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Azido-alkynylation of alkenes through radical-polar crossover†

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We report an azido-alkynylation of alkenes allowing a straightforward access to homopropargylic azides by combining hypervalent iodine reagents and alkynyl-trifluoroborate salts. The design of a photocatalytic redox-neutral radical polar crossover process was key to develop this transformation. A variety of homopropargylic azides possessing electron-rich and -poor aryls, heterocycles or ether substituents could be accessed in 34–84% yield. The products are synthetically useful building blocks that could be easily transformed into pyrroles or bioactive amines.

Introduction

The azide moiety is widely recognized as a versatile functional group (FG) and it has found broad application in the pharmaceutical industry[1] and in material science.[2] It is both a form of protected amine and a powerful synthetic handle with a unique downstream chemistry.[3] In recent years, the renaissance of radical chemistry triggered by photoredox catalysis led to the development of novel methods to introduce azides in organic molecules.[4] In particular, the formation of azide radicals and their addition onto alkenes was demonstrated to be an efficient strategy for the synthesis of difunctionalized products (Scheme 1A).[4a,f] After addition of the azide radical, different substituents including heteroatoms[5] and aryls[6] have been introduced on the intermediate carbon-centered radical. This represents a powerful strategy to quickly gain molecular complexity with the benefit of a highly regiospecific outcome resulting from the formation of the more stable carbon-centered radical.

Among all the difunctionalization methods developed, one of the potentially most useful – the azido-alkynylation – has surprisingly not yet been explored, except for the single example of the azido-alkynylation of phenyl-vinyl ketone in 28% yield reported as part of a mechanistic study (Scheme 1B).[7] Alkynes are highly useful handles for further derivatization *via* cycloaddition or other triple bond functionalization methods.[8] In this specific case, the resulting homopropargylic azides are interesting synthetic intermediates known to undergo cyclization to form pyrroles.[9] Moreover, upon reduction they would afford homopropargylic amines which can be found in bioactive molecules.[10] Homopropargylic azides are currently accessed from epoxides using a sequence of ring opening with lithium acetylide, mesylation of the resulting alcohol and displacement by azide anions.[9d,f] Consequently, more direct synthetic approaches to access such motifs would be of general interest and high synthetic value.

Developing a radical azido-alkynylation of alkenes would initially involve azide radical addition to the double bond. From there multiple approaches could be envisaged to transfer the alkyne to the intermediate carbon radical (Scheme 1B).[11] Classical strategies based on the recombination with a metal acetylide followed by reductive elimination[12] would not be compatible in the case of azidation (Scheme 1B1). Copper acetylides are the most classical intermediates used in this chemistry but the presence of azides, free alkynes and copper would lead to cycloaddition reactions.[1b] Additionally, copper catalysts and different azide sources are known to effectively promote the diazidation of alkenes, often proceeding *via* radical intermediates.[13] It is therefore not surprising that no azido-alkynylation following this mechanism has been reported so far. A second approach solely based on open-shell species would use SOMOphilic alkynes in an addition–elimination process to provide the desired product (Scheme 1B2).[12a,14] Nevertheless, this system would have major limitations as commonly used alkyne-transfer reagents (ethynylbenziodoxolone and alkynyl sulfones) often require aryl substituents to perform efficiently.[15] Moreover, while frequently used to trap alkyl radicals, only a few examples exist for more stabilized benzylic radicals and are often associated with a lower yield,[16] a narrow scope[17] or a high excess of radical.[18] All those factors could explain why there is only one report of such an approach for azido-alkynylation proceeding in 28% yield on phenyl vinyl ketone as a very activated substrate.[7]

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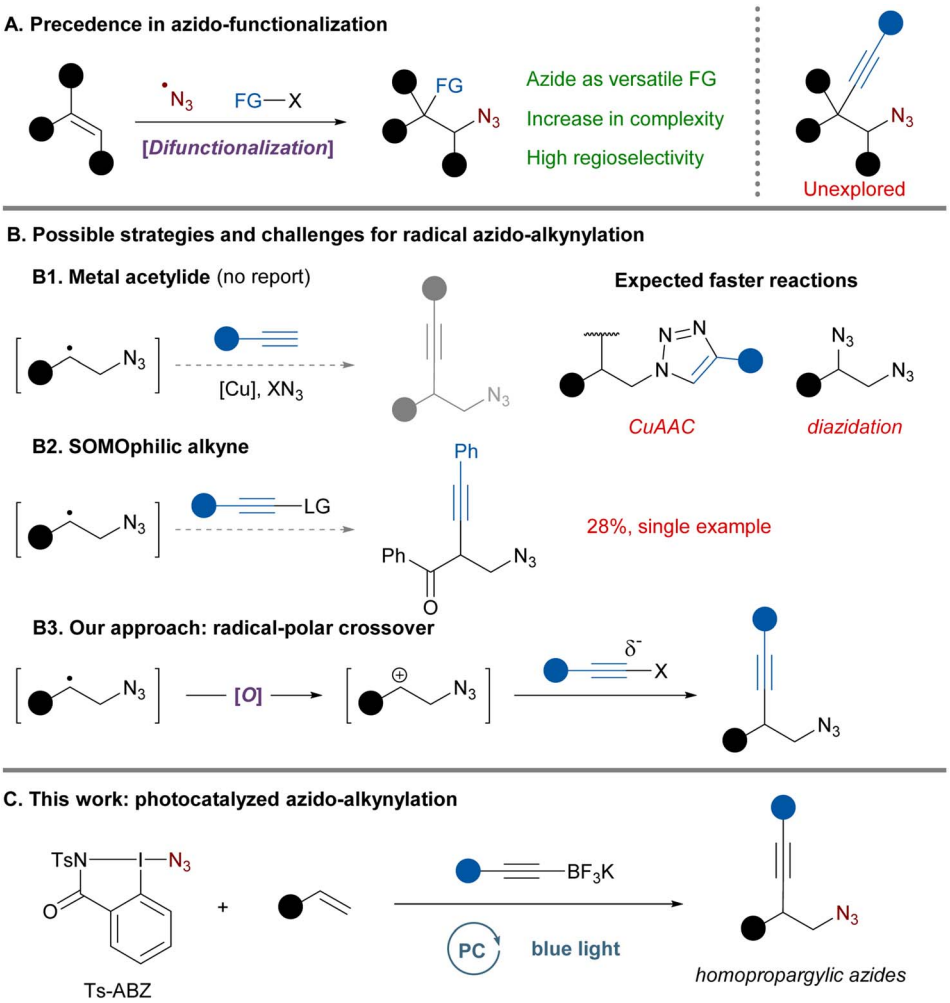
† Electronic supplementary information (ESI) available: Experimental procedures, characterization data and scan of NMR spectra. ESI references are given in note 33. Details for accessing crystallographic data is given in note 31. ESI references are given in note 32. For accessing raw data, please see the data availability statement. CCDC 2264031 and 2243553. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3sc03309k

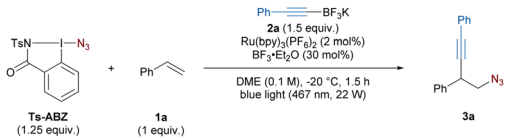


Scheme 1 Azido-functionalization state of the art and challenges.

In order to overcome this gap in existing synthetic methodologies, we thought of an alternative pathway involving the merger of radical and polar chemistry.[19] Transformations involving radical-polar crossover (RPC) mechanisms have recently received increased attention as they enable the combination of orthogonal reagents only active in either radical or polar regime. Additionally, redox-neutral processes can be developed by careful design of the catalytic cycle. Upon oxidation of the intermediate C-centered radical, the carbocation formed could be trapped by a nucleophilic alkyne affording the desired product (Scheme 1B3). In fact, Xu[20] and Molander[21] elegantly demonstrated that alkene radical cations and benzylic carbocations could be trapped by nucleophilic trifluoroborate salts. In addition, rare cases of RPC reactions involving azide radicals have been reported, but the nucleophiles were limited to methanol,[13b] carboxylic acids[22] or alkyl groups during a semipinacol rearrangement.[23]

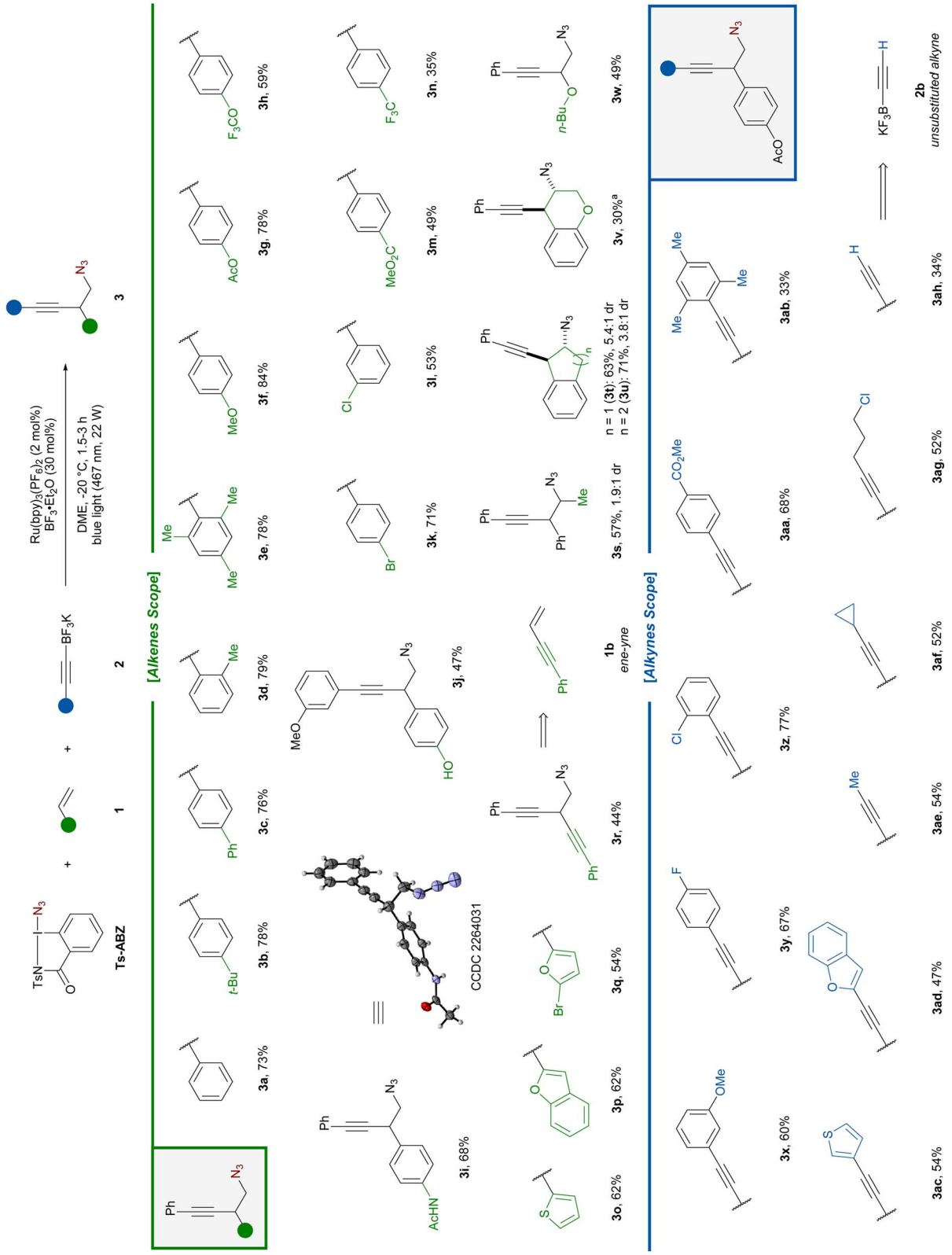
Although the envisaged 3-component synthesis of homopropargylic azides based on a RPC approach looks promising, there are still significant challenges to overcome: a non-nucleophilic azide radical precursor needs to be selected to

Table 1 Reaction optimization[a]



Entry	Variation from standard conditions	Yield[b] (%)
1	None	74
2	**Ts-ABZ** as limiting reagent	69
3	**2a** as limiting reagent	44
4	$C = 0.05$ M	74
5	$C = 0.2$ M	60
6	Room temperature	50
7	No $BF_3 \cdot Et_2O$	49
8	No light or photocatalyst	<5

[a] Reactions were carried out on 0.1 mmol scale. Light irradiation was carried out using a single Kessil lamp. [b] NMR yield determined using CH_2Br_2 as internal standard.



Scheme 2 Scope of the azido-alkynylation. Reaction conditions: **1** (1 equiv.), **2** (1.5 equiv.), **Ts-ABZ** (1.25 equiv.), $Ru(bpy)_3(PF_6)_2$ (2 mol%), $BF_3 \cdot Et_2O$ (30 mol%), DME (0.1 M), −20 °C, blue light (467 nm, 22 W), 1.5 to 3 h. The major diastereoisomer is drawn, the dr was determined on the crude reaction mixture by ^1H NMR. [a]Only diastereoisomer observed.

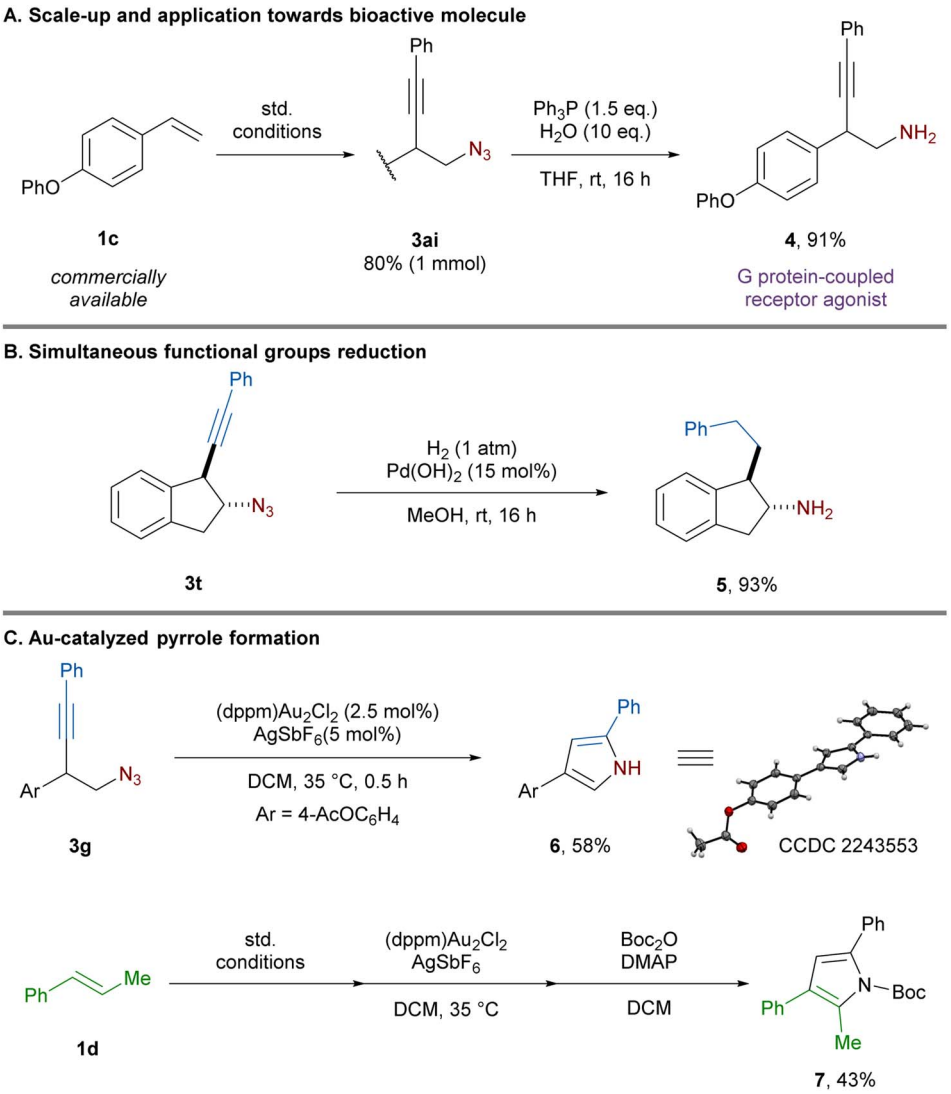
limit diazidation and a nucleophilic alkyne efficient enough for carbocation trapping before decomposition is required. Herein, we report the photocatalyzed azido-alkynylation of styrenes using the combination of an azidoiodane reagent and alkynyl-trifluoroborate salts (Scheme 1C). Using this radical-polar crossover strategy a large variety of homopropargylic azides could be accessed in a single step.

Results and discussion

Following optimization studies, the azido-alkynylation of styrene **1a** was achieved using **Ts-ABZ** as azide radical source upon single electron reduction. This hypervalent iodine reagent is a safer version of the more commonly used azidobenziodoxolone, also known as Zhdankin reagent,[24] which showed an explosion hazard.[23] Potassium alkynyl-trifluoroborates were selected as nucleophilic alkynes as they had been previously employed for the trapping of similar carbocations.[20,21] The reaction was performed under photoredox conditions with $BF_3 \cdot Et_2O$ as additive to afford **3a** in 74% yield after 1.5 hours at −20 °C (Table 1, entry 1).

Both styrene (**1a**) and **Ts-ABZ** can be used as the limiting reagent, but a lower yield was observed when 1.0 equivalent of **2a** was used (entries 1–3). Lower and higher concentrations had little to no impact on the reaction outcome (entries 4 and 5). Raising the temperature to 21 °C led to a decrease in yield (entry 6). A similar result was observed when $BF_3 \cdot Et_2O$ was not added (entry 7). Finally, control experiments in the absence of light or photocatalyst afforded only traces of the desired product (entry 8). Full optimization tables, including screening of photocatalyst, solvents, equivalents, light sources and additives can be found in the ESI (Tables S1–S8).†

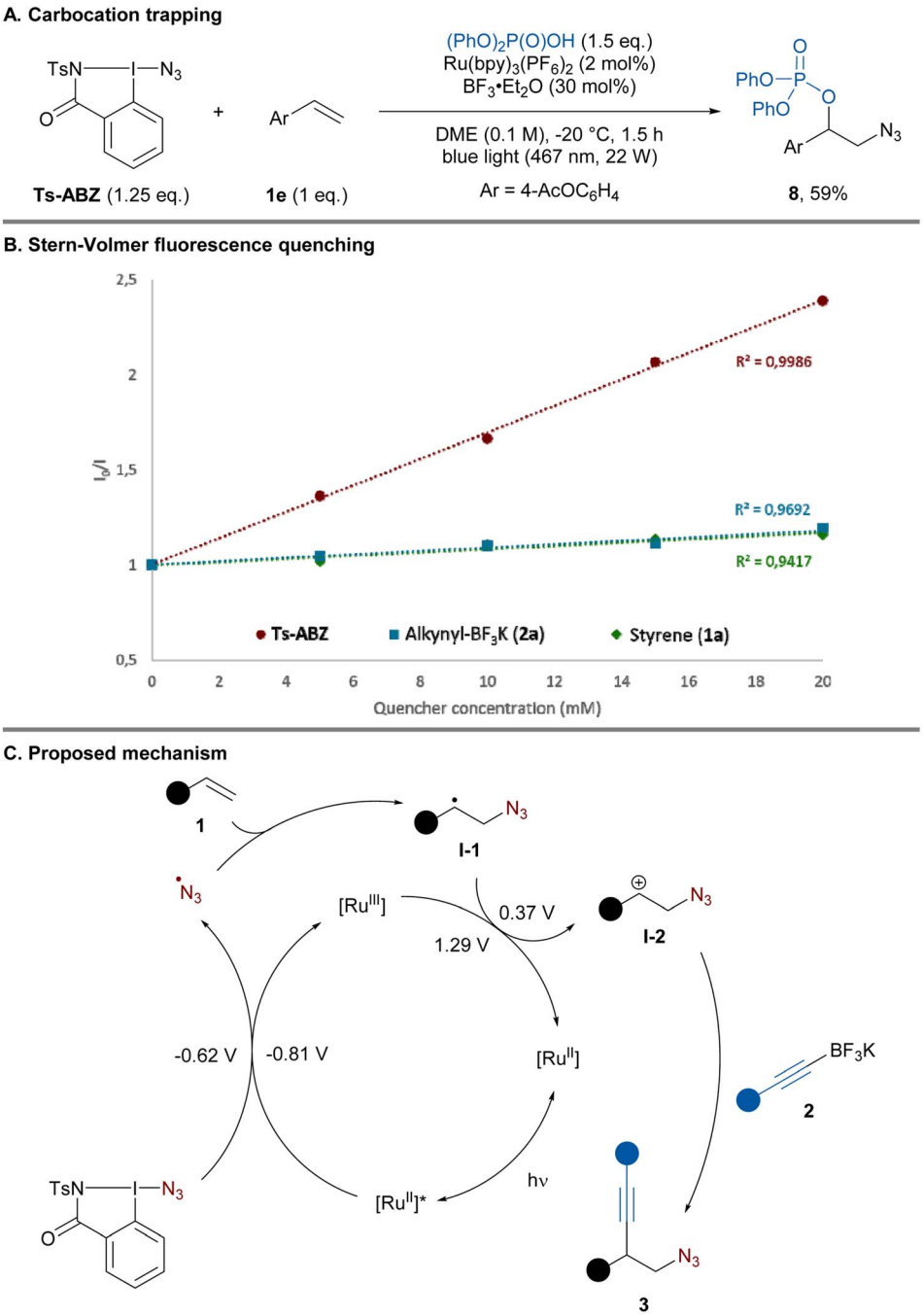
With optimized conditions in hand, the scope of styrenes was investigated (Scheme 2). In all reactions, full conversion of the alkene was achieved. As no other small molecule side products were observed, we assign the different isolated yields observed to different levels of oligomerization/polymerization of the alkenes. The model substrate **3a** was obtained in 73%



Scheme 3 Product modifications.

yield on a 0.3 mmol scale. Styrenes bearing a *tert*-butyl or a phenyl group in *para* position gave products **3b** and **3c** in 78% and 76% yield, respectively. Steric hindrance on the aryl ring was well tolerated as **3d** and **3e** possessing one or two *ortho* substituents could be obtained in >78% yield. Oxygen-substituted aryls with substituents such as methoxy and acetoxy could also be used (**3f–g**). A slight decreased in yield was observed in the presence of the medicinal chemistry relevant trifluoromethoxy substituent (**3h**).[25] Pleasingly, the presence of nucleophilic functional groups, which could have compete with **2a** for the trapping of the carbocation, did not hinder the reaction: products **3i** or **3j** bearing an acetamide and a free phenol could be accessed in 68% and 47% yield, respectively. Additionally, an X-ray structure of **3i** was obtained. Halogen-substituted arenes afforded the corresponding azido-alkynylated products **3k–l** in 71% and 53% yield, respectively.

Electron-withdrawing group (EWG), which could be expected to destabilize the carbocation intermediate, were still tolerated in the reaction. Substrates bearing a *para* ester and CF_3 group afforded the corresponding products **3m** and **3n** in 49% and



Scheme 4 Mechanistic experiments and proposed mechanism.

35% yield. Moreover, homopropargylic azides **3o–p** containing electron-rich heterocycles such as thiophene and benzofuran were obtained in 62% yield. Carrying out the reaction on a sensitive bromo-substituted vinyl-furan, which quickly polymerizes after synthesis, successfully gave product **3q** in 54% yield.

Eneyne **1b** could be exclusively 1,2-functionalized to give diyne **3r** in 44% yield. The reaction tolerated β-substitution on the styrene: product **3s** bearing a methyl substituent was obtained in 57% yield as a 1.9 : 1 mixture of diastereoisomers. Using the less flexible cyclic indene, the diastereoselectivity of the reaction could be increased to 5.4 : 1 in favor of the *trans* **3t** isomer. Increasing the ring size slightly improved the yield, but lowered the dr (**3u**). When chromene was used, the azido-alkynylated product **3v** was formed in 30% yield. No other diastereoisomer was observed. Gratifyingly, vinyl butyl ether could be azido-alkynylated to afford **3w** in 49% yield. Unfortunately, alkenes bearing aliphatic substituents only could not be used.

Next, the scope of nucleophilic alkynes was studied. Aryl-alkynes bearing either EDG (OMe) or EWG (F, Cl, CO_2Me) at different positions gave the corresponding products **3x–aa** in 60–77% yield. In this case, the steric hindrance of the nucleophile seems to be an important factor as the use of mesityl-alkyne led to **3ab** in only 33% yield. We were pleased to see that heteroaryl such at 3-thiophene or 2-benzofuran afforded the desired product **3ac** and **3ad** in 54% and 47% yield, respectively. Alkyl-substituted alkynes bearing methyl, cyclopropyl or a propyl chain possessing a chloride were well tolerated affording the corresponding products **3ae–ag** in 52–54% yields. Finally, using unsubstituted alkynyl-BF_3K **2b**, terminal alkyne **3ah** was obtained in 34% yield allowing for potential further diversification *via* cross-coupling.

To demonstrate the synthetic utility of the homopropargylic azides, various post functionalizations were carried out (Scheme 3). First, the azido-alkynylation was performed on 1 mmol scale using styrene **1c** bearing a *para* phenoxy group affording the desired product **3ai** in 80% yield under the same reaction conditions. Further reduction of the azide afforded primary amine **4** in high yield. The corresponding HCl salt is a known agonist for G protein-coupled receptors currently synthesized through a 4-step sequence in 19% overall yield.[10d]

Upon reduction of both the alkyne and azide, **5** was obtained in 93% yield affording a formal 2-step amino-alkylation. Pyrroles play a crucial role in the pharmaceutical industry as they are one of the most frequently encountered heterocycles in bioactive compounds.[26] Applying conditions developed by Toste using gold catalysis,[9a] homopropargylic azide **3g** underwent 5-*endo-dig* cyclization to afford **6**. Non-cyclic β-substituted alkenes afforded poor diastereoselectivity in the azido-alkynylation reaction (Scheme 2, **3s**). This issue is inconsequential for pyrrole synthesis, as all stereoisomers are converted in a single product. For example, styrene **1d** was effectively converted to trisubstituted pyrrole 7 in 43% yield over a 3 step-sequence of azido-alkynylation, cyclization and protection.

To gain insight into the reaction mechanism, control experiments were performed. In the absence of light and photocatalyst only traces of the product could be obtained (Table 1, entry 8). Replacing the alkyne nucleophile by diphenyl phosphate led to the formation of azido-phosphonylated product **8** in 59% yield, presumably resulting from trapping of the carbocation intermediate (Scheme 4A).

Next, Stern–Volmer quenching experiments were performed. **Ts-ABZ** proved to be the most efficient quencher of the excited state photocatalyst compared to alkyne **2a** and styrene **1a** (Scheme 4B). Based on these experiments and literature precedents, a plausible mechanism could be proposed (Scheme 4C).[13b,20,21] Under blue light irradiation, excited state $Ru(bpy)_3^{2+*}$ ($E_{1/2}$ [Ru^{III}/Ru^{II*}] = −0.86 V *vs.* SCE)[27] is capable of reducing **Ts-ABZ** ($E_{1/2}^{red}$ = −0.62 V *vs.* SCE)[28] generating the azide radical. Addition of the latter to alkene **1** would lead to carbon-centered radical **I-1** ($E_{1/2}^{ox}$ = 0.37 V *vs.* SCE)[29] which can be oxidized by the previously formed $Ru(bpy)^{3+}$ ($E_{1/2}$ [Ru^{III}/Ru^{II}] = + 1.29 V *vs.* SCE)[27] regenerating the ground state photocatalyst. Finally, the resulting carbocation **I-2** would be trapped by the nucleophilic alkynyl-BF_3K **2** affording homopropargylic azide **3**. Establishing the mechanism of this addition step would need further studies, but a concerted C–C bond formation and C–B bond cleavage could be operative, in analogy to what has been proposed for alkenyl boronate salts.[20] The exact role of $BF_3 \cdot Et_2O$ is still unclear, it is known to abstract fluoride from alkynyl-BF_3K to form alkynyl-BF_2.[30] Control experiment involving preformation of alkynyl-BF_2 and its subsequent addition instead of $BF_3 \cdot Et_2O$ led to comparable yield hinting at the potential formation of alkynyl-BF_2 under the standard conditions (see the ESI† Section 9.3).

Conclusions

In summary, a photocatalyzed azido-alkynylation of alkenes using **Ts-ABZ** as azide radical source and nucleophilic alkynyltrifluoroborate salts was developed. The reaction proceeds in high yield for electron-rich and electron-poor styrenes. Various aryl-, alkyl- or unsubstituted alkynes were successfully transferred to generate azido-alkynylated scaffolds. Moreover, heterocycles were compatible on both the alkene and alkyne fragment. The homopropargylic azides could be further derivatized, giving access to valuable pyrroles and the efficient 2-step synthesis of a G protein-coupled receptor agonist. The reaction is proposed to proceed through an overall redox-neutral process *via* a radical-polar crossover mechanism.[31,32]

Data availability

ESI† available: Experimental procedures, characterization data and scan of NMR spectra. Crystallographic data is available at CCDC (see note 31). Raw data for compound characterization, including NMR, IR and MS is available at zenodo.org: **https://doi.org/10.5281/zenodo.8239023**.

Author contributions

J. B. conceived the project, optimized the reaction, performed the investigation on the scope of the reaction, the modification of the products and prepared the experimental parts and first

draft of the manuscript. J. W. supervised the project, edited the manuscript and proofread the experimental part.

Conflicts of interest

There are no conflicts to declare.

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Supporting Information for

Azido-Alkynylation of Alkenes

Through Radical-Polar Crossover

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1. General Methods

All reactions were carried out under air unless stated otherwise. Reactions requiring heating were carried out using DrySyn heating block. 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. 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, 40 g, 80 g, 120 g). When indicated purification were performed on activated neutral aluminium oxide (Brockmann activity I). TLC was performed on Merck silica gel 60 F_{254} 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: 77.2 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” (440 nm, 40 W) were performed in test tubes (14 mL, soda-lime glass, wall thickness = 0.8 mm) 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. Reactions using “Kessil lamp” of 467 nm or 440 nm used the corresponding models PR160L-467 or PRL160L-440.

2. Picture of the Photochemistry Set-Up

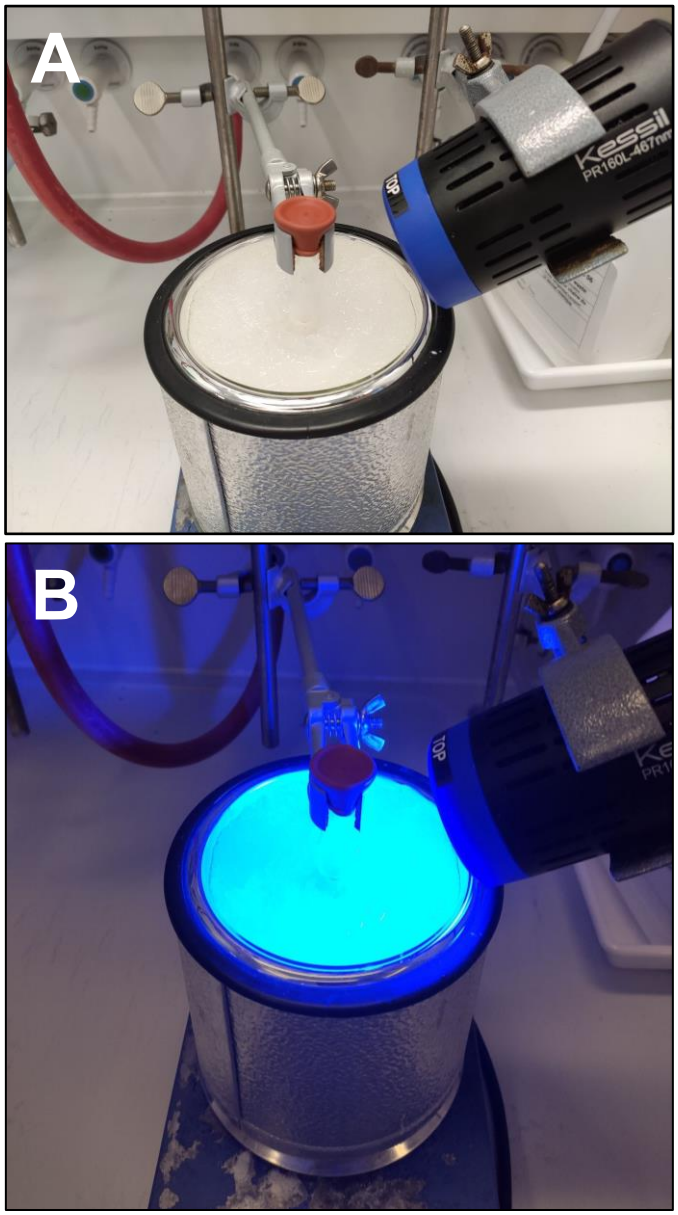


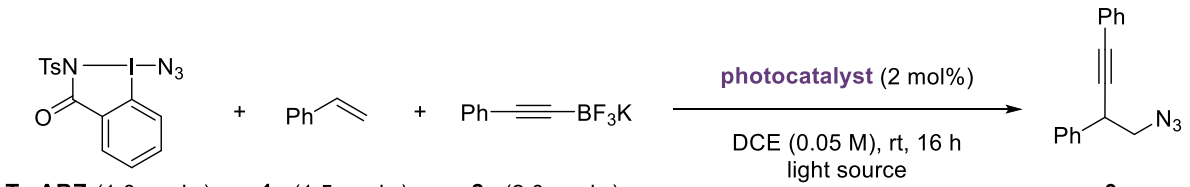
Figure S1: A) Picture of the set-up before turning on the Kessil lamp. B) Picture of the set-up during the reaction.

The Kessil lamp was placed diagonally at a distance of ~4 cm from the top of the reaction vessel (test tube or round-bottom flask). The latter was immersed in a bath of ice and salt (-20 °C) contained in a Dewar. For the optimized conditions the lamp intensity was set at 50% (22 W).

3. Reaction Optimization

Optimization protocol (0.1 mmol scale):

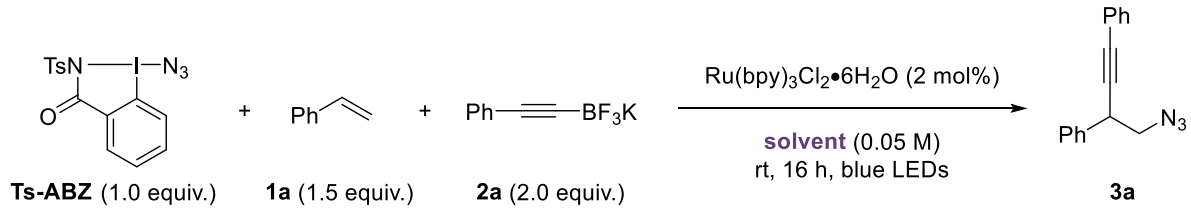
An oven-dried test tube charged with the solid reagents was evacuated and backfilled with N_2 (3x). Dry degassed solvent and the liquid reagents were added and the mixture was cooled to the desired temperature (if relevant). Then, additive (if relevant) was added and the reaction was stirred under light irradiation. The reaction mixture was filtered through a short plug of silica and eluted with DCM then concentrated *in vacuo*. ^{1}H NMR yield was determined by dissolving crude **3a** in $CDCl_3$ and adding CH_2Br_2 (3.5 µL, 0.049 mmol, 0.49 equiv.) as internal standard. The signal at 4.13 ppm was used to determine the yield.



Ts-ABZ (1.0 equiv.) **1a** (1.5 equiv.) **2a** (2.0 equiv.) **3a**

entry	photocatalyst	light source	NMR yield (%)
1	$Cu(dap)_2Cl$	blue LEDs	17
2	$Cu(dap)_2Cl$	green LEDs	21
3	$Ir(ppy)_3$	blue LEDs	n.o
4	$[Ir(dtbbpy)(ppy)_2]PF_6$	blue LEDs	<5%
5	$Ru(bpy)_3Cl_2•6H_2O$	blue LEDs	17
6	$Ru(bpz)_3(PF6)_2$	blue LEDs	n.o
7	4DPAIPN	blue LEDs	<5%
8	4ClDPAIPN	blue LEDs	10
9	4tBuCzIPN	blue LEDs	n.o
10	DPZ	blue LEDs	<5%
11	Rose Bengal	green LEDs	n.o

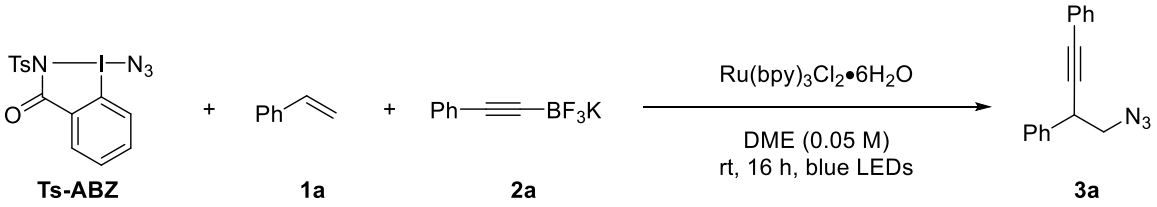
Table S1: Photocatalyst screening. n.o = not observed. [a]$Ru(bpy)_3Cl_2•6H_2O$ was selected as it afforded less diazidation.



Ts-ABZ (1.0 equiv.) **1a** (1.5 equiv.) **2a** (2.0 equiv.) **3a**

entry	solvent	NMR yield (%)
1	DCE	17
2	$CHCl_3$	16
3	CH_3CN	9
4	DMF	n.o
5	DMSO	n.o
6	acetone	<5%
7	EtOAc	15
8	THF	8
9	dioxane	14
10	DME	36
11	DME/HFIP (9:1)	39
12	DME/TFE (9:1)	31

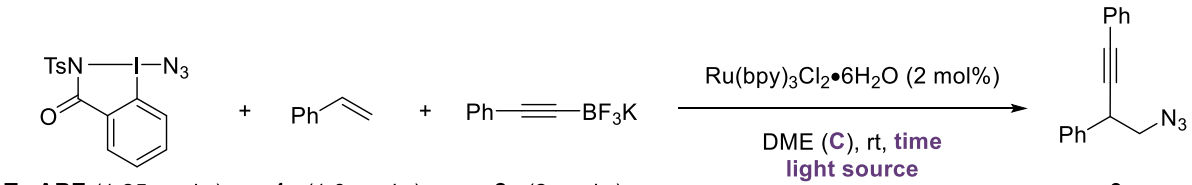
Table S2: Solvent screening. n.o = not observed.



Ts-ABZ **1a** **2a** **3a**

entry	**Ts-ABZ** equiv.	**1a** equiv.	**2a** equiv.	PC (mol%)	NMR yield (%)
1	1	1.5	2	2	36
2	1.25	1	2	2	42
3	1.5	1	2	2	41
4	1.25	1	1.25	2	39
5	1.25	1	3	2	44
6	1.5	1.5	1	2	43
7	1.25	1	2	1	40
8	1.25	1	2	5	39

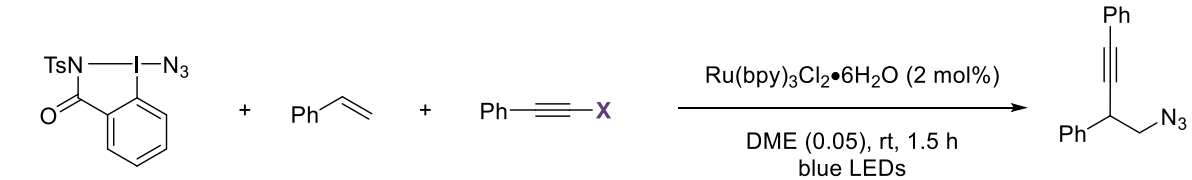
Table S3: Equivalent screening. PC = photocatalyst



Ts-ABZ (1.25 equiv.) **1a** (1.0 equiv.) **2a** (2 equiv.) **3a**

entry	reaction time (h)	light source	Concentration (M)	NMR yield (%)
1	16	blue LEDs (40 W)	0.05	42
2	2	blue LEDs (40 W)	0.05	43
3	1	blue LEDs (40 W)	0.05	39
4	0.16	blue LEDs (40 W)	0.05	21
5	1.5	kessil 467 nm (44 W)	0.05	42
6	1.5	kessil 467 nm (22 W)	0.05	42
7	1.5	kessil 440 nm (45 W)	0.05	41
8	4	CFL (8 W)	0.05	38
9	1.5	green LEDs (40 W)	0.05	35
10	1.5	blue LEDs (40 W)	0.05	42
11	1.5	blue LEDs (40 W)	0.025	36
12	1.5	blue LEDs (40 W)	0.1	41
13	1.5	blue LEDs (40 W)	0.2	41

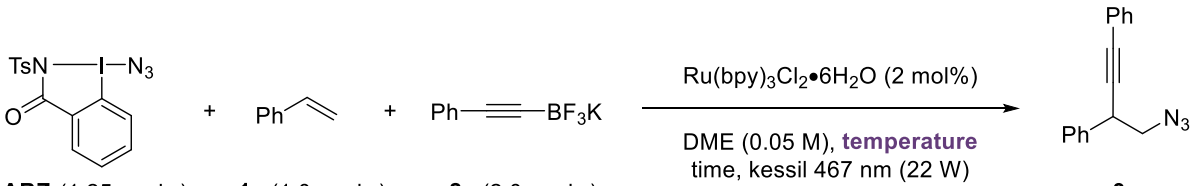
Table S4: Reaction time, light source and concentration screening. Blue/green LEDs refers to LEDs strip attached on a crystallization flask.



Ts-ABZ (1.25 equiv.) **1a** (1.0 equiv.) **2** (2.0 equiv.) **3a**

entry	**X**	NMR yield (%)
1	BF_3K	42
2	BF_3[TBA]	14
3	TMS	n.o

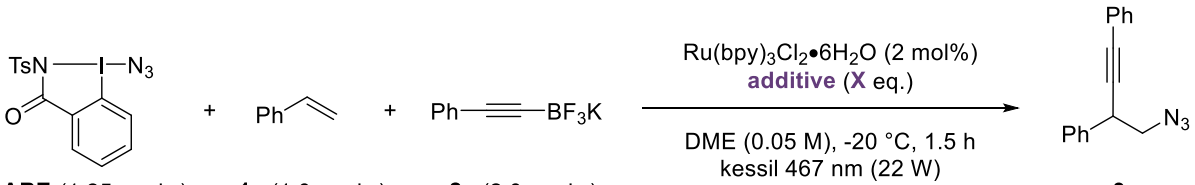
Table S5: Alkyne source screening. n.o = not observed.



Ts-ABZ (1.25 equiv.) **1a** (1.0 equiv.) **2a** (2.0 equiv.) **3a**

entry	T (°C)	method of cooling	time (h)	NMR yield (%)
1	rt	none	1.5	42
2	0	immersion cooler	1.5	50
3	-20	immersion cooler	1.5	52
4	-20	ice and salt bath	1.5	53[a]
5	-46	immersion cooler	3	46

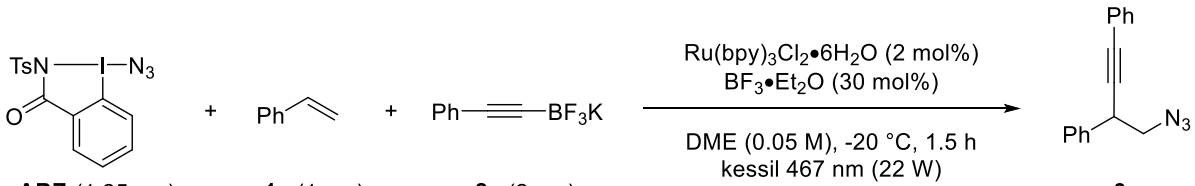
Table S6: Temperature screening. An immersion cooler was immersed in EtOAc. [a]Although there is little difference in yield between 0 and -20 °C we observed a better mass balance in the latter.



Ts-ABZ (1.25 equiv.) **1a** (1.0 equiv.) **2a** (2.0 equiv.) **3a**

entry	additive	equivalent	NMR yield (%)
1	none		53
2	MS 4Å	50 mg / 0.1 mmol	51
3	TMSCl	1 equiv.	40
4	TFAA	1 equiv.	54
5	$(TMS)_2O$	1 equiv.	48
6	$B(OTFE)_3$	1 equiv.	53
7	$BF_3•Et_2O$	1 equiv.	75
8	$BF_3•Et_2O$	2 equiv.	37
9	$BF_3•Et_2O$	0.5 equiv.	73
10	$BF_3•Et_2O$	0.3 equiv.	72

Table S7: Additive screening.



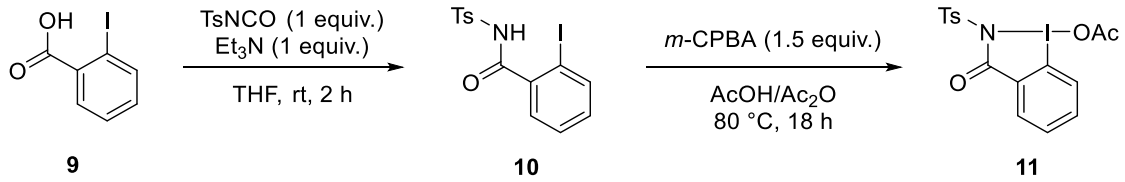
Ts-ABZ (1.25 eq.) **1a** (1 eq.) **2a** (2 eq.) **3a**

entry	change from standard condition	NMR yield (%)
1	none	72
2	C = 0.1 M	75
3	C = 0.1 M, **2a** (1.5 equiv.)	74
4	C = 0.1 M, **2a** (1.25 equiv.)	71
5	C = 0.1 M, **2a** (1.5 equiv.), no degassing	65
6	C = 0.1 M, **2a** (1.5 equiv.), $Ru(bpy)_3(PF_6)_2$ (2 mol%)	74
7	C = 0.1 M, **2a** (1.5 equiv.), $Ru(bpy)_3(PF_6)_2$ (2 mol%), DME/CH_3CN (9:1)	66
8	C = 0.1 M, **2a** (1.5 equiv.), $Ru(bpy)_3(PF_6)_2$ (2 mol%), *p*-ABSA instead of **Ts-ABZ**	n.o

Table S8: Fine-tuning of the reaction condition. n.o = not observed.

4. Synthesis of Hypervalent Iodine Reagents

3-Oxo-2-tosyl-2,3-dihydro-1*H*-1λ^3-benzo[*d*][1,2]iodazol-1-yl acetate (11):



9 **10** **11**

Following a reported procedure,[1] an oven dried round-bottom flask charged with 2-iodobenzoic acid (**9**) (10 g, 40 mmol, 1.0 equiv.) was evacuated and backfilled with N_2 (3x) then dry THF (115 mL) and *p*-toluenesulfonyl isocyanate (6.2 mL, 40 mmol, 1.0 equiv.) were added. Finally, triethylamine (5.6 mL, 40 mmol, 1.0 equiv.) was added dropwise under N_2, a slightly exothermic reaction began in addition to gas release. The reaction was stirred at rt for 2 h. The mixture was diluted with EtOAc (150 mL) and washed with 1 M aq. HCl (2 x 100 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was used in the next step without further purification.

Following a reported procedure,[2] to a round-bottom flask charged with a solution of crude 2-iodo-*N*-tosylbenzamide (**10**) in a mixture of AcOH (70 mL) and Ac_2O (70 mL) was added *m*-CPBA (13.5 g, 60.5 mmol, 1.50 equiv., 77%). The reaction was stirred at 80 °C for 18 h covered from light. The mixture was left to cool to rt then pentane (100 mL) was added. The precipitate was filtered and washed with pentane (2 x 30 mL) and Et_2O (2 x 30 mL) and dried on the frit to afford 3-oxo-2-tosyl-2,3-dihydro-1*H*-1λ^3-benzo[*d*][1,2]iodazol-1-yl acetate (**11**) (7.74 g, 16.8 mmol, 42%) as an off white solid.

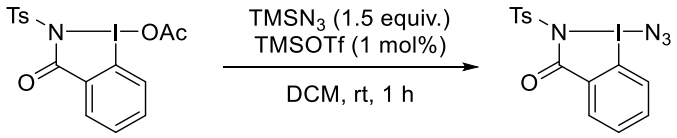
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.7, 1.6 Hz, 1H, Ar*H*), 8.04 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.99 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.87 – 7.81 (m, 1H, Ar*H*), 7.67 – 7.62 (m, 1H, Ar*H*), 7.33 (d, *J* = 8.1 Hz, 2H, Ar*H*), 2.42 (s, 3H, C*H*$_3$), 2.25 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 162.3, 145.2, 136.4, 135.8, 133.0, 132.5, 131.3, 129.8, 129.8, 128.7, 116.8, 21.8, 20.9. Spectroscopic data was consistent with the values reported in the literature.[2]

1-Azido-2-tosyl-1,2-dihydro-3*H*-1λ^3-benzo[*d*][1,2]iodazol-3-one (Ts-ABZ):

Caution: Even though **Ts-ABZ** has a much safer safety profile than the most commonly used azidobenziodoxolone (ABX) care has to be taken when preparing it.[3] The synthesis and filtration were carried out behind a blast shield wearing anti cut gloves (HyFlex 11-541) below regular nitrile gloves. The scale described in the procedure below was the largest scale the reaction was carried on. To synthesize larger amount of the reagent we performed the reaction in multiple batches in parallel and filtered them individually. **Ts-ABZ** batches were stored in

[1] V. Smyrnov, B. Muriel, J. Waser, *Org. Lett.* **2021**, *23*, 5435–5439.
[2] X.-G. Yang, F.-H. Du, J.-J. Li, C. Zhang, *Chem. - Eur. J.* **2022**, *28*, e202200272.
[3] S. Alazet, J. Preindl, R. Simonet-Davin, S. Nicolai, A. Nanchen, T. Meyer, J. Waser, *J. Org. Chem.* **2018**, *83*, 12334–12356.

plastic containers and kept in the fridge at 4 °C. During the course of this project this synthesis was performed 34 times without incident with an average yield of 86%.



11 **Ts-ABZ**

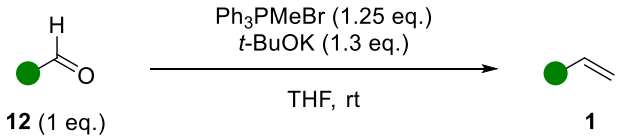
Following a reported procedure,[1] an oven dried flask containing a solution of 3-oxo-2-tosyl-2,3-dihydro-1*H*-1λ^3-benzo[*d*][1,2]iodazol-1-yl acetate (**11**) (919 mg, 2.00 mmol, 1.0 equiv.) in dry DCM (10 mL) was cooled to 0 °C then $TMSN_3$ (0.40 mL, 3.0 mmol, 1.5 equiv.) was added dropwise followed by two drops of TMSOTf (approximation: 4.0 µL, 20 µmol, 1 mol%). The reaction was stirred at rt for 1 h and pentane (30 mL) was added to induce further precipitation (usually precipitation already starts to occur during the reaction). The solid was filtered, washed with pentane (3 x 20 mL) and dried on the frit for 2 min to afford **Ts-ABZ** (778 mg, 1.76 mmol, 88% yield) as an off white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar*H*), 8.07 – 8.00 (m, 3H, Ar*H*), 7.93 – 7.86 (m, 1H, Ar*H*), 7.70 (td, *J* = 7.6, 0.7 Hz, 1H, Ar*H*), 7.33 (d, *J* = 8.1 Hz, 2H, Ar*H*), 2.42 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 145.1, 136.5, 136.0, 133.0, 132.8, 131.8, 129.8, 128.6, 127.3, 116.2, 21.8.

5. Synthesis of Alkenes

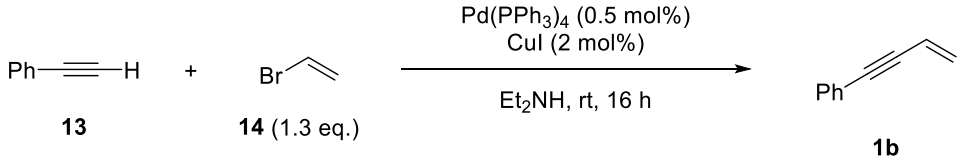
The following alkenes were commercially available: styrene, 4-*tert*-butylstyrene, 4-vinylbiphenyl, 2-methylstyrene, 2,4,6-trimethylstyrene, 4-vinylanisole, 4-vinylphenyl acetate, 4-bromostyrene, 3-chlorostyrene, 4-vinylbenzoate, 4-(trifluoromethyl)styrene, 2-vinylthiophene, *trans*-β-methylstyrene, indene, 1,2-dihydronaphthalene, vinyl butyl ether, 1-phenoxy-4-vinylbenzene.

General procedure A:



Following a reported procedure,[4] an oven dried round-bottom flask charged with methyltriphenylphosphonium bromide (1.79 g, 5.00 mmol, 1.25 equiv.) and potassium *tert*-butoxide (584 mg, 5.20 mmol, 1.30 equiv.) was evacuated and backfilled with N_2. Dry THF (11 mL) was added and the mixture was stirred at rt for 30 min. A solution of aldehyde **12** (4.00 mmol, 1 equiv.) in dry THF (5 mL) was added dropwise over 5 min and the reaction was stirred at rt under N_2 until full conversion was observed by TLC. The reaction was quenched with 35 mL of a sat. sol. of NH_4Cl and the mixture was extracted with 3 x 40 mL of Et_2O or EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography to obtain alkene **1**.

But-3-en-1-yn-1-ylbenzene (1b):



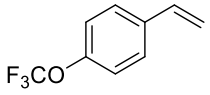
Compound 1b was synthesized following a reported procedure.[5] An oven dried round-bottom flask charged with CuI (19 mg, 0.10 mmol, 2 mol%) and $Pd(PPh_3)_4$ (30 mg, 25 µmol, 0.5 mol%) was evacuated and backfilled with N_2 (3x) then degassed Et_2NH (2.5 mL) was added. The mixture was cooled to 0 °C and phenylacetylene (**13**) (0.55 mL, 5.0 mmol, 1.00 equiv.) and a solution of vinyl bromide (**14**) (6.5 mL, 6.5 mmol, 1 M in THF, 1.30 equiv.) were added. The reaction was stirred at rt for 16 h under N_2 atmosphere. The reaction was quenched with water (~15 mL) then extracted with 3 x 15 mL of a mixture of pentane/Et_2O (1:1). The combined

[4] R. J. Maza, E. Davenport, N. Miralles, J. J. Carbó, E. Fernández, *Org. Lett.* **2019**, *21*, 2251–2255.
[5] Y. Zhang, B. Yu, B. Gao, T. Zhang, H. Huang, *Org. Lett.* **2019**, *21*, 535–539.

organic layers were washed with 20 mL of 1 M aq. HCl, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was loaded on celite and purified by column chromatography (pentane) to afford but-3-en-1-yn-1-ylbenzene (**1b**) (566 mg, 4.42 mmol, 88%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H, Ar*H*), 7.35 – 7.29 (m, 3H, Ar*H*), 6.03 (dd, *J* = 17.5, 11.1 Hz, 1H, *H*C=CH_2), 5.74 (dd, *J* = 17.5, 2.1 Hz, 1H, HC=C*H*$_2$), 5.55 (dd, *J* = 11.1, 2.1 Hz, 1H, HC=C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 128.4, 128.4, 127.0, 123.3, 117.3, 90.1, 88.2. Spectroscopic data was consistent with the values reported in the literature.[5]

1-(Trifluoromethoxy)-4-vinylbenzene (1f):

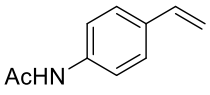


1f

Synthesized following **general procedure A** starting from 4-(trifluoromethoxy)benzaldehyde (0.57 mL, 4.0 mmol). The reaction was carried out for 1 h and extractions were performed with Et_2O. The crude product was loaded on celite and purified by column chromatography (pentane) to afford 1-(trifluoromethoxy)-4-vinylbenzene (**1f**) (441 mg, 2.34 mmol, 59%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H, Ar*H*), 7.17 (d, *J* = 8.1 Hz, 2H, Ar*H*), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H, *H*C=CH_2), 5.73 (dd, *J* = 17.6, 0.5 Hz, 1H, HC=C*H*$_2$), 5.29 (dd, *J* = 10.9, 0.4 Hz, 1H, HC=C*H*$_2$).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8 (m), 136.4, 135.6, 127.6, 121.2, 120.6 (q, *J* = 257.0 Hz), 115.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.9. Spectroscopic data was consistent with the values reported in the literature.[6]

***N*-(4-Vinylphenyl)acetamide (1g):**



1g

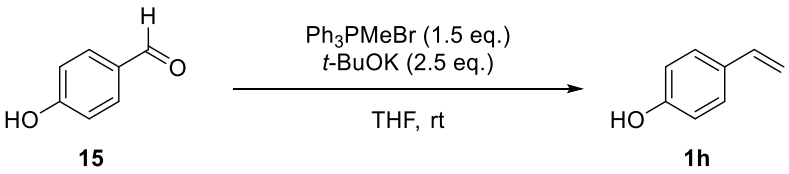
Synthesized following **general procedure A** starting from 4-acetamidobenzaldehyde (653 mg, 4.00 mmol). The reaction was carried out for 3.5 h and extractions were performed with EtOAc. The crude product was purified by column chromatography (pentane/EtOAc, 6:4) to afford *N*-(4-vinylphenyl)acetamide (**1g**) (520 mg, 3.00 mmol, 75%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.39 – 7.30 (m, 3H, Ar*H* + N*H*Ac), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H, *H*C=CH_2), 5.68 (d, *J* = 17.6 Hz, 1H, HC=C*H*$_2$), 5.19 (d, *J* = 10.9 Hz, 1H, HC=C*H*$_2$), 2.17 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 137.6, 136.2,

[6] M. Su, X. Huang, C. Lei, J. Jin, *Org. Lett.* **2022**, *24*, 354–358.

133.9, 127.0, 119.9, 113.2, 24.8. Spectroscopic data was consistent with the values reported in the literature.[7]

4-Vinylphenol (1h):

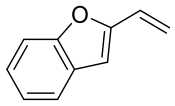


15 **1h**

Compound **1f** was synthesized following a reported procedure.[8] An oven dried round-bottom flask charged with methyltriphenylphosphonium bromide (2.14 g, 6.00 mmol, 1.50 equiv.) and potassium *tert*-butoxide (1.12 g, 10.0 mmol, 2.50 equiv.) was evacuated and backfilled with N_2. Dry THF (11 mL) was added and the mixture was stirred at rt for 30 min. A solution of 4-hydroxybenzaldehyde (**15**) (488 mg, 4.00 mmol, 1.00 equiv.) in dry THF (5 mL) was added dropwise over 5 min and the reaction was stirred at rt for 3.5 h under N_2. The reaction was quenched with 35 mL of a sat. sol. of NH_4Cl and the mixture was extracted with 3 x 40 mL of Et_2O or EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (pentane/EtOAc, 9:1) to afford 4-vinylphenol (**1f**) (388 mg, 3.23 mmol, 81%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H, Ar*H*), 6.82 – 6.77 (m, 2H, Ar*H*), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H, *H*C=CH$_2$), 5.61 (dd, *J* = 17.6, 0.8 Hz, 1H, HC=C*H*$_2$), 5.13 (dd, *J* = 10.9, 0.8 Hz, 1H, HC=C*H*$_2$), 4.86 (s, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 136.3, 130.8, 127.8, 115.5, 111.8. Spectroscopic data was consistent with the values reported in the literature.[7]

2-Vinylbenzofuran (1i):



1i

Synthesized following **general procedure A** starting from 2-benzofurancarboxaldehyde (0.49 mL, 4.0 mmol). The reaction was carried out for 1 h and extractions were performed with Et_2O. The crude product was loaded on celite and purified by column chromatography (pentane) to afford 2-vinylbenzofuran (**1i**) (465 mg, 3.23 mmol, 81%) as a colorless oil.

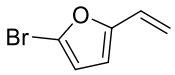
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H, Ar*H*), 7.48 – 7.44 (m, 1H, Ar*H*), 7.31 – 7.24 (m, 1H, Ar*H*), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H, Ar*H*), 6.65 (dd, *J* = 17.5, 11.3 Hz, 1H, *H*C=CH$_2$), 6.60 (s, 1H, OC=C*H*), 5.97 (dd, *J* = 17.5, 0.7 Hz, 1H, HC=C*H*$_2$), 5.39 (dd, *J* = 11.2, 1.0 Hz, 1H,

[7] M.-J. Zhou, L. Zhang, G. Liu, C. Xu, Z. Huang, *J. Am. Chem. Soc.* **2021**, *143*, 16470–16485.
[8] F. C. Demidoff, F. P. de Souza, C. D. Netto, *Synthesis* **2017**, *49*, 5217–5223.

HC=C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 154.9, 129.0, 125.4, 124.8, 122.9, 121.1, 115.9, 111.2, 104.9. Spectroscopic data was consistent with the values reported in the literature.[9]

Note: Product was stored at -20 °C after isolation.

2-Bromo-5-vinylfuran (1j):



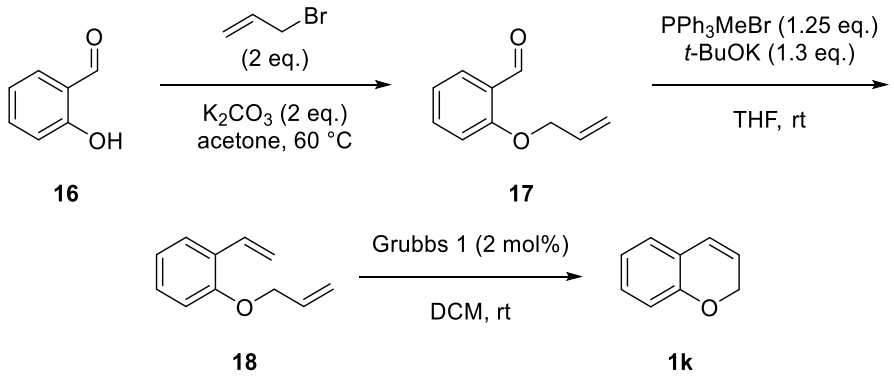
1j

Synthesized following **general procedure A** starting from 5-bromo-2-furaldehyde (700 mg, 4.00 mmol). The reaction was carried out for 1 h and extractions were performed with Et_2O. The crude product was loaded on celite and purified by column chromatography (pentane) to afford 2-bromo-5-vinylfuran (**1j**) (491 mg, 2.84 mmol, 71%) as a light orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (dd, *J* = 17.5, 11.3 Hz, 1H, *H*C=CH$_2$), 6.29 (d, *J* = 3.3 Hz, 1H, Ar*H*), 6.21 (d, *J* = 3.3 Hz, 1H, Ar*H*), 5.65 (dd, *J* = 17.4, 0.7 Hz, 1H, HC=C*H*$_2$), 5.17 (dd, *J* = 11.3, 0.9 Hz, 1H, HC=C*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 124.3, 121.8, 113.1, 113.0, 110.4. Spectroscopic data was consistent with the values reported in the literature.[10]

Note: Product was stored at -20 °C after isolation. It was used the next day in the azido-alkynylation reaction. We observed substantial degradation after 2-3 days of storage.

