Tosyloxybenziodoxolone: A Platform for Performing the Umpolung of Alkynes in One-pot Transformations

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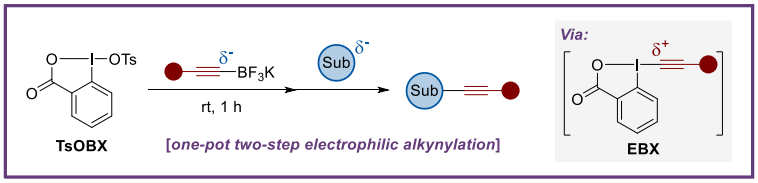


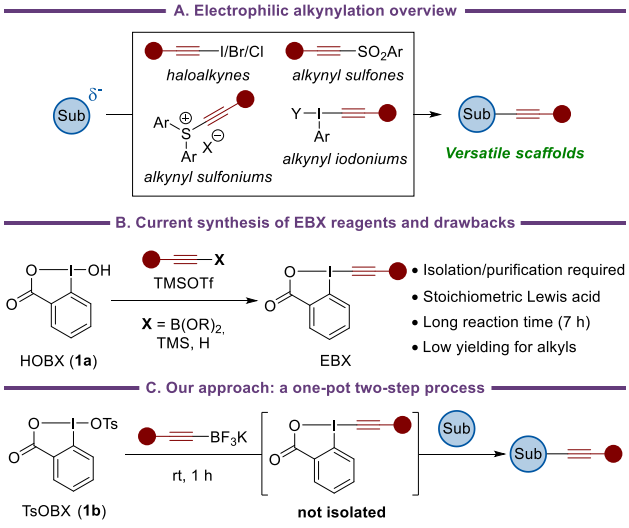
ABSTRACT: Ethynylbenziodoxolones (EBXs) are commonly encountered reagents for the electrophilic alkynylation of nucleophiles. Herein, we report a one-pot two-step process for EBX generation and their direct application in substrate functionalization. Our approach enables to bypass the originally mandatory isolation and purification of the reagents, resulting in a more efficient synthesis. We could apply this process to seven different transformations involving both two- and one- electron nucleophiles to obtain a large variety of alkynylated products.

Alkynes are important motifs that can be found in bioactive molecules, inducing rigidity and lipophilicity,[1] in highly conjugated systems such as semiconductors[2] and in valuable building blocks for synthetic and medicinal chemistry. The carbon-carbon triple bond represents a versatile synthetic handle for further transformations such as cycloadditions, difunctionalizations, metathesis or reduction.[3] Transfer of an alkyne to a molecule usually takes place by a Sonogashira cross-coupling or by reaction of acetylides with an electrophilic functional group.[3b] Although these methods represent a straightforward pathway for the introduction of triple bonds, they are limited to alkyne introduction at an electrophilic position.

The reverse approach utilizing electrophilic alkynylation reagents enables further scaffold diversity by reaction with nucleophilic partners. This Umpolung approach requires pre-activation of the alkyne to make it a viable electrophile. Different classes of reagents have been developed: haloalkynes,[4] alkynyl sulfones,[5] alkynyl sulfoniums[6] and alkynyl iodoniums (Scheme 1A).[7] The latter were especially successful and allowed the development of multiple new transformations. In the last decade, Ethynylbenziodoxolones (EBXs) in particular have become reagents of choice due to their increased stability compared to the non-cyclic alkynyl iodonium salts.[8] They can be used under a broader variety of conditions involving transition metals[9] and free radicals,[10] which were previously not well tolerated.

EBXs are most often synthesized from HOBX (**1a**) and the corresponding silyl alkynes under strong Lewis acidic conditions (Scheme 1B).[11] Higher yields can be obtained using alkynyl boronic esters, but the instability and low yielding synthesis of these compounds makes them less practical. More recently, Olofsson and co-workers developed a one-pot synthesis of the reagents starting from 2-iodobenzoic acid using *m*-CPBA and *p*-TsOH, but relying on the use of alkynyl boronic esters in a trifluoroethanol/dichloromethane mixture to get high yields.[12]

Scheme 1. (A) Electrophilic alkyne sources; (B) EBX synthesis; (C) Our one-pot two-step approach.



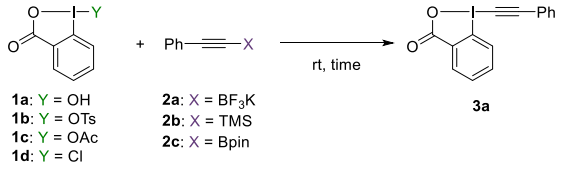
In this context, modification of the alkyne substituent is tedious due to the necessity to isolate and purify the reagent for each modification. Especially non-crystalline alkyl-substituted EBXs are purified by column chromatography, which usually leads to a substantial loss of material. This constitutes a major obstacle to the broad application of EBXs in synthetic chemistry. A more efficient method giving EBXs directly with high purity is therefore highly desirable. In addition, this would open the way to subsequent alkynylation of the substrates in a single pot. However, such process will not only require high purity of the EBXs. The stoichiometric amount of strong Lewis acid used and the formation of by-products are further issues that could prevent the subsequent alkynylation step. In addition, tolerance

to different reaction conditions and solvents would be important to enable diverse applications. For a successful one-pot process, EBX formation would therefore need to be additive-free, high yielding, fast and tolerant to different solvents.

Herein, we report the reaction of TsOBX (**1b**) and stable and easy to handle alkynyltrifluoroborates for the fast and highly efficient formation of EBX reagents without using Lewis acids (Scheme 1C). The reagents are generated in high purity without the need for purification. This allowed us to develop efficient one-pot processes involving both polar and radical methods, affording a variety of alkynylated products starting from the same hypervalent iodine precursor.

In the search for an alkyne precursor more nucleophilic than silyl alkynes, but without the stability issues associated with alkynyl boronic esters, we became interested in using alkynyltrifluoroborate salts. This class of boron species has been demonstrated to be less sensitive than boronic acids and boronic esters.[13] In the context of hypervalent iodine reagents synthesis, they have been used once for accessing alkynyliodonium salts starting from *p*-iodotoluene difluoride, but the yield of this transformation was highly dependent on the alkyne substituent.[14] We started our investigation by using potassium phenylethynyltrifluoborate (**2a**) in acetonitrile with 10% of HFIP to help the solubilization of the hypervalent iodine reagent (HIR). We examined different substituents on the iodine centre with increasing leaving group ability (Table 1, entries 1-3). Having a hydroxide (**1a**), acetate (**1c**) or chloride (**1d**) resulted in only trace amount of the desired product **3a**.

Table 1. Optimization of the formation of EBX 3a.[a]



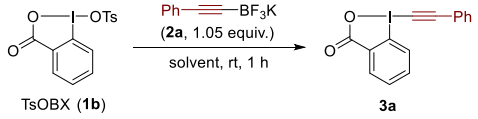
entry	HIR	alkyne (equiv.)	solvent	time (h)	yield[b]
1	**1a**	**2a** (1.5)	CH_3CN/HFIP (9:1)	16	<5%
2	**1c**	**2a** (1.5)	CH_3CN/HFIP (9:1)	16	<5%
3	**1d**	**2a** (1.5)	CH_3CN/HFIP (9:1)	16	<5%
4	**1b**	**2a** (1.5)	CH_3CN/HFIP (9:1)	16	86%
5	**1b**	**2a** (1.5)	CH_3CN	16	59%
6	**1b**	**2a** (1.5)	CH_3CN	1.5	90%
7	**1b**	**2a** (1.05)	CH_3CN	1	95%
8	**1b**	**2a** (1.05)	DCE	1	89%
9	**1b**	**2b** (1.5)	DCE	20	59%
10	**1b**	**2c** (1.05)	CH_3CN	1	55%
11	**1b**	**2c** (1.5)	CH_3CN	1	79%

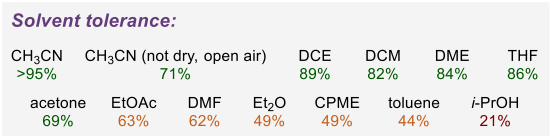
[a]Reaction conditions: HIR **1** (1.0 equiv.), alkyne **2** (1.05-1.5 equiv.), solvent (0.1 M), rt, reactions were carried out under N_2 atmosphere. [b]NMR yield determined using CH_2Br_2 as internal standard.

We turned to the more reactive TsOBX (**1b**). This compound can be easily prepared starting from hydroxybenziodoxolone (**1a**) using *p*-TsOH in acetic anhydride or by a one-pot procedure directly from 2-iodobenzoic acid.[11a,15] It has found only limited use as oxidant[16] or in tosyloxylation reaction.[17] When **1b** was used we observed a drastic increase in reactivity and **3a** was obtained in 86% yield (entry 4). The desired product can still be formed in 59% yield without HFIP (Entry 5). We found out that by reducing the reaction time to 1.5 hours the yield could be increased to 90% even in pure acetonitrile (entry 6). Fine tuning of the reaction conditions by further decreasing the reaction time to 1 hour and the amount of the alkyne to 1.05 equivalents afforded near quantitative yield (entry 7). Replacing acetonitrile by DCE had little impact on the reaction (entry 8). Using TMS-alkyne **2b** resulted in a drop of yield and required substantially longer reaction time (entry 9). Alkynylboronic ester **2c** afforded only moderate yield with 1.05 equivalents, a higher yield was obtained with 1.5 equivalents, but the result was still inferior than with **2a** (entries 10 and 11).

We further wanted to determine the solvent compatibility of the reaction since it will affect the variety of transformations that could be performed in a one-pot process. We found out that using wet HPLC grade acetonitrile under air afforded **3a** in a slightly diminished yield (Scheme 2). Chlorinated solvents (DCE, DCM) as well as polar ethers (DME, THF) were well tolerated with yields above 80% in all cases. Acetone, ethyl acetate and DMF showed diminished yields. We observed a decrease in yield when less polar solvents were used, such as Et_2O, CPME and toluene. The reaction was not compatible with alcohols such as *i*-PrOH, probably due to the competitive substitution of the tosyloxy group by the solvent.

Scheme 2. Solvent tolerance for the formation of EBX 3a.[a]

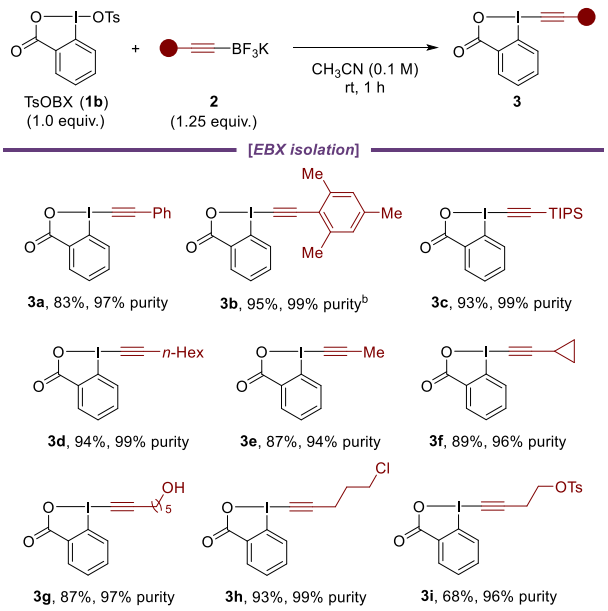




[a]NMR yields are displayed, determined using CH_2Br_2 as internal standard.

Before developing one-pot procedures, it was important to assess the generality of our conditions by synthesizing different EBXs and checking their purity. We found that after 1 hour of reaction a simple basic work-up and a pentane wash of the crude solid afforded the EBXs in high yield and purity, rendering further purification unnecessary (Scheme 3). Aryl and TIPS substituted reagents (**3a-c**) were accesses in near quantitative yields and 97-99% purity. We were pleased to see that our procedure allowed the formation of alkyl-EBXs in high yields (**3d-3f**). Accessing these compounds was often low yielding unless the sensitive boronic esters were used.[18] In contrast, the alkynylboronate salts used in our method were stable solid compounds accessed in good yield from the terminal alkynes (see Supporting Information). Furthermore, we could incorporate a free alcohol (**3g**) in 87% yield and both a chloride and a tosylate leaving groups (**3h** and **3i**) in 93% and 68% yield respectively.

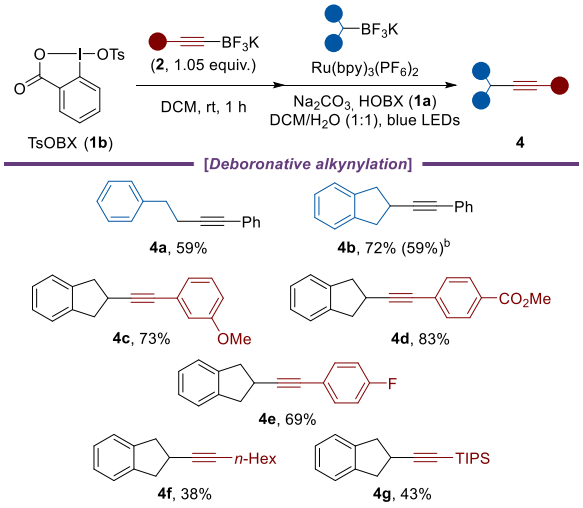
Scheme 3. Synthesis and isolation of EBX reagents 3a-i.



[b]The reaction was stirred at rt for 2 h. The purity was determined by ^{1}H NMR (See Supporting Information or details).

Having established that aryl-, alkyl- and TIPS-EBX are accessible in high yields and purity using our conditions, we turned to one-pot two-step alkynylations. We began with the deboronative alkynylation reported by Chen and co-workers.[19,20] After preformation of **3a** for 1 hour, the substrates and reagents needed were added and the reaction mixture was stirred under blue light irradiation for 16 hours (Scheme 4). We were pleased to see that **4a**, resulting from the alkynylation of the corresponding primary radical, was obtained in 59% yield.

Scheme 4. Scope of the deboronative alkynylation.[a]

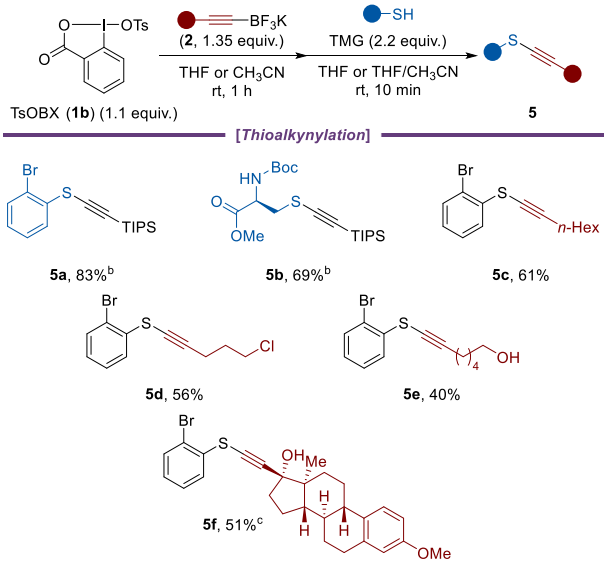


[a]Reaction conditions: 1) TsOBX (**1b**) (1.0 equiv.), alkynyl-BF_3K **2** (1.05 equiv.), DCM (2 mL), rt, 1 h. 2) alkyl-BF_3K (1.5 equiv.), $Ru(bpy)_3(PF_6)_2$ (2 mol%), HOBX (**1a**) (0.5 equiv.), Na_2CO_3 (2.0 equiv.), H_2O (2 mL), blue LEDs, rt, 16 h. Reactions performed on 0.4 mmol scale. Yields are based on TsOBX (**1b**). [b]Reaction performed on 1 mmol scale.

By changing to a secondary radical, we could obtain a 72% yield of **4b**, compared to 85% reported using an isolated EBX reagent **3a**. This reaction could be performed on a 1 mmol scale with a small decrease in yield. Thanks to this one-pot two-step process we could easily vary the alkyne introduced. Both electrons donating (**4c**) and electron withdrawing substituents (**4d-e**) are well tolerated. Notably, up to 83% yield (for **4d**) could be obtained further illustrating the efficacy of our process with TsOBX as the limiting reagent. Alkyl and TIPS alkynes could be transferred in diminished yield (**4f-g**), in accordance with the known lower reactivity of the corresponding EBXs with radicals.[21]

Next, we explored polar chemistry and selected the thioalkynylation developed by our group.[22] We were pleased to see that **5a** could be obtained in 83% yield by adding a solution of 2-bromothiophenol and tetramethylguanidine (TMG) to the preformed EBX **3c** (Scheme 5). A protected cysteine could be used to obtain **5b** in 69% yield. Replacing the TIPS group on the alkyne by a hexyl chain was tolerated (**5c**). More sensitive alkynes bearing a chlorine leaving group or an alcohol afforded the corresponding products in moderate yields (**5d-e**). Mestranol, a synthetic estrogen that is used in contraceptive pills,[23] could be functionalized to give **5f** in 51% yield showing tolerance of a free propargylic alcohol.

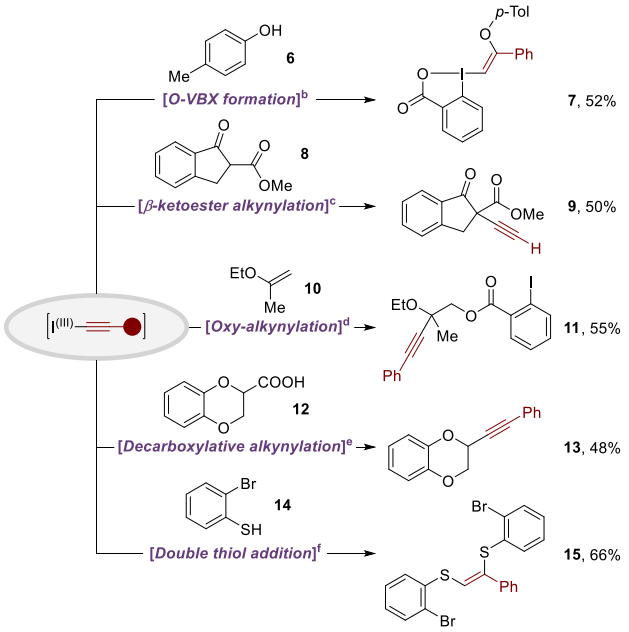
Scheme 5. Scope of the thioalkynylation.[a]



[a]Reaction conditions: 1) TsOBX (**1b**) (1.1 equiv.), alkynyl-BF_3K **2** (1.35 equiv.), CH_3CN (2 mL), rt, 1 h. 2) thiol (1.0 equiv.), TMG (2.2 equiv.), THF (1.5 mL), rt, 10 min. Reaction performed on 0.4 mmol scale. Yields are based on the thiol. [b]THF (3 mL total) was used in both steps. [c]2) TMG (1.05 equiv.), $NaHCO_3$ (1.5 equiv.).

Finally, we explored other transformations using one-pot two-step protocols (Scheme 6). *O*-VBX **7** could be formed in 52% yield from *p*-cresol (**6**) under basic conditions.[24] Using ethynyltrifluoroborate we could access the crude unsubstituted EBX. It was directly used for the α-alkynylation of β-ketoester **8** in the presence of DBU in moderate yield.[25] This reagent is instable and requires care for isolation.[26] Therefore, the *in situ* deprotection of silyl-EBXs has been more often used.[27] Further photoredox reactions were then attempted, the oxy-alkynylation of enol ether **10** afforded **11** with transfer of both the alkyne and carboxylate from the EBX reagent.[21d] Using conditions developed by Xiao and co-workers, the decarboxylative alkynylation of **12** could be performed to give **13** in 48% yield.[28] 1,2-Dithioalkene **15** could be synthetized in 66% yield using Miyake's conditions with an excess of thiol and base.[18b]

Scheme 6. Scope of other transformations.[a]



Reaction conditions: [a]For the pre-formation of the EBX, see Supporting Information. Yields are based on the limiting reagent (either TsOBX (**1b**) or nucleophile). [b]TsOBX (**1b**) (1.0 equiv.), **6** (1.0 equiv.), Cs_2CO_3 (2.0 equiv.), DCE (0.1 M), rt, 16 h. [c]TsOBX (**1b**) (1.1 equiv.), **8** (1.0 equiv.), DBU (1.2 equiv.), CH_3CN (0.08 M), rt, 2 h. [d]TsOBX (**1b**) (1.0 equiv.), **10** (1.5 equiv.), 4-ClCzIPN (2 mol%), **1c** (0.5 equiv.), Na_2CO_3 (2.0 equiv.), DCM (0.13 M), blue LEDs, rt, 16 h. [e]TsOBX (**1b**) (1.5 equiv.), **12** (1.0 equiv.), [Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF_6 (3 mol%), Cs_2CO_3 (3.0 equiv.), DCM (0.07 M), blue LEDs, rt, 16 h. [f]TsOBX (**1b**) (1.0 equiv.), **14** (4.0 equiv.), Cs_2CO_3 (5.0 equiv.), DMA/CH_3CN (1.5:1; 0.08 M), rt, 16 h.

In summary, we have developed new conditions for the formation of EBX reagents using tosyloxybenziodoxolone (TsOBX, **1b**) and alkynyltrifluoroborate salts. The reaction proceeds rapidly and in high yield without additives. Thanks to these conditions, we could develop one-pot two-step processes: the pre-formed reagent was directly used in seven different reactions to obtain a variety of alkynylated products. This method enables easy modification of the alkyne by bypassing the isolation and purification of the intermediate EBXs. Further development of this chemistry will consist in the diversification of the functional group that can be transferred to the hypervalent iodine.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and analytical data for all new compounds. The Supporting Information is available free of charge on the ACS Publications website.

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(19) Huang, H.; Zhang, G.; Gong, L.; Zhang, S.; Chen, Y. Visible-Light-Induced Chemoselective Deboronative Alkynylation under Biomolecule-Compatible Conditions. *J. Am. Chem. Soc.* **2014**, *136* (6), 2280–2283.

(20) The use of alkyltrifluoroborates as substrates made this transformation a logical starting point for our investigation as similar boron-based by-products should be formed in both EBX formation and the subsequent alkynylation reaction.

(21) Selected examples: (a) Huang, H.; Zhang, G.; Chen, Y. Dual Hypervalent Iodine(III) Reagents and Photoredox Catalysis Enable Decarboxylative Ynonylation under Mild Conditions. *Angew. Chem. Int. Ed.* **2015**, *54* (27), 7872–7876. (b) Jia, K.; Li, J.; Chen, Y. Selective P−C(Sp^3) Bond Cleavage and Radical Alkynylation of α-Phosphorus Alcohols by Photoredox Catalysis. *Chem. - Eur. J.* **2018**, *24* (13), 3174–3177. (c) Le Vaillant, F.; Garreau, M.; Nicolai, S.; Gryn'ova, G.; Corminboeuf, C.; Waser, J. Fine-Tuned Organic Photoredox Catalysts for Fragmentation-Alkynylation Cascades of Cyclic Oxime Ethers. *Chem. Sci.* **2018**, *9* (27), 5883–5889. (d) Amos, S. G. E.; Nicolai, S.; Waser, J. Photocatalytic Umpolung of *N* - and *O* -Substituted Alkenes for the Synthesis of 1,2-Amino Alcohols and Diols. *Chem. Sci.* **2020**, *11* (41), 11274–11279.

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Supporting Information for

Tosyloxybenziodoxolone: A Platform for Performing the Umpolung of Alkynes in One-pot Transformations

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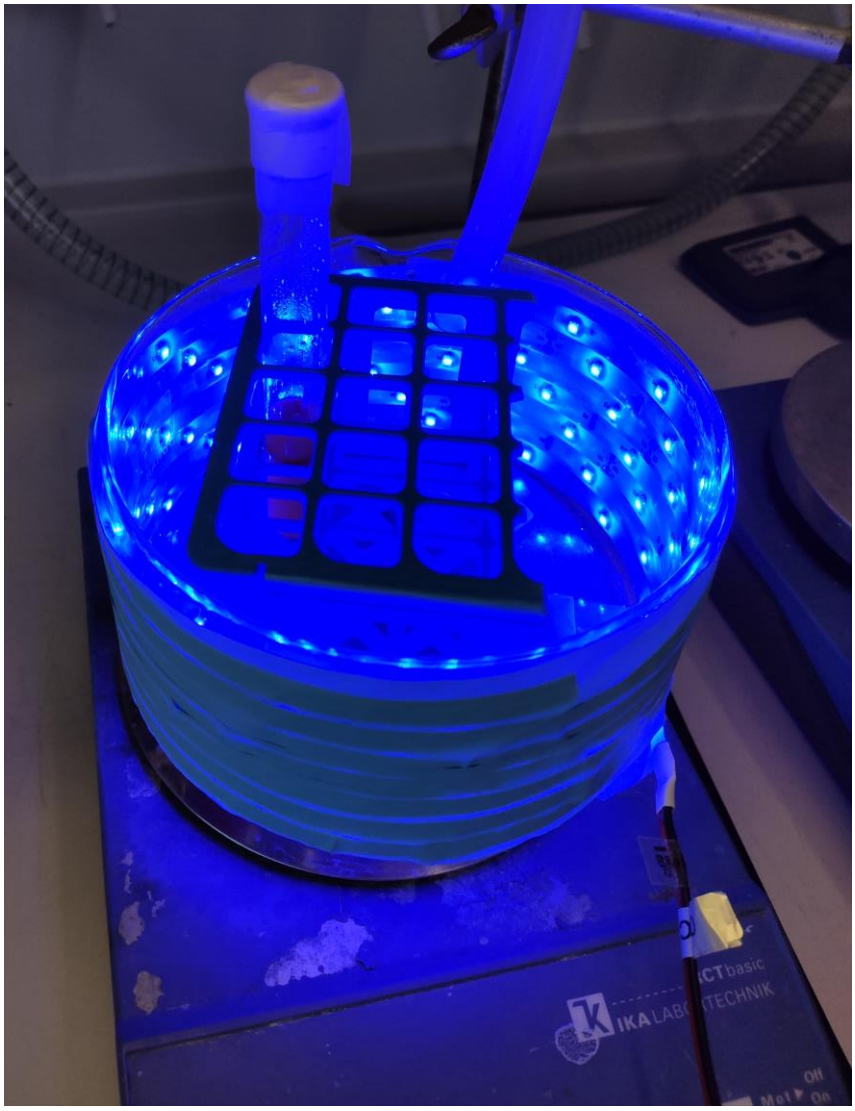
1. General Methods

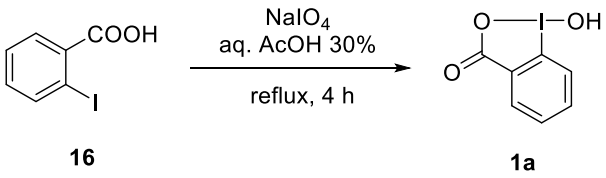
All reactions were carried out under air unless stated otherwise. For flash chromatography, distilled technical grade solvents were used. THF, toluene, Et_2O and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content <10 ppm, Karl-Fischer titration). Solvents were degassed by bubbling with a balloon of argon or by Freeze-Pump-Thaw when mentioned. All chemicals were purchased from Acros, Aldrich, Combi-blocks, Fluka, Fluorochem, Merck, TCI or VWR and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Silicycle silica 40-63 µm (230-400 mesh), using the solvents indicated as eluent with 0.1-0.5 bar pressure or using Biotage Isolera Spektra One with pre-packaged silica cartridges purchased from Buchi, models: Sepacore or GraceResolve (4 g, 12 g, 25 g, 40g, 80g, 120g). TLC was performed on Merck silica gel 60 F254 TLC glass plates and visualized with UV light and potassium permanganate or *p*-anisaldehyde stain. ^{1}H-NMR spectra were recorded on a Bruker DPX-400 400 MHz spectrometer in chloroform-d, DMSO-d_6 or acetone-d_6. All signals are reported in ppm using the residual solvent signal as internal reference (chloroform-d: 7.26 ppm, DMSO-d_6: 2.50 ppm, acetone-d_6: 2.06 ppm). The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, bs = broad signal, coupling constant(s) in Hz, integration, assignment). ^{13}C-NMR spectra were recorded with {^{1}H} decoupling on a Bruker DPX-400 101 MHz spectrometer in chloroform-d, DMSO-d_6 or acetone-d_6. All signals are reported in ppm using the residual solvent signal as internal reference (chloroform-d: 77.0 ppm, DMSO-d_6: 39.5 ppm, acetone-d_6: 206.3 and 29.8 ppm). ^{19}F-NMR spectra were recorded with {^{1}H} decoupling on a Bruker DPX-400 376 MHz spectrometer in chloroform-d, DMSO-d_6 or acetone-d_6. ^{11}B-NMR spectra were recorded on a Bruker DPX-400 128 MHz spectrometer in DMSO-d_6 or acetone-d_6. 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 a LTQOrbitrap Elite instrument (Thermofisher) operated in the positive ionization mode. Reactions under blue LEDs irradiation were performed in test tubes (14 mL) which were placed at the center of a crystallization flask. On this flask were attached the blue LEDs (RUBAN LED 5MÈTRES - 60LED/M -3528 BLEU - IP65 with Transformateur pour Ruban LED 24W/2A/12V, bought directly on RubanLED.com). The distance between the LEDs and the test tubes was approximatively 3 cm. Long irradiation resulted in temperature increasing up to 35 °C during overnight reactions, a flow of air was maintained in the crystallization flask during reactions.

2. Picture of the photochemistry set-up



3. Preparation of Hypervalent Iodine Reagents

1-Hydroxy-1,2-benziodoxol-3-(1*H*)-one (HOBX, 1a):

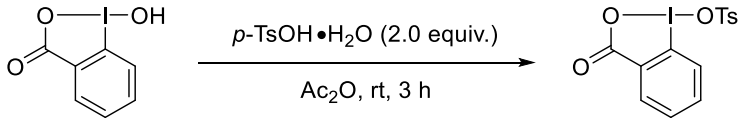


16 **1a**

Following an adapted version of a reported procedure,[1] $NaIO_4$ (18.1 g, 84.7 mmol, 1.05 equiv) and 2-iodobenzoic acid (**16**) (20.0 g, 80.6 mmol, 1.00 equiv) were suspended in a mixture of AcOH (36 mL) and water (84 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (100 mL) and allowed to cool to room temperature protected from light. The crude product was collected by filtration, washed on the filter with ice water (3 x 50 mL) and acetone (3 x 50 mL), and air-dried in the dark to give the pure product **1a** (20.0 g, 75.7 mmol, 94%) as a white solid. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.02 (dd, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 7.97 (m, 1H, Ar*H*), 7.85 (dd, *J* = 8.2, 0.7 Hz, 1H, Ar*H*), 7.71 (td, *J* = 7.6, 1.2 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4. Spectroscopic data was consistent with the values reported in the literature.[1]

1-(*p*-Methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (TsOBX, 1b):

Synthesis of this reagent can be carried out using two different procedures:



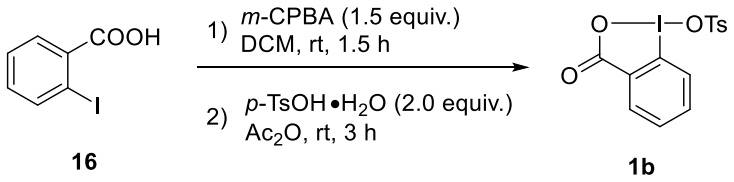
1a **1b**

Compound **1b** was synthesized following an adapted version of a reported procedure.[2] *p*-TsOH•H_2O (5.71 g, 30.0 mmol, 2.0 equiv.) was added portionwise to an oven-dried flask containing a suspension of 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one (**1a**) (3.96 g, 15.0 mmol, 1.0 equiv.) in acetic anhydride (15 mL). After 5 min, a slightly exothermic reaction began and the mixture turned into a clear slightly yellow solution. The reaction was stirred at rt under N_2 for 3 h. During the course of the reaction precipitation of the product as a white solid might occur. Dry Et_2O (40 mL) was added and the mixture was cooled to 0 °C for 10 min. At this point precipitation of the product should have occurred. The solid was filtered and washed with dry

[1] L. Kraszkiewicz, L. Skulski, *Arkivoc* **2003**, *2003*, 120.
[2] M. Nappi, C. He, W. G. Whitehurst, B. G. N. Chappell, M. J. Gaunt, *Angew. Chem. Int. Ed.* **2018**, *57*, 3178–3182.

Et_2O (4 x 40 mL) then dried *in vacuo* to afford 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (4.75 g, 11.4 mmol, 76%) as a white solid.

Note: The product is slightly hygroscopic, when filtering it using vacuum filtration it is advised to avoid extensive drying on the frit. Just removing the ether is enough to collect it properly and further drying can be carried *in vacuo*.



16 **1b**

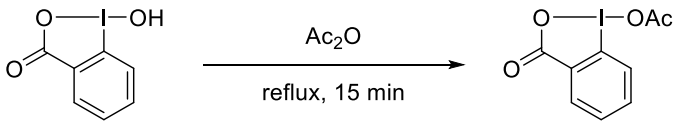
Compound **1b** was synthesized following an adapted version of a reported procedure.[3] *m*-CPBA (1.36 g, 6.0 mmol, 1.5 equiv., 77% purity) was added to an oven-dried flask containing a suspension of 2-iodobenzoic acid (**16**) (1.0 g, 4.0 mmol, 1.0 equiv.) in dry DCM (12 mL). After 5 minutes, precipitation of a white solid occurs. The reaction was stirred at rt under N_2 for 1.5 h then acetic anhydride (4 mL) was added followed by the portionwise addition of *p*-TsOH•H_2O (1.53 g, 8.06 mmol, 2.0 equiv.). After 5 min, a slightly exothermic reaction began and the mixture turned into a clear slightly yellow solution. The reaction was stirred at rt under N_2 for 3 h. The DCM was removed *in vacuo*, dry Et_2O (40 mL) was added and the mixture was cooled to 0 °C for 10 min. At this point precipitation of the product should have occurred. The solid was filtered and washed with dry Et_2O (4 x 20 mL) then dried *in vacuo* to afford 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (0.87 g, 2.1 mmol, 52%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (dd, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 7.98 – 7.93 (m, 1H, Ar*H*), 7.83 (dd, *J* = 8.1, 0.9 Hz, 1H, Ar*H*), 7.70 (td, *J* = 7.4, 1.0 Hz, 1H, Ar*H*), 7.51 – 7.46 (m, 2H, Ar*H*), 7.15 – 7.10 (m, 2H, Ar*H*), 2.28 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.9, 145.2, 138.1, 134.6, 131.5, 131.2, 130.5, 128.3, 126.4, 125.6, 120.5, 20.9. HRMS (APCI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{12}IO_5S^+$ 418.9445; Found 418.9437. Spectroscopic data was consistent with the values reported in the literature.[2]

Note: We observed a slow solubilization of **1b** if dry DMSO is used. We think water present in DMSO help the solubilization and that when dry DMSO is used the solubilization happen after a couple of minutes (~5min) due to the progressive absorption of the water present in the air by the solvent.

1-Acetoxy-1,2-benziodoxol-3-(1*H*)-one (1c):

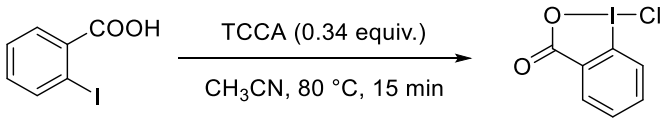
[3] Y. Yamamoto, H. Togo, *Synlett* **2005**, *2005*, 2486–2488.



1a **1c**

Following a reported procedure,[4] a suspension of **1a** (5.0 g, 19 mmol, 1 equiv.) in acetic anhydride (19 mL) was refluxed until total dissolution (~15 min). The resulting clears solution was allowed to cool to room temperature and then cooled to 5 °C in the fridge. The white crystals were filtered, washed with pentane (3 x 30 mL) and dried under reduced pressure to afford 1-Acetoxy-1,2-benziodoxol-3-(1*H*)-one (**1c**) (5.0 g, 16 mmol, 86%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar*H*), 8.01 (dd, *J* = 8.1, 0.9 Hz, 1H, Ar*H*), 7.97 – 7.88 (m, 1H, Ar*H*), 7.72 (td, *J* = 7.4, 1.0 Hz, 1H, Ar*H*), 2.26 (s, 3H, C*H*$_3$CO). Spectroscopic data was consistent with the values reported in the literature.[5]

1-Chloro-1,2-benziodoxol-3-(1*H*)-one (1d):



16 **1d**

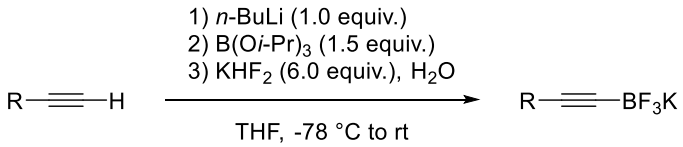
Compound **1c** was synthesized following a reported procedure.[6] An oven-dried 2-neck round bottom flask charged with **1a** (500 mg, 2.02 mmol, 1.00 equiv.) and equipped with a condenser was evacuated and backfilled with N_2 (3x). Dry acetonitrile (4 mL) was added and the mixture was heated to 80 °C (become a clear solution). A hot (35-40 °C) solution of trichloroisocyanuric acid (159 mg, 0.685 mmol, 0.34 equiv.) in dry acetonitrile (1 mL) was added dropwise over 5 min. The reaction was stirred at 80 °C for 10 min then immediately filtered over a hot plug of silica and eluted with 15 mL of hot acetonitrile. The filtrate was concentrated in vacuo to afford 1-chloro-1,2-benziodoxol-3-(1*H*)-one (**1d**) (386 mg, 1.37 mmol, 68%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 7.5, 1.6 Hz, 1H), 8.22 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.04 – 7.95 (m, 1H), 7.80 (td, *J* = 7.4, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 136.8, 133.6, 132.0, 128.8, 127.0, 117.2. Spectroscopic data was consistent with the values reported in the literature.[6]

4. Synthesis of Potassium Trifluoroborate Salts

[4] E. Grenet, J. Waser, *Org. Lett.* **2018**, *20*, 1473–1476.
[5] S. Bertho, R. Rey-Rodriguez, C. Colas, P. Retailleau, I. Gillaizeau, *Chem. - Eur. J.* **2017**, *23*, 17674–17677.
[6] D. L. Poeira, J. Macara, H. Faustino, J. A. S. Coelho, P. M. P. Gois, M. M. B. Marques, *Eur. J. Org. Chem.* **2019**, *2019*, 2695–2701.

General note: It is known that carbons linked to the boron atom are difficult to be observed by ^{13}C NMR due to a broadening of the signal caused by the quadrupole moment of ^{11}B nuclei. This implies that the carbon directly linked to the boron (in alkyl-BF_3K) or the two carbon of the alkyne (in alkynyl-BF_3K) are too broad to be properly visible.[7] Therefore, they are not listed in the characterization data.

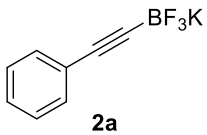
General procedure A:



Adapted version of a reported procedure.[8] An oven-dried round-bottom flask (PFA), charged with alkyne (1.0 equiv.) if solid, was evacuated and backfilled with N_2 (3x). Then, alkyne (if liquid) and dry THF (0.3 M) were added. The mixture was cooled to -78 °C and a solution of *n*-BuLi (2.5 M, 1.0 equiv.) in hexane was added dropwise under N_2. The reaction was stirred at -78 °C for 1 h and B(O*i*-Pr)$_3$ (1.5 equiv.) was added quickly. The reaction was stirred 10 min at -78 °C then 2 h at rt. The mixture was cooled to 0 °C and a saturated solution of KHF_2 (6.0 equiv.) in water (40% of THF volume + additional 40% to rinse the remaining solid) was added. The reaction was stirred at rt open to air for 2 h 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, this process was repeated 2 more times. The combined 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 potassium alkynyltrifluoroborate.

Note: This purification procedure usually affords the pure desired product. If it is not the case a more classical recrystallization from acetone followed by precipitation with Et_2O can be performed.

Potassium trifluoro(phenylethynyl)borate (2a):

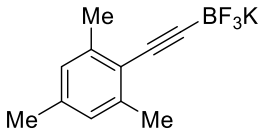


2a

[7] R. A. Oliveira, R. O. Silva, G. A. Molander, P. H. Menezes, *Magn. Reson. Chem.* **2009**, *47*, 873–878.
[8] D. A. Mundal, K. E. Lutz, R. J. Thomson, *J. Am. Chem. Soc.* **2012**, *134*, 5782–5785.

Synthesized following **general procedure A** starting from phenylacetylene (1.53 g, 1.65 mL, 15.0 mmol). Potassium trifluoro(phenylethynyl)borate (**2a**) (2.60 g, 12.5 mmol, 83%) was obtained 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-d_6) δ -135.0. Spectroscopic data was consistent with the values reported in the literature.[9]

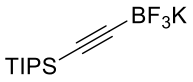
Potassium trifluoro(mesitylethynyl)borate (17):



17

Synthesized following **general procedure A** starting from 2-ethynyl-1,3,5-trimethylbenzene (0.950 g, 1.03 mL, 6.3 mmol). Potassium trifluoro(mesitylethynyl)borate (**17**) (1.23 g, 4.94 mmol, 78%) was obtained as a white solid. Mp (Dec.): 233 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 6.79 (s, 2H, Ar*H*), 2.34 (s, 6H, *CH*$_3$), 2.20 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, acetone-d_6) δ 140.0, 135.9, 127.9, 124.0, 21.3, 21.2. ^{19}F NMR (377 MHz, acetone-d_6) δ -134.3. ^{11}B NMR (128 MHz, acetone-d_6) δ -1.0 (q, *J* = 37.3 Hz). HRMS (APPI/LTQ-Orbitrap) m/z: $[M-K]^-$ Calcd for $C_{11}H_{11}BF_3^-$ 211.0911; Found 211.0901.

Potassium trifluoro((triisopropylsilyl)ethynyl)borate (18):



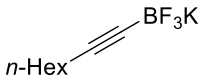
18

Synthesized following **general procedure A** starting from ethynyltriisopropylsilane (1.37 g, 1.68 mL, 7.5 mmol). Potassium trifluoro((triisopropylsilyl)ethynyl)borate (**18**) (1.75 g, 6.08 mmol, 81%) was obtained as a white solid. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.10 – 1.04 (m, 21H, *TIPS*). ^{13}C NMR (101 MHz, acetone-d_6) δ 19.1, 12.2. ^{19}F NMR (376 MHz, acetone-d_6) δ -135.1. Spectroscopic data was consistent with the values reported in the literature.[10]

Potassium trifluoro(oct-1-yn-1-yl)borate (19):

[9] G. A. Molander, B. W. Katona, F. Machrouhi, *J. Org. Chem.* **2002**, *67*, 8416–8423.

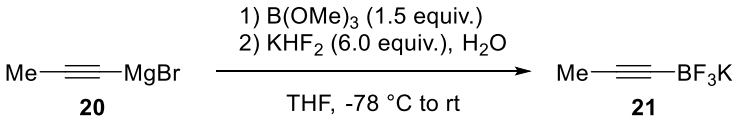
[10] K. Stout, T. P. J. Peters, M. F. J. Mabesoone, F. L. L. Visschers, E. M. Meijer, J.-R. Klop, J. van den Berg, P. B. White, A. E. Rowan, R. J. M. Nolte, J. A. A. W. Elemans, *Eur. J. Org. Chem.* **2020**, *2020*, 7087–7100.



19

Synthesized following **general procedure A** starting from oct-1-yne (0.83 g, 1.1 mL, 7.5 mmol). Potassium trifluoro(oct-1-yn-1-yl)borate (19) (1.32 g, 6.10 mmol, 81%) was obtained as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.00 – 1.93 (m, 2H, C≡CC*H*$_2$), 1.39 – 1.18 (m, 8H, C*H*$_2$), 0.86 (t, *J* = 7.0 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (101 MHz, DMSO-d_6) δ 31.0, 29.0, 28.1, 22.1, 18.9, 14.0. ^{19}F NMR (376 MHz, DMSO-d_6) δ -131.0. Spectroscopic data was consistent with the values reported in the literature.[11]

Potassium trifluoro(prop-1-yn-1-yl)borate (21):

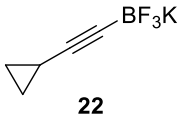


20 **21**

Compound **20** was synthesized following an adapted version of a reported procedure.[12] An oven-dried round-bottom flask (PFA) was evacuated and backfilled with N_2 (3x). Then, a solution of 1-propynylmagnesium bromide (**20**) (15 mL, 7.5 mmol, 0.5 M, 1.0 equiv.) in THF and dry THF (15 mL) were added. The solution was cooled to -78 °C and B(OMe)$_3$ (1.25 mL, 11.3 mmol, 1.5 equiv.) was added quickly under N_2. The reaction was stirred 1 h at -78 °C then 1.5 h at -20 °C. A saturated solution of KHF_2 (3.5 g, 45 mmol, 6.0 equiv.) in water (10 mL + additional 10 mL to rinse the remaining solid) was added. The reaction was stirred at rt open air for 2 h then concentrated *in vacuo*. The wet solid obtained was further dried by co-evaporation with acetone. To the dry solid was added acetone (~30 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, this process was repeated 2 more times. The combined filtrates were concentrated *in vacuo* to approximately 1/3 of the initial volume. Et_2O (~30 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 potassium trifluoro(prop-1-yn-1-yl)borate (**21**) (0.95 g, 6.5 mmol, 87%) as a white solid. Mp (Dec.): 238 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.64 – 1.58 (m, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, acetone-d_6) δ 4.0. ^{19}F NMR (376 MHz, acetone-d_6) δ -134.7 (dd, *J* = 76.0, 37.4 Hz). ^{11}B NMR (128 MHz, acetone-d_6) δ -1.7 (q, *J* = 38.2 Hz). HRMS (ESI/QTOF) m/z: [M-K]$^-$ Calcd for $C_3H_3BF_3^-$ 107.0285; Found 107.0285.

[11] K. Jouvin, F. Couty, G. Evano, *Org. Lett.* **2010**, *12*, 3272–3275.
[12] P. B. Brady, E. M. Carreira, *Org. Lett.* **2015**, *17*, 3350–3353.

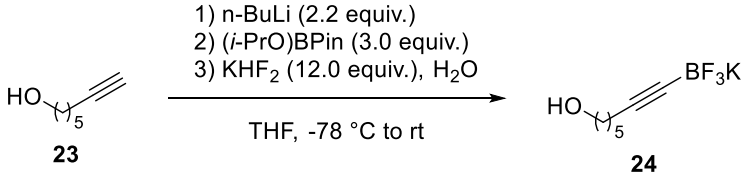
Potassium (cyclopropylethynyl)trifluoroborate (22):



22

Synthesized following **general procedure A** starting from ethynylcyclopropane (0.50 g, 0.64 mL, 7.5 mmol). Potassium (cyclopropylethynyl)trifluoroborate (**22**) (0.86 g, 5.0 mmol, 67%) was obtained as a white solid. Mp (Dec.): 250 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.12 – 1.01 (m, 1H, C*H*), 0.61 – 0.54 (m, 2H, CH_2), 0.42 – 0.36 (m, 2H, CH_2). ^{13}C NMR (101 MHz, DMSO-d_6) δ 7.4, 0.1. ^{19}F NMR (377 MHz, DMSO-d_6) δ -131.1. ^{11}B NMR (128 MHz, DMSO-d_6) δ -2.1 (q, *J* = 37.5 Hz). HRMS (ESI/QTOF) m/z: $[M-K]^-$ Calcd for $C_5H_5BF_3^-$ 133.0442; Found 133.0444.

Potassium trifluoro(7-hydroxyhept-1-yn-1-yl)borate (24):



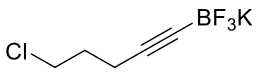
23 **24**

Compound **24** was synthesized following an adapted version of a reported procedure.[13] An oven-dried round-bottom flask (PFA) was evacuated and backfilled with N_2 (3x). Then, hept-6-yn-1-ol (**23**) (0.94 mL, 7.5 mmol, 1.0 equiv.) and dry THF (25 mL) were added. The mixture was cooled to -78 °C and a solution of *n*-BuLi (6.60 mL, 16.5 mmol, 2.5 M, 2.2 equiv.) in hexane was added dropwise under N_2. The reaction was stirred at -78 °C for 1 h and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.65 mL, 22.5 mmol, 3.0 equiv.) was added quickly. The reaction was warmed to -20 °C and stirred for 1 h. A saturated solution of KHF_2 (7.03 g, 90.0 mmol, 12.0 equiv.) in water (20 mL + additional 10 mL to rinse the remaining solid) was added. The reaction was stirred at rt open to air for 1 h then concentrated *in vacuo*. The wet solid obtained was further dried by co-evaporation with acetone. To the dry solid was added acetone (~30 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, this process was repeated 2 more times. The combined filtrates were concentrated *in vacuo* to approximately 1/3 of the initial volume. Et_2O (~40 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* then recrystallized in acetone using Et_2O to induce precipitation to afford potassium trifluoro(7-hydroxyhept-1-yn-1-yl)borate (**24**) (0.91 g, 4.2 mmol, 56%) as a white solid. Mp (Dec.): 260 °C; ^{1}H NMR (400

[13] J. D. Kirkham, S. J. Edeson, S. Stokes, J. P. A. Harrity, *Org. Lett.* **2012**, *14*, 5354–5357.

MHz, DMSO-d_6) δ 4.34 (t, *J* = 5.2 Hz, 1H, CH_2OH), 3.37 (q, *J* = 5.3 Hz, 2H, CH_2OH), 2.01 – 1.92 (m, 2H, C≡C-CH_2), 1.45 – 1.27 (m, 6H, CH_2). ^{13}C NMR (101 MHz, DMSO-d_6) δ 60.7, 32.2, 29.0, 25.0, 19.0. ^{19}F NMR (376 MHz, DMSO-d_6) δ -131.0. ^{11}B NMR (128 MHz, DMSO-d_6) δ -1.9. HRMS (ESI/QTOF) m/z: $[M-K]^-$ Calcd for $C_7H_{11}BF_3O^-$ 179.0861; Found 179.0862.

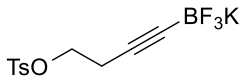
Potassium (5-chloropent-1-yn-1-yl)trifluoroborate (25):



25

Synthesized following **general procedure A** starting from 5-chloropent-1-yne (0.77 g, 0.80 mL, 7.5 mmol). Potassium (5-chloropent-1-yn-1-yl)trifluoroborate (**25**) (1.28 g, 6.14 mmol, 82%) was obtained as a white solid. ^{1}H NMR (400 MHz, acetone-d_6) δ 3.70 (t, *J* = 6.6 Hz, 2H, CH_2Cl), 2.24 – 2.17 (m, 2H, C≡C-CH_2), 1.85 (p, *J* = 6.7 Hz, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (101 MHz, acetone-d_6) δ 44.9, 33.1, 17.3. ^{19}F NMR (376 MHz, acetone-d_6) δ -134.6. Spectroscopic data was consistent with the values reported in the literature.[9]

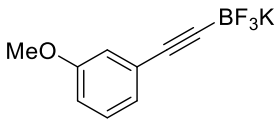
Potassium trifluoro(4-(tosyloxy)but-1-yn-1-yl)borate (26):



26

Synthesized following **general procedure A** starting from but-3-yn-1-yl 4-methylbenzenesulfonate (1.75 g, 1.73 mL, 7.5 mmol). Potassium trifluoro(4-(tosyloxy)but-1-yn-1-yl)borate (**26**) (1.9 g, 5.7 mmol, 77%) was obtained as a beige solid. Mp (Dec.): 156 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.88 – 7.81 (m, 2H, Ar*H*), 7.51 – 7.46 (m, 2H, Ar*H*), 3.99 (t, *J* = 7.3 Hz, 2H, CH_2OTs), 2.45 (s, 3H, CH_3), 2.38 (tq, *J* = 7.3, 1.8 Hz, 2H, C≡C-CH_2). ^{13}C NMR (101 MHz, acetone-d_6) δ 145.8, 134.2, 130.9, 128.7, 70.0, 21.5, 20.8. ^{19}F NMR (377 MHz, acetone-d_6) δ -135.0 (dd, *J* = 71.8, 32.1 Hz). ^{11}B NMR (128 MHz, acetone-d_6) δ -1.8 (q, *J* = 37.0 Hz). HRMS (ESI/QTOF) m/z: $[M-K]^-$ Calcd for $C_{11}H_{11}BF_3O_3S^-$ 291.0480; Found 291.0478.

Potassium trifluoro((3-methoxyphenyl)ethynyl)borate (27):

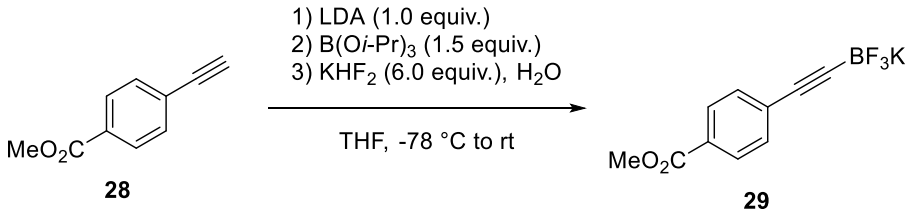


27

Synthesized following **general procedure A** starting from 1-ethynyl-3-methoxybenzene (1.0 g, 0.97 mL, 7.5 mmol). Potassium trifluoro((3-methoxyphenyl)ethynyl)borate (**27**) (0.91 g, 3.8 mmol, 51%) was obtained as a white solid. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.15 (t, *J* = 8.0

Hz, 1H, Ar*H*), 6.93 – 6.84 (m, 2H, Ar*H*), 6.78 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H, Ar*H*), 3.76 (s, 3H, OC*H*$_3$). ^{13}C NMR (101 MHz, acetone-d$_6$) δ 160.3, 129.8, 128.3, 124.5, 117.1, 113.7, 55.4. ^{19}F NMR (377 MHz, acetone-d$_6$) δ -135.0 (dd, *J* = 70.9, 30.5 Hz). Spectroscopic data was consistent with the values reported in the literature.[14]

Potassium trifluoro((4-(methoxycarbonyl)phenyl)ethynyl)borate (29):



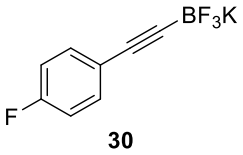
28 **29**

Compound **29** was synthesized following an adapted version of a reported procedure.[8,15] An oven-dried round-bottom flask (PFA) was evacuated and backfilled with N_2 (3x). Then, freshly distilled diisopropylamine (1.05 mL, 7.50 mmol, 1.0 equiv.) and dry THF (15 mL) were added. The mixture was cooled to 0 °C and a solution of *n*-BuLi (3.0 mL, 7.5 mmol, 2.5 M, 1.0 equiv.) in hexane was added dropwise under N_2. The reaction was stirred at 0 °C for 0.5 h then cooled to -78 °C. A solution of methyl 4-ethynylbenzoate (1.2 g, 7.5 mmol, 1.0 equiv.) in dry THF (10 mL) was added dropwise. The reaction was stirred at -78 °C for 0.5 h then B(O*i*-Pr)$_3$ (2.60 mL, 11.3 mmol, 1.5 equiv.) was added quickly. The reaction was stirred 10 min at -78 °C then 2 h at rt. The mixture was cooled to 0 °C and a saturated solution of KHF_2 (3.52 g, 45.0 mmol, 6.0 equiv.) in water (10 mL + additional 10 mL to rinse the remaining solid) was added. The reaction was stirred at rt open to air for 2 h then concentrated *in vacuo*. The wet solid obtained was further dried by co-evaporation with acetone. To the dry solid was added acetone (~30 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, this process was repeated 2 more times. The combined filtrates were concentrated *in vacuo* to approximately 1/3 of the initial volume. Et_2O (~40 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 potassium trifluoro((4-(methoxycarbonyl)phenyl)ethynyl)borate (**29**) (0.80 g, 3.0 mmol, 40%) as a beige solid. Mp (Dec.): 220 °C; ^{1}H NMR (400 MHz, acetone-d$_6$) δ 7.92 – 7.85 (m, 2H, Ar*H*), 7.45 – 7.38 (m, 2H, Ar*H*), 3.86 (s, 3H, OC*H*$_3$). ^{13}C NMR (101 MHz, acetone-d$_6$) δ 167.0, 132.5, 132.1, 129.9, 128.7, 52.3. ^{19}F NMR (376 MHz, acetone-d$_6$) δ -135.4. ^{11}B NMR (128 MHz, acetone-d$_6$) δ -1.4 (q, *J* = 34.8 Hz). HRMS (ESI/QTOF) m/z: [M-K]$^-$ Calcd for $C_{10}H_7BF_3O_2^-$ 227.0497; Found 227.0501.

[14] J. H. Song, P. Choi, S. E. Lee, K. H. Jeong, T. Kim, K. S. Kang, Y. S. Choi, J. Ham, *Eur. J. Org. Chem.* **2013**, *2013*, 6249–6253.

[15] For LDA preparation see: S. Jansone-Popova, J. A. May, *J. Am. Chem. Soc.* **2012**, *134*, 17877–17880.

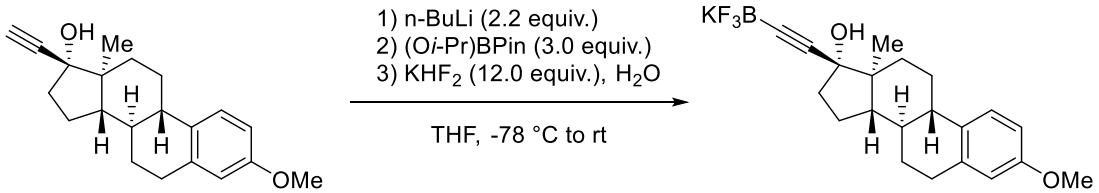
Potassium trifluoro((4-fluorophenyl)ethynyl)borate (30):



30

Synthesized following **general procedure A** starting from 1-ethynyl-4-fluorobenzene (0.90 g, 0.86 mL, 7.5 mmol). Potassium trifluoro((4-fluorophenyl)ethynyl)borate (**30**) (1.11 g, 4.91 mmol, 65%) was obtained as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 – 7.28 (m, 2H), 7.14 – 7.07 (m, 2H). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.38 – 7.30 (m, 2H, Ar*H*), 7.06 – 6.98 (m, 2H, Ar*H*). ^{13}C NMR (101 MHz, acetone-d_6) δ 162.2 (d, *J* = 244.5 Hz), 134.0 (d, *J* = 8.0 Hz), 123.7, 115.8 (d, *J* = 21.9 Hz). ^{19}F NMR (376 MHz, acetone-d_6) δ -115.9, -135.1. ^{1}H NMR in DMSO was consistent with the values reported in the literature.[8]

Potassium trifluoro(((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)borate (32):

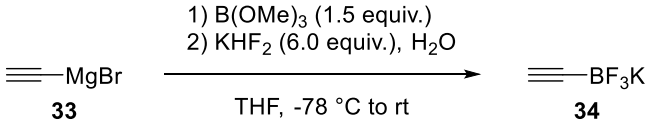


31 **32**

Compound **32** was synthesized following an adapted version of a reported procedure.[13] An oven-dried round-bottom flask (PFA) charged with (8*R*,9*S*,13*S*,14*S*,17*R*)-17-ethynyl-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-ol (**31**) (1.0 g, 3.2 mmol, 1.0 equiv.) was evacuated and backfilled with N_2 (3x). Dry THF (22 mL) was added, the mixture was cooled to -78 °C and a solution of *n*-BuLi (2.8 mL, 7.1 mmol, 2.5 M, 2.2 equiv.) in hexane was added dropwise under N_2. The reaction was stirred at -78 °C for 1 h and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.0 mL, 9.7 mmol, 3.0 equiv.) was added quickly. The reaction was warmed to -20 °C and stirred for 1 h. A saturated solution of KHF_2 (3.02 g, 38.7 mmol, 12.0 equiv.) in water (9 mL + additional 9 mL to rinse the remaining solid) was added. The reaction was stirred at rt open air for 1 h then concentrated *in vacuo*. The wet solid obtained was further dried by co-evaporation with acetone. To the dry solid was added acetone (~30 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, this process was repeated 2 more times. The combined filtrates were concentrated *in vacuo* to approximately 1/3 of the initial volume. Et_2O (~40 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, dried *in vacuo* then recrystallized in acetone using

Et_2O to induce precipitation to afford potassium trifluoro(((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)borate (**32**) (0.53 g, 1.3 mmol, 40%) as a white solid. Mp (Dec.): 257 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.18 (d, *J* = 8.6 Hz, 1H, Ar*H*), 6.67 (dd, *J* = 8.6, 2.8 Hz, 1H, Ar*H*), 6.59 (d, *J* = 2.7 Hz, 1H, Ar*H*), 4.79 (s, 1H, O*H*), 3.69 (s, 3H, OC*H*$_3$), 2.77 (q, *J* = 4.3 Hz, 2H, C*H*$_2$), 2.38 – 2.23 (m, 1H, C*H*$_2$), 2.02 (ddd, *J* = 12.9, 9.9, 6.1 Hz, 2H, C*H*$_2$ + C*H*), 1.91 (td, *J* = 13.2, 4.2 Hz, 1H, C*H*$_2$), 1.85 – 1.72 (m, 2H, C*H*$_2$), 1.72 – 1.52 (m, 3H, C*H*$_2$ + C*H*), 1.35 – 1.17 (m, 4H, C*H*$_2$ + C*H*), 0.71 (s, 3H, C-C*H*$_3$). ^{13}C NMR (101 MHz, DMSO-d_6)[16] δ 157.0, 137.4, 132.3, 126.2, 113.4, 111.5, 78.2, 54.9, 48.6, 46.5, 43.3, 32.6, 29.4, 27.0, 26.3, 22.6, 13.0. ^{19}F NMR (376 MHz, DMSO-d_6) δ -130.6. ^{11}B NMR (128 MHz, DMSO-d_6) δ -1.7. HRMS (ESI/QTOF) m/z: [M-K]$^-$ Calcd for $C_{21}H_{25}BF_3O_2^-$ 377.1905; Found 377.1919.

