Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-Catalyzed Remote Nucleophilic Substitution of 5-Ethynylthiophene Esters

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Table of Contents

1. General Information

Unless otherwise noted, all commercially available compounds were used without further purification. Dry solvents (MeOH, CH_2Cl_2, THF, toluene) were purified by distillation over the drying agents.

All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent. Compounds were visualized by irradiation with UV light or potassium permanganate staining. Flash column chromatography was performed using 200-300 or 300-400 mesh silica gel. All air- and moisture-sensitive reactions were performed under the atmosphere of N_2 in fire dried glasswares.

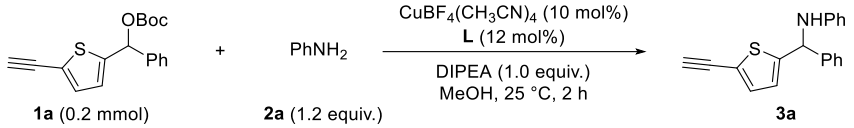
^{1}H-NMR spectra were recorded on 400 or 600 MHz spectrophotometers, ^{13}C-NMR spectra were recorded on 100 or 150 MHz with complete proton decoupling spectrophotometers using $CDCl_3$ as solvent. Data were reported in the following order: chemical shift (δ) values are reported in ppm with the solvent resonance as internal standard ($CDCl_3$: δ = 7.26 ppm for ^{1}H-NMR, δ = 77.16 ppm for ^{13}C-NMR); multiplicities are indicated brs (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz).

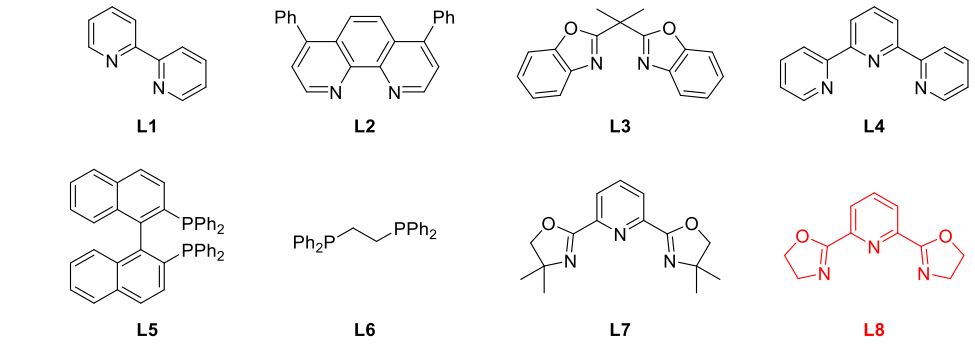
All air- and moisture-sensitive reactions were performed under the atmosphere of N_2 in fire dried glasswares.

HR-MS was recorded on Agilent technologies 6224 TOF LC/MS instrument or Bruker ultrafleXtreme MALDI-TOF/TOF mass spectrometer.

2. Optimization Studies

Table S1. The Effect of the Ligands on the Reaction. [a]

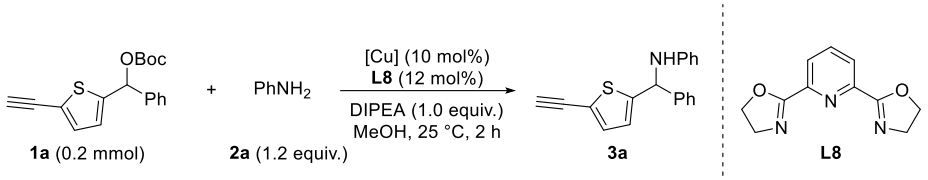




Entry	L	Yield of 3a (%)[b]
1	**L1**	11
2	**L2**	12
3	**L3**	62
4	**L4**	66
5	**L5**	69
6	**L6**	70
7	**L7**	74
8	**L8**	79

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), MeOH (0.1 M), DIPEA (1.0 equiv.), $CuBF_4(CH_3CN)_4$ (10 mol%), **L** (12 mol%), 25 °C, 2 h, under air. [b]Isolated yield after purification by column chromatography. DIPEA = *N*, *N*-diisopropylethylamine.

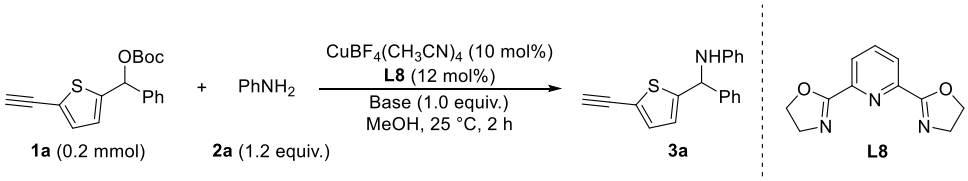
Table S2. The Effect of the Copper Salts on the Reaction. [a]



Entry	[Cu]	Yield of 3a (%)[b]
1	$CuBF_4(CH_3CN)_4$	79
2	$CuPF_6(CH_3CN)_4$	39
3	CuCl	69
4	CuBr	62
5	CuI	55
6	$Cu(OTf)_2$	66
7	$CuSO_4$	52
8	$Cu(OAc)_2•H_2O$	60

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), MeOH (0.1 M), DIPEA (1.0 equiv.), [Cu] (10 mol%), **L8** (12 mol%), 25 ℃, 2 h, under air. [b]Isolated yield after purification by column chromatography. DIPEA = *N*, *N*-diisopropylethylamine.

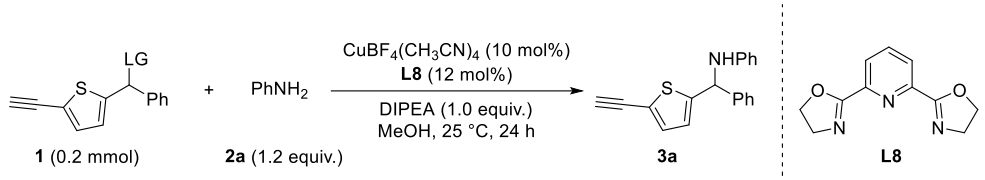
Table S3. The Effect of Base on the Reaction. [a]



Entry	Base	Yield of 3a (%)[b]
1	DIPEA	79
2	Et_3N	45
3	No Base	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), MeOH (0.1 M), Base (1.0 equiv.), $CuBF_4(CH_3CN)_4$ (10 mol%), **L8** (12 mol%), 25 ℃, 2 h, under air. [b]Isolated yield after purification by column chromatography. DIPEA = *N*, *N*-diisopropylethylamine.

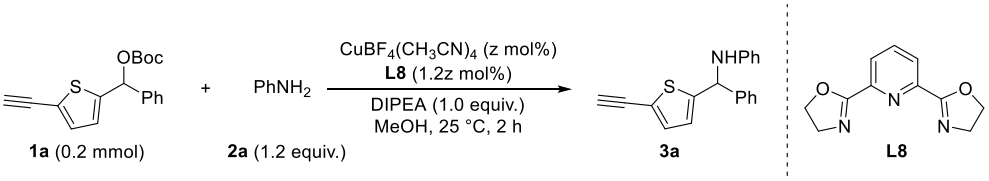
Table S4. The Effect of Leaving Groups on the Reaction. [a]



Entry	1	LG	Yield of 3a (%)[b]
1	**1a**	OBoc	79
2	**1b**	OAc	52
3	**1c**	OBz	43

[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.24 mmol), MeOH (0.1 M), DIPEA (1.0 equiv.), $CuBF_4(CH_3CN)_4$ (10 mol%), **L8** (12 mol%), 25 °C, 24 h, under air. [b]Isolated yield after purification by column chromatography. DIPEA = *N*, *N*-diisopropylethylamine.

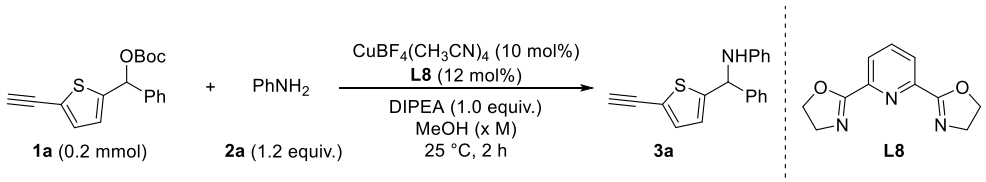
Table S5. The Effect of Catalytic Loading of Copper Salt on the Reaction. [a]



Entry	[Cu] (z mol%)	Yield of 3a (%)[b]
1	5	56
2[c]	5	68
3	10	79

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), MeOH (0.1 M), DIPEA (1.0 equiv.), $CuBF_4(CH_3CN)_4$ (z mol%), **L8** (1.2z mol%), 25 °C, 2 h, under air. [b]Isolated yield after purification by column chromatography. [c]MeOH (0.2 M). DIPEA = *N*, *N*-diisopropylethylamine.

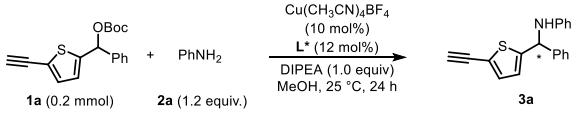
Table S6. The Effect of Concentration on the Reaction. [a]

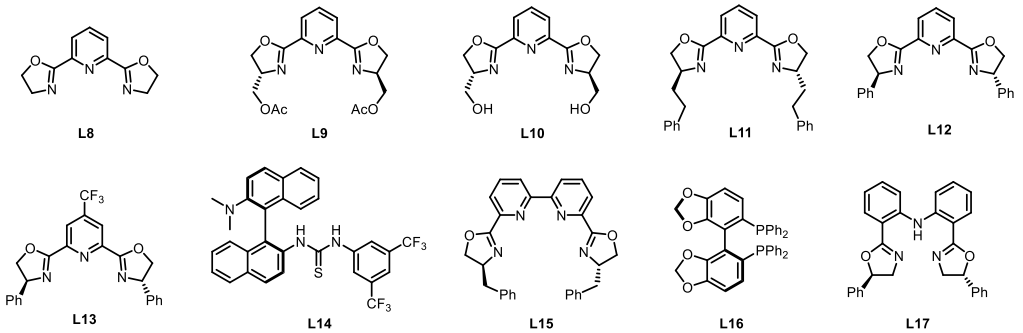


Entry	MeOH (M)	Yield of 3a (%)[b]
1	0.2	82
2	0.1	79

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), MeOH (x M), DIPEA (1.0 equiv.), $CuBF_4(CH_3CN)_4$ (10 mol%), **L8** (12 mol%), 25 °C, 2 h, under air. [b]Isolated yield after purification by column chromatography. DIPEA = *N*, *N*-diisopropylethylamine.

Table S7. The Effect of the Chiral Ligands on the Reaction. [a]





Entry	L*	Yield of 3a (%)[b]	ee of 3a (%)[c]
1	**L8**	82	-
2	**L9**	98	-6
3	**L10**	98	-3
4	**L11**	98	2
5	**L12**	99	16
6	**L13**	97	3
7	**L14**	92	3
8	**L15**	99	6
9	**L16**	48	5
10	**L17**	93	14

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), MeOH (0.2 M), DIPEA (1.0 equiv.), $CuBF_4(CH_3CN)_4$ (10 mol%), **L*** (12 mol%), 25 °C, 24 h, under air. [b]Isolated yield after purification by column chromatography. [c]Enantiomeric excess of **3** was determined by HPLC analysis using a chiral stationary phase. DIPEA = *N*, *N*-diisopropylethylamine.

3. Experimental Procedures

Procedure A: Procedures for the synthesis of 5-ethynylthiophene esters 1.

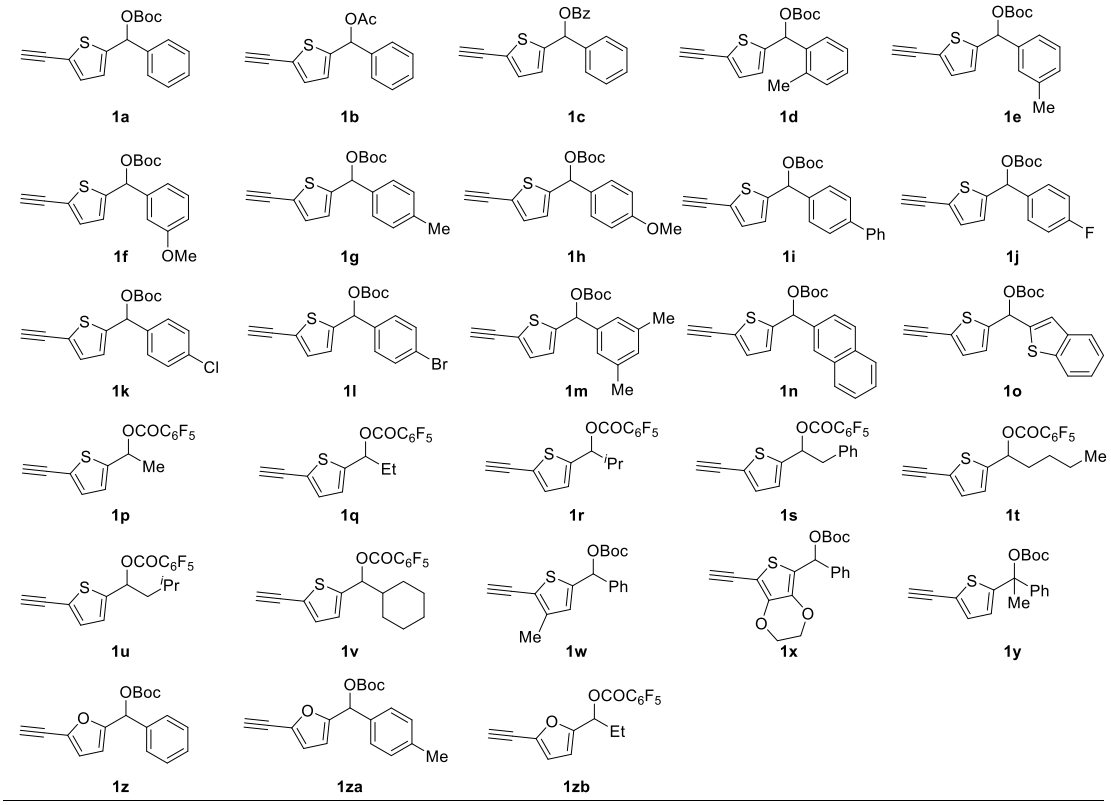
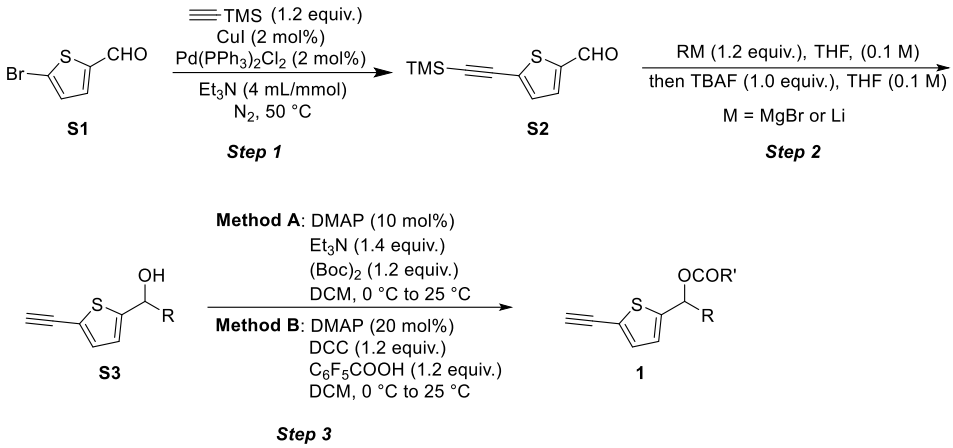


Figure S1. The summary of 5-ethynylthiophene esters.

Synthesis of 5-ethynylthiophene esters **1**



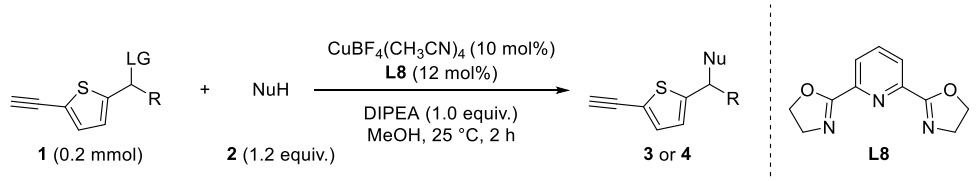
Step 1: A flame-dried 200 mL Schlenk flask was charged with $Pd(PPh_3)_4$ (2 mol%), CuI (2 mol%), **S1** (1.0 equiv.) and Et_3N (4 mL/mmol) under nitrogen atmosphere. After stirring at 50 °C for 30 minutes, trimethylsilylacetylene (1.2 equiv.) was added dropwise and then the mixture was stirred at 50 °C for 24 h. After the starting material **S1** was consumed, the mixture was passed through a short pad of diatomite with *n*-hexane as eluent. The solution was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (EtOAc/Petroleum ether = 1:100) to give the corresponding product **S2**.

Step 2: A dry 100 mL Schlenk flask equipped with a magnetic stir bar was added aldehyde **S2** (1.0 equiv.) and anhydrous THF (0.1 M) under nitrogen atmosphere. Then aryl metal reagent (1.2 equiv.) was added dropwise at -78 or 0 ºC and the mixture was warmed to room temperature and stirred until **S2** was consumed. The reaction was quenched with saturated NH_4Cl solution and the aqueous phase was extracted with EtOAc (15 mL×3). The combined organic layer was dried with anhydrous Na_2SO_4, filtered, the solvent was concentrated *in vacuo* and the residue in THF (0.1 M) was added TBAF (1.0 M in THF, 1.0 equiv.) at 0 ºC. After stirring for 30 min, the reaction was quenched with water, and the aqueous layer was extracted with ethyl acetate (15 mL×3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (EtOAc/Petroleum ether = 1:20) to give the corresponding alcohol **S3**.

Step 3: In a 100 mL round bottom flask, the alcohol **S4** (1.0 equiv.), DMAP (10 or 20 mol%) in DCM was cooled to 0 ºC, then Et_3N (1.4 equiv.) and di-tert-butyl dicarbonate (1.2 equiv.) or pentafluorobenzoic acid (1.2 equiv.) and DCC (1.2 equiv.) were added to the mixture. After stirring for 1 h at 0 ºC, the reaction mixture was allowed to warm to room temperature and stirred for 4–24

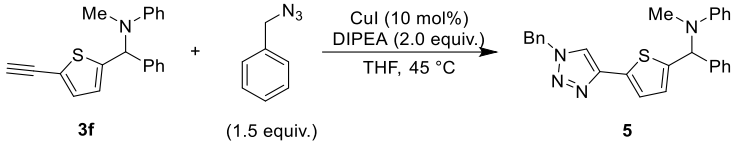
h. The resulting suspension was quenched with water and extracted with CH_2Cl_2 (15 mL×3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel (EtOAc/Petroleum ether/Et_3N = 1:100:1) to give the substrates **1**.

Procedure B: General procedure for copper-catalyzed nucleophilic substitution of 5-ethynylthiophene carbonates.

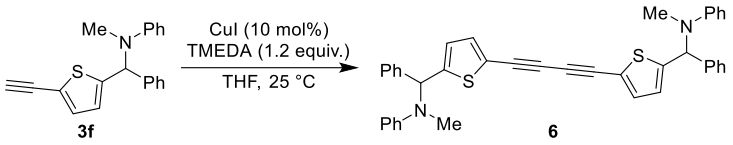


In a flame-dried 10.0 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with $CuBF_4(CH_3CN)_4$ (10 mol%), **L8** (12 mol%) in MeOH (0.2 mL). Then the mixture was stirred at 25 °C for 1 h. To the resulting mixture was added yne-thiophene carbonates **1** (0.2 mmol, 1.0 equiv.), nucleophiles **2** (1.2 equiv.) and DIPEA (1.0 equiv.) in MeOH (0.8 mL). After the mixture was stirred at 25 °C for 12–48 h, and then transferred into a round bottom flask with CH_2Cl_2 (5.0 mL) and concentrated *in vacuo*. The obtained residue was then purified by column chromatography on silica gel with petroleum ether/ethyl acetate as eluent, affording the desired products **3** or **4**.

Procedure C: General procedure for the transformation of product.

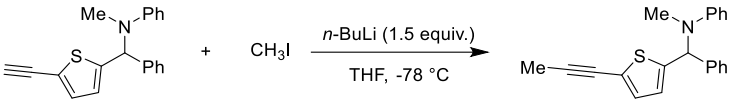


A dry 25 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with CuI (10 mol%), **3f** (0.2 mmol, 1.0 equiv.), benzyl azide (1.5 equiv.), DIPEA (2.0 equiv.) in anhydrous THF (2 mL) under nitrogen atmosphere. After the reaction was stirred at 45 ˚C for 24 h and then transferred into a round bottom flask with CH_2Cl_2 (5.0 mL) and concentrated *in vacuo*. The obtained residue was purified by flash column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) to give the target product **5** in 96% yield.



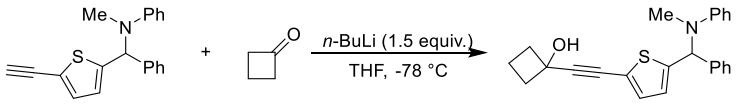
3f **6**

A dry 25 mL Schlenk tube equipped with a magnetic stir bar was added CuI (10 mol%), **3f** (0.2 mmol, 1.0 equiv.), TMEDA (1.2 equiv.) in anhydrous THF (1 mL) was stirred at 25 °C for 48 h under nitrogen atmosphere. Then, the solvent was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (EtOAc/Petroleum ether = 1:20) to give the target product **6** in 81% yield.

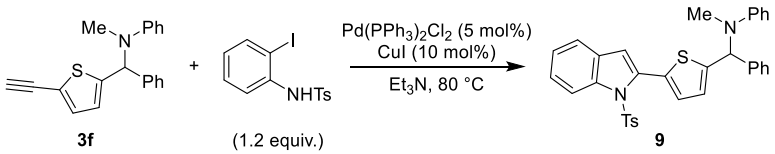


3f (3.0 equiv.) **7**

A dry 25 mL Schlenk tube equipped with a magnetic stir bar was added **3f** (0.2 mmol, 1.0 equiv.) in anhydrous THF (1 mL). Then *n*-BuLi (2.5 M in hexane, 1.5 equiv.) was added at -78 °C under nitrogen atmosphere. After stirring for 30 min, methyl iodide (3.0 equiv.) was added at -78 °C and then the reaction mixture was warmed to room temperature and stirred for 21 h. When the reaction was completed as monitored by TLC, the solution was quenched with saturated NH_4Cl solution and then extracted with ethyl acetate (5 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation under reduced pressure, the residue was purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:100) to give the target product **7** in 78% yield.



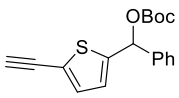
A dry 25 mL Schlenk tube equipped with a magnetic stir bar was added **3f** (0.2 mmol, 1.0 equiv.) in anhydrous THF (1 mL). Then *n*-BuLi (2.5 M in hexane, 1.5 equiv.) was added at -78 °C under nitrogen atmosphere. After stirring for 30 min, then cyclobutanone (2.0 equiv.) was added at -78 °C and the reaction mixture was warmed to room temperature. When the reaction was completed as monitored by TLC, the solution was quenched with saturated NH_4Cl solution and then extracted with ethyl acetate (5 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and evaporation under reduced pressure, the residue was purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5) to give the target product **8** in 86% yield.



A dry 25 mL Schlenk tube equipped with a magnetic stir bar was added **3f** (0.2 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%), ArI (1.2 equiv.) and Et_3N (2 ml) under nitrogen atmosphere. Then the mixture was stirred at 80 °C for 40 h. After the reaction was cooled to room temperature, the reaction mixture was passed through a short pad of diatomite with *n*-hexane as eluent. The solvent was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) to give the target product **9** in 92% yield.

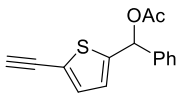
4. Products Date Characterization

***tert*-butyl ((5-ethynylthiophen-2-yl)(phenyl)methyl) carbonate**



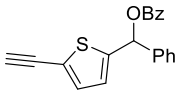
1a: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.2 Hz, 2H), 7.40–7.35 (m, 3H), 7.10 (d, *J* = 3.8 Hz, 1H), 6.79 (d, *J* = 3.8 Hz, 1H), 6.77 (s, 1H), 3.32 (s, 1H), 1.48 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.7, 145.5, 138.9, 132.8, 128.8, 128.7, 126.8, 126.4, 122.9, 83.1, 81.9, 75.5, 62.6, 27.9; **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{18}O_2SNa^+$ $[M+Na]^+$ 337.0869, found: 337.0865.

(5-ethynylthiophen-2-yl)(phenyl)methyl acetate



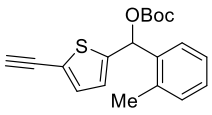
1b: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.44–7.35 (m, 5H), 7.11 (d, *J* = 3.8 Hz, 1H), 7.02 (s, 1H), 6.78 (dd, *J* = 3.8, 1.0 Hz, 1H), 3.33 (s, 1H), 2.16 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 169.9, 145.8, 139.0, 132.8, 128.8, 128.7, 126.9, 126.4, 122.8, 81.9, 76.8, 72.7, 21.3; **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{13}O_2S^+$ $[M+H]^+$ 257.0631, found: 257.0629.

(5-ethynylthiophen-2-yl)(phenyl)methyl benzoate



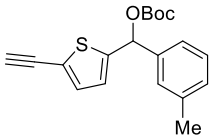
1c: yellow oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.20–8.18 (m, 2H), 7.60–7.57 (m, 3H), 7.51–7.41 (m, 5H), 7.33 (s, 1H), 7.17 (d, *J* = 3.8 Hz, 1H), 6.91 (d, *J* = 3.8 Hz, 1H), 3.39 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.3, 145.7, 139.1, 133.4, 132.8, 129.9, 129.7, 128.8, 128.7, 128.5, 126.9, 126.4, 122.8, 82.1, 76.7, 73.3; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{14}O_2SNa^+$ $[M+Na]^+$ 341.0607, found: 341.0607.

***tert*-butyl ((5-ethynylthiophen-2-yl)(*o*-tolyl)methyl) carbonate**



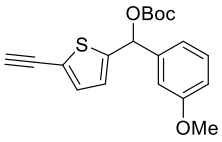
1d: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 1H), 7.26–7.24 (m, 2H), 7.16 (d, *J* = 5.6 Hz, 1H), 7.08 (d, *J* = 3.8 Hz, 1H), 6.92 (s, 1H), 6.74 (d, *J* = 3.8 Hz, 1H), 3.31 (s, 1H), 2.30 (s, 3H), 1.47 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.8, 144.7, 137.3, 135.2, 132.8, 130.7, 128.5, 127.0, 126.5, 126.0, 123.1, 83.0, 81.9, 76.8, 72.4, 27.9, 19.3; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{20}O_3SNa^+$ $[M+Na]^+$ 351.1025, found: 351.1023.

***tert*-butyl ((5-ethynylthiophen-2-yl)(*m*-tolyl)methyl) carbonate**



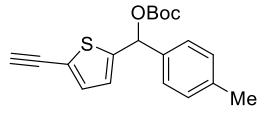
1e: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 3H), 7.14 (d, *J* = 7.0 Hz, 1H), 7.09 (d, *J* = 3.8 Hz, 1H), 6.79 (d, *J* = 3.8 Hz, 1H), 6.73 (s, 1H), 3.31 (s, 1H), 2.35 (s, 3H), 1.48 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.7, 145.7, 138.8, 138.5, 132.8, 129.5, 128.7, 127.4, 126.3, 123.8, 122.8, 83.1, 81.9, 76.8, 75.5, 27.9, 21.6; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{20}O_3SNa^+$ $[M+Na]^+$ 351.1025, found: 351.1021.

***tert*-butyl ((5-ethynylthiophen-2-yl)(3-methoxyphenyl)methyl) carbonate**



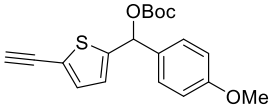
1f: yellow oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 3.8 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 2.0 Hz, 1H), 6.87 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.81 (dd, *J* = 3.8, 0.8 Hz, 1H), 6.74 (s, 1H), 3.80 (s, 3H), 3.32 (s, 1H), 1.48 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 159.9, 152.7, 145.3, 140.4, 132.8, 129.9, 126.5, 123.0, 119.0, 114.2, 112.2, 83.2, 81.9, 76.8, 75.3, 55.4, 27.9; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{20}O_4SNa^+$ $[M+Na]^+$ 367.0975, found: 367.0977.

***tert*-butyl ((5-ethynylthiophen-2-yl)(*p*-tolyl)methyl) carbonate**



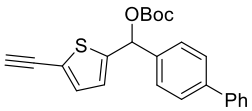
1g: yellow oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 3.8 Hz, 1H), 6.79 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.75 (s, 1H), 3.32 (s, 1H), 2.36 (s, 3H), 1.48 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.7, 145.8, 138.6, 136.0, 132.8, 129.4, 126.8, 126.3, 121.1, 83.0, 81.8, 76.8, 75.5, 27.9, 21.3; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{20}O_3SNa^+$ $[M+Na]^+$ 351.1025, found: 351.1022.

***tert*-butyl ((5-ethynylthiophen-2-yl)(4-methoxyphenyl)methyl) carbonate**



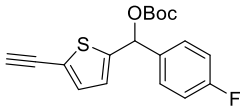
1h: brown oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 3.8 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.78 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.73 (s, 1H), 3.81 (s, 3H), 3.32 (s, 1H), 1.48 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 159.9, 152.7, 146.0, 132.8, 131.1, 128.4, 126.1, 122.7, 114.1, 83.0, 81.8, 76.8, 75.4, 55.4, 27.9; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{20}O_4SNa^+$ $[M+Na]^+$ 367.0975, found: 367.0972.

[1,1'-biphenyl]-4-yl(5-ethynylthiophen-2-yl)methyl *tert*-butyl carbonate



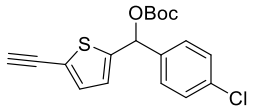
1i: brown oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 8.0 Hz, 4H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 3.8 Hz, 1H), 6.87 (dd, *J* = 3.8, 0.8 Hz, 1H), 6.85 (s, 1H), 3.35 (s, 1H), 1.52 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.7, 145.4, 141.6, 140.6, 137.9, 132.9, 128.9, 127.6, 127.5, 127.3, 127.2, 126.5, 123.0, 83.2, 82.0, 76.8, 75.3, 27.9; **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{22}O_3SNa^+$ $[M+Na]^+$ 413.1182, found: 413.1183.

***tert*-butyl ((5-ethynylthiophen-2-yl)(4-fluorophenyl)methyl) carbonate**



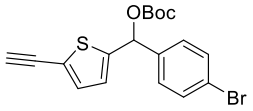
1j: brown oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 2H), 7.10 (d, *J* = 3.8 Hz, 1H), 7.06 (t, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 3.8, 1H), 6.75 (s, 1H), 3.33 (s, 1H), 1.48 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 247.8 Hz), 152.6, 145.2, 134.8 (d, *J* = 3.2 Hz), 132.8, 128.8 (d, *J* = 8.4 Hz), 126.4, 123.0, 115.7 (d, *J* = 21.8 Hz), 83.3, 82.1, 76.7, 74.9, 27.9; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -112.9; **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{17}FO_3SNa^+$ $[M+Na]^+$ 355.0775, found: 355.0775.

***tert*-butyl ((4-chlorophenyl)(5-ethynylthiophen-2-yl)methyl) carbonate**



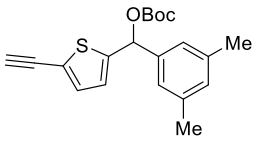
1k: brown oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.39–7.34 (m, 4H), 7.10 (d, *J* = 3.8 Hz, 1H), 6.78 (d, *J* = 3.8 Hz, 1H), 6.74 (s, 1H), 3.34 (s, 1H), 1.48 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.4, 144.7, 137.4, 134.4, 132.7, 128.8, 128.1, 126.4, 123.1, 83.1, 82.3, 76.6, 74.6, 27.7; **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{17}ClO_3SNa^+$ $[M+Na]^+$ 371.0479, found: 371.0476.

(4-bromophenyl)(5-ethynylthiophen-2-yl)methyl *tert*-butyl carbonate



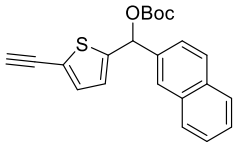
1l: brown oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 3.8 Hz, 1H), 6.78 (d, *J* = 3.8 Hz, 1H), 6.72 (s, 1H), 3.33 (s, 1H), 1.48 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.5, 144.7, 138.0, 132.8, 131.9, 128.5, 126.5, 123.2, 122.7, 83.3, 82.2, 76.6, 74.8, 27.8; **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{17}BrO_3SNa^+$ $[M+Na]^+$ 414.9974, found: 414.9975.

***tert*-butyl ((3,5-dimethylphenyl)(5-ethynylthiophen-2-yl)methyl) carbonate**



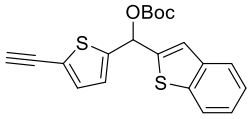
1m: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 3.8 Hz, 1H), 7.07 (s, 2H), 6.99 (s, 1H), 6.83 (dd, *J* = 3.8, 0.8 Hz, 1H), 6.74 (s, 1H), 3.34 (s, 1H), 2.33 (s, 6H), 1.51 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.7, 145.8, 138.7, 138.3, 132.7, 130.3, 126.2, 124.5, 122.7, 82.9, 81.9, 76.8, 75.6, 27.8, 21.4; **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{15}OS^+$ $[M+H]^+$ 243.0838, found: 243.0835.

***tert*-butyl ((5-ethynylthiophen-2-yl)(naphthalen-2-yl)methyl) carbonate**



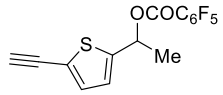
1n: brown solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.87–7.84 (m, 3H), 7.52–7.49 (m, 3H), 7.10 (d, *J* = 3.8 Hz, 1H), 6.94 (s, 1H), 6.83 (dd, *J* = 3.8, 0.8 Hz, 1H), 3.32 (s, 1H), 1.49 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.7, 145.3, 136.2, 133.3, 133.1, 132.8, 128.7, 128.3, 127.8, 126.5(9), 126.5(5), 126.5, 125.9, 124.4, 123.0, 83.2, 82.0, 76.8, 75.6, 27.8; **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{21}O_3S^+$ $[M+H]^+$ 365.1206, found: 365.1203.

benzo[*b*]thiophen-2-yl(5-ethynylthiophen-2-yl)methyl *tert*-butyl carbonate



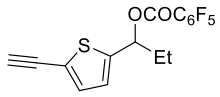
1o: brown solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 3H), 7.14 (d, *J* = 3.4 Hz, 1H), 7.10 (s, 1H), 6.99 (d, *J* = 3.4 Hz, 1H), 3.34 (s, 1H), 1.49 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.4, 143.6, 142.3, 140.0, 139.0, 132.8, 126.6, 124.9, 124.6, 124.1, 123.3, 123.2, 122.5, 83.5, 82.2, 76.7, 71.9, 27.8; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}O_3S_2Na^+$ $[M+Na]^+$ 393.0590, found: 393.0591.

1-(5-ethynylthiophen-2-yl)ethyl 2,3,4,5,6-pentafluorobenzoate



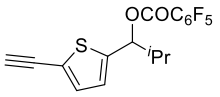
1p: white solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 3.8 Hz, 1H), 6.99 (d, *J* = 3.8 Hz, 1H), 6.34 (q, *J* = 6.6 Hz, 1H), 3.34 (s, 1H), 1.76 (d, *J* = 6.6 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 158.1, 145.5 (dm, *J* = 258.6 Hz), 144.8, 143.4 (dm, *J* = 259.6 Hz), 137.7 (dm, *J* = 255.8 Hz), 132.7, 125.9, 122.6, 108.0 (m), 81.9, 76.4, 70.3, 21.7; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -137.8 (m, 2F), -148.1 (m, 1F), -160.2 (m, 2F); **HR-MS** (ESI) *m/z* calcd for $C_{15}H_8F_5O_2S^+$ $[M+H]^+$ 347.0160, found: 347.0161.

1-(5-ethynylthiophen-2-yl)propyl 2,3,4,5,6-pentafluorobenzoate



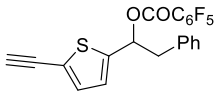
1q: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 3.8 Hz, 1H), 6.99 (d, *J* = 3.8 Hz, 1H), 6.13 (t, *J* = 7.0 Hz, 1H), 3.34 (s, 1H), 2.15–1.98 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 158.4, 145.5 (dm, *J* = 270.4 Hz), 143.7, 143.4 (dm, *J* = 259.8 Hz), 137.9 (dm, *J* = 271.6 Hz), 132.8, 126.5, 122.7, 108.0 (m), 82.0, 76.7, 75.4, 29.5, 10.0; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -137.8 (m, 2F), -148.3 (m, 1F), -160.3 (m, 2F); **HR-MS** (ESI) *m/z* calcd for $C_{16}H_9F_5O_2SNa^+$ $[M+Na]^+$ 383.0136, found: 383.0133.

1-(5-ethynylthiophen-2-yl)-2-methylpropyl 2,3,4,5,6-pentafluorobenzoate



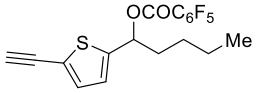
1r: yellow oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 3.8 Hz, 1H), 6.95 (d, *J* = 3.8 Hz, 1H), 5.94 (d, *J* = 7.8 Hz, 1H), 3.34 (s, 1H), 2.28–2.19 (m, 1H), 1.07 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 158.2, 145.7 (dm, *J* = 258.6 Hz), 143.4 (dm, *J* = 259.6 Hz), 143.0, 137.6 (dm, *J* = 252.8 Hz), 132.6, 126.7, 122.4, 107.9 (m), 81.9, 79.2, 76.5, 34.2, 18.5; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -137.6 (m, 2F), -148.2 (m, 1F), -160.2 (m, 2F); **HR-MS** (ESI) *m/z* calcd for $C_{17}H_{11}F_5O_2SNa^+$ $[M+Na]^+$ 397.0292, found: 397.0294.

1-(5-ethynylthiophen-2-yl)-2-phenylethyl 2,3,4,5,6-pentafluorobenzoate



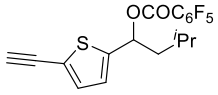
1s: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.29–7.23 (m, 3H), 7.18 (d, *J* = 6.6 Hz, 2H), 7.10 (d, *J* = 3.8 Hz, 1H), 6.88 (d, *J* = 3.8 Hz, 1H), 6.42 (t, *J* = 7.2 Hz, 1H), 3.41–3.35 (m, 1H), 3.35 (s, 1H), 3.29–3.21 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 158.1, 145.6 (dm, *J* = 259.6 Hz), 143.5 (dm, *J* = 260.2 Hz), 143.1, 137.8 (dm, *J* = 256.4 Hz), 135.5, 132.8, 129.5, 128.7, 127.3, 126.7, 122.8, 107.7 (m), 82.2, 76.6, 74.7, 42.8; **^{19}F-NMR** -137.3 (m, 2F), -147.8 (m, 1F), -160.2 (m, 2F); **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{11}F_5O_2SNa^+$ $[M+Na]^+$ 445.0292, found: 445.0295.

1-(5-ethynylthiophen-2-yl)pentyl 2,3,4,5,6-pentafluorobenzoate



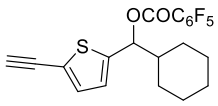
1t: yellow oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 3.8 Hz, 1H), 6.99 (d, *J* = 3.8 Hz, 1H), 6.20 (t, *J* = 7.2 Hz, 1H), 3.34 (s, 1H), 2.15–1.93 (m, 2H), 1.45–1.32 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 158.3, 145.5 (dm, *J* = 258.6 Hz), 144.0, 143.4 (dm, *J* = 259.8 Hz), 137.6 (dm, *J* = 253.4 Hz), 132.8, 126.5, 122.6, 108.2 (m), 81.9, 76.6, 74.1, 35.9, 27.6, 22.3, 13.9; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -137.8 (m, 2F), -148.4 (m, 1F), -160.3 (m, 2F); **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{14}F_5O_2S^+$ $[M+H]^+$ 389.0629, found: 389.0627.

1-(5-ethynylthiophen-2-yl)-3-methylbutyl 2,3,4,5,6-pentafluorobenzoate



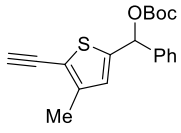
1u: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 3.8 Hz, 1H), 7.01 (d, *J* = 3.8 Hz, 1H), 6.29 (dd, *J* = 8.2, 6.4 Hz, 1H), 3.35 (s, 1H), 2.10–2.00 (m, 1H), 1.86–1.76 (m, 1H), 1.72–1.66 (m, 1H), 0.99 (d, *J* = 4.8 Hz, 3H), 0.97 (d, *J* = 4.8 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 158.4, 145.5 (dm, *J* = 253.6 Hz), 144.1, 143.4 (dm, *J* = 259.8 Hz), 137.6 (dm, *J* = 253.0 Hz), 132.8, 126.7, 122.8, 108.2 (m), 82.0, 76.7, 72.5, 45.0, 24.8, 22.6; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -137.8 (m, 2F), -148.2 (m, 1F), -160.2 (m, 2F); **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{14}F_5O_2S^+$ $[M+H]^+$ 389.0629, found: 389.0628.

cyclohexyl(5-ethynylthiophen-2-yl)methyl 2,3,4,5,6-pentafluorobenzoate



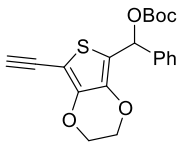
1v: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 3.6 Hz, 1H), 6.94 (d, *J* = 3.6 Hz, 1H), 5.97 (d, *J* = 8.2 Hz, 1H), 3.34 (s, 1H), 1.99–1.86 (m, 2H), 1.79–1.55 (m, 4H), 1.28–1.00 (m, 5H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 158.3, 145.5 (dm, *J* = 258.8 Hz), 143.4 (dm, *J* = 259.8 Hz), 143.1, 137.6 (dm, *J* = 252.4 Hz), 132.7, 126.8, 122.5, 108.1 (m), 82.0, 78.5, 76.7, 43.4, 29.0, 26.2, 25.8; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -137.6 (m, 2F), -148.4 (m, 1F), -160.4 (m, 2F); **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{16}F_5O_2S^+$ $[M+H]^+$ 415.0786, found: 415.0789.

***tert*-butyl ((5-ethynyl-4-methylthiophen-2-yl)(phenyl)methyl) carbonate**



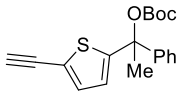
1w: yellow oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.40–7.34 (m, 3H), 6.74 (s, 1H), 6.68 (s, 1H), 3.44 (s, 1H), 2.24 (s, 3H), 1.49 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.7, 143.7, 143.6, 138.9, 128.7, 128.6, 128.5, 126.8, 118.2, 84.0, 83.0, 76.5, 75.5, 27.9, 15.1; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{20}O_3SNa^+$ $[M+Na]^+$ 351.1025, found: 351.1026.

***tert*-butyl ((7-ethynyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)(phenyl)methyl) carbonate**



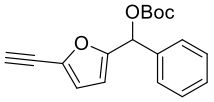
1x: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.43–7.41 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.32–7.30 (m, 1H), 6.87 (s, 1H), 4.28–4.25 (m, 2H), 4.23–4.20 (m, 2H), 3.46 (s, 1H), 1.47 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.5, 145.1, 138.6, 138.1, 128.7, 128.5, 126.4, 118.0, 97.2, 84.7, 82.9, 74.3, 72.2, 65.2, 64.6, 27.9; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{20}O_5SNa^+$ $[M+Na]^+$ 395.0924, found: 395.0925.

***tert*-butyl (1-(5-ethynylthiophen-2-yl)-1-phenylethyl) carbonate**



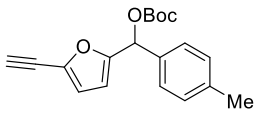
1y: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.39–7.28 (m, 5H), 7.08 (d, *J* = 3.8 Hz, 1H), 6.76 (d, *J* = 3.8 Hz, 1H), 3.31 (s, 1H), 2.25 (s, 3H), 1.42 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.4, 151.2, 144.3, 132.6, 128.4, 127.8, 125.3, 125.1, 122.0, 83.1, 82.3, 81.8, 76.9, 28.0, 27.8; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{20}O_3SNa^+$ $[M+Na]^+$ 351.1025, found: 351.1024.

***t*ert-butyl ((5-ethynylfuran-2-yl)(phenyl)methyl) carbonate**



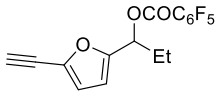
1z: brown oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.0 Hz, 2H), 7.37 (q, *J* = 8.6, 7.6 Hz, 3H), 6.59 (s, 1H), 6.55 (d, *J* = 3.4 Hz, 1H), 6.15 (d, *J* = 3.4 Hz, 1H), 3.38 (s, 1H), 1.47 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.4, 152.6, 136.8, 136.7, 128.8, 128.7, 127.2, 116.9, 110.5, 83.1, 82.4, 73.8, 73.3, 27.8; **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{18}O_4Na^+$ $[M+Na]^+$ 321.1097, found: 321.1095.

***tert*-butyl ((5-ethynylfuran-2-yl)(*p*-tolyl)methyl) carbonate**



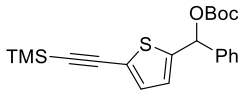
1za: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 3.6 Hz, 2H), 6.15 (s, 1H), 3.37 (s, 1H), 2.35 (s, 3H), 1.47 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.6, 152.5, 138.5, 136.6, 133.8, 129.3, 127.1, 116.8, 110.3, 82.8, 82.3, 73.8, 73.2, 27.7, 21.2; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{20}O_4Na^+$ $[M+Na]^+$ 335.1254, found: 335.1255.

1-(5-ethynylfuran-2-yl)propyl 2,3,4,5,6-pentafluorobenzoate



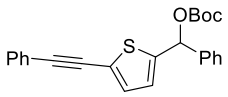
1zb: yellow oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 6.58 (d, *J* = 3.4 Hz, 1H), 6.40 (d, *J* = 3.4 Hz, 1H), 5.97 (t, *J* = 7.0 Hz, 1H), 3.38 (s, 1H), 2.13–2.06 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 158.3, 152.5, 145.5 (dm, *J* = 258.0 Hz), 143.3 (dm, *J* = 259.4 Hz), 137.9 (dm, *J* = 253.2 Hz), 136.4, 116.8, 110.3, 108.1 (m), 82.2, 73.5, 72.6, 25.7, 9.5; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -137.9 (m, 2F), -148.5 (m, 1F), -160.4 (m, 2F); **HR-MS** (ESI) *m/z* calcd for $C_{16}H_9F_5O_3Na^+$ $[M+Na]^+$ 367.0364, found: 367.0366.

***tert*-butyl (phenyl(5-((trimethylsilyl)ethynyl)thiophen-2-yl)methyl) carbonate**



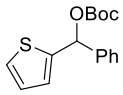
10: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.0 Hz, 2H), 7.39–7.33 (m, 3H), 7.05 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 1.48 (s, 9H), 0.23 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.7, 145.2, 139.0, 132.3, 128.7, 128.6, 126.8, 126.4, 124.2, 99.6, 97.4, 83.0, 75.5, 27.9, -0.1; **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{27}O_3SSi^+$ $[M+H]^+$ 387.1445, found: 387.1446.

***tert*-butyl (phenyl(5-(phenylethynyl)thiophen-2-yl)methyl) carbonate**



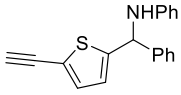
11: yellow solid; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.51–7.48 (m, 4H), 7.43–7.38 (m, 3H), 7.36–7.34 (m, 3H), 7.13 (d, *J* = 3.8 Hz, 1H), 6.87 (d, *J* = 3.8 Hz, 1H), 6.84 (s, 1H), 1.52 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.7, 145.1, 139.0, 131.6, 131.5, 128.7, 128.6(3), 128.5(7), 128.5, 126.8, 126.7, 124.3, 122.8, 93.7, 83.0, 82.5, 75.6, 27.9; **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{22}O_3SNa^+$ $[M+Na]^+$ 413.1182, found: 413.1181.

***tert*-butyl (phenyl(thiophen-2-yl)methyl) carbonate**



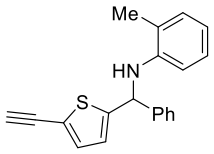
12: yellow oil; According to procedure A; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.40–7.37 (m, 2H), 7.35–7.33 (m, 1H), 7.28 (dd, *J* = 4.8, 1.6 Hz, 1H), 6.95–6.93 (m, 2H), 6.88 (s, 1H), 1.49 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.8, 143.4, 139.5, 128.6, 128.4, 126.9, 126.7(3), 126.6(6), 126.4, 82.8, 75.7, 27.9; **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{18}O_3SNa^+$ $[M+Na]^+$ 313.0869, found: 313.0868.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)aniline**



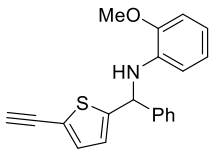
3a: 82% yield; white solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.44–7.33 (m, 5H), 7.19–7.14 (m, 3H), 6.79–6.75 (m, 2H), 6.63 (d, *J* = 8.0 Hz, 2H), 5.72 (s, 1H), 4.35 (brs, 1H), 3.32 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.2, 146.7, 142.0, 133.3, 129.3, 129.1, 128.2, 127.2, 124.8, 121.5, 118.5, 113.8, 81.5, 77.2, 59.0; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{15}NSNa^+$ $[M+Na]^+$ 312.0817, found: 312.0819.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-2-methylaniline**



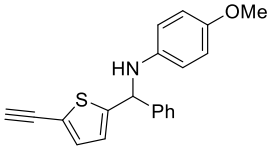
3ba: 80% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.46–7.44 (m, 2H), 7.41–7.38 (m, 2H), 7.36–7.32 (m, 1H), 7.15 (d, *J* = 3.8 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 3.6 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.78 (s, 1H), 4.22 (brs, 1H), 3.33 (s, 1H), 2.23 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.4, 144.6, 142.0, 133.3, 130.3, 129.1, 128.2, 127.2, 124.9, 122.5, 121.6, 118.2, 111.4, 81.6, 77.2, 58.8, 17.8; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}NS^+$ $[M+H]^+$ 304.1154, found: 304.1151.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-2-methoxyaniline**



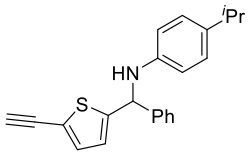
3bb: 75% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 3.8 Hz, 1H), 6.85–6.80 (m, 3H), 6.77–6.73 (m, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 5.74 (s, 1H), 5.02 (brs, 1H), 3.88 (s, 3H), 3.34 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.4, 146.9, 142.1, 136.7, 133.2, 129.0, 128.0, 127.2, 124.8, 121.4, 121.2, 117.7, 111.4, 109.6, 81.5, 71.2, 58.8, 55.5; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}NOS^+$ $[M+H]^+$ 320.1104, found: 320.1106.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-4-methoxyaniline**



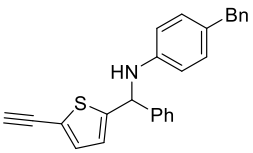
3ca: 79% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.38–7.35 (m, 2H), 7.33–7.29 (m, 1H), 7.12 (d, *J* = 3.8 Hz, 1H), 6.77–6.73 (m, 3H), 6.58 (d, *J* = 8.8 Hz, 2H), 5.62 (s, 1H), 4.11 (brs, 1H), 3.73 (s, 3H), 3.31 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.8, 150.7, 142.2, 140.9, 133.3, 129.0, 128.1, 127.2, 124.6, 121.4, 115.1, 114.8, 81.5, 77.2, 59.9, 55.8; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}NOSNa^+$ $[M+Na]^+$ 342.0923, found: 342.0922.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-4-isopropylaniline**



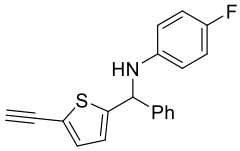
3cb: 99% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 6.8 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.37–7.32 (m, 1H), 7.16 (d, *J* = 3.8 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 3.8 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 2H), 5.71 (s, 1H), 4.29 (brs, 1H), 3.33 (s, 1H), 2.84 (q, *J* = 7.0 Hz, 1H), 1.25 (d, *J* = 7.0 Hz, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.6, 144.8, 142.2, 139.0, 133.3, 129.0, 128.1, 127.2(0), 127.1(7), 124.7, 121.4, 113.8, 81.5, 77.2, 59.3, 33.3, 24.3; **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{22}NS^+$ $[M+H]^+$ 332.1467, found: 332.1469.

4-benzyl-*N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)aniline



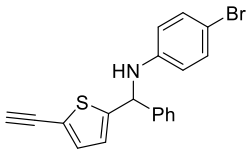
3cc: 85% yield; yellow solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.37–7.29 (m, 4H), 7.27–7.23 (m, 2H), 7.16–7.12 (m, 4H), 7.07 (d, *J* = 3.8 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 3.8 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 2H), 5.62 (s, 1H), 4.22 (brs, 1H), 3.82 (s, 2H), 3.25 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.4, 145.0, 142.1, 141.8, 133.3, 131.2, 129.7, 129.0, 128.9, 128.5, 128.1, 127.2, 126.0, 124.7, 121.5, 113.9, 81.6, 77.2, 59.2, 41.1; **HR-MS** (ESI) *m/z* calcd for $C_{26}H_{21}NSNa^+$ $[M+Na]^+$ 402.1287, found: 402.1288.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-4-fluoroaniline**



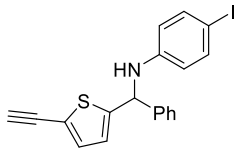
3cd: 95% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.43–7.37 (m, 4H), 7.35–7.32 (m, 1H), 7.14 (d, *J* = 3.8 Hz, 1H), 6.87 (t, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 3.8 Hz, 1H), 6.57–6.54 (m, 2H), 5.65 (s, 1H), 4.27 (brs, 1H), 3.33 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 156.4 (d, *J* = 236.4 Hz), 150.0, 143.0 (d, *J* = 2.2 Hz), 141.8, 133.3, 129.1, 128.2, 127.2, 124.8, 121.6, 115.8 (d, *J* = 22.4 Hz), 114.7 (d, *J* = 7.4 Hz), 81.6, 77.1, 59.6; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -126.5; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{14}FNSNa^+$ $[M+Na]^+$ 330.0723, found: 330.0722.

4-bromo-*N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)aniline



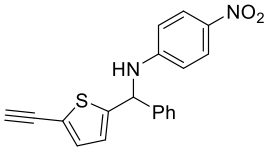
3ce: 94% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.33–7.30 (m, 4H), 7.30–7.28 (m, 1H), 7.19–7.16 (m, 2H), 7.07 (d, *J* = 3.8 Hz, 1H), 6.71 (d, *J* = 3.8 Hz, 1H), 6.43 (d, *J* = 8.8 Hz, 2H), 5.61 (s, 1H), 4.32 (brs, 1H), 3.27 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.4, 145.6, 141.4, 133.3, 132.0, 129.1, 128.3, 127.1, 125.0, 121.7, 115.4, 110.3, 81.7, 77.0, 58.9; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{14}BrNSNa^+$ $[M+Na]^+$ 389.9923, found: 389.9925.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-4-iodoaniline**



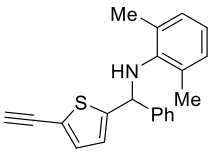
3cf: 97% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 6H), 7.35–7.32 (m, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.77 (d, *J* = 3.8 Hz, 1H), 6.40 (d, *J* = 7.2 Hz, 2H), 5.67 (s, 1H), 4.39 (brs, 1H), 3.33 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.4, 146.2, 141.4, 137.9, 133.3, 129.1, 128.3, 127.1, 125.0, 121.8, 116.0, 81.8, 77.0, 79.6, 58.7; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{15}INS^+$ $[M+H]^+$ 415.9964, found: 415.9966.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-4-nitroaniline**



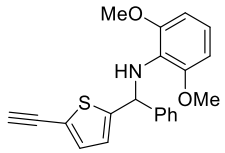
3cg: 96% yield; yellow solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.2 Hz, 2H), 7.40–7.34 (m, 5H), 7.13 (d, *J* = 3.8 Hz, 1H), 6.78 (d, *J* = 3.8 Hz, 1H), 6.57 (d, *J* = 9.2 Hz, 2H), 5.82 (s, 1H), 5.18 (brs, 1H), 3.33 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.5, 147.5, 140.2, 139.0, 133.3, 129.3, 128.7, 127.1, 126.2, 125.7, 122.4, 112.4, 82.1, 76.7, 58.1; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{14}N_2O_2SNa^+$ $[M+Na]^+$ 357.0668, found: 357.0669.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-2,6-dimethylaniline**



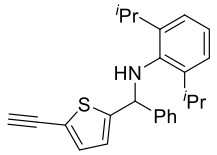
3da: 92% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.35–7.32 (m, 3H), 7.30–7.28 (m, 2H), 7.18 (d, *J* = 3.8 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.88–6.84 (m, 1H), 6.63 (d, *J* = 2.6 Hz, 1H), 5.37 (s, 1H), 3.71 (brs, 1H), 3.35 (s, 1H), 2.06 (s, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.2, 144.0, 143.0, 133.4, 130.1, 129.0, 128.7, 128.0, 127.4, 124.9, 122.6, 121.0, 81.3, 77.4, 62.6, 18.6; **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{19}NSNa^+$ $[M+Na]^+$ 340.1130, found: 340.1132.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-2,6-dimethoxyaniline**



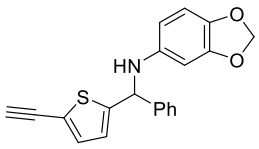
3db: 93% yield; white solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.0 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.21 (d, *J* = 2.6 Hz, 1H), 7.04 (d, *J* = 3.8 Hz, 1H), 6.73 (t, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 3.8 Hz, 1H), 6.45 (d, *J* = 8.4 Hz, 2H), 6.21 (s, 1H), 4.75 (brs, 1H), 3.74 (s, 6H), 3.26 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.6, 150.8, 142.8, 132.9, 128.4, 127.5, 127.4, 125.2, 124.7, 120.9, 120.6, 104.9, 81.1, 77.4, 59.4, 56.1; **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{19}NO_2SNa^+$ $[M+Na]^+$ 372.1029, found: 372.1027.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-2,6-diisopropylaniline**



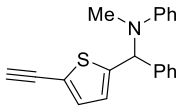
3dc: 91% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.29–7.26 (m, 3H), 7.22–7.20 (m, 2H), 7.13 (d, *J* = 3.8 Hz, 1H), 7.02 (s, 3H), 6.56 (d, *J* = 3.8 Hz, 1H), 5.14 (s, 1H), 3.74 (brs, 1H), 3.29 (s, 1H), 2.85 (q, *J* = 6.8 Hz, 2H), 1.10 (d, *J* = 6.8 Hz, 6H), 0.94 (d, *J* = 6.8 Hz, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.1, 142.5, 142.4, 140.7, 133.4, 128.7, 128.0, 127.7, 125.0, 124.0, 123.6, 121.0, 81.2, 77.5, 65.7, 27.8, 24.2; **HR-MS** (ESI) *m/z* calcd for $C_{25}H_{27}NSNa^+$ $[M+Na]^+$ 396.1756, found: 396.1755.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)benzo[*d*][1,3]dioxol-5-amine**



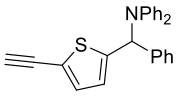
3e: 95% yield; yellow solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.41–7.33 (m, 5H), 7.13 (d, *J* = 3.8 Hz, 1H), 6.76 (d, *J* = 3.8 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.25 (d, *J* = 2.4 Hz, 1H), 6.05 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.83 (s, 2H), 5.61 (s, 1H), 4.16 (brs, 1H), 3.32 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.3, 148.3, 142.4, 142.0, 140.4, 133.3, 129.0, 128.1, 127.2, 124.7, 121.5, 108.6, 105.8, 100.8, 96.9, 81.6, 77.2, 59.9; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{16}NO_2S^+$ $[M+H]^+$ 334.0896, found: 334.0896.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-*N*-methylaniline**



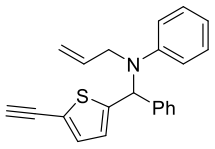
3f: 96% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.34–7.23 (m, 7H), 7.14 (d, *J* = 3.8 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 3.8 Hz, 1H), 6.28 (s, 1H), 3.30 (s, 1H), 2.75 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.7, 147.6, 139.3, 133.1, 129.3, 128.6, 128.3, 128.0, 126.4, 121.5, 118.1, 114.0, 81.6, 77.2, 63.8, 34.2; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}NS^+$ $[M+H]^+$ 304.1154, found: 304.1151.

***N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)-*N*-phenylaniline**



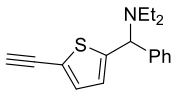
3g: 68% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 3H), 7.13 (t, *J* = 7.8 Hz, 3H), 7.06–7.04 (m, 2H), 6.92–6.85 (m, 6H), 6.73 (d, *J* = 3.8 Hz, 1H), 6.48 (s, 1H), 3.26 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 147.9, 146.9, 140.2, 132.9, 129.5, 129.1, 128.4, 127.7, 127.0, 123.3(4), 122.3(2), 121.8, 121.1, 117.9, 81.6, 77.2, 65.0; **HR-MS** (ESI) *m/z* calcd for $C_{25}H_{20}NS^+$ $[M+H]^+$ 366.1311, found: 366.1312.

***N*-allyl-*N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)aniline**



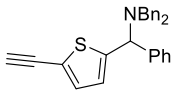
3h: 83% yield; colorless oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.27–7.24 (m, 4H), 7.20–7.15 (m, 3H), 7.10 (d, *J* = 3.8 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 3.8 Hz, 1H), 6.23 (s, 1H), 5.63–5.57 (m, 1H), 5.05–4.95 (m, 2H), 3.92–3.79 (m, 2H), 3.28 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 148.7, 147.8, 139.5, 135.4, 133.1, 129.1, 128.7, 128.6, 128.0, 126.7, 121.6, 118.7, 116.4, 115.8, 81.5, 77.2, 64.2, 50.6; **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{19}NSNa^+$ $[M+Na]^+$ 352.1130, found: 352.1132.

***N*-ethyl-*N*-((5-ethynylthiophen-2-yl)(phenyl)methyl)ethanamine**



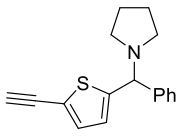
3i: 91% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.36–7.32 (m, 2H), 7.30–7.28 (m, 1H), 7.11 (d, *J* = 3.8 Hz, 1H), 6.69 (d, *J* = 3.8 Hz, 1H), 5.09 (s, 1H), 3.33 (s, 1H), 2.63 (q, *J* = 6.8 Hz, 2H), 2.43 (q, *J* = 6.8 Hz, 2H), 1.07 (t, *J* = 7.2 Hz, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.2, 140.0, 132.8, 128.9, 128.3, 127.5, 125.2, 121.0, 81.1, 77.7, 65.7, 43.5, 12.5; **HR-MS** (ESI) *m/z* calcd for $C_{17}H_{19}NSNa^+$ $[M+Na]^+$ 292.1130, found: 292.1133.

***N*,*N*-dibenzyl-1-(5-ethynylthiophen-2-yl)-1-phenylmethanamine**



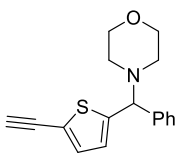
3j: 93% yield; yellow solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 4H), 7.49–7.46 (m, 2H), 7.43–7.36 (m, 7H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 3.8 Hz, 1H), 6.60 (d, *J* = 3.2 Hz, 1H), 5.17 (s, 1H), 3.92 (s, 2H), 3.40 (s, 1H), 3.31 (s, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.5, 139.4, 136.0, 133.0, 130.1, 128.7, 128.6, 128.3, 128.1, 127.2, 126.4, 121.3, 81.3, 77.6, 63.3, 54.0; **HR-MS** (ESI) *m/z* calcd for $C_{27}H_{23}NSNa^+$ $[M+Na]^+$ 416.1443, found: 416.1441.

1-((5-ethynylthiophen-2-yl)(phenyl)methyl)pyrrolidine



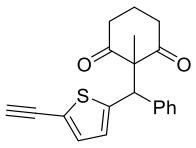
3k: 80% yield; white solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.26–7.23 (m, 1H), 7.04 (d, *J* = 3.8 Hz, 1H), 6.81 (d, *J* = 3.8 Hz, 1H), 4.46 (s, 1H), 3.29 (s, 1H), 2.47 (d, *J* = 9.4 Hz, 4H), 1.78 (d, *J* = 6.6 Hz, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.5, 142.8, 132.6, 128.6, 127.7, 127.5, 123.8, 121.1, 81.1, 77.5, 71.3, 53.5, 23.6; **HR-MS** (ESI) *m/z* calcd for $C_{17}H_{18}NS^+$ $[M+H]^+$ 268.1154, found: 268.1154.

4-((5-ethynylthiophen-2-yl)(phenyl)methyl)morpholine



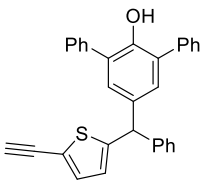
3l: 73% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.8 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.24–7.22 (m, 1H), 7.05 (d, *J* = 3.6 Hz, 1H), 6.76 (d, *J* = 3.6 Hz, 1H), 4.52 (s, 1H), 3.69 (t, *J* = 4.6 Hz, 4H), 3.30 (s, 1H), 2.42 (t, *J* = 4.6 Hz, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.4, 140.0, 132.8, 128.7, 128.3, 127.9, 125.2, 121.8, 81.5, 77.3, 71.7, 67.2, 52.2; **HR-MS** (ESI) *m/z* calcd for $C_{17}H_{18}NOS^+$ $[M+H]^+$ 284.1104, found: 284.1105.

2-((5-ethynylthiophen-2-yl)(phenyl)methyl)-2-methylcyclohexane-1,3-dione



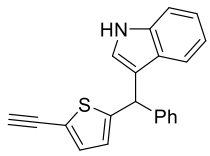
3m: 87% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.34–7.32 (m, 2H), 7.30–7.28 (m, 3H), 7.12 (d, *J* = 3.8 Hz, 1H), 6.89 (d, *J* = 3.8 Hz, 1H), 5.12 (s, 1H), 3.34 (s, 1H), 2.69–2.62 (m, 2H), 2.58–2.51 (m, 2H), 1.84–1.81 (m, 1H), 1.72–1.69 (m, 1H), 1.29 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 210.1, 144.7, 138.7, 132.7, 129.8, 128.6, 127.9, 127.6, 121.8, 81.5, 77.0, 68.8, 52.2, 39.3, 21.2, 16.9; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}O_2SNa^+$ $[M+Na]^+$ 345.0920, found: 345.0922.

5'-((5-ethynylthiophen-2-yl)(phenyl)methyl)-[1,1':3',1''-terphenyl]-2'-ol



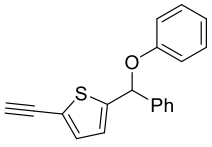
3n: 70% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 4H), 7.46 (t, *J* = 7.6 Hz, 5H), 7.38 (d, *J* = 6.6 Hz, 2H), 7.31 (d, *J* = 6.8 Hz, 2H), 7.28 (s, 1H), 7.26 (s, 2H), 7.14 (s, 2H), 6.63 (d, *J* = 3.8 Hz, 1H), 5.62 (s, 1H), 5.41 (brs, 1H), 3.31 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.9, 148.4, 143.3, 137.5, 135.5, 133.1, 130.3, 129.5, 129.0, 128.8(5), 128.8(3), 128.7, 127.9, 127.1, 126.3, 121.2, 81.3, 77.3, 51.9; **HR-MS** (ESI) *m/z* calcd for $C_{31}H_{22}OSNa^+$ $[M+Na]^+$ 465.1284, found: 465.1282.

3-((5-ethynylthiophen-2-yl)(phenyl)methyl)-1*H*-indole



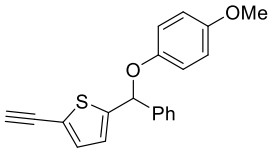
3o: 83% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.98 (brs, 1H), 7.37–7.33 (m, 6H), 7.31–7.27 (m, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 3.8 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.78 (s, 1H), 6.69 (d, *J* = 3.8 Hz, 1H), 5.85 (s, 1H), 3.30 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.0, 143.2, 136.6, 133.1, 128.6, 128.5, 127.0, 126.6, 125.7, 123.7, 122.4, 120.6, 119.8, 119.7, 119.2, 111.3, 81.1, 77.5, 44.3; **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{15}NSNa^+$ $[M+Na]^+$ 336.0817, found: 336.0818.

2-ethynyl-5-(phenoxy(phenyl)methyl)thiophene



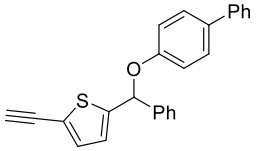
3p: 86% yield; yellow solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 3.8 Hz, 1H), 6.93–6.89 (m, 3H), 6.71 (d, *J* = 3.8 Hz, 1H), 6.32 (s, 1H), 3.27 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 157.6, 147.5, 140.2, 132.9, 129.6, 128.9, 128.5, 126.7, 125.4, 122.5, 121.7, 116.3, 81.8, 77.0, 78.0; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{14}OSNa^+$ $[M+Na]^+$ 313.0658, found: 313.0656.

2-ethynyl-5-((4-methoxyphenoxy)(phenyl)methyl)thiophene



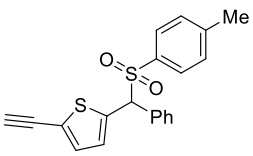
3q: 90% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.0 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.35–7.31 (m, 1H), 7.11 (d, *J* = 3.8 Hz, 1H), 6.92–6.89 (m, 2H), 6.79–6.77 (m, 2H), 6.74 (d, *J* = 3.8 Hz, 1H), 6.25 (s, 1H), 3.74 (s, 3H), 3.33 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.6, 151.7, 147.8, 140.4, 132.9, 128.8, 128.4, 126.8, 125.3, 122.4, 117.8, 114.6, 81.8, 79.2, 77.0, 55.7; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}O_2S^+$ $[M+H]^+$ 321.0944, found: 321.0943.

2-(([1,1'-biphenyl]-4-yloxy)(phenyl)methyl)-5-ethynylthiophene



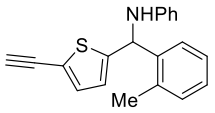
3r: 84% yield; white solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.54–7.48 (m, 6H), 7.42 (t, *J* = 7.4 Hz, 4H), 7.38–7.30 (m, 2H), 7.14 (d, *J* = 3.4 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 3.4 Hz, 1H), 6.41 (s, 1H), 3.35 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 157.2, 147.4, 140.7, 140.1, 134.8, 132.9, 129.0, 128.8, 128.6, 128.3, 126.9(0), 126.8(6), 126.7, 125.4, 122.6, 116.6, 81.9, 78.2, 77.0; **HR-MS** (ESI) *m/z* calcd for $C_{25}H_{19}OS^+$ $[M+H]^+$ 367.1151, found: 367.1153.

2-ethynyl-5-(phenyl(tosyl)methyl)thiophene



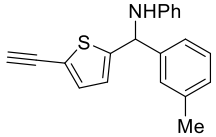
3s: 92% yield; yellow solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.50–7.46 (m, 4H), 7.35–7.32 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 3.4 Hz, 1H), 7.06 (d, *J* = 3.8 Hz, 1H), 5.47 (s, 1H), 3.36 (s, 1H), 2.37 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 145.0, 136.1, 134.2, 132.8, 132.2, 130.0, 129.5(0), 129.4(7), 129.3(0), 129.2(6), 128.8, 123.8, 82.4, 76.5, 72.3, 21.8; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{16}O_2S_2Na^+$ $[M+Na]^+$ 375.0484, found: 375.0486.

***N*-((5-ethynylthiophen-2-yl)(*o*-tolyl)methyl)aniline**



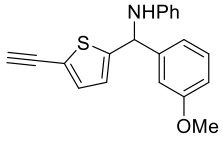
4a: 93% yield; white solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.0 Hz, 1H), 7.22–7.13 (m, 6H), 6.76–6.73 (m, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 5.86 (s, 1H), 4.28 (brs, 1H), 3.32 (s, 1H), 2.38 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.3, 146.7, 139.8, 135.8, 133.3, 130.9, 129.4, 128.0, 126.7, 126.6, 125.2, 121.6, 118.4, 113.4, 81.5, 77.2, 55.3, 19.4; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}NSNa^+$ $[M+Na]^+$ 326.0974, found: 326.0975.

***N*-((5-ethynylthiophen-2-yl)(*m*-tolyl)methyl)aniline**



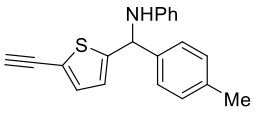
4b: 94% yield; white solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.23–7.17 (m, 3H), 7.15–7.09 (m, 4H), 6.76–6.70 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 2H), 5.63 (s, 1H), 4.30 (brs, 1H), 3.27 (s, 1H), 2.33 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.4, 146.8, 142.0, 138.8, 133.3, 129.3, 128.9, 127.9, 124.7, 124.2, 121.4, 118.5, 113.8, 81.5, 77.2, 59.1, 21.6; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}NSNa^+$ $[M+Na]^+$ 326.0974, found: 326.0976.

***N*-((5-ethynylthiophen-2-yl)(3-methoxyphenyl)methyl)aniline**



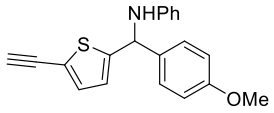
4c: 81% yield; white solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.0 Hz, 1H), 7.19–7.15 (m, 2H), 7.14 (d, *J* = 3.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.98 (s, 1H), 6.87 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.80 (d, *J* = 3.8 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.4 Hz, 2H), 5.68 (s, 1H), 4.37 (brs, 1H), 3.81 (s, 3H), 3.32 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 160.1, 150.0, 146.7, 143.6, 133.3, 130.1, 129.3, 124.8, 121.5, 119.5, 118.5, 113.8, 113.4, 112.9, 81.5, 77.2, 59.0, 55.4; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}NOS^+$ $[M+H]^+$ 320.1104, found: 320.1101.

***N*-((5-ethynylthiophen-2-yl)(*p*-tolyl)methyl)aniline**



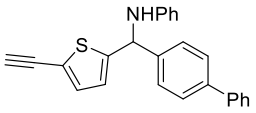
4d: 70% yield; white solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.20–7.17 (m, 4H), 7.14 (d, *J* = 3.8 Hz, 1H), 6.79–6.74 (m, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 5.69 (s, 1H), 4.33 (brs, 1H), 3.32 (s, 1H), 2.37 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.6, 146.8, 139.1, 137.9, 133.3, 129.7, 129.3, 127.1, 124.7, 121.1, 118.5, 113.8, 81.4, 77.2, 58.7, 21.3; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}NS^+$ $[M+H]^+$ 304.1154, found: 304.1155.

***N*-((5-ethynylthiophen-2-yl)(4-methoxyphenyl)methyl)aniline**



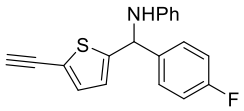
4e: 62% yield; yellow solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.19–7.14 (m, 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.79–6.74 (m, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 5.67 (s, 1H), 4.32 (brs, 1H), 3.82 (s, 3H), 3.32 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 159.4, 150.7, 146.7, 134.2, 133.3, 129.3, 128.4, 124.6, 121.3, 118.4, 114.3, 113.7, 81.5, 77.2, 58.4, 55.4; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{18}NOS^+$ $[M+H]^+$ 320.1104, found: 320.1101.

***N*-([1,1'-biphenyl]-4-yl(5-ethynylthiophen-2-yl)methyl)aniline**



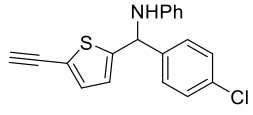
4f: 83% yield; white solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 4H), 7.52–7.46 (m, 4H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.25–7.16 (m, 3H), 6.85 (d, *J* = 3.8 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 2H), 5.79 (s, 1H), 4.41 (brs, 1H), 3.35 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.1, 146.7, 141.0, 140.9, 140.6, 133.3, 129.3, 128.9, 127.8, 127.6(3), 127.5(5), 127.2, 124.9, 121.6, 118.6, 113.8, 81.6, 77.1, 58.7; **HR-MS** (ESI) *m/z* calcd for $C_{25}H_{19}NSNa^+$ $[M+Na]^+$ 388.1130, found: 388.1133.

***N*-((5-ethynylthiophen-2-yl)(4-fluorophenyl)methyl)aniline**



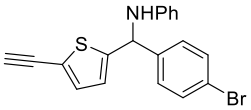
4g: 89% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.41–7.37 (m, 2H), 7.19–7.13 (m, 3H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.79–6.75 (m, 2H), 6.60 (d, *J* = 8.0 Hz, 2H), 5.70 (s, 1H), 4.30 (brs, 1H), 3.33 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 246.8 Hz), 149.8, 146.5, 137.7 (d, *J* = 3.2 Hz), 133.3, 129.4, 128.9 (d, *J* = 8.2 Hz), 124.9, 121.8, 118.7, 116.0 (d, *J* = 21.6 Hz), 113.8, 81.7, 77.0, 58.2; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -114.0; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{14}FNSNa^+$ $[M+Na]^+$ 330.0723, found: 330.0720.

***N*-((4-chlorophenyl)(5-ethynylthiophen-2-yl)methyl)aniline**



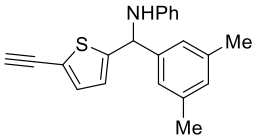
4h: 69% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.38–7.33 (m, 4H), 7.19–7.13 (m, 3H), 6.80–6.76 (m, 2H), 6.60 (d, *J* = 7.6 Hz, 2H), 5.69 (s, 1H), 4.32 (brs, 1H), 3.34 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.3, 146.4, 140.4, 133.9, 133.3, 129.4, 129.2, 128.5, 125.1, 121.9, 118.8, 113.8, 81.8, 76.9, 58.2; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{15}ClNS^+$ $[M+H]^+$ 324.0608, found: 324.0606.

***N*-((4-bromophenyl)(5-ethynylthiophen-2-yl)methyl)aniline**



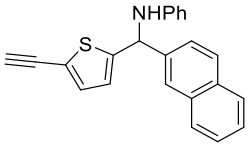
4i: 77% yield; brown oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.19–7.13 (m, 3H), 6.80–6.75 (m, 2H), 6.60 (d, *J* = 7.6 Hz, 2H), 5.67 (s, 1H), 4.32 (brs, 1H), 3.34 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.2, 146.3, 140.9, 133.3, 132.2, 129.4, 128.9, 125.1, 122.0, 121.9, 118.8, 113.8, 81.8, 76.9, 58.3; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{14}BrNSNa^+$ $[M+Na]^+$ 389.9923, found: 389.9924.

***N*-((3,5-dimethylphenyl)(5-ethynylthiophen-2-yl)methyl)aniline**



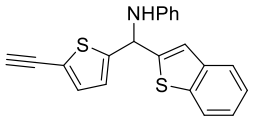
4j: 72% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.20–7.14 (m, 3H), 7.03 (s, 2H), 6.97 (s, 1H), 6.81 (d, *J* = 3.8 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 5.63 (s, 1H), 4.33 (brs, 1H), 3.32 (s, 1H), 2.33 (s, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.7, 146.9, 142.1, 138.7, 133.4, 129.8, 129.3, 124.9, 124.5, 121.3, 118.4, 113.7, 81.4, 77.3, 59.2, 21.5; **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{19}NSNa^+$ $[M+Na]^+$ 340.1130, found: 340.1131.

***N*-((5-ethynylthiophen-2-yl)(naphthalen-2-yl)methyl)aniline**



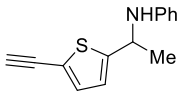
4k: 72% yield; brown solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.90–7.83 (m, 4H), 7.55–7.50 (m, 3H), 7.20–7.16 (m, 3H), 6.82–6.76 (m, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 5.89 (s, 1H), 4.45 (brs, 1H), 3.33 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.9, 146.7, 139.3, 133.5, 133.3, 133.2, 129.4, 129.0, 128.2, 127.8, 126.5, 126.4, 126.0, 125.1, 121.7, 118.6, 113.9, 81.7, 77.2, 59.1; **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{17}NSNa^+$ $[M+Na]^+$ 362.0974, found: 362.0971.

***N*-(benzo[*b*]thiophen-2-yl(5-ethynylthiophen-2-yl)methyl)aniline**



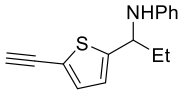
4l: 68% yield; white solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.36–7.29 (m, 3H), 7.20–7.15 (m, 3H), 6.94 (d, J = 3.8 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.05 (s, 1H), 4.47 (brs, 1H), 3.33 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 148.4, 146.8, 146.1, 139.7, 139.5, 133.3, 129.4, 125.3, 124.6(4), 124.6(1), 123.8, 122.6, 122.2, 122.0, 119.2, 114.0, 81.8, 77.0, 55.1; **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{15}NS_2Na^+$ $[M+Na]^+$ 368.0538, found: 368.0536.

***N*-(1-(5-ethynylthiophen-2-yl)ethyl)aniline**



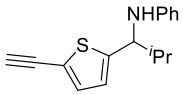
4m: 93% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.19–7.13 (m, 3H), 6.84 (d, *J* = 3.8 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 4.75 (q, *J* = 6.4 Hz, 1H), 3.99 (brs, 1H), 3.30 (s, 1H), 1.62 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.1, 146.7, 133.3, 129.3, 122.8, 120.2, 118.2, 113.6, 81.1, 77.2, 49.9, 24.8; **HR-MS** (ESI) *m/z* calcd for $C_{14}H_{14}NS^+$ $[M+H]^+$ 228.0841, found: 228.0839.

***N*-(1-(5-ethynylthiophen-2-yl)propyl)aniline**



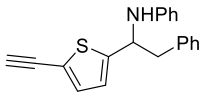
4n: 97% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.19–7.14 (m, 3H), 6.85 (d, *J* = 3.8 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 7.4 Hz, 2H), 4.51 (t, *J* = 6.6 Hz, 1H), 4.02 (brs, 1H), 3.31 (s, 1H), 1.96–1.88 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.0, 147.0, 133.2, 129.3, 123.5, 120.2, 118.1, 113.5, 81.1, 77.4, 56.0, 31.8, 10.7; **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{16}NS^+$ $[M+H]^+$ 242.0998, found: 242.0996.

***N*-(1-(5-ethynylthiophen-2-yl)-2-methylpropyl)aniline**



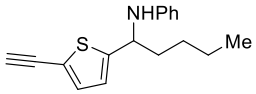
4o: 98% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.18–7.14 (m, 3H), 6.82 (d, *J* = 3.6 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.4 Hz, 2H), 4.40 (d, *J* = 5.8 Hz, 1H), 4.06 (brs, 1H), 3.31 (s, 1H), 2.17–2.05 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 50.8, 147.2, 133.1, 129.3, 124.1, 120.2, 118.0, 113.5, 81.1, 77.4, 60.2, 35.3, 19.4; **HR-MS** (ESI) *m/z* calcd for $C_{16}H_{18}NS^+$ $[M+H]^+$ 256.1154, found: 256.1152.

***N*-(1-(5-ethynylthiophen-2-yl)-2-phenylethyl)aniline**



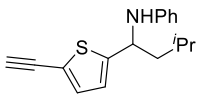
4p: 75% yield; yellow solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.45–7.41 (m, 1H), 7.33–7.28 (m, 3H), 7.16–7.13 (m, 3H), 7.11 (s, 1H), 6.77–6.69 (m, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 4.85 (t, *J* = 7.0 Hz, 1H), 4.13 (brs, 1H), 3.31 (s, 1H), 3.18 (d, *J* = 7.0 Hz, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.3, 146.7, 136.8, 133.3, 129.4, 129.3, 128.7, 127.1, 123.6, 120.4, 118.5, 113.9, 81.2, 68.6, 55.7, 45.1; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}NSNa^+$ $[M+Na]^+$ 326.0974, found: 326.0976.

***N*-(1-(5-ethynylthiophen-2-yl)pentyl)aniline**



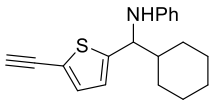
4q: 90% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.19–7.14 (m, 3H), 6.84 (d, *J* = 3.6 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.4 Hz, 2H), 4.57 (t, *J* = 6.8 Hz, 1H), 4.02 (brs, 1H), 3.31 (s, 1H), 1.96–1.82 (m, 2H), 1.46–1.35 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.4, 147.0, 133.2, 129.3, 123.3, 120.1, 118.1, 113.5, 81.1, 77.4, 54.5, 38.7, 28.3, 22.6, 14.1; **HR-MS** (ESI) *m/z* calcd for $C_{17}H_{19}NSNa^+$ $[M+Na]^+$ 292.1130, found: 292.1131.

***N*-(1-(5-ethynylthiophen-2-yl)-3-methylbutyl)aniline**



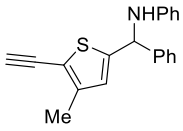
4r: 77% yield; yellow oil; According to procedure B;**^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.17–7.12 (m, 3H), 6.84 (d, *J* = 3.8 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 4.64 (t, *J* = 6.6 Hz, 1H), 3.97 (brs, 1H), 3.30 (s, 1H), 1.84–1.74 (m, 2H), 1.73–1.69 (m, 1H), 1.01 (d, *J* = 5.8 Hz, 3H), 0.96 (d, *J* = 5.8 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.8, 146.9, 133.2, 129.3, 123.2, 120.1, 118.1, 113.5, 81.1, 77.4, 52.6, 48.5, 25.1, 22.8; **HR-MS** (ESI) *m/z* calcd for $C_{17}H_{20}NS^+$ $[M+H]^+$ 270.1311, found: 270.1311.

***N*-(cyclohexyl(5-ethynylthiophen-2-yl)methyl)aniline**



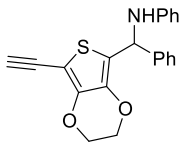
4s: 86% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.17–7.13 (m, 3H), 6.81 (d, *J* = 3.8 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 4.39 (d, *J* = 6.0 Hz, 1H), 4.10 (brs, 1H), 3.31 (s, 1H), 1.95–1.92 (m, 1H), 1.83–1.77 (m, 2H), 1.72–1.67 (m, 3H), 1.30–1.26 (m, 2H), 1.18–1.12 (m, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.0, 147.3, 133.1, 129.2, 124.1, 120.1, 117.9, 113.4, 81.1, 77.4, 59.7, 45.3, 30.0, 29.5, 26.4; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{21}NSNa^+$ $[M+Na]^+$ 318.1287, found: 318.1288.

***N*-((5-ethynyl-4-methylthiophen-2-yl)(phenyl)methyl)aniline**



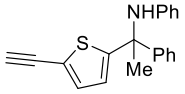
4t: 91% yield; brown oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.45–7.33 (m, 5H), 7.18 (t, *J* = 7.8 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.67–6.62 (m, 3H), 5.66 (s, 1H), 4.33 (brs, 1H), 3.44 (s, 1H), 2.27 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 148.4, 146.8, 144.1, 142.1, 129.3, 129.0, 128.1, 127.2, 127.0, 118.5, 116.8, 113.8, 83.6, 76.8, 59.0, 15.3; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}NSNa^+$ $[M+Na]^+$ 326.0974, found: 326.0974.

***N*-((7-ethynyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)(phenyl)methyl)aniline**



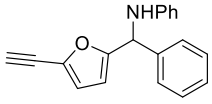
4u: 80% yield; white solid; According to procedure B;**^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 5.75 (s, 1H), 4.30–4.27 (m, 2H), 4.24 (brs, 1H), 4.21–4.14 (m, 2H), 3.46 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 146.9, 145.5, 141.4, 136.8, 129.2, 129.0, 128.0, 127.1, 122.6, 118.5, 113.8, 95.7, 84.4, 74.6, 65.3, 64.6, 55.5; **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{17}NO_2SNa^+$ $[M+Na]^+$ 370.0872, found: 370.0874.

***N*-(1-(5-ethynylthiophen-2-yl)-1-phenylethyl)aniline**



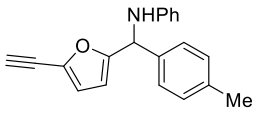
4v: 51% yield; yellow solid; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 3.6 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 3.6 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 2H), 4.44 (brs, 1H), 3.31 (s, 1H), 2.14 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 155.4, 146.1, 145.3, 133.0, 128.9, 128.7, 127.5, 126.4, 124.5, 121.5, 118.5, 116.5, 81.5, 61.2, 28.4; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}NSNa^+$ $[M+Na]^+$ 326.0974, found: 326.0976.

***N*-((5-ethynylfuran-2-yl)(phenyl)methyl)aniline**



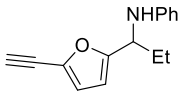
4w: 89% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.44–7.41 (m, 3H), 7.39–7.34 (m, 2H), 7.20–7.16 (m, 2H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.63–6.60 (m, 3H), 6.17 (d, *J* = 2.6 Hz, 1H), 5.59 (s, 1H), 4.36 (brs, 1H), 3.42 (s, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 156.8, 146.8, 140.0, 135.9, 129.3, 129.0, 128.1, 127.4, 118.3, 117.3, 113.6, 108.7, 82.3, 74.0, 57.1; **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{16}NO^+$ $[M+H]^+$ 274.1226, found: 274.1227.

***N*-((5-ethynylfuran-2-yl)(*p*-tolyl)methyl)aniline**



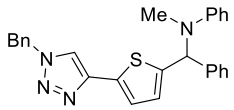
4x: 90% yield; yellow oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.21–7.16 (m, 4H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.63–6.60 (m, 3H), 6.18 (d, *J* = 3.4 Hz, 1H), 5.55 (s, 1H), 4.33 (brs, 1H), 3.41 (s, 1H), 2.38 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 157.0, 146.8, 137.9, 137.0, 135.8, 129.6, 129.3, 127.3, 118.2, 117.3, 113.6, 108.5, 82.2, 74.1, 56.9, 21.3; **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{17}NONa^+$ $[M+Na]^+$ 310.1202, found: 310.1203.

***N*-(1-(5-ethynylfuran-2-yl)propyl)aniline**



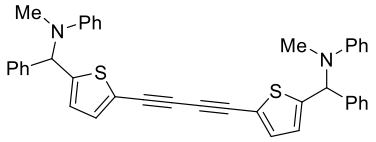
4y: 77% yield; colorless oil; According to procedure B; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.8 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 3.4 Hz, 1H), 6.16 (d, *J* = 3.4 Hz, 1H), 4.38 (brs, 1H), 3.93 (s, 1H), 3.43 (s, 1H), 2.01–1.86 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 158.0, 147.0, 135.2, 129.3, 117.9, 117.2, 113.4, 107.4, 82.0, 74.3, 53.6, 28.3, 10.5; **HR-MS** (ESI) *m/z* calcd for $C_{15}H_{15}NONa^+$ $[M+Na]^+$ 248.1046, found: 248.1043.

***N*-((5-(1-benzyl-1*H*-1,2,3-triazol-4-yl)thiophen-2-yl)(phenyl)methyl)-*N*-methylaniline**



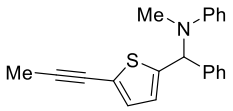
5: 96% yield; yellow solid; According to procedure C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.33–7.29 (m, 7H), 7.24–7.18 (m, 6H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.75–6.72 (m, 2H), 6.30 (s, 1H), 5.46 (s, 2H), 2.76 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.7, 144.8, 143.2, 139.7, 134.5, 132.4, 129.2, 128.8, 128.5, 128.2, 128.1, 127.7, 127.2, 123.9, 119.0, 117.7, 113.7, 63.4, 54.2, 34.2; **HR-MS** (ESI) *m/z* calcd for $C_{27}H_{24}N_4SNa^+$ $[M+Na]^+$ 459.1614, found: 459.1616.

***N*,*N*'-((buta-1,3-diyne-1,4-diylbis(thiophene-5,2-diyl))bis(phenylmethylene))bis(*N*-methylaniline)**



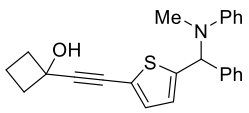
6: 81% yield; yellow solid; According to procedure C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.30–7.28 (m, 5H), 7.23–7.20 (m, 8H), 7.18–7.16 (m, 3H), 6.80–6.73 (m, 6H), 6.66 (d, *J* = 3.8 Hz, 2H), 6.24 (s, 2H), 2.70 (s, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.7, 149.3, 139.2, 134.6, 129.3, 128.7, 128.4, 128.0, 126.8, 121.5, 118.2, 114.1, 78.2, 77.1, 64.1, 34.3; **HR-MS** (ESI) *m/z* calcd for $C_{40}H_{32}N_2S_2Na^+$ $[M+Na]^+$ 627.1899, found: 627.1898.

***N*-methyl-*N*-(phenyl(5-(prop-1-yn-1-yl)thiophen-2-yl)methyl)aniline**



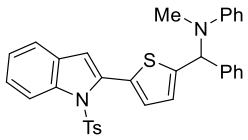
7: 78% yield; yellow oil; According to procedure C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.40–7.34 (m, 5H), 7.32–7.28 (m, 2H), 7.04 (d, *J* = 3.8 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 3.4 Hz, 1H), 6.33 (s, 1H), 2.83 (s, 3H), 2.11 (s, 3H); **^{13}C-NMR** (100 MHz, CDCl3) δ 149.8, 145.6, 139.7, 130.8, 129.3, 128.6, 128.3, 127.8, 126.5, 123.9, 117.8, 113.9, 90.4, 73.1, 63.6, 34.2, 4.8; **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{19}NSNa^+$ $[M+Na]^+$ 340.1130, found: 340.1132.

1-((5-((methyl(phenyl)amino)(phenyl)methyl)thiophen-2-yl)ethynyl)cyclobutan-1-ol



8: 86% yield; yellow oil; According to procedure C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.33–7.25 (m, 5H), 7.22 (d, *J* = 5.8 Hz, 2H), 7.07 (d, *J* = 3.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 3.6 Hz, 1H), 6.27 (s, 1H), 2.75 (s, 3H), 2.52–2.48 (m, 2H), 2.44 (brs, 1H), 2.35–2.27 (m, 2H), 1.87–1.81 (m, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.7, 147.2, 139.5, 132.2, 129.3, 128.6, 128.3, 127.9, 126.5, 122.2, 118.0, 113.9, 96.6, 77.0, 68.4, 63.7, 38.6, 34.2, 13.1; **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{23}NOSNa^+$ $[M+Na]^+$ 396.1393, found: 396.1395.

***N*-methyl-*N*-(phenyl(5-(1-tosyl-1*H*-indol-2-yl)thiophen-2-yl)methyl)aniline**



9: 92% yield; yellow solid; According to procedure C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.38–7.33 (m, 6H), 7.30 (d, *J* = 2.2 Hz, 1H), 7.28 (d, *J* = 2.6 Hz, 2H), 7.26 (s, 2H), 7.23 (d, *J* = 3.8 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 3.8 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.62 (s, 1H), 6.38 (s, 1H), 2.83 (s, 3H), 2.26 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.7, 146.6, 144.7, 139.7, 138.4, 134.9, 134.1, 131.6, 130.5, 130.0, 129.4, 129.3, 128.6, 128.3, 127.8, 126.8, 125.2, 124.3, 120.8, 117.8, 116.5, 114.3, 113.8, 63.5, 34.3, 21.6; **HR-MS** (ESI) *m/z* calcd for $C_{33}H_{29}N_2O_2S_2^+$ $[M+H]^+$ 549.1665, found: 549.1666.

5. X-ray Crystallographic Data

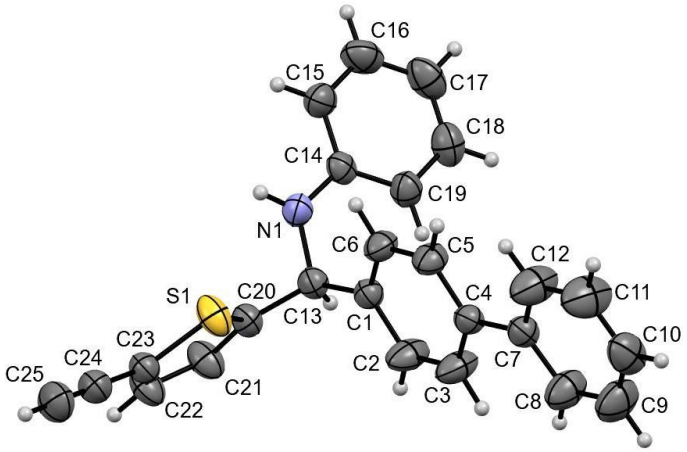


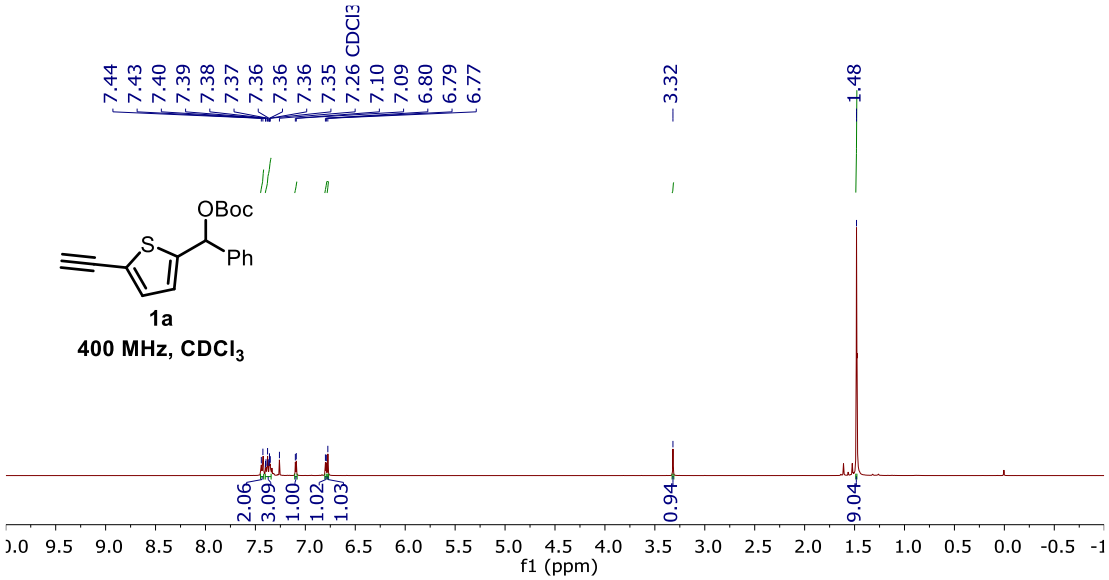
Figure S2. Single-crystal X-ray Structure of **4f**

Method for single crystals cultivation: **4f** (20.0 mg) was dissolved in *n*-hexane/ dichloromethane (v/v =90:10, 2.0 mL) in a vial at room temperature. The vial was properly sealed with parafilm and kept at 25 °C to allow the slow evaporation of the solvents until a single crystal was obtained. The absolute configuration of compound **4f** is determined by anomalous dispersion with Ga Kα radiation (λ =0.71073 Å) as X-ray source for X-ray diffraction experiment, and a Flack parameter of 0.05(3) is obtained as result. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2339912.

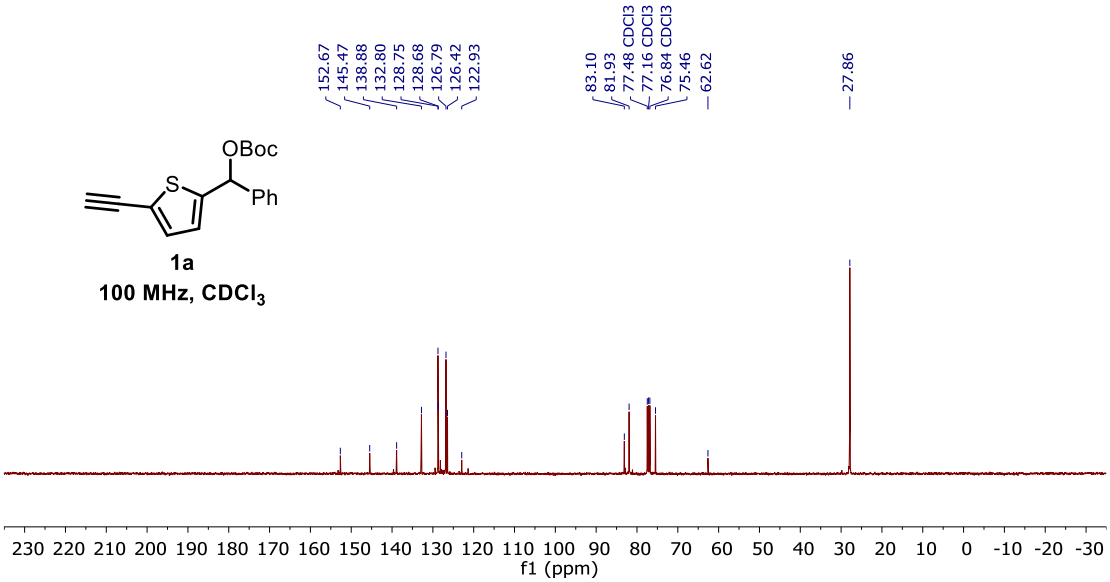
Table S8. Crystal data and structure refinement for **4f**

Identification code	**4f**	
Empirical formula	$C_{25}H_{19}NS$	
Formula weight	365.47	
Temperature	296(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 8.9563(16) Å	α = 90°.
	b = 5.8840(10) Å	β = 91.049(3)°.
	c = 18.577(3) Å	γ = 90°.
Volume	978.8(3) $Å^3$	
Z	2	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	0.174 mm^{-1}	
F(000)	384	
Crystal size	0.3 x 0.2 x 0.2 mm^3	
Theta range for data collection	2.507 to 32.039°.	
Index ranges	-12<=h<=12, -8<=k<=7, -26<=l<=26	
Reflections collected	10573	
Independent reflections	5811 [R(int) = 0.0282]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7463 and 0.6001	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5811 / 1 / 244	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.1168	
R indices (all data)	R1 = 0.0499, wR2 = 0.1245	
Absolute structure parameter	0.05(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.268 and -0.214 $e.Å^{-3}$	

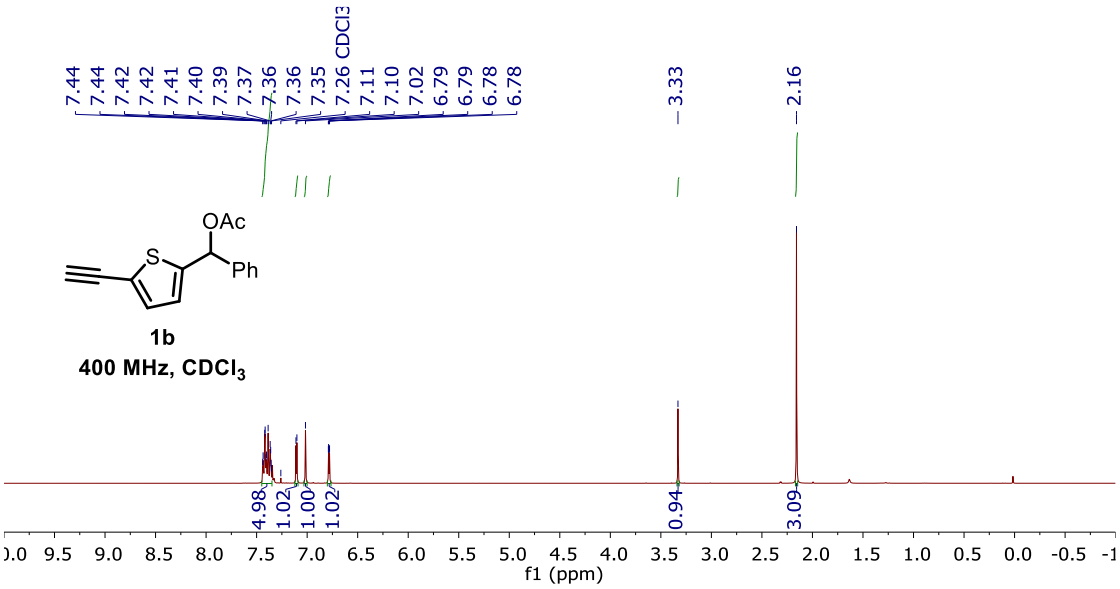
6. NMR Spectra



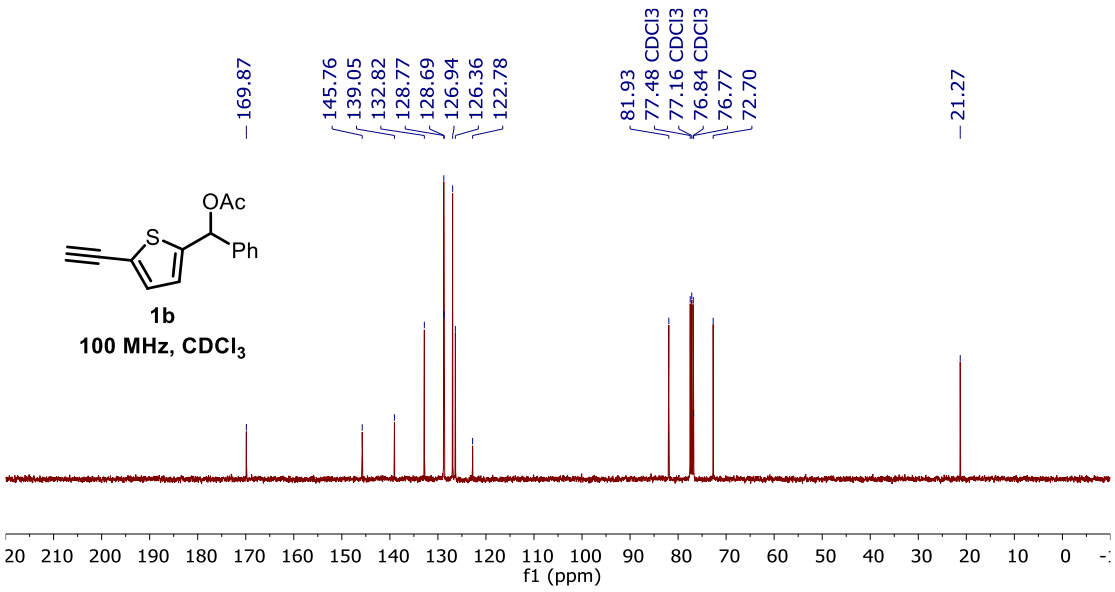
^{1}H NMR spectrum of **1a**



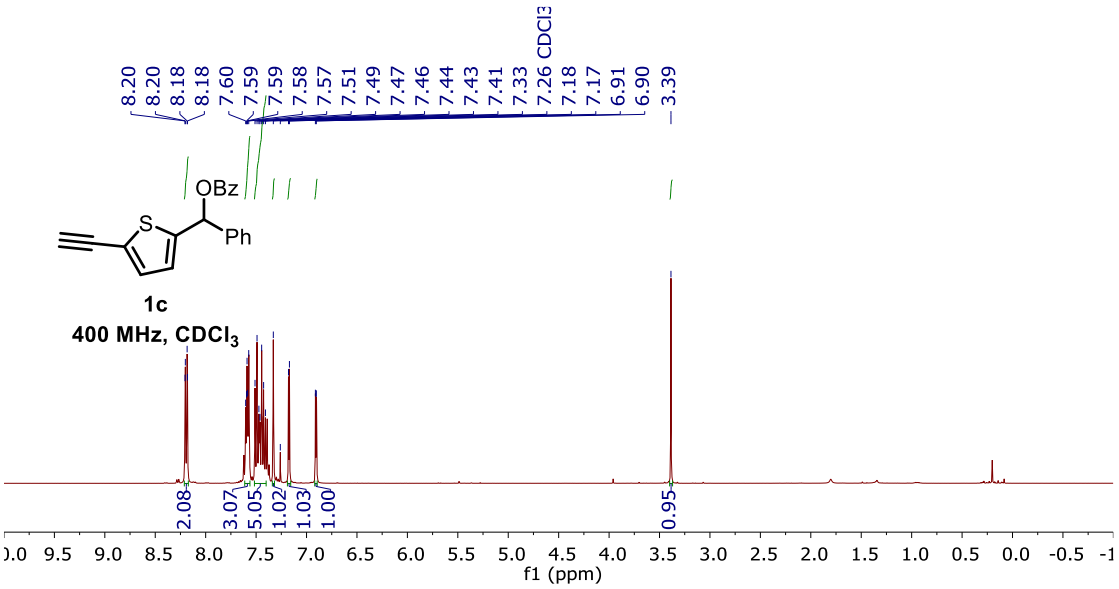
^{13}C NMR spectrum of **1a**



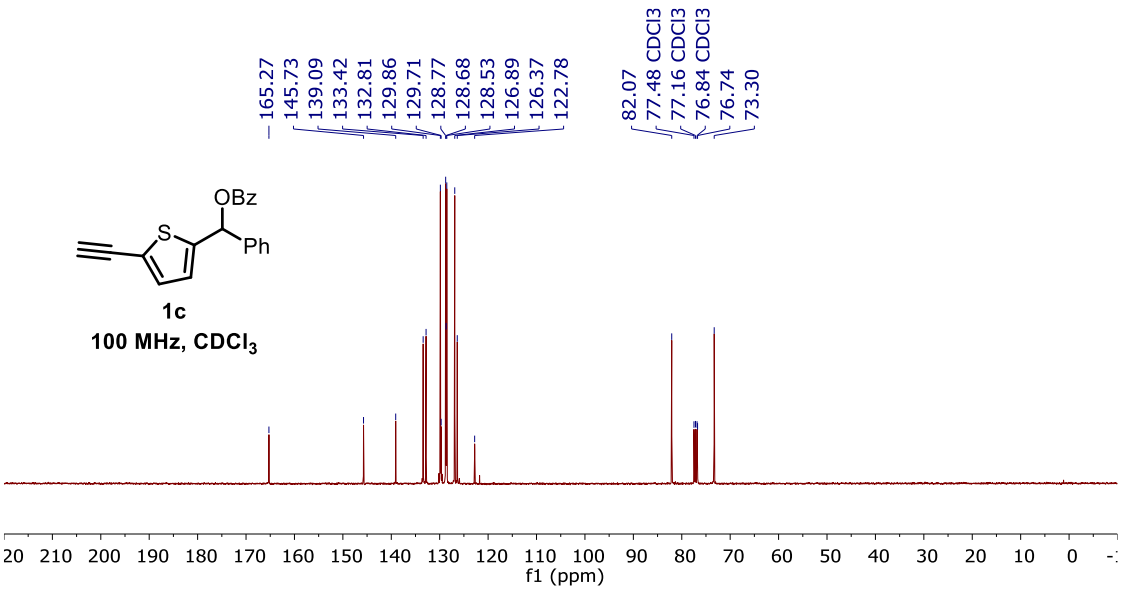
^{1}H NMR spectrum of **1b**



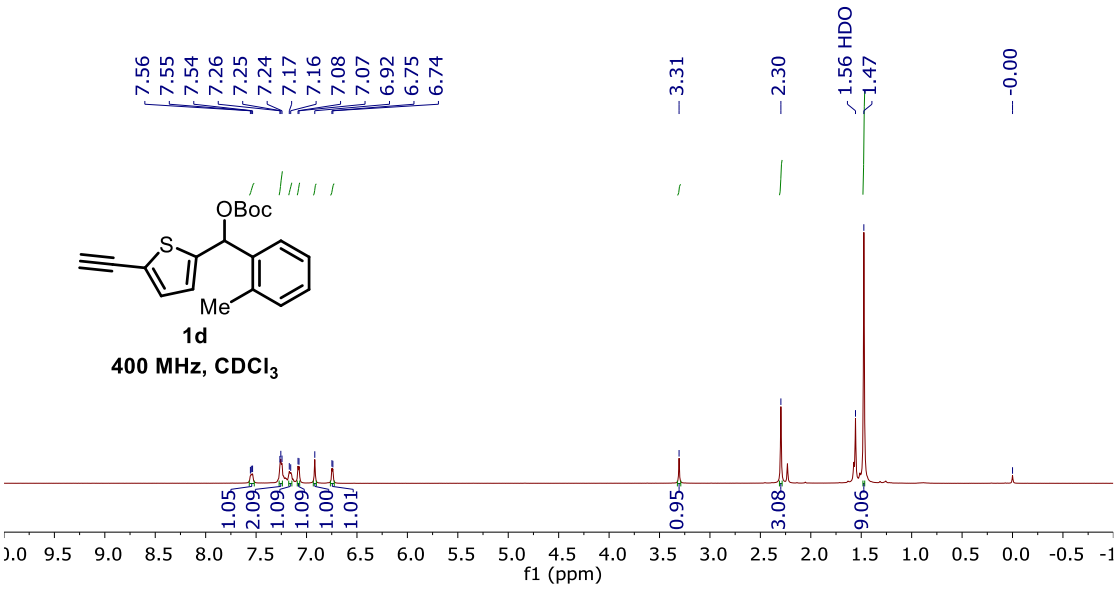
^{13}C NMR spectrum of **1b**



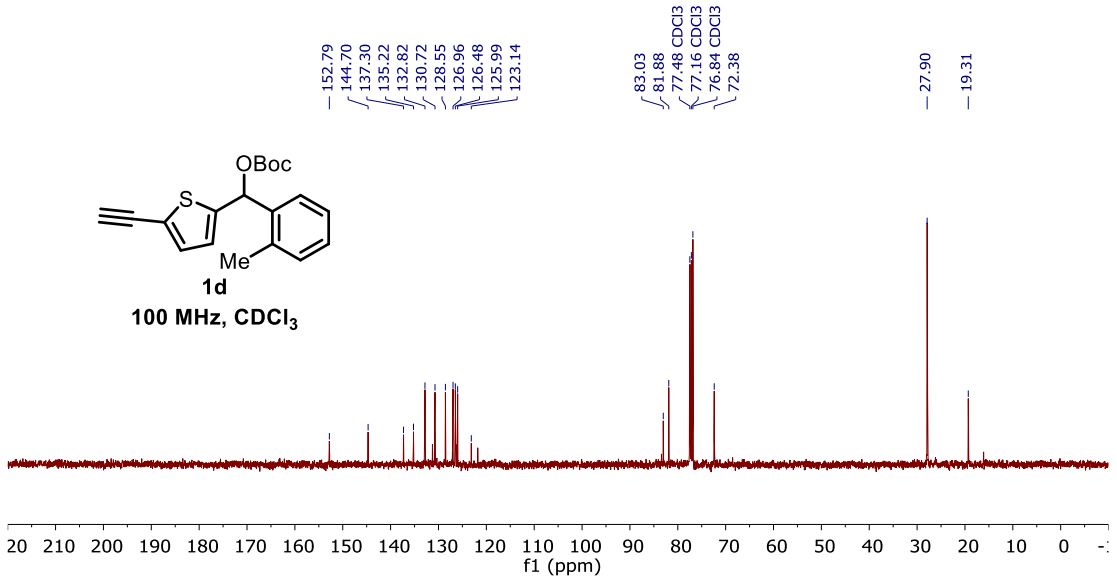
^{1}H NMR spectrum of **1c**



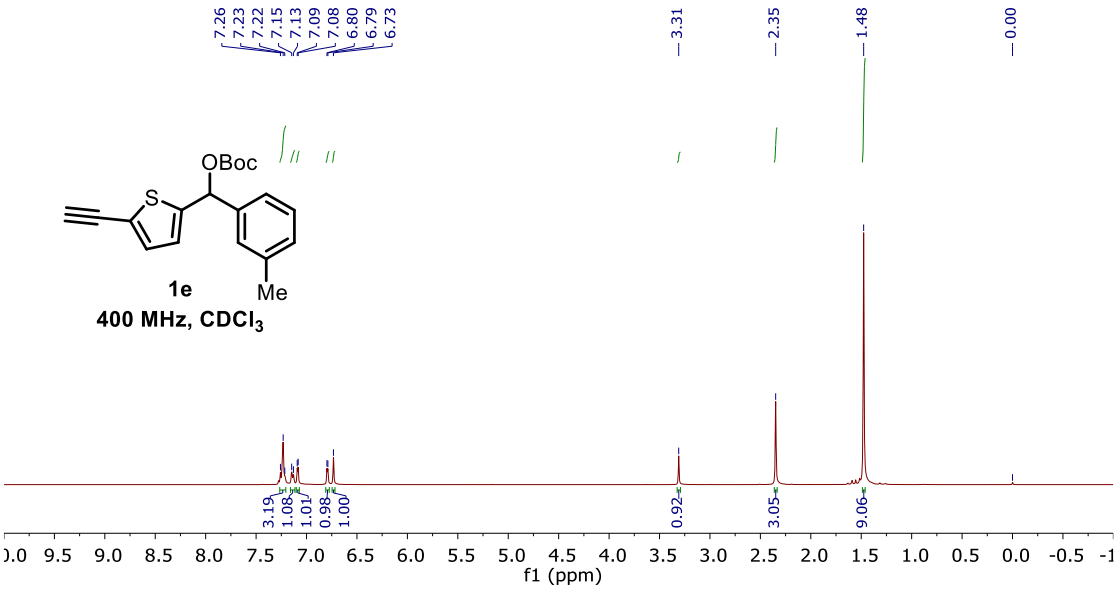
^{13}C NMR spectrum of **1c**



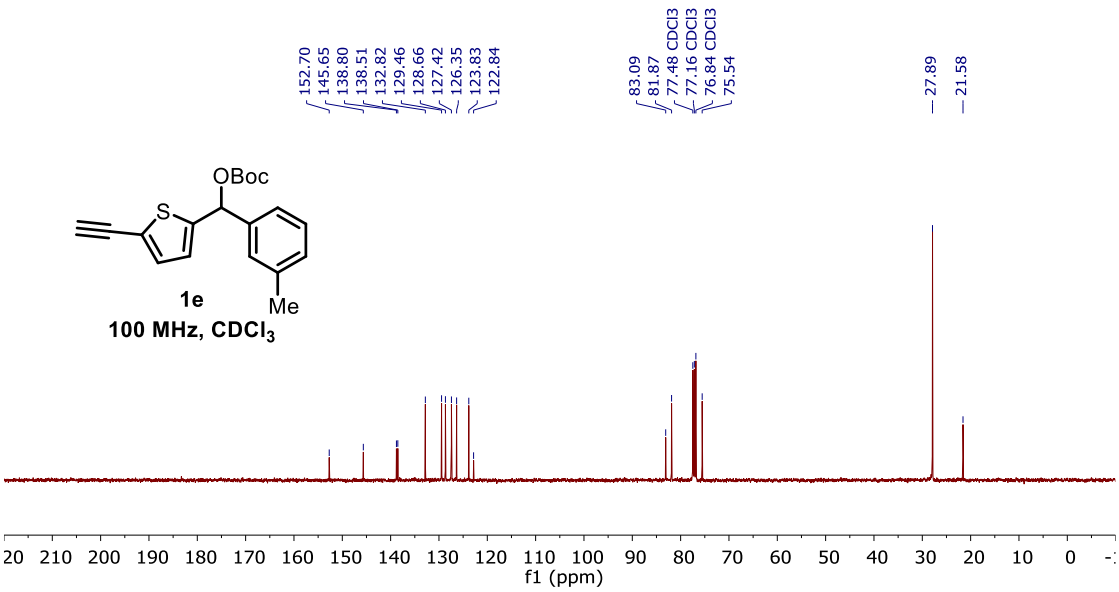
^{1}H NMR spectrum of **1d**



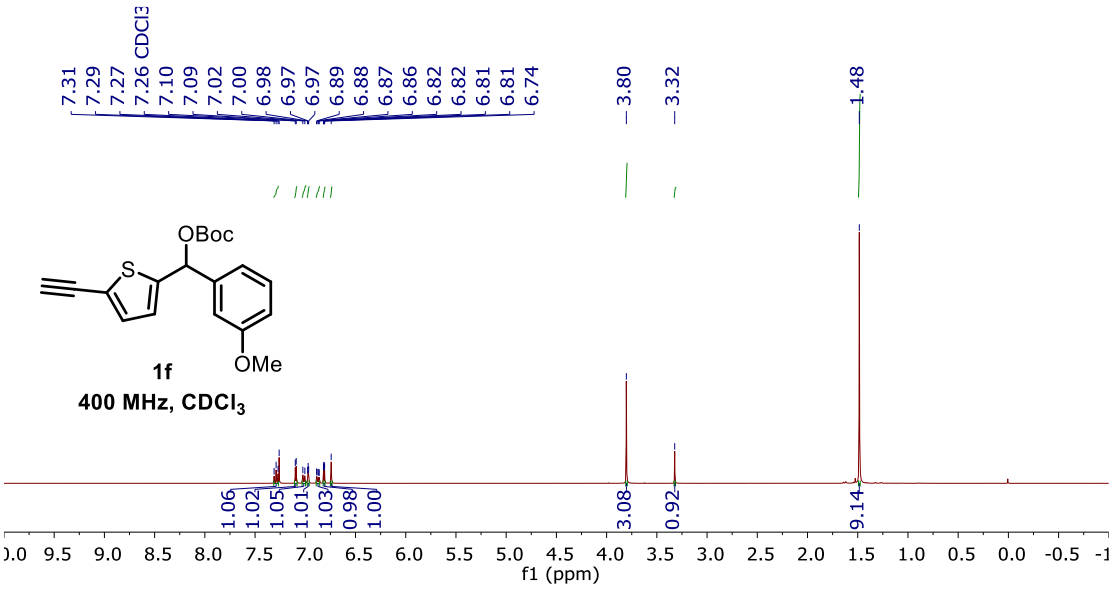
^{13}C NMR spectrum of **1d**



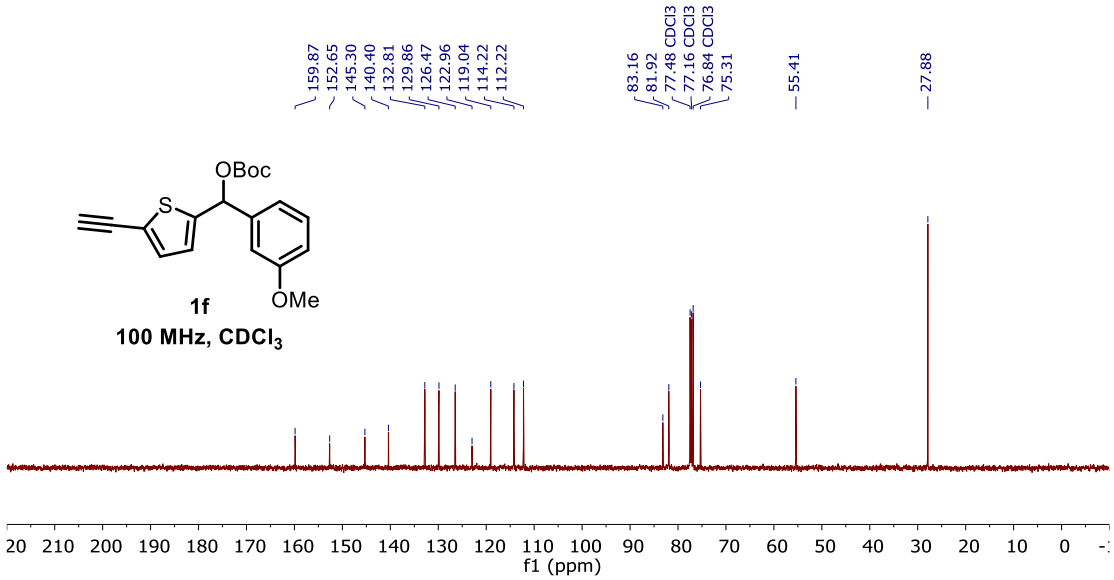
^{1}H NMR spectrum of **1e**



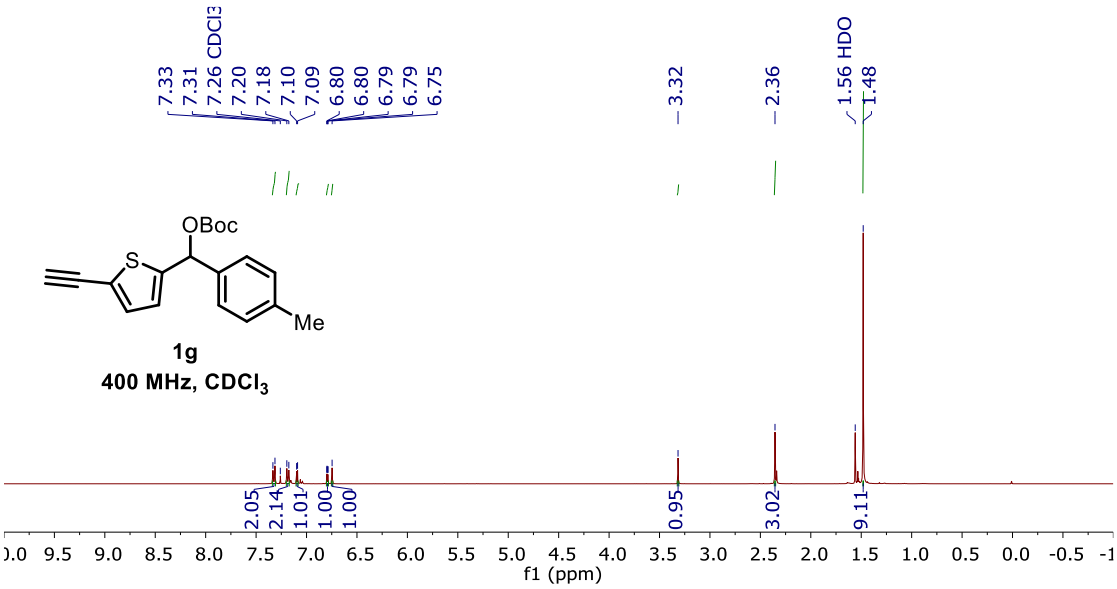
^{13}C NMR spectrum of **1e**



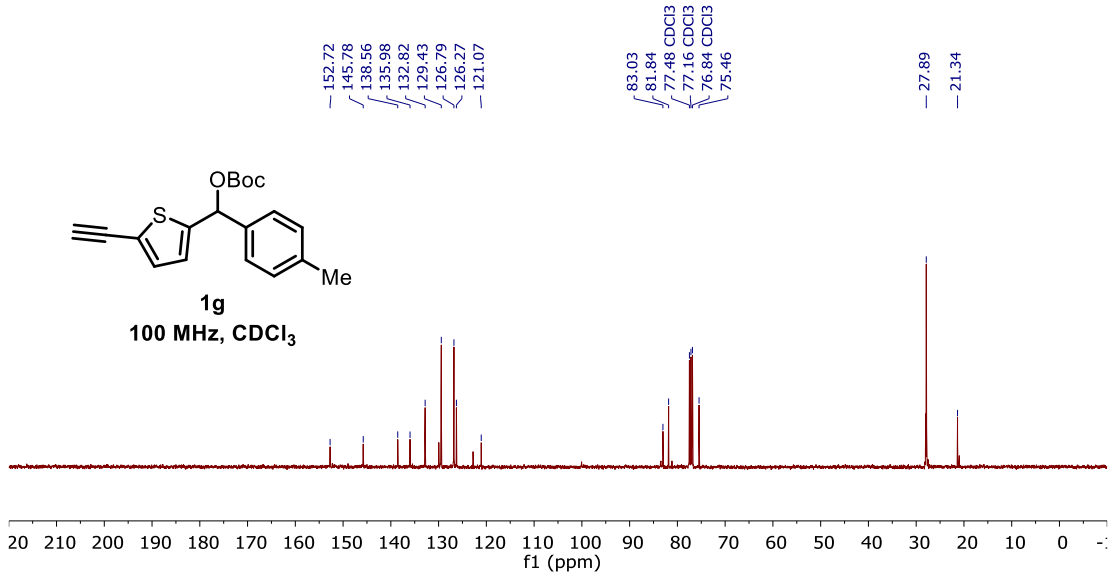
^{1}H NMR spectrum of **1f**



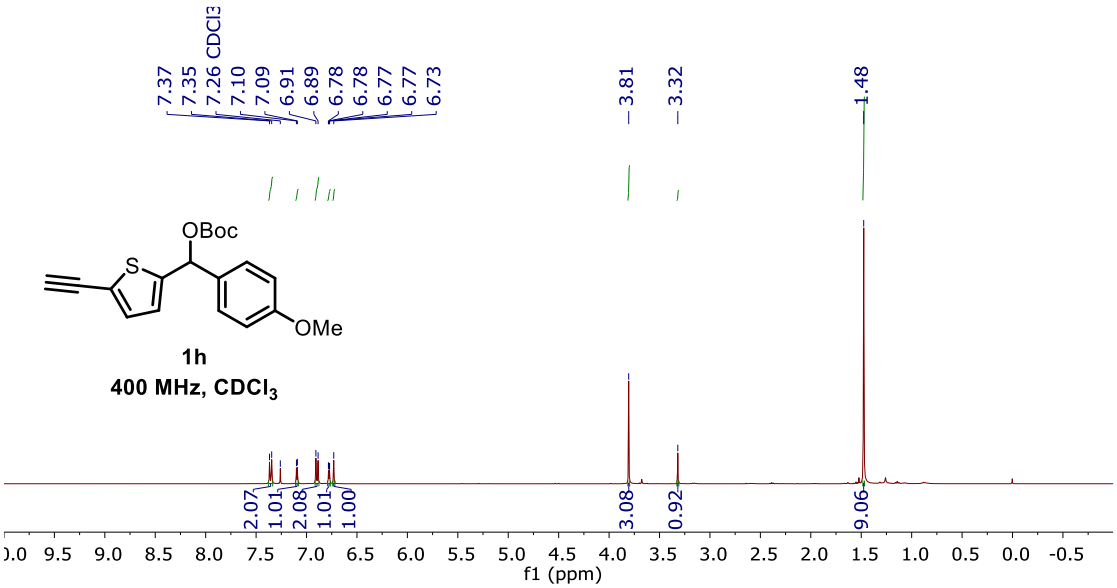
^{13}C NMR spectrum of **1f**



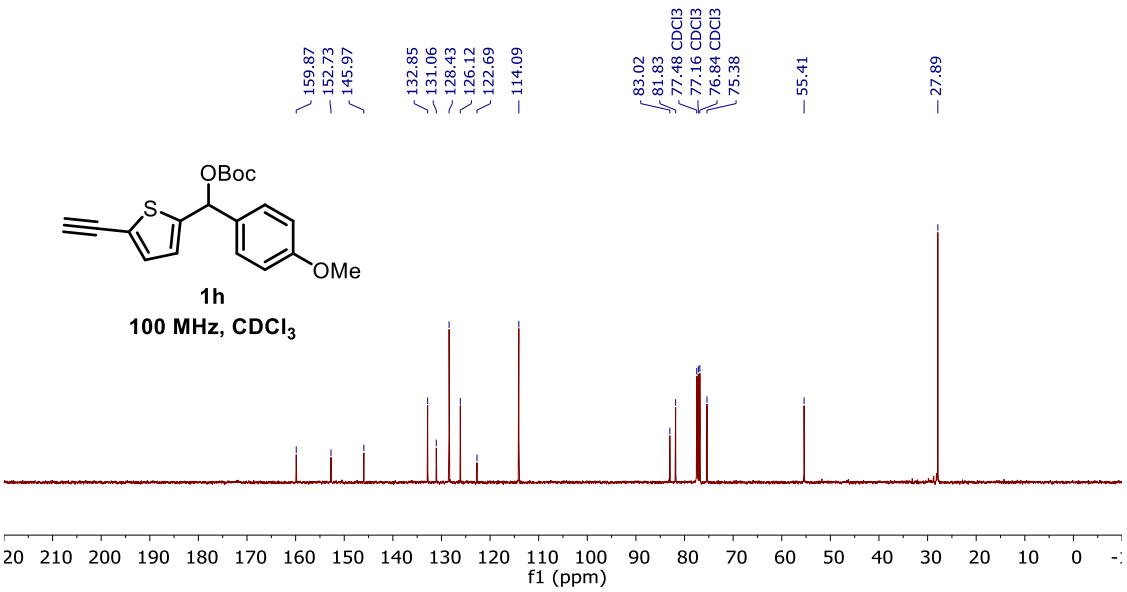
^{1}H NMR spectrum of **1g**



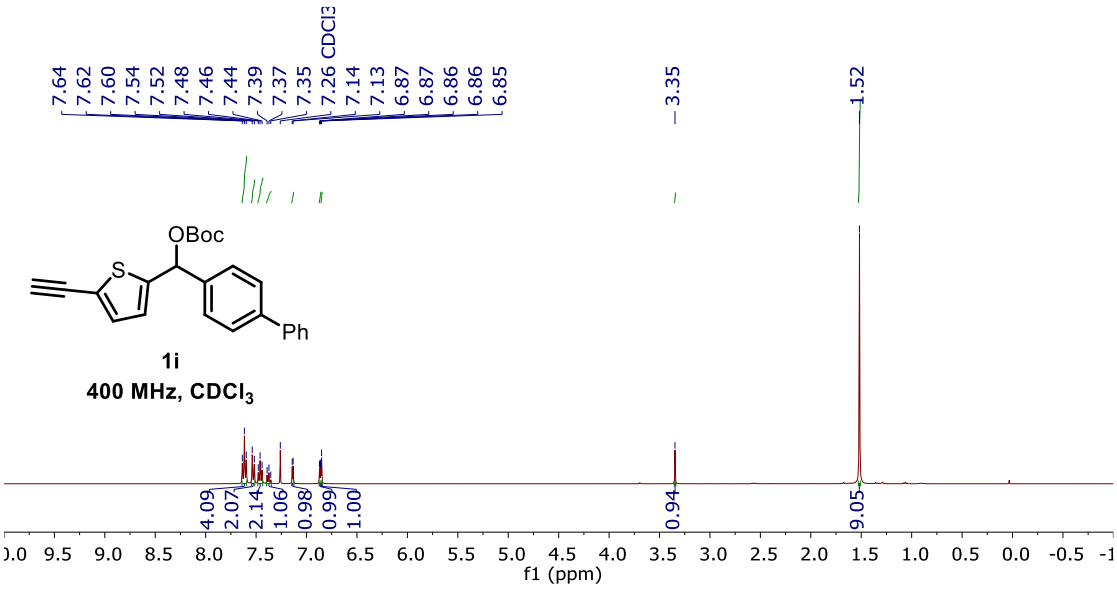
^{13}C NMR spectrum of **1g**



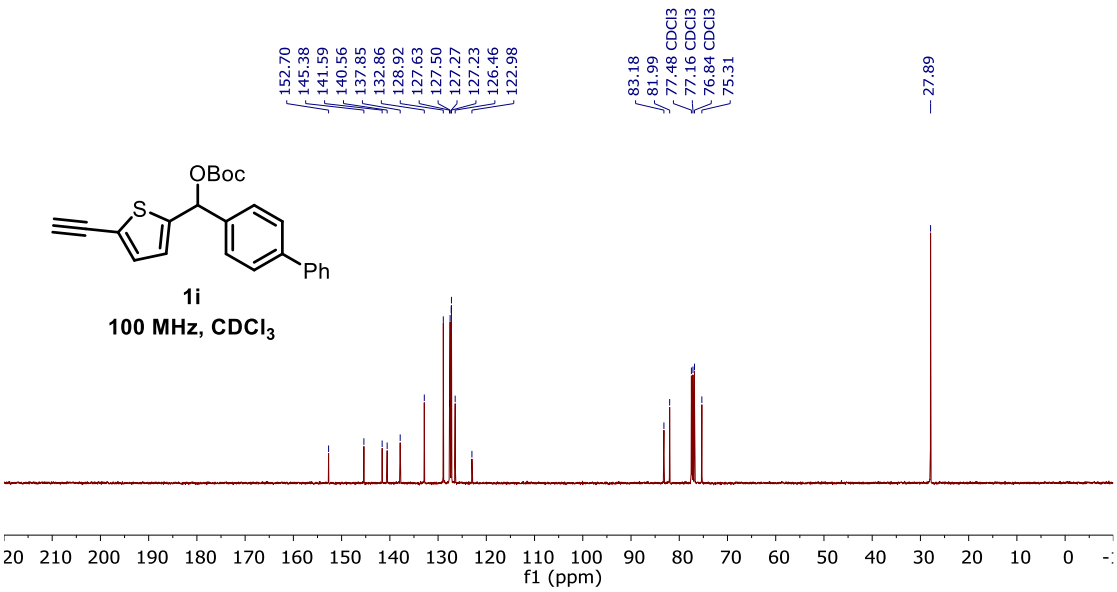
^{1}H NMR spectrum of **1h**



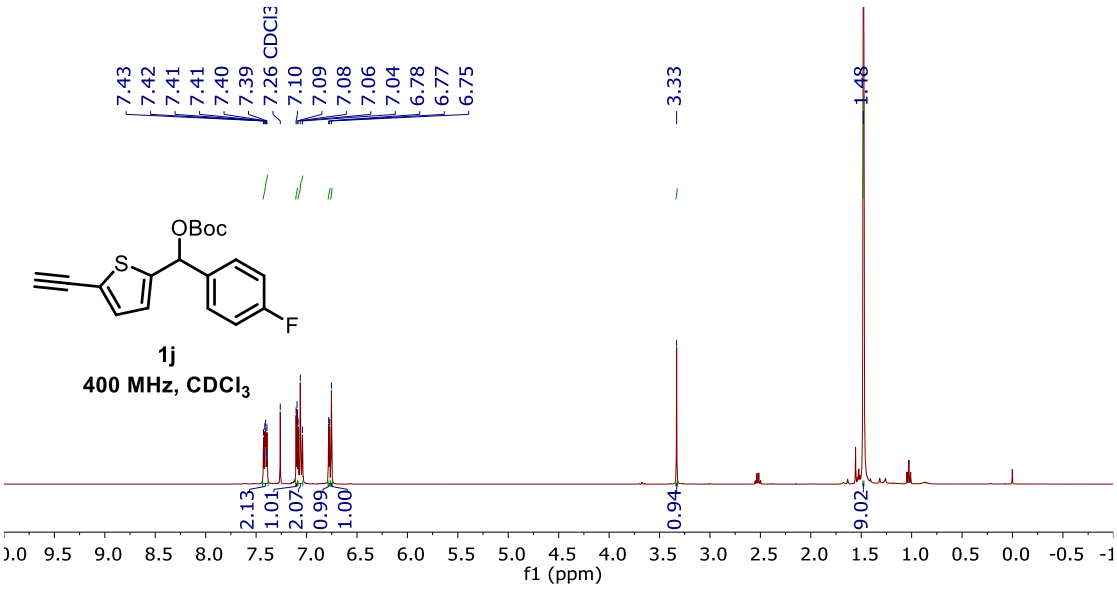
^{13}C NMR spectrum of **1h**



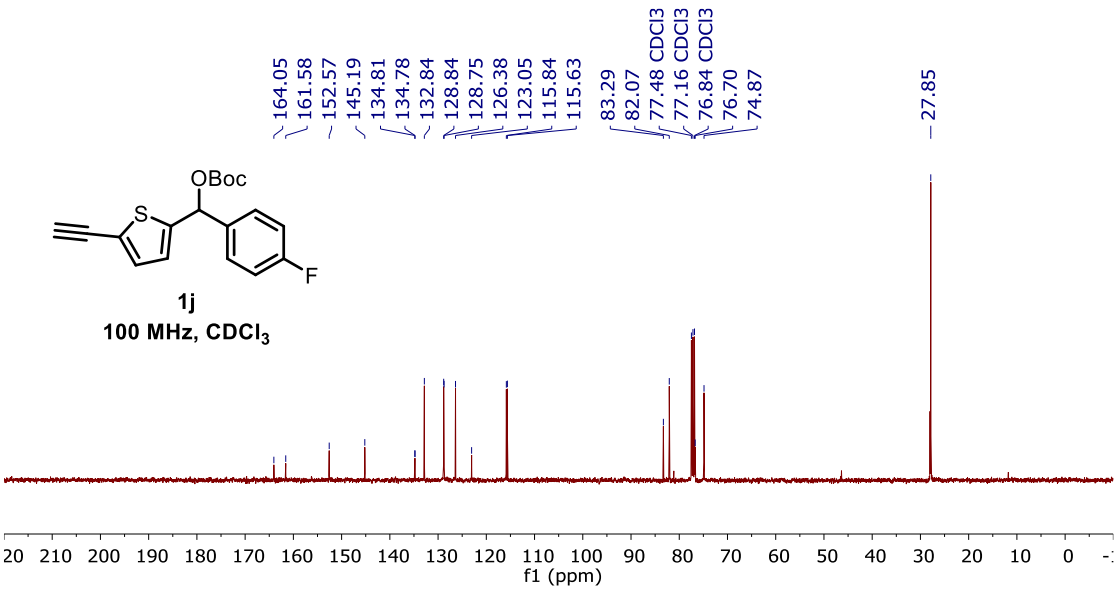
^{1}H NMR spectrum of **1i**



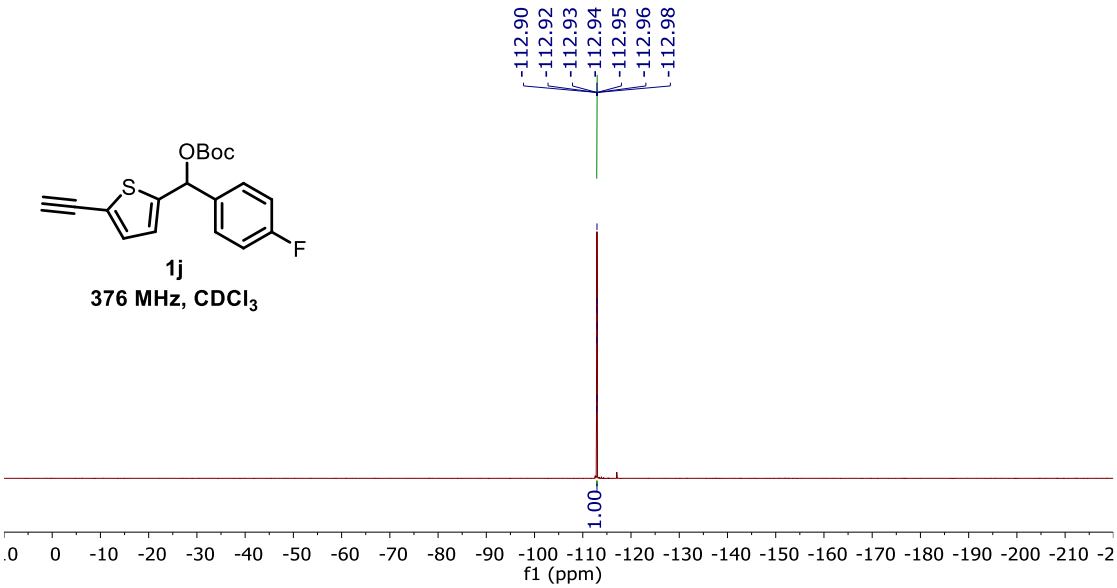
^{13}C NMR spectrum of **1i**



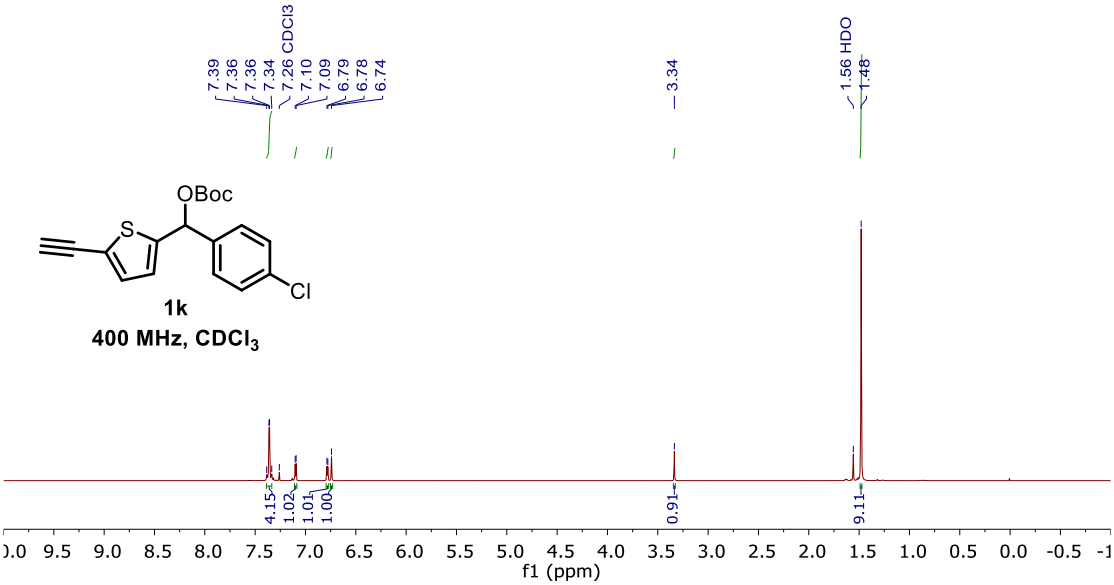
^{1}H NMR spectrum of **1j**



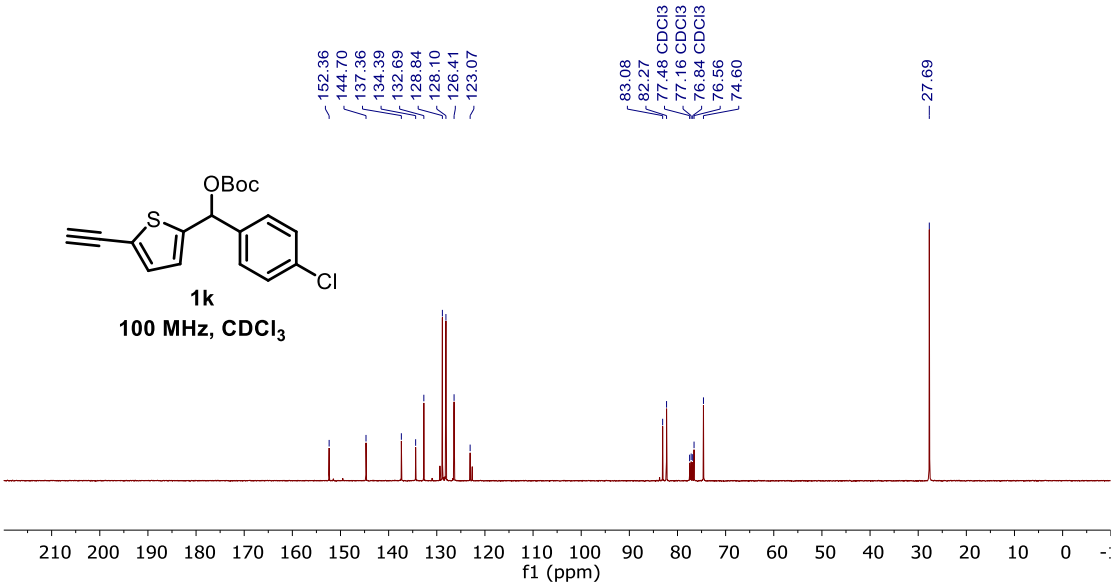
^{13}C NMR spectrum of **1j**



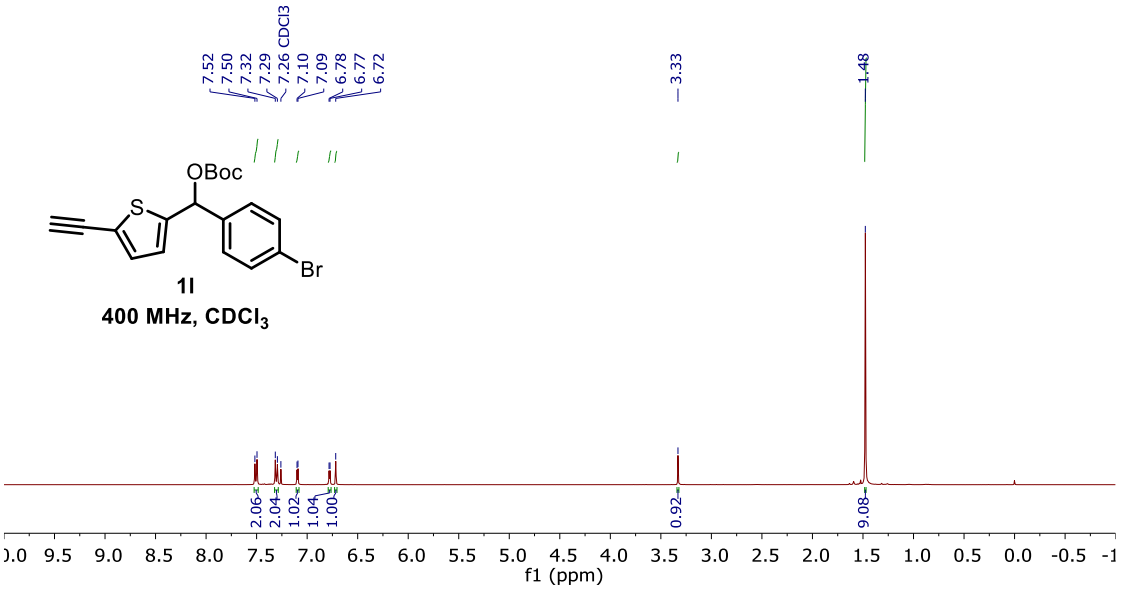
^{19}F NMR spectrum of **1j**



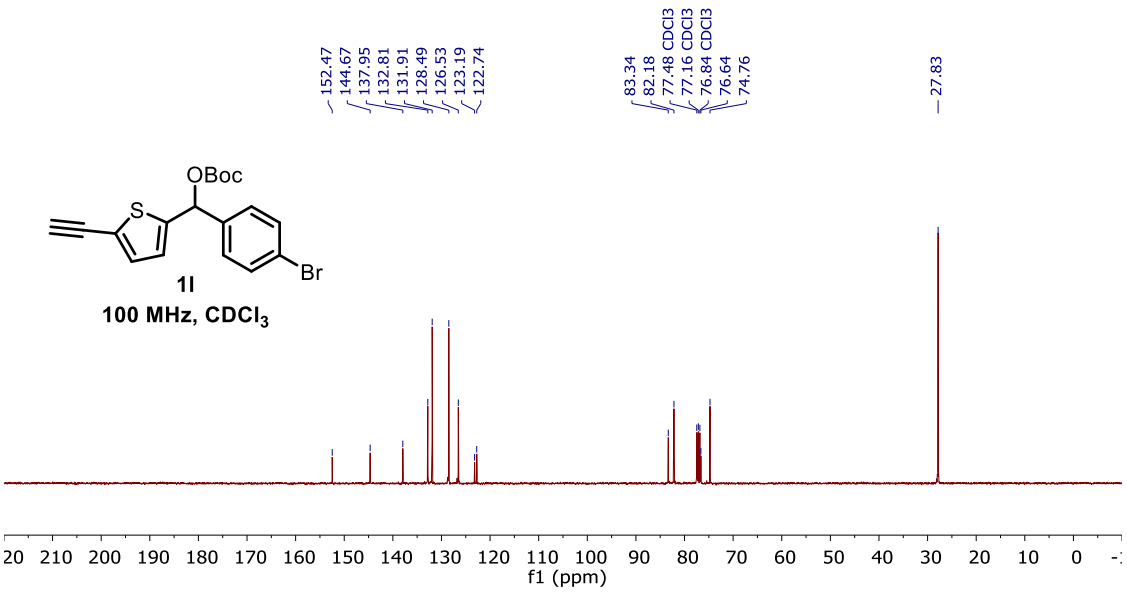
^{1}H NMR spectrum of **1k**



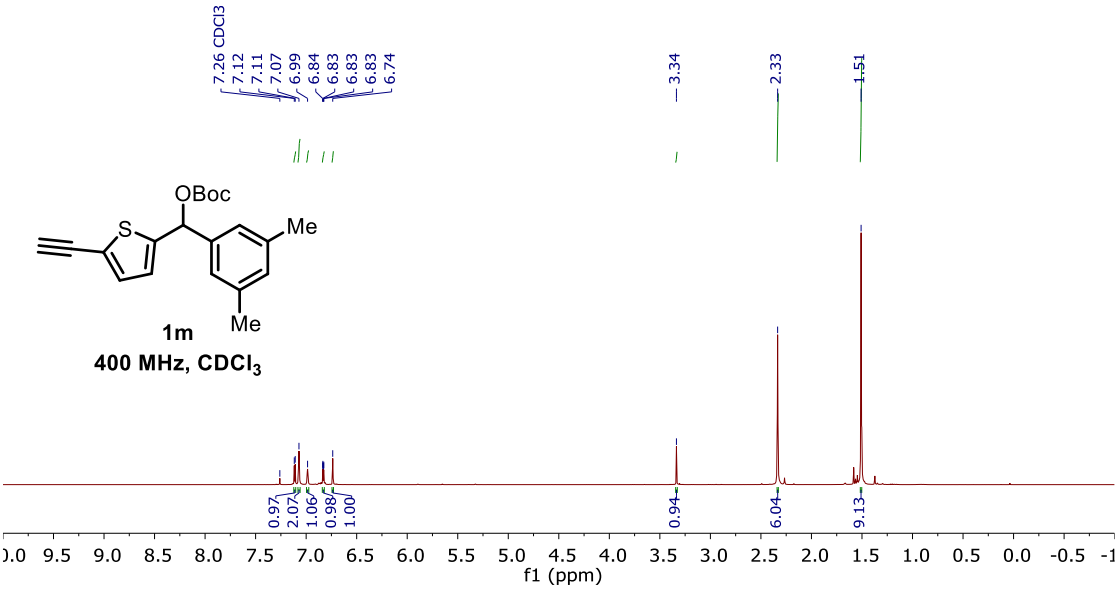
^{13}C NMR spectrum of **1k**



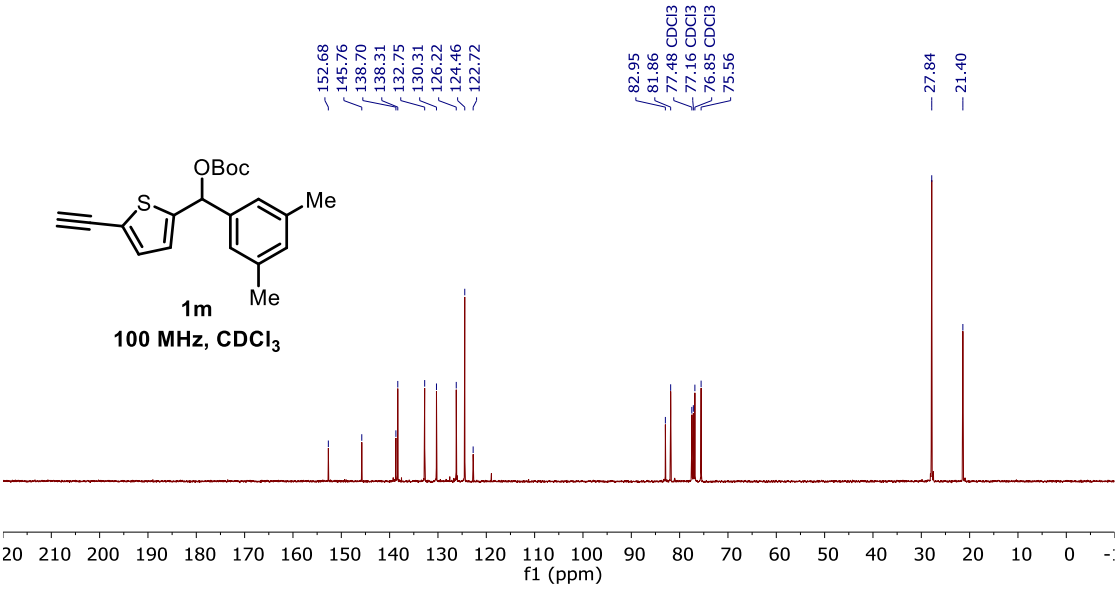
^{1}H NMR spectrum of **1l**



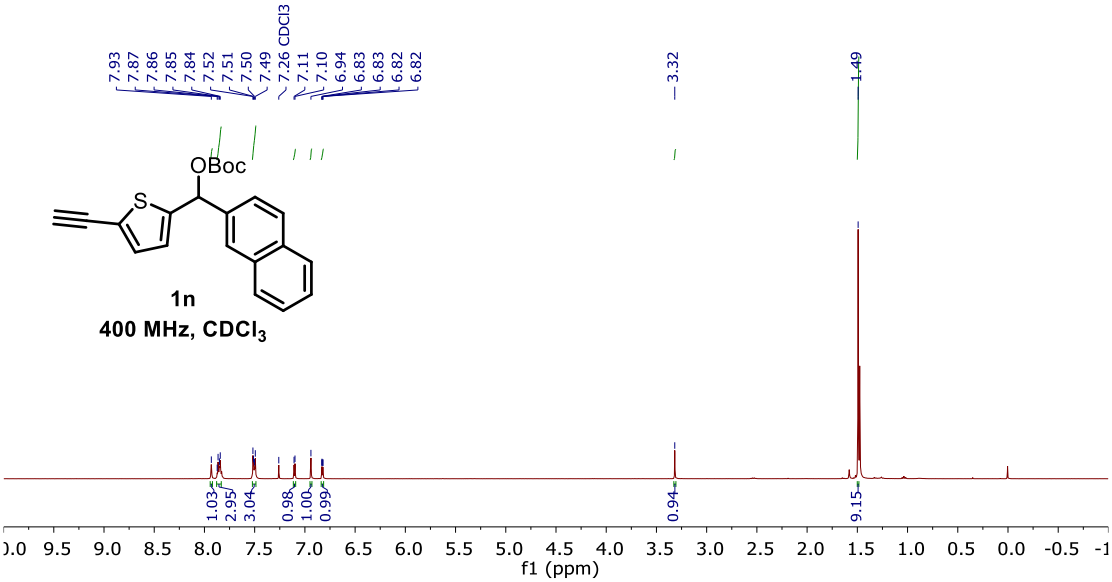
^{13}C NMR spectrum of **1l**



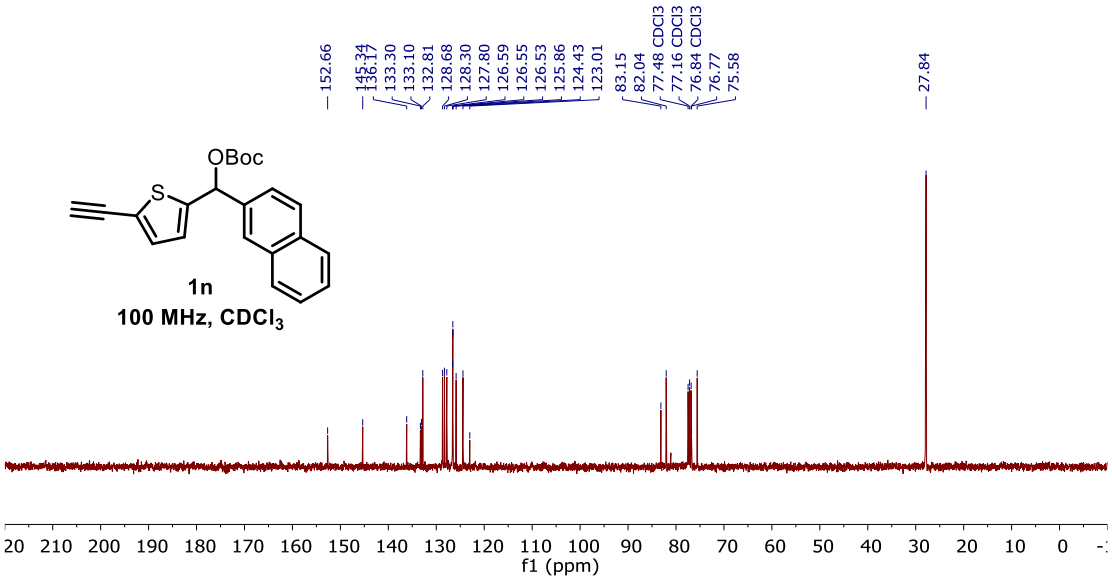
^{1}H NMR spectrum of **1m**



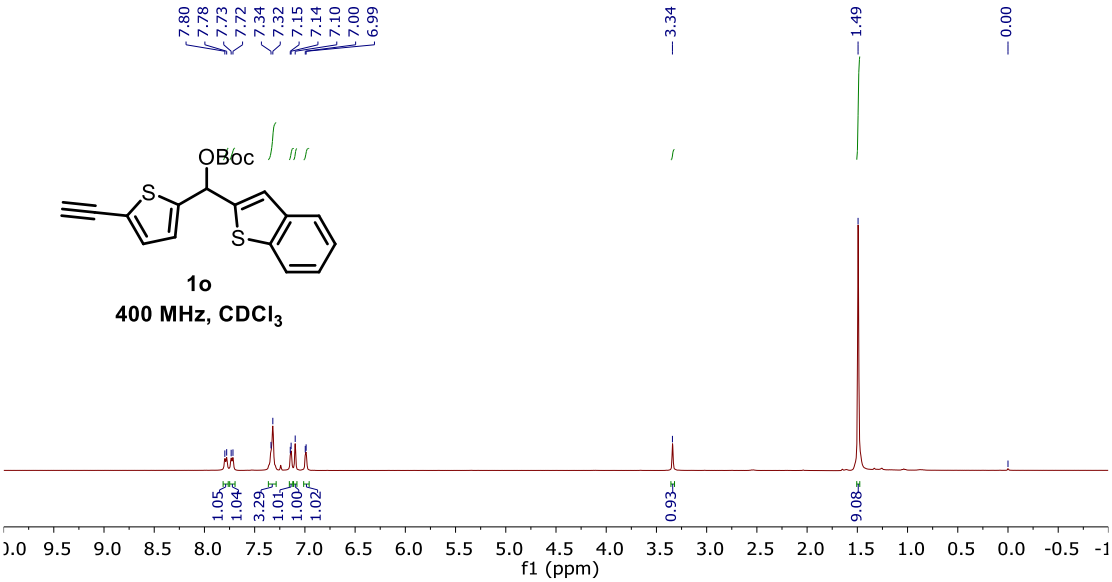
^{13}C NMR spectrum of **1m**



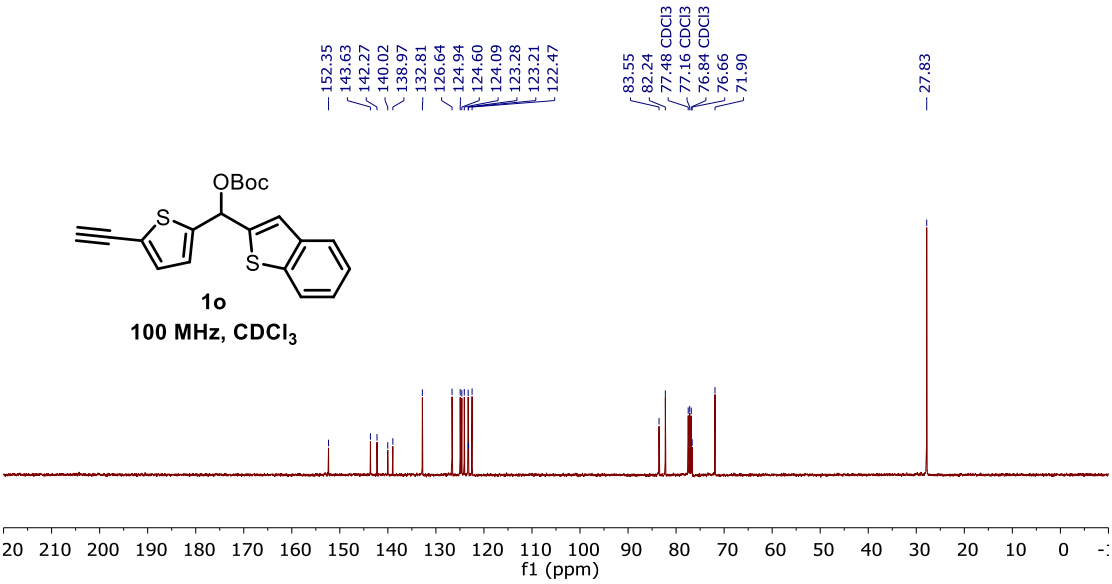
^{1}H NMR spectrum of **1n**



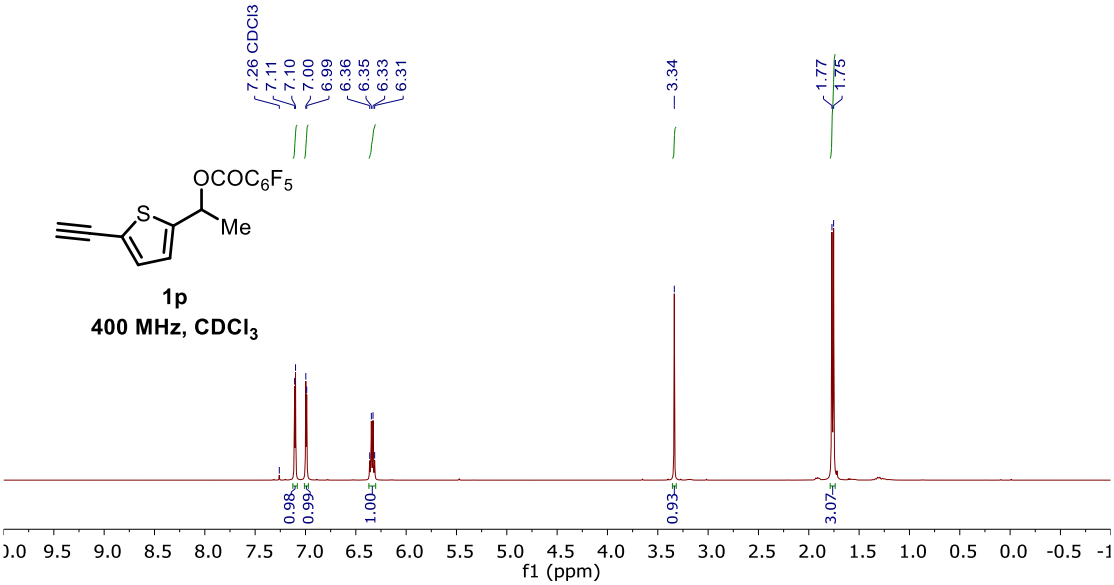
^{13}C NMR spectrum of **1n**



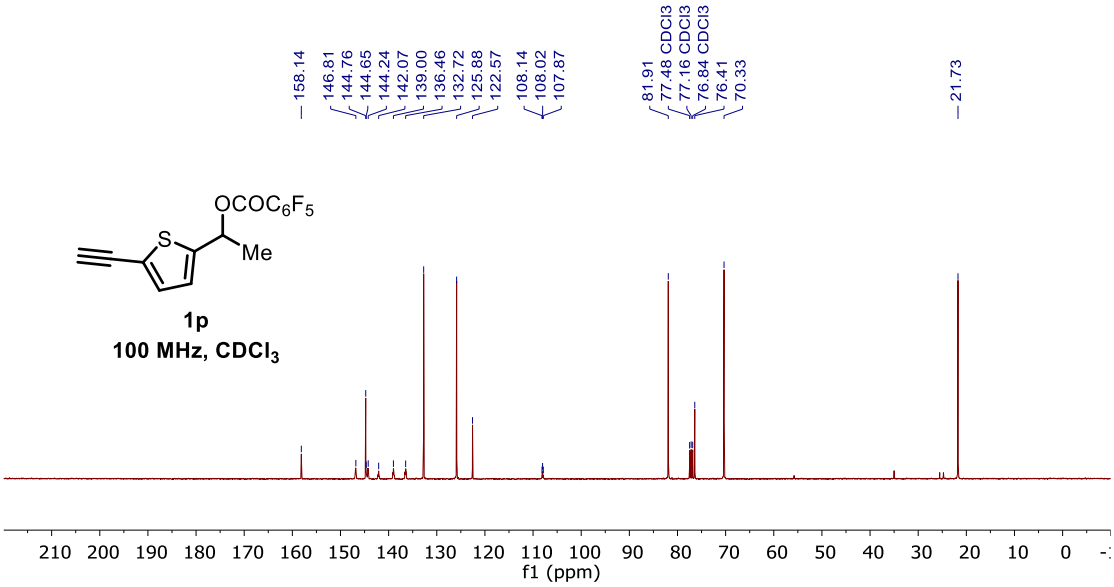
^{1}H NMR spectrum of **1o**



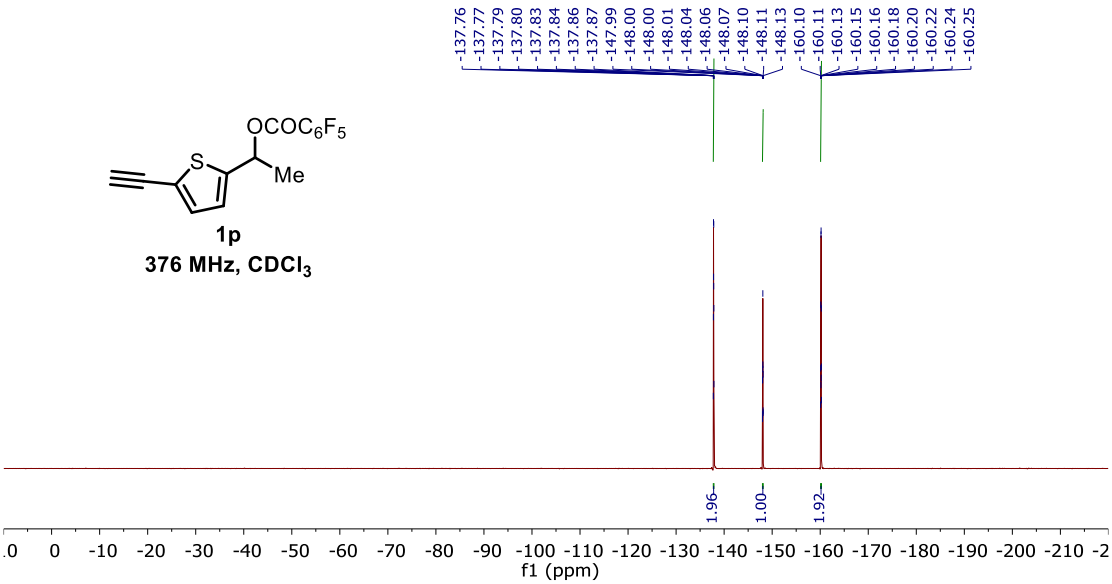
^{13}C NMR spectrum of **1o**



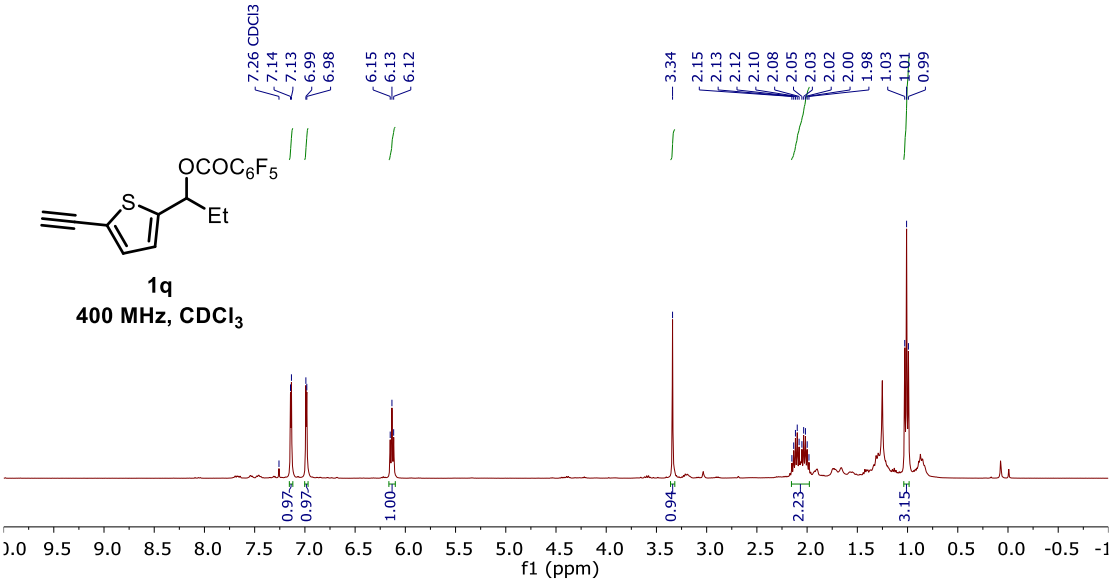
^{1}H NMR spectrum of **1p**



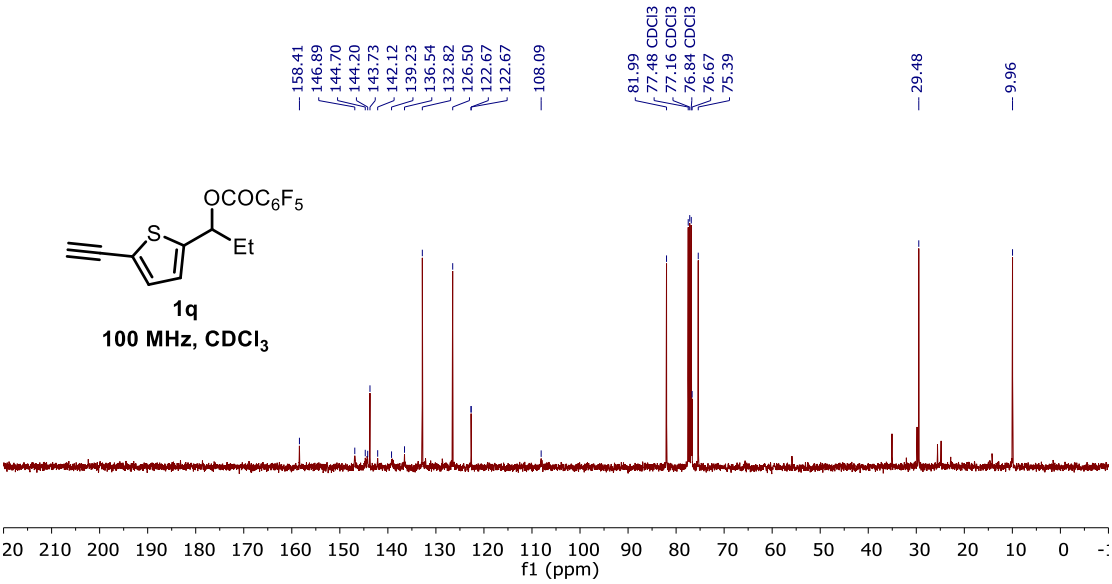
^{13}C NMR spectrum of **1p**



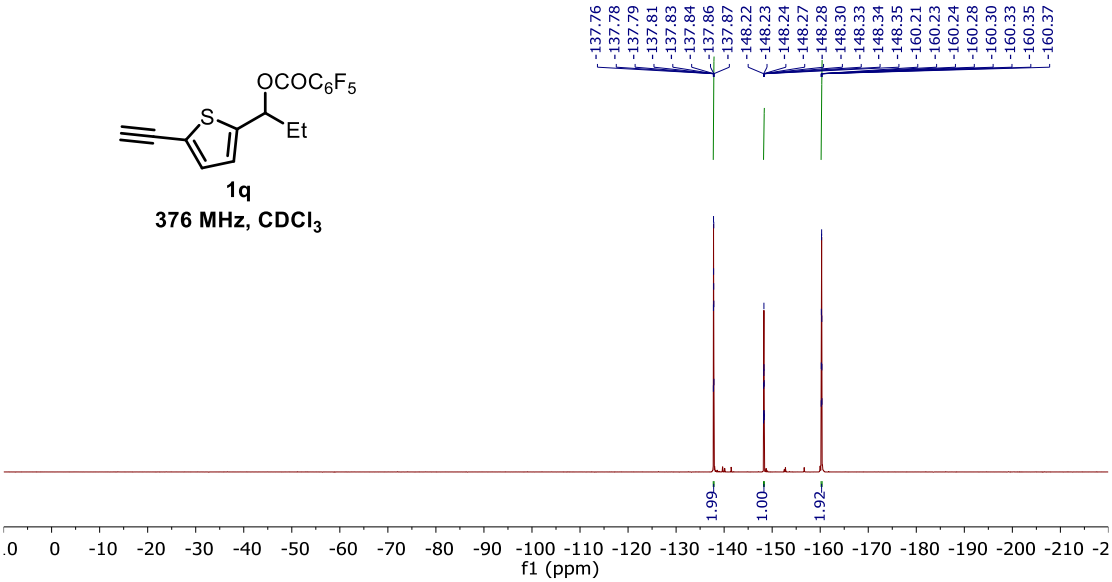
^{19}F NMR spectrum of **1p**



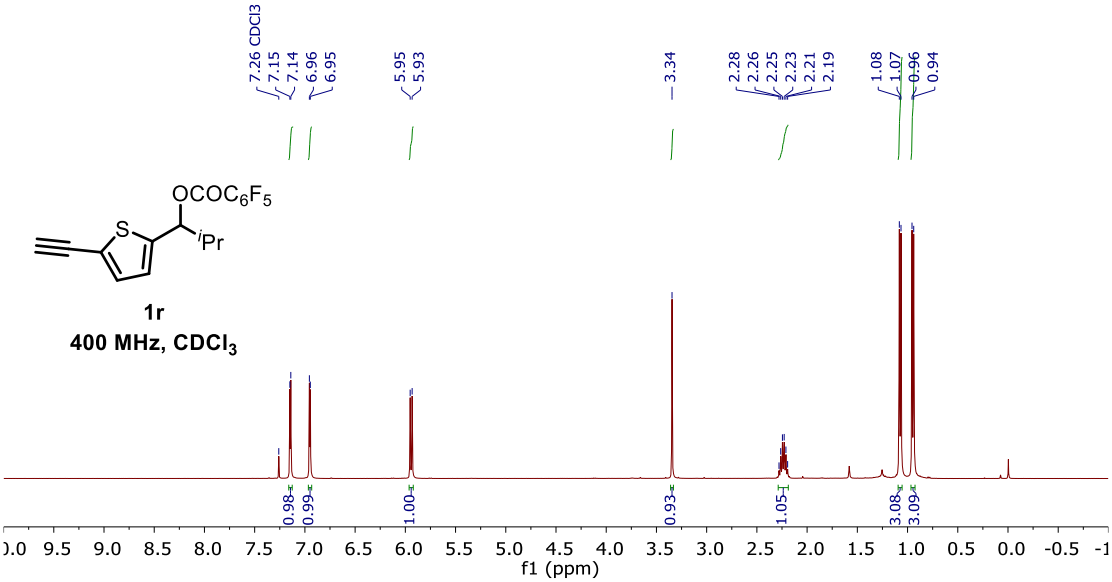
^{1}H NMR spectrum of **1q**



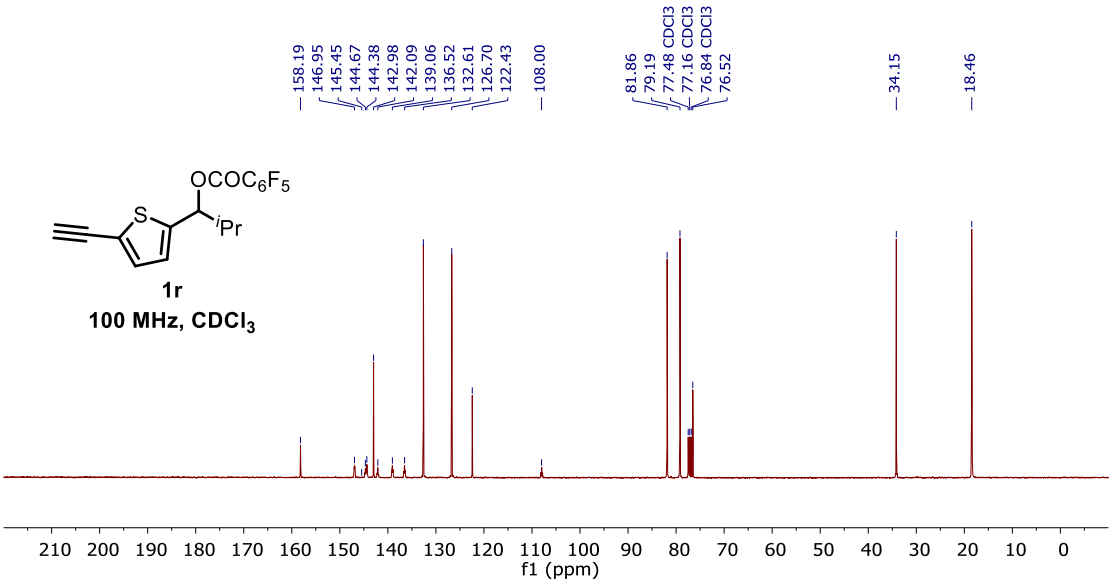
^{13}C NMR spectrum of **1q**



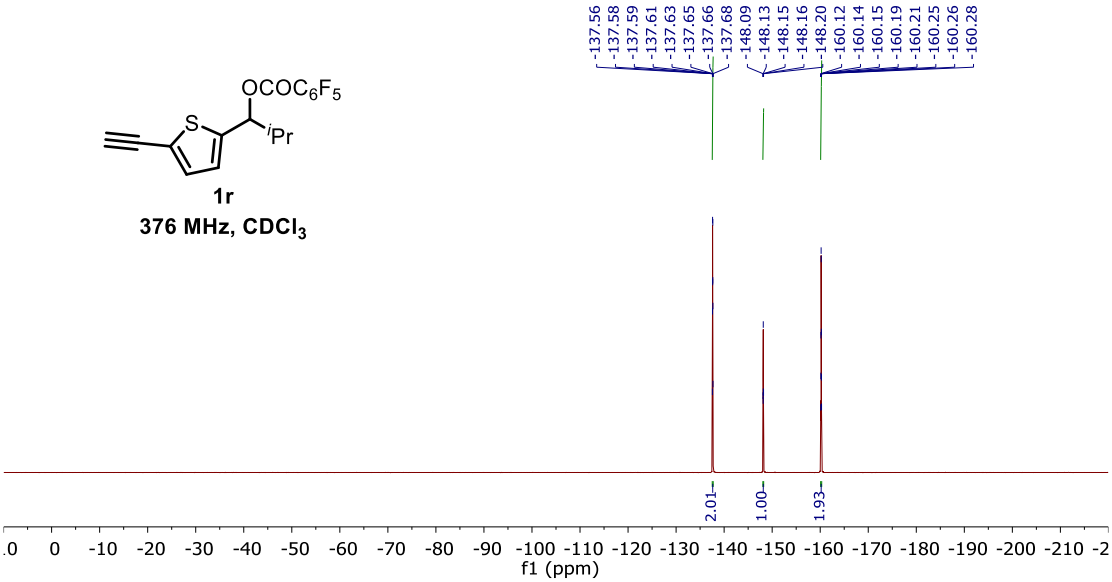
^{19}F NMR spectrum of **1q**



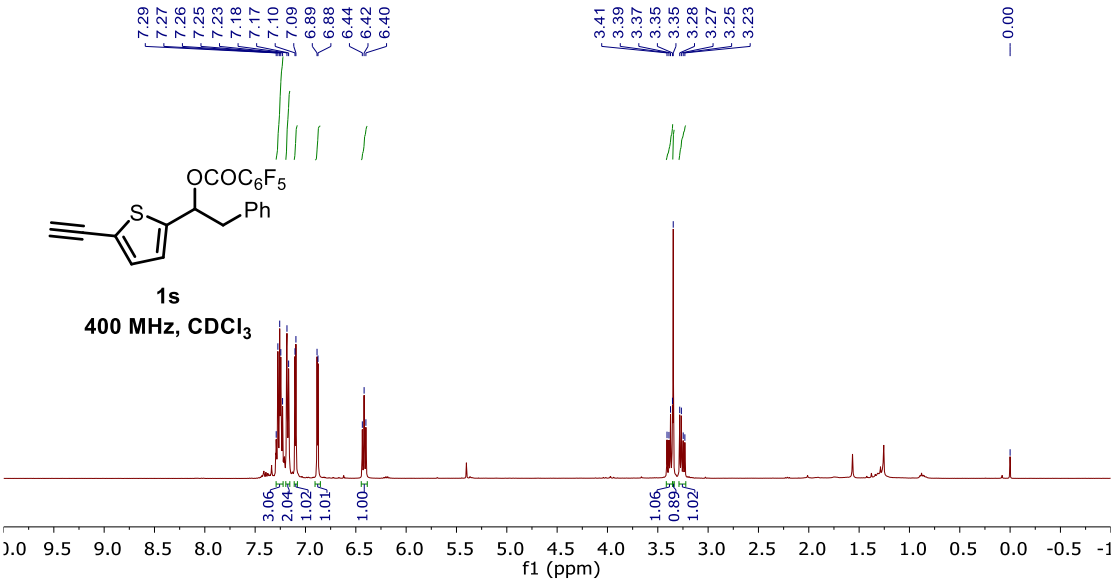
^{1}H NMR spectrum of **1r**



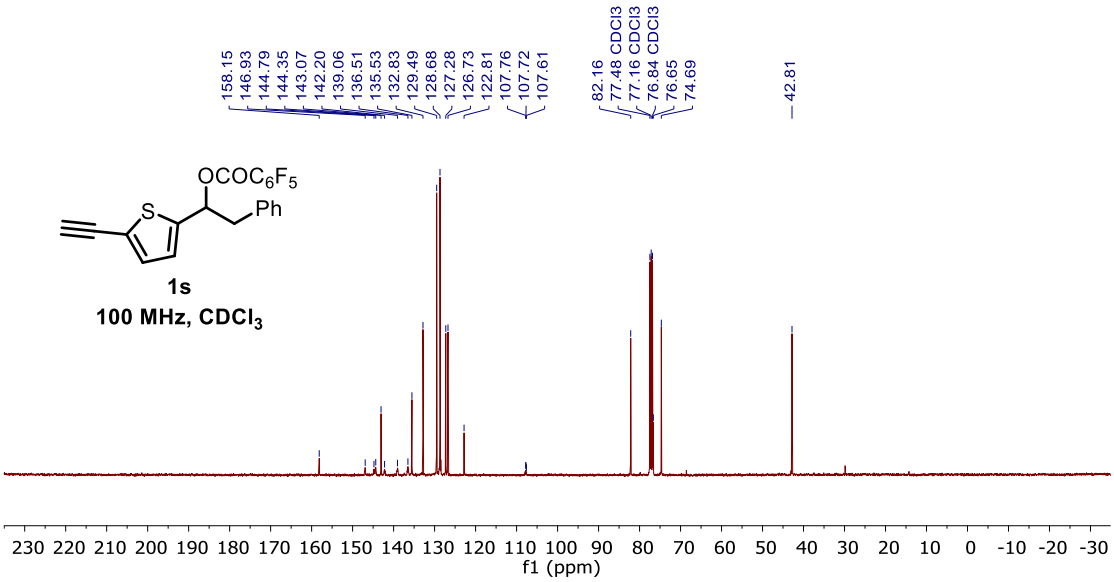
^{13}C NMR spectrum of **1r**



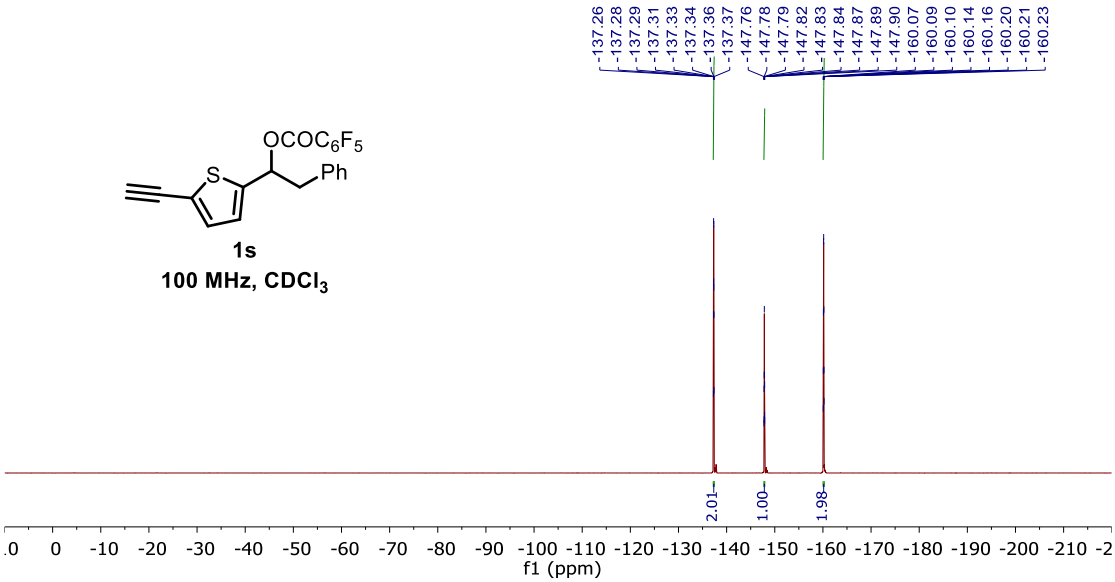
^{19}F NMR spectrum of **1r**



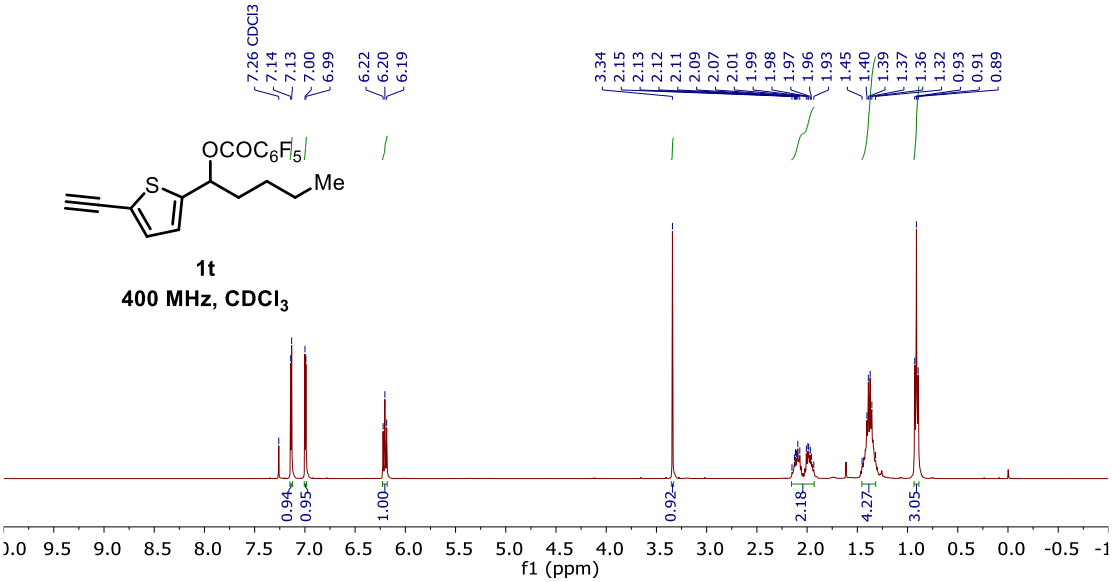
^{1}H NMR spectrum of **1s**



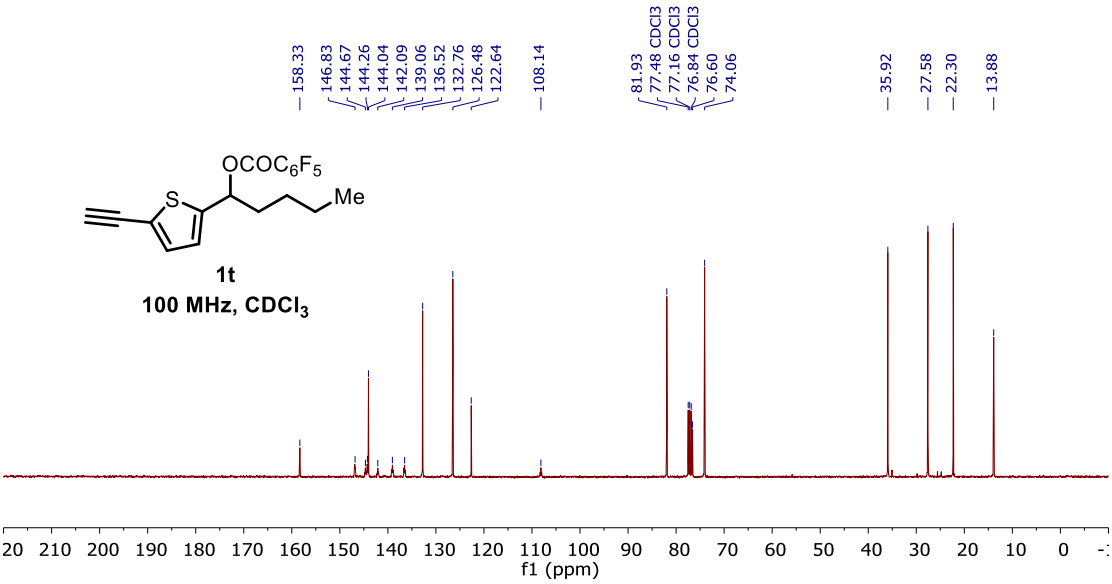
^{13}C NMR spectrum of **1s**



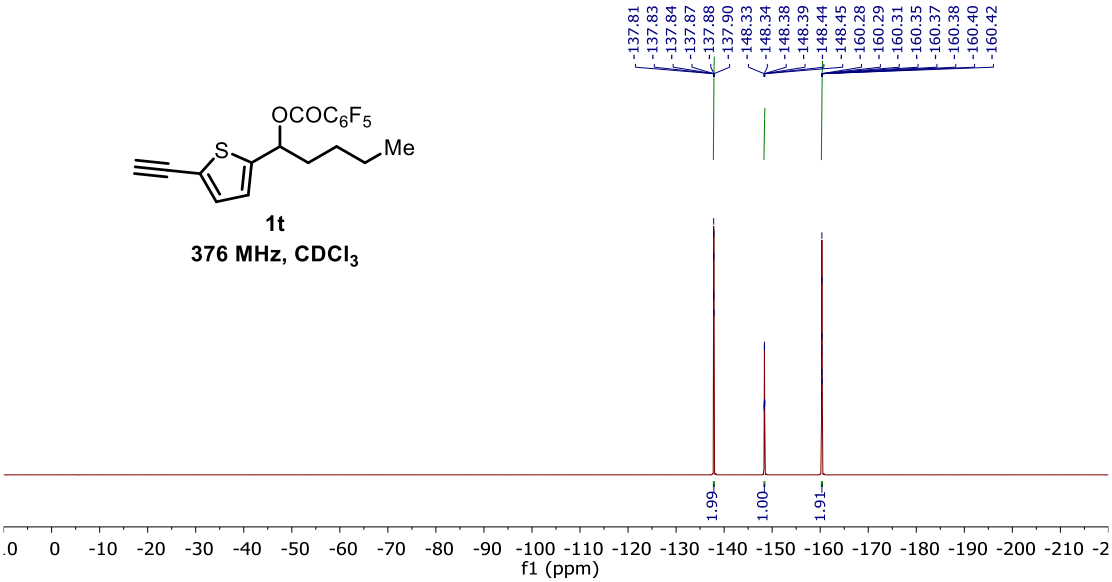
^{19}F NMR spectrum of **1s**



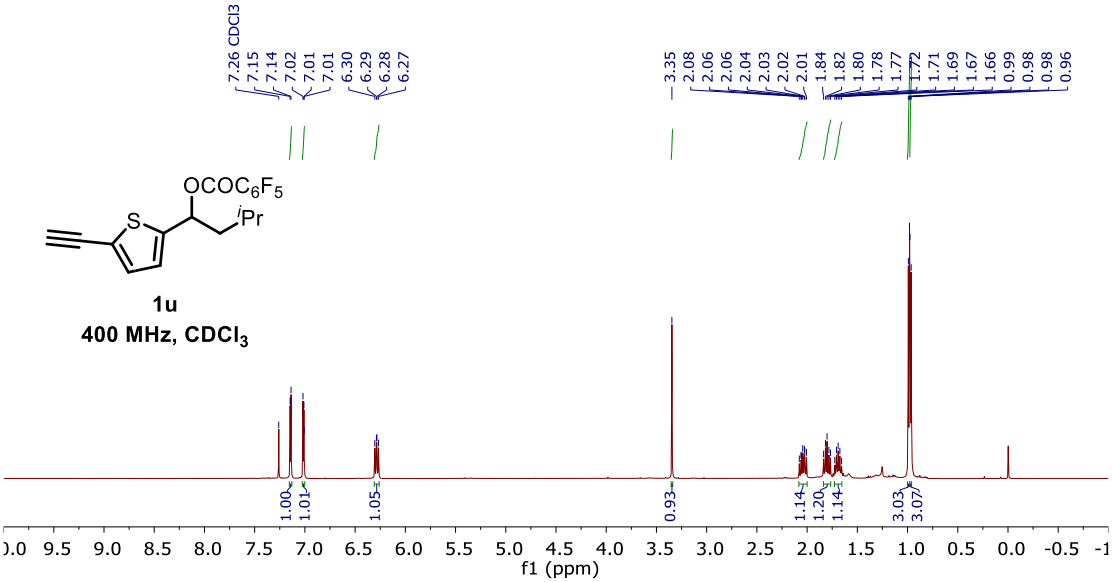
^{1}H NMR spectrum of **1t**



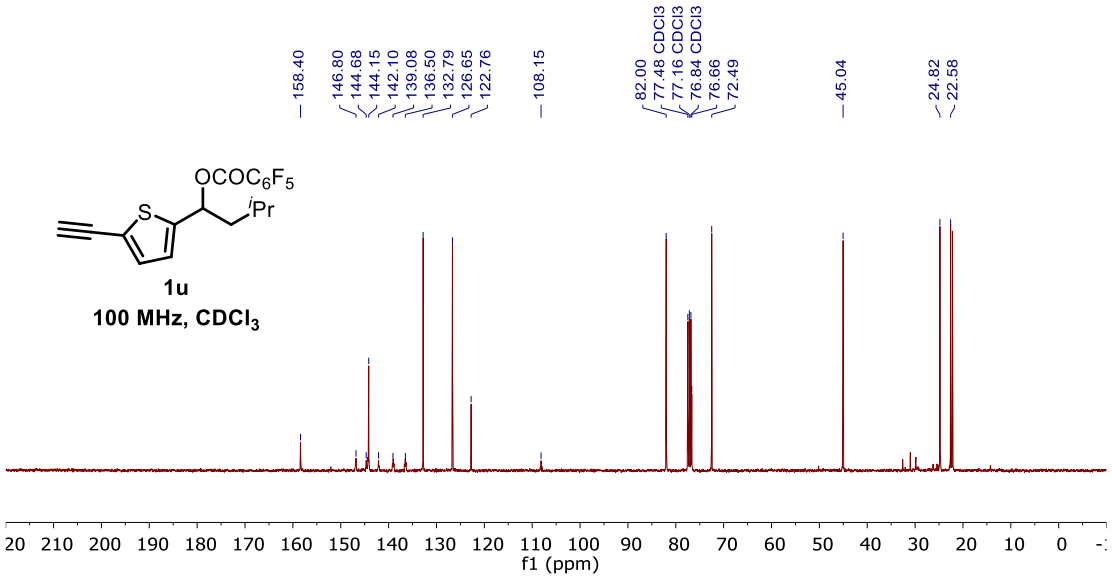
^{13}C NMR spectrum of **1t**



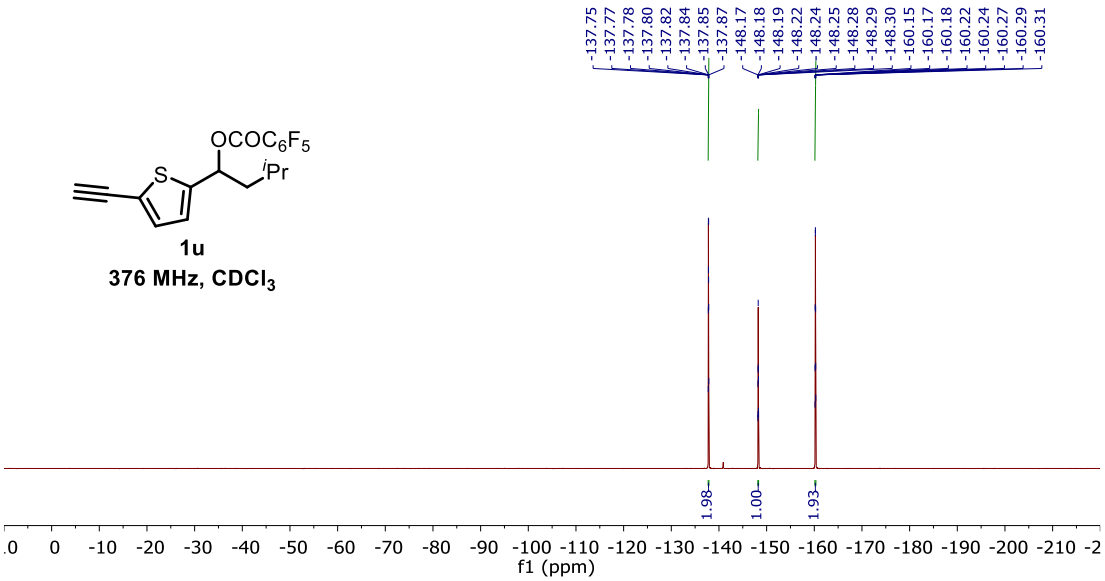
^{19}F NMR spectrum of **1t**



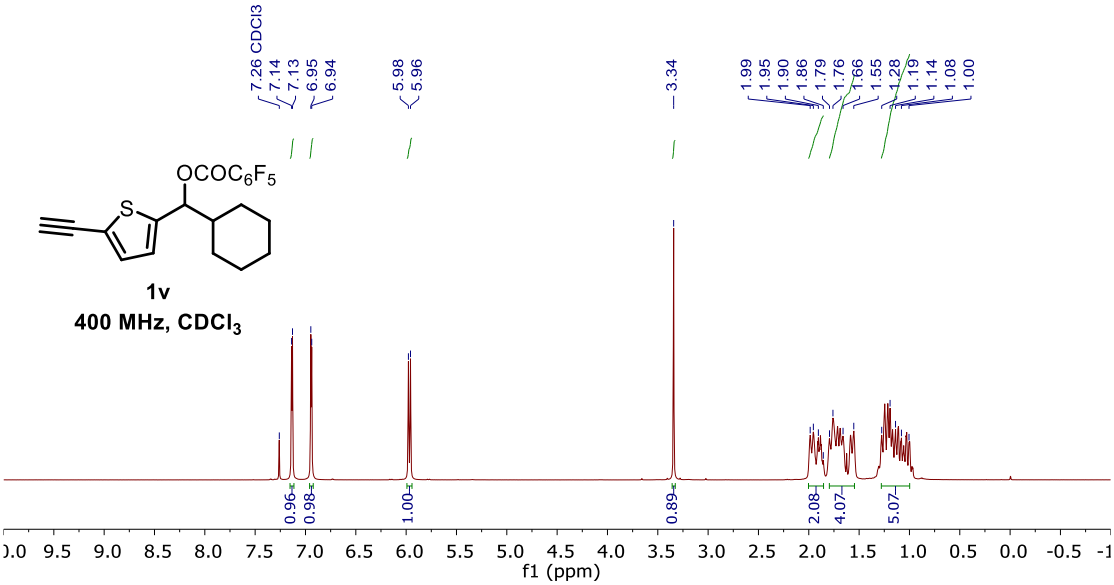
^{1}H NMR spectrum of **1u**



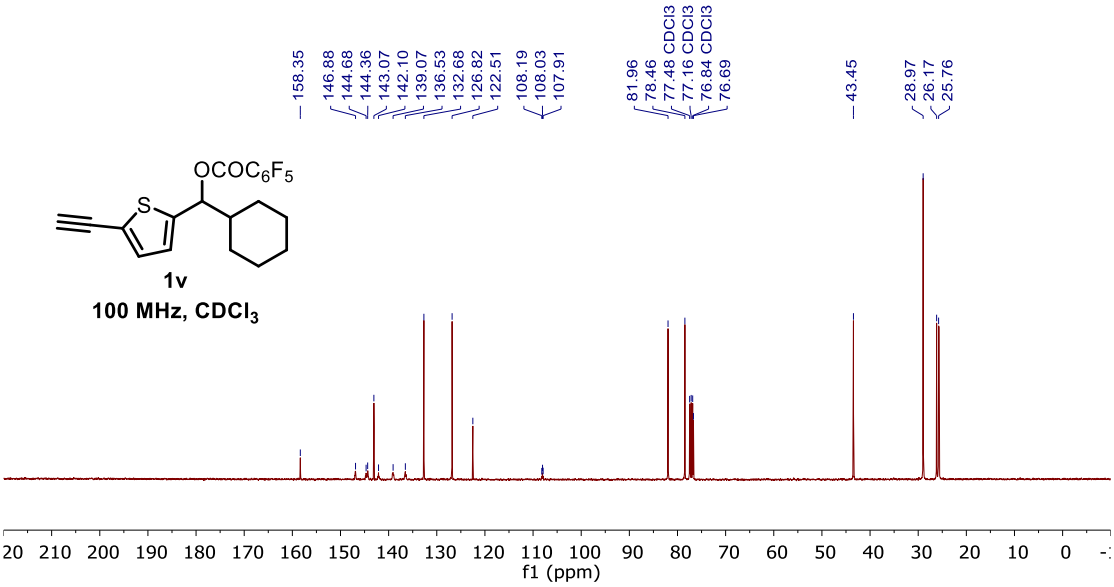
^{13}C NMR spectrum of **1u**



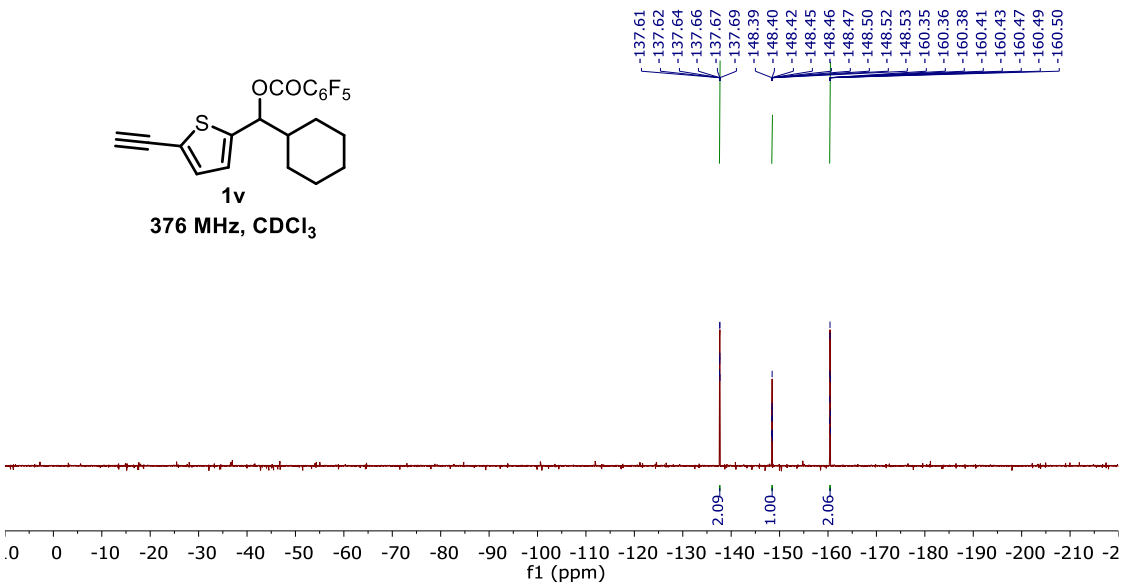
^{19}F NMR spectrum of **1u**



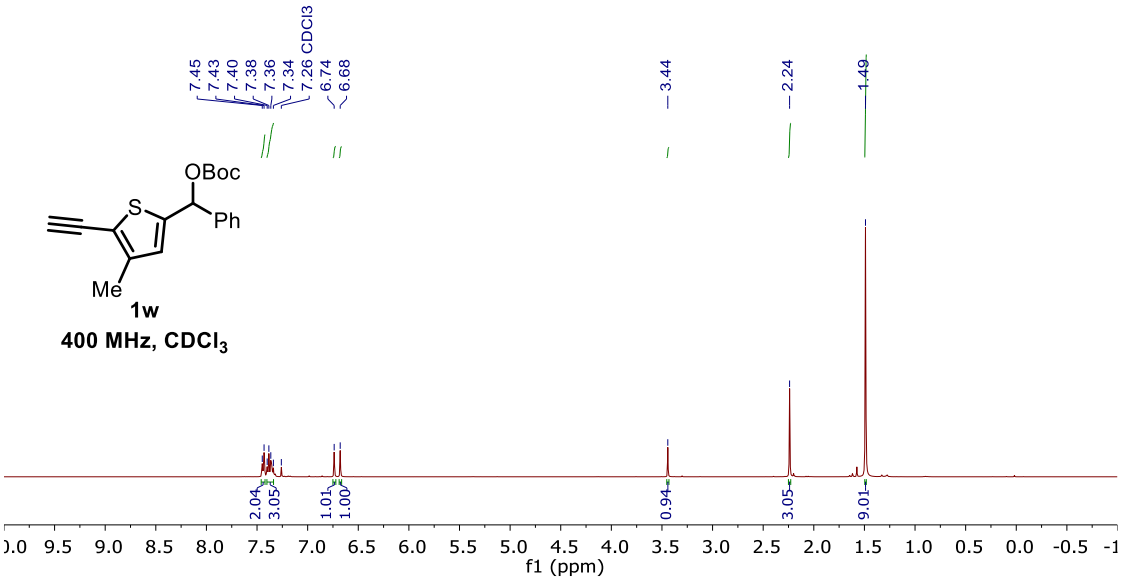
^{1}H NMR spectrum of **1v**



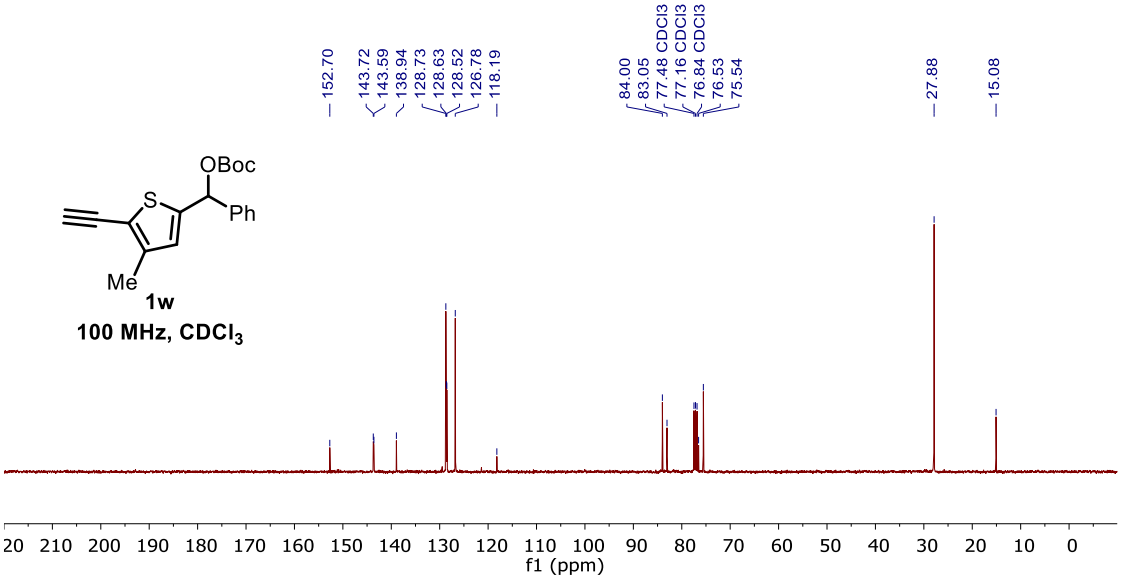
^{13}C NMR spectrum of **1v**



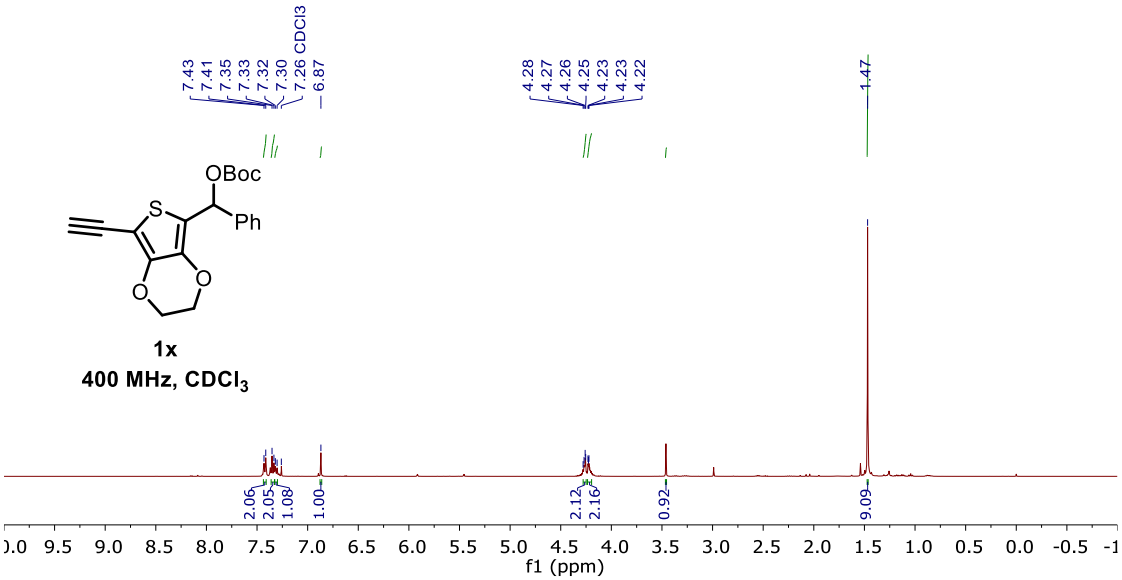
^{19}F NMR spectrum of **1v**



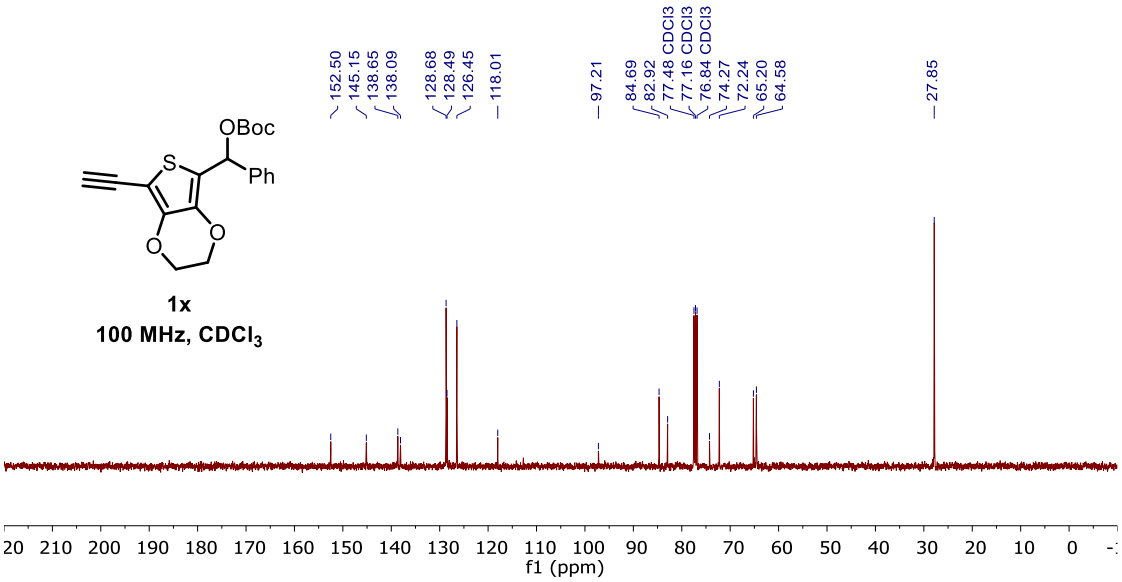
^{1}H NMR spectrum of **1w**



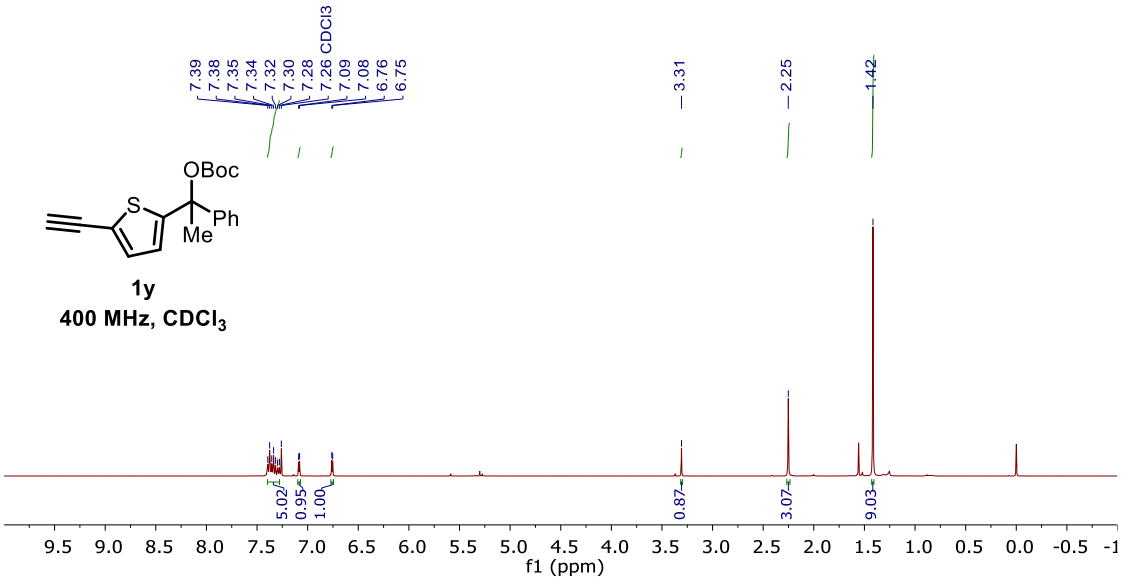
^{13}C NMR spectrum of **1w**



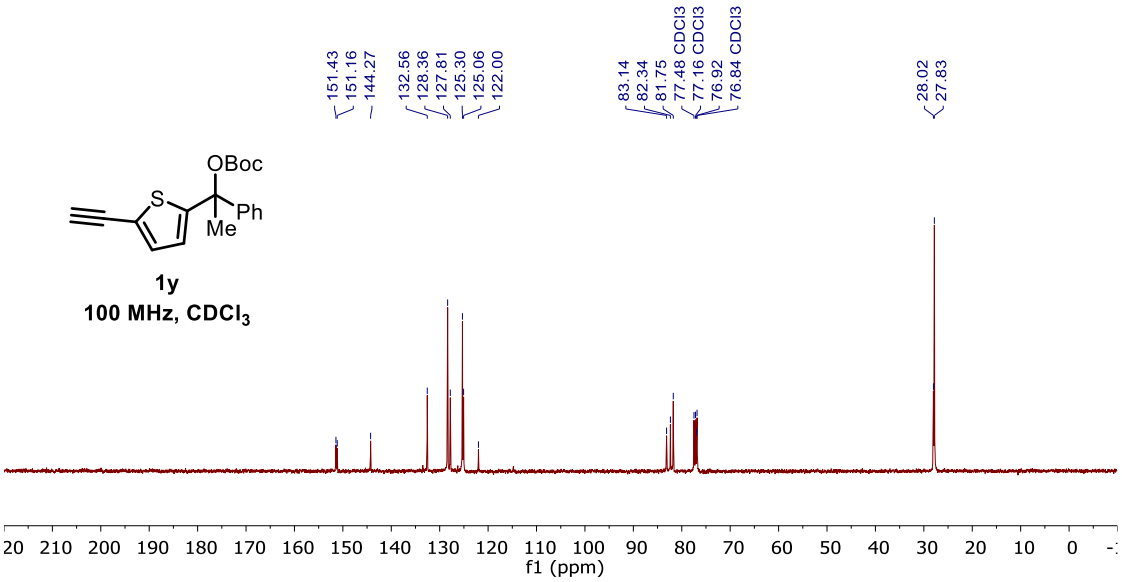
^{1}H NMR spectrum of **1x**



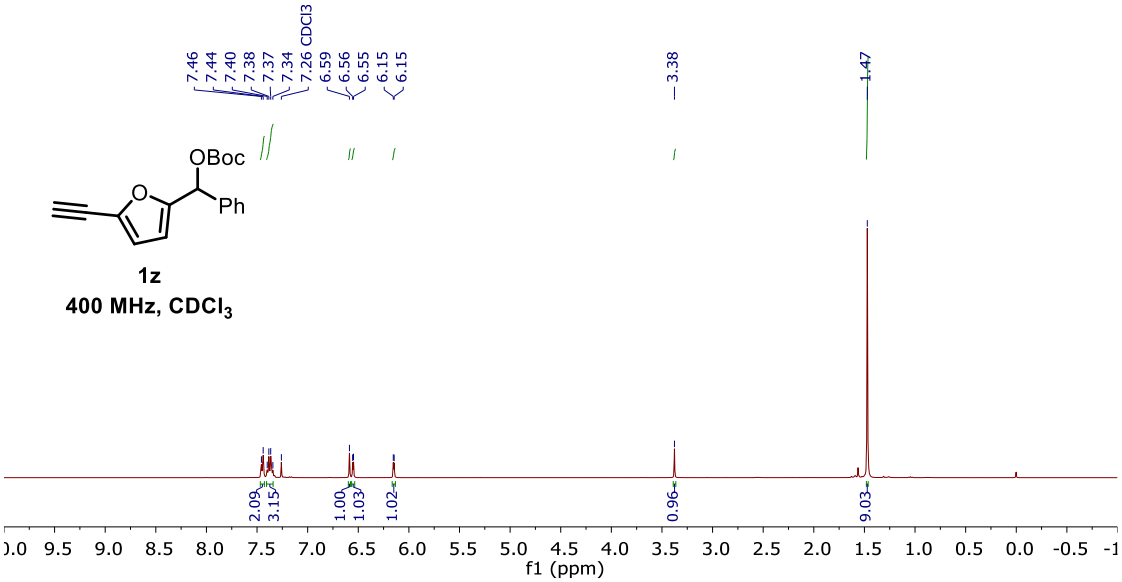
^{13}C NMR spectrum of **1x**



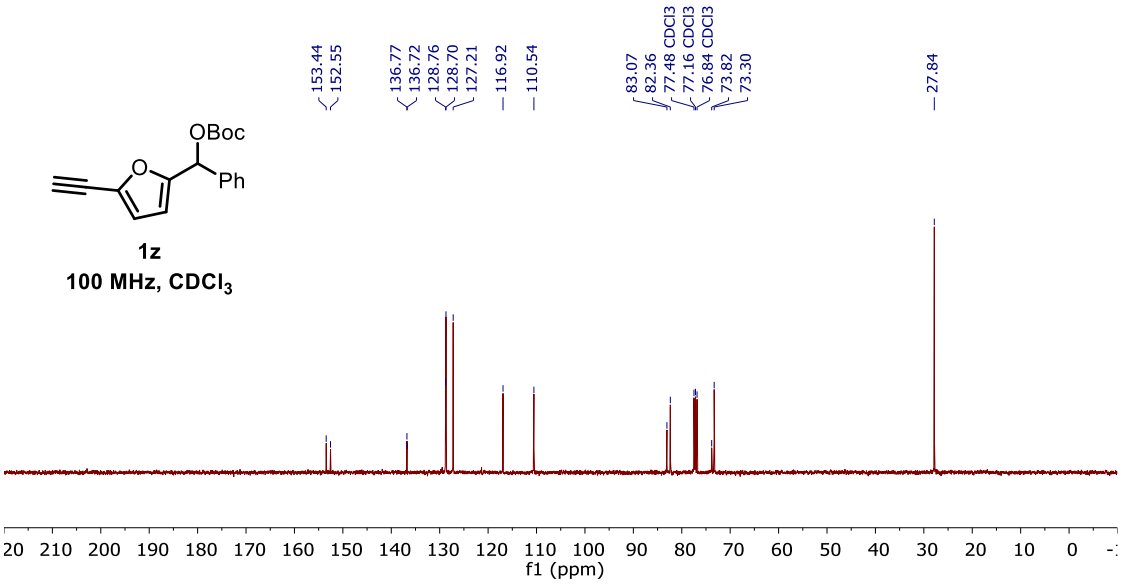
^{1}H NMR spectrum of **1y**



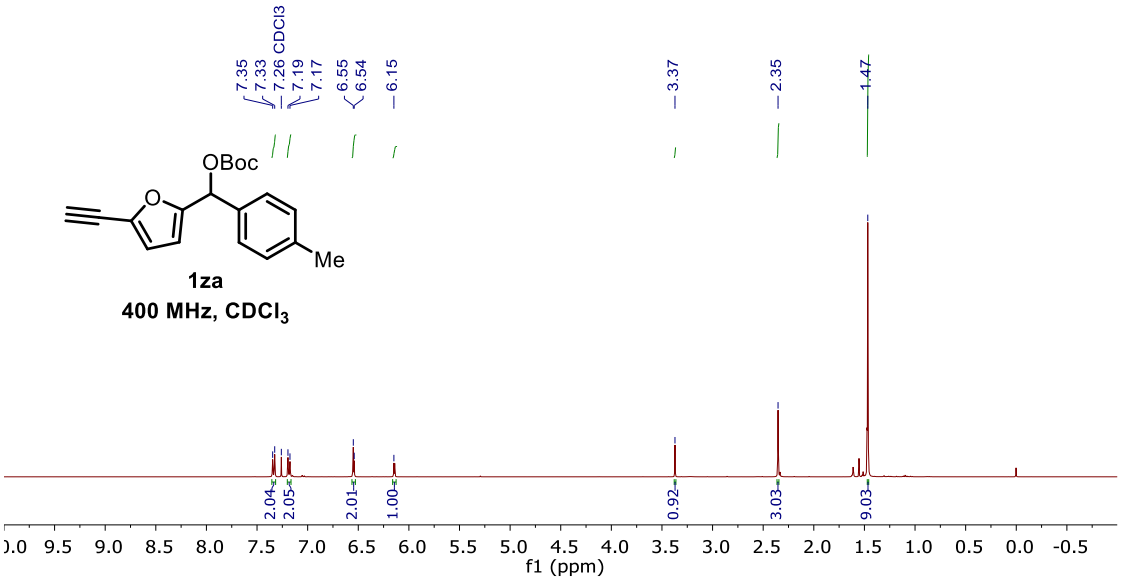
^{13}C NMR spectrum of **1y**



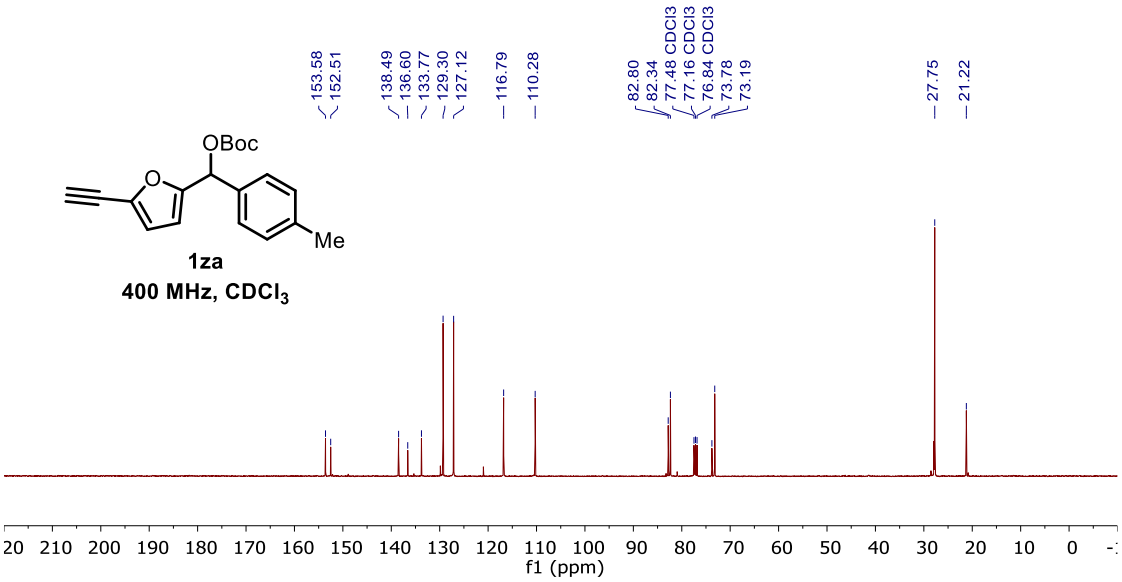
^{1}H NMR spectrum of **1z**



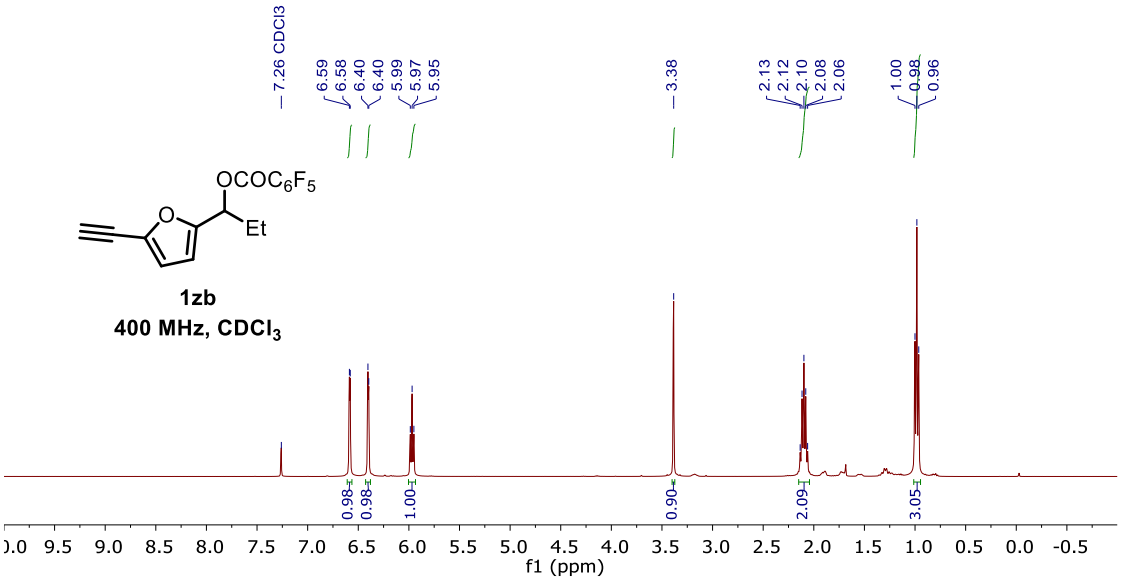
^{13}C NMR spectrum of **1z**



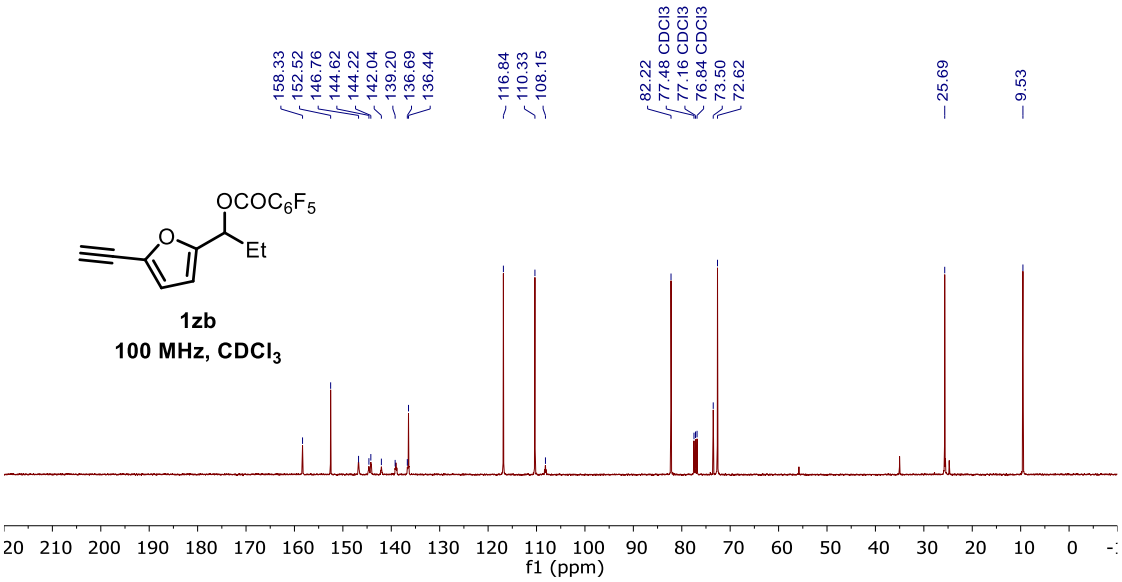
^{1}H NMR spectrum of **1za**



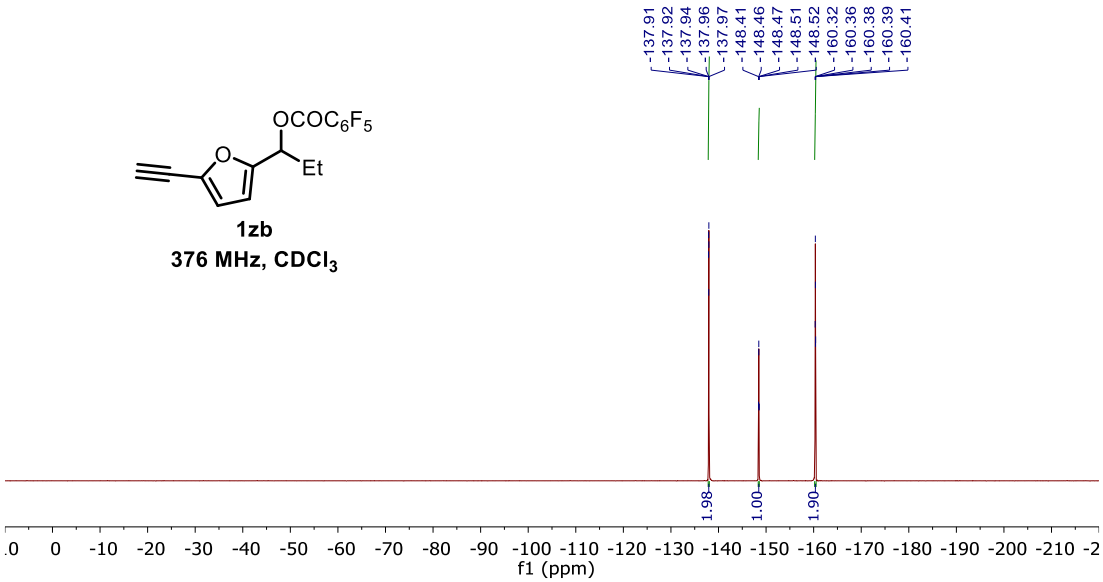
^{13}C NMR spectrum of **1za**



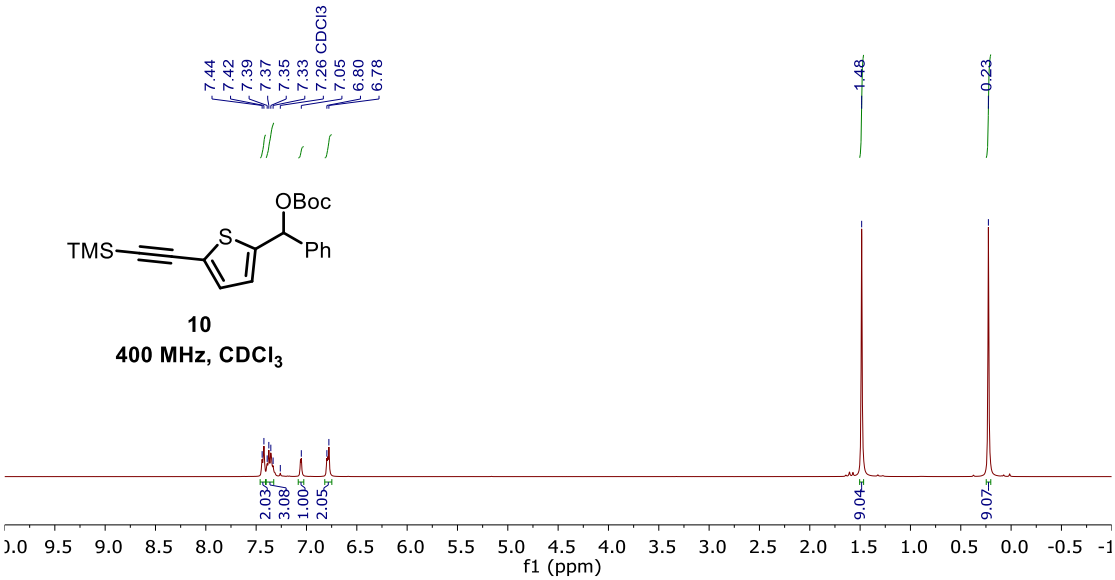
^{1}H NMR spectrum of **1zb**



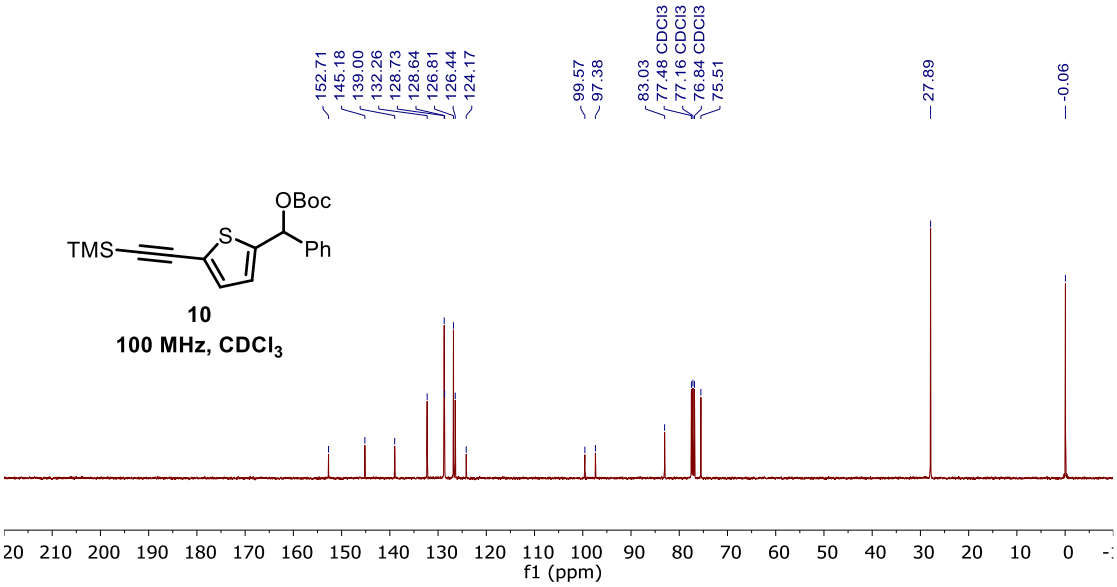
^{13}C NMR spectrum of **1zb**



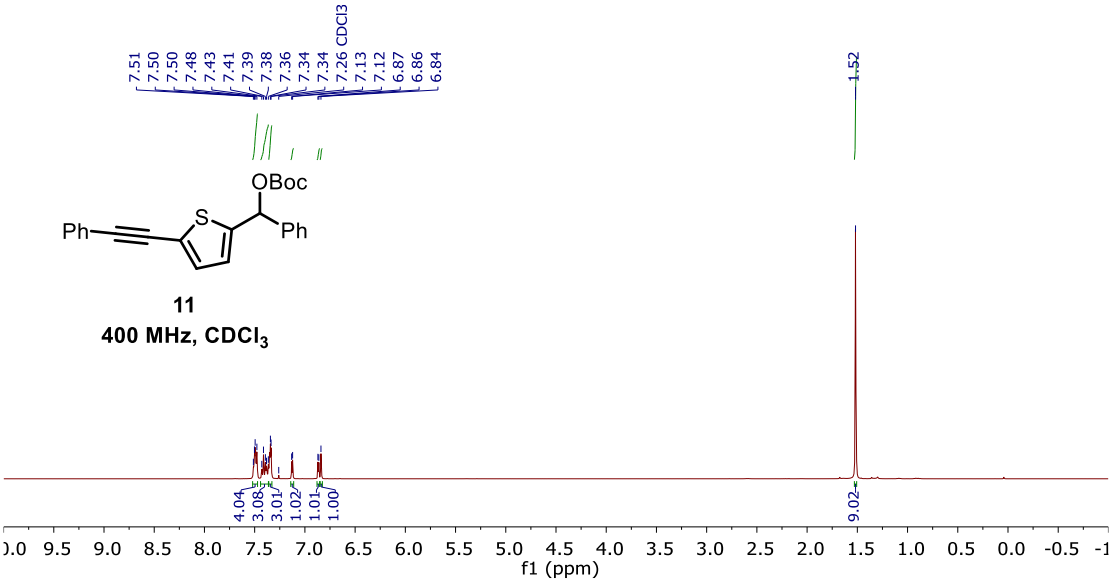
^{19}F NMR spectrum of **1zb**



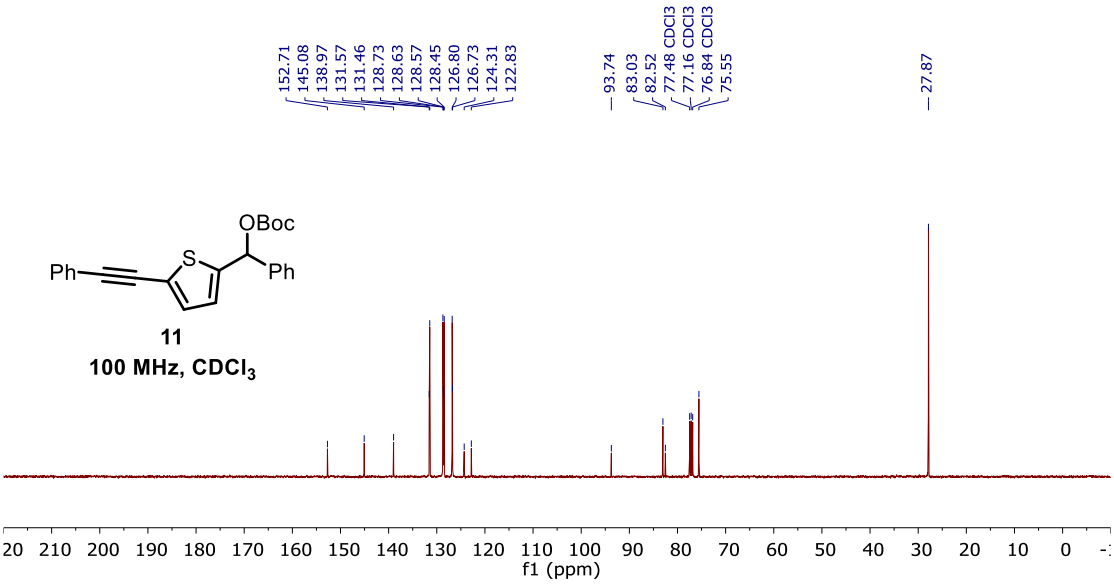
^{1}H NMR spectrum of **10**



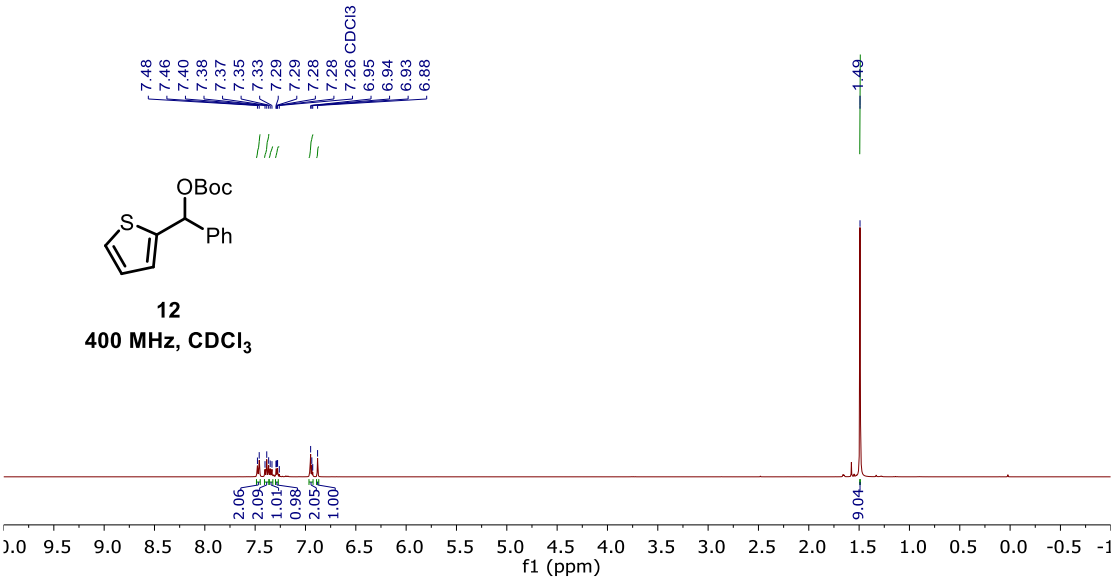
^{13}C NMR spectrum of **10**



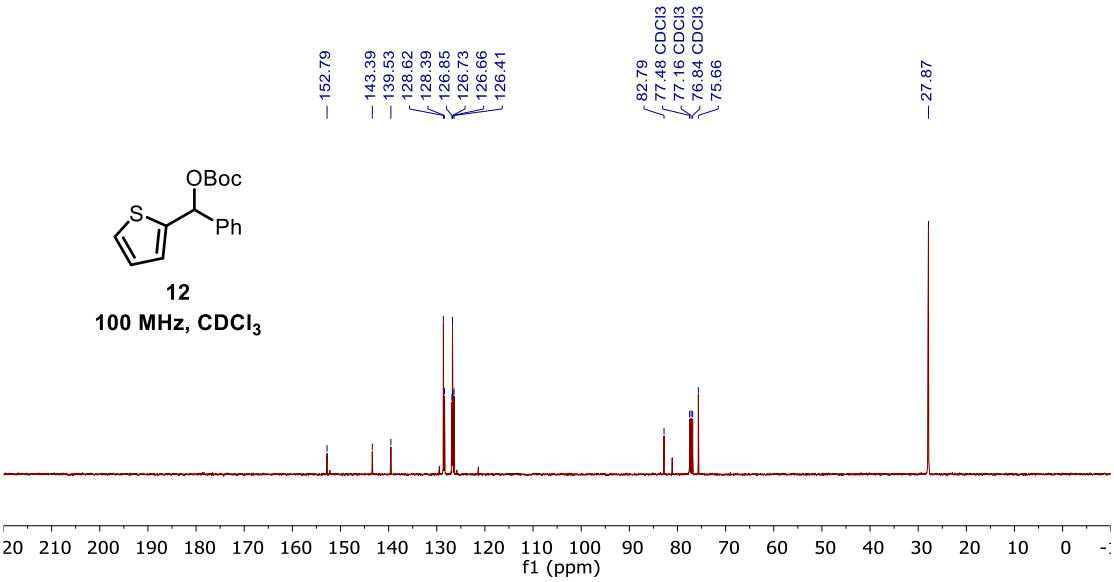
^{1}H NMR spectrum of **11**



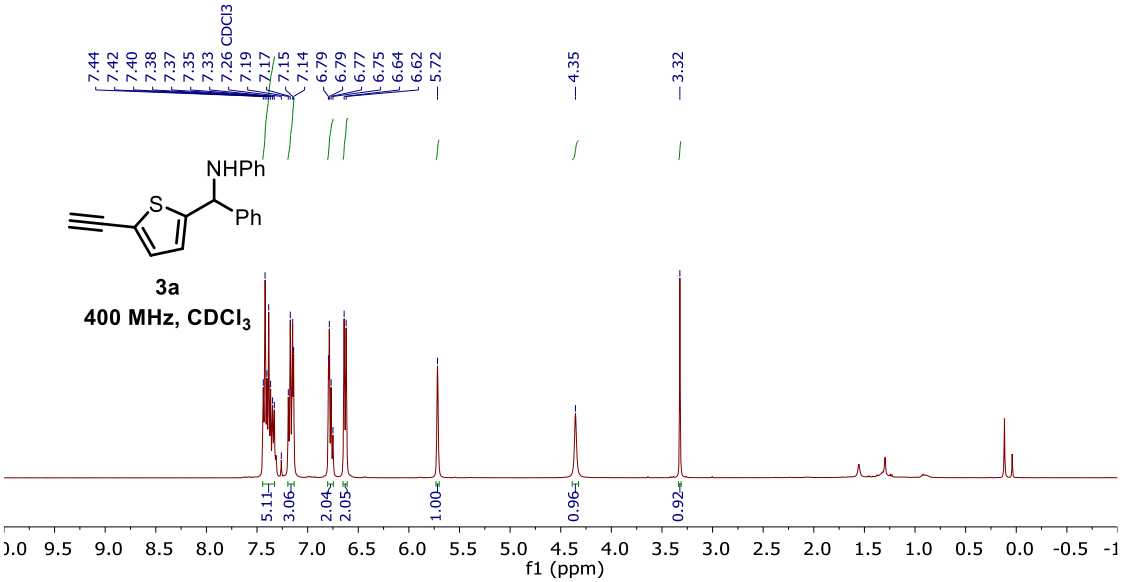
^{13}C NMR spectrum of **11**



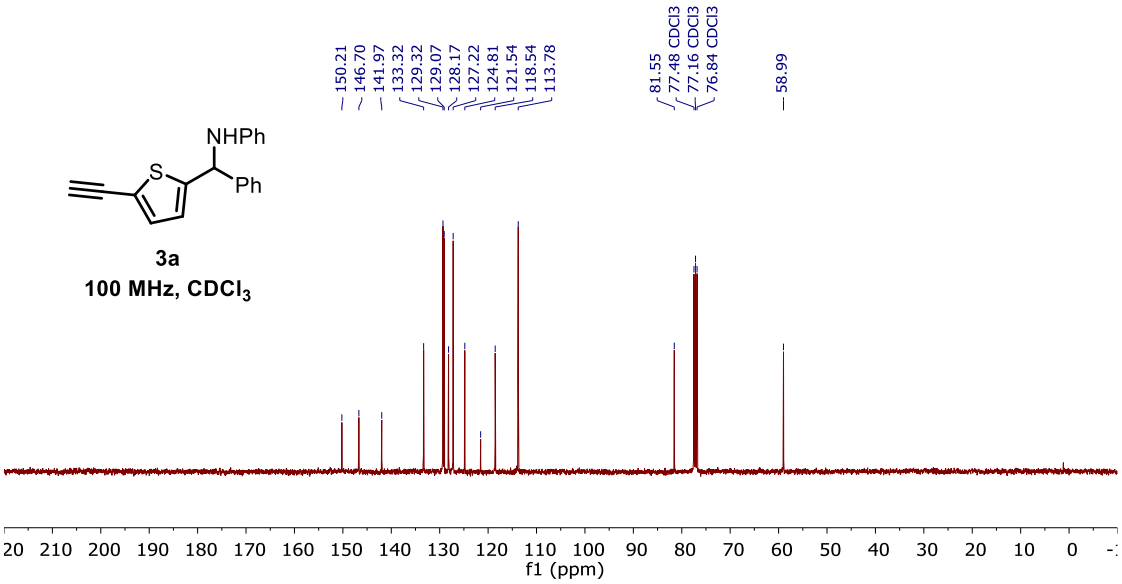
^{1}H NMR spectrum of **12**



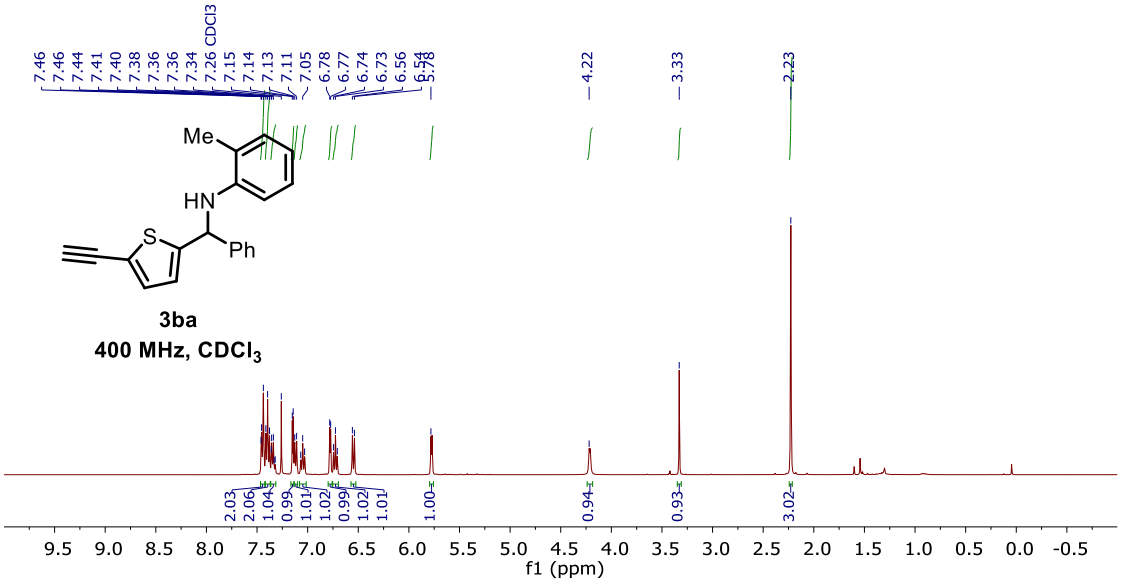
^{13}C NMR spectrum of **12**



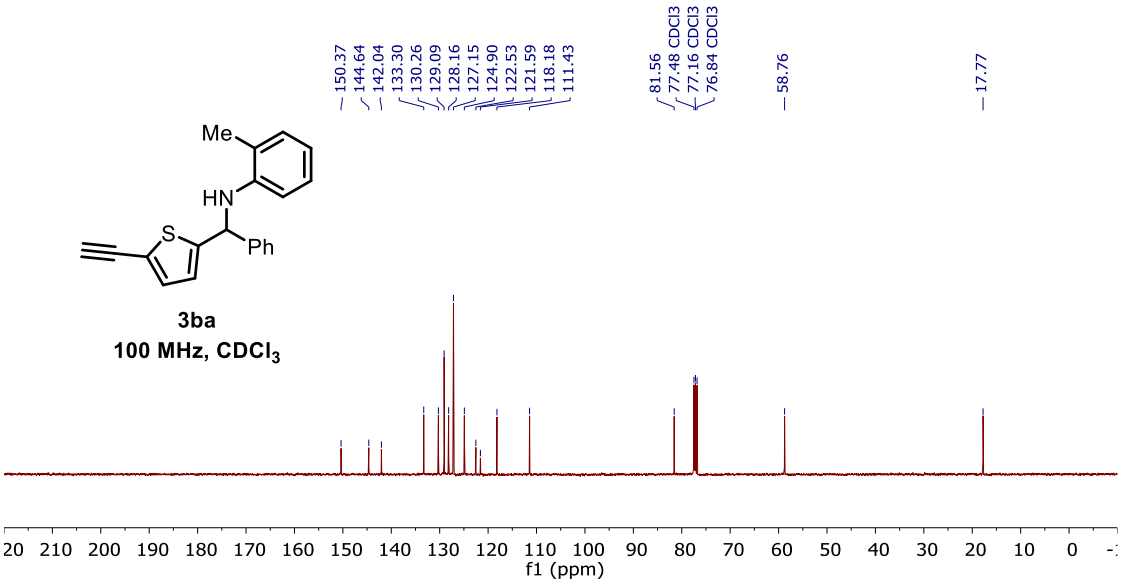
^{1}H NMR spectrum of **3a**



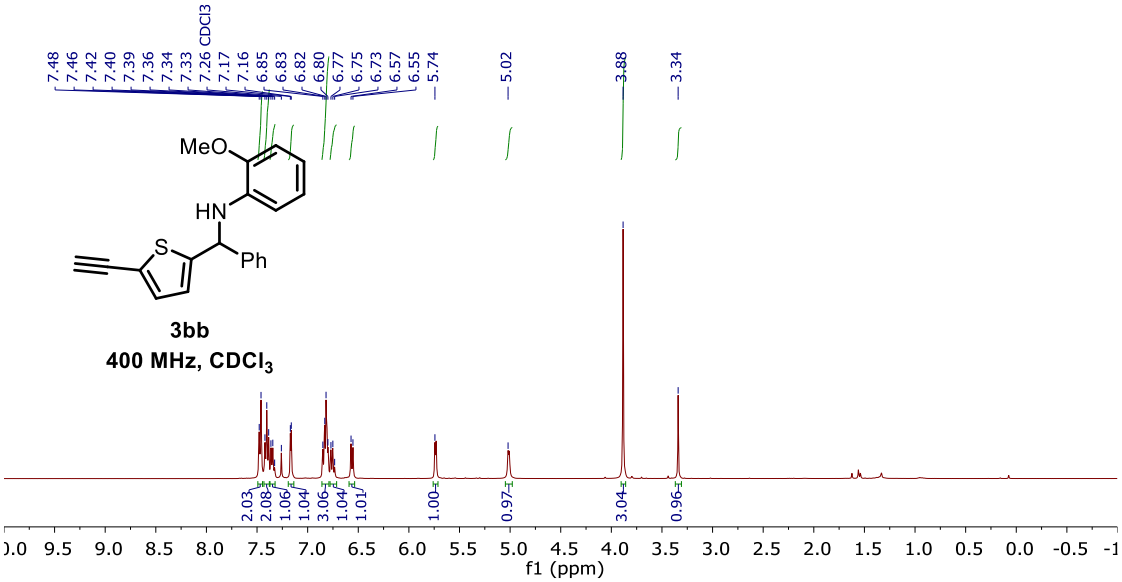
^{13}C NMR spectrum of **3a**



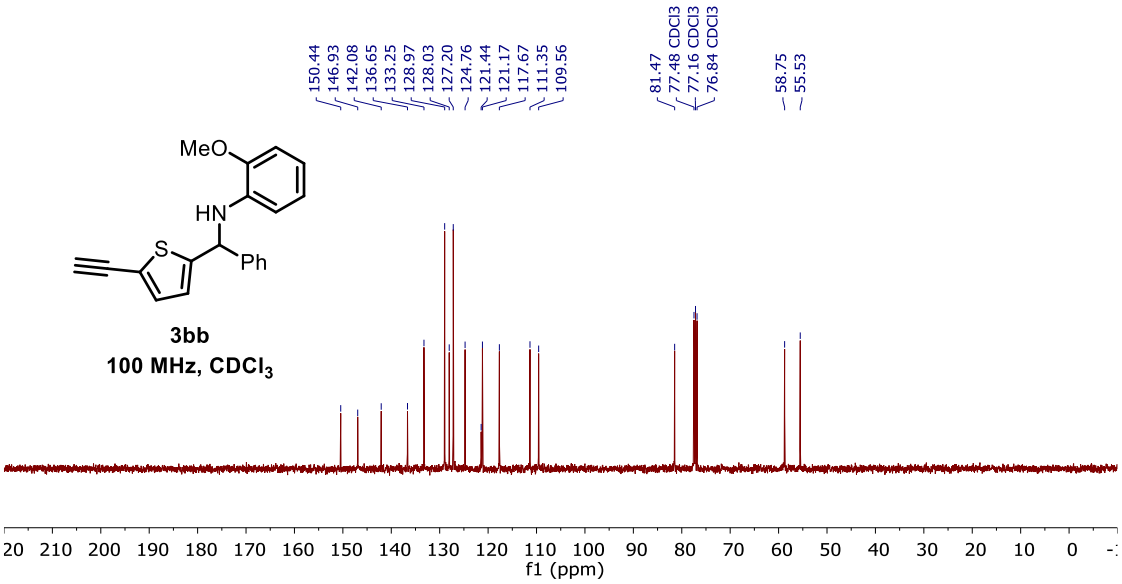
^{1}H NMR spectrum of **3ba**



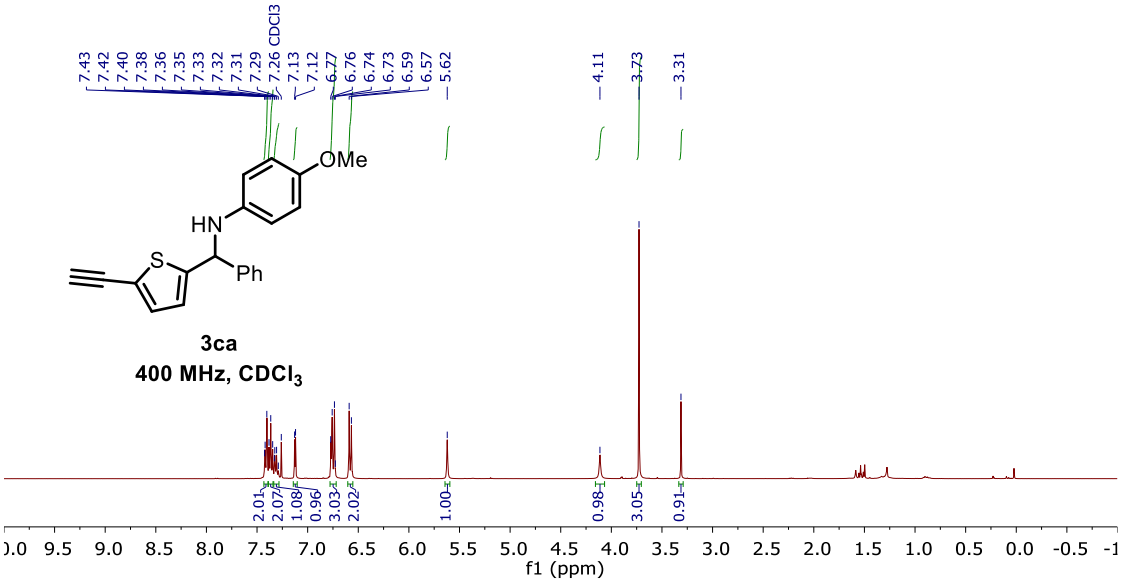
^{13}C NMR spectrum of **3ba**



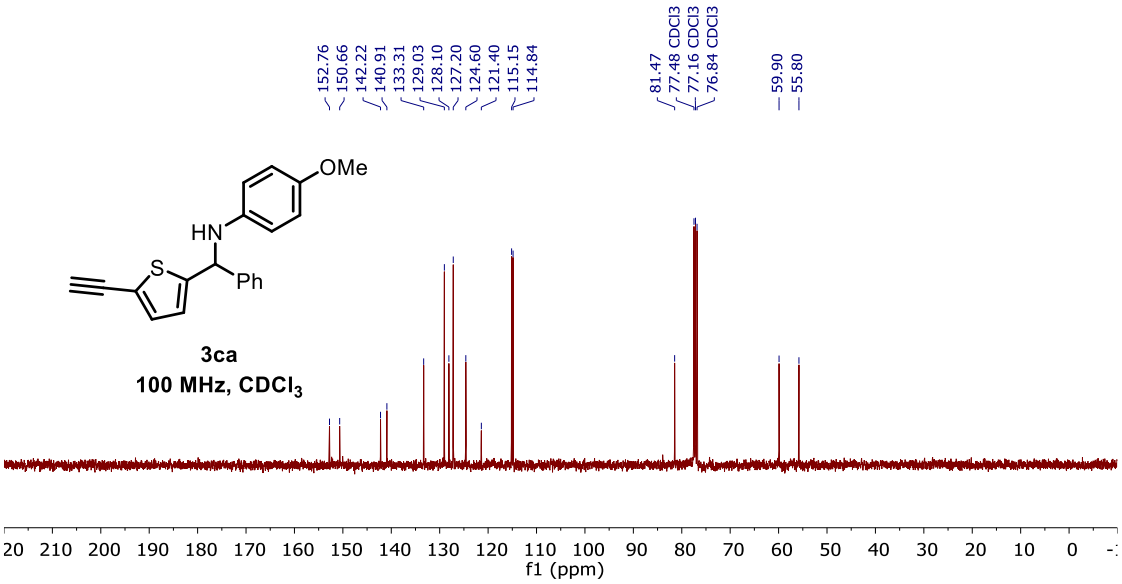
^{1}H NMR spectrum of **3bb**



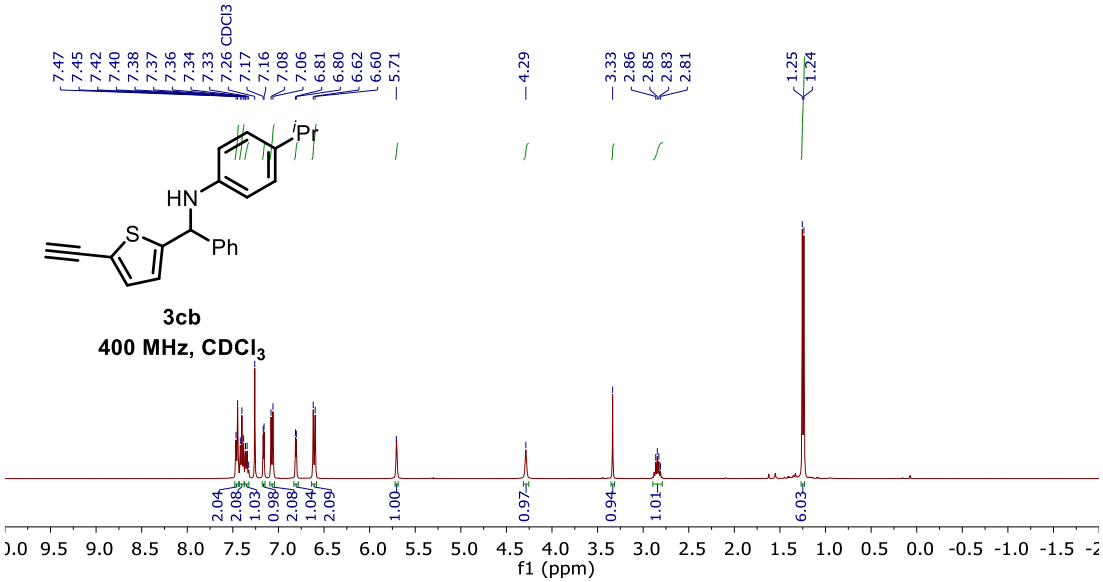
^{13}C NMR spectrum of **3bb**



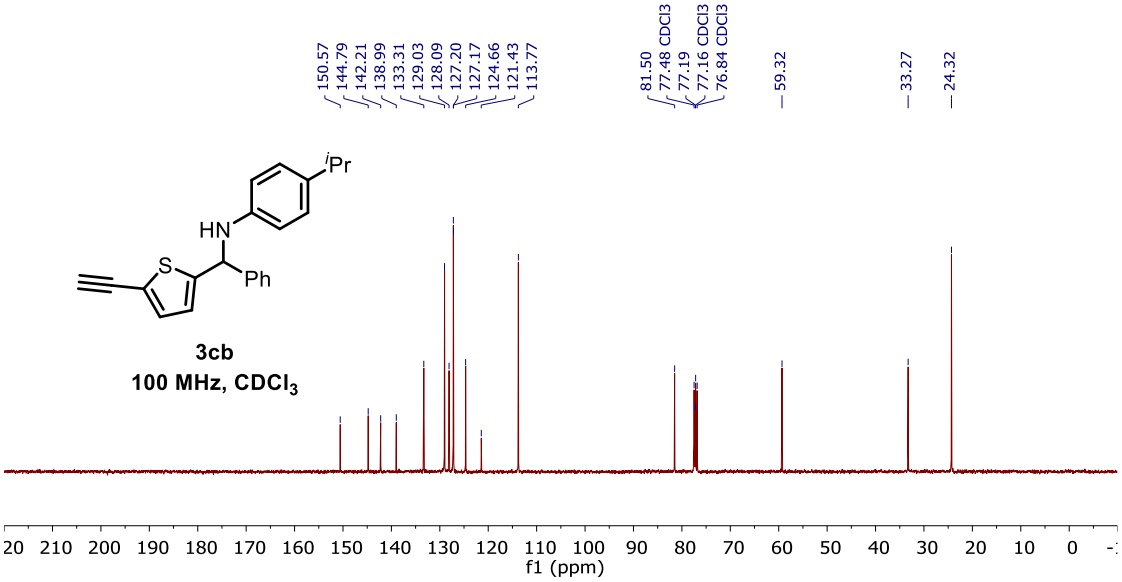
^{1}H NMR spectrum of **3ca**



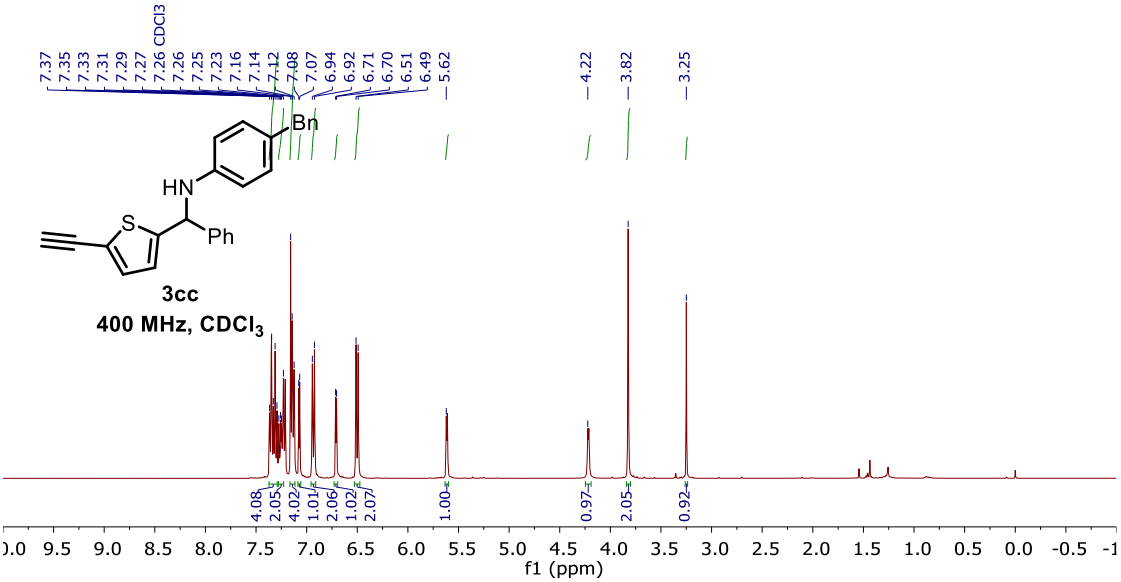
^{13}C NMR spectrum of **3ca**



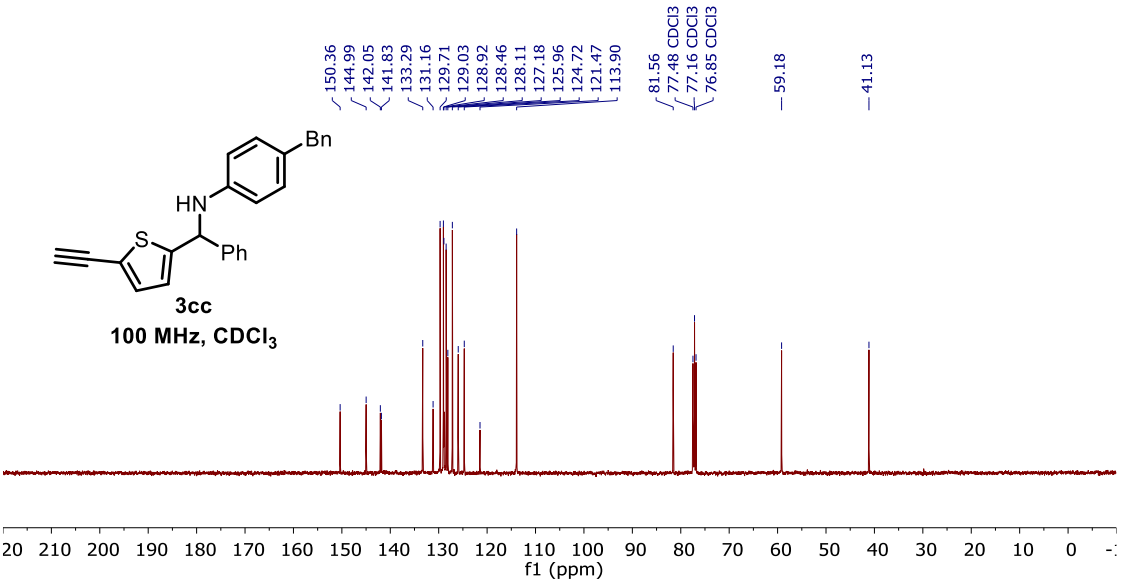
^{1}H NMR spectrum of **3cb**



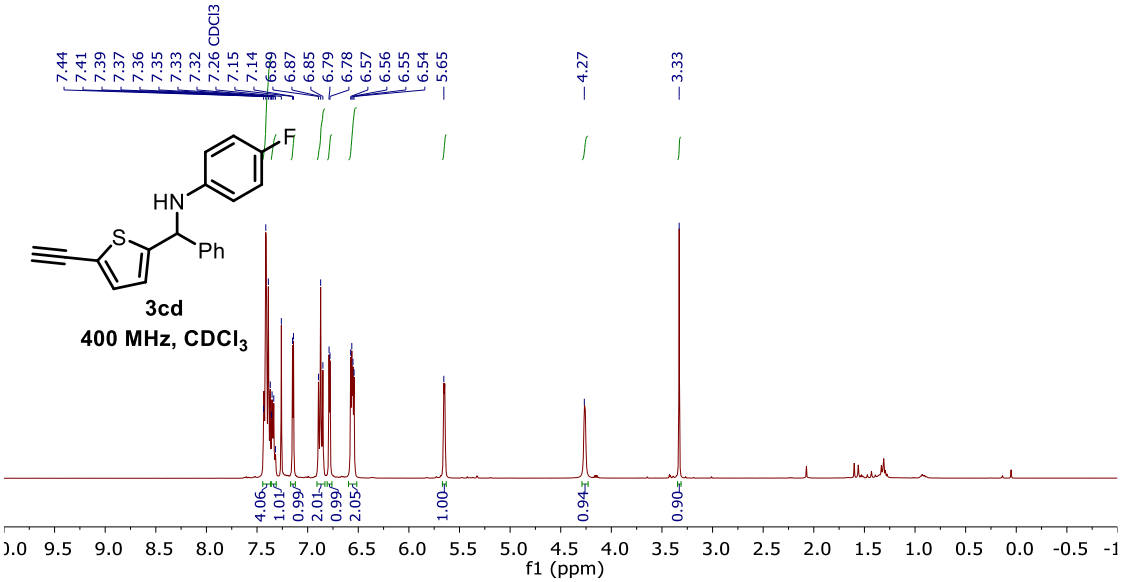
^{13}C NMR spectrum of **3cb**



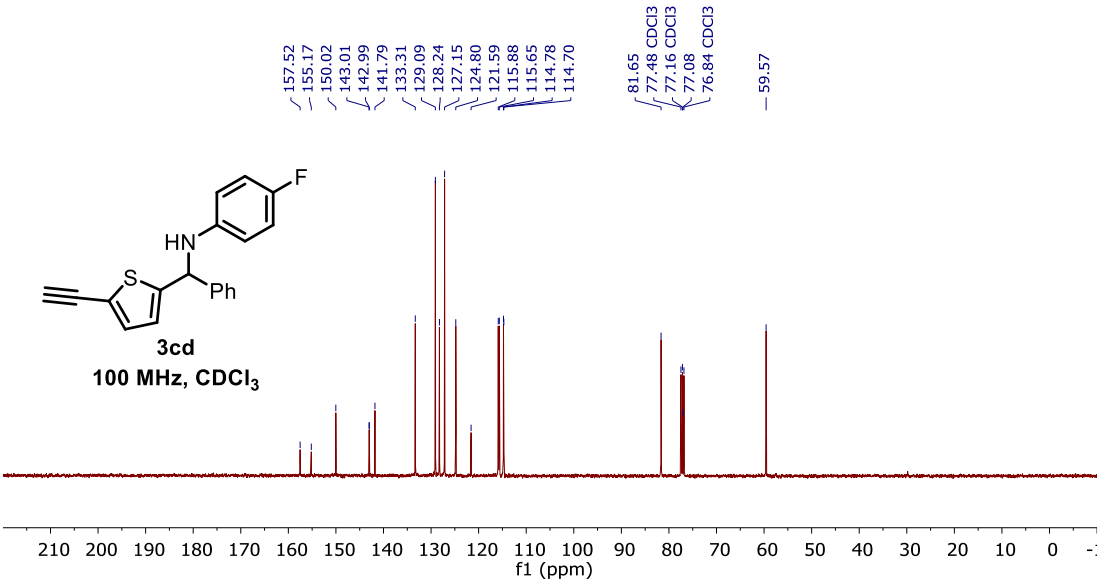
^{1}H NMR spectrum of **3cc**



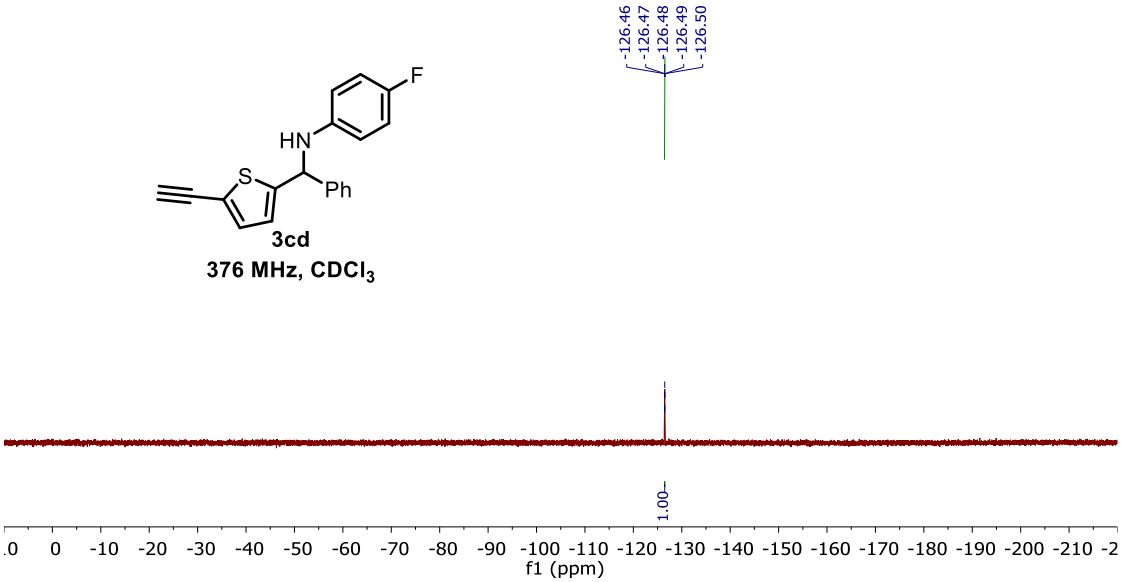
^{13}C NMR spectrum of **3cc**



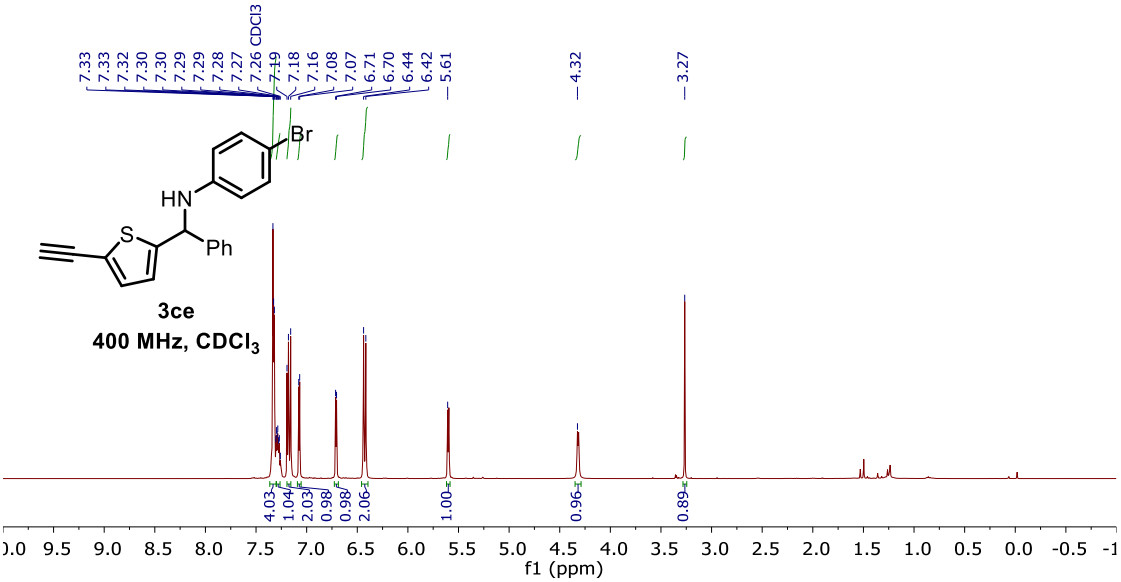
^{1}H NMR spectrum of **3cd**



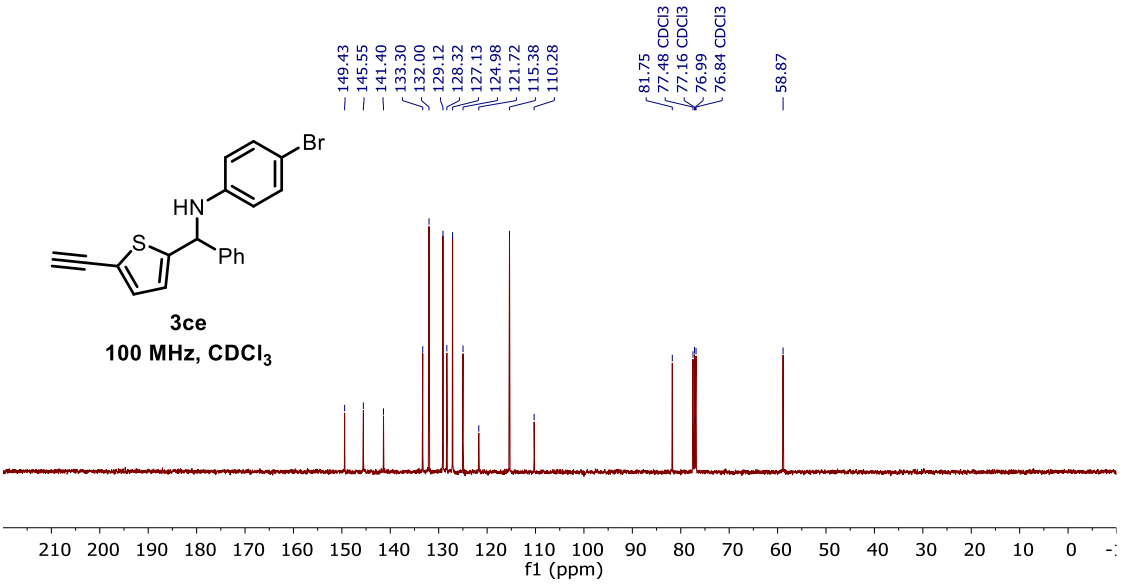
^{13}C NMR spectrum of **3cd**



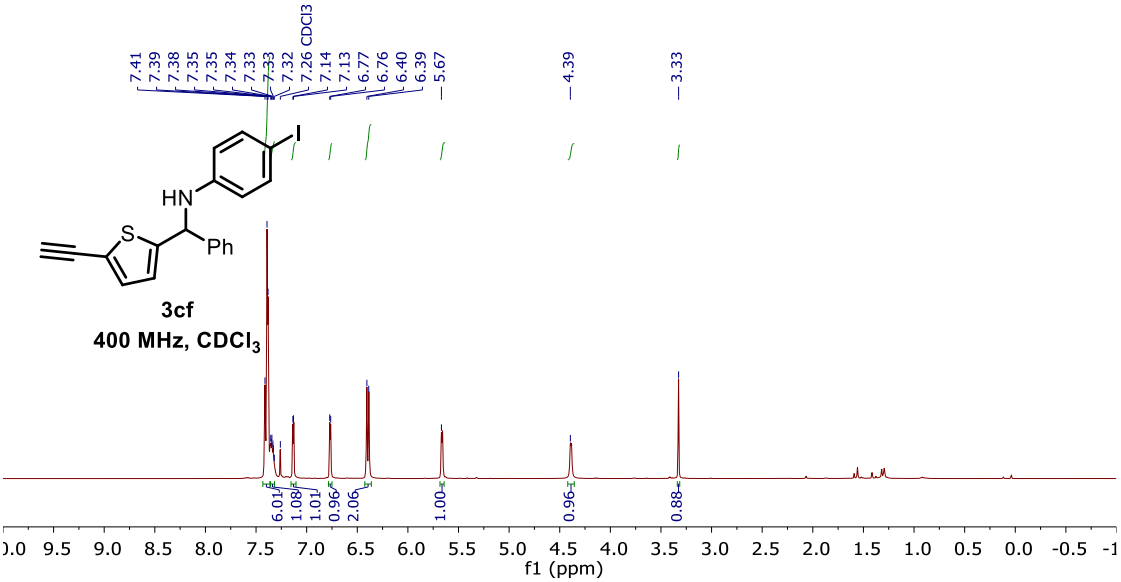
^{19}F NMR spectrum of **3cd**



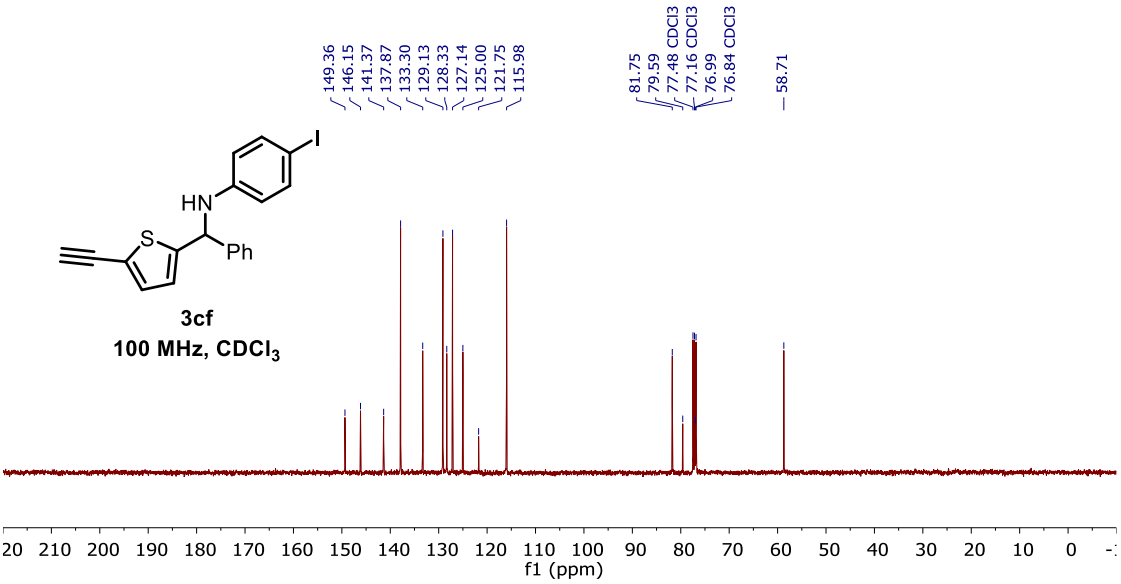
^{1}H NMR spectrum of **3ce**



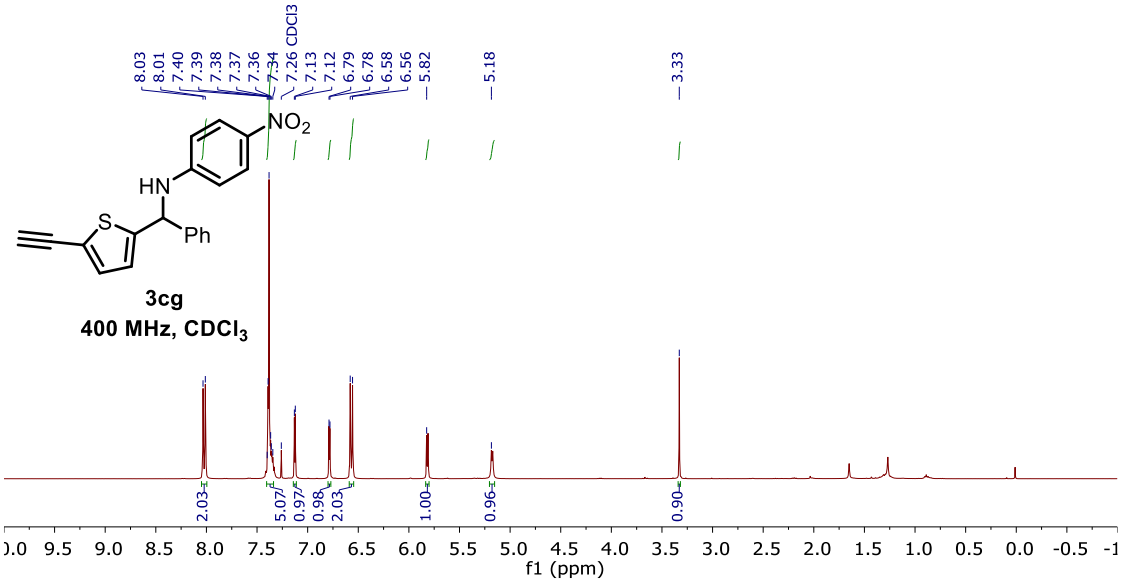
^{13}C NMR spectrum of **3ce**



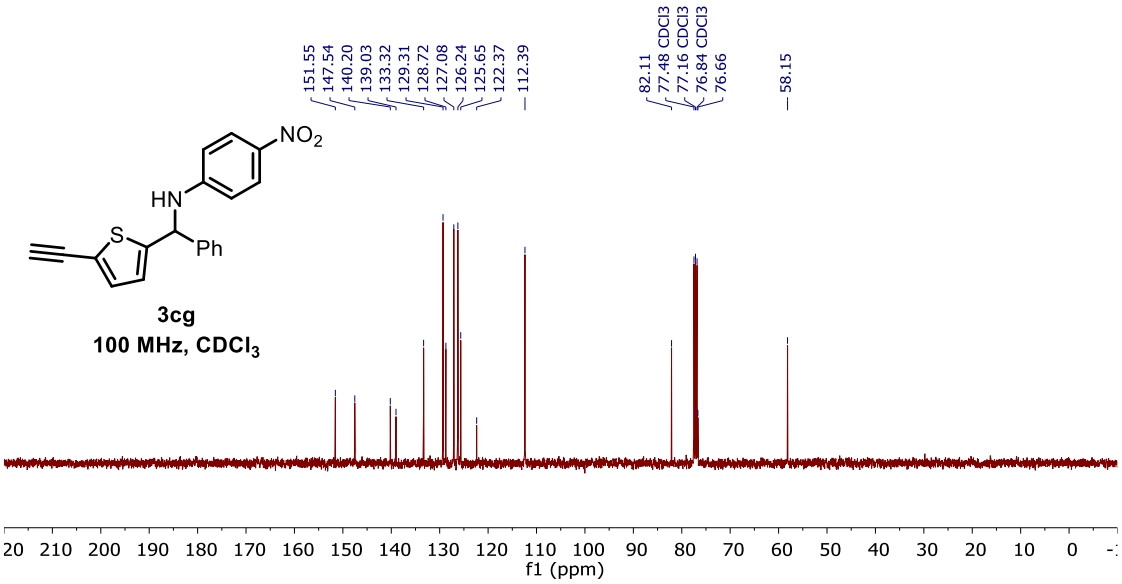
^{1}H NMR spectrum of **3cf**



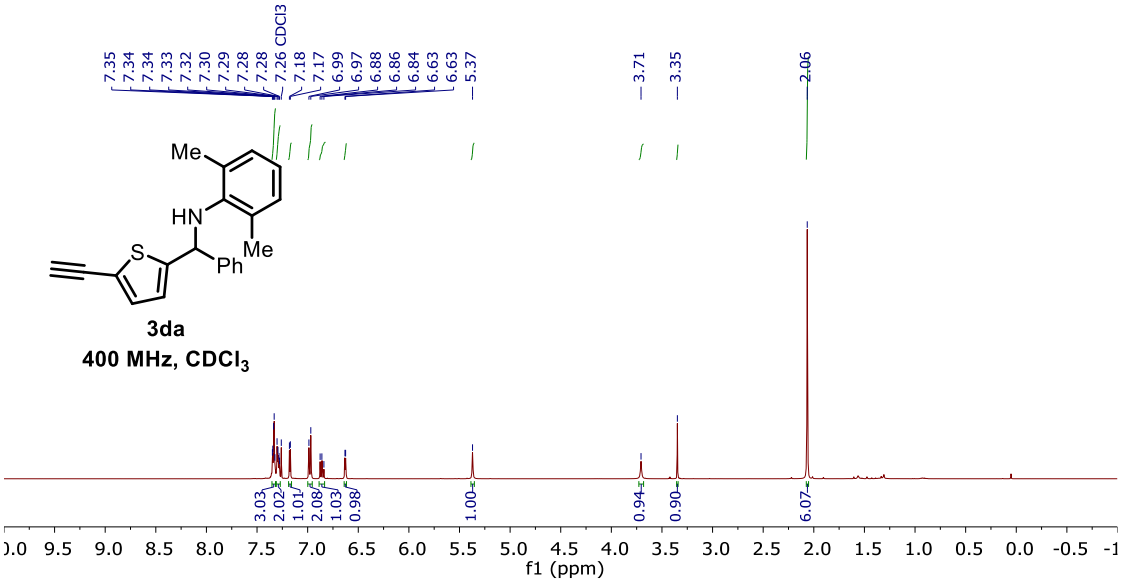
^{13}C NMR spectrum of **3cf**



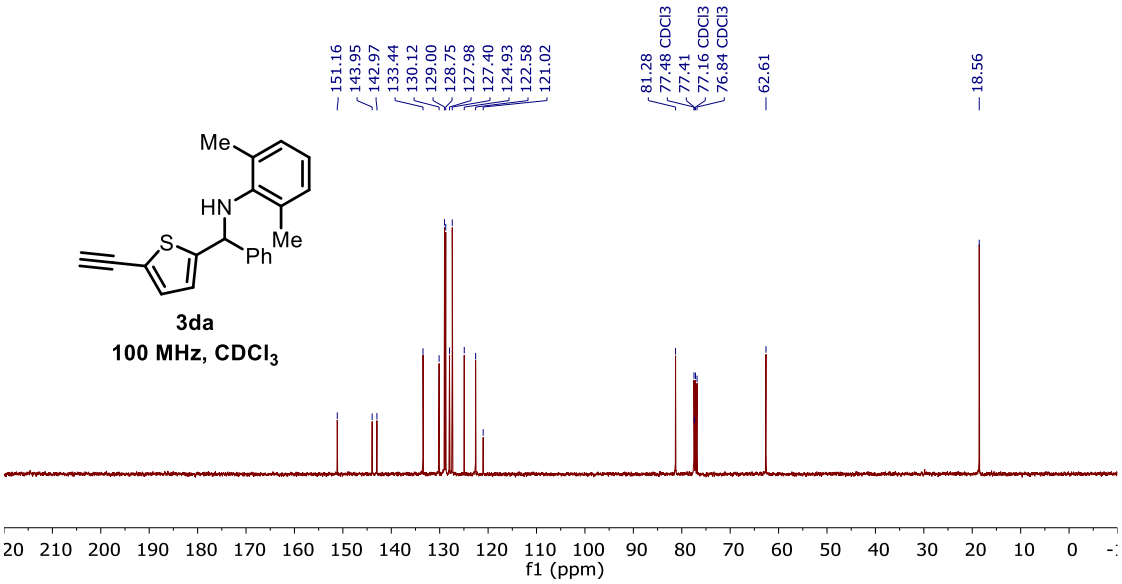
^{1}H NMR spectrum of **3cg**



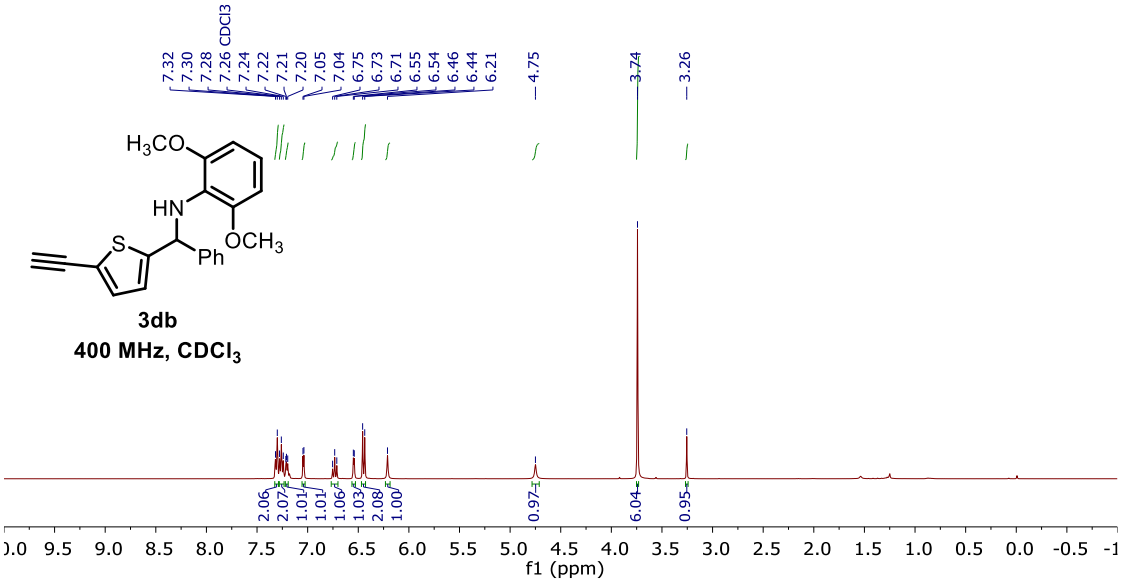
^{13}C NMR spectrum of **3cg**



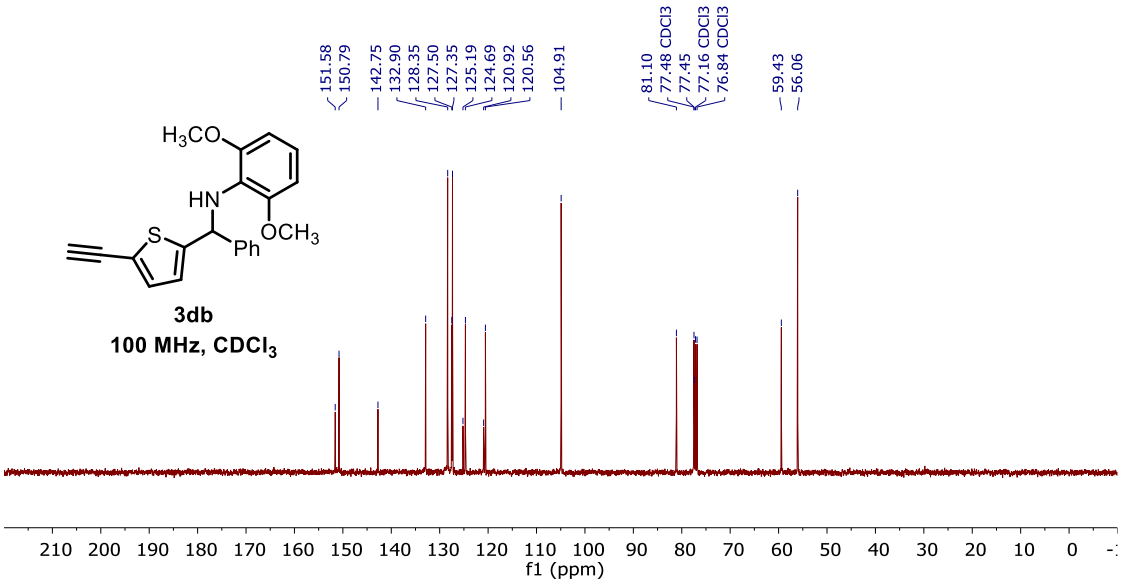
^{1}H NMR spectrum of **3da**



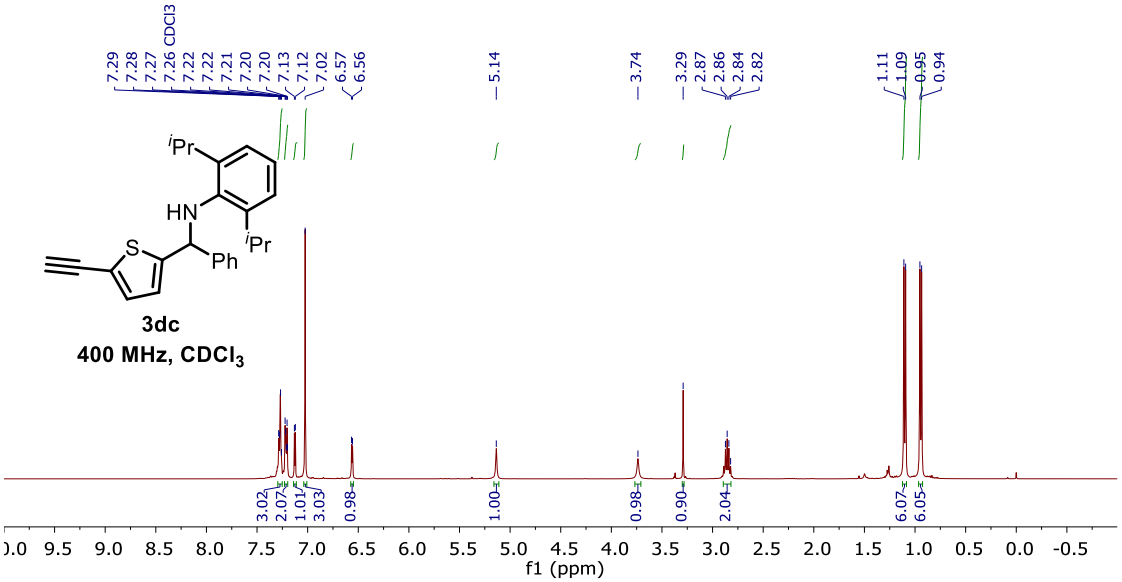
^{13}C NMR spectrum of **3da**



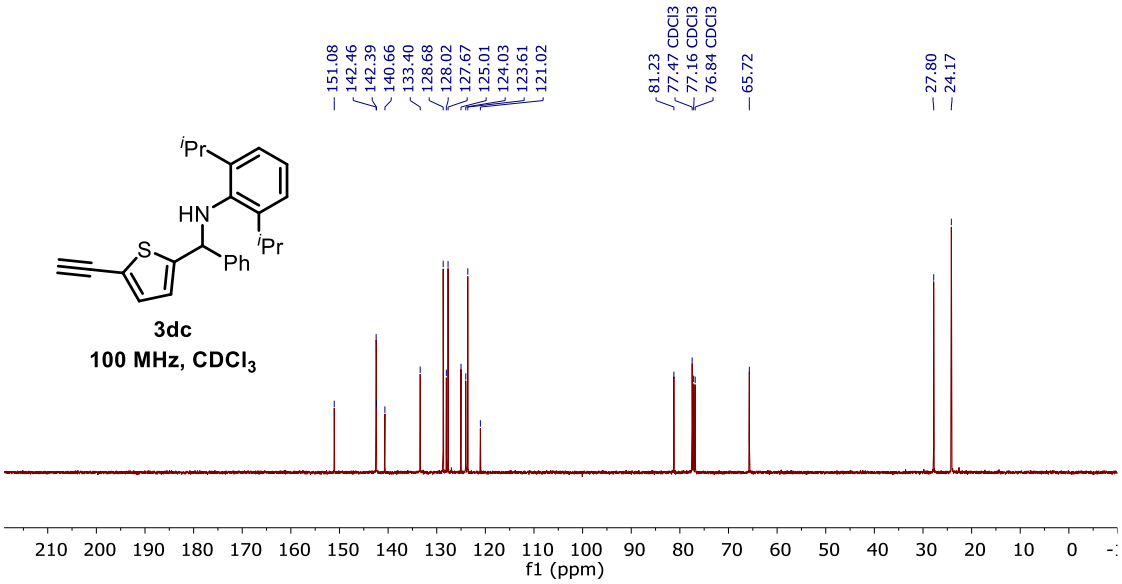
^{1}H NMR spectrum of **3db**



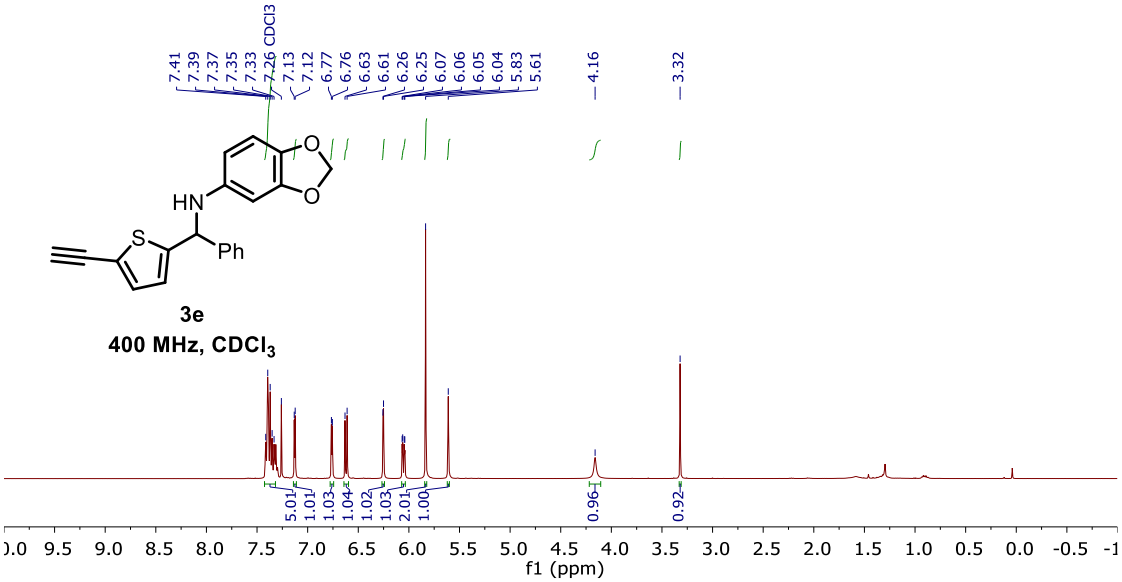
^{13}C NMR spectrum of **3db**



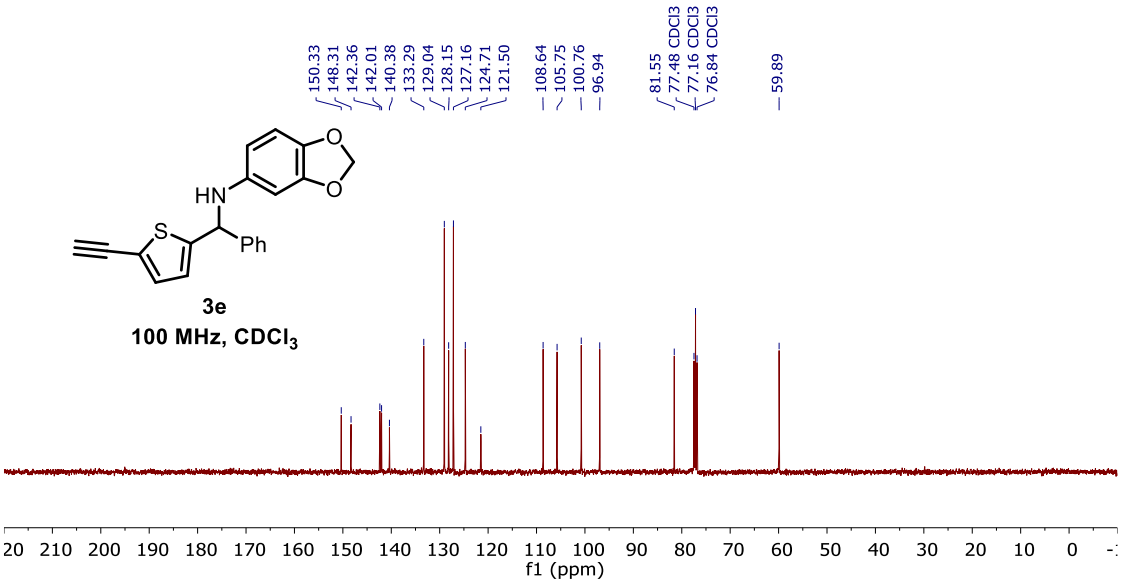
^{1}H NMR spectrum of **3dc**



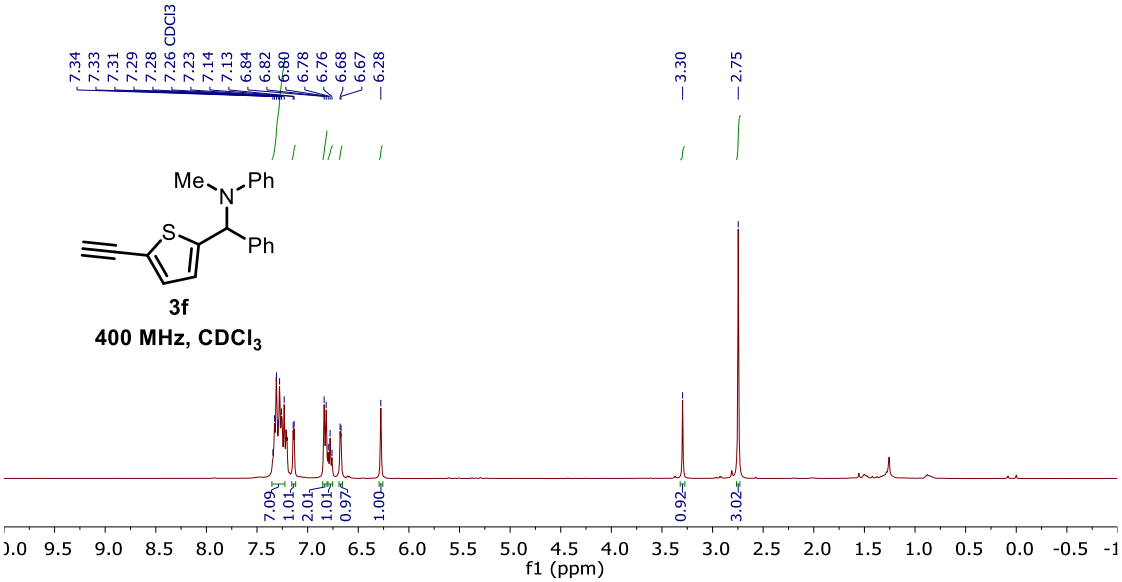
^{13}C NMR spectrum of **3dc**



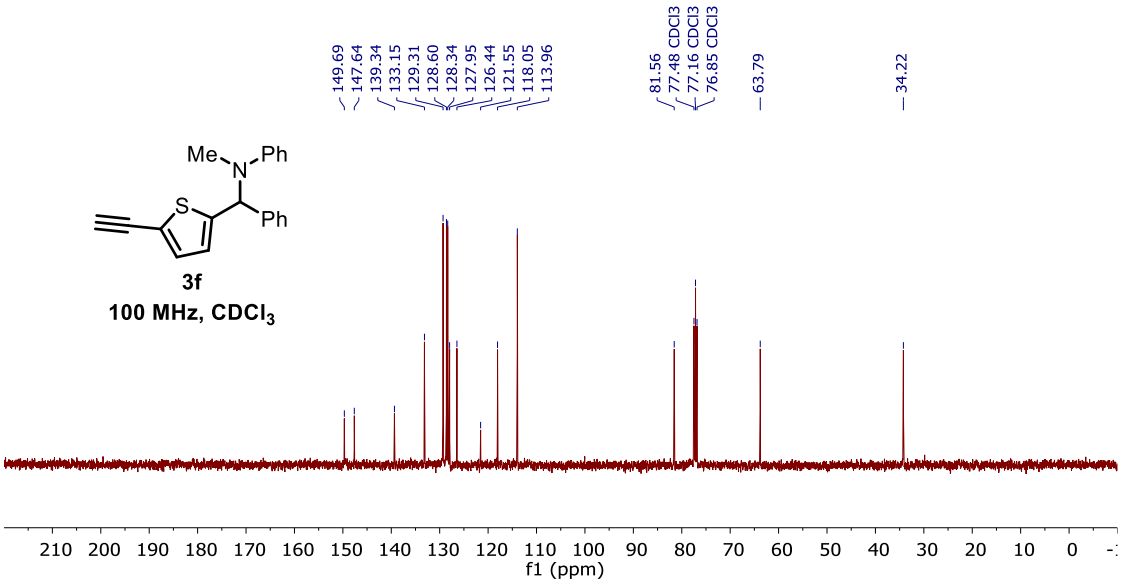
^{1}H NMR spectrum of **3e**



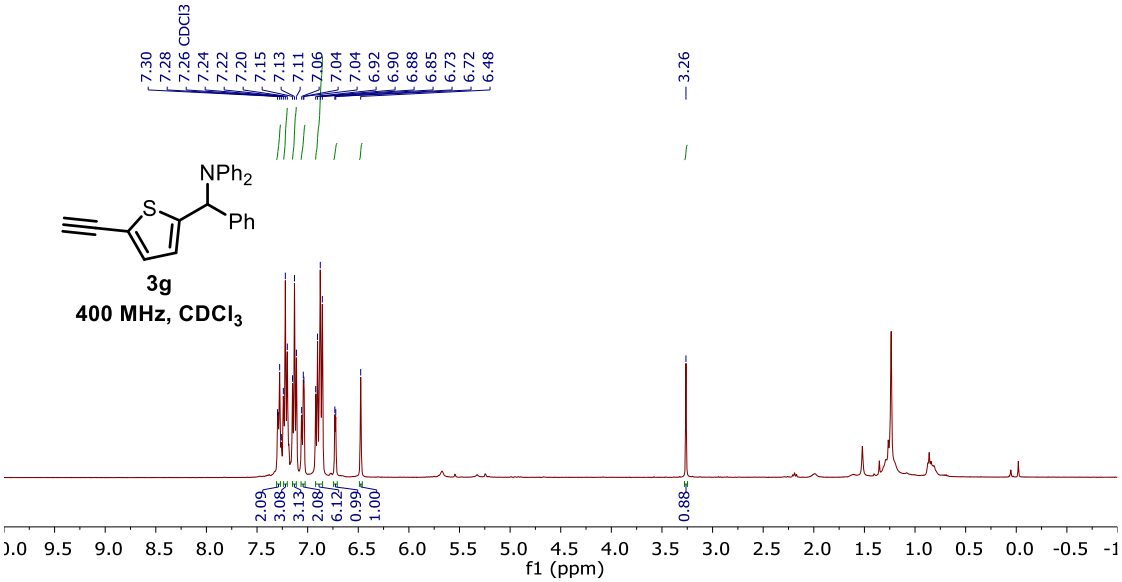
^{13}C NMR spectrum of **3e**



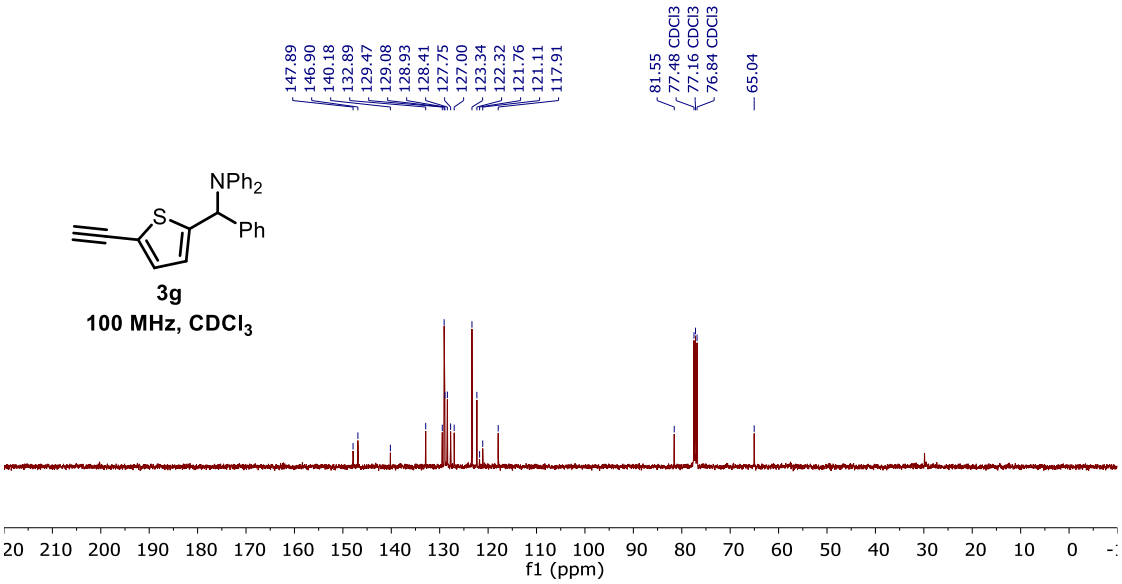
^{1}H NMR spectrum of **3f**



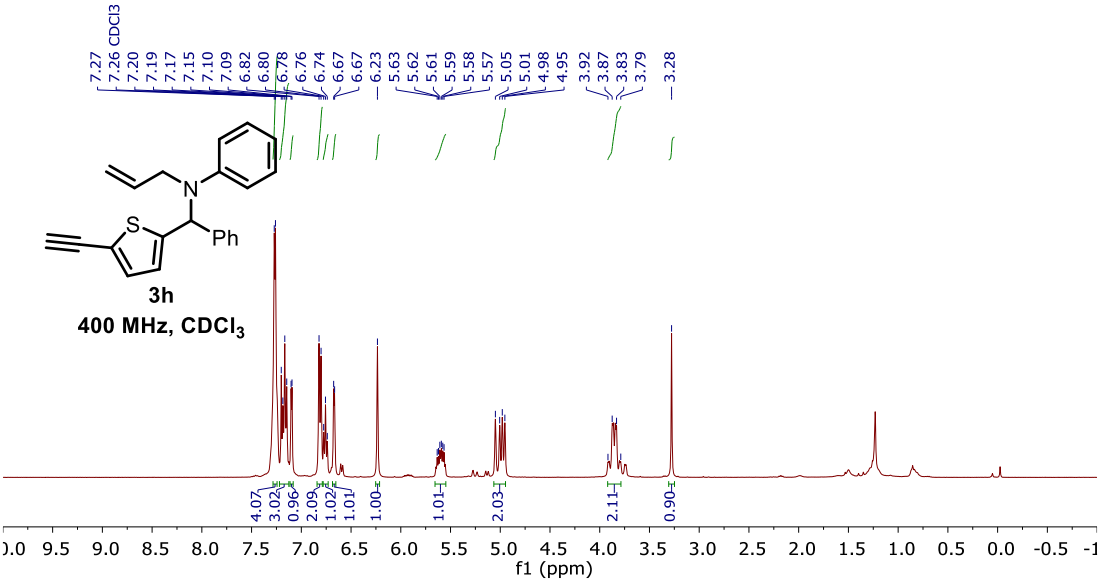
^{13}C NMR spectrum of **3f**



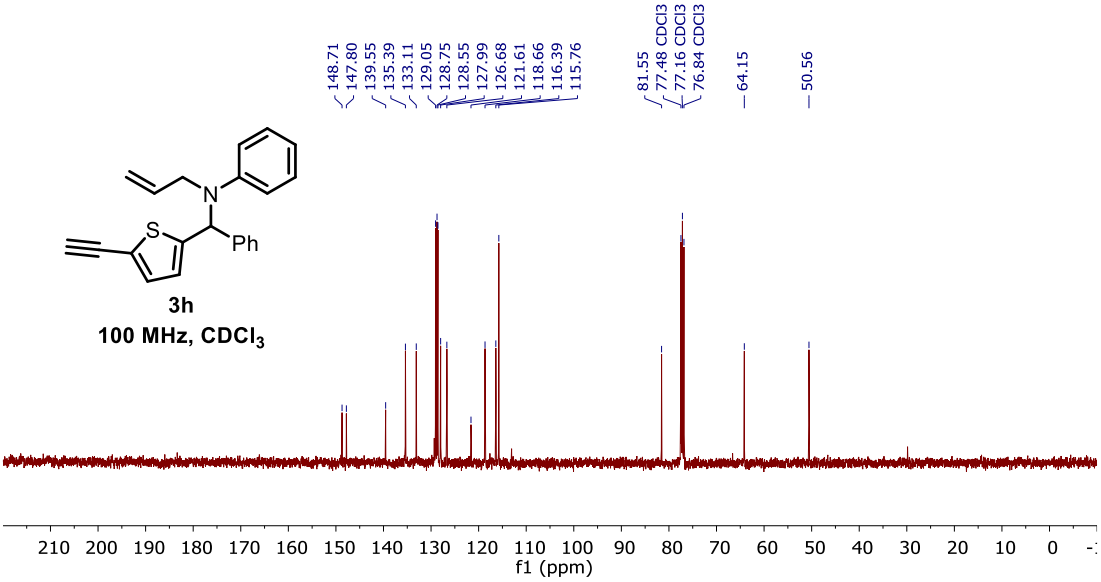
^{1}H NMR spectrum of **3g**



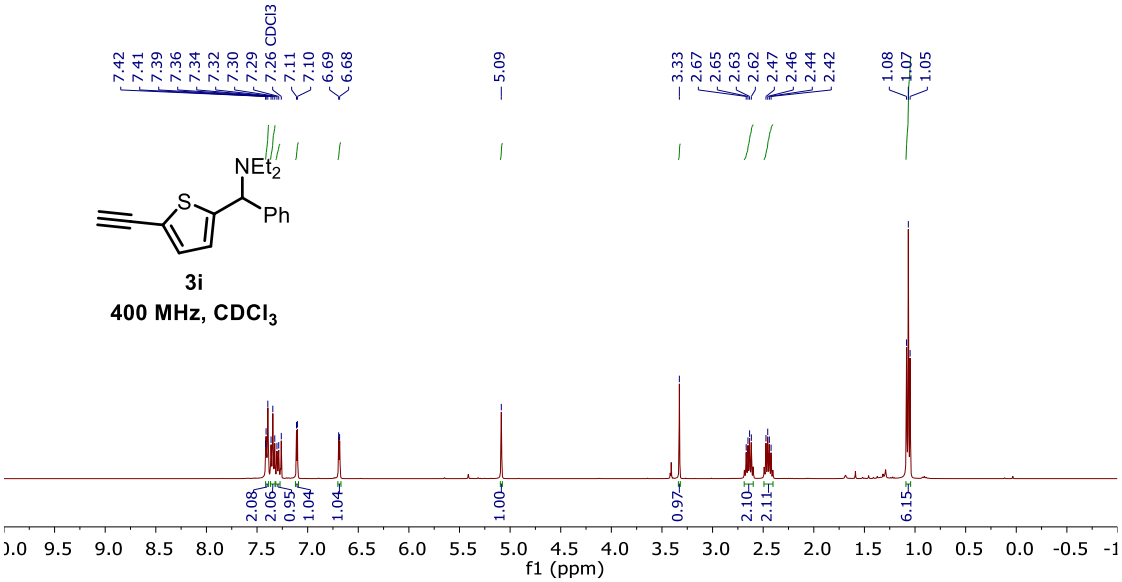
^{13}C NMR spectrum of **3g**



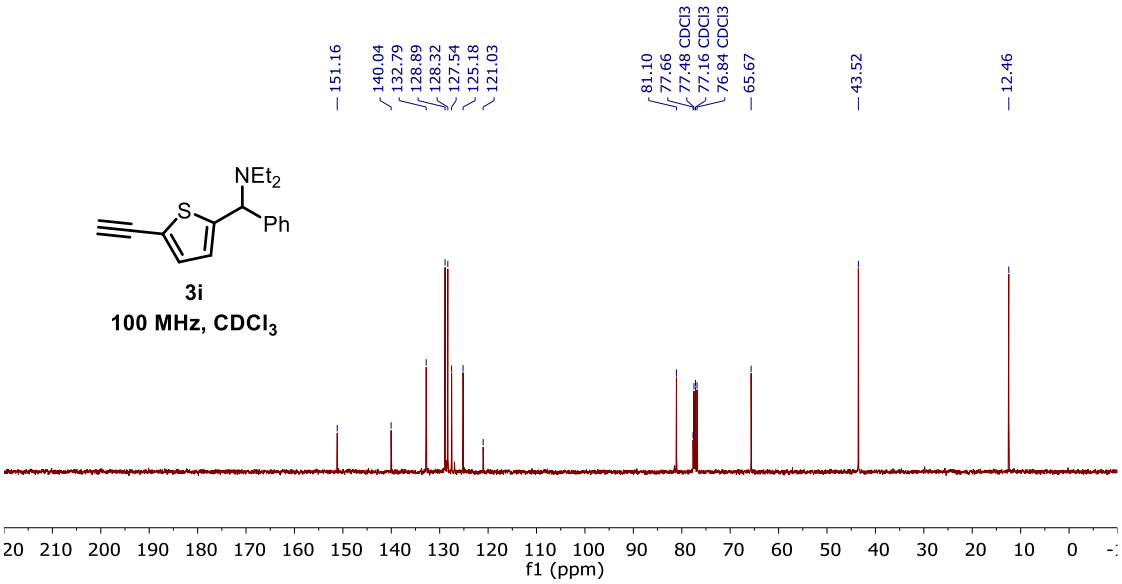
^{1}H NMR spectrum of **3h**



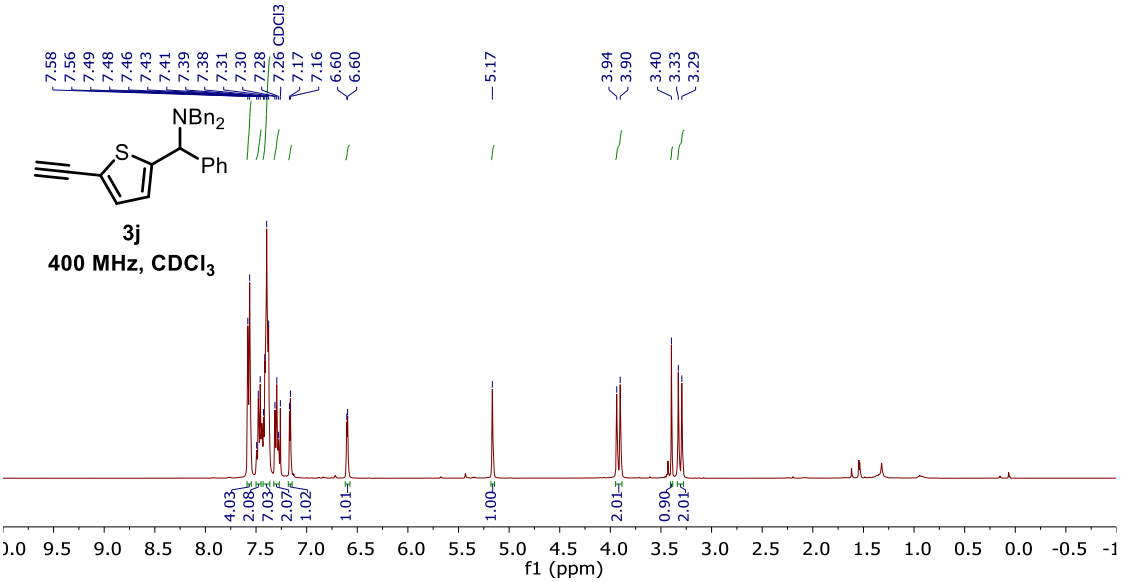
^{13}C NMR spectrum of **3h**



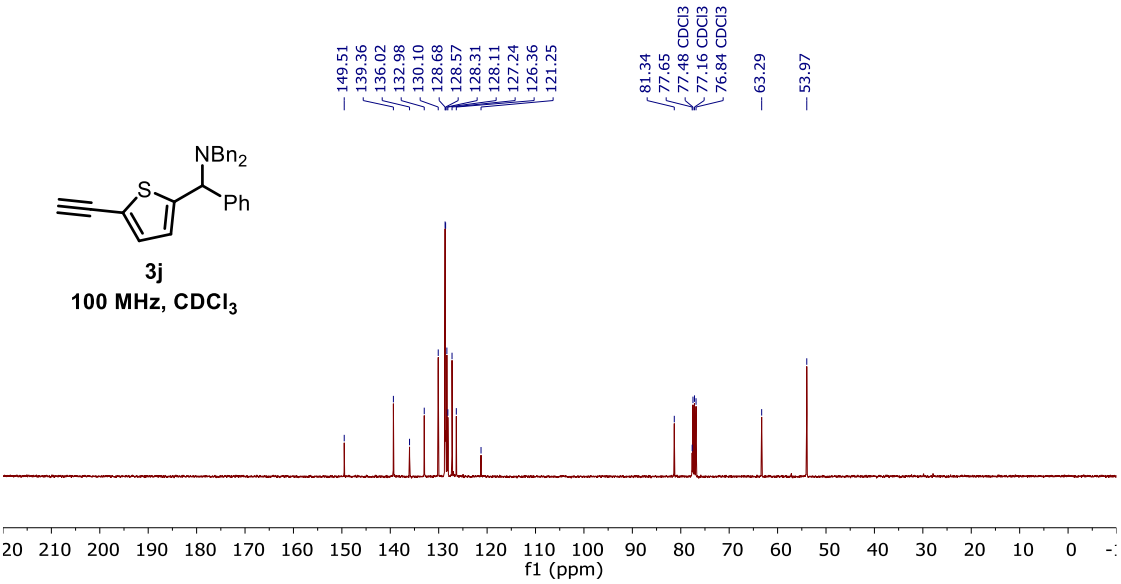
^{1}H NMR spectrum of **3i**



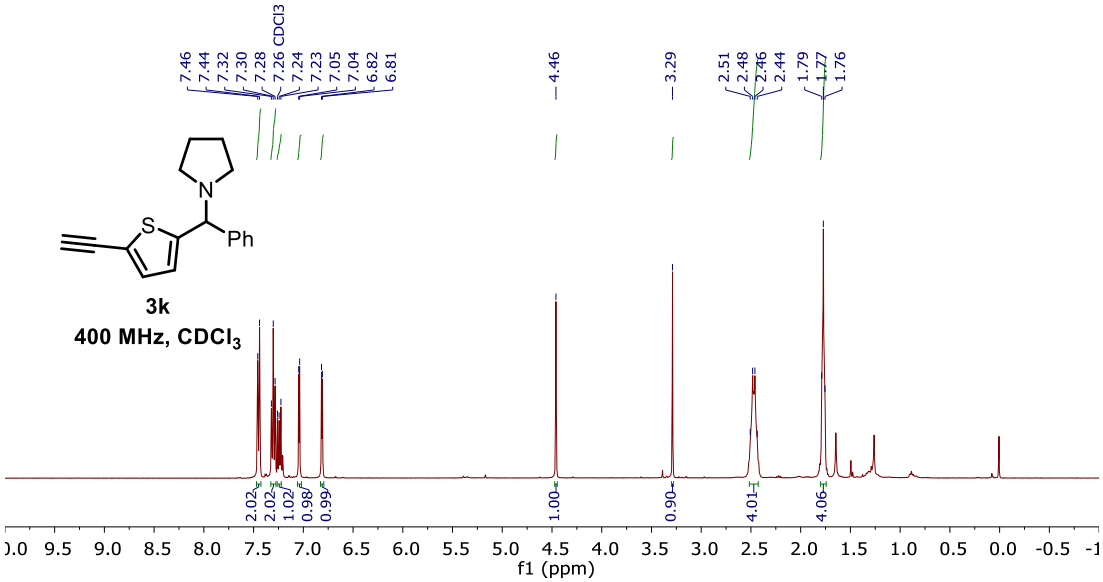
^{13}C NMR spectrum of **3i**



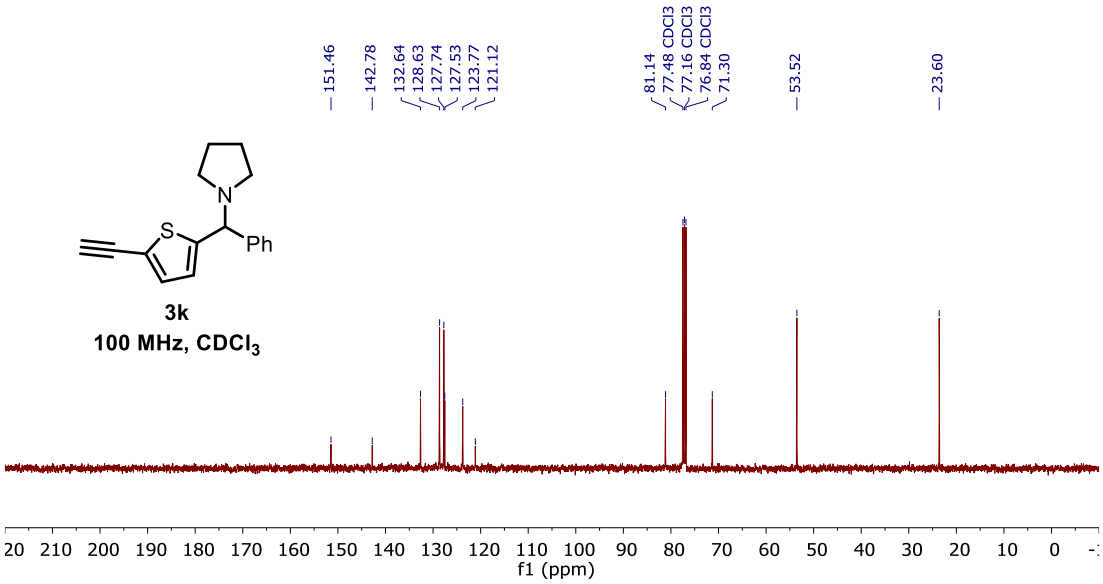
^{1}H NMR spectrum of **3j**



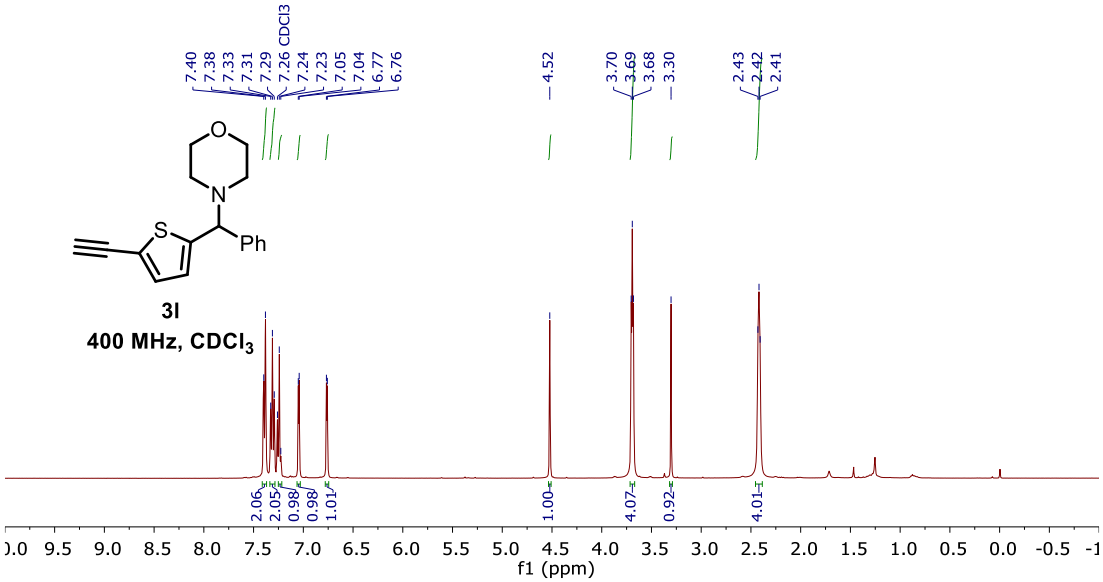
^{13}C NMR spectrum of **3j**



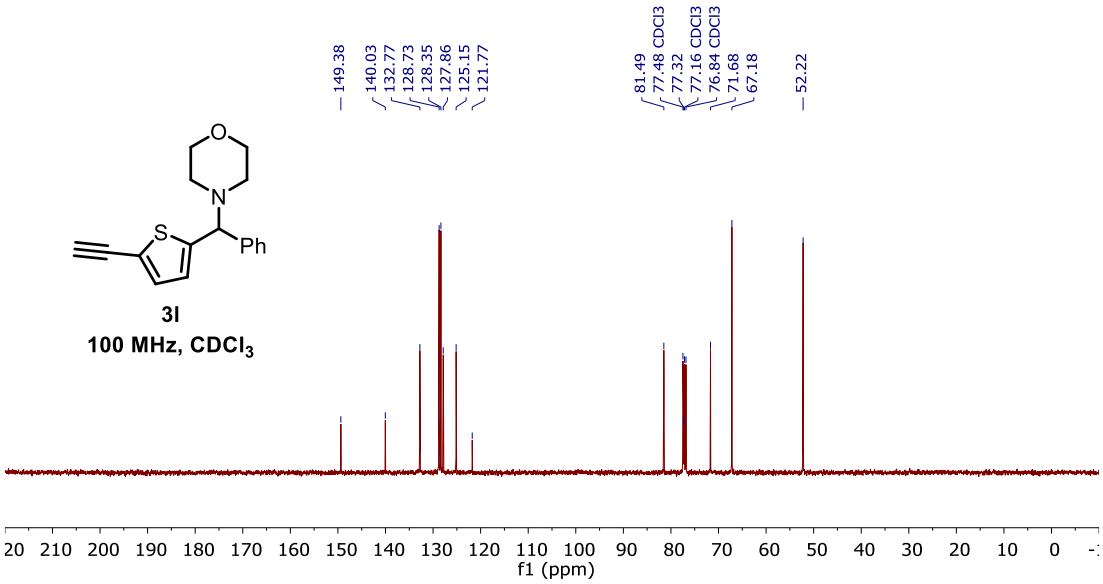
^{1}H NMR spectrum of **3k**



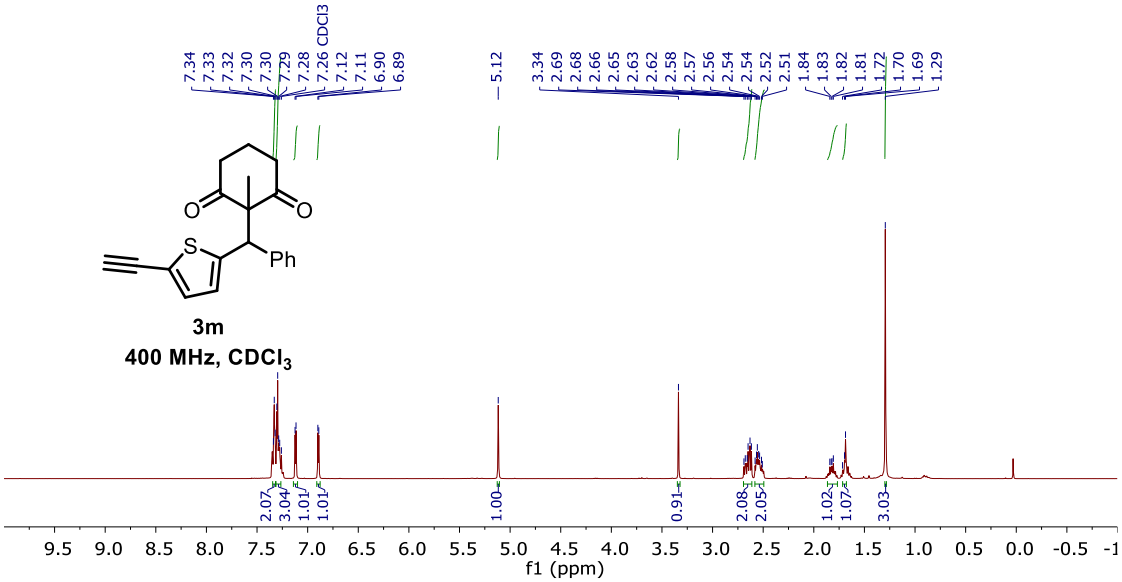
^{13}C NMR spectrum of **3k**



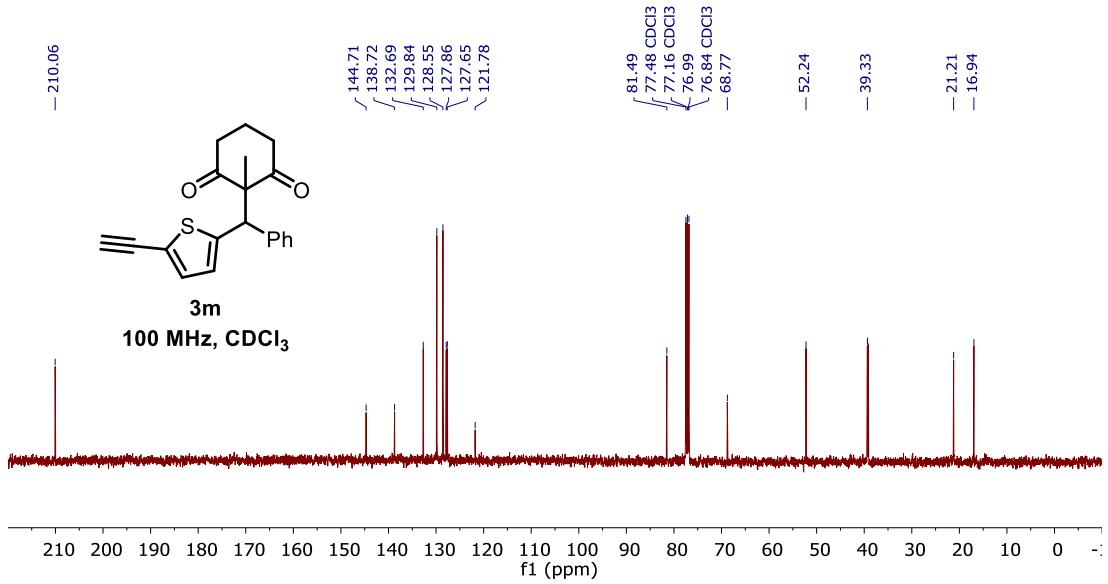
^{1}H NMR spectrum of **3l**



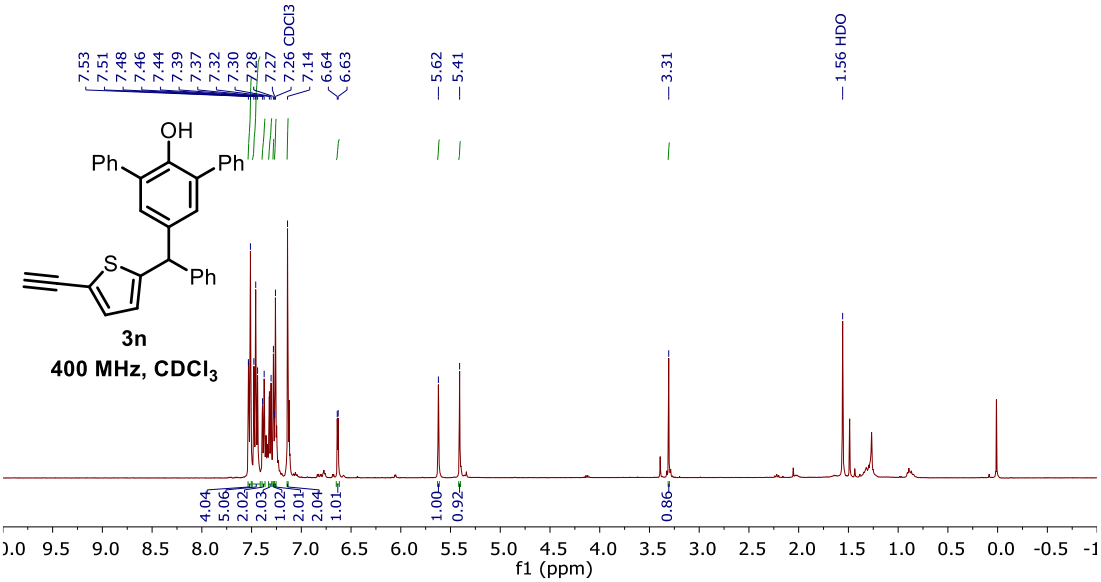
^{13}C NMR spectrum of **3l**



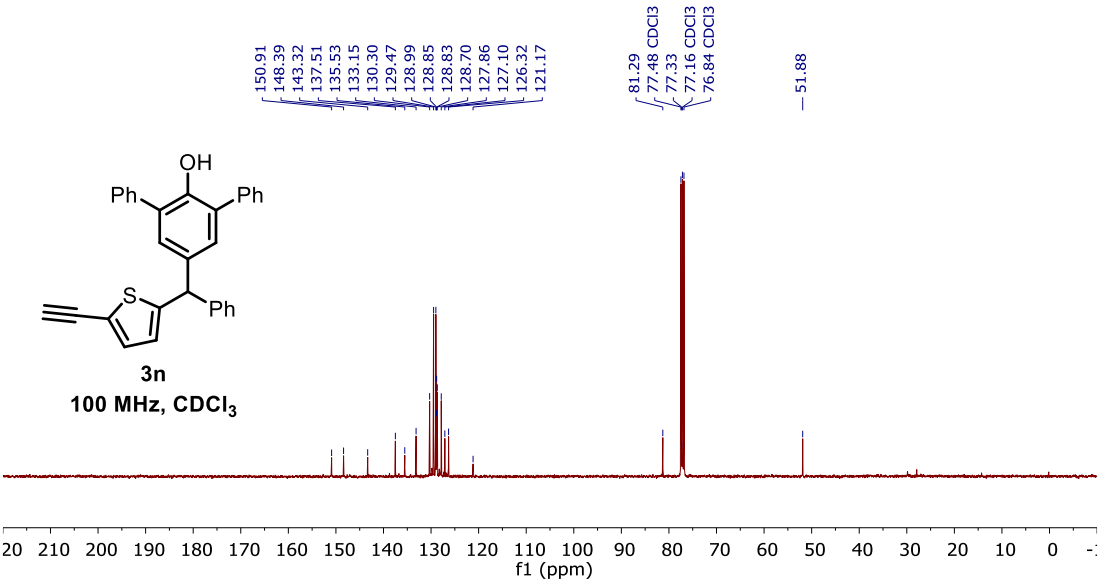
^{1}H NMR spectrum of **3m**



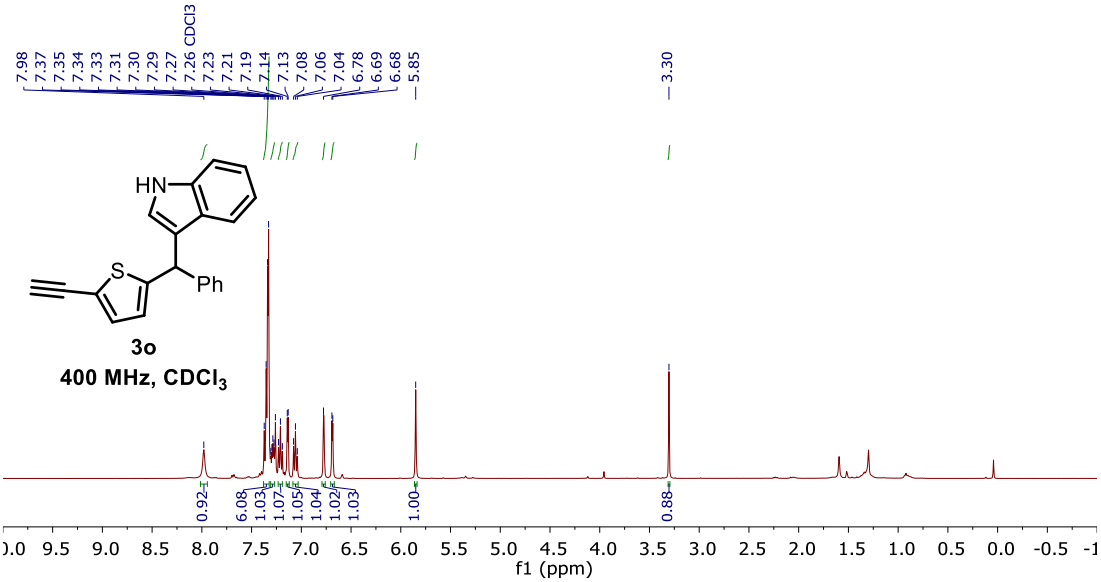
^{13}C NMR spectrum of **3m**



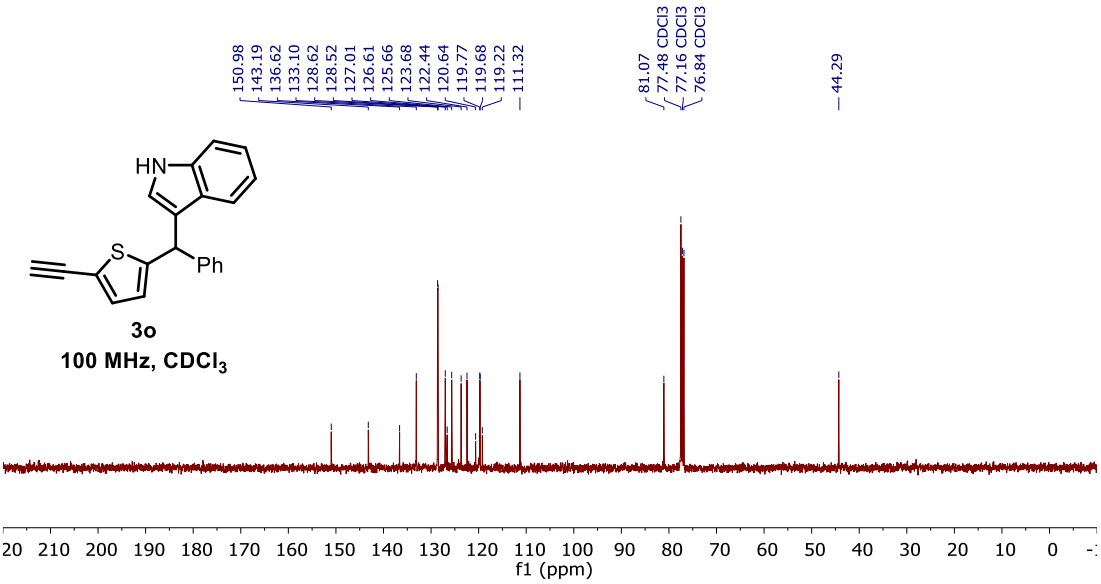
^{1}H NMR spectrum of **3n**



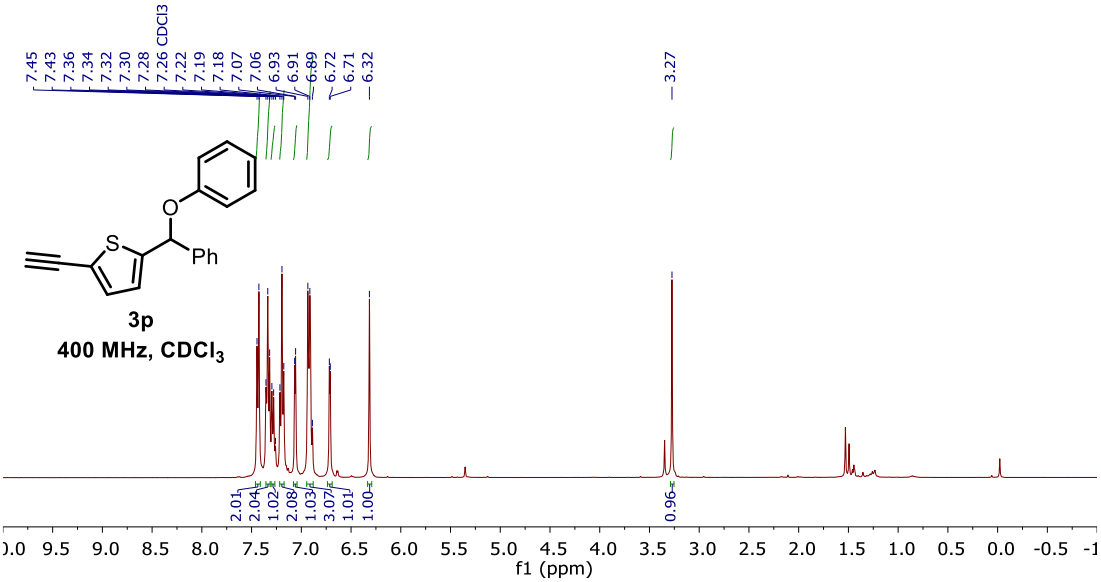
^{13}C NMR spectrum of **3n**



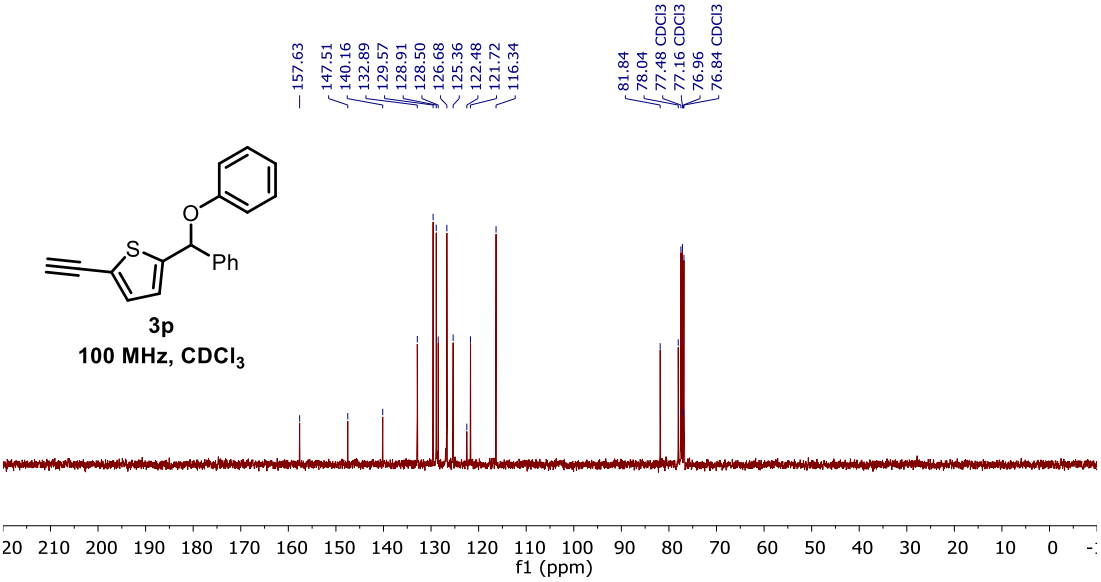
^{1}H NMR spectrum of **3o**



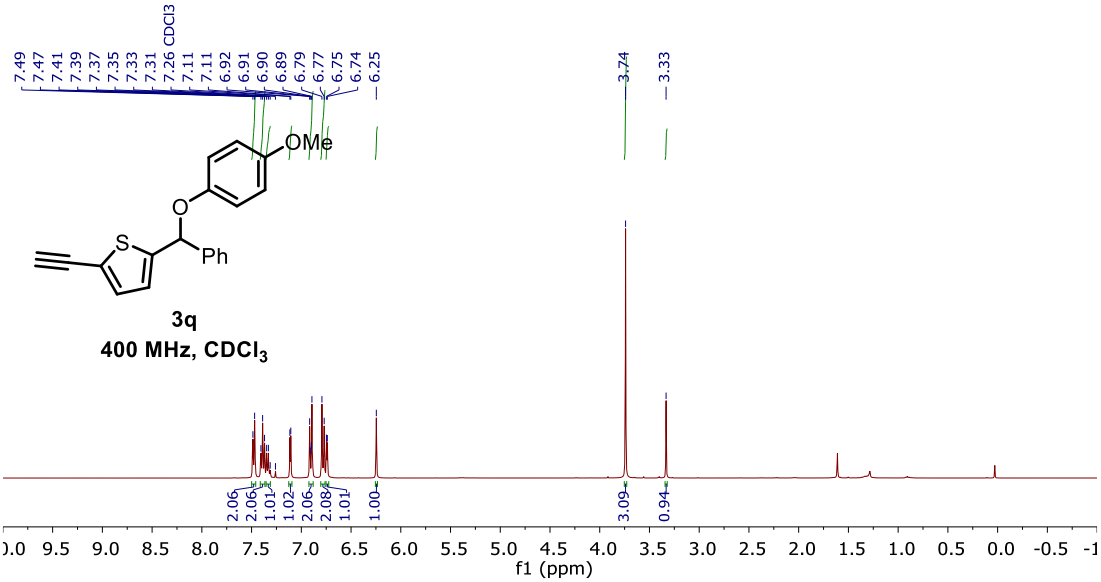
^{13}C NMR spectrum of **3o**



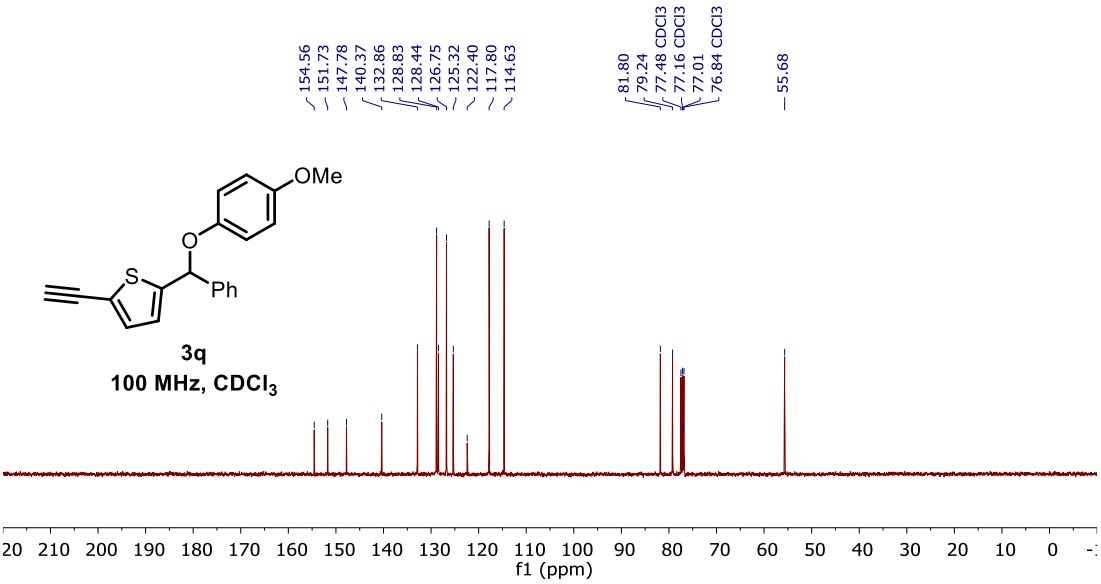
^{1}H NMR spectrum of **3p**



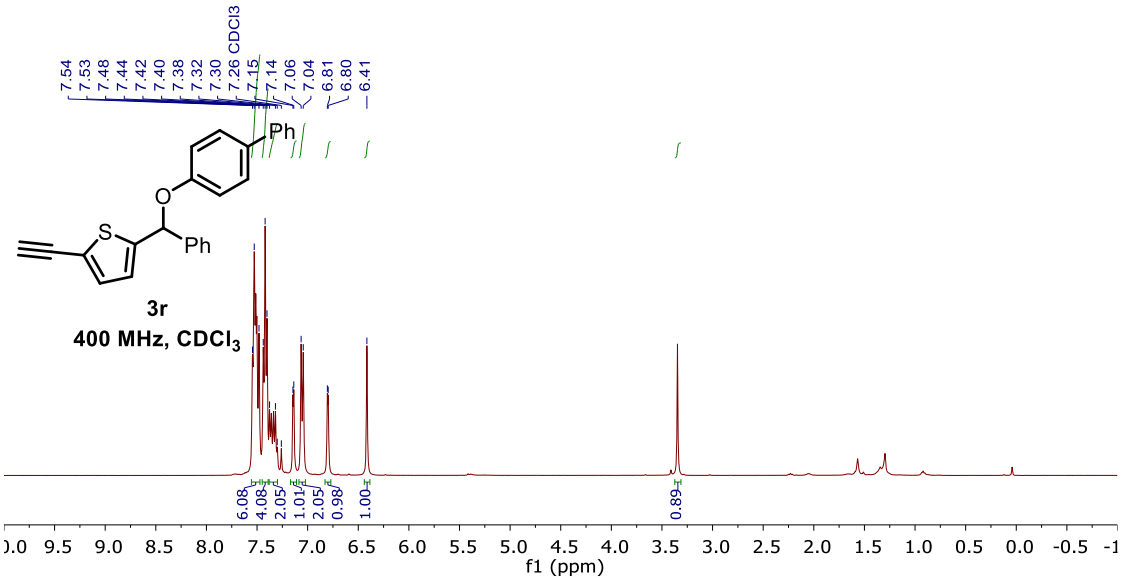
^{13}C NMR spectrum of **3p**



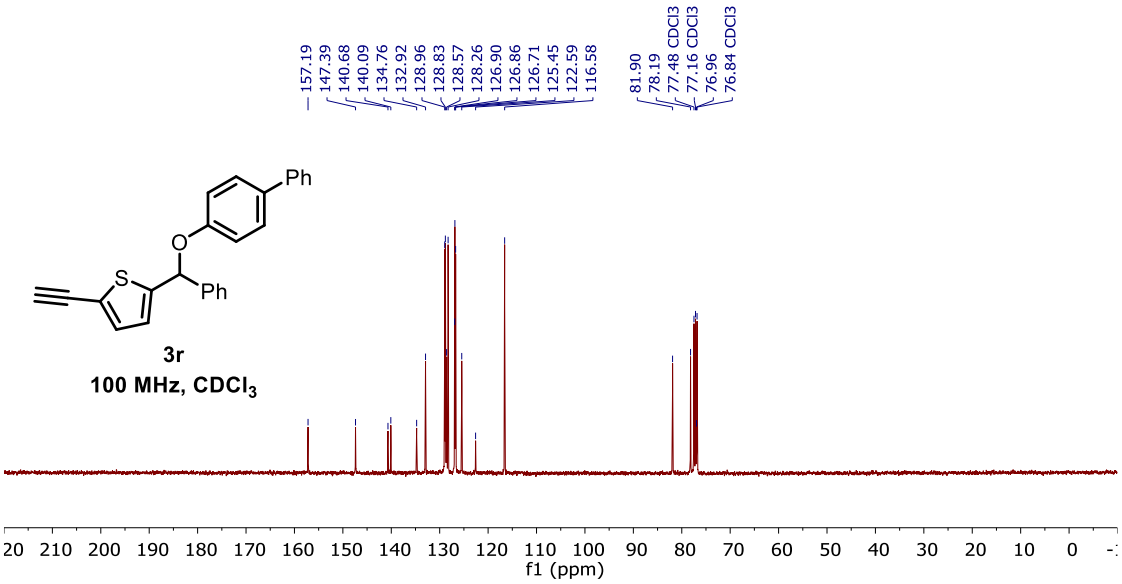
^{1}H NMR spectrum of **3q**



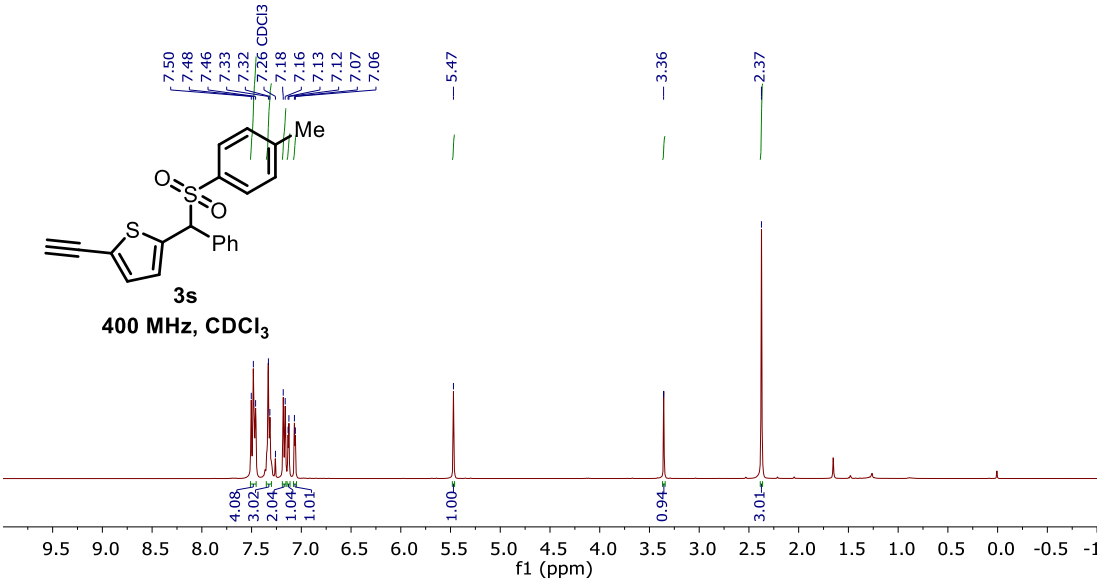
^{13}C NMR spectrum of **3q**



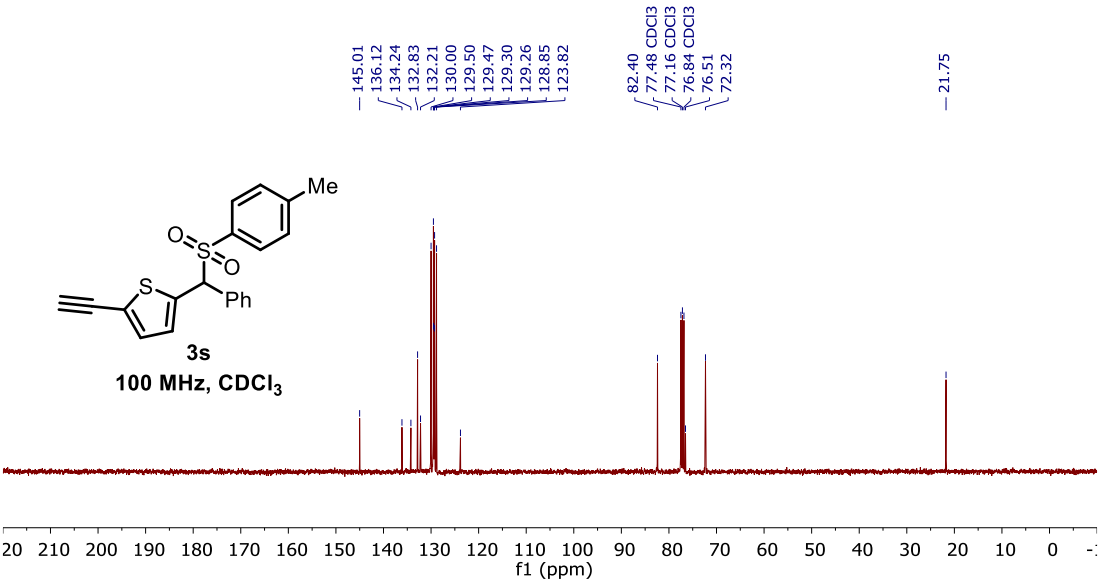
^{1}H NMR spectrum of **3r**



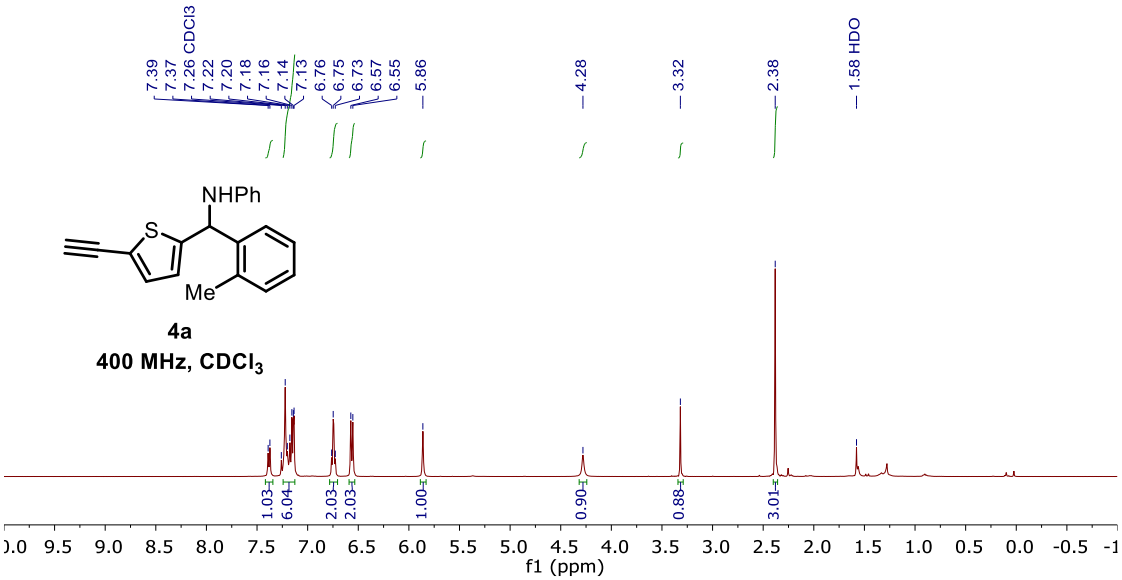
^{13}C NMR spectrum of **3r**



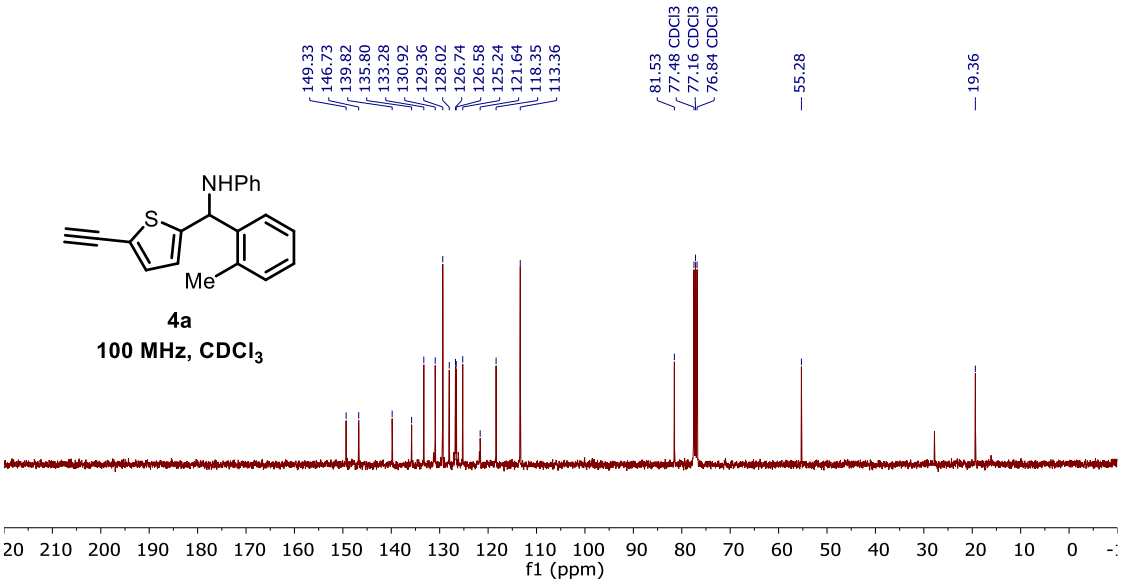
^{1}H NMR spectrum of **3s**



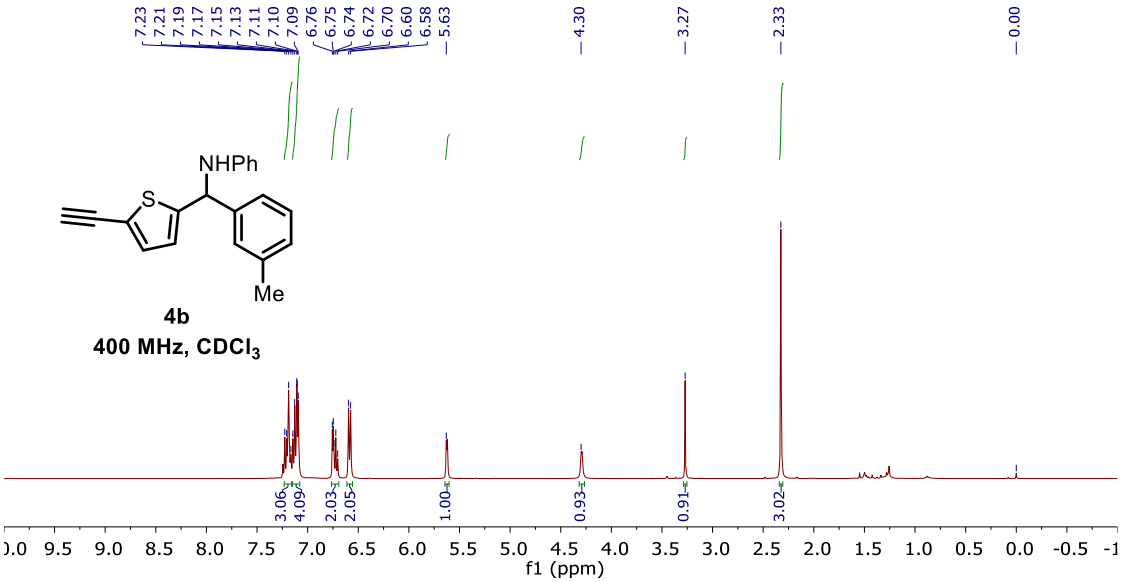
^{13}C NMR spectrum of **3s**



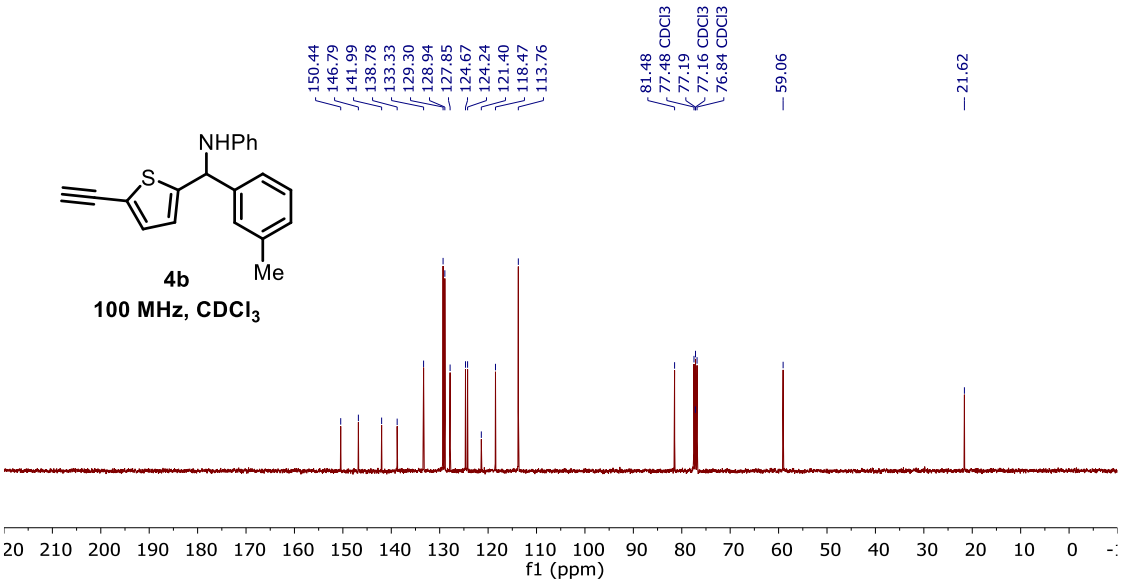
^{1}H NMR spectrum of **4a**



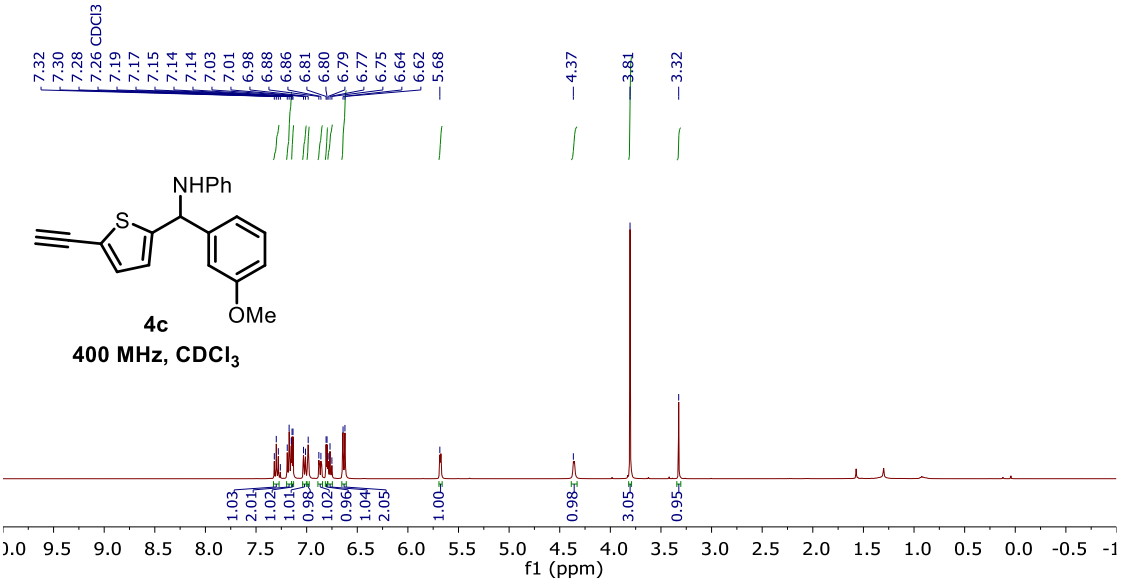
^{13}C NMR spectrum of **4a**



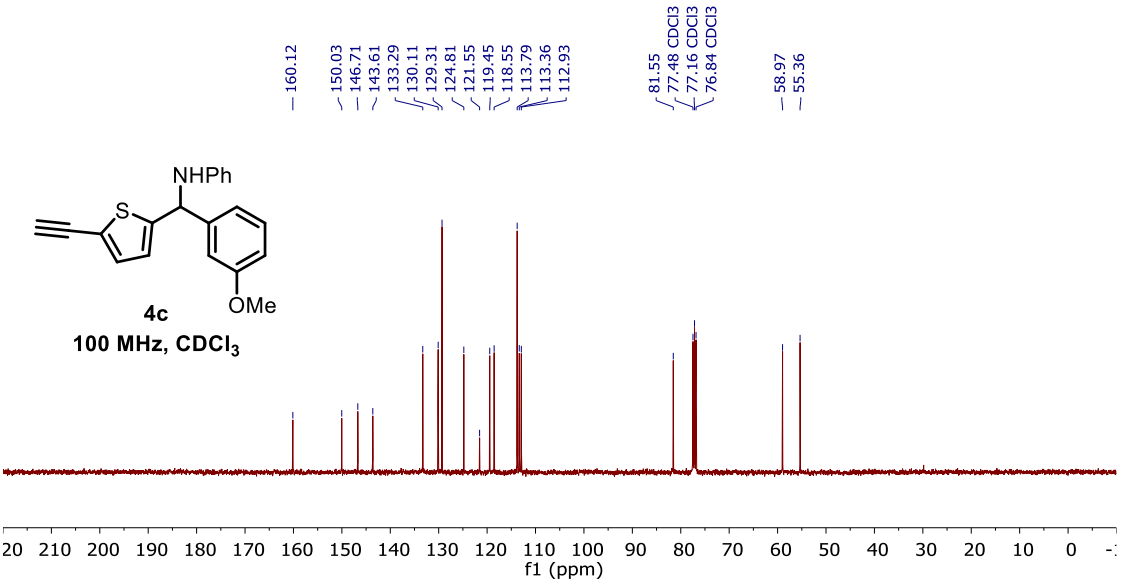
^{1}H NMR spectrum of **4b**



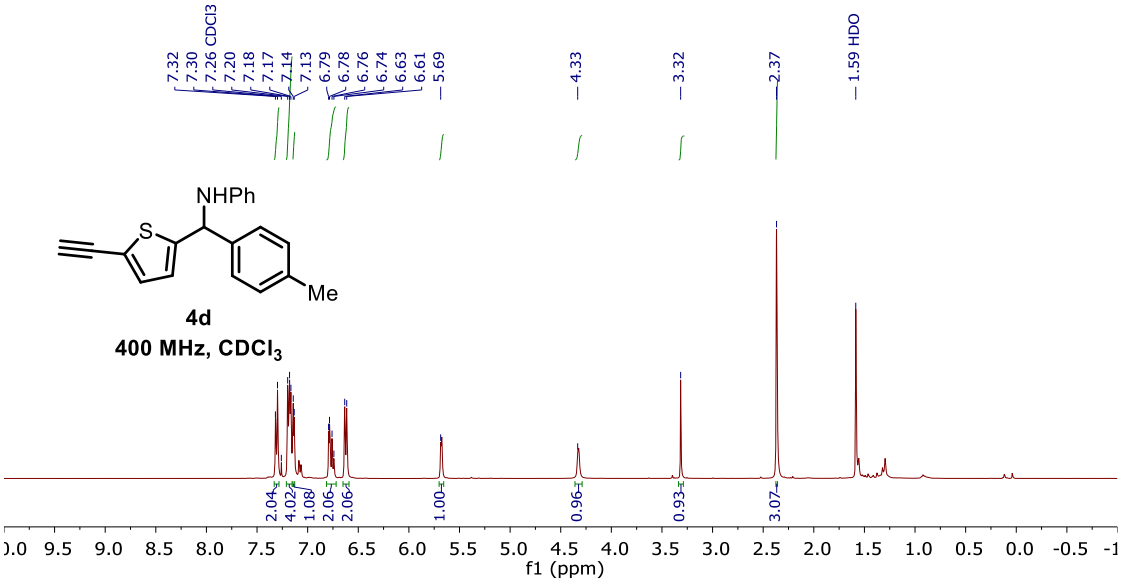
^{13}C NMR spectrum of **4b**



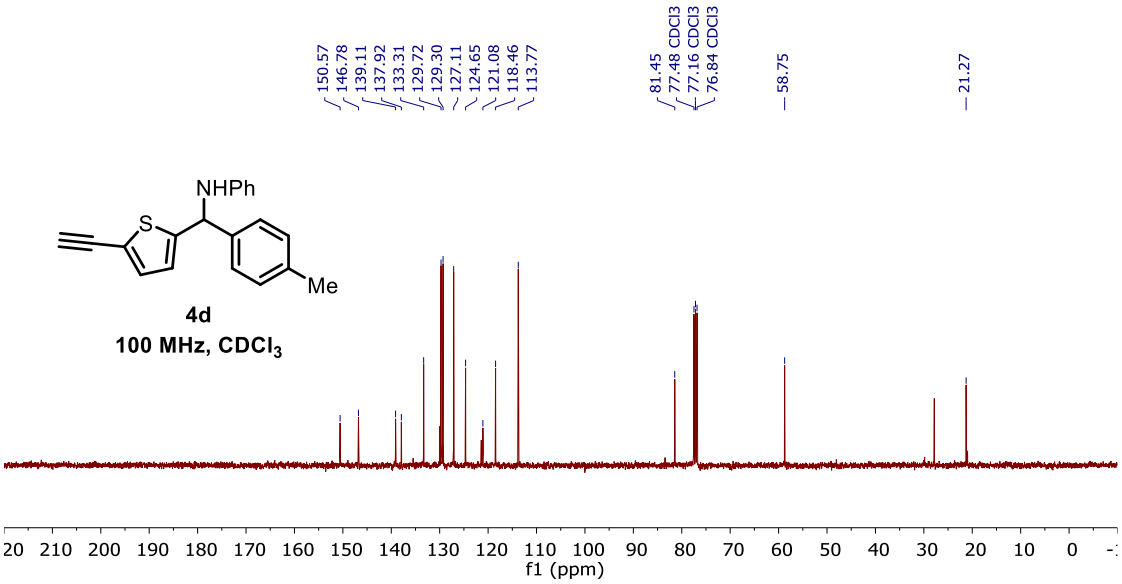
^{1}H NMR spectrum of **4c**



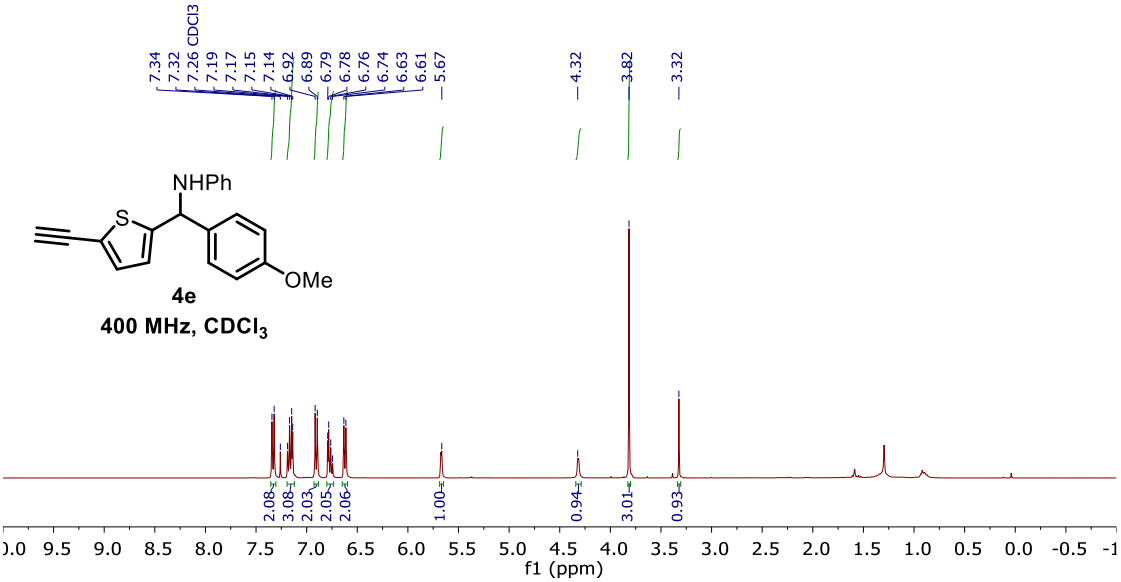
^{13}C NMR spectrum of **4c**



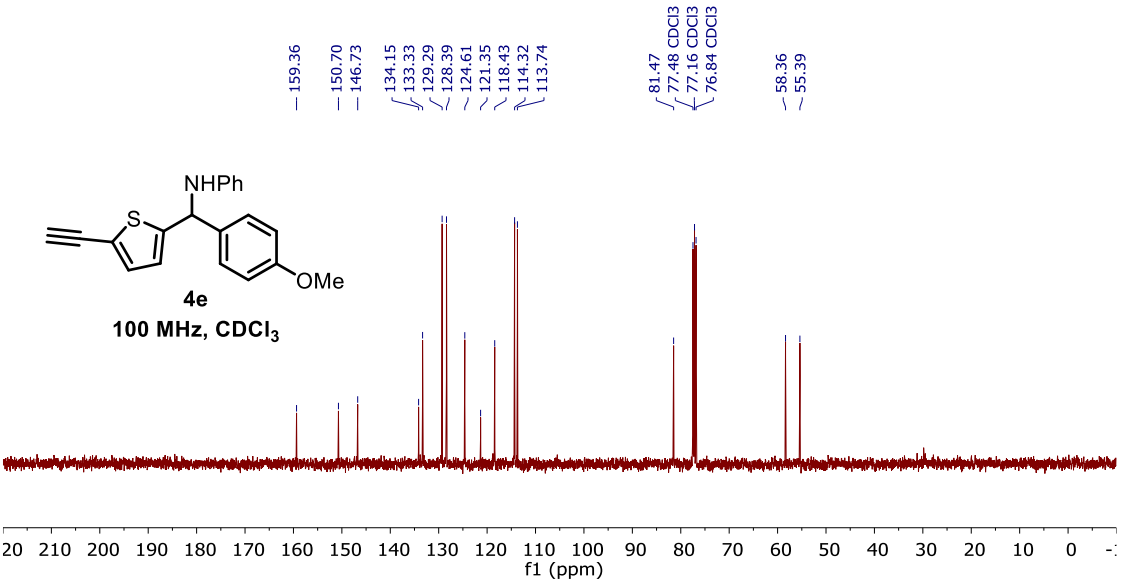
^{1}H NMR spectrum of **4d**



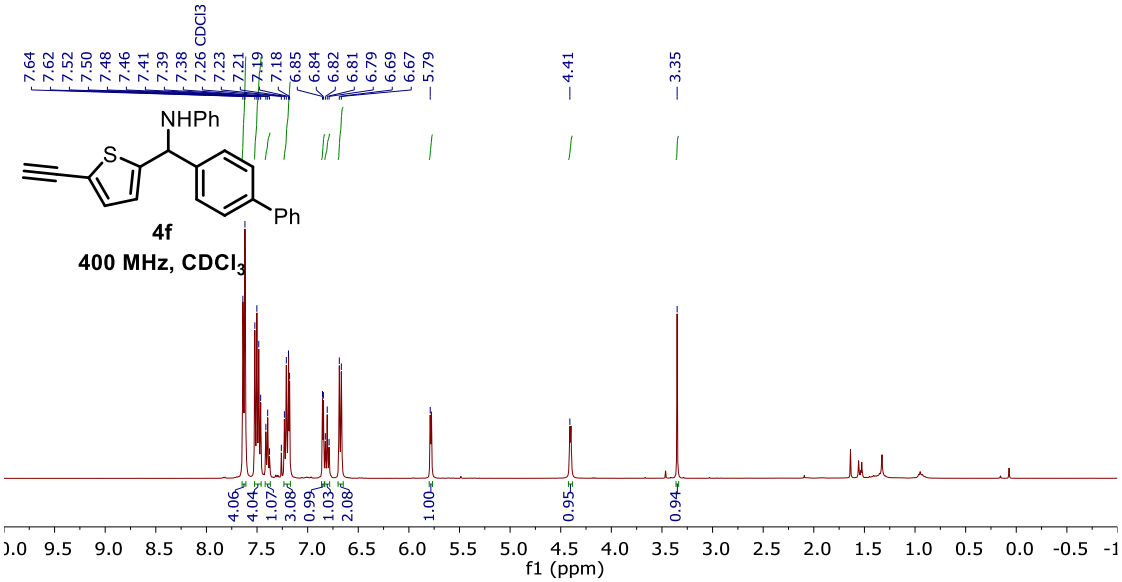
^{13}C NMR spectrum of **4d**



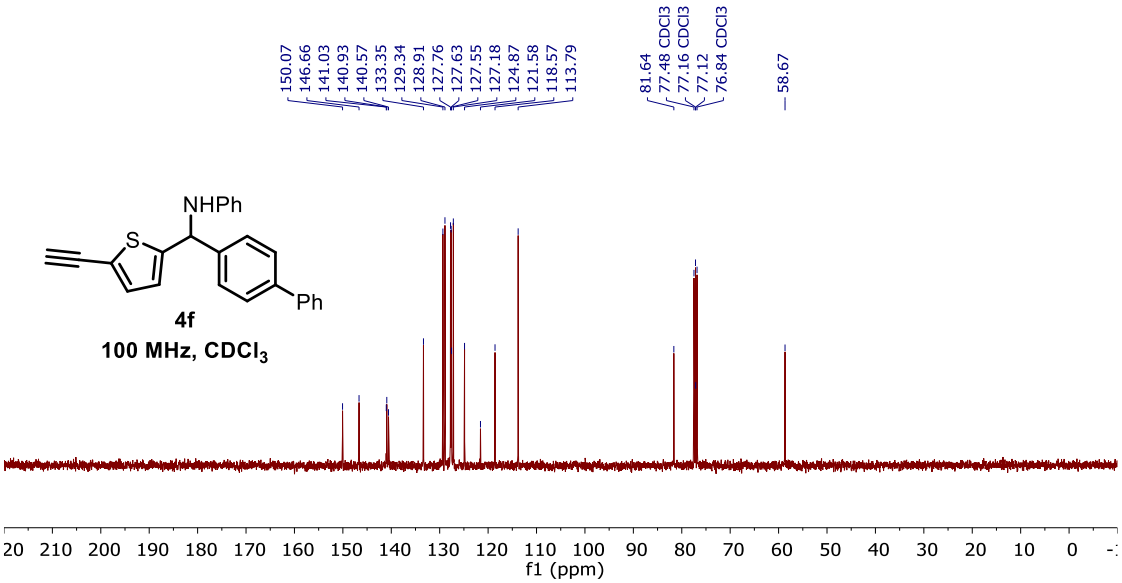
^{1}H NMR spectrum of **4e**



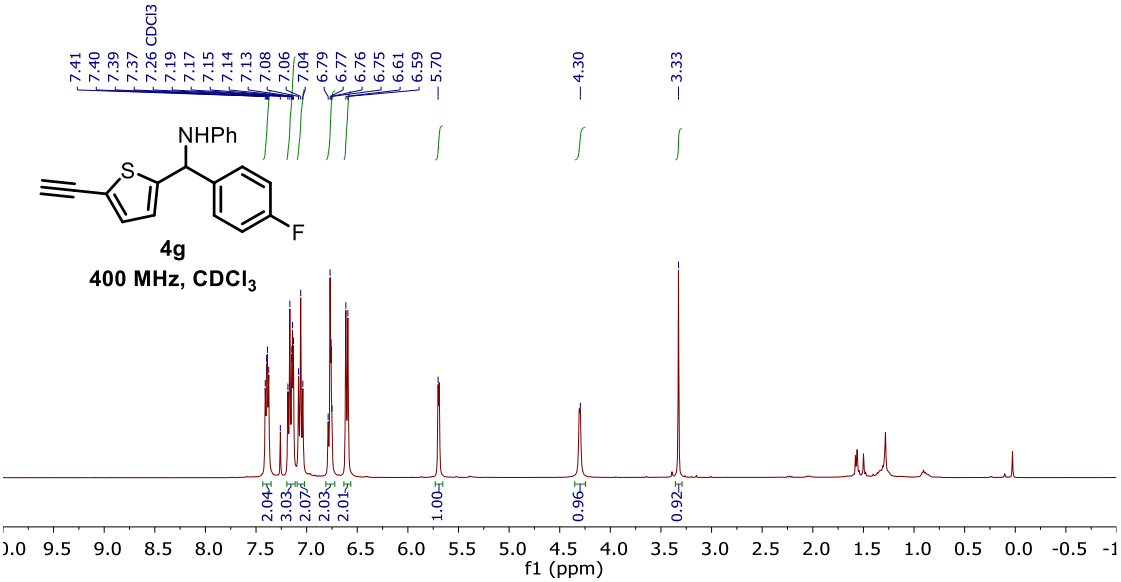
^{13}C NMR spectrum of **4e**



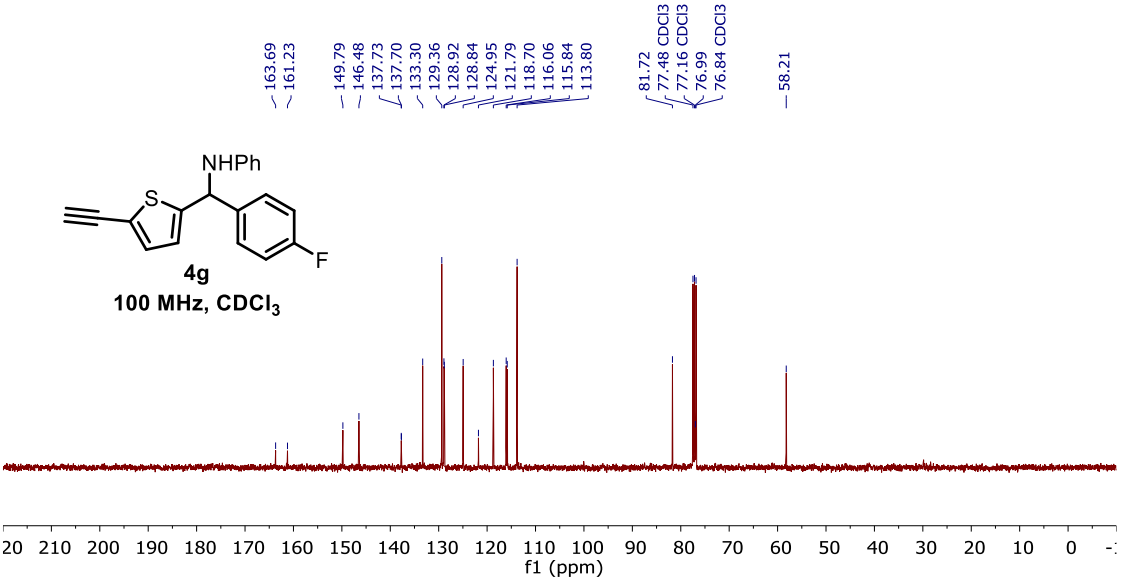
^{1}H NMR spectrum of **4f**



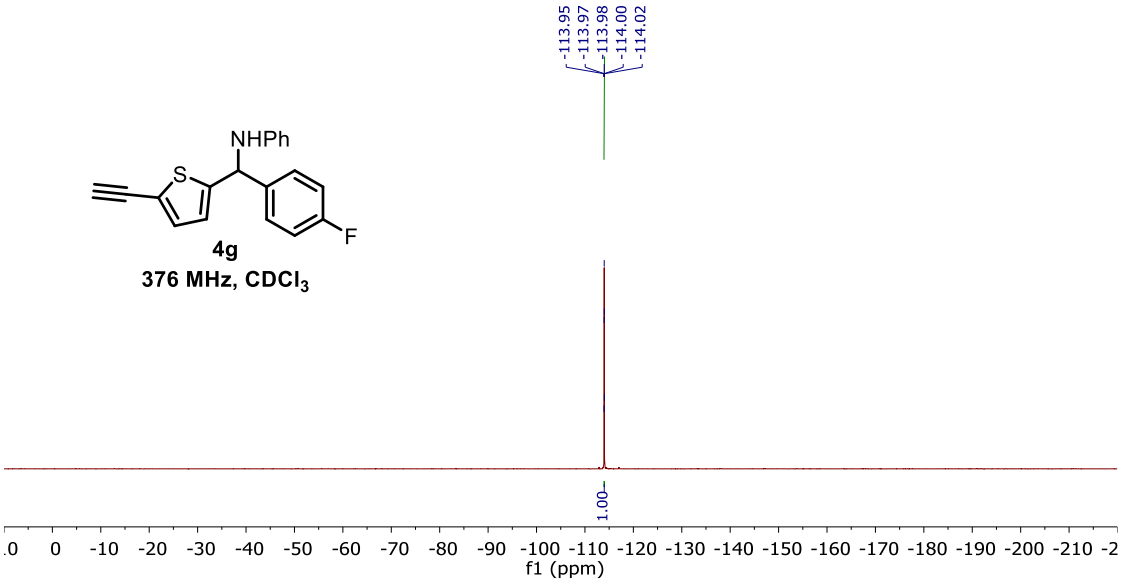
^{13}C NMR spectrum of **4f**



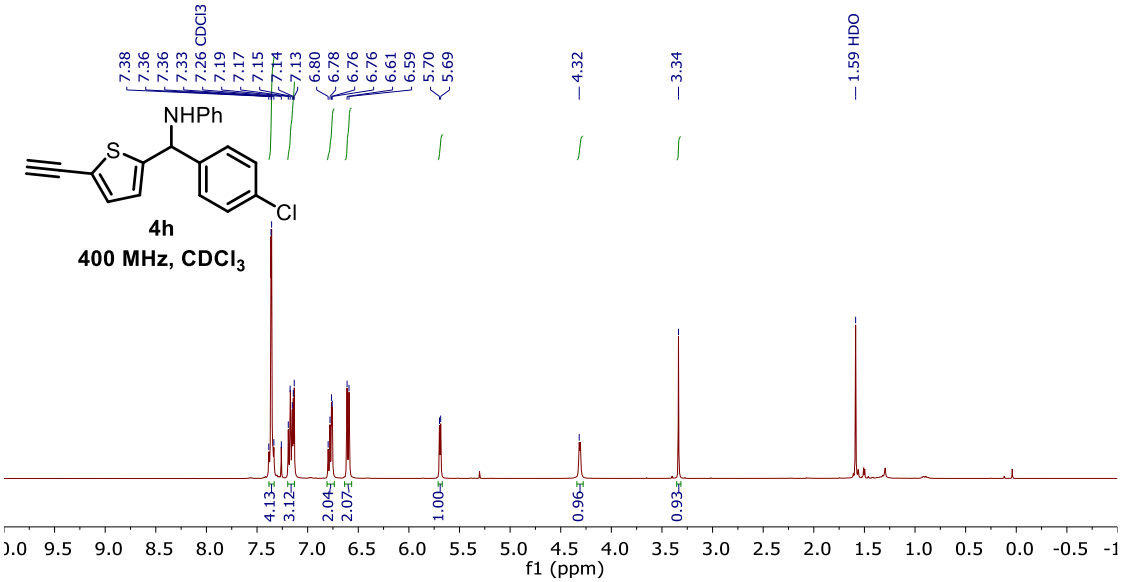
^{1}H NMR spectrum of **4g**



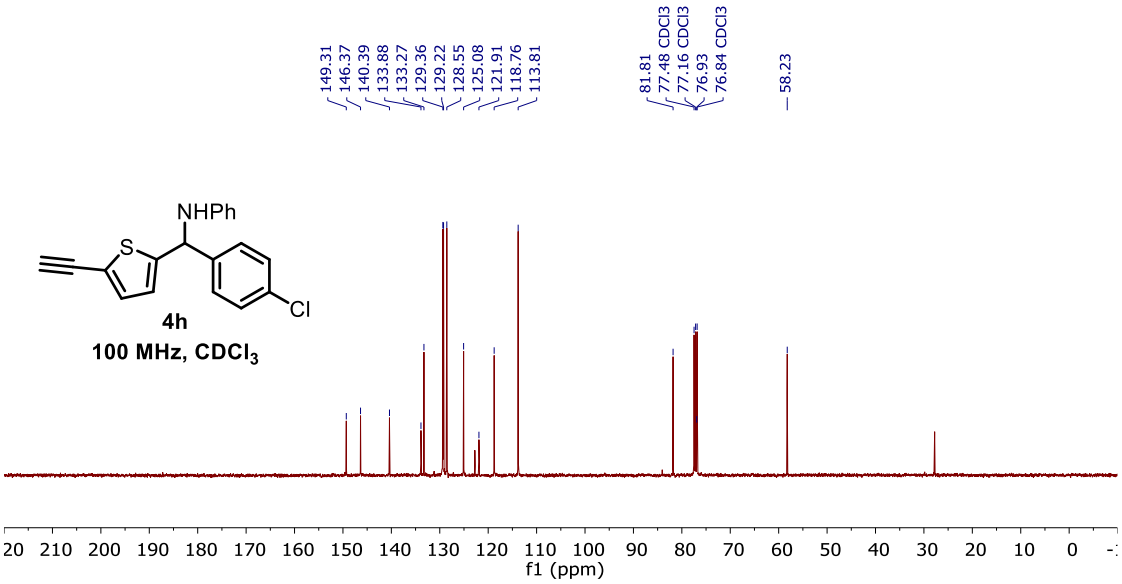
^{13}C NMR spectrum of **4g**



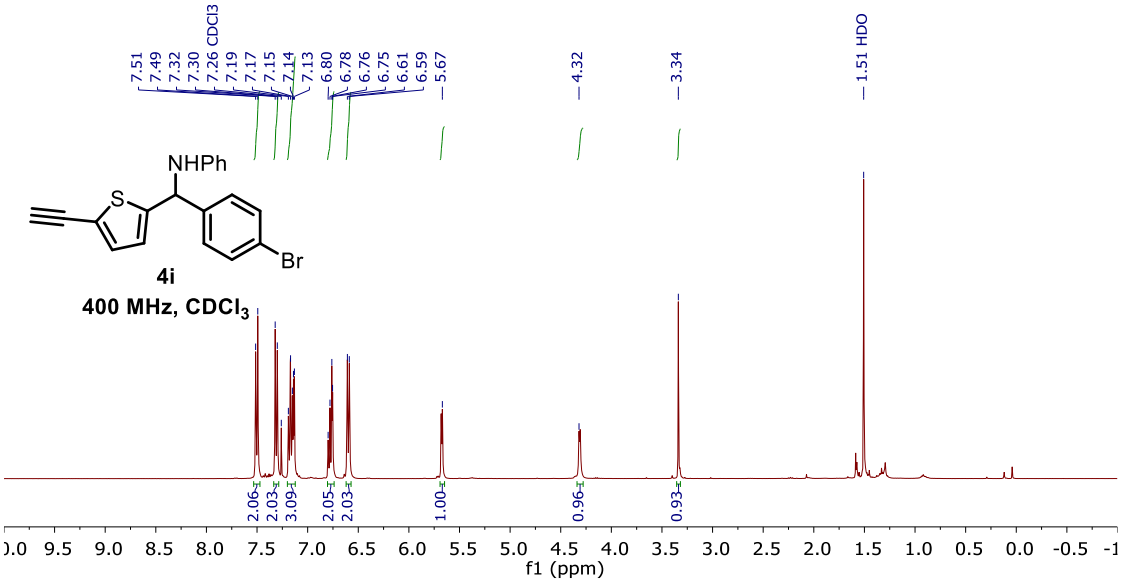
^{19}F NMR spectrum of **4g**



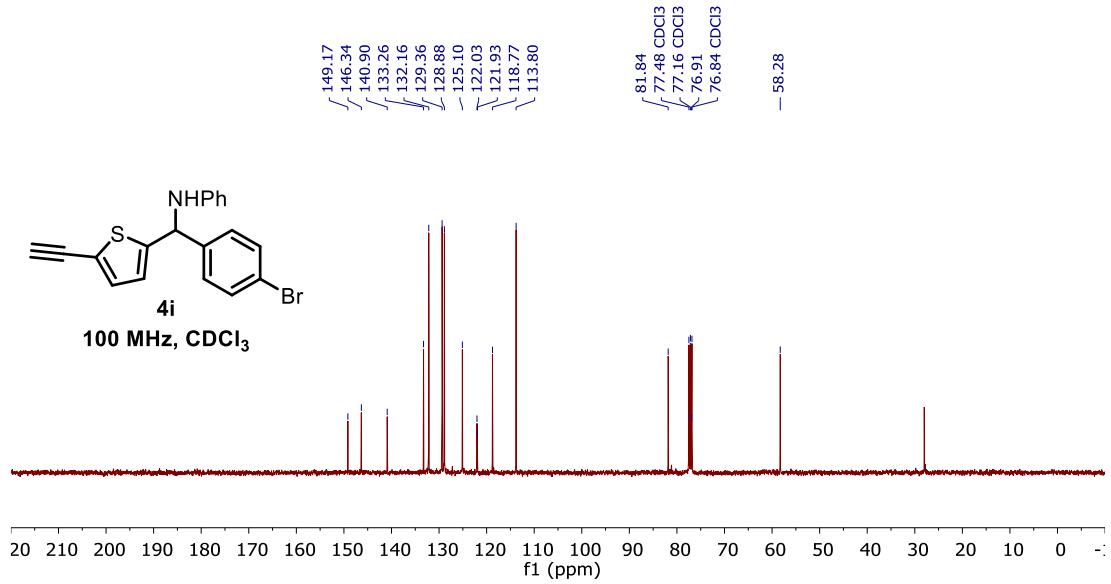
^{1}H NMR spectrum of **4h**



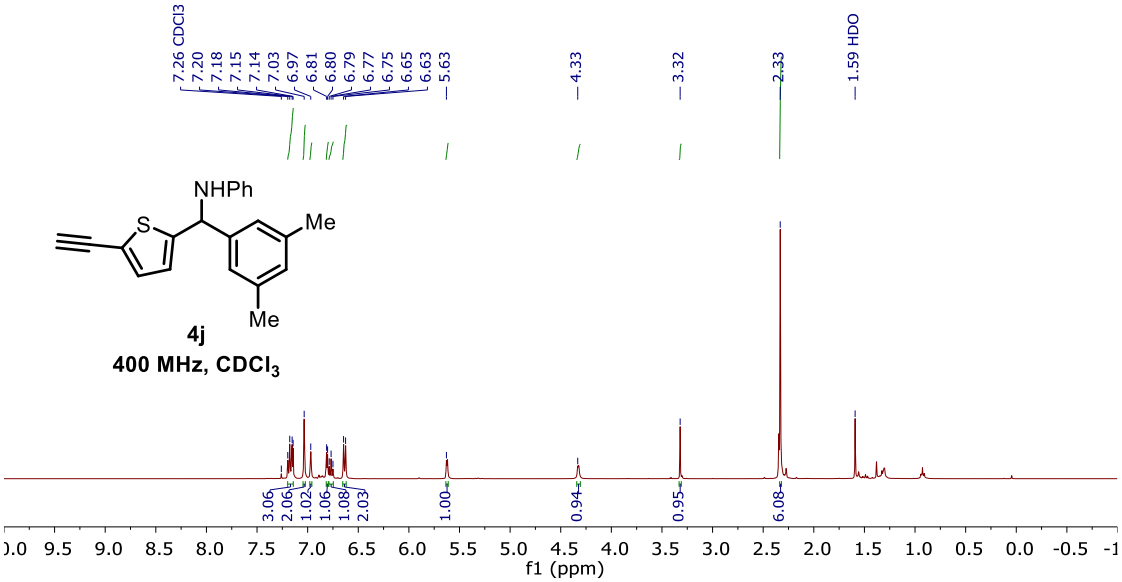
^{13}C NMR spectrum of **4h**



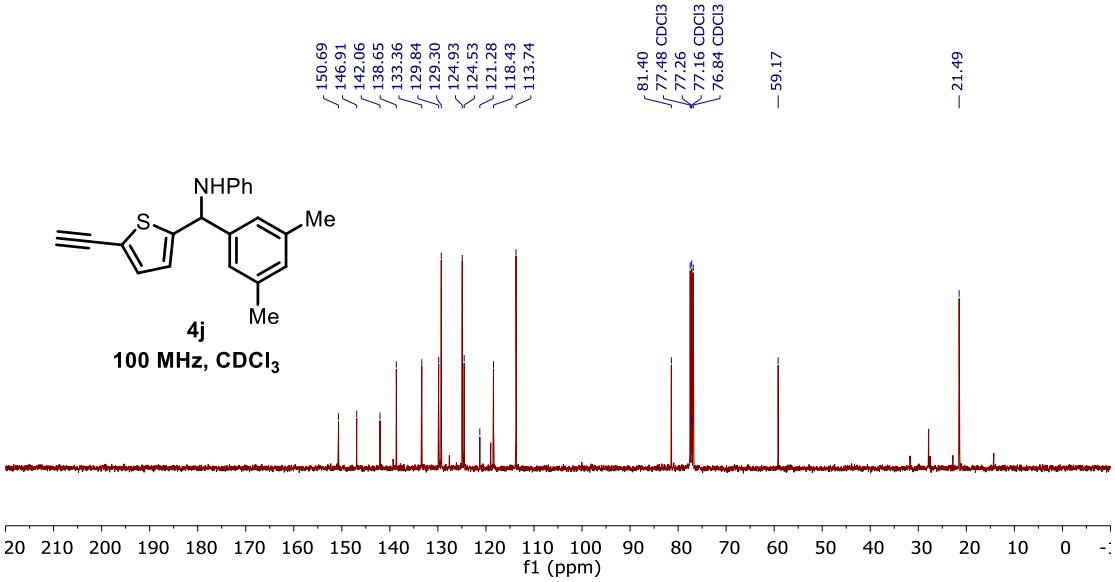
^{1}H NMR spectrum of **4i**



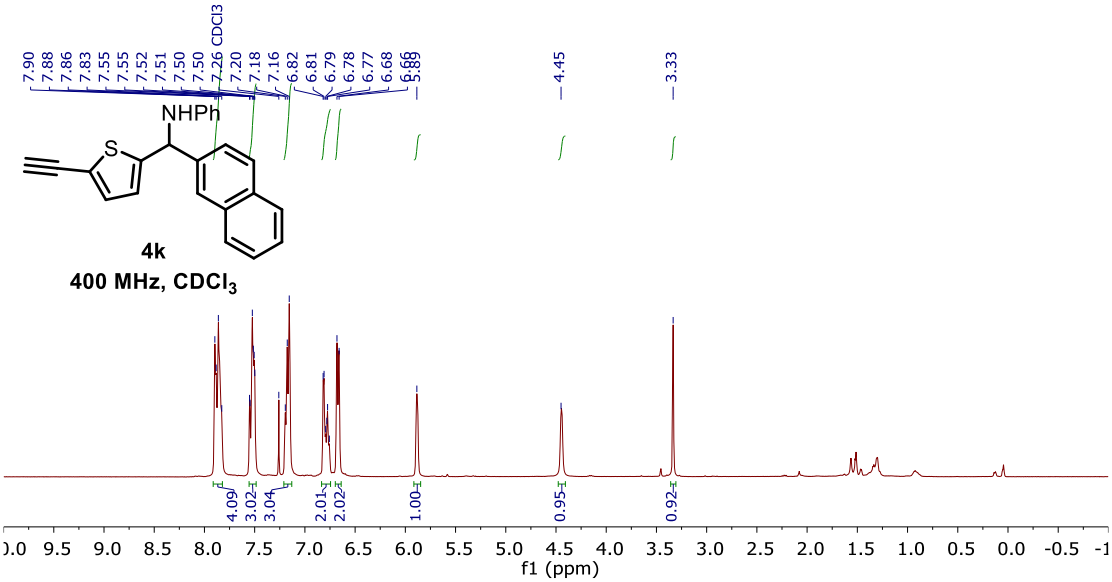
^{13}C NMR spectrum of **4i**



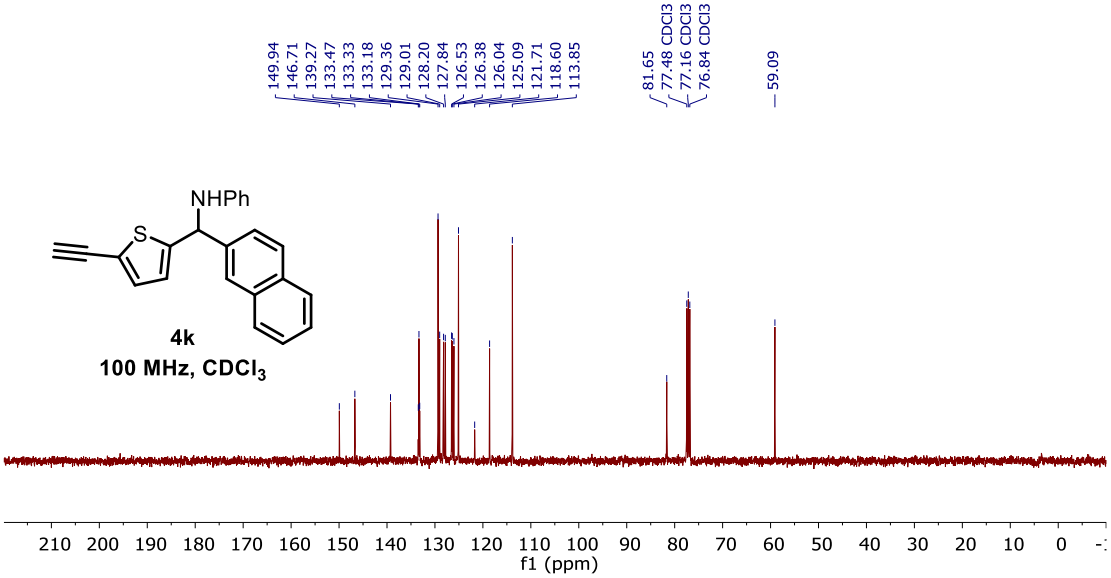
^{1}H NMR spectrum of **4j**



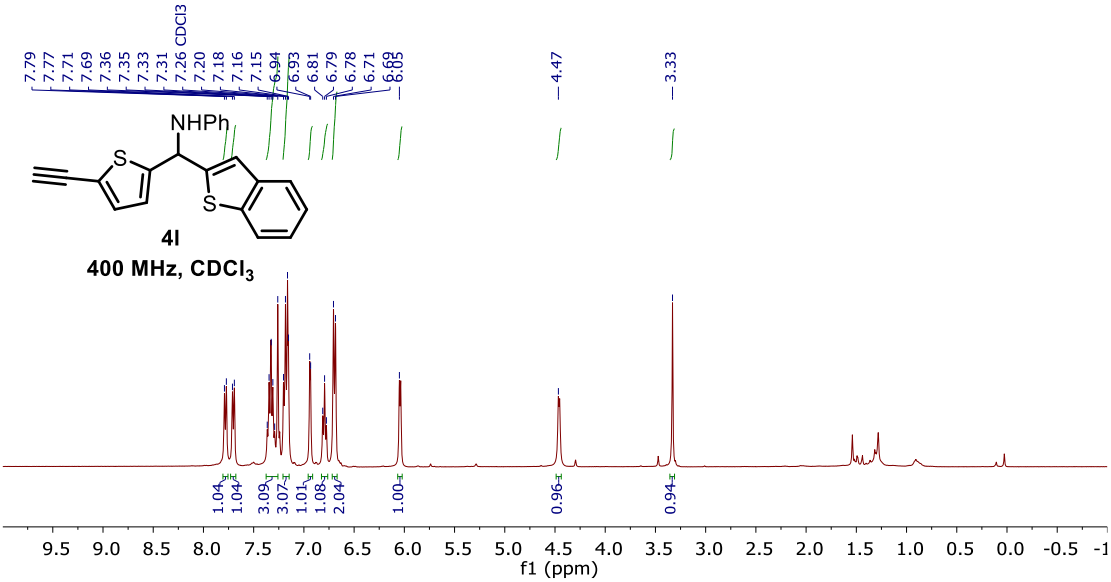
^{13}C NMR spectrum of **4j**



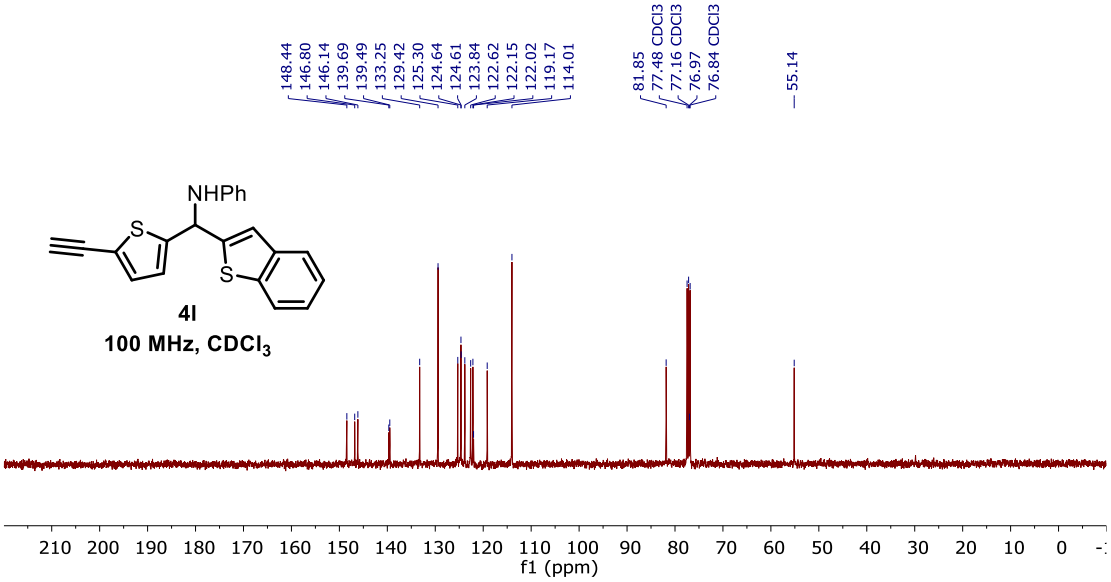
^{1}H NMR spectrum of **4k**



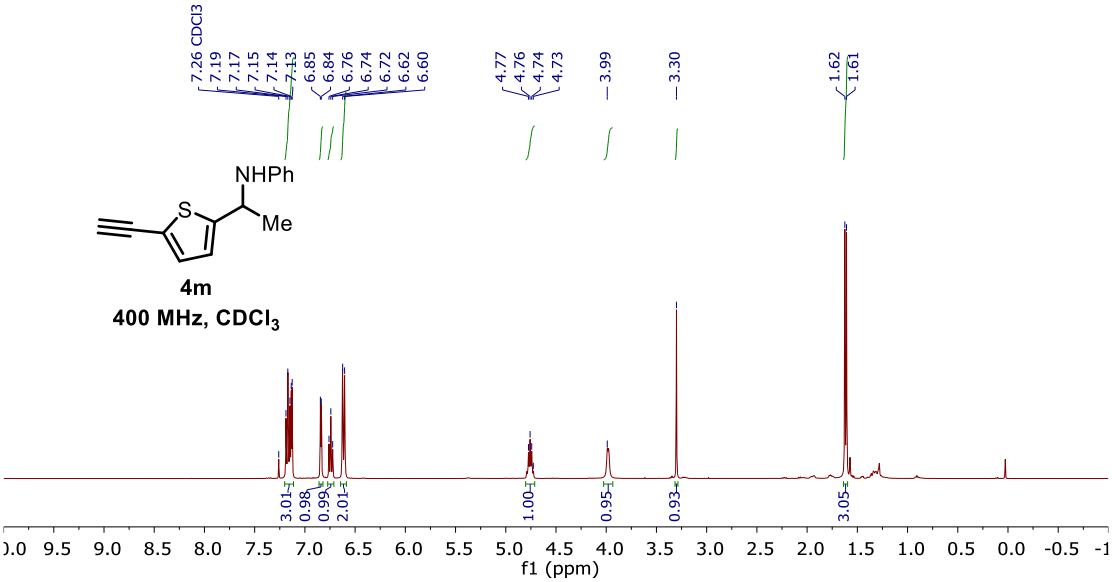
^{13}C NMR spectrum of **4k**



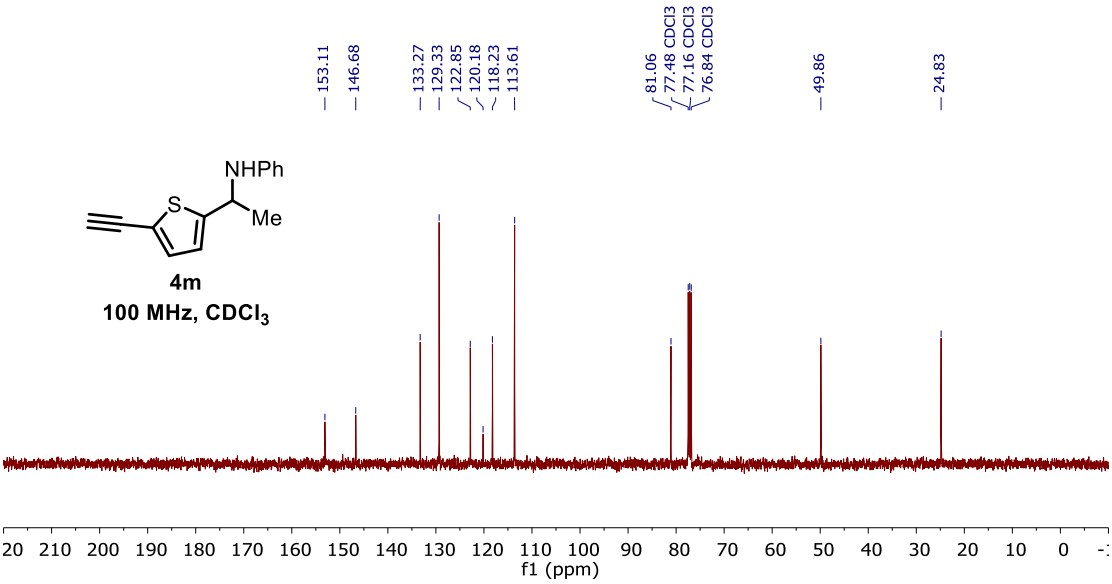
^{1}H NMR spectrum of **4l**



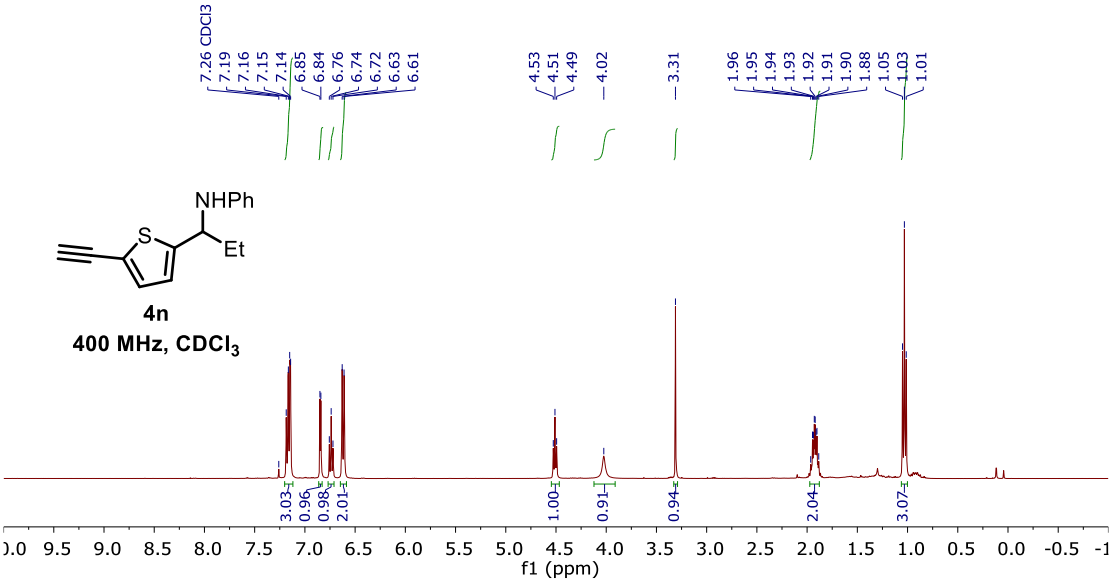
^{13}C NMR spectrum of **4l**



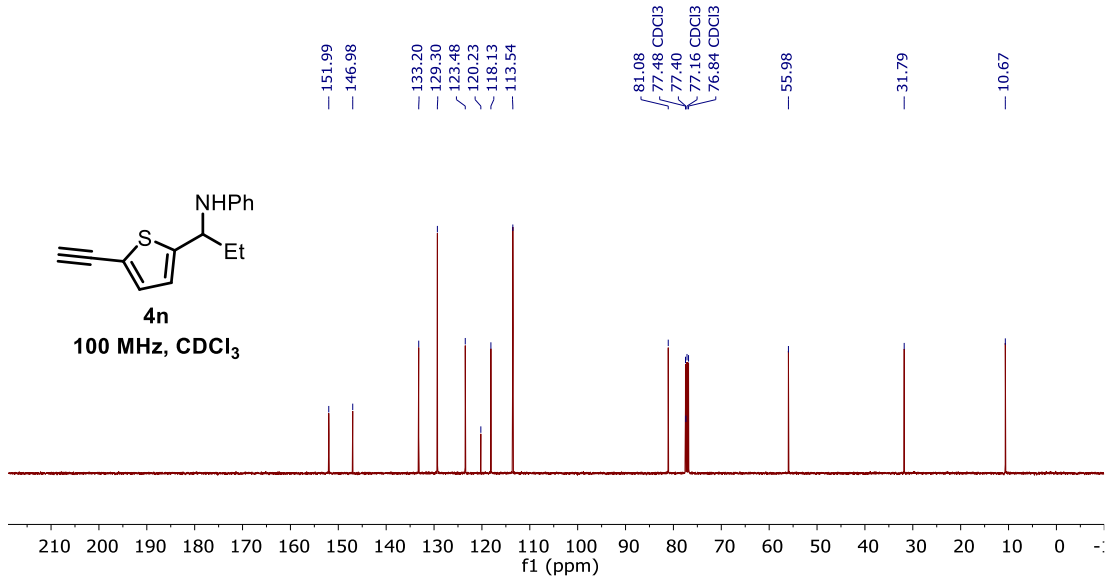
^{1}H NMR spectrum of **4m**



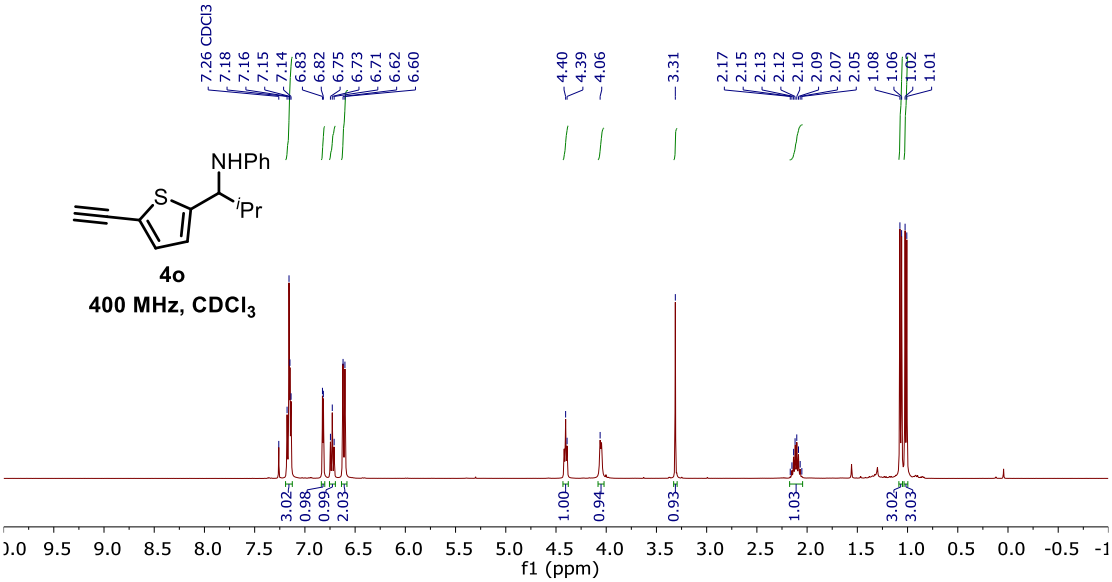
^{13}C NMR spectrum of **4m**



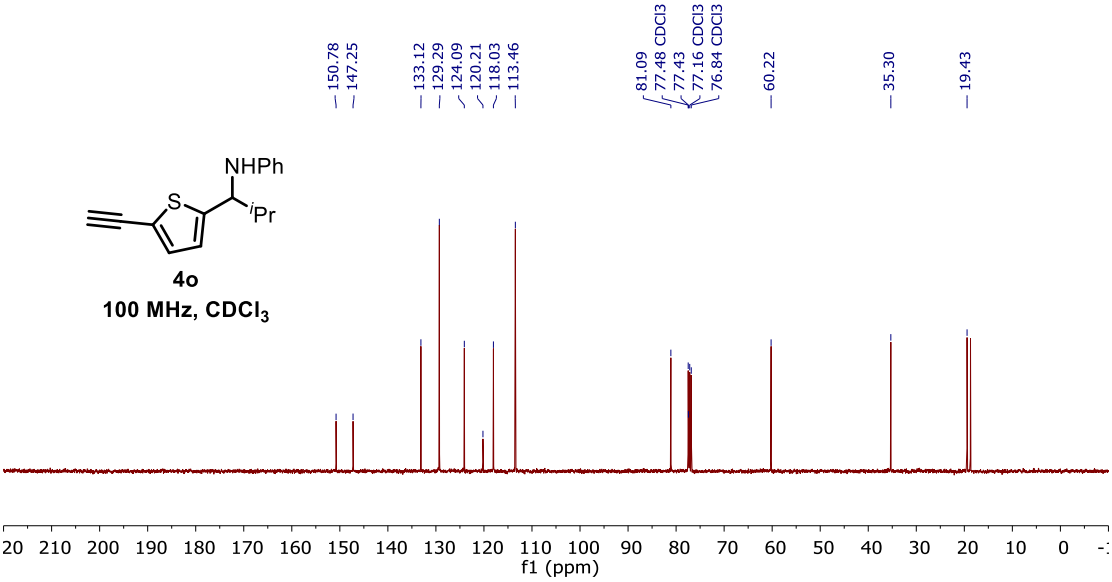
^{1}H NMR spectrum of **4n**



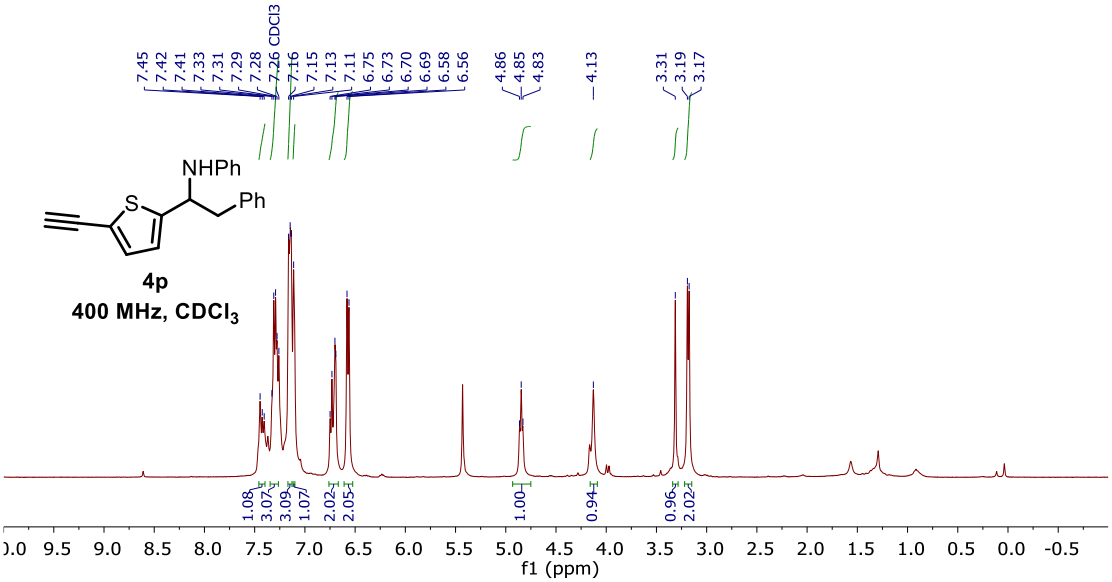
^{13}C NMR spectrum of **4n**



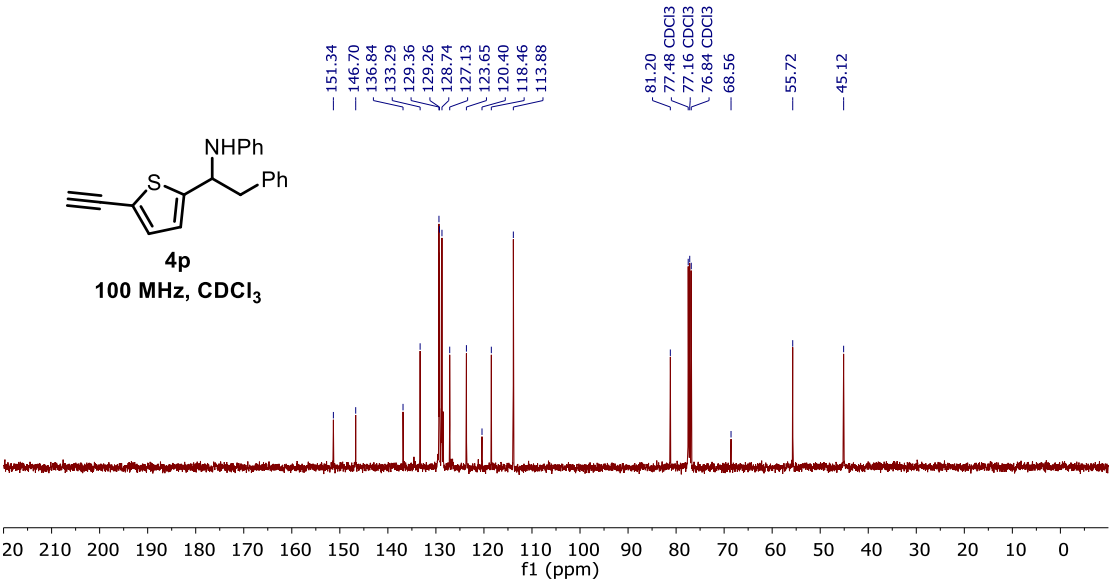
^{1}H NMR spectrum of **4o**



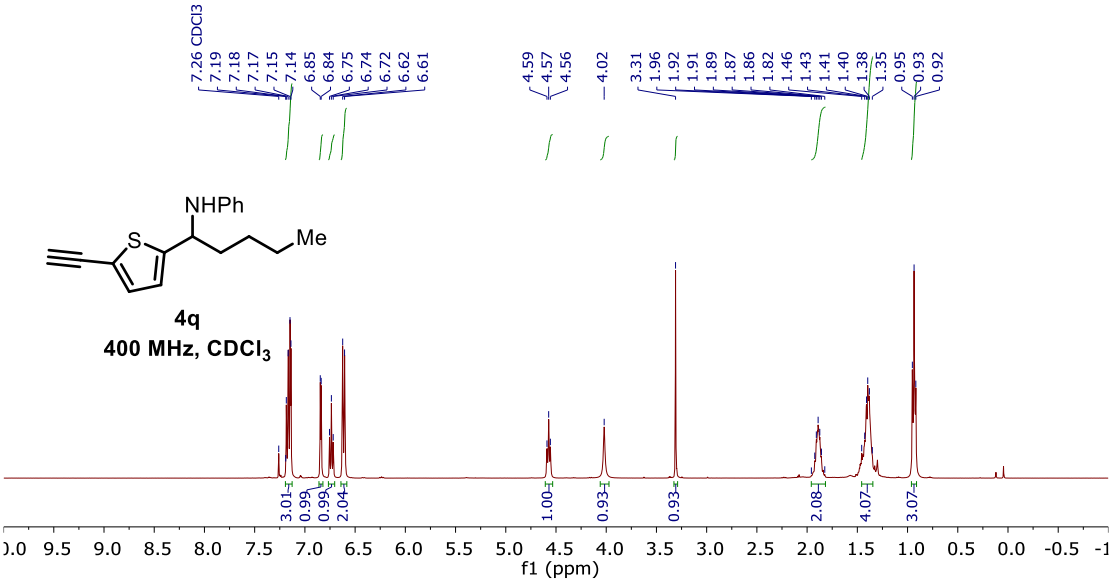
^{13}C NMR spectrum of **4o**



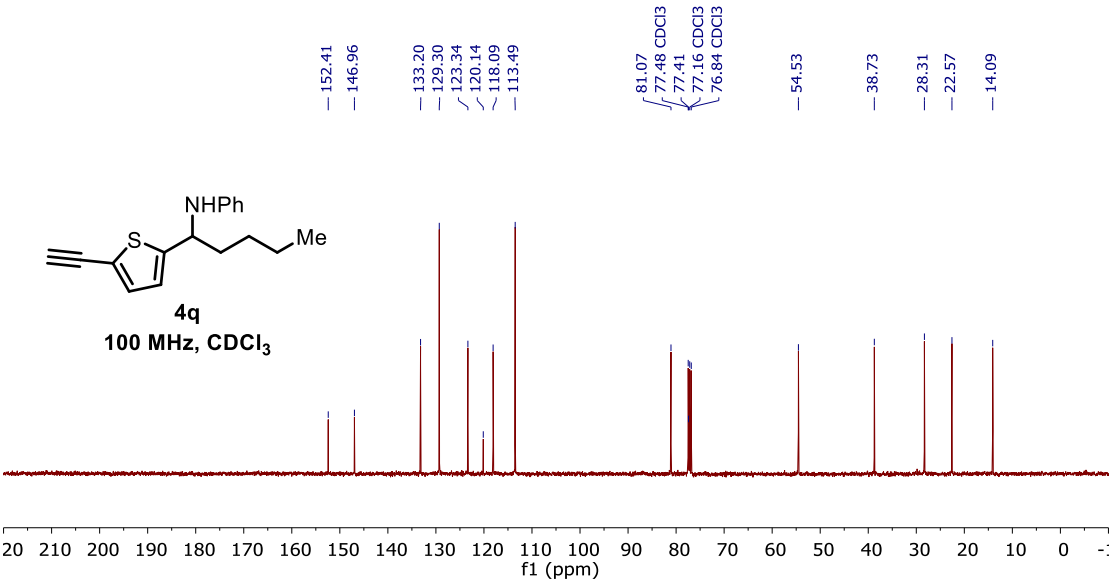
^{1}H NMR spectrum of **4p**



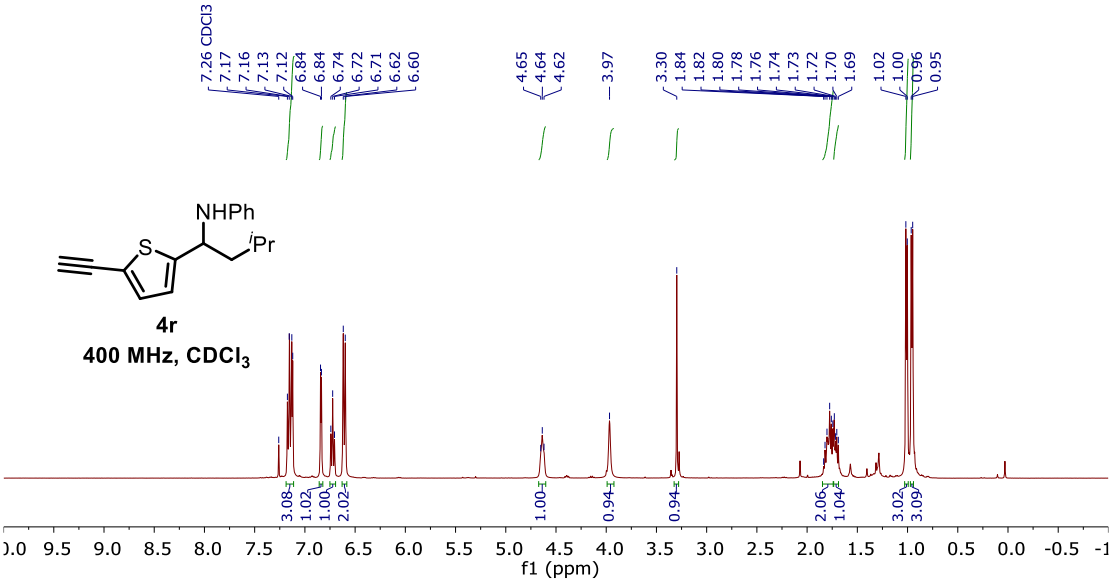
^{13}C NMR spectrum of **4p**



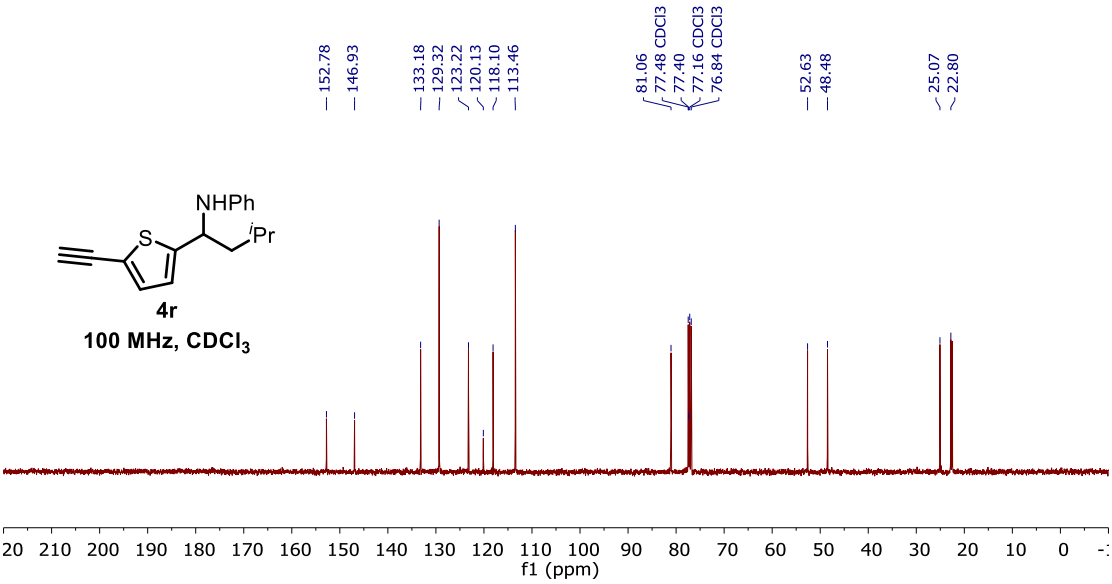
^{1}H NMR spectrum of **4q**



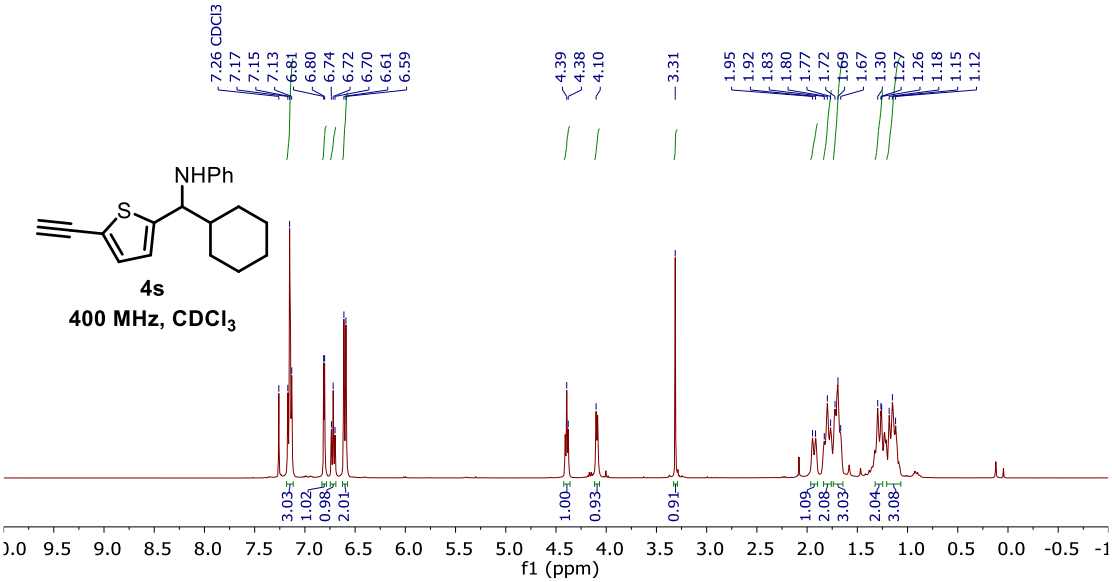
^{13}C NMR spectrum of **4q**



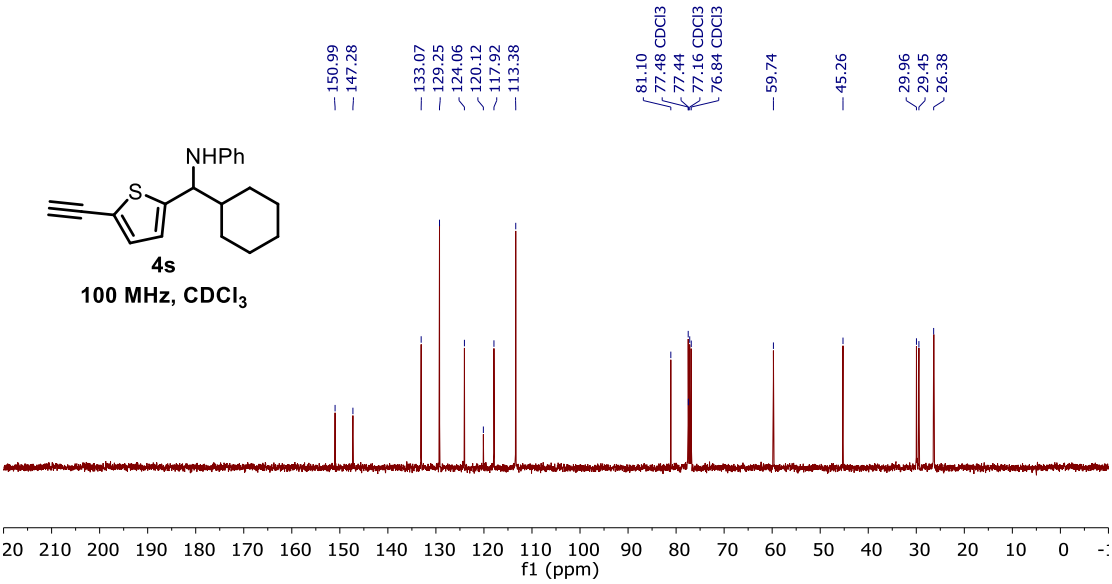
^{1}H NMR spectrum of **4r**



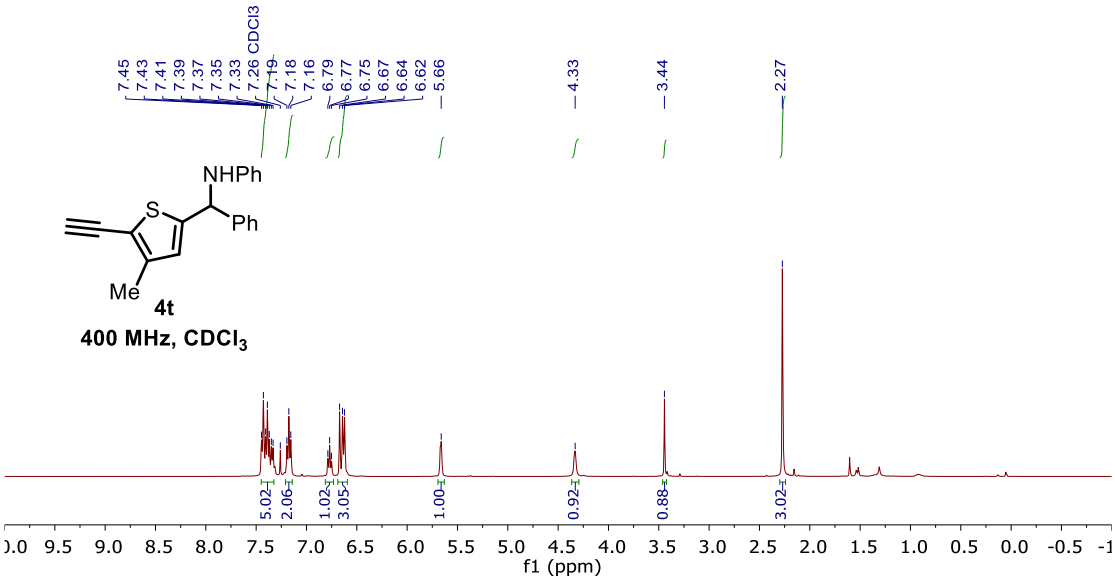
^{13}C NMR spectrum of **4r**



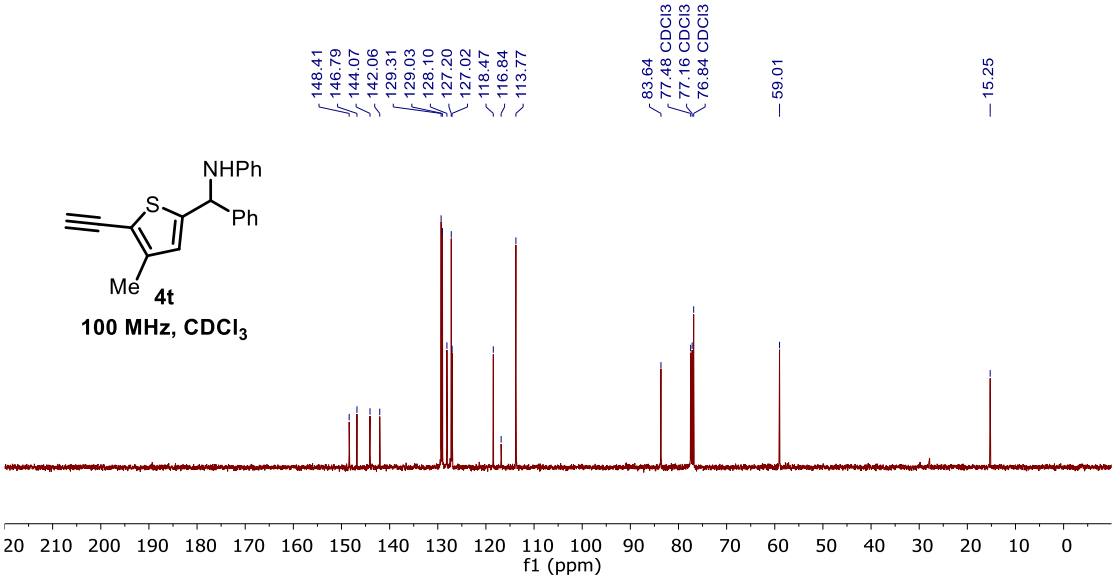
^{1}H NMR spectrum of **4s**



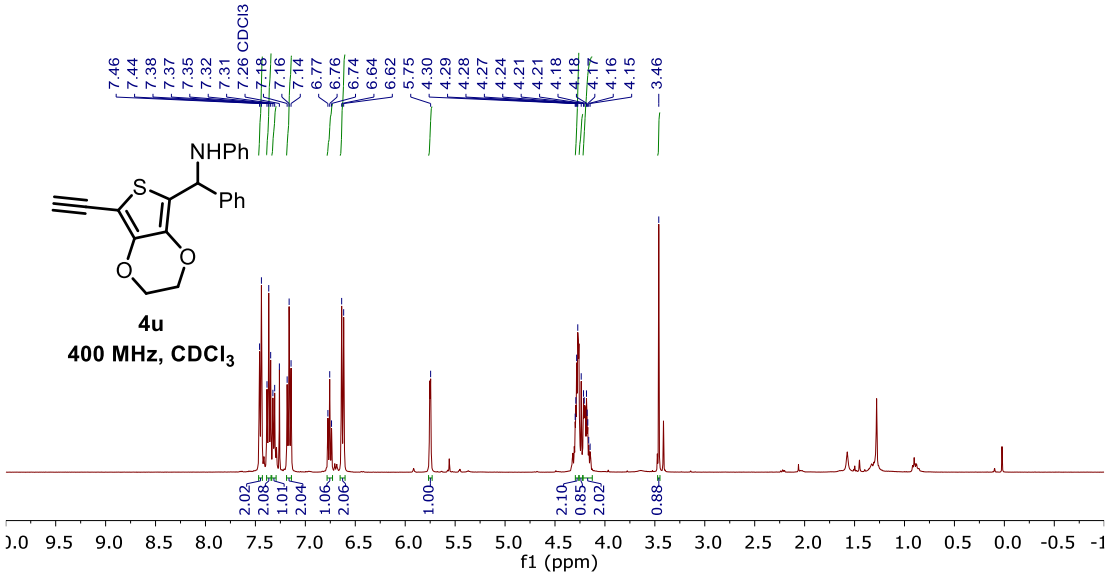
^{13}C NMR spectrum of **4s**



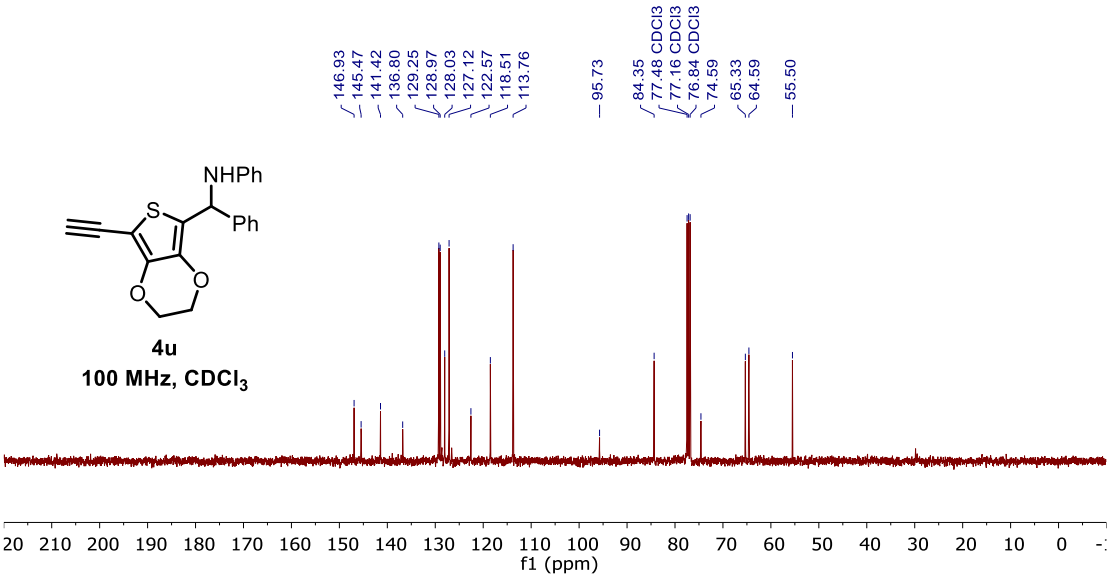
^{1}H NMR spectrum of **4t**



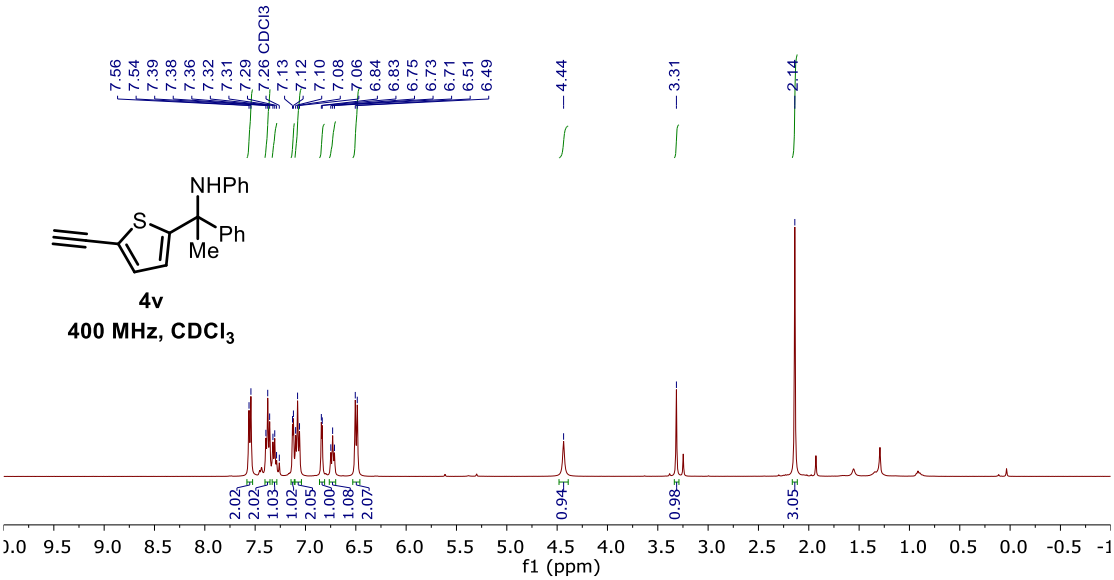
^{13}C NMR spectrum of **4t**



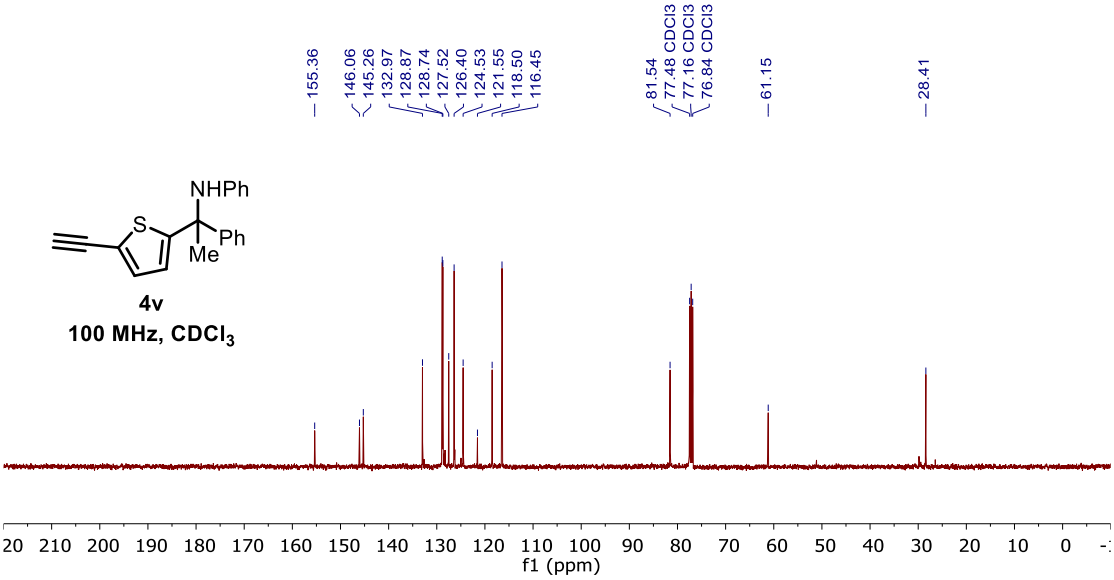
^{1}H NMR spectrum of **4u**



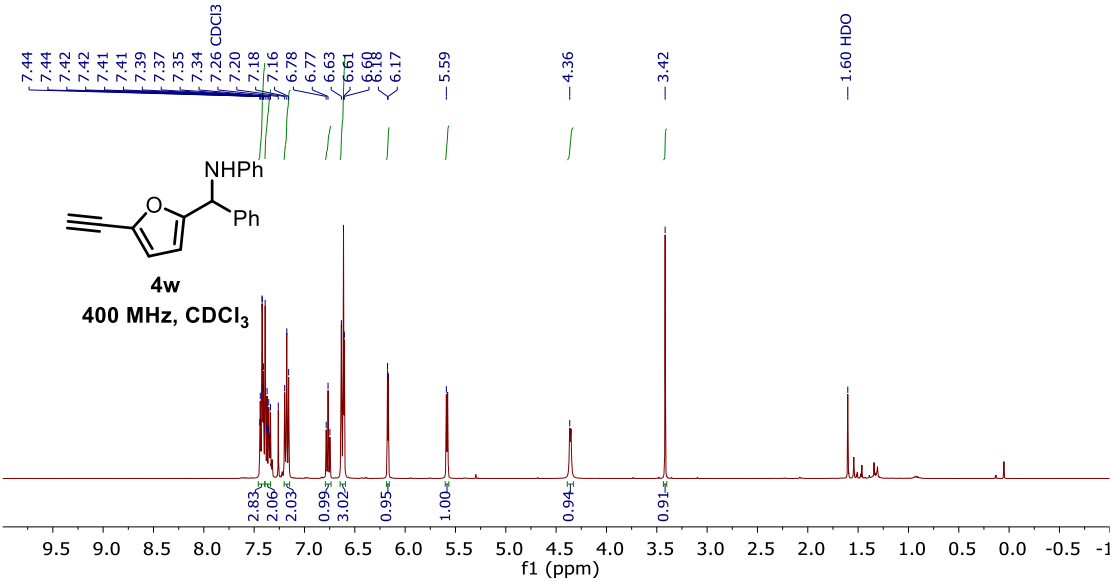
^{13}C NMR spectrum of **4u**



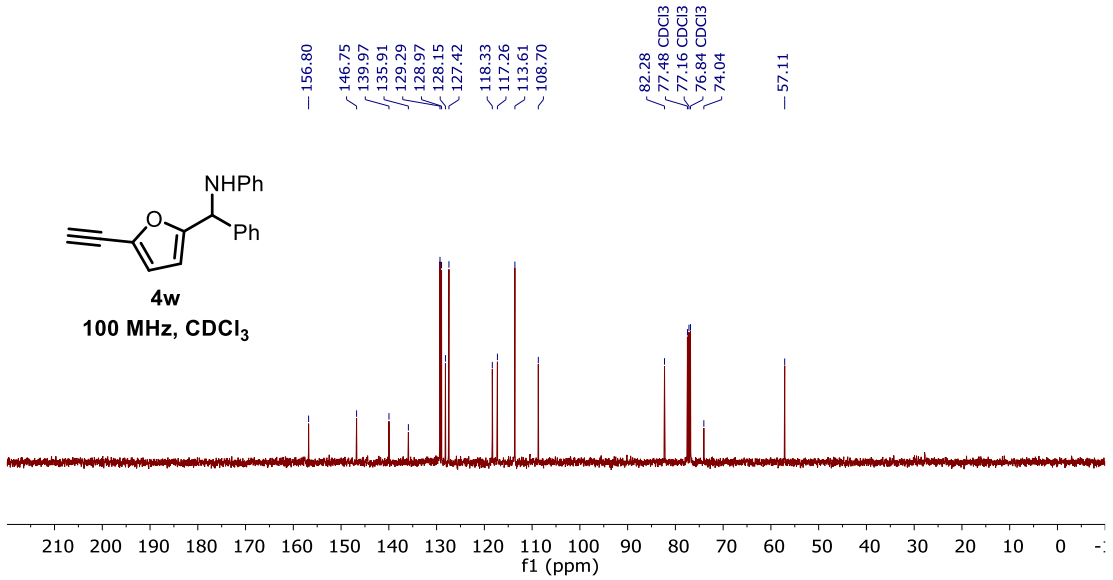
^{1}H NMR spectrum of **4v**



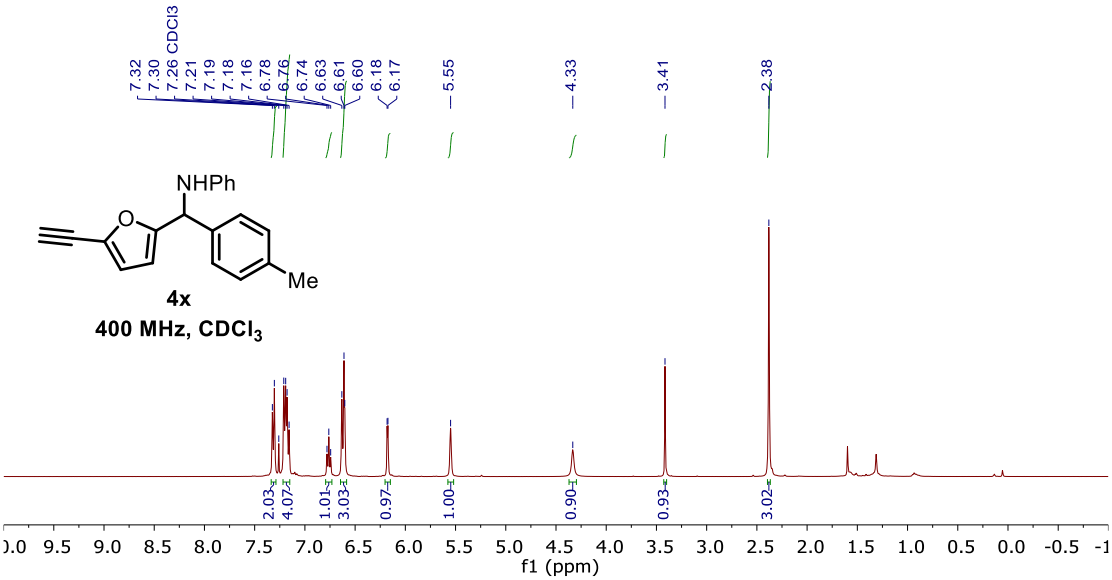
^{13}C NMR spectrum of **4v**



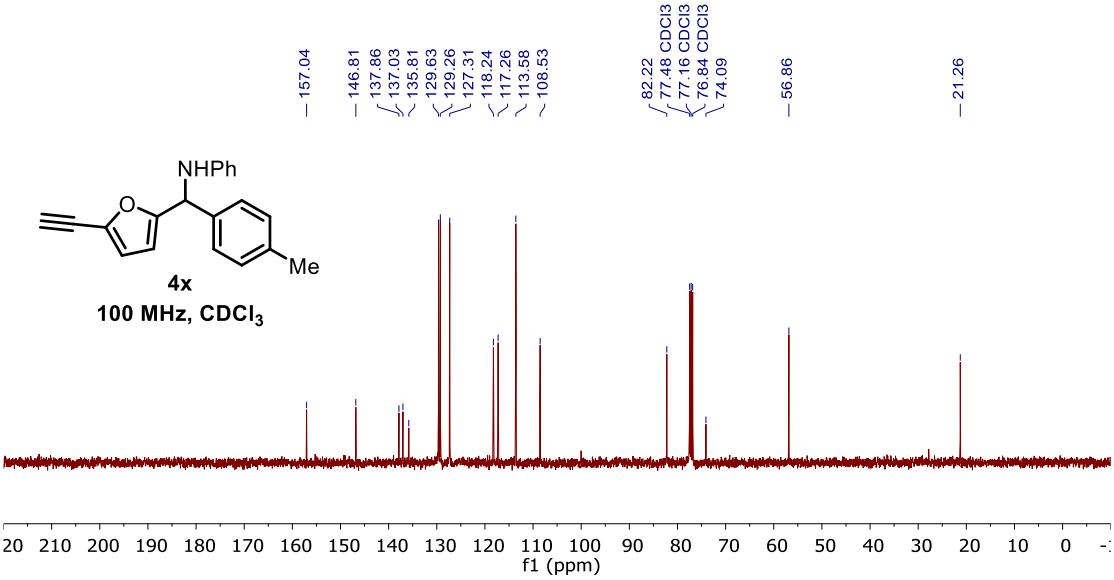
^{1}H NMR spectrum of **4w**



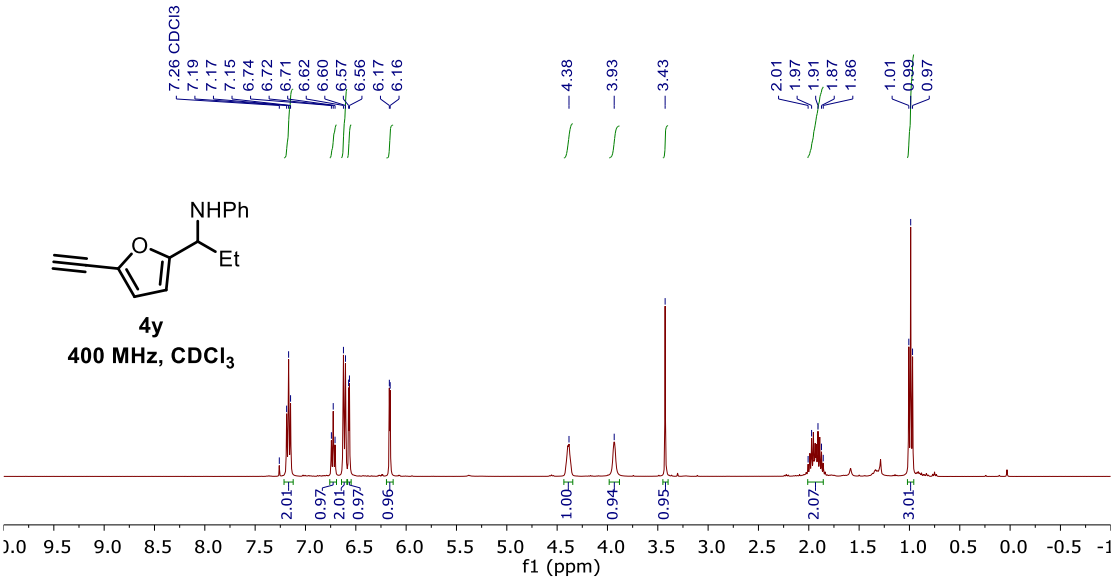
^{13}C NMR spectrum of **4w**



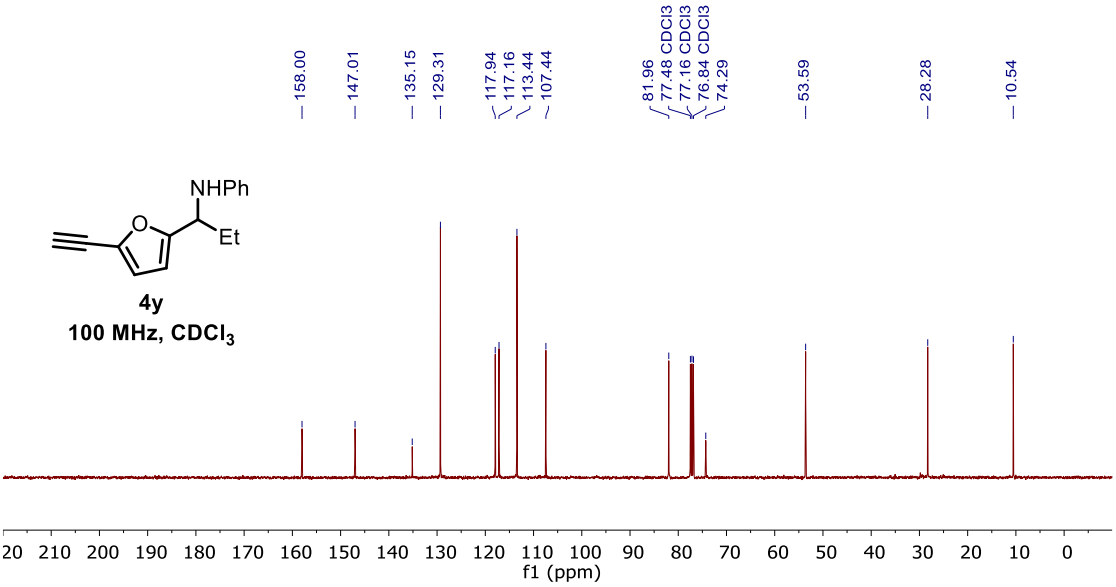
^{1}H NMR spectrum of **4x**



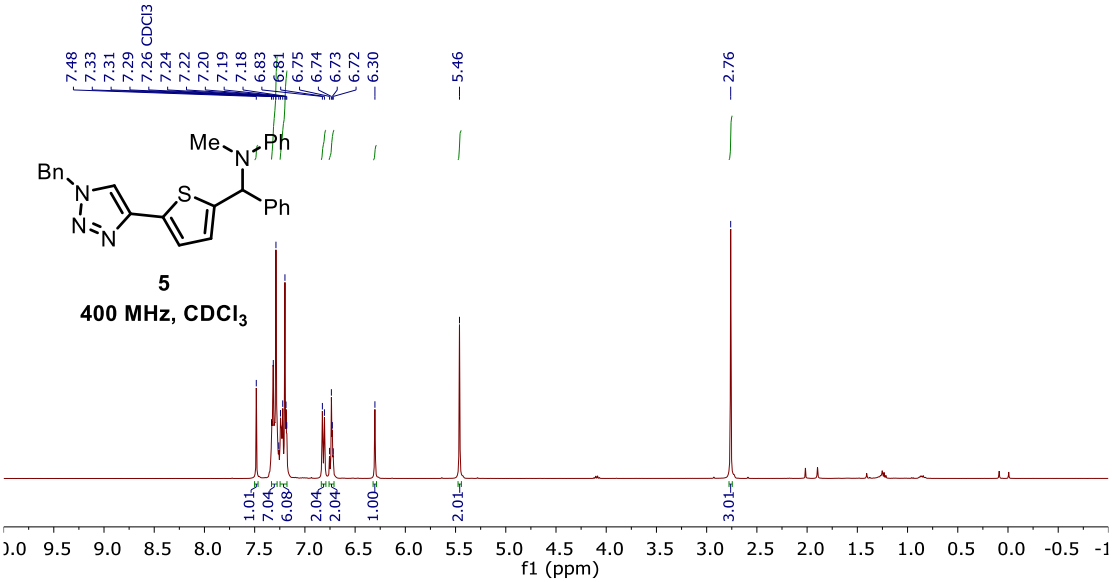
^{13}C NMR spectrum of **4x**



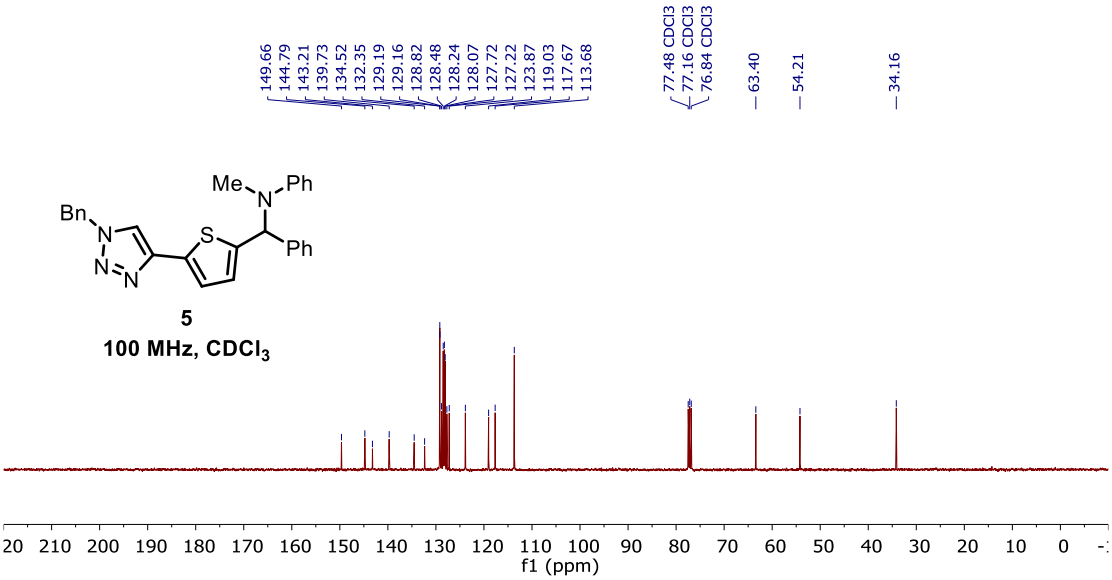
^{1}H NMR spectrum of **4y**



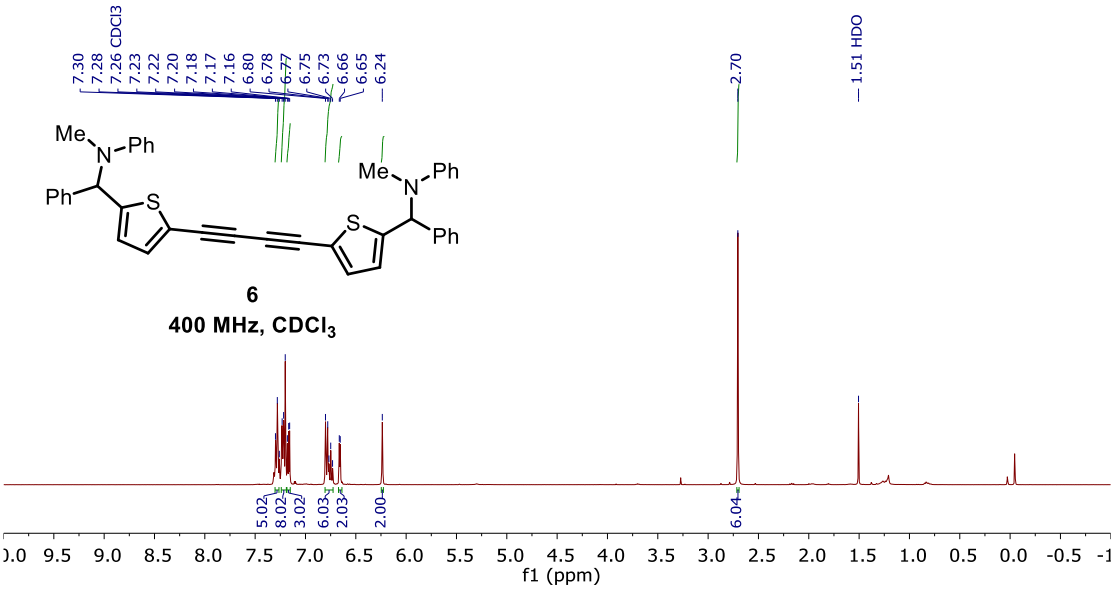
^{13}C NMR spectrum of **4y**



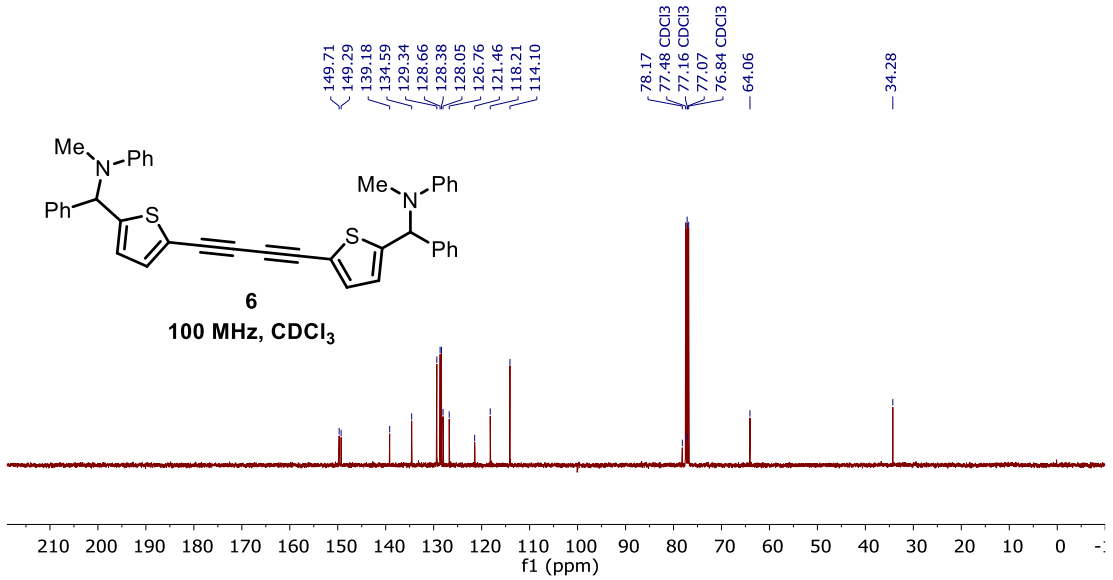
^{1}H NMR spectrum of **5**



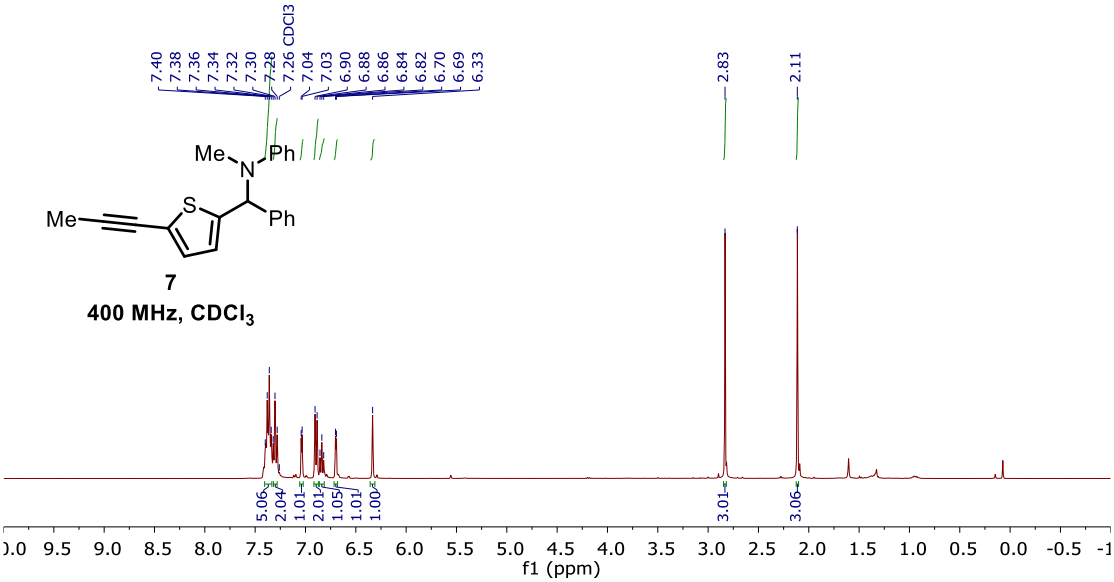
^{13}C NMR spectrum of **5**



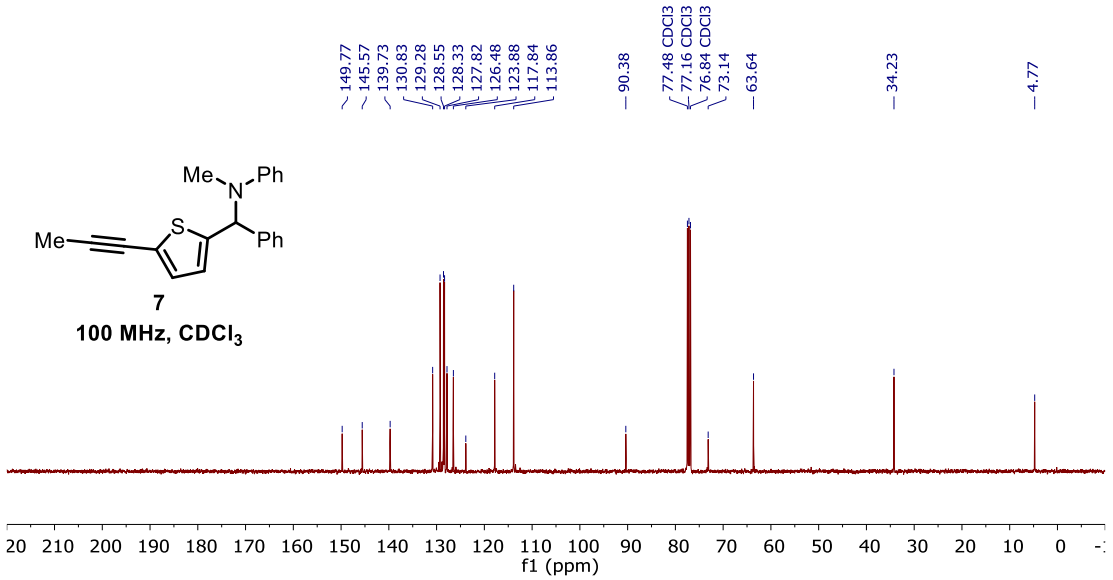
^{1}H NMR spectrum of **6**



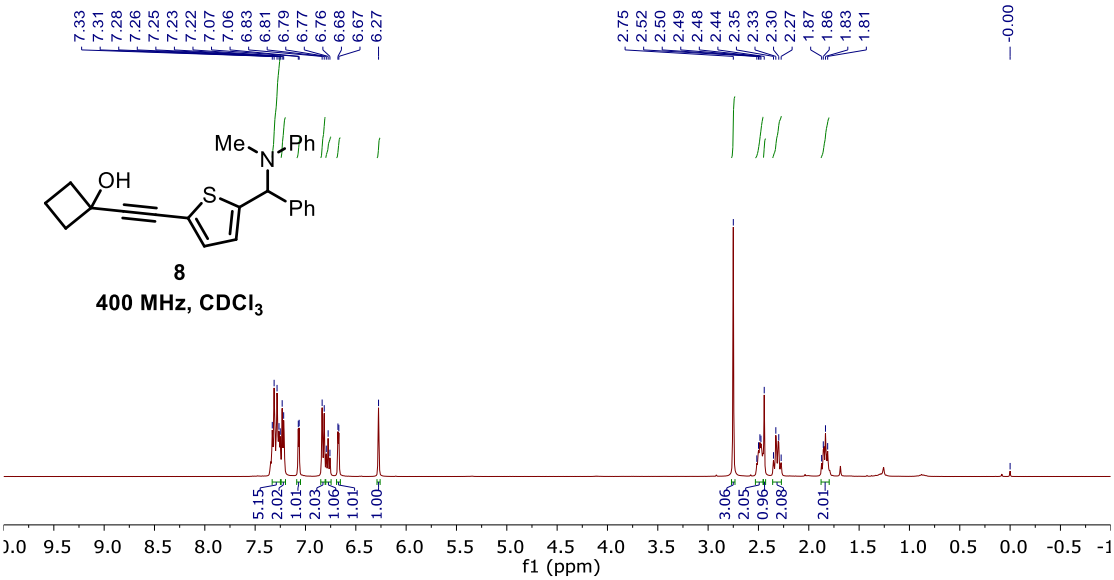
^{13}C NMR spectrum of **6**



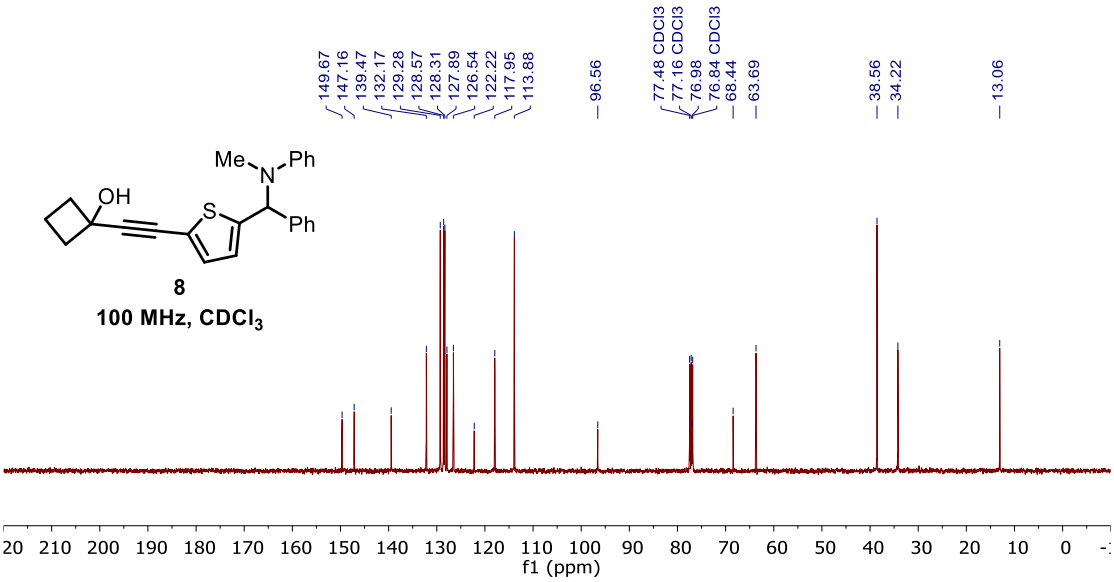
^{1}H NMR spectrum of **7**



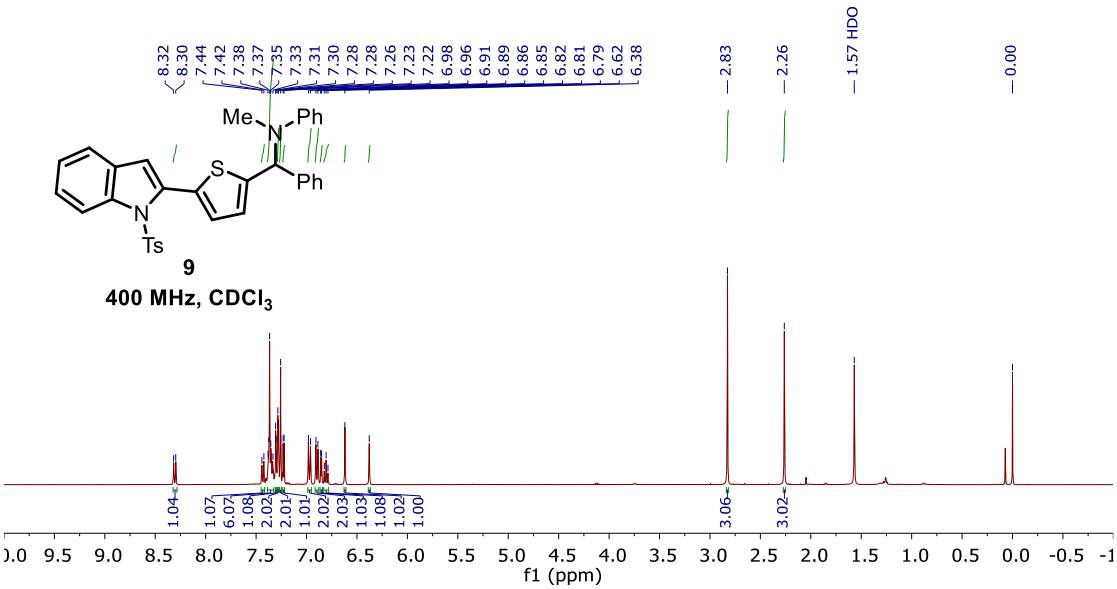
^{13}C NMR spectrum of **7**



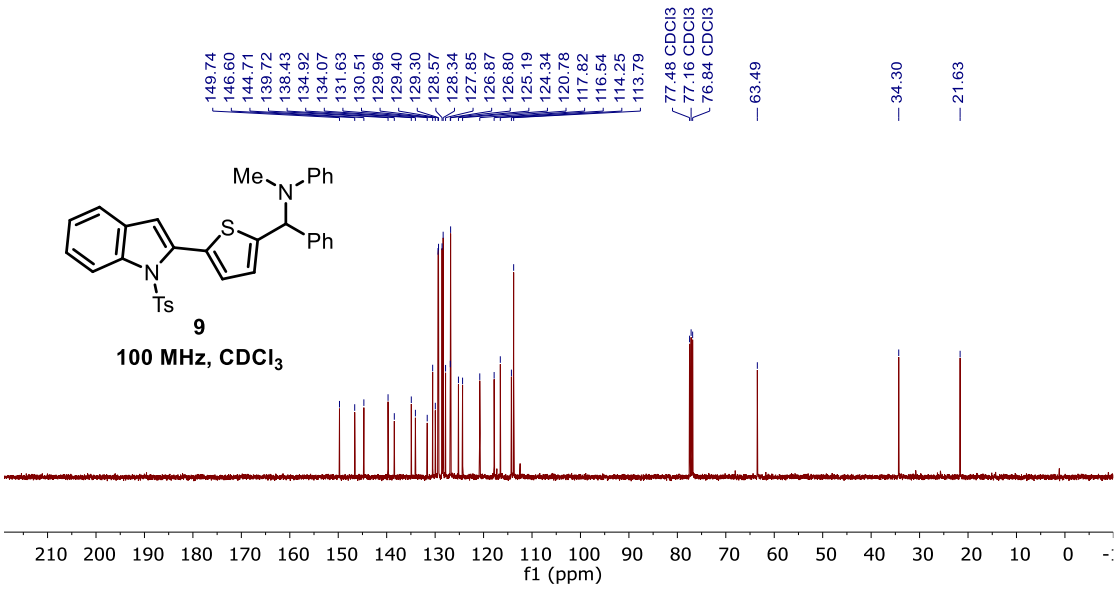
^{1}H NMR spectrum of **8**



^{13}C NMR spectrum of **8**



^{1}H NMR spectrum of **9**



^{13}C NMR spectrum of **9**