2*H*-Chromene (1k):



16 **17** **18** **1k**

Following a reported procedure,[4,11] to a round-bottom flask charged with a suspension of K_2CO_3 (4.15 g, 30.0 mmol, 2.0 equiv.) in acetone (45 mL) were added 2-hydroxybenzaldehyde (**16**) (1.6 mL, 15 mmol, 1.0 equiv.) and allyl bromide (2.6 mL, 30 mmol, 2.0 equiv). The reaction was heated to 60 °C for 3 h. The mixture was filtered over a plug of celite, eluted with acetone

[9] H. Seo, A. Liu, T. F. Jamison, *J. Am. Chem. Soc.* **2017**, *139*, 13969–13972.
[10] Y. Yamamoto, Y. Yamada, H. Sajiki, Y. Sawama, *Bull. Chem. Soc. Jpn.* **2020**, *93*, 1419–1423.
[11] X.-S. Liang, R.-D. Li, W. Sun, Z. Liu, X.-C. Wang, *ACS Catal.* **2022**, *12*, 9153–9158.

and concentrated *in vacuo* to afford 2-(allyloxy)benzaldehyde (**17**). The crude product was used in the next step without further purification.

An oven dried round-bottom flask charged with methyltriphenylphosphonium bromide (6.7 g, 19 mmol, 1.25 equiv.) and potassium *tert*-butoxide (2.2 g, 20 mmol, 1.30 equiv.) was evacuated and backfilled with N_2. Dry THF (45 mL) was added and the mixture was stirred at rt for 30 min. A solution of crude aldehyde **17** previously prepared in dry THF (15 mL) was added dropwise over 5 min and the reaction was stirred at rt under N_2 for 1 h. The reaction was quenched with 60 mL of a sat. sol. of NH_4Cl and the mixture was extracted with 3 x 60 mL of EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was loaded on celite and purified by column chromatography (pentane) to afford 1-(allyloxy)-2-vinylbenzene (**18**) (1.78 g, 11.1 mmol, 74% over 2 steps) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.6, 1.7 Hz, 1H, Ar*H*), 7.21 (ddd, *J* = 8.3, 7.5, 1.7 Hz, 1H, Ar*H*), 7.10 (dd, *J* = 17.8, 11.2 Hz, 1H, ArC*H*=CH_2), 6.97 – 6.91 (m, 1H, Ar*H*), 6.87 (dd, *J* = 8.3, 0.8 Hz, 1H, Ar*H*), 6.14 – 6.03 (m, 1H, CH_2C*H*=CH_2), 5.75 (dd, *J* = 17.8, 1.5 Hz, 1H, ArCH=C*H*$_2$), 5.43 (dq, *J* = 17.3, 1.7 Hz, 1H, CH_2CH=C*H*$_2$), 5.32 – 5.23 (m, 2H, CH_2CH=C*H*$_2$ + ArCH=C*H*$_2$), 4.57 (dt, *J* = 5.1, 1.6 Hz, 2H, OC*H*$_2$CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 133.5, 131.8, 128.9, 127.2, 126.7, 121.0, 117.5, 114.5, 112.5, 69.3. Spectroscopic data was consistent with the values reported in the literature.[12]

Following a reported procedure,[11] to an oven-dried round-bottom flask containing a solution of 1-(allyloxy)-2-vinylbenzene (**18**) (320 mg, 2.00 mmol, 1.0 equiv.) in dry DCM (10 mL) was added Grubbs 1 catalyst (33 mg, 40 µmol, 0.02 equiv.). The reaction was stirred at rt for 2 h. The crude mixture was concentrated *in vacuo*, loaded on celite and purified by column chromatography (pentane/Et_2O, 100:0 to 97:3) to afford 2*H*-chromene (**1k**) (180 mg, 1.36 mmol, 68%) as a colorless oil.

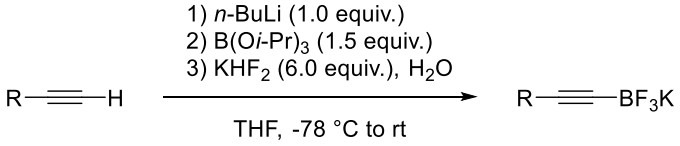
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (td, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 6.96 (dd, *J* = 7.4, 1.7 Hz, 1H, Ar*H*), 6.86 (td, *J* = 7.4, 1.1 Hz, 1H, Ar*H*), 6.77 (d, *J* = 8.1 Hz, 1H, Ar*H*), 6.42 (dt, *J* = 9.9, 1.6 Hz, 1H, ArC*H*=CH), 5.77 (dt, *J* = 9.8, 3.6 Hz, 1H,CH=C*H*CH_2), 4.82 (dd, *J* = 3.6, 1.9 Hz, 2H, OC*H*$_2$CH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 129.3, 126.7, 124.7, 122.5, 122.1, 121.5, 115.9, 65.7. Spectroscopic data was consistent with the values reported in the literature.[12]

[12] F. Yang, K. Rauch, K. Kettelhoit, L. Ackermann, *Angew. Chem. Int. Ed.* **2014**, *53*, 11285–11288.

6. Synthesis of Potassium Trifluoroborate Salts

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 two carbons of the alkyne (in alkynyl-BF_3K) are too broad to be properly visible.[13] Therefore, they are not listed in the characterization data.

General procedure B:

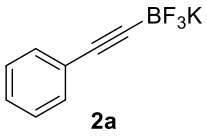


Following a reported procedure,[14,15] an oven-dried round-bottom flask (PFA), charged with alkyne (1.0 equiv.) if solid, was evacuated and backfilled with N_2 (3x). Then, alkyne (if liquid) and dry THF (0.3 M) were added. The mixture was cooled to -78 °C and a solution of *n*-BuLi (2.5 M, 1.0 equiv.) 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 toluene (3x). 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 (KHF_2) in the reaction flask. Acetone was once again added and the process (heating for 15 min then collection of the liquid) was repeated 2 more times. The combined acetone filtrates were concentrated *in vacuo* to approximately 1/3 of the initial volume. Et_2O (~60 mL) was added causing a white solid to precipitate. The mixture was cooled to 0 °C for 10 min then filtered. The solid obtained was washed with Et_2O and dried in vacuo to afford the desired potassium alkynyl-trifluoroborate.

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

Potassium trifluoro(phenylethynyl)borate (2a):

[13] R. A. Oliveira, R. O. Silva, G. A. Molander, P. H. Menezes, *Magn. Reson. Chem.* **2009**, *47*, 873–878.
[14] D. A. Mundal, K. E. Lutz, R. J. Thomson, *J. Am. Chem. Soc.* **2012**, *134*, 5782–5785.
[15] J. Borrel, J. Waser, *Org. Lett.* **2022**, *24*, 142–146.

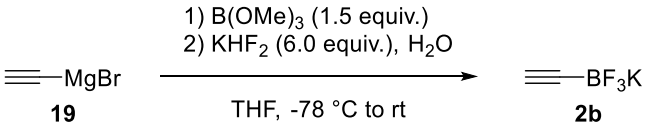


2a

Synthesized following **general procedure B** 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.[16]

Potassium ethynyltrifluoroborate (2b):

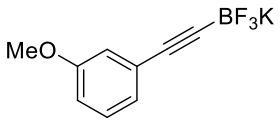


Compound **2b** was synthesized following a reported procedure.[17] An oven-dried round-bottom flask (PFA) was evacuated and backfilled with N_2 (3x). Then, a solution of ethynylmagnesium bromide (**19**) (30.0 mL, 15.0 mmol, 0.5 M, 1.0 equiv.) in THF and dry THF (30 mL) were added. The solution was 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. Acetone was once again added and the process (heating for 15 min then collection of the liquid) was repeated 2 more times. The combined acetone filtrates were concentrated *in vacuo* to approximately 1/3 of the initial volume. Et_2O (~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 (**2b**) (1.17 g, 8.86 mmol, 59%) as a white solid.

^{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. Spectroscopic data was consistent with the values reported in the literature.[15]

[16] G. A. Molander, B. W. Katona, F. Machrouhi, *J. Org. Chem.* **2002**, *67*, 8416–8423.
[17] P. B. Brady, E. M. Carreira, *Org. Lett.* **2015**, *17*, 3350–3353.

Potassium trifluoro((3-methoxyphenyl)ethynyl)borate (2c):

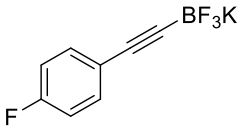


2c

Synthesized following **general procedure B** starting from 1-ethynyl-3-methoxybenzene (1.0 g, 0.97 mL, 7.5 mmol). Potassium trifluoro((3-methoxyphenyl)ethynyl)borate (**2c**) (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, OCH_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.[18]

Potassium trifluoro((4-fluorophenyl)ethynyl)borate (2d):

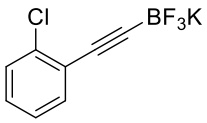


2d

Synthesized following **general procedure B** starting from 1-ethynyl-4-fluorobenzene (0.90 g, 0.86 mL, 7.5 mmol). Potassium trifluoro((4-fluorophenyl)ethynyl)borate (**2d**) (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, Ar*H*), 7.14 – 7.07 (m, 2H, Ar*H*). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.38 – 7.30 (m, 2H, Ar*H*), 7.06 – 6.98 (m, 2H). ^{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. Spectroscopic data was consistent with the values reported in the literature.[14]

Potassium ((2-chlorophenyl)ethynyl)trifluoroborate (2e):



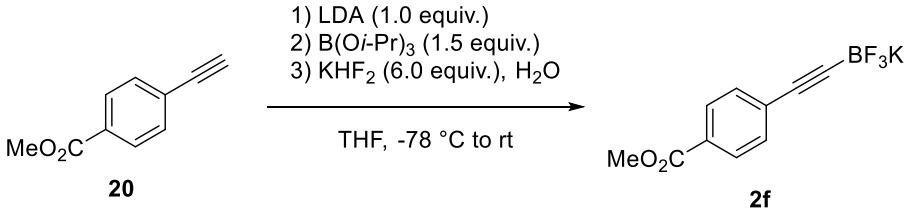
2e

[18] 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.

Synthesized following **general procedure B** starting from 1-chloro-2-ethynylbenzene (1.0 g, 0.91 mL, 7.5 mmol). Potassium ((2-chlorophenyl)ethynyl)trifluoroborate (**2e**) (712 mg, 2.94 mmol, 39%) was obtained as a white solid.

Mp (Dec.): 272 °C; ^{1}H NMR (400 MHz, Acetone) δ 7.45 – 7.39 (m, 1H, Ar*H*), 7.39 – 7.33 (m, 1H, Ar*H*), 7.23 – 7.16 (m, 2H, Ar*H*). ^{13}C NMR (101 MHz, Acetone) δ 135.6, 134.4, 129.7, 128.4, 127.3, 127.0. ^{19}F NMR (376 MHz, Acetone) δ -135.1. ^{11}B NMR (128 MHz, Acetone) δ -1.3 (q, *J* = 35.3 Hz). HRMS (ESI/QTOF) m/z: $[M-K]^-$ Calcd for $C_8H_4BClF_3^-$ 203.0052; Found 203.0053.

Potassium trifluoro((4-(methoxycarbonyl)phenyl)ethynyl)borate (2f):



20 **2f**

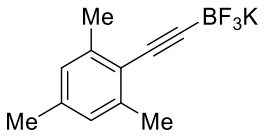
Compound **2f** was synthesized following a reported procedure.[15,19] An oven-dried round-bottom flask (PFA) was evacuated and backfilled with N_2 (3x). Then, freshly distilled diisopropylamine (1.05 mL, 7.50 mmol, 1.0 equiv.) and dry THF (15 mL) were added. The mixture was cooled to 0 °C and a solution 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 (**20**) (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. Acetone was once again added and the process (heating for 15 min then collection of the liquid) was repeated 2 more times. The combined acetone filtrates were concentrated *in vacuo* to approximately 1/3 of the initial volume. Et_2O (~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 (**2f**) (0.80 g, 3.0 mmol, 40%) as a beige solid.

^{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

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

NMR (376 MHz, acetone-d_6) δ -135.4. Spectroscopic data was consistent with the values reported in the literature.[15]

Potassium trifluoro(mesitylethynyl)borate (2g):

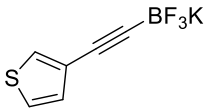


2g

Synthesized following **general procedure B** starting from 2-ethynyl-1,3,5-trimethylbenzene (0.950 g, 1.03 mL, 6.3 mmol). Potassium trifluoro(mesitylethynyl)borate (**2g**) (1.23 g, 4.94 mmol, 78%) was obtained as a white solid.

^{1}H NMR (400 MHz, acetone-d_6) δ 6.79 (s, 2H, Ar*H*), 2.34 (s, 6H, C*H*$_3$), 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. Spectroscopic data was consistent with the values reported in the literature.[15]

Potassium trifluoro(thiophen-3-ylethynyl)borate (2h):

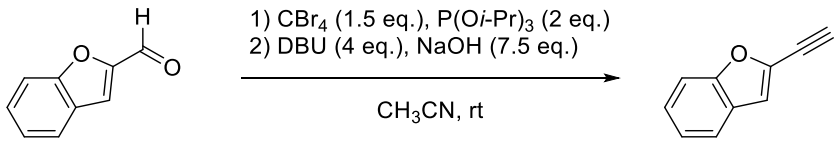


2h

Synthesized following **general procedure B** starting from 3-ethynylthiophene (0.85 g, 0.77 mL, 7.5 mmol). Potassium trifluoro(thiophen-3-ylethynyl)borate (**2h**) (1.29 g, 6.01 mmol, 80%) was obtained as a light brown solid.

Mp (Dec.): 248 °C; ^{1}H NMR (400 MHz, Acetone) δ 7.33 (dd, *J* = 4.9, 3.0 Hz, 1H, Ar*H*), 7.29 (dd, *J* = 3.0, 1.2 Hz, 1H, Ar*H*), 7.00 (dd, *J* = 4.9, 1.2 Hz, 1H, Ar*H*). ^{13}C NMR (101 MHz, Acetone) δ 131.0, 126.9, 126.4, 125.5. ^{19}F NMR (376 MHz, Acetone) δ -135.0. ^{11}B NMR (128 MHz, Acetone) δ -1.3 (q, *J* = 36.4 Hz). HRMS (ESI/QTOF) m/z: $[M-K]^-$ Calcd for $C_6H_3BF_3S^-$ 175.0006; Found 175.0012.

2-Ethynylbenzofuran (19):

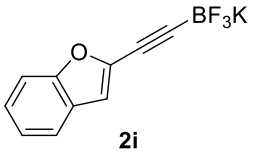


21 **22**

Compound **22** was synthesized following a reported procedure.[20] An oven-dried round-bottom flask charged with CBr_4 (5.0 g, 15 mmol, 1.5 equiv.) was evacuated and backfilled with N_2 (3x) then dry CH_3CN (20 mL) and 2-benzofurancarboxaldehyde (**21**) (1.2 mL, 10 mmol, 1.0 equiv.) were added. The mixture was cooled to 0 °C and triisopropyl phosphite (4.9 mL, 20 mmol, 2.0 equiv) was added dropwise over 5 min then DBU (6.0 mL, 40 mmol, 4.0 equiv) was added dropwise over 15 minutes. The mixture was stirred at 0 °C for 10 min then at rt for 20 min. Grinded NaOH (3.0 g, 75 mmol, 7.5 equiv) was added and the reaction was stirred at rt for 4 h under N_2 atmosphere. Water (30 mL) and brine (50 mL) were added and the mixture was extracted with 3 x 70 mL of EtOAc. The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was loaded on celite and purified by column chromatography (pentane) to afford 2-ethynylbenzofuran (**22**) (516 mg, 3.63 mmol, 36%) as an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 1H, Ar*H*), 7.49 – 7.44 (m, 1H, Ar*H*), 7.36 (td, *J* = 7.8, 1.3 Hz, 1H, Ar*H*), 7.30 – 7.21 (m, 1H, Ar*H*), 7.01 (d, *J* = 0.5 Hz, 1H, OC=C*H*), 3.50 (s, 1H, C≡C*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 137.8, 127.3, 126.1, 123.5, 121.5, 112.8, 111.5, 83.5, 74.2. Spectroscopic data was consistent with the values reported in the literature.[20]

Potassium (benzofuran-2-ylethynyl)trifluoroborate (2i):

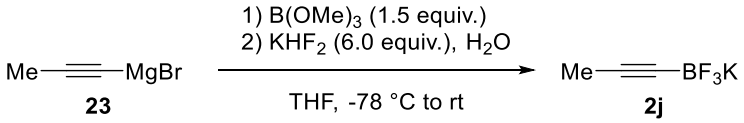


2i

Synthesized following **general procedure B** starting from 2-ethynylbenzofuran (**22**) (500 mg, 3.52 mmol). After recrystallization (acetone/Et_2O) potassium (benzofuran-2-ylethynyl)trifluoroborate (**2i**) (568 mg, 2.29 mmol, 65%) was obtained as a white solid.

^{1}H NMR (400 MHz, DMSO) δ 7.59 – 7.54 (m, 1H, Ar*H*), 7.51 – 7.45 (m, 1H, Ar*H*), 7.30 (dd, *J* = 6.0, 1.4 Hz, 1H, Ar*H*), 7.22 (td, *J* = 7.6, 1.0 Hz, 1H, Ar*H*), 6.92 (s, 1H, OC=C*H*). ^{13}C NMR (101 MHz, DMSO) δ 153.5, 140.4, 127.7, 124.8, 123.1, 120.9, 110.7, 108.6. Spectroscopic data was consistent with the values reported in the literature.[21]

Potassium trifluoro(prop-1-yn-1-yl)borate (2j):



23 **2j**

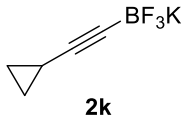
Compound **2j** was synthesized following a reported procedure.[15] An oven-dried round-bottom flask (PFA) was evacuated and backfilled with N_2 (3x). Then, a solution of 1-

[20] Y. Thummala, G. V. Karunakar, V. R. Doddi, *Adv. Synth. Catal.* **2019**, *361*, 611–616.
[21] J.-F. Wang, X. Meng, C.-H. Zhang, C.-M. Yu, B. Mao, *Org. Lett.* **2020**, *22*, 7427–7432.

propynylmagnesium bromide (**23**) (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. Acetone was once again added and the process (heating for 15 min then collection of the liquid) was repeated 2 more times. The combined acetone filtrates were concentrated *in vacuo* to approximately 1/3 of the initial volume. Et_2O (~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 (**2j**) (0.95 g, 6.5 mmol, 87%) as a white solid.

^{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. Spectroscopic data was consistent with the values reported in the literature.[15]

Potassium (cyclopropylethynyl)trifluoroborate (2k):

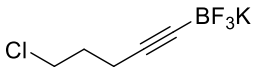


2k

Synthesized following **general procedure B** starting from ethynylcyclopropane (0.50 g, 0.64 mL, 7.5 mmol). Potassium (cyclopropylethynyl)trifluoroborate (**2k**) (0.86 g, 5.0 mmol, 67%) was obtained as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.12 – 1.01 (m, 1H, C*H*), 0.61 – 0.54 (m, 2H, C*H*$_2$), 0.42 – 0.36 (m, 2H, C*H*$_2$). ^{13}C NMR (101 MHz, DMSO-d_6) δ 7.4, 0.1. ^{19}F NMR (377 MHz, DMSO-d_6) δ -131.1. Spectroscopic data was consistent with the values reported in the literature.[15]

Potassium (5-chloropent-1-yn-1-yl)trifluoroborate (2l):



2l

Synthesized following **general procedure B** starting from 5-chloropent-1-yne (0.77 g, 0.80 mL, 7.5 mmol). Potassium (5-chloropent-1-yn-1-yl)trifluoroborate (**2l**) (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, C*H*$_2$Cl), 2.24 – 2.17 (m, 2H, C≡C-C*H*$_2$), 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,

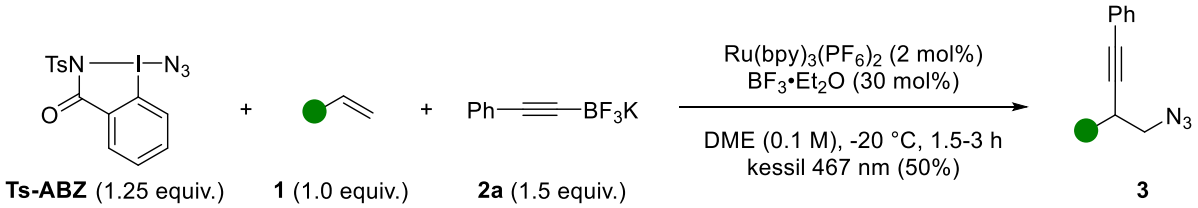
17.3. ^{19}F NMR (376 MHz, acetone-d_6) δ -134.6. Spectroscopic data was consistent with the values reported in the literature.[16]

7. Azido-Alkynylation

General Note: We observed that the homopropargylic azides synthetized in this work tend to slowly decompose even when stored in the fridge at 4 °C

7.1 Scope of Alkenes

General procedure C:

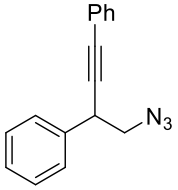


Ts-ABZ (1.25 equiv.) **1** (1.0 equiv.) **2a** (1.5 equiv.) **3**

An oven-dried test tube charged with $Ru(bpy)_3(PF_6)_2$ (5.2 mg, 6.0 µmol, 0.02 equiv.), **Ts-ABZ** (166 mg, 0.375 mmol, 1.25 equiv.), potassium trifluoro(phenylethynyl)borate (**2a**) (94 mg, 0.45 mmol, 1.50 equiv.) and alkene (**1**) (if solid, 0.30 mmol, 1.00 equiv.) was evacuated and backfilled with N_2 (3x). Dry degassed DME (2.7 mL) and alkene (**1**) (if liquid, 0.30 mmol, 1.00 equiv.) were added and the mixture was cooled to -20 °C. Then, a stock solution of BF_3•Et_2O (11 µL, 90 µmol, 0.30 equiv.) in dry degassed DME (0.34 mL) was added and the reaction was stirred under blue LEDs irradiation (1 x Kessil 467 nm, 50% intensity 22 W) at -20 °C until full conversion was observed (1.5-3 h). The reaction mixture was filtered through a short plug of silica and eluted with DCM or EtOAc then concentrated *in vacuo*. The crude product was purified by column chromatography to afford **3**.

Note: Commercially available liquid alkenes were eluted through a short plug of basic Al_2O_3 before use. DME was sparged with argon for 0.5 h before use. Cooling was performed using a Dewar filled with a mixture of ice and salt. We did not observe significant rise in temperature after 1.5 h (which is enough in most cases to reach full conversion). In the case of longer reactions, the cold bath was replaced with a new one after 1.5 h. For further details on the photochemistry set-up see Figure S1.

(4-Azidobut-1-yne-1,3-diyl)dibenzene (3a):

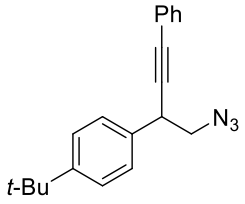


3a

Synthesized following **general procedure C** starting from styrene (**1a**) (35 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 85:15) to afford (4-azidobut-1-yne-1,3-diyl)dibenzene (**3a**) (55 mg, 0.22 mmol, 73%) as a yellow oil.

R_f (pentane/toluene, 7:3): 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 4H, Ar*H*), 7.42 – 7.36 (m, 2H, Ar*H*), 7.35 – 7.30 (m, 4H, Ar*H*), 4.13 (t, *J* = 6.8 Hz, 1H, C*H*C≡C), 3.63 (dd, *J* = 12.0, 7.6 Hz, 1H, CH_2N$_3$), 3.53 (dd, *J* = 12.0, 6.2 Hz, 1H, CH_2N$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 131.7, 128.8, 128.3, 128.3, 127.9, 127.8, 123.0, 87.9, 84.9, 57.3, 39.6. HRMS (APPI/LTQ-Orbitrap) m/z: $[M-N_2+H]^+$ Calcd for $C_{16}H_{14}N^+$ 220.1121; Found 220.1120.

1-(1-Azido-4-phenylbut-3-yn-2-yl)-4-(tert-butyl)benzene (3b):

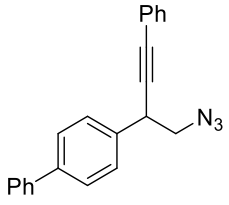


3b

Synthesized following **general procedure C** starting from 4-*tert*-butylstyrene (55 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 95:5 to 90:10) to afford 1-(1-azido-4-phenylbut-3-yn-2-yl)-4-(tert-butyl)benzene (**3b**) (71 mg, 0.24 mmol, 78%) as a colorless oil.

R_f (pentane/toluene, 85 :15) : 0.27; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H, Ar*H*), 7.45 – 7.39 (m, 4H, Ar*H*), 7.36 – 7.30 (m, 3H, Ar*H*), 4.12 (dd, *J* = 7.7, 6.1 Hz, 1H, C*H*C≡C), 3.63 (dd, *J* = 12.0, 7.8 Hz, 1H, CH_2N$_3$), 3.53 (dd, *J* = 12.0, 6.1 Hz, 1H, CH_2N$_3$), 1.35 (s, 9H, *t*-Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 135.2, 131.8, 128.4, 128.3, 127.6, 125.9, 123.2, 88.3, 84.8, 57.4, 39.3, 34.7, 31.5. HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}N_3^+$ 304.1808; Found 304.1804.

4-(1-Azido-4-phenylbut-3-yn-2-yl)-1,1'-biphenyl (3c):

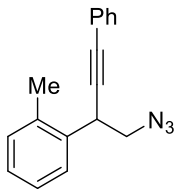


3c

Synthesized following **general procedure C** starting from 4-vinylbiphenyl (54 mg, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 90:10 to 80:20) to afford 4-(1-azido-4-phenylbut-3-yn-2-yl)-1,1'-biphenyl (**3c**) (74 mg, 0.23 mmol, 76%) as a yellow oil.

R_f (pentane/toluene, 7:3): 0.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 4H, Ar*H*), 7.58 – 7.51 (m, 4H, Ar*H*), 7.49 – 7.44 (m, 2H, Ar*H*), 7.41 – 7.32 (m, 4H, Ar*H*), 4.19 (t, *J* = 6.6 Hz, 1H, C*H*C≡C), 3.69 (dd, *J* = 12.0, 7.6 Hz, 1H, CH_2N_3), 3.59 (dd, *J* = 12.0, 6.2 Hz, 1H, CH_2N_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ[22] 140.9, 140.7, 137.3, 131.9, 128.9, 128.4, 128.4, 127.7, 127.5, 127.2, 123.1, 88.0, 85.1, 57.3, 39.4. HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}N_3^+$ 324.1495; Found 324.1497.

1-(1-Azido-4-phenylbut-3-yn-2-yl)-2-methylbenzene (3d):

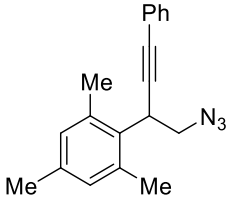


3d

Synthesized following **general procedure C** starting from 2-methylstyrene (39 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 90:10 to 85:15) to afford 1-(1-azido-4-phenylbut-3-yn-2-yl)-2-methylbenzene (**3d**) (62 mg, 0.24 mmol, 79%) as a yellow oil.

R_f (pentane/toluene, 7:3): 0.57; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 1H, Ar*H*), 7.51 – 7.45 (m, 2H, Ar*H*), 7.34 – 7.29 (m, 3H, Ar*H*), 7.29 – 7.18 (m, 3H, Ar*H*), 4.35 (dd, *J* = 8.1, 5.8 Hz, 1H, C*H*C≡C), 3.60 (dd, *J* = 12.0, 8.2 Hz, 1H, CH_2N_3), 3.49 (dd, *J* = 12.0, 5.8 Hz, 1H, CH_2N_3), 2.42 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 135.4, 131.8, 130.9, 128.4, 128.3, 128.2, 127.8, 126.8, 123.2, 88.7, 84.3, 56.2, 36.2, 19.4. HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M-N_2+H]^+$ Calcd for $C_{17}H_{16}N^+$ 234.1277; Found 234.1277.

2-(1-Azido-4-phenylbut-3-yn-2-yl)-1,3,5-trimethylbenzene (3e):



3e

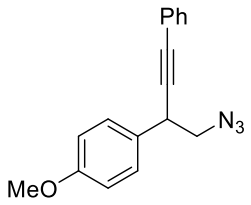
Synthesized following **general procedure C** starting from 2,4,6-trimethylstyrene (48 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 97.5:2.5) to

[22] One aromatic carbon was not resolved.

afford 2-(1-azido-4-phenylbut-3-yn-2-yl)-1,3,5-trimethylbenzene (**3e**) (68 mg, 0.24 mmol, 78%) as a yellow oil.

R_f (pentane/Et_2O, 95:5): 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H, Ar*H*), 7.35 – 7.30 (m, 3H, Ar*H*), 6.91 (s, 2H, Ar*H*), 4.61 (dd, *J* = 8.6, 7.0 Hz, 1H, C*H*C≡C), 3.83 (dd, *J* = 12.0, 8.8 Hz, 1H, C*H*$_2$$N_3$), 3.49 (dd, *J* = 12.0, 6.9 Hz, 1H, C*H*$_2$$N_3$), 2.54 (s, 6H, C*H*$_3$), 2.30 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 136.8, 131.6, 131.0, 130.4, 128.4, 128.1, 123.4, 88.5, 84.1, 53.9, 34.1, 21.0, 20.9. HRMS (APPI/LTQ-Orbitrap) m/z: $[M-N_2+H]^+$ Calcd for $C_{19}H_{20}N^+$ 262.1590; Found 262.1590.

1-(1-Azido-4-phenylbut-3-yn-2-yl)-4-methoxybenzene (3f):

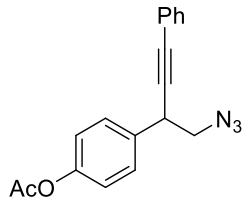


3f

Synthesized following **general procedure C** starting from 4-vinylanisole (40 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 97.5:2.5 to 95:5) to afford 1-(1-azido-4-phenylbut-3-yn-2-yl)-4-methoxybenzene (**3f**) (70 mg, 0.25 mmol, 84%) as a yellow oil.

R_f (pentane/Et_2O, 9:1): 0.35; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H, Ar*H*), 7.41 – 7.36 (m, 2H, Ar*H*), 7.34 – 7.30 (m, 3H, Ar*H*), 6.95 – 6.89 (m, 2H, Ar*H*), 4.10 – 4.05 (m, 1H, C*H*C≡C), 3.82 (s, 3H, OC*H*$_3$), 3.60 (dd, *J* = 12.0, 7.6 Hz, 1H, C*H*$_2$$N_3$), 3.50 (dd, *J* = 12.0, 6.3 Hz, 1H, C*H*$_2$$N_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 131.8, 130.3, 129.0, 128.4, 128.4, 123.1, 114.3, 88.4, 84.8, 57.5, 55.5, 38.9. HRMS (APPI/LTQ-Orbitrap) m/z: $[M-N_2+H]^+$ Calcd for $C_{17}H_{16}NO^+$ 250.1226; Found 250.1226.

4-(1-Azido-4-phenylbut-3-yn-2-yl)phenyl acetate (3g):

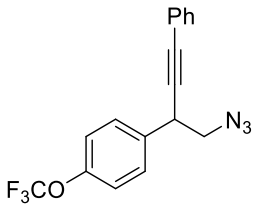


3g

Synthesized following **general procedure C** starting from 4-vinylphenyl acetate (**1e**) (46 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 90:10 to 85:15) to afford 4-(1-azido-4-phenylbut-3-yn-2-yl)phenyl acetate (**3g**) (71 mg, 0.23 mmol, 78%) as a yellow oil.

R_f (pentane/Et_2O, 8:2): 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 4H, Ar*H*), 7.36 – 7.30 (m, 3H, Ar*H*), 7.14 – 7.08 (m, 2H, Ar*H*), 4.13 (dd, *J* = 7.5, 6.2 Hz, 1H, C*H*C≡C), 3.62 (dd, *J* = 12.0, 7.6 Hz, 1H, CH_2N_3), 3.52 (dd, *J* = 12.0, 6.1 Hz, 1H, CH_2N_3), 2.31 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 150.2, 135.8, 131.8, 129.0, 128.5, 128.4, 122.9, 122.0, 87.7, 85.2, 57.3, 39.2, 21.2. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{15}N_3NaO_2^+$ 328.1056; Found 328.1056.

1-(1-Azido-4-phenylbut-3-yn-2-yl)-4-(trifluoromethoxy)benzene (3h):

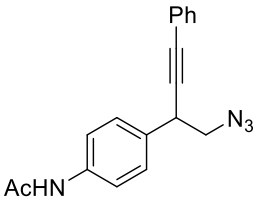


3h

Synthesized following **general procedure C** starting from a solution of 1-(trifluoromethoxy)-4-vinylbenzene (**1f**) (56 mg, 0.30 mmol, 1.00 equiv.) in dry degassed DME (0.5 mL). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 9:1) to afford 1-(1-azido-4-phenylbut-3-yn-2-yl)-4-(trifluoromethoxy)benzene (**3h**) (59 mg, 0.18 mmol, 59%) as a colorless oil.

R_f (pentane/toluene, 85:15): 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 4H, Ar*H*), 7.35 – 7.31 (m, 3H, Ar*H*), 7.24 (d, *J* = 8.0 Hz, 2H, Ar*H*), 4.14 (t, *J* = 6.8 Hz, 1H, C*H*C≡C), 3.63 (dd, *J* = 12.0, 7.2 Hz, 1H, CH_2N_3), 3.53 (dd, *J* = 12.0, 6.3 Hz, 1H, CH_2N_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9 (q, *J* = 1.8 Hz), 137.0, 131.8, 129.4, 128.6, 128.5, 122.8, 121.4, 120.6 (q, *J* = 257.2 Hz), 87.3, 85.5, 57.3, 39.1. ^{19}F NMR (376 MHz, CDCl3) δ -57.9. HRMS (APPI/LTQ-Orbitrap) m/z: $[M-N_2+H]^+$ Calcd for $C_{17}H_{13}F_3NO^+$ 304.0944; Found 304.0946

***N*-(4-(1-Azido-4-phenylbut-3-yn-2-yl)phenyl)acetamide (3i):**

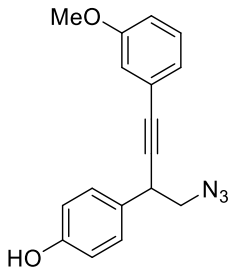


3i

Synthesized following **general procedure C** starting from *N*-(4-vinylphenyl)acetamide (**1g**) (52 mg, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, EtOAc was used for the silica plug. The crude product was dissolved in DCM (15 mL), the solution was washed with 3 x 10 mL of a sat. sol. of $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (pentane/EtOAc, 6:4 to 5:5) to afford *N*-(4-(1-azido-4-phenylbut-3-yn-2-yl)phenyl)acetamide (**3i**) (62 mg, 0.20 mmol, 68%) as a yellow solid.

R_f (pentane/EtOAc, 4:6): 0.45; Mp (Dec.): 139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 4H, Ar*H*), 7.41 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.35 – 7.29 (m, 3H, Ar*H*), 7.22 (bs, 1H, N*H*Ac), 4.09 (t, *J* = 6.8 Hz, 1H, C*H*C≡C), 3.60 (dd, *J* = 12.0, 7.5 Hz, 1H, C*H*$_2$N$_3$), 3.50 (dd, *J* = 12.0, 6.2 Hz, 1H, C*H*$_2$N$_3$), 2.18 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ[23] 168.4, 137.5, 134.1, 131.8, 128.6, 128.4, 123.0, 120.3, 87.9, 85.1, 57.4, 39.2, 24.8. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{16}N_4NaO^+$ 327.1216; Found 327.1212.

4-(1-Azido-4-(3-methoxyphenyl)but-3-yn-2-yl)phenol (3j):



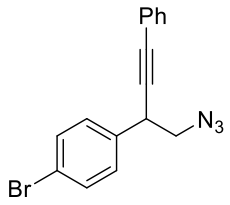
3j

An oven-dried test tube charged with $Ru(bpy)_3(PF_6)_2$ (5.2 mg, 6.0 µmol, 2 mol%), **Ts-ABZ** (166 mg, 0.375 mmol, 1.25 equiv.), potassium trifluoro((3-methoxyphenyl)ethynyl)borate (**2c**) (107 mg, 0.450 mmol, 1.50 equiv.) and 4-vinylphenol (**1h**) (36 mg, 0.30 mmol, 1.00 equiv.) was evacuated and backfilled with N_2 (3x). Dry degassed DME (2.7 mL) was added and the mixture was cooled to -20 °C. Then, a stock solution of BF_3•Et_2O (11.1 µL, 90.0 µmol, 0.30 equiv.) in dry degassed DME (0.34 mL) was added and the reaction was stirred under blue LEDs irradiation (1 x Kessil 467 nm 50% intensity, 22W) at -20 °C for 1.5 h. The reaction mixture was filtered through a short plug of silica and eluted with DCM then concentrated *in vacuo*. The crude product was purified by column chromatography (pentane/EtOAc, 85:15 to 80:20) to afford 4-(1-azido-4-(3-methoxyphenyl)but-3-yn-2-yl)phenol (**3j**) (41 mg, 0.14 mmol, 47%) as an orange oil.

R_f (pentane/EtOAc, 75:25): 0.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H, Ar*H*), 7.25 – 7.19 (m, 1H Ar*H*), 7.11 – 7.06 (m, 1H Ar*H*), 7.02 (dd, *J* = 2.4, 1.4 Hz, 1H Ar*H*), 6.89 (ddd, *J* = 8.4, 2.6, 0.8 Hz, 1H Ar*H*), 6.87 – 6.81 (m, 2H Ar*H*), 5.19 (bs, 1H, O*H*), 4.06 (t, *J* = 6.9 Hz, 1H, C*H*C≡C), 3.80 (s, 3H, OC*H*$_3$), 3.59 (dd, *J* = 12.0, 7.5 Hz, 1H, C*H*$_2$N$_3$), 3.49 (dd, *J* = 12.0, 6.2 Hz, 1H, C*H*$_2$N$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 155.2, 130.4, 129.5, 129.2, 124.4, 124.1, 116.6, 115.8, 115.0, 88.2, 84.8, 57.5, 55.4, 38.9. HRMS (APPI/LTQ-Orbitrap) m/z: $[M-N_2+H]^+$ Calcd for $C_{17}H_{16}NO_2^+$ 266.1176; Found 266.1176.

1-(1-Azido-4-phenylbut-3-yn-2-yl)-4-bromobenzene (3k):

[23] One aromatic carbon was not resolved.

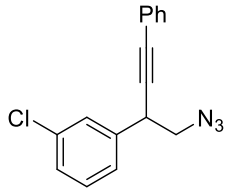


3k

Synthesized following **general procedure C** starting from 4-bromostyrene (41 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 90:10 to 85:15) to afford 1-(1-azido-4-phenylbut-3-yn-2-yl)-4-bromobenzene (**3k**) (69 mg, 0.21 mmol, 71%) as a yellow oil.

R_f (pentane/toluene, 7:3): 0.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 4H, Ar*H*), 7.38 – 7.30 (m, 5H, Ar*H*), 4.08 (t, *J* = 6.8 Hz, 1H, C*H*C≡C), 3.62 (dd, *J* = 12.0, 7.3 Hz, 1H, CH_2N_3), 3.52 (dd, *J* = 12.0, 6.3 Hz, 1H, CH_2N_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 132.0, 131.8, 129.7, 128.6, 128.5, 122.8, 121.8, 87.3, 85.4, 57.1, 39.2. HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}BrN_3^+$ 326.0287; Found 326.0286.

1-(1-Azido-4-phenylbut-3-yn-2-yl)-3-chlorobenzene (3l):

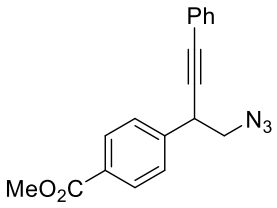


3l

Synthesized following **general procedure C** starting from 3-chlorostyrene (38 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 90:10 to 85:15) to afford 1-(1-azido-4-phenylbut-3-yn-2-yl)-3-chlorobenzene (**3l**) (45 mg, 0.16 mmol, 53%) as a yellow oil.

R_f (pentane/toluene, 8:2): 0.24; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 3H, Ar*H*), 7.37 – 7.28 (m, 6H, Ar*H*), 4.10 (t, *J* = 6.8 Hz, 1H, C*H*C≡C), 3.63 (dd, *J* = 12.0, 7.3 Hz, 1H, CH_2N_3), 3.54 (dd, *J* = 12.0, 6.3 Hz, 1H, CH_2N_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 134.8, 131.9, 130.2, 128.6, 128.5, 128.2, 128.1, 126.2, 122.8, 87.1, 85.5, 57.2, 39.4. HRMS (APPI/LTQ-Orbitrap) m/z: $[M-N_2+H]^+$ Calcd for $C_{16}H_{13}ClN^+$ 254.0731; Found 254.0737.

Methyl 4-(1-azido-4-phenylbut-3-yn-2-yl)benzoate (3m):

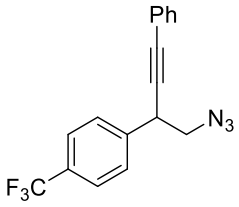


3m

Synthesized following **general procedure C** starting from methyl 4-vinylbenzoate (49 mg, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 3 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 9:1) to afford methyl 4-(1-azido-4-phenylbut-3-yn-2-yl)benzoate (**3m**) (45 mg, 0.18 mmol, 49%) as a yellow oil.

R_f (pentane/Et_2O, 8:2): 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H, Ar*H*), 7.57 – 7.52 (m, 2H, Ar*H*), 7.51 – 7.46 (m, 2H, Ar*H*), 7.36 – 7.30 (m, 3H, Ar*H*), 4.18 (t, *J* = 6.7 Hz, 1H, C*H*C≡C), 3.93 (s, 3H, C*H*$_3$), 3.65 (dd, *J* = 12.0, 7.3 Hz, 1H, C*H*$_2$$N_3$), 3.56 (dd, *J* = 12.0, 6.3 Hz, 1H, C*H*$_2$$N_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 143.4, 131.8, 130.2, 129.8, 128.6, 128.5, 128.1, 122.8, 87.1, 85.5, 57.1, 52.3, 39.7. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{15}N_3NaO_2^+$ 328.1056; Found 328.1061.

1-(1-Azido-4-phenylbut-3-yn-2-yl)-4-(trifluoromethyl)benzene (3n):

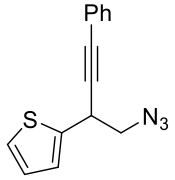


3n

Synthesized following **general procedure C** starting from 4-(trifluoromethyl)styrene (46 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 3 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 90:10 to 85:15) to afford 1-(1-azido-4-phenylbut-3-yn-2-yl)-4-(trifluoromethyl)benzene (**3n**) (33 mg, 0.11 mmol, 35%) as a yellow oil.

R_f (pentane/toluene, 85:15): 0.38; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.59 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.50 – 7.46 (m, 2H, Ar*H*), 7.36 – 7.31 (m, 3H, Ar*H*), 4.18 (t, *J* = 6.7 Hz, 1H, C*H*C≡C), 3.66 (dd, *J* = 12.1, 7.1 Hz, 1H, C*H*$_2$$N_3$), 3.57 (dd, *J* = 12.1, 6.3 Hz, 1H, C*H*$_2$$N_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 131.9, 130.2 (q, *J* = 32.7 Hz), 128.7, 128.5, 128.5, 125.9 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 272.1 Hz), 122.7, 86.9, 85.7, 57.1, 39.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. HRMS (APPI/LTQ-Orbitrap) m/z: $[M-N_2+H]^+$ Calcd for $C_{17}H_{13}F_3N^+$ 288.0995; Found 288.0995.

2-(1-Azido-4-phenylbut-3-yn-2-yl)thiophene (3o):

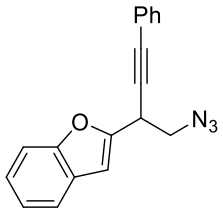


3o

Synthesized following **general procedure C** starting from a solution of 2-vinylthiophene (35 mg, 0.30 mmol, 1.00 equiv.) in dry degassed DME (0.5 mL). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 90:10 to 85:15) to afford 2-(1-azido-4-phenylbut-3-yn-2-yl)thiophene (**3o**) (47 mg, 0.19 mmol, 62%) as a yellow oil.

R_f (pentane/toluene, 7:3): 0.55; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H, Ar*H*), 7.37 – 7.31 (m, 3H, Ar*H*), 7.28 (dd, *J* = 5.1, 1.2 Hz, 1H, Ar*H*), 7.16 – 7.11 (m, 1H, Ar*H*), 7.01 (dd, *J* = 5.1, 3.5 Hz, 1H, Ar*H*), 4.39 (t, *J* = 6.6 Hz, 1H, C*H*C≡C), 3.70 (dd, *J* = 12.0, 7.2 Hz, 1H, CH_2N$_3$), 3.61 (dd, *J* = 12.0, 6.2 Hz, 1H, CH_2N$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 131.9, 128.6, 128.4, 127.1, 125.8, 125.2, 122.7, 87.4, 84.7, 57.4, 35.0. HRMS (APPI/LTQ-Orbitrap) m/z: [M-N_2+H]$^+$ Calcd for $C_{14}H_{12}NS^+$ 226.0685; Found 226.0687.

2-(1-Azido-4-phenylbut-3-yn-2-yl)benzofuran (3p):

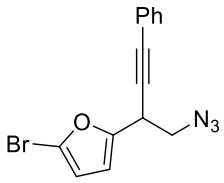


3p

Synthesized following **general procedure C** starting from a solution of 2-vinylbenzofuran (**1i**) (43 mg, 0.30 mmol, 1.00 equiv.) in dry degassed DME (0.5 mL). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 85:15) to afford 2-(1-azido-4-phenylbut-3-yn-2-yl)benzofuran (**3p**) (54 mg, 0.19 mmol, 62%) as a yellow oil.

R_f (pentane/toluene, 8:2): 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.45 (m, 4H, Ar*H*), 7.37 – 7.32 (m, 3H, Ar*H*), 7.33 – 7.19 (m, 2H, Ar*H*), 6.84 (s, 1H, OC=C*H*), 4.37 (t, *J* = 6.0 Hz, 1H, C*H*C≡C), 3.83 (dd, *J* = 11.1, 4.7 Hz, 1H, CH_2N$_3$), 3.79 (dd, *J* = 12.1, 4.9 Hz, 1H, CH_2N$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 153.9, 132.0, 128.7, 128.5, 128.3, 124.4, 123.1, 122.6, 121.1, 111.3, 105.0, 84.9, 84.8, 54.1, 34.2. HRMS (APPI/LTQ-Orbitrap) m/z: [M-N_2+H]$^+$ Calcd for $C_{18}H_{14}NO^+$ 260.1070; Found 260.1071.

2-(1-Azido-4-phenylbut-3-yn-2-yl)-5-bromofuran (3q):

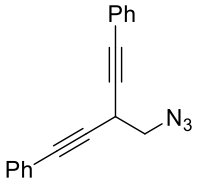


3q

Synthesized following **general procedure C** starting from a solution of 2-bromo-5-vinylfuran (**1j**) (52 mg, 0.30 mmol, 1.00 equiv.) in dry degassed DME (0.5 mL). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 9:1) to afford 2-(1-azido-4-phenylbut-3-yn-2-yl)-5-bromofuran (**3q**) (52 mg, 0.16 mmol, 54%) as an orange oil.

R_f (pentane/toluene, 8:2): 0.43; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H, Ar*H*), 7.36 – 7.30 (m, 3H, Ar*H*), 6.40 (dd, *J* = 3.3, 0.9 Hz, 1H, Ar*H*), 6.30 (d, *J* = 3.3 Hz, 1H, Ar*H*), 4.20 (t, *J* = 6.0 Hz, 1H, C*H*C≡C), 3.68 (dd, *J* = 6.2, 2.5 Hz, 2H, C$H_2$$N_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 131.9, 128.7, 128.5, 122.5, 121.5, 112.4, 110.7, 84.7, 84.5, 54.2, 33.8. HRMS (APPI/LTQ-Orbitrap) m/z: $[M\text{-}N_2+H]^+$ Calcd for $C_{14}H_{11}BrNO^+$ 288.0019; Found 288.0025.

(3-(Azidomethyl)penta-1,4-diyne-1,5-diyl)dibenzene (3r):

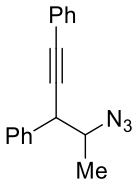


3r

Synthesized following **general procedure C** starting from a solution of but-3-en-1-yn-1-ylbenzene (**1b**) (39 mg, 0.30 mmol, 1.00 equiv.) in dry degassed DME (0.5 mL). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 85:15) to afford (3-(azidomethyl)penta-1,4-diyne-1,5-diyl)dibenzene (**3r**) (36 mg, 0.13 mmol, 44%) as a yellow oil.

R_f (pentane/toluene, 8:2): 0.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 4H, Ar*H*), 7.37 – 7.29 (m, 6H, Ar*H*), 4.09 (t, *J* = 6.7 Hz, 1H, C*H*C≡C), 3.64 (d, *J* = 6.7 Hz, 2H, C$H_2$$N_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.0, 128.7, 128.4, 122.6, 84.4, 83.2, 55.1, 26.8. HRMS (APPI/LTQ-Orbitrap) m/z: $[M\text{-}N_2+H]^+$ Calcd for $C_{18}H_{14}N^+$ 244.1121; Found 244.1121.

(4-Azidopent-1-yne-1,3-diyl)dibenzene (3s):

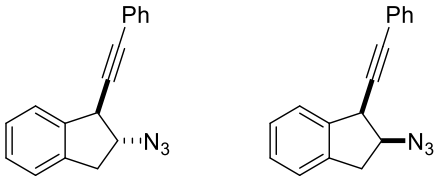


3s

Synthesized following **general procedure C** starting from *trans*-β-methylstyrene (**1d**) (36 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. Crude ^{1}H NMR of the mixture showed a diastereomeric ratio of 1.9:1 using peaks at 4.08 and 3.98 ppm. The crude product was purified by column chromatography (pentane/Et_2O, 99:1 to 98:2) to afford an inseparable mixture of diastereoisomers (4-azidopent-1-yne-1,3-diyl)dibenzene (**3s**) (45 mg, 0.17 mmol, 57%) as a yellow oil.

R_f (pentane/Et_2O, 97.5:2.5): 0.54; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 8H, Ar*H* major + minor), 7.42 – 7.36 (m, 4H, Ar*H* major + minor), 7.35 – 7.30 (m, 8H, Ar*H* major + minor), 4.08 (d, *J* = 6.1 Hz, 1H, C*H*C≡C major), 3.98 (d, *J* = 5.4 Hz, 1H, C*H*C≡C minor), 3.83 – 3.75 (m, 1H, C*H*N_3 minor), 3.71 (p, *J* = 6.5 Hz, 1H, C*H*N_3 major), 1.40 (d, *J* = 6.6 Hz, 3H, C*H*$_3$ major), 1.38 (d, *J* = 6.7 Hz, 3H, C*H*$_3$ minor). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 138.1, 131.8, 131.8, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 127.8, 127.7, 123.2, 123.2, 87.6, 87.4, 85.7, 85.4, 62.1, 62.0, 45.4, 45.2, 17.7, 16.0. HRMS (APPI/LTQ-Orbitrap) m/z: $[M-N_2+H]^+$ Calcd for $C_{17}H_{16}N^+$ 234.1277; Found 234.1288.

2-Azido-1-(phenylethynyl)-2,3-dihydro-1*H*-indene (3t/3t'):



3t **3t'**

Synthesized following **general procedure C** starting from indene (35 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. Crude ^{1}H NMR of the mixture showed a diastereomeric ratio of 5.4:1 (*trans*:*cis*) using peaks at 4.46 and 4.38 ppm. The crude product was purified by column chromatography (pentane/toluene, 9:1 to 8:2).

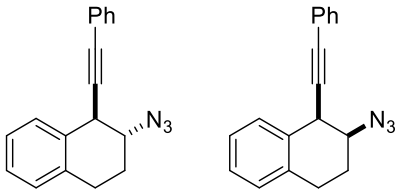
trans diastereoisomer (major): 1,2-*trans*-2-azido-1-(phenylethynyl)-2,3-dihydro-1*H*-indene (**3t**) (49 mg, 0.19 mmol, 63%) yellow oil. The *trans* configuration was determined using ^{1}H-^{1}H NOESY experiment on the reduced product (see product **5** in section 8.3)

R_f (pentane/toluene, 7:3): 0.46; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 3H, Ar*H*), 7.35 – 7.21 (m, 6H, Ar*H*), 4.38 (q, *J* = 8.3 Hz, 1H, C*H*N_3), 4.22 (d, *J* = 8.1 Hz, 1H, C*H*C≡C), 3.32 (dd, *J* = 15.5, 7.4 Hz, 1H, ArC*H*$_2$), 2.95 (dd, *J* = 15.5, 8.6 Hz, 1H, ArC*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 138.7, 131.9, 128.4, 128.3, 128.1, 127.7, 124.8, 124.6, 123.1, 88.0, 83.9, 68.7, 43.7, 37.4. HRMS (APPI/LTQ-Orbitrap) m/z: $[M-N_2]^+$ Calcd for $C_{17}H_{13}N^+$ 231.1043; Found 231.1043.

cis diastereoisomer (minor): 1,2-*cis*-2-azido-1-(phenylethynyl)-2,3-dihydro-1*H*-indene (**3t'**), the yield was determined only by crude ^{1}H NMR (12%) using CH_2Br_2 (10.6 µL, 0.150 mmol, 0.50 equiv.) as internal standard. An analytically pure sample was obtained by preparative TLC (pentane/toluene, 1:1).

R_f (pentane/toluene, 7:3): 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 3H, Ar*H*), 7.34 – 7.30 (m, 3H, Ar*H*), 7.28 – 7.25 (m, 3H, Ar*H*), 4.49 – 4.43 (m, 2H, C*H*C≡C + C*H*N_3), 3.26 – 3.16 (m, 1H, ArC*H*$_2$), 3.13 – 3.06 (m, 1H, ArC*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 139.3, 132.0, 128.4, 128.3, 128.0, 127.7, 124.9, 124.7, 123.2, 85.6, 85.5, 65.4, 43.6, 38.1. HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M\text{-}N_2+H]^+$ Calcd for $C_{17}H_{14}N^+$ 232.1121; Found 232.1122.

2-Azido-1-(phenylethynyl)-1,2,3,4-tetrahydronaphthalene (3u/3u'):



3u **3u'**

Synthesized following **general procedure C** starting from 1,2-dihydronaphthalene (39 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. Crude ^{1}H NMR of the mixture showed a diastereomeric ratio of 3.8:1 (*trans*:*cis*) using peaks at 2.08 and 1.89 ppm. The crude product was purified by column chromatography (pentane/toluene, 9:1 to 8:2). Relative configuration of the diastereoisomers were determined by analogy to **3t/3t'** where the major product is *trans*.

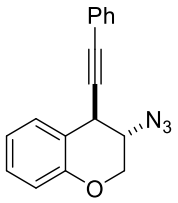
trans diastereoisomer (major): 1,2-*trans*-2-azido-1-(phenylethynyl)-1,2,3,4-tetrahydronaphthalene (**3u**) (50 mg, 0.18 mmol, 61%) yellow oil.

R_f (pentane/toluene, 8:2): 0.42; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 1H, Ar*H*), 7.50 – 7.44 (m, 2H, Ar*H*), 7.34 – 7.29 (m, 3H, Ar*H*), 7.25 – 7.19 (m, 2H, Ar*H*), 7.12 (d, *J* = 6.8 Hz, 1H, Ar*H*), 4.04 (d, *J* = 8.2 Hz, 1H, C*H*C≡C), 4.01 – 3.95 (m, 1H, C*H*N_3), 3.00 – 2.93 (m, 2H, ArC*H*$_2$), 2.36 – 2.27 (m, 1H, $ArCH_2CH_2$), 1.96 – 1.83 (m, 1H, $ArCH_2CH_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6, 133.7, 131.9, 129.3, 128.8, 128.4, 128.3, 127.3, 126.7, 123.2, 89.5, 83.8, 62.5, 39.2, 27.4, 27.2. HRMS (APPI/LTQ-Orbitrap) m/z: $[M\text{-}N_2+H]^+$ Calcd for $C_{18}H_{16}N^+$ 246.1277; Found 246.1269.

cis diastereoisomer (minor): 1,2-*cis*-2-azido-1-(phenylethynyl)-1,2,3,4-tetrahydronaphthalene (**3u'**) (8 mg, 0.03 mmol, 10%) orange oil.

R_f (pentane/toluene, 8:2): 0.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 3H, Ar*H*), 7.31 – 7.27 (m, 3H, Ar*H*), 7.24 – 7.18 (m, 2H, Ar*H*), 7.15 – 7.10 (m, 1H, Ar*H*), 4.27 (d, *J* = 4.3 Hz, 1H, C*H*C≡C), 4.01 (ddd, *J* = 8.5, 4.3, 2.8 Hz, 1H, C*H*N_3), 3.08 (dt, *J* = 17.2, 6.5 Hz, 1H, ArC*H*$_2$), 2.87 (dt, *J* = 17.2, 6.9 Hz, 1H, ArC*H*$_2$), 2.37 – 2.27 (m, 1H, $ArCH_2CH_2$), 2.13 – 2.04 (m, 1H, $ArCH_2CH_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 133.9, 131.9, 129.6, 129.0, 128.3, 128.2, 127.5, 126.6, 123.3, 88.2, 85.0, 59.6, 38.3, 26.5, 25.6. HRMS (APPI/LTQ-Orbitrap) m/z: $[M\text{-}N_2+H]^+$ Calcd for $C_{18}H_{16}N^+$ 246.1277; Found 246.1275.

3,4-*trans*-3-Azido-4-(phenylethynyl)chromane (3v):

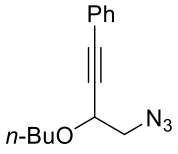


3v

Synthesized following **general procedure C** starting from a solution of 2*H*-chromene (**1k**) (40 mg, 0.30 mmol, 1.00 equiv.) in dry degassed DME (0.5 mL). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/toluene, 85:15 to 80:20) to afford 3,4-*trans*-3-azido-4-(phenylethynyl)chromane (**3v**) (24 mg, 0.090 mmol, 30%) as a yellow oil. Relative configuration of the diastereoisomer was determined by analogy to **3t/3t'** where the major product is *trans*.

R_f (Pentane/Toluene, 75:25): 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 3H, Ar*H*), 7.34 – 7.29 (m, 3H, Ar*H*), 7.25 – 7.18 (m, 1H, Ar*H*), 6.99 (td, *J* = 7.5, 1.2 Hz, 1H, Ar*H*), 6.88 (dd, *J* = 8.2, 1.1 Hz, 1H, Ar*H*), 4.43 (dd, *J* = 10.9, 2.0 Hz, 1H, OC*H*$_2$CH), 4.13 – 4.01 (m, 3H, OC*H*$_2$CH + C*H*N_3 + C*H*C≡C). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 131.9, 130.0, 129.1, 128.6, 128.4, 122.7, 121.7, 119.3, 117.0, 87.9, 84.4, 65.9, 58.3, 35.2. HRMS (APPI/LTQ-Orbitrap) m/z: [M-N_2+H]$^+$ Calcd for $C_{17}H_{14}NO^+$ 248.1070; Found 248.1080.

(4-Azido-3-butoxybut-1-yn-1-yl)benzene (3w):



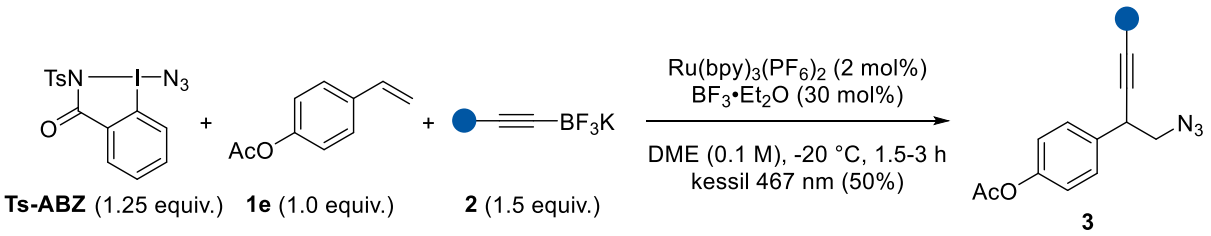
3w

Synthesized following **general procedure C** starting from vinyl butyl ether (39 µL, 0.30 mmol, 1.00 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 99:1 to 98:2) to afford (4-azido-3-butoxybut-1-yn-1-yl)benzene (**3w**) (36 mg, 0.15 mmol, 49%) as a slightly yellow oil.

R_f (pentane/Et_2O, 95:5): 0.55; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H, Ar*H*), 7.35 – 7.30 (m, 3H, Ar*H*), 4.43 (dd, *J* = 7.6, 4.0 Hz, 1H, C*H*C≡C), 3.86 (dt, *J* = 9.1, 6.5 Hz, 1H, C*H*$_2$O), 3.61 – 3.47 (m, 2H, C*H*$_2$O + C*H*$_2N_3$), 3.38 (dd, *J* = 12.8, 4.0 Hz, 1H, C*H*$_2N_3$), 1.68 – 1.60 (m, 2H, C*H*$_2CH_2$O), 1.49 – 1.39 (m, 2H, C*H*$_2CH_3$), 0.95 (t, *J* = 7.4 Hz, 3H, CH_2C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.9, 128.9, 128.5, 122.3, 87.1, 85.3, 69.9, 69.5, 54.7, 31.8, 19.4, 14.0. HRMS (ESI/QTOF) m/z: [M+Na]$^+$ Calcd for $C_{14}H_{17}N_3NaO^+$ 266.1264; Found 266.1260.