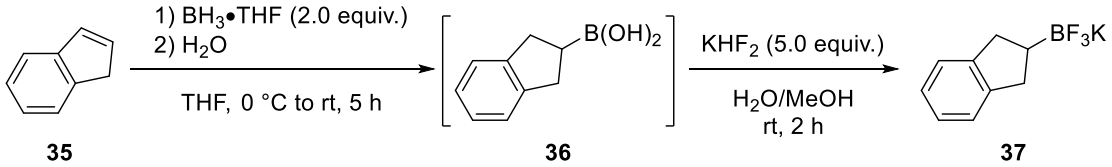
Potassium ethynyltrifluoroborate (34):



Compound **34** was synthesized following an adapted version of a reported procedure.[12] An oven-dried round-bottom flask (PFA) was evacuated and backfilled with N_2 (3x). Then, a solution of ethynylmagnesium bromide (**33**) (30.0 mL, 15.0 mmol, 0.5 M, 1.0 equiv.) in THF and dry THF (30 mL) were added. The solution was cooled to -78 °C and $B(OMe)_3$ (2.5 mL, 22 mmol, 1.5 equiv.) was added quickly under N_2. The reaction was stirred 1 h at -78 °C then 1.5 h at -20 °C. A saturated solution of KHF_2 (7.03 g, 90.0 mmol, 6.0 equiv.) in water (20 mL + additional 20 mL to rinse the remaining solid) was added. The reaction was stirred at rt open air for 2 h then concentrated *in vacuo*. The wet solid obtained was further dried by co-evaporation with acetone. To the dry solid was added acetone (~30 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, this process was repeated 2 more times. The combined filtrates were concentrated *in vacuo* to approximately 1/3 of the initial volume. Et_2O (~30 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 potassium ethynyltrifluoroborate (**34**) (1.17 g, 8.86 mmol, 59%) as a white solid. Mp (Dec.): 216 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.67 (d, *J* = 5.4 Hz, 1H, C≡C*H*). ^{13}C NMR (101 MHz, acetone-d_6) not observed. ^{19}F NMR (376 MHz, acetone-d_6) δ -135.5. ^{11}B NMR (128 MHz, acetone-d_6) δ -2.0 (qd, *J* = 36.1, 3.7 Hz). HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: [M-K]$^-$ Calcd for $C_2HBF_3^-$ 93.0129; Found 93.0128.

[16]Two carbon signals are hidden under the DMSO signal.

Potassium (2,3-dihydro-1*H*-inden-2-yl)trifluoroborate (37):



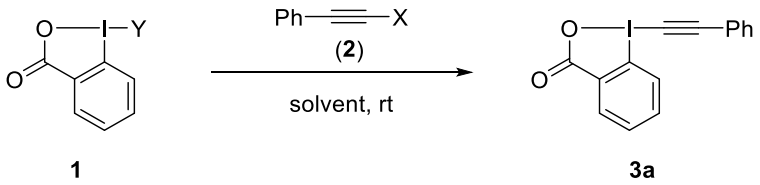
Compound **37** was synthesized following an adapted version of a reported procedure.[17] An oven dried round-bottom flask was evacuated and backfilled with N_2 (3x). A solution of BH_3•THF (40.0 mL, 40.0 mmol, 1 M, 2.0 equiv.) was added and cooled to 0 °C. A solution of indene (**35**) (2.3 mL, 20.0 mmol, 1.0 equiv.) in dry THF (4 mL) was added under N_2 and the reaction was warm to rt and stirred for 2 h. The mixture was cooled to 0 °C and water (4 mL) was added dropwise. The reaction was stirred at rt for 3 h. The mixture was concentrated *in vacuo* to remove the THF then EtOAc (50 mL) was added. The organic layer was collected, washed with water (25 mL) and brine (2 x 25 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford crude boronic acid **36** as an oil.

To a round-bottom flask (PFA) charged with a saturated solution of KHF_2 (7.81 g, 100 mmol, 5.0 equiv.) in water (30 mL) was added a solution of crude **36** in MeOH (40 mL). The reaction was stirred at rt open air for 2 h then was concentrated *in vacuo*. The wet solid obtained was further dried by co-evaporation with acetone. To the dry solid was added acetone (~30 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, this process was repeated 2 more times. The combined filtrates were concentrated *in vacuo* to approximately 1/3 of the initial volume. Et_2O (~40 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 potassium (2,3-dihydro-1*H*-inden-2-yl)trifluoroborate (**3**7) (1.55 g, 6.90 mmol, 34%) as a white solid. ^{1}H NMR (400 MHz, acetone-d_6) δ 7.07 (dd, *J* = 5.3, 3.3 Hz, 2H, Ar*H*), 6.95 (dd, *J* = 5.5, 3.1 Hz, 2H, Ar*H*), 2.75 (dd, *J* = 9.9, 3.6 Hz, 4H, ArC*H*$_2$), 1.38 – 1.21 (m, 1H, C*H*-BF_3K). ^{13}C NMR (101 MHz, acetone-d_6) δ 148.3, 125.6, 124.6, 36.8. ^{19}F NMR (376 MHz, acetone-d_6) δ -146.3 (d, *J* = 92.8 Hz). Spectroscopic data was consistent with the values reported in the literature.[18]

[17] W.-Z. Weng, H. Liang, B. Zhang, *Org. Lett.* **2018**, *20*, 4979–4983.
[18] H. Huang, G. Zhang, L. Gong, S. Zhang, Y. Chen, *J. Am. Chem. Soc.* **2014**, *136*, 2280–2283.

5. Purification-free Synthesis of EBX Reagents

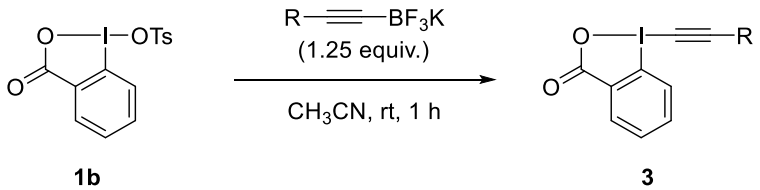
Optimization procedure:



1 **3a**

A capped oven dried microwave vial charged with hypervalent iodine reagent **1** (0.10 mmol, 1.0 equiv.) and alkyne **2** (1.05-1.50 equiv.) was evacuated and backfilled with N_2 (3x). Solvent was added under N_2 and the reaction was stirred at rt for the indicated amount of time. To the mixture was added a sat. sol. of $NaHCO_3$ (2 mL) and the mixture was vigorously stirred open to air for 1 h. Water (2 mL) was added and the mixture was extracted with 4 x 3 mL of DCM, the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford **3a**. ^{1}H NMR yield was determined dissolving **3a** in $CDCl_3$ and adding CH_2Br_2 (3.6 µL, 0.051 mmol, 0.51 equiv.) as internal standard.

General procedure B:



1b **3**

A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (167 mg, 0.400 mmol, 1.0 equiv.) and potassium alkynyltrifluoroborate (0.50 mmol, 1.25 equiv.) was evacuated and backfilled with N_2 (3x). Dry acetonitrile (4 mL) was added under N_2 and the reaction was stirred at rt for 1 h. To the mixture was added a sat. sol. of $NaHCO_3$ (8 mL) and the mixture was vigorously stirred open to air for 1 h. Water (10 mL) was added and the mixture was extracted with 3 x 20 mL of DCM, the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude EBX was triturated in pentane, which induced precipitation if it was an oil. The pentane layer was discarded with care to leave the solid in the flask. This process was repeated 2 more times then the solid was dried *in vacuo* to afford **3**.

Note: Purity of the product obtained was determined using ^{1}H NMR by dissolving the entirety of the compound in $CDCl_3$ (~4 mL) and adding CH_2Br_2 (14.0 µL, 0.1975 mmol, 0.49 equiv.) as internal standard.

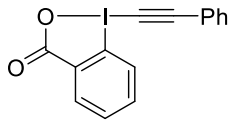
Purity is determined based on the signal of CH_2Br_2 (4.93 ppm) normalize at I = 1 and an aromatic signal of the EBX corresponding to 1 H:

$$n(EBX)_{eff} = \frac{\frac{I_{EBX}}{N_{EBX}} * n_{std} * N_{std}}{I_{std}} = \frac{\frac{I_{EBX}}{1} * 0.1975 * 2}{1} = I_{EBX} * 0.3950$$

$$p_{EBX} = \frac{n(EBX)_{eff}}{n(EBX)_{theo}} = \frac{n(EBX)_{eff}}{\frac{m_{EBX}}{MW_{EBX}}}$$

$n(EBX)_{eff}$: moles of EBX determined by NMR (in mmol).
$n(EBX)_{theo}$: moles of EBX calculated from the mass obtained if 100% pure (in mmol).
I_{EBX}: Integral of the EBX signal.
I_{std}: Integral of the standard (CH_2Br_2) signal.
N_{EBX}: Number of protons corresponding the EBX signal.
N_{std}: Number of protons corresponding the standard (CH_2Br_2) signal.
m_{EBX}: mass of EBX obtained at the end of the reaction (in mg).
MW_{EBX}: Molecular weight of the EBX (in mg/mmol)
p_{EBX}: purity of the EBX

1-[Phenylethynyl]-1,2-benziodoxol-3-(1*H*)-one (3a):



3a

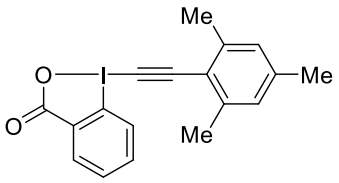
Synthesized following **general procedure B** starting from potassium trifluoro(phenylethynyl)borate (**2a**) (104 mg, 0.500 mmol). 1-[Phenylethynyl]-1,2-benziodoxol-3-(1*H*)-one (**3a**) (119.7 mg, 0.3318 mmol, 83%, 97% purity) was obtained as a slightly yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.37 (m, 1H, Ar*H*), 8.29 – 8.22 (m, 1H, Ar*H*), 7.81 – 7.72 (m, 2H, Ar*H*), 7.63 – 7.57 (m, 2H, Ar*H*), 7.52 – 7.39 (m, 3H, Ar*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 135.0, 133.0, 132.6, 131.7, 131.5, 130.9, 128.9, 126.4, 120.7, 116.3, 106.7, 50.3. Spectroscopic data was consistent with the values reported in the literature.[19]

$$n(EBX)_{eff} = 0.84 * 0.3950 = 0.3318\, mmol$$

$$p_{EBX} = \frac{0.3318}{\frac{119.7}{348.14}} = 0.9651 = 97\%\, purity$$

1-[Mesitylethynyl]-1,2-benziodoxol-3-(1*H*)-one (3b):

[19] D. P. Hari, J. Waser, *J. Am. Chem. Soc.* **2016**, *138*, 2190–2193.



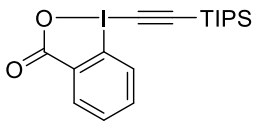
3b

Synthesized following **general procedure B** starting from potassium trifluoro(mesitylethynyl)borate (**17**) (125 mg, 0.500 mmol). The reaction was stirred at rt for 2 h. 1-[Mesitylethynyl]-1,2-benziodoxol-3-(1*H*)-one (**3b**) (148.2 mg, 0.3792 mmol, 95%, 99% purity) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.38 (m, 1H, Ar*H*), 8.33 – 8.25 (m, 1H, Ar*H*), 7.79 – 7.71 (m, 2H, Ar*H*), 6.95 (s, 2H, Mes*H*), 2.47 (s, 6H, C*H*$_3$), 2.34 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 142.4, 141.0, 134.9, 132.7, 131.7, 131.6, 128.3, 126.2, 117.6, 116.7, 105.6, 55.7, 21.7, 21.3. Spectroscopic data was consistent with the values reported in the literature.[20]

$$n(EBX)_{eff} = 0.96 * 0.3950 = 0.3792\ mmol$$

$$p_{EBX} = \frac{0.3792}{\frac{148.2}{390.21}} = 0.9984 = 99\%\ purity$$

1-[(Triisopropylsilyl)ethynyl]-1,2-benziodoxol-3-(1*H*)-one (3c):



3c

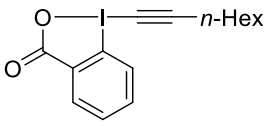
Synthesized following **general procedure B** starting from Potassium trifluoro((triisopropylsilyl)ethynyl)borate (**18**) (144 mg, 0.500 mmol). 1-[(Triisopropylsilyl)ethynyl]-1,2-benziodoxol-3-(1*H*)-one (**3c**) (159.9 mg, 0.3713 mmol, 93%, 99% purity) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.37 (m, 1H, Ar*H*), 8.33 – 8.24 (m, 1H, Ar*H*), 7.79 – 7.70 (m, 2H, Ar*H*), 1.18 – 1.10 (m, 21H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 134.8, 132.5, 131.6, 131.6, 126.2, 115.7, 114.3, 64.8, 18.6, 11.3. Spectroscopic data was consistent with the values reported in the literature.[19]

$$n(EBX)_{eff} = 0.94 * 0.3950 = 0.3713\ mmol$$

[20] R. Frei, M. D. Wodrich, D. P. Hari, P. A. Borin, C. Chauvier, J. Waser, *J. Am. Chem. Soc.* **2014**, *136*, 16563–16573.

$$p_{EBX} = \frac{\frac{0.3713}{159.9}}{428.38} = 0.9947 = 99\%\ purity$$

1-[Oct-1-yn-1-yl]-1,2-benziodoxol-3-(1*H*)-one (3d):



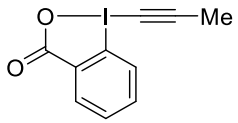
3d

Synthesized following **general procedure B** starting from Potassium trifluoro(oct-1-yn-1-yl)borate (**19**) (108 mg, 0.500 mmol). 1-[Oct-1-yn-1-yl]-1,2-benziodoxol-3-(1*H*)-one (**3d**) (134.8 mg, 0.3753 mmol, 94%, 99% purity) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.34 (m, 1H, Ar*H*), 8.21 – 8.13 (m, 1H, Ar*H*), 7.78 – 7.68 (m, 2H, Ar*H*), 2.58 (t, *J* = 7.1 Hz, 2H, C≡C-CH_2), 1.64 (p, *J* = 7.2 Hz, 2H, CH_2), 1.50 – 1.39 (m, 2H, CH_2), 1.38 – 1.25 (m, 4H, CH_2), 0.90 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 134.7, 132.5, 131.7, 131.6, 126.2, 115.7, 109.9, 39.4, 31.3, 28.7, 28.3, 22.6, 20.6, 14.2. Spectroscopic data was consistent with the values reported in the literature.[20]

$$n(EBX)_{eff} = 0.95 * 0.3950 = 0.3753\ mmol$$

$$p_{EBX} = \frac{\frac{0.3753}{134.8}}{356.20} = 0.9917 = 99\%\ purity$$

1-[Prop-1-yn-1-yl]-1,2-benziodoxol-3-(1*H*)-one (3e):



3e

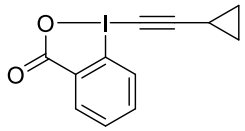
Synthesized following **general procedure B** starting from potassium trifluoro(prop-1-yn-1-yl)borate (**21**) (73.0 mg, 0.500 mmol). 1-[Prop-1-yn-1-yl]-1,2-benziodoxol-3-(1*H*)-one (**3e**) (105.9 mg, 0.3476 mmol, 87%, 94% purity) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.33 (m, 1H, Ar*H*), 8.22 – 8.13 (m, 1H, Ar*H*), 7.79 – 7.67 (m, 2H, Ar*H*), 2.26 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$)[21] δ 166.6, 134.8, 132.5, 131.6, 126.3, 115.6, 105.1, 39.0, 5.7. Spectroscopic data was consistent with the values reported in the literature.[20]

$$n(EBX)_{eff} = 0.88 * 0.3950 = 0.3476\ mmol$$

[21]One aromatic carbon signal was not resolved, consistent with literature.

$$p_{EBX} = \frac{0.3476}{\frac{105.9}{286.07}} = 0.9390 = 94\%\ purity$$

1-[Cyclopropylethynyl]-1,2-benziodoxol-3-(1*H*)-one (3f):



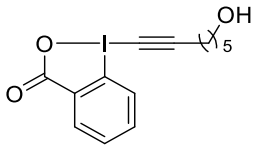
3f

Synthesized following **general procedure B** starting from potassium (cyclopropylethynyl)trifluoroborate (**22**) (86.0 mg, 0.500 mmol). 1-[Cyclopropylethynyl]-1,2-benziodoxol-3-(1*H*)-one (**3f**) (115.7 mg, 0.3555 mmol, 89%, 96% purity) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.34 (m, 1H, Ar*H*), 8.18 – 8.12 (m, 1H, Ar*H*), 7.79 – 7.68 (m, 2H, Ar*H*), 1.65 – 1.56 (m, 1H, C*H*), 1.05 – 0.97 (m, 2H, CH_2), 0.97 – 0.91 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 134.7, 132.4, 131.6, 131.5, 126.2, 115.9, 113.4, 35.1, 9.8, 1.1. Spectroscopic data was consistent with the values reported in the literature.[20]

$$n(EBX)_{eff} = 0.90 * 0.3950 = 0.3555\ mmol$$

$$p_{EBX} = \frac{0.3555}{\frac{115.7}{312.10}} = 0.9590 = 96\%\ purity$$

1-[7-Hydroxyhept-1-yn-1-yl]-1,2-benziodoxol-3-(1*H*)-one (3g):



3g

Synthesized following **general procedure B** starting from potassium trifluoro(7-hydroxyhept-1-yn-1-yl)borate (**24**) (109 mg, 0.500 mmol). 1-[7-Hydroxyhept-1-yn-1-yl]-1,2-benziodoxol-3-(1*H*)-one (**3g**) (128.0 mg, 0.3476 mmol, 87%, 97% purity) as a beige solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.2, 2.0 Hz, 1H, Ar*H*), 8.20 – 8.13 (m, 1H, Ar*H*), 7.74 (pd, *J* = 7.2, 1.6 Hz, 2H, Ar*H*), 3.69 (t, *J* = 6.1 Hz, 2H, CH_2OH), 2.62 (t, *J* = 7.0 Hz, 2H, C≡C-CH_2CH$_2$), 1.93 (s, 1H, O*H*), 1.75 – 1.51 (m, 6H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$)[22] δ 166.9, 134.8, 132.4,

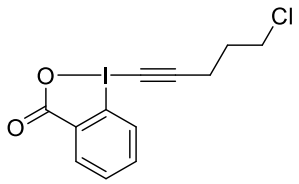
[22]One aromatic carbon signal is not resolved, probably two signals overlapping at 131.6 ppm.

131.6, 126.4, 115.7, 109.6, 62.5, 39.5, 32.1, 28.1, 25.3, 20.6. Spectroscopic data was consistent with the values reported in the literature.[20]

$$n(EBX)_{eff} = 0.88 * 0.3950 = 0.3476\, mmol$$

$$p_{EBX} = \frac{0.3476}{\frac{128.0}{358.17}} = 0.9726 = 97\%\, purity$$

1-[5-Chloropent-1-yn-1-yl]-1,2-benziodoxol-3-(1*H*)-one (3h):



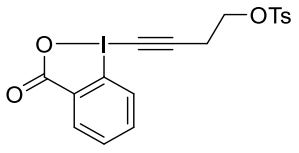
3h

Synthesized following **general procedure B** starting from potassium (5-chloropent-1-yn-1-yl)trifluoroborate (**25**) (104 mg, 0.500 mmol). 1-[5-Chloropent-1-yn-1-yl]-1,2-benziodoxol-3-(1*H*)-one (**3h**) (129.9 mg, 0.3713 mmol, 93%, 99% purity) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.34 (m, 1H, Ar*H*), 8.20 – 8.13 (m, 1H, Ar*H*), 7.81 – 7.69 (m, 2H, Ar*H*), 3.70 (t, *J* = 6.1 Hz, 2H, CH_2CH_2Cl), 2.82 (t, *J* = 6.9 Hz, 2H, C≡C-CH_2CH_2), 2.10 (p, *J* = 6.8 Hz, 2H, CH_2CH_2CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 134.9, 132.6, 131.7, 131.6, 126.3, 115.7, 107.2, 43.3, 41.3, 30.8, 18.0. Spectroscopic data was consistent with the values reported in the literature.[20]

$$n(EBX)_{eff} = 0.94 * 0.3950 = 0.3713\, mmol$$

$$p_{EBX} = \frac{0.3713}{\frac{129.9}{348.56}} = 0.9963 = 99\%\, purity$$

1-[4-(Tosyloxy)but-1-yn-1-yl]-1,2-benziodoxol-3-(1*H*)-one (3i):



3i

Synthesized following **general procedure B** starting from potassium trifluoro(4-(tosyloxy)but-1-yn-1-yl)borate (**26**) (112 mg, 0.500 mmol). 1-[4-(Tosyloxy)but-1-yn-1-yl]-1,2-benziodoxol-3-(1*H*)-one (**3i**) (132.8 mg, 0.2706 mmol, 68%, 96% purity) was obtained as a beige solid. Mp (Dec.): 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.4, 1.7 Hz, 1H, Ar*H*), 8.20 (dd, *J* = 8.3, 1.0 Hz, 1H, Ar*H*), 7.83 – 7.77 (m, 3H, Ar*H*), 7.74 (td, *J* = 7.3, 1.0 Hz, 1H, Ar*H*), 7.36 –

7.30 (m, 2H, Ar*H*), 4.22 (t, *J* = 6.2 Hz, 2H, CH_2CH_2OTs), 2.96 (t, *J* = 6.2 Hz, 2H, C≡C-CH_2CH_2), 2.41 (s, 3H, $ArCH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 145.6, 135.3, 132.6, 132.5, 131.7, 131.3, 130.2, 128.1, 126.7, 115.7, 102.7, 67.0, 43.4, 21.8, 21.6. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}IO_5S^+$ 470.9758; Found 470.9771.

For the determination of the purity of **3i** the signal from the EBX was changed to a triplet at 4.22 ppm (2H) due to some impurity overlapping the aromatic signals.

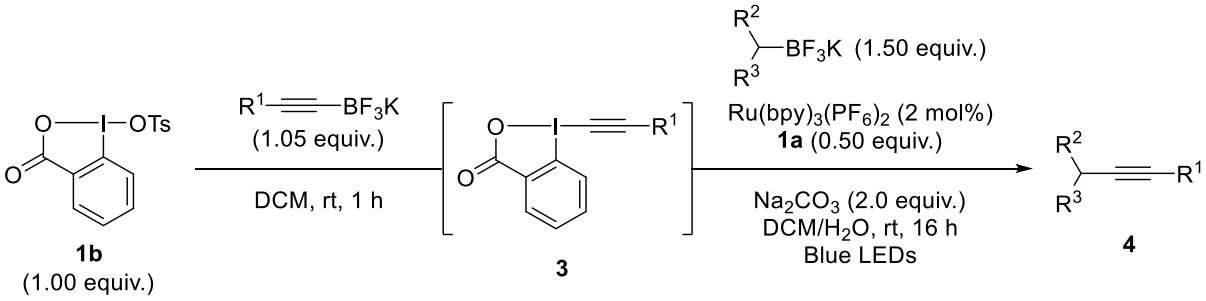
$$n(EBX)_{eff} = \frac{1.37}{2} * 0.3950 = 0.2706\ mmol$$

$$p_{EBX} = \frac{0.2706}{\frac{132.8}{470.28}} = 0.9582 = 96\%\ purity$$

6. One-pot two-step Transformations

6.1 Deboronative Alkynylation

General procedure C:

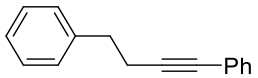


A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (167 mg, 0.400 mmol, 1.00 equiv.) and potassium alkynyltrifluoroborate (0.420 mmol, 1.05 equiv.) was evacuated and backfilled with N_2 (3x). Dry DCM (2 mL), previously degassed with argon for 30 min, was added under N_2 and the reaction was stirred at rt for 1 h. A solution of Na_2CO_3 (84.8 mg, 0.800 mmol, 2.00 equiv.) in water (1 mL), previously degassed with argon for 30 min, was added under N_2 and the mixture was stirred vigorously for 5 min.

A test tube charged with $Ru(bpy)_3(PF_6)_2$ (6.9 mg, 8.0 µmol, 0.02 equiv.), 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one (**1a**) (52.8 mg, 0.200 mmol, 0.50 equiv.) and potassium alkyltrifluoroborate (0.600 mmol, 1.50 equiv.) was evacuated and backfilled with N_2 (3x). The biphasic solution of crude **3** was added under N_2 (+ 1 mL of water and DCM to rinse the vial containing the solution). The reaction was stirred to rt under blue LEDs irradiation for 16 h. Water (20 mL) was added and the mixture was extracted with DCM (3 x 20 mL), the combined

organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude compound was purified by column chromatography to afford **4**.

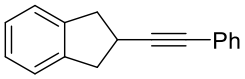
But-1-yne-1,4-diyldibenzene (4a):



4a

Synthesized following **general procedure C** starting from potassium trifluoro(phenylethynyl)borate (**2a**) (87.4 mg, 0.420 mmol) and potassium trifluoro(phenethyl)borate (127.2 mg, 0.6000 mmol). The crude product was purified by column chromatography (Pentane) to afford but-1-yne-1,4-diyldibenzene (**4a**) (48.5 mg, 0.235 mmol, 59%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.23 (m, 10H, Ar*H*), 2.95 (t, *J* = 7.5 Hz, 2H, ArC*H*$_2$CH$_2$), 2.72 (t, *J* = 7.5 Hz, 2H, C≡C-C*H*$_2$CH$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 131.7, 128.7, 128.5, 128.3, 127.8, 126.4, 124.0, 89.6, 81.4, 35.3, 21.8. Spectroscopic data was consistent with the values reported in the literature.[18]

2-(Phenylethynyl)-2,3-dihydro-1*H*-indene (4b):



4b

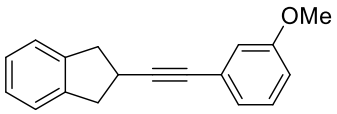
Synthesized following **general procedure C** starting from potassium trifluoro(phenylethynyl)borate (**2a**) (87.4 mg, 0.420 mmol) and potassium (2,3-dihydro-1*H*-inden-2-yl)trifluoroborate (**37**) (134.4 mg, 0.6000 mmol). The crude product was purified by column chromatography (Pentane) to afford 2-(phenylethynyl)-2,3-dihydro-1*H*-indene (**4b**) (63.3 mg, 0.290 mmol, 72%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H, Ar*H*), 7.33 – 7.27 (m, 3H, Ar*H*), 7.27 – 7.22 (m, 2H, Ar*H*), 7.22 – 7.16 (m, 2H, Ar*H*), 3.46 (p, *J* = 8.5 Hz, 1H, C≡C-C*H*(CH$_2$)$_2$), 3.33 (dd, *J* = 15.1, 7.9 Hz, 2H, ArC*H*$_2$CH), 3.15 (dd, *J* = 15.3, 8.8 Hz, 2H, ArC*H*$_2$CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 131.8, 128.3, 127.8, 126.7, 124.5, 123.9, 93.1, 80.7, 40.5, 30.9. Spectroscopic data was consistent with the values reported in the literature.[18]

Large scale synthesis of 4b:

A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (418 mg, 1.00 mmol, 1.00 equiv.) and potassium trifluoro(phenylethynyl)borate (**2a**) (218 mg, 1.05 mmol, 1.05 equiv.) was evacuated and backfilled with N_2 (3x). Dry DCM (5 mL), previously degassed with argon for 30 min, was added under N_2 and the reaction was stirred at rt for 1 h. A solution of Na_2CO_3 (212 mg, 2.00 mmol, 2.00 equiv.) in water (2.5 mL), previously degassed with argon for 30 min, was added under N_2 and the mixture was stirred vigorously for 5 min.

A test tube charged with $Ru(bpy)_3(PF_6)_2$ (17.2 mg, 20.0 µmol, 0.02 equiv.), 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one (**1a**) (132 mg, 0.500 mmol, 0.50 equiv.) and potassium (2,3-dihydro-1*H*-inden-2-yl)trifluoroborate (**37**) (336 mg, 1.50 mmol, 1.50 equiv.) was evacuated and backfilled with N_2 (3x). The biphasic solution of crude **3** was added under N_2 (+ 2.5 mL of water and 1 mL of DCM to rinse the vial containing the solution). The reaction was stirred to rt under blue LEDs irradiation for 16 h. Water (20 mL) was added and the mixture was extracted with DCM (3 x 30 mL), the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude compound was purified by column chromatography (Pentane) to afford 2-(phenylethynyl)-2,3-dihydro-1*H*-indene (**4b**) (130 mg, 0.594 mmol, 59%) as a white solid.

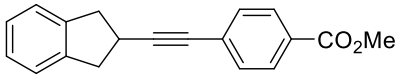
2-((3-Methoxyphenyl)ethynyl)-2,3-dihydro-1*H*-indene (4c):



4c

Synthesized following **general procedure C** starting from potassium trifluoro((3-methoxyphenyl)ethynyl)borate (**27**) (100 mg, 0.420 mmol) and potassium (2,3-dihydro-1*H*-inden-2-yl)trifluoroborate (**37**) (134 mg, 0.600 mmol). The crude product was purified by column chromatography (Pentane/DCM, 1:0 to 85:15) to afford 2-((3-methoxyphenyl)ethynyl)-2,3-dihydro-1*H*-indene (**4c**) (72.8 mg, 0.293 mmol, 73%) as a colorless amorphous solid. R_f (Pentane/DCM, 85:15) = 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H, Ar*H*), 7.21 – 7.17 (m, 3H, Ar*H*), 7.02 (dt, *J* = 7.6, 1.2 Hz, 1H, Ar*H*), 6.96 (dd, *J* = 2.6, 1.4 Hz, 1H, Ar*H*), 6.85 (ddd, *J* = 8.4, 2.7, 1.0 Hz, 1H, Ar*H*), 3.80 (s, 3H, OC*H*$_3$), 3.45 (p, *J* = 8.6 Hz, 1H, C≡C-C*H*$(CH_2)_2$), 3.33 (dd, *J* = 15.1, 7.9 Hz, 2H, ArC*H*$_2$CH), 3.15 (dd, *J* = 15.3, 8.8 Hz, 2H, ArC*H*$_2$CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 142.1, 129.4, 126.7, 124.9, 124.5, 124.3, 116.5, 114.5, 93.0, 80.6, 55.4, 40.4, 30.9. HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}O^+$ 249.1274; Found 249.1268.

Methyl 4-((2,3-dihydro-1*H*-inden-2-yl)ethynyl)benzoate (4d):

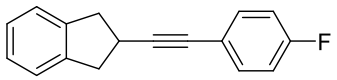


4d

Synthesized following **general procedure C** starting from potassium trifluoro((4-(methoxycarbonyl)phenyl)ethynyl)borate (**29**) (112 mg, 0.420 mmol) and (2,3-dihydro-1*H*-inden-2-yl)trifluoroborate (**37**) (134 mg, 0.600 mmol). The crude product was purified by column chromatography (Pentane/DCM, 1:0 to 7:3) to afford methyl 4-((2,3-dihydro-1*H*-inden-2-yl)ethynyl)benzoate (**4d**) (91.8 mg, 0.332 mmol, 83%) as a white solid. R_f (Pentane/DCM, 7:3) = 0.33; Mp: 102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H, Ar*H*), 7.56 – 7.50 (m, 2H, Ar*H*), 7.34 – 7.28 (m, 2H, Ar*H*), 7.28 – 7.23 (m, 2H, Ar*H*), 3.98 (s,

3H, OC*H*$_3$), 3.53 (p, *J* = 8.4 Hz, 1H, C≡C-C*H*(CH$_2$)$_2$), 3.40 (dd, *J* = 14.9, 7.6 Hz, 2H, ArC*H*$_2$CH), 3.21 (dd, *J* = 15.3, 8.5 Hz, 2H, ArC*H*$_2$CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 141.9, 131.7, 129.5, 129.1, 128.7, 126.8, 124.5, 96.6, 80.2, 52.3, 40.3, 30.9. HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}O_2^+$ 277.1223; Found 277.1226.

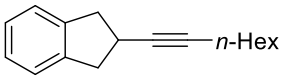
2-((4-Fluorophenyl)ethynyl)-2,3-dihydro-1*H*-indene (4e):



4e

Synthesized following **general procedure C** starting from potassium trifluoro((4-fluorophenyl)ethynyl)borate (**30**) (95 mg, 0.42 mmol) and (2,3-dihydro-1*H*-inden-2-yl)trifluoroborate (**37**) (134 mg, 0.600 mmol). The crude product was purified by column chromatography (Pentane/DCM, 1:0 to 85:15) to afford 2-((4-fluorophenyl)ethynyl)-2,3-dihydro-1*H*-indene (**4e**) (65.2 mg, 0.276 mmol, 69%) as a colorless amorphous solid. R_f (Pentane/DCM; 95:5) = 0.63; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H, Ar*H*), 7.26 – 7.22 (m, 2H, Ar*H*), 7.21 – 7.15 (m, 2H, Ar*H*), 7.03 – 6.95 (m, 2H, Ar*H*), 3.44 (p, *J* = 8.6 Hz, 1H, C≡C-C*H*(CH$_2$)$_2$), 3.32 (dd, *J* = 15.0, 7.9 Hz, 2H, ArC*H*$_2$CH), 3.13 (dd, *J* = 15.2, 8.6 Hz, 2H, ArC*H*$_2$CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 248.5 Hz), 142.1, 133.5 (d, *J* = 8.2 Hz), 126.7, 124.5, 119.9 (d, *J* = 3.6 Hz), 115.5 (d, *J* = 21.9 Hz), 92.8, 79.7, 40.4, 30.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.1. HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{17}H_{13}F^+$ 236.0996; Found 236.0994.

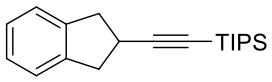
2-(Oct-1-yn-1-yl)-2,3-dihydro-1*H*-indene (4f):



4f

Synthesized following **general procedure C** starting from potassium trifluoro(oct-1-yn-1-yl)borate (**19**) (91 mg, 0.42 mmol) and (2,3-dihydro-1*H*-inden-2-yl)trifluoroborate (**37**) (134 mg, 0.600 mmol). The crude product was purified by column chromatography (Pentane) to afford 2-(oct-1-yn-1-yl)-2,3-dihydro-1*H*-indene (**4f**) (34.1 mg, 0.151 mmol, 38%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.11 (m, 4H, Ar*H*), 3.26 – 3.14 (m, 3H, ArC*H*$_2$CH + C≡C-C*H*(CH$_2$)$_2$), 3.04 – 2.92 (m, 2H, ArC*H*$_2$CH), 2.17 (td, *J* = 7.1, 1.7 Hz, 2H, C≡C-C*H*$_2$CH$_2$), 1.54 – 1.44 (m, 2H, C*H*$_2$), 1.42 – 1.23 (m, 6H, C*H*$_2$), 0.90 (t, *J* = 6.9 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 126.5, 124.4, 83.3, 80.7, 40.8, 31.5, 30.5, 29.2, 28.7, 22.7, 19.0, 14.2. Spectroscopic data was consistent with the values reported in the literature.[18]

((2,3-Dihydro-1*H*-inden-2-yl)ethynyl)triisopropylsilane (4g):

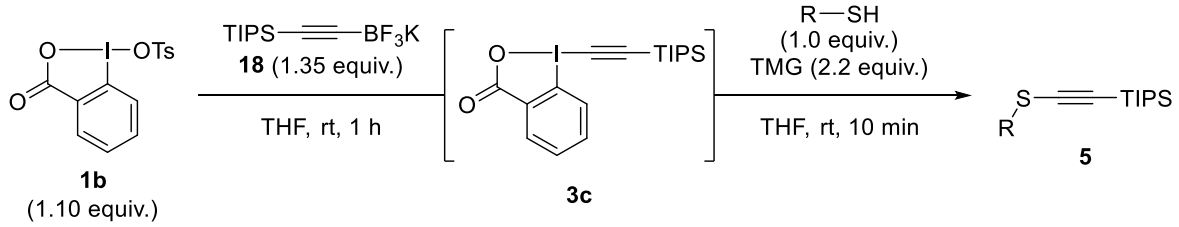


4g

Synthesized following **general procedure C** starting from potassium trifluoro((triisopropylsilyl)ethynyl)borate (**18**) (121 mg, 0.420 mmol) and (2,3-dihydro-1*H*-inden-2-yl)trifluoroborate (**37**) (134 mg, 0.600 mmol). The crude product was purified by column chromatography (Pentane) to afford ((2,3-dihydro-1*H*-inden-2-yl)ethynyl)triisopropylsilane (**4g**) (50.8 mg, 0.170 mmol, 43%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 4H, Ar*H*), 3.34 – 3.20 (m, 3H, ArC*H*$_2$CH + C≡C-C*H*$(CH_2)_2$), 3.13 – 3.00 (m, 2H, ArC*H*$_2$CH), 1.13 – 0.97 (m, 21H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 126.6, 124.4, 112.4, 80.3, 40.9, 31.3, 18.8, 11.4. Spectroscopic data was consistent with the values reported in the literature.[18]

6.2 Thiolakynylation

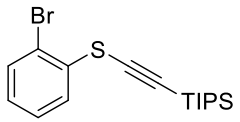
General procedure D:



A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (184 mg, 0.440 mmol, 1.10 equiv.) and potassium trifluoro((triisopropylsilyl)ethynyl)borate (**18**) (156 mg, 0.540 mmol, 1.35 equiv.) was evacuated and backfilled with N_2 (3x). Dry THF (2 mL) was added under N_2 and the reaction was stirred at rt for 1 h. To the mixture was added distilled 1,1,3,3-tetramethylguanidine (55 µL, 0.44 mmol, 1.10 equiv.) and it was stirred at rt for 5 min.

To a microwave vial containing a solution of thiol (0.40 mmol, 1.00 equiv.) in dry THF (0.5 mL) was added 1,1,3,3-tetramethylguanidine (55 µL, 0.44 mmol, 1.10 equiv.). The mixture was stirred at rt open to air for 5 min then the solution of crude **3c** was added (+ THF (0.5 mL) to rinse the vial). The reaction was stirred at rt open to air for 10 min then a sat. sol. of $NaHCO_3$ (15 mL) was added. The mixture was extracted with EtOAc (3 x 20 mL), the combined layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography to obtain **5**.

(((2-Bromophenyl)thio)ethynyl)triisopropylsilane (5a):



5a

Synthesized following **general procedure D** starting from 2-bromothiophenol (**14**) (48 µL, 0.40 mmol). The crude product was purified by column chromatography (Pentane) to afford (((2-bromophenyl)thio)ethynyl)triisopropylsilane (**5a**) (126 mg, 0.332 mmol, 83%, 97% purity) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar*H*), 7.49 (dd, *J* = 7.9, 1.3 Hz, 1H, Ar*H*), 7.39 – 7.32 (m, 1H, Ar*H*), 7.12 – 7.05 (m, 1H, Ar*H*), 1.18 – 1.12 (m, 21H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7, 132.8, 128.2, 127.5, 127.2, 119.6, 105.4, 90.8, 18.8, 11.5. Spectroscopic data was consistent with the values reported in the literature.[23]

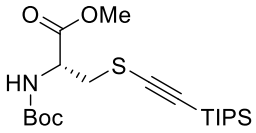
Note: The impurity observed is (triisopropylsilyl)acetylene (**38**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 1H, C≡C*H*), 1.09 (m, 21H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 94.9, 86.4, 18.6, 11.2.

Purity was determined using the C≡C*H* signal of **38** and an Ar*H* signal of **5a**:

$$p = \frac{I_{product} * MW_{product}}{\left(I_{product} * MW_{product}\right) + \left(I_{byproduct} * MW_{byproduct}\right)}$$

$$p = \frac{1 * 369.44}{(1 * 369.44) + (0.06 * 182.38)} = 0.971 = 97\%\ purity$$

Methyl *N*-(*tert*-butoxycarbonyl)-*S*-((triisopropylsilyl)ethynyl)-*L*-cysteinate (5b):



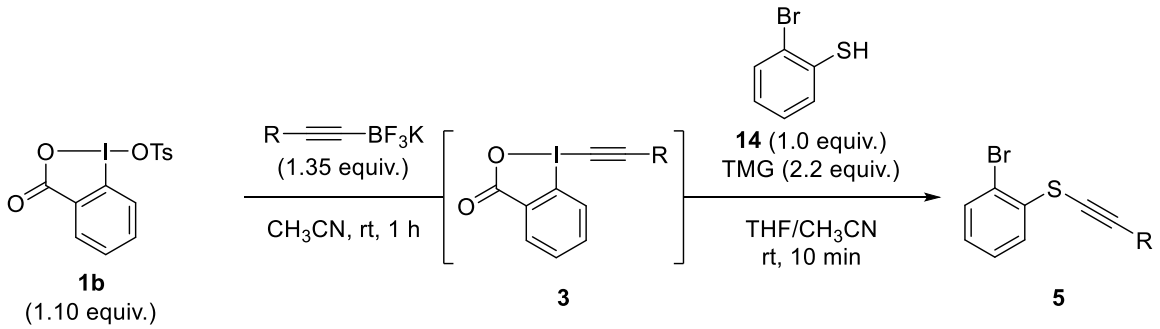
5b

Synthesized following **general procedure D** starting from *N*-(*tert*-Butoxycarbonyl)-*L*-cysteine methyl ester (97.0 mg, 0.40 mmol). The crude product was purified by column chromatography (Pentane/EtOAc, 95:5) to afford methyl *N*-(*tert*-butoxycarbonyl)-*S*-((triisopropylsilyl)ethynyl)-*L*-cysteinate (**5b**) (114 mg, 0.275 mmol, 69%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (d, *J* = 8.4 Hz, 1H, BocN*H*), 4.74 – 4.62 (m, 1H, C*H*NHBoc), 3.78 (s, 3H, OCH_3), 3.25 (dd, *J* = 13.6, 4.2 Hz, 1H, SCH_2CH), 3.13 (dd, *J* = 13.6, 5.9 Hz, 1H, SCH_2CH), 1.44 (s, 9H, C(CH_3)$_3$), 1.10 – 1.04 (m, 21H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 155.3, 98.3, 94.6,

[23] R. Frei, J. Waser, *J. Am. Chem. Soc.* **2013**, *135*, 9620–9623.

80.5, 54.0, 52.8, 38.6, 28.4, 18.7, 11.4. Spectroscopic data was consistent with the values reported in the literature.[23]

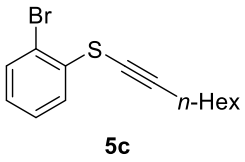
General procedure E:



A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (184 mg, 0.440 mmol, 1.10 equiv.) and potassium alkynyltrifluoroborate (0.54 mmol, 1.35 equiv.) was evacuated and backfilled with N_2 (3x). Dry CH_3CN (2 mL) was added under N_2 and the reaction was stirred at rt for 1 h. To the mixture was added distilled 1,1,3,3-tetramethylguanidine (55 µL, 0.44 mmol, 1.10 equiv.) and it was stirred at rt for 5 min.

To a microwave vial containing a solution of 2-bromothiophenol (**14**) (48 µL, 0.40 mmol, 1.00 equiv.) in dry THF (0.75 mL) was added 1,1,3,3-tetramethylguanidine (55 µL, 0.44 mmol, 1.10 equiv.). The mixture was stirred at rt open to air for 5 min then the solution of crude **3c** was added (+ THF (0.75 mL) to rinse the vial). The reaction was stirred at rt open to air for 10 min then a sat. sol. of $NaHCO_3$ (15 mL) was added. The mixture was extracted with Et_2O (3 x 20 mL), the combined layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography to obtain **5**.

(2-Bromophenyl)(oct-1-yn-1-yl)sulfane (5c):

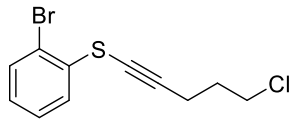


5c

Synthesized following **general procedure E** starting from potassium trifluoro(oct-1-yn-1-yl)borate (**19**) (117 mg, 0.540 mmol). The crude product was purified by column chromatography (Pentane) to afford (2-bromophenyl)(oct-1-yn-1-yl)sulfane (**5c**) (73 mg, 0.24 mmol, 61%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar*H*), 7.47 (dd, *J* = 7.9, 1.3 Hz, 1H, Ar*H*), 7.37 – 7.31 (m, 1H, Ar*H*), 7.09 – 7.03 (m, 1H, Ar*H*), 2.48 (t, *J* = 7.1 Hz, 2H, C≡C-C*H*$_2$CH$_2$), 1.67 – 1.57 (m, 2H, C*H*$_2$), 1.50 – 1.41 (m, 2H, C*H*$_2$), 1.38 – 1.28 (m, 4H, C*H*$_2$), 0.91 (t, *J* = 7.1 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ

135.7, 132.7, 128.1, 127.1, 126.9, 119.3, 102.1, 64.5, 31.4, 28.7, 28.7, 22.7, 20.5, 14.2. Spectroscopic data was consistent with the values reported in the literature.[20]

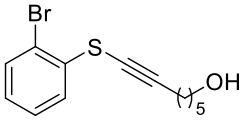
(2-Bromophenyl)(5-chloropent-1-yn-1-yl)sulfane (5d):



5d

Synthesized following **general procedure E** starting from potassium (5-chloropent-1-yn-1-yl)trifluoroborate (**25**) (113 mg, 0.540 mmol). The crude product was purified by column chromatography (Pentane) to afford (2-bromophenyl)(5-chloropent-1-yn-1-yl)sulfane (**5d**) (65 mg, 0.22 mmol, 56%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar*H*), 7.48 (dd, *J* = 7.9, 1.3 Hz, 1H, Ar*H*), 7.39 – 7.32 (m, 1H, Ar*H*), 7.11 – 7.04 (m, 1H, Ar*H*), 3.70 (t, *J* = 6.3 Hz, 2H, $CH_2C\mathit{H}_2Cl$), 2.70 (t, *J* = 6.8 Hz, 2H, C≡C-$C\mathit{H}_2CH_2$), 2.07 (p, *J* = 6.5 Hz, 2H, $CH_2C\mathit{H}_2CH_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 132.8, 128.2, 127.4, 126.9, 119.5, 99.7, 66.2, 43.7, 31.3, 17.9. Spectroscopic data was consistent with the values reported in the literature.[20]

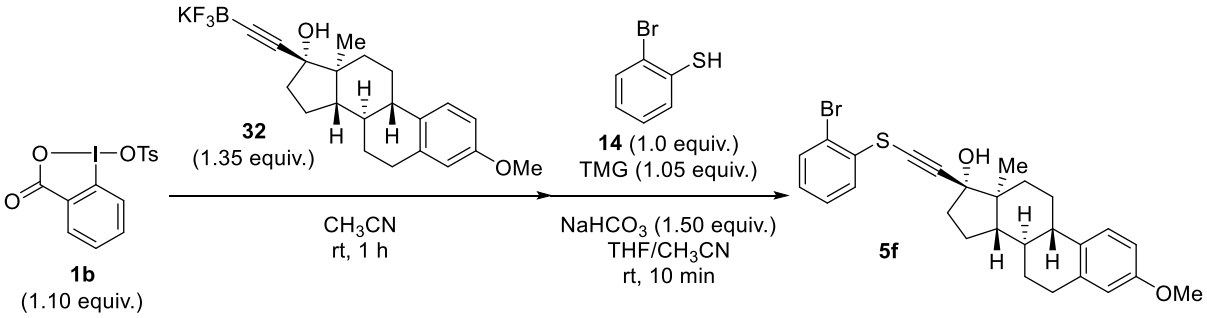
7-((2-Bromophenyl)thio)hept-6-yn-1-ol (5e):



5e

Synthesized following **general procedure E** starting from potassium trifluoro(7-hydroxyhept-1-yn-1-yl)borate (**24**) (118 mg, 0.540 mmol). The crude product was purified by column chromatography (Pentane/EtOAc, 95:5 to 65:35) to afford 7-((2-Bromophenyl)thio)hept-6-yn-1-ol (**5e**) (47.3 mg, 0.158 mmol, 40%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar*H*), 7.47 (dd, *J* = 7.9, 1.3 Hz, 1H, Ar*H*), 7.37 – 7.31 (m, 1H, Ar*H*), 7.10 – 7.02 (m, 1H, Ar*H*), 3.66 (t, *J* = 6.4 Hz, 2H, $CH_2C\mathit{H}_2OH$), 2.50 (t, *J* = 7.0 Hz, 2H, C≡C-$C\mathit{H}_2CH_2$), 1.71 – 1.57 (m, 4H, $C\mathit{H}_2$), 1.57 – 1.39 (m, 3H, $C\mathit{H}_2$ + O*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 132.7, 128.1, 127.2, 126.8, 119.4, 101.7, 64.8, 62.9, 32.3, 28.5, 25.2, 20.5. Spectroscopic data was consistent with the values reported in the literature.[20]

(8*R*,9*S*,13*S*,14*S*,17*S*)-17-(((2-Bromophenyl)thio)ethynyl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (5f):

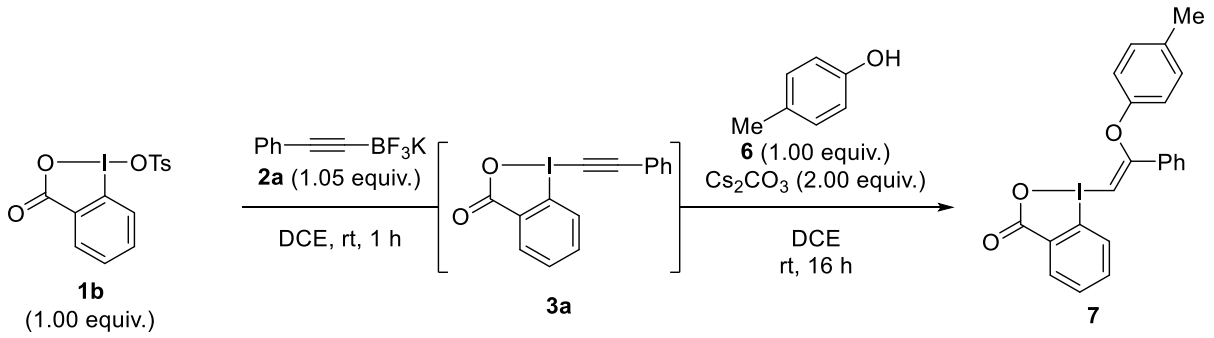


A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (184 mg, 0.440 mmol, 1.10 equiv.) and **32** (225 mg, 0.540 mmol, 1.35 equiv.) was evacuated and backfilled with N_2 (3x). Dry CH_3CN (2 mL) was added under N_2 and the reaction was stirred at rt for 1 h. To the mixture was added $NaHCO_3$ (50 mg, 0.60 mmol, 1.50 equiv.) and it was stirred at rt for 15 min open to air.

To a microwave vial containing a solution of 2-bromothiophenol (**14**) (48 µL, 0.40 mmol, 1.00 equiv.) in dry THF (0.75 mL) was added 1,1,3,3-tetramethylguanidine (53 µL, 0.42 mmol, 1.05 equiv.). The mixture was stirred at rt open to air for 5 min then the solution of crude EBX was added (+ THF (0.75 mL) to rinse the vial). The reaction was stirred at rt open to air for 10 min then a sat. sol. of $NaHCO_3$ (15 mL) was added. The mixture was extracted with Et_2O (3 x 20 mL), the combined layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography (Toluene/DCM, 1:1) to obtain (8*R*,9*S*,13*S*,14*S*,17*S*)-17-(((2-bromophenyl)thio)ethynyl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (**5f**) (102 mg, 0.205 mmol, 51%) as a slightly yellow solid. R_f (Toluene/DCM, 1:1) = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar*H*), 7.50 (dd, *J* = 7.9, 1.3 Hz, 1H, Ar*H*), 7.39 – 7.33 (m, 1H, Ar*H*), 7.21 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.12 – 7.06 (m, 1H, Ar*H*), 6.72 (dd, *J* = 8.6, 2.8 Hz, 1H, Ar*H*), 6.64 (d, *J* = 2.6 Hz, 1H, Ar*H*), 3.78 (s, 3H, OC*H*$_3$), 2.90 – 2.83 (m, 2H, C*H*$_2$), 2.49 – 2.34 (m, 2H, C*H*$_2$), 2.23 (td, *J* = 11.2, 4.2 Hz, 1H, ArC*H*(CH)(CH$_2$)), 2.18 – 2.08 (m, 1H, C*H*$_2$), 2.06 (bs, 1H, O*H*), 1.95 – 1.72 (m, 5H, C*H*$_2$ + C*H*), 1.57 – 1.31 (m, 4H, C*H*$_2$ + C*H*), 0.93 (s, 3H, C-C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 138.1, 134.8, 132.9, 132.6, 128.3, 127.6, 127.1, 126.5, 119.8, 113.9, 111.6, 104.3, 81.3, 72.1, 55.3, 50.0, 48.0, 43.7, 39.6, 39.5, 33.3, 30.0, 27.4, 26.6, 23.1, 13.0. HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{27}H_{29}BrO_2S^+$ 496.1066; Found 496.1062.

6.3 *O*-VBX Formation:

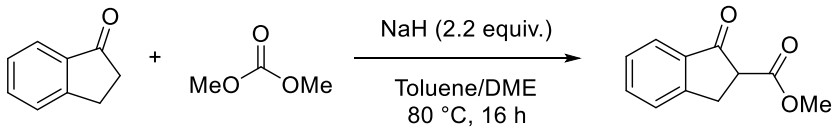
(*Z*)-1-[2-phenyl-2-(p-tolyloxy)vinyl]-1,2-benziodoxol-3-(1*H*)-one (7):



A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (167 mg, 0.400 mmol, 1.00 equiv.) and potassium trifluoro(phenylethynyl)borate (**2a**) (87 mg, 0.420 mmol, 1.05 equiv.) was evacuated and backfilled with N_2 (3x). Dry DCE (4 mL) was added under N_2 and the reaction was stirred at rt for 1 h. To the mixture was added Cs_2CO_3 (261 mg, 0.800 mmol, 2.0 equiv.) and it was stirred at rt for 15 min. Then, *p*-cresol (**6**) (43.3 mg, 0.400 mmol, 1.0 equiv.) was added and the reaction was stirred at rt for 16 h. A sat. sol. of $NaHCO_3$ (8 mL) was added and the mixture was stirred vigorously for 1 h. The mixture was extracted with DCM (3 x 20 mL), the combined layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (DCM/MeOH, 1:0 to 9:1) to obtain (*Z*)-1-[2-phenyl-2-(p-tolyloxy)vinyl]-1,2-benziodoxol-3-(1*H*)-one (**7**) (94 mg, 0.21 mmol, 52%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.41 (m, 1H, Ar*H*), 7.68 – 7.56 (m, 5H, Ar*H*), 7.48 – 7.37 (m, 3H, Ar*H*), 7.02 – 6.96 (m, 2H, Ar*H*), 6.77 – 6.72 (m, 2H, Ar*H*), 6.62 (s, 1H, C=C*H*), 2.22 (s, 3H, ArC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 165.5, 153.6, 133.6, 133.5, 133.5, 133.0, 131.7, 131.4, 130.8, 130.5, 129.2, 127.8, 125.4, 116.9, 114.5, 86.5, 20.6. Spectroscopic data was consistent with the values reported in the literature.[24]

6.4 β-Ketoester Alkynylation

Methyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (8):

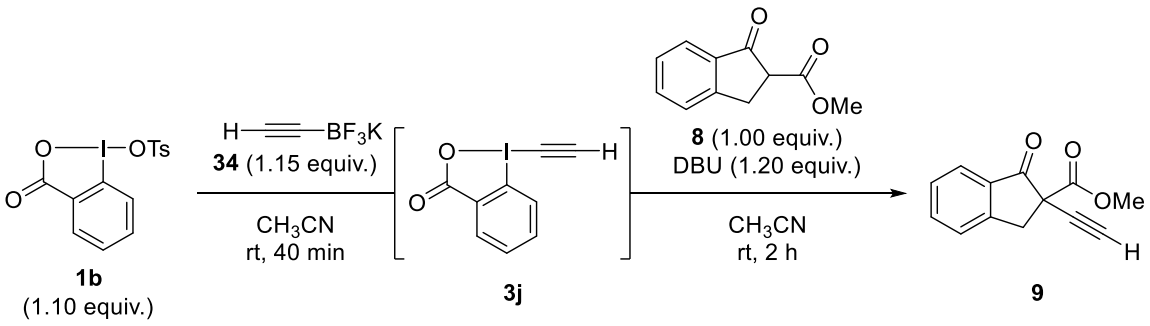


Compound **40** was synthesized following an adapted version of a reported procedure.[25] An oven dried 3-neck round bottom flask equipped with a condenser and charged with NaH (2.00 g, 49.9 mmol, 2.2 equiv.) was evacuated and backfilled with N_2 (3x). The solid was washed with pentane (3x) then dry toluene (94 mL), dry DME (11 mL) and dimethyl carbonate (**40**) (4.8

[24] N. Declas, J. Waser, *Angew. Chem. Int. Ed.* **2020**, *59*, 18256–18260.
[25] M. Rogers, C. Margot, C. Vuilleumier, B. Smith, S. Fitzgerald, M. Reiter, S. Nicolai, WO 2017005517A1, 2017.

mL, 56.7 mmol, 2.5 equiv.) were added under N_2. The mixture was heated to 80 °C and a solution of 2,3-dihydro-1*H*-inden-1-one (**39**) (3.00 g, 22.7 mmol, 1.0 equiv.) in dry toluene (11 mL) was added dropwise over 1 h under vigorous stirring. The reaction was stirred at 80 °C for 15 h then was allowed to cooled to rt. The mixture was diluted with Et_2O (50 mL) and 100 mL of a sat. sol. of $NaHCO_3$ was added. The mixture was extracted with Et_2O (3 x 100 mL), the combined organic layers were washed with brine (2 x 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was purified by column chromatography (Pentane/EtOAc, 1:0 to 85:15) to afford methyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**8**) (2.92 g, 15.3 mmol, 68%) as an orange oil which solidify in the fridge. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.67 – 7.60 (m, 1H, Ar*H*), 7.54 – 7.49 (m, 1H, Ar*H*), 7.42 – 7.38 (m, 1H, Ar*H*), 3.80 (s, 3H, OC*H*$_3$), 3.74 (dd, *J* = 8.3, 4.1 Hz, 1H, C*H*), 3.57 (dd, *J* = 17.3, 4.0 Hz, 1H, C*H*$_2$), 3.38 (dd, *J* = 17.3, 8.4 Hz, 1H, C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 169.7, 153.7, 135.6, 135.4, 128.0, 126.7, 124.9, 53.3, 53.0, 30.4. Spectroscopic data was consistent with the values reported in the literature.[26]

Methyl 2-ethynyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (9):



A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (184 mg, 0.440 mmol, 1.10 equiv.) and potassium ethynyltrifluoroborate (**34**) (60.7 mg, 0.460 mmol, 1.15 equiv.) was evacuated and backfilled with N_2 (3x). Dry CH_3CN (4 mL) was added under N_2 and the reaction was stirred at rt for 40 min.

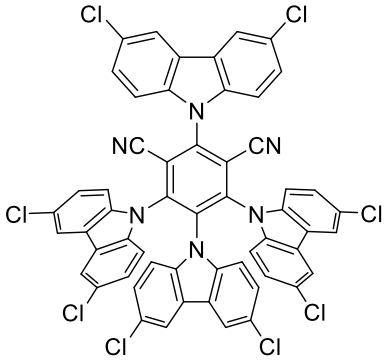
To a microwave vial containing a solution of methyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**8**) (76.1 mg, 0.400 mmol, 1.00 equiv.) in dry CH_3CN (0.8 mL) was added DBU (72 µL, 0.48 mmol, 1.20 equiv.). The mixture was stirred at rt 5 min then was added to the crude solution of **3j** (+ 0.2 mL of CH_3CN to rinse the vial). The reaction was stirred at rt for 2 h then Et_2O (10 mL) and a sat. sol. of $NaHCO_3$ (20 mL) were added. The mixture was extracted with Et_2O (3 x 20 mL), the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude compound was purified by column chromatography (Pentane/EtOAc, 98:2 to 85:15) to afford methyl 2-ethynyl-1-oxo-2,3-dihydro-1*H*-indene-2-

[26] M. V. Vita, J. Waser, *Org. Lett.* **2013**, *15*, 3246–3249.

carboxylate (**9**) (43.1 mg, 0.201 mmol, 50%) as a colorless amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 1H, Ar*H*), 7.67 (td, *J* = 7.5, 1.2 Hz, 1H, Ar*H*), 7.52 – 7.47 (m, 1H, Ar*H*), 7.47 – 7.39 (m, 1H, Ar*H*), 3.93 (d, *J* = 17.1 Hz, 1H, C*H*$_2$), 3.80 (s, 3H, OC*H*$_3$), 3.52 (d, *J* = 17.2 Hz, 1H, C*H*$_2$), 2.42 (s, 1H, C≡C*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 168.3, 152.3, 136.2, 133.2, 128.4, 126.5, 126.0, 80.0, 72.5, 55.4, 54.0, 40.6. Spectroscopic data was consistent with the values reported in the literature.[27]

6.5 Oxy-alkynylation of Enol Ether

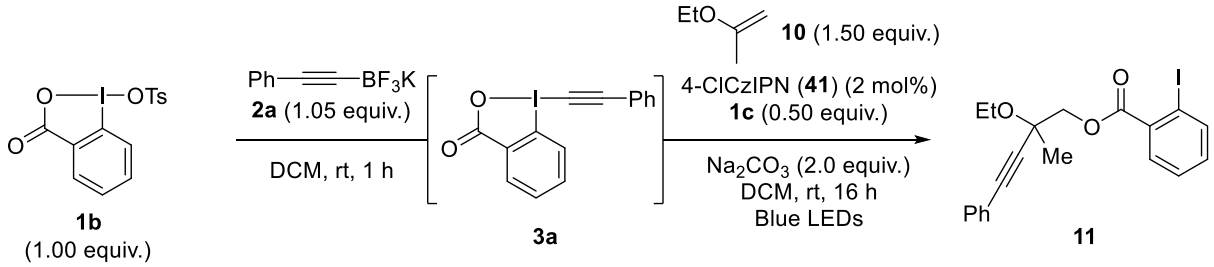
(2r,4s,5r)-2,4,5,6-Tetrakis(3,6-dichloro-9*H*-carbazol-9-yl)isophthalonitrile (4-ClCzIPN, 41):



4-ClCzIPN (**41**)

Compound **41** was synthesized following a reported procedure.[28]

2-Ethoxy-2-methyl-4-phenylbut-3-yn-1-yl 2-iodobenzoate (11):



A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (167 mg, 0.400 mmol, 1.00 equiv.) and potassium trifluoro(phenylethynyl)borate (**2a**) (87.4 mg, 0.420 mmol, 1.05 equiv.) was evacuated and backfilled with N_2 (3x). Dry DCM (1.5 mL), previously degassed by freeze-pump-thaw, was

[27] D. Fernández González, J. P. Brand, J. Waser, *Chem. - Eur. J.* **2010**, *16*, 9457–9461.
[28] S. G. E. Amos, D. Cavalli, F. Le Vaillant, J. Waser, *Angew. Chem. Int. Ed.* **2021**, *60*, 23827–23834.

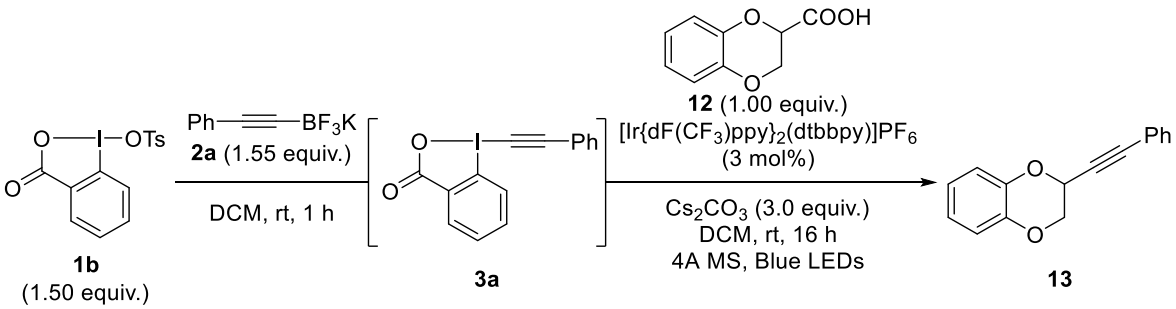
added under N_2. The reaction was stirred at rt for 1 h then Na_2CO_3 (84.8 mg, 0.800 mmol, 2.00 equiv.) was added under a flow of N_2 and the mixture was stirred at rt for 15 min.

An oven-dried test tube charged with 4-ClCzIPN (**41**) (8.5 mg, 8.0 µmol, 0.02 equiv.) and 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**1c**) (61.2 mg, 0.200 mmol, 0.50 equiv.) was evacuated and backfilled with N_2 (3x). The crude suspension of **3a** was added (+ DCM (1.0 mL) to rinse the vial). The mixture was degassed with argon for 5 min then 2-ethoxyprop-1-ene (**10**) (71 µL, 0.60 mmol, 1.50 equiv.) was added. The reaction was stirred at rt under blue LEDs irradiation for 16 h. Then, DCM (5 mL) and a sat. sol. of $NaHCO_3$ (20 mL) were added and the mixture was extracted with DCM (3 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was dissolved in DCM and Et_3N (~2 mL), a solid deposit for column chromatography was prepared using silica (~3 g). The crude was purified by column chromatography (Pentane/EtOAc, 1:0 to 95:5) to afford 2-ethoxy-2-methyl-4-phenylbut-3-yn-1-yl 2-iodobenzoate (**11**) (95.3 mg, 0.219 mmol, 55%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.2 Hz, 1H, Ar*H*), 7.90 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.45 – 7.41 (m, 2H, Ar*H*), 7.39 (dd, *J* = 7.7, 1.2 Hz, 1H, Ar*H*), 7.34 – 7.29 (m, 3H, Ar*H*), 7.16 (t, *J* = 7.7 Hz, 1H, Ar*H*), 4.59 (d, *J* = 11.2 Hz, 1H, C_qCH_2), 4.43 (d, *J* = 11.2 Hz, 1H, C_qCH_2), 3.78 (qd, *J* = 7.0, 0.8 Hz, 2H, OCH_2CH_3), 1.66 (s, 3H, C_qCH_3), 1.25 (t, *J* = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 141.5, 134.9, 132.9, 131.9, 131.4, 128.7, 128.4, 128.0, 122.4, 94.5, 87.8, 86.7, 72.4, 69.1, 60.3, 24.9, 15.9. Spectroscopic data was consistent with the values reported in the literature.[29]

Note: 2-ethoxyprop-1-ene (**10**) was eluted through a short column a basic Al_2O_3 before used.

6.6 Decarboxylative Alkynylation

2-(Phenylethynyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (13):



A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (125 mg, 0.300 mmol, 1.50 equiv.) and potassium trifluoro(phenylethynyl)borate (**2a**) (64.5 mg, 0.310 mmol, 1.55 equiv.) was evacuated and backfilled with N_2 (3x). Dry DCM (2 mL), previously degassed by freeze-pump-thaw, was

[29] S. G. E. Amos, S. Nicolai, J. Waser, *Chem. Sci.* **2020**, *11*, 11274–11279.

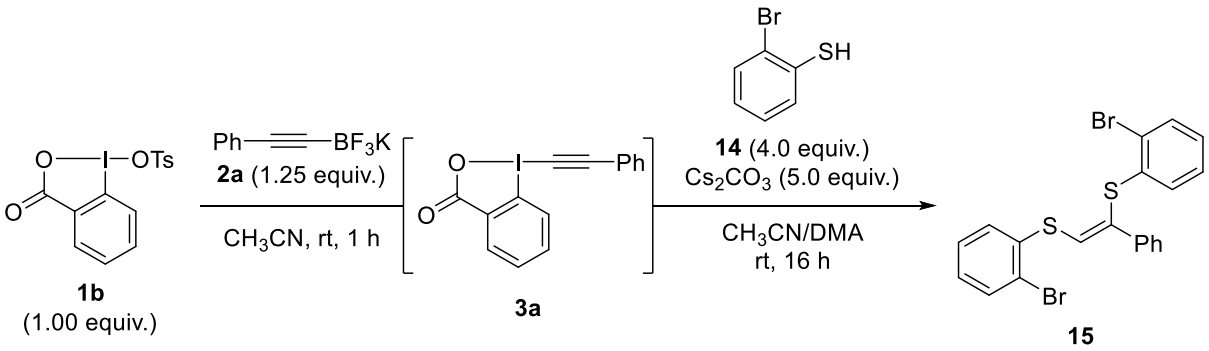
added under N_2. The reaction was stirred at rt for 1 h then Cs_2CO_3 (97.8 mg, 0.300 mmol, 1.50 equiv.) was added under a flow of N_2 and the mixture was stirred at rt for 15 min.

An oven-dried test tube charged with 4Å molecular sieve (20 g, powder), 1,4-benzodioxane-2-carboxylic acid (**12**) (36.4 mg, 0.200 mmol, 1.00 equiv.), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (6.8 mg, 6.0 µmol, 0.03 equiv.) and Cs_2CO_3 (97.8 mg, 0.300 mmol, 1.50 equiv.) was evacuated and backfilled with N_2 (3x). The crude suspension of **3a** was added (+ DCM (1.0 mL) to rinse the vial). The reaction mixture was degassed with argon for 5 min then was stirred under blue LEDs irradiation for 16 h. Then, DCM (5 mL) and a sat. sol. of $NaHCO_3$ (15 mL) were added and the mixture was extracted with DCM (3 x 15 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography (Pentane/DCM, 95:5) to afford 2-(phenylethynyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (**13**) (22.8 mg, 96.5 µmol, 48%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H, Ar*H*), 7.37 – 7.30 (m, 3H, Ar*H*), 7.00 – 6.95 (m, 1H, Ar*H*), 6.95 – 6.86 (m, 3H, Ar*H*), 5.13 (dd, *J* = 7.4, 2.5 Hz, 1H, C*H*), 4.45 (dd, *J* = 11.3, 2.5 Hz, 1H, CH_2), 4.22 (dd, *J* = 11.3, 7.4 Hz, 1H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 142.5, 132.2, 129.2, 128.5, 122.1, 122.0, 121.7, 117.8, 117.4, 87.9, 82.6, 67.6, 64.7. Spectroscopic data was consistent with the values reported in the literature.[30]

Note: Prior to use the 4Å molecular sieve was activated by heating it >300 °C under vacuum for 10 min.

6.7 Synthesis of 1,2-Dithioalkene

(*Z*)-(1-Phenylethene-1,2-diyl)bis((2-bromophenyl)sulfane) (15)



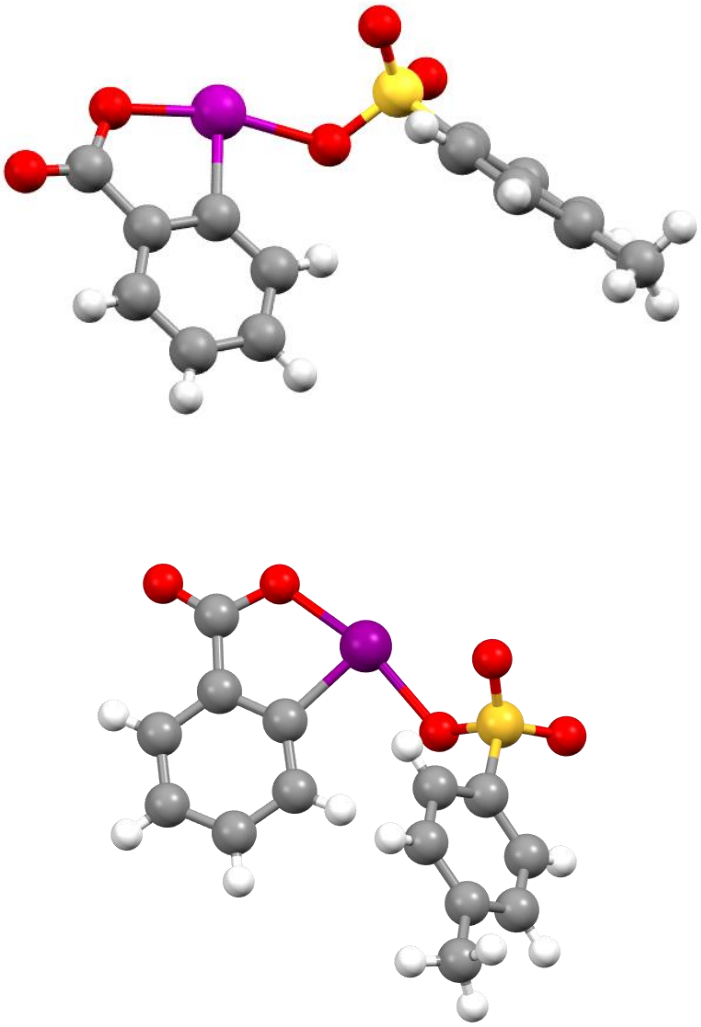
A capped oven dried microwave vial charged with 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one (**1b**) (83.6 mg, 0.200 mmol, 1.00 equiv.) and potassium trifluoro(phenylethynyl)borate (**2a**) (52.0 mg, 0.250 mmol, 1.25 equiv.) was evacuated and backfilled with N_2 (3x). Dry CH_3CN (1 mL), previously degassed with argon for 30 min, was

[30] Q.-Q. Zhou, W. Guo, W. Ding, X. Wu, X. Chen, L.-Q. Lu, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2015**, *54*, 11196–11199.

added under N_2 and the reaction was stirred at rt for 1 h. Then, Cs_2CO_3 (65.2 mg, 0.20 mmol, 1.00 equiv.) was added and the mixture was stirred at rt for 15 min.

A capped oven dried microwave vial charged with Cs_2CO_3 (261 mg, 0.800 mmol, 4.00 equiv.) was evacuated and backfilled with N_2 (3x). Dry DMA (0.75 mL), previously degassed with argon for 30 min, and 2-bromothiophenol (**14**) (96 µL, 0.80 mmol, 4.00 equiv.) was added under N_2. The solution of crude **3a** was added (+ 0.75 mL of DMA to rinse the vial) under N_2 and the reaction was stirred at rt for 16 h. Then, water (10 mL) and a sat. sol. of $NaHCO_3$ (5 mL) were added and the mixture was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine (2 x 15 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude mixture was purified by preparative TLC (Pentane/DCM, 95:5) to afford (*Z*)-(1-phenylethene-1,2-diyl)bis((2-bromophenyl)sulfane) (**15**) (63.0 mg, 0.132 mmol, 66%) as a colorless oil. R_f (Pentane/DCM, 95:5) = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.60 – 7.54 (m, 3H), 7.49 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.33 (td, *J* = 7.6, 1.4 Hz, 1H), 7.30 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 7.13 – 7.04 (m, 2H), 6.97 – 6.92 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 136.2, 136.2, 135.9, 133.7, 133.1, 132.0, 130.7, 129.1, 128.9, 128.7, 128.3, 128.2, 127.8, 127.1, 126.8, 125.9, 122.8. HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}Br_2S_2^+$ 476.8976; Found 476.8967.

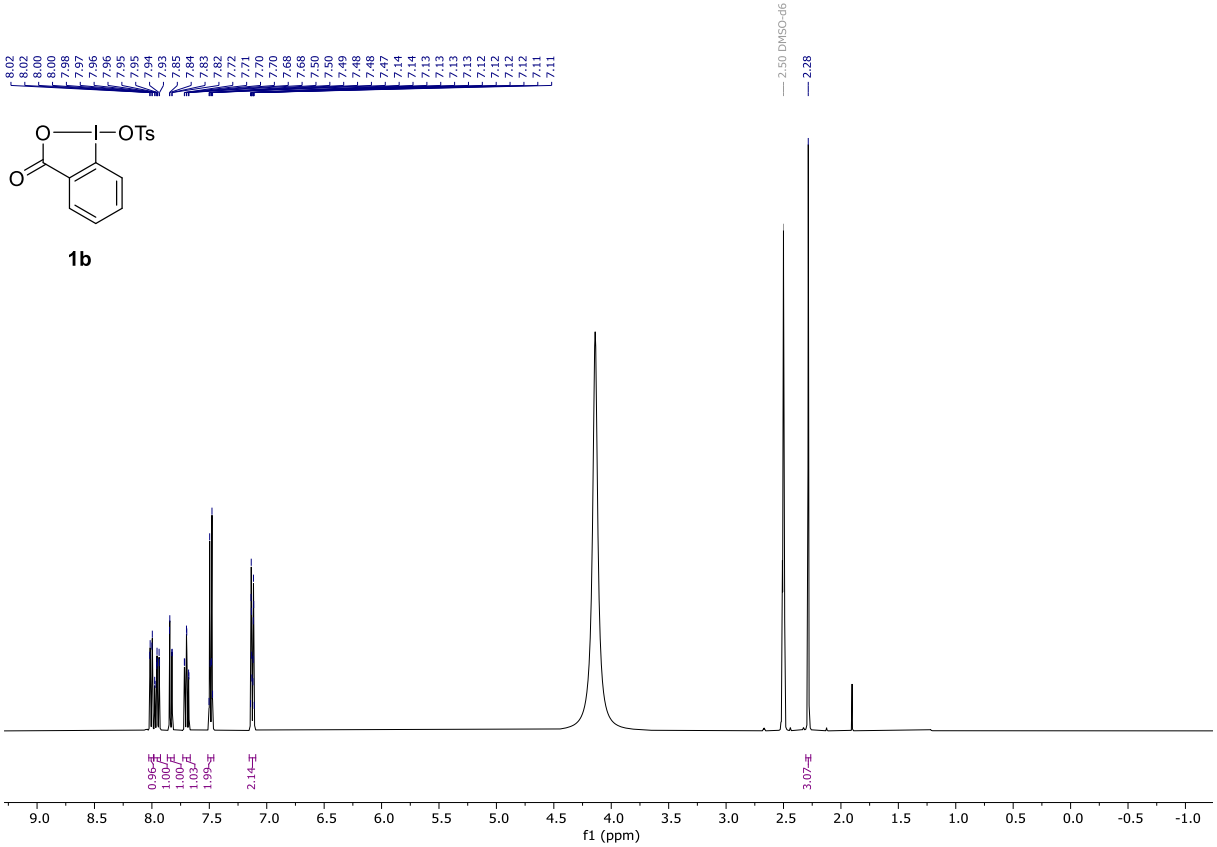
7. Crystal structure of TsOBX (1b)



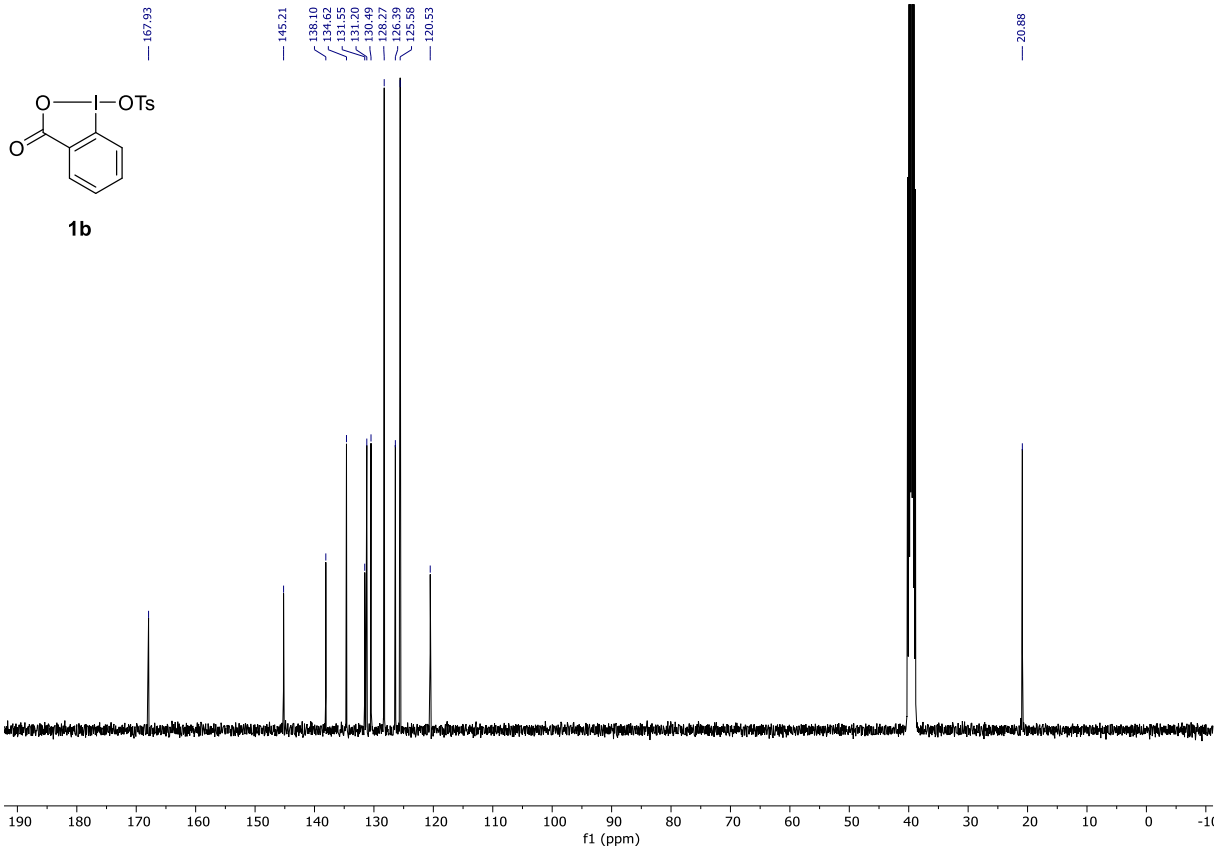
Crystals were grown using a batch of TsOBX (**1b**) which upon synthesis was immediately stored in a glovebox filled with N_2. Recrystallization of **1b** (150 mg, 0.359 mmol) from this batch was performed in dry boiling DCE (13 mL) under N_2 using oven-dried glassware outside of the glovebox. The compound did not seem to be soluble and the suspension was left to cool slowly over 16 h. Some small crystals formed on the side of the flask and were collected. Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (CCDC 2117886) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

8. NMR Spectra

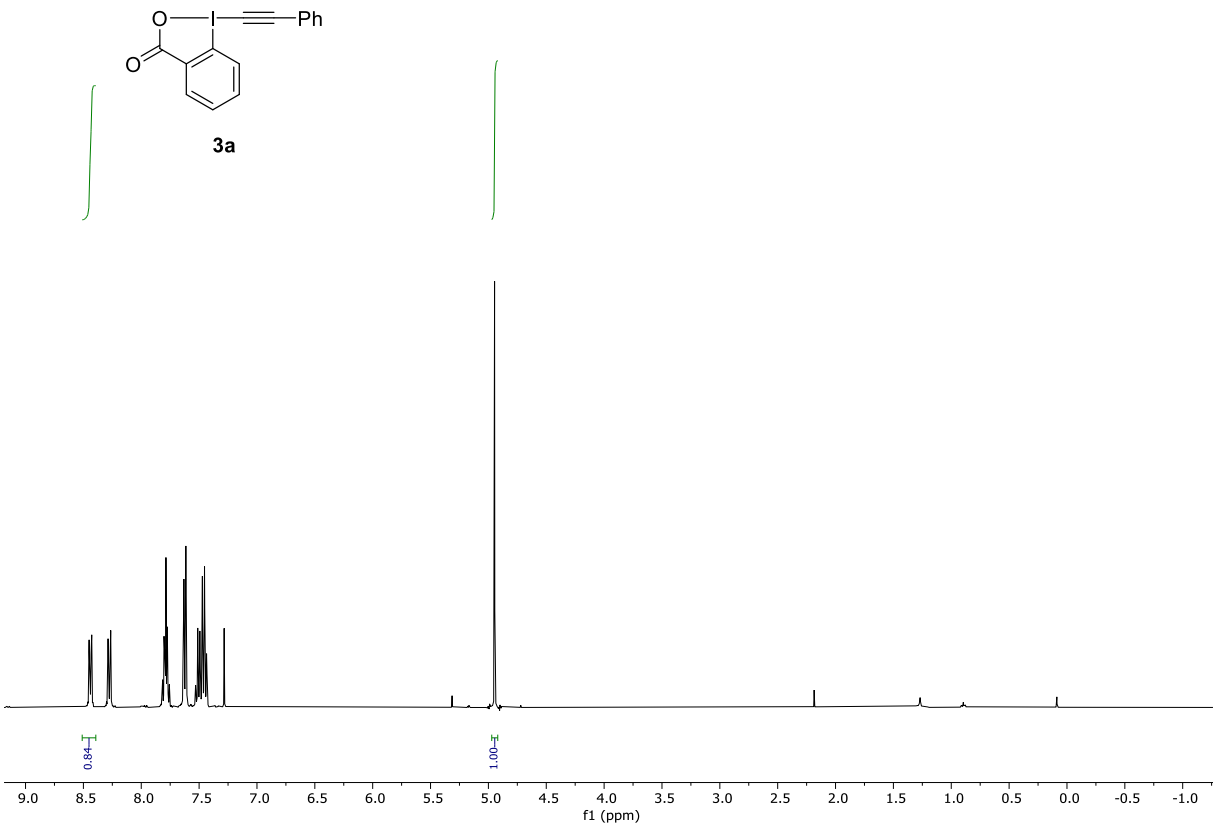
^{1}H NMR (400 MHz, DMSO-d_6) of compound **1b**:



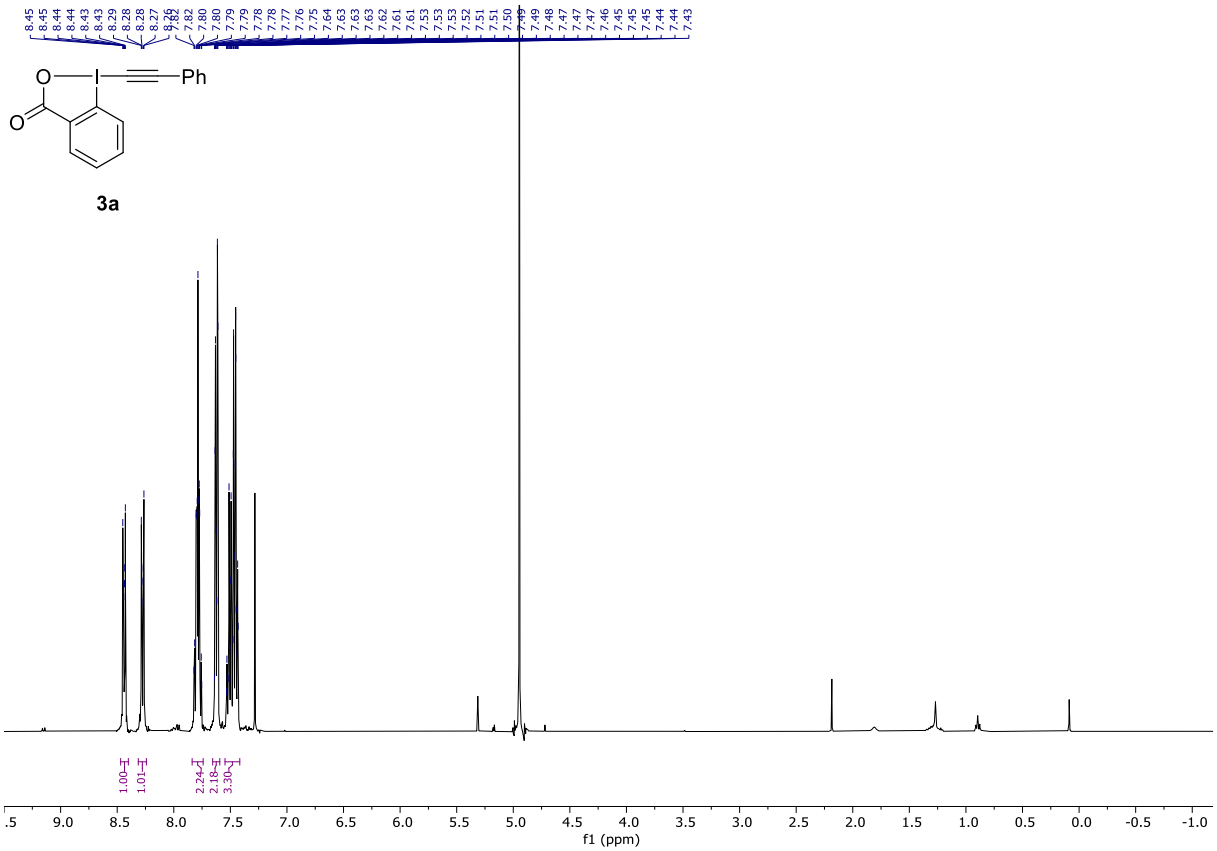
^{13}C NMR (101 MHz, DMSO-d_6) of compound **1b**:



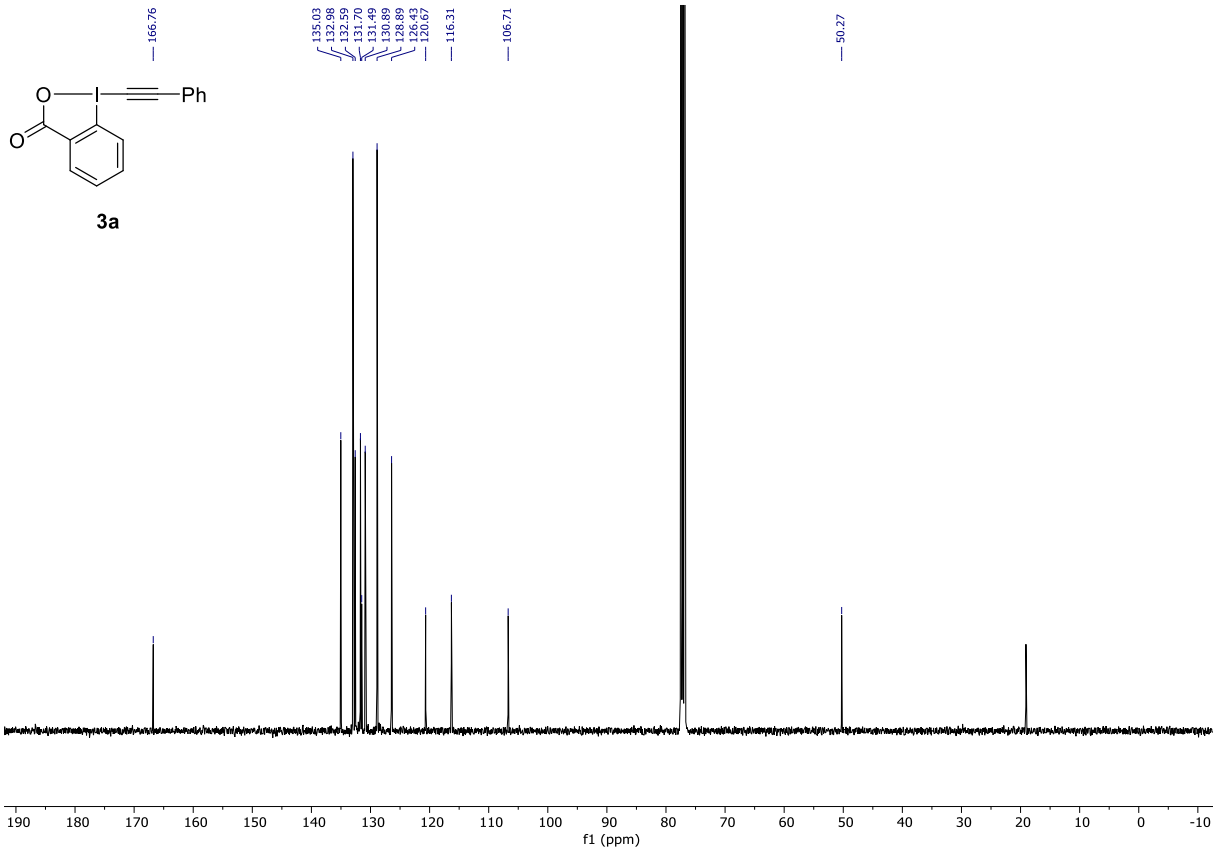
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a** (purity determination):



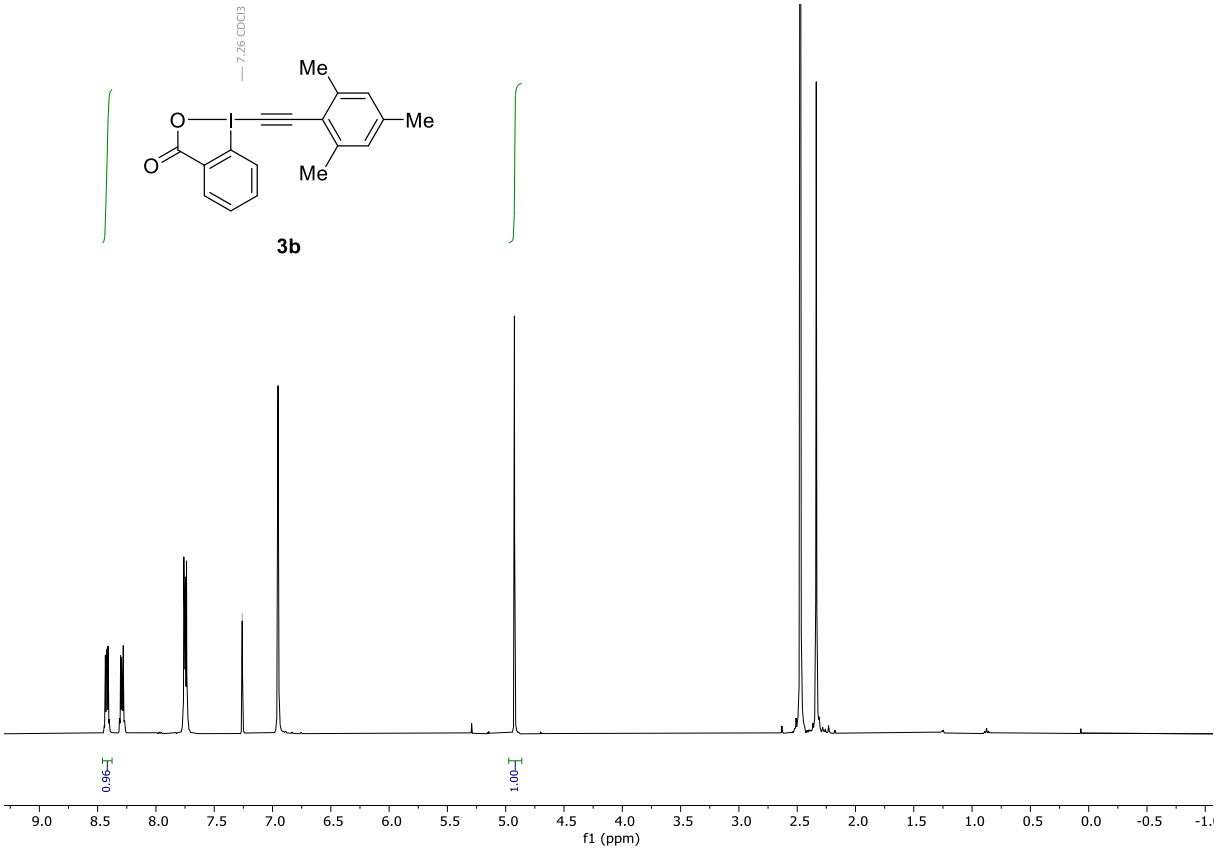
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**:



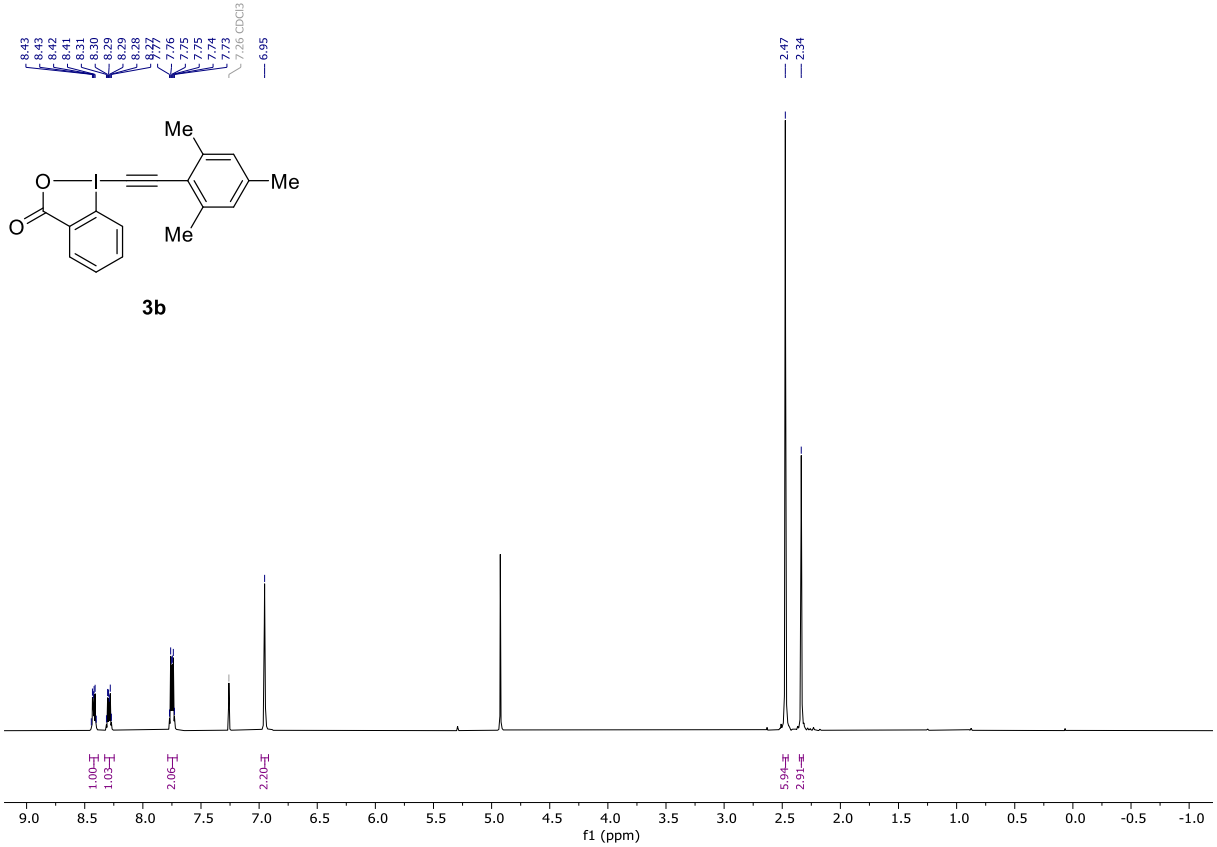
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3a**:



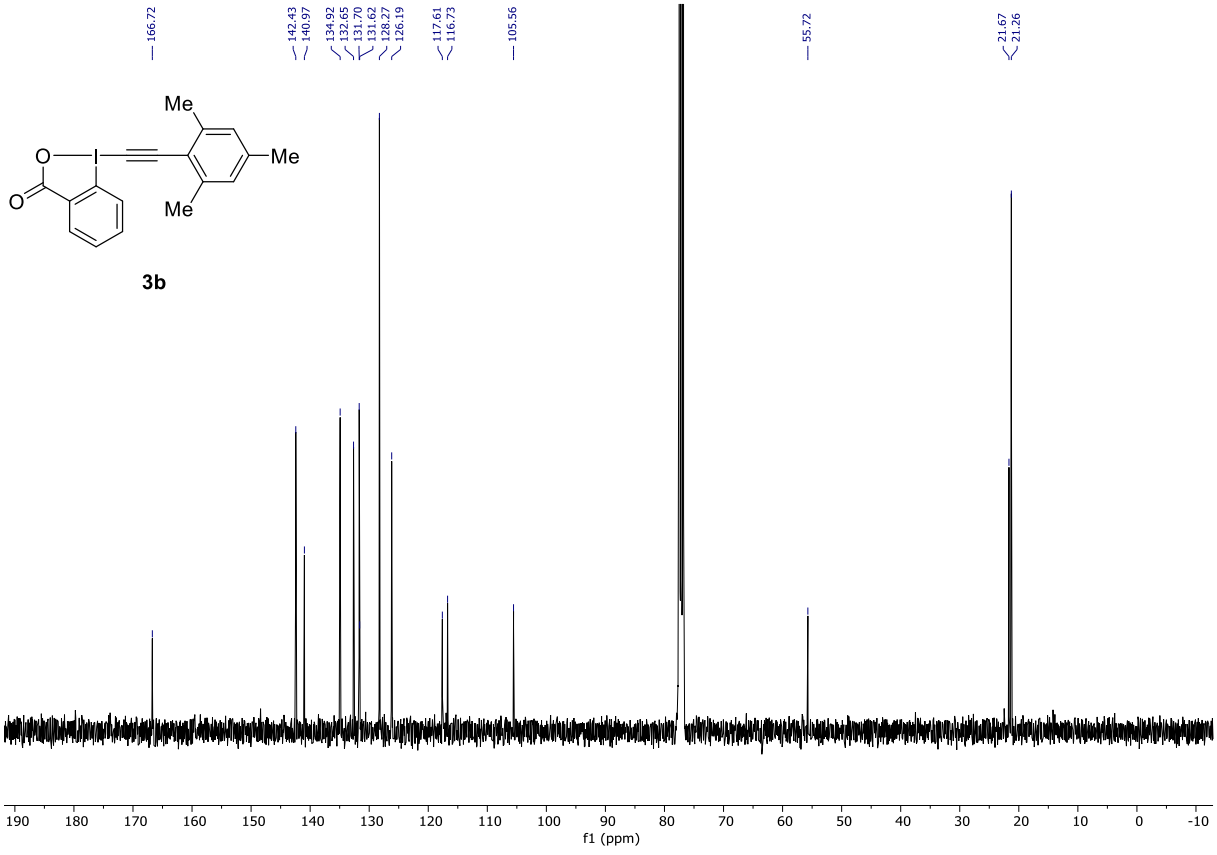
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b** (purity determination):



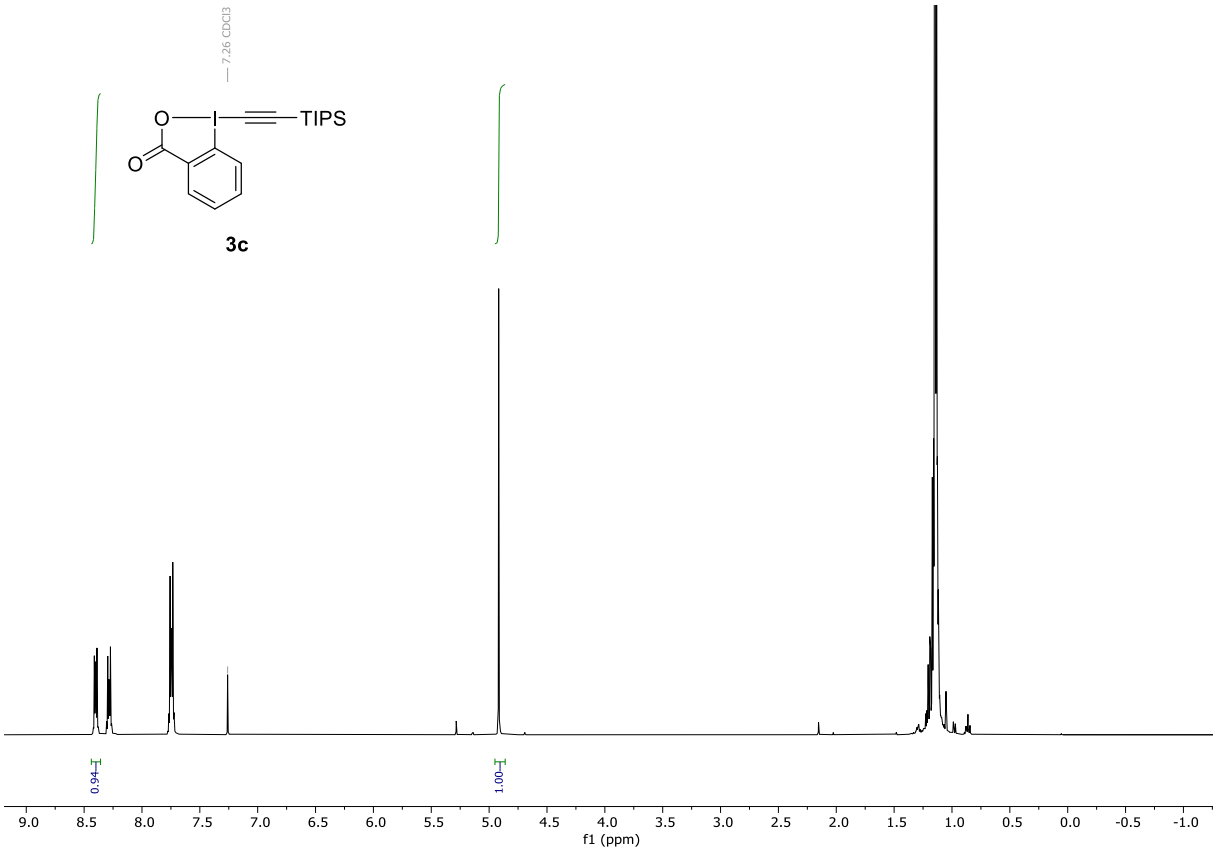
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**:



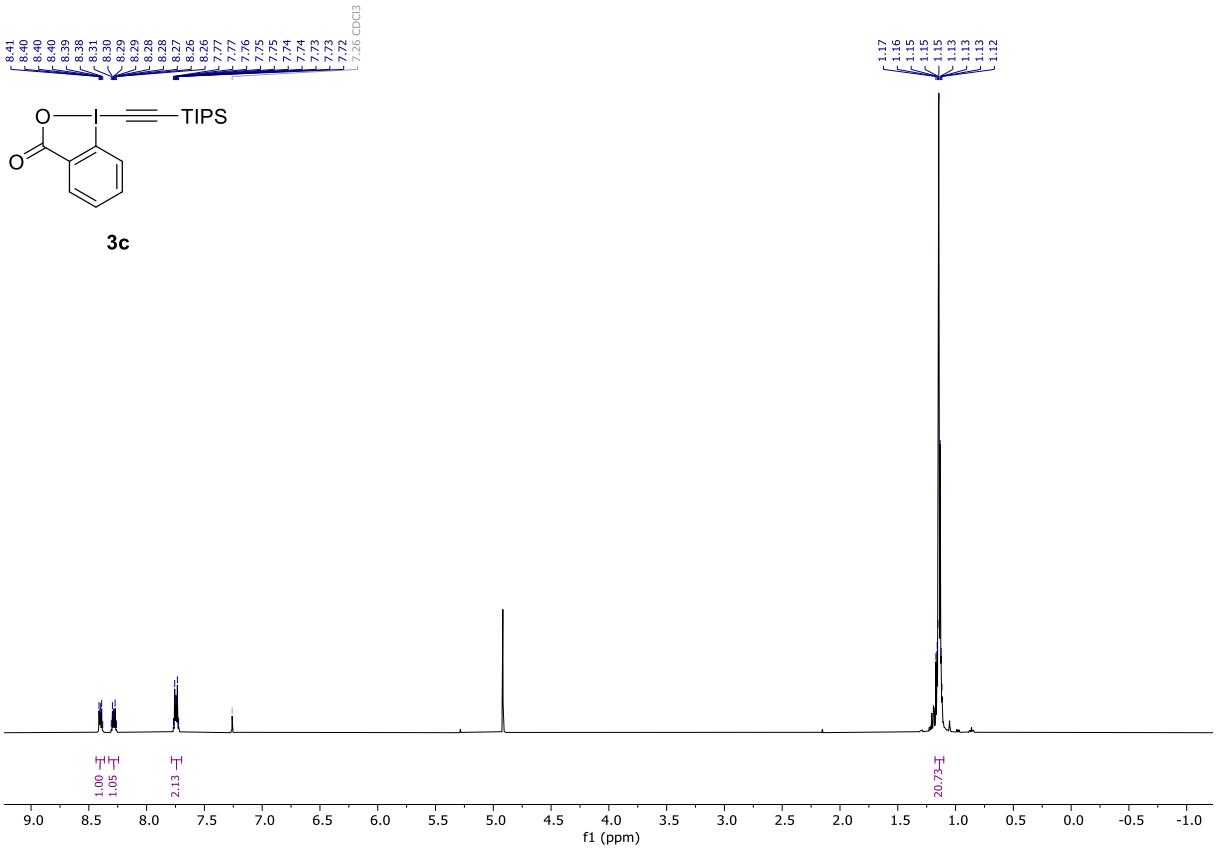
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3b**:



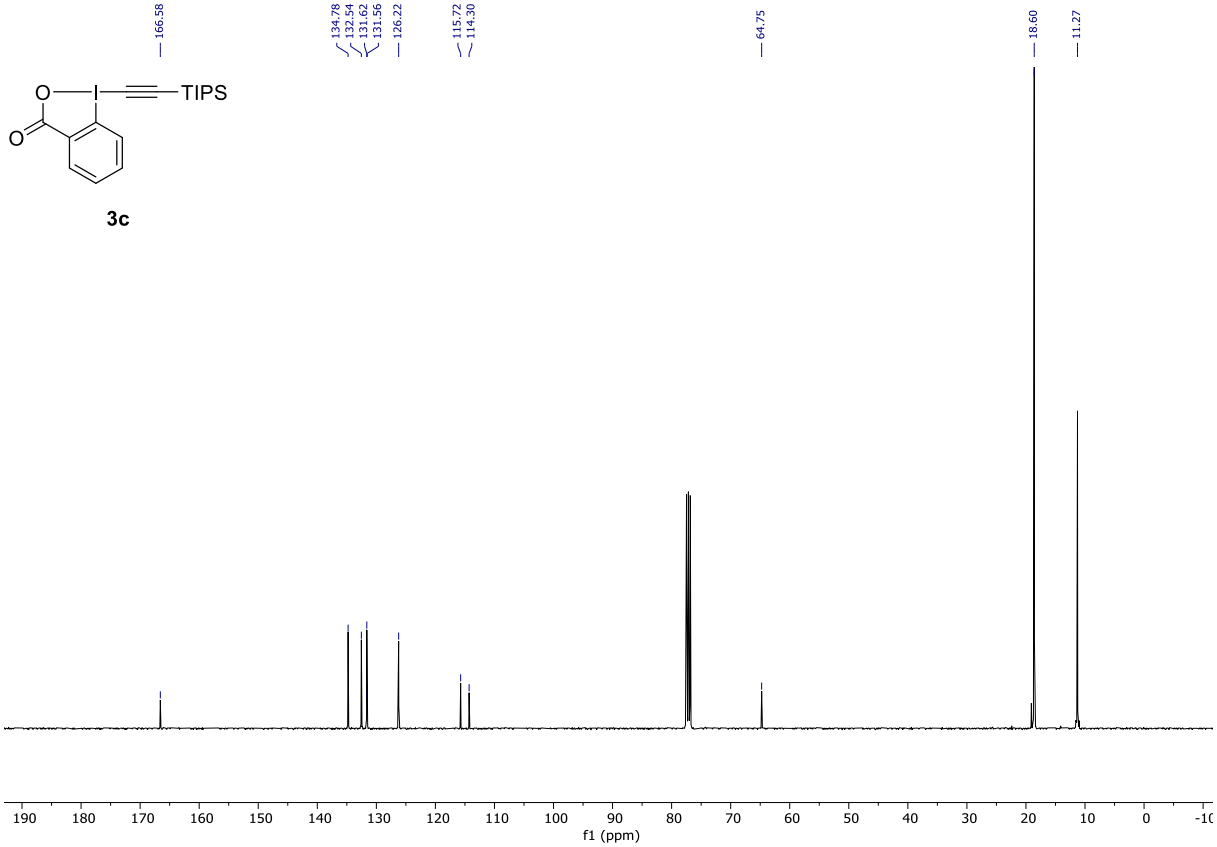
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c** (purity determination):



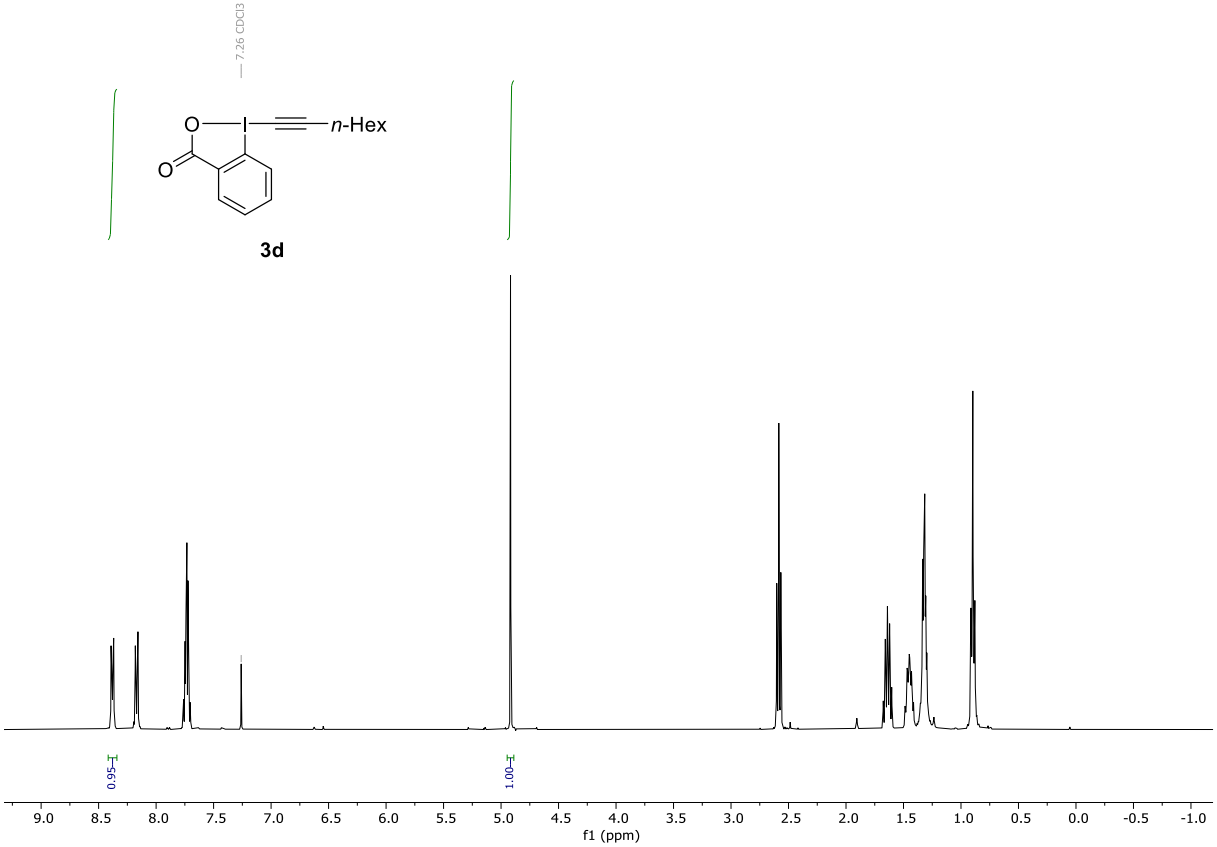
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**:



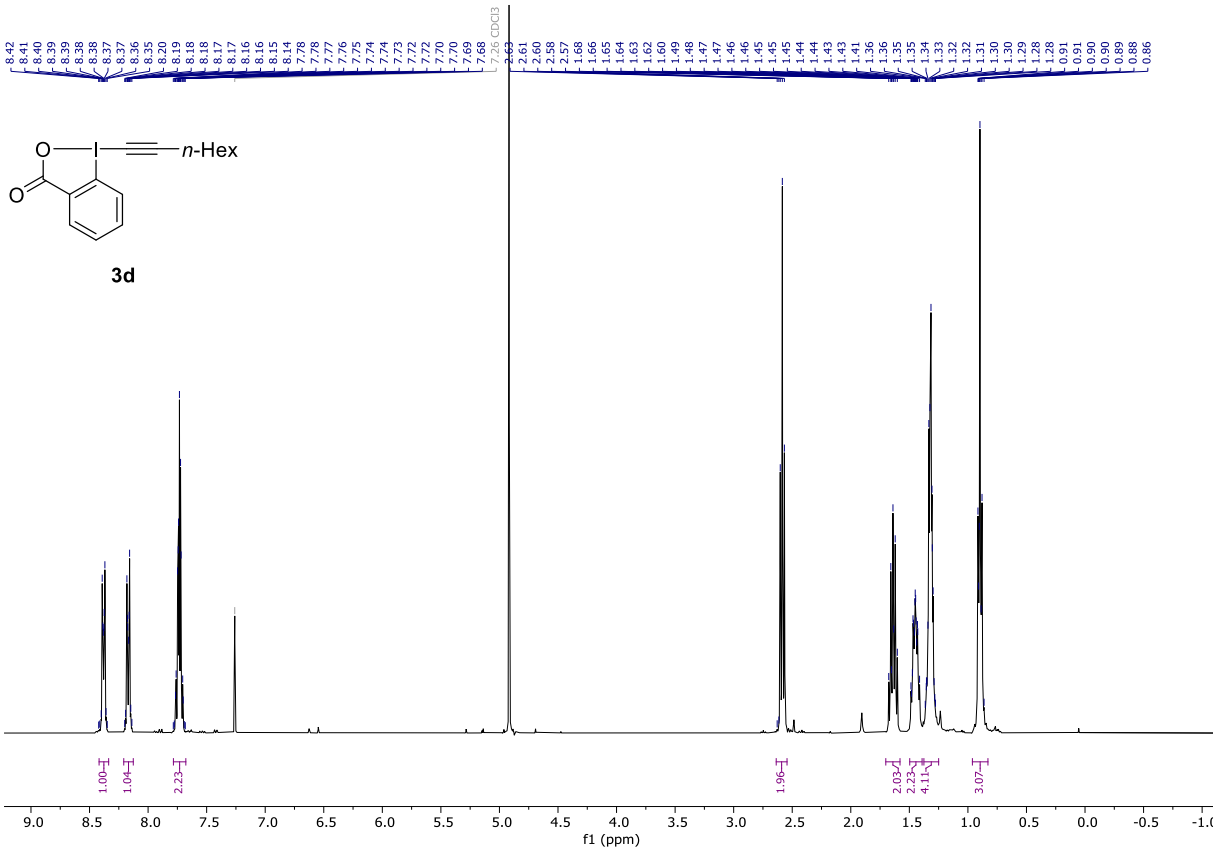
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3c**:



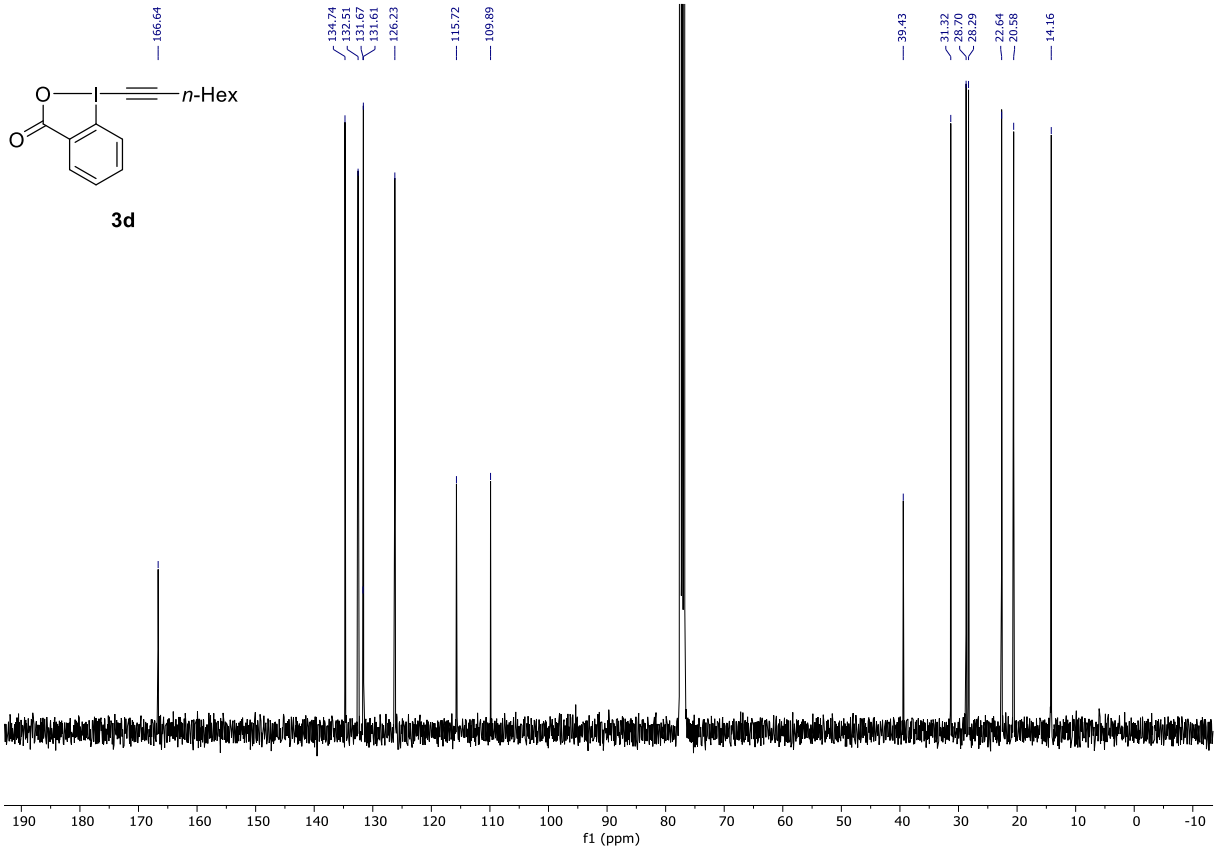
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d** (purity determination):



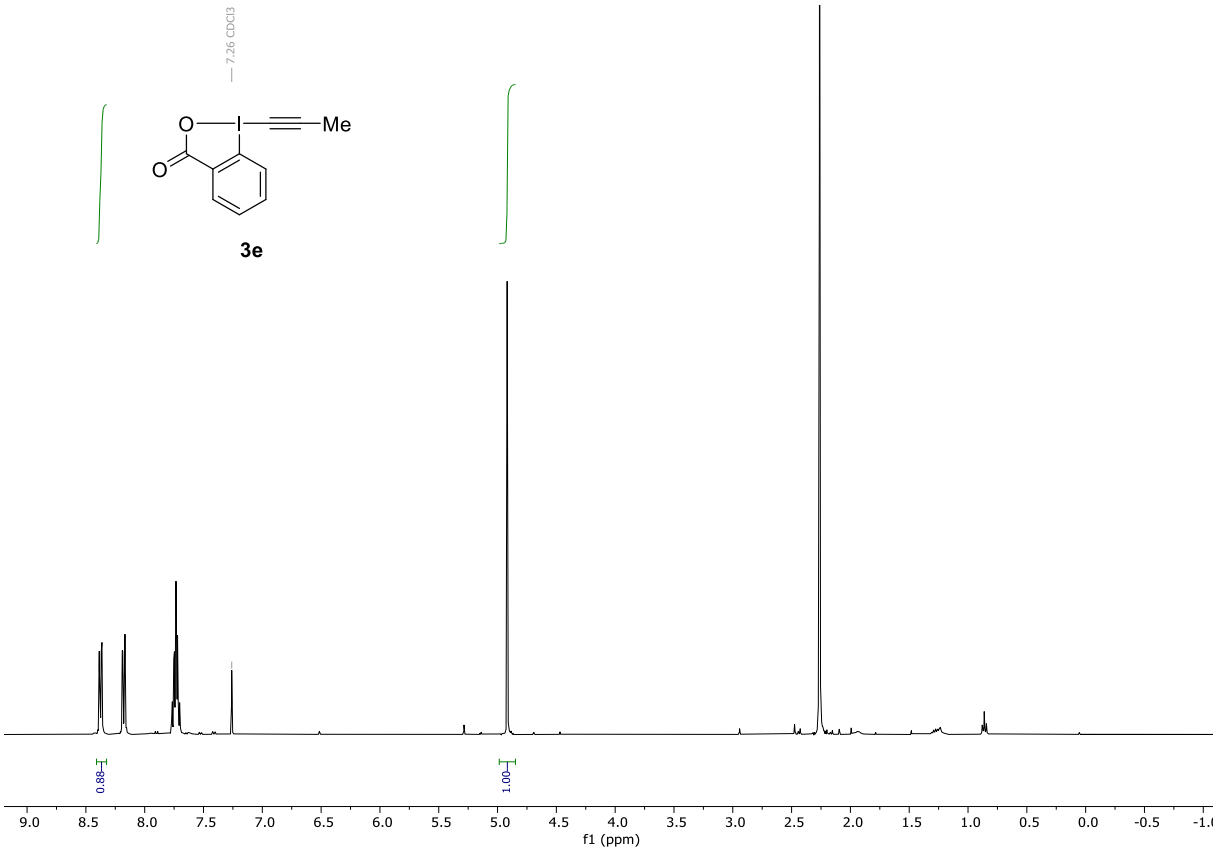
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**:



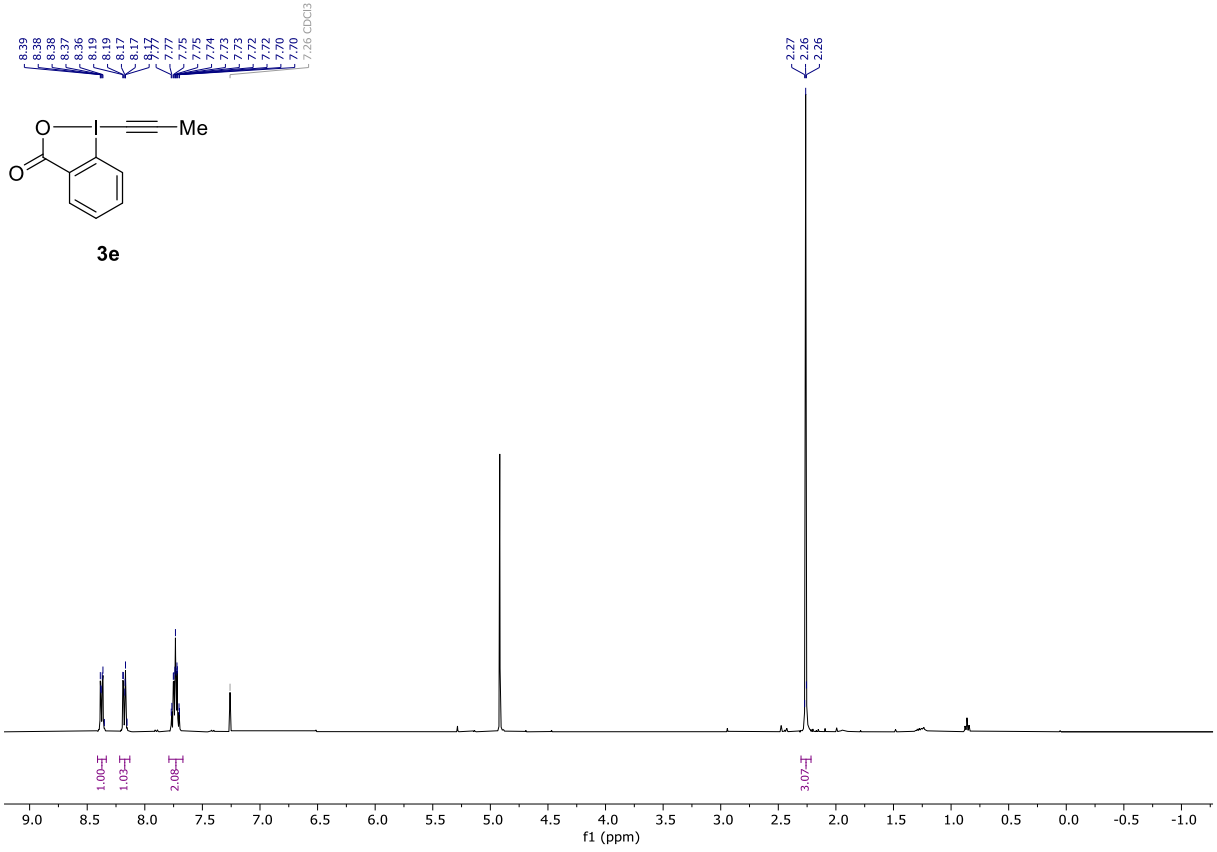
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3d**:



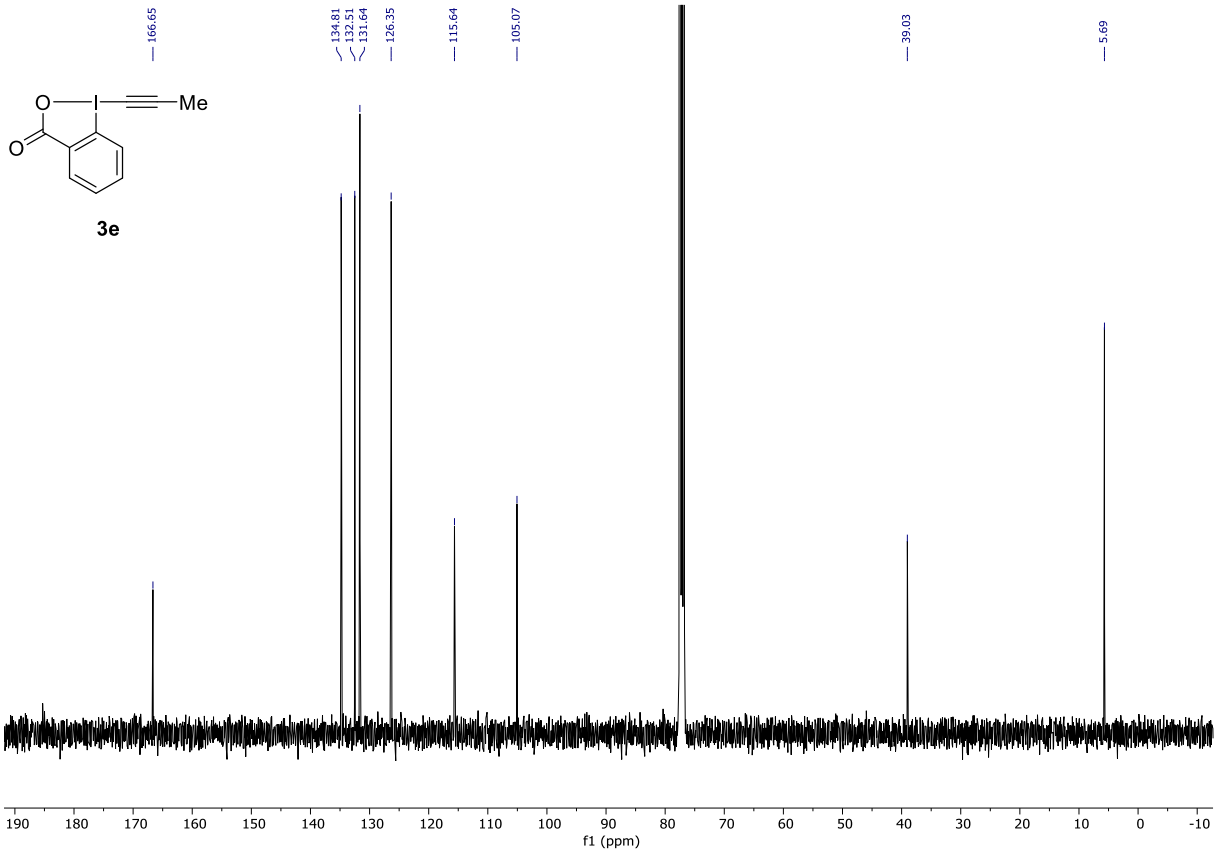
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e** (purity determination):



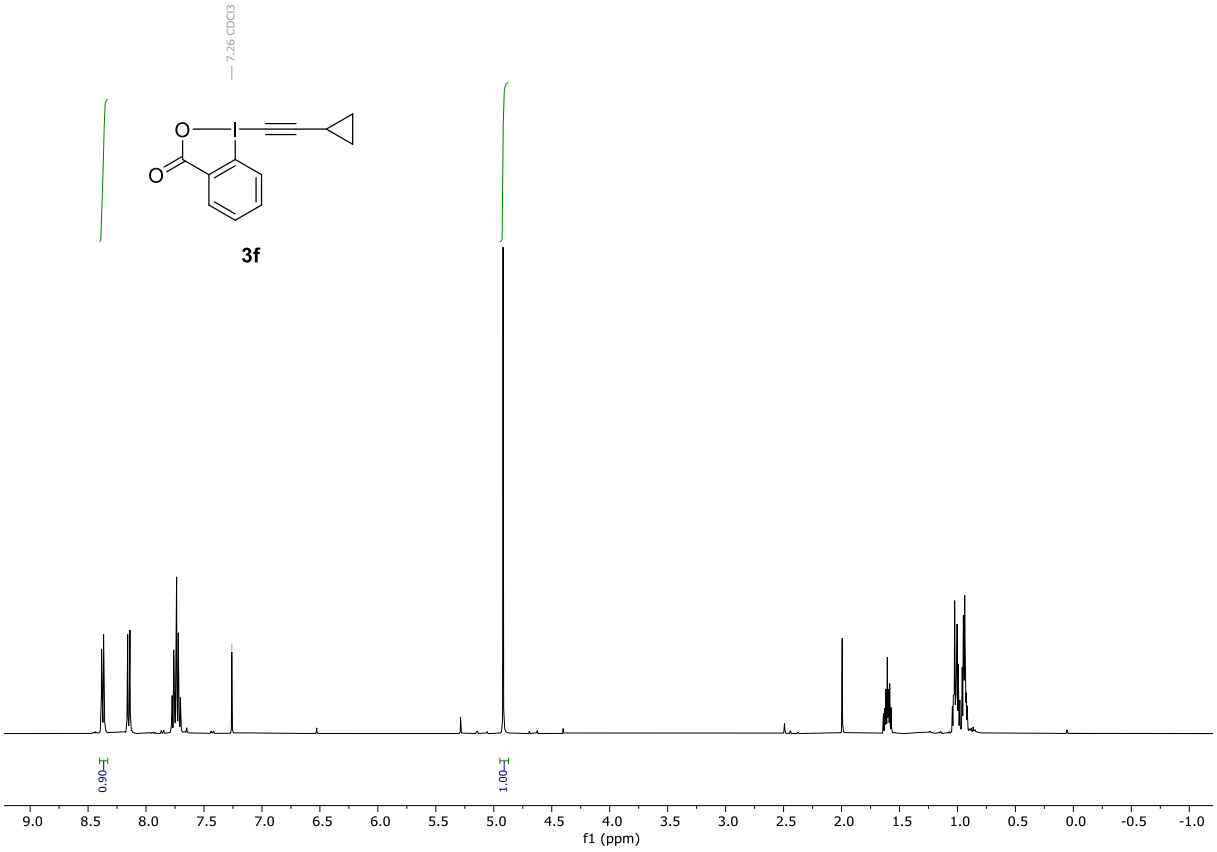
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**:



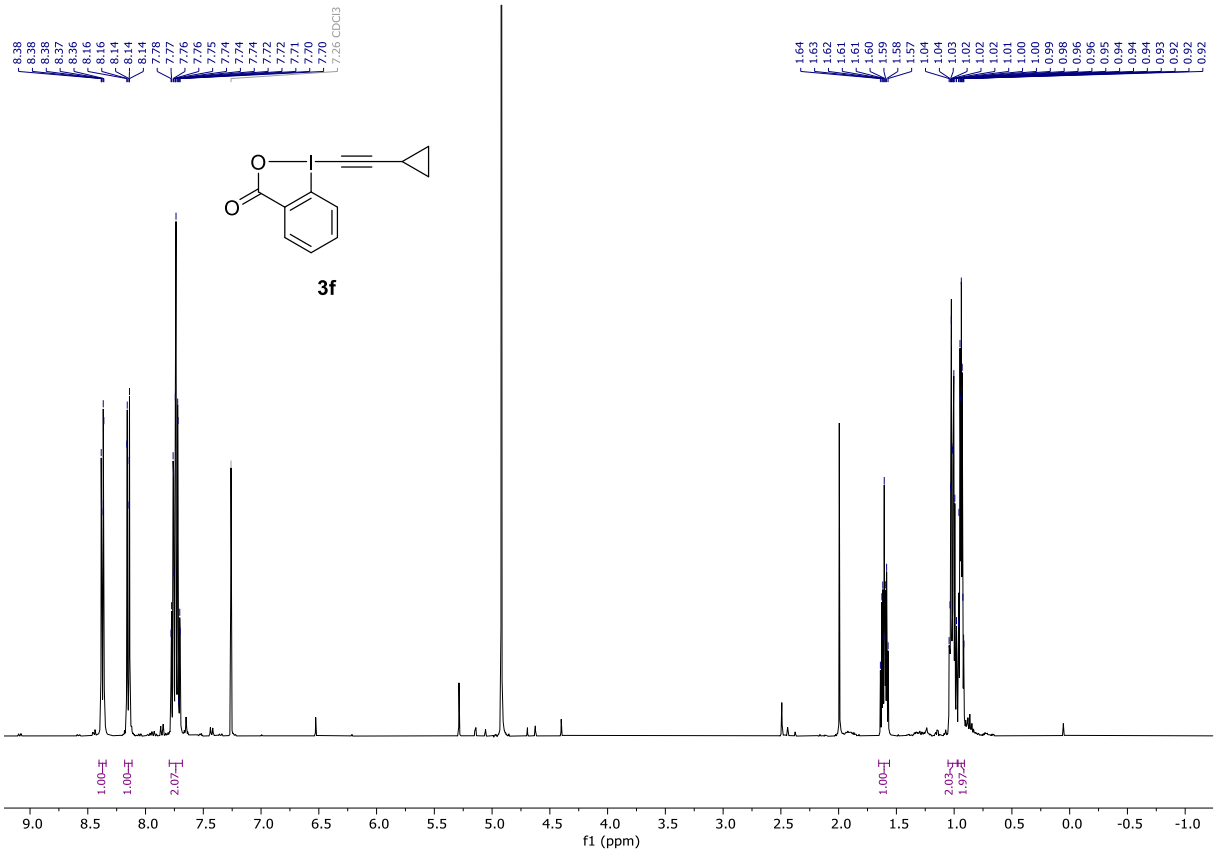
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3e**:



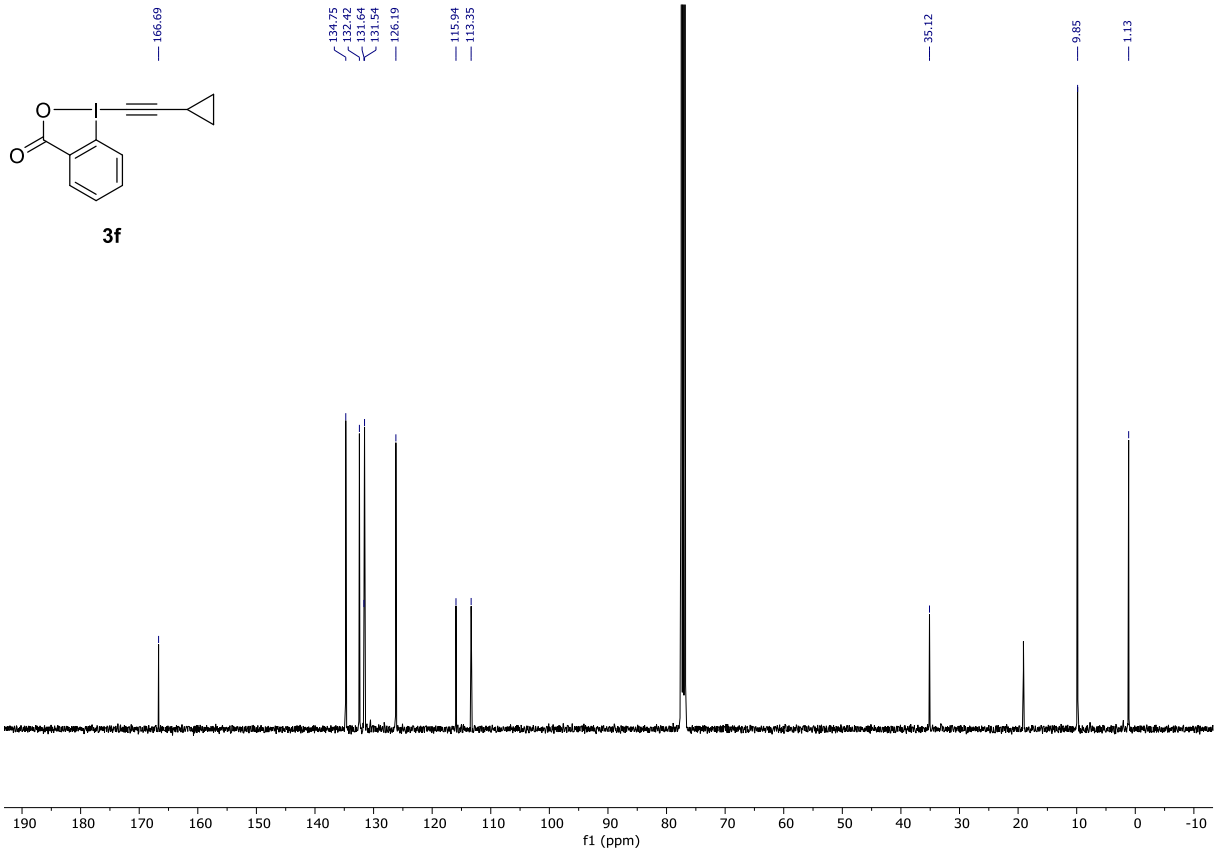
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f** (purity determination):



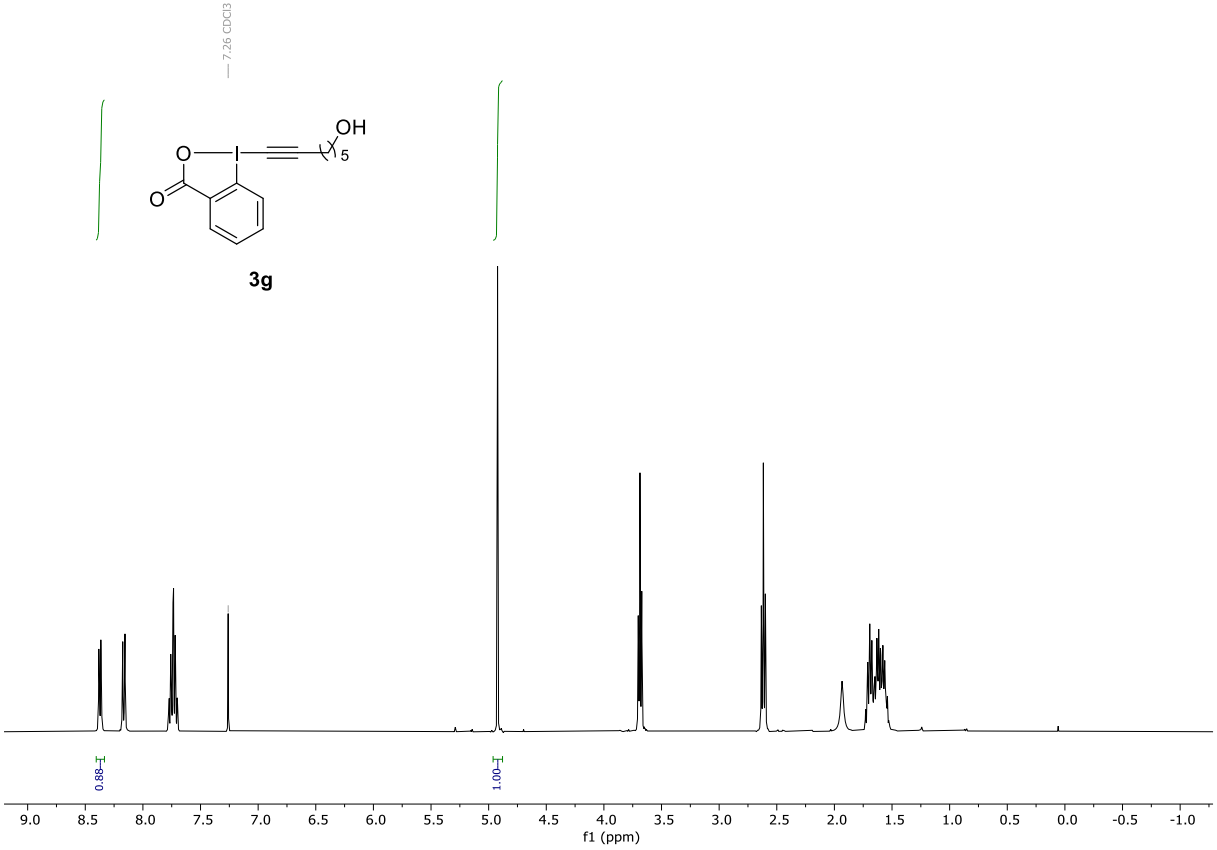
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**:



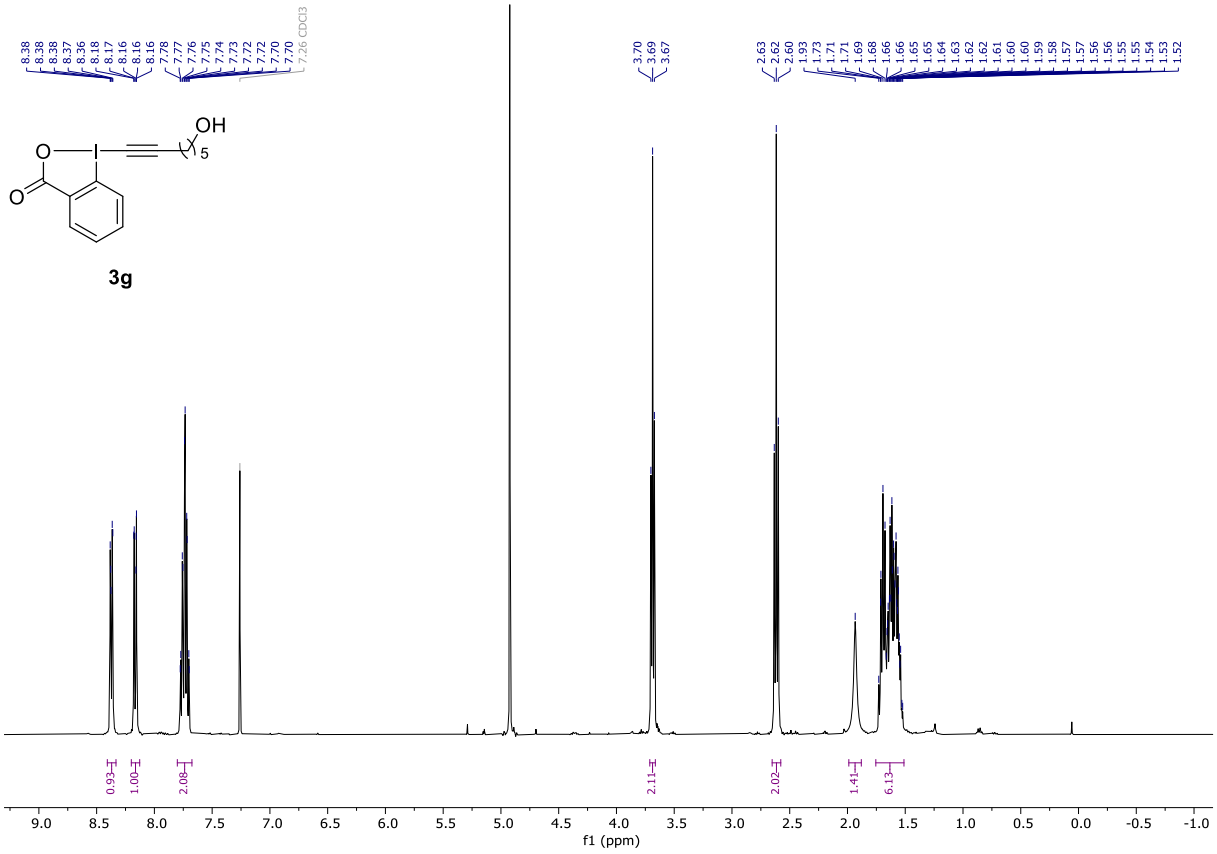
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3f**:



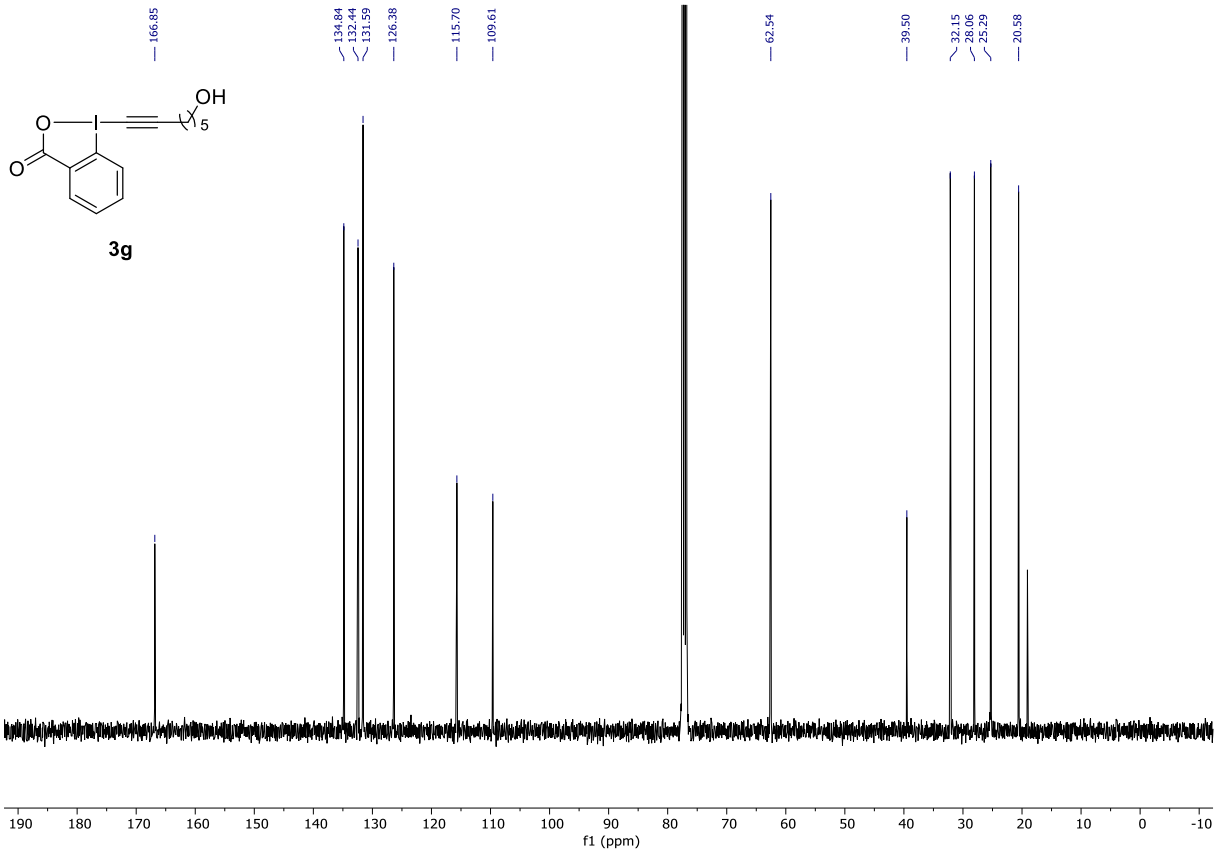
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g** (purity determination):



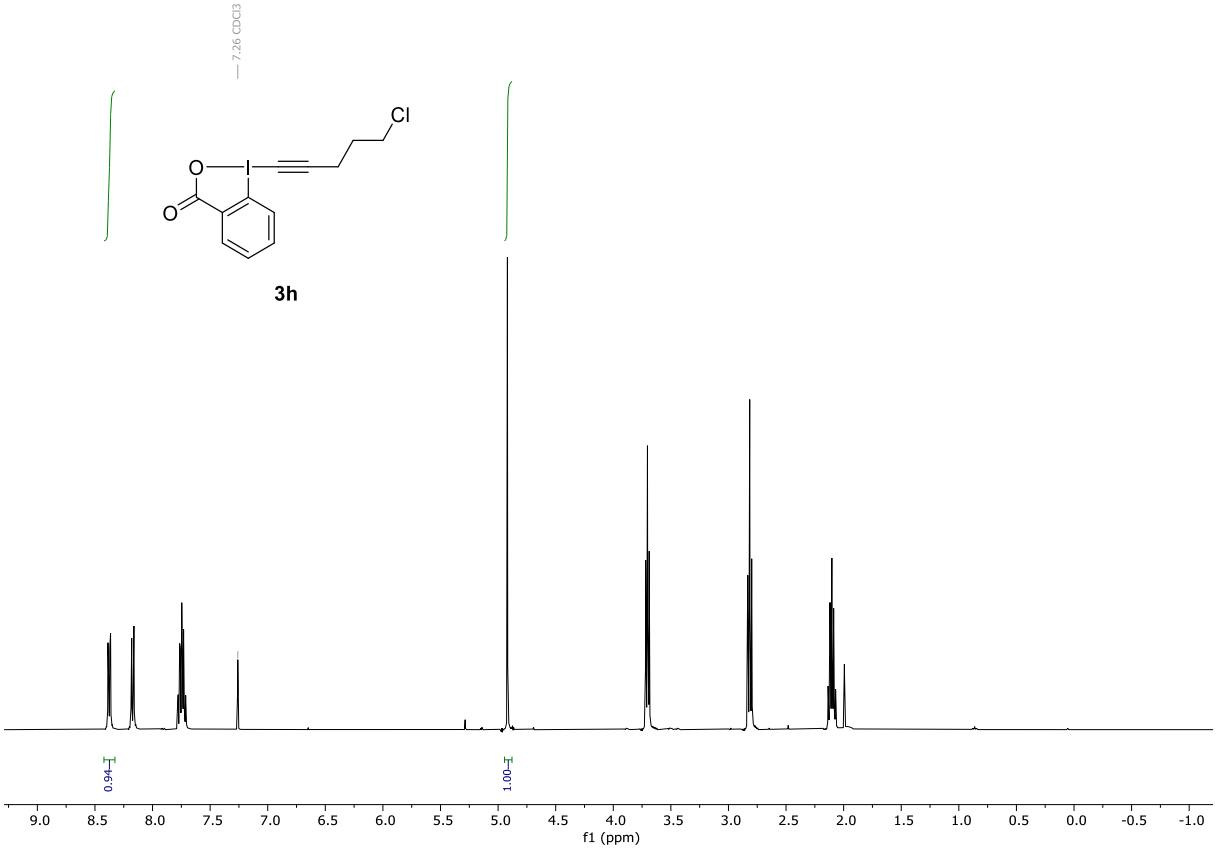
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**:



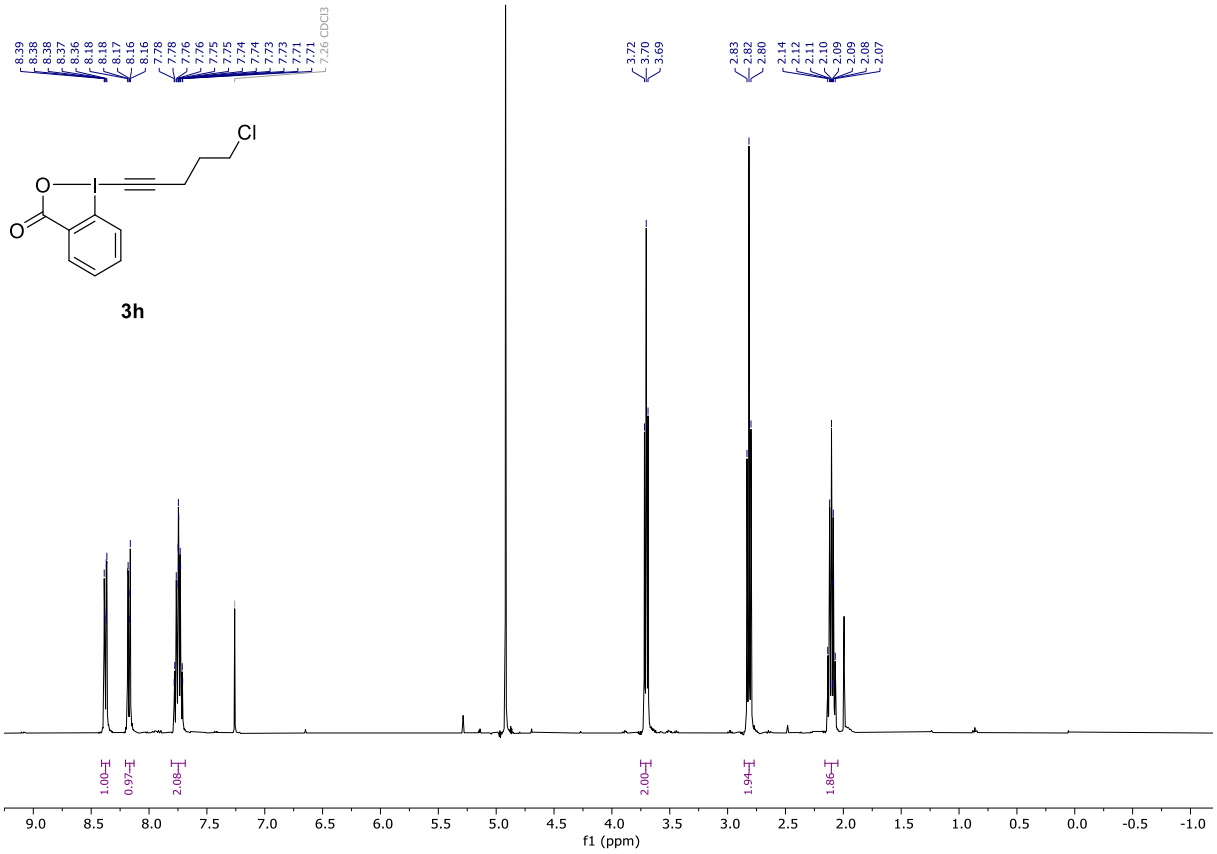
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3g**:



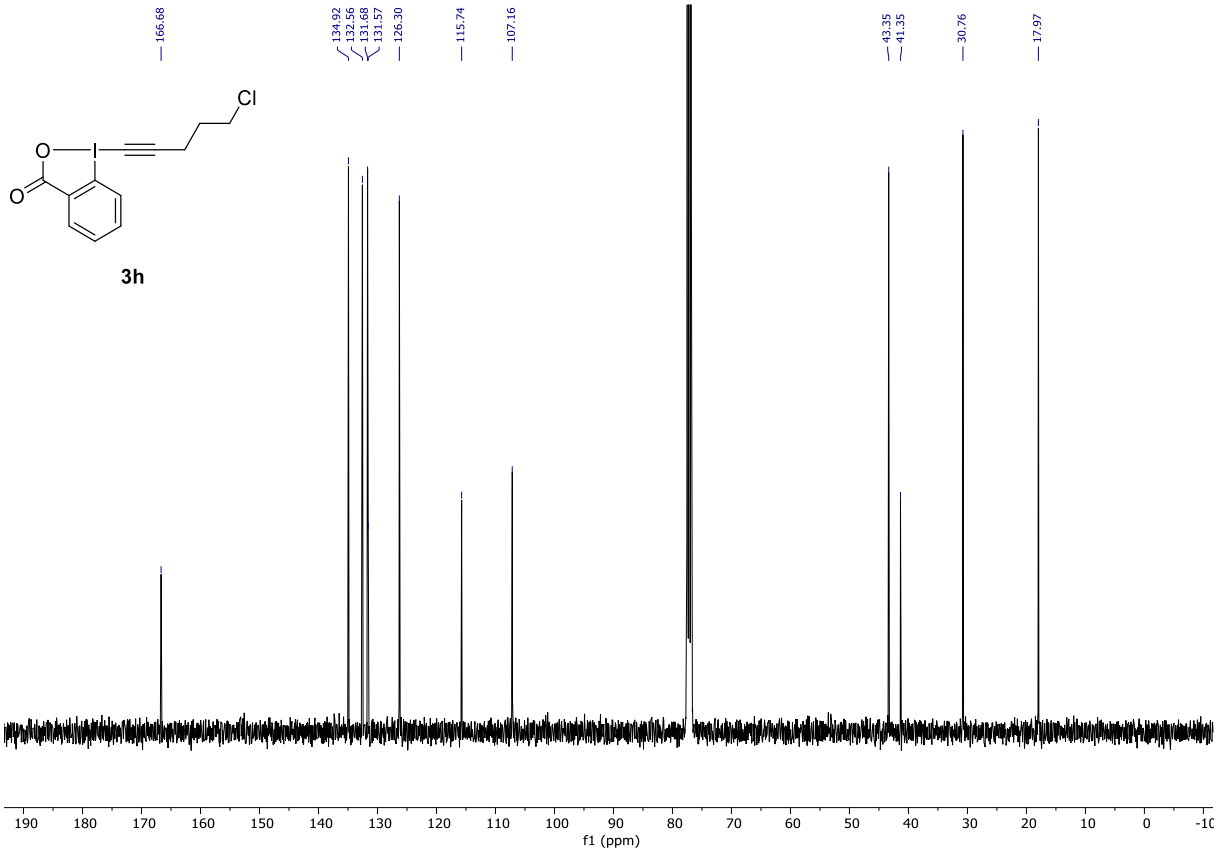
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h** (purity determination):



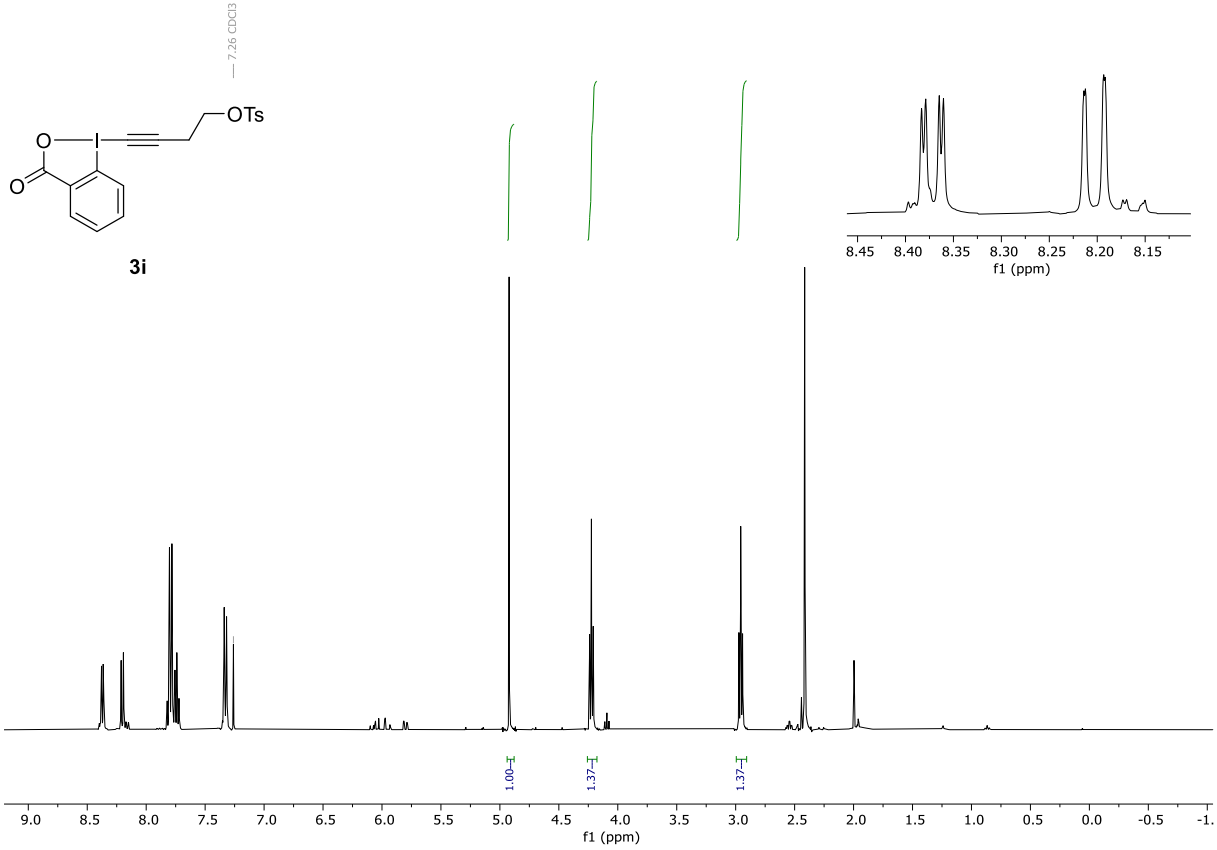
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**:



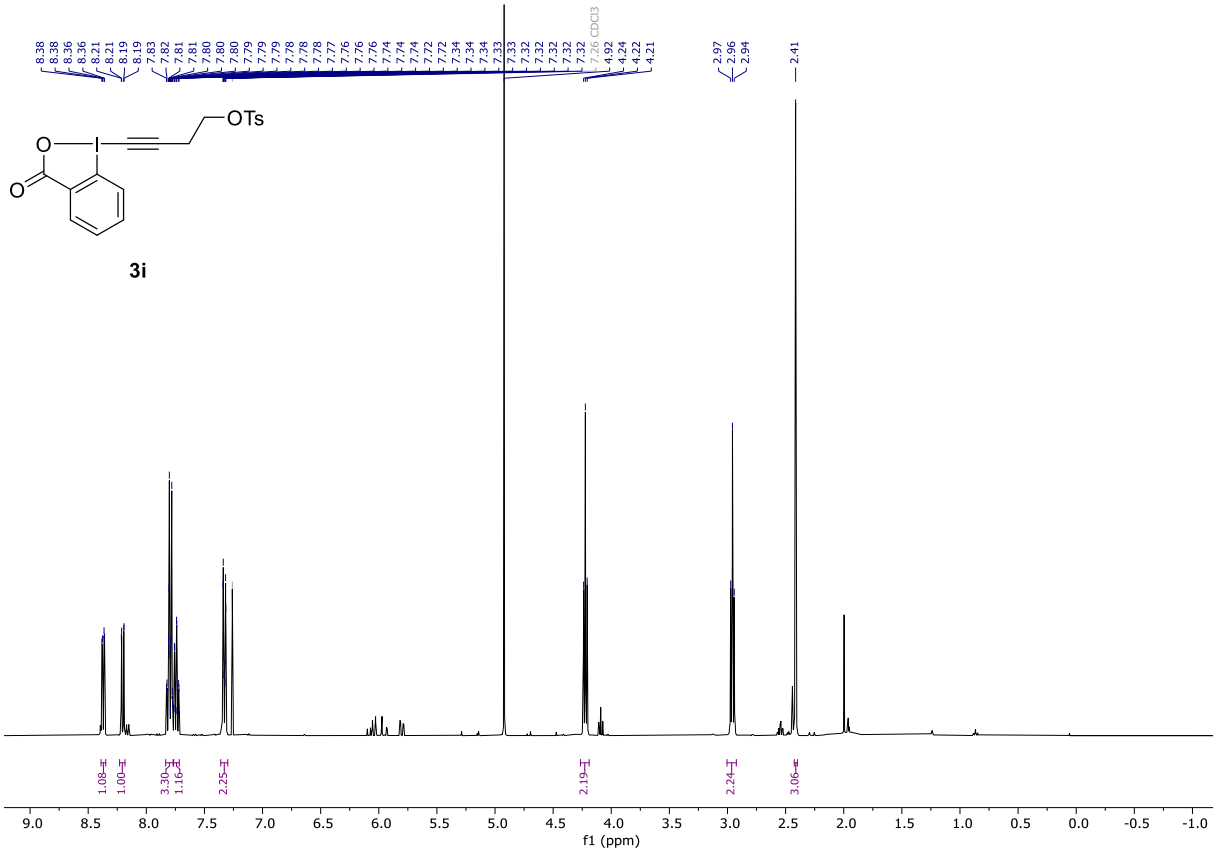
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3h**:



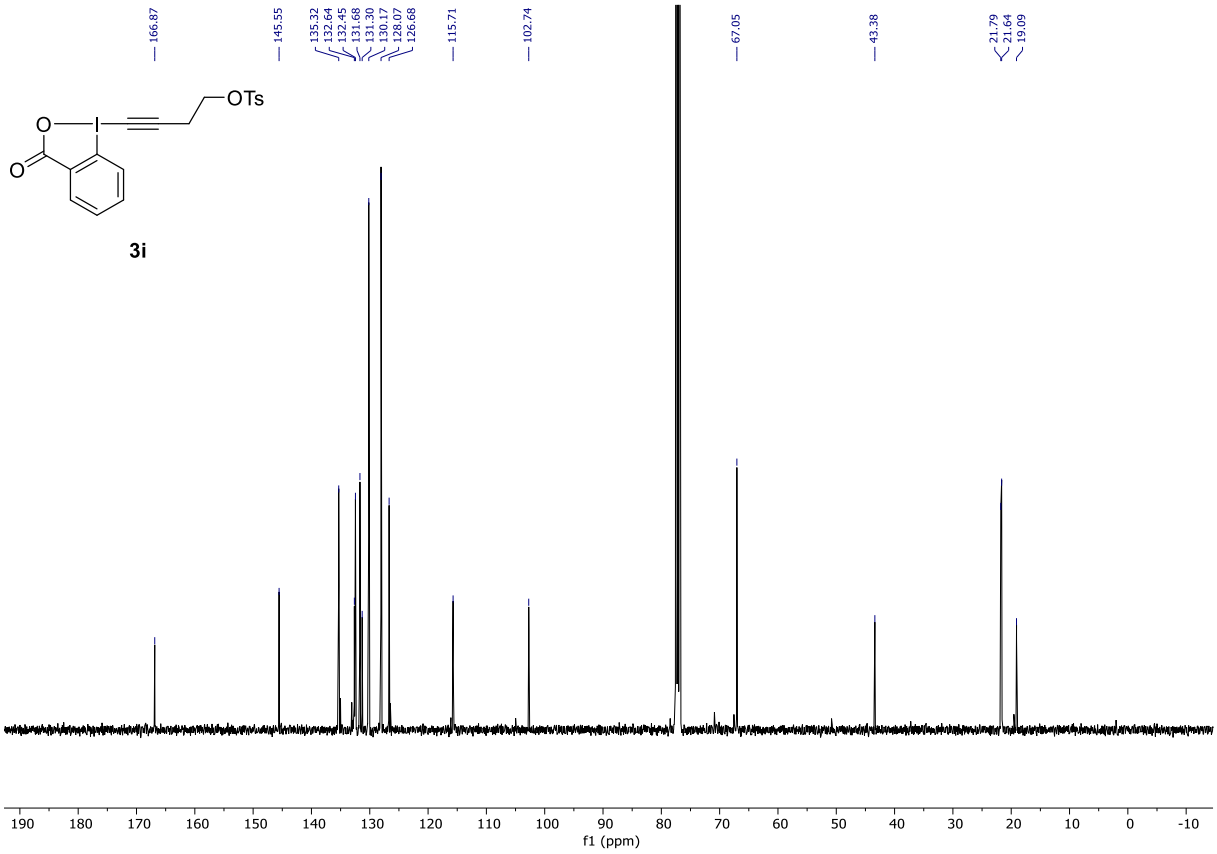
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i** (purity determination):



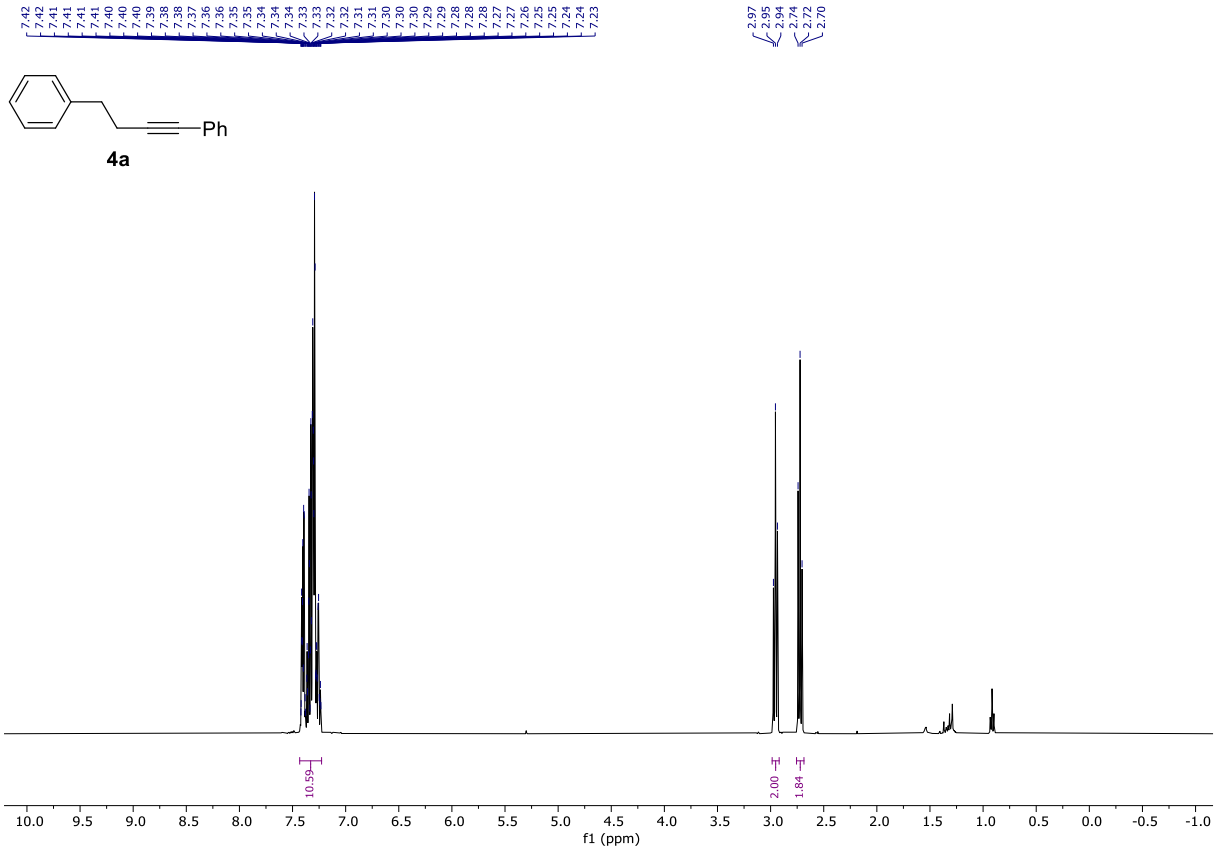
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**:



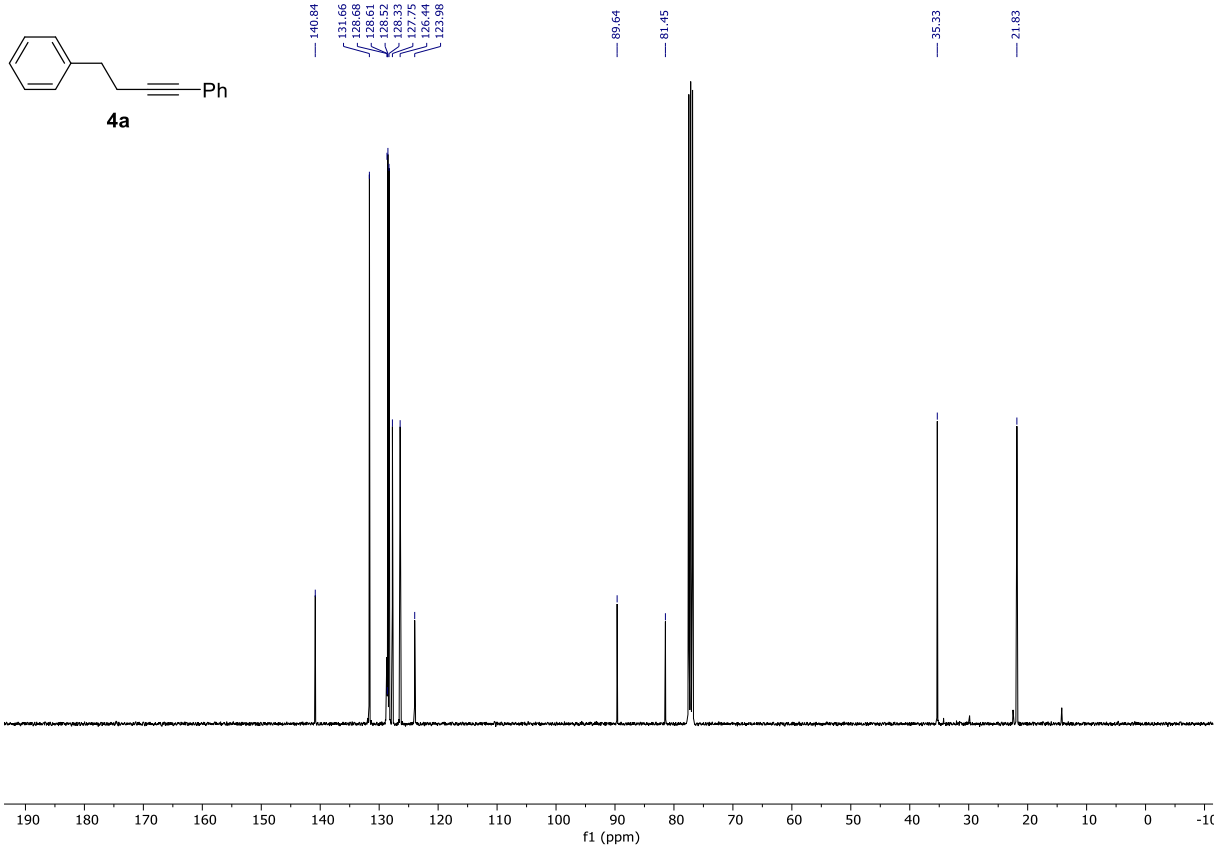
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3i**:



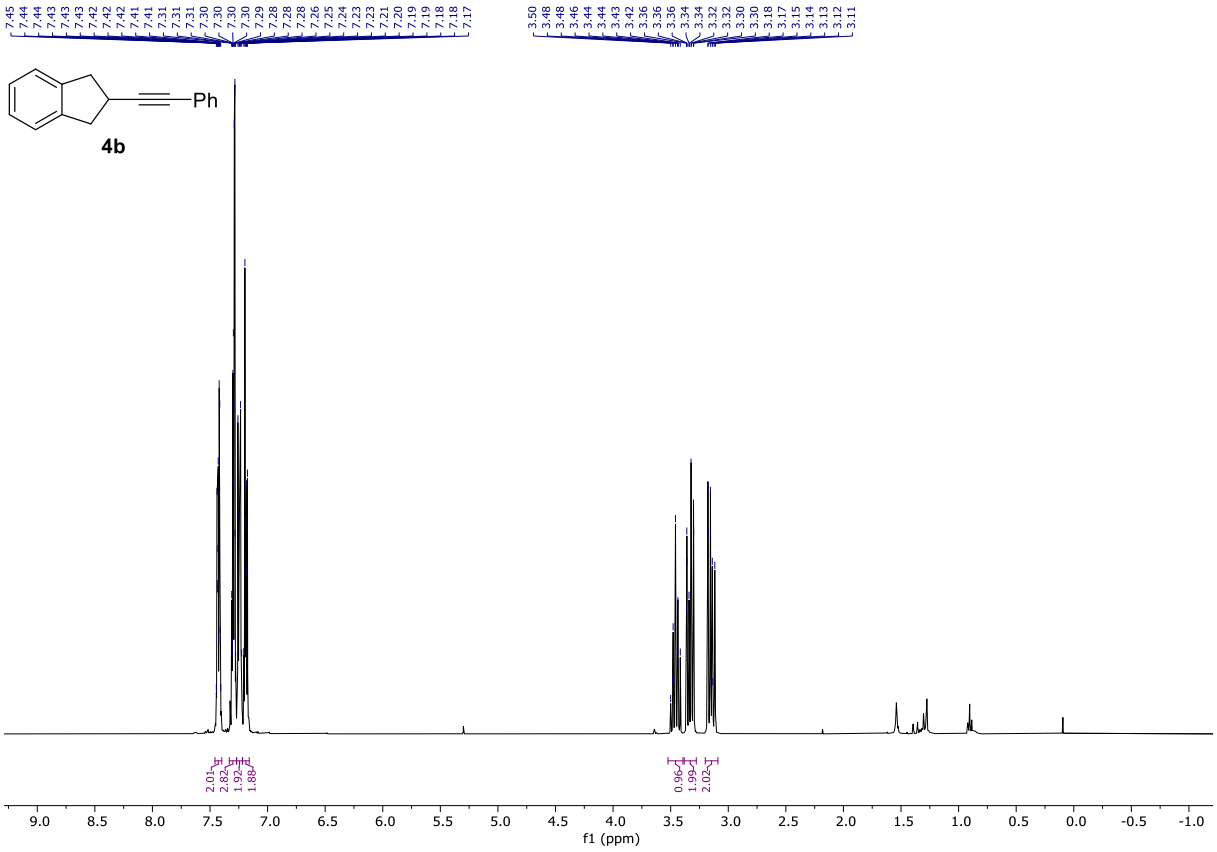
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a**:



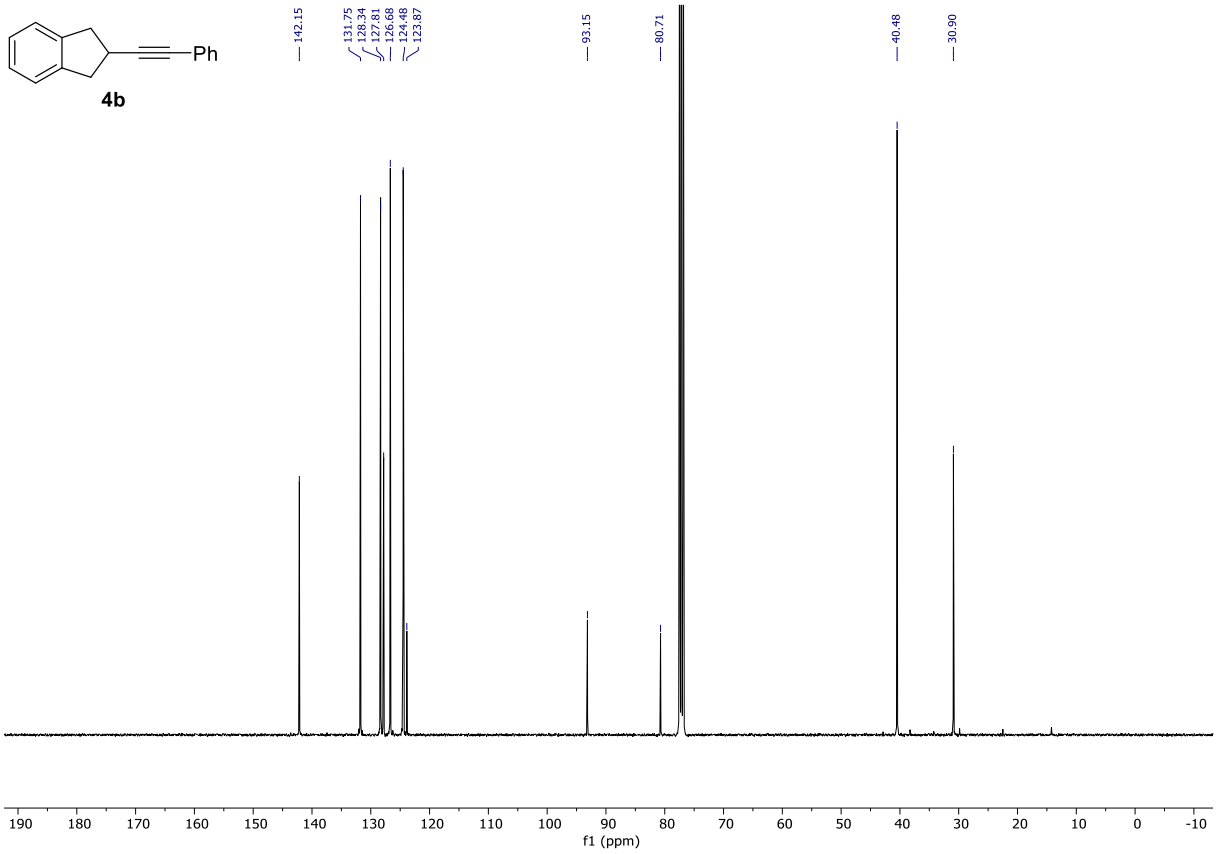
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4a**:



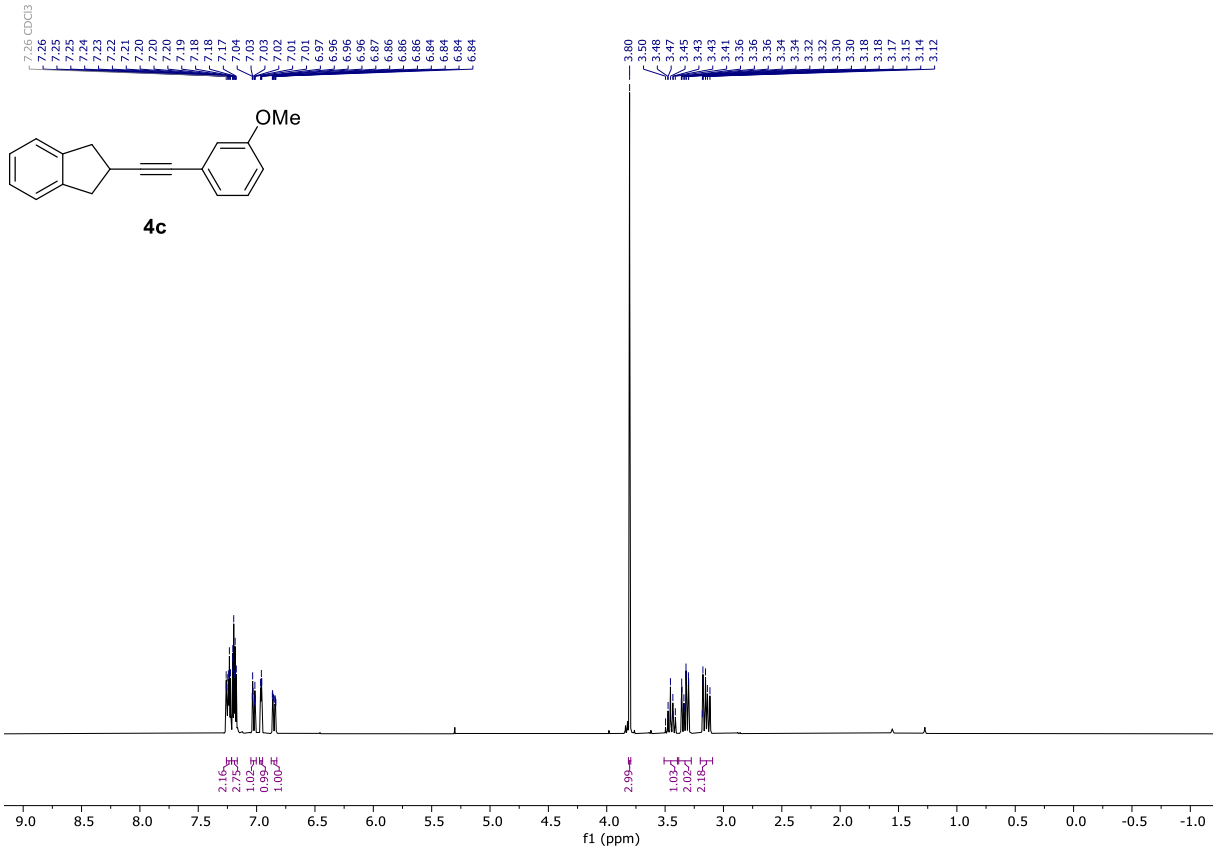
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b**:



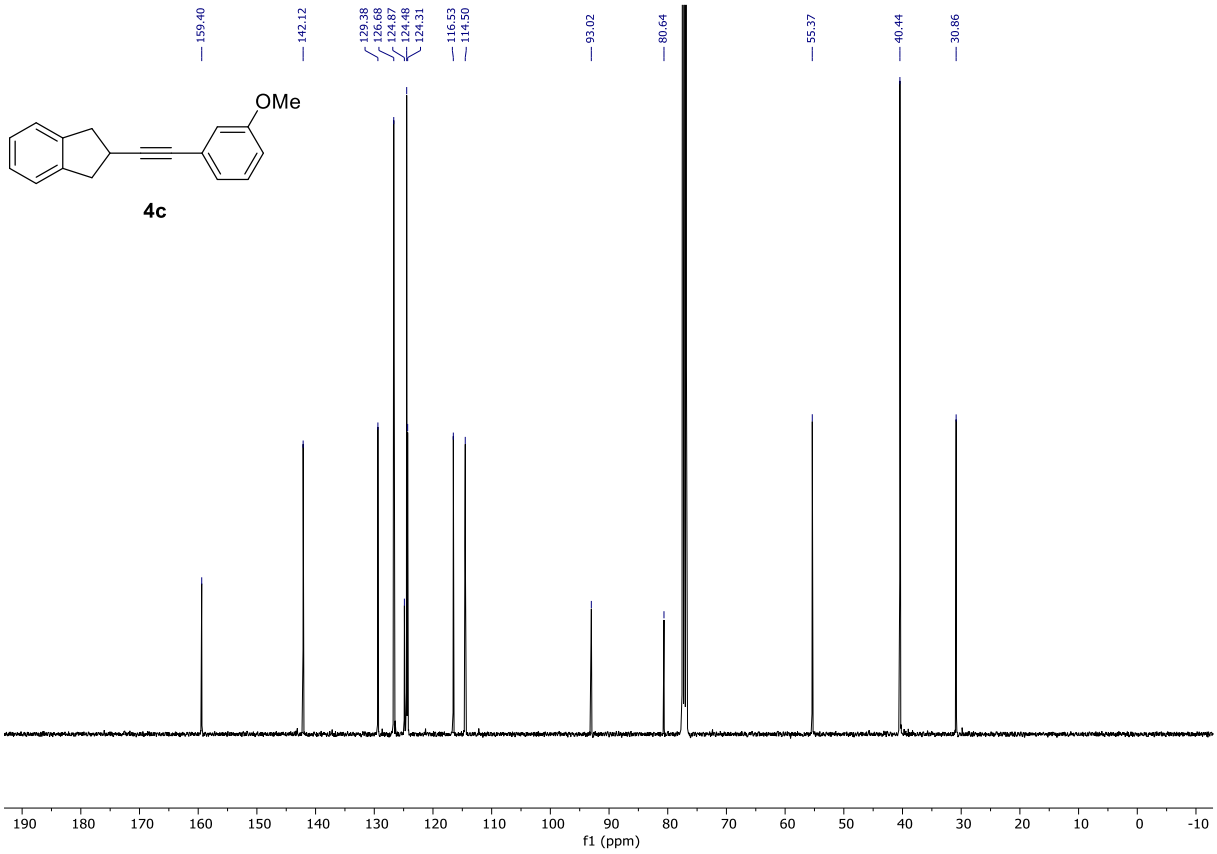
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4b**:



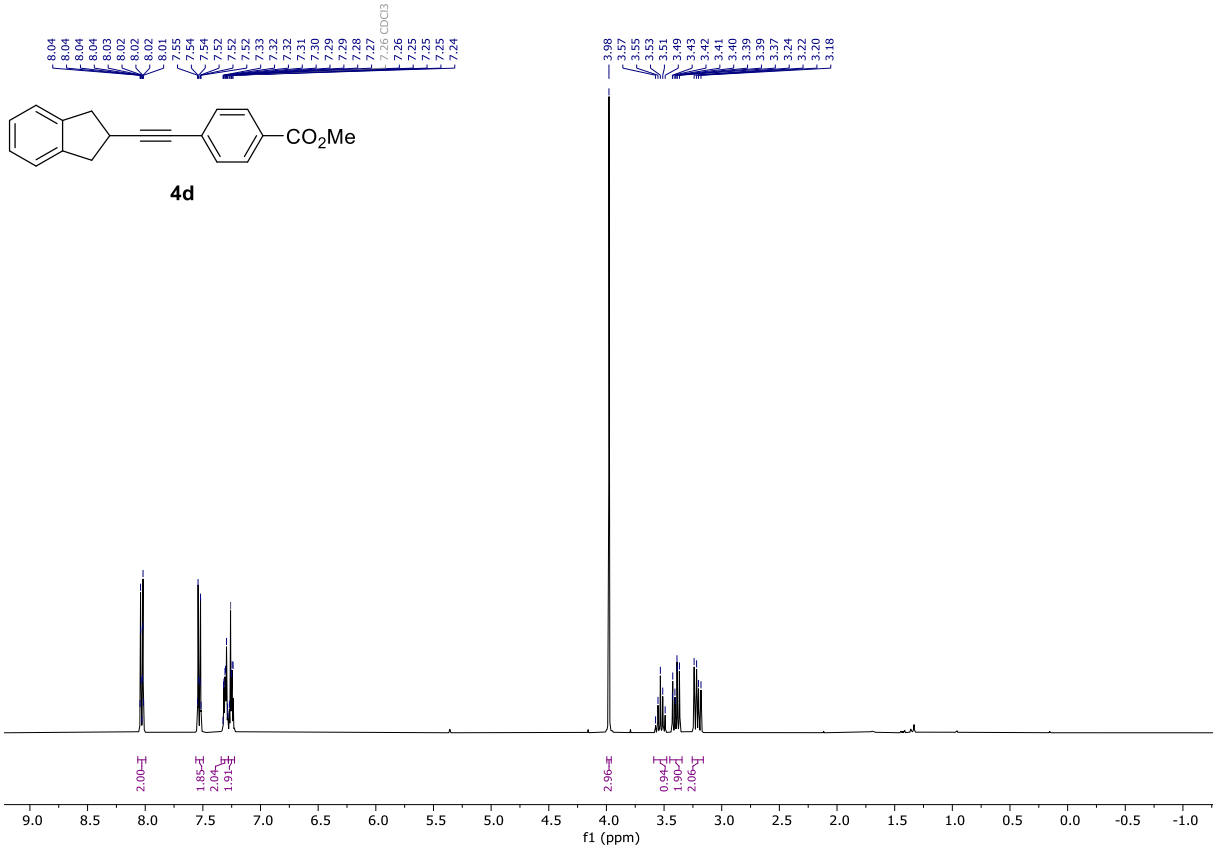
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4c**:



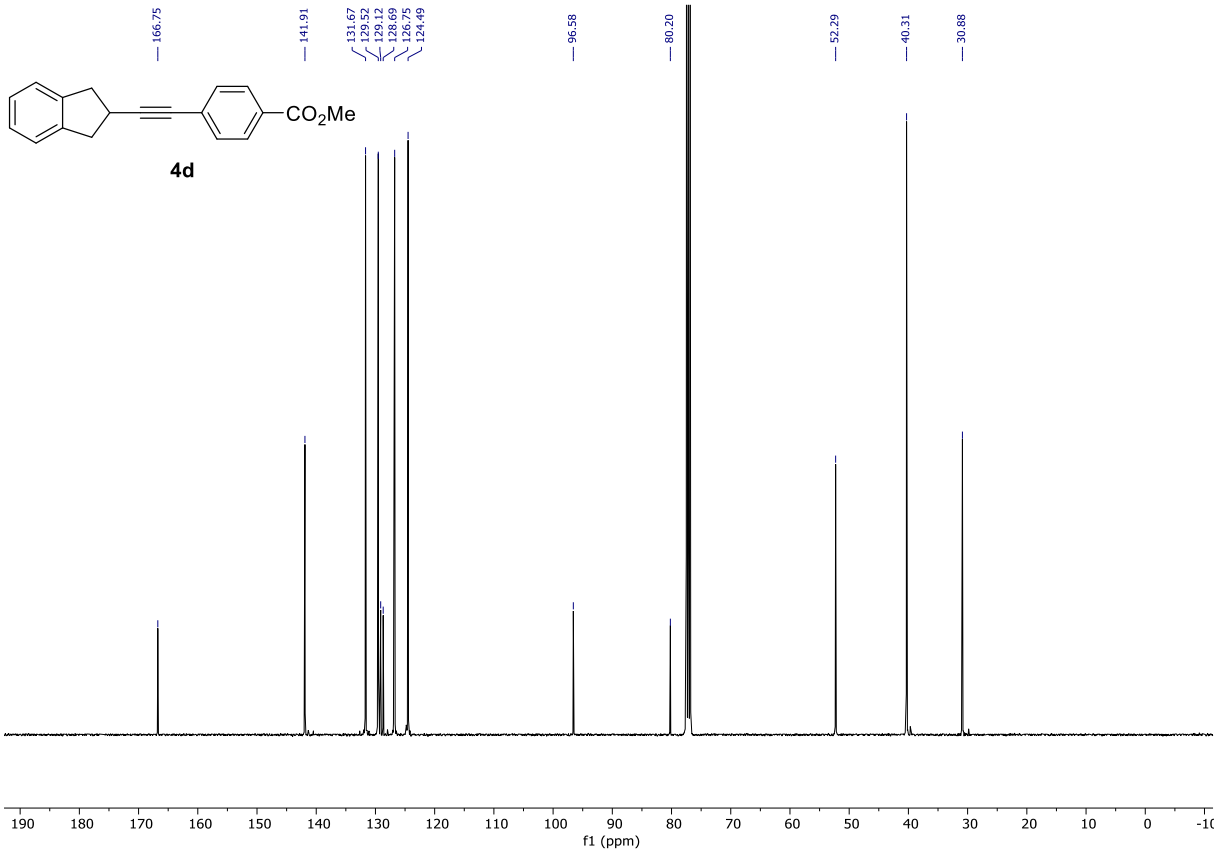
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4c**:



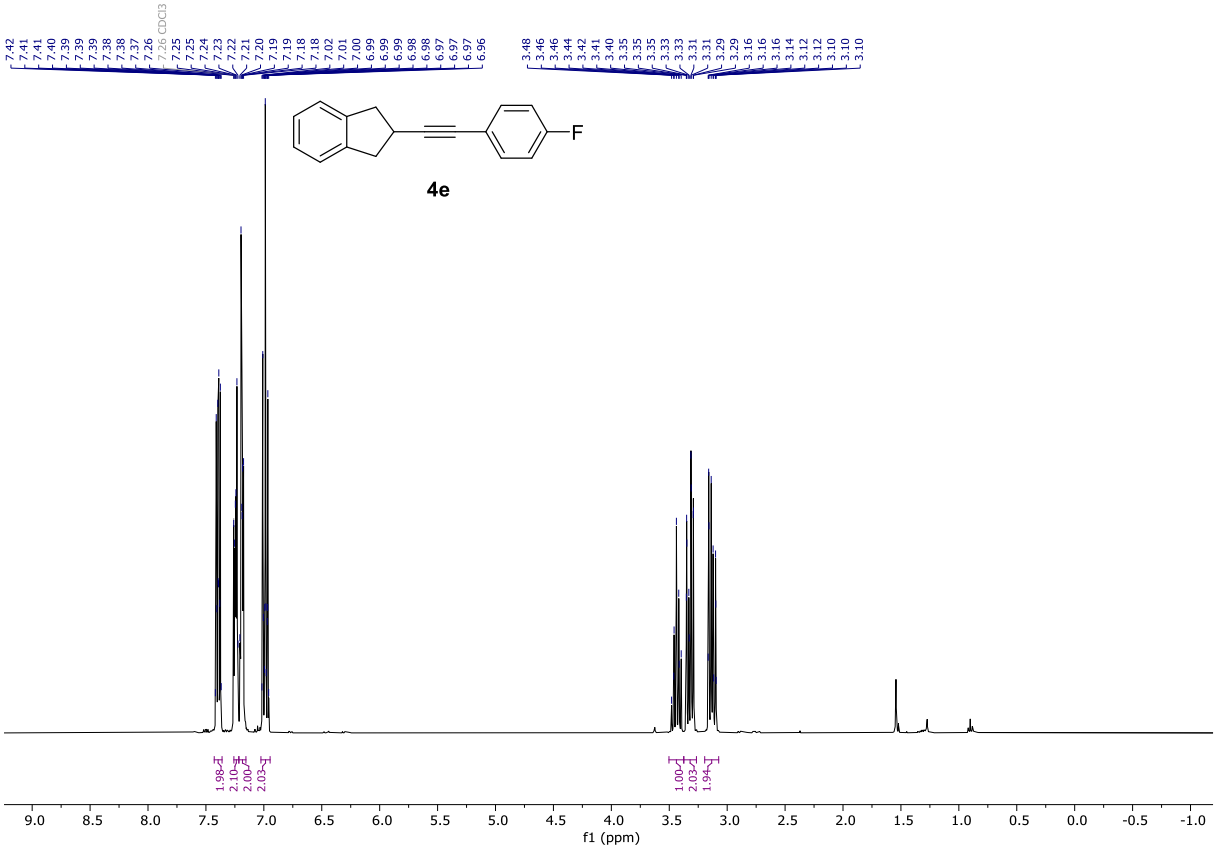
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d**:



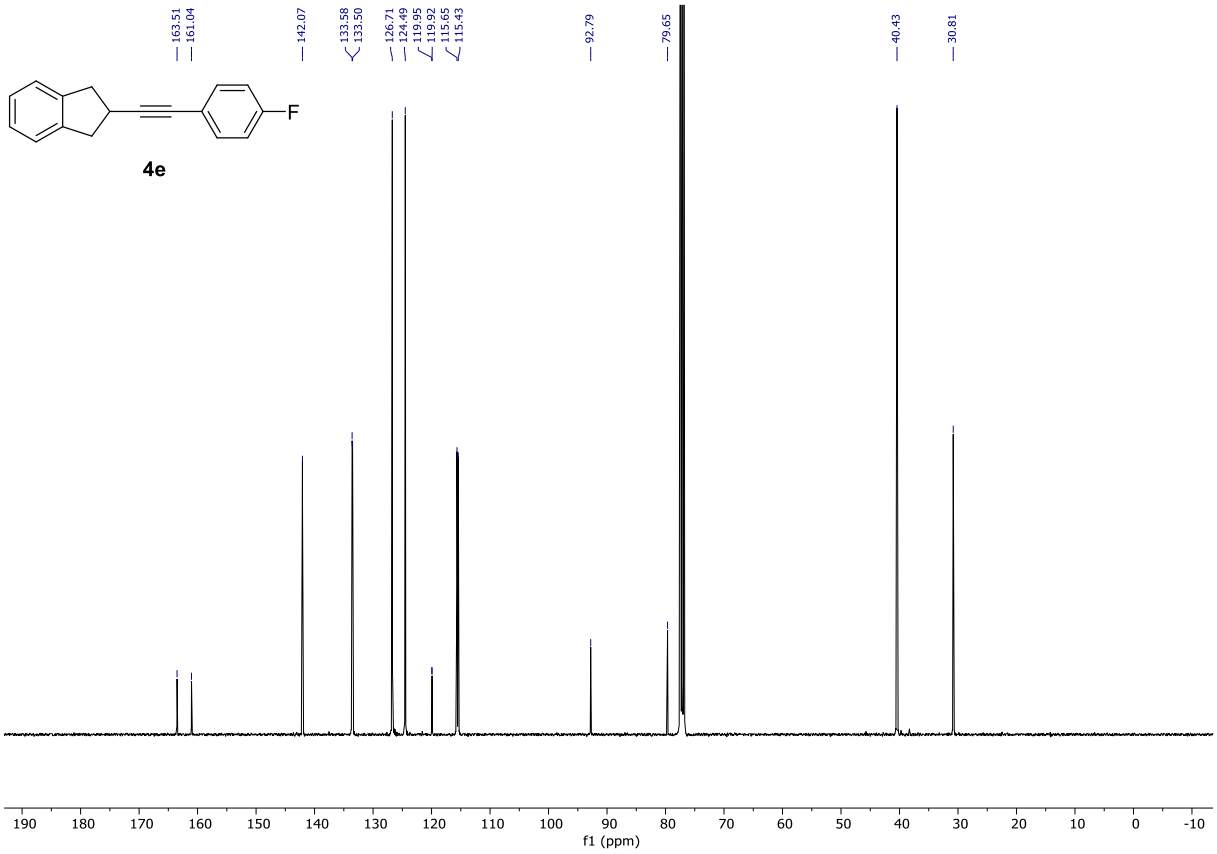
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4d**:



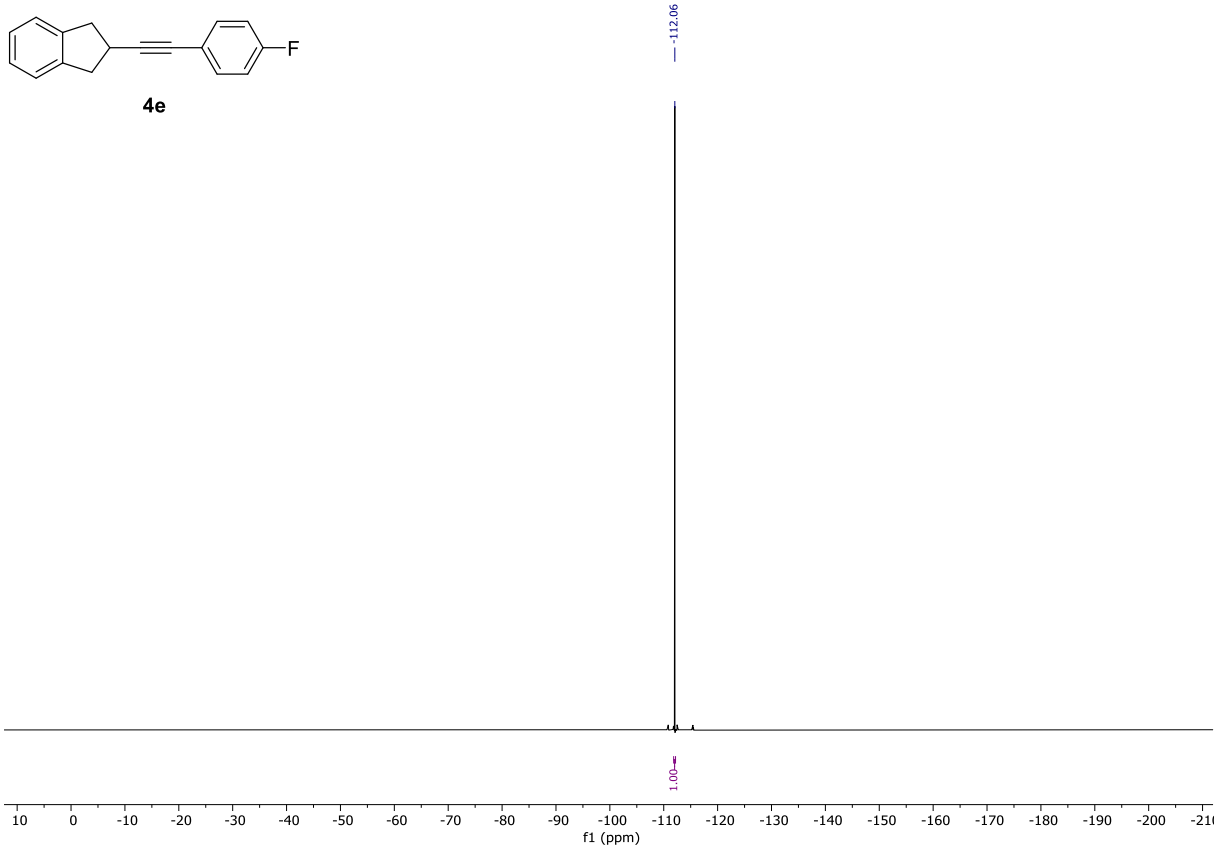
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4e**:



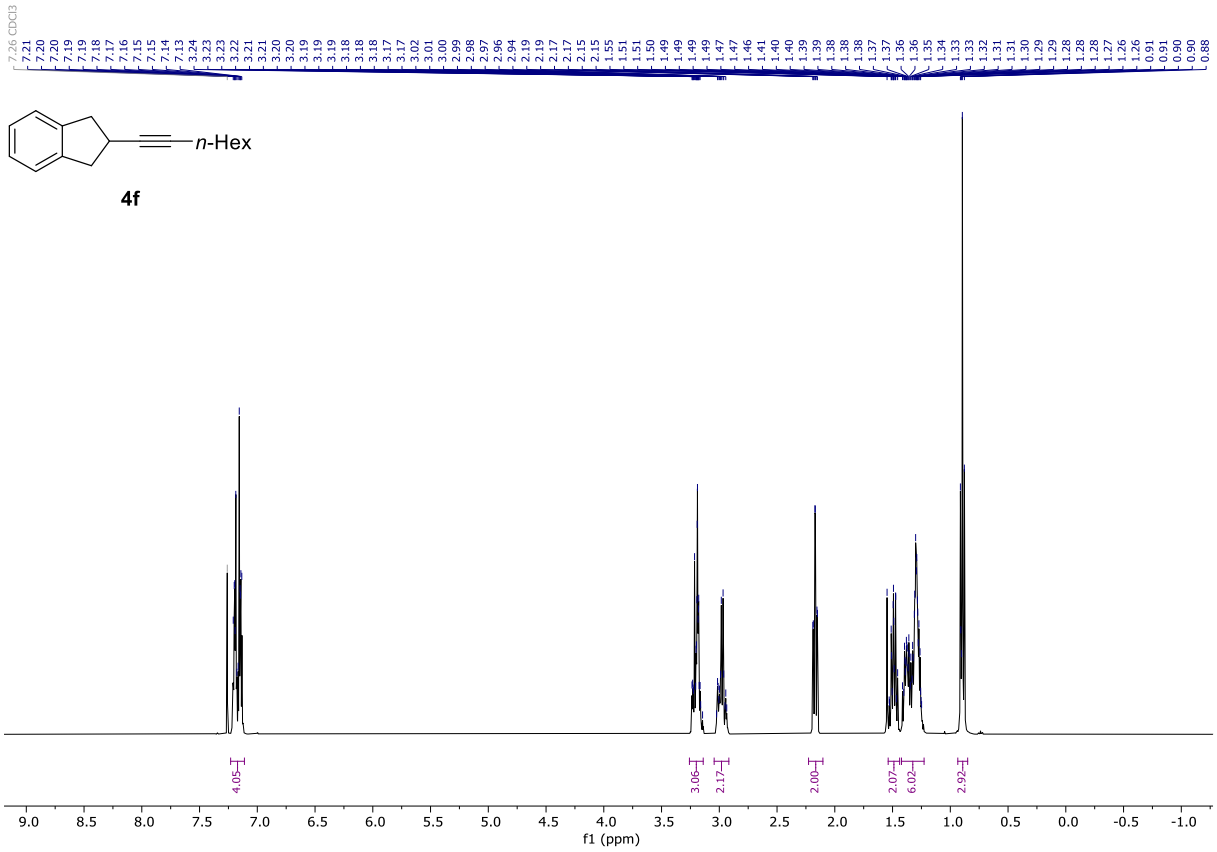
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4e**:



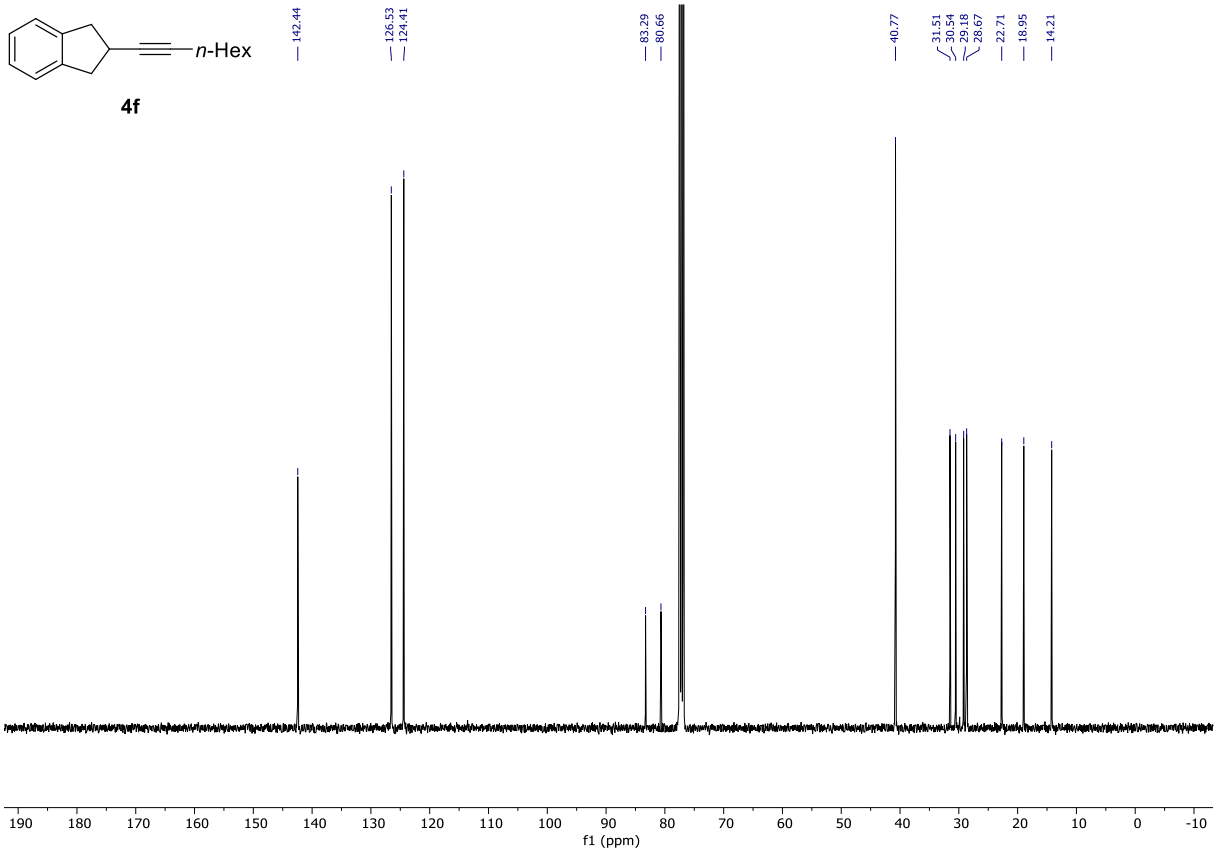
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4e**:



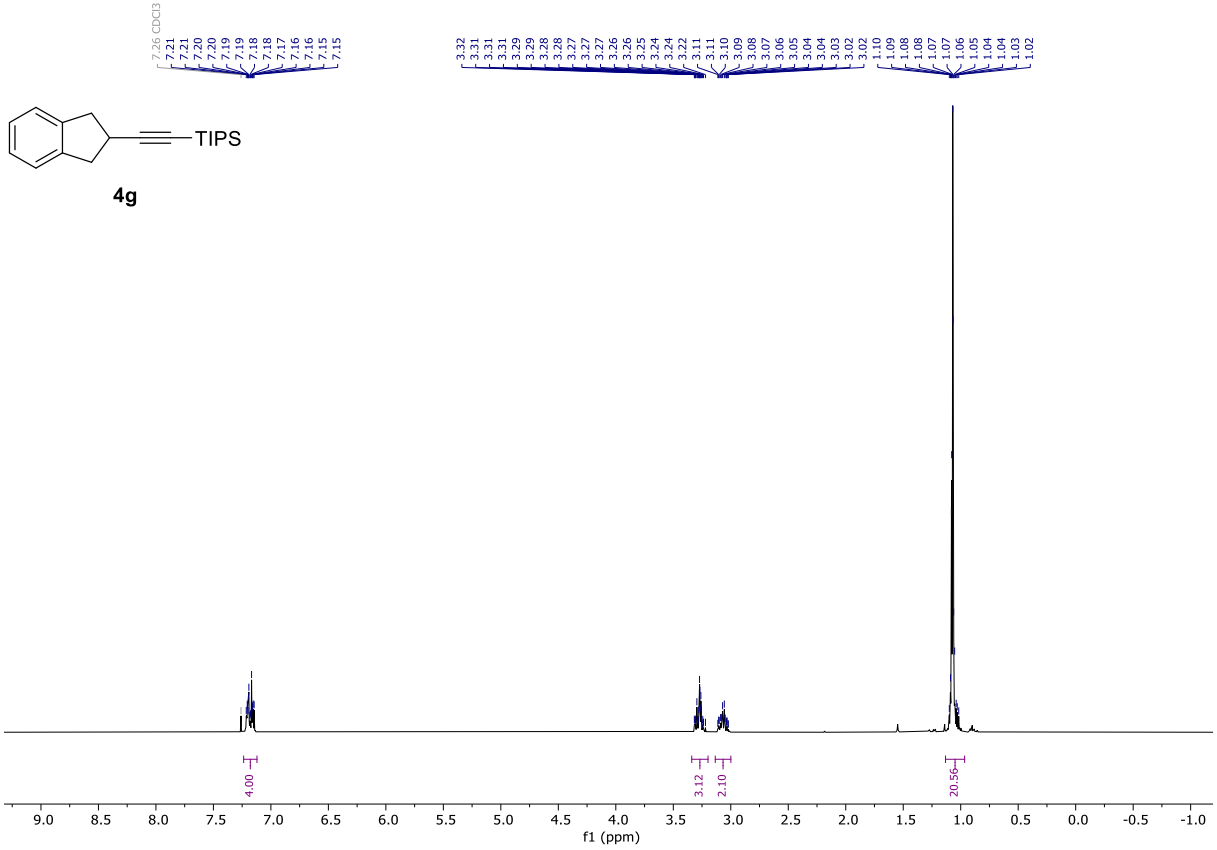
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4f**:



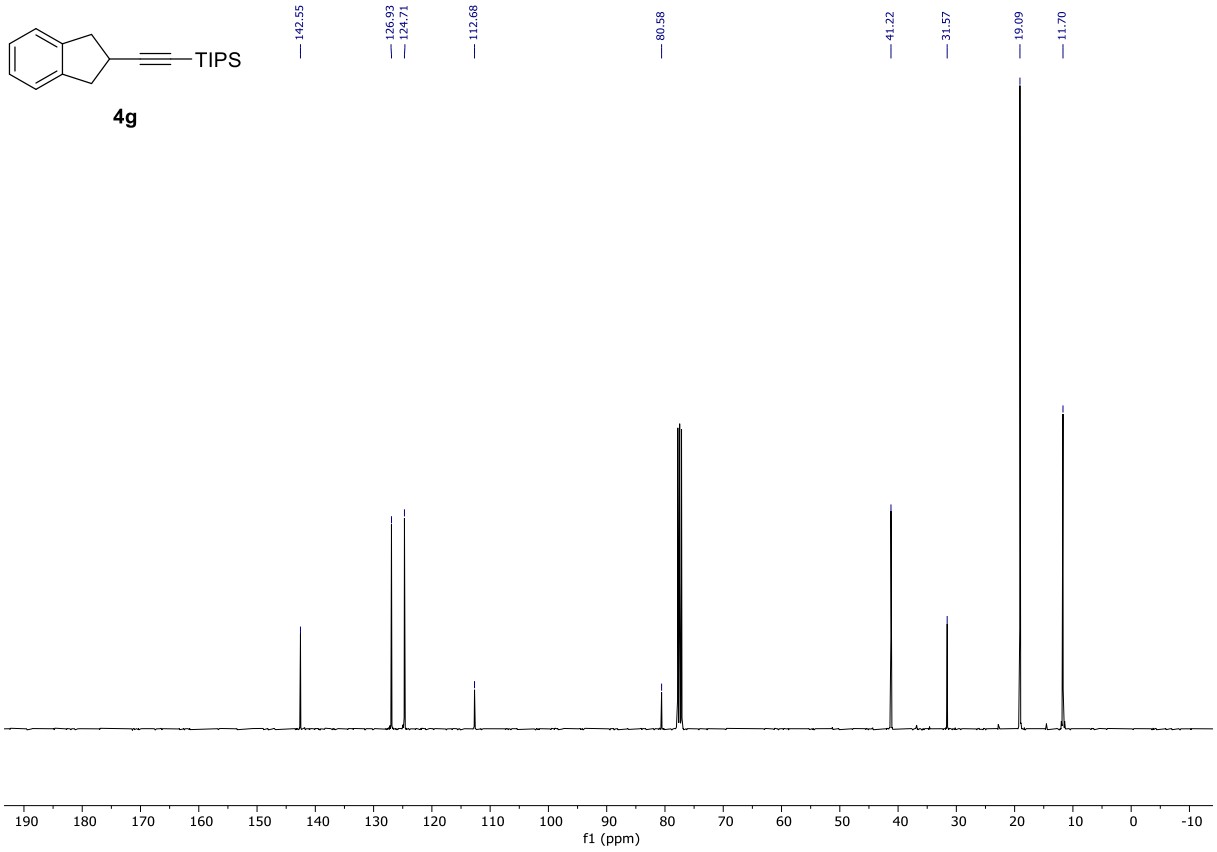
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4f**:



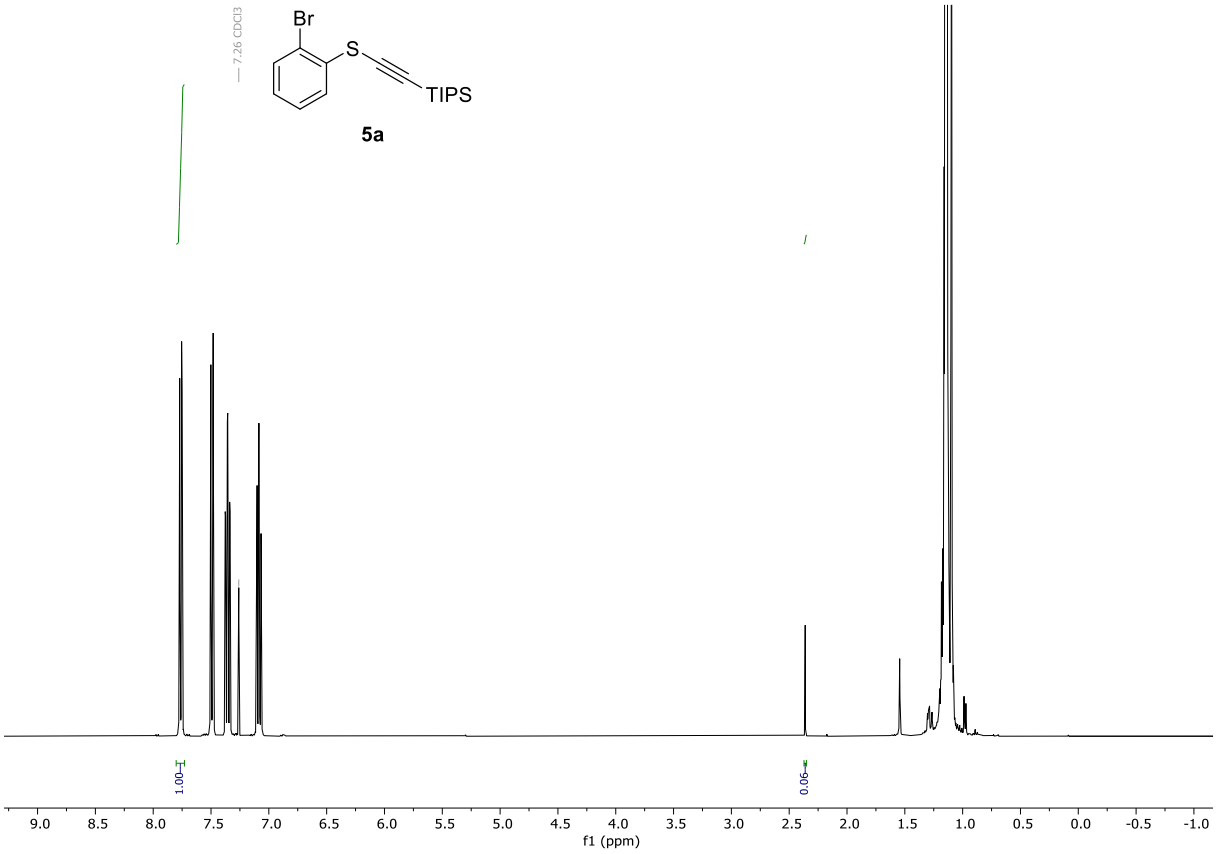
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4g**:



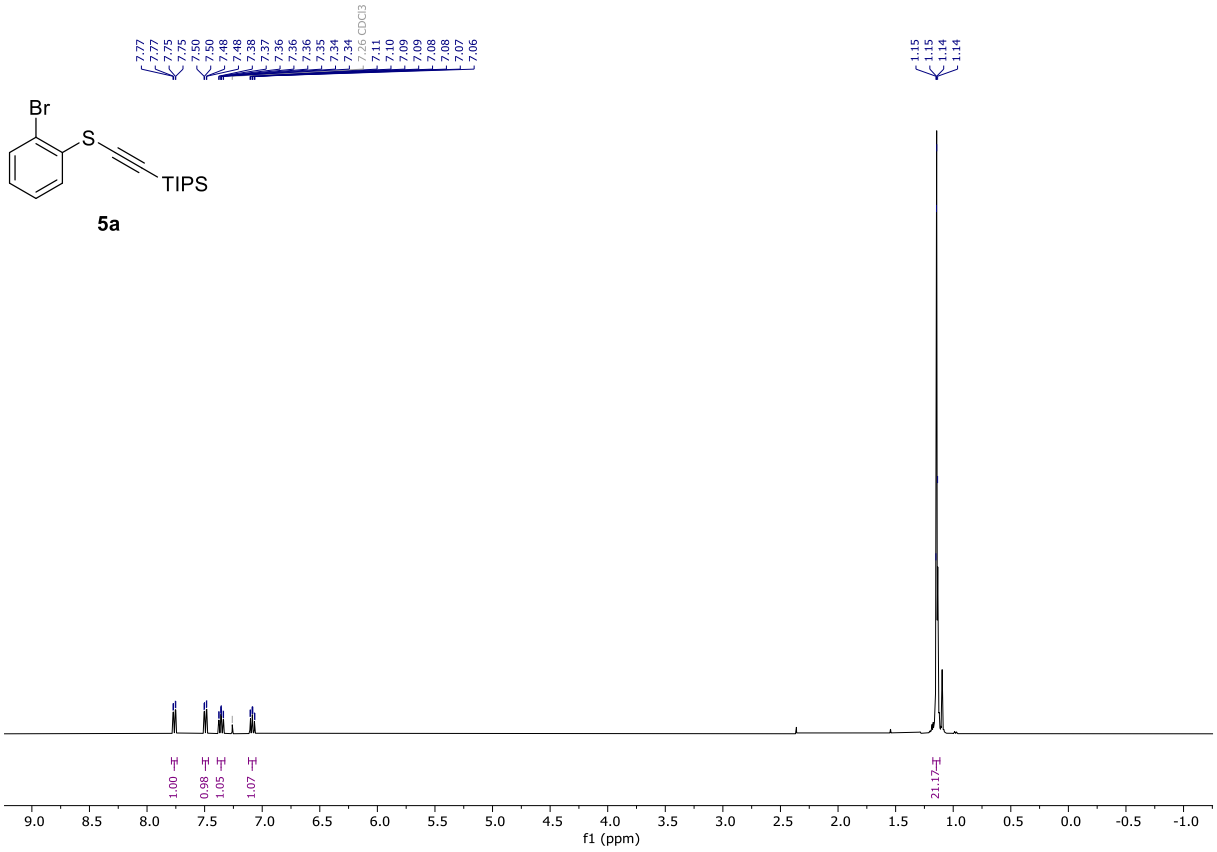
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4g**:



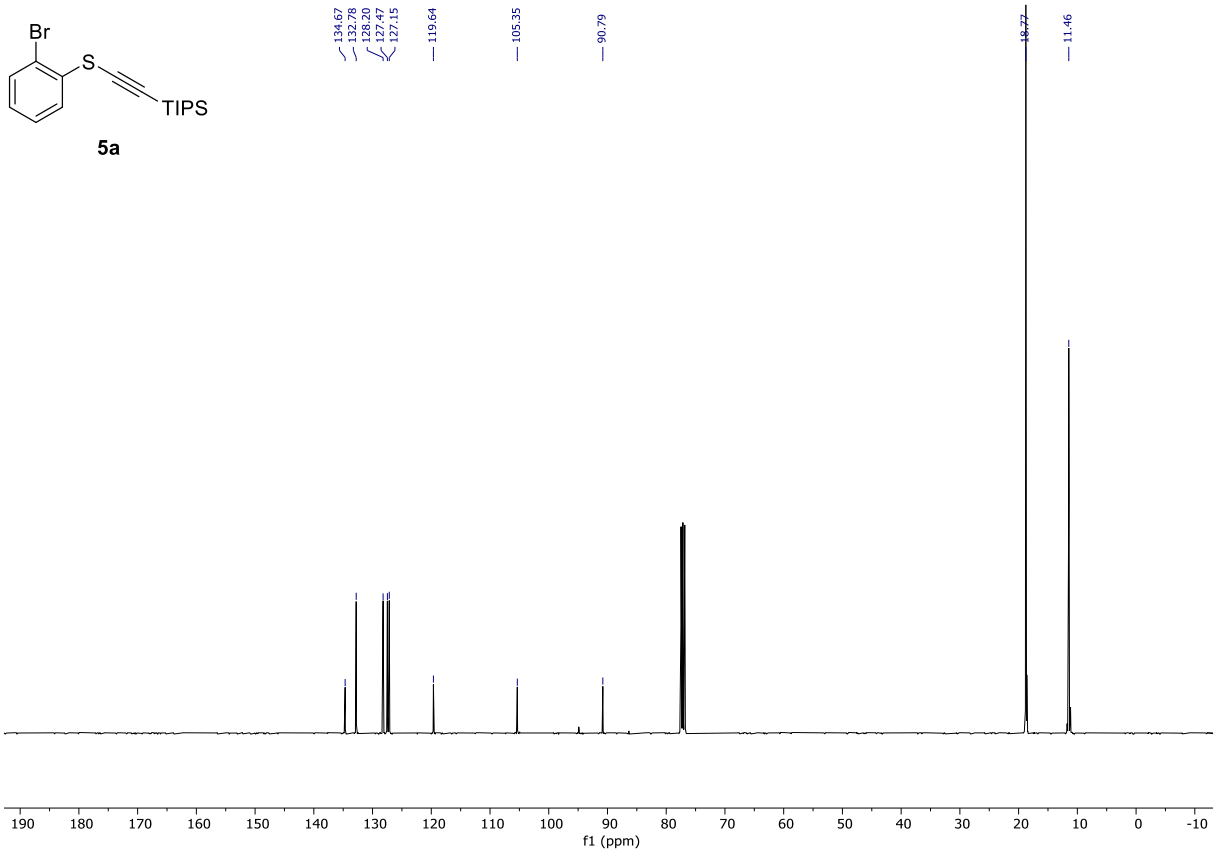
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5a** (purity determination):



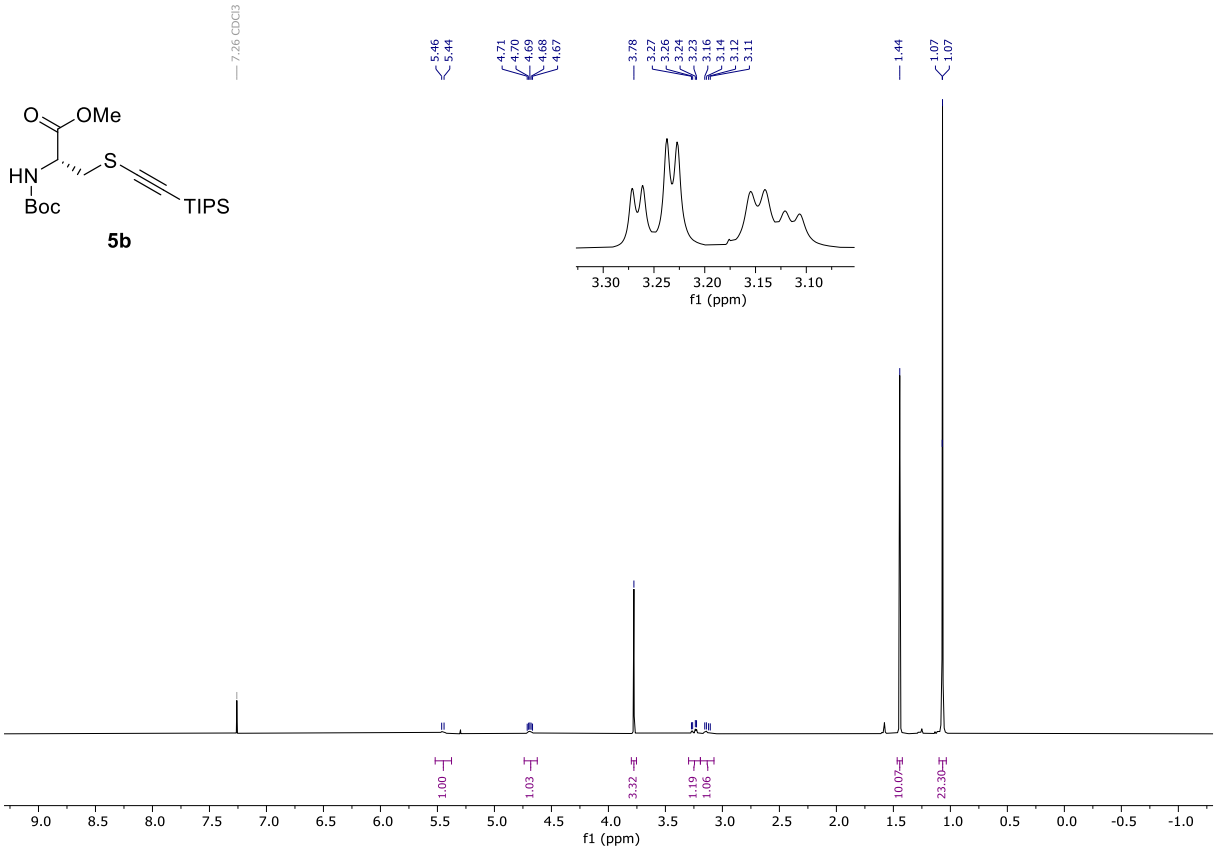
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5a**:



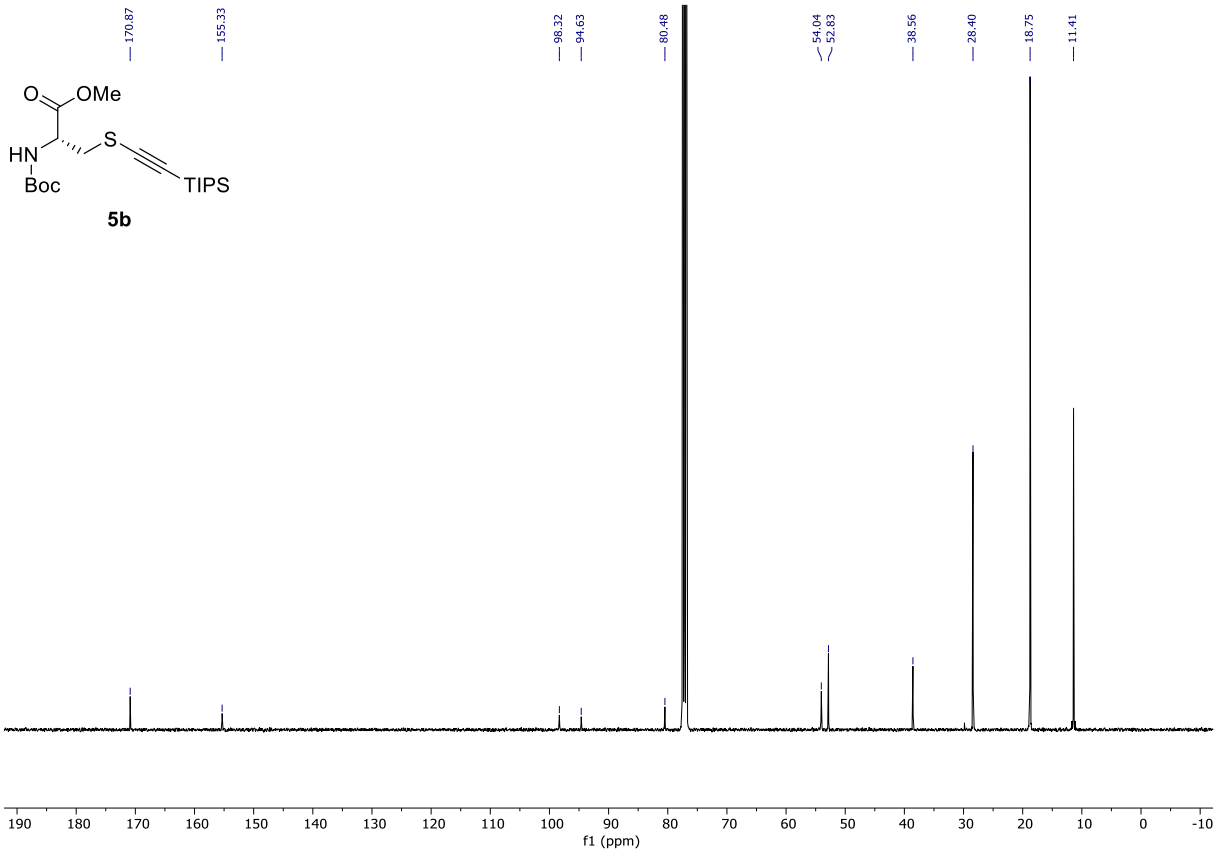
^{13}C NMR (101 MHz, $CDCl_3$) of compound **5a**:



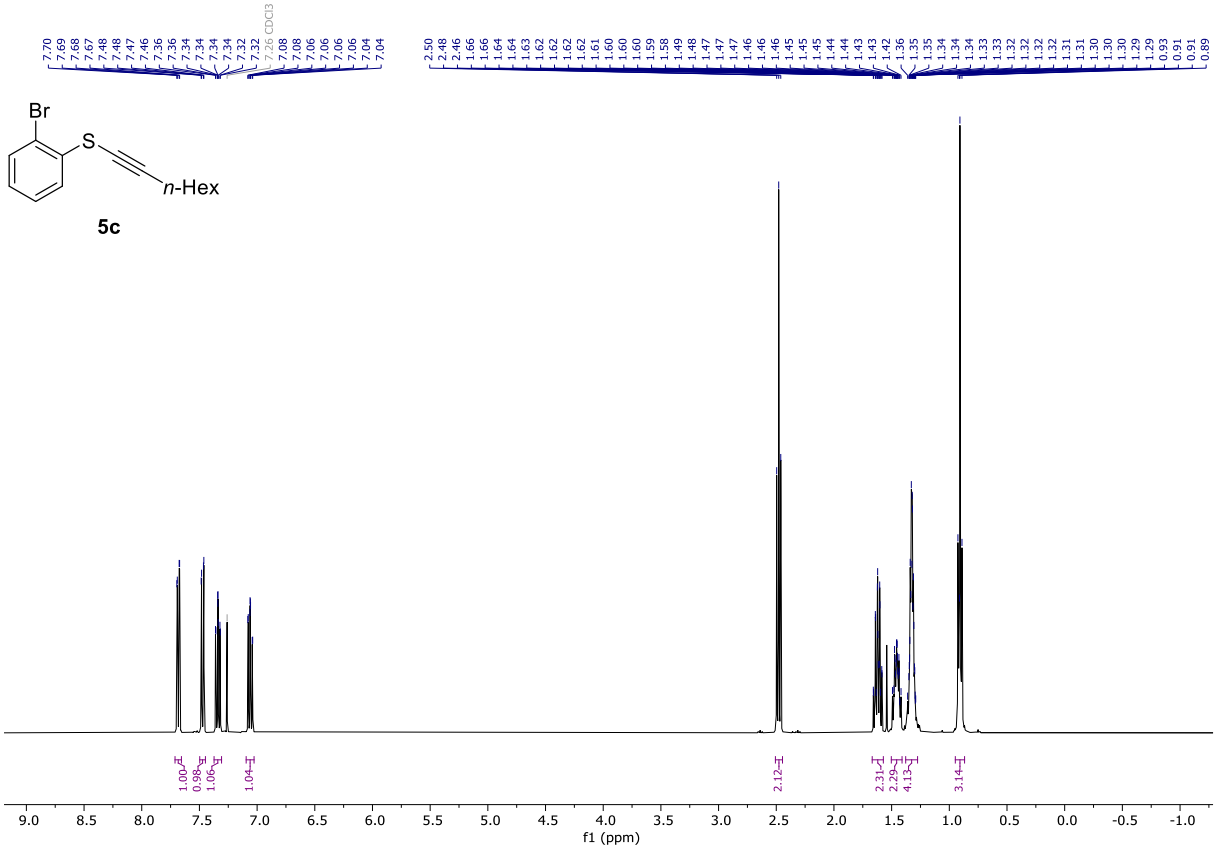
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5b**:



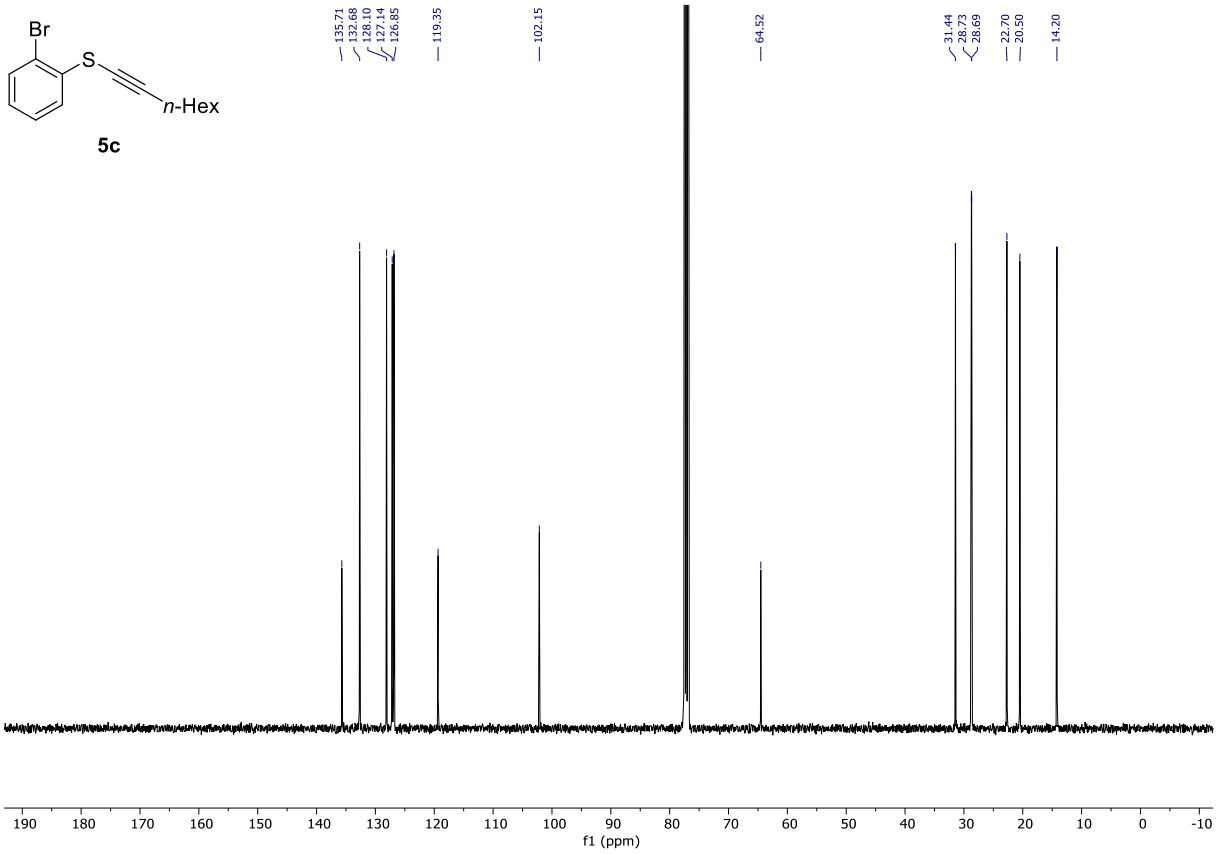
^{13}C NMR (101 MHz, $CDCl_3$) of compound **5b**:



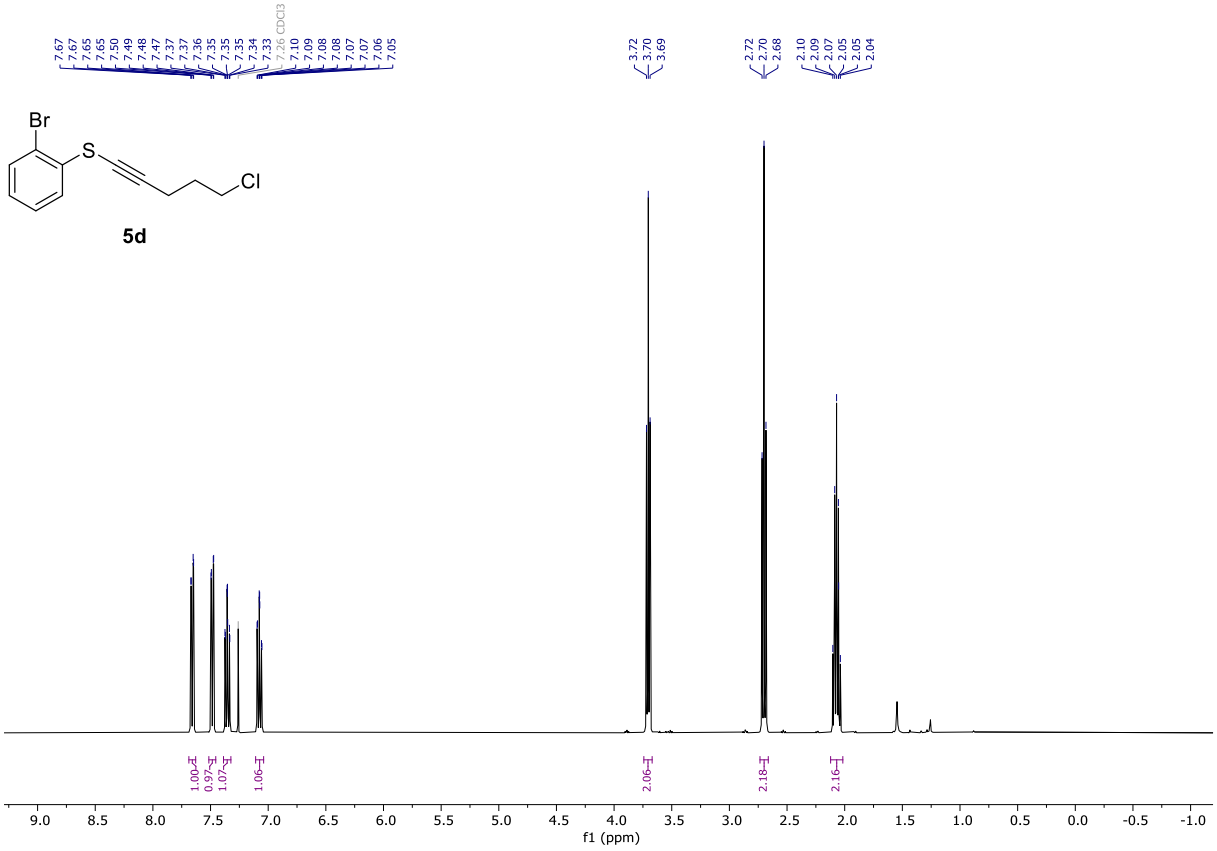
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5c**:



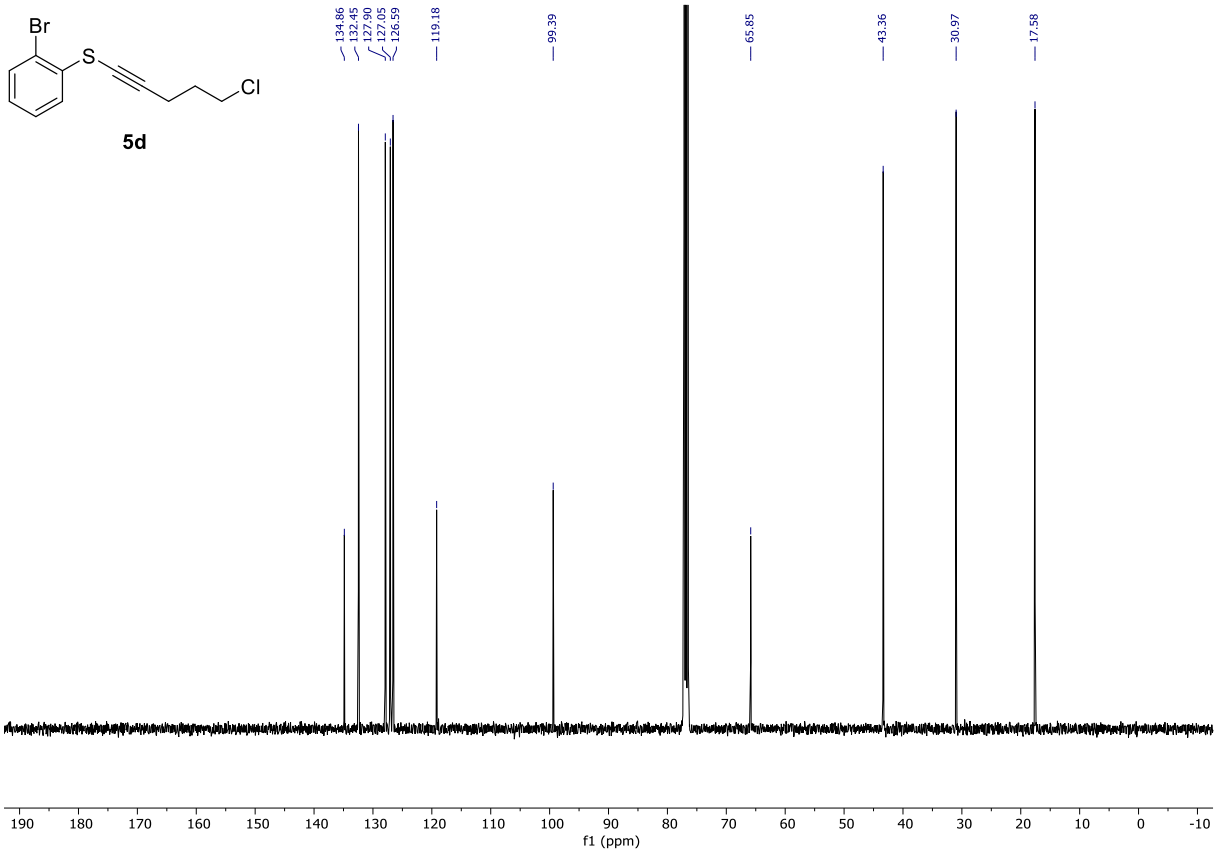
^{13}C NMR (101 MHz, $CDCl_3$) of compound **5c**:



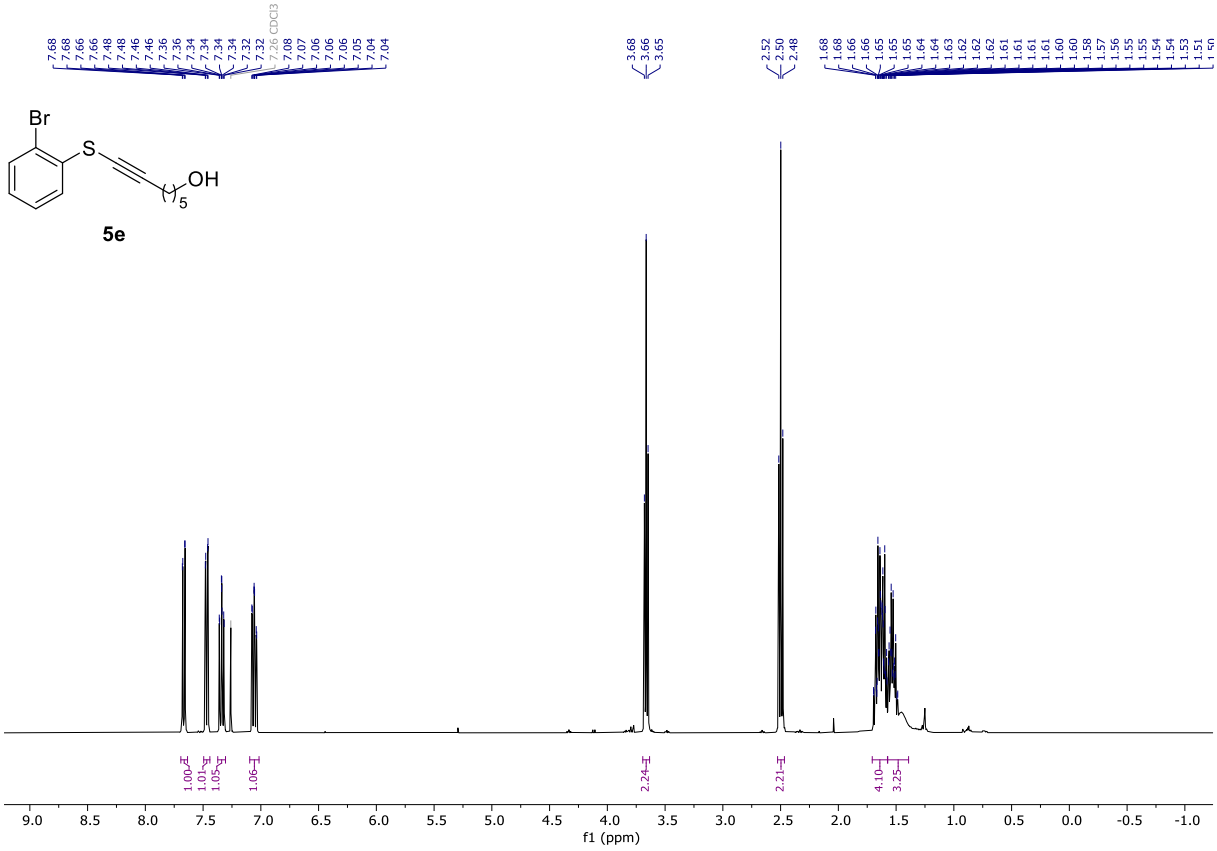
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5d**:



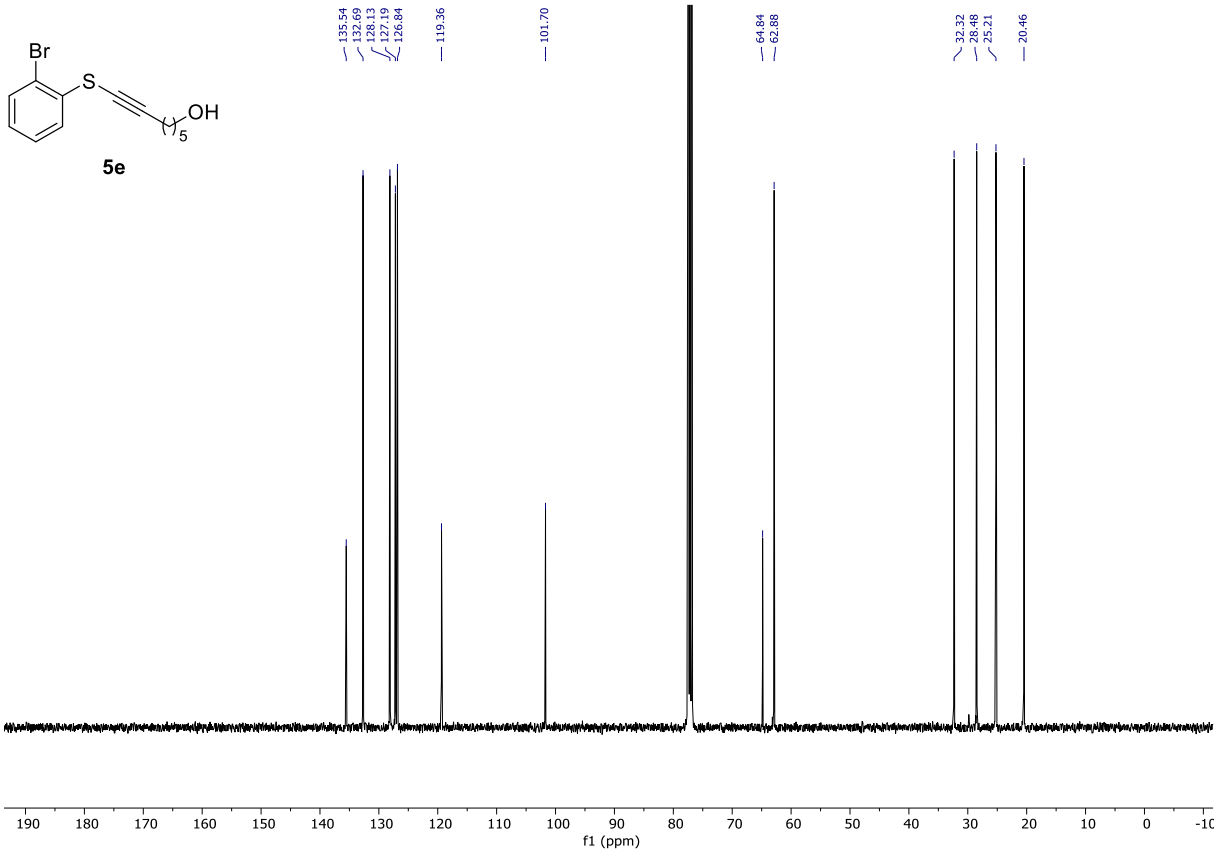
^{13}C NMR (101 MHz, $CDCl_3$) of compound **5d**:



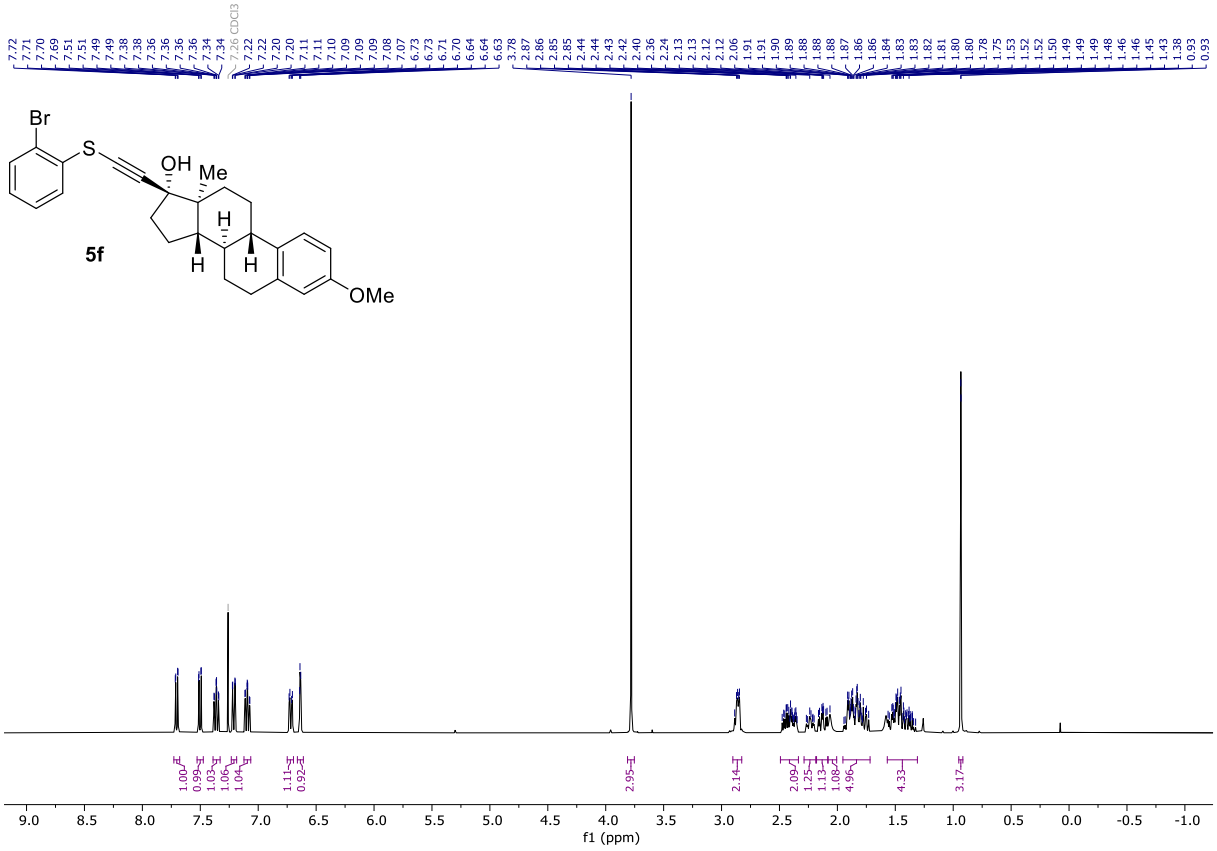
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5e**:



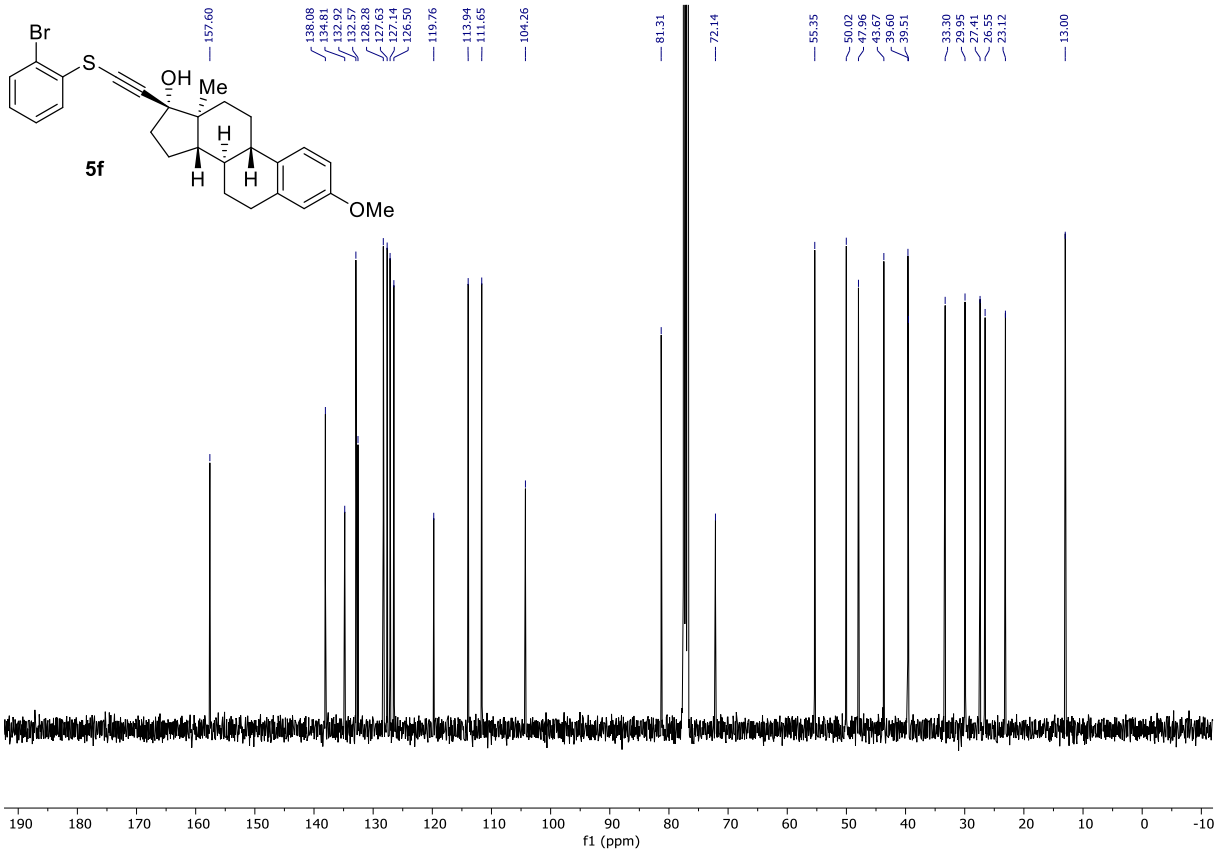
^{13}C NMR (101 MHz, $CDCl_3$) of compound **5e**:



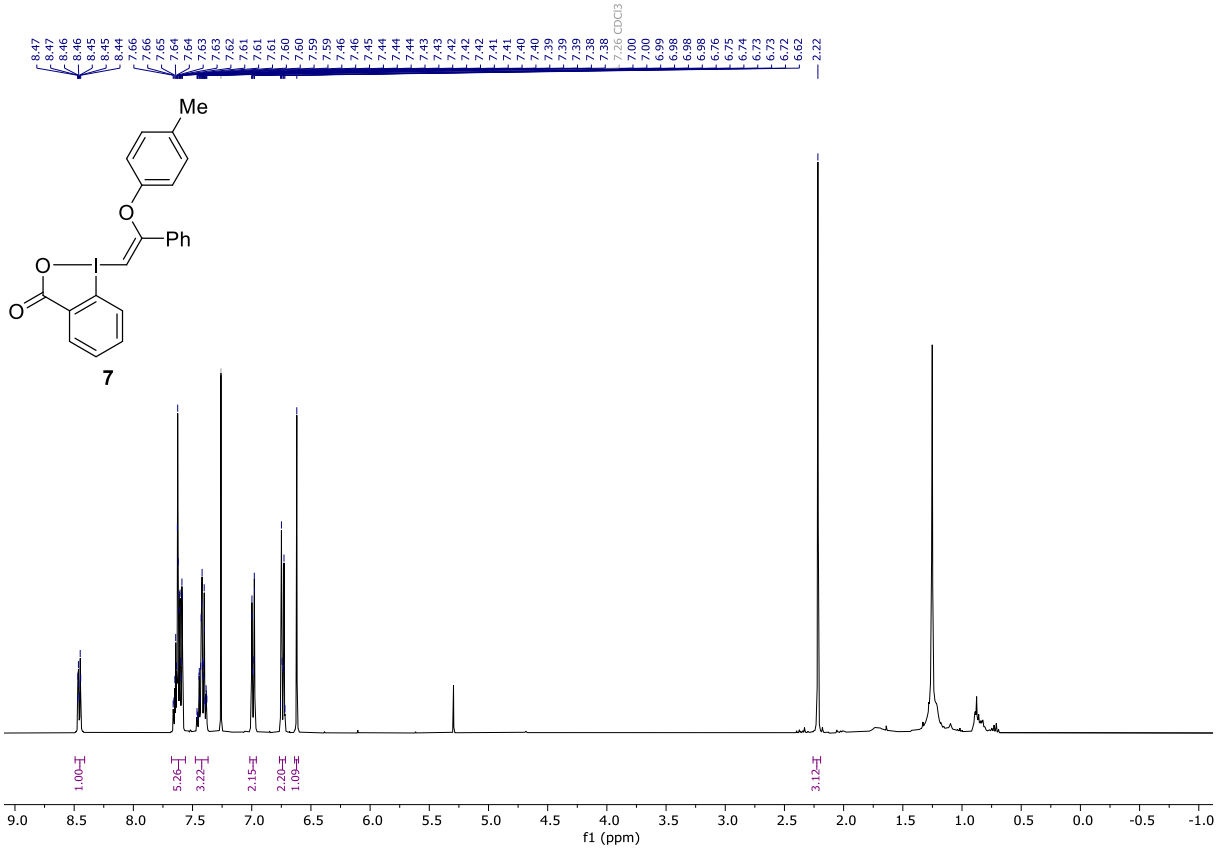
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5f**:



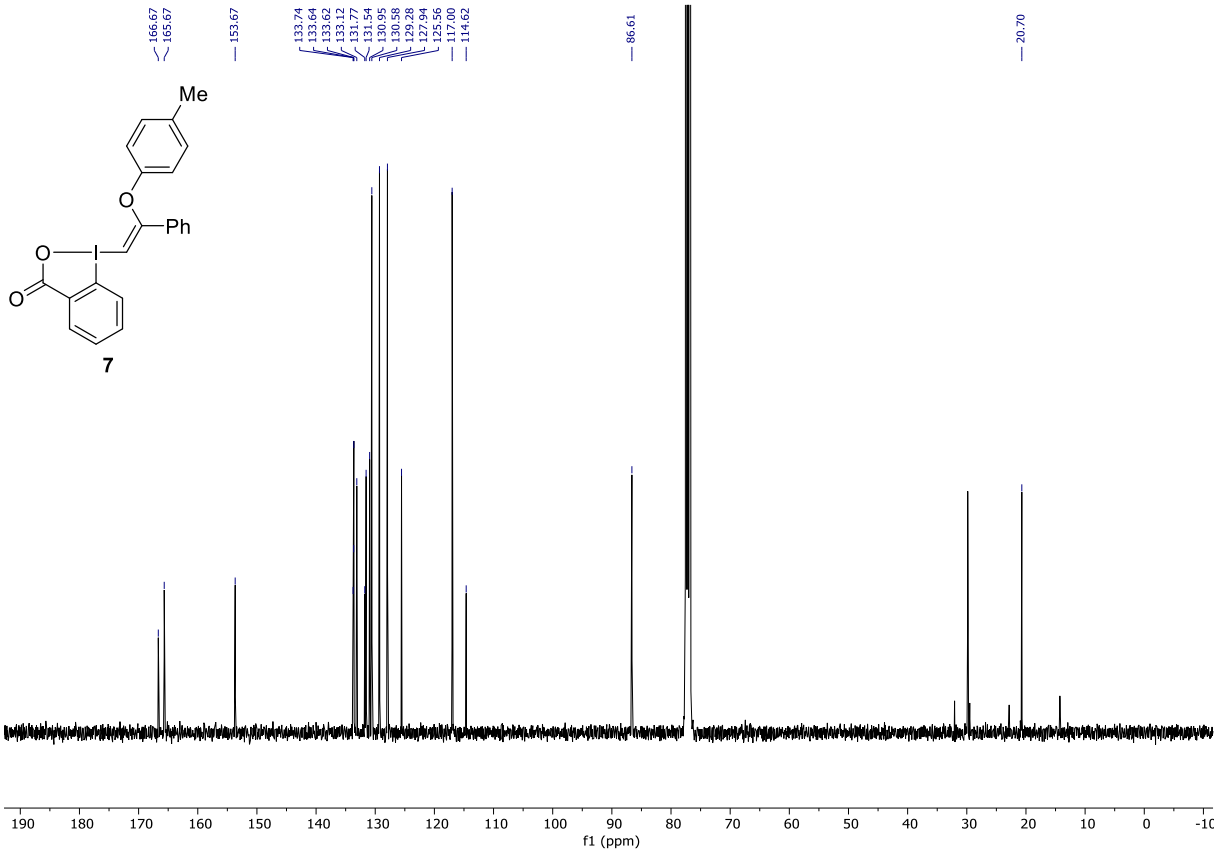
^{13}C NMR (101 MHz, $CDCl_3$) of compound **5f**:



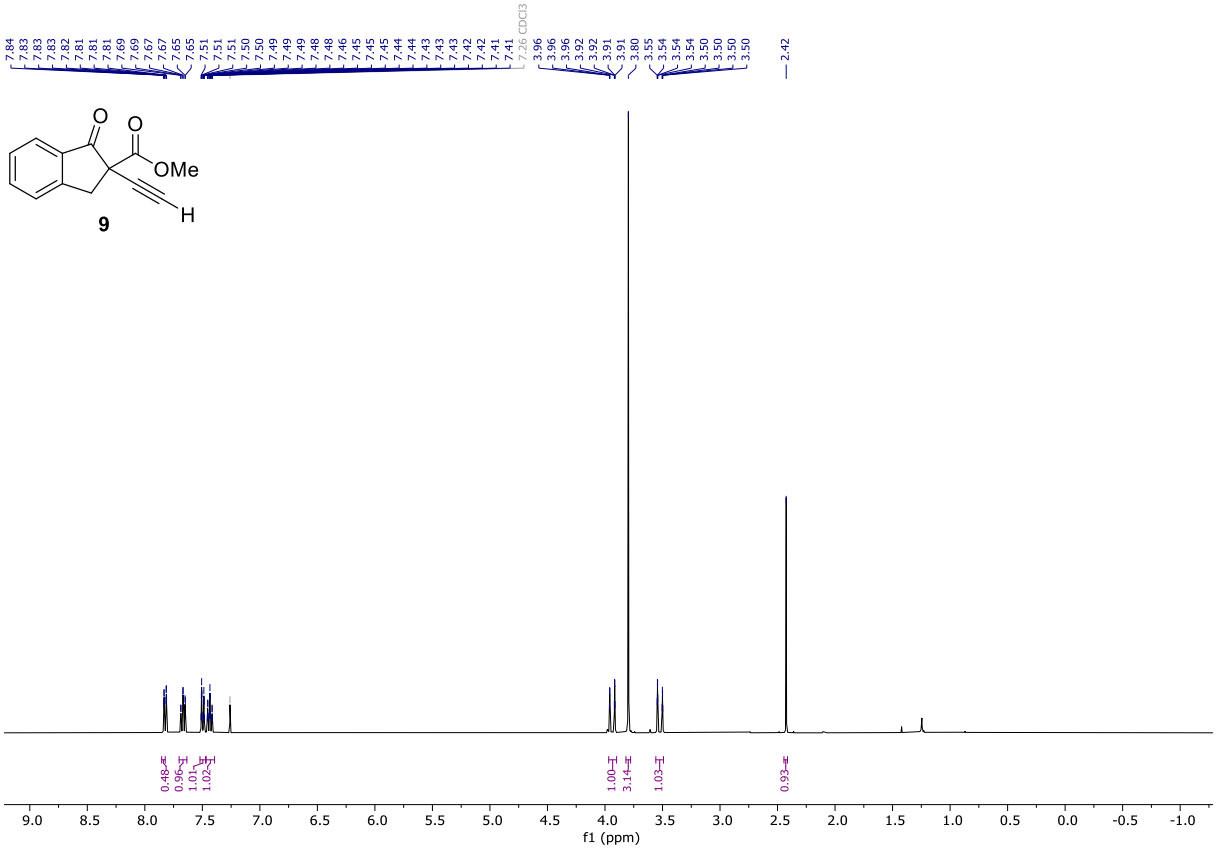
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7**:



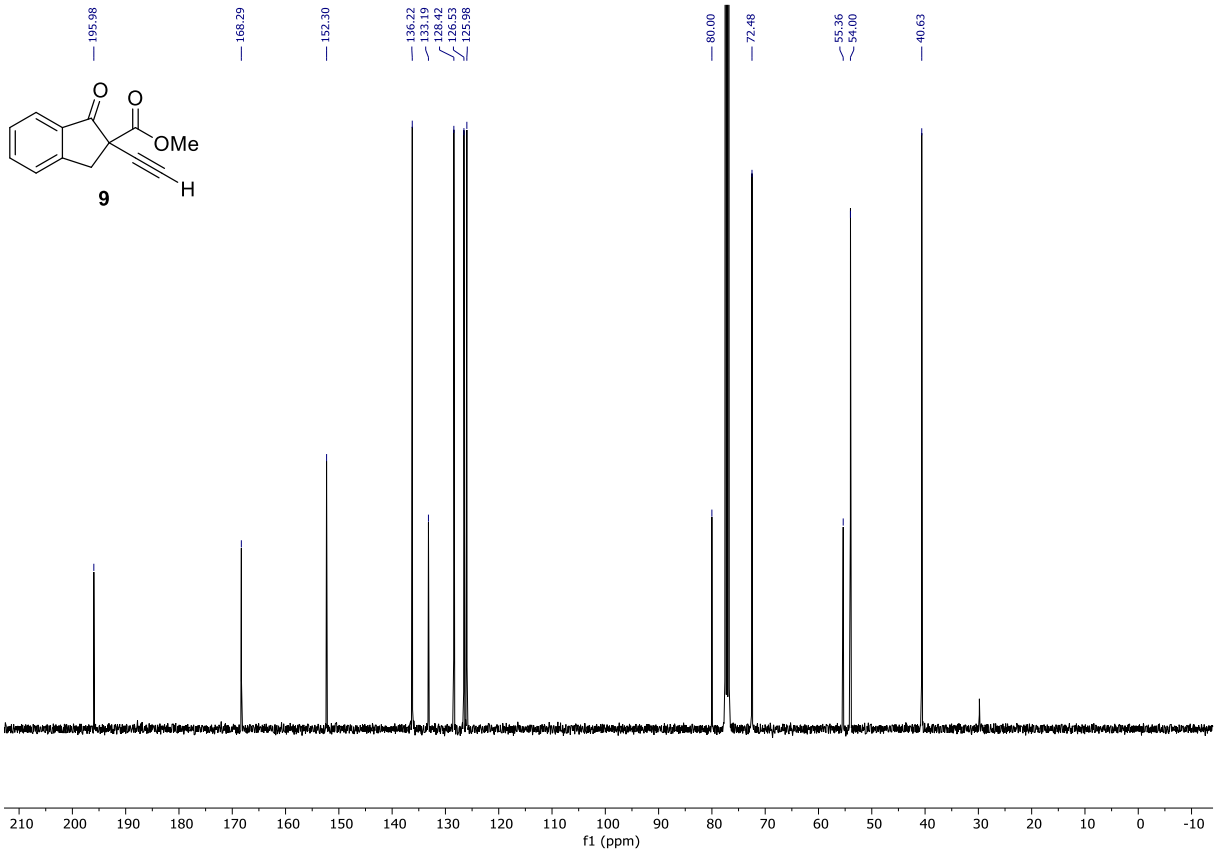
^{13}C NMR (101 MHz, $CDCl_3$) of compound **7**:



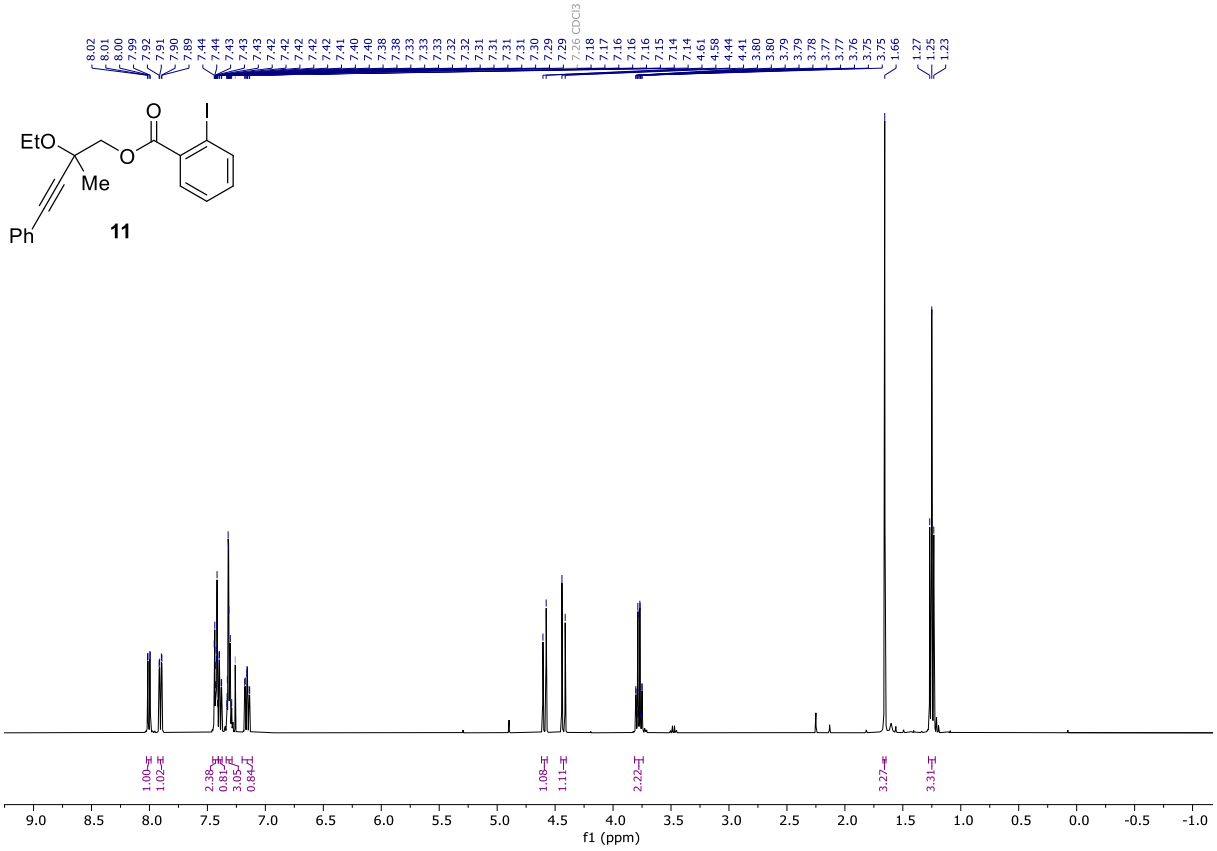
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9**:



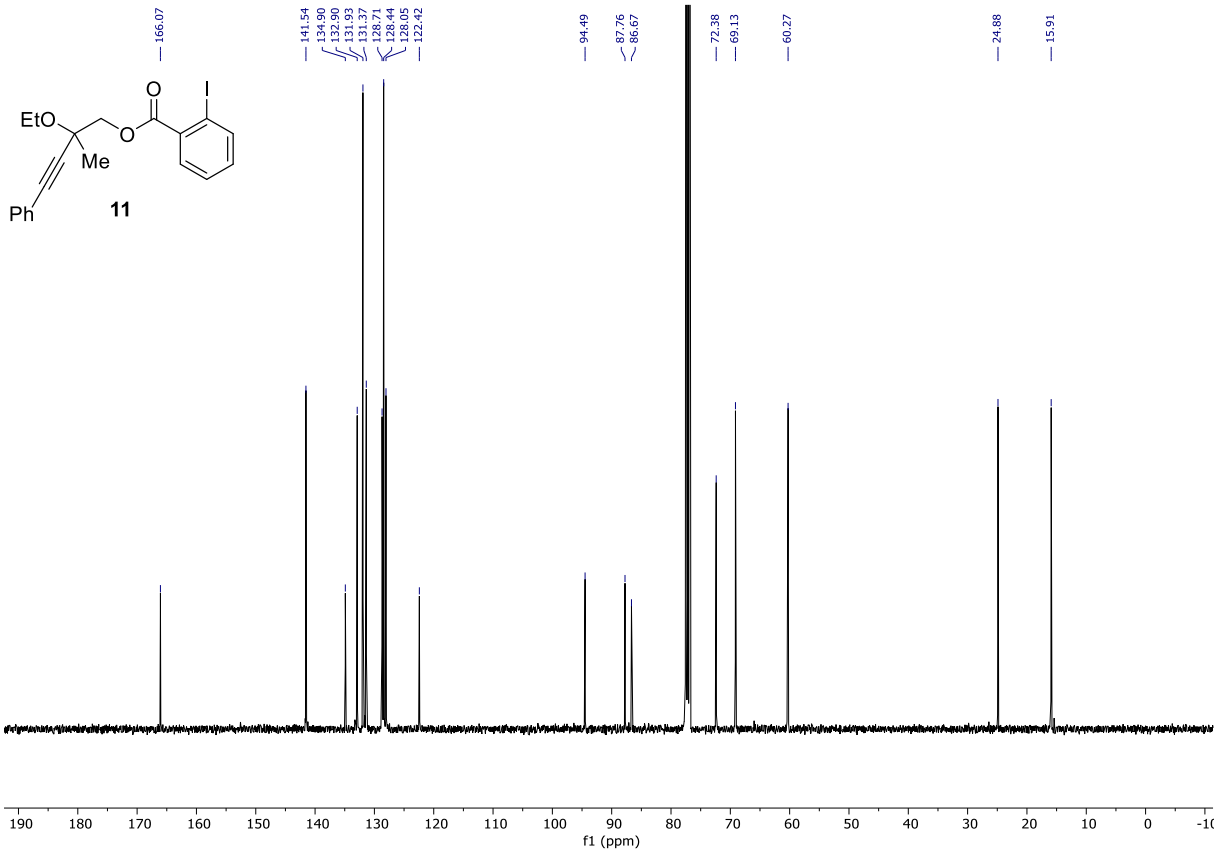
^{13}C NMR (101 MHz, $CDCl_3$) of compound **9**:



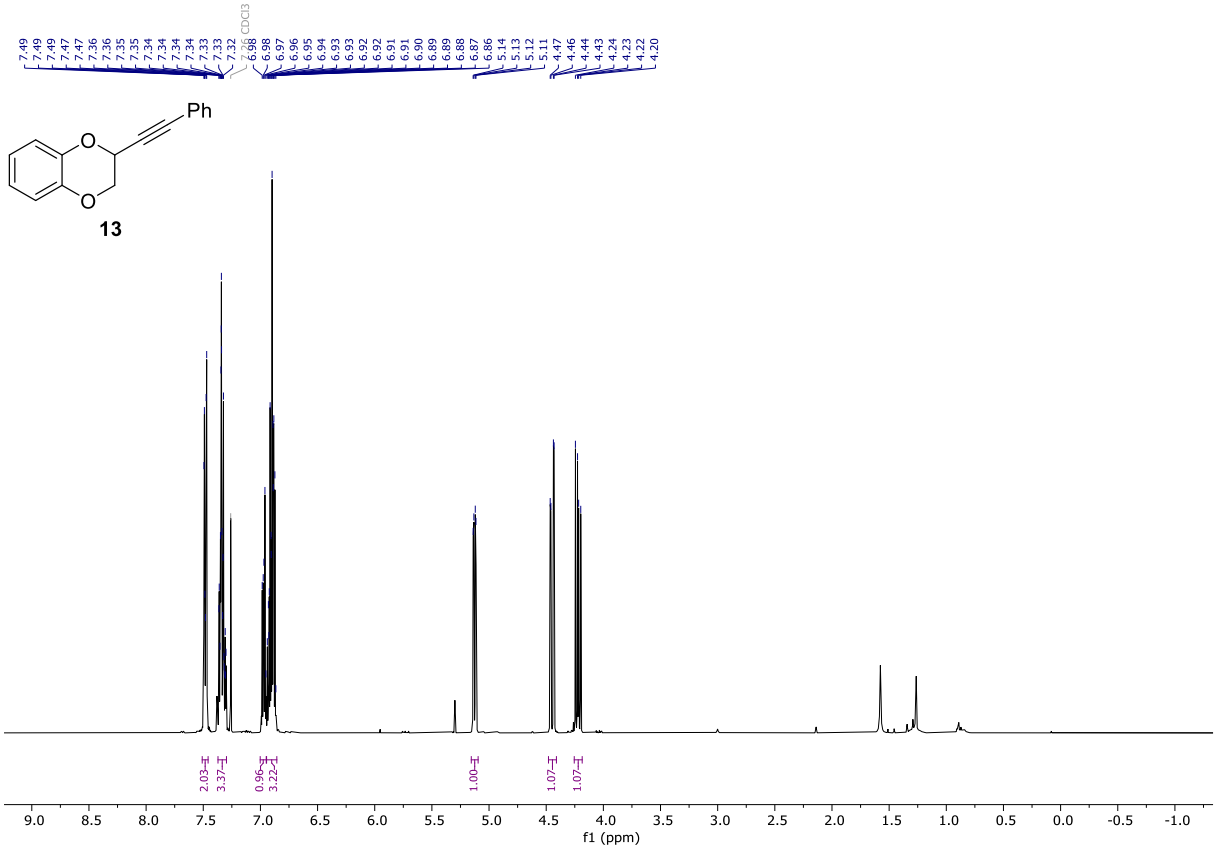
^{1}H NMR (400 MHz, $CDCl_3$) of compound **11**:



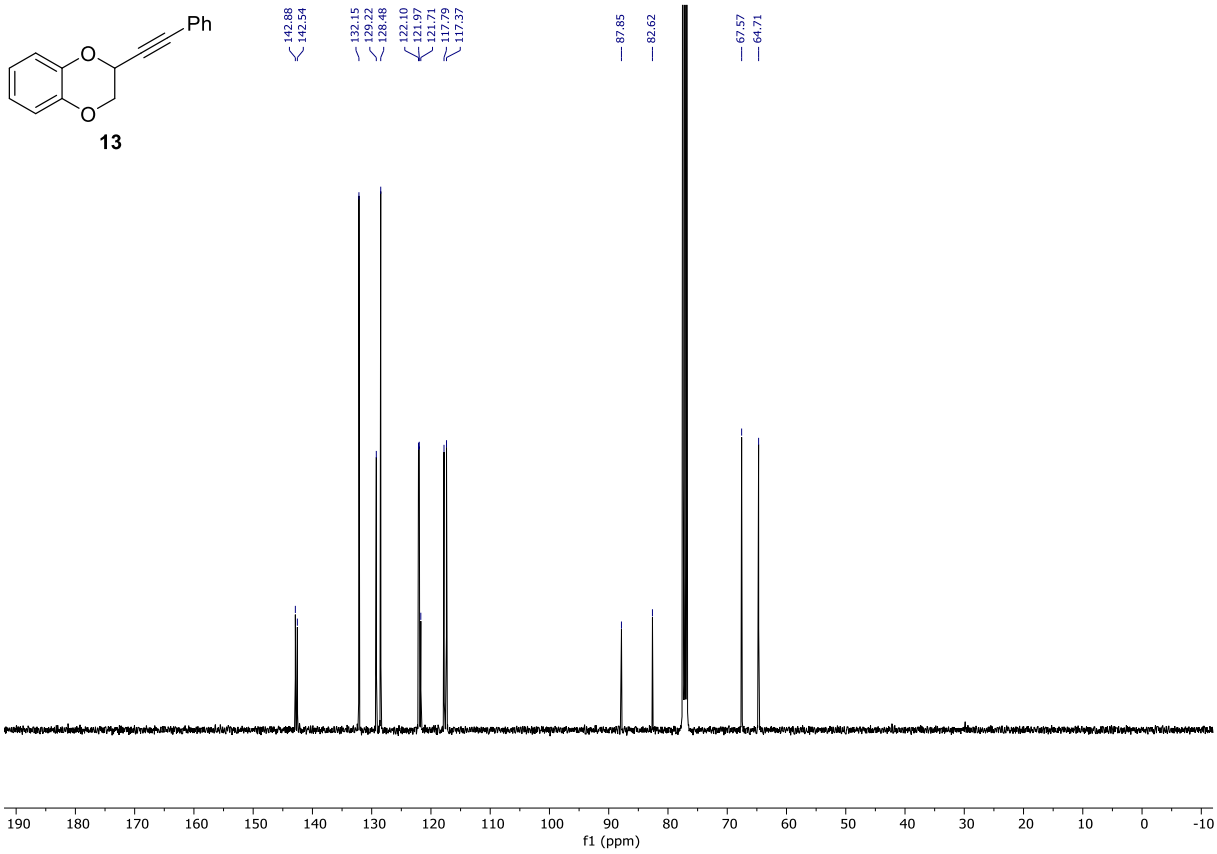
^{13}C NMR (101 MHz, $CDCl_3$) of compound **11**:



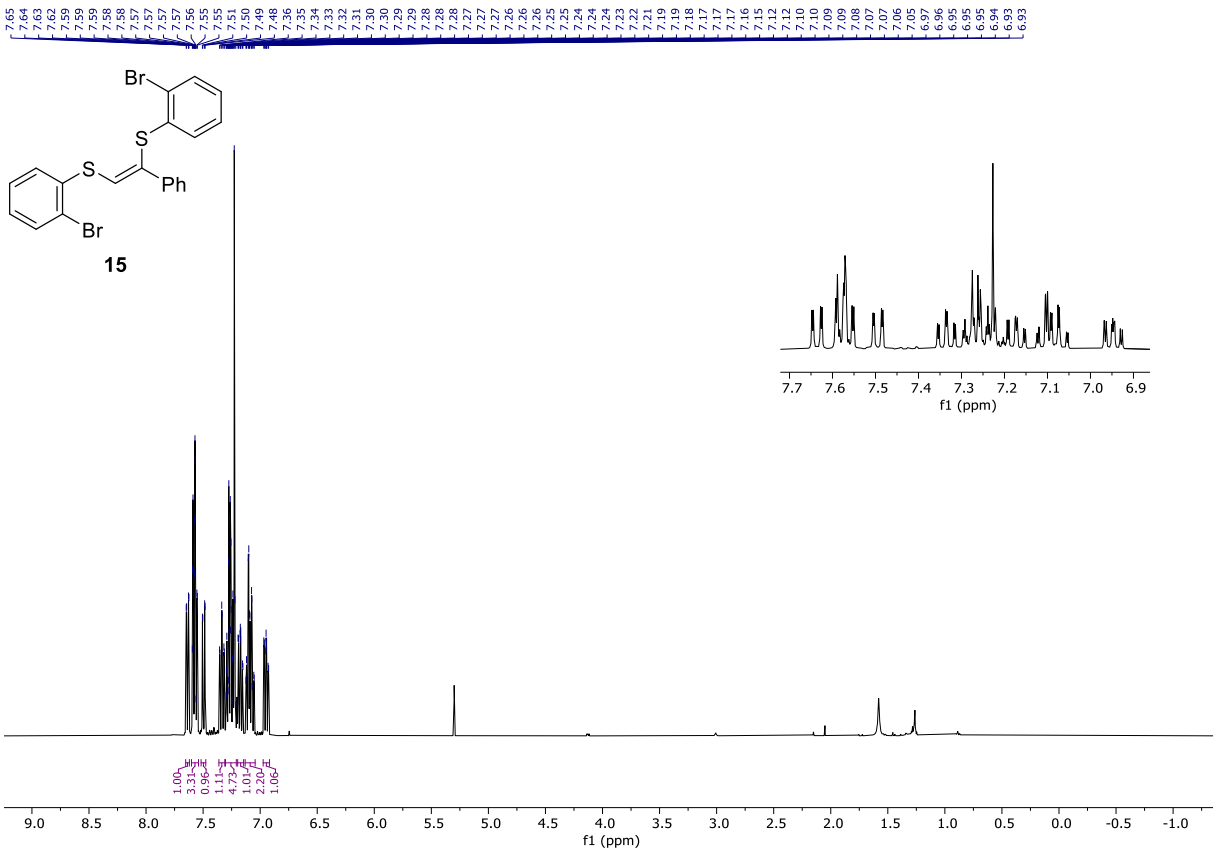
^{1}H NMR (400 MHz, $CDCl_3$) of compound **13**:



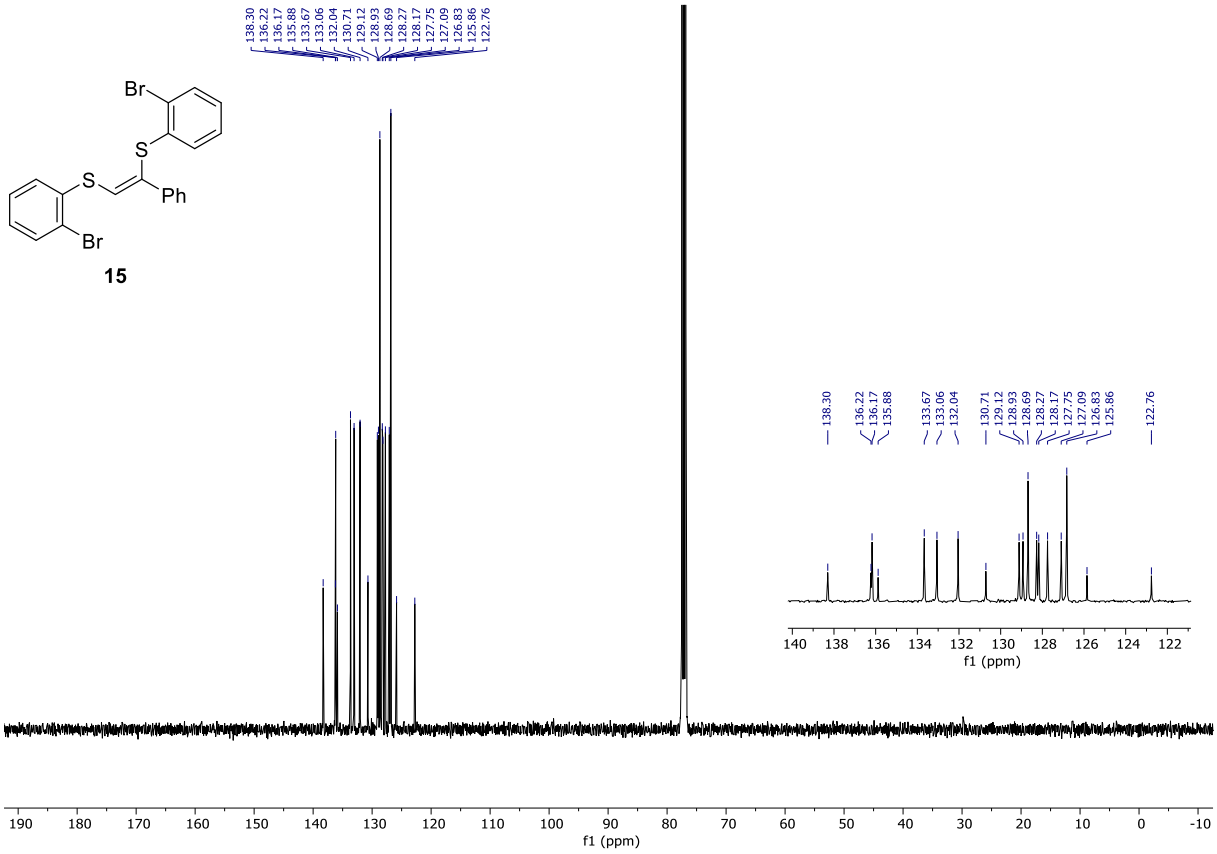
^{13}C NMR (101 MHz, $CDCl_3$) of compound **13**:



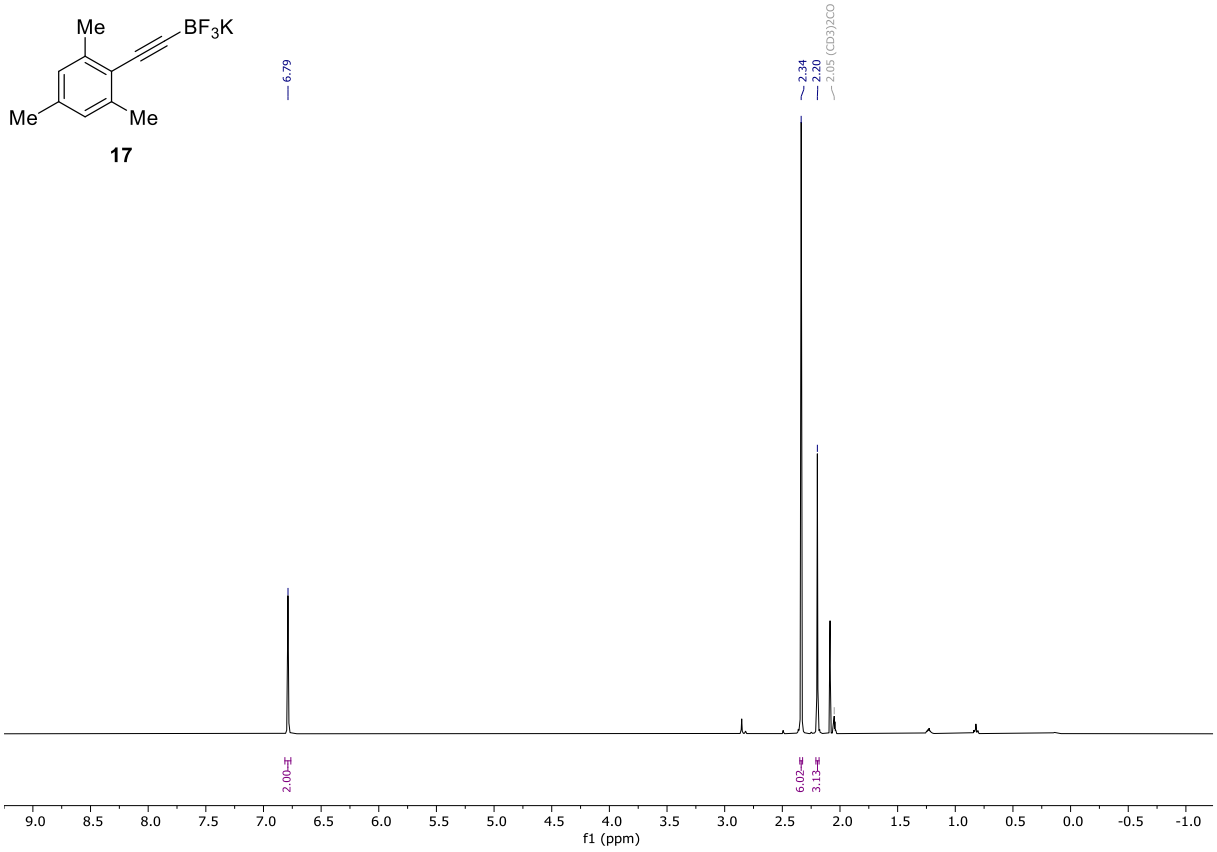
^{1}H NMR (400 MHz, $CDCl_3$) of compound **15**:



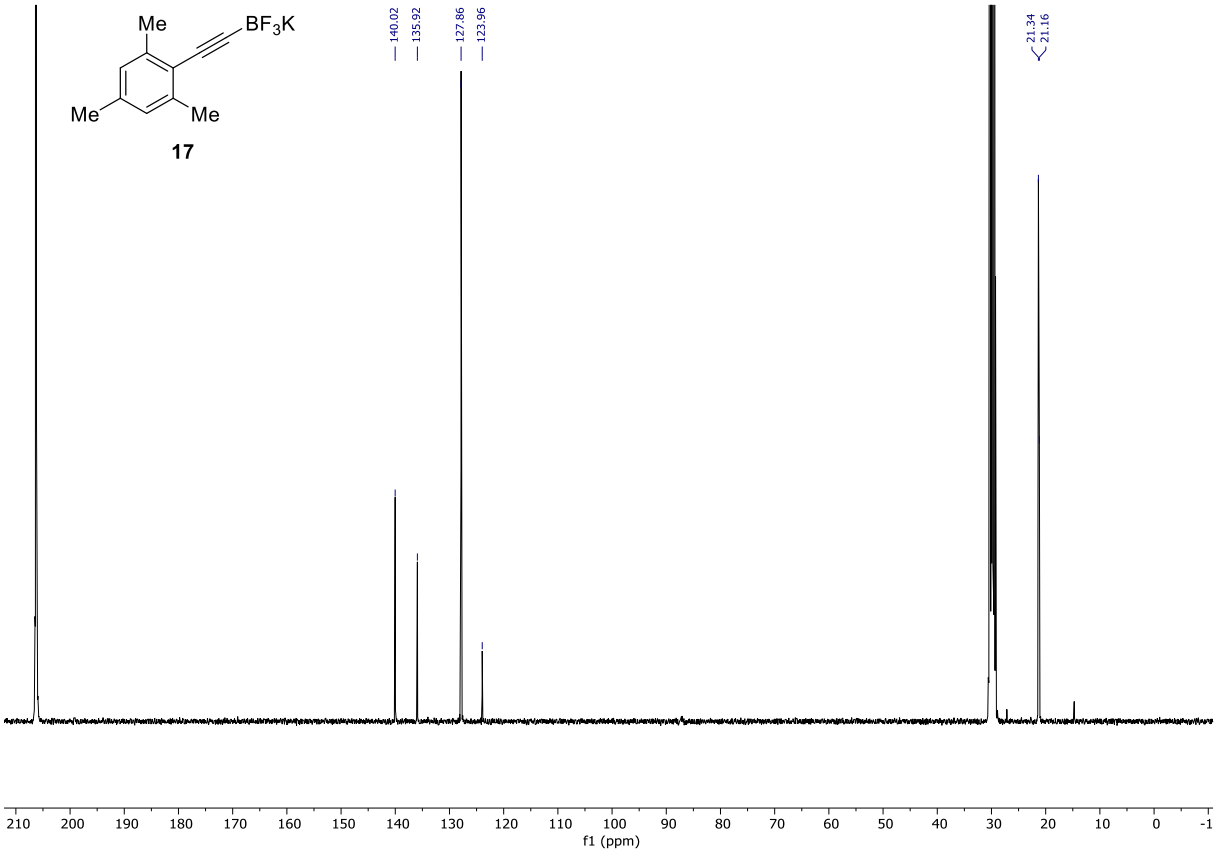
^{13}C NMR (101 MHz, $CDCl_3$) of compound **15**:



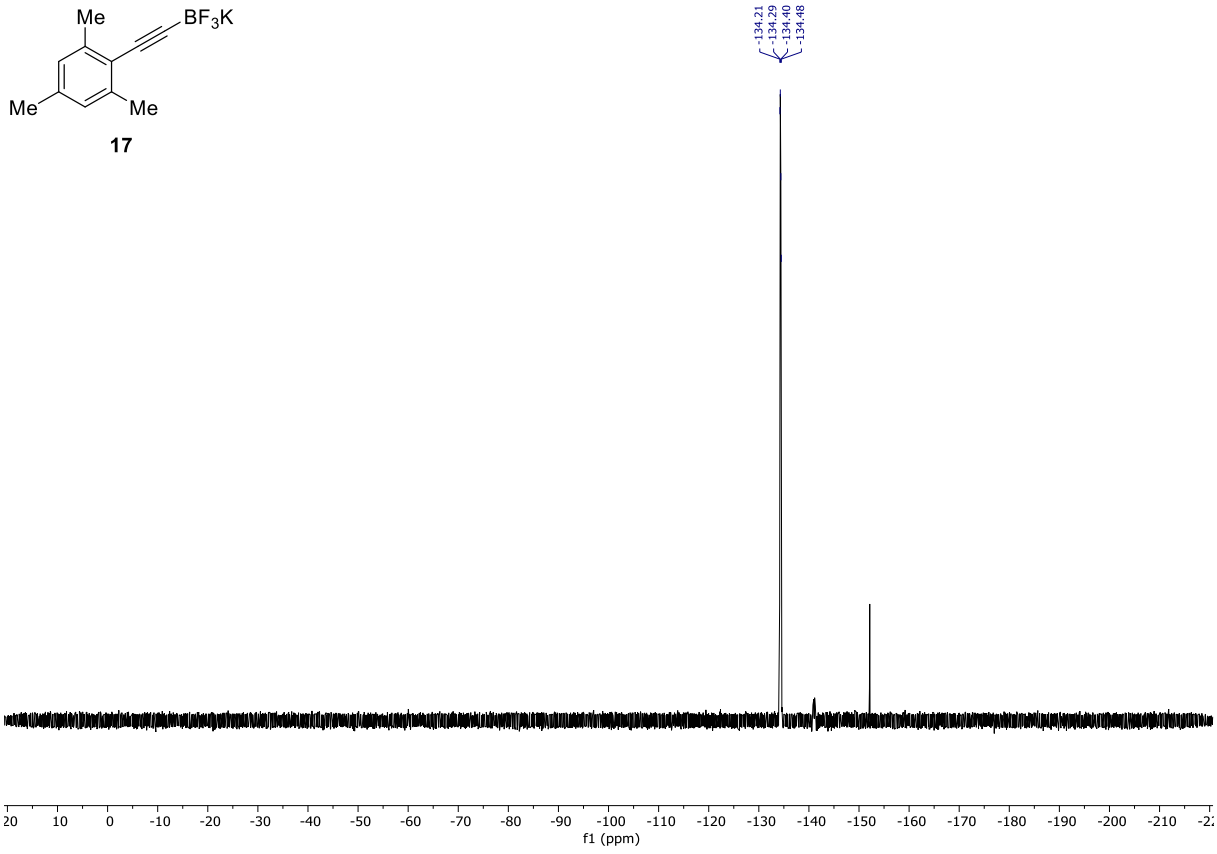
^{1}H NMR (400 MHz, acetone-d_6) of compound **17**:



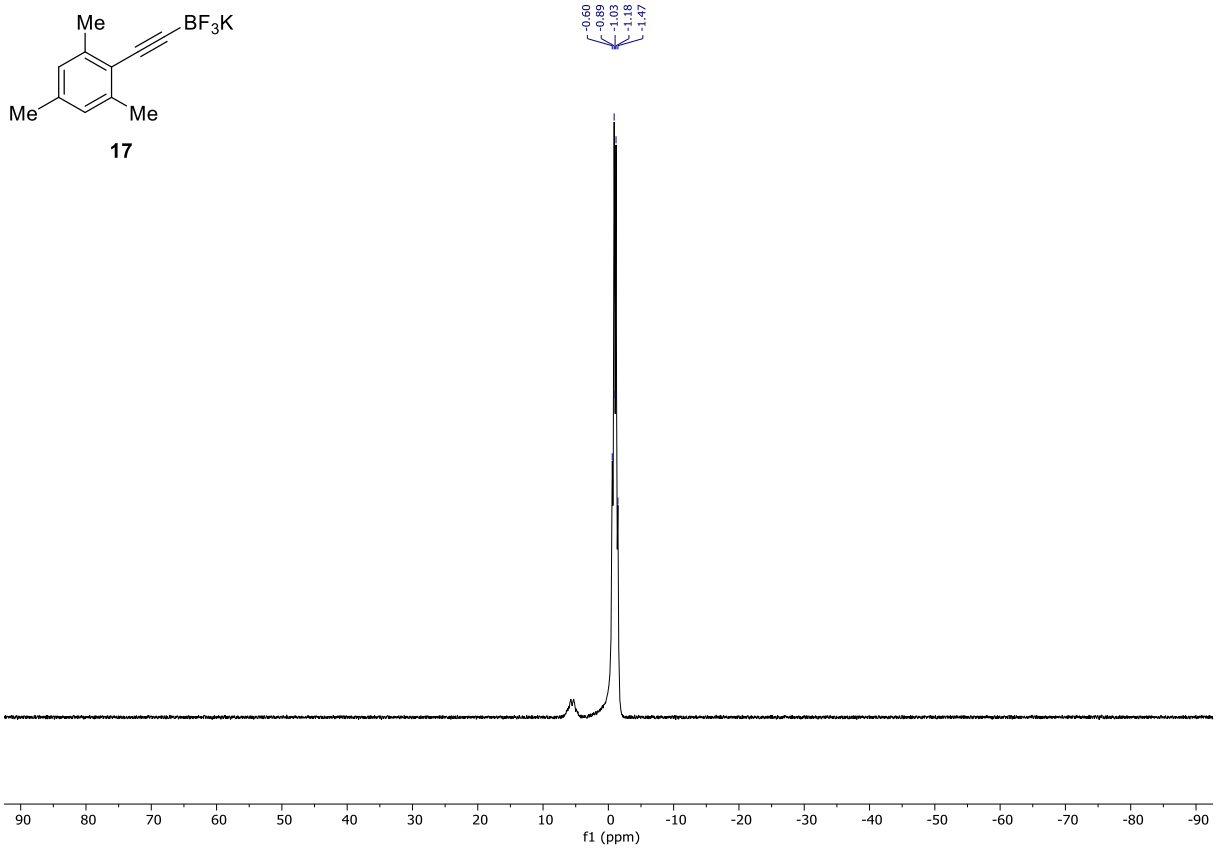
^{13}C NMR (101 MHz, acetone-d_6) of compound **17**:



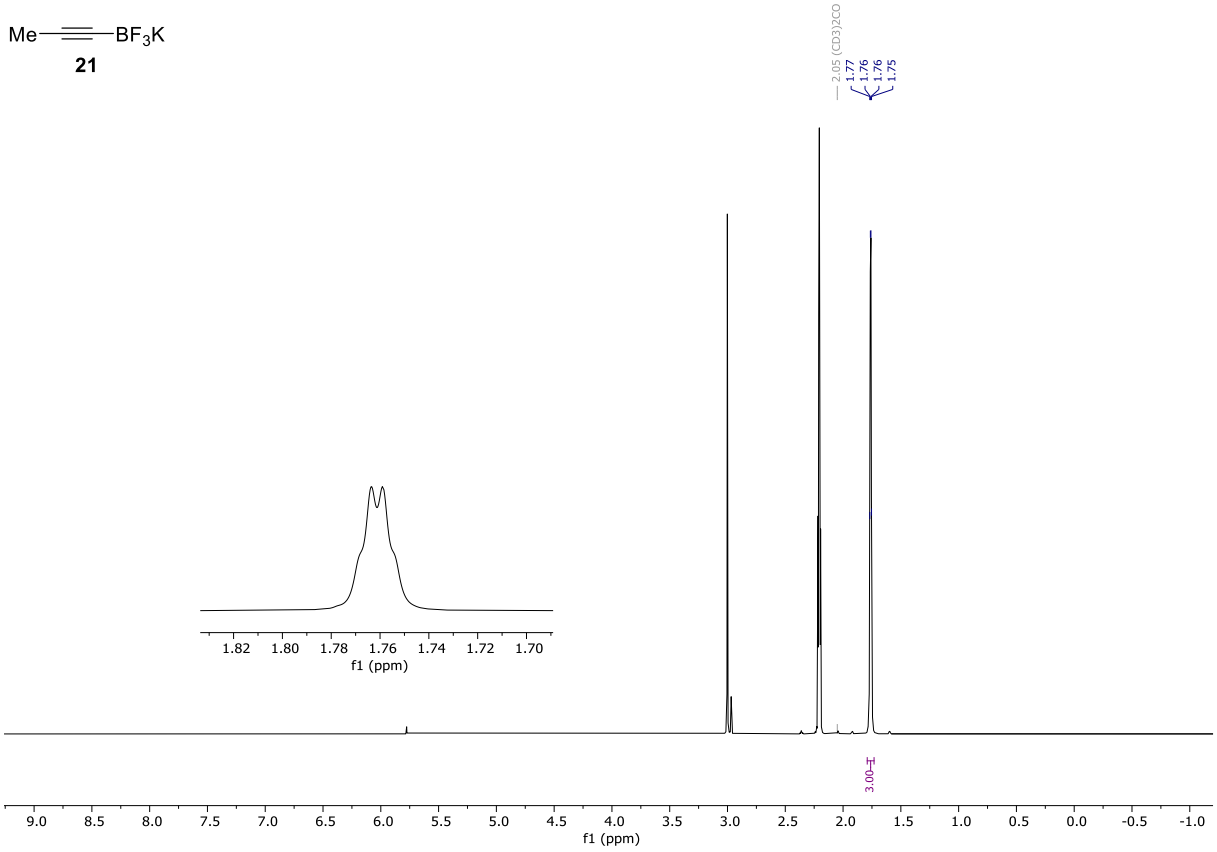
^{19}F NMR (377 MHz, acetone-d_6) of compound **17**:



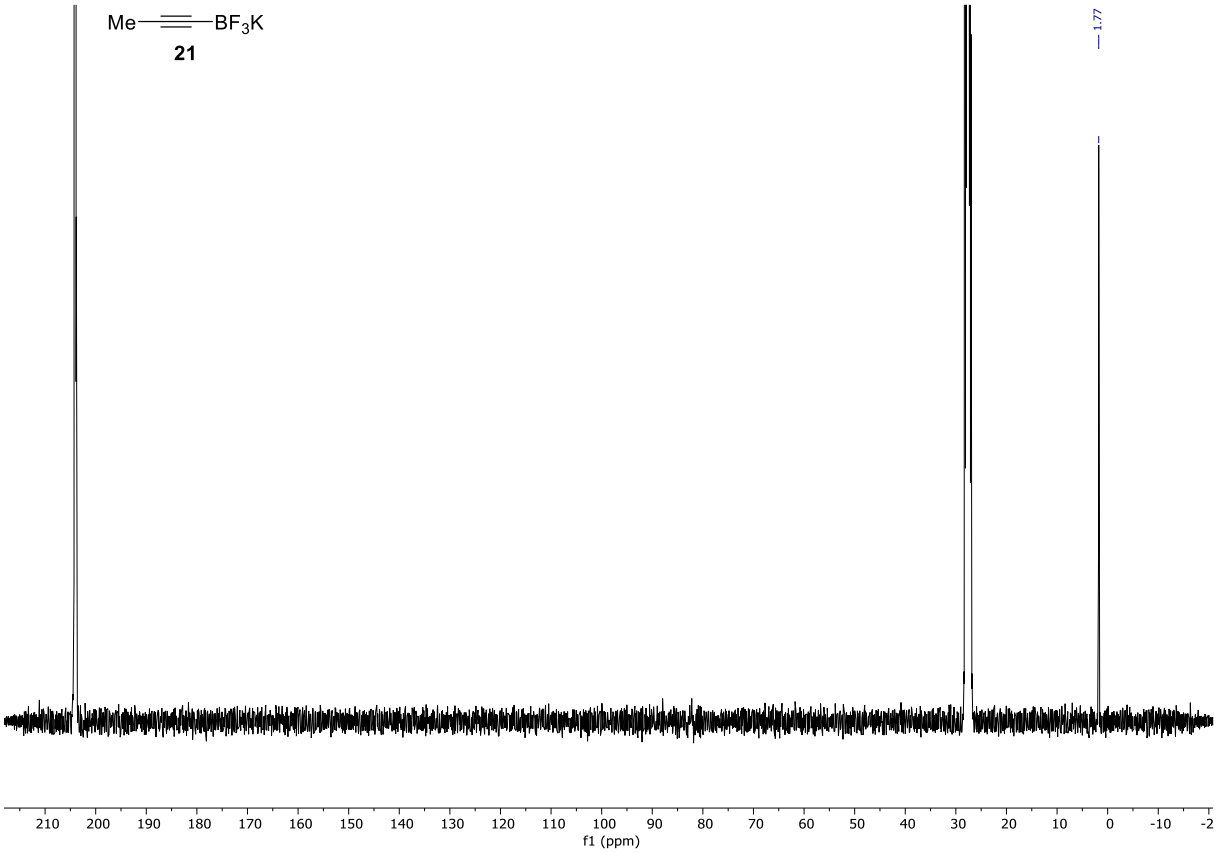
^{11}B NMR (128 MHz, acetone-d_6) of compound **17**:



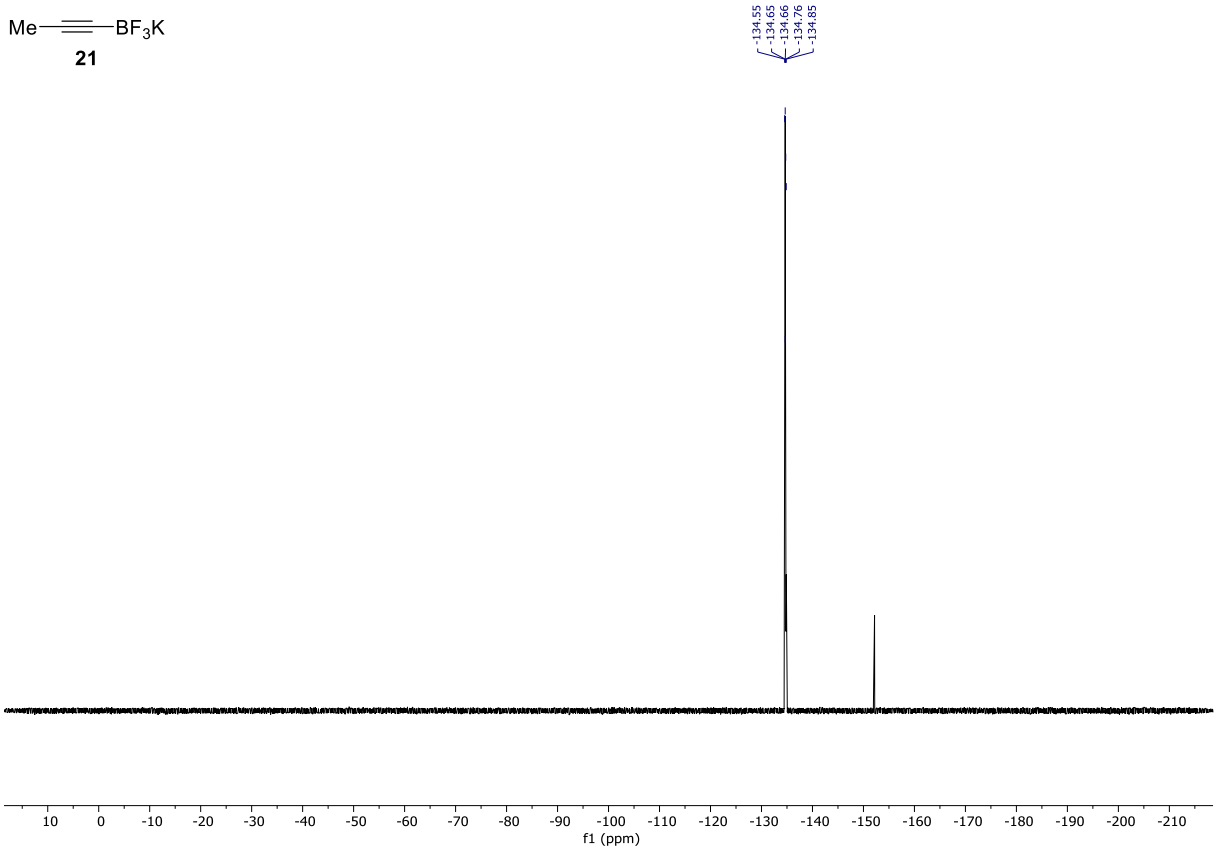
^{1}H NMR (400 MHz, acetone-d_6) of compound **21**:



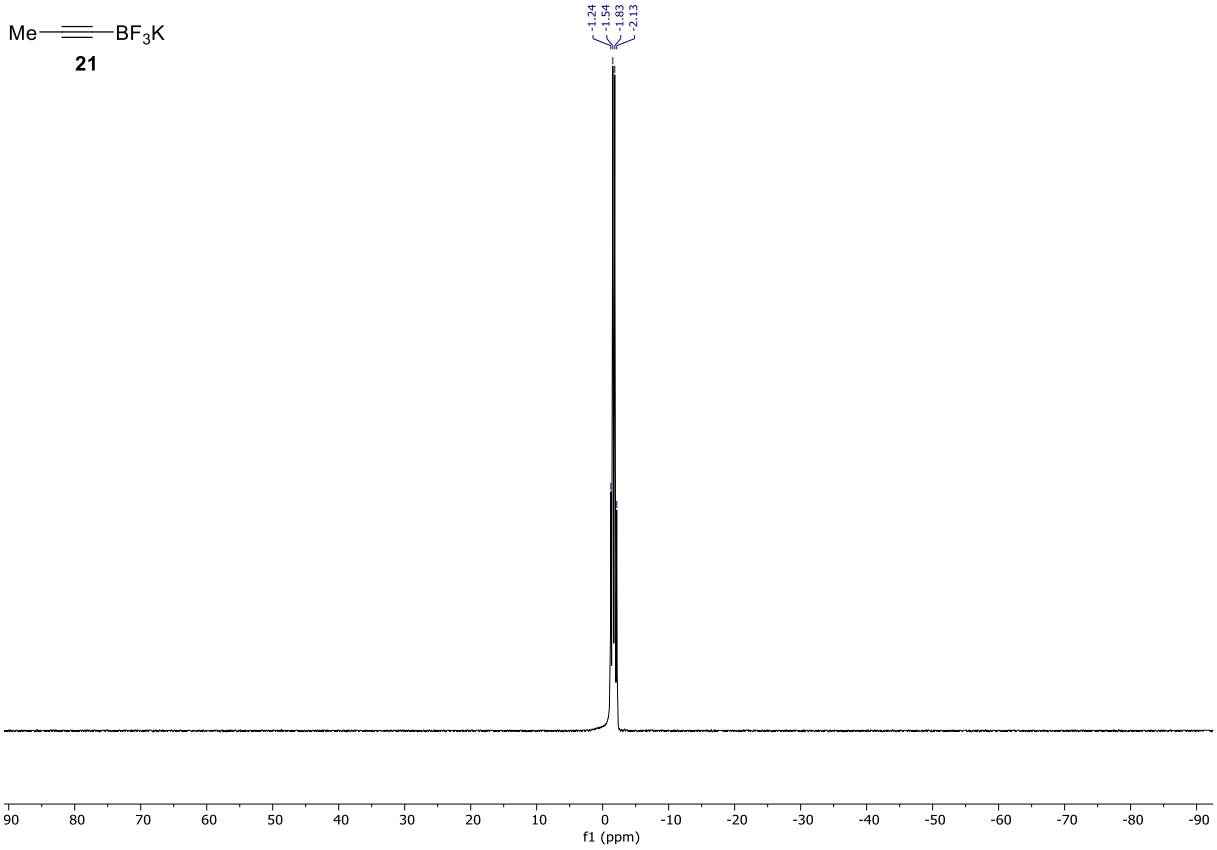
^{13}C NMR (101 MHz, acetone-d_6) of compound **21**:



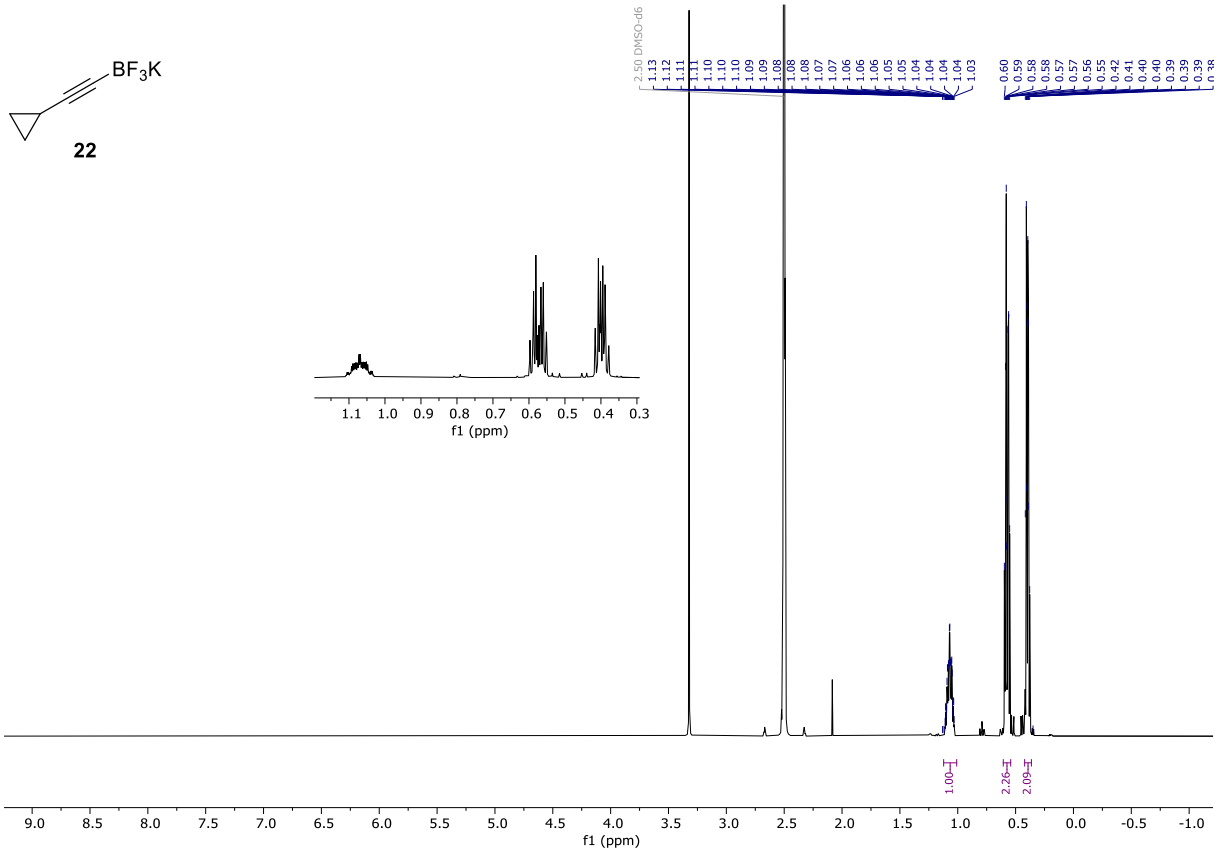
^{19}F NMR (376 MHz, acetone-d_6) of compound **21**:



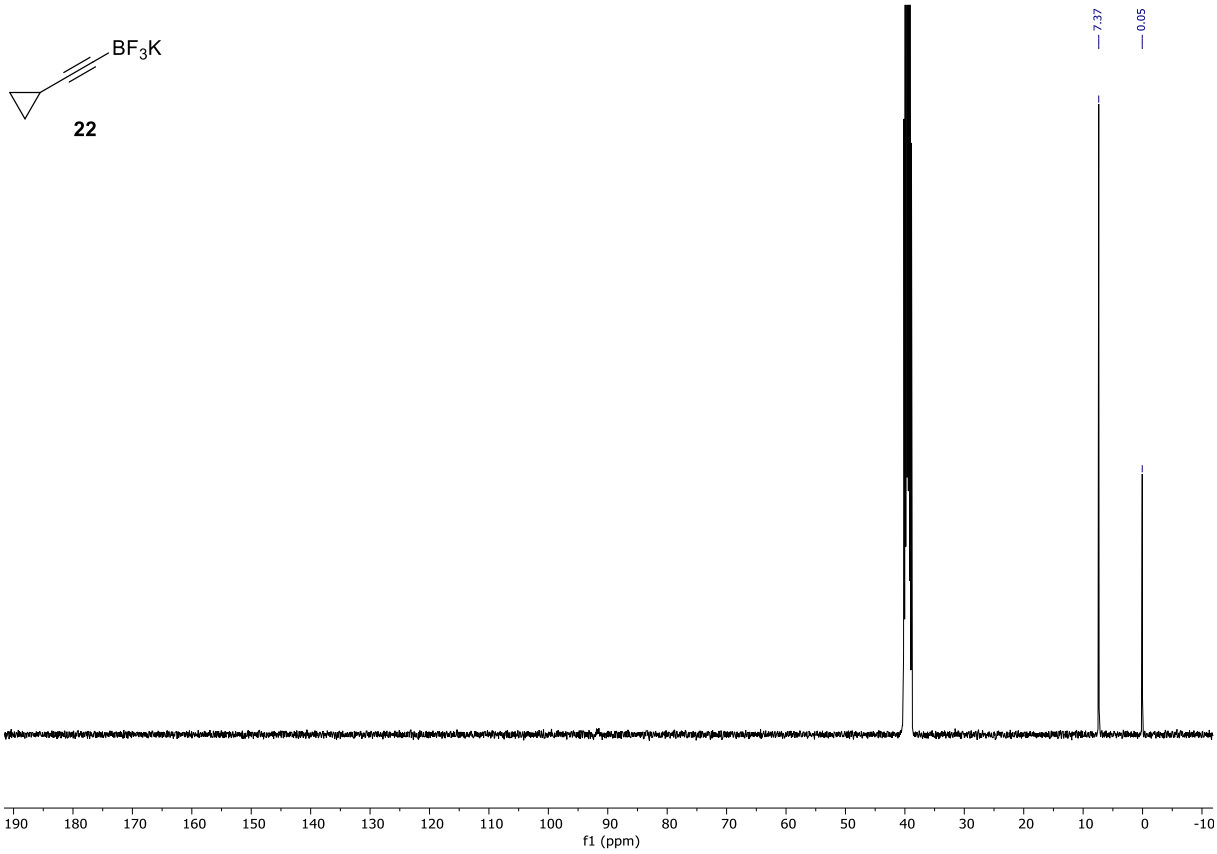
^{11}B NMR (128 MHz, acetone-d_6) of compound **21**:



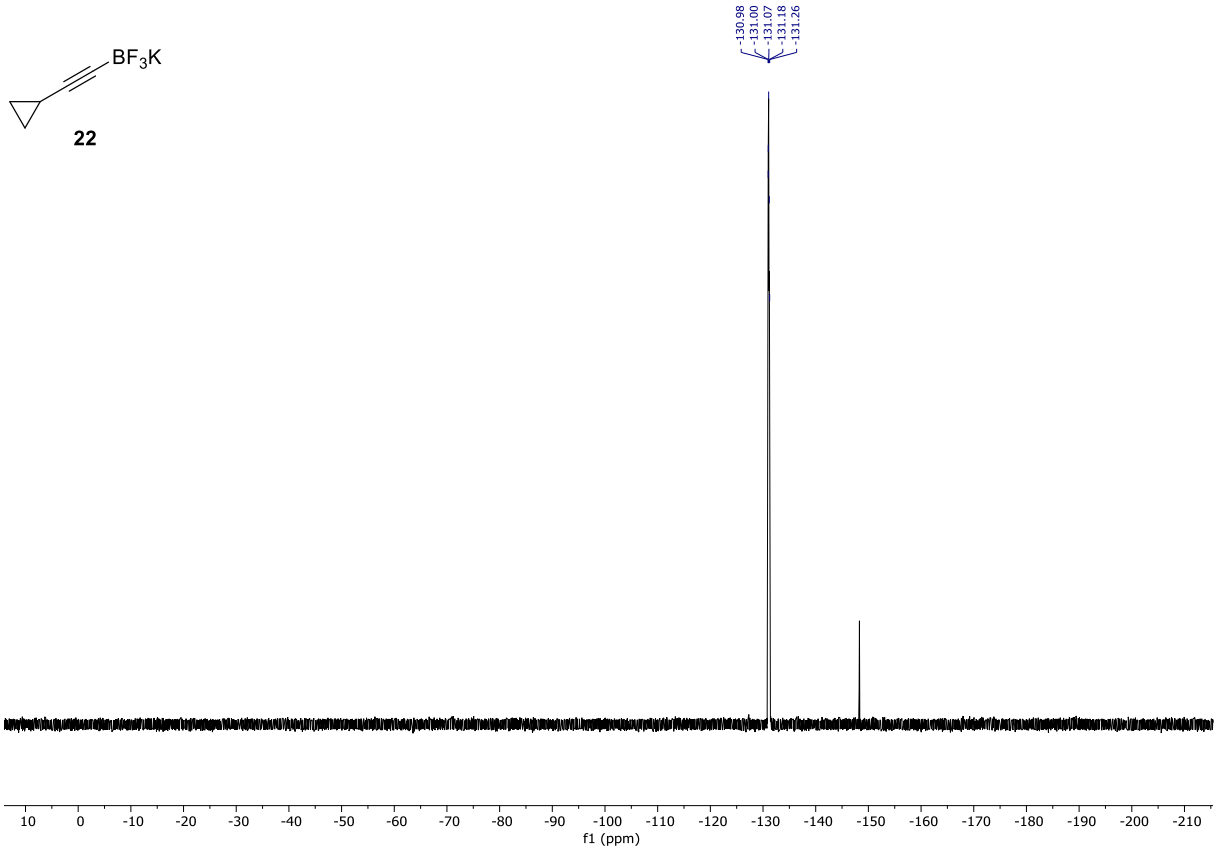
^{1}H NMR (400 MHz, acetone-d_6) of compound **22**:



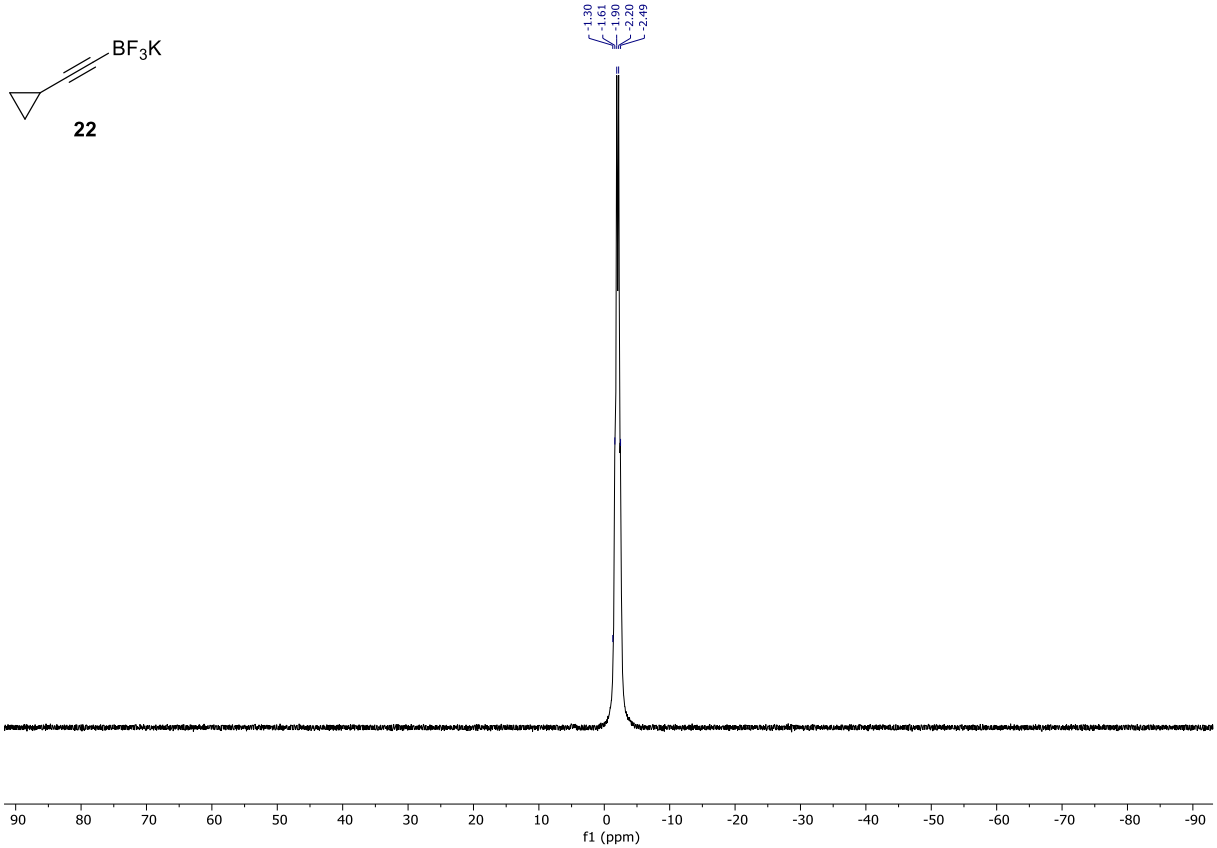
^{13}C NMR (101 MHz, acetone-d_6) of compound **22**:



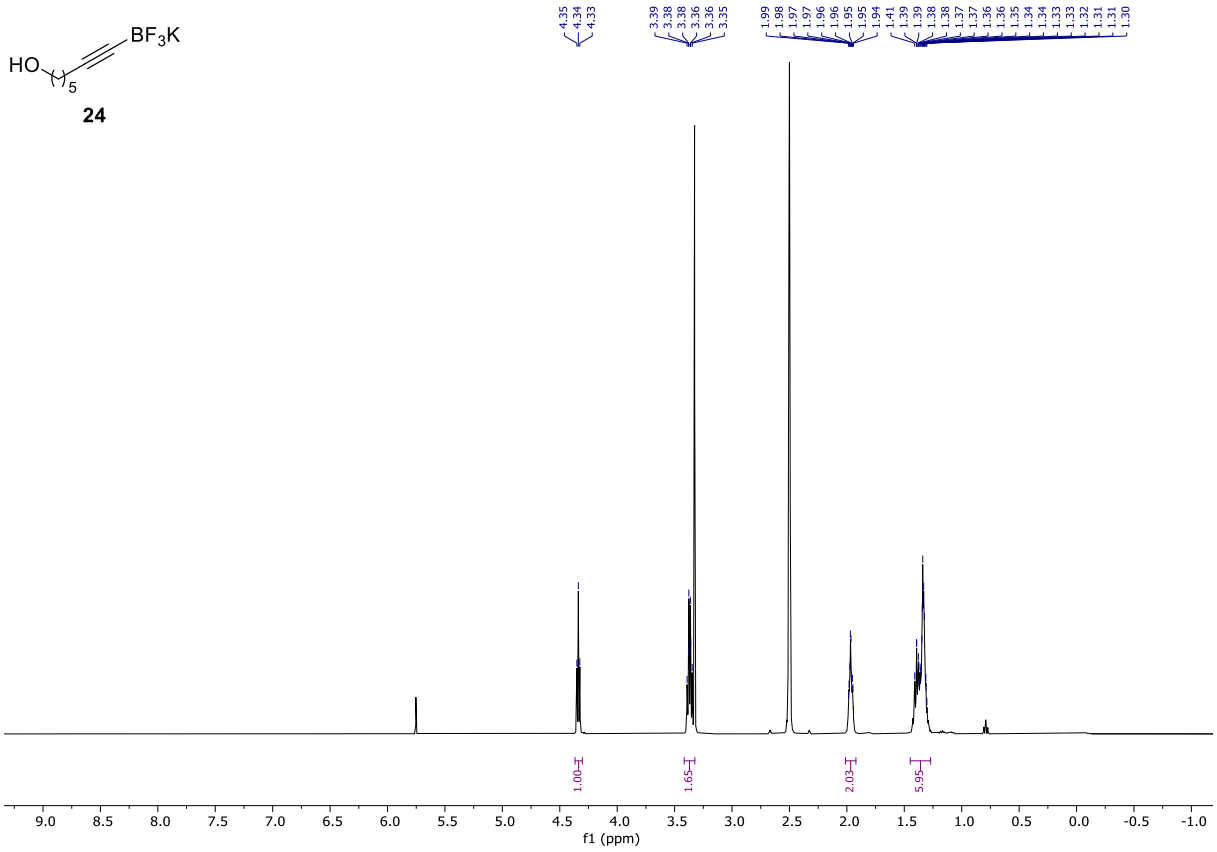
^{19}F NMR (376 MHz, acetone-d_6) of compound **22**:



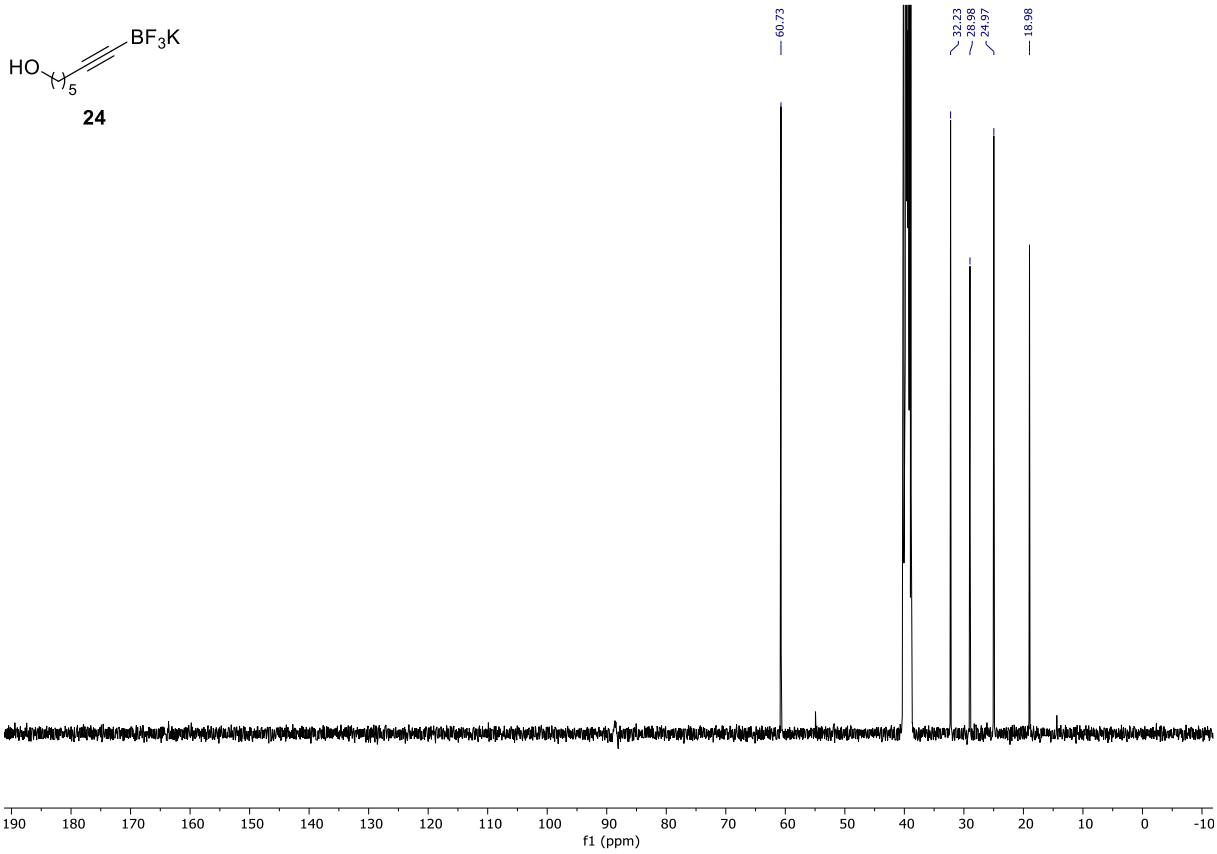
^{11}B NMR (128 MHz, acetone-d_6) of compound **22**:



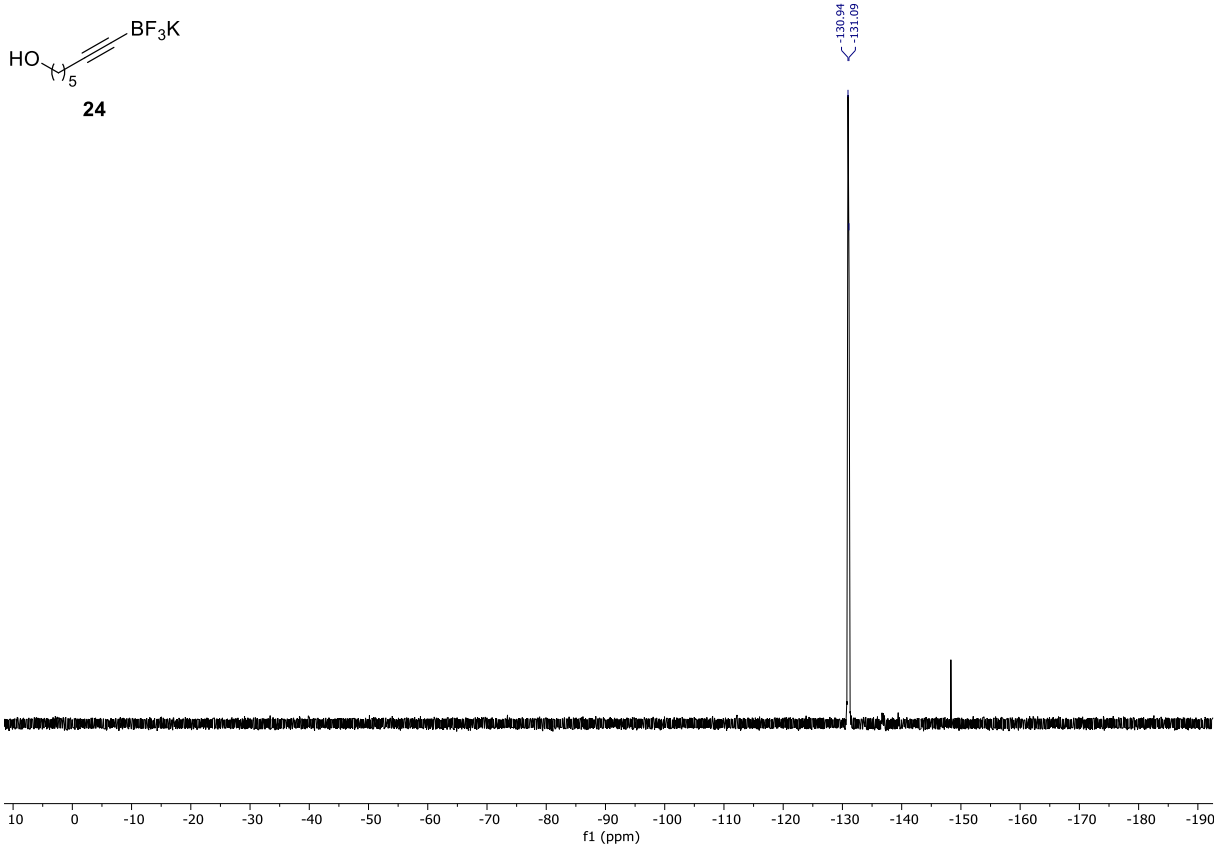
^{1}H NMR (400 MHz, DMSO-d_6) of compound **24**:



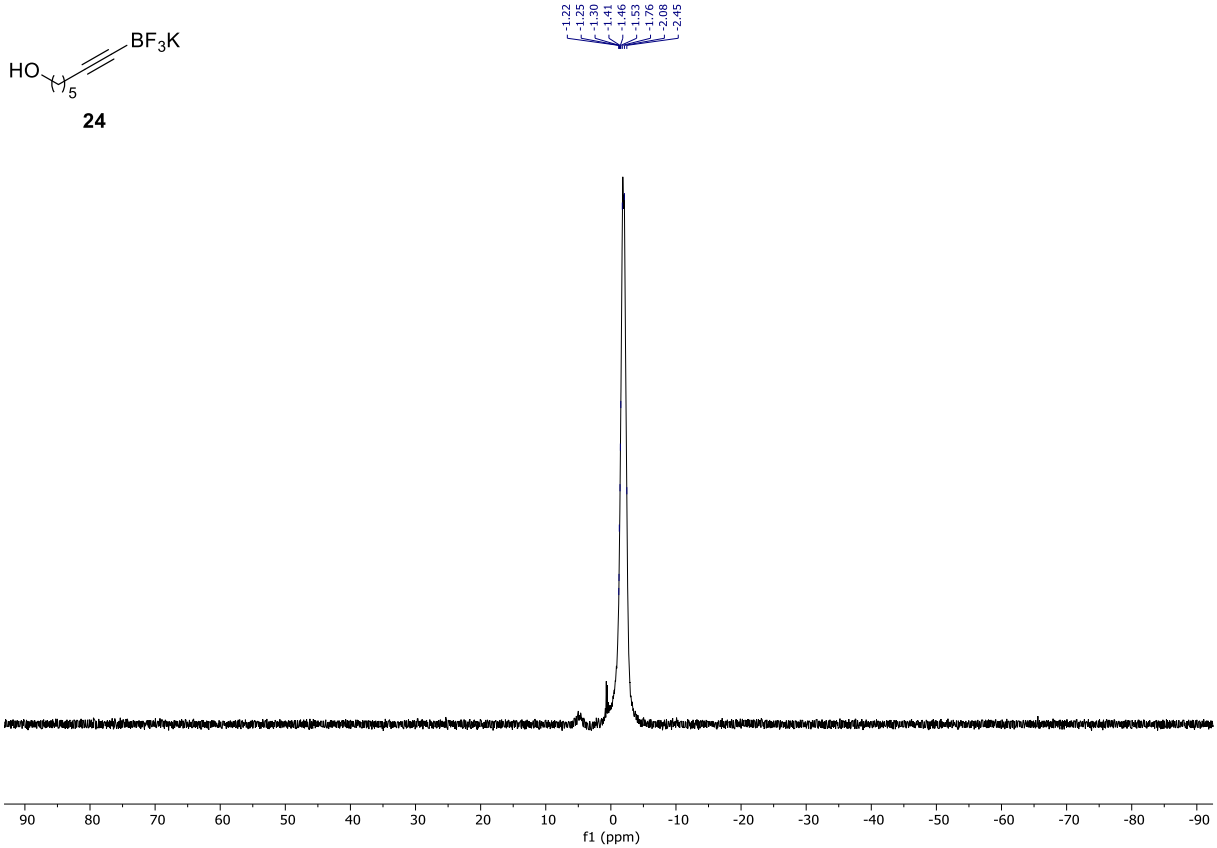
^{13}C NMR (101 MHz, DMSO-d_6) of compound **24**:



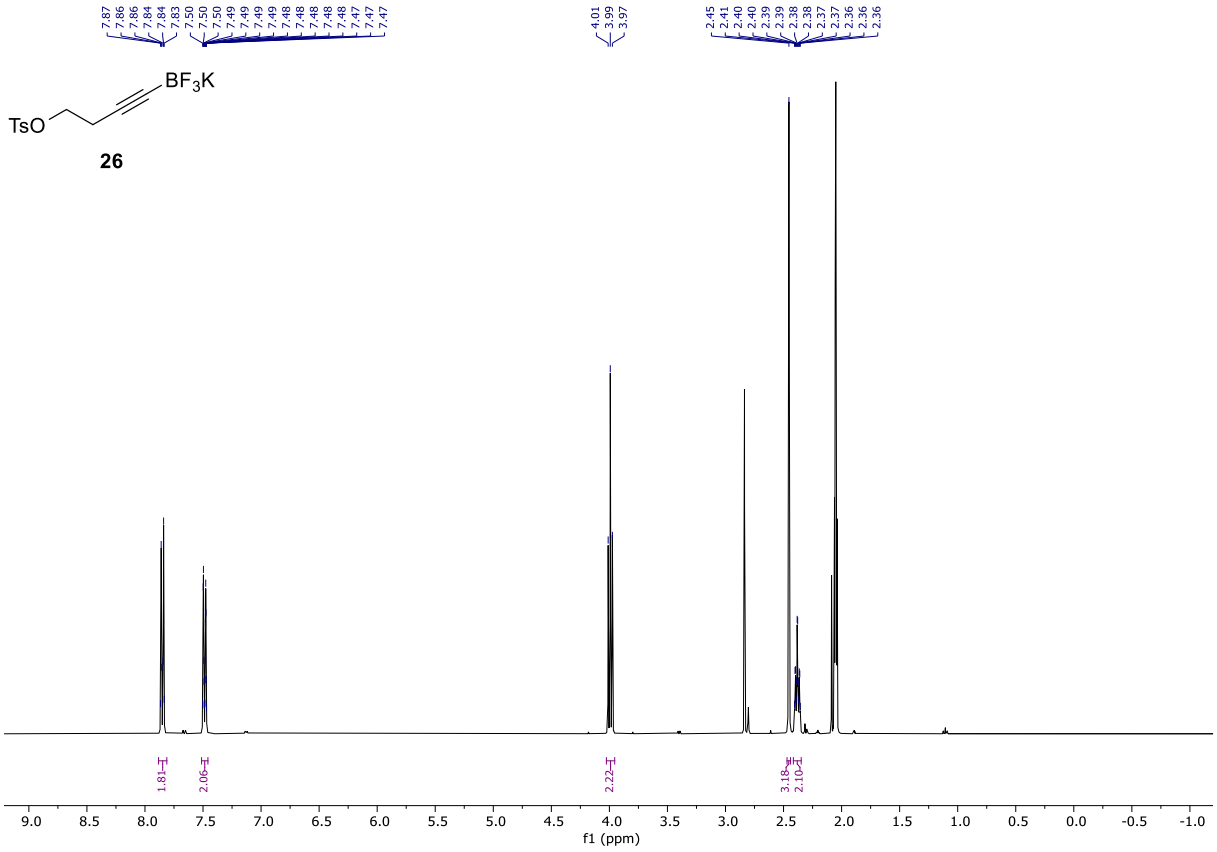
^{19}F NMR (376 MHz, DMSO-d_6) of compound **24**:



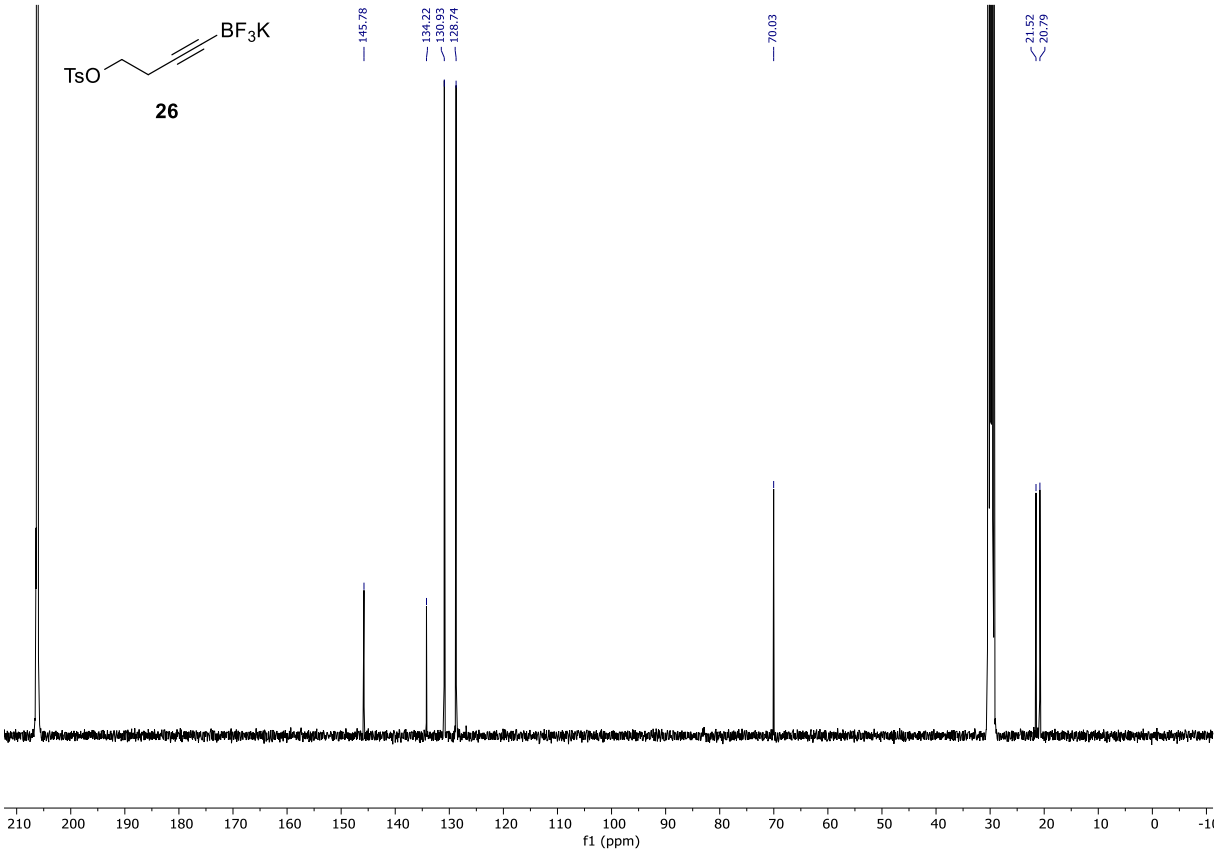
^{11}B NMR (128 MHz, DMSO-d_6) of compound **24**:



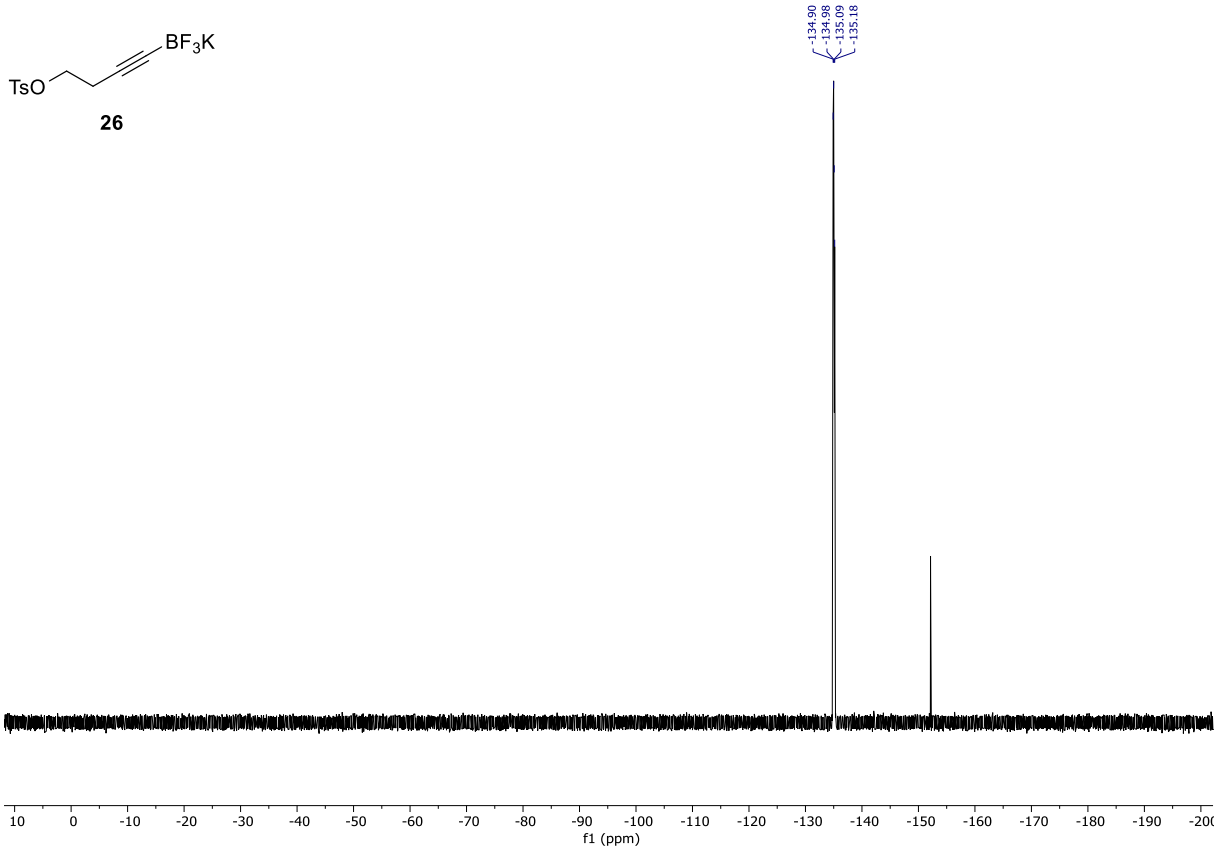
^{1}H NMR (400 MHz, acetone-d_6) of compound **26**:



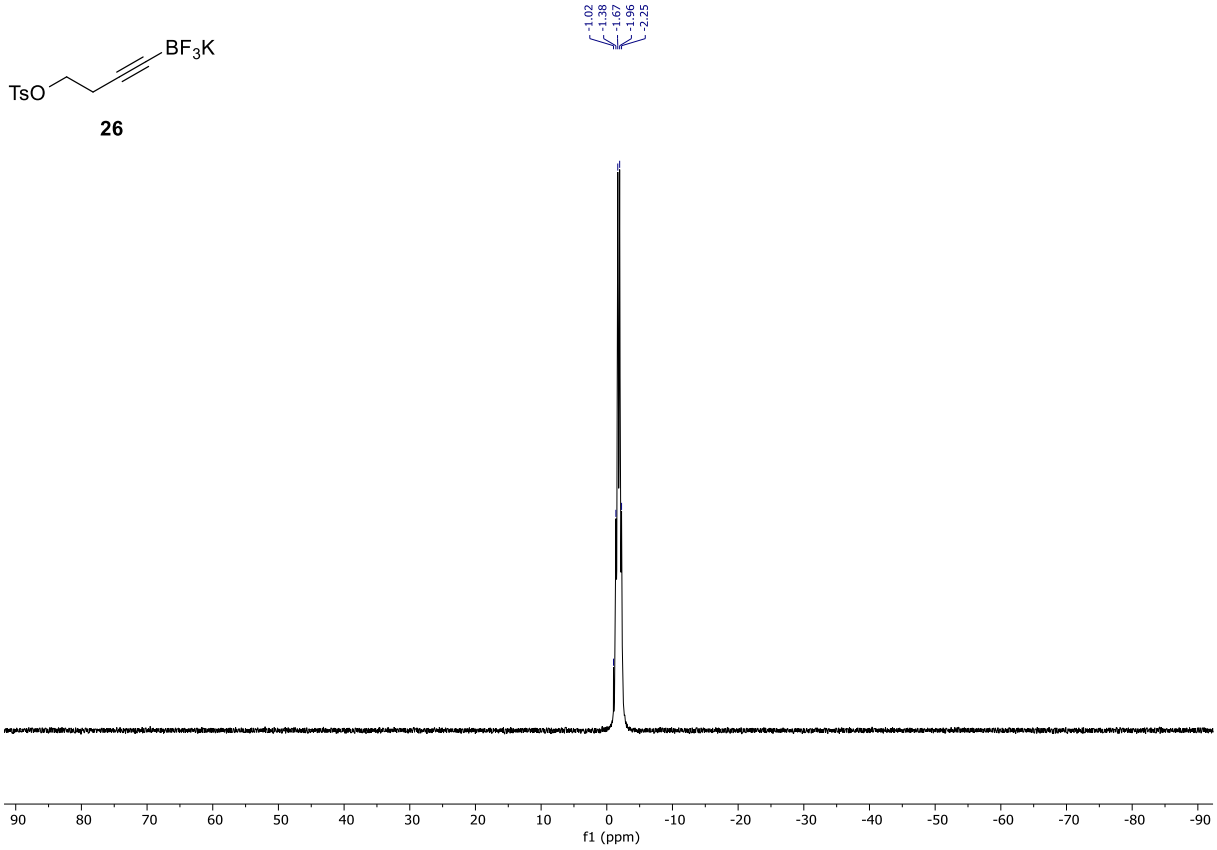
^{13}C NMR (101 MHz, acetone-d_6) of compound **26**:



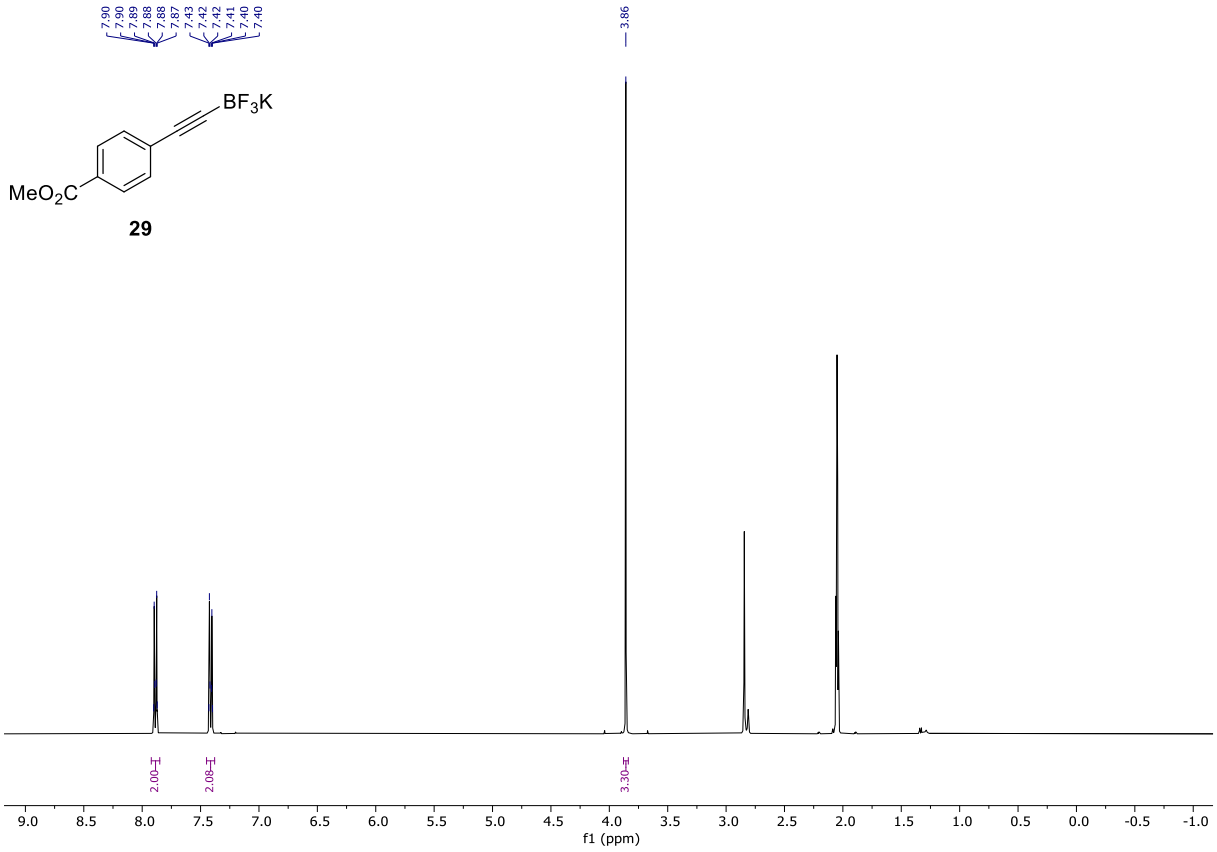
^{19}F NMR (376 MHz, acetone-d_6) of compound **26**:



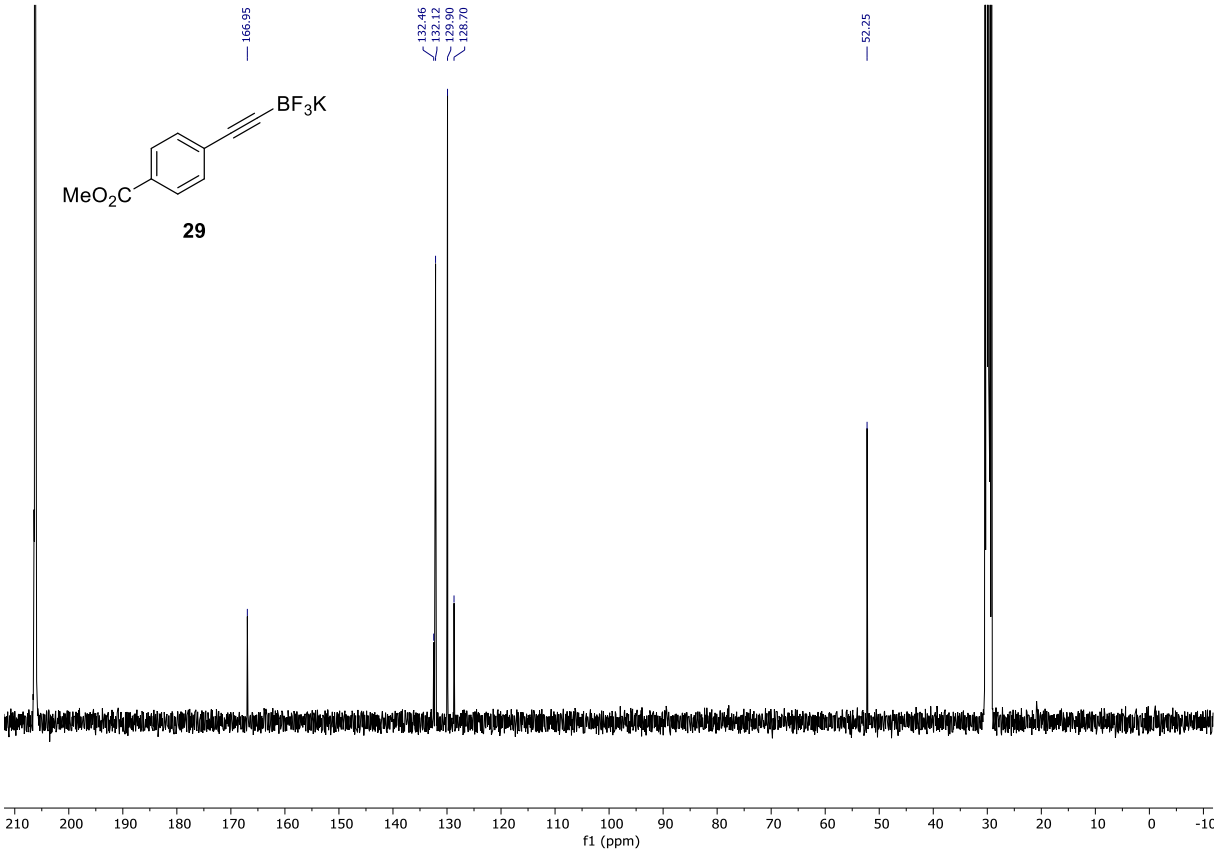
^{11}B NMR (128 MHz, acetone-d_6) of compound **26**:



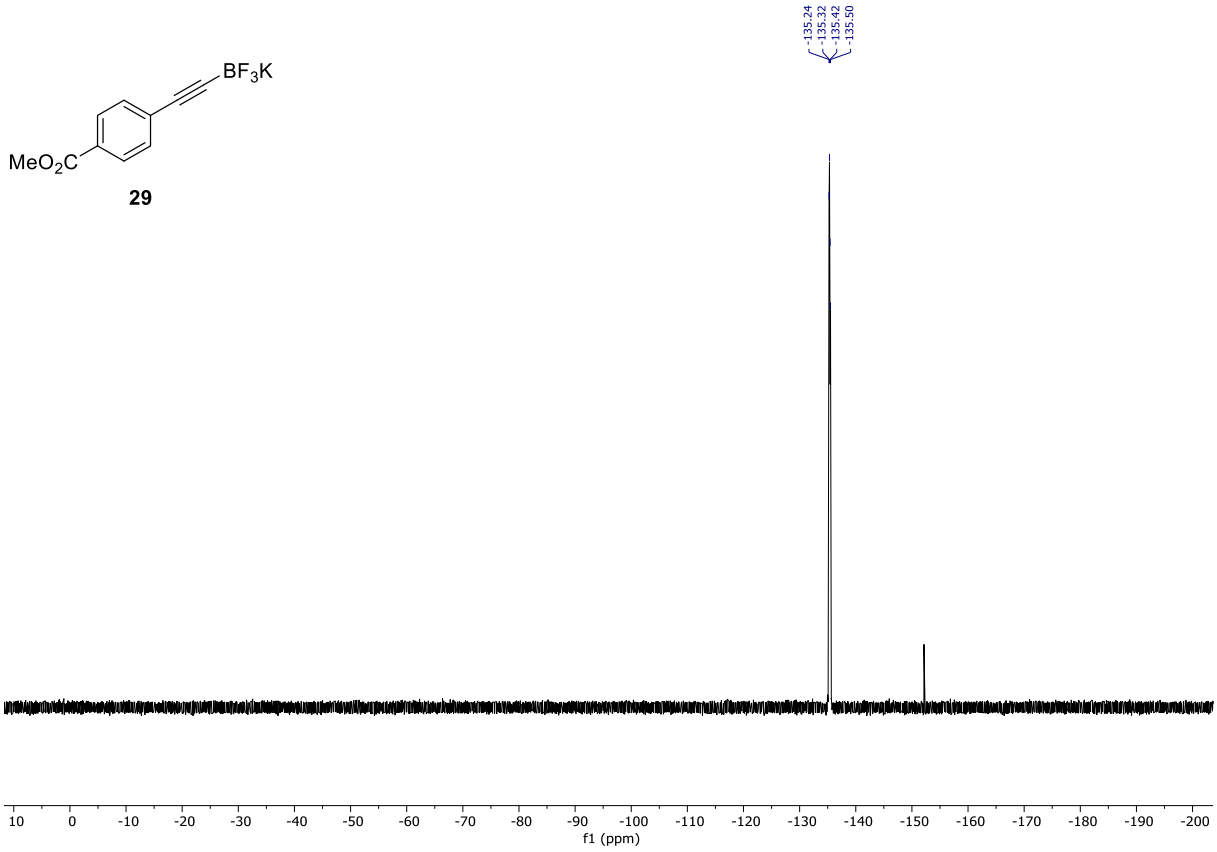
^{1}H NMR (400 MHz, acetone-d_6) of compound **29**:



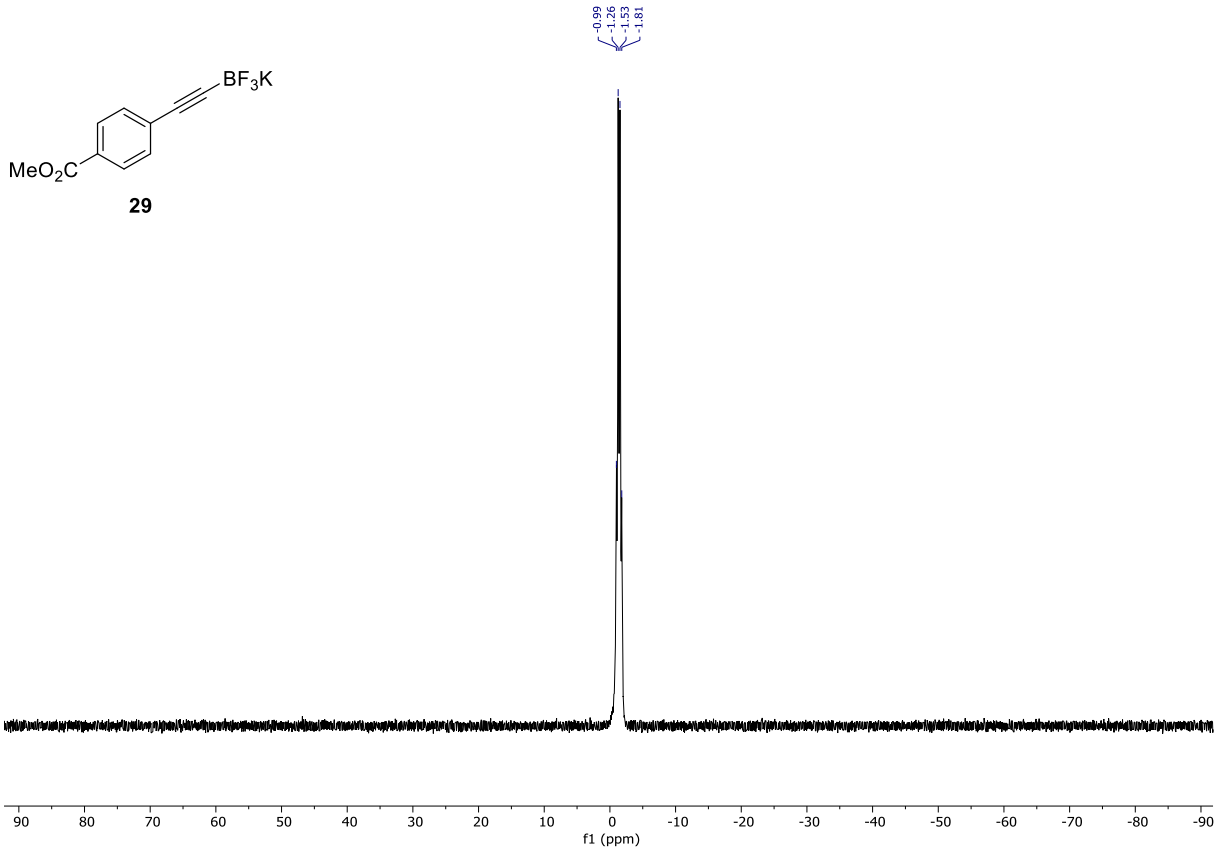
^{13}C NMR (101 MHz, acetone-d_6) of compound **29**:



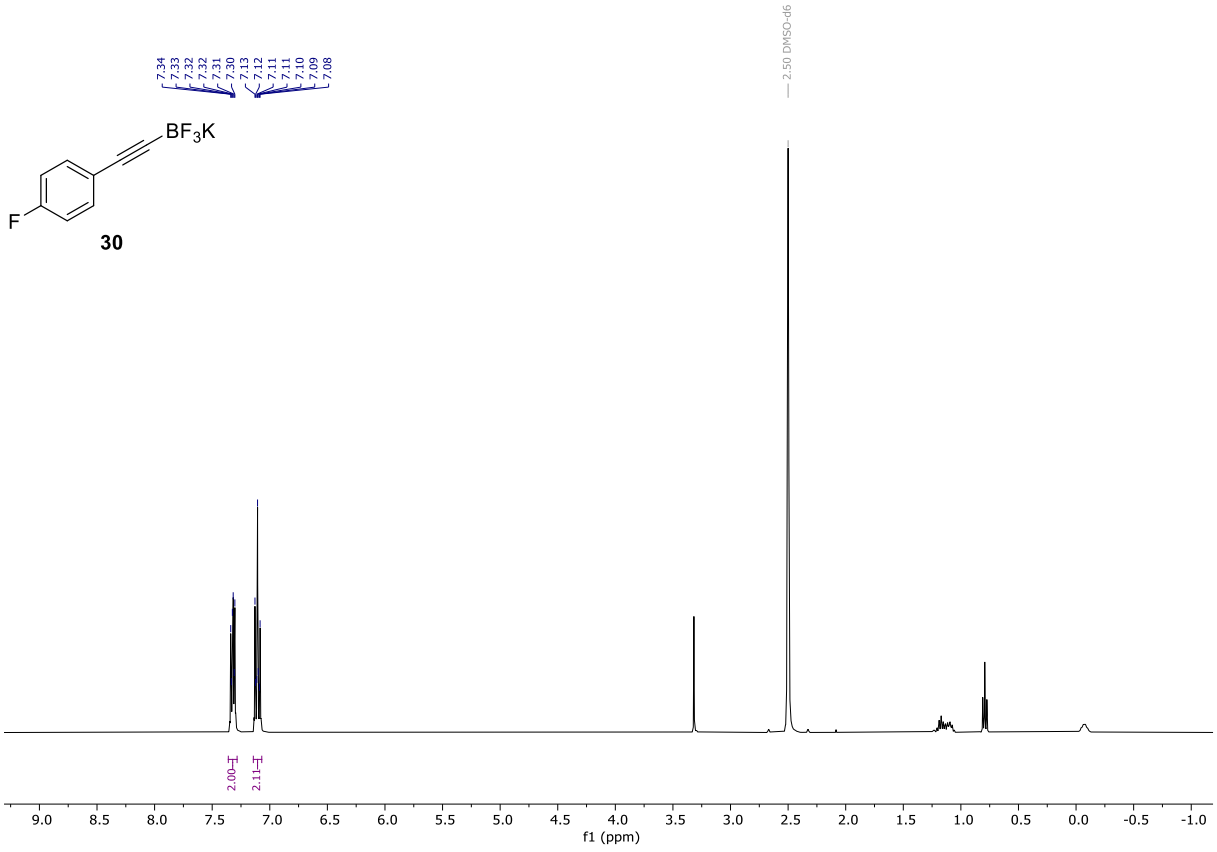
^{19}F NMR (376 MHz, acetone-d_6) of compound **29**:



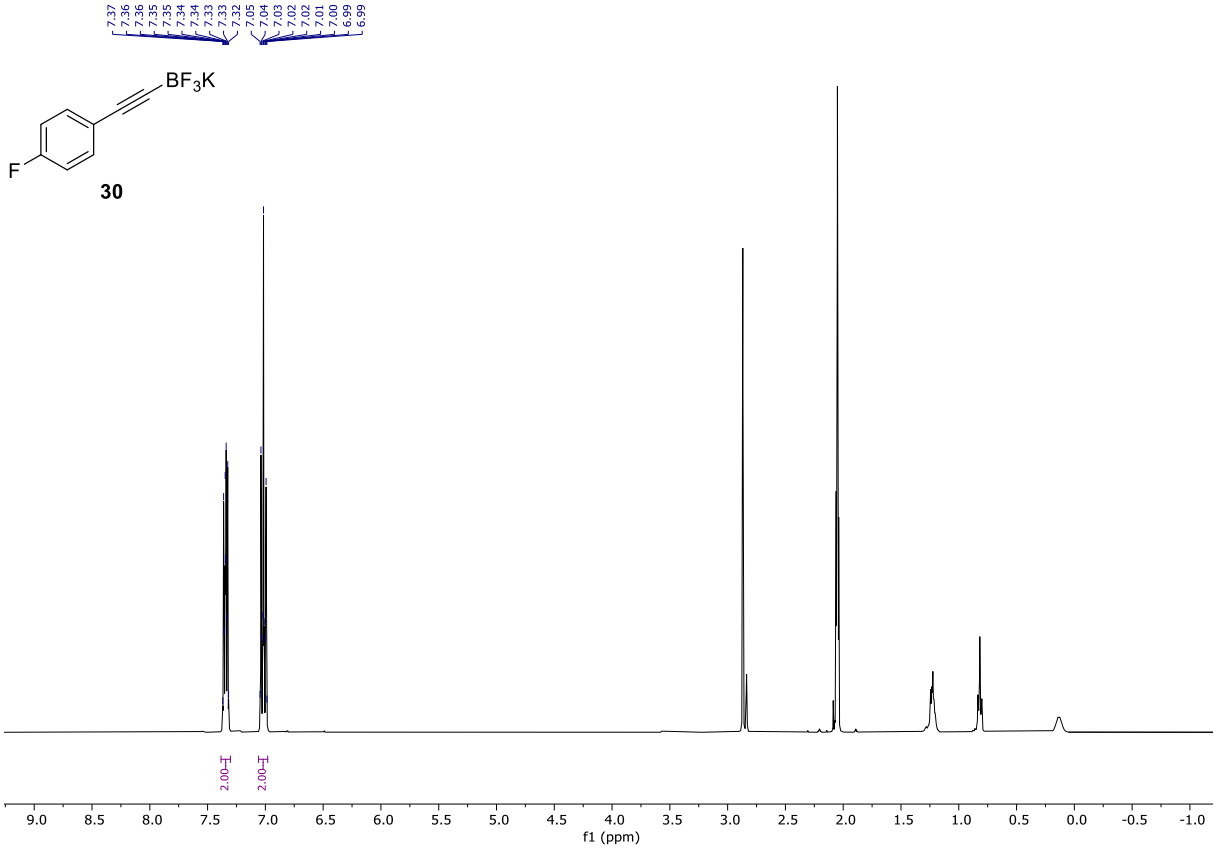
^{11}B NMR (128 MHz, acetone-d_6) of compound **29**:



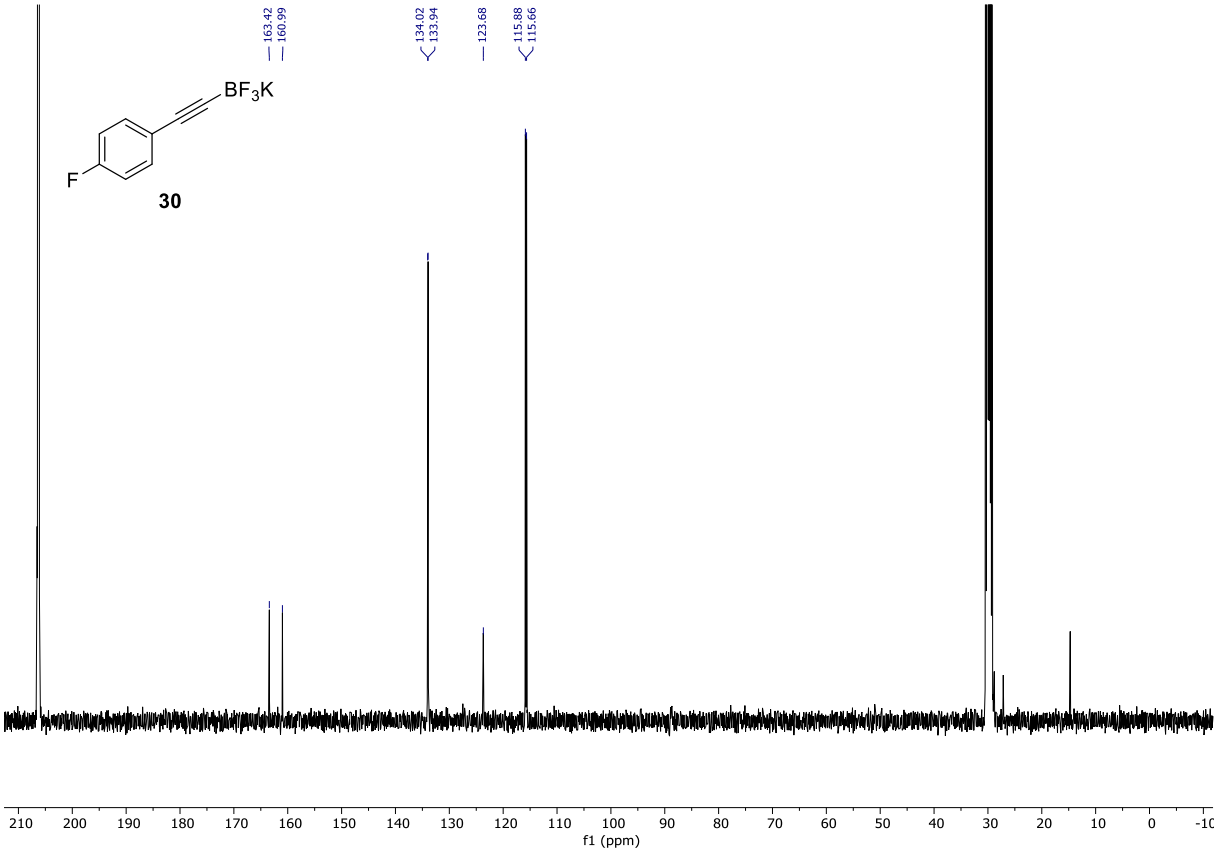
^{1}H NMR (400 MHz, DMSO-d_6) of compound **30**:



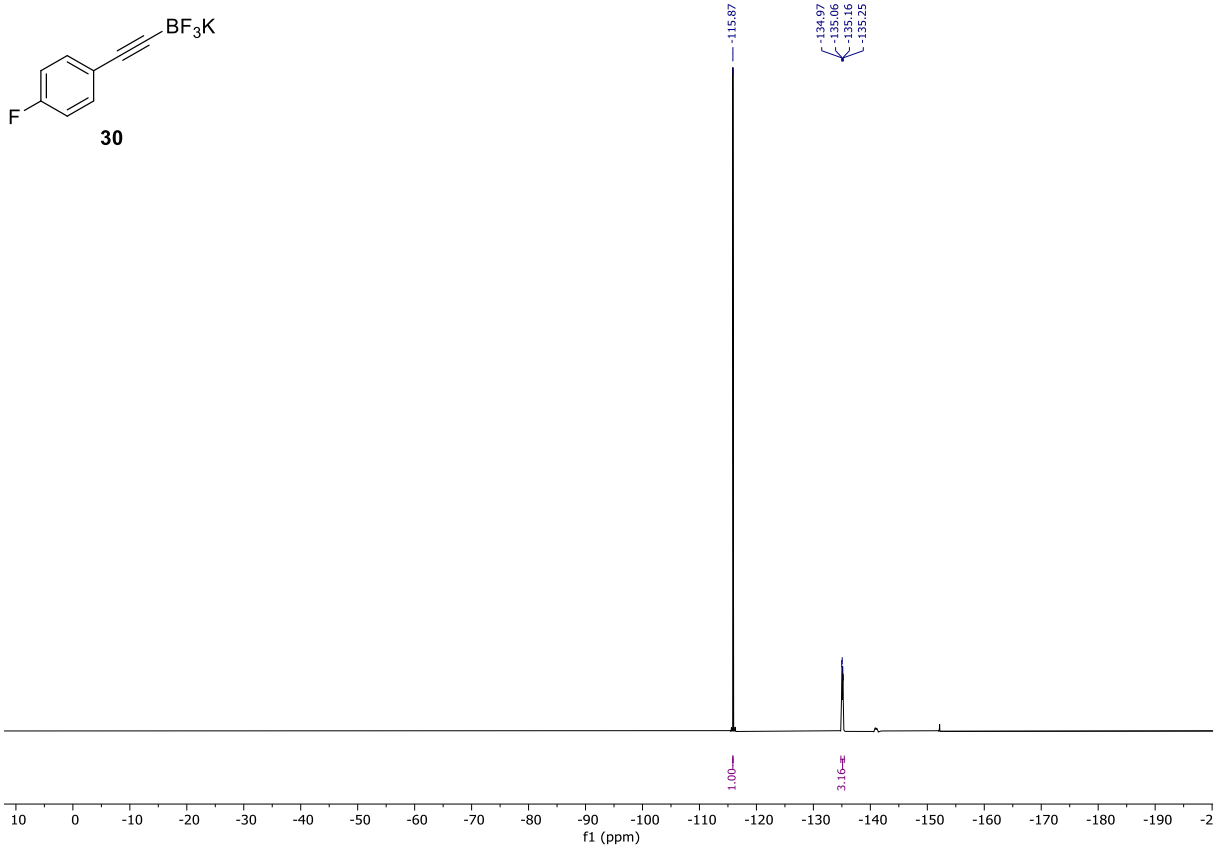
^{1}H NMR (400 MHz, acetone-d_6) of compound **30**:



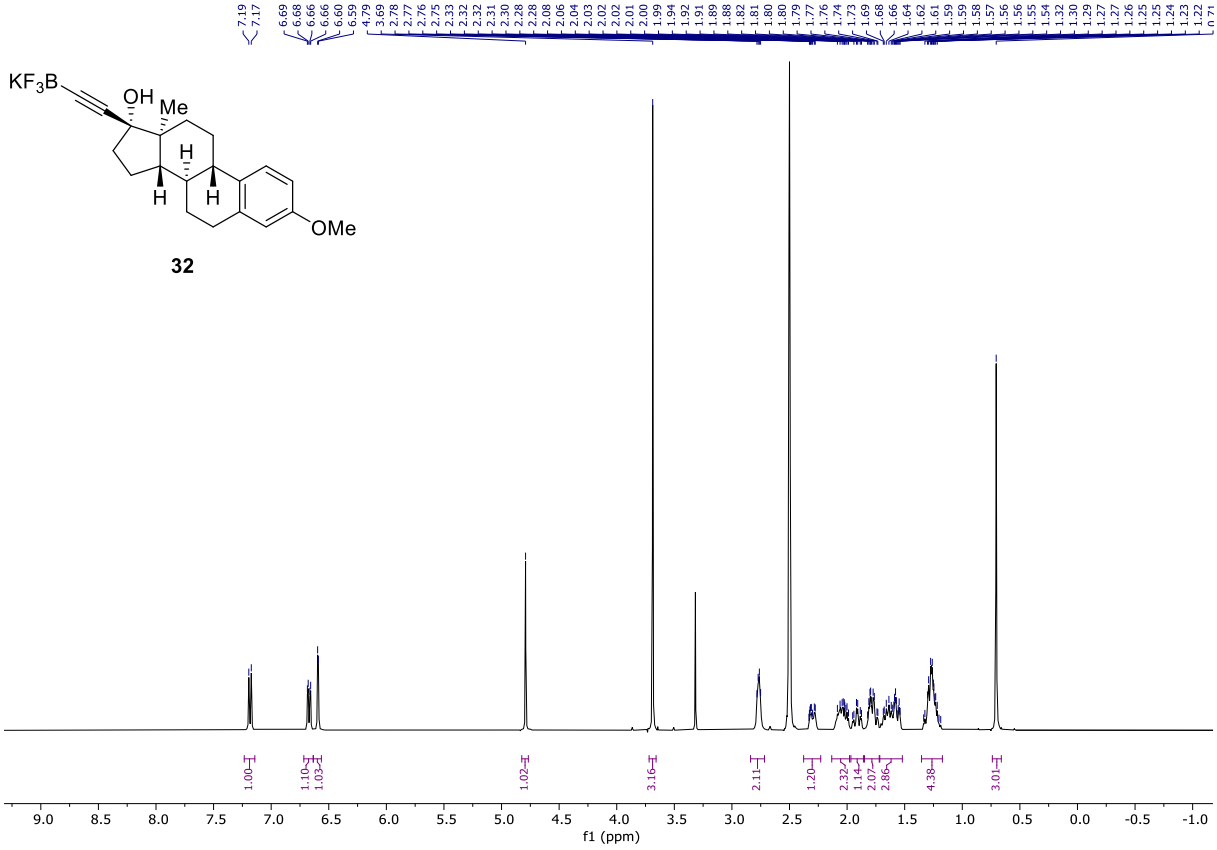
^{13}C NMR (101 MHz, acetone-d_6) of compound **30**:



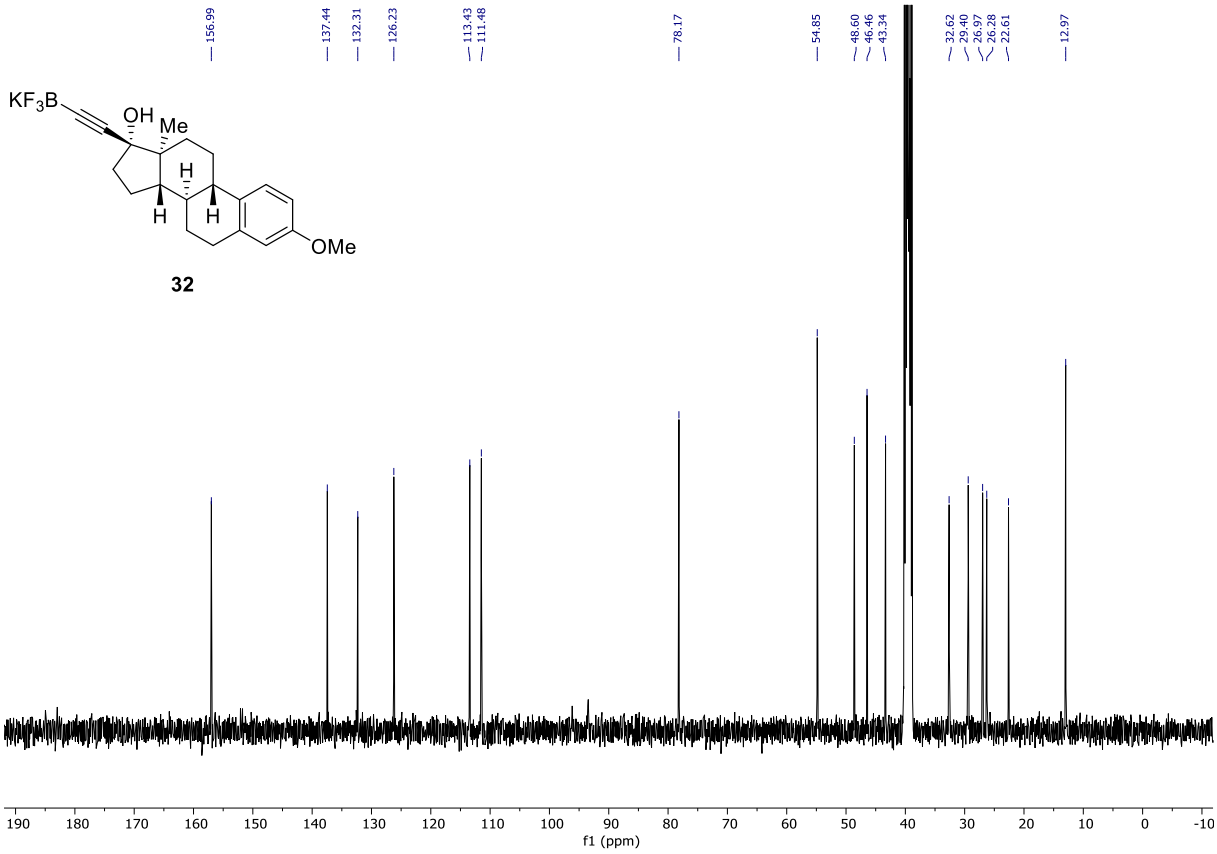
^{19}F NMR (376 MHz, acetone-d_6) of compound **30**:



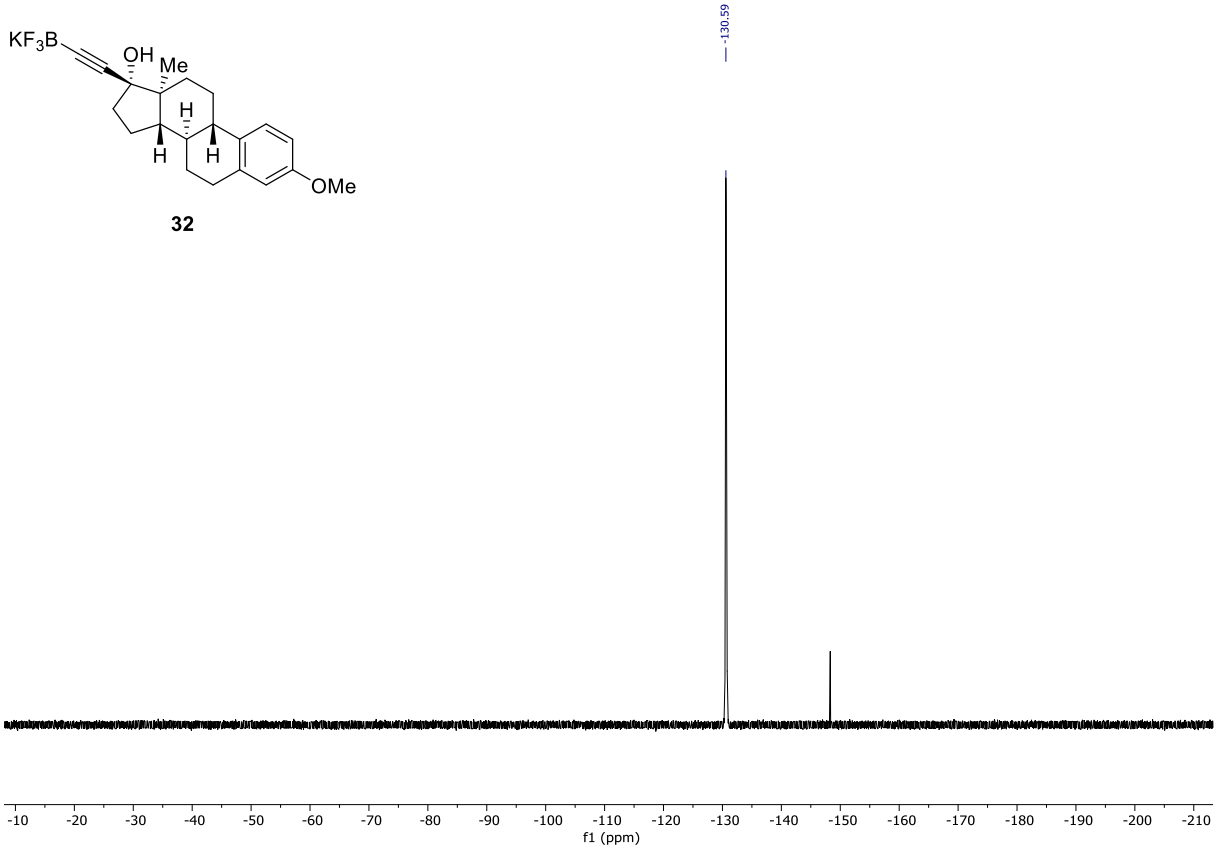
^{1}H NMR (400 MHz, DMSO-d_6) of compound **32**:



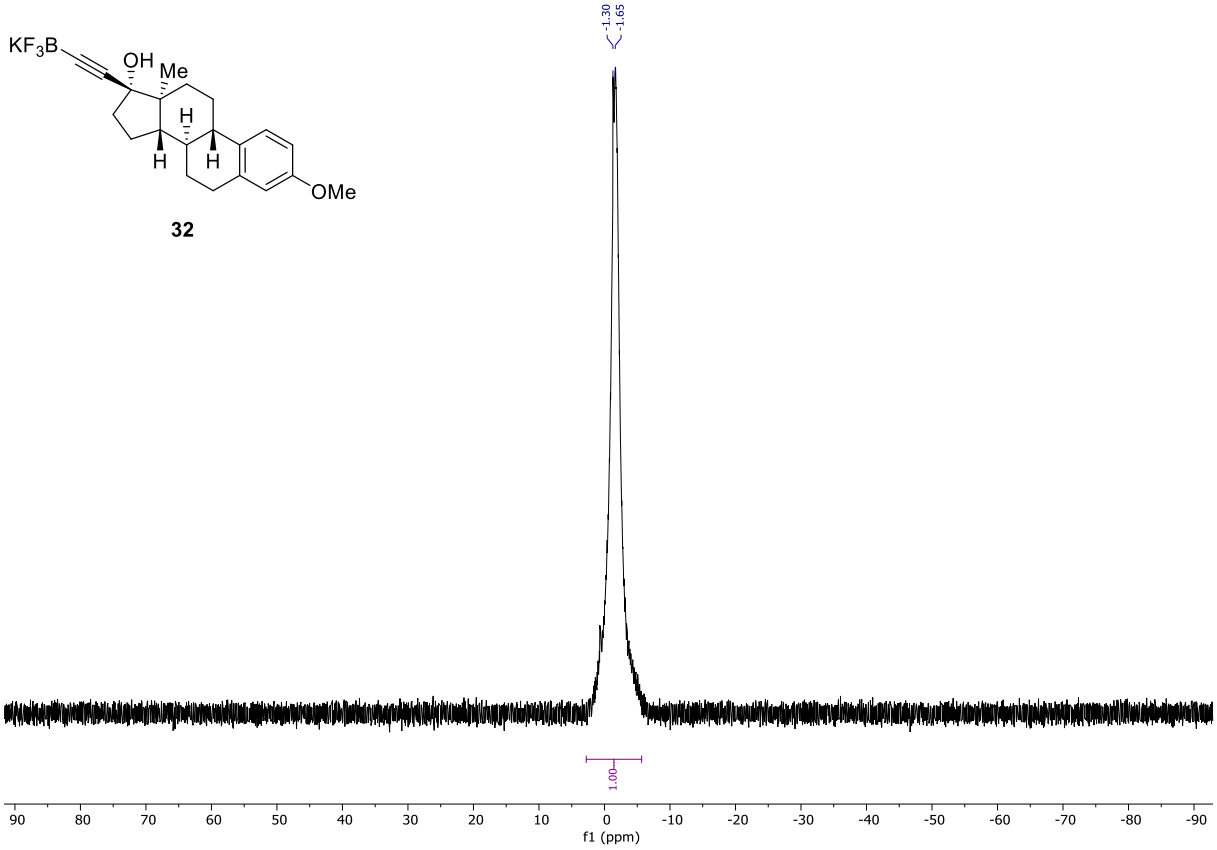
^{13}C NMR (101 MHz, DMSO -d_6) of compound **32**:



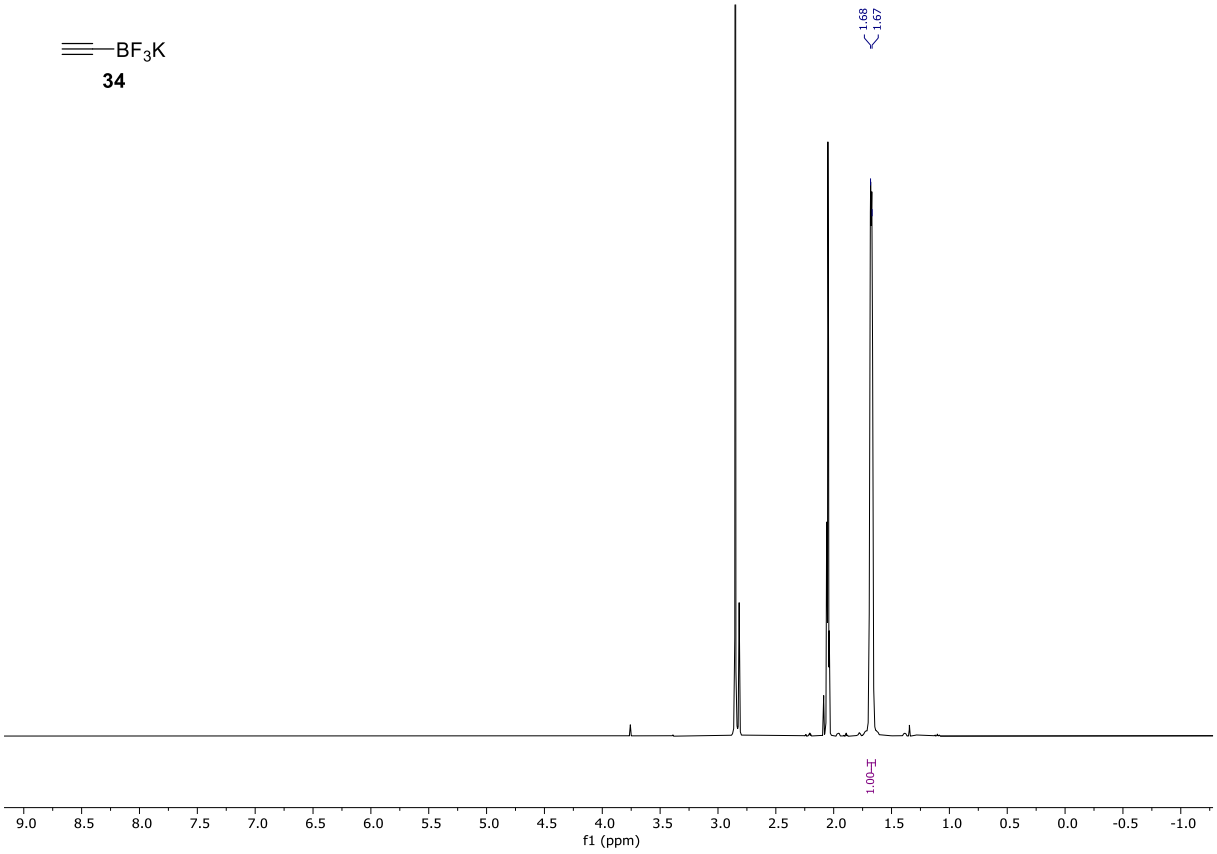
^{19}F NMR (376 MHz, DMSO -d_6) of compound **32**:



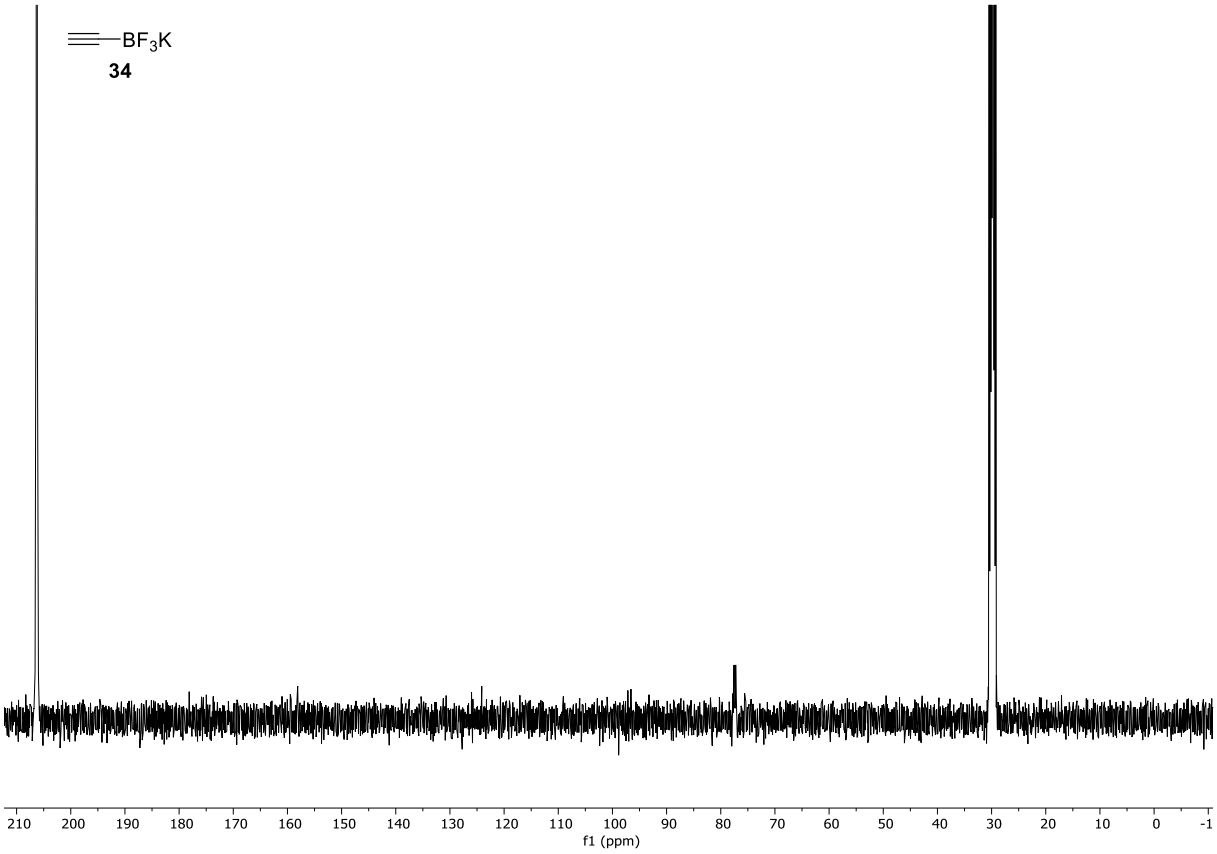
^{11}B NMR (128 MHz, DMSO -d_6) of compound **32**:



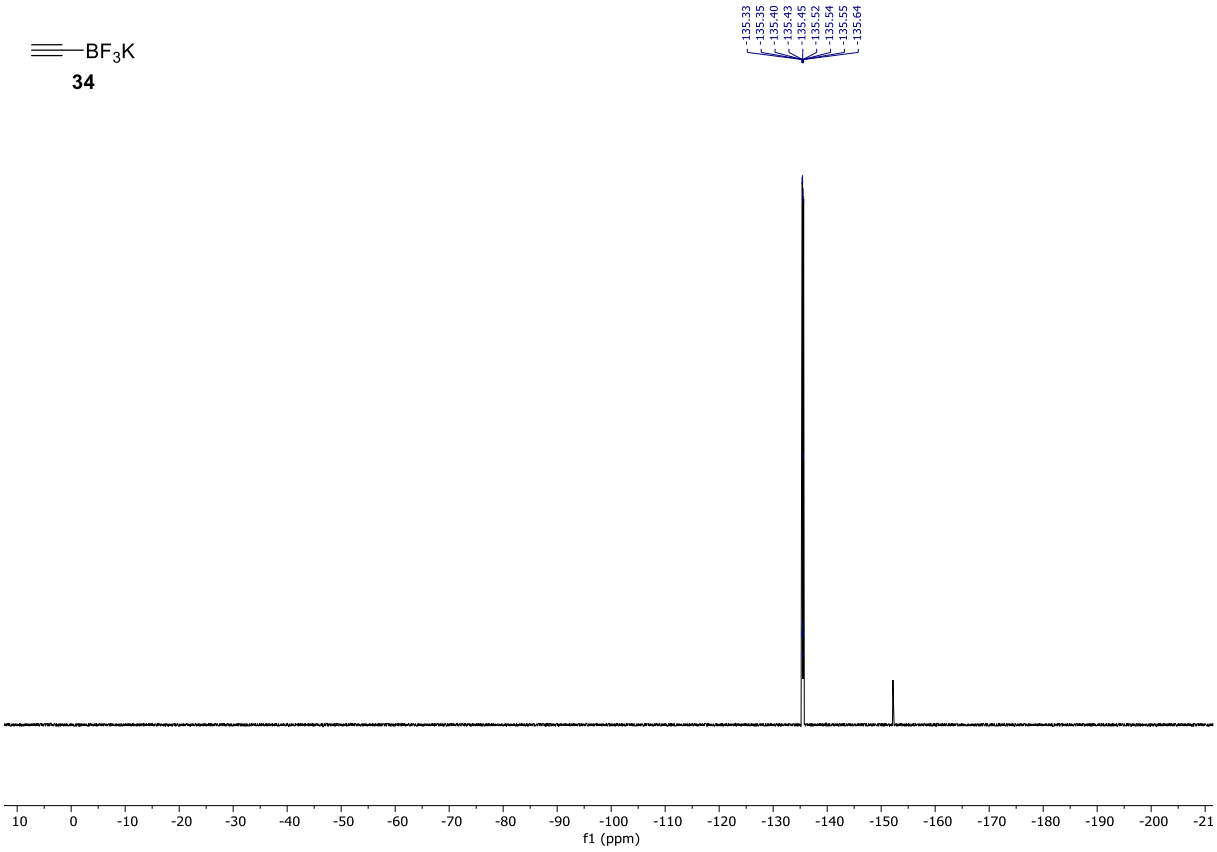
^{1}H NMR (400 MHz, acetone-d_6) of compound **34**:



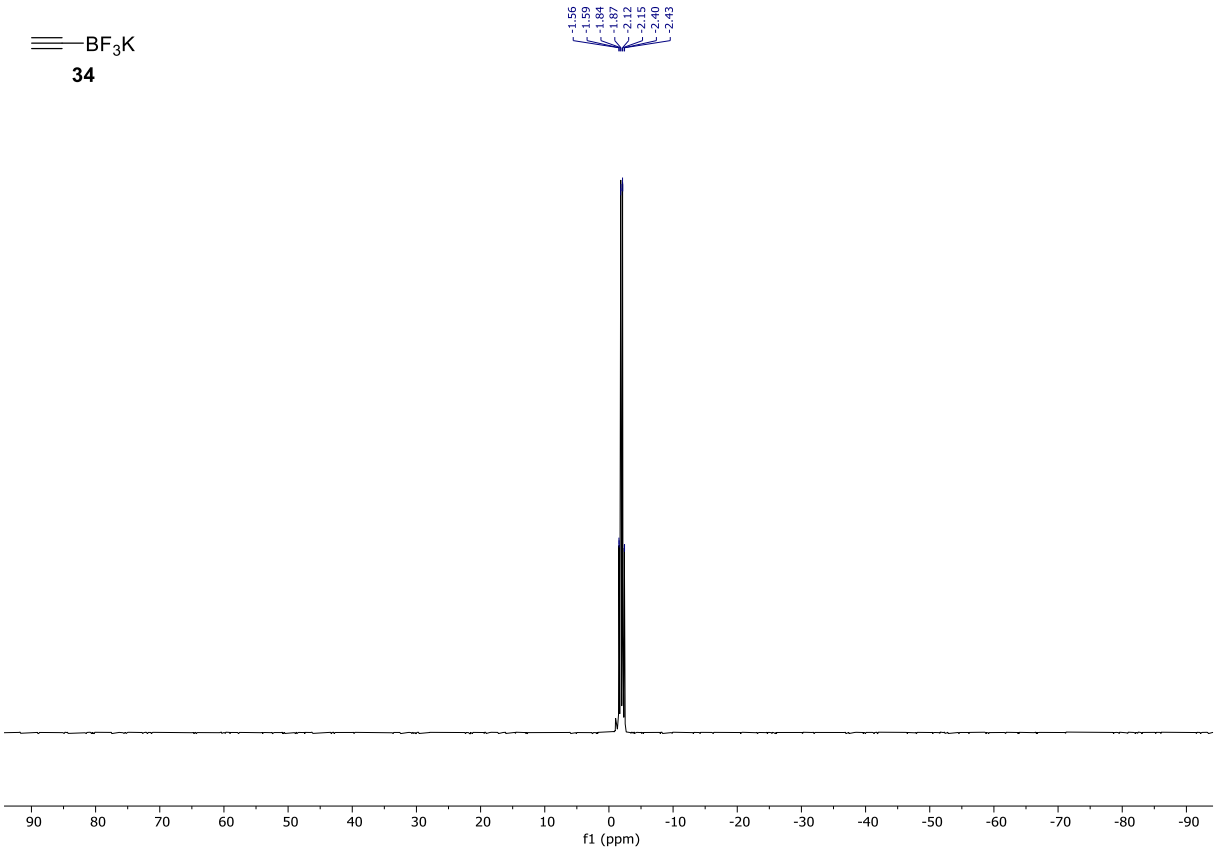
^{13}C NMR (101 MHz, acetone-d_6) of compound **34**:



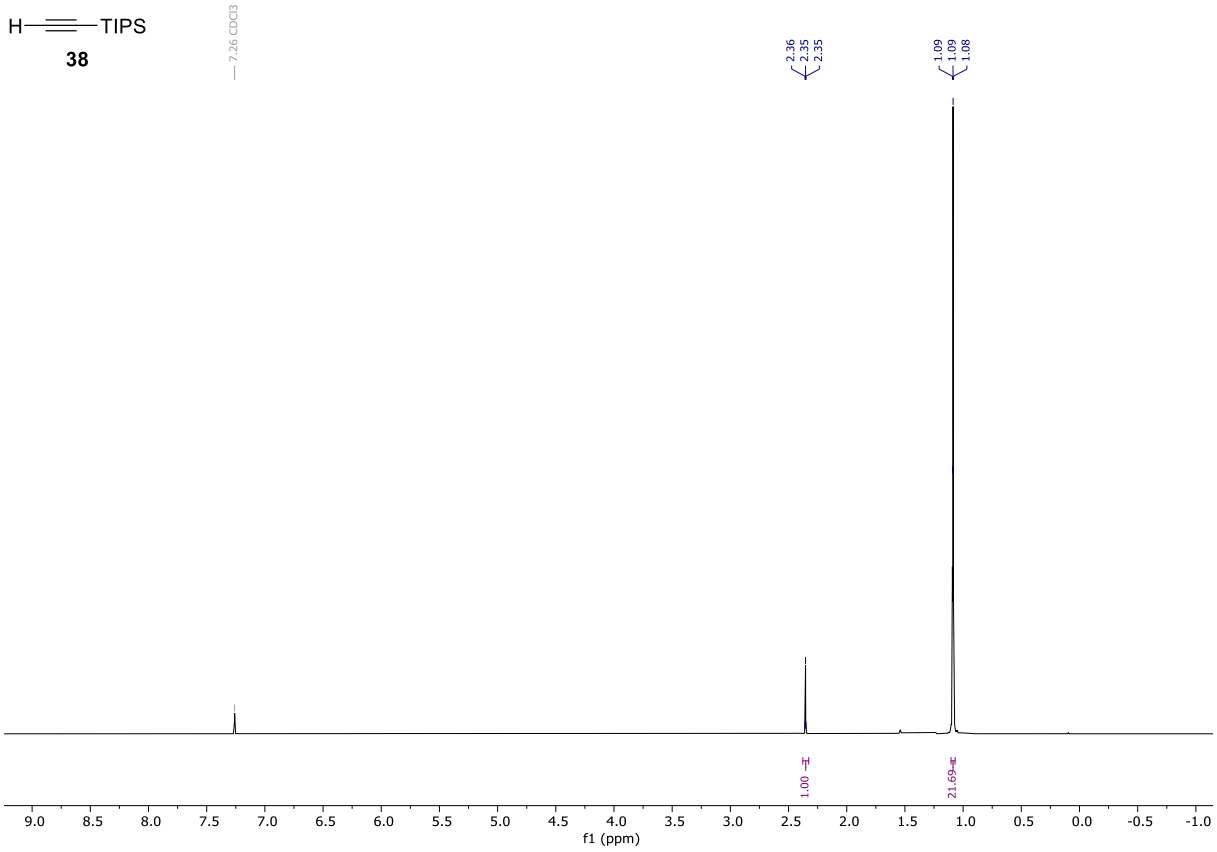
^{19}F NMR (376 MHz, acetone-d_6) of compound **34**:



^{11}B NMR (128 MHz, acetone-d_6) of compound **34**:



^{1}H NMR (400 MHz, $CDCl_3$) of compound **38**:



^{13}C NMR (101 MHz, $CDCl_3$) of compound **38**: