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Accessing elusive σ-type cyclopropenium cation equivalents through redox gold catalysis

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Xiangdong Li [1], Matthew D. Wodrich [2] & Jérôme Waser [1]

Cyclopropenes are the smallest unsaturated carbocycles. Removing one substituent from cyclopropenes leads to cyclopropenium cations (C_3^+ systems, CPCs). Stable aromatic π-type CPCs were discovered by Breslow in 1957 by removing a substituent on the aliphatic position. In contrast, σ-type CPCs—formally accessed by removing one substituent on the alkene—are unstable and relatively unexplored. Here we introduce electrophilic cyclopropenyl-gold(III) species as equivalents of σ-type CPCs, which can then react with terminal alkynes and vinylboronic acids. With catalyst loadings as low as 2 mol%, the synthesis of highly functionalized alkynyl- or alkenyl-cyclopropenes proceeded under mild conditions. A class of hypervalent iodine reagents—the cyclopropenyl benziodoxoles (CpBXs)—enabled the direct oxidation of gold(I) to gold(III) with concomitant transfer of a cyclopropenyl group. This protocol was general, tolerant to numerous functional groups and could be used for the late-stage modification of complex natural products, bioactive molecules and pharmaceuticals.

The search for reactive functional groups and synthons has long been one of the most productive wellsprings of discovery in chemistry, enabling the design and development of novel transformations[1] and opening opportunities for drug discovery[2]. As recent striking examples, Suero and colleagues unveiled the dual radical and carbene character of carbyne equivalents generated in situ from a hypervalent iodine reagent bearing a diazo ester[3], and Garg and colleagues demonstrated that 1,2,3-cyclohexatriene is a powerful and versatile reagent in synthetic chemistry[4]. The search for synthetic equivalents for not-yet-existing synthons thus continues to drive progress in synthetic chemistry by enabling unprecedented bond disconnections.

Cyclopropenes, the smallest cyclic alkenes, possess substantial strain energy (54.6 kcal mol^{-1})[5], which leads to a unique reactivity in ring-opening transformations[6–8] and C=C bond functionalization[9–11]. The π-type cyclopropenium cations (CPCs, **I**)[12,13], a C_3^+ system generated by removing one substituent from the aliphatic C1 site of cyclopropenes, possess extraordinary stability (Fig. 1a, (1)) due to the aromatic character of this system[14]. Neutral cyclopropene precursors are easily ionized, because the aromaticity helps to offset the cost of generating the positive charge[15,16]. Since their discovery, π-type CPCs **I** have led to important advances in aromaticity theory[14], catalysis[17] and material science[18]. The π-type CPCs **I** also provide a good platform for the synthesis of functionalized cyclopropenes of type **A** by the addition of nucleophiles on the C3 position[19]. In contrast, σ-type CPCs **II**, formally generated from cyclopropenes by removing one substituent from the C1 or the C2 position, have remained unexplored in synthetic chemistry (Fig. 1a, (2)). In σ-type CPCs **II**, the empty σ-orbital is perpendicular to the C1–C2 π-orbital, thereby making the positive charge localized on a single carbon atom without aromatic stabilization. As such, free σ-type CPCs **II** decay rapidly into propargylic cations **III** and give open-chain products of type **C**[20,21]. Therefore, σ-type CPCs **II** can usually not be used to access C1/C2-substituted cyclopropenes of type **B**, making this class of products more difficult to access. Chemists have therefore developed synthetic equivalents of σ-type CPCs, but only with limited

[1]Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland. [2]Laboratory for Computational Molecular Design, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland. e-mail: jerome.waser@epfl.ch

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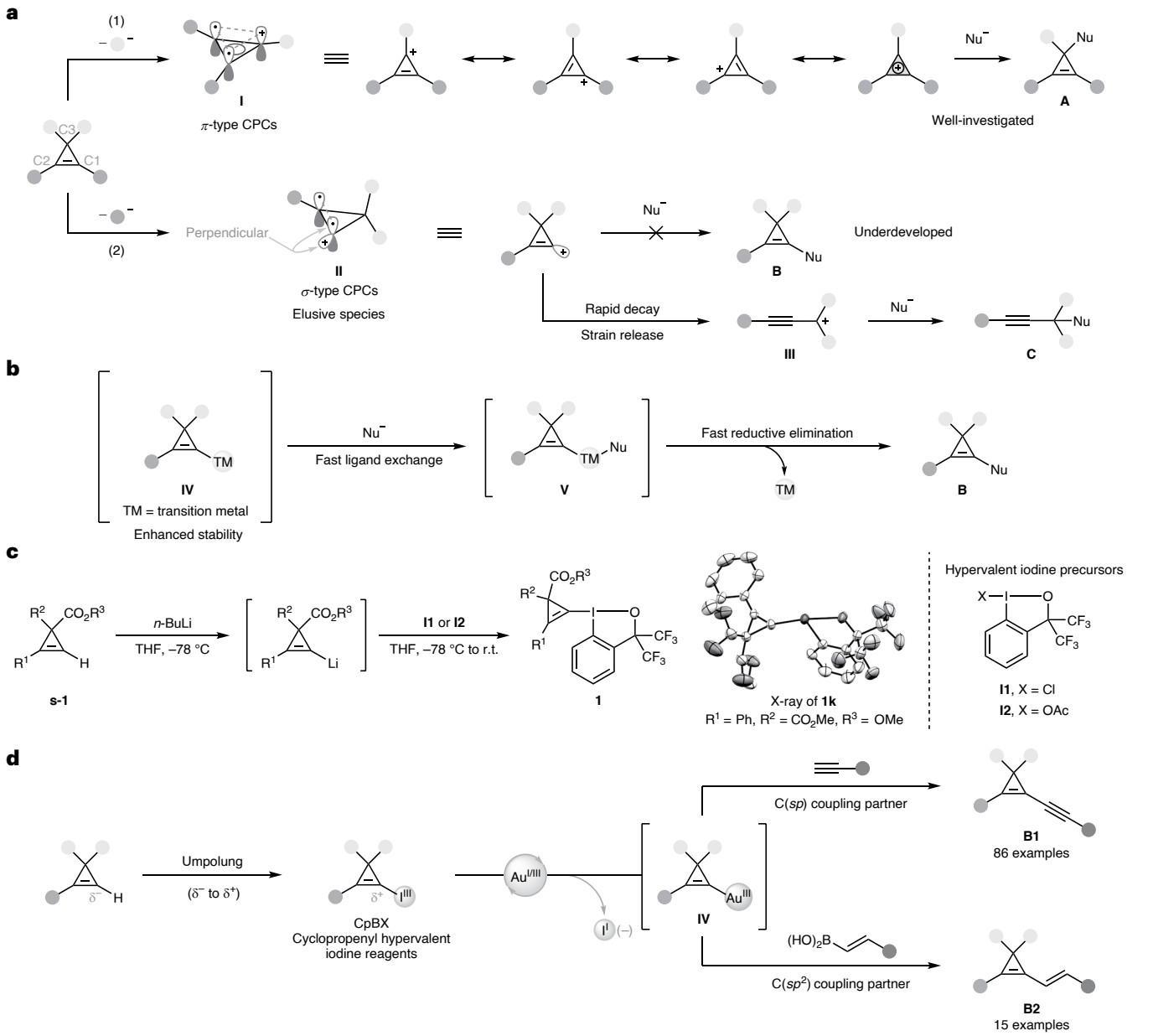

Fig. 1 | Structure of *π*-type and *σ*-type CPCs and our design. a, Bonding analysis and reactivity of *π*-type and *σ*-type CPCs **I** and **II**. **b**, Design of transition metal-based *σ*-type CPC equivalents. **c**, Synthesis of CpBXs via a cyclopropenyl lithium intermediate. **d**, Development of iodine(III)-based electrophilic *σ*-type CPC precursors by an umpolung strategy and *σ*-type CPC transfer reactions to terminal alkynes and vinylboronic acids via redox gold catalysis. Nu, nucleophile.

success. Cyclopropenyl bromides[22] or iodides[23,24] can act as *σ*-type CPC precursors in the presence of a palladium catalyst, but this approach has been limited to 3-difluoromethylated or 3,3′-difluoro cyclopropenes in cross-coupling with terminal alkynes, alkenes or aryl boronic acids. Considering the versatile role of cyclopropenes in synthetic chemistry[25], chemical biology[26], and medicinal[27] and material[28] chemistry, the availability of broadly applicable synthetic equivalents of *σ*-type CPCs would facilitate the synthesis of functionalized cyclopropenes and accelerate progress in these areas.

Our strategy was based on the generation of a transient electrophilic cyclopropenyl-metal species **IV**, which could act as a *σ*-type CPC equivalent through ligand exchange with a nucleophile to give **V**, followed by fast reductive elimination (Fig. 1b). Key design elements are good stability of the transient organometallic intermediate **IV**, fast ligand exchange and reductive elimination, and especially catalytic generation of **IV**, as the use of stoichiometric transition-metal reagents would be not sustainable. Based on the limitations of the reported approaches using cyclopropenyl bromides and iodides[22–24], more reactive yet stable precursors will be needed for our strategy. Over the past three decades, hypervalent iodine reagents (HIRs) have been broadly applied for the umpolung of nucleophiles owing to their unique combination of extreme leaving-group ability, stability and availability[29–33]. Building on our previous studies on hypervalent iodine-based reagents[34], we attempted the synthesis of the proposed *σ*-type CPC precursors by mixing iodine(III) compounds and nucleophilic cyclopropenyl partners (Fig. 1c). The cyclopropenyl organolithium reagents could be generated through deprotonation of cyclopropenes **s-1** with *n*-butyllithium at −78 °C. Addition of hypervalent iodine precursors **I1** or **I2** then gave various cyclopropenyl benziodoxoles (CpBXs) **1** in good yields (see Supplementary Section 2.3 for details). The structure of CpBX **1k** was confirmed by X-ray crystallography. The CpBX compounds are stable and easy to manipulate.

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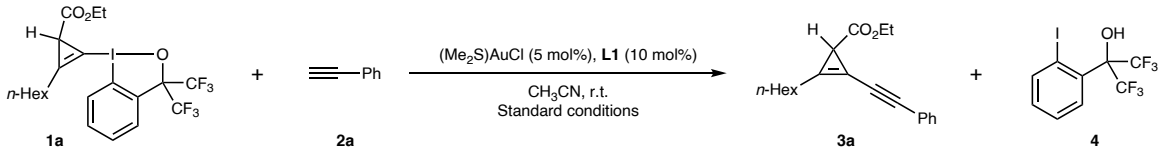
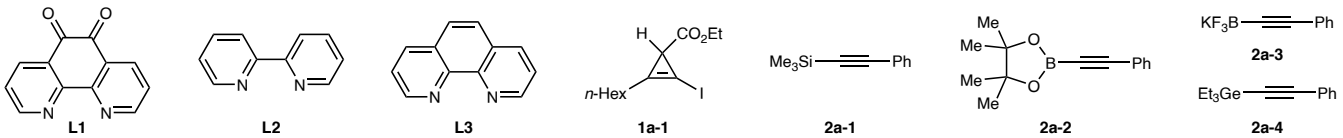
Table 1 | Optimization of the gold-catalysed σ-type CPC transfer reaction



Entry	Variations from the standard conditions	Time (h)	Yield of **3a** (%)[a]	Recovery of **1a** (%)[a]	Yield of **4** (%)[a]
1	None	2	96	0	99
2	Without $(Me_2S)AuCl$	24	0	99	–
3	Without **L1**	8	84	–	97
4	$(PhCN)_2PdCl_2$ or $NiCl_2$(glyme) instead of $(Me_2S)AuCl$, 50 °C	12	0	99	–
5	**L1** (25 mol%) was used	2	95	–	99
6	PPh_3AuNTf_2 instead of $(Me_2S)AuCl$	24	1	72	22
7	**L2** instead of **L1**	5	95	–	95
8	**L3** instead of **L1**	4	96	–	97
9	CH_2Cl_2 instead of CH_3CN	24	88	–	94
10	THF instead of CH_3CN	13	93	–	98
11	AuCl instead of $(Me_2S)AuCl$	4	93	–	94
12	$AuCl_3$ instead of $(Me_2S)AuCl$	24	15	69	30
13	$AuCl_3$ instead of $(Me_2S)AuCl$, 40 °C	6	69	–	98
14	**1a-1** instead of **1a**, **L1** (25 mol%), 50 °C	15	0	–[b]	–
15	**2a-1** instead of **2a**	4	80	–	81
16	**2a-2** instead of **2a**	2	96	–	96
17	**2a-3** instead of **2a**	24	0	90	9
18	**2a-4** instead of **2a**	24	10	82	16



Reactions performed on a 0.1 mmol scale. [a]Yields or recoveries were determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard. [b]98% NMR recovery of **1a-1**.

In this Article we describe the application of these CpBX reagents as σ-type CPC synthetic equivalents together with gold catalysis[35] (Fig. 1d). We demonstrate that the oxidative addition of CpBXs to the gold catalyst occurs under mild conditions[36], thus giving access to the σ-type CPC synthetic equivalent **IV** with high functional-group tolerance. Using terminal alkynes or vinylboronic acids as coupling partners, alkynyl- or alkenyl-cyclopropenes **B1** and **B2** were accessed, often in close to quantitative yields. Concerning cyclopropenyl-gold species, Hashmi and colleagues disclosed that stoichiometric Au(I)–cyclopropenyl complexes can be used as aurated carbenoids or quasi-carbene precursors[37]. In contrast, the transient Au(III)–cyclopropenyl species in our study reacted as σ-type CPC equivalents. Our findings reveal that the reactivity of σ-type CPC equivalents can be harnessed based on a gold redox process[38–40] that enables the divergent synthesis of functionalized cyclopropenes. In addition, the obtained alkynyl–cyclopropenes can serve as versatile building blocks to access valuable functionalized cyclopropenes, cyclopropanes and conjugated enynes. The power of the transformation is further highlighted in the late-stage modification of complex natural products, bioactive molecules and drugs.

Results and discussion

Reaction development

The success of the proposed σ-type CPC transfer reaction hinged on our hypothesis that transition-metal catalysts would prefer to cleave the C–I(III) bond of CpBXs (oxidative addition) rather than the C–C bond of cyclopropenes (ring-opening reactions). Furthermore, coordination of the nucleophilic reaction partner and subsequent reductive elimination will need to be efficient to overcome the expected limited stability of the formed cyclopropenyl intermediate. Terminal alkynes are well-established partners for cross-coupling reactions and are widely represented in commercially available compounds and pharmaceuticals[41]. The cross-coupling between CpBXs and terminal alkynes would give access to useful alkynyl–cyclopropene building blocks. The synthesis of such compounds has been reported by Hashmi and colleagues using a reverse polarity approach (cyclopropenes as nucleophiles and ethynylbenziodoxole (EBX) reagents as electrophiles)[42]. However, terminal cyclopropenes with two electron-withdrawing groups are required for efficient C–H activation, resulting in a narrow scope. Monocyclopropenation of 1,3-diynes by transition-metal-catalysed reaction of diazo compounds or their surrogates is also a viable process affording alkynyl cyclopropenes[43–46], but is limited to symmetrical 1,3-diynes. Therefore, the coupling of CpBX **1a** bearing one ester group on the C3 position and phenylacetylene (**2a**) was selected as our prototypical system. A wide range of transition-metal catalysts and ligands were investigated, and the selected conditions are presented in Table 1 (a complete list of the conditions screened is provided in Supplementary Section 4). We identified the commercial complex $(Me_2S)AuCl$ as an effective transition-metal catalyst, together with

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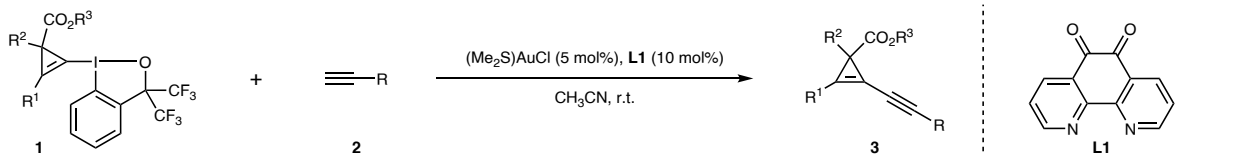
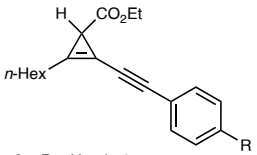
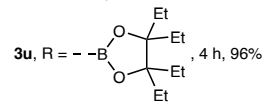
Table 2 | Scope of the gold-catalysed *σ*-type CPC transfer to terminal alkynes



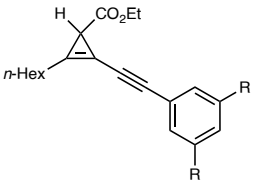
Scope of **2**



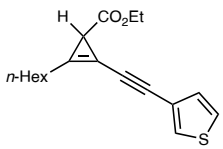
3a, R = H, 2 h, 95%
3b, R = *n*-Pent, 3 h, 89%
3c, R = , 2 h, 89%
3d, R = Ph, 3 h, 91%
3f, R = CF_3, 6 h, 94%
3g, R = NO_2, 6 h, 87%
3h, R = CO_2Me, 8 h, 92%
3i, R = CHO, 4 h, 87%
3j, R = CO_2H, 9 h, 86%
3n, R = OCF_3, 4 h, 92%
3o, R = NHCbz, 6 h, 91%
3q, R = Br, 4 h, 88%
3r, R = I, 3 h, 92%
3s, R = $SiMe_3$, 3 h, 84%
3t, R = $GeEt_3$, 3 h, 76%



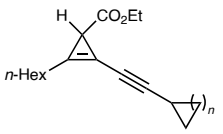
3u, R = , 4 h, 96%



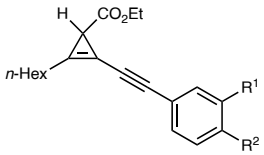
3e, R = CF_3, 6 h, 92%
3m, R = OMe, 4 h, 92%



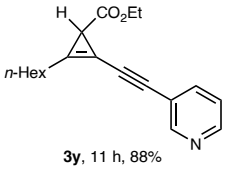
3x, 3 h, 94%



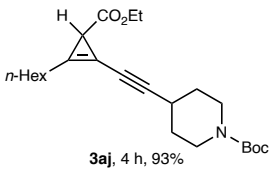
3ac, *n* = 3, 3 h, 83%
3ad, *n* = 1, 4 h, 94%



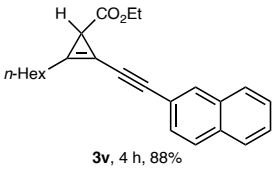
3k, R^1 = CO_2H, R^2 = H, 6 h, 78%
3l, R^1 = OMe, R^2 = H, 5 h, 90%
3p, R^1 = R^2 = Cl, 4 h, 91%



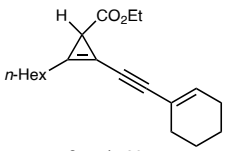
3y, 11 h, 88%



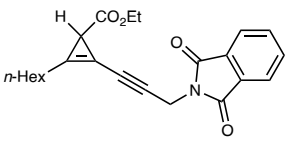
3aj, 4 h, 93%



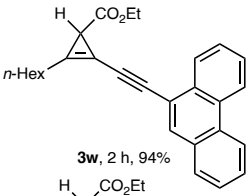
3v, 4 h, 88%



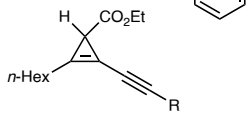
3z, 4 h, 90%



3ak, 3 h, 95%

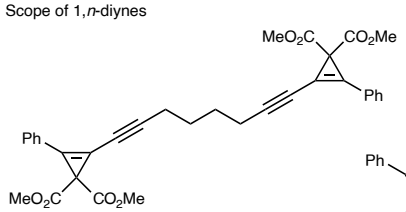


3w, 2 h, 94%

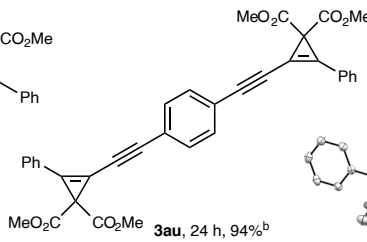


3aa, R = *n*-Hex, 6 h, 94%
3ab, R = *n*-$C_{12}H_{25}$, 3 h, 90%
3ae, R = $(CH_2)_4Cl$, 6 h, 88%
3af, R = $(CH_2)_2Br$, 3 h, 90%
3ag, R = $(CH_2)_3I$, 6 h, 82%
3ah, R = $(CH_2)_5OH$, 6 h, 87%
3ai, R = $(CH_2)_2OTBS$, 6 h, 87%
3al, R = $C(Me)_2OH$, 4 h, 96%
3am, R = CH_2OBn, 5 h, 85%
3an, R = CH_2OPh, 3 h, 90%
3ao, R = CH_2OBz, 3 h, 93%
3ap, R = $(CH_2)_2CO_2Me$, 2 h, 87%
3aq, R = $(CH_2)_3CN$, 3 h, 90%
3ar, R = CO_2Et, 9 h, 84%
3as, R = H, 18 h, 46%[a]

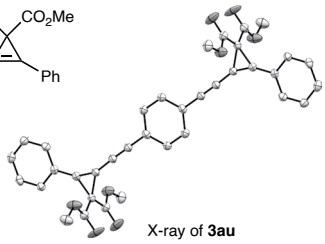
Scope of 1,*n*-diynes



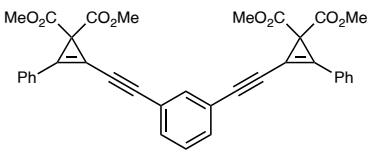
3at, 24 h, 84%[b]



3au, 24 h, 94%[b]

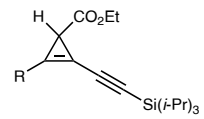


X-ray of **3au**

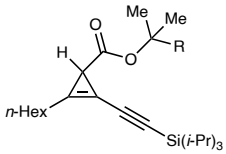


3av, 24 h, 92%[b]

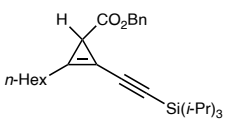
Scope of **1**



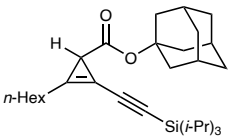
3aw, R = *n*-Hex, 6 h, 93%
3ax, R = $(CH_2)_2Ph$, 4 h, 91%



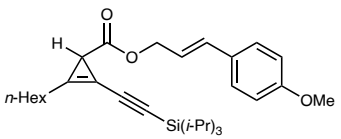
3ay, R = Me, 4 h, 96%
3az, R = Ph, 4 h, 91%



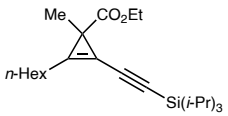
3ba, 5 h, 91%



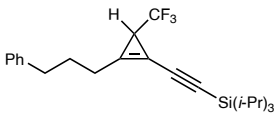
3bb, 5 h, 94%



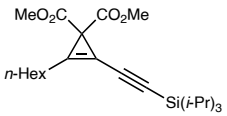
3bc, 10 h, 89%



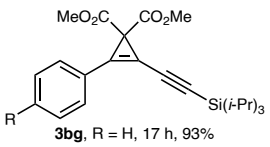
3bd, 6 h, 89%



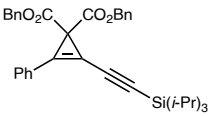
3be, 24 h, 78%[c,d,e]



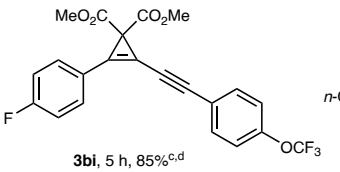
3bf, 24 h, 91%



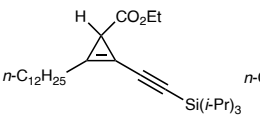
3bg, R = H, 17 h, 93%
3bh, R = F, 4 h, 82%[c,d]
3bj, R = Br, 36 h, 88%[d]



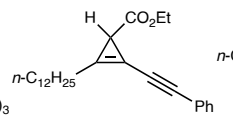
3bk, 2 h, 80%[c,d]



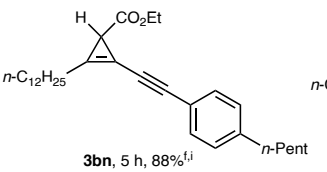
3bi, 5 h, 85%[c,d]



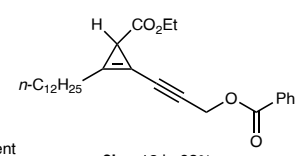
3bl, 12 h, 92%[f,g]



3bm, 7 h, 93%[f,h]



3bn, 5 h, 88%[f,i]



3bo, 12 h, 93% [f,j]

Reaction conditions: CpBX **1** (0.2 mmol, 1.0 equiv.), terminal alkyne **2** (0.2 mmol, 1.0 equiv.), $(Me_2S)AuCl$ (5 mol%) and **L1** (10 mol%) were stirred in CH_3CN (2.0 ml) at room temperature for the indicated time, unless noted otherwise. Isolated yields are given. Bz, benzoyl; Cbz, carbobenzyloxy; TBS, *tert*-butyldimethylsilyl. [a]An acetylene balloon (1 atm) and **L1** (25 mol%) were used at 40 °C. [b]CpBX **1k** (0.4 mmol, 2.0 equiv.), diyne **2** (0.2 mmol, 1.0 equiv.), $(Me_2S)AuCl$ (10 mol%) and **L1** (20 mol%) were used. [c]Reactions carried out at 40 °C. [d]0.1 mmol scale. [e]CpBX **1j** (1.5 equiv.) and **L1** (25 mol%) were used instead. [f]$(Me_2S)AuCl$ (2 mol%) and **L1** (4 mol%) were used instead. [g]2 mmol scale. [h]1.2 mmol scale. [i]0.6 mmol scale. [j]1.8 mmol scale.

ligand **L1**, to deliver the cross-coupled product **3a** in 96% NMR yield in CH_3CN at room temperature (r.t., entry 1). Without $(Me_2S)AuCl$, no desired product was obtained (entry 2), and without **L1**, a drop in yield and a longer reaction time were observed (entry 3). Palladium or nickel, commonly used catalysts for C–C bond formation[47], did not promote the desired transformation, even when a higher reaction temperature was applied, thus underscoring the specific role of gold in catalysing the *σ*-type CPC transfer reaction (entry 4). This result is noteworthy, given that gold(I) species are difficult to oxidize (Au(III)/Au(I) = 1.41 V) when compared to palladium(0) (Pd(II)/Pd(0) = 0.91 V) or nickel (0) (Ni(II)/Ni(0) = −0.24 V)[48,49]. Our findings further highlight the unique properties of hypervalent iodine reagents to promote redox-gold catalysis[42,50–52]. Increasing the amount of **L1** to 25 mol% afforded almost the same yield of **3a** as with 10 mol% (entry 5). PPh_3-ligated gold catalysts, previously shown to be the optimal catalysts for alkynylation using EBXs[53,54], were ineffective (entry 6). Other gold catalysts coordinated by strong *σ*-donating ligands all failed to give **3a** (Supplementary Table 1). Electron-deficient **L1** was found to be superior in accelerating the reaction than its more electron-rich analogues **L2** or **L3** (entries 7 and 8)[55]. The screening of solvents revealed that CH_3CN was the optimal solvent compared with less polar ones, such as CH_2Cl_2 or tetrahydrofuran (THF; entries 9 and 10). A similar catalytic performance was also observed with AuCl as the catalyst, albeit a longer reaction time was necessary for the full conversion of **1a** (entry 11). The slightly lower reaction rate observed when using AuCl as the catalyst might be attributed to a necessary dissociative process of the polymeric gold(I) source compared to monomeric $(Me_2S)AuCl$. Replacing $(Me_2S)AuCl$ with $AuCl_3$ resulted in a drop in the yield of **3a**, which could be improved when increasing the temperature to 40 °C (entries 12 and 13). The sluggish performance for the reaction using $AuCl_3$ as catalyst could be attributed to an additional induction period needed to generate the catalytically active Au(I) species[56]. As a control experiment, the use of cyclopropenyl iodide **1a-1** as the coupling partner did not yield any desired product under the standard conditions, highlighting the importance of the hypervalent iodine reagent for successful oxidative addition (entry 14). Although alkynyl silane **2a-1**[57] (entry 15) and alkynyl pinacol boronate **2a-2** (entry 16) also gave good yields of **3a**, other acetylide surrogates, such as potassium alkynyltrifluoroborate **2a-3** (entry 17) and alkynylgermane **2a-4**[58] (entry 18) were less efficient. It is noteworthy that the iodoarene **4** obtained during the reaction can be recovered and recycled for the synthesis of hypervalent iodine precursors **I1** or **I2** (Supplementary Sections 5 and 6 provide details).

Scope of *σ*-type CPC transfer to terminal alkynes

With the optimal conditions in hand, we explored the scope and limitations of this *σ*-type CPC transfer reaction in terms of both functional-group compatibility and structural diversity. We first examined variation of the terminal alkyne component (Table 2). Our process worked well for terminal alkynes with aryl rings substituted with alkyl (**3b**), alkenyl (**3c**), phenyl (**3d**), CF_3 (**3e**–**3f**), nitro (**3g**), ester (**3h**), aldehyde (**3i**) and carboxylic acid (**3j**–**3k**) groups in the *para* and *meta* positions. Electron-donating functionalities on the aryl substituent of the terminal alkyne, such as methoxy (**3l**–**3m**), trifluoromethoxy (**3n**) and carbamate (**3o**), were well tolerated. Functionalities, such as halogens (-Cl, -Br and -I, **3p**–**3r**), which can react in the presence of many transition-metal catalysts, remained intact using our protocol, thus highlighting the orthogonal reactivity of gold over palladium or nickel catalysis and allowing the installation of halogen handles for further diversification. Intriguingly, terminal alkynes bearing functionalities such as aryl silane[59] (**3s**), aryl germane[60] (**3t**) and aryl boronate[61] (**3u**), previously reported to be suitable coupling partners in redox gold catalysis, remained untouched, thus underscoring the chemoselectivity of the *σ*-type CPC transfer reaction for alkynes. Additionally, this gold-catalysed cross-coupling system was shown to tolerate polyaromatic or heteroaryl-substituted alkynes, as exemplified by the synthesis of alkynylcyclopropenes substituted with naphthalene (**3v**), phenanthrene (**3w**), thiophene (**3x**) and pyridine (**3y**) moieties. A conjugated enyne was also tolerated (**3z**). The use of aliphatic terminal alkyl alkynes as coupling partners was also successful and further illustrated the compatibility of the process with a broad range of functionalities, including alkyls (**3aa**–**3ab**), cyclic alkanes (**3ac**–**3ad**), a chloride (**3ae**), a bromide (**3af**), an iodide (**3ag**), free alcohols (**3ah**, **3al**), a silyl ether (**3ai**), a cyclic carbamate (**3aj**), an imide (**3ak**), a benzylic ether (**3am**), a phenyl ether (**3an**), an ester (**3ao**, **3ap**) and a cyano (**3aq**) group. In particular, a propargyl benzoate, which is known to easily undergo a 1,2-migration using gold catalysis[62], could also be accommodated, furnishing **3ao** in 93% yield. Ethyl propiolate was also suitable for this reaction, giving **3ar** in 84% yield. Acetylene gas itself, which is of particular interest owing to its availability in bulk quantity[63], led to **3as** in moderate yield, although a higher ligand loading and higher reaction temperature were required. Notably, 1,*n*-diynes tethered by an alkyl chain or an aromatic framework underwent smooth double cross-coupling in excellent yields (**3at**–**3av**). The structure of **3au** with two alkynylcyclopropene units attached to the *para* positions of benzene was confirmed by X-ray crystallography. Next, we examined the scope of CpBXs using silyl-substituted terminal alkynes as the representative coupling partners. CpBXs bearing different alkyl substituents (R^1) attached to the cyclopropene were suitable reaction partners and furnished products **3aw** and **3ax** in >90% yield. CpBXs featuring various ester substituents provided products **3ay** to **3bc** in excellent yields. CpBX **1i** bearing an additional alkyl substituent at the C3 position of the cyclopropenyl moiety underwent coupling with ethynyltriisopropylsilane to give tetrasubstituted alkynylcyclopropene **3bd** in 89% yield. Remarkably, trifluoromethyl-substituted CpBX **1j** could also be used in our gold-catalysed *σ*-type CPC transfer protocol to give **3be** in 78% yield. Furthermore, CpBXs derived from cyclopropenes bearing two methyl ester substituents[42,64] at the C3 position were also excellent substrates, as showcased by the formation of alkyl- (**3bf**), phenyl- (**3bg**), fluoroaryl- (**3bh**–**3bi**) and bromoaryl- (**3bj**) substituted alkynylcyclopropenes. Other esters at the C3 position were also tolerated (**3bk**). For some substrates, the reaction temperature was increased to 40 °C to increase the reaction rate. To demonstrate the practical utility of our method, the synthesis of representative alkynylcyclopropenes **3bl**, **3bm**, **3bn** and **3bo** was performed with decreased catalyst loading (2 mol% $(Me_2S)AuCl$ and 4 mol% **L1**) on 2.0, 1.2, 0.6 and 1.8 mmol scales, respectively. The products were obtained in comparable yields, albeit with extended reaction times.

Late-stage functionalization[65] has emerged as an appealing strategy for the identification of bioactive compounds and requires further extension of the boundaries of modern synthesis in its ability to build and tolerate molecular complexity. Pleasingly, late-stage modification of complex natural products modified with a propargylic alkyne handle, such as (−)-camphanic acid (**3bp**) and (−)-borneol (**3bq**), as well as biologically relevant molecules such as L-propargylglycine (**3br**), L-phenylalanine (**3bs**), α-D-allofuranose (**3bt**) and D-biotin (**3bu**) could be achieved efficiently, thus confirming the generality of our method (Table 3). We next evaluated a selection of drug derivatives, including sulbactam (**3bv**), fenofibric acid (**3bw**), ciprofibrate (**3bx**), naproxen (**3by**), oxaprozin (**3bz**), isoxepac (**3ca**), febuxostat (**3cb**), indomethacin (**3cc**), mestranol (**3cd**) and norethindrone (**3ce**), resulting in the formation of the corresponding modified drug molecules in 83–99% yield. Remarkably, the sensitive core heterocyclic fragments in ezetimibe (**3cf**), artesunate (**3cg**) and gibberellic acid (**3ch**) were also well tolerated in the cross-coupling.

Scope of *σ*-type CPC transfer to vinylboronic acids

To expand the generality of our method, other potential acceptors for *σ*-type CPCs were also examined. Following extensive screening of various sp^2-hybridized coupling partners, we were pleased to find that vinylboronic acids (**5**) also participate in the *σ*-type CPCs transfer

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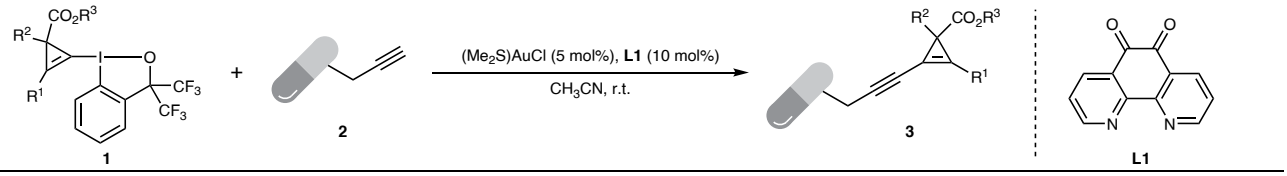
Table 3 | Late-stage functionalization of bioactive natural and synthetic molecules



From (1*S*)-(–)-camphanic acid
3bp, 3 h, 91%[a,b]

From (–)-borneol
3bq, 60 h, 79%

From L-propargylglycine
3br, 24 h, 86%[a,c] (*d.r. = 1:1)

From L-phenylalanine
3bs, 18 h, 74%[a]

From α-D-allofuranose
3bt, 2 h, 96%[a,b]

From D-biotin
3bu, 11 h, 90%[a,b]

From sulbactam
3bv, 17 h, 83%[a]

From fenofibric acid
3bw, 18 h, 85%

From ciprofibrate
3bx, 3 h, 94%[a,c]

From naproxen
3by, 12 h, 89%[a,b]

From oxaprozin
3bz, 22 h, 97%[b]

From isoxepac
3ca, 22 h, 95%[b]

From febuxostat
3cb, 3 h, 99%[b]

From indomethacin
3cc, 16 h, 88%[a,b]

From mestranol
3cd, 24 h, 95%

From norethindrone
3ce, 24 h, 92%

From ezetimibe
3cf, 12 h, 77%[a,b]

From artesunate
3cg, 28 h, 82%[b,d]

From gibberellic acid
3ch, 4 h, 95%[a,b]

Reaction conditions: **1** (0.1 mmol, 1.0 equiv.), **2** (0.1 mmol, 1.0 equiv.), $(Me_2S)AuCl$ (5 mol%) and **L1** (10 mol%) were stirred in CH_3CN (2.0 ml) at room temperature for the indicated time, unless noted otherwise. Isolated yields are given. [a]Reactions carried out at 40 °C. [b]**1** (0.12 mmol, 1.2 equiv.) was used instead. [c]**1** (0.13 mmol, 1.3 equiv.) was used instead. [d]Reactions carried out at 30 °C.

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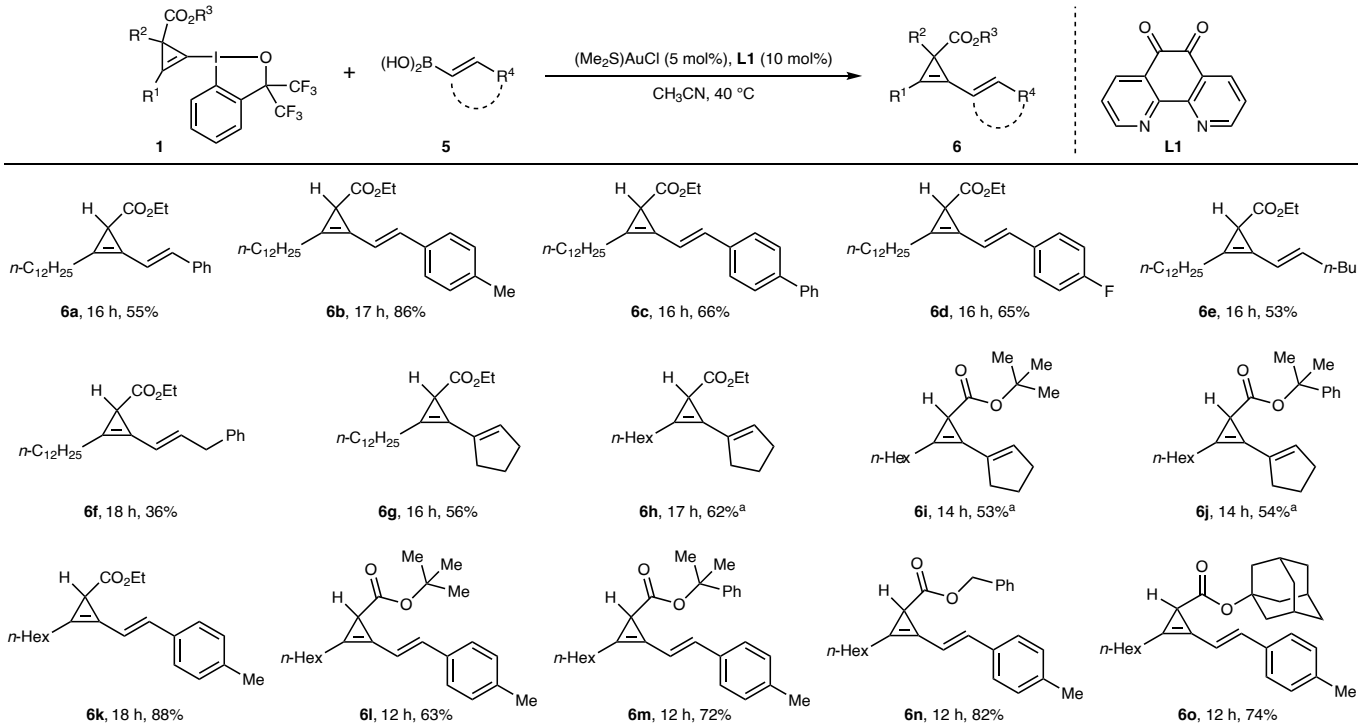
Table 4 | Scope of the gold-catalysed *σ*-type CPC transfer to vinylboronic acids



Reaction conditions: **1** (0.13 mmol, 1.3 equiv.), **5** (0.1 mmol, 1.0 equiv.), (Me_2S)AuCl (5 mol%) and **L1** (10 mol%) were stirred in CH_3CN (2.0 ml) at 40 °C for the indicated time, unless noted otherwise. Isolated yields are given. [a]**1** (1.0 equiv.) was used instead.

reaction. With only minor modification of the standard conditions (optimization details are provided in Supplementary Table 6), the scope of this *σ*-type CPC transfer reaction to vinylboronic acids was explored. As shown in Table 4, vinylboronic acids bearing aromatic rings with different electronic properties (**6a**–**6c**) or a halogen substituent (**6d**) gave the desired products in 55–86% yield. Vinylboronic acids with an alkyl group (**6e**) or a benzyl group (**6f**) on the alkene were tolerated. Cyclic disubstituted-vinylboronic acids were also suitable substrates, furnishing the corresponding coupled products **6g**–**6j** in 53–62% yields. In addition, the scope of CpBXs was investigated with (*E*)-(4-methylstyryl)boronic acid **5b**. To our delight, CpBXs **1** bearing various alkyl substituents on the ester underwent coupling smoothly with vinylboronic acid **5b** to give vinyl–cyclopropenes **6k**–**6o** in 63–88% yield. The use of other nucleophilic partners such as allenamides or indoles was not successful (details are provided in Supplementary Section 6.3).

Synthetic transformations

The alkynyl–cyclopropene products are versatile building blocks for the synthesis of substituted cyclopropenes, functionalized cyclopropanes or ring-opening products (Fig. 2). Selective reduction of the ester functionality in **3bm** with diisobutylaluminium hydride (DIBAL-H)[66] afforded hydroxymethylcyclopropene **7** in 94% yield. Alternatively, the alkene unit and the ester functionality in **3bn** were both reduced when treated with $LiAlH_4$ (ref. 67) to provide cyclopropane **10** in 32% yield with excellent diastereoselectivity. Moreover, **7** could serve as starting material for a copper-catalysed carbomagnesiation reaction proceeding in a regio- and diastereoselective manner[68]. The in situ-formed cyclopropyl metal species could be quenched by methanol and allyl bromide, affording polysubstituted cyclopropanes **8** and **9**, respectively. Saponification of **3bm** using sodium hydroxide furnished cyclopropene carboxylic acid **11** in 82% yield. Interestingly, **3bo** could be readily converted into conjugated enyne **12** with excellent stereoselectivity in the presence of a cationic gold(I)–carbene complex[69]. Gold carbene **18**, presumably generated via 1,2-benzoyloxy migration of **3bo**, can be proposed as the key reactive intermediate, which then underwent ring-opening of the cyclopropene (a complete speculative mechanism is provided in Supplementary Fig. 1). A Diels–Alder reaction of **3bo** with 2,3-dimethylbutadiene gave fused bicycle **13** in 89% yield and >20:1 diastereoselectivity (d.r.). Additionally, desilylation of **3bl** using tetrabutylammonium fluoride (TBAF)[70] allowed access to cyclopropene **14** bearing a terminal alkyne, which can itself serve as a suitable partner in the gold-catalysed *σ*-type CPC transfer reaction, affording non-symmetrical 1,2-bis-cyclopropenyl substituted alkyne **15**. A gold-catalysed cross-coupling of **14** with hypervalent iodine reagent **19** (ref. 53) gave cyclopropenyl 1,3-diyne **16** in 86% yield. Finally, copper(I)-catalysed alkyne–azide cycloaddition[71] of **14** and benzyl azide provided cyclopropenyl triazole **17** in 72% yield.

Mechanistic investigations

To gain some insights into the reaction mechanism[72,73], we first attempted to identify the active gold species at the start of the catalytic cycle. We prepared the ligand-free polymeric gold(I)–phenylacetylide **20**[74] and the cationic gold(I)–ethylene complex **21**[75] as potential gold sources (Fig. 3a). We first investigated the use of 5 mol% **20** in the cross-coupling of CpBX **1a** and terminal alkyne **2a** under the standard conditions. No cross-coupled product was observed (Fig. 3b, entry 2). Running the reaction at 40 °C for 24 h, only 7% yield of product **3a** was observed with most **1a** (87%) recovered (Fig. 3b, entry 3). These results do not support a catalytic cycle involving the direct oxidation of a gold(I)–acetylide complex by CpBX **1**. When the cationic gold(I)–ethylene complex **21** was used, a 10% yield of **3a** was observed at room temperature after 2 h (Fig. 3b, entry 4). The yield could be improved to 57% by running the reaction at 40 °C for 10 h with full conversion of

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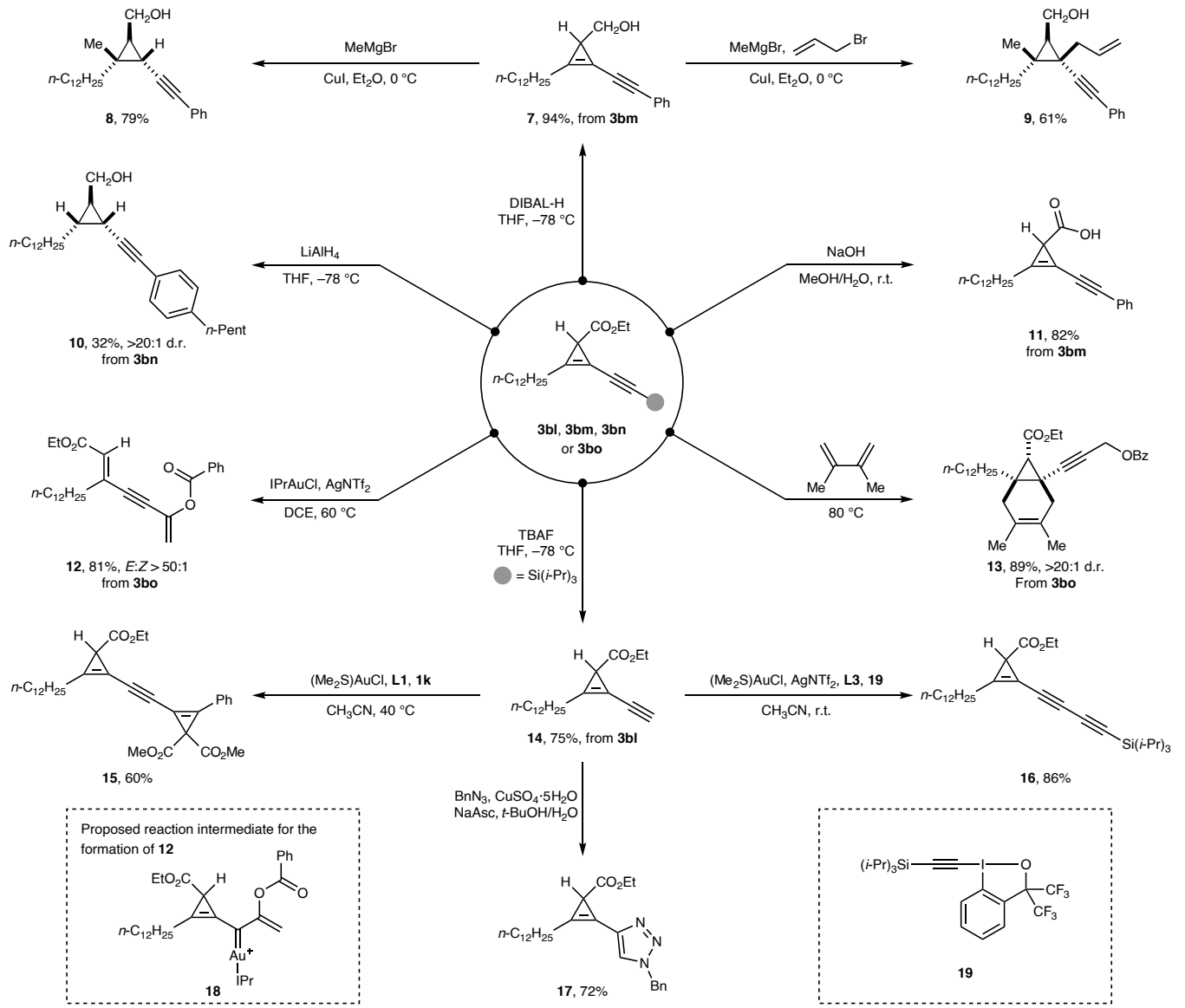

Fig. 2 | Synthetic modifications of the alkynylcyclopropenes. The obtained alkynylcyclopropenes can be used as precursors for accessing different types of functionalized cyclopropenes, cyclopropanes or ring-opening products. Reduction of alkynyl–cyclopropene **3bm** with DIBAL-H gave cyclopropene **7**, which was converted into alkynyl cyclopropane carbinol **8** and **9** by copper-catalysed carbomagnesiation quenched by methanol and allyl bromide, respectively. Reduction of **3bn** by $LiAlH_4$ afforded cyclopropane **10**. Saponification of **3bm** using sodium hydroxide afforded cyclopropene **11**. Gold(I)-catalysed ring-opening of **3bo** via gold carbene **18** furnished **12**. Diels–Alder reaction of **3bo** with 2,3-dimethylbutadiene produced fused bicycle **13**. Desilylation of **3bl** using TBAF led to the formation of **14**, which could be converted into cyclopropenes **15** and **16** by gold-catalysed cross-coupling with **1k** and **19**, respectively. Copper(I)-catalysed alkyne–azide cycloaddition of **14** and benzyl azide gave triazole **17**. NaAsc, (+)-sodium L-ascorbate; IPr, 2,6-bis(diisopropylphenyl)imidazole-2-ylidene; DCE, 1,2-dichloroethane; Tf, trifluoromethanesulfonyl. Supplementary Section 7 provides all the experimental details.

1a (Fig. 3b, entry 5), indicating that the cationic gold(I) species can be oxidized by CpBX **1**. The poor catalytic performance of cationic gold(I) complex **21** under the standard conditions could be attributed to the formation of a catalytically inert gold(I)–acetylide in the presence of an excess of terminal alkyne (Supplementary Section 8.3 presents more details). In contrast, when 5 mol% of **21** and 5 mol% of NBu_4Cl were used, **3a** was obtained in 94% yield (Fig. 3b, entry 6), with an efficiency similar to the one observed under standard conditions (Fig. 3b, entry 1). A control experiment using $NaHCO_3$ (3.0 equiv.) as an additive did not show any improvement (Fig. 3b, entry 7), supporting the important role of chloride. To support this hypothesis, other halogenide additives were examined. Bromide exhibited a similar effect on the reaction outcome (Fig. 3b, entry 8). In contrast, the use of fluoride and iodide nearly completely suppressed the formation of **3a** (Fig. 3b, entries 9 and 10). A catalytically active tricoordinated gold(I) chloride species[55], **22**, undergoing oxidative addition onto CpBX **1** would be in accordance with these observations (Fig. 3c). The NMR spectra of **22** prepared independently by mixing an equimolar amount of **21** and NBu_4Cl in CD_2Cl_2 showed symmetric ligand backbone signals, which were distinct from those of **21** or **L1** (spectra details are provided in Supplementary Fig. 3). Species **22** is therefore proposed to be a fluxional species with fast exchange of the coordination sites of gold(I) to the two nitrogen atoms of **L1**[76]. A weak coordination of the gold centre to CpBX **1** would afford transient π-type Au(I) species **VI**. Subsequently, oxidation of gold(I) to gold(III) with the concomitant transfer of the cyclopropenyl moiety from iodine to gold via a concerted four-membered ring

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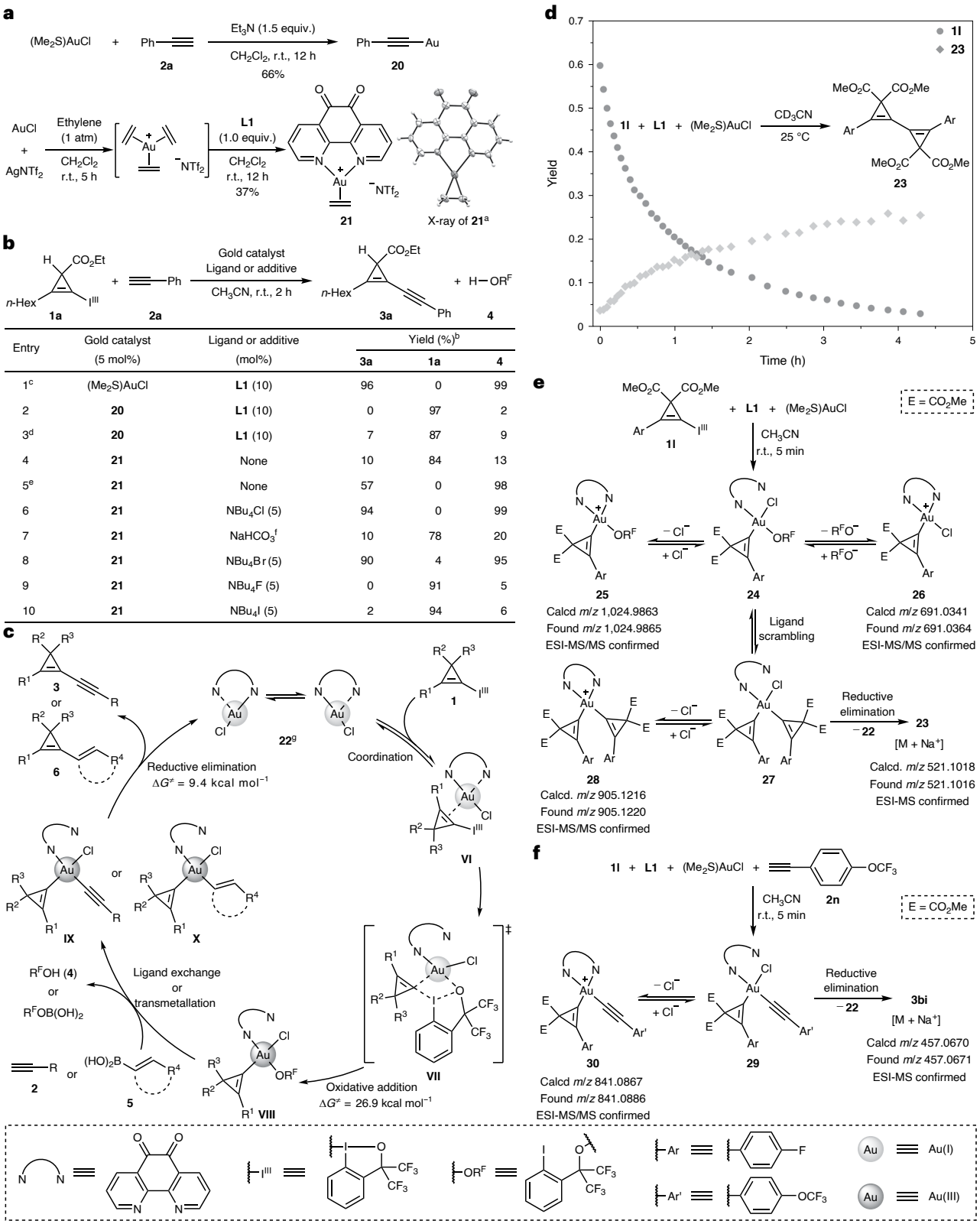

Entry	Gold catalyst (5 mol%)	Ligand or additive (mol%)	Yield (%)[b] 3a	1a	4
1[c]	$(Me_2S)AuCl$	**L1** (10)	96	0	99
2	**20**	**L1** (10)	0	97	2
3[d]	**20**	**L1** (10)	7	87	9
4	**21**	None	10	84	13
5[e]	**21**	None	57	0	98
6	**21**	NBu_4Cl (5)	94	0	99
7	**21**	$NaHCO_3$[f]	10	78	20
8	**21**	NBu_4Br (5)	90	4	95
9	**21**	NBu_4F (5)	0	91	5
10	**21**	NBu_4I (5)	2	94	6

Fig. 3 | Mechanistic studies on the gold-catalysed *σ*-type CPC transfer reaction. a, Preparation of gold(I)–phenylacetylide **20** and cationic gold(I)–ethylene complex **21**. **b**, Control experiments for determining the catalytically active species. Gold(I)–acetylide complex **20** was not a competent catalyst. Chloride plays a crucial role in accelerating the coupling reaction. **c**, Proposed reaction mechanism. **d**, Reaction profile of the stoichiometric reaction of CpBX **1l** and $(Me_2S)AuCl$, with **L1** as the ligand. **e**, ESI-MS/MS analysis of the stoichiometric reaction of CpBX **1l**, $(Me_2S)AuCl$ and **L1** supporting the formation of intermediate **VIII**. **f**, ESI-MS/MS analysis of the stoichiometric reaction of CpBX **1l**, $(Me_2S)AuCl$, **L1** and alkyne **2n** supporting the formation of intermediate **IX**. [a]Solid-state structure of 21, with thermal displacement ellipsoids given at 50% probability. The counterion is omitted for clarity. [b]Determined by ^1H NMR. [c]Standard condition (Table 1, entry 1). [d]Reaction carried out at 40 °C for 24 h. [e]Reaction carried out at 40 °C for 10 h. [f]$NaHCO_3$ (3.0 equiv.) was used. [g]**22** is proposed to be a fluxional species with fast exchange of the coordination sites of gold(I) to the two nitrogen atoms of L1. ESI, electrospray ionization.

transition state **VII** would generate the square-planar Au(III)–cyclopropenyl species **VIII**[77]. The highly electrophilic and reactive species **VIII** would capture terminal alkyne **2** via ligand exchange or undergo transmetallation with vinylboronic acid **5** to generate gold(III) species **IX** or **X**, which, upon reductive elimination, would yield cross-coupled products **3** or **6**, respectively, and regenerate the gold(I) catalyst **22**.

We next performed further computations and mechanistic experiments to support the proposed catalytic cycle and the putative Au(III)–cyclopropenyl species. First, we used density functional theory (DFT) at the B3PW91-D3(BJ)/def2-TZVP//PBE0-D3(BJ)/def2-SVP level (Supplementary Section 8.8 and Supplementary Fig. 19) to further assess the feasibility of the key oxidative addition and reductive elimination steps. Activation energies of 26.9 kcal mol^{-1} and 9.4 kcal mol^{-1} were obtained for the oxidative addition and reductive elimination processes, respectively. This further supported that both steps were feasible, even if the energy for the oxidative addition step remains a little high when considering the reaction rate. We then used ^{19}F NMR spectroscopy to monitor the stoichiometric reaction of an equimolar amount of CpBX **1l**, $(Me_2S)AuCl$ and **L1** in CD_3CN at ambient temperature. As shown in Fig. 3d, CpBX **1l** readily reacted with gold(I) and was completely consumed within 5 h, thus confirming the reactivity of CpBX **1** with gold(I) species. Intriguingly, the homo-coupled product **23** was formed, which may originate from the labile Au(III)–cyclopropenyl species **24** (vide infra). To further probe the intermediacy of the proposed Au(III)–cyclopropenyl species **VIII**, we then used electrospray ionization mass spectrometry (ESI-MS) techniques to monitor the reaction mixture. As shown in Fig. 3e, a reaction mixture of equimolar **1l**, $(Me_2S)AuCl$ and **L1** in CH_3CN (at room temperature for 5 min) was subjected to high-resolution mass analysis. Although **24** was not observed directly by mass spectrometry due to its electroneutral nature, cationic Au(III) species **25** and **26** derived from **24** by losing one anionic fragment were both observed by ESI-MS and structurally confirmed by tandem mass spectrometry (MS/MS) (Supplementary Section 8.6). Interestingly, the cationic Au(III)-bis(cyclopropenyl) species **28**, derived from **27** by losing chloride, was also observed, indicating the mechanism for the formation of **23**, that is, ligand scrambling[78] of **24** to **27** followed by reduction elimination to furnish **23**. Finally, we sought to gain support for the putative Au(III) species **IX**, a key organogold species in the catalytic cycle to connect the transmetallation and reductive elimination step. As shown in Fig. 3f, a reaction mixture of equimolar **1l**, $(Me_2S)AuCl$, **L1** and terminal alkyne **2n** in CH_3CN was subjected to high-resolution mass analysis. Gratifyingly, the expected cationic Au(III) species **30**, derived from **29** by losing chloride, was observed by ESI-MS and further structurally determined by MS/MS analysis, thus providing direct evidence for the participation of Au(III)–cyclopropenyl species **IX** in the catalytic cycle. Overall, these experiments support the mechanism proposed in Fig. 3c well, even if it is not completely certain which of the chloride or cationic species is on or off the catalytic cycle.

Conclusion

In summary, we have developed broadly applicable synthetic equivalents of the elusive and untapped σ-type CPCs. The required CpBXs, newly designed iodine(III)-based precursors of σ-type CPCs, can be prepared from readily available reagents. Gold(I) complexes were used as catalysts for the intermolecular σ-type CPC transfer reaction of CpBXs **1** to terminal alkynes or vinylboronic acids under mild conditions, providing straightforward access to alkynyl–cyclopropenes and vinyl–cyclopropenes. The gold-catalysed protocol exhibited a broad substrate scope and tolerated numerous functional groups. This protocol can be further applied to the late-stage elaboration of complex organic compounds and drug molecules containing an alkyne handle. The alkynyl–cyclopropene products have been shown to be versatile synthetic intermediates for downstream diversification. Mechanistic studies support the intermediacy of a highly electrophilic cyclopropenyl–Au(III) species as a σ-type CPC equivalent and provide evidence for the crucial role of chloride as a supporting ligand for efficient coupling. Our work therefore substantially extends the chemical diversity of easily accessible cyclopropene building blocks, with applications in synthetic and medicinal chemistry, and will inspire other researchers in the design of new synthons based on the merger of hypervalent iodine reagents and redox gold catalysis.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41557-024-01535-8.

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Methods

General procedure for the synthesis of cyclopropenyl benziodoxoles 1 (CpBXs)

An oven-dried Schlenk tube was charged with a magnetic stirring bar and the terminal cyclopropene **s-1** (4.00 mmol, 1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. THF (40 ml) was added by syringe and the Schlenk tube was placed at −78 °C in a dry ice/acetone bath. We then added *n*-butyllithium (2.5 M in hexane; typically, 4.2 mmol, 1.7 ml, 1.05 equiv.) dropwise via a syringe pump over 5 min, and the reaction mixture was stirred at −78 °C for an additional 10 min. Hypervalent iodine precursor **I1** (typically, 4.40 mmol, 1.78 g, 1.10 equiv.) was added in one portion under nitrogen. The reaction mixture was stirred at −78 °C for 15 min, then the cooling bath was removed. The reaction mixture was allowed to warm to room temperature gradually (typically for ~15 min) while stirring. The reaction mixture was then quenched by adding saturated aqueous $NaHCO_3$ (40 ml). The organic layer was removed, and the remaining aqueous portion was extracted with EtOAc (3 × 10 ml). The combined organic portions were dried over Na_2SO_4, filtered, and the volatiles removed under reduced pressure. The crude product was purified by flash chromatography on silica gel, and the fractions that contained the product were collected and concentrated by rotary evaporation to afford the purified compound.

General procedure for the synthesis of alkynyl–cyclopropenes 3

An oven-dried 10-ml Schlenk tube with a magnetic stirring bar was sequentially charged with **L1** (4.20 mg, 20.0 µmol, 10.0 mol%), $(Me_2S)AuCl$ (2.95 mg, 10.0 µmol, 5.0 mol%), terminal alkyne **2** (200 µmol, 1.00 equiv.) and CpBX **1** (200 µmol, 1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (2.0 ml) was added by syringe. If **2** was a liquid, it was added last. The reaction mixture was stirred at room temperature (~21 °C) for the specified time. The reaction mixture was then filtered through a silica gel pad and washed with CH_2Cl_2 (3 × 5 ml). Excess solvent was removed under reduced pressure and the desired product **3** was obtained by column chromatography on silica gel.

General procedure for the synthesis of vinyl–cyclopropenes 6

An oven-dried 10-ml Schlenk tube with a magnetic stirring bar was sequentially charged with **L1** (2.10 mg, 10.0 µmol, 10.0 mol%), $(Me_2S)AuCl$ (1.47 mg, 5.00 µmol, 5.0 mol%), vinylboronic acid **5** (100 µmol, 1.00 equiv.) and CpBX **1** (typically, 130 µmol, 1.30 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (2.0 ml) was added by syringe. The reaction mixture was stirred at 40 °C for the specified time. The reaction mixture was then filtered through a silica gel pad and eluted with CH_2Cl_2 (3 × 5 ml). The solvent was removed under reduced pressure, and the resulting crude residue was subjected to a short column chromatography stage (silica). The fractions that contained the products were collected and analysed by ^1H NMR spectroscopy. The recovered sample was purified by flash column chromatography (C18 reverse phase) to give cross-coupled product **6**.

Data availability

Materials and methods, experimental procedures, computational details, mechanistic studies, ^1H NMR spectra, ^{13}C NMR spectra, ^{11}B NMR spectra, ^{19}F NMR spectra and mass spectrometry data, as well as all other supporting data for the article, are available in the Supplementary Information. Raw data for compound characterization are available with free access on zenodo.org: https://doi.org/10.5281/zenodo.10674147 (ref. 79). Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition nos. CCDC 2260609 (**1k**), 2260610 (**3au**) and 2260611 (**21**). Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/. Source data are provided with this paper.

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Author contributions

X.L. performed the experiments. M.D.W. conducted the density functional theory calculations. X.L. and J.W. contributed to the design of the study, data analysis and writing of the paper.

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Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Jérôme Waser.

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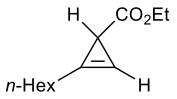
1. General Information

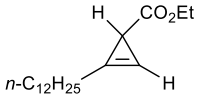
All reactions were carried out using standard Schlenk technique under nitrogen unless otherwise stated. All reagents were purchased from major commercial suppliers (Sigma-Aldrich, Merck, Fluorochem, Combi-blocks, Fluka, Apollo Scientific, Fischer Scientific, Tokyo Chemical Industry, Acros Organics) and used as such unless otherwise noted. Dry solvents (DCM, THF, MeCN, toluene and Et_2O) were obtained fresh from an Innovative Technology solvent purification system having been passed through anhydrous alumina columns. 1,2-Dichloroethane (99.5%, extra dry over molecular sieve, AcrosSeal®) was purchased from Thermo Scientific Chemicals. Unless otherwise stated, solvents were used without further drying or degassing. (Me_2S)AuCl and 1,10-phenanthroline-5,6-dione (**L1**) used in the σ-type CPC transfer reactions were purchased from Sigma-Aldrich and Combi-Blocks, respectively. The AuCl (97%, 99.99%-Au) was purchased from abcr GmbH. Gold(III) chloride (99%) was purchased from Sigma-Aldrich. Ethyl diazoacetate (contains ≥13 wt. % dichloromethane) was purchased from Sigma-Aldrich (E22201-100G) and used without further purification. Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel 60 F_{254} TLC glass plates and visualized with ultraviolet irradiation (254 nm) and/or potassium permanganate stain. Flash column chromatography (FCC) was carried out using Biotage Isolera One with pre-packaged silica cartridges (EcoFlex Silica 4 g, 12 g, 25 g, 40g, 80g, 120g) purchased from Büchi or C18 reverse phase chromatography (Aquarius C18AQ 20 g; 100 Å, Spherical, 30 μm, Flow rate: 10-25 mL/min). ^{1}H NMR spectra were recorded on a Bruker Ascend™ 400 400 MHz spectrometer and reported as chemical shifts (δ) in parts per million (ppm) relative to the residual non-deuterated solvent signal as internal reference (chloroform-*d*: 7.26 ppm; DMSO-d_6: 2.50 ppm; acetoned-d_6: 2.06 ppm; CD_3CN: 1.94 ppm). ^{13}C NMR spectra were recorded with {^{1}H} decoupling on a Bruker Ascend™ 400 101 MHz spectrometer and reported in ppm using the residual solvent signal as internal reference (chloroform-*d*: 77.16 ppm; DMSO-d_6: 39.52 ppm; acetoned-d_6: 29.84 ppm; CD_3CN: 1.32 ppm). ^{19}F-NMR spectra were recorded with {^{1}H} decoupling on a Bruker Ascend™ 400 376 MHz spectrometer. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, sept = septet, br = broad, m = multiplet), coupling constants (Hz) and integration. NMR spectra were processed with MestReNova (version 14.2.1). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL. Electrospray-ionisation HRMS data were acquired on a Q-Tof Ultima mass spectrometer (Waters) or a Q-Tof 6530 Accurate mass spectrometer (Agilent) operated in the positive ionization mode and fitted with a standard Z-spray ion source equipped with the Lock-Spray interface. Data from the Lock-Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. Atmospheric pressure photo-ionisation (APPI) HRMS measurements were done on an LTQ Orbitrap Elite instrument (Thermofisher) operated in the positive ionization mode. The raw data obtained from the Q-TOF Waters instrument does not consider the mass of the electron for the ion, the obtained raw data has been corrected by removing (positive ionization) or adding (negative ionization) the mass of the electron (0.5 mDa). Infrared spectra were recorded using a JASCO FT/IR-4100 Fourier Transform Infrared Spectrometer at room temperature, and the stretching frequencies are reported in wavenumbers (cm^{-1}) (s = strong, m = medium, w = weak). Elemental Analyses were performed using an UNICUBE analyzer (Elementar, France) operated in the CHNS mode. Melting points were measured using a Büchi Melting Point B-540 and were uncorrected. The specific rotation was measured with a Jasco P-2000 polarimeter at 20 °C. The given specific rotation is the mean value from 10 measurements. The concentration for the specific rotation measurements is given in 10 mg/mL.

2. Development of σ-type cyclopropenium cations transfer reagents

2.1. Synthesis of terminal cyclopropenes by rhodium catalysis



s-1a



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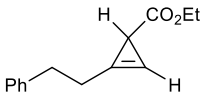
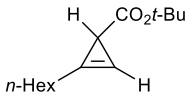


s-1c



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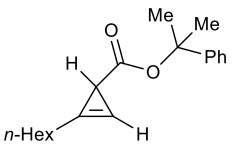

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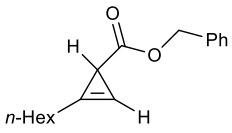

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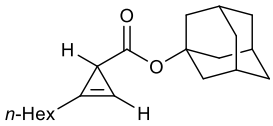
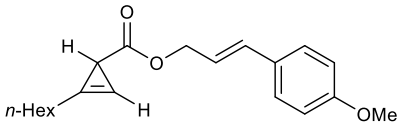


s-1g



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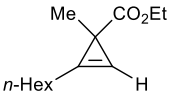

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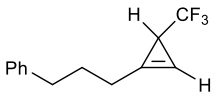
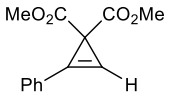
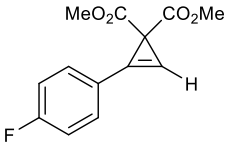


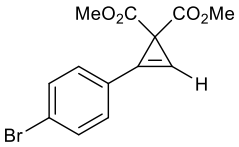
s-1j



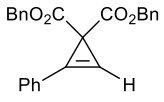
s-1k



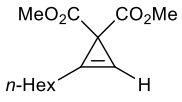
s-1l



s-1m

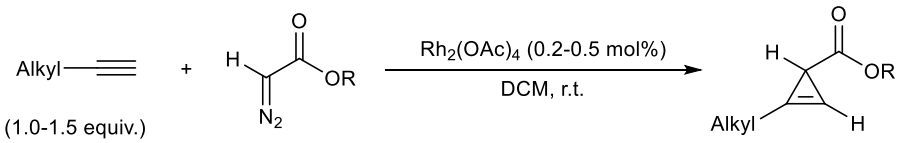


s-1n



s-1o

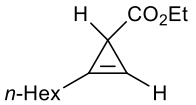
General Procedure A (**GPA**)[1]:



s-1

GPA: To a stirred solution of $Rh_2(OAc)_4$ (0.2-0.5 mol%) and terminal alkyne (1.0-1.5 equiv.) in CH_2Cl_2 (1.00-1.50 M) at room temperature was added a solution of diazo ester (1.0 equiv.) in CH_2Cl_2 (1.00 M) via syringe pump over 8 h under nitrogen. After the addition was complete, the mixture was stirred for additional 8 h, filtered through a short pad of Celite® eluting with CH_2Cl_2, and concentrated under reduced pressure. Purification of the residue by column chromatography (pentane/ethyl acetate) to afford **s-1**.

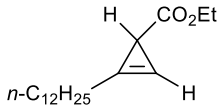
2.1.1. Synthesis and characterization of ethyl 2-hexylcycloprop-2-ene-1-carboxylate (s-1a)



s-1a

Following **GPA**, oct-1-yne (1.65 g, 15.0 mmol, 1.50 equiv.), ethyl diazoacetate (1.21 mL, 10.0 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (22.1 mg, 50.0 μmol, 0.5 mol%) and CH_2Cl_2 (20 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **s-1a** in 79% yield (1.55 g, 7.88 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 40:1) = 0.23; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.32 (q, *J* = 1.5 Hz, 1H, C=C*H*), 4.21 – 4.05 (m, 2H, OCH_2CH$_3$), 2.49 (td, *J* = 7.3, 1.4 Hz, 2H, CH$_2$CH_2C), 2.12 (d, *J* = 1.5 Hz, 1H, C*H*CO$_2$Et), 1.64 – 1.51 (m, 2H, CH_2CH$_2$C), 1.44 – 1.20 (m, 9H, CH_2 & OCH$_2$CH_3), 0.96 – 0.82 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 115.8, 94.0, 60.3, 31.6, 28.9, 26.8, 25.1, 22.7, 19.9, 14.5, 14.2. The NMR spectroscopic data is consistent with previous report[2].

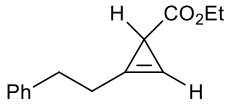
2.1.2. Synthesis and characterization of ethyl 2-dodecylcycloprop-2-ene-1-carboxylate (s-1b)



s-1b

Following **GPA**, tetradec-1-yne (1.94 g, 10.0 mmol, 1.0 equiv.), ethyl diazoacetate (1.21 mL, 10.0 mmol, 1.0 equiv.), $Rh_2(OAc)_4$ (22.1 mg, 50.0 μmol, 0.5 mol%) and CH_2Cl_2 (20 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **s-1b** in 70% yield (1.97 g, 7.03 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 20:1) = 0.44; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.31 (q, *J* = 1.5 Hz, 1H, C=C*H*), 4.18 – 4.06 (m, 2H, OCH_2CH$_3$), 2.48 (td, *J* = 7.3, 1.4 Hz, 2H, CH$_2$CH_2C), 2.12 (d, *J* = 1.5 Hz, 1H, C*H*CO$_2$Et), 1.61 – 1.54 (m, 2H, CH_2CH$_2$C), 1.39 – 1.19 (m, 21H, CH_2 & OCH$_2$CH_3), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 115.8, 94.0, 60.3, 32.1, 29.80, 29.78, 29.76, 29.7, 29.5, 29.4, 29.3, 26.8, 25.1, 22.8, 19.9, 14.5, 14.3; **IR** (ν_{max}, cm^{-1}) 2955 (m), 2925 (s), 2855 (s), 1725 (s), 1465 (m), 1370 (w), 1339 (w), 1253 (m), 1183 (s), 1038 (m), 960 (w), 745 (w); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{32}NaO_2^+$ 303.2295; Found 303.2295.

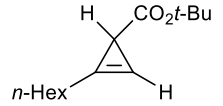
2.1.3. Synthesis and characterization of ethyl 2-phenethylcycloprop-2-ene-1-carboxylate (s-1c)



s-1c

Following **GPA**, but-3-yn-1-ylbenzene (1.95 g, 15.0 mmol, 1.50 equiv.), ethyl diazoacetate (1.21 mL, 10.0 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (8.84 mg, 20.0 μmol, 0.2 mol%) and CH_2Cl_2 (20 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **s-1c** in 67% yield (1.46 g, 6.74 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 20:1) = 0.29; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H, Ar*H*), 7.24 – 7.16 (m, 3H, Ar*H*), 6.36 (q, *J* = 1.4 Hz, 1H, C=C*H*), 4.20 – 4.04 (m, 2H, OCH_2CH$_3$), 2.95 – 2.88 (m, 2H, CH$_2$CH_2), 2.86 – 2.78 (m, 2H, CH_2CH$_2$), 2.14 (d, *J* = 1.5 Hz, 1H, C*H*CO$_2$Et), 1.25 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3). The NMR spectroscopic data is consistent with previous report[1].

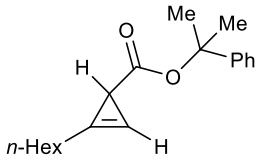
2.1.4. Synthesis and characterization of *tert*-butyl 2-hexylcycloprop-2-ene-1-carboxylate (s-1d)



s-1d

Following **GPA**, oct-1-yne (482 mg, 4.37 mmol, 1.5 equiv.), *tert*-butyl 2-diazoacetate (414 mg, 2.92 mmol, 1.0 equiv.), $Rh_2(OAc)_4$ (6.44 mg, 14.6 μmol, 0.5 mol%) and CH_2Cl_2 (10 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **s-1d** in 53% yield (350 mg, 1.56 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 20:1) = 0.41; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.29 (q, *J* = 1.5 Hz, 1H, C=C*H*), 2.47 (tt, *J* = 7.2, 1.6 Hz, 2H, CH$_2$CH_2C), 2.02 (d, *J* = 1.6 Hz, 1H, C*H*CO$_2$), 1.61 – 1.53 (m, 2H, CH_2CH$_2$C), 1.43 (s, 9H, C(CH_3)$_3$), 1.40 – 1.25 (m, 6H, CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.2, 116.1, 94.3, 79.7, 31.7, 29.0, 28.3, 26.9, 25.1, 22.7, 20.8, 14.2; **IR** (ν_{max}, cm^{-1}) 2958 (m), 2930 (m), 2860 (w), 1801 (w), 1720 (s), 1458 (w), 1391 (w), 1367 (m), 1346 (m), 1273 (w), 1254 (m), 1213 (m), 1153 (s), 963 (m), 858 (w), 741 (m); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{14}H_{24}NaO_2^+$ 247.1669; Found 247.1677.

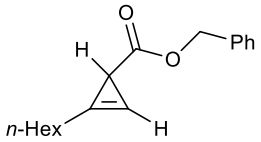
2.1.5. Synthesis and characterization of 2-phenylpropan-2-yl 2-hexylcycloprop-2-ene-1-carboxylate (s-1e)



s-1e

Following **GPA**, oct-1-yne (491 mg, 4.46 mmol, 1.50 equiv.), 2-phenylpropan-2-yl 2-diazoacetate[3] (606 mg, 2.97 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (6.60 mg, 14.9 μmol, 0.5 mol%) and CH_2Cl_2 (10 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **s-1e** in 63% yield (537 mg, 1.88 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 20:1) = 0.36; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H, Ar*H*), 7.24 – 7.20 (m, 1H, Ar*H*), 6.32 (q, *J* = 1.5 Hz, 1H, C=C*H*), 2.48 (tt, *J* = 7.2, 1.3 Hz, 2H, CH_2CH_2C), 2.14 (d, *J* = 1.5 Hz, 1H, $CHCO_2$), 1.78 (s, 3H, $C(CH_3)$), 1.75 (s, 3H, $C(CH_3)$), 1.61 – 1.53 (m, 2H, CH_2CH_2C), 1.40 – 1.23 (m, 6H, CH_2), 0.89 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.4, 146.6, 128.3, 126.9, 124.4, 116.0, 94.2, 81.1, 31.7, 29.1, 29.0, 28.6, 26.9, 25.2, 22.7, 20.8, 14.2; **IR** (ν_{max}, cm^{-1}) 2979 (m), 2957 (m), 2929 (m), 2863 (m), 2858 (m), 1802 (w), 1726 (s), 1496 (m), 1449 (m), 1382 (m), 1270 (m), 1191 (s), 1136 (s), 1102 (s), 1076 (m), 1031 (m), 967 (m), 763 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{26}NaO_2^+$ 309.1825; Found 309.1829.

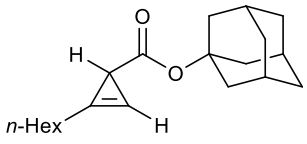
2.1.6. Synthesis and characterization of benzyl 2-hexylcycloprop-2-ene-1-carboxylate (s-1f)



s-1f

Following **GPA**, oct-1-yne (3.31 g, 30.0 mmol, 1.50 equiv.), benzyl 2-diazoacetate (90% w/w in CH_2Cl_2, 3.92 g, 20.0 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (44.2 mg, 100 μmol, 0.5 mol%) and CH_2Cl_2 (30 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **s-1f** in 62% yield (3.21 g, 12.4 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 40:1) = 0.19; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H, Ar*H*), 6.34 (q, *J* = 1.5 Hz, 1H, C=C*H*), 5.20 – 5.05 (m, 2H, OCH_2Ph), 2.49 (td, *J* = 7.3, 1.4 Hz, 2H, CH_2CH_2C), 2.19 (d, *J* = 1.6 Hz, 1H, $CHCO_2$), 1.66 – 1.46 (m, 2H, CH_2CH_2C), 1.42 – 1.18 (m, 6H, CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.6, 136.6, 128.6, 128.2, 128.1, 115.7, 94.0, 66.1, 31.6, 28.9, 26.7, 25.1, 22.7, 19.9, 14.2. The NMR spectroscopic data is consistent with previous report[4].

2.1.7. Synthesis and characterization of adamantan-1-yl 2-hexylcycloprop-2-ene-1-carboxylate (s-1g)

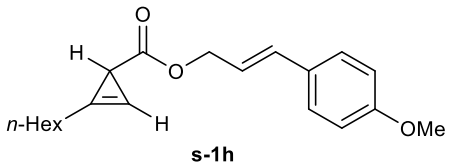


s-1g

Following **GPA**, oct-1-yne (331 mg, 3.00 mmol, 1.50 equiv.), adamantan-1-yl 2-diazoacetate[7] (459 mg, 2.00 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (4.40 mg, 10.0 μmol, 0.5 mol%) and CH_2Cl_2 (10 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **s-1g** in 70% yield (421 mg, 1.39 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 40:1) = 0.22; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.28 (q, *J* = 1.4 Hz, 1H, C=C*H*), 2.46 (tt, *J* = 7.2, 1.6 Hz, 2H, CH_2CH_2C), 2.17 – 2.11 (m, 3H,

C*H*(adamantyl)), 2.11 – 2.07 (m, 6H, C*H*$_2$(adamantyl)), 2.01 (d, *J* = 1.6 Hz, 1H, C*H*CO$_2$), 1.69 – 1.60 (m, 6H, C*H*$_2$(adamantyl)), 1.59 – 1.52 (m, 2H, C*H*$_2$CH$_2$C), 1.40 – 1.23 (m, 6H, C*H*$_2$), 0.88 (t, *J* = 6.8 Hz, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.9, 116.1, 94.3, 79.8, 41.6, 36.4, 31.6, 31.0, 28.9, 26.9, 25.1, 22.7, 20.9, 14.2; **IR** (ν_{max}, cm^{-1}) 2954 (w), 2912 (m), 2855 (m), 1800 (w), 1712 (m), 1456 (m), 1346 (m), 1256 (m), 1181 (s), 1103 (w), 1056 (s), 971 (m), 734 (s); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{30}NaO_2^+$ 325.2138; Found 325.2136.

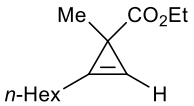
2.1.8. Synthesis and characterization of (*E*)-3-(4-methoxyphenyl)allyl 2-hexylcycloprop-2-ene-1-carboxylate (s-1h)



s-1h

Following **GPA**, oct-1-yne (260 mg, 2.36 mmol, 1.50 equiv.), (*E*)-3-(4-methoxyphenyl)allyl 2-diazoacetate[5] (366 mg, 1.57 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (3.50 mg, 7.85 μmol, 0.5 mol%) and CH_2Cl_2 (10 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **s-1h** in 65% yield (321 mg, 1.02 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 5:1) = 0.49; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H, Ar*H*), 6.92 – 6.78 (m, 2H, Ar*H*), 6.68 – 6.50 (m, 1H, C=C*H*), 6.34 (q, *J* = 1.4 Hz, 1H, CH$_2$C*H*=CH), 6.16 (dt, *J* = 15.8, 6.6 Hz, 1H, CH$_2$CH=C*H*), 4.71 (ddd, *J* = 6.7, 3.4, 1.3 Hz, 2H, C*H*$_2$CH=CH), 3.81 (s, 3H, OC*H*$_3$), 2.50 (td, *J* = 7.4, 1.4 Hz, 2H, CH$_2$C*H*$_2$C), 2.17 (d, *J* = 1.6 Hz, 1H, C*H*CO$_2$), 1.63 – 1.53 (m, 2H, C*H*$_2$CH$_2$C), 1.43 – 1.19 (m, 6H, C*H*$_2$), 0.87 (t, *J* = 6.8 Hz, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.6, 159.6, 133.7, 129.3, 128.0, 121.5, 115.7, 114.1, 94.0, 65.3, 55.4, 31.6, 28.9, 26.8, 25.1, 22.7, 19.9, 14.2; **IR** (ν_{max}, cm^{-1}) 3144 (w), 2957 (m), 2930 (m), 2859 (m), 1721 (m), 1607 (m), 1512 (s), 1464 (m), 1378 (w), 1337 (w), 1305 (w), 1248 (s), 1169 (s), 1032 (m), 966 (m), 836 (m), 808 (w), 719 (w); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{26}NaO_3^+$ 337.1774; Found 337.1788.

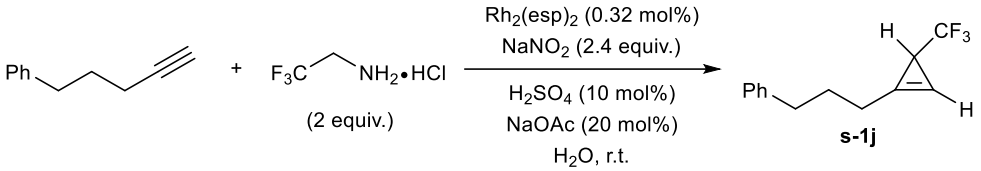
2.1.9. Synthesis and characterization of ethyl 2-hexyl-1-methylcycloprop-2-ene-1-carboxylate (s-1i)



s-1i

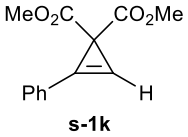
Following **GPA**, oct-1-yne (579 mg, 5.25 mmol, 1.50 equiv.), ethyl diazoalaninate (448 mg, 3.50 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (7.74 mg, 17.5 μmol, 0.5 mol%) and CH_2Cl_2 (15 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **s-1i** in 42% yield (313 mg, 1.49 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 20:1) = 0.34; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.38 (td, *J* = 1.4, 0.7 Hz, 1H, C=C*H*), 4.15 – 3.97 (m, 2H, OC*H*$_2$CH$_3$), 2.44 (td, *J* = 7.3, 1.4 Hz, 2H, CH$_2$C*H*$_2$C), 1.59 – 1.47 (m, 2H, C*H*$_2$CH$_2$C), 1.42 – 1.23 (m, 9H, C*H*$_2$ & CC*H*$_3$), 1.20 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), 0.97 – 0.77 (m, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.8, 121.5, 100.0, 60.3, 31.6, 29.0, 27.0, 24.5, 24.3, 22.6, 20.8, 14.5, 14.1. The NMR spectroscopic data is consistent with previous report[6].

2.1.10. Synthesis and characterization of (3-(3-(trifluoromethyl)cycloprop-1-en-1-yl)propyl)benzene (s-1j)



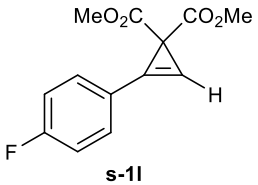
Following a reported procedure[7]: An oven-dried 100 mL Schlenk tube was sequentially charged with a magnetic stir-bar, $Rh_2(esp)_2$ (24.2 mg, 31.7 μmol, 0.32 mol%) and NaOAc (164 mg, 2.00 mmol, 20 mol%). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, distilled water (36 mL) was added under nitrogen. To this stirring mixture was added trifluoroethylamine hydrochloride (2.71 g, 20.0 mmol, 2.00 equiv.), H_2SO_4 (53.6 μL, 1.00 mmol, 10 mol%) and pent-4-yn-1-ylbenzene (1.44 g, 10.0 mmol, 1.0 equiv.) sequentially. Then, aqueous $NaNO_2$ (1.66 g, 24.0 mmol, 2.40 equiv.; dissolved in 20 mL of water) was added by syringe pump over 10 hours. After additional 4 hours, CH_2Cl_2 and water were added, and the water layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic portions were dried with Na_2SO_4 and evaporated under reduced pressure. The resulting crude residue was purified by column chromatography on silica gel (eluent: pentane) to afford **s-1j** in 34% yield (774 mg, 3.42 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 40:1) = 0.47; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H, Ar*H*), 7.25 – 7.15 (m, 3H, Ar*H*), 6.43 (hept, *J* = 1.6 Hz, 1H, C=C*H*), 2.70 (dd, *J* = 8.4, 6.8 Hz, 2H, CH_2CH_2C), 2.53 (td, *J* = 7.3, 1.3 Hz, 2H, CH_2CH_2C), 2.01 – 1.92 (m, 3H, $CHCF_3$ & CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 128.6, 128.6, 126.6 (q, *J* = 275.6 Hz), 126.2, 116.7 (q, *J* = 2.7 Hz), 95.0 (q, *J* = 3.3 Hz), 35.3, 28.4, 24.5, 19.2 (q, *J* = 39.3 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -67.0; **IR** (ν_{max}, cm^{-1}) 3151 (w), 3029 (w), 2944 (w), 2864 (w), 1497 (w), 1455 (w), 1366 (w), 1275 (s), 1120 (s), 953 (w), 829 (m), 745 (m); **HRMS** (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{13}H_{13}F_3^+$ 226.0964; Found 226.0967.

2.1.11. Synthesis and characterization of dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (s-1k)



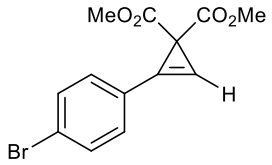
Following **GPA**, phenylacetylene (0.98 mL, 8.91 mmol, 1.50 equiv.), dimethyl diazomalonate (940 mg, 5.94 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (13.1 mg, 29.7 μmol, 0.5 mol%) and CH_2Cl_2 (10 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **s-1k** in 62% yield (850 mg, 3.66 mmol) as a colourless solid. **TLC**: R_f (*n*-hexane: EtOAc = 5:1) = 0.24; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H, Ar*H*), 7.54 – 7.30 (m, 3H, Ar*H*), 6.89 (s, 1H, C=C*H*), 3.73 (s, 6H, OCH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 130.7, 130.5, 129.0, 124.1, 112.4, 95.4, 52.5, 32.9. The NMR spectroscopic data is consistent with previous report[8].

2.1.12. Synthesis and characterization of dimethyl 2-(4-fluorophenyl)cycloprop-2-ene-1,1-dicarboxylate (s-1l)



Following **GPA**, 1-ethynyl-4-fluorobenzene (961 mg, 8.00 mmol, 1.00 equiv.), dimethyl diazomalonate (1.27 g, 8.00 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (17.7 mg, 40.0 μmol, 0.5 mol%) and CH_2Cl_2 (8.0 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **s-1l** in 48% yield (961 mg, 3.84 mmol) as a colourless solid. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.25; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.57 (m, 2H, Ar*H*), 7.21 – 7.07 (m, 2H, Ar*H*), 6.86 (s, 1H, C=C*H*), 3.73 (s, 6H, OCH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 165.3, 162.8, 132.6 (d, *J* = 8.8 Hz), 120.4 (d, *J* = 3.3 Hz), 116.4 (d, *J* = 22.3 Hz), 111.5, 95.0 (d, *J* = 2.6 Hz), 52.6, 33.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.1. The NMR spectroscopic data is consistent with previous report[9].

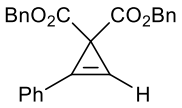
2.1.13. Synthesis and characterization of dimethyl 2-(4-bromophenyl)cycloprop-2-ene-1,1-dicarboxylate (s-1m)



s-1m

Following **GPA**, starting from dimethyl 2-diazomalonate (395 mg, 2.50 mmol, 1.00 equiv.) and 1-bromo-4-ethynylbenzene (1.36 g, 7.50 mmol, 3.00 equiv.), the product **s-1m** was obtained after purification by column chromatography (SiO_2, pentane: EtOAc = 95:5 to 85:15) as a pale-yellow oil (554 mg, 1.78 mmol, 71% yield). **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.28; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H, Ar*H*), 7.51 – 7.46 (m, 2H, Ar*H*), 6.94 (s, 1H, C=C*H*), 3.73 (s, 6H, CO_2CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.0, 132.4, 131.9, 125.4, 123.1, 111.7, 96.4, 52.7, 33.0. The NMR spectroscopic data is consistent with previous report[7].

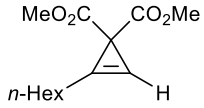
2.1.14. Synthesis and characterization of dibenzyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate (s-1n)



s-1n

Following **GPA**, phenylacetylene (613 mg, 6.00 mmol, 1.50 equiv.), dibenzyl 2-diazomalonate (1.24 g, 4.00 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (8.80 mg, 20.0 μmol, 0.5 mol%) and CH_2Cl_2 (20 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **s-1n** in 48% yield (734 mg, 1.91 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 5:1) = 0.32; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 2H, Ar*H*), 7.40 (dd, *J* = 5.0, 2.0 Hz, 3H, Ar*H*), 7.31 – 7.19 (m, 10H, Ar*H*), 6.89 (s, 1H, C=C*H*), 5.16 (s, 4H, OCH_2Ph); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 135.9, 130.7, 130.5, 129.0, 128.6, 128.2, 128.0, 124.0, 112.5, 95.3, 67.0, 33.5. The NMR spectroscopic data is consistent with previous report[7].

2.1.15. Synthesis and characterization of dimethyl 2-hexylcycloprop-2-ene-1,1-dicarboxylate (s-1o)

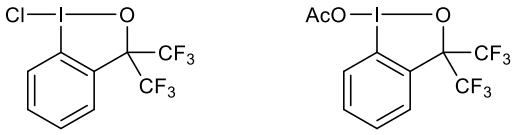


s-1o

Following **GPA**, oct-1-yne (1.1 mL, 7.50 mmol, 1.50 equiv.), dimethyl 2-diazomalonate (791 mg, 5.00 mmol, 1.00 equiv.), $Rh_2(OAc)_4$ (4.40 mg, 10.0 μmol, 0.2 mol%) and CH_2Cl_2 (10 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **s-1o** in 69% yield (832 mg,

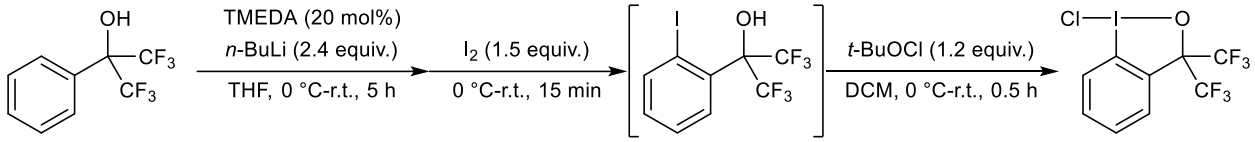
3.46 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.28; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.35 (t, *J* = 1.5 Hz, 1H, C=C*H*), 3.71 (s, 6H, CO_2CH_3), 2.54 (td, *J* = 7.4, 1.5 Hz, 2H, CH_2CH_2C), 1.66 – 1.51 (m, 2H, CH_2CH_2C), 1.46 – 1.18 (m, 6H, CH_2), 1.02 – 0.75 (m, 3H, CH_3). The NMR spectroscopic data is consistent with previous report[10].

2.2. Synthesis of hypervalent iodine precursor



I1 **I2**

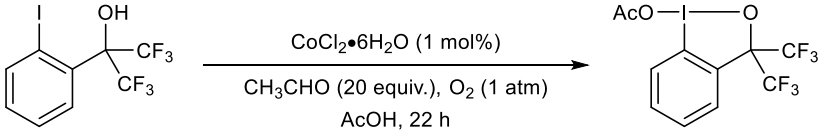
2.2.1. Synthesis and characterization of 1-chloro-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (I1)[11]



4 **I1**

Under nitrogen, TMEDA (1.2 mL, 8.00 mmol, 20.0 mol%) was added to a solution of *n*-BuLi (2.5 M in hexane, 38.4 mL, 96 mmol, 2.40 equiv.). After 15 min, the cloudy solution was cooled to 0 °C and 1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-ol (9.77 g, 40.0 mmol, 1.00 equiv.) in THF (10 mL) was added dropwise. The reaction was stirred at 0 °C for 30 min and then at room temperature for 5 hours. I_2 (15.2 g, 60.0 mmol, 1.50 equiv.) was then added in several portions at 0 °C and the mixture was stirred at 0 °C for 5 min and room temperature for 10 min. The reaction was quenched with saturated NH_4Cl (sat. aq., 10 mL). Et_2O (20 mL) was added and the layers were separated. The aqueous layer was then extracted with Et_2O (10 mL × 2). The organic layers were combined, washed twice with sodium bisulfite solution ($NaHSO_3$, ⩾37% in water; 10 mL), dried over Na_2SO_4, and filtered. The resulting solvent was evaporated under the reduced pressure to afford 1,1,1,3,3,3-hexafluoro-2-(2-iodophenyl)propan-2-ol (**4**) as an brown oil which was used without further purification. The crude product was dissolved in CH_2Cl_2 (10 mL) under air. *t*-BuOCl (5.21 g, 48.0 mmol, 1.20 equiv.) was then added dropwise at 0 °C. The resulting suspension was stirred under room temperature for 30 min. Then, the reaction mixture was filtered and washed with CH_2Cl_2 (10 mL) and pentane (10 mL) to afford 1-chloro-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (**I1**) in 58% yield (9.38 g, 23.2 mmol) as a yellow solid. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.17 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.08 – 8.04 (m, 1H), 7.96 – 7.92 (m, 1H), 7.86 – 7.83 (m, 1H); **^{13}C NMR** (101 MHz, Acetone-d_6) δ 135.2, 133.1, 132.9, 130.5 (m), 130.0, 124.1 (q, *J* = 288.7 Hz), 114.1, 86.2 (m); **^{19}F NMR** (377 MHz, Acetone-d_6) δ -76.5. The NMR spectroscopic data is consistent with previous report[12].

2.2.2. Synthesis and characterization of 3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (I2)[13]

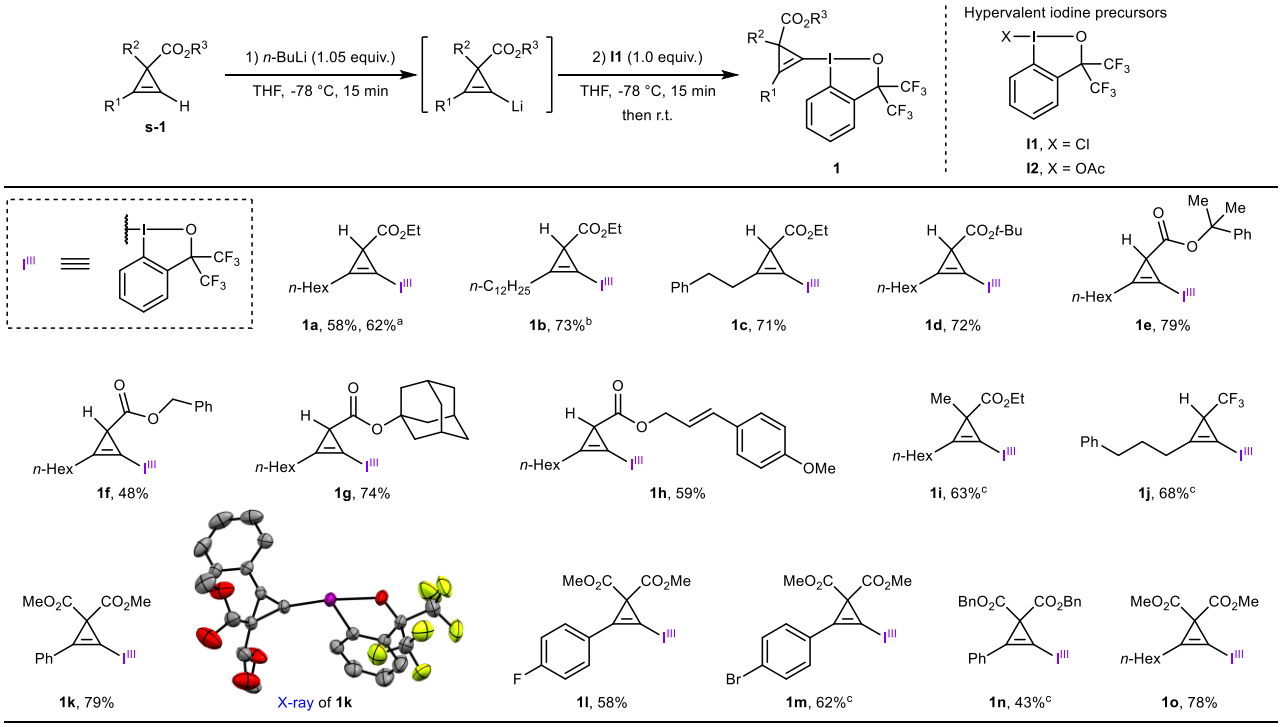


4 **I2**

An oven-dried Schlenk tube was charged with a magnetic stir-bar and $CoCl_2 \cdot 6H_2O$ (32.5 mg, 137 μmol, 1.00 mol%). The Schlenk tube was then evacuated and backfilled with oxygen for three times. After that, 1,1,1,3,3,3-hexafluoro-2-(2-iodophenyl)propan-2-ol (**4**) (5.05 g, 13.7 mmol, 1.00 equiv. dissolved

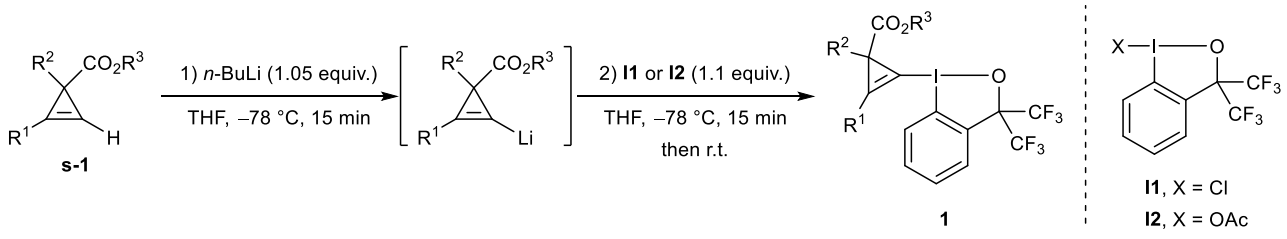
in 68 mL glacial AcOH) and acetaldehyde (137 mmol, 7.7 mL, 10.0 equiv.) were added by syringe. The reaction mixture was stirred under 1 atm O_2, delivered by inflated balloon at 21 °C for 12 hours. After that, additional acetaldehyde (137 mmol, 7.7 mL, 10.0 equiv.) was added by syringe. The reaction mixture was stirred under 1 atm O_2 and 21 °C for additional 10 hours. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (20 mL). The organic layer was washed with distilled water (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$ and solvent was removed in vacuo to afford the oily product. Pentane (150 mL) was added gradually to the flask containing the product, which caused a precipitation. Filtration of the resulting suspension afforded 3,3-bis(trifluoromethyl)-1λ³-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl acetate (**I2**) as a white solid in 56% yield (3.28 g, 7.67 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 1H), 7.86 – 7.45 (m, 3H), 2.18 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.7, 133.6, 131.7, 131.2, 130.4, 129.8 (m), 123.2 (q, *J* = 289.3 Hz), 115.9, 85.8 (m), 20.6; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -75.9. The NMR spectroscopic data is consistent with previous report[14].

2.3. Synthesis of σ-type cyclopropenium cations transfer reagents CpBXs



Reaction conditions: (1) Terminal cyclopropenes (1.0 equiv.), *n*-butyllithium (1.05 equiv.), THF (0.1 M), -78 °C for 15 min; (2) **I1** (1.0 equiv.), −78 °C for 15 min, then warm up to room temperature. [a]**I2** was used instead of **I1**. [b]**I1** (1.1 equiv.) was used. [c]N_2(l)/ethanol bath (−116 °C) and THF/Et_2O = 1:1 as the mixed solvents were used instead of THF.

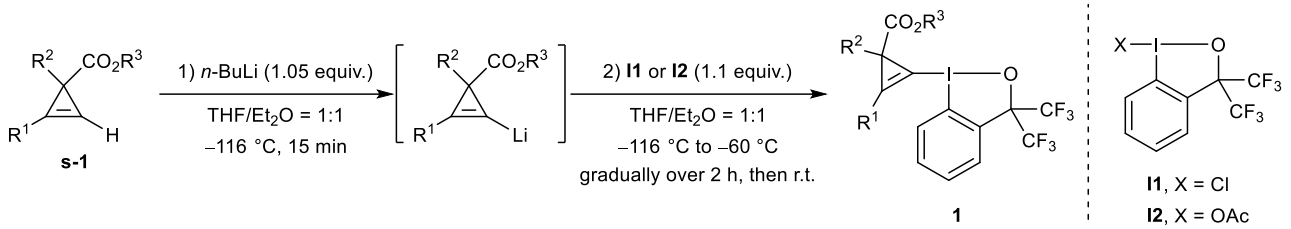
General Procedure B (**GPB**): Synthesis of σ-type cyclopropenium cation transfer reagents (CpBXs). **GPB** was applied for the synthesis of **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1k**, **1l** and **1o**.



GPB: An oven-dried Schlenk tube was charged with a magnetic stir-bar and terminal cyclopropene **s-1** (1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, THF (typically, 0.10 M) was added by syringe and the Schlenk tube was placed at −78 °C in a dry ice/acetone bath. *n*-Butyllithium (2.5 M in hexane; 1.05 equiv.) was added dropwise by a syringe pump

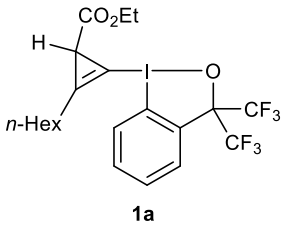
over 5 min and the reaction mixture was stirred at −78 °C for additional 10 min. Then, hypervalent iodine precursor **I1** or **I2** (1.10 equiv.) was added in one portion under nitrogen. The reaction mixture was stirred at −78 °C for 15 min, then the cooling bath was removed. The reaction mixture was allowed to warm to room temperature gradually (typically, ca. 15 min) while keeping stirring. The reaction mixture was then quenched by adding saturated aqueous $NaHCO_3$ (10 ml/mmol). The organic phase was removed, and the remaining aqueous portion was extracted with EtOAc. The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel, and the fractions that contained the product were collected and concentrated by rotary evaporation to afford the purified compound **1**.

General Procedure C (**GPC**): Synthesis of σ-type cyclopropenium cation transfer reagents (CpBXs). **GPC** was applied for the synthesis of **1i**, **1j**, **1m** and **1n**.



GPC: An oven-dried Schlenk tube was charged with a magnetic stir-bar and terminal cyclopropene **s-1** (1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, THF/Et_2O = 1:1 was added by syringe and the Schlenk tube was placed at −116 °C in a liquid nitrogen/ethanol bath. *n*-Butyllithium (2.5 M in hexane; 1.05 equiv.) was added dropwise by a syringe pump over 5 min and the reaction mixture was stirred at −116 °C for additional 10 min. Then, hypervalent iodine precursor **I1** or **I2** (1.1 equiv.) was added in one portion under nitrogen. The reaction mixture was stirred in the cooling bath without adding more liquid nitrogen for additional 2 hours, thus resulting a gradual warm-up of the stirring mixture to ca. −60 °C. Then, the cooling bath was removed. The reaction mixture was allowed to warm further to room temperature naturally (typically, ca. 15 min) while keeping stirring. The reaction mixture was then quenched by adding saturated aqueous $NaHCO_3$ (10 ml/mmol). The organic phase was removed, and the remaining aqueous portion was extracted with EtOAc (3 × 10 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel, and the fractions that contained the product were collected and concentrated by rotary evaporation to afford the purified compound **1**.

2.3.1. Synthesis and characterization of ethyl 2-(3,3-bis(trifluoromethyl)-1λ³-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-hexylcycloprop-2-ene-1-carboxylate (1a)

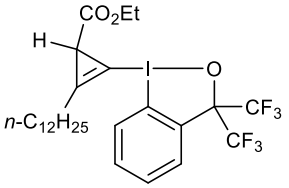


Following **GPB**, **s-1a** (1.96 g, 10.0 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 4.0 mL, 10.0 mmol, 1.00 equiv.), **I1** (4.05 g, 10.0 mmol, 1.00 equiv.) and THF (30 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **1a** in 58% yield (3.30 g, 5.85 mmol) as a colourless oil, which turned to be solidified when stored in the freezer.

In a second reaction, **s-1a** (1.96 g, 10.0 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 4.2 mL, 10.5 mmol, 1.05 equiv.), **I2** (4.28 g, 10.0 mmol, 1.00 equiv.) and THF (30 mL) were used, which afforded **1a** in 62% yield (3.49 g, 6.18 mmol).

M.p. 54 – 55 °C. **TLC**: R_f (*n*-hexane: EtOAc = 5:1) = 0.28; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 1H, Ar*H*), 7.71 (dd, *J* = 8.2, 1.2 Hz, 1H, Ar*H*), 7.64 (td, *J* = 7.4, 1.2 Hz, 1H, Ar*H*), 7.57 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H, Ar*H*), 4.17 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 2.70 (t, *J* = 7.3 Hz, 2H, CH$_2$C*H*$_2$C), 2.64 (s, 1H, C*H*CO$_2$), 1.73 – 1.57 (m, 2H, C*H*$_2$CH$_2$C), 1.44 – 1.32 (m, 2H, C*H*$_2$), 1.29 – 1.23 (m, 7H, C*H*$_2$ & OCH$_2$C*H*$_3$), 0.94 – 0.76 (m, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 133.8, 132.8, 131.1, 130.9, 130.3 (hept, *J* = 2.5 Hz), 129.4, 123.8 (q, *J* = 291.6 Hz), 111.7, 81.1 (hept, *J* = 29.2 Hz), 80.4, 61.1, 31.5, 29.0, 27.0, 26.3, 26.1, 22.6, 14.4, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.1 (m); **IR** (ν_{max}, cm^{-1}) 2960 (w), 2932 (w), 2861 (w), 1809 (w), 1717 (m), 1565 (w), 1465 (w), 1441 (w), 1370 (w), 1337 (w), 1264 (m), 1178 (s), 1150 (s), 1021 (w), 965 (m), 949 (s), 761 (m), 754 (m), 730 (s); **HRMS** (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{21}H_{24}F_6IO_3^+$ 565.0669; Found 565.0686.

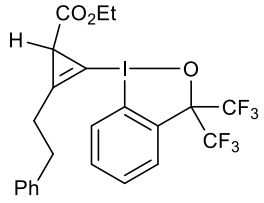
2.3.2. Synthesis and characterization of ethyl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-dodecylcycloprop-2-ene-1-carboxylate (1b)



1b

Following **GPB**, **s-1b** (1.35 g, 4.83 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 2.0 mL, 5.07 mmol, 1.05 equiv.), **I1** (2.15 g, 5.31 mmol, 1.10 equiv.) and THF (20 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **1b** in 73% yield (2.27 g, 3.51 mmol) as a colourless oil, which turned to be solidified when stored in the freezer. **M.p.** 39 – 40 °C. **TLC**: R_f (*n*-hexane: EtOAc = 3:1) = 0.55; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dq, *J* = 7.8, 1.5 Hz, 1H, Ar*H*), 7.72 (dd, *J* = 8.2, 1.2 Hz, 1H, Ar*H*), 7.65 (td, *J* = 7.4, 1.2 Hz, 1H, Ar*H*), 7.58 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H, Ar*H*), 4.18 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 2.71 (t, *J* = 7.3 Hz, 2H, CH$_2$C*H*$_2$C), 2.64 (s, 1H, C*H*CO$_2$), 1.72 – 1.58 (m, 2H, C*H*$_2$CH$_2$C), 1.43 – 1.33 (m, 2H, C*H*$_2$), 1.33 – 1.14 (m, 19H, C*H*$_2$ & OCH$_2$C*H*$_3$), 0.87 (t, *J* = 6.8 Hz, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 133.8, 132.9, 131.1, 130.9, 130.4 (m), 129.4, 123.8 (q, *J* = 290.8 Hz), 111.7, 81.2 (hept, *J* = 29.3 Hz), 80.5, 61.2, 32.0, 29.73 (2C), 29.69, 29.6, 29.5, 29.4, 29.3, 27.0, 26.4, 26.2, 22.8, 14.5, 14.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.1 (m); **IR** (ν_{max}, cm^{-1}) 2928 (m), 2855 (m), 1811 (w), 1721 (m), 1565 (w), 1465 (w), 1442 (w), 1371 (w), 1335 (w), 1264 (s), 1180 (s), 1149 (s), 1020 (w), 964 (m), 950 (s), 867 (w), 757 (m), 727 (m); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{27}H_{35}F_6INaO_3^+$ 671.1427; Found 671.1435.

2.3.3. Synthesis and characterization of ethyl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-phenethylcycloprop-2-ene-1-carboxylate (1c)

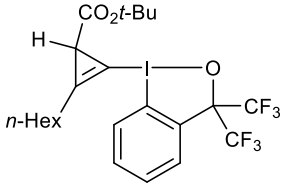


1c

Following **GPB**, **s-1c** (865 mg, 4.00 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 1.6 mL, 4.00 mmol, 1.00 equiv.), **I1** (1.62 g, 4.00 mmol, 1.00 equiv.) and THF (24 mL) were used. Column

chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **1c** in 71% yield (1.66 g, 2.84 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.26; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.71 – 7.58 (m, 1H, Ar*H*), 7.58 – 7.44 (m, 2H, Ar*H*), 7.36 – 7.12 (m, 5H, Ar*H*), 4.19 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 3.19 – 3.08 (m, 2H, C*H*$_2$), 3.08 – 2.95 (m, 2H, C*H*$_2$), 2.62 (s, 1H, C*H*CO$_2$), 1.30 (t, *J* = 7.2 Hz, 3H, OCH$_2$C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 139.5, 132.8, 132.5, 130.9, 130.7, 130.2 (m), 129.3, 128.9, 128.3, 126.9, 123.8 (q, *J* = 290.8 Hz), 111.6, 81.6, 81.1 (hept, *J* = 29.4 Hz), 61.2, 32.1, 27.3, 26.9, 14.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.0; **IR** (ν_{max}, cm^{-1}) 3066 (w), 3030 (w), 2982 (w), 2933 (w), 1810 (w), 1715 (m), 1440 (w), 1264 (m), 1178 (s), 1149 (s), 1133 (s), 1021 (m), 964 (m), 949 (s), 866 (w), 795 (w), 753 (m), 730 (s); **HRMS** (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{23}H_{20}F_6IO_3^+$ 585.0356; Found 585.0351.

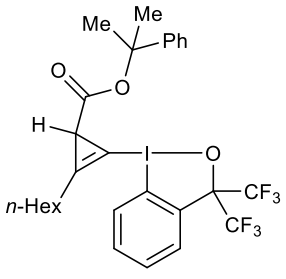
2.3.4. Synthesis and characterization of *tert*-butyl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-hexylcycloprop-2-ene-1-carboxylate (1d)



1d

Following **GPB**, **s-1d** (329 mg, 1.47 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 0.62 mL, 1.54 mmol, 1.05 equiv.), **I1** (593 mg, 1.47 mmol, 1.00 equiv.) and THF (15 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **1d** in 72% yield (627 mg, 1.06 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.43; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dq, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 7.71 – 7.60 (m, 2H, Ar*H*), 7.56 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H, Ar*H*), 2.70 (td, *J* = 7.2, 1.4 Hz, 2H, CH$_2$C*H*$_2$C), 2.56 (s, 1H, C*H*CO$_2$), 1.68 – 1.61 (m, 2H, C*H*$_2$CH$_2$C), 1.46 (s, 9H, C(C*H*$_3$)$_3$), 1.43 – 1.34 (m, 2H, C*H*$_2$), 1.33 – 1.24 (m, 4H, C*H*$_2$), 0.93 – 0.79 (m, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 134.5, 132.8, 131.1, 130.9, 130.4 (m), 129.5, 123.9 (q, *J* = 290.4 Hz), 111.7, 81.3, 81.1 (hept, *J* = 29.2 Hz), 81.0, 31.5, 29.1, 28.28, 28.25, 26.5, 26.2, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.1 (m); **IR** (ν_{max}, cm^{-1}) 2961 (w), 2934 (w), 2861 (w), 1807 (w), 1713 (m), 1462 (w), 1369 (w), 1265 (m), 1179 (s), 1148 (s), 965 (m), 950 (s), 762 (m); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{23}H_{27}F_6INaO_3^+$ 615.0801; Found 615.0810.

2.3.5. Synthesis and characterization of 2-phenylpropan-2-yl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-hexylcycloprop-2-ene-1-carboxylate (1e)

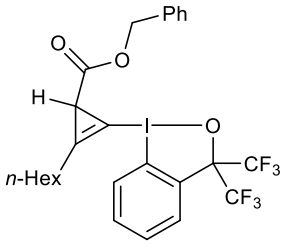


1e

Following **GPB**, **s-1e** (411 mg, 1.44 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 0.60 mL, 1.51 mmol, 1.05 equiv.), **I1** (581 mg, 1.44 mmol, 1.00 equiv.) and THF (15 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **1d** in 79% yield (744 mg, 1.14 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 10:1) = 0.13; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dq, *J* = 7.8, 1.4 Hz, 1H, Ar*H*), 7.69 – 7.55 (m, 2H, Ar*H*), 7.43 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H, Ar*H*), 7.39 – 7.31 (m, 2H, Ar*H*), 7.33 – 7.25 (m, 2H, Ar*H*), 7.27 – 7.16 (m, 1H, Ar*H*), 2.73 – 2.69 (m, 2H, CH$_2$C*H*$_2$C),

2.68 (s, 1H, C*H*CO_2), 1.82 (s, 3H, C(CH_3)), 1.81 (s, 3H, C(CH_3)), 1.73 – 1.58 (m, 2H, C$H_2$$CH_2$C), 1.47 – 1.35 (m, 2H, CH_2), 1.32 – 1.38 (m, 4H, CH_2), 0.95 – 0.80 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 145.7, 134.1, 133.0, 131.0, 130.8, 130.3 (m), 129.5, 128.4, 127.2, 124.3, 123.9 (q, *J* = 290.8 Hz), 111.5, 82.5, 81.1 (hept, *J* = 29.3 Hz), 80.7, 31.5, 29.1, 29.0, 28.6, 28.0, 26.5, 26.2, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.1 (m); **IR** (ν_{max}, cm^{-1}) 3069 (w), 2933 (w), 2863 (w), 1808 (w), 1718 (m), 1465 (w), 1265 (s), 1179 (s), 1151 (s), 1133 (s), 1102 (m), 965 (s), 946 (s), 762 (m), 730 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{29}F_6INaO_3^+$ 677.0958; Found 677.0975.

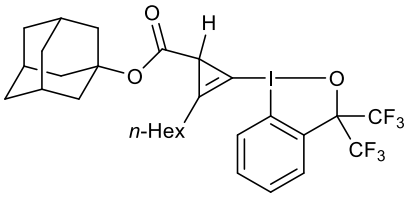
2.3.6. Synthesis and characterization of benzyl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-hexylcycloprop-2-ene-1-carboxylate (1f)



1f

Following **GPB**, **s-1f** (517 mg, 2.00 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 0.84 mL, 2.10 mmol, 1.05 equiv.), **I1** (809 mg, 2.00 mmol, 1.00 equiv.) and THF (20 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **1f** in 48% yield (599 mg, 956 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.38; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dq, *J* = 7.8, 1.4 Hz, 1H, Ar*H*), 7.66 (dd, *J* = 8.3, 1.0 Hz, 1H, Ar*H*), 7.63 (td, *J* = 7.5, 1.1 Hz, 1H, Ar*H*), 7.45 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H, Ar*H*), 7.39 – 7.30 (m, 5H, Ar*H*), 5.16 (d, *J* = 2.5 Hz, 2H, OCH_2Ph), 2.71 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.70 (s, 1H, C*H*CO_2), 1.69 – 1.57 (m, 2H, C$H_2$$CH_2$C), 1.42 – 1.32 (m, 2H, CH_2), 1.31 – 1.20 (m, 4H, CH_2), 0.95 – 0.78 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 135.8, 133.6, 132.9, 131.1, 130.8, 130.4 (m), 129.3, 128.8, 128.6, 128.5, 123.8 (q, *J* = 290.7 Hz), 111.7, 81.2 (hept, *J* = 29.1 Hz), 80.4, 67.1, 31.5, 29.1, 27.0, 26.4, 26.2, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.1 (m); **IR** (ν_{max}, cm^{-1}) 2957 (w), 2932 (w), 2859 (w), 1811 (w), 1720 (m), 1565 (w), 1464 (w), 1440 (w), 1379 (w), 1340 (w), 1265 (m), 1215 (m), 1179 (s), 1150 (s), 1003 (w), 965 (m), 949 (s), 755 (m), 730 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{25}F_6INaO_3^+$ 649.0645; Found 649.0657.

2.3.7. Synthesis and characterization of adamantan-1-yl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-hexylcycloprop-2-ene-1-carboxylate (1g)

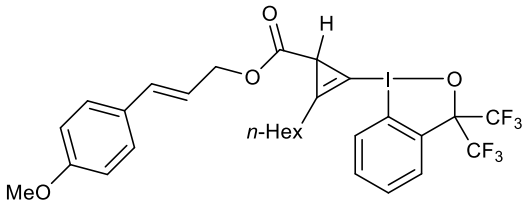


1g

Following **GPB**, **s-1g** (367 mg, 1.21 mmol, 1.0 equiv.), *n*-butyllithium (2.5 M in hexane; 1.3 mL, 1.27 mmol, 1.05 equiv.), **I1** (489 mg, 1.21 mmol, 1.00 equiv.) and THF (20 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **1g** in 74% yield (598 mg, 892 μmol) as a colourless oil, which turned to be solidified when stored in the freezer. **M.p.** 73 – 75 °C. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 1H, Ar*H*), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H, Ar*H*), 7.61 (td, *J* = 7.4, 1.2 Hz, 1H, Ar*H*), 7.54 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H, Ar*H*), 2.67 (td, *J* = 7.2, 2.3 Hz, 2H, CH_2CH_2C), 2.53 (s, 1H, C*H*CO_2), 2.17 – 2.10 (m, 3H, C*H*(adamantyl)), 2.10 – 2.04 (m, 6H, CH_2(adamantyl)), 1.73 – 1.52 (m, 8H, CH_2 & CH_2(adamantyl)), 1.46 – 1.31 (m, 2H, CH_2), 1.26 (dt,

J = 7.5, 3.8 Hz, 4H, C*H*$_2$), 0.89 – 0.76 (m, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 134.5, 132.8, 131.1, 130.9, 130.4, 129.5, 123.9 (q, *J* = 290.8 Hz), 111.7, 81.4, 81.06, 81.14 (hept, *J* = 29.3 Hz), 41.6, 36.3, 31.5, 31.0, 29.1, 28.3, 26.5, 26.2, 22.6, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.1 (m); **IR** (ν_{max}, cm^{-1}) 2917 (m), 2857 (w), 1810 (w), 1712 (m), 1457 (w), 1347 (w), 1264 (m), 1179 (s), 1151 (s), 1051 (m), 965 (s), 950 (s), 760 (m), 730 (s); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{29}H_{33}F_6INaO_3^+$ 693.1271; Found 693.1271.

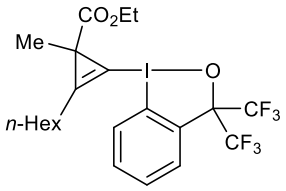
2.3.8. Synthesis and characterization of (*E*)-3-(4-methoxyphenyl)allyl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-hexylcycloprop-2-ene-1-carboxylate (1h)



1h

Following **GPB**, **s-1h** (297 mg, 946 µmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 0.40 mL, 993 µmol, 1.05 equiv.), **I1** (383 mg, 946 µmol, 1.00 equiv.) and THF (20 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **1h** in 59% yield (382 mg, 559 µmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 1H, Ar*H*), 7.72 (dd, *J* = 8.1, 1.2 Hz, 1H, Ar*H*), 7.60 (td, *J* = 7.4, 1.2 Hz, 1H, Ar*H*), 7.53 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H, Ar*H*), 7.36 – 7.27 (m, 2H, Ar*H*), 6.90 – 6.80 (m, 2H, Ar*H*), 6.60 (d, *J* = 15.8 Hz, 1H, CH_2CH=C*H*), 6.14 (dt, *J* = 15.8, 6.7 Hz, 1H, CH_2C*H*=CH), 4.76 (dd, *J* = 6.7, 1.3 Hz, 2H, C*H*$_2$CH=CH), 3.79 (s, 3H, OC*H*$_3$), 2.72 (t, *J* = 7.3 Hz, 2H, CH_2C*H*$_2$C), 2.69 (s, 1H, C*H*CO_2), 1.81 – 1.56 (m, 2H, C*H*$_2$$CH_2$C), 1.43 – 1.32 (m, 2H, C*H*$_2$), 1.32 – 1.20 (m, 4H, C*H*$_2$), 0.93 – 0.72 (m, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 159.8, 134.5, 133.7, 132.9, 131.0, 130.8, 130.3, 129.4, 128.8, 128.0, 123.8 (q, *J* = 290.9 Hz), 120.6, 114.1, 111.6, 81.1 (hept, *J* = 29.4 Hz), 80.3, 66.0, 55.3, 31.4, 29.0, 27.0, 26.3, 26.1, 22.5, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.1 (m); **IR** (ν_{max}, cm^{-1}) 2956 (w), 2933 (w), 2860 (w), 1811 (w), 1717 (m), 1608 (w), 1512 (m), 1464 (w), 1441 (w), 1264 (m), 1179 (s), 1150 (s), 1035 (w), 965 (m), 943 (m), 739 (s); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{29}H_{33}F_6INaO_3^+$ 693.1271; Found 693.1271.

2.3.9. Synthesis and characterization of ethyl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-hexyl-1-methylcycloprop-2-ene-1-carboxylate (1i)

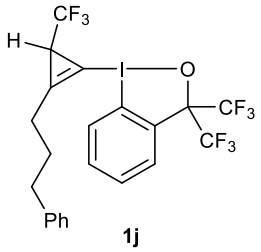


1i

Following **GPC**, **s-1i** (377 mg, 1.79 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 0.75 mL, 1.88 mmol, 1.05 equiv.), **I1** (724 mg, 1.79 mmol, 1.00 equiv.), THF (10 mL) and Et_2O (10 mL) were used. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **1i** in 63% yield (657 mg, 1.14 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 5:1) = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dq, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 7.74 (dd, *J* = 8.2, 1.1 Hz, 1H, Ar*H*), 7.65 (ddd, *J* = 7.8, 7.2, 1.1 Hz, 1H, Ar*H*), 7.55 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H, Ar*H*), 4.15 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$$CH_3$), 2.67 (t, *J* = 7.3 Hz, 2H, CH_2C*H*$_2$C), 1.68 – 1.58 (m, 2H, C*H*$_2$$CH_2$C), 1.50 (s, 3H, C(C*H*$_3$)), 1.45 – 1.33 (m, 2H, C*H*$_2$), 1.33 – 1.20 (m, 7H, C*H*$_2$ & OCH$_2$C*H*$_3$), 0.95 – 0.79 (m, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.4, 140.9, 132.7, 131.13, 131.06, 130.4 (m), 129.5, 123.9 (q, *J* = 291.3 Hz), 111.4, 87.8, 81.0 (hept, *J* = 29.4 Hz),

61.4, 32.7, 31.5, 29.1, 26.6, 25.6, 22.6, 20.7, 14.5, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.1 (m); **IR** (ν_{max}, cm^{-1}) 3073 (w), 2959 (w), 2931 (w), 2861 (w), 1800 (w), 1714 (m), 1565 (w), 1465 (w), 1441 (w), 1380 (w), 1260 (s), 1215 (m), 1178 (s), 1151 (s), 1132 (m), 1116 (s), 1025 (w), 965 (m), 950 (s), 795 (w), 759 (m), 730 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{26}F_6IO_3^+$ 579.0825; Found 579.0827.

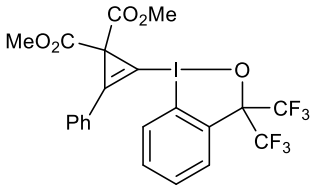
2.3.10. Synthesis and characterization of 1-(2-(3-phenylpropyl)-3-(trifluoromethyl)cycloprop-1-en-1-yl)-3,3-bis(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (1j)



1j

Following **GPC**, **s-1j** (385 mg, 1.70 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 0.71 mL, 1.79 mmol, 1.05 equiv.), **I1** (688mg, 1.70 mmol, 1.00 equiv.), THF (10 mL) and Et_2O (10 mL) were used. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **1j** in 68% yield (682 mg, 1.15 mmol) as a colourless oil, which turned to be solidified when stored in the freezer. **M.p.** 102 – 104 °C. **TLC**: R_f (*n*-hexane: EtOAc = 5:1) = 0.37; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dq, *J* = 7.8, 1.4 Hz, 1H, Ar*H*), 7.68 (td, *J* = 7.5, 1.1 Hz, 1H, Ar*H*), 7.57 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H, Ar*H*), 7.39 (dd, *J* = 8.3, 1.0 Hz, 1H, Ar*H*), 7.35 – 7.27 (m, 2H, Ar*H*), 7.25 – 7.19 (m, 1H, Ar*H*), 7.19 – 7.12 (m, 2H, Ar*H*), 2.78 – 2.71 (m, 4H, CH_2), 2.46 (q, *J* = 4.5 Hz, 1H, C*H*(CF_3)), 2.03 (pent, *J* = 7.4 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.7, 132.94, 132.91, 131.3, 130.8, 130.7 (m), 128.8, 128.6, 128.4, 126.5, 125.7 (q, *J* = 275.5 Hz), 123.8 (q, *J* = 290.8 Hz), 111.5, 81.4 (d, *J* = 2.6 Hz), 81.3 (hept, *J* = 29.4 Hz), 35.4, 27.9, 26.4 (q, *J* = 39.6 Hz), 25.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.5 (CHCF_3), -76.0 (m, C(CF_3)$_2$); **IR** (ν_{max}, cm^{-1}) 3030 (w), 2943 (w), 2864 (w), 1797 (w), 1605 (w), 1497 (w), 1364 (w), 1266 (s), 1217 (m), 1183 (s), 1150 (s), 1131 (s), 965 (s), 952 (s), 829 (w), 754 (m), 730 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}F_9IO^+$ 595.0175; Found 595.0184.

2.3.11. Synthesis and characterization of dimethyl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (1k)

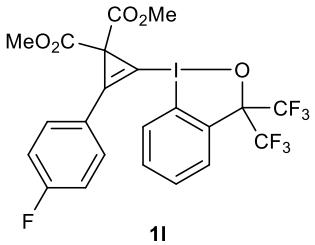


1k

Following **GPB**, **s-1k** (994 mg, 4.28 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 1.8 mL, 4.49 mmol, 1.05 equiv.), **I1** (1.73 g, 4.28 mmol, 1.00 equiv.) and THF (40 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **1k** in 79% yield (2.02 g, 3.37 mmol) as a colourless solid. **M.p.** 121 – 124 °C. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.23; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 1H, Ar*H*), 7.84 (dd, *J* = 8.4, 1.0 Hz, 1H, Ar*H*), 7.71 – 7.66 (m, 1H, Ar*H*), 7.66 – 7.61 (m, 2H, Ar*H*), 7.60 – 7.46 (m, 4H, Ar*H*), 3.79 (s, 6H, OCH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 133.2, 132.3, 131.4, 130.9, 130.8, 130.5 (m), 129.5, 129.4, 126.8, 123.7 (q, *J* = 290.5 Hz), 123.4, 111.8, 81.4 (hept, *J* = 29.6 Hz), 80.1, 53.0, 37.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.0; **IR** (ν_{max}, cm^{-1}) 3069 (w), 2956 (w), 2847 (w), 1923 (w), 1793 (w), 1729 (m), 1437 (m), 1265 (s), 1181 (s), 1147 (s), 1062

(m), 950 (s), 756 (s), 730 (s); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{15}F_6INaO_5^+$ 622.9761; Found 622.9778.

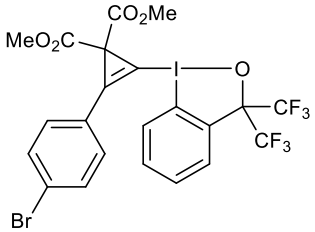
2.3.12. Synthesis and characterization of dimethyl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-(4-fluorophenyl)cycloprop-2-ene-1,1-dicarboxylate (1l)



1l

Following **GPB**, **s-1l** (751 mg, 3.00 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 1.3 mL, 3.15 mmol, 1.05 equiv.), **I1** (1.21 g, 3.00 mmol, 1.00 equiv.) and THF (15 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **1l** in 58% yield (1.08 g, 1.75 mmol) as a colourless oil, which turned to be an amorphous solid when stored in the freezer. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.17; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 1H, Ar*H*), 7.80 (dd, *J* = 8.4, 1.0 Hz, 1H, Ar*H*), 7.72 – 7.60 (m, 3H, Ar*H*), 7.59 – 7.54 (m, 1H, Ar*H*), 7.23 – 7.15 (m, 2H, Ar*H*), 3.79 (s, 6H, OCH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 165.0 (d, *J* = 255.7 Hz), 133.2, 133.1 (d, *J* = 9.2 Hz), 131.4, 130.9, 130.6 (m), 129.3, 125.9, 123.7 (q, *J* = 290.5 Hz), 119.8 (d, *J* = 3.3 Hz), 117.0 (d, *J* = 22.4 Hz), 111.7, 81.4 (hept, *J* = 29.7 Hz), 79.7 (d, *J* = 3.2 Hz), 53.1, 37.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.9 (C(CF_3)$_2$), -104.7 (Ar*F*); **IR** (ν_{max}, cm^{-1}) 3076 (w), 2957 (w), 2849 (w), 1926 (w), 1794 (w), 1732 (s), 1602 (m), 1504 (m), 1465 (w), 1438 (m), 1263 (s), 1237 (s), 1183 (s), 1148 (s), 1065 (m), 1013 (w), 965 (m), 950 (s), 842 (m), 798 (w), 759 (m); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{14}F_7INaO_5^+$ 640.9666; Found 640.9677.

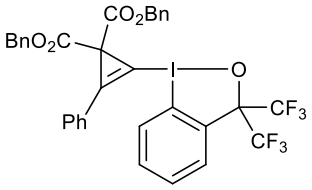
2.3.13. Synthesis and characterization of dimethyl 2-(3,3-bis(trifluoromethyl)-1λ^3-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-(4-bromophenyl)cycloprop-2-ene-1,1-dicarboxylate (1m)



1m

Following **GPC**, **s-1m** (350 mg, 1.12 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 0.47 mL, 1.18 mmol, 1.05 equiv.), **I1** (455mg, 1.12 mmol, 1.00 equiv.), THF (10 mL) and Et_2O (10 mL) were used. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **1m** in 62% yield (475 mg, 699 μmol) as a colourless solid. **M.p.** 150 – 152 °C. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.20; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.78 (dd, *J* = 8.3, 1.1 Hz, 1H, Ar*H*), 7.74 – 7.61 (m, 3H, Ar*H*), 7.56 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H, Ar*H*), 7.52 – 7.43 (m, 2H, Ar*H*), 3.79 (s, 6H, OCH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 133.3, 132.9, 132.0, 131.5, 130.8, 130.6 (m), 129.3, 127.2, 125.9, 123.7 (q, *J* = 290.5 Hz), 122.3, 111.8, 81.4 (hept, *J* = 29.7 Hz), 81.3, 53.1, 37.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.9; **IR** (ν_{max}, cm^{-1}) 2955 (w), 1797 (w), 1730 (m), 1585 (w), 1482 (m), 1464 (w), 1438 (m), 1398 (w), 1288 (s), 1267 (s), 1184 (s), 1150 (s), 1134 (m), 1068 (m), 1012 (m), 967 (m), 953 (m), 829 (m), 755 (m), 731 (m); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{14}BrF_6INaO_5^+$ 700.8866; Found 700.8885.

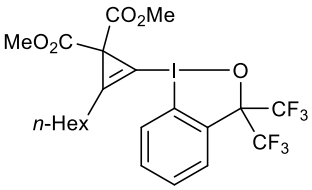
2.3.14. Synthesis and characterization of dibenzyl 2-(3,3-bis(trifluoromethyl)-1λ³-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (1n)



1n

Following **GPC**, **s-1n** (550 mg, 1.43 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 0.60 mL, 1.50 mmol, 1.05 equiv.), **I1** (578 mg, 1.43 mmol, 1.00 equiv.), THF (20 mL) and Et_2O (20 mL) were used. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **1n** in 43% yield (467 mg, 620 µmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.33; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 1H, Ar*H*), 7.68 (dd, *J* = 8.3, 0.9 Hz, 1H, Ar*H*), 7.59 – 7.52 (m, 3H, Ar*H*), 7.51 – 7.40 (m, 3H, Ar*H*), 7.30 – 7.12 (m, 11H, Ar*H*), 5.26 – 5.09 (m, 4H, OCH_2Ph); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 135.4, 133.2, 132.3, 131.3, 130.8, 130.6, 130.4 (m), 129.4, 129.3, 128.7, 128.5, 128.1, 126.9, 123.7 (q, *J* = 290.6 Hz), 123.3, 111.7, 81.4 (hept, *J* = 29.4 Hz), 80.0, 67.7, 38.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.9; **IR** (ν_{max}, cm^{-1}) 3068 (w), 3034 (w), 2957 (w), 2891 (w), 2237 (w), 2139 (w), 1959 (w), 1736 (m), 1584 (w), 1498 (w), 1455 (w), 1257 (s), 1213 (s), 1193 (s), 1180 (s), 1147 (m), 1109 (m), 1015 (w), 963 (m), 946 (m), 926 (m), 755 (s), 729 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{23}F_6INaO_5^+$ 775.0387; Found 775.0394.

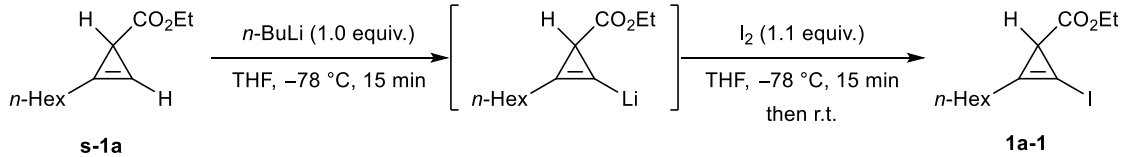
2.3.15. Synthesis and characterization of dimethyl 2-(3,3-bis(trifluoromethyl)-1λ³-benzo[*d*][1,2]iodaoxol-1(3*H*)-yl)-3-hexylcycloprop-2-ene-1,1-dicarboxylate (1o)



1o

Following **GPB**, **s-1o** (240 mg, 1.00 mmol, 1.00 equiv.), *n*-butyllithium (2.5 M in hexane; 0.42 mL, 1.05 mmol, 1.05 equiv.), **I1** (405 g, 1.00 mmol, 1.00 equiv.) and THF (10 mL) were used. Column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **1o** in 78% yield (475 mg, 781 µmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 4:1) = 0.27; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 1H, Ar*H*), 7.75 (dd, *J* = 8.2, 1.1 Hz, 1H, Ar*H*), 7.62 (td, *J* = 7.4, 1.1 Hz, 1H, Ar*H*), 7.54 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H, Ar*H*), 3.72 (s, 6H, OCH_3), 2.70 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 1.61 (pent, *J* = 7.3 Hz, 2H, CH_2CH_2C), 1.44 – 1.28 (m, 2H, CH_2), 1.28 – 1.13 (m, 4H, CH_2), 0.83 – 0.77 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 132.9, 131.2, 131.0, 130.8, 130.2 (m), 129.5, 123.6 (q, *J* = 290.6 Hz), 111.4, 81.1 (hept, *J* = 29.5 Hz), 79.1, 52.7, 37.5, 31.3, 28.9, 26.0, 25.1, 22.4, 13.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.0; **IR** (ν_{max}, cm^{-1}) 2956 (w), 2931 (w), 2859 (w), 1813 (w), 1726 (m), 1464 (w), 1437 (m), 1281 (m), 1265 (s), 1216 (m), 1181 (s), 1149 (s), 1134 (m), 1065 (m), 966 (m), 950 (s), 837 (w), 754 (m), 730 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{24}F_6IO_5^+$ 609.0567; Found 609.0576.

2.4. Synthesis and characterization of ethyl 2-hexyl-3-iodocycloprop-2-ene-1-carboxylate (1a-1)

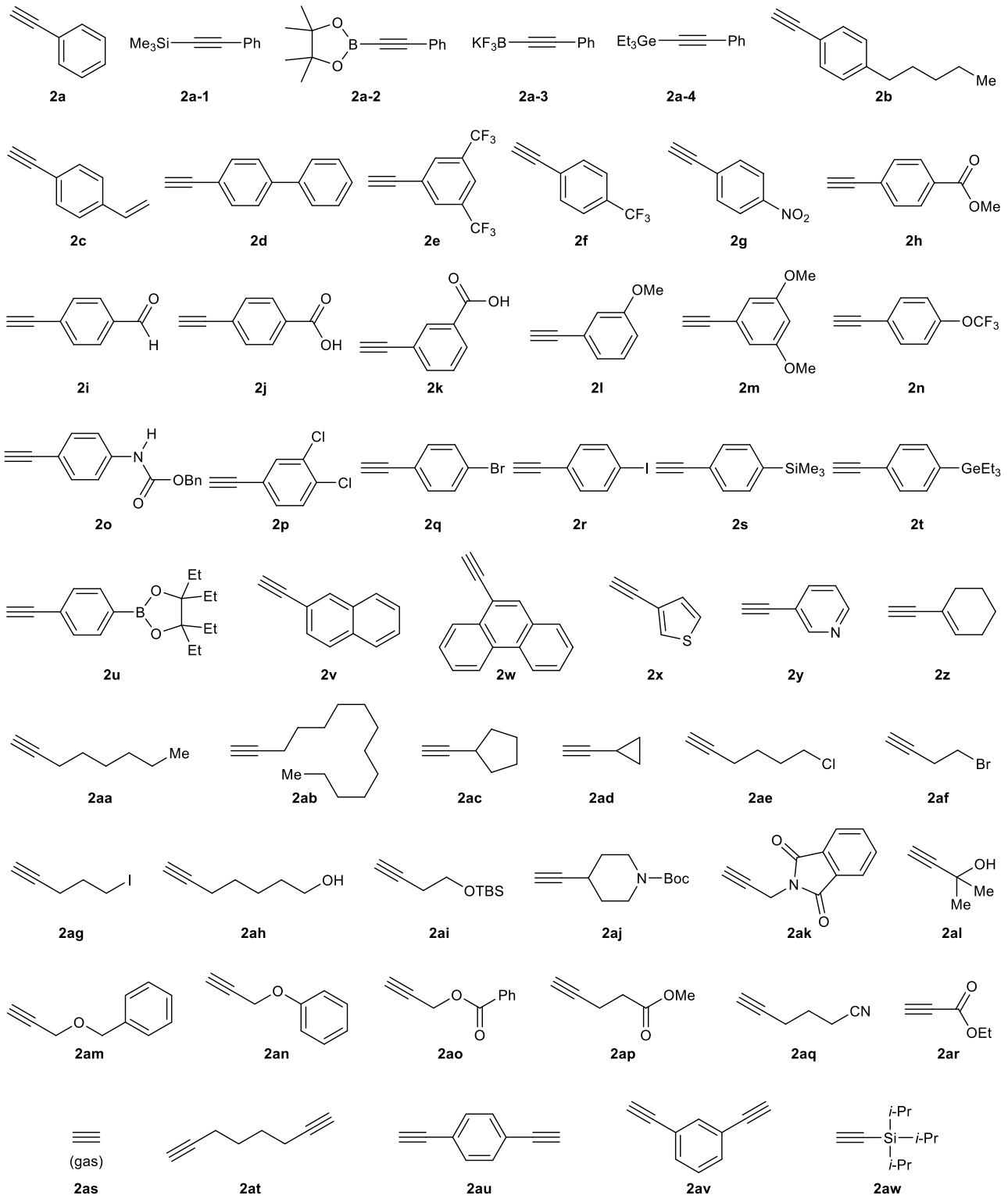


s-1a **1a-1**

An oven-dried Schlenk tube was charged with a magnetic stir-bar and terminal cyclopropene **s-1a** (589 mg, 3.00 mmol, 1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, THF (30 mL) was added by syringe and the Schlenk tube was placed at −78 °C in a dry ice/acetone bath. *n*-Butyllithium (2.5 M in hexane; 1.2 mL, 3.00 mmol, 1.00 equiv.) was added dropwise by a syringe pump over 5 min and the reaction mixture was stirred at −78 °C for additional 10 min. Then, elemental iodine (838 mg, 3.30 mmol, 1.10 equiv.) was added in one portion under nitrogen. The reaction mixture was stirred at −78 °C for 15 min, then the cooling bath was removed. The reaction mixture was allowed to warm to room temperature gradually (ca. 15 min) while keeping stirring. The reaction mixture was then quenched by adding sodium bisulfite solution ($NaHSO_3$, ⩾37% in water; 10 mL). The organic phase was separated, and the remaining aqueous portion was extracted with EtOAc (3 × 10 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 20:1), and the fractions that contained the product were collected and concentrated by rotary evaporation to afford the purified compound **1a-1** in 59% yield (575 mg, 1.78 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 20:1) = 0.33; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.14 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 2.49 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.45 (s, 1H, $CHCO_2$), 1.68 – 1.52 (m, 2H, CH_2CH_2C), 1.44 – 1.20 (m, 9H, CH_2 & OCH_2CH_3), 0.96 – 0.83 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 125.3, 60.7, 46.7, 31.6, 29.0, 26.7, 26.0, 25.1, 22.7, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 2955 (m), 2929 (m), 2858 (w), 1720 (s), 1643 (w), 1607 (w), 1463 (m), 1391 (w), 1371 (m), 1320 (w), 1302 (w), 1255 (m), 1180 (s), 1131 (w), 1095 (w), 1026 (m), 891 (w), 865 (w), 799 (w), 724 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{19}INaO_2^+$ 345.0322; Found 345.0329**.**

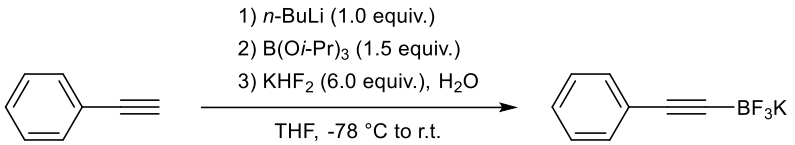
3. Synthesis and characterisation of terminal alkynes and alkyne surrogates

3.1. Terminal alkynes and alkyne surrogates



Terminal alkyne **2a**, **2b**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j**, **2k**, **2l**, **2m**, **2n**, **2p**, **2q**, **2v**, **2w**, **2x**, **2y**, **2z**, **2aa**, **2ab**, **2ac**, **2ad**, **2ae**, **2af**, **2ag**, **2ah**, **2ai**, **2aj**, **2ak**, **2al**, **2am**, **2an**, **2ao**, **2ap**, **2aq**, **2ar**, **2as**, **2at**, **2au**, **2av**, **2aw** and terminal alkyne surrogates **2a-1**, **2a-2** were commercially available and used as received.

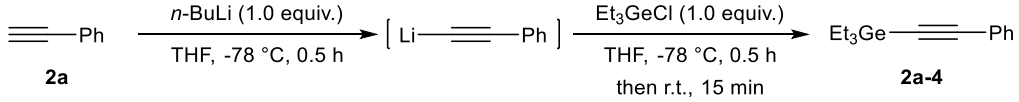
3.1.1. Synthesis and characterization of potassium trifluoro(phenylethynyl)borate (2a-3)[15]



2a **2a-3**

An oven-dried round-bottom flask, charged with a magnetic stir-bar was evacuated and backfilled with N_2 (3 times). Then, phenylacetylene **2a** (1.53 g, 15.0 mmol, 1.00 equiv.) and dry THF (50 mL) were added. The mixture was cooled to -78 °C and a solution of *n*-BuLi (2.5 M, 6.0 mL, 15.0 mmol, 1.00 equiv.) in hexane was added dropwise under N_2. The reaction was stirred at -78 °C for 1 hour and B(O*i*-Pr)$_3$ (4.23 g, 22.5 mmol, 1.50 equiv.) was added quickly. The reaction was stirred 10 min at -78 °C then 2 hours at room temperature. The mixture was cooled to 0 °C and a saturated solution of KHF_2 (7.03 g, 90.0 mmol, 6.00 equiv.) in water (20 mL + 20 mL to rinse the remaining solid) was added. The reaction was stirred at room temperature open to air for 2 hours then concentrated in vacuo. The wet solid obtained was further dried by co-evaporation with acetone. To the dry solid was added acetone (~50 mL) and the resulting mixture was placed on a rotary evaporator and rotated rapidly at atmospheric pressure with the bath set at 45 °C for 15 minutes. The flask was removed and the mixture carefully filtered taking care to leave the insoluble material in the reaction flask. Acetone was once again added and the process (heating for 15 min then collection of the liquid) was repeated 2 more times. The combined acetone filtrates were concentrated in vacuo to approximately 1/3 of the initial volume. Et_2O (~60 mL) was added causing a white solid to precipitate. The mixture was cooled to 0 °C for 10 min then filtered. The solid obtained was washed with Et_2O and dried in vacuo to afford the desired **2a-3** in 83% yield (2.60 g, 12.5 mmol) as a white solid. **^{1}H NMR** (400 MHz, acetone-d$_6$) δ 7.35 – 7.29 (m, 2H, Ar*H*), 7.27 – 7.17 (m, 3H, Ar*H*); **^{13}C NMR** (101 MHz, acetone-d$_6$) δ 132.1, 128.8, 127.4, 127.2; **^{19}F NMR** (376 MHz, acetone-d6) δ -135.0. The NMR spectroscopic data is consistent with previous report[16].

3.1.2. Synthesis and characterization of triethyl(phenylethynyl)germane (2a-4)[17]

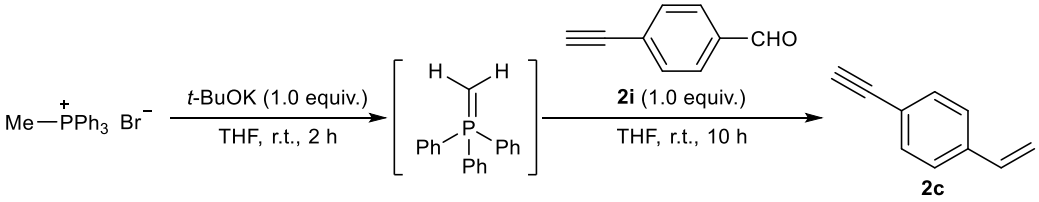


2a **2a-4**

An oven-dried Schlenk tube was charged with a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, ethynylbenzene **2a** (0.22 mL, 2.00 mmol, 1.00 equiv.) and THF (10 mL) was added by syringe and the Schlenk tube was placed at −78 °C in a dry ice/acetone bath. *n*-Butyllithium (2.5 M in hexane; 2.00 mmol, 0.80 mL, 1.00 equiv.) was added dropwise by a syringe pump over 5 min and the reaction mixture was stirred at −78 °C for additional 25 min. Then, Et_3GeCl (2.00 mmol, 391 mg, 1.00 equiv.) was added dropwise under nitrogen. The reaction mixture was stirred at −78 °C for 30 min, then the cooling bath was removed. The reaction mixture was allowed to warm to room temperature gradually while keeping stirring for additional 15 min. The reaction mixture was then quenched by adding saturated aqueous NH_4Cl (10 mL). The organic phase was removed, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent : pentane). Terminal alkyne surrogate **2a-4** was obtained in 98% yield (509 mg, 1.95 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane) = 0.54; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.38 (m, 2H, Ar*H*), 7.34 – 7.17 (m, 3H, Ar*H*), 1.14 (t, *J* = 7.8 Hz, 9H, Ge(CH_2CH_3)$_3$), 0.93 (qd, *J* = 7.7, 1.1 Hz, 6H, Ge(CH_2CH_3)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.1, 128.3, 128.1, 123.9, 106.1, 92.2, 9.2, 6.0; **HRMS** (ESI/QTOF) m/z: [M +

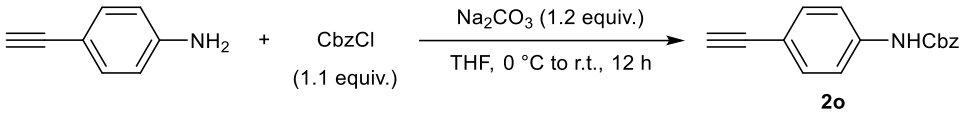
Ag]$^+$ Calcd for $C_{14}H_{20}AgGe^+$ 368.9822; Found 368.9820. The spectroscopic data is consistent with previous report[18].

3.1.3. Synthesis and characterization of 1-ethynyl-4-vinylbenzene (2c)[19]



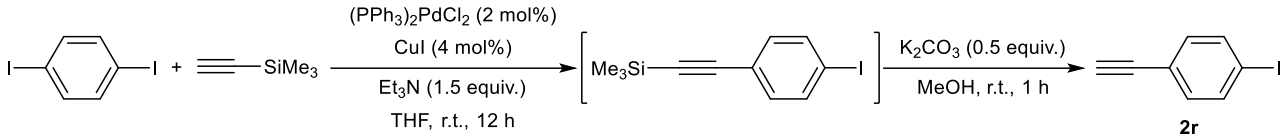
In a nitrogen-filled glovebox, a 50 ml Schlenk tube was sequentially charged with a magnetic stir bar and *t*-BuOK (224 mg, 2.00 mmol, 1.00 equiv.). The tube was then tightly sealed with a rubber cap. The tube was brought out of the glovebox. After that, THF (10 mL) and methyltriphenylphosphonium bromide (714 mg, 2.00 mmol, 1.00 equiv.) was added sequentially. The reaction mixture was stirred under room temperature for 2 hours. Then 4-ethynylbenzaldehyde **2i** (260 mg, 2.00 mmol, 1.00 equiv.) was added in one portion. The reaction mixture was stirred under room temperature for additional 10 hours. The reaction mixture was then filtered through a silica gel pad and washed with EtOAc. The organic solution of crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane). Terminal alkyne **2c** was obtained in 65% yield (167 mg, 1.30 mmol) as a colorless oil. **TLC**: R_f (*n*-hexane) = 0.56; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H, Ar*H*), 7.41 – 7.32 (m, 2H, Ar*H*), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H, C*H*=CH_2), 5.77 (dd, *J* = 17.6, 0.8 Hz, 1H, CH=CH_2), 5.30 (dd, *J* = 10.9, 0.8 Hz, 1H, CH=CH_2), 3.11 (s, 1H, C≡C*H*); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1, 136.3, 132.5, 126.3, 121.5, 115.2, 83.8, 77.9; **HRMS** (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{10}H_8^+$ 128.0621; Found 128.0622. The spectroscopic data is consistent with previous report[20].

3.1.4. Synthesis and characterization of benzyl (4-ethynylphenyl)carbamate (2o)[21]



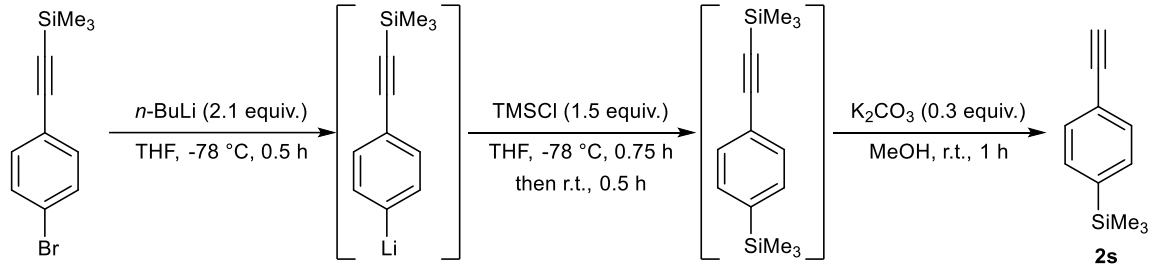
An oven-dried Schlenk tube was charged with a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, 4-ethynylaniline (234 mg, 2.00 mmol, 1.00 equiv.), Na_2CO_3 (254 mg, 2.40 mmol, 1.20 equiv.) and THF (10 mL) were added and the resulting mixture was stirred at 0 °C. Then, benzyl chloroformate (CbzCl; 2.20 mmol, 0.31 mL, 1.10 equiv.) was added dropwise by a syringe pump and the reaction mixture was stirred at room temperature for 12 hours. The reaction mixture was then quenched by adding saturated aqueous NH_4Cl (10 mL). The organic phase was collected, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/EtOAc = 10:1). Terminal alkyne **2o** was obtained in 99% yield (497 mg, 1.98 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane: EtOAc = 10:1) = 0.24; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.30 (m, 9H, Ar*H*), 6.82 (s, 1H, N*H*), 5.20 (s, 2H, CH_2Ph), 3.04 (s, 1H, C≡C*H*); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.1, 138.4, 135.9, 133.2, 128.8, 128.6, 128.5, 118.3, 117.0, 83.5, 76.7, 67.3. The spectroscopic data is consistent with previous report[22].

3.1.5. Synthesis and characterization of 1-ethynyl-4-iodobenzene (2r)[23]



An oven-dried Schlenk tube was charged with $(PPh_3)_2PdCl_2$ (56.2 mg, 80.0 µmol, 2.00 mol%), CuI (30.5 mg, 160 µmol, 4.00 mol%), 1,4-diiodobenzene (1.32 g, 4.00 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, THF (10 mL) was added by syringe and the reaction mixture was stirred under room temperature. Then, ethynyltrimethylsilane (393 mg, 4.00 mmol, 1.00 equiv.) was added dropwise by a syringe and the reaction mixture was stirred at room temperature for additional 12 hours. The reaction mixture was then quenched by adding saturated aqueous NH_4Cl (10 mL). The organic phase was collected, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude residue was dissolved by MeOH (10 mL) under air. Then, K_2CO_3 (276 mg, 2.00 mmol, 0.500 equiv.) was added. The reaction mixture was stirred under room temperature for 1 hour. The reaction mixture was then diluted by adding deionized water (20 mL) and EtOAc (20 mL). The organic phase was collected, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent : pentane). Terminal alkyne **2r** was obtained in 31% yield (283 mg, 1.24 mmol) as a white solid. **TLC**: R_f (*n*-hexane) = 0.60;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.57 (m, 2H, Ar*H*), 7.25 – 7.09 (m, 2H, Ar*H*), 3.13 (s, 1H, C≡C*H*);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.6, 133.7, 121.7, 95.0, 82.8, 78.8. The spectroscopic data is consistent with previous report[24].

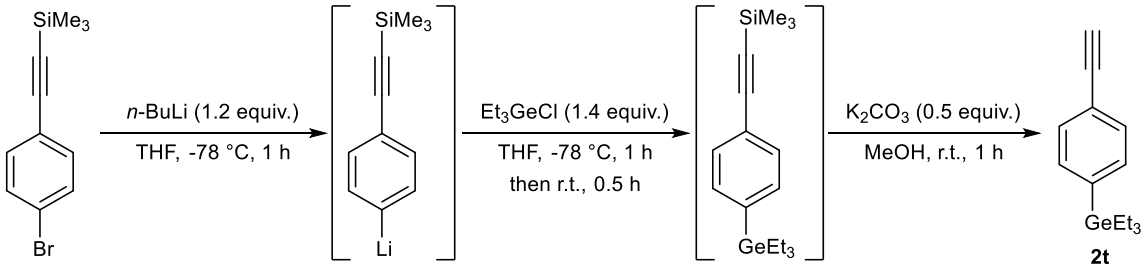
3.1.6. Synthesis and characterization of (4-ethynylphenyl)trimethylsilane (2s)[25]



An oven-dried Schlenk tube was charged with ((4-bromophenyl)ethynyl)trimethylsilane (506 mg, 2.00 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, THF (10 mL) was added by syringe and the Schlenk tube was placed at −78 °C in a dry ice/acetone bath. *n*-Butyllithium (2.5 M in hexane; 4.20 mmol, 1.68 mL, 2.10 equiv.) was added dropwise by a syringe pump over 5 min and the reaction mixture was stirred at −78 °C for additional 25 min. Then, TMSCl (3.00 mmol, 381 µL, 1.50 equiv.) was added dropwise under nitrogen. The reaction mixture was stirred at −78 °C for 45 min, then the cooling bath was removed. The reaction mixture was allowed to warm to room temperature gradually while keeping stirring for 30 min. The reaction mixture was then quenched by adding saturated aqueous NH_4Cl (10 mL). The organic phase was collected, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude residue was dissolved by MeOH (10 mL) under air. Then, K_2CO_3 (82.9 mg, 600 µmol, 0.300 equiv.) was added. The reaction mixture was stirred under room temperature for 1 hour. The reaction mixture was then diluted by adding deionized water (20 mL) and EtOAc (20 mL). The organic phase was collected, and the remaining aqueous portion was extracted with EtOAc

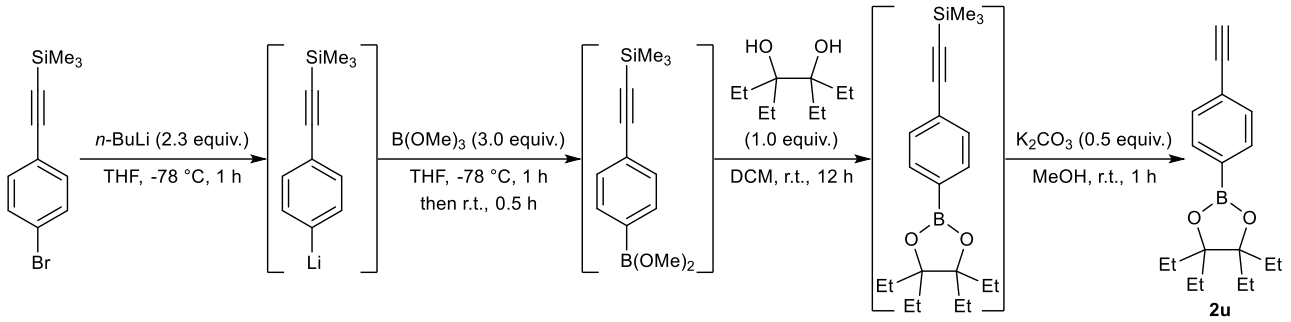
(3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent : pentane). Terminal alkyne **2s** was obtained in 77% yield (268 mg, 1.54 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane) = 0.38; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 4H, Ar*H*), 3.09 (s, 1H, C≡C*H*), 0.27 (s, 9H, Si(C*H*$_3$)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 133.3, 131.3, 122.5, 83.9, 77.6, -1.1. The spectroscopic data is consistent with previous report[26].

3.1.7. Synthesis and characterization of triethyl(4-ethynylphenyl)germane (2t)[27]



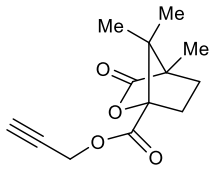
An oven-dried Schlenk tube was charged with ((4-bromophenyl)ethynyl)trimethylsilane (506 mg, 2.00 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, THF (10 mL) was added by syringe and the Schlenk tube was placed at −78 °C in a dry ice/acetone bath. *n*-Butyllithium (2.5 M in hexane; 2.40 mmol, 0.96 mL, 1.20 equiv.) was added dropwise by a syringe pump over 5 min and the reaction mixture was stirred at −78 °C for additional 55 min. Then, Et_3GeCl (2.80 mmol, 547 mg, 1.40 equiv.) was added dropwise under nitrogen. The reaction mixture was stirred at −78 °C for 1 hour, then the cooling bath was removed. The reaction mixture was allowed to warm to room temperature gradually while keeping stirring for 30 min. The reaction mixture was then quenched by adding saturated aqueous NH_4Cl (10 mL). The organic phase was removed, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude residue was dissolved by MeOH (10 mL) under air. Then, K_2CO_3 (138 mg, 1.00 mmol, 0.500 equiv.) was added. The reaction mixture was stirred under room temperature for 1 hour. The reaction mixture was then diluted by adding deionized water (20 mL) and EtOAc (20 mL). The organic phase was removed, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane). Terminal alkyne **2t** was obtained in 89% yield (463 mg, 1.78 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane) = 0.52; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.42 – 7.35 (m, 2H, Ar*H*), 3.07 (s, 1H, C≡C*H*), 1.11 – 0.93 (m, 15H, Ge(C*H*$_2$C*H*$_3$)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 134.0, 131.4, 121.8, 84.0, 77.3, 9.0, 4.3; **IR** (ν_{max}, cm^{-1}) 3300 (m), 3065 (w), 2952 (m), 2930 (m), 2906 (m), 2871 (m), 2391 (w), 2186 (w), 2108 (w), 1912 (w), 1805 (w), 1458 (m), 1231 (w), 1083 (m), 1015 (m), 970 (w), 819 (s); **HRMS** (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{21}Ge^+$ 263.0850; Found 263.0857.

3.1.8. Synthesis and characterization of 4,4,5,5-tetraethyl-2-(4-ethynylphenyl)-1,3,2-dioxaborolane (2u)[28]

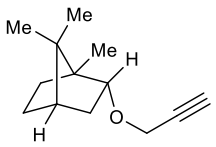


An oven-dried Schlenk tube was charged with ((4-bromophenyl)ethynyl)trimethylsilane (506 mg, 2.00 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, THF (10 mL) was added by syringe and the Schlenk tube was placed at −78 °C in a dry ice/acetone bath. *n*-Butyllithium (2.5 M in hexane; 4.60 mmol, 1.8 mL, 2.30 equiv.) was added dropwise by a syringe pump over 5 min and the reaction mixture was stirred at −78 °C for additional 55 min. Then, $B(OMe)_3$ (6.00 mmol, 0.67 mL, 3.00 equiv.) was added dropwise under nitrogen. The reaction mixture was stirred at −78 °C for 1 hour, then the cooling bath was removed. The reaction mixture was allowed to warm to room temperature gradually while keeping stirring for 30 min. The reaction mixture was then quenched by adding saturated aqueous NH_4Cl (10 mL). The organic phase was removed, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude residue was dissolved in DCM (10 mL) under air. Then, 3,4-diethylhexane-3,4-diol (349 mg, 2.00 mmol, 1.00 equiv.) was added. The reaction mixture was stirred under room temperature for 12 hours. The reaction mixture was then diluted by adding deionized water (10 mL) and DCM (10 mL). The organic phase was removed, and the remaining aqueous portion was extracted with DCM (3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude residue was dissolved by MeOH (10 mL) under air. Then, K_2CO_3 (138 mg, 1.00 mmol, 0.500 equiv.) was added. The reaction mixture was stirred under room temperature for 1 hour. The reaction mixture was then diluted by adding deionized water (20 mL) and EtOAc (20 mL). The organic phase was removed, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane). Terminal alkyne **2u** was obtained in 83% yield (474mg, 1.67 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 40:1) = 0.24; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 2H, Ar*H*), 7.52 – 7.43 (m, 2H, Ar*H*), 3.13 (s, 1H, C≡C*H*), 1.86 – 1.59 (m, 8H, CCH_2CH$_3$), 0.96 (t, *J* = 7.5 Hz, 12H, CCH$_2$CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.7, 131.4, 124.7, 89.2, 84.0, 78.3, 26.6, 9.0; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 28.9; **IR** (ν_{max}, cm^{-1}) 3301 (w), 2979 (m), 2945 (m), 2885 (w), 2108 (w), 1932 (w), 1722 (w), 1607 (m), 1547 (w), 1511 (w), 1460 (w), 1400 (s), 1364 (s), 1350 (s), 1292 (m), 1260 (m), 1180 (w), 1090 (s), 1021 (w), 958 (w), 921 (s), 838 (m), 772 (w), 741 (m); **HRMS** (APPI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{18}H_{26}BO_2^+$ 285.2020; Found 285.2027.

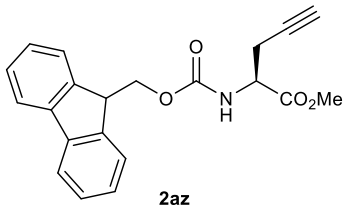
3.2. Terminal alkynes tethered with natural products, bioactive molecules and pharmaceuticals



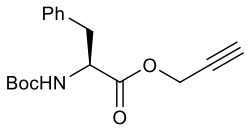
2ax
From (1*S*)-(-)-camphanic acid



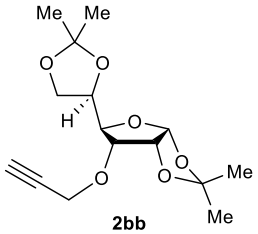
2ay
From (-)-borneol



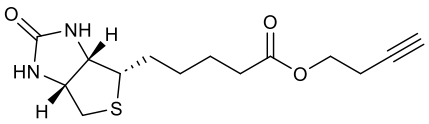
2az
From L-propargylglycine



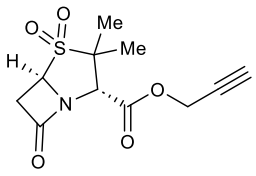
2ba
From L-phenylalanine



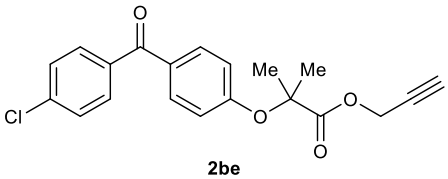
2bb
From α-D-allofuranose



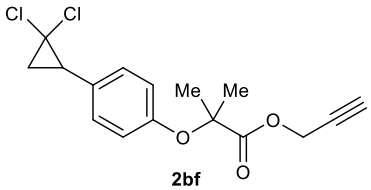
2bc
From D-biotin



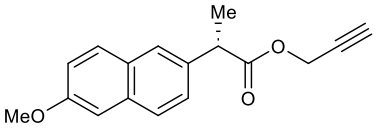
2bd
From Sulbactam



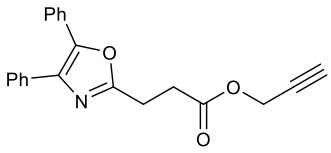
2be
From fenofibric acid



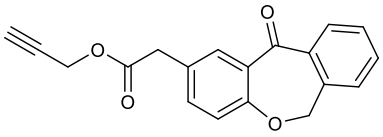
2bf
From ciprofibrate



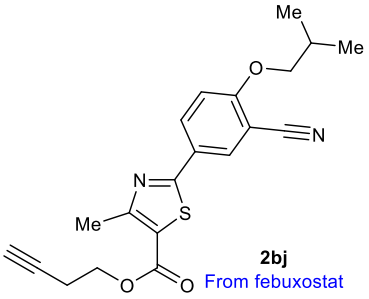
2bg
From naproxen



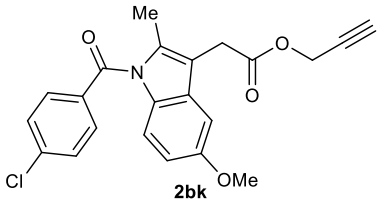
2bh
From oxaprozin



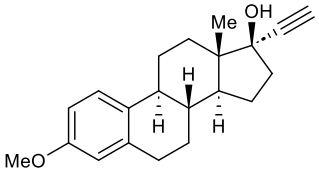
2bi
From isoxepac



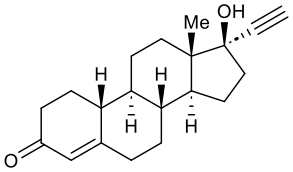
2bj
From febuxostat



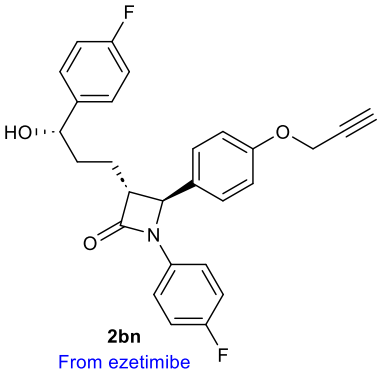
2bk
From indomethacin



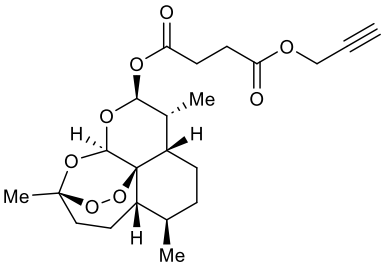
2bl
From mestranol



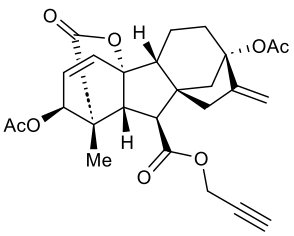
2bm
From norethindrone



2bn
From ezetimibe



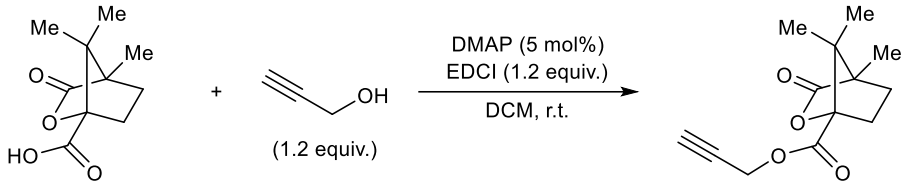
2bo
From artesunate



2bp
From gibberellic acid

Alkyne derivative **2bl** and **2bm** were commercially available and used as received. Alkyne derivative **2ax**, **2ay**, **2az**, **2ba**, **2bb**, **2bc**, **2bd**, **2be**, **2bf**, **2bg**, **2bh**, **2bi**, **2bj**, **2bk**, **2bn**, **2bo** and **2bp** were prepared according to the following procedures:

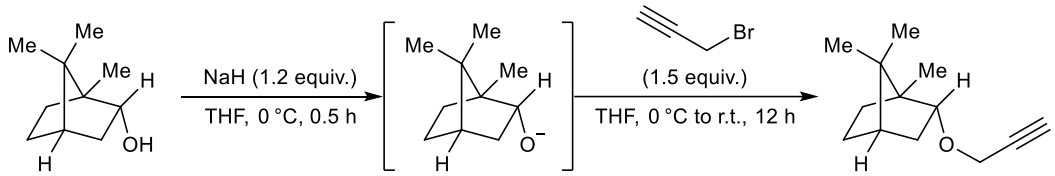
3.2.1. Synthesis and characterization of prop-2-yn-1-yl (1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (2ax)[29]



(1*S*)-(-)-Camphanic acid **2ax**

A mixture of 4-(dimethylamino)pyridine (DMAP; 6.10 mg, 50.0 µmol, 5.00 mol%), *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 230 mg, 1.20 mmol, 1.20 equiv.), (1*S*)-(−)-camphanic acid (198 mg, 1.00 mmol, 1.00 equiv.), prop-2-yn-1-ol (67.3 mg, 1.20 mmol, 1.20 equiv.) and DCM (10 mL) was stirred under room temperature for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1). Alkyne derivative **2ax** was obtained in 65% yield (155 mg, 654 µmol) as a colourless solid. **M.p.** 52 – 53 °C. **ORD**: $[\alpha]_D^{20}$ = -22.4 (c = 1.00, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.31; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.82 (dd, *J* = 2.5, 1.1 Hz, 2H, OCH_2), 2.51 (t, *J* = 2.4 Hz, 1H, C≡C*H*), 2.45 (ddd, *J* = 13.4, 10.7, 4.2 Hz, 1H, CH_2), 2.05 (ddd, *J* = 13.6, 9.3, 4.5 Hz, 1H, CH_2), 1.93 (ddd, *J* = 13.2, 10.7, 4.6 Hz, 1H, CH_2), 1.70 (ddd, *J* = 13.4, 9.4, 4.3 Hz, 1H, CH_2), 1.12 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 0.99 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.0, 167.0, 90.9, 77.0, 75.8, 54.9, 54.7, 52.9, 30.7, 29.1, 16.9, 16.8, 9.8; **IR** (ν_{max}, cm^{-1}) 3278 (w), 2971 (w), 2940 (w), 2881 (w), 2130 (w), 1787 (s), 1757 (s), 1744 (s), 1474 (w), 1447 (w), 1399 (w), 1381 (w), 1335 (w), 1312 (m), 1269 (s), 1226 (w), 1168 (m), 1102 (s), 1057 (s), 1020 (m), 959 (m), 932 (m), 795 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}NaO_4^+$ 259.0941; Found 259.0949.

3.2.2. Synthesis and characterization of (1*S*,2*R*,4*S*)-1,7,7-trimethyl-2-(prop-2-yn-1-yloxy)bicyclo[2.2.1]heptane (2ay)[30]

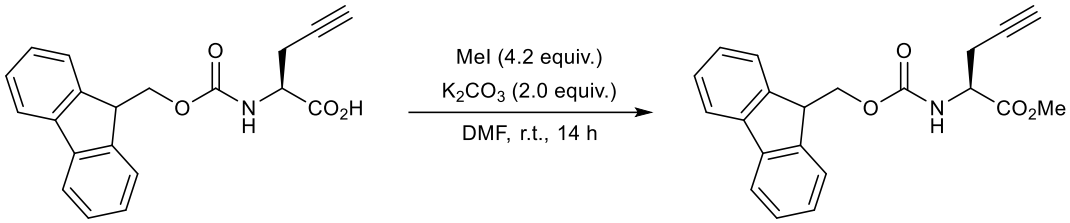


(-)-Borneol **2ay**

An oven-dried Schlenk tube was charged with (-)-borneol (674 mg, 4.37 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, THF (10 mL) was added by syringe and the Schlenk tube was placed at 0 °C in an ice/water bath. Subsequently, NaH (60% dispersion in mineral oil; 5.24 mmol, 210 mg, 1.20 equiv.) was added in several portions and the reaction mixture was stirred at 0 °C for 30 min. Then, 3-bromoprop-1-yne (6.56 mmol, 780 mg, 1.50 equiv.) was added dropwise under nitrogen. Then the cooling bath was removed. The reaction mixture was stirred under room temperature for 12 hours. The reaction mixture was then quenched under 0 °C by adding saturated aqueous NH_4Cl (10 mL) and diluted with EtOAc (10 mL). The organic phase was removed, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were washed with brine, dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane). Alkyne derivative **2ay** was obtained in 58% yield (488 mg, 2.54 mmol) as a colourless oil. **ORD**: $[\alpha]_D^{20}$ = -74.8 (c = 0.26, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.17; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.24 – 4.03 (m, 2H, OCH_2), 3.78 (ddd, *J* = 9.4, 3.4, 1.8 Hz, 1H,

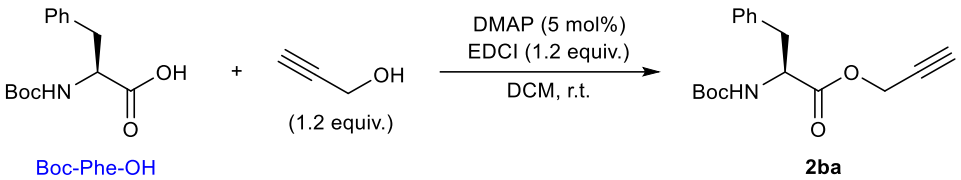
OC*H*), 2.37 (t, *J* = 2.4 Hz, 1H, C≡C*H*), 2.14 (dddd, *J* = 12.9, 9.4, 4.8, 3.2 Hz, 1H, CH_2), 1.95 (ddd, *J* = 11.9, 9.6, 4.4 Hz, 1H, CH_2), 1.77 – 1.58 (m, 2H, CH_2), 1.33 – 1.16 (m, 2H, CH_2), 1.06 (dd, *J* = 13.1, 3.4 Hz, 1H, C*H*), 0.88 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 0.85 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 84.5, 81.0, 73.6, 57.4, 49.3, 48.0, 45.1, 36.0, 28.3, 26.7, 19.9, 19.0, 13.9; **HRMS** (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{13}H_{20}O^+$ 192.1509; Found 192.1512. The spectroscopic data is consistent with previous report[31].

3.2.3. Synthesis and characterization of methyl (*S*)-2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)pent-4-ynoate (2az)[32]



An oven-dried Schlenk tube was charged with Fmoc-L-propargylglycine (335 mg, 1.00 mmol, 1.00 equiv.), K_2CO_3 (276 mg, 2.00 mmol, 2.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, dimethylformamide (DMF; 10 mL) was added by syringe and the resulting mixture was stirring under room temperature. Subsequently, MeI (4.20 mmol, 0.26 mL, 4.20 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 14 hours. The reaction mixture was then filtered through a silica gel pad and washed with EtOAc (3 × 5 mL). The organic solution of the crude product was washed with brine (3 × 10 mL), deionized water (3 × 10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 3:1). Alkyne derivative **2az** was obtained in 94% yield (327 mg, 936 μmol) as a colorless solid. ^{13}C NMR showed the formation of rotamers (1:1 based on ^{13}C NMR) even if under 60 °C. **ORD**: $[\alpha]_D^{20}$ = +45.9 (c = 0.21, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.23; **^{1}H NMR** (400 MHz, $CDCl_3$, 60 °C) δ 7.77 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.68 – 7.56 (m, 2H, Ar*H*), 7.40 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.32 (tt, *J* = 7.4, 1.2 Hz, 2H, Ar*H*), 5.61 (bs, 1H, N*H*), 4.54 (bs, 1H, NC*H*), 4.44 (d, *J* = 7.1 Hz, 2H, CH_2(fluorenyl)), 4.26 (t, *J* = 7.0 Hz, 1H, C*H*(fluorenyl)), 3.80 (s, 3H, OCH_3), 2.78 (bs, 2H, CH_2C≡CH), 2.07 (t, *J* = 2.7 Hz, 1H, C≡C*H*); **^{13}C NMR** (101 MHz, $CDCl_3$, 60 °C) δ 170.8, 155.7 (bs), 144.1*, 144.0*, 141.5, 127.9, 127.23#, 127.22#, 125.2, 120.1, 78.5 (bs), 71.9, 67.5, 52.8, 52.7 (bs), 47.5, 22.9. *These two signals are assigned to one certain aryl carbon atom on the 9-fluorenyl group, which has also been reported by a previous study[33]; #These two signals are assigned to another one certain aryl carbon atom on the 9-fluorenyl group. **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{19}NNaO_4^+$ 372.1206; Found 372.1209. The NMR spectroscopic data is consistent with the previous reports[20,34,35].

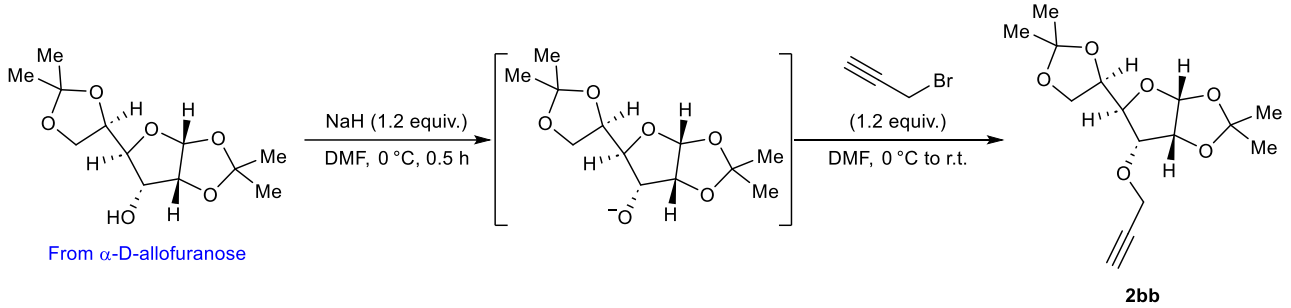
3.2.4. Synthesis and characterization of methyl prop-2-yn-1-yl (*tert*-butoxycarbonyl)-*L*-phenylalaninate (2ba)[36]



A mixture of 4-(dimethylamino)pyridine (DMAP; 6.10 mg, 50.0 μmol, 5.00 mol%), *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 230 mg, 1.20 mmol, 1.20 equiv.), Boc-L-phenylalanine (265 mg, 1.00 mmol, 1.00 equiv.), prop-2-yn-1-ol (67.3 mg, 1.20 mmol, 1.20 equiv.) and DCM (10 mL) was stirred under room temperature for 12 hours. The reaction mixture was then

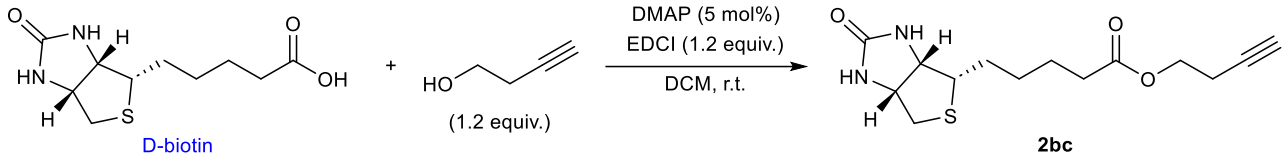
filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1). Alkyne derivative **2ba** was obtained in 84% yield (256 mg, 844 μmol) as a colourless oil. **ORD**: $[\alpha]_D^{20}$ = +12.1 (c = 0.81, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.20; **^{1}H NMR** (400 MHz, $CDCl_3$, 60 °C) δ 7.36 – 7.23 (m, 3H, Ar*H*), 7.22 – 7.15 (m, 2H, Ar*H*), 4.91 (bs, 1H, N*H*), 4.74 (qd, *J* = 15.5, 2.4 Hz, 2H, OCH_2), 4.63 (bs, 1H, NC*H*), 3.34 – 2.91 (m, 2H, PhCH_2), 2.51-2.50 (m, 1H, C≡C*H*), 1.45 (s, 9H, OC(CH_3)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$, 60 °C) δ 171.3, 155.1 (bs), 136.0, 129.6, 128.8, 127.3, 80.3 (bs), 77.3, 75.5, 54.8 (bs), 52.7, 38.5, 28.5; **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{17}H_{21}NNaO_4^+$ 326.1363; Found 326.1366. The NMR spectroscopic data is consistent with the previous report[37].

3.2.5. Synthesis and characterization of (3a*R*,5*S*,6*R*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(prop-2-yn-1-yloxy)tetrahydrofuro[2,3-*d*][1,3]dioxole (2bb)[38]



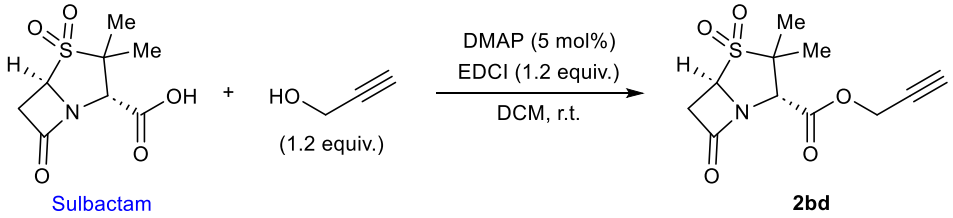
An oven-dried Schlenk tube was charged with 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (521 mg, 2.00 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, DMF (5 mL) was added by syringe and the Schlenk tube was placed at 0 °C in an ice/water bath. Subsequently, NaH (60% dispersion in mineral oil; 2.40 mmol, 96.0 mg, 1.20 equiv.) was added in several portions and the reaction mixture was stirred at 0 °C for 30 min. Then, 3-bromoprop-1-yne (2.40 mmol, 286 mg, 1.20 equiv.) was added dropwise under nitrogen. Then the cooling bath was removed. The reaction mixture was stirred under room temperature for 10 hours. The reaction mixture was then quenched under 0 °C by adding saturated aqueous NH_4Cl (5 mL) and diluted with EtOAc (10 mL). The organic phase was removed, and the remaining aqueous portion was extracted with EtOAc (3 × 5 mL). The combined organic portions were washed with brine (3 × 15 mL), deionized water (3 × 15 mL), dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane). Alkyne derivative **2bb** was obtained in 95% yield (569 mg, 1.91 mmol) as a colourless solid. **M.p.** 118 – 120 °C. **ORD**: $[\alpha]_D^{20}$ = +106.8 (c = 0.35, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 5:1) = 0.29; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.78 (d, *J* = 3.7 Hz, 1H, C*H*), 4.71 (t, *J* = 4.0 Hz, 1H, C*H*), 4.46 – 4.23 (m, 3H, OCH_2 & C*H*), 4.18 – 4.04 (m, 2H, C*H*), 4.05 – 3.93 (m, 2H, OCH_2), 2.47 (t, *J* = 2.4 Hz, 1H, C≡C*H*), 1.56 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.34 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 113.2, 109.9, 103.9, 79.3, 78.0, 77.9, 77.0, 75.6, 74.9, 65.2, 57.5, 26.9, 26.6, 26.4, 25.3; **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{22}NaO_6^+$ 321.1309; Found 321.1310. The spectroscopic data is consistent with previous report[39].

3.2.6. Synthesis and characterization of but-3-yn-1-yl 5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)pentanoate (2bc)[40]



A mixture of 4-(dimethylamino)pyridine (DMAP; 12.2 mg, 100 µmol, 5.00 mol%), *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 460 mg, 2.40 mmol, 1.20 equiv.), D-biotin (489 mg, 2.00 mmol, 1.00 equiv.), but-3-yn-1-ol (168 mg, 2.40 mmol, 1.20 equiv.) and DCM (10 mL) was stirred under room temperature for 3 days. The reaction mixture was then filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: DCM/MeOH = 20:1). Alkyne derivative **2bc** was obtained in 81% yield (480 mg, 1.62 mmol) as a colourless solid. **M.p.** 118 – 121 °C. **ORD**: $[\alpha]_D^{20}$ = +54.1 (c = 0.20, $CHCl_3$). **TLC**: R_f (DCM/MeOH = 20:1) = 0.26; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.92 (bs, 1H, N*H*), 5.42 (bs, 1H, N*H*), 4.50 (ddd, *J* = 7.7, 5.0, 1.2 Hz, 1H, C*H*), 4.31 (dd, *J* = 7.8, 4.6 Hz, 1H, C*H*), 4.18 (td, *J* = 6.8, 0.8 Hz, 2H, CH_2), 3.15 (ddd, *J* = 8.1, 6.5, 4.6 Hz, 1H, C*H*), 2.91 (ddd, *J* = 12.9, 5.0, 1.2 Hz, 1H, CH_2), 2.74 (d, *J* = 12.8 Hz, 1H, CH_2), 2.52 (td, *J* = 6.7, 2.6 Hz, 2H, CH_2), 2.36 (t, *J* = 7.5 Hz, 2H, CH_2), 2.01 (t, *J* = 2.7 Hz, 1H, C≡C*H*), 1.69 (ttd, *J* = 10.6, 5.8, 2.6 Hz, 4H, CH_2), 1.57 – 1.36 (m, 2H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 163.7, 80.3, 70.1, 62.2, 62.1, 60.3, 55.6, 40.7, 33.9, 28.44, 28.37, 24.9, 19.1; **IR** (ν_{max}, cm^{-1}) 3343 (w), 3252 (m), 3201 (m), 3117 (w), 3065 (w), 2914 (w), 2849 (w), 1736 (m), 1706 (s), 1473 (m), 1420 (m), 1356 (w), 1317 (w), 1267 (m), 1212 (w), 1173 (s), 1105 (m), 1075 (w), 993 (w), 878 (w), 860 (w), 730 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}N_2NaO_3S^+$ 319.1087; Found 319.1092.

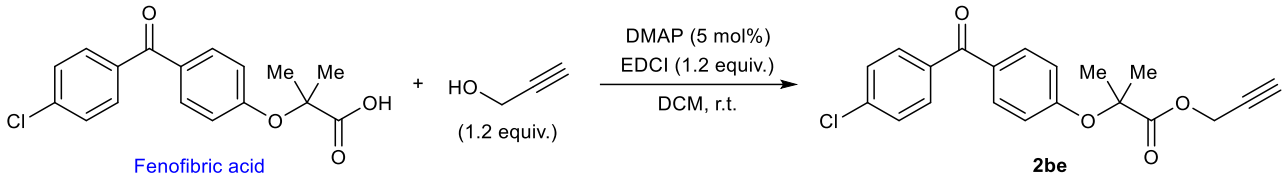
3.2.7. Synthesis and characterization of prop-2-yn-1-yl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (2bd)[40]



A mixture of 4-(dimethylamino)pyridine (DMAP; 6.10 mg, 50.0 µmol, 5.00 mol%), *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 230 mg, 1.20 mmol, 1.20 equiv.), Sulbactam (233 mg, 1.00 mmol, 1.00 equiv.), prop-2-yn-1-ol (67.3 mg, 1.20 mmol, 1.20 equiv.) and DCM (10 mL) was stirred under room temperature for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1). Alkyne derivative **2bd** was obtained in 87% yield (237 mg, 873 µmol) as a colourless oil. **ORD**: $[\alpha]_D^{20}$ = +220.7 (c = 0.25, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.15; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.90 (dd, *J* = 15.5, 2.5 Hz, 1H, CH_2), 4.72 (dd, *J* = 15.5, 2.5 Hz, 1H, CH_2), 4.62 (dd, *J* = 4.1, 2.2 Hz, 1H, C*H*), 4.42 (s, 1H, C*H*), 3.57 – 3.38 (m, 2H, CH_2), 2.55 (t, *J* = 2.5 Hz, 1H, C≡C*H*), 1.64 (s, 3H, CH_3), 1.45 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8, 166.4, 76.4, 76.4, 63.1, 63.0, 61.2, 53.5, 38.5, 20.4, 18.7; **IR** (ν_{max}, cm^{-1}) 3644 (w), 3283 (w), 2989 (w), 2130 (w), 1793 (s), 1762 (s), 1466 (w), 1442 (w), 1398 (w), 1376 (w), 1319 (s), 1274 (m), 1184 (s), 1157 (s), 1118 (s), 1085 (m), 1023 (m), 996 (m), 944 (s), 902 (w), 861 (w),

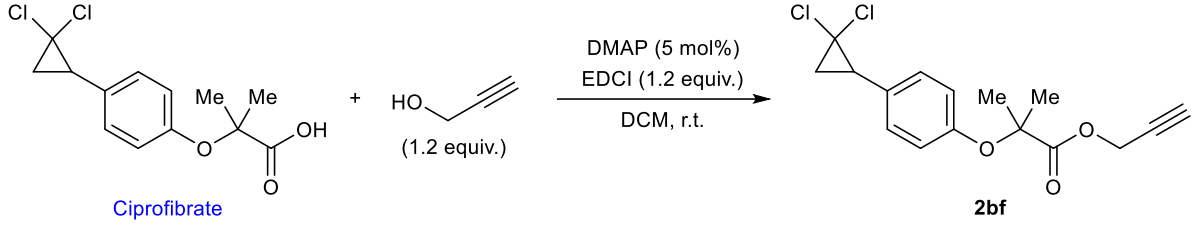
828 (w), 775 (w), 736 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{13}NNaO_5S^+$ 294.0407; Found 294.0408.

3.2.8. Synthesis and characterization of prop-2-yn-1-yl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (2be)[40]



A mixture of 4-(dimethylamino)pyridine (DMAP; 6.10 mg, 50.0 µmol, 5.00 mol%), *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 230 mg, 1.20 mmol, 1.20 equiv.), Fenofibric acid (319 mg, 1.00 mmol, 1.00 equiv.), prop-2-yn-1-ol (67.3 mg, 1.20 mmol, 1.20 equiv.) and DCM (5 mL) was stirred under room temperature for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1). Alkyne derivative **2be** was obtained in 72% yield (257 mg, 721 µmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.20; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.65 (m, 4H, Ar*H*), 7.52 – 7.39 (m, 2H, Ar*H*), 6.94 – 6.83 (m, 2H, Ar*H*), 4.77 (d, *J* = 2.4 Hz, 2H, OCH_2), 2.48 (t, *J* = 2.5 Hz, 1H, C≡C*H*), 1.69 (s, 6H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.4, 173.1, 159.5, 138.6, 136.5, 132.1, 131.3, 130.8, 128.7, 117.8, 79.4, 76.9, 75.6, 53.1, 25.5; **IR** (ν_{max}, cm^{-1}) 3296 (w), 3072 (w), 2997 (w), 2942 (w), 2129 (w), 1922 (w), 1742 (m), 1653 (m), 1598 (s), 1505 (m), 1386 (w), 1305 (m), 1278 (s), 1247 (s), 1170 (s), 1130 (s), 1090 (s), 1013 (m), 989 (m), 959 (m), 927 (s), 852 (m), 839 (m), 762 (s), 738 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{17}ClNaO_4^+$ 379.0708; Found 379.0712.

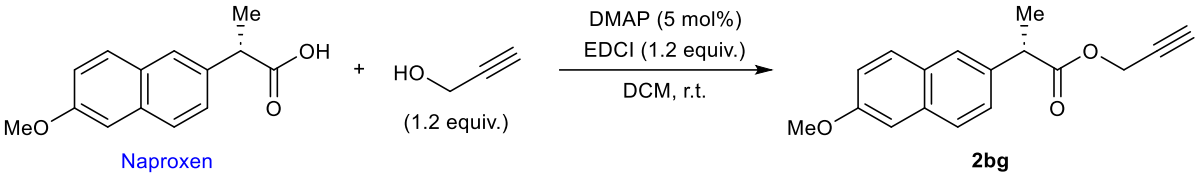
3.2.9. Synthesis and characterization of prop-2-yn-1-yl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (2bf)[40]



A mixture of 4-(dimethylamino)pyridine (DMAP; 6.10 mg, 50.0 µmol, 5.00 mol%), *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 230 mg, 1.20 mmol, 1.20 equiv.), Ciprofibrate (289 mg, 1.00 mmol, 1.00 equiv.), prop-2-yn-1-ol (67.3 mg, 1.20 mmol, 1.20 equiv.) and DCM (10 mL) was stirred under room temperature for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 20:1). Alkyne derivative **2bf** was obtained in 74% yield (241 mg, 736 µmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 – 7.03 (m, 2H, Ar*H*), 6.91 – 6.77 (m, 2H, Ar*H*), 4.76 (d, *J* = 2.5 Hz, 2H, OCH_2), 2.83 (dd, *J* = 10.7, 8.3 Hz, 1H, C*H*), 2.47 (t, *J* = 2.5 Hz, 1H, C≡C*H*), 1.94 (dd, *J* = 10.7, 7.4 Hz, 1H, CH_2), 1.77 (dd, *J* = 8.4, 7.4 Hz, 1H, CH_2), 1.61 (s, 6H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 154.8, 129.8, 128.7, 119.3, 79.3, 75.4, 61.0, 52.9, 35.0, 26.0, 25.44, 25.43; **IR** (ν_{max}, cm^{-1}) 3296 (w), 2996 (w), 2130 (w), 1742 (m), 1611 (w), 1510 (m), 1465 (w), 1436 (w), 1385 (w), 1367 (w), 1274 (m), 1239 (m), 1173 (m), 1127 (s), 1051 (w), 1012 (w), 989 (w), 966 (w), 932 (w),

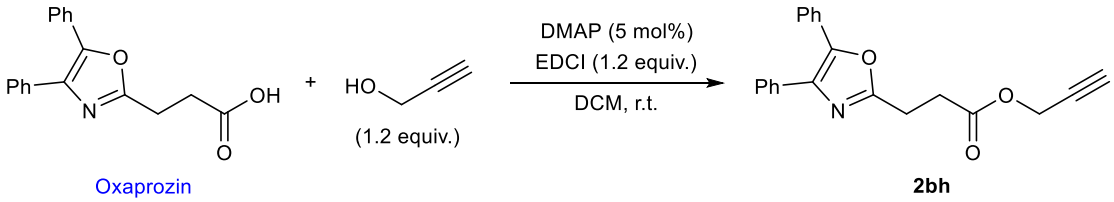
889 (w), 835 (m), 761 (m), 734 (w); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{16}Cl_2NaO_3^+$ 349.0369; Found 349.0376.

3.2.10. Synthesis and characterization of prop-2-yn-1-yl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (2bg)[40]



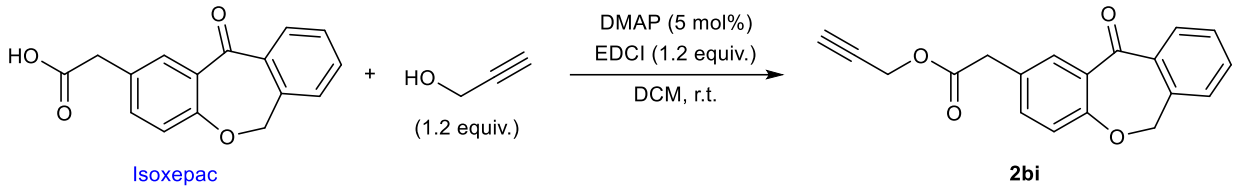
A mixture of 4-(dimethylamino)pyridine (DMAP; 6.10 mg, 50.0 mmol, 5.00 mol%), *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 230 mg, 1.20 mmol, 1.20 equiv.), Naproxen (230 mg, 1.00 mmol, 1.00 equiv.), prop-2-yn-1-ol (67.3 mg, 1.20 mmol, 1.20 equiv.) and DCM (10 mL) was stirred under room temperature for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1). Alkyne derivative **2bg** was obtained in 94% yield (254 mg, 945 μmol) as a colourless solid. **M.p.** 69 – 70 °C. **ORD**: $[\alpha]_D^{20}$ = +30.9 (c = 0.16, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.28; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H, Ar*H*), 7.69 – 7.65 (m, 1H, Ar*H*), 7.41 (dd, *J* = 8.5, 1.9 Hz, 1H, Ar*H*), 7.19 – 7.07 (m, 2H, Ar*H*), 4.81 – 4.49 (m, 2H, OCH_2), 3.92 (s, 3H, OCH_3), 3.91 (q, *J* = 7.1 Hz, 1H, C*H*), 2.43 (t, *J* = 2.5 Hz, 1H, C≡C*H*), 1.60 (d, *J* = 7.2 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 157.8, 135.2, 133.9, 129.4, 129.0, 127.4, 126.3, 126.2, 119.2, 105.7, 77.7, 75.0, 55.5, 52.4, 45.3, 18.7; **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{17}H_{16}NaO_3^+$ 291.0992; Found 291.0982. The NMR spectroscopic data is consistent with previous report[41].

3.2.11. Synthesis and characterization of prop-2-yn-1-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (2bh)[40]



A mixture of 4-(dimethylamino)pyridine (DMAP; 6.10 mg, 50.0 mmol, 5.00 mol%), *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 230 mg, 1.20 mmol, 1.20 equiv.), Oxaprozin (293 mg, 1.00 mmol, 1.00 equiv.), prop-2-yn-1-ol (67.3 mg, 1.20 mmol, 1.20 equiv.) and DCM (10 mL) was stirred under room temperature for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1). Alkyne derivative **2bh** was obtained in 97% yield (320 mg, 966 μmol) as a colourless solid. **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.52; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H, Ar*H*), 7.60 – 7.54 (m, 2H, Ar*H*), 7.41 – 7.28 (m, 6H, Ar*H*), 4.74 (d, *J* = 2.4 Hz, 2H, OCH_2), 3.32 – 3.14 (m, 2H, CH_2), 2.99 – 2.96 (m, 2H, CH_2), 2.46 (t, *J* = 2.5 Hz, 1H, C≡C*H*); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 161.6, 145.6, 135.3, 132.5, 129.1, 128.8, 128.7, 128.6, 128.2, 128.0, 126.6, 77.6, 75.2, 52.4, 31.0, 23.5; **HRMS** (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{21}H_{18}NO_3^+$ 332.1281; Found 332.1279. The NMR spectroscopic data is consistent with previous report[42].

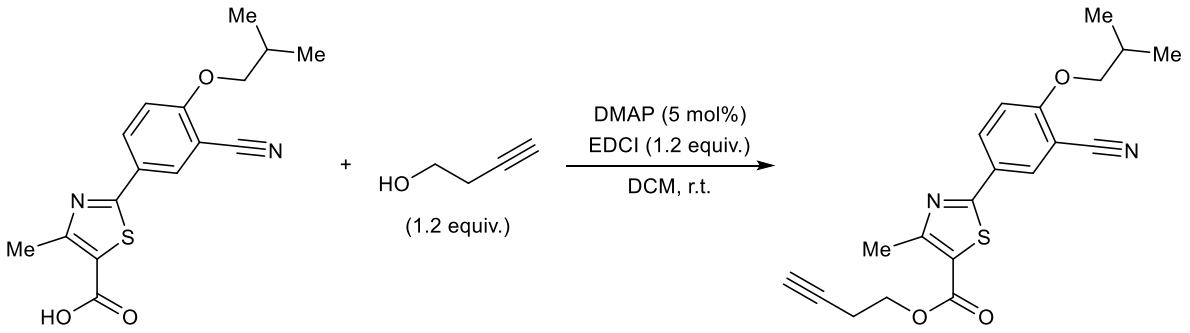
3.2.12. Synthesis and characterization of prop-2-yn-1-yl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (2bi)[40]



Isoxepac **2bi**

A mixture of 4-(dimethylamino)pyridine (DMAP; 6.10 mg, 50.0 μmol, 5.00 mol%), *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 230 mg, 1.20 mmol, 1.20 equiv.), Isoxepac (268 mg, 1.00 mmol, 1.00 equiv.), prop-2-yn-1-ol (67.3 mg, 1.20 mmol, 1.20 equiv.) and DCM (10 mL) was stirred under room temperature for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1). Alkyne derivative **2bi** was obtained in 96% yield (295 mg, 962 μmol) as a colourless solid. **M.p.** 96 – 98 °C. **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.89 (dd, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 7.56 (td, *J* = 7.4, 1.4 Hz, 1H, Ar*H*), 7.51 – 7.40 (m, 2H, Ar*H*), 7.36 (dd, *J* = 7.4, 1.3 Hz, 1H, Ar*H*), 7.03 (d, *J* = 8.4 Hz, 1H, Ar*H*), 5.19 (s, 2H, CH_2), 4.71 (d, *J* = 2.4 Hz, 2H, CH_2), 3.70 (s, 2H, CH_2), 2.48 (t, *J* = 2.5 Hz, 1H, C≡C*H*); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.9, 170.7, 160.7, 140.6, 136.4, 135.6, 132.9, 132.7, 129.6, 129.4, 128.0, 127.3, 125.3, 121.3, 77.5, 75.3, 73.8, 52.6, 39.9; **IR** (ν_{max}, cm^{-1}) 3284 (w), 3065 (w), 3033 (w), 2974 (w), 2950 (w), 2921 (w), 2872 (w), 2129 (w), 1799 (w), 1739 (s), 1646 (m), 1611 (m), 1601 (m), 1570 (w), 1489 (s), 1453 (w), 1414 (m), 1376 (w), 1300 (s), 1285 (m), 1242 (m), 1221 (m), 1202 (m), 1139 (s), 1121 (s), 1013 (s), 964 (w), 938 (w), 860 (w), 830 (m), 800 (w), 762 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{14}NaO_4^+$ 329.0784; Found 329.0784.

3.2.13. Synthesis and characterization of but-3-yn-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (2bj)[40]

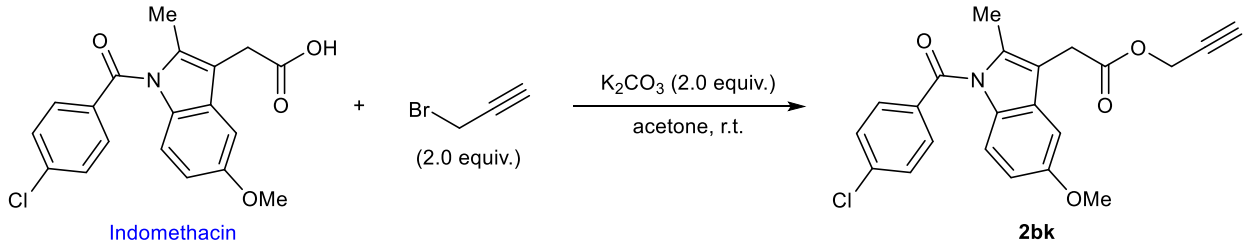


Febuxostat **2bj**

A mixture of 4-(dimethylamino)pyridine (DMAP; 6.10 mg, 50.0 mmol, 5.00 mol%), *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 230 mg, 1.20 mmol, 1.20 equiv.), Febuxostat (316 mg, 1.00 mmol, 1.00 equiv.), but-3-yn-1-ol (84.1 mg, 1.20 mmol, 1.20 equiv.) and DCM (10 mL) was stirred under room temperature for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1). Alkyne derivative **2bj** was obtained in 84% yield (308 mg, 835 μmol) as a colourless solid. **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.48; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.3 Hz, 1H, Ar*H*), 8.09 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar*H*), 7.01 (d, *J* = 8.9 Hz, 1H, Ar*H*), 4.41 (t, *J* = 6.7 Hz, 2H, CH_2), 3.90 (d, *J* = 6.5 Hz, 2H, CH_2), 2.77 (s, 3H, CH_3), 2.66 (td, *J* = 6.7, 2.7 Hz, 2H, CH_2), 2.20 (dt, *J* = 13.3, 6.7 Hz, 1H, C*H*), 2.04 (t, *J* = 2.7 Hz,

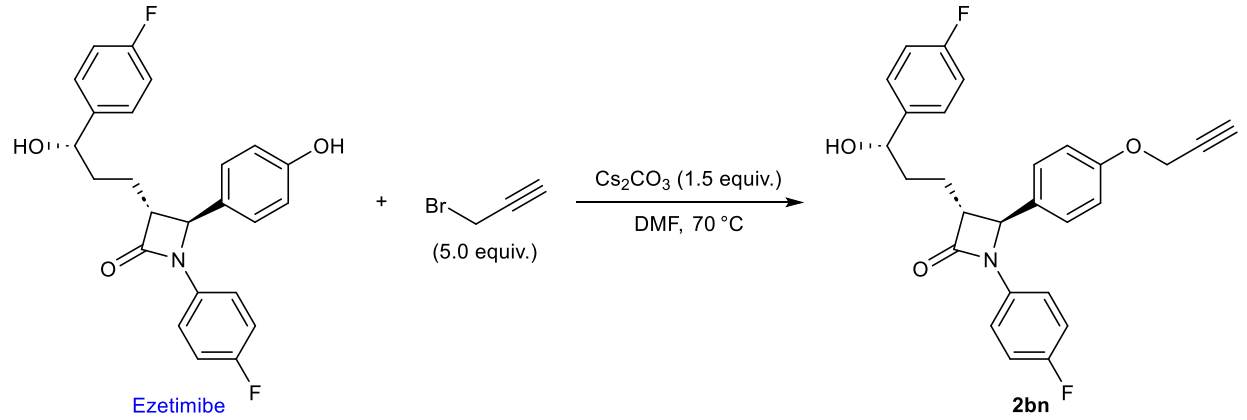
1H, C≡C*H*), 1.09 (d, *J* = 6.7 Hz, 6H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 162.7, 161.9, 161.8, 132.7, 132.3, 126.1, 121.6, 115.5, 112.8, 103.2, 79.9, 75.9, 70.4, 63.0, 28.3, 19.3, 19.2, 17.7; **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}N_2O_3S^+$ 369.1267; Found 369.1254. The spectroscopic data is consistent with previous report[43].

3.2.14. Synthesis and characterization of prop-2-yn-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (2bk)[44]



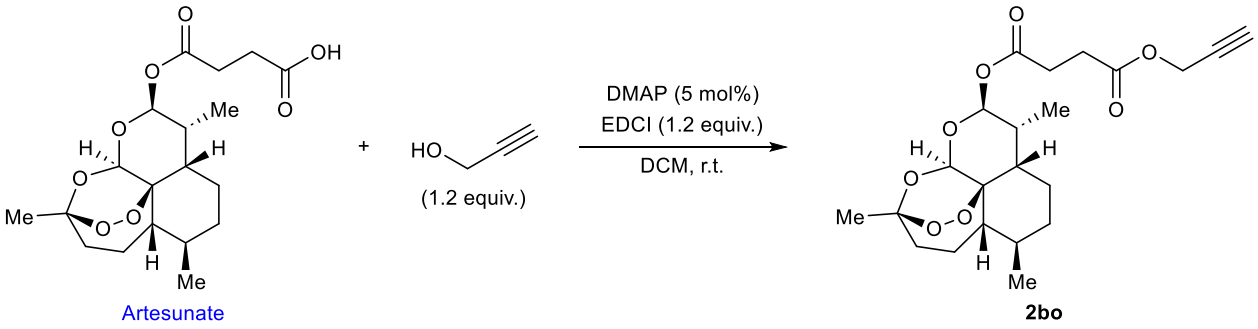
An oven-dried Schlenk tube was charged with Indomethacin (358 mg, 1.00 mmol, 1.00 equiv.), K_2CO_3 (276 mg, 2.00 mmol, 2.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, acetone (10 mL) was added by syringe and the resulting mixture was stirring under room temperature. Subsequently, 3-bromoprop-1-yne (2.00 mmol, 238 mg, 2.00 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with EtOAc (3 × 5 mL). The solvent was removed under reduced pressure. The resulting residue was dissolved in EtOAc (15 mL) and the organic solution of the crude product was washed with brine (15 mL), deionized water (15 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1). Alkyne derivative **2bk** was obtained in 98% yield (388 mg, 980 μmol) as a colourless oil, which turned to be solidified when stored in the freezer. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 2H, Ar*H*), 7.50 – 7.42 (m, 2H, Ar*H*), 6.96 (d, *J* = 2.5 Hz, 1H, Ar*H*), 6.87 (d, *J* = 9.1 Hz, 1H, Ar*H*), 6.67 (dd, *J* = 9.0, 2.5 Hz, 1H, Ar*H*), 4.71 (d, *J* = 2.5 Hz, 2H, C*H*$_2$), 3.84 (s, 3H, C*H*$_3$), 3.72 (s, 2H, C*H*$_2$), 2.48 (t, *J* = 2.5 Hz, 1H, C≡C*H*), 2.39 (s, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 168.4, 156.2, 139.4, 136.3, 134.0, 131.3, 130.9, 130.6, 129.3, 115.1, 112.1, 112.0, 101.3, 77.6, 75.3, 55.8, 52.6, 30.2, 13.5; **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}ClNO_4^+$ 396.0997; Found 396.0982. The NMR spectroscopic data is consistent with the previous reports[45].

3.2.15. Synthesis and characterization of (3*R*,4*S*)-1-(4-fluorophenyl)-3-((*S*)-3-(4-fluorophenyl)-3-hydroxypropyl)-4-(4-(prop-2-yn-1-yloxy)phenyl)azetidin-2-one (2bn)[46]



An oven-dried Schlenk tube was charged with Ezetimibe (409 mg, 1.00 mmol, 1.00 equiv.), Cs_2CO_3 (489 mg, 1.50 mmol, 1.50 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. After that, dimethylformamide (DMF; 10 mL) was added by syringe and the resulting mixture was stirring under room temperature. Subsequently, 3-bromoprop-1-yne (5.00 mmol, 595 mg, 5.00 equiv.) was added dropwise and the reaction mixture was stirred at 70 °C for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with EtOAc (3 × 5 mL). The organic solution of the crude product was washed with brine (3 × 15 mL), deionized water (3 × 15 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1). Alkyne derivative **2bn** was obtained in 71% yield (319 mg, 712 µmol) as a colourless oil. **ORD**: $[\alpha]_D^{20}$ = -42.8 (c = 0.33, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 1:1) = 0.61; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.10 (m, 6H, Ar*H*), 7.00 – 6.77 (m, 6H, Ar*H*), 4.66 – 4.59 (m, 1H, O*H*), 4.61 (d, *J* = 2.4 Hz, 2H, CH_2), 4.50 (d, *J* = 2.3 Hz, 1H, C*H*), 2.99 (td, *J* = 7.4, 2.5 Hz, 1H, C*H*), 2.45 (t, *J* = 2.4 Hz, 1H, C≡C*H*), 2.25 (d, *J* = 3.7 Hz, 1H, C*H*), 2.01 – 1.71 (m, 4H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 162.3 (d, *J* = 245.5 Hz), 159.1 (d, *J* = 243.8 Hz), 157.9, 140.2 (d, *J* = 3.2 Hz), 134.0 (d, *J* = 2.8 Hz), 130.5, 127.5 (d, *J* = 8.1 Hz), 127.3, 118.5 (d, *J* = 7.9 Hz), 116.0 (d, *J* = 22.7 Hz), 115.7, 115.5 (d, *J* = 21.4 Hz), 78.4, 76.0, 73.2, 61.2, 60.5, 56.0, 36.7, 25.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.9 (Ar*F*), -118.0 (Ar*F*); **IR** (ν_{max}, cm^{-1}) 3294 (w), 3066 (w), 2928 (w), 2862 (w), 2122 (w), 1894 (w), 1736 (s), 1607 (w), 1510 (s), 1387 (m), 1219 (s), 1156 (w), 1140 (w), 1025 (m), 833 (s), 735 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{23}F_2NNaO_3^+$ 470.1538; Found 470.1540.

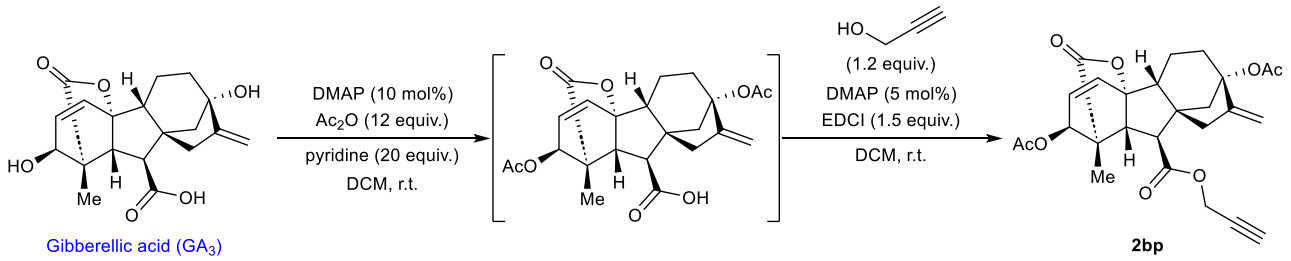
3.2.16. Synthesis and characterization of prop-2-yn-1-yl ((3*R*,5a*S*,6*R*,8a*S*,9*R*,10*S*,12*R*,12a*R*)-3,6,9-trimethyldecahydro-12*H*-3,12-epoxy[1,2]dioxepino[4,3-*i*]isochromen-10-yl) succinate (2bo)[40]



A mixture of 4-(dimethylamino)pyridine (DMAP; 6.10 mg, 50.0 mmol, 5.00 mol%), *N*-ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 230 mg, 1.20 mmol, 1.20 equiv.), Artesunate (384 mg, 1.00 mmol, 1.00 equiv.), prop-2-yn-1-ol (67.3 mg, 1.20 mmol, 1.20 equiv.) and DCM (10 mL) was stirred under room temperature for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with DCM (3 × 5 mL). The organic solution of the crude product was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1). Alkyne derivative **2bo** was obtained in 82% yield (345 mg, 816 µmol) as a colourless oil. **ORD**: $[\alpha]_D^{20}$ = +6.7 (c = 0.20, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.37; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.79 (d, *J* = 9.8 Hz, 1H, C*H*), 5.43 (s, 1H, C*H*), 4.69 (td, *J* = 2.5, 0.6 Hz, 2H, CH_2), 2.81 – 2.61 (m, 4H, CH_2), 2.57 (dtd, *J* = 9.9, 7.3, 4.6 Hz, 1H, C*H*), 2.47 (t, *J* = 2.5 Hz, 1H, C≡C*H*), 2.43 – 2.30 (m, 1H, C*H*), 2.03 (ddd, *J* = 14.6, 4.9, 3.0 Hz, 1H, C*H*), 1.89 (ddt, *J* = 13.5, 6.6, 3.6 Hz, 1H, C*H*), 1.74 (ddq, *J* = 19.7, 13.4, 3.6 Hz, 2H, CH_2), 1.65 – 1.58 (m, 1H, C*H*), 1.55 – 1.20 (m, 7H, C*H* & CH_3), 1.07 – 0.95 (m, 1H, C*H*), 0.96 (d, *J* = 5.9 Hz, 3H, CH_3), 0.85 (d, *J* = 7.1 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.5, 171.1, 104.6, 92.4, 91.7, 80.2, 77.6, 75.2, 52.4, 51.7, 45.4, 37.4, 36.3, 34.2, 31.9, 29.2, 28.8, 26.1, 24.7, 22.1, 20.4, 12.2; **HRMS** (ESI/QTOF)

m/z: [M + Na]$^+$ Calcd for $C_{22}H_{30}NaO_8^+$ 445.1833; Found 445.1828. The spectroscopic data is consistent with previous report[47].

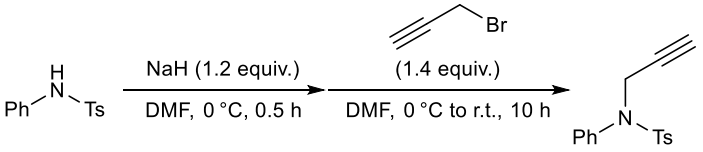
3.2.17. Synthesis and characterization of (1*S*,2*S*,4a*R*,4b*R*,7*S*,9a*S*,10*S*,10a*R*)-1-methyl-8-methylene-13-oxo-10-((prop-2-yn-1-yloxy)carbonyl)-1,2,5,6,8,9,10,10a-octahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[*a*]azulene-2,7(4b*H*)-diyl diacetate (2bp)[40]



To a solution of gibberellic acid (GA_3; 693 mg, 2.00 mmol, 1.00 equiv.), acetic anhydride (Ac_2O; 2.3 mL, 24.0 mmol, 12.0 equiv.) and DMAP (24.4 mg, 200 μmol, 10.0 mol%) in anhydrous DCM (20 mL) at room temperature was added pyridine (3.2 mL, 40.0 mmol, 20.0 equiv.). After the addition, the mixture was allowed to stir for 48 hours at room temperature before addition of 10 mL of deionized water. After extraction with DCM (10 mL × 2), the organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a colourless oil. The crude was then dissolved in DCM (15 mL). To the solution was sequentially added *N*-ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI; 460 mg, 2.40 mmol, 1.20 equiv.), prop-2-yn-1-ol (135 mg, 2.40 mmol, 1.20 equiv.) and DMAP (12.2 mg, 100 μmol, 5.00 mol%). After the addition, the mixture was allowed to stir for 12 hours at room temperature before addition of 15 mL of deionized water. The organic phase was removed, and the remaining aqueous portion was extracted with DCM (3 × 5.0 mL). The combined organic portions were washed with brine, dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 3:1). Alkyne derivative **2bp** was obtained in 29% yield (272 mg, 580 μmol) as a colourless solid. **ORD**: $[\alpha]_D^{20}$ = +152.5 (c = 0.22, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.16; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.35 (dd, *J* = 9.3, 0.8 Hz, 1H, C*H*=CH), 5.85 (dd, *J* = 9.3, 3.8 Hz, 1H, CH=C*H*), 5.31 (dd, *J* = 3.8, 0.8 Hz, 1H, CH_2=C), 5.16 (dd, *J* = 3.2, 1.5 Hz, 1H, CH_2=C), 4.98 – 4.97 (m, 1H, C*H*), 4.72 (dd, *J* = 2.5, 0.6 Hz, 2H, CH_2), 3.31 (d, *J* = 11.0 Hz, 1H, C*H*), 2.78 (d, *J* = 11.0 Hz, 1H, C*H*), 2.49 (t, *J* = 2.4 Hz, 1H, C≡C*H*), 2.42 – 2.21 (m, 4H, CH_2), 2.18 – 2.12 (m, 1H, C*H*), 2.09 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.04 – 1.87 (m, 2H, CH_2), 1.81 – 1.60 (m, 2H, CH_2), 1.13 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.0, 171.1, 170.1, 169.9, 153.4, 134.3, 129.3, 108.4, 89.9, 84.1, 77.1, 75.6, 70.2, 53.5, 52.5, 52.2, 51.3, 51.1, 50.2, 42.5, 39.9, 36.3, 22.1, 20.9, 16.9, 14.4; **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{28}NaO_8^+$ 491.1676; Found 491.1668. The spectroscopic data is consistent with previous report[48].

3.3. Synthesis and characterization of *N*-allenamides

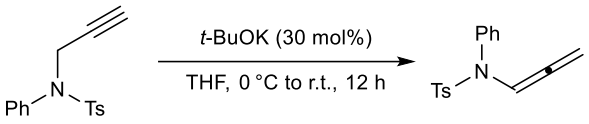
3.3.1 Synthesis of 4-methyl-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide



The product 4-methyl-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide was prepared following the procedure described in the literature[49]. Under argon, to a cooled (0 °C) solution of 4-methyl-*N*-phenylbenzenesulfonamide (742 mg, 3.00 mmol, 1.00 equiv.) in dry DMF (10 mL), NaH (60 wt.% in mineral oil, 144 mg, 3.6 mmol, 1.20 equiv.) was added in one portion. After stirring for 30 min at 0 °C, propargyl bromide (500 mg, 4.2 mmol, 1.40 equiv.) was added and the mixture was stirred at room

temperature for additional 10 h. The resulting mixture was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic portions were washed with brine, dried over Na_2SO_4, filtered and the volatiles removed under reduced pressure. The crude product was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 20:1). 4-Methyl-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide was obtained in 97% yield (832 mg, 2.91 mmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.34; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H, Ar*H*), 7.35 – 7.27 (m, 3H, Ar*H*), 7.24 – 7.20 (m, 4H, Ar*H*), 4.43 (d, *J* = 2.5 Hz, 2H, NCH_2), 2.40 (s, 3H, CH_3), 2.17 (t, *J* = 2.5 Hz, 1H, C≡C*H*); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 139.3, 135.5, 129.3, 129.1, 128.4, 128.2, 128.0, 78.1, 73.9, 41.1, 21.6. The spectroscopic data is consistent with previous report[49].

3.3.2 Synthesis of 4-methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide



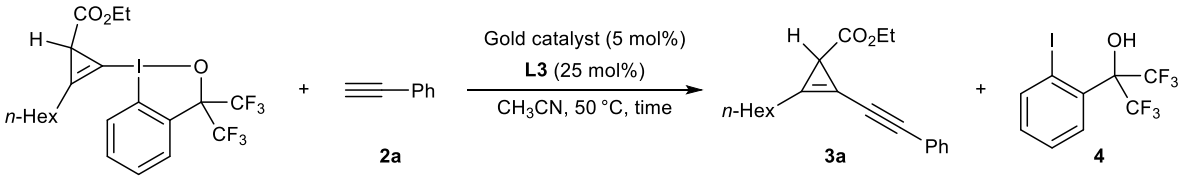
The product 4-methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide was prepared following the procedure described in the literature[50]. To a solution of 4-methyl-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (641 mg, 2.25 mmol, 1.00 equiv.) in 10 ml of anhydrous THF under argon atmosphere at 0 °C was added in one portion of *t*-BuOK (75.6 mg, 674 μmol, 0.300 equiv.). The reaction was allowed to stir at room temperature. After 12 h the mixture was diluted with Et_2O (10 mL), and then filtrated over celite. The residue was washed with diethyl ether (3 × 10 mL). The collected filtrate was concentrated in vacuo and the residue was purified via flash chromatography on silica gel (eluent: pentane/ethyl acetate = 30:1). 4-Methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide was obtained in 70% yield (446 mg, 1.56 mmol) as a colourless solid. **TLC**: R_f (*n*-hexane/EtOAc = 30:1) = 0.48; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 2H, Ar*H*), 7.33 – 7.22 (m, 5H, Ar*H*), 7.10 (t, *J* = 6.3 Hz, 1H, C*H*=C=CH_2), 7.05 – 6.94 (m, 2H, Ar*H*), 5.01 (s, 1H, CH=C=CH_2), 5.00 (s, 1H, CH=C=CH_2), 2.42 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.1, 144.0, 137.3, 135.3, 129.6, 128.8, 128.7, 127.8, 102.5, 87.6, 21.7. The spectroscopic data is consistent with previous report[50].

4. Optimization of σ-type cyclopropenium cation transfer reaction with terminal alkynes

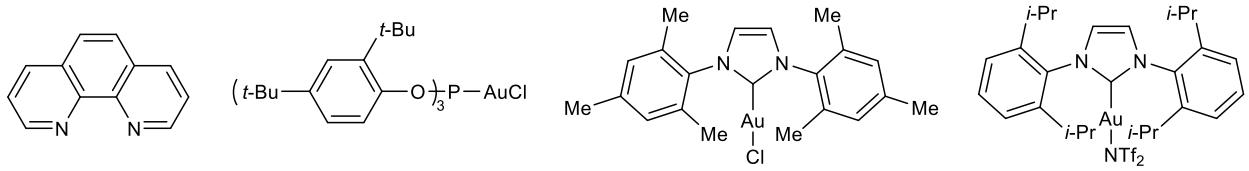
4.1. Evaluation of gold catalysts

An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, **L3** (4.50 mg, 25.0 μmol, 25.0 mol%), gold catalyst (5.00 μmol, 5.00 mol%) and CpBX **1a** (56.4 mg, 0.100 mmol, 1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (0.10 M; 1.0 mL) and terminal alkyne **2a** (11 μL, 0.100 mmol, 1.00 equiv.) were added by syringe. The reaction mixture was stirred at 50 °C for the specified time. The resulting reaction mixture was diluted with CH_2Cl_2 (5.0 mL) and filtered through a short pad of silica gel by eluting with CH_2Cl_2 (3 × 5.0 mL). The filtrate was then concentrated to dryness and the residue was subjected to flash column chromatography on silica gel (eluent: pentane/EtOAc = 20:1). The fractions that contained the product **3a** and **4** were collected and concentrated by rotary evaporation. The yields of **3a** and **4** were obtained by quantitative ^{1}H NMR analysis using CH_2Br_2 (^{1}H NMR δ 4.92) as the internal standard.

Table 1 | Evaluation of gold catalysts



Entry	Gold catalyst	Time (h)	Yield (%)	
			3a	**4**
1	PPh_3AuCl	10	trace	-
2	AuCl	10	94	96
3	$AuCl_3$	10	90	99
4	$AuBr_3$	10	85	93
5	$PPhMe_2AuCl$	10	trace	-
6	$Au(OAc)_3$	10	18	22
7	PPh_3AuMe	10	trace	-
8	Au_2O_3[a]	10	35	42
9	$(ArO)_3PAuCl$	10	trace	-
10	IMesAuCl	10	0	-
11	$(Me_2S)AuCl$	2	97	99
12	PPh_3AuNTf_2	9	trace	92
13	$IPrAuNTf_2$	9	0	96
14	$HAuCl_4 \bullet xH_2O$	9	77	97
15[b]	none	9	0	-

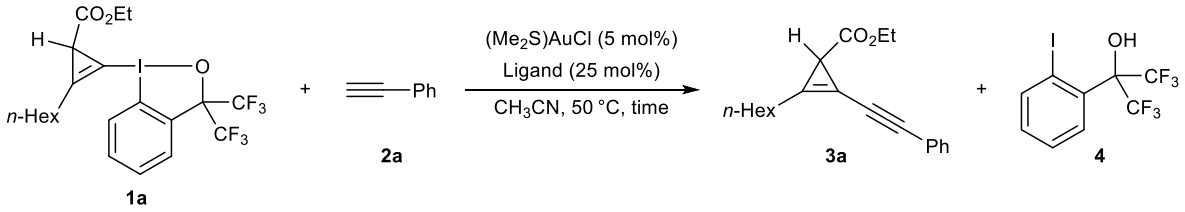


Reactions performed on a 0.100 mmol scale. Yields were determined by ^1H NMR spectroscopy using dibromomethane as the internal standard. [a]Au_2O_3 (2.50 mol%) was used instead. [b]**1a** was recovered in 99% NMR yield.

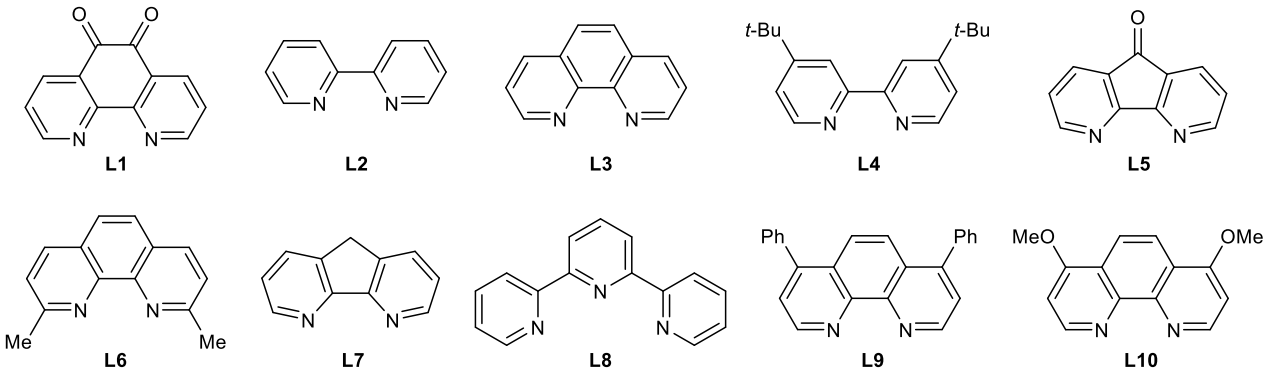
4.2. Evaluation of bidentate ligands

An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, bidentate ligand (25.0 μmol, 25.0 mol%), $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%) and CpBX **1a** (56.4 mg, 0.100 mmol, 1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (0.10 M; 1.0 mL) and terminal alkyne **2a** (11 μL, 0.100 mmol, 1.00 equiv.) were added by syringe. The reaction mixture was stirred at 50 °C for the specified time. The resulting reaction mixture was diluted with CH_2Cl_2 (5.0 mL) and filtered through a short pad of silica gel by eluting with CH_2Cl_2 (3 × 5.0 mL). The filtrate was then concentrated to dryness and the residue was subjected to flash column chromatography on silica gel (eluent: pentane/EtOAc = 20:1). The fractions that contained the product **3a** and **4** were collected and concentrated by rotary evaporation. The yields of **3a** and **4** were obtained by quantitative ^1H NMR analysis using CH_2Br_2 (^1H NMR δ 4.92) as the internal standard.

Table 2 | Evaluation of bidentate ligands



Entry	Ligand	Time (h)	Yield (%)	
			3a	**4**
1	**L1**	2	97	99
2	**L2**	11	92	97
3	**L3**	3	93	91
4	**L4**	11	90	93
5	**L5**	11	84	87
6	**L6**	11	80	85
7	**L7**	11	10	16
8	**L8**	11	29	32
9	**L9**	11	90	94
10	**L10**	11	27	34
11	none	9	55	66

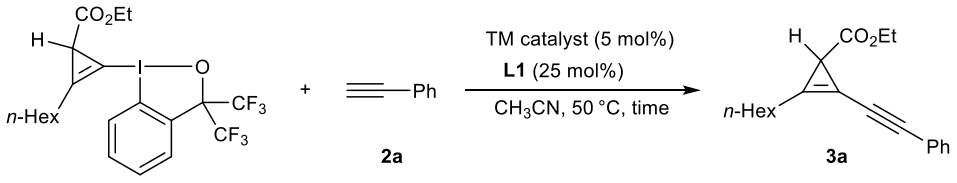


Reactions performed on a 0.100 mmol scale. Yields were determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.

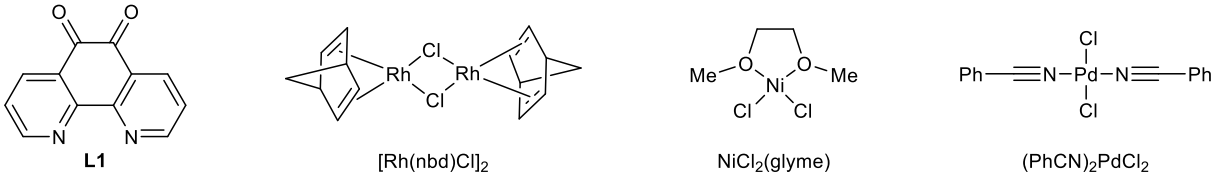
4.3. Evaluation of transition metal catalysts

An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, **L1** (5.25 mg, 25.0 µmol, 25.0 mol%), transition metal catalyst (TM catalyst; 5.00 µmol, 5.00 mol%) and CpBX **1a** (56.4 mg, 0.100 mmol, 1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (0.10 M; 1.0 mL) and terminal alkyne **2a** (11 µL, 0.100 mmol, 1.00 equiv.) were added by syringe. The reaction mixture was stirred at 50 °C for the specified time. The resulting reaction mixture was diluted with CH_2Cl_2 (5.0 mL) and filtered through a short pad of silica gel by eluting with CH_2Cl_2 (3 × 5.0 mL). The filtrate was then concentrated to dryness and the residue was subjected to flash column chromatography on silica gel (eluent: pentane/EtOAc = 20:1). The fractions that contained the product **3a** and the remaining CpBX **1a** were collected separately and concentrated by rotary evaporation. The yields of **3a** and the recoveries of **1a** were obtained by quantitative ^{1}H NMR analysis using CH_2Br_2 (^{1}H NMR δ 4.92) as the internal standard.

Table 3 | Evaluation of transition metal catalysts



Entry	Transition metal catalyst	Time (h)	Yield (%)	
			3a	**1a**
1	$[Rh(nbd)Cl]_2$[a]	12	0	95
2	$FeCl_2$	12	0	99
3	$PtCl_2$	12	0	98
4	$RuCl_3$	12	0	99
5	AgCl	12	0	99
6	$(PhCN)_2PdCl_2$	12	0	99
7	$NiCl_2$(glyme)	12	0	99
8	CuCl	12	trace	78
9	$(Me_2S)AuCl$	2	97	0

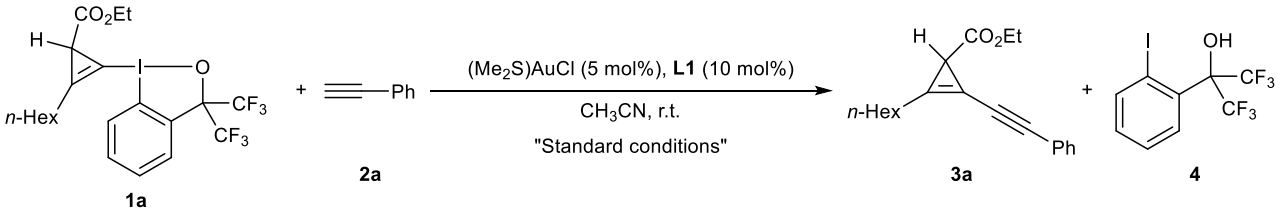


Reactions performed on a 0.100 mmol scale. Yields were determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard.
[a]$[Rh(nbd)Cl]_2$ (2.50 mol%) was used instead.

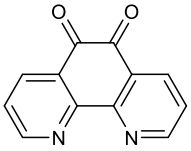
4.4. Variations from the standard condition

An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, ligand, catalyst and CpBX **1a** (56.4 mg, 0.100 mmol, 1.00 equiv.) or **1a-1** (32.2 mg, 0.100 mmol, 1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, solvent (0.10 M; 1.0 mL) and terminal alkyne **2a** (11 μL, 0.100 mmol, 1.00 equiv.) or its surrogates were added. The reaction mixture was stirred at the indicated temperature for the specified time. The resulting reaction mixture was diluted with CH_2Cl_2 (5.0 mL)and filtered through a short pad of silica gel by eluting with CH_2Cl_2 (3 × 5.0 mL). The filtrate was then concentrated to dryness and the residue was subjected to flash column chromatography on silica gel (eluent: pentane/EtOAc = 20:1 to 5:1). The fractions that contained the product **3a**, **4** and the remaining CpBX **1a** or **1a-1** were collected separately and concentrated by rotary evaporation. The yields of **3a**, **4** and the recoveries of **1a** or **1a-1** were obtained by quantitative ^{1}H NMR analysis using CH_2Br_2 (^{1}H NMR δ 4.92) as the internal standard.

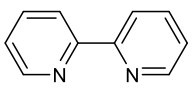
Table 4 | Variations from the standard conditions



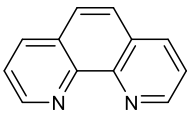
Entry	Variations from the "standard conditions"	Time (h)	Yield (%)[a]		
			3a	**1a**	**4**
1	none	2	96	0	99
2	without $(Me_2S)AuCl$	24	0	99	-
3	without **L1**	8	84	-	97
4	$(PhCN)_2PdCl_2$ or $NiCl_2$(glyme) instead of $(Me_2S)AuCl$, 50 °C	12	0	99	-
5	**L1** (25 mol%) was used	2	95	-	99
6	PPh_3AuNTf_2 instead of $(Me_2S)AuCl$	24	1	72	22
7	**L2** instead of **L1**	5	95	-	95
8	**L3** instead of **L1**	4	96	-	97
9	DCM instead of CH_3CN	24	88	-	94
10	THF instead of CH_3CN	13	93	-	98
11	AuCl instead of $(Me_2S)AuCl$	4	93	-	94
12	$AuCl_3$ instead of $(Me_2S)AuCl$	24	15	69	30
13	$AuCl_3$ instead of $(Me_2S)AuCl$, 40 °C	6	69	-	98
14	**1a-1** instead of **1a**, **L1** (25 mol%), 50 °C	15	0	-[b]	-
15	**2a-1** instead of **2a**	4	80	-	81
16	**2a-2** instead of **2a**	2	96	-	96
17	**2a-3** instead of **2a**	24	0	90	9
18	**2a-4** instead of **2a**	24	10	82	16



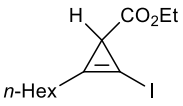
L1



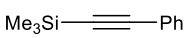
L2



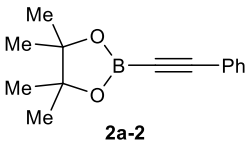
L3



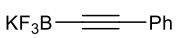
1a-1



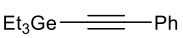
2a-1



2a-2



2a-3

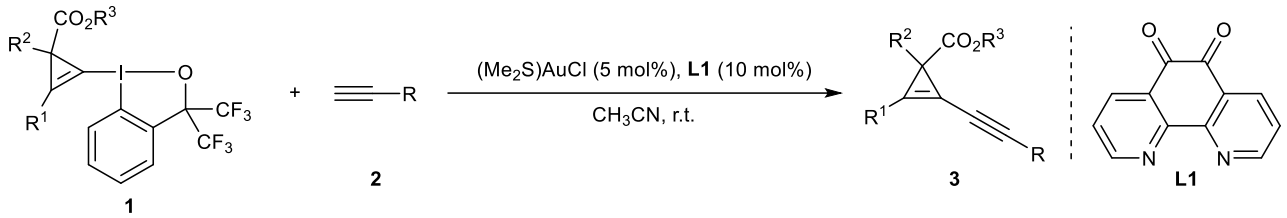


2a-4

Reactions performed on a 100 µmol scale. [a]Yields or recovery were determined by ^1H NMR spectroscopy using dibromomethane as the internal standard. [b]98% NMR recovery of **1a-1**.

5. Substrate scope of σ-type cyclopropenium cation transfer to terminal alkyne

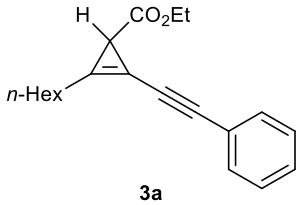
General Procedure D (**GPD**) for the gold-catalysed σ-type cyclopropenium cation transfer to terminal alkyne:



GPD: An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), terminal alkyne **2** (0.200 mmol, 1.00 equiv.) and CpBX **1** (0.200 mmol, 1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (0.10 M; 2.0 mL) was added by syringe; if **2** was a liquid, it was added last. The reaction mixture was stirred at room temperature (ca. 21 °C) for the specified time. The reaction mixture was then filtered through a silica gel pad and washed with CH_2Cl_2 (3 × 5.0 mL). Excess solvent was removed under reduced pressure and the desired product **3** was obtained by column chromatography on silica gel. The by-product **4** is a volatile colourless liquid. Thus, the fractions that contained **4** were collected and concentrated by rotary evaporation (vacuum pressure higher than 100 mBar, 40 °C water bath) to afford a concentrated solution of **4** in EtOAc. The yield of **4**[51] was determined by quantitative ^{1}H NMR analysis of the collected residue using CH_2Br_2 (^{1}H NMR δ 4.92) as the internal standard.

5.1. Substrate scope of terminal alkyne

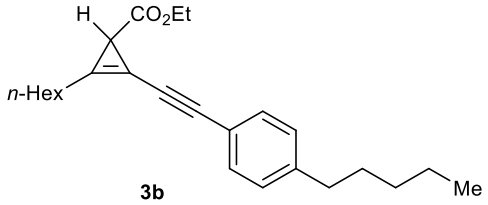
5.1.1. Synthesis and characterization of ethyl 2-hexyl-3-(phenylethynyl)cycloprop-2-ene-1-carboxylate (3a)



3a

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2a** (22 μL, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 2 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3a** in 95% yield (56.5 mg, 191 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.48; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.42 (m, 2H, Ar*H*), 7.37 – 7.30 (m, 3H, Ar*H*), 4.23 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 2.58 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.50 (s, 1H, $CHCO_2$), 1.74 – 1.57 (m, 2H, CH_2CH_2C), 1.47 – 1.36 (m, 2H, CH_2), 1.36 – 1.21 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.98 – 0.81 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 131.9, 129.1, 128.5, 122.5, 116.9, 99.0, 90.6, 76.7, 60.6, 31.6, 28.9, 26.7, 26.1, 25.3, 22.6, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 2971 (m), 2928 (m), 2858 (m), 2121 (w), 1858 (w), 1753 (w), 1721 (s), 1490 (m), 1369 (m), 1335 (m), 1249 (m), 1188 (s), 1026 (m), 756 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{24}NaO_2^+$ 319.1669; Found 319.1667.

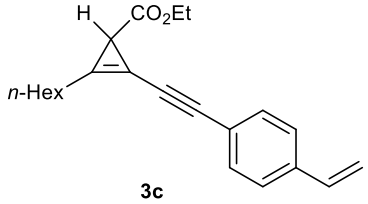
5.1.2. Synthesis and characterization of ethyl 2-hexyl-3-((4-pentylphenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3b)



3b

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2b** (34.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3b** in 89% yield (65.0 mg, 177 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.56; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H, Ar*H*), 7.18 – 7.10 (m, 2H, Ar*H*), 4.23 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 2.62 – 2.56 (m, 4H, CH_2), 2.49 (s, 1H, $CHCO_2$), 1.68 – 1.53 (m, 4H, CH_2), 1.48 – 1.37 (m, 2H, CH_2), 1.37 – 1.21 (m, 11H, CH_2 & $CO_2CH_2CH_3$), 0.89 (td, *J* = 7.0, 4.9 Hz, 6H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 144.4, 131.8, 128.6, 119.6, 116.3, 99.3, 90.7, 76.1, 60.6, 36.0, 31.6, 31.5, 31.0, 28.9, 26.7, 26.1, 25.3, 22.7, 22.6, 14.5, 14.2, 14.1; **IR** (ν_{max}, cm^{-1}) 2956 (s), 2930 (s), 2871 (m), 2858 (m), 2197 (m), 1725 (s), 1653 (m), 1606 (s), 1509 (w), 1466 (m), 1413 (w), 1373 (w), 1334 (w), 1179 (m), 1095 (m), 1022 (m), 839 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}NaO_5^+$ 389.1359; Found 389.1362.

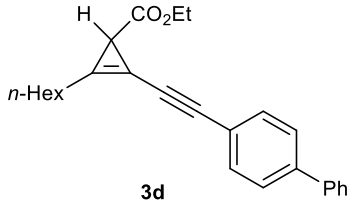
5.1.3. Synthesis and characterization of ethyl 2-hexyl-3-((4-vinylphenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3c)



3c

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2c** (25.6 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 2 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3c** in 89% yield (57.3 mg, 178 μmol) as a colourless oil and **4** in 92% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.61; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H, Ar*H*), 7.40 – 7.33 (m, 2H, Ar*H*), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H, CH=CH_2), 5.78 (dd, *J* = 17.6, 0.8 Hz, 1H, CH=CH_2), 5.31 (dd, *J* = 10.9, 0.8 Hz, 1H, CH=CH_2), 4.27 – 4.08 (m, 2H, $CO_2CH_2CH_3$), 2.59 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.50 (s, 1H, $CHCO_2$), 1.72 – 1.60 (m, 2H, CH_2CH_2C), 1.49 – 1.37 (m, 2H, CH_2), 1.37 – 1.16 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.96 – 0.81 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 138.3, 136.3, 132.1, 126.3, 121.7, 117.0, 115.4, 99.0, 90.6, 77.4, 60.7, 31.6, 29.0, 26.7, 26.1, 25.3, 22.7, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 2955 (m), 2928 (m), 2859 (m), 2202 (w), 1714 (s), 1649 (m), 1602 (m), 1509 (w), 1466 (m), 1407 (m), 1376 (m), 1265 (s), 1202 (s), 1181 (s), 1092 (s), 1018 (s), 835 (m), 736 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{27}O_2^+$ 323.2006; Found 323.2013.

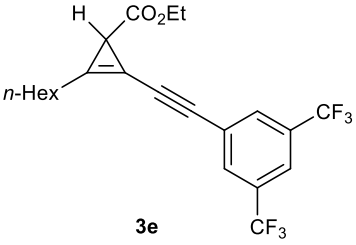
5.1.4. Synthesis and characterization of ethyl 2-([1,1'-biphenyl]-4-ylethynyl)-3-hexylcycloprop-2-ene-1-carboxylate (3d)



3d

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2d** (35.7 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3d** in 91% yield (67.6 mg, 181 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.46; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.52 (m, 6H, Ar*H*), 7.47 – 7.43 (m, 2H, Ar*H*), 7.39 – 7.34 (s, 1H, Ar*H*), 4.25 – 4.13 (m, 2H, $CO_2CH_2CH_3$), 2.61 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.52 (s, 1H, $CHCO_2$), 1.72 – 1.62 (m, 2H, CH_2CH_2C), 1.47 – 1.38 (m, 2H, CH_2), 1.38 – 1.23 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 1.03 – 0.81 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 141.8, 140.3, 132.3, 129.0, 127.9, 127.2, 121.4, 117.0, 98.9, 90.6, 77.4, 60.7, 31.6, 29.0, 26.7, 26.1, 25.4, 22.7, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 2979 (w), 2956 (m), 2928 (m), 2858 (m), 2196 (w), 1777 (w), 1711 (s), 1601 (m), 1486 (m), 1407 (w), 1267 (m), 1180 (m), 1094 (w), 1026 (m), 1007 (m), 842 (m), 764 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}O_2^+$ 373.2162; Found 373.2160.

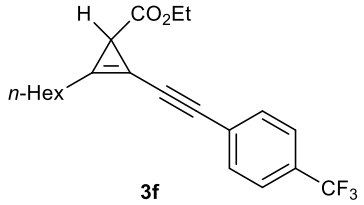
5.1.5. Synthesis and characterization of ethyl 2-((3,5-bis(trifluoromethyl)phenyl)ethynyl)-3-hexylcycloprop-2-ene-1-carboxylate (3e)



3e

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2e** (47.6 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3e** in 92% yield (79.7 mg, 184 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.68; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H, Ar*H*), 7.83 – 7.81 (m, 1H, Ar*H*), 4.18 (qd, *J* = 7.1, 4.1 Hz, 2H, $CO_2CH_2CH_3$), 2.62 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.54 (s, 1H, $CHCO_2$), 1.75 – 1.58 (m, 2H, CH_2CH_2C), 1.52 – 1.37 (m, 2H, CH_2), 1.37 – 1.19 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.96 – 0.79 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 132.2 (q, *J* = 33.8 Hz), 131.7 (m), 124.9, 123.0 (q, *J* = 272.9 Hz), 122.4 (hept, *J* = 3.8 Hz), 120.5, 95.5, 89.9, 80.3, 60.8, 31.6, 28.9, 26.6, 26.3, 25.5, 22.7, 14.5, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.3; **IR** (ν_{max}, cm^{-1}) 2961 (w), 2934 (w), 2863 (w), 2218 (w), 1725 (m), 1617 (w), 1465 (w), 1386 (m), 1277 (s), 1175 (s), 1133 (s), 1027 (w), 899 (m), 848 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}F_6O_2^+$ 433.1597; Found 433.1597.

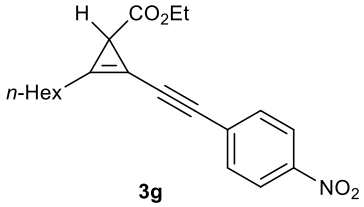
5.1.6. Synthesis and characterization of ethyl 2-hexyl-3-((4-(trifluoromethyl)phenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3f)



3f

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2f** (34.0 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3f** in 94% yield (68.8 mg, 189 μmol) as a colorless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.55; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (s, 4H, Ar*H*), 4.17 (qt, *J* = 6.9, 3.5 Hz, 2H, $CO_2CH_2CH_3$), 2.60 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.53 (s, 1H, $CHCO_2$), 1.70 – 1.59 (m, 2H, CH_2CH_2C), 1.46 – 1.36 (m, 2H, CH_2), 1.36 – 1.20 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.93 – 0.84 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 132.1, 130.7 (q, *J* = 32.7 Hz), 126.3, 125.5 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.2 Hz), 118.9, 97.3, 90.2, 79.1, 60.7, 31.6, 28.9, 26.6, 26.2, 25.4, 22.6, 14.5, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.9; **IR** (ν_{max}, cm^{-1}) 2957 (w), 2932 (w), 2867 (w), 2208 (w), 1725 (m), 1617 (w), 1469 (w), 1407 (w), 1323 (s), 1167 (m), 1129 (s), 1106 (m), 1065 (s), 1017 (m), 841 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}F_3O_2^+$ 365.1723; Found 365.1722.

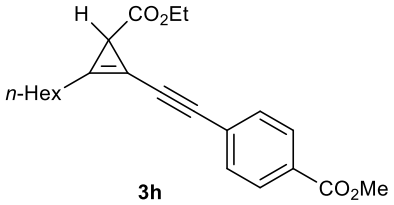
5.1.7. Synthesis and characterization of ethyl 2-hexyl-3-((4-nitrophenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3g)



3g

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2g** (29.4 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3g** in 87% yield (59.3 mg, 174 μmol) as a light-yellow oil and **4** in 88% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 – 8.15 (m, 2H, Ar*H*), 7.66 – 7.57 (m, 2H, Ar*H*), 4.23 – 4.12 (m, 2H, $CO_2CH_2CH_3$), 2.61 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.54 (s, 1H, $CHCO_2$), 1.70 – 1.57 (m, 2H, CH_2CH_2C), 1.44 – 1.36 (m, 2H, CH_2), 1.36 – 1.20 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.82 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 147.5, 132.6, 129.3, 123.8, 120.4, 96.7, 90.0, 81.8, 60.8, 31.5, 28.9, 26.6, 26.3, 25.5, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2961 (m), 2928 (m), 2856 (w), 2211 (w), 1858 (w), 1724 (m), 1593 (m), 1520 (s), 1466 (w), 1341 (s), 1182 (m), 1108 (w), 1023 (w), 854 (s), 749 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}NO_4^+$ 342.1700; Found 342.1698.

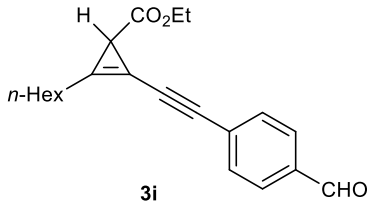
5.1.8. Synthesis and characterization of methyl 4-((3-(ethoxycarbonyl)-2-hexylcycloprop-1-en-1-yl)ethynyl)benzoate (3h)



3h

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2h** (32.0 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 8 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3h** in 92% yield (65.5 mg, 185 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.36; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 2H, Ar*H*), 7.58 – 7.46 (m, 2H, Ar*H*), 4.22 – 4.10 (m, 2H, $CO_2CH_2CH_3$), 3.90 (s, 3H, CO_2CH_3), 2.59 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.51 (s, 1H, $CHCO_2$), 1.70 – 1.56 (m, 2H, CH_2CH_2C), 1.45 – 1.35 (m, 2H, CH_2), 1.35 – 1.19 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.77 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 166.5, 131.7, 130.2, 129.6, 127.1, 118.7, 98.0, 90.3, 79.5, 60.7, 52.4, 31.5, 28.9, 26.6, 26.2, 25.4, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2954 (m), 2932 (m), 2859 (w), 2204 (w), 1724 (s), 1605 (m), 1464 (w), 1436 (m), 1405 (w), 1371 (w), 1276 (s), 1177 (m), 1107 (m), 1018 (m), 861 (m), 769 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{27}O_4^+$ 355.1904; Found 355.1902.

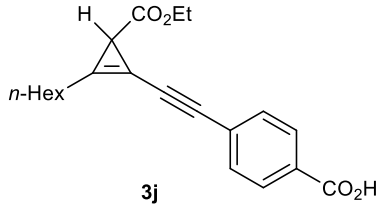
5.1.9. Synthesis and characterization of ethyl 2-((4-formylphenyl)ethynyl)-3-hexylcycloprop-2-ene-1-carboxylate (3i)



3i

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2i** (26.0 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 20:1) afforded **3i** in 87% yield (56.5 mg, 174 μmol) as a colorless oil and **4** in 97% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.26; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.00 (s, 1H, C*H*O), 7.89 – 7.78 (m, 2H, Ar*H*), 7.67 – 7.54 (m, 2H, Ar*H*), 4.23 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 2.60 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.52 (s, 1H, $CHCO_2$), 1.71 – 1.57 (m, 2H, CH_2CH_2C), 1.44 – 1.36 (m, 2H, CH_2), 1.35 – 1.20 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.76 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.4, 174.0, 136.0, 132.4, 129.6, 128.6, 119.3, 97.8, 90.2, 80.5, 60.7, 31.5, 28.9, 26.6, 26.2, 25.4, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (w), 2930 (m), 2858 (w), 2203 (w), 1717 (m), 1702 (s), 1602 (m), 1562 (w), 1466 (w), 1411 (w), 1302 (m), 1266 (m), 1204 (s), 1095 (w), 1016 (m), 831 (m), 735 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O_3^+$ 325.1798; Found 325.1798.

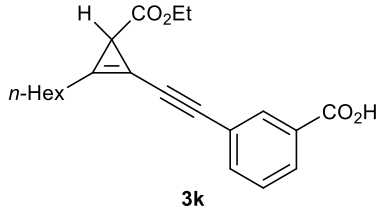
5.1.10. Synthesis and characterization of 4-((3-(ethoxycarbonyl)-2-hexylcycloprop-1-en-1-yl)ethynyl)benzoic acid (3j)



3j

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2j** (29.2 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 9 hours. Flash column chromatography on silica gel (eluent: DCM/MeOH = 20:1) afforded **3j** in 86% yield (58.7 mg, 172 μmol) as a colourless solid and **4** in 95% NMR yield. **M.p.** 87 – 89 °C. **TLC**: R_f (DCM/MeOH = 20:1) = 0.27; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (bs, 1H, CO_2H), 8.07 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.56 (d, *J* = 7.9 Hz, 2H, Ar*H*), 4.25 – 4.13 (m, 2H, $CO_2CH_2CH_3$), 2.61 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.54 (s, 1H, $CHCO_2$), 1.67 – 1.61 (m, 2H, CH_2CH_2C), 1.45 – 1.37 (m, 2H, CH_2), 1.33 – 1.25 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.91 – 0.85 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 171.3, 131.8, 130.2, 129.5, 127.9, 118.9, 97.9, 90.3, 79.9, 60.8, 31.6, 28.9, 26.6, 26.2, 25.4, 22.6, 14.5, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2932 (m), 2853 (w), 1729 (s), 1689 (s), 1682 (s), 1604 (m), 1558 (w), 1465 (w), 1426 (m), 1316 (m), 1296 (s), 1280 (m), 1185 (s), 1017 (m), 952 (w), 859 (m), 775 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O_4^+$ 341.1747; Found 341.1748.

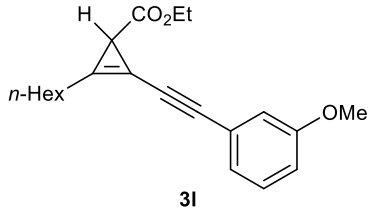
5.1.11. Synthesis and characterization of 3-((3-(ethoxycarbonyl)-2-hexylcycloprop-1-en-1-yl)ethynyl)benzoic acid (3k)



3k

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2k** (29.2 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: DCM/MeOH = 20:1) afforded **3k** in 78% yield (52.9 mg, 155 μmol) as a colourless oil and **4** in 90% NMR yield. **TLC**: R_f (DCM/MeOH = 20:1) = 0.31; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (bs, 1H, CO_2H), 8.23 (t, *J* = 1.7 Hz, 1H, Ar*H*), 8.07 (dt, *J* = 7.9, 1.4 Hz, 1H, Ar*H*), 7.69 (dt, *J* = 7.8, 1.4 Hz, 1H, Ar*H*), 7.45 (t, *J* = 7.8 Hz, 1H, Ar*H*), 4.25 – 4.13 (m, 2H, $CO_2CH_2CH_3$), 2.60 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.53 (s, 1H, $CHCO_2$), 1.72 – 1.54 (m, 2H, CH_2CH_2C), 1.45 – 1.37 (m, 2H, CH_2), 1.36 – 1.25 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 1.00 – 0.74 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 171.1, 136.6, 133.6, 130.6, 130.0, 128.8, 123.2, 118.1, 97.6, 90.4, 77.8, 60.8, 31.6, 28.9, 26.7, 26.2, 25.4, 22.6, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 2958 (w), 2929 (m), 2859 (w), 2200 (w), 1722 (s), 1697 (s), 1603 (w), 1581 (w), 1444 (m), 1412 (m), 1372 (w), 1336 (w), 1300 (w), 1266 (w), 1186 (m), 1168 (m), 1096 (w), 1023 (w), 916 (w), 755 (m), 737 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O_4^+$ 341.1747; Found 341.1743.

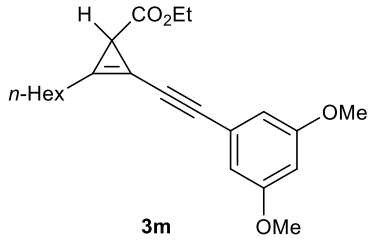
5.1.12. Synthesis and characterization of ethyl 2-hexyl-3-((3-methoxyphenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3l)



3l

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2l** (26.4 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 5 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3l** in 90% yield (58.8 mg, 180 μmol) as a colorless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.48; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.18 (m, 1H, Ar*H*), 7.08 (dt, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 7.01 (dd, *J* = 2.7, 1.4 Hz, 1H, Ar*H*), 6.90 (ddd, *J* = 8.4, 2.6, 1.0 Hz, 1H, Ar*H*), 4.23 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 3.79 (s, 3H, OCH_3), 2.58 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.50 (s, 1H, $CHCO_2$), 1.70 – 1.55 (m, 2H, CH_2CH_2C), 1.40 (dq, *J* = 8.5, 6.7 Hz, 2H, CH_2), 1.36 – 1.22 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.80 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 159.4, 129.5, 124.4, 123.4, 117.1, 116.4, 115.9, 98.9, 90.5, 76.5, 60.6, 55.4, 31.5, 28.9, 26.7, 26.1, 25.2, 22.6, 14.5, 14.1; **IR** (ν_{max}, cm^{-1}) 2956 (m), 2930 (m), 2858 (m), 2193 (w), 1858 (w), 1723 (s), 1597 (m), 1575 (m), 1489 (m), 1465 (m), 1321 (m), 1291 (m), 1213 (m), 1178 (s), 1094 (w), 1039 (s), 870 (m), 853 (m), 785 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{27}O_3^+$ 327.1955; Found 327.1949.

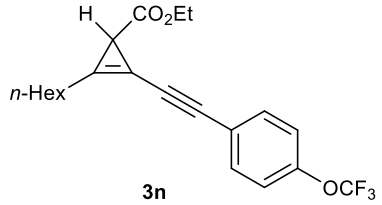
5.1.13. Synthesis and characterization of ethyl 2-((3,5-dimethoxyphenyl)ethynyl)-3-hexylcycloprop-2-ene-1-carboxylate (3m)



3m

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2m** (32.4 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **3m** in 92% yield (65.7 mg, 184 μmol) as a colorless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 2.3 Hz, 2H, Ar*H*), 6.46 (t, *J* = 2.3 Hz, 1H, Ar*H*), 4.22 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 3.77 (s, 6H, OCH_3), 2.58 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.49 (s, 1H, $CHCO_2$), 1.68 – 1.56 (m, 2H, CH_2CH_2C), 1.44 – 1.37 (m, 2H, CH_2), 1.35 – 1.24 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.91 – 0.87 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 160.6, 123.7, 117.2, 109.5, 102.7, 99.0, 90.5, 76.2, 60.6, 55.5, 31.6, 28.9, 26.7, 26.1, 25.3, 22.6, 14.5, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (w), 2932 (m), 2858 (w), 2193 (w), 1855 (w), 1800 (w), 1721 (m), 1591 (s), 1458 (m), 1418 (m), 1345 (w), 1205 (s), 1182 (s), 1154 (s), 1063 (m), 1024 (w), 931 (w), 836 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{29}O_4^+$ 357.2060; Found 357.2057.

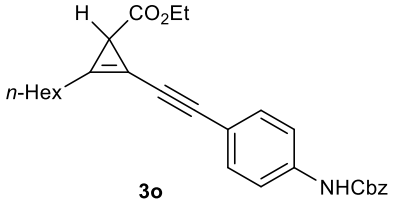
5.1.14. Synthesis and characterization of ethyl 2-hexyl-3-((4-(trifluoromethoxy)phenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3n)



3n

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2n** (37.2 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 20:1) afforded **3n** in 92% yield (69.7 mg, 183 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.58; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 2H, Ar*H*), 7.22 – 7.10 (m, 2H, Ar*H*), 4.23 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 2.59 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.50 (s, 1H, $CHCO_2$), 1.68 – 1.57 (m, 2H, CH_2CH_2C), 1.44 – 1.36 (m, 2H, CH_2), 1.36 – 1.20 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.97 – 0.77 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 149.5 (d, *J* = 2.0 Hz), 133.4, 121.3, 121.0, 120.5 (q, *J* = 258.0 Hz), 117.9, 97.4, 90.4, 77.6, 60.7, 31.6, 28.9, 26.7, 26.2, 25.3, 22.7, 14.5, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.8; **IR** (ν_{max}, cm^{-1}) 2960 (w), 2932 (w), 2863 (w), 2205 (w), 1725 (m), 1603 (w), 1507 (m), 1373 (w), 1253 (s), 1206 (s), 1163 (s), 1095 (w), 1018 (m), 923 (w), 853 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}F_3O_3^+$ 381.1672; Found 381.1672.

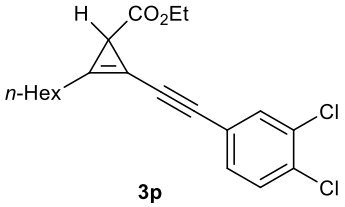
5.1.15. Synthesis and characterization of ethyl 2-((4-(((benzyloxy)carbonyl)amino)phenyl)ethynyl)-3-hexylcycloprop-2-ene-1-carboxylate (3o)



3o

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2o** (50.3 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 20:1) afforded **3o** in 91% yield (81.0 mg, 182 μmol) as a colourless oil and **4** in 96% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.14; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 9H, Ar*H*), 7.21 (s, 1H, N*H*), 5.19 (s, 2H, OCH_2Ph), 4.22 – 4.09 (m, 2H, $CO_2CH_2CH_3$), 2.56 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.50 (s, 1H, $CHCO_2$), 1.66 – 1.58 (m, 2H, CH_2CH_2C), 1.48 – 1.12 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 1.02 – 0.75 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 153.2, 138.9, 136.0, 132.8, 128.7, 128.5, 128.4, 118.3, 117.0, 116.3, 99.0, 90.5, 76.1, 67.2, 60.7, 31.5, 28.9, 26.7, 26.0, 25.2, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 3336 (w), 2957 (w), 2929 (w), 2869 (w), 2858 (w), 2193 (w), 1734 (m), 1704 (s), 1590 (m), 1524 (s), 1456 (w), 1410 (m), 1315 (m), 1210 (s), 1179 (s), 1047 (s), 837 (m), 742 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{32}NO_4^+$ 446.2326; Found 446.2327.

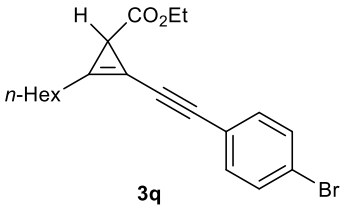
5.1.16. Synthesis and characterization of ethyl 2-((3,4-dichlorophenyl)ethynyl)-3-hexylcycloprop-2-ene-1-carboxylate (3p)



3p

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2p** (34.2 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 40:1) afforded **3p** in 91% yield (66.4 mg, 182 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.59; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.9 Hz, 1H, Ar*H*), 7.40 (d, *J* = 8.3 Hz, 1H, Ar*H*), 7.29 (dd, *J* = 8.3, 1.9 Hz, 1H, Ar*H*), 4.23 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 2.59 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.50 (s, 1H, $CHCO_2$), 1.67 – 1.59 (m, 2H, CH_2CH_2C), 1.44 – 1.36 (m, 2H, CH_2), 1.35 – 1.25 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.94 – 0.81 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 133.6, 133.4, 132.8, 130.9, 130.6, 122.5, 118.8, 96.4, 90.1, 78.7, 60.7, 31.5, 28.9, 26.6, 26.2, 25.3, 22.6, 14.5, 14.1; **IR** (ν_{max}, cm^{-1}) 2958 (m), 2929 (m), 2858 (m), 2206 (w), 1725 (s), 1587 (w), 1466 (s), 1375 (m), 1248 (m), 1182 (s), 1132 (s), 1031 (s), 880 (m), 822 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}Cl_2O_2^+$ 365.1070; Found 365.1066.

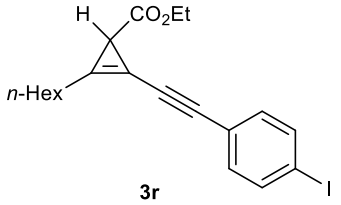
5.1.17. Synthesis and characterization of ethyl 2-((4-bromophenyl)ethynyl)-3-hexylcycloprop-2-ene-1-carboxylate (3q)



3q

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2q** (36.2 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3q** in 88% yield (65.7 mg, 175 μmol) as a colourless oil and **4** in 89% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.47; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H, Ar*H*), 7.40 – 7.30 (m, 2H, Ar*H*), 4.23 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 2.58 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.49 (s, 1H, $CHCO_2$), 1.69 – 1.55 (m, 2H, CH_2CH_2C), 1.44 – 1.36 (m, 2H, CH_2), 1.35 – 1.25 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.94 – 0.79 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 133.2, 131.8, 123.5, 121.5, 117.8, 97.8, 90.4, 77.9, 60.7, 31.5, 28.9, 26.6, 26.1, 25.3, 22.6, 14.5, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2932 (m), 2859 (m), 2201 (w), 1723 (s), 1584 (m), 1486 (m), 1467 (m), 1395 (m), 1369 (m), 1248 (m), 1184 (s), 1094 (m), 1070 (s), 1028 (m), 1010 (s), 823 (s), 737 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}BrO_2^+$ 375.0954; Found 375.0953.

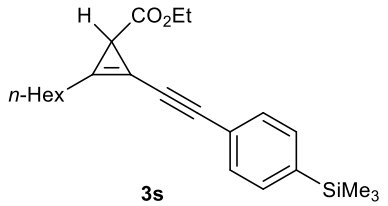
5.1.18. Synthesis and characterization of ethyl 2-hexyl-3-((4-iodophenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3r)



3r

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 µmol, 5.00 mol%), **L1** (4.20 mg, 20.0 µmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2r** (45.6 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3r** in 92% yield (77.5 mg, 184 µmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.46; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.60 (m, 2H, Ar*H*), 7.23 – 7.13 (m, 2H, Ar*H*), 4.22 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 2.58 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.49 (s, 1H, $CHCO_2$), 1.71 – 1.54 (m, 2H, CH_2CH_2C), 1.44 – 1.36 (m, 2H, CH_2), 1.35 – 1.23 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.78 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 137.7, 133.2, 122.0, 117.8, 98.0, 95.3, 90.4, 78.1, 60.6, 31.5, 28.9, 26.6, 26.2, 25.3, 22.6, 14.5, 14.1; **IR** (ν_{max}, cm^{-1}) 2954 (m), 2929 (m), 2857 (m), 2200 (w), 1722 (s), 1601 (w), 1580 (m), 1483 (m), 1466 (m), 1391 (m), 1369 (w), 1264 (m), 1181 (m), 1095 (m), 1057 (m), 1032 (m), 1006 (s), 819 (s), 737 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}IO_2^+$ 423.0816; Found 423.0809.

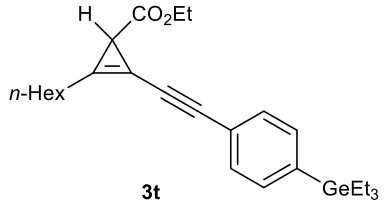
5.1.19. Synthesis and characterization of ethyl 2-hexyl-3-((4-(trimethylsilyl)phenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3s)



3s

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 µmol, 5.00 mol%), **L1** (4.20 mg, 20.0 µmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2s** (34.9 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3s** in 84% yield (61.8 mg, 168 µmol) as a colourless oil and **4** in 92% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 4H, Ar*H*), 4.24 – 4.12 (m, 2H, $CO_2CH_2CH_3$), 2.59 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.50 (s, 1H, $CHCO_2$), 1.70 – 1.57 (m, 2H, CH_2CH_2C), 1.45 – 1.37 (m, 2H, CH_2), 1.36 – 1.21 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.98 – 0.84 (m, 3H, CH_3), 0.27 (s, 9H, $Si(CH_3)_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 142.2, 133.3, 130.9, 122.7, 116.9, 99.2, 90.7, 77.0, 60.6, 31.6, 28.9, 26.7, 26.1, 25.3, 22.7, 14.5, 14.2, -1.1; **IR** (ν_{max}, cm^{-1}) 2956 (m), 2933 (m), 2860 (w), 2201 (w), 1724 (m), 1601 (w), 1467 (w), 1392 (w), 1250 (m), 1185 (m), 1109 (w), 1095 (w), 1030 (w), 842 (s), 822 (s), 757 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{33}O_2Si^+$ 369.2244; Found 369.2247.

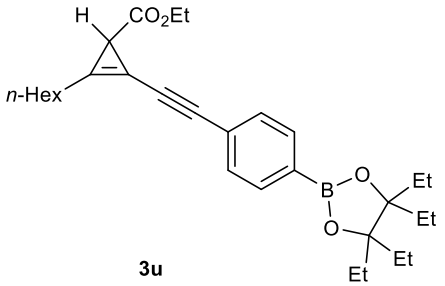
5.1.20. Synthesis and characterization of ethyl 2-hexyl-3-((4-(triethylgermyl)phenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3t)



3t

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2t** (52.2 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3t** in 76% yield (68.9 mg, 151 μmol) as a colourless oil and **4** in 97% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 4H, Ar*H*), 4.17 (qq, *J* = 7.0, 3.7 Hz, 2H, $CO_2CH_2CH_3$), 2.59 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.50 (s, 1H, $CHCO_2$), 1.74 – 1.57 (m, 2H, CH_2CH_2C), 1.47 – 1.37 (m, 2H, CH_2), 1.37 – 1.22 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 1.09 – 0.93 (m, 15H, $Ge(CH_2CH_3)_3$), 0.93 – 0.85 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 142.1, 134.0, 130.9, 122.1, 116.7, 99.3, 90.7, 76.8, 60.6, 31.6, 28.9, 26.7, 26.1, 25.3, 22.7, 14.5, 14.2, 9.0, 4.3; **IR** (ν_{max}, cm^{-1}) 2954 (s), 2930 (s), 2908 (s), 2871 (s), 2198 (m), 1725 (s), 1602 (m), 1463 (m), 1427 (m), 1183 (s), 1084 (m), 1018 (s), 972 (w), 819 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{39}GeO_2^+$ 457.2156; Found 457.2159.

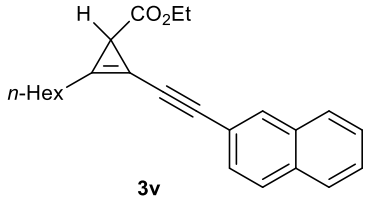
5.1.21. Synthesis and characterization of ethyl 2-hexyl-3-((4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3u)



3u

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2u** (56.8 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 40:1) afforded **3u** in 96% yield (92.2 mg, 193 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.47 (d, *J* = 8.2 Hz, 2H, Ar*H*), 4.23 – 4.12 (m, 2H, $CO_2CH_2CH_3$), 2.59 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.50 (s, 1H, $CHCO_2$), 1.85 – 1.59 (m, 10H, CH_2), 1.47 – 1.36 (m, 2H, CH_2), 1.36 – 1.22 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.96 (t, *J* = 7.4 Hz, 12H, CH_3), 0.93 – 0.85 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 134.8, 131.0, 124.9, 117.4, 99.2, 90.6, 89.2, 77.8, 60.6, 31.6, 29.0, 26.7, 26.6, 26.2, 25.4, 22.7, 14.5, 14.2, 9.0; The carbon attached to boron was not observed due to quadrupolar relaxation; **^{11}B NMR** (128 MHz, $CDCl_3$) δ 29.3; **IR** (ν_{max}, cm^{-1}) 2979 (m), 2937 (m), 2885 (m), 2200 (w), 1727 (m), 1647 (w), 1606 (m), 1512 (w), 1460 (m), 1400 (s), 1366 (s), 1352 (s), 1312 (m), 1291 (m), 1263 (m), 1181 (m), 1091 (s), 1021 (m), 921 (s), 836 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{44}BO_4^+$ 479.3327; Found 479.3328.

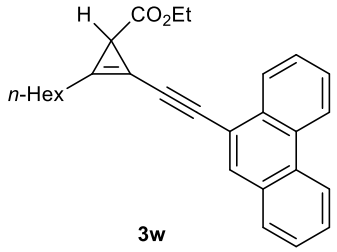
5.1.22. Synthesis and characterization of ethyl 2-hexyl-3-(naphthalen-2-ylethynyl)cycloprop-2-ene-1-carboxylate (3v)



3v

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2v** (30.4 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3v** in 88% yield (60.9 mg, 176 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.51; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.6 Hz, 1H, Ar*H*), 7.84 – 7.77 (m, 3H, Ar*H*), 7.57 – 7.46 (m, 3H, Ar*H*), 4.26 – 4.14 (m, 2H, $CO_2CH_2CH_3$), 2.62 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.55 (s, 1H, $CHCO_2$), 1.73 – 1.60 (m, 2H, CH_2CH_2C), 1.49 – 1.39 (m, 2H, CH_2), 1.39 – 1.21 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.96 – 0.84 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 133.2, 133.0, 132.1, 128.23, 128.20, 128.0, 127.9, 127.2, 126.8, 119.8, 117.1, 99.4, 90.7, 77.0, 60.6, 31.6, 29.0, 26.7, 26.2, 25.4, 22.7, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 3059 (w), 2955 (m), 2928 (s), 2857 (m), 2188 (w), 1854 (w), 1792 (w), 1723 (s), 1597 (m), 1502 (w), 1465 (m), 1368 (m), 1332 (w), 1246 (m), 1180 (s), 1095 (w), 1022 (m), 954 (w), 894 (m), 859 (s), 817 (s), 747 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{27}O_2^+$ 347.2006; Found 347.2006.

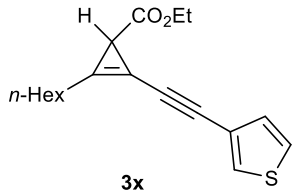
5.1.23. Synthesis and characterization of ethyl 2-hexyl-3-(phenanthren-9-ylethynyl)cycloprop-2-ene-1-carboxylate (3w)



3w

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2w** (40.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 2 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3w** in 94% yield (74.3 mg, 187 μmol) as a colourless oil and **4** in 96% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.48; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 – 8.57 (m, 2H, Ar*H*), 8.47 – 8.37 (m, 1H, Ar*H*), 8.07 (s, 1H, Ar*H*), 7.86 (dd, *J* = 7.9, 1.5 Hz, 1H, Ar*H*), 7.74 – 7.63 (m, 3H, Ar*H*), 7.62 – 7.58 (m, 1H, Ar*H*), 4.29 – 4.18 (m, 2H, $CO_2CH_2CH_3$), 2.72 – 2.65 (m, 2H, CH_2CH_2C), 2.64 (s, 1H, $CHCO_2$), 1.79 – 1.68 (m, 2H, CH_2CH_2C), 1.59 – 1.43 (m, 2H, CH_2), 1.43 – 1.23 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 1.02 – 0.85 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 132.8, 131.1, 130.9, 130.7, 130.1, 128.9, 128.0, 127.34, 127.27, 127.1, 127.0, 122.9, 122.8, 119.0, 117.5, 97.4, 90.7, 81.0, 60.7, 31.6, 29.0, 26.8, 26.3, 25.6, 22.7, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 3062 (w), 2955 (m), 2928 (m), 2857 (m), 2189 (w), 1854 (w), 1720 (m), 1604 (w), 1451 (m), 1369 (w), 1242 (w), 1177 (m), 1029 (m), 892 (w), 763 (m), 748 (s), 724 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{29}O_2^+$ 397.2162; Found 397.2165.

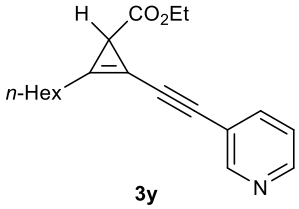
5.1.24. Synthesis and characterization of ethyl 2-hexyl-3-(thiophen-3-ylethynyl)cycloprop-2-ene-1-carboxylate (3x)



3x

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2x** (21.6 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3x** in 94% yield (56.7 mg, 188 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.34; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 3.0, 1.1 Hz, 1H, Ar*H*), 7.28 (dd, *J* = 5.0, 3.0 Hz, 1H, Ar*H*), 7.15 (dd, *J* = 5.0, 1.1 Hz, 1H, Ar*H*), 4.23 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 2.57 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.49 (s, 1H, $CHCO_2$), 1.67 – 1.59 (m, 2H, CH_2CH_2C), 1.44 – 1.37 (m, 2H, CH_2), 1.35 – 1.21 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.83 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 130.0, 129.9, 125.7, 121.7, 116.7, 94.2, 90.5, 76.4, 60.6, 31.6, 28.9, 26.7, 26.1, 25.3, 22.7, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 3110 (w), 2957 (m), 2930 (s), 2870 (m), 2858 (m), 2196 (w), 1722 (s), 1599 (w), 1514 (w), 1466 (m), 1370 (w), 1248 (m), 1211 (m), 1182 (s), 1096 (w), 1026 (m), 870 (m), 783 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}O_2S^+$ 303.1413; Found 303.1406.

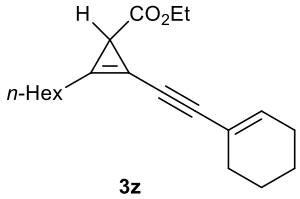
5.1.25. Synthesis and characterization of ethyl 2-hexyl-3-(pyridin-3-ylethynyl)cycloprop-2-ene-1-carboxylate (3y)



3y

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2y** (20.6 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 11 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3y** in 88% yield (52.3 mg, 176 μmol) as a colourless oil and **4** in 94% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.34; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 2.2, 0.9 Hz, 1H, Ar*H*), 8.53 (dd, *J* = 4.9, 1.7 Hz, 1H, Ar*H*), 7.75 (dt, *J* = 7.9, 1.9 Hz, 1H, Ar*H*), 7.29 – 7.23 (m, 1H, Ar*H*), 4.22 – 4.10 (m, 2H, $CO_2CH_2CH_3$), 2.59 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.51 (s, 1H, $CHCO_2$), 1.70 – 1.53 (m, 2H, CH_2CH_2C), 1.43 – 1.35 (m, 2H, CH_2), 1.34 – 1.20 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 0.93 – 0.80 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 152.4, 149.2, 138.7, 123.2, 119.8, 118.8, 95.4, 90.1, 80.0, 60.7, 31.5, 28.9, 26.6, 26.2, 25.3, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2928 (m), 2856 (m), 2213 (w), 1856 (w), 1724 (s), 1476 (m), 1407 (m), 1368 (w), 1334 (w), 1247 (m), 1180 (s), 1096 (w), 1022 (m), 805 (m), 703 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}NO_2^+$ 298.1802; Found 298.1802.

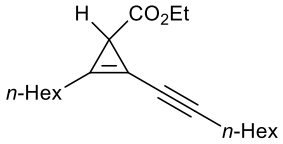
5.1.26. Synthesis and characterization of ethyl 2-(cyclohex-1-en-1-ylethynyl)-3-hexylcycloprop-2-ene-1-carboxylate (3z)



3z

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2z** (21.2 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3z** in 90% yield (54.3 mg, 181 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.33; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.21 (tt, *J* = 3.8, 1.7 Hz, 1H, C=C*H*), 4.19 – 4.07 (m, 2H, $CO_2CH_2CH_3$), 2.51 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.39 (s, 1H, $CHCO_2$), 2.17 – 2.09 (m, 4H, CH_2), 1.66 – 1.54 (m, 6H, CH_2), 1.44 – 1.16 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.74 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 137.3, 120.5, 115.1, 101.0, 90.7, 74.0, 60.5, 31.6, 28.9, 28.8, 26.7, 25.9, 25.1, 22.6, 22.3, 21.5, 14.5, 14.1; **IR** (ν_{max}, cm^{-1}) 2953 (m), 2935 (m), 2860 (m), 2193 (w), 1719 (s), 1462 (m), 1371 (m), 1242 (m), 1182 (s), 1095 (m), 1031 (m), 862 (w), 736 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{29}O_2^+$ 301.2162; Found 301.2161.

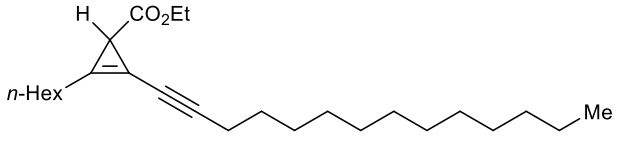
5.1.27. Synthesis and characterization of ethyl 2-hexyl-3-(oct-1-yn-1-yl)cycloprop-2-ene-1-carboxylate (3aa)



3aa

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aa** (22.0 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3aa** in 94% yield (57.4 mg, 189 μmol) as a colourless oil and **4** in 95% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.63; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.19 – 4.07 (m, 2H, $CO_2CH_2CH_3$), 2.48 (t, *J* = 7.3 Hz, 2H, CH_2), 2.39 (t, *J* = 7.1 Hz, 2H, CH_2), 2.34 (s, 1H, $CHCO_2$), 1.64 – 1.49 (m, 4H, CH_2), 1.45 – 1.20 (m, 15H, CH_2 & $CO_2CH_2CH_3$), 0.90 – 0.85 (m, 6H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 113.6, 101.4, 91.1, 67.9, 60.4, 31.6, 31.4, 28.9, 28.7, 28.4, 26.7, 25.8, 24.8, 22.6 (2C), 20.1, 14.5, 14.1 (2C); **IR** (ν_{max}, cm^{-1}) 2957 (s), 2931 (s), 2871 (m), 2859 (m), 2215 (w), 1720 (s), 1660 (m), 1604 (w), 1465 (m), 1376 (m), 1265 (m), 1248 (m), 1175 (m), 1160 (m), 1027 (m), 863 (w), 738 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{33}O_2^+$ 305.2475; Found 305.2466.

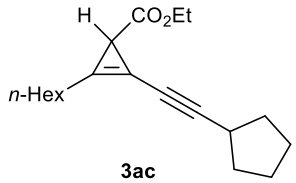
5.1.28. Synthesis and characterization of ethyl 2-hexyl-3-(tetradec-1-yn-1-yl)cycloprop-2-ene-1-carboxylate (3ab)



3ab

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ab** (38.9 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3ab** in 90% yield (70.1 mg, 180 μmol) as a colourless oil and **4** in 92% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.20 – 4.08 (m, 2H, $CO_2CH_2CH_3$), 2.48 (t, *J* = 7.2 Hz, 2H, CH_2), 2.40 (t, *J* = 7.2 Hz, 2H, CH_2), 2.35 (s, 1H, $CHCO_2$), 1.62 – 1.52 (m, 4H, CH_2), 1.46 – 1.19 (m, 27H, CH_2 & $CO_2CH_2CH_3$), 0.90 – 0.86 (m, 6H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 113.6, 101.5, 91.1, 67.9, 60.5, 32.1, 31.6, 29.81, 29.77 (2C), 29.6, 29.5, 29.3, 29.1, 28.9, 28.5, 26.7, 25.8, 24.8, 22.8, 22.7, 20.2, 14.5, 14.3, 14.2; **IR** (ν_{max}, cm^{-1}) 2955 (m), 2925 (s), 2855 (s), 2214 (w), 1716 (s), 1658 (m), 1606 (m), 1465 (m), 1376 (w), 1249 (m), 1177 (m), 1160 (m), 1034 (m), 725 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{44}NaO_2^+$ 411.3234; Found 411.3233.

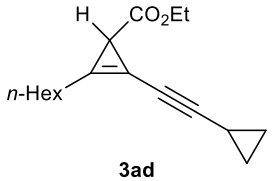
5.1.29. Synthesis and characterization of ethyl 2-(cyclopentylethynyl)-3-hexylcycloprop-2-ene-1-carboxylate (3ac)



3ac

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ac** (18.8 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3ac** in 83% yield (47.6 mg, 165 μmol) as a colourless oil and **4** in 97% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.51; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.20 – 4.08 (m, 2H, $CO_2CH_2CH_3$), 2.81 (pent, *J* = 7.5 Hz, 1H, C≡CC*H*), 2.48 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.34 (s, 1H, $CHCO_2$), 2.03 – 1.88 (m, 2H, CH_2CH_2C), 1.80 – 1.49 (m, 8H, CH_2), 1.46 – 1.16 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.80 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 113.5, 105.4, 91.1, 67.4, 60.4, 33.7, 31.6, 31.3, 28.9, 26.7, 25.8, 25.2, 24.8, 22.7, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 2955 (m), 2934 (m), 2871 (m), 2209 (w), 1733 (s), 1714 (s), 1654 (m), 1604 (m), 1456 (m), 1410 (w), 1373 (w), 1298 (w), 1250 (m), 1178 (m), 1097 (w), 1032 (m), 858 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{28}NaO_2^+$ 311.1982; Found 311.1987.

5.1.30. Synthesis and characterization of ethyl 2-(cyclopropylethynyl)-3-hexylcycloprop-2-ene-1-carboxylate (3ad)

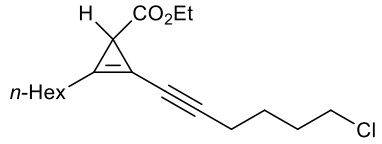


3ad

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ad** (13.2 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3ad** in 94% yield (49.1 mg, 188 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.32; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.19 – 4.08 (m, 2H, $CO_2CH_2CH_3$), 2.47 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.34 (s, 1H, $CHCO_2$), 1.61 – 1.51 (m, 2H, CH_2CH_2C), 1.48 – 1.41 (m, 1H, C≡CC*H*), 1.39 – 1.19 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.91 – 0.76 (m, 7H, CH_2 & CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 113.5, 104.4, 91.0,

63.2, 60.5, 31.6, 28.9, 26.7, 25.8, 24.9, 22.6, 14.5, 14.2, 9.1, 0.8; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2932 (m), 2861 (m), 2209 (m), 1713 (s), 1601 (m), 1465 (m), 1378 (m), 1256 (m), 1166 (m), 1094 (m), 1027 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{25}O_2^+$ 261.1849; Found 261.1854.

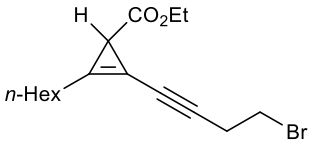
5.1.31. Synthesis and characterization of ethyl 2-(6-chlorohex-1-yn-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (3ae)



3ae

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ae** (23.3 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 40:1) afforded **3ae** in 88% yield (54.8 mg, 176 μmol) as a colourless oil and **4** in 97% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.48; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.19 – 4.07 (m, 2H, $CO_2CH_2CH_3$), 3.55 (t, *J* = 6.5 Hz, 2H, CH_2), 2.50 – 2.44 (m, 4H, CH_2), 2.34 (s, 1H, $CHCO_2$), 1.96 – 1.84 (m, 2H, CH_2CH_2C), 1.80 – 1.66 (m, 2H, CH_2), 1.63 – 1.50 (m, 2H, CH_2), 1.43 – 1.18 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.87 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 114.3, 100.2, 90.9, 68.6, 60.5, 44.5, 31.6, 31.5, 28.9, 26.6, 25.8, 25.6, 24.7, 22.6, 19.4, 14.5, 14.1; **IR** (ν_{max}, cm^{-1}) 2956 (s), 2934 (s), 2861 (m), 2218 (w), 1725 (s), 1656 (m), 1604 (m), 1462 (m), 1265 (m), 1181 (s), 1029 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{28}ClO_2^+$ 311.1772; Found 311.1771.

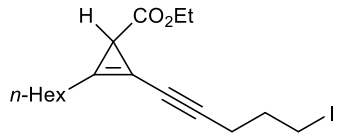
5.1.32. Synthesis and characterization of ethyl 2-(4-bromobut-1-yn-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (3af)



3af

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2af** (26.6 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3af** in 90% yield (59.1 mg, 181 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.49; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.20 – 4.08 (m, 2H, $CO_2CH_2CH_3$), 3.46 (t, *J* = 7.4 Hz, 2H, CH_2), 2.98 (t, *J* = 7.3 Hz, 2H, CH_2), 2.50 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.38 (s, 1H, $CHCO_2$), 1.63 – 1.52 (m, 2H, CH_2CH_2C), 1.42 – 1.20 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.91 – 0.84 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 115.9, 97.2, 90.5, 69.9, 60.6, 31.5, 28.9, 28.7, 26.6, 25.9, 24.8, 24.5, 22.6, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2930 (m), 2858 (m), 2240 (w), 1723 (s), 1654 (m), 1596 (m), 1466 (m), 1372 (w), 1268 (m), 1181 (s), 1096 (m), 1026 (m), 861 (w), 740 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{24}BrO_2^+$ 327.0954; Found 327.0952.

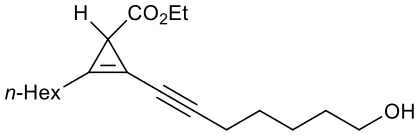
5.1.33. Synthesis and characterization of ethyl 2-hexyl-3-(5-iodopent-1-yn-1-yl)cycloprop-2-ene-1-carboxylate (3ag)



3ag

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ag** (38.8 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3ag** in 82% yield (63.5 mg, 164 μmol) as a colourless oil and **4** in 92% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.53; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.17 – 4.10 (m, 2H, $CO_2CH_2CH_3$), 3.28 (t, *J* = 6.8 Hz, 2H, CH_2), 2.56 (t, *J* = 6.8 Hz, 2H, CH_2), 2.49 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.35 (s, 1H, $CHCO_2$), 2.04 (pent, *J* = 6.8 Hz, 2H, CH_2CH_2C), 1.64 – 1.51 (m, 2H, CH_2), 1.43 – 1.17 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.94 – 0.79 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 114.7, 98.7, 90.7, 69.1, 60.5, 31.9, 31.5, 28.9, 26.6, 25.8, 24.8, 22.6, 21.2, 14.5, 14.2, 5.1; **IR** (ν_{max}, cm^{-1}) 2955 (m), 2932 (m), 2856 (m), 2219 (w), 1722 (s), 1660 (m), 1604 (m), 1466 (m), 1371 (m), 1220 (m), 1178 (s), 1025 (m), 735 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{26}IO_2^+$ 389.0972; Found 389.0971.

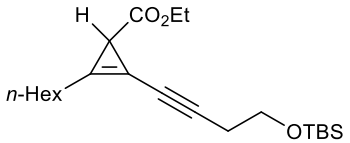
5.1.34. Synthesis and characterization of ethyl 2-hexyl-3-(7-hydroxyhept-1-yn-1-yl)cycloprop-2-ene-1-carboxylate (3ah)



3ah

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ah** (22.4 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3ah** in 87% yield (53.1 mg, 173 μmol) as a colourless oil and **4** in 96% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.17; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.18 – 4.06 (m, 2H, $CO_2CH_2CH_3$), 3.62 (t, *J* = 6.5 Hz, 2H, CH_2), 2.47 (t, *J* = 7.3 Hz, 2H, CH_2), 2.41 (t, *J* = 7.0 Hz, 2H, CH_2CH_2C), 2.33 (s, 1H, $CHCO_2$), 1.78 (bs, 1H, O*H*), 1.64 – 1.51 (m, 6H, CH_2), 1.51 – 1.41 (m, 2H, CH_2), 1.41 – 1.14 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.93 – 0.80 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 113.7, 101.0, 90.9, 68.0, 62.8, 60.5, 32.3, 31.5, 28.9, 28.2, 26.6, 25.8, 25.2, 24.7, 22.6, 20.1, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2932 (s), 2859 (m), 2348 (w), 2214 (w), 1721 (s), 1660 (m), 1607 (m), 1462 (m), 1371 (m), 1248 (m), 1178 (s), 1071 (m), 1031 (m), 866 (w), 732 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{30}NaO_3^+$ 329.2087; Found 329.2088.

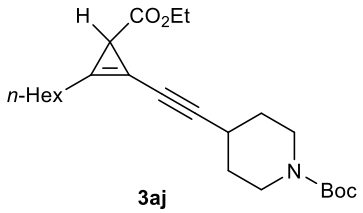
5.1.35. Synthesis and characterization of ethyl 2-(4-((*tert*-butyldimethylsilyl)oxy)but-1-yn-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (3ai)



3ai

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ai** (36.9 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3ai** in 87% yield (65.8 mg, 174 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.59; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.20 – 4.05 (m, 2H, $CO_2CH_2CH_3$), 3.76 (t, *J* = 7.0 Hz, 2H, CH_2), 2.62 (t, *J* = 7.0 Hz, 2H, CH_2), 2.48 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.35 (s, 1H, $CHCO_2$), 1.63 – 1.50 (m, 2H, CH_2CH_2C), 1.42 – 1.19 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.92 – 0.81 (m, 12H, $C(CH_3)_3$ & CH_3), 0.06 (s, 6H, $Si(CH_3)_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 114.3, 98.2, 90.9, 69.0, 61.6, 60.5, 31.6, 28.9, 26.6, 26.0, 25.8, 24.8, 24.5, 22.6, 18.5, 14.5, 14.2, -5.2; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2932 (m), 2858 (m), 2217 (w), 1725 (s), 1661 (m), 1608 (w), 1469 (m), 1372 (w), 1253 (m), 1177 (m), 1098 (m), 1035 (m), 836 (s), 777 (s), 736 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{38}NaO_3Si^+$ 401.2482; Found 401.2483.

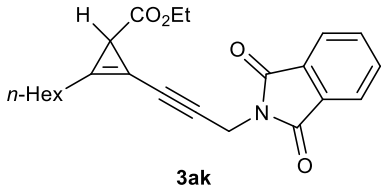
5.1.36. Synthesis and characterization of *tert*-butyl 4-((3-(ethoxycarbonyl)-2-hexylcycloprop-1-en-1-yl)ethynyl)piperidine-1-carboxylate (3aj)



3aj

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aj** (41.9 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3aj** in 93% yield (75.4 mg, 187 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.18; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.12 (qd, *J* = 7.1, 0.9 Hz, 2H, $CO_2CH_2CH_3$), 3.75 – 3.59 (m, 2H, CH_2), 3.19 – 3.12 (m, 2H, CH_2), 2.79 – 2.73 (m, 1H, C≡C*CH*), 2.47 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.34 (s, 1H, $CHCO_2$), 1.90 – 1.71 (m, 2H, CH_2CH_2C), 1.70 – 1.51 (m, 4H, CH_2), 1.42 (s, 9H, $C(CH_3)_3$), 1.39 – 1.13 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.96 – 0.73 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 154.8, 114.8, 102.4, 90.7, 79.6, 69.2, 60.4, 42.3 (bs), 31.5, 31.1, 28.8, 28.5, 28.3, 26.6, 25.8, 24.8, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2971 (m), 2956 (m), 2931 (m), 2863 (w), 2212 (w), 1725 (m), 1693 (s), 1663 (s), 1467 (m), 1422 (m), 1367 (m), 1273 (m), 1234 (m), 1162 (s), 1126 (m), 1026 (m), 865 (m), 770 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{37}NNaO_4^+$ 426.2615; Found 426.2610.

5.1.37. Synthesis and characterization of ethyl 2-(3-(1,3-dioxoisoindolin-2-yl)prop-1-yn-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (3ak)

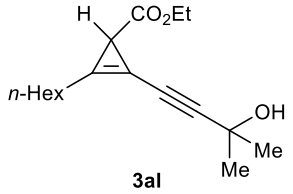


3ak

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ak** (37.0 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **3ak** in 95% yield (72.3 mg, 191 μmol) as a colourless oil and **4** in 97% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.43; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 2H, Ar*H*), 7.79 – 7.68 (m, 2H, Ar*H*), 4.65 (s, 2H, $CO_2CH_2CH_3$), 4.16 –

4.04 (m, 2H, NCH_2), 2.47 (t, J = 7.3 Hz, 2H, CH_2CH_2C), 2.35 (s, 1H, CHCO$_2$), 1.59 – 1.45 (m, 2H, CH_2CH_2C), 1.37 – 1.15 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.88 – 0.77 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 167.0, 134.3, 132.1, 123.7, 117.7, 92.9, 90.1, 70.7, 60.5, 31.4, 28.8, 28.1, 26.5, 25.9, 24.8, 22.5, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (w), 2931 (w), 2859 (w), 2226 (w), 1774 (m), 1717 (s), 1610 (w), 1468 (w), 1417 (m), 1390 (m), 1343 (m), 1315 (w), 1258 (w), 1188 (m), 1115 (m), 1087 (w), 1026 (w), 940 (m), 794 (w), 726 (s), 716 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{25}NNaO_4^+$ 402.1676; Found 402.1681.

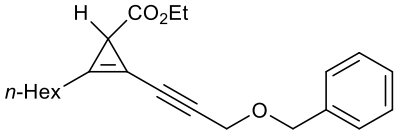
5.1.38. Synthesis and characterization of ethyl 2-hexyl-3-(3-hydroxy-3-methylbut-1-yn-1-yl)cycloprop-2-ene-1-carboxylate (3al)



3al

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2al** (16.8 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **3al** in 96% yield (53.5 mg, 192 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 5:1) = 0.27; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.19 – 4.08 (m, 2H, $CO_2CH_2CH_3$), 2.50 (t, J = 7.3 Hz, 2H, CH_2CH_2C), 2.37 (s, 1H, CHCO$_2$), 2.29 (bs, 1H, OH), 1.61 – 1.51 (m, 8H, CH_2 & C(CH_3)$_2$), 1.45 – 1.17 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.87 (t, J = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 116.5, 103.9, 90.2, 69.8, 65.8, 60.6, 31.5, 31.2, 28.9, 26.6, 25.8, 24.8, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2979 (m), 2960 (m), 2932 (m), 2859 (m), 2221 (w), 1715 (s), 1660 (m), 1609 (m), 1464 (m), 1371 (s), 1335 (m), 1246 (s), 1200 (s), 1176 (s), 1025 (m), 959 (m), 869 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{26}NaO_3^+$ 301.1774; Found 301.1778.

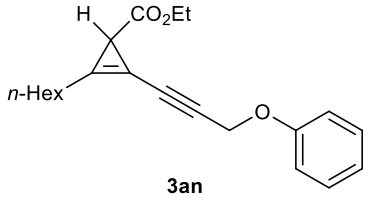
5.1.39. Synthesis and characterization of ethyl 2-(3-(benzyloxy)prop-1-yn-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (3am)



3am

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2am** (29.2 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 5 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 40:1) afforded **3am** in 85% yield (57.9 mg, 170 μmol) as a colourless oil and **4** in 91% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.20; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H, ArH), 4.62 (s, 2H, OCH_2), 4.38 (s, 2H, OCH_2), 4.21 – 4.10 (m, 2H, $CO_2CH_2CH_3$), 2.54 (t, J = 7.3 Hz, 2H, CH_2CH_2C), 2.43 (s, 1H, CHCO$_2$), 1.68 – 1.55 (m, 2H, CH_2CH_2C), 1.45 – 1.18 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.76 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 137.3, 128.6, 128.2, 128.1, 117.1, 95.6, 90.3, 74.1, 71.9, 60.6, 58.1, 31.5, 28.9, 26.6, 26.0, 25.0, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2931 (m), 2859 (m), 2221 (w), 1721 (s), 1605 (m), 1455 (m), 1372 (m), 1258 (m), 1182 (m), 1094 (s), 1072 (m), 1027 (m), 744 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{28}NaO_3^+$ 363.1931; Found 363.1930.

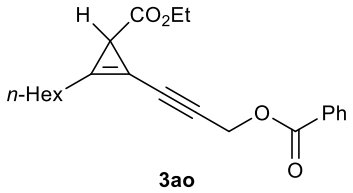
5.1.40. Synthesis and characterization of ethyl 2-hexyl-3-(3-phenoxyprop-1-yn-1-yl)cycloprop-2-ene-1-carboxylate (3an)



3an

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2an** (26.4 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 40:1) afforded **3an** in 90% yield (59.0 mg, 181 μmol) as a colourless oil and **4** in 92% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.43; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H, Ar*H*), 7.03 – 6.93 (m, 3H, Ar*H*), 4.89 (s, 2H, OCH_2), 4.20 – 4.09 (m, 2H, $CO_2CH_2CH_3$), 2.52 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.42 (s, 1H, $CHCO_2$), 1.63 – 1.51 (m, 2H, CH_2CH_2C), 1.43 – 1.15 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.96 – 0.76 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 157.7, 129.6, 121.7, 118.0, 115.0, 94.3, 90.1, 74.7, 60.6, 56.7, 31.5, 28.9, 26.5, 26.0, 25.0, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2955 (m), 2929 (m), 2858 (w), 2229 (w), 1860 (w), 1723 (m), 1599 (m), 1589 (m), 1495 (s), 1458 (w), 1370 (w), 1335 (w), 1303 (w), 1260 (m), 1213 (s), 1174 (s), 1033 (s), 1018 (m), 753 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{27}O_3^+$ 327.1955; Found 327.1955.

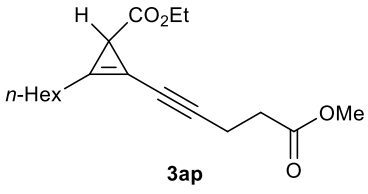
5.1.41. Synthesis and characterization of 3-(3-(ethoxycarbonyl)-2-hexylcycloprop-1-en-1-yl)prop-2-yn-1-yl benzoate (3ao)



3ao

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ao** (32.0 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3ao** in 93% yield (65.8 mg, 186 μmol) as a colourless oil and **4** in 94% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.33; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 7.97 (m, 2H, Ar*H*), 7.60 – 7.55 (m, 1H, Ar*H*), 7.51 – 7.37 (m, 2H, Ar*H*), 5.13 (s, 2H, OCH_2), 4.20 – 4.09 (m, 2H, $CO_2CH_2CH_3$), 2.53 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.43 (s, 1H, $CHCO_2$), 1.65 – 1.50 (m, 2H, CH_2CH_2C), 1.43 – 1.19 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.94 – 0.69 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 165.9, 133.5, 130.0, 129.5, 128.6, 118.3, 93.3, 90.1, 74.3, 60.7, 53.3, 31.5, 28.9, 26.6, 26.0, 25.0, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (w), 2930 (w), 2860 (w), 2233 (w), 1725 (s), 1602 (w), 1585 (w), 1452 (m), 1372 (w), 1315 (w), 1265 (s), 1177 (m), 1094 (m), 1069 (m), 1026 (m), 711 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{27}O_4^+$ 355.1904; Found 355.1903.

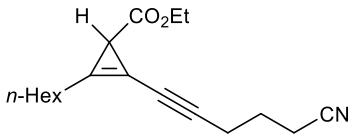
5.1.42. Synthesis and characterization of ethyl 2-hexyl-3-(5-methoxy-5-oxopent-1-yn-1-yl)cycloprop-2-ene-1-carboxylate (3ap)



3ap

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ap** (22.4 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 2 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3ap** in 87% yield (53.2 mg, 174 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.25; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.18 – 4.06 (m, 2H, $CO_2CH_2CH_3$), 3.68 (s, 3H, OCH_3), 2.76 – 2.66 (m, 2H, CH_2), 2.62 – 2.52 (m, 2H, CH_2), 2.47 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.34 (s, 1H, $CHCO_2$), 1.62 – 1.47 (m, 2H, CH_2CH_2C), 1.42 – 1.16 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.93 – 0.79 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 172.2, 114.8, 98.7, 90.7, 68.6, 60.5, 52.0, 32.9, 31.5, 28.9, 26.6, 25.8, 24.7, 22.6, 15.9, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2932 (m), 2858 (w), 2221 (w), 1738 (s), 1660 (m), 1606 (w), 1462 (w), 1439 (m), 1369 (m), 1249 (m), 1200 (m), 1167 (s), 1029 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{26}NaO_4^+$ 329.1723; Found 329.1727.

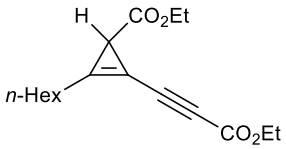
5.1.43. Synthesis and characterization of ethyl 2-(5-cyanopent-1-yn-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (3aq)



3aq

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aq** (18.6 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3aq** in 90% yield (51.6 mg, 180 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 5:1) = 0.29; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.19 – 4.07 (m, 2H, $CO_2CH_2CH_3$), 2.60 (t, *J* = 6.8 Hz, 2H, CH_2), 2.49 (td, *J* = 7.2, 1.2 Hz, 4H, CH_2), 2.36 (s, 1H, $CHCO_2$), 1.91 (pent, *J* = 7.0 Hz, 2H, CH_2CH_2C), 1.64 – 1.49 (m, 2H, CH_2), 1.43 – 1.17 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.96 – 0.72 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 119.0, 115.4, 97.7, 90.5, 69.8, 60.5, 31.5, 28.8, 26.6, 25.8, 24.7, 24.4, 22.6, 19.2, 16.3, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2956 (m), 2933 (m), 2859 (m), 2248 (w), 2218 (w), 1719 (s), 1660 (m), 1607 (m), 1457 (m), 1428 (m), 1371 (m), 1330 (w), 1250 (m), 1180 (m), 1071 (w), 1029 (m), 937 (w), 865 (w), 735 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{26}NO_2^+$ 288.1958; Found 288.1957.

5.1.44. Synthesis and characterization of ethyl 2-(3-ethoxy-3-oxoprop-1-yn-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (3ar)

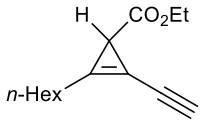


3ar

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2ar** (19.6 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 9 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3ar** in 84% yield (49.0 mg, 168 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.26 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 4.22 – 4.05 (m, 2H, $CO_2CH_2CH_3$), 2.58 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.51 (s, 1H, $CHCO_2$), 1.66 – 1.50 (m, 2H, CH_2CH_2C), 1.43 – 1.16 (m, 12H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.82 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 153.4, 125.3, 89.6, 89.0, 73.7,

62.5, 60.9, 31.4, 28.8, 26.6, 26.4, 25.6, 22.6, 14.4, 14.11, 14.09; **IR** (ν_{max}, cm^{-1}) 2981 (w), 2957 (m), 2928 (m), 2858 (w), 2234 (w), 1712 (s), 1613 (w), 1466 (w), 1369 (m), 1298 (w), 1258 (m), 1176 (m), 1160 (m), 1097 (m), 1023 (s), 858 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{25}O_4^+$ 293.1747; Found 293.1748.

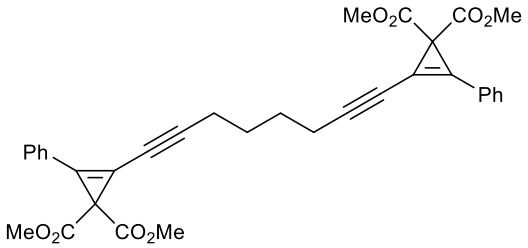
5.1.45. Synthesis and characterization of ethyl 2-ethynyl-3-hexylcycloprop-2-ene-1-carboxylate (3as)



3as

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (10.5 mg, 50.0 μmol, 25.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred under the atmosphere of acetylene (**2as**, ca. 1.0 atm.) at 40 °C for 18 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 40:1) afforded **3as** in 46% yield (20.4 mg, 92.6 μmol) as a colourless oil and **4** in 71% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.33; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.20 – 4.09 (m, 2H, $CO_2CH_2CH_3$), 3.49 (s, 1H, C≡C*H*), 2.53 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.43 (s, 1H, $CHCO_2$), 1.68 – 1.52 (m, 2H, CH_2CH_2C), 1.44 – 1.19 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.88 (t, *J* = 6.9 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 118.4, 90.3, 87.7, 71.3, 60.6, 31.5, 28.9, 26.5, 26.1, 24.9, 22.6, 14.5, 14.1; **IR** (ν_{max}, cm^{-1}) 3274 (w), 2957 (m), 2930 (m), 2859 (m), 2113 (w), 2096 (w), 1722 (s), 1611 (w), 1464 (m), 1373 (m), 1331 (m), 1298 (m), 1239 (m), 1182 (s), 1097 (m), 1029 (s), 861 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{21}O_2^+$ 221.1536; Found 221.1543.

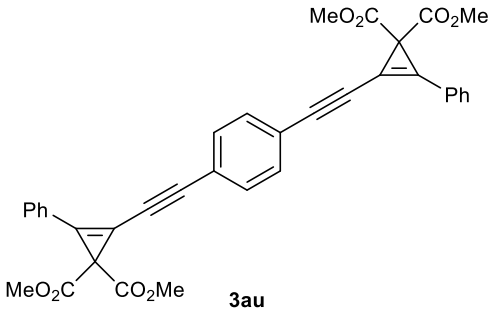
5.1.46. Synthesis and characterization of tetramethyl 3,3'-(octa-1,7-diyne-1,8-diyl)bis(2-phenylcycloprop-2-ene-1,1-dicarboxylate) (3at)



3at

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 10.0 mol%), **L1** (4.20 mg, 20.0 μmol, 20.0 mol%), CpBX **1k** (120 mg, 0.200 mmol, 2.00 equiv.), diyne **2at** (10.6 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 24 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **3at** in 84% yield (47.8 mg, 84.4 μmol) as a colorless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.14; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.53 (m, 4H, Ar*H*), 7.47 – 7.34 (m, 6H, Ar*H*), 3.74 (s, 12H, CO_2CH_3), 2.68 – 2.47 (m, 4H, CH_2), 1.81 (q, *J* = 3.0 Hz, 4H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 130.6, 130.4, 129.0, 124.5, 108.1, 104.8, 92.2, 67.3, 52.6, 36.5, 27.3, 20.0; **IR** (ν_{max}, cm^{-1}) 3059 (w), 3026 (w), 3004 (w), 2953 (w), 2899 (w), 2844 (w), 2226 (w), 2204 (w), 1726 (s), 1491 (w), 1447 (m), 1434 (m), 1333 (w), 1279 (s), 1241 (s), 1188 (w), 1059 (s), 972 (m), 919 (w), 834 (w), 763 (s), 736 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{30}NaO_8^+$ 589.1833; Found 589.1849.

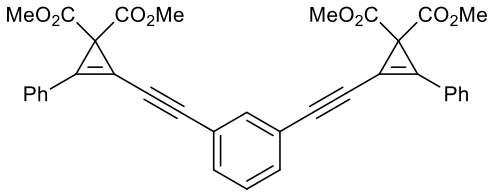
5.1.47. Synthesis and characterization of tetramethyl 3,3'-(1,4-phenylenebis(ethyne-2,1-diyl))bis(2-phenylcycloprop-2-ene-1,1-dicarboxylate) (3au)



3au

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 µmol, 10.0 mol%), **L1** (4.20 mg, 20.0 µmol, 20.0 mol%), CpBX **1k** (120 mg, 0.200 mmol, 2.00 equiv.), diyne **2au** (12.6 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 24 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **3au** in 94% yield (55.2 mg, 94.1 µmol) as a yellow solid and **4** in 98% NMR yield. **M.p.** 210 – 213 °C (decomp.). **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.18; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 4H, Ar*H*), 7.61 – 7.56 (m, 4H, Ar*H*), 7.51 – 7.42 (m, 6H, Ar*H*), 3.78 (s, 12H, CO_2CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 132.2, 131.1, 130.6, 129.2, 124.4, 123.0, 111.3, 101.7, 91.1, 78.0, 52.8, 36.9; **IR** (ν_{max}, cm^{-1}) 3026 (w), 2954 (w), 2843 (w), 2198 (m), 1744 (s), 1434 (s), 1278 (s), 1240 (m), 1187 (m), 1060 (s), 984 (w), 838 (s), 755 (s), 737 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{26}NaO_8^+$ 609.1520; Found 609.1526.

5.1.48. Synthesis and characterization of tetramethyl 3,3'-(1,3-phenylenebis(ethyne-2,1-diyl))bis(2-phenylcycloprop-2-ene-1,1-dicarboxylate) (3av)

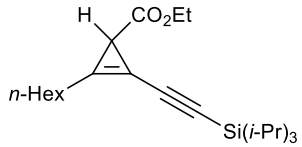


3av

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 µmol, 10.0 mol%), **L1** (4.20 mg, 20.0 µmol, 20.0 mol%), CpBX **1k** (120 mg, 0.200 mmol, 2.00 equiv.), diyne **2av** (12.6 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 24 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 3:1) afforded **3av** in 92% yield (54.2 mg, 92.4 µmol) as a light-yellow solid and **4** in 99% NMR yield. **M.p.** 175 – 176 °C. **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.15; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 1.6 Hz, 1H, Ar*H*), 7.72 – 7.66 (m, 4H, Ar*H*), 7.60 (dd, *J* = 7.8, 1.7 Hz, 2H, Ar*H*), 7.51 – 7.43 (m, 6H, Ar*H*), 7.44 – 7.35 (m, 1H, Ar*H*), 3.78 (s, 12H, CO_2CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 135.7, 133.0, 131.1, 130.6, 129.1, 128.9, 124.4, 122.5, 111.2, 101.0, 91.2, 76.5, 52.8, 36.9; **IR** (ν_{max}, cm^{-1}) 3061 (w), 3003 (w), 2952 (w), 2845 (w), 2200 (w), 1727 (s), 1591 (w), 1475 (m), 1434 (m), 1278 (s), 1242 (s), 1139 (w), 1060 (s), 973 (m), 761 (s), 736 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{26}NaO_8^+$ 609.1520; Found 609.1535.

5.2. Substrate scope of cyclopropenylbenziodoxoles CpBXs

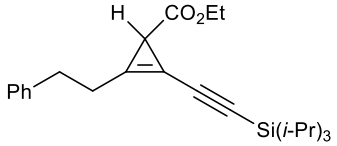
5.2.1. Synthesis and characterization of ethyl 2-hexyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1-carboxylate (3aw)



3aw

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1a** (113 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aw** (36.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3aw** in 93% yield (70.3 mg, 187 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.73; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.22 – 4.05 (m, 2H, $CO_2CH_2CH_3$), 2.51 (td, *J* = 7.1, 1.8 Hz, 2H, CH_2CH_2C), 2.42 (s, 1H, $CHCO_2$), 1.66 – 1.52 (m, 2H, CH_2CH_2C), 1.45 – 1.35 (m, 2H, CH_2), 1.35 – 1.18 (m, 7H, CH_2 & $CO_2CH_2CH_3$), 1.18 – 0.99 (m, 21H, Si(*i*-Pr)$_3$), 0.92 – 0.81 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 116.5, 103.3, 93.1, 91.1, 60.5, 31.6, 28.9, 26.6, 26.2, 25.6, 22.7, 18.7, 14.5, 14.2, 11.3; **IR** (ν_{max}, cm^{-1}) 2956 (s), 2942 (s), 2931 (s), 2897 (m), 2866 (s), 2150 (m), 1790 (w), 1728 (s), 1463 (s), 1384 (w), 1368 (m), 1332 (w), 1245 (m), 1179 (s), 1095 (w), 1073 (w), 1019 (m), 997 (m), 920 (w), 882 (s), 781 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{41}O_2Si^+$ 377.2870; Found 377.2872.

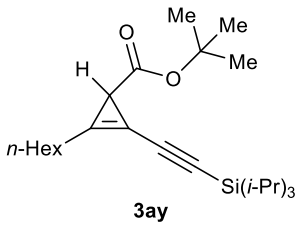
5.2.2. Synthesis and characterization of ethyl 2-phenethyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1-carboxylate (3ax)



3ax

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1c** (117 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aw** (36.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3ax** in 91% yield (72.3 mg, 182 μmol) as a colorless oil and **4** in 93% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 5H, Ar*H*), 4.24 – 4.02 (m, 2H, $CO_2CH_2CH_3$), 3.00 – 2.90 (m, 2H, CH_2), 2.90 – 2.76 (m, 2H, CH_2), 2.43 (s, 1H, $CHCO_2$), 1.24 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.14 – 1.06 (m, 21H, Si(*i*-Pr)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 140.6, 128.6, 128.5, 126.4, 115.2, 104.0, 92.9, 91.9, 60.6, 32.8, 28.1, 25.8, 18.7, 14.5, 11.3; **IR** (ν_{max}, cm^{-1}) 2944 (s), 2892 (m), 2866 (s), 2149 (m), 1789 (w), 1725 (s), 1604 (w), 1497 (m), 1465 (m), 1388 (w), 1333 (m), 1245 (m), 1181 (s), 1072 (m), 1022 (m), 997 (m), 883 (s), 783 (w), 746 (m); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{25}H_{37}O_2Si^+$ 397.2557; Found 397.2544.

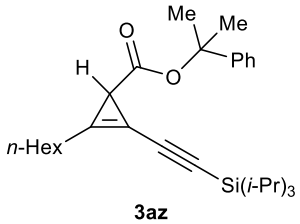
5.2.3. Synthesis and characterization of *tert*-butyl 2-hexyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1-carboxylate (3ay)



3ay

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1d** (119 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aw** (36.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3ay** in 96% yield (77.5 mg, 191 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.50 (td, *J* = 7.1, 1.7 Hz, 2H, CH_2CH_2C), 2.32 (s, 1H, $CHCO_2$), 1.68 – 1.52 (m, 2H, CH_2CH_2C), 1.42 (s, 9H, $C(CH_3)_3$), 1.44 – 1.36 (m, 2H, CH_2), 1.35 – 1.20 (m, 4H, CH_2), 1.14 – 1.02 (m, 21H, Si(*i*-Pr)$_3$), 0.97 – 0.79 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 116.9, 102.9, 93.5, 91.6, 80.2, 31.7, 28.9, 28.3, 26.7, 26.7, 26.3, 22.7, 18.7, 14.2, 11.3; **IR** (ν_{max}, cm^{-1}) 2934 (s), 2866 (s), 2149 (w), 1773 (w), 1717 (m), 1596 (w), 1463 (m), 1392 (w), 1368 (m), 1334 (w), 1252 (m), 1153 (s), 1072 (w), 997 (m), 883 (s); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{25}H_{45}O_2Si^+$ 405.3183; Found 405.3170.

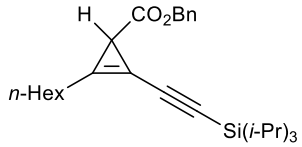
5.2.4. Synthesis and characterization of 2-phenylpropan-2-yl 2-hexyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1-carboxylate (3az)



3az

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1e** (119 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aw** (36.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3az** in 91% yield (84.5 mg, 181 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.44; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H, Ar*H*), 7.33 – 7.28 (m, 2H, Ar*H*), 7.25 – 7.19 (m, 1H, Ar*H*), 2.55 (td, *J* = 7.1, 1.6 Hz, 2H, CH_2CH_2C), 2.42 (s, 1H, $CHCO_2$), 1.79 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.63 (pent, *J* = 7.1 Hz, 2H, CH_2CH_2C), 1.47 – 1.39 (m, 2H, CH_2), 1.37 – 1.23 (m, 4H, CH_2), 1.19 – 1.06 (m, 21H, Si(*i*-Pr)$_3$), 0.94 – 0.85 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6, 146.3, 128.3, 126.9, 124.3, 116.7, 103.1, 93.4, 91.6, 81.5, 31.7, 29.3, 28.9, 28.5, 26.8, 26.7, 26.3, 22.7, 18.7, 14.2, 11.4; **IR** (ν_{max}, cm^{-1}) 2942 (m), 2865 (m), 2150 (m), 1773 (w), 1699 (m), 1463 (m), 1266 (m), 1139 (s), 1102 (m), 1073 (m), 1000 (m), 882 (s), 763 (s); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{30}H_{47}O_2Si^+$ 467.3340; Found 467.3338.

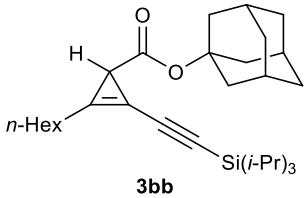
5.2.5. Synthesis and characterization of benzyl 2-hexyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1-carboxylate (3ba)



3ba

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1f** (125 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aw** (36.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 5 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 40:1) afforded **3ba** in 91% yield (79.9 mg, 182 μmol) as a colourless oil and **4** in 94% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H, Ar*H*), 5.23 – 5.07 (m, 2H, OCH_2Ph), 2.61 – 2.44 (m, 3H, C*H*CO_2 & CH_2CH_2C), 1.66 – 1.53 (m, 2H, CH_2CH_2C), 1.47 – 1.34 (m, 2H, CH_2), 1.33 – 1.22 (m, 4H, CH_2), 1.16 – 1.03 (m, 21H, Si(*i*-Pr)$_3$), 0.95 – 0.82 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 136.5, 128.6, 128.1, 128.0, 116.4, 103.5, 93.0, 91.0, 66.2, 31.6, 28.9, 26.6, 26.2, 25.6, 22.6, 18.7, 14.2, 11.3; **IR** (ν_{max}, cm^{-1}) 2956 (s), 2942 (s), 2892 (m), 2865 (s), 2150 (m), 1730 (s), 1498 (w), 1458 (m), 1381 (w), 1336 (w), 1239 (m), 1171 (s), 1072 (w), 995 (m), 883 (s), 740 (m); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{28}H_{43}O_2Si^+$ 439.3027; Found 439.3013.

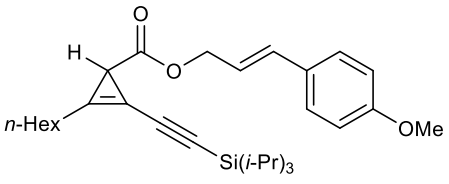
5.2.6. Synthesis and characterization of adamantan-1-yl 2-hexyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1-carboxylate (3bb)



3bb

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1g** (134 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aw** (36.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 5 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 40:1) afforded **3bb** in 94% yield (90.6 mg, 188 μmol) as a colourless oil and **4** in 96% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.47; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.56 – 2.44 (m, 2H, CH_2CH_2C), 2.31 (s, 1H, C*H*CO_2), 2.17 – 2.10 (m, 3H, C*H*(adamantyl)), 2.10 – 2.05 (m, 6H, CH_2(adamantyl)), 1.71 – 1.53 (m, 8H, CH_2), 1.45 – 1.35 (m, 2H, CH_2), 1.35 – 1.20 (m, 4H, CH_2), 1.14 – 1.03 (m, 21H, Si(*i*-Pr)$_3$), 0.93 – 0.80 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 117.0, 102.8, 93.6, 91.6, 80.2, 41.5, 36.4, 31.7, 31.0, 28.9, 26.7, 26.2, 22.7, 18.7, 14.2, 11.3; **IR** (ν_{max}, cm^{-1}) 2940 (s), 2915 (s), 2865 (s), 2149 (w), 1718 (s), 1459 (m), 1352 (m), 1248 (m), 1183 (s), 1103 (m), 1053 (s), 997 (m), 883 (s); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{31}H_{51}O_2Si^+$ 483.3653; Found 483.3644.

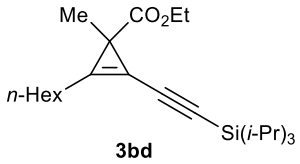
5.2.7. Synthesis and characterization of (*E*)-3-(4-methoxyphenyl)allyl 2-hexyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1-carboxylate (3bc)



3bc

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1h** (137 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aw** (36.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 10 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3bc** in 89% yield (88.0 mg, 178 μmol) as a colourless oil and **4** in 97% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.31; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H, Ar*H*), 6.91 – 6.79 (m, 2H, Ar*H*), 6.59 (dt, *J* = 15.6, 1.4 Hz, 1H, CH_2CH=C*H*), 6.15 (dt, *J* = 15.8, 6.5 Hz, 1H, CH_2C*H*=CH), 4.82 – 4.64 (m, 2H, CH_2CH=CH), 3.81 (s, 3H, OCH_3), 2.54 (td, *J* = 7.1, 2.8 Hz, 2H, CH_2CH_2C), 2.49 (s, 1H, C*H*CO_2), 1.71 – 1.52 (m, 2H, CH_2CH_2C), 1.43 – 1.36 (m, 2H, CH_2), 1.34 – 1.22 (m, 4H, CH_2), 1.14 – 1.02 (m, 21H, Si(*i*-Pr)$_3$), 0.93 – 0.82 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 159.6, 133.7, 129.3, 128.0, 121.4, 116.5, 114.1, 103.5, 93.0, 91.1, 65.4, 55.4, 31.6, 28.9, 26.6, 26.2, 25.6, 22.7, 18.7, 14.2, 11.3; **IR** (ν_{max}, cm^{-1}) 2955 (m), 2940 (m), 2896 (m), 2864 (m), 2148 (w), 1727 (m), 1608 (m), 1512 (s), 1463 (m), 1444 (w), 1248 (s), 1168 (s), 1037 (m), 964 (m), 883 (m); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{31}H_{47}O_3Si^+$ 495.3289; Found 495.3275.

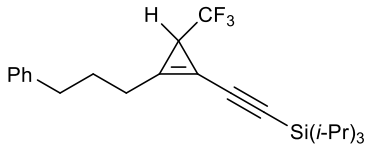
5.2.8. Synthesis and characterization of ethyl 2-hexyl-1-methyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1-carboxylate (3bd)



3bd

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1i** (116 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aw** (36.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 6 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 40:1) afforded **3bd** in 89% yield (69.2 mg, 177 μmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.31; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.17 – 3.99 (m, 2H, $CO_2CH_2CH_3$), 2.48 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 1.65 – 1.51 (m, 2H, CH_2CH_2C), 1.43 – 1.35 (m, 5H, CH_2 & CH_3), 1.34 – 1.23 (m, 4H, CH_2), 1.20 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.13 – 1.03 (m, 21H, Si(*i*-Pr)$_3$), 0.95 – 0.80 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.4, 122.2, 103.5, 96.9, 93.0, 60.5, 31.6, 30.2, 28.9, 26.8, 25.6, 22.7, 19.1, 18.7, 14.5, 14.2, 11.3; **IR** (ν_{max}, cm^{-1}) 2958 (s), 2932 (s), 2894 (m), 2866 (s), 2145 (m), 1776 (w), 1721 (s), 1464 (m), 1388 (w), 1267 (s), 1252 (s), 1171 (m), 1112 (s), 1074 (w), 1019 (m), 996 (m), 946 (w), 883 (s), 766 (m); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{24}H_{43}O_2Si^+$ 391.3027; Found 391.3012.

5.2.9. Synthesis and characterization of triisopropyl((2-(3-phenylpropyl)-3-(trifluoromethyl)cycloprop-1-en-1-yl)ethynyl)silane (3be)

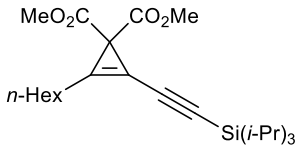


3be

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (5.25 mg, 25.0 μmol, 25.0 mol%), CpBX **1j** (59.4 mg, 0.100 mmol, 1.00 equiv.), terminal alkyne **2aw** (27.4 mg, 0.150 mmol, 1.50 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 24 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3be** in 78% yield (31.8 mg, 78.2 μmol) as a colourless oil and **4** in 81% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.75; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H, Ar*H*), 7.25 – 7.16 (m, 3H, Ar*H*), 2.73 (t, *J* = 7.6 Hz, 2H, CH_2), 2.55 (t, *J* = 7.0 Hz, 2H, CH_2), 2.29 (q, *J* = 4.4 Hz, 1H, C*H*(CF_3)), 2.01 – 1.93 (m, 2H, CH_2), 1.18 – 1.06 (m, 21H, Si(*i*-Pr)$_3$);

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 128.7, 128.6, 126.2, 125.7 (q, *J* = 275.8 Hz), 116.3 (q, *J* = 3.0 Hz), 104.8, 92.5, 91.7 (q, *J* = 3.9 Hz), 35.1, 28.3, 25.4, 24.3 (q, *J* = 39.2 Hz), 18.7, 11.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.8; **IR** (ν_{max}, cm^{-1}) 2945 (m), 2894 (w), 2867 (m), 2154 (w), 1497 (w), 1462 (w), 1359 (w), 1270 (m), 1185 (w), 1134 (s), 1075 (w), 997 (w), 920 (w), 883 (m), 805 (w), 745 (w); **HRMS** (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{24}H_{33}F_3Si^+$ 406.2298; Found 406.2302.

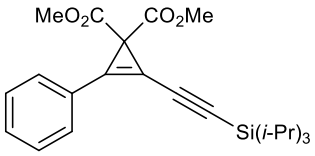
5.2.10. Synthesis and characterization of dimethyl 2-hexyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1,1-dicarboxylate (3bf)



3bf

Following **GPD**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1o** (60.8 mg, 0.100 mmol, 1.00 equiv.), terminal alkyne **2aw** (18.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 24 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3bf** in 91% yield (38.2 mg, 90.8 μmol) as a colourless oil and **4** in 95% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.39; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.72 (s, 6H, CO_2CH_3), 2.56 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 1.65 – 1.58 (m, 2H, CH_2CH_2C), 1.42 – 1.35 (m, 2H, CH_2), 1.34 – 1.18 (m, 4H, CH_2), 1.14 – 1.03 (m, 21H, Si(*i*-Pr)$_3$), 0.95 – 0.80 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 113.6, 104.6, 91.1, 90.6, 52.4, 37.0, 31.5, 28.8, 26.4, 25.2, 22.6, 18.6, 14.2, 11.2; **IR** (ν_{max}, cm^{-1}) 2946 (m), 2894 (m), 2866 (m), 2155 (w), 1733 (s), 1463 (m), 1434 (m), 1385 (w), 1279 (s), 1245 (s), 1173 (m), 1105 (w), 1063 (s), 997 (m), 883 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{41}O_4Si^+$ 421.2769; Found 421.2775.

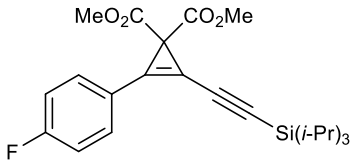
5.2.11. Synthesis and characterization of dimethyl 2-phenyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1,1-dicarboxylate (3bg)



3bg

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1k** (120 mg, 0.200 mmol, 1.00 equiv.), terminal alkyne **2aw** (36.5 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 17 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3bg** in 93% yield (76.8 mg, 186 μmol) as a colourless solid and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.16; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 2H, Ar*H*), 7.48 – 7.37 (m, 3H, Ar*H*), 3.74 (s, 6H, CO_2CH_3), 1.24 – 1.04 (m, 21H, Si(*i*-Pr)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 130.8, 130.6, 129.1, 124.6, 109.6, 108.5, 92.0, 91.4, 52.6, 37.1, 18.7, 11.3; **IR** (ν_{max}, cm^{-1}) 2948 (m), 2892 (m), 2866 (m), 2147 (w), 1734 (s), 1464 (m), 1439 (m), 1281 (s), 1245 (s), 1142 (w), 1063 (s), 1016 (m), 883 (m), 761 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{32}NaO_4Si^+$ 435.1962; Found 435.1973. The NMR spectroscopic data is consistent with previous report[52].

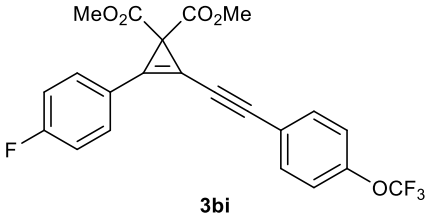
5.2.12. Synthesis and characterization of dimethyl 2-(4-fluorophenyl)-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1,1-dicarboxylate (3bh)



3bh

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1l** (61.8 mg, 0.100 mmol, 1.00 equiv.), terminal alkyne **2aw** (18.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3bh** in 82% yield (35.4 mg, 82.2 μmol) as a colourless solid and **4** in 96% NMR yield. **M.p.** 105 – 107 °C. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.54 (m, 2H, Ar*H*), 7.20 – 7.06 (m, 2H, Ar*H*), 3.75 (s, 6H, CO_2CH_3), 1.24 – 1.02 (m, 21H, Si(*i*-Pr)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.4, 164.1 (d, *J* = 253.5 Hz), 132.7 (d, *J* = 8.9 Hz), 121.0 (d, *J* = 3.3 Hz), 116.5 (d, *J* = 22.4 Hz), 108.7, 108.6, 91.6 (d, *J* = 2.8 Hz), 91.2, 52.7, 37.1, 18.7, 11.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.2; **IR** (ν_{max}, cm^{-1}) 2948 (m), 2896 (m), 2867 (m), 2723 (w), 2147 (w), 1743 (s), 1599 (m), 1504 (m), 1463 (m), 1438 (m), 1411 (w), 1277 (s), 1236 (s), 1192 (w), 1153 (m), 1063 (s), 1022 (m), 996 (m), 882 (m), 838 (m), 788 (w), 741 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{31}FNaO_4Si^+$ 453.1868; Found 453.1868.

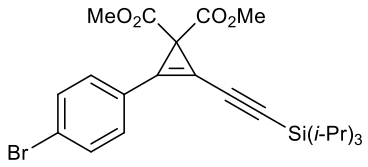
5.2.13. Synthesis and characterization of dimethyl 2-(4-fluorophenyl)-3-((4-(trifluoromethoxy)phenyl)ethynyl)cycloprop-2-ene-1,1-dicarboxylate (3bi)



3bi

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1l** (61.8 mg, 0.100 mmol, 1.00 equiv.), terminal alkyne **2n** (18.6 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 5 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3bi** in 85% yield (37.1 mg, 85.4 μmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.43; **^{1}H NMR** (400 MHz, CD_3CN) δ 7.78 – 7.66 (m, 4H, Ar*H*), 7.38 – 7.34 (m, 2H, Ar*H*), 7.32 – 7.23 (m, 2H, Ar*H*), 3.72 (s, 6H, CO_2CH_3); **^{13}C NMR** (101 MHz, CD_3CN) δ 167.0, 165.2 (d, *J* = 251.8 Hz), 150.9 (q, *J* = 2.0 Hz), 135.0, 133.8 (d, *J* = 9.1 Hz), 122.4, 121.8 (d, *J* = 3.3 Hz), 121.4 (q, *J* = 256.8 Hz), 121.3, 117.6 (d, *J* = 22.8 Hz), 111.8, 101.6, 91.6 (d, *J* = 2.8 Hz), 76.6, 53.3, 37.8; **^{19}F NMR** (376 MHz, CD_3CN) δ -58.5 (OCF_3), -108.4 (Ar*F*); **IR** (ν_{max}, cm^{-1}) 3106 (w), 3076 (w), 3005 (w), 2956 (w), 2852 (w), 2208 (w), 1733 (s), 1602 (m), 1502 (m), 1437 (w), 1247 (s), 1217 (s), 1159 (s), 1061 (s), 1017 (w), 974 (w), 924 (w), 840 (s), 815 (w), 743 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{14}F_4NaO_5^+$ 457.0670; Found 457.0662.

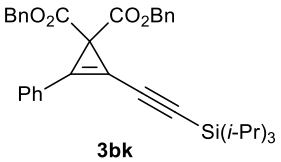
5.2.14. Synthesis and characterization of dimethyl 2-(4-bromophenyl)-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1,1-dicarboxylate (3bj)



3bj

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1m** (67.9 mg, 0.100 mmol, 1.00 equiv.), terminal alkyne **2aw** (18.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 36 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3bj** in 88% yield (43.3 mg, 88.1 μmol) as a colorless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.36; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H, Ar*H*), 7.52 – 7.42 (m, 2H, Ar*H*), 3.74 (s, 6H, CO_2CH_3), 1.24 – 1.03 (m, 21H, Si(*i*-Pr)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 132.4, 131.8, 125.5, 123.5, 109.6, 108.6, 92.8, 91.1, 52.7, 37.0, 18.7, 11.3; **IR** (ν_{max}, cm^{-1}) 2948 (m), 2892 (m), 2866 (m), 2145 (w), 1734 (s), 1585 (m), 1484 (m), 1463 (m), 1435 (m), 1397 (w), 1277 (s), 1243 (s), 1142 (w), 1065 (s), 1009 (s), 976 (w), 882 (m), 826 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{31}BrNaO_4Si^+$ 513.1067; Found 513.1074.

5.2.15. Synthesis and characterization of dibenzyl 2-phenyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1,1-dicarboxylate (3bk)

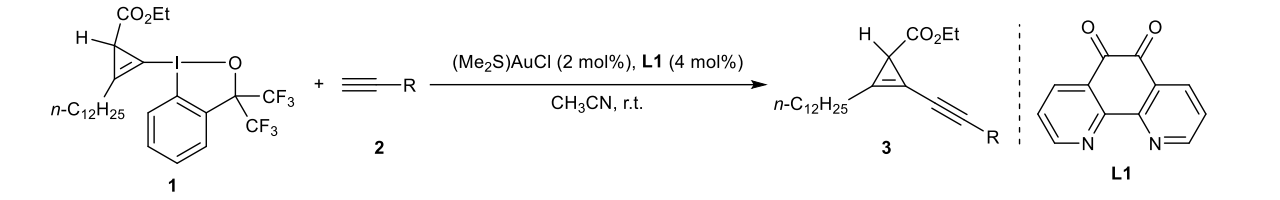


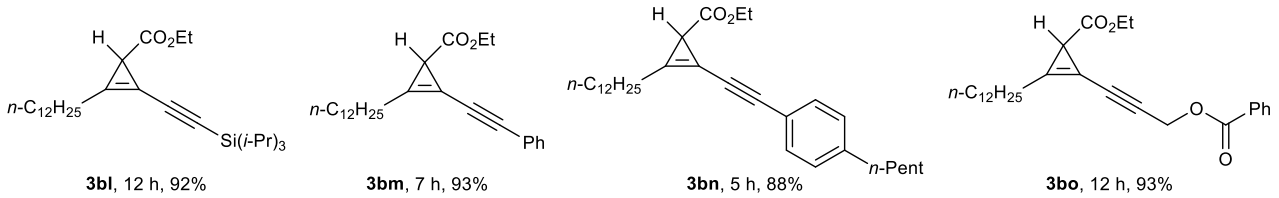
3bk

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1n** (75.2 mg, 0.100 mmol, 1.00 equiv.), terminal alkyne **2aw** (18.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 2 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3bk** in 80% yield (45.2 mg, 80.0 μmol) as a colorless oil and **4** in 95% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.37; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.56 (m, 2H, Ar*H*), 7.42 (tt, *J* = 3.9, 2.4 Hz, 3H, Ar*H*), 7.29 (s, 10H, Ar*H*), 5.36 – 5.09 (m, 4H, OCH_2Ph), 1.22 – 1.05 (m, 21H, Si(*i*-Pr)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 135.9, 130.8, 130.7, 129.0, 128.5, 128.0, 127.7, 124.5, 109.7, 108.5, 91.8, 91.4, 67.0, 37.4, 18.7, 11.3; **IR** (ν_{max}, cm^{-1}) 3065 (w), 3034 (w), 2944 (m), 2865 (m), 2146 (w), 1732 (s), 1498 (m), 1456 (m), 1376 (w), 1271 (s), 1226 (s), 1140 (w), 1055 (s), 1015 (m), 883 (m), 759 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{40}NaO_4Si^+$ 587.2588; Found 587.2582.

5.3. Scale up experiment of σ-type cyclopropenium cation transfer to terminal alkyne

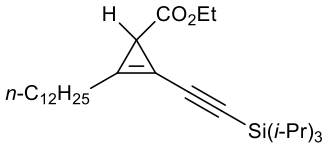
Table 5 | Scale up experiment





Reaction conditions: CpBX **1** (1.00 equiv.), terminal alkyne **2** (1.00 equiv.), $(Me_2S)AuCl$ (2.00 mol%) and **L1** (4.00 mol%) in CH_3CN were stirred at room temperature for the indicated time.

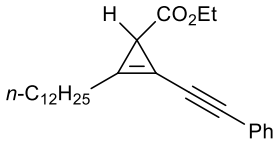
5.3.1. Synthesis and characterization of ethyl 2-dodecyl-3-((triisopropylsilyl)ethynyl)cycloprop-2-ene-1-carboxylate (3bl)



3bl

Following **GPD**, a mixture of $(Me_2S)AuCl$ (11.8 mg, 40.0 μmol, 2.00 mol%), **L1** (16.8 mg, 80.0 μmol, 4.00 mol%), CpBX **1b** (1.29 g, 2.00 mmol, 1.00 equiv.), terminal alkyne **2aw** (365mg, 2.00 mmol, 1.00 equiv.) and CH_3CN (20 mL) was stirred at room temperature for 12 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3bl** in 92% yield (851.6 mg, 1.85 mmol) as a colourless oil and **4** in 99% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.33; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.22 – 4.07 (m, 2H, $CO_2CH_2CH_3$), 2.52 (td, J = 7.1, 2.0 Hz, 2H, CH_2CH_2C), 2.43 (s, 1H, $CHCO_2$), 1.68 – 1.53 (m, 2H, CH_2CH_2C), 1.45 – 1.35 (m, 2H, CH_2), 1.34 – 1.19 (m, 19H, CH_2 & $CO_2CH_2CH_3$), 1.16 – 1.03 (m, 21H, Si(*i*-Pr)$_3$), 0.96 – 0.81 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 116.6, 103.3, 93.1, 91.1, 60.5, 32.1, 29.82, 29.81, 29.79, 29.7, 29.51, 29.49, 29.3, 26.7, 26.2, 25.7, 22.8, 18.7, 14.5, 14.3, 11.4; **IR** (ν_{max}, cm^{-1}) 2956 (m), 2925 (s), 2861 (s), 2149 (w), 1728 (s), 1464 (m), 1370 (w), 1333 (w), 1245 (m), 1179 (s), 1073 (w), 1020 (m), 997 (m), 921 (w), 885 (m), 724 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{52}NaO_2Si^+$ 483.3629; Found 483.3622.

5.3.2. Synthesis and characterization of ethyl 2-dodecyl-3-(phenylethynyl)cycloprop-2-ene-1-carboxylate (3bm)

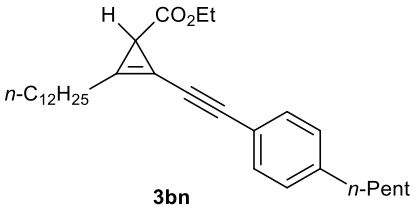


3bm

Following **GPD**, a mixture of $(Me_2S)AuCl$ (7.07 mg, 24.0 μmol, 2.00 mol%), **L1** (10.1 mg, 48.0 μmol, 4.00 mol%), CpBX **1b** (778 mg, 1.20 mmol, 1.00 equiv.), terminal alkyne **2a** (0.13 mL, 1.20 mmol, 1.00 equiv.) and CH_3CN (12 mL) was stirred at room temperature for 7 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3bm** in 93% yield (427

mg, 1.12 mmol) as a colourless oil and **4** in 98% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.39; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.43 (m, 2H, Ar*H*), 7.39 – 7.28 (m, 3H, Ar*H*), 4.24 – 4.12 (m, 2H, $CO_2CH_2CH_3$), 2.59 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.50 (s, 1H, $CHCO_2$), 1.71 – 1.59 (m, 2H, CH_2CH_2C), 1.44 – 1.37 (m, 2H, CH_2), 1.35 – 1.21 (m, 19H, CH_2 & $CO_2CH_2CH_3$), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 131.9, 129.1, 128.5, 122.5, 117.0, 99.0, 90.6, 76.7, 60.6, 32.1, 29.82, 29.78, 29.77, 29.7, 29.5, 29.4, 29.3, 26.7, 26.1, 25.3, 22.8, 14.5, 14.3; **IR** (ν_{max}, cm^{-1}) 3058 (w), 2926 (m), 2854 (w), 2200 (w), 1720 (m), 1606 (w), 1490 (w), 1464 (w), 1372 (w), 1332 (w), 1260 (w), 1185 (m), 1094 (w), 1026 (w), 737 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{37}O_2^+$ 381.2788; Found 381.2779.

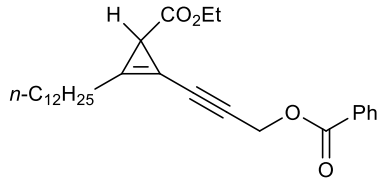
5.3.3. Synthesis and characterization of ethyl 2-dodecyl-3-((4-pentylphenyl)ethynyl)cycloprop-2-ene-1-carboxylate (3bn)



3bn

Following **GPD**, a mixture of (Me_2S)AuCl (3.53 mg, 12.0 μmol, 2.00 mol%), **L1** (5.04 mg, 24.0 μmol, 4.00 mol%), CpBX **1b** (389 mg, 0.600 mmol, 1.00 equiv.), terminal alkyne **2b** (103 mg, 0.600 mmol, 1.00 equiv.) and CH_3CN (6.0 mL) was stirred at room temperature for 5 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 50:1) afforded **3bn** in 88% yield (239 mg, 530 μmol) as a colourless oil and **4** in 95% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.34 (m, 2H, Ar*H*), 7.18 – 7.08 (m, 2H, Ar*H*), 4.23 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 2.62 – 2.56 (m, 4H, CH_2), 2.49 (s, 1H, $CHCO_2$), 1.68 – 1.57 (m, 4H, CH_2), 1.51 – 1.13 (m, 25H, CH_2 & $CO_2CH_2CH_3$), 0.90 – 0.86 (m, 6H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 144.4, 131.8, 128.6, 119.7, 116.3, 99.3, 90.7, 76.1, 60.6, 36.1, 32.1, 31.6, 31.0, 29.82, 29.79, 29.77, 29.7, 29.5, 29.4, 29.3, 26.8, 26.1, 25.3, 22.8, 22.6, 14.5, 14.3, 14.1; **IR** (ν_{max}, cm^{-1}) 2955 (m), 2925 (s), 2855 (s), 2201 (w), 1857 (w), 1725 (s), 1607 (w), 1509 (w), 1464 (m), 1370 (w), 1334 (w), 1248 (m), 1180 (s), 1093 (w), 1024 (m), 942 (w), 910 (w), 836 (w), 798 (w), 733 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{47}O_2^+$ 451.3571; Found 451.3577.

5.3.4. Synthesis and characterization of 3-(2-dodecyl-3-(ethoxycarbonyl)cycloprop-1-en-1-yl)prop-2-yn-1-yl benzoate (3bo)



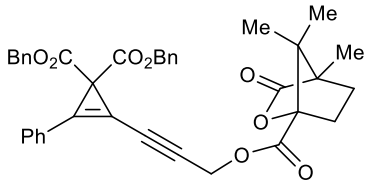
3bo

Following **GPD**, a mixture of (Me_2S)AuCl (10.6 mg, 36.0 μmol, 2.00 mol%), **L1** (15.1 mg, 72.0 μmol, 4.00 mol%), CpBX **1b** (1.17 g, 1.80 mmol, 1.00 equiv.), terminal alkyne **2ao** (288 mg, 1.80 mmol, 1.00 equiv.) and CH_3CN (18 mL) was stirred at room temperature for 12 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3bo** in 93% yield (736 mg, 1.68 mmol) as a colourless oil and **4** in 97% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.20; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 – 7.97 (m, 2H, Ar*H*), 7.63 – 7.53 (m, 1H, Ar*H*), 7.48 – 7.44 (m, 2H, Ar*H*), 5.13 (s, 2H, OCH_2), 4.21 – 4.09 (m, 2H, $CO_2CH_2CH_3$), 2.53 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.44 (s, 1H, $CHCO_2$), 1.68 – 1.46 (m, 2H, CH_2CH_2C), 1.47 – 1.11 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 165.9, 133.5, 130.0, 129.5, 128.6, 118.3, 93.3, 90.1, 74.3, 60.7, 53.3, 32.1, 29.79, 29.78, 29.7, 29.6, 29.5, 29.4, 29.3, 26.6, 26.1, 25.1, 22.8, 14.5, 14.3; **IR** (ν_{max}, cm^{-1})

2926 (m), 2854 (m), 2232 (w), 1725 (s), 1603 (w), 1452 (w), 1370 (w), 1264 (s), 1179 (m), 1094 (s), 1069 (m), 1027 (m), 912 (w), 734 (m), 711 (s); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{28}H_{38}NaO_4^+$ 461.2662; Found 461.2659.

5.4. Late-stage functionalization of bioactive and drug molecules

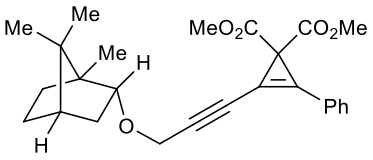
5.4.1. Synthesis and characterization of dibenzyl 2-phenyl-3-(3-(((1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carbonyl)oxy)prop-1-yn-1-yl)cycloprop-2-ene-1,1-dicarboxylate (3bp)



3bp

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1n** (90.3 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2ax** (23.6 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3bp** in 91% yield (56.3 mg, 91.0 μmol) as a colourless oil and **4** in 87% NMR yield based on **1n**. **ORD**: $[\alpha]_D^{20}$ = -3.0 (c = 0.17, $CHCl_3$); **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.11; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 2H, Ar*H*), 7.49 – 7.41 (m, 3H, Ar*H*), 7.35 – 7.25 (m, 10H, Ar*H*), 5.22 (s, 4H, OCH_2Ph), 5.13 (d, *J* = 1.7 Hz, 2H, OCH_2), 2.48 (ddd, *J* = 13.5, 10.7, 4.3 Hz, 1H, CH_2), 2.09 (ddd, *J* = 13.7, 9.3, 4.6 Hz, 1H, CH_2), 1.96 (ddd, *J* = 13.2, 10.8, 4.6 Hz, 1H, CH_2), 1.73 (ddd, *J* = 13.4, 9.3, 4.3 Hz, 1H, CH_2), 1.14 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 0.99 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.9, 168.6, 166.9, 135.7, 131.3, 130.8, 129.1, 128.6, 128.2, 127.8, 124.0, 112.2, 95.7, 90.9, 90.3, 73.5, 67.2, 54.9, 54.7, 53.5, 37.1, 30.7, 29.0, 16.85, 16.77, 9.8; **IR** (ν_{max}, cm^{-1}) 3061 (w), 2976 (w), 2193 (w), 1789 (w), 1732 (m), 1588 (w), 1568 (w), 1496 (w), 1452 (w), 1377 (w), 1335 (w), 1310 (w), 1265 (m), 1233 (m), 1181 (w), 1102 (w), 1058 (m), 1019 (w), 993 (w), 910 (w), 732 (s); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{38}H_{34}NaO_8^+$ 641.2146; Found 641.2154.

5.4.2. Synthesis and characterization of dimethyl 2-phenyl-3-(3-(((1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)prop-1-yn-1-yl)cycloprop-2-ene-1,1-dicarboxylate (3bq)

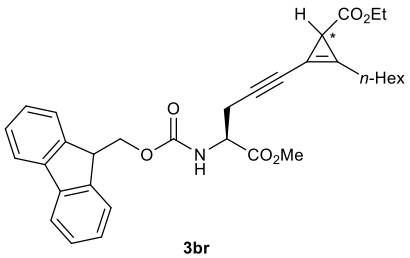


3bq

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1k** (60.0 mg, 0.100 mmol, 1.00 equiv.), alkyne derivative **2ay** (19.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 60 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3bq** in 79% yield (33.3 mg, 78.8 μmol) as a colourless oil and **4** in 87% NMR yield. **ORD**: $[\alpha]_D^{20}$ = -27.1 (c = 0.19, $CHCl_3$); **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.19; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 2H, Ar*H*), 7.52 – 7.39 (m, 3H, Ar*H*), 4.52 – 4.26 (m, 2H, OCH_2), 3.86 – 3.77 (m, 1H, OC*H*), 3.74 (s, 6H, CO_2CH_3), 2.22 – 2.15 (m, 1H, CH_2), 2.00 – 1.94 (m, 1H, CH_2), 1.75 – 1.65 (m, 2H, CH_2), 1.35 – 1.17 (m, 2H, CH_2), 1.11 (dd, *J* = 13.2, 3.3 Hz, 1H, C*H*), 0.91 (s, 3H, CH_3), 0.87 (s, 3H, CH_3), 0.86 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 130.9, 130.6, 129.1, 124.4, 110.1, 100.8, 91.4, 85.3, 71.8, 58.5, 52.7, 49.4, 48.0, 45.1, 36.6, 36.2, 28.3, 26.7, 19.9, 19.0, 13.9; **IR** (ν_{max}, cm^{-1}) 2952 (m), 2877 (m), 2190 (w), 1731 (s), 1589 (w), 1566 (w), 1448 (m), 1436

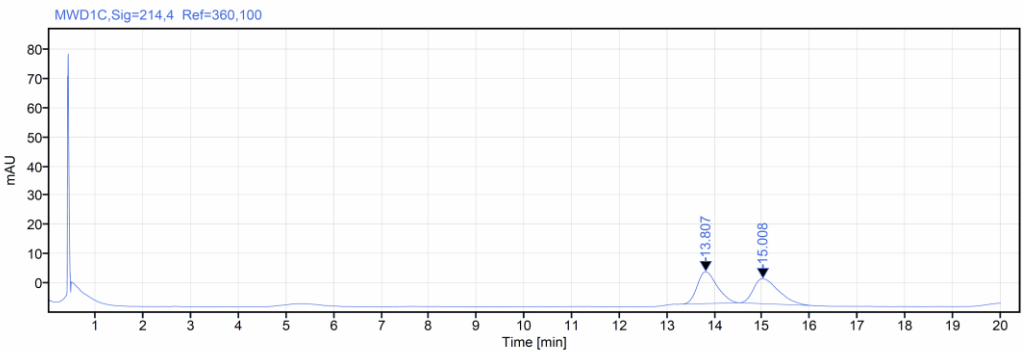
(m), 1351 (w), 1282 (m), 1240 (s), 1189 (w), 1112 (m), 1089 (m), 1066 (s), 977 (w), 763 (m), 740 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{30}NaO_5^+$ 445.1985; Found 445.1988.

5.4.3. Synthesis and characterization of ethyl 2-((*S*)-4-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-5-methoxy-5-oxopent-1-yn-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (3br)



3br

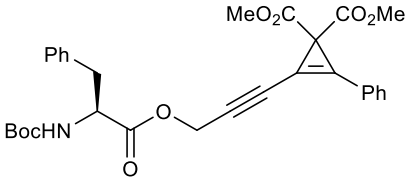
Following **GPD**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1a** (73.4 mg, 0.130 mmol, 1.30 equiv.), alkyne derivative **2az** (34.9 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 24 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 3:1) afforded **3br** in 86% yield (46.8 mg, 86.1 μmol, diastereomer ratio, 1:1) as a colourless oil and **4** in 93% NMR yield based on **1a**. ^{13}C NMR showed the formation of rotamers even if under 60 °C. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$, 60 °C) δ 7.76 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.60 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.39 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.31 (t, *J* = 7.4 Hz, 2H, Ar*H*), 5.59 (bs, 1H, N*H*), 4.57 (bs, 1H, C*H*CO_2Me), 4.43 (d, *J* = 7.1 Hz, 2H, CH_2(fluorenyl)), 4.25 (t, *J* = 7.0 Hz, 1H, C*H*(fluorenyl)), 4.15 (q, *J* = 7.2 Hz, 2H, $CO_2CH_2CH_3$), 3.79 (s, 3H, CO_2CH_3), 3.01 (bs, 2H, $CH_2C{\equiv}C$), 2.51 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.39 (s, 1H, $CHCO_2$), 1.71 – 1.52 (m, 2H, CH_2CH_2C), 1.51 – 1.12 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.89 (t, *J* = 6.7 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$, 60 °C) δ 174.0, 170.7, 155.7 (bs), 144.1#, 144.0#, 141.6, 127.9, 127.27£, 127.25£, 125.2, 120.1, 116.3, 94.5, 90.9, 71.43$, 71.40$, 67.54*, 67.52*, 60.5, 52.9 (bs), 52.8, 47.5, 31.5, 28.9, 26.7, 26.0, 25.1, 24.5, 22.6, 14.5, 14.0; #These two signals are assigned to one certain quaternary aryl carbon atom on the 9-fluorenyl group; £These two signals are assigned to one certain aryl (C-H) carbon atom on the 9-fluorenyl group; $These two signals are assigned to one certain quaternary carbon atom; *These two signals are assigned to one certain carbon atom; **IR** (ν_{max}, cm^{-1}) 3054 (w), 2958 (w), 2931 (w), 2859 (w), 2308 (w), 1750 (w), 1721 (m), 1617 (w), 1515 (w), 1449 (w), 1373 (w), 1335 (w), 1265 (m), 1207 (m), 1185 (m), 1080 (w), 1030 (w), 870 (w), 734 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{37}NNaO_6^+$ 566.2513; Found 566.2522. The ratio of the two diastereomer (see below) was determined by chiral supercritical fluid chromatography (SFC).



Signal: MWD1C,Sig=214,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.807	MM m	1.23	317.08	10.90	50.21	
15.008	MM m	1.78	314.38	8.56	49.79	
		Sum	**631.46**			

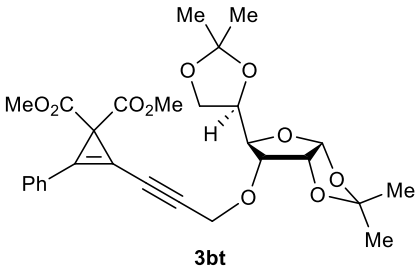
5.4.4. Synthesis and characterization of dimethyl 2-(3-(((*tert*-butoxycarbonyl)-*L*-phenylalanyl)oxy)prop-1-yn-1-yl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (3bs)



3bs

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1k** (60.0 mg, 0.100 mmol, 1.00 equiv.), alkyne derivative **2ba** (34.9 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 18 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **3bs** in 74% yield (39.4 mg, 73.8 μmol) as a colourless oil and **4** in 99% NMR yield. **ORD**: $[\alpha]_D^{20}$ = -23.5 (c = 0.20, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.23; **^{1}H NMR** (400 MHz, $CDCl_3$, 60 °C) δ 7.69 – 7.64 (m, 2H, Ar*H*), 7.49 – 7.45 (m, 3H, Ar*H*), 7.35 – 7.27 (m, 2H, Ar*H*), 7.27 – 7.18 (m, 3H, Ar*H*), 5.12 – 4.96 (m, 2H, OCH_2), 4.94 (bs, 1H, N*H*), 4.66 (bs, 1H, NC*H*), 3.78 (s, 6H, CO_2CH_3), 3.21 – 3.10 (m, 2H, CH_2Ph), 1.45 (s, 9H, C(CH_3)$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$, 60 °C) δ 171.2, 169.3, 155.1, 135.9, 131.2, 130.8, 129.5, 129.2, 128.8, 127.3, 124.4, 112.5, 96.1, 91.0, 80.3, 73.4, 54.8, 53.3, 52.6, 38.5, 37.0, 28.5; **IR** (ν_{max}, cm^{-1}) 3381 (w), 2959 (w), 1726 (s), 1497 (m), 1436 (m), 1392 (m), 1370 (m), 1345 (m), 1278 (s), 1245 (s), 1163 (s), 1106 (m), 1061 (s), 1023 (m), 975 (m), 763 (s), 735 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{31}NNaO_8^+$ 556.1942; Found 556.1946.

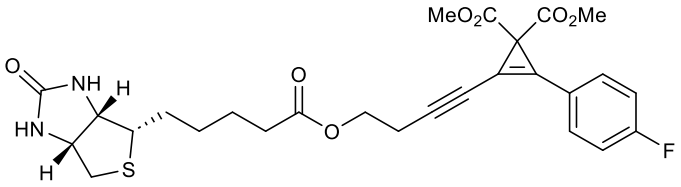
5.4.5. Synthesis and characterization of dimethyl 2-(3-(((3a*R*,5*S*,6*R*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)prop-1-yn-1-yl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (3bt)



3bt

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1k** (72.0 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2bb** (29.8 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 2 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3bt** in 96% yield (50.5 mg, 95.5 μmol) as a colourless oil and **4** in 95% NMR yield based on **1k**. **ORD**: $[\alpha]_D^{20}$ = +72.5 (c = 0.22, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 2:1) = 0.21; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 2H, Ar*H*), 7.45 – 7.41 (m, 3H, Ar*H*), 5.80 (d, *J* = 3.7 Hz, 1H, C*H*), 4.77 (t, *J* = 3.9 Hz, 1H, C*H*), 4.72 – 4.53 (m, 2H, OCH_2), 4.37 (td, *J* = 6.9, 3.1 Hz, 1H, C*H*), 4.17 – 4.07 (m, 2H, OCH_2), 4.07 – 3.95 (m, 2H, C*H*), 3.73 (s, 6H, CO_2CH_3), 1.58 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.35 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.4, 131.1, 130.6, 129.1, 124.1, 113.2, 111.2, 109.9, 103.9, 98.6, 90.8, 78.1, 78.0, 77.8, 74.9, 73.4, 65.3, 58.6, 52.7, 36.6, 26.9, 26.6, 26.4, 25.3; **IR** (ν_{max}, cm^{-1}) 3061 (w), 2988 (w), 2953 (w), 2903 (w), 2191 (w), 1732 (s), 1440 (w), 1375 (m), 1247 (s), 1217 (m), 1164 (m), 1132 (m), 1101 (m), 1062 (s), 1024 (s), 974 (m), 918 (w), 870 (m), 852 (m), 764 (m), 735 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{32}NaO_{10}^+$ 551.1888; Found 551.1887.

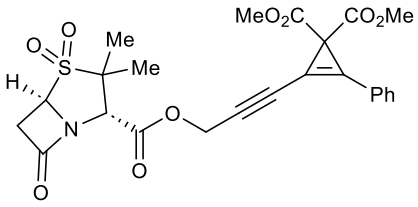
5.4.6. Synthesis and characterization of dimethyl 2-(4-fluorophenyl)-3-(4-((5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)pentanoyl)oxy)but-1-yn-1-yl)cycloprop-2-ene-1,1-dicarboxylate (3bu)



3bu

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1l** (74.2 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2bc** (29.6 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 11 hours. Flash column chromatography on silica gel (eluent: DCM/MeOH = 20:1) afforded **3bu** in 90% yield (49.1 mg, 90.2 μmol) as a colourless oil and **4** in 98% NMR yield based on **1l**. **ORD**: $[\alpha]_D^{20}$ = +28.6 (c = 0.11, $CHCl_3$). **TLC**: R_f (DCM/MeOH = 20:1) = 0.23; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.54 (m, 2H, Ar*H*), 7.19 – 7.07 (m, 2H, Ar*H*), 5.89 (bs, 1H, N*H*), 5.41 (bs, 1H, N*H*), 4.49 – 4.45 (m, 1H, C*H*), 4.29 – 4.25 (m, 3H, C*H* & OCH_2), 3.74 (s, 6H, CO_2CH_3), 3.16 – 3.11 (m, 1H, C*H*), 2.98 – 2.64 (m, 4H, CH_2), 2.37 (t, *J* = 7.5 Hz, 2H, CH_2), 1.76 – 1.60 (m, 4H, CH_2), 1.57 – 1.32 (m, 2H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 169.6, 164.0 (d, *J* = 253.4 Hz), 163.7, 132.6 (d, *J* = 8.8 Hz), 120.8 (d, *J* = 3.3 Hz), 116.5 (d, *J* = 22.4 Hz), 108.2, 100.7, 91.4 (d, *J* = 2.8 Hz), 68.2, 62.1, 61.5, 60.2, 55.5, 52.8, 40.7, 36.6, 33.9, 28.4, 28.3, 24.9, 21.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.3; **IR** (ν_{max}, cm^{-1}) 3057 (w), 2953 (w), 2234 (w), 1730 (m), 1703 (m), 1600 (w), 1506 (w), 1454 (w), 1436 (w), 1266 (m), 1239 (m), 1156 (w), 1064 (m), 841 (w), 733 (s); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{27}H_{29}FN_2NaO_7S^+$ 567.1572; Found 567.1575.

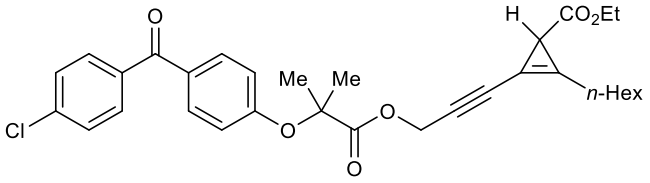
5.4.7. Synthesis and characterization of dimethyl 2-(3-(((2*S*,5*R*)-3,3-dimethyl-4,4-dioxido-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carbonyl)oxy)prop-1-yn-1-yl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (3bv)



3bv

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1k** (60.0 mg, 0.100 mmol, 1.00 equiv.), alkyne derivative **2bd** (27.1 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 17 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 2:1) afforded **3bv** in 83% yield (41.8 mg, 83.3 μmol) as a colourless oil and **4** in 99% NMR yield. **ORD**: $[\alpha]_D^{20}$ = +150.2 (c = 0.27, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 1:1) = 0.49; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 2H, Ar*H*), 7.51 – 7.42 (m, 3H, Ar*H*), 5.22 – 4.94 (m, 2H, OCH_2), 4.64 (dd, *J* = 4.3, 2.1 Hz, 1H, NC*H*), 4.45 (s, 1H, C*H*CO_2), 3.74 (s, 6H, CO_2CH_3), 3.55 – 3.36 (m, 2H, CH_2), 1.65 (s, 3H, CH_3), 1.46 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8, 169.2, 166.4, 131.5, 130.8, 129.2, 123.9, 112.6, 94.9, 90.1, 74.1, 63.1, 63.0, 61.2, 54.2, 52.8, 38.5, 36.7, 20.4, 18.7; **IR** (ν_{max}, cm^{-1}) 3058 (w), 2989 (w), 2950 (w), 1802 (w), 1766 (w), 1732 (w), 1437 (w), 1325 (w), 1266 (m), 1184 (w), 1159 (w), 1119 (w), 1065 (w), 964 (w), 910 (w), 732 (s); **HRMS** (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{24}H_{23}NNaO_9S^+$ 524.0986; Found 524.0997.

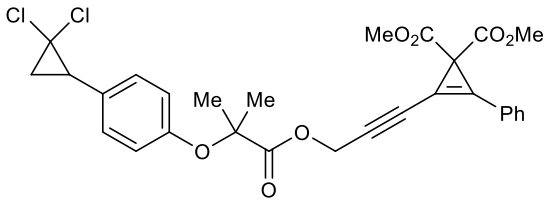
5.4.8. Synthesis and characterization of ethyl 2-(3-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)prop-1-yn-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (3bw)



3bw

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1a** (56.4 mg, 0.100 mmol, 1.00 equiv.), alkyne derivative **2be** (35.7 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 18 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3bw** in 85% yield (46.8 mg, 84.9 μmol) as a colourless oil and **4** in 95% NMR yield. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.15; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 8.3 Hz, 4H, Ar*H*), 7.53 – 7.36 (m, 2H, Ar*H*), 6.98 – 6.79 (m, 2H, Ar*H*), 4.97 (s, 2H, $CO_2CH_2CH_3$), 4.11 (q, *J* = 7.0 Hz, 2H, OCH_2), 2.49 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.39 (s, 1H, $CHCO_2$), 1.68 (s, 6H, $OCCH_3$), 1.61 – 1.48 (m, 2H, CH_2CH_2C), 1.38 – 1.13 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.86 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.2, 173.8, 173.0, 159.4, 138.5, 136.4, 132.1, 131.3, 130.8, 128.6, 118.8, 117.8, 92.3, 89.8, 79.4, 74.8, 60.7, 53.9, 31.5, 28.8, 26.5, 26.0, 25.5, 25.4, 24.9, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (w), 2934 (w), 2871 (w), 2232 (w), 1925 (w), 1744 (m), 1723 (m), 1655 (m), 1597 (s), 1505 (w), 1466 (w), 1390 (w), 1369 (w), 1304 (m), 1279 (s), 1248 (s), 1172 (s), 1129 (s), 1090 (m), 1014 (m), 953 (w), 928 (s), 853 (m), 844 (m), 763 (s), 737 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{36}ClO_6^+$ 551.2195; Found 551.2188.

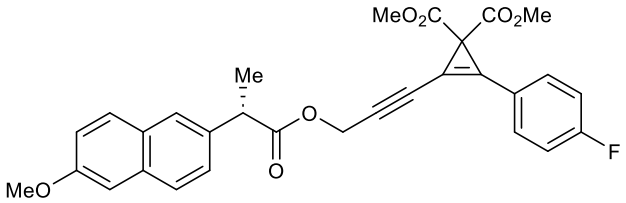
5.4.9. Synthesis and characterization of dimethyl 2-(3-((2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoyl)oxy)prop-1-yn-1-yl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (3bx)



3bx

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1k** (78.0 mg, 0.130 mmol, 1.30 equiv.), alkyne derivative **2bf** (32.7 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3bx** in 94% yield (52.6 mg, 94.4 μmol) as a colourless oil and **4** in 95% NMR yield based on **1k**. **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.37; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.57 (m, 2H, Ar*H*), 7.51 – 7.41 (m, 3H, Ar*H*), 7.16 – 7.07 (m, 2H, Ar*H*), 6.90 – 6.81 (m, 2H, Ar*H*), 5.06 (s, 2H, OCH_2), 3.75 (s, 6H, CO_2CH_3), 2.75 (dd, *J* = 10.7, 8.3 Hz, 1H, C*H*), 1.83 (dd, *J* = 10.7, 7.4 Hz, 1H, CH_2), 1.71 (dd, *J* = 8.4, 7.4 Hz, 1H, CH_2), 1.63 (s, 6H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 169.3, 154.7, 131.3, 130.7, 129.8, 129.2, 128.8, 124.1, 119.3, 112.1, 96.1, 90.6, 79.3, 73.1, 60.9, 53.5, 52.8, 36.7, 34.9, 25.8, 25.5, 25.4; **IR** (ν_{max}, cm^{-1}) 3060 (w), 2995 (w), 2953 (w), 2844 (w), 2194 (w), 1732 (s), 1610 (w), 1583 (w), 1571 (w), 1511 (m), 1435 (m), 1386 (w), 1368 (w), 1342 (w), 1270 (s), 1242 (s), 1195 (w), 1175 (m), 1125 (s), 1061 (m), 958 (w), 834 (w), 765 (s), 736 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{26}Cl_2NaO_7^+$ 579.0948; Found 579.0955.

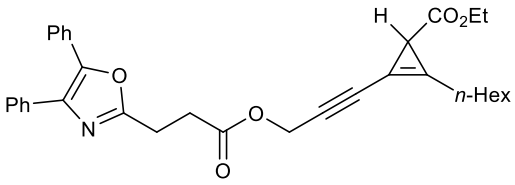
5.4.10. Synthesis and characterization of dimethyl (*S*)-2-(4-fluorophenyl)-3-(3-((2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)prop-1-yn-1-yl)cycloprop-2-ene-1,1-dicarboxylate (3by)



3by

Following **GPD**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1l** (74.2 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2bg** (26.8 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 12 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1) afforded **3by** in 89% yield (46.1 mg, 89.3 μmol) as a colourless oil and **4** in 98% NMR yield based on **1l**. **ORD**: $[\alpha]_D^{20}$ = -28.2 (c = 0.43, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.19; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 3H, Ar*H*), 7.64 – 7.54 (m, 2H, Ar*H*), 7.42 (dd, *J* = 8.5, 1.9 Hz, 1H, Ar*H*), 7.18 – 7.04 (m, 4H, Ar*H*), 5.13 – 4.78 (m, 2H, OCH_2), 3.94 (q, *J* = 7.2 Hz, 1H, C*H*), 3.91 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 1.62 (d, *J* = 7.2 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 169.3, 164.3 (d, *J* = 253.9 Hz), 157.9, 135.1, 133.9, 132.9 (d, *J* = 8.9 Hz), 129.4, 129.0, 127.4, 126.22, 126.19, 120.6 (d, *J* = 3.3 Hz), 119.2, 116.6 (d, *J* = 22.4 Hz), 110.7, 105.7, 96.8, 90.4 (d, *J* = 2.8 Hz), 72.6, 55.4, 53.0, 52.8, 45.3, 36.7, 18.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -106.6; **IR** (ν_{max}, cm^{-1}) 2954 (m), 2926 (m), 2848 (w), 2197 (w), 1734 (s), 1633 (w), 1603 (m), 1506 (m), 1484 (w), 1460 (w), 1437 (m), 1392 (w), 1367 (w), 1235 (s), 1177 (s), 1152 (s), 1062 (m), 927 (m), 841 (m), 730 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{25}FNaO_7^+$ 539.1477; Found 539.1475.

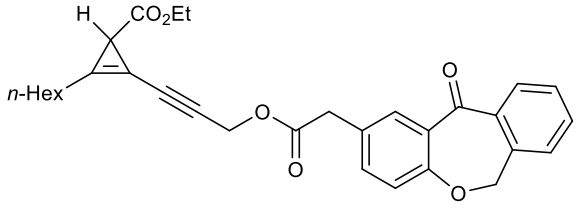
5.4.11. Synthesis and characterization of ethyl 2-(3-((3-(4,5-diphenyloxazol-2-yl)propanoyl)oxy)prop-1-yn-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (3bz)



3bz

Following **GPD**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1a** (67.7 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2bh** (33.1 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 22 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) afforded **3bz** in 97% yield (51.2 mg, 97.4 μmol) as a colourless oil and **4** in 98% NMR yield based on **1a**. **TLC**: R_f (*n*-hexane/EtOAc = 5:1) = 0.26; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H, Ar*H*), 7.60 – 7.53 (m, 2H, Ar*H*), 7.40 – 7.28 (m, 6H, Ar*H*), 4.95 (s, 2H, OCH_2), 4.21 – 4.09 (m, 2H, $CO_2CH_2CH_3$), 3.32 – 3.12 (m, 2H, CH_2), 3.00 – 2.96 (m, 2H, CH_2), 2.52 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.42 (s, 1H, C*H*CO_2), 1.65 – 1.53 (m, 2H, CH_2CH_2C), 1.44 – 1.18 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.95 – 0.76 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 171.3, 161.5, 145.6, 135.2, 132.5, 129.0, 128.8, 128.7, 128.6, 128.2, 128.0, 126.6, 118.4, 93.0, 90.0, 74.3, 60.7, 53.1, 31.5, 31.0, 28.9, 26.5, 26.0, 25.0, 23.5, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 3058 (w), 2956 (m), 2931 (m), 2860 (w), 2229 (w), 1738 (s), 1683 (m), 1597 (m), 1581 (m), 1503 (w), 1447 (m), 1373 (w), 1328 (w), 1244 (m), 1210 (m), 1156 (s), 1054 (m), 1022 (m), 964 (m), 871 (w), 766 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{36}NO_5^+$ 526.2588; Found 526.2601.

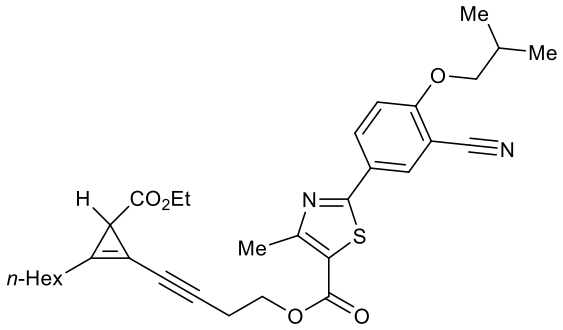
5.4.12. Synthesis and characterization of ethyl 2-hexyl-3-(3-(2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetoxy)prop-1-yn-1-yl)cycloprop-2-ene-1-carboxylate (3ca)



3ca

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1a** (67.7 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2bi** (30.6 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 22 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **3ca** in 95% yield (47.5 mg, 94.9 μmol) as a colourless oil and **4** in 99% NMR yield based on **1a**. **TLC**: R_f (*n*-hexane/EtOAc = 5:1) = 0.24; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.88 (dd, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 7.55 (td, *J* = 7.4, 1.4 Hz, 1H, Ar*H*), 7.50 – 7.39 (m, 2H, Ar*H*), 7.35 (dd, *J* = 7.5, 1.3 Hz, 1H, Ar*H*), 7.03 (d, *J* = 8.4 Hz, 1H, Ar*H*), 5.18 (s, 2H, OCH_2), 4.91 (s, 2H, OCH_2), 4.20 – 4.08 (m, 2H, $CO_2CH_2CH_3$), 3.70 (s, 2H, CH_2), 2.53 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.42 (s, 1H, $CHCO_2$), 1.64 – 1.51 (m, 2H, CH_2CH_2C), 1.44 – 1.15 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 0.97 – 0.78 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.9, 174.0, 170.7, 160.7, 140.5, 136.4, 135.6, 132.9, 132.7, 129.6, 129.4, 127.9, 127.3, 125.3, 121.3, 118.4, 93.0, 90.0, 74.4, 73.7, 60.7, 53.3, 39.9, 31.5, 28.9, 26.5, 26.0, 25.0, 22.6, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2930 (m), 2863 (w), 2233 (w), 1738 (s), 1721 (s), 1649 (m), 1611 (m), 1494 (m), 1455 (m), 1414 (m), 1372 (m), 1300 (s), 1243 (s), 1186 (s), 1138 (s), 1122 (s), 1016 (s), 936 (w), 831 (w), 761 (m), 737 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{32}NaO_6^+$ 523.2091; Found 523.2090.

5.4.13. Synthesis and characterization of 4-(3-(ethoxycarbonyl)-2-hexylcycloprop-1-en-1-yl)but-3-yn-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (3cb)

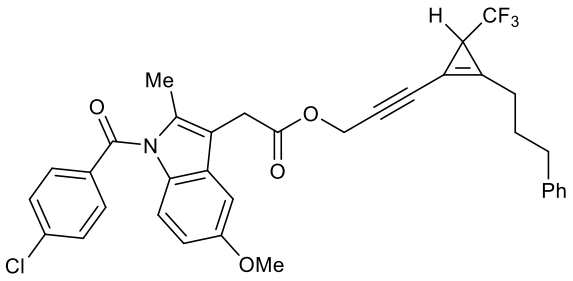


3cb

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1a** (67.7 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2bj** (36.9 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 3 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 3:1) afforded **3cb** in 99% yield (55.8 mg, 99.2 μmol) as a colourless oil and **4** in 98% NMR yield based on **1a**. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.34; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.3 Hz, 1H, Ar*H*), 8.08 (dd, *J* = 8.9, 2.3 Hz, 1H, Ar*H*), 7.00 (d, *J* = 8.9 Hz, 1H, Ar*H*), 4.42 (t, *J* = 6.7 Hz, 2H, OCH_2), 4.18 – 4.06 (m, 2H, $CO_2CH_2CH_3$), 3.88 (d, *J* = 6.5 Hz, 2H, OCH_2), 2.88 (t, *J* = 6.7 Hz, 2H, CH_2), 2.75 (s, 3H, CH_3), 2.49 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.37 (s, 1H, $CHCO_2$), 2.24 – 2.14 (m, 1H, $CH_2CH(CH_3)_2$), 1.66 – 1.48 (m, 2H, CH_2CH_2C), 1.47 – 1.16 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 1.07 (d, *J* = 6.8 Hz, 6H, $CH_2CH(CH_3)_2$), 0.92 – 0.75 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 167.6, 162.6, 161.8, 161.7, 132.7, 132.2, 126.0, 121.5, 115.5, 115.4, 112.7, 103.1, 96.0, 90.6,

75.8, 69.8, 62.7, 60.5, 31.5, 28.8, 28.2, 26.6, 25.9, 24.8, 22.6, 20.7, 19.1, 17.7, 14.4, 14.1; **IR** (ν_{max}, cm^{-1}) 2959 (m), 2932 (m), 2878 (w), 2229 (w), 1861 (w), 1716 (s), 1604 (m), 1509 (m), 1464 (w), 1450 (m), 1432 (m), 1373 (m), 1328 (m), 1295 (m), 1259 (s), 1183 (s), 1095 (s), 1041 (m), 1012 (s), 820 (w), 759 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{39}N_2O_5S^+$ 563.2574; Found 563.2562.

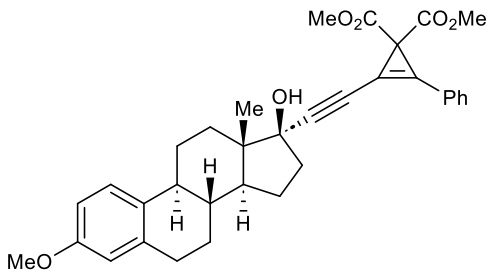
5.4.14. Synthesis and characterization of 3-(2-(3-phenylpropyl)-3-(trifluoromethyl)cycloprop-1-en-1-yl)prop-2-yn-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (3cc)



3cc

Following **GPD**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1j** (71.3 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2bk** (39.6 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 16 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 8:1) afforded **3cc** in 88% yield (54.7 mg, 88.2 μmol) as a colourless oil and **4** in 87% NMR yield based on **1j**. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.44; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 2H, Ar*H*), 7.54 – 7.41 (m, 2H, Ar*H*), 7.35 – 7.27 (m, 2H, Ar*H*), 7.25 – 7.12 (m, 3H, Ar*H*), 6.98 (d, *J* = 2.5 Hz, 1H, Ar*H*), 6.88 (d, *J* = 9.0 Hz, 1H, Ar*H*), 6.68 (dd, *J* = 9.0, 2.5 Hz, 1H, Ar*H*), 4.94 (s, 2H, OCH_2), 3.83 (s, 3H, OCH_3), 3.74 (s, 2H, CH_2), 2.71 – 2.68 (m, 2H, CH_2), 2.56 (t, *J* = 7.2 Hz, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.29 (q, *J* = 4.4 Hz, 1H, C*H*(CF_3)), 2.07 – 1.88 (m, 2H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 168.4, 156.2, 141.2, 139.4, 136.3, 133.9, 131.3, 130.9, 130.6, 129.2, 128.6 (2C), 126.2, 125.4 (q, *J* = 275.5 Hz), 118.5 (q, *J* = 3.1 Hz), 115.1, 112.0, 112.0, 101.2, 94.1, 90.6 (q, *J* = 4.0 Hz), 73.8, 55.8, 53.2, 35.2, 30.2, 28.2, 25.4, 24.0 (q, *J* = 39.3 Hz), 13.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.8; **IR** (ν_{max}, cm^{-1}) 3063 (w), 3029 (w), 2939 (w), 2860 (w), 2835 (w), 2232 (w), 1744 (m), 1683 (m), 1595 (w), 1478 (m), 1456 (m), 1400 (w), 1357 (m), 1321 (m), 1267 (m), 1223 (m), 1131 (s), 1087 (m), 1065 (m), 1037 (m), 1017 (m), 986 (w), 925 (w), 913 (w), 832 (m), 805 (w), 751 (m), 741 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{29}ClF_3NNaO_4^+$ 642.1629; Found 642.1644.

5.4.15. Synthesis and characterization of dimethyl 2-(((8*R*,9*S*,13*S*,14*S*,17*S*)-17-hydroxy-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)ethynyl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (3cd)

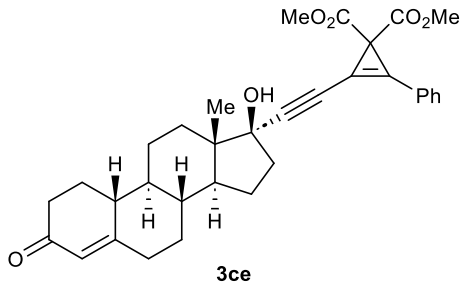


3cd

Following **GPD**, a mixture of $(Me_2S)AuCl$ (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1k** (120 mg, 0.200 mmol, 1.00 equiv.), alkyne derivative **2bl** (62.1 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 24 hours. Flash column

chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **3cd** in 95% yield (103 mg, 190 μmol) as a colourless solid and **4** in 95% NMR yield. **M.p.** 135 – 138 °C. **ORD**: $[\alpha]_D^{20}$ = -34.1 (c = 0.32, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.14; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.58 (m, 2H, Ar*H*), 7.48 – 7.41 (m, 3H, Ar*H*), 7.25 – 7.20 (m, 1H, Ar*H*), 6.73 (dd, *J* = 8.6, 2.8 Hz, 1H, Ar*H*), 6.65 (d, *J* = 2.7 Hz, 1H, Ar*H*), 3.78 (s, 3H, OCH_3), 3.75 (s, 6H, CO_2CH_3), 3.01 – 2.74 (m, 2H, CH_2), 2.49 – 2.37 (m, 3H, O*H* & CH_2), 2.29 – 2.22 (m, 1H, C*H*), 2.15 – 2.08 (m, 1H, C*H*), 1.94 – 1.70 (m, 5H, C*H* & CH_2), 1.56 – 1.36 (m, 4H, CH_2), 0.95 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 157.6, 138.1, 132.5, 130.9, 130.5, 129.1, 126.5, 124.3, 113.9, 111.6, 109.8, 106.9, 91.4, 81.0, 72.3, 55.3, 52.7, 50.1, 48.2, 43.7, 39.6, 39.0, 36.7, 33.3, 29.9, 27.4, 26.5, 23.1, 13.0; **IR** (ν_{max}, cm^{-1}) 3464 (w), 2935 (m), 2870 (m), 2210 (w), 1730 (m), 1609 (m), 1576 (w), 1499 (m), 1434 (m), 1281 (s), 1248 (s), 1187 (w), 1066 (s), 841 (w), 762 (m), 735 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{36}NaO_6^+$ 563.2404; Found 563.2408.

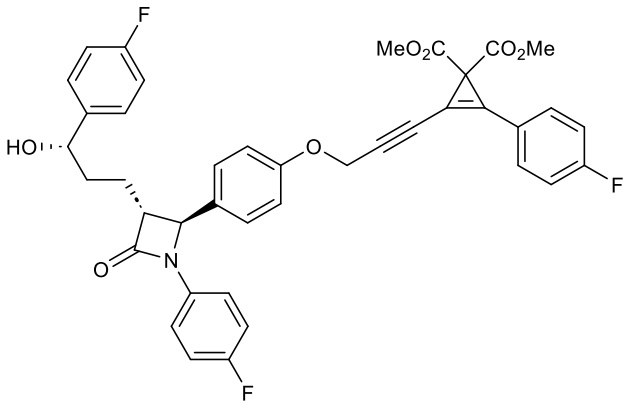
5.4.16. Synthesis and characterization of dimethyl 2-(((8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-hydroxy-13-methyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)ethynyl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (3ce)



3ce

Following **GPD**, a mixture of (Me_2S)AuCl (2.95 mg, 10.0 μmol, 5.00 mol%), **L1** (4.20 mg, 20.0 μmol, 10.0 mol%), CpBX **1k** (120 mg, 0.200 mmol, 1.00 equiv.), alkyne derivative **2bm** (59.7 mg, 0.200 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at room temperature for 24 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **3ce** in 92% yield (97.6 mg, 185 μmol) as a colourless oil and **4** in 99% NMR yield. **ORD**: $[\alpha]_D^{20}$ = -54.6 (c = 0.30, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 2:1) = 0.12; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.52 (m, 2H, Ar*H*), 7.49 – 7.32 (m, 3H, Ar*H*), 5.82 (s, 1H, C*H*=C), 3.71 (s, 6H, CO_2CH_3), 2.90 (s, 1H, O*H*), 2.52 – 2.32 (m, 3H, C*H* & CH_2), 2.32 – 2.14 (m, 3H, CH_2), 2.14 – 1.98 (m, 2H, CH_2), 1.98 – 1.60 (m, 5H, C*H* & CH_2), 1.43 – 1.47 (m, 2H, CH_2), 1.43 – 1.20 (m, 3H, CH_2), 1.16 – 1.00 (m, 1H, C*H*), 0.94 (s, 3H, CH_3), 0.93 –0.83 (m, 1H, C*H*); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.1, 169.6, 166.7, 130.9, 130.4, 129.0, 124.6, 124.2, 109.7, 106.8, 91.2, 80.6, 72.2, 52.6, 49.7, 49.0, 47.8, 42.6, 41.1, 38.8, 36.6, 36.5, 35.5, 32.8, 30.6, 26.6, 26.3, 23.1, 12.9; **IR** (ν_{max}, cm^{-1}) 3414 (w), 2951 (m), 2869 (m), 2210 (w), 1730 (s), 1658 (s), 1619 (m), 1448 (m), 1434 (m), 1246 (s), 1132 (w), 1062 (s), 969 (w), 885 (w), 763 (s), 733 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{36}NaO_6^+$ 551.2404; Found 551.2414.

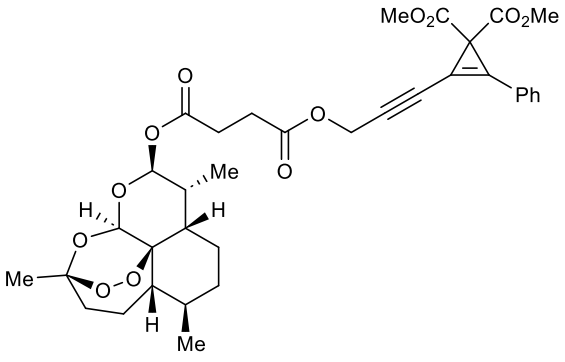
5.4.17. Synthesis and characterization of dimethyl 2-(4-fluorophenyl)-3-(3-(4-((2S,3R)-1-(4-fluorophenyl)-3-((S)-3-(4-fluorophenyl)-3-hydroxypropyl)-4-oxoazetidin-2-yl)phenoxy)prop-1-yn-1-yl)cycloprop-2-ene-1,1-dicarboxylate (3cf)



3cf

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1l** (74.2 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2bn** (44.8 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 12 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **3cf** in 77% yield (53.5 mg, 76.9 μmol) as a colourless oil and **4** in 96% NMR yield based on **1l**. **ORD**: $[\alpha]_D^{20}$ = -22.4 (c = 0.30, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 2:1) = 0.11; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 2H, Ar*H*), 7.31 – 7.25 (m, 4H, Ar*H*), 7.25 – 7.19 (m, 2H, Ar*H*), 7.17 – 7.06 (m, 2H, Ar*H*), 7.02 – 6.96 (m, 4H, Ar*H*), 6.96 – 6.86 (m, 2H, Ar*H*), 4.96 (s, 2H, OCH_2), 4.70 (t, *J* = 6.0 Hz, 1H, C*H*), 4.59 (d, *J* = 2.3 Hz, 1H, C*H*), 3.721 (s, 3H, CO_2CH_3), 3.718 (s, 3H, CO_2CH_3), 3.10 – 3.05 (m, 1H, C*H*), 2.50 (s, 1H, O*H*), 2.09 – 1.80 (m, 4H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 167.7, 164.3 (d, *J* = 254.2 Hz), 162.3 (d, *J* = 245.7 Hz), 159.1 (d, *J* = 243.3 Hz), 157.9, 140.2 (d, *J* = 3.1 Hz), 133.9 (d, *J* = 2.7 Hz), 132.9 (d, *J* = 9.0 Hz), 130.8, 127.5 (d, *J* = 8.1 Hz), 127.3, 120.5 (d, *J* = 3.3 Hz), 118.5 (d, *J* = 7.8 Hz), 116.6 (d, *J* = 22.3 Hz), 116.0 (d, *J* = 22.7 Hz), 115.8, 115.4 (d, *J* = 21.3 Hz), 110.7, 97.4, 90.3 (d, *J* = 2.9 Hz), 73.4, 73.2, 61.1, 60.5, 57.0, 52.8, 36.7 (2C), 25.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -106.3 (Ar*F*), -114.9 (Ar*F*), -117.9 (Ar*F*); **IR** (ν_{max}, cm^{-1}) 3465 (w), 2953 (w), 2926 (w), 2856 (w), 2197 (w), 1731 (s), 1602 (m), 1508 (s), 1435 (w), 1389 (m), 1285 (m), 1220 (s), 1157 (m), 1102 (w), 1064 (m), 1016 (m), 836 (s), 737 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{40}H_{32}F_3NNaO_7^+$ 718.2023; Found 718.2029.

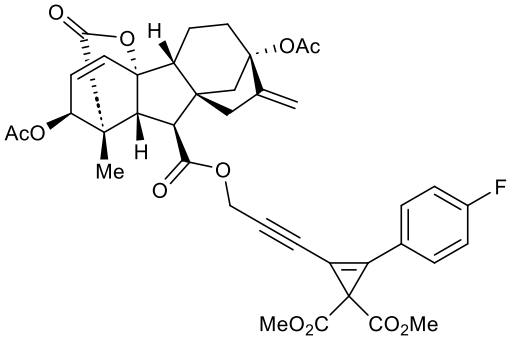
5.4.18. Synthesis and characterization of dimethyl 2-(3-((4-oxo-4-(((3*R*,5a*S*,6*R*,8a*S*,9*R*,10*S*,12*R*,12a*R*)-3,6,9-trimethyldecahydro-12*H*-3,12-epoxy[1,2]dioxepino[4,3-*i*]isochromen-10-yl)oxy)butanoyl)oxy)prop-1-yn-1-yl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (3cg)



3cg

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1k** (72.0 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2bo** (42.3 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 30 °C for 28 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1) afforded **3cg** in 82% yield (53.8 mg, 82.4 μmol) as a colourless oil and **4** in 99% NMR yield based on **1k**. **ORD**: $[\alpha]_D^{20}$ = +8.2 (c = 0.51, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 3:1) = 0.11; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.58 (m, 2H, Ar*H*), 7.52 – 7.37 (m, 3H, Ar*H*), 5.79 (d, *J* = 9.8 Hz, 1H, C*H*), 5.42 (s, 1H, C*H*), 4.98 (d, *J* = 2.7 Hz, 2H, OCH_2), 3.74 (s, 6H, CO_2CH_3), 2.85 – 2.63 (m, 4H, CH_2), 2.60 – 2.51 (m, 1H, C*H*), 2.40 – 2.32 (m, 1H, C*H*), 2.05 – 1.99 (m, 1H, C*H*), 1.96 – 1.82 (m, 1H, C*H*), 1.78 – 1.65 (m, 2H, CH_2), 1.60 (dt, *J* = 13.7, 4.4 Hz, 1H, C*H*), 1.51 – 1.38 (m, 4H, CH_2 & CH_3), 1.36 – 1.22 (m, 3H, CH_2), 1.08 – 0.90 (m, 4H, C*H* & CH_3), 0.85 (d, *J* = 7.1 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 171.0, 169.3, 131.2, 130.7, 129.1, 124.1, 111.7, 104.6, 96.5, 92.4, 91.6, 90.7, 80.2, 72.9, 53.0, 52.7, 51.6, 45.3, 37.3, 36.6, 36.3, 34.2, 31.9, 29.2, 28.8, 26.1, 24.7, 22.1, 20.3, 12.2; **IR** (ν_{max}, cm^{-1}) 3061 (w), 2952 (m), 2928 (m), 2878 (w), 1736 (s), 1436 (m), 1377 (w), 1348 (w), 1281 (m), 1248 (s), 1201 (m), 1148 (s), 1101 (m), 1036 (s), 1014 (s), 974 (m), 945 (w), 925 (w), 877 (m), 845 (w), 827 (w), 765 (m), 735 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{40}NaO_{12}^+$ 675.2412; Found 675.2393.

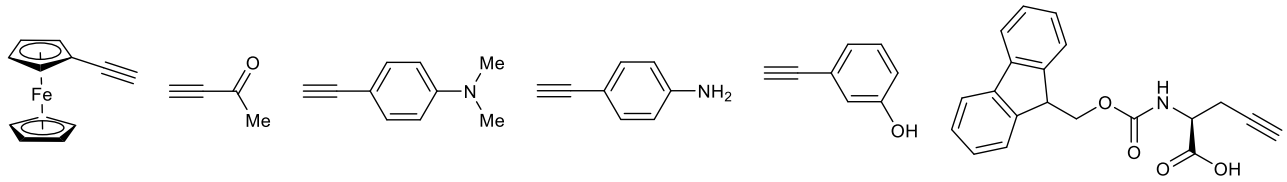
5.4.19. Synthesis and characterization of dimethyl 2-(3-(((1*S*,2*S*,4a*R*,4b*R*,7*S*,9a*S*,10*S*,10a*R*)-2,7-diacetoxy-1-methyl-8-methylene-13-oxo-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[a]azulene-10-carbonyl)oxy)prop-1-yn-1-yl)-3-(4-fluorophenyl)cycloprop-2-ene-1,1-dicarboxylate (3ch)



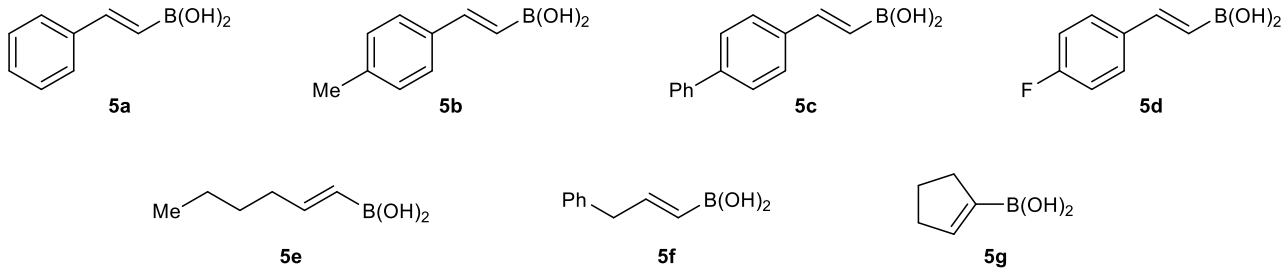
3ch

Following **GPD**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1k** (72.0 mg, 0.120 mmol, 1.20 equiv.), alkyne derivative **2bo** (42.3 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (4.0 mL) was stirred at 40 °C for 4 hours. Flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 2:1) afforded **3ch** in 95% yield (67.9 mg, 94.7 μmol) as a colourless solid and **4** in 95% NMR yield based on **1k**. **M.p.** 172 – 174 °C. **ORD**: $[\alpha]_D^{20}$ = +128.7 (c = 0.23, $CHCl_3$). **TLC**: R_f (*n*-hexane/EtOAc = 2:1) = 0.19; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.53 (m, 2H, Ar*H*), 7.20 – 7.03 (m, 2H, Ar*H*), 6.36 (d, *J* = 9.3 Hz, 1H, CHCH=C*H*), 5.92 – 5.81 (m, 1H, CHC*H*=CH), 5.32 (d, *J* = 3.7 Hz, 1H, C*H*CH=CH), 5.22 – 5.12 (m, 1H, C=CH_2), 5.11 – 4.92 (m, 3H, C=CH_2 & OCH_2), 3.73 (s, 6H, CO_2CH_3), 3.34 (d, *J* = 10.9 Hz, 1H, C*H*), 2.83 (d, *J* = 11.0 Hz, 1H, C*H*), 2.46 – 2.25 (m, 4H, CH_2), 2.21 – 2.16 (m, 1H, C*H*), 2.09 (s, 3H, CH_3), 2.06 – 1.88 (m, 5H, CH_2 & CH_3), 1.84 – 1.64 (m, 2H, CH_2), 1.15 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.9, 171.0, 170.1, 169.9, 169.1, 164.3 (d, *J* = 254.1 Hz), 153.3, 134.2, 132.9 (d, *J* = 8.9 Hz), 129.3, 120.5 (d, *J* = 3.3 Hz), 116.6 (d, *J* = 22.4 Hz), 111.1, 108.6, 96.0, 90.0 (d, *J* = 2.8 Hz), 89.9, 84.1, 73.1, 70.2, 53.6, 53.2, 52.8, 52.2, 51.3, 51.1, 50.2, 42.6, 40.0, 36.7, 36.3, 22.1, 20.9, 16.9, 14.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -106.4; **IR** (ν_{max}, cm^{-1}) 2989 (w), 2955 (w), 2882 (w), 2849 (w), 1781 (m), 1734 (s), 1599 (w), 1506 (w), 1436 (w), 1372 (m), 1281 (m), 1231 (s), 1155 (m), 1094 (w), 1058 (m), 1026 (m), 975 (m), 897 (w), 842 (m), 736 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{39}H_{37}FNaO_{12}^+$ 739.2161; Found 739.2163.

5.4.20. Unsuccessful substrates



6. Substrate scope of σ-type cyclopropenium cation transfer to vinylboronic acid

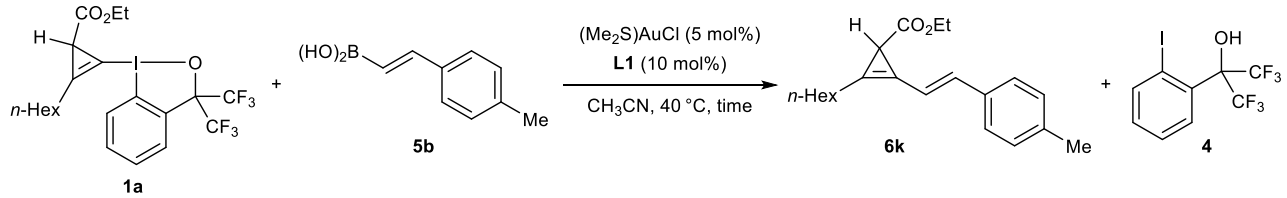


Vinylboronic acid **5a**, **5b**, **5c**, **5d**, **5e**, **5f**, **5g** were commercially available and used as received.

6.1. Optimization of σ-type cyclopropenium cation transfer to vinylboronic acid

An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), vinylboronic acid **5b** (16.2 mg, 0.100 mmol, 1.00 equiv.) and CpBX **1a** (1.00 – 2.00 equiv.); if the additive was used, it was added last. The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (0.050 M; 2.0 mL) was added by syringe. The reaction mixture was stirred at 40 °C for the specified time. The resulting reaction mixture was diluted with CH_2Cl_2 (5.0 mL) and filtered through a short pad of silica gel by eluting with CH_2Cl_2 (3 × 5.0 mL). The filtrate was then concentrated to dryness and the residue was subjected to flash column chromatography on silica gel (eluent: pentane/EtOAc = 20:1). The fractions that contained the product **6k**, **4** and the remaining CpBX **1a** were collected separately and concentrated by rotary evaporation. The yields of **6k**, **4** and the recovery of **1a** were obtained by quantitative ^{1}H NMR analysis using CH_2Br_2 (^{1}H NMR δ 4.92) as the internal standard.

Table 6 | Optimization of σ-type cyclopropenium cation transfer to vinylboronic acid

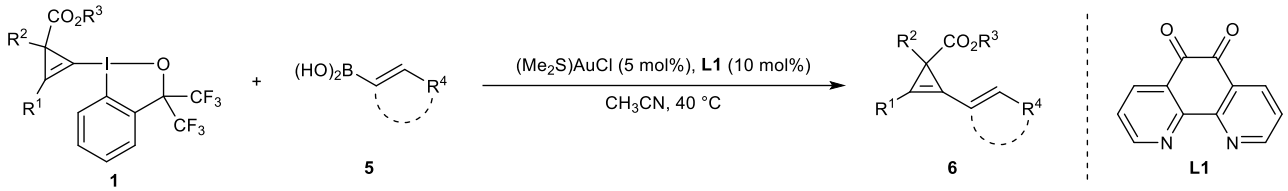


Entry	**1a** (equiv.)	**5b** (equiv.)	Additive (equiv.)	Time (h)	Yield of **6k** (%)[a]	Yield of **4** (%)[b]	Recovery of **1a** (%)[b]
1	1.0	1.0	none	10	71	99	0
2	1.0	1.0	CsF (1.0)	3	trace	60	0
3	1.3	1.0	none	5	85	99	0
4	1.5	1.0	none	5	64	89	10
5	2.0	1.0	none	12	59	96	0

Reactions performed on a 100 μmol scale. Yields and recovery were determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard. [a]Yield was determined based on **5b**. [b]Yield and recovery were determined based on **1a**.

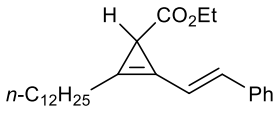
6.2. Survey of gold-catalysed σ-type cyclopropenium cation transfer to vinylboronic acid

General procedure E (**GPE**) for gold-catalysed σ-type cyclopropenium cation transfer to vinylboronic acid:



GPE: An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), vinylboronic acid **5** (0.100 mmol, 1.00 equiv.) and CpBX **1** (0.130 mmol, 1.30 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (0.10 M; 2.0 mL) was added by syringe. The reaction mixture was stirred at 40 °C for the specified time. The reaction mixture was then filtered through a silica gel pad and washed with CH_2Cl_2 (3 × 5.0 mL). The solvent was removed under reduced pressure, and the resulting crude residue was subjected to a short column chromatography (silica). The fractions that contained the products were collected and analysed by ^{1}H NMR spectroscopy. The recovered sample was purified by flash column chromatography (C18 reverse phase) to give the cross-coupled product **6**.

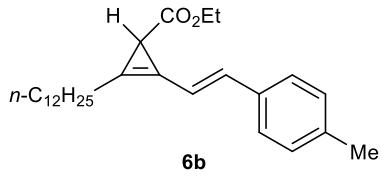
6.2.1. Synthesis and characterization of ethyl (*E*)-2-dodecyl-3-styrylcycloprop-2-ene-1-carboxylate (6a)



6a

Following **GPE**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1b** (84.3 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5a** (14.8 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 16 hours. Analysis of the crude product gave 57% NMR yield of **6a** and the by-product **4** was observed in 96% NMR yield based on **1b**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6a** in 55% yield (21.1 mg, 55.2 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.28; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H, Ar*H*), 7.39 – 7.30 (m, 2H, Ar*H*), 7.30 – 7.23 (m, 1H, Ar*H*), 6.90 (d, *J* = 15.6 Hz, 1H, C*H*=CH), 6.71 (d, *J* = 15.6 Hz, 1H, CH=C*H*), 4.22 – 4.10 (m, 2H, $CO_2CH_2CH_3$), 2.58 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.33 (s, 1H, $CHCO_2$), 1.71 – 1.56 (m, 2H, CH_2CH_2C), 1.49 – 1.14 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 0.97 – 0.77 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.9, 138.1, 136.5, 128.8, 128.6, 127.1, 113.0, 111.7, 103.5, 60.2, 32.1, 29.82, 29.79 (2C), 29.7, 29.51, 29.48, 29.4, 27.2, 25.7, 22.8, 22.0, 14.6, 14.3; **IR** (ν_{max}, cm^{-1}) 2954 (m), 2925 (s), 2854 (s), 1710 (s), 1630 (m), 1593 (m), 1465 (m), 1450 (m), 1404 (w), 1376 (m), 1304 (w), 1245 (m), 1203 (m), 1178 (m), 1150 (m), 1094 (w), 1073 (m), 1030 (m), 971 (w), 863 (w), 753 (m); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{26}H_{39}O_2^+$ 383.2945; Found 383.2945.

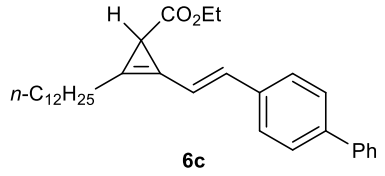
6.2.2. Synthesis and characterization of ethyl (*E*)-2-dodecyl-3-(4-methylstyryl)cycloprop-2-ene-1-carboxylate (6b)



6b

Following **GPE**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1b** (84.3 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5b** (16.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 17 hours. Analysis of the crude product gave 88% NMR yield of **6b** and the by-product **4** was observed in 98% NMR yield based on **1b**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6b** in 86% yield (34.2 mg, 86.2 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H, Ar*H*), 7.17 – 7.12 (m, 2H, Ar*H*), 6.84 (d, *J* = 15.6 Hz, 1H, C*H*=CH), 6.68 (d, *J* = 15.6 Hz, 1H, CH=C*H*), 4.21 – 4.10 (m, 2H, $CO_2CH_2CH_3$), 2.57 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.35 (s, 3H, CH_3), 2.31 (s, 1H, $CHCO_2$), 1.74 – 1.52 (m, 2H, CH_2CH_2C), 1.45 – 1.13 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.9, 138.6, 138.1, 133.7, 129.5, 127.0, 112.0, 111.0, 103.6, 60.2, 32.1, 29.82, 29.79 (2C), 29.7, 29.51, 29.48, 29.4, 27.2, 25.7, 22.8, 22.0, 21.4, 14.6, 14.3; **IR** (ν_{max}, cm^{-1}) 3026 (w), 2950 (m), 2854 (s), 1867 (w), 1721 (s), 1604 (w), 1512 (w), 1463 (m), 1369 (w), 1331 (w), 1302 (w), 1243 (m), 1173 (s), 1095 (w), 1036 (m), 997 (w), 959 (m), 943 (w), 854 (w), 803 (m), 723 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{41}O_2^+$ 397.3101; Found 397.3096.

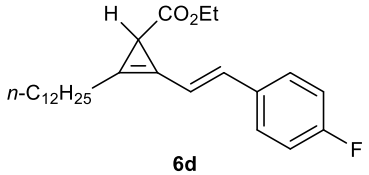
6.2.3. Synthesis and characterization of ethyl (*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-3-dodecylcycloprop-2-ene-1-carboxylate (6c)



6c

Following **GPE**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1b** (84.3 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5c** (22.4 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 16 hours. Analysis of the crude product gave 67% NMR yield of **6c** and the by-product **4** was observed in 98% NMR yield based on **1b**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6c** in 66% yield (30.2 mg, 65.8 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.24; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 4H, Ar*H*), 7.52 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.49 – 7.41 (m, 2H, Ar*H*), 7.41 – 7.31 (m, 1H, Ar*H*), 6.94 (d, *J* = 15.6 Hz, 1H, C*H*=CH), 6.75 (d, *J* = 15.6 Hz, 1H, CH=C*H*), 4.23 – 4.11 (m, 2H, $CO_2CH_2CH_3$), 2.60 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.35 (s, 1H, $CHCO_2$), 1.81 – 1.60 (m, 2H, CH_2CH_2C), 1.50 – 1.13 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 1.08 – 0.77 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.9, 141.3, 140.6, 137.6, 135.5, 129.0, 127.6, 127.53, 127.48, 127.1, 113.0, 111.8, 103.6, 60.3, 32.1, 29.83, 29.80 (2C), 29.7, 29.51, 29.48, 29.4, 27.2, 25.8, 22.8, 22.0, 14.6, 14.3; **IR** (ν_{max}, cm^{-1}) 3418 (w), 3031 (w), 2924 (s), 2853 (s), 1709 (s), 1602 (m), 1486 (w), 1464 (m), 1407 (w), 1375 (w), 1245 (m), 1176 (m), 1077 (w), 1033 (m), 1007 (w), 964 (w), 835 (m), 763 (s), 727 (m); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{32}H_{43}O_2^+$ 459.3258; Found 459.3258.

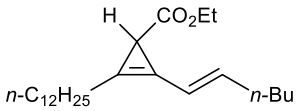
6.2.4. Synthesis and characterization of ethyl (*E*)-2-dodecyl-3-(4-fluorostyryl)cycloprop-2-ene-1-carboxylate (6d)



6d

Following **GPE**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1b** (84.3 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5d** (16.6 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 16 hours. Analysis of the crude product gave 66% NMR yield of **6d** and the by-product **4** was observed in 98% NMR yield based on **1b**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6d** in 65% yield (26.2 mg, 65.4 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.27; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.33 (m, 2H, Ar*H*), 7.09 – 6.95 (m, 2H, Ar*H*), 6.81 (d, *J* = 15.6 Hz, 1H, C*H*=CH), 6.66 (d, *J* = 15.6 Hz, 1H, CH=C*H*), 4.21 – 4.10 (m, 2H, $CO_2CH_2CH_3$), 2.58 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.32 (s, 1H, $CHCO_2$), 1.70 – 1.58 (m, 2H, CH_2CH_2C), 1.46 – 1.18 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 0.93 – 0.80 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.8, 162.9 (d, *J* = 248.8 Hz), 136.8, 132.7 (d, *J* = 3.4 Hz), 128.7 (d, *J* = 8.1 Hz), 115.9 (d, *J* = 21.8 Hz), 112.9 (d, *J* = 2.5 Hz), 111.8, 103.3, 60.3, 32.1, 29.82, 29.79 (2C), 29.7, 29.51, 29.47, 29.4, 27.2, 25.7, 22.8, 21.9, 14.6, 14.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.8; **IR** (ν_{max}, cm^{-1}) 2926 (s), 2855 (s), 1865 (w), 1720 (s), 1599 (m), 1509 (s), 1464 (m), 1369 (w), 1332 (w), 1235 (s), 1176 (s), 1161 (s), 1094 (w), 1036 (m), 1000 (w), 958 (m), 856 (w), 820 (m); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{26}H_{38}FO_2^+$ 401.2850; Found 401.2850.

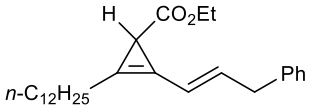
6.2.5. Synthesis and characterization of ethyl (*E*)-2-dodecyl-3-(hex-1-en-1-yl)cycloprop-2-ene-1-carboxylate (6e)



6e

Following **GPE**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1b** (84.3 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5e** (12.8 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 16 hours. Analysis of the crude product gave 55% NMR yield of **6e** and the by-product **4** was observed in 88% NMR yield based on **1b**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6e** in 53% yield (19.3 mg, 53.2 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.34; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.18 (dt, *J* = 15.2, 1.5 Hz, 1H, C*H*=CH), 5.92 (dt, *J* = 14.7, 7.0 Hz, 1H, CH=C*H*), 4.12 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 2.48 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.27 – 2.12 (m, 3H, $CHCO_2$ & CH_2), 1.65 – 1.52 (m, 2H, CH_2CH_2C), 1.47 – 1.14 (m, 25H, CH_2 & $CO_2CH_2CH_3$), 0.91 – 0.86 (m, 6H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.2, 142.1, 114.8, 108.0, 103.2, 60.1, 32.5, 32.1, 31.1, 29.81, 29.79 (2C), 29.7, 29.51, 29.47, 29.4, 27.2, 25.4, 22.8, 22.4, 21.8, 14.6, 14.3, 14.0; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2926 (s), 2855 (m), 1724 (m), 1464 (w), 1369 (w), 1333 (w), 1244 (w), 1174 (m), 1094 (w), 1038 (w), 961 (w); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{24}H_{43}O_2^+$ 363.3258; Found 363.3207.

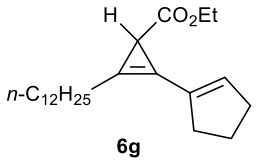
6.2.6. Synthesis and characterization of ethyl (*E*)-2-dodecyl-3-(3-phenylprop-1-en-1-yl)cycloprop-2-ene-1-carboxylate (6f)



6f

Following **GPE**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1b** (84.3 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5f** (16.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 18 hours. Analysis of the crude product gave 37% NMR yield of **6f** and the by-product **4** was observed in 84% NMR yield based on **1b**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6f** in 36% yield (14.4 mg, 36.3 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.29; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H, Ar*H*), 7.25 – 7.14 (m, 3H, Ar*H*), 6.22 (dt, *J* = 15.1, 1.5 Hz, 1H, C*H*=CH), 6.07 (dt, *J* = 15.1, 6.8 Hz, 1H, CH=C*H*), 4.12 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 3.53 (d, *J* = 6.7 Hz, 2H, CH_2Ph), 2.49 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.19 (s, 1H, $CHCO_2$), 1.66 – 1.50 (m, 2H, CH_2CH_2C), 1.45 – 1.15 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 1.00 – 0.78 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.0, 139.8, 139.3, 128.9, 128.7, 126.5, 116.2, 109.3, 103.0, 60.1, 39.1, 32.1, 29.81, 29.78 (2C), 29.7, 29.50, 29.46, 29.4, 27.2, 25.4, 22.8, 21.8, 14.5, 14.3; **IR** (ν_{max}, cm^{-1}) 3028 (w), 2956 (m), 2925 (s), 2854 (s), 1875 (w), 1724 (s), 1457 (m), 1368 (w), 1333 (w), 1245 (m), 1173 (s), 1036 (w), 961 (m), 734 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{41}O_2^+$ 397.3101; Found 397.3102.

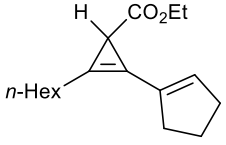
6.2.7. Synthesis and characterization of ethyl 2-(cyclopent-1-en-1-yl)-3-dodecylcycloprop-2-ene-1-carboxylate (6g)



6g

Following **GPE**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1b** (84.3 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5g** (11.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 16 hours. Analysis of the crude product gave 59% NMR yield of **6g** and the by-product **4** was observed in 95% NMR yield based on **1b**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6g** in 56% yield (19.5 mg, 56.3 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.33; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.86 – 5.84 (m, 1H, C=C*H*), 4.20 – 4.05 (m, 2H, $CO_2CH_2CH_3$), 2.69 – 2.41 (m, 6H, CH_2), 2.22 (s, 1H, $CHCO_2$), 2.05 – 1.92 (m, 2H, CH_2), 1.67 – 1.54 (m, 2H, CH_2), 1.45 – 1.19 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 0.93 – 0.79 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.2, 135.0, 130.5, 108.6, 101.1, 60.1, 34.1, 33.0, 32.1, 29.80, 29.78 (2C), 29.7, 29.5 (2C), 29.4, 27.5, 25.5, 23.9, 22.8, 22.4, 14.6, 14.3; **IR** (ν_{max}, cm^{-1}) 3429 (w), 2925 (s), 2853 (s), 1874 (w), 1724 (s), 1607 (w), 1464 (m), 1369 (w), 1323 (w), 1244 (m), 1174 (s), 1095 (w), 1037 (m), 1003 (w), 950 (w), 811 (w), 723 (w); **HRMS** (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{23}H_{39}O_2^+$ 347.2945; Found 347.2945.

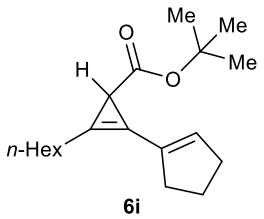
6.2.8. Synthesis and characterization of ethyl 2-(cyclopent-1-en-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (6h)



6h

Following **GPE**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1a** (56.4 mg, 0.100 mmol, 1.00 equiv.), vinylboronic acid **5g** (11.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 17 hours. Analysis of the crude product gave 63% NMR yield of **6h** and the by-product **4** was observed in 99% NMR yield. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6h** in 62% yield (16.3 mg, 62.1 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.86 – 5.84 (m, 1H, C=C*H*), 4.21 – 4.05 (m, 2H, $CO_2CH_2CH_3$), 2.70 – 2.32 (m, 6H, CH_2), 2.22 (s, 1H, $CHCO_2$), 2.08 – 1.84 (m, 2H, CH_2), 1.64 – 1.57 (m, 2H, CH_2), 1.46 – 1.13 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 1.02 – 0.73 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.2, 135.0, 130.6, 108.6, 101.1, 60.1, 34.1, 33.0, 31.7, 29.1, 27.5, 25.5, 23.9, 22.7, 22.5, 14.6, 14.2; **IR** (ν_{max}, cm^{-1}) 2956 (s), 2931 (s), 2858 (m), 1722 (s), 1587 (w), 1465 (m), 1373 (w), 1335 (w), 1303 (w), 1249 (m), 1185 (s), 1096 (w), 1034 (m), 865 (w), 744 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{27}O_2^+$ 263.2006; Found 263.2004.

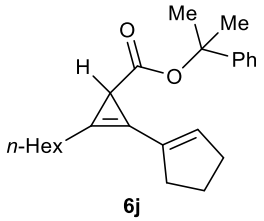
6.2.9. Synthesis and characterization of *tert*-butyl 2-(cyclopent-1-en-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (6i)



6i

Following **GPE**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1d** (59.2 mg, 0.100 mmol, 1.00 equiv.), vinylboronic acid **5g** (11.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 14 hours. Analysis of the crude product gave 53% NMR yield of **6i** and the by-product **4** was observed in 98% NMR yield. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6i** in 53% yield (15.4 mg, 53.0 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.38; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.84 – 5.81 (m, 1H, C=C*H*), 2.73 – 2.34 (m, 6H, CH_2), 2.13 (s, 1H, $CHCO_2$), 2.06 – 1.90 (m, 2H, CH_2), 1.64 – 1.56 (m, 2H, CH_2), 1.54 – 1.21 (m, 15H, CH_2 & $CO_2C(CH_3)_3$), 1.02 – 0.69 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.6, 134.5, 130.8, 109.0, 101.4, 79.6, 34.1, 33.0, 31.8, 29.1, 28.4, 27.6, 25.5, 23.9, 23.4, 22.7, 14.2; **IR** (ν_{max}, cm^{-1}) 2958 (m), 2931 (m), 2856 (m), 1720 (s), 1458 (w), 1367 (m), 1345 (w), 1324 (w), 1253 (w), 1211 (w), 1154 (s), 1004 (w), 957 (w), 853 (w), 813 (w), 734 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{30}NaO_2^+$ 313.2138; Found 313.2153.

6.2.10. Synthesis and characterization of 2-phenylpropan-2-yl 2-(cyclopent-1-en-1-yl)-3-hexylcycloprop-2-ene-1-carboxylate (6j)

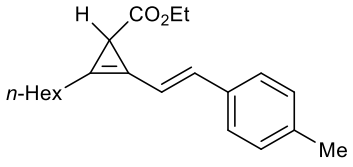


6j

Following **GPE**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1e** (65.4 mg, 0.100 mmol, 1.00 equiv.), vinylboronic acid **5g** (11.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 14 hours. Analysis of the crude product gave 55% NMR yield of **6j** and the by-product **4** was observed in 99% NMR yield. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6j** in 54% yield (19.1 mg, 54.2 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.32; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.08 (m,

5H, Ar*H*), 5.95 – 5.77 (m, 1H, C=C*H*), 2.66 – 2.34 (m, 6H, CH_2), 2.23 (s, 1H, C*H*CO_2), 2.03 – 1.95 (m, 2H, CH_2), 1.80 – 1.73 (m, 6H, CH_3), 1.69 – 1.50 (m, 2H, CH_2), 1.47 – 1.16 (m, 6H, CH_2), 0.89 (t, *J* = 6.6 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 146.8, 134.7, 130.8, 128.2, 126.8, 124.4, 108.9, 101.4, 80.9, 34.1, 33.1, 31.7, 29.2, 29.0, 28.9, 27.6, 25.6, 23.9, 23.5, 22.7, 14.2; **IR** (ν_{max}, cm^{-1}) 2955 (s), 2930 (s), 2857 (m), 1724 (s), 1602 (w), 1496 (w), 1465 (w), 1450 (m), 1382 (w), 1365 (w), 1344 (w), 1324 (w), 1270 (m), 1249 (m), 1187 (m), 1139 (s), 1101 (m), 1077 (w), 957 (w), 845 (w), 765 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{32}NaO_2^+$ 375.2295; Found 375.2291.

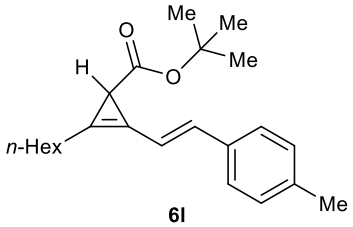
6.2.11. Synthesis and characterization of ethyl (*E*)-2-hexyl-3-(4-methylstyryl)cycloprop-2-ene-1-carboxylate (6k)



6k

Following **GPE**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1a** (73.4 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5b** (16.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 18 hours. Analysis of the crude product gave 90% NMR yield of **6k** and the by-product **4** was observed in 99% NMR yield based on **1a**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6k** in 88% yield (27.6 mg, 88.3 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.27; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H, Ar*H*), 7.16 – 7.13 (m, 2H, Ar*H*), 6.85 (d, *J* = 15.6 Hz, 1H, C*H*=CH), 6.68 (d, *J* = 15.6 Hz, 1H, CH=C*H*), 4.21 – 4.10 (m, 2H, $CO_2CH_2CH_3$), 2.57 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.34 (s, 3H, CH_3), 2.32 (s, 1H, C*H*CO_2), 1.68 – 1.60 (m, 2H, CH_2CH_2C), 1.46 – 1.17 (m, 9H, CH_2 & $CO_2CH_2CH_3$), 1.03 – 0.76 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.9, 138.6, 138.1, 133.7, 129.5, 127.0, 112.0, 111.0, 103.6, 60.2, 31.7, 29.1, 27.2, 25.7, 22.7, 21.9, 21.4, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 3026 (w), 2957 (m), 2928 (s), 2858 (m), 1866 (w), 1720 (s), 1602 (w), 1512 (w), 1465 (w), 1369 (w), 1332 (w), 1244 (m), 1175 (s), 1097 (w), 1036 (m), 960 (m), 856 (w), 805 (m), 730 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{29}O_2^+$ 313.2162; Found 313.2168.

6.2.12. Synthesis and characterization of *tert*-butyl (*E*)-2-hexyl-3-(4-methylstyryl)cycloprop-2-ene-1-carboxylate (6l)

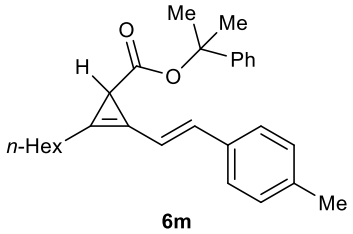


6l

Following **GPE**, a mixture of (Me_2S)AuCl (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1d** (77.0 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5b** (16.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 12 hours. Analysis of the crude product gave 64% NMR yield of **6l** and the by-product **4** was observed in 96% NMR yield based on **1d**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6l** in 63% yield (21.5 mg, 63.1 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.29; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H, Ar*H*), 7.16 – 7.12 (m, 2H, Ar*H*), 6.84 (d, *J* = 15.5 Hz, 1H, C*H*=CH), 6.67 (d, *J* = 15.5 Hz, 1H, CH=C*H*), 2.56 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.35 (s, 3H, CH_3), 2.21 (s, 1H, C*H*CO_2), 1.72 – 1.55 (m, 2H, CH_2CH_2C), 1.50 – 1.22 (m, 15H, CH_2 & $CO_2C(CH_3)_3$), 0.98 – 0.83 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3, 138.5, 137.7, 133.9, 129.5, 127.0, 112.4, 111.4, 104.0, 79.7, 31.7, 29.1, 28.4, 27.3, 25.8,

23.0, 22.7, 21.4, 14.2; **IR** (ν_{max}, cm^{-1}) 2957 (m), 2929 (m), 2859 (m), 1714 (s), 1599 (w), 1509 (w), 1455 (w), 1367 (m), 1335 (w), 1253 (m), 1148 (s), 997 (w), 961 (m), 851 (w), 802 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{32}NaO_2^+$ 363.2295; Found 363.2295.

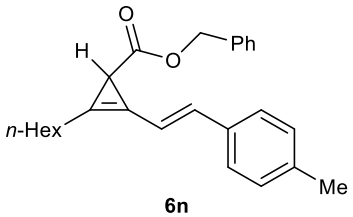
6.2.13. Synthesis and characterization of 2-phenylpropan-2-yl (*E*)-2-hexyl-3-(4-methylstyryl)cycloprop-2-ene-1-carboxylate (6m)



6m

Following **GPE**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1e** (85.1 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5b** (16.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 12 hours. Analysis of the crude product gave 73% NMR yield of **6m** and the by-product **4** was observed in 95% NMR yield based on **1e**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6m** in 72% yield (28.9 mg, 71.8 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.24; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 4H, Ar*H*), 7.34 – 7.26 (m, 2H, Ar*H*), 7.26 – 7.13 (m, 3H, Ar*H*), 6.91 (d, *J* = 15.5 Hz, 1H, C*H*=CH), 6.75 (d, *J* = 15.6 Hz, 1H, CH=C*H*), 2.62 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.40 (s, 3H, CH_3), 2.33 (s, 1H, $CHCO_2$), 1.82 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.73 – 1.65 (m, 2H, CH_2CH_2C), 1.51 – 1.22 (m, 6H, CH_2), 1.02 – 0.82 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 146.6, 138.6, 138.1, 133.8, 129.6, 128.2, 127.0, 126.8, 124.4, 112.3, 111.2, 104.1, 80.9, 31.7, 29.3, 29.1, 28.6, 27.3, 25.8, 23.0, 22.7, 21.5, 14.2; **IR** (ν_{max}, cm^{-1}) 3029 (w), 2949 (m), 2932 (s), 2859 (m), 1723 (s), 1605 (w), 1512 (w), 1455 (w), 1379 (w), 1249 (m), 1184 (m), 1138 (s), 1102 (m), 1076 (w), 1000 (w), 959 (m), 849 (w), 802 (m), 766 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{34}NaO_2^+$ 425.2451; Found 425.2435.

6.2.14. Synthesis and characterization of benzyl (*E*)-2-hexyl-3-(4-methylstyryl)cycloprop-2-ene-1-carboxylate (6n)

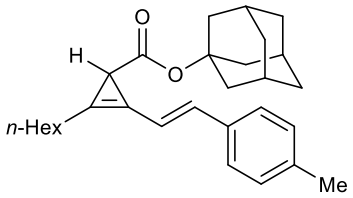


6n

Following **GPE**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1f** (81.4 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5b** (16.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 12 hours. Analysis of the crude product gave 85% NMR yield of **6n** and the by-product **4** was observed in 93% NMR yield based on **1f**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6n** in 82% yield (30.8 mg, 82.2 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.22; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.27 (m, 7H, Ar*H*), 7.16 (d, *J* = 7.9 Hz, 2H, Ar*H*), 6.86 (d, *J* = 15.6 Hz, 1H, C*H*=CH), 6.68 (d, *J* = 15.6 Hz, 1H, CH=C*H*), 5.24 – 5.11 (m, 2H, OCH_2Ph), 2.58 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.39 (s, 1H, $CHCO_2$), 2.36 (s, 3H, CH_3), 1.78 – 1.53 (m, 2H, CH_2CH_2C), 1.48 – 1.16 (m, 6H, CH_2), 1.02 – 0.75 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.8, 138.7, 138.4, 136.8, 133.6, 129.5, 128.6, 128.0 (2C), 127.0, 111.9, 110.8, 103.6, 65.9, 31.6, 29.1, 27.2, 25.7, 22.7, 22.0, 21.4, 14.2; **IR** (ν_{max}, cm^{-1}) 3433 (w), 3029 (w), 2954 (m), 2928 (s), 2858 (m), 1717 (s), 1599 (m), 1512 (w), 1456 (m), 1379 (w), 1331 (w), 1239 (m), 1159 (s),

999 (m), 961 (m), 805 (m), 737 (m); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{31}O_2^+$ 375.2319; Found 375.2304.

6.2.15. Synthesis and characterization of adamantan-1-yl 2-hexyl-3-((*E*)-4-methylstyryl)cycloprop-2-ene-1-carboxylate (6o)

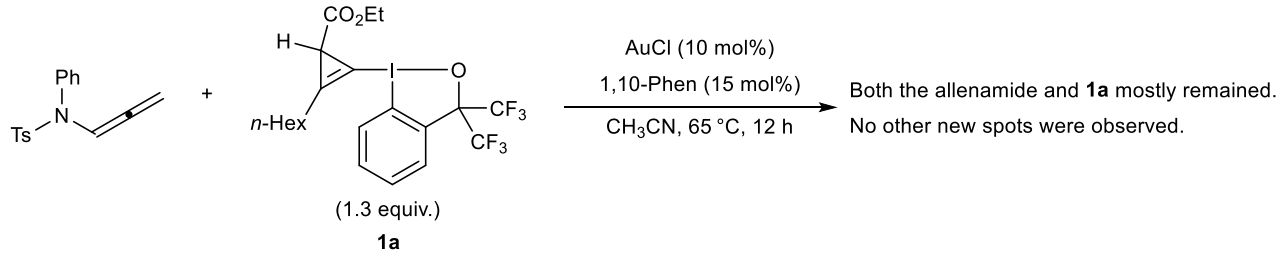


6o

Following **GPE**, a mixture of $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), CpBX **1g** (87.2 mg, 0.130 mmol, 1.30 equiv.), vinylboronic acid **5b** (16.2 mg, 0.100 mmol, 1.00 equiv.) and CH_3CN (2.0 mL) was stirred at 40 °C for 12 hours. Analysis of the crude product gave 77% NMR yield of **6o** and the by-product **4** was observed in 95% NMR yield based on **1g**. Flash column chromatography (C18 reverse phase; eluent: CH_3CN/H_2O = 1:9 to 9:1) afforded **6o** in 74% yield (31.1 mg, 74.3 μmol) as a colourless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.30; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H, Ar*H*), 7.17 – 7.12 (m, 2H, Ar*H*), 6.83 (d, *J* = 15.6 Hz, 1H, C*H*=CH), 6.68 (d, *J* = 15.5 Hz, 1H, CH=C*H*), 2.56 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.35 (s, 3H, CH_3), 2.20 (s, 1H, , $CHCO_2$), 2.16 – 2.05 (m, 9H, C*H*(adamantyl) & CH_2(adamantyl)), 1.74 – 1.56 (m, 8H, CH_2), 1.49 – 1.21 (m, 6H, CH_2), 0.96 – 0.84 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.0, 138.4, 137.7, 133.9, 129.5, 127.0, 112.4, 111.5, 104.1, 79.7, 41.6, 36.4, 31.7, 31.0, 29.1, 27.3, 25.7, 23.1, 22.7, 21.4, 14.2; **IR** (ν_{max}, cm^{-1}) 3028 (w), 2913 (s), 2856 (s), 1712 (s), 1602 (m), 1514 (w), 1456 (m), 1348 (w), 1251 (m), 1179 (s), 1105 (w), 1061 (s), 967 (m), 805 (m), 737 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{38}NaO_2^+$ 441.2764; Found 441.2782.

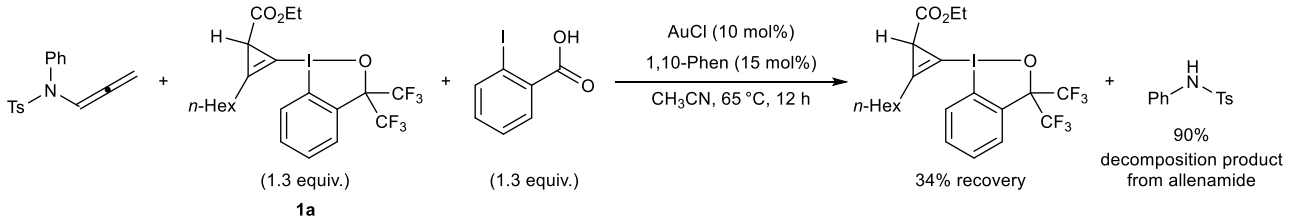
6.3. Attempts of gold-catalysed σ-type cyclopropenium cation transfer to other substrates

6.3.1 Gold-catalysed σ-type cyclopropenium cation transfer reaction of CpBXs with allenamides



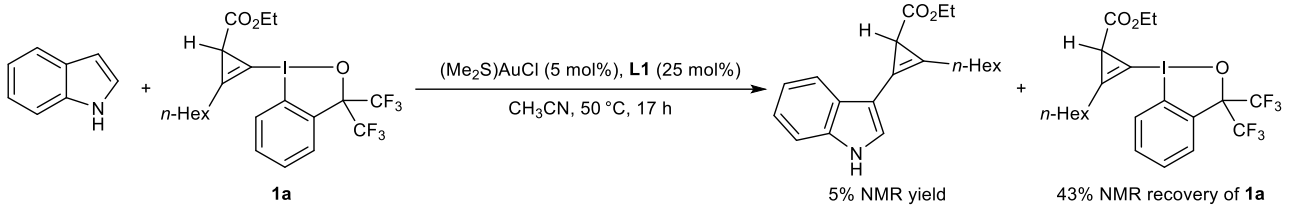
The reaction was run according to a previously reported procedure[53]. An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, 1,10-phenanthroline (2.70 mg, 15.0 μmol, 15.0 mol%), 4-methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (28.5 mg, 100 μmol, 1.00 equiv.) and CpBX **1a** (73.4 mg, 130 μmol, 1.30 equiv.). The Schlenk tube was then introduced into a glovebox and AuCl (2.32 mg, 10.0 μmol, 10.0 mol%) was added. The Schlenk tube was then taken out of the glovebox. Subsequently, CH_3CN (0.05 M; 2.0 mL) was added by syringe. The reaction mixture was stirred at 65 °C for 12 hours. Thin layer chromatography indicated that both the allenamide and CpBX **1a** mostly remained, and no other new spots were observed.

6.3.2 Gold-catalysed σ-type cyclopropenium cation transfer reaction of CpBXs with allenamides in the presence of 2-iodobenzoic acid



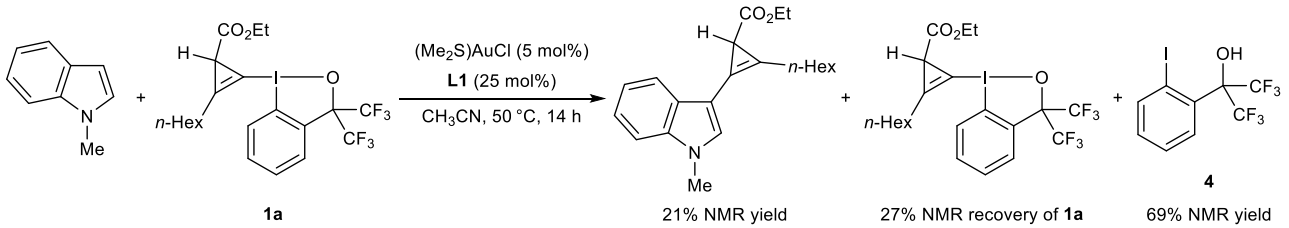
The reaction was run according to a previously reported procedure[53]. An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, 1,10-phenanthroline (2.70 mg, 15.0 µmol, 15.0 mol%), 4-methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (28.5 mg, 100 µmol, 1.00 equiv.), 2-iodobenzoic acid (32.2 mg, 130 µmol, 1.30 equiv.) and CpBX **1a** (73.4 mg, 130 µmol, 1.30 equiv.). The Schlenk tube was then introduced into a glovebox and AuCl (2.32 mg, 10.0 µmol, 10.0 mol%) was added. The Schlenk tube was then taken out of the glovebox. Subsequently, CH_3CN (0.05 M; 2.0 mL) was added by syringe. The reaction mixture was stirred at 65 °C for 12 hours. The reaction mixture was then filtered through a silica gel pad and washed with CH_2Cl_2 (3 × 5.0 mL). The solvent was removed under reduced pressure, and the resulting crude residue was subjected to preparative thin-layer chromatography (eluent: hexane/ethyl acetate = 10:1). The major new spot was isolated and indentified to be 4-methyl-*N*-phenylbenzenesulfonamide (22.3 mg, 90.2 µmol, 90% yield), which comes from the decomposition of the substrate 4-methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide. The CpBX **1a** was recovered in 34% yield (24.7 mg). Apart from those, no other prominent new spots were observed.

6.3.3 Gold-catalysed σ-type cyclopropenium cation transfer reaction of CpBXs with indole



An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, **L1** (5.25 mg, 25.0 µmol, 25.0 mol%), (Me_2S)AuCl (1.47 mg, 5.00 µmol, 5.00 mol%), indole (11.7 mg, 100 µmol, 1.00 equiv.) and CpBX **1a** (56.43 mg, 100 µmol, 1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (0.05 M; 2.0 mL) was added by syringe. The reaction mixture was stirred at 50 °C for 17 hours. The reaction mixture was then filtered through a silica gel pad and washed with CH_2Cl_2 (3 × 5.0 mL). The solvent was removed under reduced pressure, and the resulting crude residue was subjected to a flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 4:1). The fractions that contained the products were collected and analysed by ^1H NMR spectroscopy. Analysis of the product fraction gave 5% NMR yield of the desired product and CpBX **1a** was recovered in 43% NMR yield.

6.3.4 Gold-catalysed σ-type cyclopropenium cation transfer reaction of CpBXs with 1-methyl-1*H*-indole

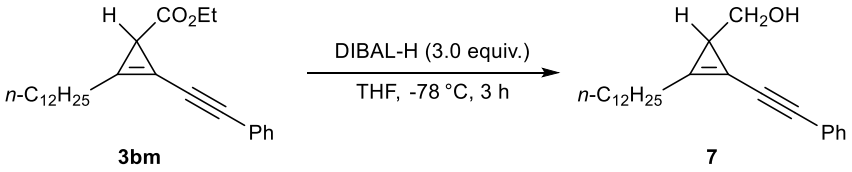


An oven-dried 10 mL Schlenk tube was sequentially charged with a magnetic stir-bar, **L1** (5.25 mg, 25.0 µmol, 25.0 mol%), (Me_2S)AuCl (1.47 mg, 5.00 µmol, 5.00 mol%), 1-methyl-1*H*-indole (13.1 mg, 100 µmol, 1.00 equiv.) and CpBX **1a** (56.43 mg, 100 µmol, 1.00 equiv.). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (0.05 M; 2.0 mL) was added by syringe. The reaction mixture was stirred at 50 °C for 14 hours. The reaction mixture was then filtered through a silica gel pad and washed with CH_2Cl_2 (3 × 5.0 mL). The solvent was removed under reduced pressure, and the resulting crude residue was subjected to a flash column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1). The fractions that contained the products were collected and analysed by ^{1}H NMR spectroscopy. Analysis of the product fraction gave 21% NMR yield of the desired product and CpBX **1a** was recovered in 27% NMR yield. The by-product **4** was observed in 69% NMR yield.

7. Transformations of products and applications

7.1. Selective reduction of alkynyl-cyclopropenes using DIBAL-H[54]

7.1.1. Synthesis and characterization of (2-dodecyl-3-(phenylethynyl)cycloprop-2-en-1-yl)methanol (7)

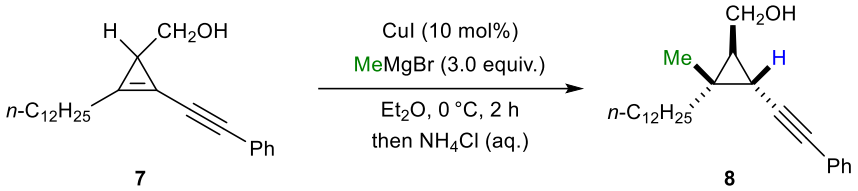


A 25 mL Schlenk tube was charged with **3bm** (190 mg, 0.500 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, THF (0.1 M; 5.0 mL) was added by syringe and the Schlenk tube was placed at −78 °C in a dry ice/acetone bath. After that, diisobutylaluminum hydride (DIBAL-H, 1.0 M in toluene; 1.50 mmol, 1.5 mL, 3.00 equiv.) was added dropwise by a syringe pump over 5 min and the reaction mixture was stirred at −78 °C for additional 3 hours. Then the cooling bath was removed. The reaction mixture was allowed to warm to room temperature gradually (ca. 20 min) while keeping stirring. The reaction mixture was then quenched by adding saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc (10 ml × 3). The combined organic layers were successively washed with brine and H_2O, then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: pentane/EtOAc = 10:1) to give the desired product **7** in 94% yield (159 mg, 469 µmol) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H, Ar*H*), 7.39 – 7.30 (m, 3H, Ar*H*), 3.72 – 3.63 (m, 2H, C*H*$_2$OH), 2.59 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.11 (t, *J* = 4.4 Hz, 1H, C*H*CH_2OH), 1.68 – 1.60 (m, 2H, C*H*$_2CH_2C$), 1.45 – 1.21 (m, 19H, C*H*$_2$ & O*H*), 0.96 – 0.81 (m, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.7, 128.8, 128.5, 128.3, 123.1, 100.2, 96.9, 79.0, 67.5, 32.1, 29.83, 29.79 (2C), 29.7, 29.51 (2C), 29.45, 27.5, 27.2, 26.4, 22.8, 14.3; **IR** (ν_{max}, cm^{-1}) 3359 (w), 2924 (s), 2852 (s), 2203 (w), 1821 (w), 1595 (w), 1490 (w), 1465 (m), 1443 (w),

1054 (w), 1018 (m), 755 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{34}NaO^+$ 361.2502; Found 361.2506.

7.2. Hydroalkylation of alkynyl-cyclopropene 7 via copper-catalyzed carbomagnesiation[55]

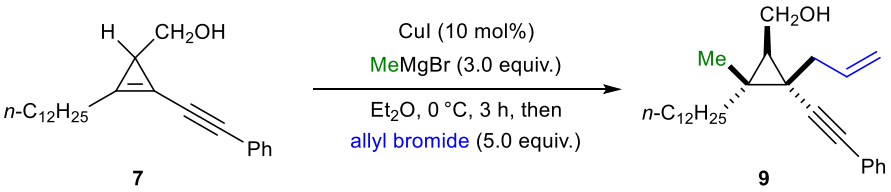
7.2.1. Synthesis and characterization of (2-dodecyl-2-methyl-3-(phenylethynyl)cyclopropyl)methanol (8)



A 10 mL Schlenk tube was charged with **7** (33.9 mg, 0.100 mmol, 1.00 equiv.), copper iodide (CuI; 1.90 mg, 10.0 μmol, 10.0 mol%) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, Et_2O (0.05 M; 2.0 mL) was added by syringe and the mixture was stirred at room temperature. Then methylmagnesium bromide (MeMgBr, 3.0 M in Et_2O; 0.10 mL, 0.300 mmol, 3.00 equiv.) was added dropwise. The resulting reaction mixture was stirred at room temperature for 2 hours. Then the mixture was quenched by adding saturated aqueous NH_4Cl (1.0 mL) and extracted with EtOAc (5.0 ml × 3). The combined organic layers were successively washed with brine and H_2O, then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: pentane/EtOAc = 10:1) to give the hydroalkylation product **8** in 79% yield (28.0 mg, 79.0 μmol) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 10:1) = 0.07; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H, Ar*H*), 7.19 – 7.08 (m, 3H, Ar*H*), 3.74 – 3.64 (m, 1H, C*H*$_2$OH), 3.51 – 3.41 (m, 1H, C*H*$_2$OH), 1.48 – 1.06 (m, 25H, C*H* & C*H*$_2$ & O*H*), 1.03 (s, 3H, C*H*$_3$), 0.76 (t, *J* = 6.7 Hz, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.6, 128.3, 127.6, 124.2, 90.3, 79.1, 62.7, 37.5, 36.1, 32.1, 30.1, 29.9, 29.82 (2C), 29.79 (2C), 29.5, 28.2, 26.7, 22.8, 19.5, 17.5, 14.3; **IR** (ν_{max}, cm^{-1}) 3366 (w), 2950 (m), 2925 (s), 2853 (s), 2222 (m), 1599 (w), 1490 (w), 1463 (m), 1445 (m), 1379 (w), 1253 (w), 1069 (m), 1023 (m), 907 (w), 754 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{38}NaO^+$ 377.2815; Found 377.2813.

7.3. Difunctionalization of alkynyl-cyclopropene 7 via copper-catalyzed carbomagnesiation[33]

7.3.1. Synthesis and characterization of (2-allyl-3-dodecyl-3-methyl-2-(phenylethynyl)cyclopropyl)methanol (9)

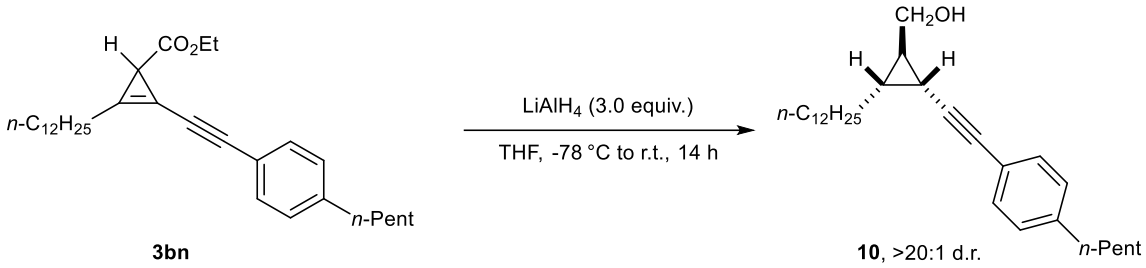


A 10 mL Schlenk tube was charged with **7** (33.9 mg, 0.100 mmol, 1.00 equiv.), copper iodide (CuI; 1.90 mg, 10.0 μmol, 10.0 mol%) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, Et_2O (0.05 M; 2.0 mL) was added by syringe and the mixture was stirred at room temperature. Then methylmagnesium bromide (MeMgBr, 3.0 M in Et_2O; 0.10 mL, 0.300 mmol, 3.00 equiv.) was added dropwise. The resulting reaction mixture was stirred at room temperature for 3 hours. Allyl bromide (43.3 μL, 0.500 mmol, 5.00 equiv.) was added dropwise to the reaction mixture. The resulting reaction mixture was stirred at room temperature for additional 5 hours. Then the mixture was quenched by adding saturated aqueous NH_4Cl (1.0 mL) and extracted with EtOAc (5.0 ml × 3). The combined organic layers were successively washed with brine and H_2O, then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The

residue was purified by column chromatography on silica gel (eluent: pentane/EtOAc = 10:1) to give the difunctionalization product **9** in 61% yield (24.2 mg, 61.3 μmol) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 5:1) = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H, Ar*H*), 7.24 – 7.13 (m, 3H, Ar*H*), 6.07 – 5.97 (m, 1H, CH_2CH=CH_2), 5.12 (dq, *J* = 17.2, 1.7 Hz, 1H, CH_2CH=CH_2), 5.08 – 5.04 (m, 1H, CH_2CH=CH_2), 3.65 (d, *J* = 7.7 Hz, 2H, CH_2CH=CH_2), 2.37 – 2.20 (m, 2H, CH_2OH), 1.66 – 1.39 (m, 3H, C*H* & CH_2), 1.39 – 1.10 (m, 21H, CH_2 & O*H*), 1.04 (s, 3H, CH_3), 0.90 – 0.70 (m, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.8, 131.6, 128.3, 127.5, 124.3, 116.4, 94.1, 79.4, 59.7, 39.9, 37.7, 33.5, 32.1, 30.12, 30.06, 29.9, 29.84, 29.82 (2C), 29.80, 29.5, 26.7, 25.1, 22.8, 14.3, 13.1; **IR** (ν_{max}, cm^{-1}) 3359 (w), 2926 (s), 2854 (s), 2221 (w), 1642 (w), 1598 (w), 1493 (w), 1463 (w), 1068 (w), 1004 (m), 912 (m), 755 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{42}NaO^+$ 417.3128; Found 417.3129.

7.4. Selective reduction of alkynyl-cyclopropenes using $LiAlH_4$[56]

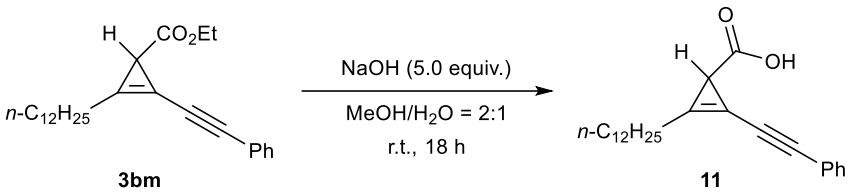
7.4.1. Synthesis and characterization of (2-dodecyl-3-((4-pentylphenyl)ethynyl)cyclopropyl)methanol (10)



A 25 mL Schlenk tube was charged with **3bn** (45.1 mg, 0.100 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, THF (0.05 M; 2.0 mL) was added by syringe and the Schlenk tube was placed at −78 °C in a dry ice/acetone bath. After that, lithium aluminum hydride ($LiAlH_4$, 2.4 M in THF; 0.300 mmol, 0.13 mL, 3.00 equiv.) was added dropwise and then the reaction mixture was stirred with the dry ice/acetone bath. The reaction mixture was allowed to warm to room temperature naturally over 14 hours while keeping stirring. The reaction mixture was then quenched by adding saturated aqueous NH_4Cl (2.0 mL) and extracted with EtOAc (10 ml × 3). The combined organic layers were successively washed with brine and H_2O, then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: pentane/EtOAc = 8:1) to give the reduced product **10** in 32% yield (13.2 mg, 32.1 μmol, >20:1 dr. based on ^{1}H NMR) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H, Ar*H*), 7.13 – 7.00 (m, 2H, Ar*H*), 3.74 (dd, *J* = 11.5, 7.1 Hz, 1H, CH_2OH), 3.64 (dd, *J* = 11.5, 7.7 Hz, 1H, CH_2OH), 2.63 – 2.49 (m, 2H, CH_2Ph), 1.74 – 1.52 (m, 3H, C*H* & CH_2), 1.52 – 1.16 (m, 28H, C*H* & CH_2 & O*H*), 1.10 (t, *J* = 4.8 Hz, 1H, C*H*), 0.90 – 0.86 (m, 6H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.7, 131.6, 128.4, 121.0, 91.4, 77.0, 62.0, 35.9, 32.1, 31.6, 31.1, 29.84 (2C), 29.81 (2C), 29.78, 29.7, 29.6, 29.5, 29.4, 28.0, 27.7, 22.8, 22.7, 14.3, 14.2, 12.6; **IR** (ν_{max}, cm^{-1}) 2954 (m), 2926 (s), 2855 (m), 2225 (w), 1800 (w), 1739 (m), 1512 (w), 1462 (w), 1443 (w), 1323 (w), 1287 (w), 1267 (w), 1253 (w), 1185 (w), 1160 (w), 1121 (w), 1064 (w), 1024 (w), 837 (w), 761 (w); **HRMS** (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{47}O^+$ 411.3621; Found 411.3620.

7.5. Saponification of alkynyl-cyclopropene 3bm[57]

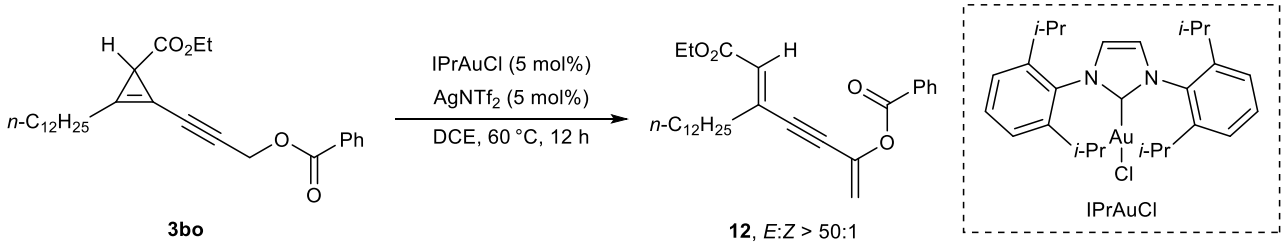
7.5.1. Synthesis and characterization of 2-dodecyl-3-(phenylethynyl)cycloprop-2-ene-1-carboxylic acid (11)



NaOH (20.0 mg, 0.500 mmol, 5.00 equiv.) was added to a 10 mL vial that contained the **3bm** (38.1 mg, 0.100 mmol, 1.00 equiv.), MeOH (0.25 mL) and deionized water (0.13 mL). The mixture was stirred under room temperature for 18 hours. The mixture was acidified by adding aqueous HCl (1.0 M, 0.50 mL) and extracted with DCM (5.0 ml × 4). The combined organic layers were successively washed with brine and H_2O, then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (C18 reverse phase) to give the saponification product **11** in 82% yield (29.0 mg, 82.3 μmol) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.10; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.56 (bs, 1H, CO_2H), 7.60 – 7.45 (m, 2H, Ar*H*), 7.40 – 7.29 (m, 3H, Ar*H*), 2.66 – 2.54 (m, 2H, CH_2CH_2C), 2.51 (s, 1H, $CHCO_2$), 1.72 – 1.59 (m, 2H, CH_2CH_2C), 1.51 – 1.11 (m, 18H, CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.1, 132.0, 129.2, 128.5, 122.4, 116.0, 99.2, 90.3, 76.2, 32.1, 29.80, 29.78, 29.74, 29.65, 29.5, 29.4, 29.3, 26.7, 26.1, 25.0, 22.8, 14.3; **IR** (ν_{max}, cm^{-1}) 2924 (s), 2853 (m), 2535 (w), 2204 (w), 1861 (w), 1692 (s), 1490 (w), 1462 (w), 1423 (m), 1271 (m), 1232 (m), 1072 (w), 999 (w), 944 (w), 919 (w), 755 (s); **HRMS** (ESI/QTOF) m/z: $[M + H_{-1}]^-$ Calcd for $C_{24}H_{31}O_2^-$ 351.2330; Found 351.2323.

7.6. Gold(I)-catalysed rearrangement of propargylic benzoate and ring-opening cascade

7.6.1. Synthesis and characterization of (*E*)-5-(2-ethoxy-2-oxoethylidene)heptadec-1-en-3-yn-2-yl benzoate (12)



In a nitrogen-filled glovebox, a 10 ml Schlenk tube was sequentially charged with IPrAuCl (6.20 mg, 5.00 μmol, 5.00 mol%) and $AgNTf_2$ (1.90 mg, 5.00 μmol, 5.00 mol%). A magnetic stir bar was added to the Schlenk tube. The tube was then sealed with a rubber cap. The Schlenk tube was brought out of the glovebox and 1,2-dichloroethane (DCE; 1.0 mL) was added. The mixture was stirred under room temperature for 5 min. Then, **3bo** (43.9 mg, 0.100 mmol, 1.00 equiv., dissolved in 2.0 mL DCE) was added. The resulting mixture was stirred under 60 °C for 12 hours. The reaction mixture was then filtered through a silica gel pad and eluted with CH_2Cl_2 (3 × 5.0 mL). The solvent was removed under reduced pressure, and the resulting crude residue was purified by flash column chromatography on silica gel (eluent: pentane/EtOAc = 10:1) to give the ring-opening product **12** in 81% yield (35.4 mg, 80.7 μmol, *E*: *Z* > 50:1 base on ^{1}H NMR) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.33; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 – 8.05 (m, 2H, Ar*H*), 7.66 – 7.57 (m, 1H, Ar*H*), 7.51 – 7.45 (m, 2H, Ar*H*), 6.10 – 6.09 (m, 1H, C=C*H*), 5.46 (d, *J* = 1.8 Hz, 1H, C=CH_2), 5.42 (d, *J* = 1.8 Hz, 1H, C=CH_2), 4.15 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 2.76 – 2.72 (m, 2H, CH_2C=CH), 1.59 – 1.48 (m, 2H, CH_2), 1.36 – 1.16 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 164.1, 141.5, 136.2, 133.8,

130.3, 129.1, 128.7, 125.6, 113.5, 90.8, 87.4, 60.3, 32.1, 31.9, 29.79 (2C), 29.77, 29.7, 29.52, 29.49, 29.4, 28.5, 22.8, 14.33, 14.26; **IR** (ν_{max}, cm^{-1}) 2925 (s), 2855 (m), 1746 (s), 1717 (s), 1629 (m), 1603 (m), 1458 (w), 1455 (m), 1370 (w), 1245 (s), 1192 (s), 1174 (s), 1084 (s), 1065 (s), 1027 (m), 881 (m), 707 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{39}O_4^+$ 439.2843; Found 439.2849.

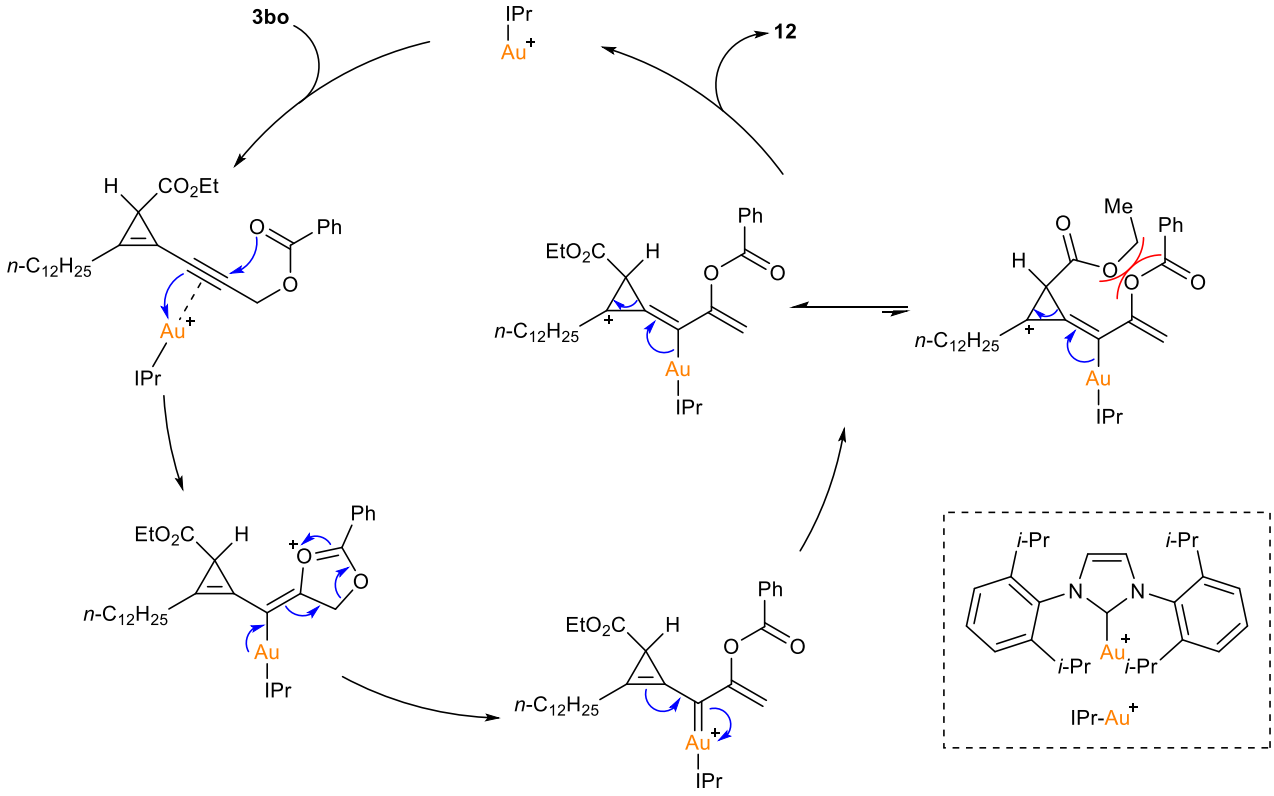
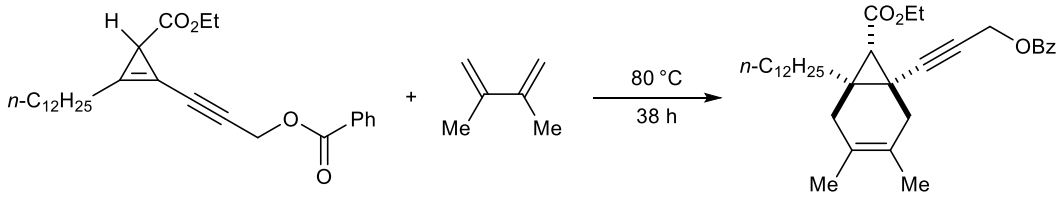


Fig. 1 | Proposed mechanism of gold(I)-catalysed 1,2-benzoyloxy migration of propargylic benzoate and ring-opening cascade.

7.7. Diels–Alder reaction of 3bo with 2,3-dimethylbutadiene[58]

7.7.1. Synthesis and characterization of ethyl 1-(3-(benzoyloxy)prop-1-yn-1-yl)-6-dodecyl-3,4-dimethylbicyclo[4.1.0]hept-3-ene-7-carboxylate (13)



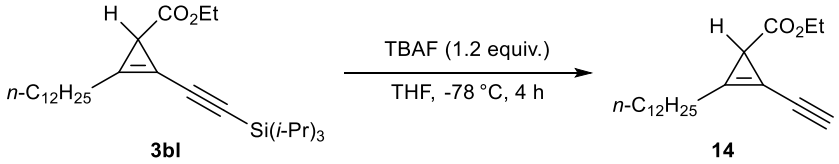
3bo **13**, >20:1 d.r.

A solution of **3bo** (43.9 mg, 0.100 mmol, 1.00 equiv.) in 2,3-dimethylbutadiene (0.50 mL) was heated at 80 °C in a sealed tube for 38 hours. After being cooled to room temperature, the mixture was concentrated and purified by column chromatography on silica gel (eluent: pentane/EtOAc = 10:1) to give the cycloaddition product **13** in 89% yield (46.4 mg, 89.1 μmol, dr. >20:1 based on ^{1}H NMR) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.27; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 – 8.00 (m, 2H, Ar*H*), 7.62 – 7.50 (m, 1H, Ar*H*), 7.42 (t, *J* = 7.7 Hz, 2H, Ar*H*), 4.98 (s, 2H, C*H*$_2$OBz), 4.17 – 4.05 (m, 2H, $CO_2CH_2CH_3$), 2.57 – 2.43 (m, 2H, C*H*$_2$), 2.23 (s, 2H, C*H*$_2$), 2.10 – 1.90 (m, 2H, C*H*$_2$), 1.88 (s, 1H, C*H*CO_2), 1.83 – 1.73 (m, 1H, C*H*$_2$), 1.72 – 1.61 (m, 2H, C*H*$_2$), 1.60 – 1.51 (m, 6H, C*H*$_3$), 1.51 – 1.11 (m, 20H, C*H*$_2$ & $CO_2CH_2CH_3$), 0.87 (t, *J* = 6.8 Hz, 3H, C*H*$_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 166.0, 133.1, 130.0, 129.9, 128.4, 122.1, 121.5, 87.0, 76.2, 60.2, 53.6, 37.7, 36.0, 34.9, 32.0, 30.6, 30.2, 30.1, 29.9, 29.84, 29.80,

29.78 (2C), 29.5, 26.6, 26.5, 22.8, 19.1, 18.7, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 2925 (s), 2855 (m), 2247 (w), 1728 (s), 1602 (w), 1451 (m), 1416 (w), 1372 (m), 1314 (w), 1266 (s), 1148 (s), 1098 (s), 1068 (m), 1027 (w), 957 (w), 711 (s); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{48}NaO_4^+$ 543.3445; Found 543.3436.

7.8. Desilylation of 3bl using TBAF to terminal cyclopropenyl alkyne 14[59]

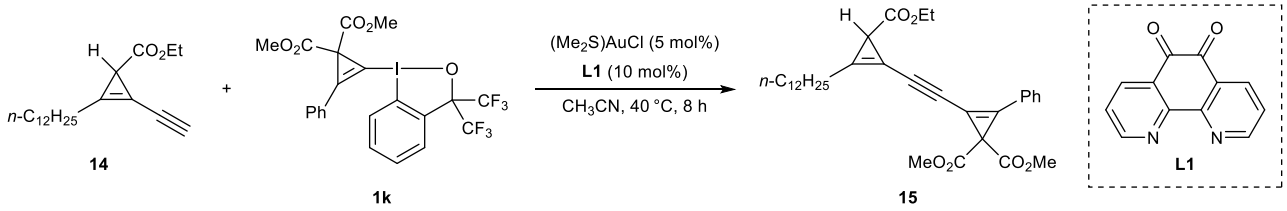
7.8.1. Synthesis and characterization of ethyl 2-dodecyl-3-ethynylcycloprop-2-ene-1-carboxylate (14)



A 25 mL Schlenk tube was charged with **3bl** (286 mg, 0.622 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, THF (5.0 mL) was added by syringe and the Schlenk tube was placed at −78 °C in a dry ice/acetone bath. After that, tetrabutylammonium fluoride (TBAF, 1.0 M in THF; 0.746 mmol, 0.75 mL, 1.20 equiv.) was added dropwise by a syringe pump over 5 min and the reaction mixture was stirred at −78 °C for additional 4 hours. Then the cooling bath was removed. The reaction mixture was allowed to warm to room temperature gradually (ca. 20 min) while keeping stirring. The reaction mixture was then quenched by adding saturated aqueous NH_4Cl (5.0 mL) and extracted with EtOAc (10 ml × 3). The combined organic layers were successively washed with brine and H_2O, then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: pentane/EtOAc = 20:1) to give the desilylation product **14** in 75% yield (141 mg, 464 μmol) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.38; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.21 – 4.10 (m, 2H, $CO_2CH_2CH_3$), 3.49 (s, 1H, C≡C*H*), 2.53 (t, *J* = 7.2 Hz, 2H, CH_2CH_2C), 2.43 (s, 1H, $CHCO_2$), 1.68 – 1.53 (m, 2H, CH_2CH_2C), 1.44 – 1.16 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 0.88 (t, *J* = 6.7 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 118.5, 90.3, 87.7, 71.3, 60.7, 32.1, 29.793, 29.787, 29.7, 29.6, 29.5, 29.4, 29.2, 26.6, 26.1, 25.0, 22.8, 14.5, 14.3; **IR** (ν_{max}, cm^{-1}) 3306 (w), 2950 (m), 2926 (s), 2855 (s), 2114 (w), 1846 (w), 1727 (s), 1465 (w), 1371 (w), 1334 (w), 1252 (w), 1186 (s), 1095 (w), 1028 (w), 722 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{32}NaO_2^+$ 327.2295; Found 327.2308.

7.9. Gold-catalysed σ-type CPCs transfer reaction for the synthesis of non-symmetrical 1,2-bis-cyclopropenyl substituted alkyne

7.9.1. Synthesis and characterization of dimethyl 2-((2-dodecyl-3-(ethoxycarbonyl)cycloprop-1-en-1-yl)ethynyl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (15)

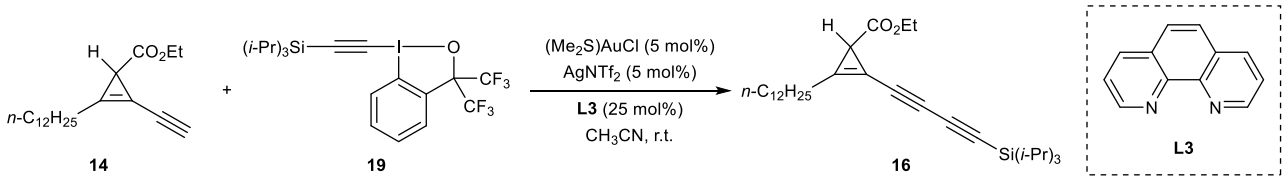


An oven-dried 10 mL Schlenk tube was sequentially charged with **14** (30.5 mg, 0.100 mmol, 1.00 equiv.), **L1** (2.10 mg, 10.0 μmol, 10.0 mol%), $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), CpBX **1k** (72.0 mg, 0.120 mmol, 1.20 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (0.05 M; 2.0 mL) was added by syringe. The reaction mixture was stirred at 40 °C for 8 hours. The resulting reaction mixture was then filtered

through a silica gel pad and eluted with CH_2Cl_2 (3 × 5.0 mL). The solvent was removed under reduced pressure, and the resulting crude residue was purified by flash column chromatography on silica gel (eluent: pentane/EtOAc = 5:1) to give the cross-coupled product **15** in 60% yield (32.2 mg, 60.2 μmol) as a colorless oil. The by-product **4** was recovered in 99% NMR yield based on **1k**. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.60 (m, 2H, Ar*H*), 7.47 – 7.42 (m, 3H, Ar*H*), 4.27 – 4.08 (m, 2H, $CO_2CH_2CH_3$), 3.75 (s, 6H, CO_2CH_3), 2.62 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.57 (s, 1H, $CHCO_2$), 1.70 – 1.56 (m, 2H, CH_2CH_2C), 1.48 – 1.16 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 0.87 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 169.3, 131.3, 130.8, 129.2, 124.4, 122.3, 112.5, 90.8, 90.0, 89.5, 84.6, 60.9, 52.8, 37.2, 32.0, 29.78, 29.76 (2C), 29.6, 29.5, 29.4, 29.3, 26.6, 26.5, 26.1, 22.8, 14.5, 14.2; **IR** (ν_{max}, cm^{-1}) 2946 (m), 2928 (s), 2856 (m), 2189 (w), 1873 (w), 1732 (s), 1602 (w), 1436 (m), 1369 (w), 1281 (m), 1245 (s), 1184 (s), 1063 (m), 1031 (w), 763 (w); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{42}NaO_6^+$ 557.2874; Found 557.2876.

7.10. Au-Ag bimetallic catalysis providing unsymmetrical cyclopropenyl 1,3-diyne[60]

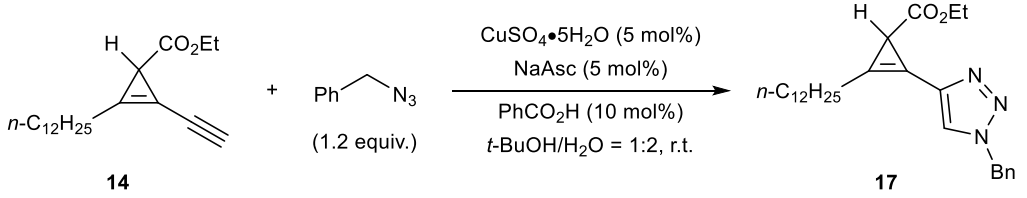
7.10.1. Synthesis and characterization of ethyl 2-dodecyl-3-((triisopropylsilyl)buta-1,3-diyn-1-yl)cycloprop-2-ene-1-carboxylate (16)



An oven-dried 10 mL Schlenk tube was sequentially charged with **14** (30.5 mg, 0.100 mmol, 1.00 equiv.), **L3** (4.51 mg, 25.0 μmol, 25.0 mol%), $(Me_2S)AuCl$ (1.47 mg, 5.00 μmol, 5.00 mol%), **19** (55.0 mg, 0.100 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, $AgNTf_2$ (1.90 mg, 5.00 μmol, 5.00 mol%) and CH_3CN (0.05 M; 2.0 mL) was added. The reaction mixture was stirred at room temperature for 1 hour. The resulting reaction mixture was then filtered through a silica gel pad and eluted with CH_2Cl_2 (3 × 5 mL). The solvent was removed under reduced pressure, and the resulting crude residue was purified by flash column chromatography on silica gel (eluent: pentane/EtOAc = 20:1) to give the cross-coupled product **16** in 86% yield (41.9 mg, 86.4 μmol) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 20:1) = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.22 – 4.06 (m, 2H, $CO_2CH_2CH_3$), 2.54 (t, *J* = 7.3 Hz, 2H, CH_2CH_2C), 2.48 (s, 1H, $CHCO_2$), 1.66 – 1.53 (m, 2H, CH_2CH_2C), 1.40 – 1.19 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 1.14 – 0.97 (m, 21H, Si(*i*-Pr)$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 120.7, 92.1, 90.2, 89.1, 84.4, 62.7, 60.8, 32.1, 29.79, 29.77, 29.7, 29.6, 29.5, 29.3, 29.2, 26.6 (2C), 25.9, 22.8, 18.7, 14.5, 14.3, 11.4; **IR** (ν_{max}, cm^{-1}) 2952 (s), 2927 (s), 2859 (s), 2189 (w), 2102 (w), 1847 (w), 1730 (s), 1465 (m), 1387 (w), 1368 (w), 1333 (m), 1249 (m), 1181 (s), 1095 (w), 1076 (w), 1018 (m), 998 (m), 892 (w); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{53}O_2Si^+$ 485.3809; Found 485.3820.

7.11. Copper(I)-catalysed alkyne-azide cycloaddition of 14 and benzyl azide[61]

7.11.1. Synthesis and characterization of ethyl 2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-3-dodecylcycloprop-2-ene-1-carboxylate (17)

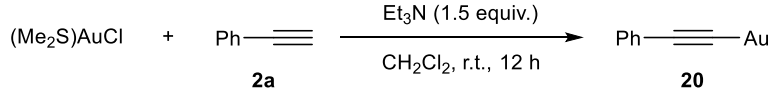


An oven-dried 10 mL Schlenk tube was sequentially charged with **14** (30.5 mg, 0.100 mmol, 1.00 equiv.), $CuSO_4 \cdot 5H_2O$ (1.25 mg, 5.00 μmol, 5.00 mol%), sodium ascorbate (NaAsc; 0.99 mg, 5.00 μmol, 5.00 mol%), $PhCO_2H$ (1.22 mg, 0.100 mmol, 10.0 mol%) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, *t*-BuOH (1.0 mL), deionized water (2.0 mL) and benzyl azide (16.0 mg, 0.120 mmol, 1.20 equiv.) was added. The reaction mixture was stirred at room temperature for 2 hours. The resulting reaction mixture was then diluted by adding CH_2Cl_2 (2.0 mL) and further extracted with CH_2Cl_2 (5.0 ml × 3). The combined organic layers were successively washed with brine and H_2O, then dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: pentane/EtOAc = 3:1) to give the cycloaddition product **17** in 72% yield (31.5 mg, 72.0 μmol) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.22; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (s, 1H, triazole), 7.33 – 7.27 (m, 3H, Ar*H*), 7.25 – 7.14 (m, 2H, Ar*H*), 5.54 – 5.37 (m, 2H, NCH_2Ph), 4.08 – 4.00 (m, 2H, $CO_2CH_2CH_3$), 2.57 (t, *J* = 7.4 Hz, 2H, CH_2CH_2C), 2.38 (s, 1H, C*H*CO_2), 1.65 – 1.57 (m, 2H, CH_2CH_2C), 1.41 – 1.06 (m, 21H, CH_2 & $CO_2CH_2CH_3$), 0.80 (t, *J* = 6.8 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.4, 137.2, 134.3, 129.3, 129.0, 128.3, 123.5, 111.3, 95.2, 60.4, 54.4, 32.0, 29.8, 29.7 (2C), 29.6, 29.5, 29.4 (2C), 27.1, 25.4, 22.8, 22.3, 14.4, 14.2; **IR** (ν_{max}, cm^{-1}) 3133 (w), 2925 (s), 2852 (m), 1897 (w), 1721 (s), 1459 (m), 1369 (w), 1335 (w), 1249 (m), 1184 (s), 1039 (m), 1004 (w), 802 (w), 723 (s); **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{40}N_3O_2^+$ 438.3115; Found 438.3120.

8. Mechanistic investigations

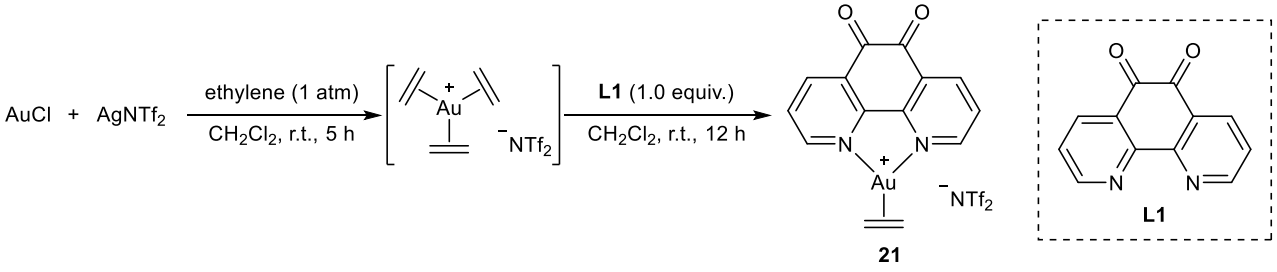
8.1. Preparation of potential gold catalysts

8.1.1. Preparation of the ligand-free polymeric gold(I)-phenylacetylide (20)[62]



A 10 mL Schlenk tube containing a stirring bar was charged with $(Me_2S)AuCl$ (147 mg, 0.500 mmol, 1.00 equiv.), dichloromethane (3.0 mL) and phenylacetylene **2a** (55 μL, 0.500 mmol, 1.00 equiv.) under air, sequentially. While stirring, Et_3N (104 μL, 0.750 mmol, 1.50 equiv.) was added dropwise, which resulted in the immediate formation of a yellow precipitate. After stirring for 12 hours at room temperature, the precipitate was filtered, washed with dichloromethane and dried under vacuum to give **20** in 66% yield (99.0 mg, 332 μmol) as a grey solid. **Anal**. Calcd for C_8H_5Au: C, 32.23; H, 1.69; N, 0.00; S, 0.00. Found: C, 31.69; H, 1.65; N, 0.03; S, 0.00.

8.1.2. Preparation of cationic gold(I)-ethylene complex (21)[63]



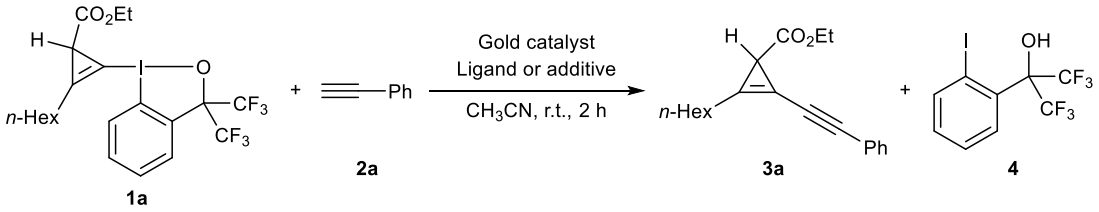
In a nitrogen-filled glovebox, a 100 ml Schlenk tube was sequentially charged with AuCl (93.0 mg, 0.400 mmol, 1.00 equiv.) and a magnetic stir bar then wrapped with foil to protect the contents from light. The Schlenk tube was then sealed with a rubber cap and brought out of the glovebox. Subsequently, the Schlenk tube was evacuated and backfilled with ethylene gas for three times by a balloon filled with ethylene (ca. 1 atm.). To the Schlenk tube was added dry CH_2Cl_2 (2.0 mL). The resulting solution was stirred for 5 min at room temperature. After that, a solution of $AgNTf_2$ (155 mg,

0.400 mmol, 1.00 equiv.) in CH_2Cl_2 (25 mL) was added via a syringe pump over 30 min. After the addition was complete, the mixture was stirred for additional 4.5 hours at room temperature. The resulting suspension[64] was filtered through a syringe filter (membrane-⌀: 25 mm; pore size: 0.2 μm). The filtrate was directly introduced into another 100 ml Schlenk tube (wrapped with aluminium foil and filled with nitrogen) charged with **L1** (84.1 mg, 0.400 mmol, 1.00 equiv.) and a magnetic stir bar. The resulting mixture was stirred at room temperature for 12 hours and then filtered through a syringe filter (membrane-⌀: 25 mm; pore size: 0.2 μm). The filtrate was directly introduced into a third 100 ml Schlenk tube (wrapped with aluminium foil and filled with nitrogen). Dry Et_2O (25 mL) was added slowly as a layer. The Schlenk tube was kept standing at room temperature with a balloon filled with nitrogen for 24 h, which gave a crystalline solid. After decanting the solvent, the solid was washed with Et_2O (3 × 10 mL) and dried in vacuo to afford the gold(I)-ethylene complex **21** (107 mg, 149 μmol, 37% yield) as a light-yellow crystal. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 9.09 (d, *J* = 4.9 Hz, 2H, Ar*H*), 8.83 (dd, *J* = 8.0, 1.6 Hz, 2H, Ar*H*), 8.06 (dd, *J* = 8.0, 5.2 Hz, 2H, Ar*H*), 4.01 (s, 4H, CH_2=CH_2); **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 175.2, 156.8, 151.2, 141.1, 130.2, 129.8, 120.0 (q, *J* = 321.6 Hz), 65.0; **^{19}F NMR** (376 MHz, CD_2Cl_2) δ -79.3; **IR** (ν_{max}, cm^{-1}) 3100 (w), 2982 (w), 2939 (w), 2888 (w), 1701 (m), 1577 (m), 1478 (w), 1432 (w), 1350 (s), 1335 (m), 1300 (w), 1194 (s), 1136 (m), 1053 (m), 934 (w), 818 (w), 791 (w), 734 (m), 710 (w); **HRMS** (ESI^+) m/z Calcd. for $C_{14}H_{10}AuN_2O_2$ $[M\text{-}NTf_2]^+$ 435.0402, found 435.0413; **Anal**. Calcd for $C_{12}H_6N_2O_2 \bullet C_2AuF_6NO_4S_2 \bullet C_2H_4$: C, 26.86; H, 1.41; N, 5.87; S, 8.96. Found: C, 28.09; H, 1.47; N, 6.14; S, 8.64.

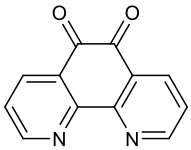
8.2. Control experiments for determining the catalytically active species

An oven-dried 10 mL Schlenk tube was sequentially charged with gold catalyst [(Me_2S)AuCl, **20** or **21**; 5.00 μmol, 5.00 mol%], **L1** (if used; 2.10 mg, 10.0 μmol, 10.0 mol%) or additive (if used; NBu_4X, X = Cl, F, Br, I; 5.00 μmol, 5.00 mol%), $NaHCO_3$ (if used; 25.2 mg, 0.300 mmol, 3.00 equiv.), CpBX **1a** (56.4 mg, 0.100 mmol, 1.00 equiv.) and a magnetic stir-bar. The Schlenk tube was then evacuated and backfilled with nitrogen three times. Subsequently, CH_3CN (0.10 M; 1.0 mL) and terminal alkyne **2a** (11 μL, 0.100 mmol, 1.00 equiv.) were added by syringe. The reaction mixture was stirred at room temperature for 2 hours (unless otherwise noted). The resulting reaction mixture was diluted with CH_2Cl_2 and filtered through a short pad of silica gel by eluting with CH_2Cl_2 (3 × 5.0 mL). The filtrate was then concentrated to dryness and the residue was subjected to flash column chromatography on silica gel (eluent: pentane/EtOAc = 20:1 to 5:1). The fractions that contained the product **3a**, **4** and the remained CpBX **1a** were collected and concentrated by rotary evaporation. The yields of **3a**, **4** and the recoveries of **1a** were obtained by quantitative ^{1}H NMR analysis using CH_2Br_2 (^{1}H NMR δ 4.92) as the internal standard.

Table 7 | Control experiments for determining the catalytically active species

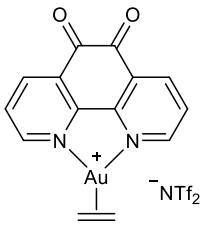


Entry	Gold catalyst (5 mol%)	Ligand or additive (mol%)	Yield of **3a** (%)[a]	Recovery of **1a** (%)[a]	Yield of **4** (%)[a]
1[b]	$(Me_2S)AuCl$	**L1** (10)	96	0	99
2	**20**	**L1** (10)	0	97	2
3[c]	**20**	**L1** (10)	7	87	9
4	**21**	none	10	84	13
5[d]	**21**	none	57	0	98
6	**21**	NBu_4Cl (5)	94	0	99
7	**21**	$NaHCO_3$[e]	10	78	20
8	**21**	NBu_4Br (5)	90	4	95
9	**21**	NBu_4F (5)	0	91	5
10	**21**	NBu_4I (5)	2	94	6



L1

20



21

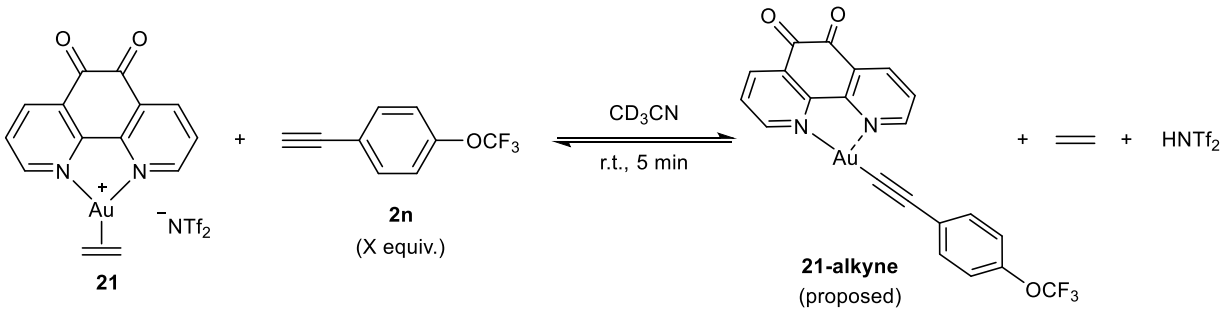
Reactions performed on a 100 μmol scale. [a]Yields or recovery were determined by ^1H NMR spectroscopy using dibromomethane as the internal standard. [b]Standard condition. [c]Reaction carried out at 40 °C for 24 h. [d]Reaction carried out at 40 °C for 10 h. [e]$NaHCO_3$ (3.00 equiv.) was used.

These results disfavour a catalytic cycle involving a direct oxidation of gold(I)-acetylide by CpBX, and cationic gold(I) species are competent in catalysing the reaction.

8.3. Stoichiometric reaction of cationic gold(I)-ethylene complex 21 and terminal alkyne 2n

To a 1.5 mL dry vial were sequentially added 1,3,5-tris(trifluoromethyl)benzene (internal standard) and 1-ethynyl-4-(trifluoromethoxy)benzene **2n** (1.00 or 20.0 equiv.). The vial was introduced into a nitrogen-filled glovebox. Then, the cationic gold(I)-ethylene complex **21** (1.00 equiv.) and CD_3CN (0.75 mL) was added. The vial was capped and shaken violently for 30 seconds. The resulting solution was transferred into a J. Young NMR tube and subjected to NMR spectroscopy analysis immediately. The yields of the proposed **21-alkyne** (δ –58.5 ppm) were determined by ^{19}F NMR analysis.

Table 8 | Generation of L1-ligated gold(I)-acetylide from cationic gold(I) species and alkyne



Entry	Reaction scale (μmol)	Initial concentration of **21** (mM)	Equiv. of **2n**	Yield of **21-alkyne** (proposed) (%)[a]
1	10	13.33	1.0	15
2	10	13.33	20.0	50
3	3.75	5	20.0	39
4	1.875	2.5	20.0	35

[a]Yields were determined by ^{19}F NMR spectroscopy.

The above experimental results showed that increasing the equivalent of terminal alkyne **2n** or the initial concentration of cationic gold(I)-ethylene complex **21** can push the equilibrium forward, thus affording higher yield of the proposed **L1**-ligated gold(I)-acetylide **21-alkyne**. Especially, the experimental result showed in entry 3 (Table 8) mimics the reaction condition in Table 7, entry 4. Both reaction conditions (Table 7, entry 4 and Table 8, entry 3) exhibited the same stoichiometric ratio of **21** and the terminal alkyne, as well as the same initial concentration of **21**. Therefore, it is reasonable to postulate that near 40% of the cationic gold(I)-ethylene complex **21** turned into the **L1**-ligated gold(I)-acetylide **21-alkyne** during the first 5 minutes for the reaction showed in Table 7, entry 4. However, extremely low yield of the desired cross-coupled product **3a** was observed and most of the oxidant **1a** was recovered in this case, which indicated that the **L1**-ligated gold(I)-acetylide **21-alkyne** is a catalytically inert species towards the oxidation of **1a**. Thus, gold(I)-acetylide is less likely involved in the productive catalytic cycle. The in-situ formation of the catalytically inactive species, i.e. gold(I)-acetylide, explained the low catalytic activity of cationic gold(I)-ethylene complex **21** towards the coupling reaction.

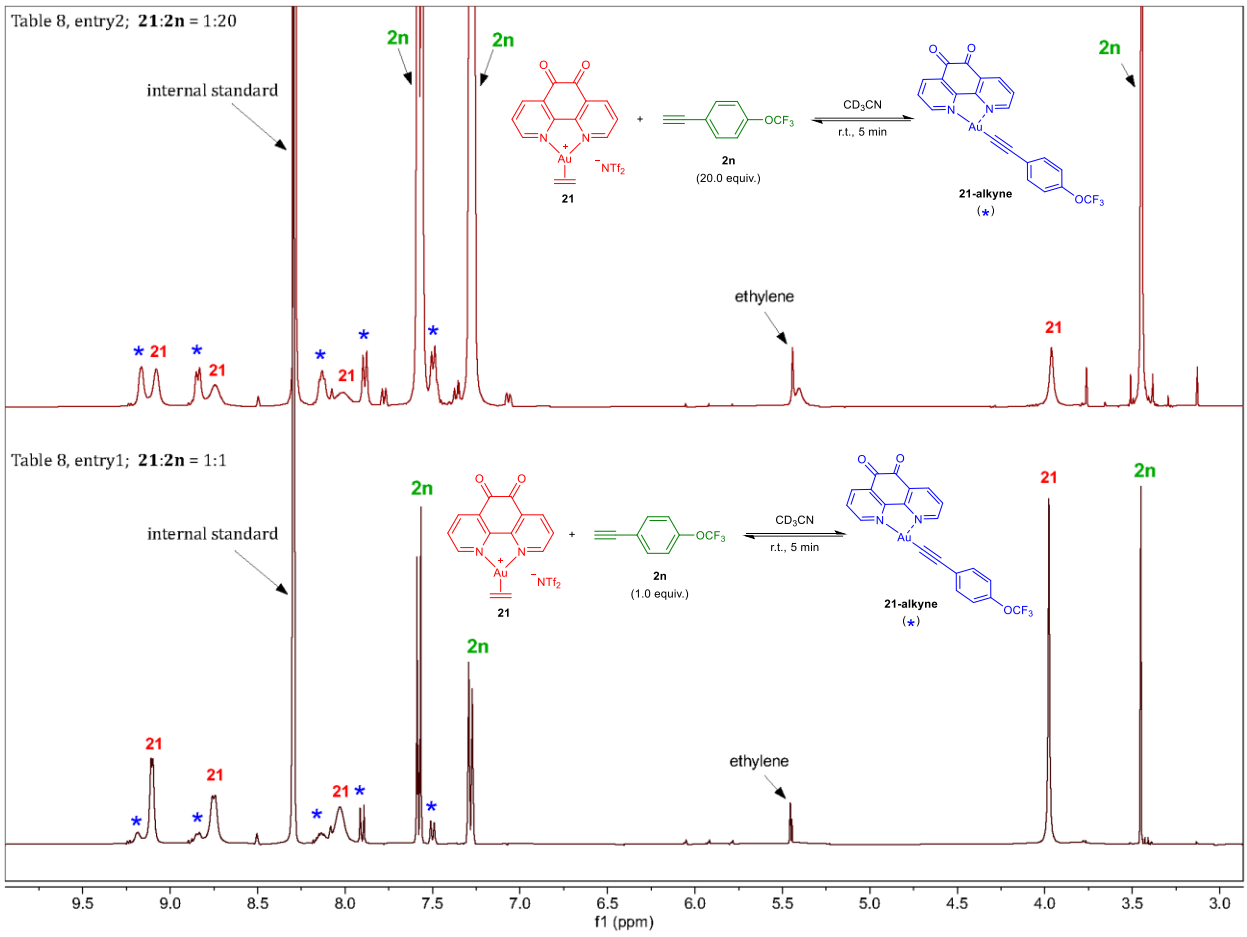


Fig. 2 | Stacked ^{1}H NMR spectra (CD_3CN, 25 °C) of stoichiometry study. The bottom ^{1}H NMR spectrum revealed the experiment showed in Table 8, entry 1; the top ^{1}H NMR spectrum revealed the experiment showed in Table 8, entry 2. The stacked spectra showed clearly that increasing the equivalent of **2n** led an increased consumption of cationic gold(I)-ethylene complex **21**, and gave an increased yield of the proposed **L1**-ligated gold(I)-acetylide **21-alkyne**. The ^{1}H NMR signals assigned to **21-alkyne** has been labelled with asterisk (*) in blue.

8.4. Generation of L1-ligated AuCl 22 from cationic gold(I)-ethylene complex 21 and Bu_4NCl

To a 1.5 mL dry vial were added tetrabutylammonium chloride (Bu_4NCl; 1.39 mg, 5.00 μmol, 1.00 equiv.). The vial was introduced into a nitrogen-filled glovebox. Then, the cationic gold(I)-ethylene complex **21** (3.6 mg, 5.00 μmol, 1.00 equiv.) and CD_2Cl_2 (0.75 mL) were sequentially added. The vial was capped and shaken violently for 20 seconds. The resulting solution was transferred into a J. Young NMR tube and subjected to NMR spectroscopy analysis immediately.

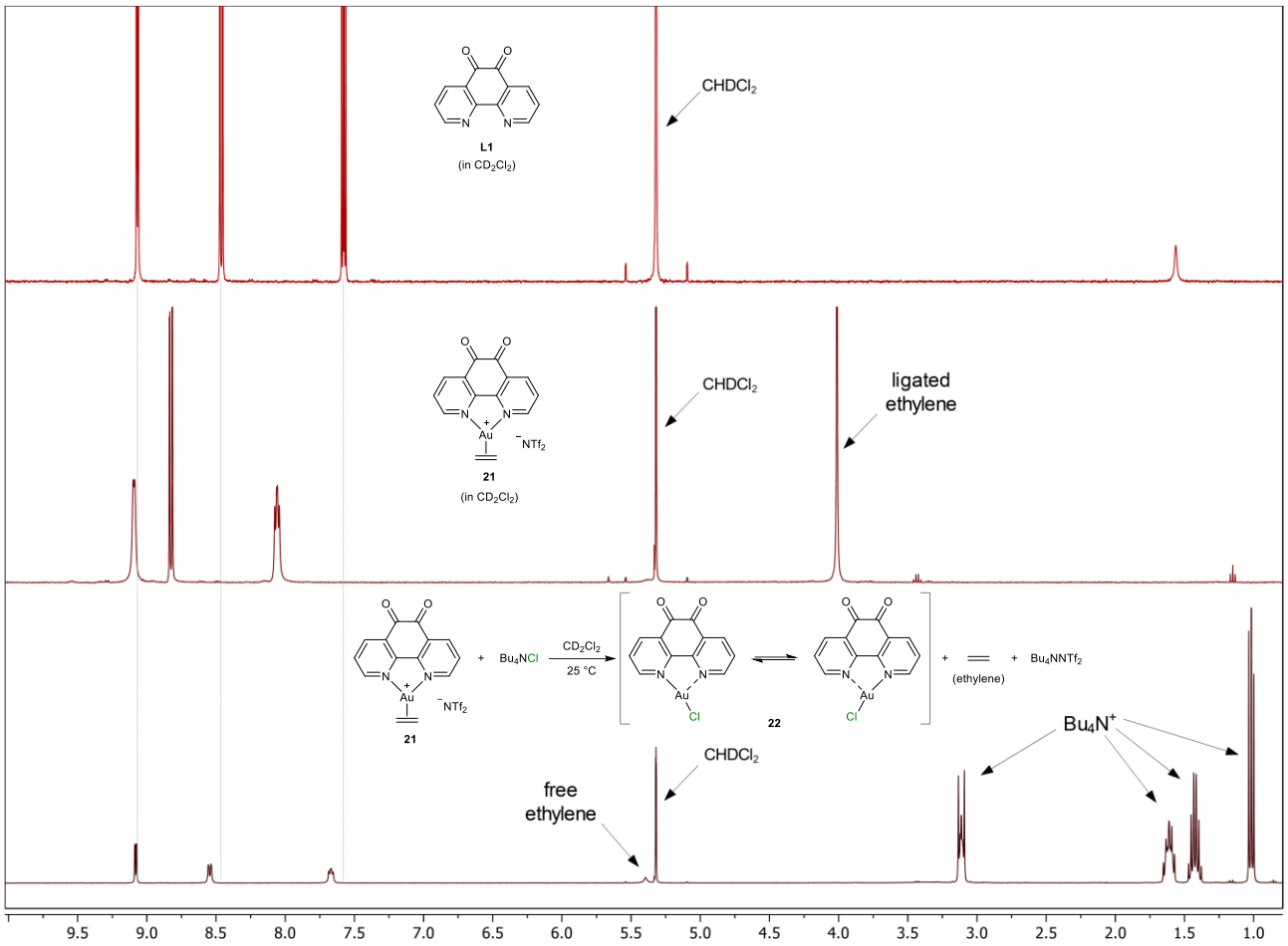


Fig. 3 | Stacked ^{1}H NMR spectra of equimolar mixture of 21 and NBu_4Cl in CD_2Cl_2 at 25 °C (bottom), ^{1}H NMR spectra of the authentic sample of L1 (top) and the cationic gold(I)-ethylene complex 21 (middle) in CD_2Cl_2 at 25 °C for reference. The bottom ^{1}H NMR spectrum showed that upon mixing cationic gold(I)-ethylene complex **21** and NBu_4Cl in CD_2Cl_2, a new set of proton signals derived from the ligand **L1** arose and the signals assigned to the free ethylene were also observed. Such results suggest that the ethylene ligand can be readily replaced by the σ-donor ligand, i.e. chloride irreversibly. The new proton signals (δ 9.2 – 7.5 ppm) can be putatively assigned to the **L1**-ligated AuCl **22**, which was envisaged to be a fluxional species in which the coordination site of gold(I) rapidly exchanges between the two nitrogen atoms of **L1**. **^{1}H NMR** of **22** (400 MHz, CD_2Cl_2) δ 9.08 (dd, *J* = 4.8, 1.8 Hz, 2H, Ar*H*), 8.55 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.67 (dd, *J* = 7.9, 4.8 Hz, 2H, Ar*H*).

8.5. Stoichiometric reaction of CpBX 1l and chloride-supported gold(I) catalyst

To a 1.5 mL dry vial were sequentially added 1,3,5-tris(trifluoromethyl)benzene (internal standard; 28.2 mg, 100 μmol, 5.00 equiv.), **L1** (4.20 mg, 20.0 μmol, 1.00 equiv.), (Me_2S)AuCl (5.89 mg, 20.0 μmol, 1.00 equiv.) and **1l** (12.4 mg, 20.0 μmol, 1.00 equiv.). The vial was introduced into a nitrogen-filled glovebox and CD_3CN (0.75 mL) was then added. The vial was capped and shaken violently for 20 seconds. The resulting solution was transferred into a J. Young NMR tube and subjected to NMR spectroscopy analysis immediately. The reaction was then monitored by NMR at 25 °C with a duration of ca. 5 hours. The conversion of **1a** and the yield of the homo-coupled product **23** were determined by ^{19}F NMR analysis.

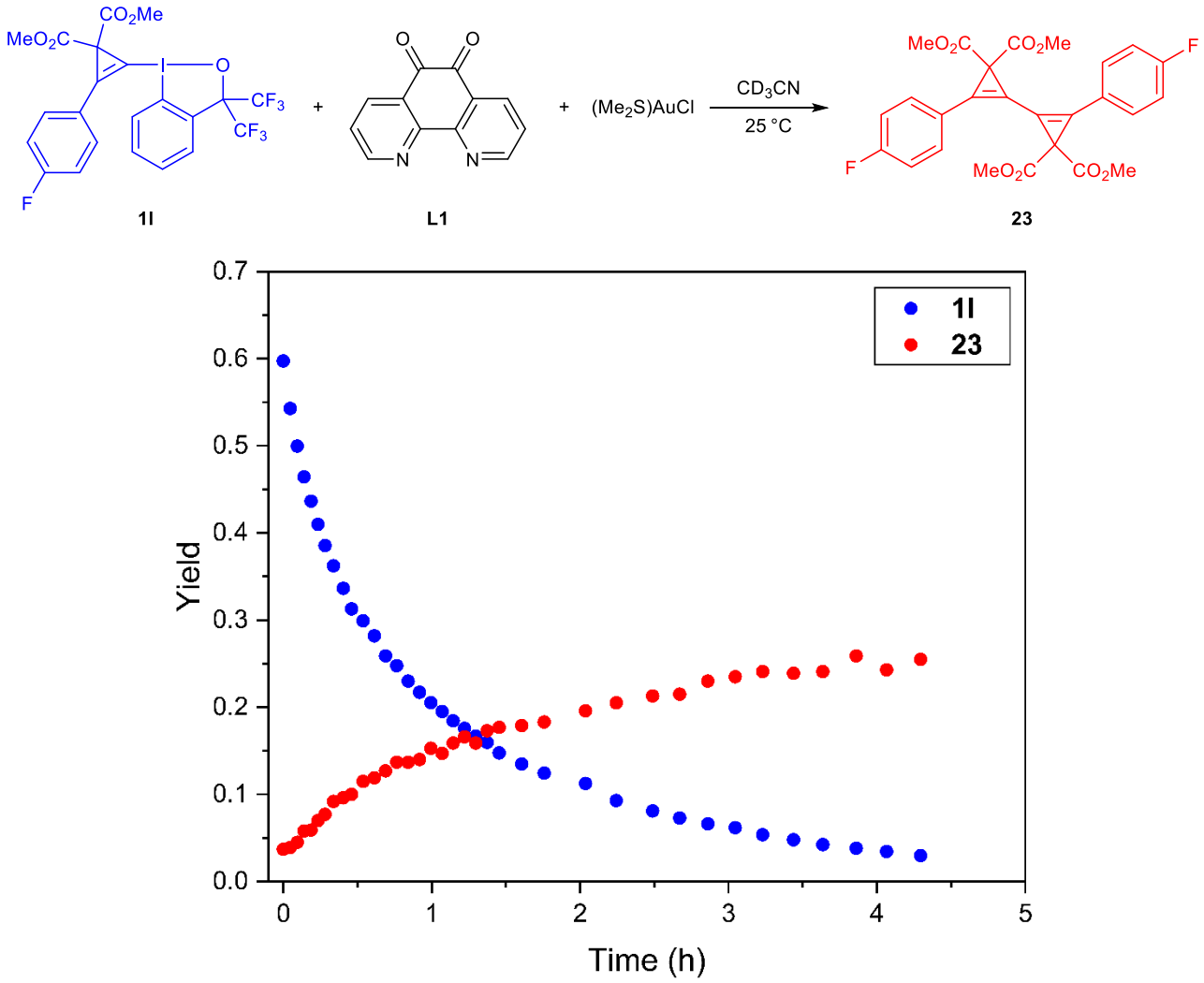


Fig. 4 | Reaction profile of the stoichiometric reaction of CpBX 1l and $(Me_2S)AuCl$ with L1 as the ligand in CD_3CN monitored by ^{19}F NMR at 25 °C. This stoichiometric reaction of CpBX **1l** and chloride-supported gold(I) catalyst clearly showed that the CpBX reagent can oxidize the gold(I) complex efficiently as proved by the full conversion of the reagent **1l** with the presence of the gold(I) species. The formation of the homo-coupled product **23** also indicated the involvement of an oxidation event (*vide infra*).

Upon the NMR monitoring experiment was done, the NMR sample was recovered and eluted with DCM. The resulting solution was filtered through a silica gel pad and eluted with CH_2Cl_2 (3 × 5.0 mL). The solvent was removed under reduced pressure, and the resulting crude residue was purified by flash column chromatography on silica gel (eluent: pentane/EtOAc = 3:1) to give the homo-coupled product **23** in 18% yield (0.90 mg, 1.81 μmol) as a colorless oil. **TLC**: R_f (*n*-hexane/EtOAc = 4:1) = 0.15; **^{1}H NMR** (400 MHz, CD_3CN) δ 7.81 – 7.78 (m, 4H, Ar*H*), 7.34 – 7.30 (m, 4H, Ar*H*), 3.71 (s, 12H, CO_2CH_3); **^{13}C NMR** (101 MHz, CD_3CN) δ 170.3, 165.5 (d, *J* = 252.5 Hz), 134.3 (d, *J* = 9.2 Hz), 121.7 (d, *J* = 3.3 Hz), 117.8 (d, *J* = 22.8 Hz), 112.5, 93.8 (d, *J* = 2.9 Hz), 53.4, 36.6; **^{19}F NMR** (376 MHz, CD_3CN) δ -108.0; **IR** (ν_{max}, cm^{-1}) 2955 (m), 2921 (s), 2851 (s), 1800 (w), 1740 (s), 1598 (m), 1502 (m), 1461 (m), 1436 (w), 1377 (w), 1287 (s), 1236 (s), 1187 (w), 1155 (m), 1067 (s), 925 (w), 842 (m); **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{20}F_2NaO_8^+$ 521.1018; Found 521.1022.

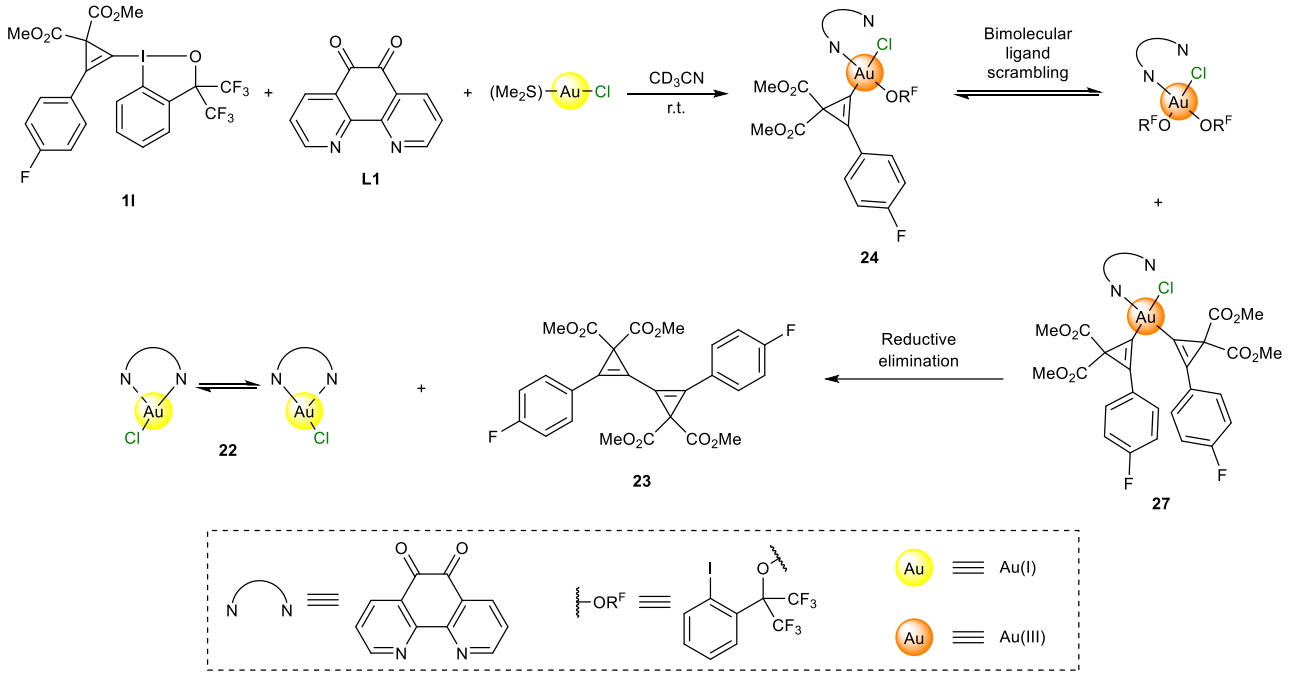


Fig. 5 | Proposed mechanism for the formation of homo-coupled product 23 by direct oxidation of gold(I) complex using CpBX. The homo-coupled product **23** can be generated by the reduction elimination of Au(III) species **27**, which can be derived from the bimolecular ligand scrambling of Au(III) species **24**.

8.6. Tandem mass spectrometry (ESI-MS/MS) analysis for the capture of active intermediates

8.6.1. General remarks

Samples were analyzed using a Waters Acquity-I-UPLC Class system (Waters Corporation, Milford, MA, USA), coupled with a Waters Vion IMS-QTof Mass Spectrometer equipped with LockSpray (Leucine-enkephalin, 200 pg/µL). The instrument was controlled by Waters UNIFI 1.9.4 (3.1.0, Waters Corporation, Milford, MA, USA). The injection volume was 5 µL, and the instrument was operated in positive polarity sensitivity mode (with a resolution of 33,000 FWHM at 556.2766 m/z). Data was acquired in HDMSe mode with a scan time of 0.036 seconds, and the recorded mass range was from 50 to 1200 m/z for both low and high energy spectra. The collision energy was ramped from 20 to 40 V, while the cone voltage was set to 30 V, capillary voltage was set to 3 kV, and the source offset was set to 50 V. The source temperature was set to 120°C, and the desolvation temperature was set to 500°C. The cone gas flow rate was set to 50 L/h, and the desolvation gas flow rate was set to 1000 L/h.

MS/MS experiments were performed on an LTQ Orbitrap FTMS instrument (LTQ Orbitrap Elite FTMS, Thermo Scientific, Bremen, Germany) operated in positive mode, coupled with a robotic chip-based nano-ESI source (TriVersa Nanomate, Advion Biosciences, Ithaca, NY, U.S.A.). A standard data acquisition and instrument control system were utilized (Thermo Scientific), while the ion source was controlled by Chipsoft 8.3.1 software (Advion BioScience). Samples were loaded onto a 96-well plate (Eppendorf, Hamburg, Germany) with an injection volume of 5 µL. The experimental conditions for the ionization voltage were +1.4 kV, and the gas pressure was set at 0.30 psi. The temperature of the ion transfer capillary was 120°C. FTMS spectra were obtained in the 80-1000 m/z range in the reduced profile mode, with a resolution set to 120,000. In all spectra, one microscan was acquired with a maximum injection time value of 1000 ms. The isolation window was set at 5 Da, and the NCE was typically between 20-24.

8.6.2. Tandem mass spectrometry for determining the intermediacy of Au(III) species 24

To a 1.5 mL dry vial were sequentially added **L1** (0.42 mg, 2.00 μmol, 1.00 equiv.), (Me_2S)AuCl (0.59 mg, 2.00 μmol, 1.00 equiv.) and **1l** (1.24 mg, 2.00 μmol, 1.00 equiv.). The vial was introduced into a nitrogen-filled glovebox and CH_3CN (1.0 mL) was then added. The vial was capped and shaken violently for 30 seconds. The resulting solution was subjected to tandem mass spectrometry (ESI-MS/MS) analysis in 5 min.

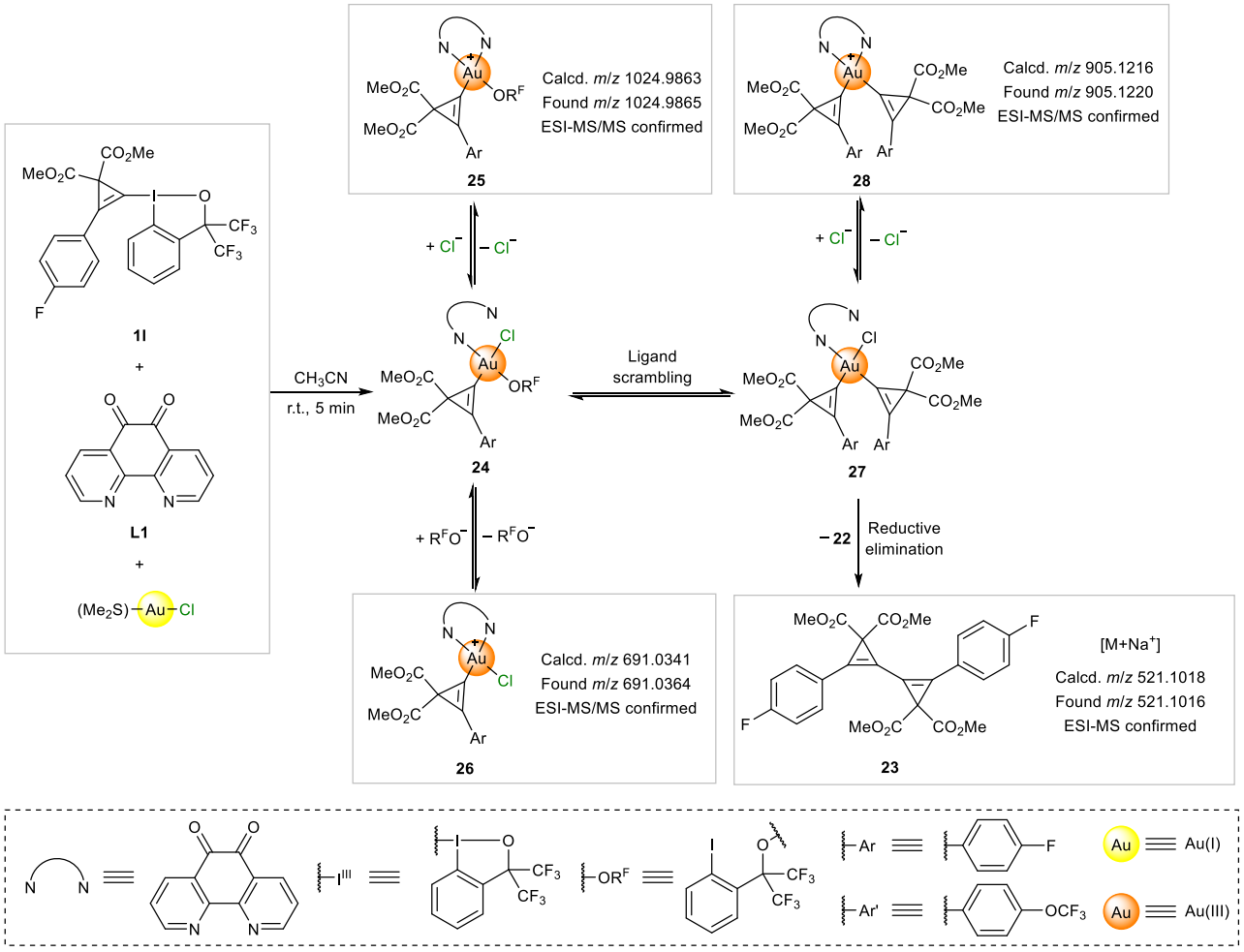


Fig. 6 | Tandem mass spectrometry (ESI-MS/MS) analysis of the stoichiometric reaction of CpBX 1l, (Me_2S)AuCl and L1 determined the formation of intermediate 24. Although **24** was not observed directly by mass spectrometry due to its electroneutral nature, cationic Au(III) species **25** and **26** derived from **24** by losing one anionic fragment were both observed by ESI-MS and structurally confirmed by tandem mass spectrometry (MS/MS) (*vide infra*). Moreover, the cationic Au(III)-bis(cyclopropenyl) species **28** derived from **27** by losing chloride was also observed, thus indicating the mechanism for the formation of **23**, i.e., ligand scrambling of **24** to **27** followed by reduction elimination to furnish **23**.

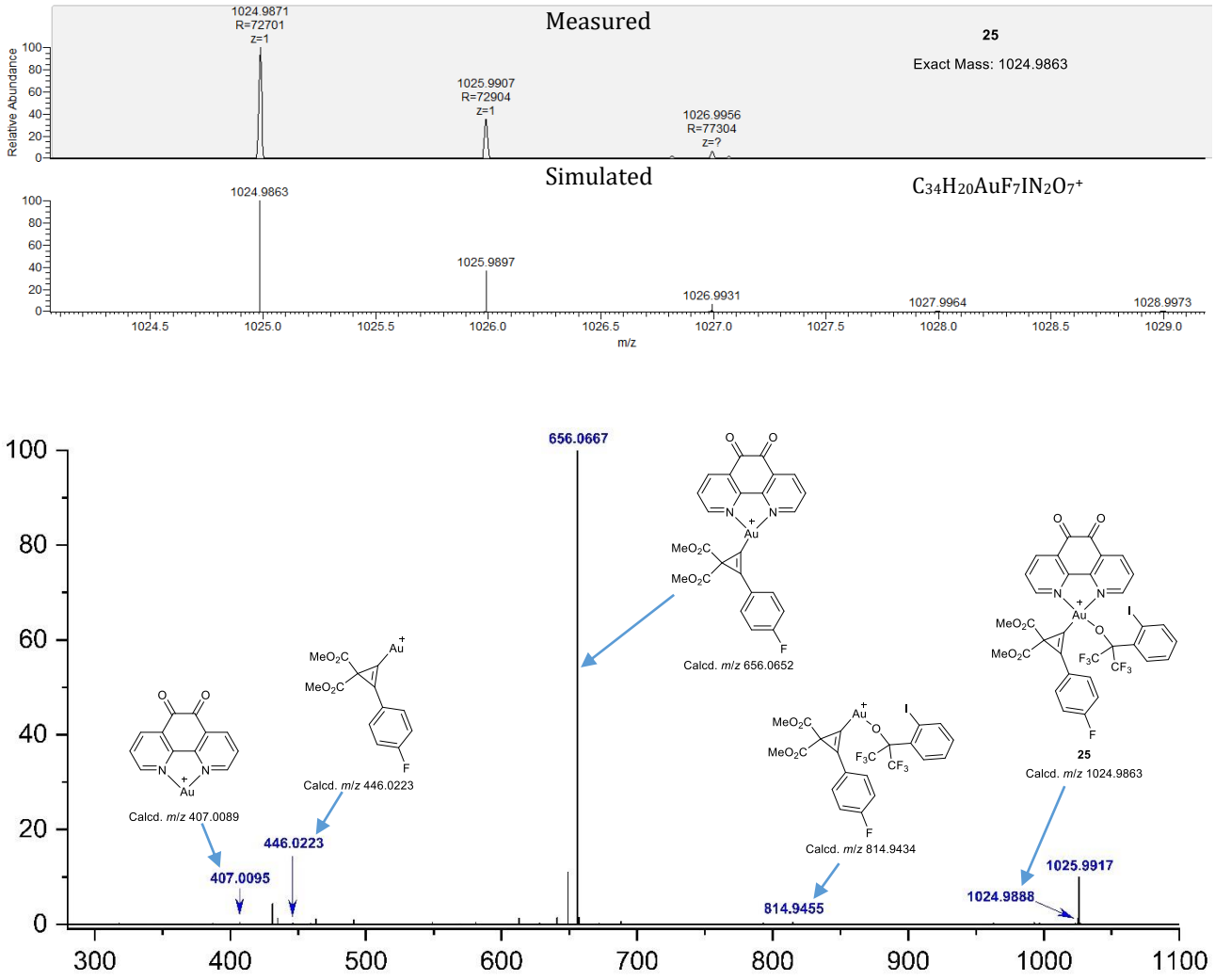
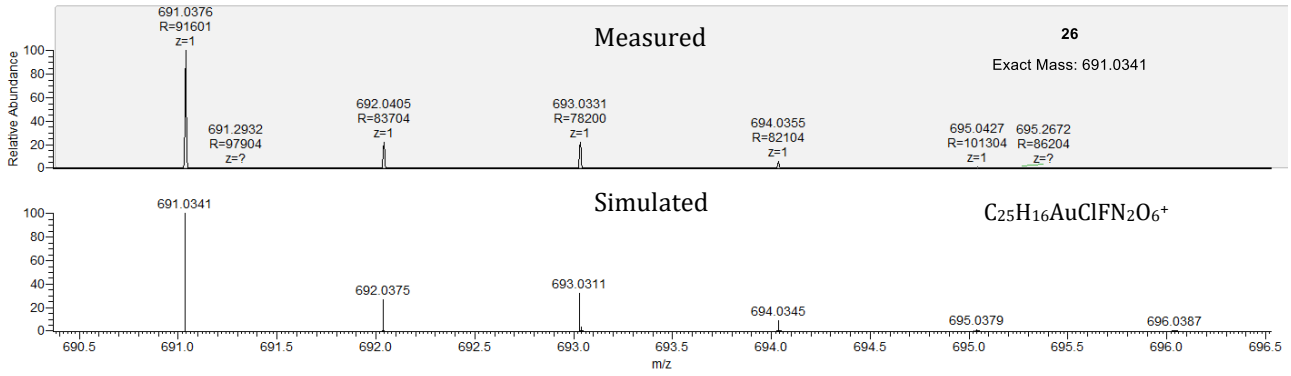


Fig. 7 | Tandem mass spectra of stoichiometric reaction of CpBX 1l, (Me_2S)AuCl and L1, isolated precursor ion *m/z* 1024.90. Cationic Au(III) species **25** derived from **24** by losing chloride was observed by ESI-MS (top) and structurally confirmed by tandem mass spectrometry (MS/MS; bottom).



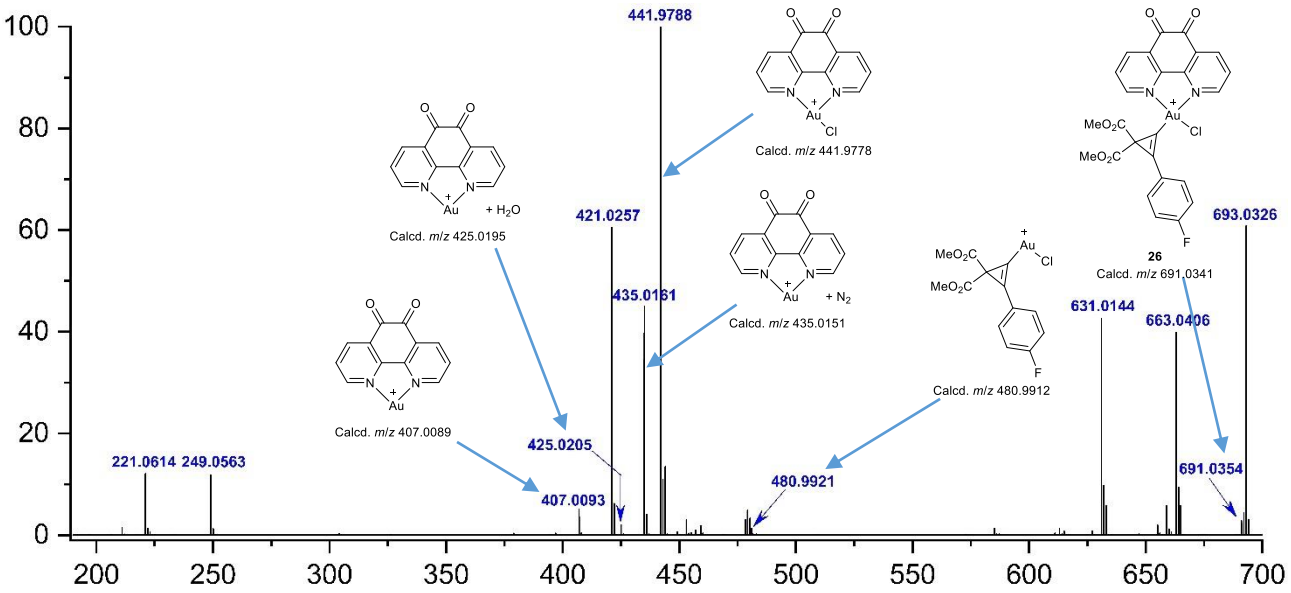


Fig. 8 | Tandem mass spectra of stoichiometric reaction of CpBX 1l, (Me_2S)AuCl and L1, isolated precursor ion *m/z* 691.03. Cationic Au(III) species **26** derived from **24** by losing R^FO^- was observed by ESI-MS (top) and structurally confirmed by tandem mass spectrometry (MS/MS; bottom).

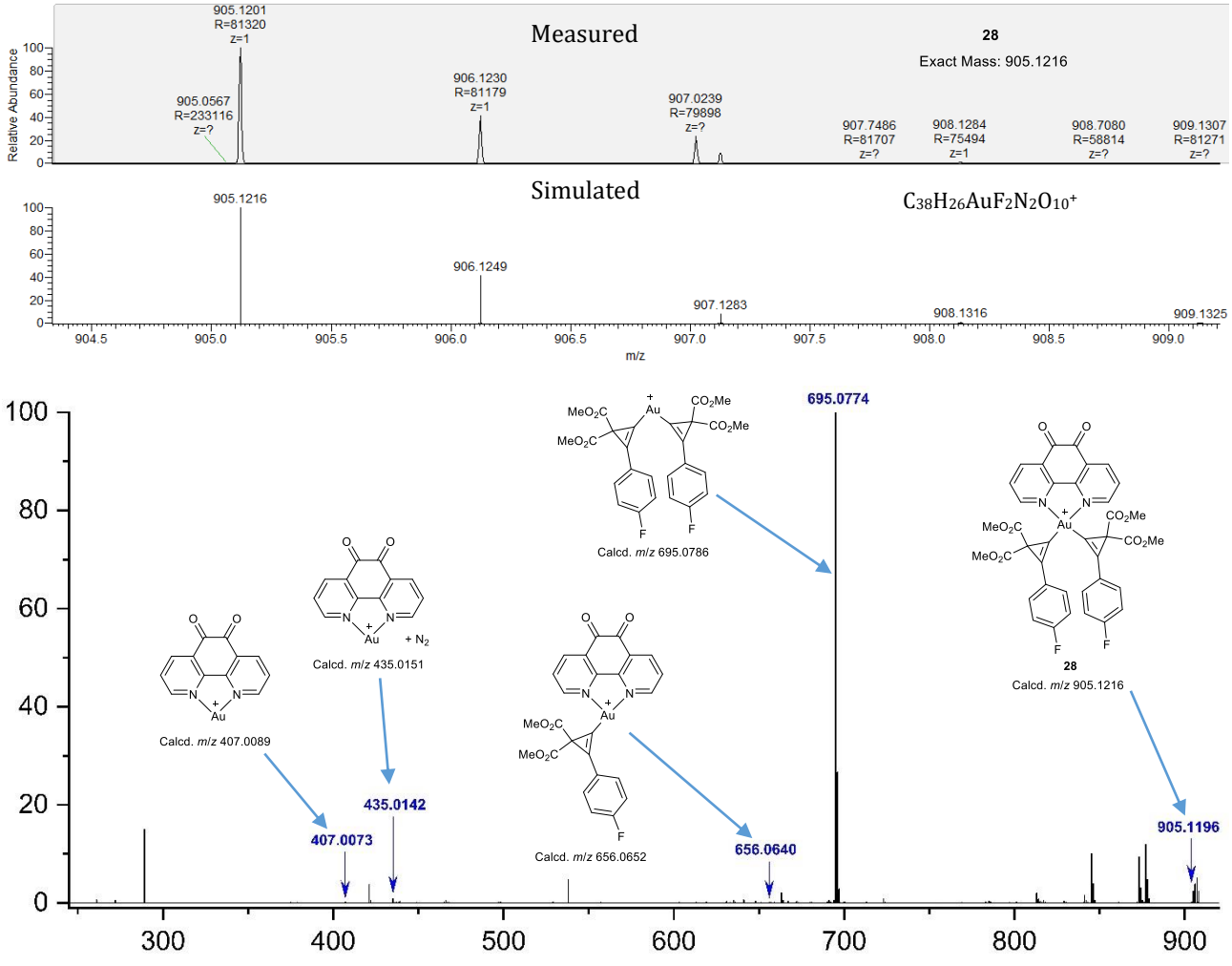


Fig. 9 | Tandem mass spectra of stoichiometric reaction of CpBX 1l, (Me_2S)AuCl and L1, isolated precursor ion *m/z* 906.00. Cationic Au(III) species **28** derived from **27** by losing chloride was observed by ESI-MS (top) and structurally confirmed by tandem mass spectrometry (MS/MS; bottom).

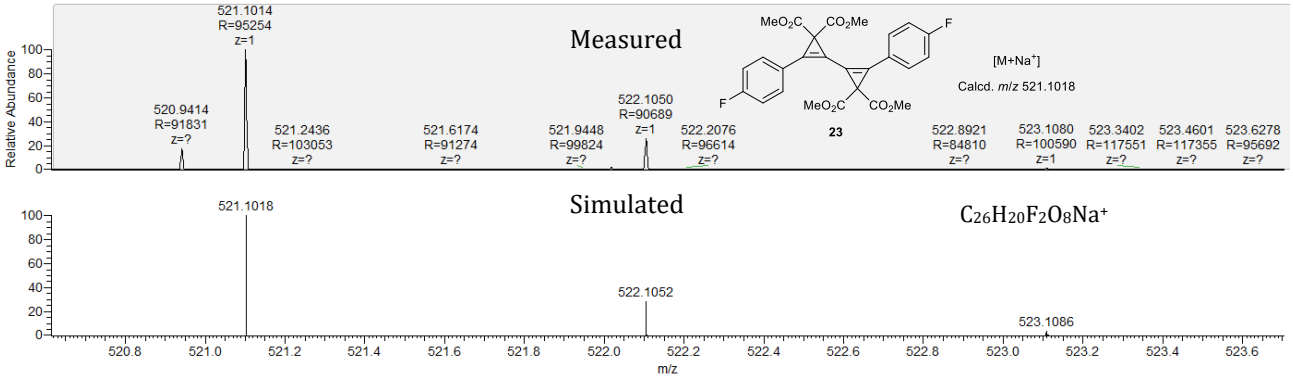


Fig. 10 | Mass spectra of stoichiometric reaction of CpBX 1l, (Me_2S)AuCl and L1. Homo-coupling product **23** derived from **27** by reduction elimination was confirmed by ESI-MS.

8.6.3. Tandem mass spectrometry for determining the intermediacy of Au(III) species 29

To a 1.5 mL dry vial were sequentially added terminal alkyne **2n** (0.37 mg, 2.00 μmol, 1.00 equiv.), **L1** (0.42 mg, 2.00 μmol, 1.00 equiv.), (Me_2S)AuCl (0.59 mg, 2.00 μmol, 1.00 equiv.) and **1l** (1.24 mg, 2.00 μmol, 1.00 equiv.). The vial was introduced into a nitrogen-filled glovebox and CH_3CN (1.0 mL) was then added. The vial was capped and shaken violently for 30 seconds. The resulting solution was subjected to tandem mass spectrometry (ESI-MS/MS) analysis in 5 min.

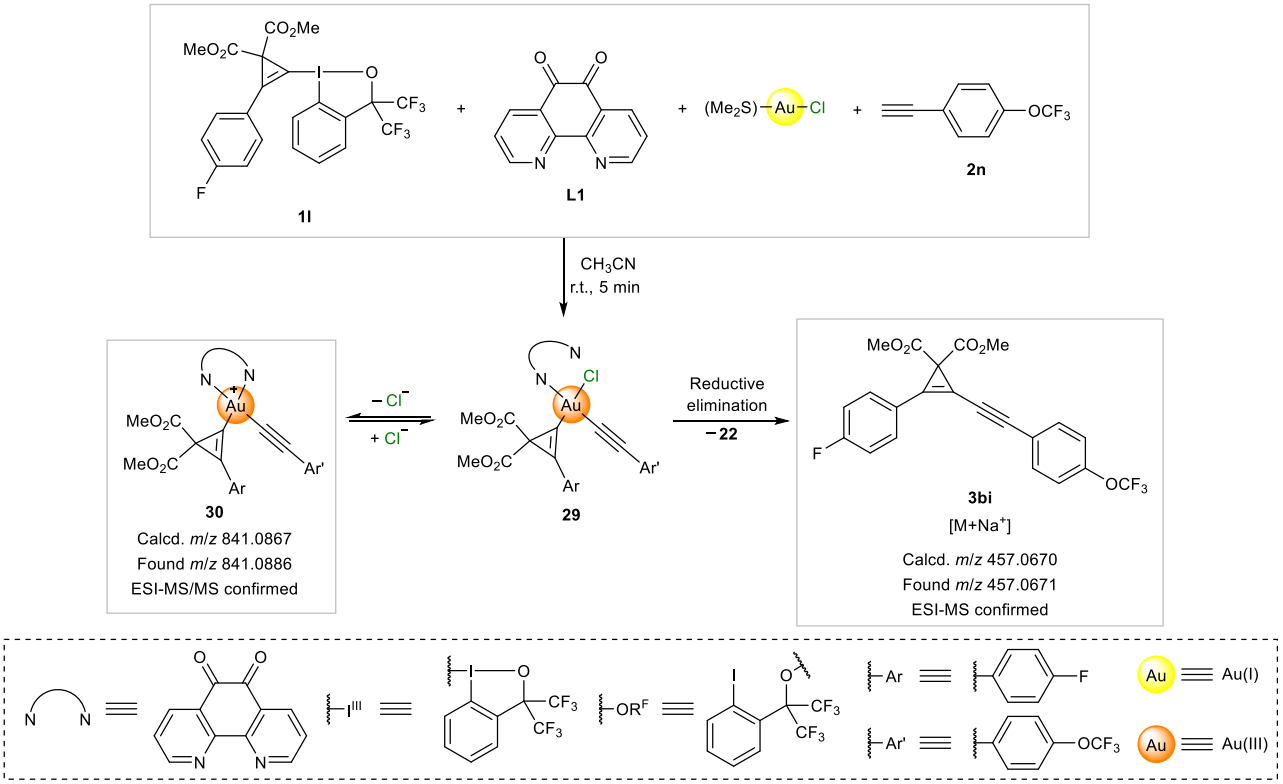


Fig. 11 | Tandem mass spectrometry (ESI-MS/MS) analysis of the stoichiometric reaction of CpBX 1l, (Me_2S)AuCl, L1 and alkyne 2n determined the formation of Au(III) intermediate 29. The cationic Au(III) species **30** derived from **29** by losing chloride was observed by ESI-MS and was further structurally determined by MS/MS analysis, thus providing direct evidence for the

participation of the Au(III)-cyclopropenyl species in the catalytic cycle. The Au(III) intermediate **29** is the key organogold species to connect the transmetallation and reductive elimination step.

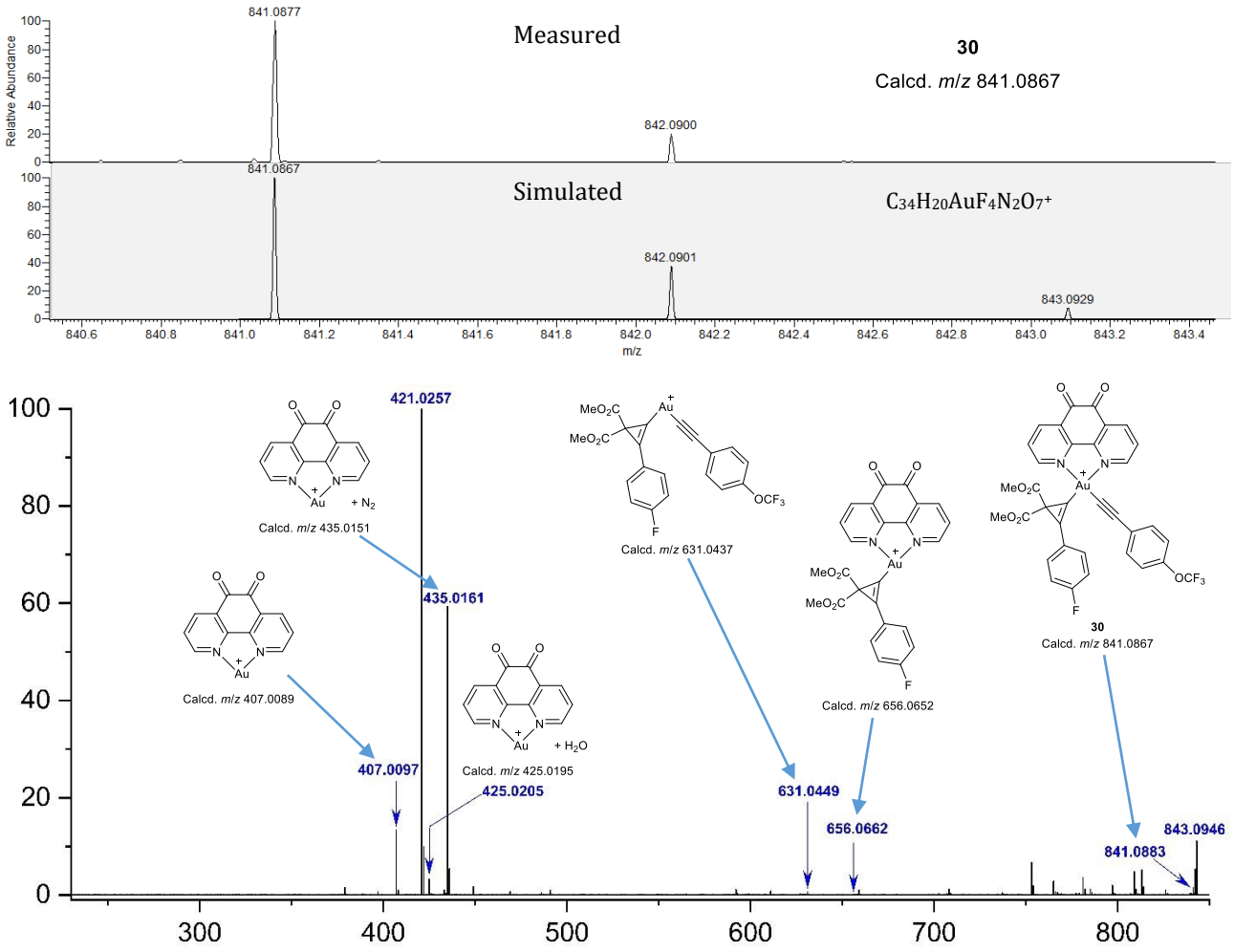


Fig. 12 | Tandem mass spectra of stoichiometric reaction of CpBX 1l, (Me_2S)AuCl, L1 and alkyne 2n, isolated precursor ion *m/z* 841.10. Cationic Au(III) species **30** derived from **29** by losing chloride was observed by ESI-MS (top) and structurally confirmed by tandem mass spectrometry (MS/MS; bottom).

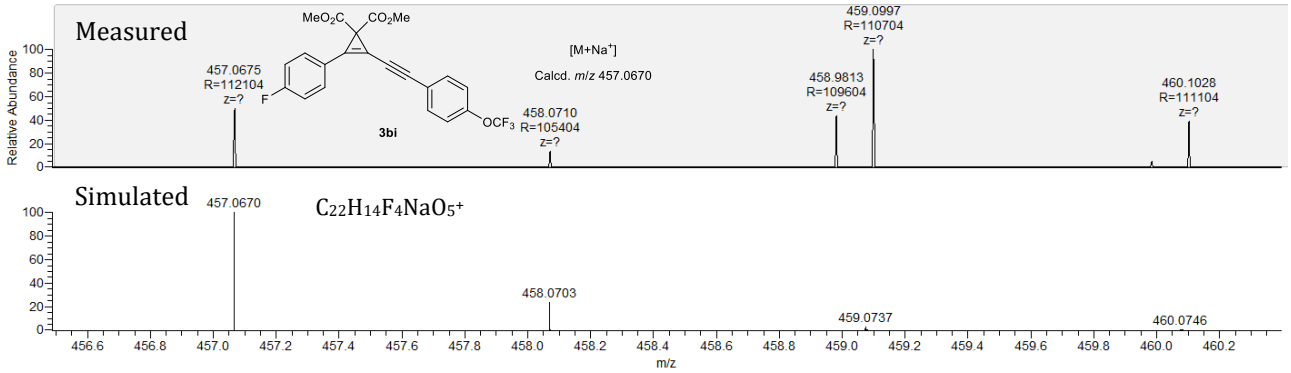


Fig. 13 | Mass spectra of stoichiometric reaction of CpBX 1l, (Me_2S)AuCl, L1 and alkyne 2n. Cross-coupling product **3bi** derived from **29** by reduction elimination was confirmed by ESI-MS.

8.6.4. Tandem mass spectrometry evidence for the oxidation event of cationic Au(I) and CpBXs

To a 1.5 mL dry vial was added CpBX **1l** (1.24 mg, 2.00 μmol, 1.00 equiv.). The vial was introduced into a nitrogen-filled glovebox. Then, gold(I)-ethylene complex **21** (1.4 mg, 2.00 μmol, 1.00 equiv.) and CH_3CN (1.0 mL) was then added. The vial was capped and shaken violently for 30 seconds. The resulting solution was subjected to tandem mass spectrometry (ESI-MS/MS) analysis in 5 min.

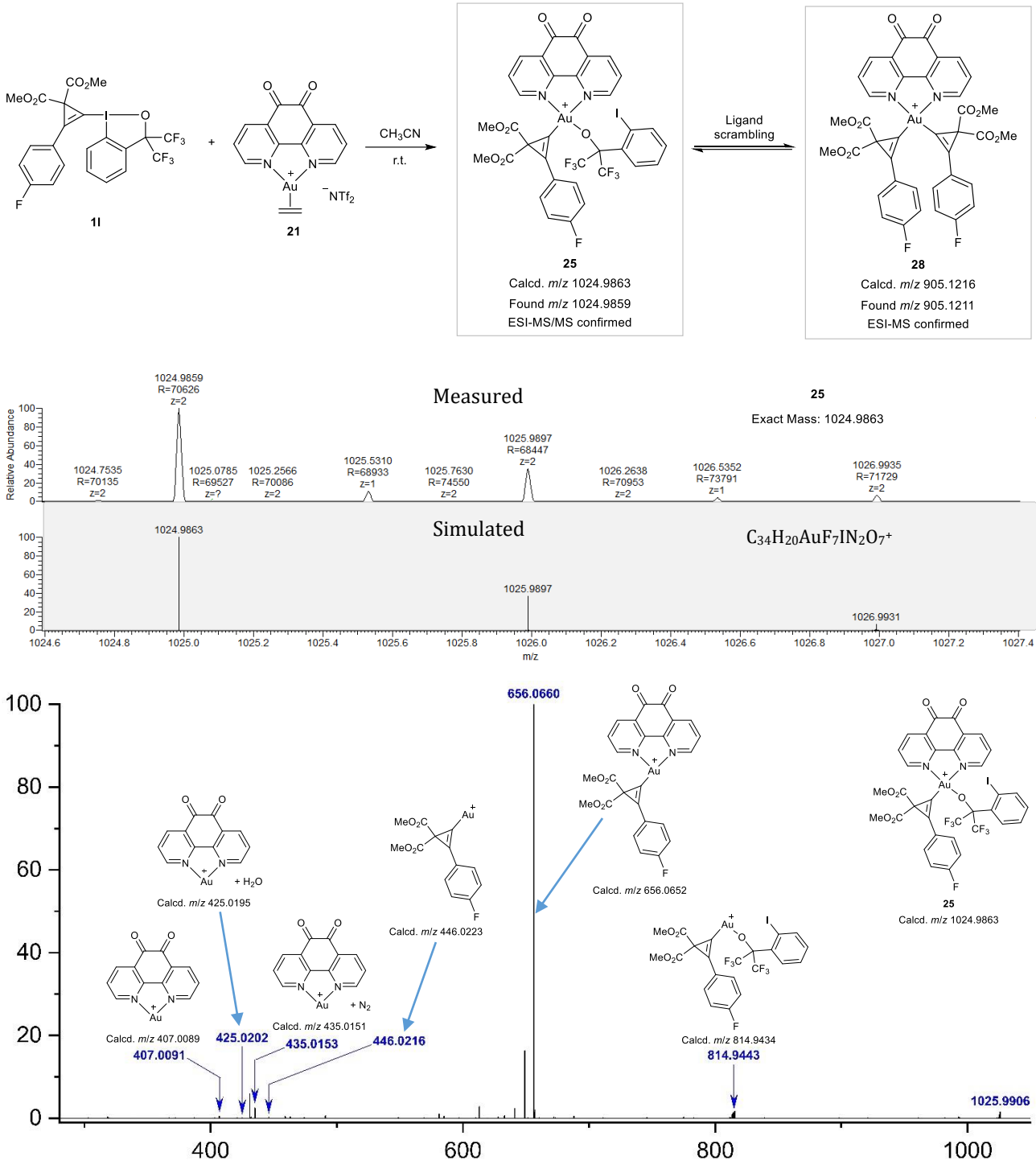


Fig. 14 | Tandem mass spectra of stoichiometric reaction of CpBX 1l and cationic gold(I)-ethylene complex 21, isolated precursor ion *m/z* 1025.00. Cationic Au(III) species **25** was observed by ESI-MS (top) and structurally confirmed by tandem mass spectrometry (MS/MS; bottom), which revealed that the CpBXs can oxidize cationic gold(I) species directly.

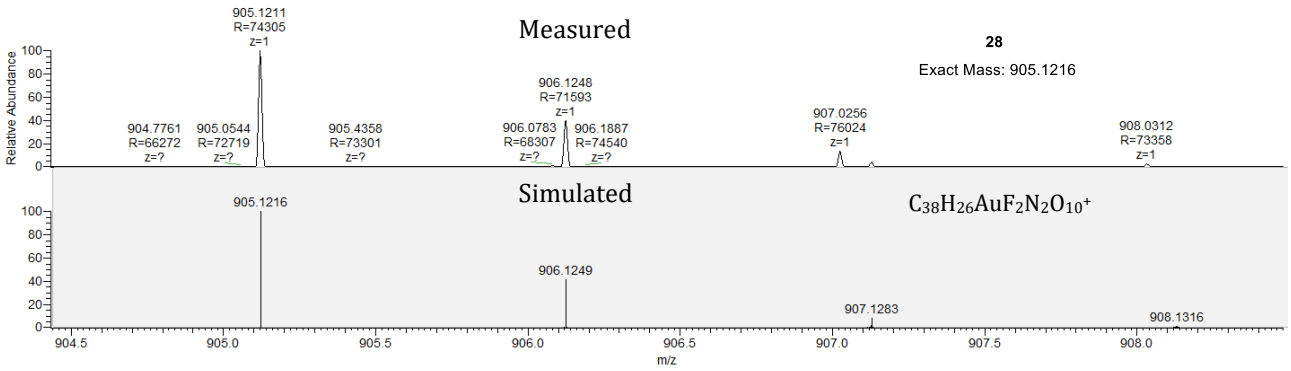


Fig. 15 | Mass spectra of stoichiometric reaction of CpBX 1l and cationic gold(I)-ethylene complex 21. Cationic Au(III) species **28** derived from **25** by ligand scrambling was observed by ESI-MS.

8.7. Stoichiometric reaction monitored by NMR

8.7.1. Stoichiometric reaction of CpBX 1l, $(Me_2S)AuCl$ and alkyne 2n with L1 as the ligand

To a 1.5 mL dry vial were sequentially added 1,3,5-tris(trifluoromethyl)benzene (internal standard; 28.2 mg, 100 μmol, 5.00 equiv.), 1-ethynyl-4-(trifluoromethoxy)benzene **2n** (3.72 mg, 20.0 μmol, 1.00 equiv.), **L1** (4.20 mg, 20.0 μmol, 1.00 equiv.), $(Me_2S)AuCl$ (5.89 mg, 20.0 μmol, 1.00 equiv.) and CpBX **1l** (12.4 mg, 20.0 μmol, 1.00 equiv.). The vial was introduced into a nitrogen-filled glovebox. Then, CD_3CN (0.75 mL) was added. The vial was capped and shaken violently for 20 seconds. The resulting solution was transferred into a J. Young NMR tube and subjected to NMR spectroscopy analysis immediately at 25 °C.

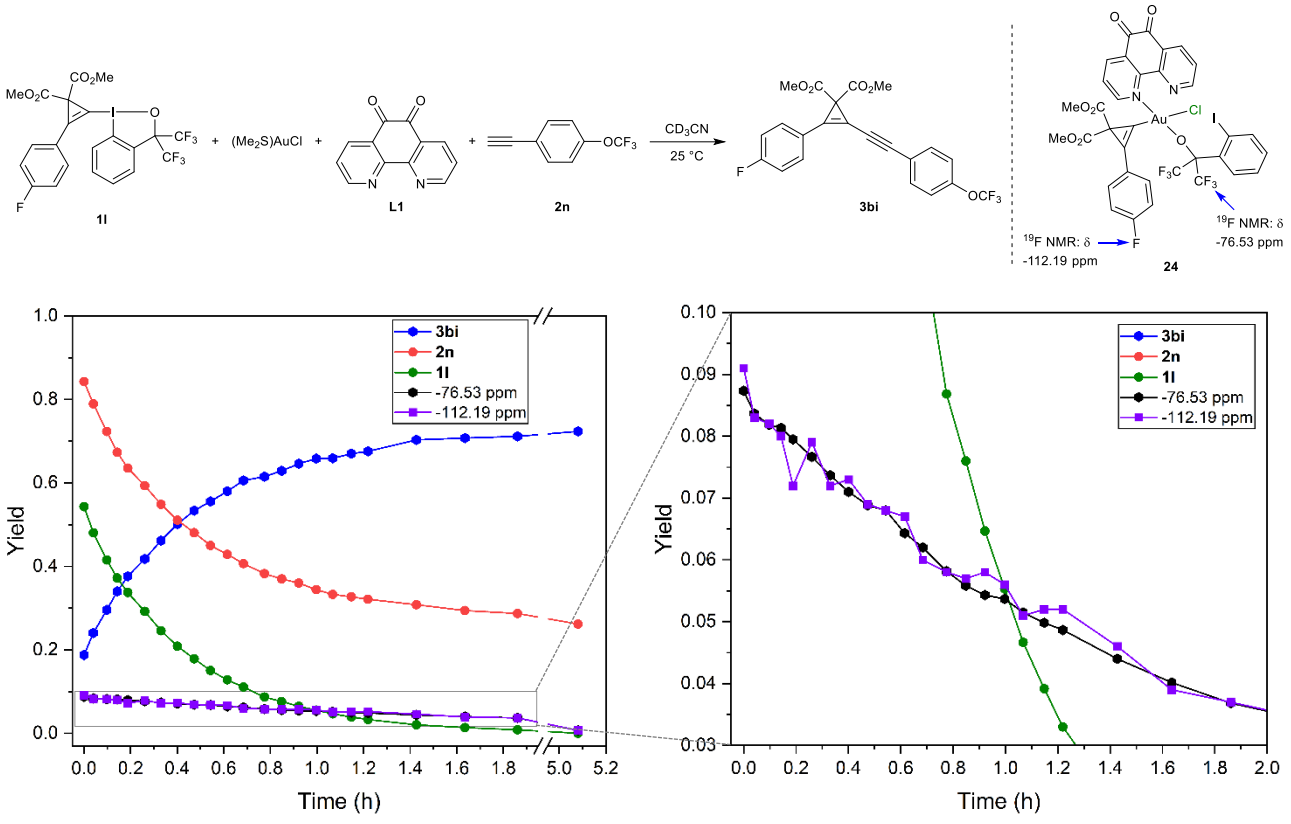


Fig. 16 | Reaction profile of the stoichiometric reaction of CpBX 1l, $(Me_2S)AuCl$ and alkyne 2n with L1 as the ligand in CD_3CN monitored by ^{19}F NMR at 25 °C. The yield of **3bi** (δ -58.58 ppm) and

the conversion of **2n** (δ -58.68 ppm), **1l** (δ -76.53 ppm) were determined by ^{19}F NMR. The NMR monitoring experiment showed that the consuming rate of CpBX **1l** is faster than that of terminal alkyne **2n**. Interestingly, two ^{19}F NMR signals (δ -76.53 ppm and -112.19 ppm) showed high correlation during the whole reaction course, thus allowing a tentative assignment of the two ^{19}F NMR signals to the proposed cyclopropenyl-Au(III) intermediate **24**.

8.7.2. Stoichiometric reaction of CpBX 1l, gold(I)-ethylene complex 21 and alkyne 2n

To a 1.5 mL dry vial were sequentially added 1,3,5-tris(trifluoromethyl)benzene (internal standard; 28.2 mg, 100 μmol, 5.00 equiv.), 1-ethynyl-4-(trifluoromethoxy)benzene **2n** (3.72 mg, 20.0 μmol, 1.00 equiv.) and CpBX **1l** (12.4 mg, 20.0 μmol, 1.00 equiv.). The vial was introduced into a nitrogen-filled glovebox. Then, gold(I)-ethylene complex **21** (14.3 mg, 20.0 μmol, 1.00 equiv.) and CD_3CN (0.75 mL) was added. The vial was capped and shaken violently for 20 seconds. The resulting solution was transferred into a J. Young NMR tube and subjected to NMR spectroscopy analysis immediately at 25 °C.

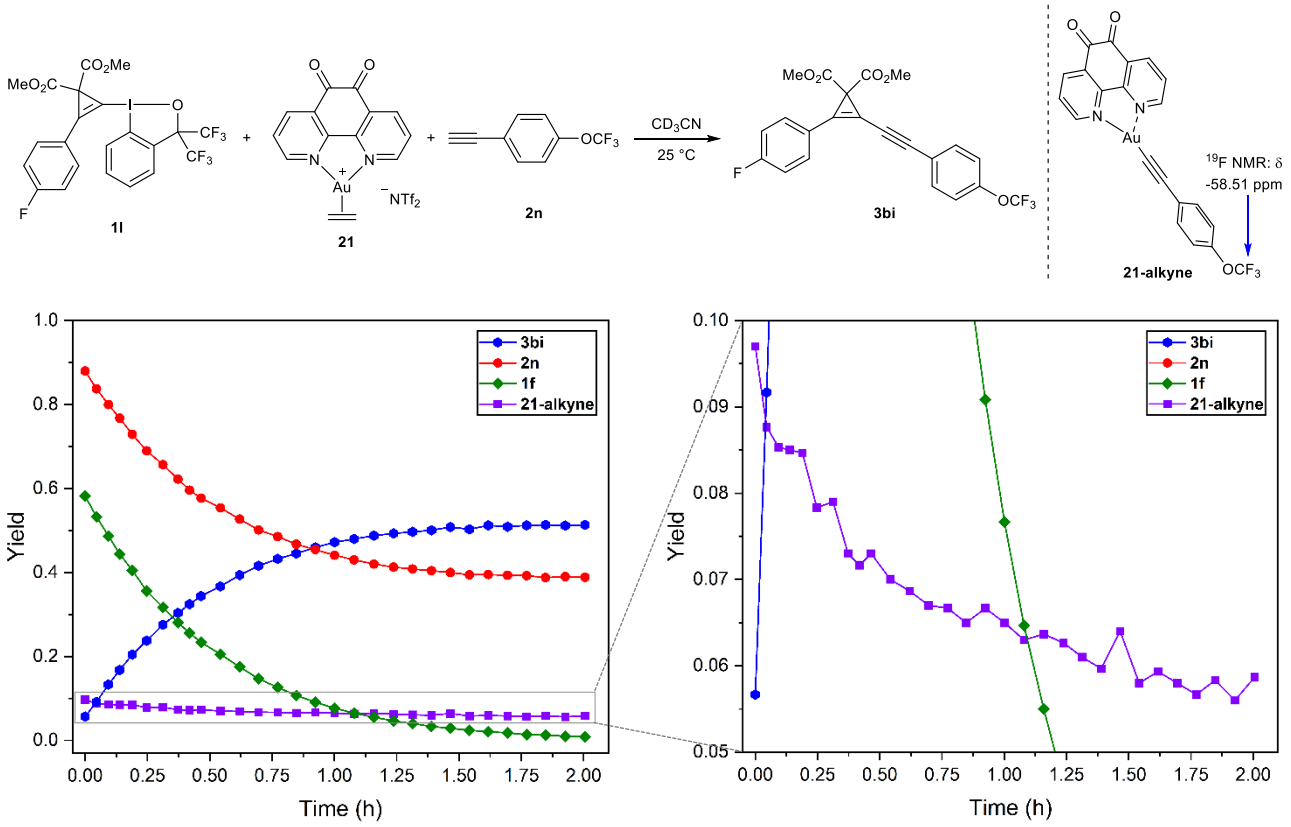


Fig. 17 | Reaction profile of the stoichiometric reaction of CpBX 1l, gold(I)-ethylene complex 21 and alkyne 2n in CD_3CN monitored by ^{19}F NMR at 25 °C. Although the gold(I)-acetylide **21-alkyne** was observed in the stoichiometric reaction, however, unlike the case in Table 7, entry 4 (**2a**:**21** = 20:1), the stoichiometric reaction of CpBX **1l**, gold complex **21** and alkyne **2n** (**2n**:**21** = 1:1) took place smoothly and the product **3bi** was observed in around 60% yield in the end, which was close to the yield observed in Table 7, entry 5. These results indicate that using excess amount of gold(I)-ethylene complex **21** can restore the catalytic activity of **21** even if partial gold(I)-ethylene complex **21** was consumed by the formation of the catalytically inert gold(I)-acetylide. However, the yield of the desired product **3bi** was comparatively lower than the one using chloride-supported Au(I) catalyst (as revealed by the case showed in Fig. 8), thus suggesting the significant role of chloride in maintaining high efficiency and turn-over number of the gold catalyst. The gradual consumption of gold(I)-acetylide **21-alkyne** in the stoichiometric reaction can be explained by the reversible release of free

terminal alkyne **2n** in view of the decreasing concentration of **2n** as the reaction going on. Alternatively, gold(I)-acetylide **21-alkyne** underwent smooth transmetallation with the cyclopropenyl-Au(III) intermediate **25** (*vide infra*), thus resulting its decreasing concentration during the reaction course.

8.7.3. Stoichiometric reaction of CpBX 1l and gold(I)-ethylene complex 21

To a 1.5 mL dry vial were sequentially added 1,3,5-tris(trifluoromethyl)benzene (internal standard; 28.2 mg, 100 μmol, 5.00 equiv.) and CpBX **1l** (12.4 mg, 20.0 μmol, 1.00 equiv.). The vial was introduced into a nitrogen-filled glovebox. Then, gold(I)-ethylene complex **21** (14.3 mg, 20.0 μmol, 1.00 equiv.) and CD_3CN (0.75 mL) was added. The vial was capped and shaken violently for 20 seconds. The resulting solution was transferred into a J. Young NMR tube and subjected to NMR spectroscopy analysis immediately at 25 °C.

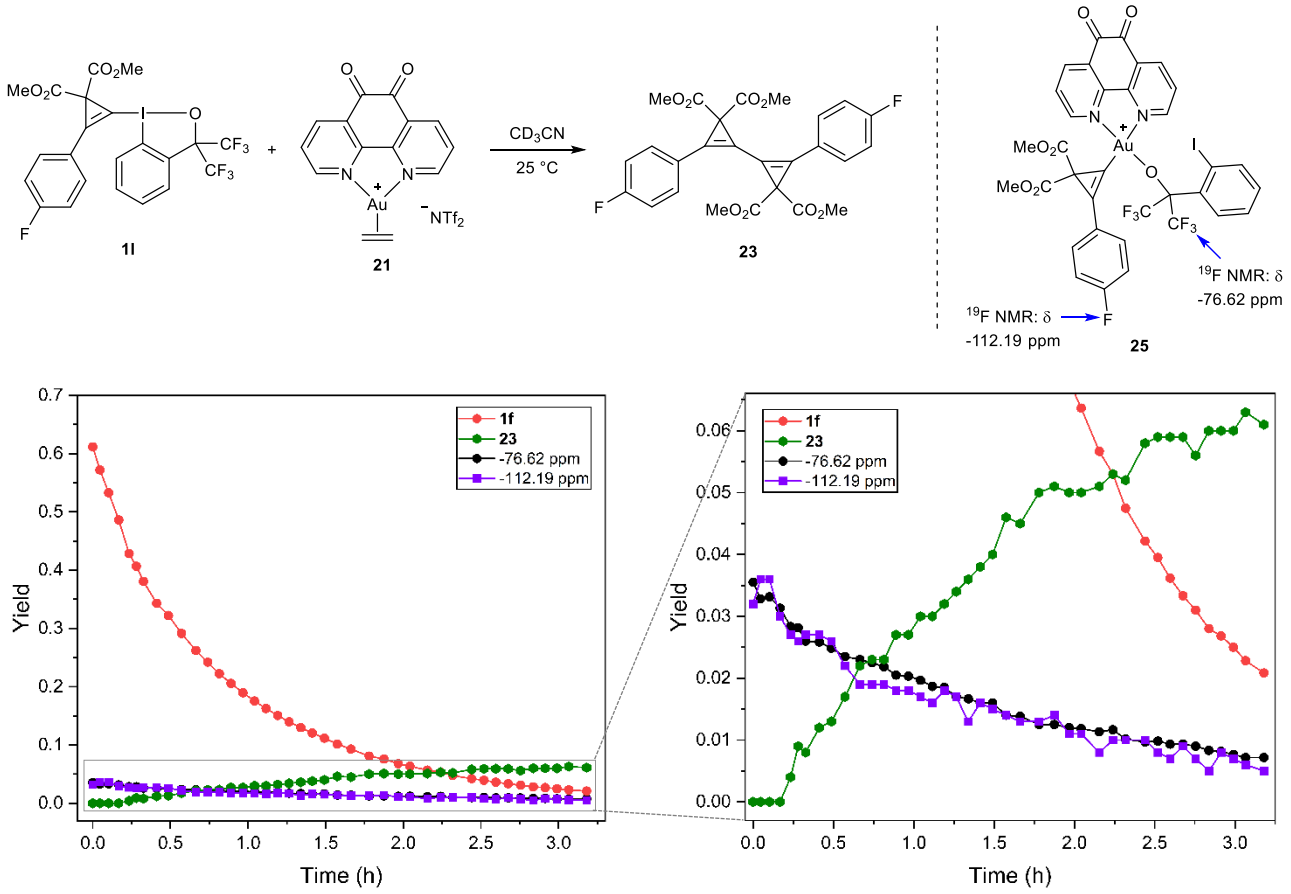


Fig. 18 | Reaction profile of the stoichiometric reaction of CpBX 1l and gold(I)-ethylene complex 21 in CD_3CN monitored by ^{19}F NMR at 25 °C. The yield of **23** (δ -107.86 ppm) and the conversion of **1l** (δ -76.71 ppm) were determined by ^{19}F NMR. The NMR monitoring experiment showed clearly that the CpBX reagents, such as **1l** can directly oxidize cationic gold(I)-ethylene complex **21**, which was also proved by the formation of the homo-coupled product **23** by ligand scrambling (the same mechanism showed in Fig. 5.) of the putative cyclopropenyl-Au(III) intermediate **25**. The relative lower yield of homo-coupled product **23** in the end of the reaction compared with the one showed in Fig. 4 (with chloride as a supporting ligand) was attributed to its relatively poorer stability of cyclopropenyl-Au(III) intermediate **25** compared with its chloride-supported counterpart **24**. Indeed, two ^{19}F NMR signals (δ -76.62 ppm and -112.19 ppm) showed high correlation during the whole reaction course, thus allowing a tentative assignment of the two ^{19}F NMR signals to the proposed cyclopropenyl-Au(III) intermediate **25**.

8.8. DFT Calculations

To gain further understanding of the catalytic cycle, we computed key energetic barriers associated with oxidative addition and reductive elimination on a model substrate (**1a**) reacting with phenylacetylene (**2a**). The geometries of all structures were first optimized at the PBE0[65,66]-D3(BJ)[67,68,69,70] /def2-SVP[71] level using the SMD implicit solvent model[72] for acetonitrile in Gaussian16.[73] Refined energy estimates were obtained by singlet point computations at the B3PW91[74,75,76]-D3(BJ)/def2-TZVP[71] level on the PBE0-D3(BJ) optimized geometries. Each species was characterized as either a minimum (zero imaginary frequencies) or a transition state (one imaginary frequency) via examination of the vibrational frequencies of the optimized structures. Free energies reported include B3PW91-D3(BJ)/def2-TZVP//PBE0-D3(BJ)/def2-SVP electronic energies along with free energy corrections (at the PBE0-D3(BJ)/def2-SVP level) using the quasi rigid-rotor harmonic oscillator model and a pressure correction for acetonitrile (19.15 mol/L) to treat translational entropy in solution using the approach of Martin, Hay, and Pratt.[77] Optimized Cartesian coordinates of all species can be found as additional supporting information files (.zip).

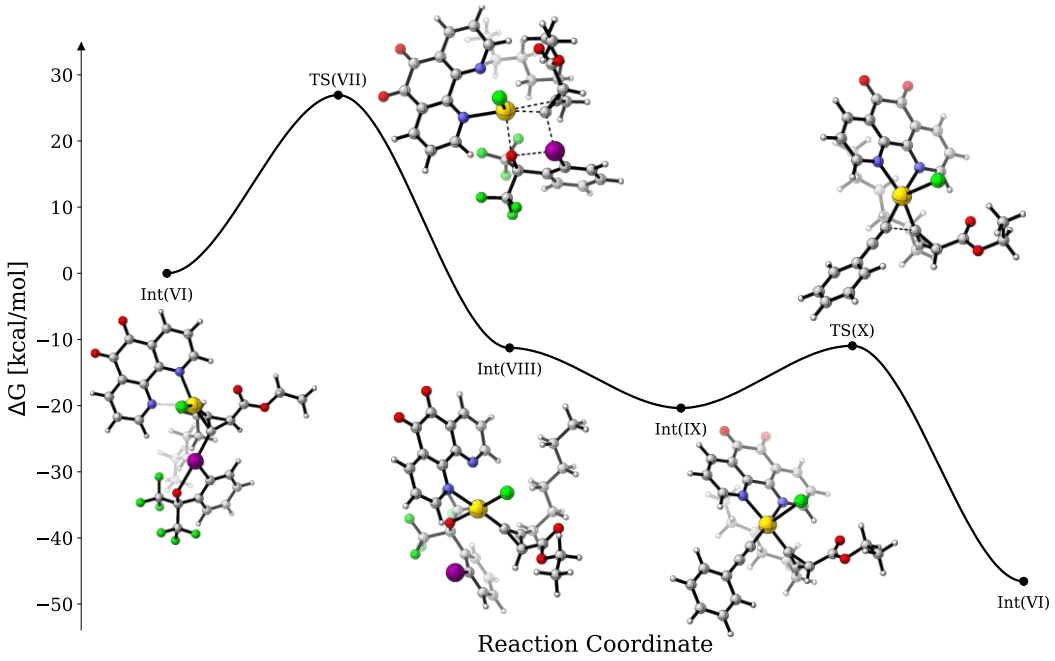


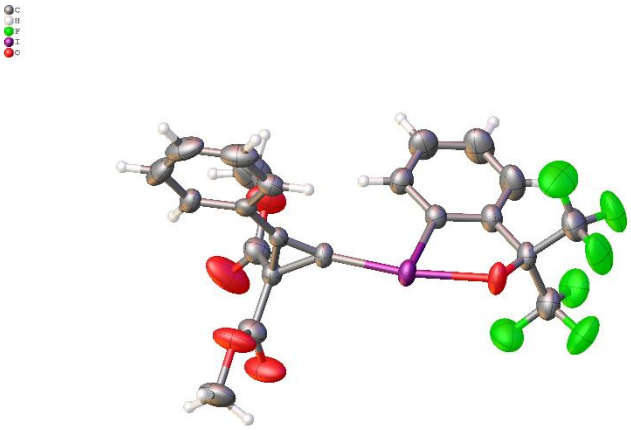
Fig. 19 | Computed free energy profile (at the B3PW91-D3(BJ)/def2-TZVP//PBE0-D3(BJ)/def2-SVP level) of the catalytic cycle. Values in kcal/mol.

Table 9 | Computed values of key species.

	PBE0-D3(BJ)/def2-SVP Electronic Energy [hartree]	PBE0-D3(BJ)/def2-SVP Free Energy Correction [hartree]	B3PW91-D3(BJ)/def2-TZVP// PBE0-D3(BJ)/def2-SVP Electronic Energy [hartree]	Total Free Energy [hartree]	ΔG (Relative to Int(VI)) [kcal/mol]
1a	-1933.530468	0.348311	-1936.710065	-1936.361754	--
2a	-307.822759	0.085690	-308.415394	-308.329704	--
3a (Product)	-925.244523	0.340375	-927.0201408	-926.6797658	--
4 (Alcohol)	-1316.201691	0.095126	-1318.181023	-1318.085897	--
Int(**VI**)	-3248.824032	0.492439	-3253.714552	-3253.222113	0.00
TS(**VII**)	-3248.785956	0.490436	-3253.669623	-3253.179187	26.94
Int(**VIII**)	-3248.849422	0.492924	-3253.732997	-3253.240073	-11.27
Int(**IX**)	-2240.476560	0.484620	-2243.982999	-2243.498379	-20.37
TS(**X**)	-2240.467656	0.483783	-2243.967175	-2243.483392	-10.96

9. Single crystal X-ray diffraction analysis

9.1. Crystal data and structure refinement for 1k



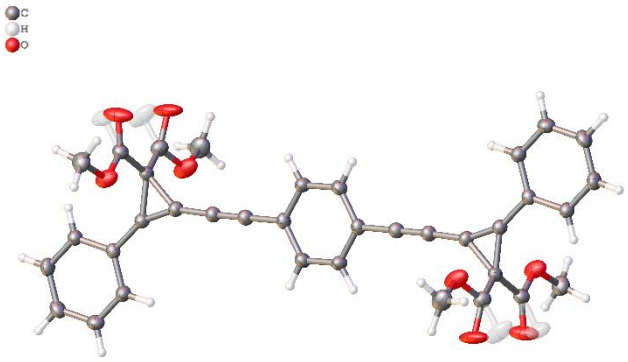
Preparation. Monocrystal suitable for X-ray diffraction analysis was grown by slow diffusion of hexane into saturated CH_2Cl_2 solution of **1k**.

Experimental. Single clear pale colourless plate-shaped crystals of **1k** were used as supplied. A suitable crystal with dimensions 0.17 × 0.15 × 0.08 mm^3 was selected and mounted on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The crystal was kept at a steady T = 229.99(10) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_{22}H_{15}F_6IO_5$, M_r = 600.24, monoclinic, $P2_1/n$ (No. 14), a = 16.6125(5) Å, b = 7.7673(2) Å, c = 18.9493(6) Å, β = 110.931(3)°, α = γ = 90°, V = 2283.74(12) Å^3, T = 229.99(10) K, Z = 4, Z' = 1, μ(Mo K$_\alpha$) = 1.482, 18406 reflections measured, 5533 unique (R_{int} = 0.0247) which were used in all calculations. The final wR_2 was 0.0749 (all data) and R_1 was 0.0322 (I≥2 σ(I)).

Compound	**1k**
CCDC code	2260609
Formula	$C_{22}H_{15}F_6IO_5$
Dcalc	1.746
μ/mm^{-1}	1.482
Formula Weight	600.24
Colour	clear pale colourless
Shape	plate-shaped
Size/mm^3	0.17×0.15×0.08
T/K	229.99(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	16.6125(5)
b/Å	7.7673(2)
c/Å	18.9493(6)
α/°	90
β/°	110.931(3)
γ/°	90
V/Å^3	2283.74(12)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K$_\alpha$
Θ_{min}/°	2.806
Θ_{max}/°	29.537
Measured Refl's.	18406
Indep't Refl's	5533
Refl's I≥2 σ(I)	4588
R_{int}	0.0247
Parameters	328
Restraints	30
Largest Peak	0.537
Deepest Hole	-0.376
GooF	1.036
wR_2 (all data)	0.0749
wR_2	0.0689
R_1 (all data)	0.0438
R_1	0.0322

9.2. Crystal data and structure refinement for 3au



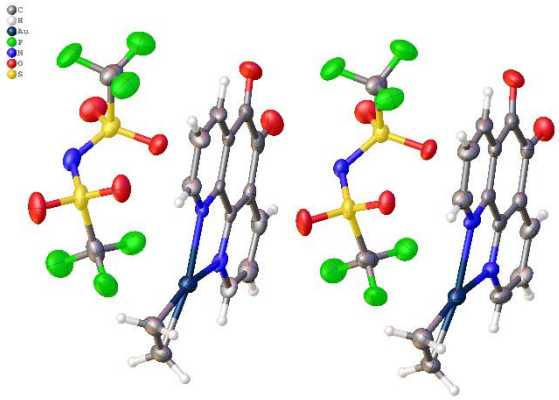
Preparation. Monocrystal suitable for X-ray diffraction analysis was grown by slow diffusion of pentane into saturated CH_2Cl_2 solution of **3au**.

Experimental. Single clear pale-yellow prism-shaped crystals of **3au** were used as supplied. A suitable crystal with dimensions 0.29 × 0.15 × 0.09 mm^3 was selected and mounted on a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The crystal was kept at a steady T = 139.99(10) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{36}H_{26}O_8$, M_r = 586.57, triclinic, P-1 (No. 2), a = 7.79978(19) Å, b = 10.2444(3) Å, c = 10.4570(3) Å, α = 64.821(3)°, β = 79.661(2)°, γ = 85.675(2)°, V = 743.89(4) Å^3, T = 139.99(10) K, Z = 1, Z' = 0.5, μ(Cu K$_\alpha$) = 0.764, 14396 reflections measured, 2921 unique (R_{int} = 0.0367) which were used in all calculations. The final wR_2 was 0.1379 (all data) and R_1 was 0.0473 (I≥2 σ(I)).

Compound	**3au**
CCDC code	2260610
Formula	$C_{36}H_{26}O_8$
$D_{calc.}$/ g cm^{-3}	1.309
μ/mm^{-1}	0.764
Formula Weight	586.57
Colour	clear pale yellow
Shape	prism-shaped
Size/mm^3	0.29×0.15×0.09
T/K	139.99(10)
Crystal System	triclinic
Space Group	P-1
a/Å	7.79978(19)
b/Å	10.2444(3)
c/Å	10.4570(3)
α/°	64.821(3)
β/°	79.661(2)
γ/°	85.675(2)
V/Å^3	743.89(4)
Z	1
Z'	0.5
Wavelength/Å	1.54184
Radiation type	Cu K$_\alpha$
Θ_{min}/°	4.736
Θ_{max}/°	74.473
Measured Refl's.	14396
Indep't Refl's	2921
Refl's I≥2 σ(I)	2526
R_{int}	0.0367
Parameters	271
Restraints	36
Largest Peak	0.293
Deepest Hole	-0.331
GooF	1.077
wR_2 (all data)	0.1379
wR_2	0.1326
R_1 (all data)	0.0533
R_1	0.0473

9.3. Crystal data and structure refinement for 21



Preparation. Monocrystal suitable for X-ray diffraction analysis was grown by slow diffusion of Et_2O (top layer) into saturated CH_2Cl_2 solution of **21** (bottom layer).

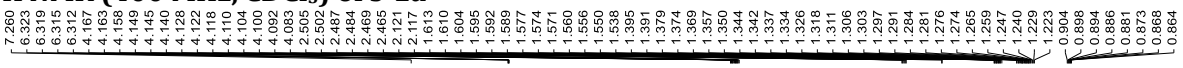
Experimental. Single clear pale colourless plate-shaped crystals of **21** were used as supplied. A suitable crystal with dimensions 0.22 × 0.05 × 0.03 mm³ was selected and mounted on a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The crystal was kept at a steady T = 140.00(10) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **olex2.refine** 1.5 (Bourhis et al., 2015) using full matrix least squares minimisation on F^2.

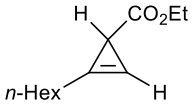
Crystal Data. $C_{16}H_{10}AuF_6N_3O_6S_2$, M_r = 715.363, monoclinic, $P2_1/n$ (No. 14), a = 16.2041(4) Å, b = 15.2787(3) Å, c = 17.5817(4) Å, β = 106.170(2)°, α = γ = 90°, V = 4180.64(16) Å³, T = 140.00(10) K, Z = 8, Z' = 2, μ(Mo K_α) = 7.333, 109486 reflections measured, 8536 unique (R_{int} = 0.0974) which were used in all calculations. The final wR_2 was 0.1072 (all data) and R_1 was 0.0427 (I≥2 σ(I))

Compound	**21**
CCDC code	2260611
Formula	$C_{16}H_{10}AuF_6N_3O_6S_2$
$D_{calc.}$/ g cm^{-3}	2.273
μ/mm^{-1}	7.333
Formula Weight	715.363
Colour	clear pale colourless
Shape	plate-shaped
Size/mm³	0.22×0.05×0.03
T/K	140.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	16.2041(4)
b/Å	15.2787(3)
c/Å	17.5817(4)
α/°	90
β/°	106.170(2)
γ/°	90
V/Å³	4180.64(16)
Z	8
Z'	2
Wavelength/Å	0.71073
Radiation type	Mo K_α
Θ_{min}/°	2.01
Θ_{max}/°	26.37
Measured Refl's.	109486
Indep't Refl's	8536
Refl's I≥2 σ(I)	7291
R_{int}	0.0974
Parameters	663
Restraints	90
Largest Peak	2.9128
Deepest Hole	-2.5025
GooF	1.0469
wR_2 (all data)	0.1072
wR_2	0.1032
R_1 (all data)	0.0526
R_1	0.0427

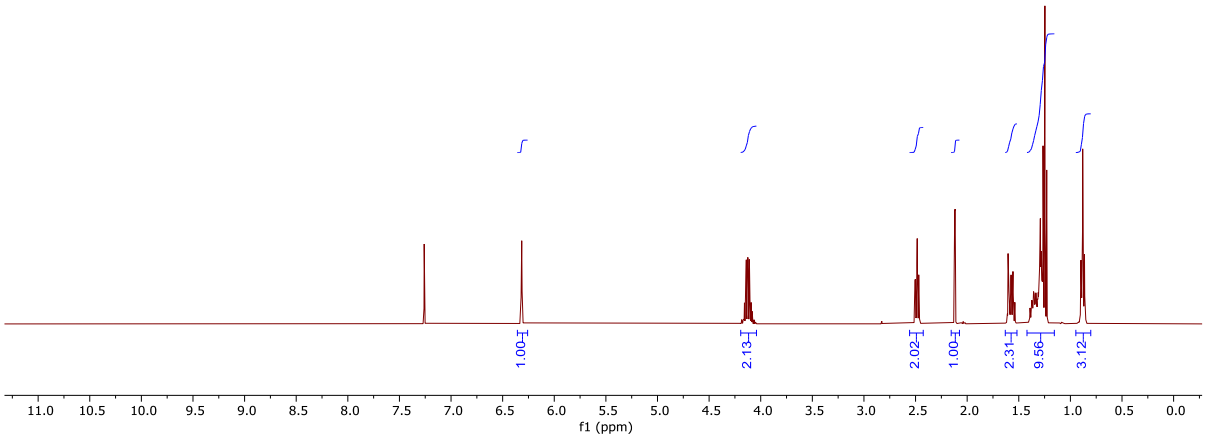
10. NMR spectra

^{1}H NMR (400 MHz, $CDCl_3$) of s-1a

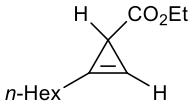




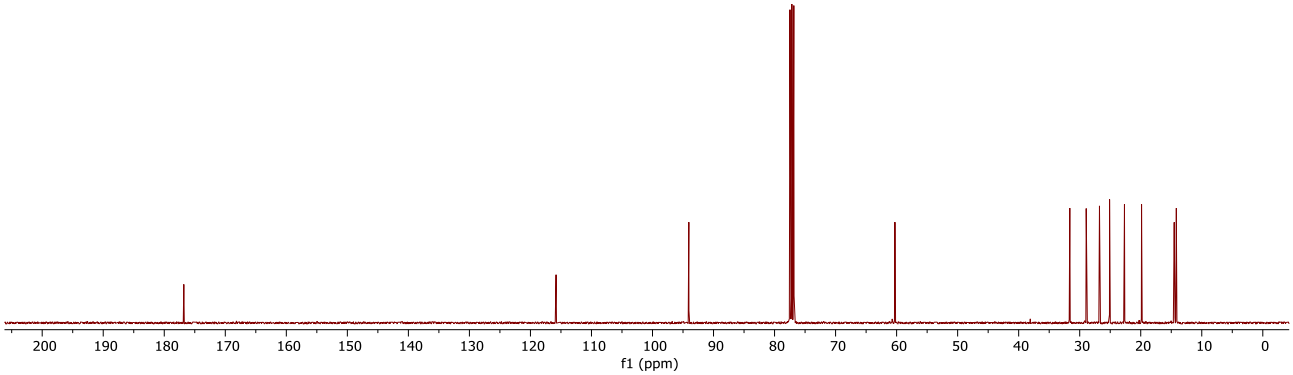
s-1a



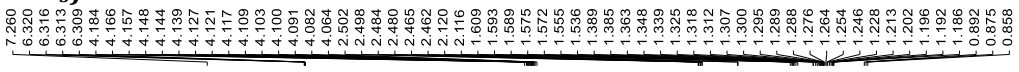
^{13}C NMR (101 MHz, $CDCl_3$) of s-1a

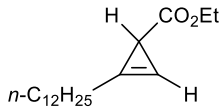


s-1a

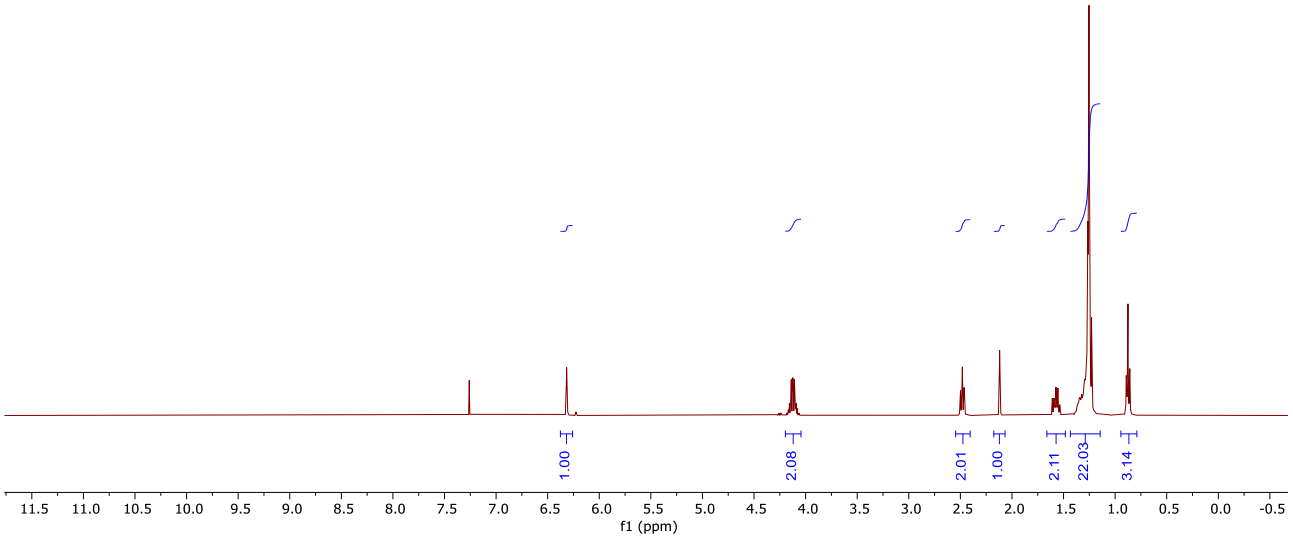


^{1}H NMR (400 MHz, $CDCl_3$) of s-1b

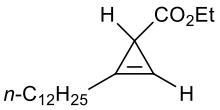




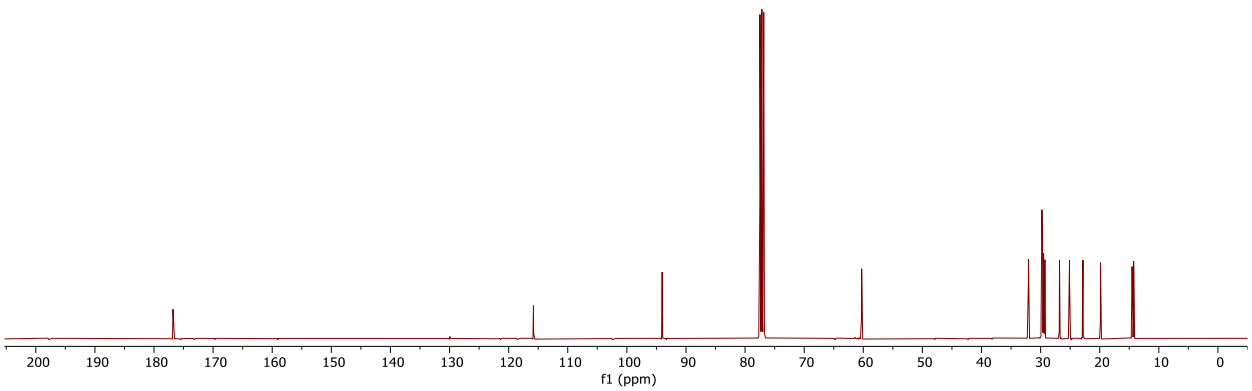
s-1b



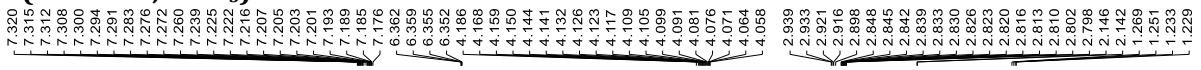
^{13}C NMR (101 MHz, $CDCl_3$) of s-1b

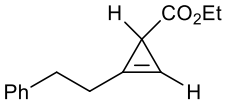


s-1b

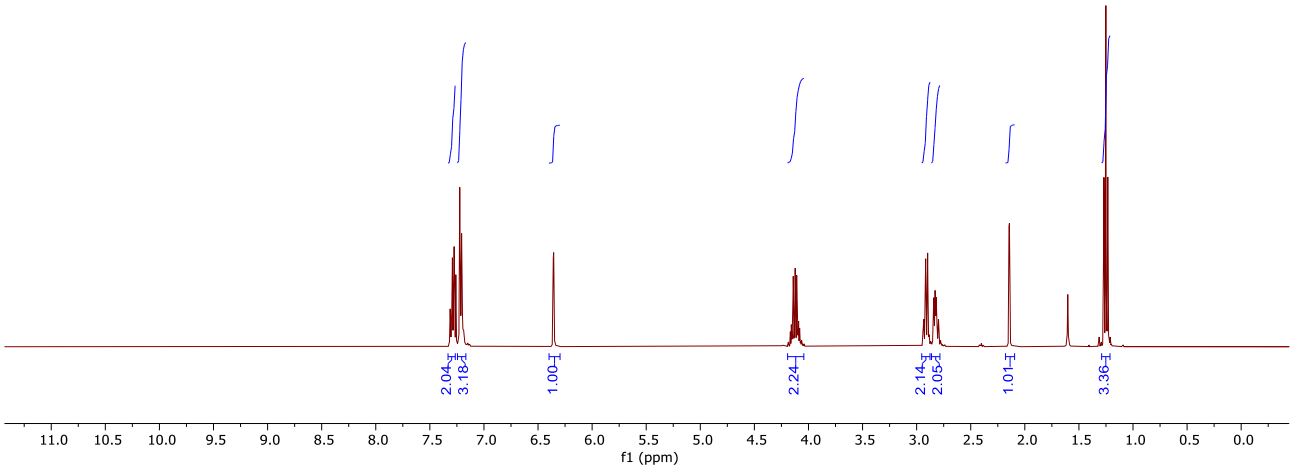


^{1}H NMR (400 MHz, $CDCl_3$) of s-1c

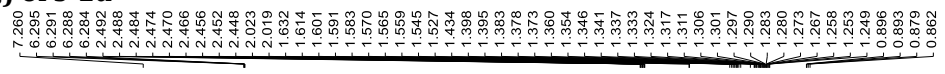


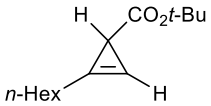


s-1c



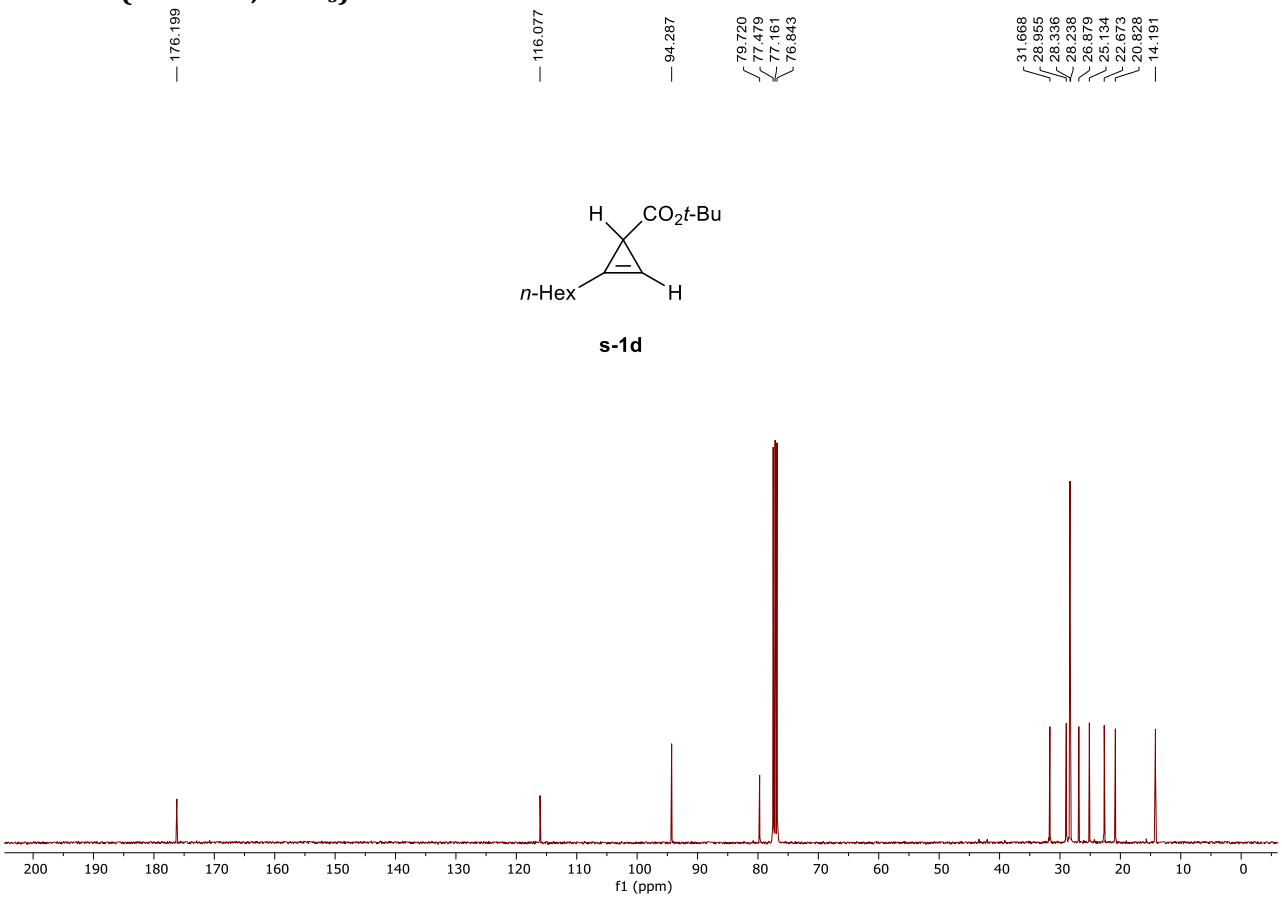
^{1}H NMR (400 MHz, $CDCl_3$) of s-1d



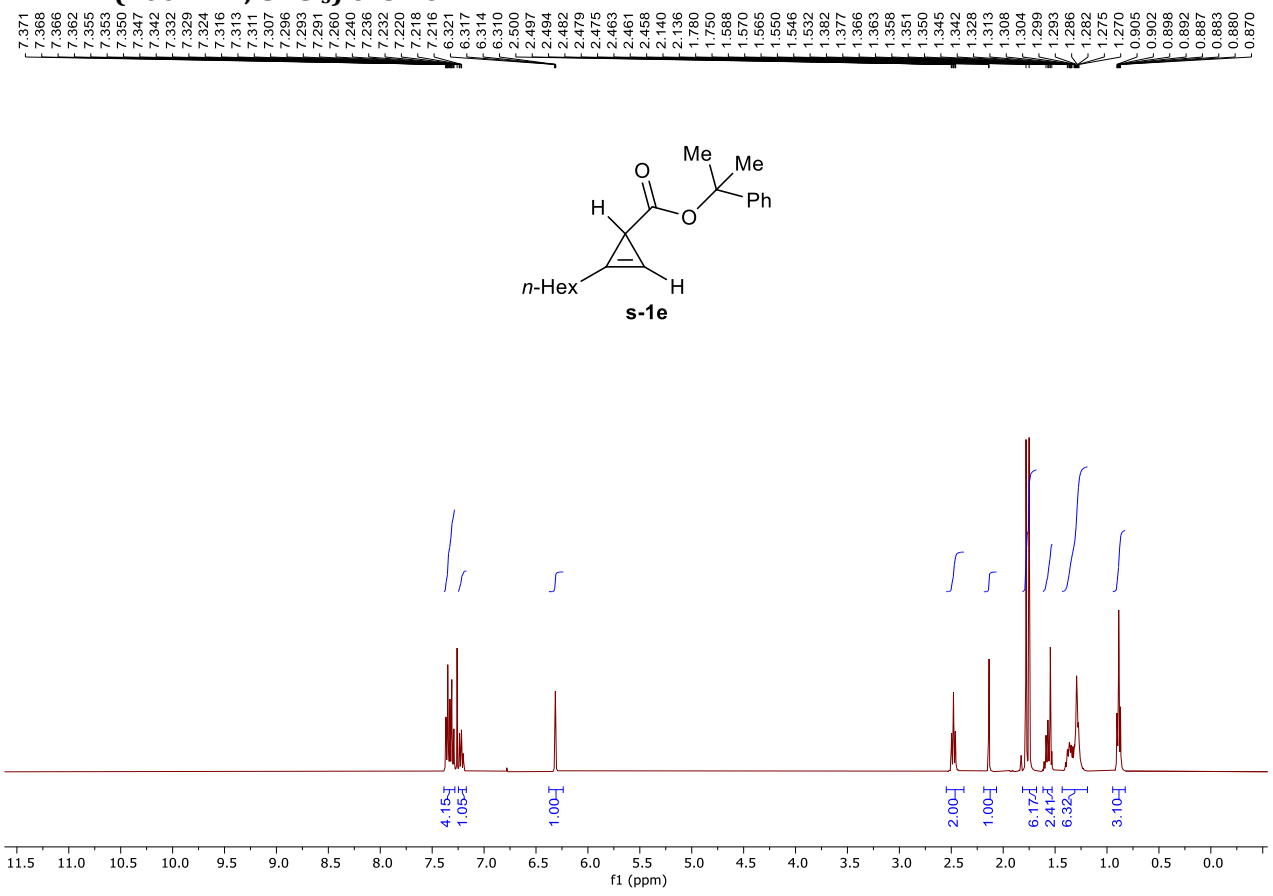


s-1d

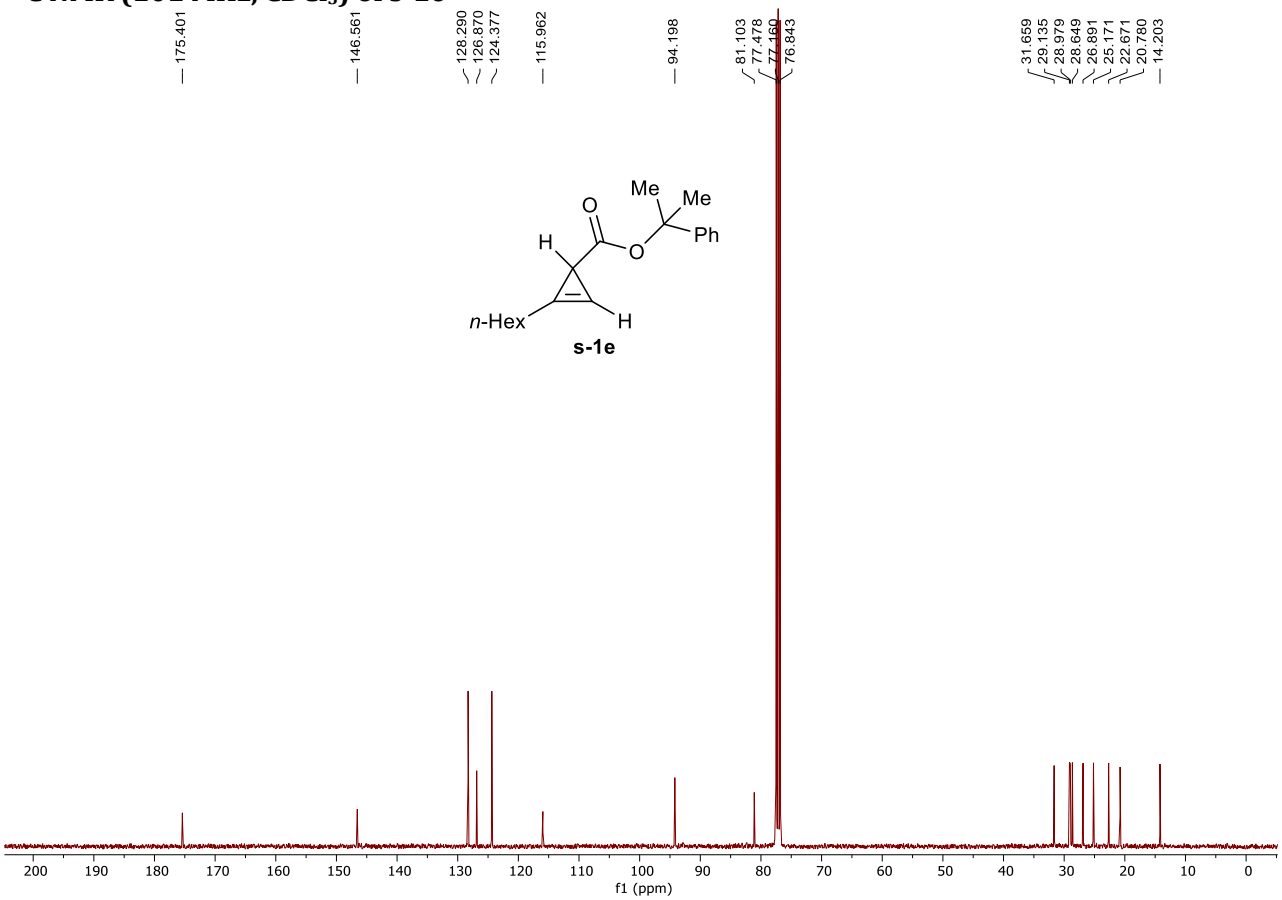
^{13}C NMR (101 MHz, $CDCl_3$) of s-1d



^{1}H NMR (400 MHz, $CDCl_3$) of s-1e

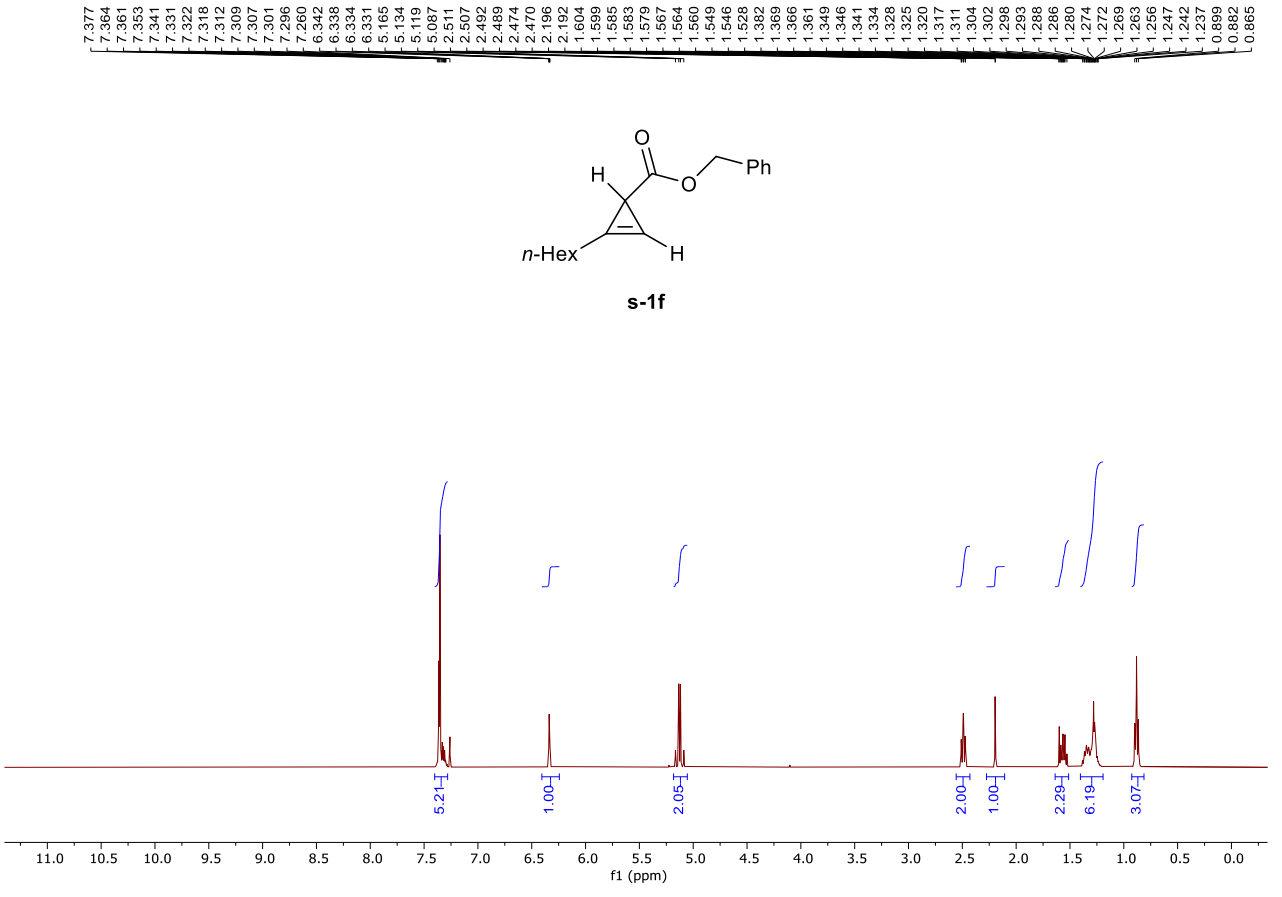


^{13}C NMR (101 MHz, $CDCl_3$) of s-1e



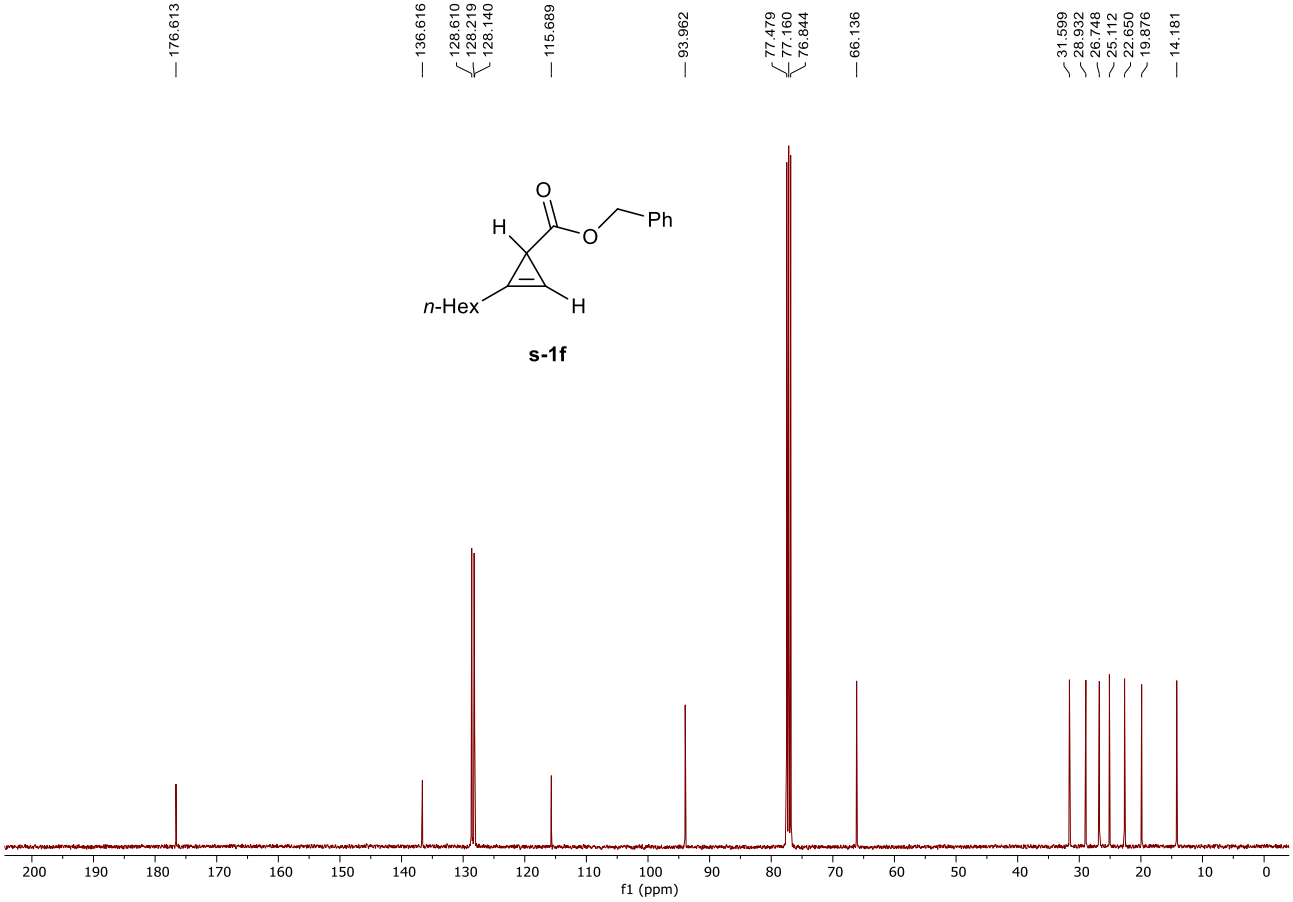
s-1e

^{1}H NMR (400 MHz, $CDCl_3$) of s-1f

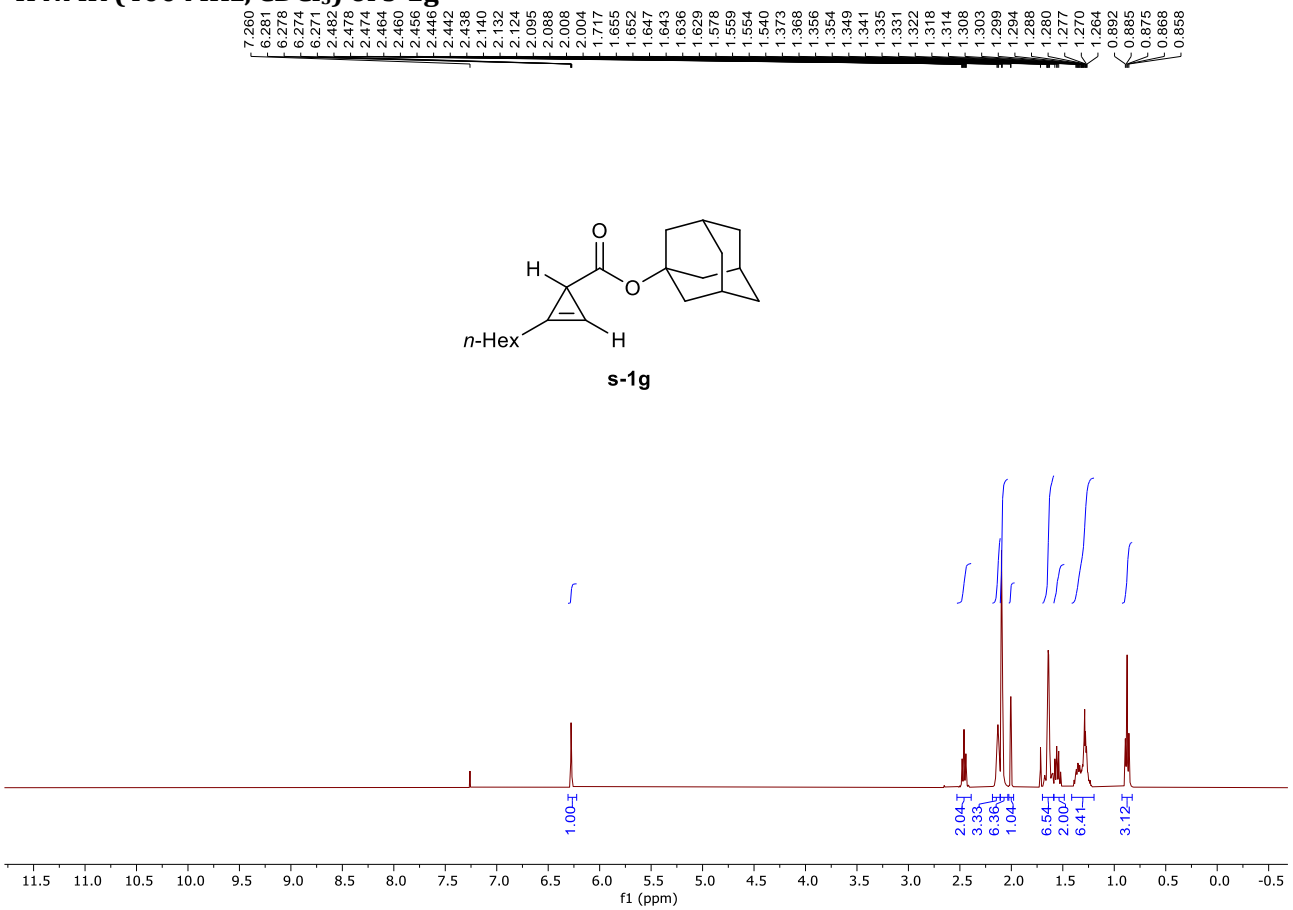


s-1f

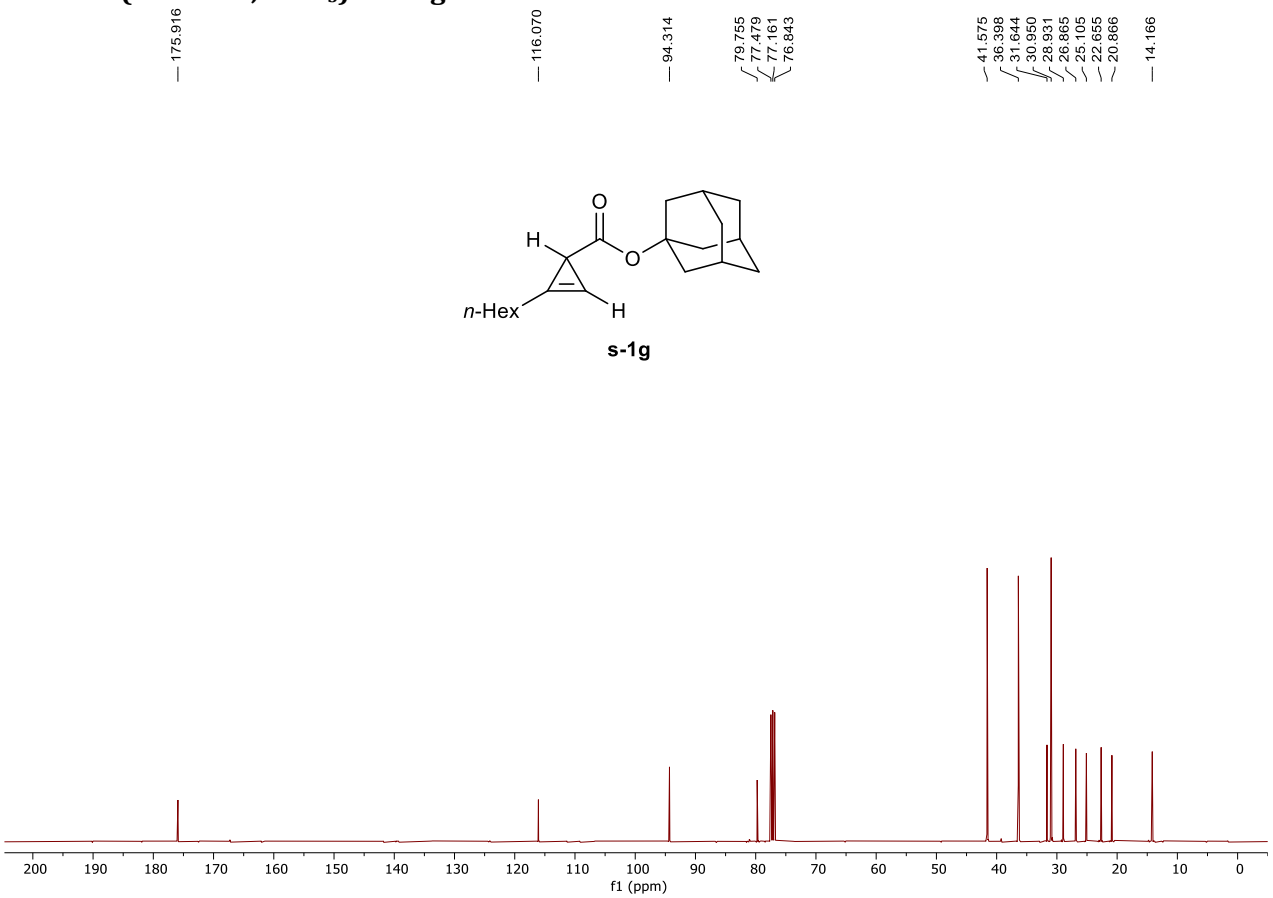
^{13}C NMR (101 MHz, $CDCl_3$) of s-1f



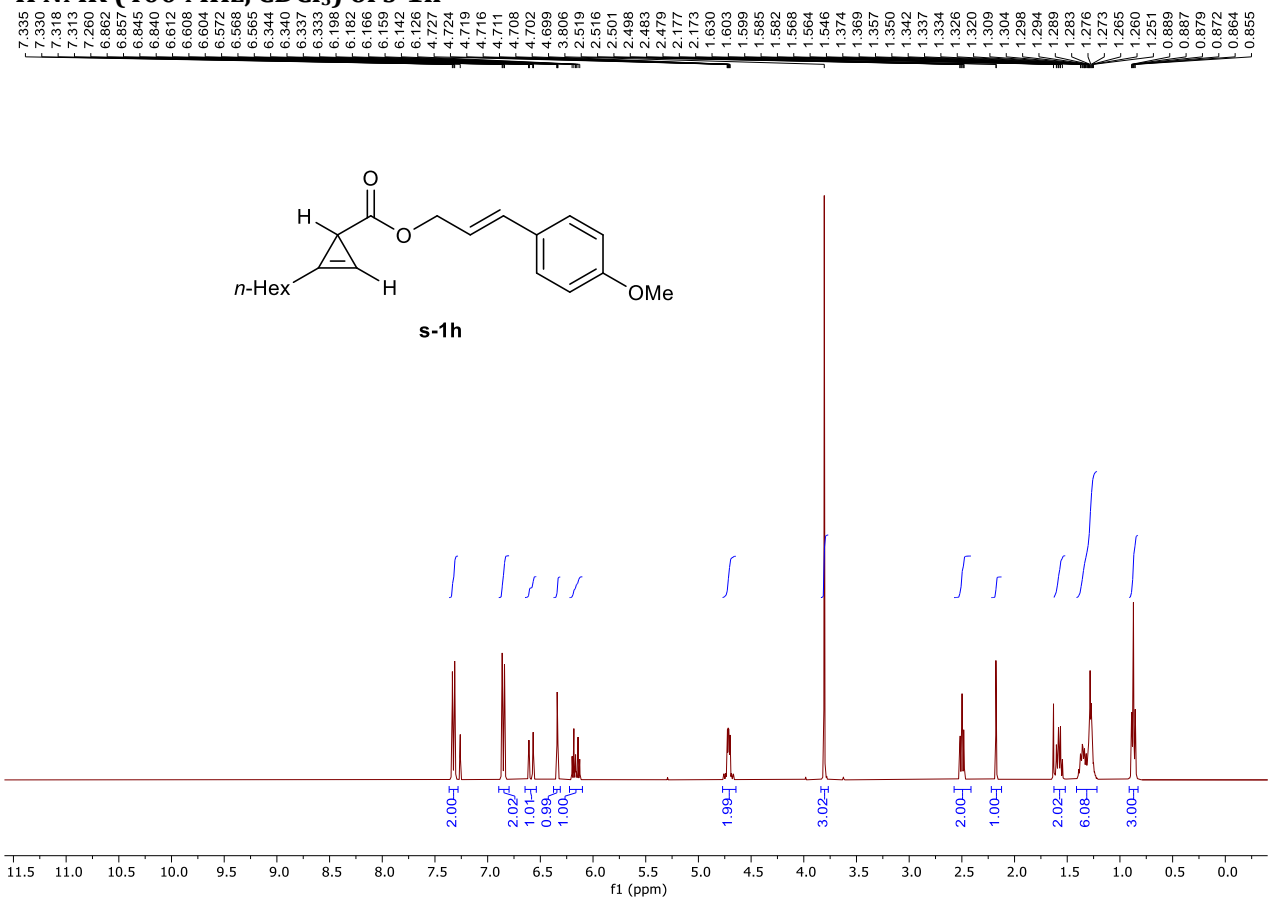
^{1}H NMR (400 MHz, $CDCl_3$) of s-1g



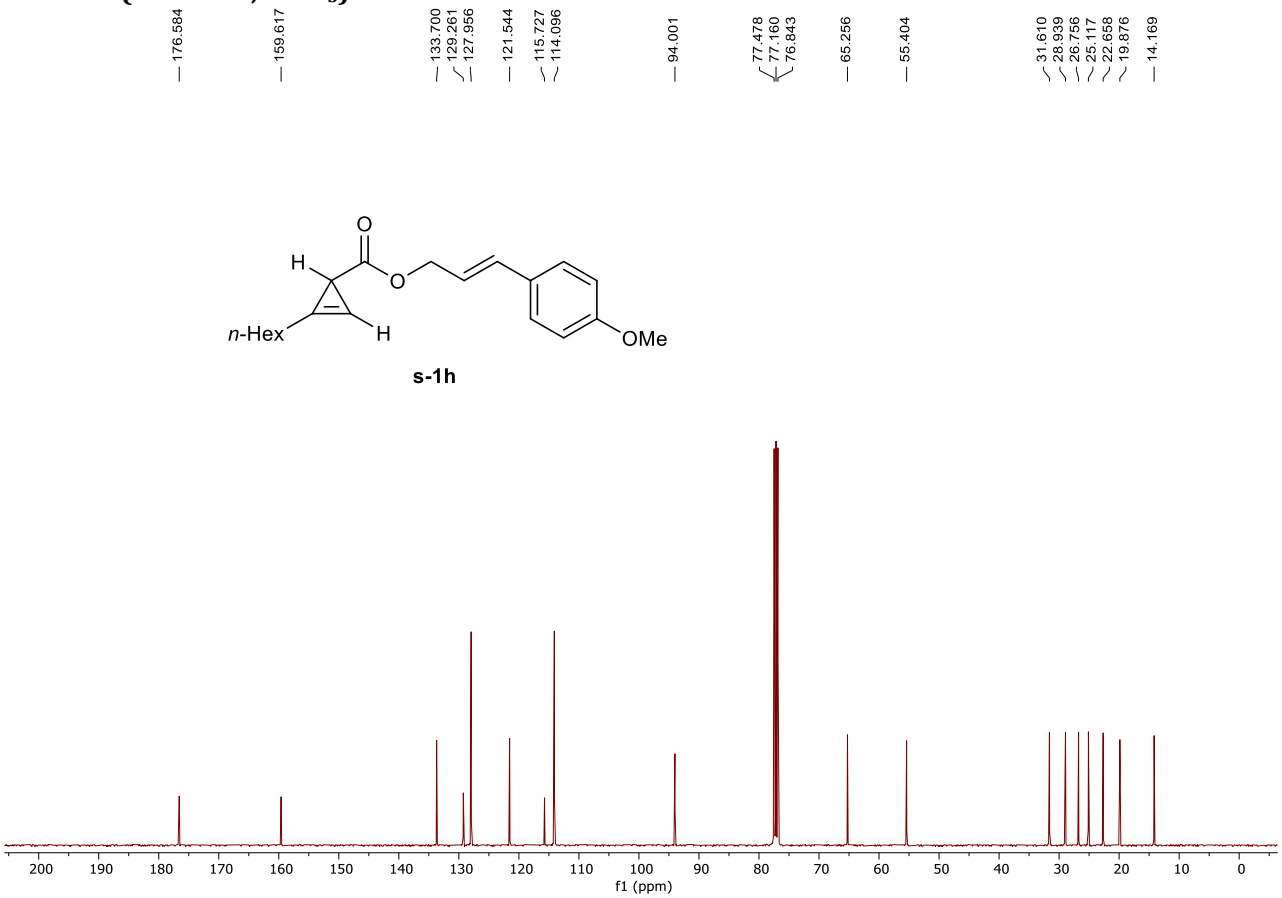
^{13}C NMR (101 MHz, $CDCl_3$) of s-1g



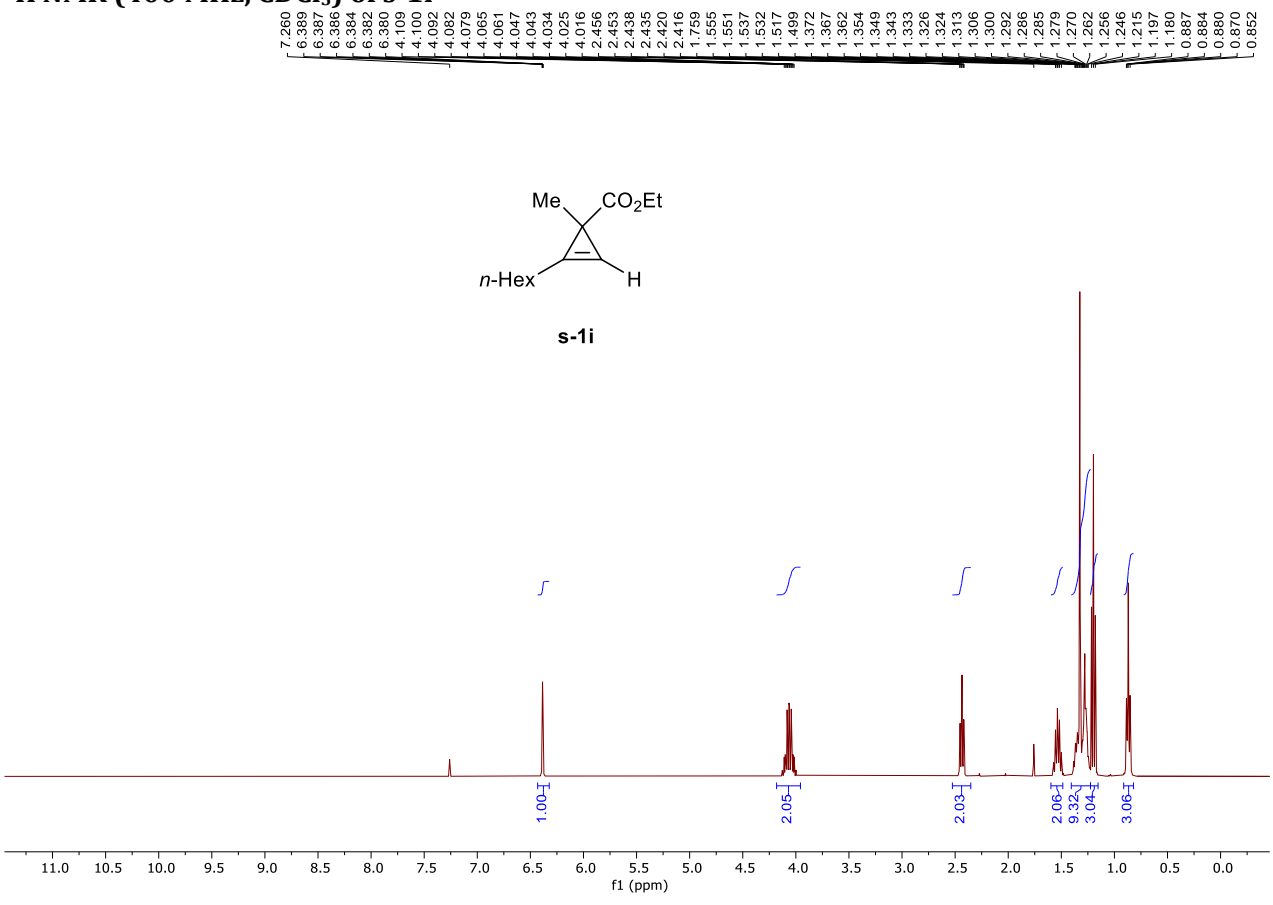
^{1}H NMR (400 MHz, $CDCl_3$) of s-1h



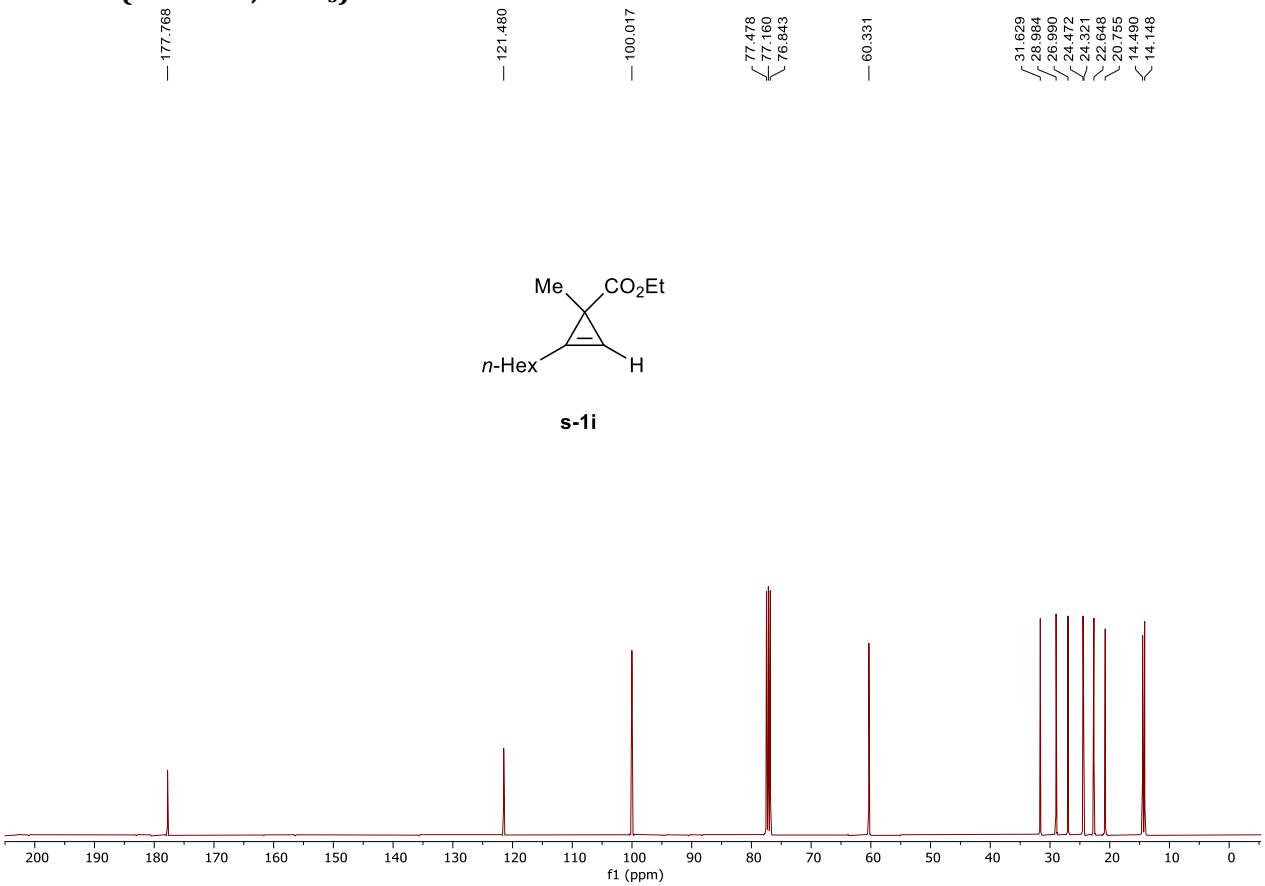
^{13}C NMR (101 MHz, $CDCl_3$) of s-1h



^{1}H NMR (400 MHz, $CDCl_3$) of s-1i

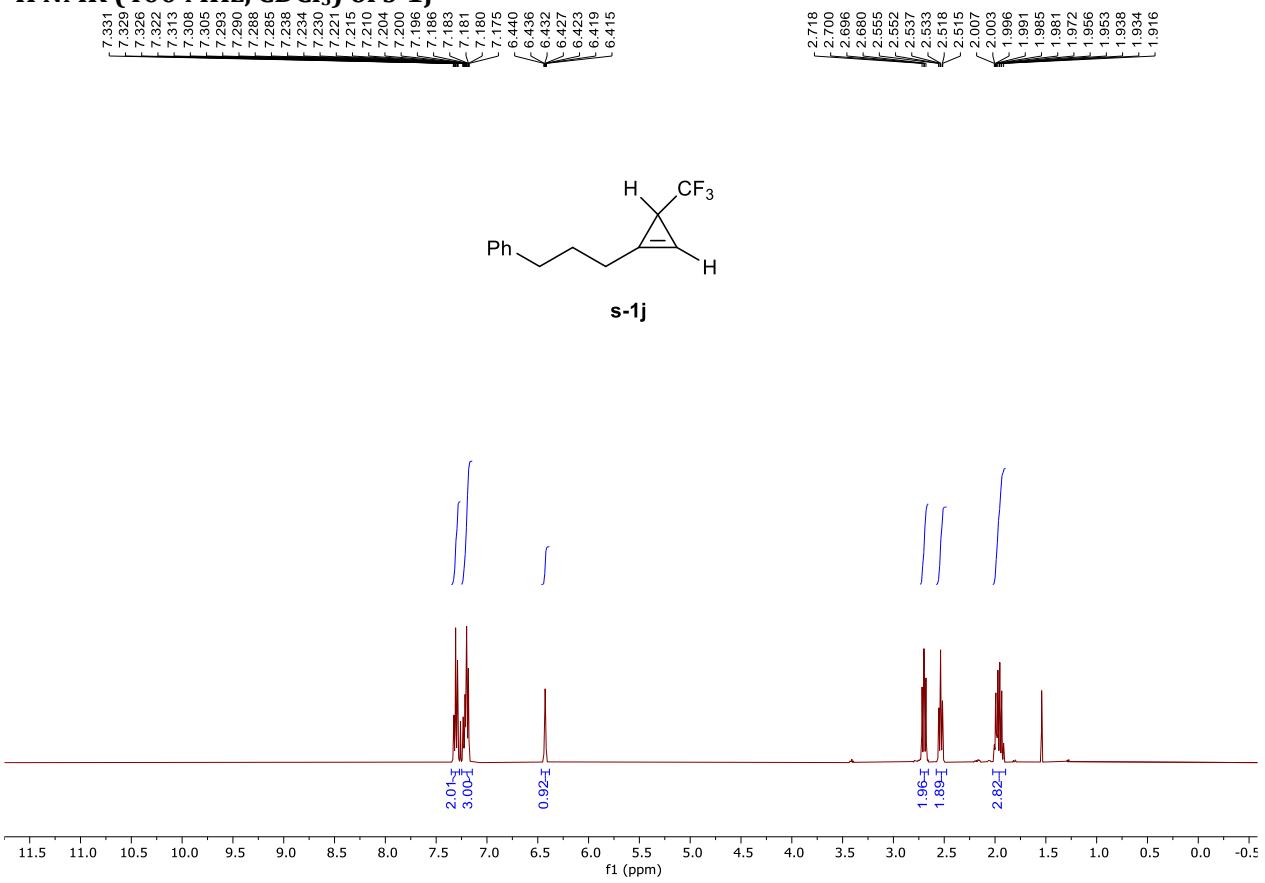


^{13}C NMR (101 MHz, $CDCl_3$) of s-1i



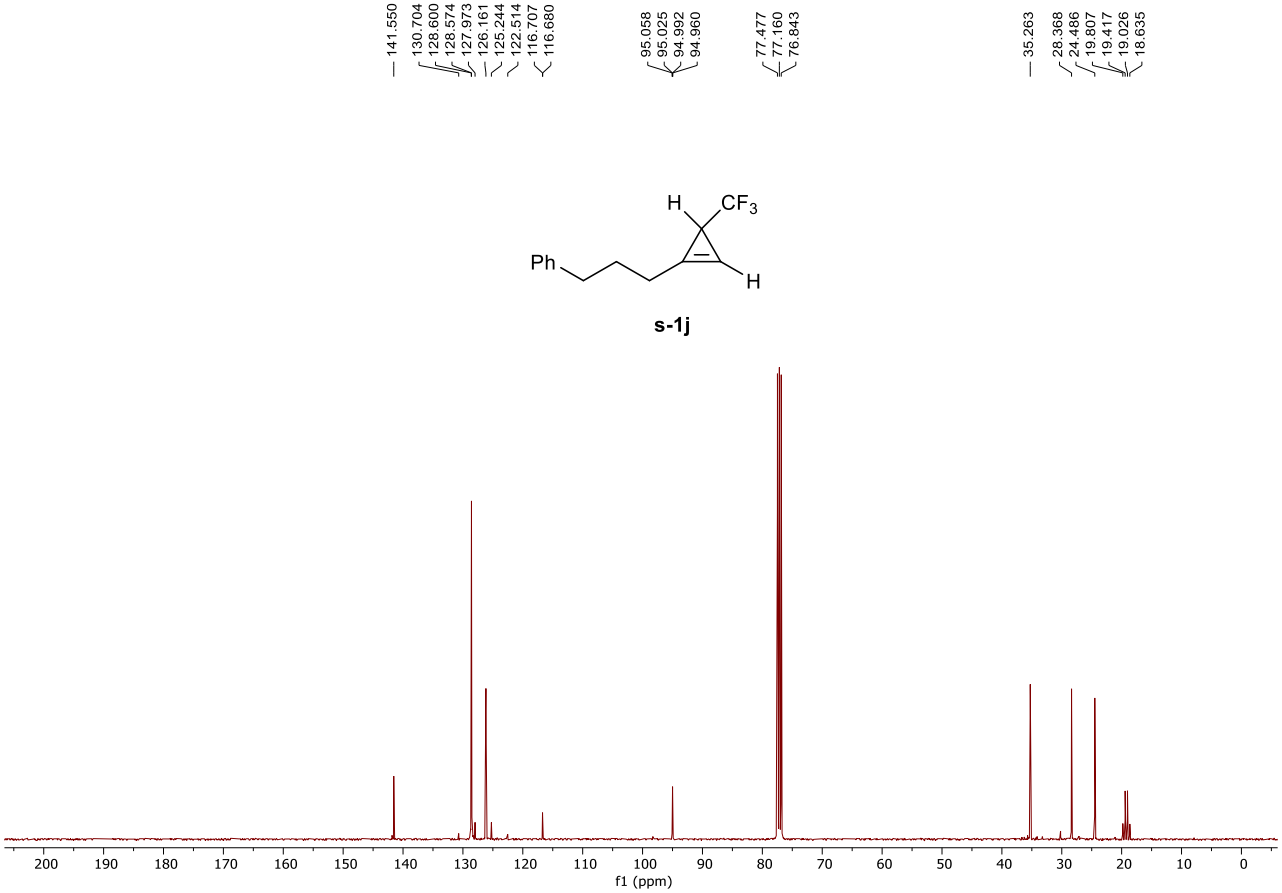
s-1i

^{1}H NMR (400 MHz, $CDCl_3$) of s-1j

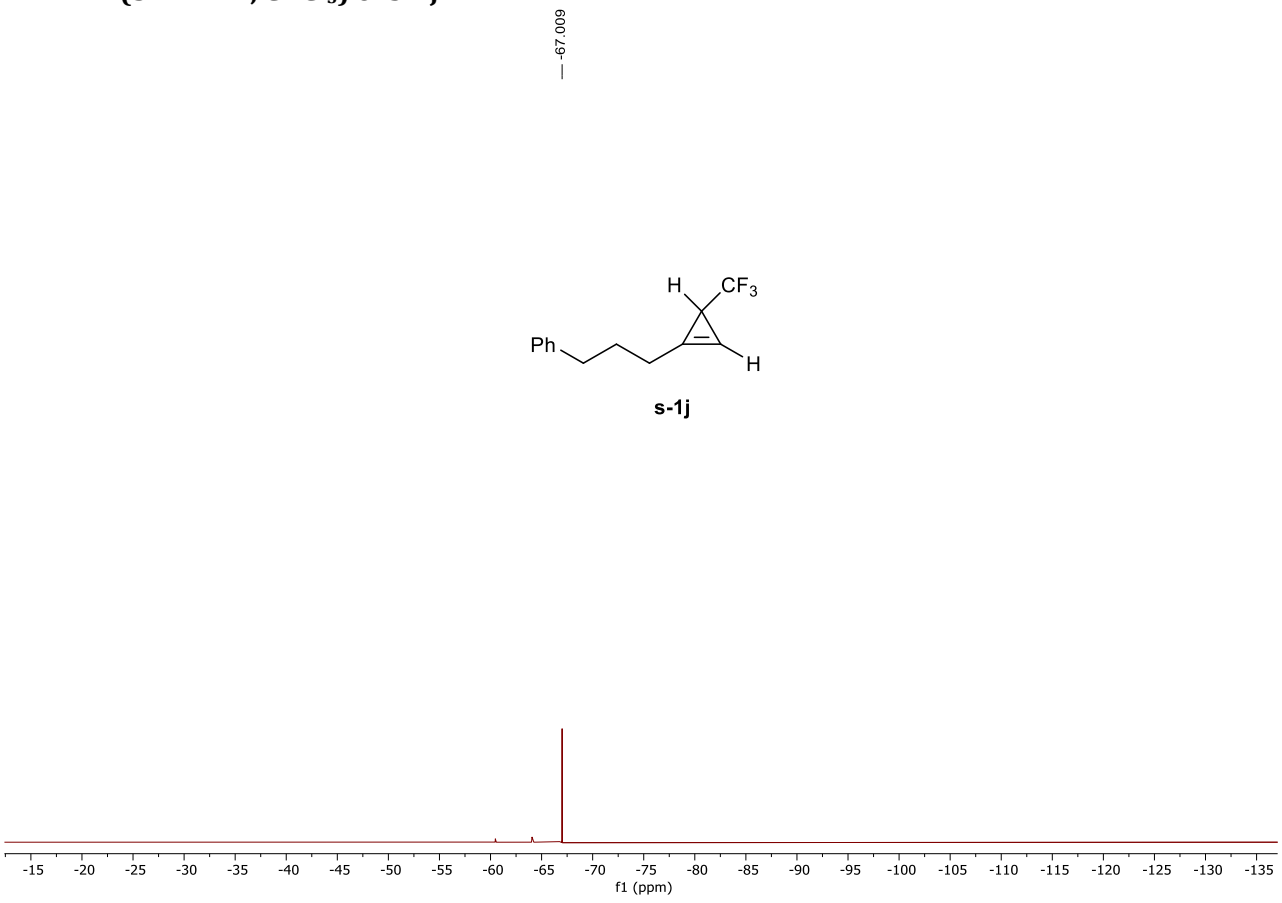


s-1j

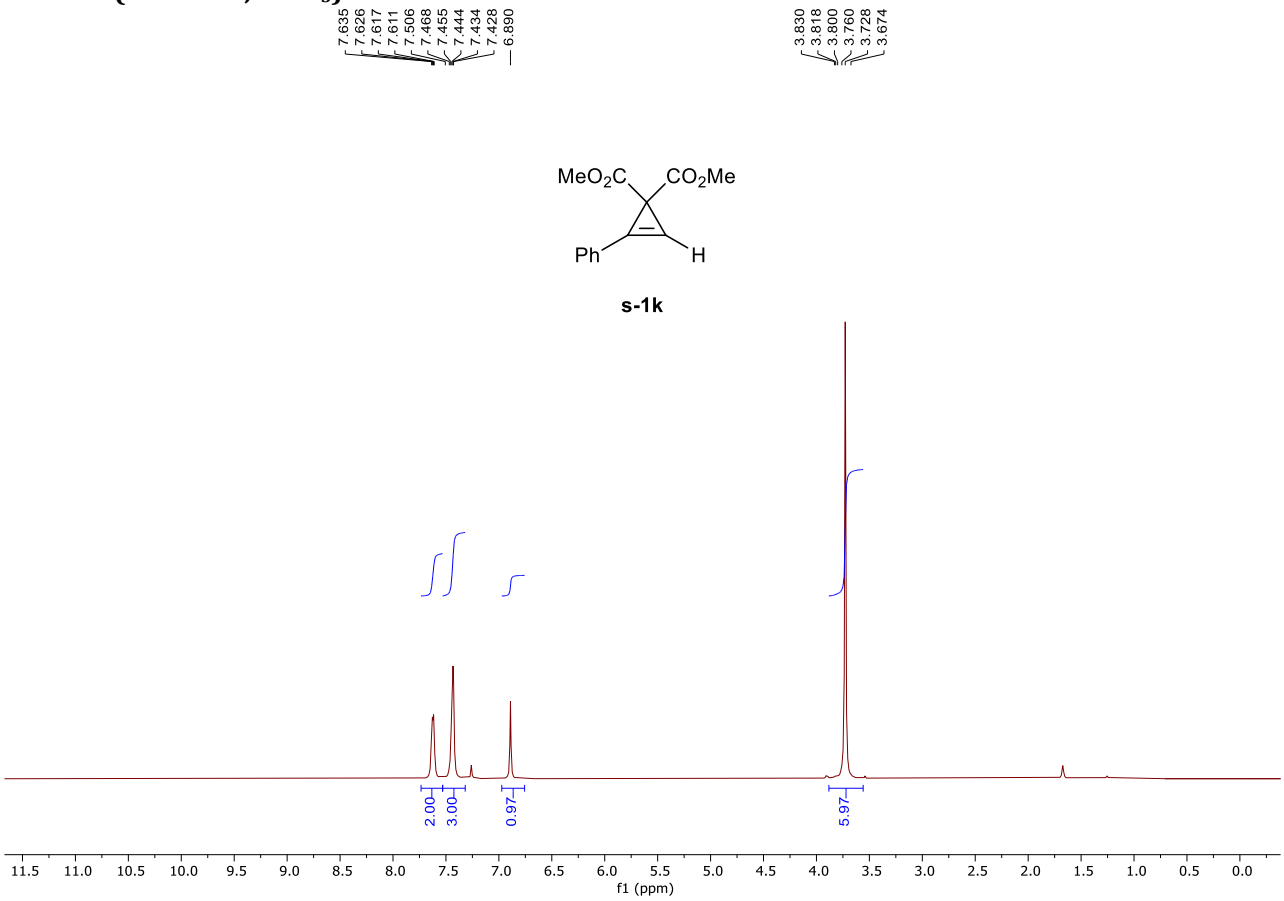
^{13}C NMR (101 MHz, $CDCl_3$) of s-1j



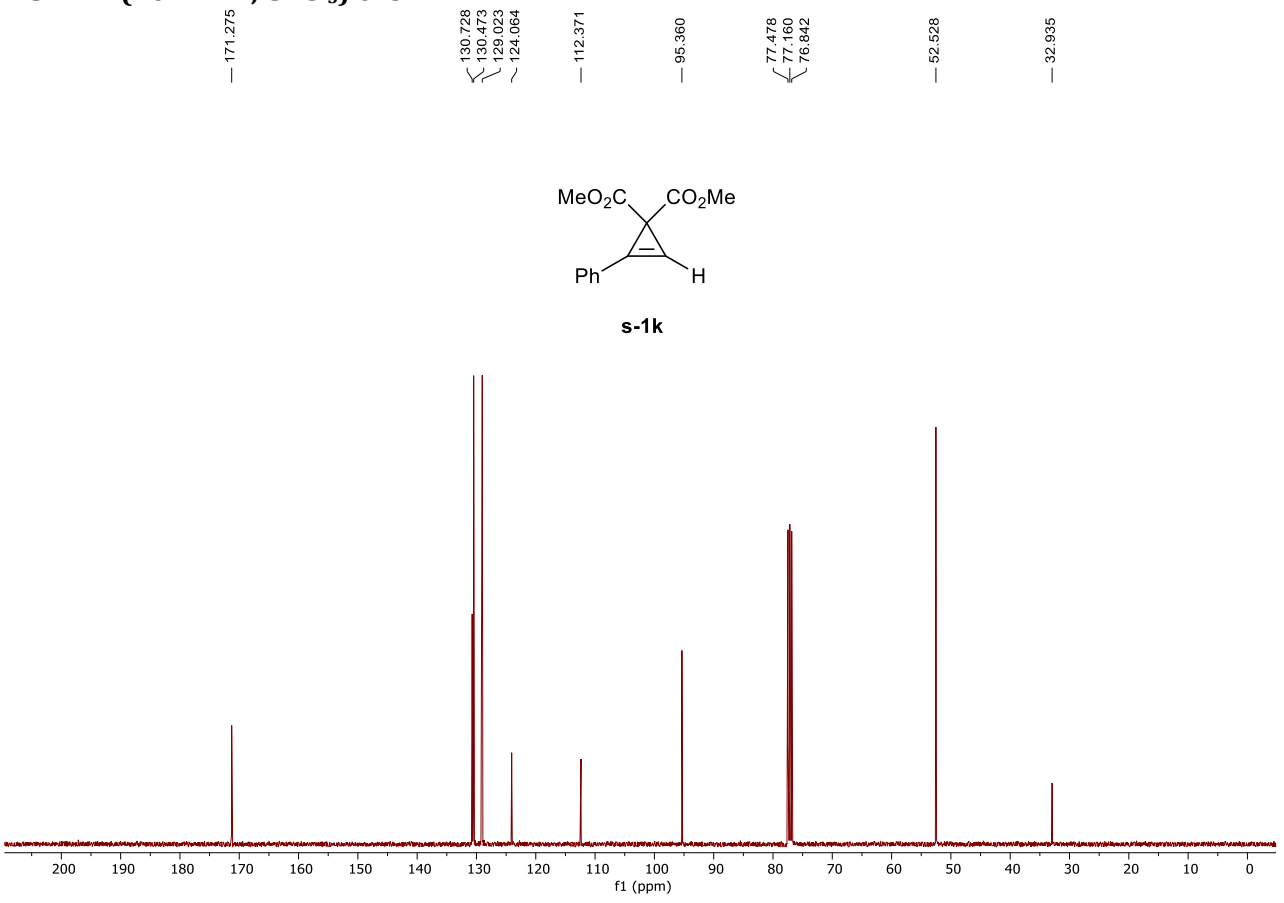
^{19}F NMR (377 MHz, $CDCl_3$) of s-1j



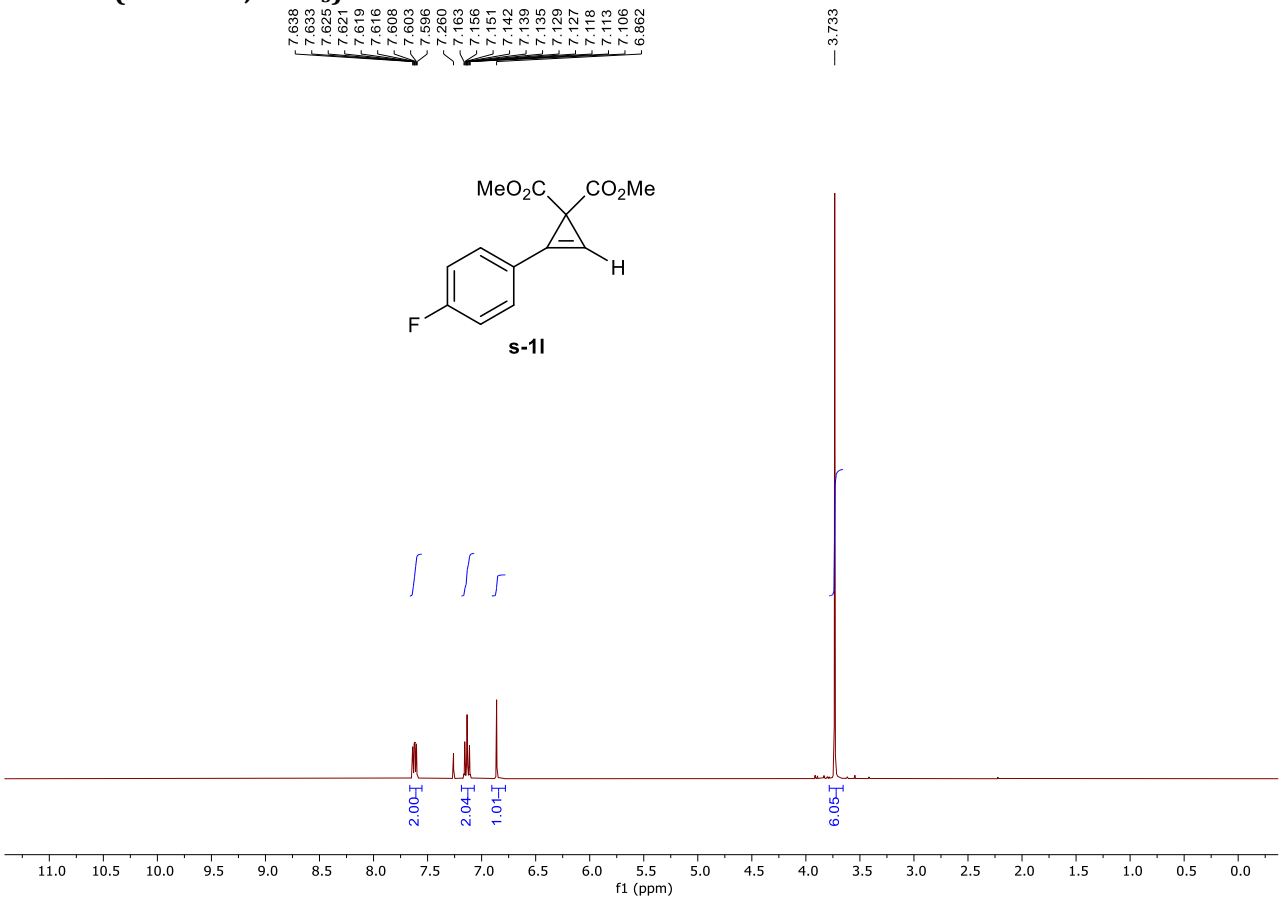
^{1}H NMR (400 MHz, $CDCl_3$) of s-1k



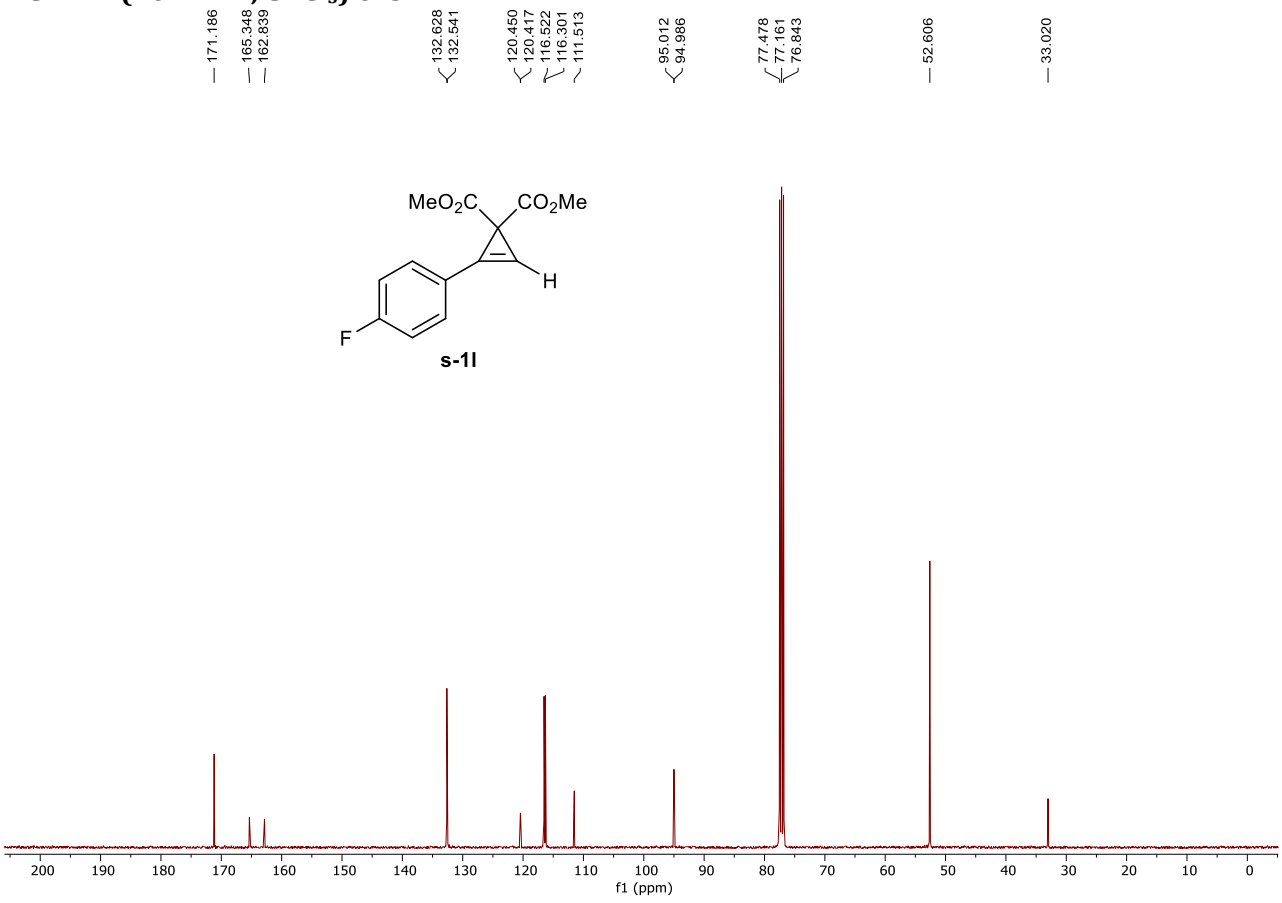
^{13}C NMR (101 MHz, $CDCl_3$) of s-1k



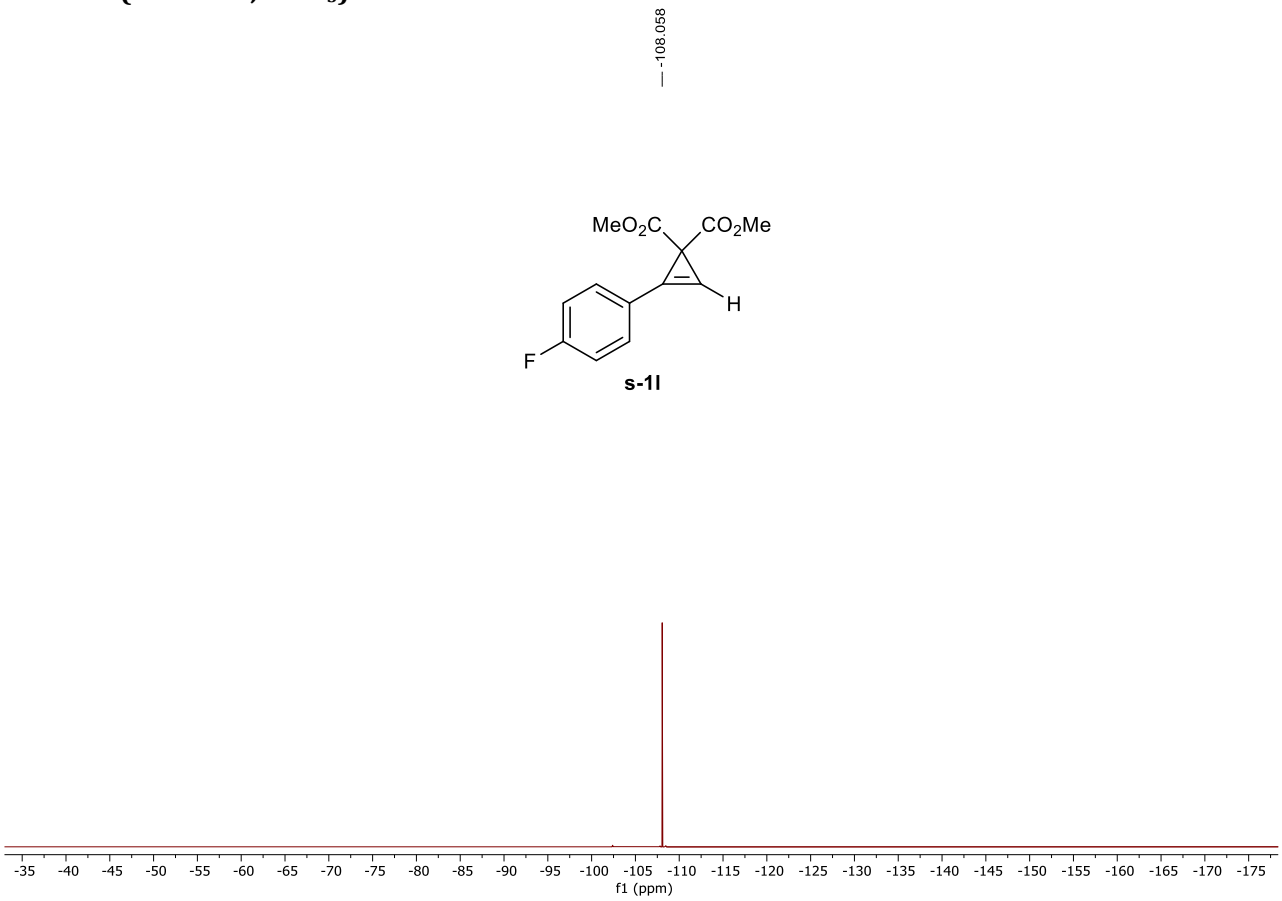
^{1}H NMR (400 MHz, $CDCl_3$) of s-1l



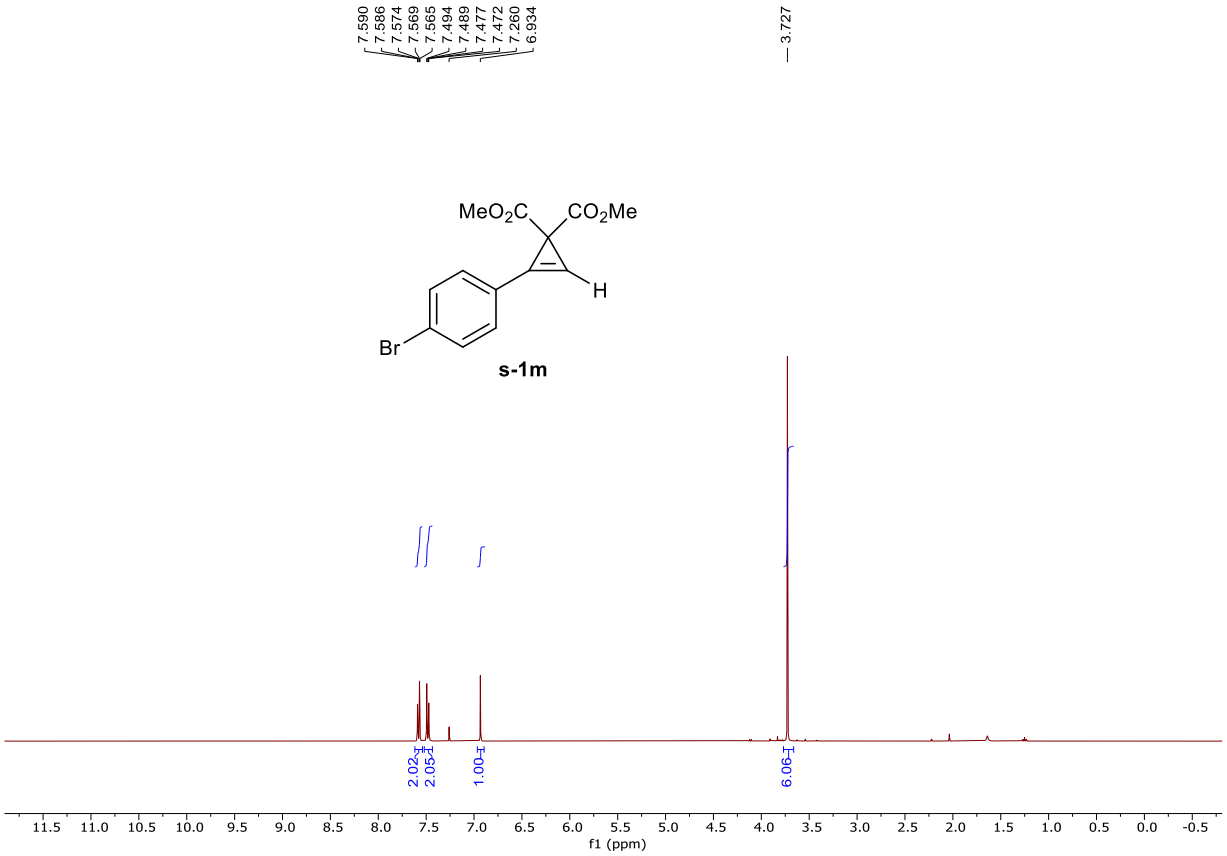
^{13}C NMR (101 MHz, $CDCl_3$) of s-1l



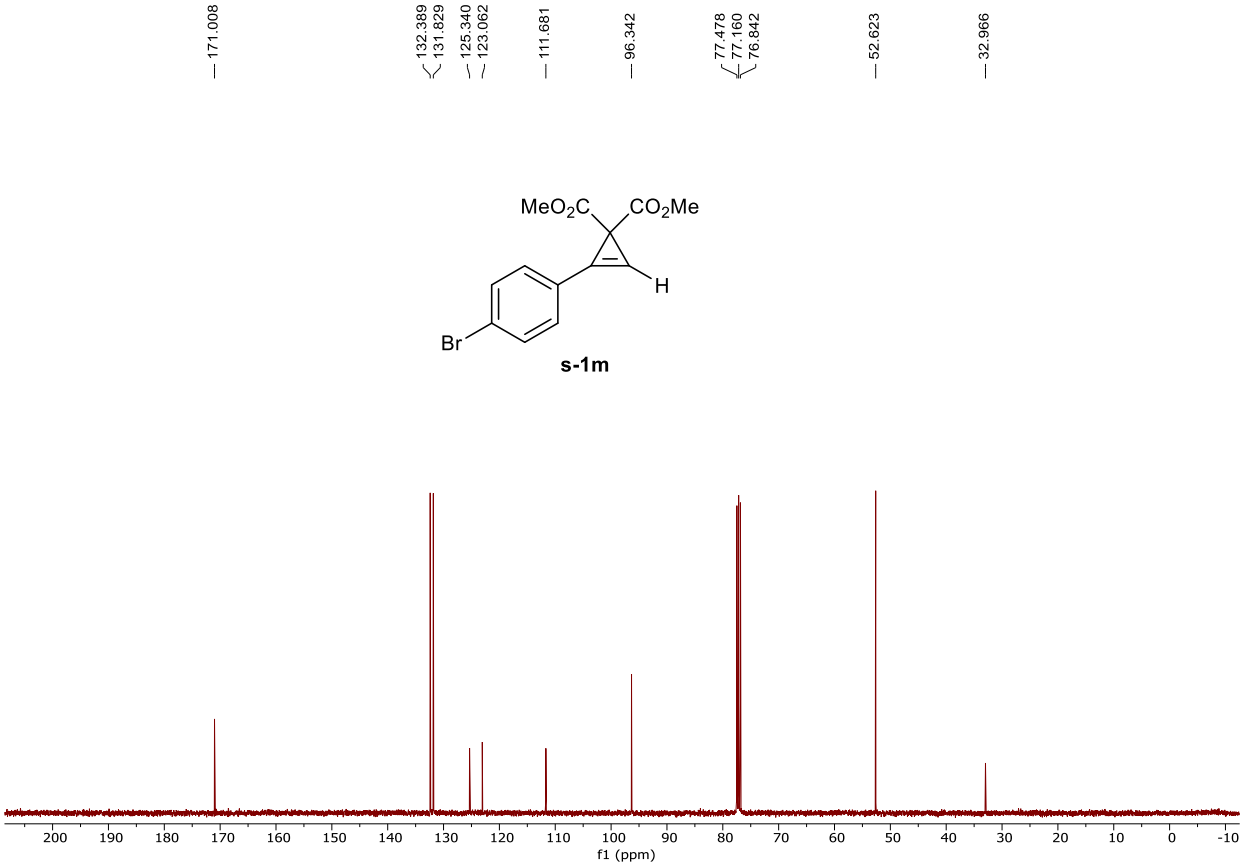
^{19}F NMR (377 MHz, $CDCl_3$) of s-1l



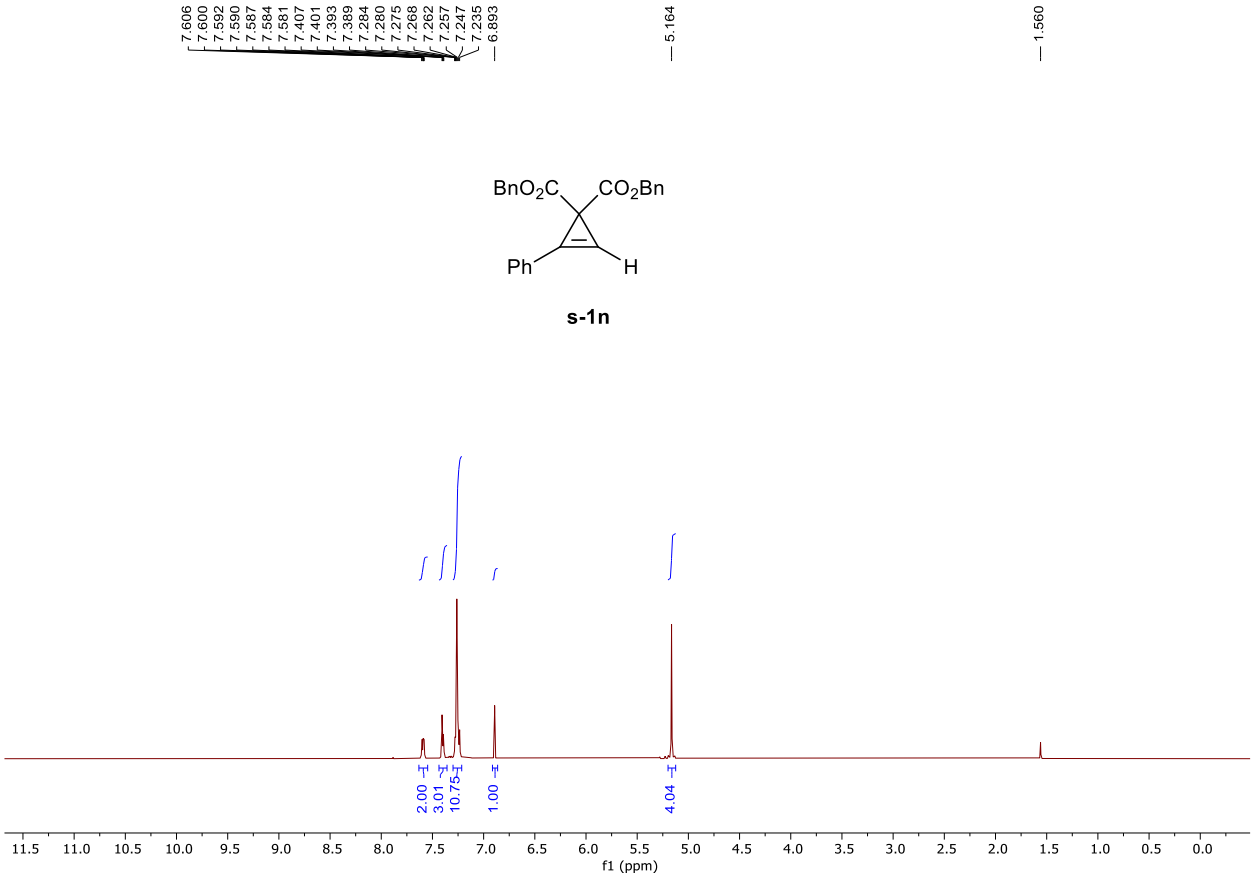
^{1}H NMR (400 MHz, $CDCl_3$) of s-1m



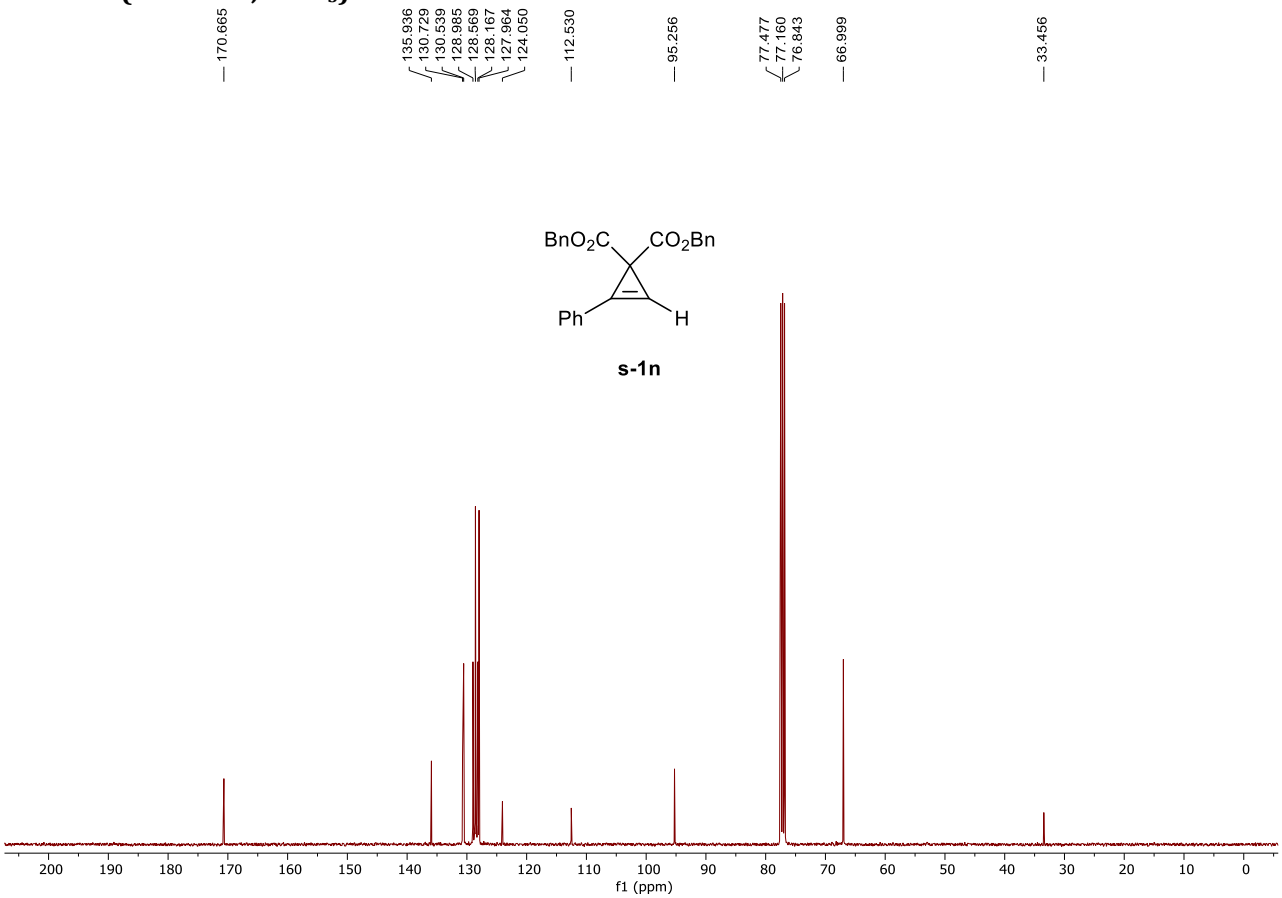
^{13}C NMR (101 MHz, $CDCl_3$) of s-1m



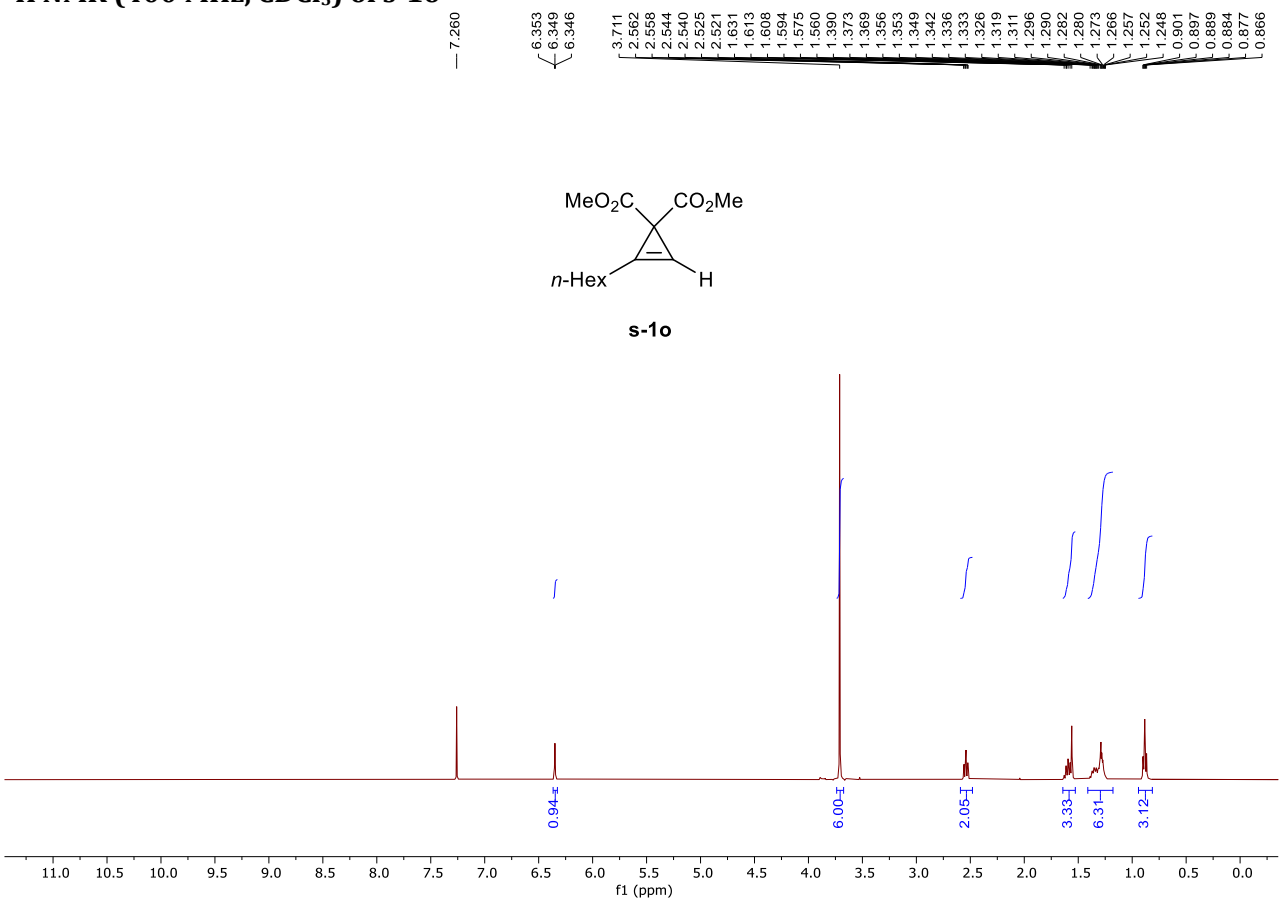
^{1}H NMR (400 MHz, $CDCl_3$) of s-1n



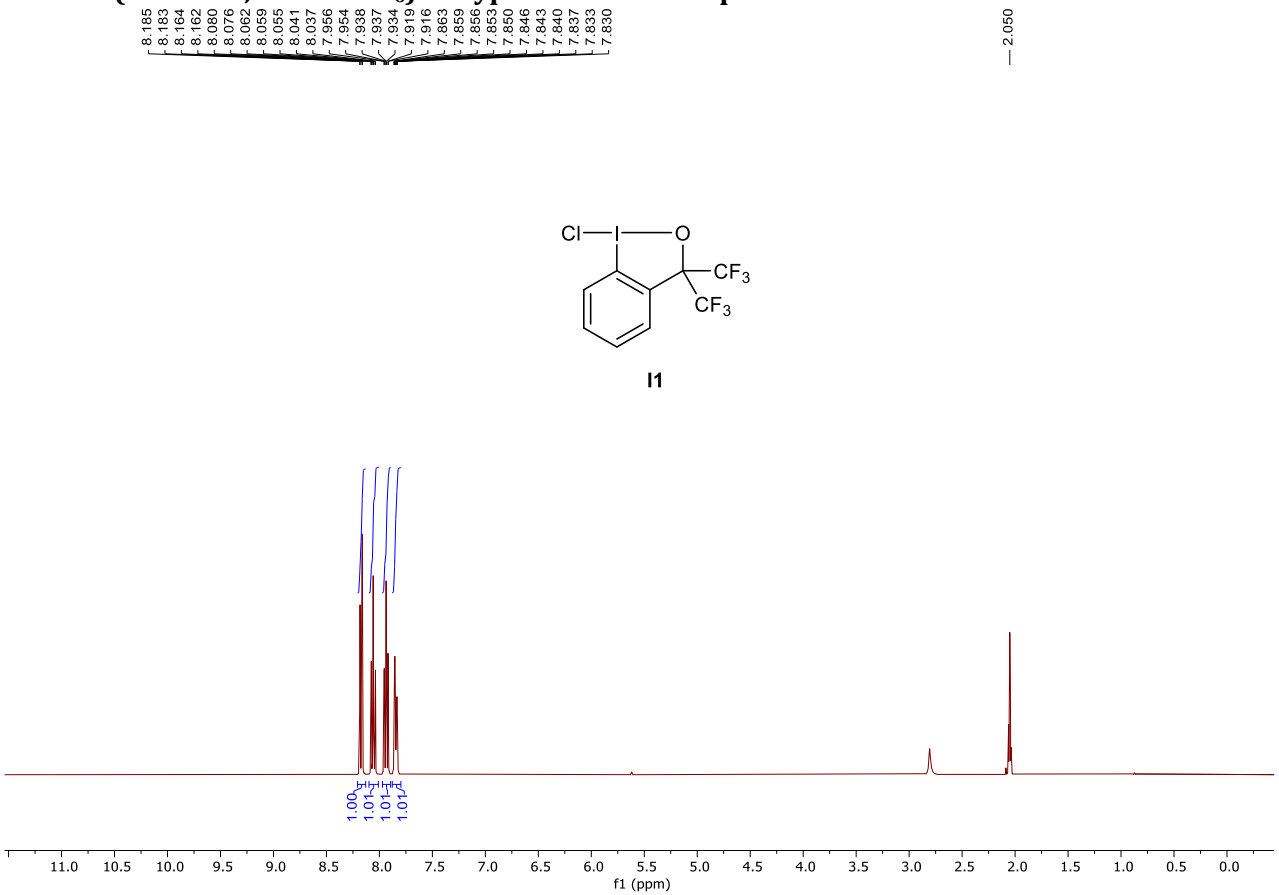
^{13}C NMR (101 MHz, $CDCl_3$) of s-1n



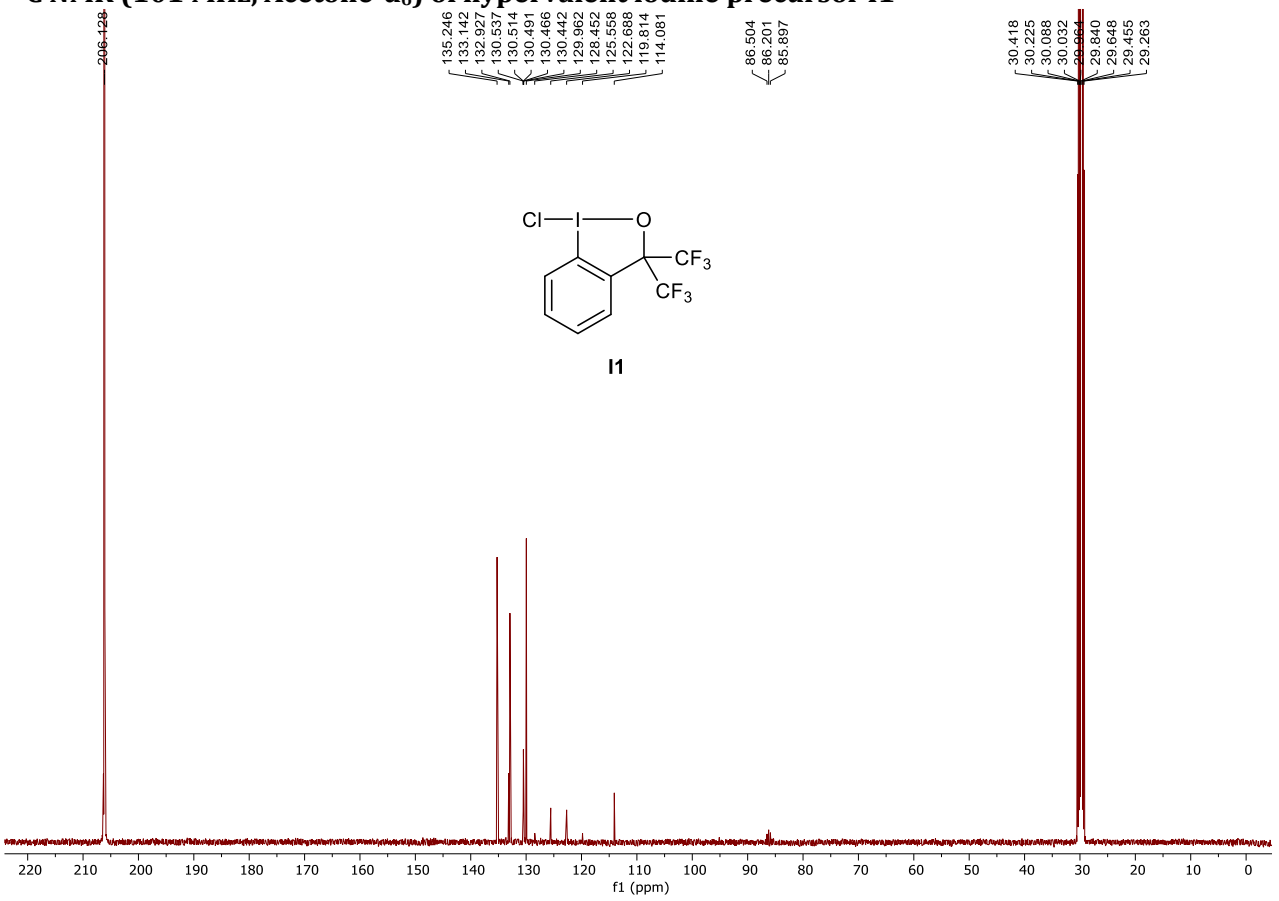
^{1}H NMR (400 MHz, $CDCl_3$) of s-1o



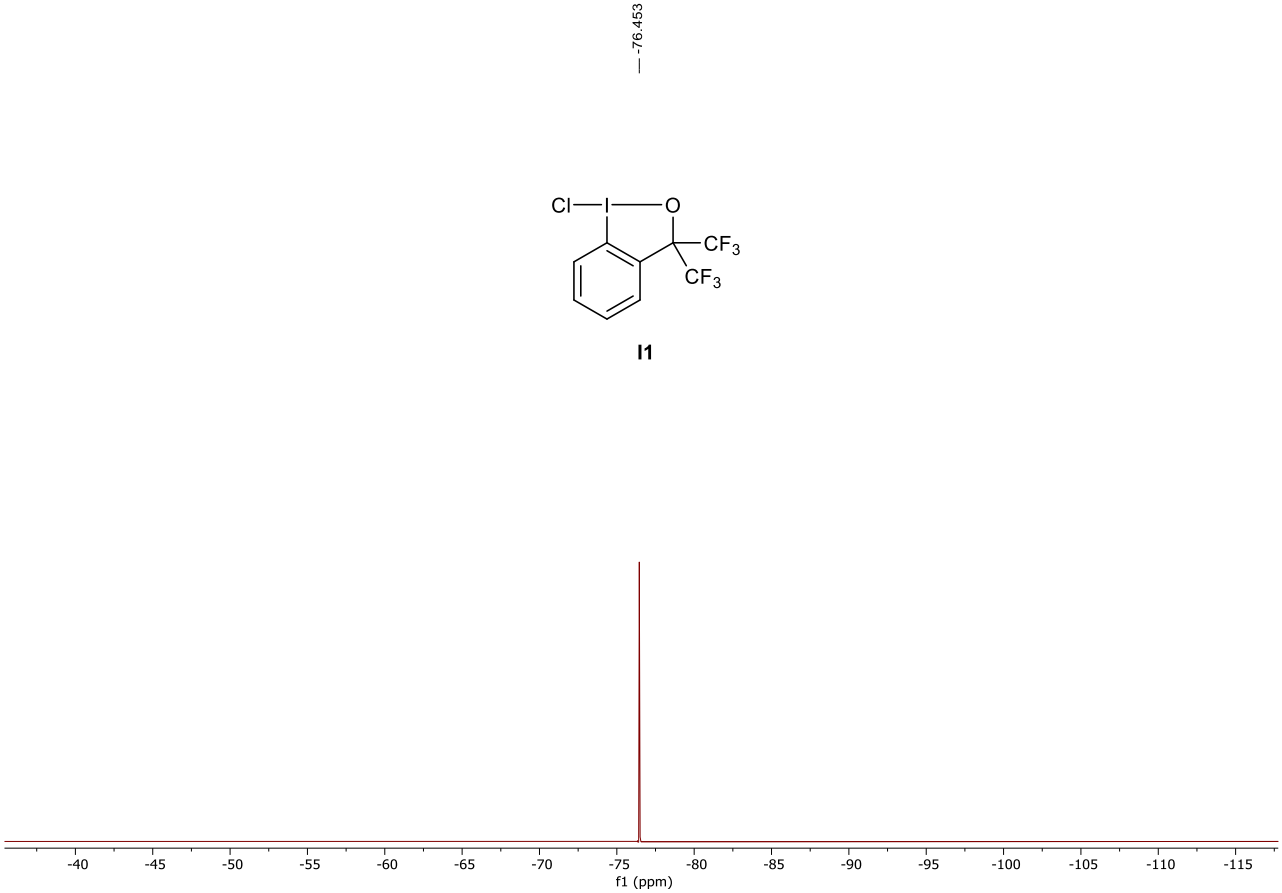
^{1}H NMR (400 MHz, Acetone-d_6) of hypervalent iodine precursor I1



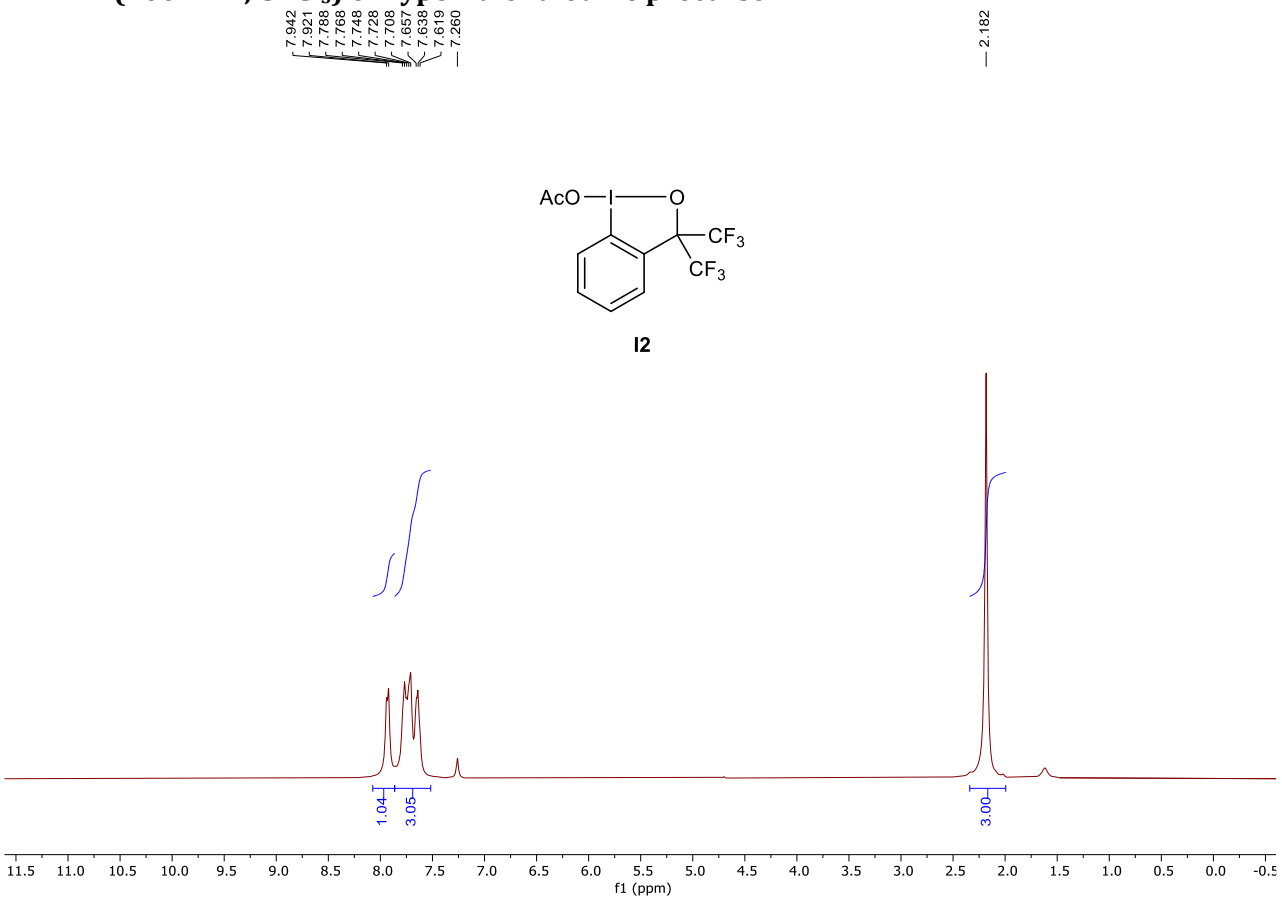
^{13}C NMR (101 MHz, Acetone-d_6) of hypervalent iodine precursor I1



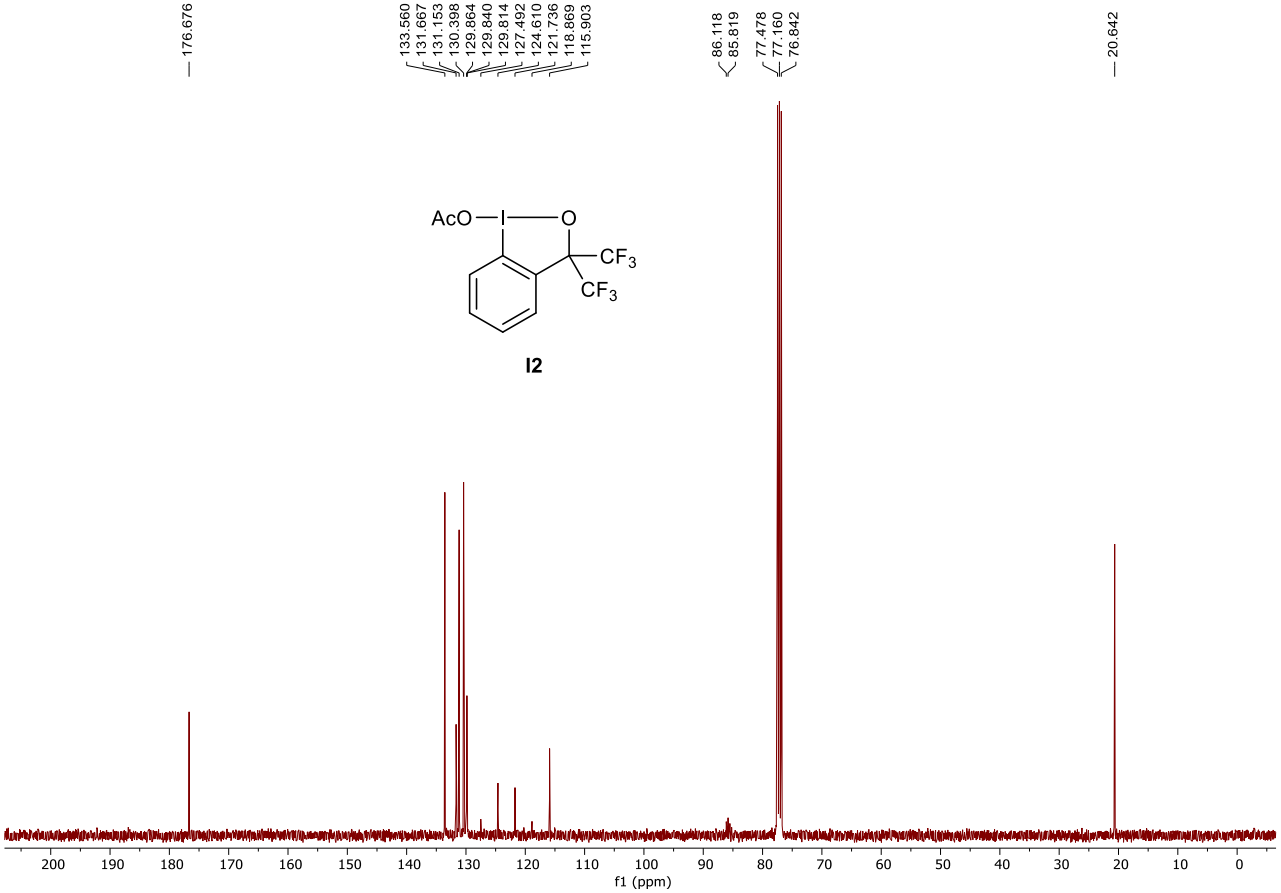
^{19}F NMR (377 MHz, Acetone-d_6) of hypervalent iodine precursor I1



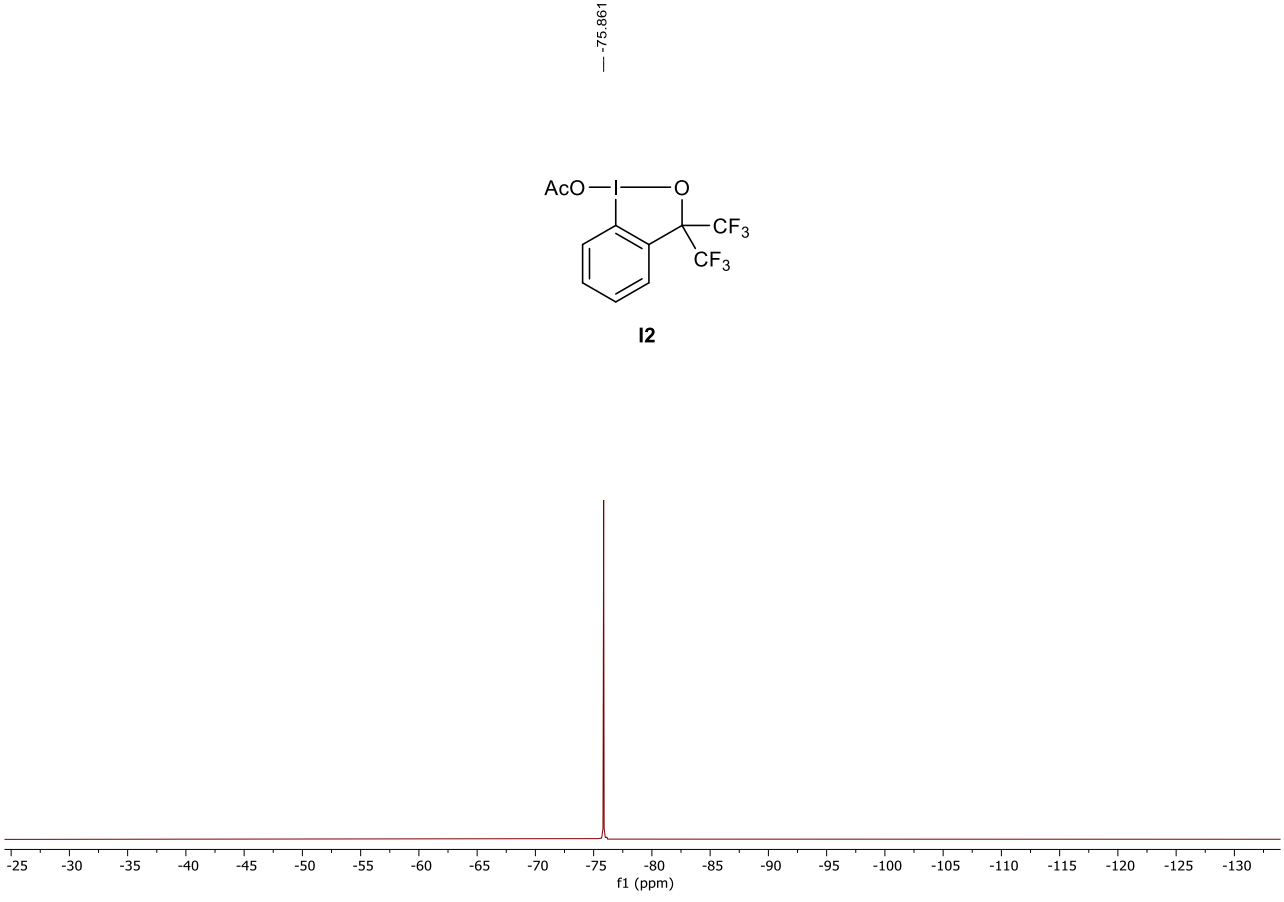
^{1}H NMR (400 MHz, $CDCl_3$) of hypervalent iodine precursor I2



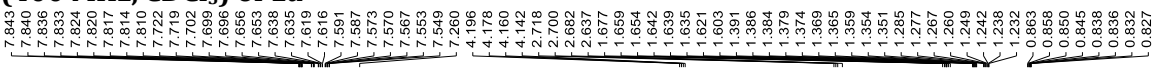
^{13}C NMR (101 MHz, $CDCl_3$) of hypervalent iodine precursor I2

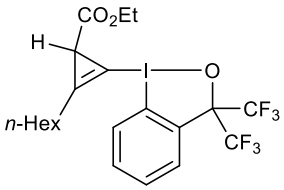


^{19}F NMR (377 MHz, $CDCl_3$) of hypervalent iodine precursor I2

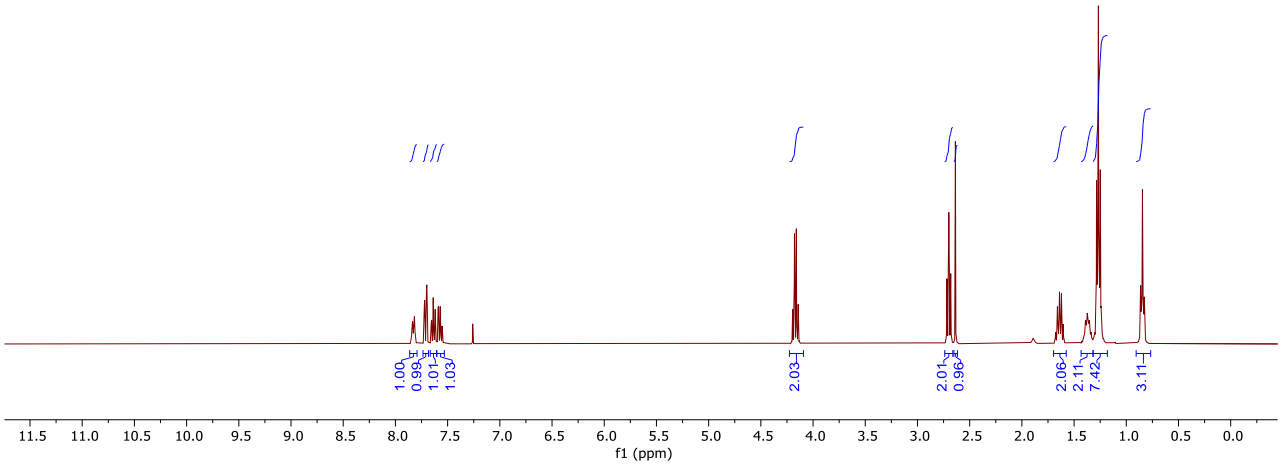


^{1}H NMR (400 MHz, $CDCl_3$) of 1a

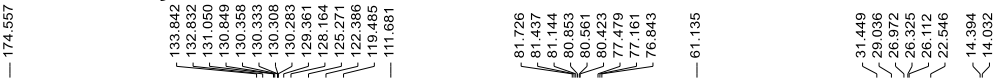


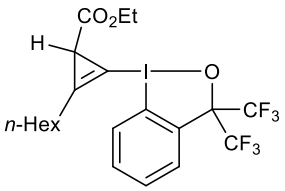


1a

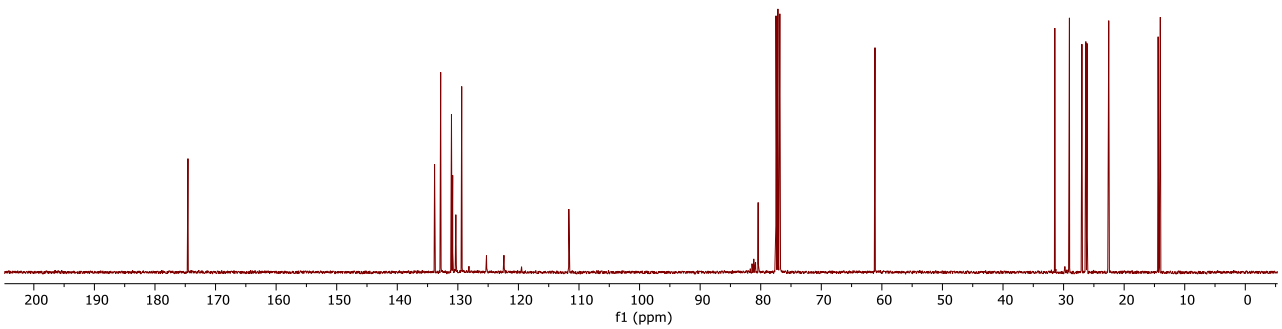


^{13}C NMR (101 MHz, $CDCl_3$) of 1a

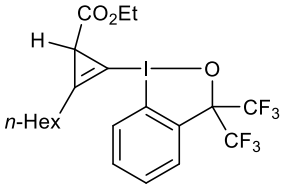




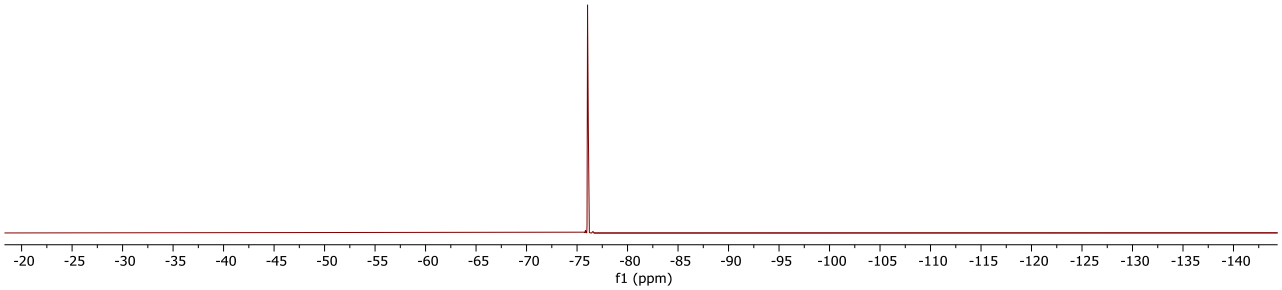
1a



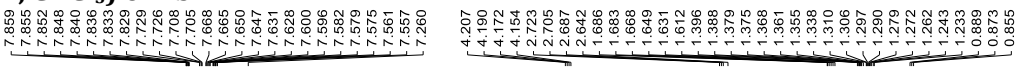
^{19}F NMR (377 MHz, $CDCl_3$) of 1a

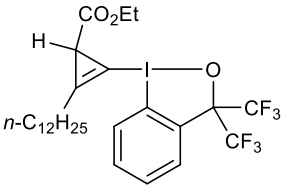


1a



^{1}H NMR (400 MHz, $CDCl_3$) of 1b





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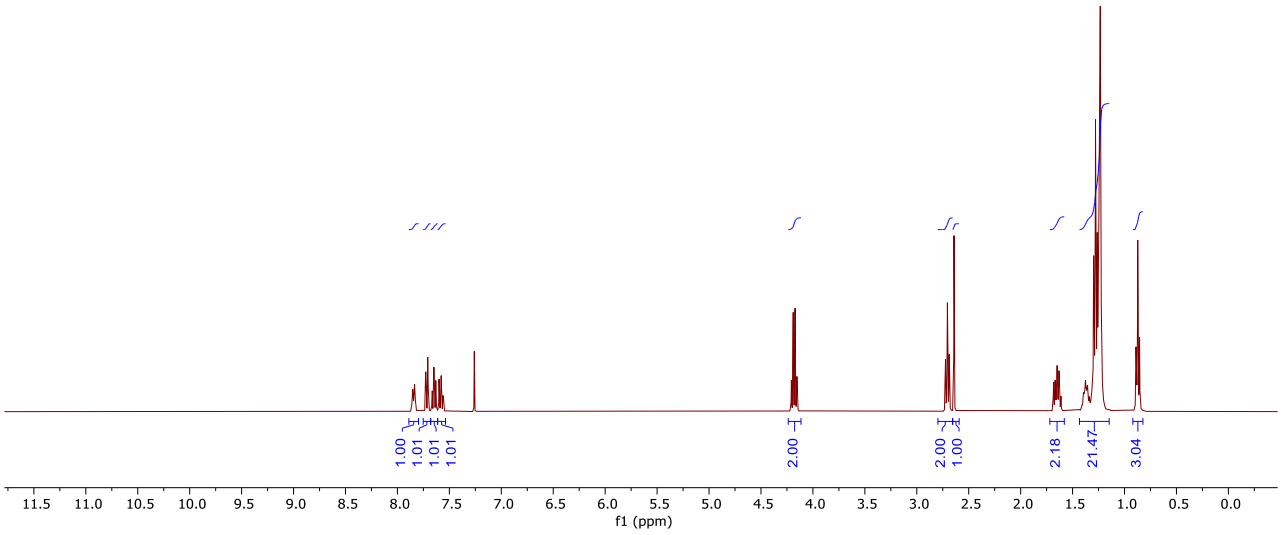
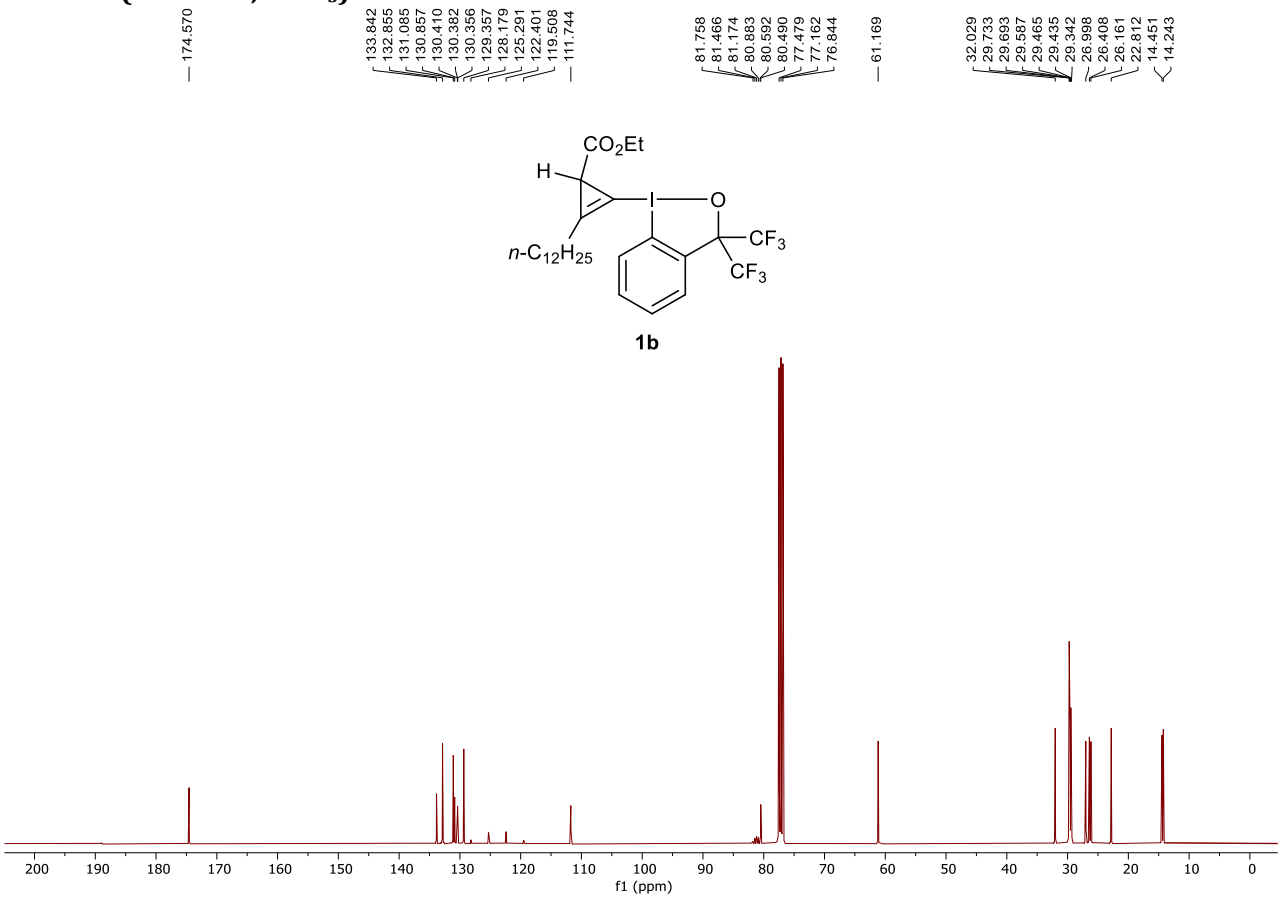
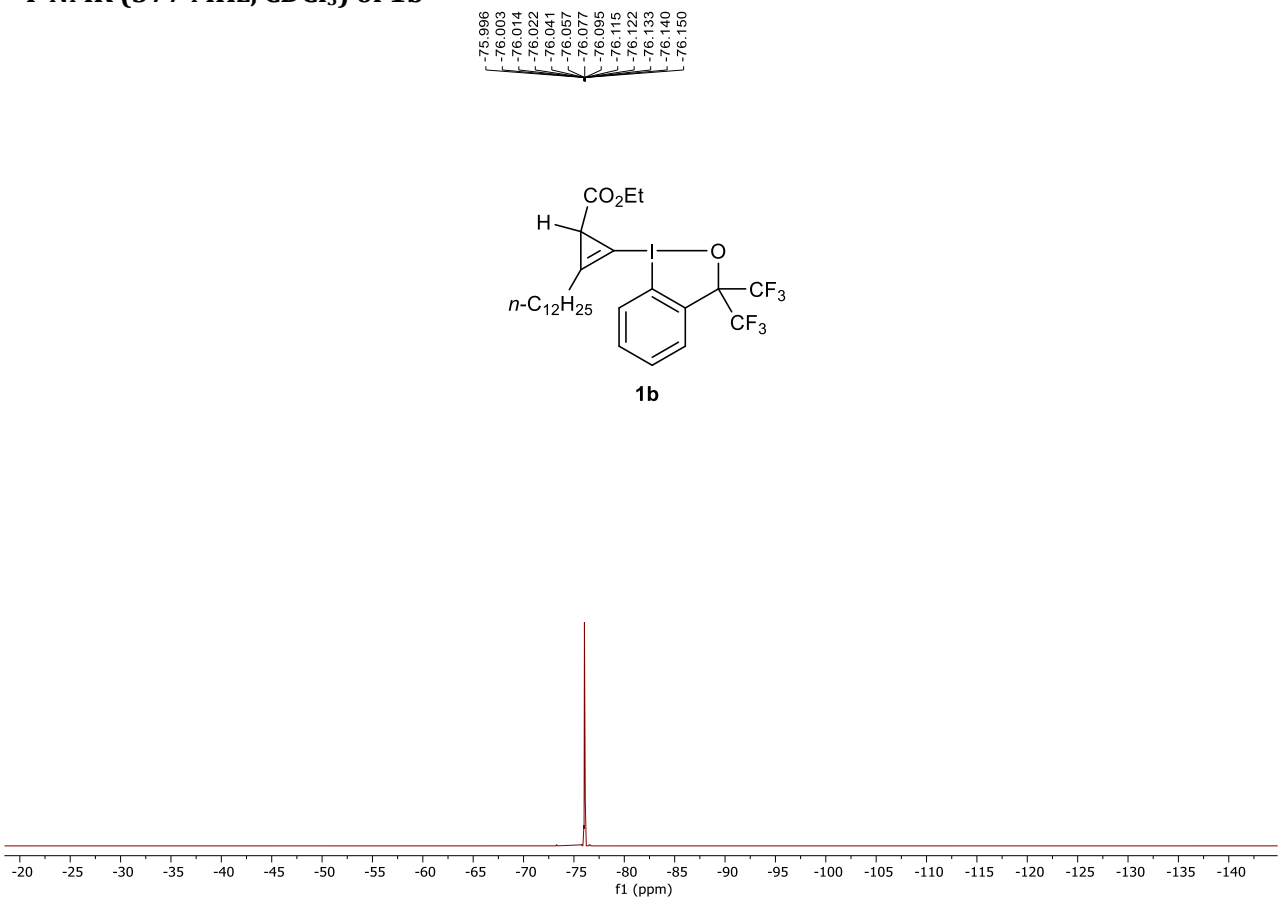


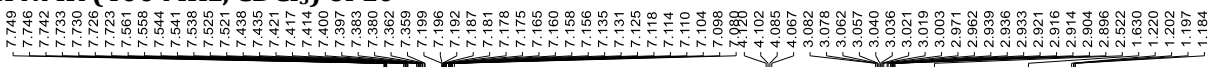
^{13}C NMR (101 MHz, $CDCl_3$) of 1b

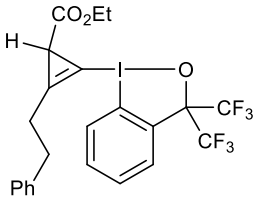


^{19}F NMR (377 MHz, $CDCl_3$) of 1b



^{1}H NMR (400 MHz, $CDCl_3$) of 1c





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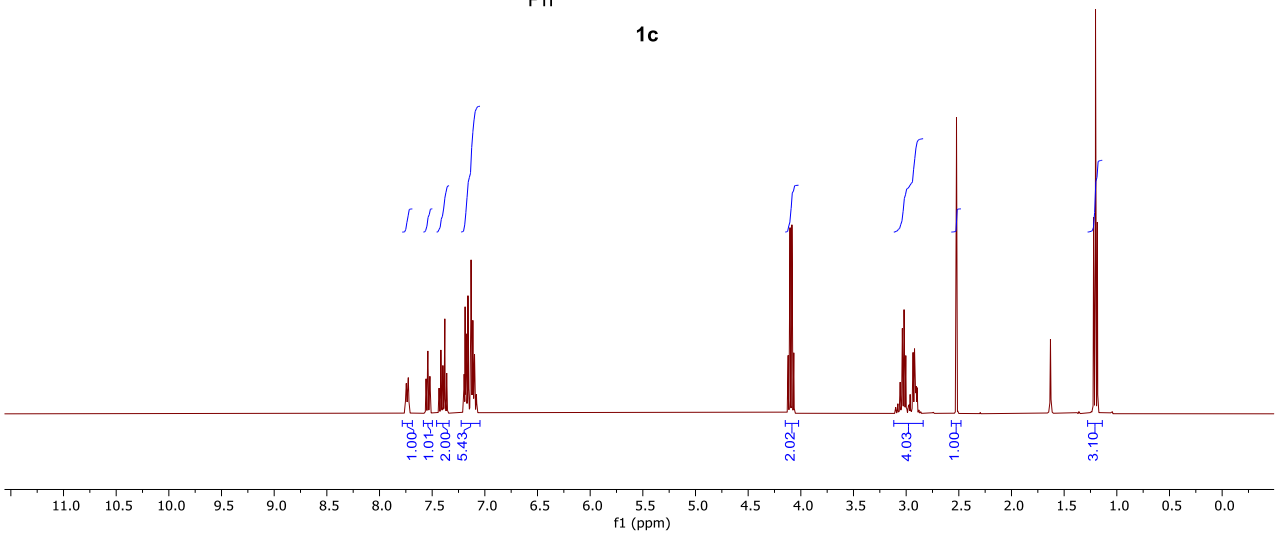
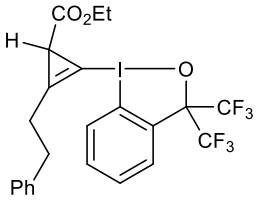
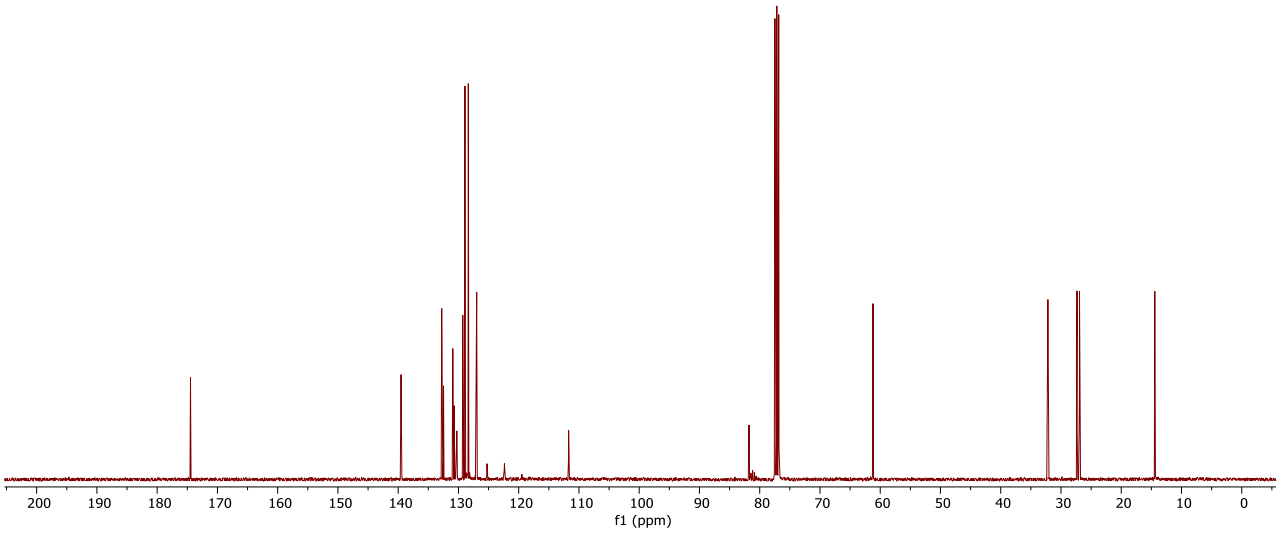


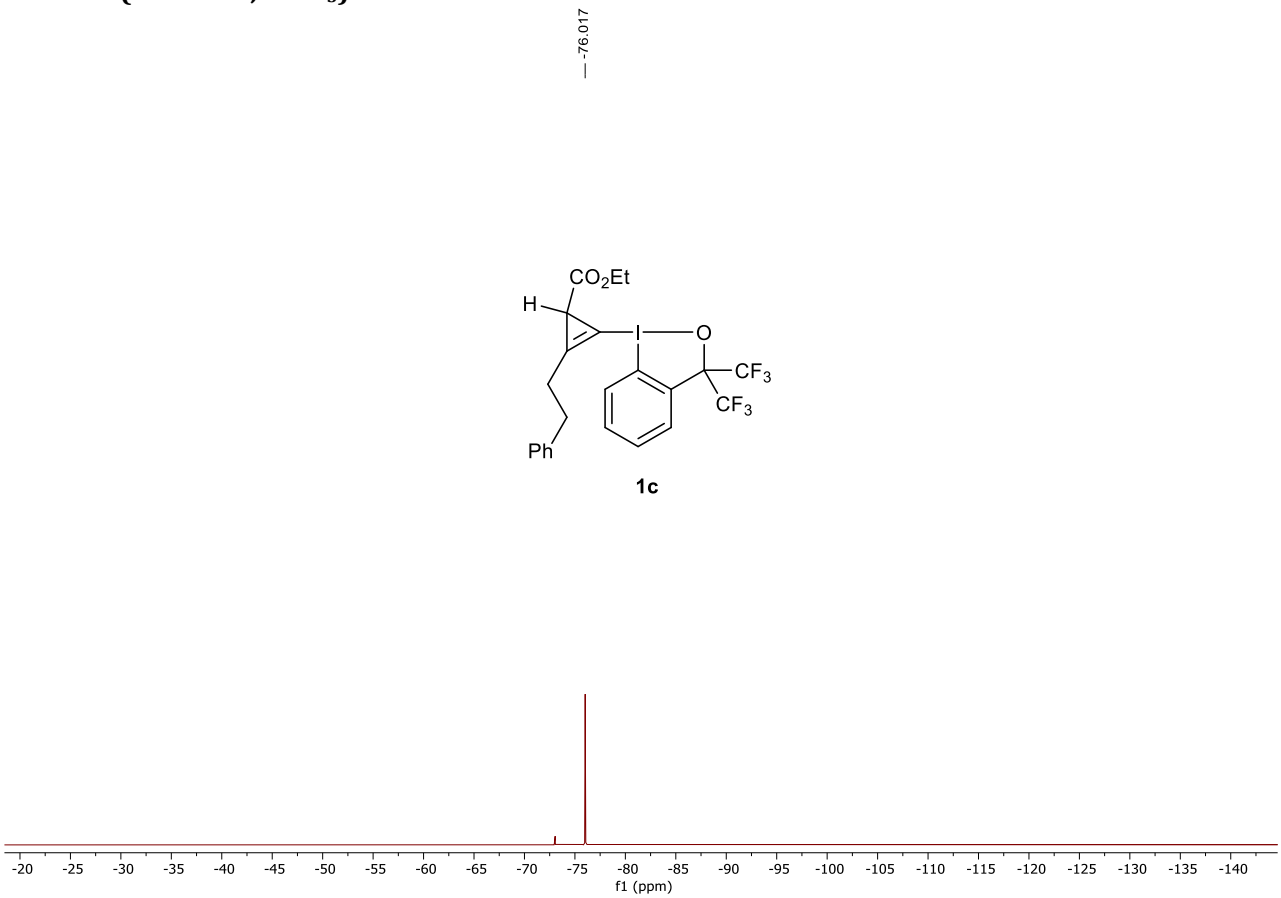
^{13}C NMR (101 MHz, $CDCl_3$) of 1c



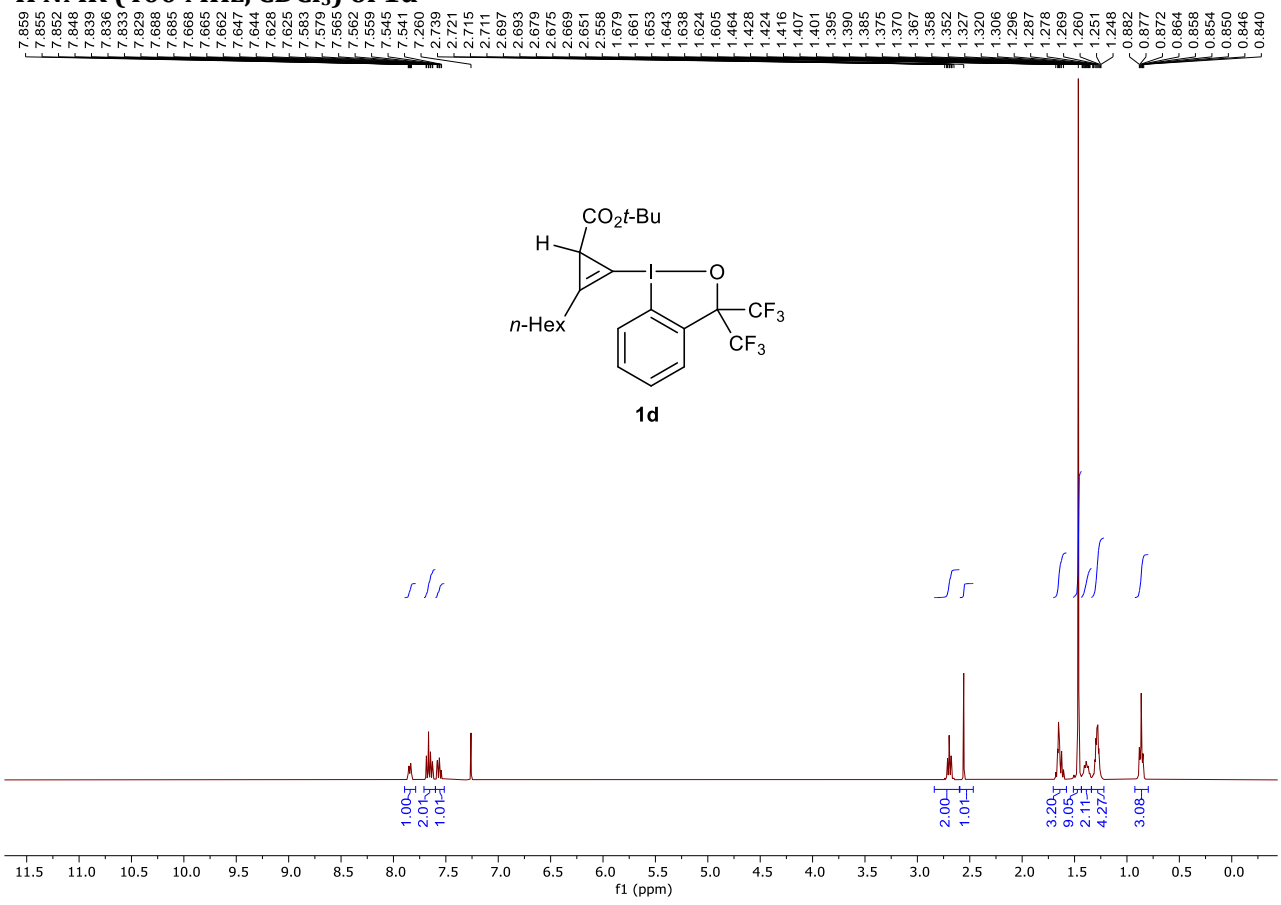
1c



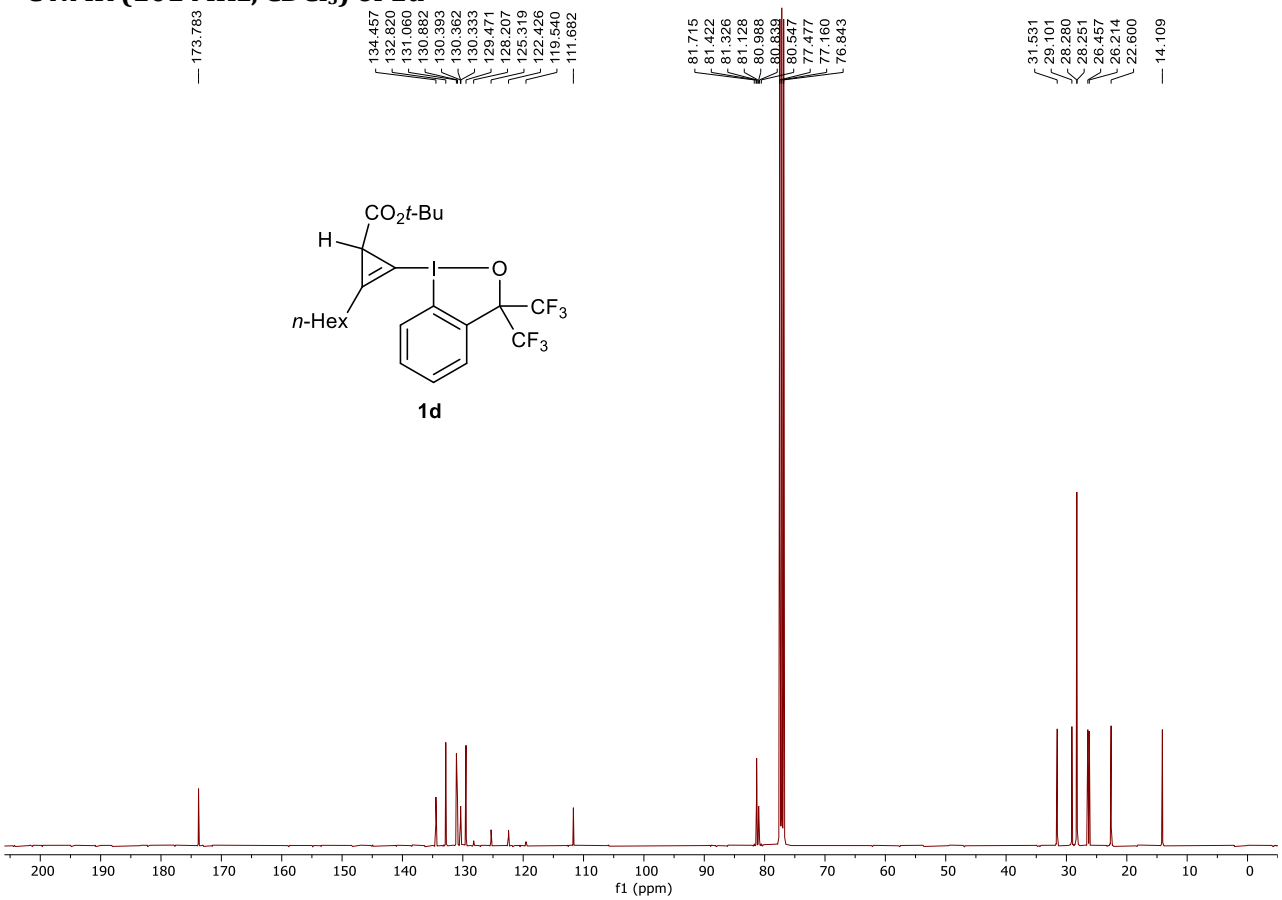
^{19}F NMR (377 MHz, $CDCl_3$) of 1c



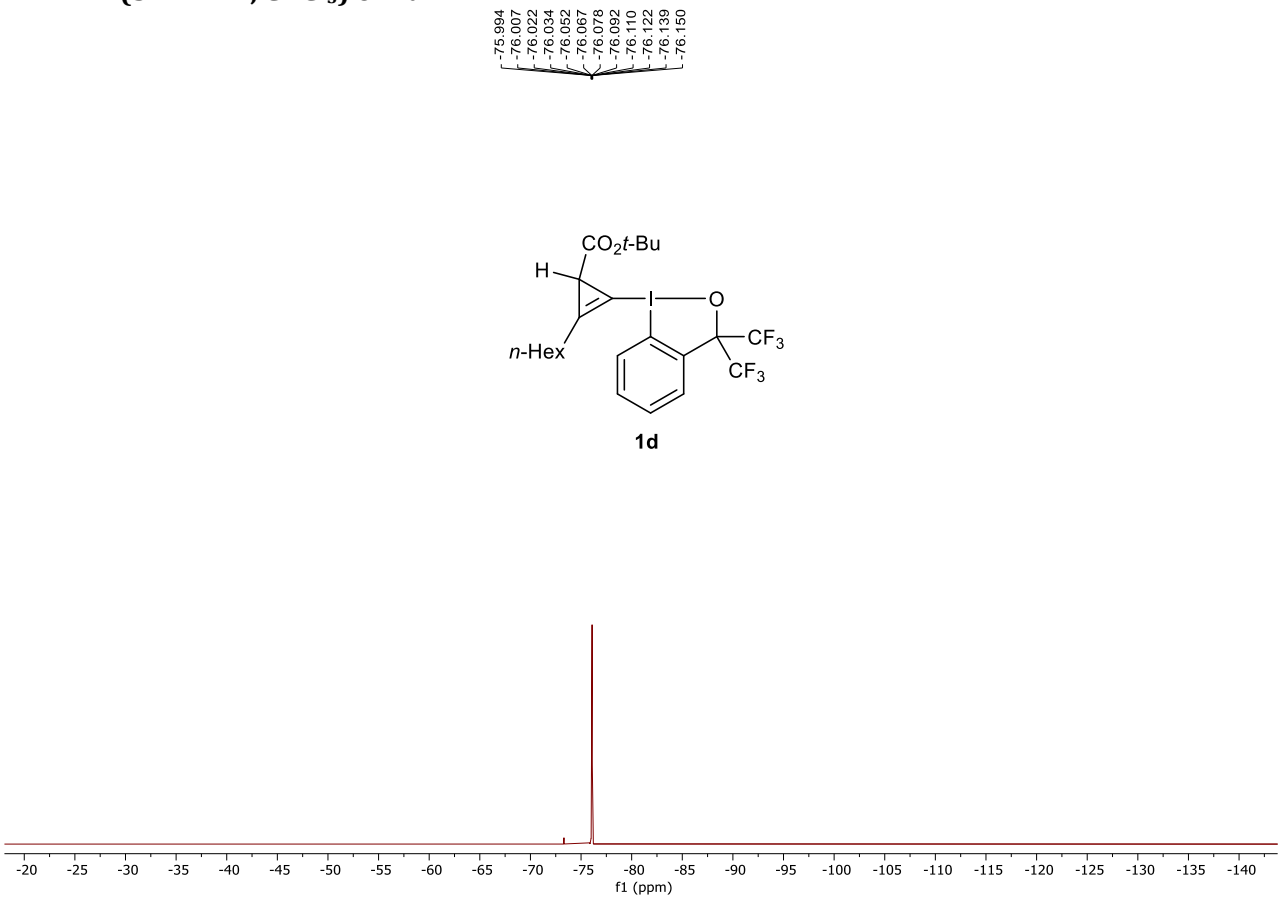
^{1}H NMR (400 MHz, $CDCl_3$) of 1d



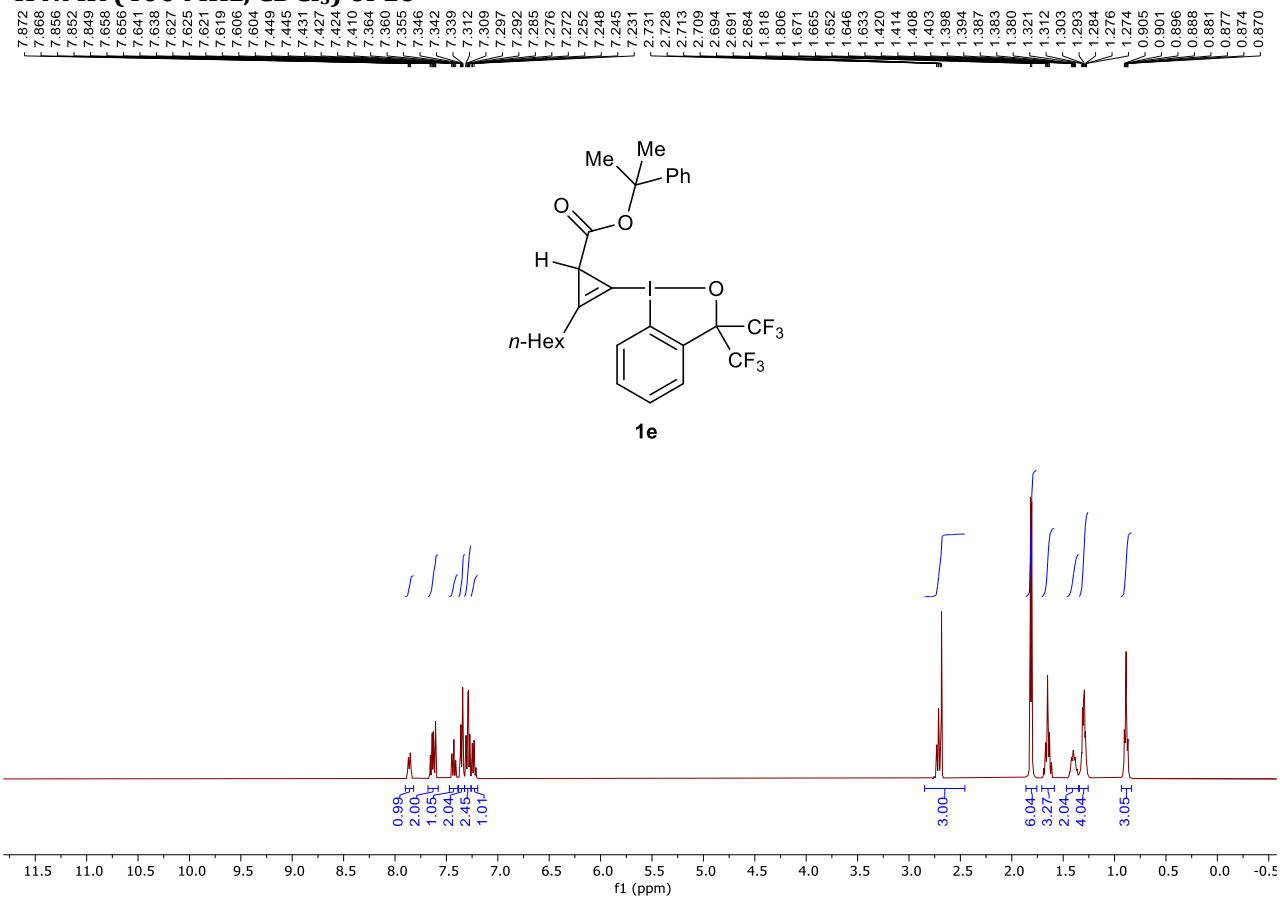
^{13}C NMR (101 MHz, $CDCl_3$) of 1d



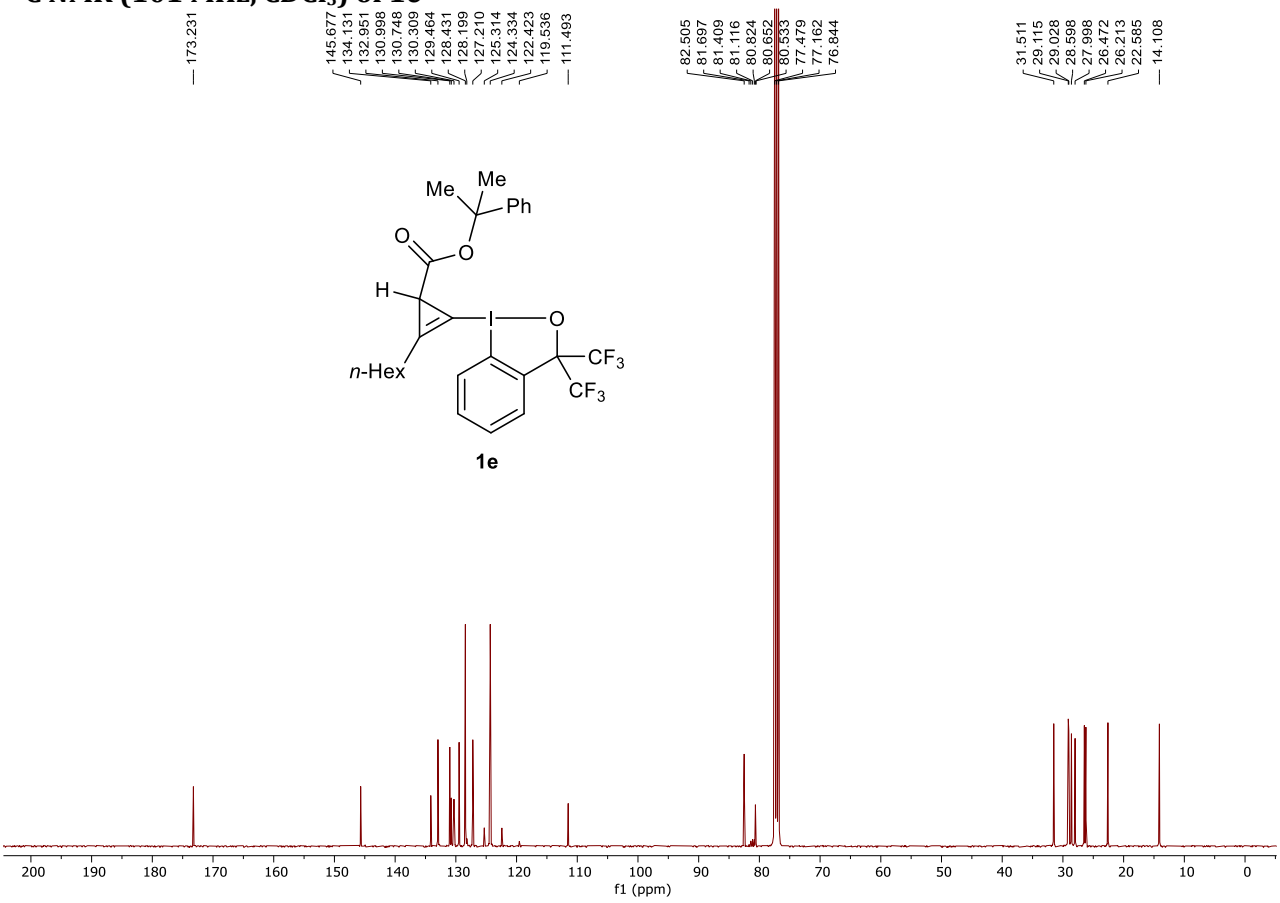
^{19}F NMR (377 MHz, $CDCl_3$) of 1d



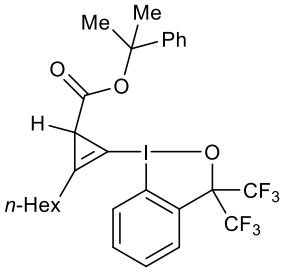
^{1}H NMR (400 MHz, $CDCl_3$) of 1e



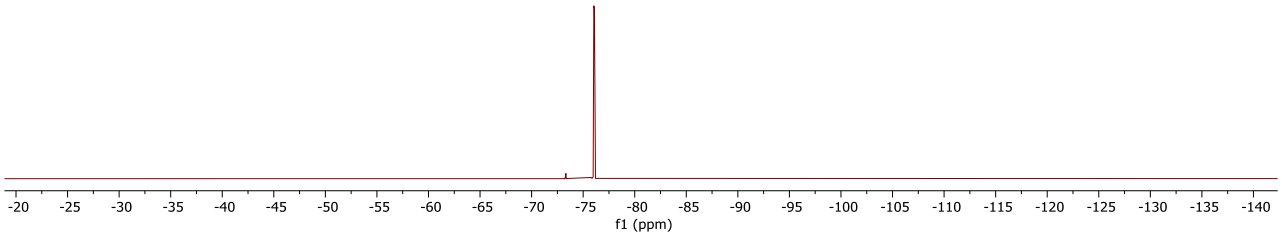
^{13}C NMR (101 MHz, $CDCl_3$) of 1e



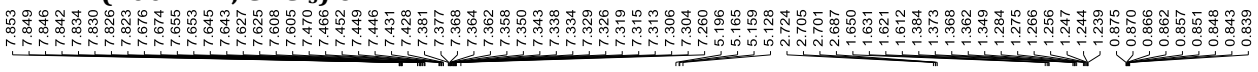
^{19}F NMR (377 MHz, $CDCl_3$) of 1e

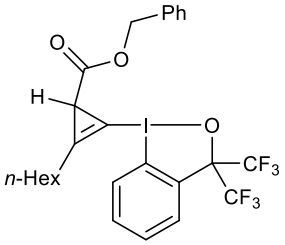


1e



^{1}H NMR (400 MHz, $CDCl_3$) of 1f





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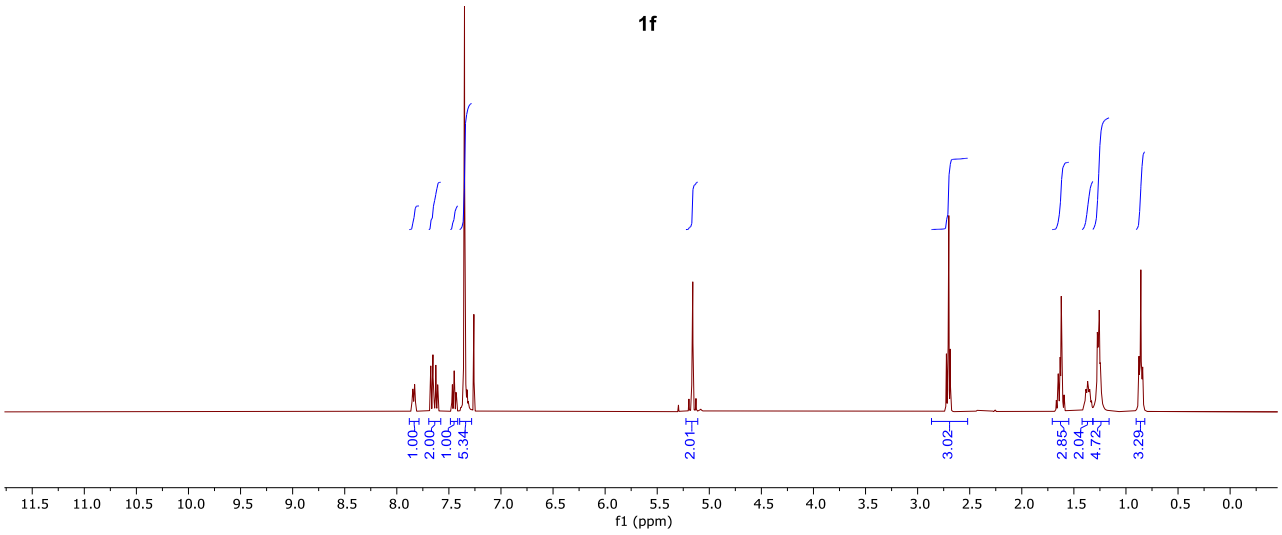
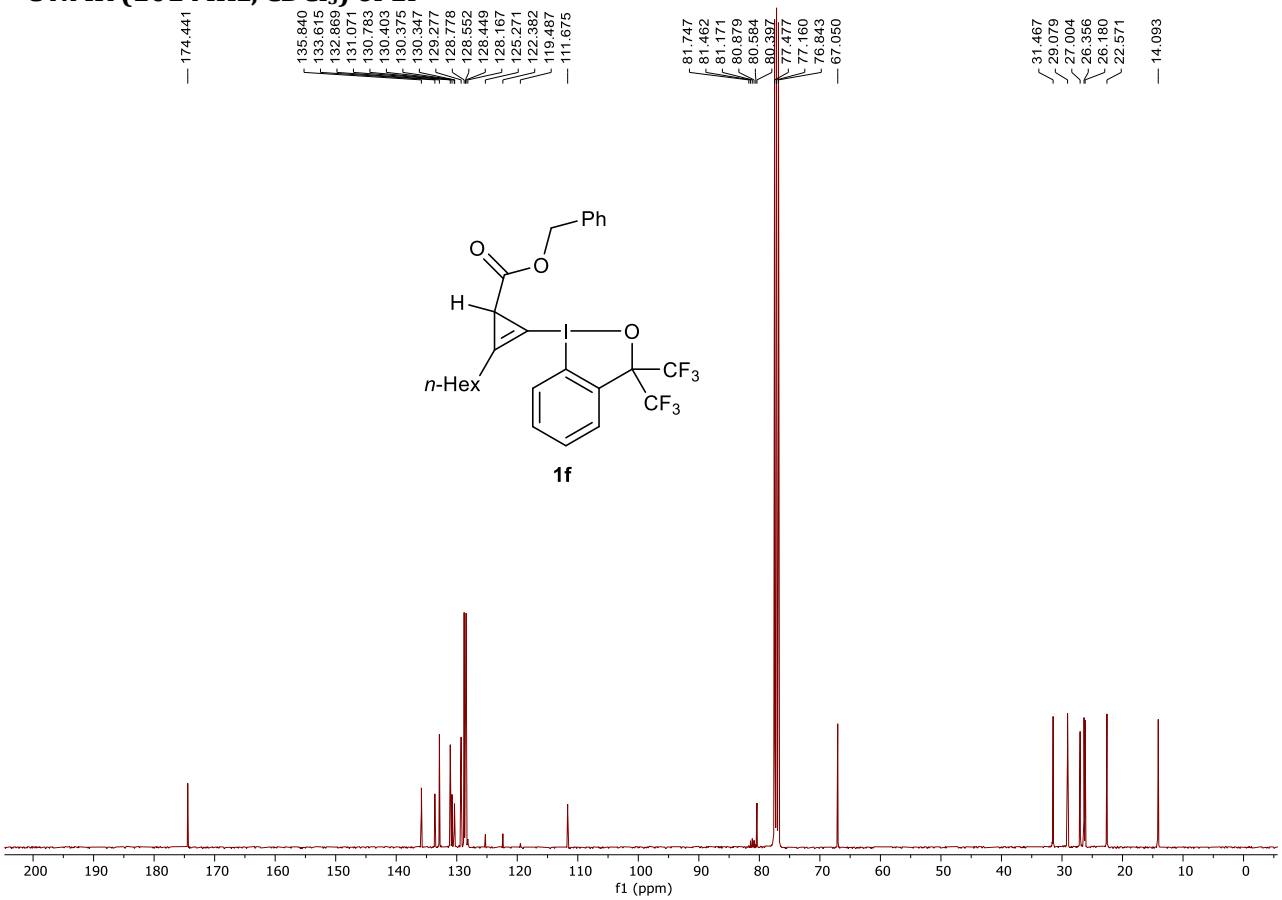
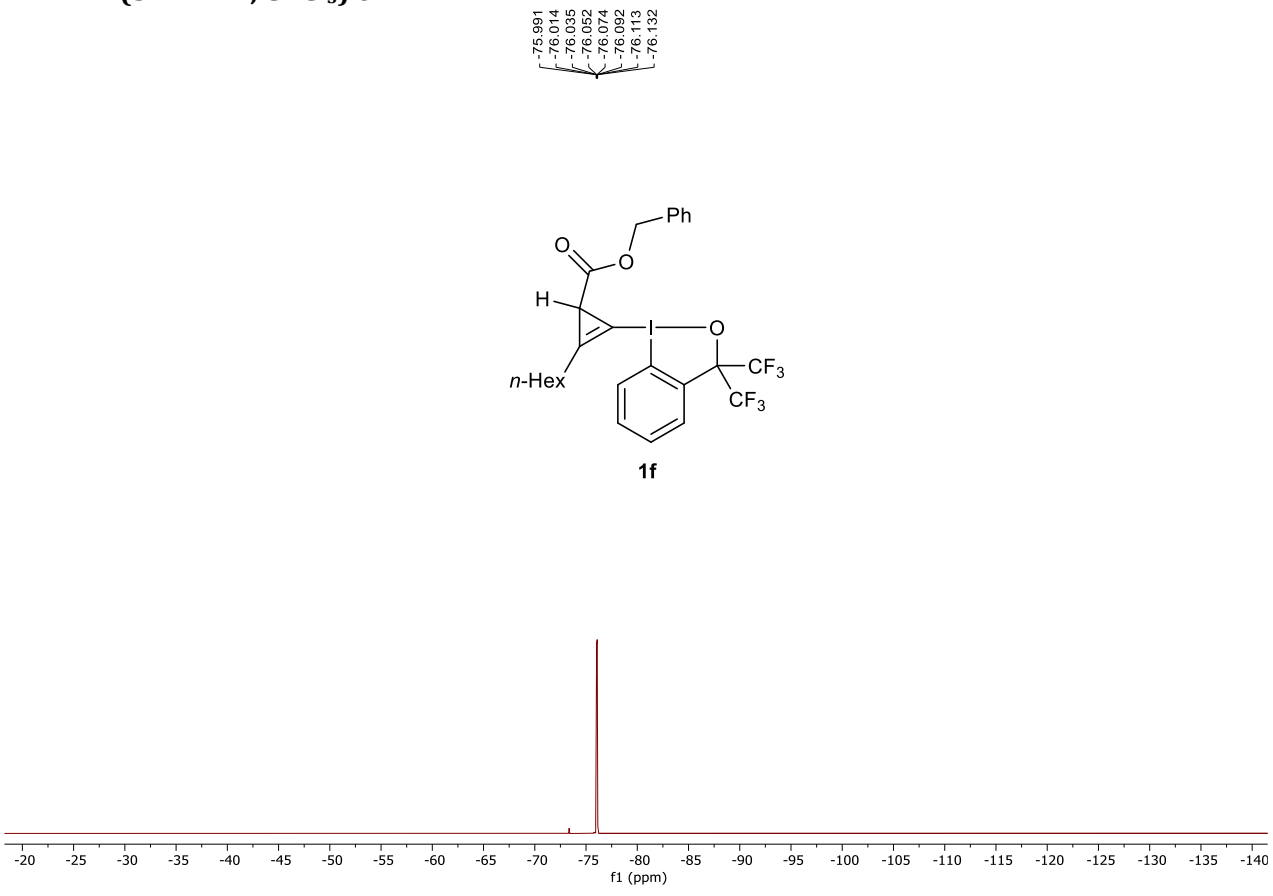


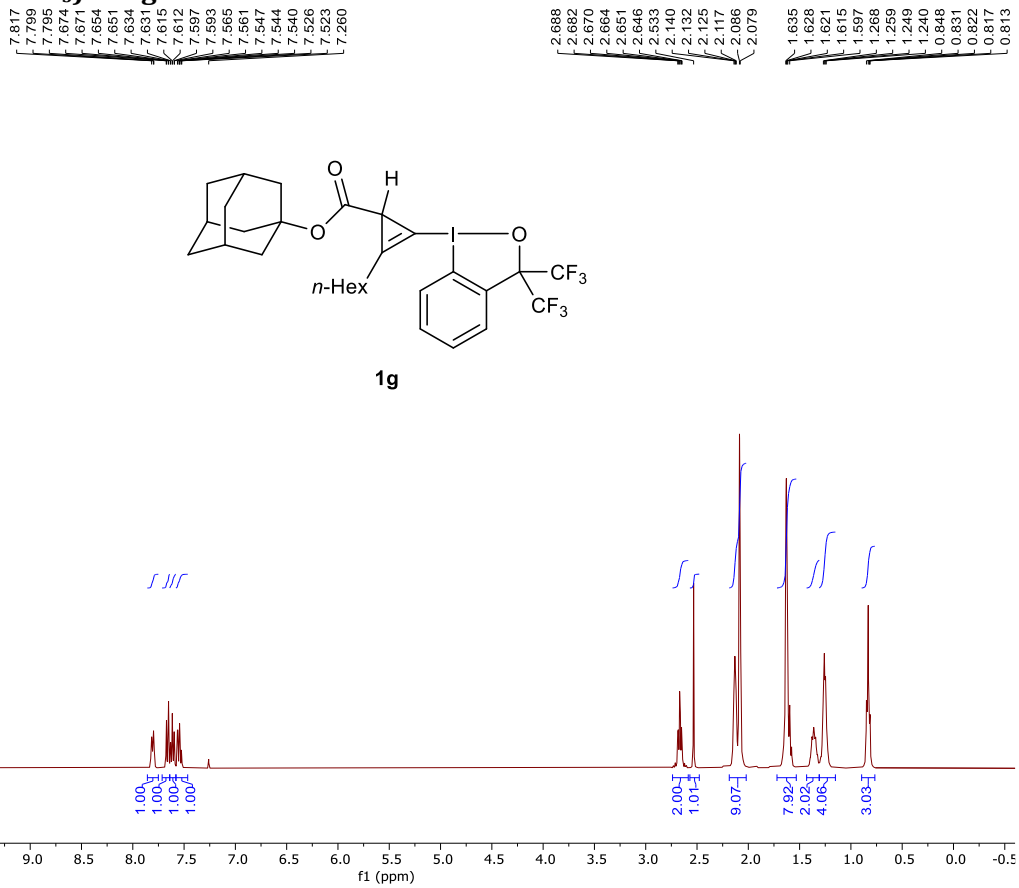
^{13}C NMR (101 MHz, $CDCl_3$) of 1f



^{19}F NMR (377 MHz, $CDCl_3$) of 1f

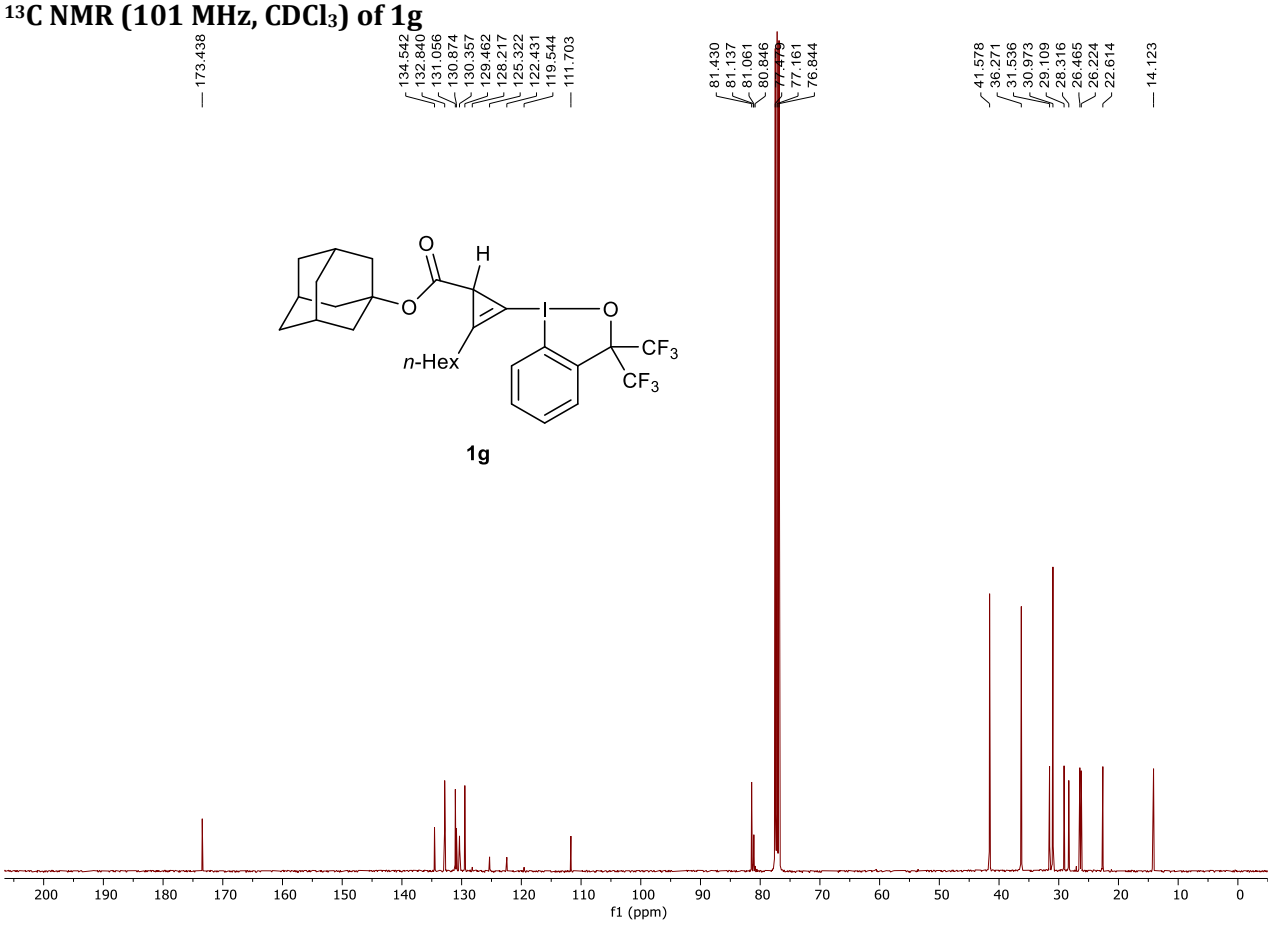


^{1}H NMR (400 MHz, $CDCl_3$) of 1g



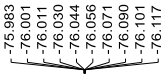
1g

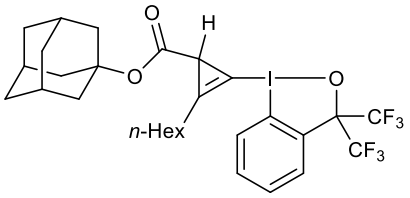
^{13}C NMR (101 MHz, $CDCl_3$) of 1g



1g

^{19}F NMR (377 MHz, $CDCl_3$) of 1g





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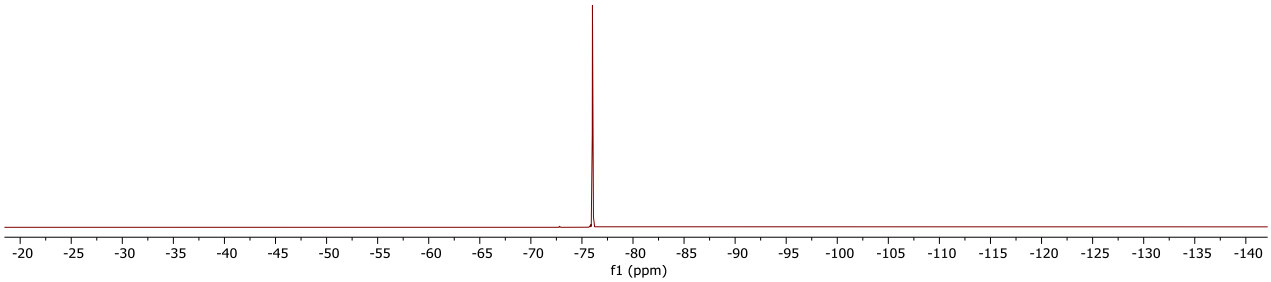
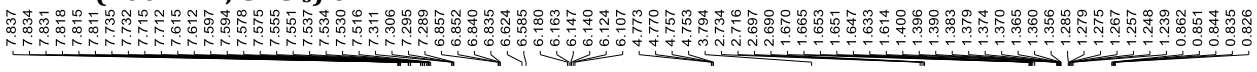
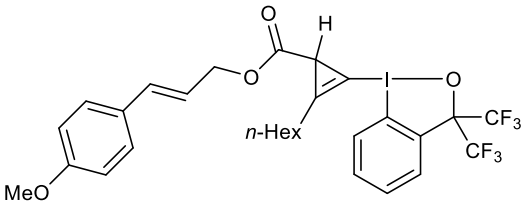
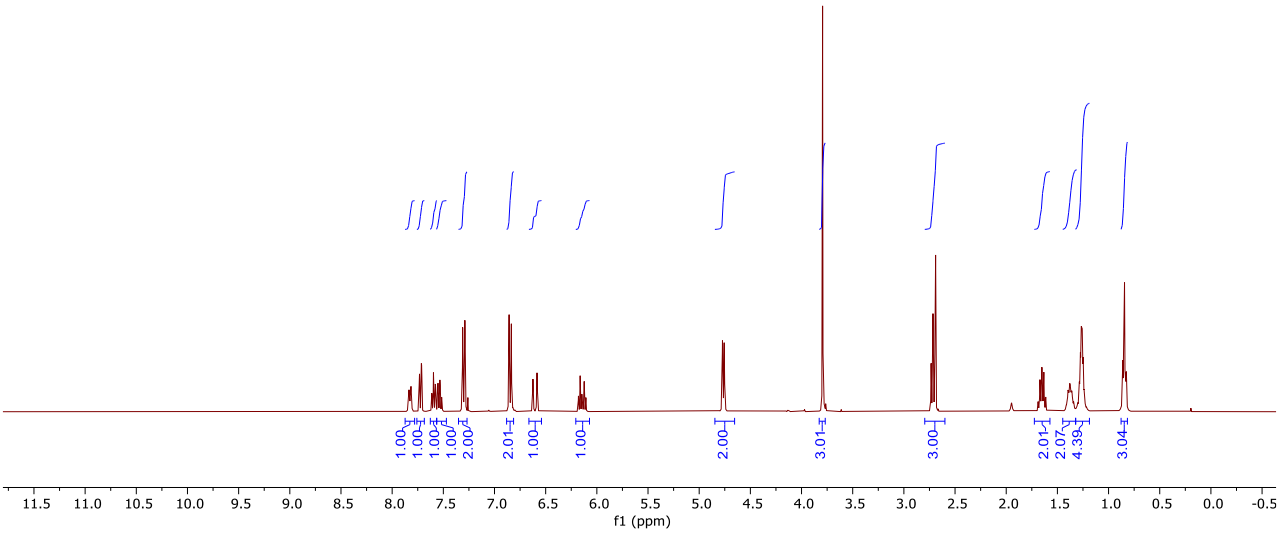


^{1}H NMR (400 MHz, $CDCl_3$) of 1h

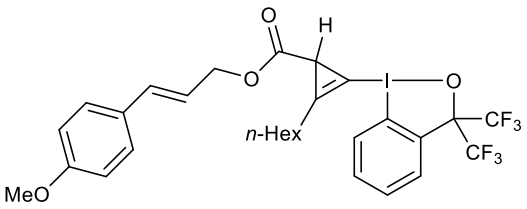




1h



^{13}C NMR (101 MHz, $CDCl_3$) of 1h



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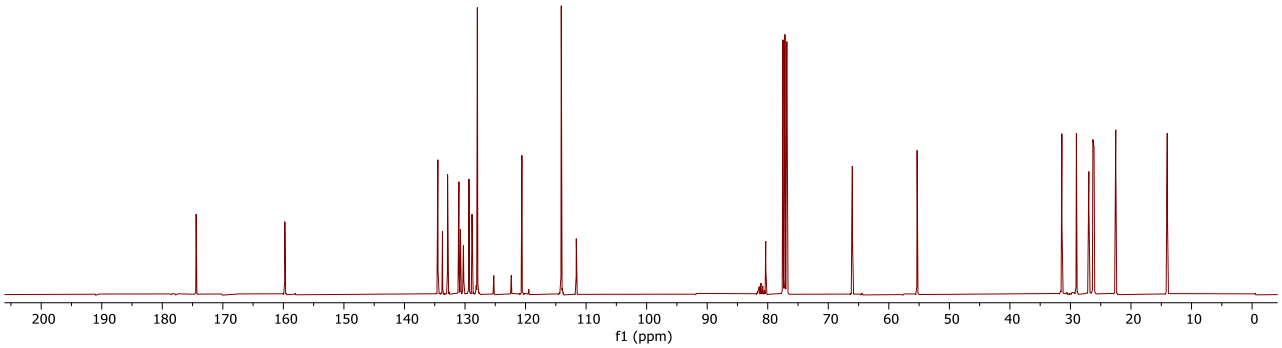
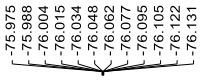
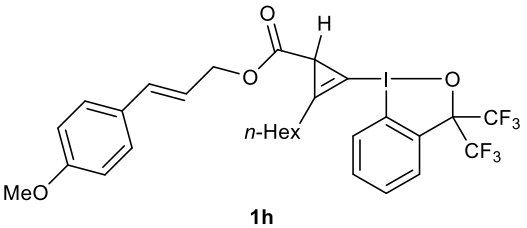


^{19}F NMR (377 MHz, $CDCl_3$) of 1h





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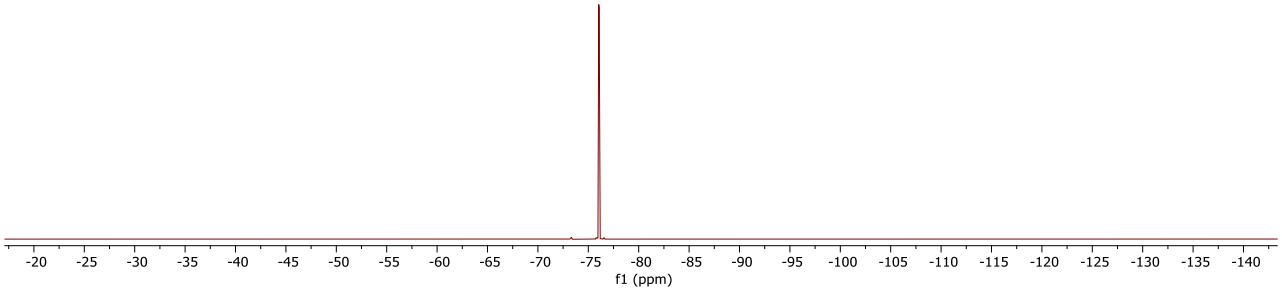
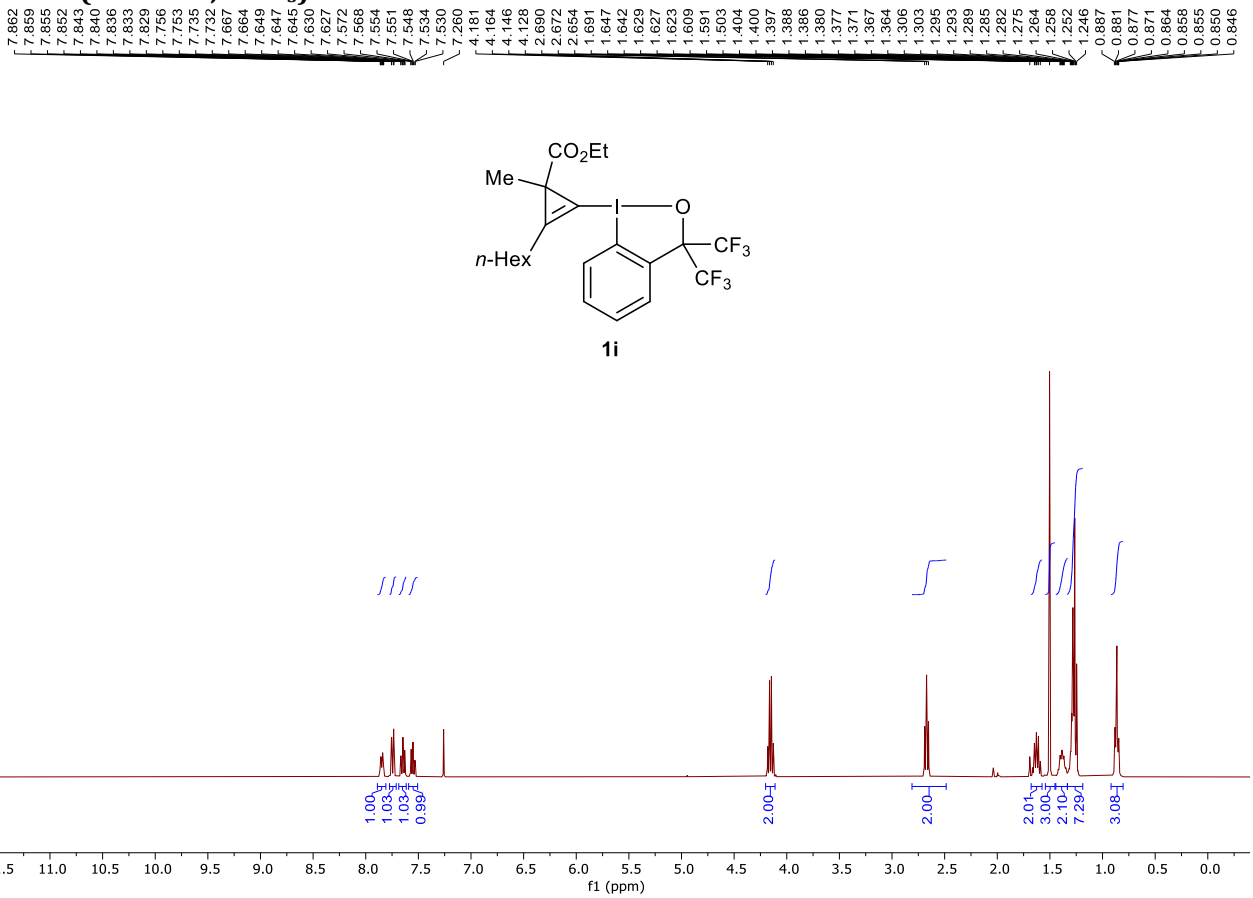
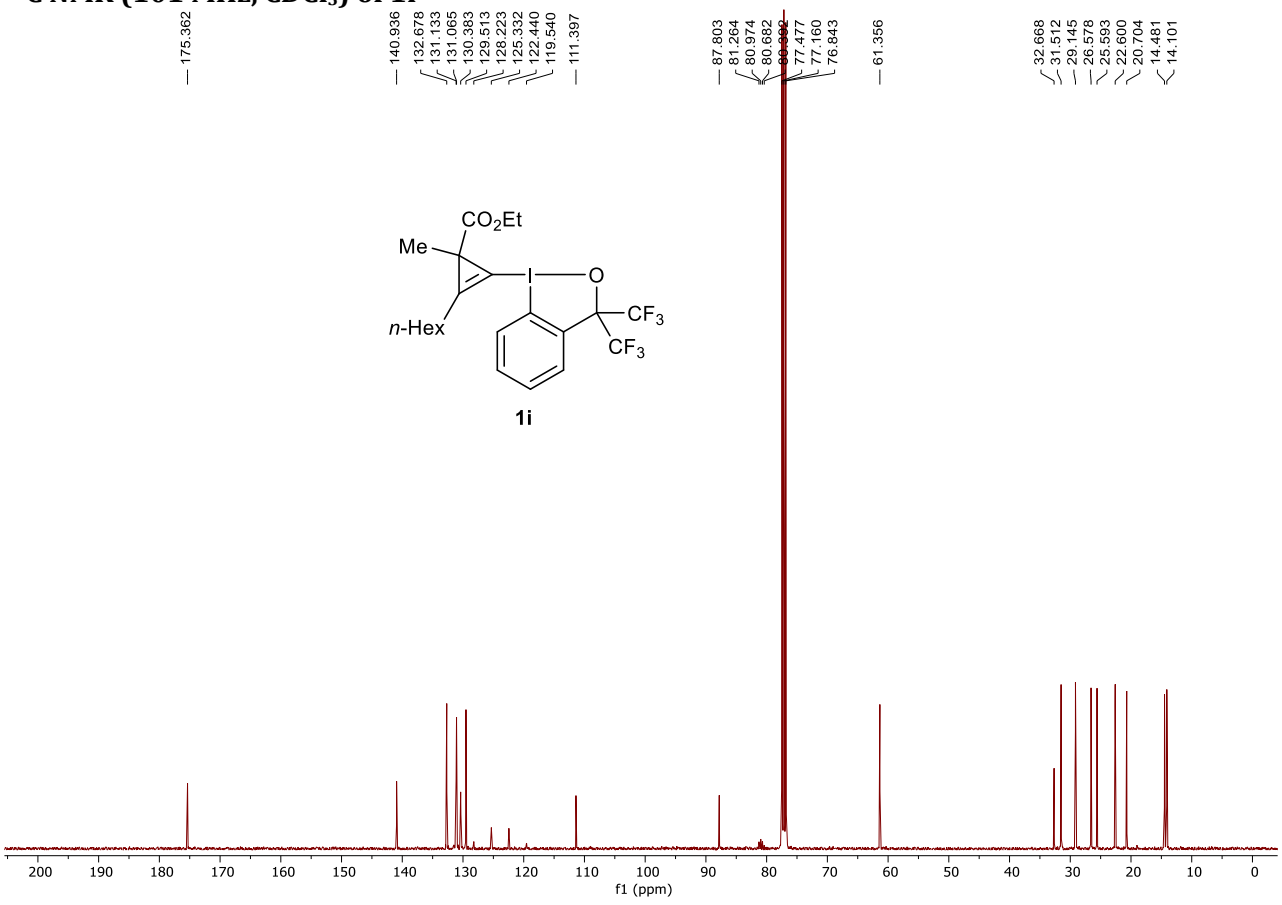


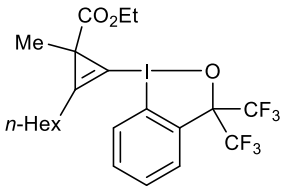
^{1}H NMR (400 MHz, $CDCl_3$) of 1i



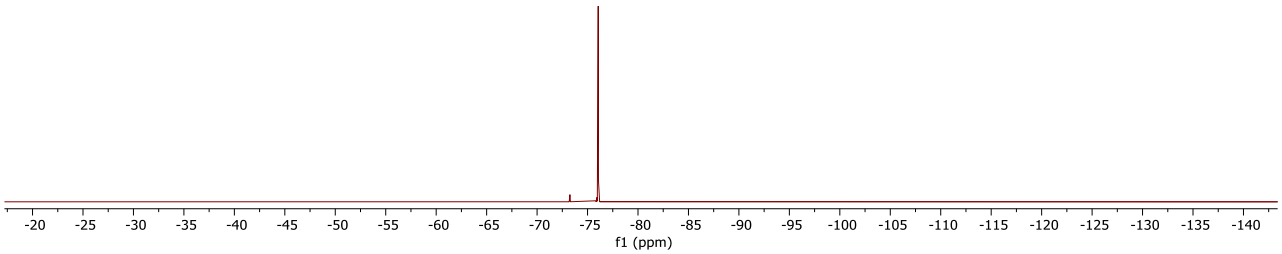
^{13}C NMR (101 MHz, $CDCl_3$) of 1i



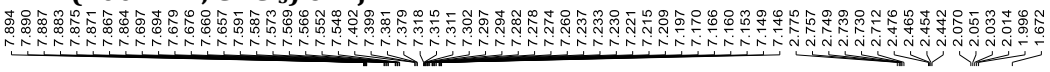
^{19}F NMR (377 MHz, $CDCl_3$) of 1i

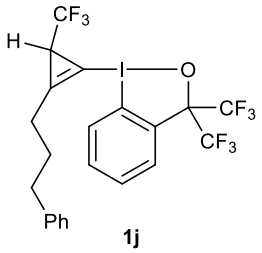


1i

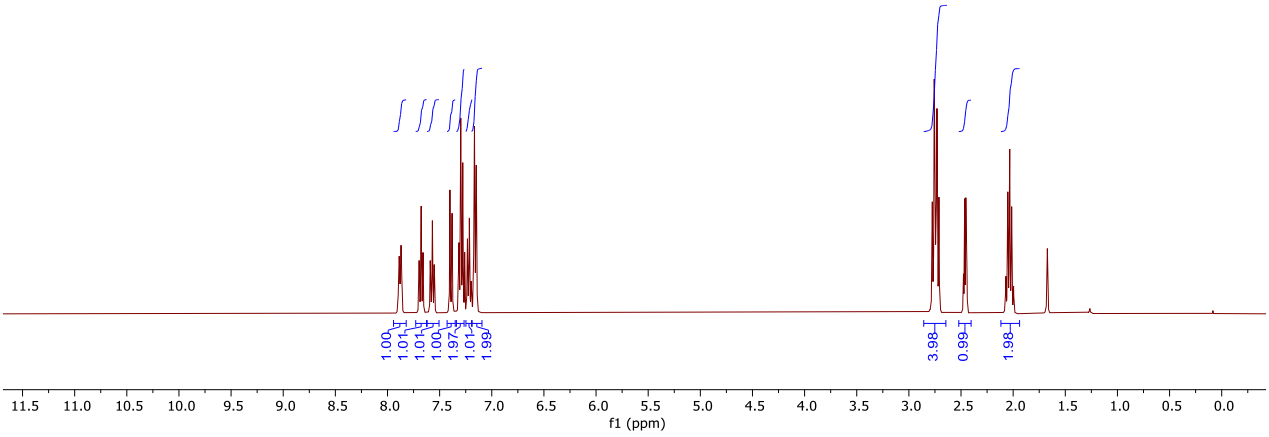


^{1}H NMR (400 MHz, $CDCl_3$) of 1j

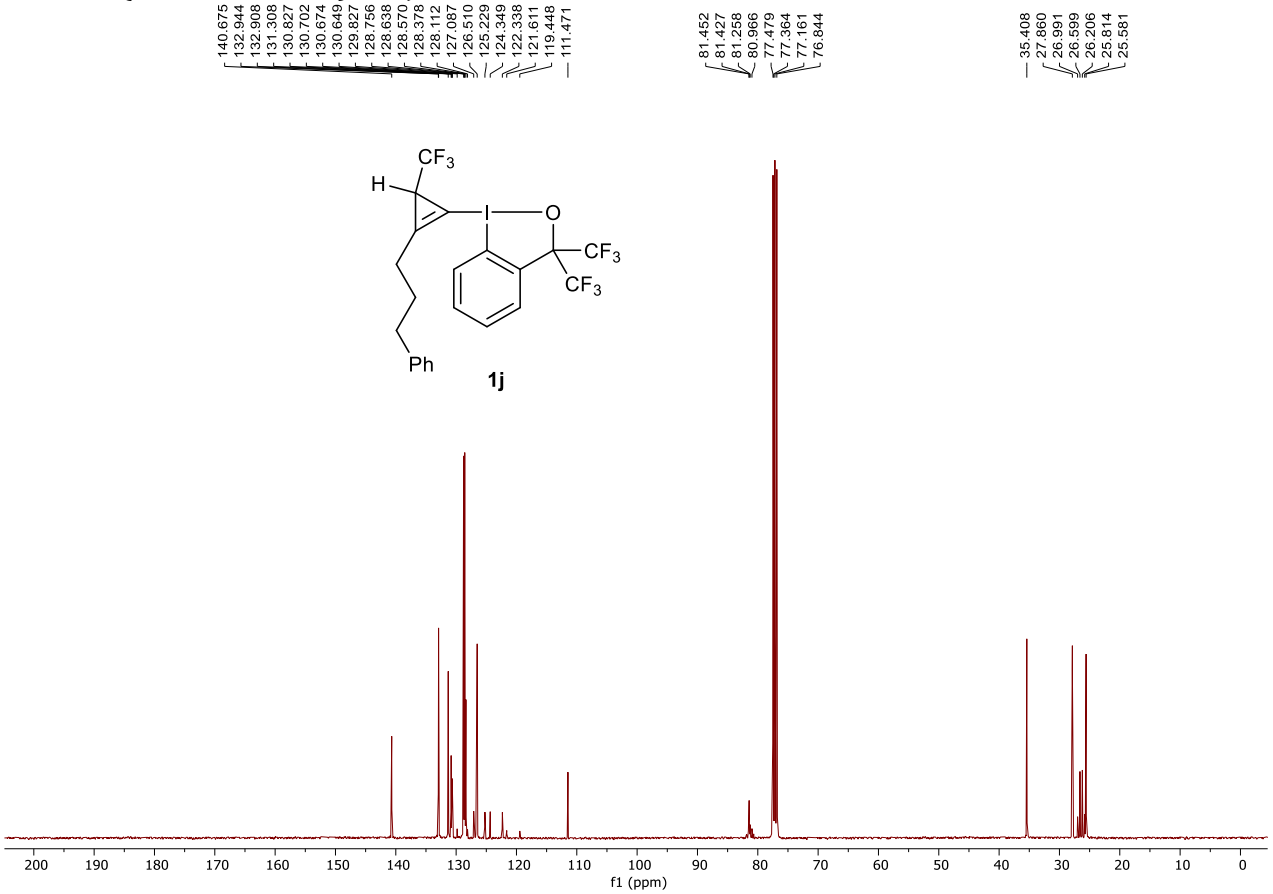




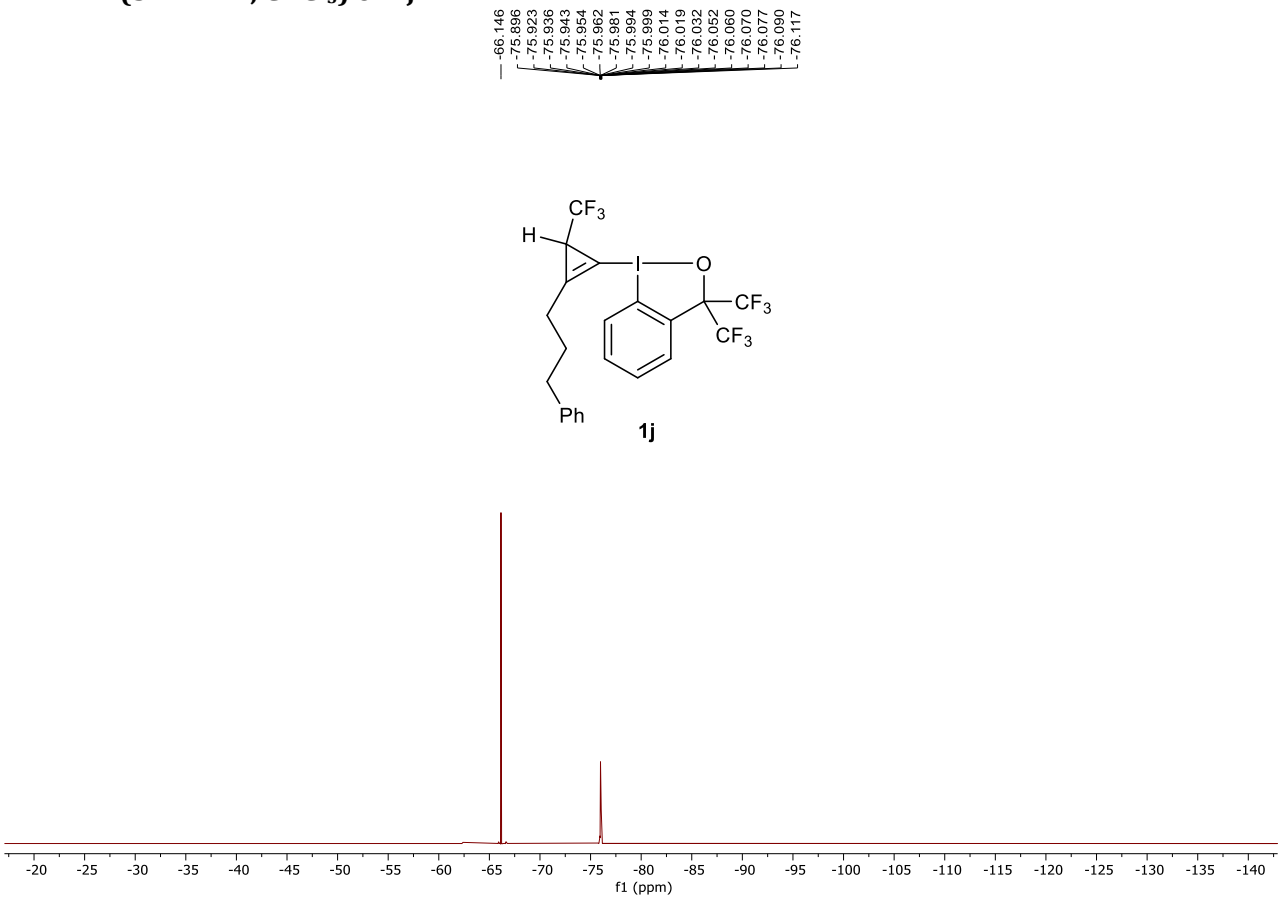
1j



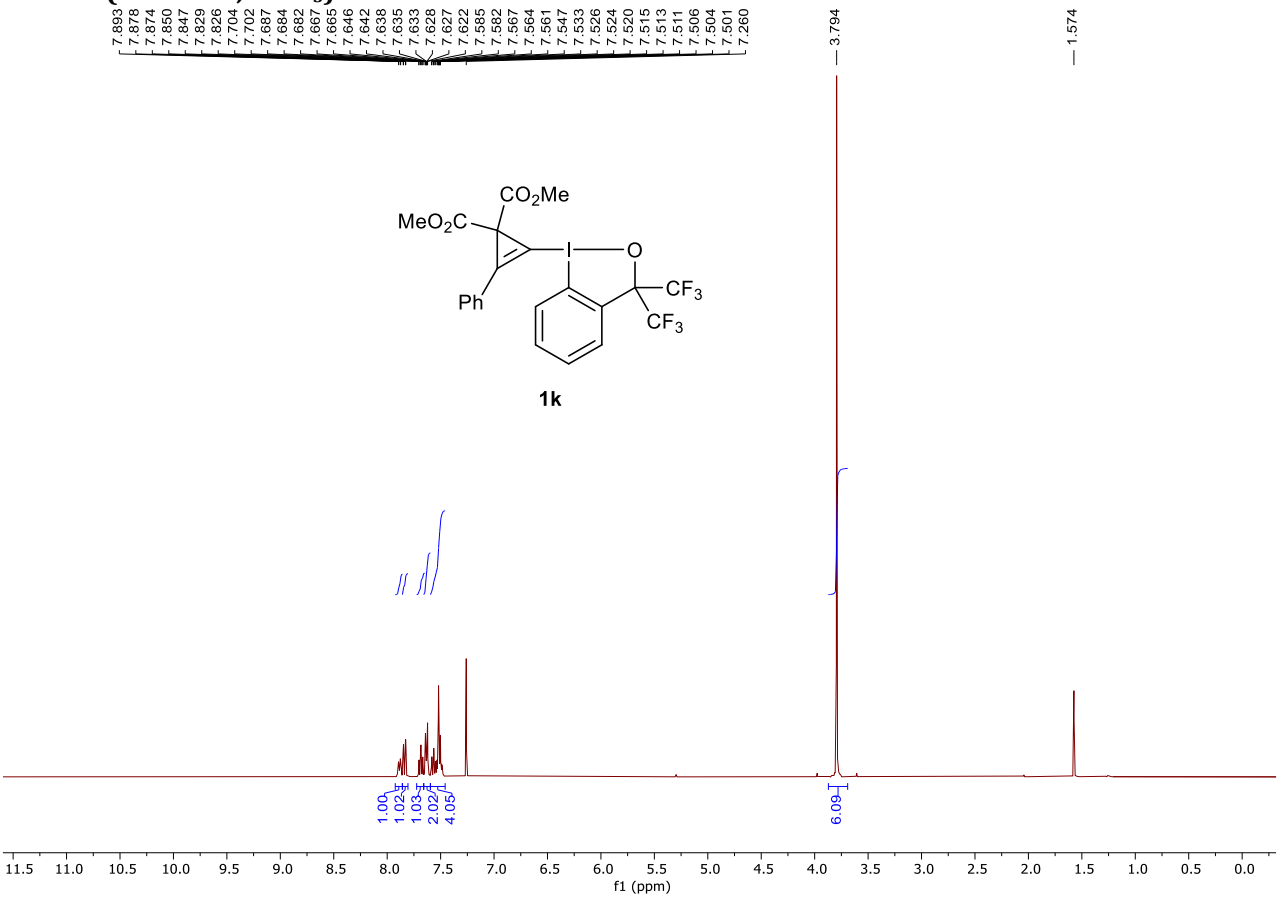
^{13}C NMR (101 MHz, $CDCl_3$) of 1j



^{19}F NMR (377 MHz, $CDCl_3$) of 1j

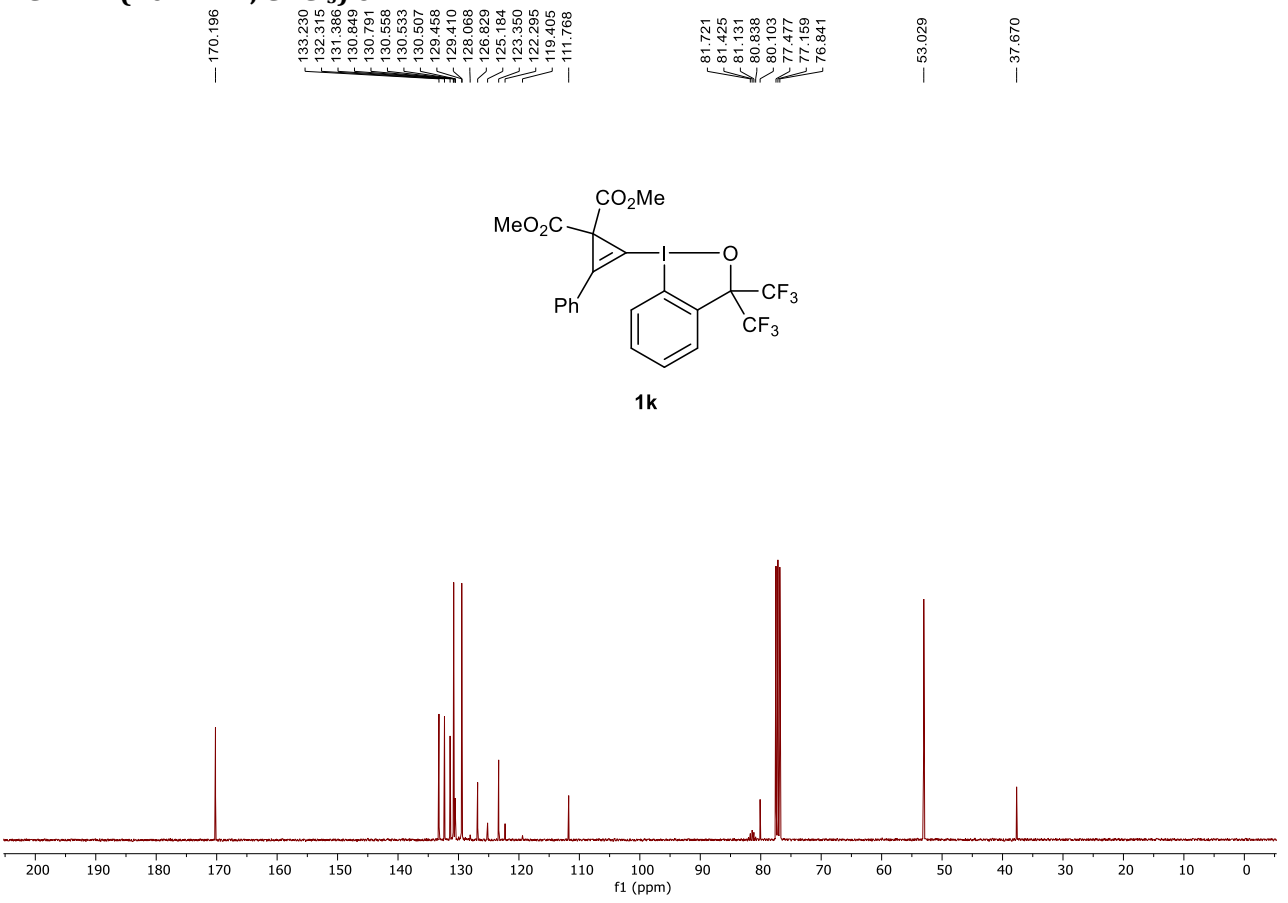


^{1}H NMR (400 MHz, $CDCl_3$) of 1k



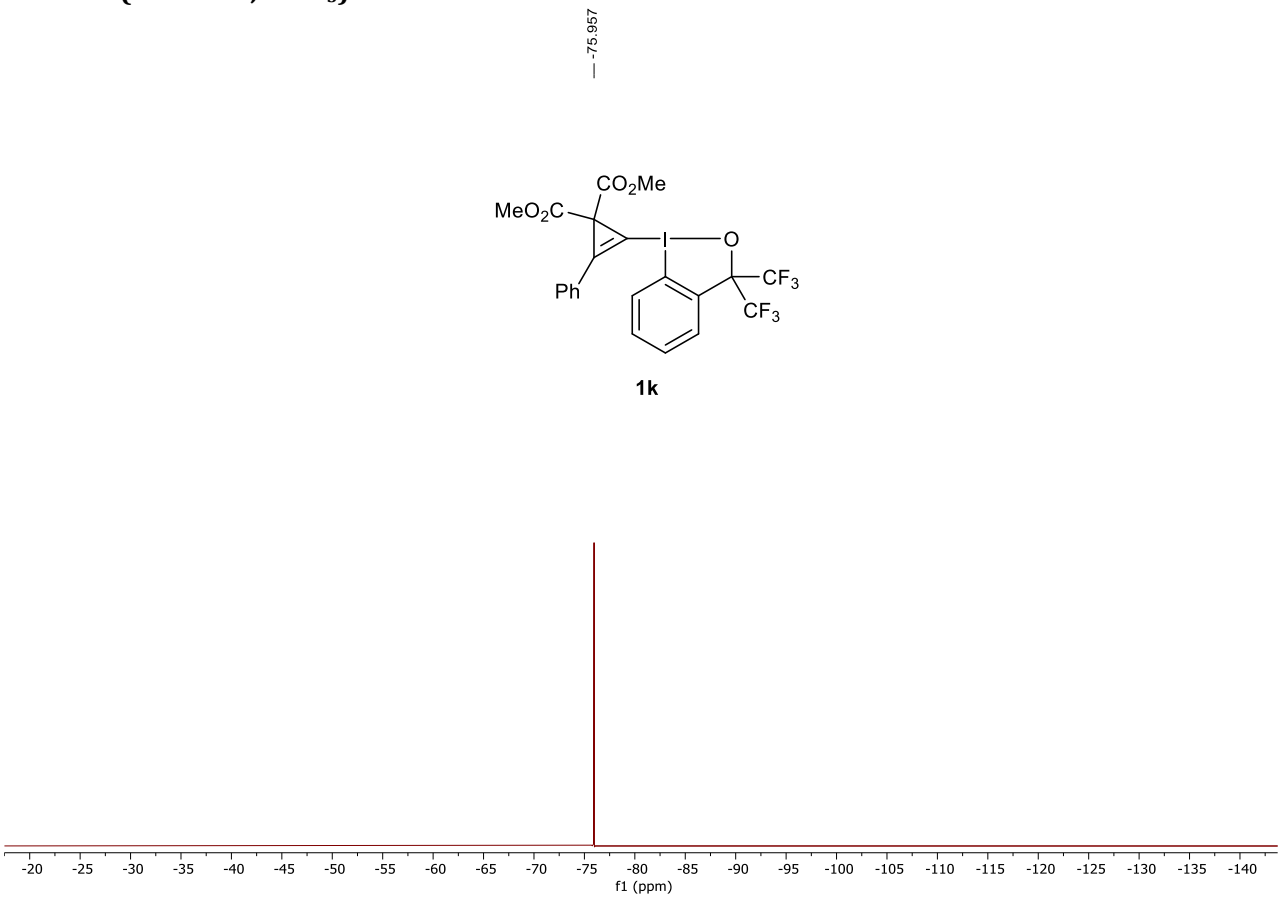
1k

^{13}C NMR (101 MHz, $CDCl_3$) of 1k

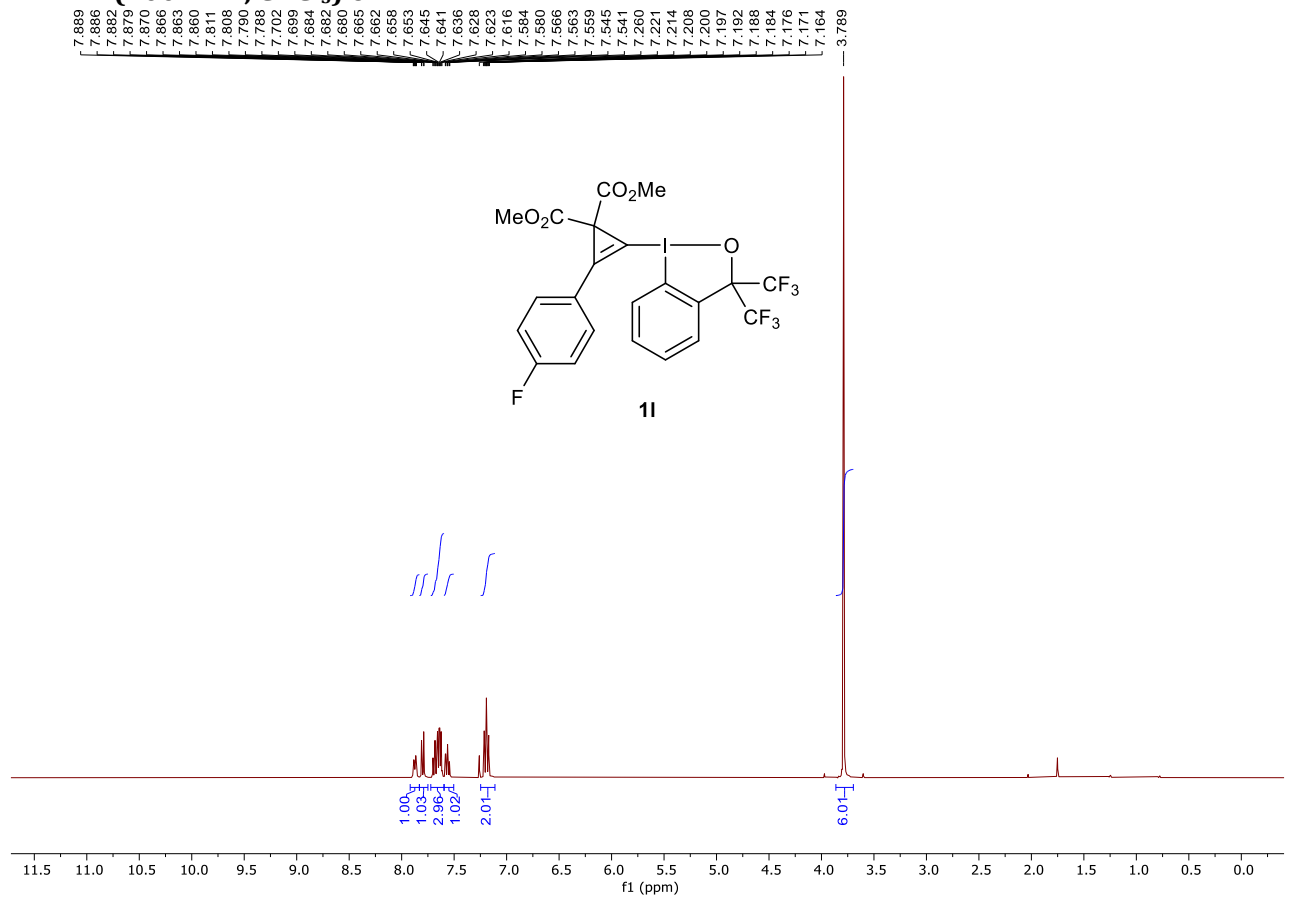


1k

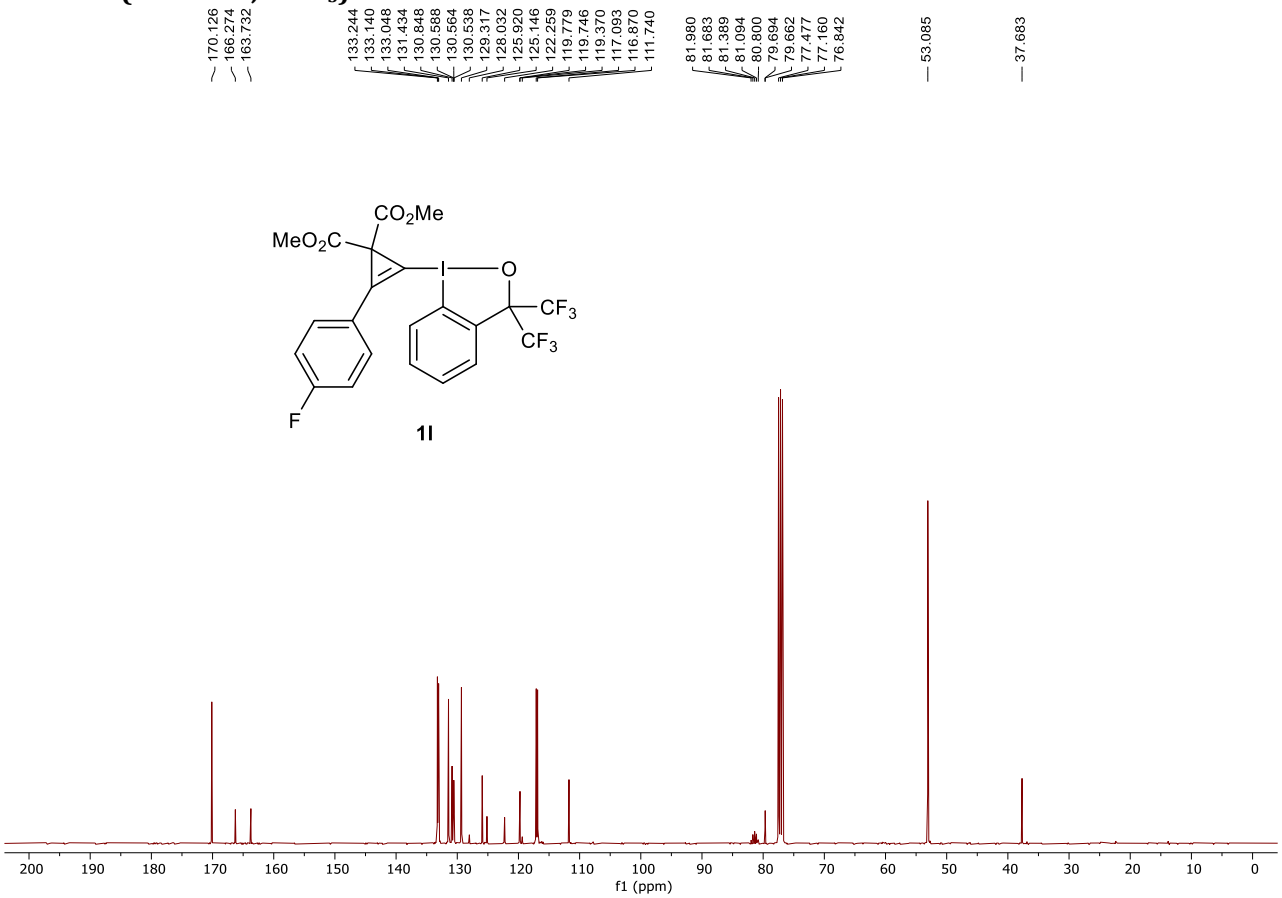
^{19}F NMR (377 MHz, $CDCl_3$) of 1k



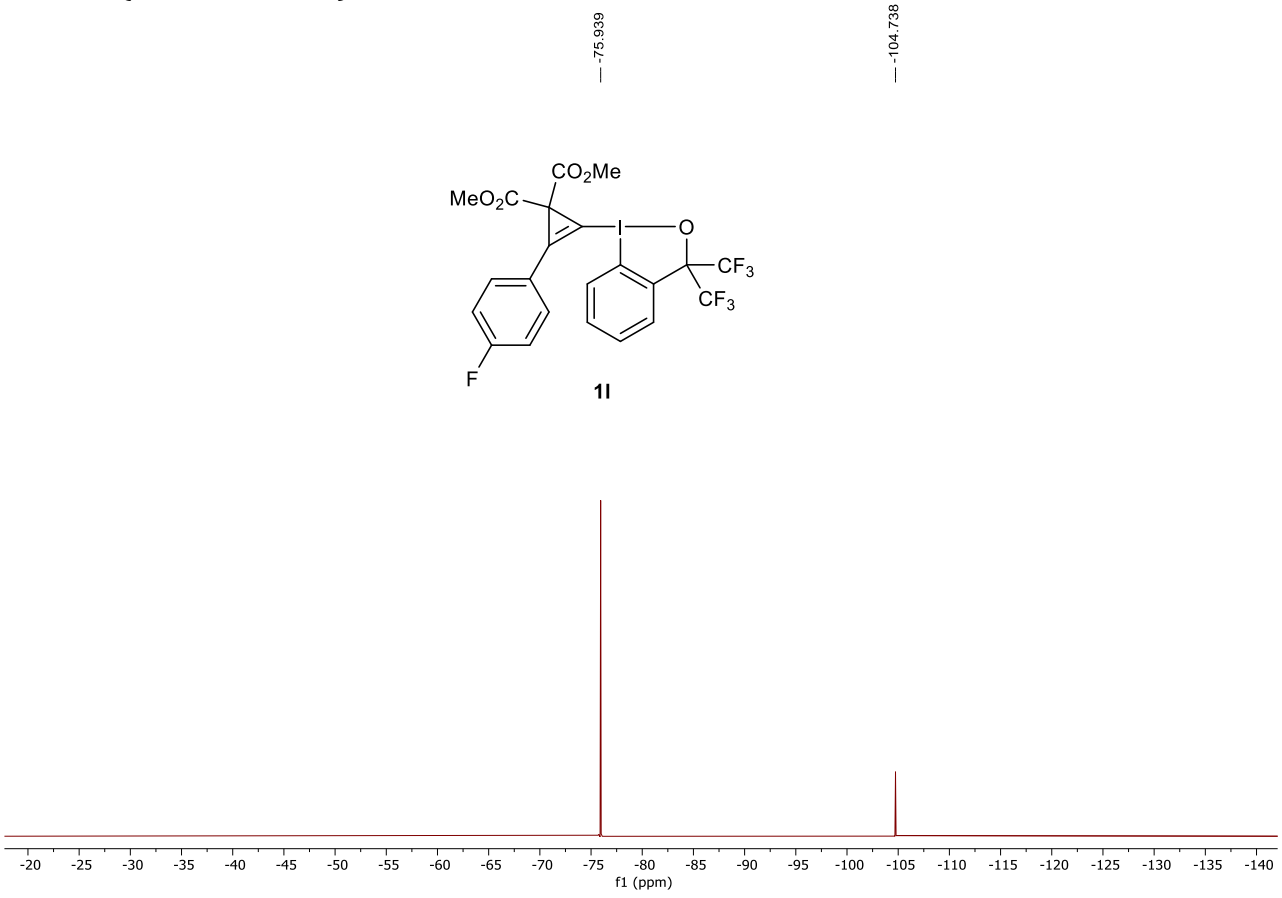
^{1}H NMR (400 MHz, $CDCl_3$) of 1l



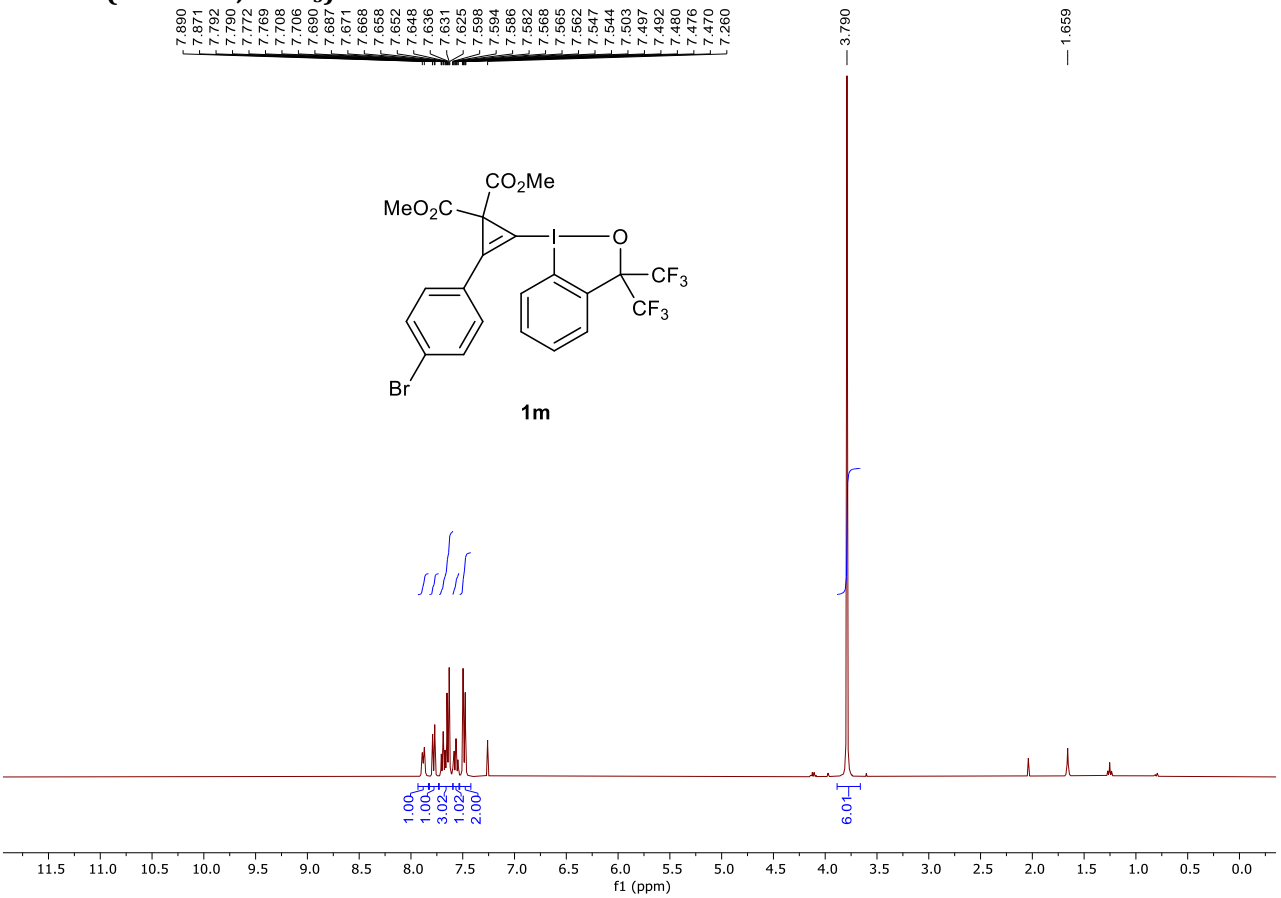
^{13}C NMR (101 MHz, $CDCl_3$) of 1l



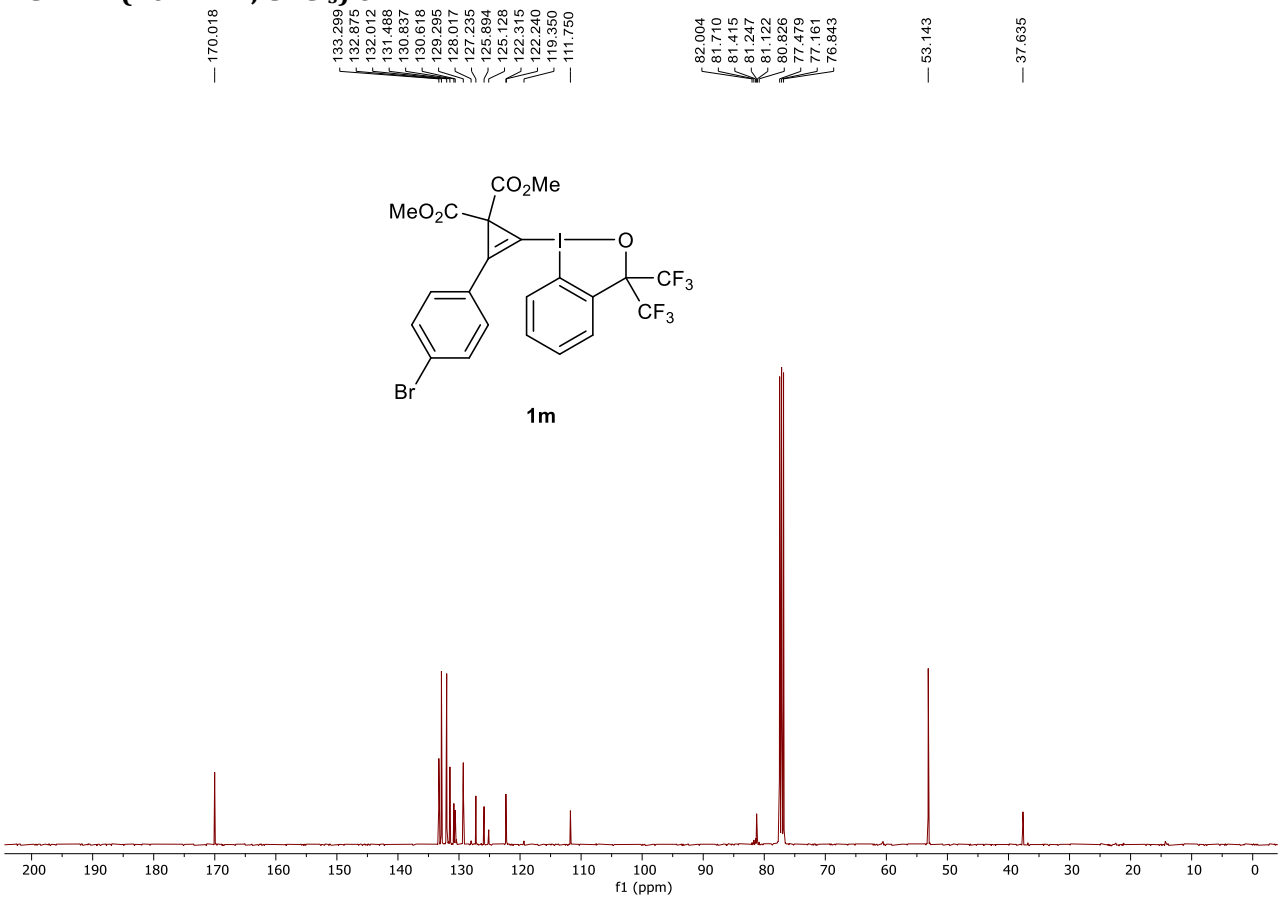
^{19}F NMR (377 MHz, $CDCl_3$) of 1l



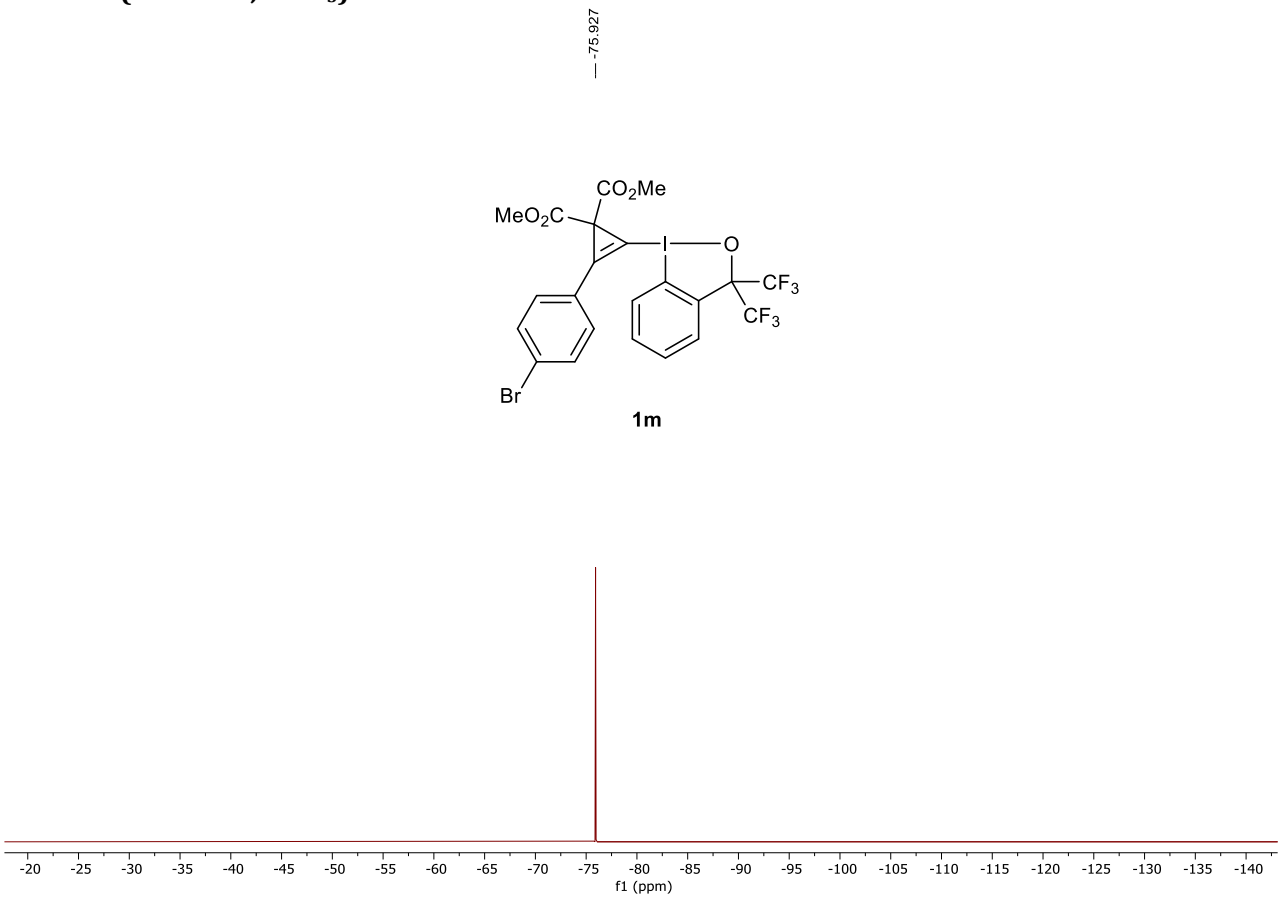
^{1}H NMR (400 MHz, $CDCl_3$) of 1m



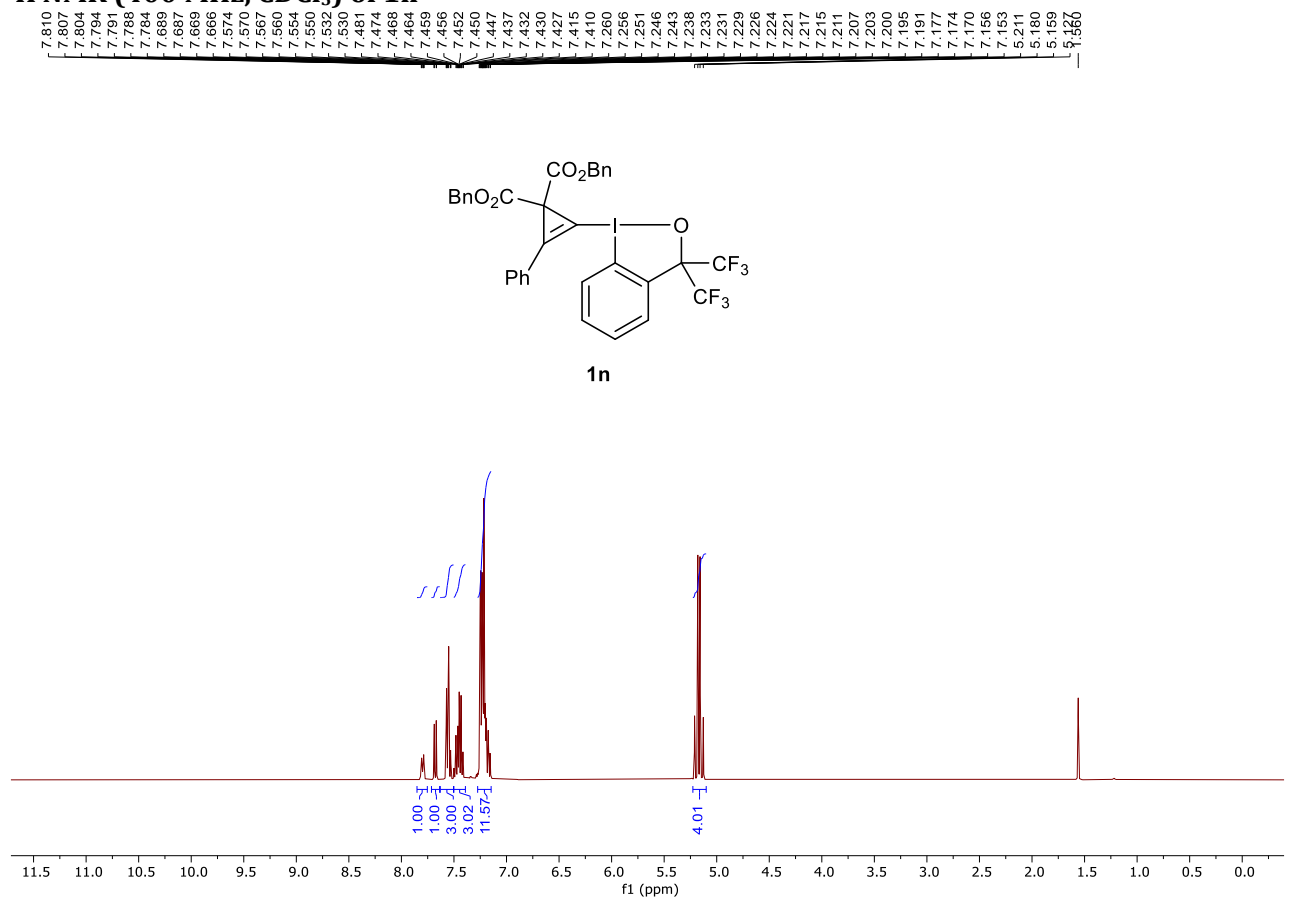
^{13}C NMR (101 MHz, $CDCl_3$) of 1m



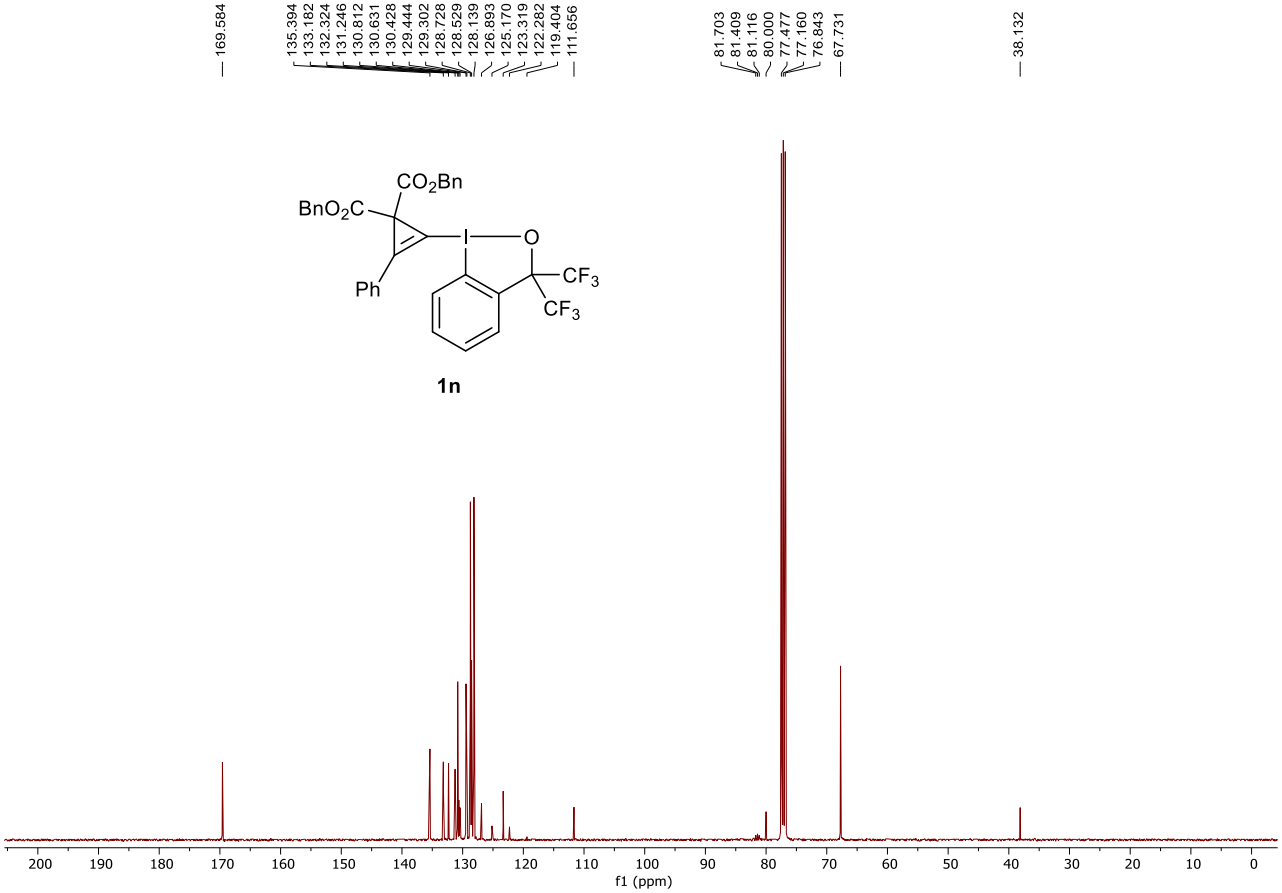
^{19}F NMR (377 MHz, $CDCl_3$) of 1m



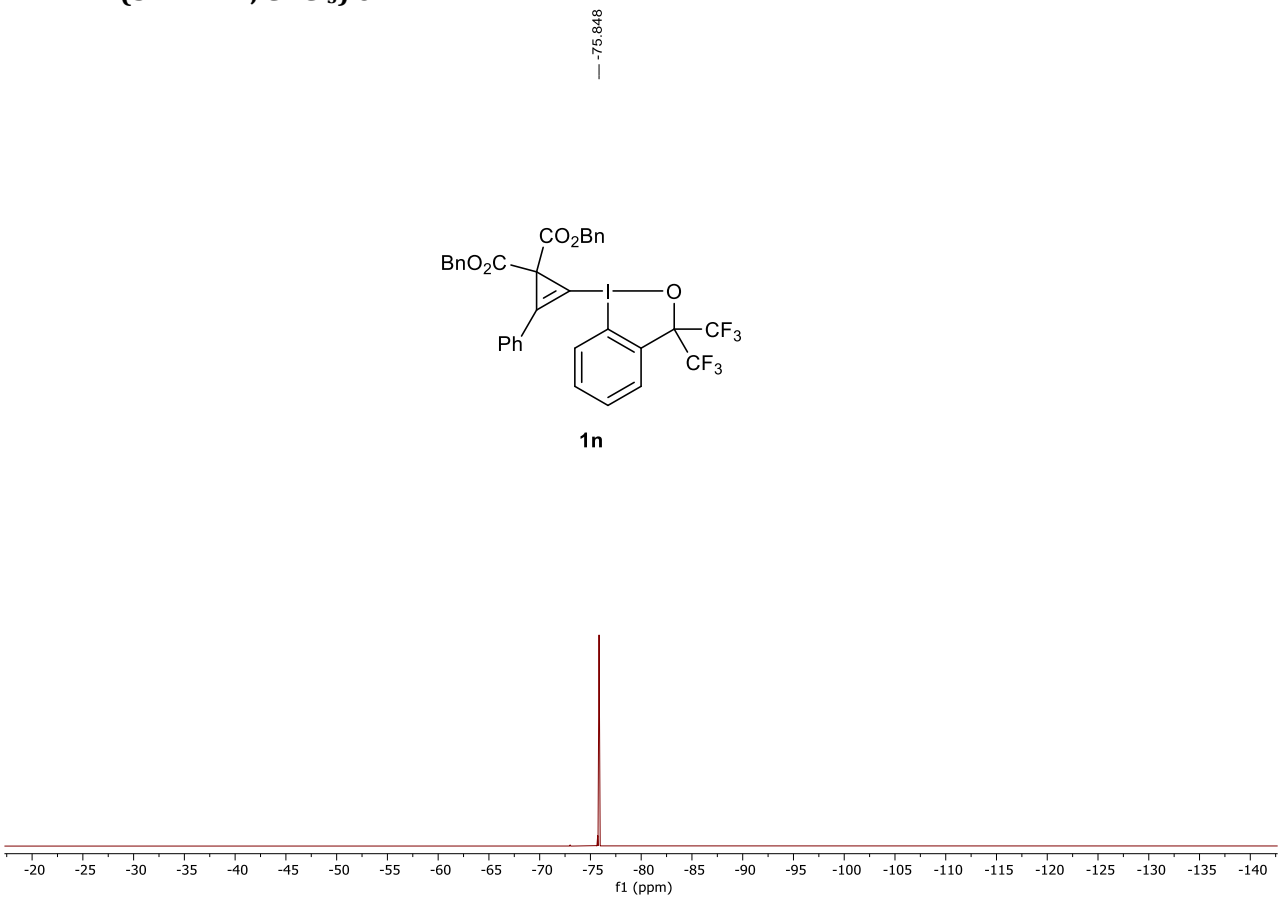
^{1}H NMR (400 MHz, $CDCl_3$) of 1n



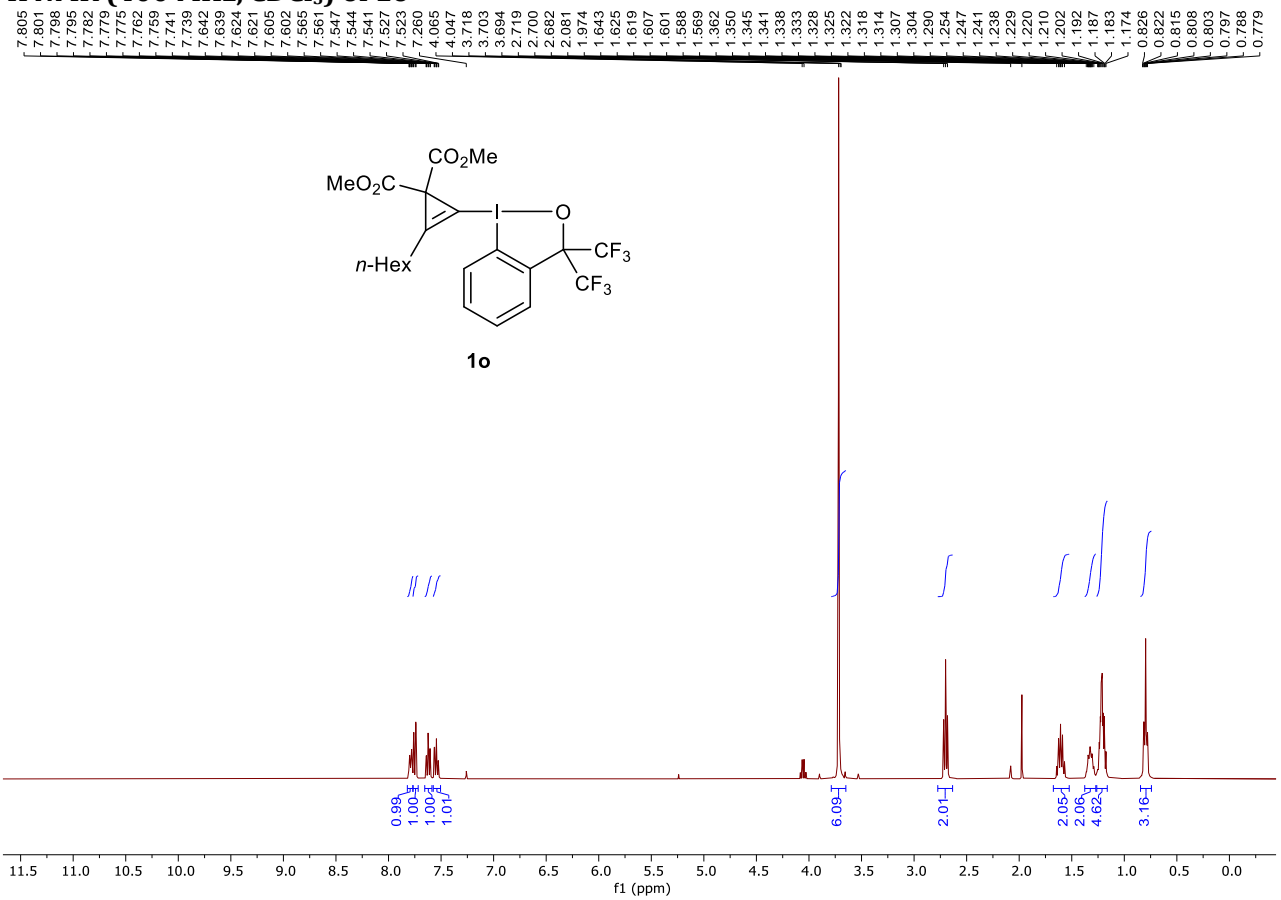
^{13}C NMR (101 MHz, $CDCl_3$) of 1n



^{19}F NMR (377 MHz, $CDCl_3$) of 1n

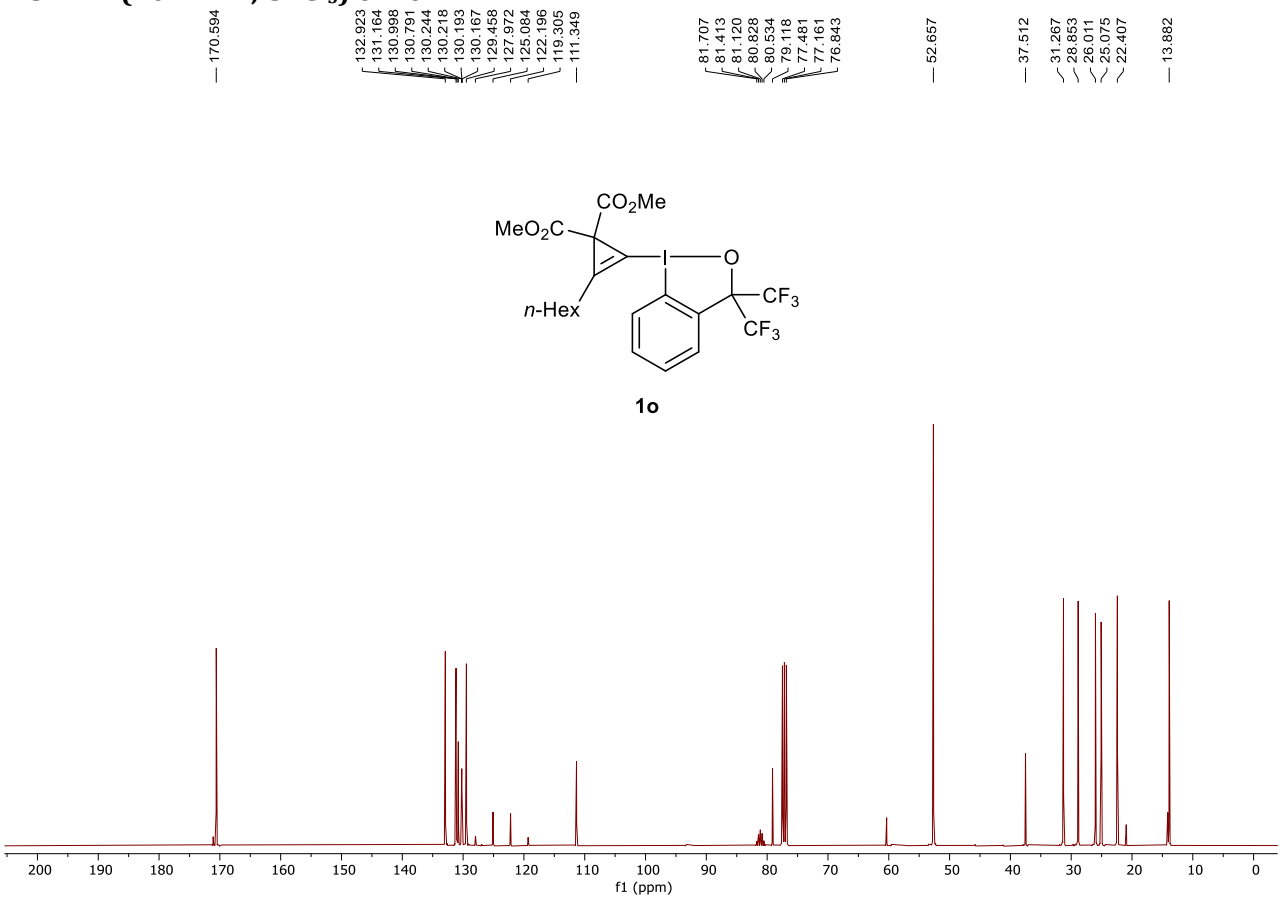


^{1}H NMR (400 MHz, $CDCl_3$) of 1o



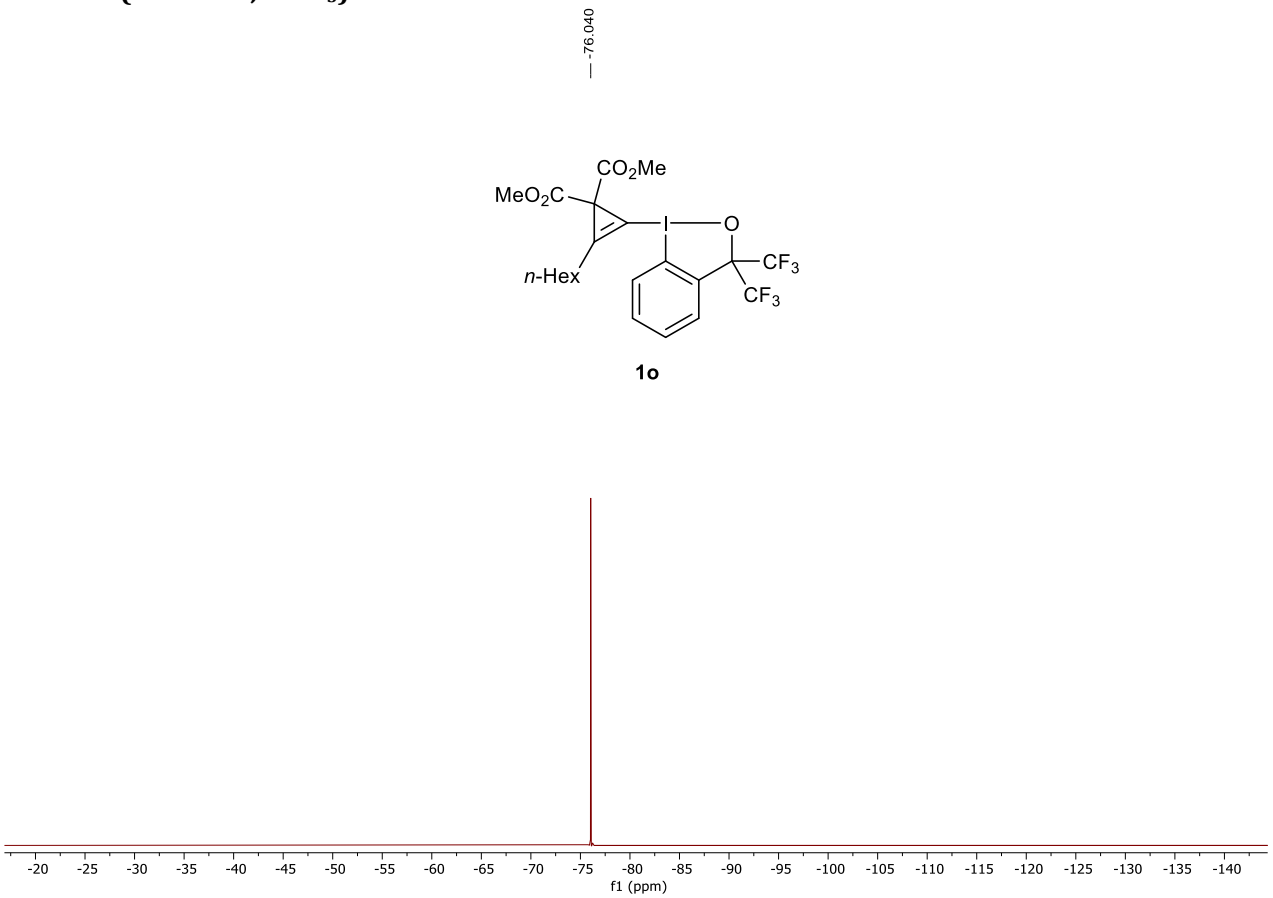
1o

^{13}C NMR (101 MHz, $CDCl_3$) of 1o



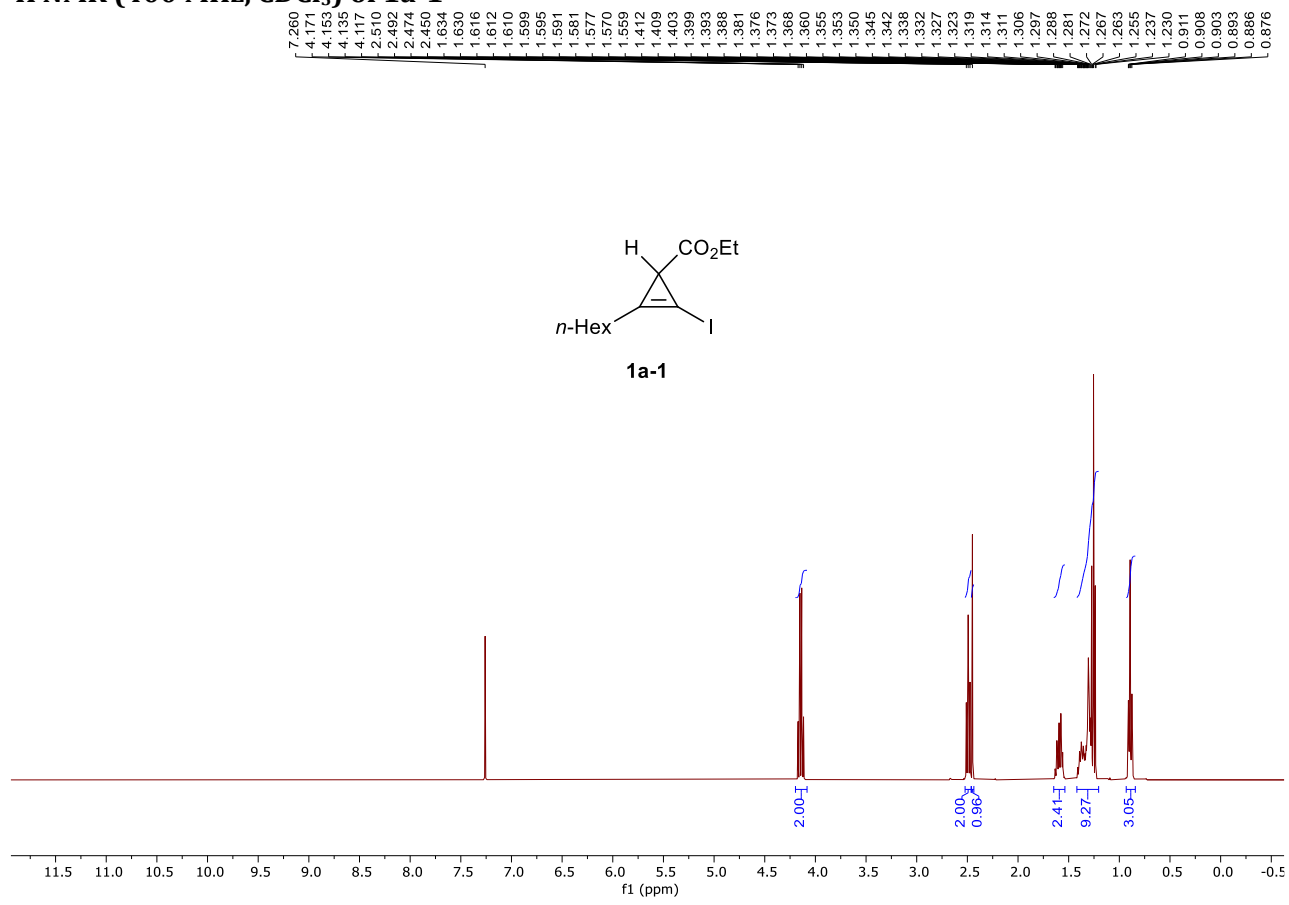
1o

^{19}F NMR (377 MHz, $CDCl_3$) of 1o



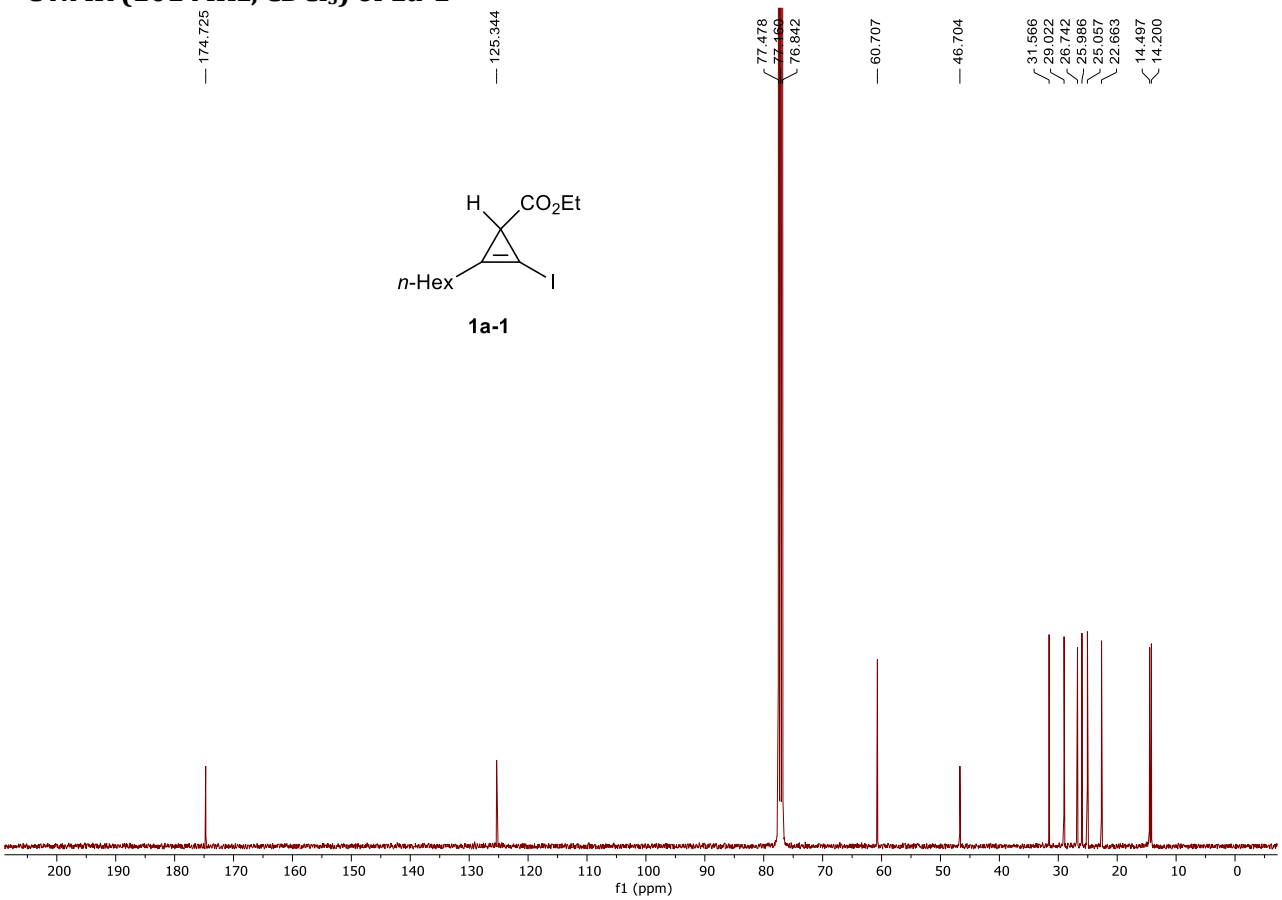
1o

^{1}H NMR (400 MHz, $CDCl_3$) of 1a-1



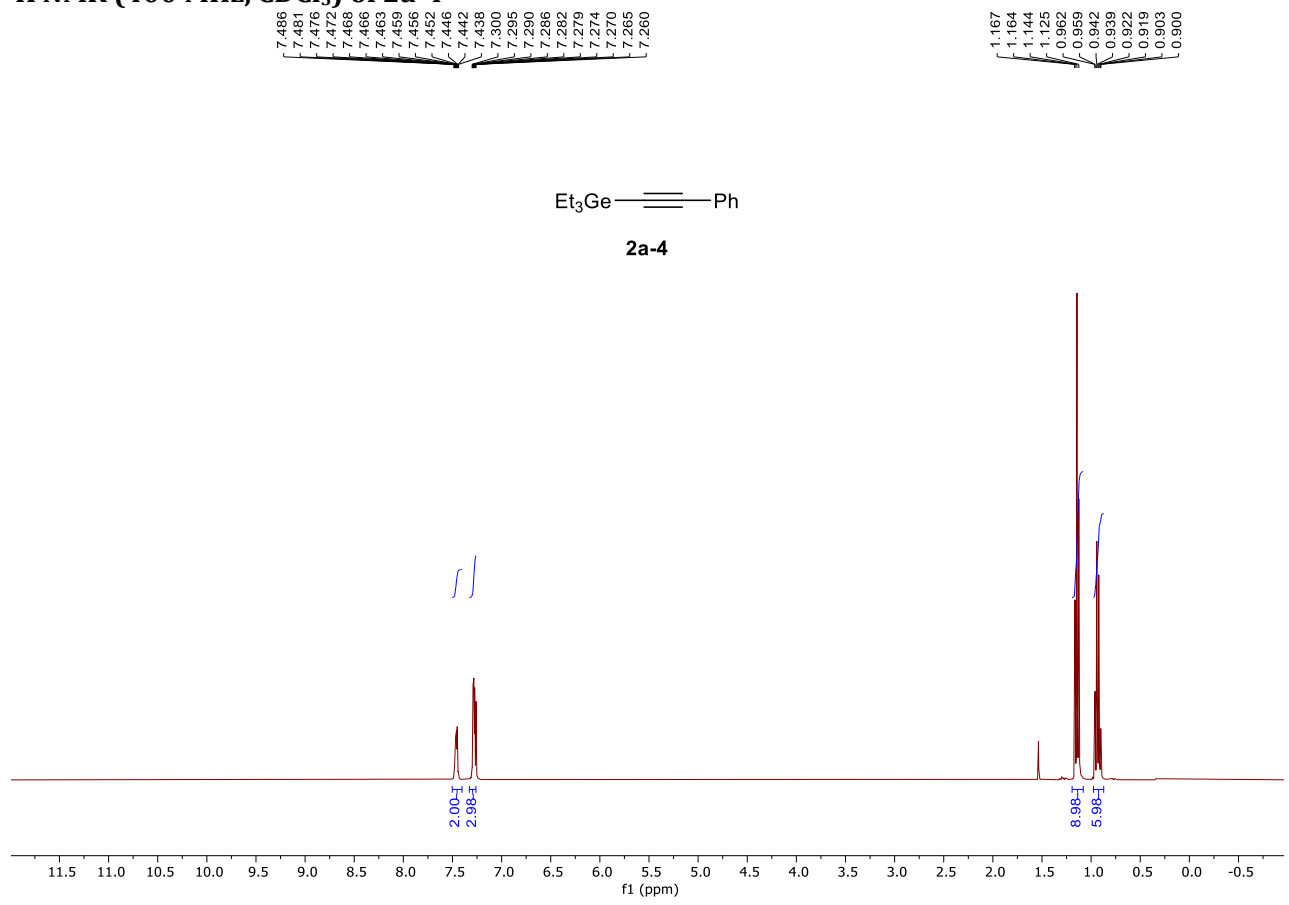
1a-1

^{13}C NMR (101 MHz, $CDCl_3$) of 1a-1



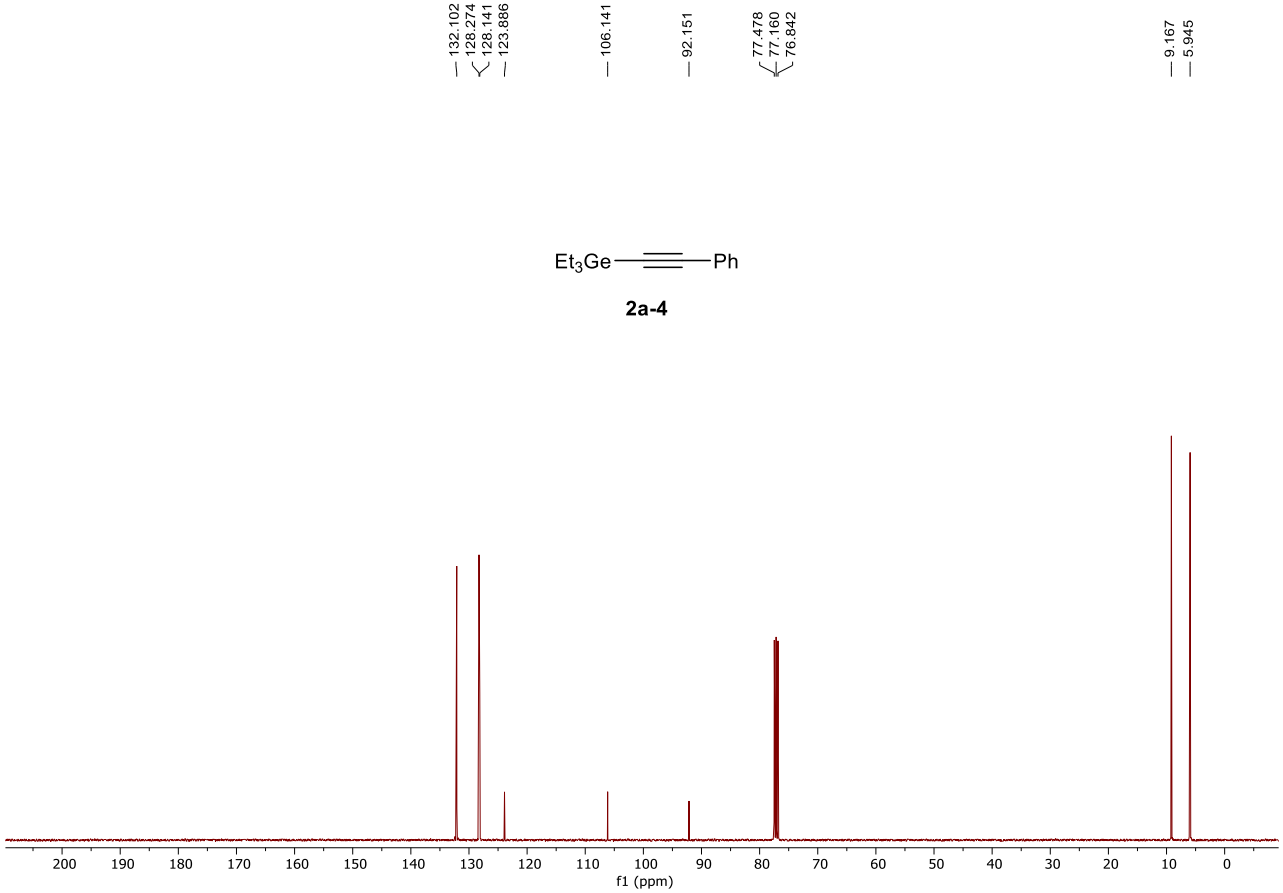
1a-1

^{1}H NMR (400 MHz, $CDCl_3$) of 2a-4



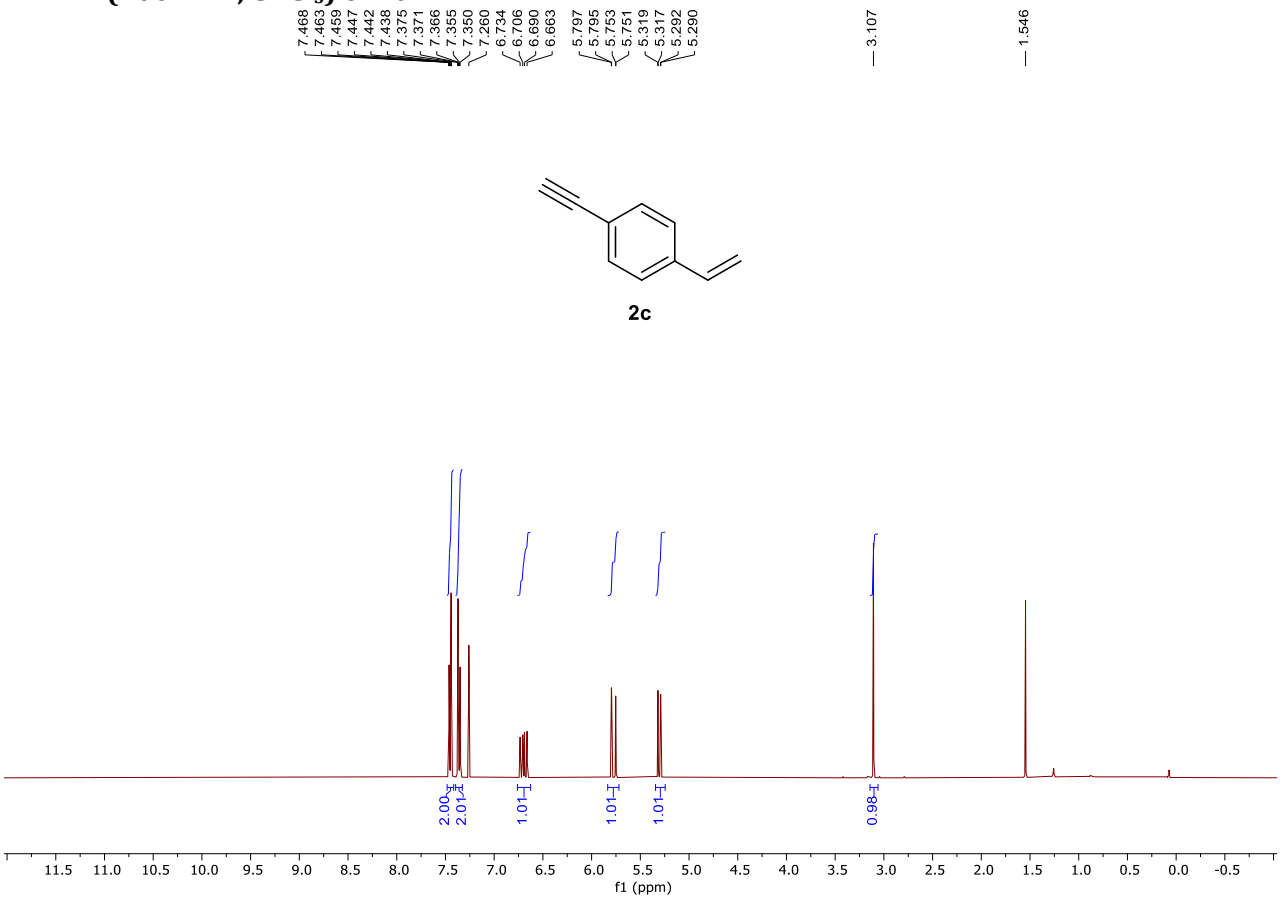
2a-4

^{13}C NMR (101 MHz, $CDCl_3$) of 2a-4



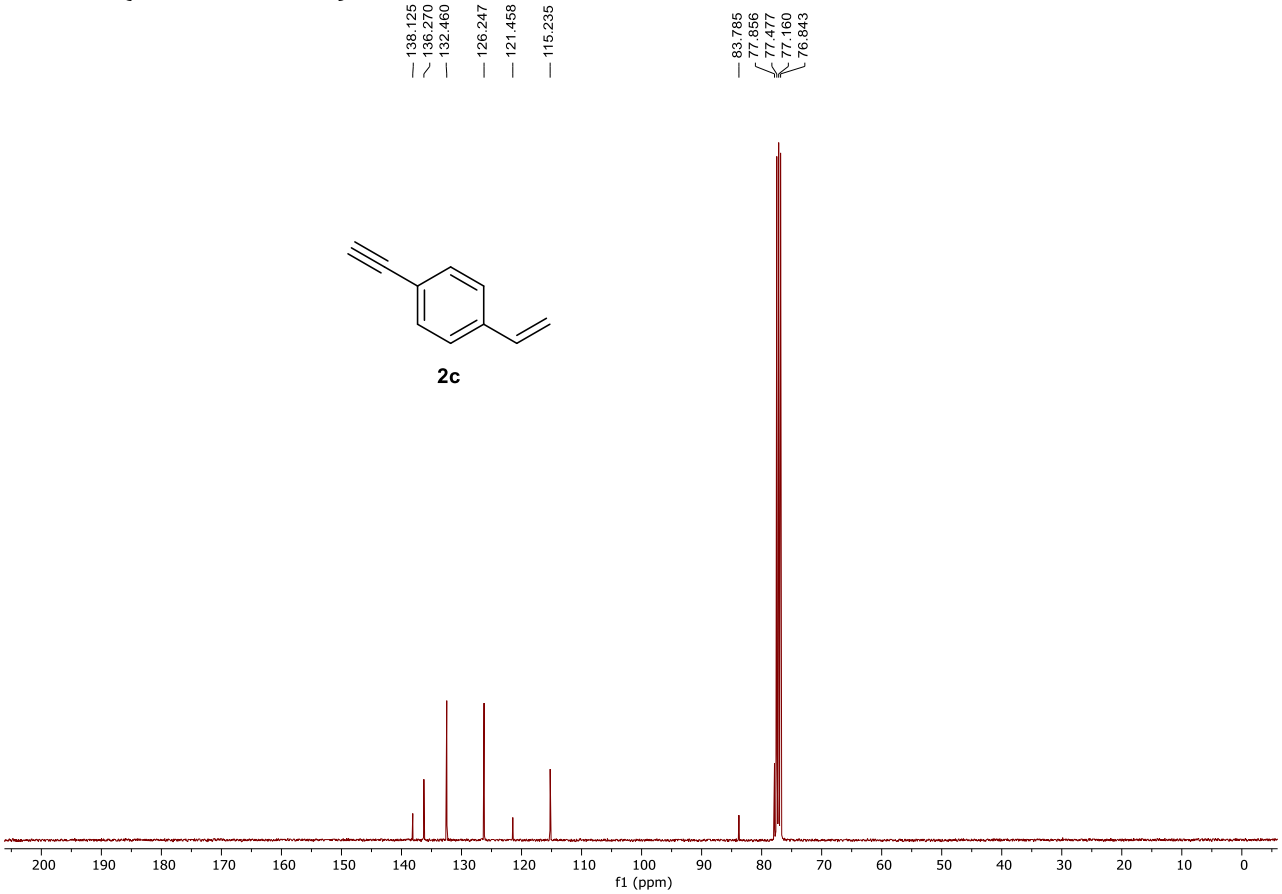
2a-4

^{1}H NMR (400 MHz, $CDCl_3$) of 2c



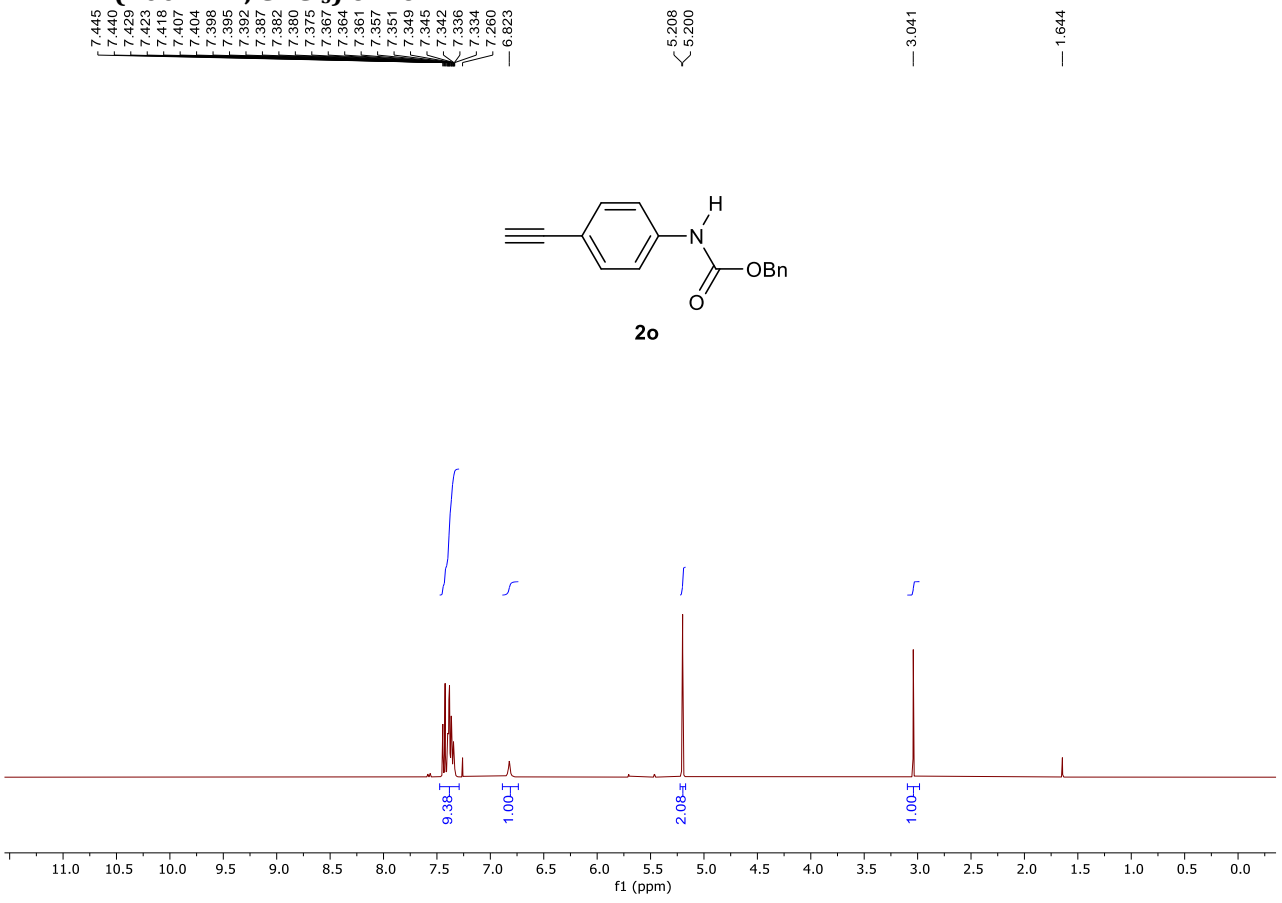
2c

^{13}C NMR (101 MHz, $CDCl_3$) of 2c



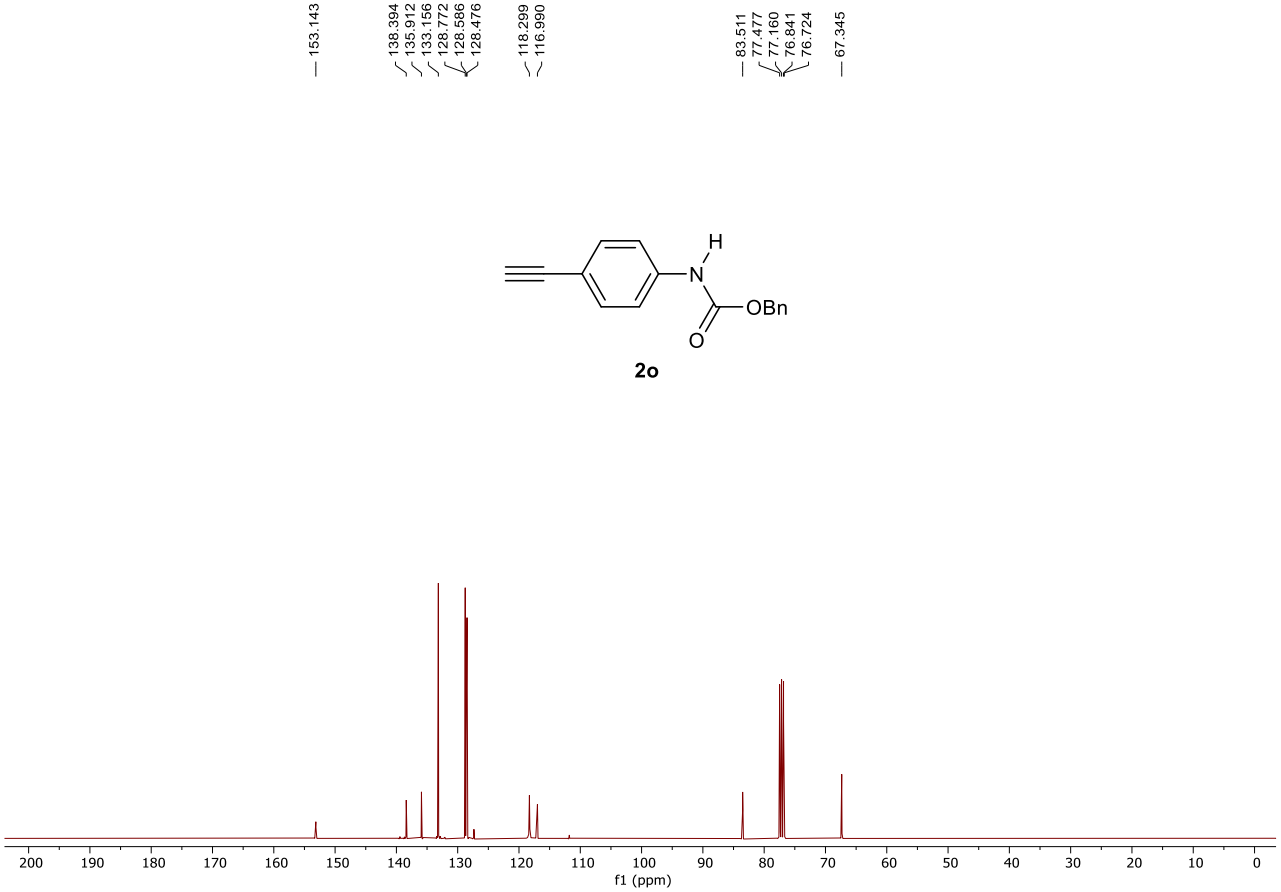
2c

^{1}H NMR (400 MHz, $CDCl_3$) of 2o



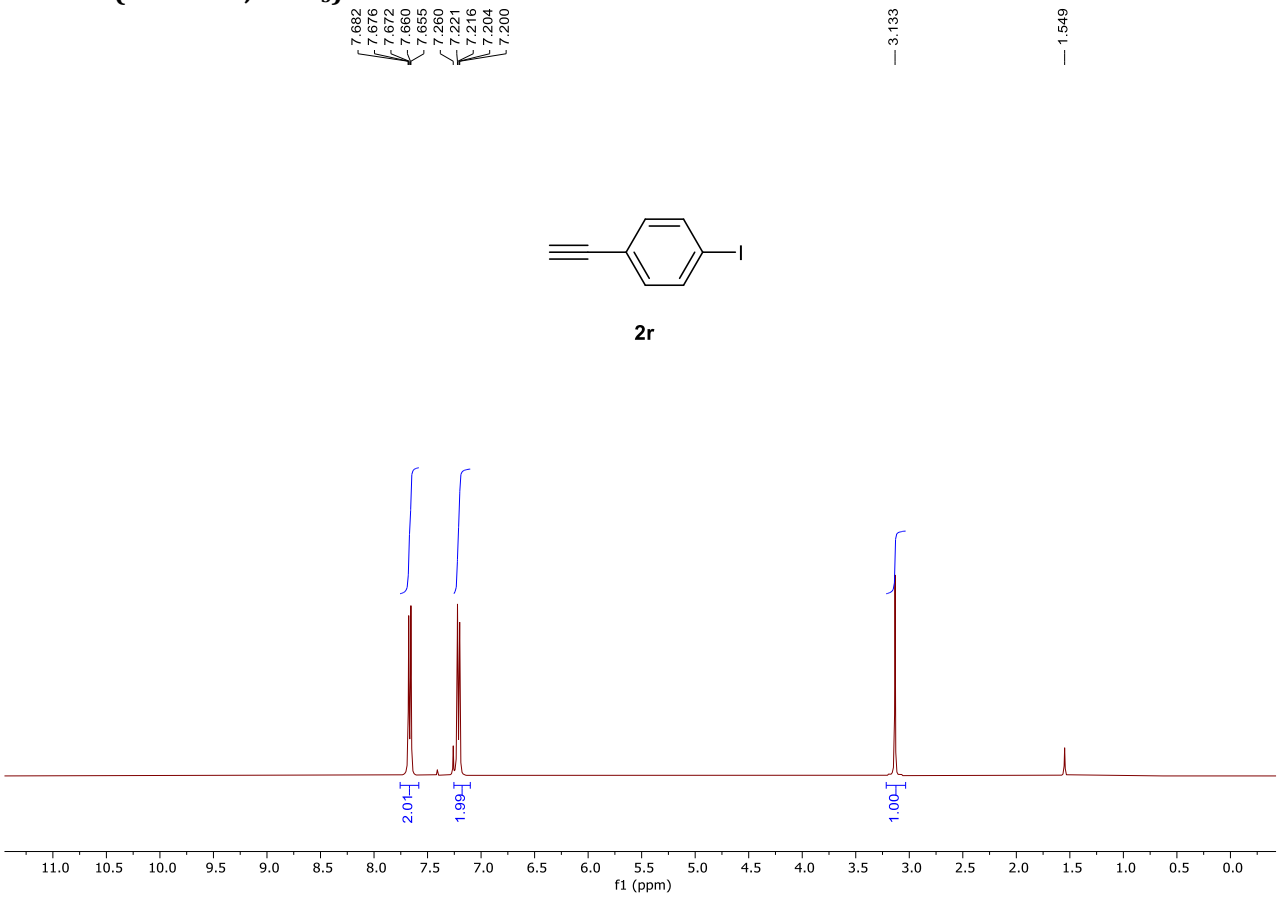
2o

^{13}C NMR (101 MHz, $CDCl_3$) of 2o



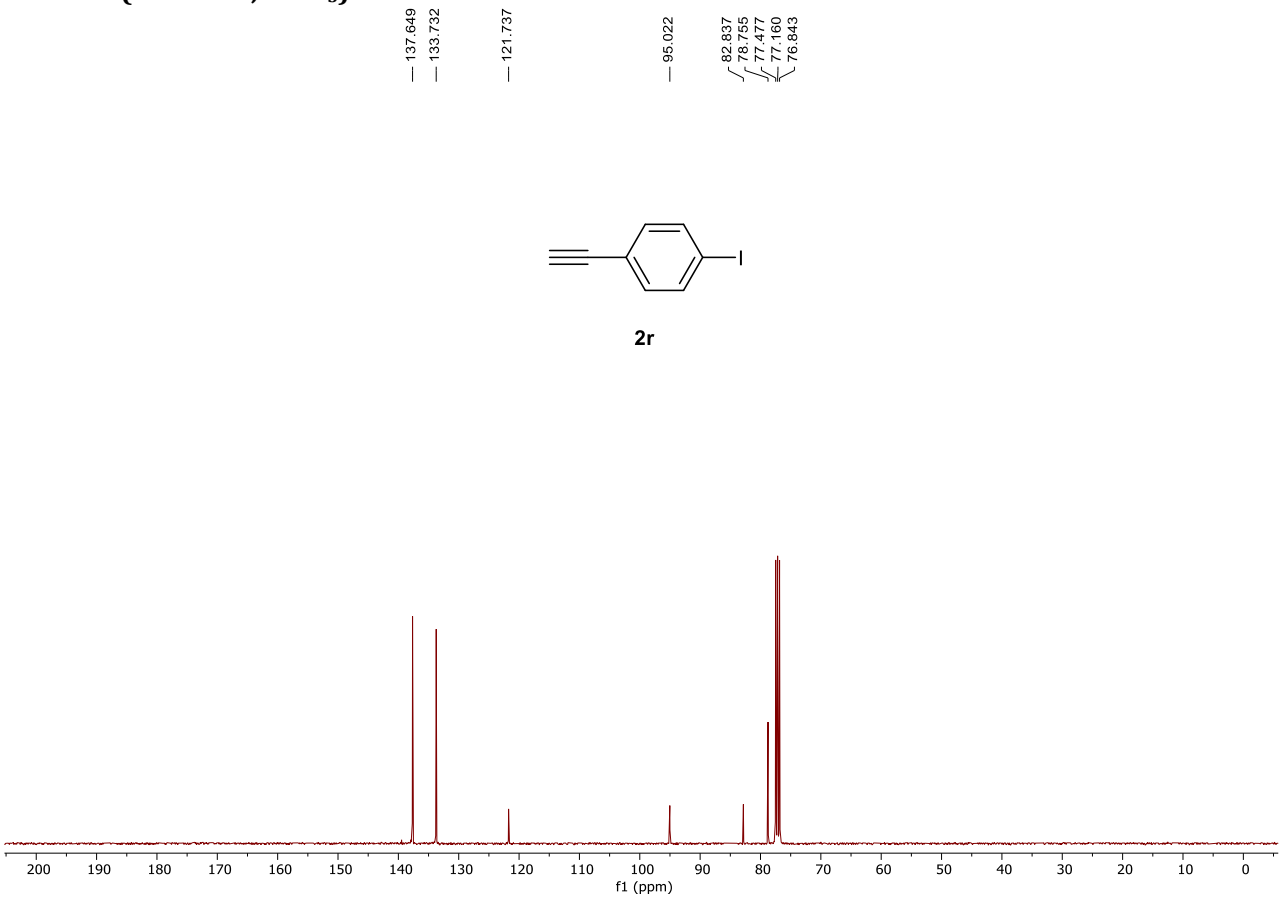
2o

^{1}H NMR (400 MHz, $CDCl_3$) of 2r

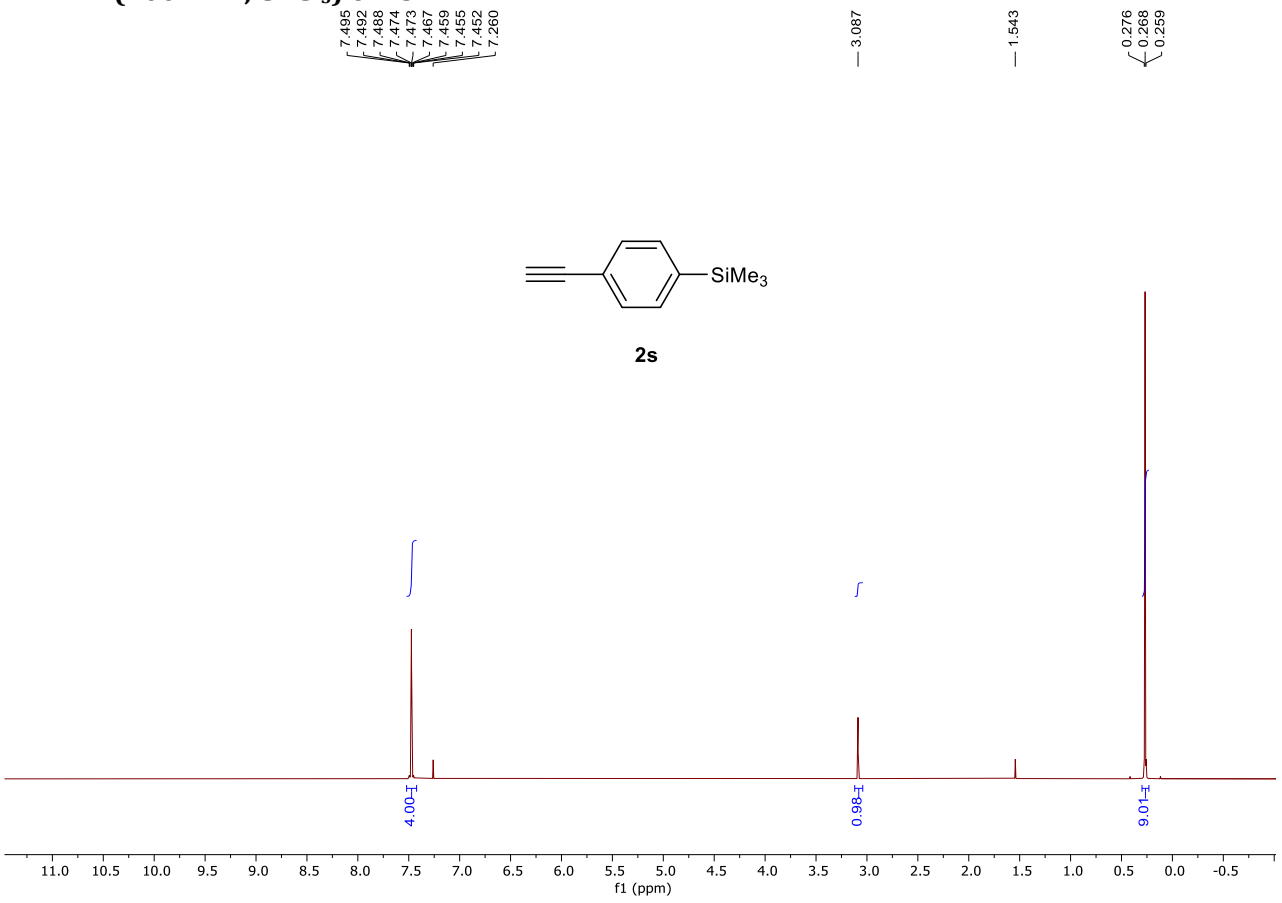


2r

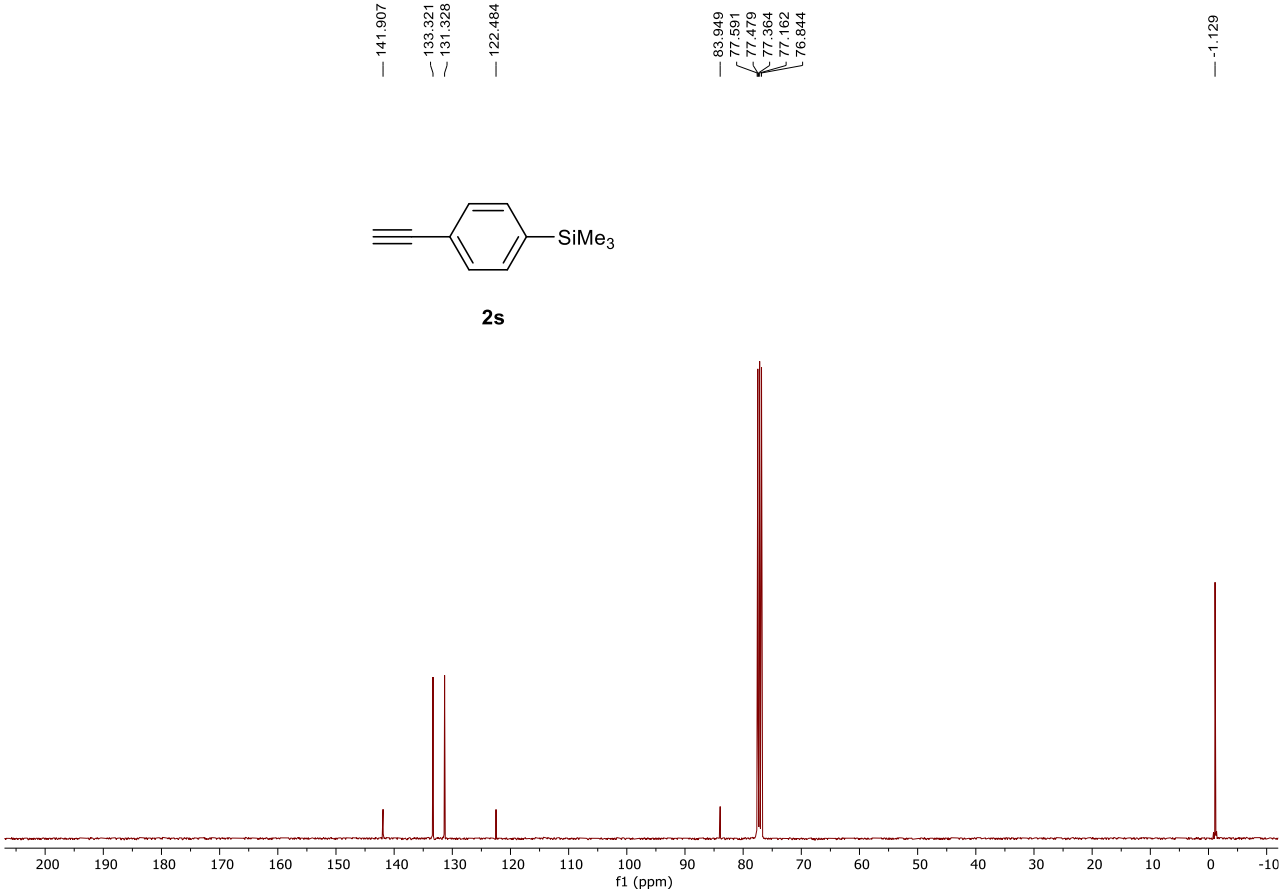
^{13}C NMR (101 MHz, $CDCl_3$) of 2r



^{1}H NMR (400 MHz, $CDCl_3$) of 2s

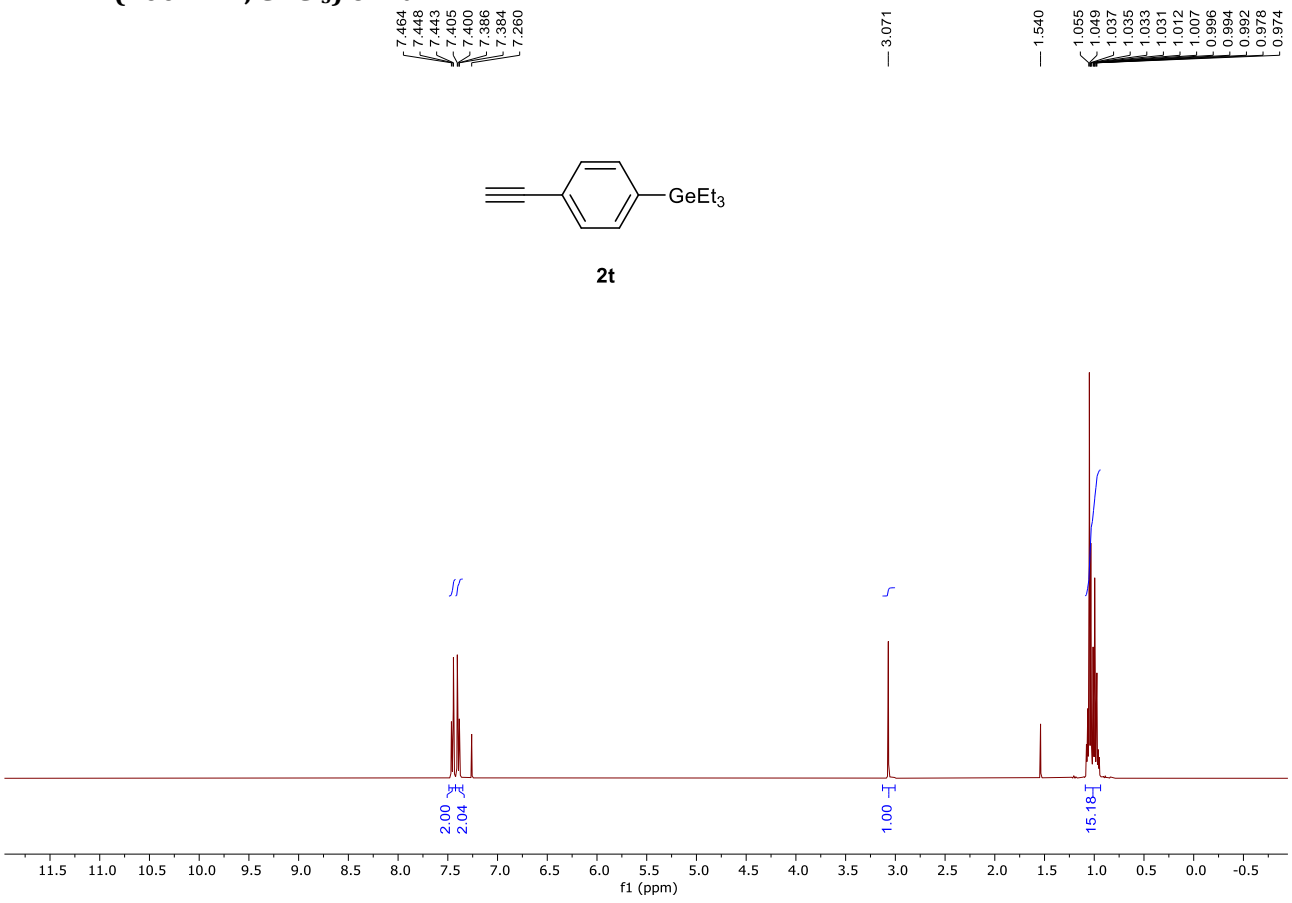


^{13}C NMR (101 MHz, $CDCl_3$) of 2s



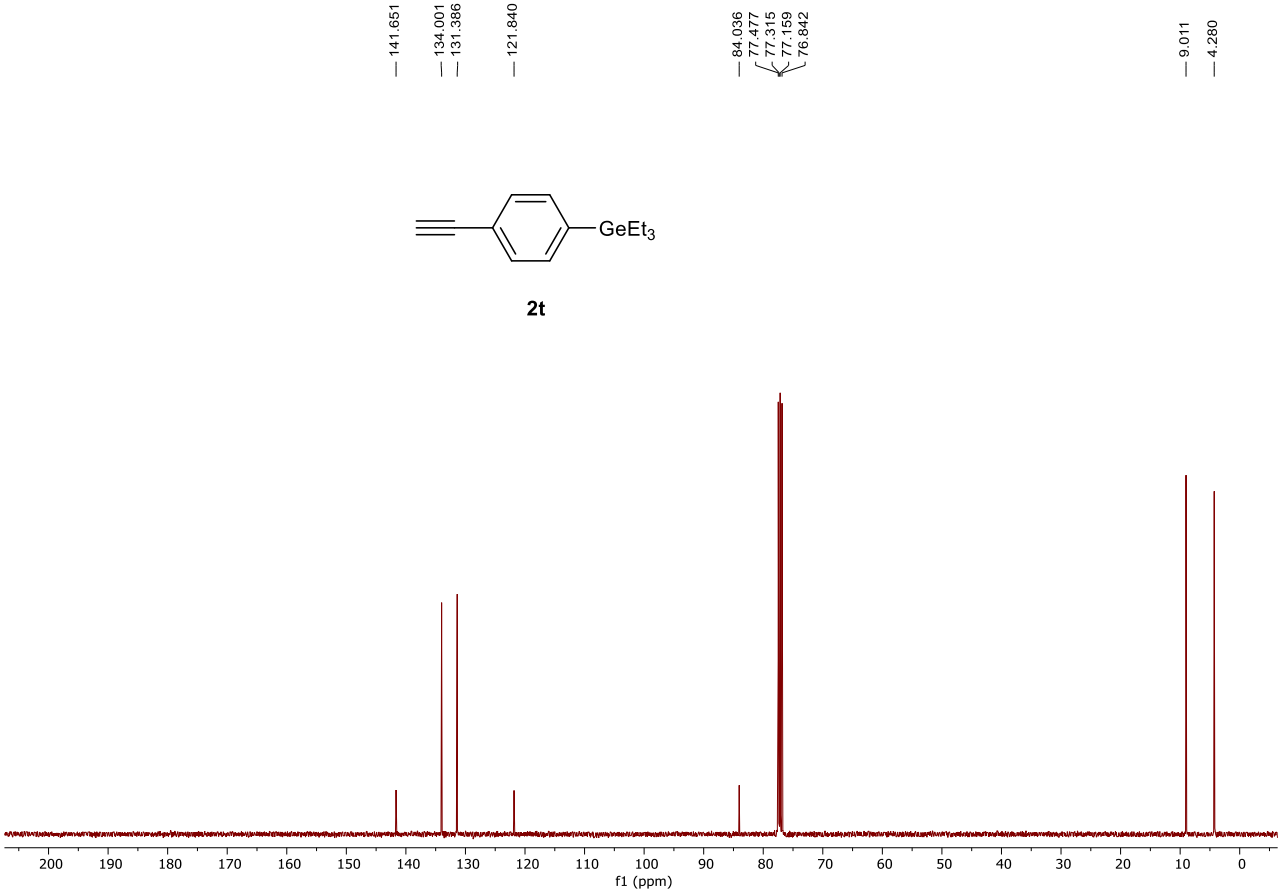
2s

^{1}H NMR (400 MHz, $CDCl_3$) of 2t



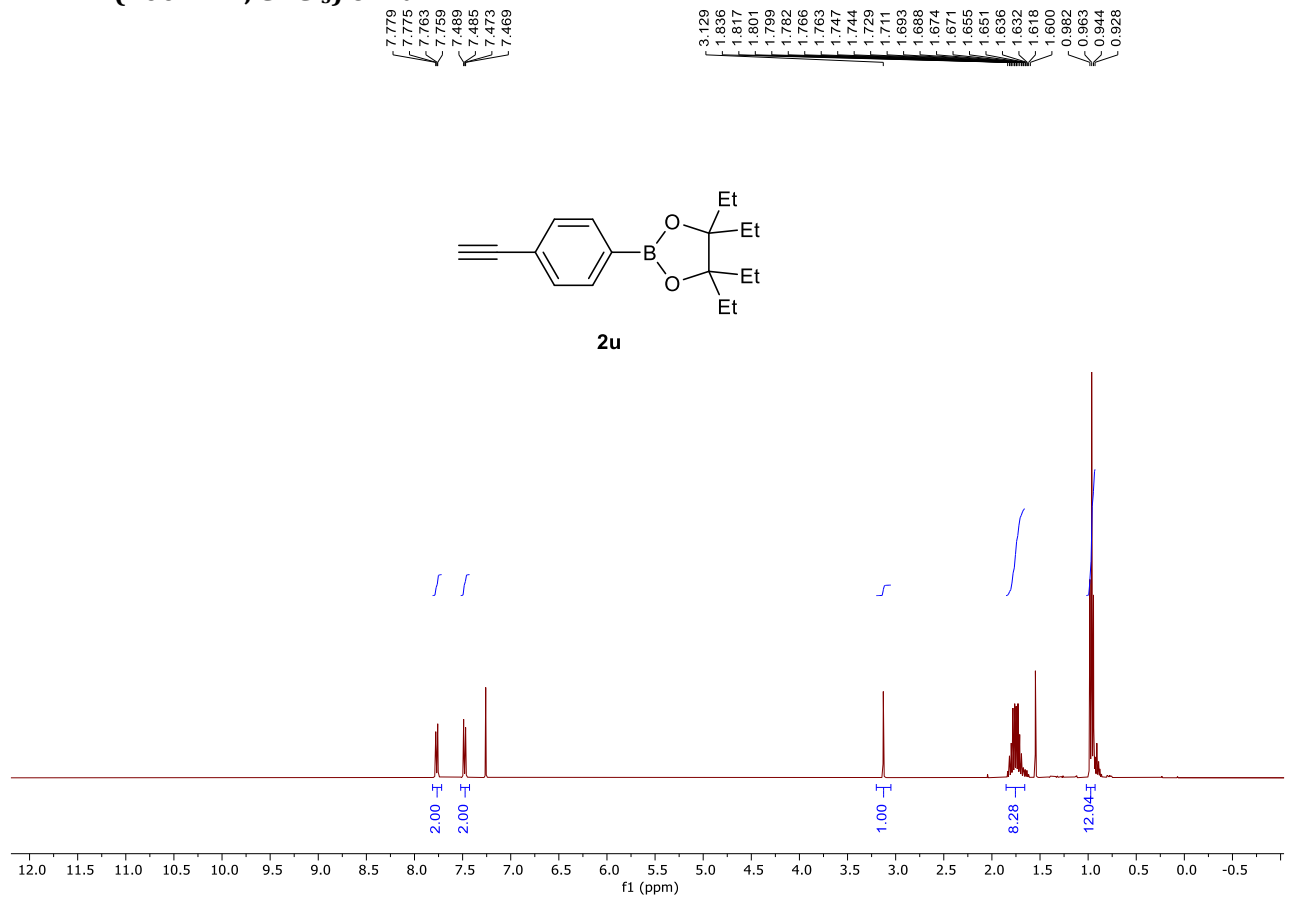
2t

^{13}C NMR (101 MHz, $CDCl_3$) of 2t



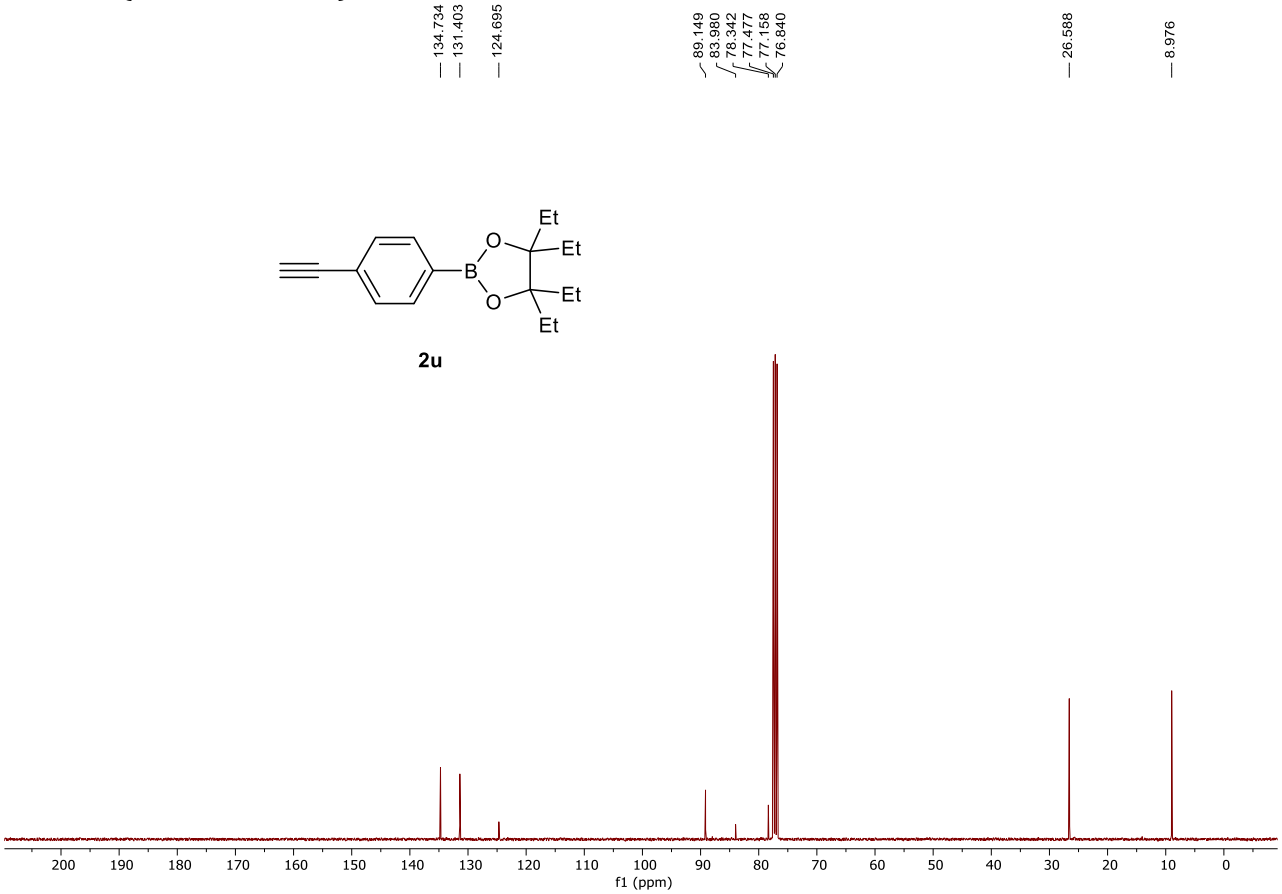
2t

^{1}H NMR (400 MHz, $CDCl_3$) of 2u

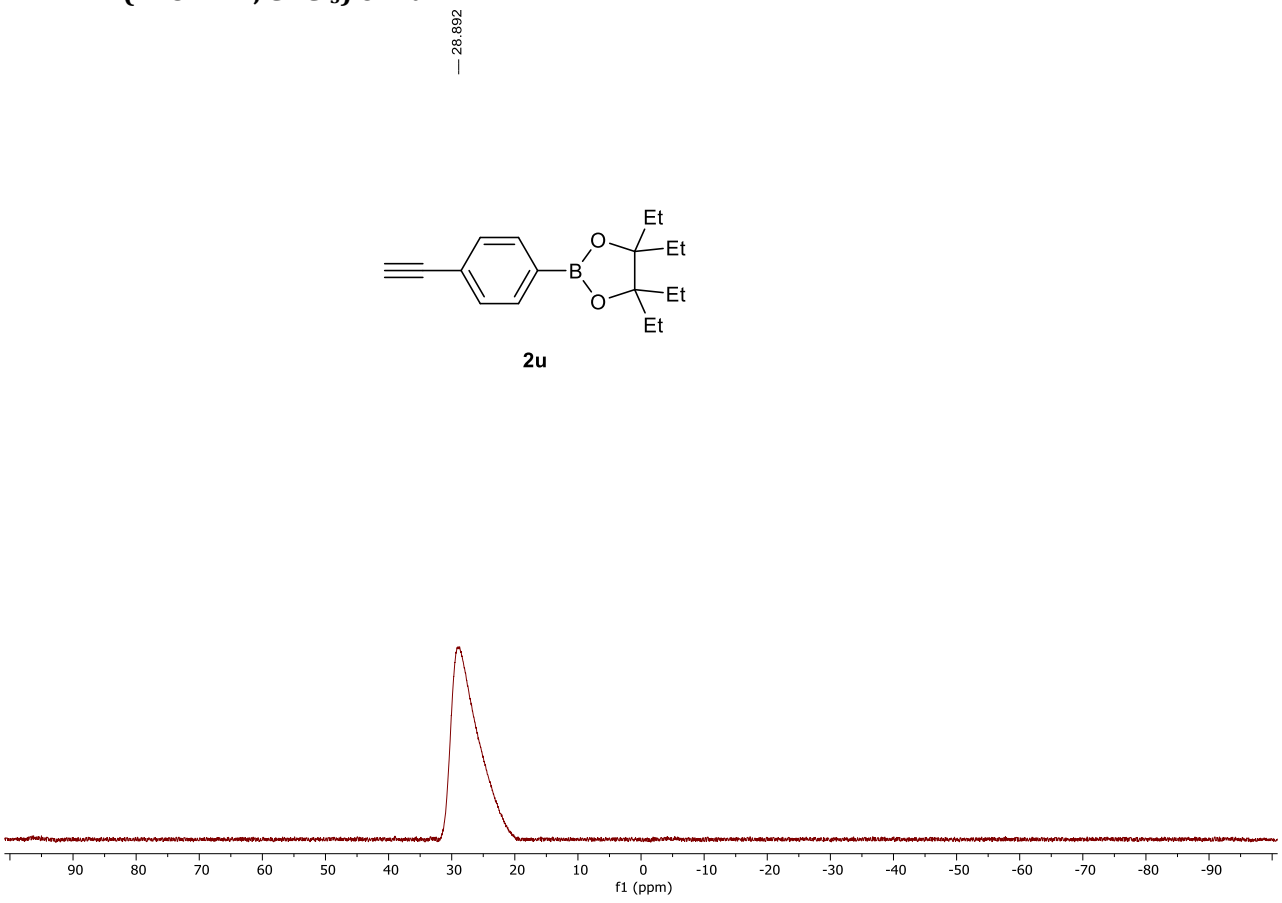


2u

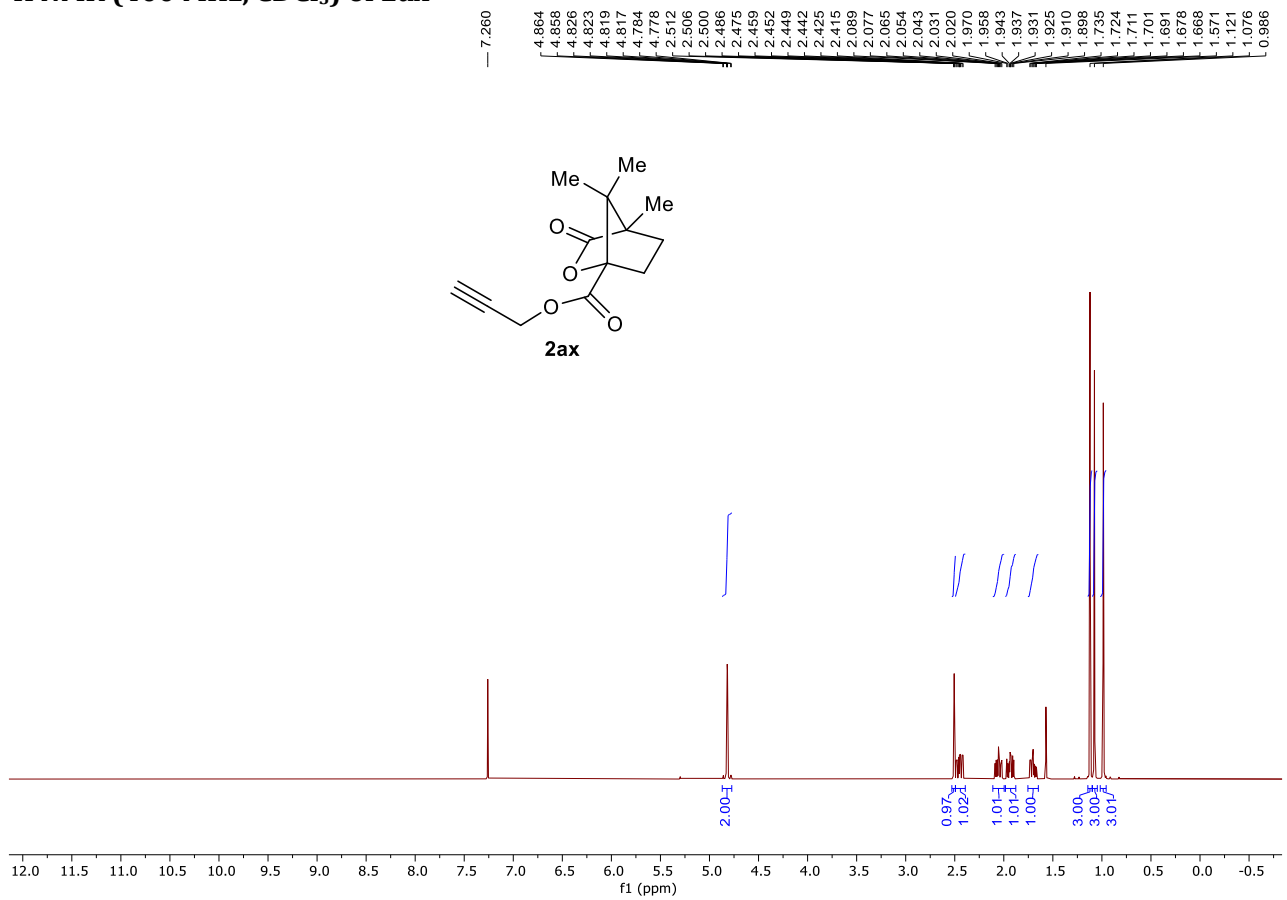
^{13}C NMR (101 MHz, $CDCl_3$) of 2u



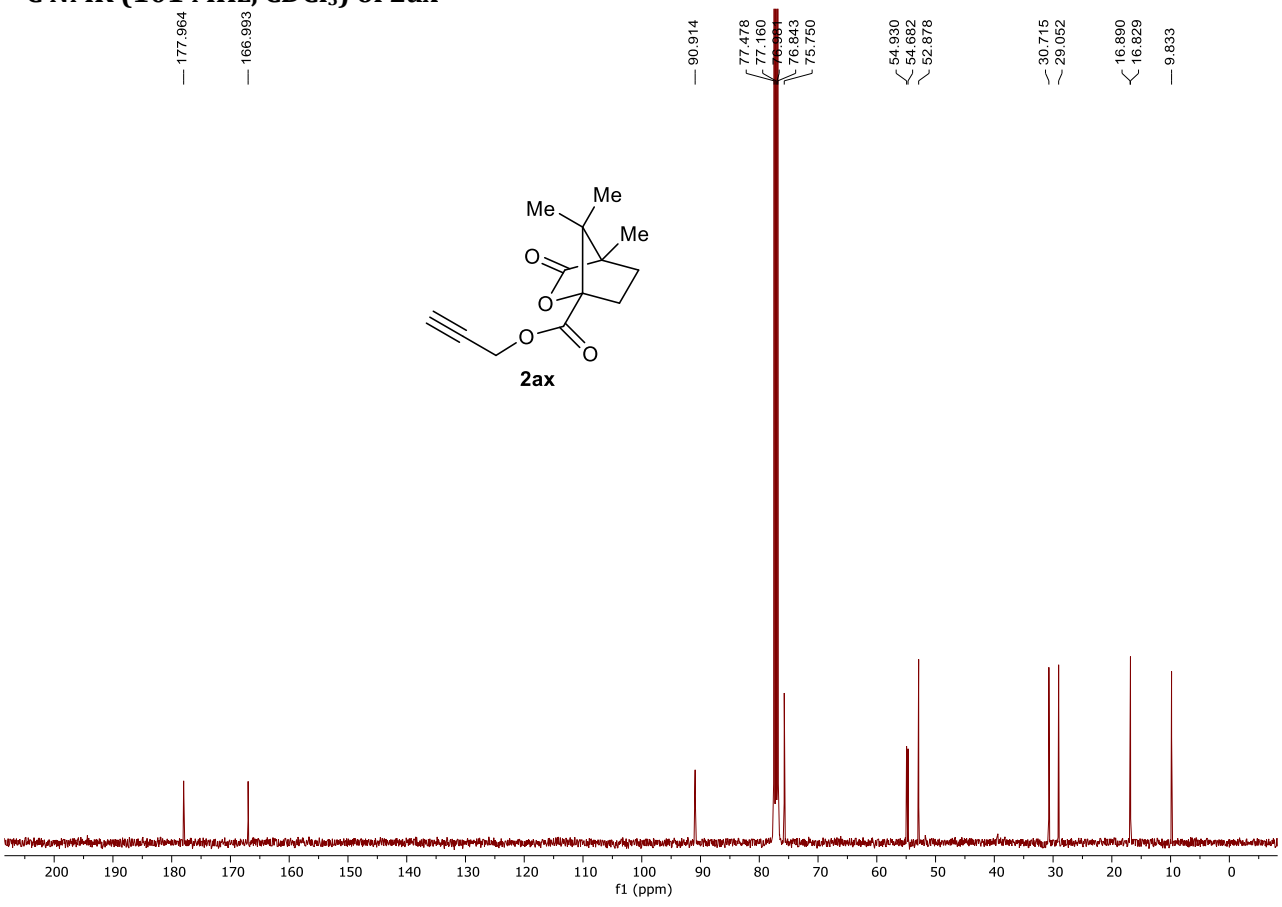
^{11}B NMR (128 MHz, $CDCl_3$) of 2u



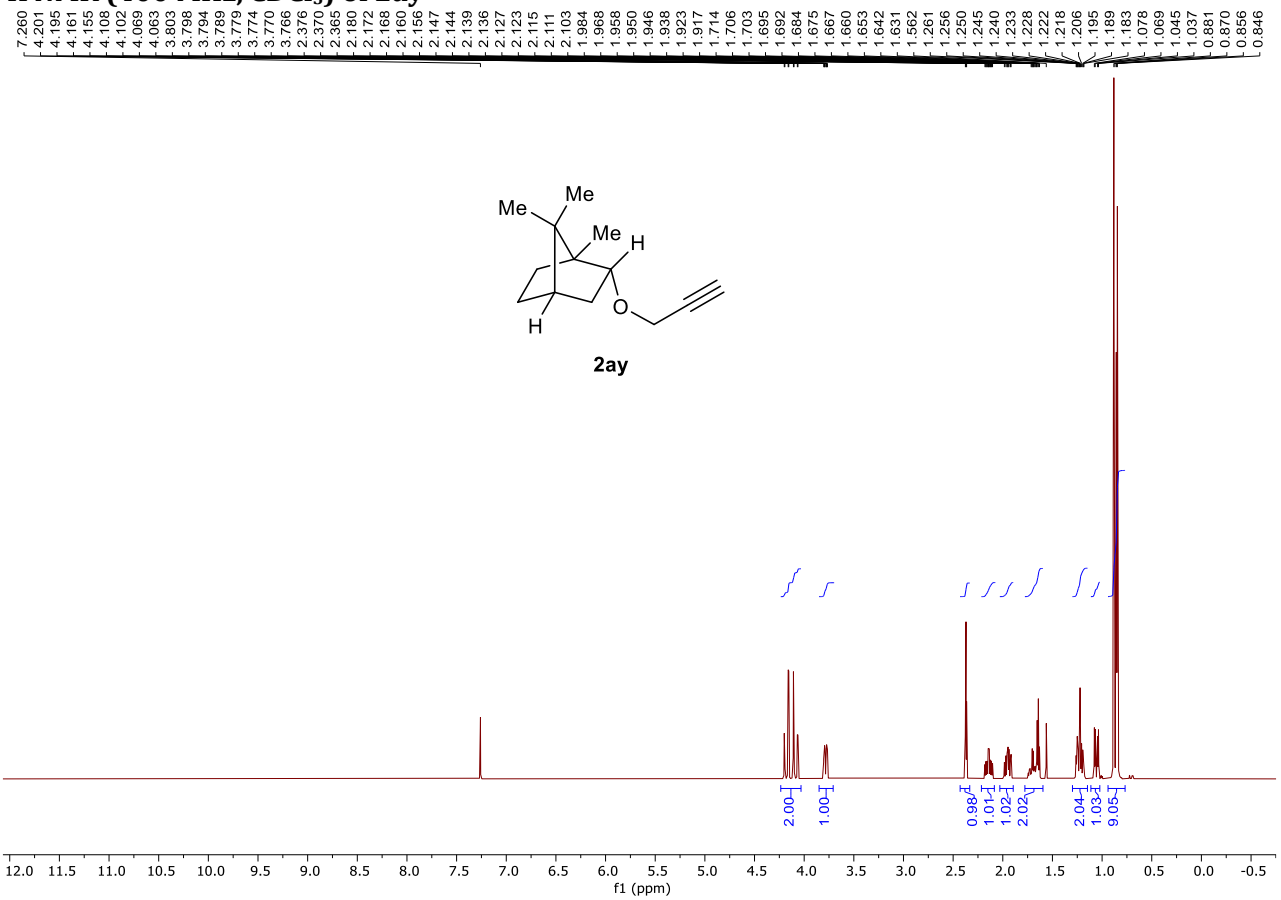
^{1}H NMR (400 MHz, $CDCl_3$) of 2ax



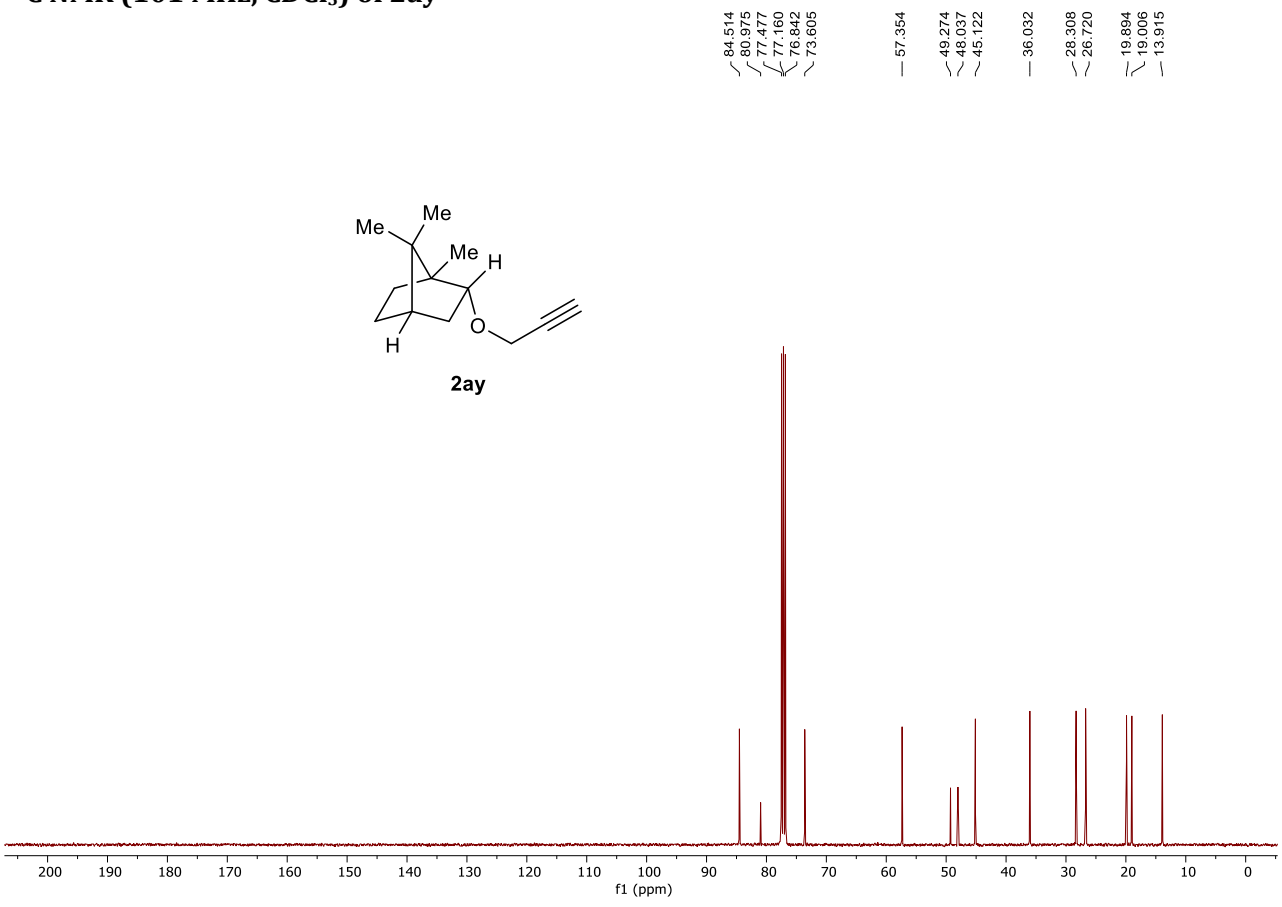
^{13}C NMR (101 MHz, $CDCl_3$) of 2ax



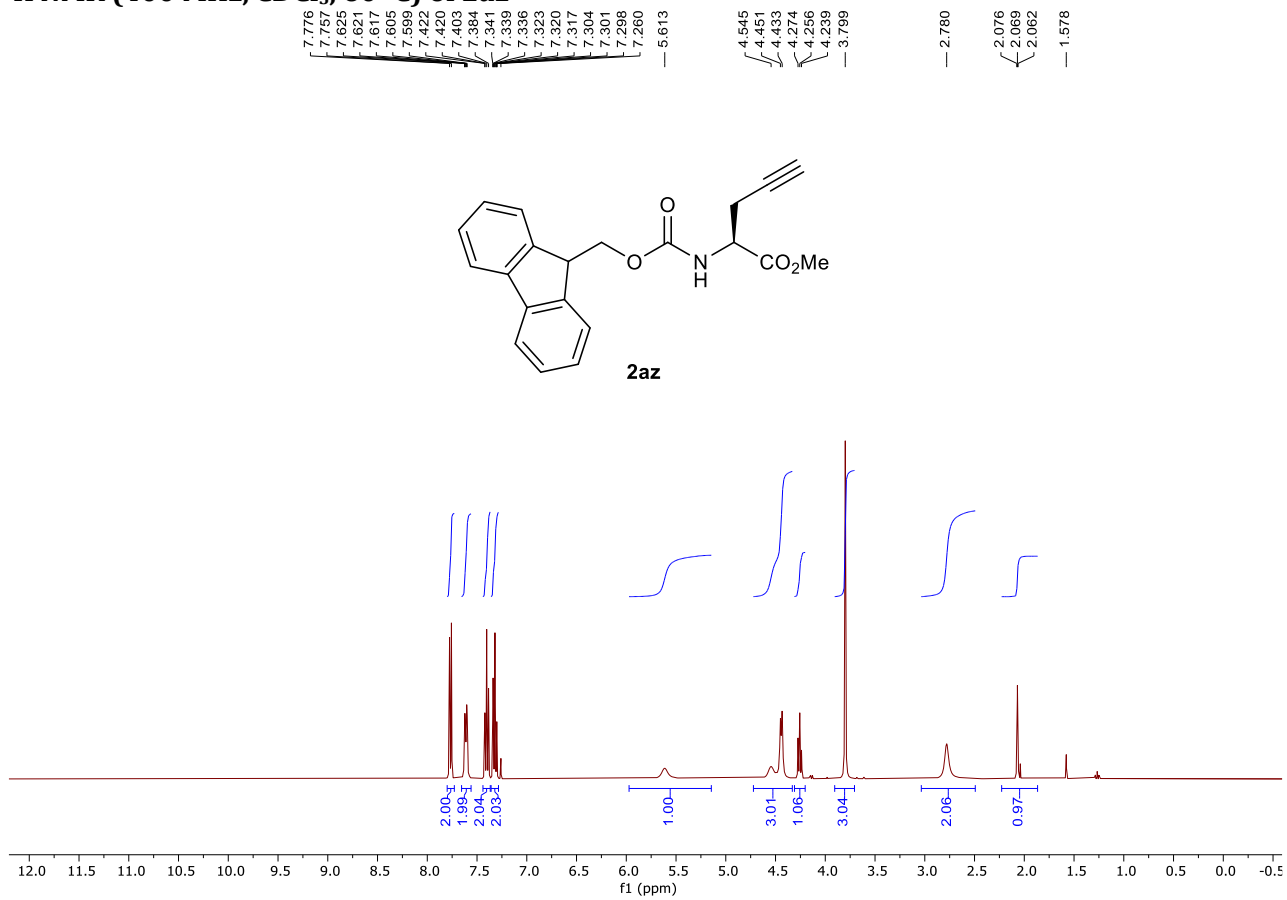
^{1}H NMR (400 MHz, $CDCl_3$) of 2ay



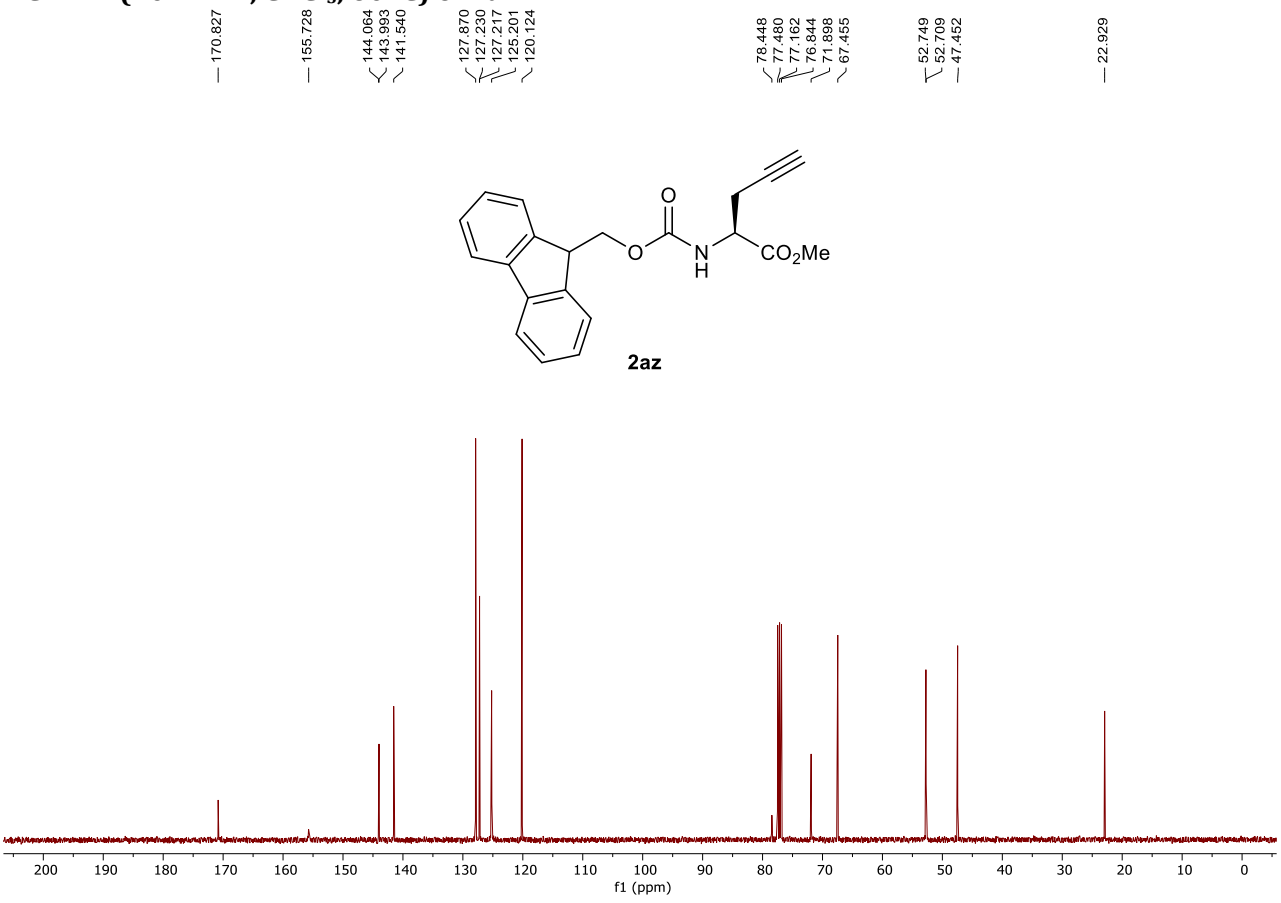
^{13}C NMR (101 MHz, $CDCl_3$) of 2ay



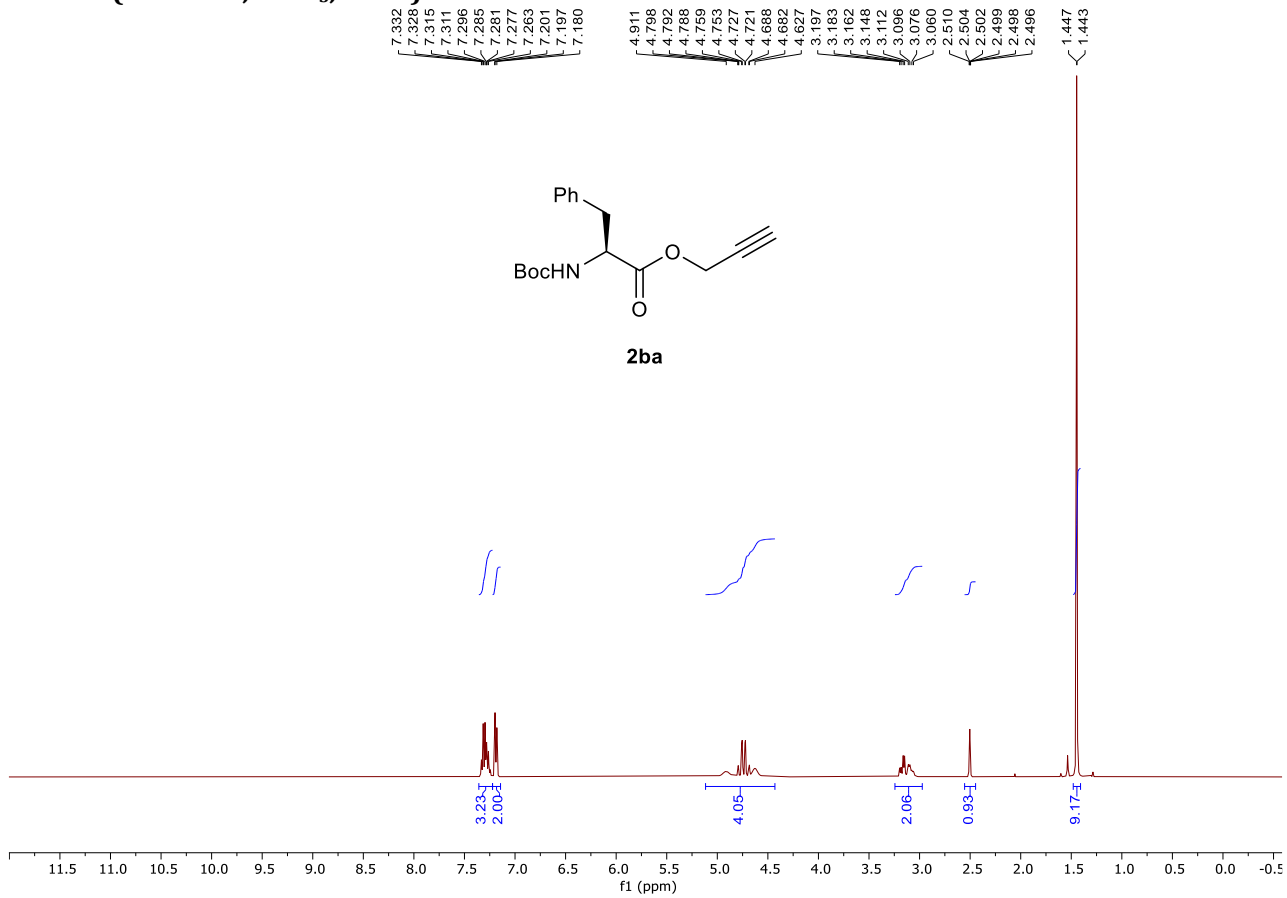
^{1}H NMR (400 MHz, $CDCl_3$, 60 °C) of 2az



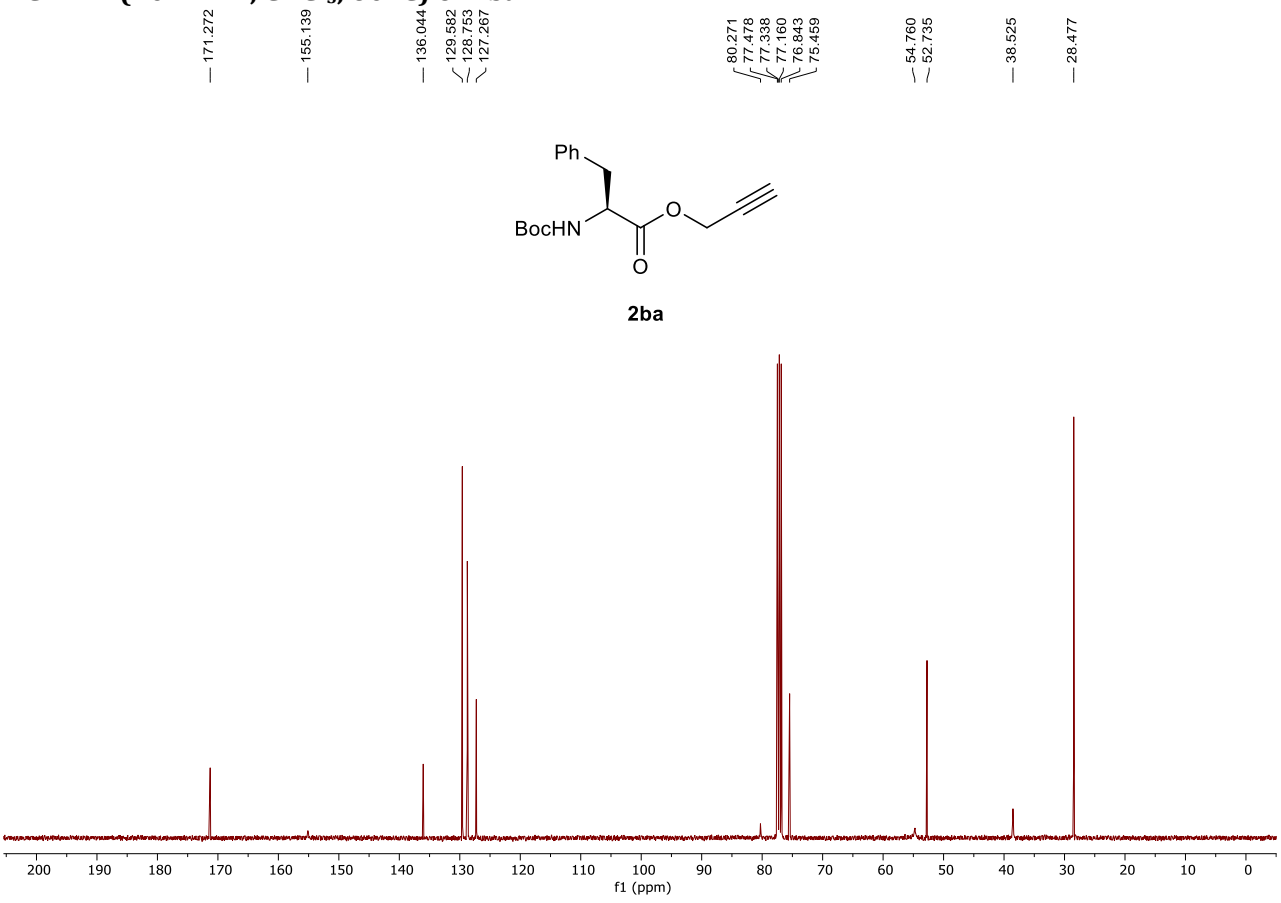
^{13}C NMR (101 MHz, $CDCl_3$, 60 °C) of 2az



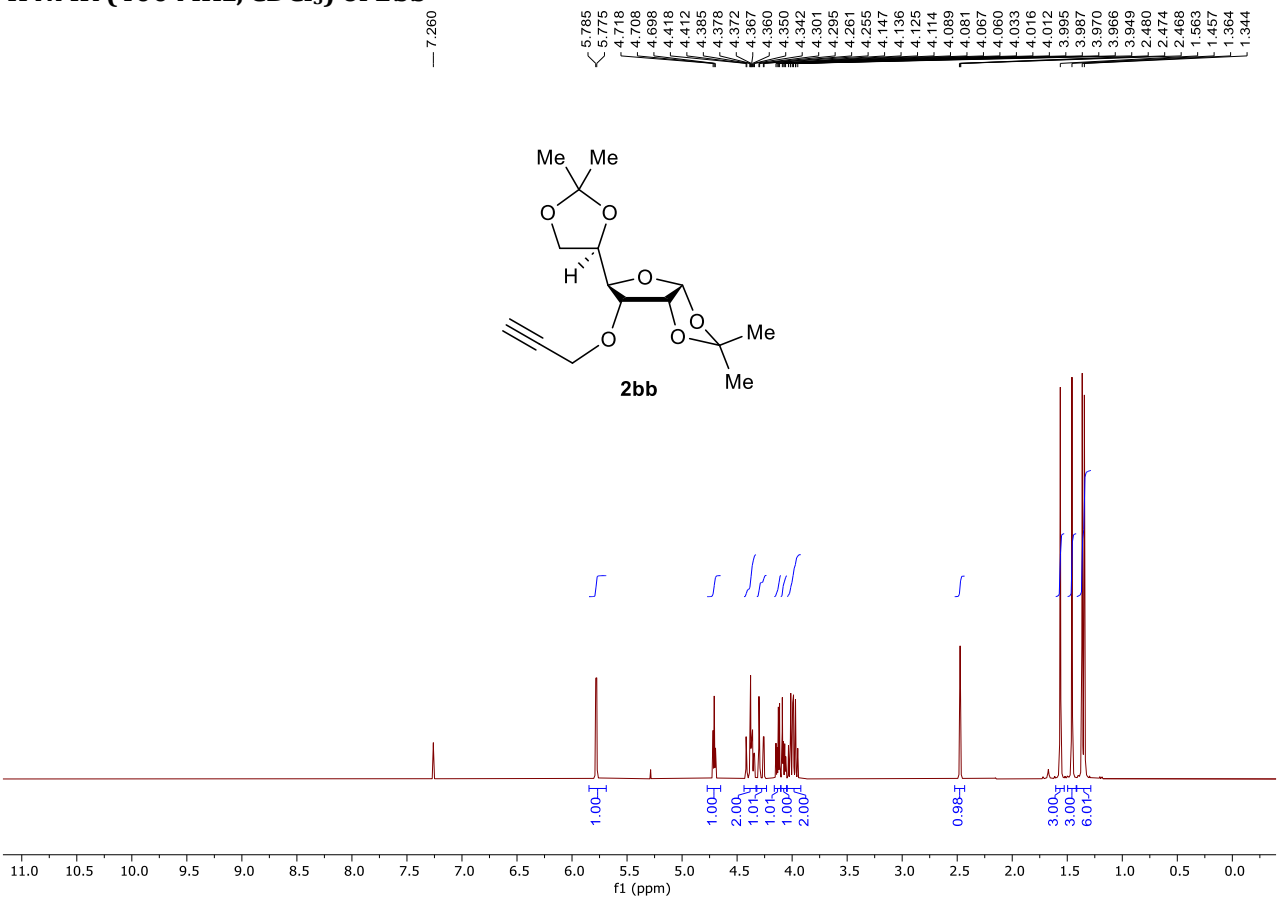
^{1}H NMR (400 MHz, $CDCl_3$, 60 °C) of 2ba



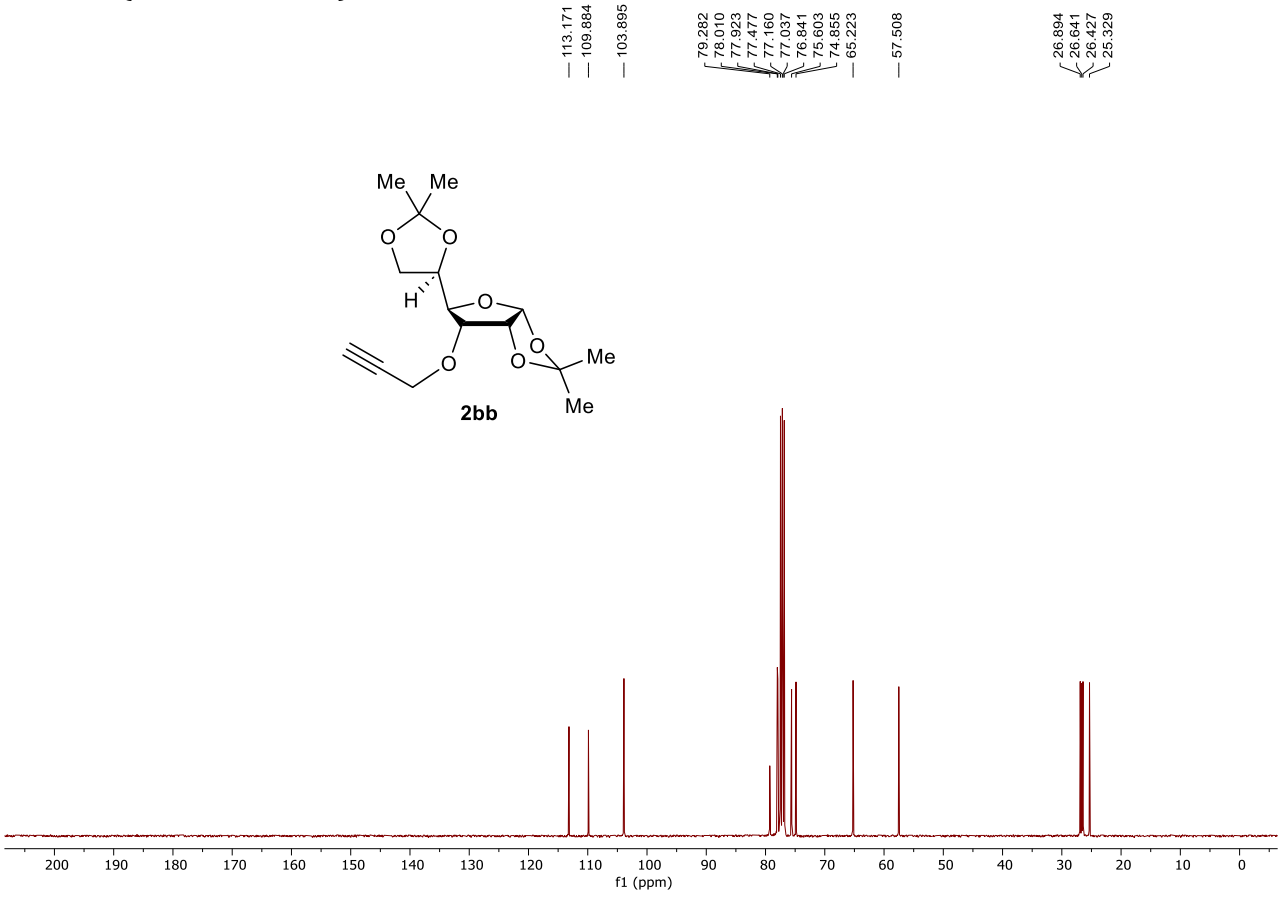
^{13}C NMR (101 MHz, $CDCl_3$, 60 °C) of 2ba



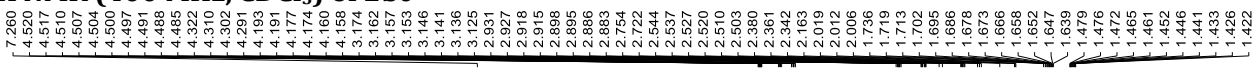
^{1}H NMR (400 MHz, $CDCl_3$) of 2bb

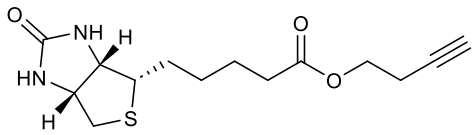


^{13}C NMR (101 MHz, $CDCl_3$) of 2bb

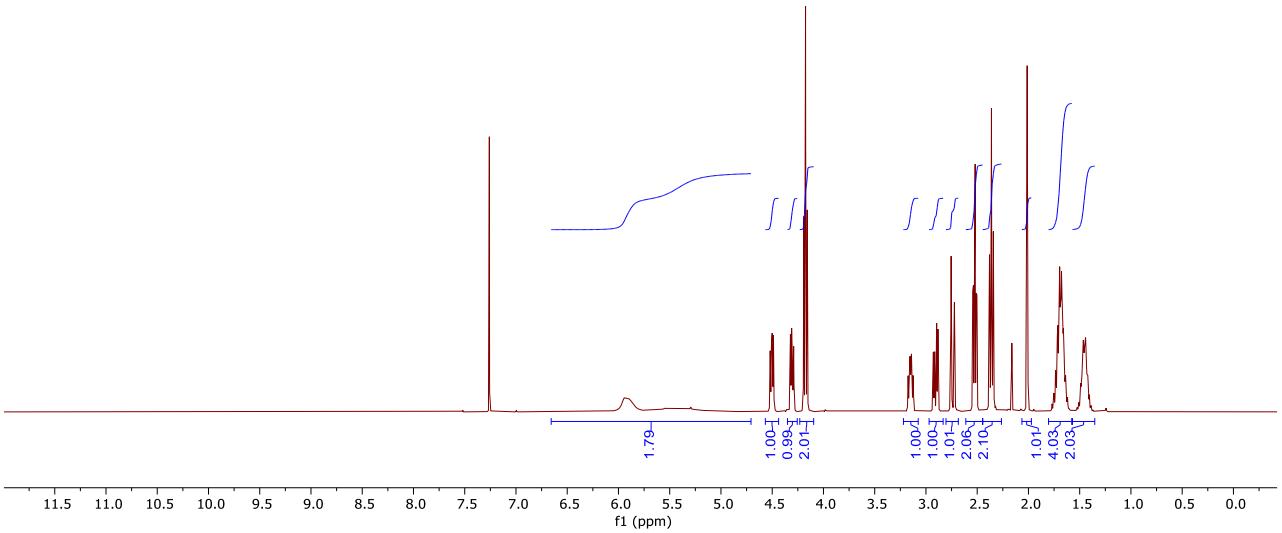


^{1}H NMR (400 MHz, $CDCl_3$) of 2bc

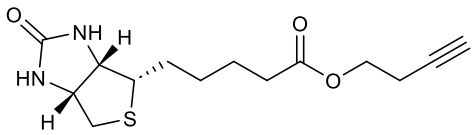




2bc

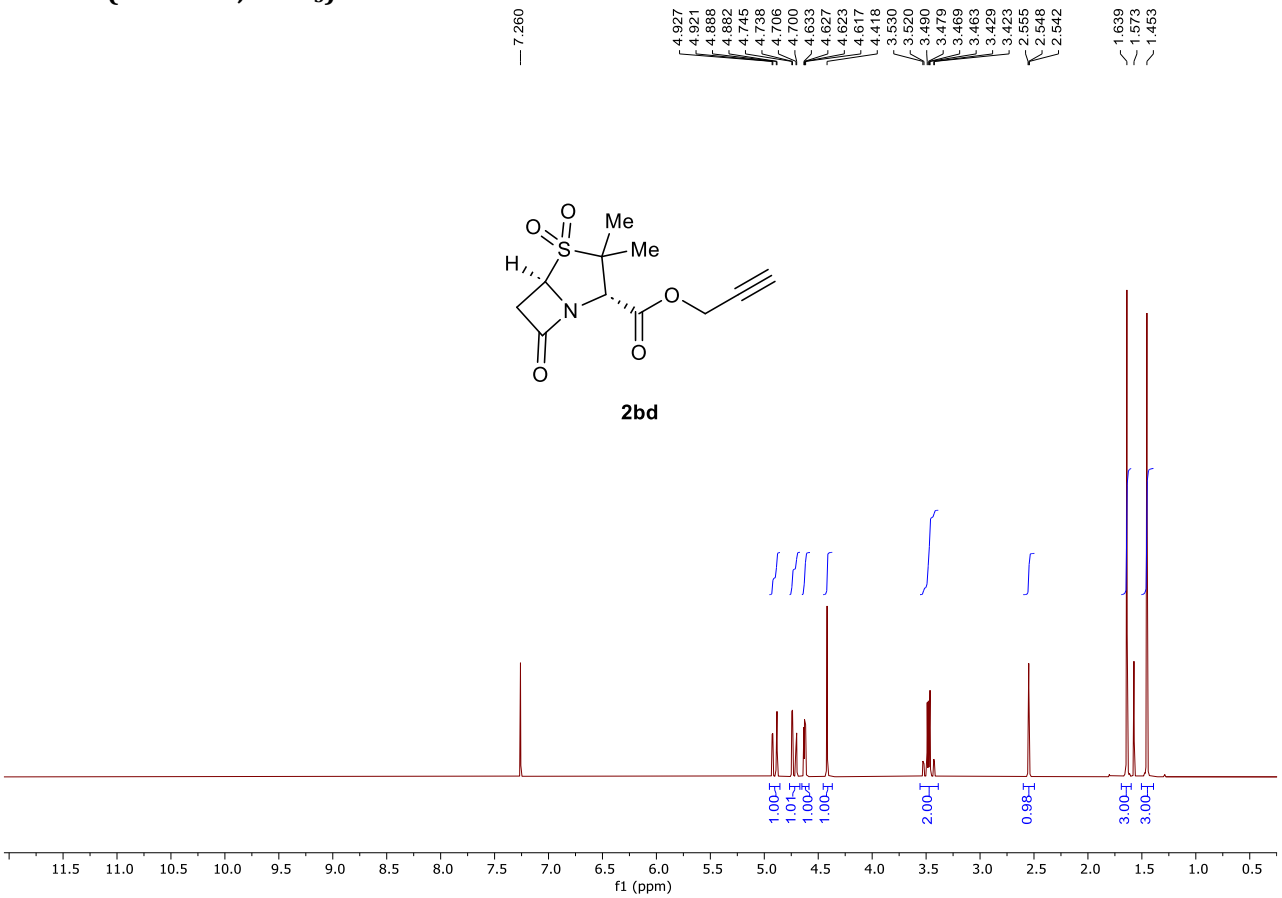


^{13}C NMR (101 MHz, $CDCl_3$) of 2bc

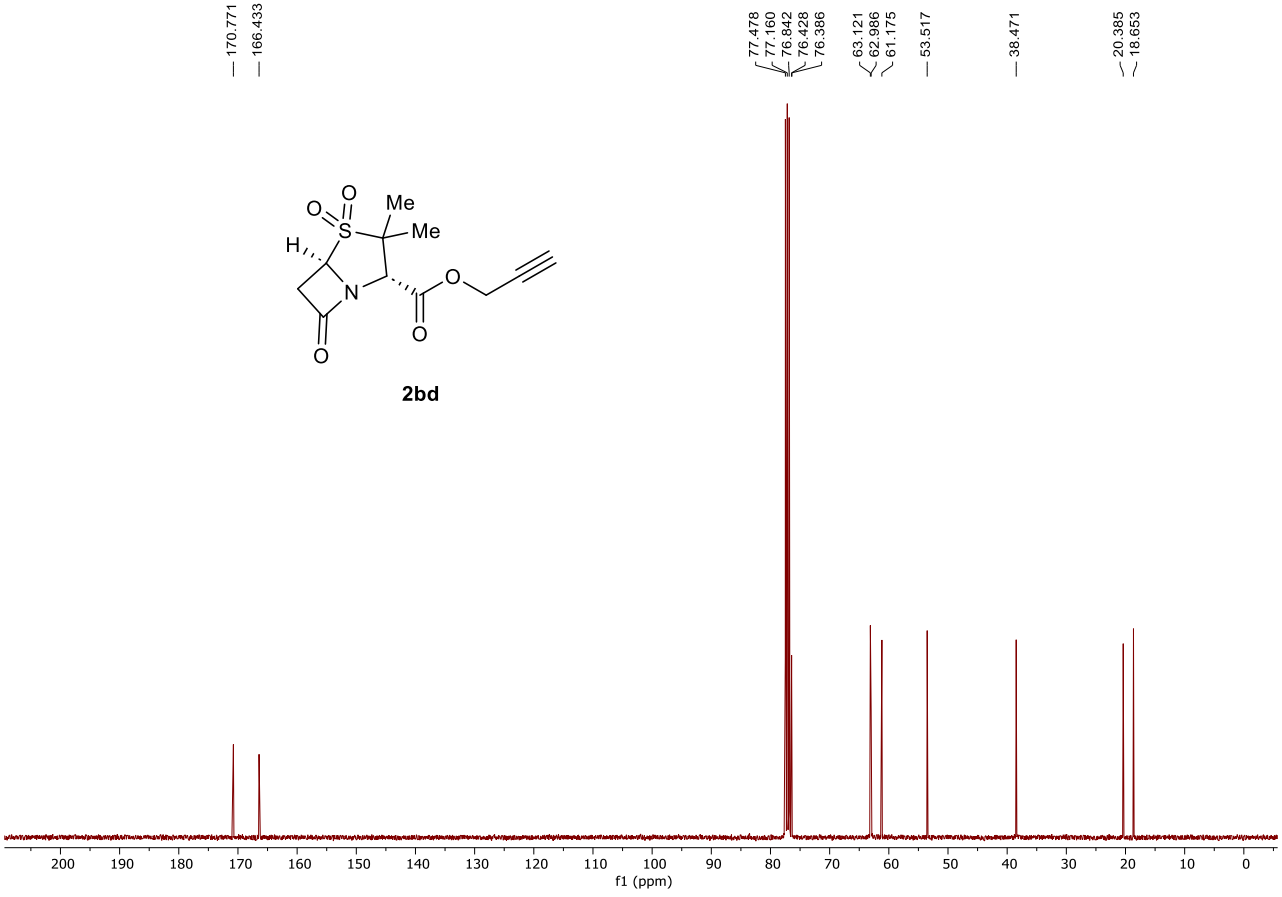


2bc

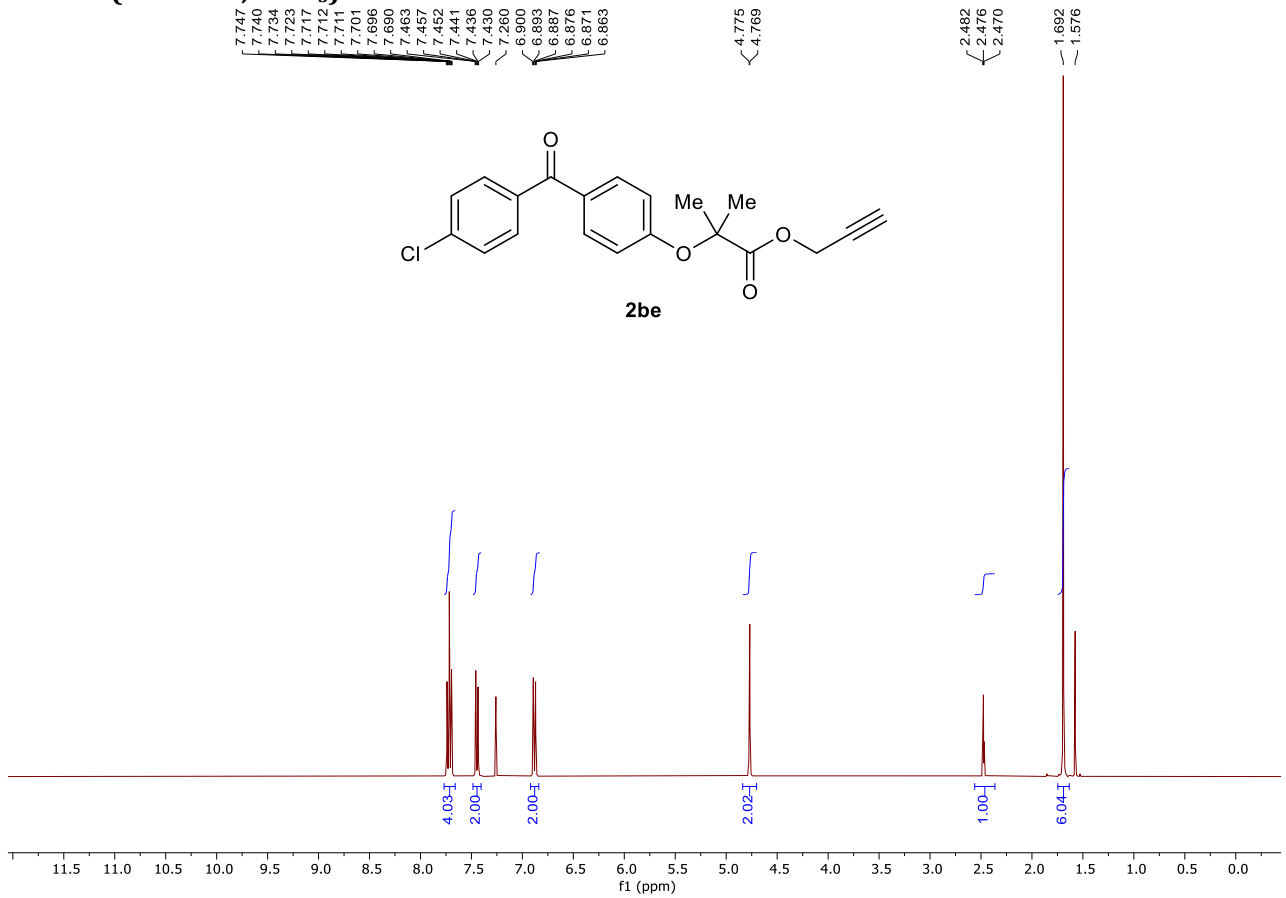
^{1}H NMR (400 MHz, $CDCl_3$) of 2bd



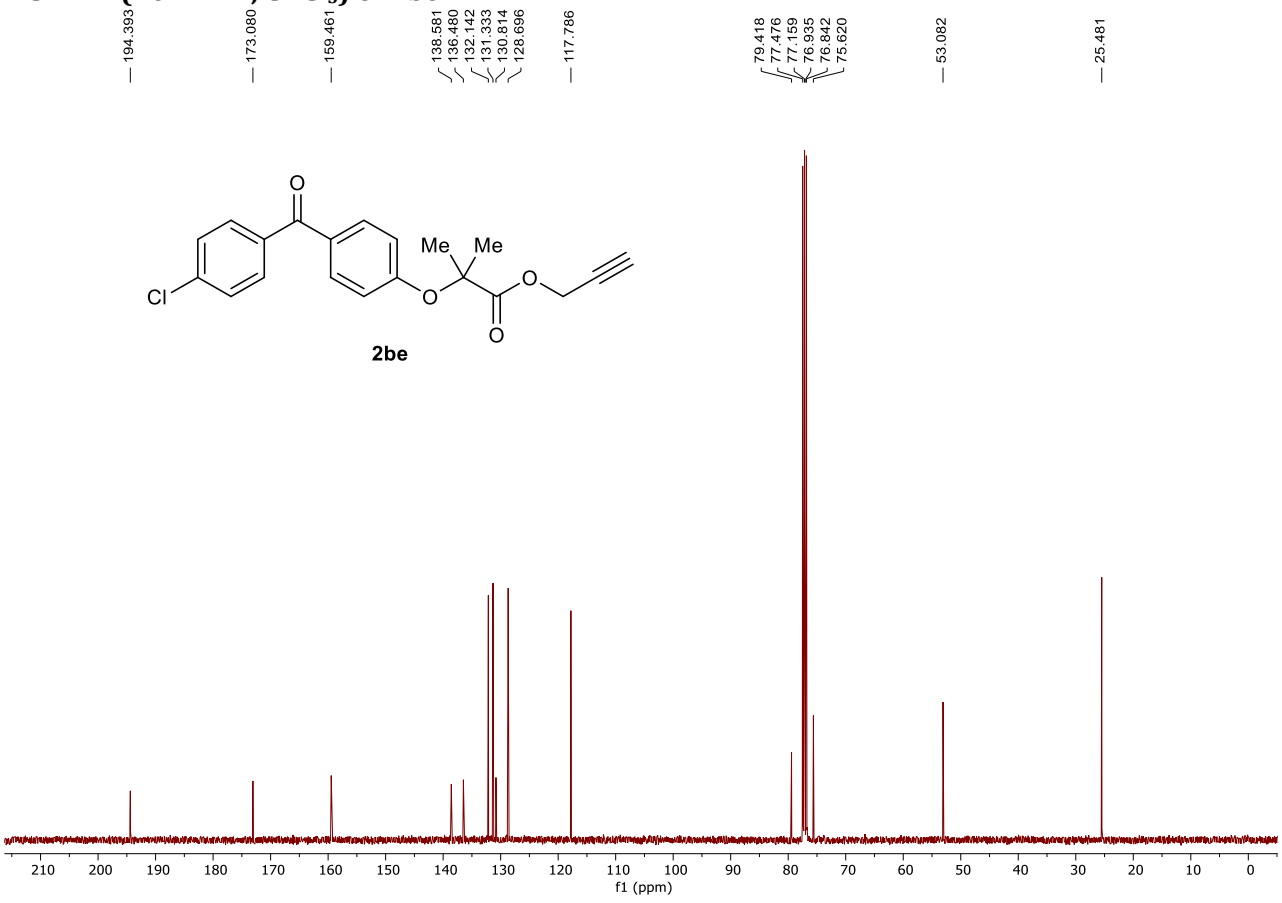
^{13}C NMR (101 MHz, $CDCl_3$) of 2bd



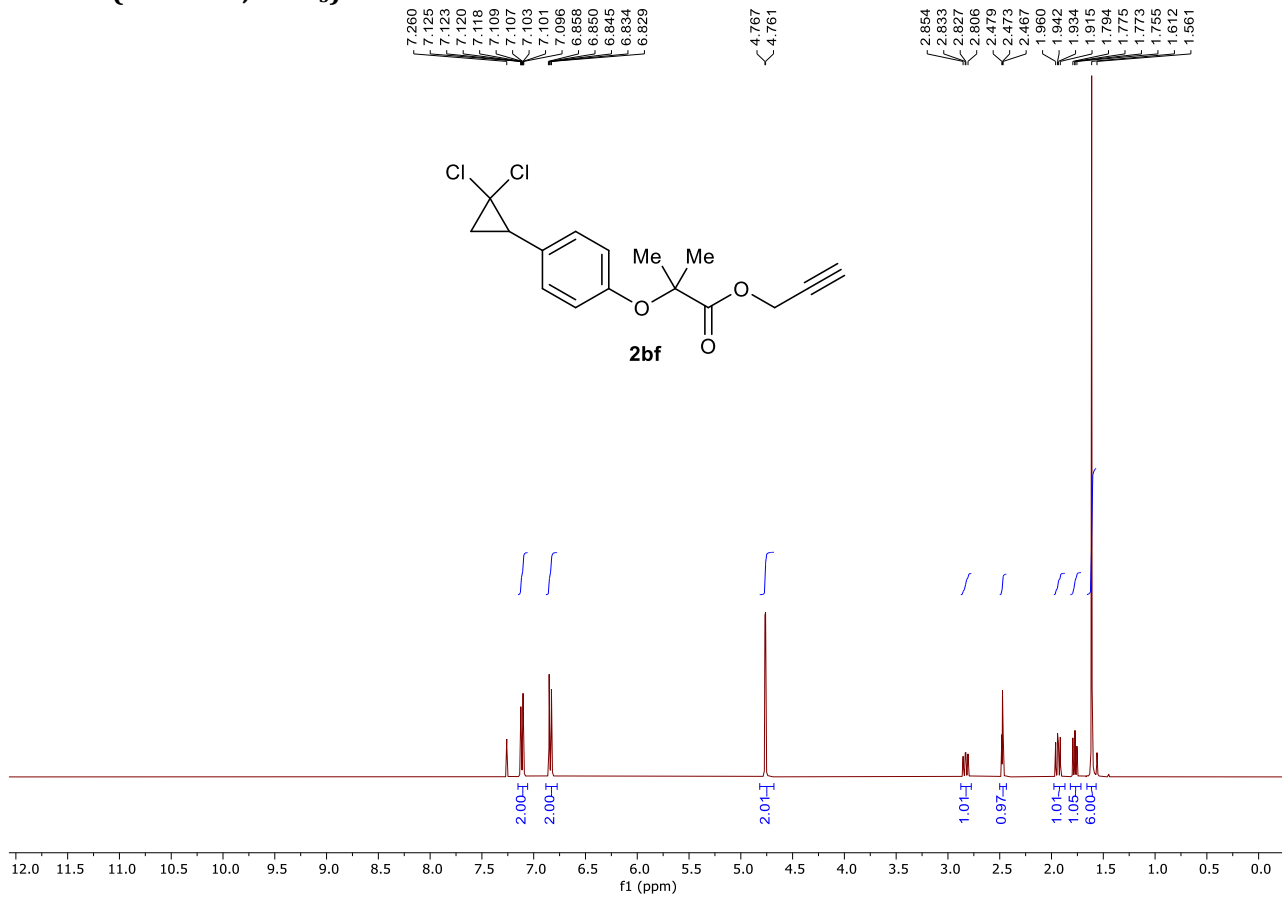
^{1}H NMR (400 MHz, $CDCl_3$) of 2be



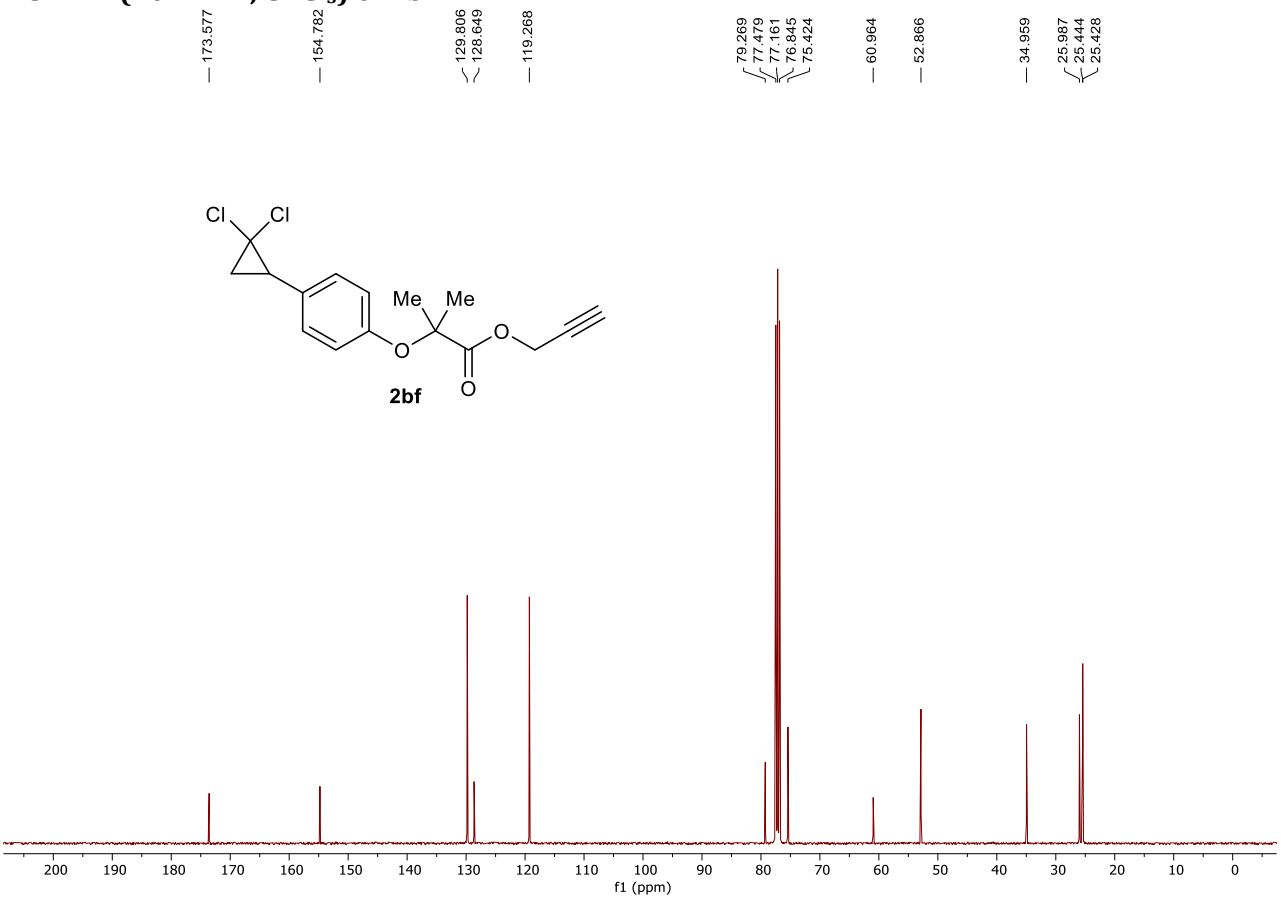
^{13}C NMR (101 MHz, $CDCl_3$) of 2be



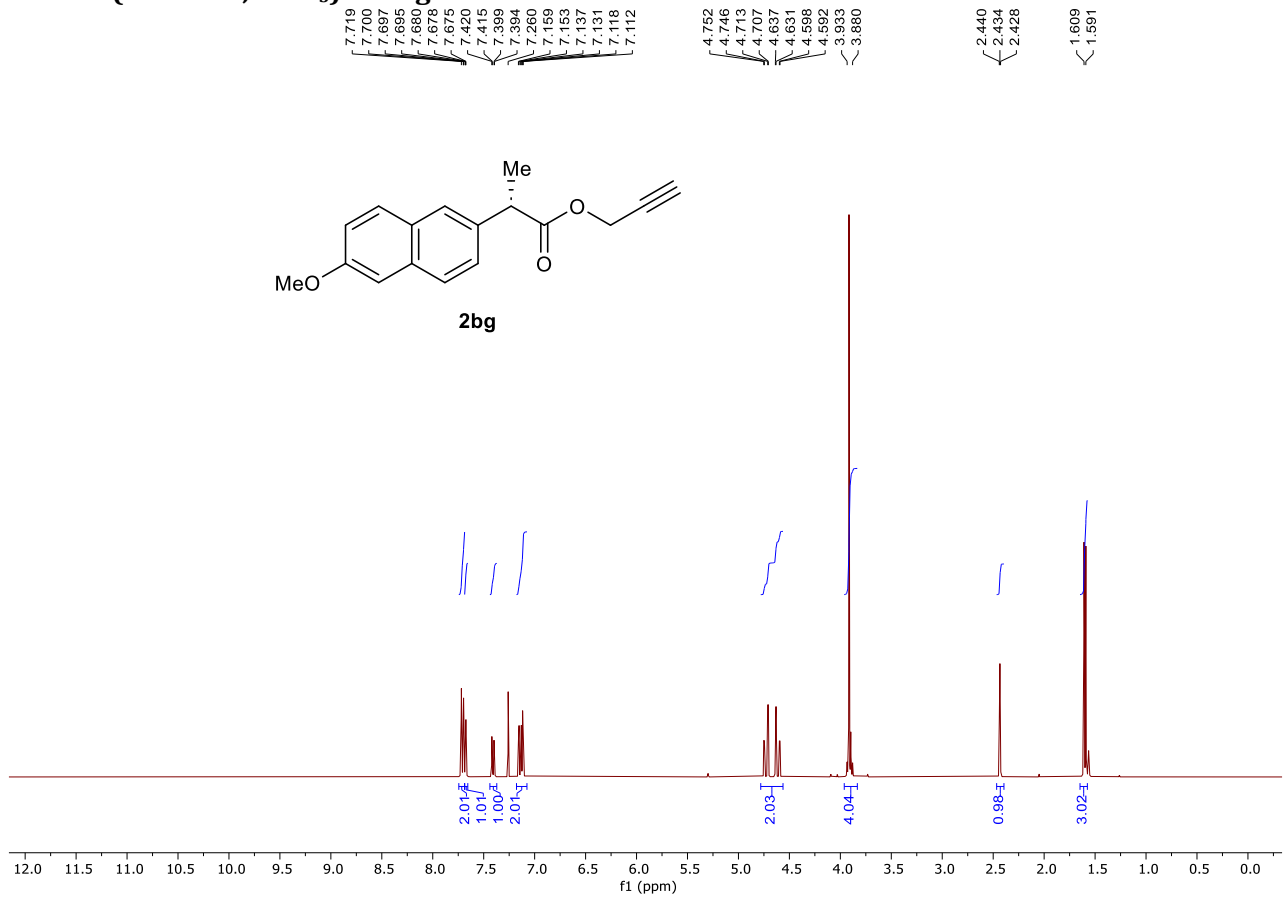
^{1}H NMR (400 MHz, $CDCl_3$) of 2bf



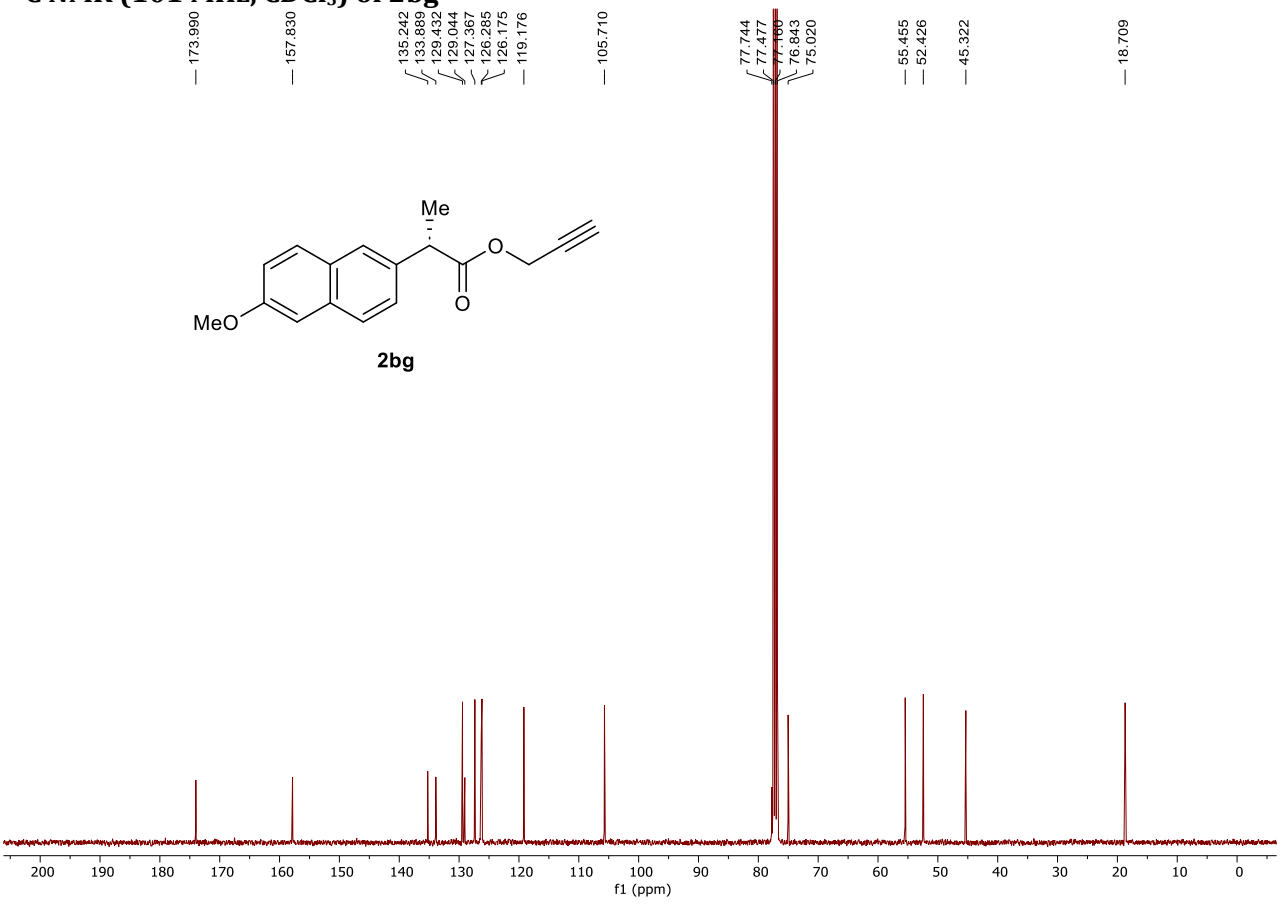
^{13}C NMR (101 MHz, $CDCl_3$) of 2bf



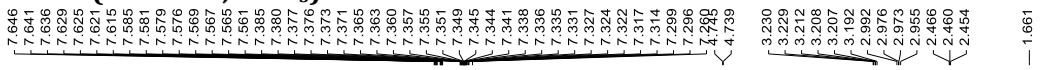
^{1}H NMR (400 MHz, $CDCl_3$) of 2bg

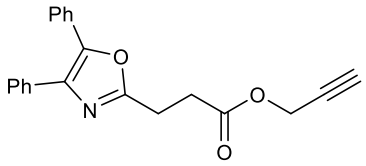


^{13}C NMR (101 MHz, $CDCl_3$) of 2bg

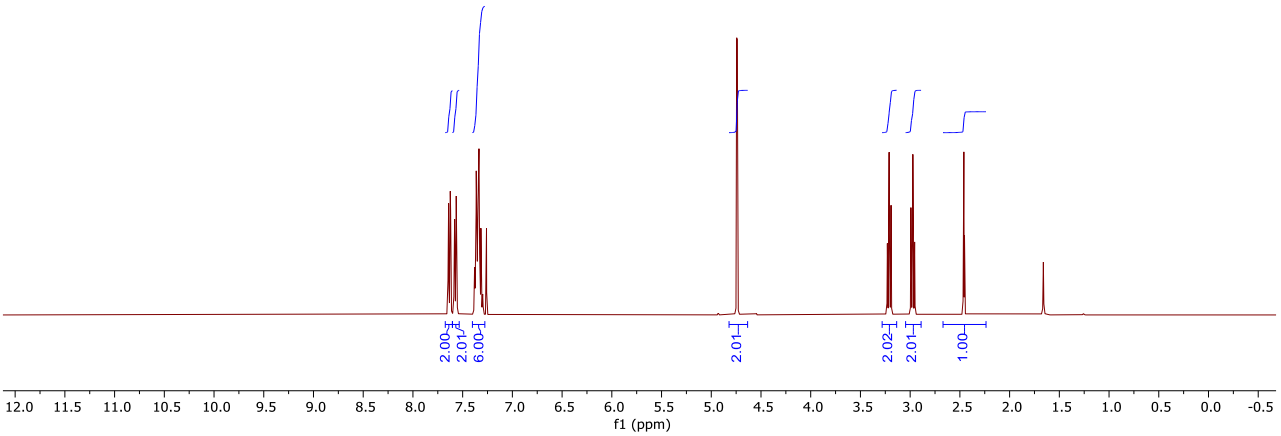


^{1}H NMR (400 MHz, $CDCl_3$) of 2bh

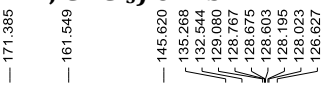


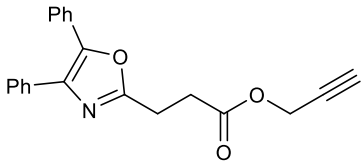


2bh



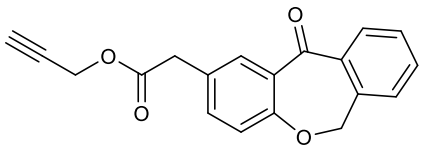
^{13}C NMR (101 MHz, $CDCl_3$) of 2bh



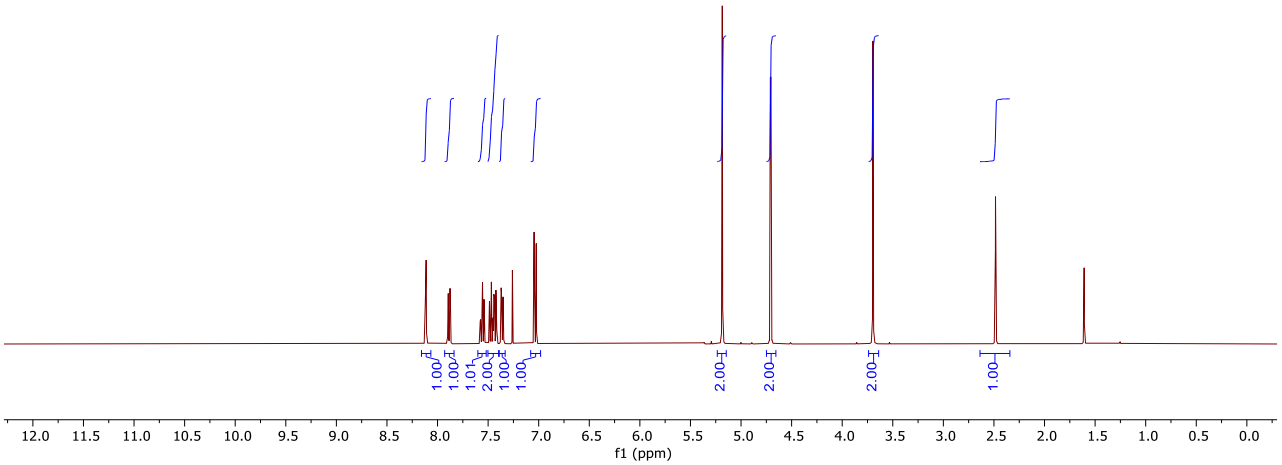


2bh

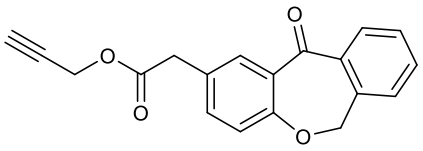
^{1}H NMR (400 MHz, $CDCl_3$) of 2bi



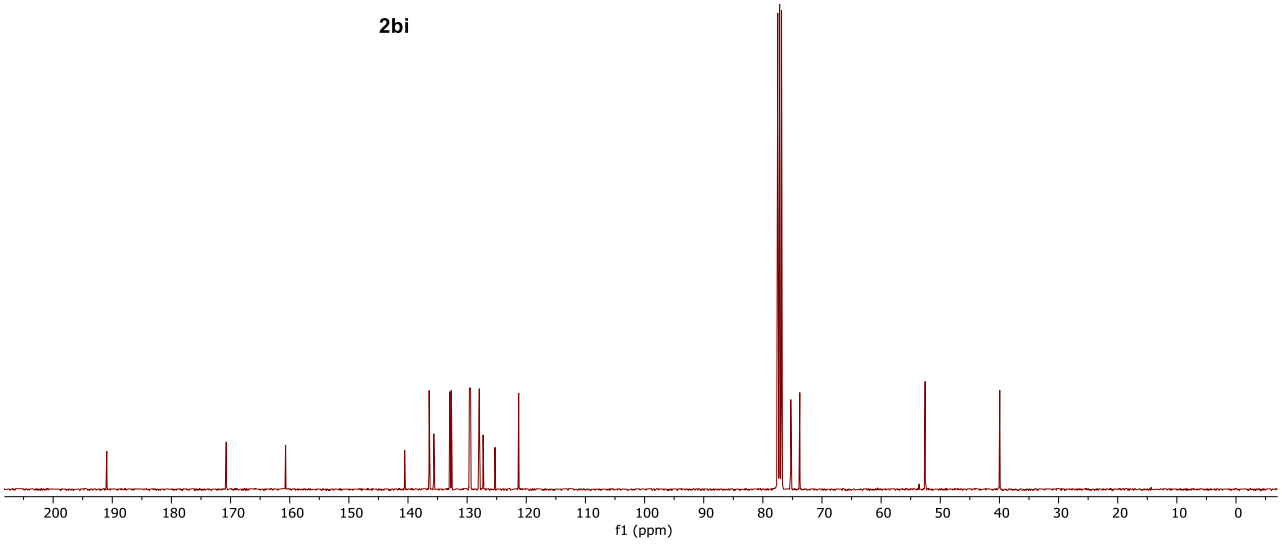
2bi



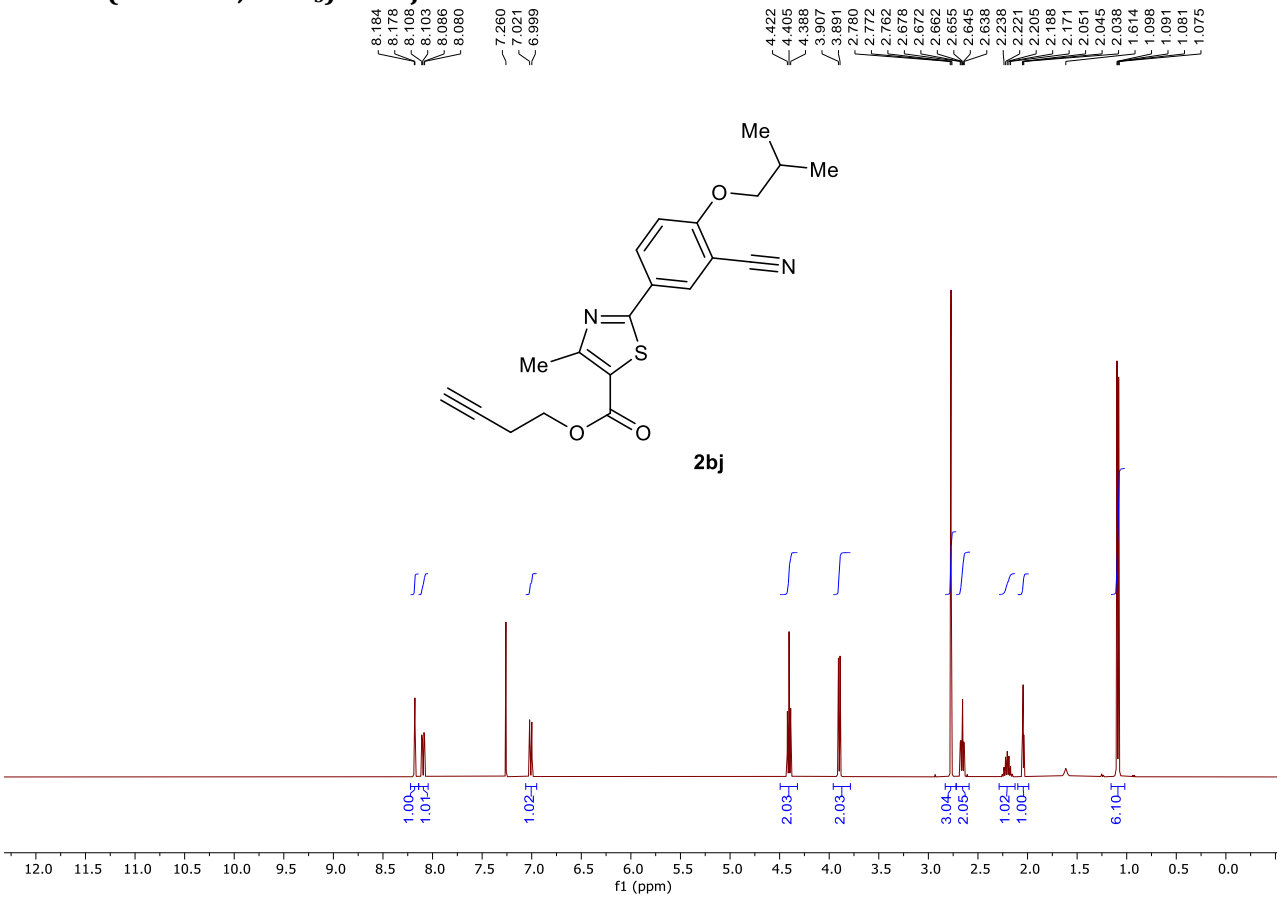
^{13}C NMR (101 MHz, $CDCl_3$) of 2bi



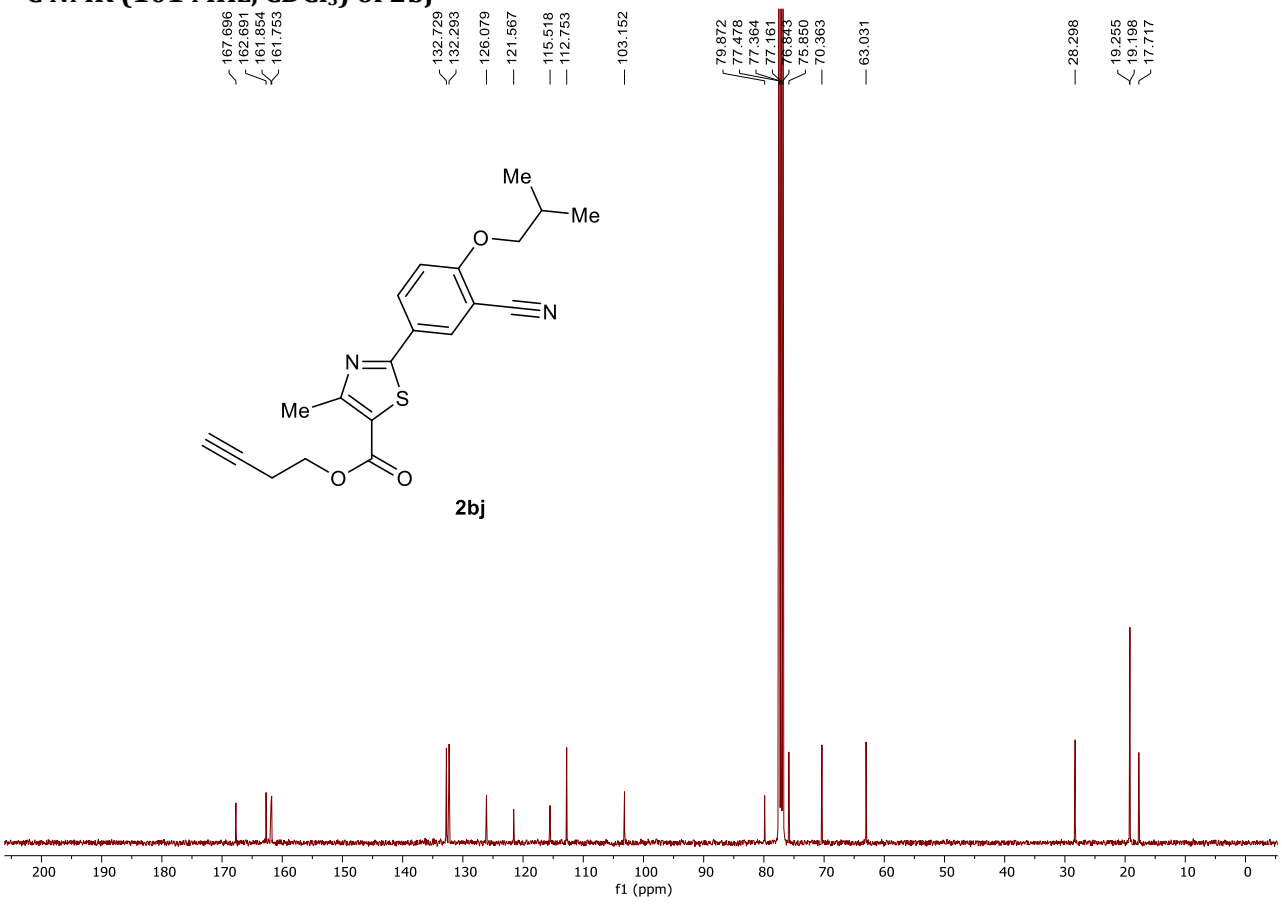
2bi



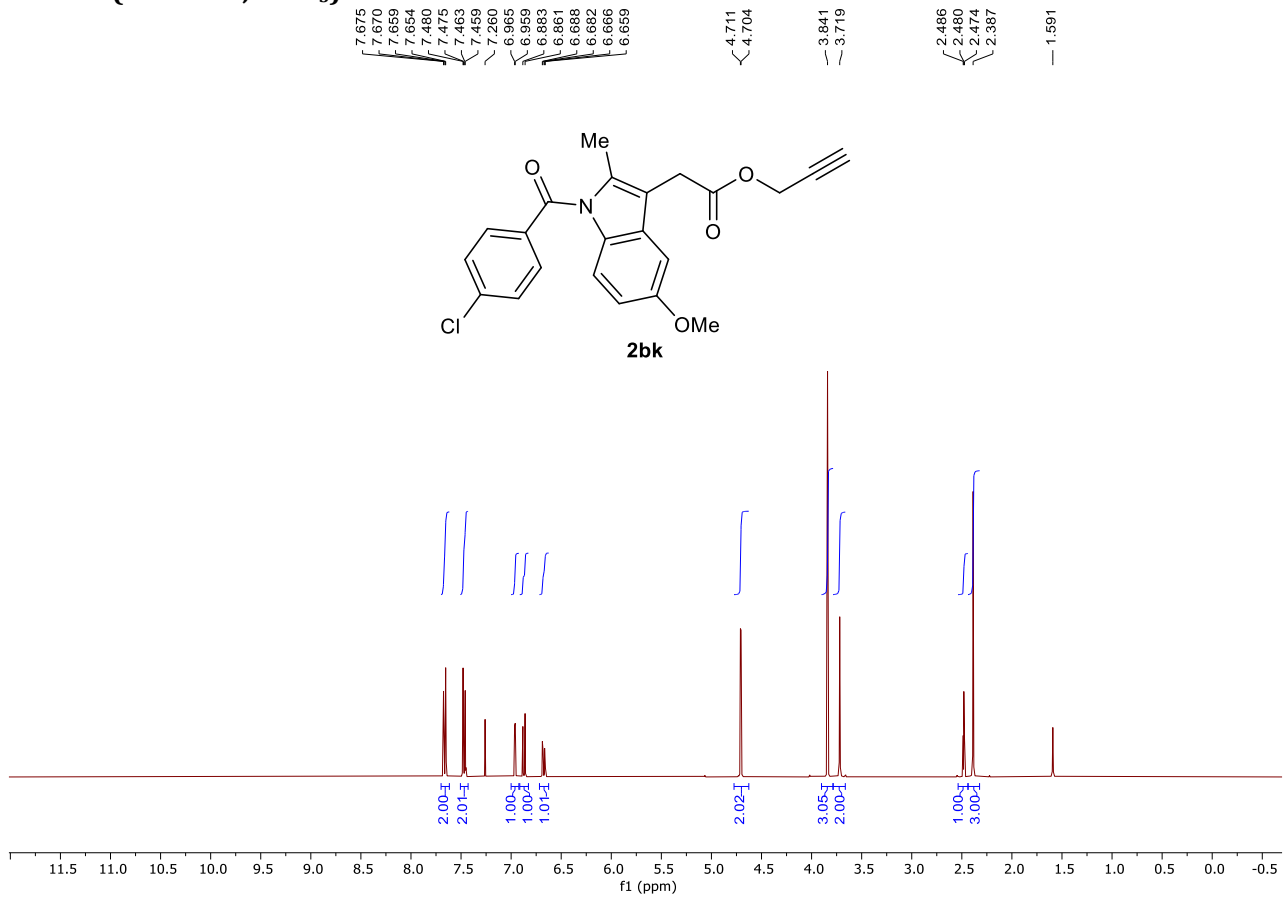
^{1}H NMR (400 MHz, $CDCl_3$) of 2bj



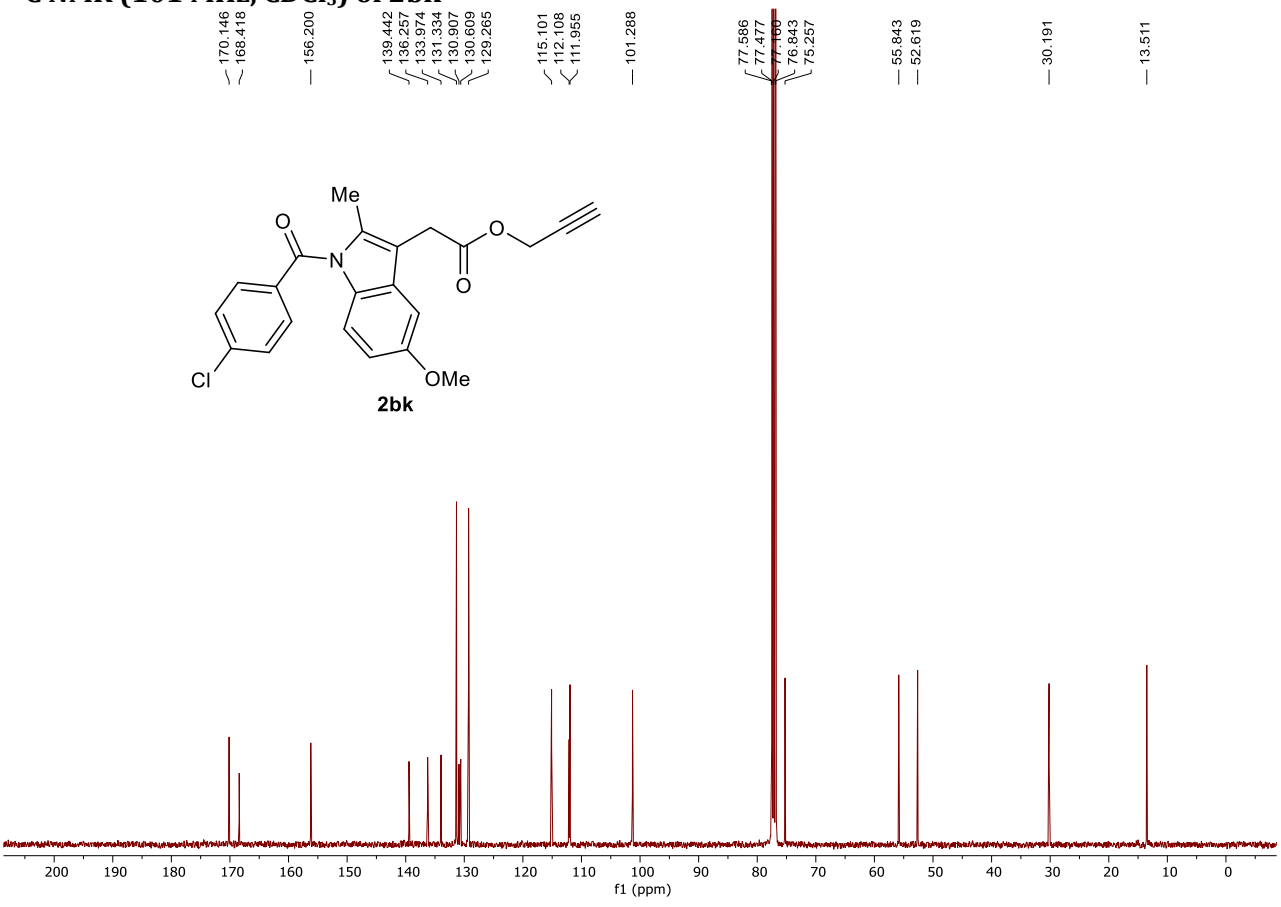
^{13}C NMR (101 MHz, $CDCl_3$) of 2bj



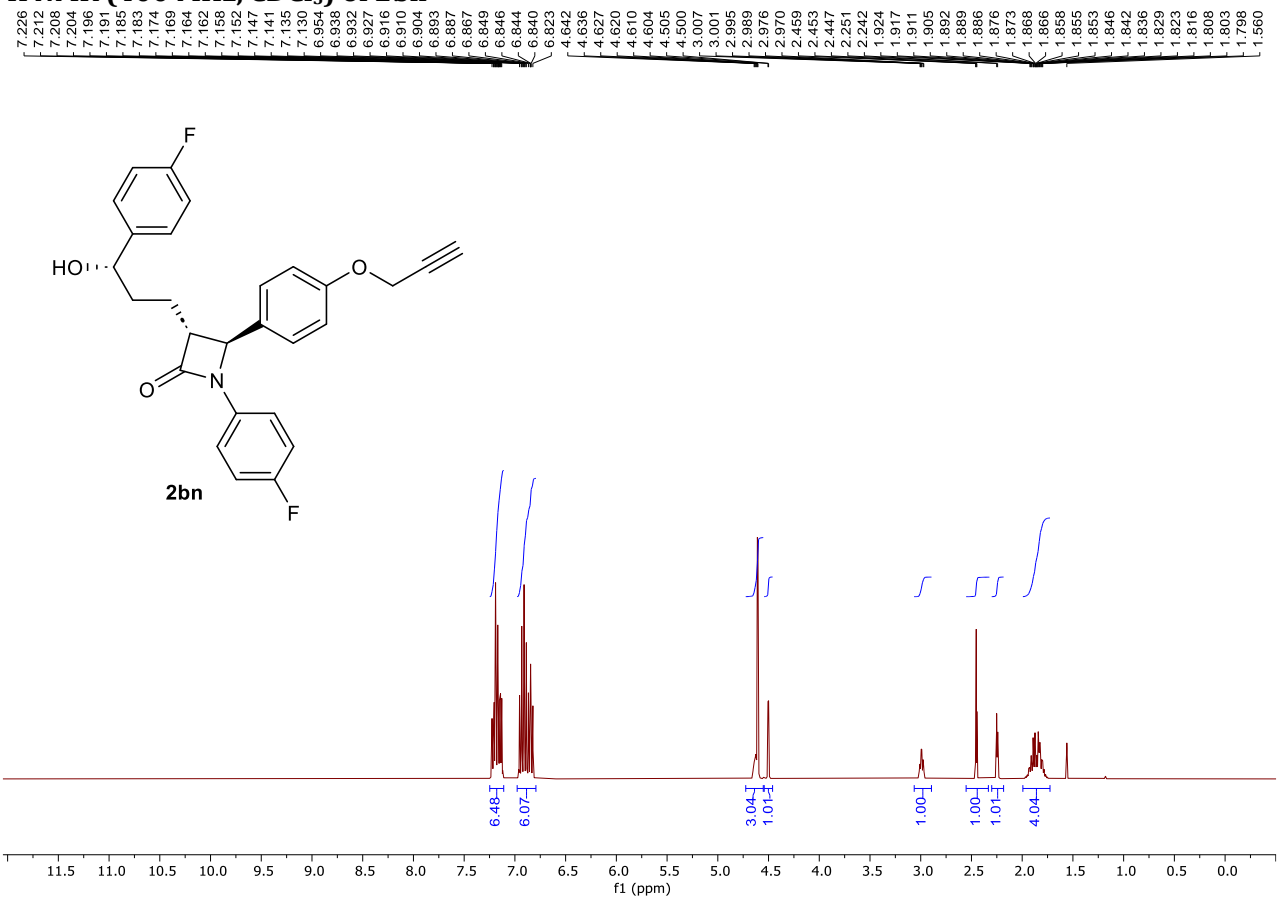
^{1}H NMR (400 MHz, $CDCl_3$) of 2bk



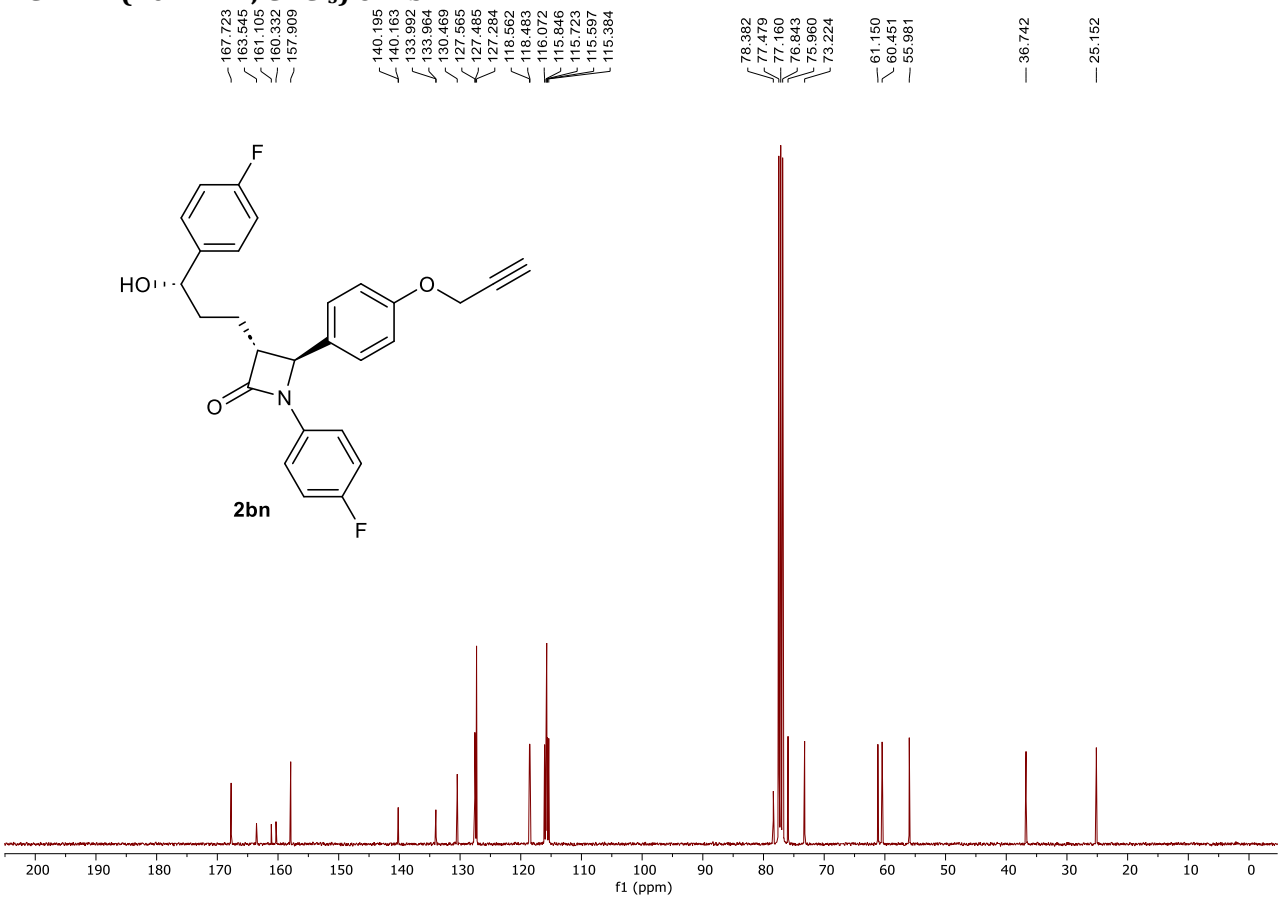
^{13}C NMR (101 MHz, $CDCl_3$) of 2bk



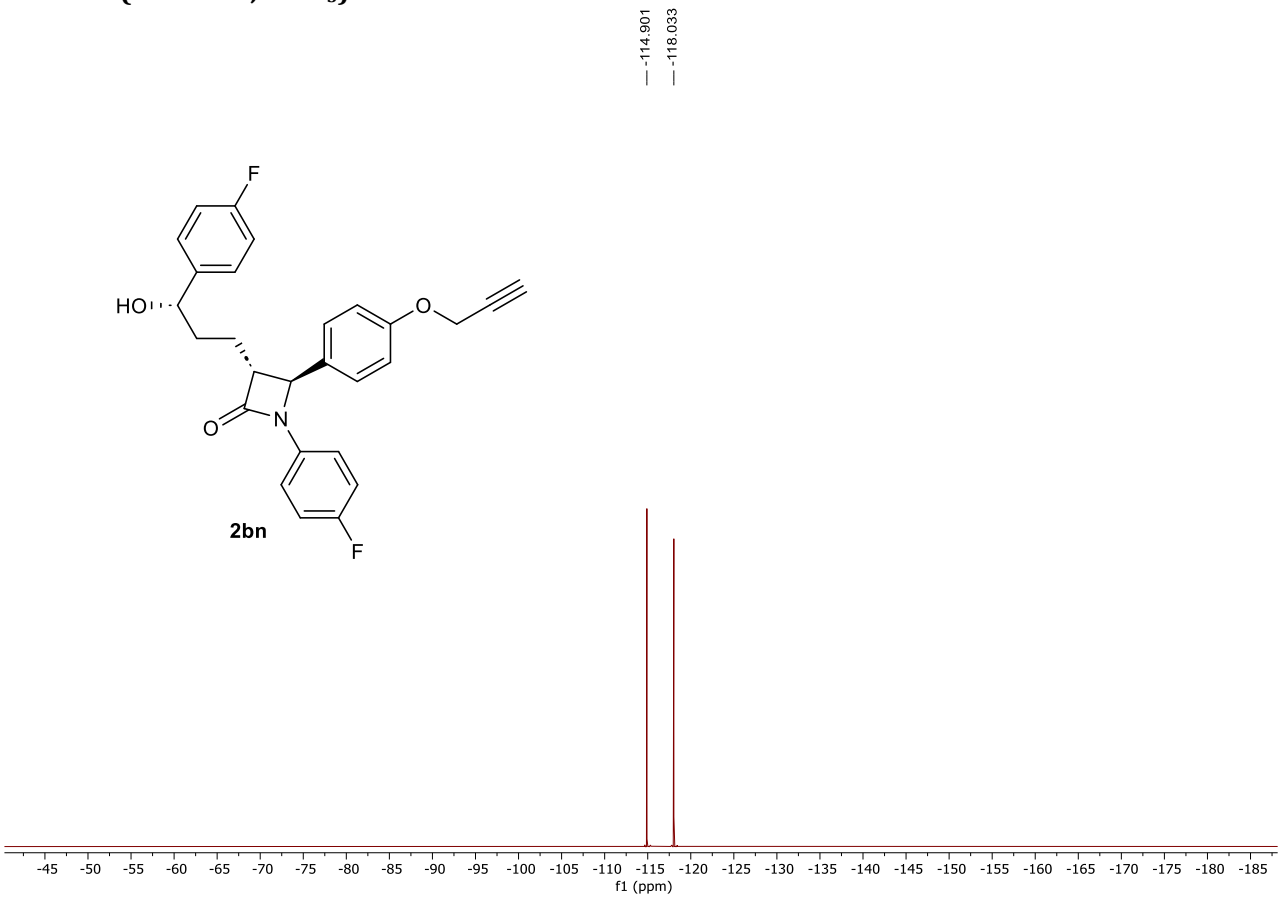
^{1}H NMR (400 MHz, $CDCl_3$) of 2bn



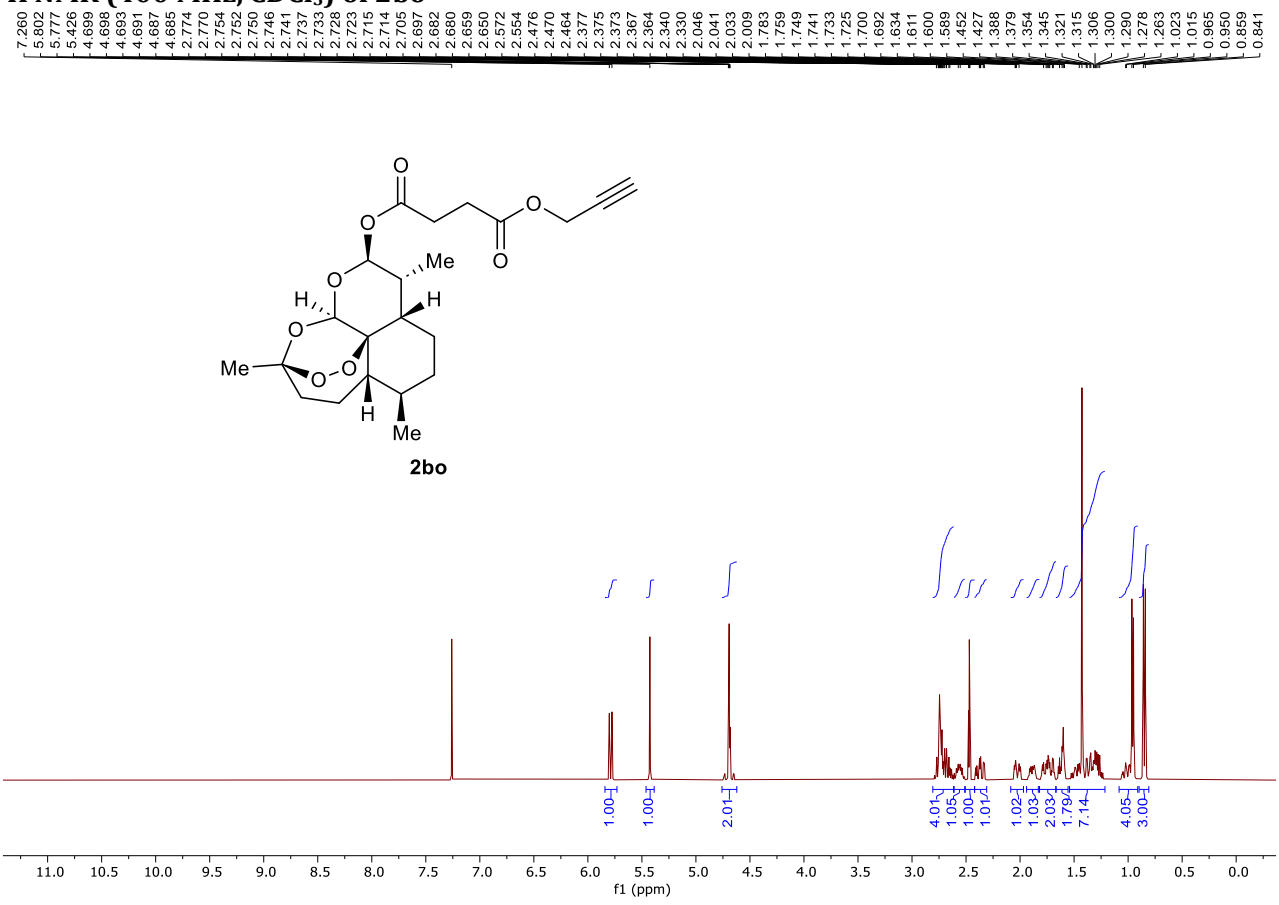
^{13}C NMR (101 MHz, $CDCl_3$) of 2bn



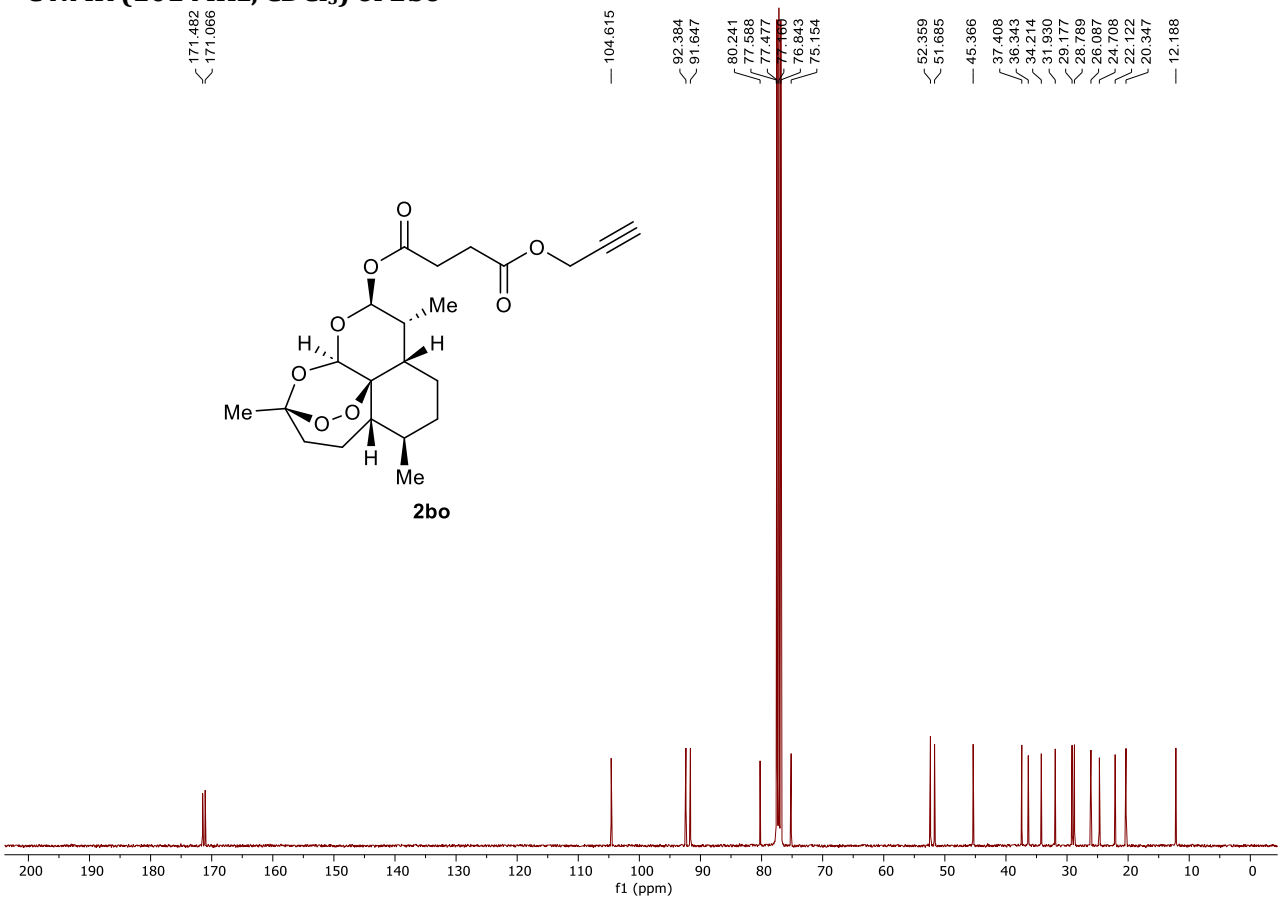
^{19}F NMR (377 MHz, $CDCl_3$) of 2bn



^{1}H NMR (400 MHz, $CDCl_3$) of 2bo

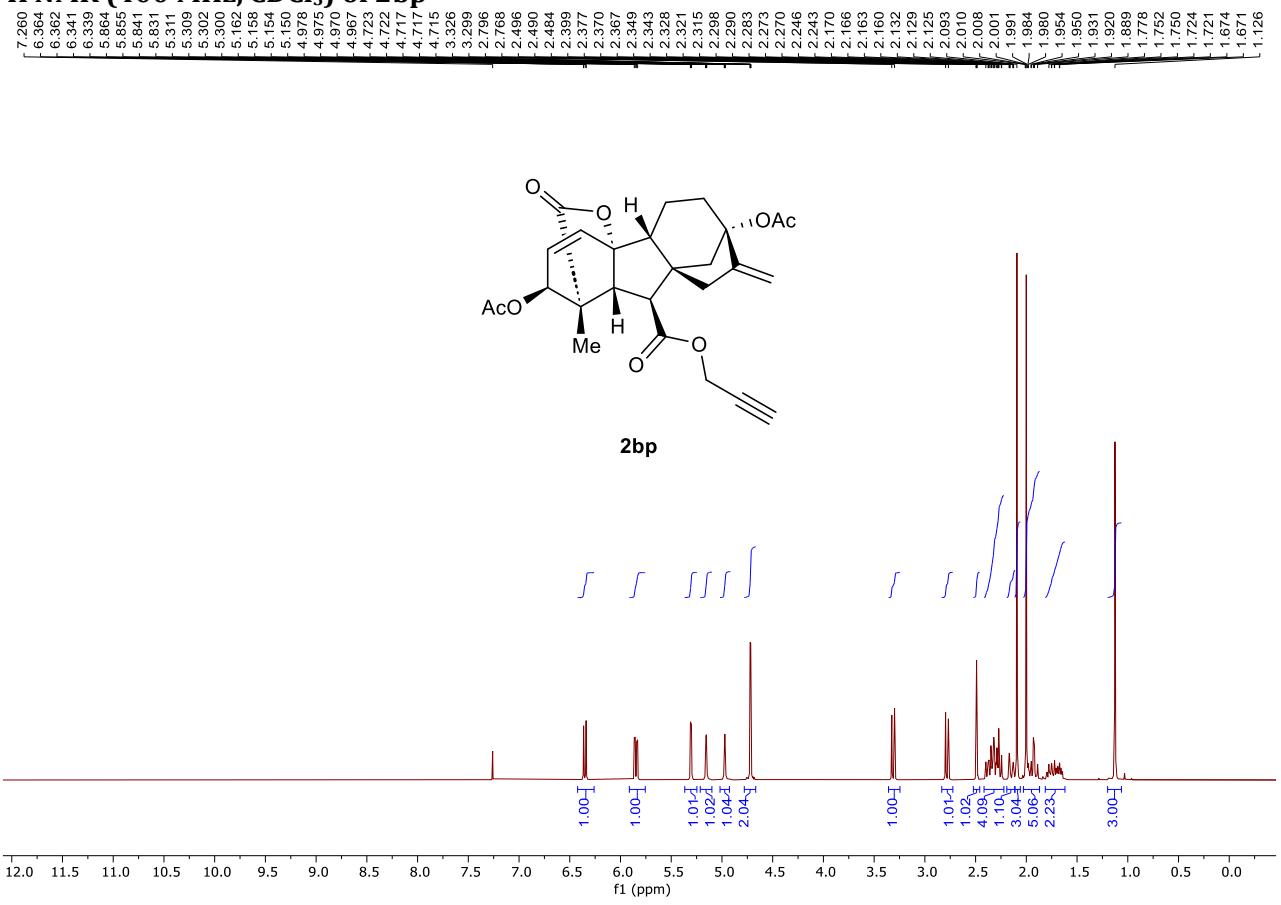


^{13}C NMR (101 MHz, $CDCl_3$) of 2bo



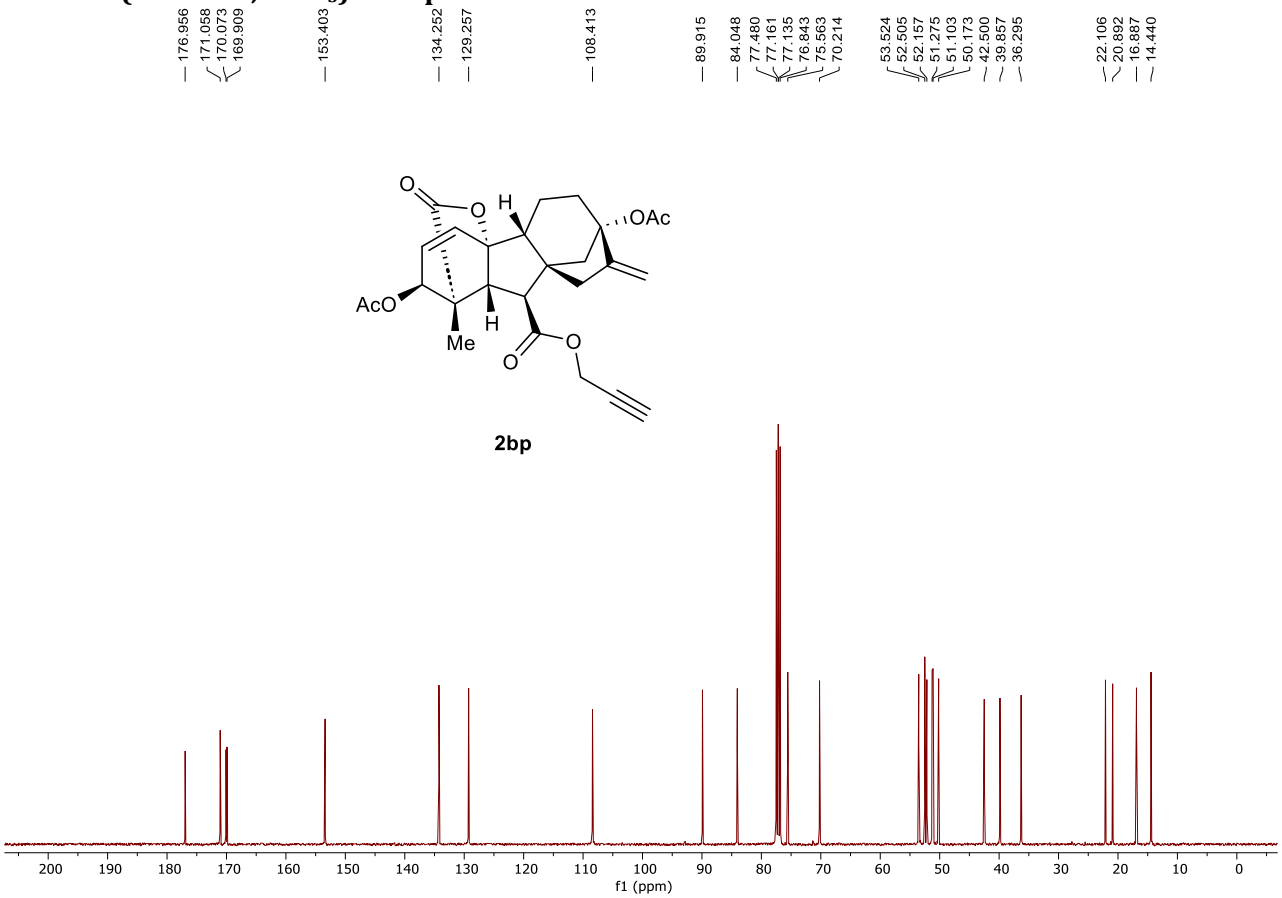
2bo

^{1}H NMR (400 MHz, $CDCl_3$) of 2bp

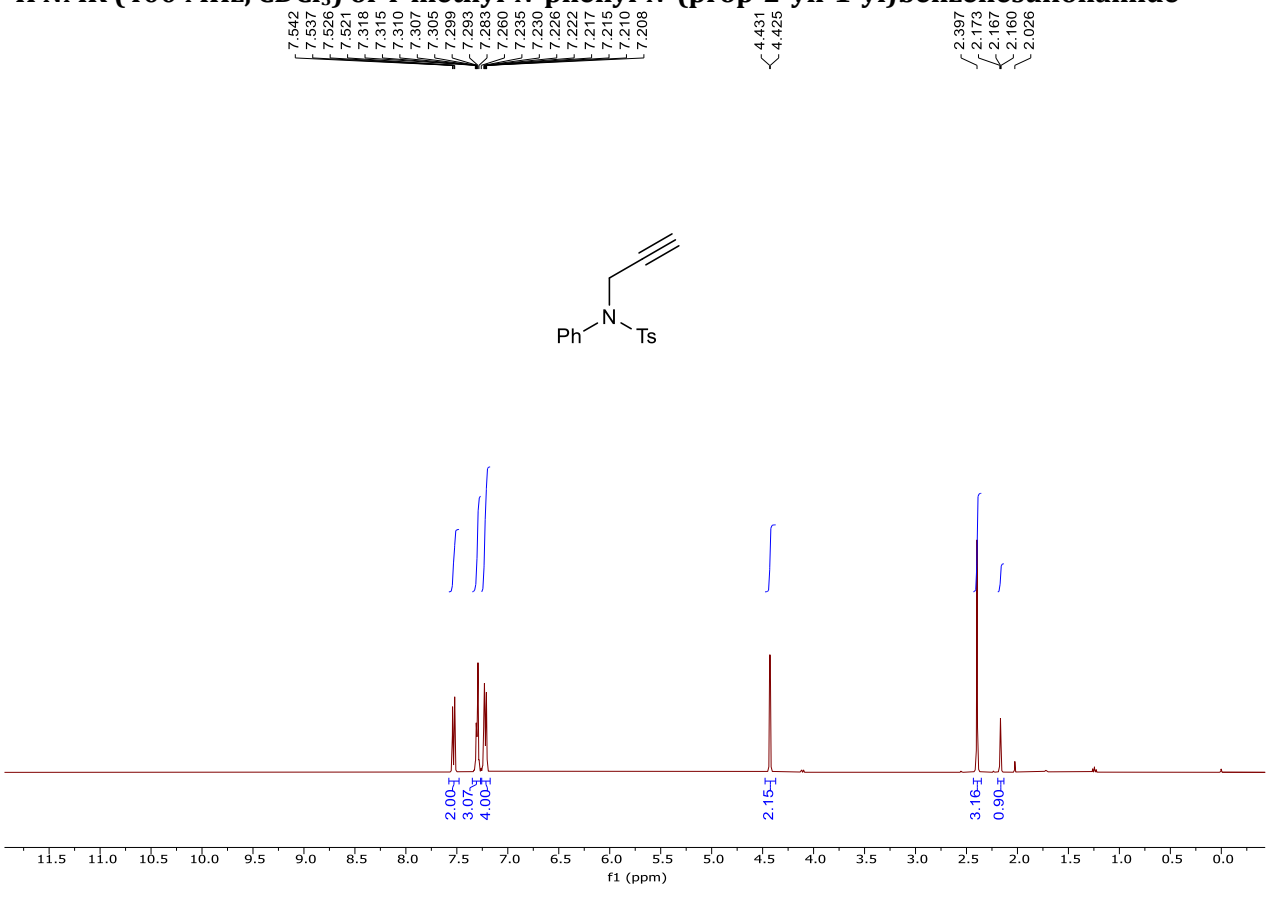


2bp

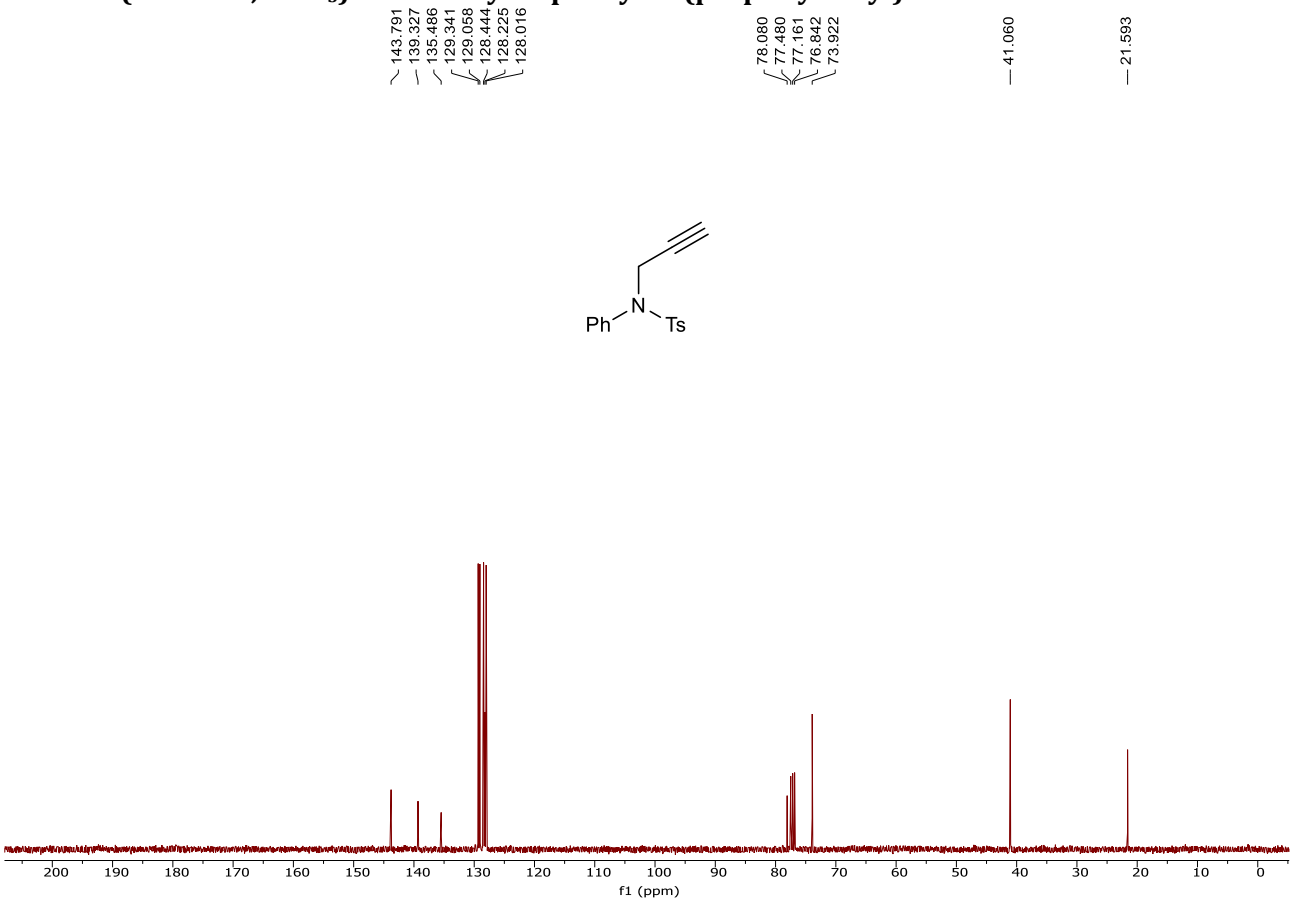
^{13}C NMR (101 MHz, $CDCl_3$) of 2bp



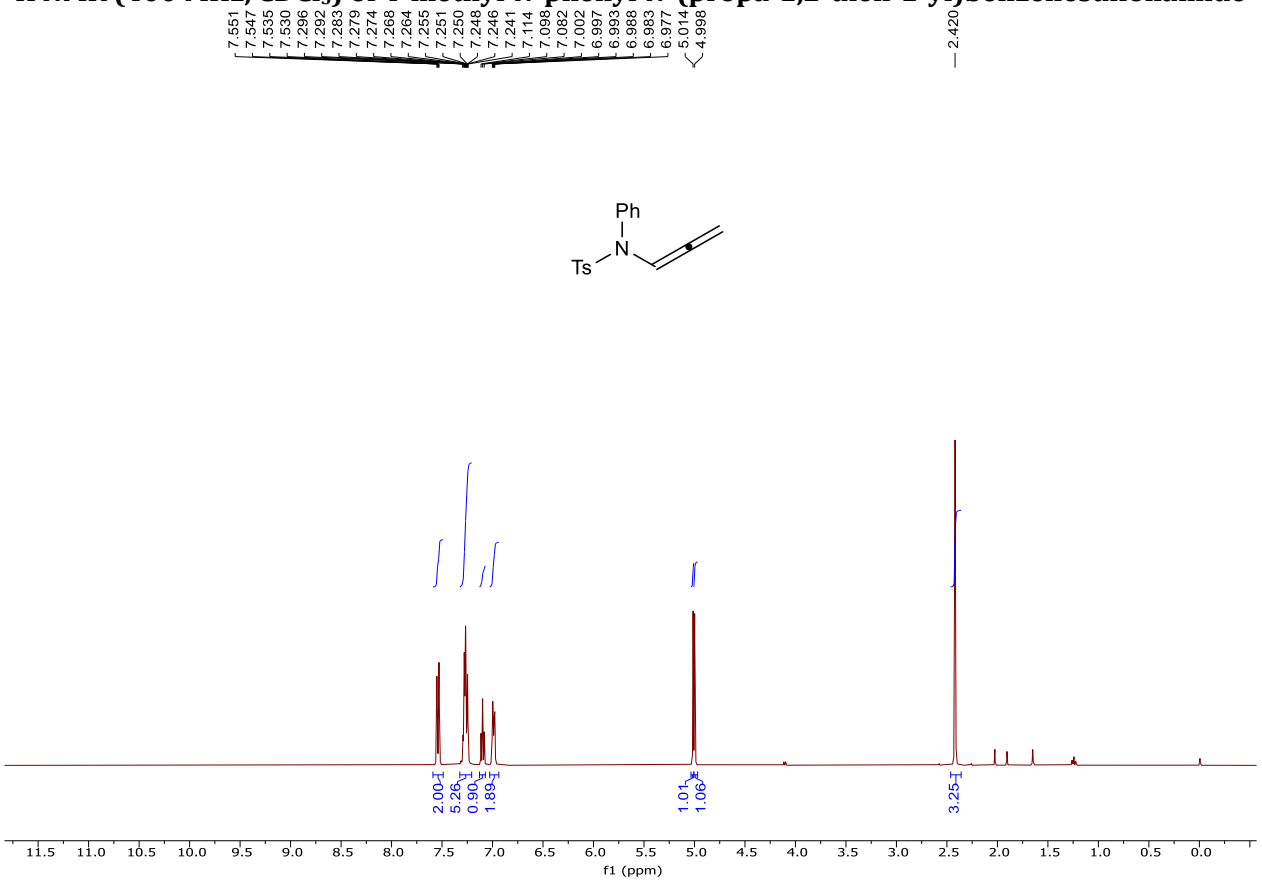
^{1}H NMR (400 MHz, $CDCl_3$) of 4-methyl-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide



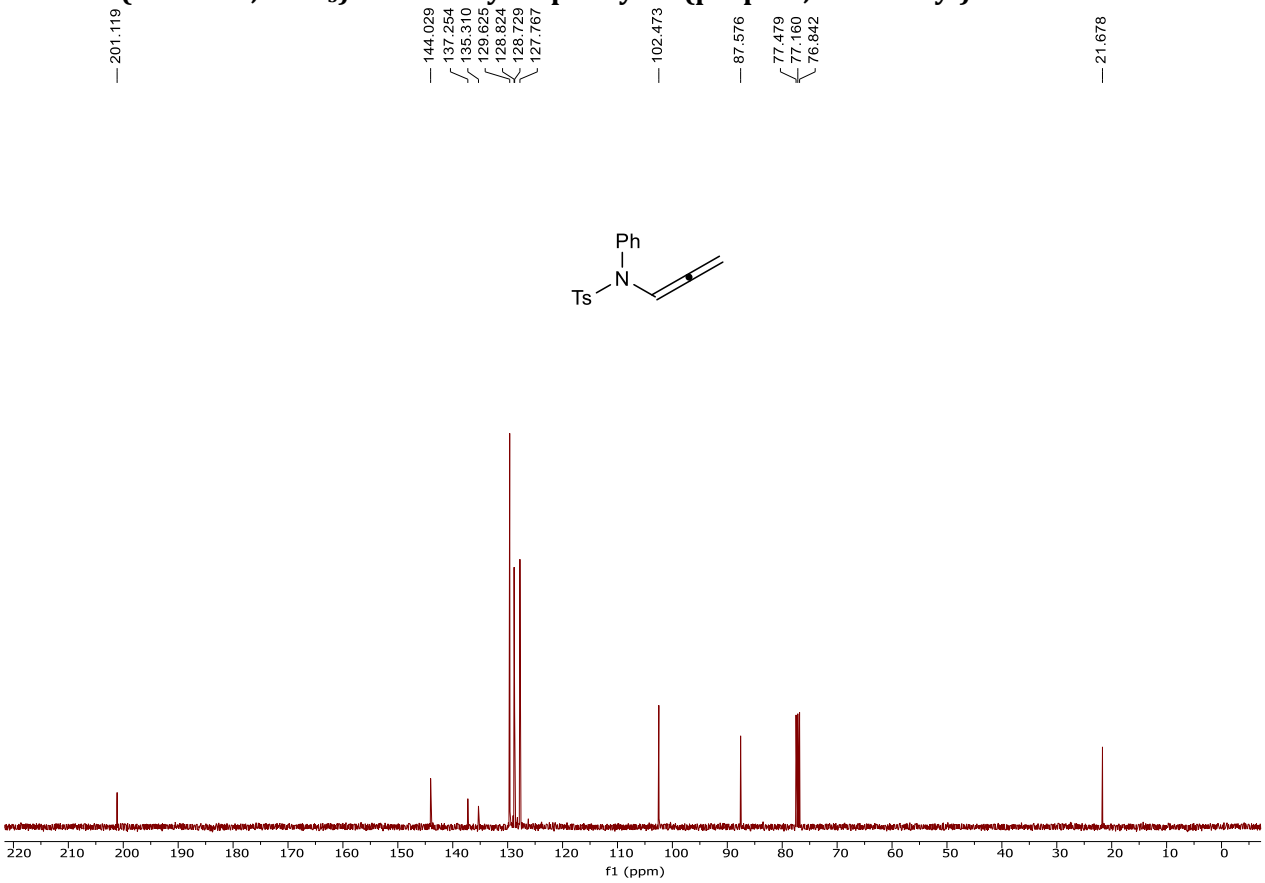
^{13}C NMR (101 MHz, $CDCl_3$) of 4-methyl-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide



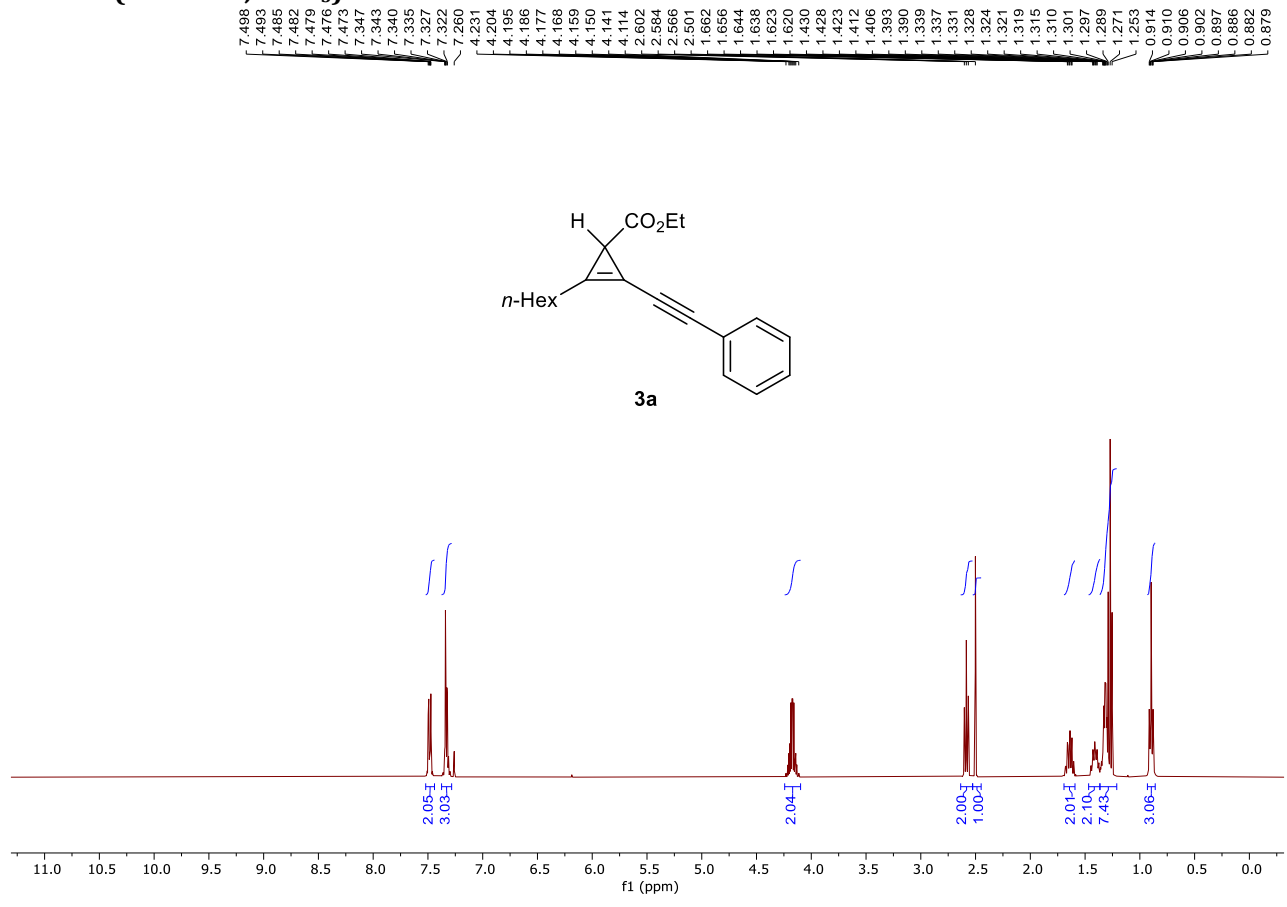
^{1}H NMR (400 MHz, $CDCl_3$) of 4-methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide



^{13}C NMR (101 MHz, $CDCl_3$) of 4-methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide

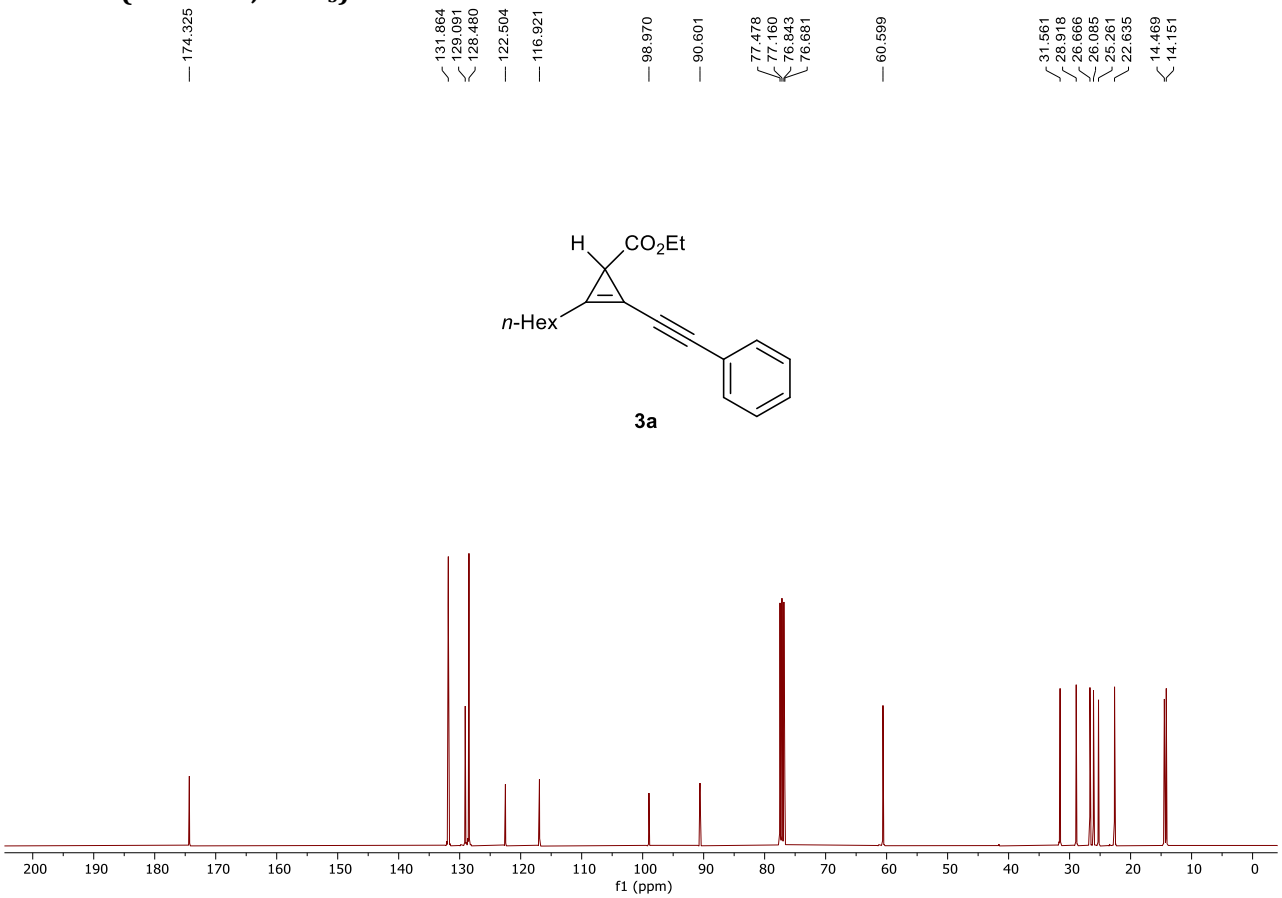


^{1}H NMR (400 MHz, $CDCl_3$) of 3a

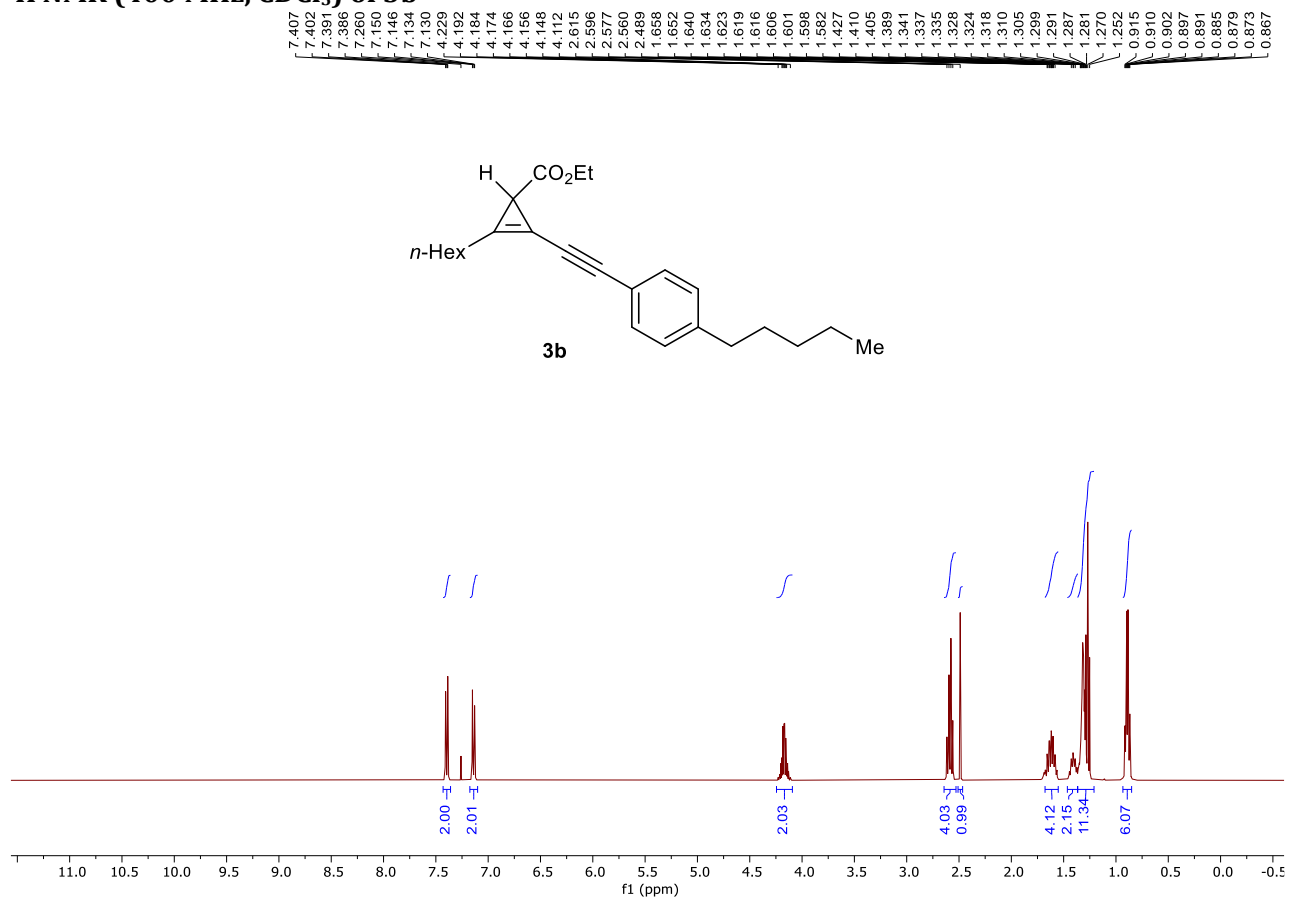


3a

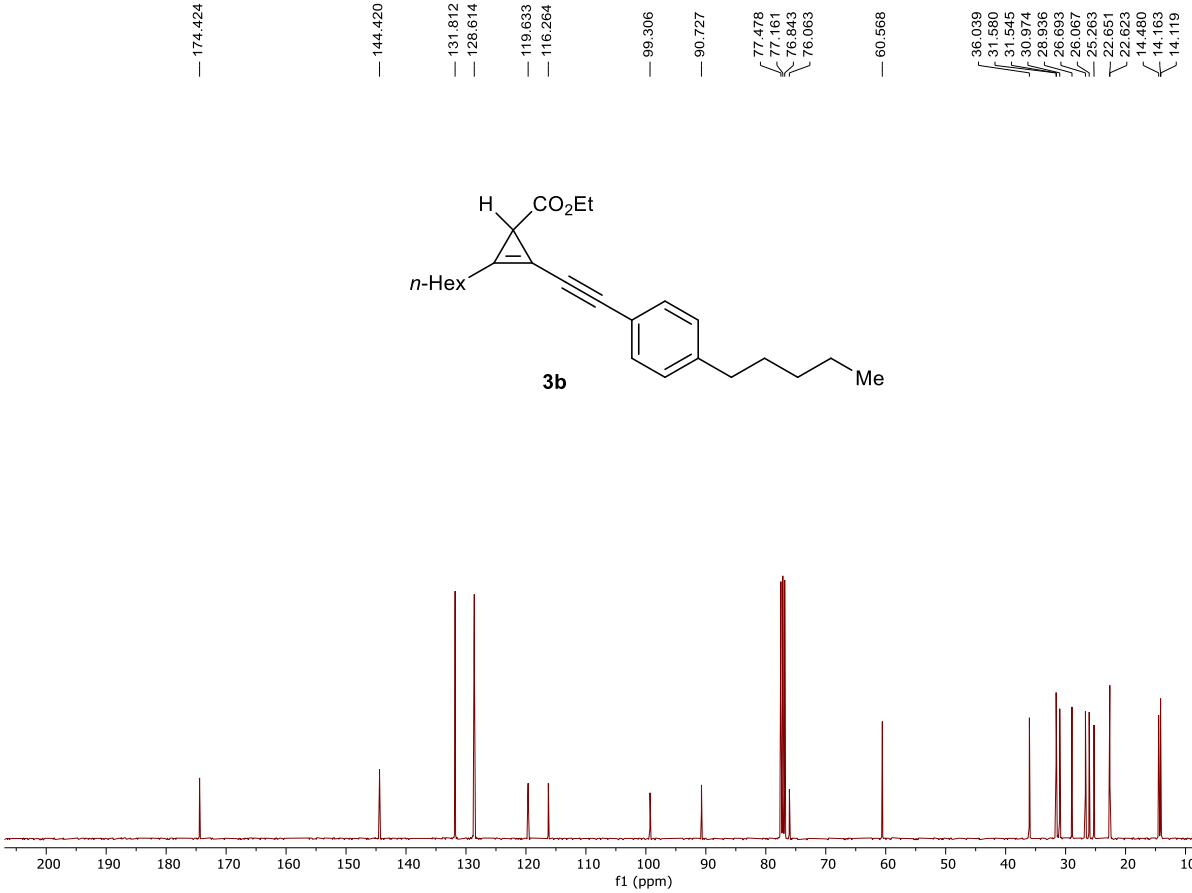
^{13}C NMR (101 MHz, $CDCl_3$) of 3a



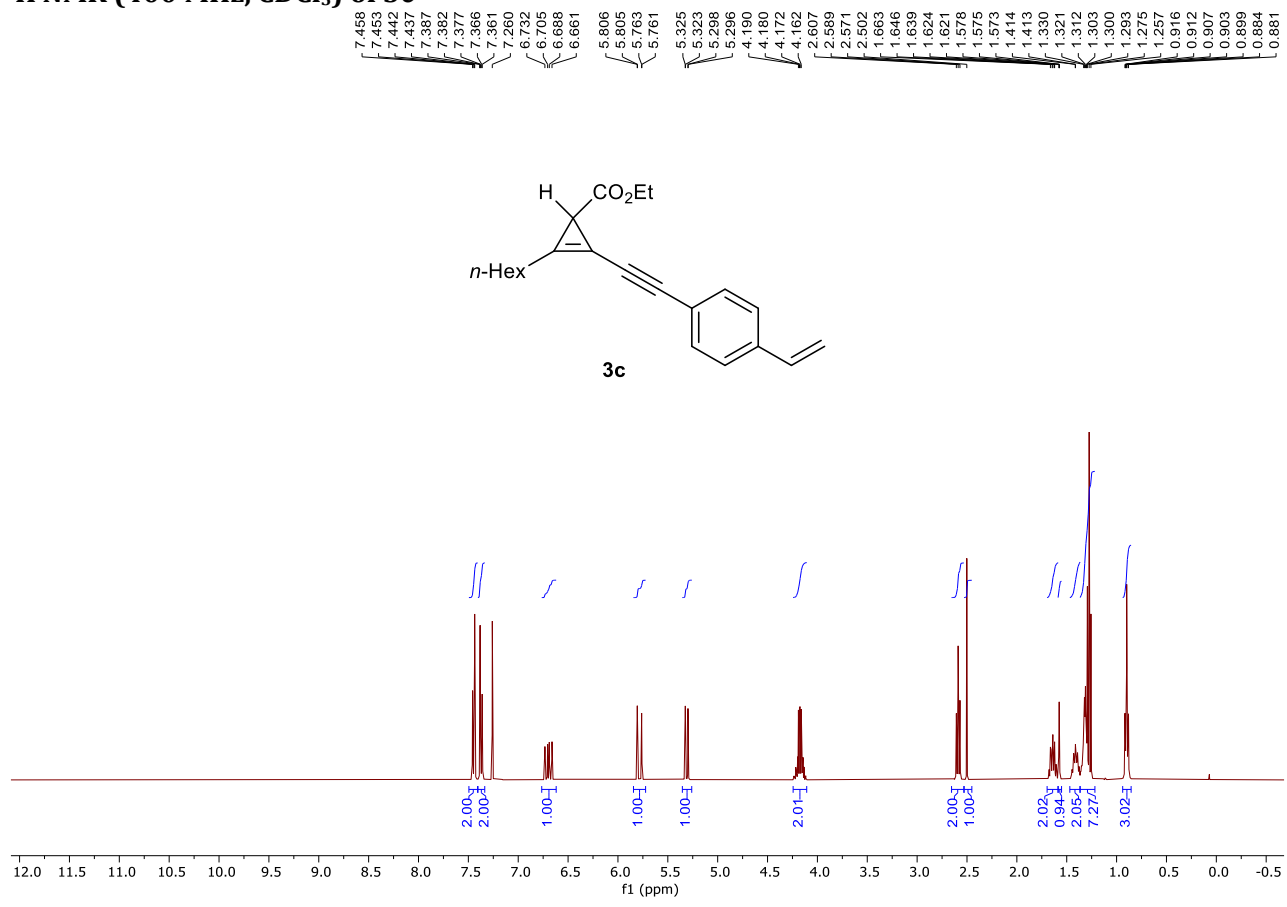
^{1}H NMR (400 MHz, $CDCl_3$) of 3b



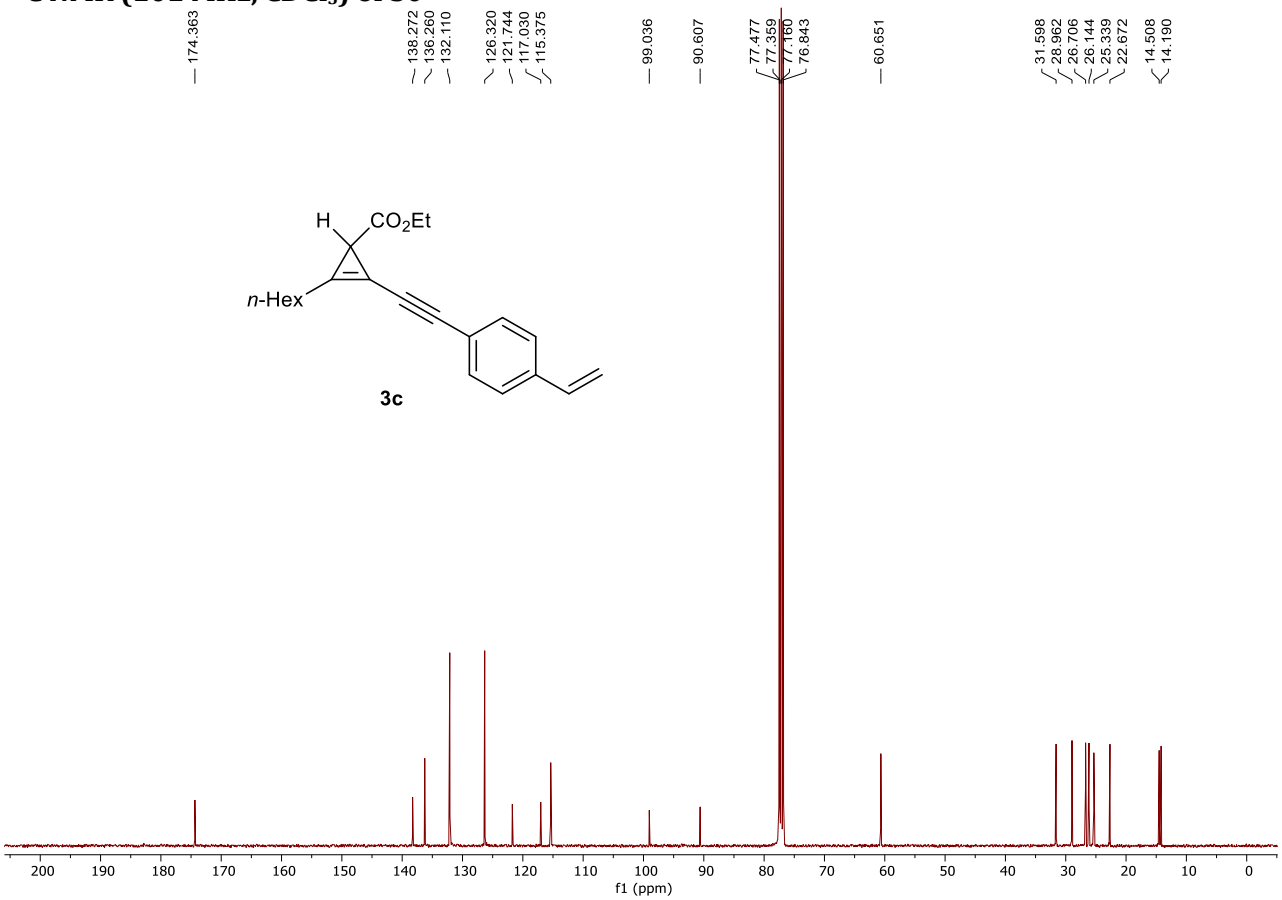
^{13}C NMR (101 MHz, $CDCl_3$) of 3b



^{1}H NMR (400 MHz, $CDCl_3$) of 3c

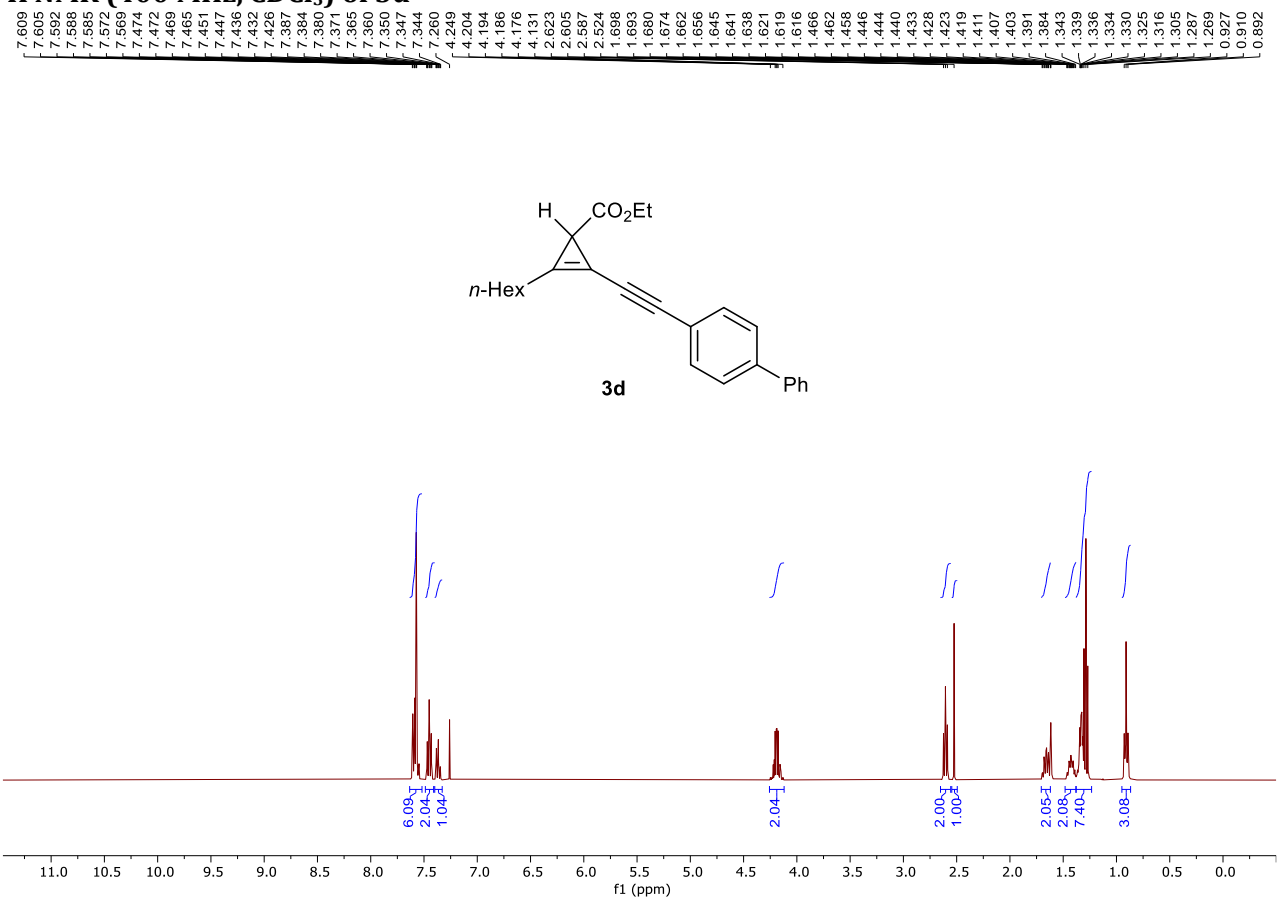


^{13}C NMR (101 MHz, $CDCl_3$) of 3c



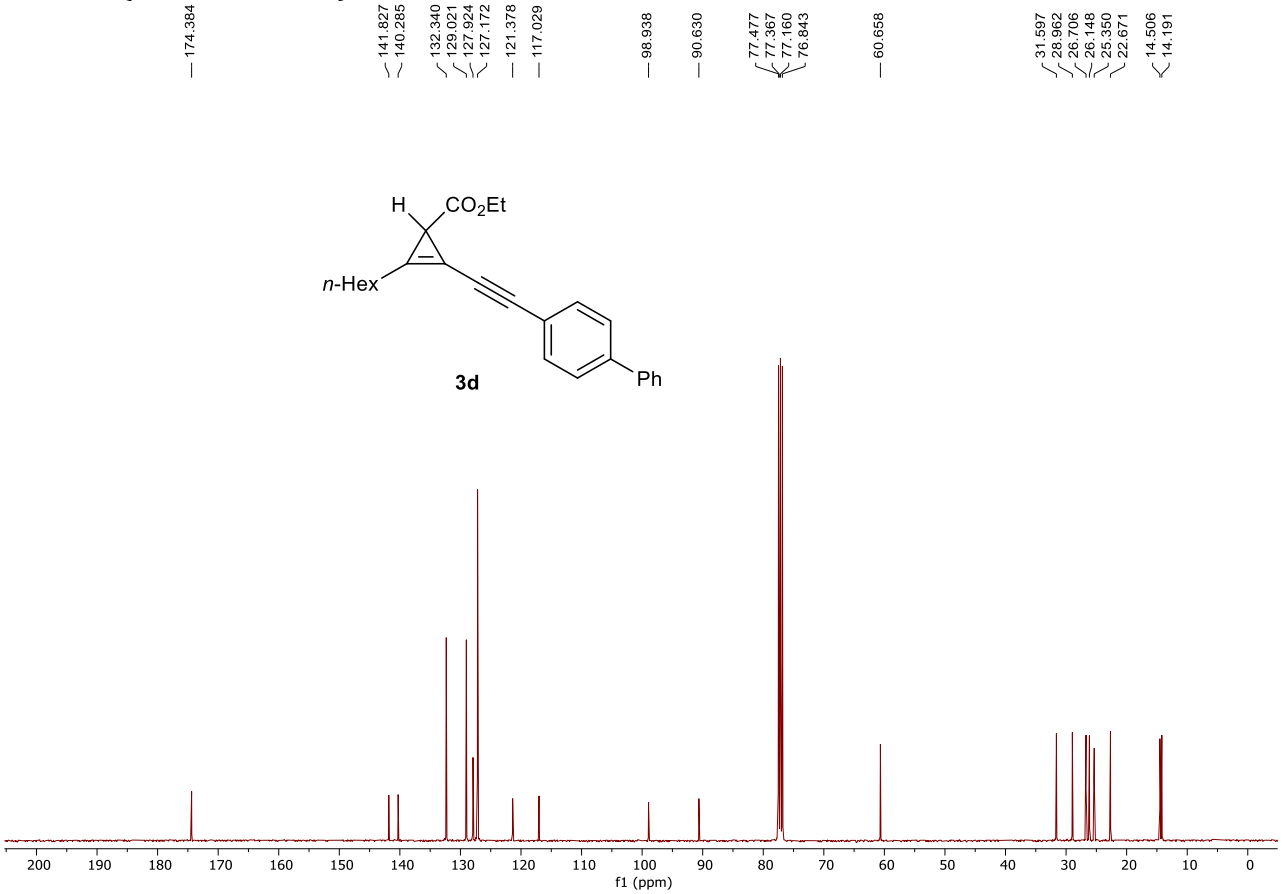
3c

^{1}H NMR (400 MHz, $CDCl_3$) of 3d

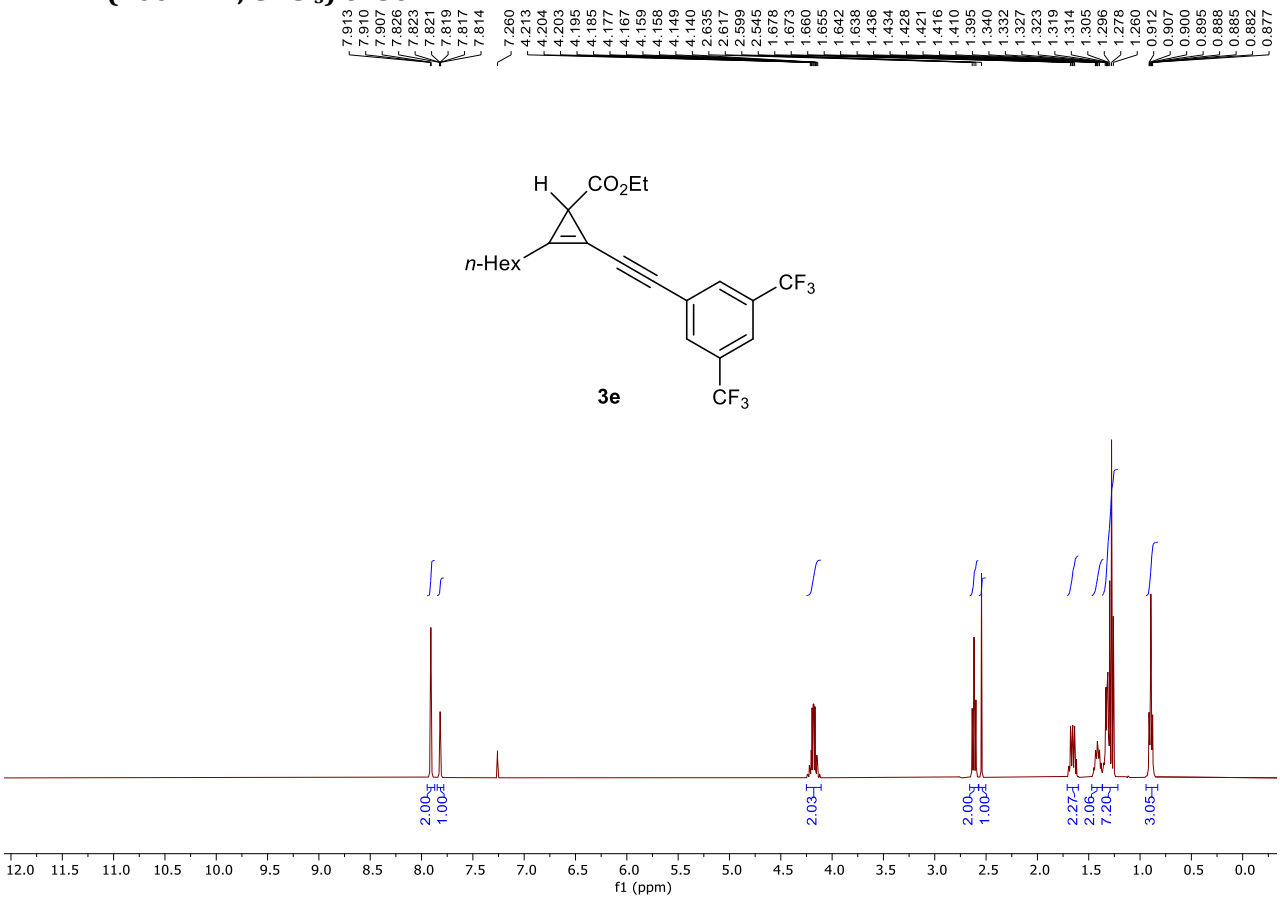


3d

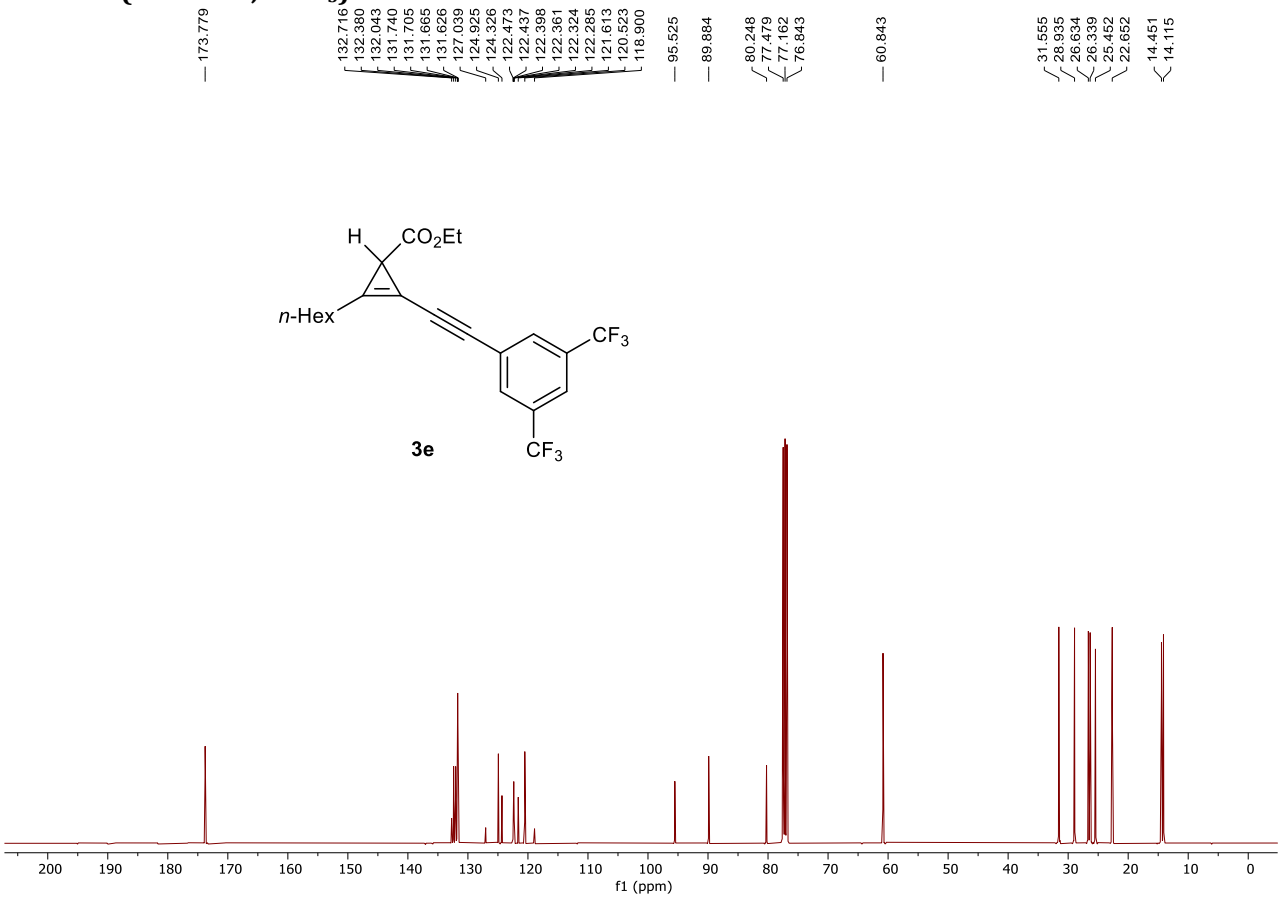
^{13}C NMR (101 MHz, $CDCl_3$) of 3d



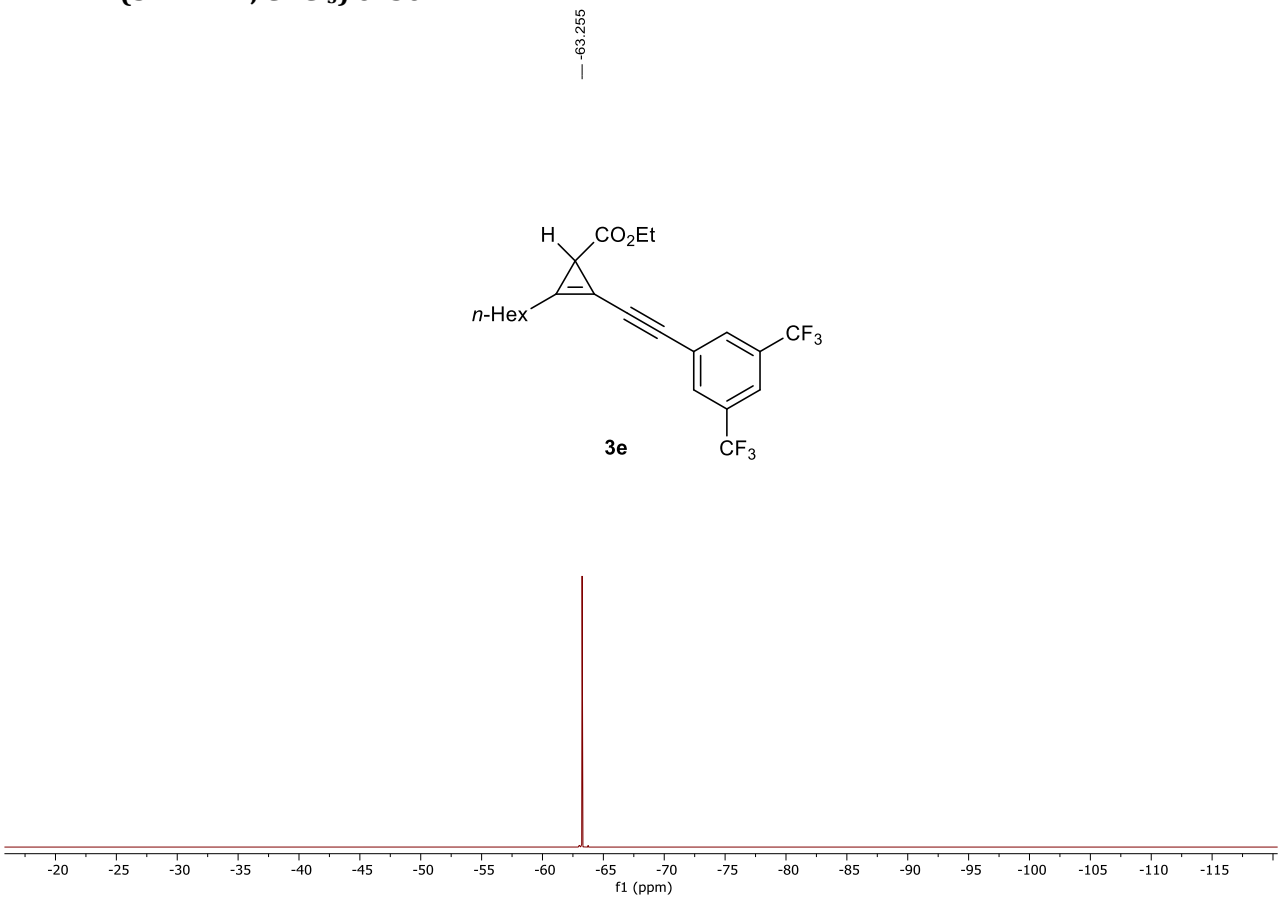
^{1}H NMR (400 MHz, $CDCl_3$) of 3e



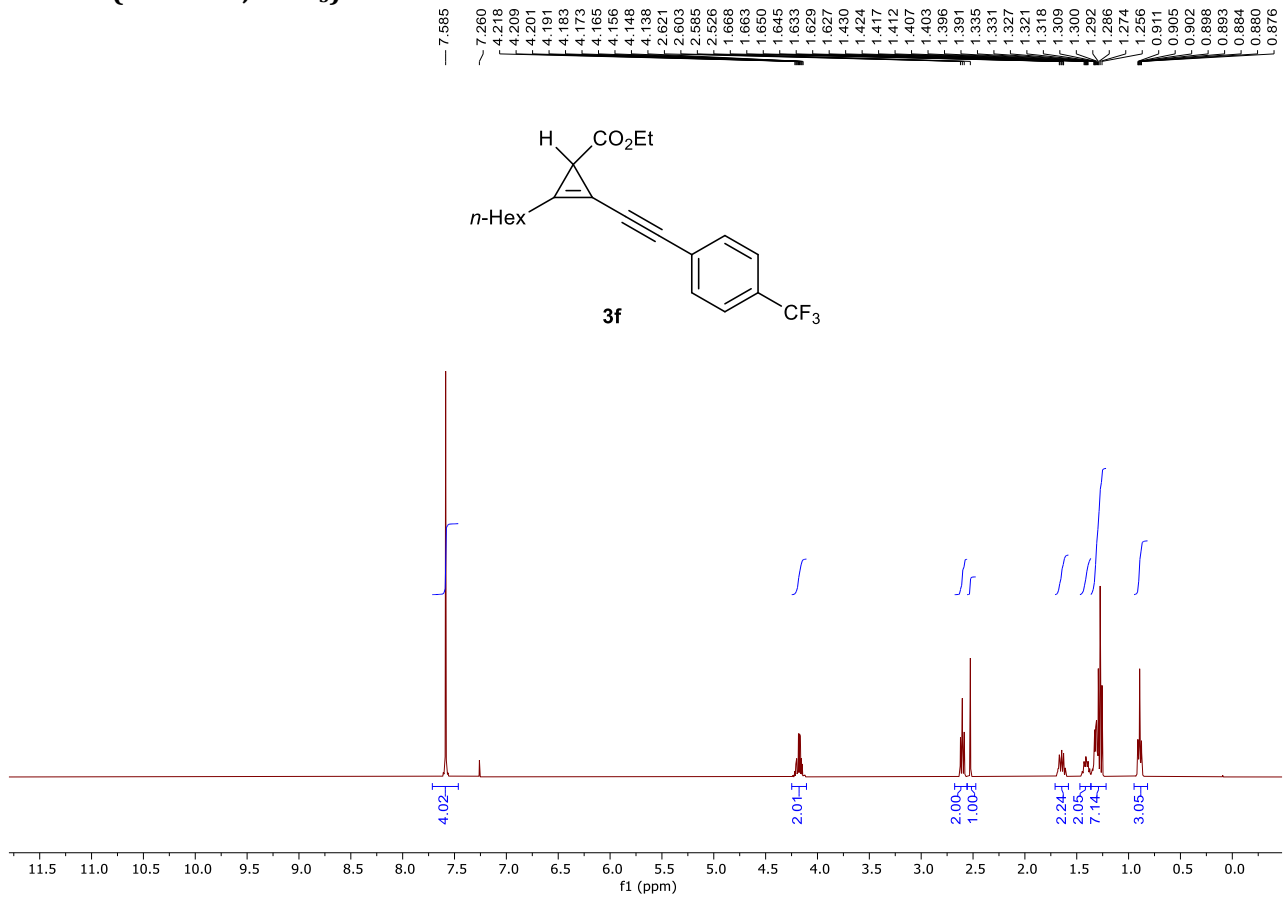
^{13}C NMR (101 MHz, $CDCl_3$) of 3e



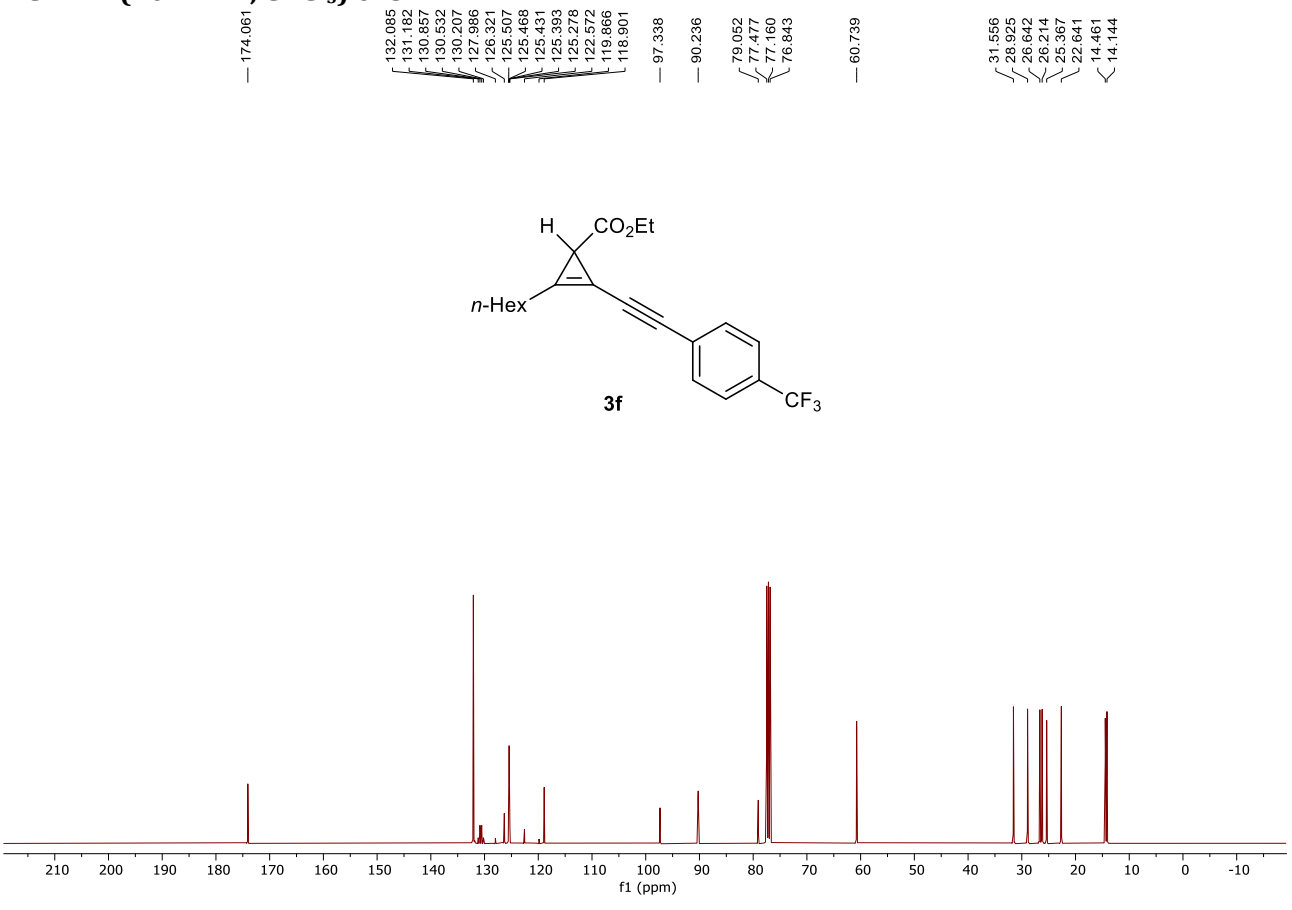
^{19}F NMR (377 MHz, $CDCl_3$) of 3e



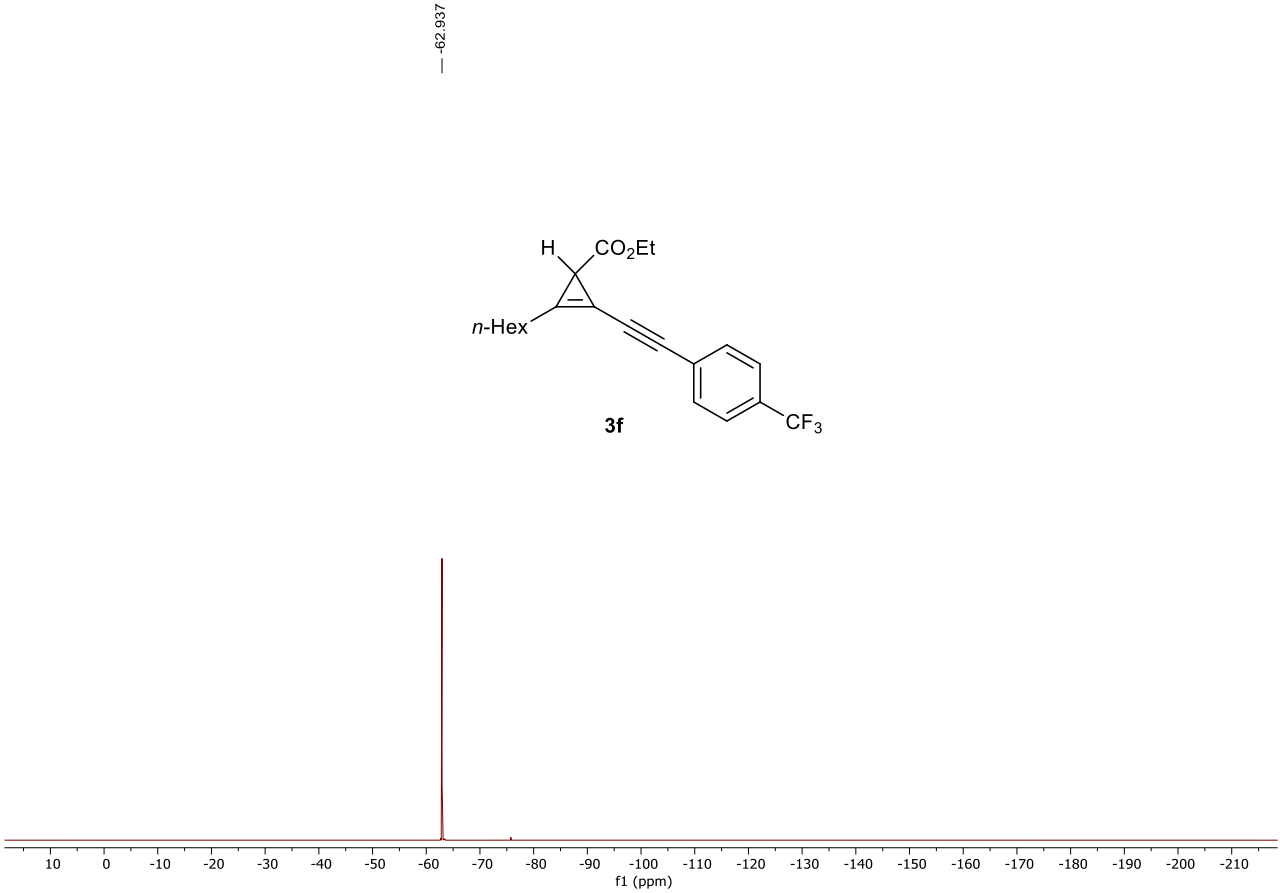
^{1}H NMR (400 MHz, $CDCl_3$) of 3f



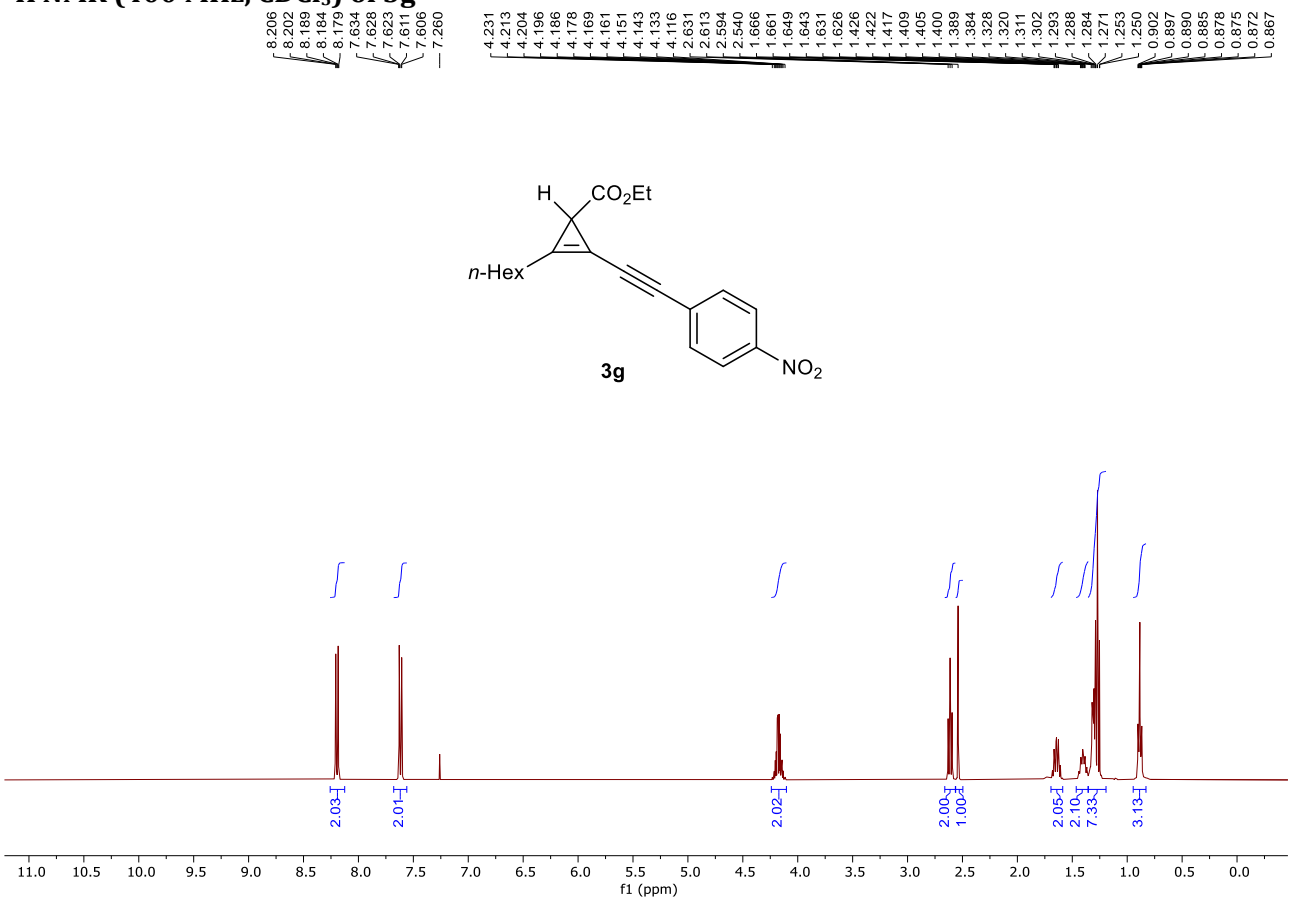
^{13}C NMR (101 MHz, $CDCl_3$) of 3f



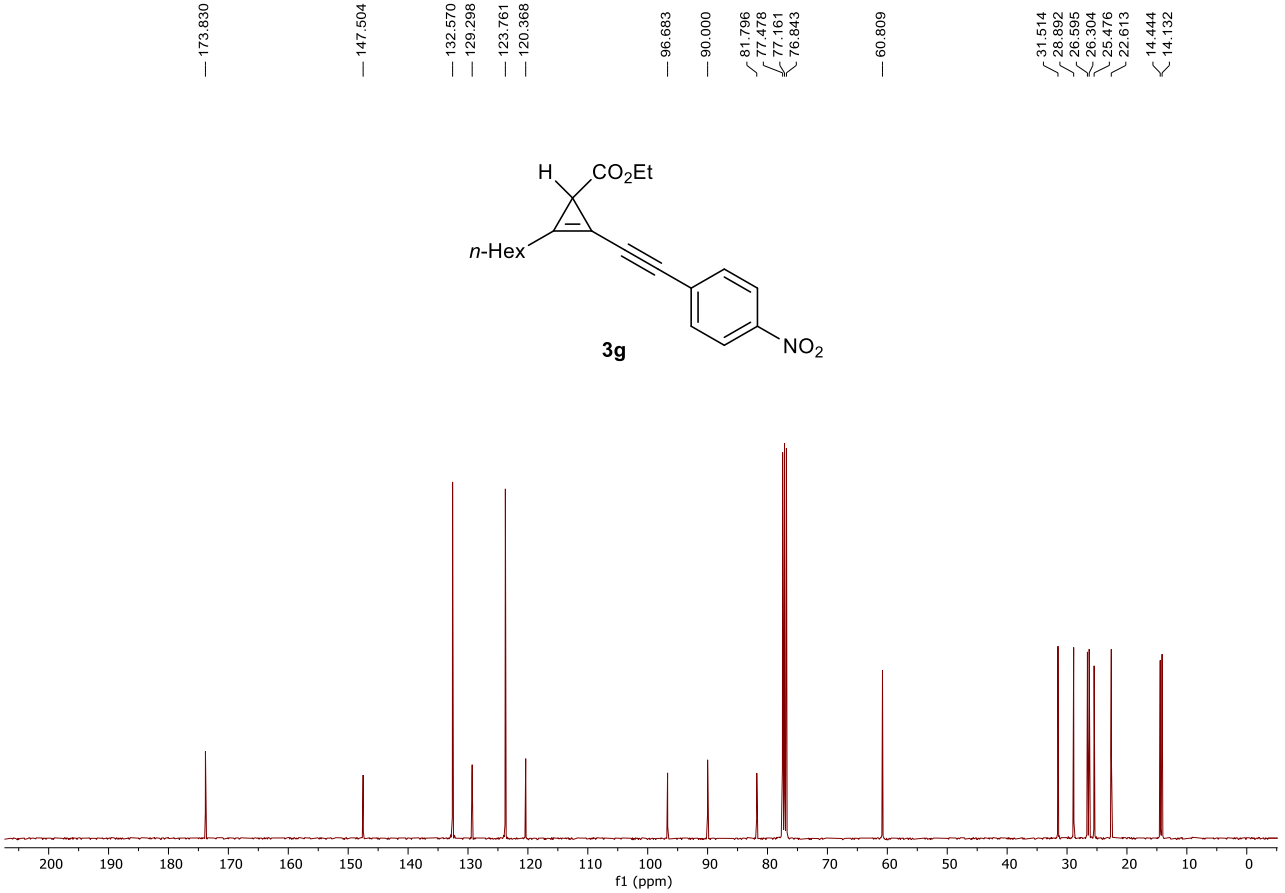
^{19}F NMR (377 MHz, $CDCl_3$) of 3f



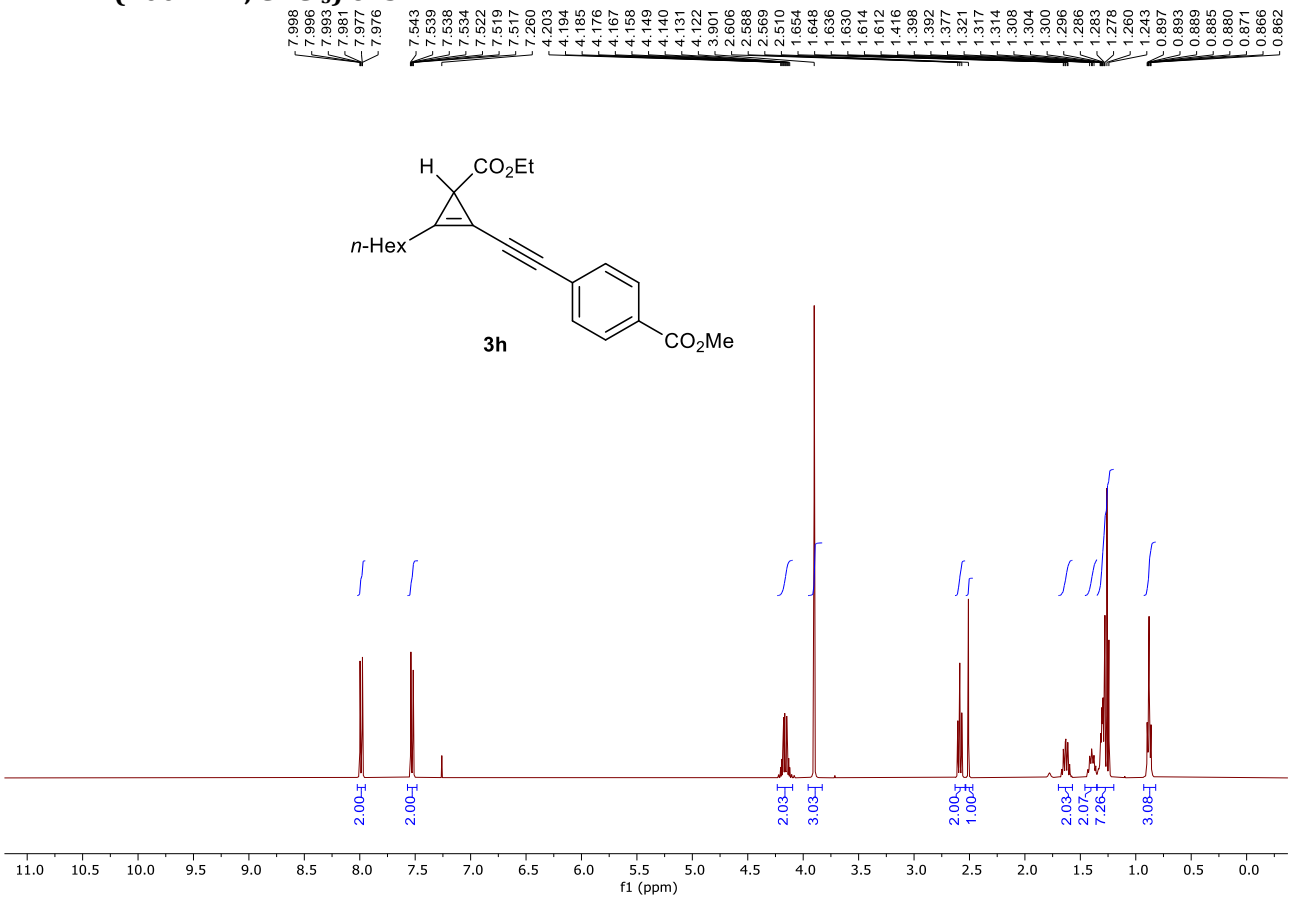
^{1}H NMR (400 MHz, $CDCl_3$) of 3g



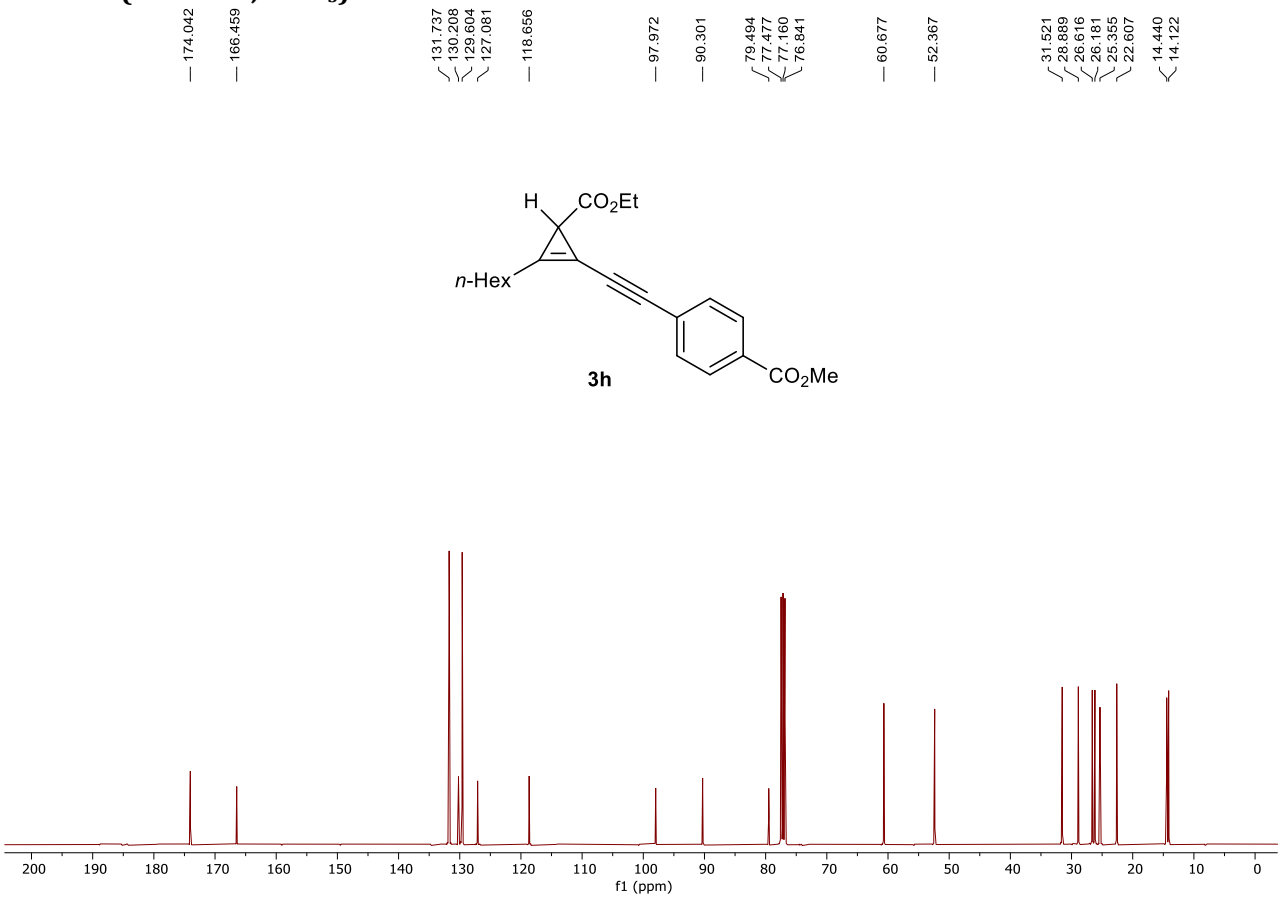
^{13}C NMR (101 MHz, $CDCl_3$) of 3g



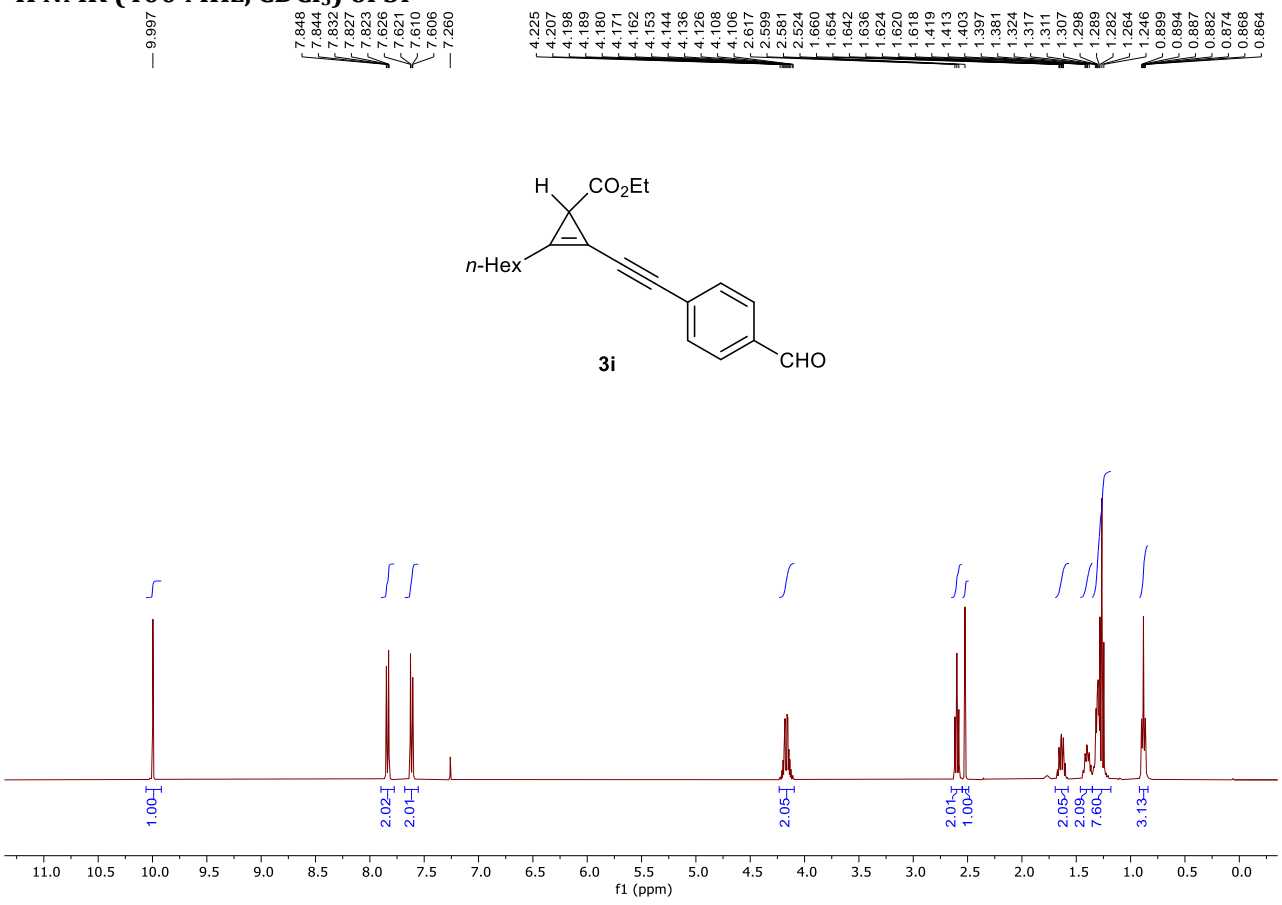
^{1}H NMR (400 MHz, $CDCl_3$) of 3h



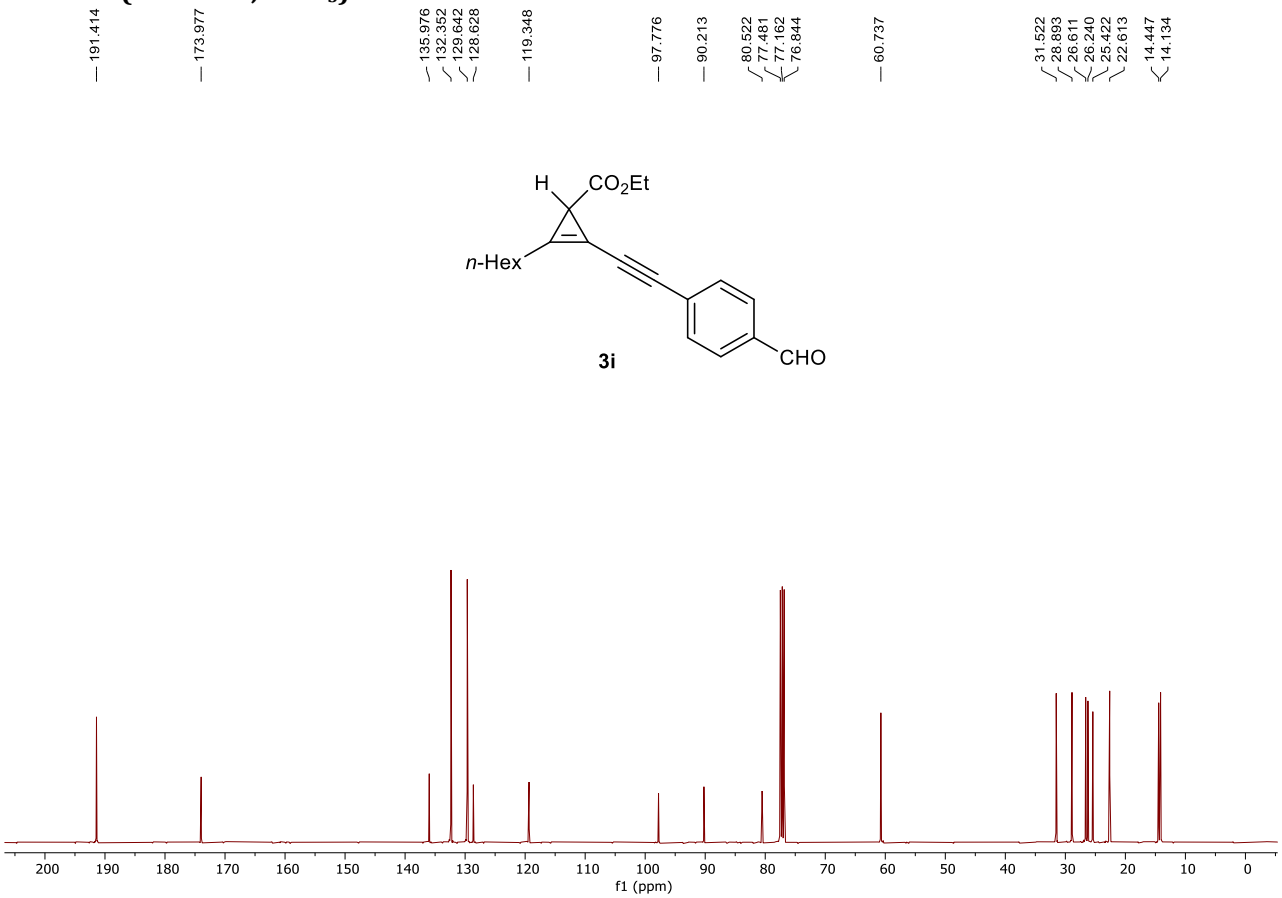
^{13}C NMR (101 MHz, $CDCl_3$) of 3h



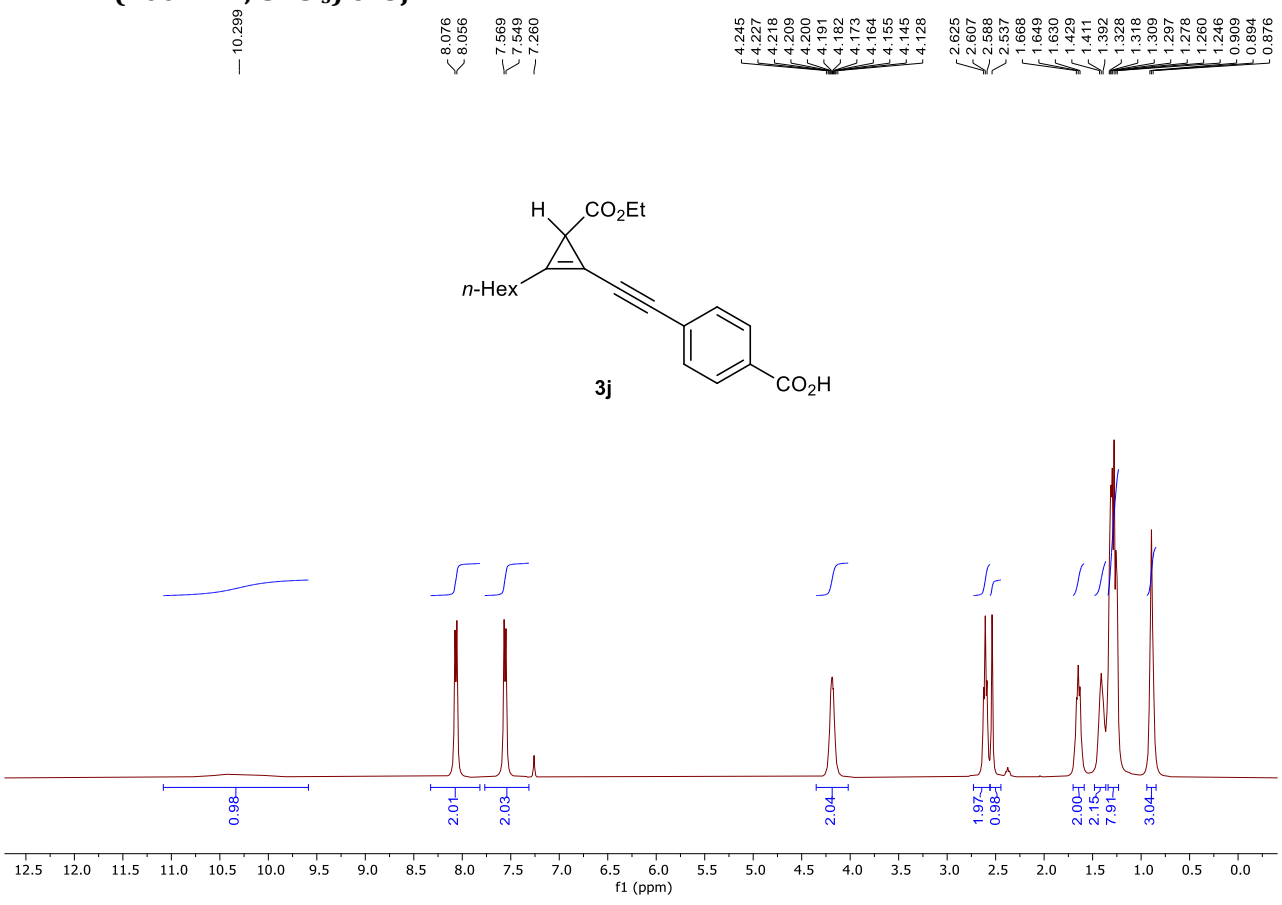
^{1}H NMR (400 MHz, $CDCl_3$) of 3i



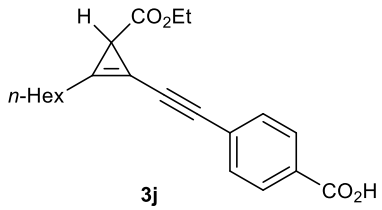
^{13}C NMR (101 MHz, $CDCl_3$) of 3i



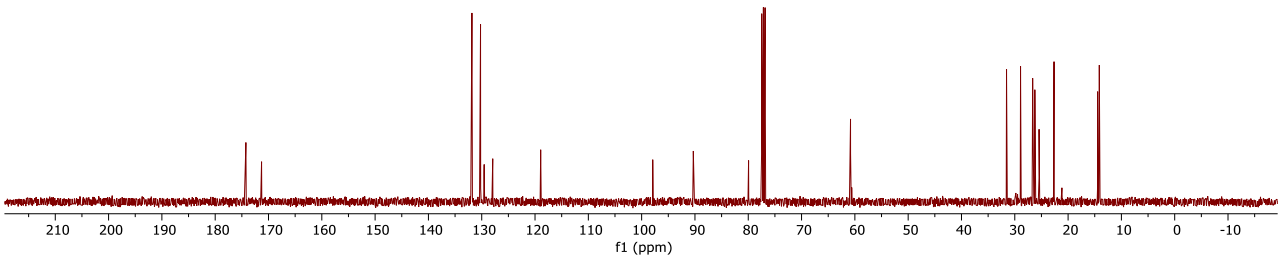
^{1}H NMR (400 MHz, $CDCl_3$) of 3j



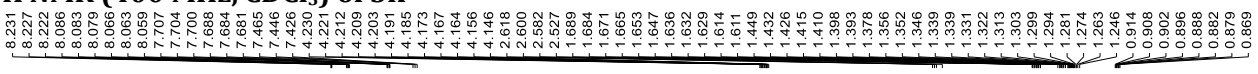
^{13}C NMR (101 MHz, $CDCl_3$) of 3j

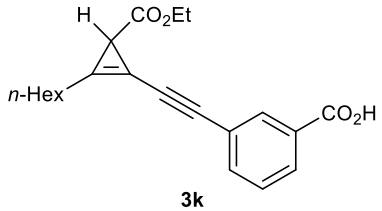


3j

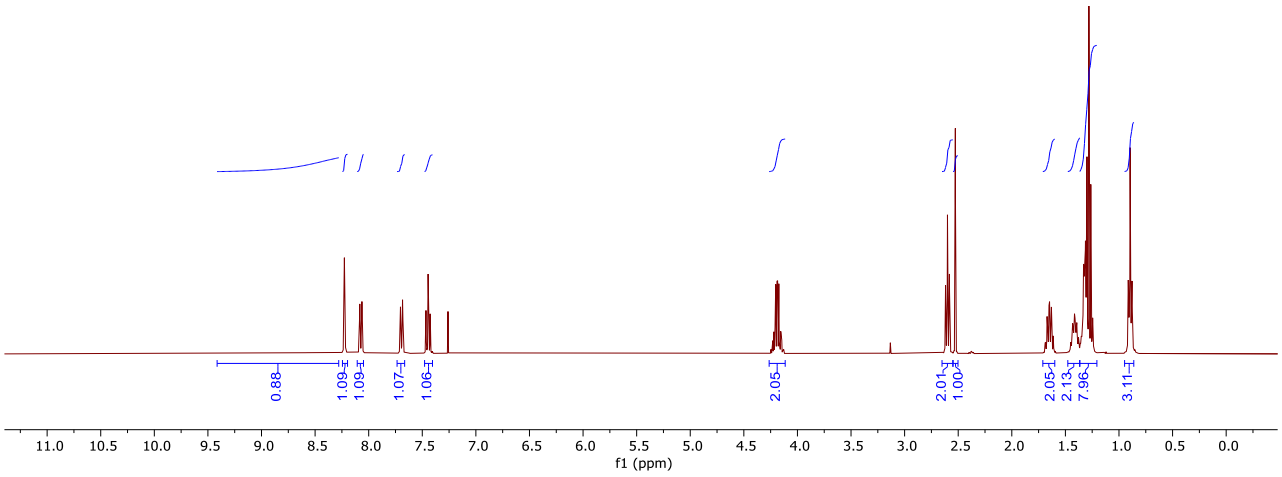


^{1}H NMR (400 MHz, $CDCl_3$) of 3k

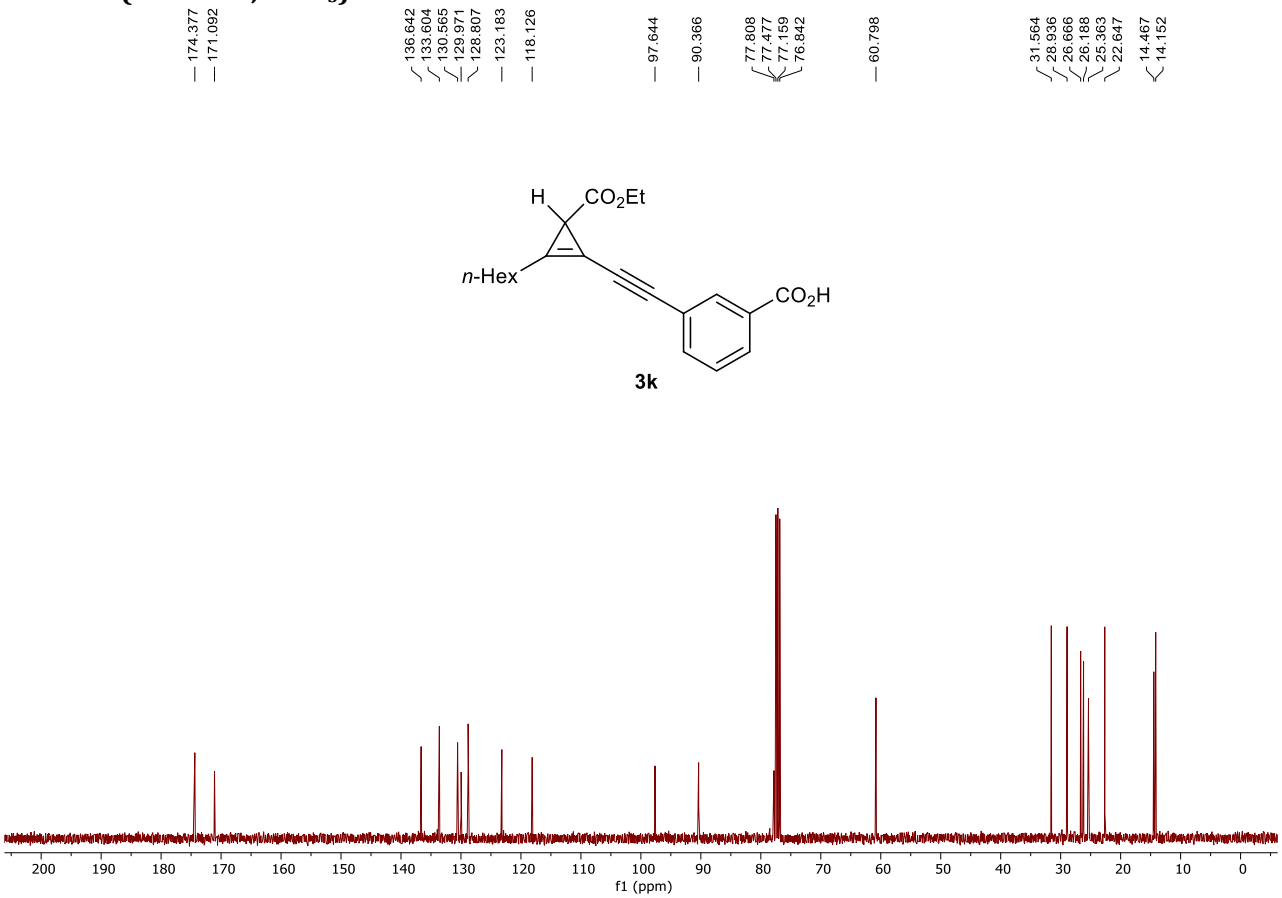




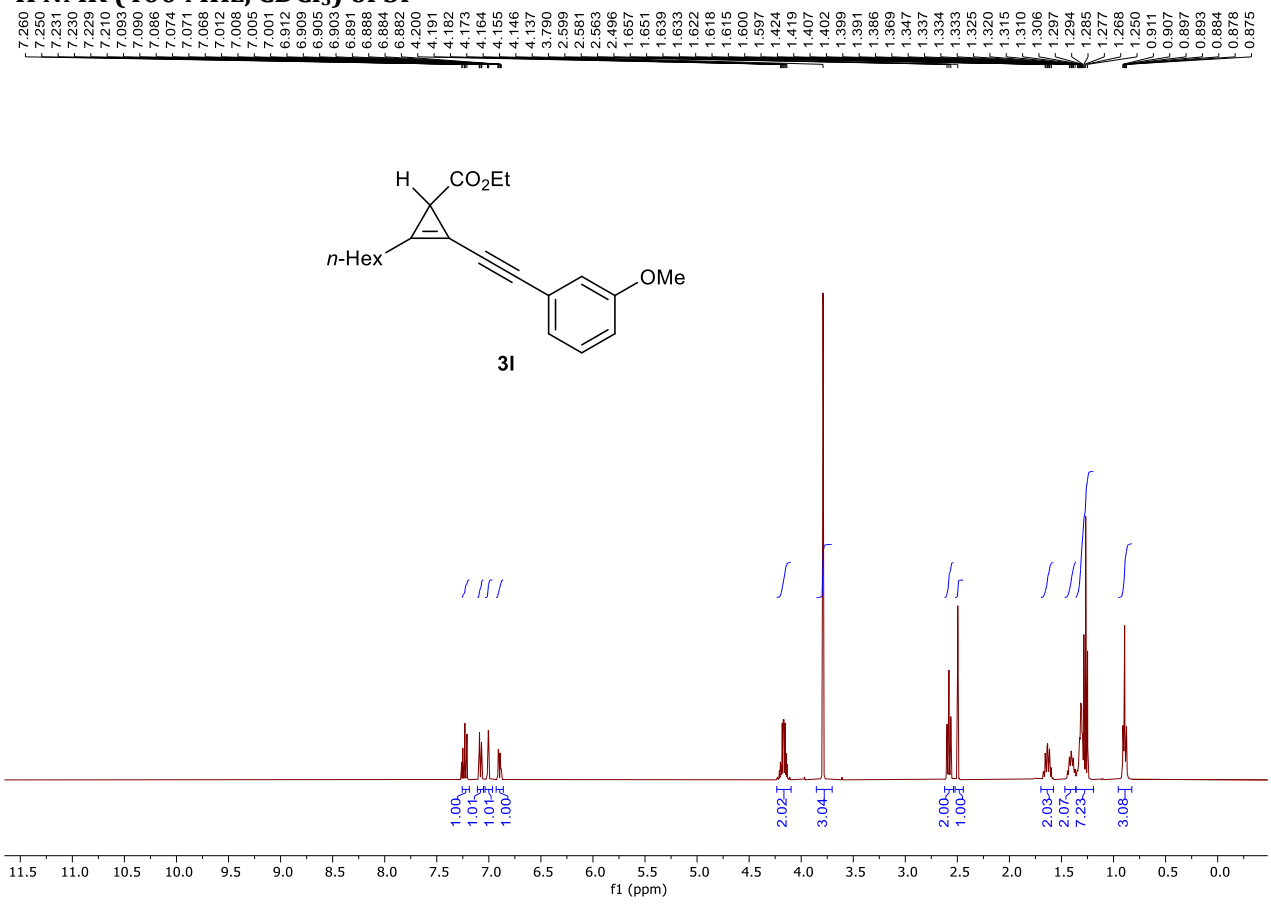
3k



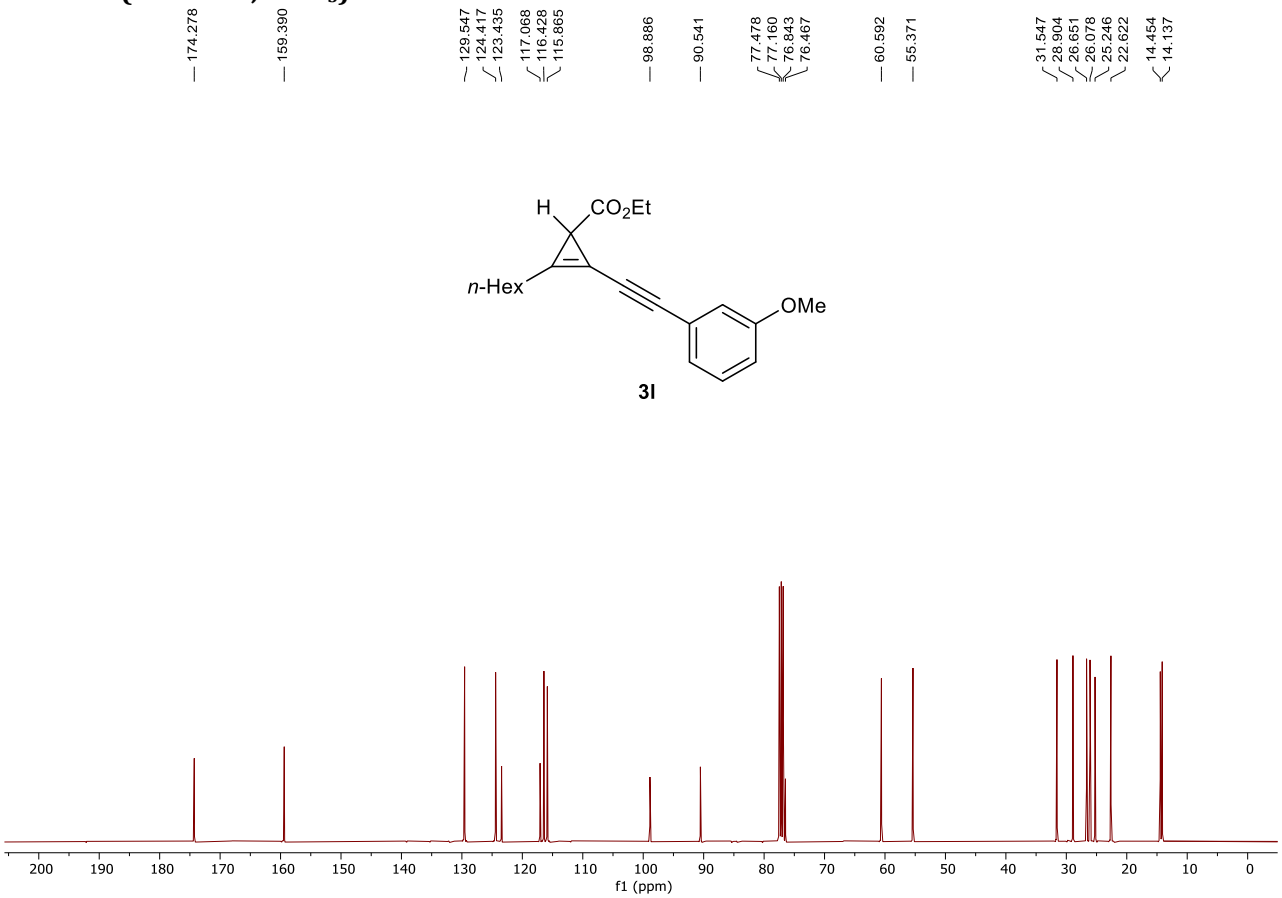
^{13}C NMR (101 MHz, $CDCl_3$) of 3k



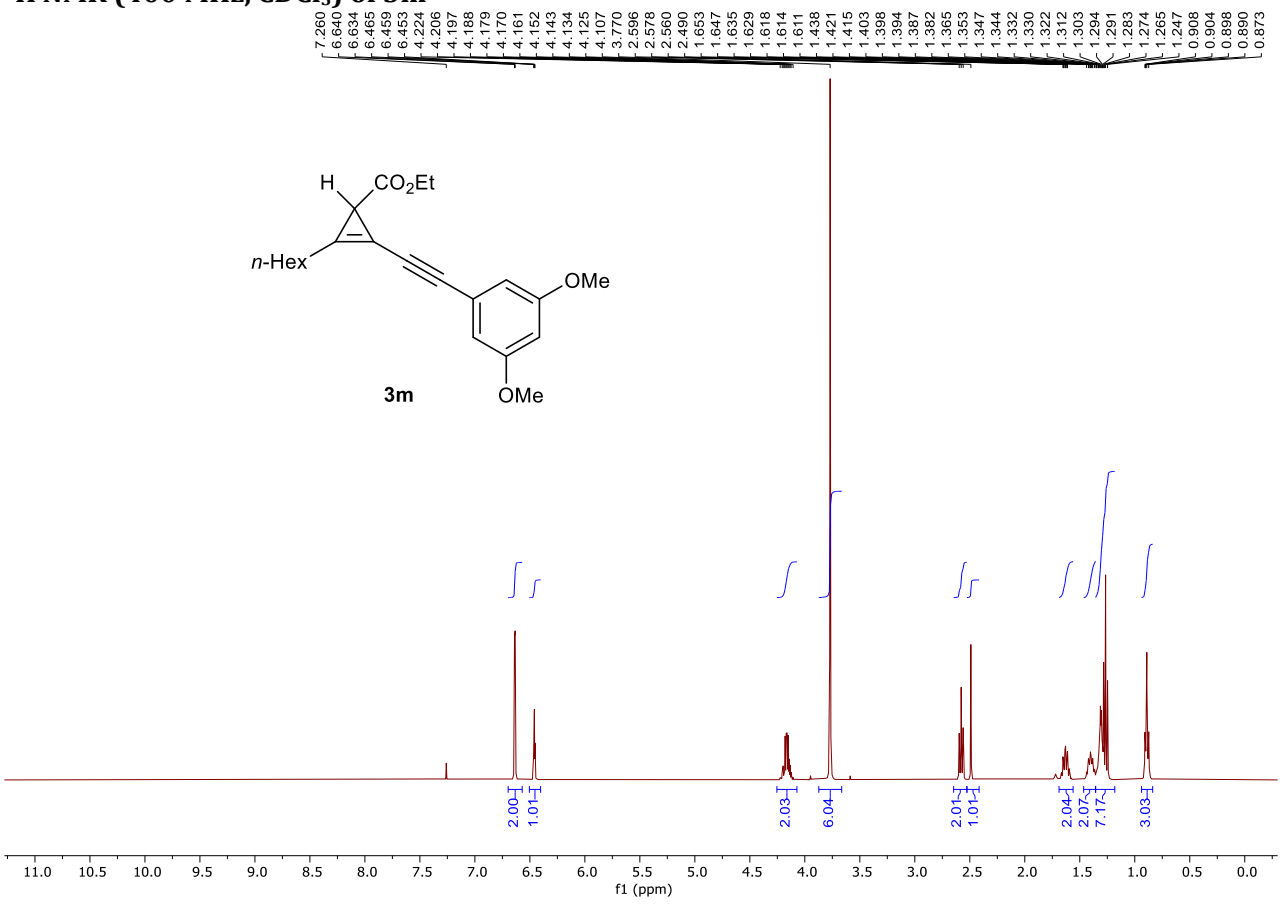
^{1}H NMR (400 MHz, $CDCl_3$) of 3l



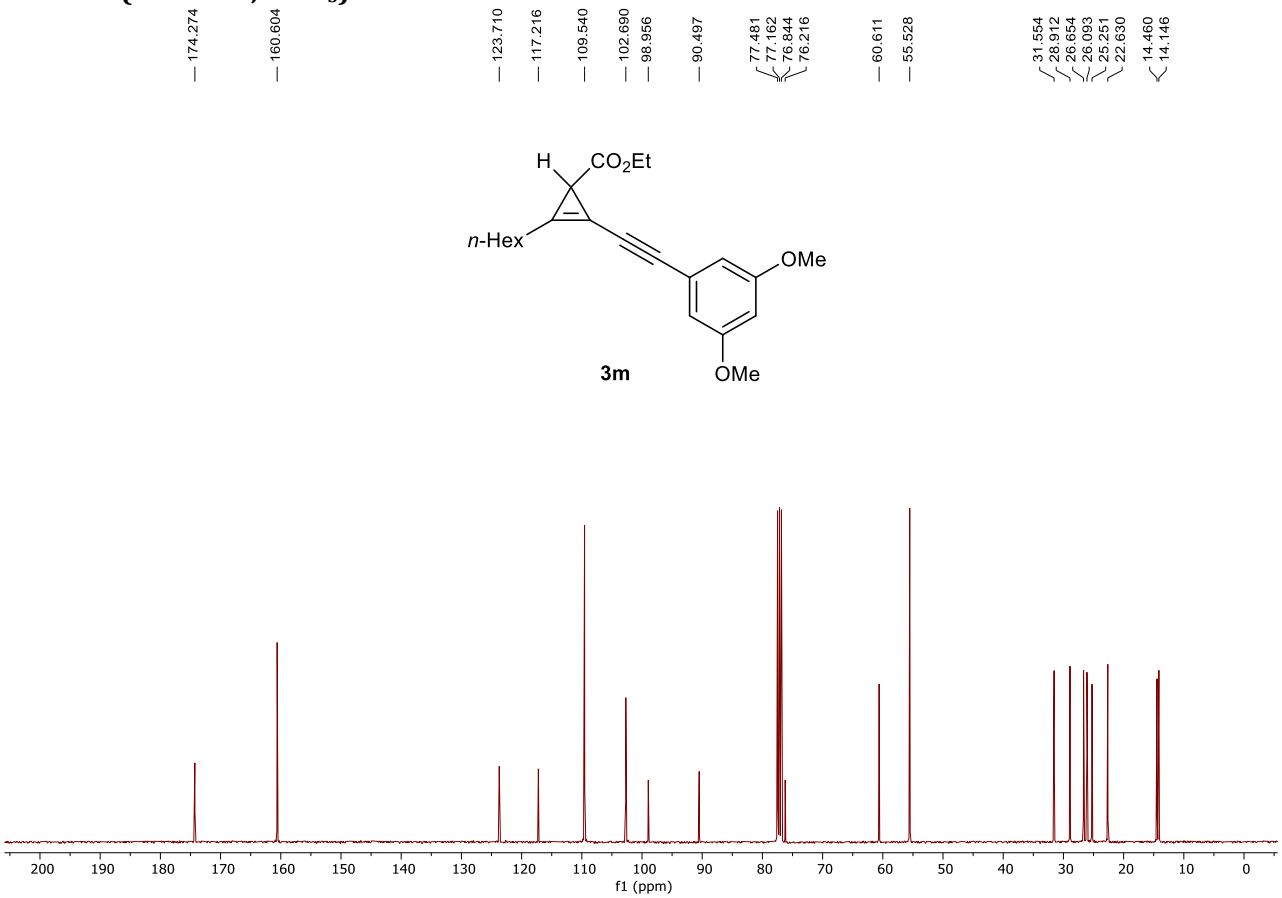
^{13}C NMR (101 MHz, $CDCl_3$) of 3l



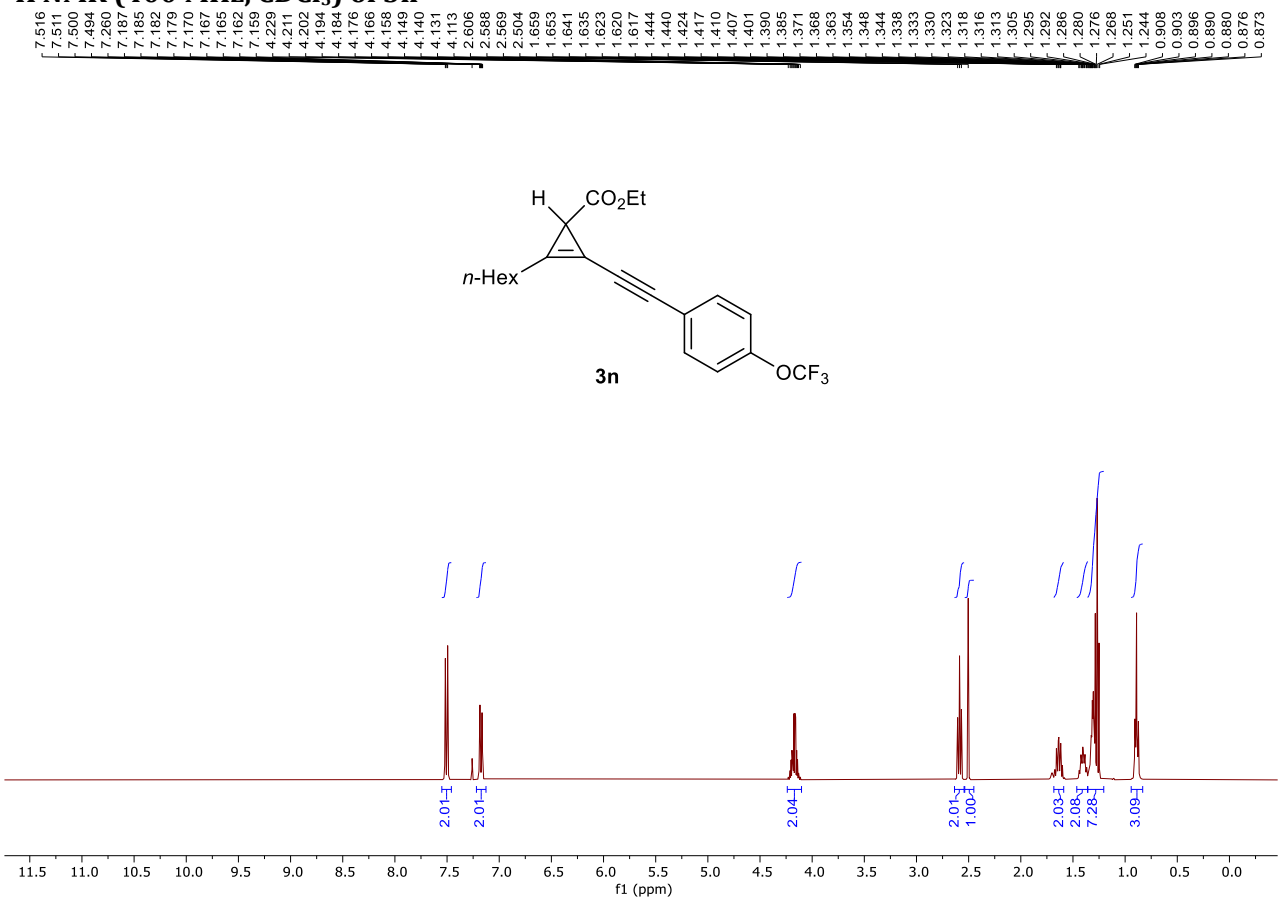
^{1}H NMR (400 MHz, $CDCl_3$) of 3m



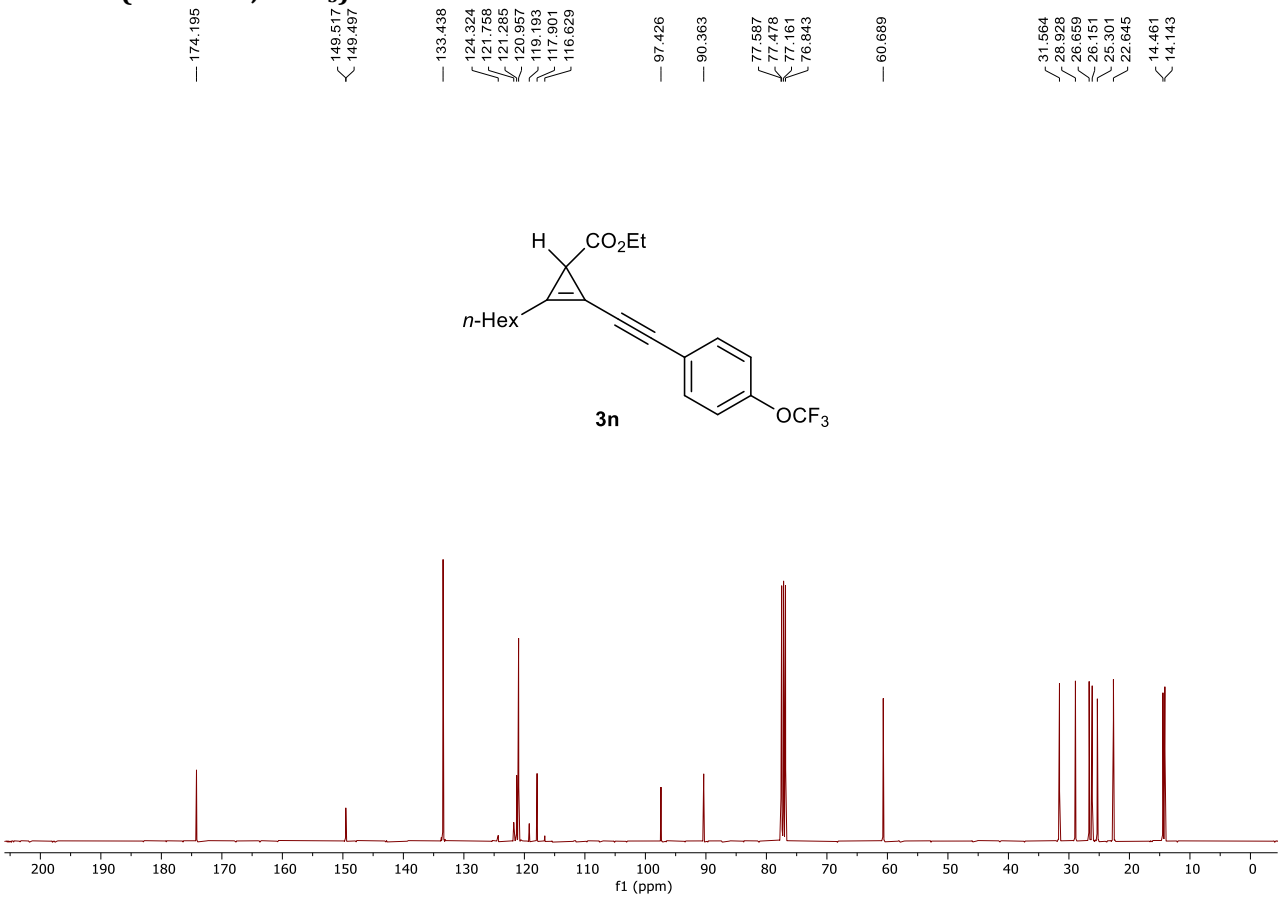
^{13}C NMR (101 MHz, $CDCl_3$) of 3m



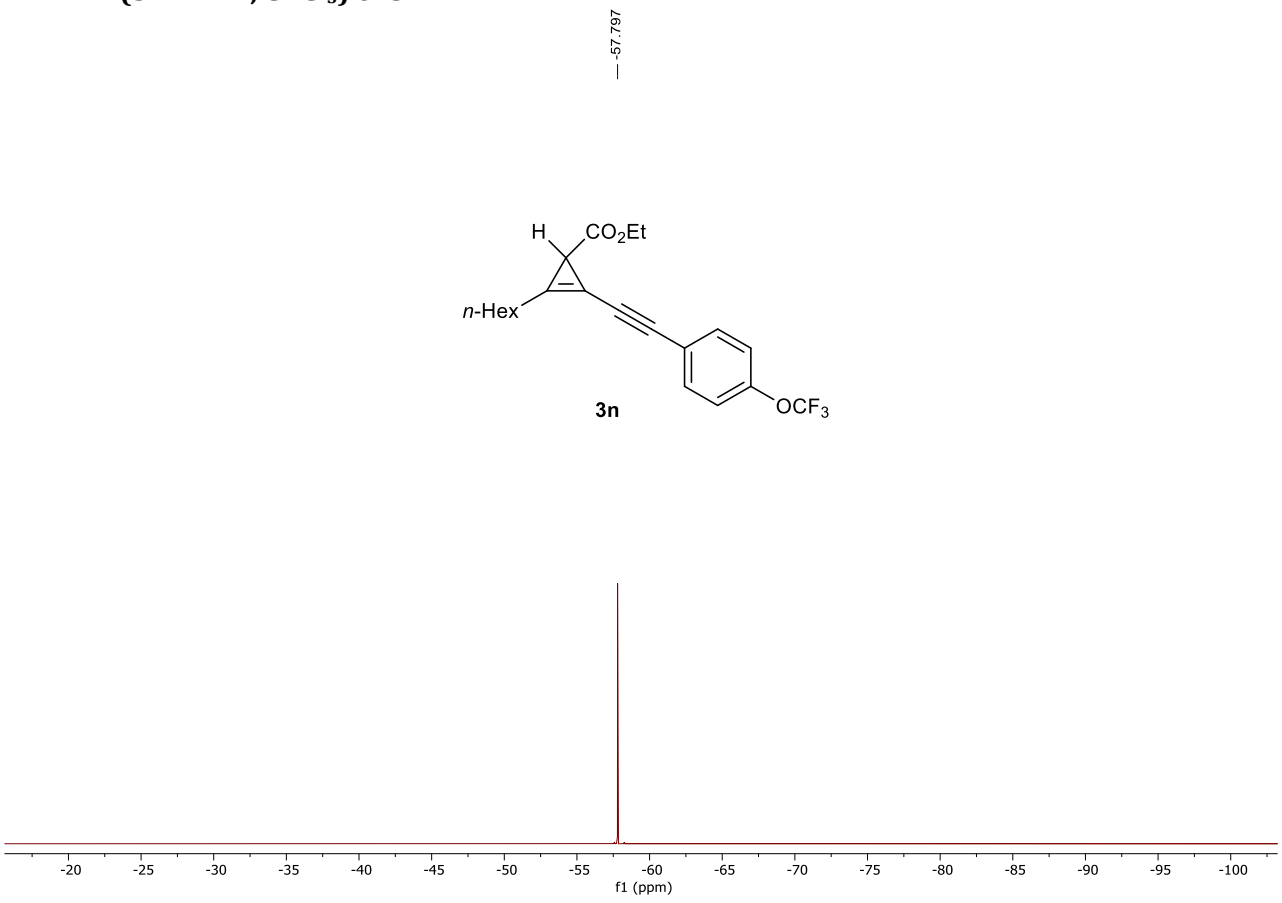
^{1}H NMR (400 MHz, $CDCl_3$) of 3n



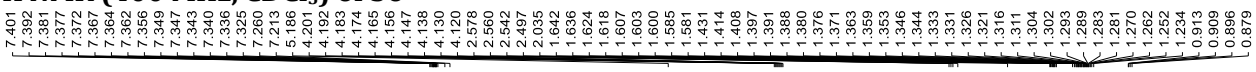
^{13}C NMR (101 MHz, $CDCl_3$) of 3n

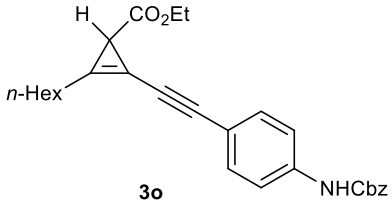


^{19}F NMR (377 MHz, $CDCl_3$) of 3n

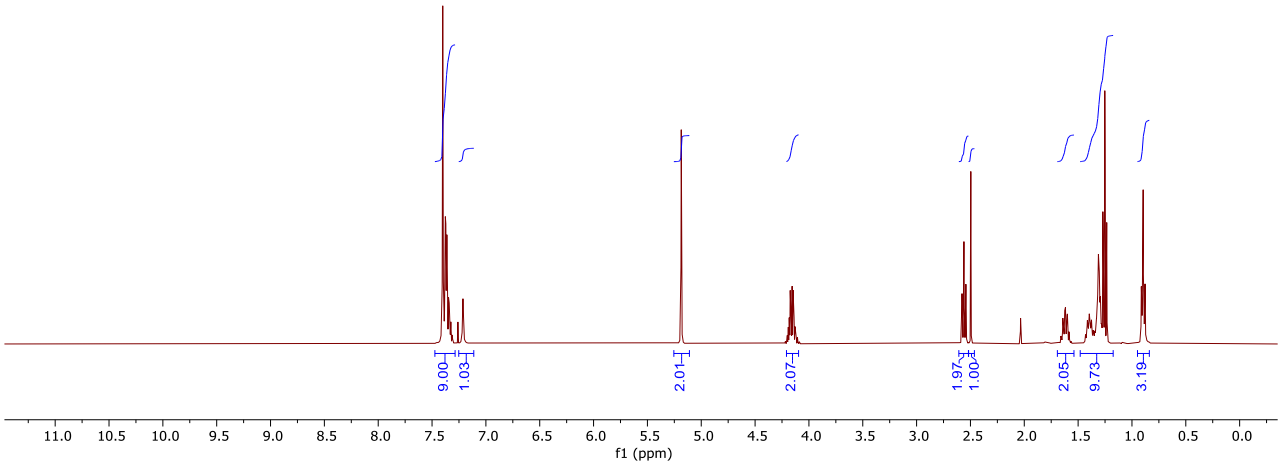


^{1}H NMR (400 MHz, $CDCl_3$) of 3o

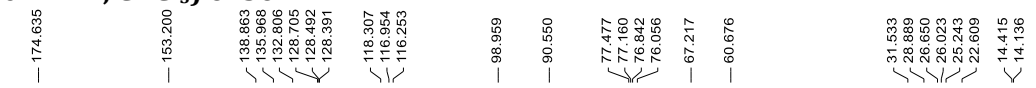


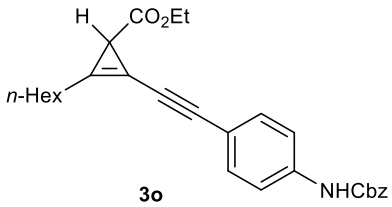


3o



^{13}C NMR (101 MHz, $CDCl_3$) of 3o





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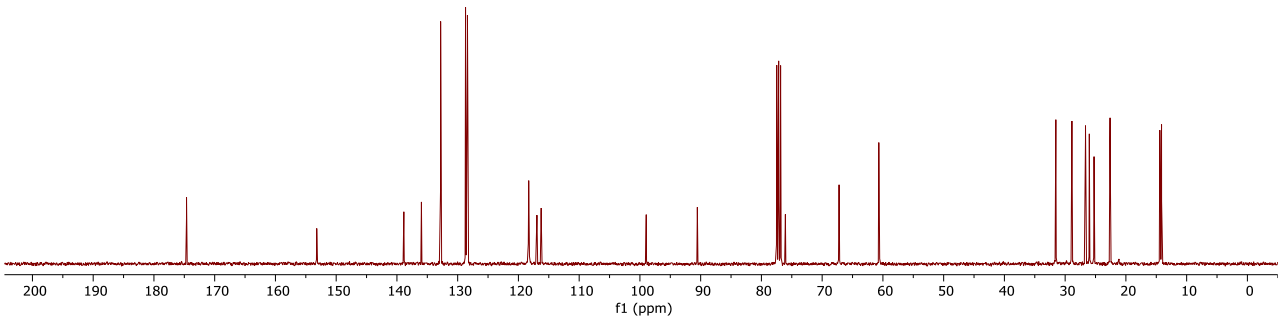
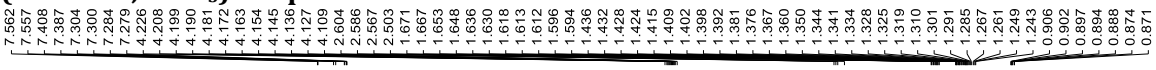
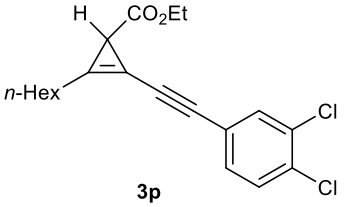


^{1}H NMR (400 MHz, $CDCl_3$) of 3p





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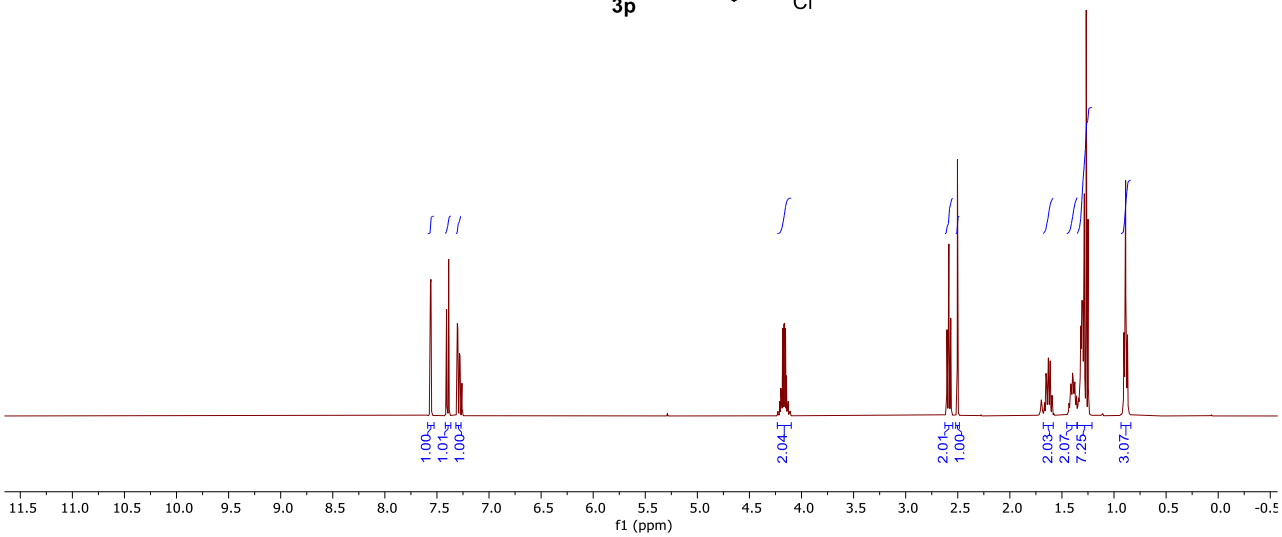
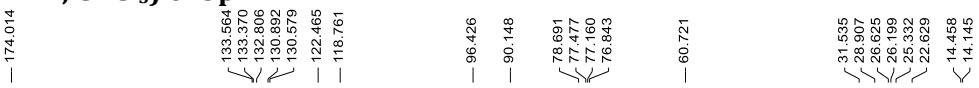
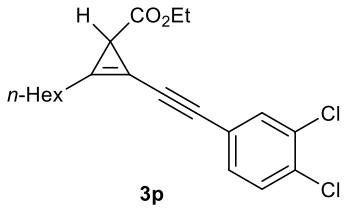


^{13}C NMR (101 MHz, $CDCl_3$) of 3p





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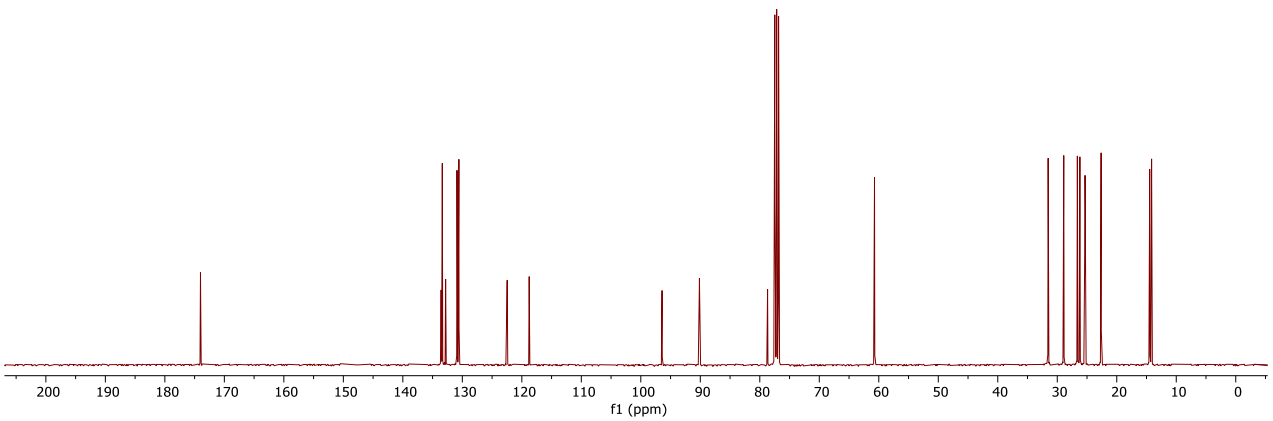
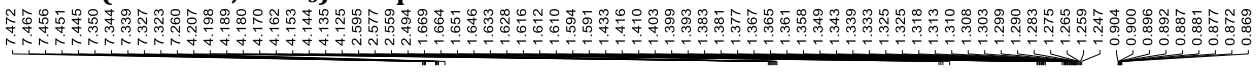
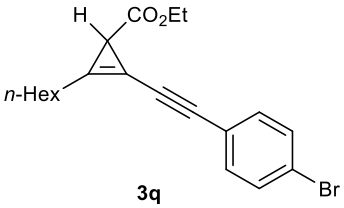


^{1}H NMR (400 MHz, $CDCl_3$) of 3q





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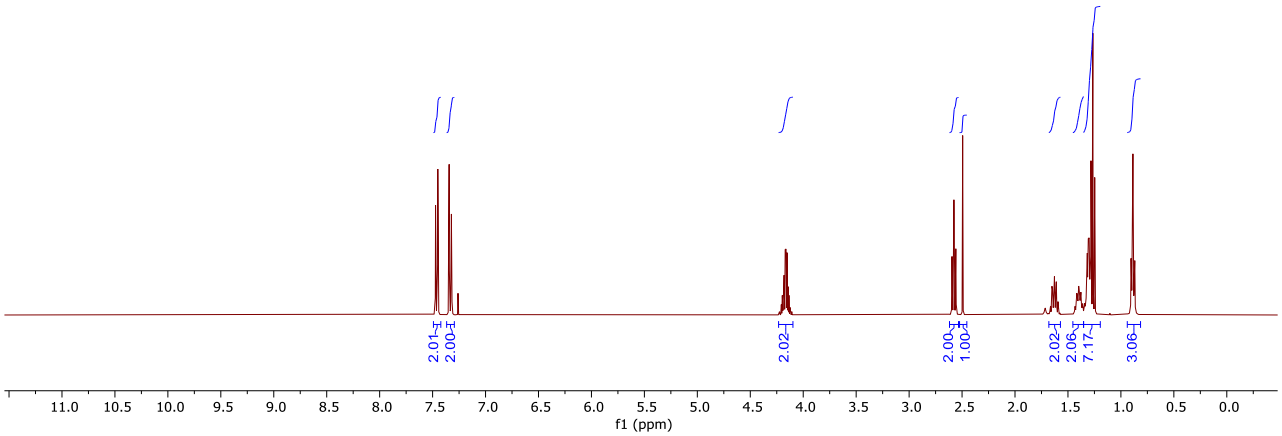
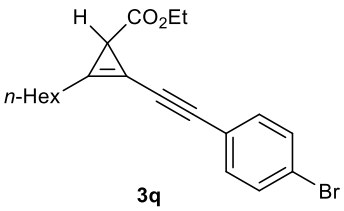


^{13}C NMR (101 MHz, $CDCl_3$) of 3q



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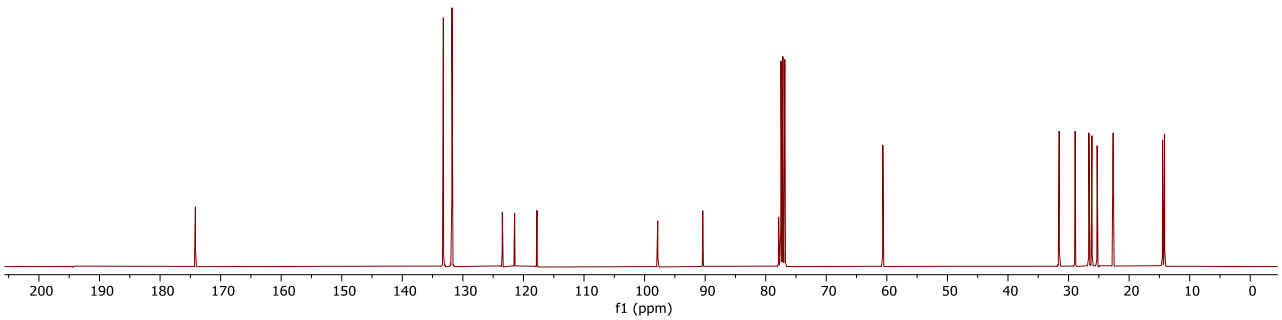
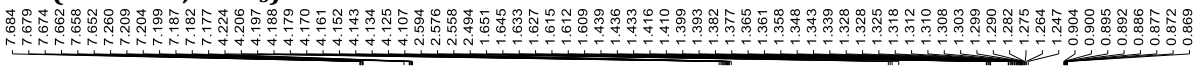
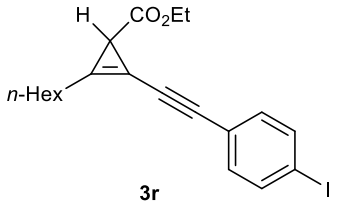
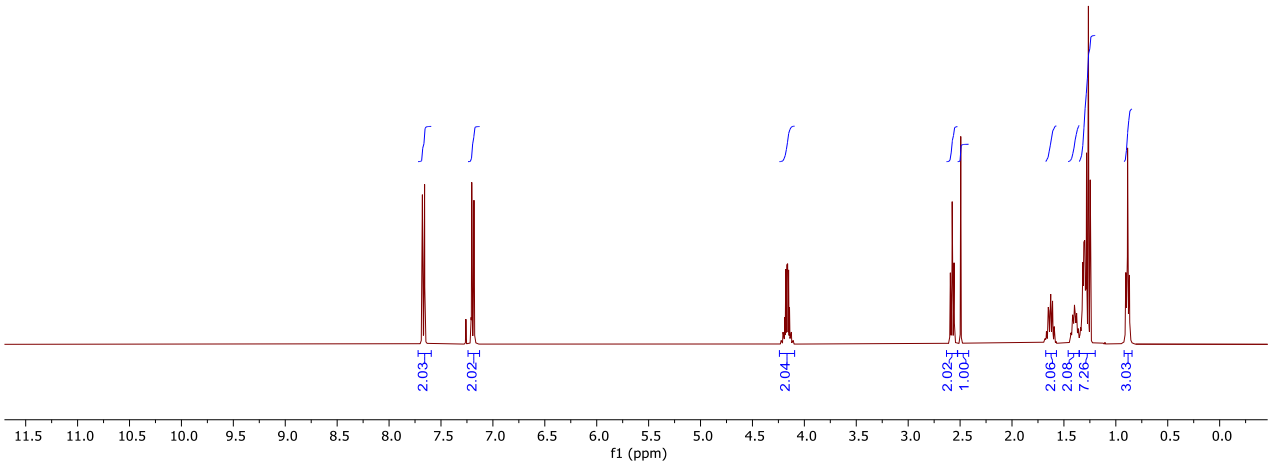


^{1}H NMR (400 MHz, $CDCl_3$) of 3r

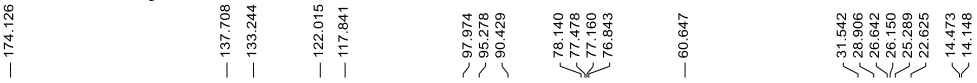


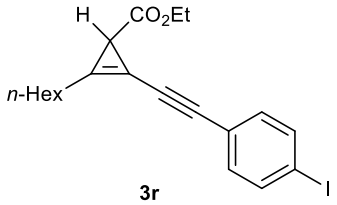


3r



^{13}C NMR (101 MHz, $CDCl_3$) of 3r





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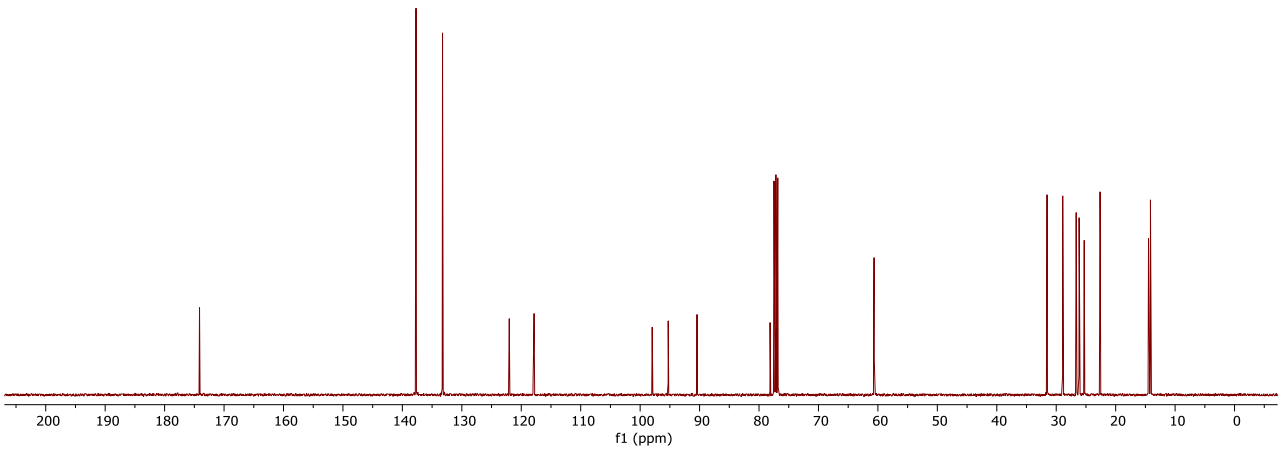
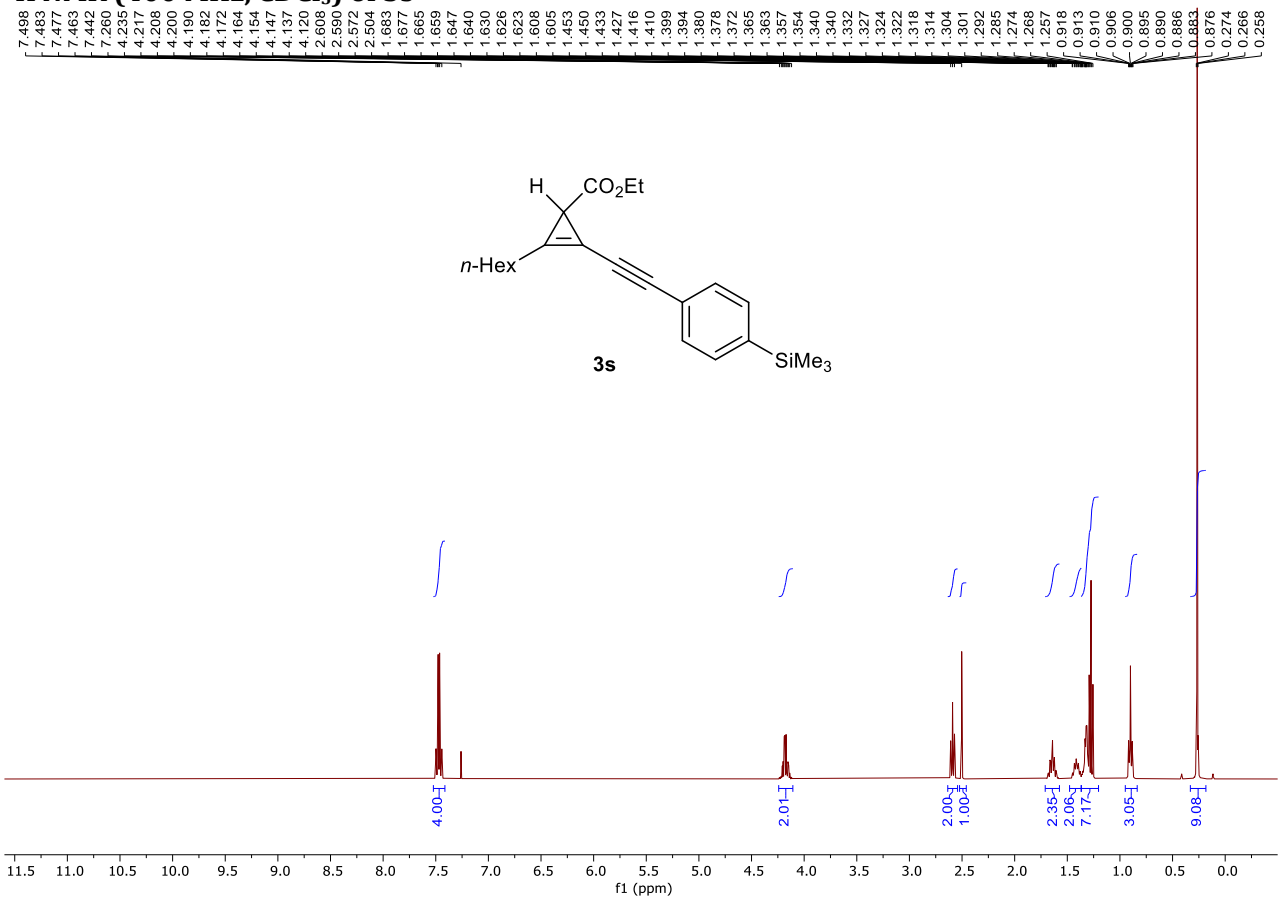
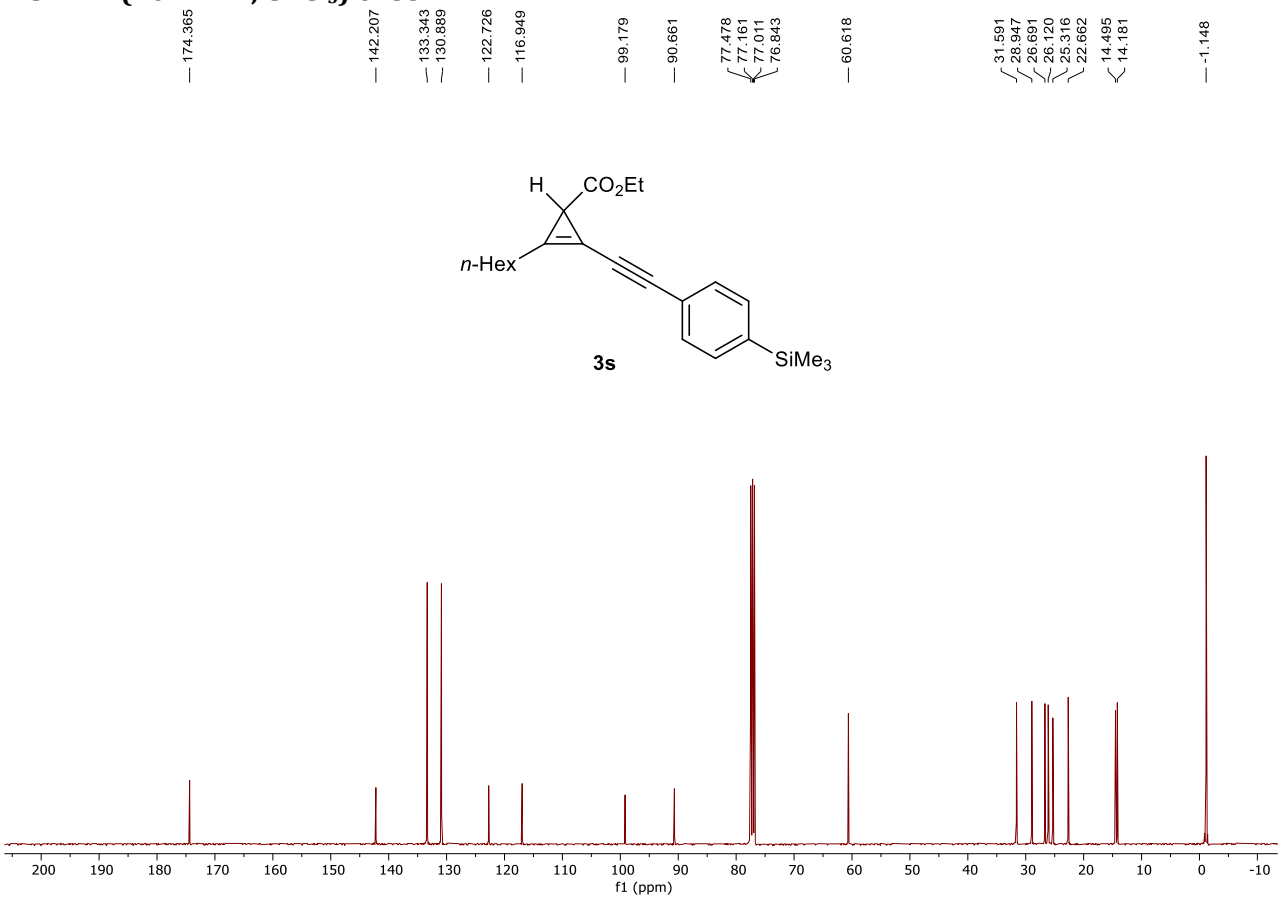


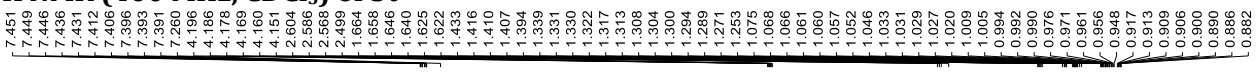
^{1}H NMR (400 MHz, $CDCl_3$) of 3s

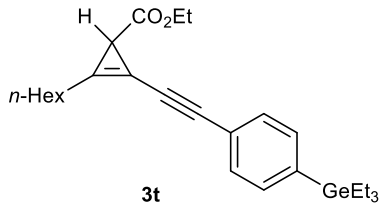


^{13}C NMR (101 MHz, $CDCl_3$) of 3s

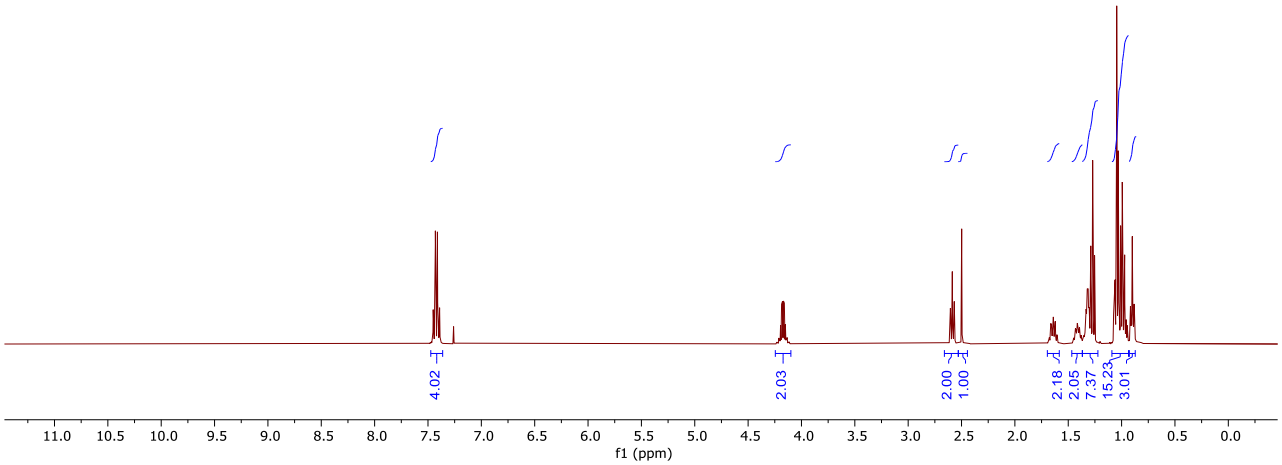


^{1}H NMR (400 MHz, $CDCl_3$) of 3t

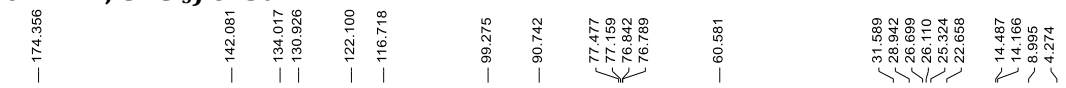


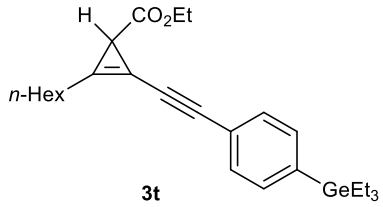


3t

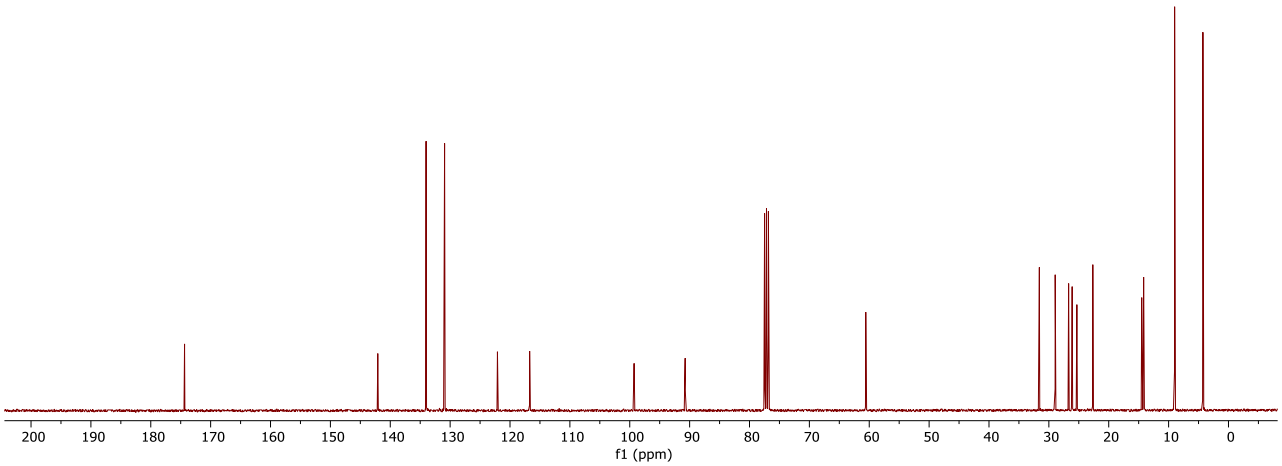


^{13}C NMR (101 MHz, $CDCl_3$) of 3t

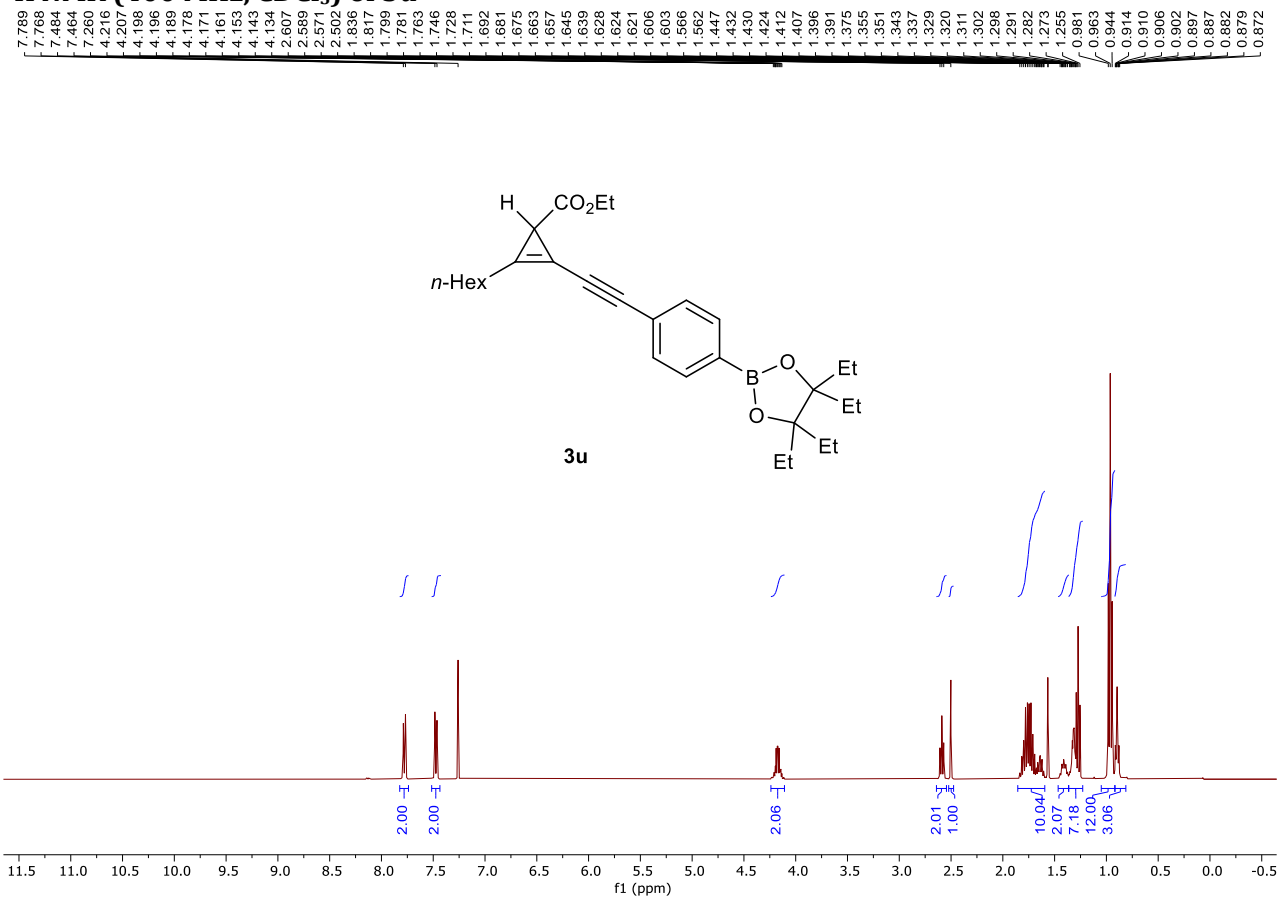




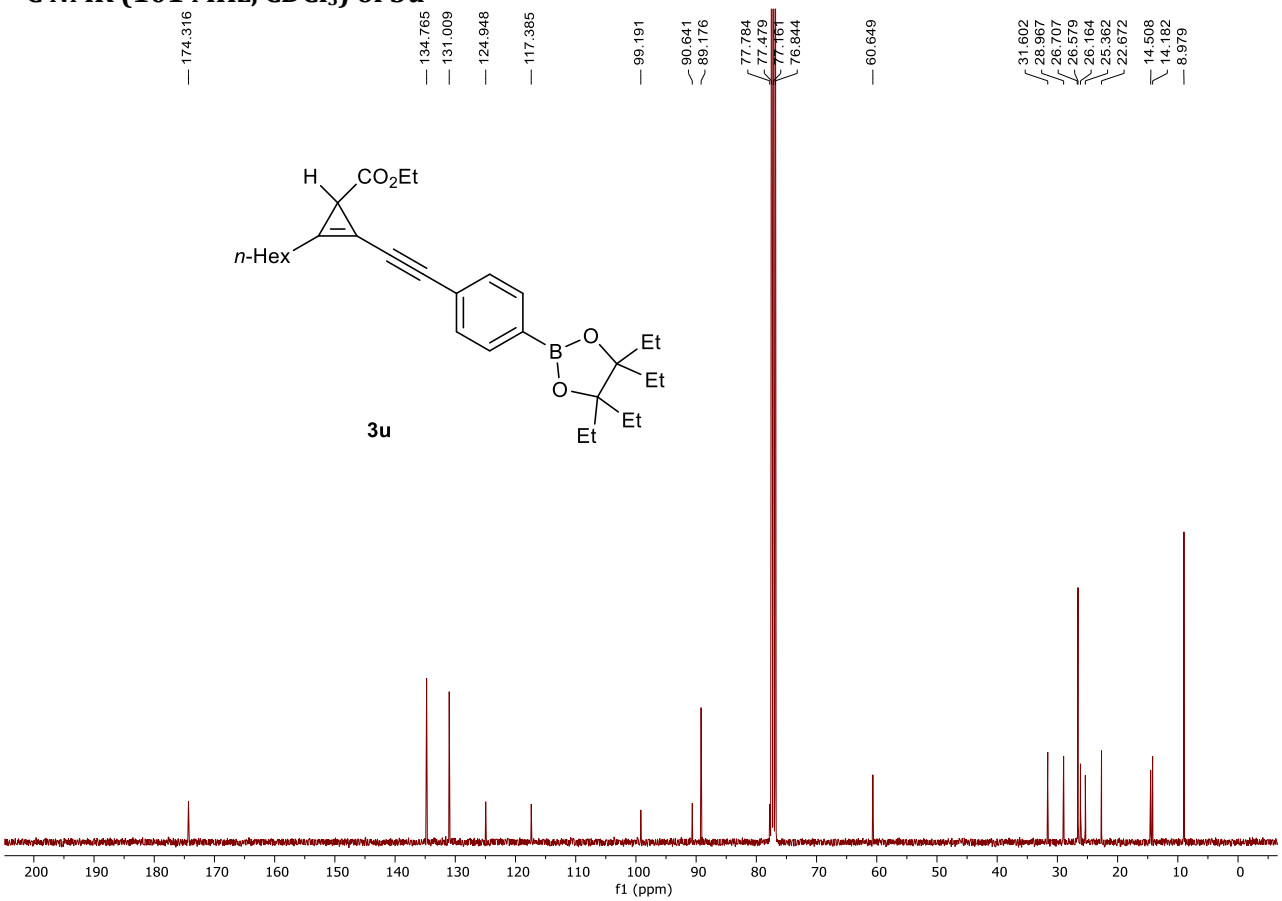
3t



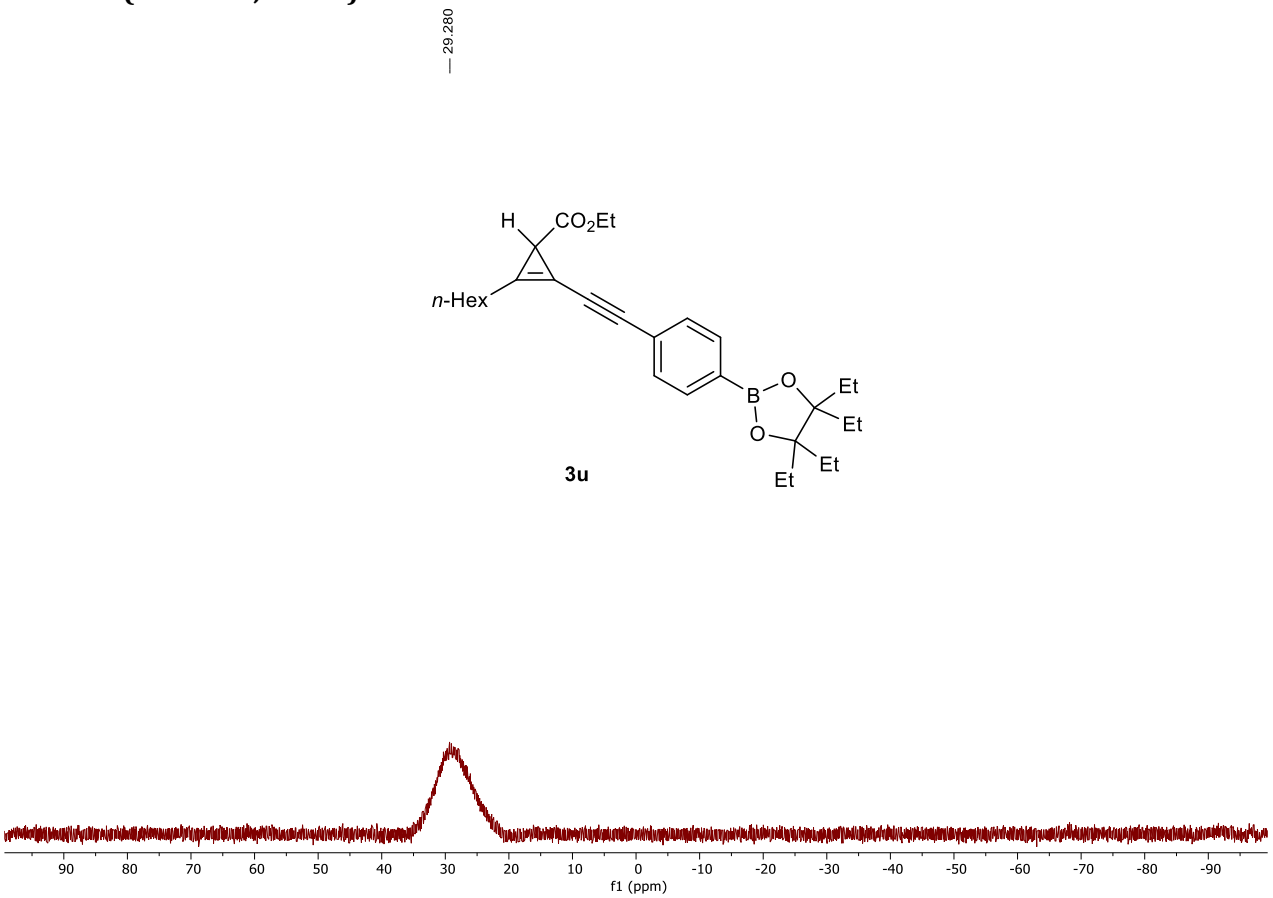
^{1}H NMR (400 MHz, $CDCl_3$) of 3u



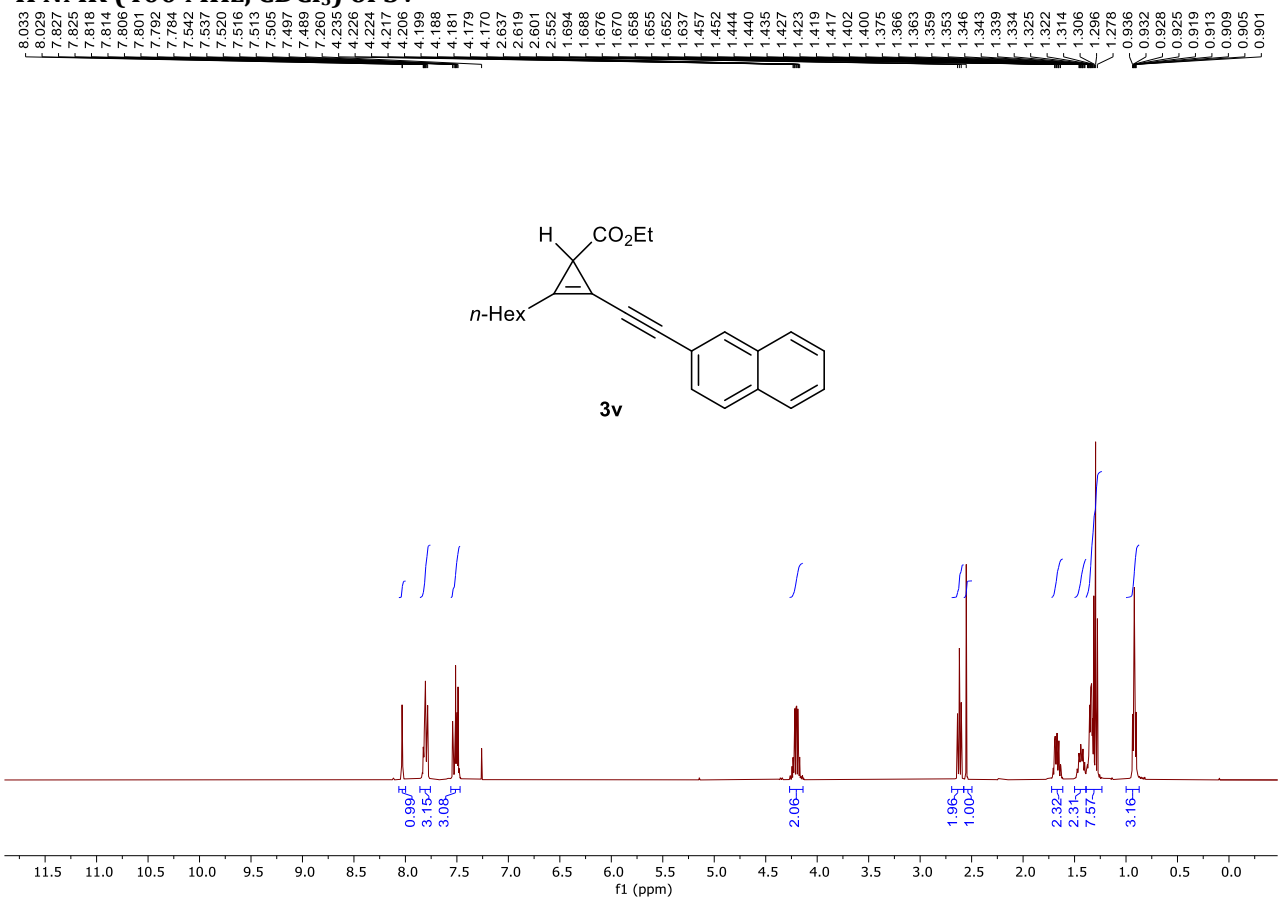
^{13}C NMR (101 MHz, $CDCl_3$) of 3u



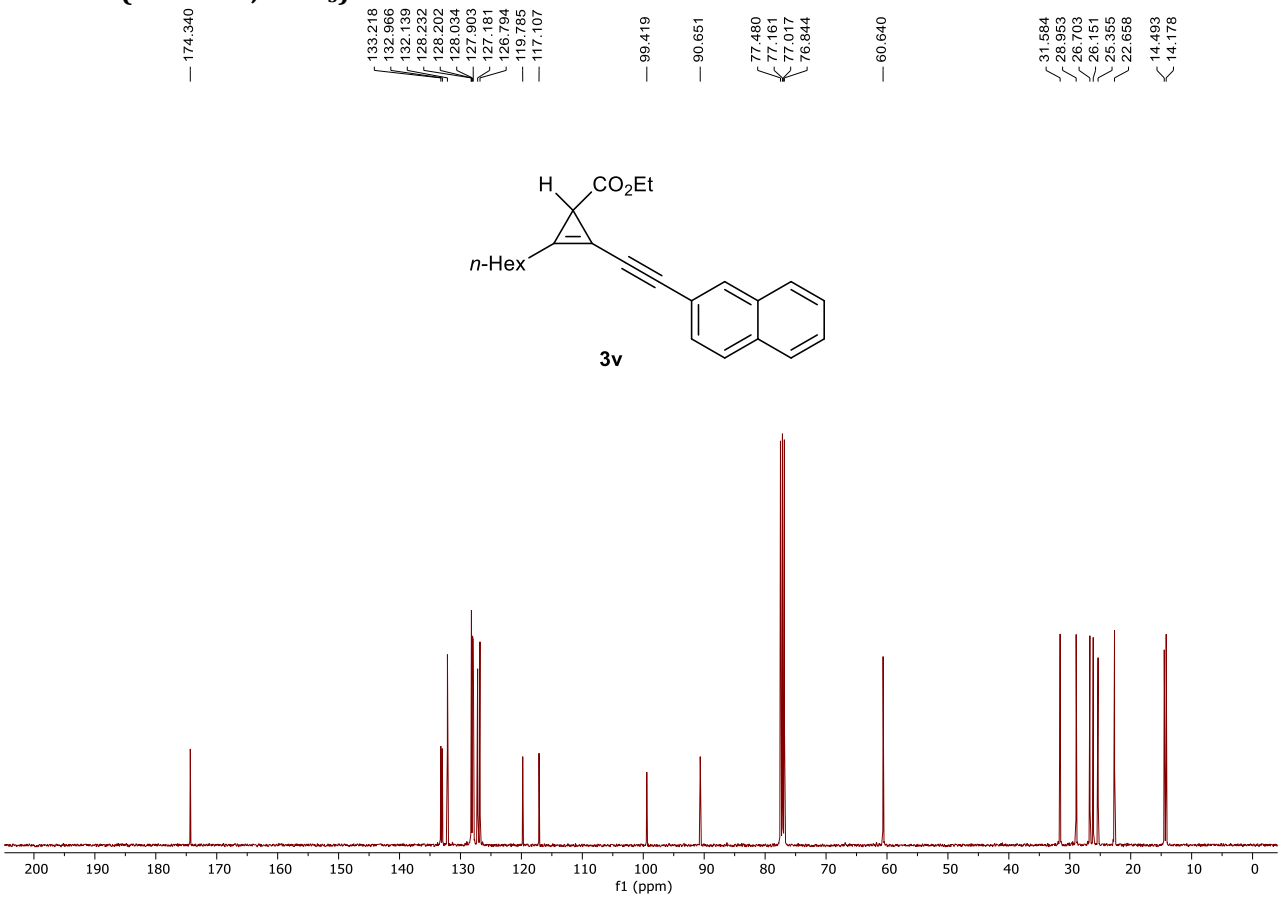
^{11}B NMR (128 MHz, CDCl3) of 3u



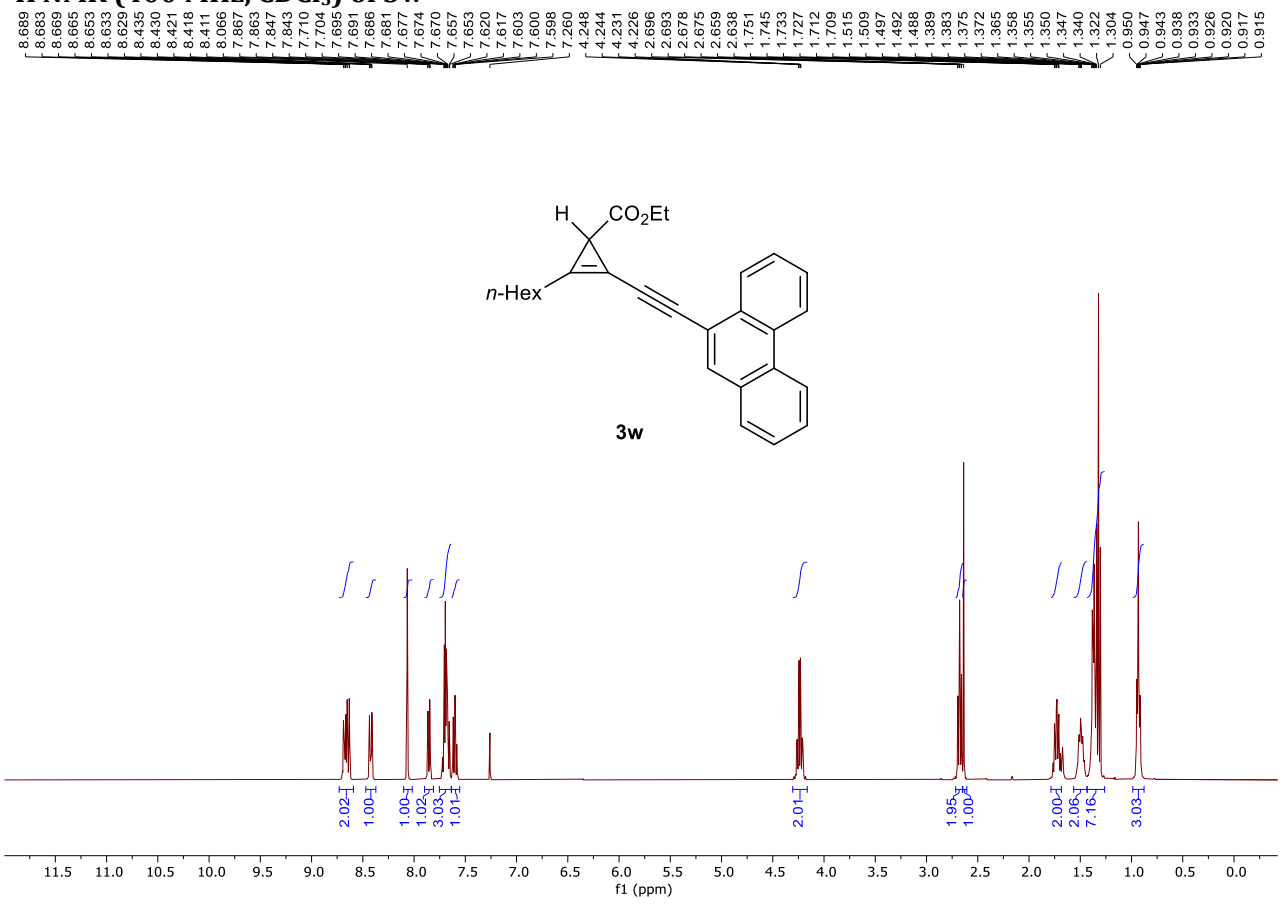
^{1}H NMR (400 MHz, $CDCl_3$) of 3v



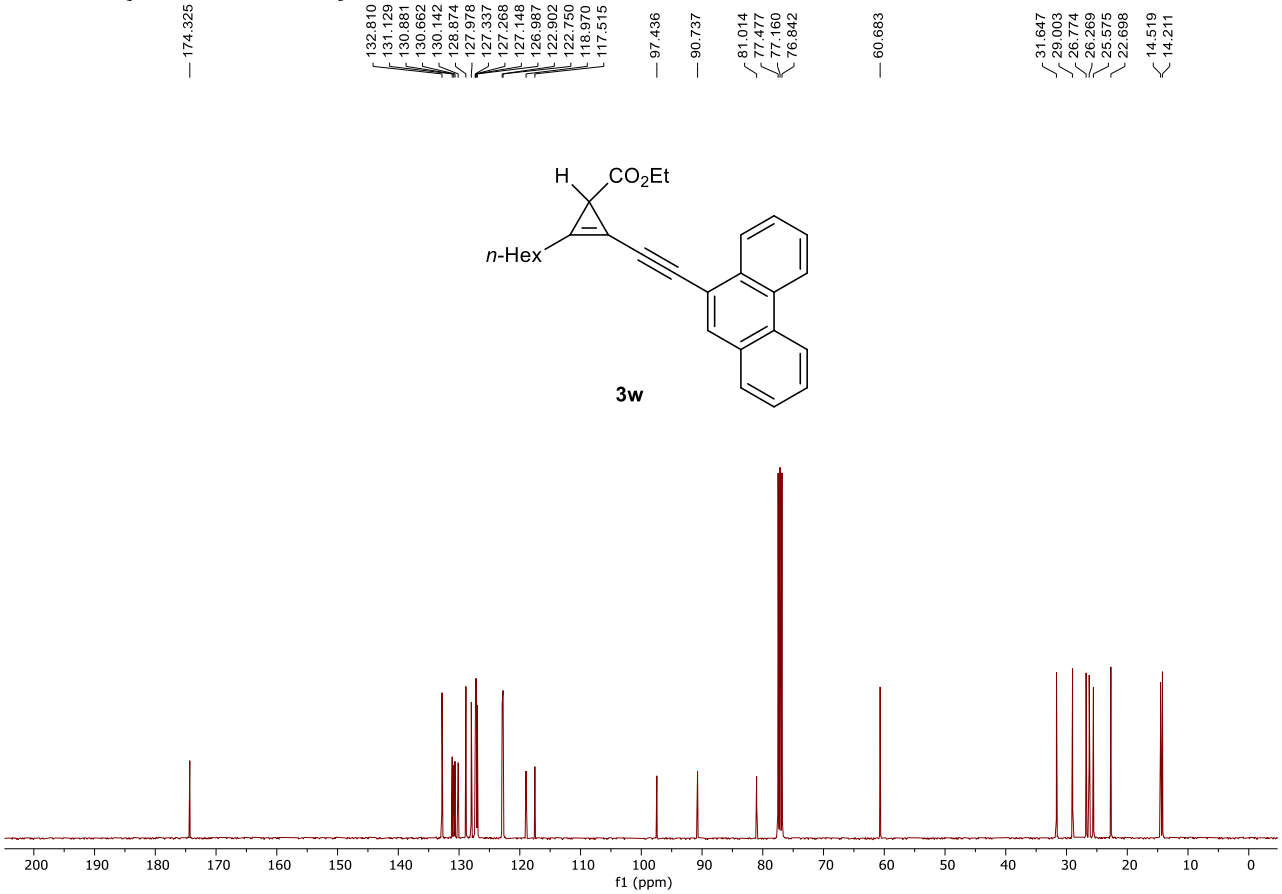
^{13}C NMR (101 MHz, $CDCl_3$) of 3v



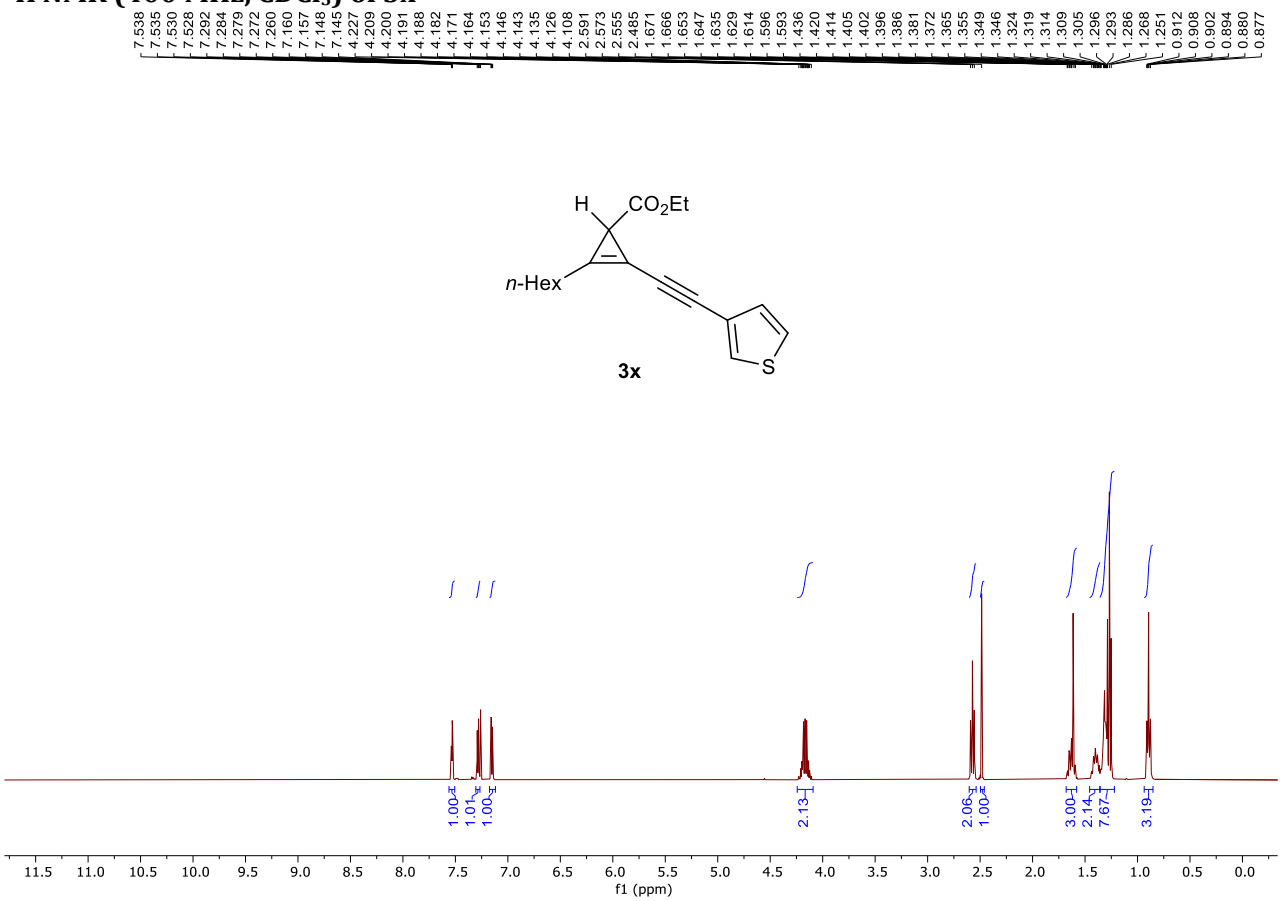
^{1}H NMR (400 MHz, $CDCl_3$) of 3w



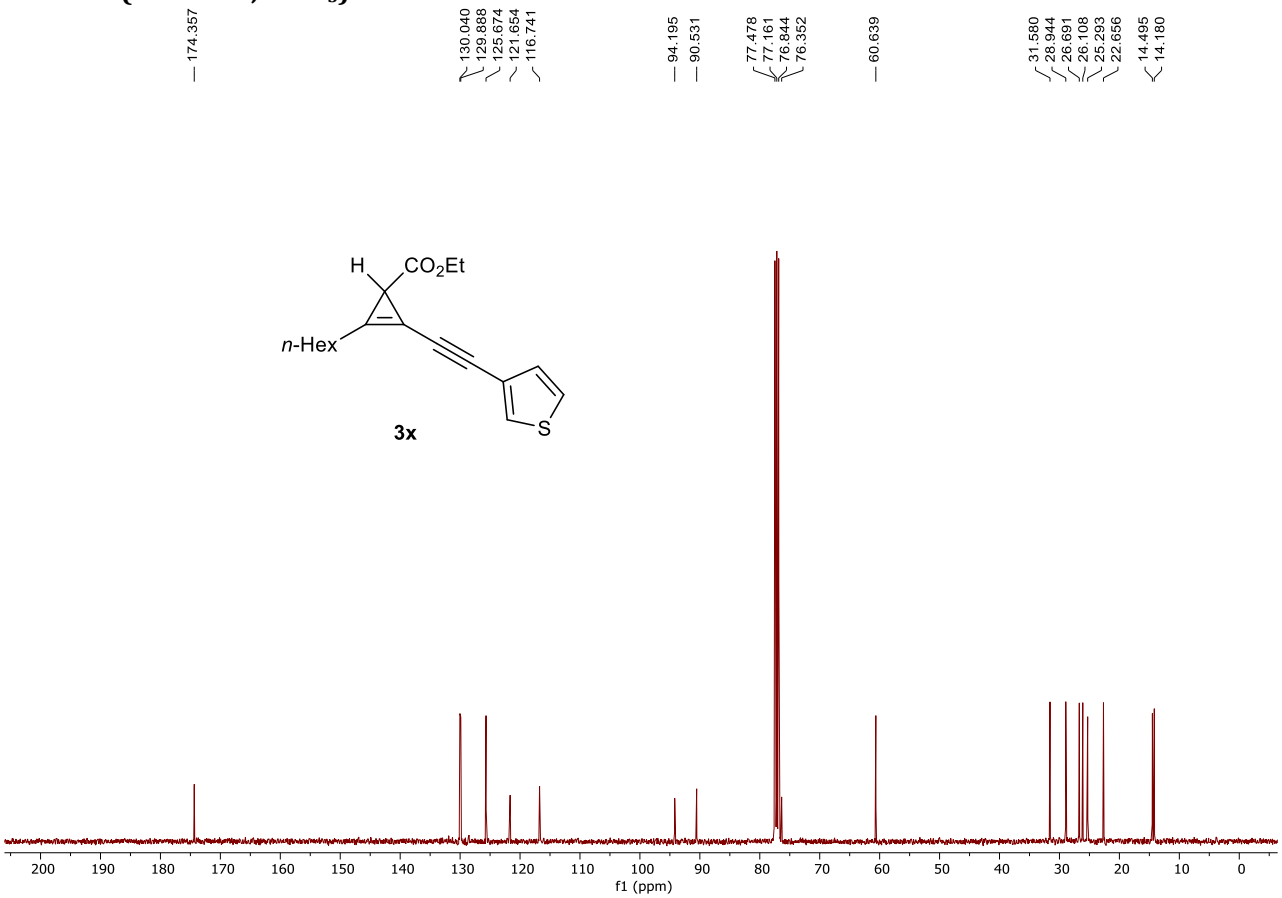
^{13}C NMR (101 MHz, $CDCl_3$) of 3w



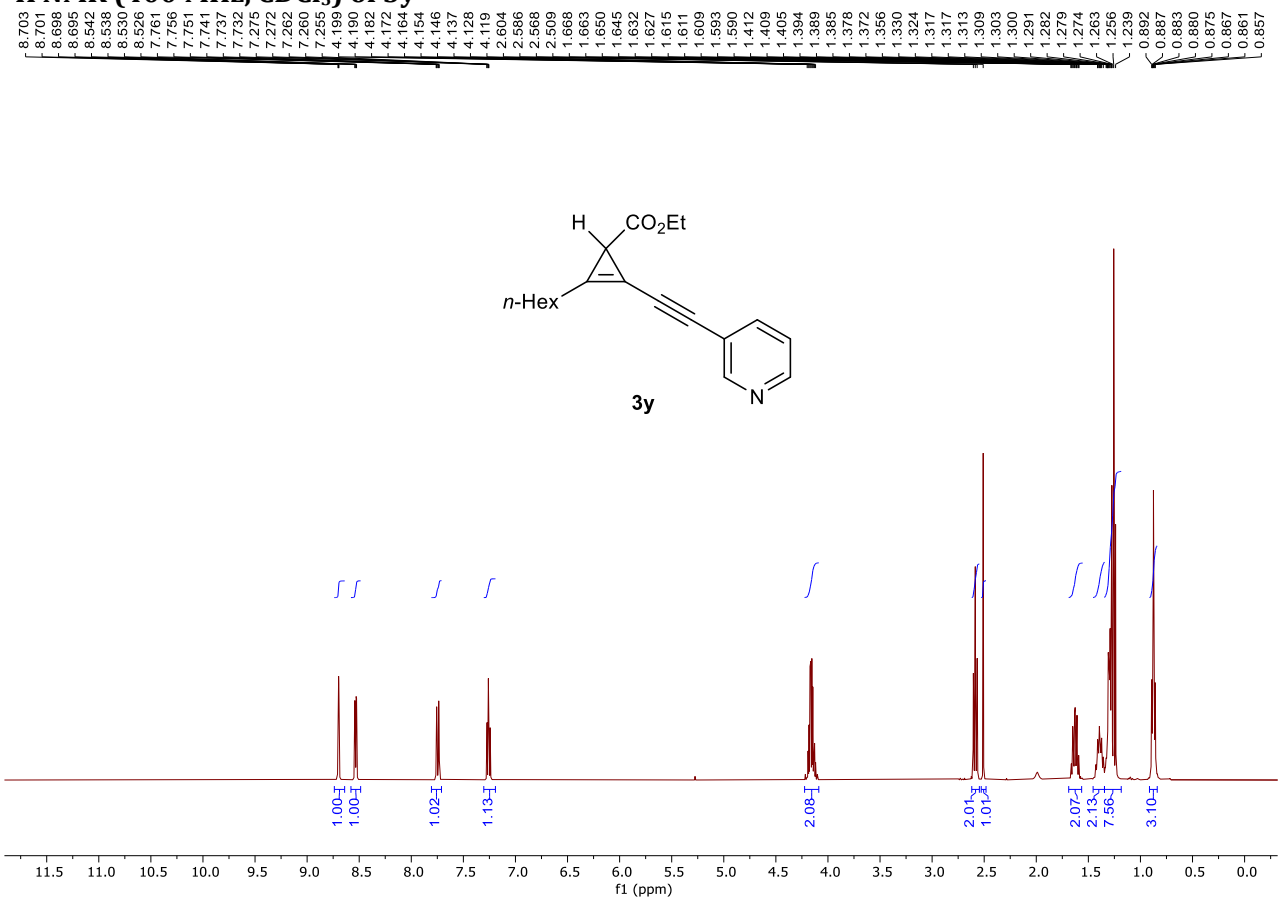
^{1}H NMR (400 MHz, $CDCl_3$) of 3x



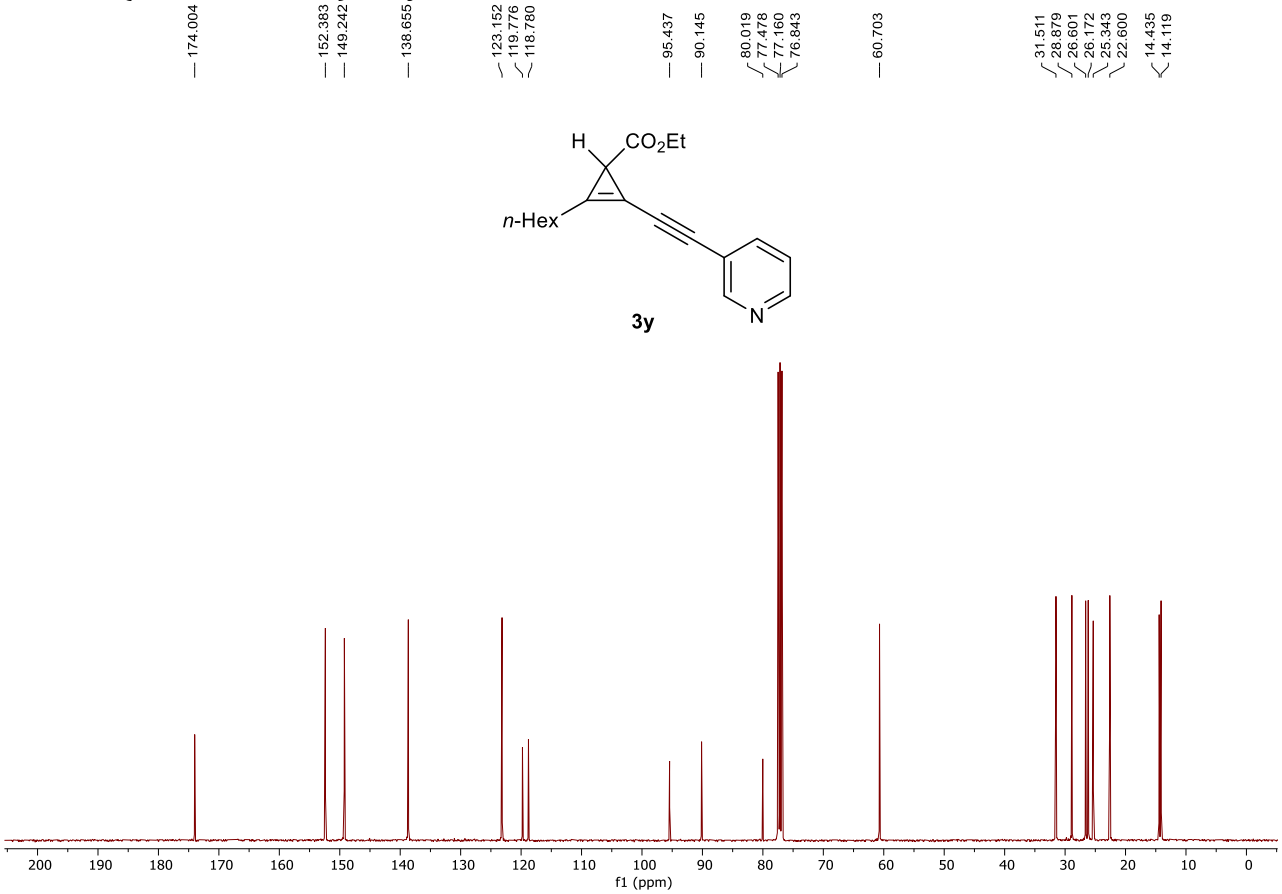
^{13}C NMR (101 MHz, $CDCl_3$) of 3x



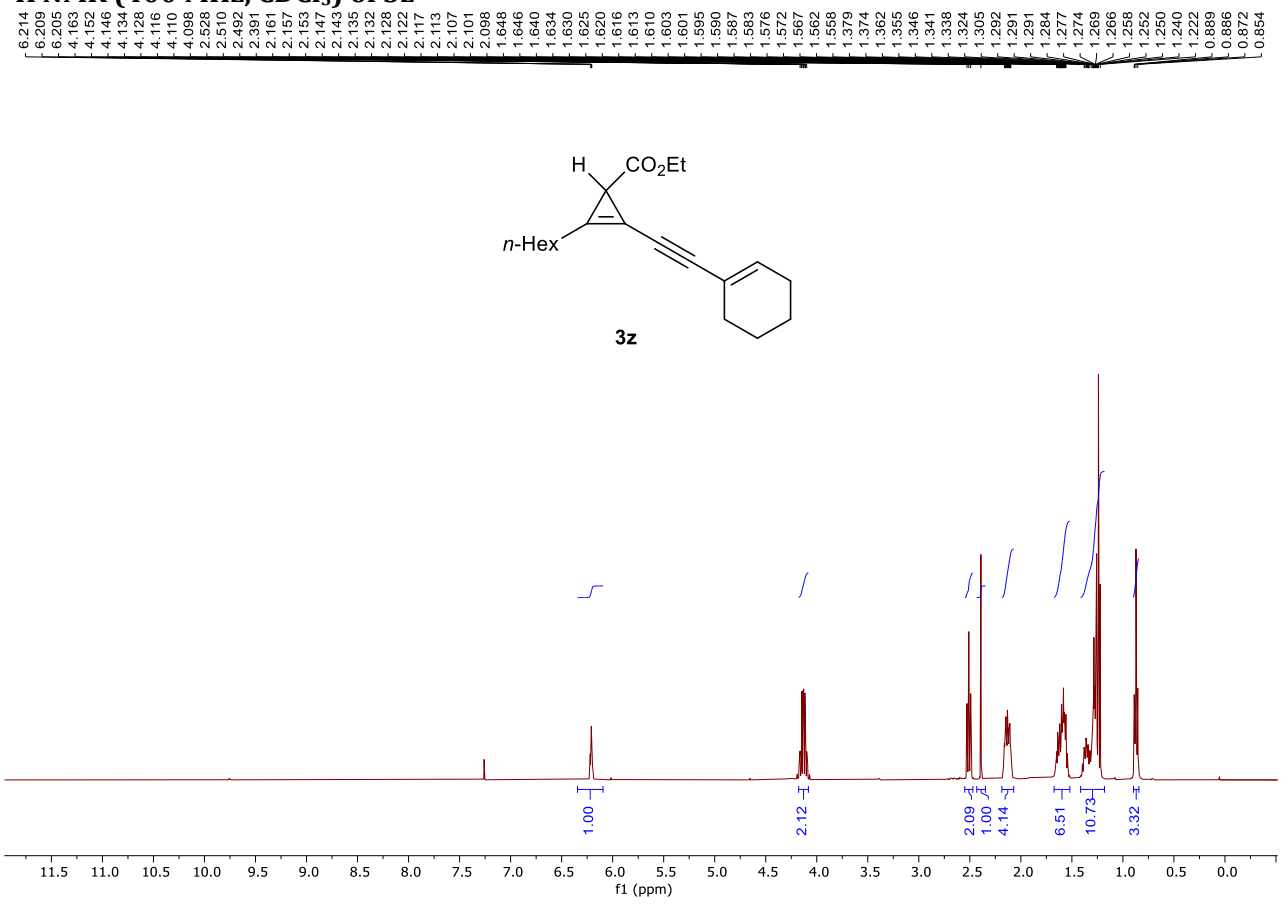
^{1}H NMR (400 MHz, $CDCl_3$) of 3y



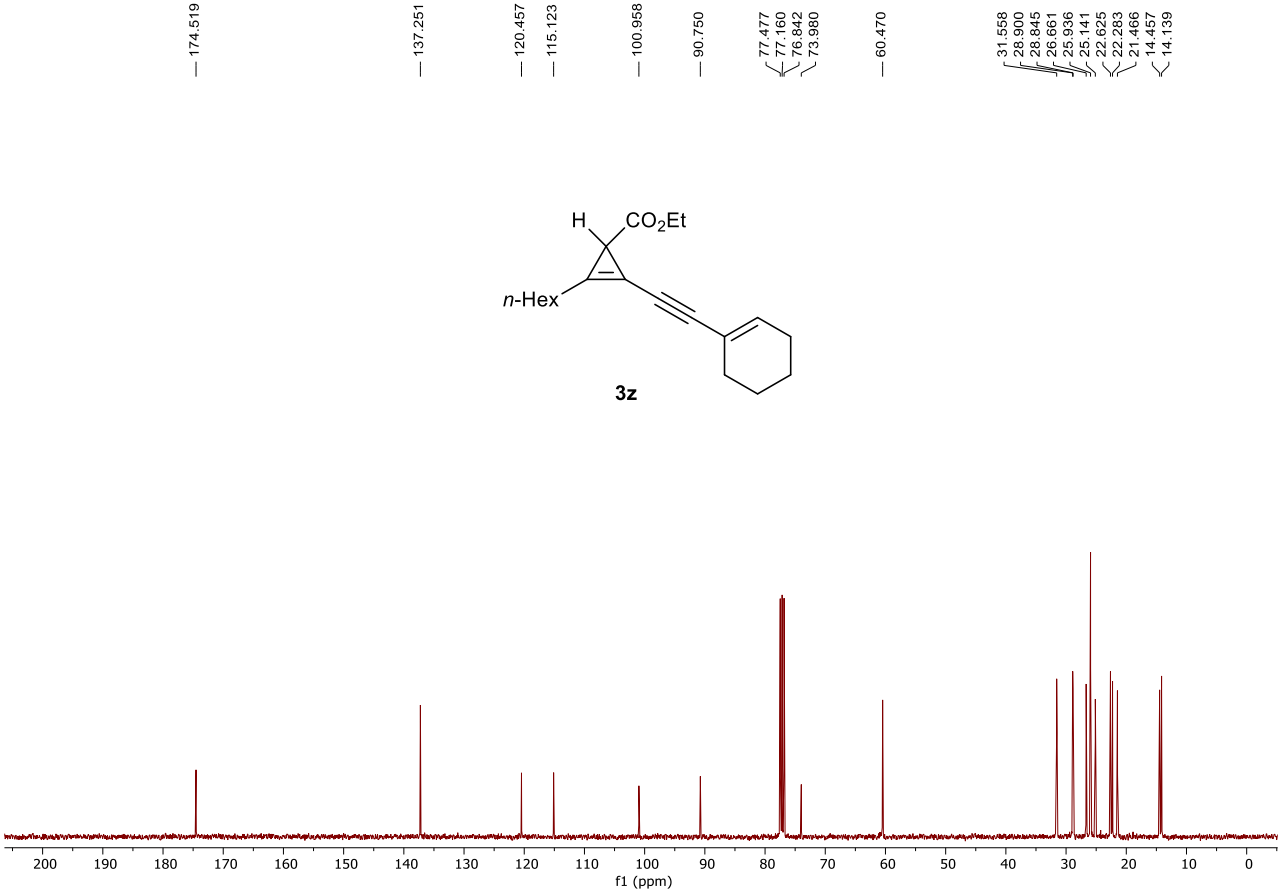
^{13}C NMR (101 MHz, $CDCl_3$) of 3y



^{1}H NMR (400 MHz, $CDCl_3$) of 3z

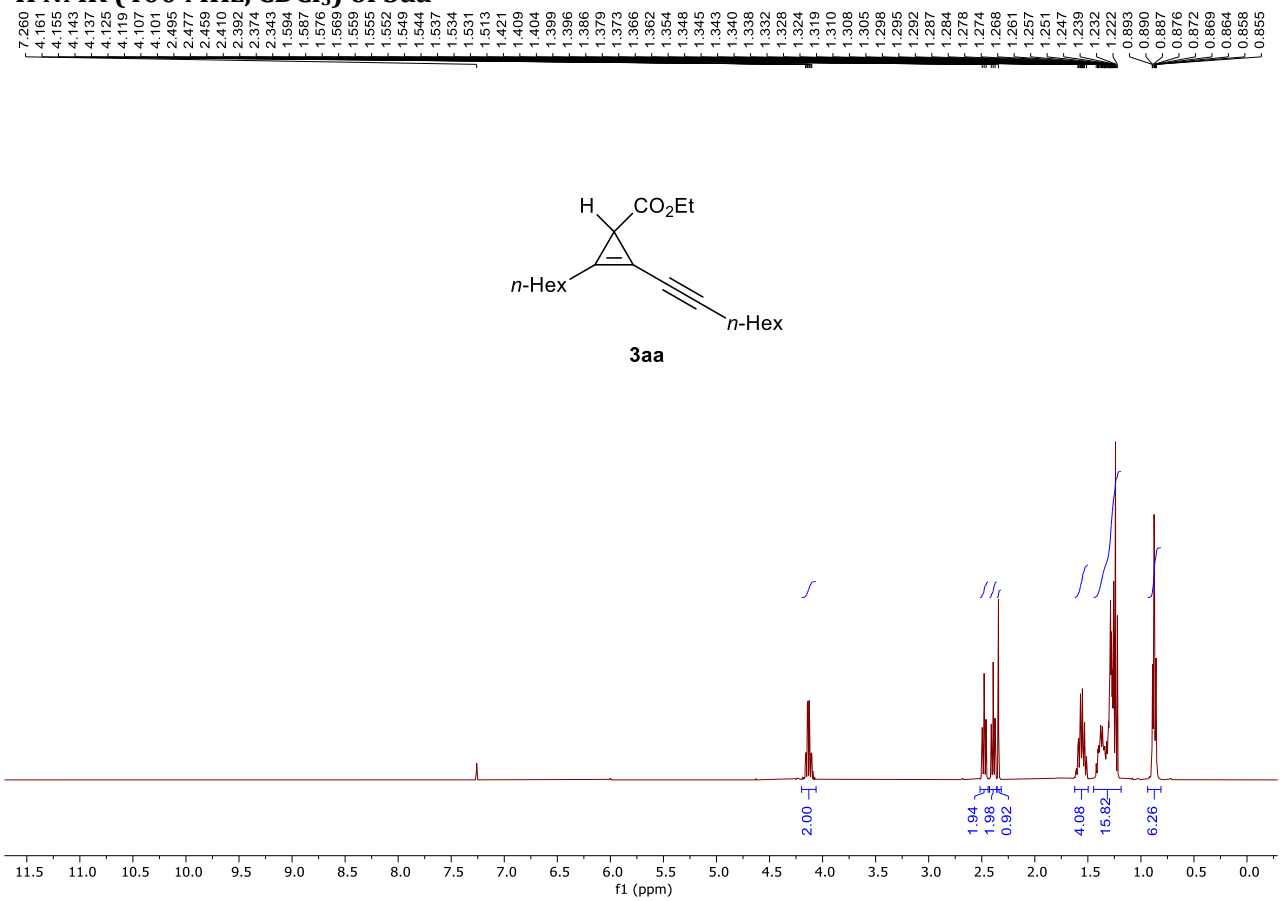


^{13}C NMR (101 MHz, $CDCl_3$) of 3z



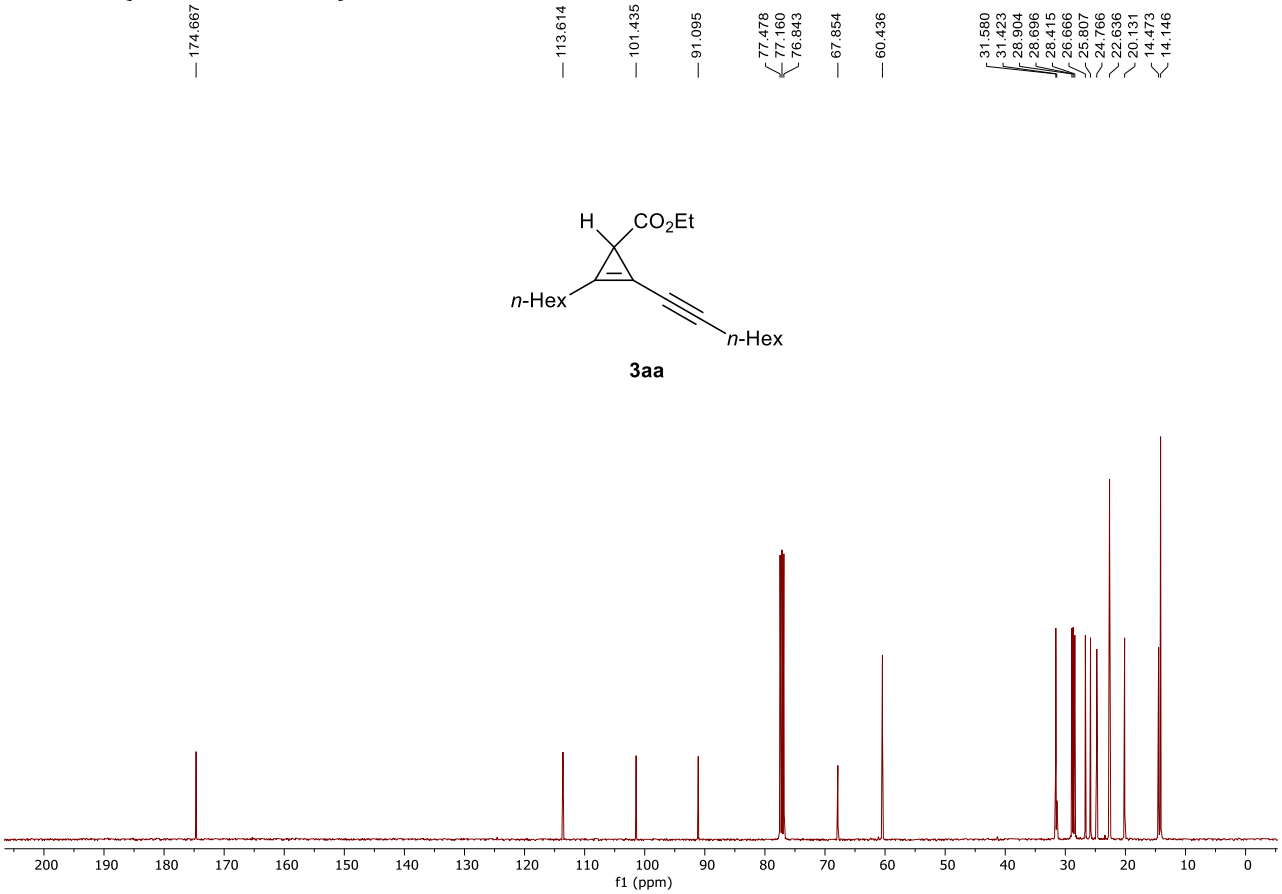
3z

^{1}H NMR (400 MHz, $CDCl_3$) of 3aa



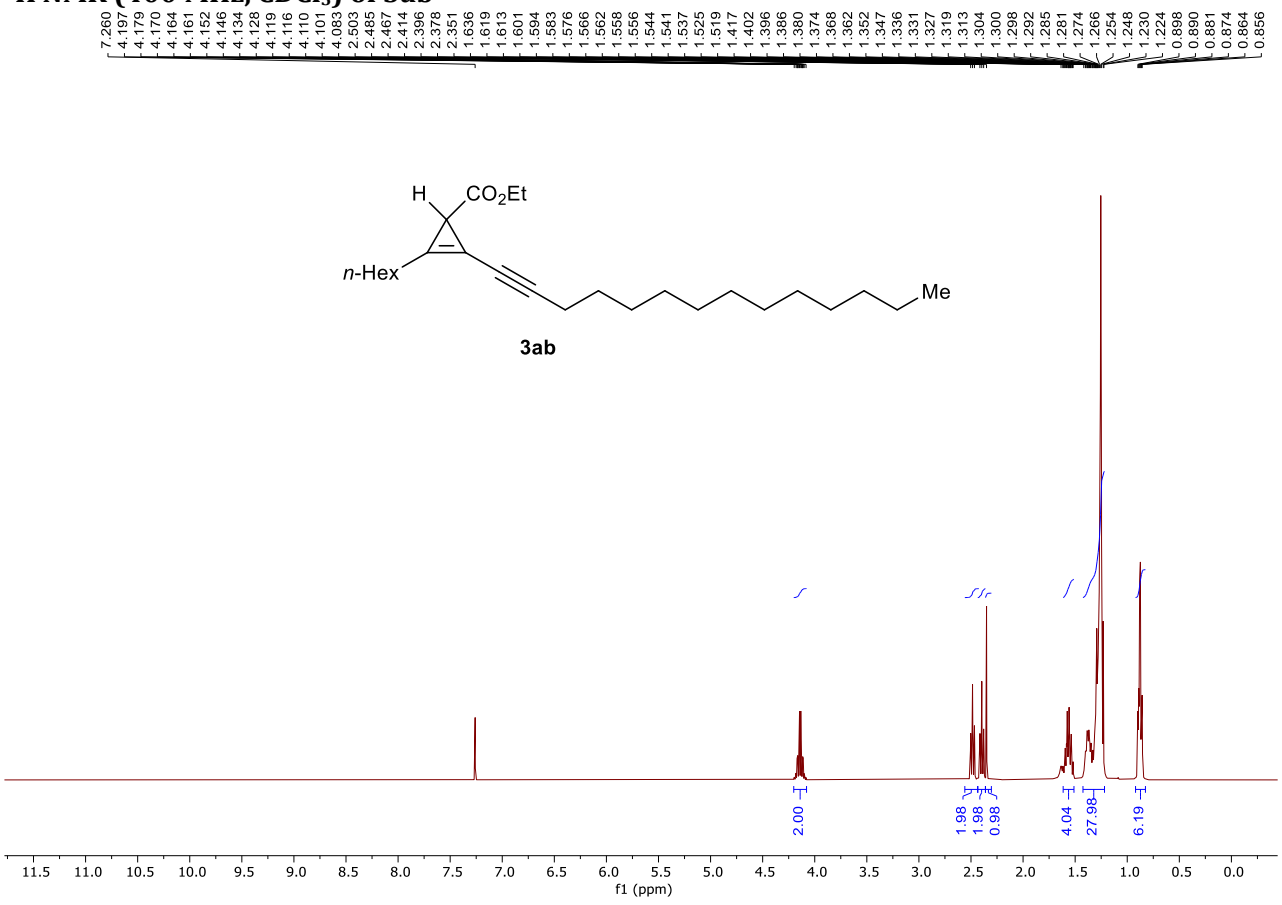
3aa

^{13}C NMR (101 MHz, $CDCl_3$) of 3aa



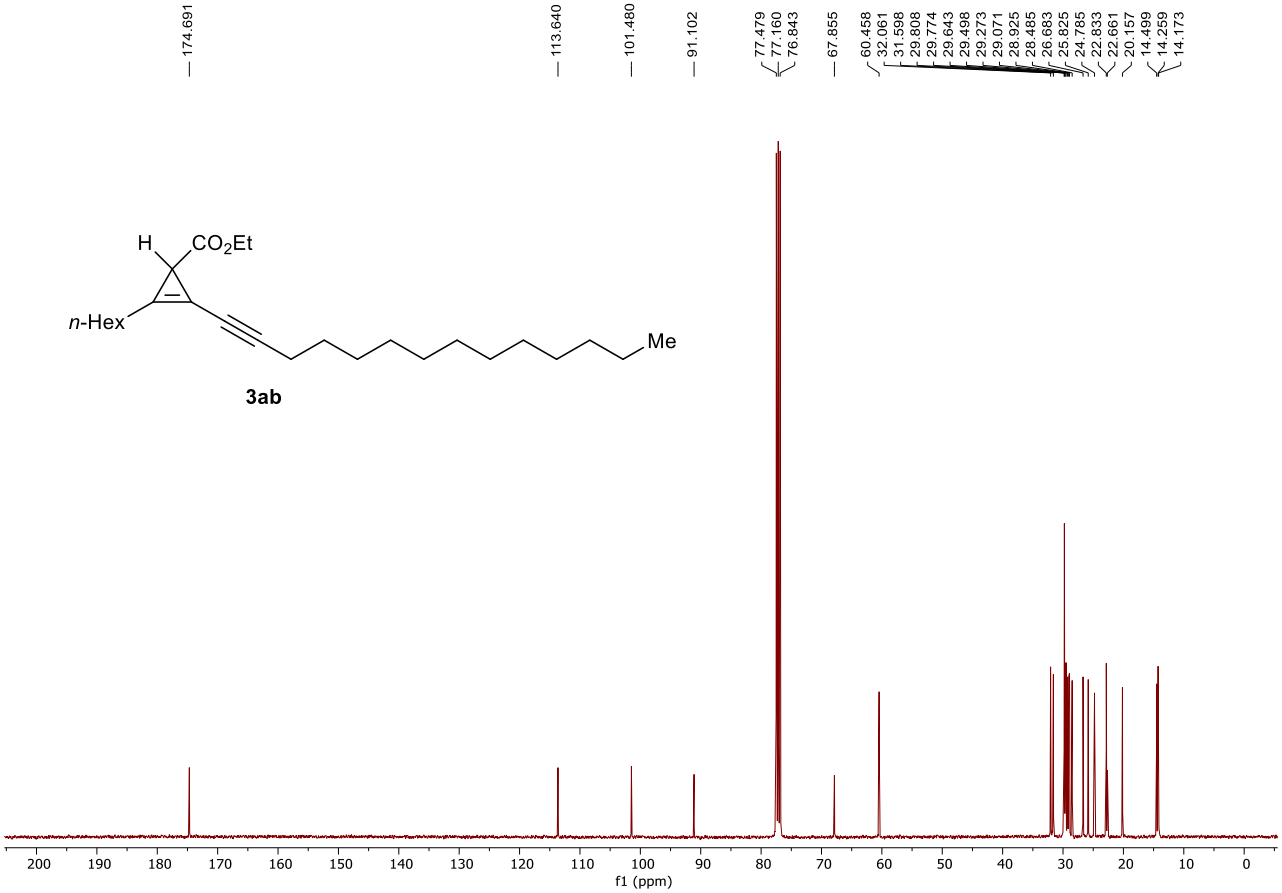
3aa

^{1}H NMR (400 MHz, $CDCl_3$) of 3ab



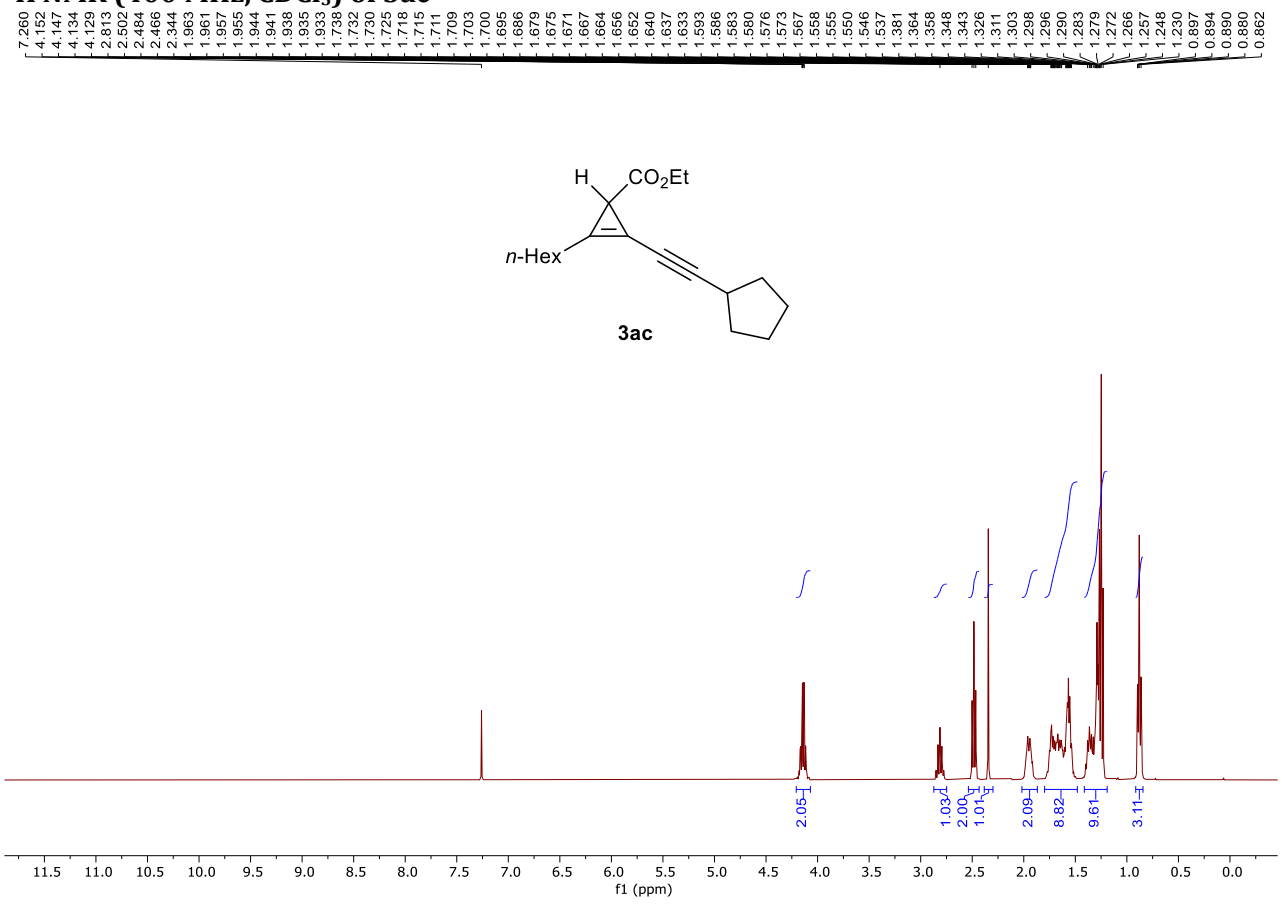
3ab

^{13}C NMR (101 MHz, $CDCl_3$) of 3ab



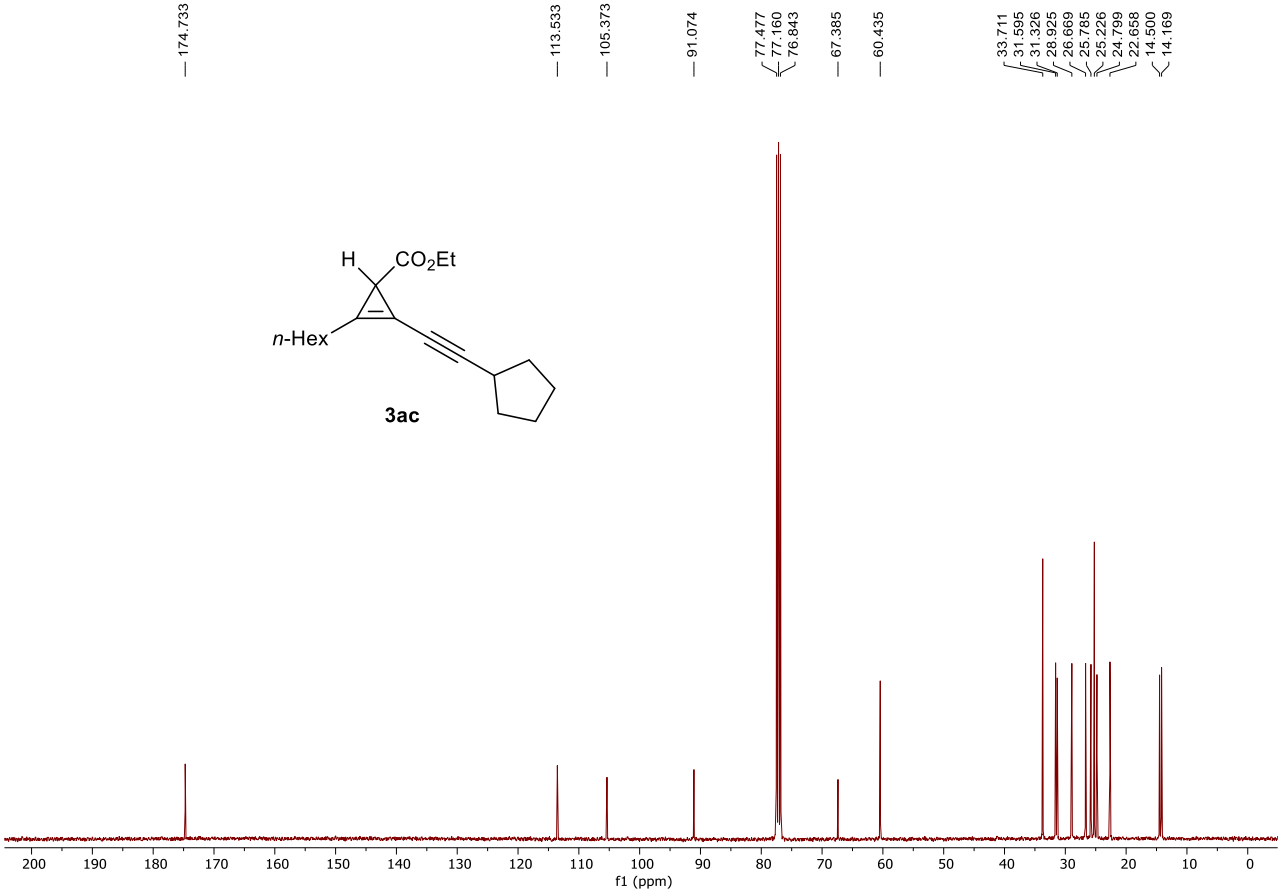
3ab

^{1}H NMR (400 MHz, $CDCl_3$) of 3ac

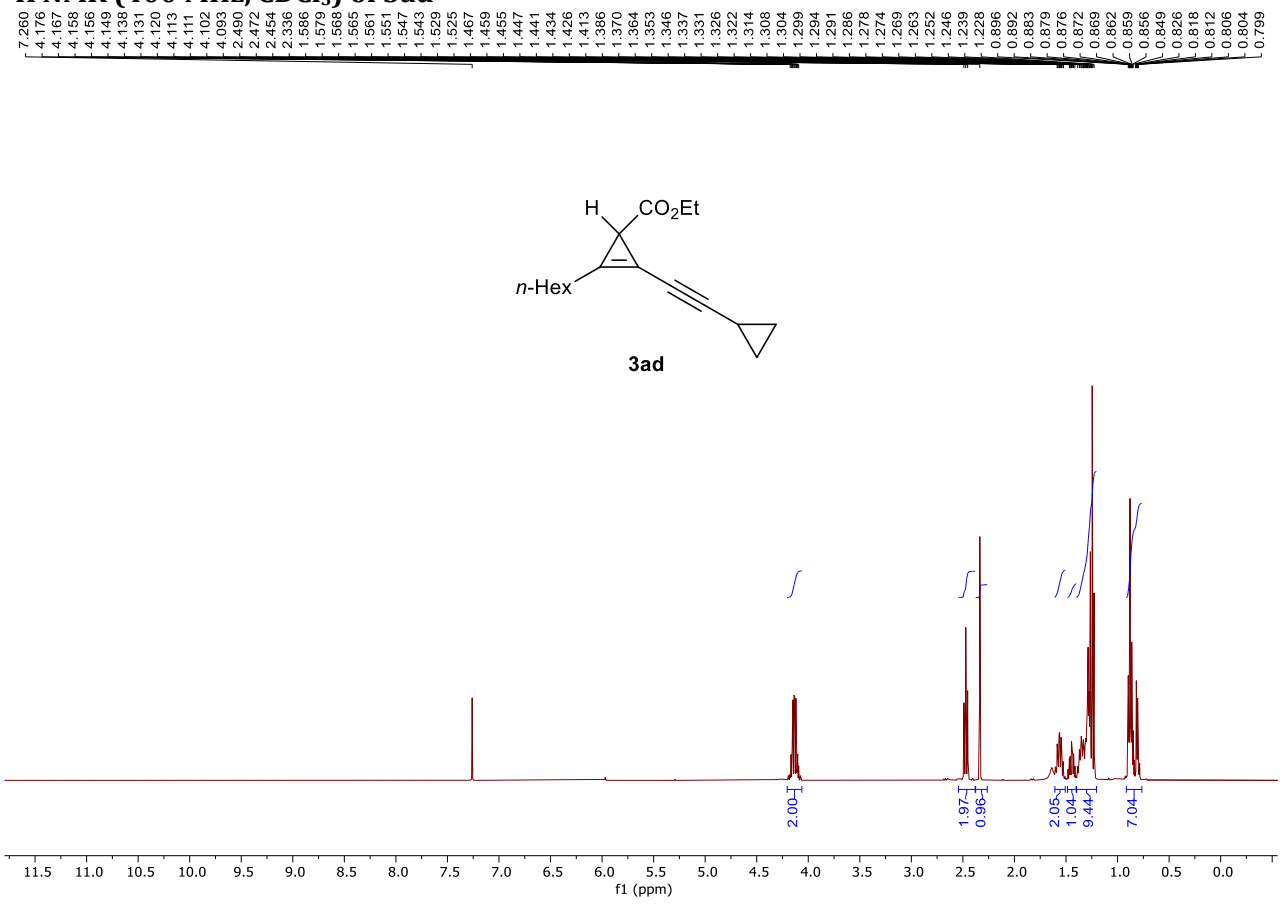


3ac

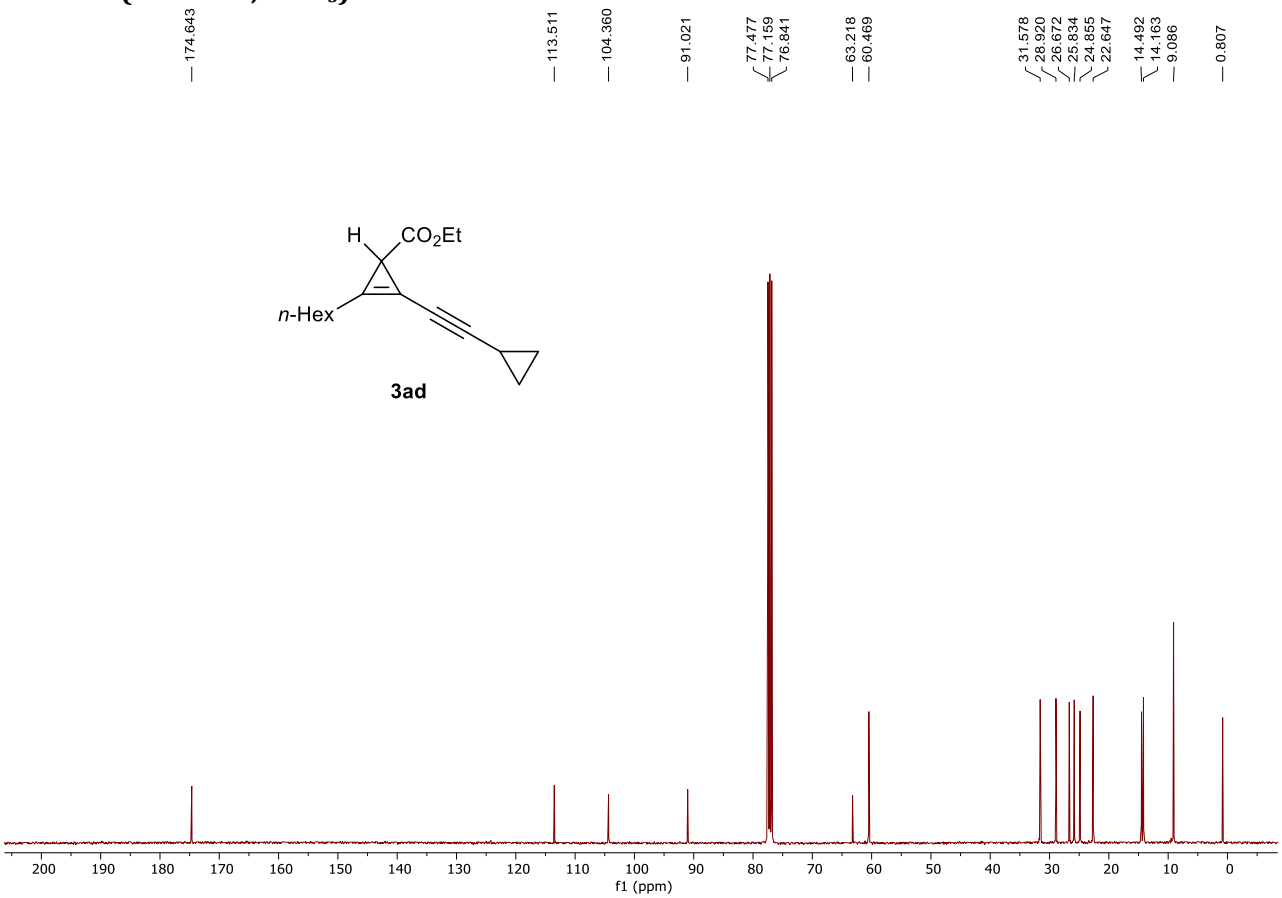
^{13}C NMR (101 MHz, $CDCl_3$) of 3ac



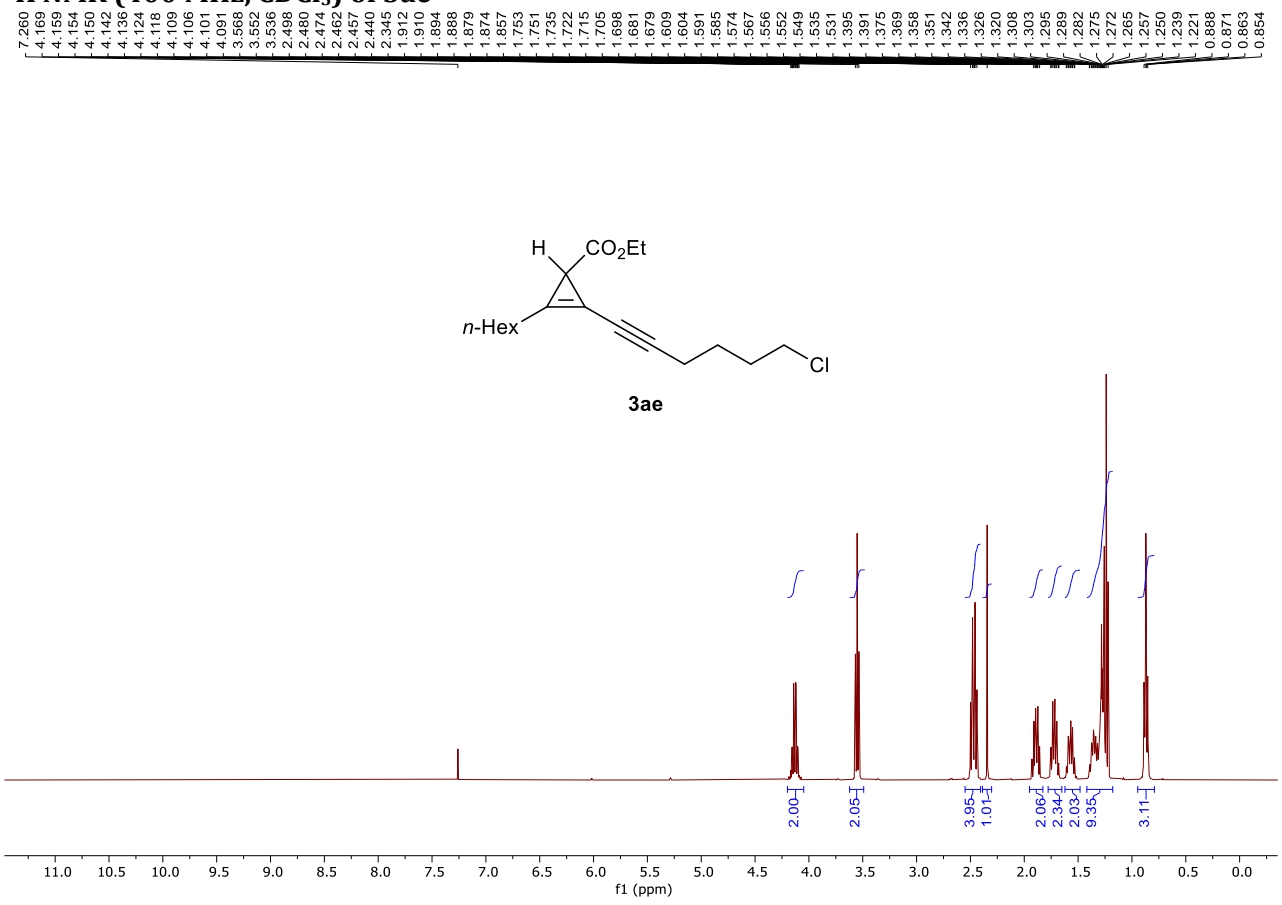
^{1}H NMR (400 MHz, $CDCl_3$) of 3ad



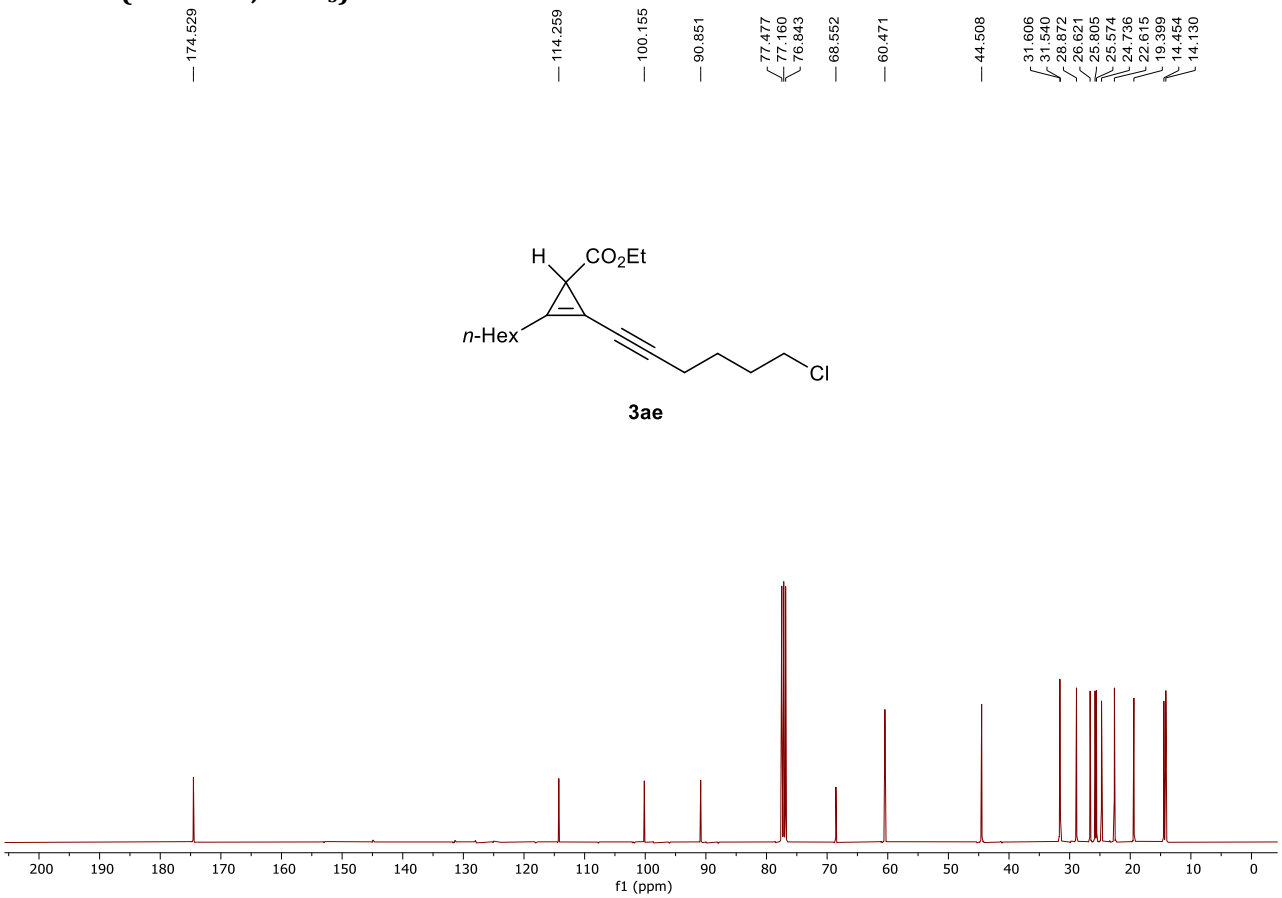
^{13}C NMR (101 MHz, $CDCl_3$) of 3ad



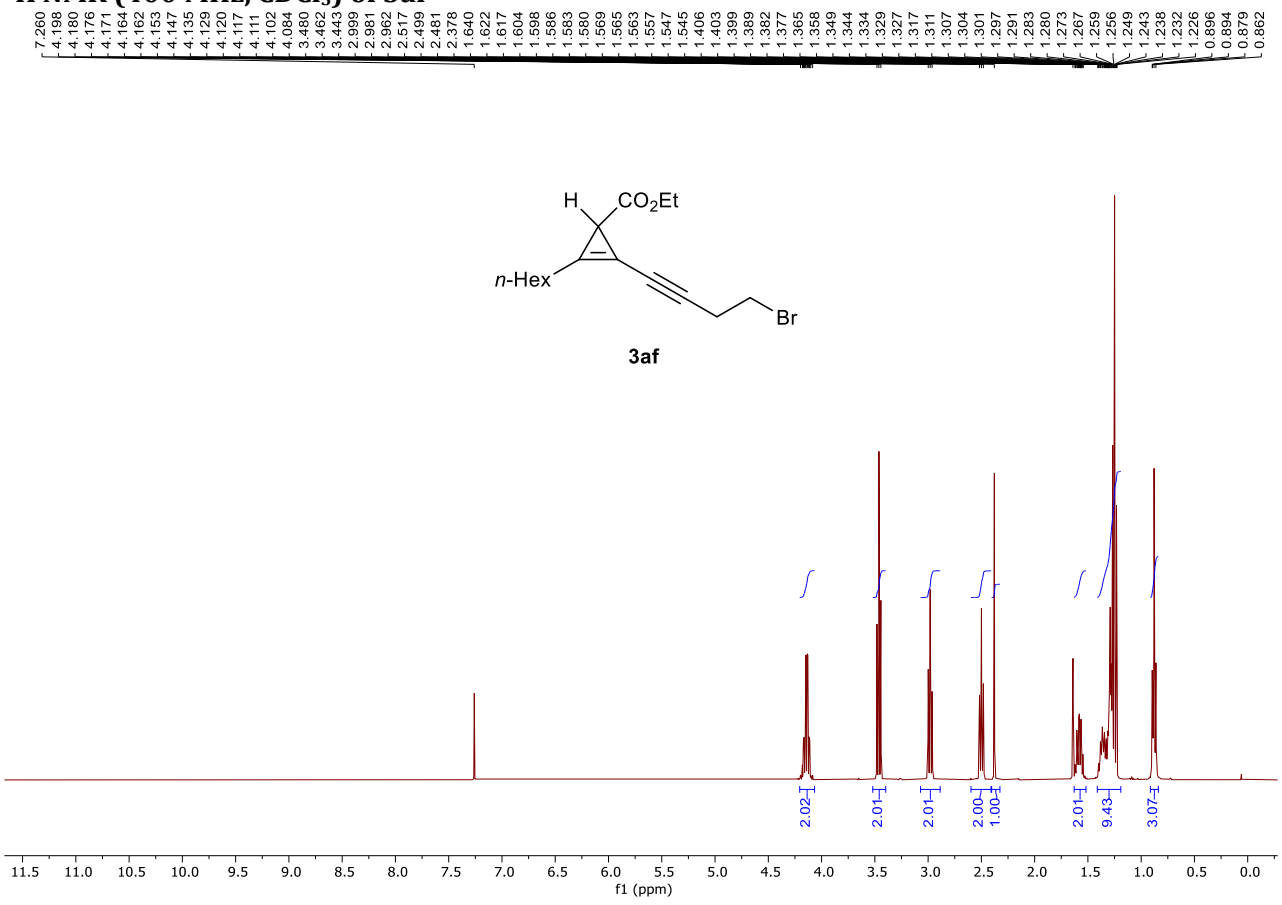
^{1}H NMR (400 MHz, $CDCl_3$) of 3ae



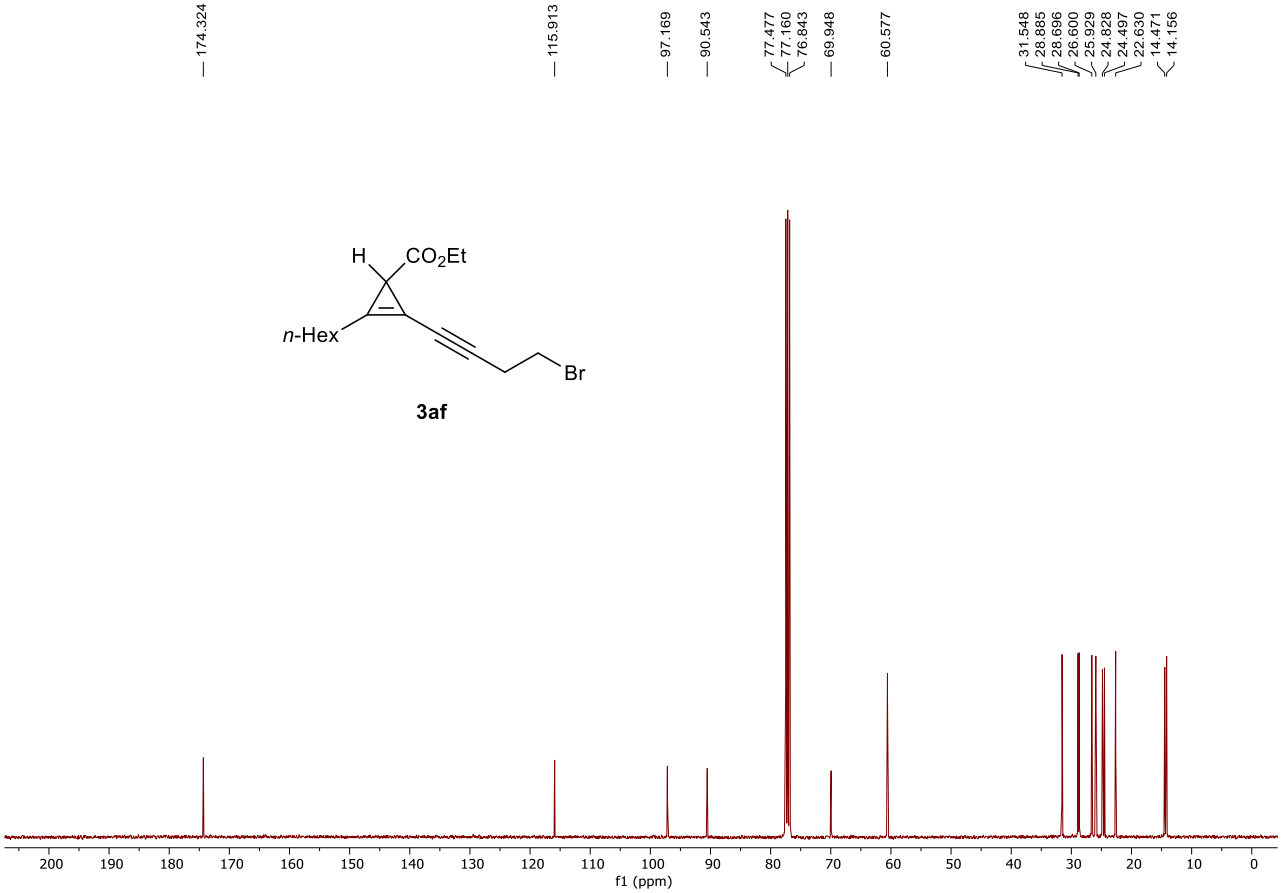
^{13}C NMR (101 MHz, $CDCl_3$) of 3ae



^{1}H NMR (400 MHz, $CDCl_3$) of 3af

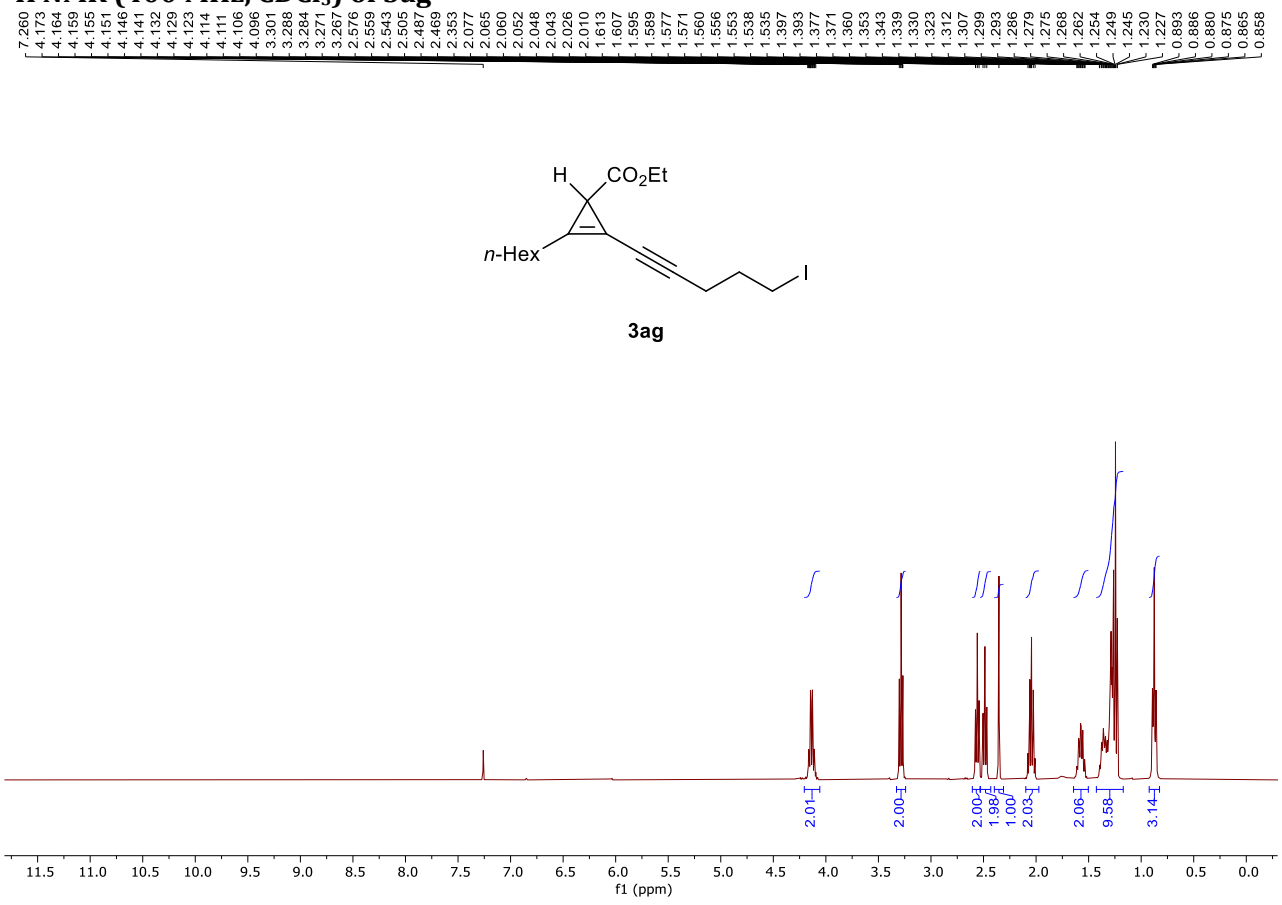


^{13}C NMR (101 MHz, $CDCl_3$) of 3af



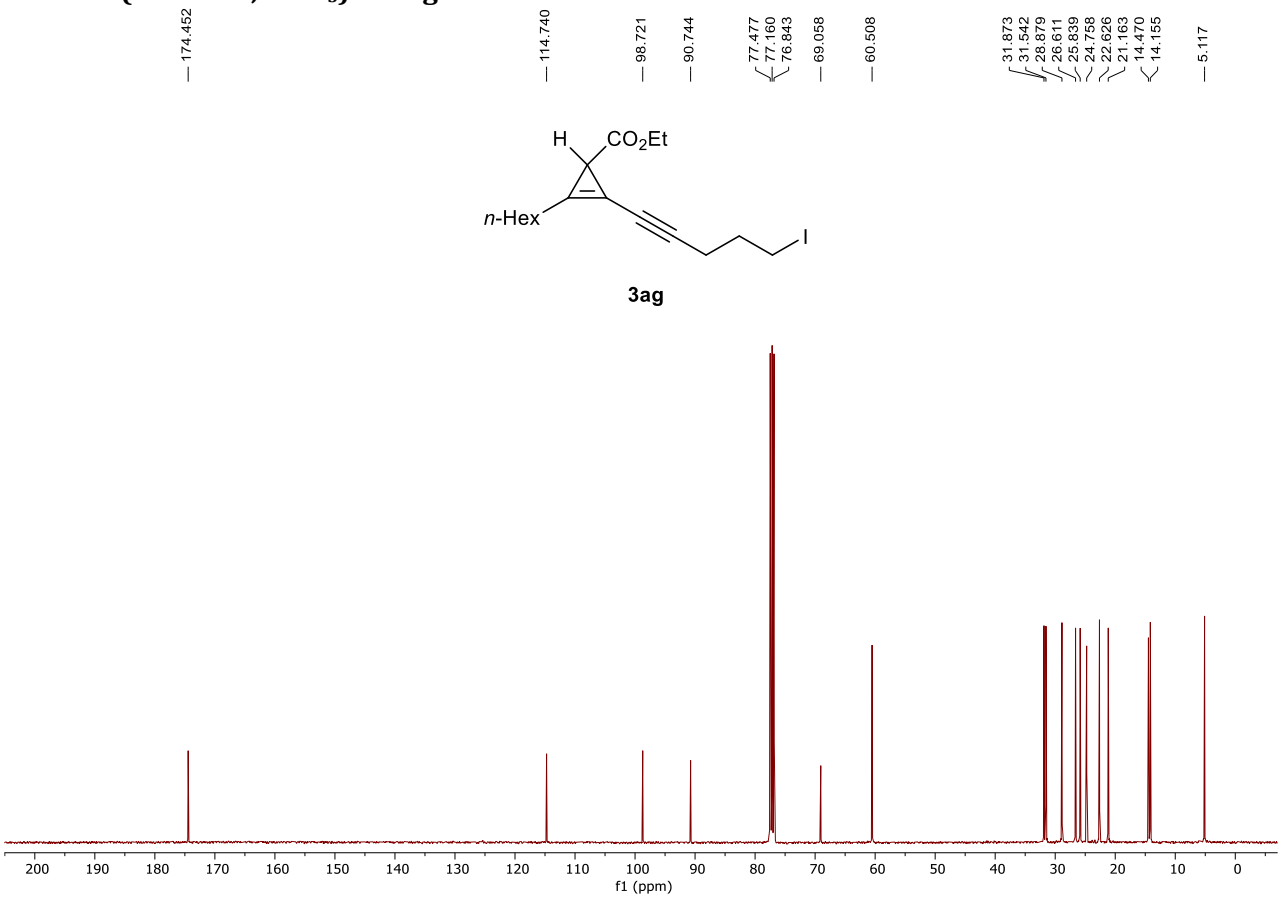
3af

^{1}H NMR (400 MHz, $CDCl_3$) of 3ag



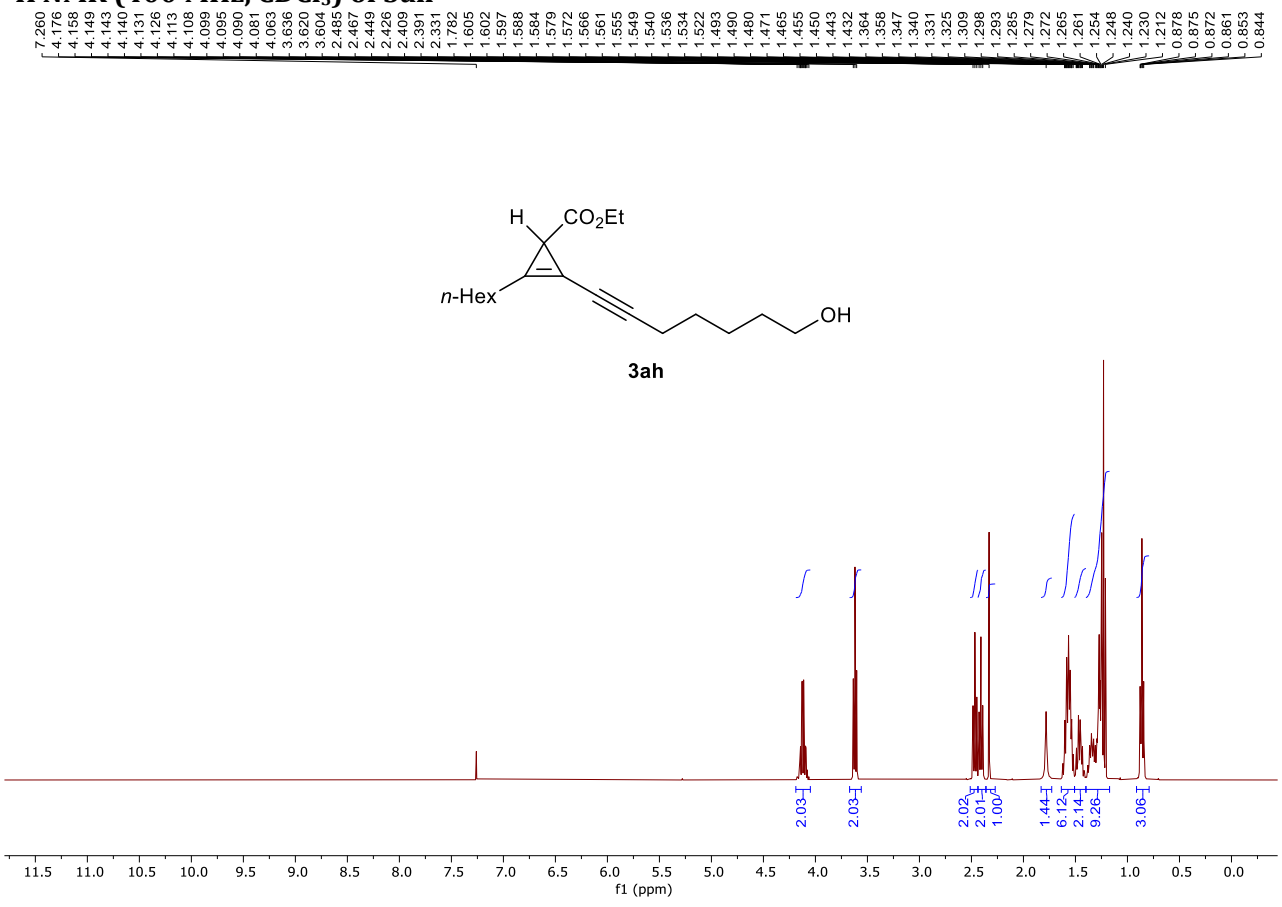
3ag

^{13}C NMR (101 MHz, $CDCl_3$) of 3ag



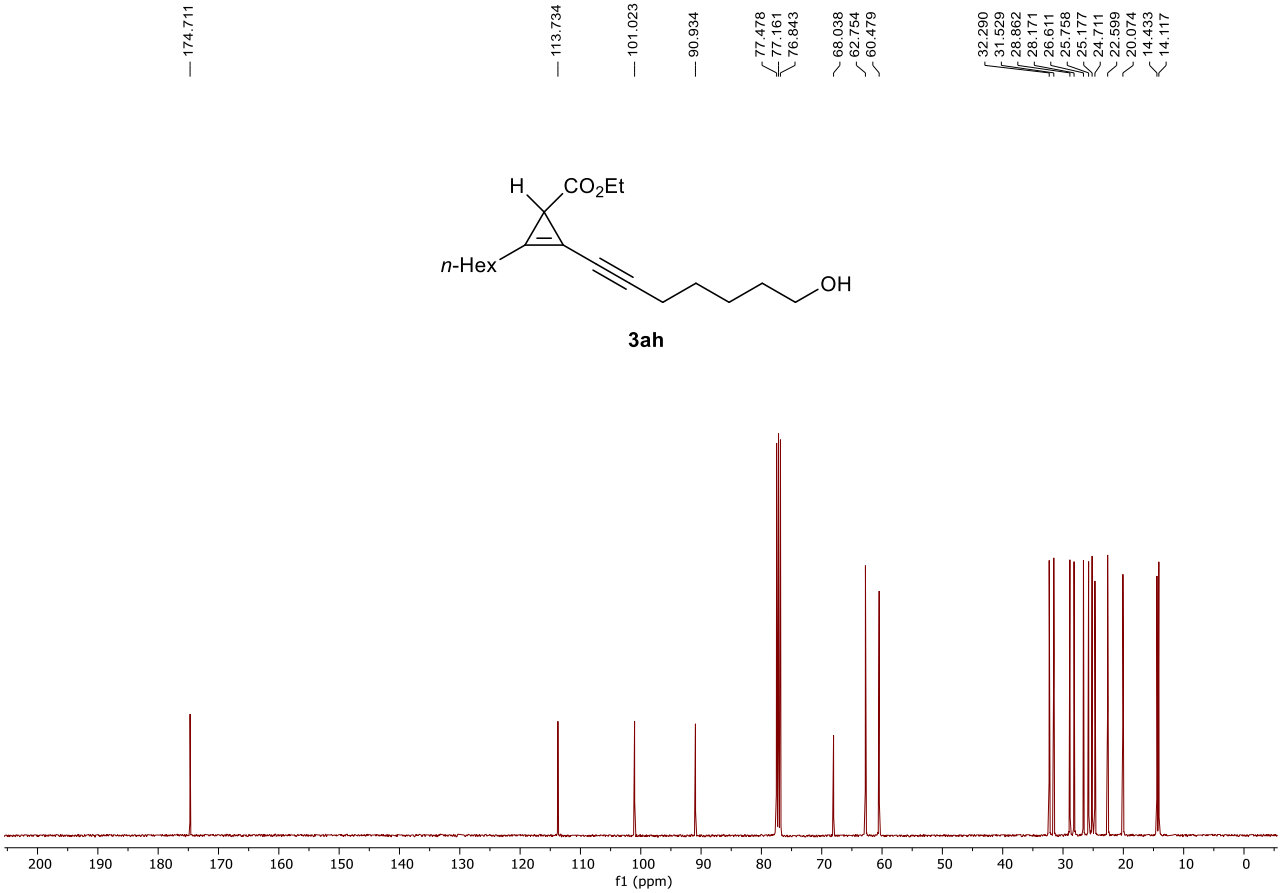
3ag

^{1}H NMR (400 MHz, $CDCl_3$) of 3ah



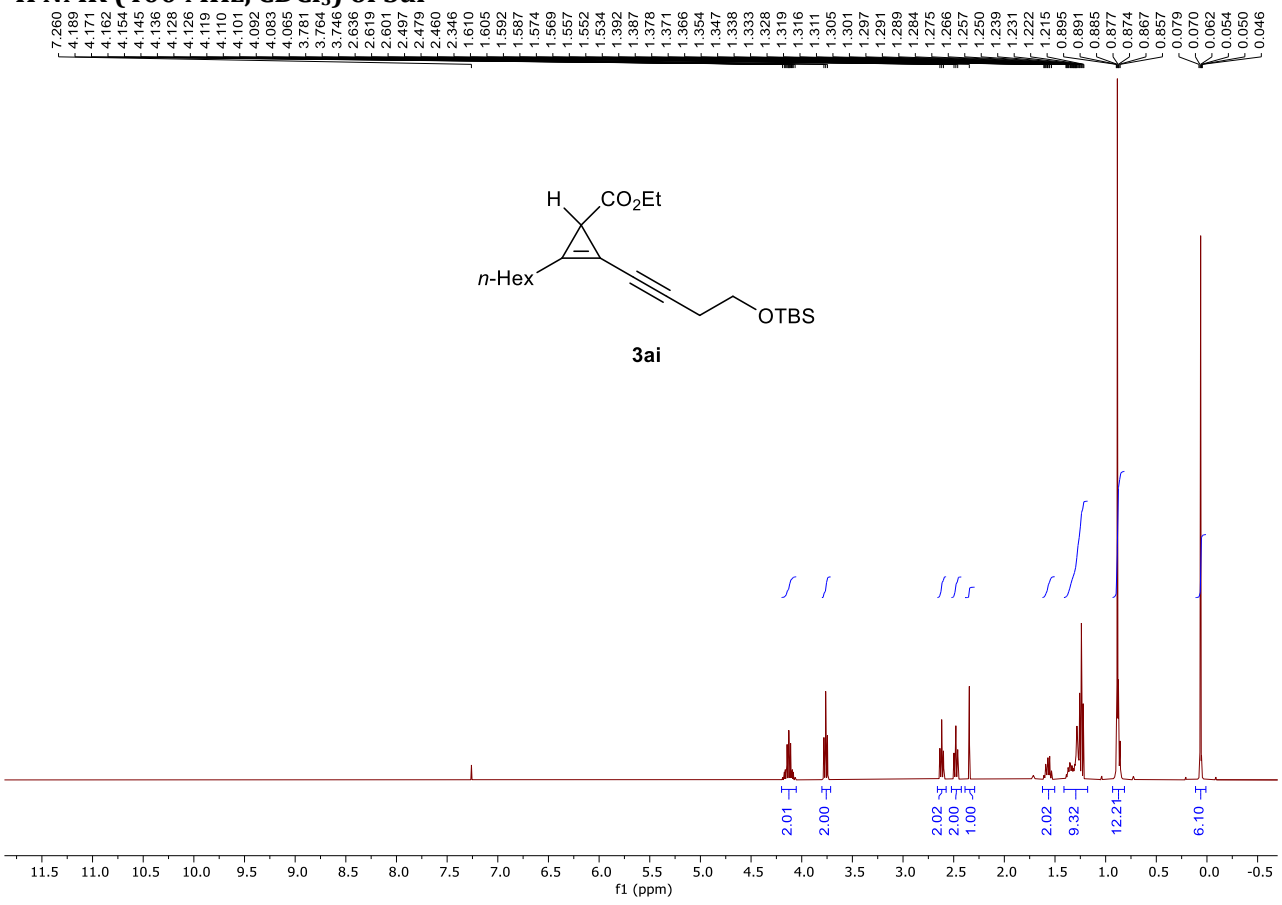
3ah

^{13}C NMR (101 MHz, $CDCl_3$) of 3ah



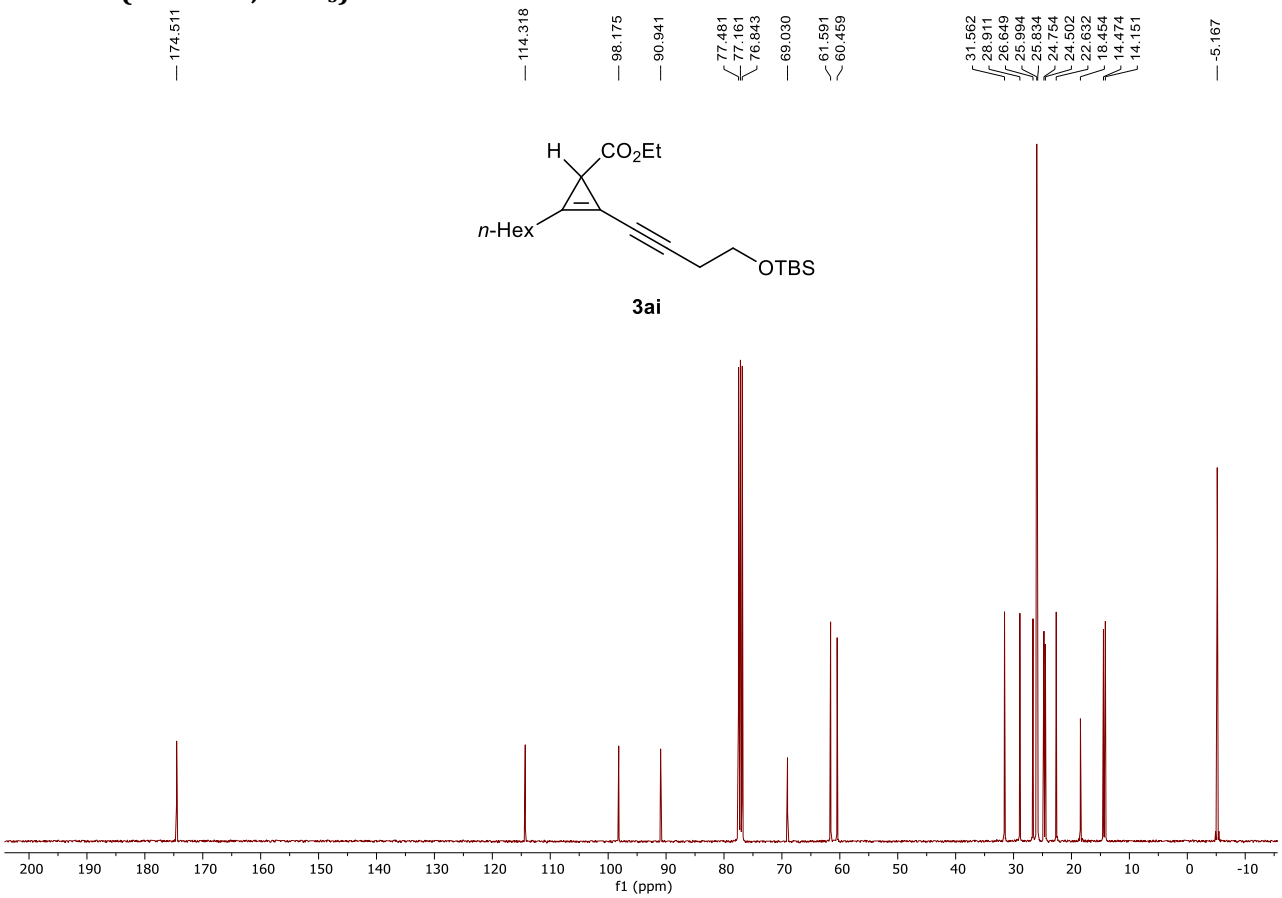
3ah

^{1}H NMR (400 MHz, $CDCl_3$) of 3ai

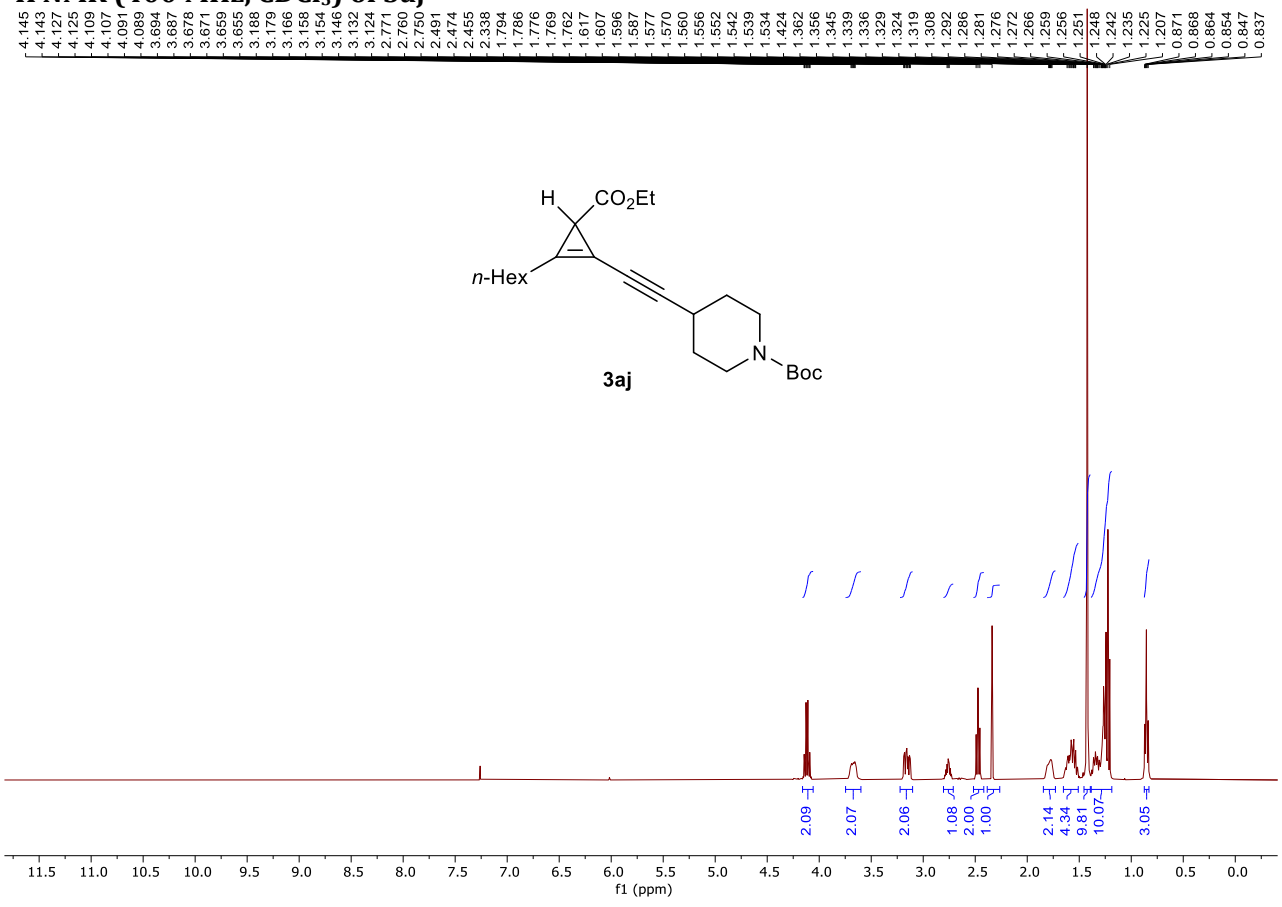


3ai

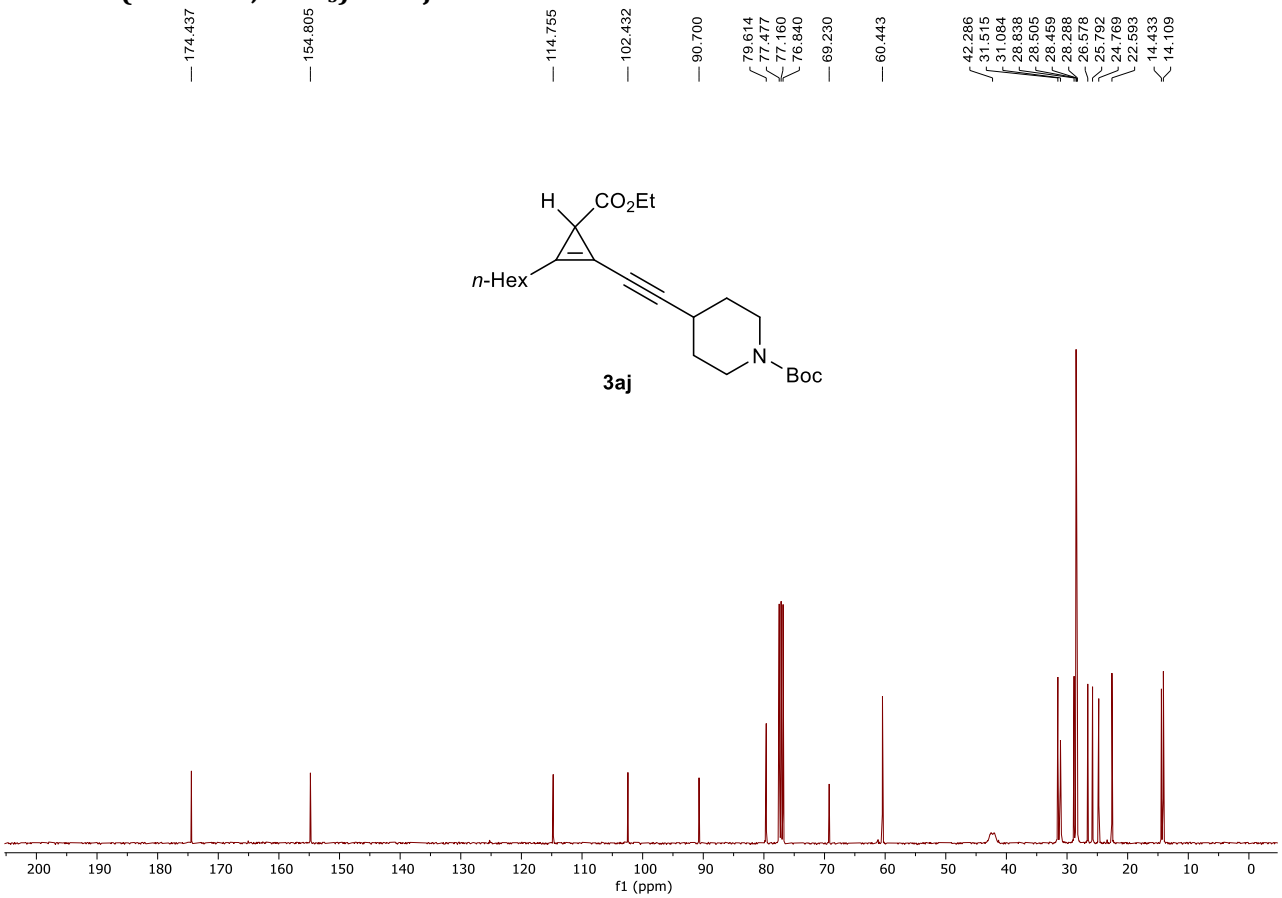
^{13}C NMR (101 MHz, $CDCl_3$) of 3ai



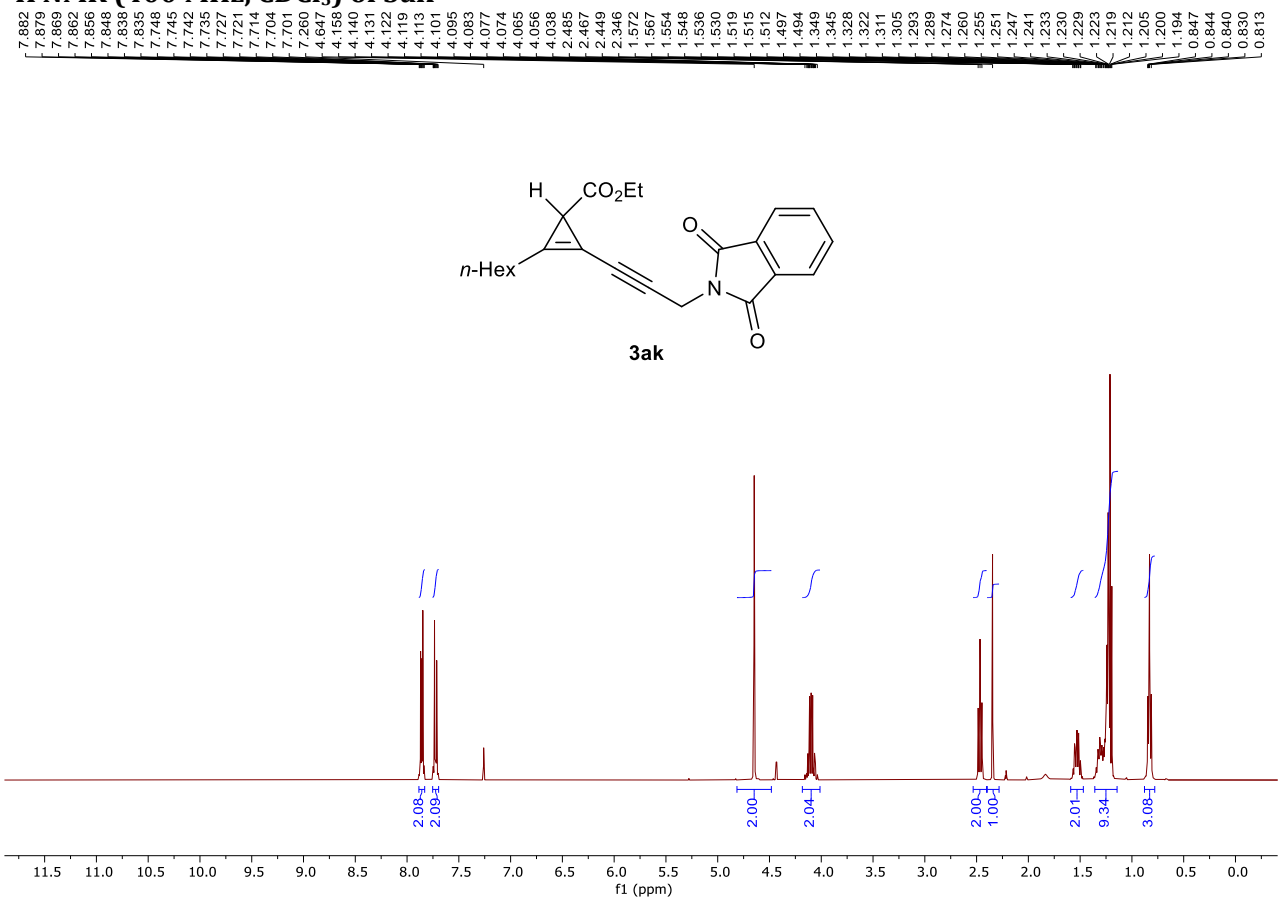
^{1}H NMR (400 MHz, $CDCl_3$) of 3aj



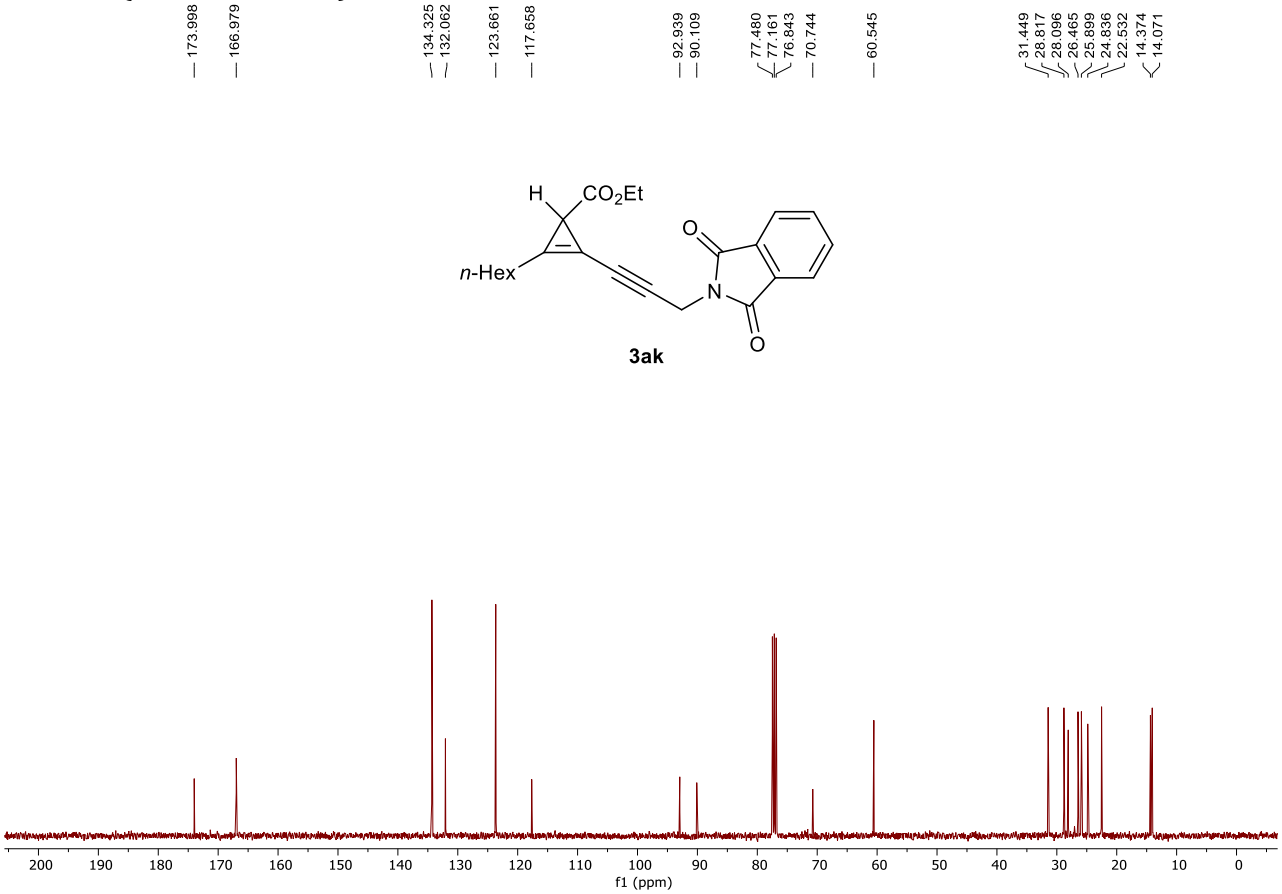
^{13}C NMR (101 MHz, $CDCl_3$) of 3aj



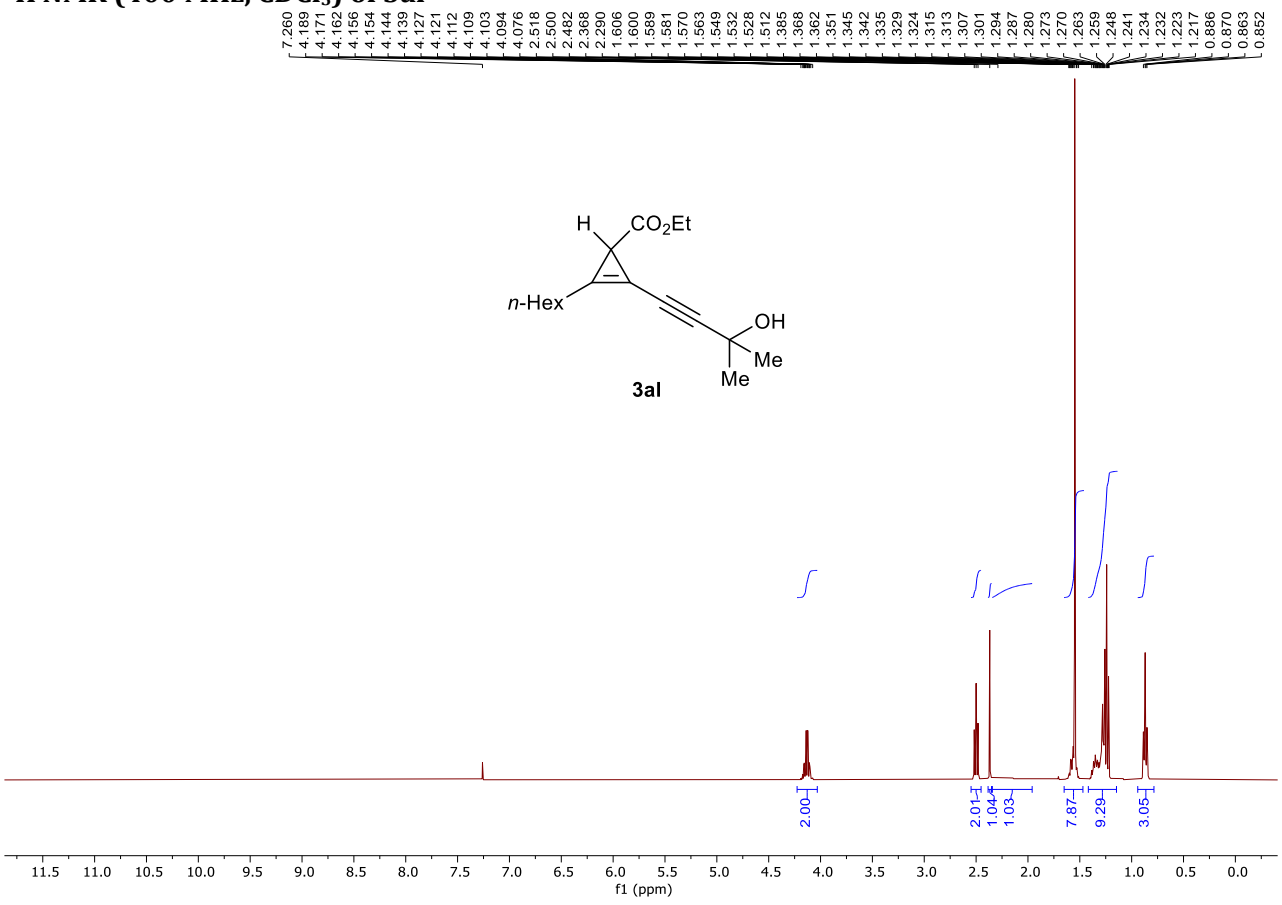
^{1}H NMR (400 MHz, $CDCl_3$) of 3ak



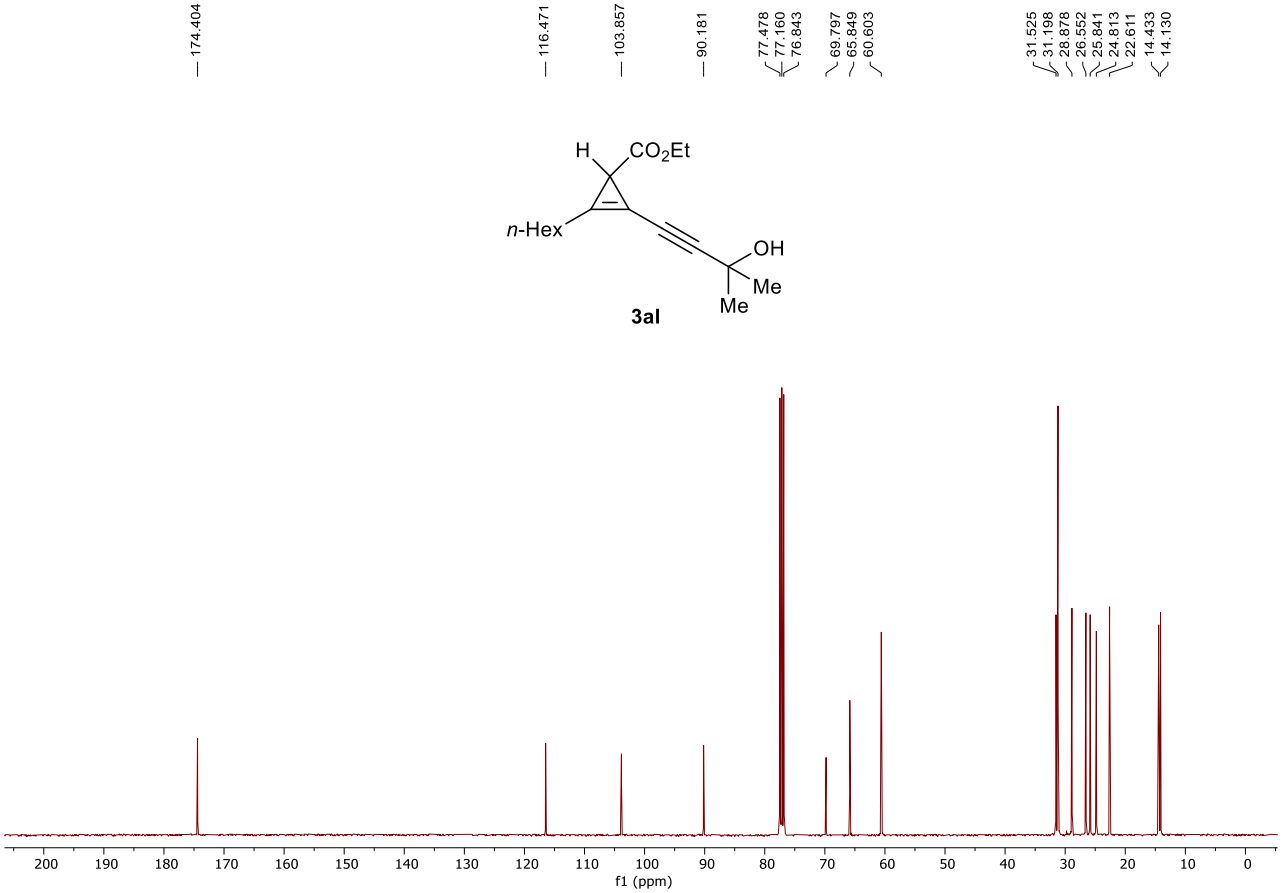
^{13}C NMR (101 MHz, $CDCl_3$) of 3ak



^{1}H NMR (400 MHz, $CDCl_3$) of 3al

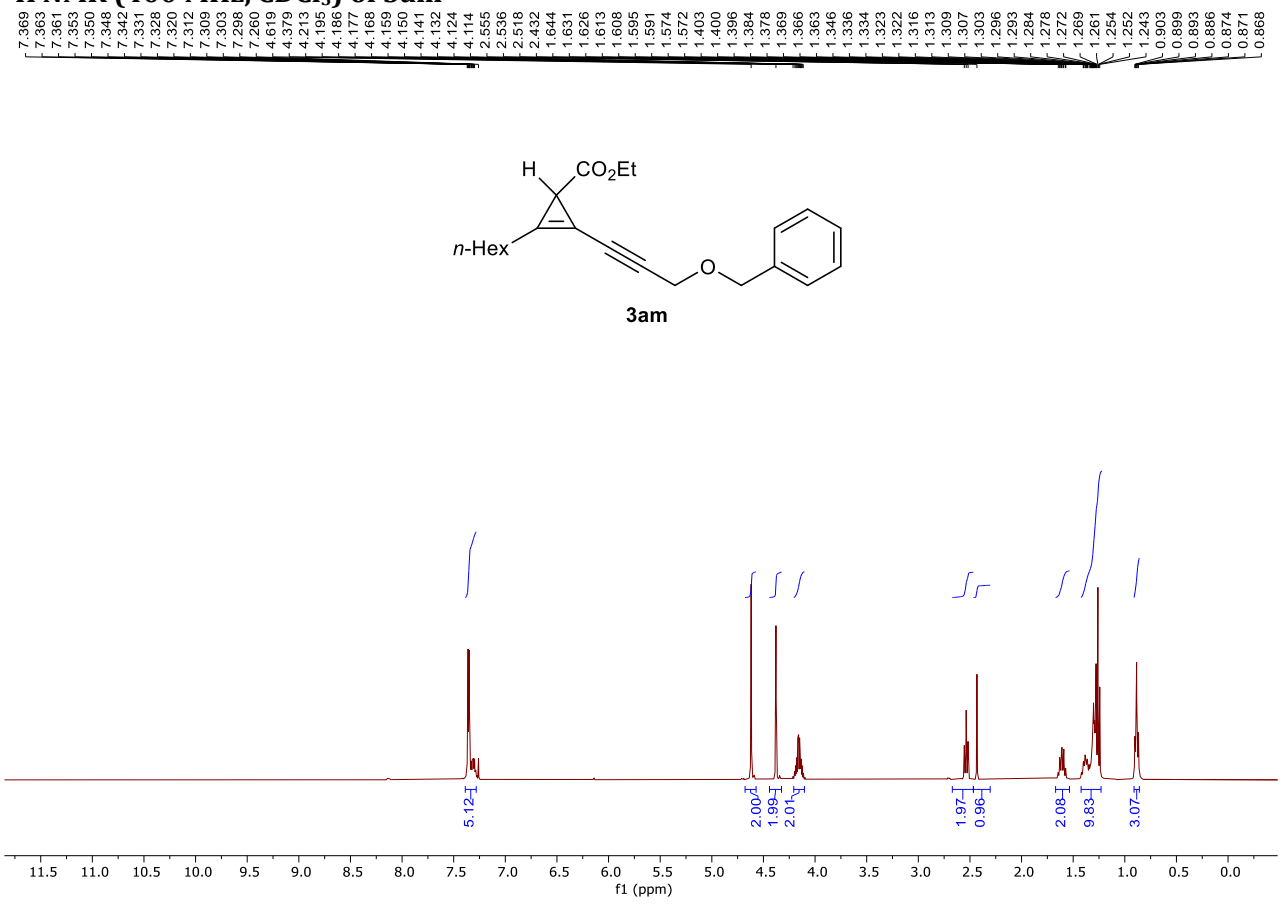


^{13}C NMR (101 MHz, $CDCl_3$) of 3al



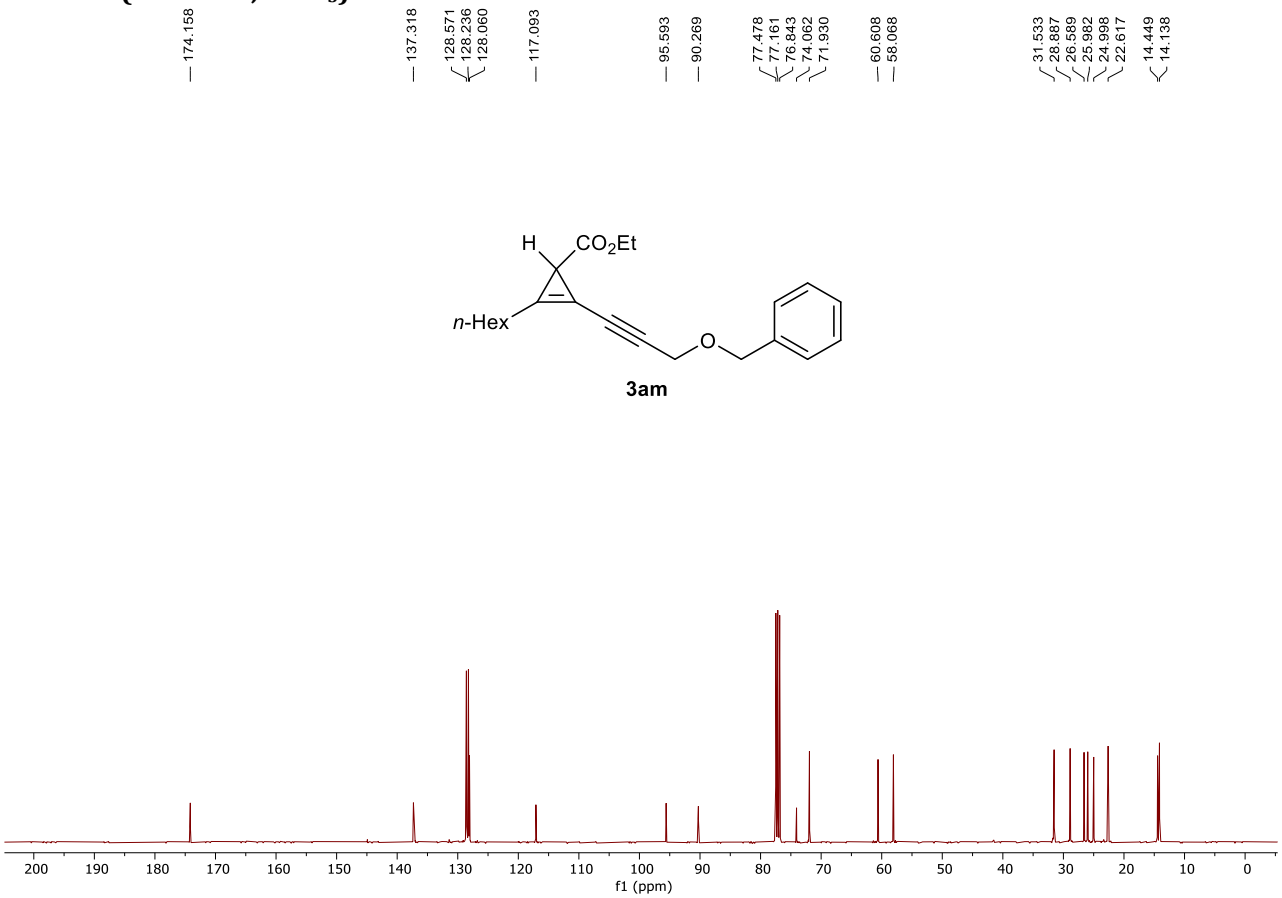
3al

^{1}H NMR (400 MHz, $CDCl_3$) of 3am

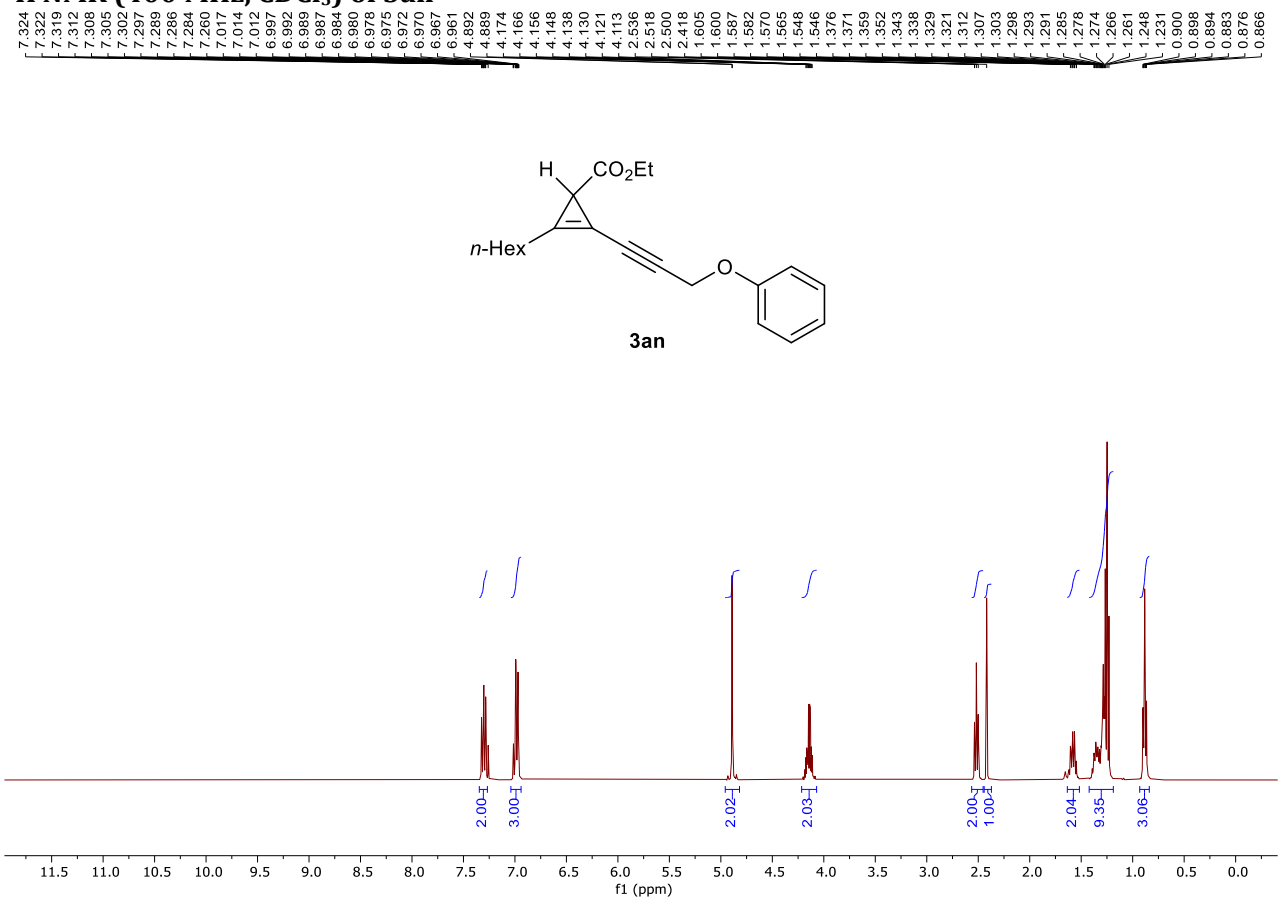


3am

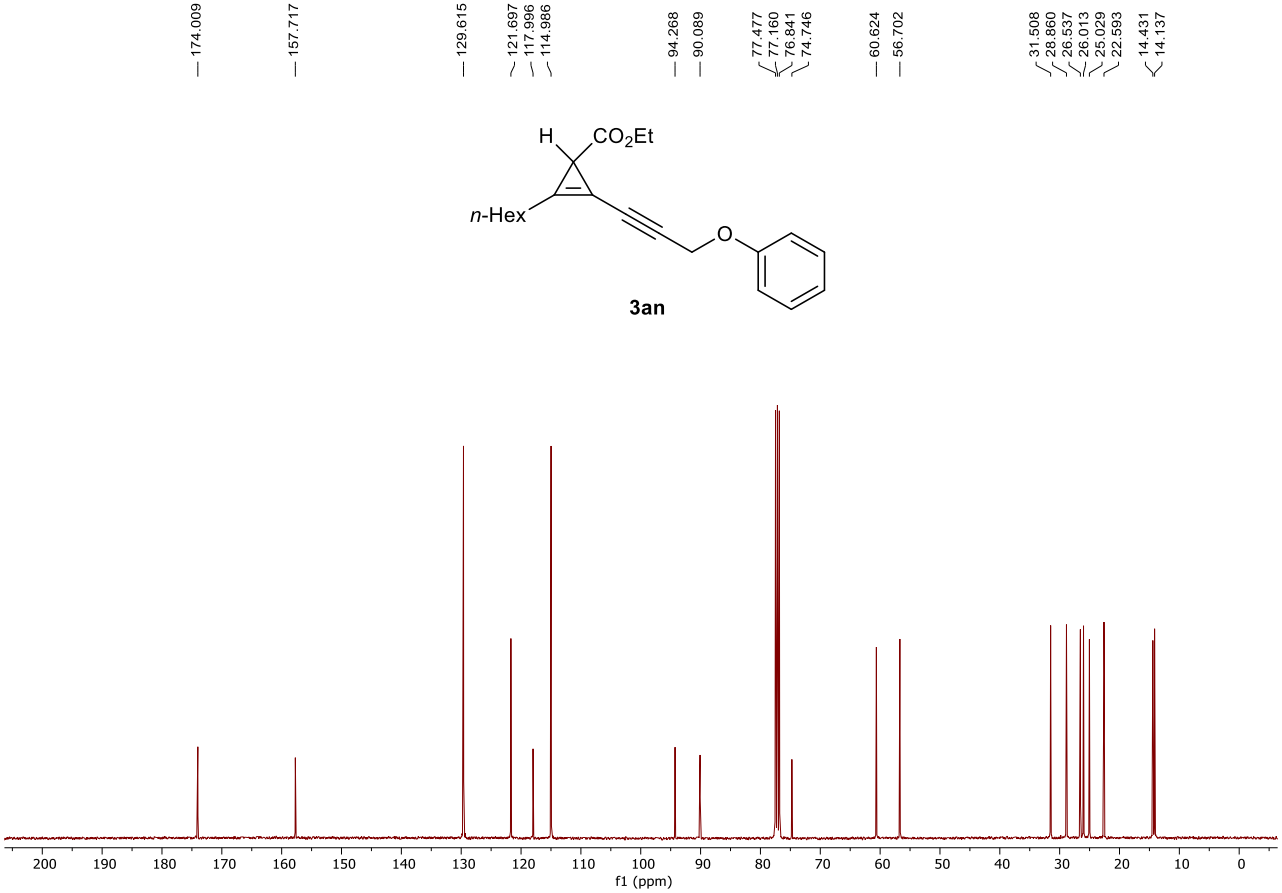
^{13}C NMR (101 MHz, $CDCl_3$) of 3am



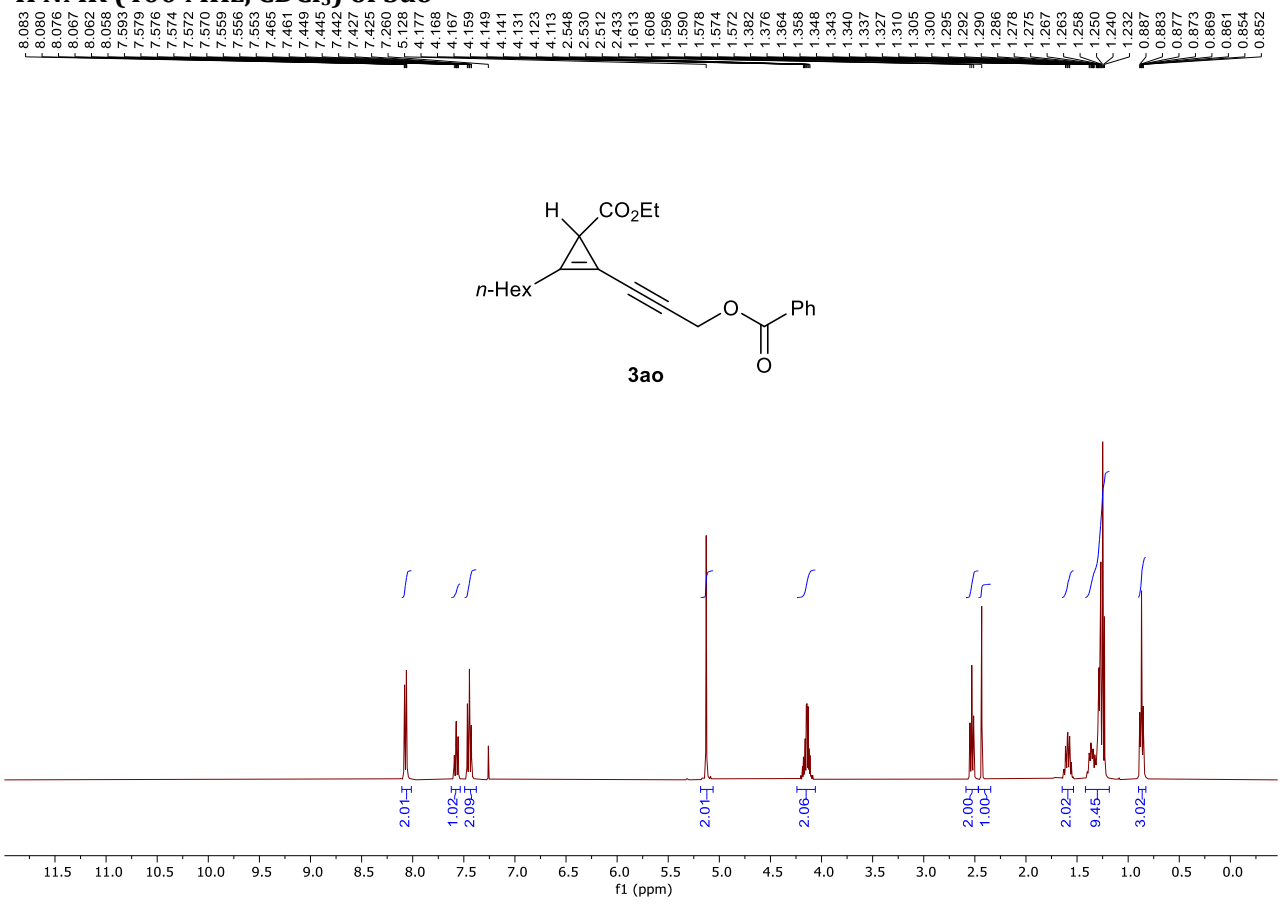
^{1}H NMR (400 MHz, $CDCl_3$) of 3an



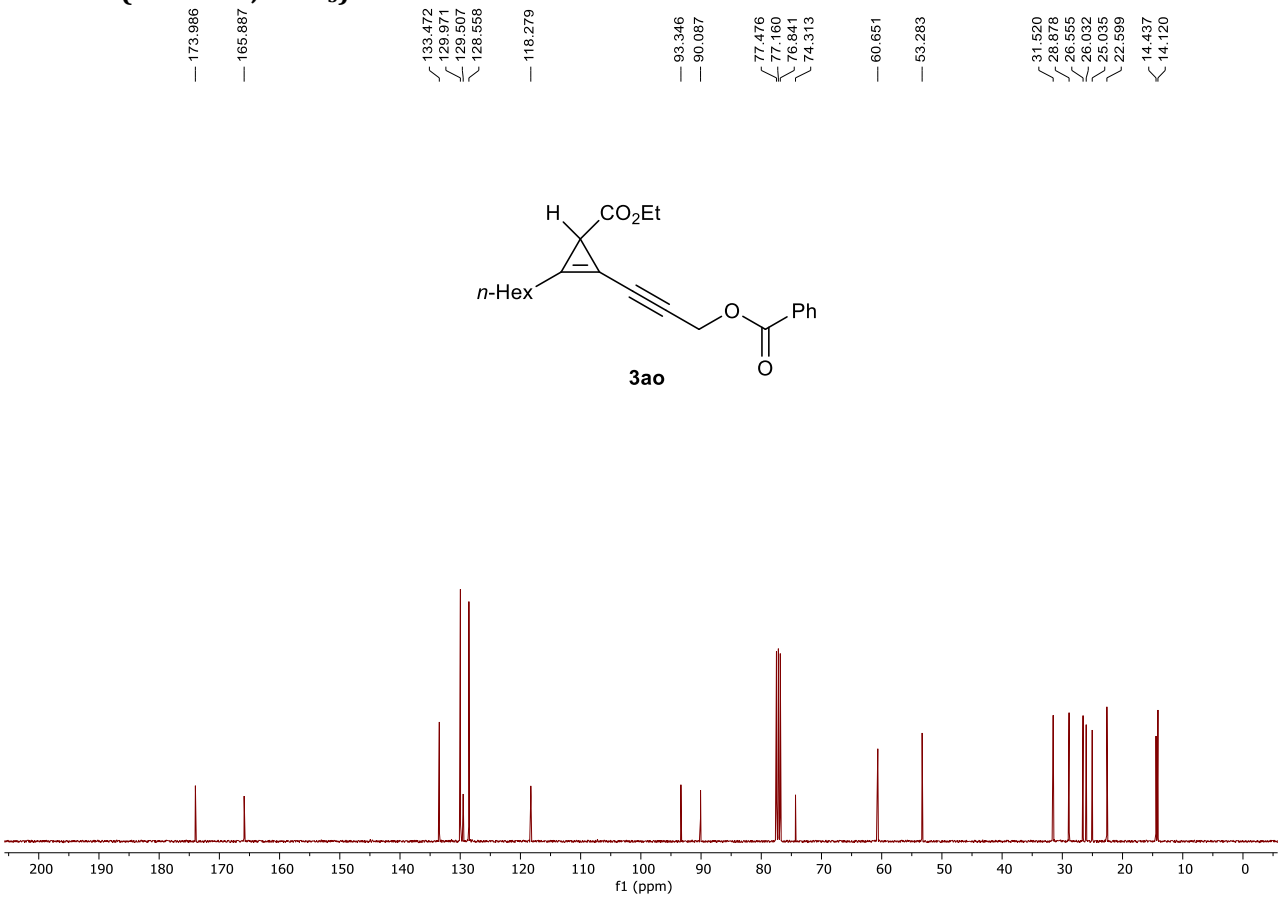
^{13}C NMR (101 MHz, $CDCl_3$) of 3an



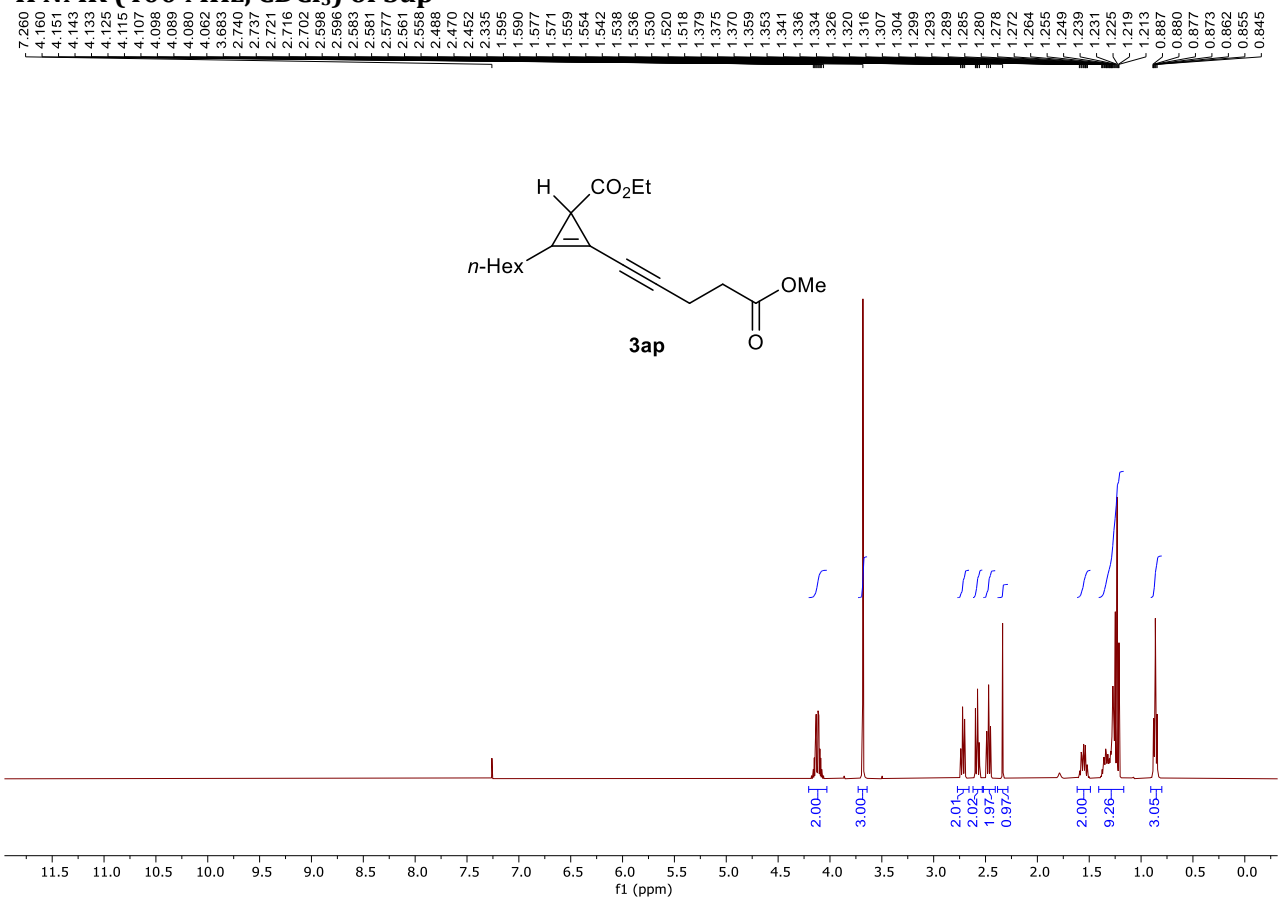
^{1}H NMR (400 MHz, $CDCl_3$) of 3ao



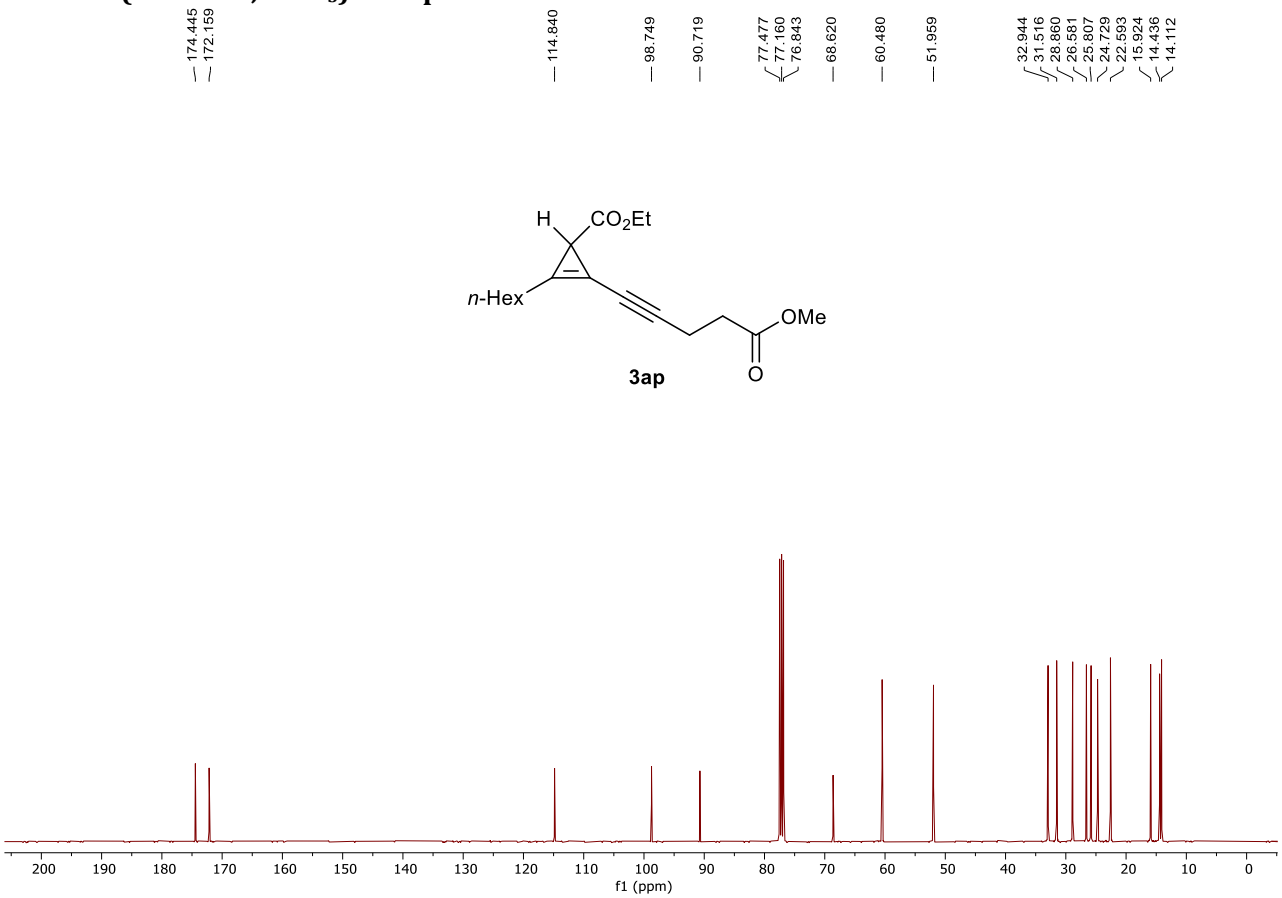
^{13}C NMR (101 MHz, $CDCl_3$) of 3ao



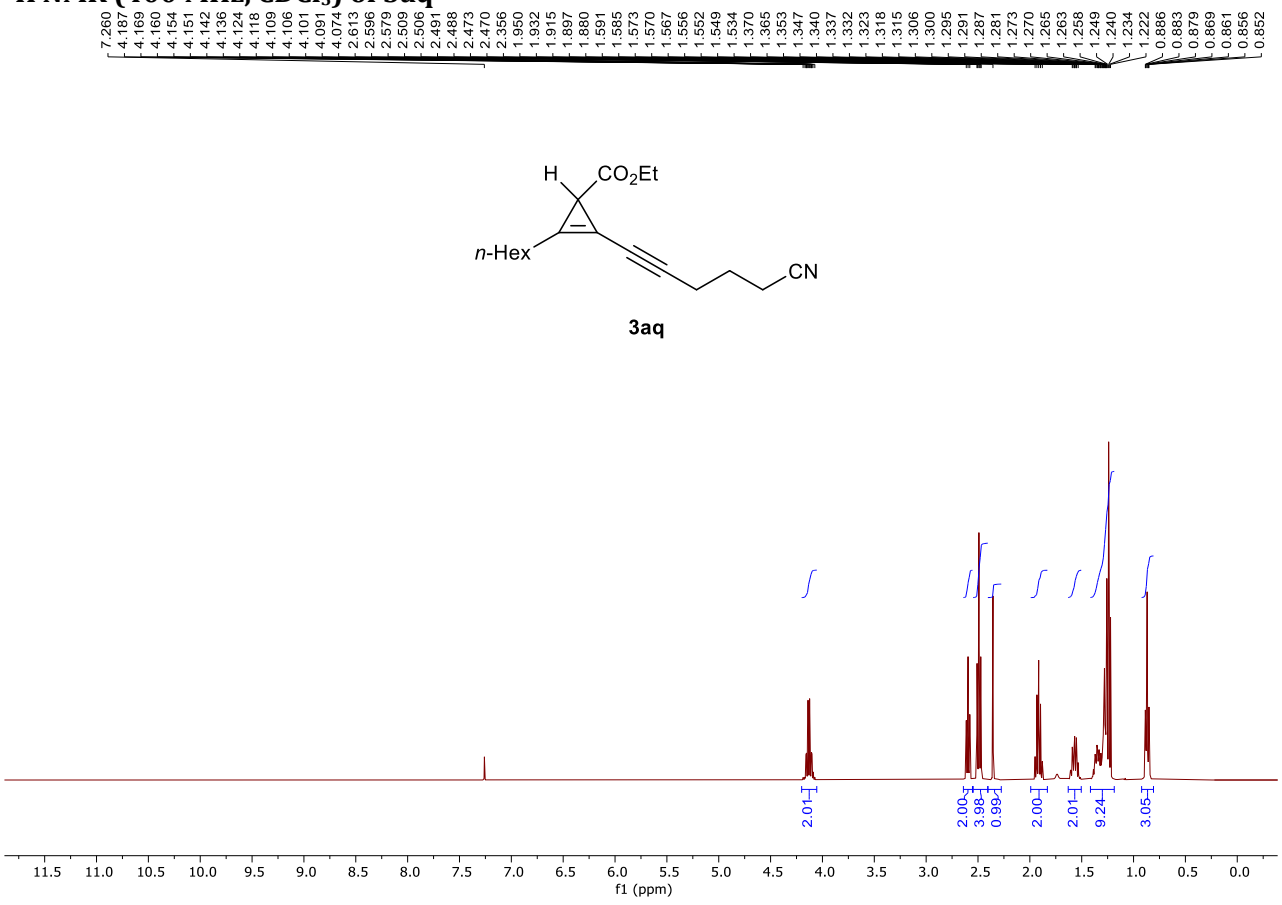
^{1}H NMR (400 MHz, $CDCl_3$) of 3ap



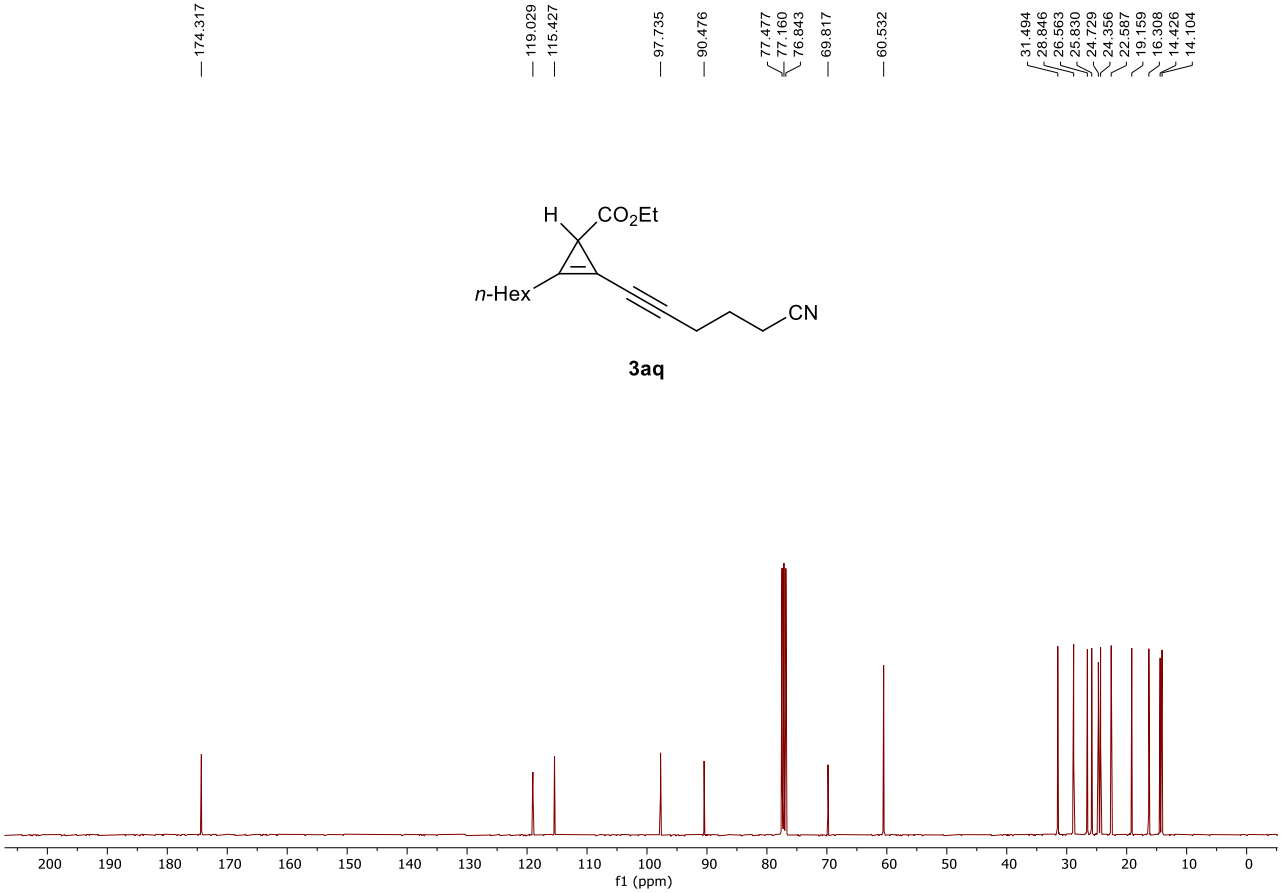
^{13}C NMR (101 MHz, $CDCl_3$) of 3ap



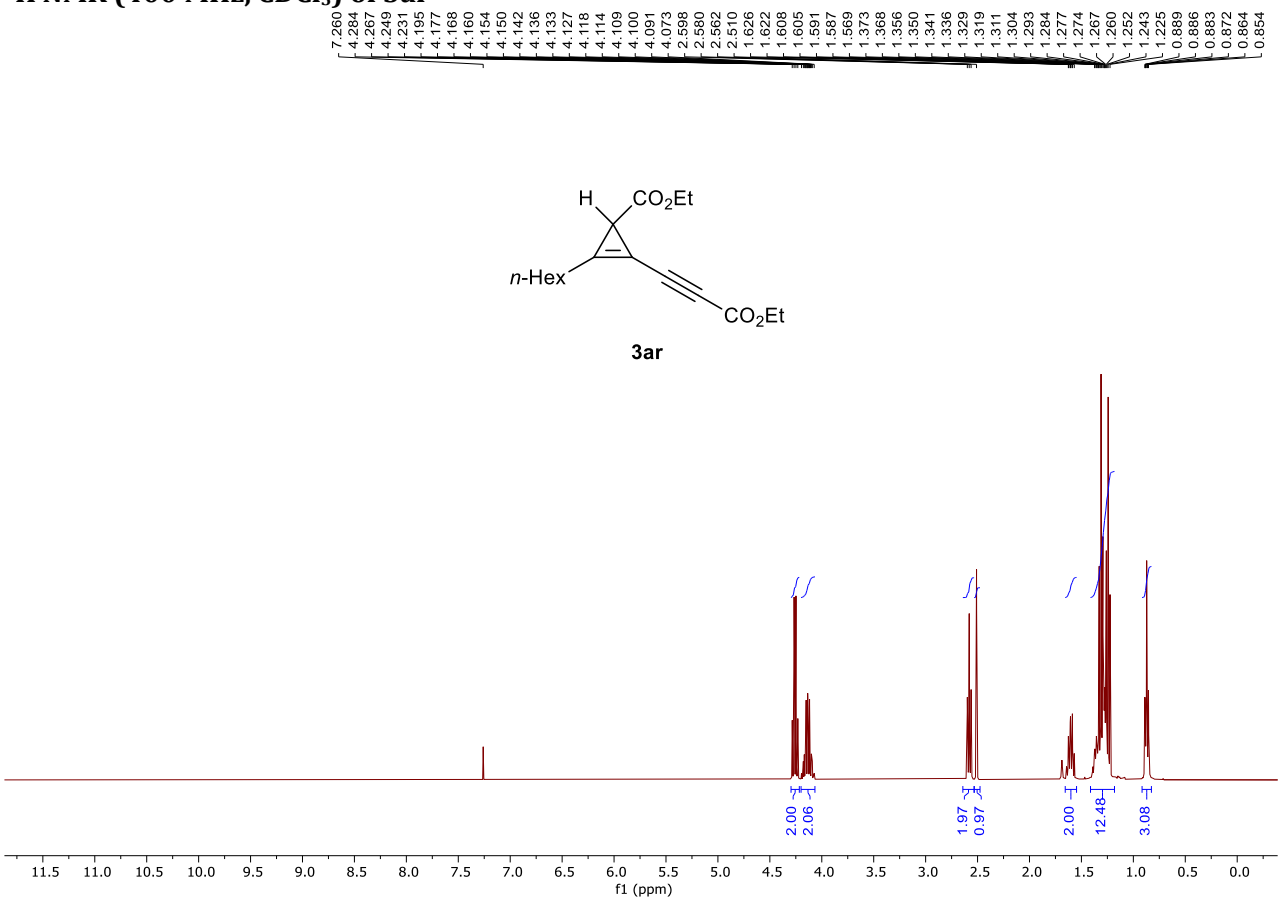
^{1}H NMR (400 MHz, $CDCl_3$) of 3aq



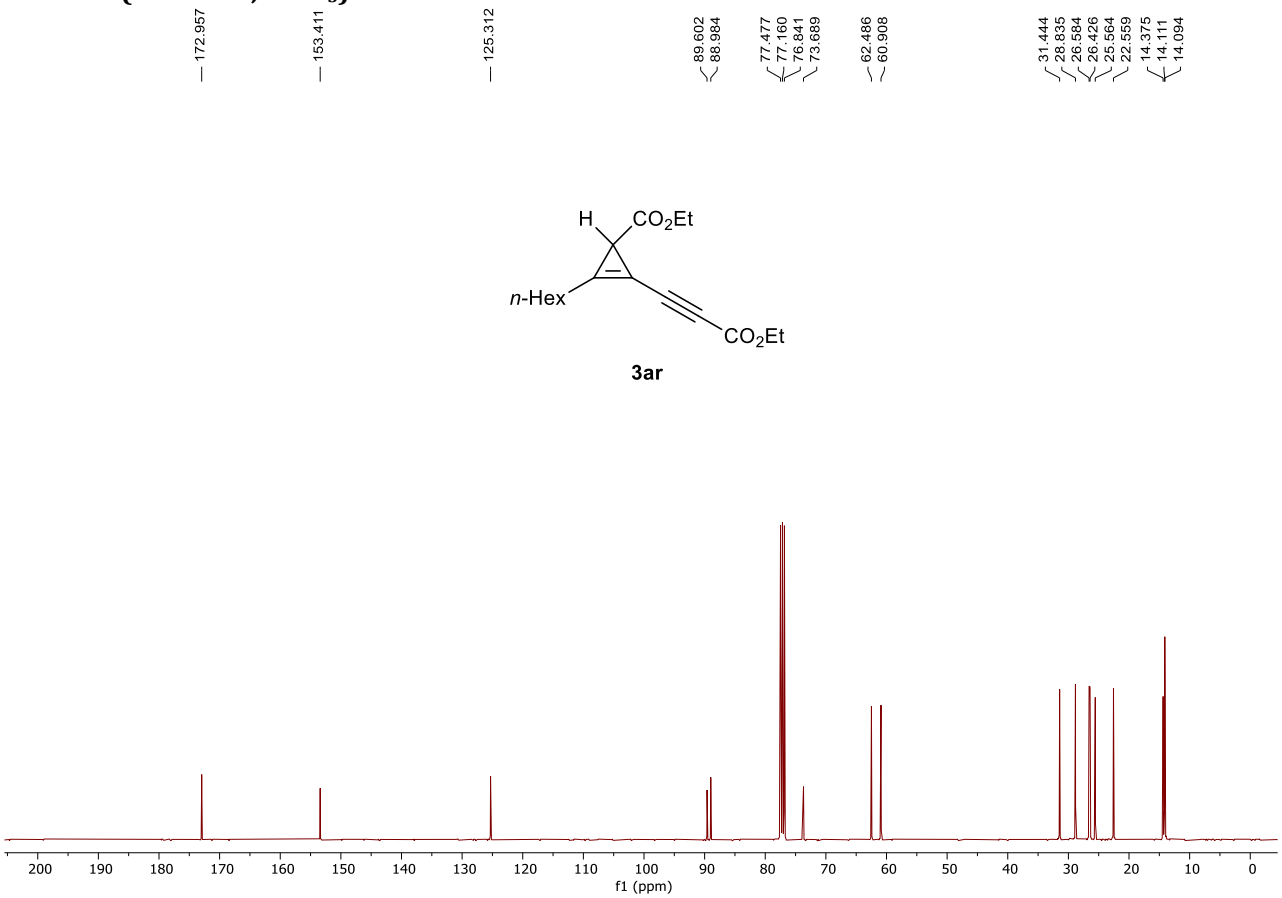
^{13}C NMR (101 MHz, $CDCl_3$) of 3aq



^{1}H NMR (400 MHz, $CDCl_3$) of 3ar

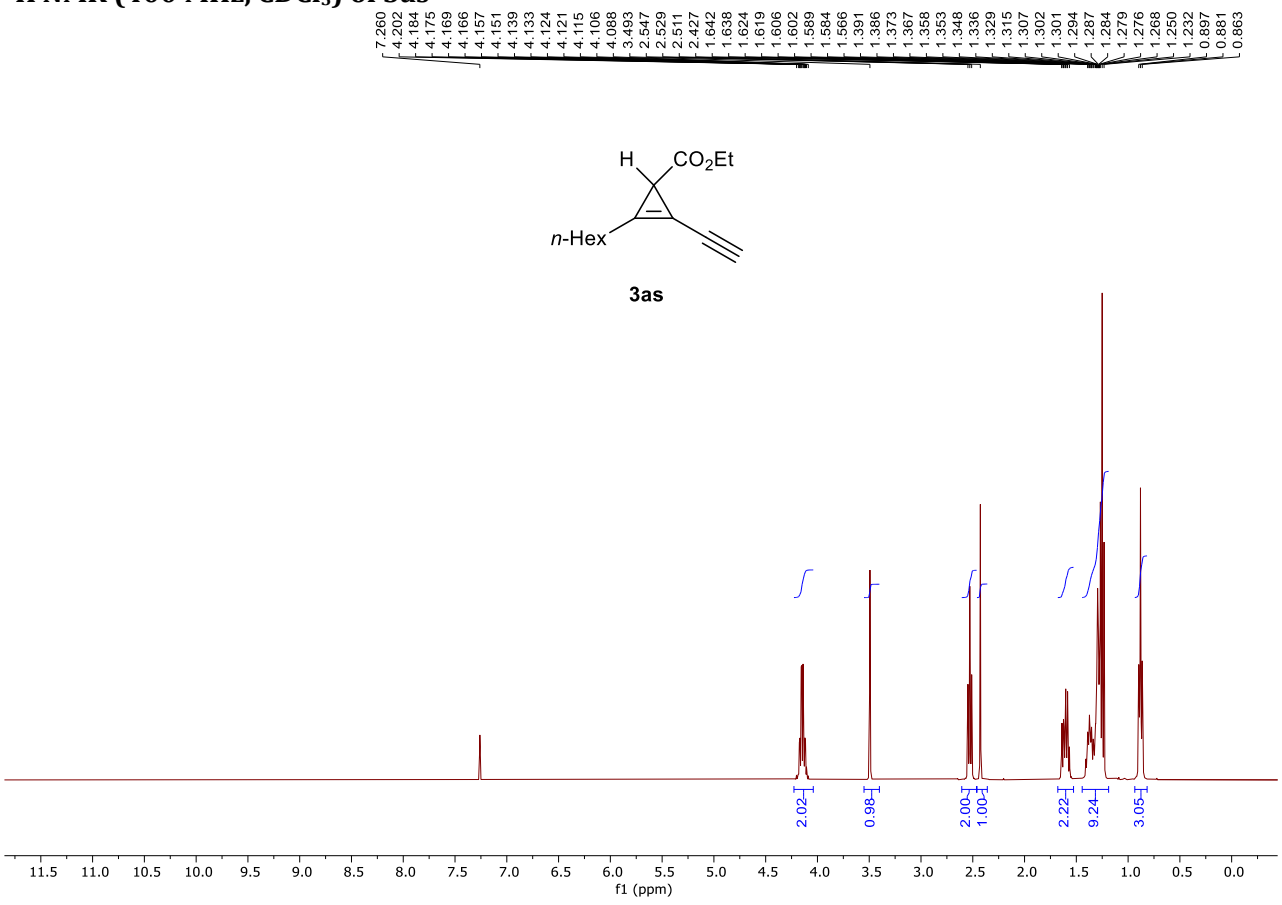


^{13}C NMR (101 MHz, $CDCl_3$) of 3ar



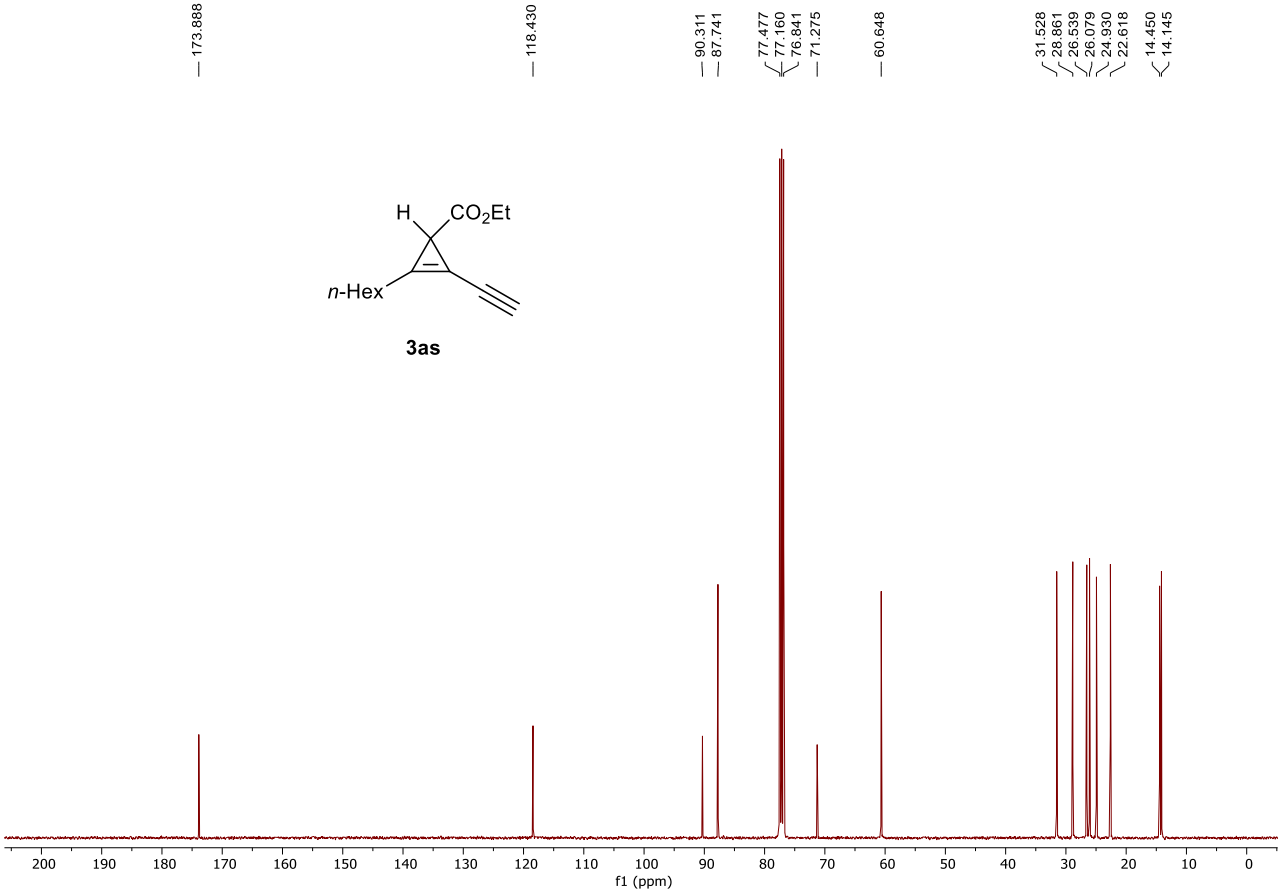
3ar

^{1}H NMR (400 MHz, $CDCl_3$) of 3as

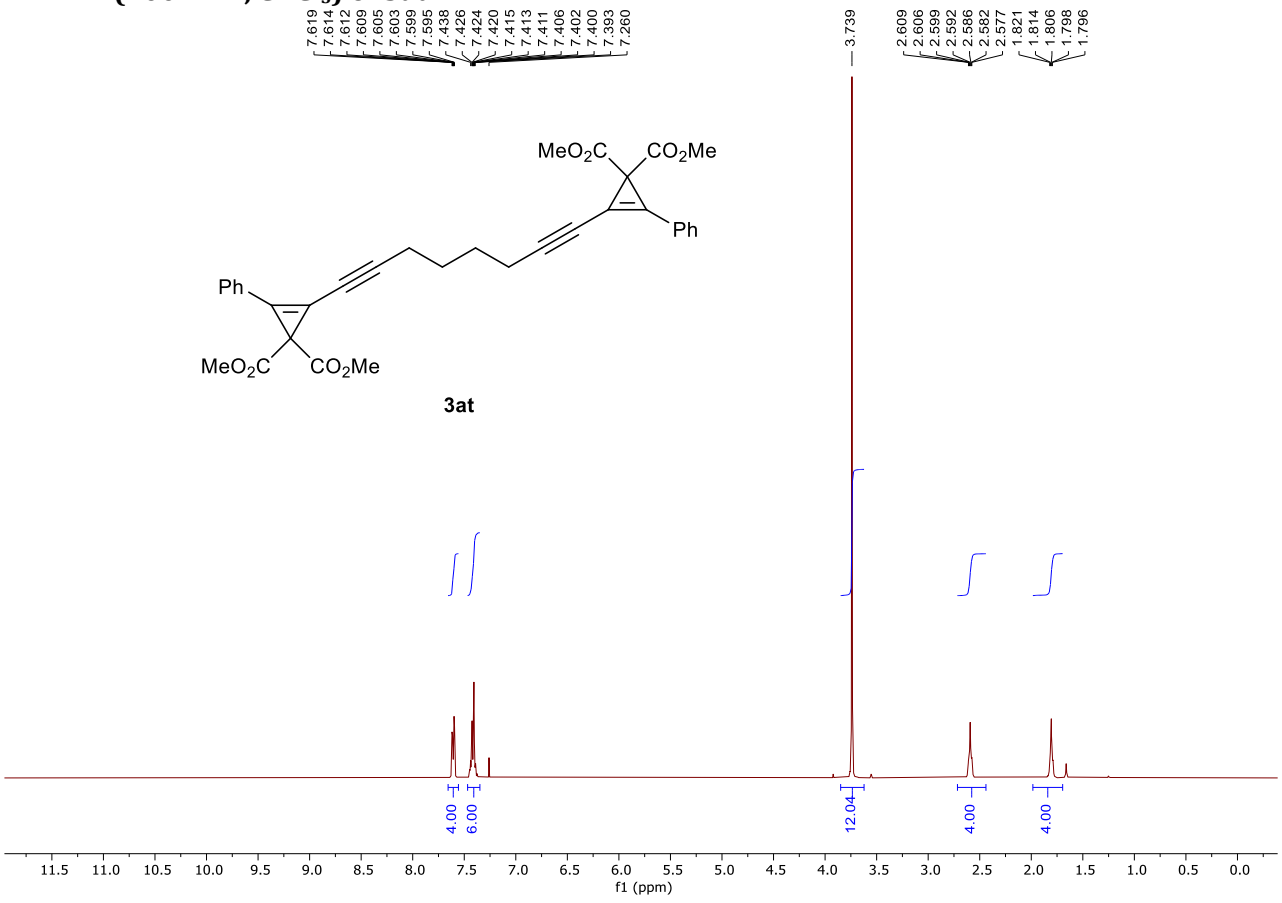


3as

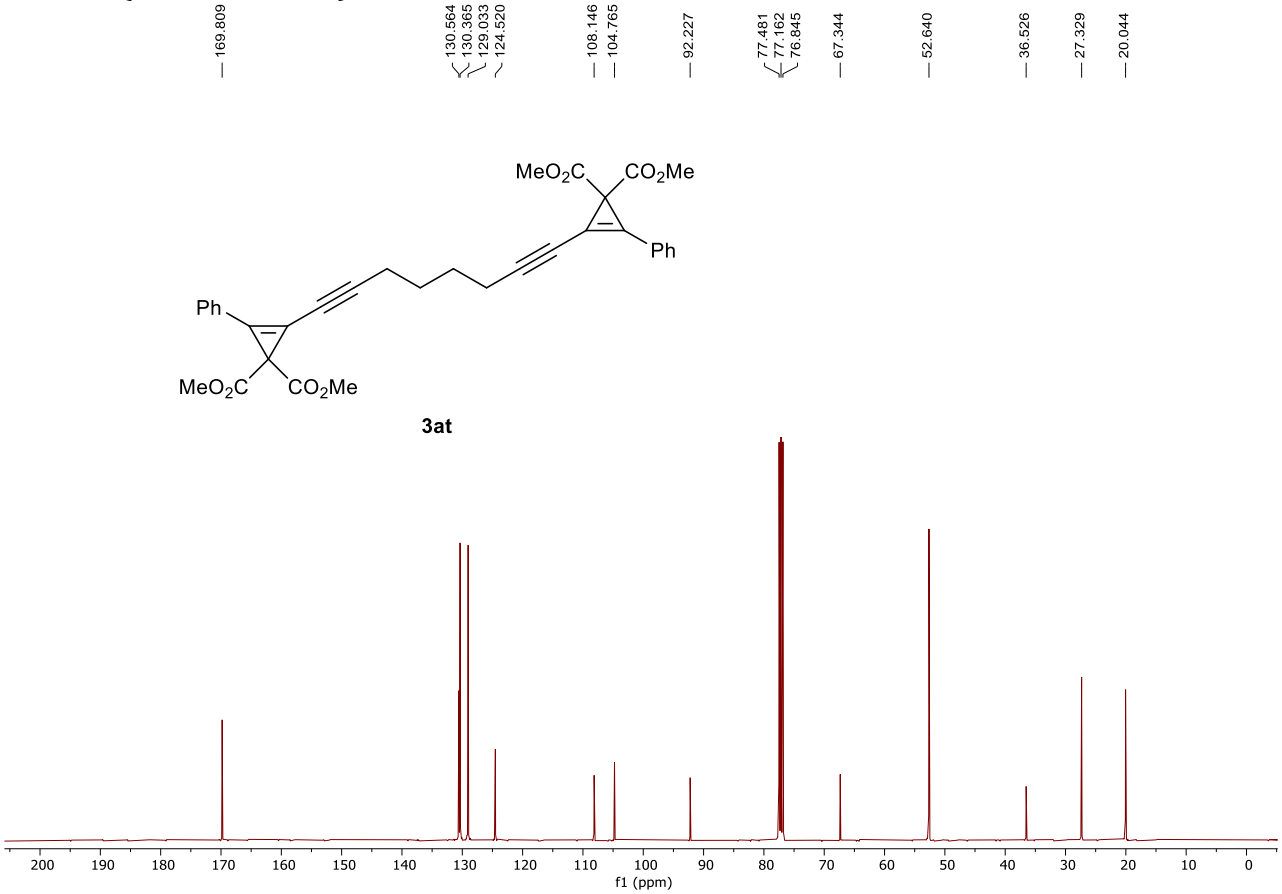
^{13}C NMR (101 MHz, $CDCl_3$) of 3as



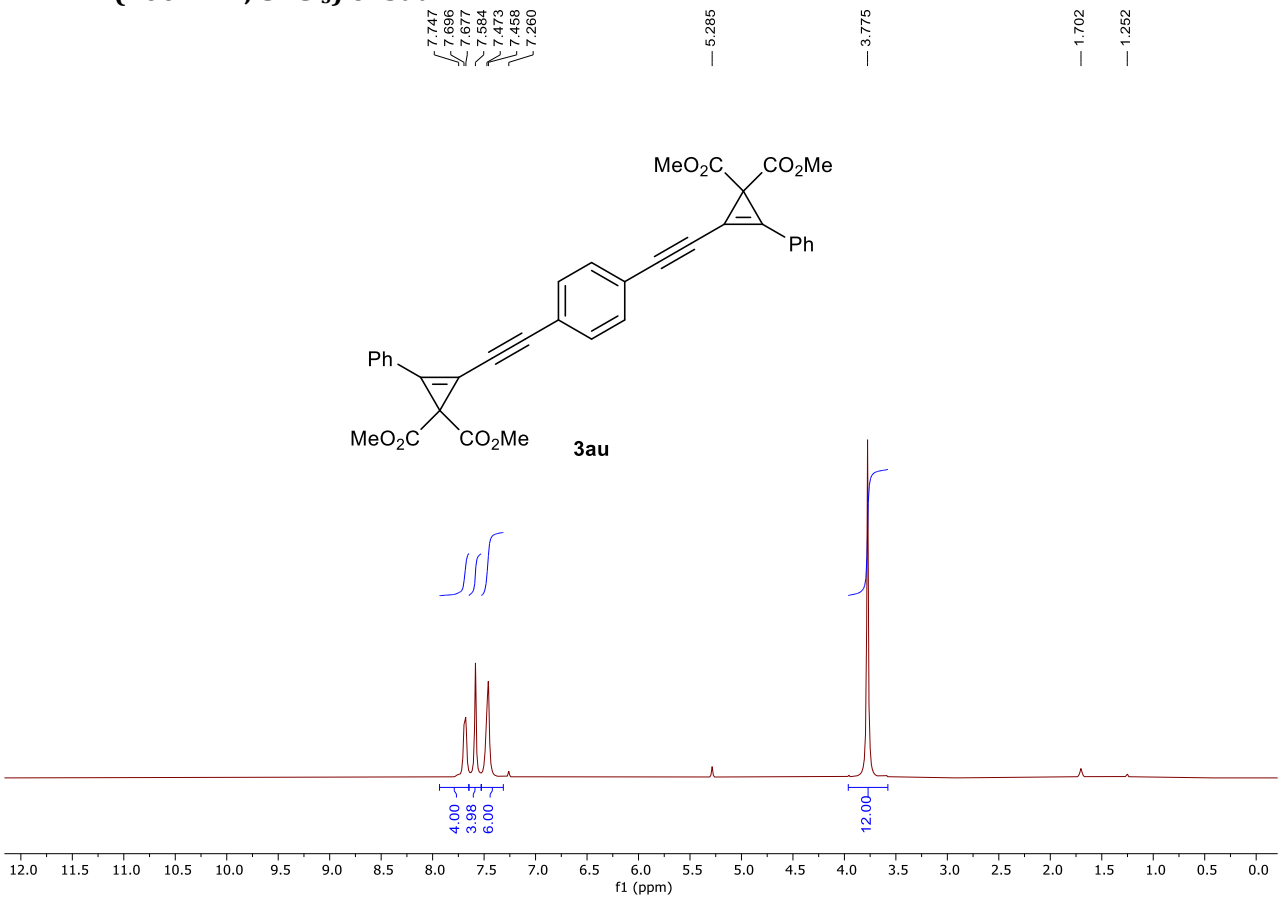
^{1}H NMR (400 MHz, $CDCl_3$) of 3at



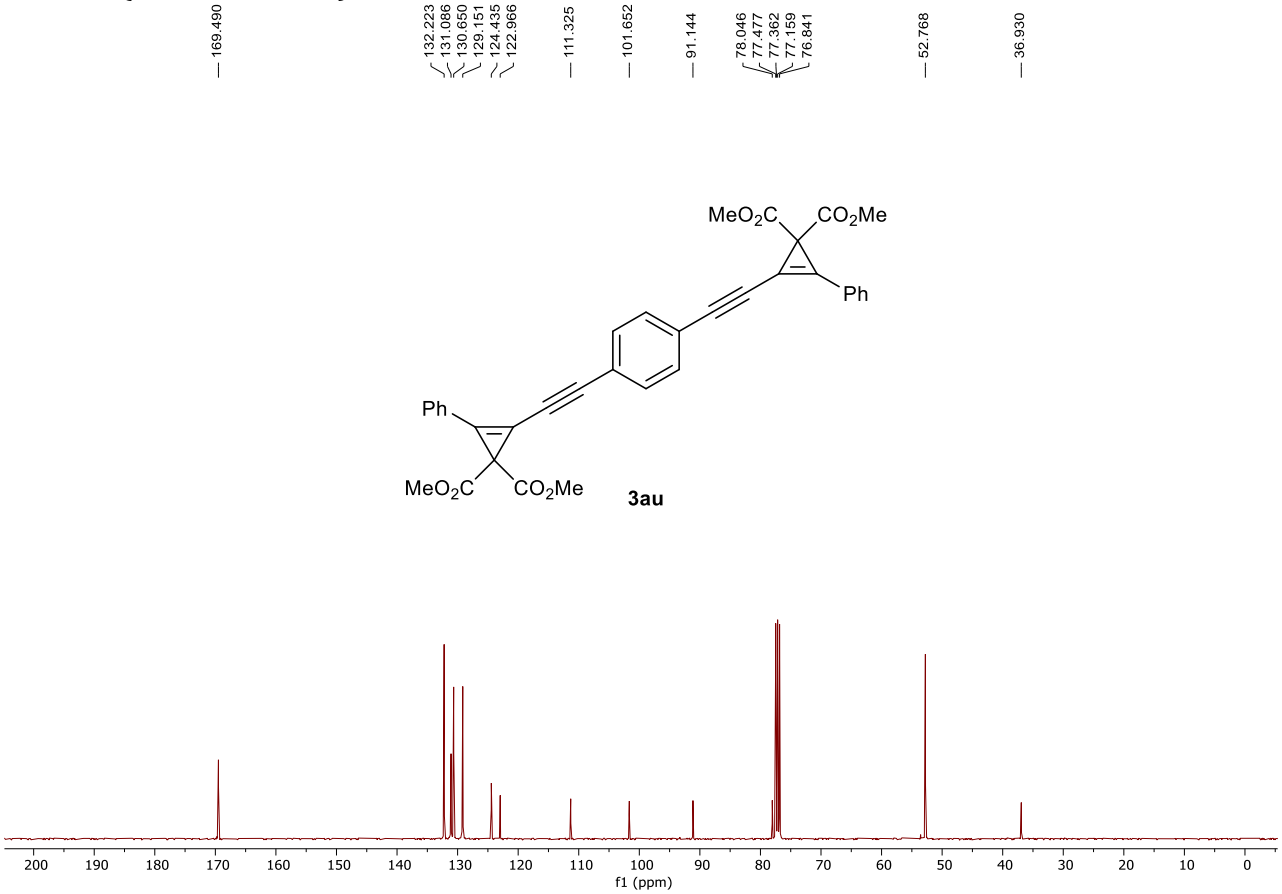
^{13}C NMR (101 MHz, $CDCl_3$) of 3at



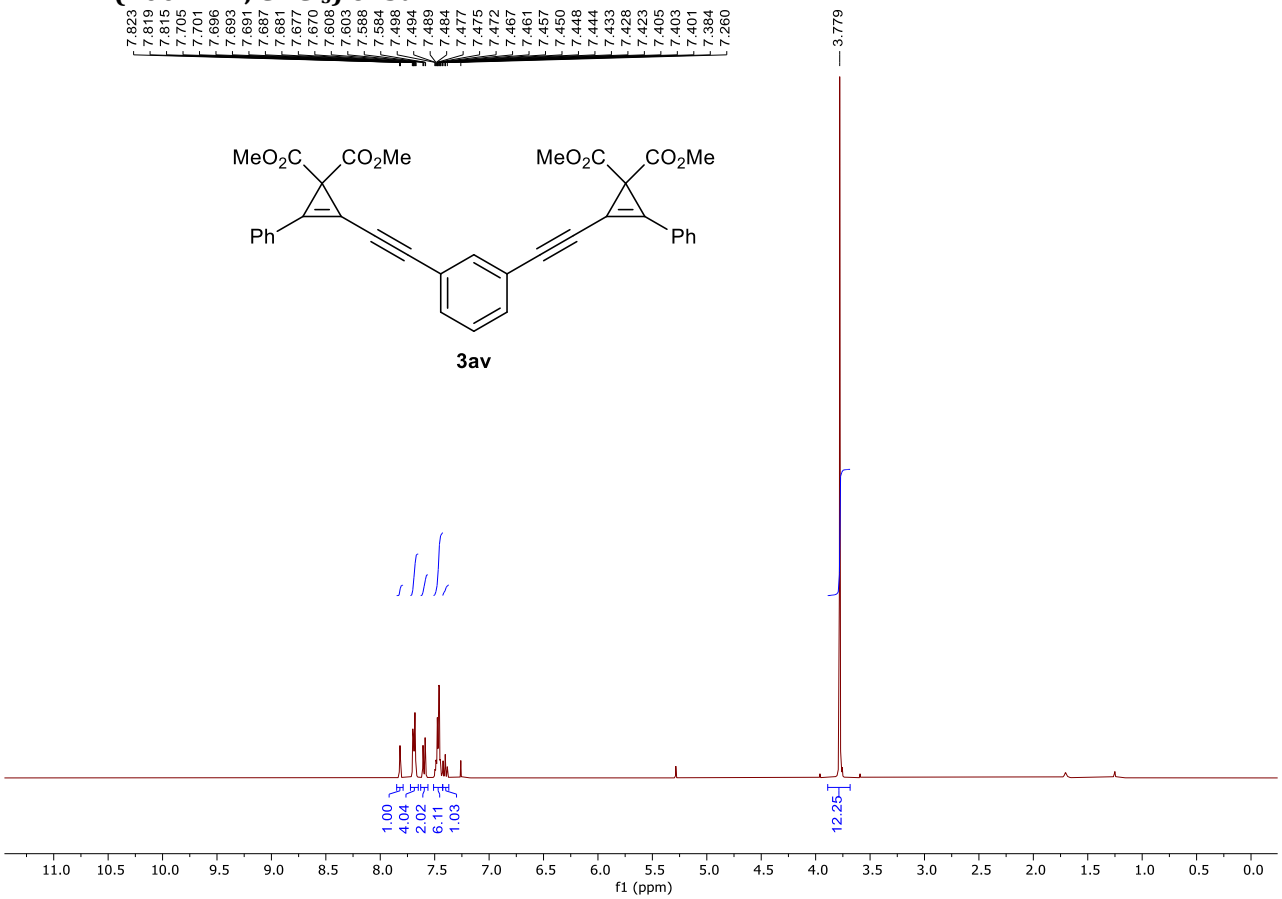
^{1}H NMR (400 MHz, $CDCl_3$) of 3au



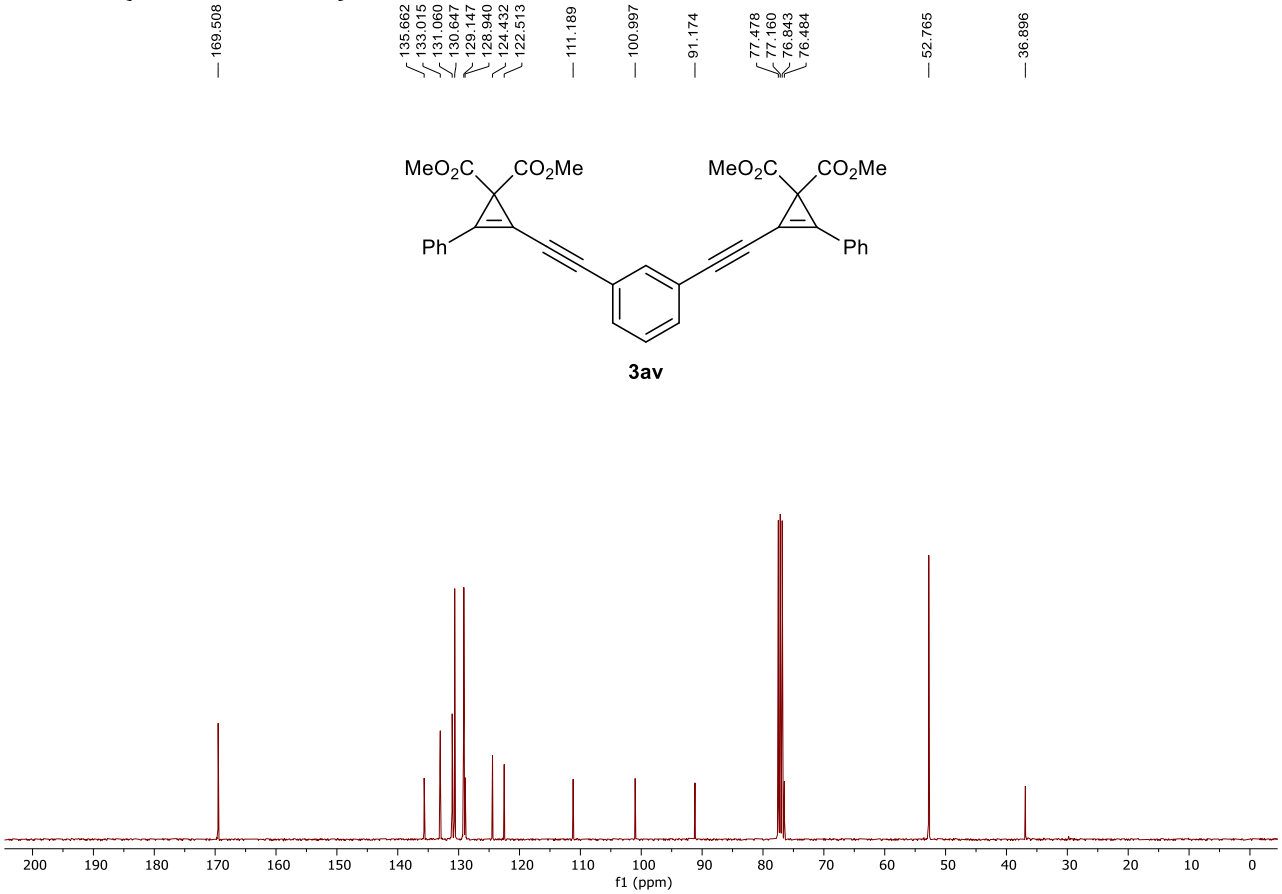
^{13}C NMR (101 MHz, $CDCl_3$) of 3au



^{1}H NMR (400 MHz, $CDCl_3$) of 3av

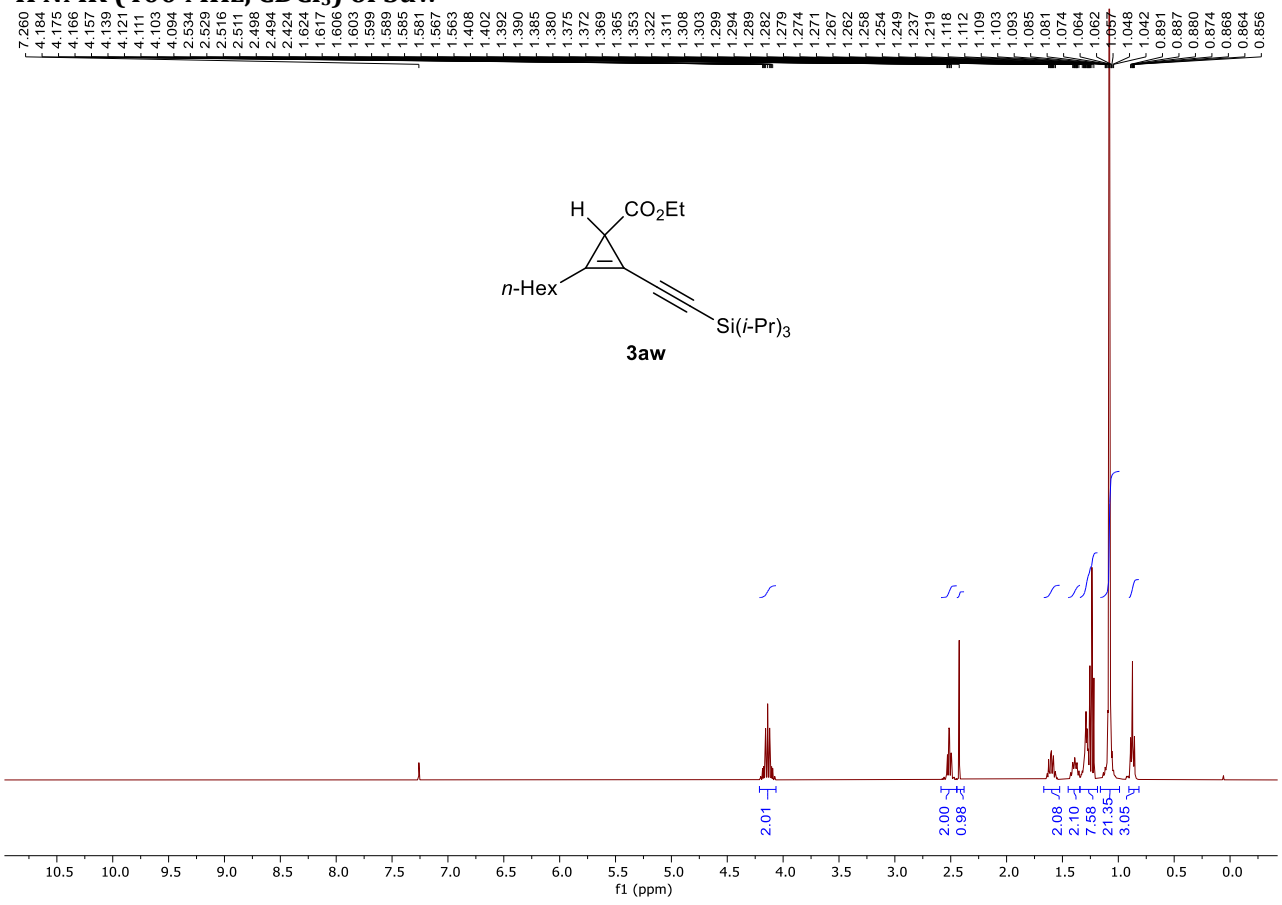


^{13}C NMR (101 MHz, $CDCl_3$) of 3av



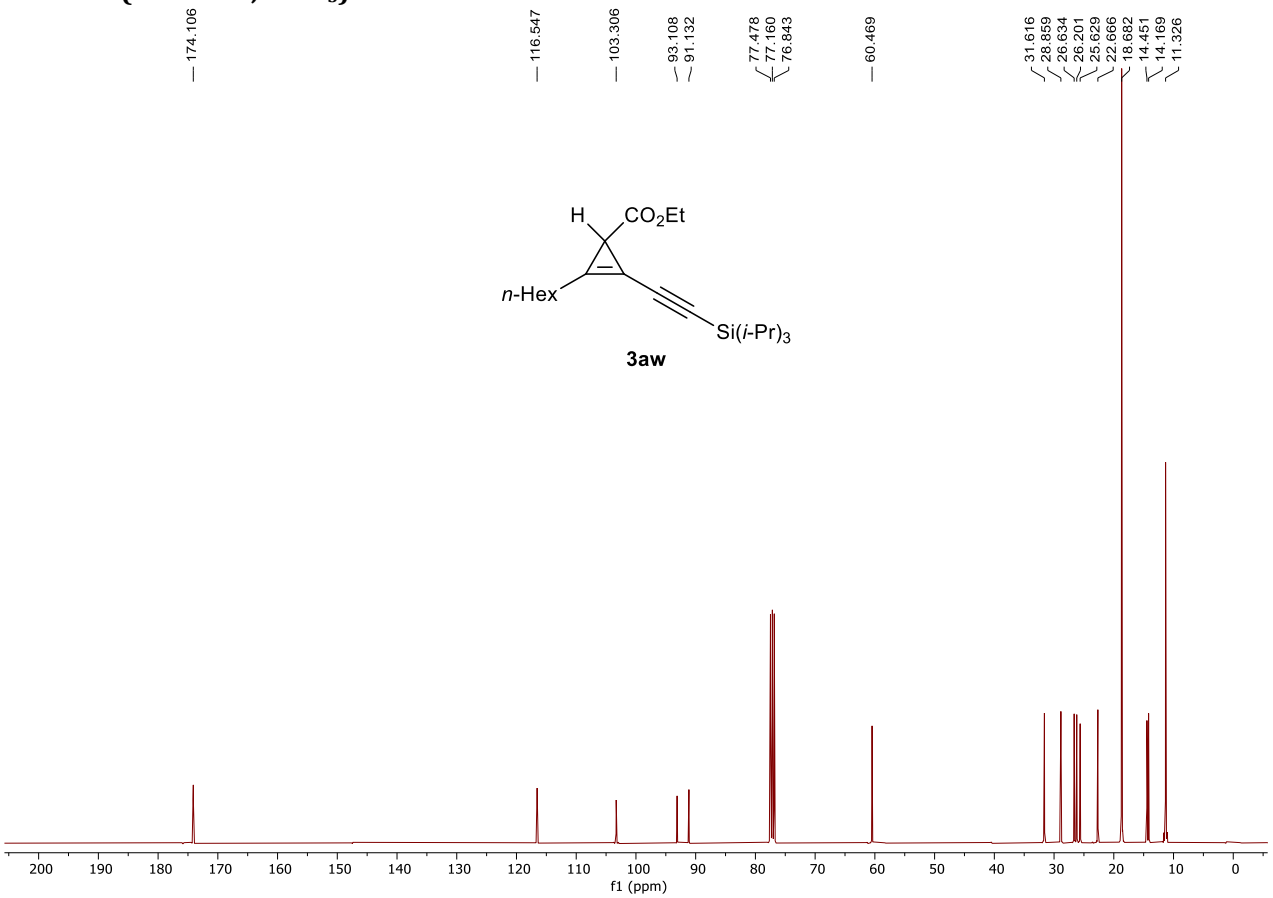
3av

^{1}H NMR (400 MHz, $CDCl_3$) of 3aw



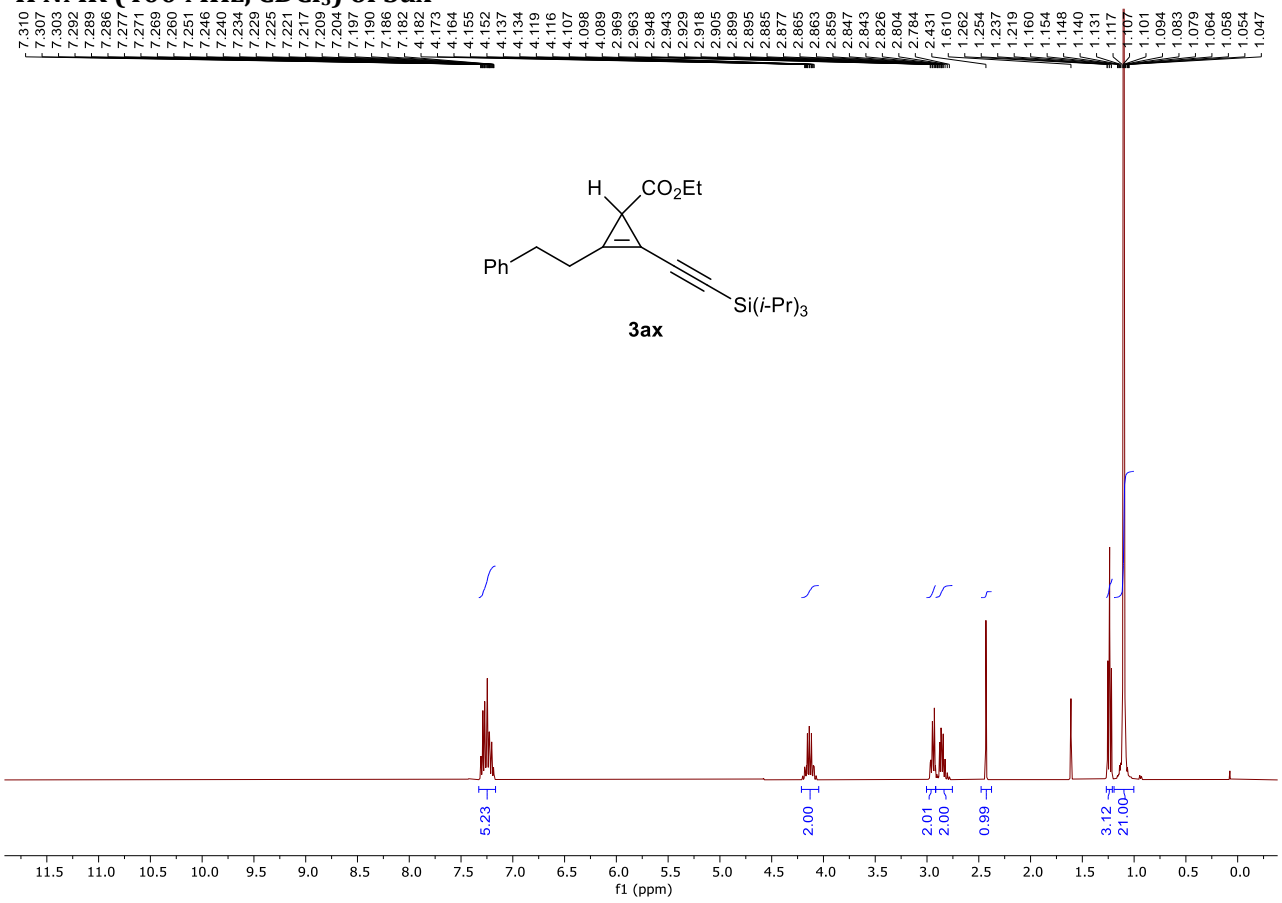
3aw

^{13}C NMR (101 MHz, $CDCl_3$) of 3aw



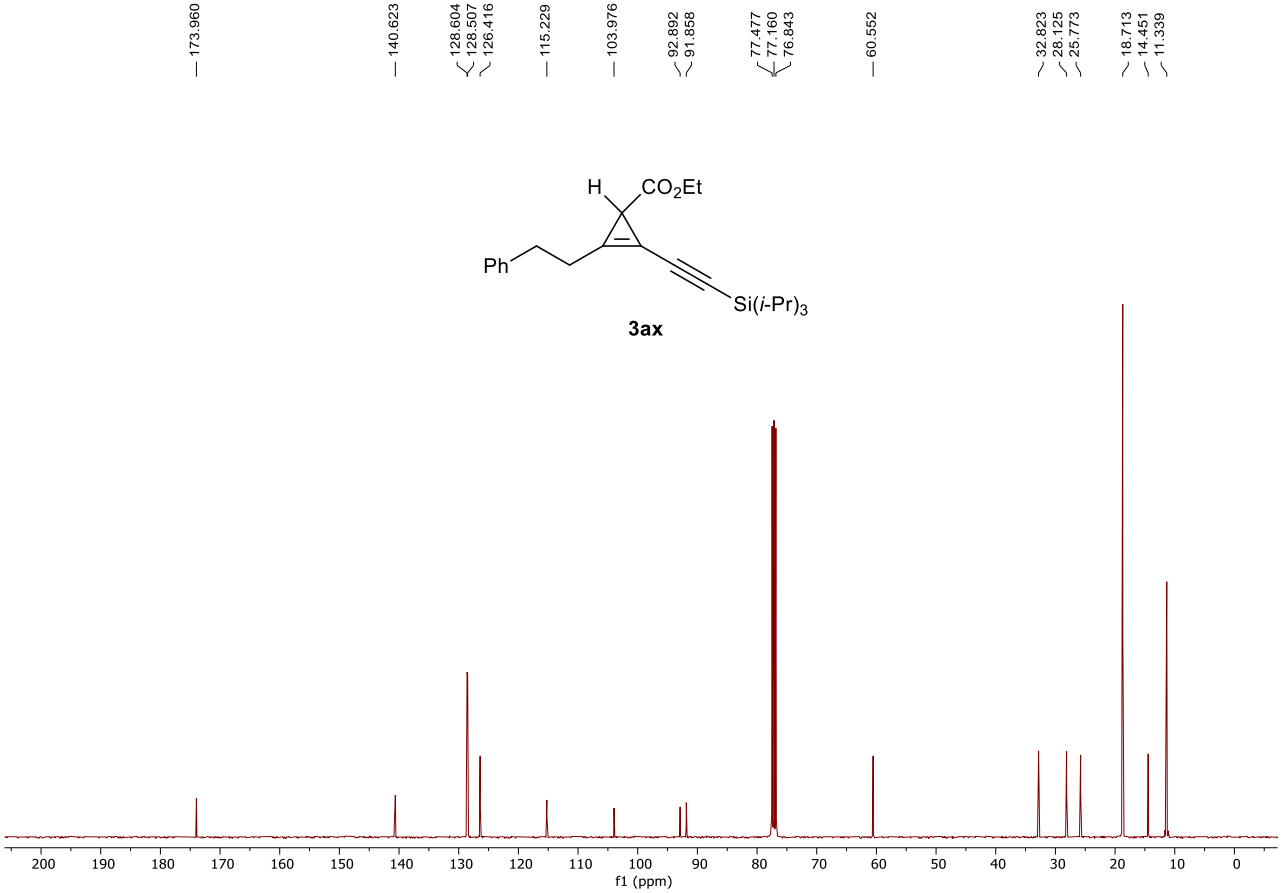
3aw

^{1}H NMR (400 MHz, $CDCl_3$) of 3ax

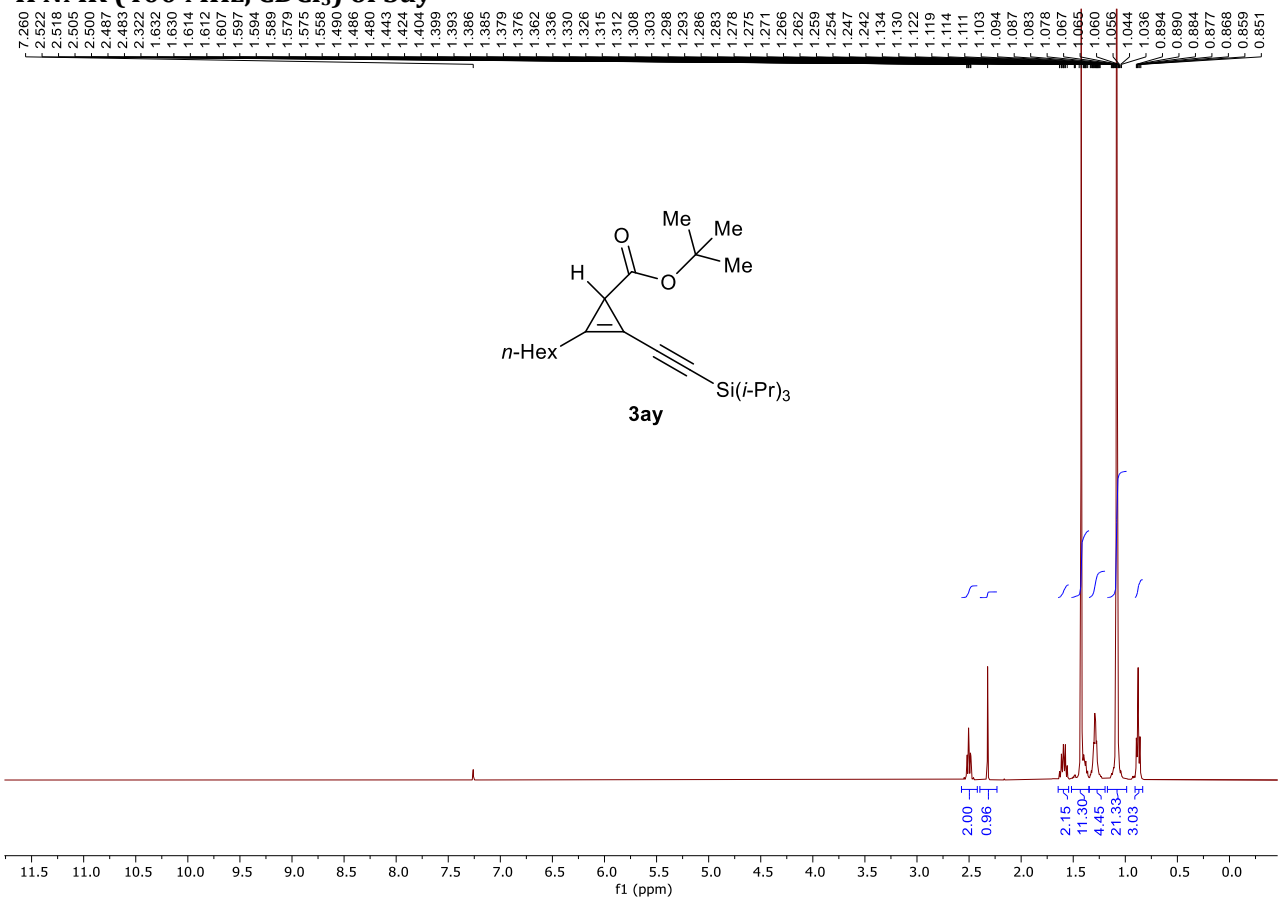


3ax

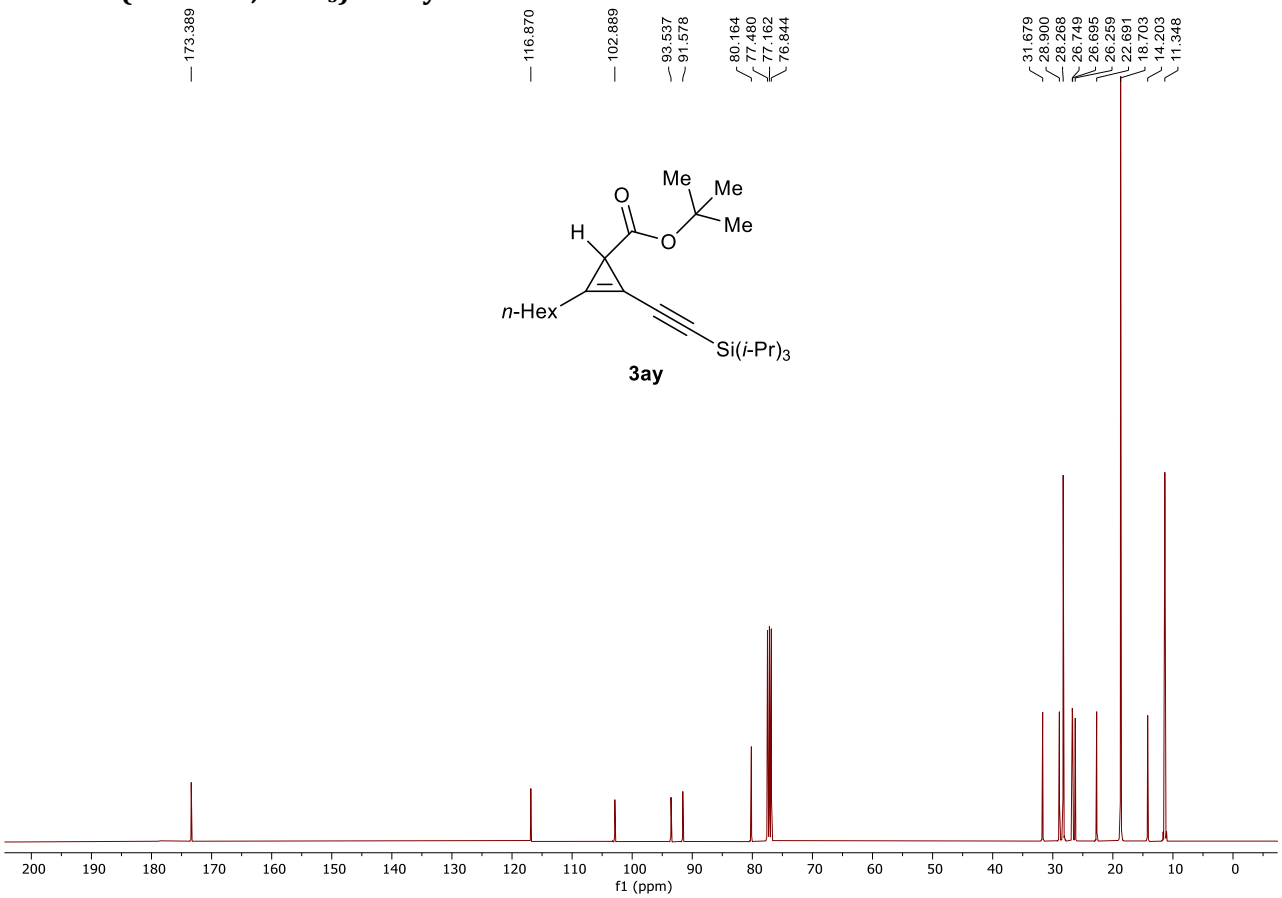
^{13}C NMR (101 MHz, $CDCl_3$) of 3ax



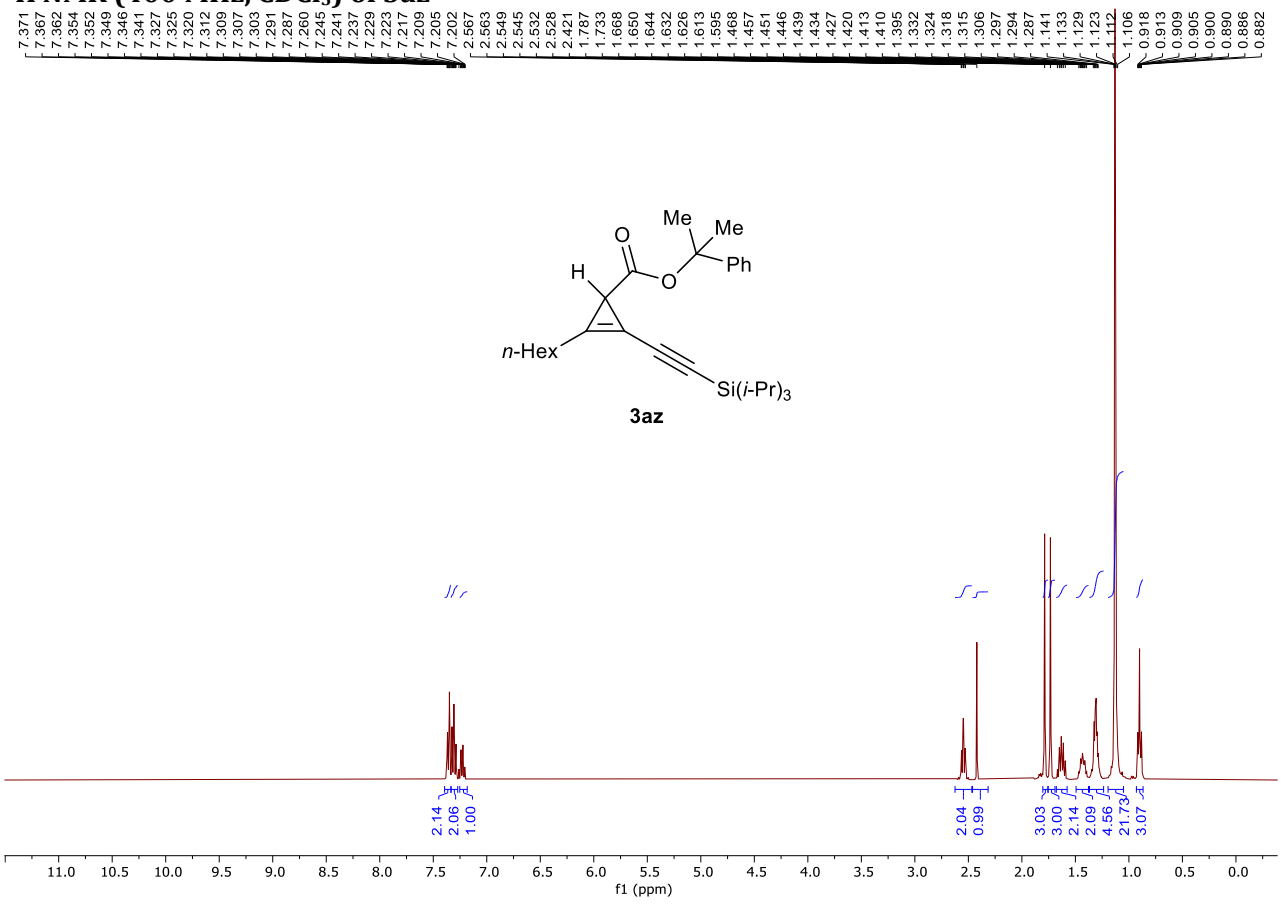
^{1}H NMR (400 MHz, $CDCl_3$) of 3ay



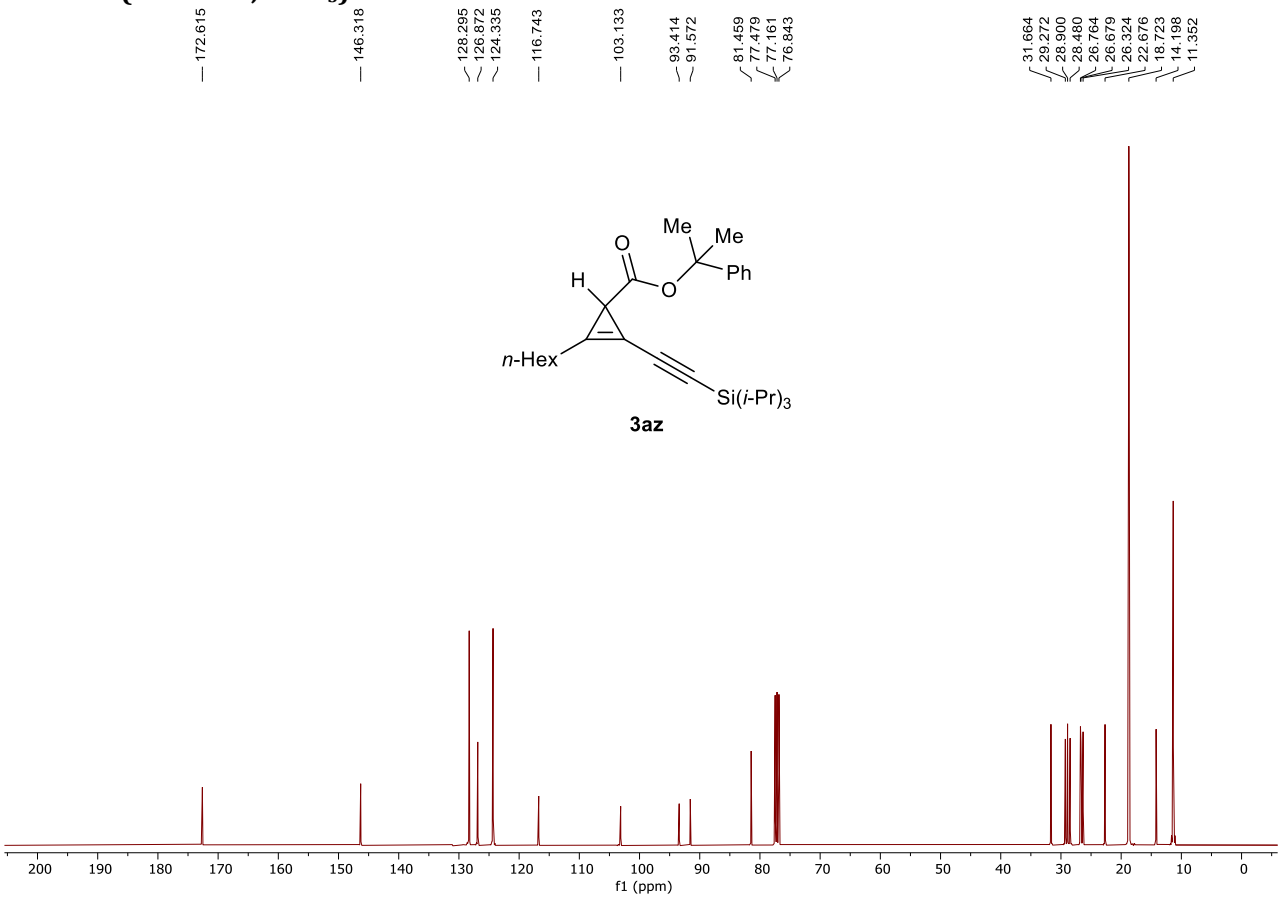
^{13}C NMR (101 MHz, $CDCl_3$) of 3ay



^{1}H NMR (400 MHz, $CDCl_3$) of 3az

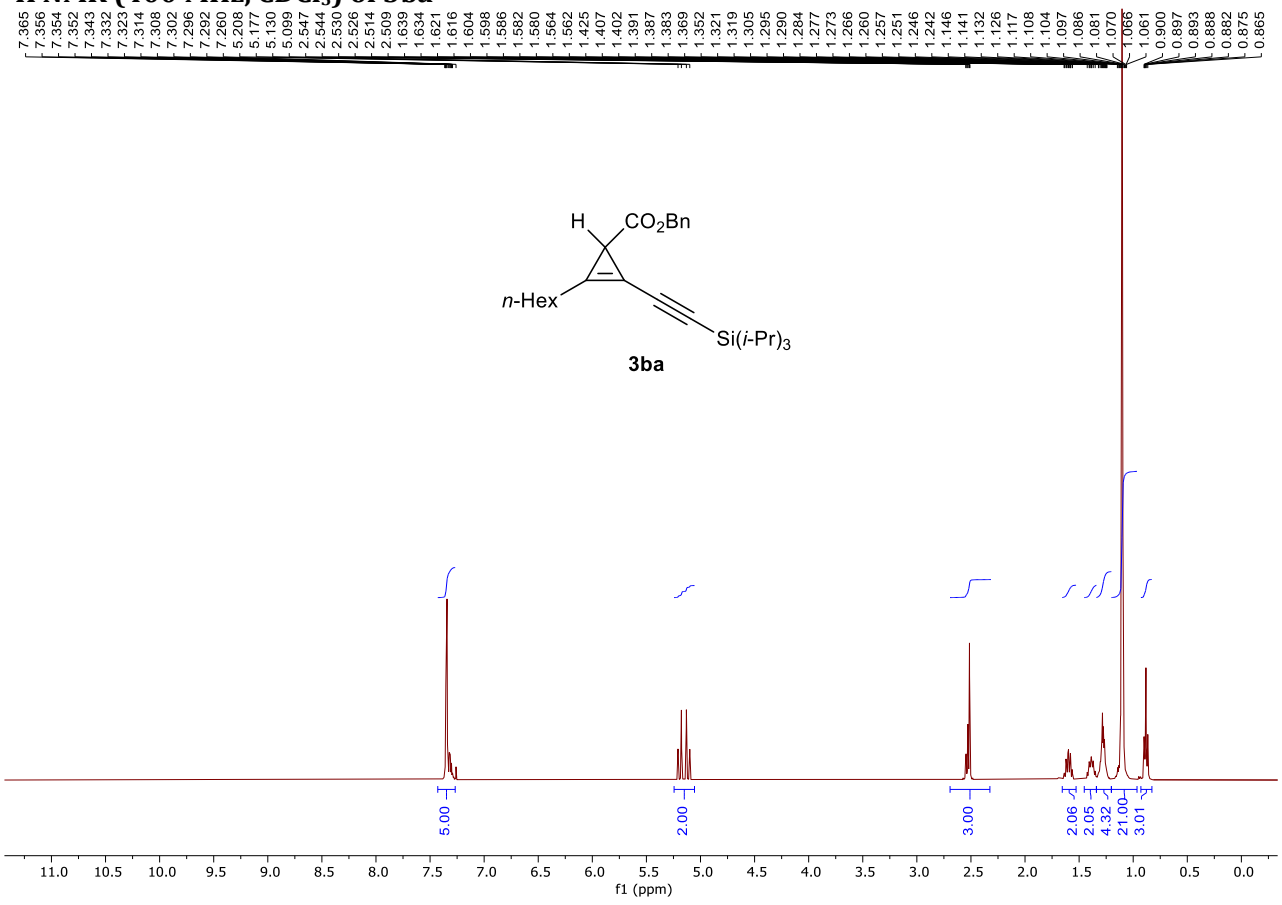


^{13}C NMR (101 MHz, $CDCl_3$) of 3az



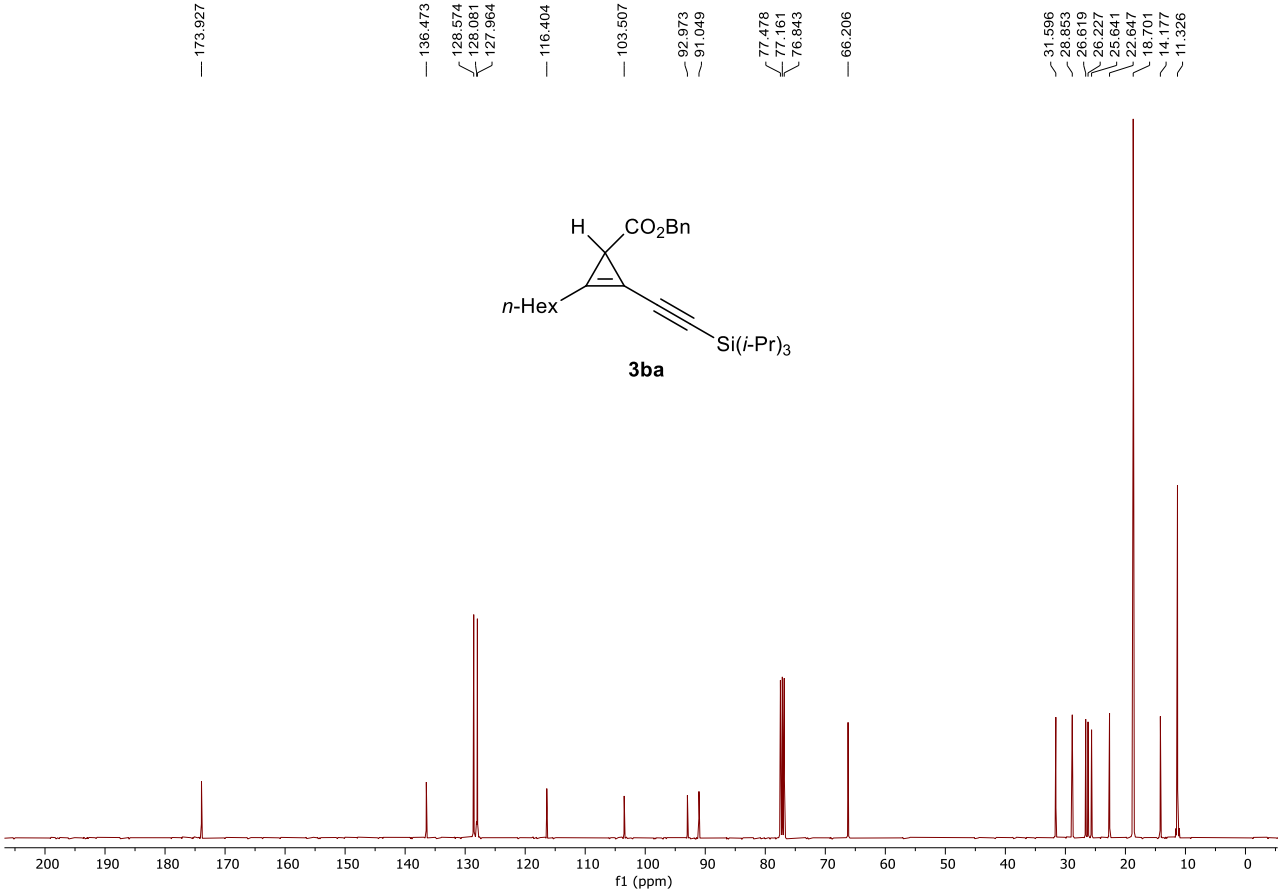
3az

^{1}H NMR (400 MHz, $CDCl_3$) of 3ba



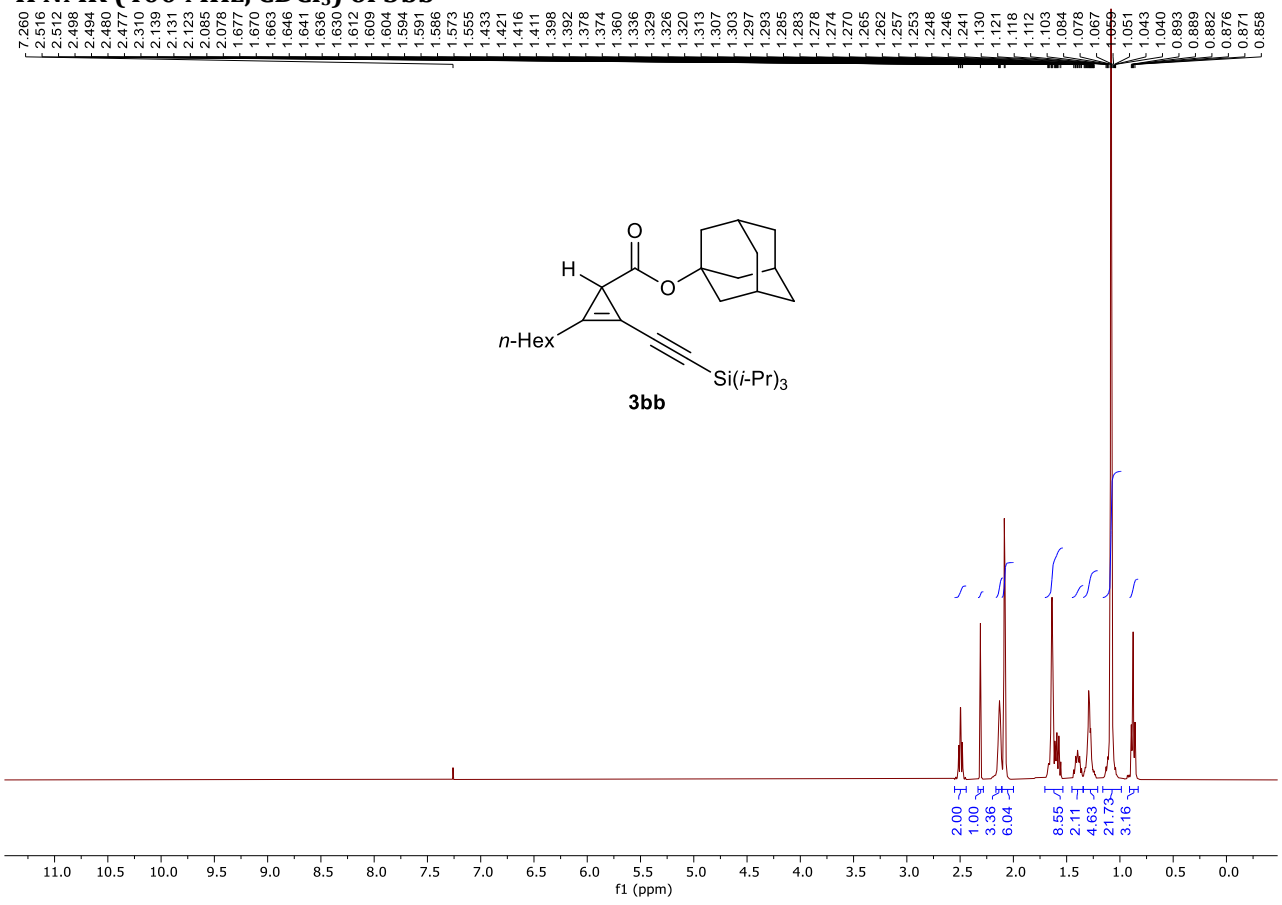
3ba

^{13}C NMR (101 MHz, $CDCl_3$) of 3ba



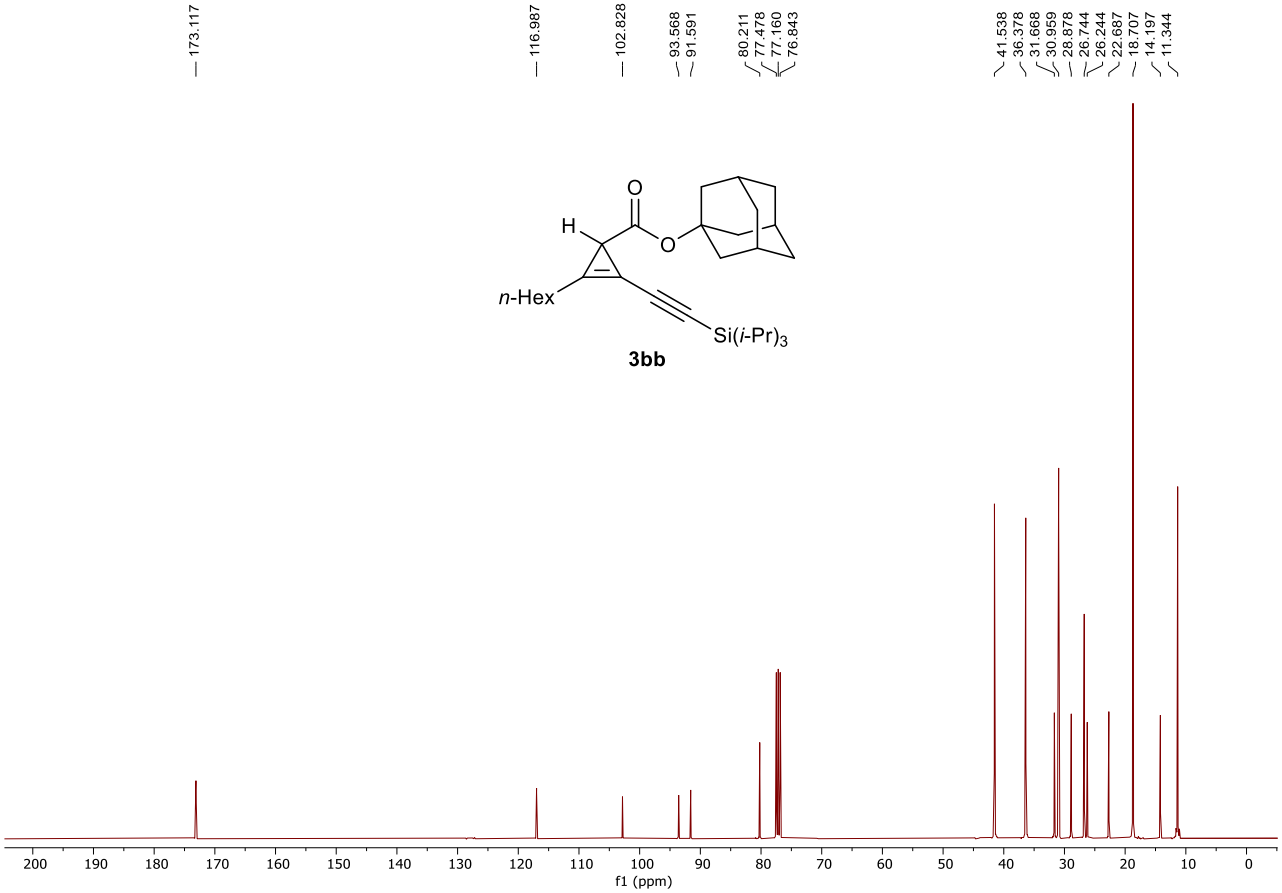
3ba

^{1}H NMR (400 MHz, $CDCl_3$) of 3bb



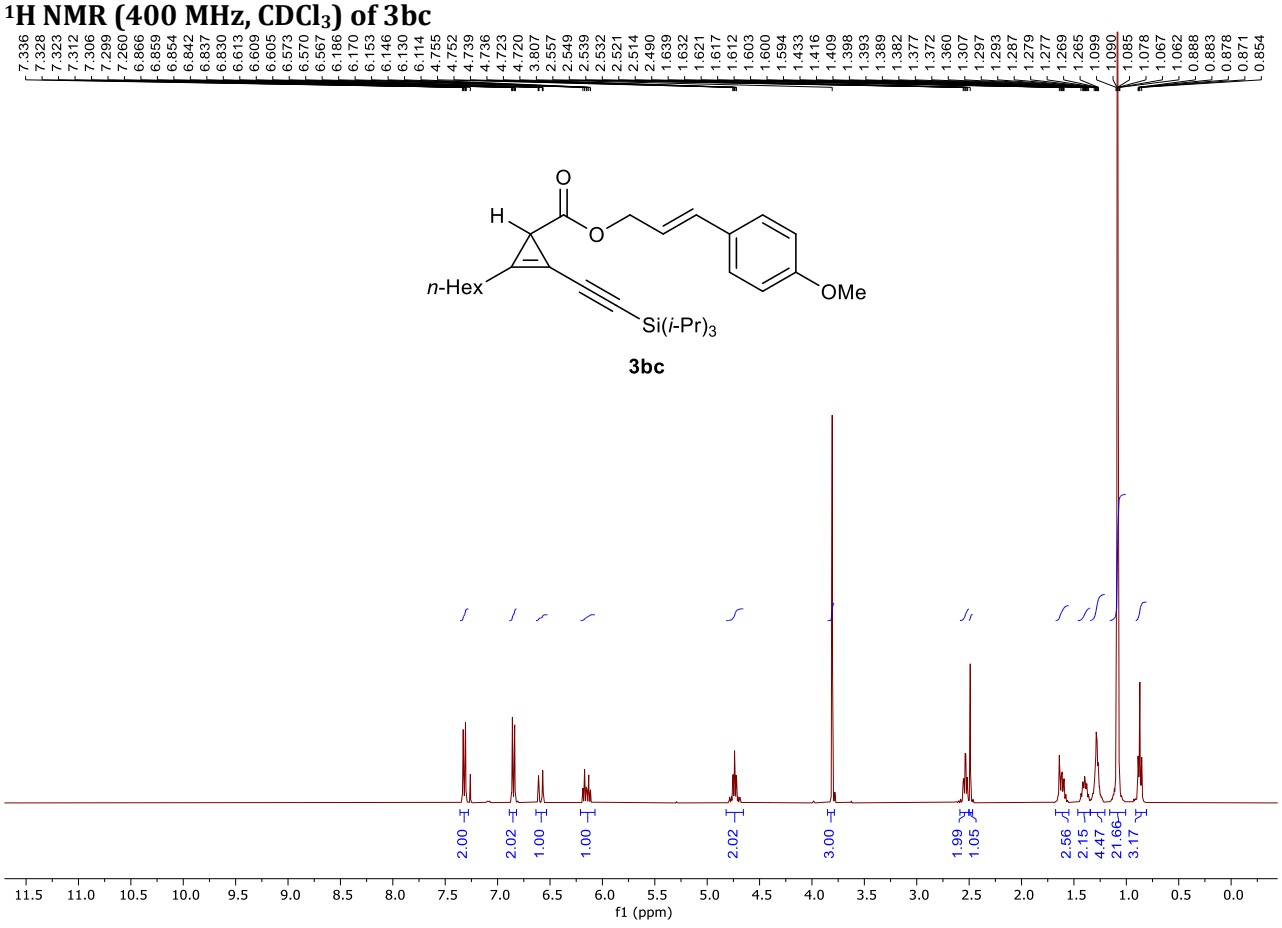
3bb

^{13}C NMR (101 MHz, $CDCl_3$) of 3bb



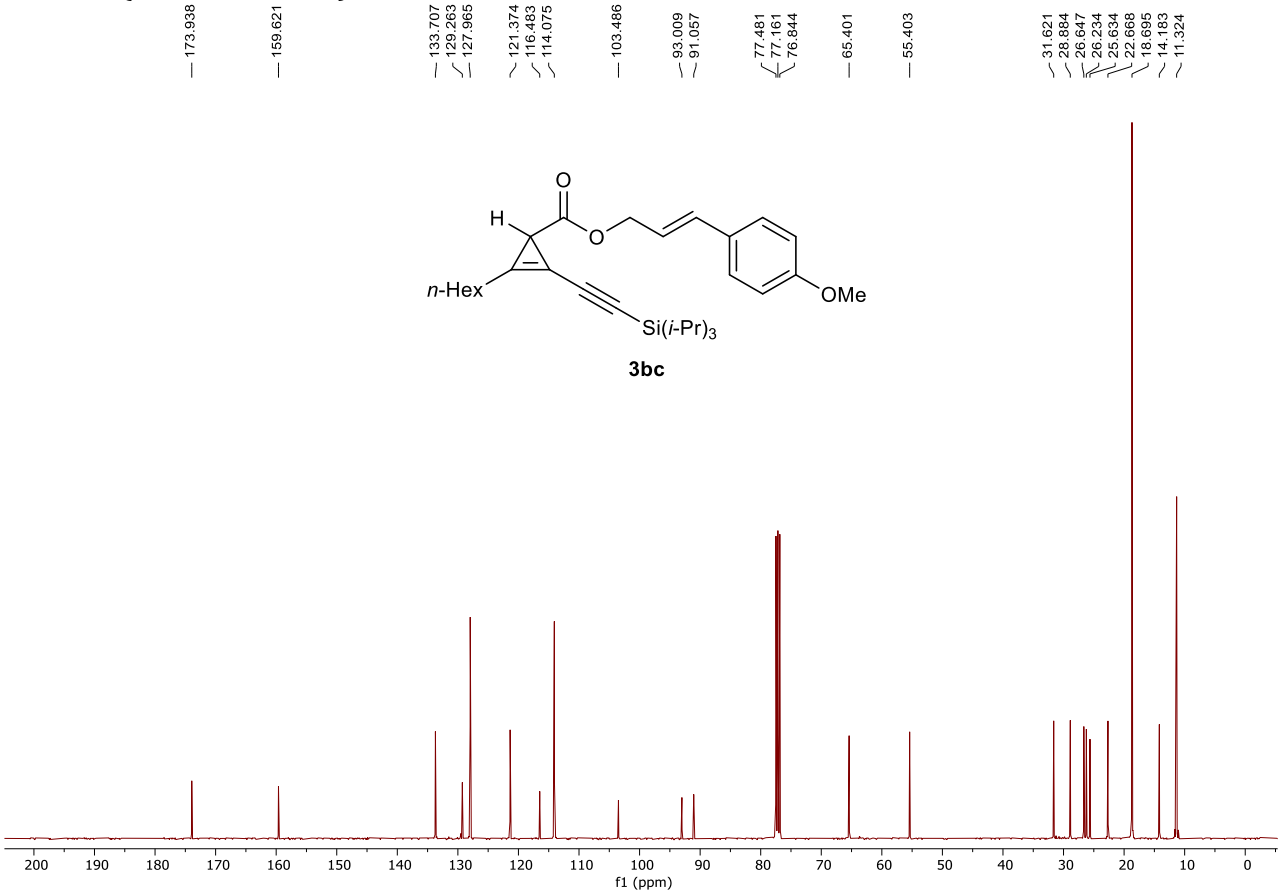
3bb

^{1}H NMR (400 MHz, $CDCl_3$) of 3bc



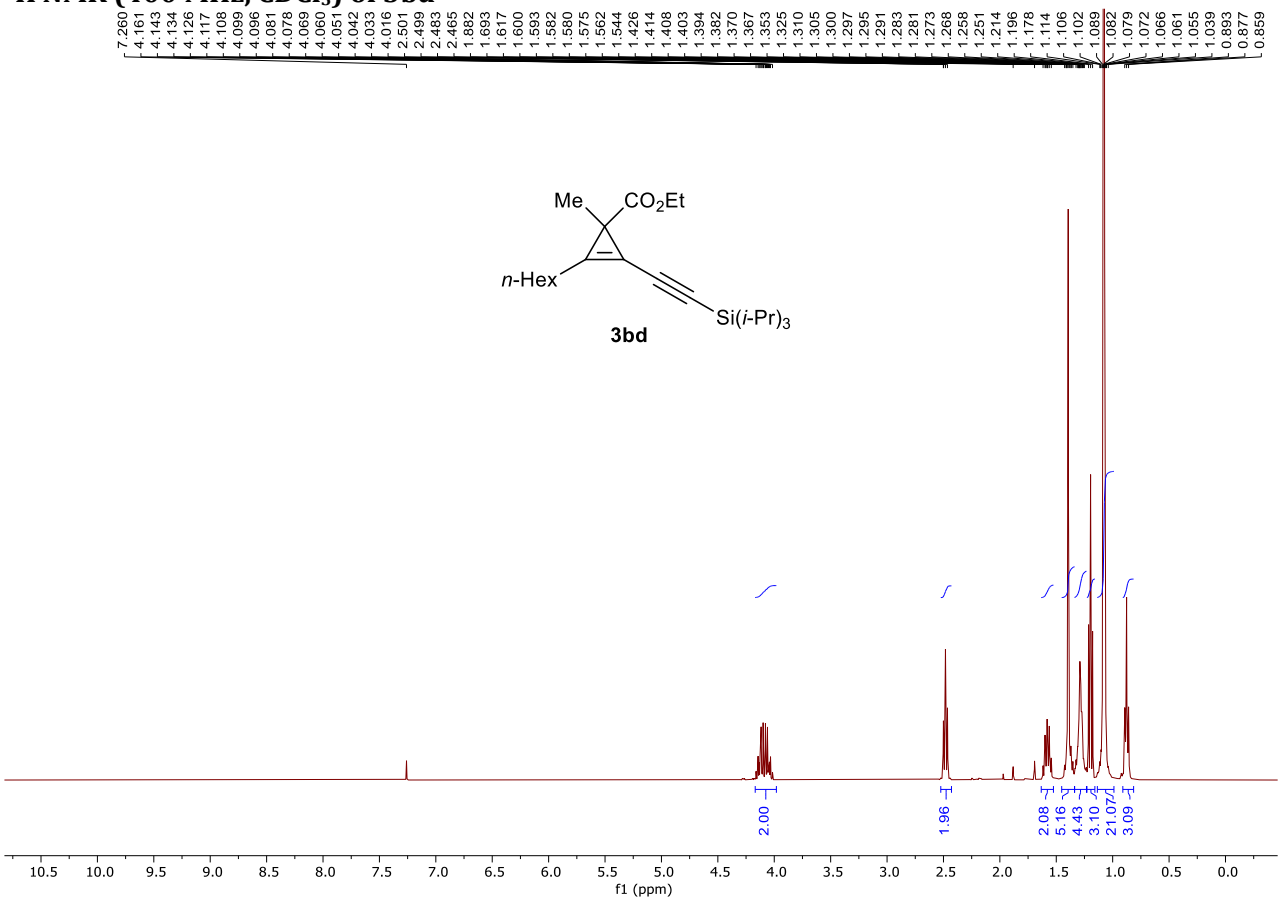
3bc

^{13}C NMR (101 MHz, $CDCl_3$) of 3bc



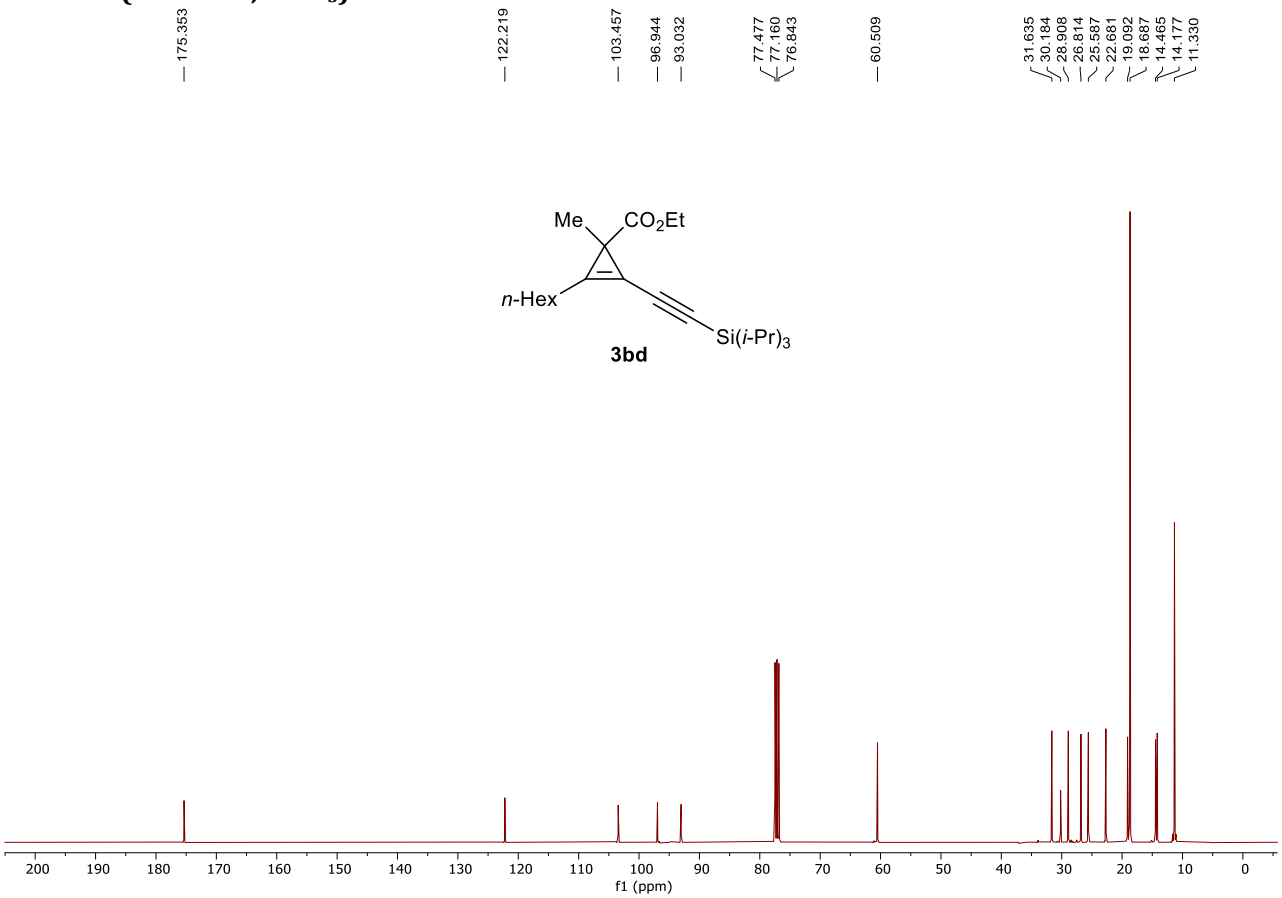
3bc

^{1}H NMR (400 MHz, $CDCl_3$) of 3bd

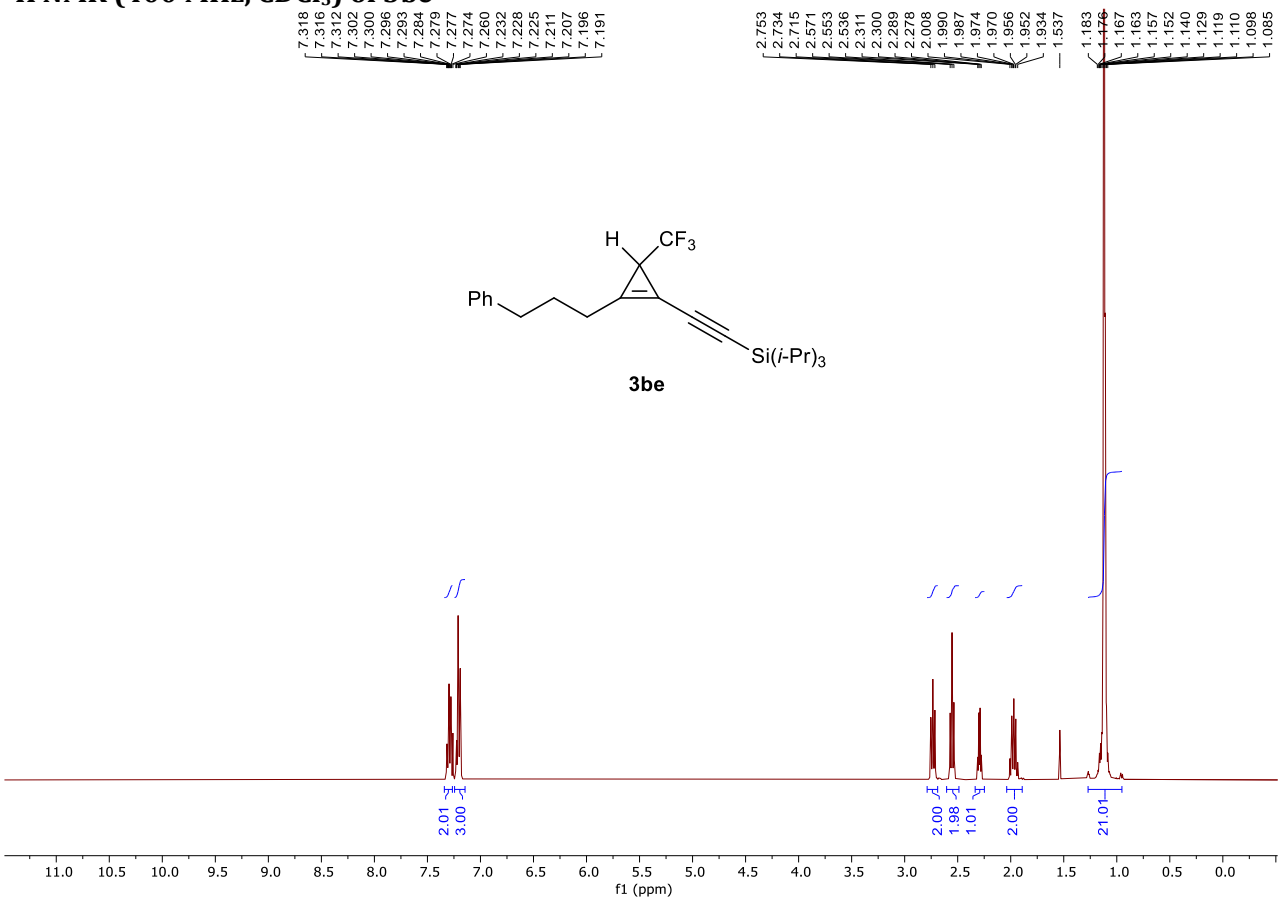


3bd

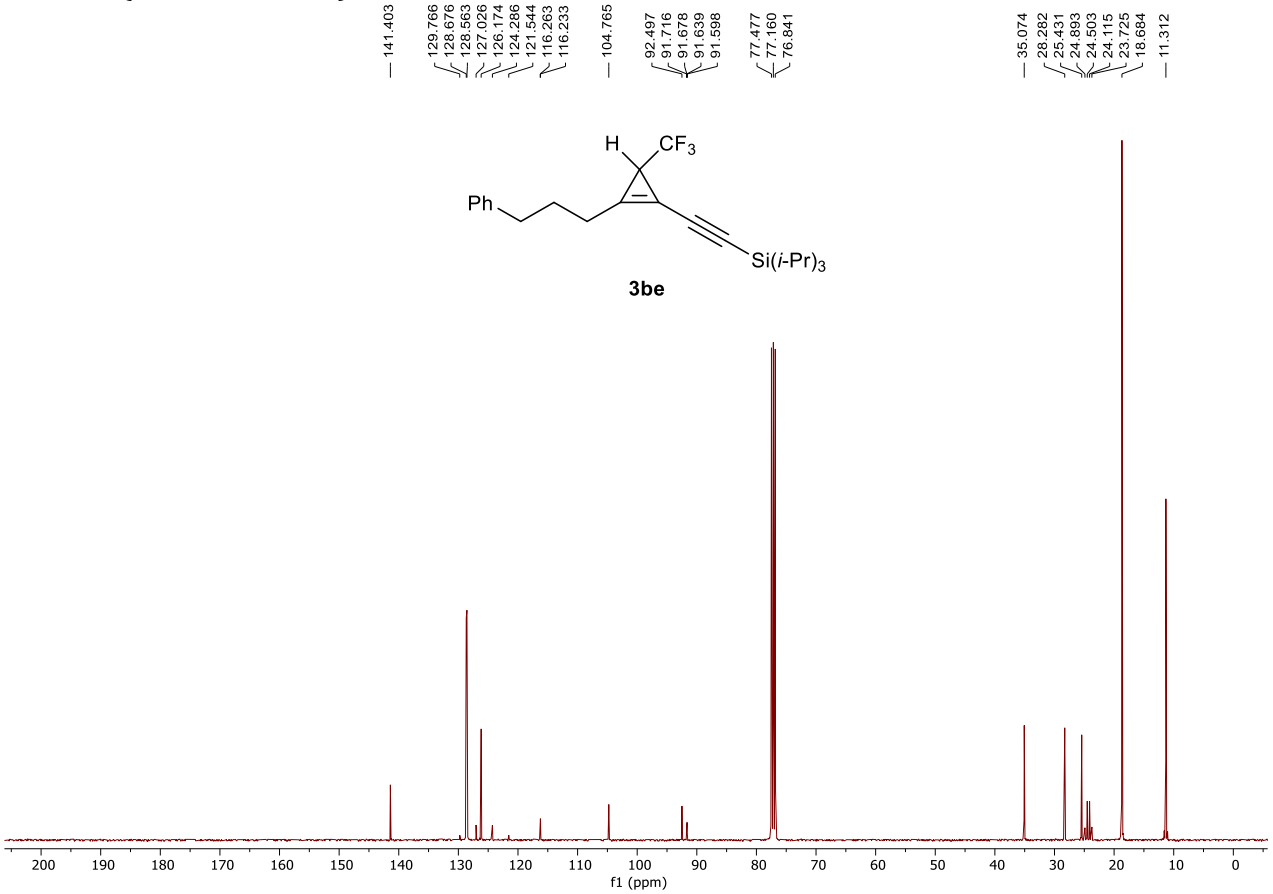
^{13}C NMR (101 MHz, $CDCl_3$) of 3bd



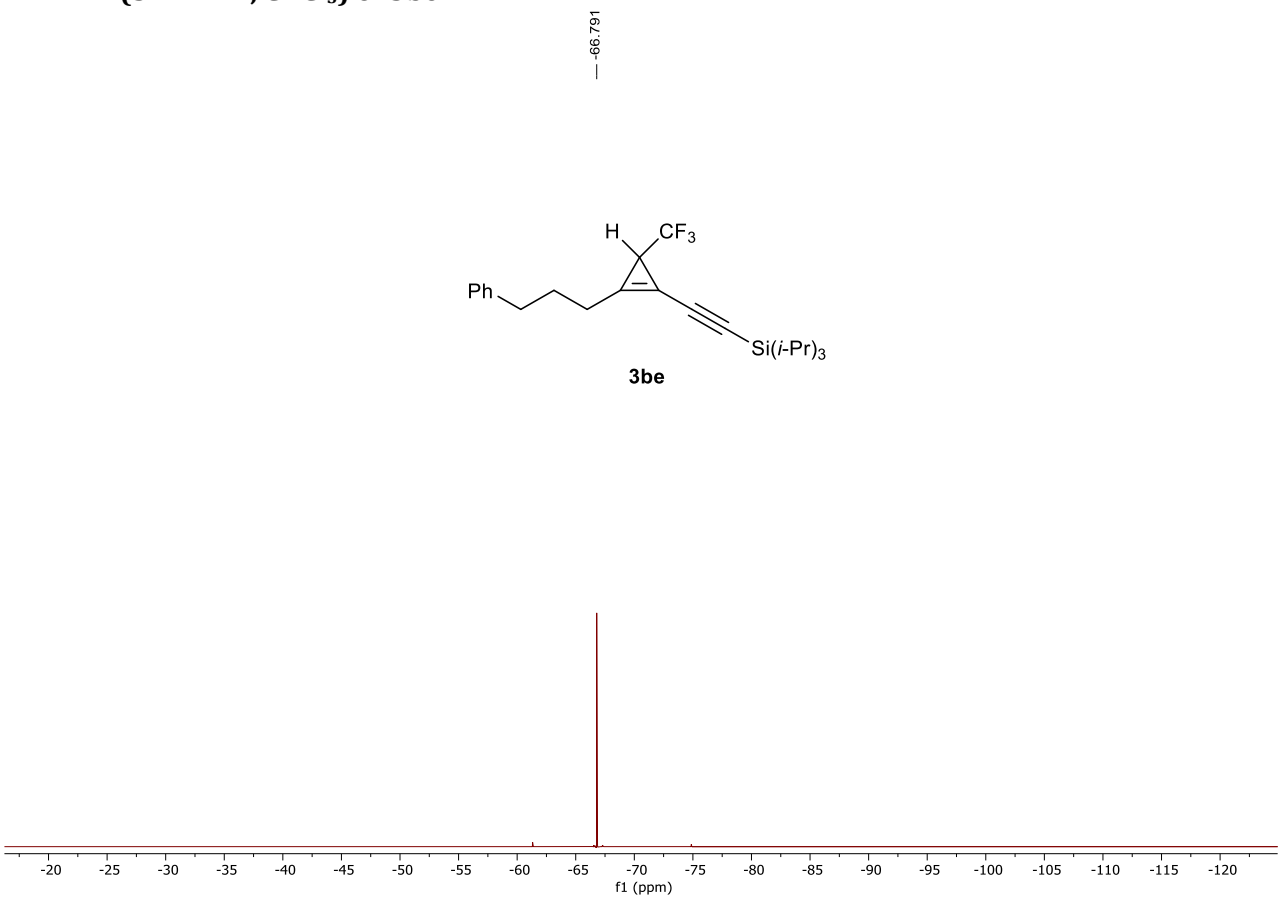
^{1}H NMR (400 MHz, $CDCl_3$) of 3be



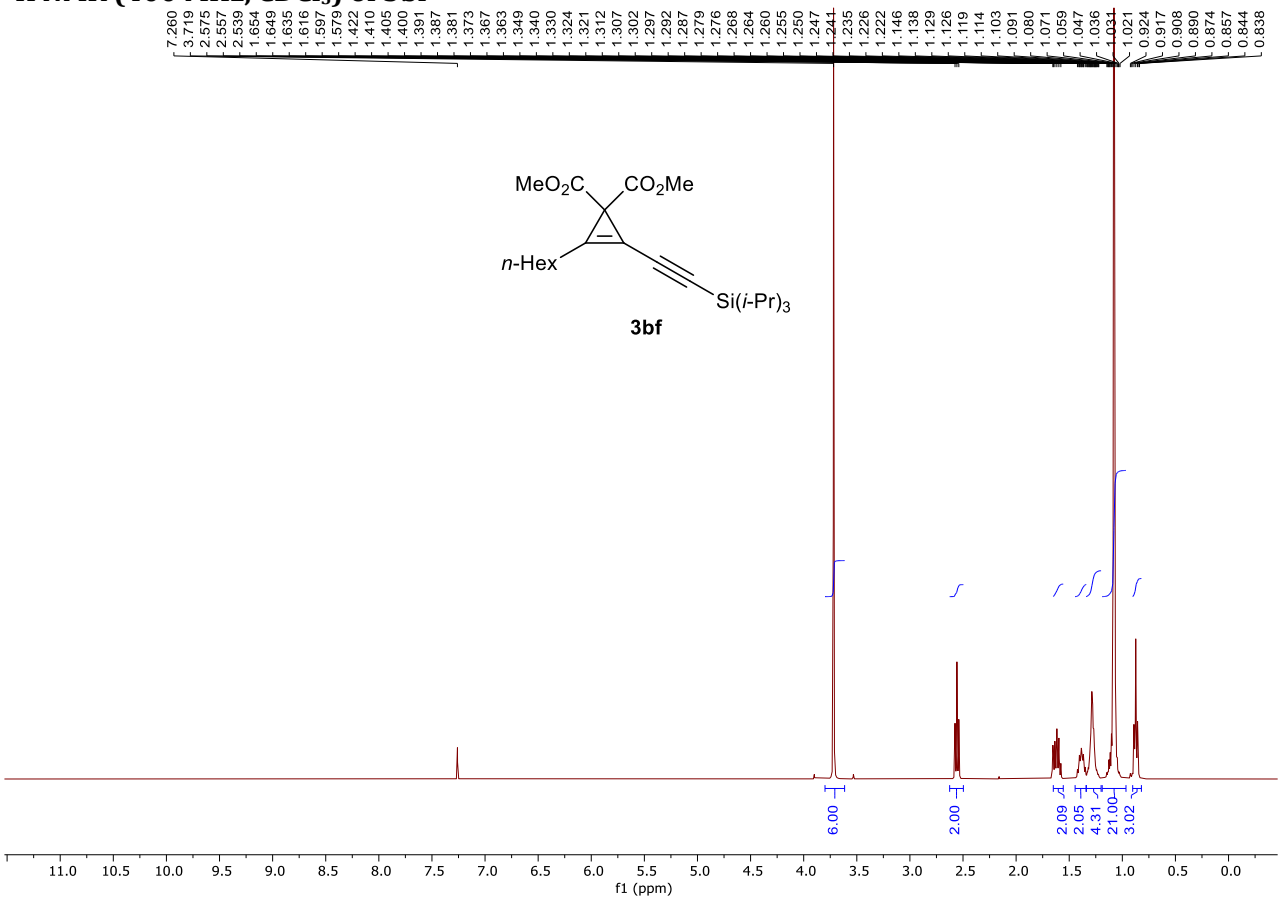
^{13}C NMR (101 MHz, $CDCl_3$) of 3be



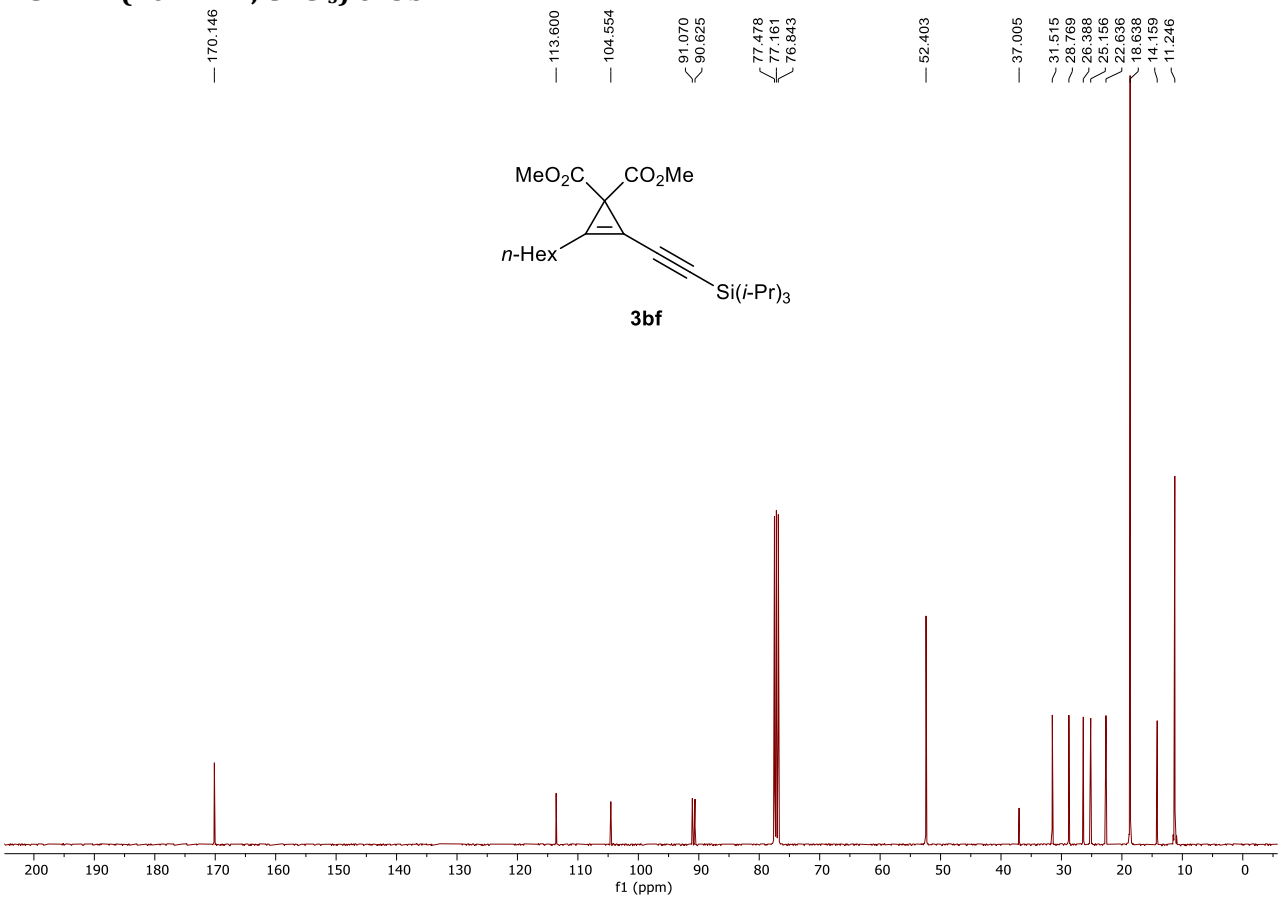
^{19}F NMR (377 MHz, $CDCl_3$) of 3be



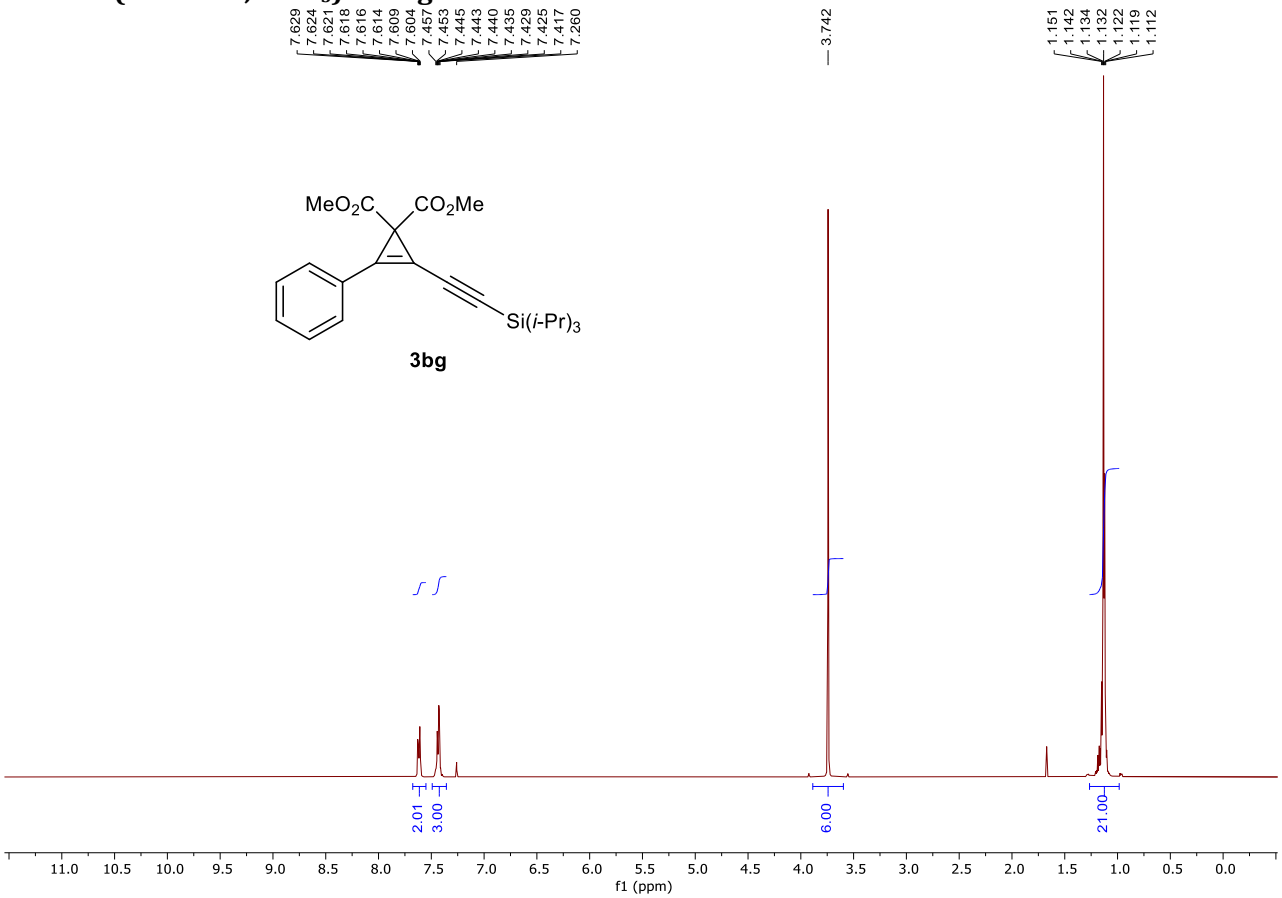
^{1}H NMR (400 MHz, $CDCl_3$) of 3bf



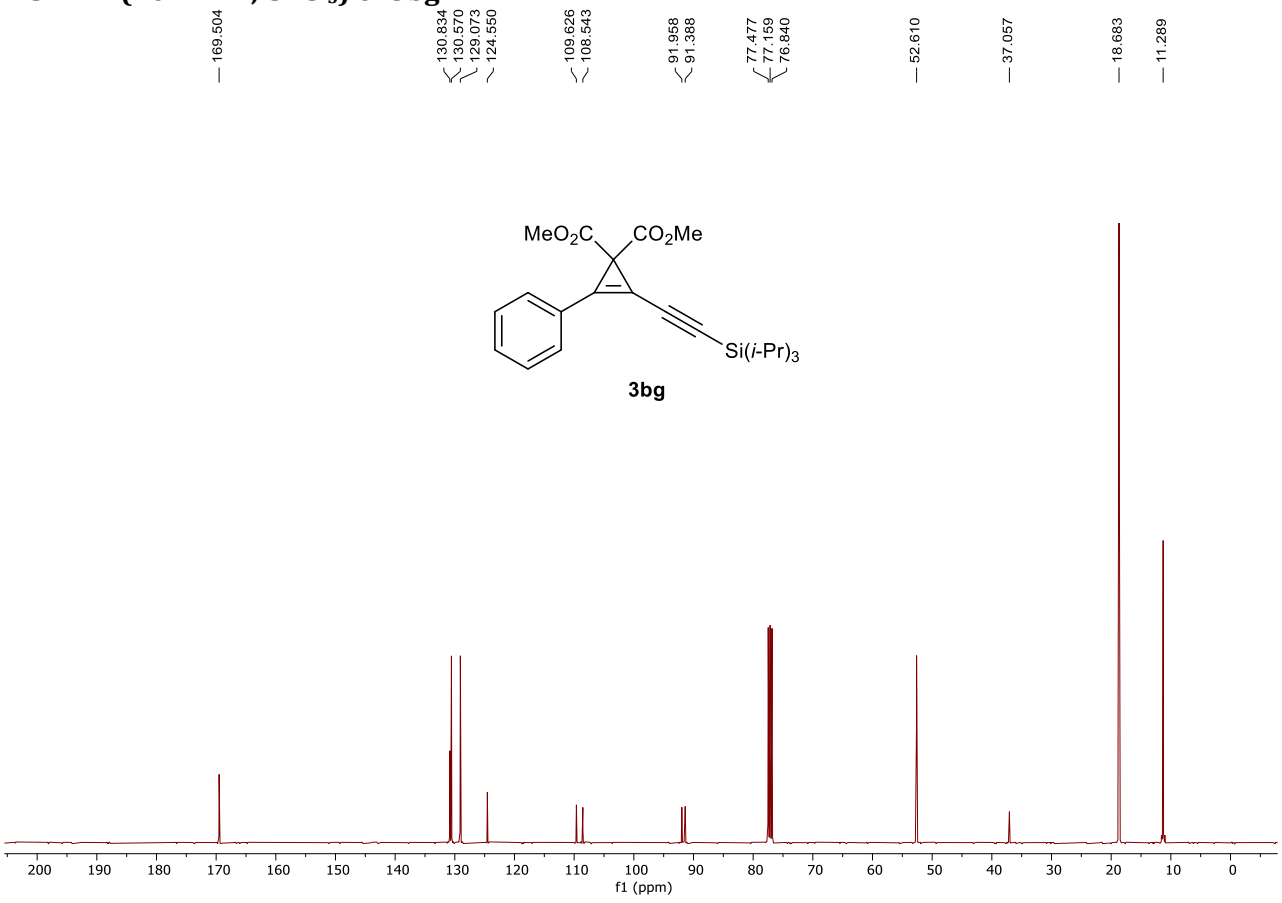
^{13}C NMR (101 MHz, $CDCl_3$) of 3bf



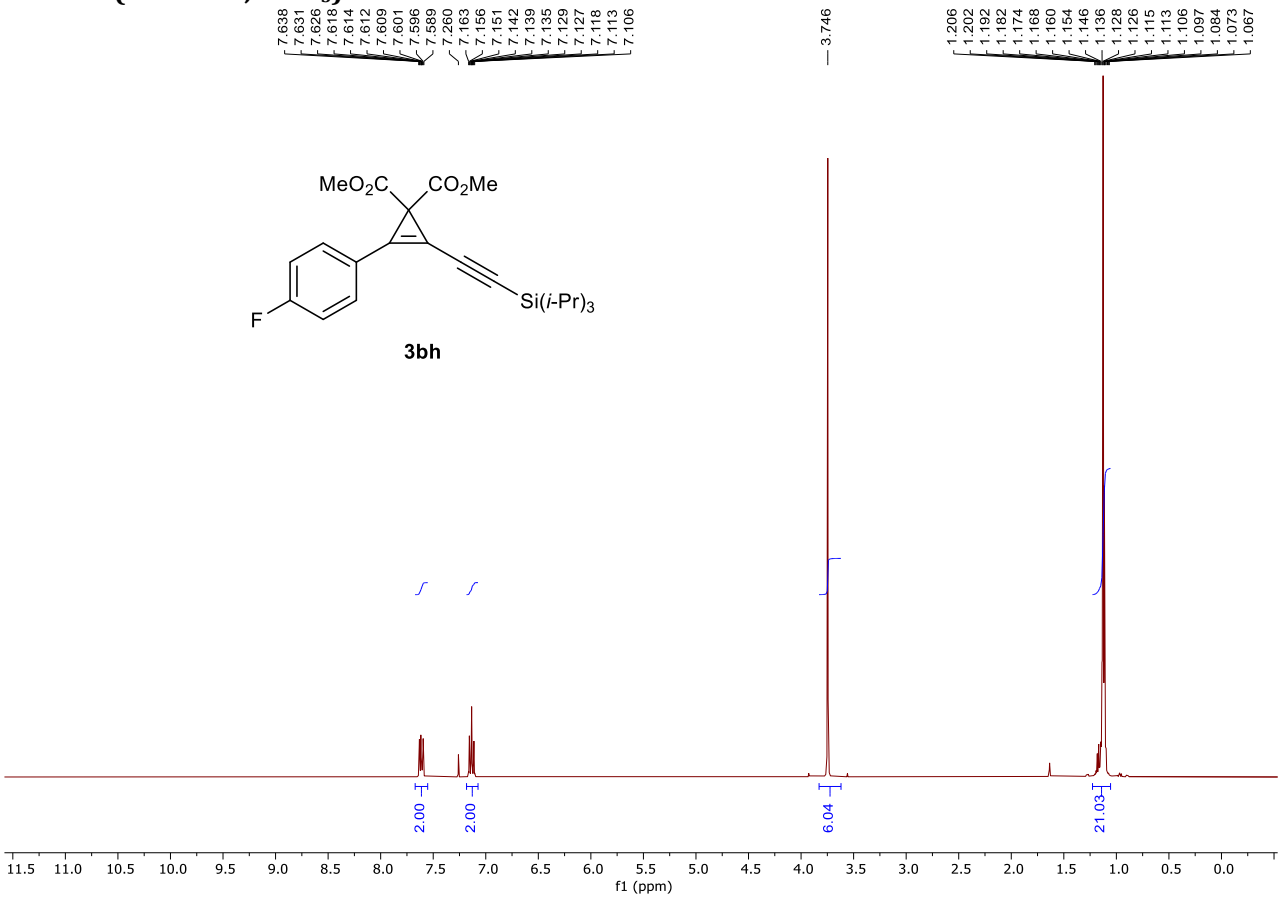
^{1}H NMR (400 MHz, $CDCl_3$) of 3bg



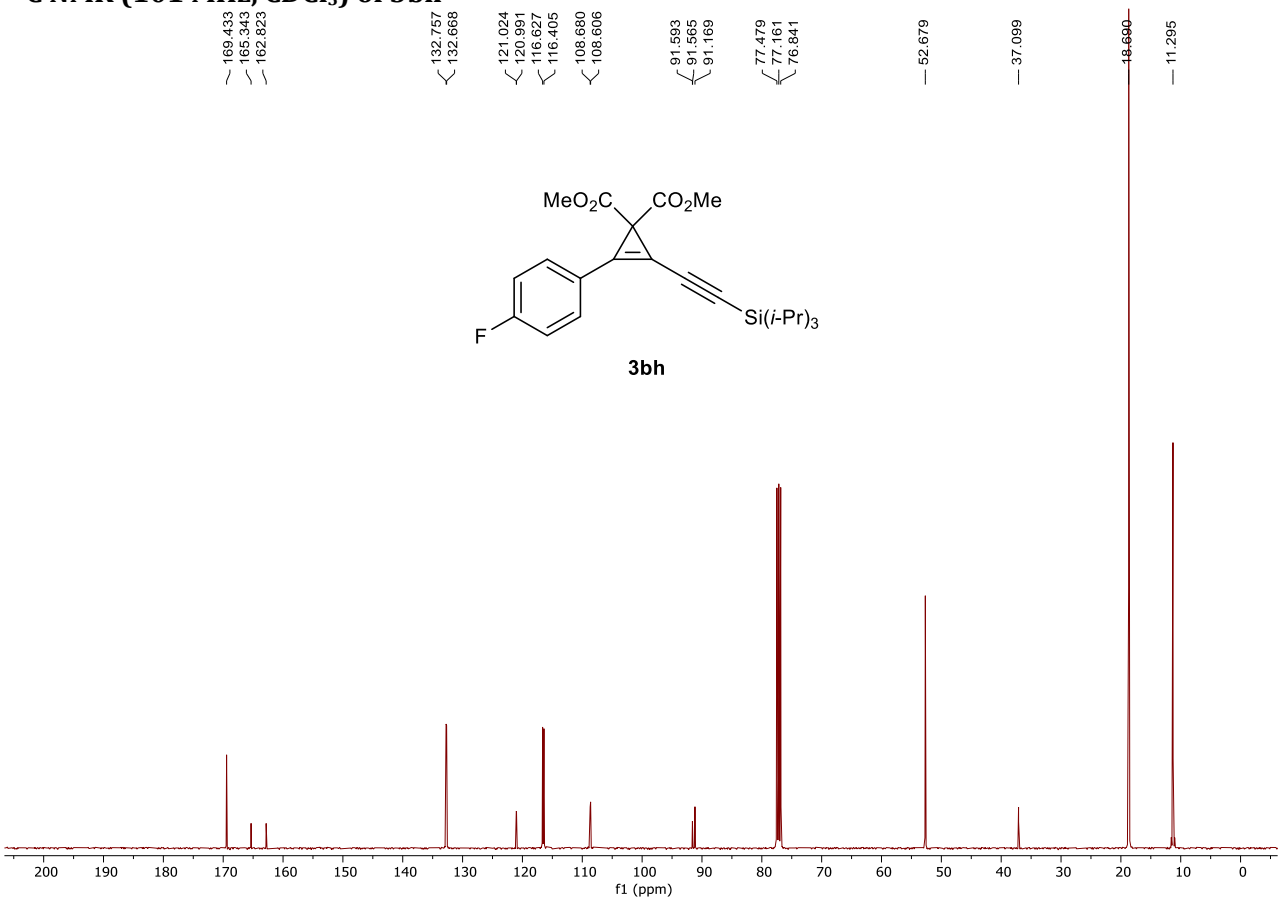
^{13}C NMR (101 MHz, $CDCl_3$) of 3bg



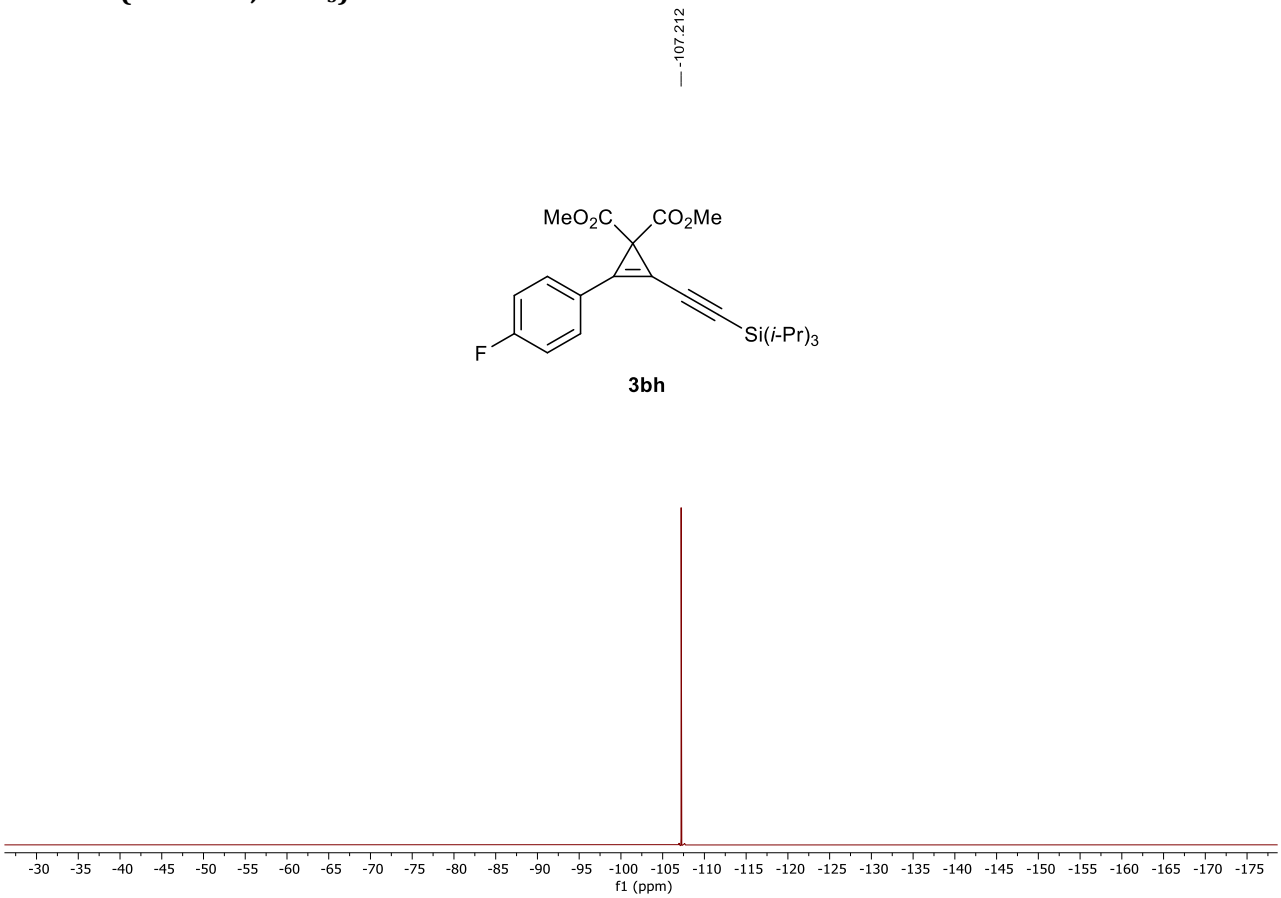
^{1}H NMR (400 MHz, $CDCl_3$) of 3bh



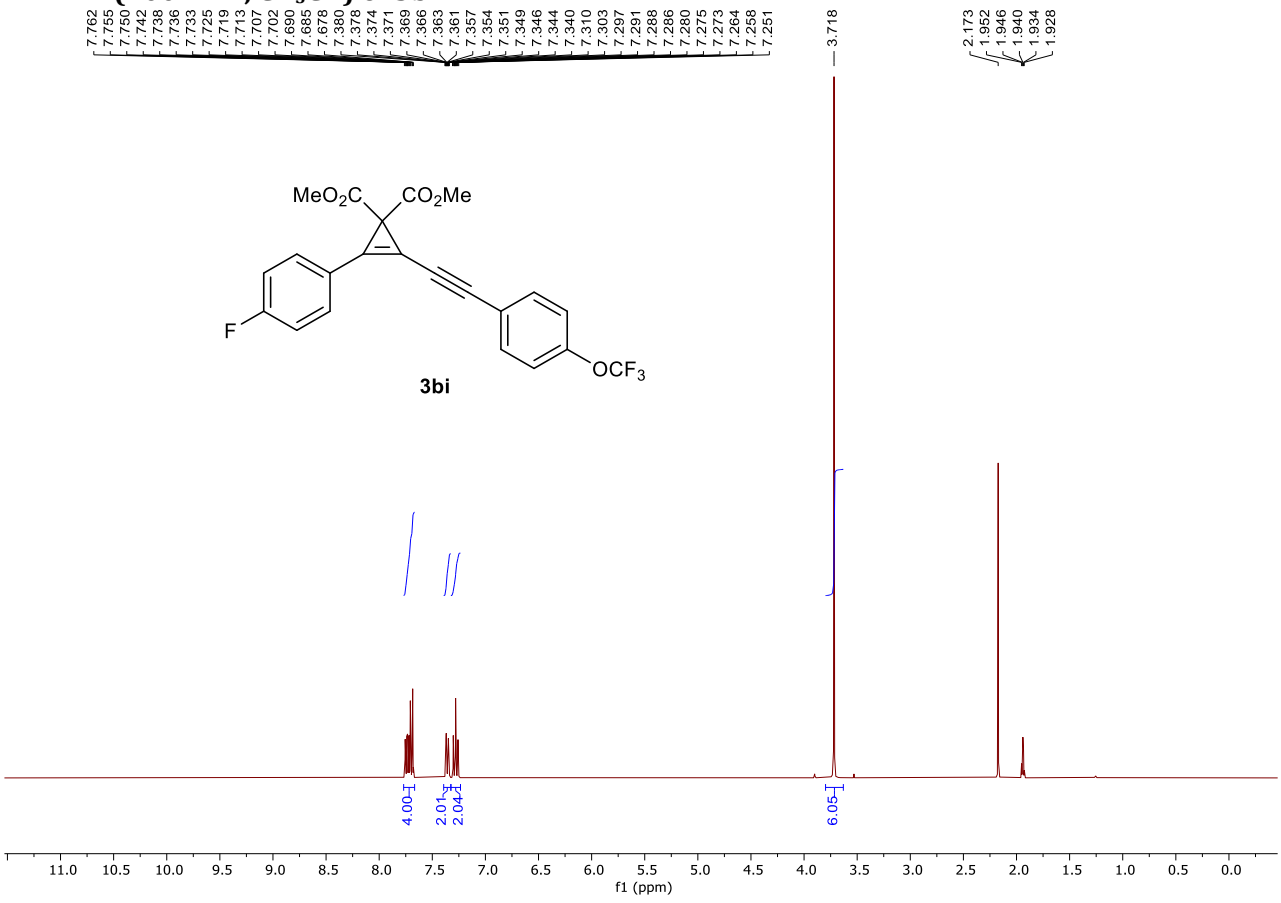
^{13}C NMR (101 MHz, $CDCl_3$) of 3bh



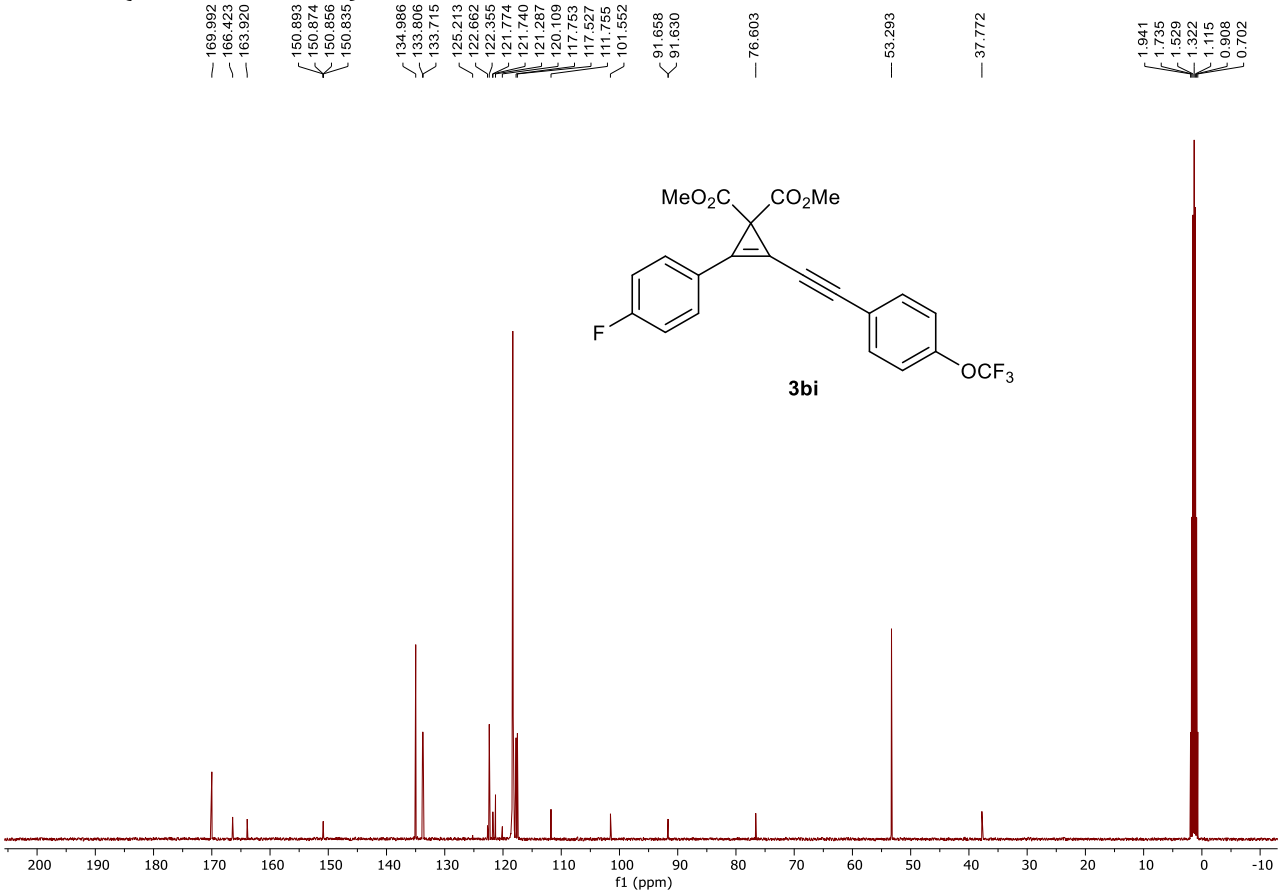
^{19}F NMR (377 MHz, $CDCl_3$) of 3bh



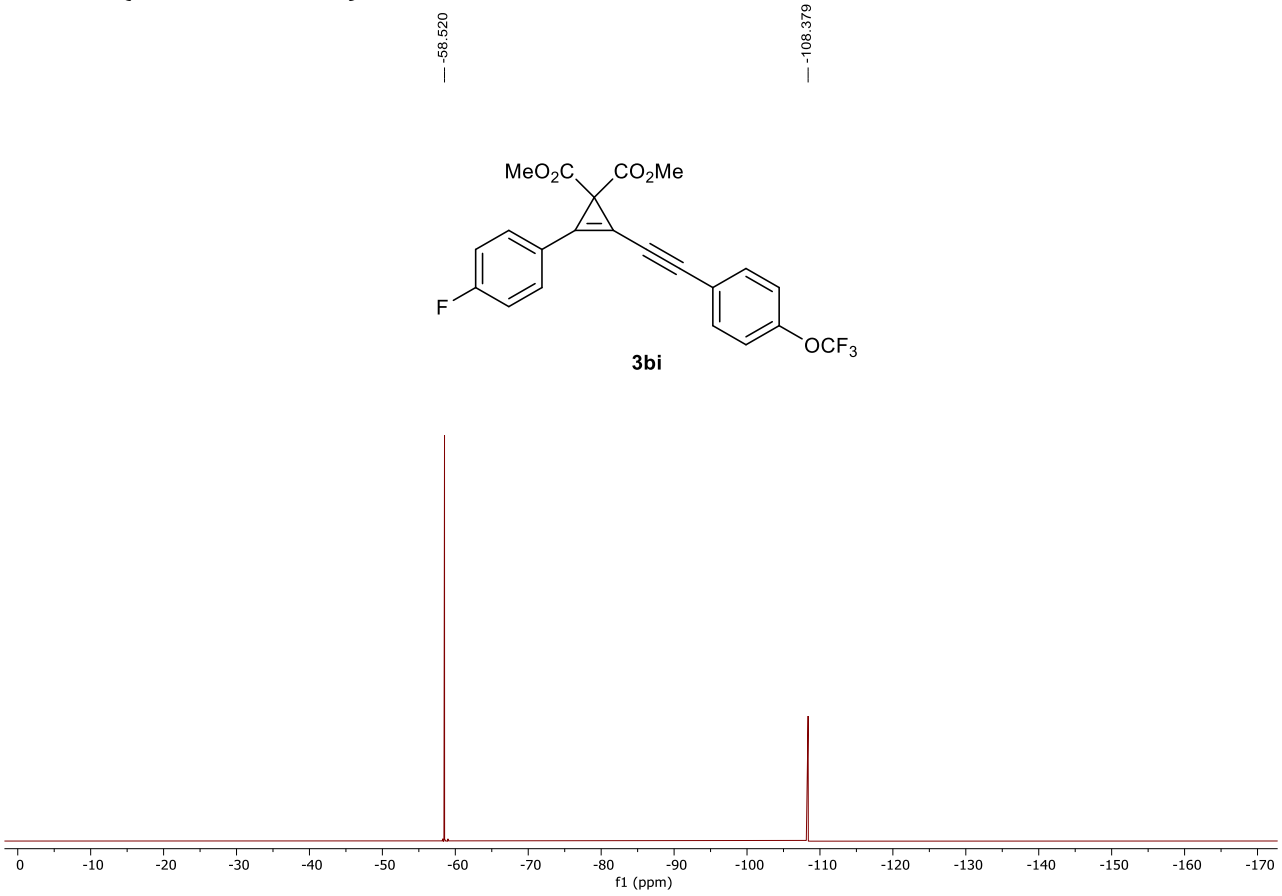
^{1}H NMR (400 MHz, CD_3CN) of 3bi



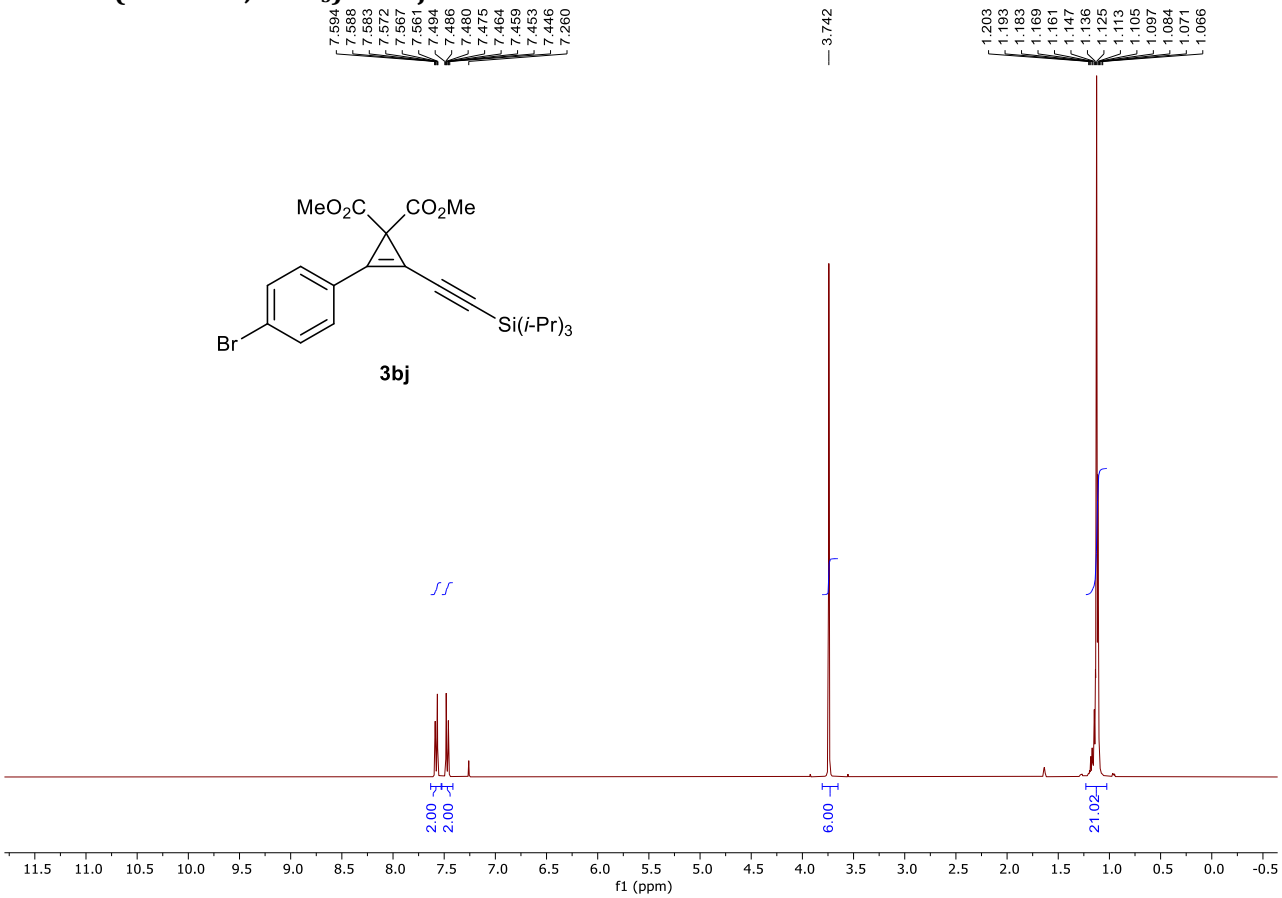
^{13}C NMR (101 MHz, CD_3CN) of 3bi



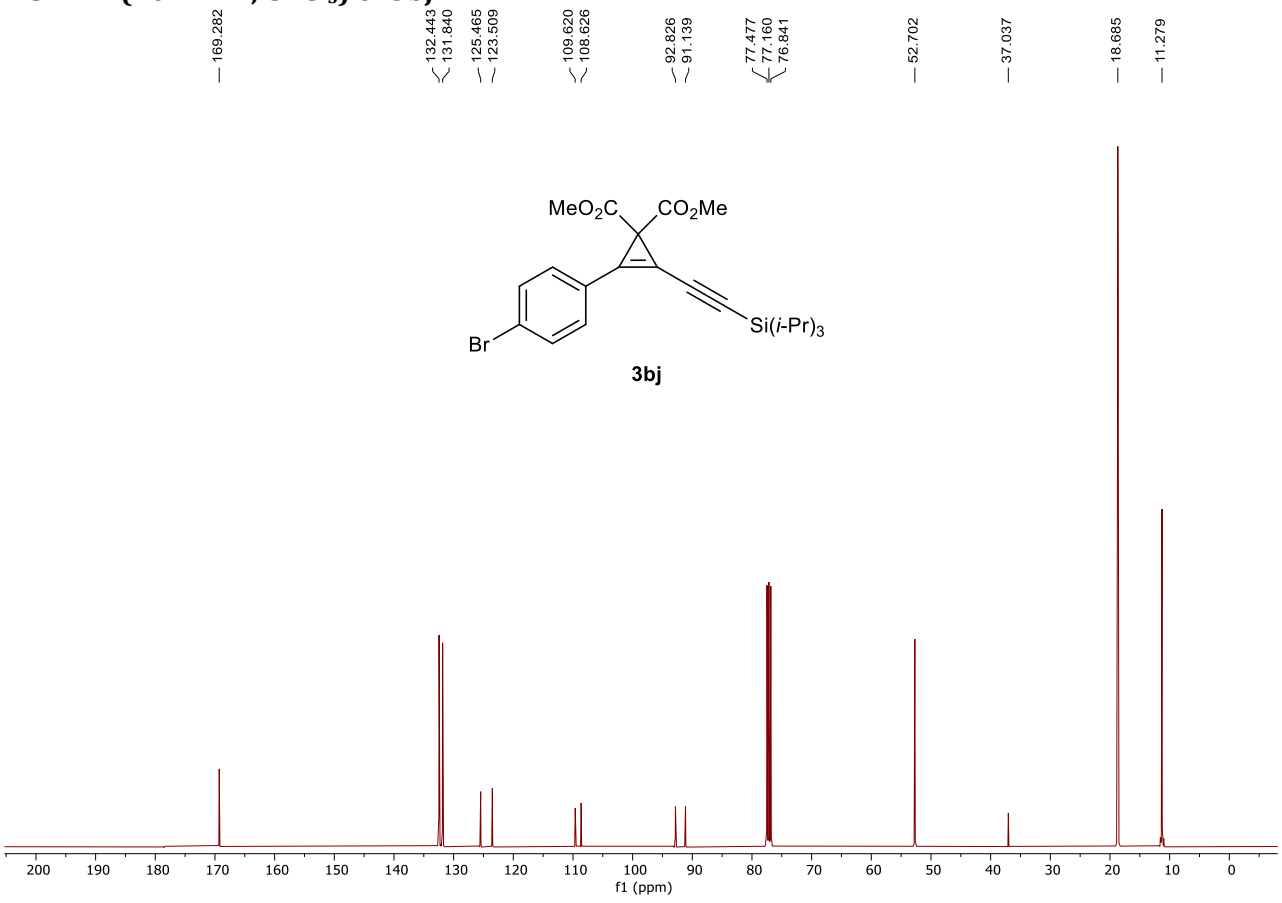
^{19}F NMR (377 MHz, CD_3CN) of 3bi



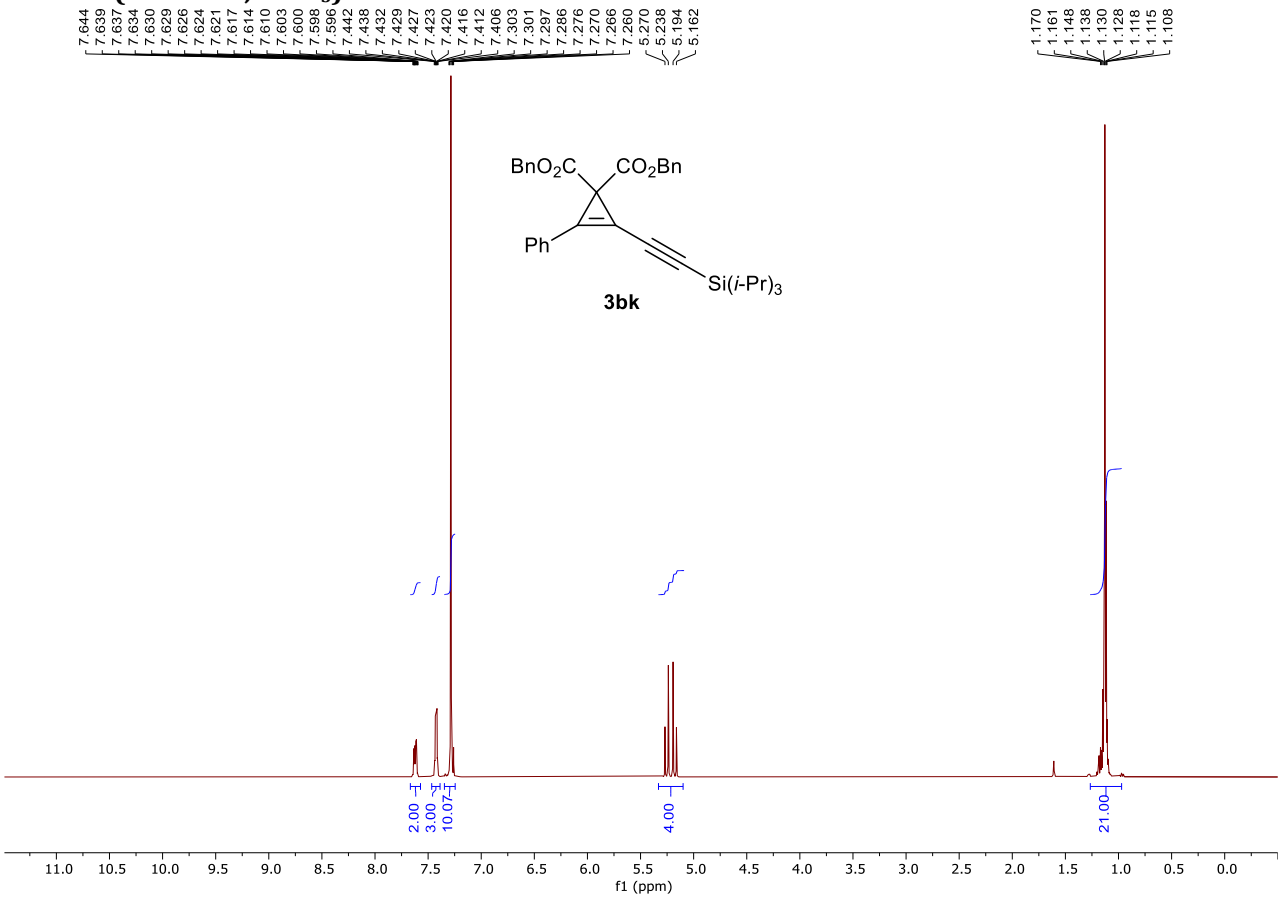
^{1}H NMR (400 MHz, $CDCl_3$) of 3bj



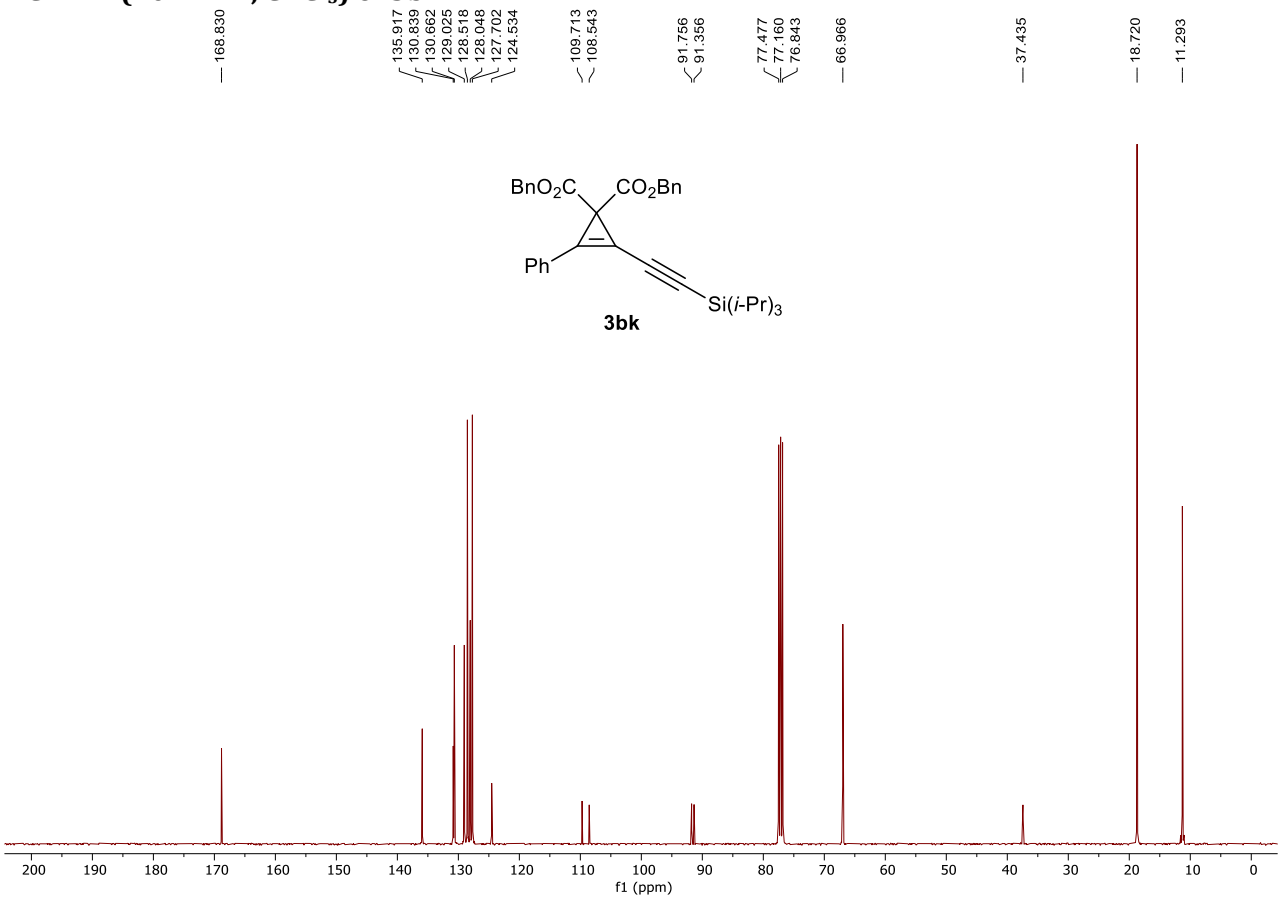
^{13}C NMR (101 MHz, $CDCl_3$) of 3bj



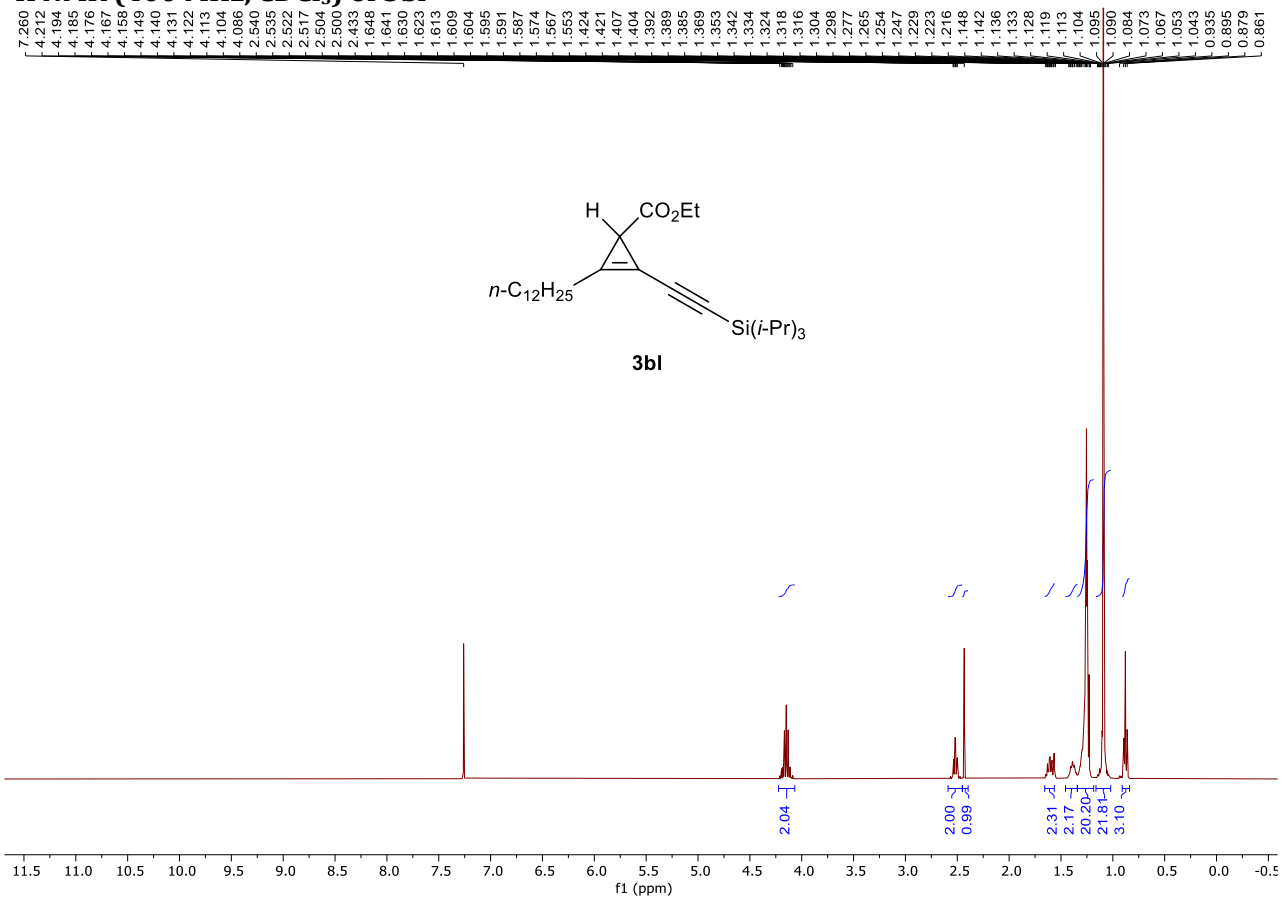
^{1}H NMR (400 MHz, $CDCl_3$) of 3bk



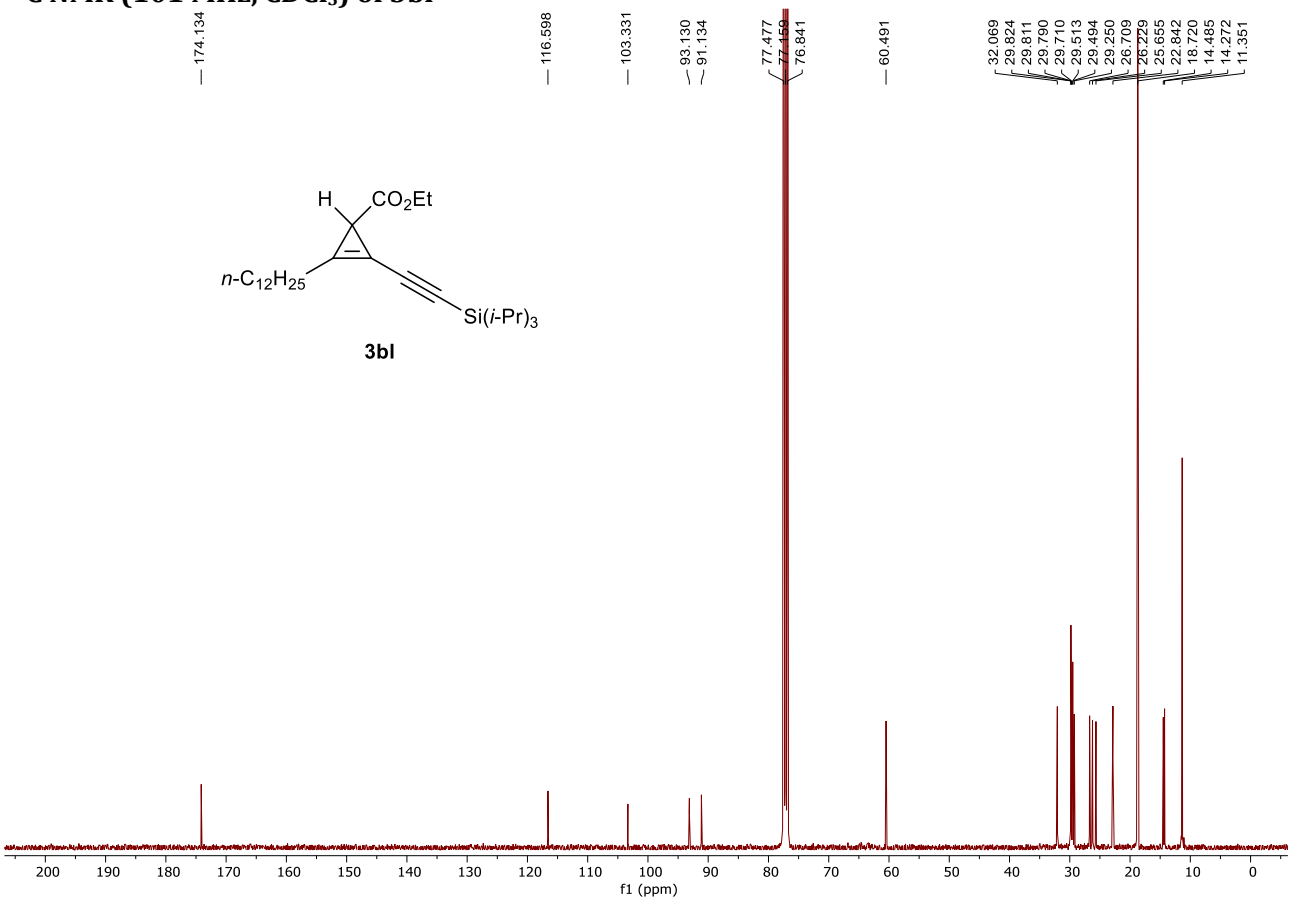
^{13}C NMR (101 MHz, $CDCl_3$) of 3bk



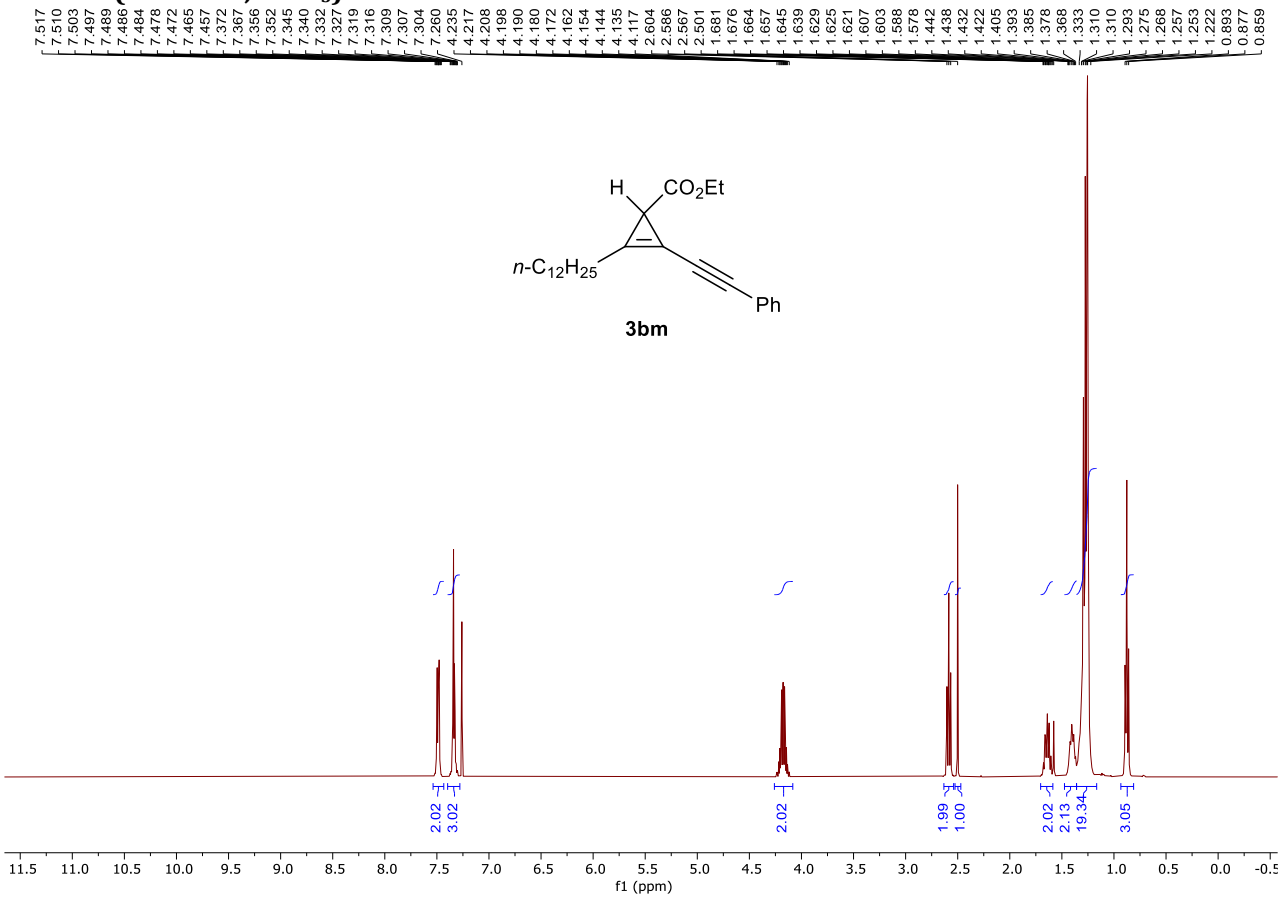
^{1}H NMR (400 MHz, $CDCl_3$) of 3bl



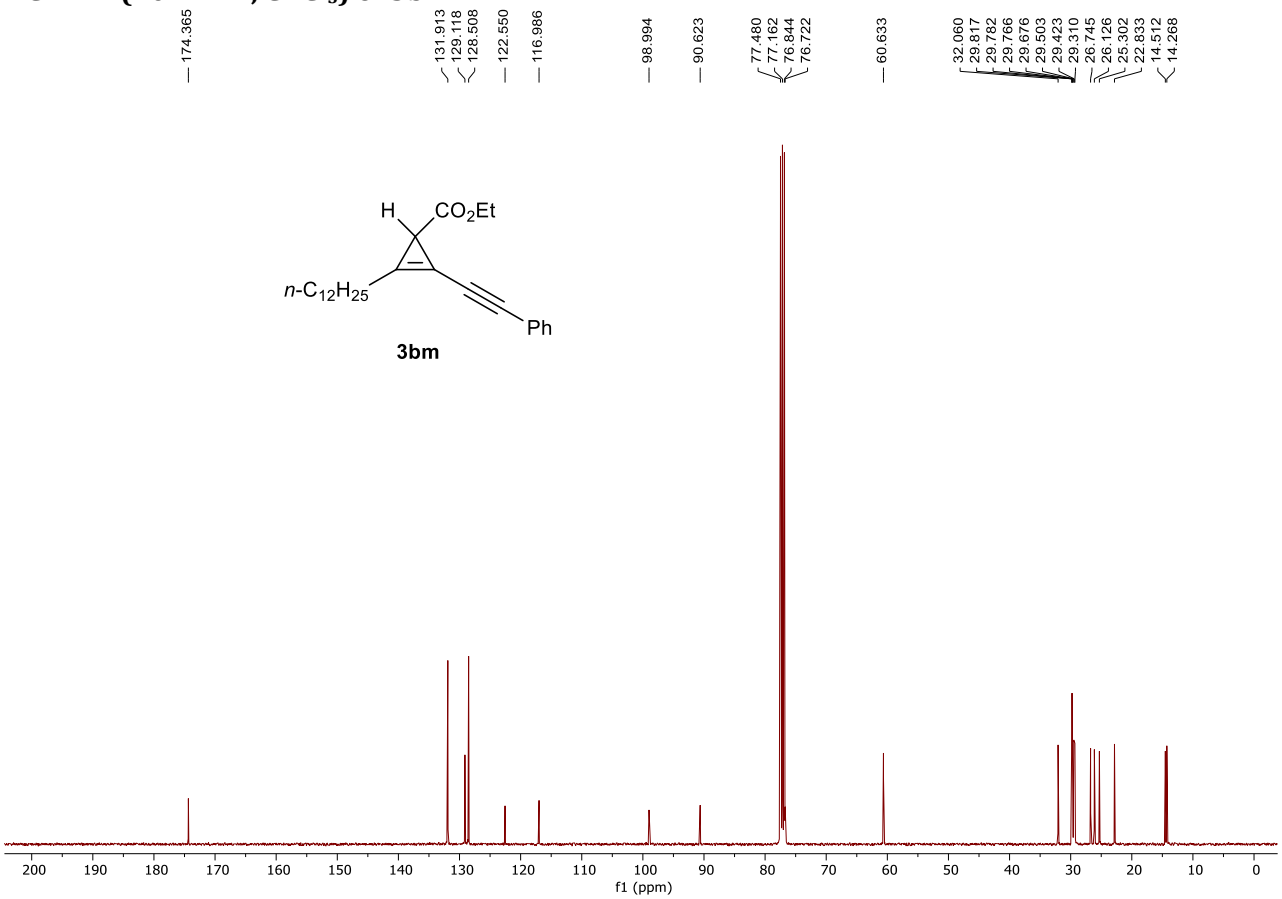
^{13}C NMR (101 MHz, $CDCl_3$) of 3bl



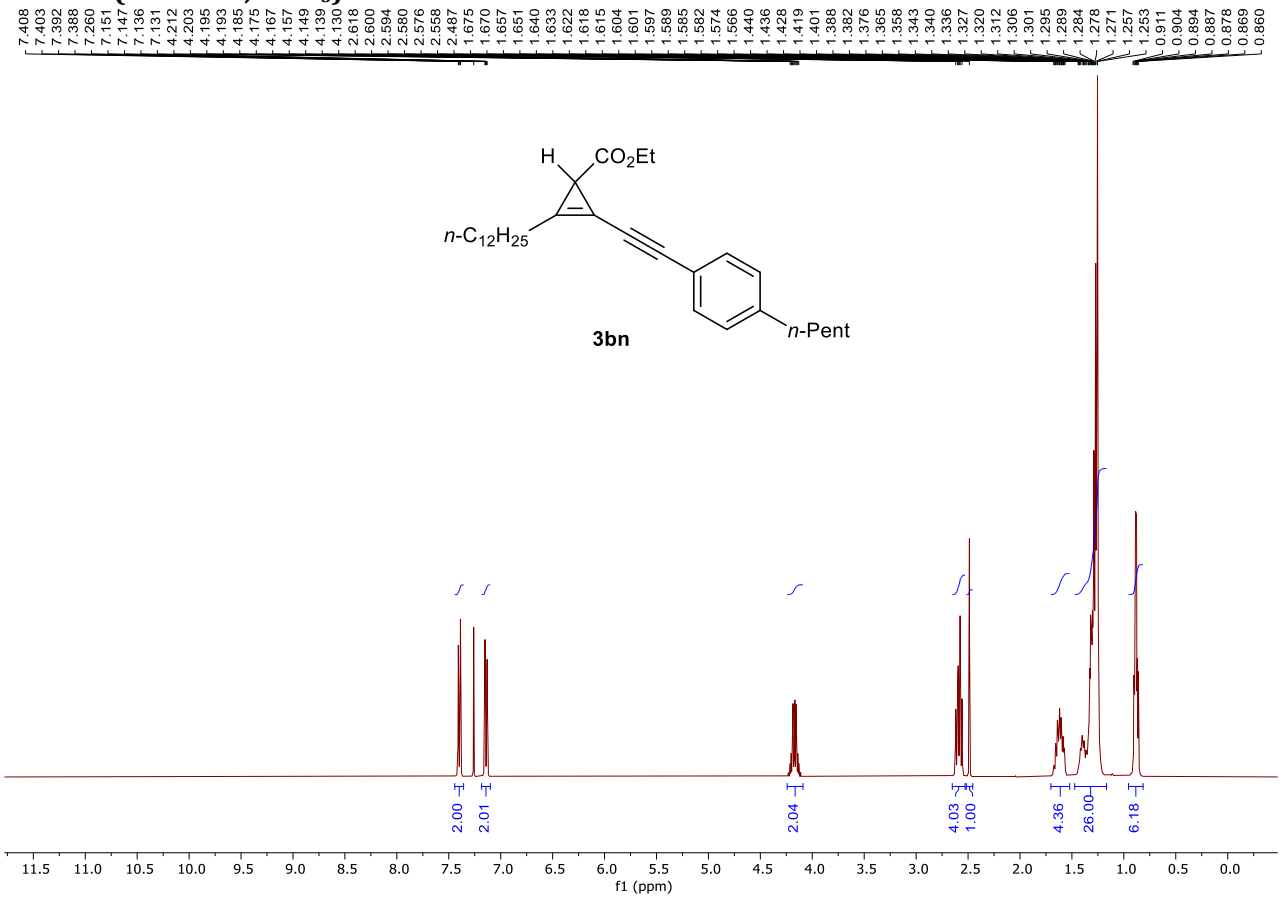
^{1}H NMR (400 MHz, $CDCl_3$) of 3bm



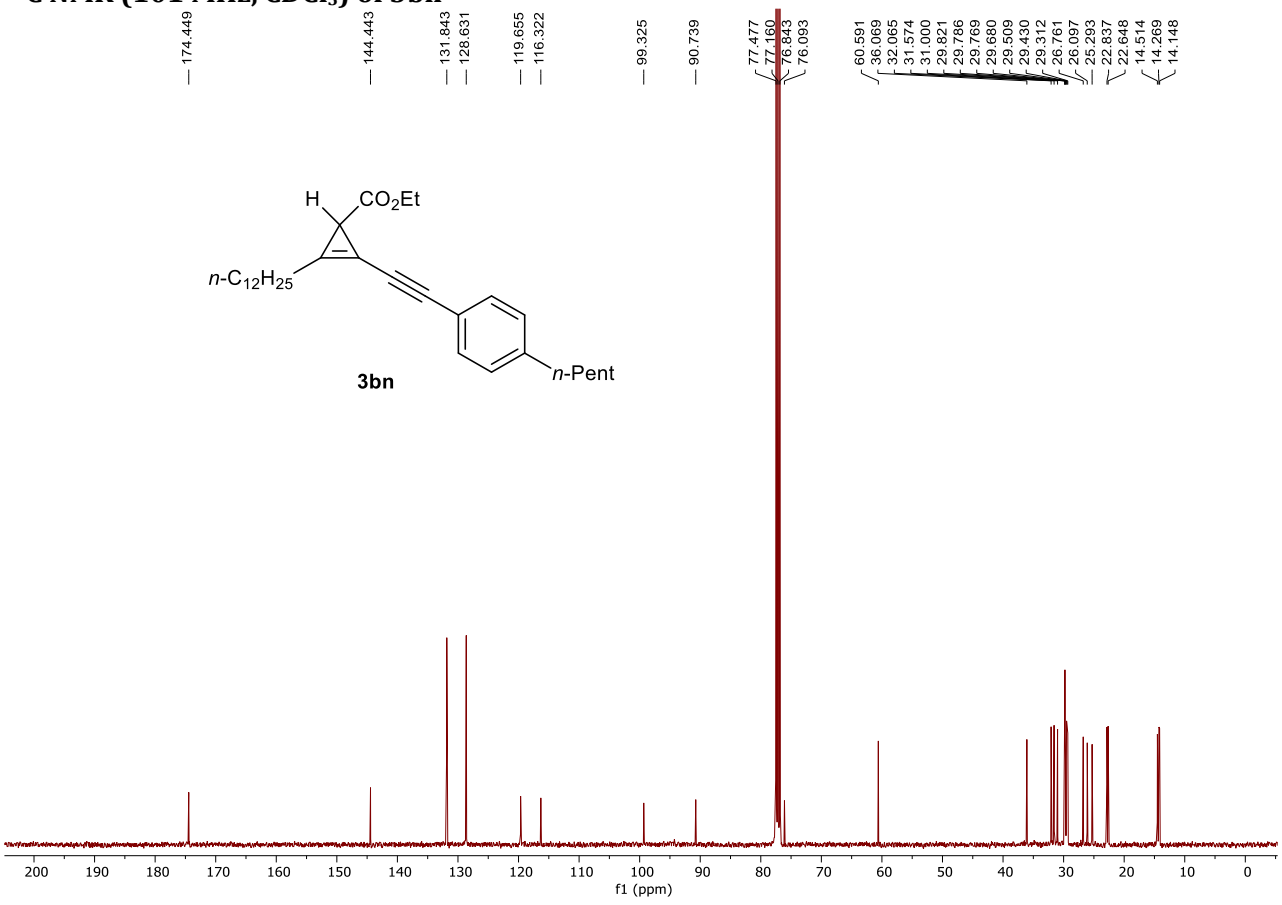
^{13}C NMR (101 MHz, $CDCl_3$) of 3bm



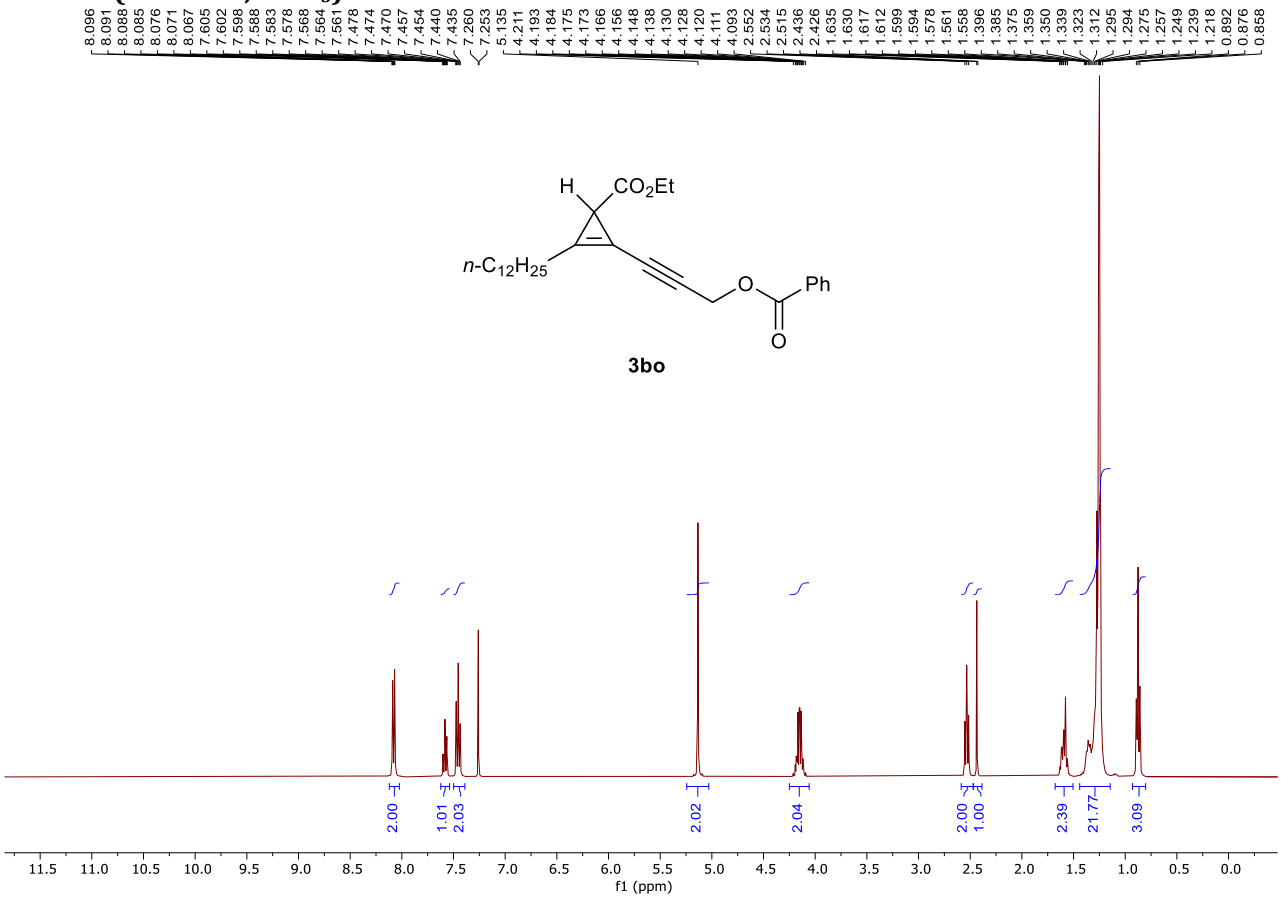
^{1}H NMR (400 MHz, $CDCl_3$) of 3bn



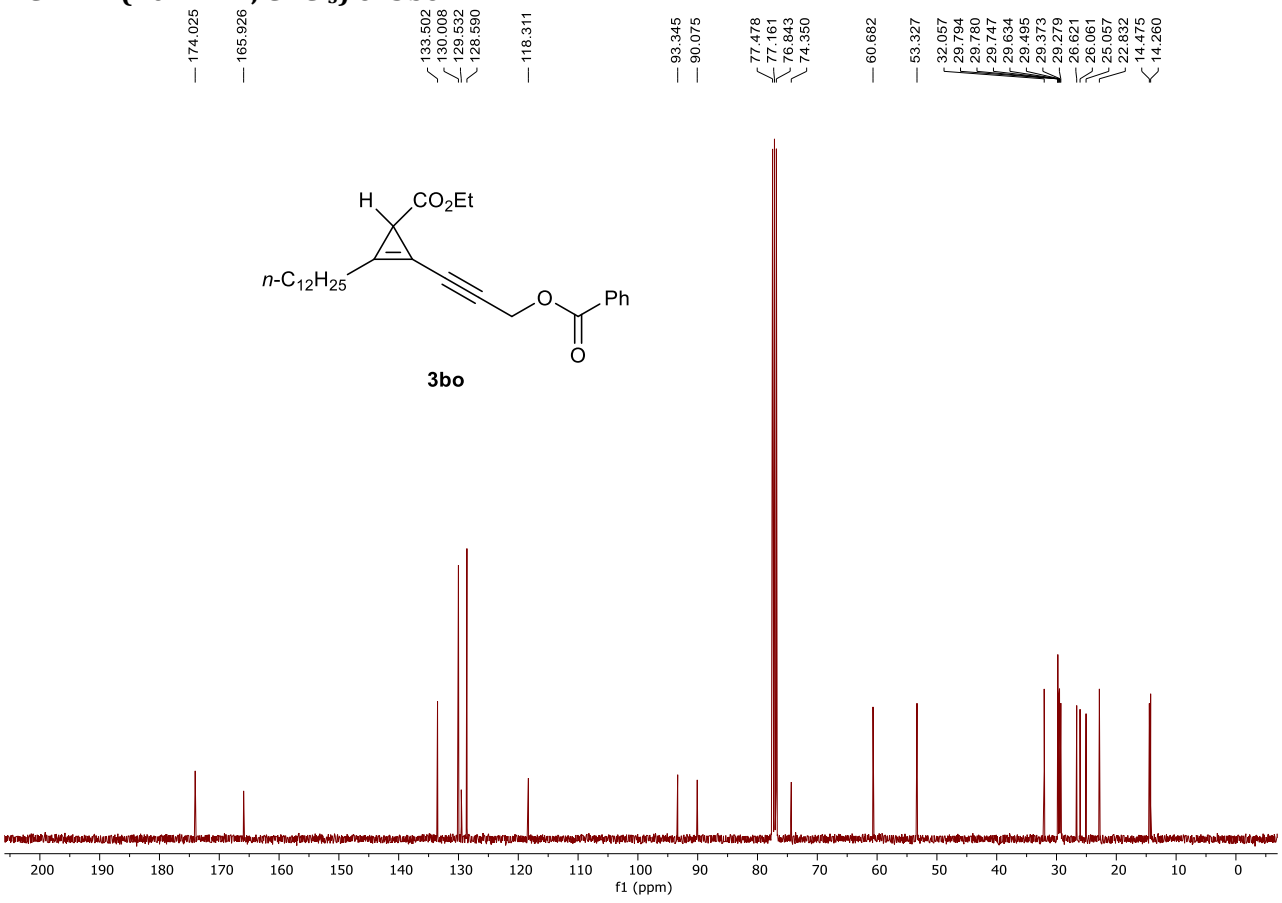
^{13}C NMR (101 MHz, $CDCl_3$) of 3bn



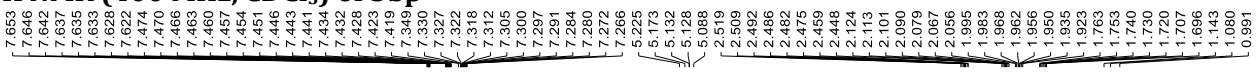
^{1}H NMR (400 MHz, $CDCl_3$) of 3bo

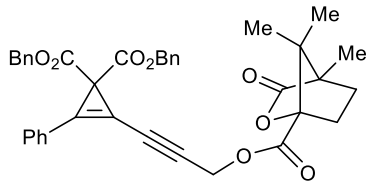


^{13}C NMR (101 MHz, $CDCl_3$) of 3bo

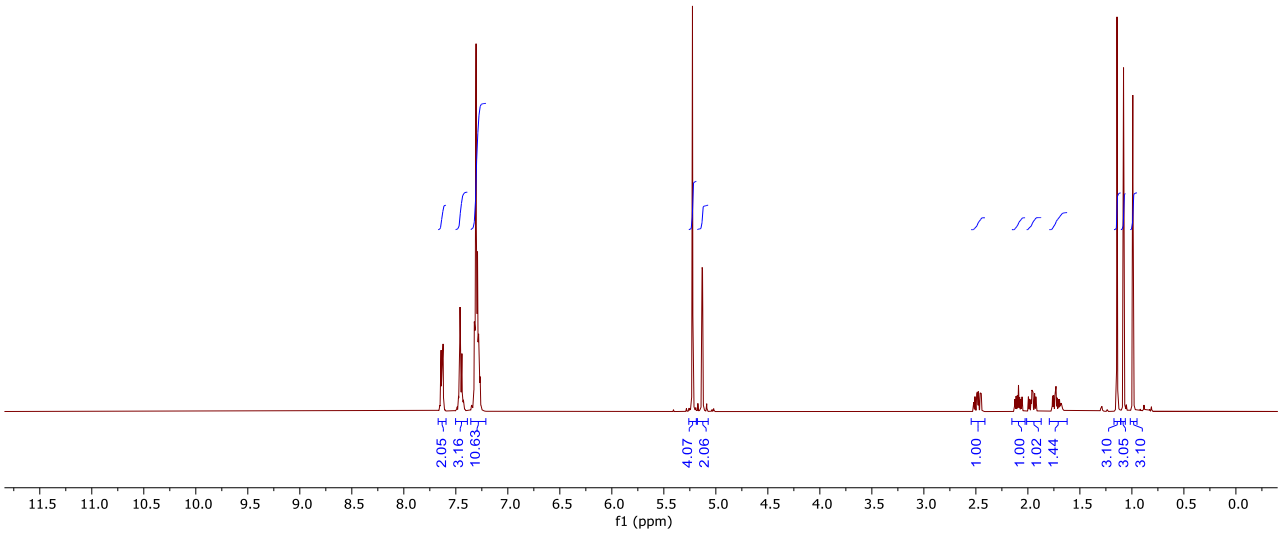


^{1}H NMR (400 MHz, $CDCl_3$) of 3bp

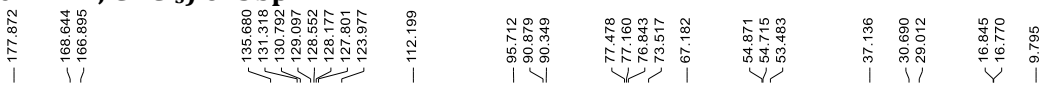


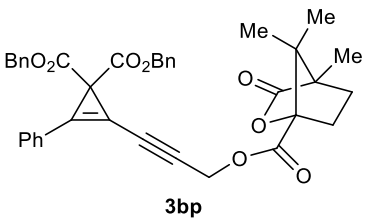


3bp



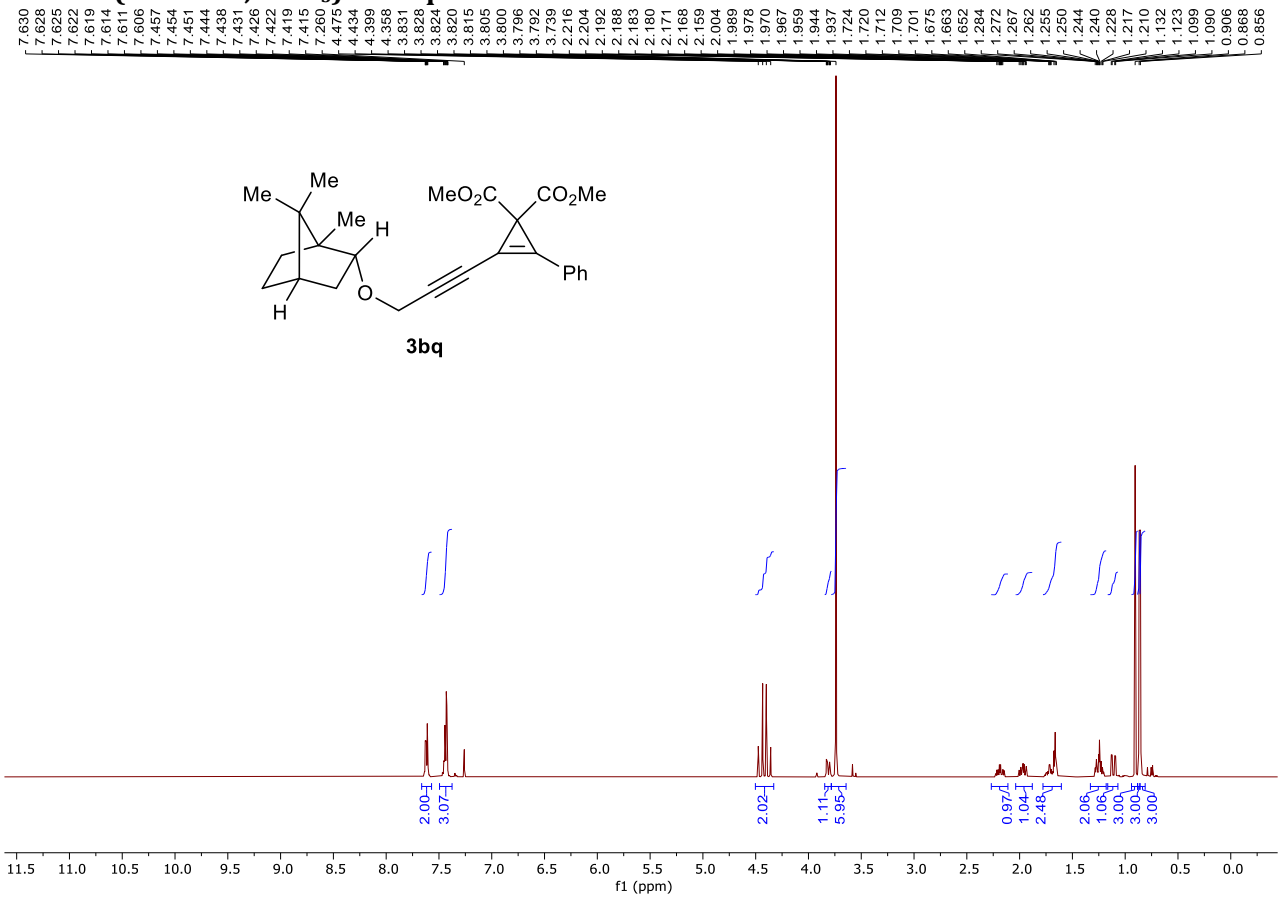
^{13}C NMR (101 MHz, $CDCl_3$) of 3bp





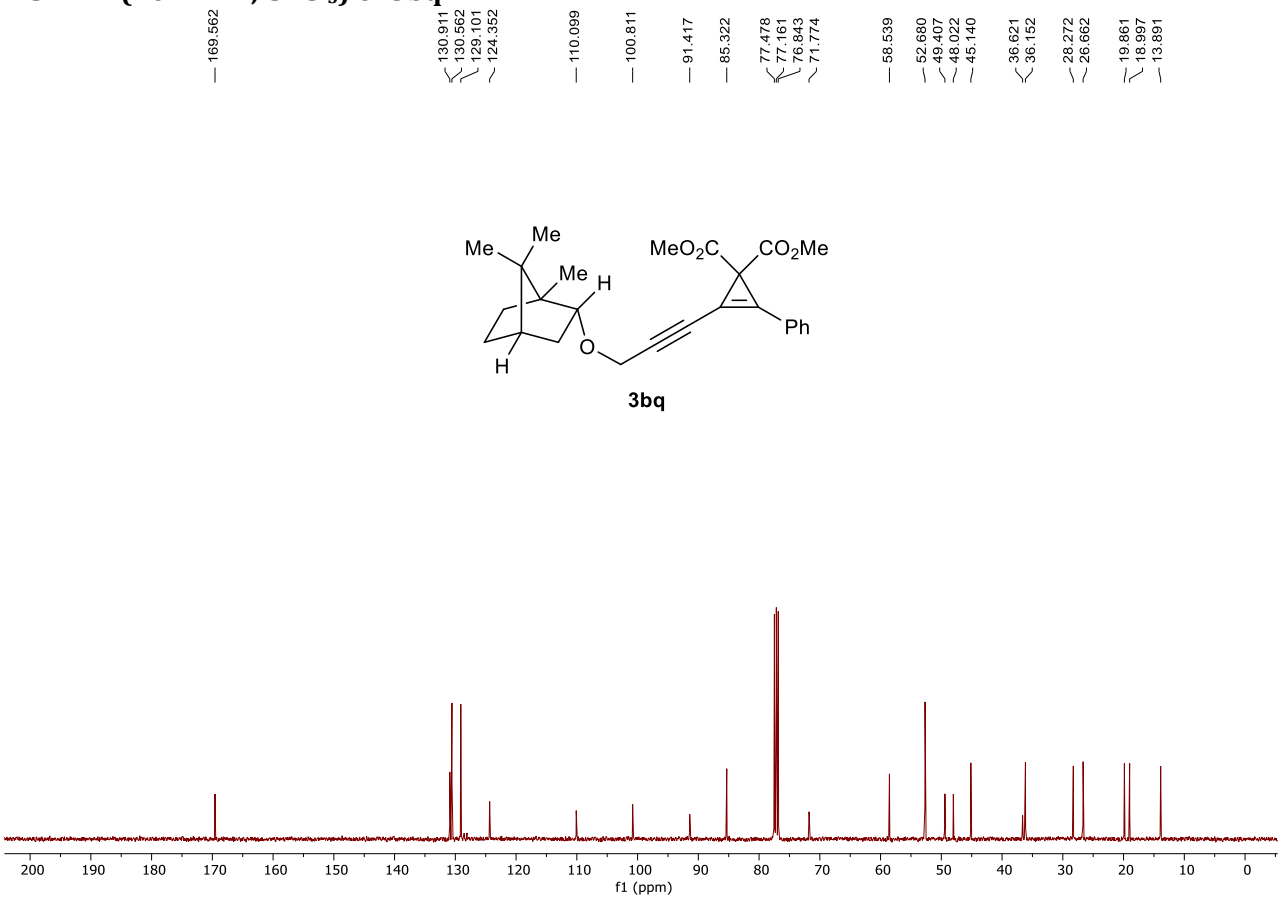
3bp

^{1}H NMR (400 MHz, $CDCl_3$) of 3bq



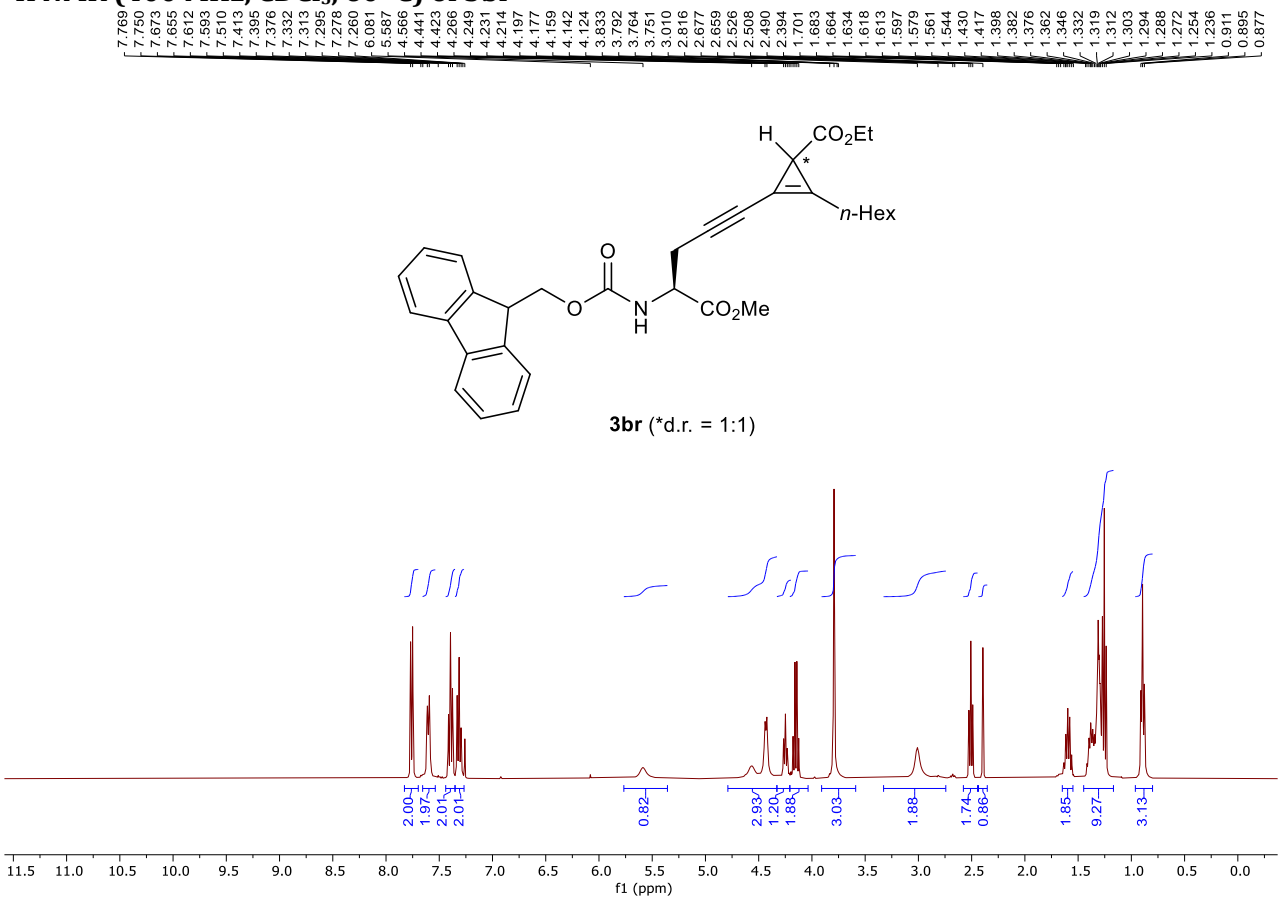
3bq

^{13}C NMR (101 MHz, $CDCl_3$) of 3bq



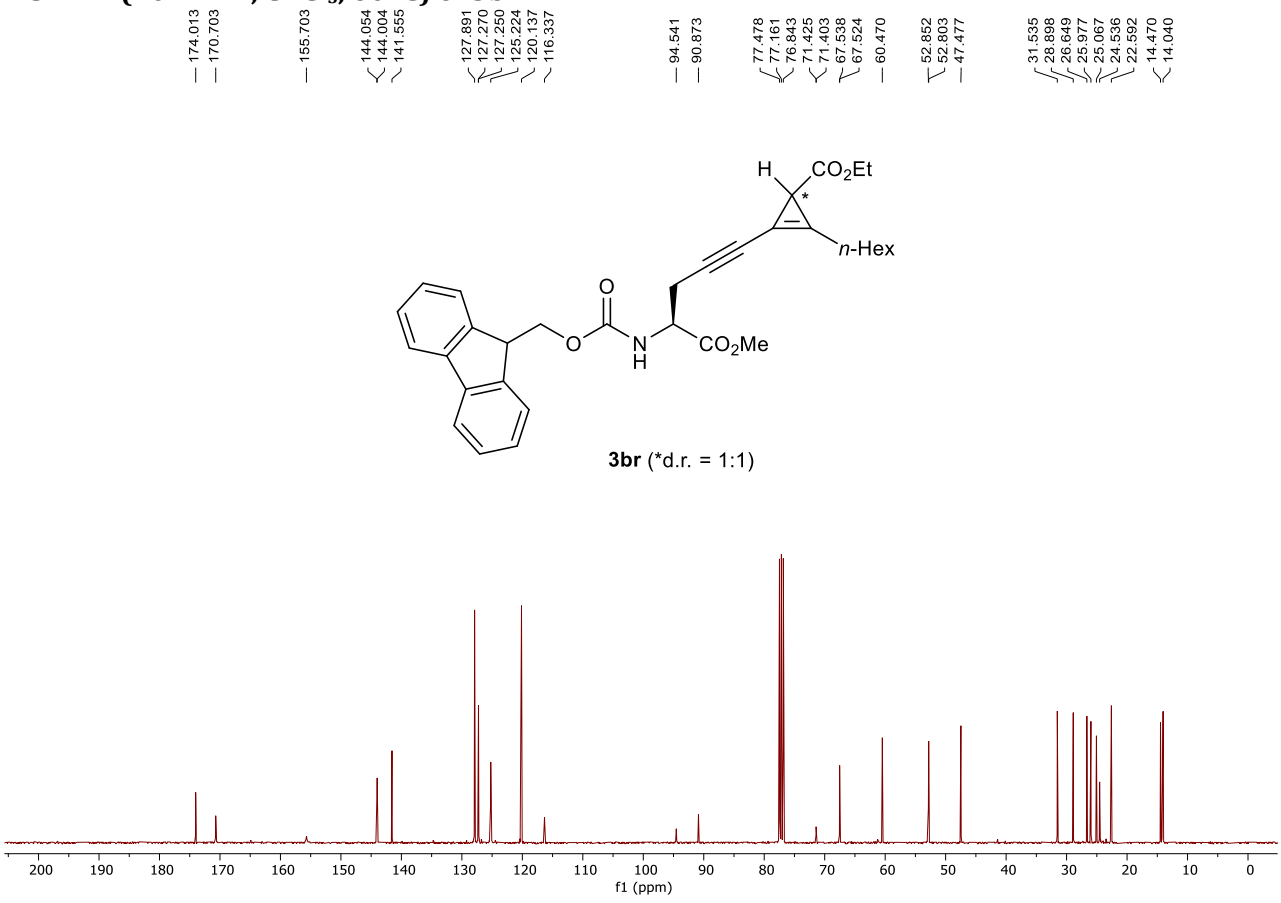
3bq

^{1}H NMR (400 MHz, $CDCl_3$, 60 °C) of 3br



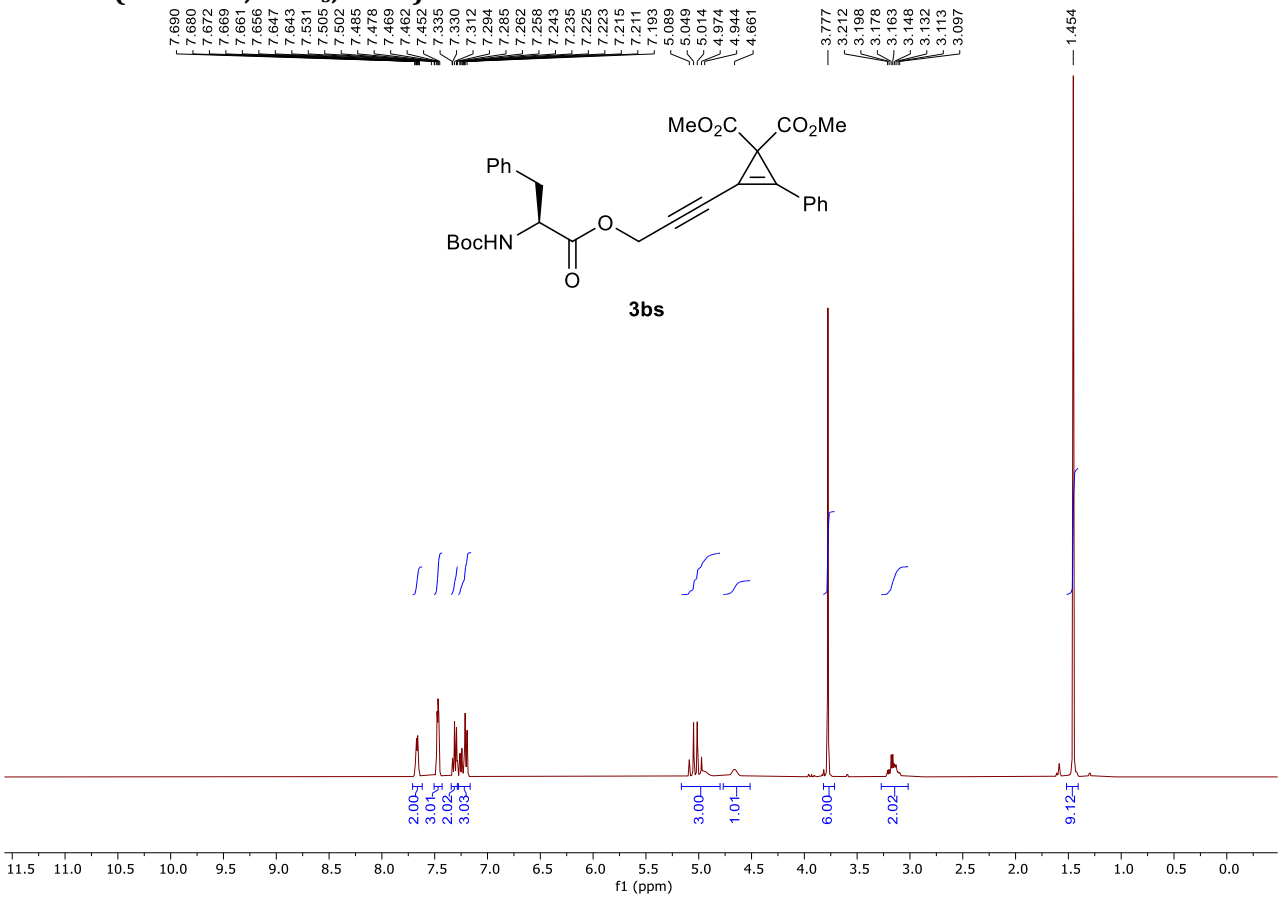
3br (*d.r. = 1:1)

^{13}C NMR (101 MHz, $CDCl_3$, 60 °C) of 3br

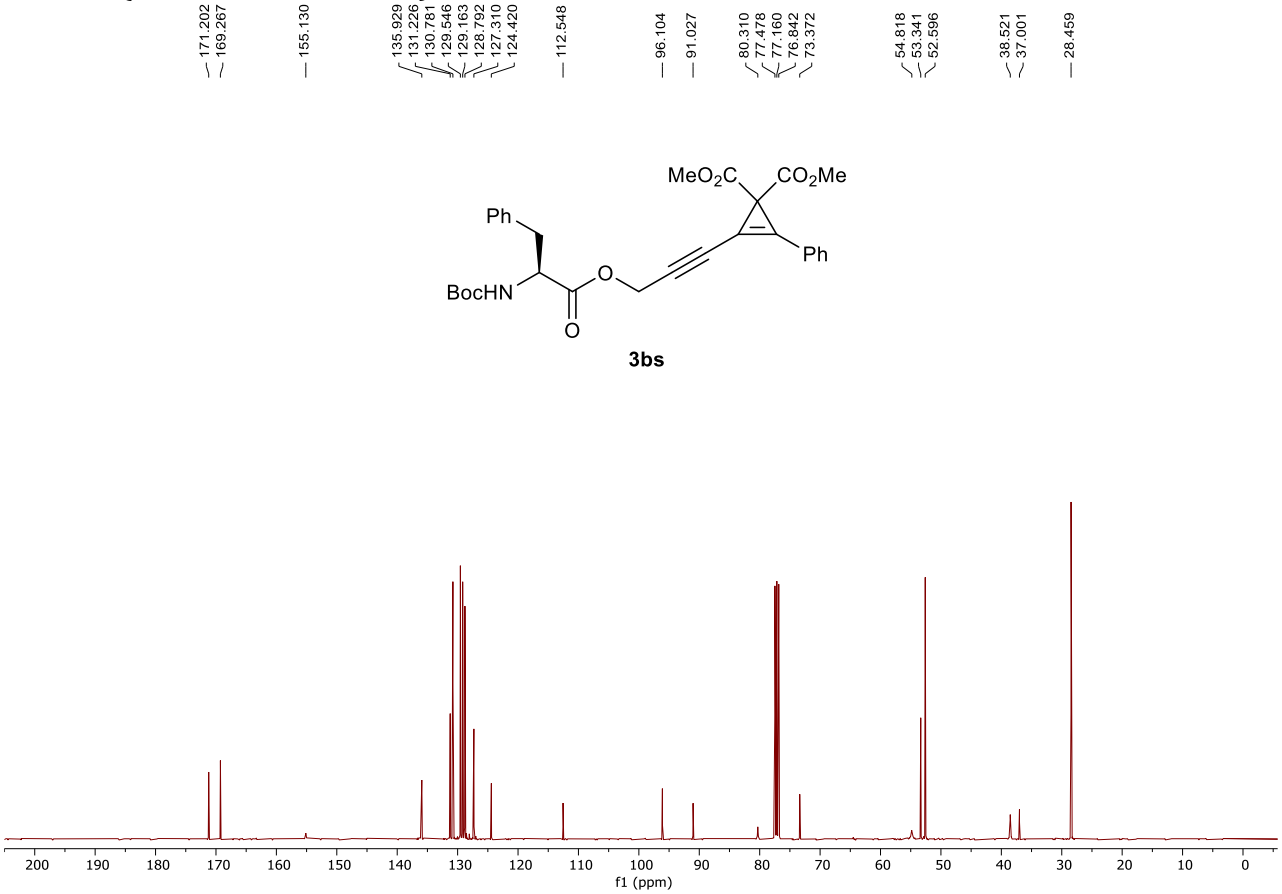


3br (*d.r. = 1:1)

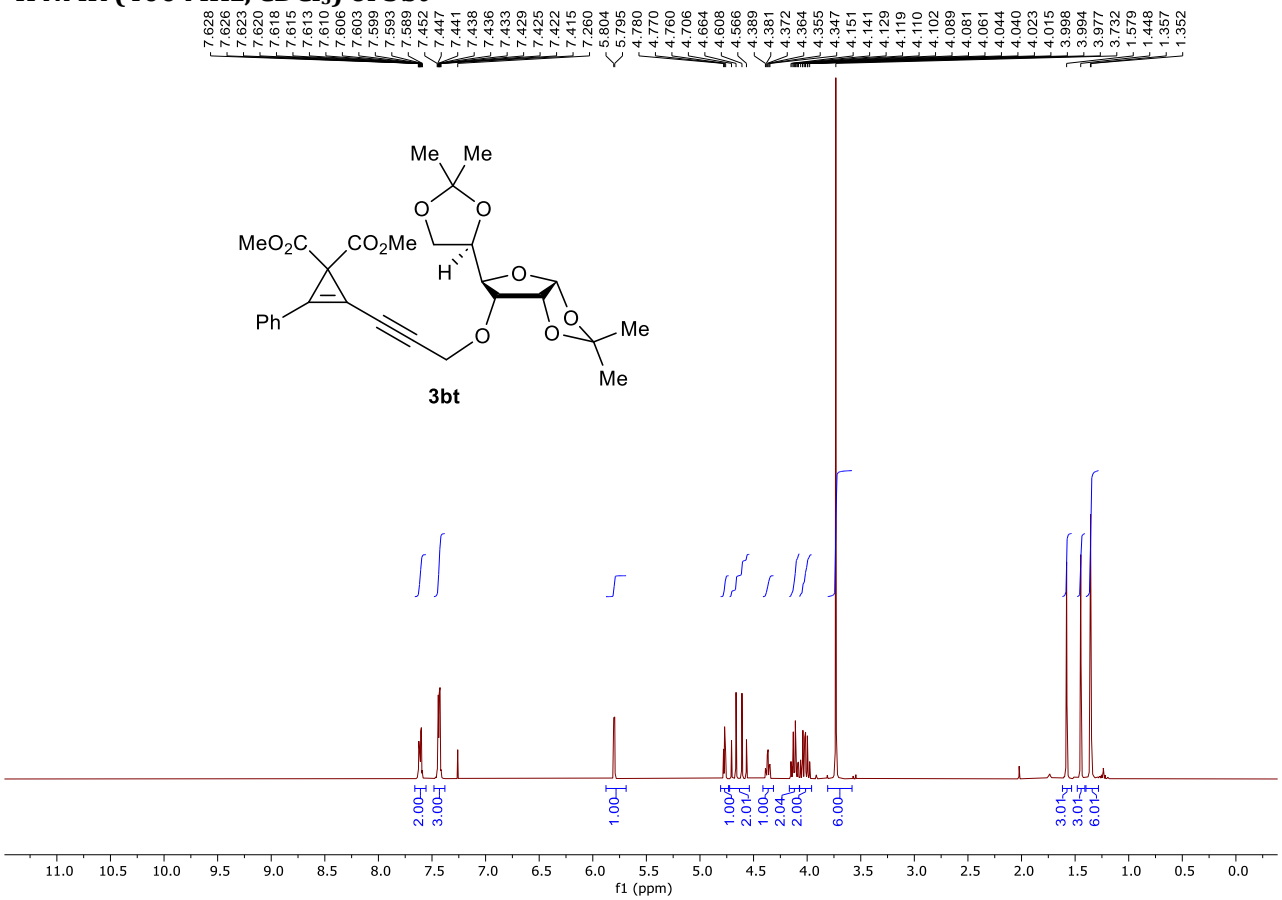
^{1}H NMR (400 MHz, $CDCl_3$, 60 °C) of 3bs



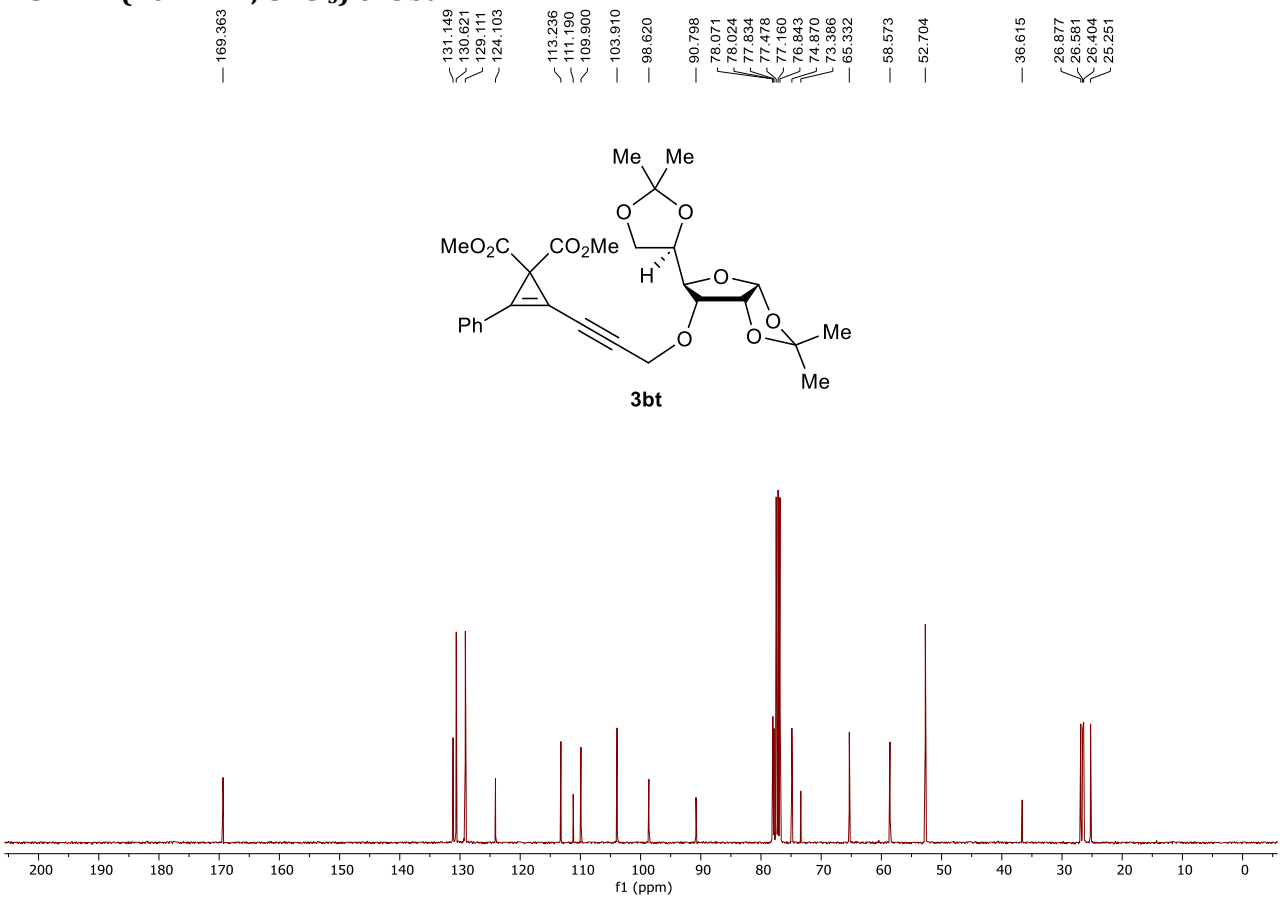
^{13}C NMR (101 MHz, $CDCl_3$, 60 °C) of 3bs



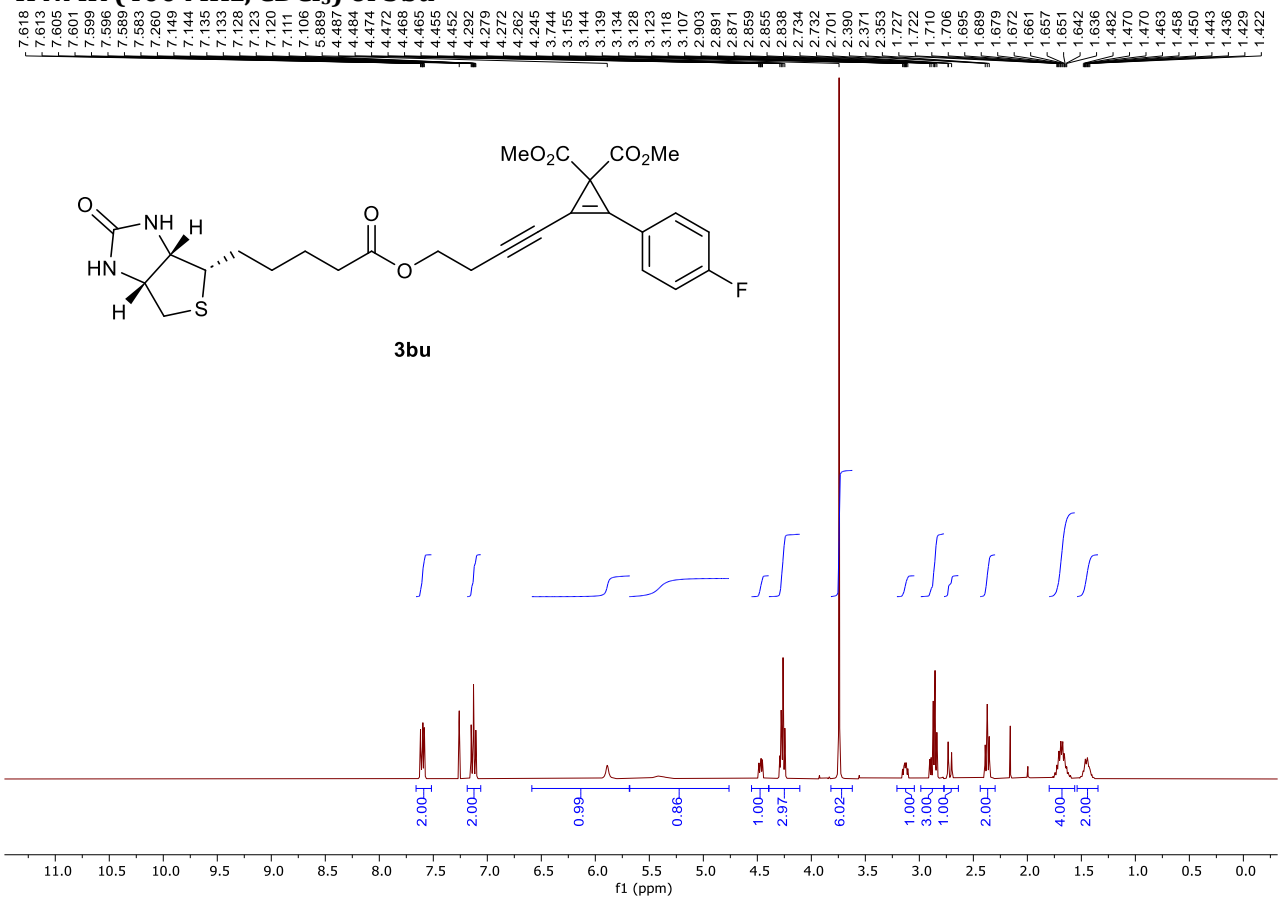
^{1}H NMR (400 MHz, $CDCl_3$) of 3bt



^{13}C NMR (101 MHz, $CDCl_3$) of 3bt

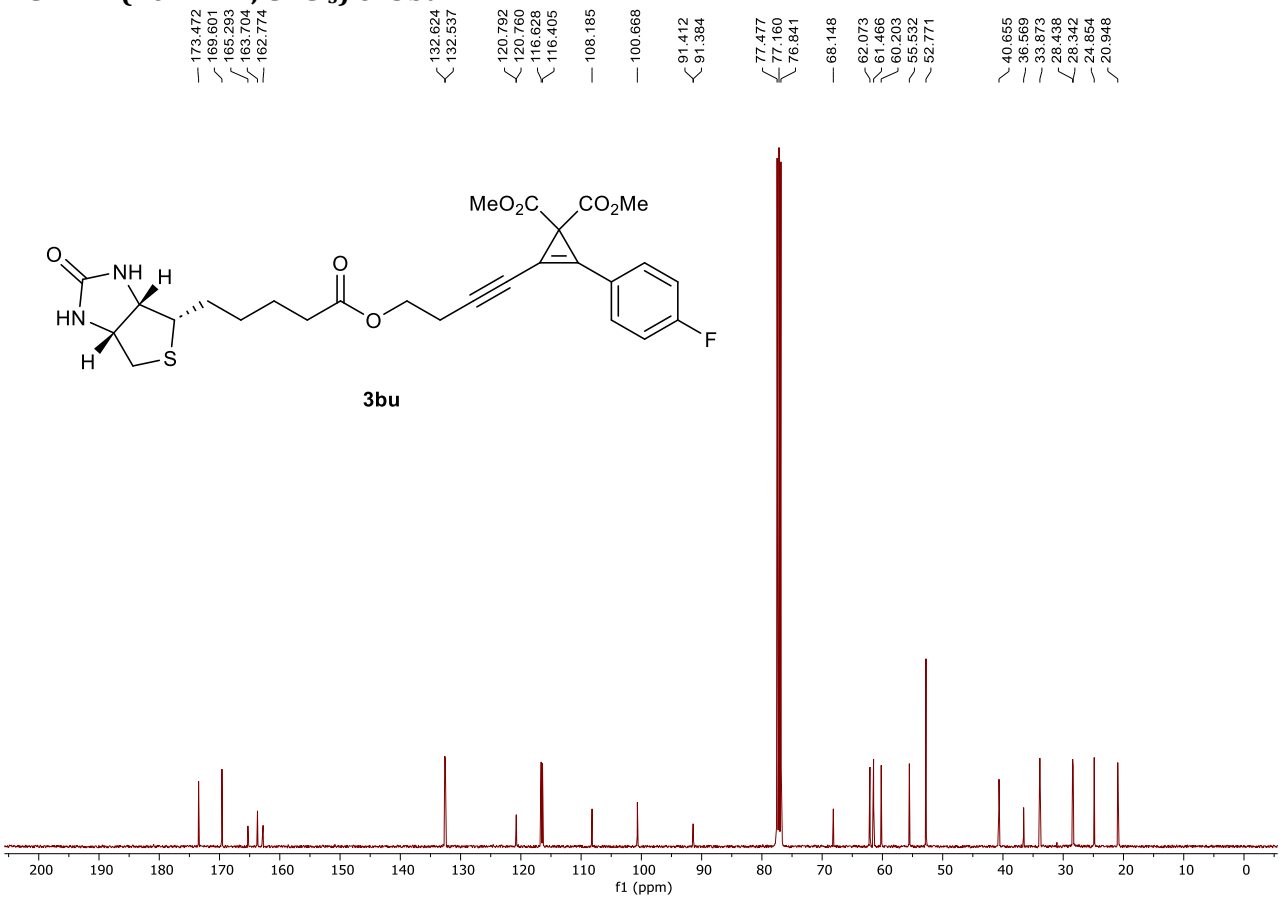


^{1}H NMR (400 MHz, $CDCl_3$) of 3bu



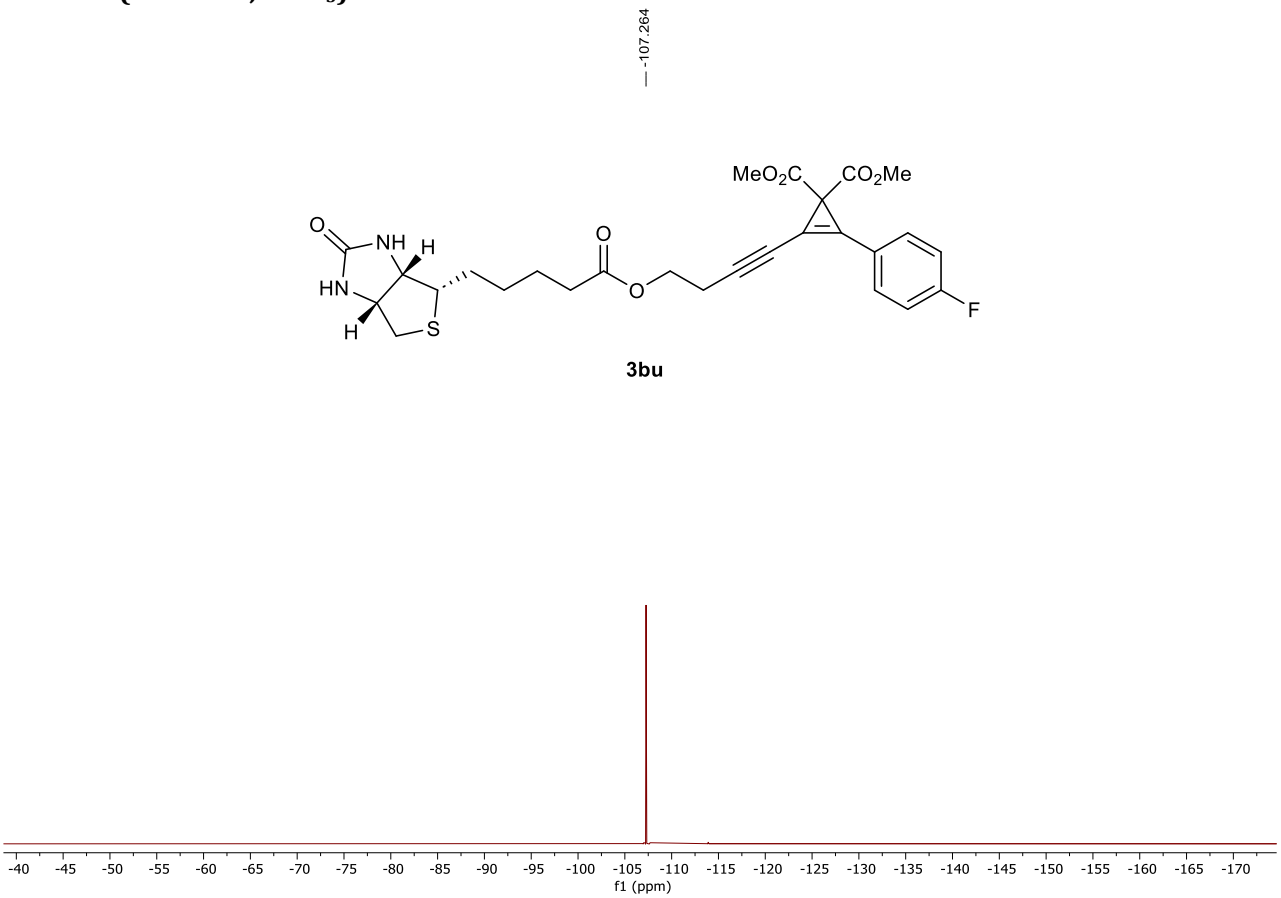
3bu

^{13}C NMR (101 MHz, $CDCl_3$) of 3bu

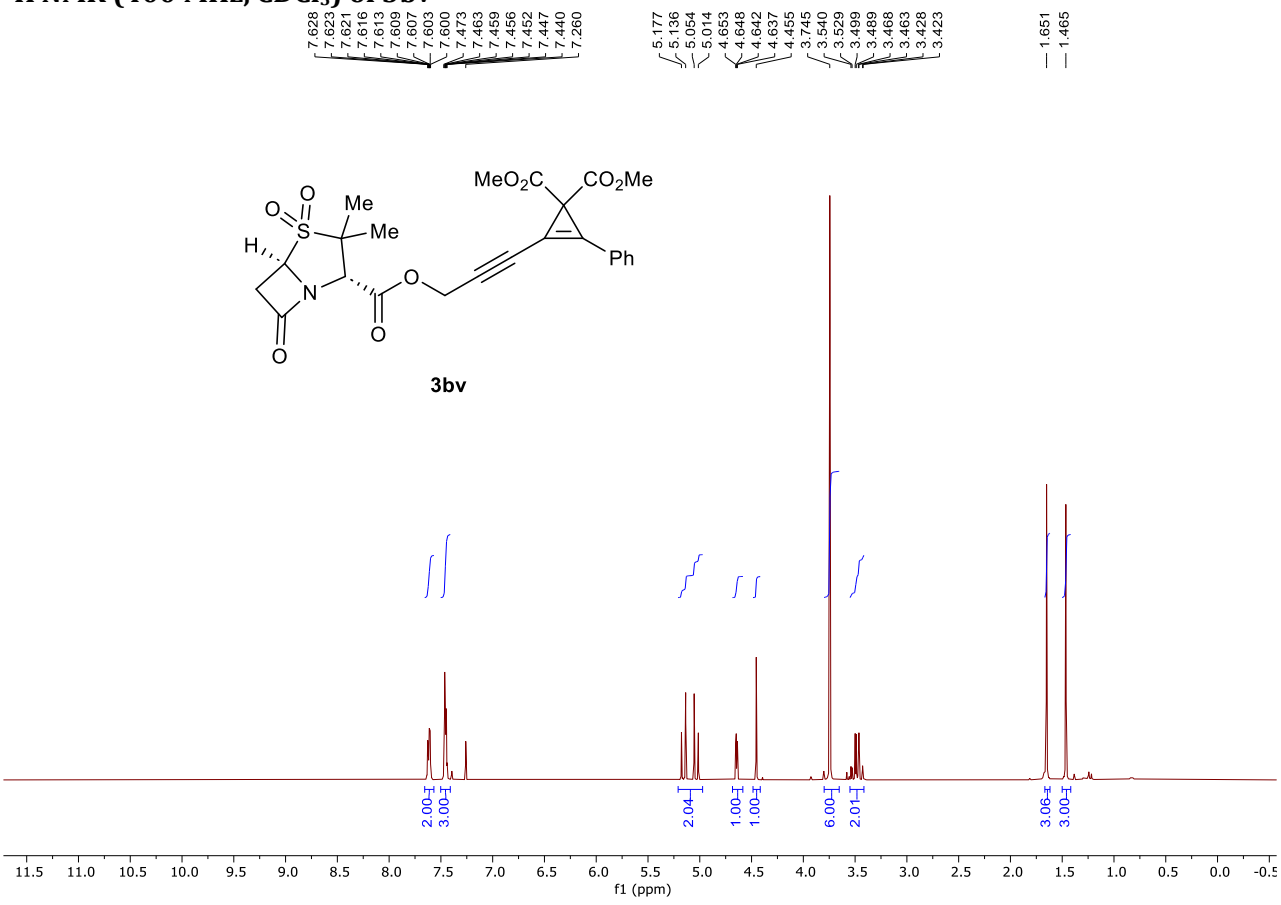


3bu

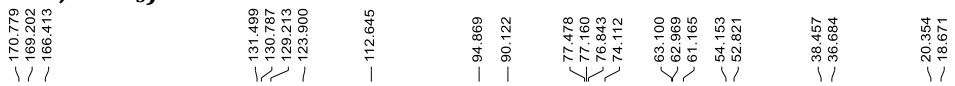
^{19}F NMR (377 MHz, $CDCl_3$) of 3bu

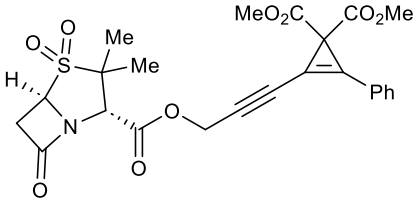


^{1}H NMR (400 MHz, $CDCl_3$) of 3bv

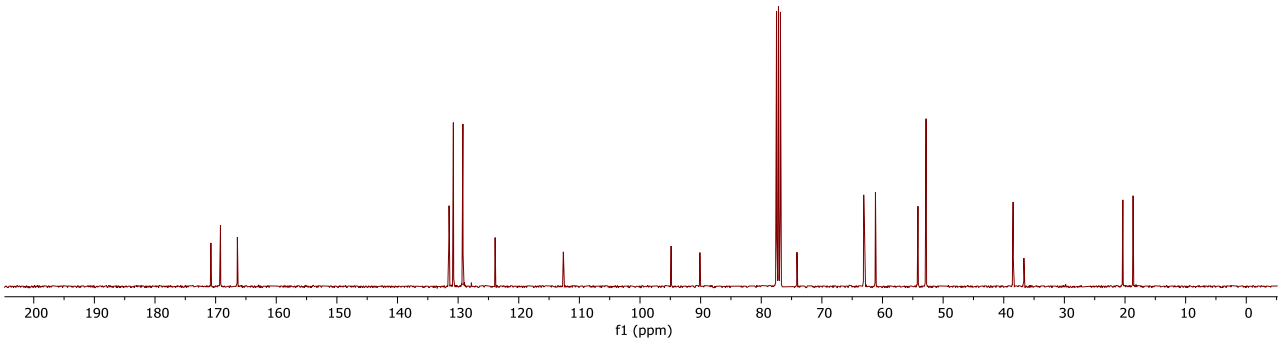


^{13}C NMR (101 MHz, $CDCl_3$) of 3bv

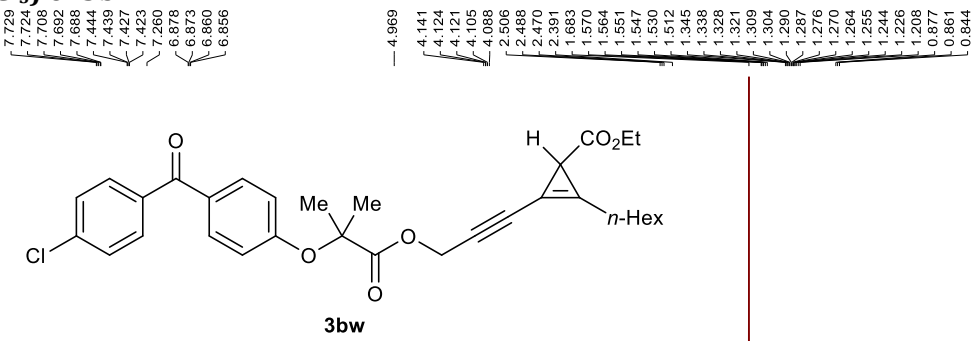




3bv

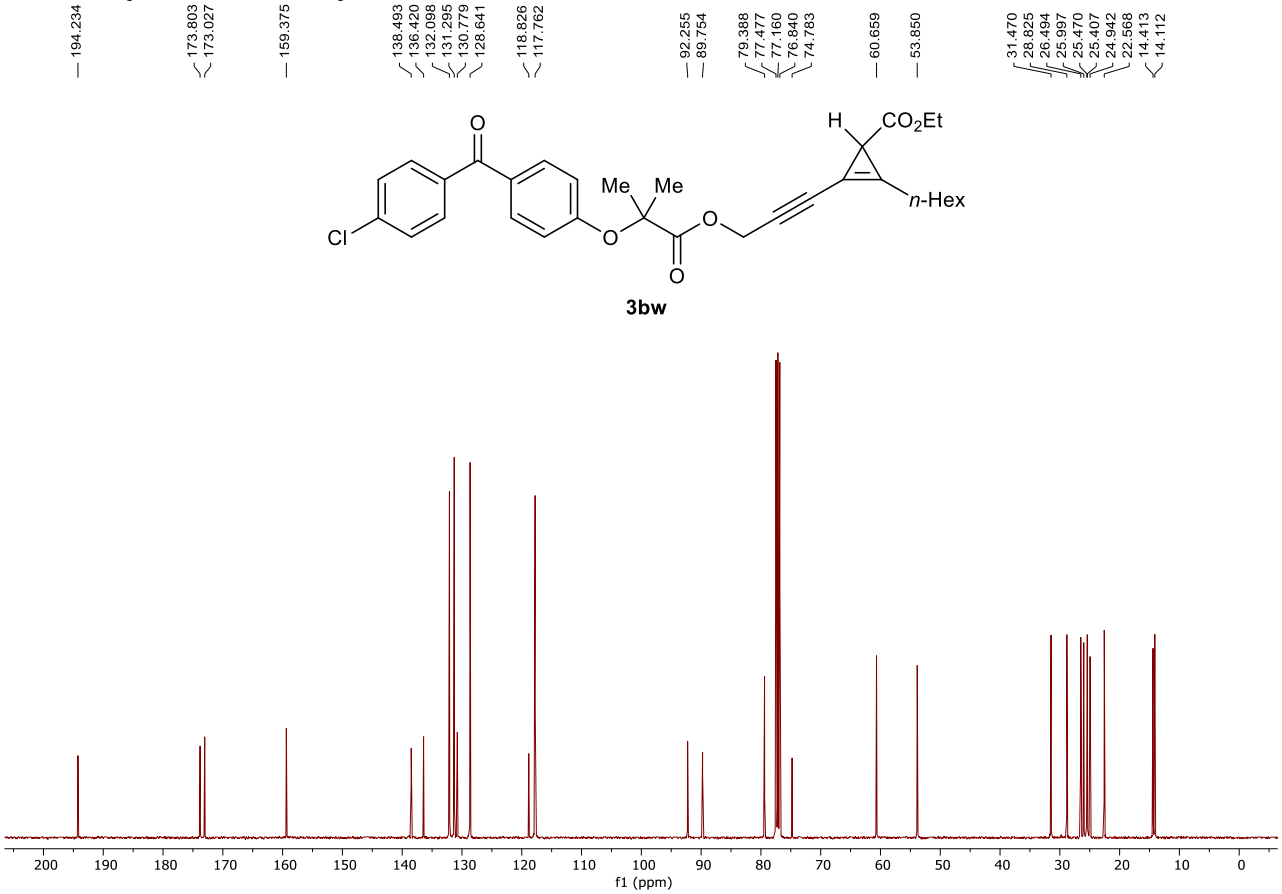


^{1}H NMR (400 MHz, $CDCl_3$) of 3bw



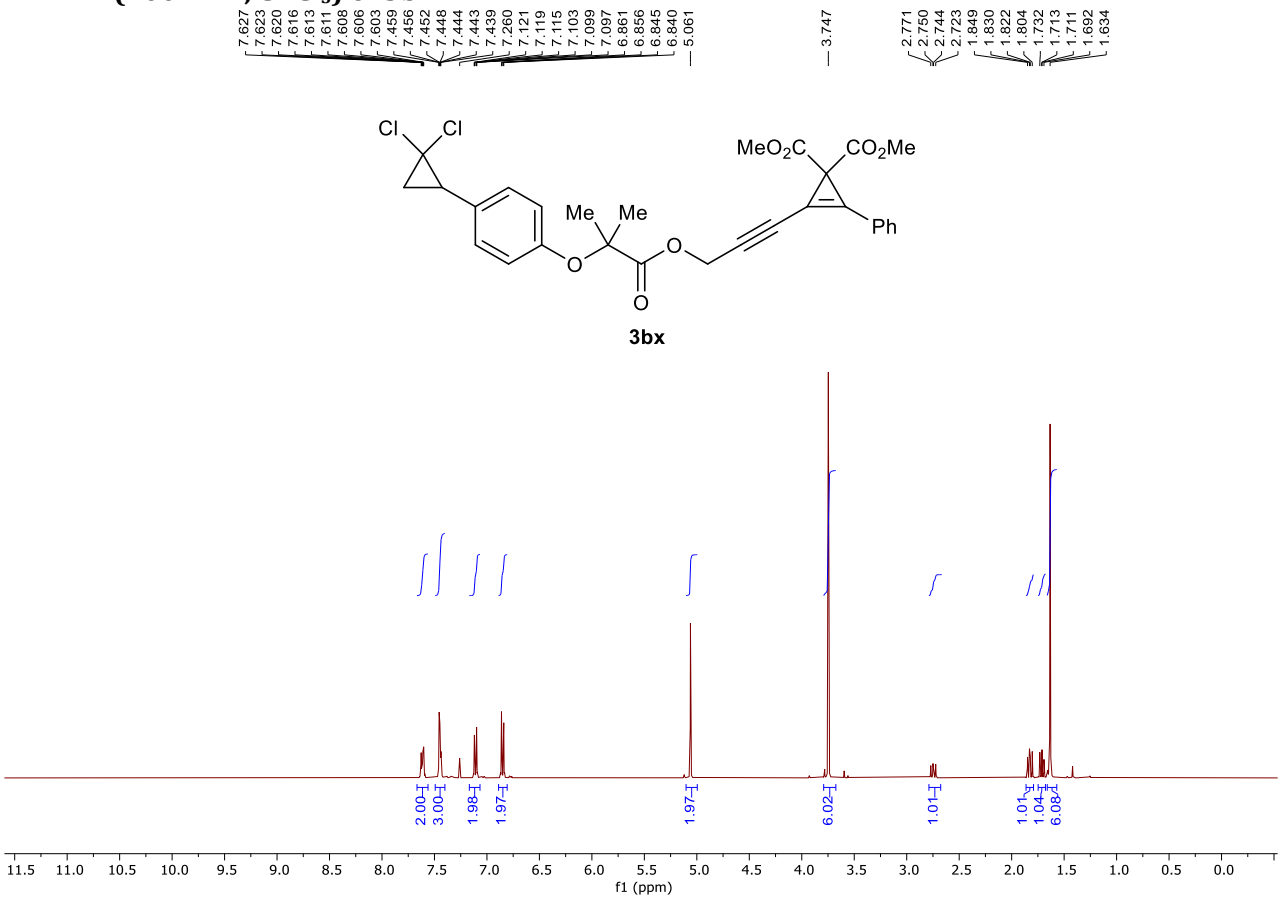
3bw

^{13}C NMR (101 MHz, $CDCl_3$) of 3bw



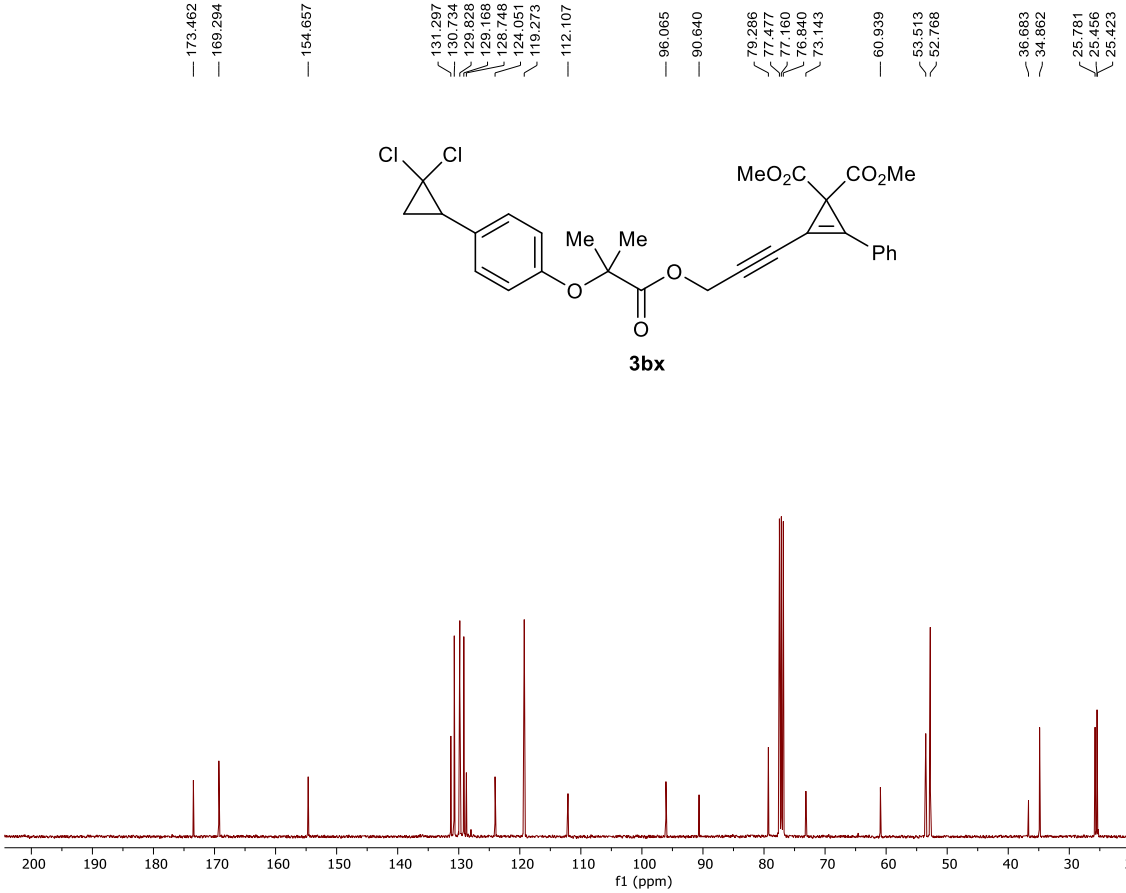
3bw

^{1}H NMR (400 MHz, $CDCl_3$) of 3bx

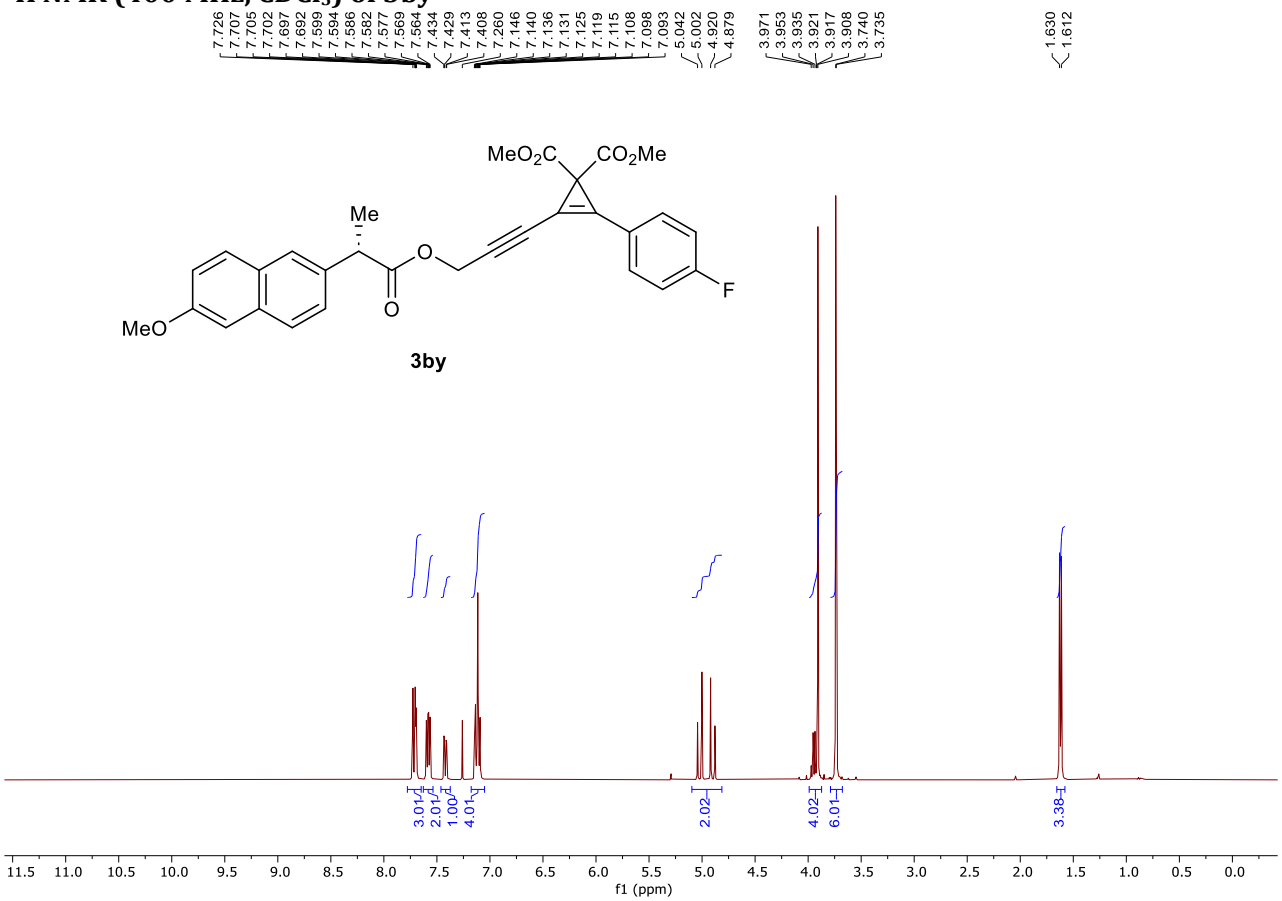


3bx

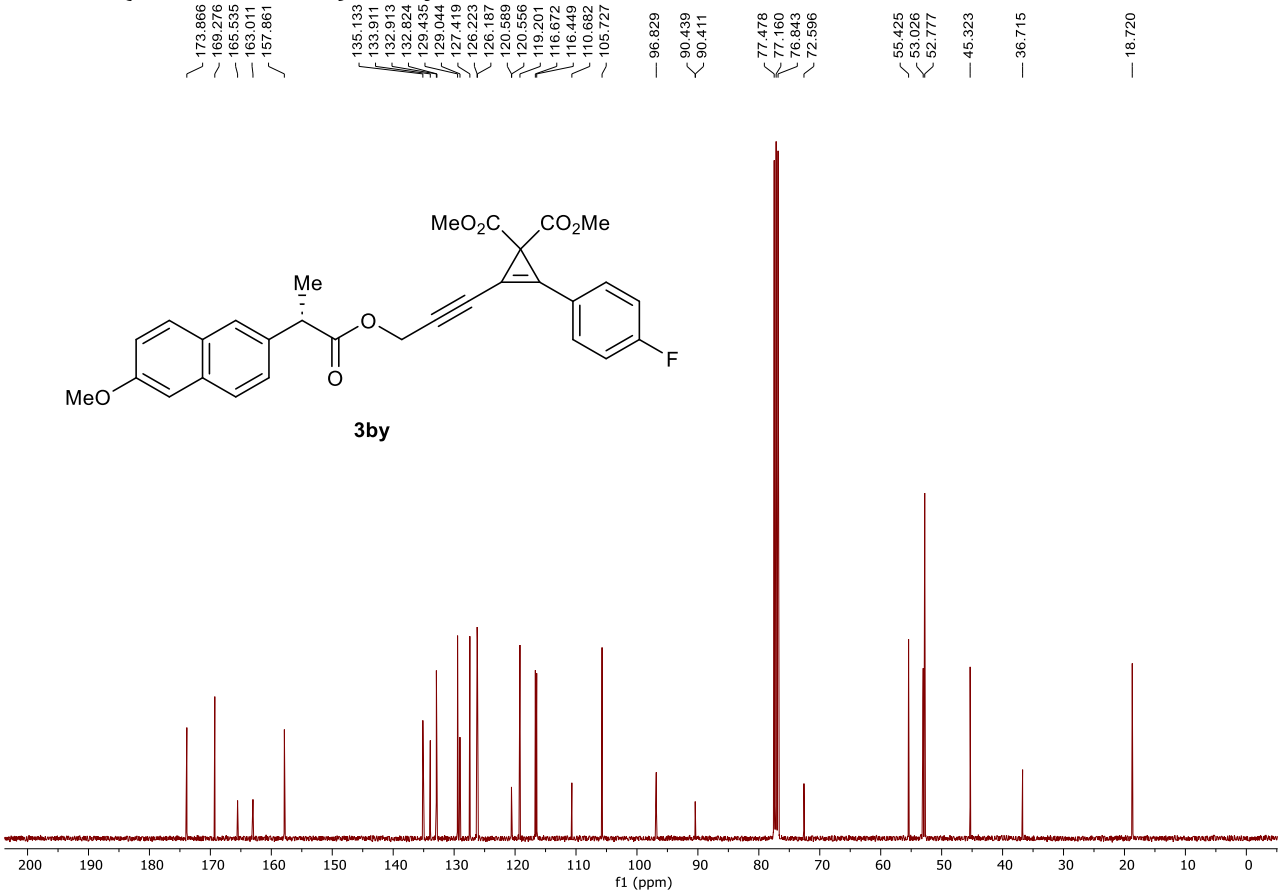
^{13}C NMR (101 MHz, $CDCl_3$) of 3bx



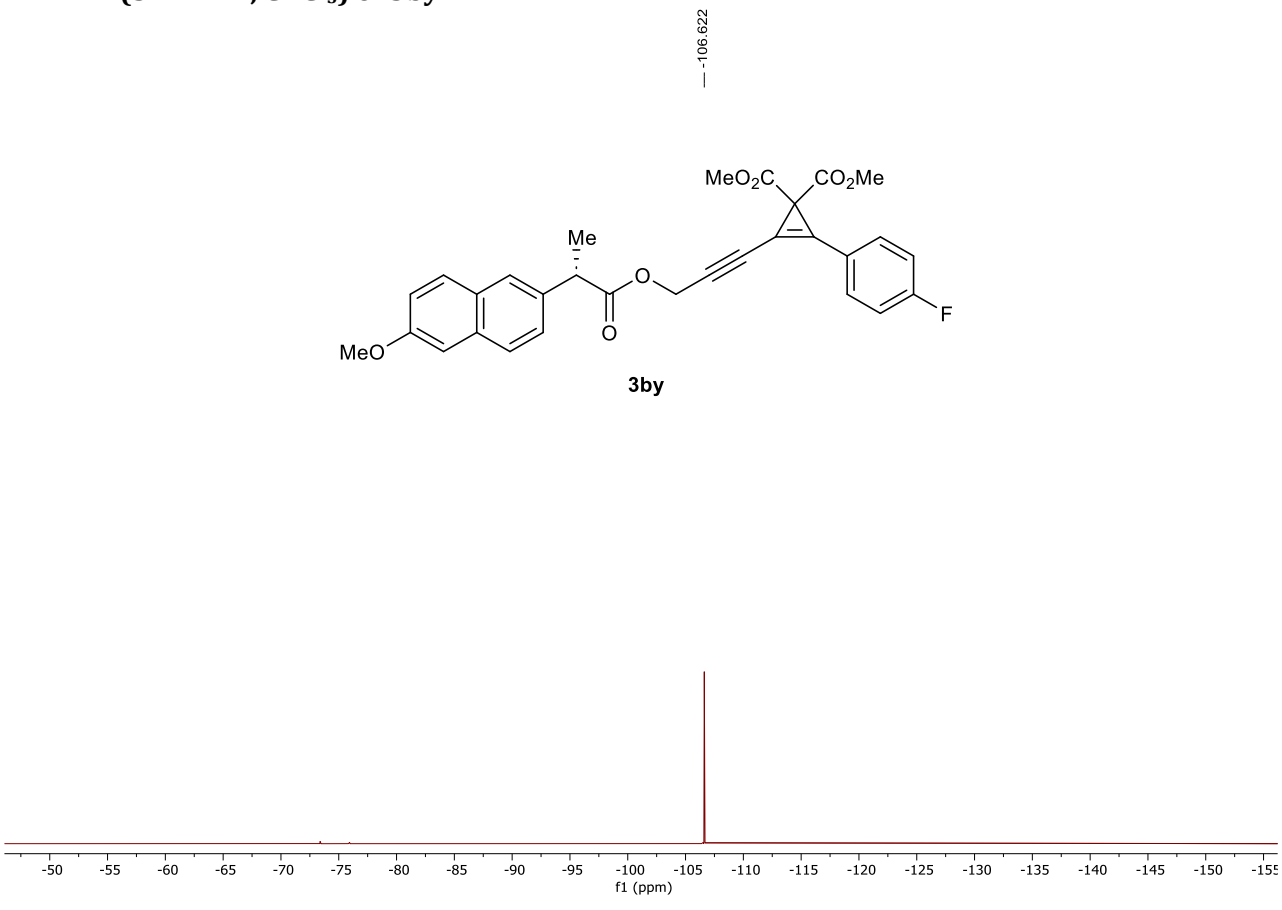
^{1}H NMR (400 MHz, $CDCl_3$) of 3by



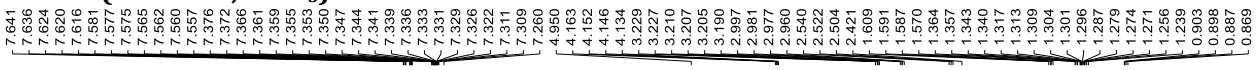
^{13}C NMR (101 MHz, $CDCl_3$) of 3by

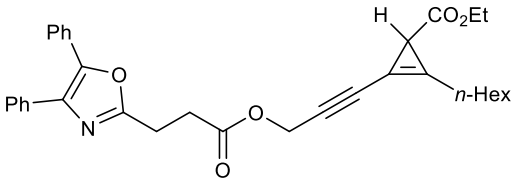


^{19}F NMR (377 MHz, $CDCl_3$) of 3by

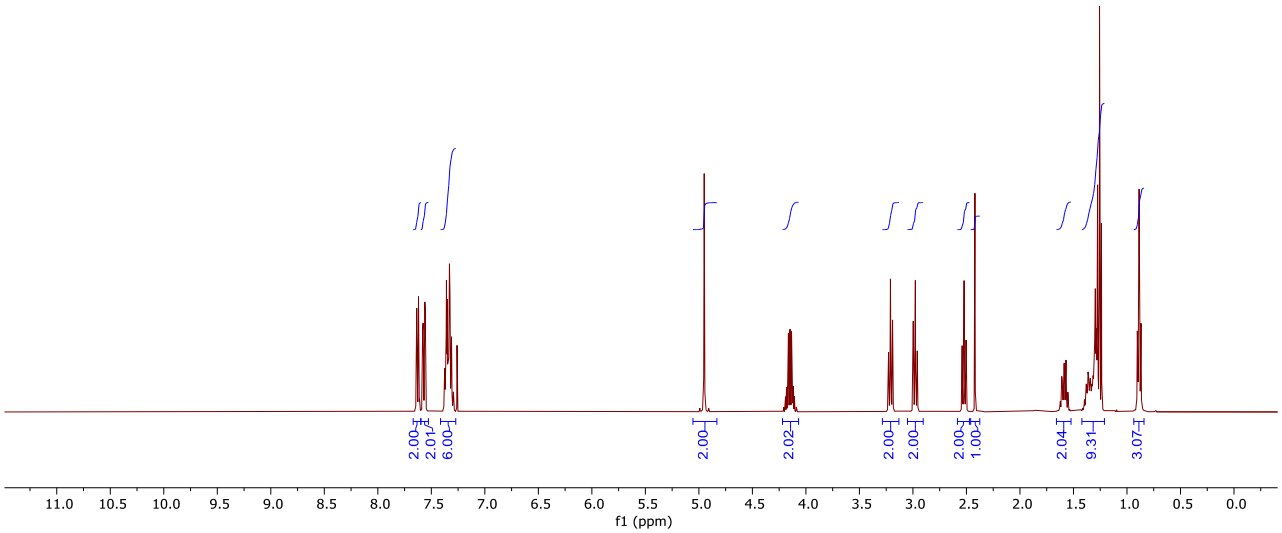


^{1}H NMR (400 MHz, $CDCl_3$) of 3bz

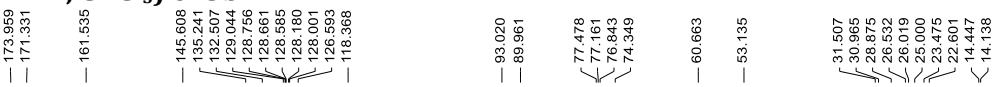


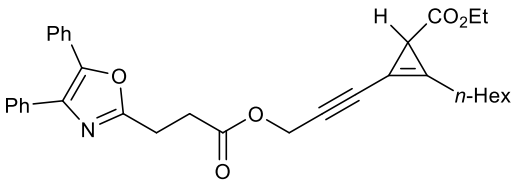


3bz



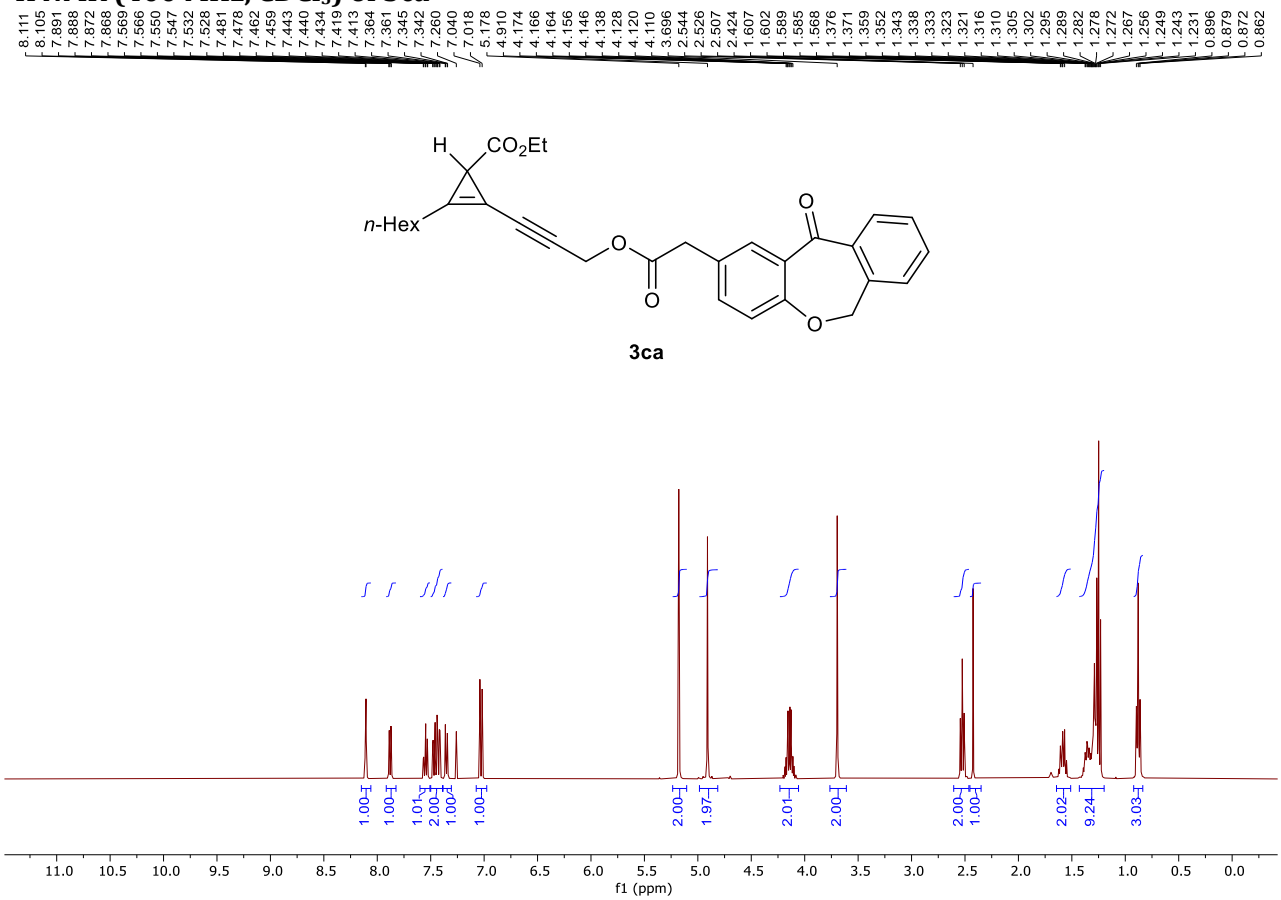
^{13}C NMR (101 MHz, $CDCl_3$) of 3bz





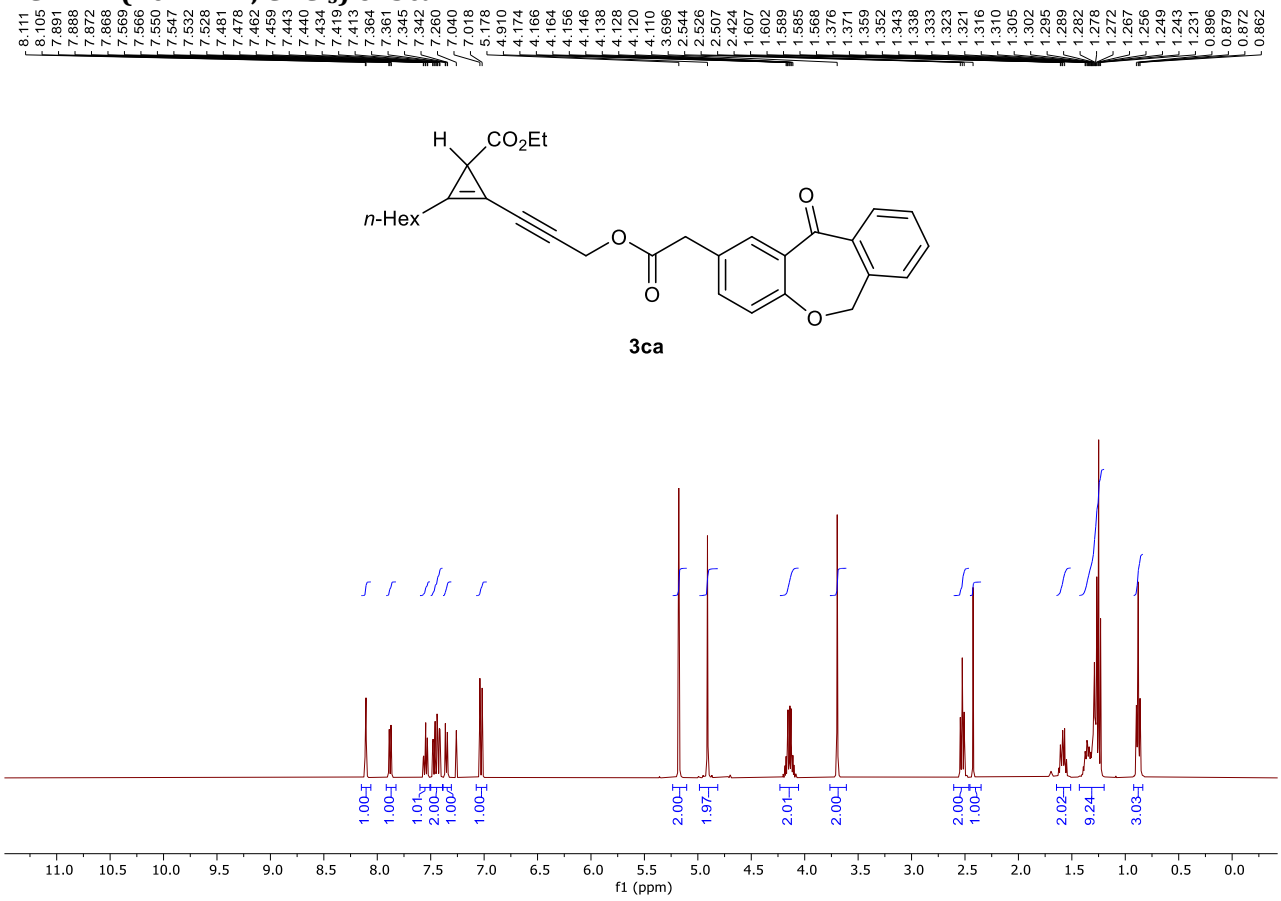
3bz

^{1}H NMR (400 MHz, $CDCl_3$) of 3ca



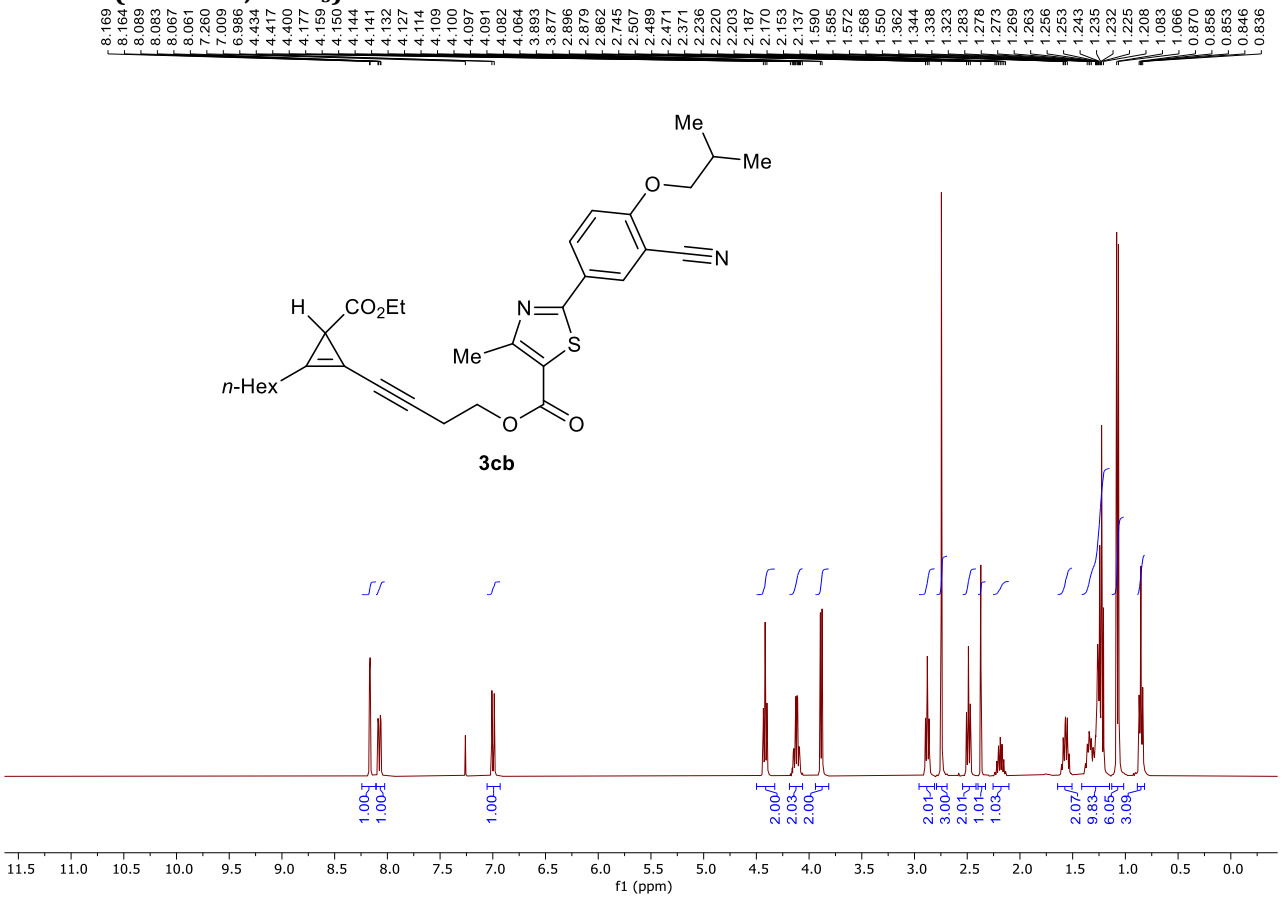
3ca

^{13}C NMR (101 MHz, $CDCl_3$) of 3ca

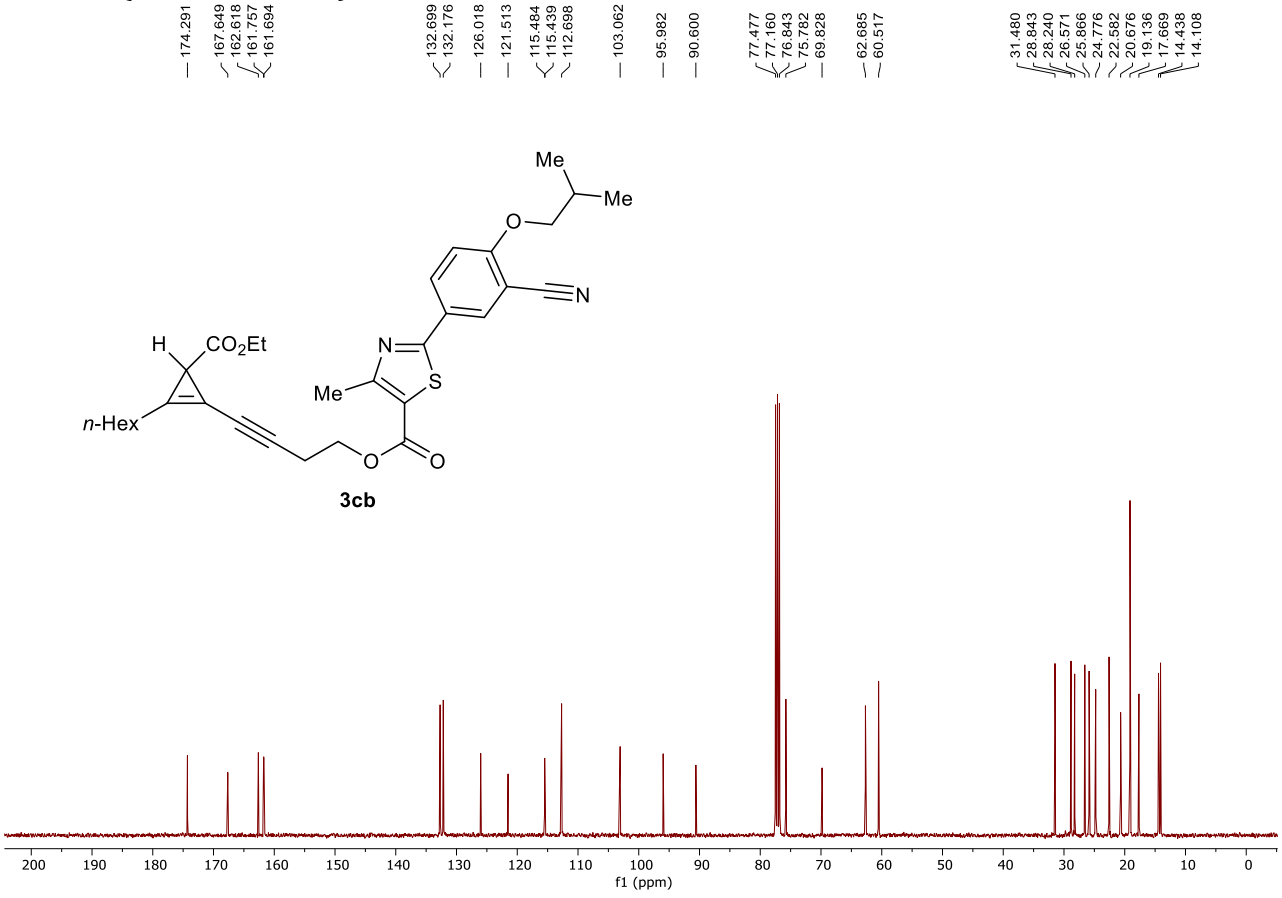


3ca

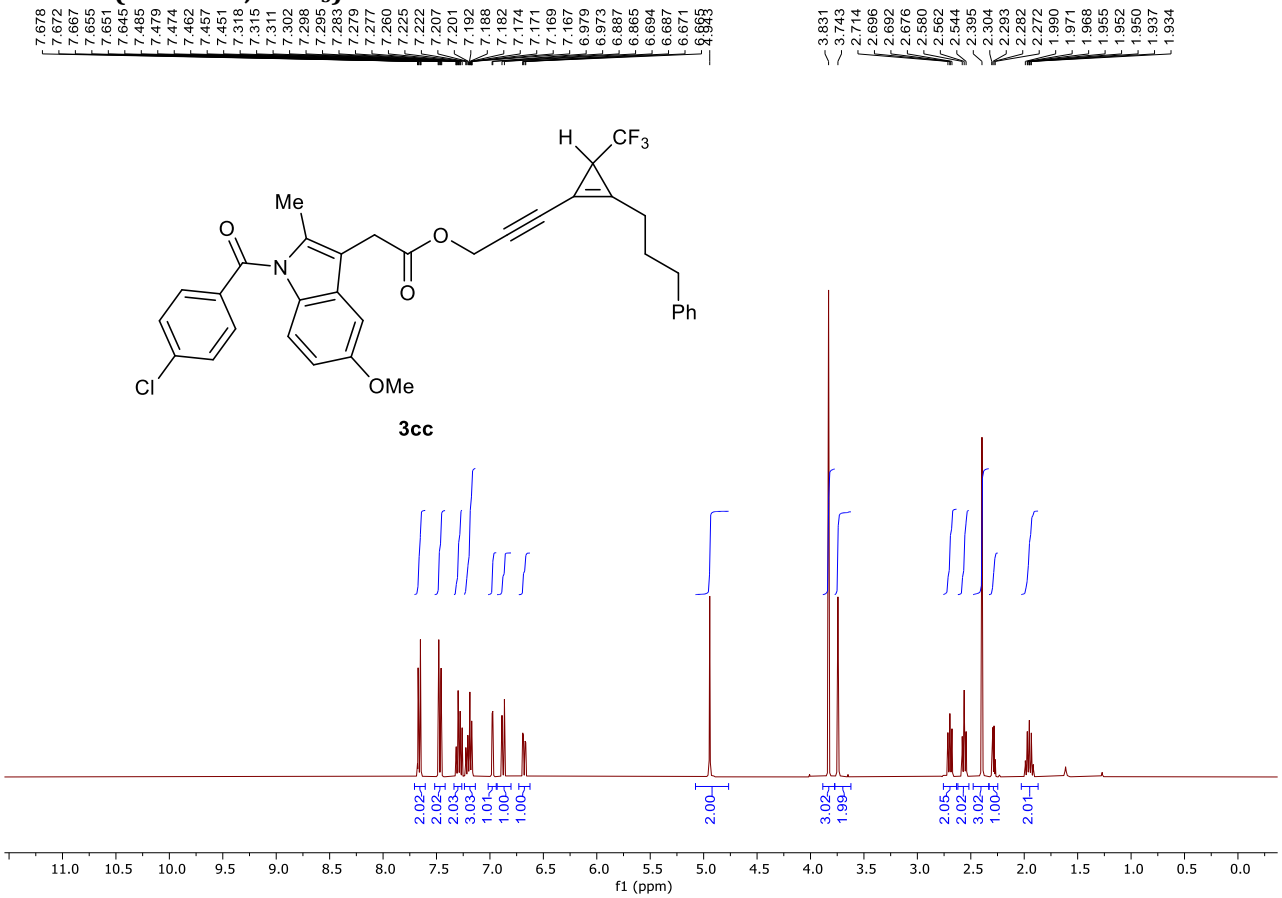
^{1}H NMR (400 MHz, $CDCl_3$) of 3cb



^{13}C NMR (101 MHz, $CDCl_3$) of 3cb

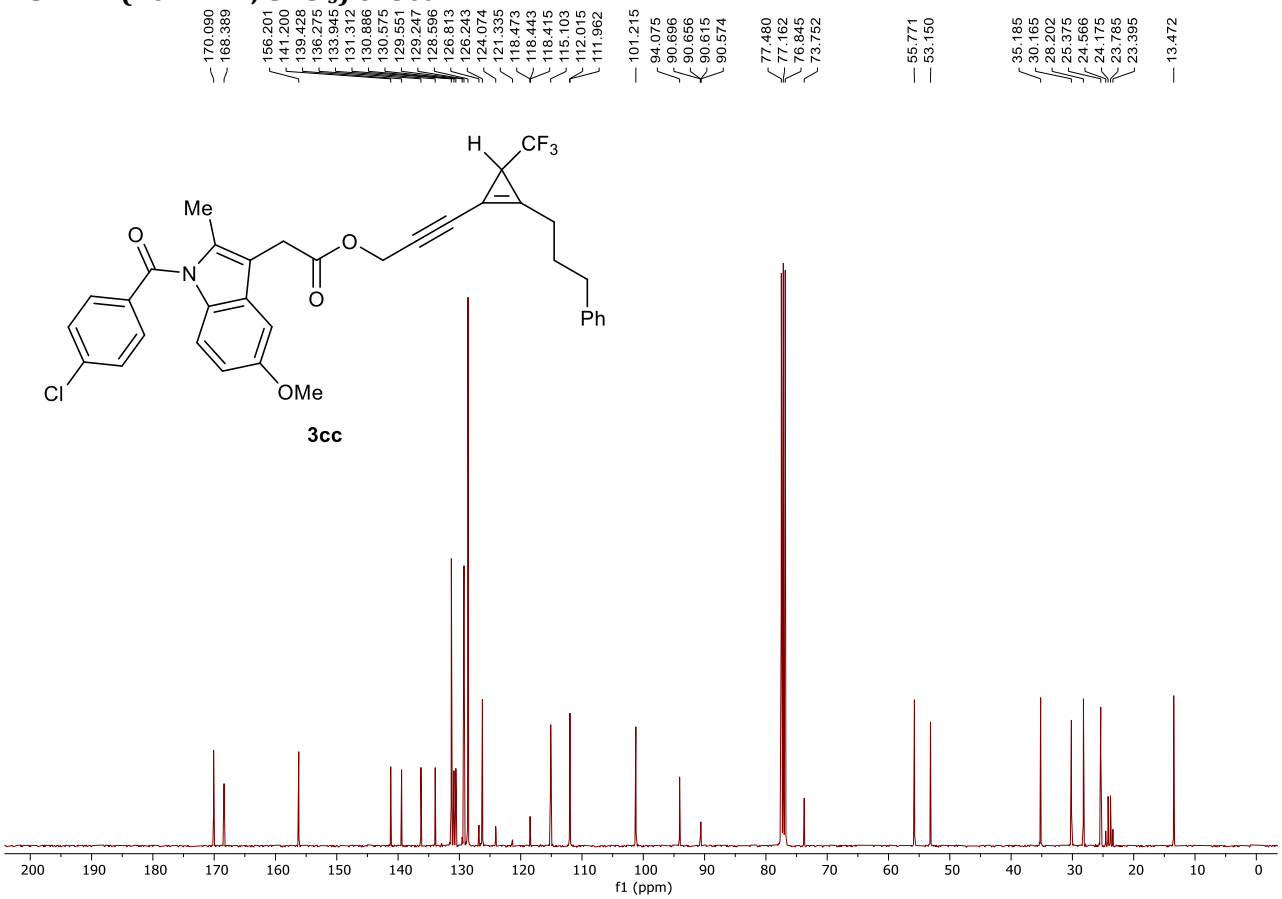


^{1}H NMR (400 MHz, $CDCl_3$) of 3cc



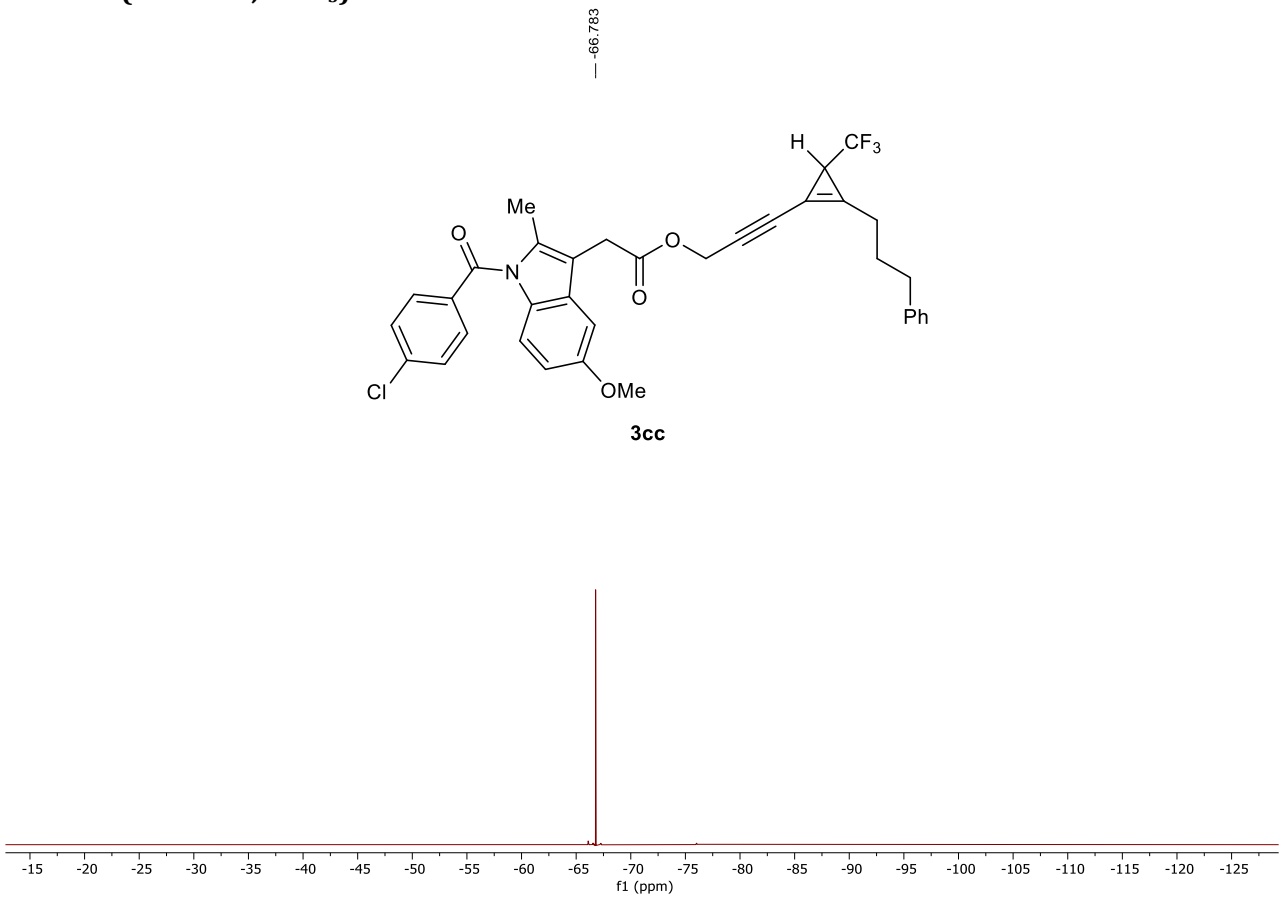
3cc

^{13}C NMR (101 MHz, $CDCl_3$) of 3cc

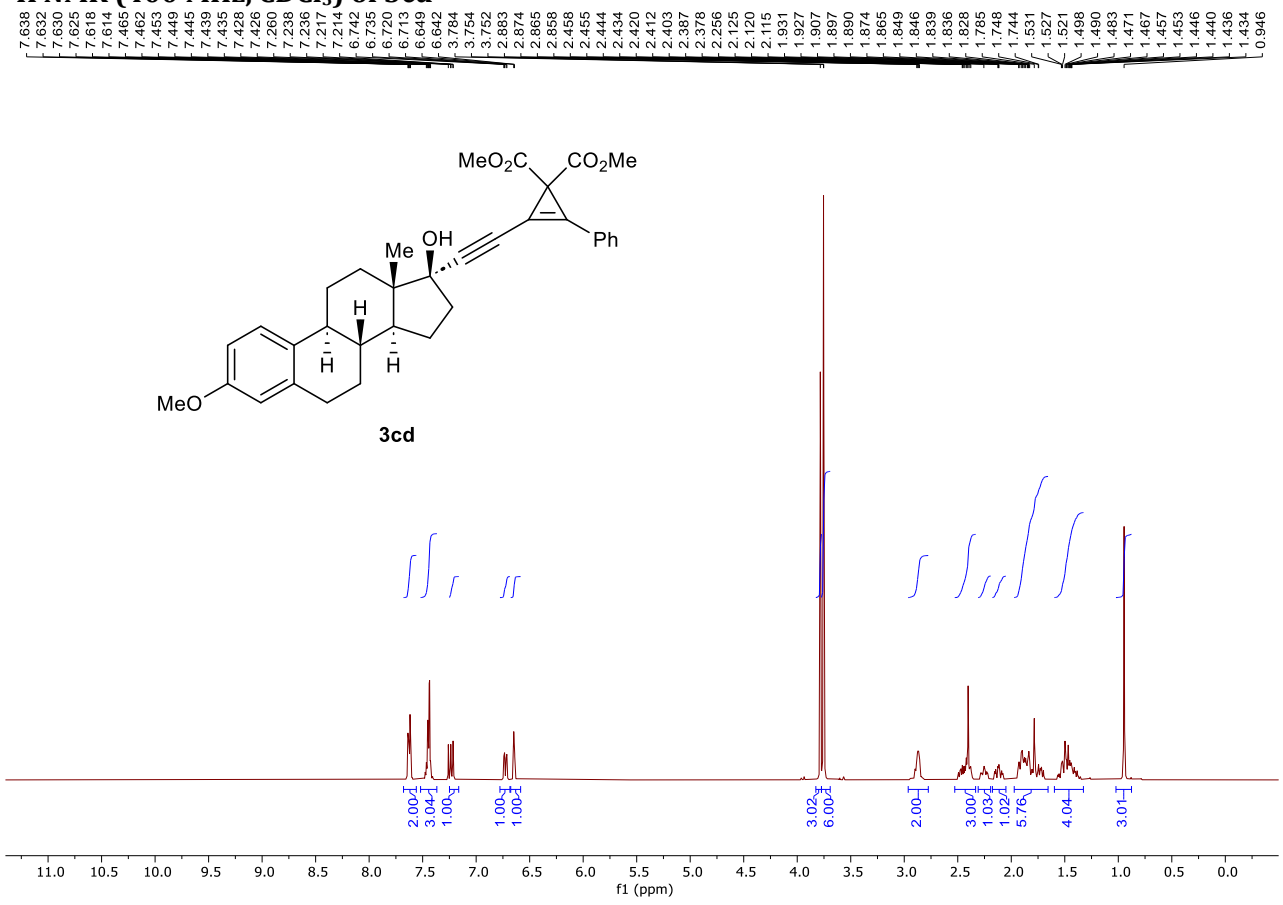


3cc

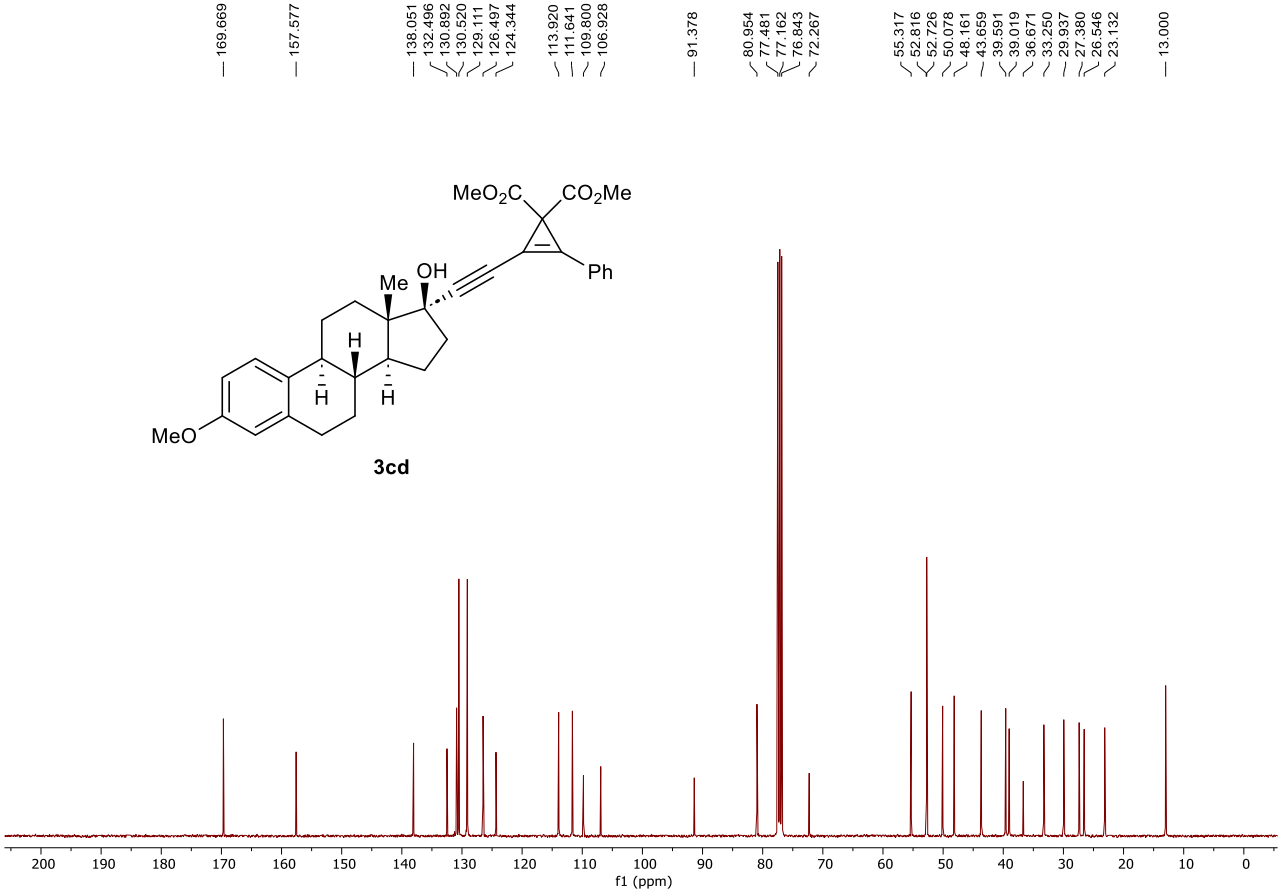
^{19}F NMR (377 MHz, $CDCl_3$) of 3cc



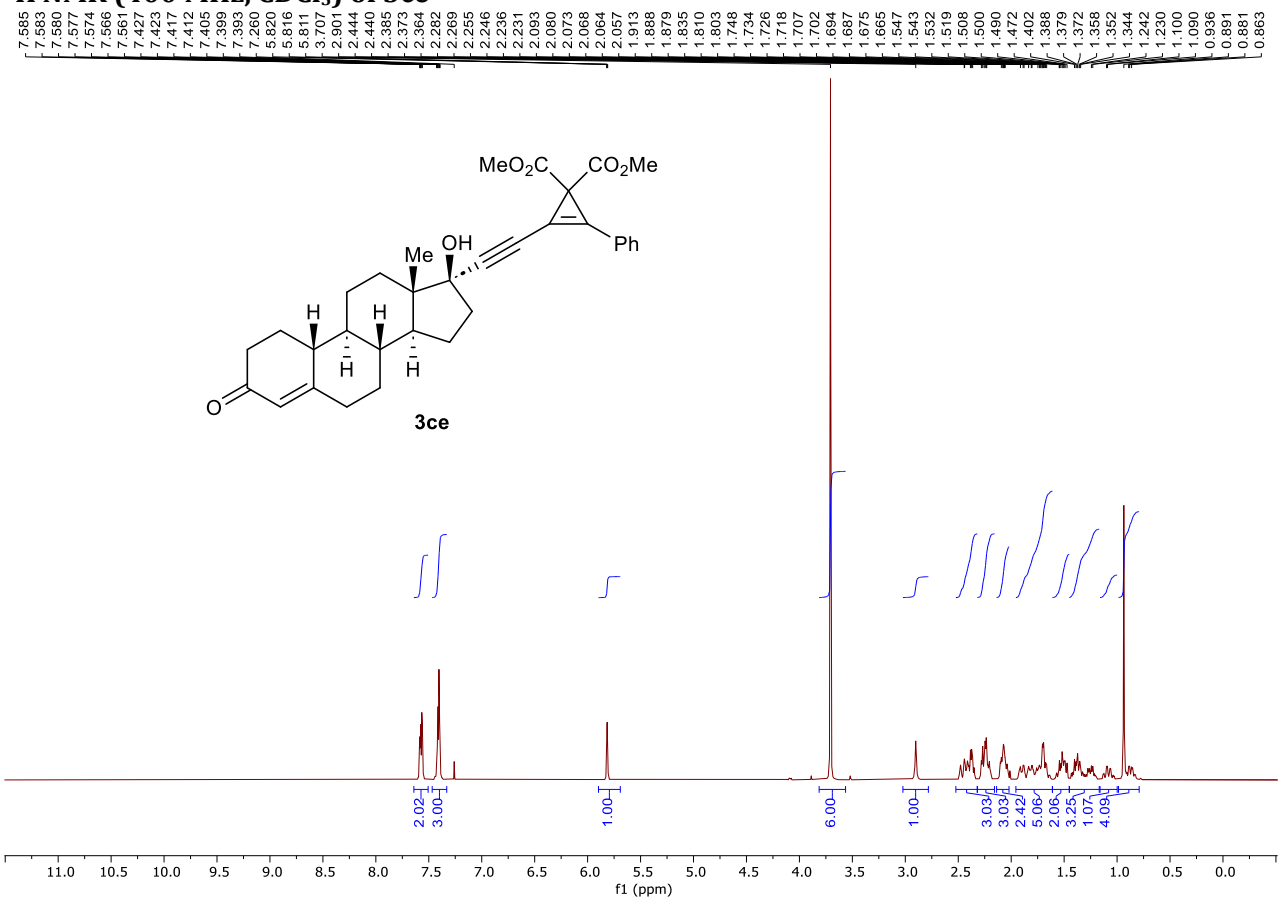
^{1}H NMR (400 MHz, $CDCl_3$) of 3cd



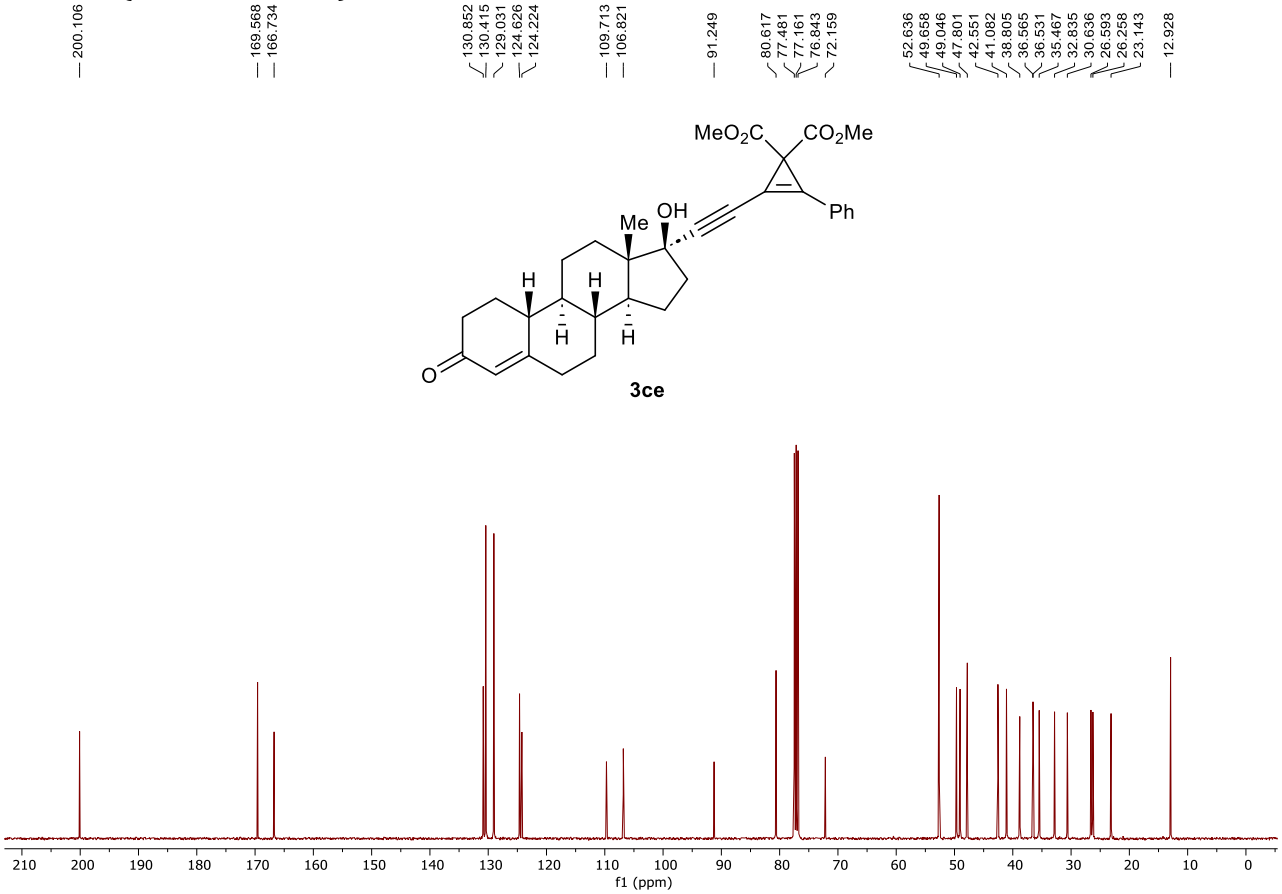
^{13}C NMR (101 MHz, $CDCl_3$) of 3cd



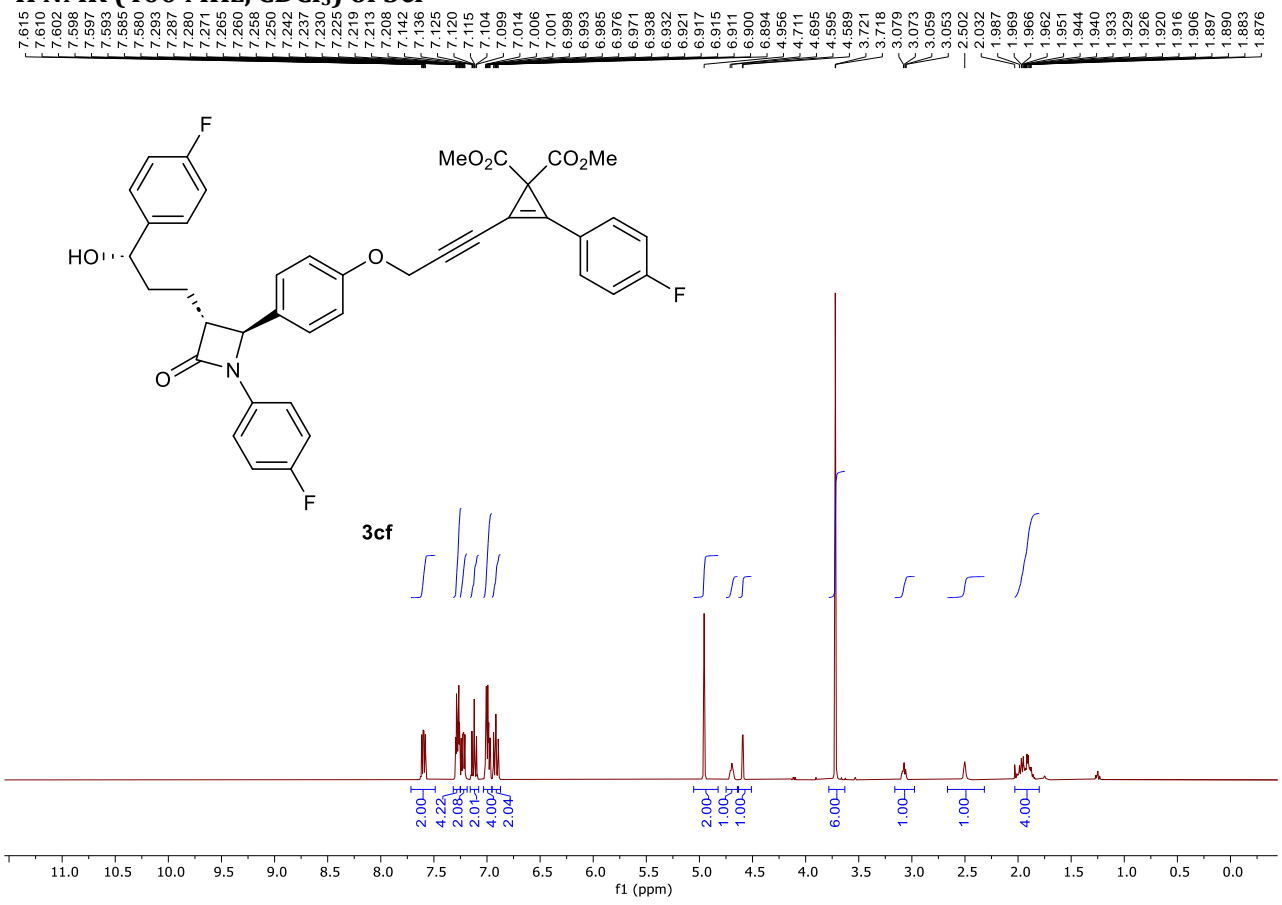
^{1}H NMR (400 MHz, $CDCl_3$) of 3ce



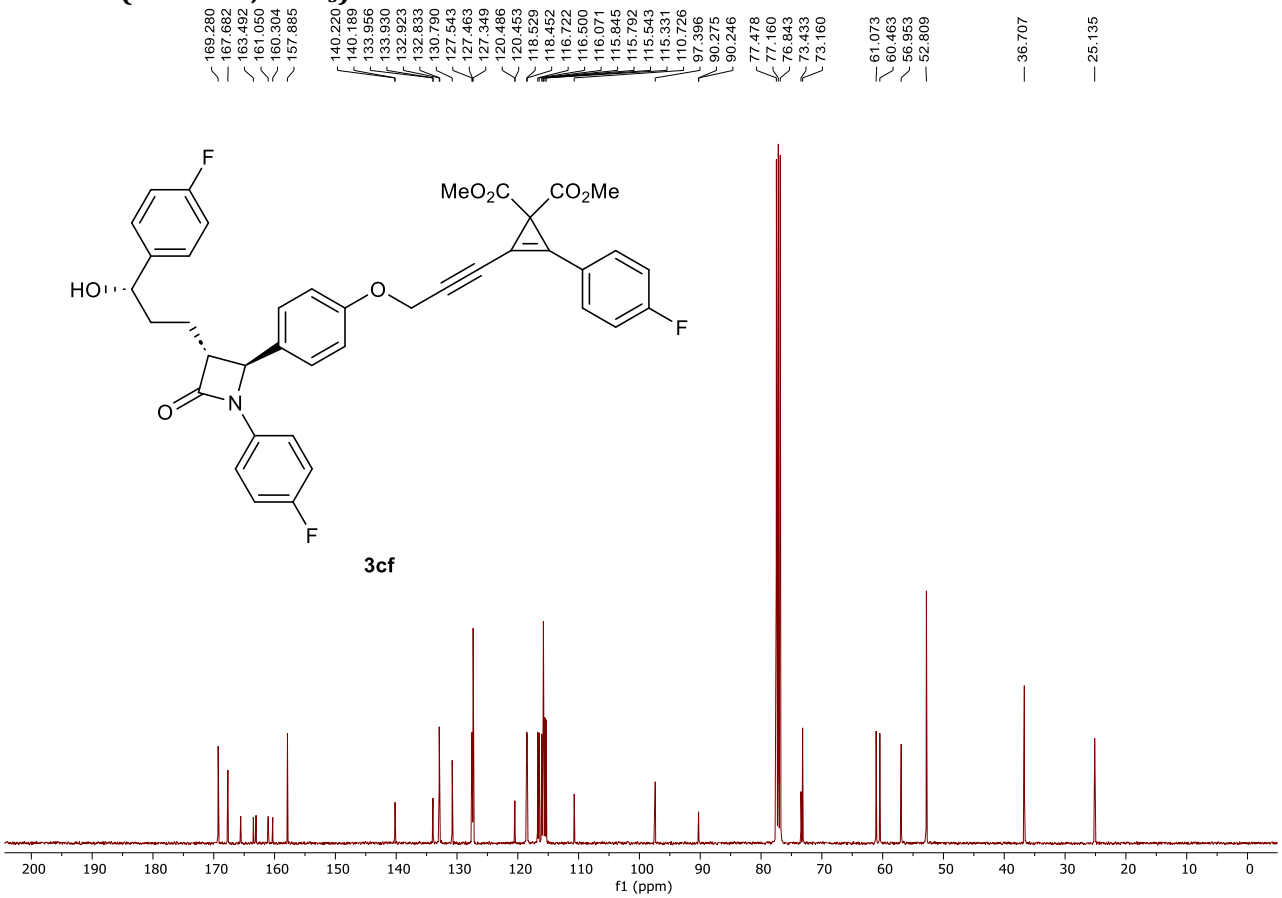
^{13}C NMR (101 MHz, $CDCl_3$) of 3ce



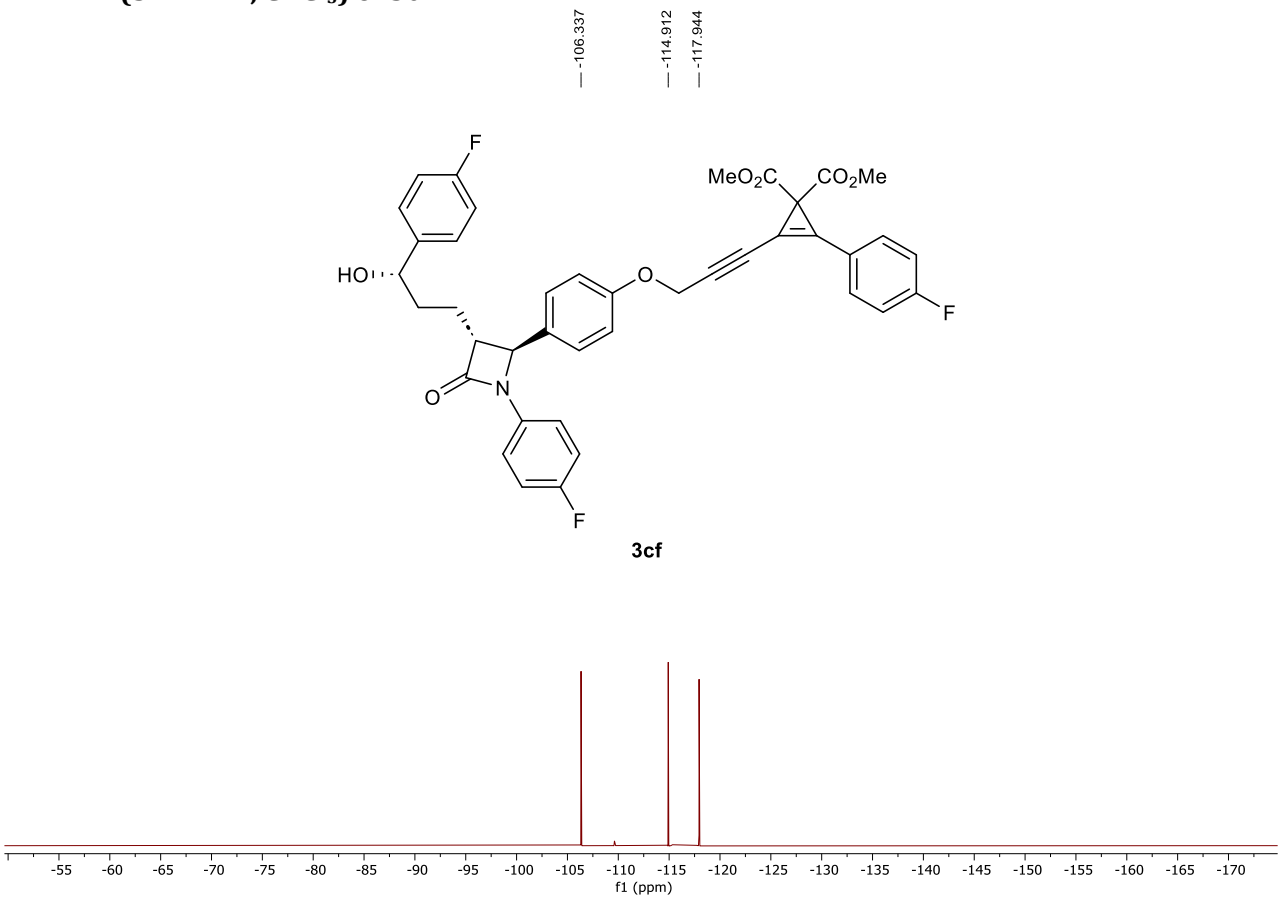
^{1}H NMR (400 MHz, $CDCl_3$) of 3cf



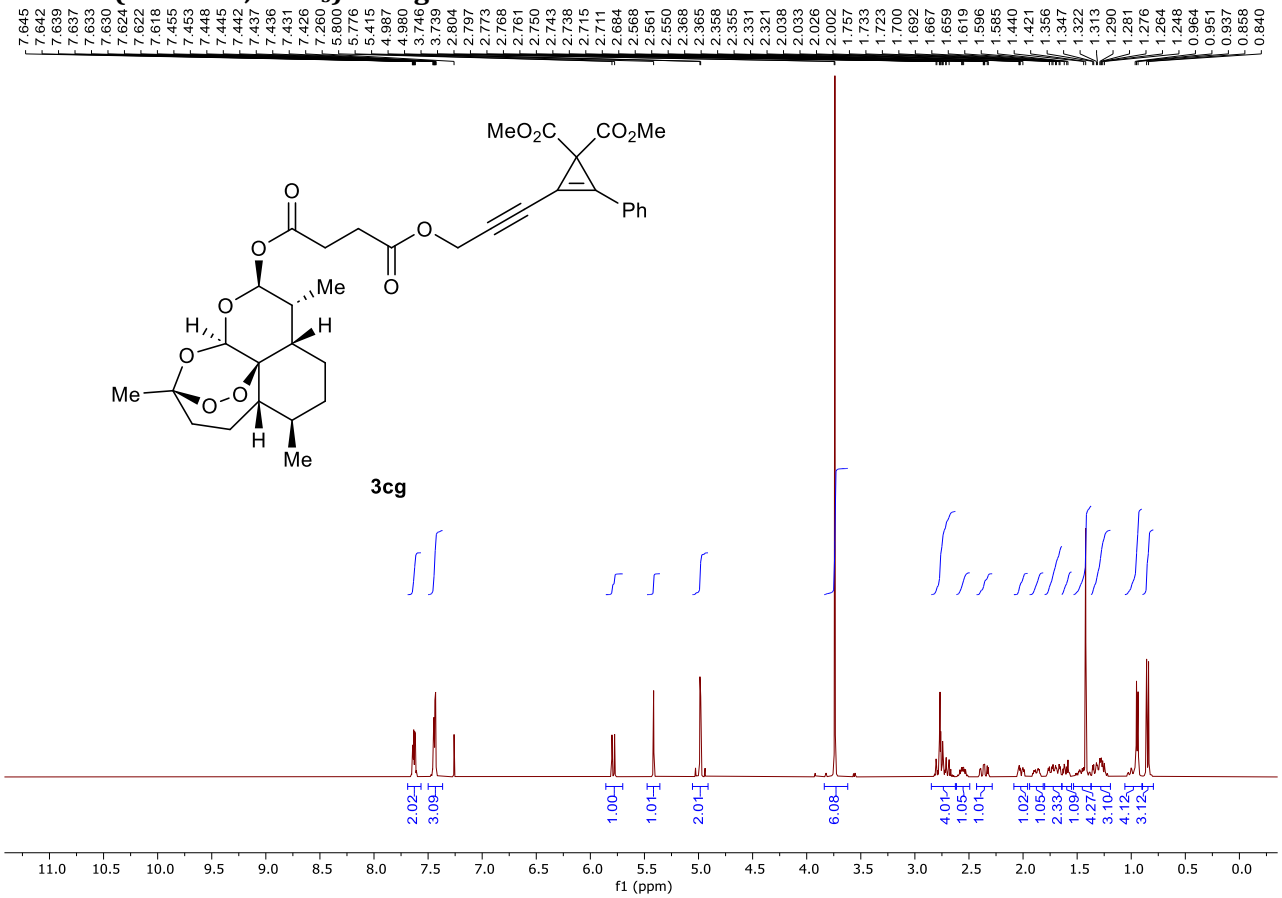
^{13}C NMR (101 MHz, $CDCl_3$) of 3cf



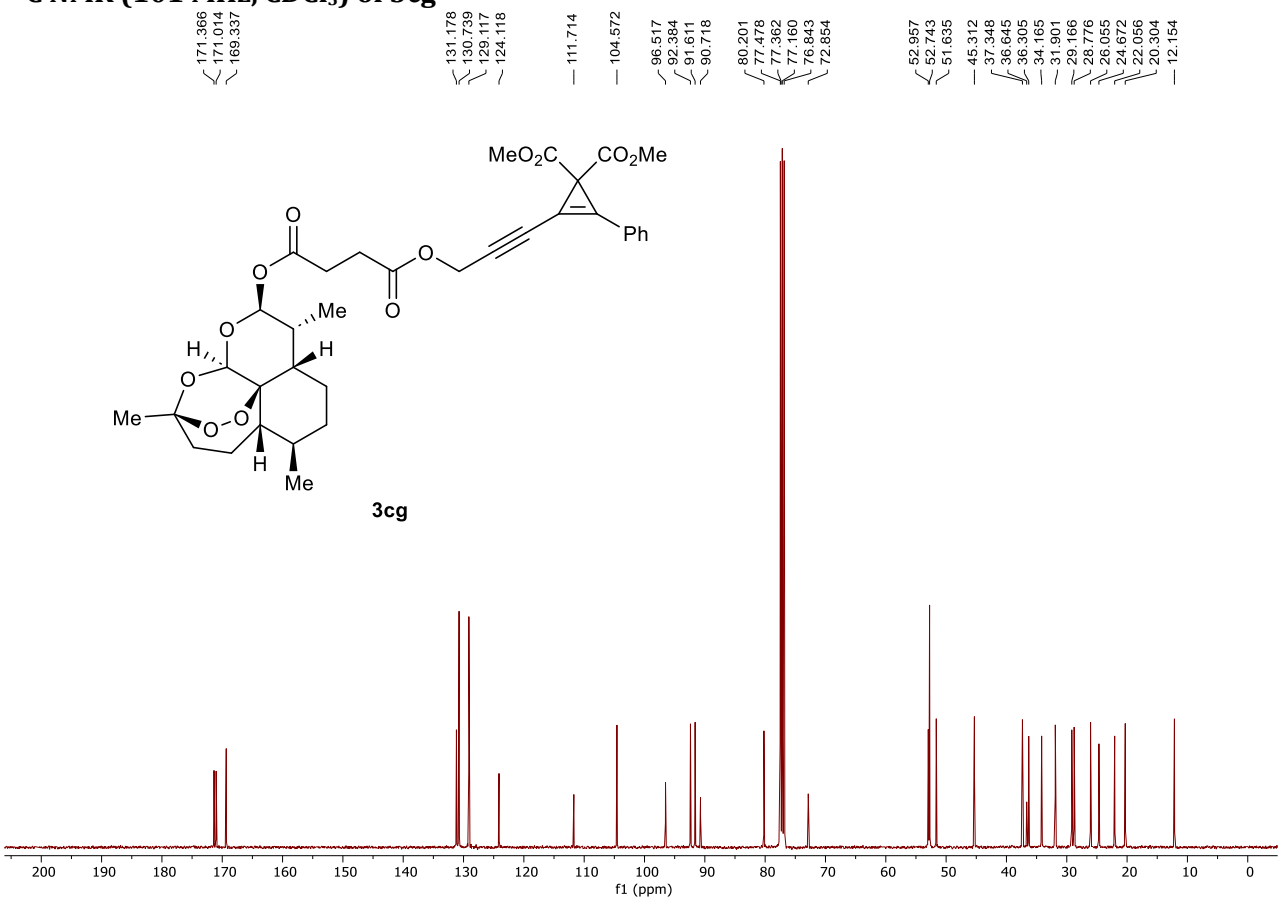
^{19}F NMR (377 MHz, $CDCl_3$) of 3cf



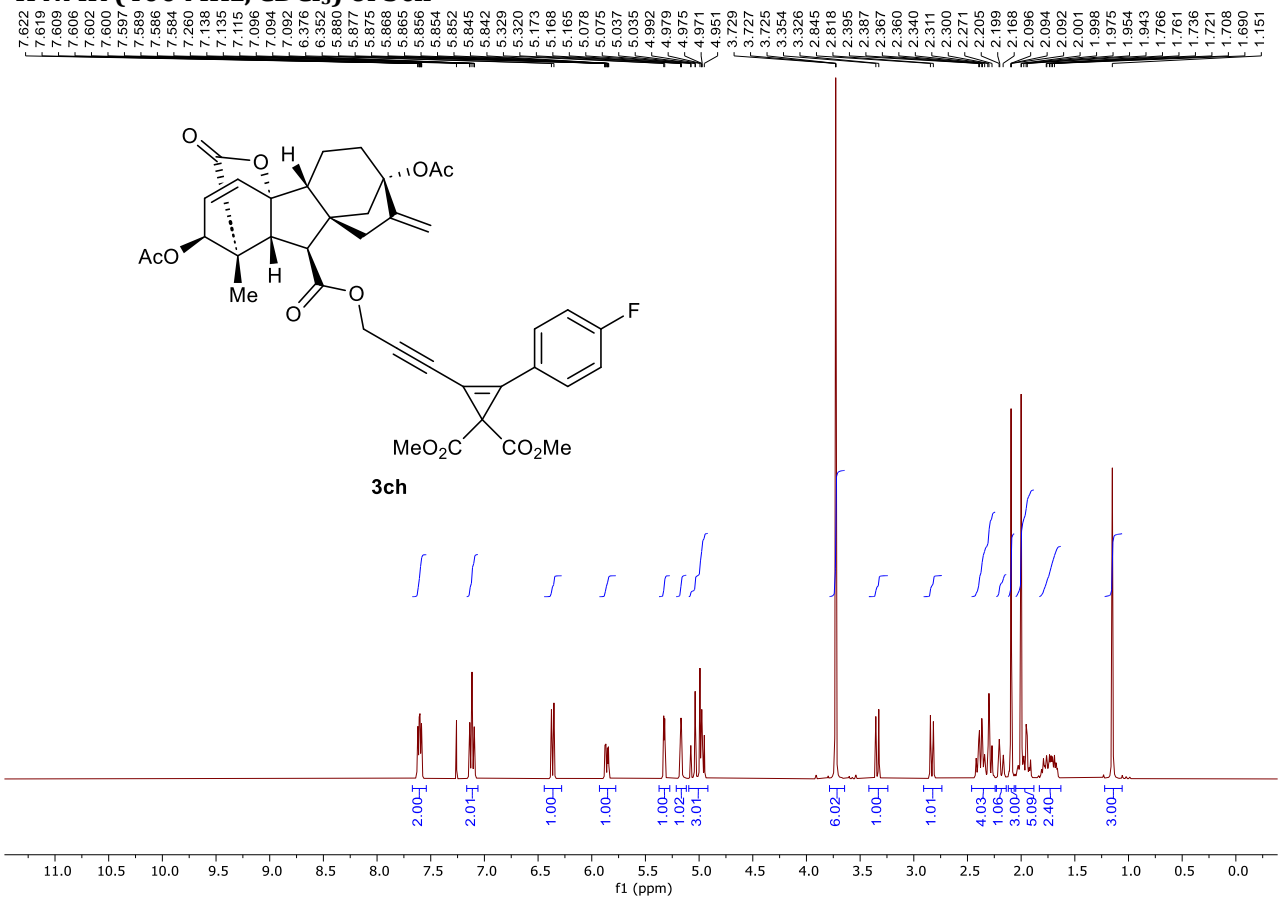
^{1}H NMR (400 MHz, $CDCl_3$) of 3cg



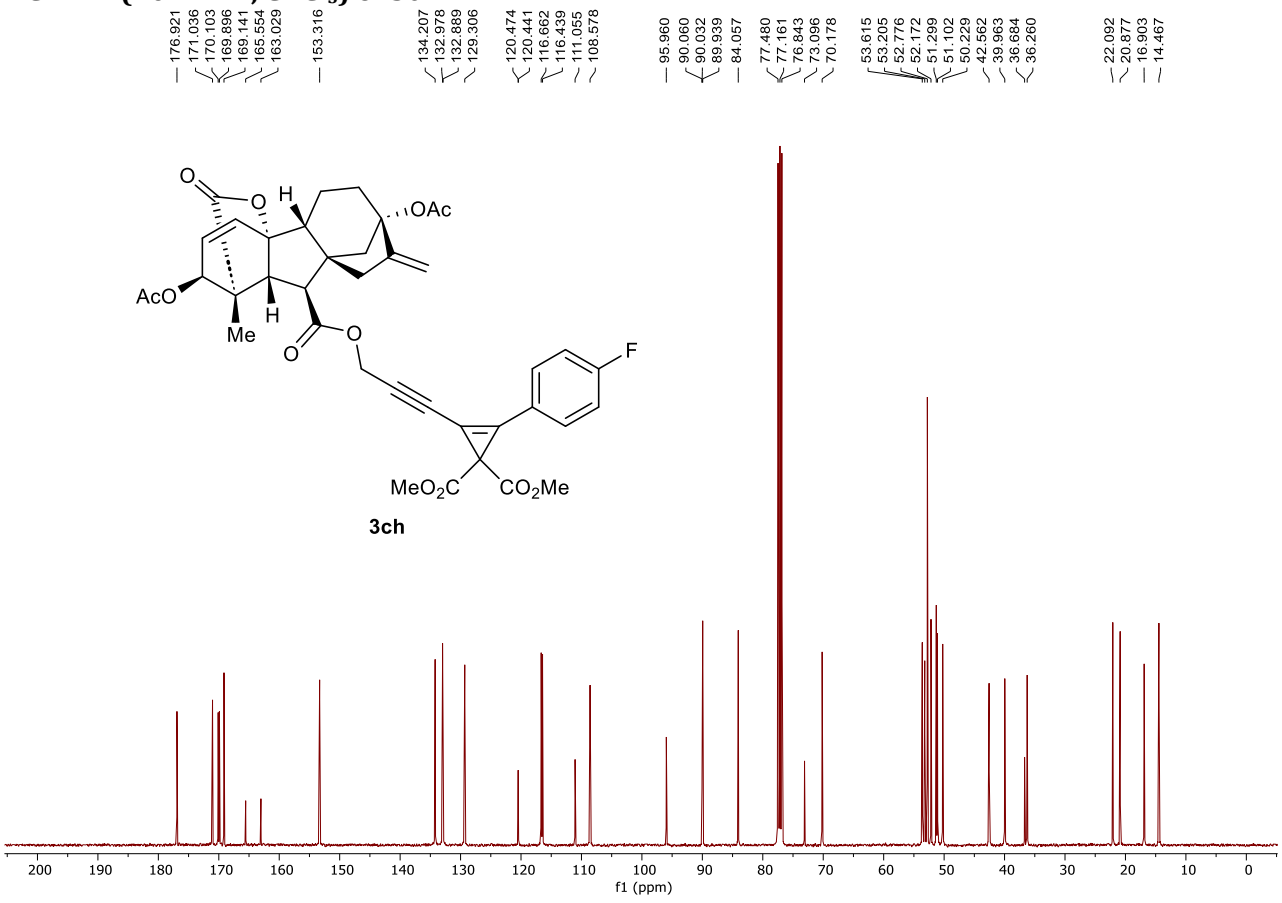
^{13}C NMR (101 MHz, $CDCl_3$) of 3cg



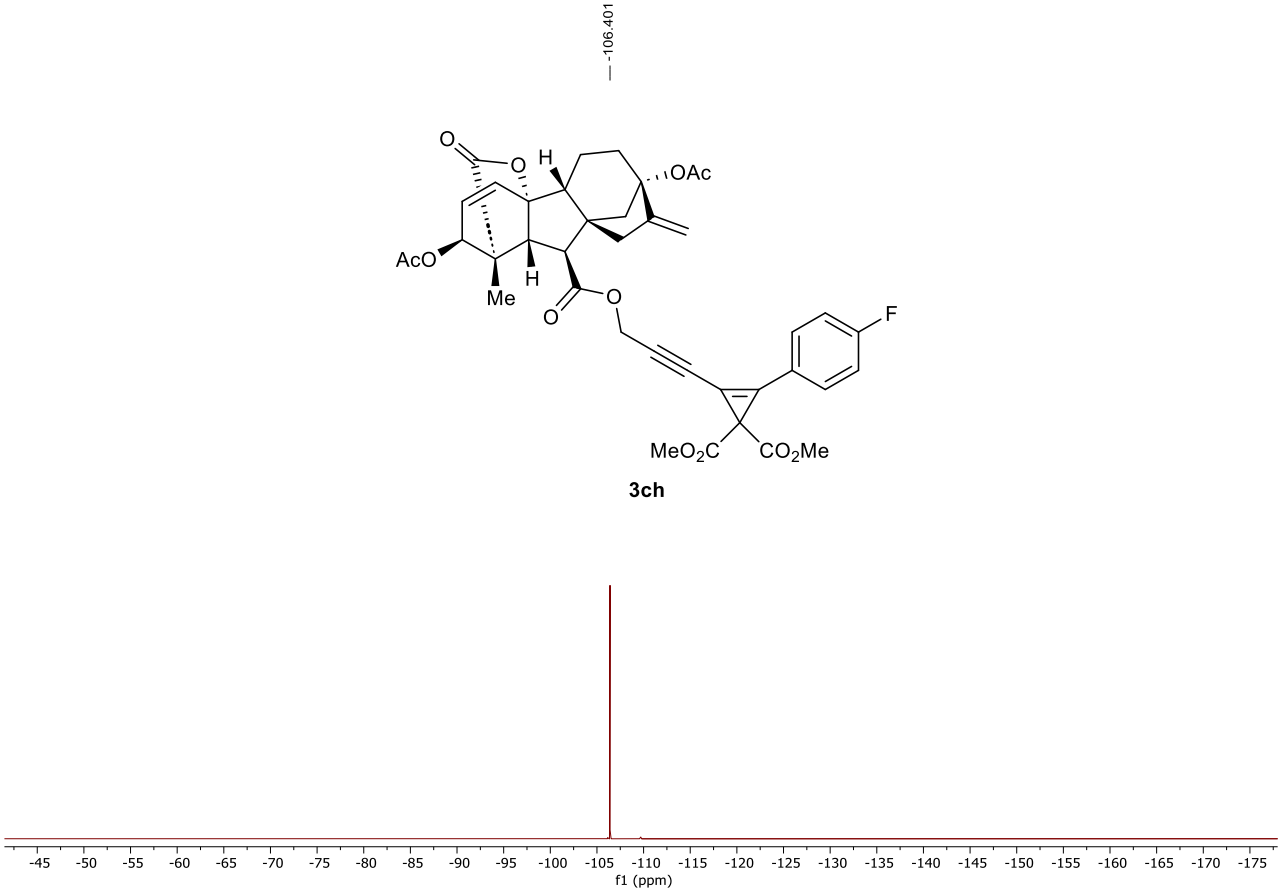
^{1}H NMR (400 MHz, $CDCl_3$) of 3ch



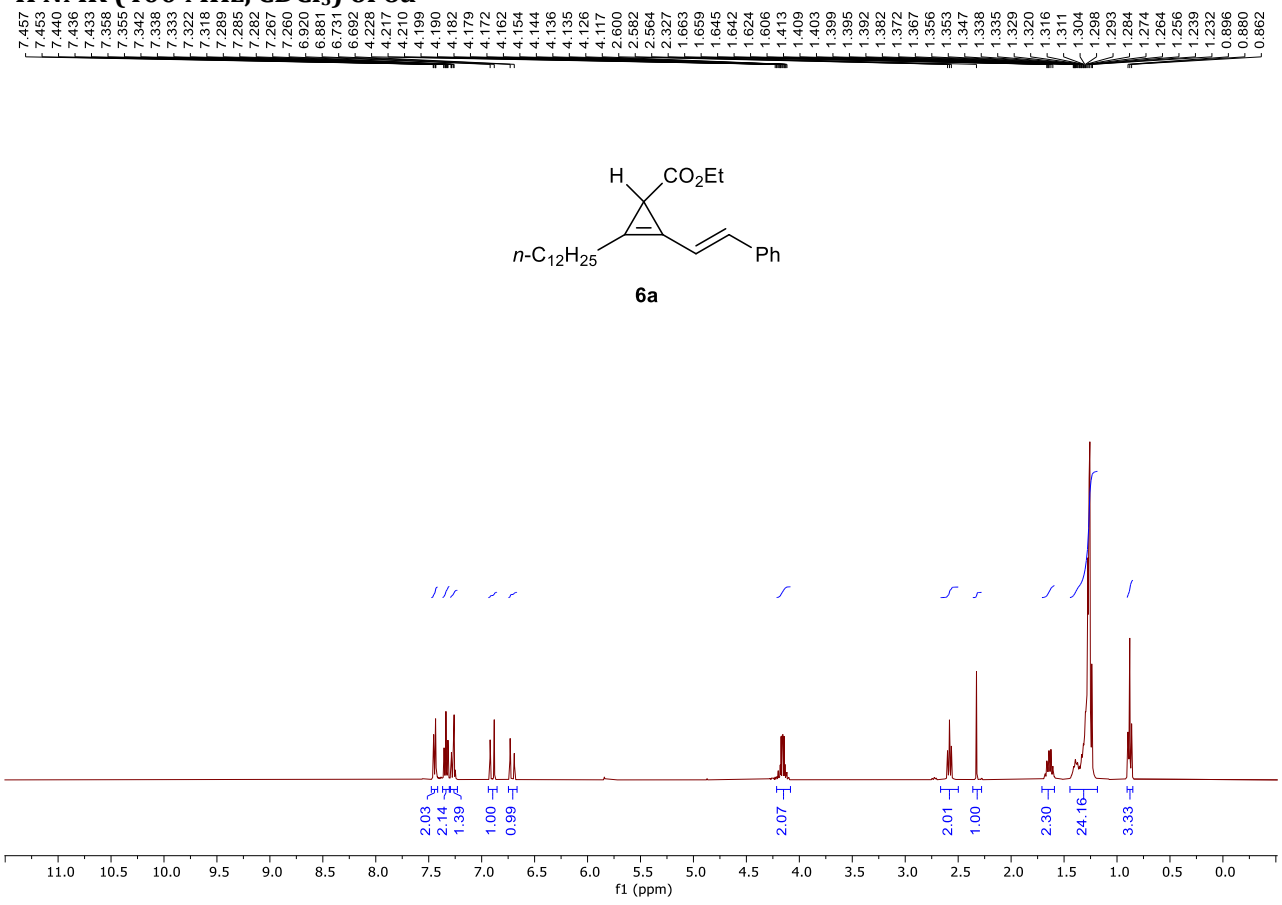
^{13}C NMR (101 MHz, $CDCl_3$) of 3ch



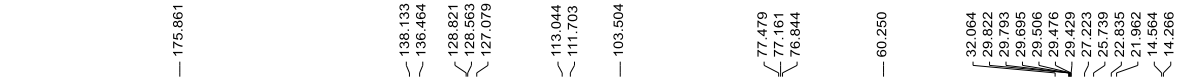
^{19}F NMR (377 MHz, $CDCl_3$) of 3ch

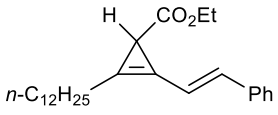


^{1}H NMR (400 MHz, $CDCl_3$) of 6a

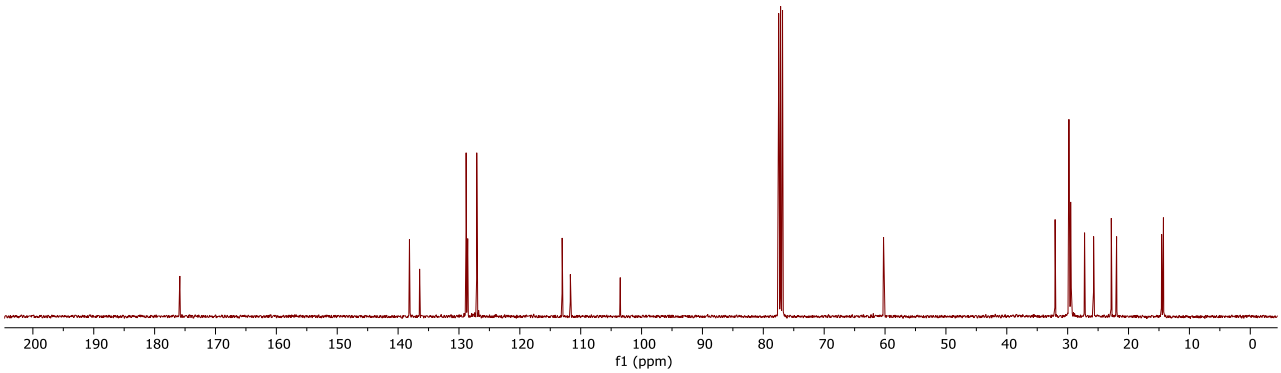


^{13}C NMR (101 MHz, $CDCl_3$) of 6a

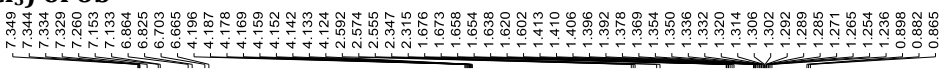


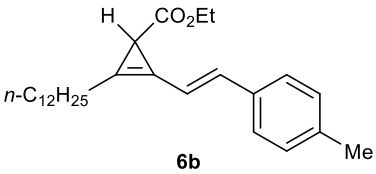


6a

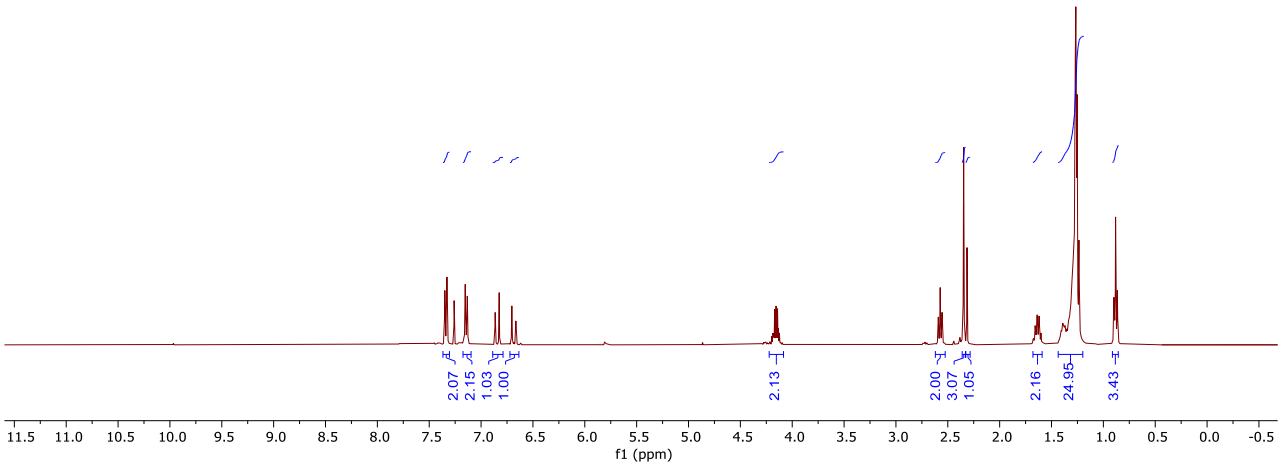


^{1}H NMR (400 MHz, $CDCl_3$) of 6b

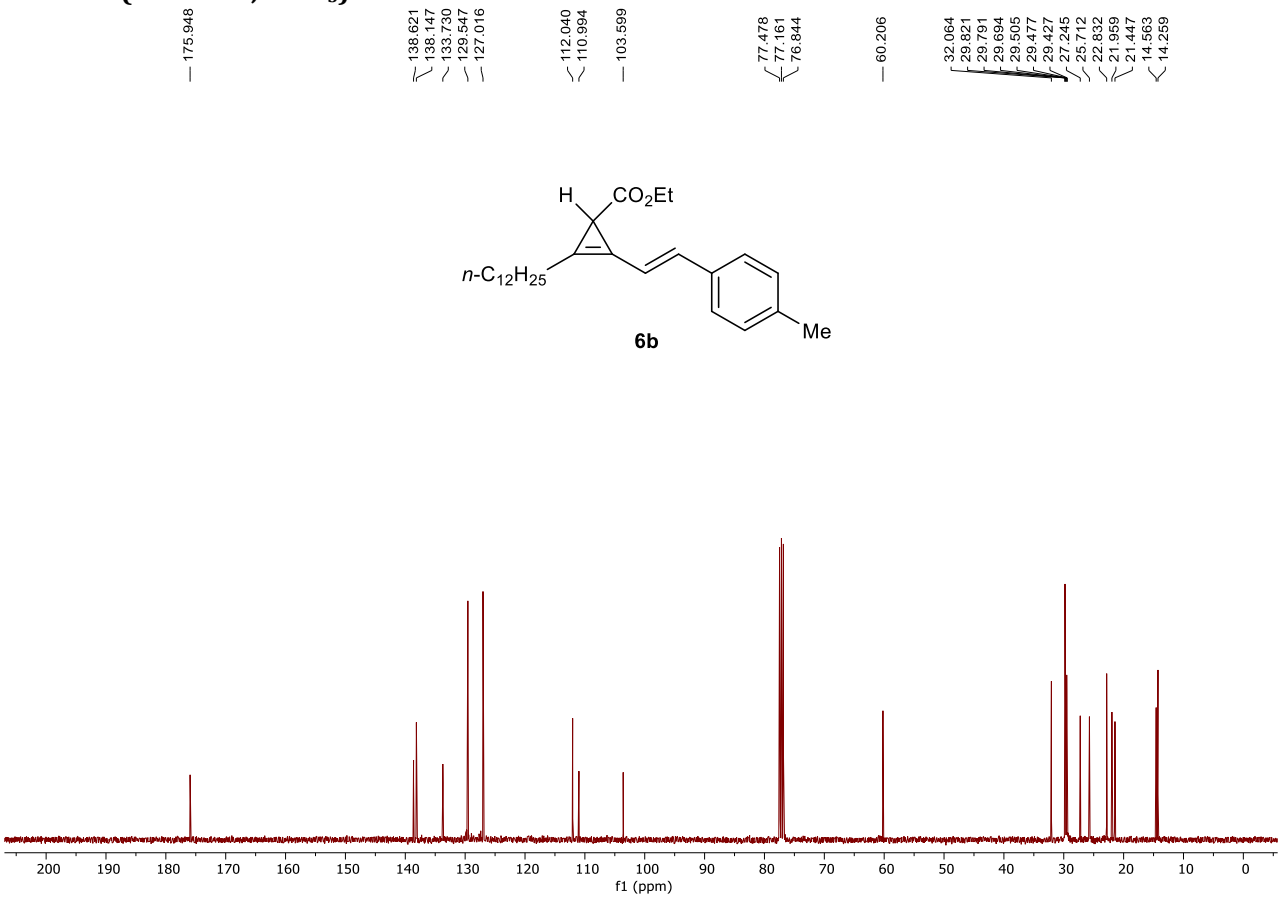




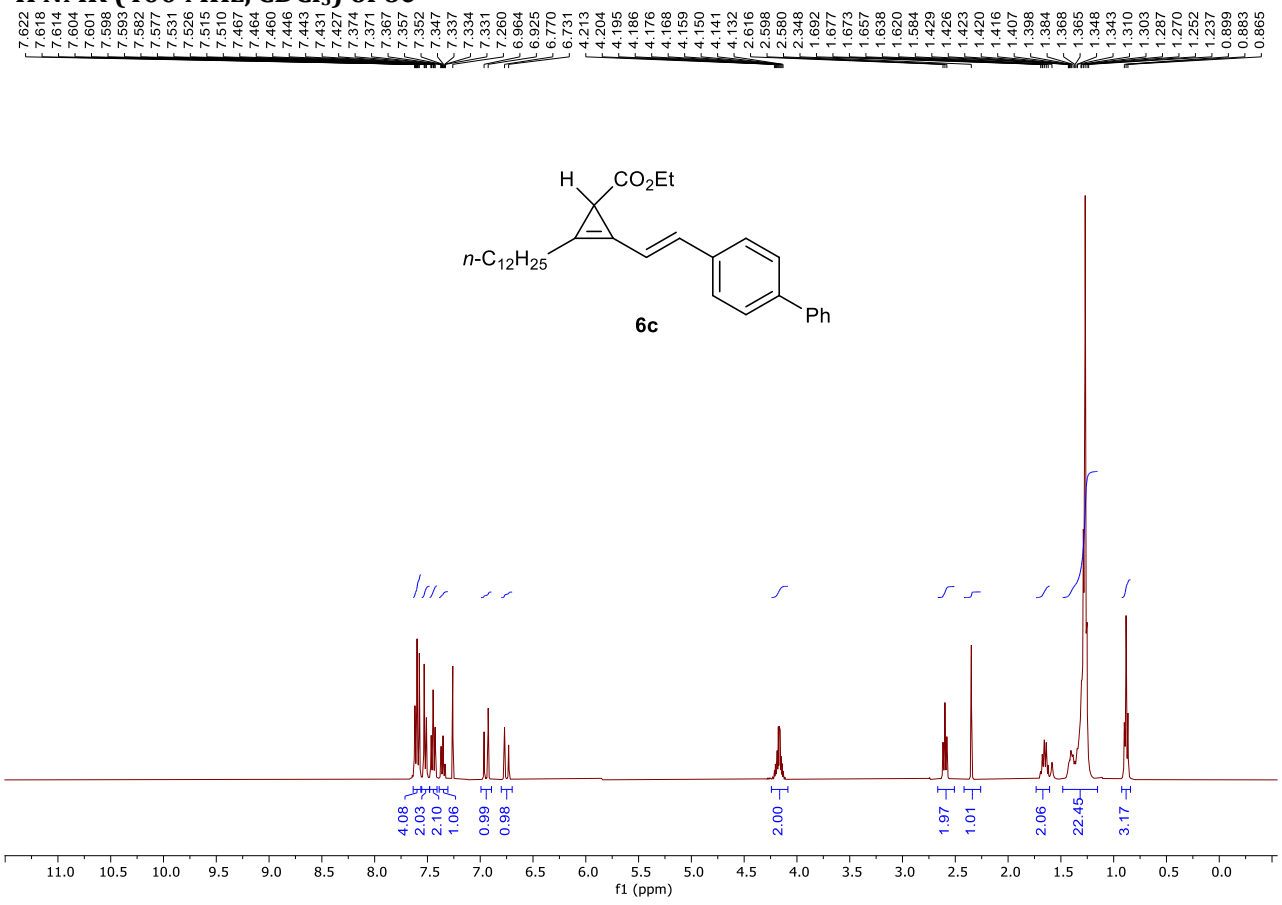
6b



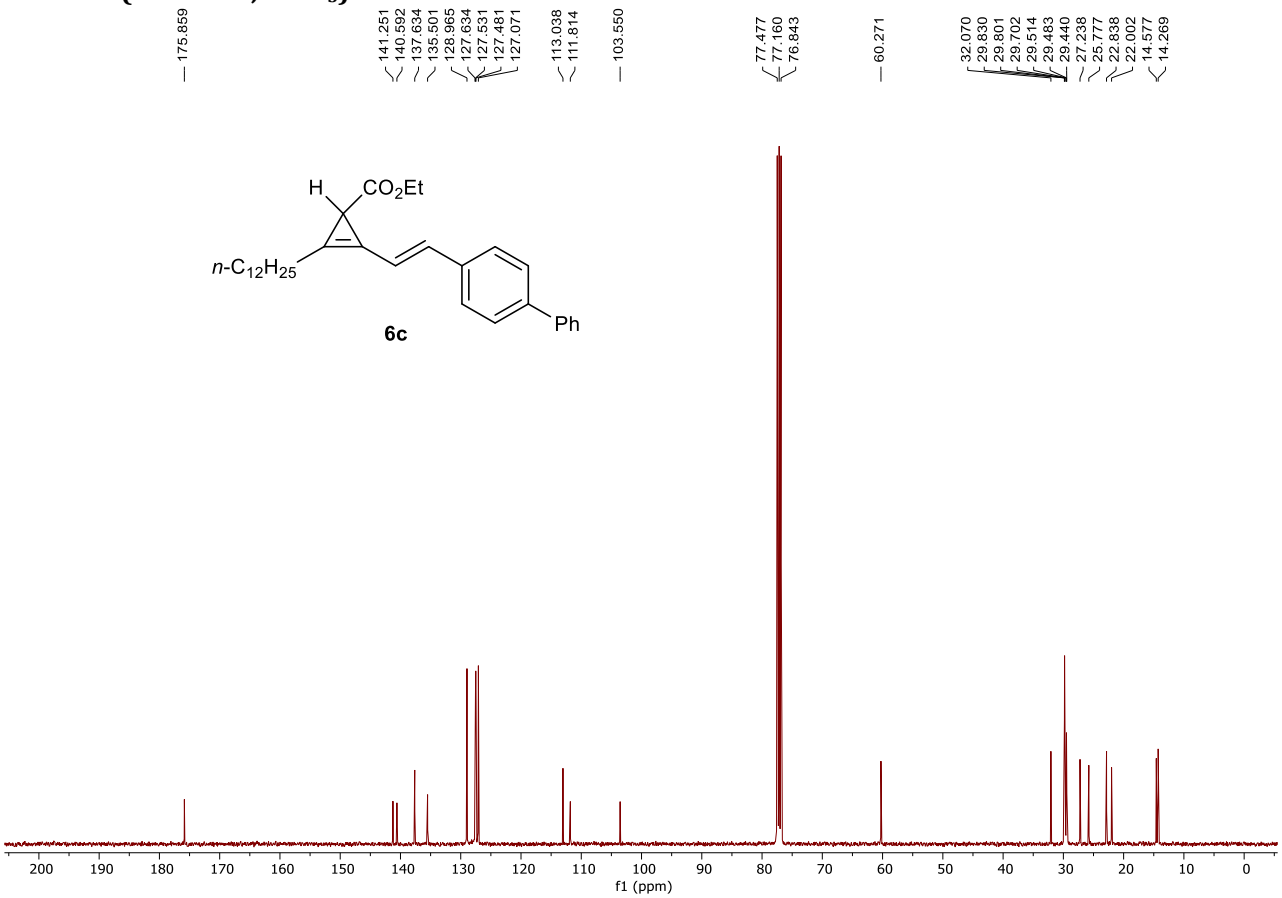
^{13}C NMR (101 MHz, $CDCl_3$) of 6b



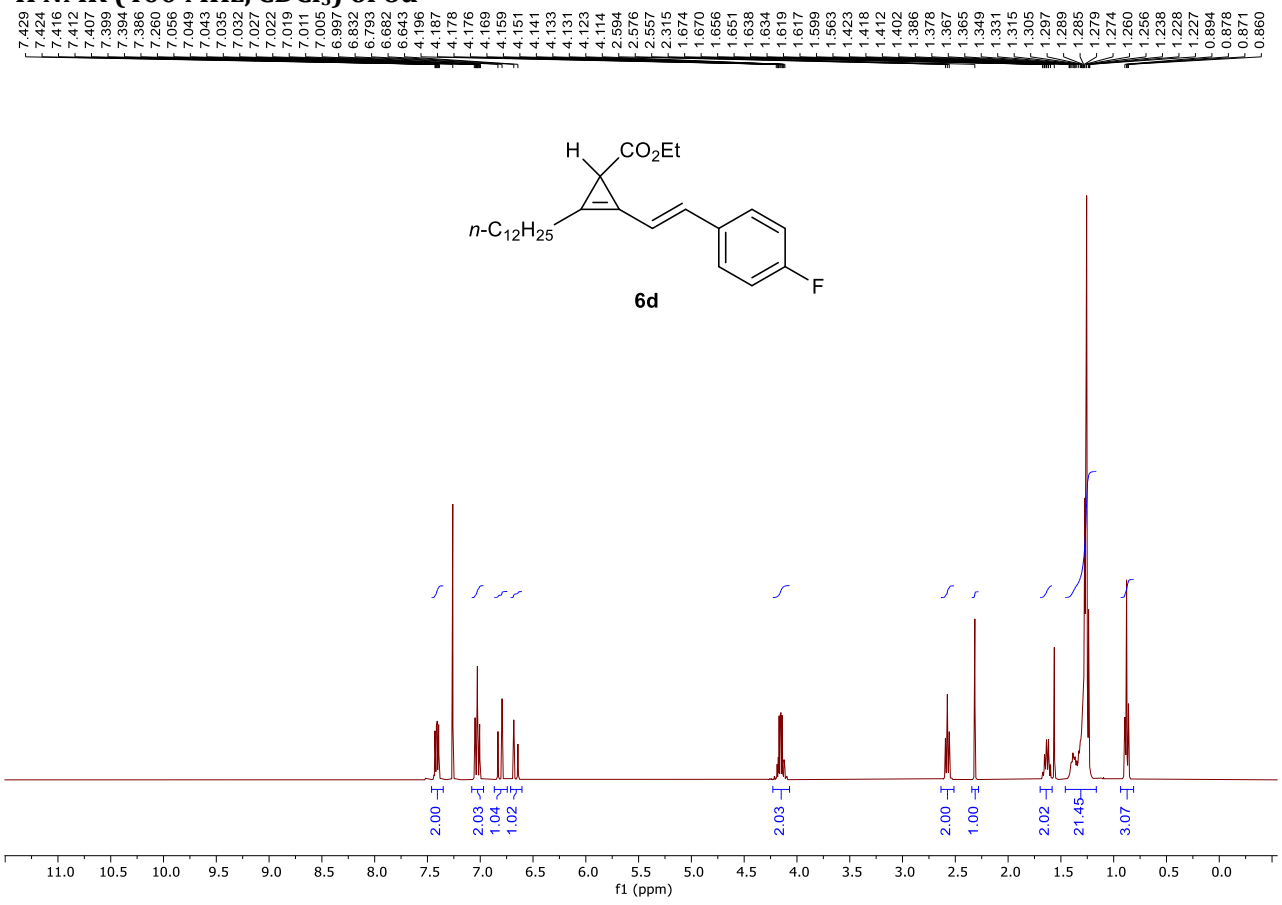
^{1}H NMR (400 MHz, $CDCl_3$) of 6c



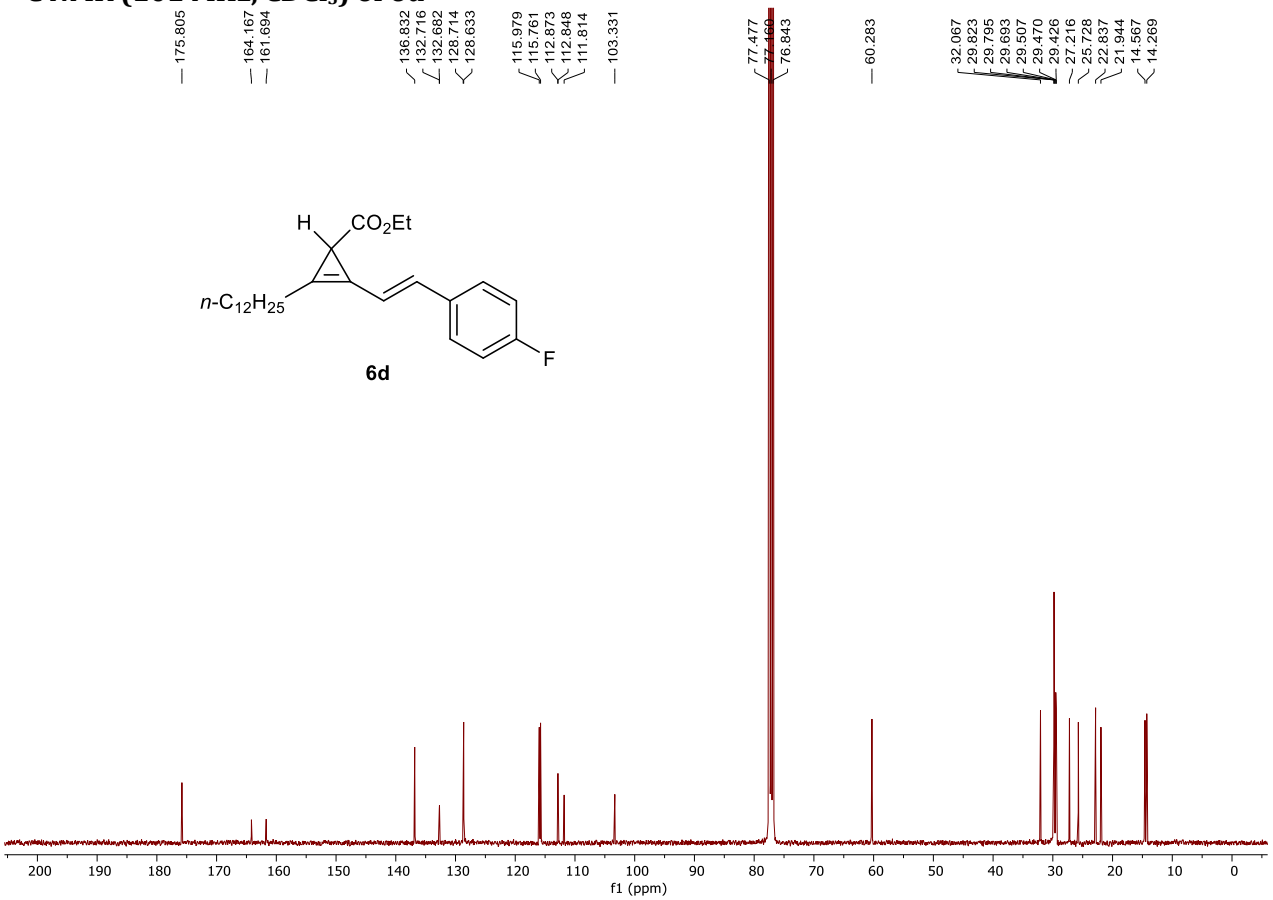
^{13}C NMR (101 MHz, $CDCl_3$) of 6c



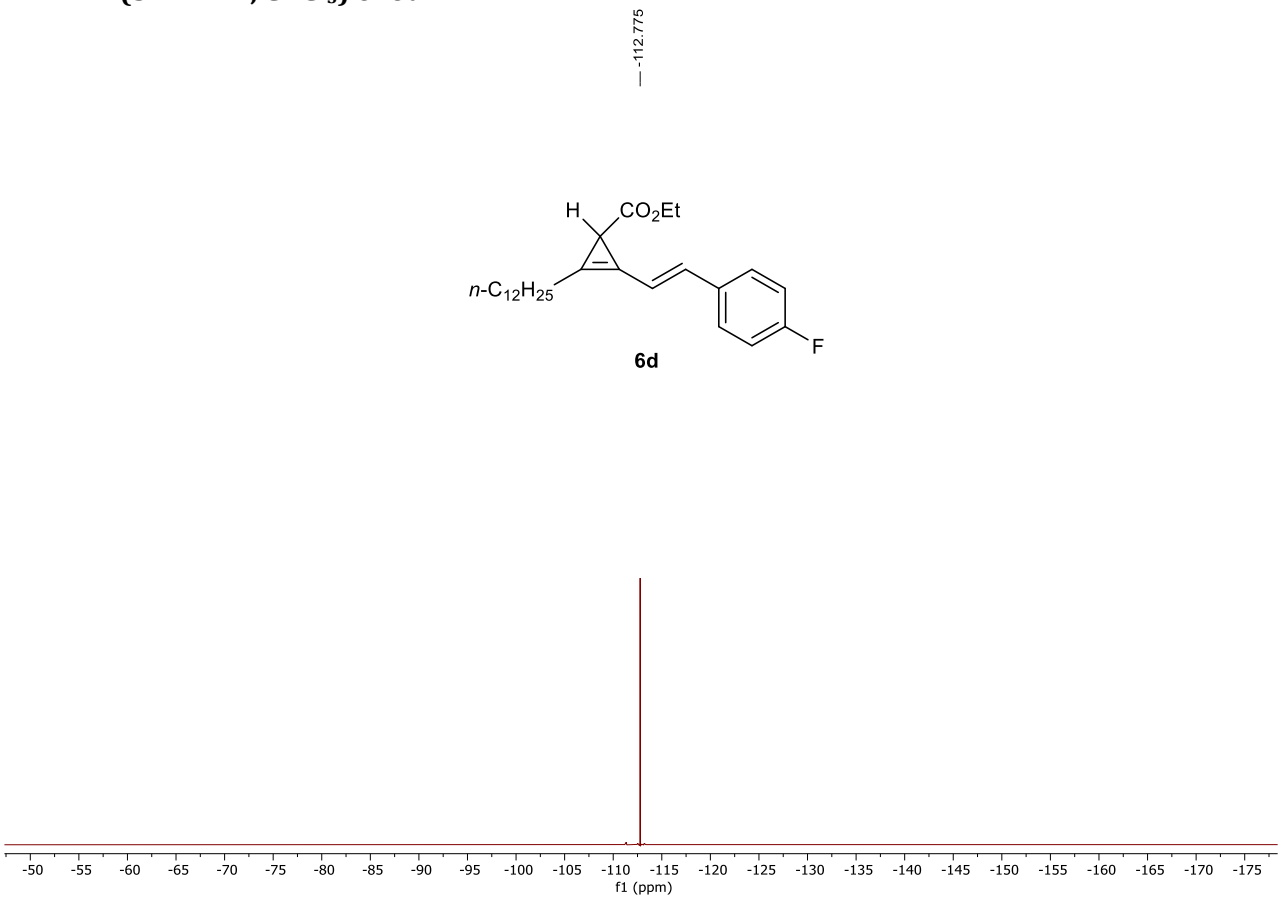
^{1}H NMR (400 MHz, $CDCl_3$) of 6d



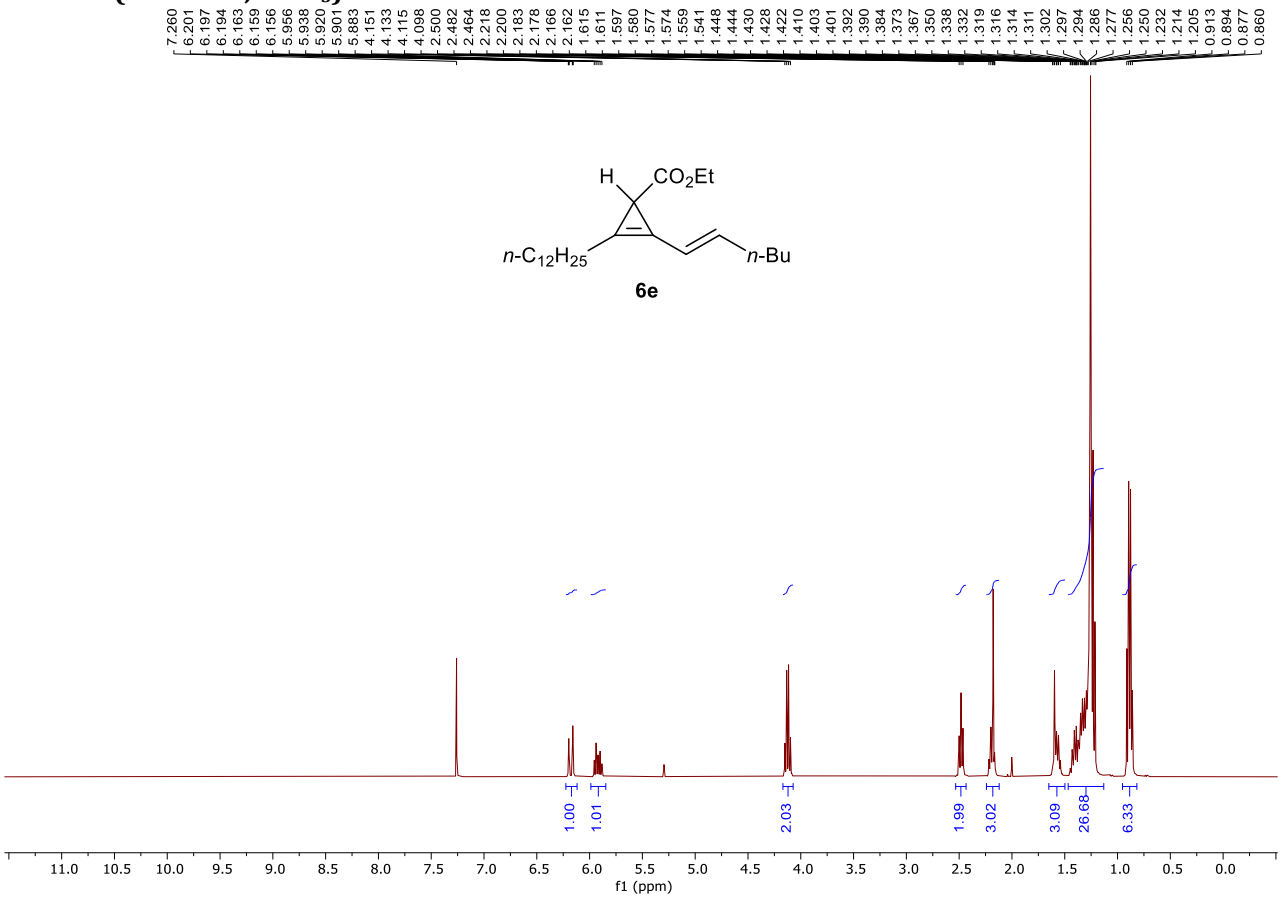
^{13}C NMR (101 MHz, $CDCl_3$) of 6d



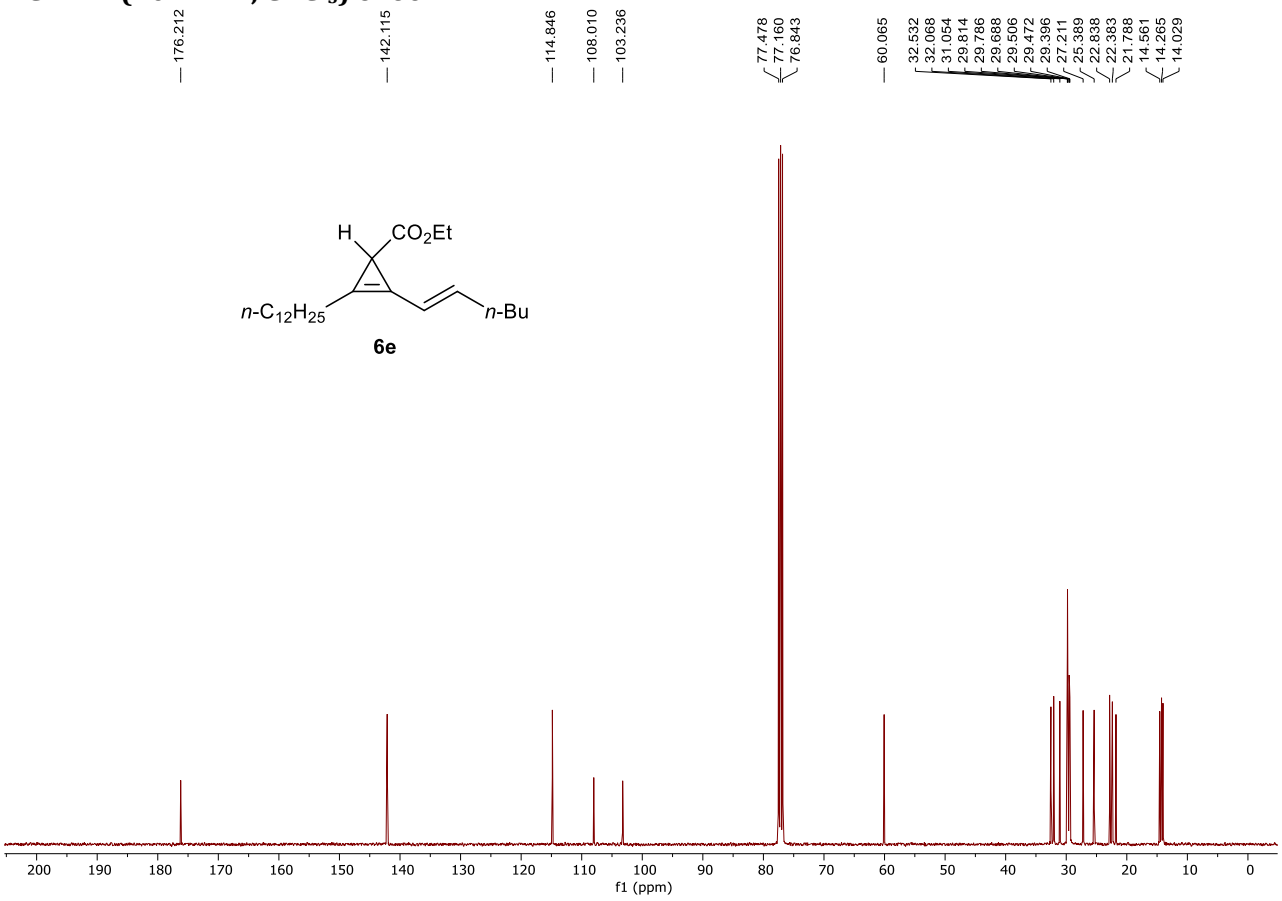
^{19}F NMR (377 MHz, $CDCl_3$) of 6d



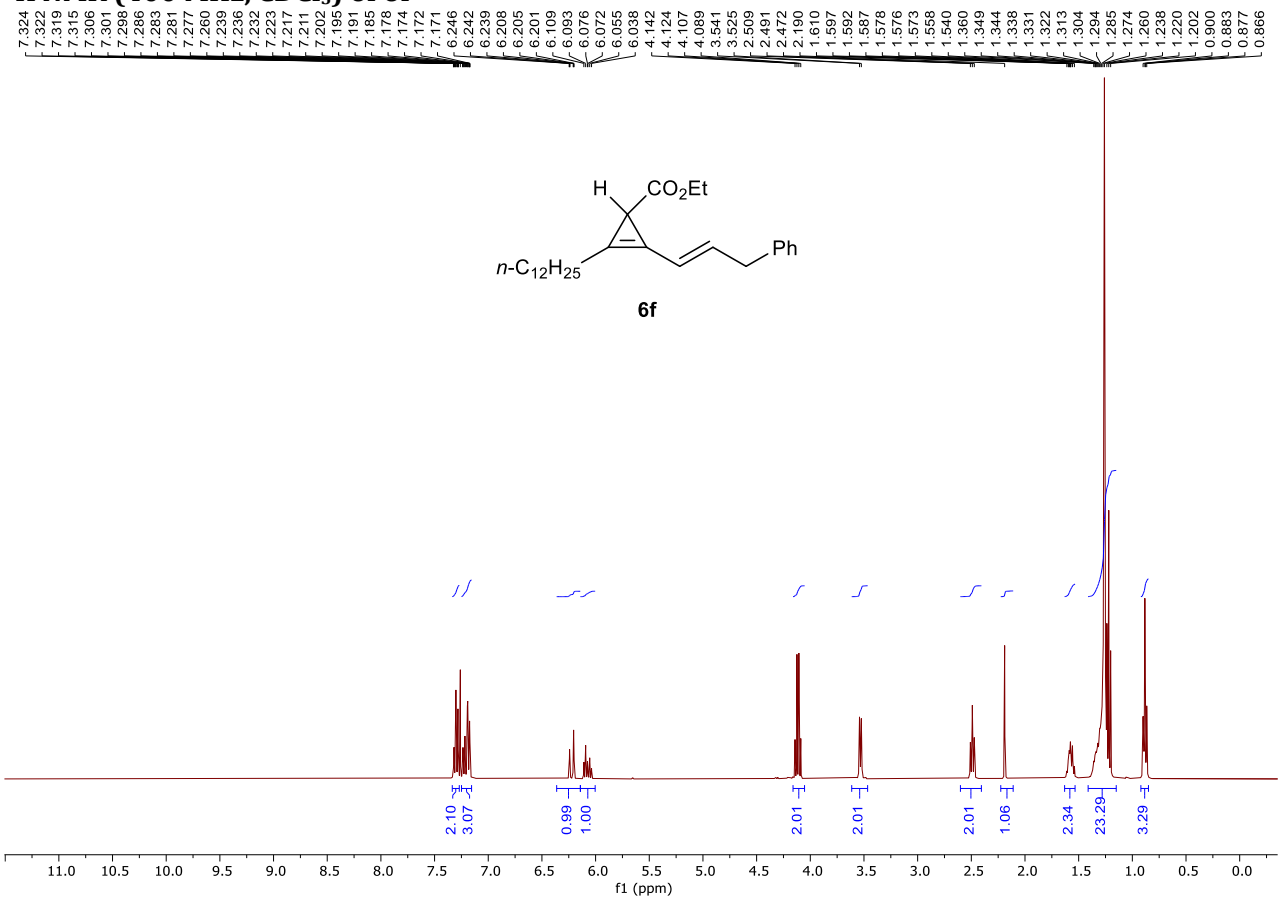
^{1}H NMR (400 MHz, $CDCl_3$) of 6e



^{13}C NMR (101 MHz, $CDCl_3$) of 6e

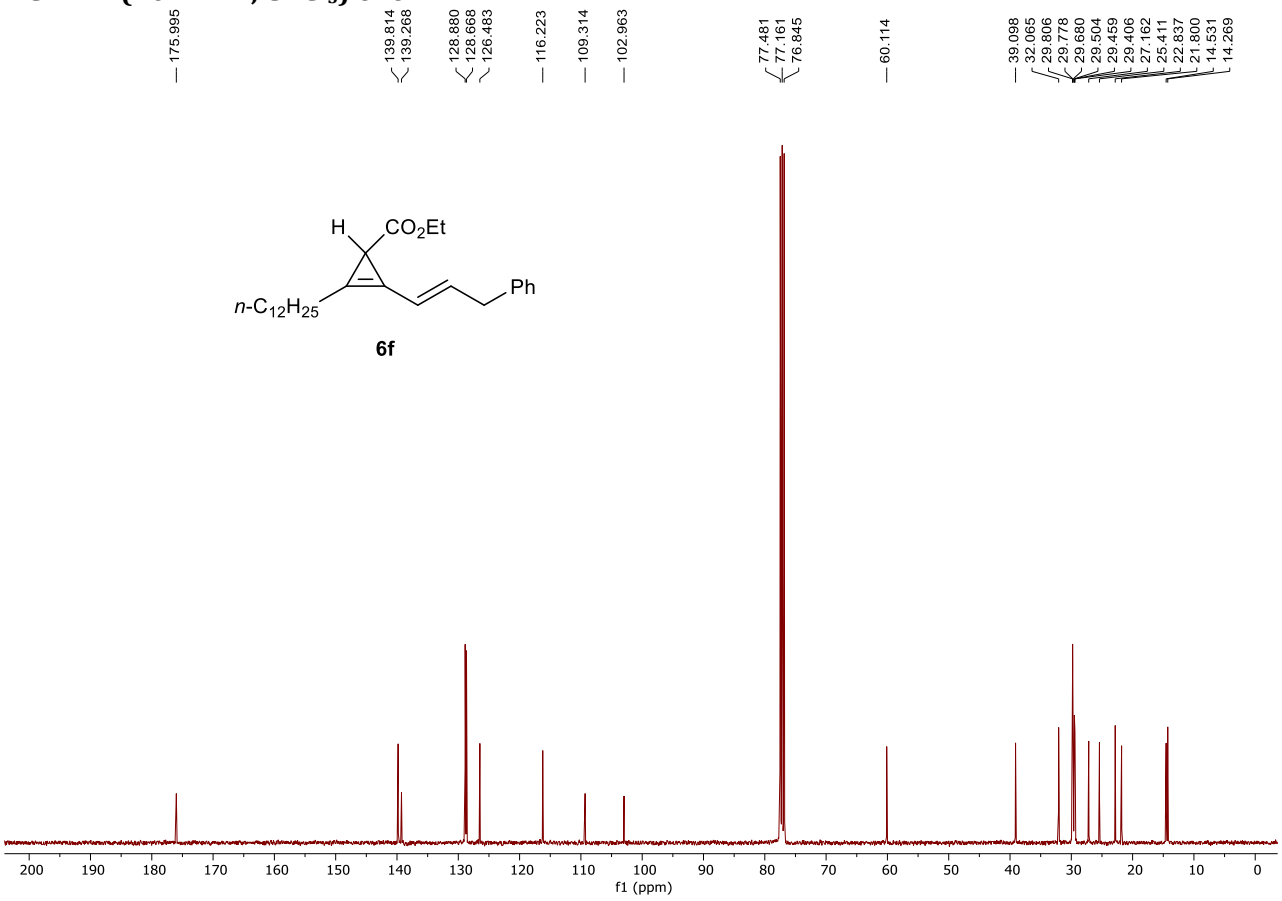


^{1}H NMR (400 MHz, $CDCl_3$) of 6f



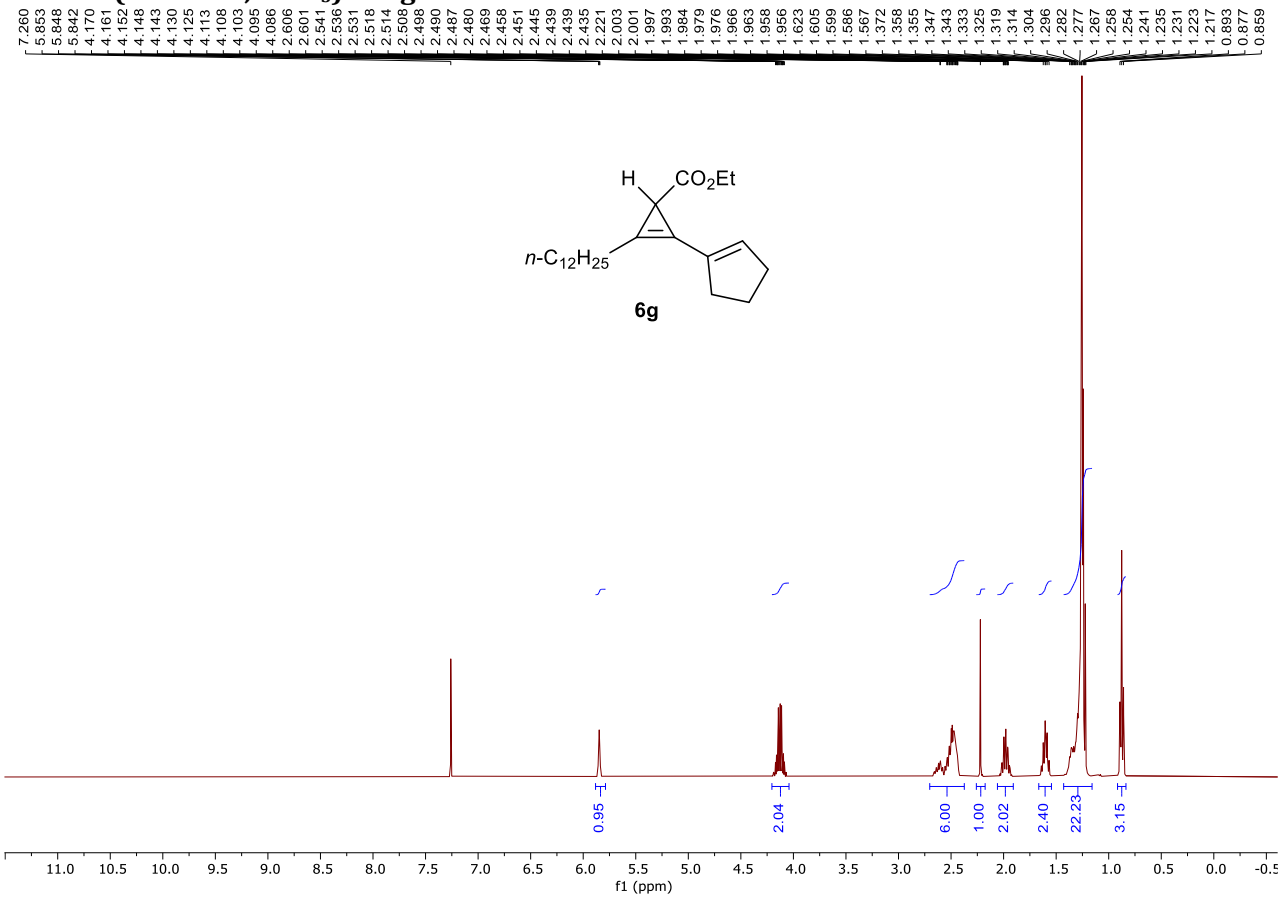
6f

^{13}C NMR (101 MHz, $CDCl_3$) of 6f

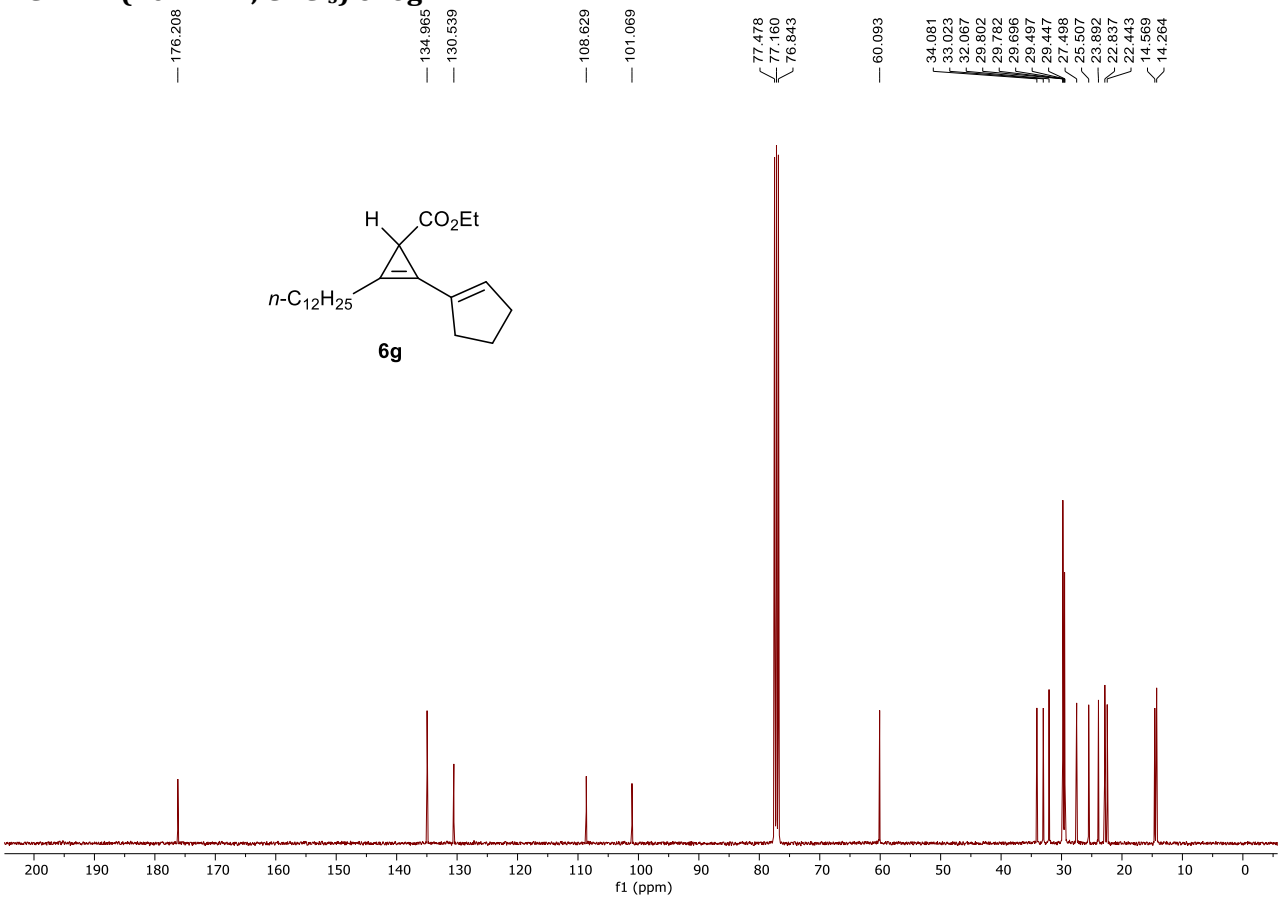


6f

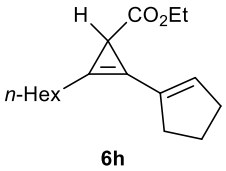
^{1}H NMR (400 MHz, $CDCl_3$) of 6g



^{13}C NMR (101 MHz, $CDCl_3$) of 6g

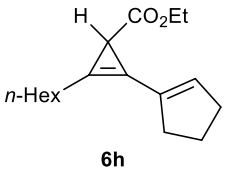


^{1}H NMR (400 MHz, $CDCl_3$) of 6h

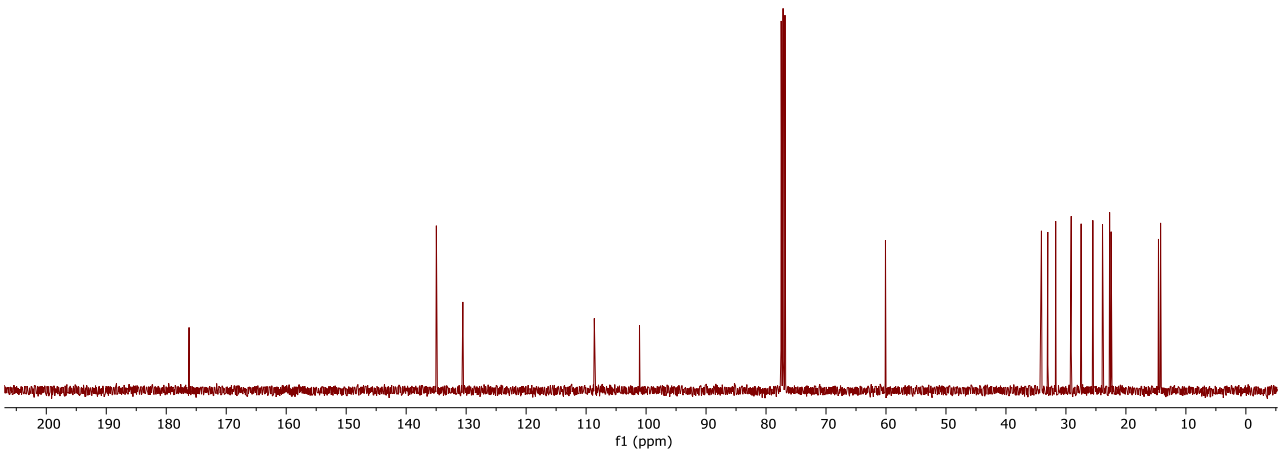


6h

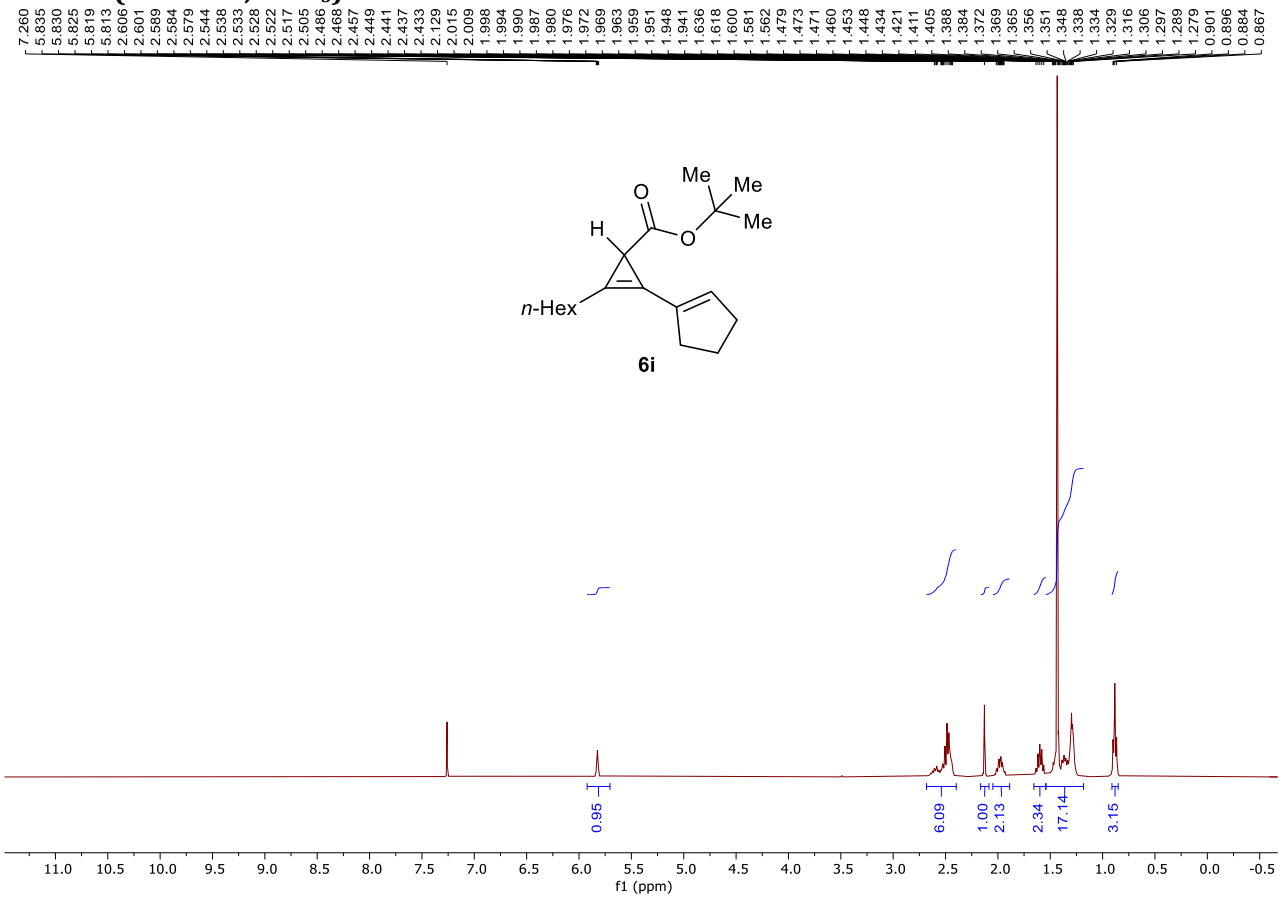
^{13}C NMR (101 MHz, $CDCl_3$) of 6h



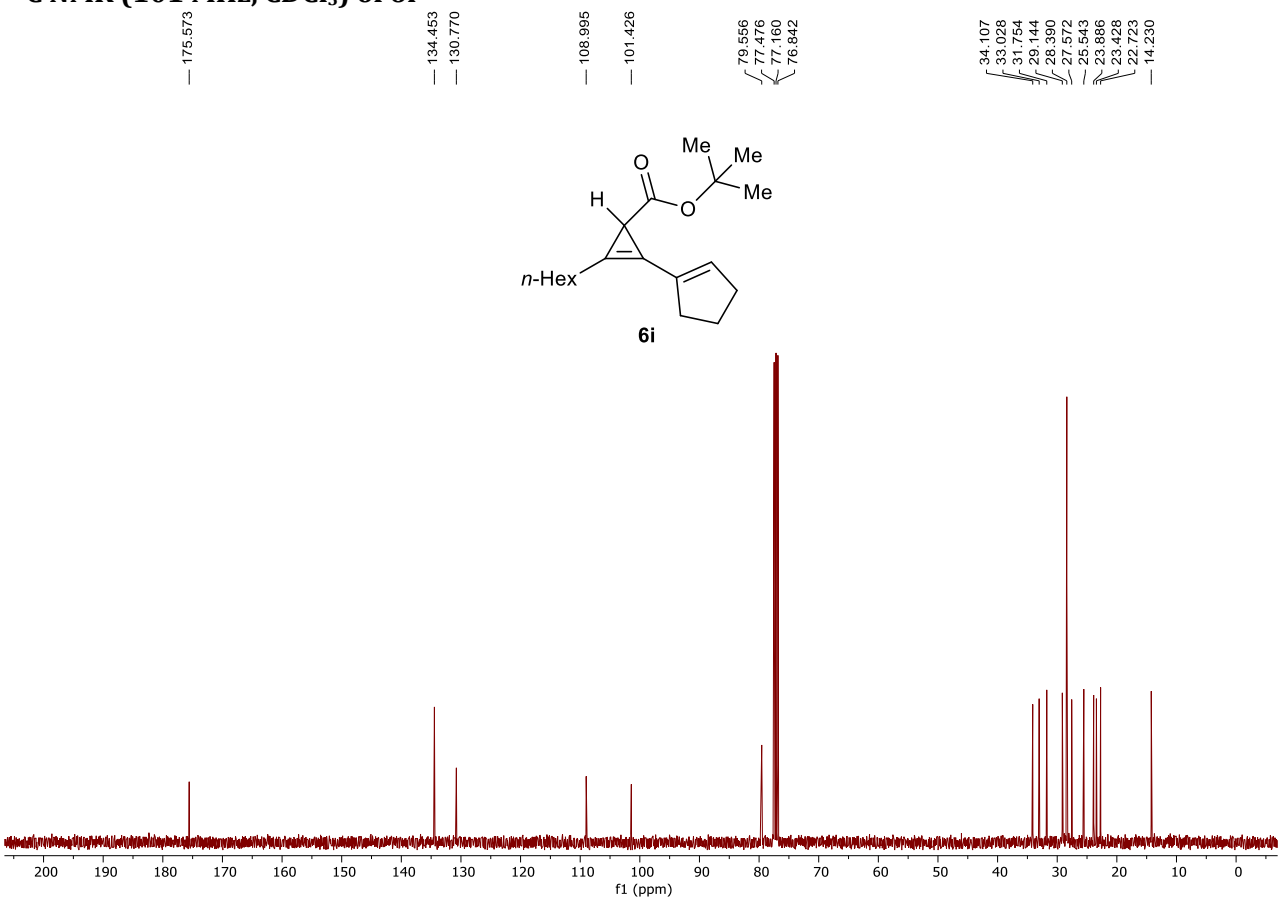
6h



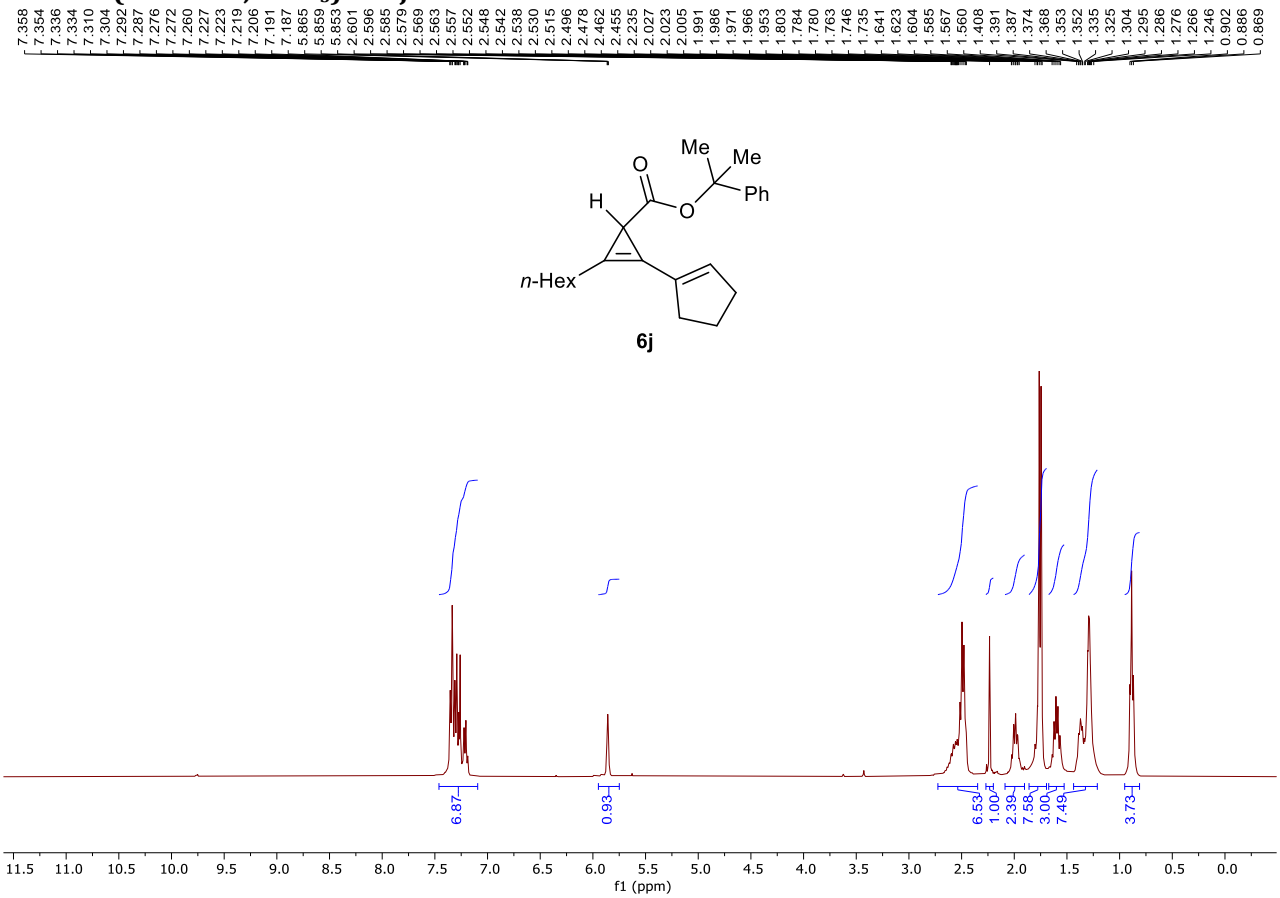
^{1}H NMR (400 MHz, $CDCl_3$) of 6i



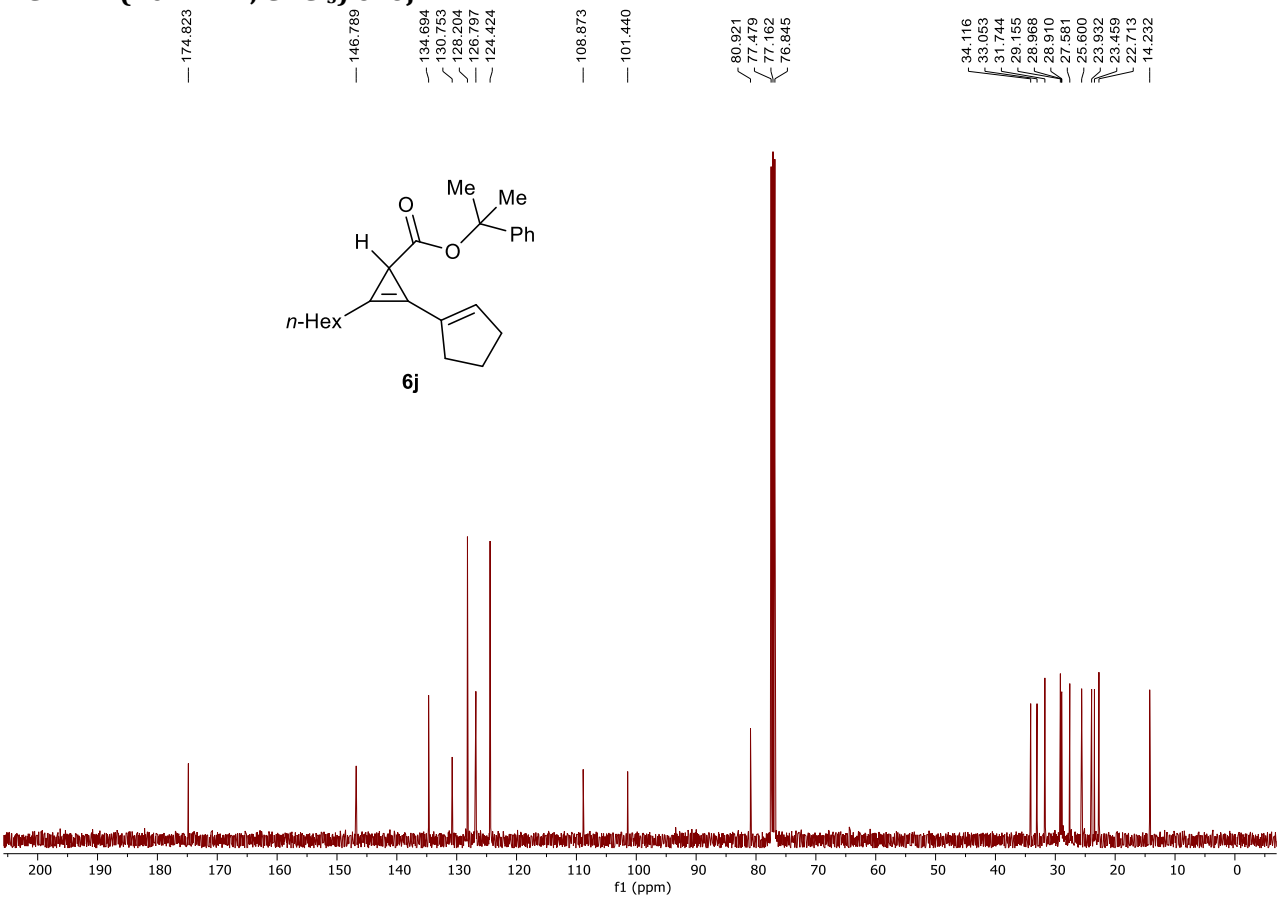
^{13}C NMR (101 MHz, $CDCl_3$) of 6i



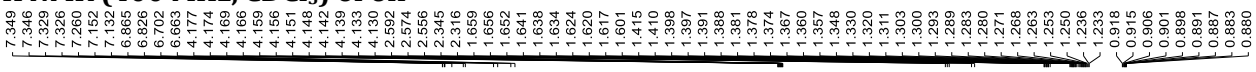
^{1}H NMR (400 MHz, $CDCl_3$) of 6j

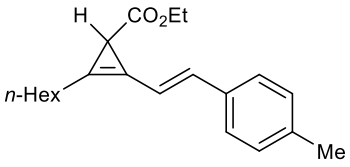


^{13}C NMR (101 MHz, $CDCl_3$) of 6j

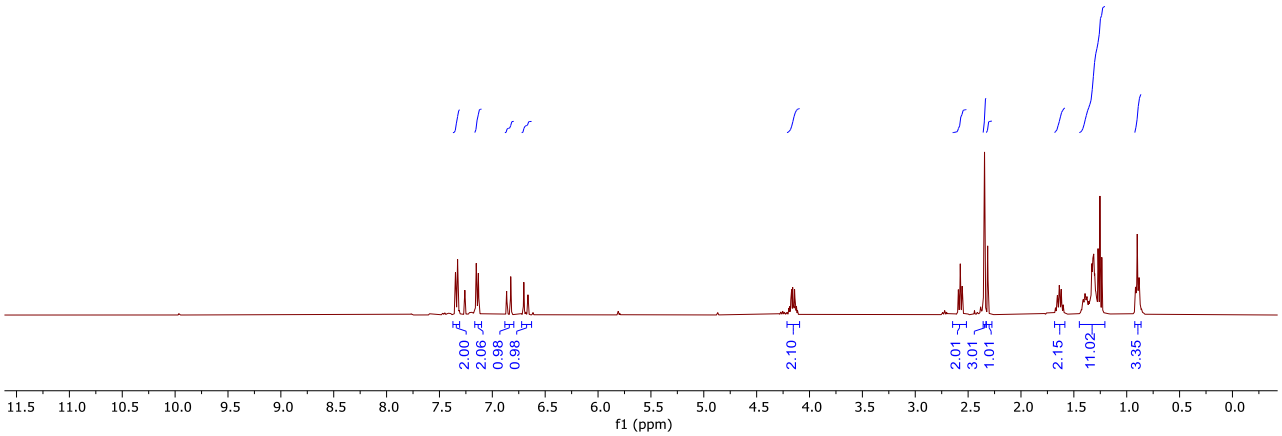


^{1}H NMR (400 MHz, $CDCl_3$) of 6k

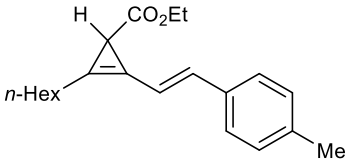




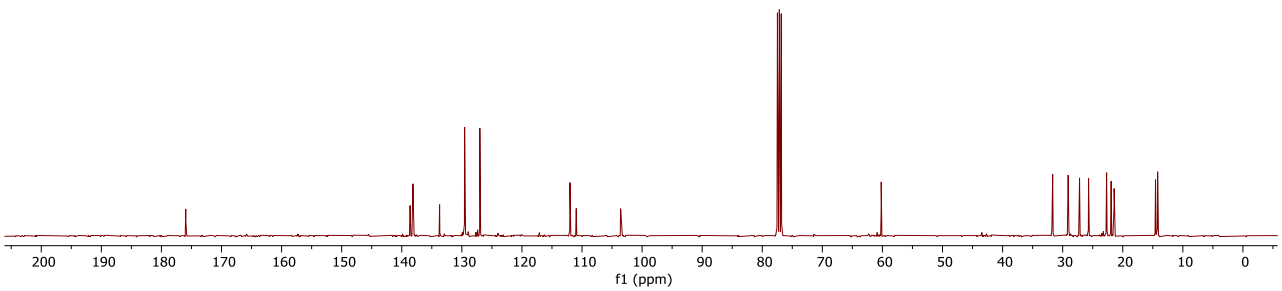
6k



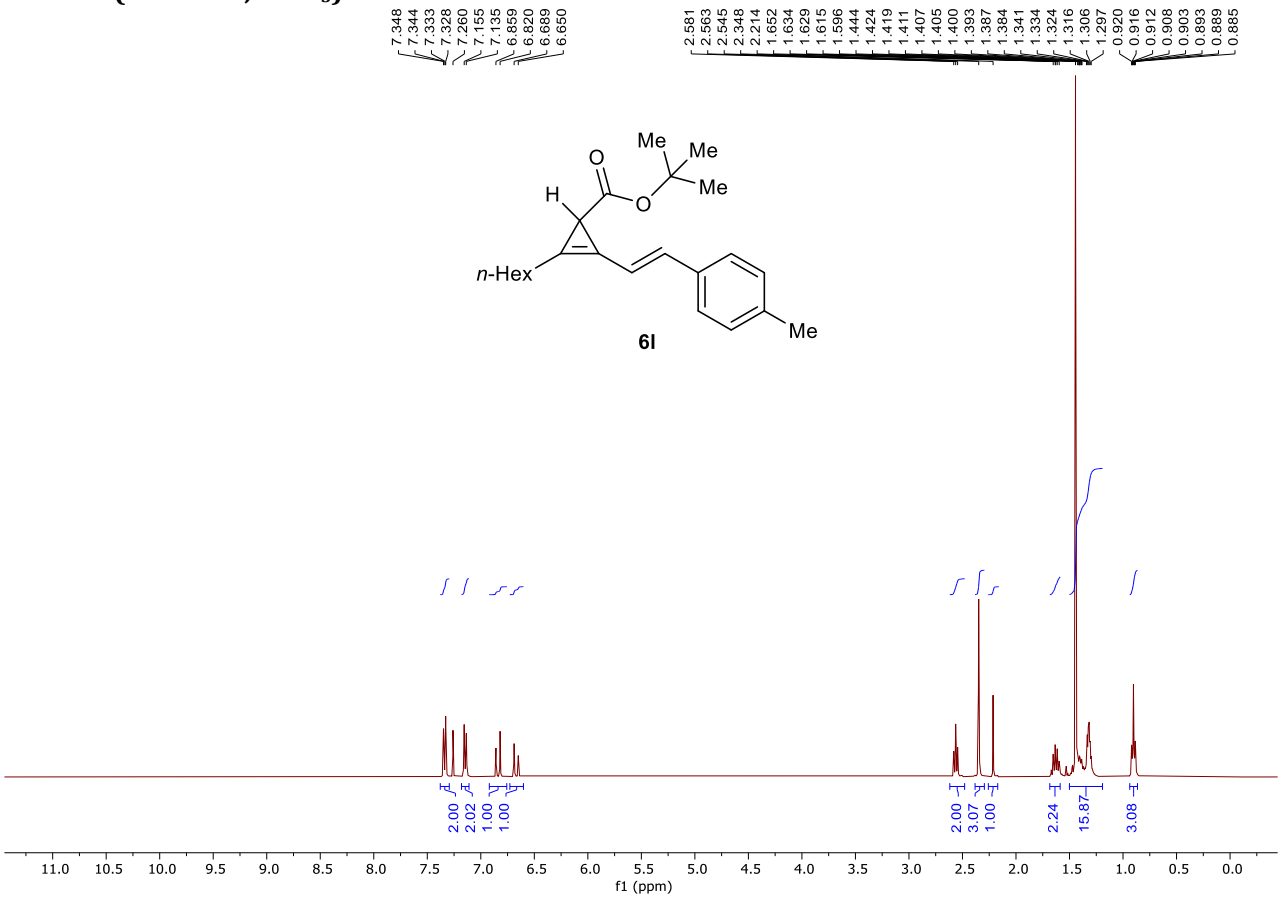
^{13}C NMR (101 MHz, $CDCl_3$) of 6k



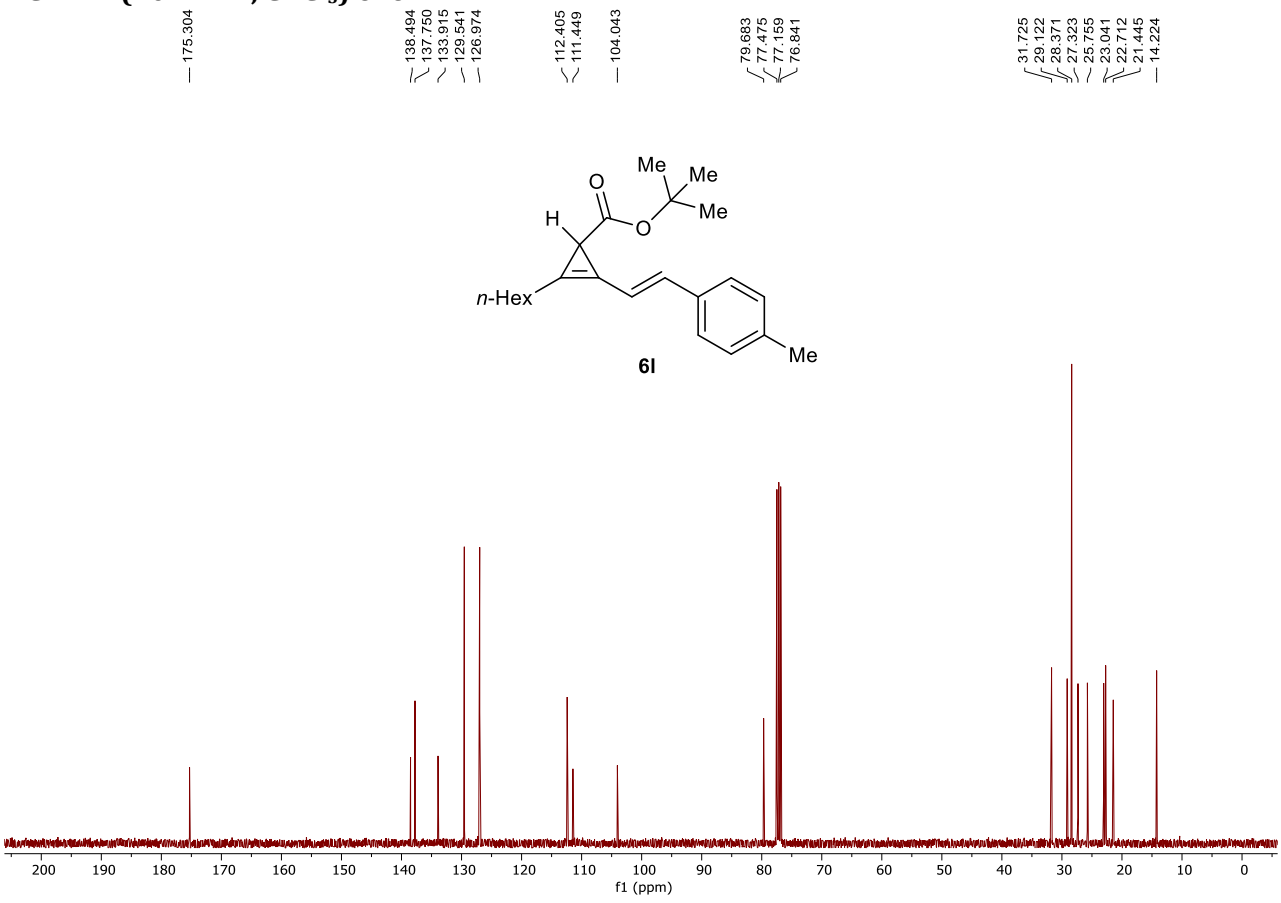
6k



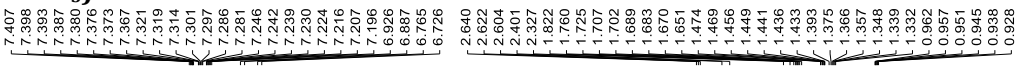
^{1}H NMR (400 MHz, $CDCl_3$) of 6l

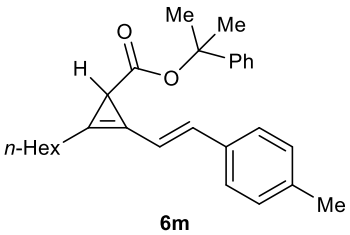


^{13}C NMR (101 MHz, $CDCl_3$) of 6l



^{1}H NMR (400 MHz, $CDCl_3$) of 6m





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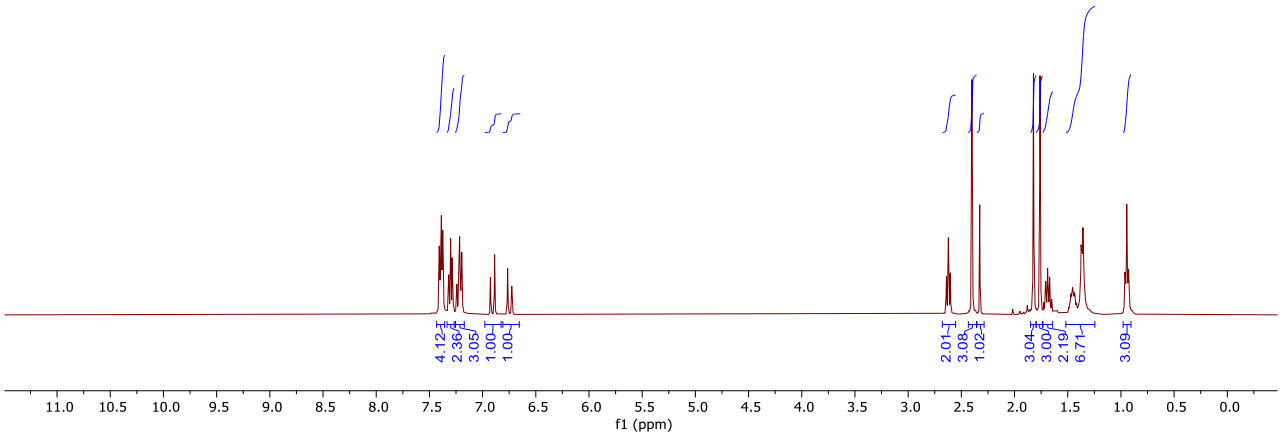
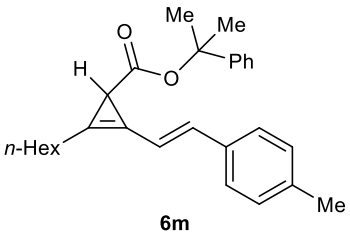
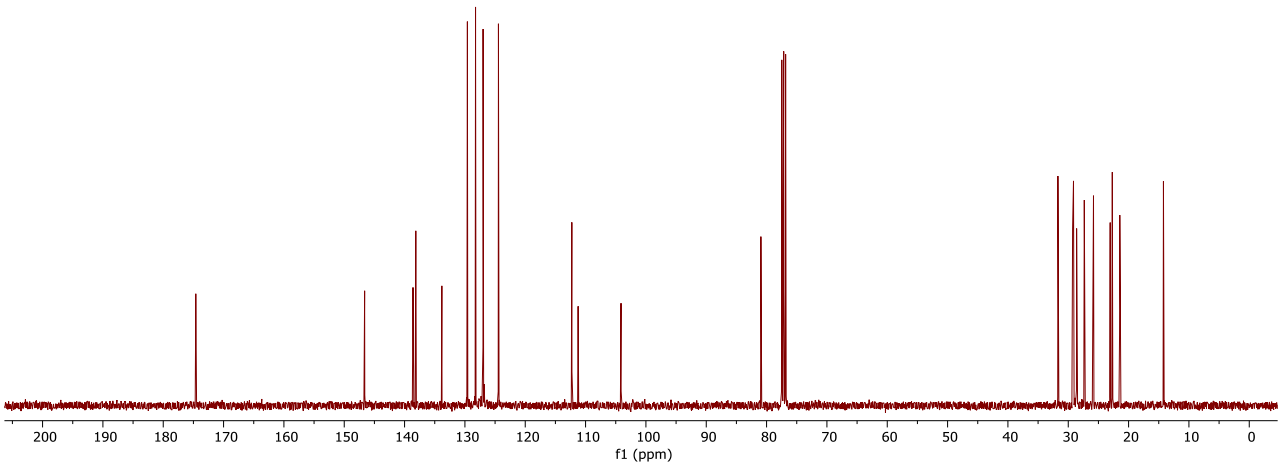


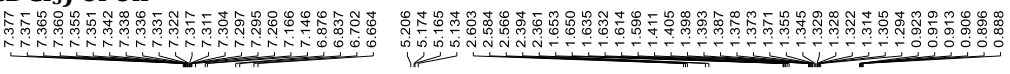
^{13}C NMR (101 MHz, $CDCl_3$) of 6m

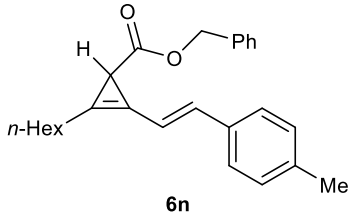


6m

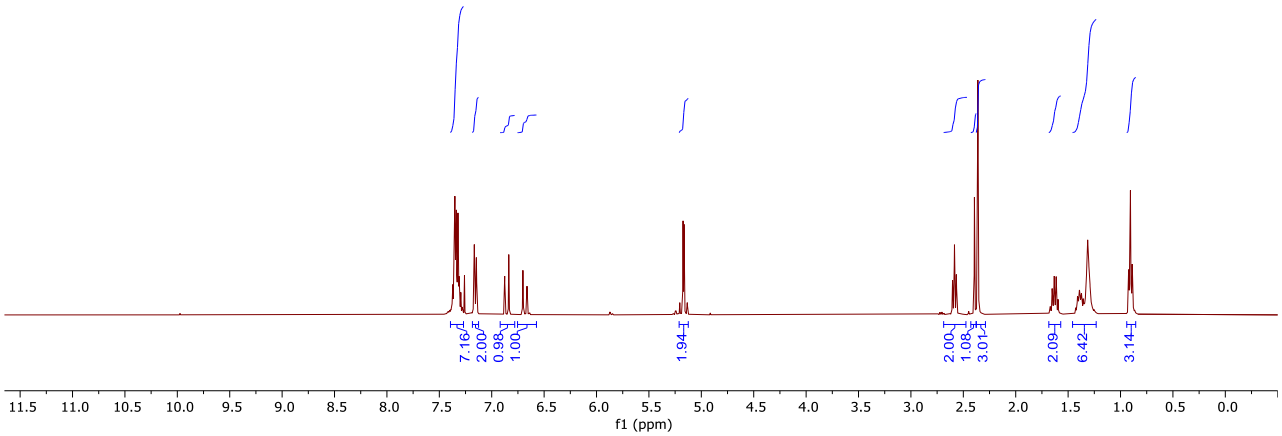


^{1}H NMR (400 MHz, $CDCl_3$) of 6n

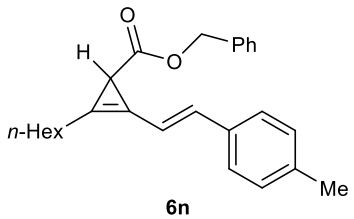




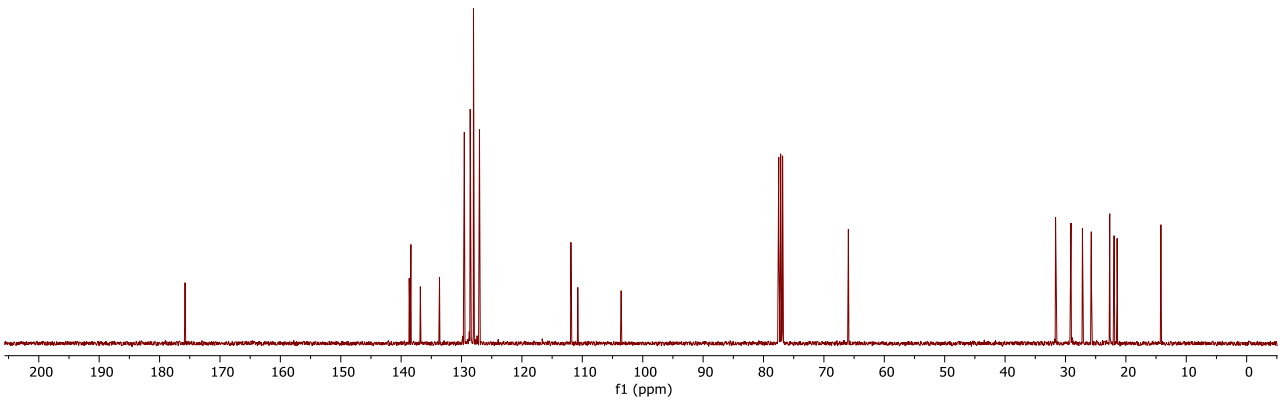
6n



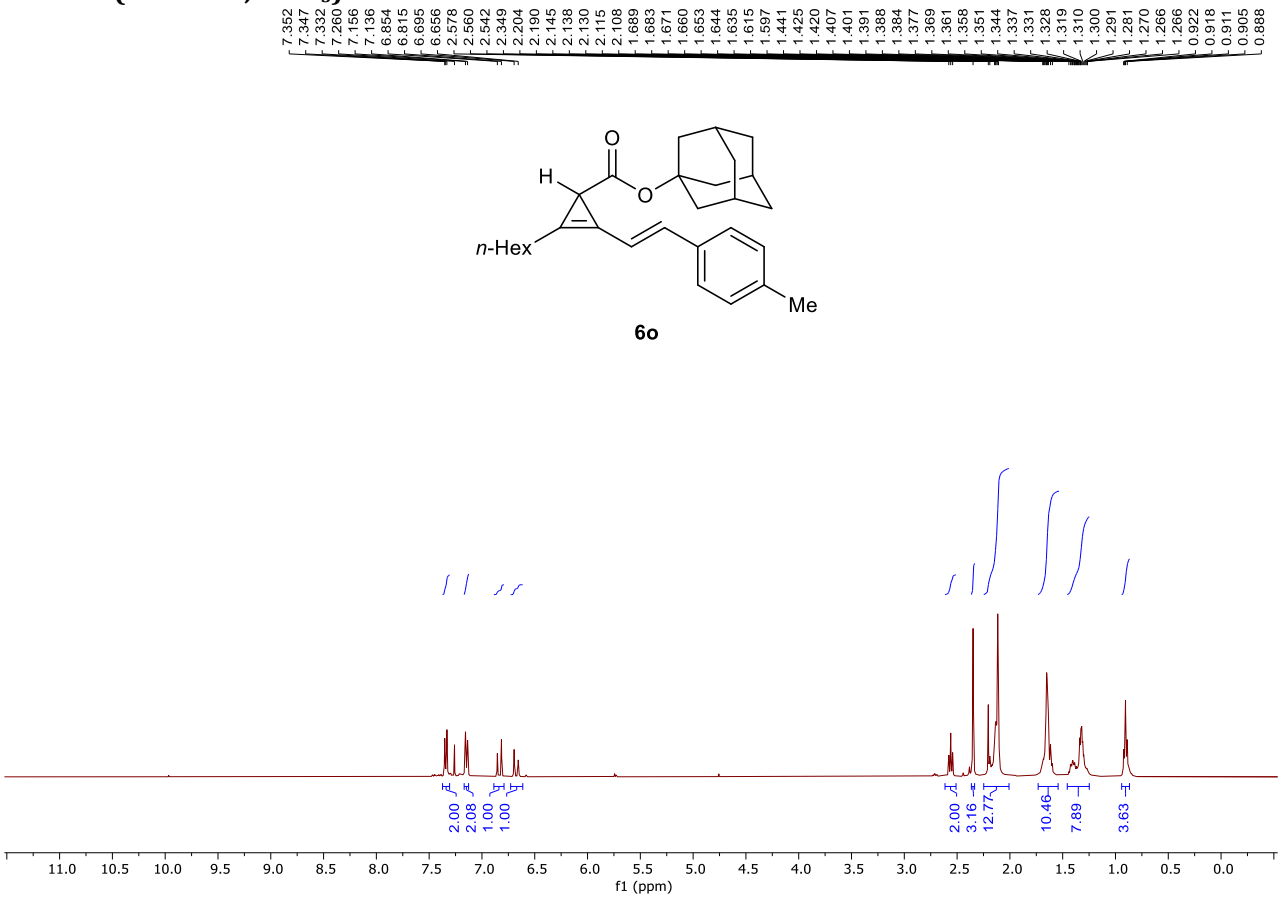
^{13}C NMR (101 MHz, $CDCl_3$) of 6n



6n

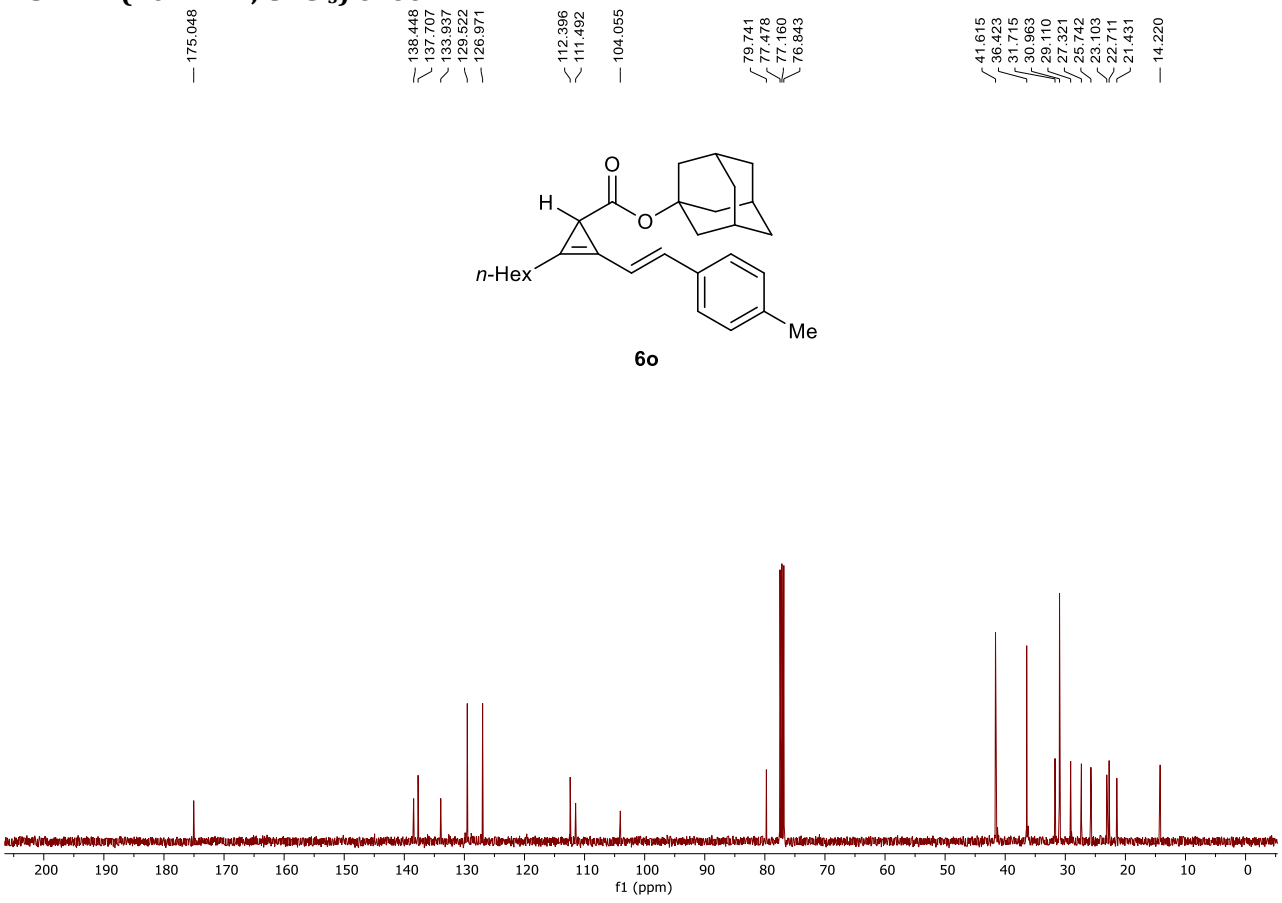


^{1}H NMR (400 MHz, $CDCl_3$) of 6o



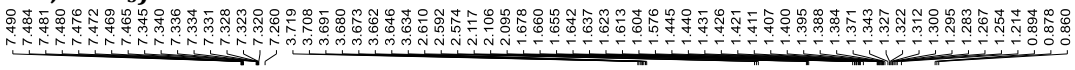
6o

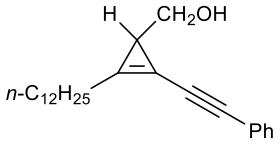
^{13}C NMR (101 MHz, $CDCl_3$) of 6o



6o

^{1}H NMR (400 MHz, $CDCl_3$) of 7





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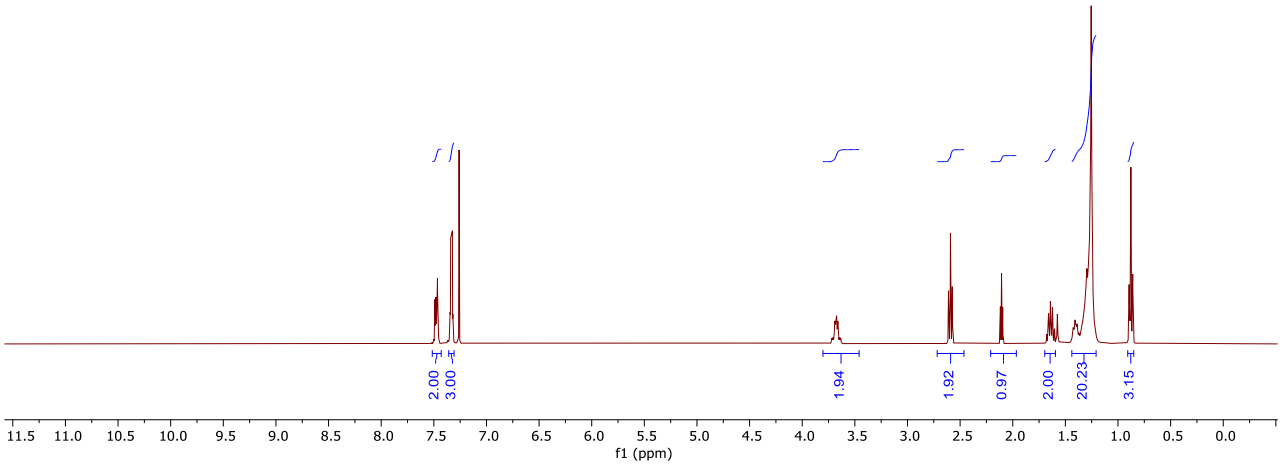
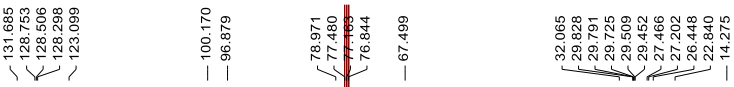
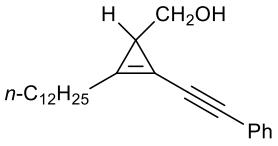


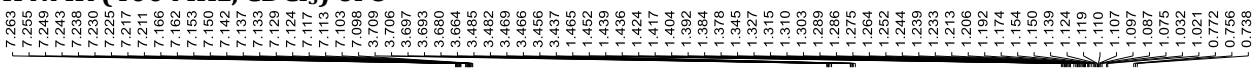
^{13}C NMR (101 MHz, $CDCl_3$) of 7

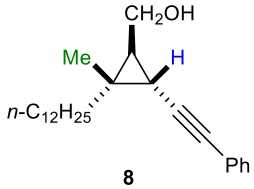




7

^{1}H NMR (400 MHz, $CDCl_3$) of 8





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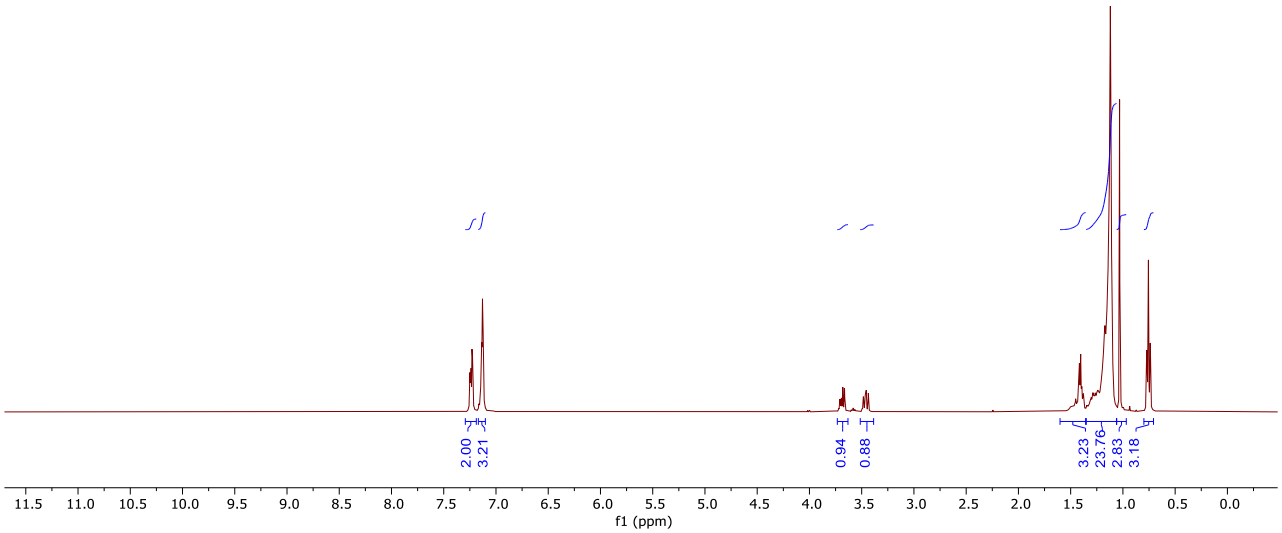
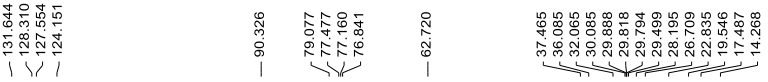
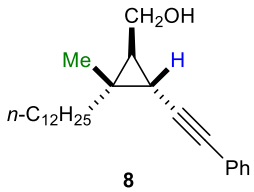


^{13}C NMR (101 MHz, $CDCl_3$) of 8





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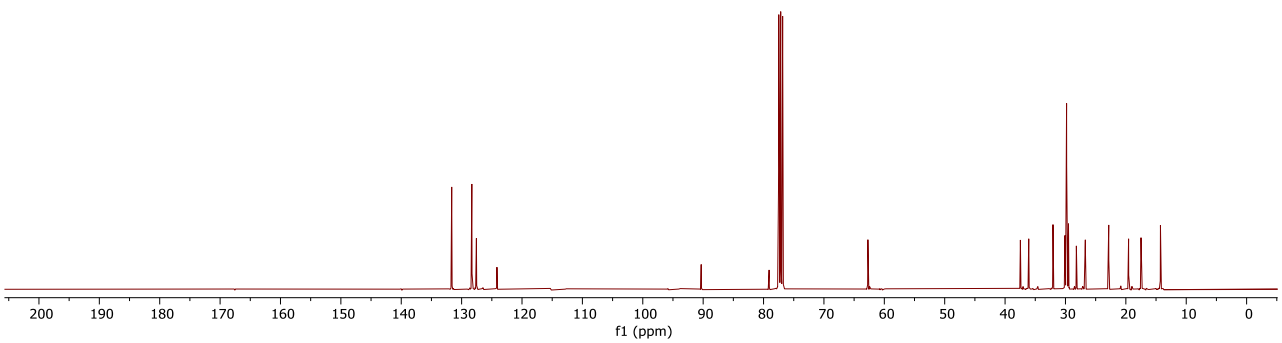
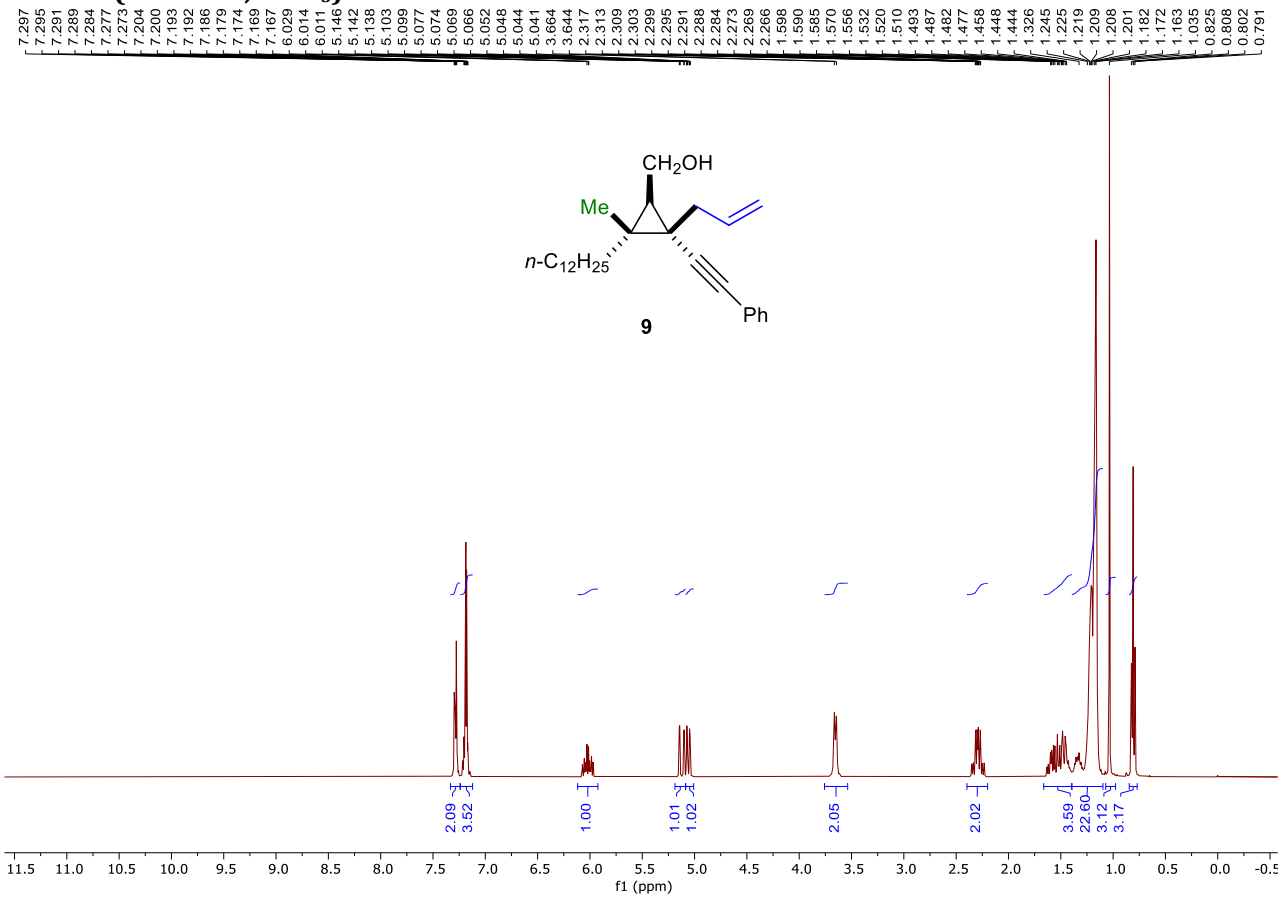
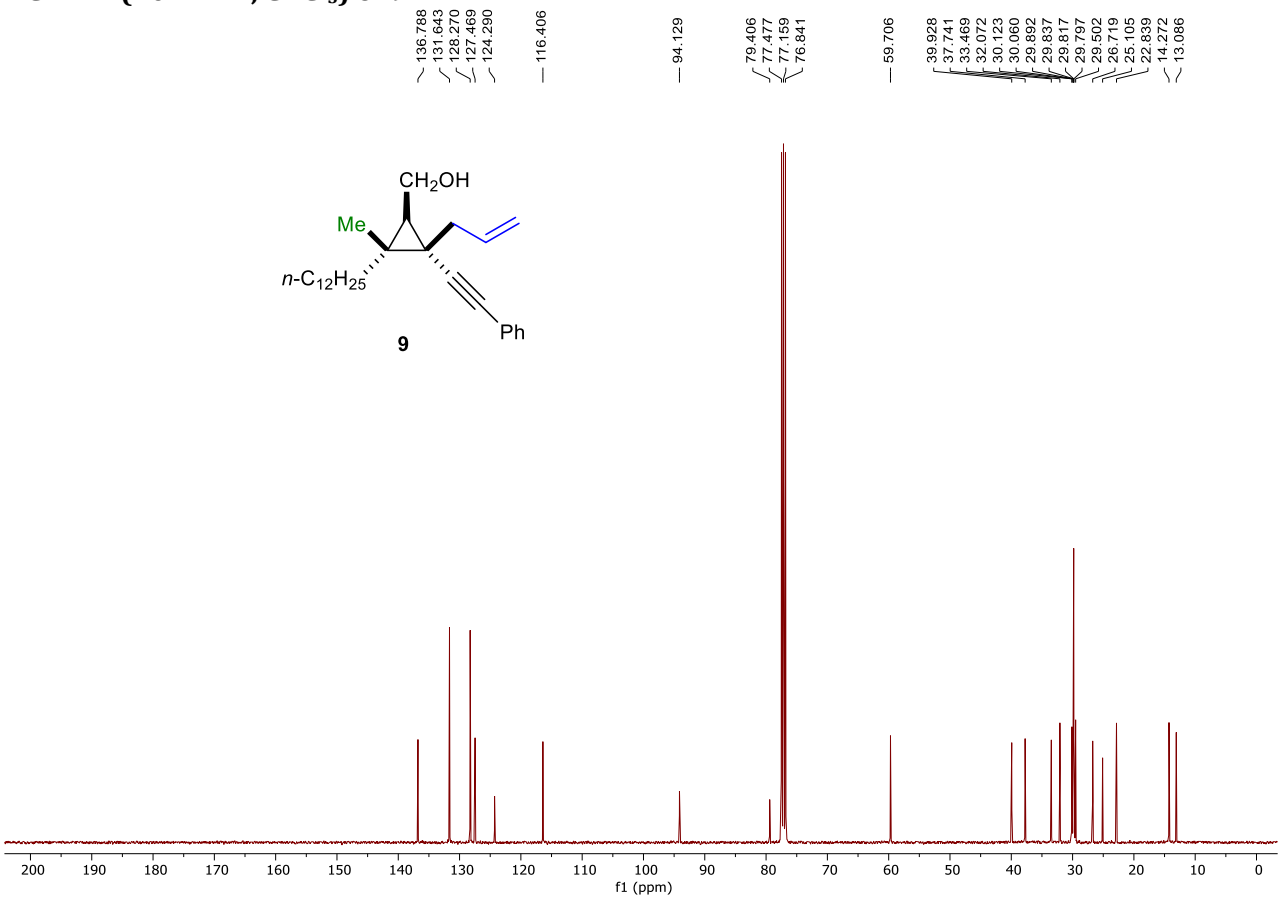


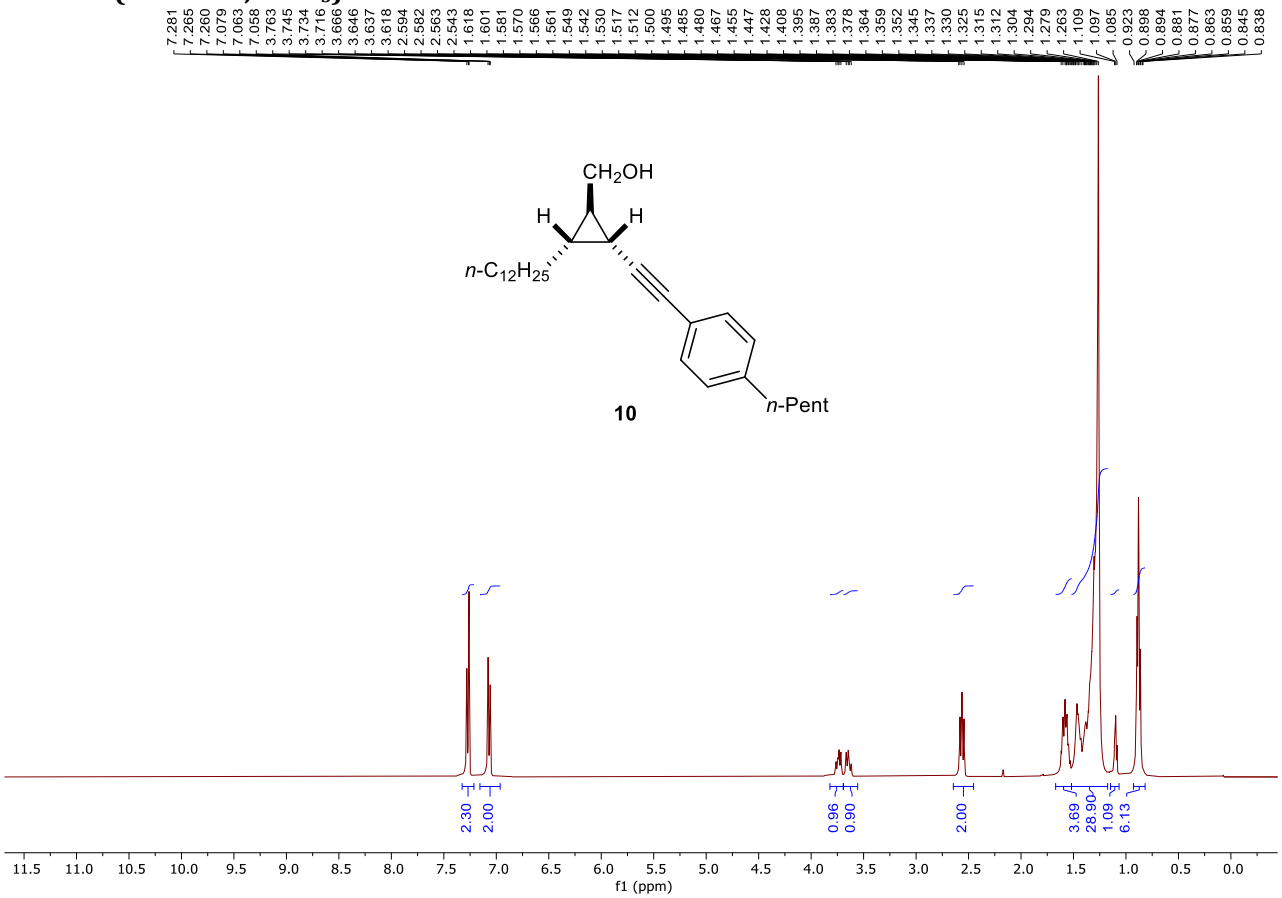
^{1}H NMR (400 MHz, $CDCl_3$) of 9



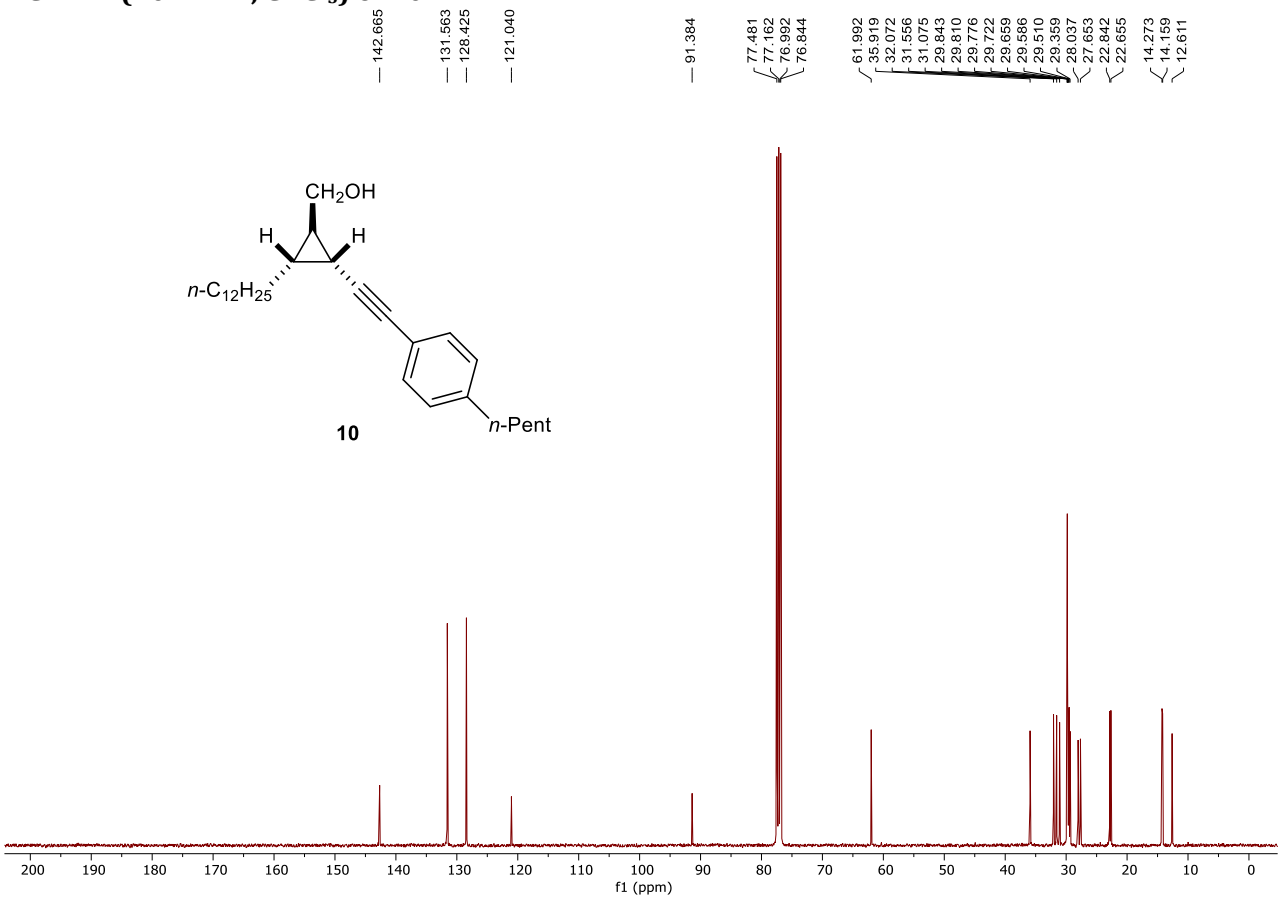
^{13}C NMR (101 MHz, $CDCl_3$) of 9



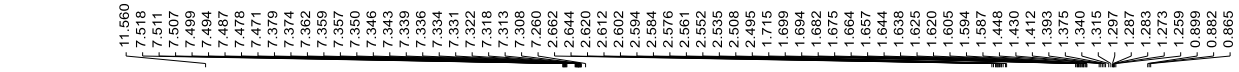
^{1}H NMR (400 MHz, $CDCl_3$) of 10

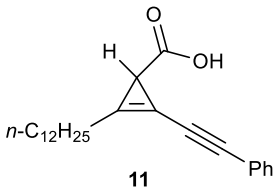


^{13}C NMR (101 MHz, $CDCl_3$) of 10



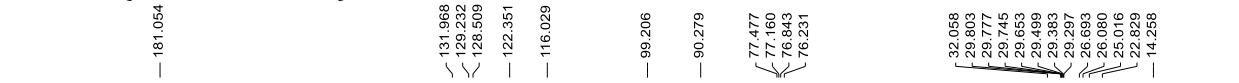
^{1}H NMR (400 MHz, $CDCl_3$) of 11

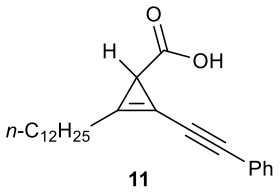




11

^{13}C NMR (101 MHz, $CDCl_3$) of 11





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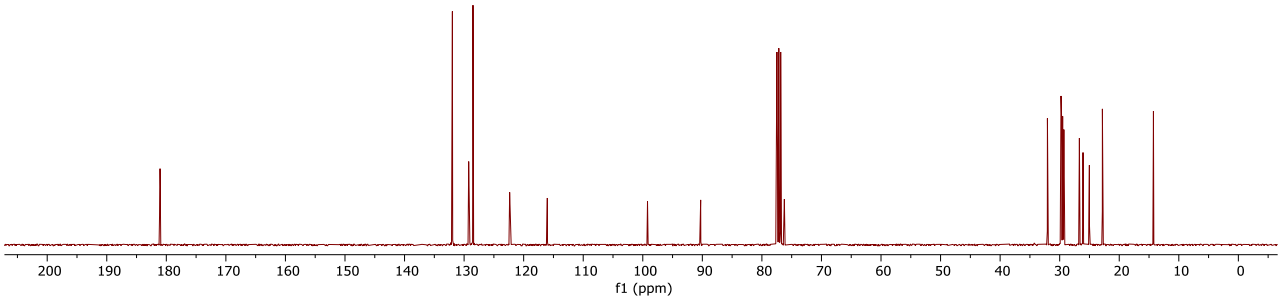
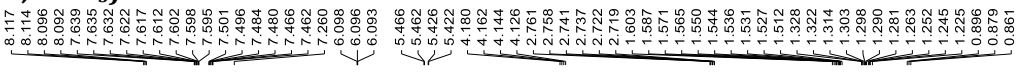
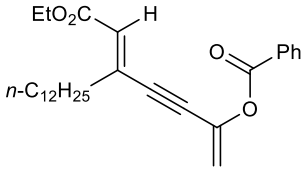


^{1}H NMR (400 MHz, $CDCl_3$) of 12





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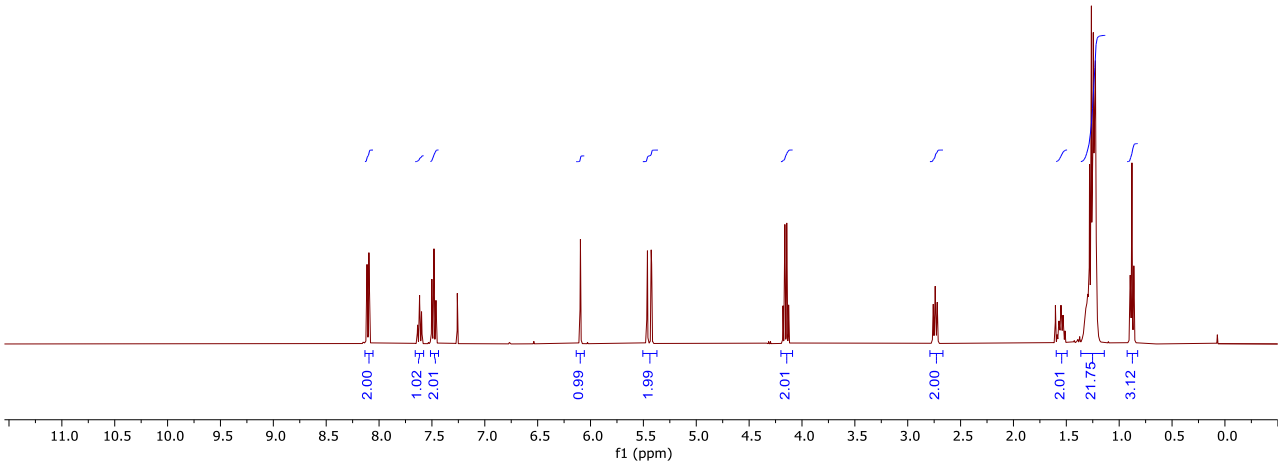
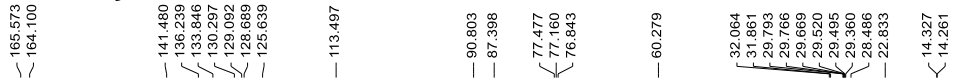
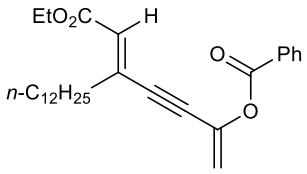


^{13}C NMR (101 MHz, $CDCl_3$) of 12





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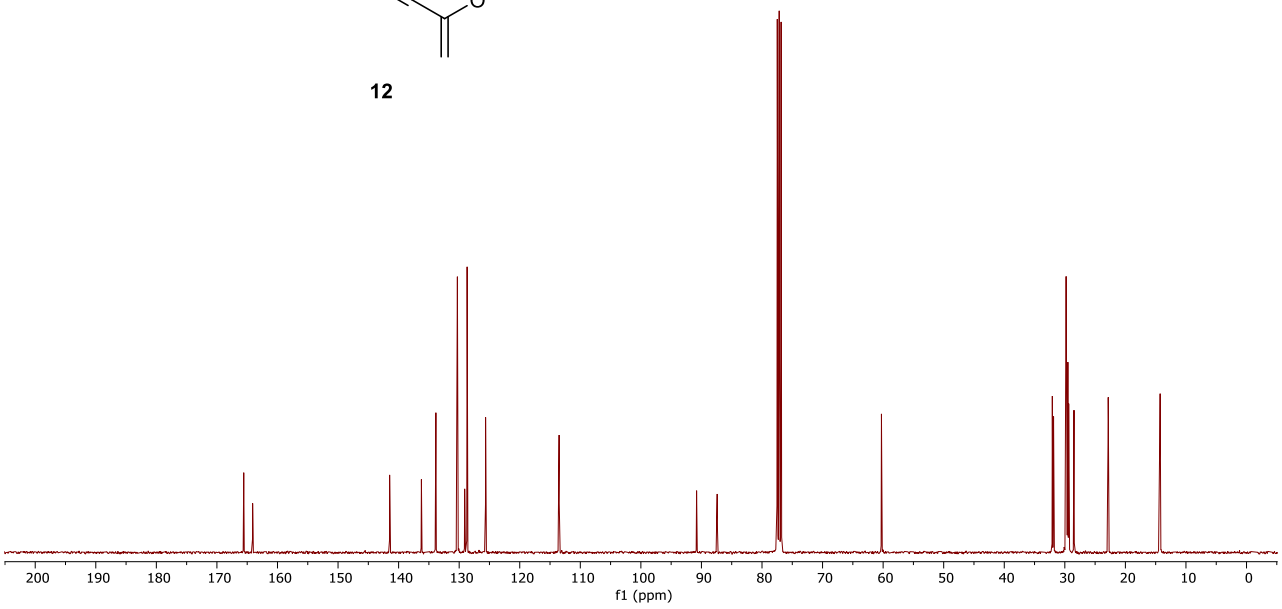
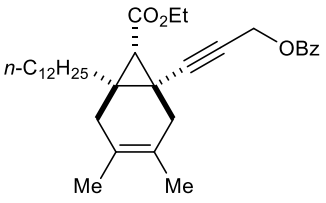
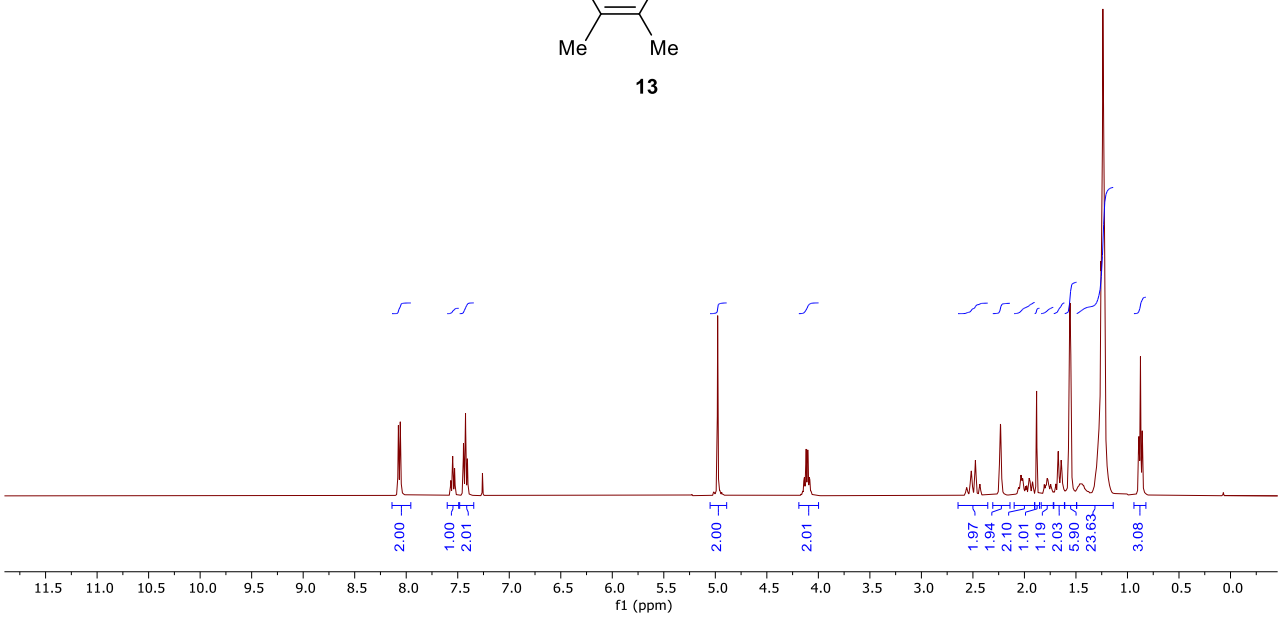


^{1}H NMR (400 MHz, $CDCl_3$) of 13

8.079 8.075 8.058 8.054 7.572 7.568 7.564 7.549 7.544 7.534 7.531 7.527 7.444 7.425 7.410 7.406 7.260 4.977 4.141 4.136 4.133 4.124 4.118 4.106 4.100 4.088 4.082 2.516 2.476 2.432 2.233 2.057 2.034 2.016 1.990 1.978 1.961 1.954 1.945 1.924 1.917 1.882 1.808 1.794 1.780 1.771 1.745 1.737 1.696 1.692 1.672 1.643 1.565 1.558 1.551 1.479 1.465 1.451 1.440 1.432 1.426 1.422 1.310 1.293 1.275 1.275 1.257 1.249 1.239 1.229 1.221 1.195 1.175 0.890 0.874 0.856

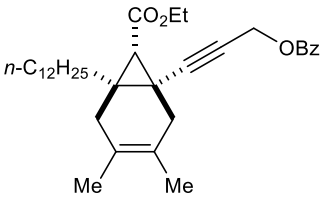


13



^{13}C NMR (101 MHz, $CDCl_3$) of 13

170.159 166.034 133.145 130.016 129.898 128.421 122.085 121.522 86.953 77.477 77.159 76.842 76.214 60.243 53.628 37.686 35.973 34.883 32.049 30.586 30.228 30.081 29.860 29.841 29.801 29.784 29.486 26.648 26.490 22.813 19.139 18.721 14.451 14.241



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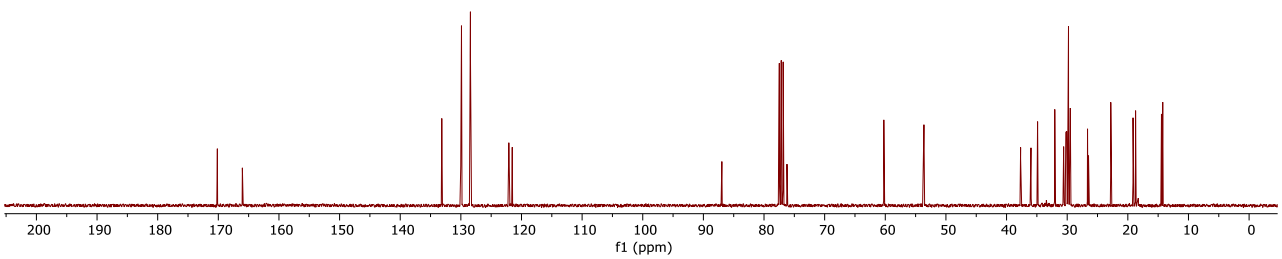

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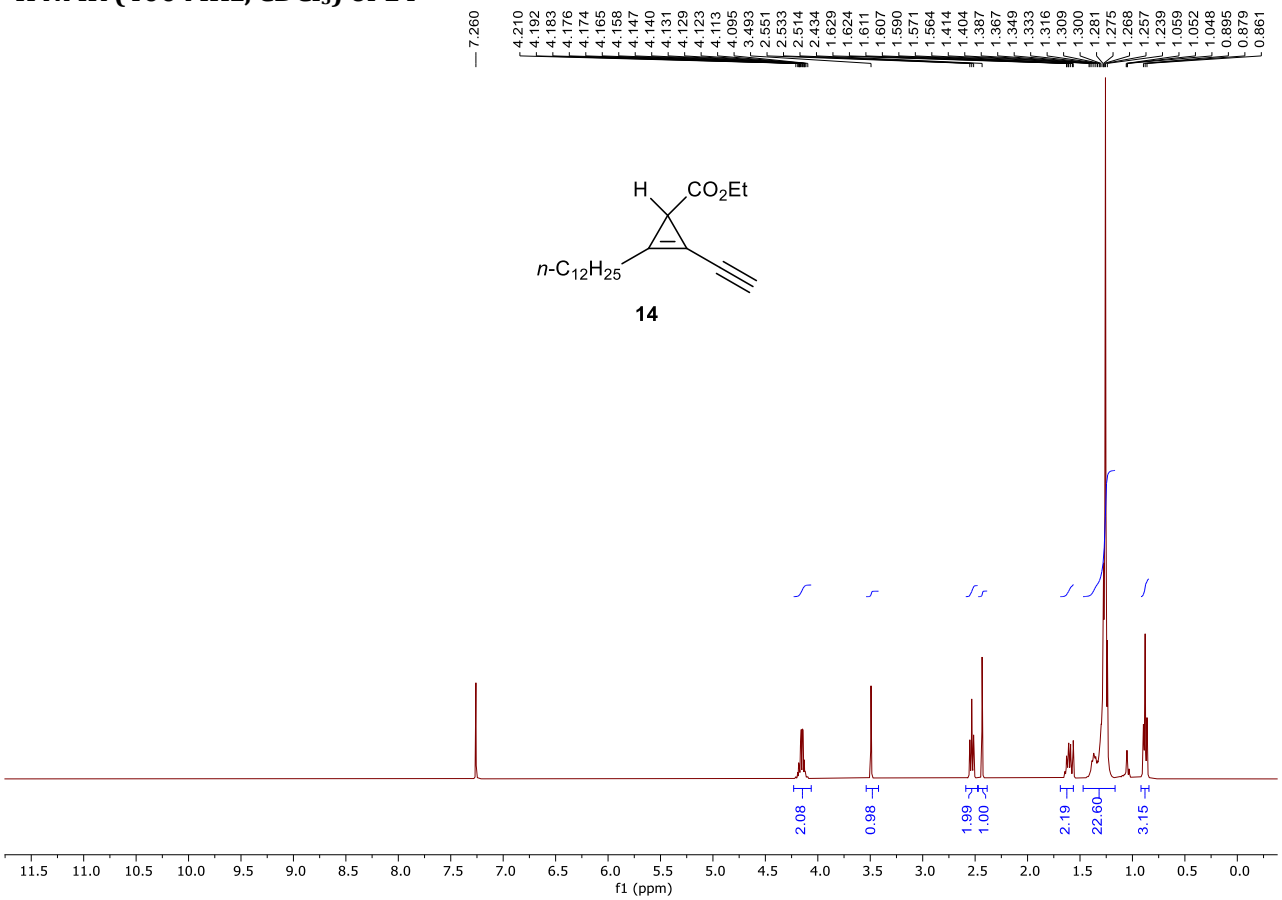

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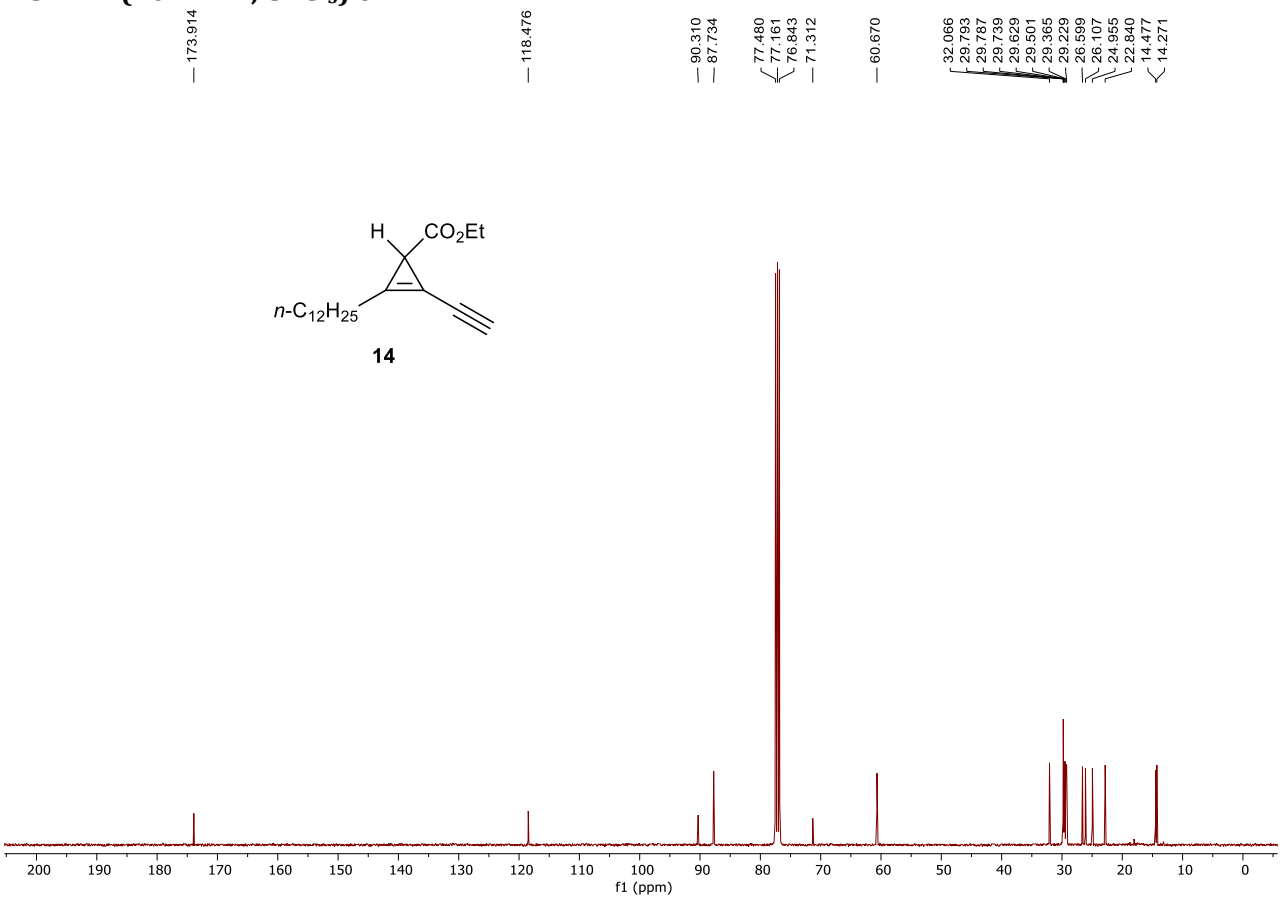

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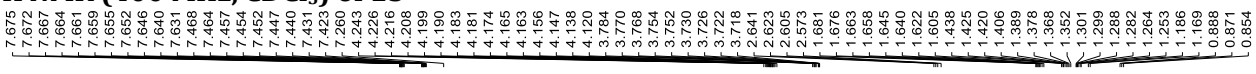

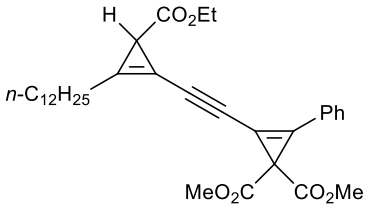

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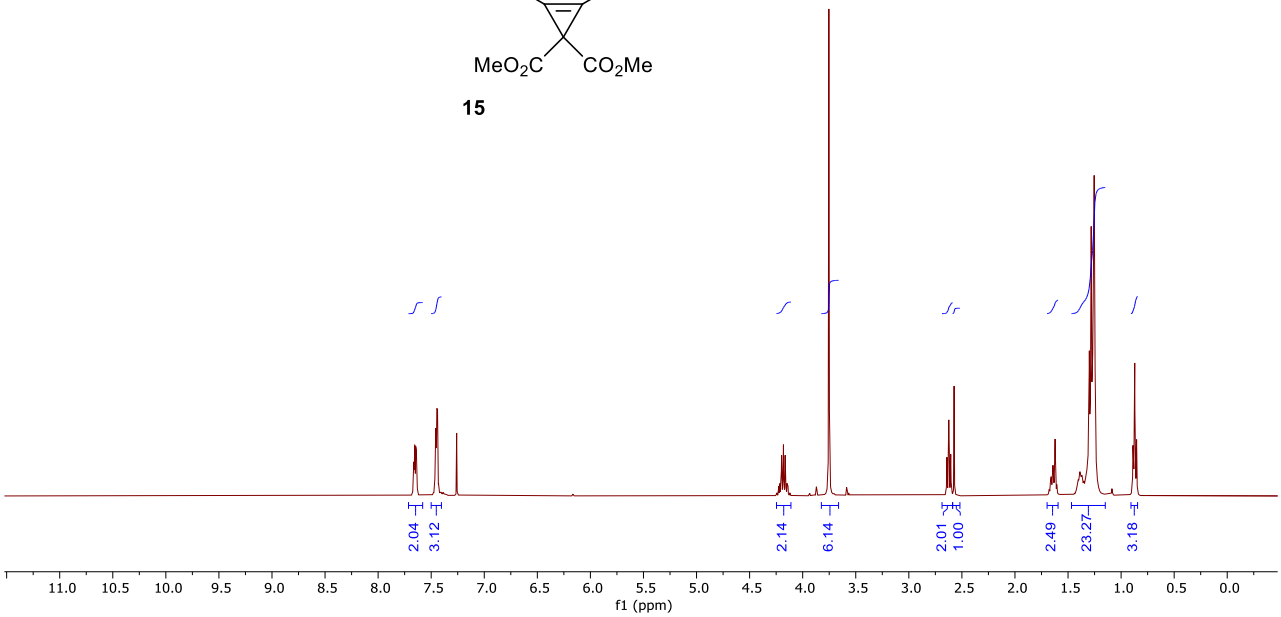

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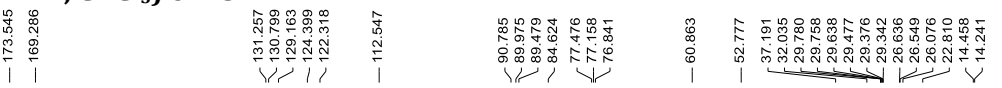

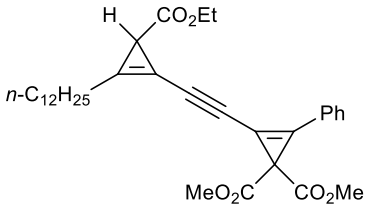

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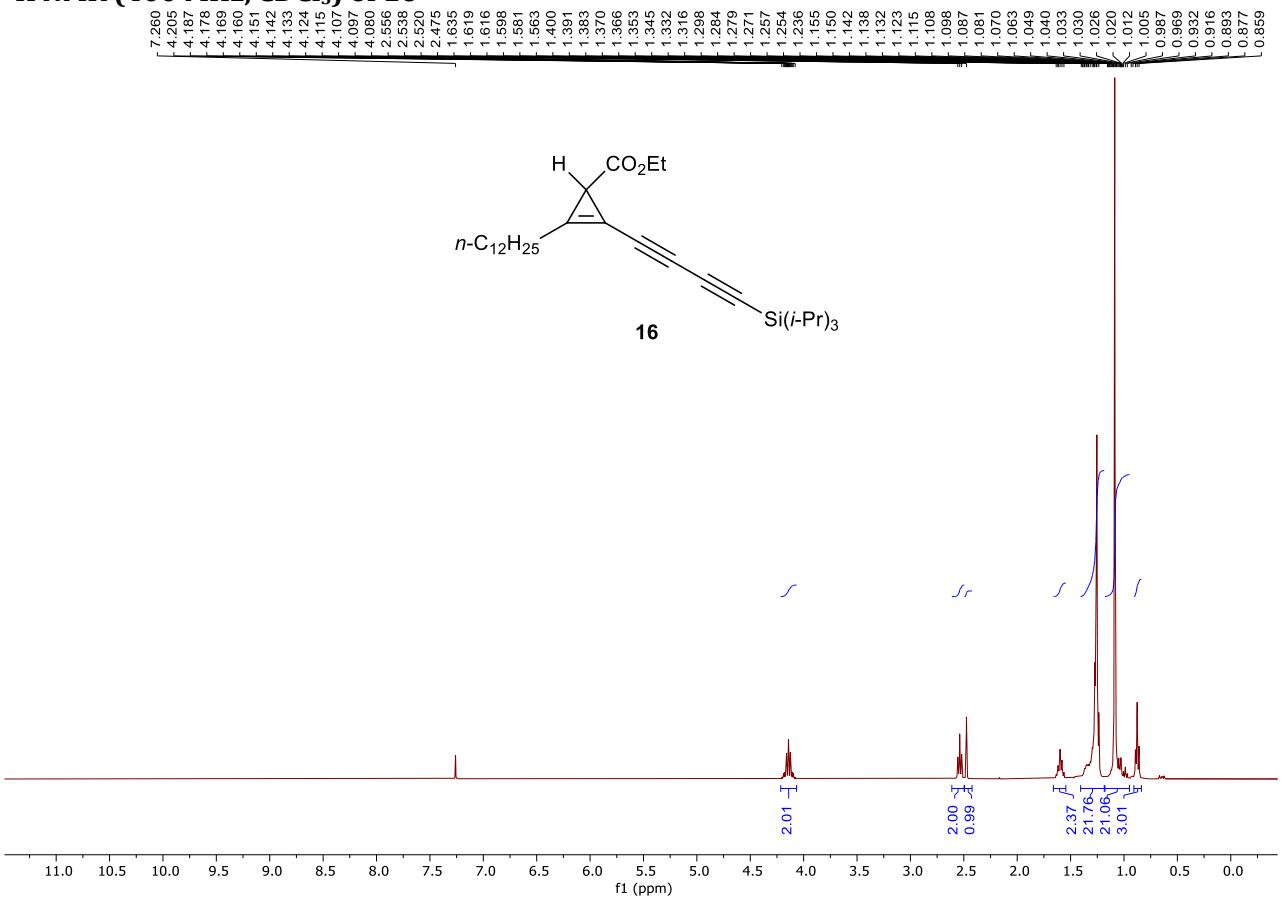
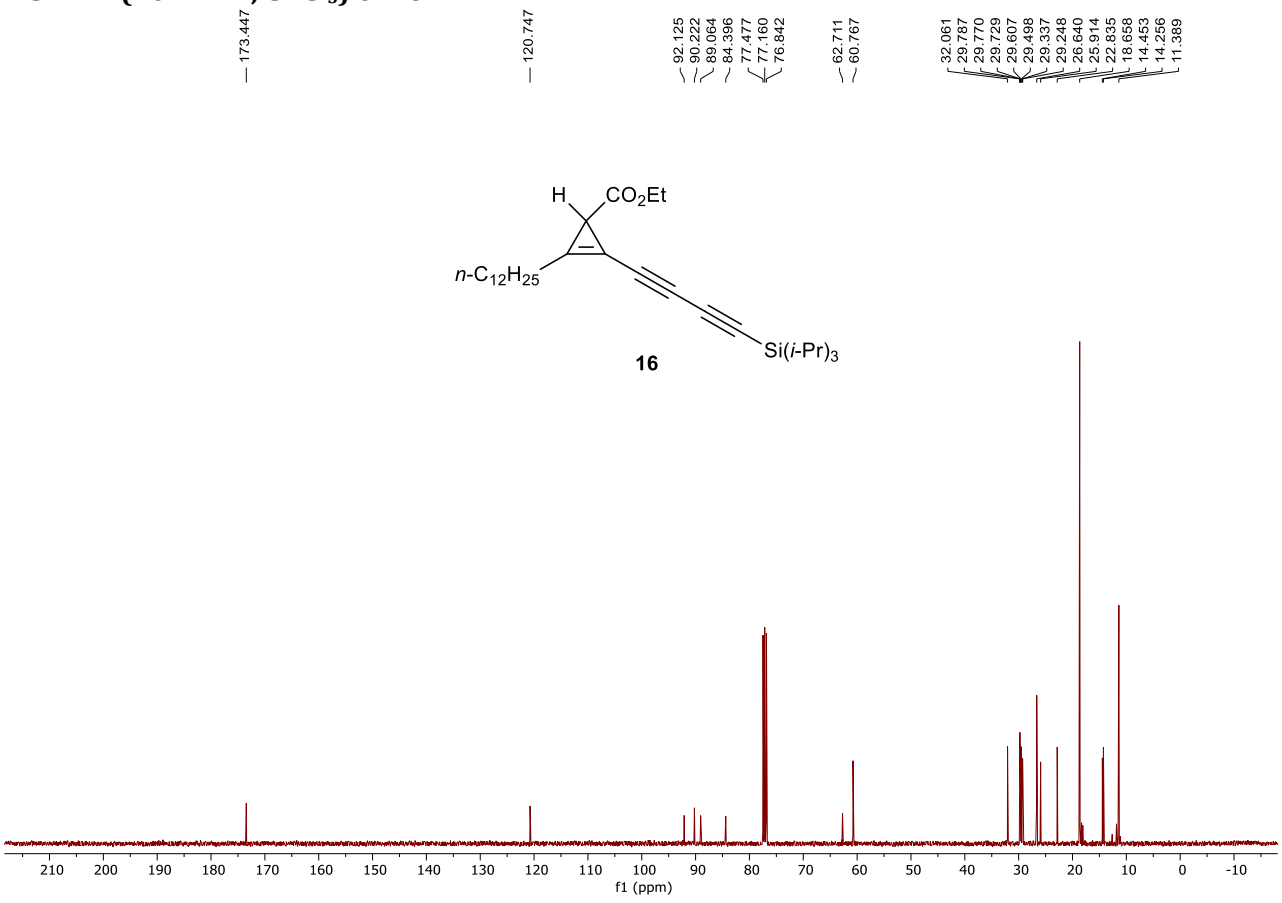
^{1}H NMR (400 MHz, $CDCl_3$) of 16



^{13}C NMR (101 MHz, $CDCl_3$) of 16



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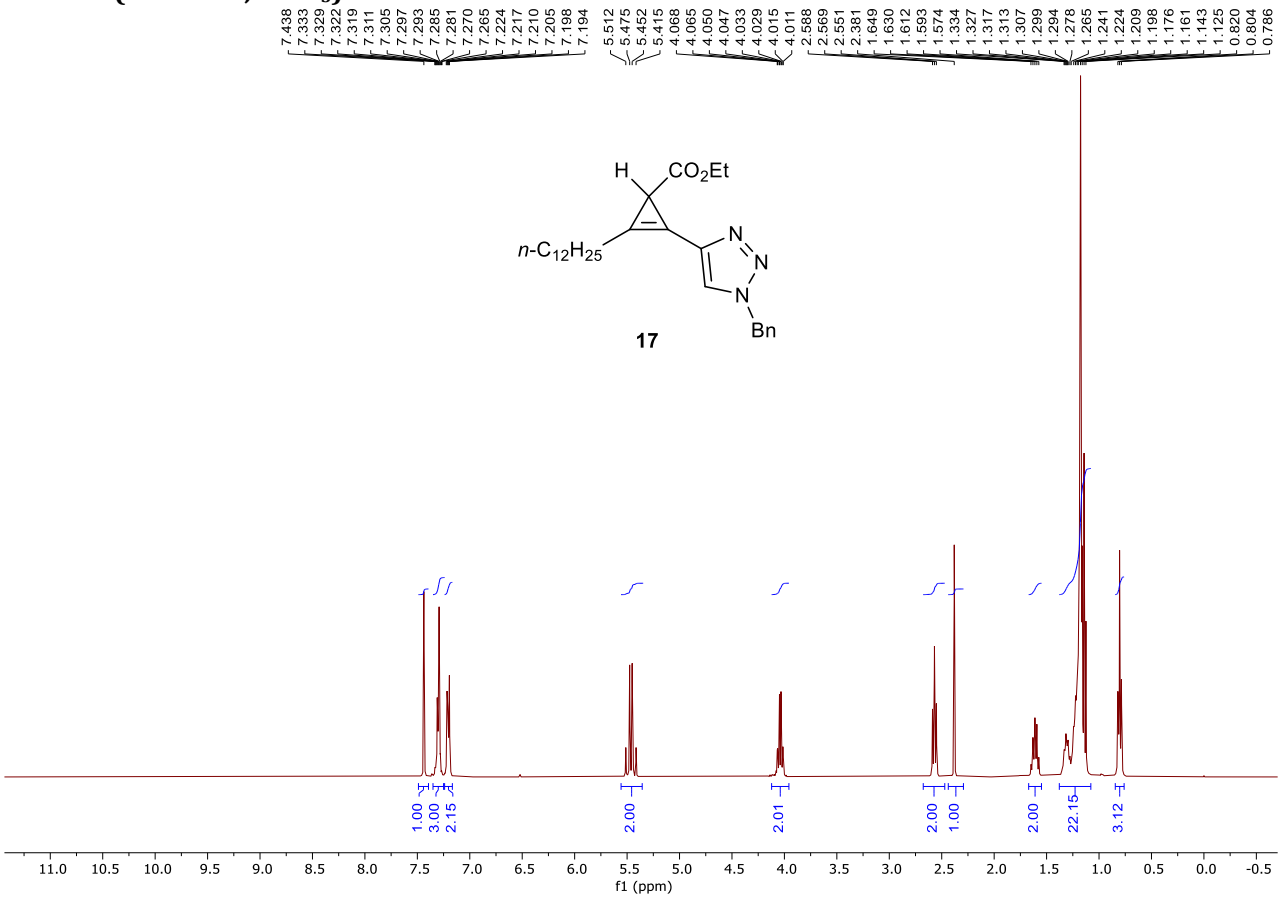

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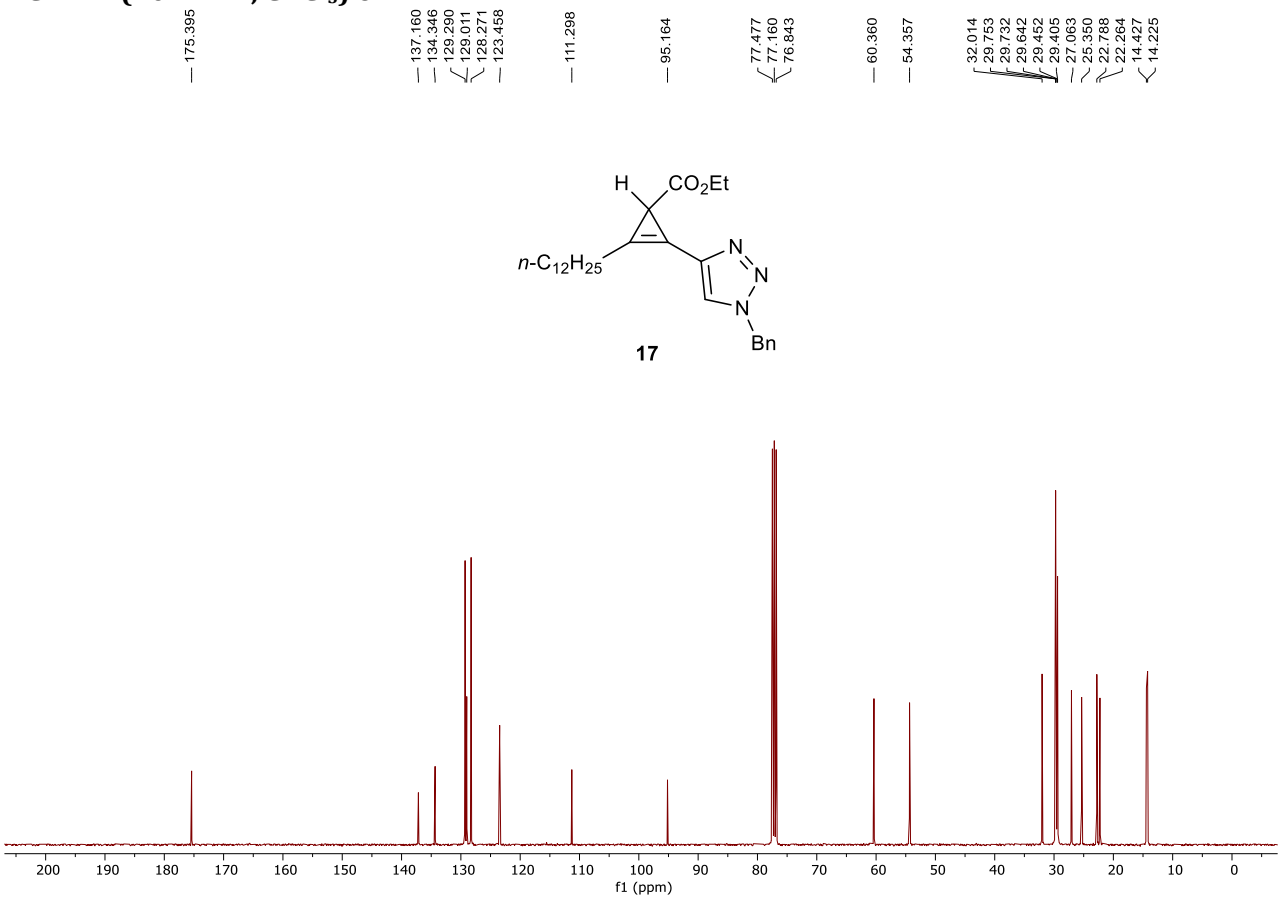
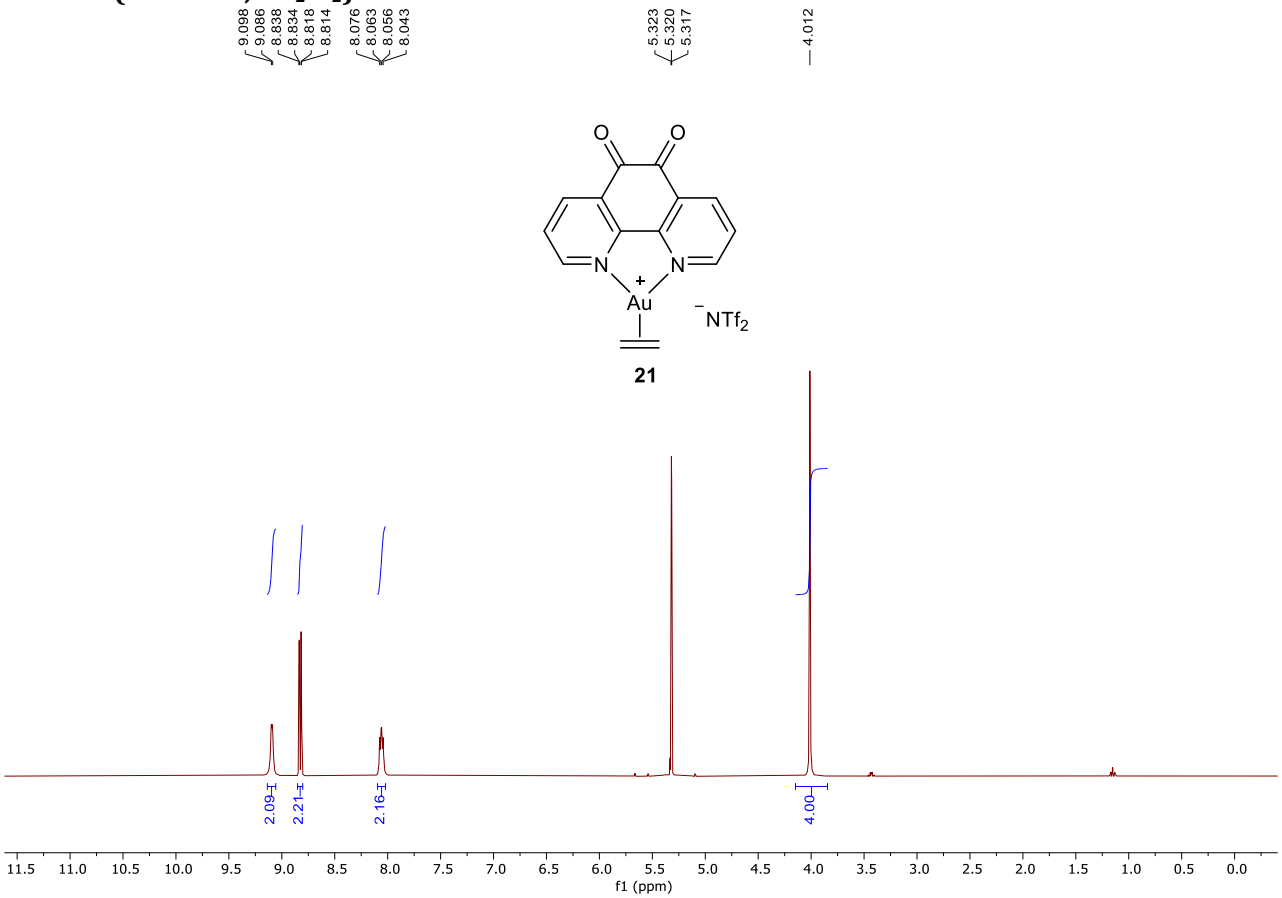
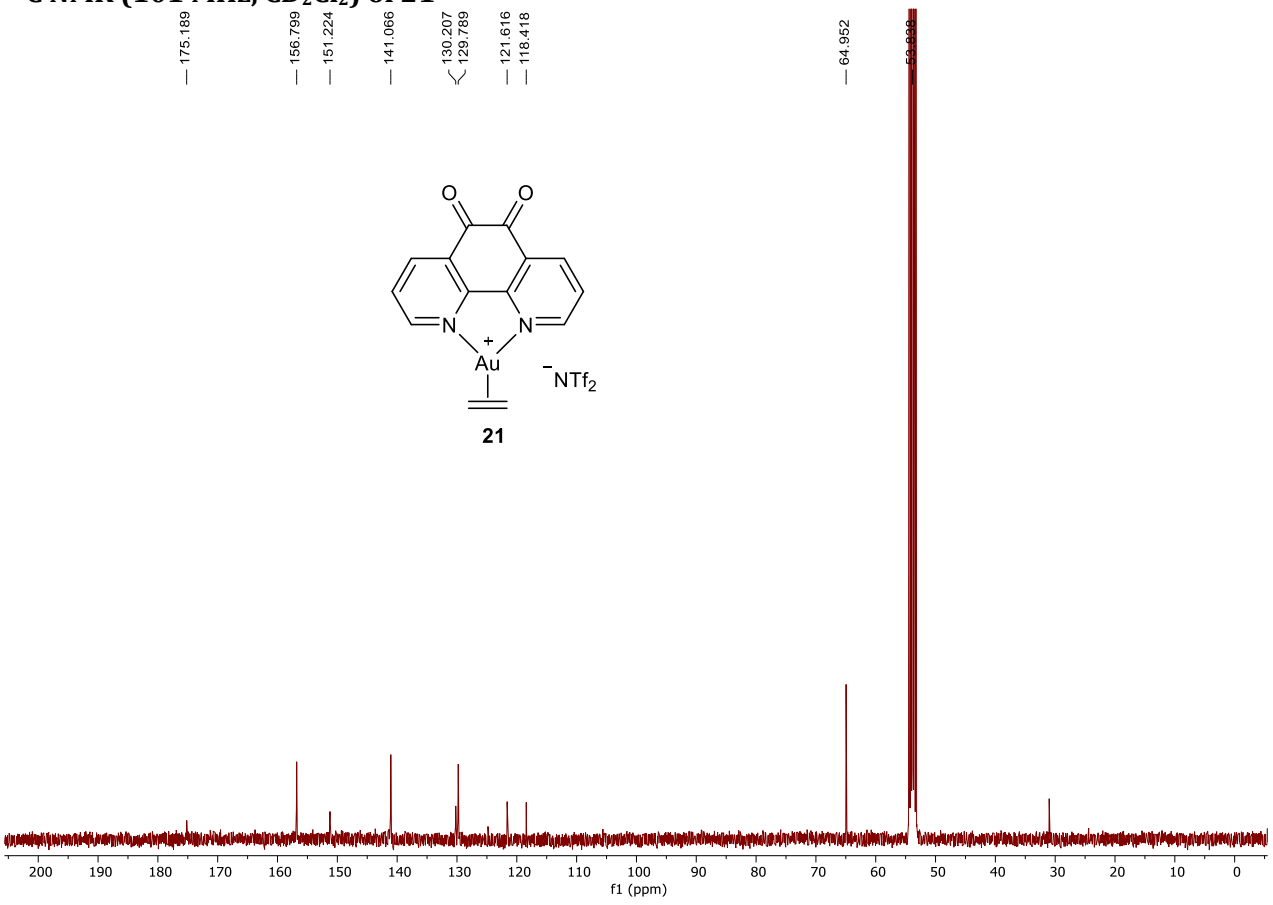


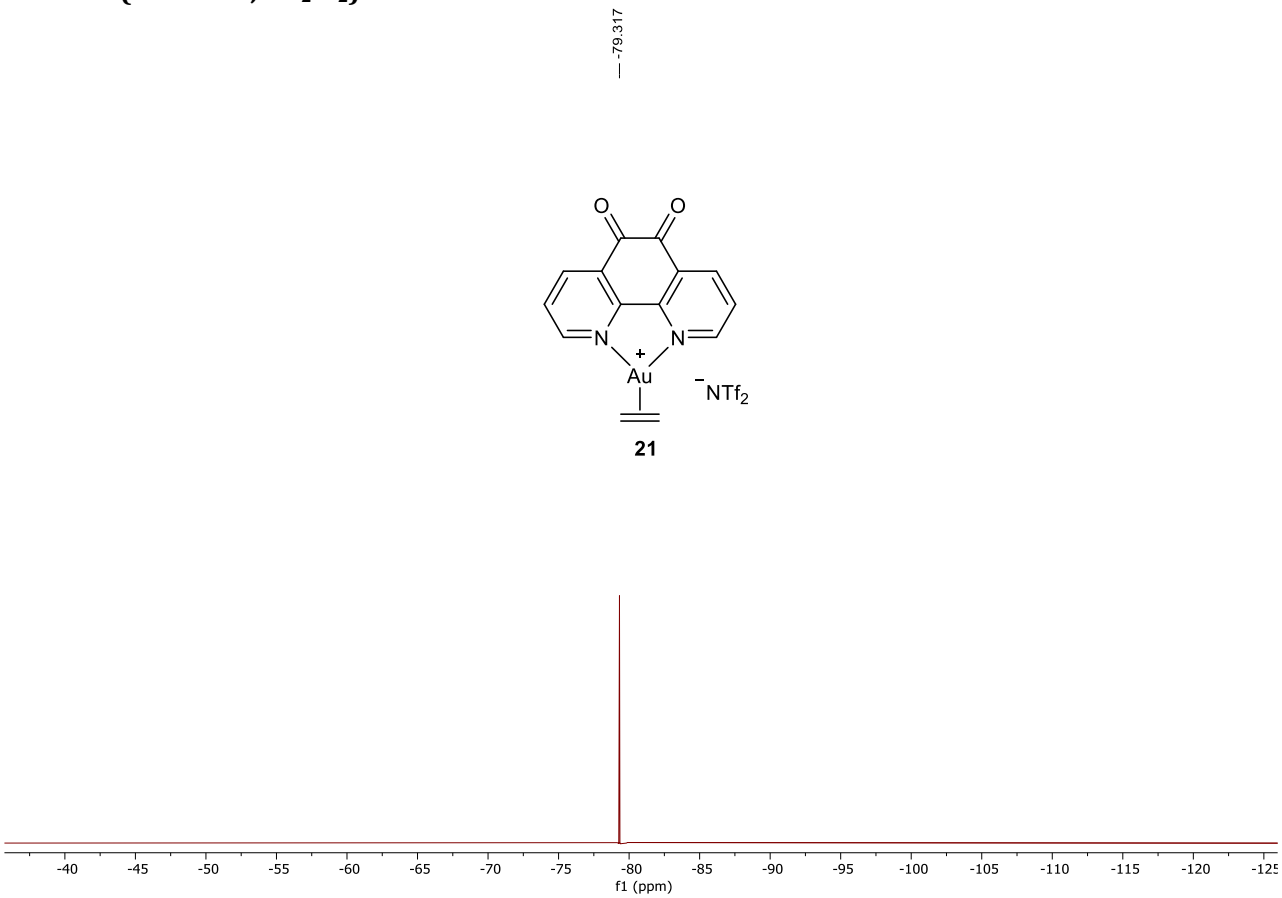
^{1}H NMR (400 MHz, CD_2Cl_2) of 21



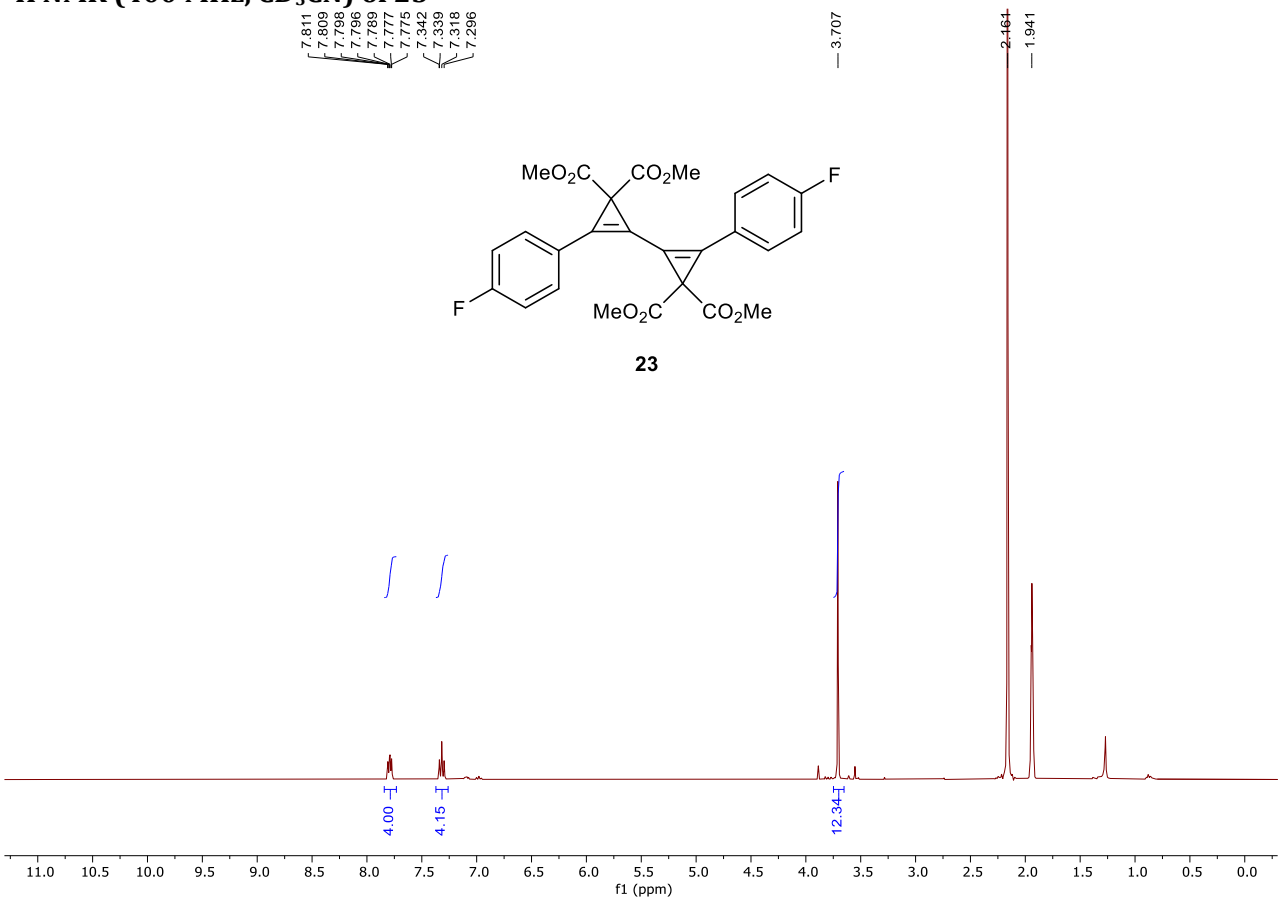
^{13}C NMR (101 MHz, CD_2Cl_2) of 21



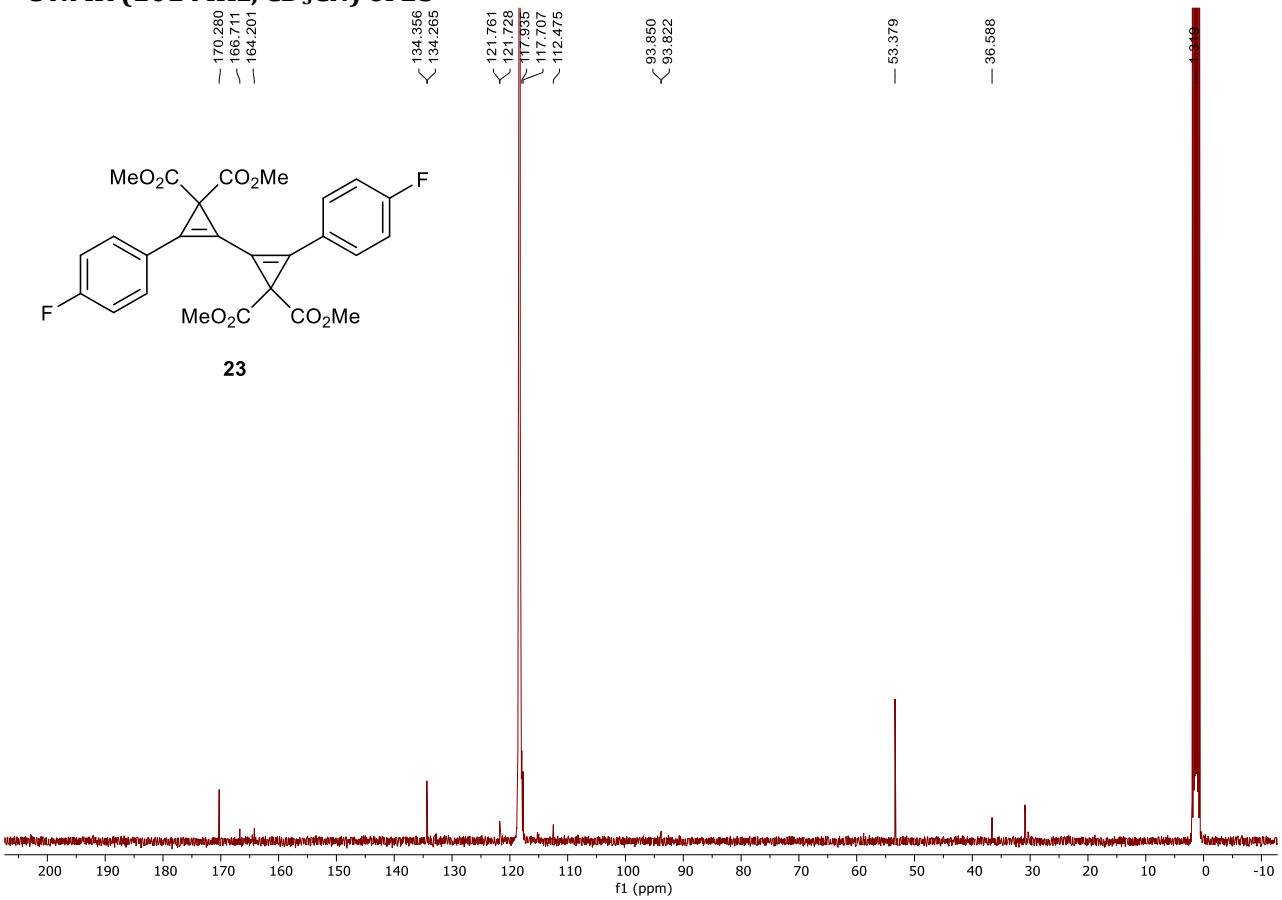
^{19}F NMR (376 MHz, CD_2Cl_2) of 21



^{1}H NMR (400 MHz, CD_3CN) of 23



^{13}C NMR (101 MHz, CD_3CN) of 23



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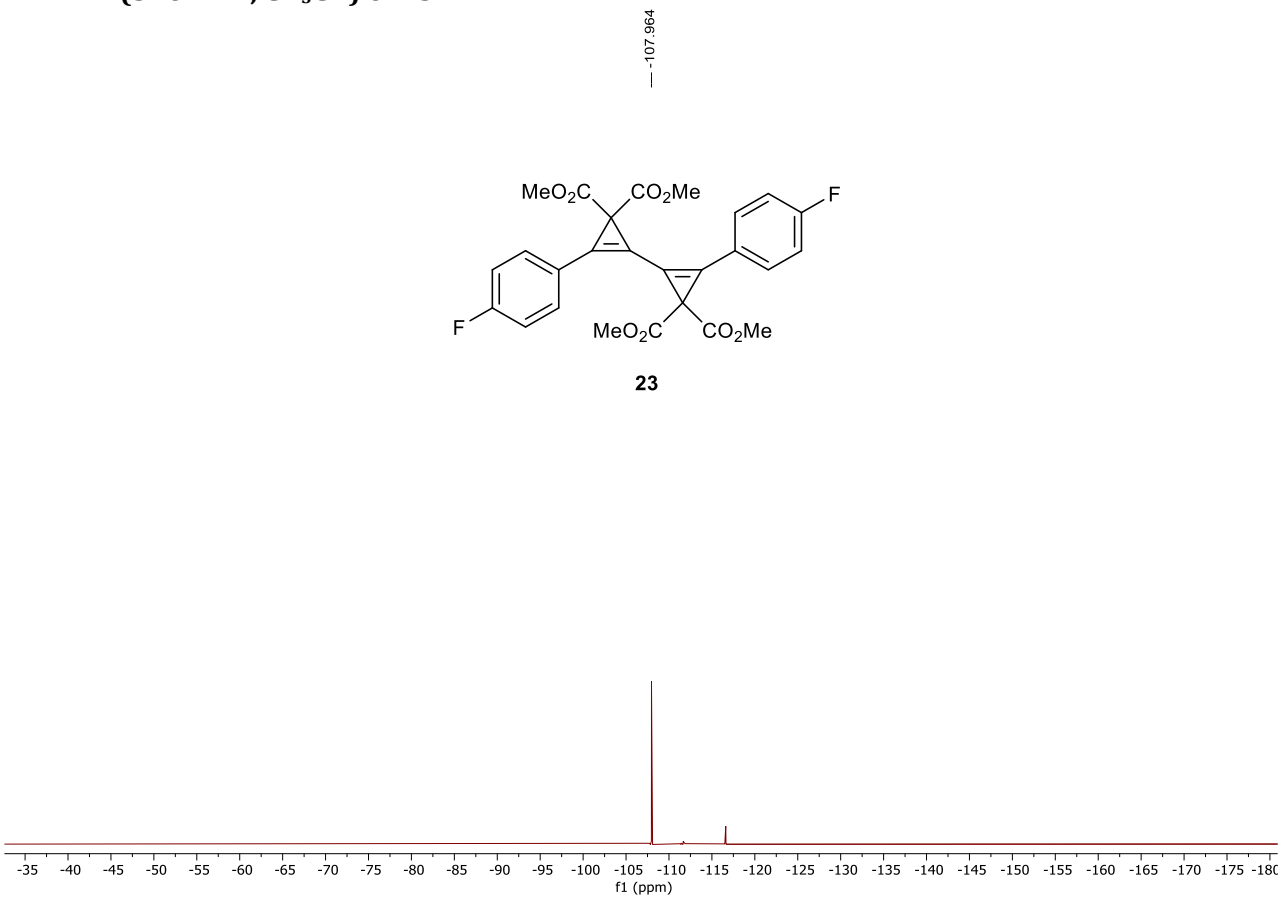
^{19}F NMR (376 MHz, CD_3CN) of 23



23

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