7.1 Scope of Alkynes

General procedure D:

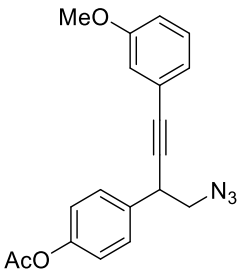


Ts-ABZ (1.25 equiv.) **1e** (1.0 equiv.) **2** (1.5 equiv.) **3**

An oven-dried test tube charged with $Ru(bpy)_3(PF_6)_2$ (5.2 mg, 6.0 µmol, 0.02 equiv.), **Ts-ABZ** (166 mg, 0.375 mmol, 1.25 equiv.) and potassium trifluoroborate **2** (0.45 mmol, 1.50 equiv.) was evacuated and backfilled with N_2 (3x). Dry degassed DME (2.7 mL) and 4-acetoxystyrene (**1e**) (46 µL, 0.30 mmol, 1.00 equiv.) were added and the mixture was cooled to -20 °C. Then, a stock solution of BF_3•Et_2O (11 µL, 90 µmol, 0.30 equiv.) in dry degassed DME (0.34 mL) was added and the reaction was stirred under blue LEDs irradiation (1 x Kessil 467 nm 50% intensity, 22 W) at -20 °C for 1.5-3 h. The reaction mixture was filtered through a short plug of silica and eluted with DCM then concentrated *in vacuo*. The crude product was purified by column chromatography to afford **3**.

Note: 4-Acetoxystyrene (**1e**) was eluted through a short plug of basic Al_2O_3 before use. DME was sparged with argon for 0.5 h before use. Cooling was performed using a Dewar filled with a mixture of ice and salt. We did not observe significant rise in temperature after 1.5 h (which is enough in most cases to reach full conversion). In the case of longer reaction, the cold bath was replaced with a new one after 1.5 h. For further details on the photochemistry set-up see Figure S1.

4-(1-Azido-4-(3-methoxyphenyl)but-3-yn-2-yl)phenyl acetate (3x):



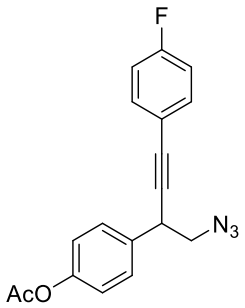
3x

Synthesized following **general procedure D** starting from potassium trifluoro((3-methoxyphenyl)ethynyl)borate (**2c**) (107 mg, 0.450 mmol, 1.50 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 85:15) to afford 4-(1-azido-4-(3-methoxyphenyl)but-3-yn-2-yl)phenyl acetate (**3x**) (60 mg, 0.18 mmol, 60%) as a yellow oil.

R_f (pentane/Et_2O, 8:2): 0.19; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H, Ar*H*), 7.27 – 7.20 (m, 1H, Ar*H*), 7.14 – 7.05 (m, 3H, Ar*H*), 7.01 (dd, *J* = 2.4, 1.4 Hz, 1H, Ar*H*), 6.89 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1H, Ar*H*), 4.16 – 4.09 (m, 1H, C*H*C≡C), 3.81 (s, 3H, OC*H*$_3$), 3.62 (dd, *J* = 12.0, 7.7 Hz, 1H, C*H*$_2$N$_3$), 3.52 (dd, *J* = 12.0, 6.1 Hz, 1H, C*H*$_2$N$_3$), 2.31 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 159.4, 150.3, 135.7, 129.5, 129.1, 124.3, 123.9, 122.1, 116.6,

115.2, 87.6, 85.1, 57.3, 55.4, 39.2, 21.3. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{17}N_3NaO_3^+$ 358.1162; Found 358.1161.

4-(1-Azido-4-(4-fluorophenyl)but-3-yn-2-yl)phenyl acetate (3y):

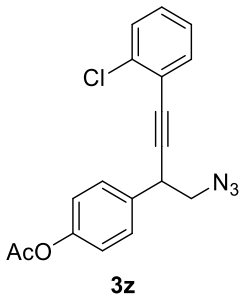


3y

Synthesized following **general procedure D** starting from potassium trifluoro((4-fluorophenyl)ethynyl)borate (**2d**) (102 mg, 0.450 mmol, 1.50 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 90:10 to 85:15) to afford 4-(1-azido-4-(4-fluorophenyl)but-3-yn-2-yl)phenyl acetate (**3y**) (65 mg, 0.20 mmol, 67%) as a yellow oil.

R_f (pentane/Et_2O, 8:2): 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.6, 4.7 Hz, 4H, Ar*H*), 7.14 – 7.08 (m, 2H, Ar*H*), 7.06 – 6.97 (m, 2H, Ar*H*), 4.14 – 4.08 (m, 1H, C*H*C≡C), 3.60 (dd, *J* = 12.0, 7.7 Hz, 1H, C$H_2$$N_3$), 3.51 (dd, *J* = 12.0, 6.0 Hz, 1H, C$H_2$$N_3$), 2.31 (s, 3H, C$H_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 162.7 (d, *J* = 249.5 Hz), 150.3, 135.7, 133.7 (d, *J* = 8.4 Hz), 129.0, 122.1, 119.0 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 22.1 Hz), 87.5 (d, *J* = 1.3 Hz), 84.2, 57.3, 39.2, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.9. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{14}FN_3NaO_2^+$ 346.0962; Found 346.0953.

4-(1-Azido-4-(2-chlorophenyl)but-3-yn-2-yl)phenyl acetate (3z):

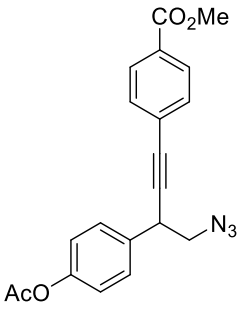


3z

Synthesized following **general procedure D** starting from potassium ((2-chlorophenyl)ethynyl)trifluoroborate (**2e**) (109 mg, 0.450 mmol, 1.50 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 90:10 to 85:15) to afford 4-(1-azido-4-(2-chlorophenyl)but-3-yn-2-yl)phenyl acetate (**3z**) (79 mg, 0.23 mmol, 77%) as a yellow oil.

R_f (pentane/Et_2O, 8:2): 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 3H, Ar*H*), 7.41 (dd, *J* = 7.9, 1.4 Hz, 1H, Ar*H*), 7.30 – 7.17 (m, 2H, Ar*H*), 7.15 – 7.07 (m, 2H, Ar*H*), 4.16 (t, *J* = 6.8 Hz, 1H, C*H*C≡C), 3.66 (dd, *J* = 12.0, 7.6 Hz, 1H, C*H*$_2$$N_3$), 3.56 (dd, *J* = 12.0, 6.3 Hz, 1H, C*H*$_2$$N_3$), 2.30 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 150.3, 136.3, 135.4, 133.6, 129.5, 129.4, 129.2, 126.6, 122.9, 122.1, 93.2, 82.1, 57.4, 39.3, 21.3. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{14}ClN_3NaO_2^+$ 362.0667; Found 362.0654.

Methyl 4-(3-(4-acetoxyphenyl)-4-azidobut-1-yn-1-yl)benzoate (3aa):

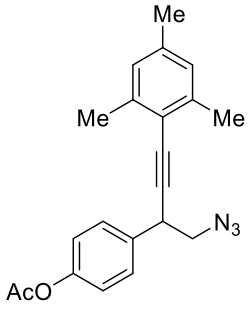


3aa

Synthesized following **general procedure D** starting from potassium trifluoro((4-(methoxycarbonyl)phenyl)ethynyl)borate (**2f**) (120 mg, 0.450 mmol, 1.50 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/EtOAc, 85:15 to 80:20) to afford methyl 4-(3-(4-acetoxyphenyl)-4-azidobut-1-yn-1-yl)benzoate (**3aa**) (74 mg, 0.20 mmol, 68%) as a yellow oil.

R_f (pentane/EtOAc, 8:2): 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H, Ar*H*), 7.55 – 7.51 (m, 2H, Ar*H*), 7.49 – 7.42 (m, 2H, Ar*H*), 7.15 – 7.08 (m, 2H, Ar*H*), 4.17 – 4.11 (m, 1H, C*H*C≡C), 3.92 (s, 3H, OC*H*$_3$), 3.63 (dd, *J* = 12.0, 7.7 Hz, 1H, C*H*$_2$$N_3$), 3.53 (dd, *J* = 12.0, 6.1 Hz, 1H, C*H*$_2$$N_3$), 2.31 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 166.7, 150.4, 135.4, 131.8, 129.8, 129.6, 129.0, 127.6, 122.2, 90.9, 84.5, 57.2, 52.4, 39.3, 21.3. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{17}N_3NaO_4^+$ 386.1111; Found 386.1101.

4-(1-Azido-4-mesitylbut-3-yn-2-yl)phenyl acetate (3ab):



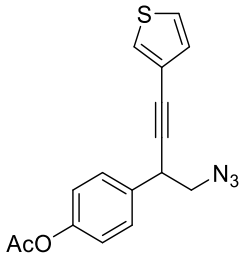
3ab

Synthesized following **general procedure D** starting from potassium trifluoro(mesitylethynyl)borate (**2g**) (113 mg, 0.450 mmol, 1.50 equiv.). The reaction was carried out for 3 h, DCM was used for the silica plug. The crude product was purified by column

chromatography (pentane/Et_2O, 95:5 to 90:10) to afford 4-(1-azido-4-mesitylbut-3-yn-2-yl)phenyl acetate (**3ab**) (35 mg, 99 µmol, 33%) as a yellow oil.

R_f (pentane/Et_2O, 9:1): 0.26; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H, Ar*H*), 7.14 – 7.08 (m, 2H, Ar*H*), 6.87 (s, 2H, Ar*H*), 4.20 (t, *J* = 6.9 Hz, 1H, C*H*C≡C), 3.64 (dd, *J* = 12.0, 7.4 Hz, 1H, CH_2N_3), 3.58 (dd, *J* = 12.0, 6.4 Hz, 1H, CH_2N_3), 2.42 (s, 6H, ArCH_3), 2.31 (s, 3H, CH_3C(O)), 2.28 (s, 3H, ArCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 150.2, 140.4, 137.8, 136.2, 129.1, 127.7, 122.0, 119.7, 95.2, 83.1, 57.9, 39.3, 21.4, 21.3, 21.2. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{21}N_3NaO_2^+$ 370.1526; Found 370.1536.

4-(1-Azido-4-(thiophen-3-yl)but-3-yn-2-yl)phenyl acetate (3ac):

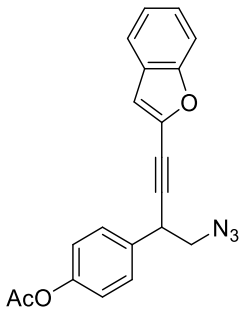


3ac

Synthesized following **general procedure D** starting from potassium trifluoro(thiophen-3-ylethynyl)borate (**2h**) (97 mg, 0.45 mmol, 1.50 equiv.). The reaction was carried out for 3 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 85:15) to afford 4-(1-azido-4-(thiophen-3-yl)but-3-yn-2-yl)phenyl acetate (**3ac**) (50 mg, 0.16 mmol, 54%) as a yellow oil.

R_f (pentane/Et_2O, 8:2): 0.29; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 3H, Ar*H*), 7.28 (dd, *J* = 5.0, 3.0 Hz, 1H, Ar*H*), 7.17 – 7.09 (m, 3H, Ar*H*), 4.14 – 4.08 (m, 1H, C*H*C≡C), 3.61 (dd, *J* = 12.0, 7.7 Hz, 1H, CH_2N_3), 3.51 (dd, *J* = 12.0, 6.1 Hz, 1H, CH_2N_3), 2.31 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 150.3, 135.7, 130.0, 129.0, 129.0, 125.4, 122.0, 121.9, 87.3, 80.4, 57.2, 39.2, 21.3. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{13}N_3NaO_2S^+$ 334.0621; Found 334.0624.

4-(1-Azido-4-(benzofuran-2-yl)but-3-yn-2-yl)phenyl acetate (3ad):

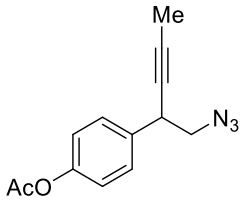


3ad

Synthesized following **general procedure D** starting from potassium (benzofuran-2-ylethynyl)trifluoroborate (**2i**) (112 mg, 0.450 mmol, 1.50 equiv.). The reaction was carried out for 3 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 8:2) to afford 4-(1-azido-4-(benzofuran-2-yl)but-3-yn-2-yl)phenyl acetate (**3ad**) (49 mg, 0.14 mmol, 47%) as a yellow oil.

R_f (pentane/Et_2O, 6:4): 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.46 (t, *J* = 8.3 Hz, 3H, Ar*H*), 7.33 (t, *J* = 7.2 Hz, 1H, Ar*H*), 7.24 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.12 (d, *J* = 8.6 Hz, 2H, Ar*H*), 6.95 (s, 1H, OC=C*H*), 4.18 (t, *J* = 6.9 Hz, 1H, C*H*C≡C), 3.68 (dd, *J* = 12.0, 7.5 Hz, 1H, C*H*$_2$N$_3$), 3.58 (dd, *J* = 12.0, 6.3 Hz, 1H, C*H*$_2$N$_3$), 2.31 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 154.8, 150.5, 138.3, 134.7, 129.1, 127.6, 125.7, 123.4, 122.2, 121.4, 111.8, 111.4, 94.1, 75.7, 56.8, 39.2, 21.3. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{15}N_3NaO_3^+$ 368.1006; Found 368.1022.

4-(1-Azidopent-3-yn-2-yl)phenyl acetate (3ae)



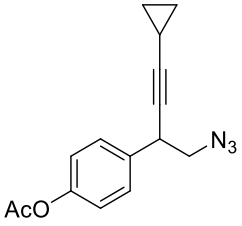
3ae

Synthesized following **general procedure D** starting from potassium trifluoro(prop-1-yn-1-yl)borate (**2j**) (66 mg, 0.45 mmol, 1.50 equiv.). The reaction was carried out for 3 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 8:2) to afford 4-(1-azidopent-3-yn-2-yl)phenyl acetate (**3ae**) (40 mg, 0.16 mmol, 54%) as a slightly yellow oil.

R_f (pentane/Et_2O, 8:2): 0.46; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H, Ar*H*), 7.10 – 7.04 (m, 2H, Ar*H*), 3.87 – 3.80 (m, 1H, C*H*C≡C), 3.47 (dd, *J* = 11.9, 7.6 Hz, 1H, C*H*$_2$N$_3$), 3.39 (dd, *J* = 11.9, 6.2 Hz, 1H, C*H*$_2$N$_3$), 2.29 (s, 3H, C*H*$_3$), 1.88 (d, *J* = 2.4 Hz, 3H, C≡CC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ[24] 169.5, 150.1, 136.3, 128.9, 121.9, 81.1, 57.5, 38.5, 21.2, 3.7. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{13}N_3NaO_2^+$ 266.0900; Found 266.0902.

4-(1-Azido-4-cyclopropylbut-3-yn-2-yl)phenyl acetate (3af):

[24] One carbon of the alkyne is overlapping with the $CDCl_3$ signal.

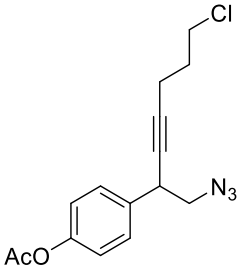


3af

Synthesized following **general procedure D** starting from potassium (cyclopropylethynyl)trifluoroborate (**2k**) (77 mg, 0.45 mmol, 1.50 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 9:1) to afford 4-(1-azido-4-cyclopropylbut-3-yn-2-yl)phenyl acetate (**3af**) (42 mg, 0.16 mmol, 52%) as a colorless oil.

R_f (pentane/Et_2O, 8:2): 0.29; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H, Ar*H*), 7.09 – 7.04 (m, 2H, Ar*H*), 3.87 – 3.80 (m, 1H, C*H*C≡C), 3.45 (dd, *J* = 11.9, 7.6 Hz, 1H, CH_2N_3), 3.36 (dd, *J* = 12.0, 6.1 Hz, 1H, CH_2N_3), 2.29 (s, 3H, CH_3), 1.34 – 1.25 (m, 1H, C*H*CH_2), 0.81 – 0.68 (m, 4H, CHCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 150.1, 136.4, 128.9, 121.8, 88.6, 73.6, 57.5, 38.6, 21.2, 8.1, -0.3. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{15}N_3NaO_2^+$ 292.1056; Found 292.1055.

4-(1-Azido-7-chlorohept-3-yn-2-yl)phenyl acetate (3ag):

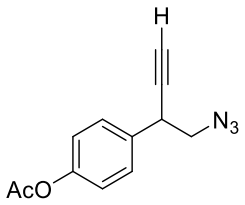


3ag

Synthesized following **general procedure D** starting from potassium (5-chloropent-1-yn-1-yl)trifluoroborate (**2l**) (94 mg, 0.45 mmol, 1.50 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 90:10 to 85:15) to afford 4-(1-azido-7-chlorohept-3-yn-2-yl)phenyl acetate (**3ag**) (47 mg, 0.16 mmol, 52%) as a yellow oil.

R_f (pentane/Et_2O, 8:2): 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H, Ar*H*), 7.10 – 7.05 (m, 2H, Ar*H*), 3.90 – 3.83 (m, 1H, C*H*C≡C), 3.66 (t, *J* = 6.3 Hz, 2H, CH_2Cl), 3.47 (dd, *J* = 12.0, 7.7 Hz, 1H, CH_2N_3), 3.40 (dd, *J* = 12.0, 6.1 Hz, 1H, CH_2N_3), 2.46 (td, *J* = 6.9, 2.2 Hz, 2H, C≡CCH_2CH_2), 2.30 (s, 3H, CH_3), 2.00 (p, *J* = 6.6 Hz, 2H, C≡CCH_2CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 150.1, 136.1, 128.9, 121.9, 83.6, 79.5, 57.5, 43.8, 38.5, 31.4, 21.2, 16.4. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{16}ClN_3NaO_2^+$ 328.0823; Found 328.0830.

4-(1-Azidobut-3-yn-2-yl)phenyl acetate (3ah):



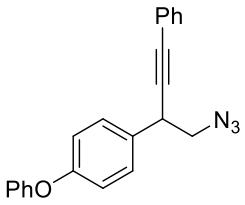
3ah

Synthesized following **general procedure D** starting from potassium ethynyltrifluoroborate (**2b**) (59 mg, 0.45 mmol, 1.50 equiv.). The reaction was carried out for 1.5 h, DCM was used for the silica plug. The crude product was purified by column chromatography (pentane/Et_2O, 90:10 to 85:15) to afford 4-(1-azidobut-3-yn-2-yl)phenyl acetate (**3ah**) (23 mg, 0.10 mmol, 34%) as a yellow oil.

R_f (pentane/Et_2O, 8:2): 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H, Ar*H*), 7.12 – 7.07 (m, 2H, Ar*H*), 3.89 (td, *J* = 7.3, 2.5 Hz, 1H, C*H*C≡C), 3.56 (dd, *J* = 12.0, 7.5 Hz, 1H, C*H*$_2$$N_3$), 3.48 (dd, *J* = 12.0, 6.3 Hz, 1H, C*H*$_2$$N_3$), 2.39 (d, *J* = 2.5 Hz, 1H, C≡C*H*), 2.30 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 150.4, 135.1, 129.0, 122.1, 82.5, 73.3, 57.1, 38.1, 21.3. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{11}N_3NaO_2^+$ 252.0743; Found 252.0734.

8. Product Modifications

8.1 Scale-up

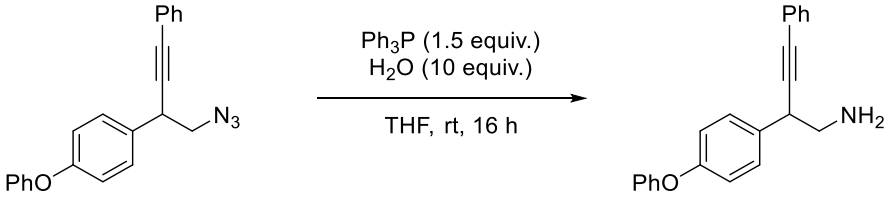


3ai

An oven-dried round-bottom flask charged with $Ru(bpy)_3(PF_6)_2$ (17.2 mg, 20.0 µmol, 2 mol%), **Ts-ABZ** (553 mg, 1.25 mmol, 1.25 equiv.), potassium trifluoro(phenylethynyl)borate (**2a**) (312 mg, 1.50 mmol, 1.50 equiv.) was evacuated and backfilled with N_2 (3x). Dry degassed DME (7.8 mL) and a solution of 1-phenoxy-4-vinylbenzene (**1c**) (207 mg, 1.00 mmol, 1.00 equiv.) in dry degassed DME (1.0 mL) were added and the mixture was cooled to -20 °C. Then, a stock solution of BF_3•Et_2O (37 µL, 0.30 mmol, 0.30 equiv.) in dry degassed DME (1.2 mL) was added and the reaction was stirred under blue LEDs irradiation (1 x Kessil 467 nm 50% intensity, 22W) at -20 °C for 1.5 h. The reaction mixture was filtered through a short plug of silica and eluted with DCM then concentrated *in vacuo*. The crude product was purified by column chromatography (pentane/Et_2O, 97.5:2.5) to afford 1-(1-azido-4-phenylbut-3-yn-2-yl)-4-phenoxybenzene (**3ai**) (271 mg, 0.799 mmol, 80%) as a yellow oil.

R_f (pentane/Et_2O, 9:1): 0.52; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H, Ar*H*), 7.45 – 7.40 (m, 2H, Ar*H*), 7.38 – 7.30 (m, 5H, Ar*H*), 7.14 – 7.09 (m, 1H, Ar*H*), 7.05 – 6.99 (m, 4H, Ar*H*), 4.11 (t, *J* = 6.8 Hz, 1H, C*H*C≡C), 3.62 (dd, *J* = 12.0, 7.4 Hz, 1H, C$H_2$$N_3$), 3.53 (dd, *J* = 12.0, 6.3 Hz, 1H, C$H_2$$N_3$). ^{13}C NMR (101 MHz, CDCl3) δ[25] 157.2, 157.0, 133.0, 131.8, 129.9, 129.3, 128.4, 123.6, 123.0, 119.2, 119.1, 88.0, 85.1, 57.5, 39.1. HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M-N_2+H]^+$ Calcd for $C_{22}H_{18}NO^+$ 312.1383; Found 312.1384.

8.2 Azide reduction



3ai **4**

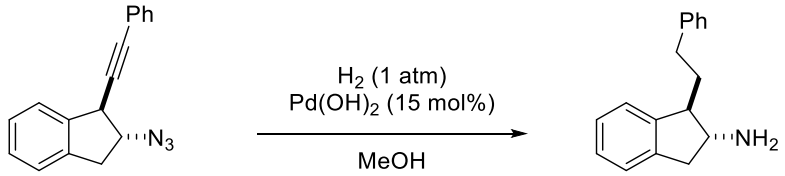
To a microwave vial containing a solution of 1-(1-azido-4-phenylbut-3-yn-2-yl)-4-phenoxybenzene (**3ai**) (34 mg, 0.10 mmol, 1.00 equiv) in THF (1 mL) were added Ph_3P (39 mg, 0.15 mmol, 1.50 equiv) and water (18 µL, 1.0 mmol, 10.0 equiv) under air. The vial was

[25] One aromatic carbon was not resolved.

capped and the reaction was stirred at rt for 16 h. The mixture was concentrated *in vacuo* then was loaded on a small plug of silica using DCM. The plug was washed with DCM then the crude product was collected using DCM/MeOH (9:1) and concentrated *in vacuo*. The crude product was purified by reverse phase column chromatography (H_2O/CH_3CN, 95:5 to 5:95) to afford 2-(4-phenoxyphenyl)-4-phenylbut-3-yn-1-amine (**4**) (29 mg, 91 µmol, 91%) as an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H, Ar*H*), 7.42 – 7.37 (m, 2H, Ar*H*), 7.37 – 7.29 (m, 5H, Ar*H*), 7.14 – 7.08 (m, 1H, Ar*H*), 7.05 – 6.98 (m, 4H, Ar*H*), 3.96 – 3.90 (m, 1H, C*H*C≡C), 3.08 (dd, *J* = 12.8, 5.6 Hz, 1H, C*H*$_2$NH$_2$), 3.01 (dd, *J* = 12.8, 7.1 Hz, 1H, C*H*$_2$NH$_2$), 1.44 (bs, 2H, N*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 156.5, 134.3, 131.9, 129.9, 129.2, 128.4, 128.2, 123.4, 123.4, 119.1, 119.0, 89.6, 84.7, 49.8, 42.5. HRMS (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO^+$ 314.1539; Found 314.1534.

8.3 Hydrogenation

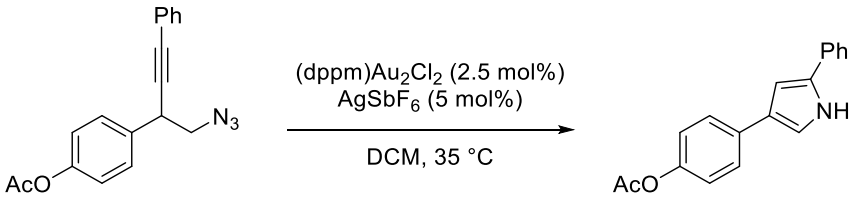


3t **5**

A capped oven-dried microwave vial charged with 2-azido-1-(phenylethynyl)-2,3-dihydro-1*H*-indene (**3t**) (31 mg, 0.12 mmol, 1.00 equiv.) was evacuated and backfilled with N_2 (3x). Then, dry MeOH (2 mL) was added. The vial was opened and $Pd(OH)_2$ (13 mg, 18 µmol, 20 wt.% on C, 0.15 equiv.) was added. The vial was capped and the mixture was sparged with H_2 for 15 min using a balloon. The reaction was stirred at rt for 16 h under H_2 atmosphere (1 atm, balloon). The mixture was sparged with N_2 for 15 min then was filtered over a syringe filter (PTFE, 0.22 µm), eluted with DCM and concentrated in vacuo to afford 1-phenethyl-2,3-dihydro-1*H*-inden-2-amine (**5**) (26 mg, 0.11 mmol, 93%) as a dark orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H, Ar*H*), 7.25 – 7.15 (m, 7H, Ar*H*), 3.53 (dt, *J* = 6.7, 4.8 Hz, 1H, C*H*NH$_2$), 3.27 (dd, *J* = 15.9, 6.8 Hz, 1H, ArC*H*$_2$CHNH$_2$), 2.88 (q, *J* = 6.4 Hz, 1H, ArC*H*), 2.82 – 2.75 (m, 2H, ArC*H*$_2$CH$_2$), 2.66 (dd, *J* = 15.9, 4.9 Hz, 1H, ArC*H*$_2$CHNH$_2$), 2.05 – 1.81 (m, 4H, ArCH$_2$C*H*$_2$ + N*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 142.4, 141.2, 128.6, 128.5, 126.9, 126.7, 126.0, 125.1, 124.6, 58.6, 54.4, 41.7, 35.1, 33.8. HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}N^+$ 238.1590; Found 238.1590.

8.4 Pyrrole formation

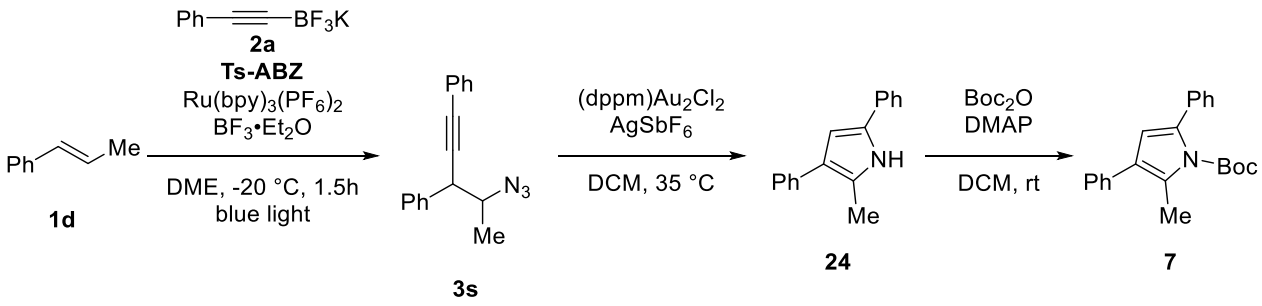


3g **6**

Adapting from a known methodology,[26] a capped oven-dried microwave vial charged with $AgSbF_6$ (1.7 mg, 5.0 µmol, 5 mol%) and $(dppm)Au_2Cl_2$ (2.1 mg, 2.5 µmol, 2.5 mol%) was evacuated and backfilled with N_2 (3x). Then, dry DCM (1 mL) was added and the mixture was stirred at rt for 2 min. A solution of 4-(1-azido-4-phenylbut-3-yn-2-yl)phenyl acetate (**3g**) (31 mg, 0.10 mmol, 1.00 equiv.) in dry DCM (1 mL) was added under N_2 and the vial was placed in a preheated heating block at 35 °C. The reaction was stirred at 35 °C for 30 min. The mixture was allowed to cool to rt, filtered over activated neutral alumina, eluted with DCM and concentrated *in vacuo*. The crude product was purified by column chromatography on activated neutral alumina (pentane/EtOAc, 95:5 to 80:20) to afford 4-(5-phenyl-1H-pyrrol-3-yl)phenyl acetate (**6**) (16 mg, 58 µmol, 58%) as a slightly yellow solid.

R_f (SiO_2, pentane/EtOAc, 7 :3): 0.43; Mp (Dec.): 176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H, N*H*), 7.58 – 7.49 (m, 4H, Ar*H*), 7.42 – 7.36 (m, 2H, Ar*H*), 7.26 – 7.22 (m, 1H, Ar*H*), 7.11 – 7.06 (m, 3H, Ar*H*), 6.78 (dd, *J* = 2.7, 1.7 Hz, 1H, Ar*H*), 2.31 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 148.9, 133.6, 133.3, 132.5, 129.1, 126.7, 126.3, 126.0, 124.0, 121.8, 115.7, 104.2, 21.3. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{15}NNaO_2^+$ 300.0995; Found 300.0994.

8.5 Telescoped protected pyrrole formation



1d **3s** **24** **7**

An oven-dried test tube charged with $Ru(bpy)_3(PF_6)_2$ (5.2 mg, 6.0 µmol, 0.02 equiv.), **Ts-ABZ** (166 mg, 0.375 mmol, 1.25 equiv.) and potassium trifluoro(phenylethynyl)borate (**2a**) (94 mg, 0.45 mmol, 1.50 equiv.) was evacuated and backfilled with N_2 (3x). Dry degassed DME (2.7 mL) and *trans-β*-methylstyrene (**1d**) (39 µL, 0.30 mmol, 1.00 equiv.) were added and the mixture was cooled to -20 °C. Then, a stock solution of BF_3•Et_2O (11 µL, 90 µmol, 0.30 equiv.) in dry degassed DME (0.34 mL) was added and the reaction was stirred under blue LEDs irradiation (1 x Kessil 467 nm 50% intensity, 22W) at -20 °C for 1.5 h. The reaction mixture

[26] D. J. Gorin, N. R. Davis, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 11260–11261.

was concentrated *in vacuo*. The crude product was dissolved in DCM, filtered through a short plug of silica and eluted with DCM then concentrated *in vacuo* to afford crude **3s**.

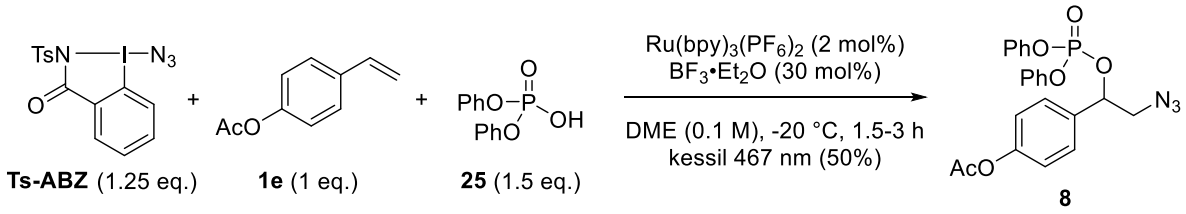
A capped oven-dried microwave vial charged with $AgSbF_6$ (5.2 mg, 15 µmol, 0.050 equiv) and $(dppm)Au_2Cl_2$ (6.4 mg, 7.5 µmol, 0.025 equiv.) was evacuated and backfilled with N_2 (3x). Then, dry DCM (3 mL) was added and the mixture was stirred at rt for 2 min. A solution of previously obtained crude **3s** in dry DCM (3 mL) was added under N_2 and the vial was placed in a preheated heating block at 35 °C. The reaction was stirred at 35 °C for 1.5 h. The mixture was allowed to cool to rt, filtered over activated neutral alumina, eluted with DCM and concentrated *in vacuo* to afford crude **24**.

A capped microwave vial charged with previously obtained crude **24** and DMAP (7.3 mg, 60 µmol, 0.20 equiv) was evacuated and backfilled with N_2 (3x). Then, dry DCM (2 mL) was added followed by the dropwise addition of a solution of Boc_2O (131 mg, 0.600 mmol, 2.00 equiv.) in dry DCM (1 mL). The reaction was stirred at rt for 1.5 h then was concentrated *in vacuo*. The crude product was purified by column chromatography (pentane/Et_2O, 98:2 to 96:4) to afford *tert*-butyl 2-methyl-3,5-diphenyl-1*H*-pyrrole-1-carboxylate (**7**) (43 mg, 0.13 mmol, 43%) as a yellow oil.

R_f (pentane/Et_2O, 95:5): 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 8H, Ar*H*), 7.32 – 7.27 (m, 2H, Ar*H*), 6.28 (s, 1H, NC=C*H*), 2.54 (s, 3H, ArC*H*$_3$), 1.28 (s, 9H, Boc). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 136.0, 135.2, 134.3, 128.8, 128.7, 128.5, 128.5, 128.0, 127.0, 126.3, 125.0, 113.6, 83.8, 27.5, 13.5. HRMS (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{23}NNaO_2^+$ 356.1621; Found 356.1620.

9. Mechanistic Studies

9.1 Carbocation trapping



Ts-ABZ (1.25 eq.) **1e** (1 eq.) **25** (1.5 eq.) **8**

An oven-dried test tube charged with $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 2.0 µmol, 0.02 equiv.), **Ts-ABZ** (55 mg, 0.13 mmol, 1.25 equiv.) and diphenyl phosphate (**25**) (38 mg, 0.15 mmol, 1.50 equiv.) was evacuated and backfilled with N_2 (3x). Dry degassed DME (0.9 mL) and 4-acetoxystyrene (**1e**) (15 µL, 0.10 mmol, 1.00 equiv.) were added and the mixture was cooled to -20 °C. Then, a stock solution of BF_3•Et_2O (3.7 µL, 30 µmol, 0.30 equiv.) in dry degassed DME (0.12 mL) was added and the reaction was stirred under blue LEDs irradiation (1 x Kessil 467 nm 50% intensity, 22 W) at -20 °C for 2 h. The reaction mixture was filtered through a short plug of silica and eluted with EtOAc then concentrated *in vacuo*. The crude product was dissolved in DCM (10 mL), the solution was washed with 3 x 10 mL of a sat. sol. of $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by

preparative TLC (pentane/EtOAc, 65:35) to afford 4-(2-azido-1-((diphenoxyphosphoryl)oxy)ethyl)phenyl acetate (**8**) (27 mg, 59 µmol, 59%) as a colorless oil.

R_f (pentane/EtOAc, 7:3): 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H, Ar*H*), 7.27 – 7.16 (m, 5H, Ar*H*), 7.15 – 7.10 (m, 1H, Ar*H*), 7.09 – 7.04 (m, 2H, Ar*H*), 7.03 – 6.98 (m, 2H, Ar*H*), 5.62 (td, *J* = 7.6, 4.3 Hz, 1H, P(O)OC*H*), 3.64 (dd, *J* = 13.2, 7.4 Hz, 1H, C*H*$_2$N$_3$), 3.53 (ddd, *J* = 13.2, 4.2, 2.5 Hz, 1H, C*H*$_2$N$_3$), 2.30 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 151.4, 150.5 (d, *J* = 7.1 Hz), 150.4 (d, *J* = 7.2 Hz), 133.9 (d, *J* = 3.0 Hz), 129.9, 129.8, 128.0, 125.6 (d, *J* = 1.1 Hz), 125.5 (d, *J* = 1.1 Hz), 122.1, 120.2 (d, *J* = 5.0 Hz), 120.1 (d, *J* = 4.9 Hz), 79.8 (d, *J* = 5.8 Hz), 56.3 (d, *J* = 7.6 Hz), 21.2. HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}N_3O_6P^+$ 454.1162; Found 454.1163.

9.2 Stern-Volmer fluorescence quenching

Due to the low solubility of the different components of the reaction in pure DME a mixture of DME/CH_3CN (9:1) was chosen for the study. We observed only a very slight decreased in yield when the reaction was carried out in this solvent mixture (Table S8, entry 7). All the solvent used during the study was dry and sparged with argon for 30 minutes before use. Stern-Volmer fluorescence quenching experiments were conducted on a Varian Cary Eclipse machine.

Preparation of the solutions:

Solution **A**: A 20 mL volumetric flask charged with $Ru(bpy)_3(PF_6)_2$ (4.3 mg, 5.0 µmol) was evacuated and backfilled with N_2 (3x). The solvent was added (~16 mL) and the flask was vigorously shaken to ensure solubilization. Solvent was further added until the line and the flask was further shaken. The solution was stored under argon atmosphere throughout the experiments.

Solution **B**: A 25 mL volumetric flask charged with potassium trifluoro(phenylethynyl)borate (**2a**) (130 mg, 0.625 mmol) was evacuated and backfilled with N_2 (3x). The solvent was added (~20 mL) and the flask was vigorously shaken to ensure solubilization. Solvent was further added until the line and the flask was further shaken. The solution was stored under argon atmosphere throughout the experiments.

Solution **C**: A 10 mL volumetric flask charged with **Ts-ABZ** (111 mg, 0.250 mmol) was evacuated and backfilled with N_2 (3x). The solvent was added (~7 mL) and the flask was vigorously shaken to ensure solubilization. Solvent was further added until the line and the flask was further shaken. The solution was stored under argon atmosphere throughout the experiments.

Solution **D**: A 5 mL volumetric flask charged with styrene (**1a**) (36 µL, 0.31 mmol) was evacuated and backfilled with N_2 (3x). The solvent was added (~3 mL) and the flask was vigorously shaken. Solvent was further added until the line and the flask was further shaken. The solution was stored under argon atmosphere throughout the experiments.

Preparation of a sample:

A quartz cuvette fitted with a septum was evacuated and backfilled with N_2 (3x). Then, 0.5 mL of solution **A**, the appropriate amount of quencher solution and solvent were added under N_2. The final volume of the solution was always 2.5 mL with a final concentration of the photocatalyst of $5x10^{-5}$ M. The mixture was vortexed for 5 s and the analysis was performed.

V_A (mL)	V_B (mL)	$V_{solvent}$	Quencher concentration (mM)
0.5	0	2	0
0.5	0.5	1.5	5
0.5	1	1	10
0.5	1.5	0.5	15
0.5	2	0	20

Table S9: Alkynyl-BF_3K **2a** as quencher (solution **B**).

V_A (mL)	V_C (mL)	$V_{solvent}$	Quencher concentration (mM)
0.5	0	2	0
0.5	0.5	1.5	5
0.5	1	1	10
0.5	1.5	0.5	15
0.5	2	0	20

Table S10: Ts-ABZ as quencher (solution **C**).

V_A (mL)	V_D (mL)	$V_{solvent}$	Quencher concentration (mM)
0.5	0	2	0
0.5	0.2	1.8	5
0.5	0.4	1.6	10
0.5	0.6	1.4	15
0.5	0.8	1.2	20

Table S11: Styrene **1a** as quencher (solution **D**).

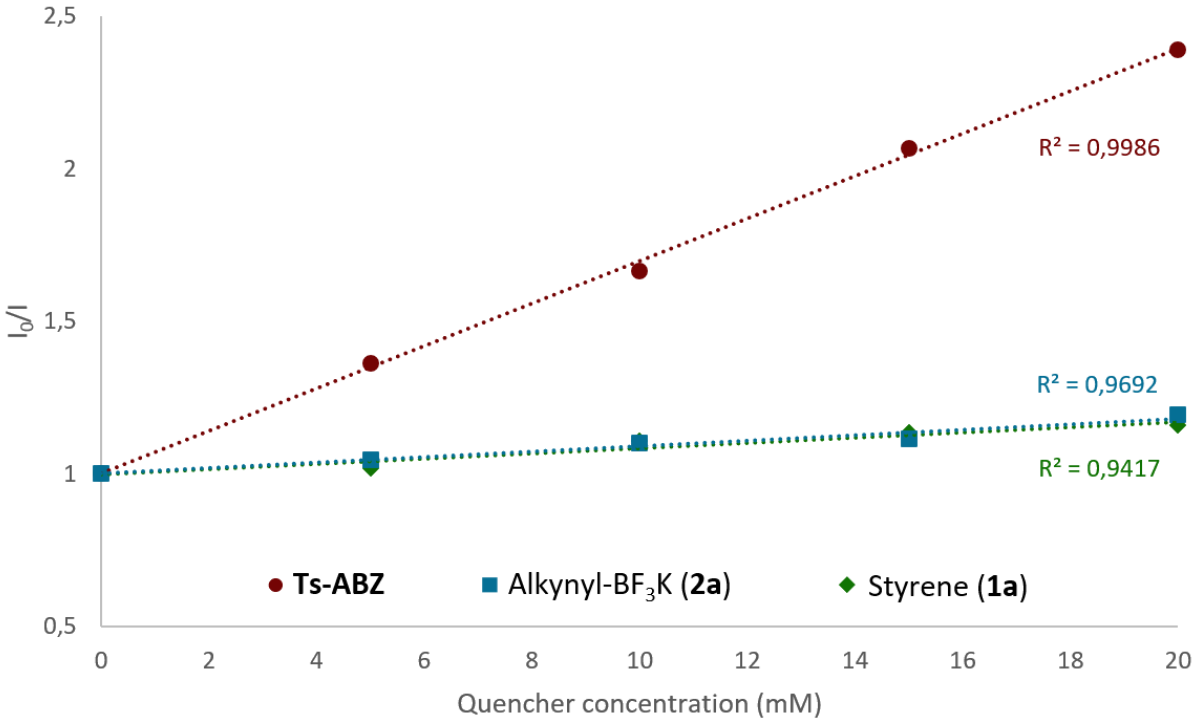


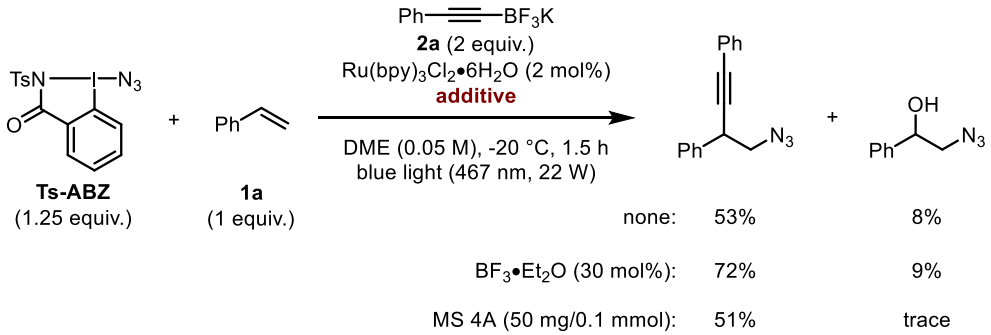
Figure S2: Stern-Volmer fluorescence quenching results.

9.3 Investigation of the BF_3•Et_2O effect

As described in the manuscript we did not reach a proper conclusion on the role of BF_3. We investigated different hypothesis for its effect:

1) It could scavenge water from the reaction mixture:

Since the reaction is occurring via the formation of a carbocation intermediate we usually observed small amount of water addition (oxy-azidation). When BF_3 is added the formation of this by-product occurs similarly.



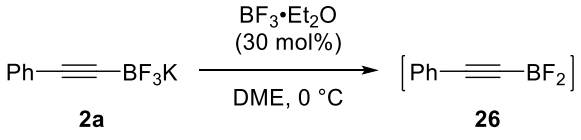
Additionally, when the reaction was performed in the presence of molecular sieves almost no oxy-azidation product was observed but the yield did not increase.

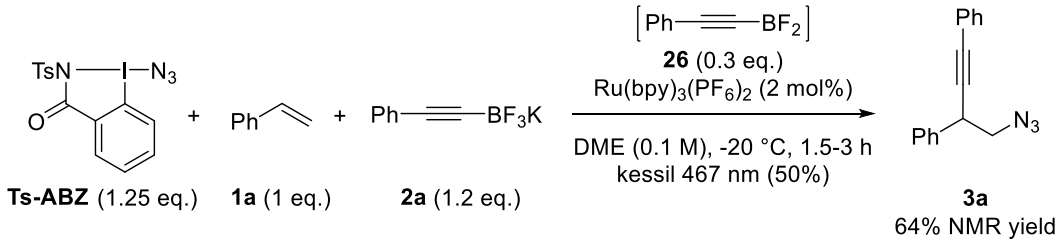
2) Activation of Ts-ABZ:

BF_3 is known to activate different hypervalent iodine reagent by coordinating the ligands.[27] In our case, NMR studies show no significant shift of the signals corresponding to Ts-ABZ in the presence of BF_3 in DME.

3) Abstraction of fluoride from alkynyl-BF_3K:

BF_3 is known to abstract fluoride from trifluoroborate salts to form BF_4^- and neutral R-BF_2 compounds. This reactivity is known for alkynyl-BF_3K[28] and a control experiment in which alkynyl-BF_2 was preformed and then added to the reaction afforded similar results as the standard conditions:





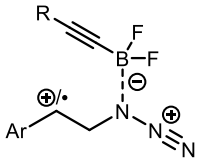
A capped oven-dried microwave vial charged with potassium trifluoro(phenylethynyl)borate (**2a**) (19 mg, 90 µmol, 0.9 equiv.) was evacuated and backfilled with N_2 (3x). Dry degassed DME (0.54 mL) was added and the solution was cooled to 0 °C. Then, a stock solution of BF_3•Et_2O (11 µL, 90 µmol, 0.9 equiv.) in dry DME (0.36 mL) was added and the mixture was stirred at 0 °C for 30 min.

An oven-dried test tube charged with $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 2.0 µmol, 0.02 equiv.), **Ts-ABZ** (55 mg, 0.13 mmol, 1.25 equiv.) and potassium trifluoro(phenylethynyl)borate (**2a**) (25 mg, 0.12 mmol, 1.20 equiv.) was evacuated and backfilled with N_2 (3x). Dry degassed DME (0.7 mL) and styrene (**1a**) (11.5 µL, 0.100 mmol, 1.00 equiv.) were added and the mixture was cooled to -20 °C. Then, the stock solution of **26** in dry degassed DME (0.34 mL, 0.3 equiv.) was added and the reaction was stirred under blue LEDs irradiation (1 x Kessil 467 nm 50% intensity, 22 W) at -20 °C for 1.5 h. The reaction mixture was filtered through a short plug of silica and eluted with DCM then concentrated *in vacuo*. Crude NMR yield of **3a** was determined to be 64% using CH_2Br_2 (3.5 µL, 50 µmol, 0.5 equiv.) as internal standard.

A control reaction was carried out in parallel using the standard conditions on 0.1 mmol scale and afforded **3a** in 71% NMR yield.

[27] A. Dasgupta, C. Thiehoff, P. D. Newman, T. Wirth, R. L. Melen, *Org. Biomol. Chem.* **2021**, *19*, 4852–4865.
[28] T. A. Mitchell, J. W. Bode, *J. Am. Chem. Soc.* **2009**, *131*, 18057–18059.

This result suggest that the 30 mol% of BF_3 are consumed to form alknyl-BF_2. The implication of this species in the reaction is not yet clear. A highly speculative explanation would rely on a potential coordination with the reactive azide intermediate (either radical or carbocation) leading to a pseudo intramolecular delivery of the alkyne, which could explain the higher yield. Similar intermolecular deliveries using oxygen anchors have been proposed.[29]



To try to probe this interaction we added a solution of alkynyl-BF_2 to benzyl azide. No NMR shift of the benzylic proton were observed.

Alknyl-BF_2 could also be directly quenched by another nucleophile in the mixture, such as 2-iodotosylbenzamide, leading to the formation of a potentially more nucleophilic tetravalent alkynyl-BF_2X^- salt.

With all the observation listed above we cannot properly conclude on the exact role of BF_3 although evidence suggest the formation of alknyl-BF_2 but its effect is still unclear. Those species are known to be in equilibrium in solution with other tetravalent boron compound which often lead to complex mechanistic scenarios.[30]

9.4 Cyclic voltammetry of Ts-ABZ

Cyclic voltammetry (CV) was performed using a BioLogic Potentiostat SP-150. Electrochemical cell consisted of a 10 mL glass sample vial (VC-4 type, ALS Co., LTD) equipped with a corresponding Teflon cap, an Ag wire coated with AgCl in 3 M NaCl as a reference electrode, a Pt wire as a counter electrode and a Pt surface with a diameter of 6 mm as a working electrode. Dry degassed solution of 0.1 M *n*-Bu_4NPF_6 in MeCN was used as a support electrolyte. A ferrocene/ferrocenium (Fc/Fc^+) couple was used as an internal reference. Conversion from Fc/Fc^+ to SCE was carried out using the reference therein.[31]

[29] (a) R. William, S. Wang, A. Mallick, X.-W. Liu, *Org. Lett.* **2016**, *18*, 4458–4461. (b) S. Roscales, V. Ortega, A. G. Csákÿ, *J. Org. Chem.* **2018**, *83*, 11425–11436.
[30] C.-V. T. Vo, T. A. Mitchell, J. W. Bode, *J. Am. Chem. Soc.* **2011**, *133*, 14082–14089.
[31] V. V. Pavlishchuk, A. W. Addison, *Inorganica Chim. Acta* **2000**, *298*, 97–102.

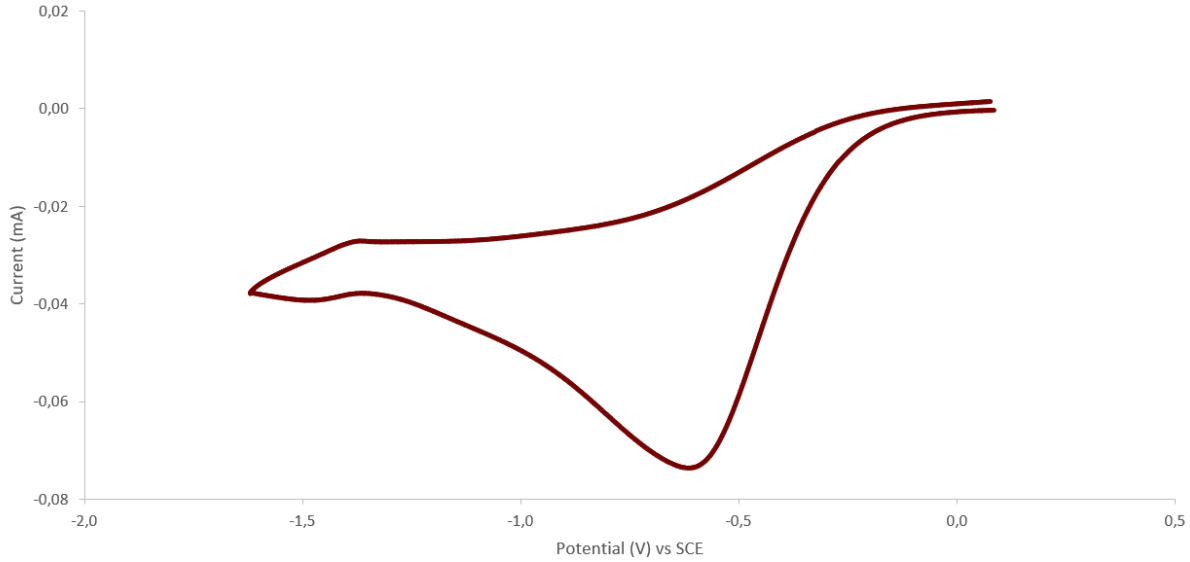


Figure S3: CV of **Ts-ABZ** vs SCE (0.1 M [TBA]PF_6 in CH_3CN), scan rate = 100 mV/s, $E_{1/2}^{red}$ = -0.62 V.

10. Crystal Structures

10.1 3i

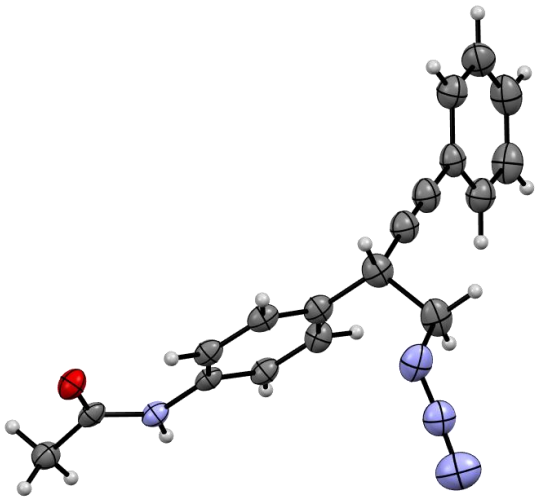


Figure S4: Ellipsoid plot (probability level 50%) of **3i**.

Compound	**3i**
Formula	$C_{18}H_{16}N_4O$
$D_{calc.}$/ g cm^{-3}	1.295
μ/mm^{-1}	0.672
Formula Weight	304.35
Colour	clear pale colourless
Shape	plate-shaped
Size/mm^3	0.24×0.20×0.07
T/K	140.00(10)
Crystal System	orthorhombic
Space Group	*Pccn*
a/Å	43.729(2)
b/Å	9.4992(4)
c/Å	7.5184(3)
α/°	90
β/°	90
γ/°	90
V/Å^3	3123.1(3)
Z	8
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K$_\alpha$
Θ_{min}/°	4.044
Θ_{max}/°	74.799
Measured Refl's.	11322
Indep't Refl's	3060
Refl's I≥2 σ(I)	2117
R_{int}	0.0431
Parameters	250
Restraints	122
Largest Peak	0.223
Deepest Hole	-0.196
GooF	1.041
wR_2 (all data)	0.1460
wR_2	0.1309
R_1 (all data)	0.0855
R_1	0.0552
CCDC number	2264031

Crystals were grown by dissolving **3i** in a small amount of DCM (~1mL), addition of hexane (~10 mL) and slow evaporation of this mixture over several days.

Analysis of the crystal: A suitable crystal with dimensions 0.24 × 0.20 × 0.07 mm^3 was selected and mounted on a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The crystal was kept at a steady T = 140.00(10) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on ***F*²**.

10.2 6

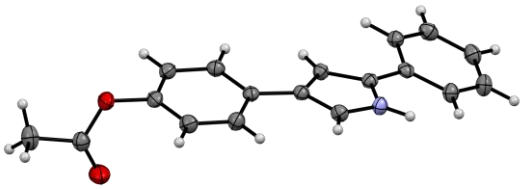


Figure S5: Ellipsoid plot (probability level 50%) of **6**.

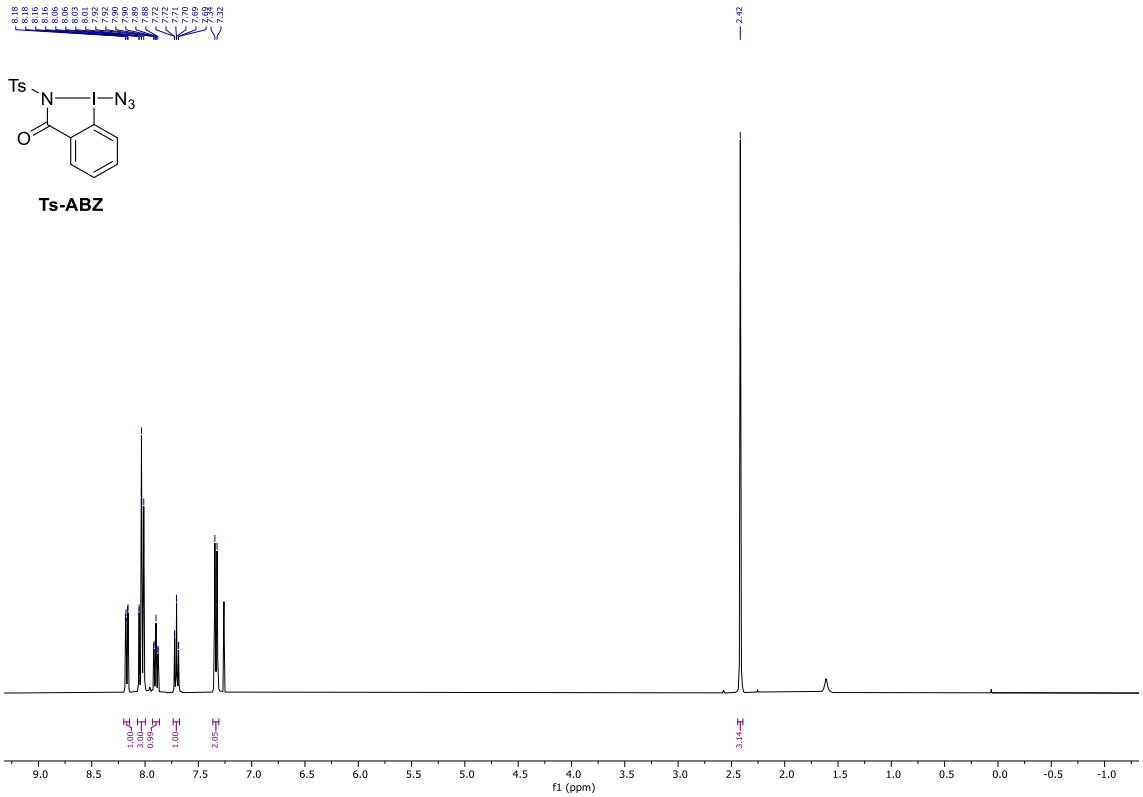
Crystals were grown by dissolving **6** in a small amount of DCM (~1mL), addition of hexane (~10 mL) and slow evaporation of this mixture over several days.

Analysis of the crystal: A suitable crystal with dimensions 0.18 × 0.14 × 0.02 mm^3 was selected and mounted on an XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The crystal was kept at a steady T = 140.00(10) K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full-matrix least-squares minimisation on F^2.

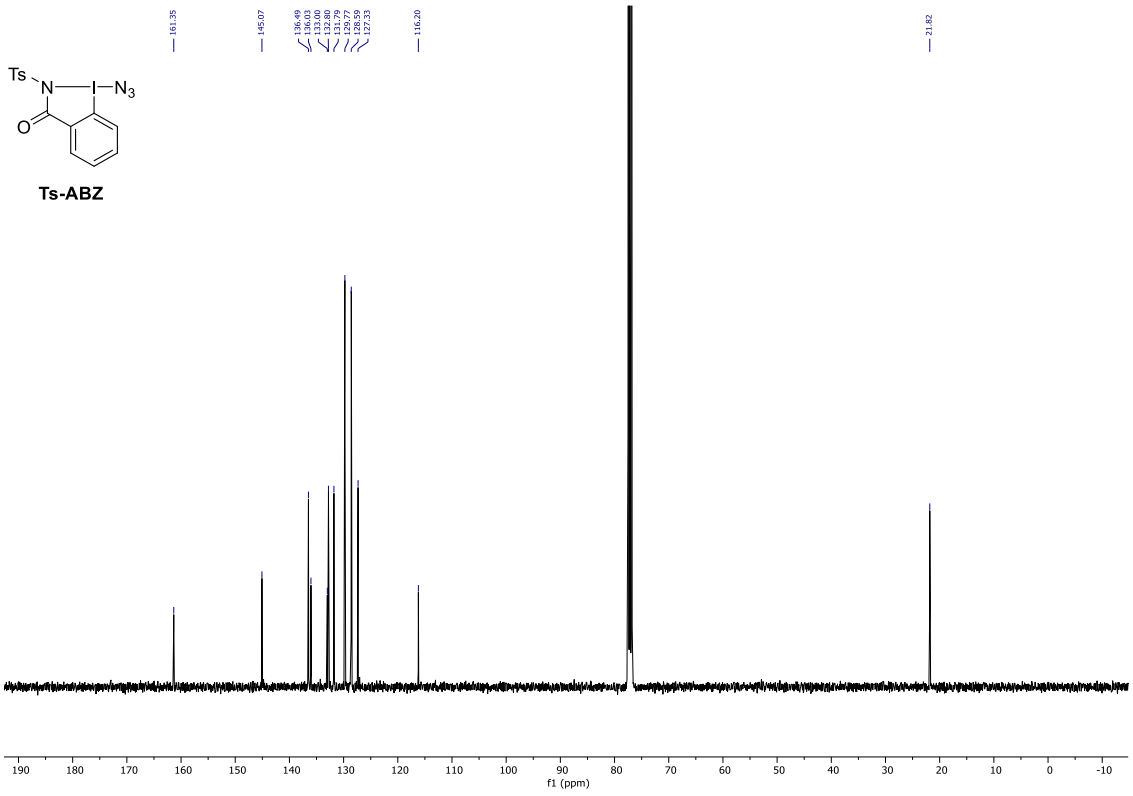
Compound	**6**
Formula	$C_{18}H_{15}NO_2$
$D_{calc.}$/ g cm^{-3}	1.294
μ/mm^{-1}	0.677
Formula Weight	277.31
Colour	colourless
Shape	plate-shaped
Size/mm^3	0.18×0.14×0.02
T/K	140.00(10)
Crystal System	orthorhombic
Flack Parameter	0.04(9)
Space Group	$P2_12_12_1$
a/Å	5.80631(11)
b/Å	7.77611(12)
c/Å	31.5189(6)
α/°	90
β/°	90
γ/°	90
V/$Å^3$	1423.09(4)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu$K\alpha$
Θ_{min}/°	2.804
Θ_{max}/°	75.554
Measured Refl's.	12451
Indep't Refl's	2932
Refl's I≥2σ(I)	2786
R_{int}	0.0183
Parameters	197
Restraints	0
Largest Peak/e $Å^{-3}$	0.211
Deepest Hole/e $Å^{-3}$	-0.148
GooF	1.034
wR_2 (all data)	0.0782
wR_2	0.0770
R_1 (all data)	0.0318
R_1	0.0297
CCDC number	2243553

11. Spectra of New Compounds

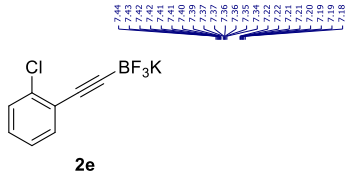
^{1}H NMR (400 MHz, $CDCl_3$) of **Ts-ABZ**:



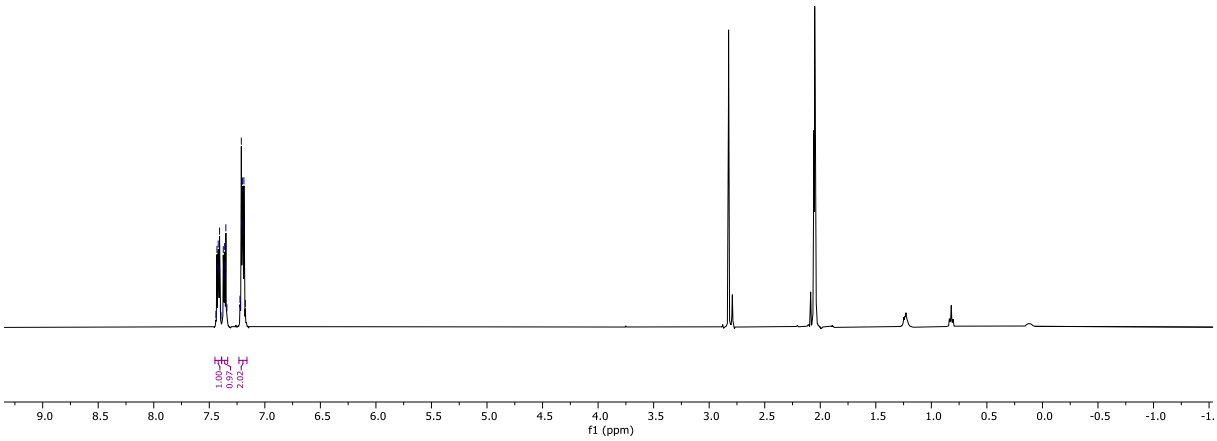
^{13}C NMR (101 MHz, $CDCl_3$) of **Ts-ABZ**:



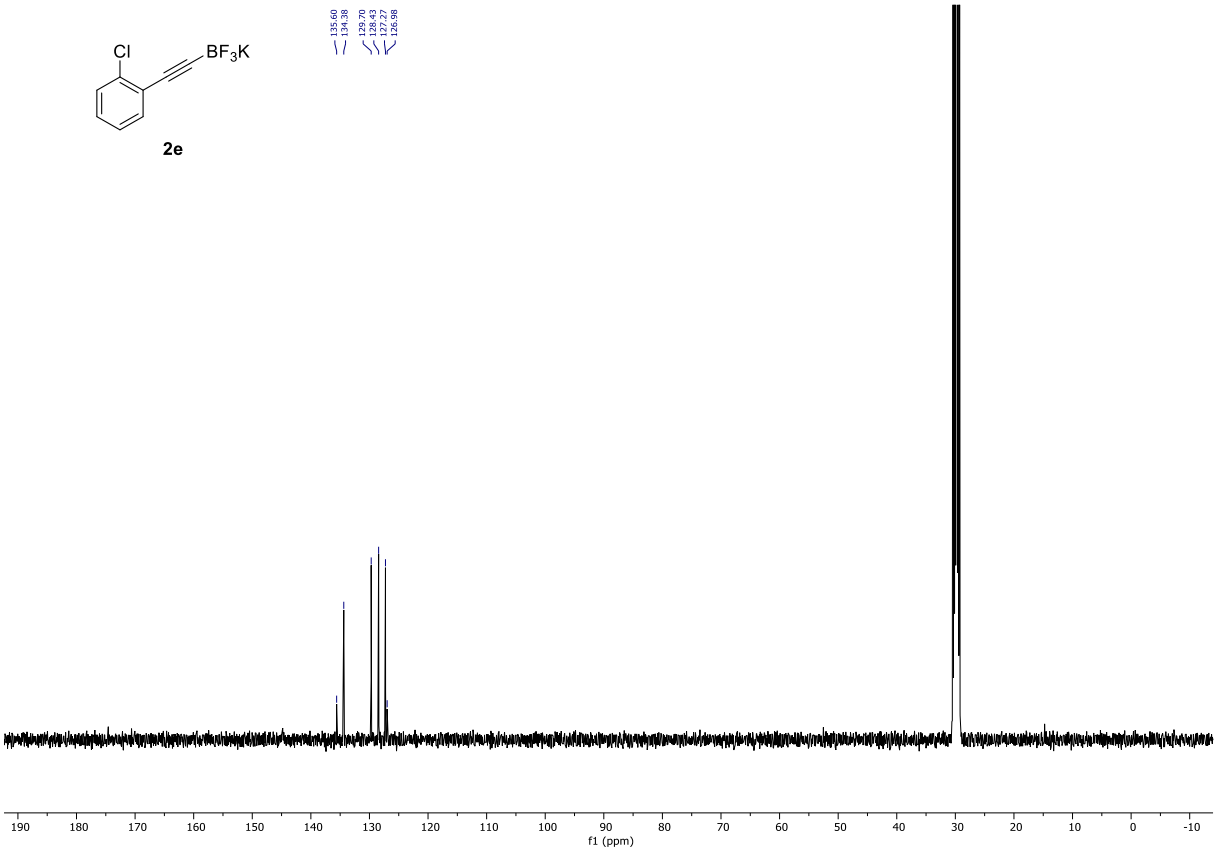
^{1}H NMR (400 MHz, acetone-d_6) of compound **2e**:



2e

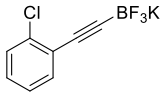


^{13}C NMR (101 MHz, acetone-d_6) of compound **2e**:

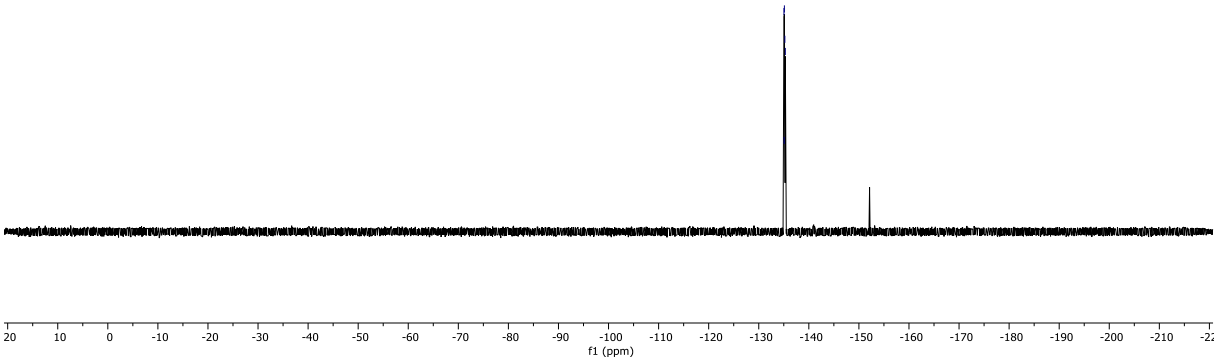


2e

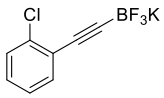
^{19}F NMR (376 MHz, acetone-d_6) of compound **2e**:



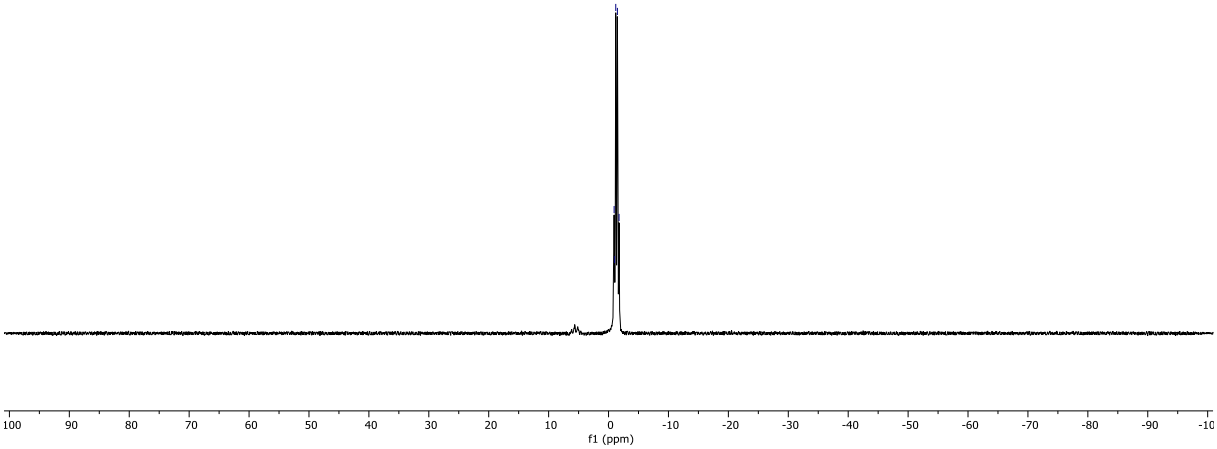
2e



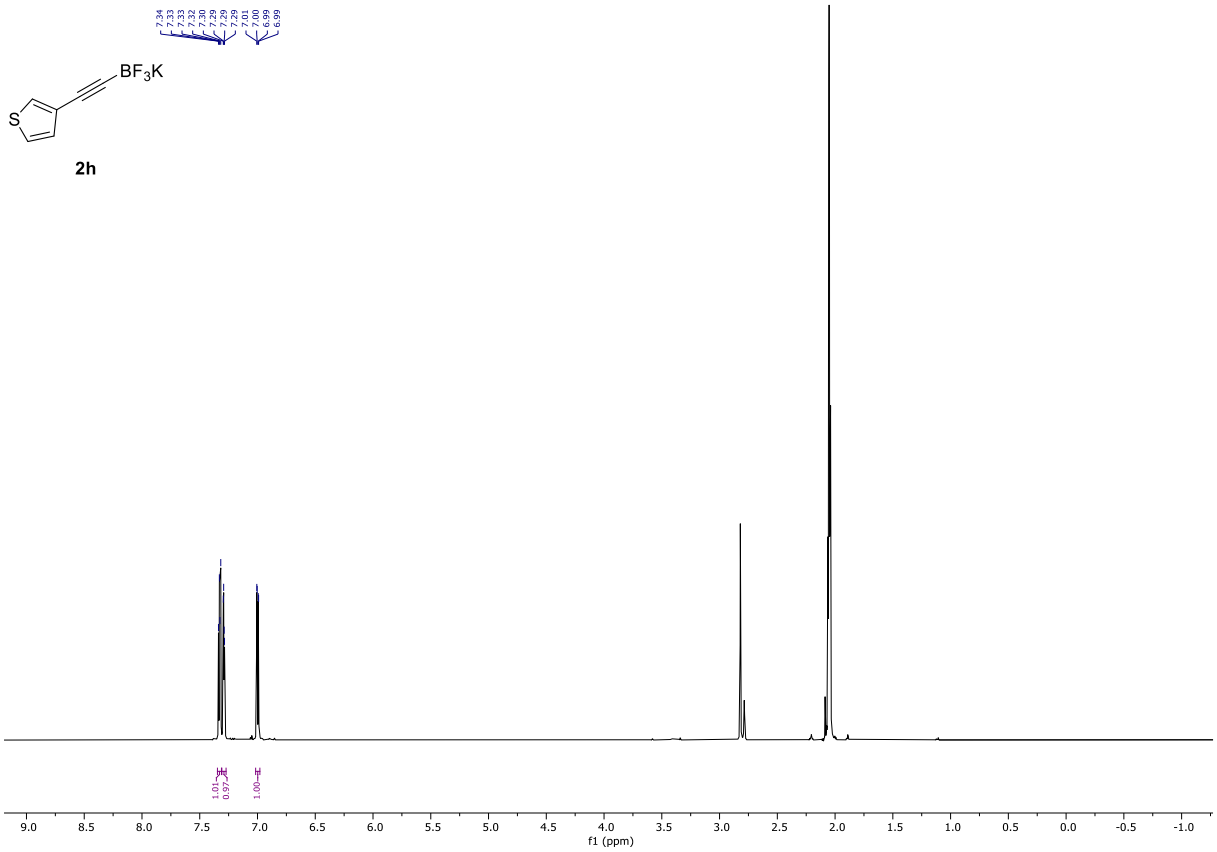
^{11}B NMR (128 MHz, acetone-d_6) of compound **2e**:



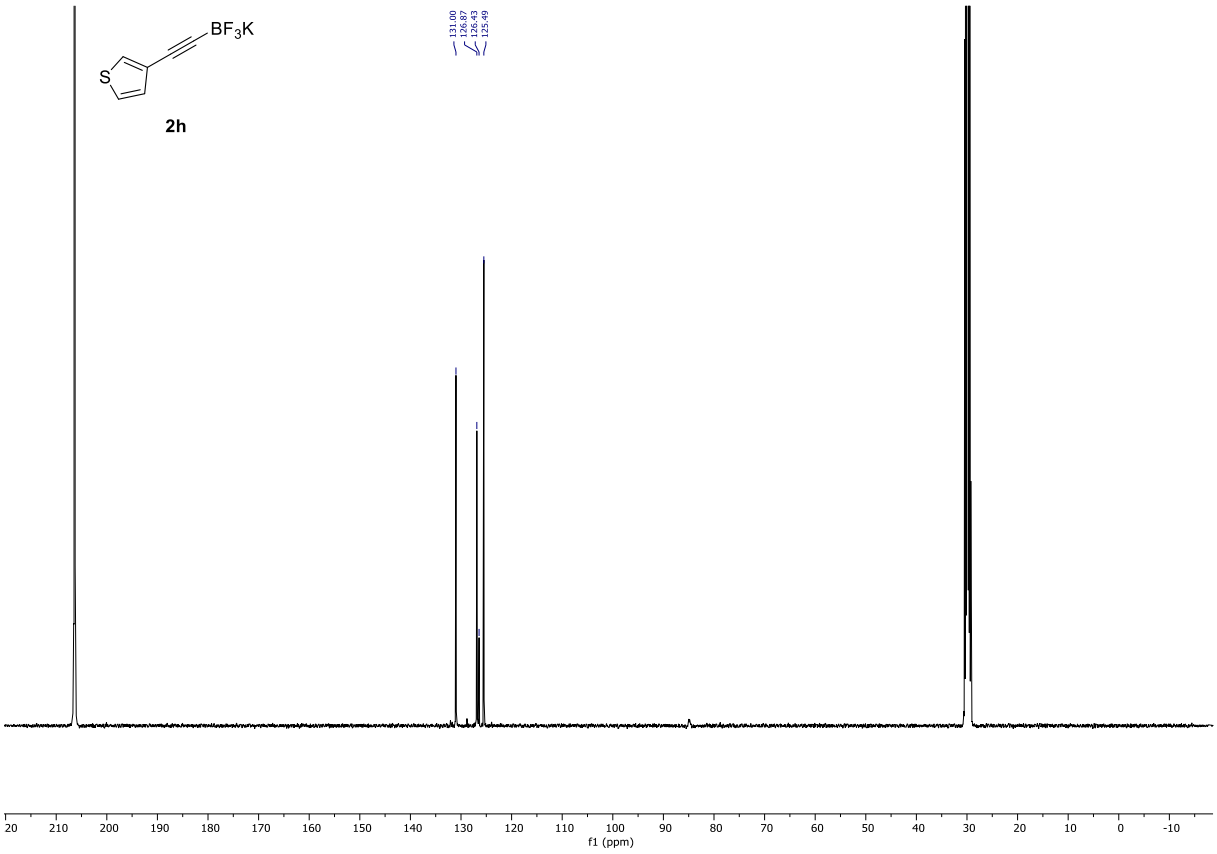
2e



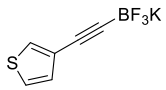
^{1}H NMR (400 MHz, acetone-d_6) of compound **2h**:



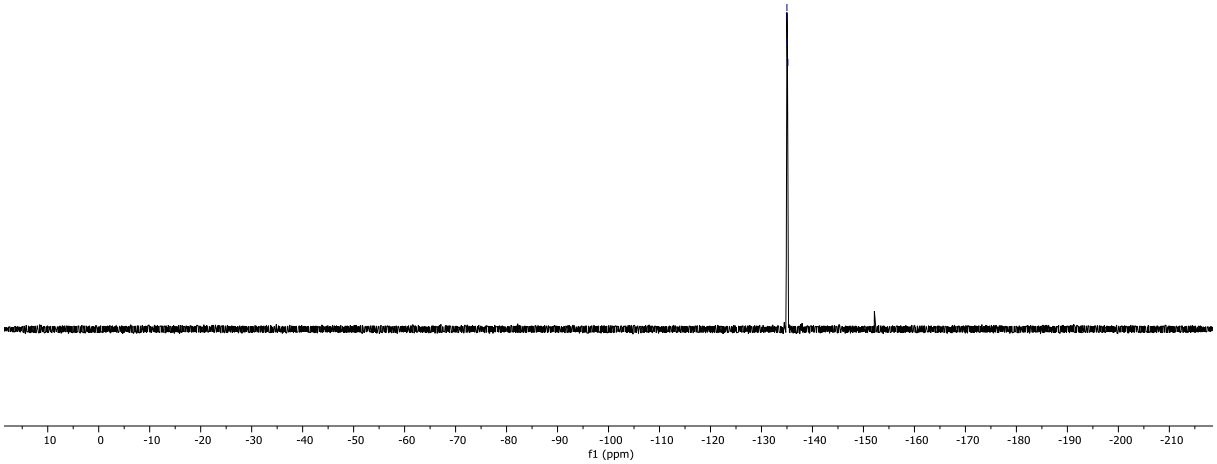
^{13}C NMR (101 MHz, acetone-d_6) of compound **2h**:



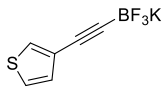
^{19}F NMR (376 MHz, acetone-d_6) of compound **2h**:



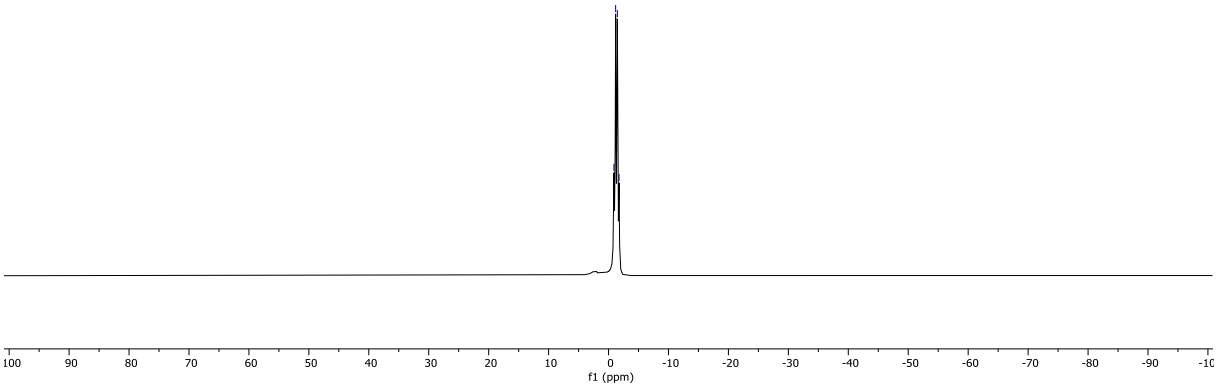
2h



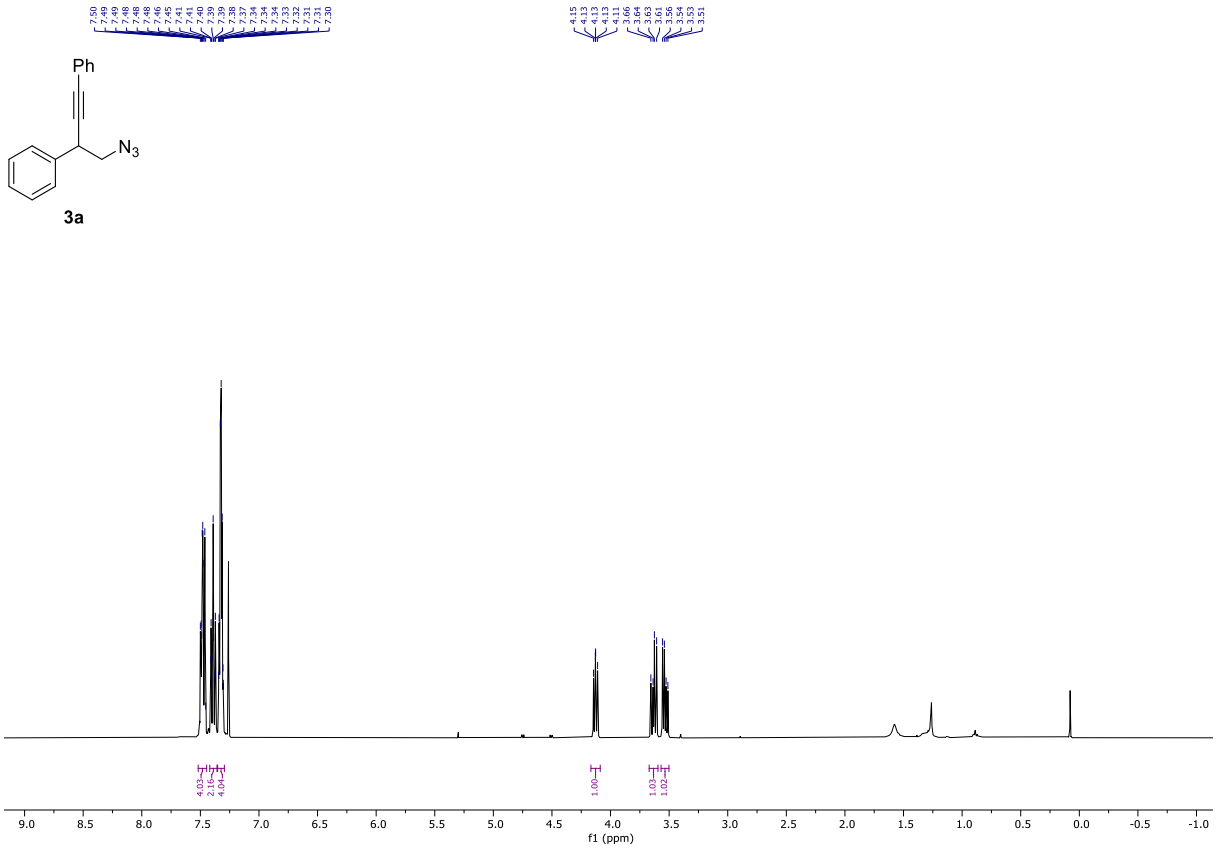
^{11}B NMR (128 MHz, acetone-d_6) of compound **2h**:



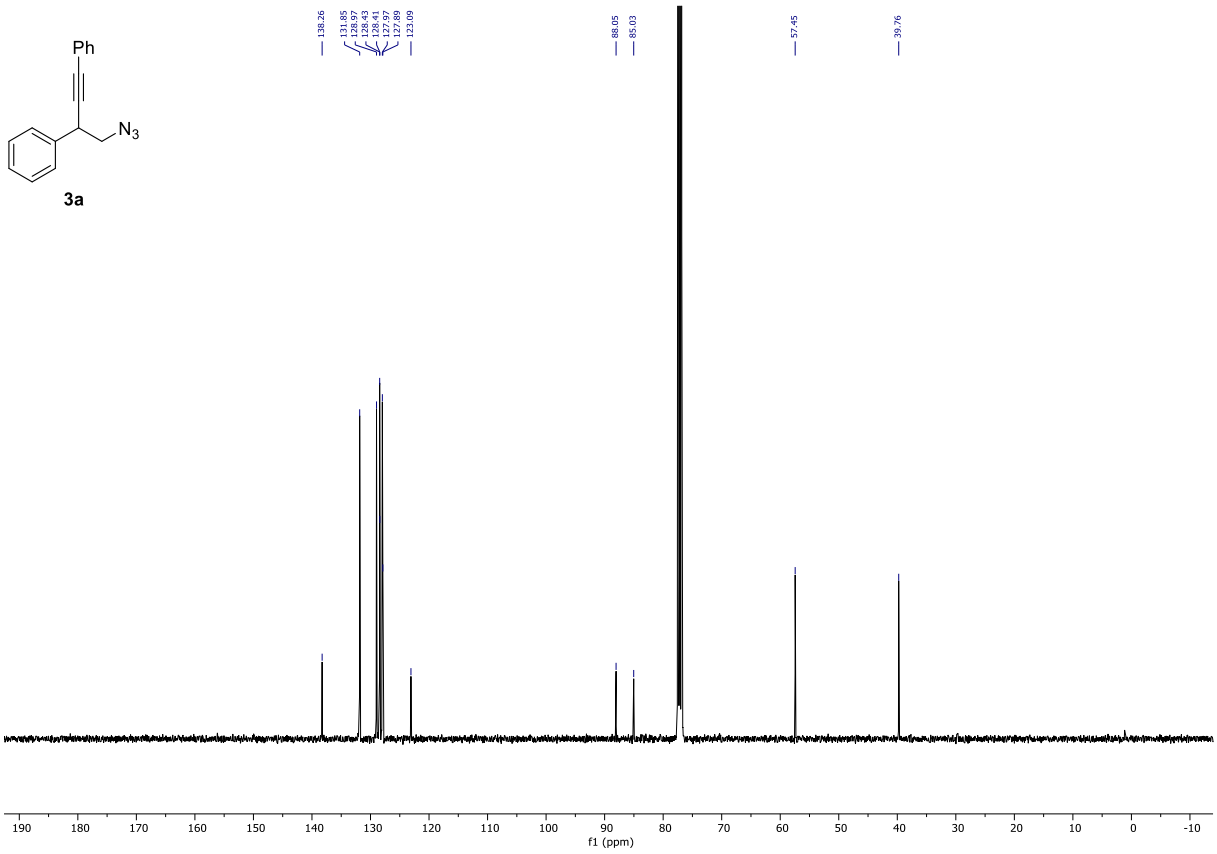
2h



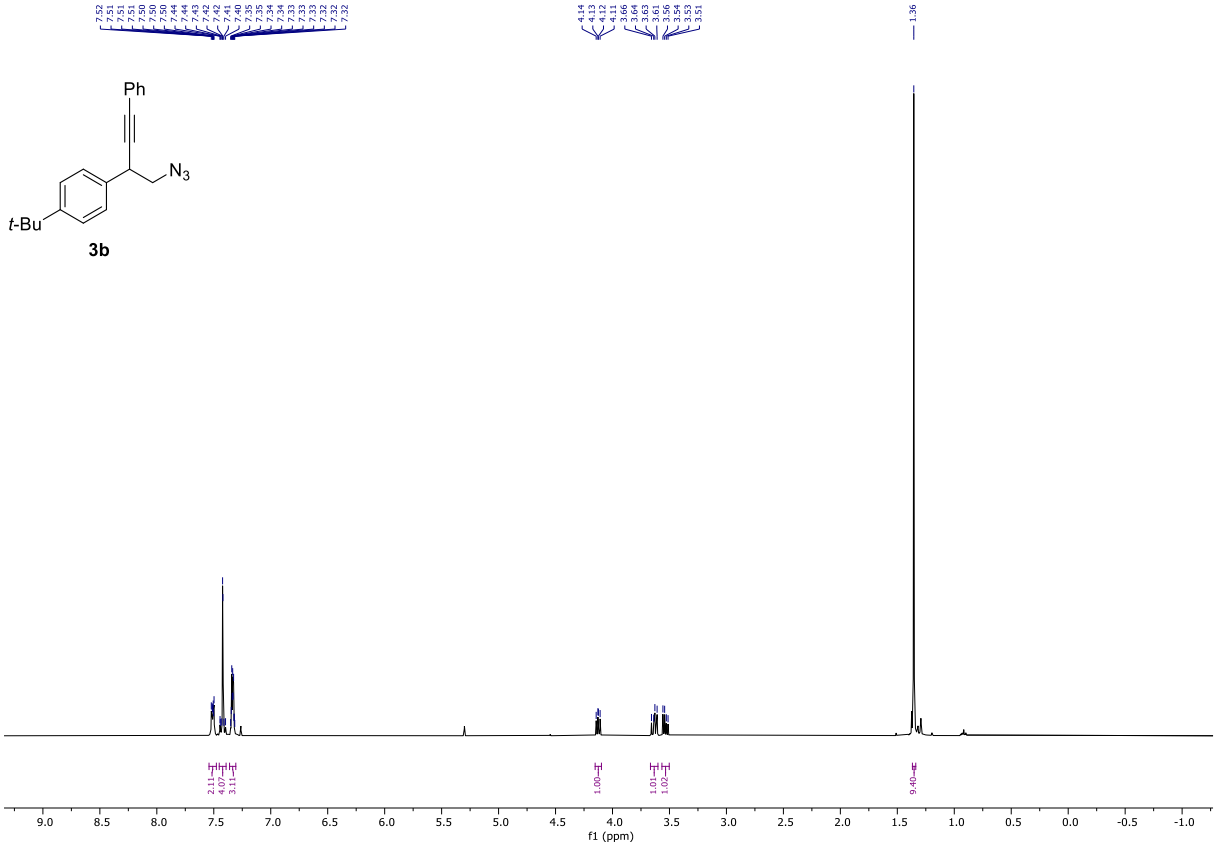
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**:



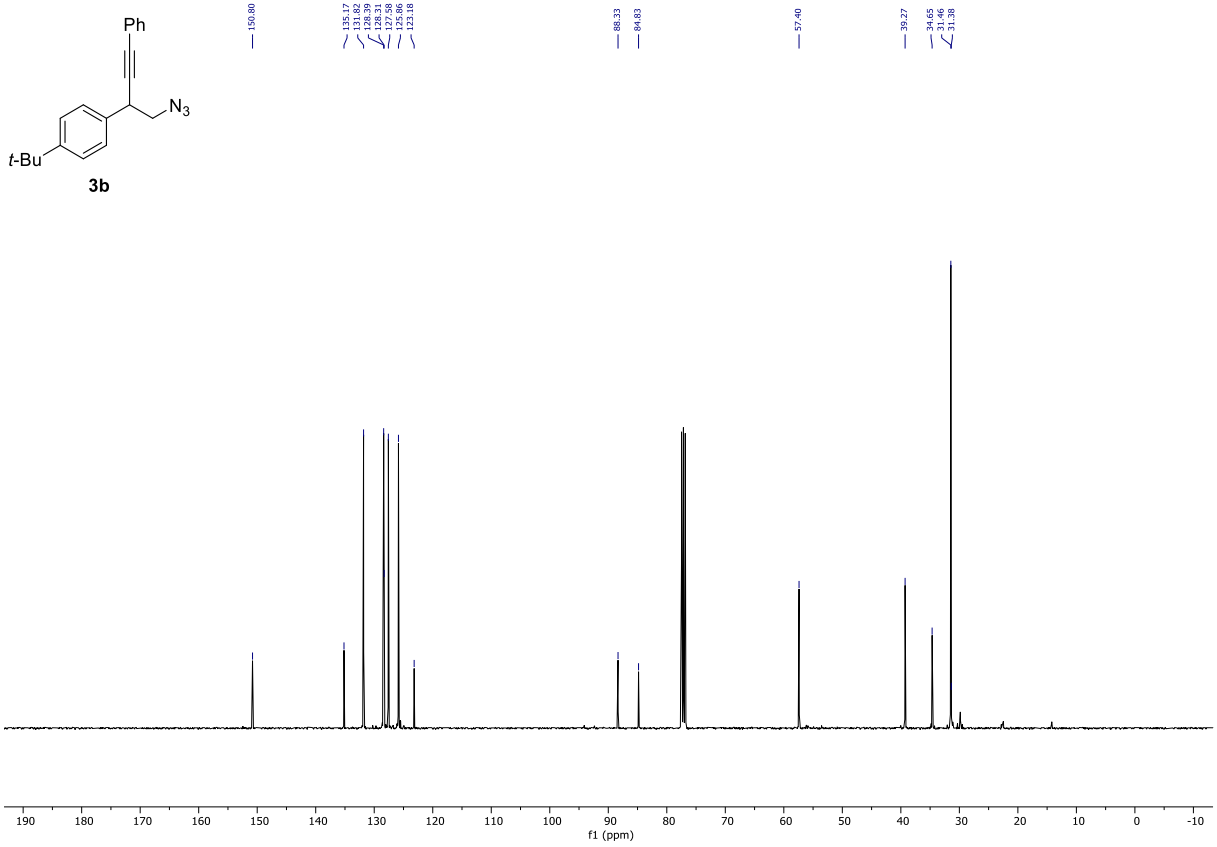
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3a**:



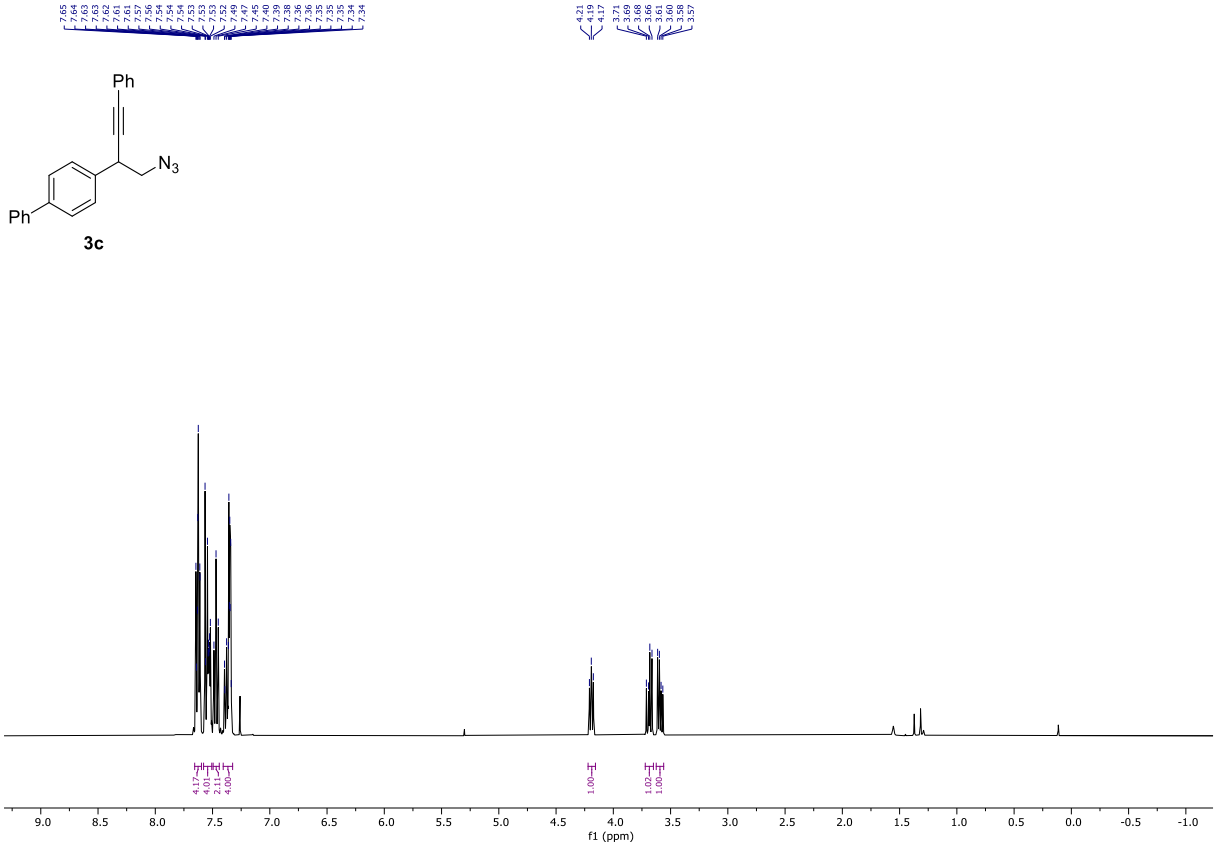
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**:



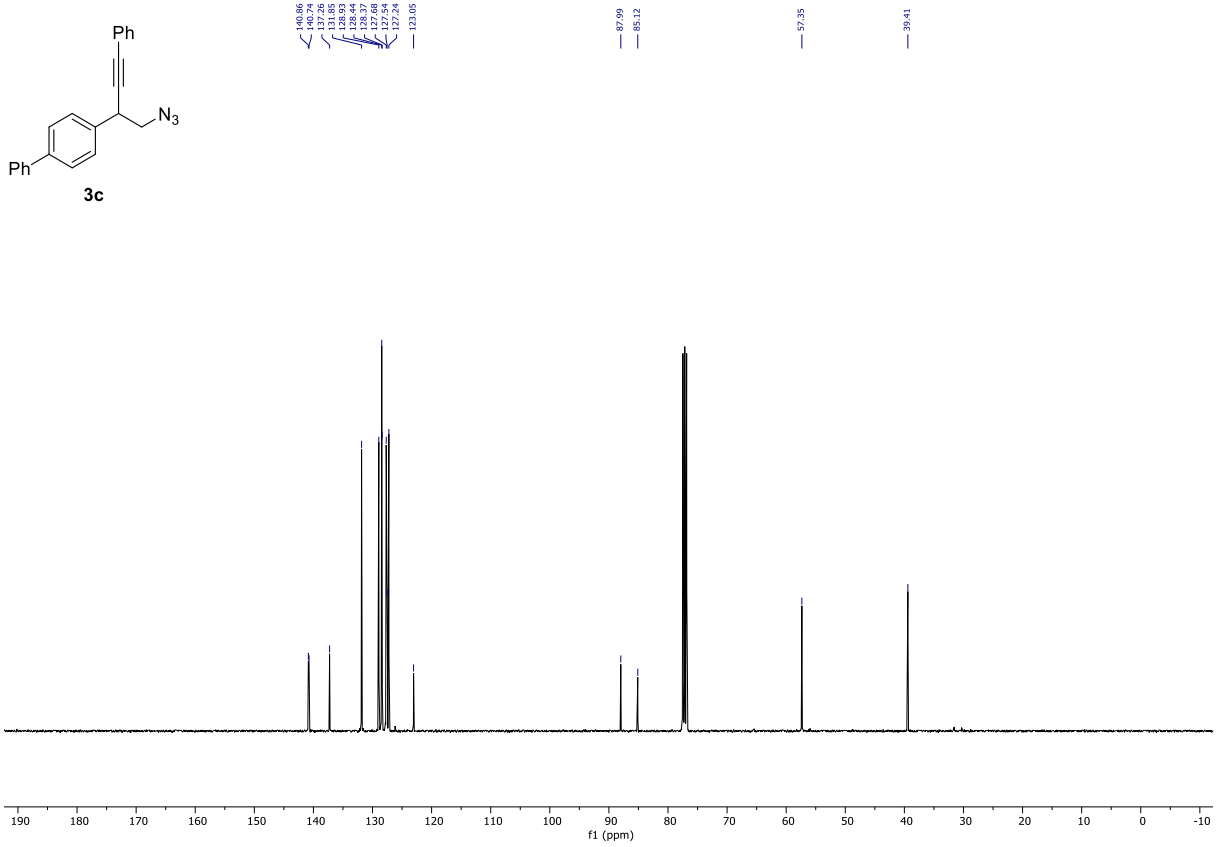
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3b**:



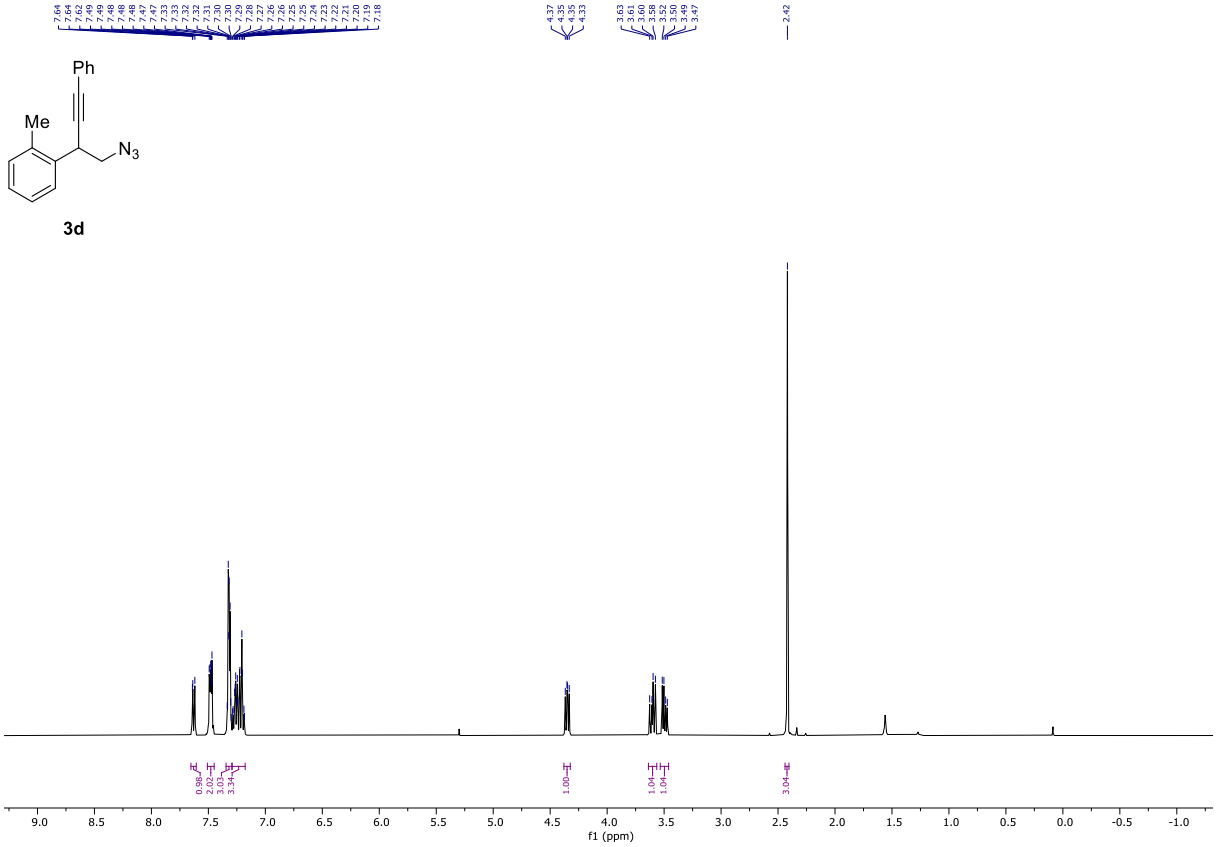
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**:



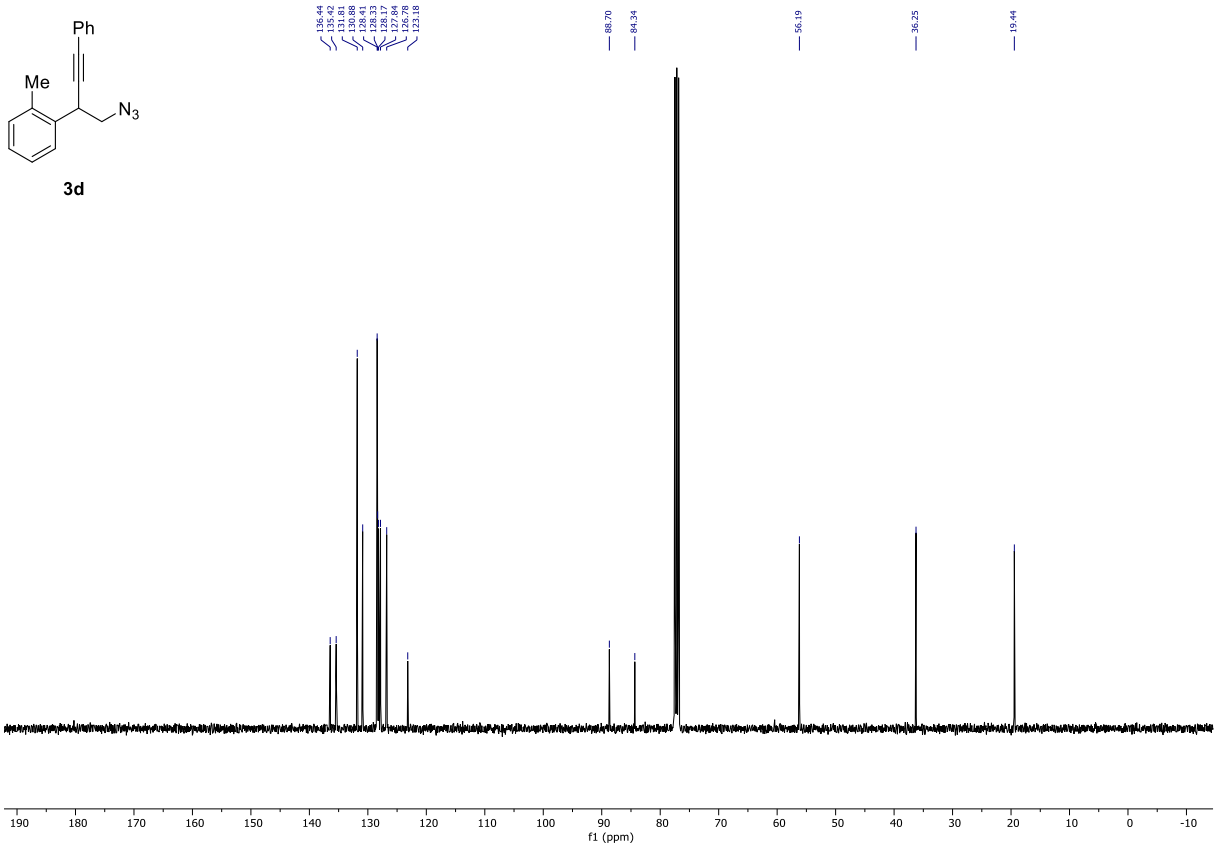
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3c**:



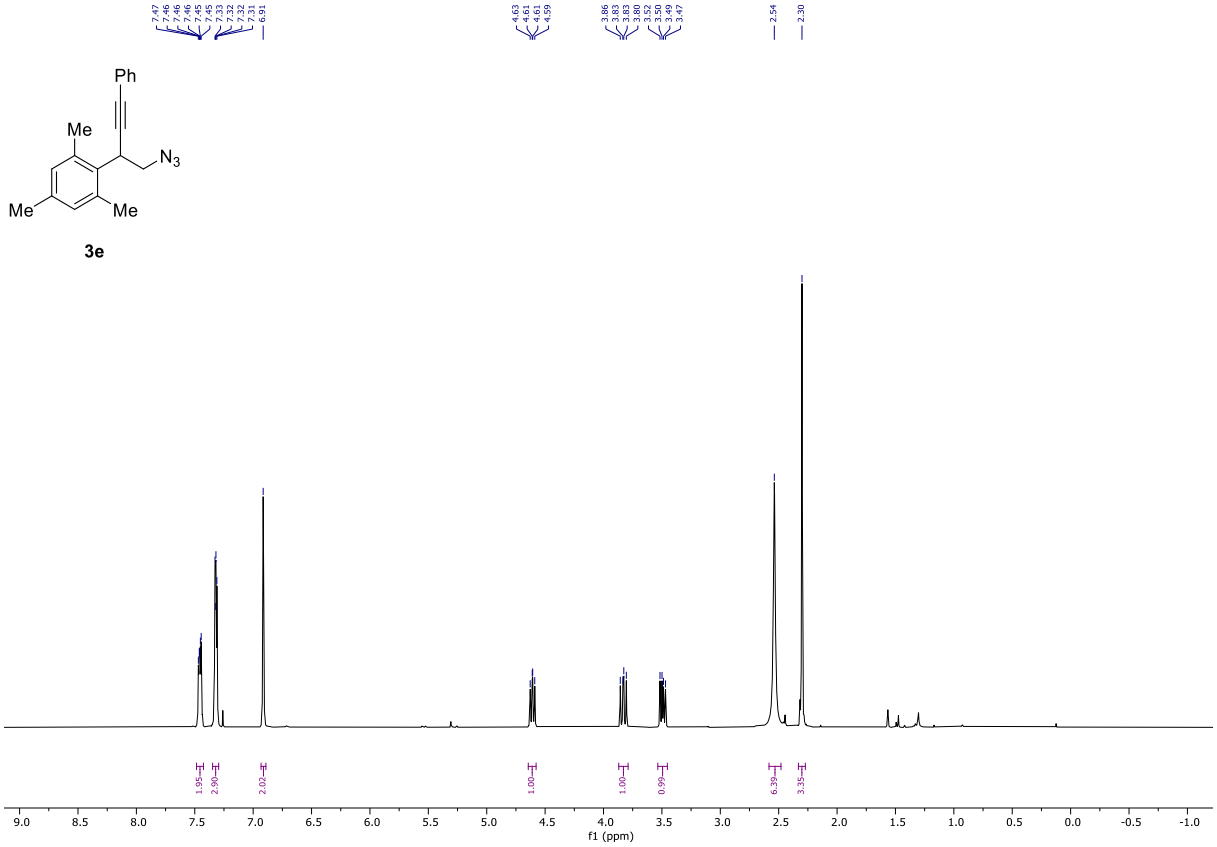
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**:



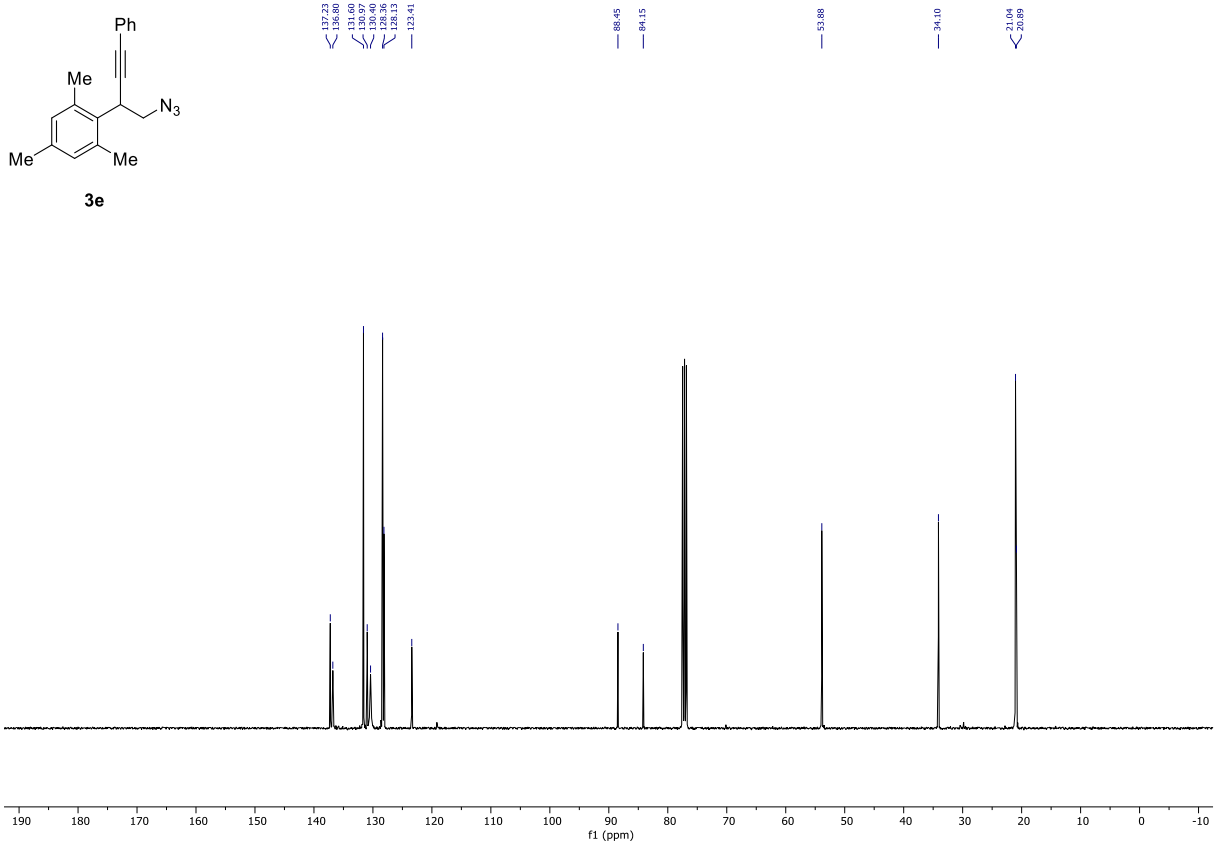
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3d**:



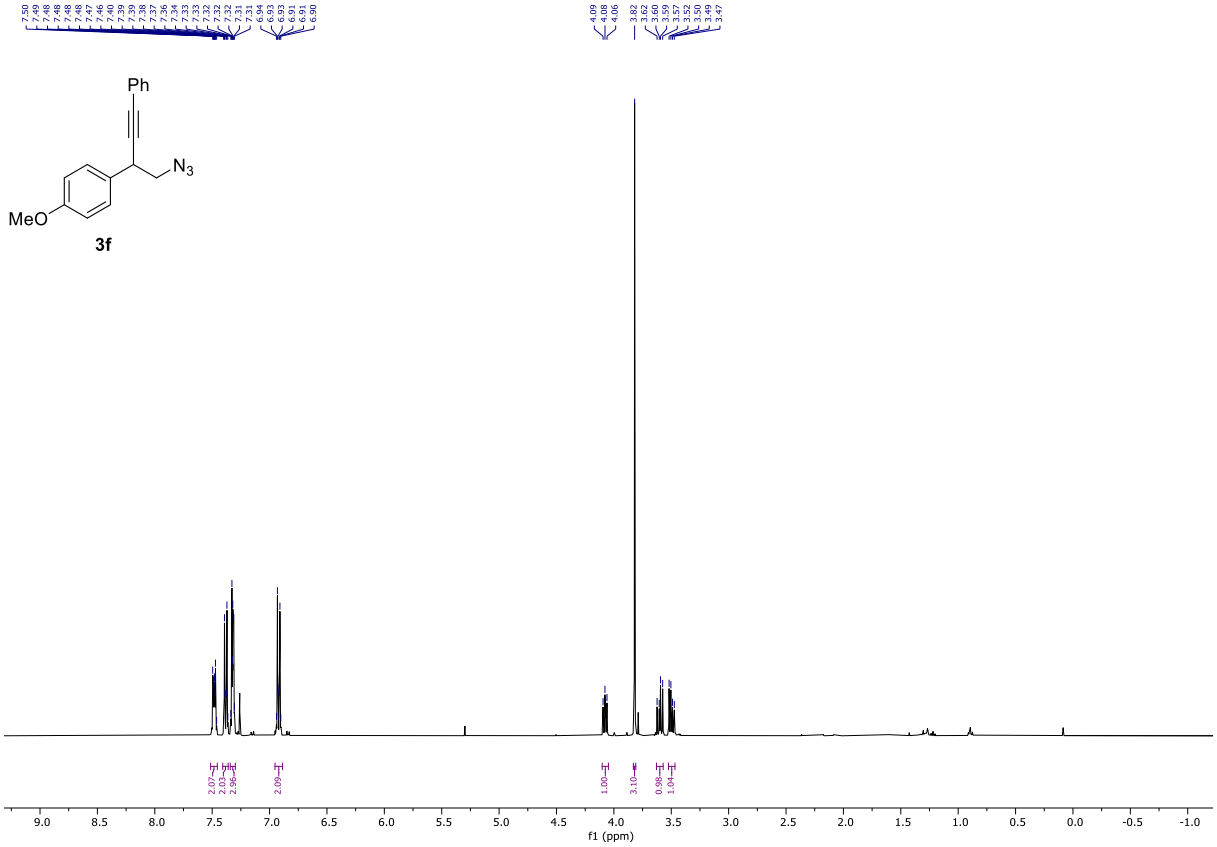
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**:



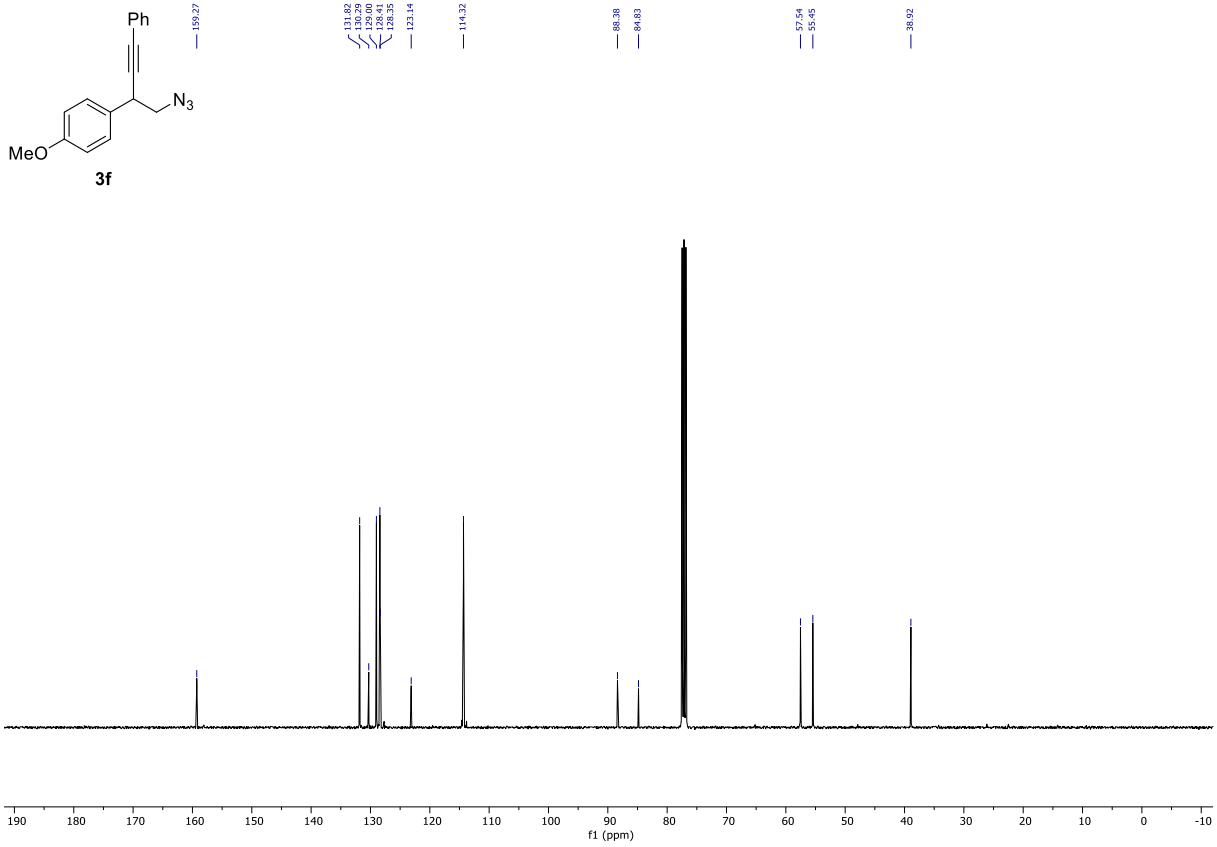
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3e**:



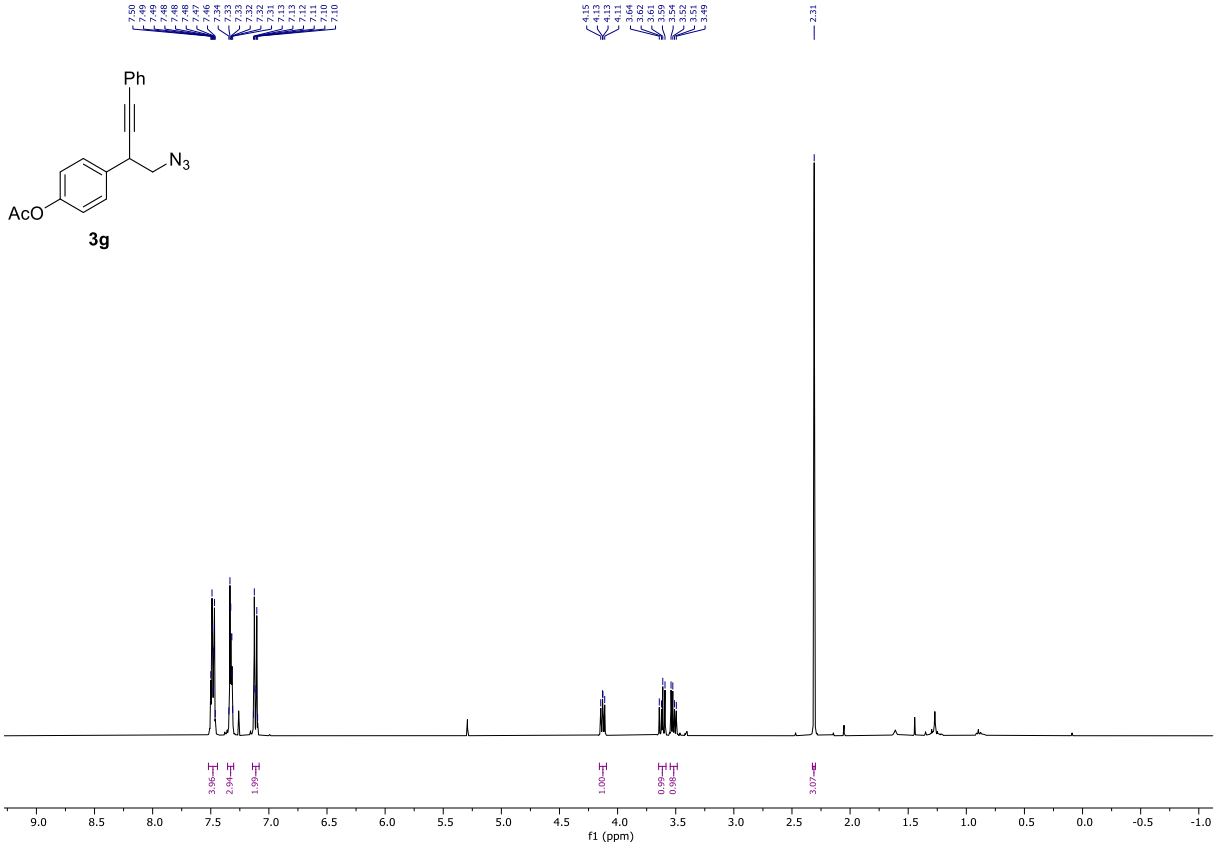
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**:



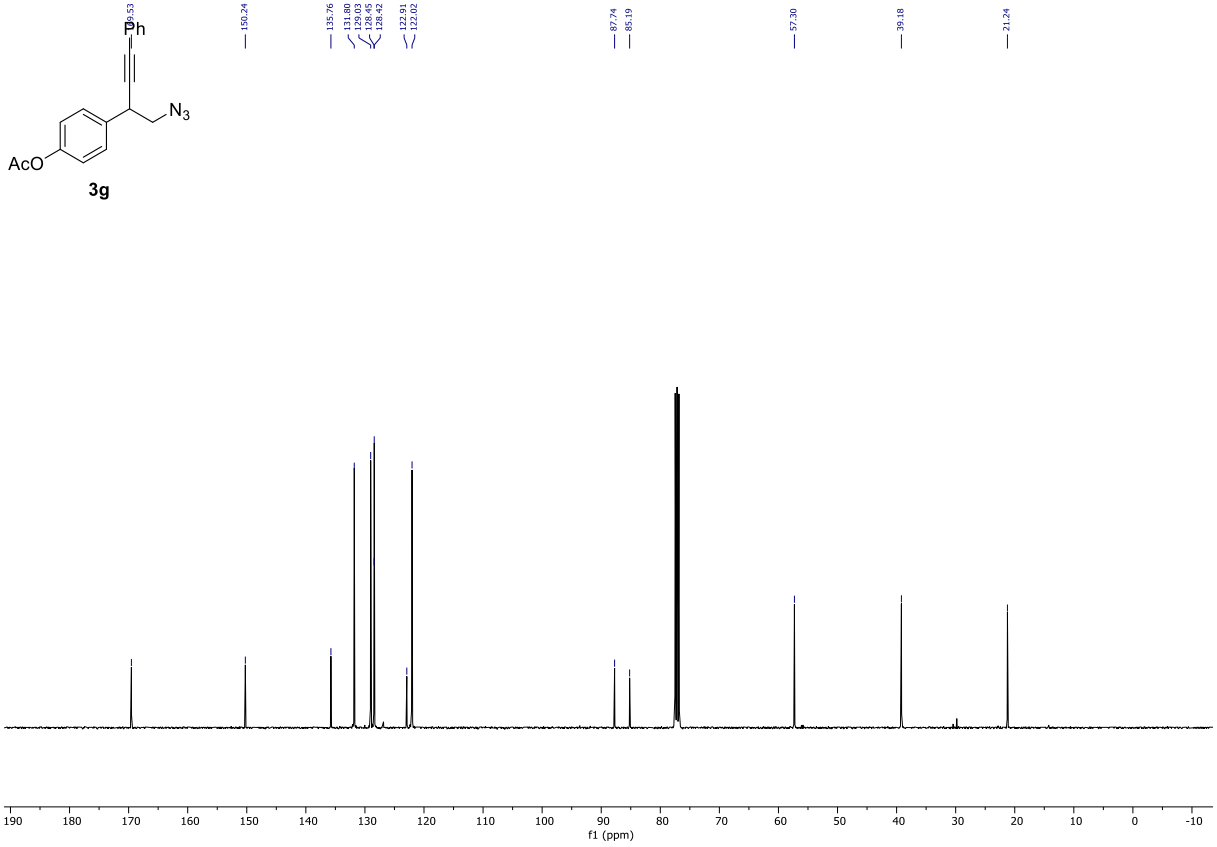
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3f**:



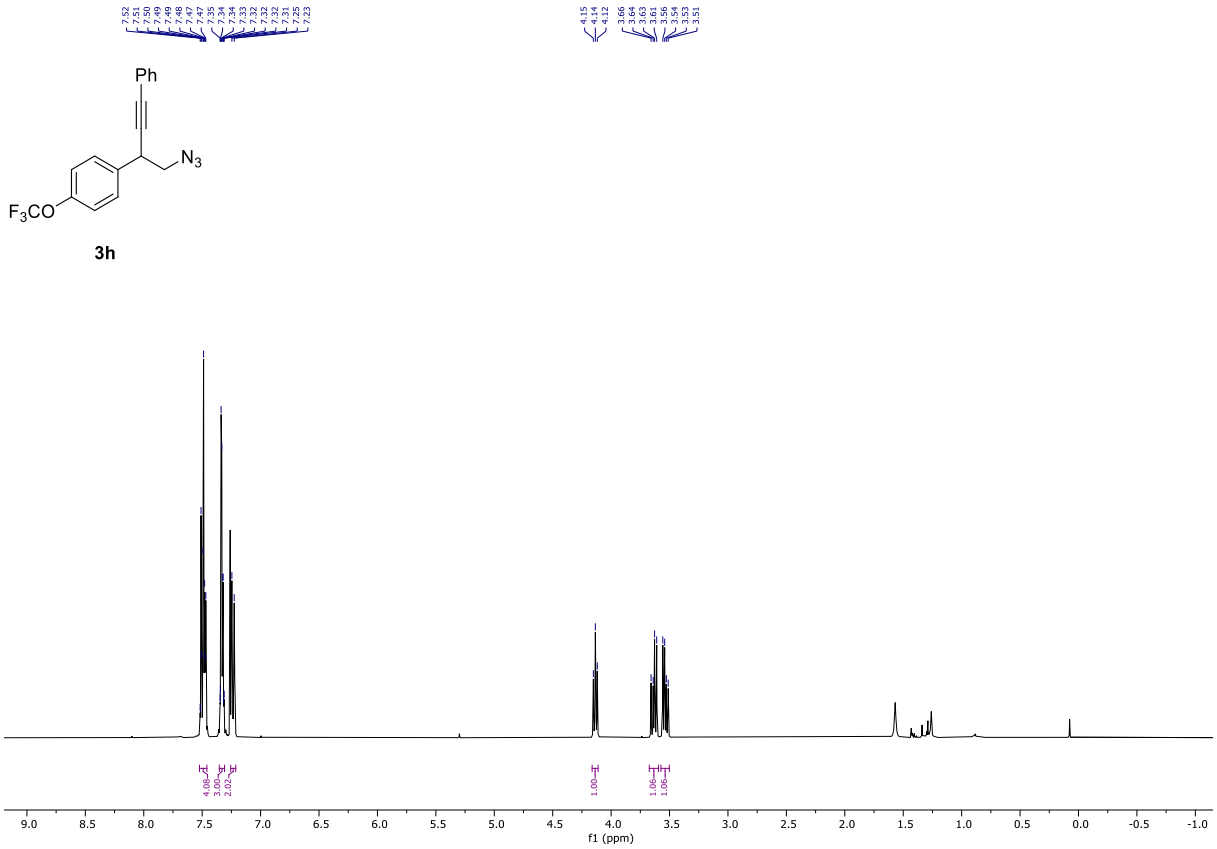
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**:



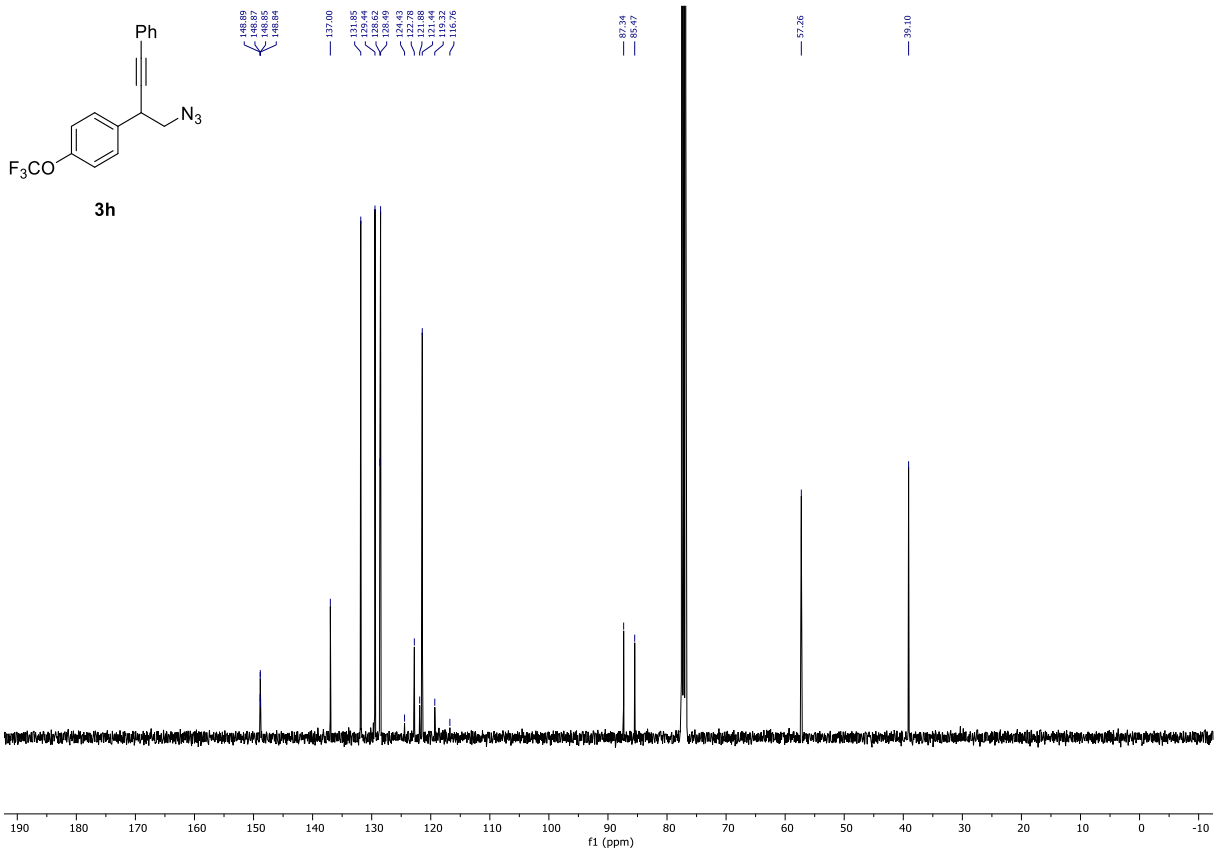
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3g**:



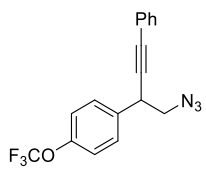
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**:



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

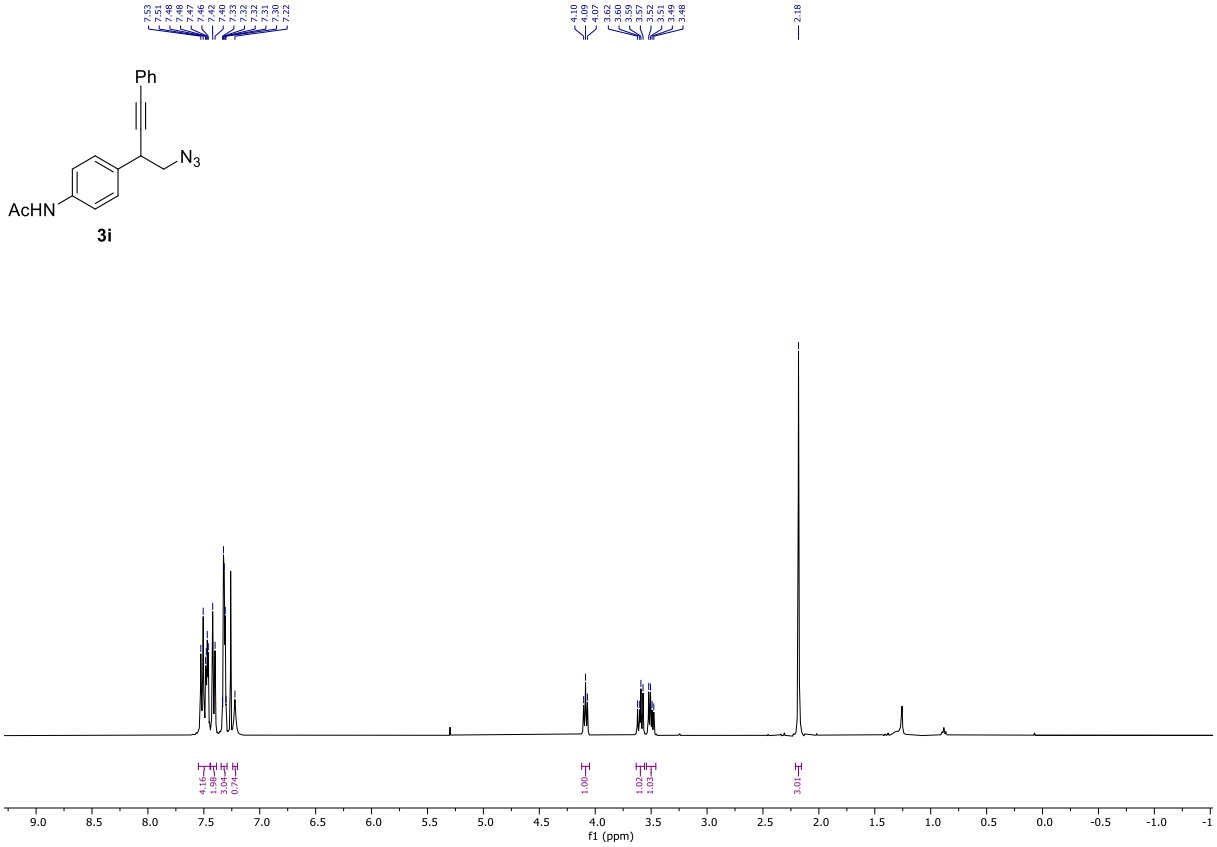


^{19}F NMR (376 MHz, $CDCl_3$) of compound **3h**:

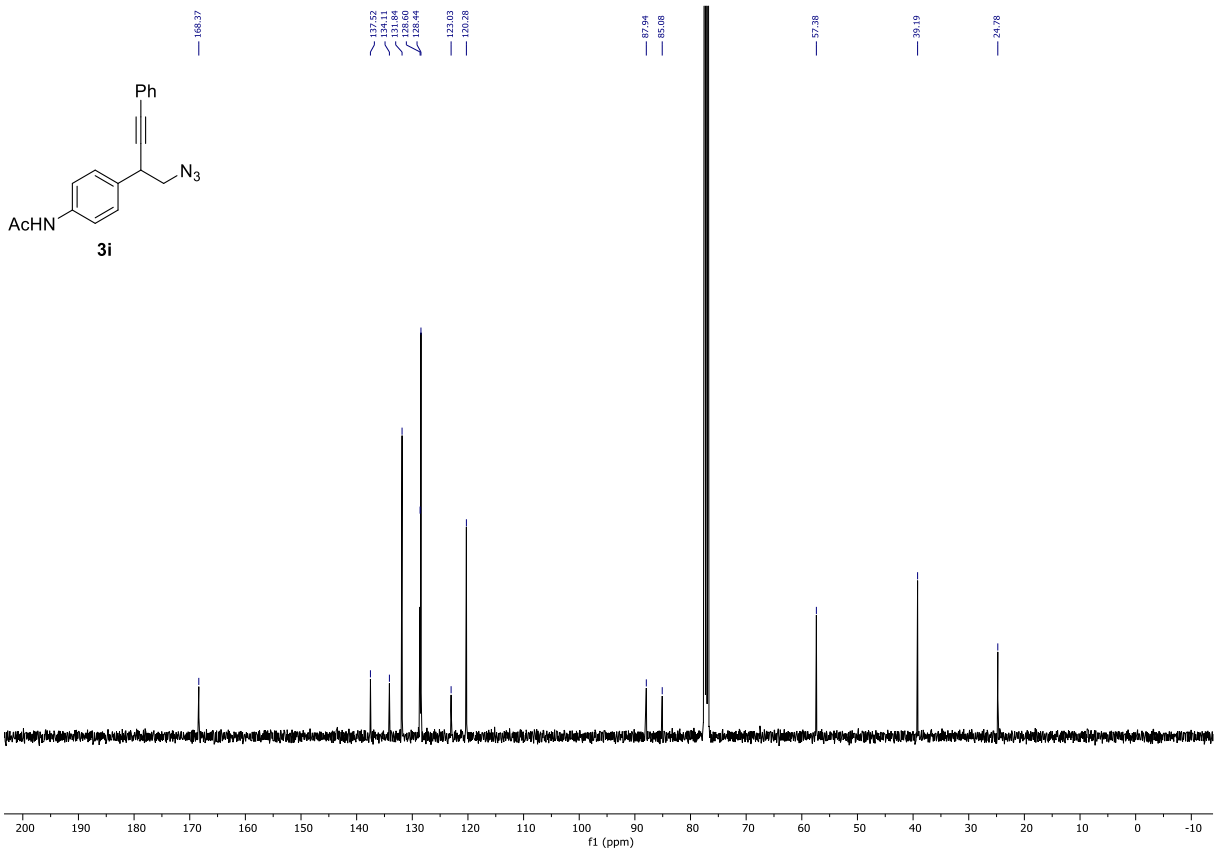


3h

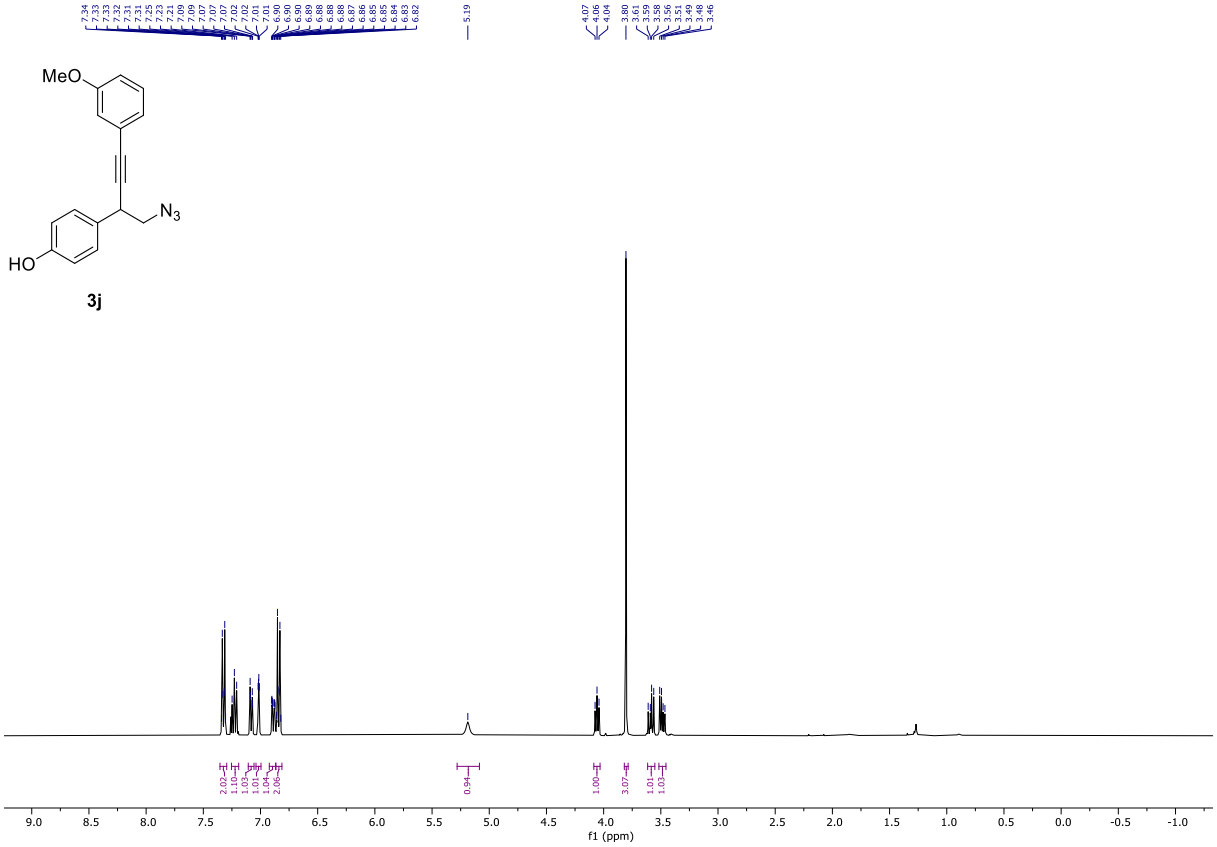
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**:



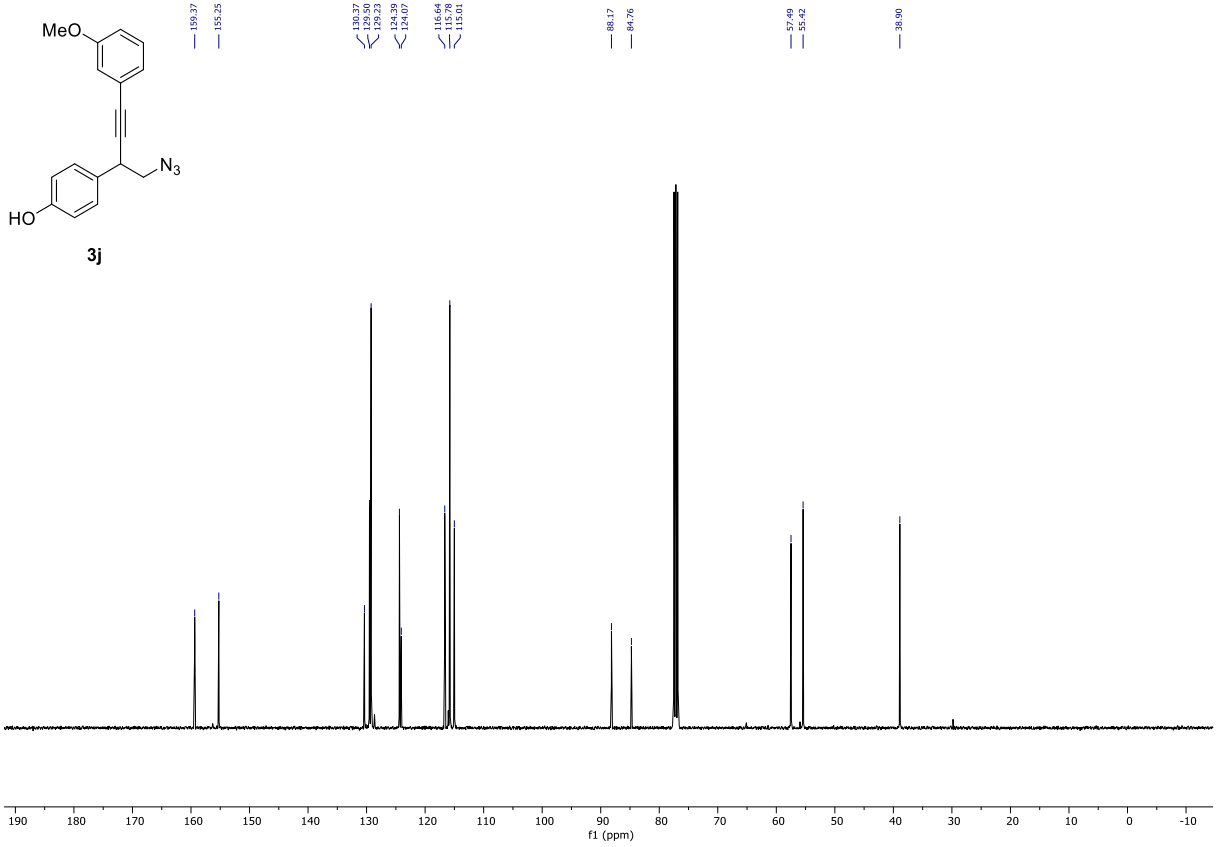
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3i**:



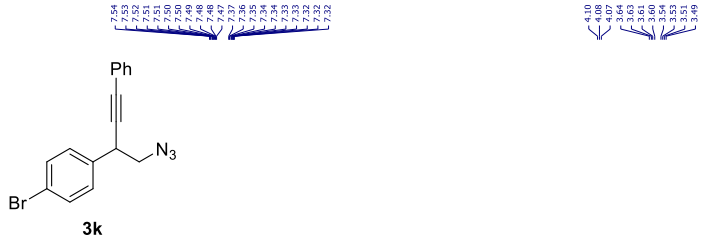
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**:



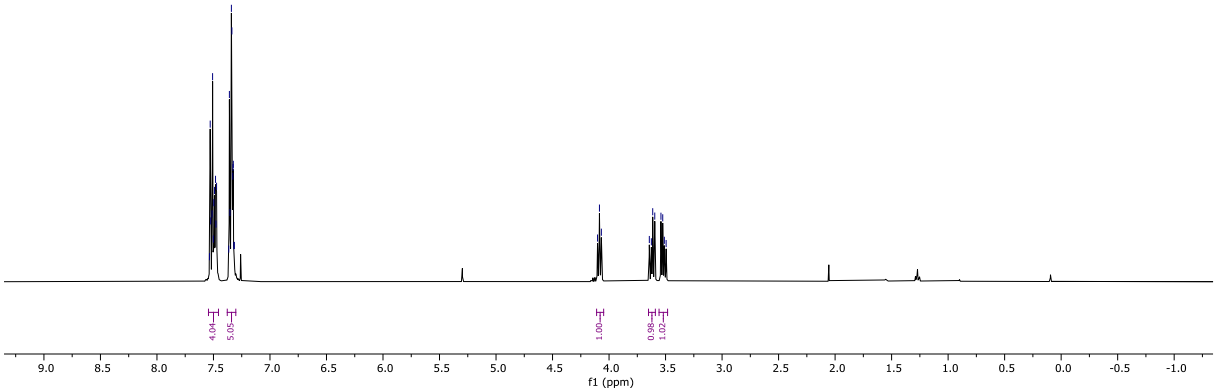
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3j**:



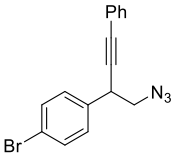
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k**:



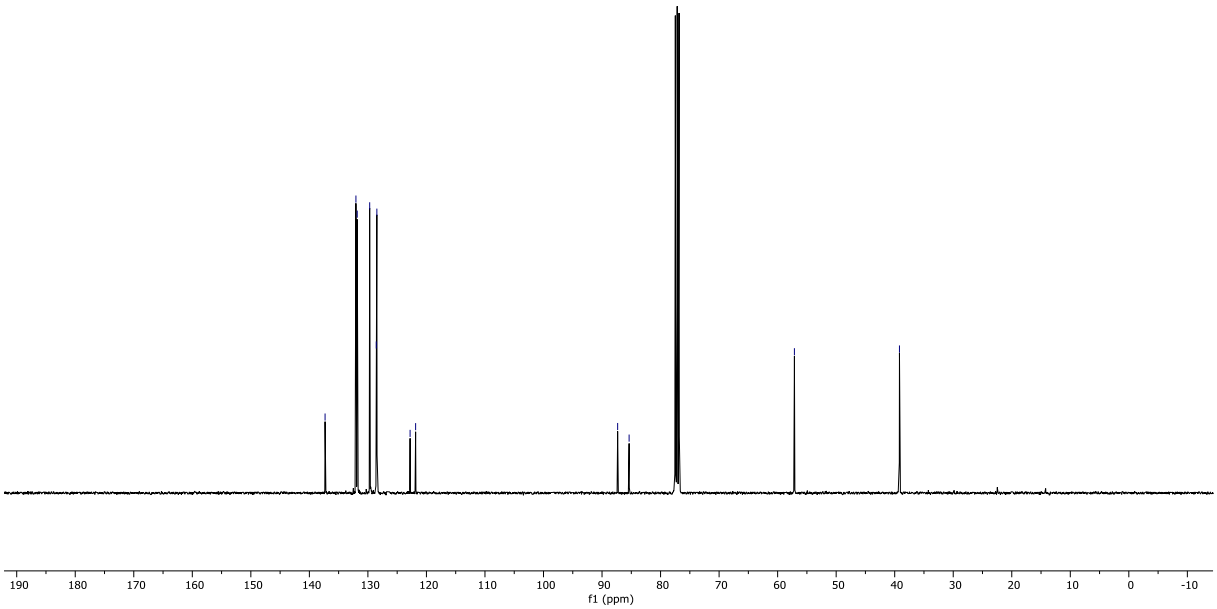
3k



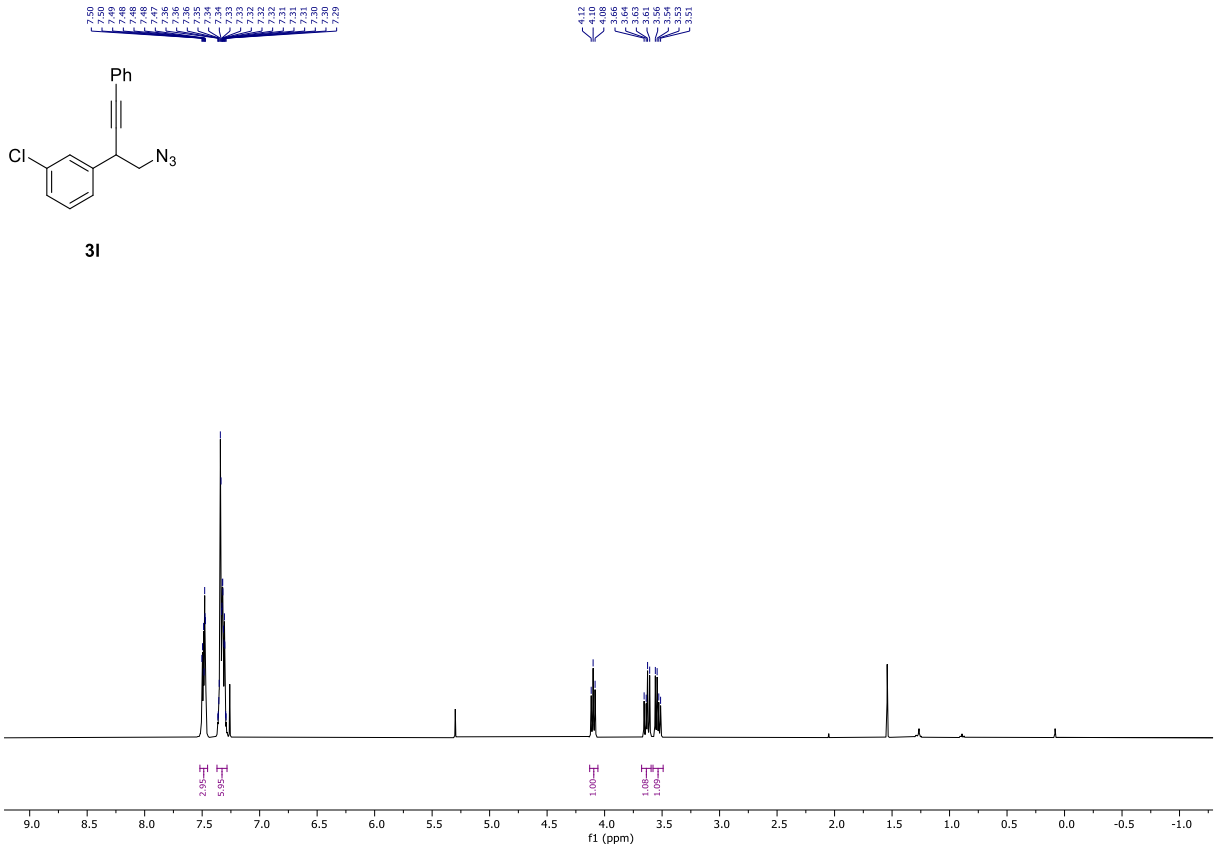
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3k**:



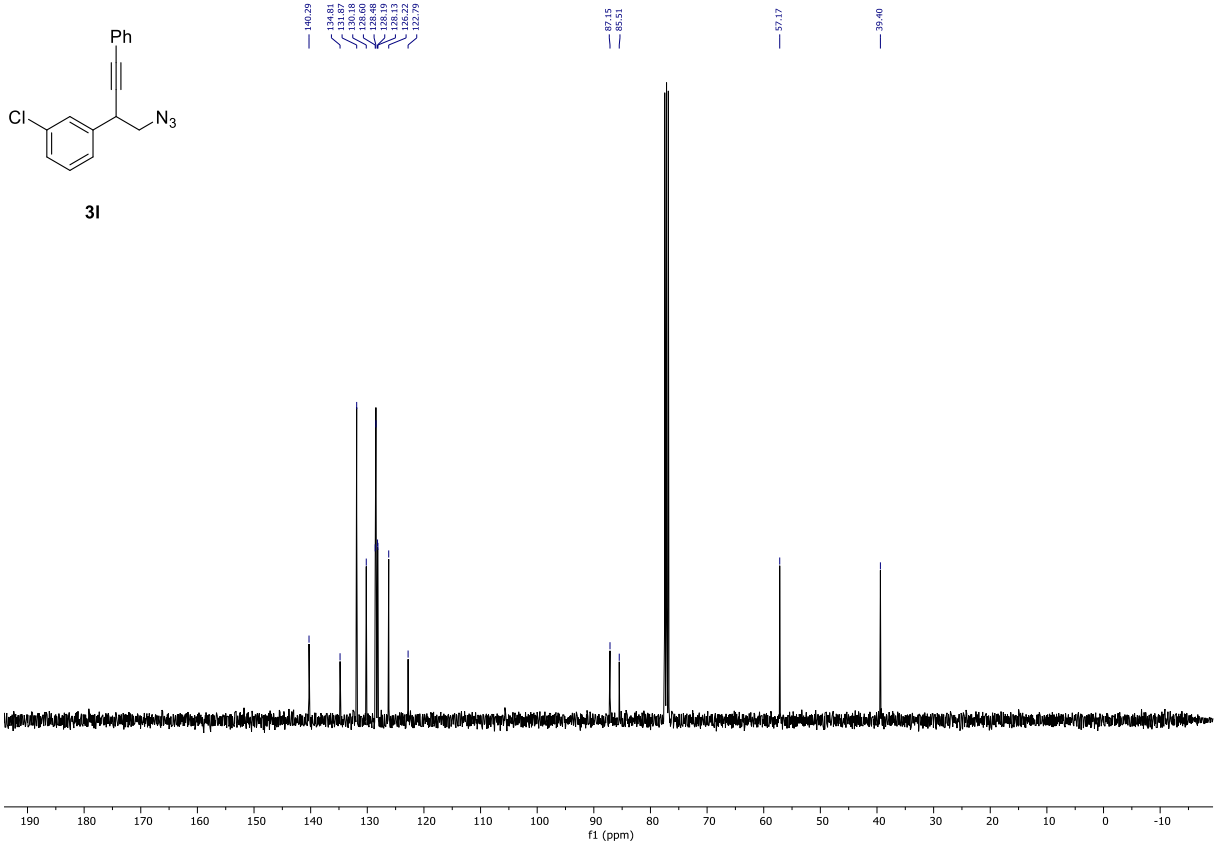
3k



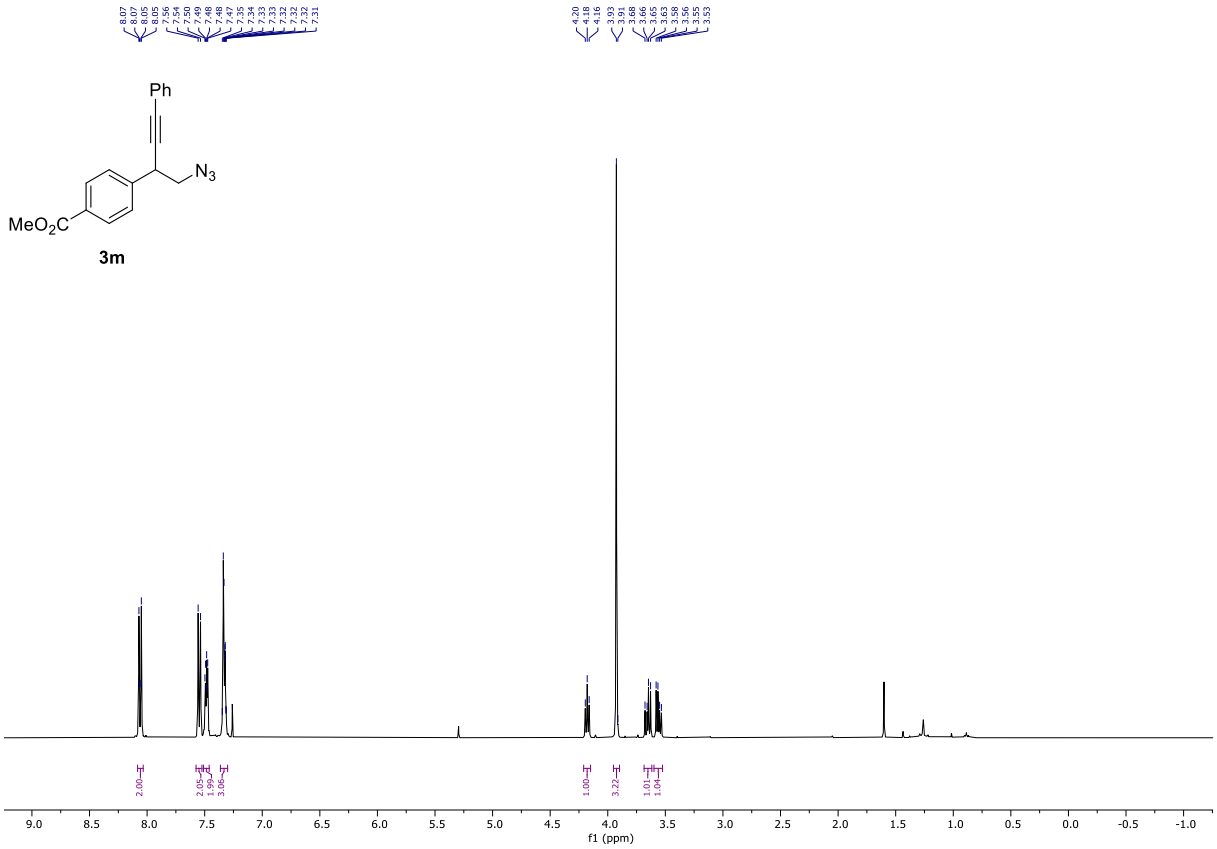
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l**:



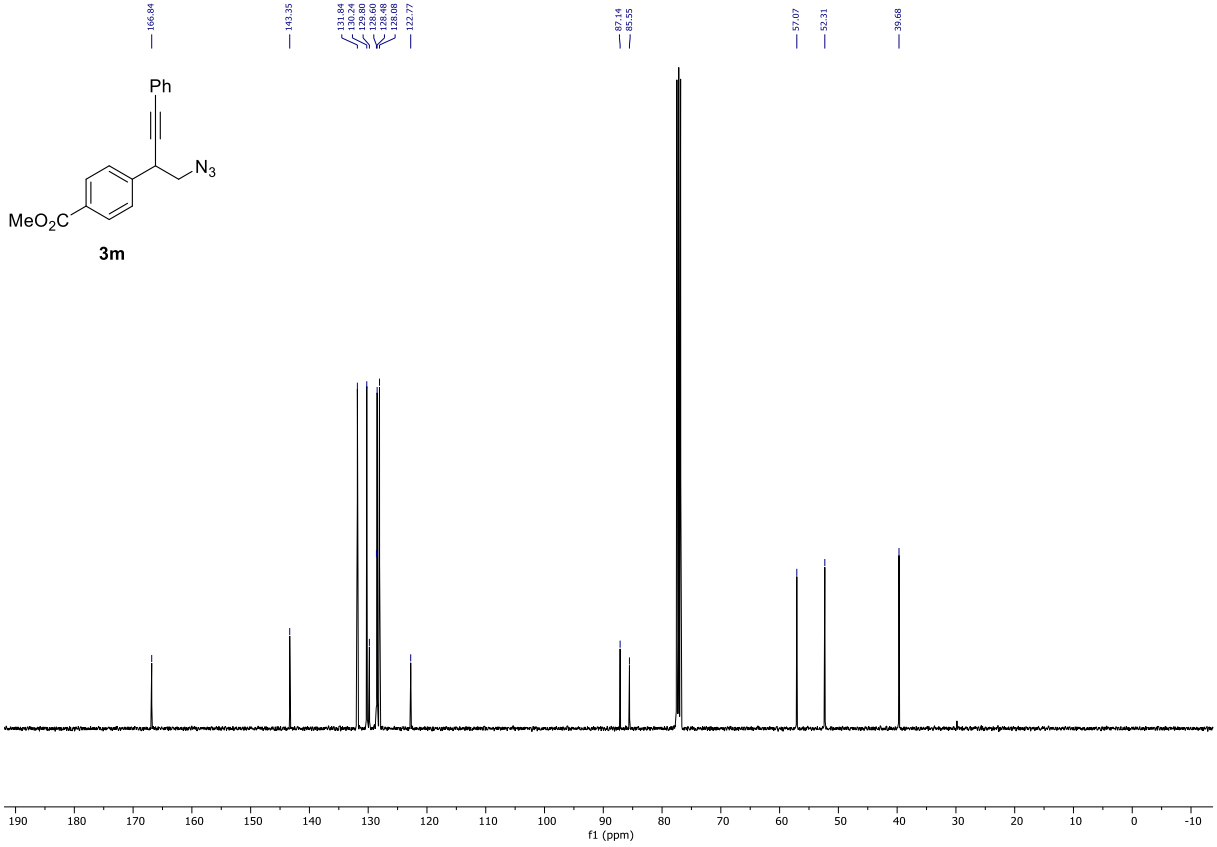
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3l**:



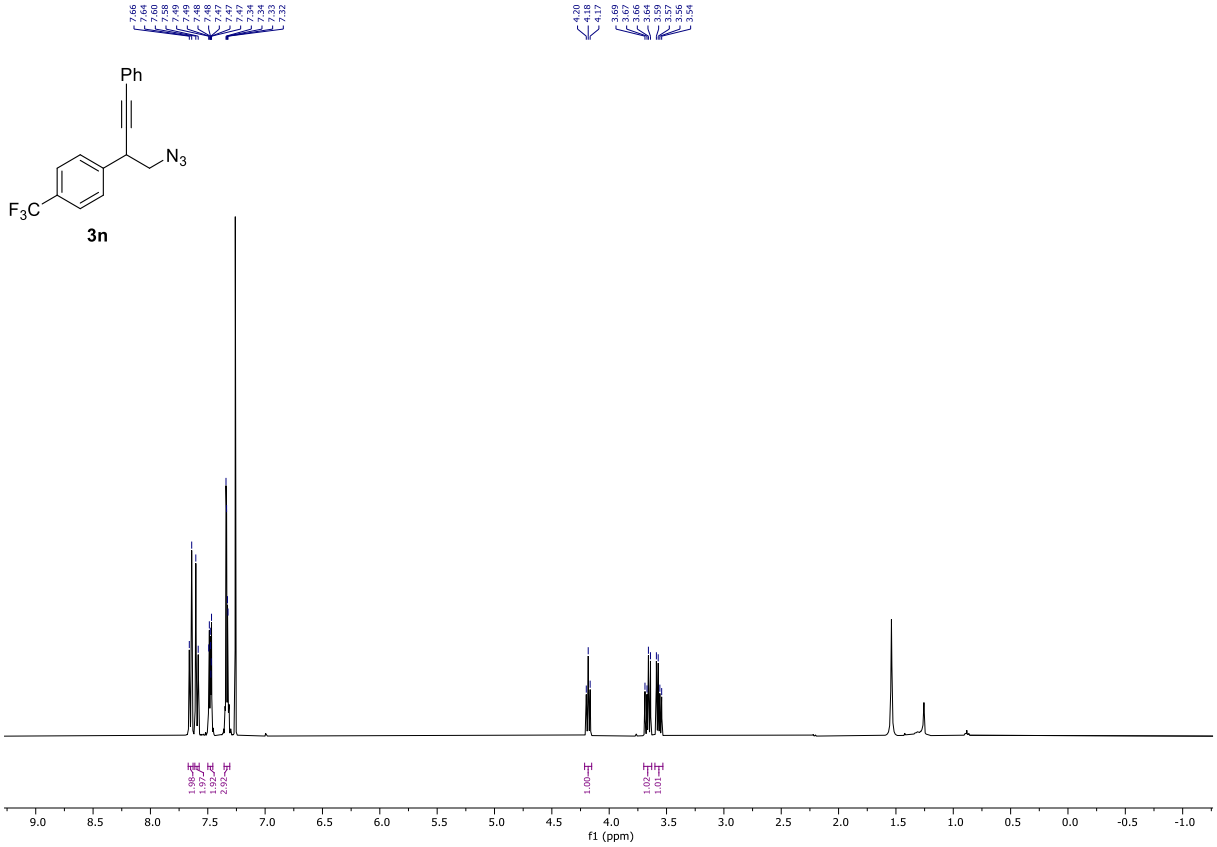
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m**:



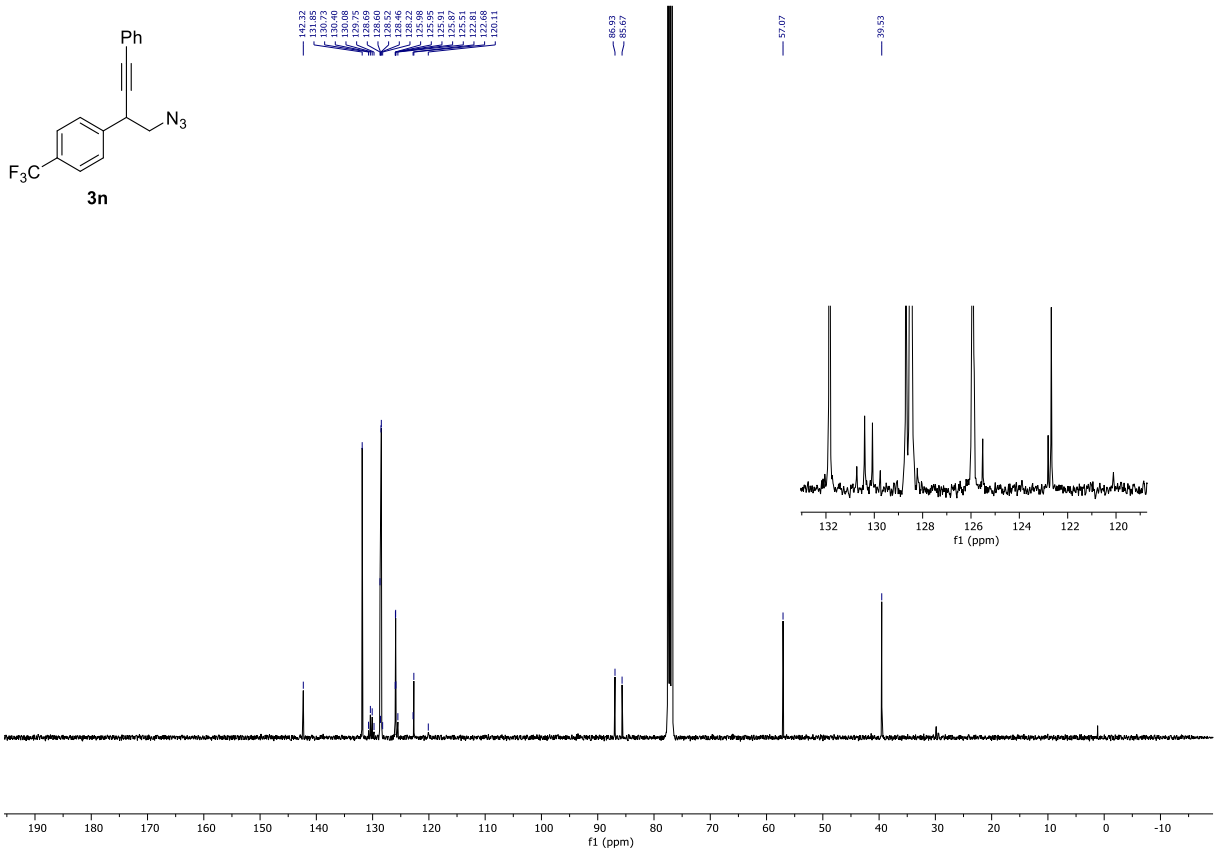
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3m**:



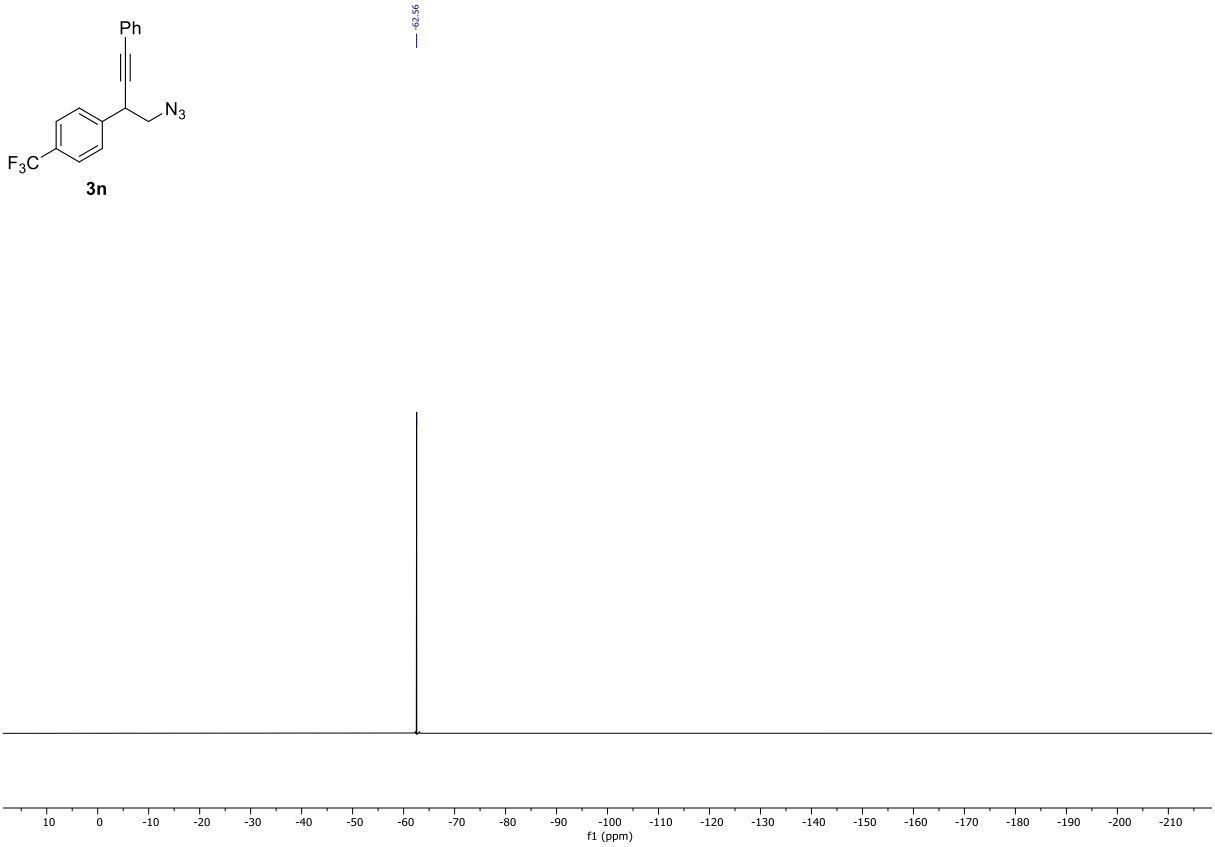
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**:



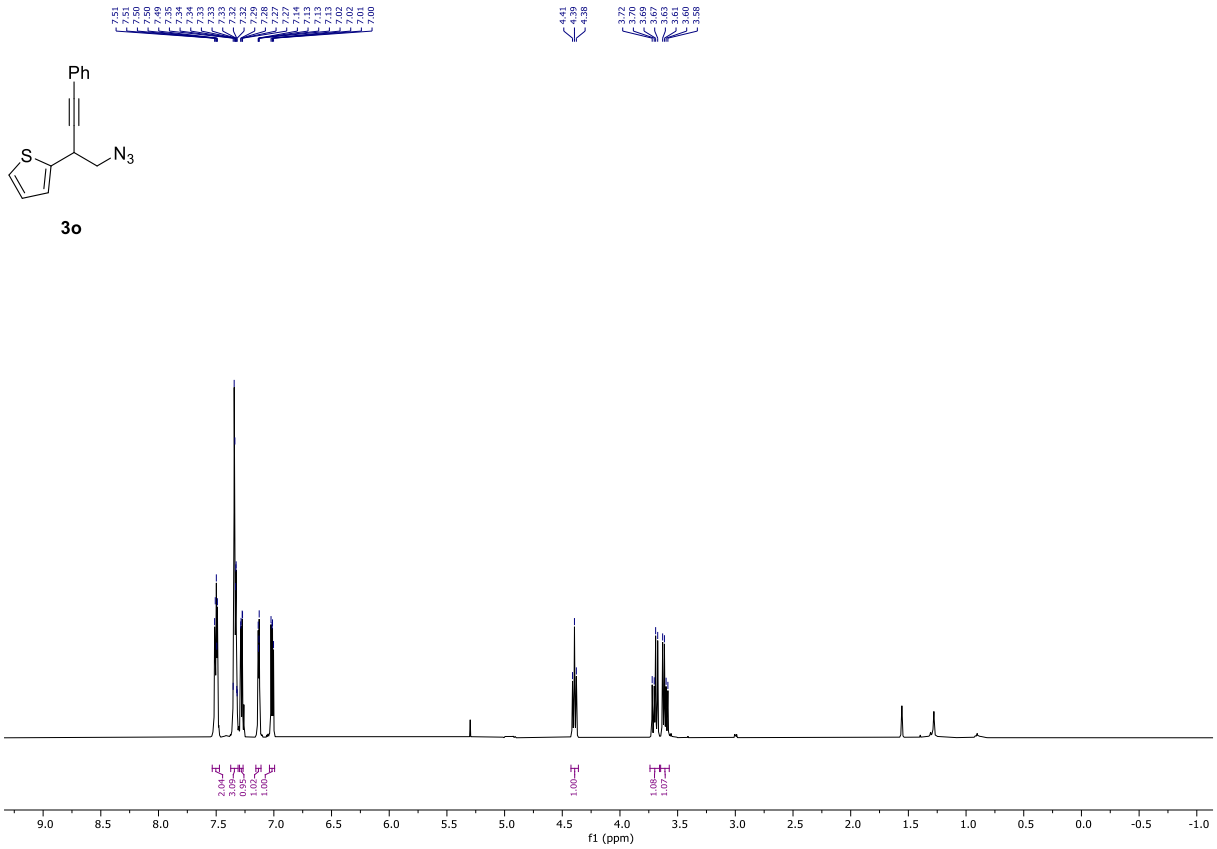
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3n**:



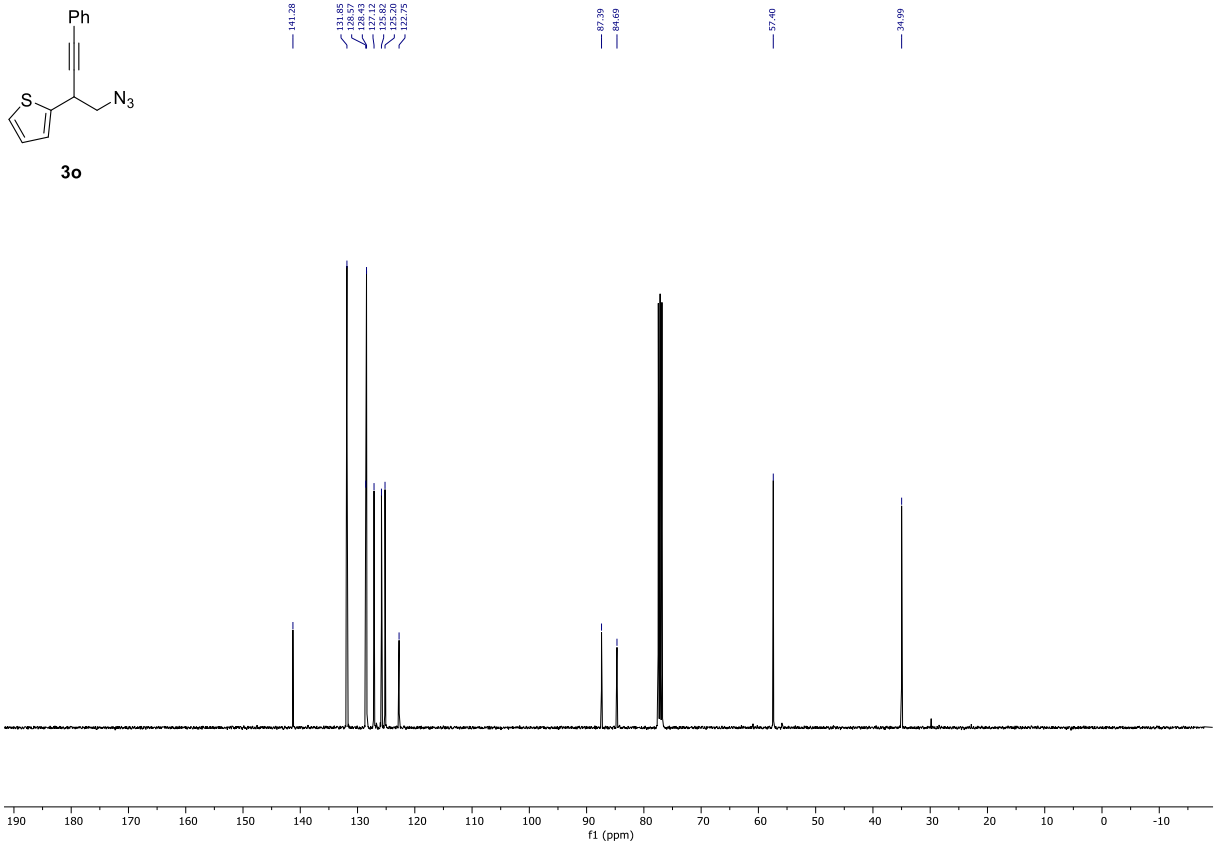
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3n**:



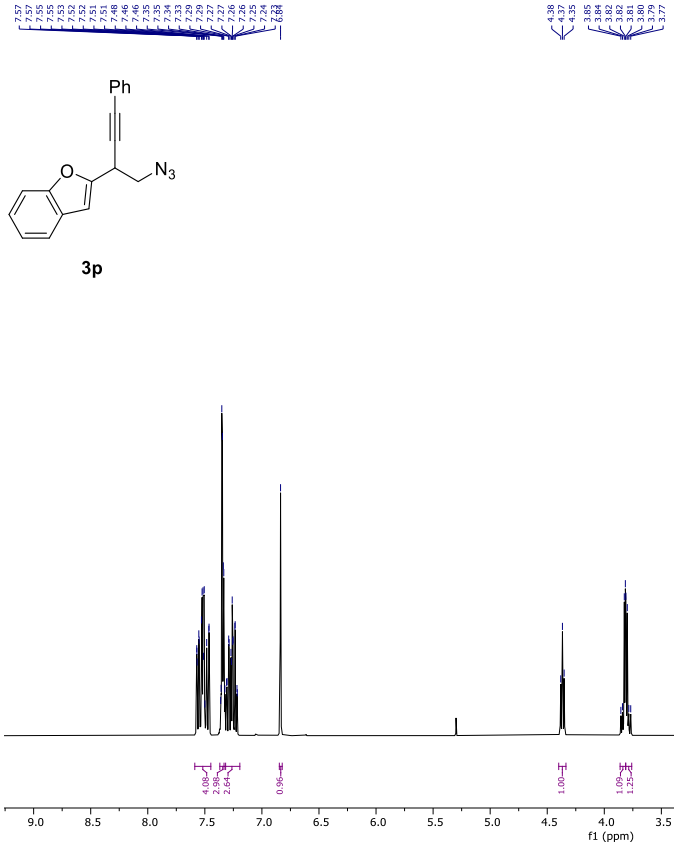
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**:



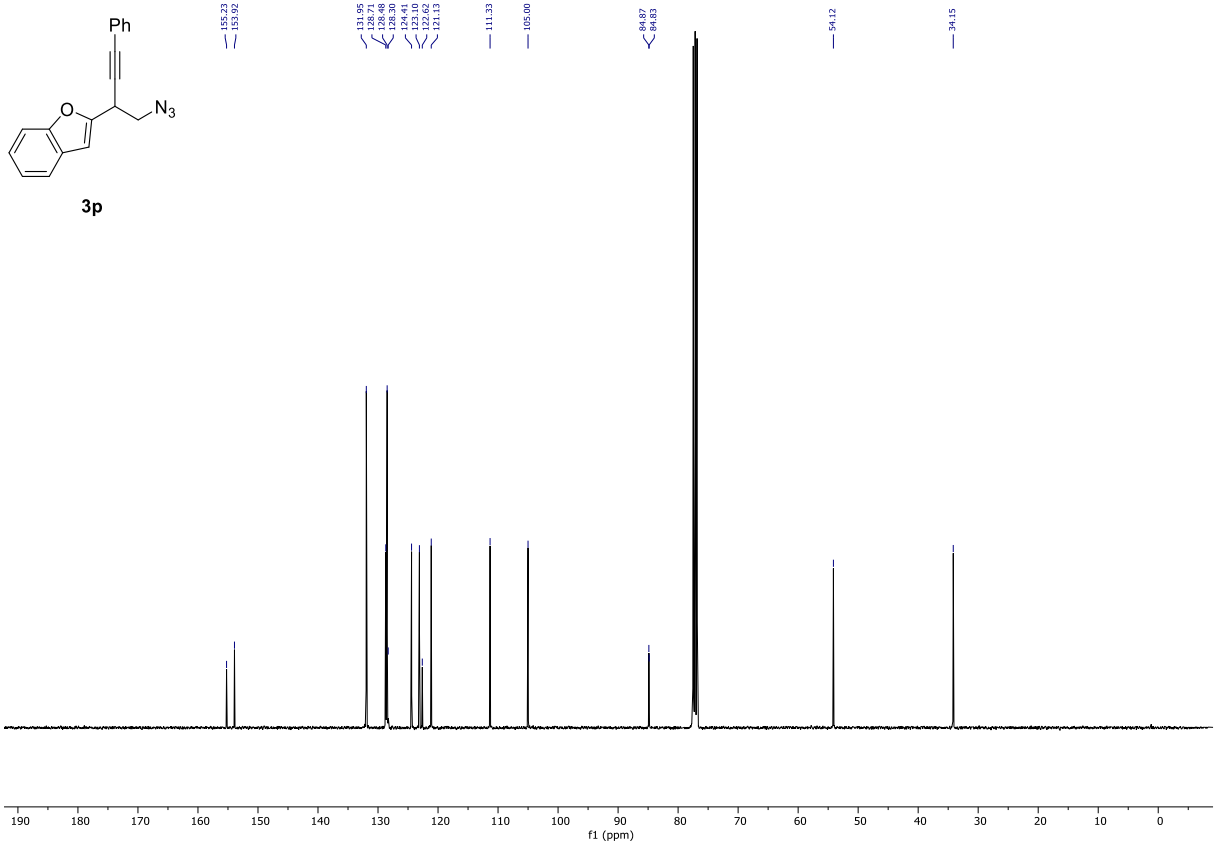
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3o**:



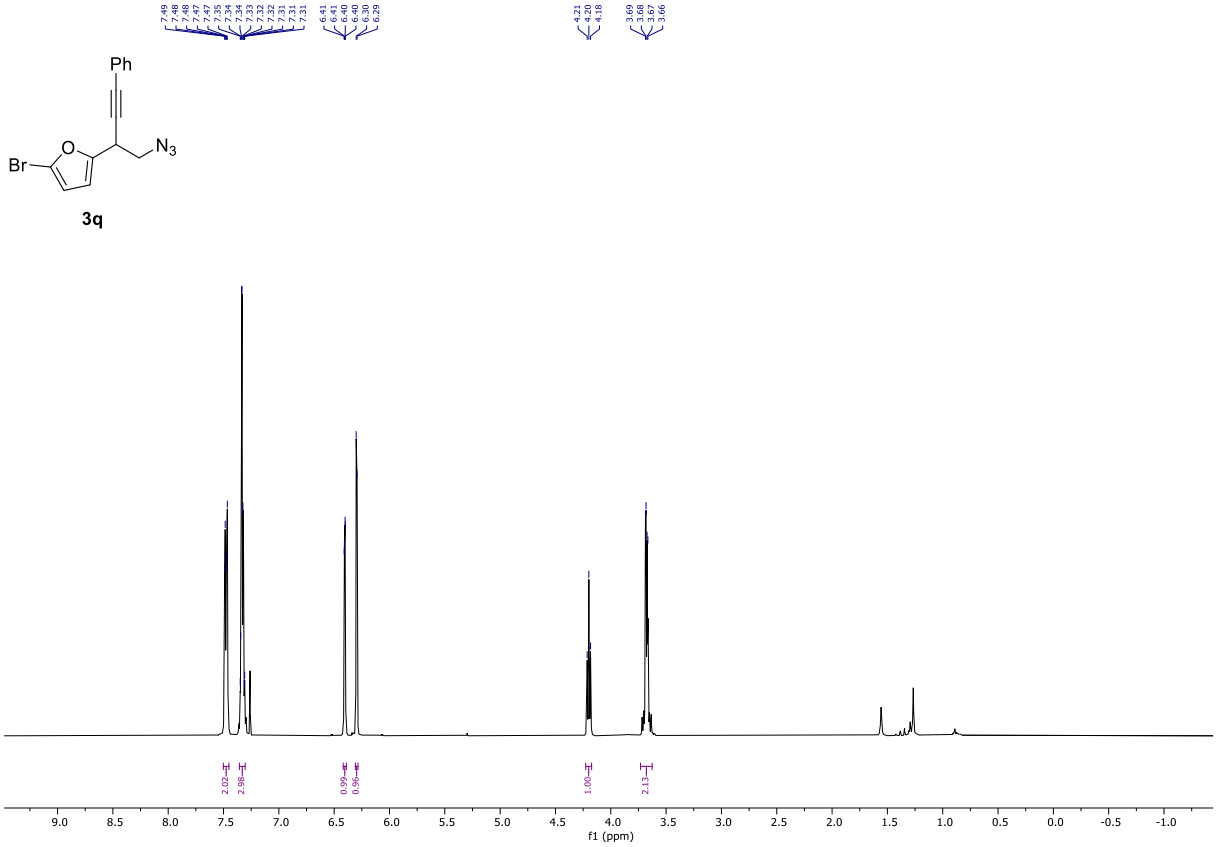
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p**:



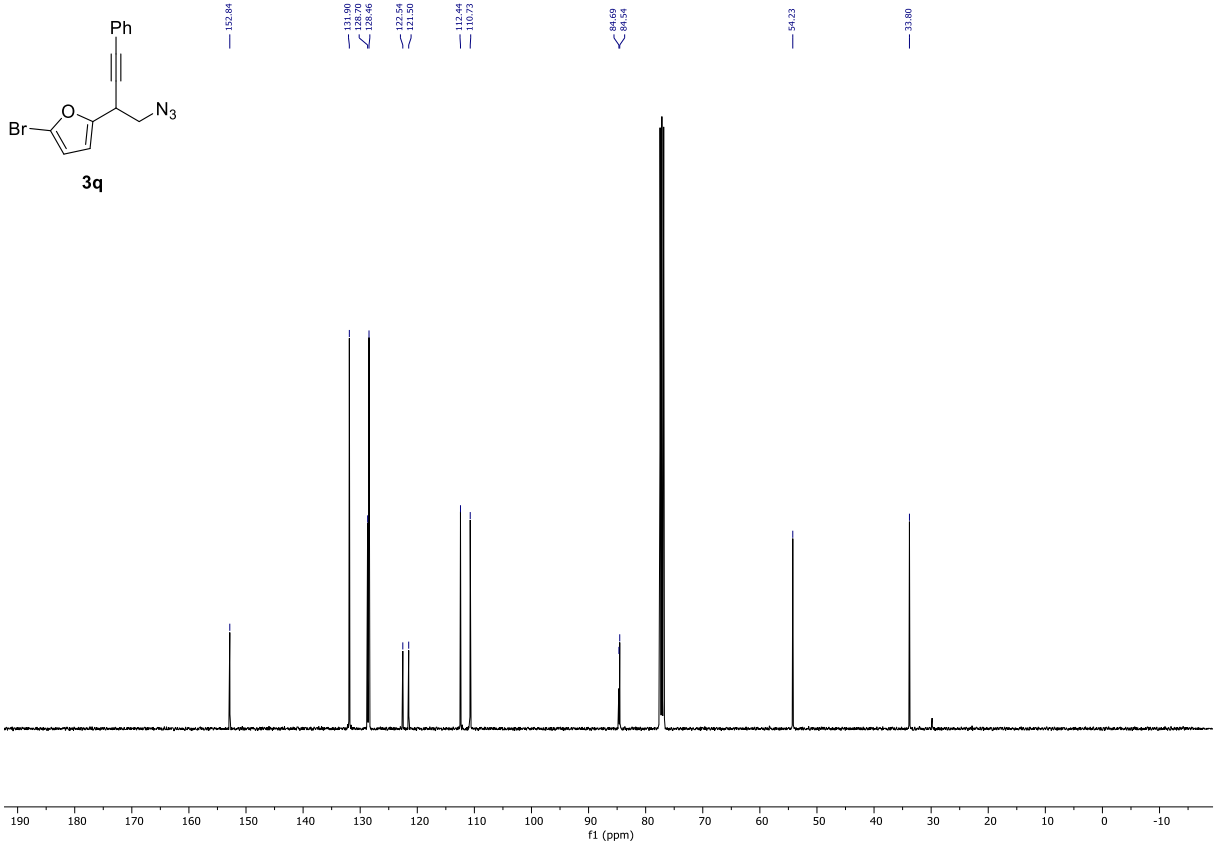
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3p**:



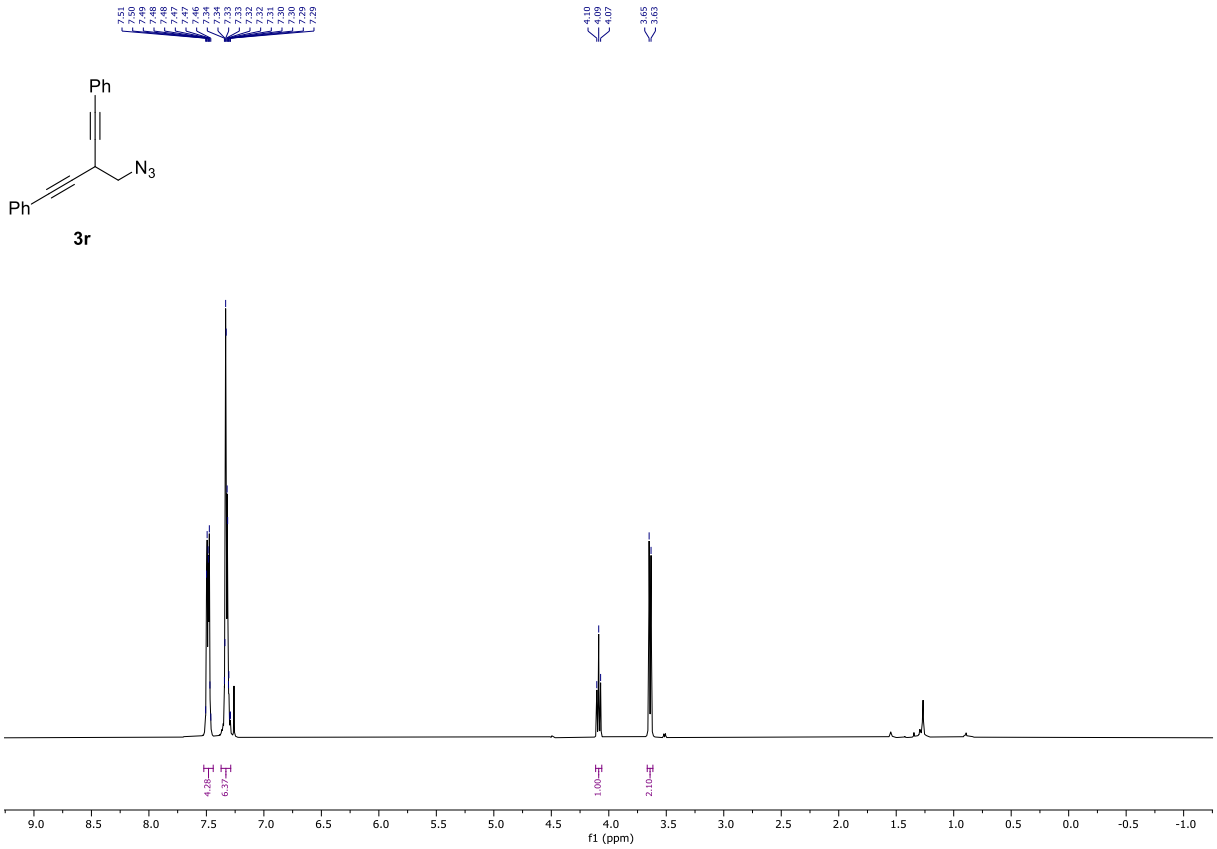
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q**:



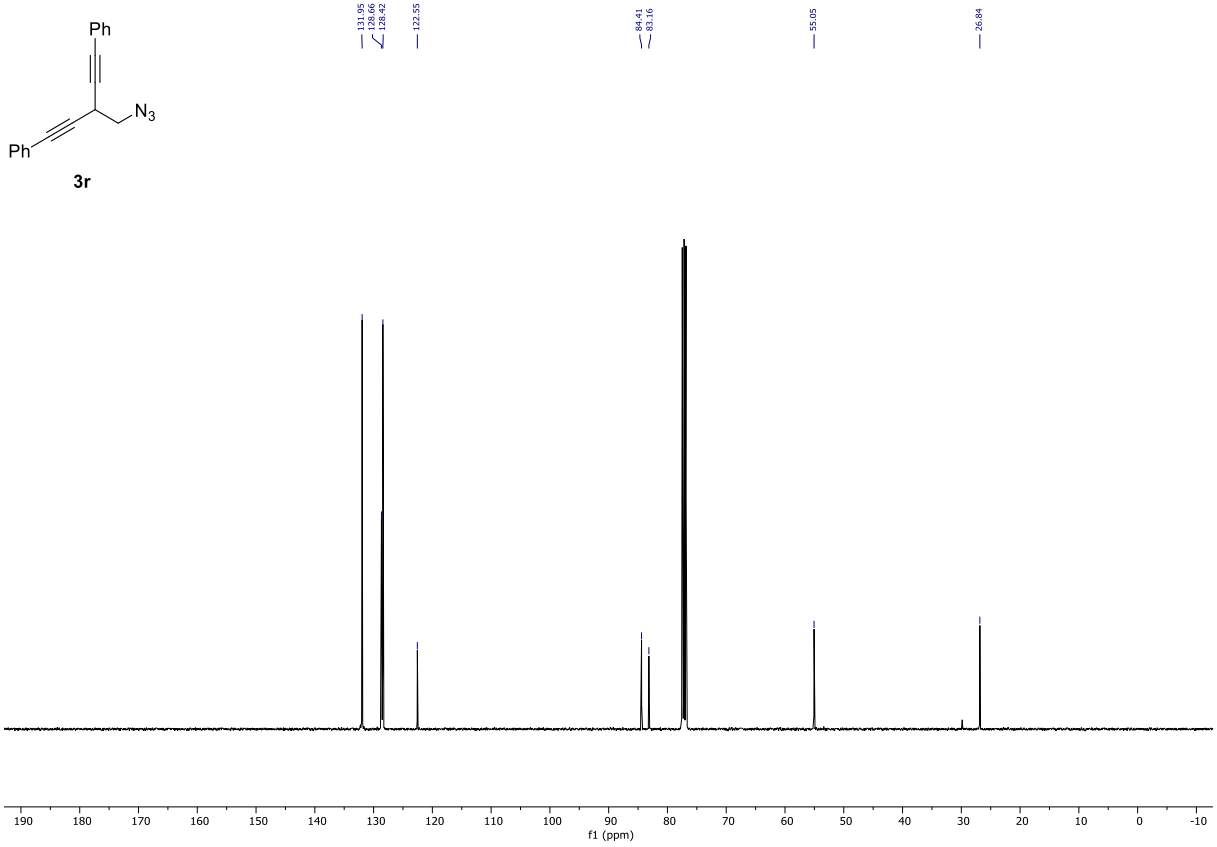
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3q**:



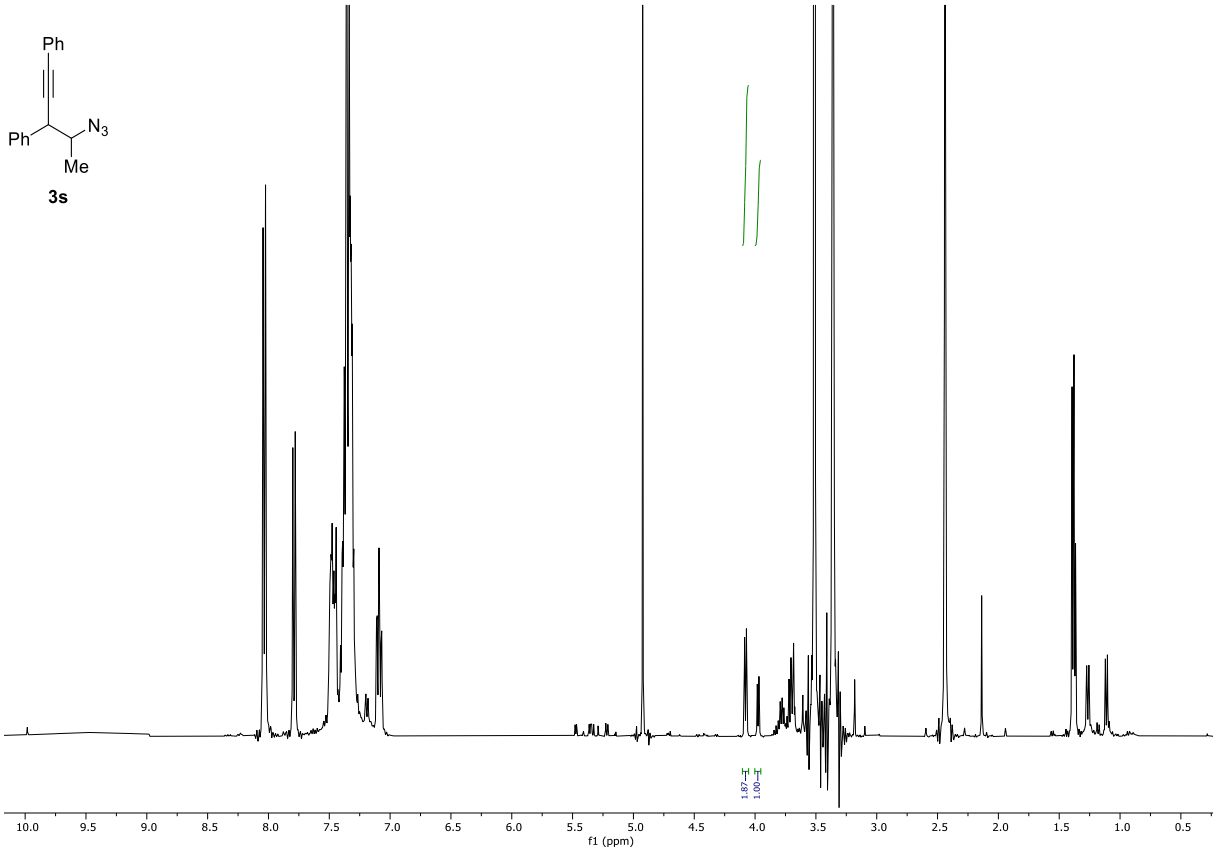
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3r**:



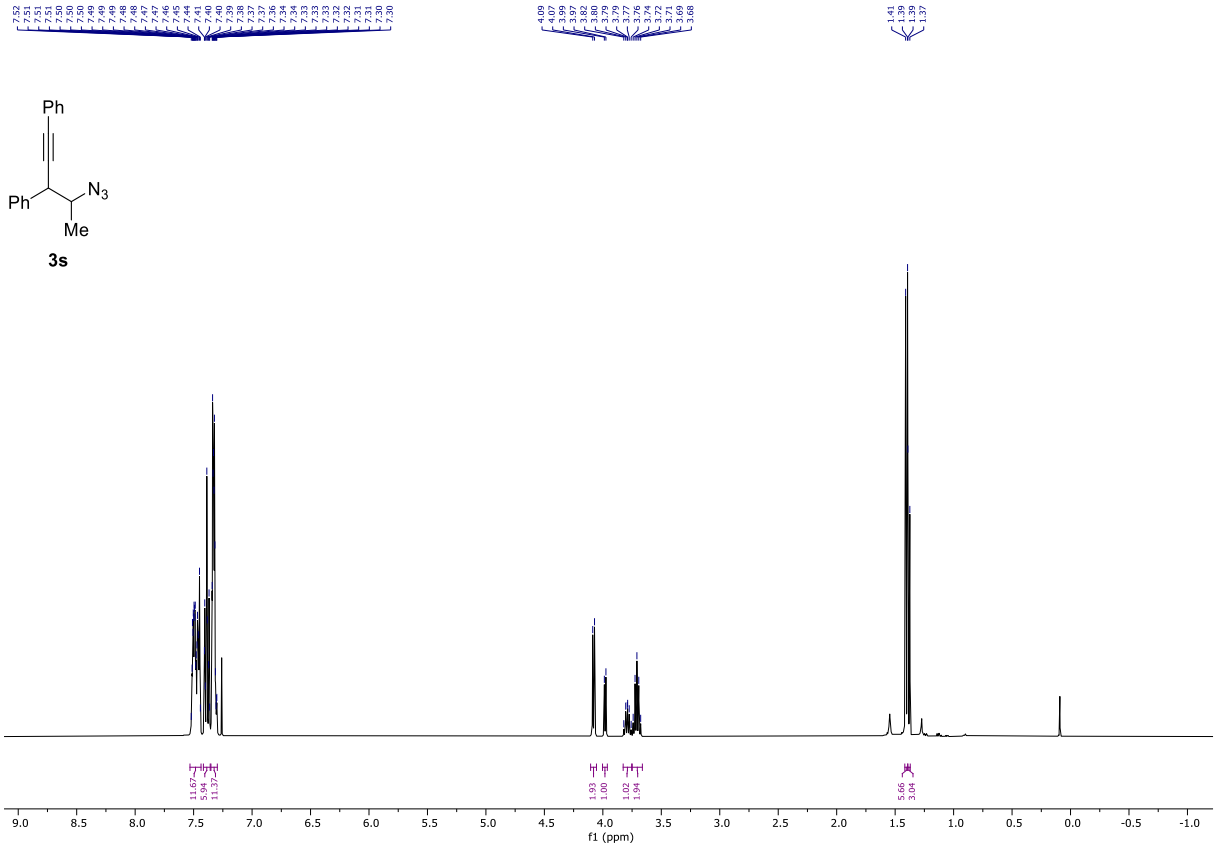
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3r**:



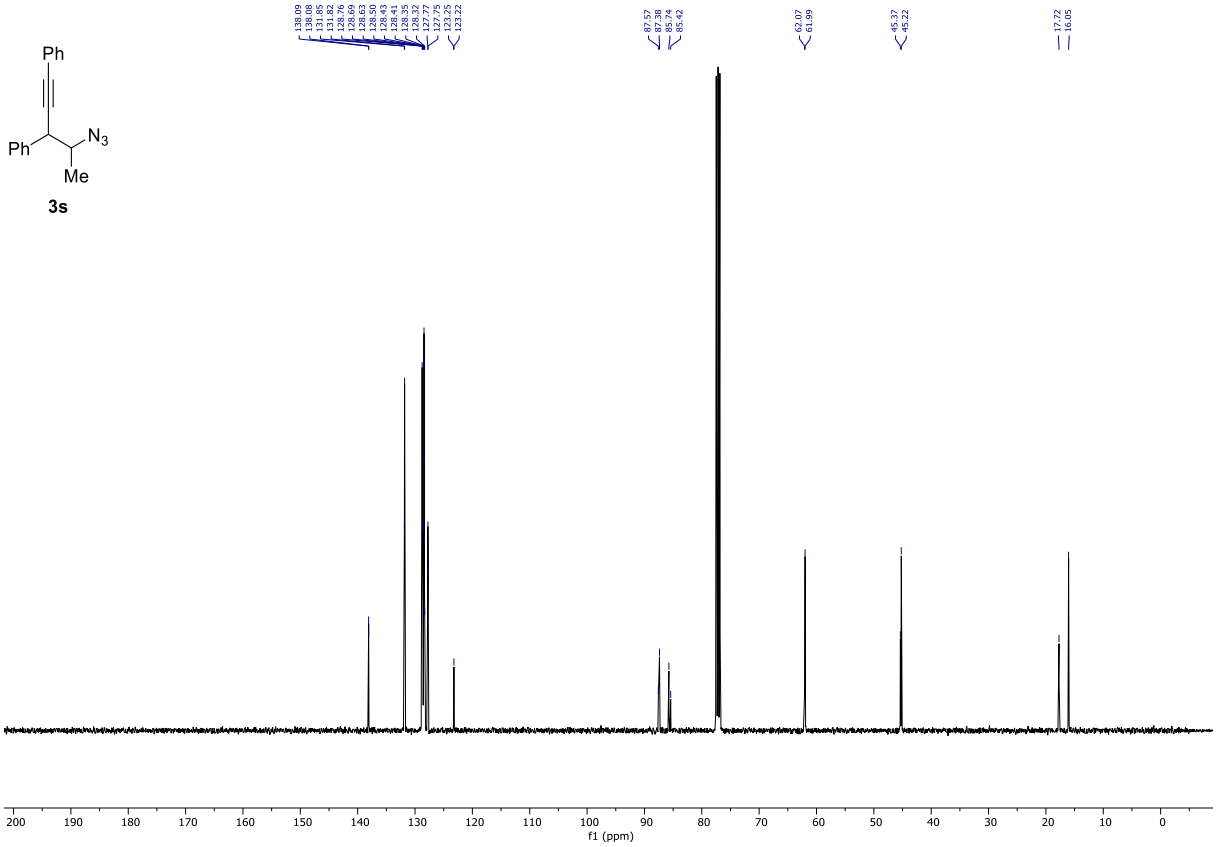
^{1}H NMR (400 MHz, $CDCl_3$) of crude compound **3s** (dr determination):



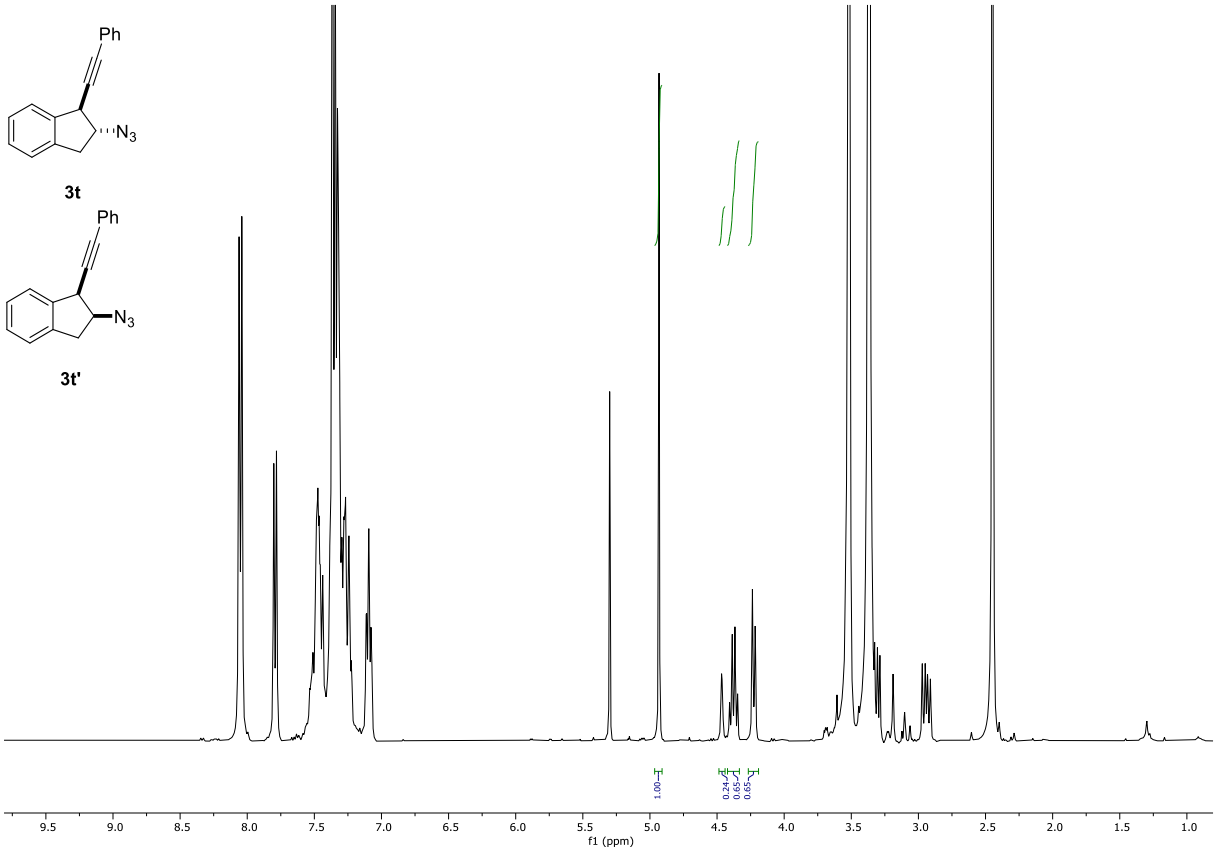
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3s**:



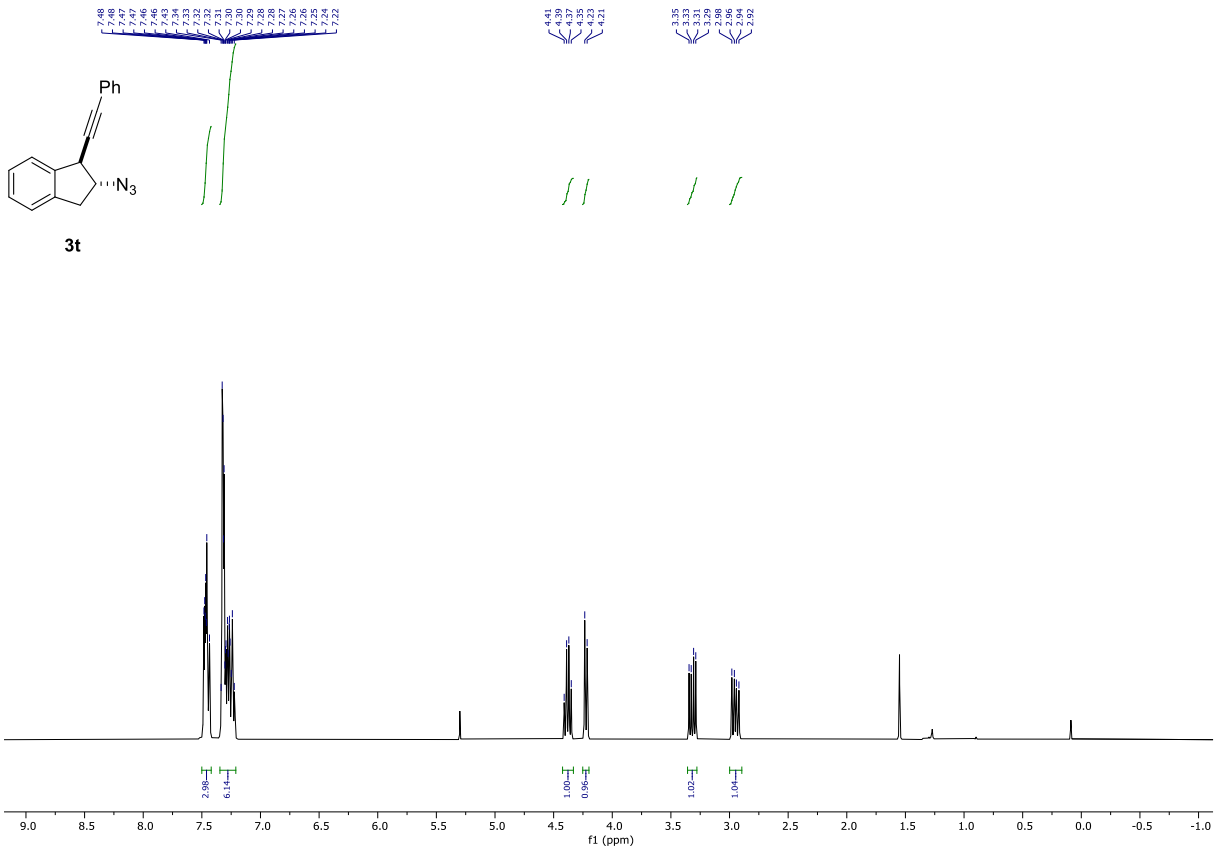
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3s**:



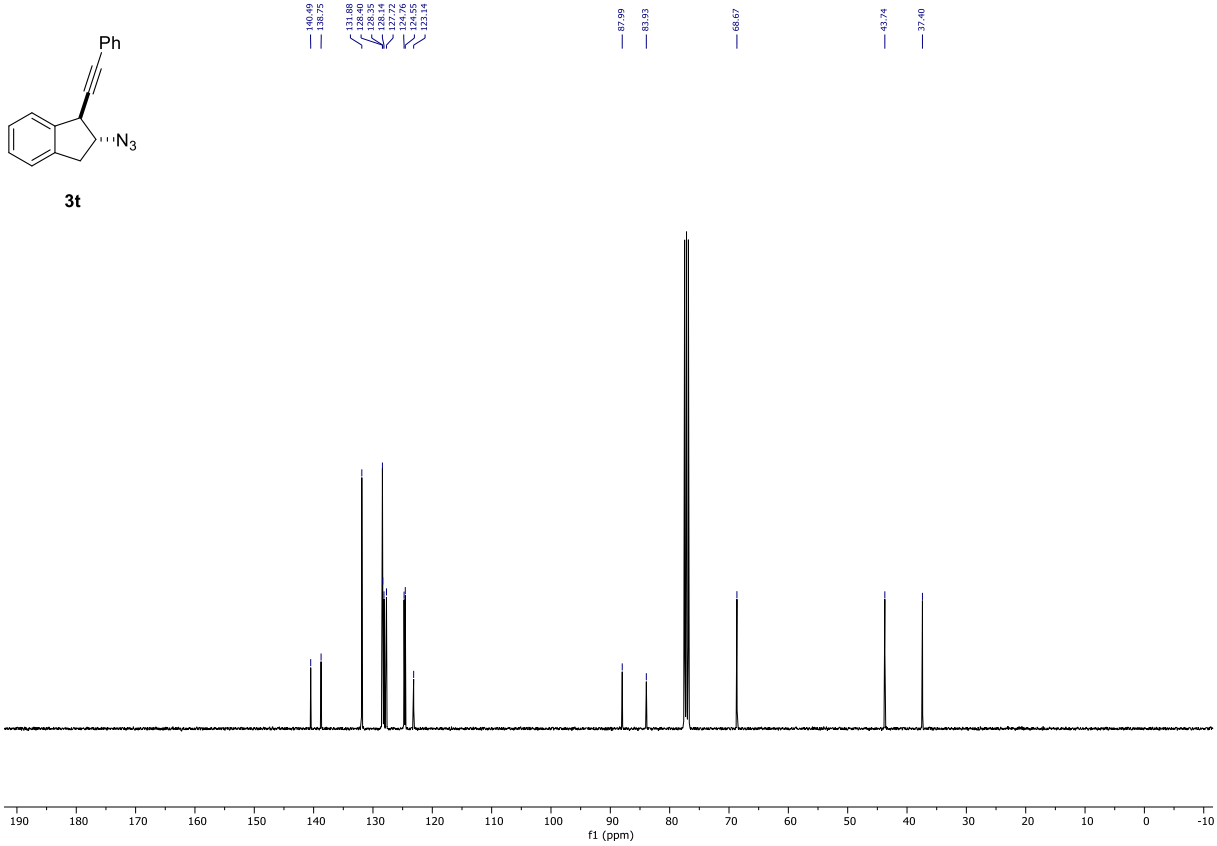
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t/3t'** (yield/dr determination):



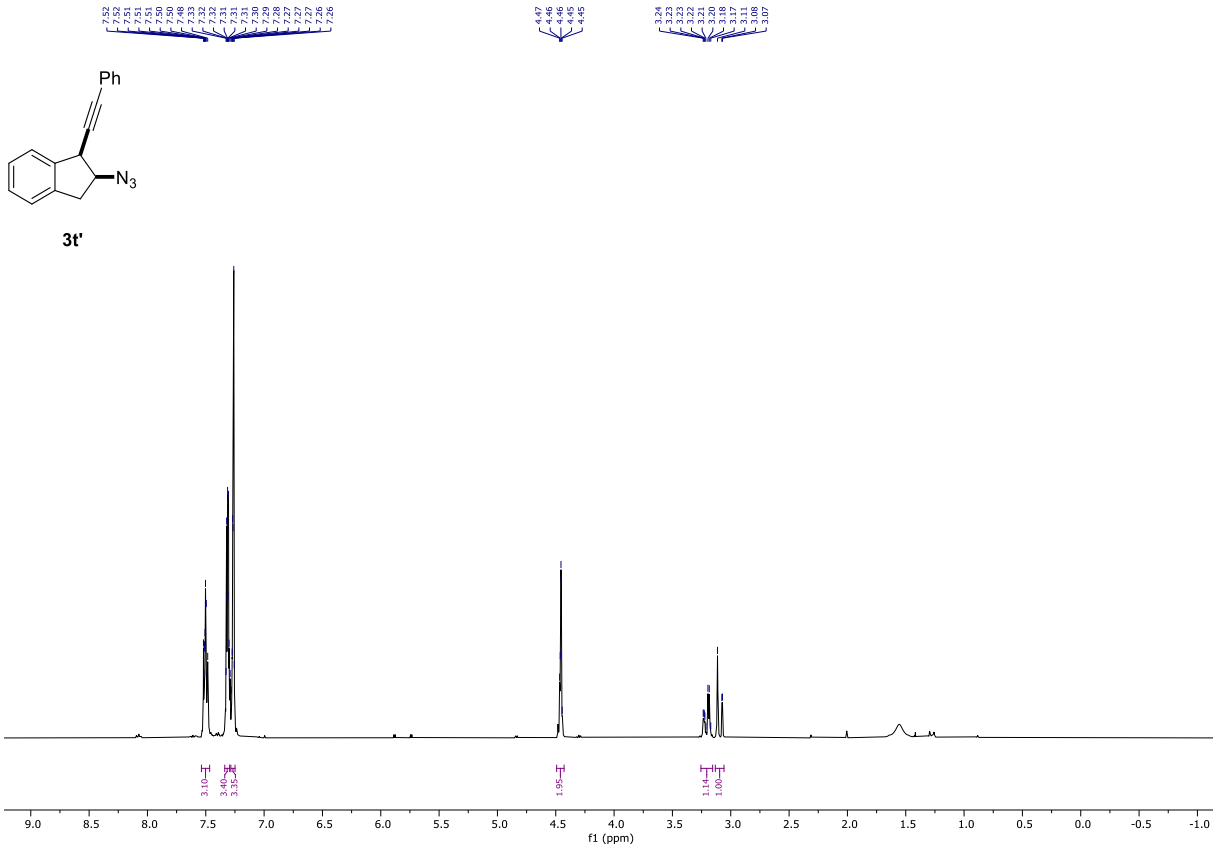
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t**:



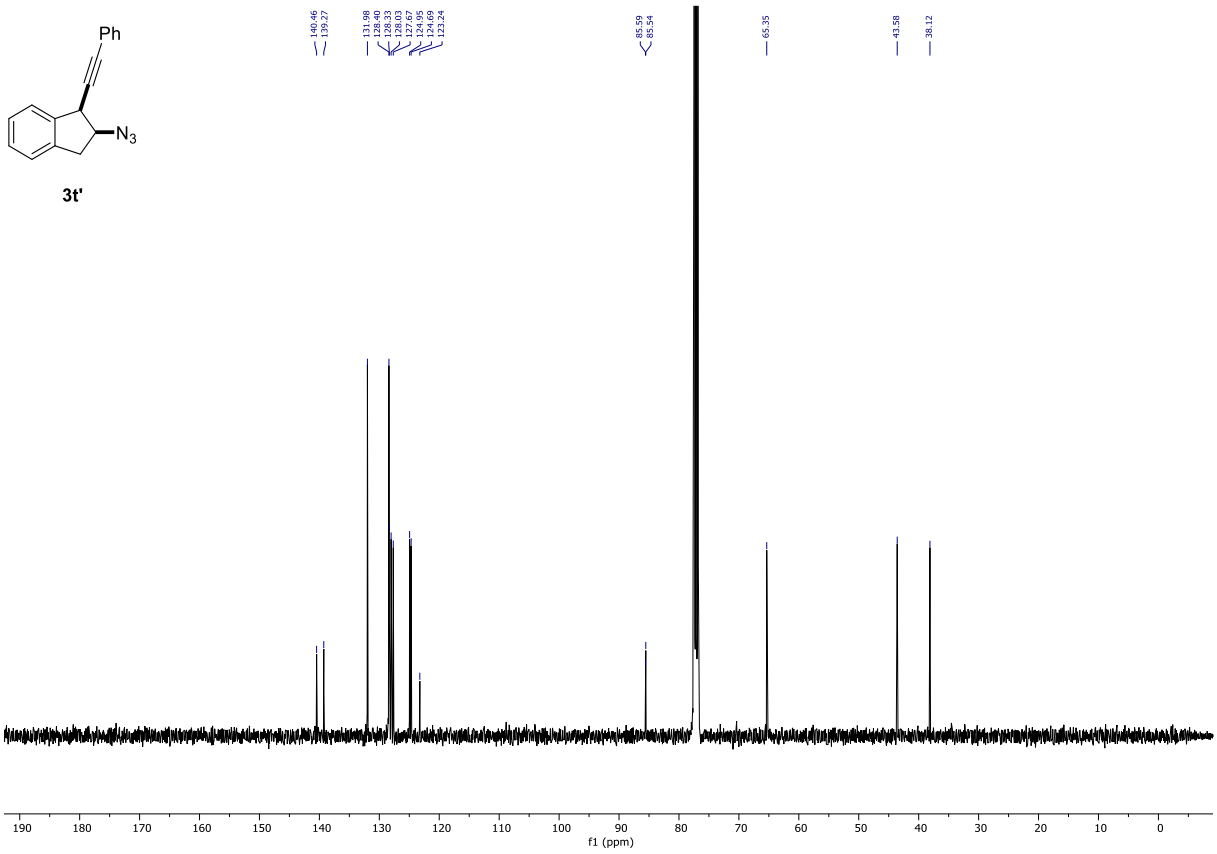
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3t**:



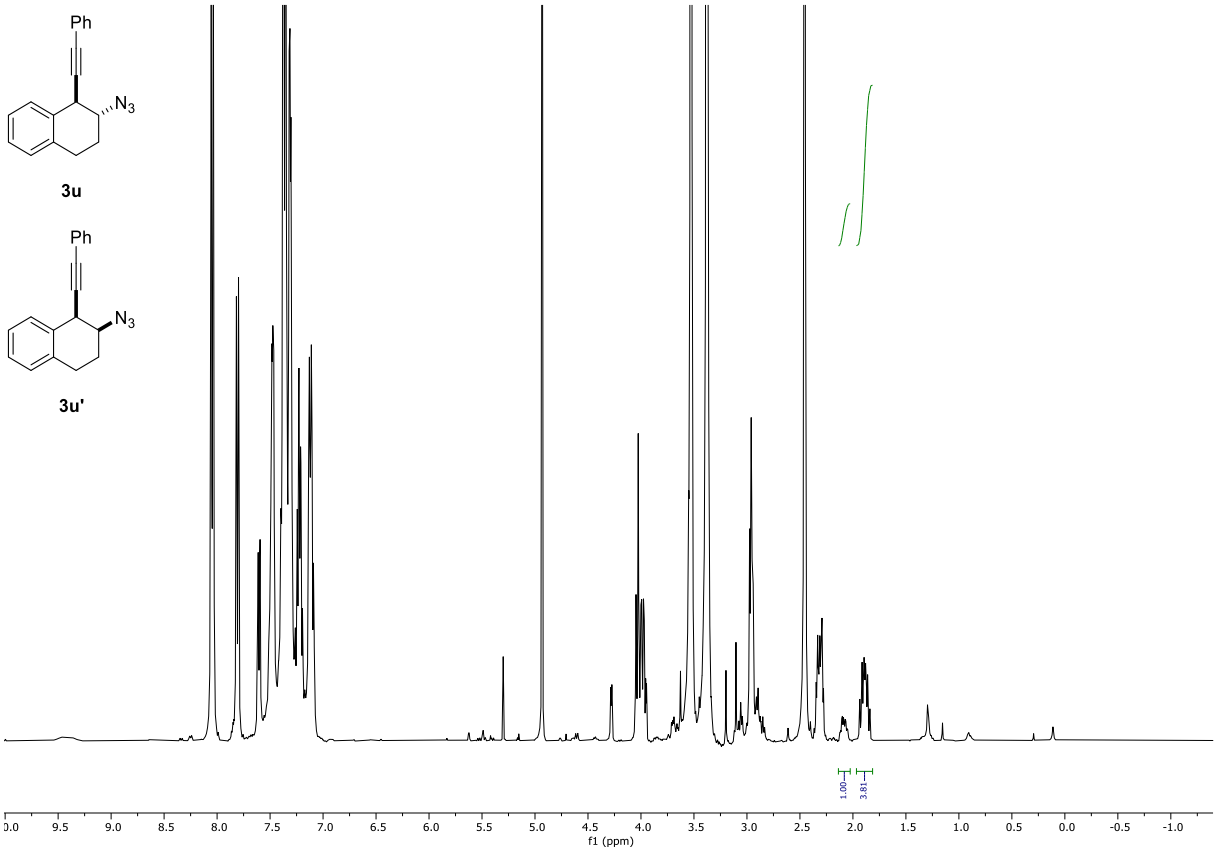
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t'**:



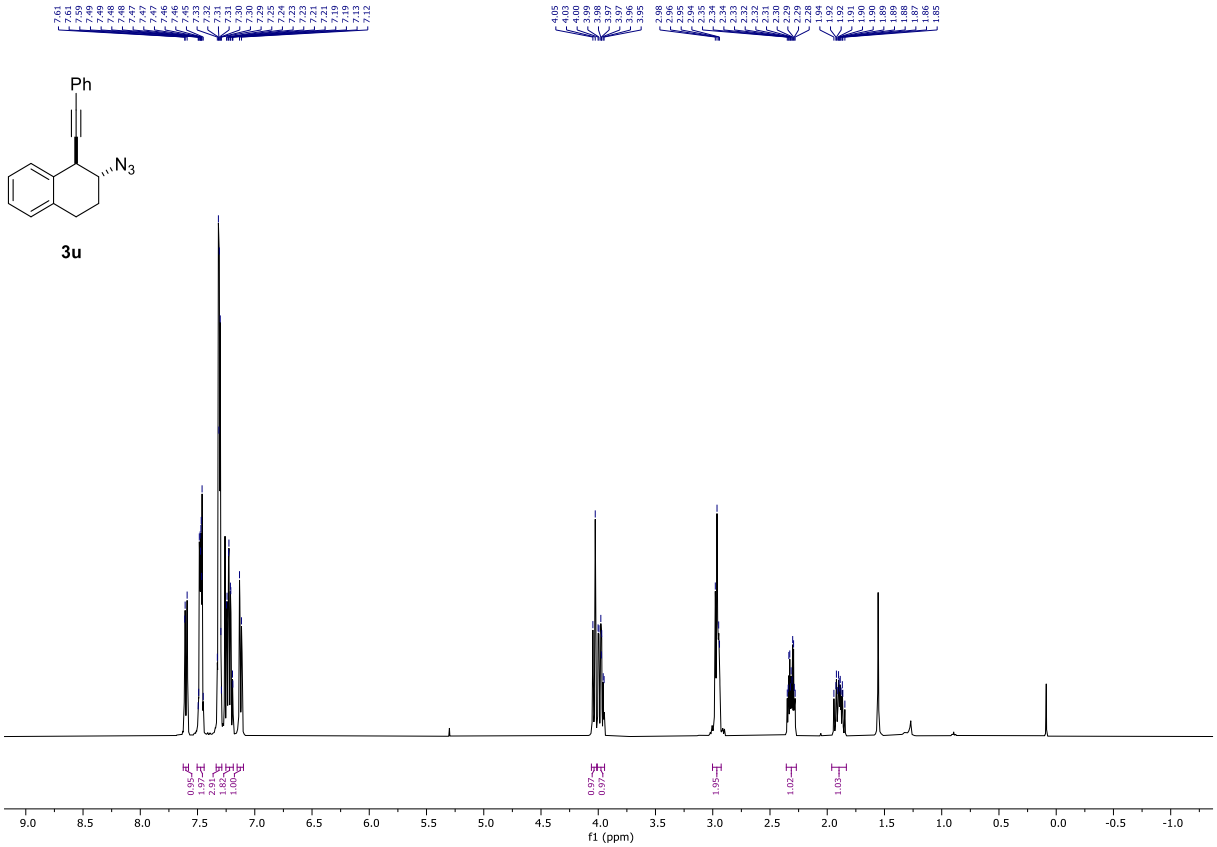
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3t'**:



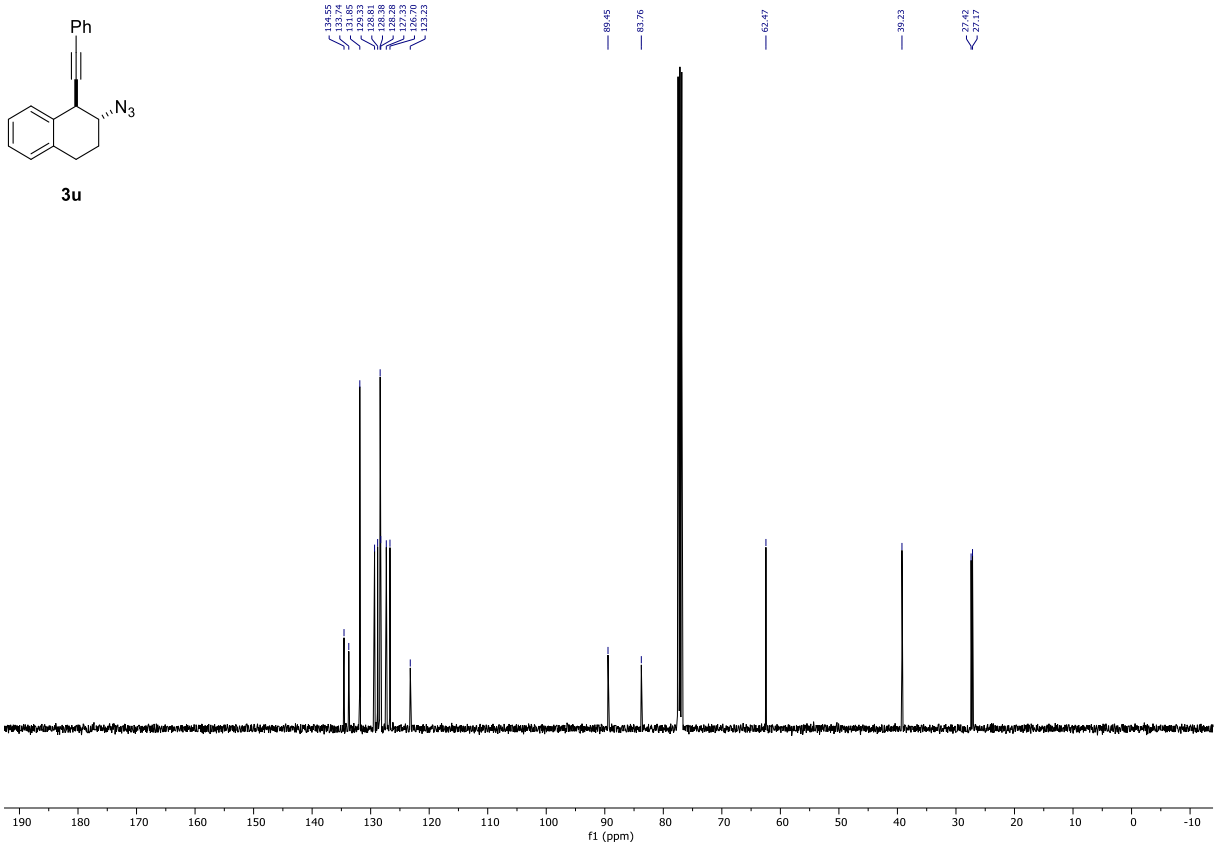
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u/3u'** (dr determination):



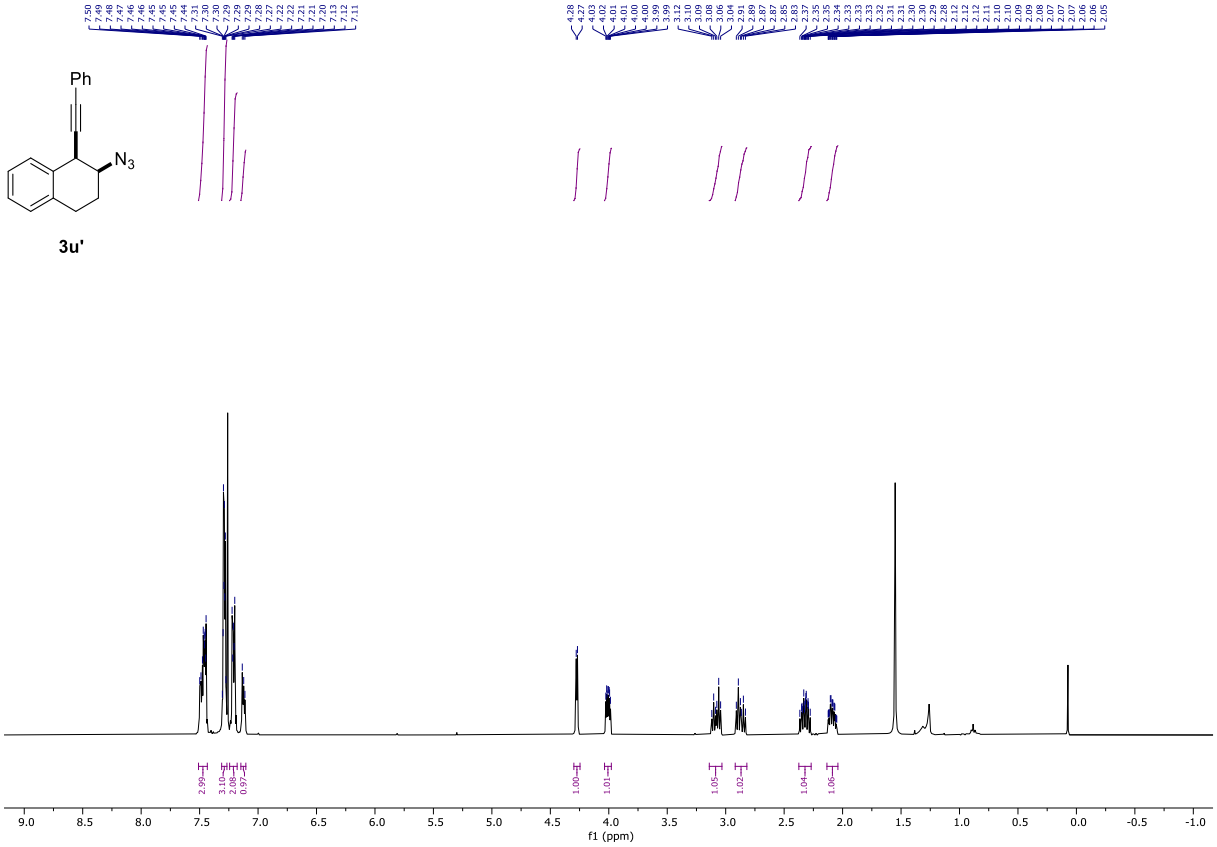
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u**:



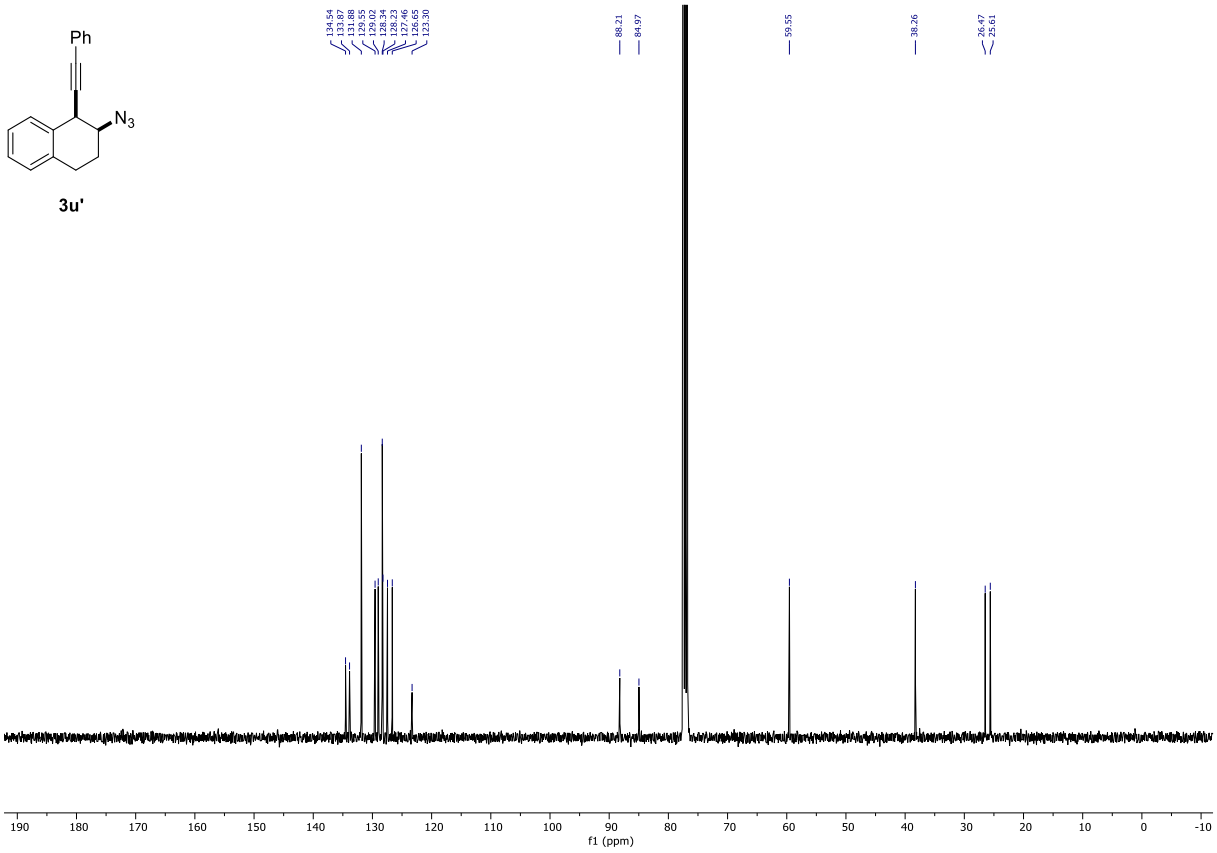
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3u**:



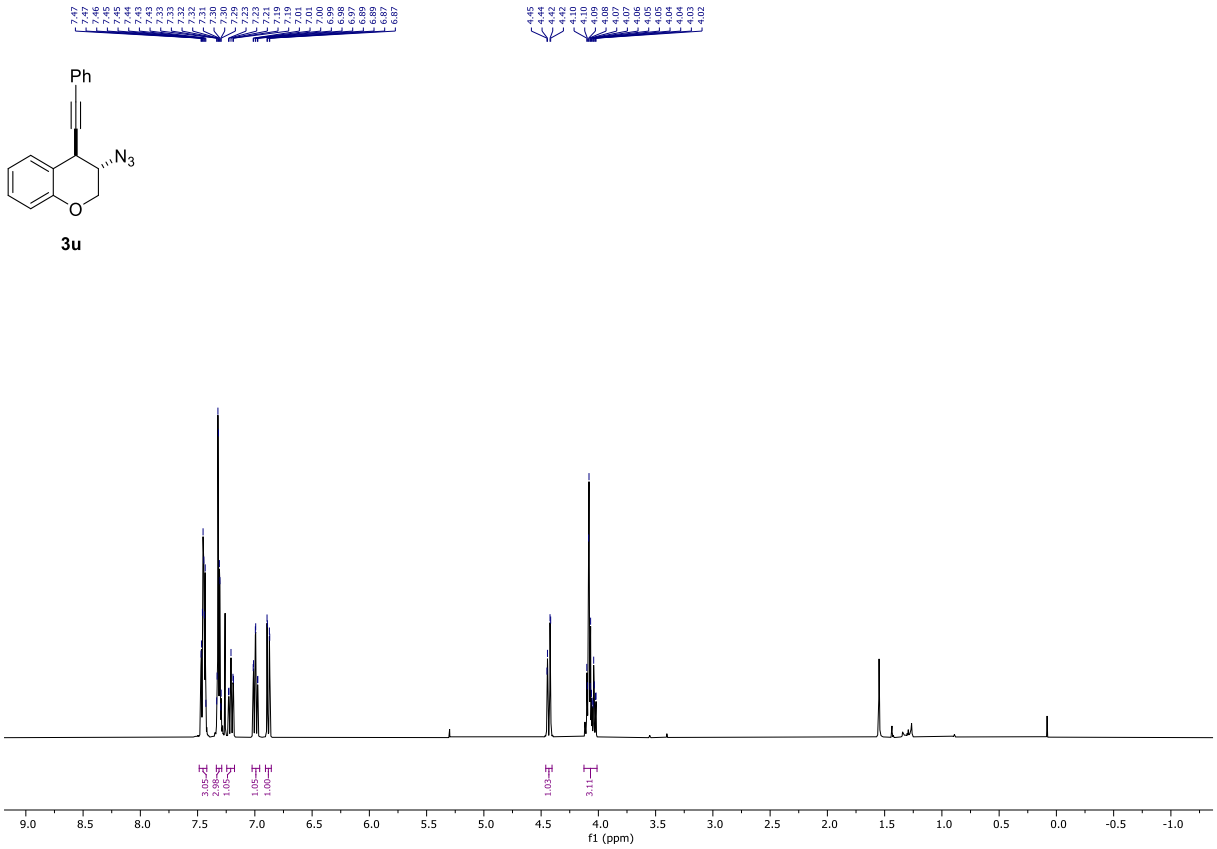
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u'**:



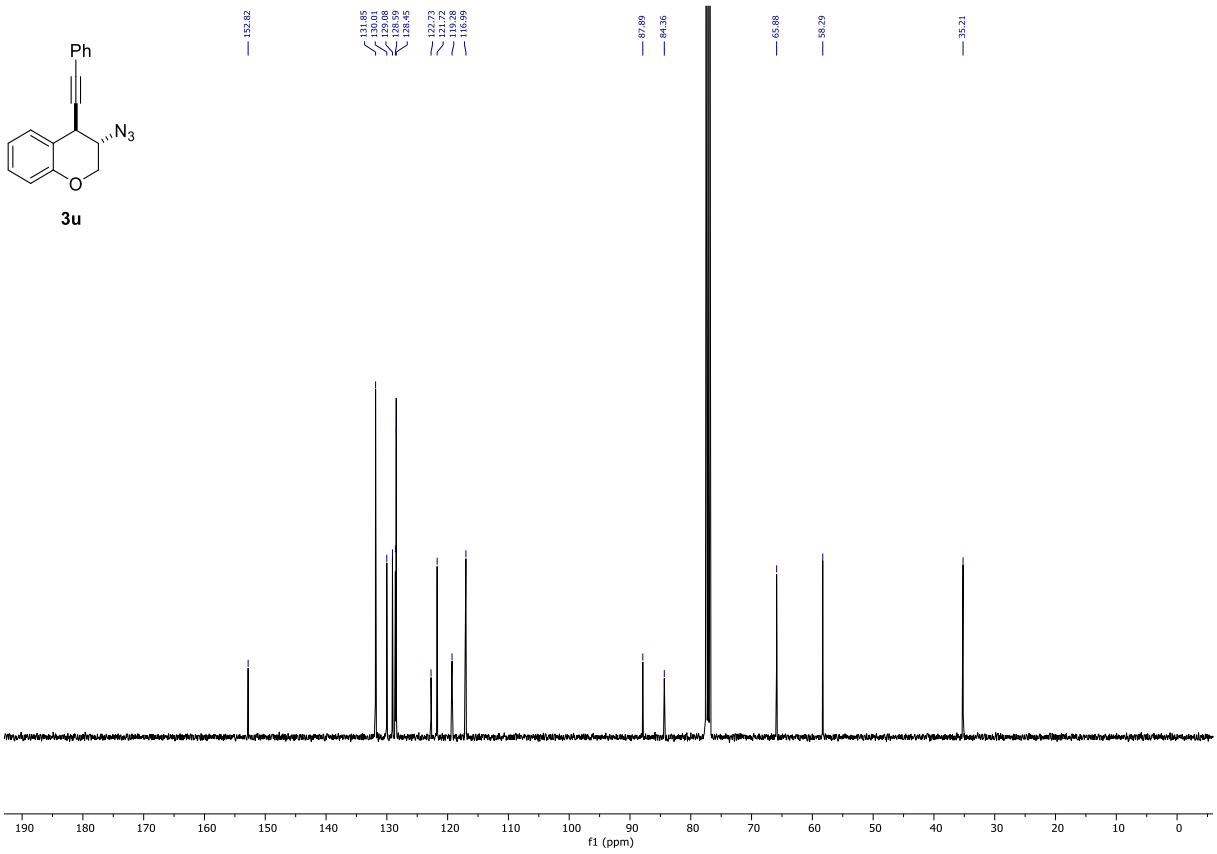
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3u'**:



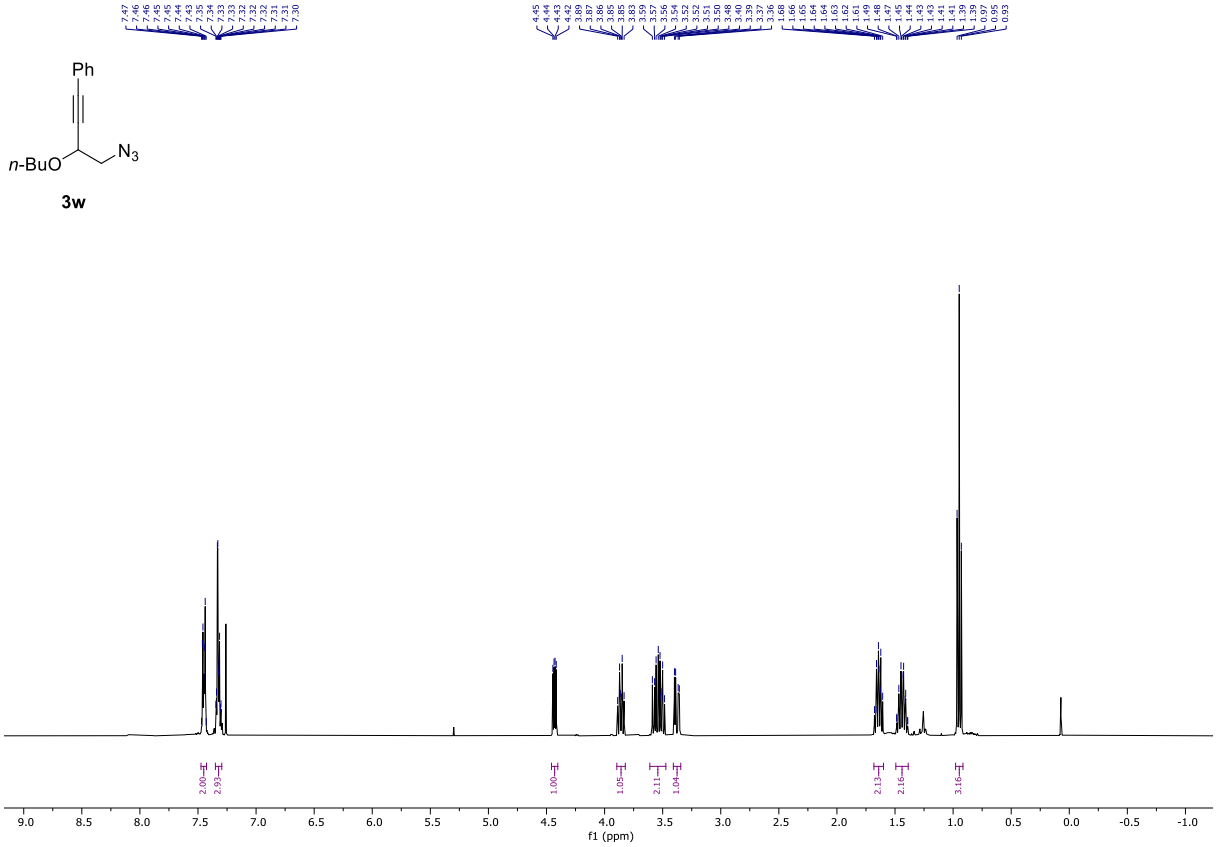
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3v**:



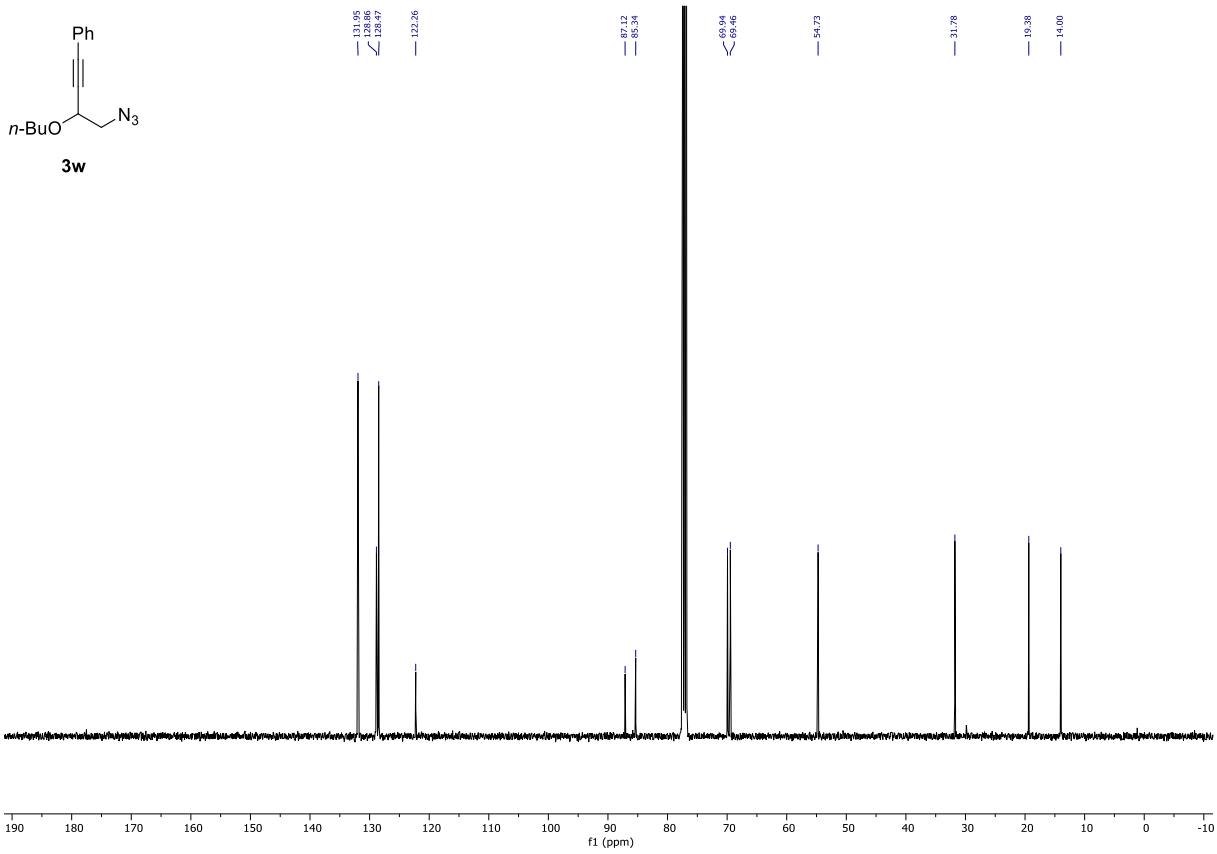
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3v**:



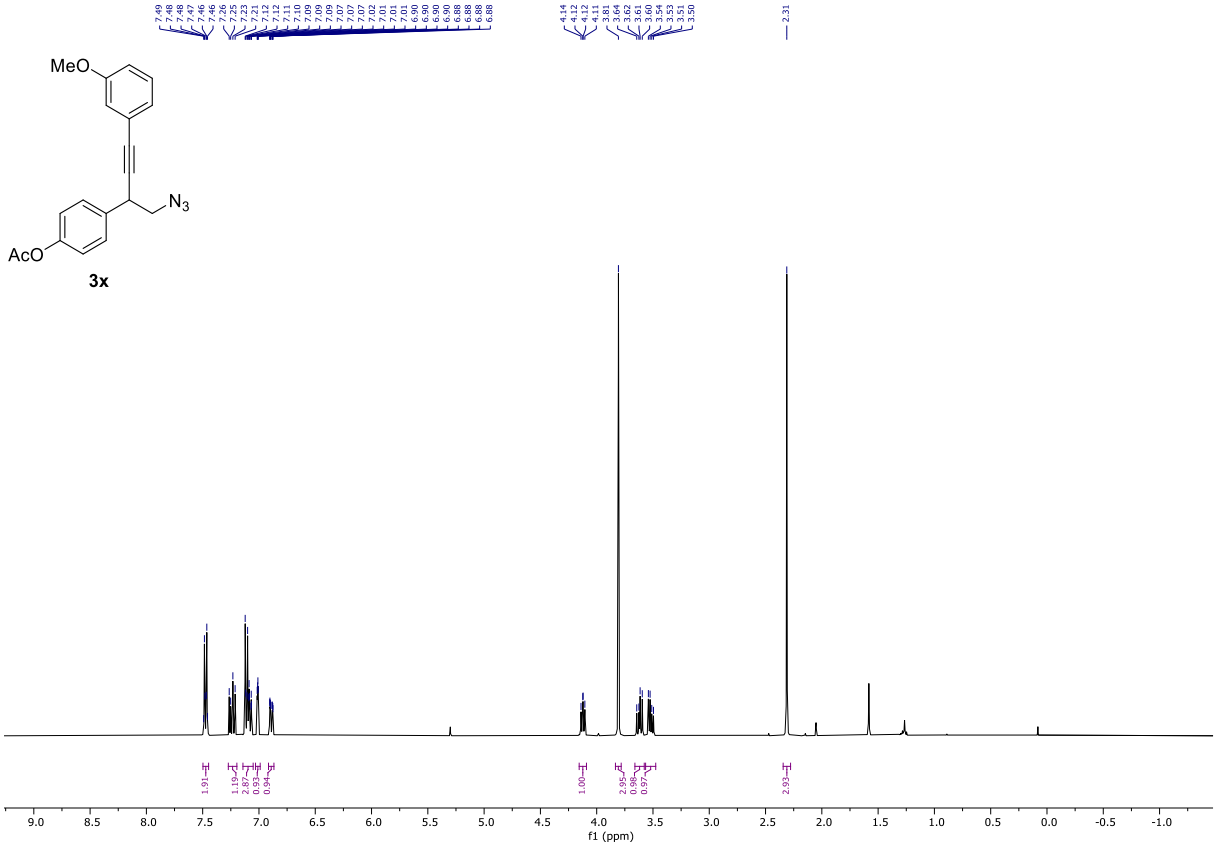
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3w**:



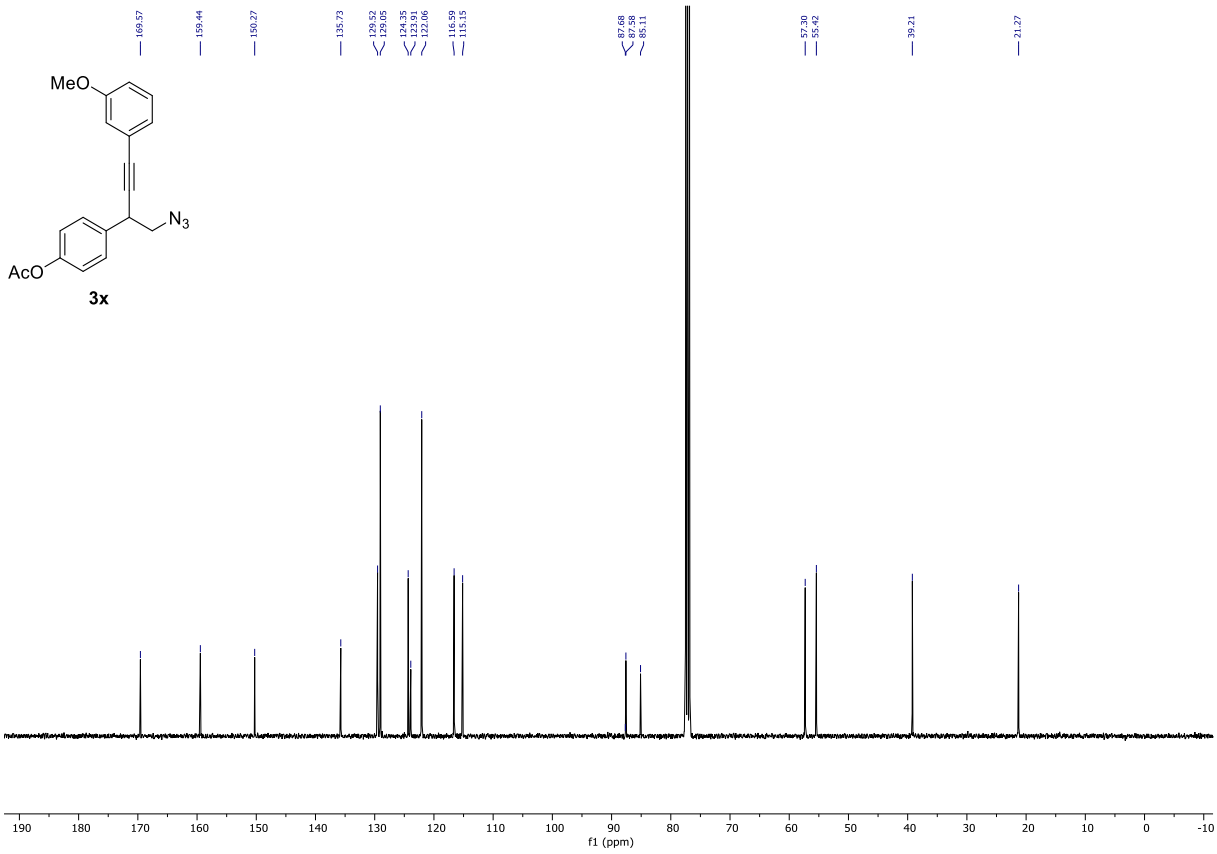
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3w**:



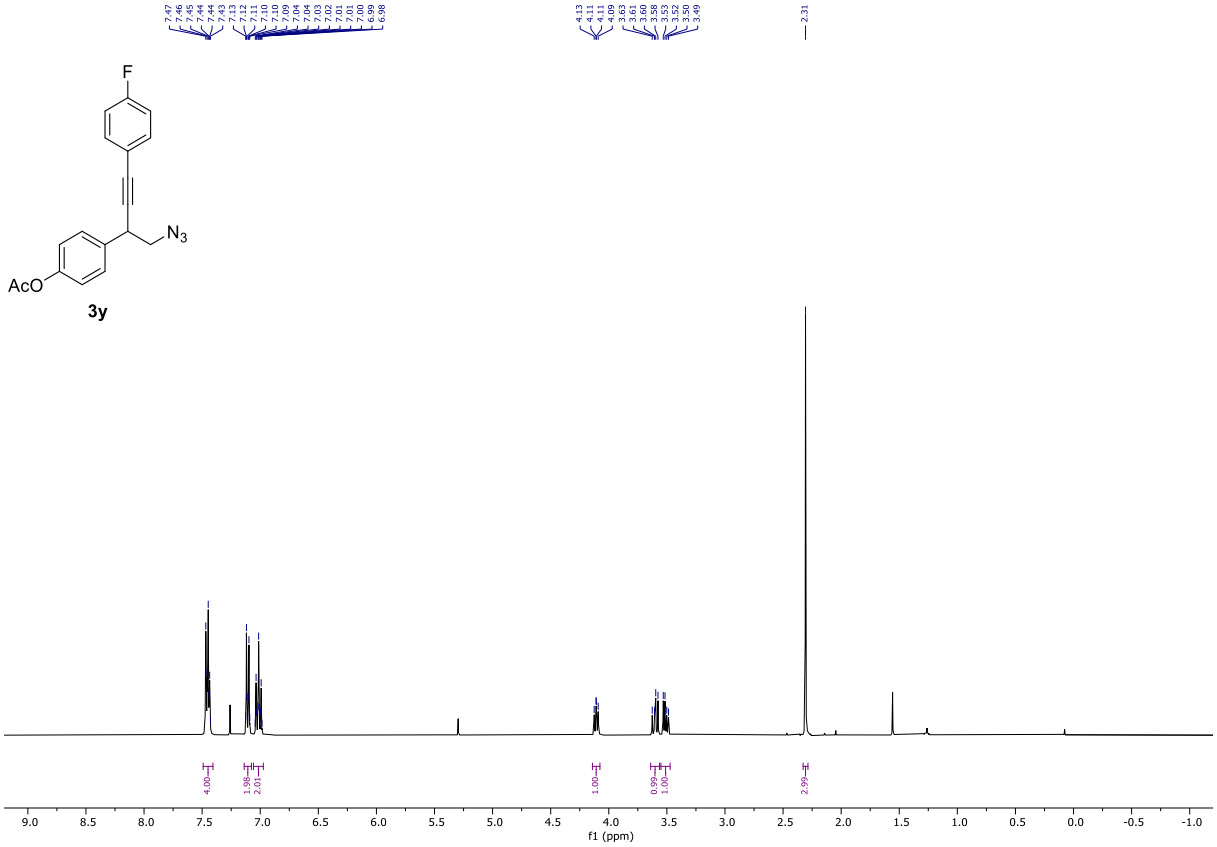
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3x**:



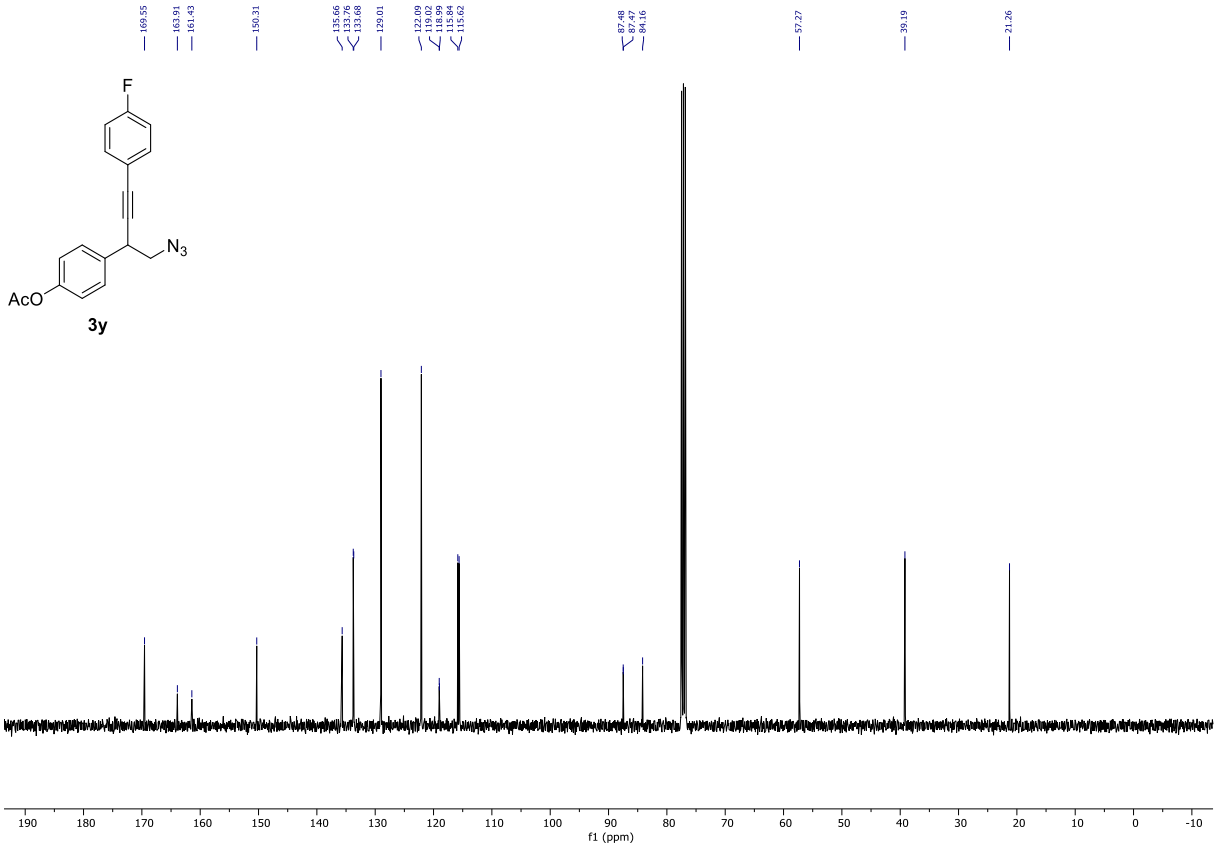
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3x**:



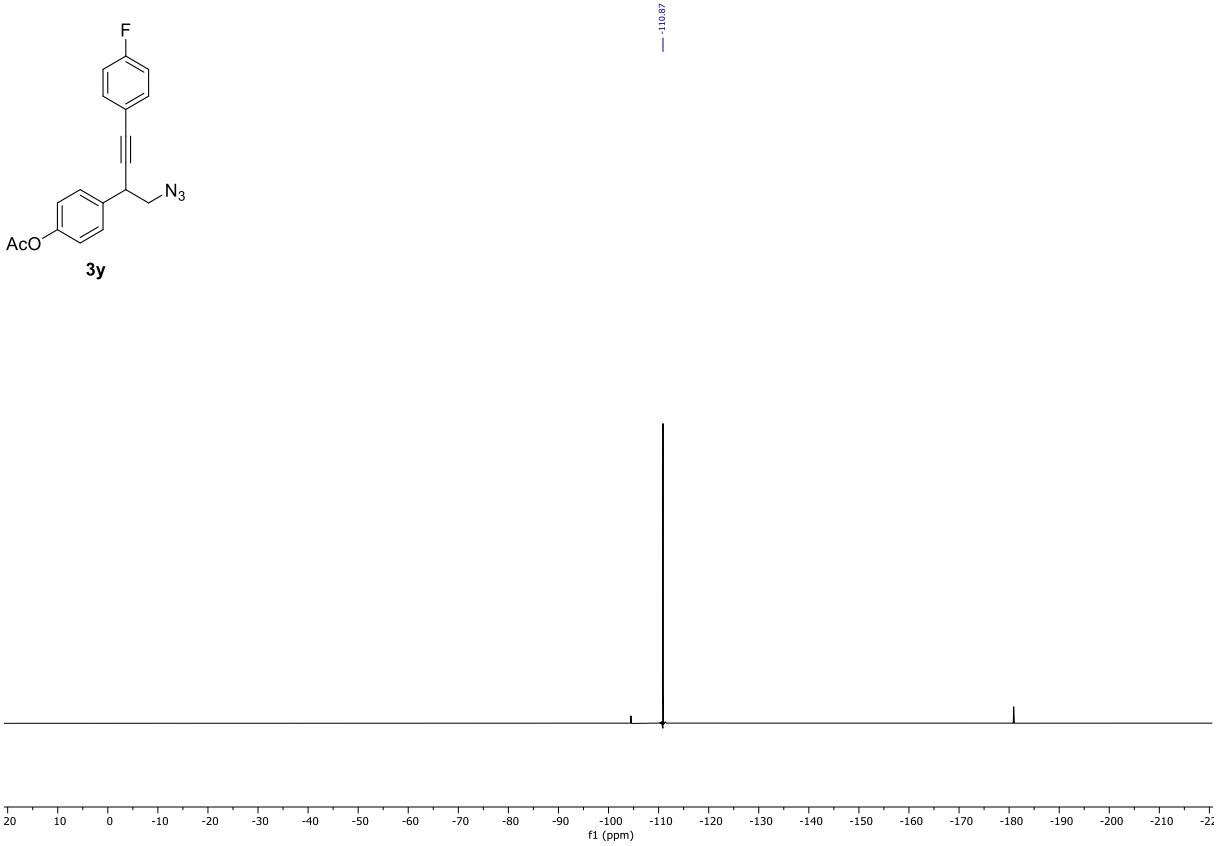
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3y**:



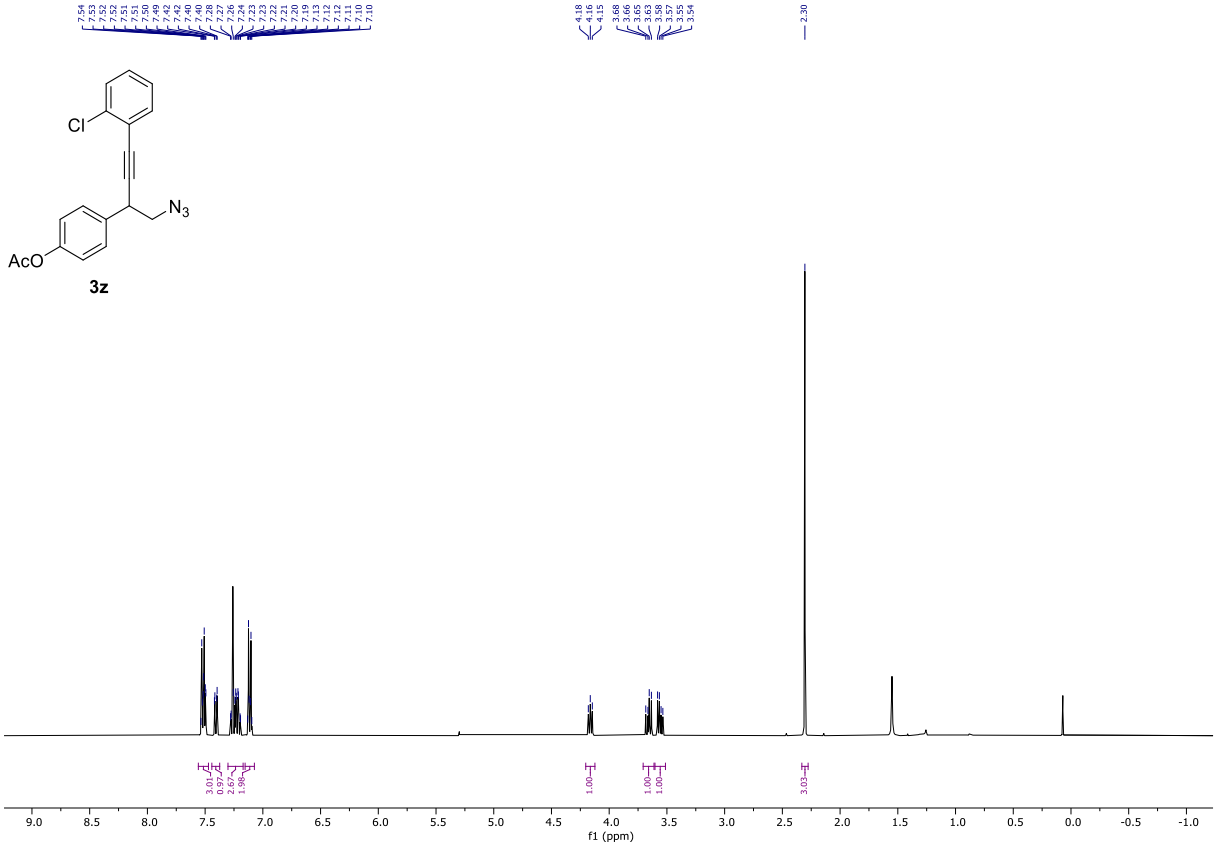
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3y**:



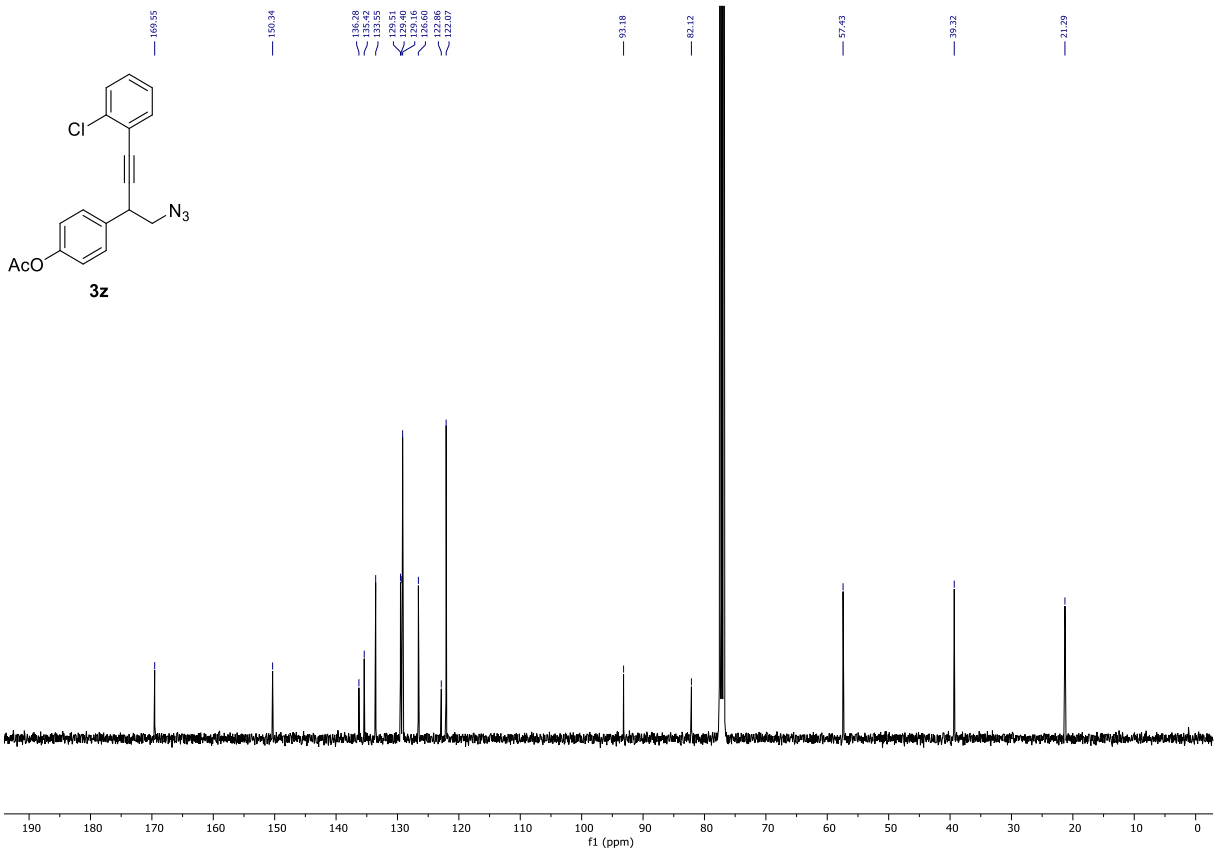
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3y**:



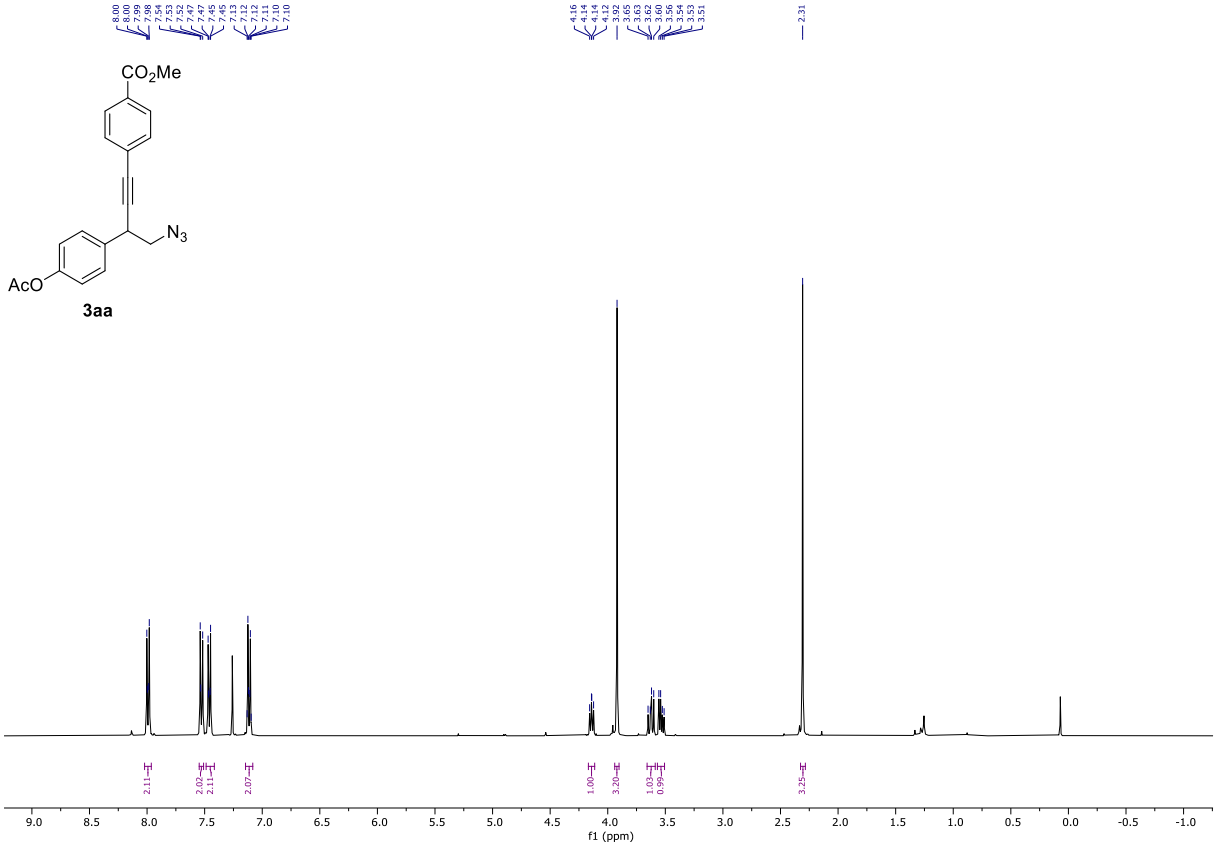
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3z**:



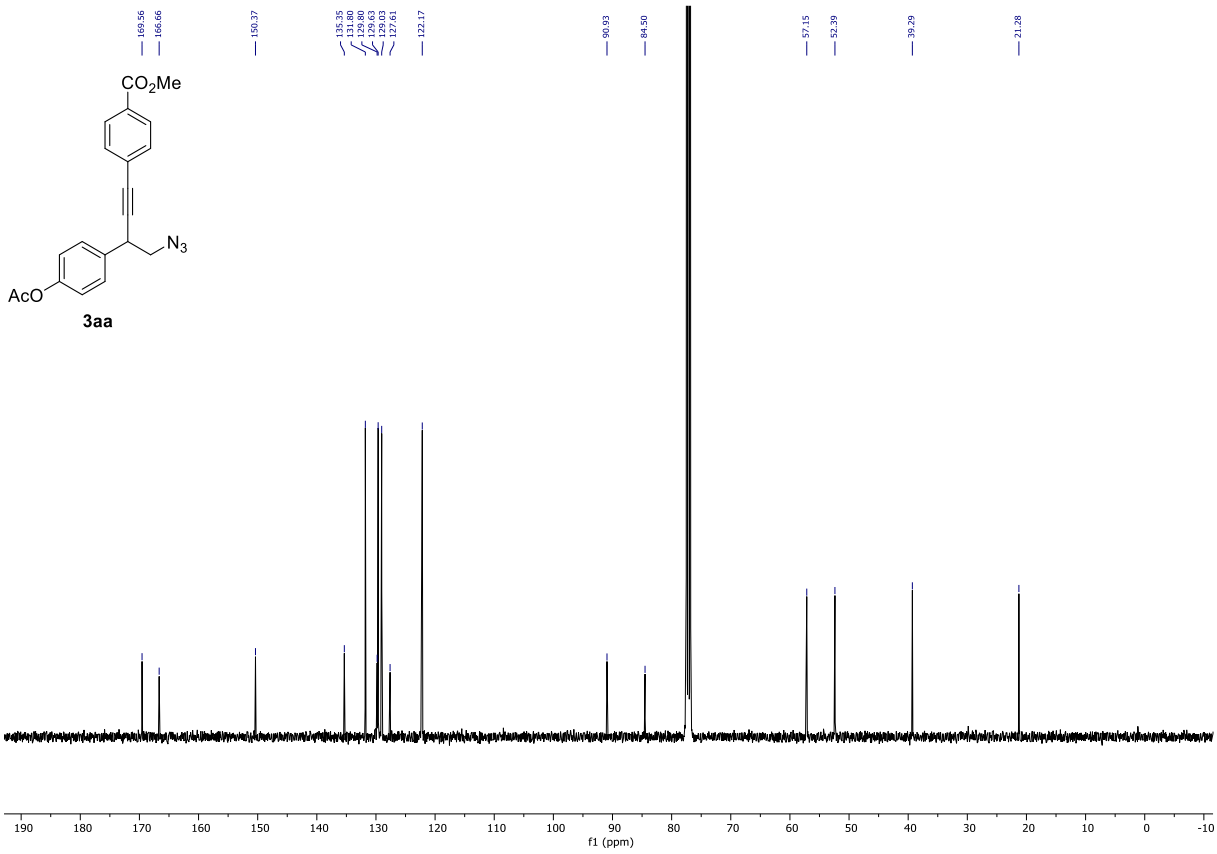
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3z**:



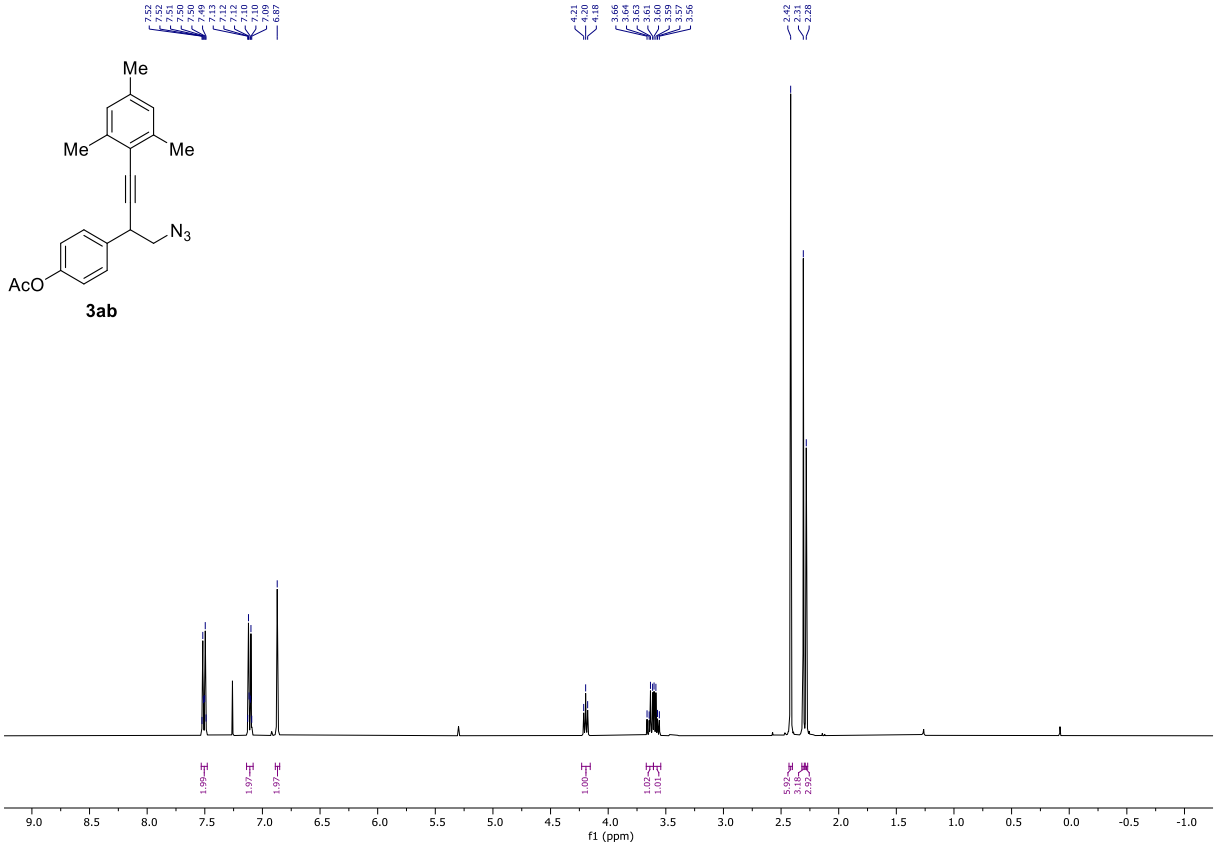
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aa**:



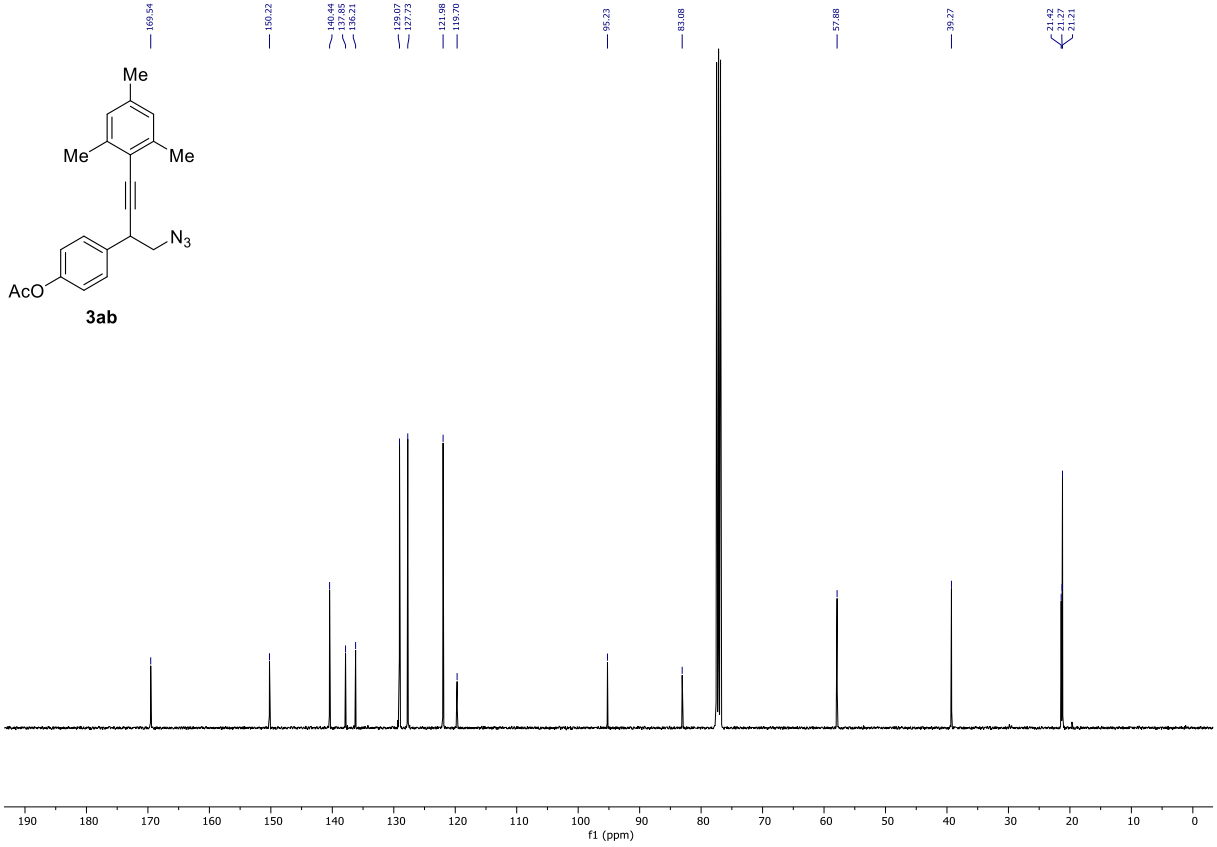
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3aa**:



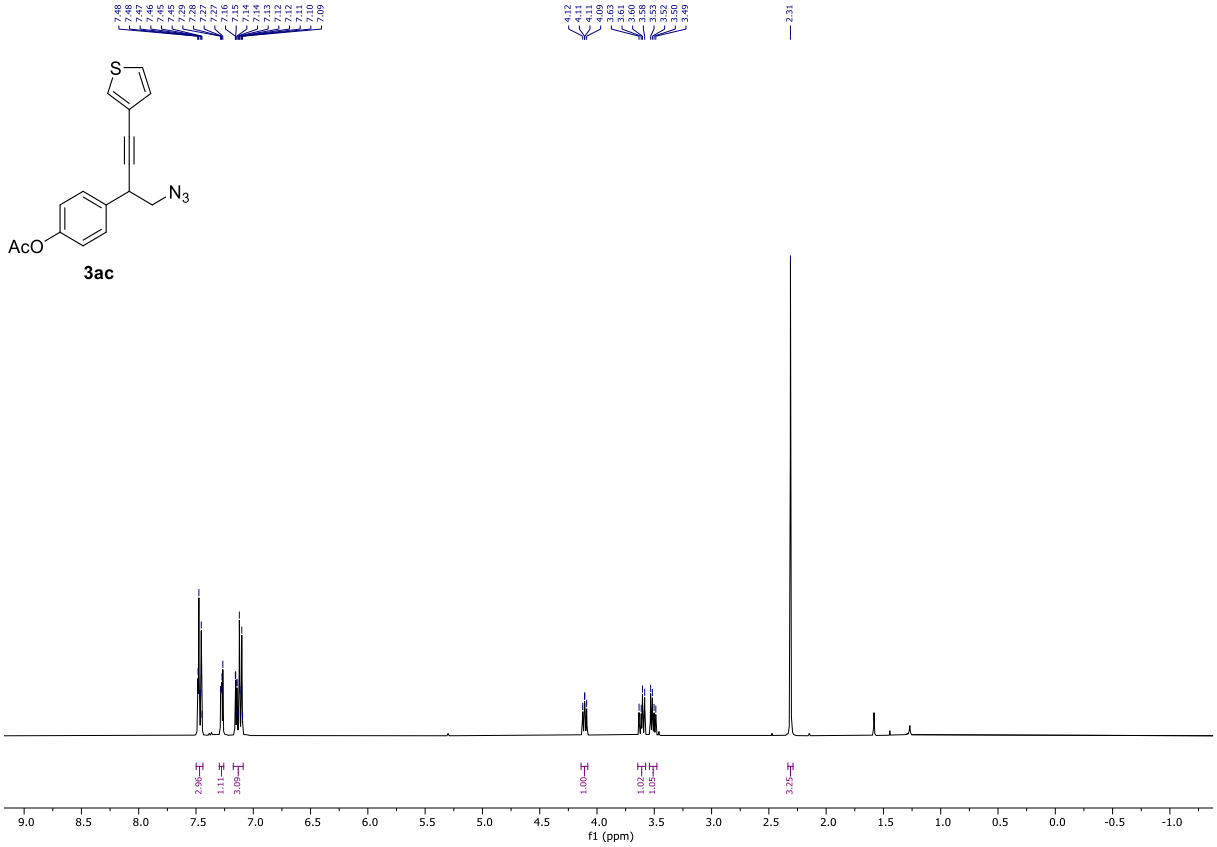
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ab**:



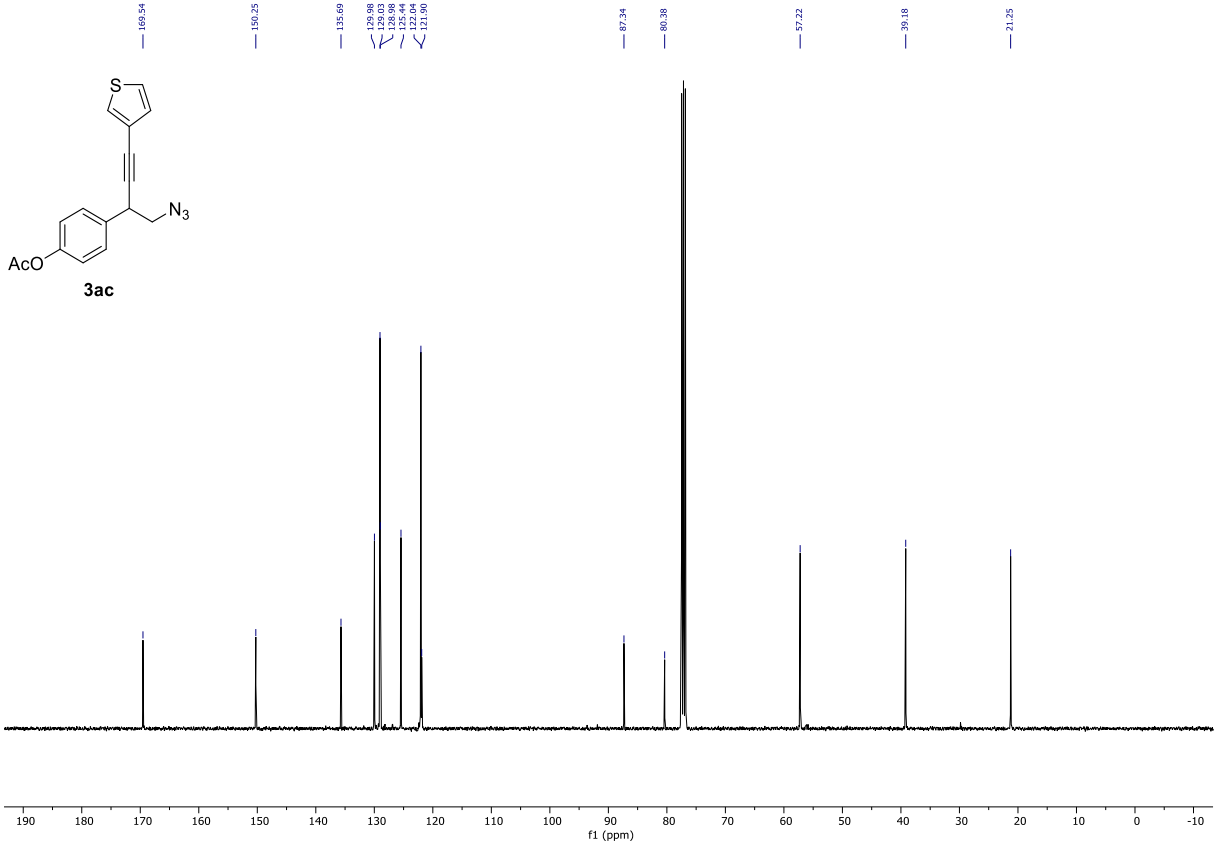
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3ab**:



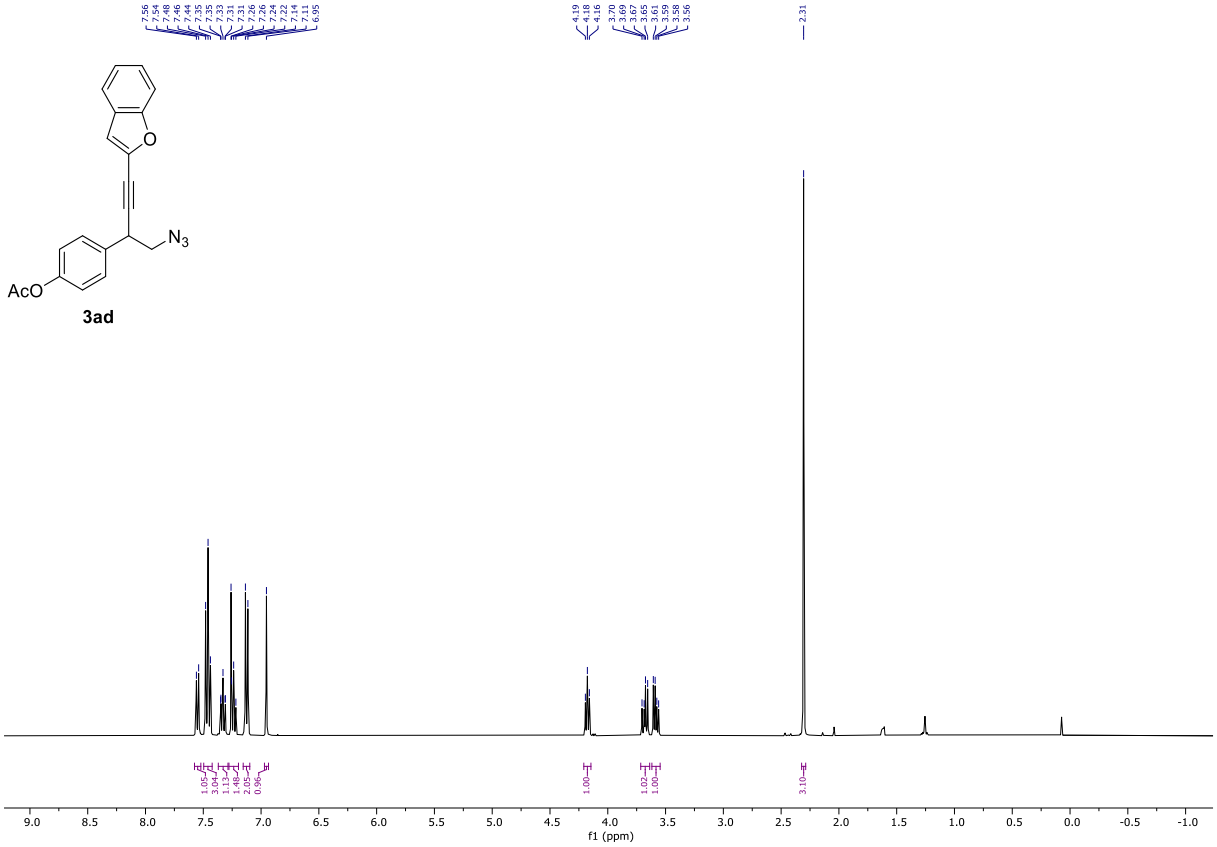
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ac**:



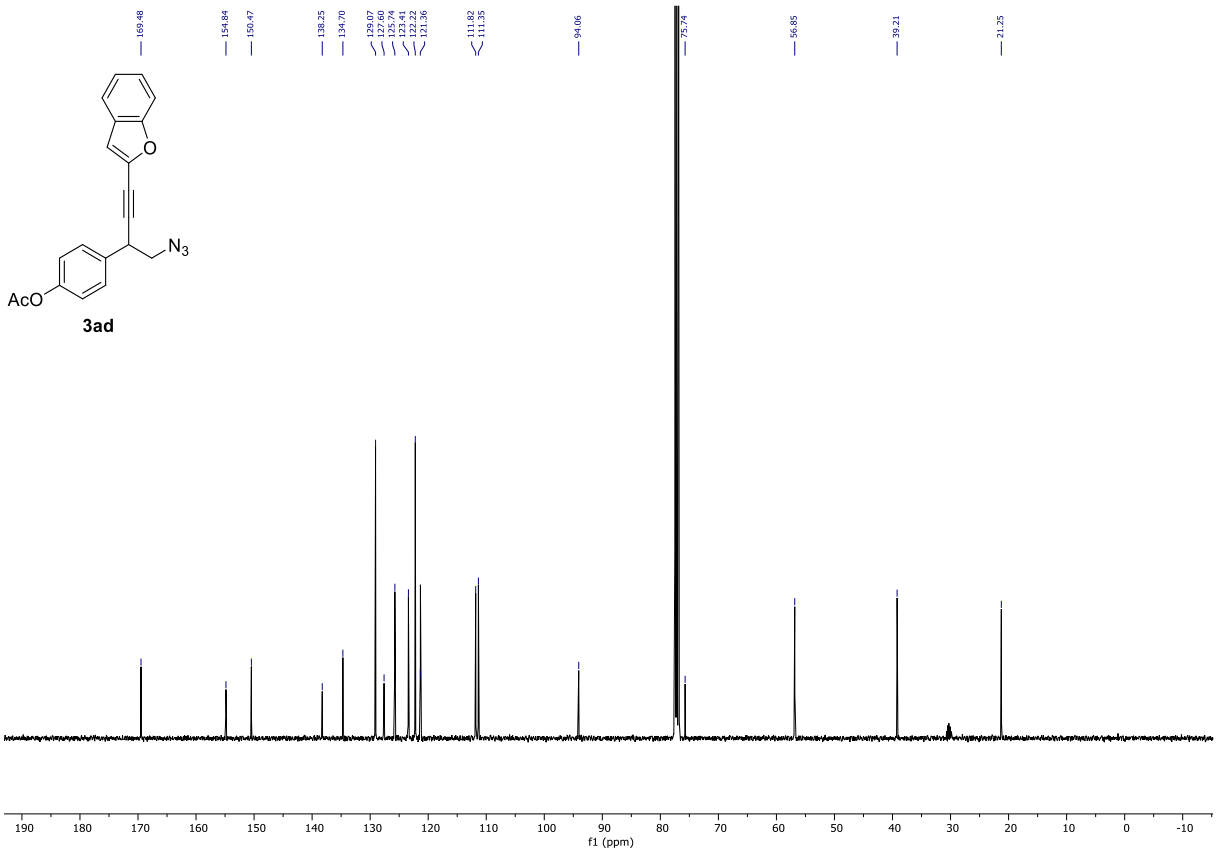
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3ac**:



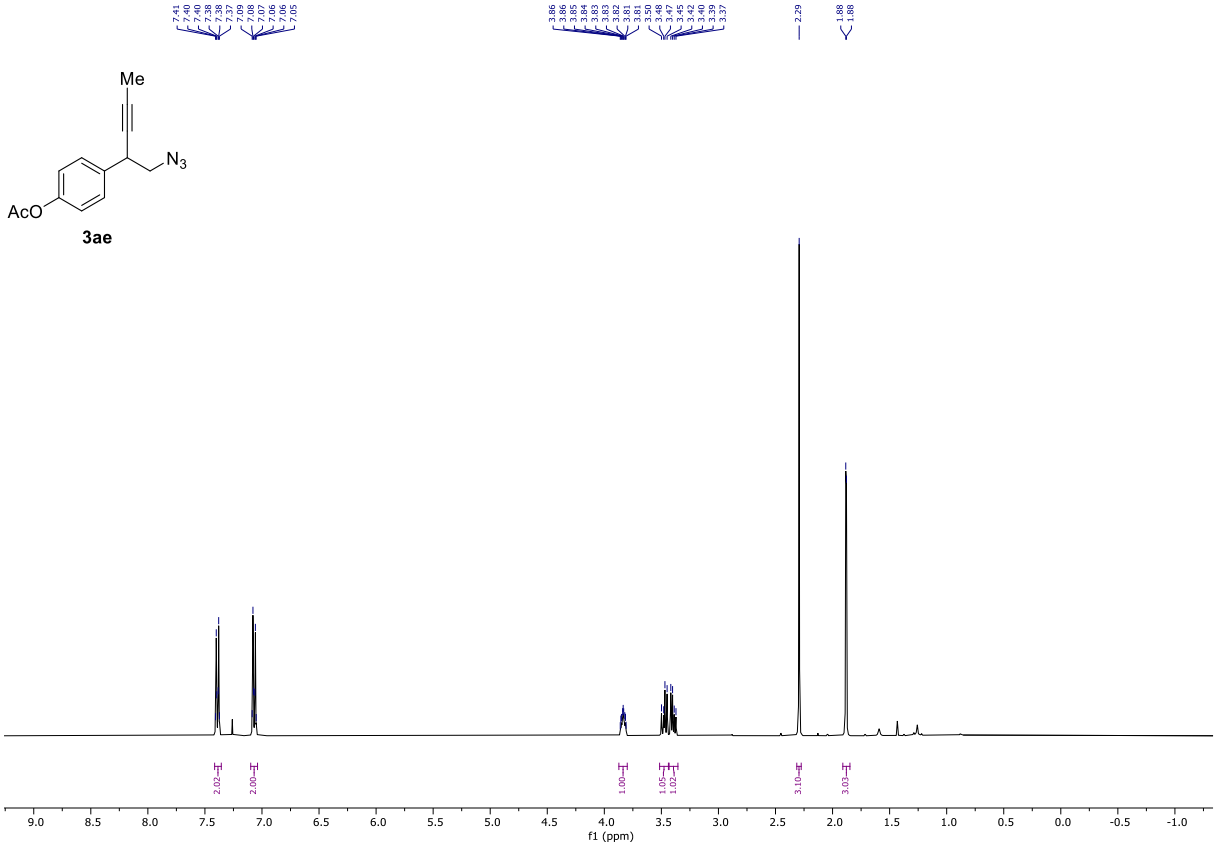
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ad**:



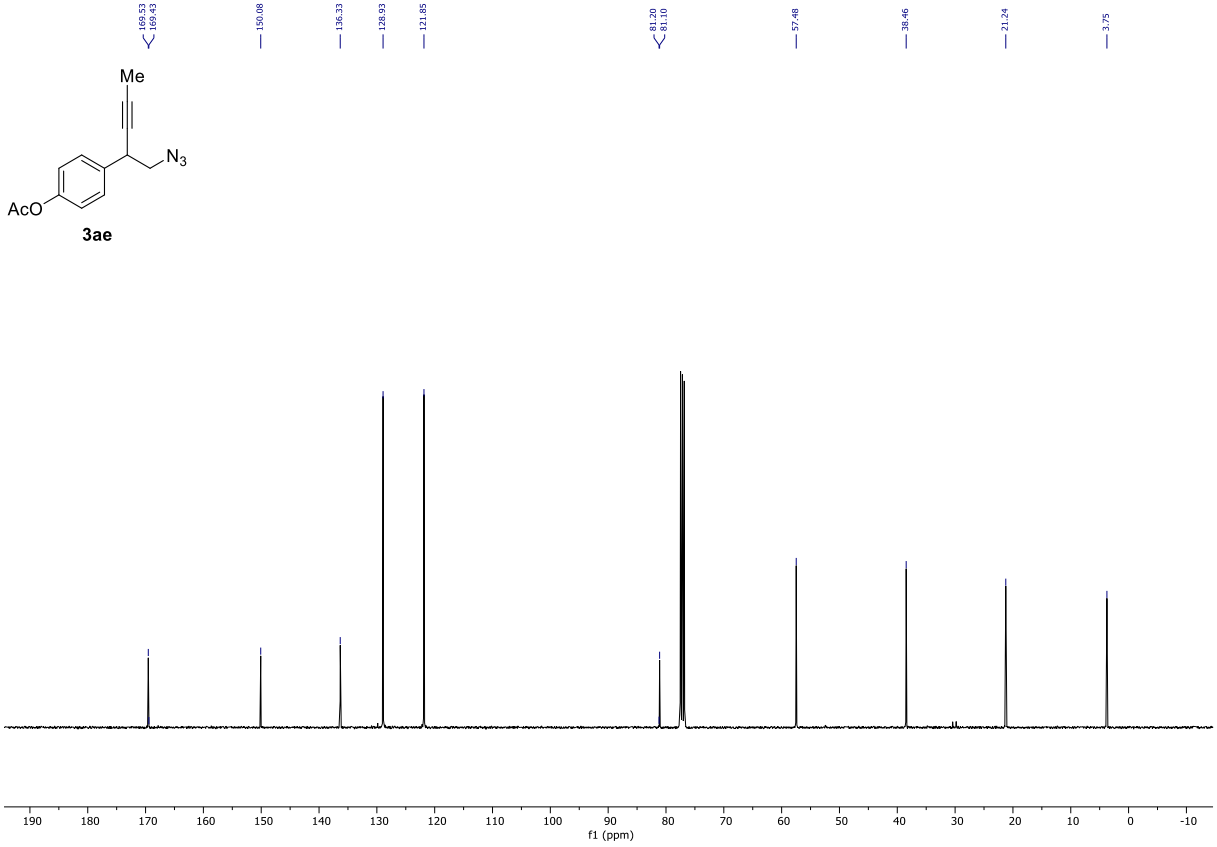
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3ad**:



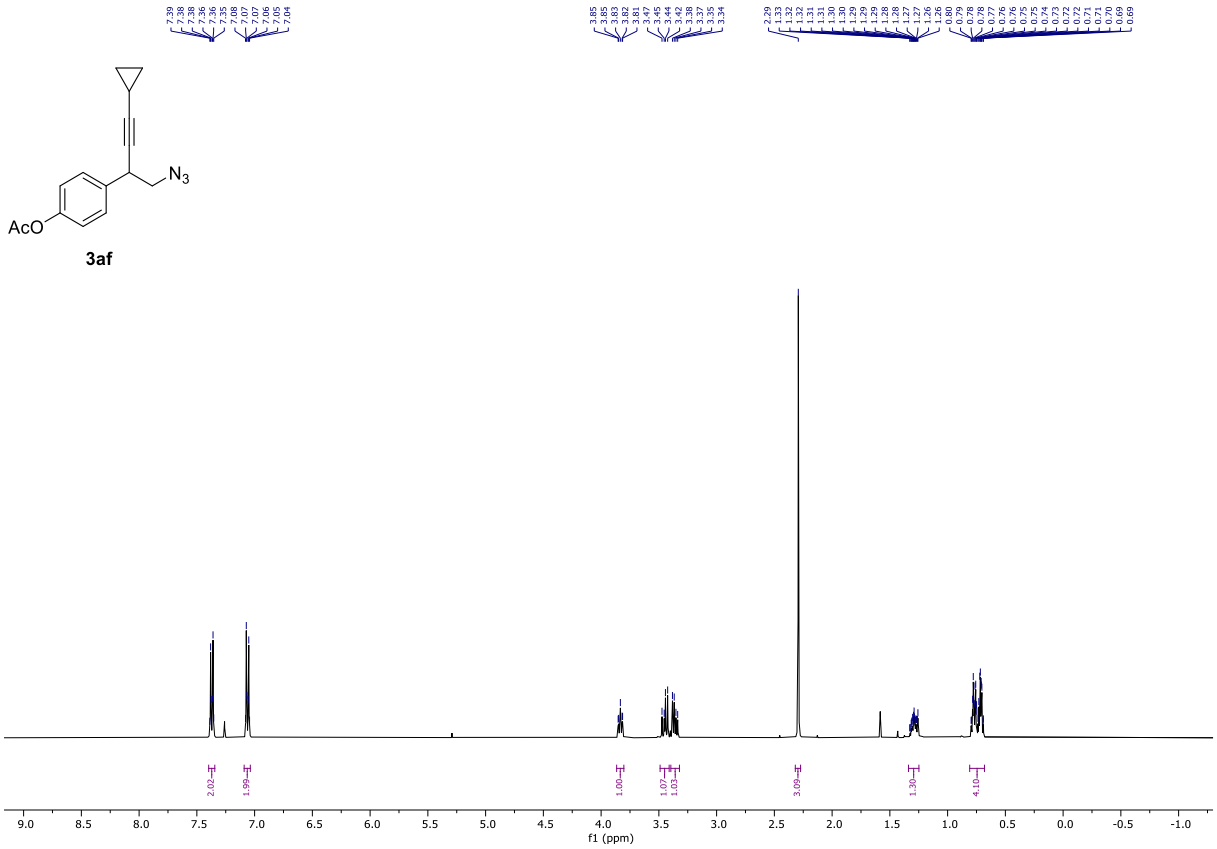
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ae**:



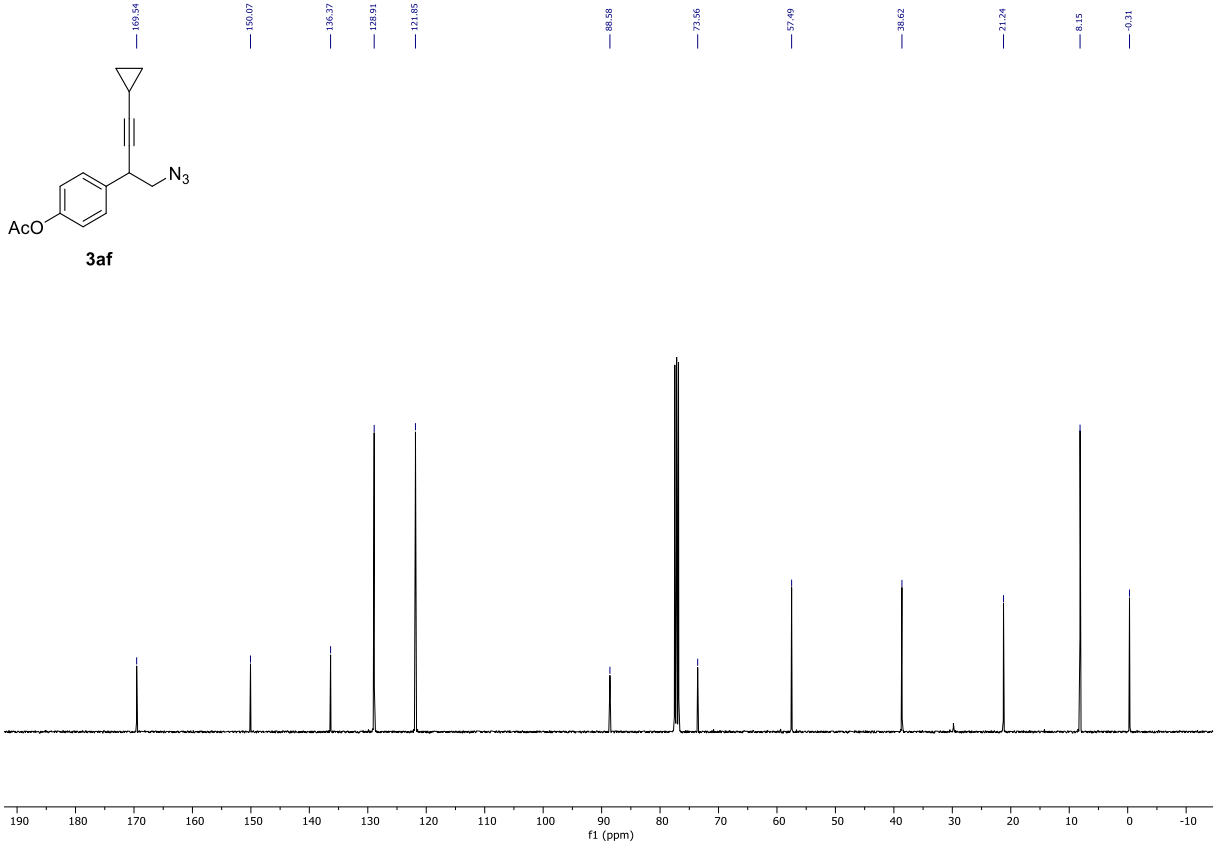
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3ae**:



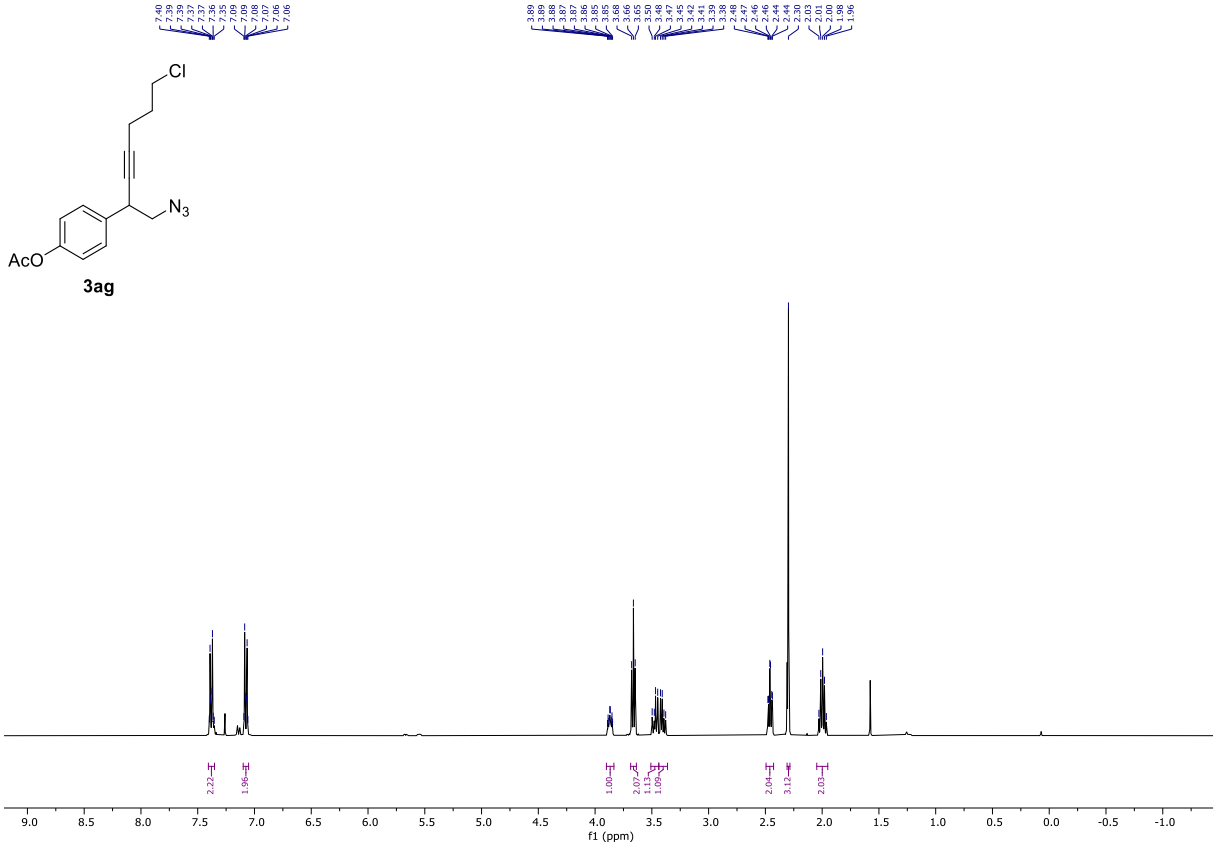
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3af**:



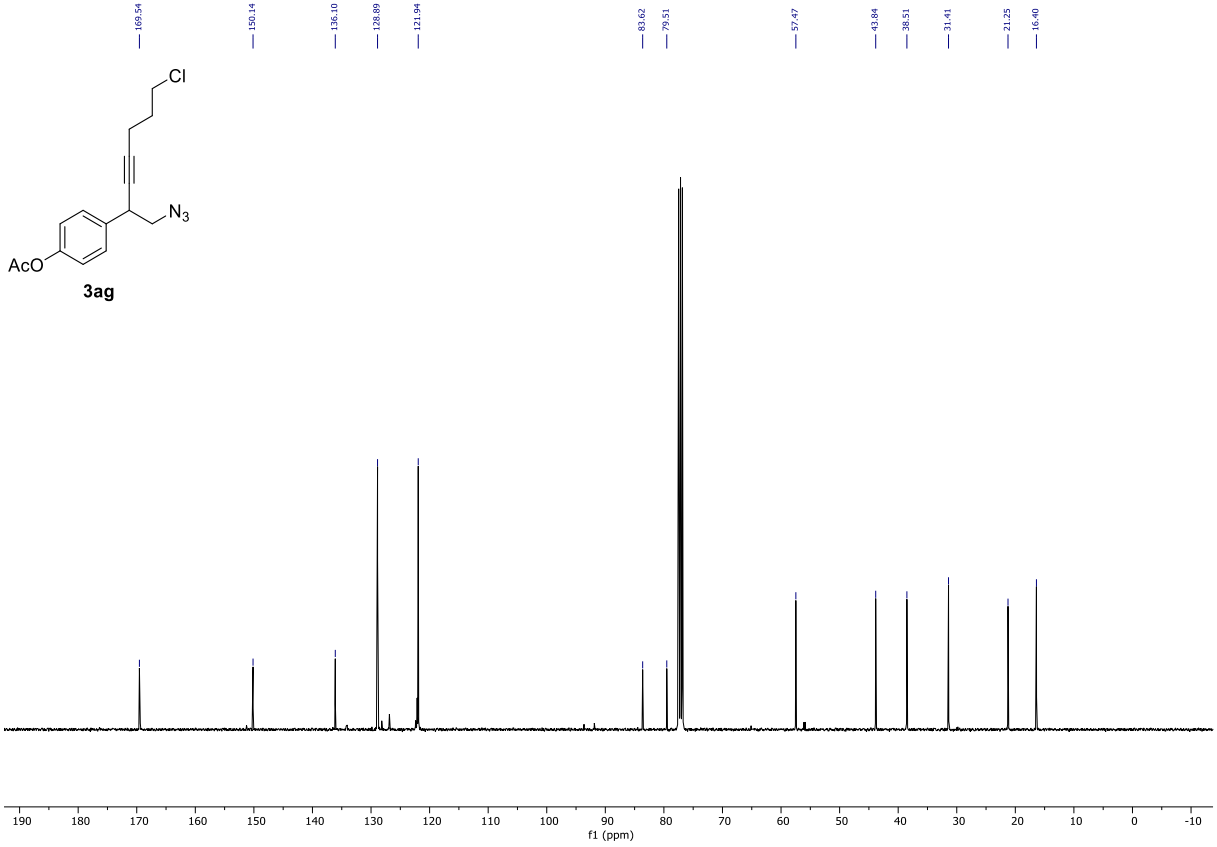
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3af**:



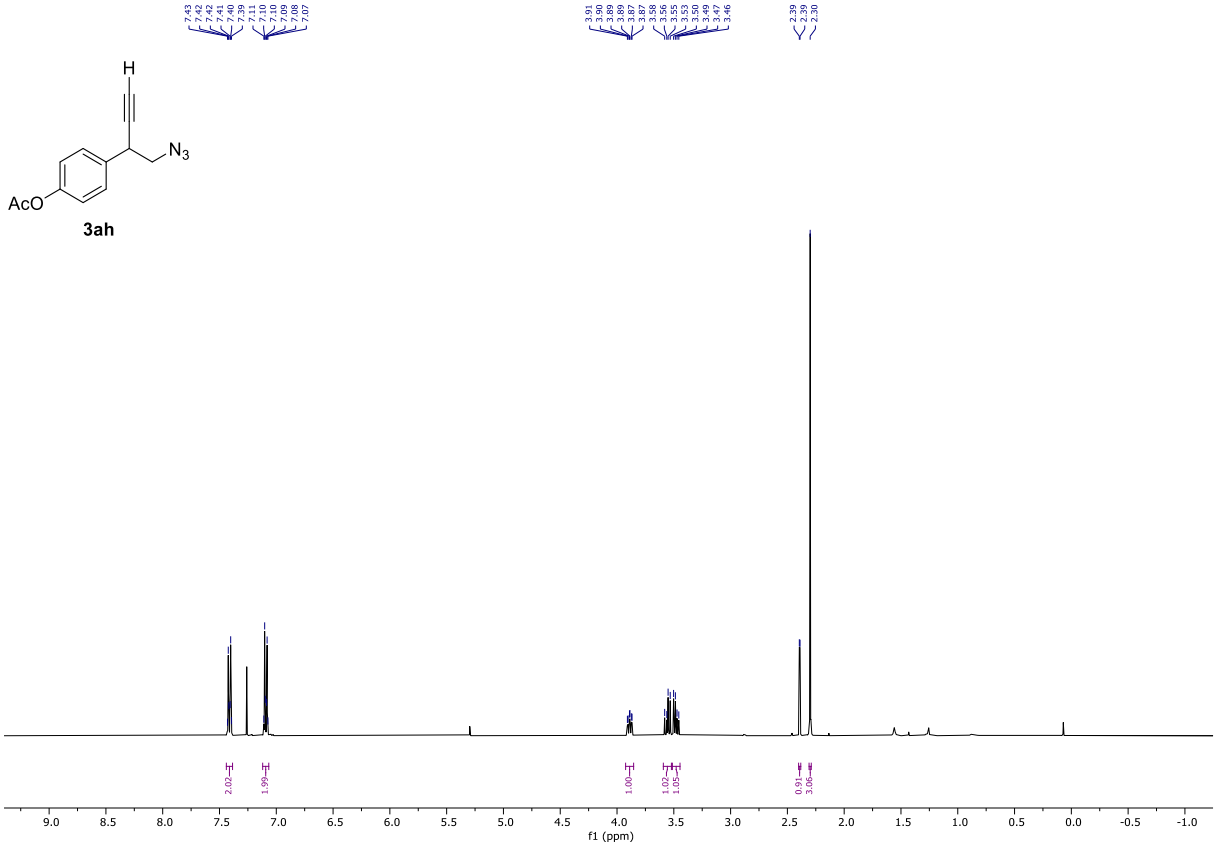
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ag**:



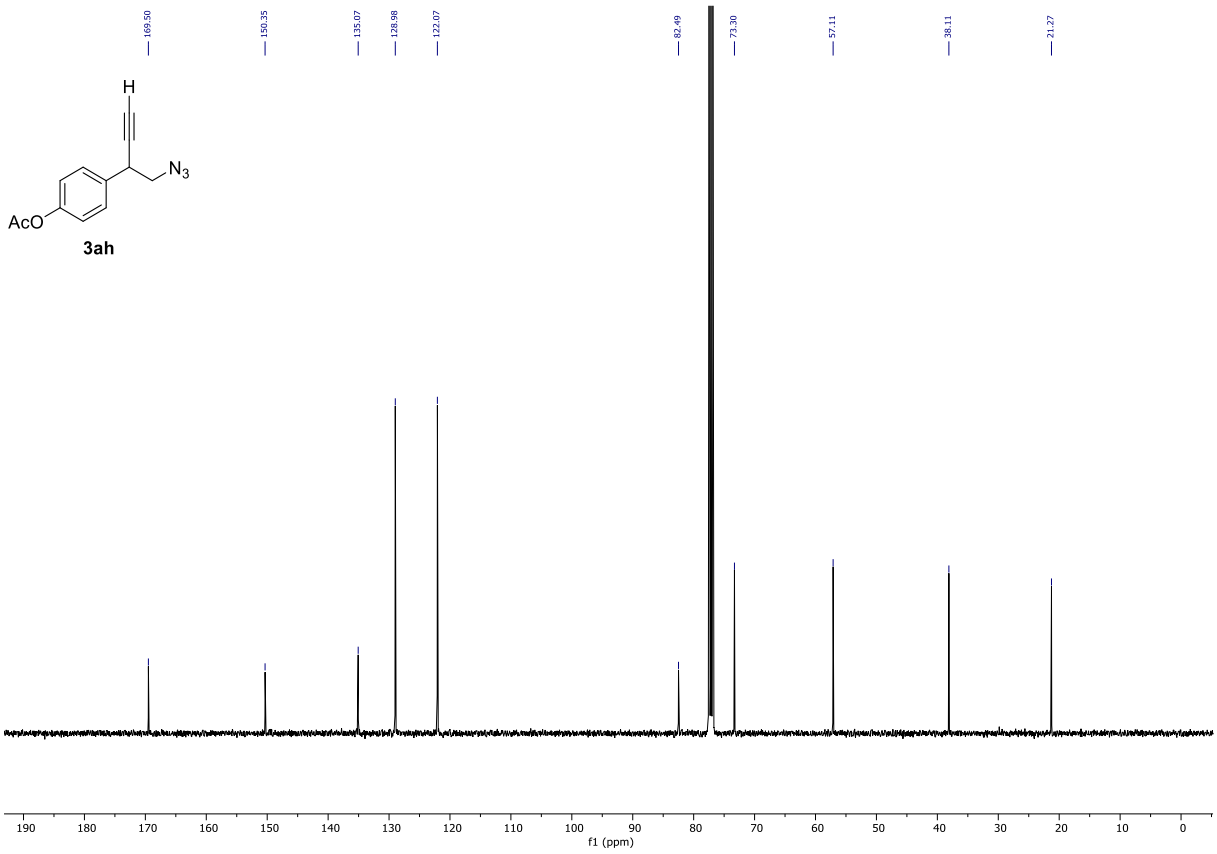
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3ag**:



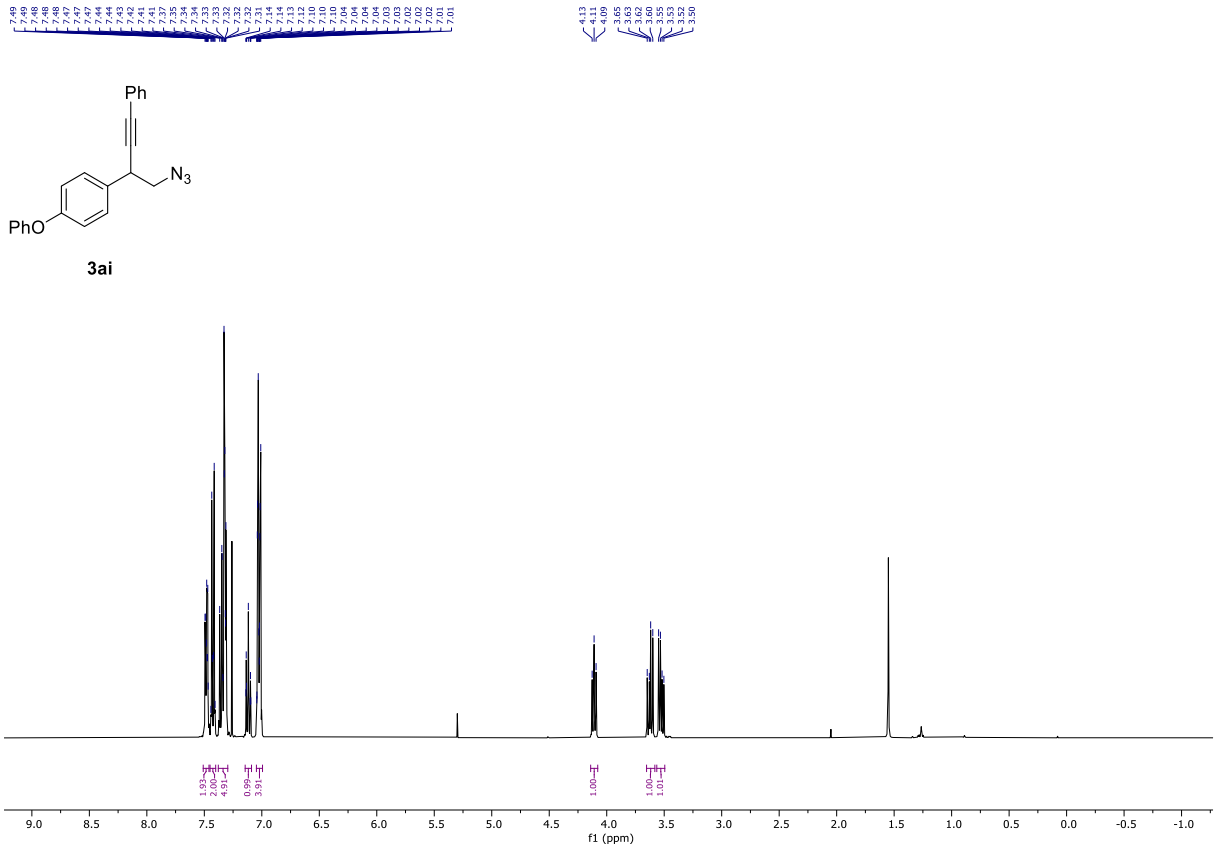
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ah**:



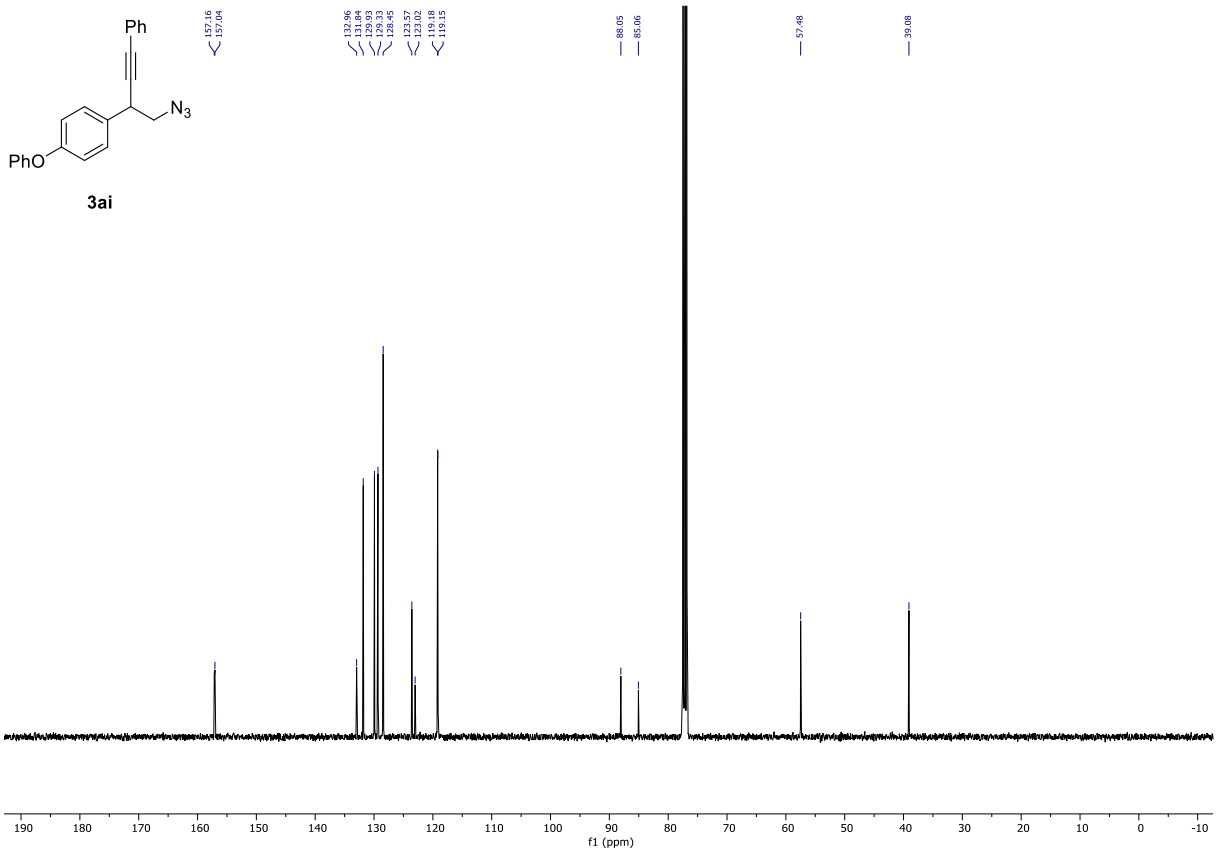
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3ah**:



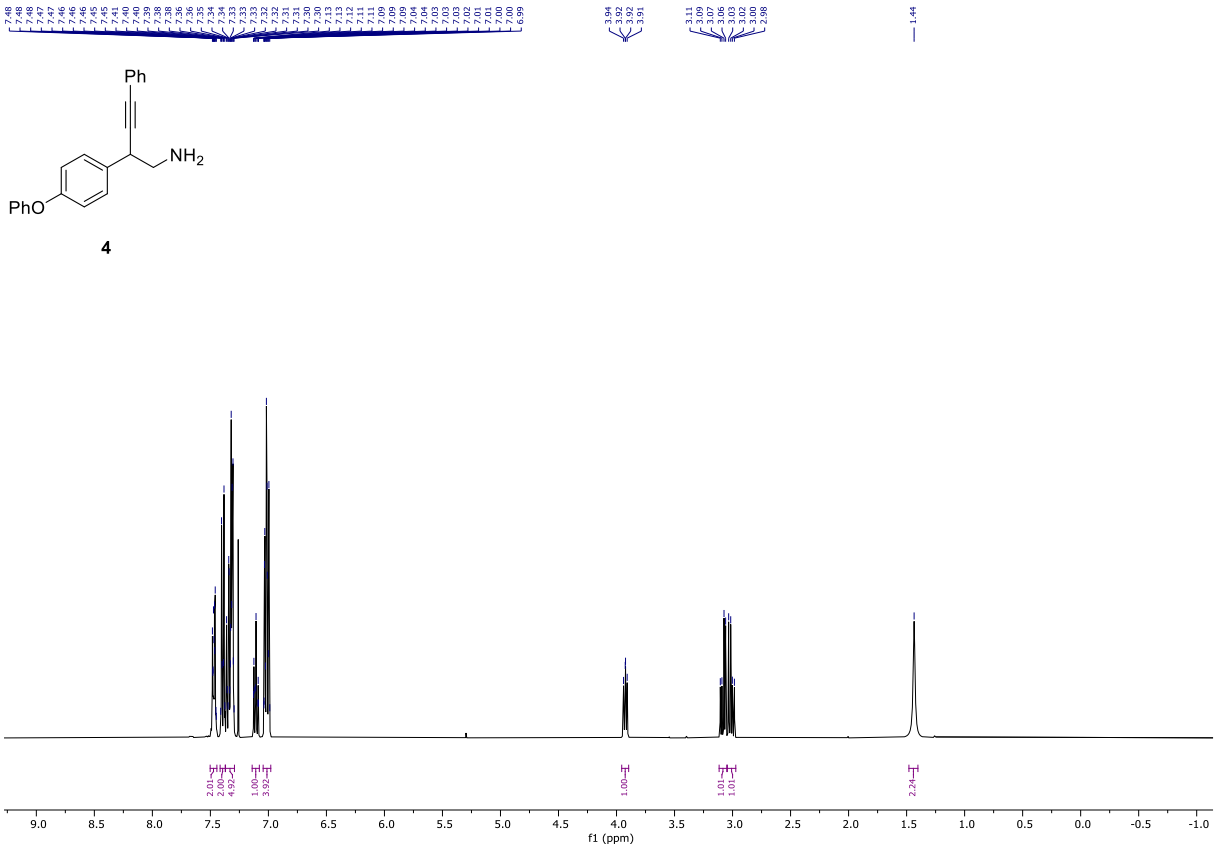
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ai**:



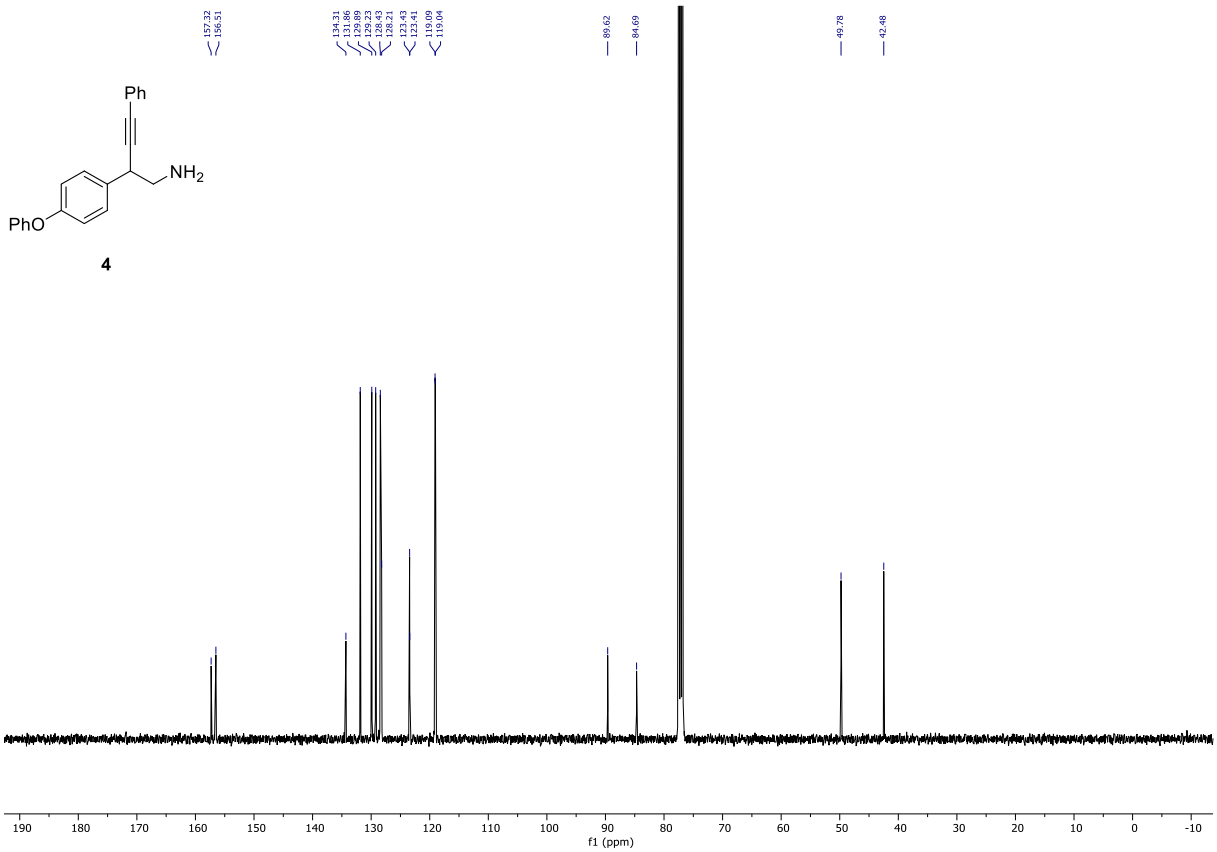
^{13}C NMR (101 MHz, $CDCl_3$) of compound **3ai**:



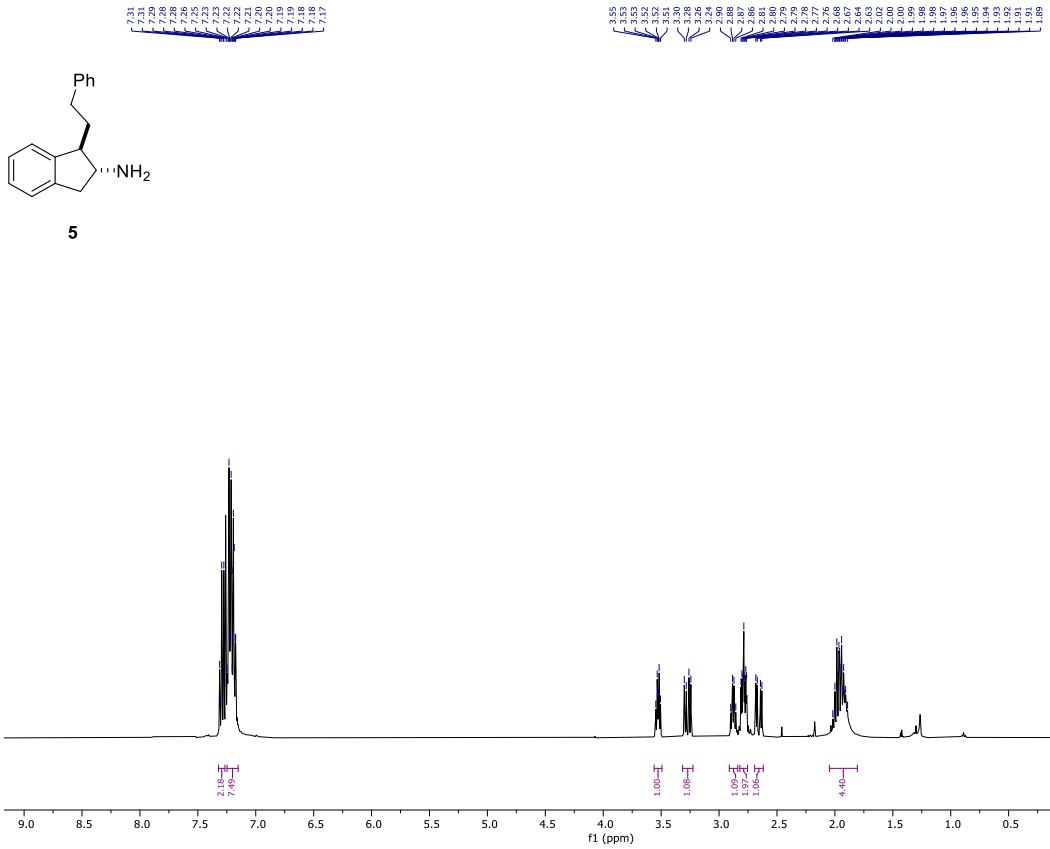
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4**:



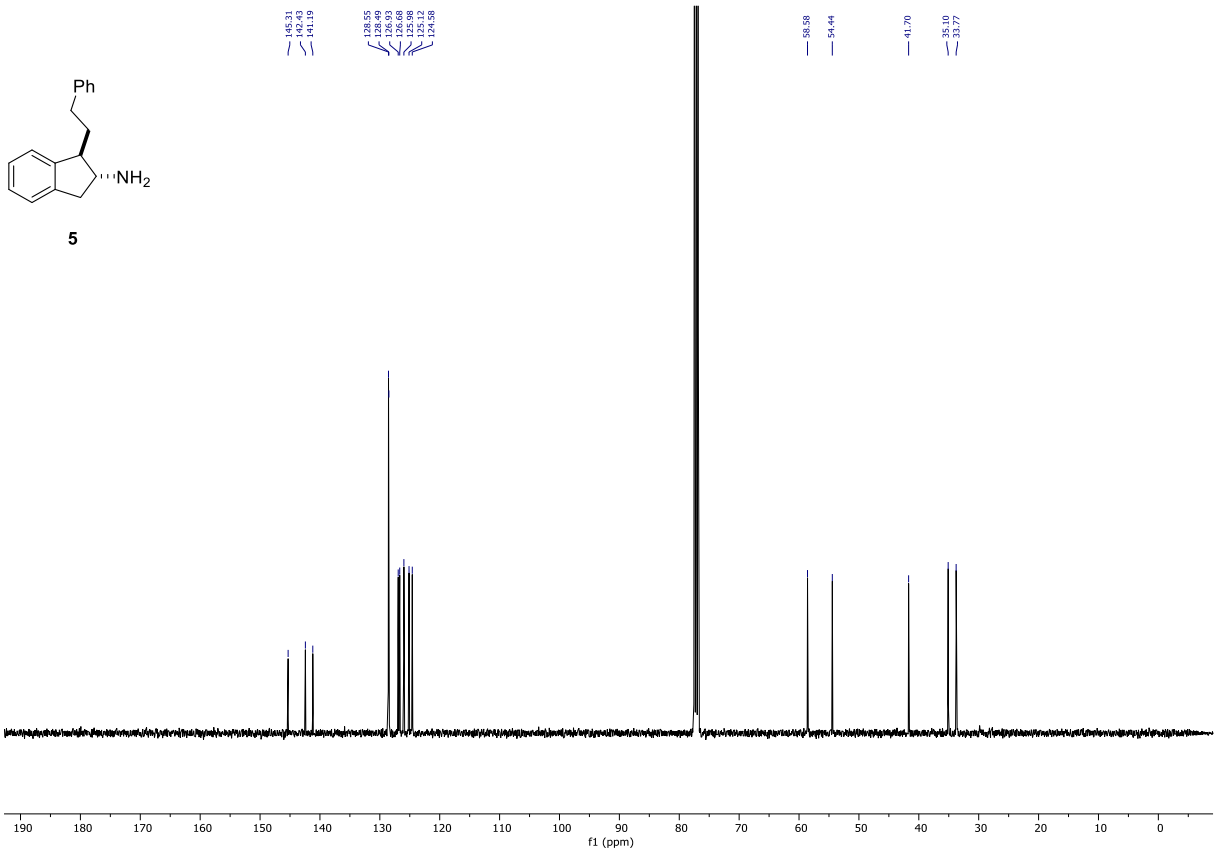
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4**:



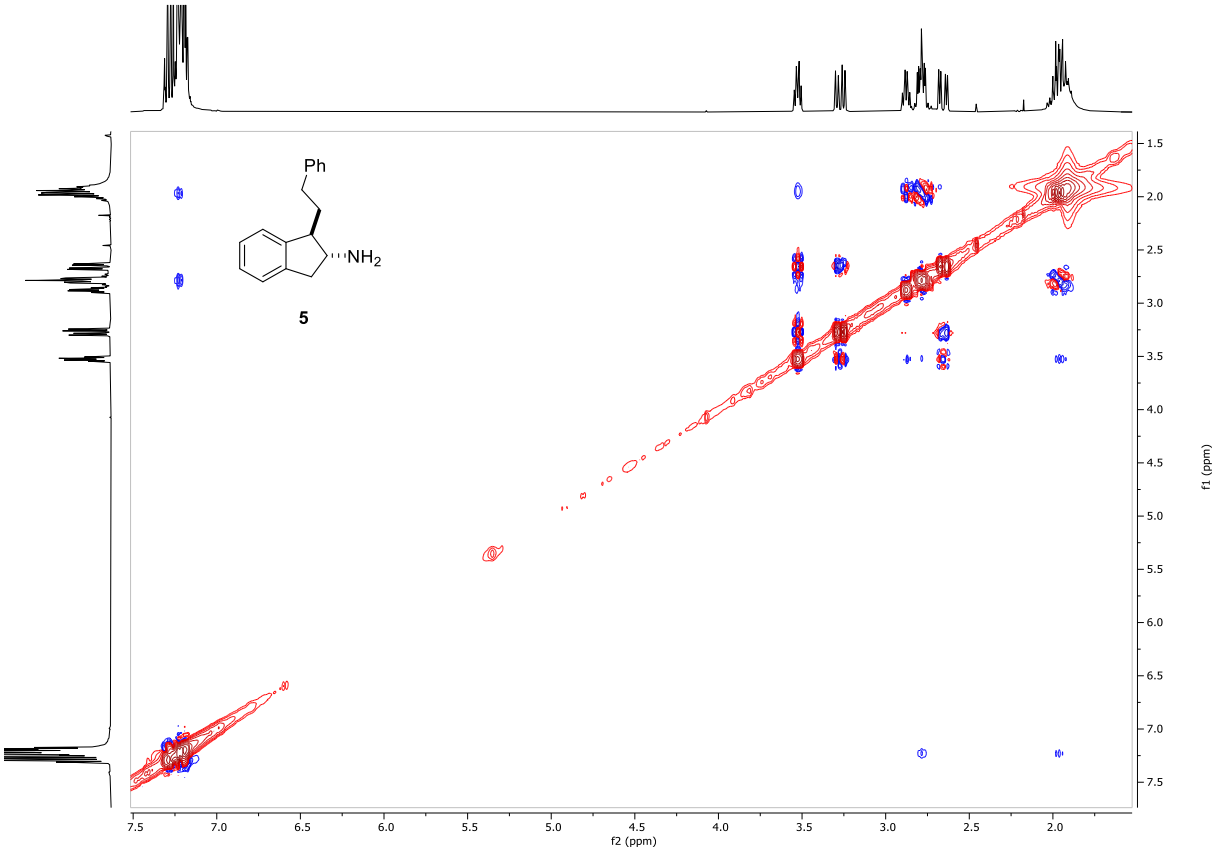
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5**:



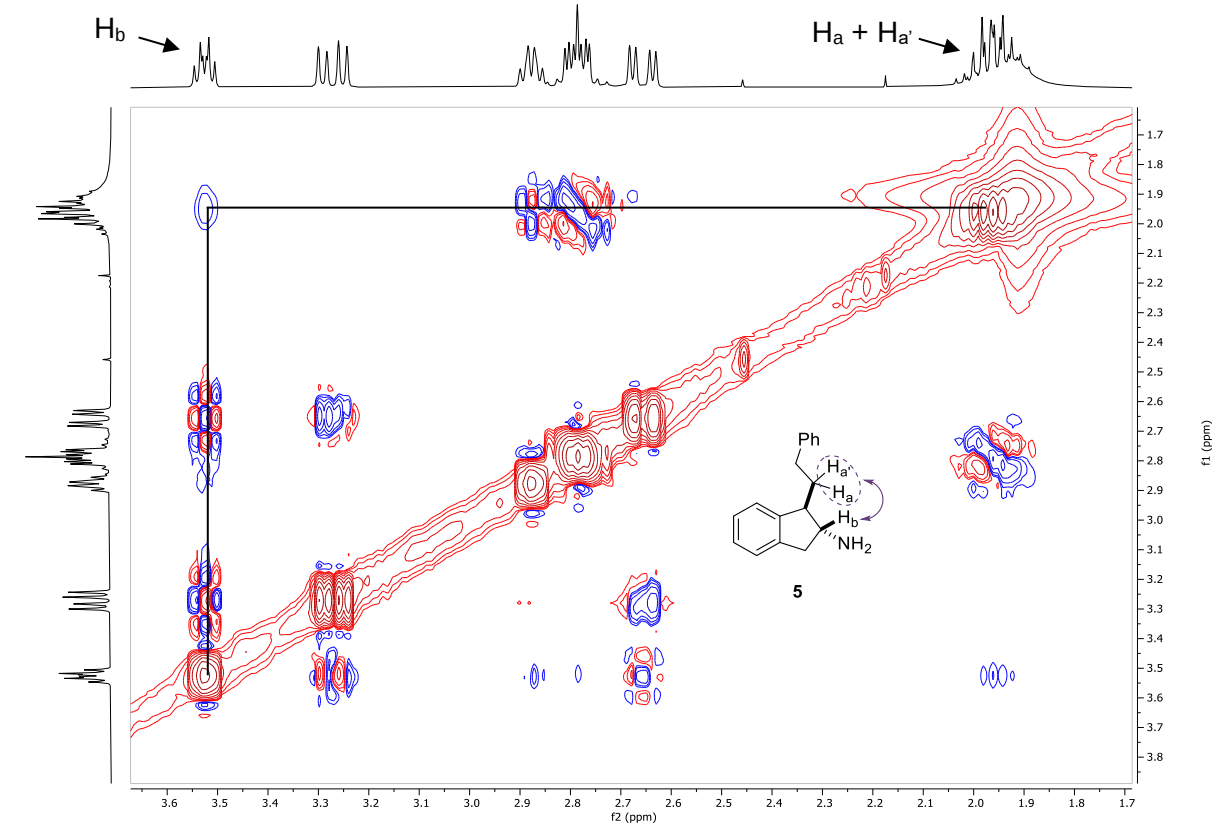
^{13}C NMR (101 MHz, $CDCl_3$) of compound **5**:



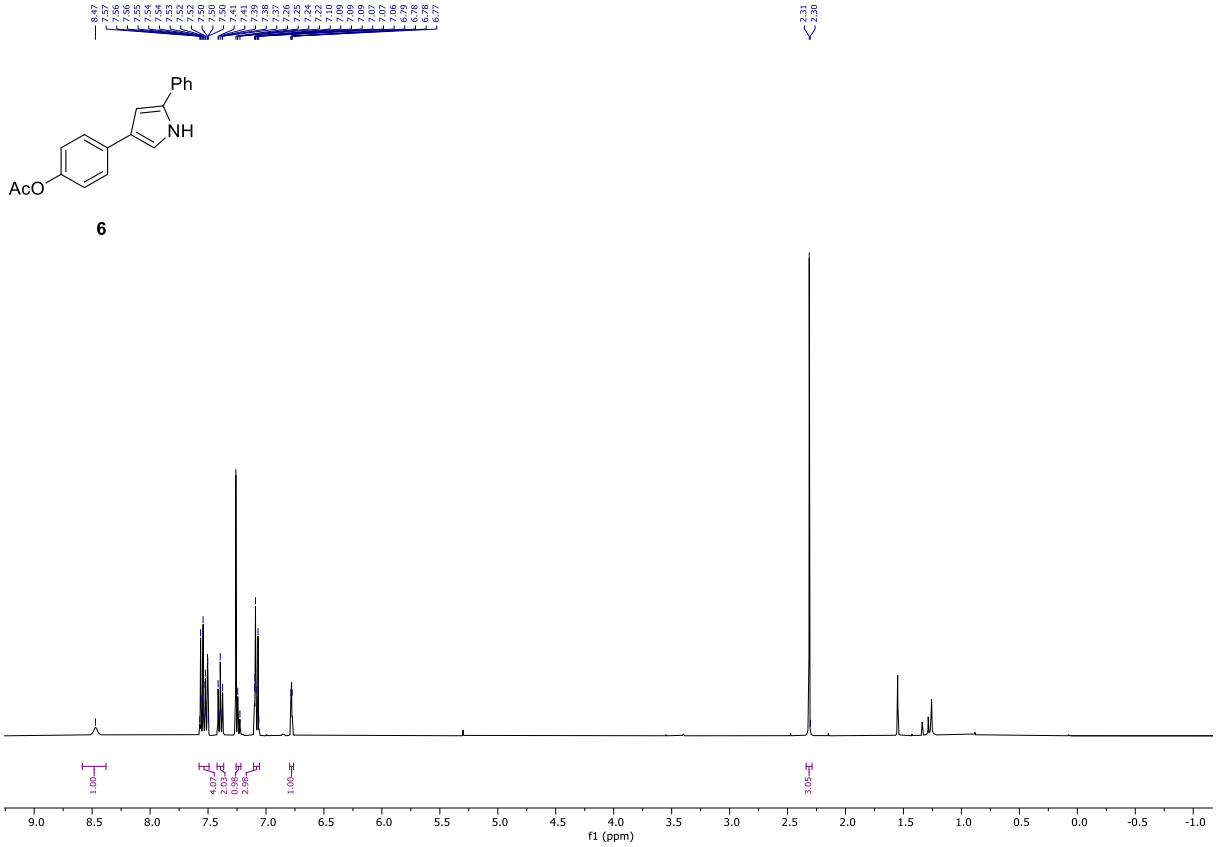
^{1}H-^{1}H NOESY NMR (400 MHz, $CDCl_3$) of compound **5**:



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

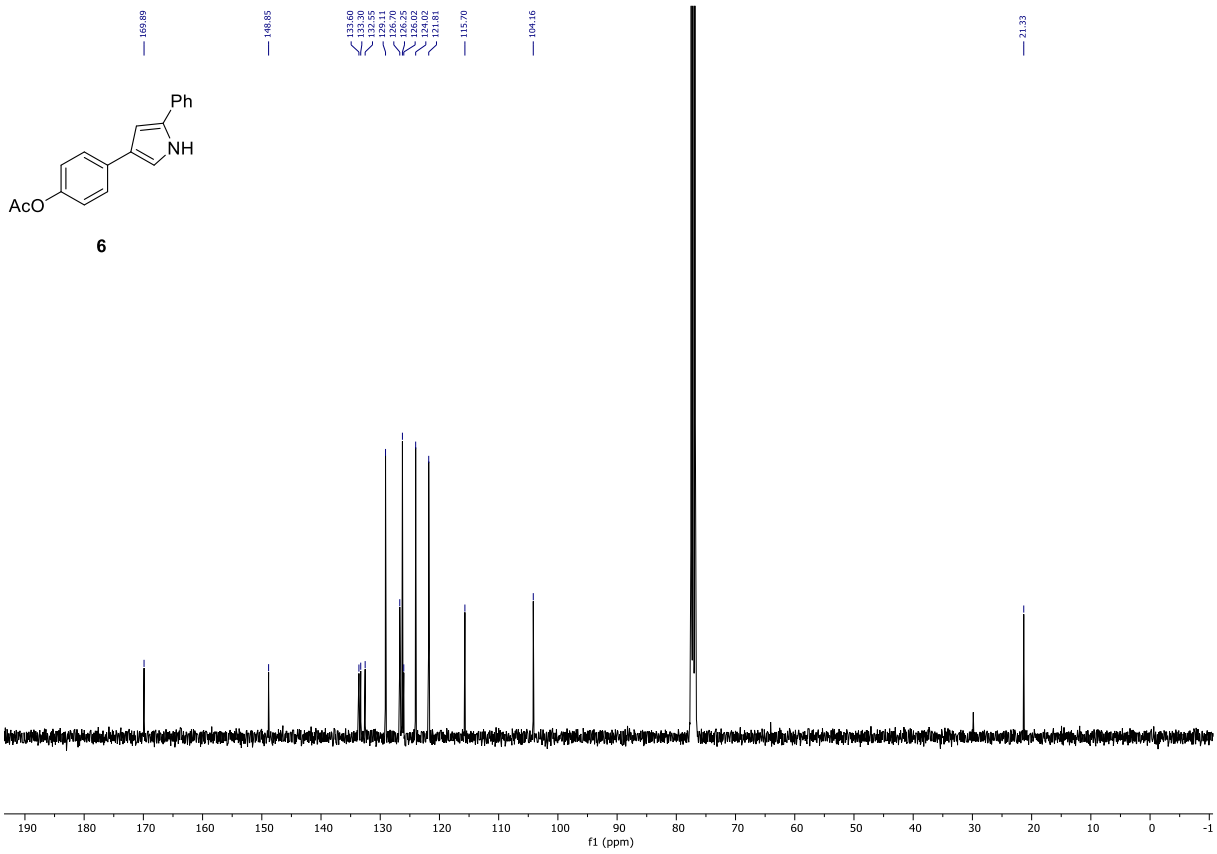


^{1}H NMR (400 MHz, $CDCl_3$) of compound **6**:



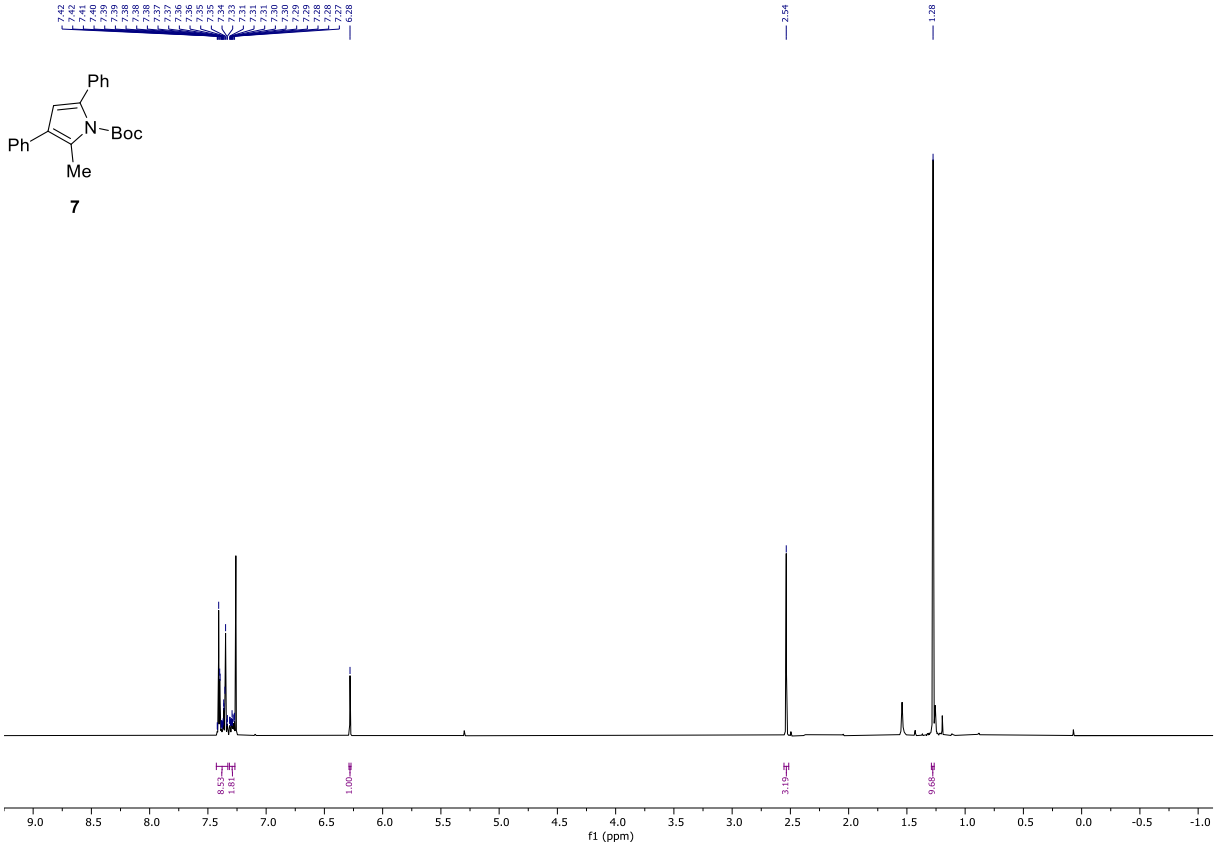
6

^{13}C NMR (101 MHz, $CDCl_3$) of compound **6**:

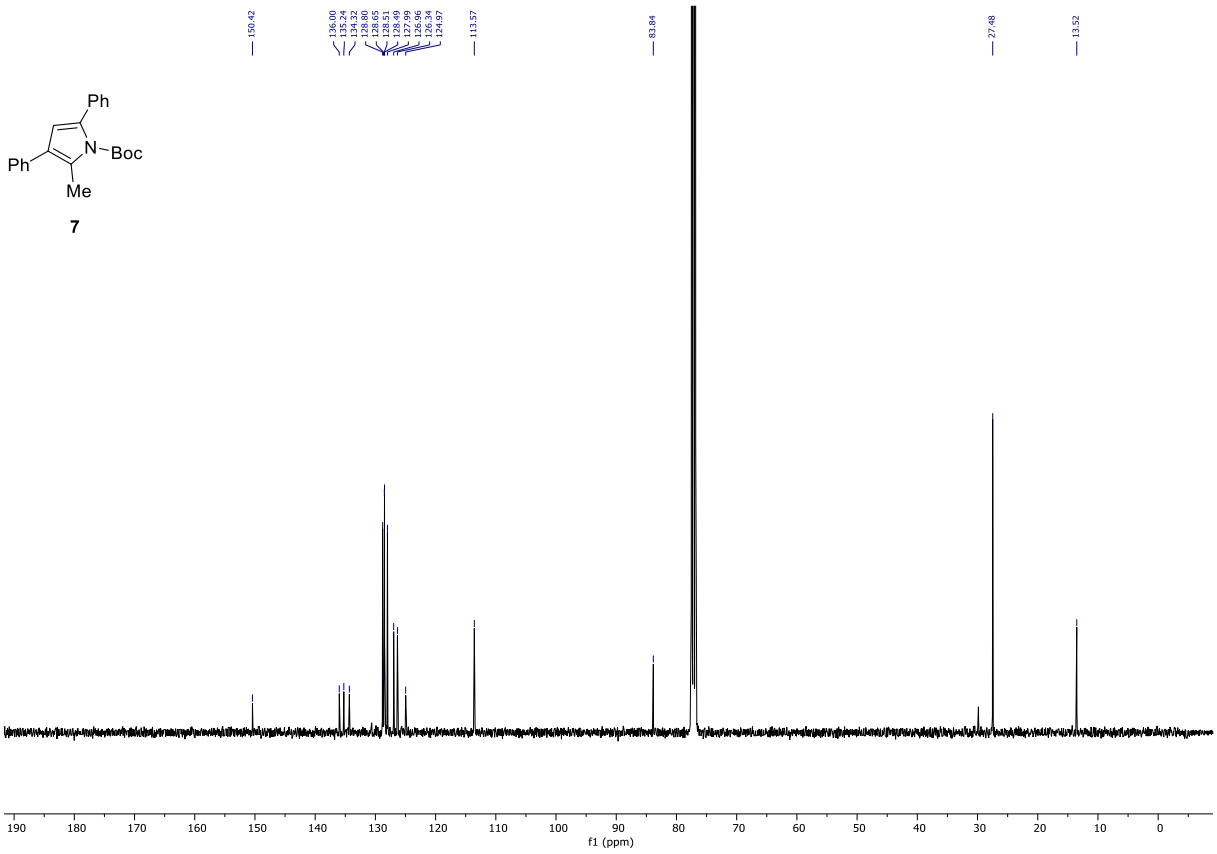


6

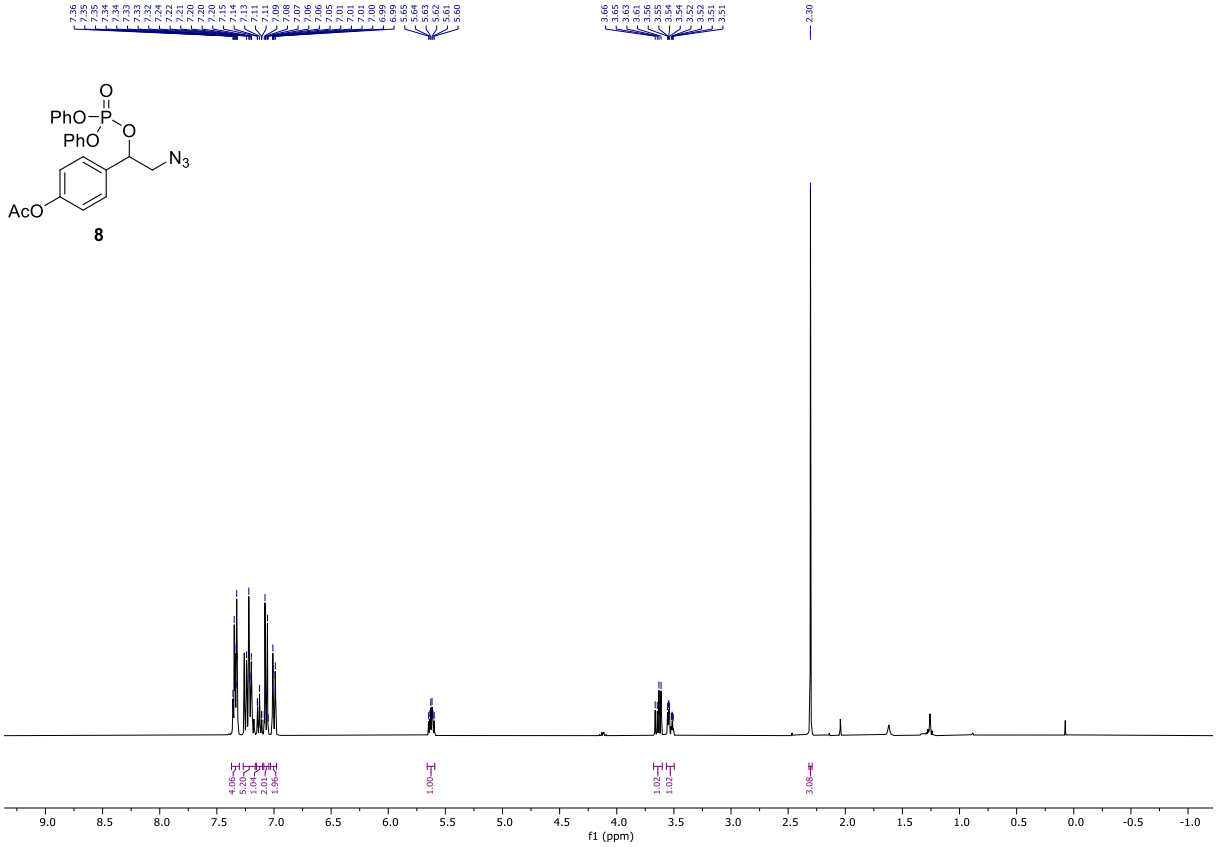
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7**:



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



^{1}H NMR (400 MHz, $CDCl_3$) of compound **8**:



^{13}C NMR (101 MHz, $CDCl_3$) of compound **8**: