Manganese(I)-catalyzed dehydrogenative borylation of terminal alkynes†

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Content

❖ General consideration

All manipulations involving air- and moisture-sensitive materials were conducted using vacuum line, Schlenk, and cannula techniques or within an MBraun inert atmosphere by using argon glovebox, unless specified otherwise. Glassware was pre-heated in a 180 °C oven before use and cleaned with base baths (KOH in EtOH) and acid baths (aqueous HCl). Reported reaction temperatures correspond to external silicone oil bath temperatures, with room temperature (rt) being approximately 25 °C. Pinacolborane (HBpin), N,N′,N′-Tetramethylethylenediamine (TMEDA) and alkyne were purchased from Sigma-Aldrich, TCI Chemicals, Alfa Aesar, Thermo Fisher Scientific and used without further purification. $CDCl_3$ (Sigma) distilled from CaH_2 under an atmosphere of argon prior to its use and stored over 4 Å molecular sieves. ^{1}H, $^{13}C\{^{1}H\}$, ^{31}P, ^{19}F and ^{11}B NMR spectra were recorded on Bruker AV-200 MHz, AV-400 MHz, and AV-500 MHz instruments at room temperature using TMS as an external standard. All chemical shifts (δ) are reported in parts-per-million (ppm, δ) downfield from residual solvent peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, etc. HRMS were recorded on a Q-TOF spectrometer (Xevo XS QTof mass spectrometer) in electrospray ionization mode. Absorption spectra were recorded using a SPECORD® 210 PLUS spectrophotometer (SPECORD® 210 PLUS, Analytik Jena, Germany). UV-Vis NIR, Agilent Technologies). The voltammetric analysis was carried out using a conventional three-electrode system (Working electrode: Platinum disk; Counter electrode: Platinum wire; Reference electrode: Ag/AgCl) by using a BASI electrochemical analyzer (Epsilon EClipse™, USA). Melting points were recorded using M-560, BUCHI Laborites AGCH-9230 Flawil 1, Switzerland. FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer with a KBr pellet in the frequency range of 4000-400 cm^{-1}. The Elemental analyses were conducted on a CHN analyzer PE-2400 (Perkin Elmer, USA). Analytical thin-layer chromatography was performed using silica gel 60F254 plates and visualized under UV light.

Synthesis and characterization for compound 1

1.1 Synthesis of [(fcbpy)Mn(CO)$_3$Br] compound (1)

0.100 g (0.29 mmol) of ligand (fcbpy) was added to a flame dried Schlenk flask and dissolved in 10 mL of dry diethyl ether. Then 0.080 g (0.29 mmol) of $Mn(CO)_5Br$ was added and the reaction mixture was refluxed for 3h. Maroon red precipitate was observed after 3h. Then, the reaction mixture was allowed to cool to room temperature and the supernatant solvent was removed by cannula filtration. The precipitate was washed two to three times (10 mL x 3) with dry diethyl ether and dried under reduced pressure. Yield: 0.119 g (74%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (d, J = 45.6 Hz, 2H),

8.10–7.78 (m, 4H), 7.45 (s, 1H), 4.77 (d, *J* = 16.7 Hz, 2H), 4.53 (s, 2H), 4.15 (s, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 222.3, 221.7, 155.9, 153.6, 151.8, 151.2, 140.6, 138.3, 134.5, 125.6, 122.2 (d, *J* = 24.1 Hz), 78.9, 71.0 (d, *J* = 12.0 Hz), 70.4, 67.7, 67.1 ppm. HRMS (ESI, m/z): calculated for $C_{23}H_{16}BrFeMnN_2O_3$: $[M\text{-}Br]^+$: 479.0020, found: 479.0427; FT-IR (KBr pellet, cm^{-1}): 2926, 2849, 2018, 1906, 1630, 1601; Mp: 192−194 °C; Anal. Calcd for Chemical Formula: $C_{23}H_{16}BrFeMnN_2O_3$: C, 49.41; H, 2.88; N, 5.01; found: C, 49.43; H, 2.89; N, 5.02.

1.2 NMR data of [(fcbpy)Mn(CO)$_3$Br] compound (1)

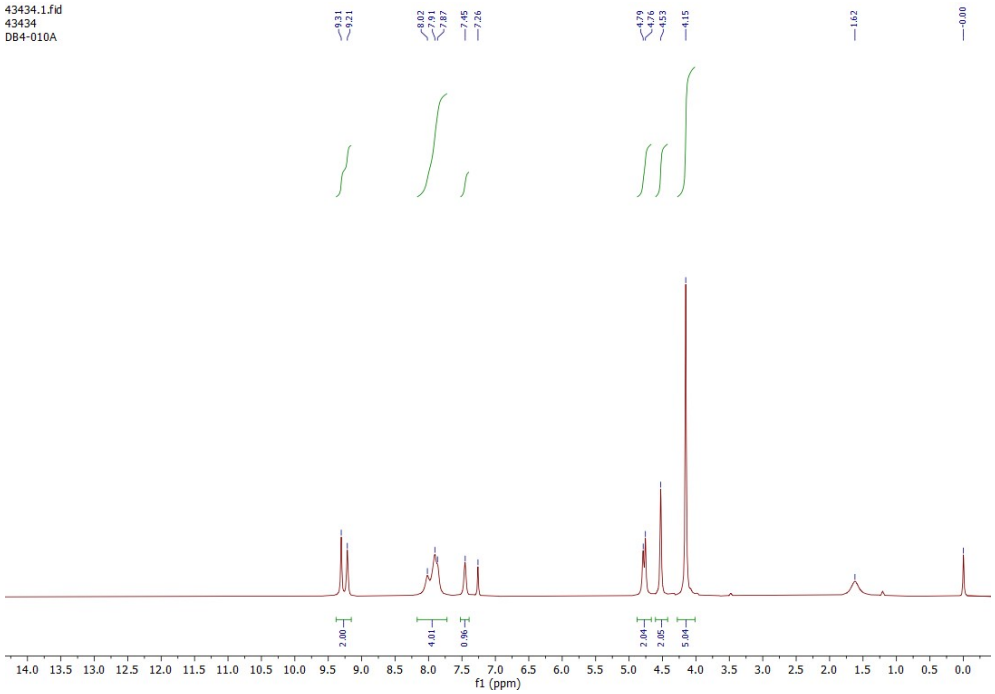


Figure S1: ^{1}H NMR spectrum of the compound **1** in $CDCl_3$ recorded at 500 MHz

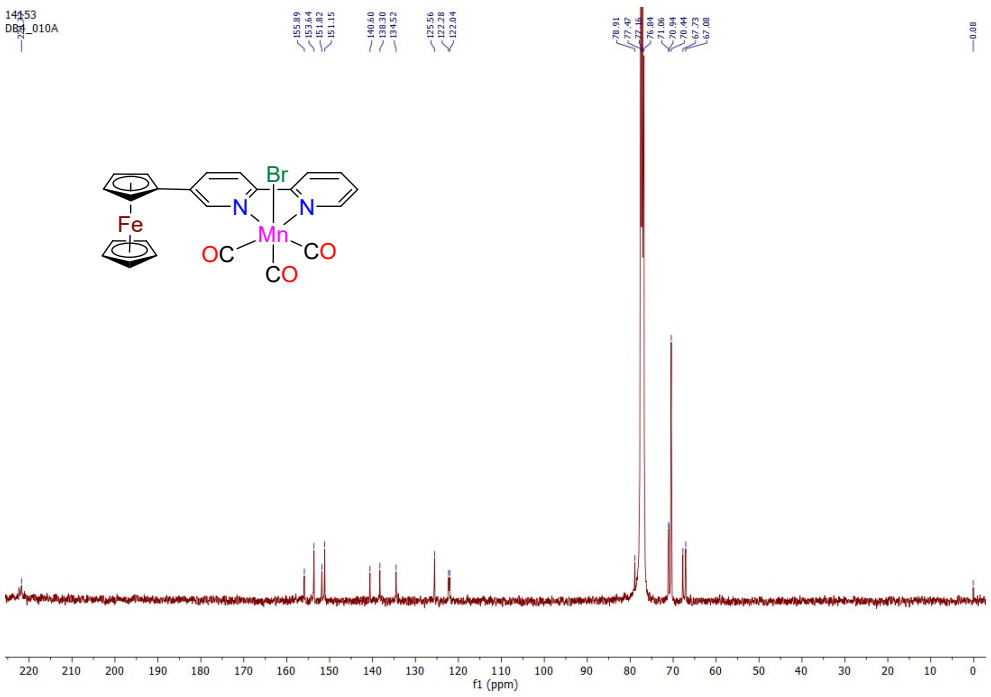


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **1** in $CDCl_3$ recorded at 100.6 MHz

1.3 HRMS data of [(fcbpy)Mn(CO)$_3$Br] complex as [1-Br]$^+$

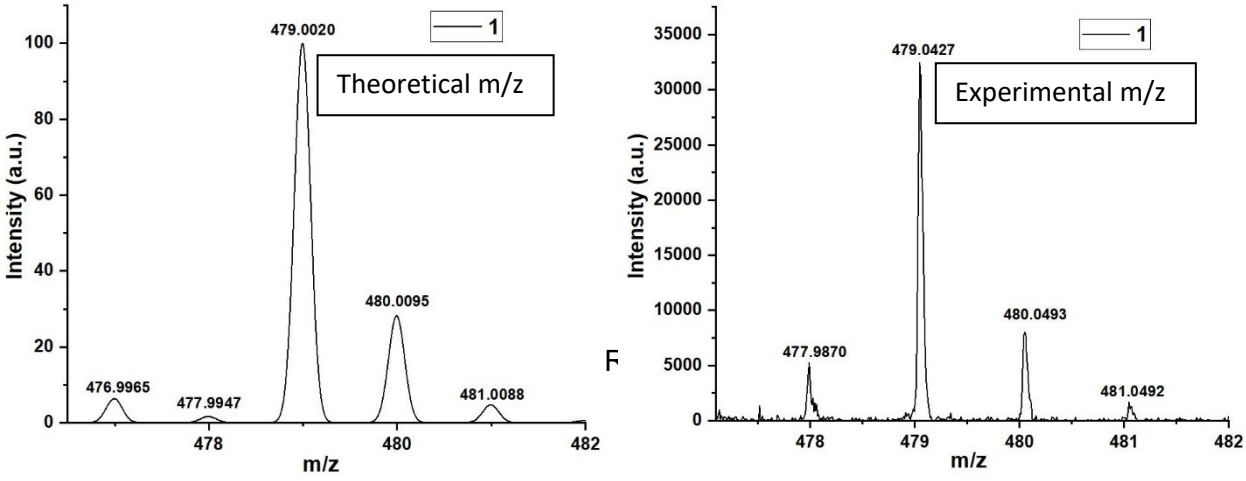


Figure S3: Theoretical and experimental m/z value of **1** (obtained as [**1**-Br]$^+$)

1.4 UV-Visible data of [(fcbpy)Mn(CO)$_3$Br] complex (1)

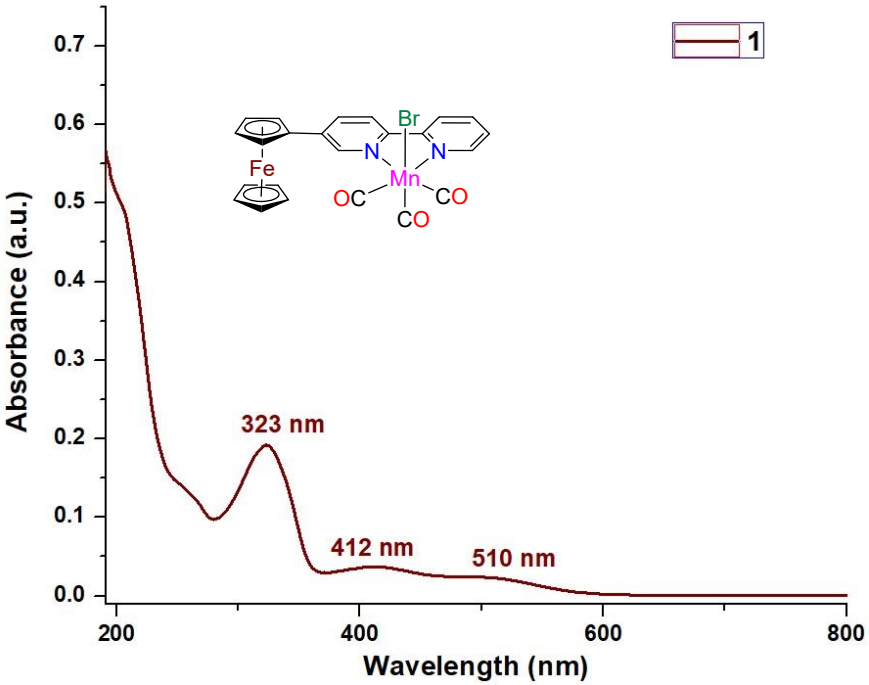


Figure S4: UV-Vis Spectrum of the compound **1**

1.5 FT-IR data of [(fcbpy)Mn(CO)$_3$Br] compound (1)

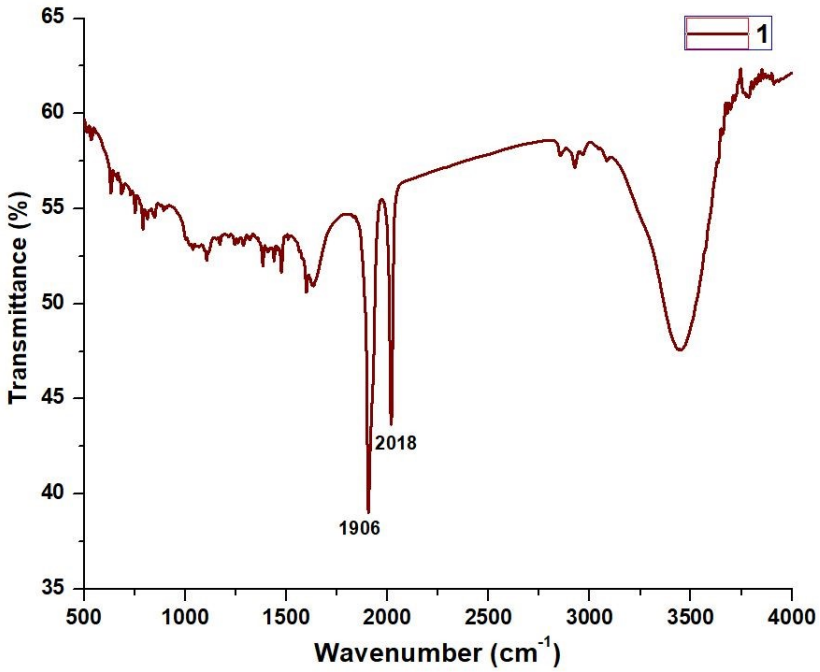


Figure S5: FT-IR Spectrum of the compound **1**

1.6 Cyclic Voltammogram of [(fcbpy)Mn(CO)$_3$Br] compound (1)

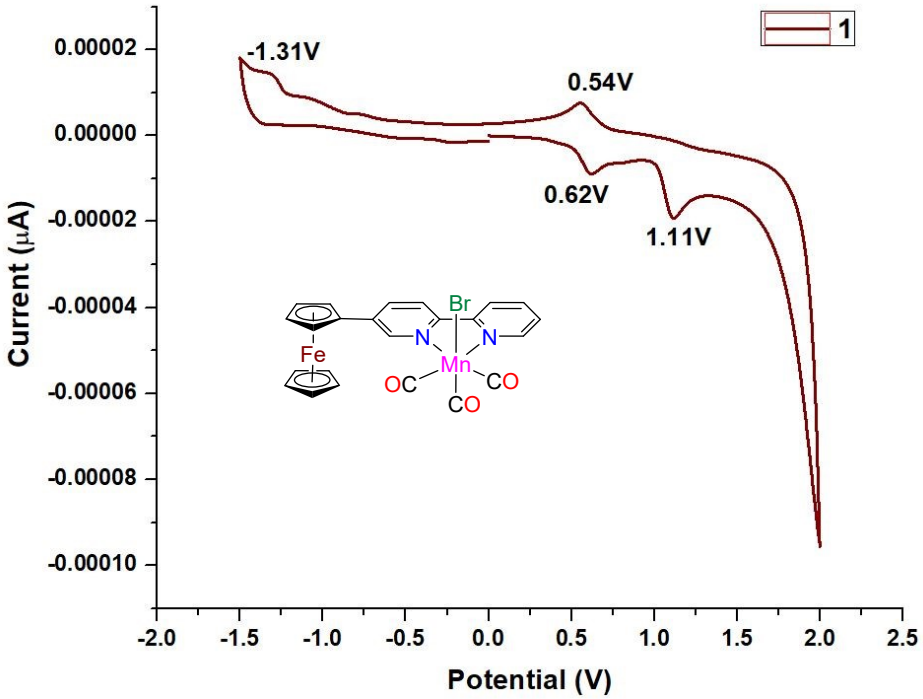
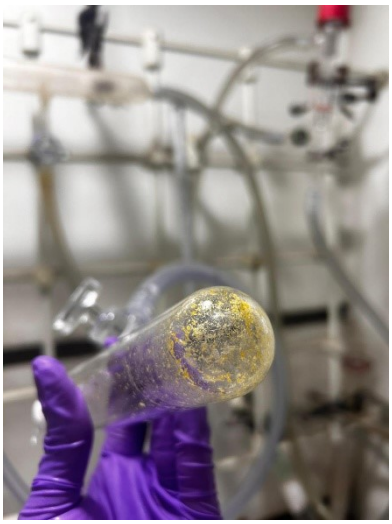


Figure S6 Full scan cyclic voltammogram from 2 to -1.5 V for **1**. Working electrode: Platinum disc; Counter electrode: Platinum Wire; Reference electrode: Ag/AgCl. Solvent: acetonitrile; Electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate; [5] = 0.001 M; Scan rate: 100 mVs^{-1}; RT

❖ **General procedure for the C–H borylation of terminal alkynes and purification of alkynyl boronic esters**

In an argon-filled glovebox, a NMR tube was loaded with **1** (1.39 mg, 0.0025 mmol), HBpin (55 µL, 0.375 mmol), N,N,N′,N′-Tetramethylethylenediamine (TMEDA) (6 µL, 0.00435 mmol), and a terminal alkyne (0.25 mmol). The reaction mixture was heated to 80 °C for 24 hours. After the reaction was complete, mesitylene (35 µL, 0.25 mmol) was added as an internal standard followed by $CDCl_3$. The reaction progress was monitored using ^{1}H NMR spectroscopy until the maximum conversion was achieved.

For purification, the above-mentioned procedure has been followed without the addition of internal standard. When the reaction was completed, it was brought into the glove-box and diluted with 3.00 mL of the chosen solvent mixture. Under an argon atmosphere, the solution was passed through a short silica gel column (2.3 g SiO_2), using 30 mL of a 1:9 Et_2O:Pentane mixture as the eluent. The resulting solution was evaporated under vacuum to obtain the alkynyl boronic esters. The isolated product was analyzed by multinuclear NMR spectroscopy. It should be noted that the ^{11}B NMR spectrum of some alkynyl borates exhibit a peak in the 20−22 ppm range, indicating a small amount of $B(OR)_3$ as a side product.



❖ **Optimization**

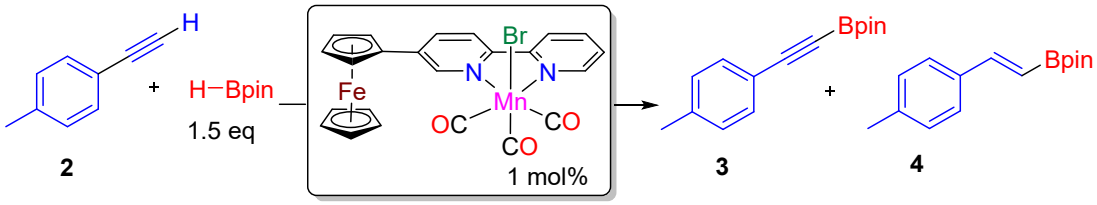
1. Optimization of the reaction components

All catalytic reactions were carried out following the general procedure using 4-ethynyltoluene as the terminal alkyne (32 µL, 0.25 mmol), along with Mn(I) (1.39 mg, 0.0025 mmol), and a borylating reagent—either HBpin (55 µL, 0.375 mmol), HBCat (40 µL, 0.375 mmol), or B_2Pin_2 (96 mg, 0.375 mmol). N,N,N′,N′-Tetramethylethylenediamine (TMEDA) (6 µL, 0.00435 mmol) was also added, and the mixture was heated at 80 °C for 24 hours. The NMR yields were measured from the crude reaction mixture using ^{1}H NMR, with mesitylene (35 µL, 0.25 mmol) as the internal standard. The % conversion and % yield obtained are reported in Table S1. From this optimization HBpin was selected as the borylating reagent because it yielded only the desired product with good efficiency.

Entry	Borylating agent	Conversion (%)	3 (%)	4 (%)
1.	HBpin	>99	94	0
2.	HBCat	>99	0	0
3.	B_2Pin_2	27	0	0

Table S1: Optimization of borylating agent for dehydrogenative borylation of 4-ethynyltoluene

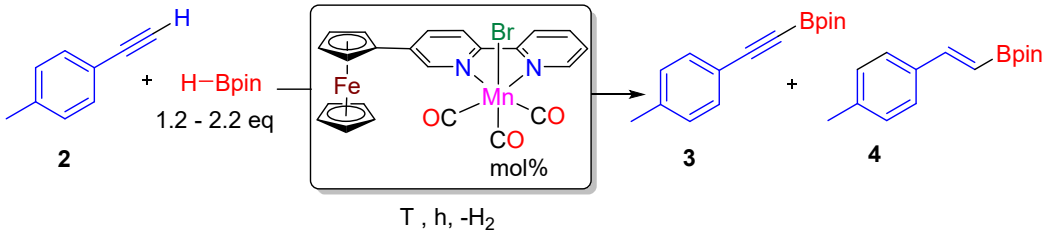
2. Optimization of the solvent



Entry	Solvent	T (°C)	Conversion (%)	3 (%)	4 (%)
1.	THF	80	42	0	trace
2.	Toluene	80	65	0	trace
3.	$CDCl_3$	80	57	0	5
4.	o-DFB	80	>99	trace	7
5.	Neat	80	>99	94	0

Table S2: Optimization of solvent (0.5 mL) for dehydrogenative borylation of 4-ethynyltoluene

3. **.Optimization of the reaction conditions**



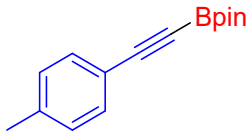
Catalytic reactions were performed using the general catalytic procedure described above, with 4-ethynyltoluene (32 µL, 0.25 mmol) as the alkyne. The % conversion and % yield obtained are reported in Table S3.

Entry	HBpin	Catalyst(%)	Temperature	Time	TMEDA(%)	3(%)	4(%)
1.	1.2	-	80 ˚C	24 h	-	-	-
2.	1.2	1 mol	80 ˚C	24 h	-	-	-
3.	1.2	1 mol	80 ˚C	48 h	-	50	21
4.	1.2	1 mol	80 ˚C	72 h	-	54	25
5.	1.2	1 mol	100 ˚C	72 h	-	8	57
6.	1.2	1 mol	80 ˚C	72 h	5 mol	15	-
7.	1.2	1 mol	80 ˚C	72 h	15 mol	71	-

8.	1.2	1 mol	80 ˚C	24 h	15 mol	78	-
9.	1.2	1 mol	60 ˚C	24 h	15 mol	66	-
10.	1.2	2 mol	80 ˚C	24 h	15 mol	64	-
11.	1.5	1 mol	80 ˚C	24 h	15 mol	94	-
12.	1.5	1 mol	80 ˚C	18 h	15 mol	75	-
13.	1.5	1 mol	80 ˚C	12 h	15 mol	71	-
14.	1.5	2 mol	80 ˚C	12 h	15 mol	36	-

Table S3: Optimazation of additives and Mn(I) for dehydrogenative borylation of 4-ethynyltoluene

❖ **Scope of Dehydrogenative borylation**



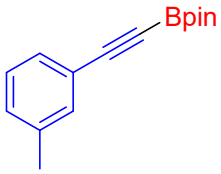
4,4,5,5-Tetramethyl-2-(p-tolylethynyl)-1,3,2-dioxaborolane (3a)

The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). Pale yellow amorphous solid, isolated yield 0.215 g (88%).[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.41 (d, J = 8.4 Hz, 2H), 7.12− 7.10 (d, J = 8.4 Hz, 2H), 2.34(s, 3H), 1.31 (s, 12H).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 139.4, 132.2, 131.7, 128.8, 118.5, 101.9, 84.0, 24.4, 21.3.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 24.8.

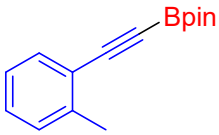


4,4,5,5-Tetramethyl-2-(m-tolylethynyl)-1,3,2-dioxaborolane (3b). The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). Pale yellow amorphous solid, isolated yield 0.180 g (74%).[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.32 (m, 1H),7.28 (s,1H), 7.21−7.19 (m, 1H), 7.17−7.15 (m, 1H), 2.30 (s, 3H), 1.31 (s, 12H).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 138.0, 133.1, 130.4, 129.7, 128.2, 121.7, 102.1, 84.4, 24.7, 21.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.4.

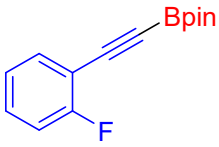


4,4,5,5-Tetramethyl-2-(o-tolylethynyl)-1,3,2-dioxaborolane (3c). The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). Deliquescent solid 0.170 g (70% yield).[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.45 (m, 2H), 7.25− 7.23 (d, J = 8.0 Hz, 1H), 7.19−7.17 (m, 1H), 7.14−7.10 (m, 1H), 2.48 (s, 3H), 1.33 (s, 12H).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 139.4, 132.2, 131.7,128.8, 118.5, 101.9, 84.0, 24.4, 21.3.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 24.4.



2-((2-Fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d).

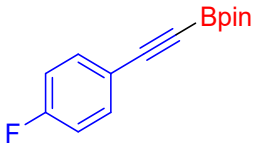
The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). White amorphous solid 0.198 g (80% yield).[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.48 (m, 1H), 7.36−7.31 (m, 1H), 7.10−7.04 (m, 2H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.6, 162.1, 134.4, 134.1, 131.3, 130.7, 124.0, 115.7, 115.5, 110.8, 110.6, 94.7, 84.6, 24.6.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.2.

^{19}F NMR: (370.50 MHz, $CCCl_3$) δ –108.3.



2-((4-Fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e).

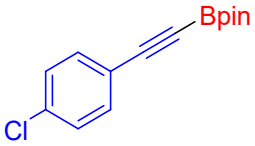
The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). Deliquescent solid 0.230 g (94% yield).[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (dt, J = 10.6, 5.2 Hz, 2H), 7.02-6.98 (t, J = 8.6 Hz, 2H), 1.31 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.8, 162.3, 135.1, 135.0, 118.4, 118.4, 116.2, 101.1, 84.9, 25.1.

^{11}B NMR: (128.34 MHz, $CDCl_3$) δ 24.3.

^{19}F NMR: (470.39 MHz, $CDCl_3$) δ –108.7.



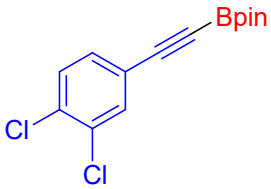
2-((4-chlorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**):

The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). White solid (0.235 g, 89 % yield).[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.30 – 7.28 (m, 2H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 135.3, 133.4, 128.4, 120.1, 100.1, 84.2, 24.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.5.



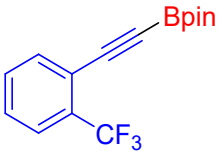
2-((3,4-dichlorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). Deliquescent solid 0.247 g (83% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.55-7.51 (1H, m), 7.35-7.33 (1H, m), 7.29-7.27 (2H, m), 1.27 (12H, s).

^{13}C{^{1}H} NMR: (125.77 MHz, $CDCl_3$) δ 133.8, 133.5, 132.4, 131.2, 130.2, 121.6, 98.82, 84.4, 24.4.

^{11}B NMR: (128.34 MHz, $CDCl_3$) δ 23.9.



4,4,5,5-tetramethyl-2-((2-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane (3h):

The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL).

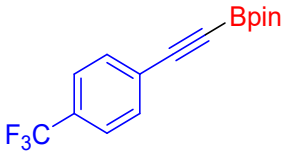
White amorphous solid (0.252 g, 85% yield).[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.49 – 7.43 (m, 2H), 1.31 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.8, 134.5, 132.1 (q, J = 29.07 Hz),131.1, 128.8, 128.4,125.6 (q, J = 6.55 Hz), 124.3, 121.6, 119.9 (q, J = 4.22 Hz), 96.3, 84.3, 24.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.9.



4,4,5,5-tetramethyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane (3i):

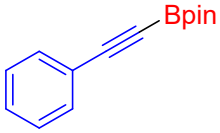
The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL), pale yellow amorphous solid (0.199 g, 67% yield)[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.5, 132.2,130.6(q, J = 30.6 Hz), 125.5 (d, J = 1.56 Hz), 125.1 (q, J = 4.83 Hz), 122.2, 119.4, 99.6, 84.5, 24.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0.



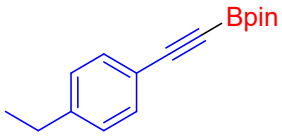
4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (3j):

The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). Pale yellow amorphous solid (0.200 g, 87% yield).[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (d, J = 7.2 Hz, 2H), 7.37–7.28 (m, 3H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.3, 131.9, 129.1, 128.5, 128.0, 121.6, 101.6, 84.2, 24.4.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.2.



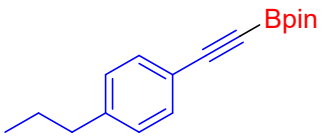
2-((4-ethylphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k):

The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). Yellow amorphous solid (0.213 g, 83% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (d, J = 8.6 Hz, 2H), 7.14-7.12 (d, J = 8.6 Hz, 2H), 2.66-2.60 (q, J = 7.6 Hz, 2H), 1.31 (s, 12H), 1.23-1.19(t, J = 8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.3, 132.9, 132.4, 128.2, 119.4, 102.5, 84.7, 29.2, 25.0, 15.5.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.4.



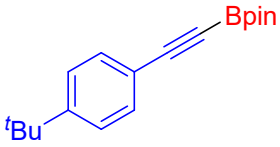
4,4,5,5-tetramethyl-2-((4-propylphenyl)ethynyl)-1,3,2-dioxaborolane (3l):

The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, pentane, 30 mL). Pale yellow amorphous solid (0.207 g, 76 % yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (d, J = 7.7 Hz, 2H), 7.13-7.10 (d, J = 7.7 Hz, 2H), 2.59-2.55 (t, J = 8 Hz, 2H), 1.65-1.59 (m, 2H) 1.32 (s, 12H), 0.94-0.90 (t, 3H, J = 7.5 Hz).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.9, 132.9, 128.9, 119.5, 84.8, 38.4, 25.1, 24.6, 14.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.5.



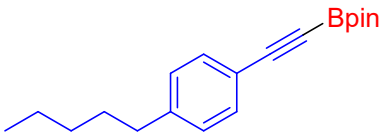
2-((4-(tert-Butyl)phenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2- dioxaborolane (3m).

The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). White amorphous solid (0.201 g, 70 % yield).[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.45 (d, J = 8 Hz, 2H), 7.34−7.32 (d, J = 8 Hz, 2H), 1.32 (s, 12H), 1.30 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.8, 132.4, 131.9, 125.3, 118.9, 102.2, 84.4, 34.9, 31.1, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.4.



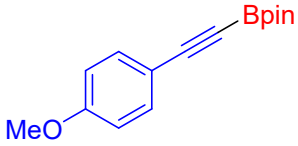
4,4,5,5-tetramethyl-2-((4-pentylphenyl)ethynyl)-1,3,2-dioxaborolane (3n):

The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:9 Et_2O:pentane, 30 mL). Pale orange liquid (0.195 g, 65 % yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.15-7.12 (m, 2H), 2.62-2.59 (t, J = 7.5 Hz, 2H), 1.63-1.60 (m, 2H), 1.33-1.28 (m, 12H - Bpin, 2H CH_2, 2H CH_2), 0.92-0.89 (t, J = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.8, 144.0, 132.6, 132.1, 128.4, 119.3, 102.3, 84.3, 35.94, 31.5, 30.9, 24.7, 22.6, 14.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.4.



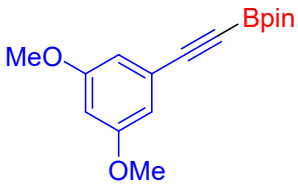
2-((4-methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o):

The crude reaction mixture was purified by flash chromatography (SiO_2, 2.30 g, 1:1 Et_2O:pentane, 30 mL). Pale yellow solid (0.235 g, 91% yield).[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 6.84 – 6.81 (m, 2H), 3.79 (s, 3H), 1.31 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.8 (d, J = 57.74 Hz), 134.6, 133.9, 114.3, 114.3, 102.3, 84.6, 55.6, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.3.



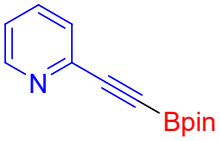
2-((3,5-dimethoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p):

NMR yield: pale yellow liquid, 67%

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (d, J = 2 Hz, 2H), 6.44 (m, 1H), 3.70 (s, 6H), 1.29 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.5, 123.1, 110.1, 103.0, 84.3, 55.3, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.4.



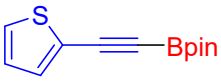
4**,4,5,5-Tetramethyl-2-(2-pyridylethynyl)-1,3,2-dioxaborolane (3q**)

NMR yield: brown liquid, 59%[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (1H, s), 7.60 (1H, s), 7.48 (1H, s), 7.22 (1H, s), 1.29 (12H, s).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)**:** δ.24.4, 82.9, 123.3, 127.3,136.0, 142.4,145.3, 149.9.

^{11}B NMR (128 MHz, $CDCl_3$)**:** δ. 24.2.



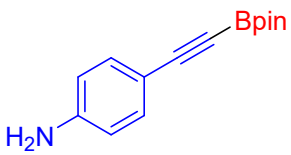
4,4,5,5-Tetramethyl-2-(2-ethynylthiophene)-1,3,2-dioxaborolane(3r):

NMR Yield: yellow oil,70%.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 3.3 Hz, 1H), 7.33 (d, J = 5.5 Hz,1H), 7.01 (t, J = 5.5 Hz, 1H), 1.37 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.1, 129.1, 127.6, 122.3, 83.2, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.4.



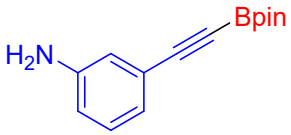
4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)aniline (3s):

NMR Yield: brown solid, 53%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.37 (d, J = 7.6 Hz, 2H), 7.08–7.06 (d, J = 7.5 Hz, 2H), 1.35 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.4, 133.3, 117.6, 113.4, 84.6, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.2.



3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)aniline (3t):

NMR Yield: brown oil, 46%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.15 – 7.13 (m, 2H), 7.02 – 7.01 (d, J = 5.6 Hz, 2H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.3, 129.4, 122.9, 122.6, 118.4, 115.9, 84.0, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 24.4.

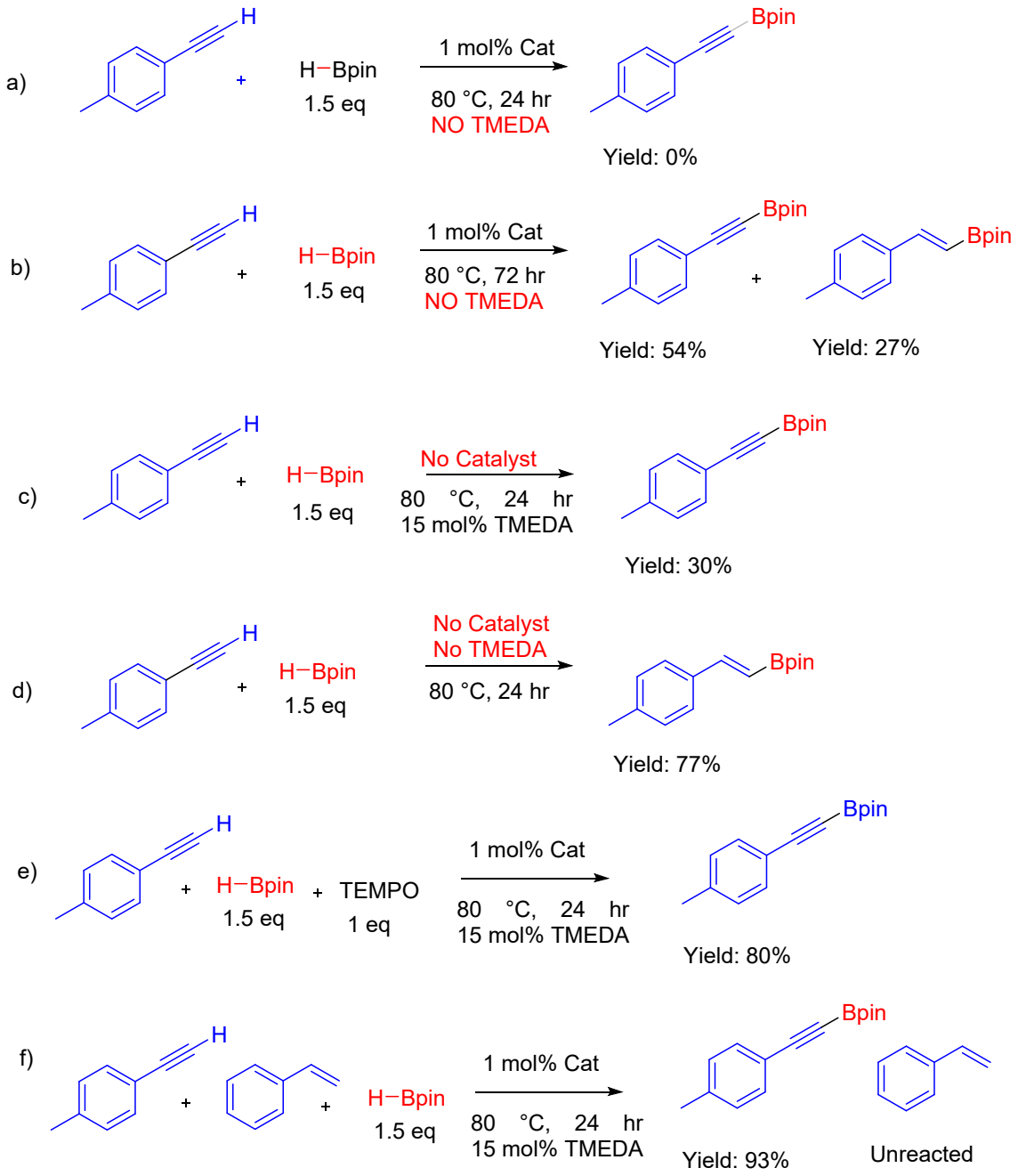
❖ **Control Reactions**

a) In an argon-filled glovebox, a J. Young NMR tube was loaded with Mn(I) (1.39 mg, 0.0025 mmol), HBpin (55 µL, 0.375 mmol), and 4-ethynyltoluene (32 µL, 0.25 mmol). The reaction mixture was heated to 80 °C for 24 hours. After the reaction was complete, mesitylene (35 µL, 0.25 mmol) was added as an internal standard followed by $CDCl_3$. The reaction progress was monitored by ^{1}H NMR, and no product formation was detected.

b) In an argon-filled glovebox, a J. Young NMR tube was loaded with Mn(I) (1.39 mg, 0.0025 mmol), HBpin (55 µL, 0.375 mmol), and 4-ethynyltoluene (32 µL, 0.25 mmol). The reaction mixture was heated to 80 °C for 72 hours. After the reaction was complete, mesitylene (35 µL, 0.25 mmol) was added as an internal standard followed by $CDCl_3$. The reaction progress was monitored by ^{1}H NMR, revealing a mixture of products. This resulted in 54% C-H borylated product and 27% hydroborated product.

c) In an argon-filled glovebox, a J. Young NMR tube was loaded with HBpin (55 µL, 0.375 mmol), N,N,N′,N′-Tetramethylethylenediamine (TMEDA) (6 µL, 0.00435 mmol) and 4-ethynyltoluene (32 µL, 0.25 mmol). The reaction mixture was heated to 80 °C for 72 hours. After the reaction was complete, mesitylene (35 µL, 0.25 mmol) was added as an internal standard followed by $CDCl_3$. The yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. This resulted in 30% C-H borylated product selectively.

d) Under an inert atmosphere, a J. Young NMR tube was loaded with HBpin (55 µL, 0.375 mmol), and 4-ethynyltoluene (32 µL, 0.25 mmol). The reaction mixture was heated to 80 °C for 24 hours. After the reaction was complete, mesitylene (35 µL, 0.25 mmol) was added as an internal standard followed by $CDCl_3$. The yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. No C–H borylation was observed, giving 77% hydroboration product.



e) In an argon-filled glovebox, a J. Young NMR tube was loaded with Mn(I) (1.39 mg, 0.0025 mmol), HBpin (55 µL, 0.375 mmol), N,N,N′,N′-Tetramethylethylenediamine (TMEDA) (6 µL, 0.00435 mmol), 4-ethynyltoluene (32 µL, 0.25 mmol) and TEMPO (30 mg, 0.25 mmol). The reaction mixture was heated to 80 °C for 24 hours. After the reaction was complete, mesitylene (35 µL, 0.25 mmol) was added as an internal standard followed by $CDCl_3$. The reaction progress was monitored by ^1H NMR, 80% of C-H borylated product was observed.

f) In an argon-filled glovebox, a J. Young NMR tube was loaded with Mn(I) (1.39 mg, 0.0025 mmol), HBpin (55 µL, 0.375 mmol), N,N,N′,N′-Tetramethylethylenediamine (TMEDA) (6 µL, 0.00435 mmol), 4-ethynyltoluene (32 µL, 0.25 mmol) and styrene (28 µL, 0.25 mmol). The reaction mixture was heated to 80 °C for 24 hours. After the reaction was complete,

mesitylene (35 µL, 0.25 mmol) was added as an internal standard followed by $CDCl_3$. The reaction progress was monitored by ^1H NMR, 93% of C-H borylated product was observed with unreacted styrene.

❖ **NMR Spectra of Isolated Compounds**

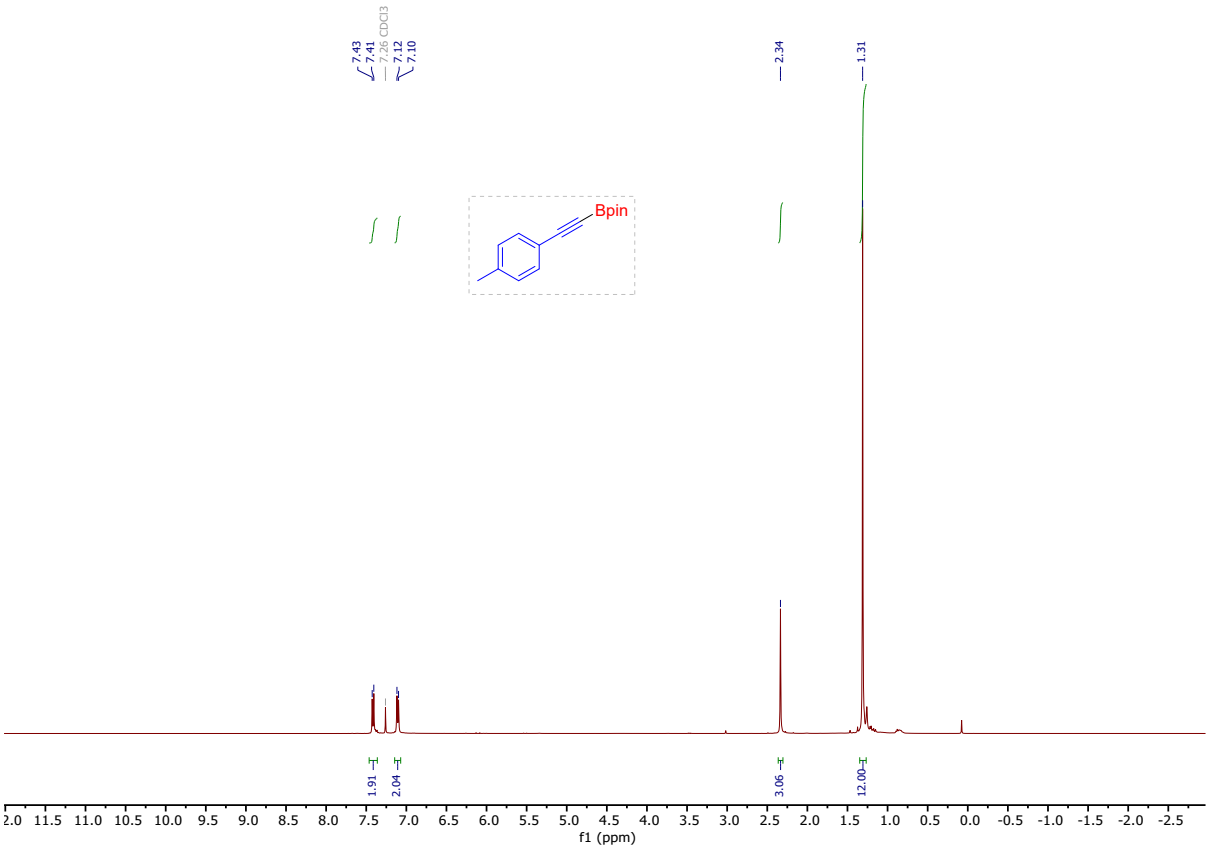


Figure S7: ^1H NMR spectrum of the compound **3a** in $CDCl_3$ recorded at 400 MHz

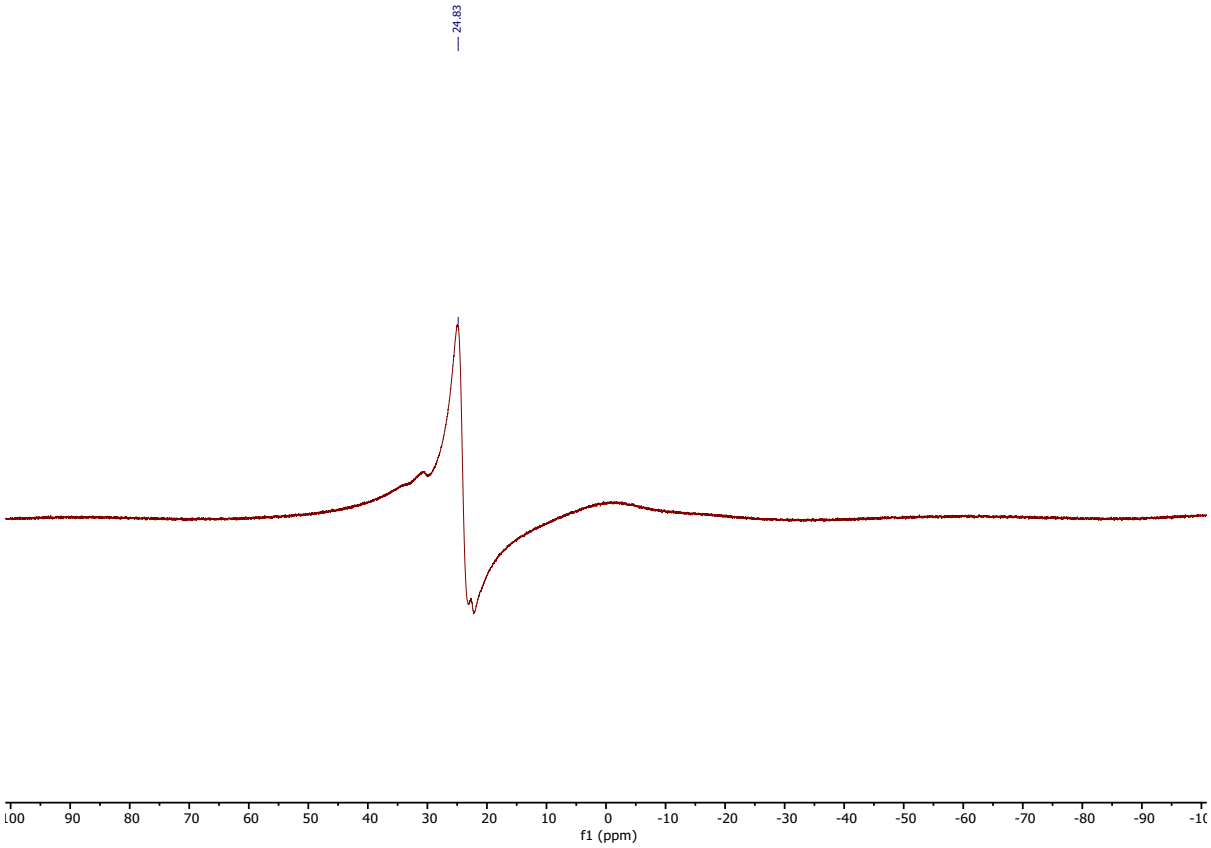


Figure S8: $^{11}B\{^1H\}$ NMR spectrum of the compound **3a** in $CDCl_3$ recorded at 128.3 MHz.

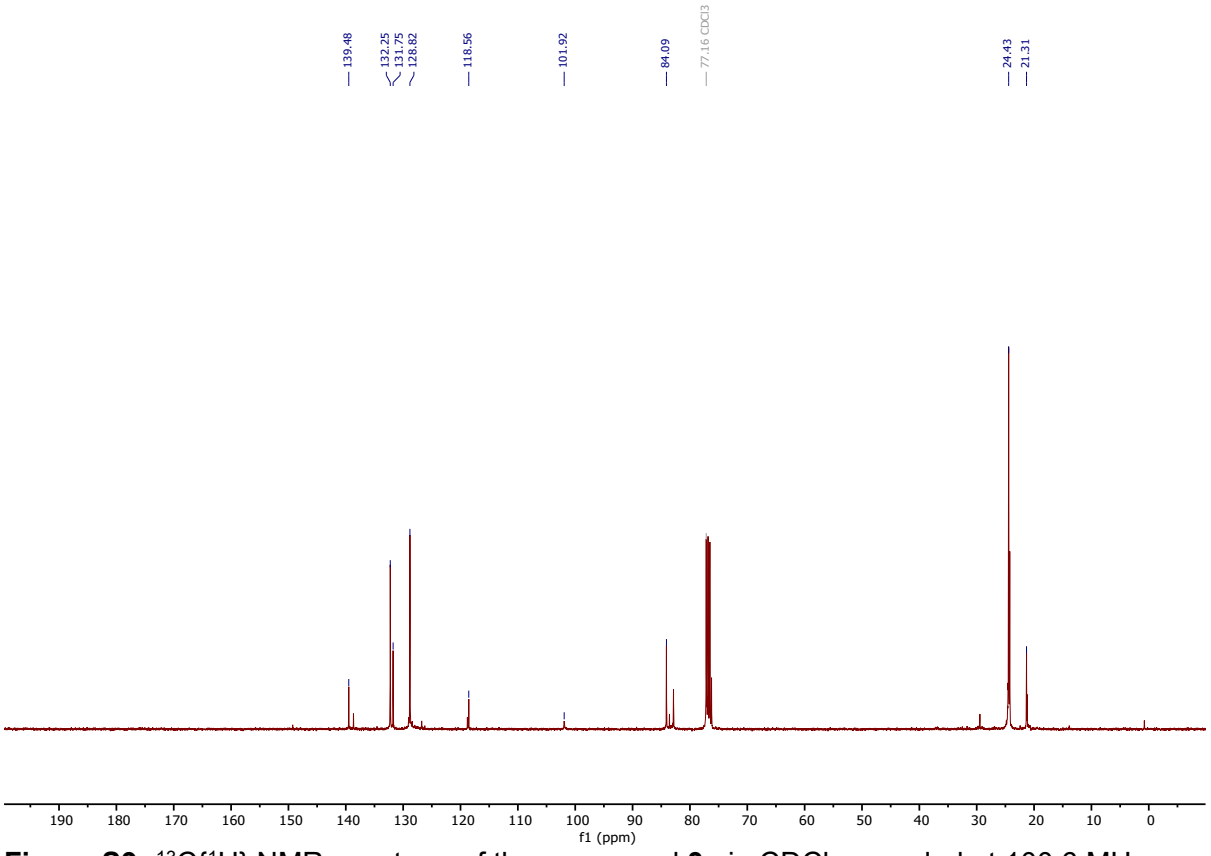


Figure S9: $^{13}C\{^1H\}$ NMR spectrum of the compound **3a** in $CDCl_3$ recorded at 100.6 MHz. Peak at 82.74 correspond to unidentified impurities.

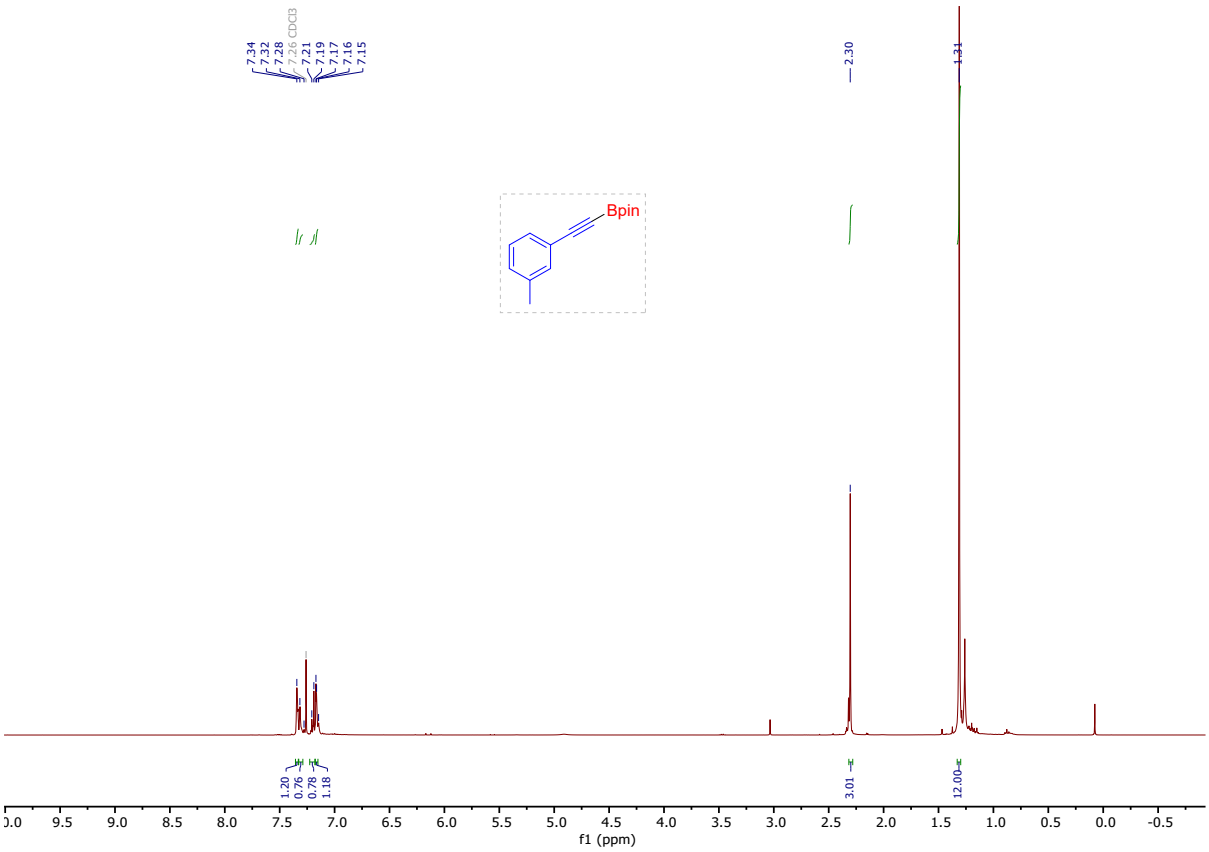


Figure S10: ^{1}H NMR spectrum of the compound **3b** in $CDCl_3$ recorded at 400 MHz

Peak at 1.25 correspond to unidentified impurities.

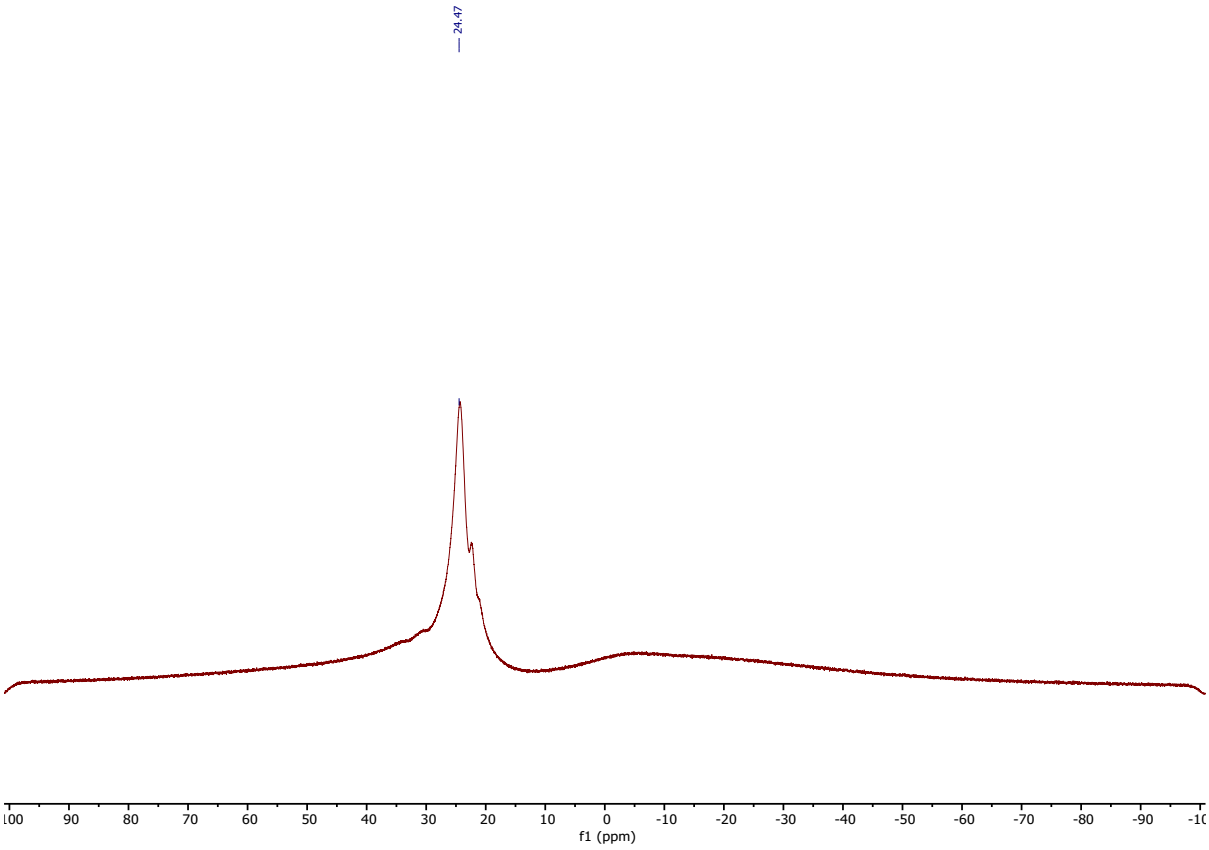


Figure S11: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3b** in $CDCl_3$ recorded at 128.3 MHz

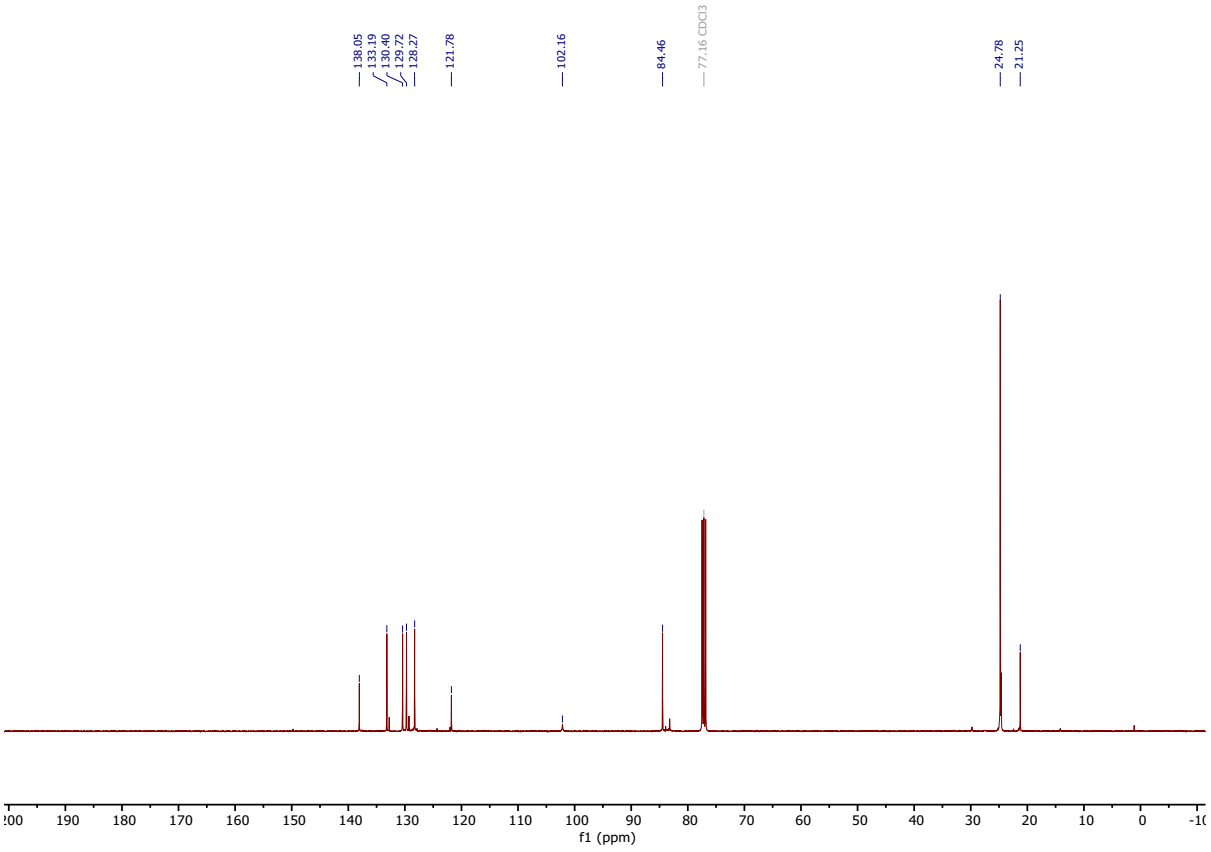


Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3b** in $CDCl_3$ recorded at 100.6 MHz

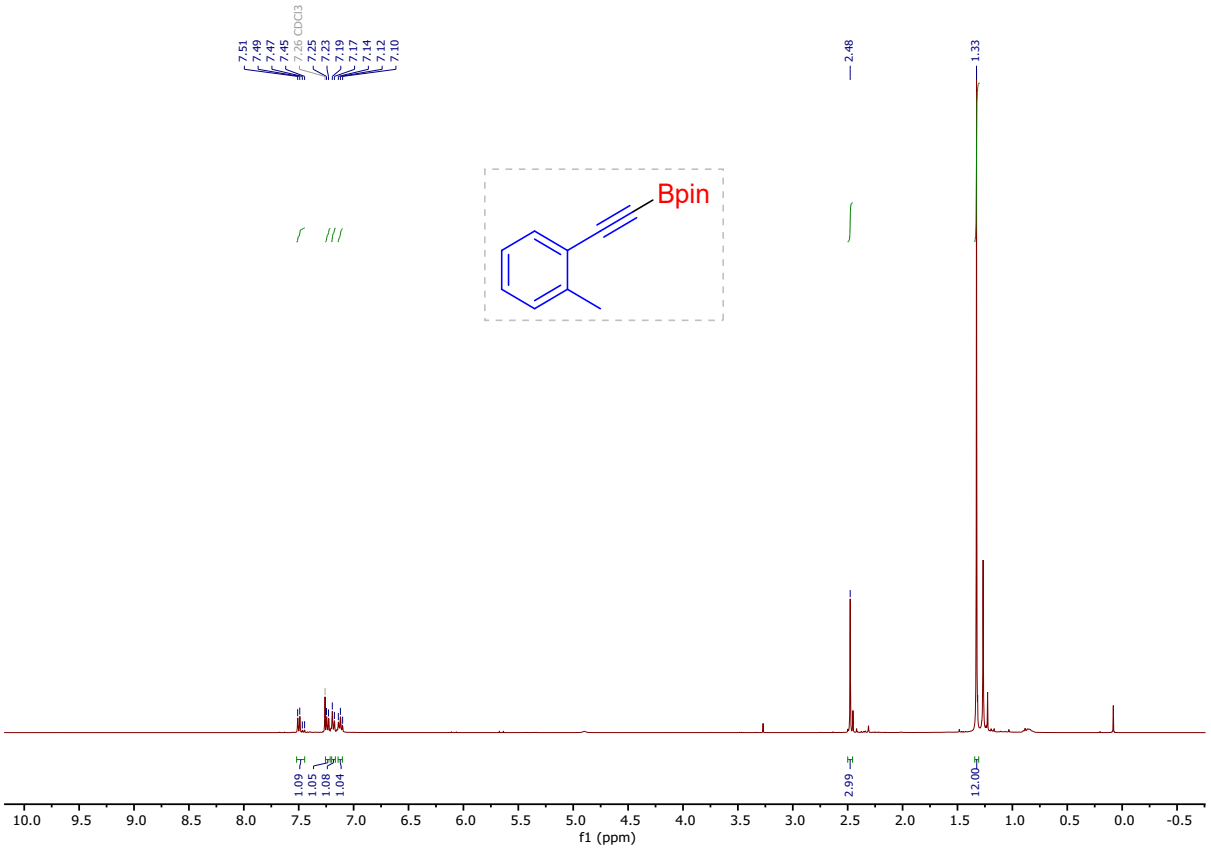


Figure S13: ^{1}H NMR spectrum of the compound **3c** in $CDCl_3$ recorded at 400 MHz

Peak at 1.27 and 1.25 correspond to unidentified impurities.

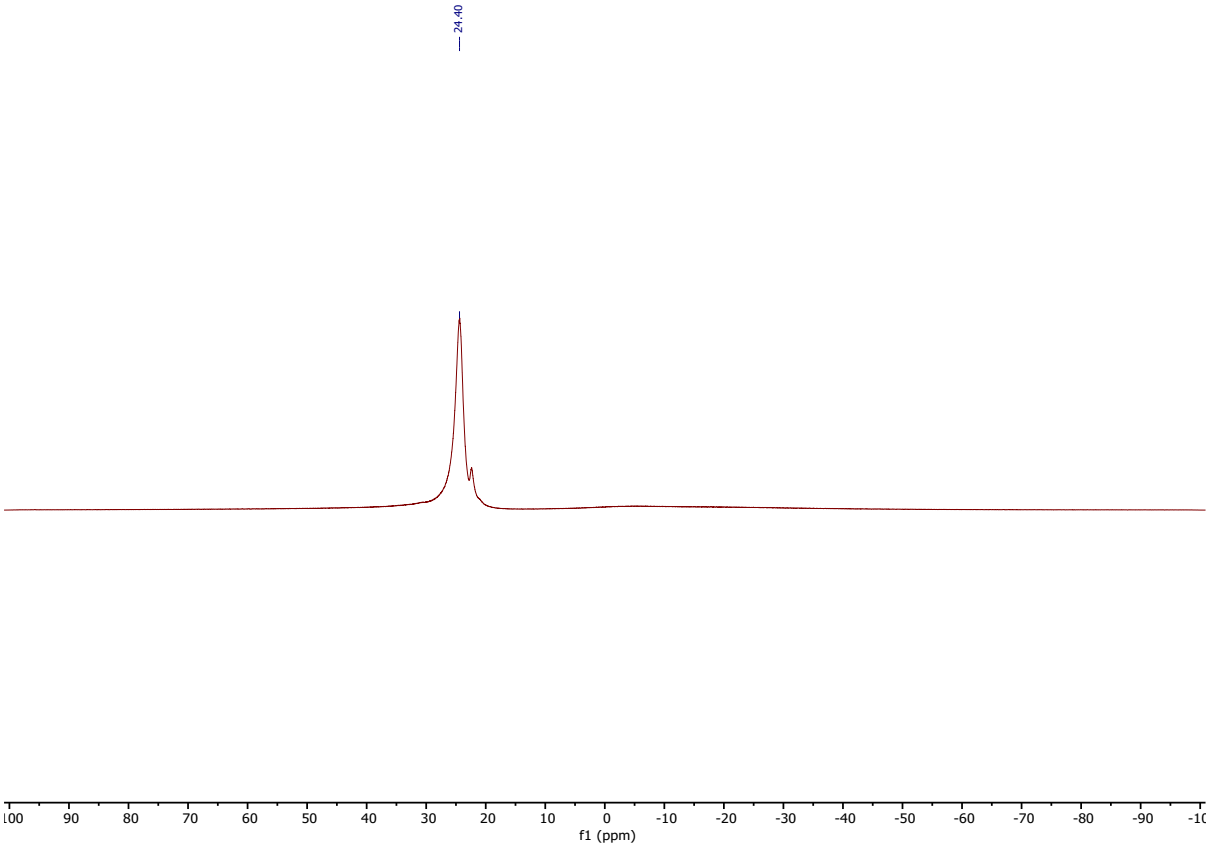


Figure S14: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3c** in $CDCl_3$ recorded at 128.3 MHz

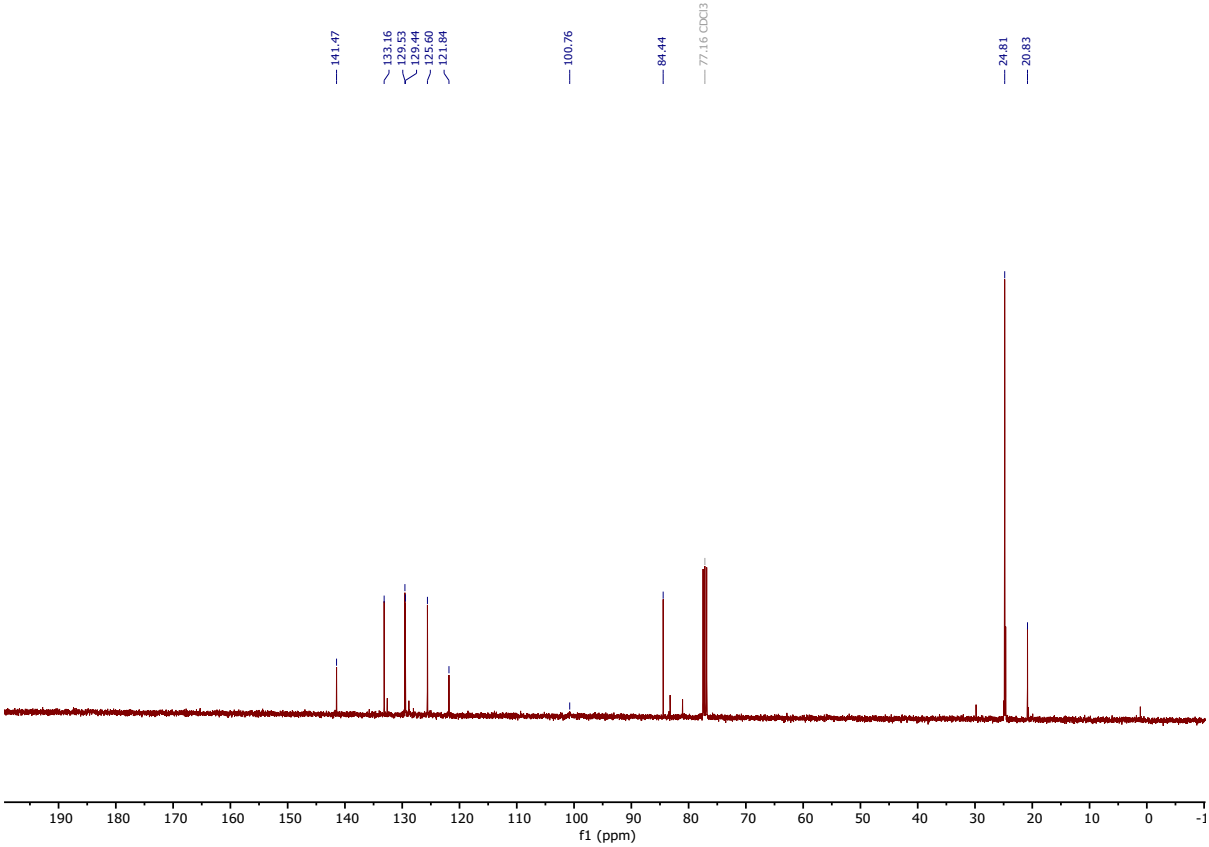


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3c** in $CDCl_3$ recorded at 100.6 MHz

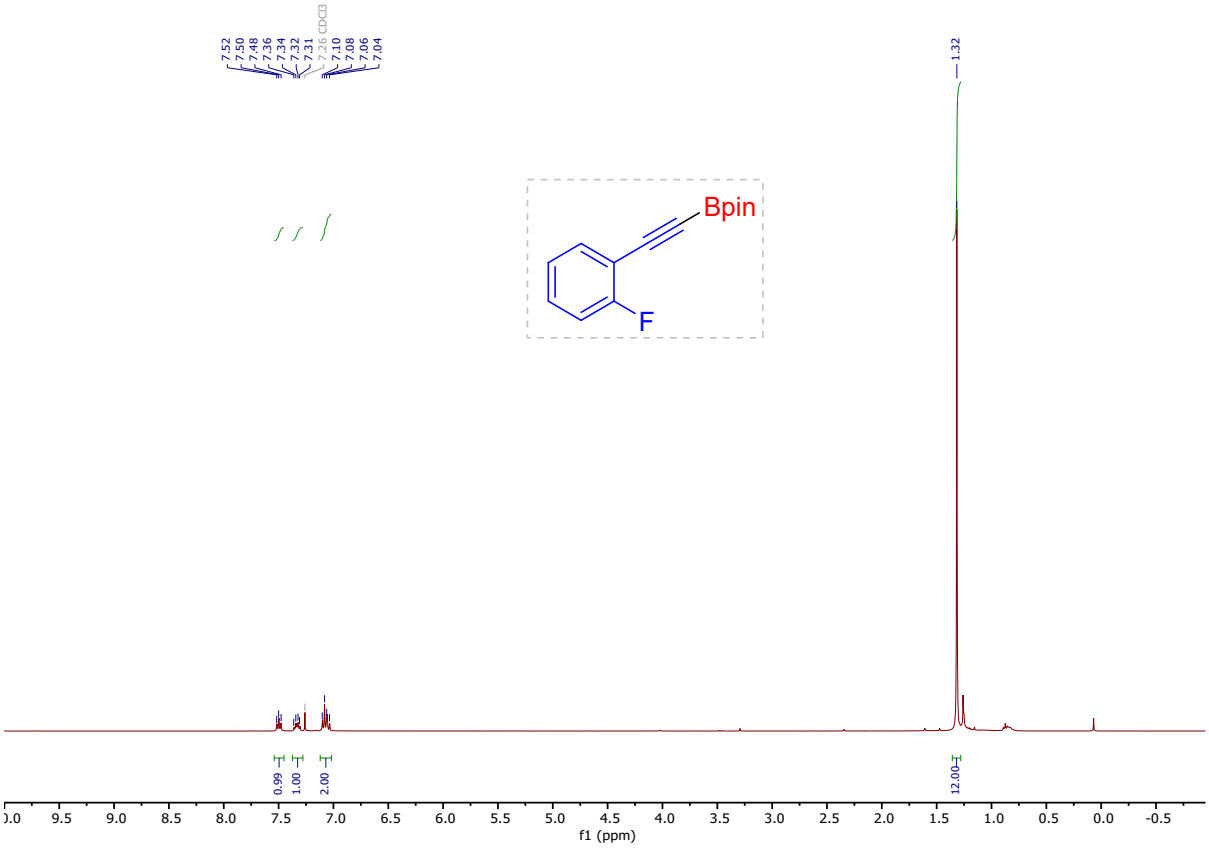


Figure S16: ^{1}H NMR spectrum of the compound **3d** in $CDCl_3$ recorded at 400 MHz

Peak at 1.26 correspond to unidentified impurities.

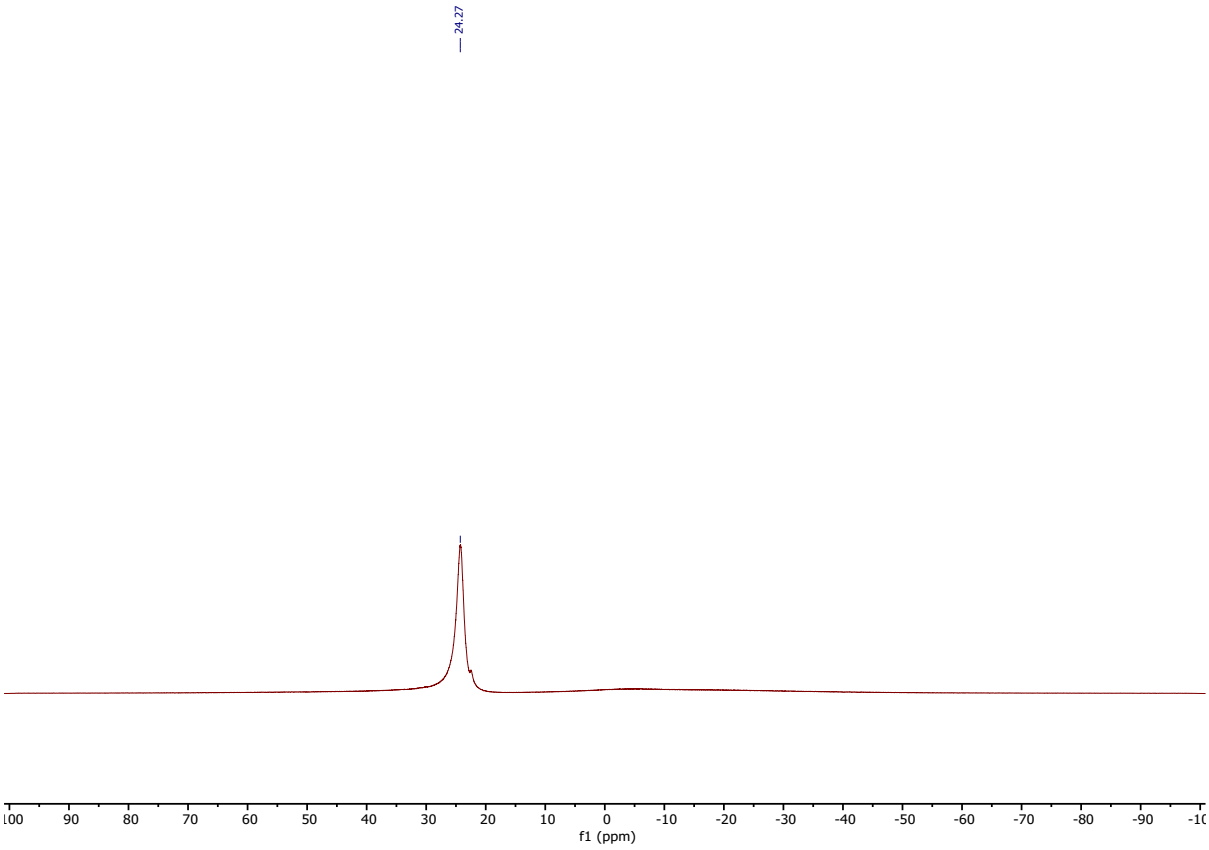


Figure S17: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3d** in $CDCl_3$ recorded at 128.3 MHz

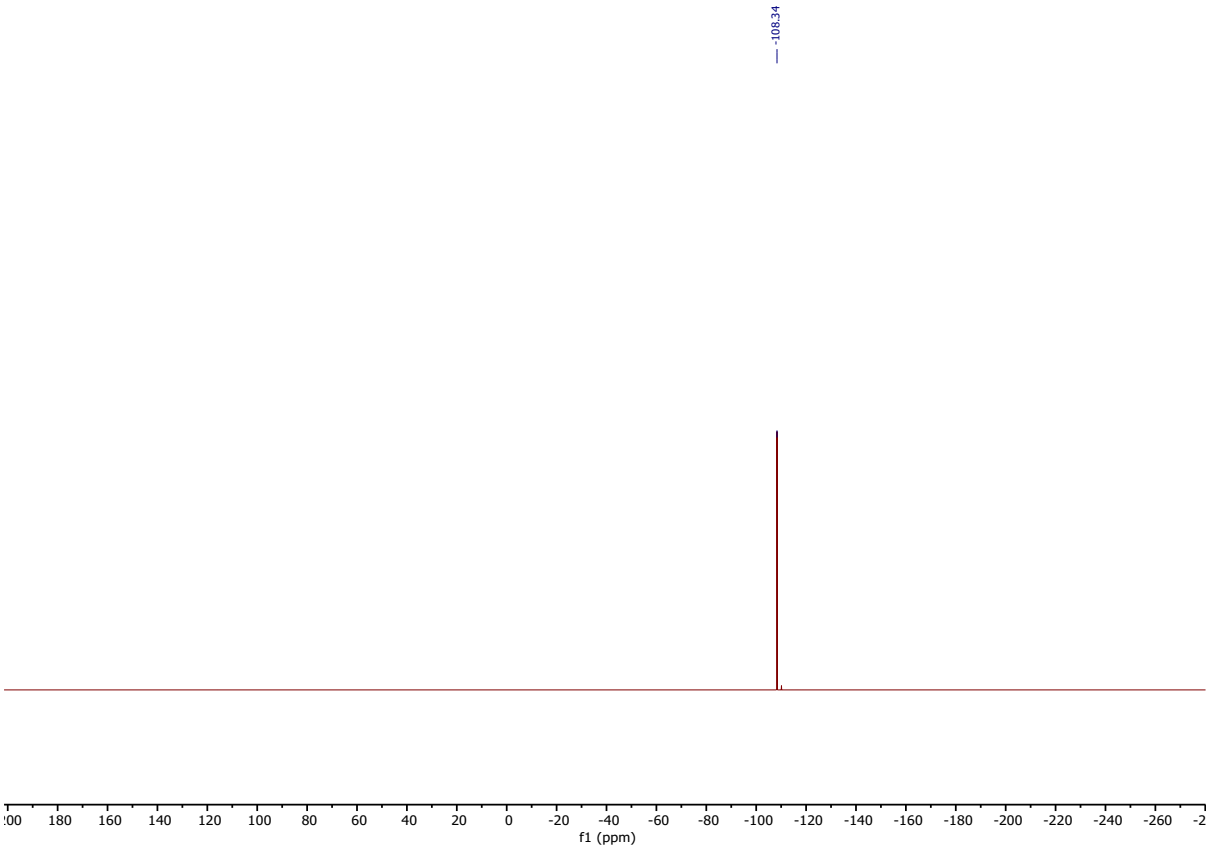


Figure S18: $^{19}F\{^{1}H\}$ NMR spectrum of the compound **3d** in $CDCl_3$ recorded at 376.5 MHz

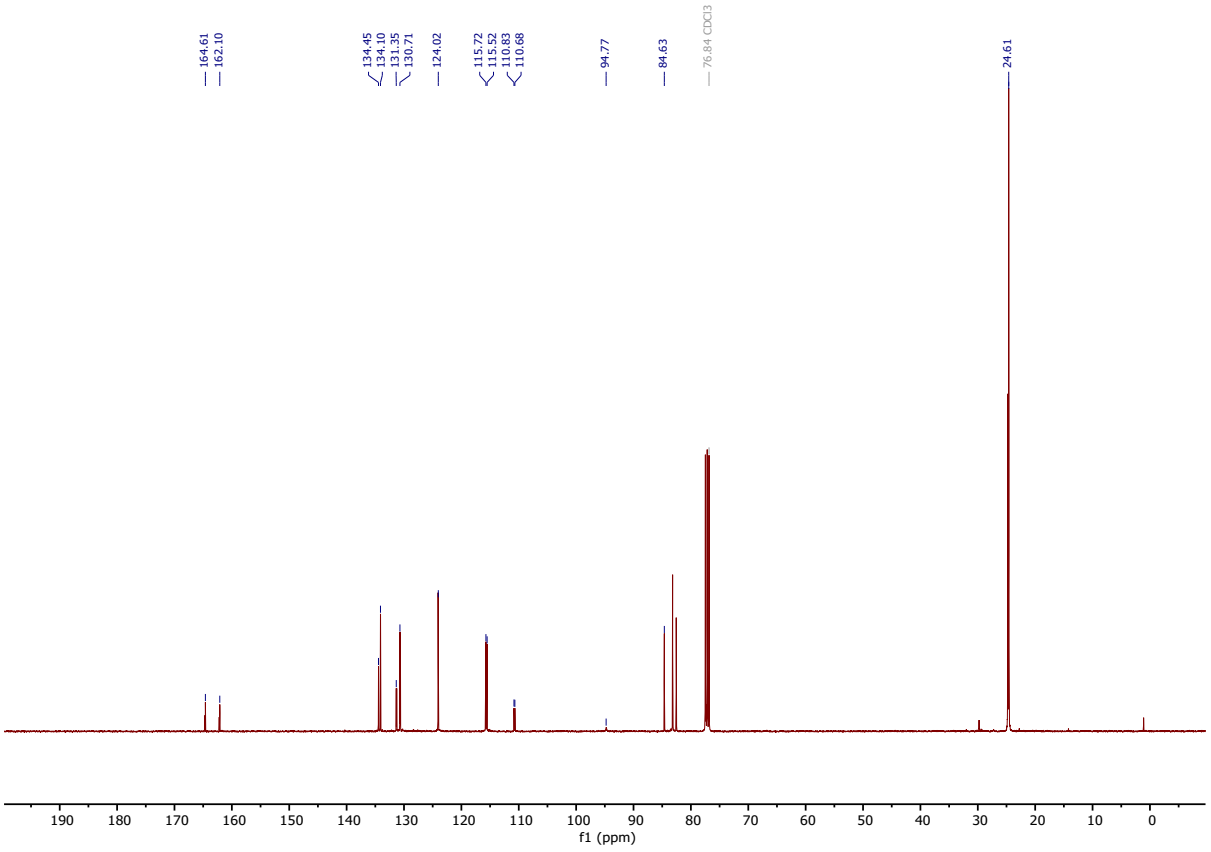


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3d** in $CDCl_3$ recorded at 100.6 MHz

Peak at 82.5 and 83.1 correspond to unidentified impurities

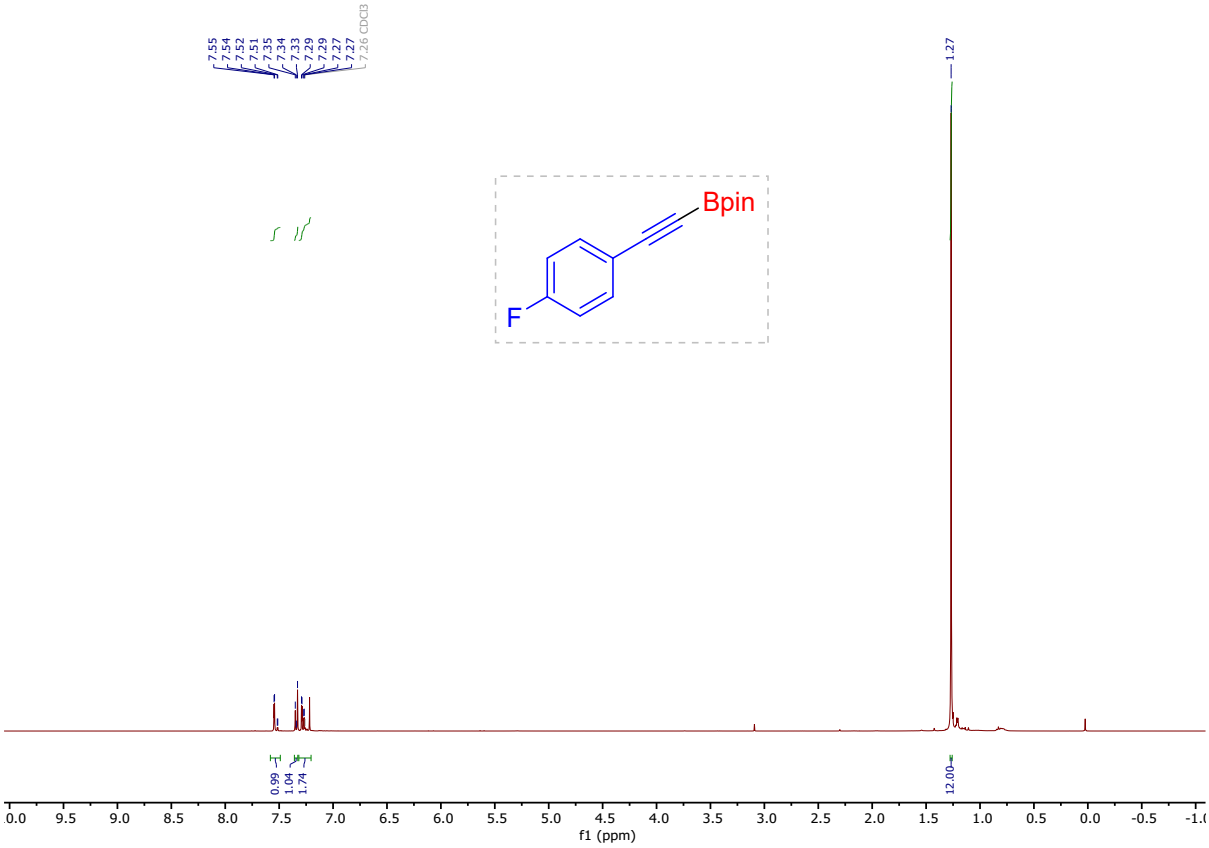


Figure S20: ^{1}H NMR spectrum of the compound **3e** in $CDCl_3$ recorded at 400 MHz

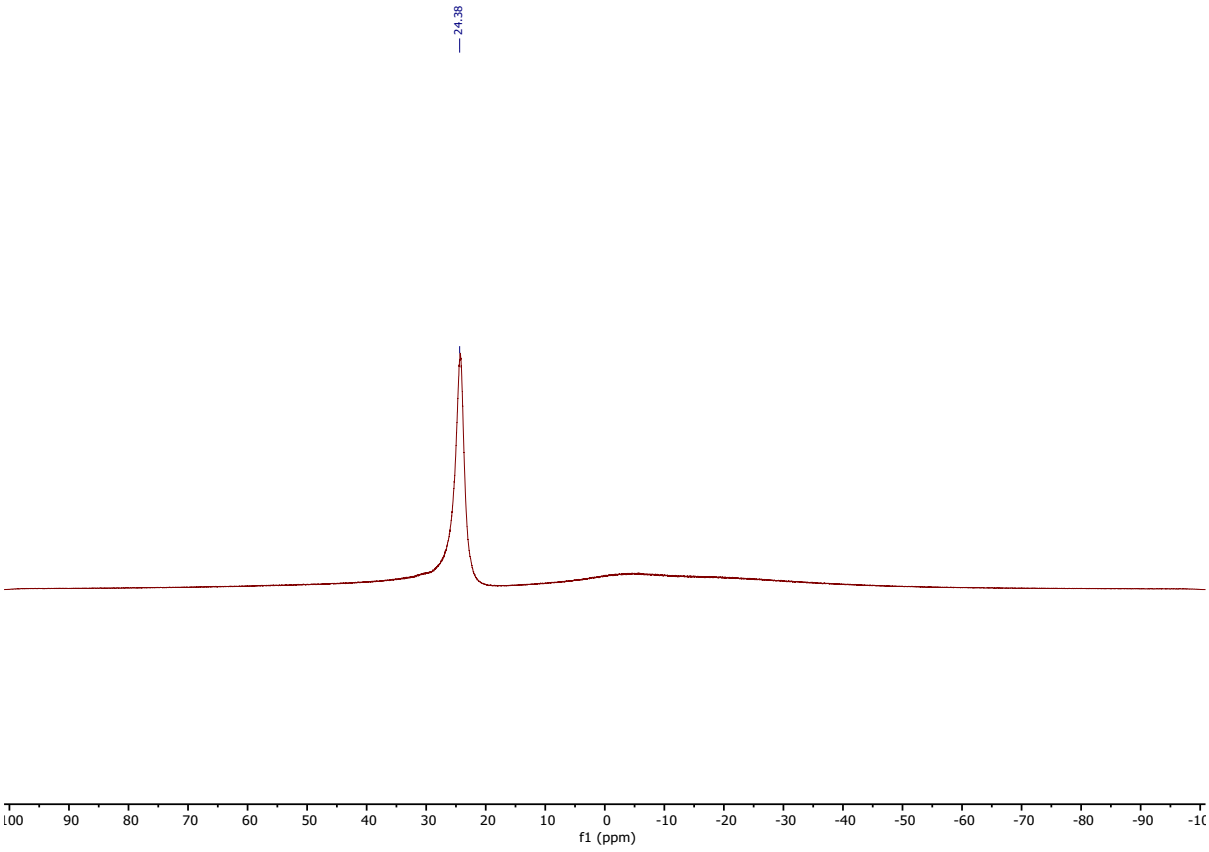


Figure S21: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3e** in $CDCl_3$ recorded at 128.3 MHz

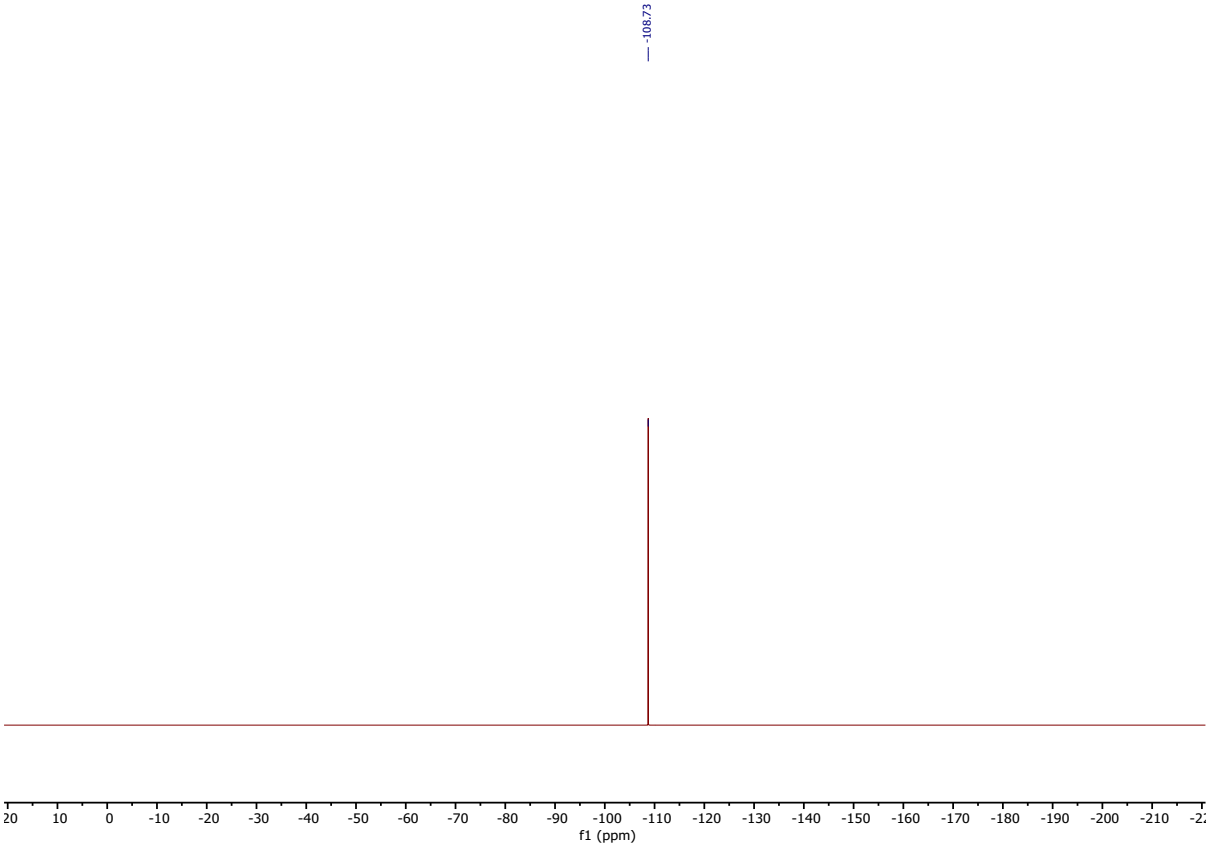


Figure S22: $^{19}F\{^{1}H\}$ NMR spectrum of the compound **3e** in $CDCl_3$ recorded at 376.5 MHz

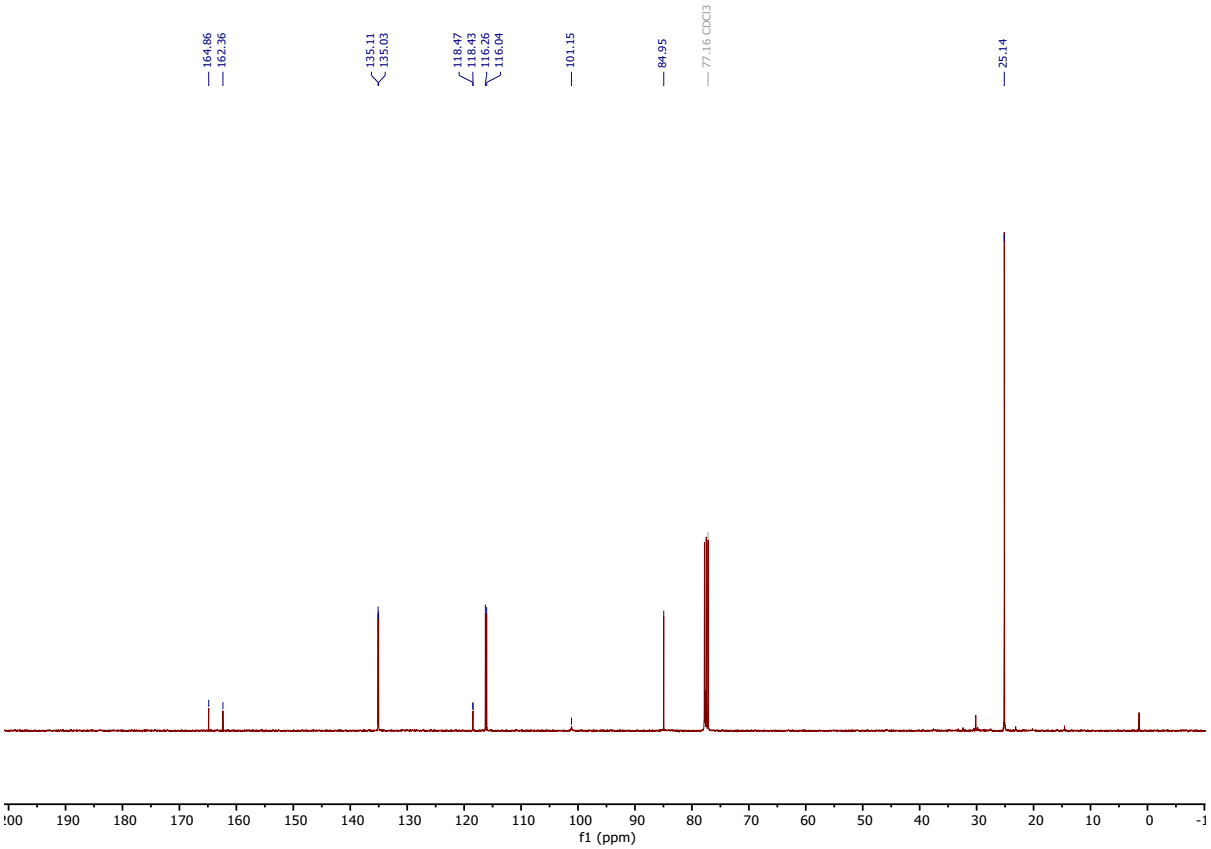


Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3e** in $CDCl_3$ recorded at 100.6 MHz

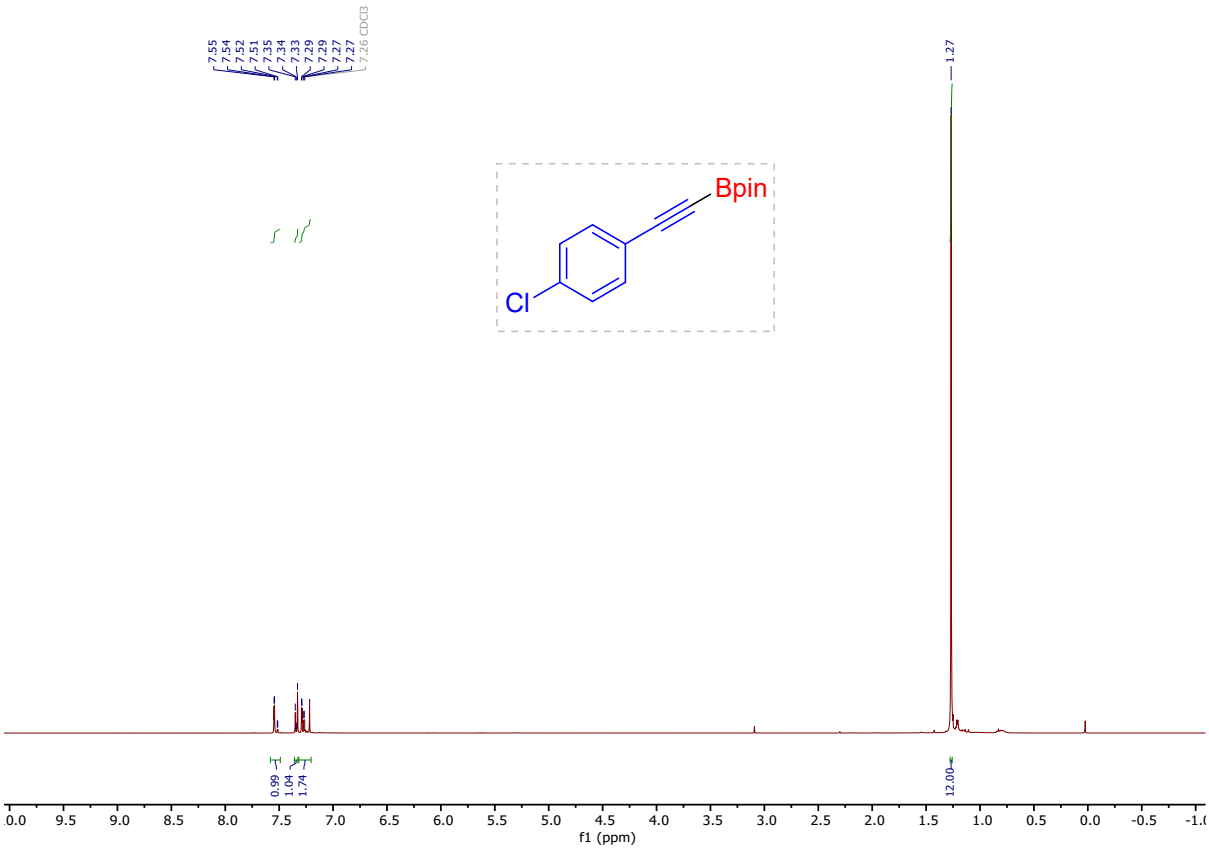


Figure S24: ^{1}H NMR spectrum of the compound **3f** in $CDCl_3$ recorded at 400 MHz

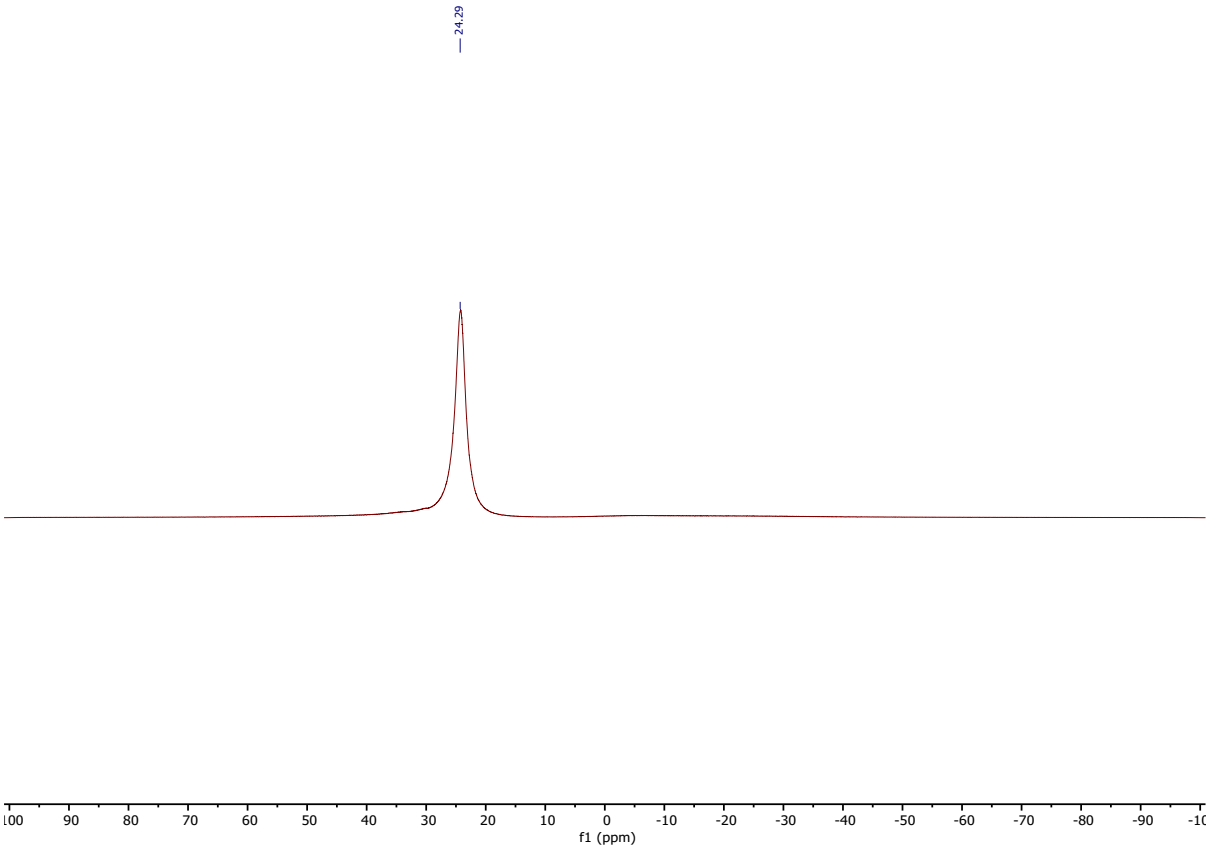


Figure S25: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3f** in $CDCl_3$ recorded at 128.3 MHz

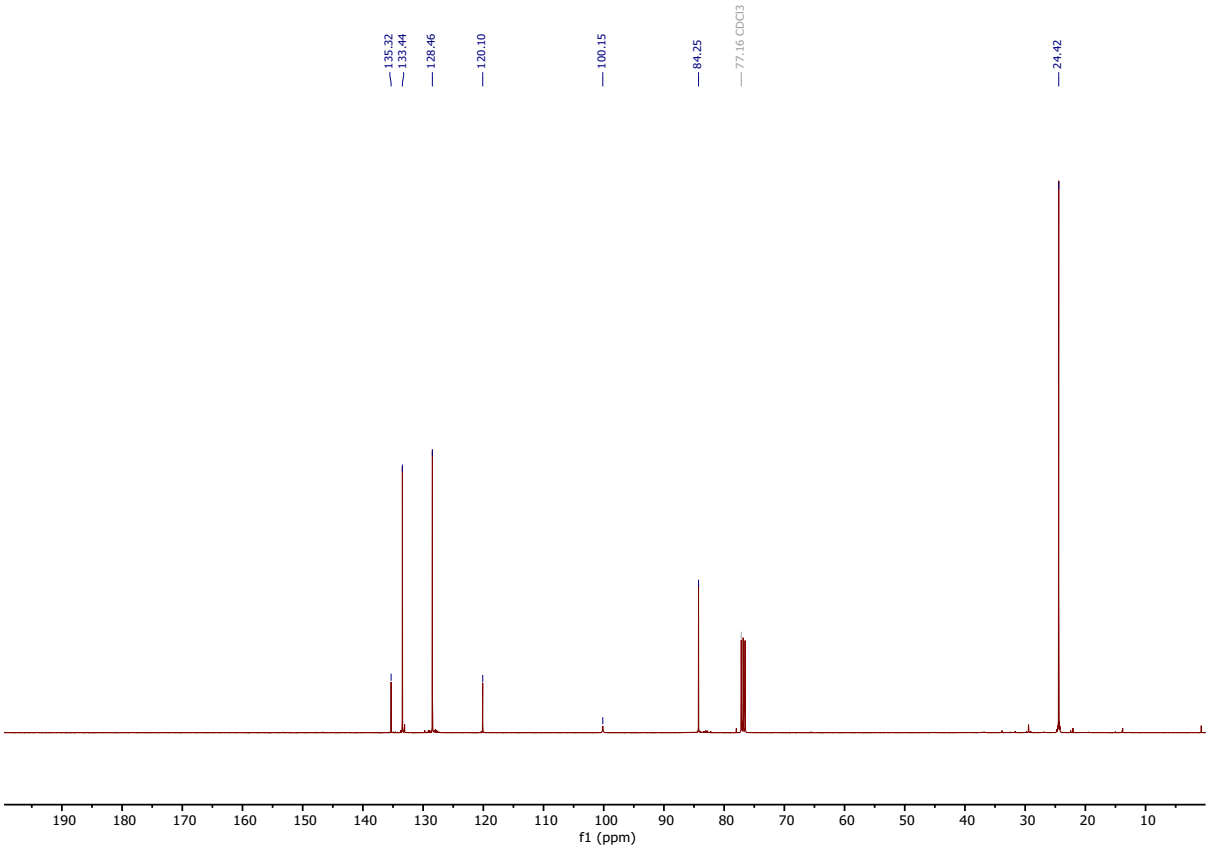


Figure S26: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3f** in $CDCl_3$ recorded at 100.6 M

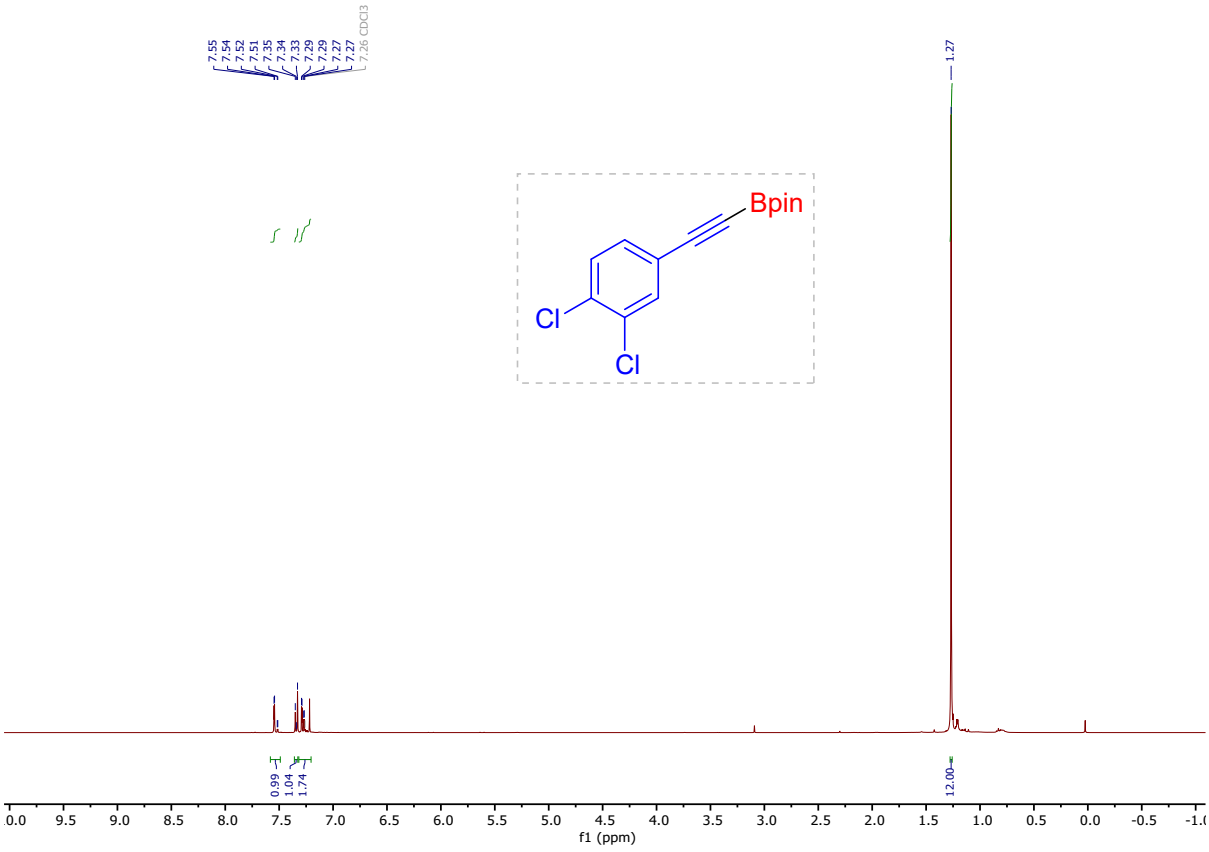


Figure S27: ^{1}H NMR spectrum of the compound **3g** in $CDCl_3$ recorded at 400 MHz

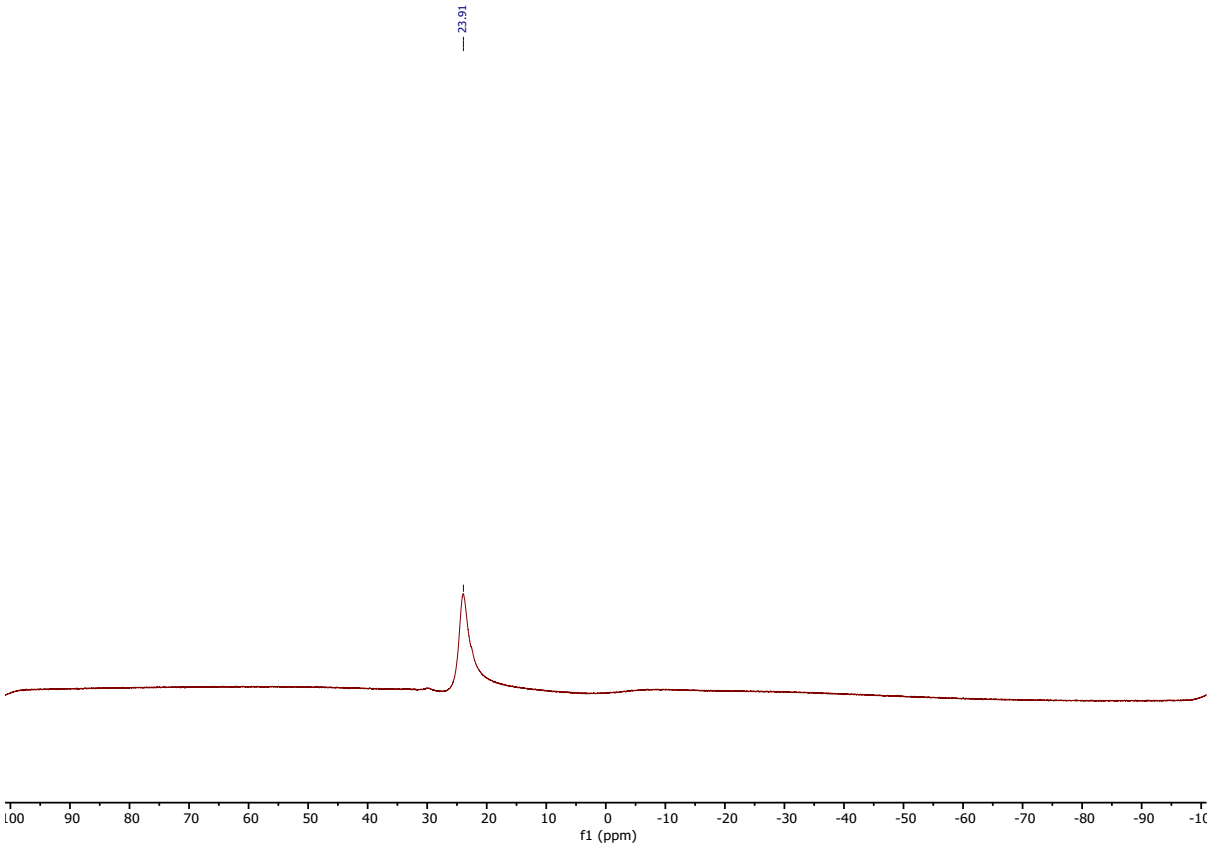


Figure S28: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3g** in $CDCl_3$ recorded at 128.3 MHz

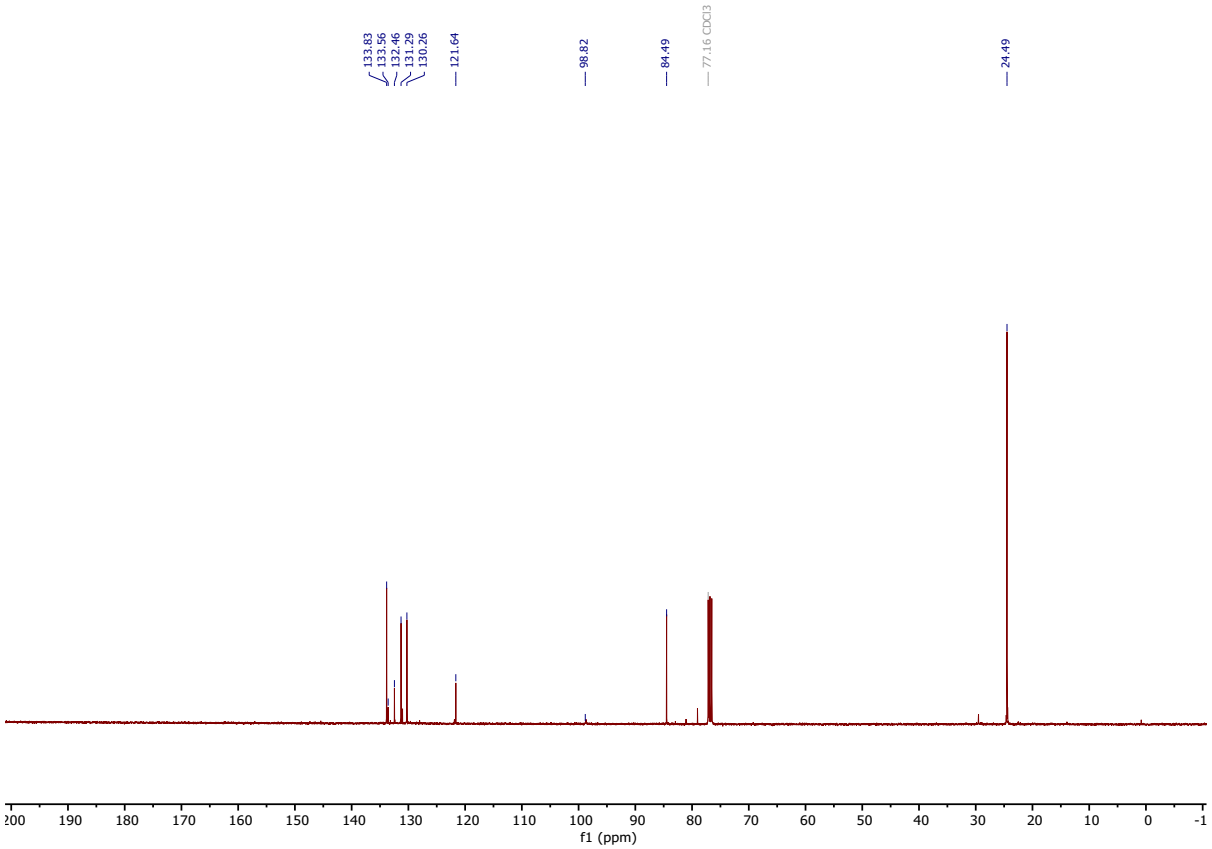


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3g** in $CDCl_3$ recorded at 100.6 MH

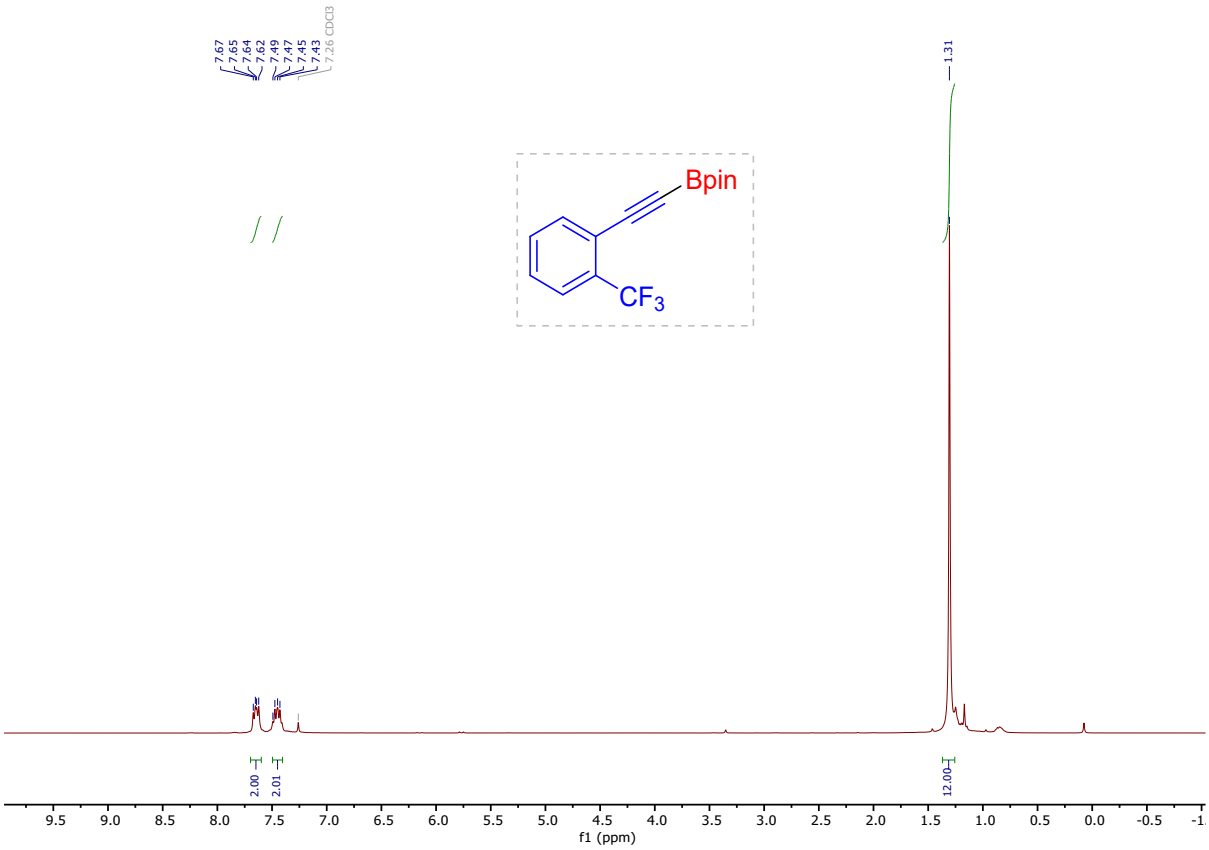


Figure S30: ^{1}H NMR spectrum of the compound **3h** in CDCl3 recorded at 400 MHz

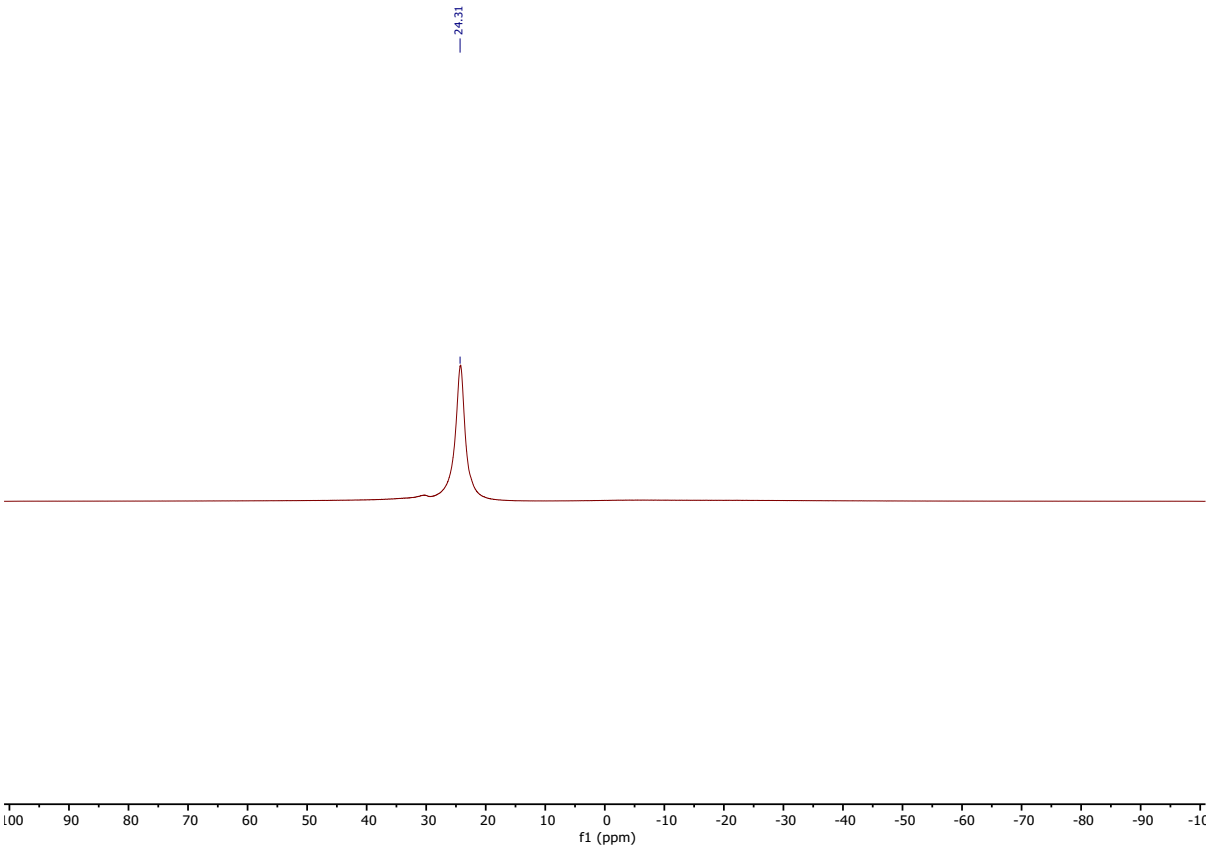


Figure S31: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3h** in $CDCl_3$ recorded at 128.3 MHz

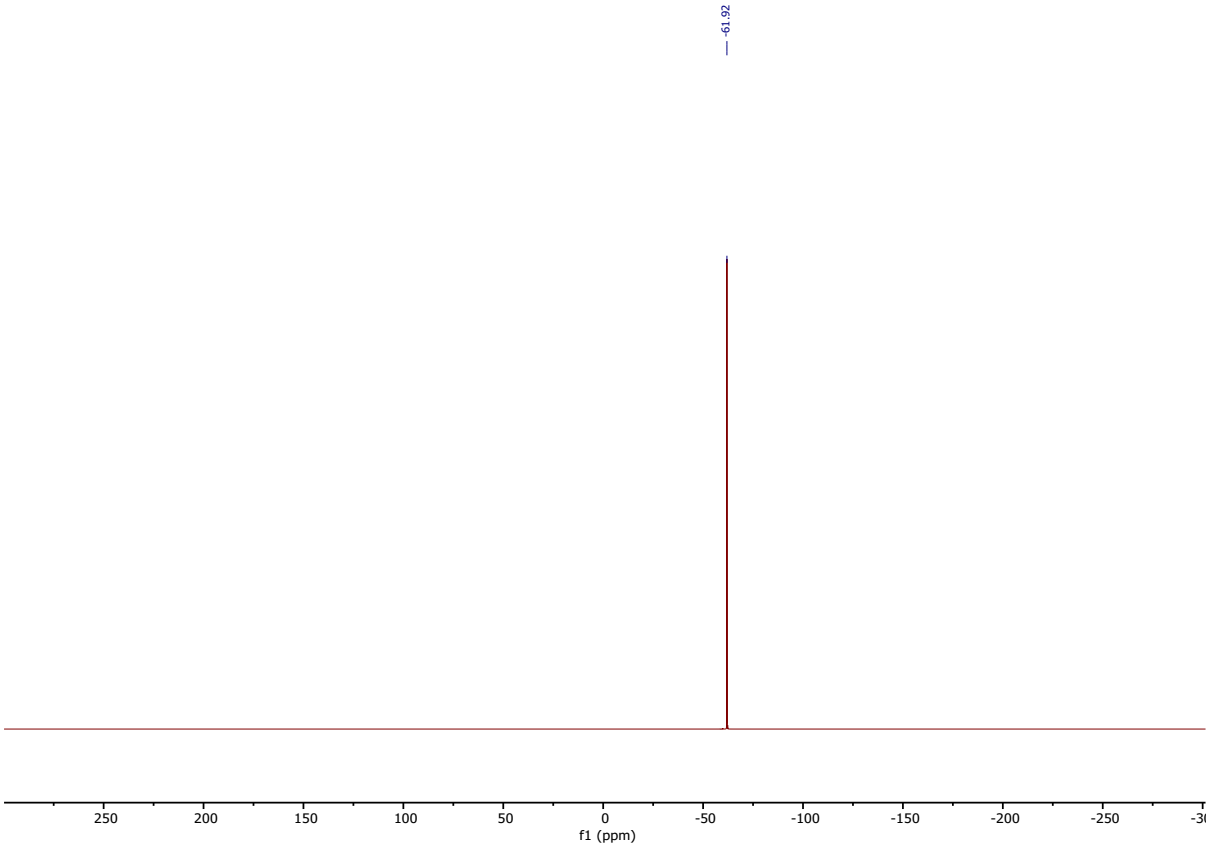


Figure S32: $^{19}F\{^{1}H\}$ NMR spectrum of the compound **3h** in $CDCl_3$ recorded at 376.5 MHz

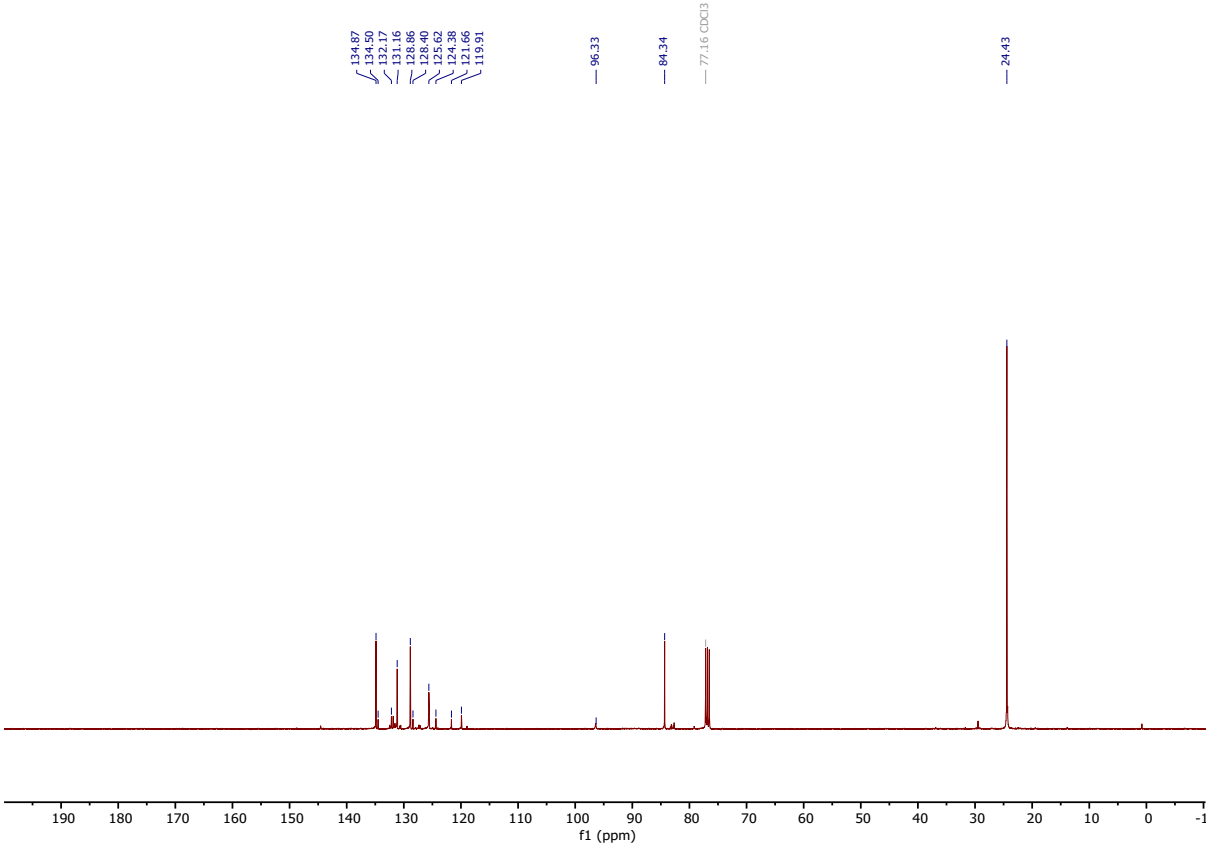


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3h** in $CDCl_3$ recorded at 100.6 MHz

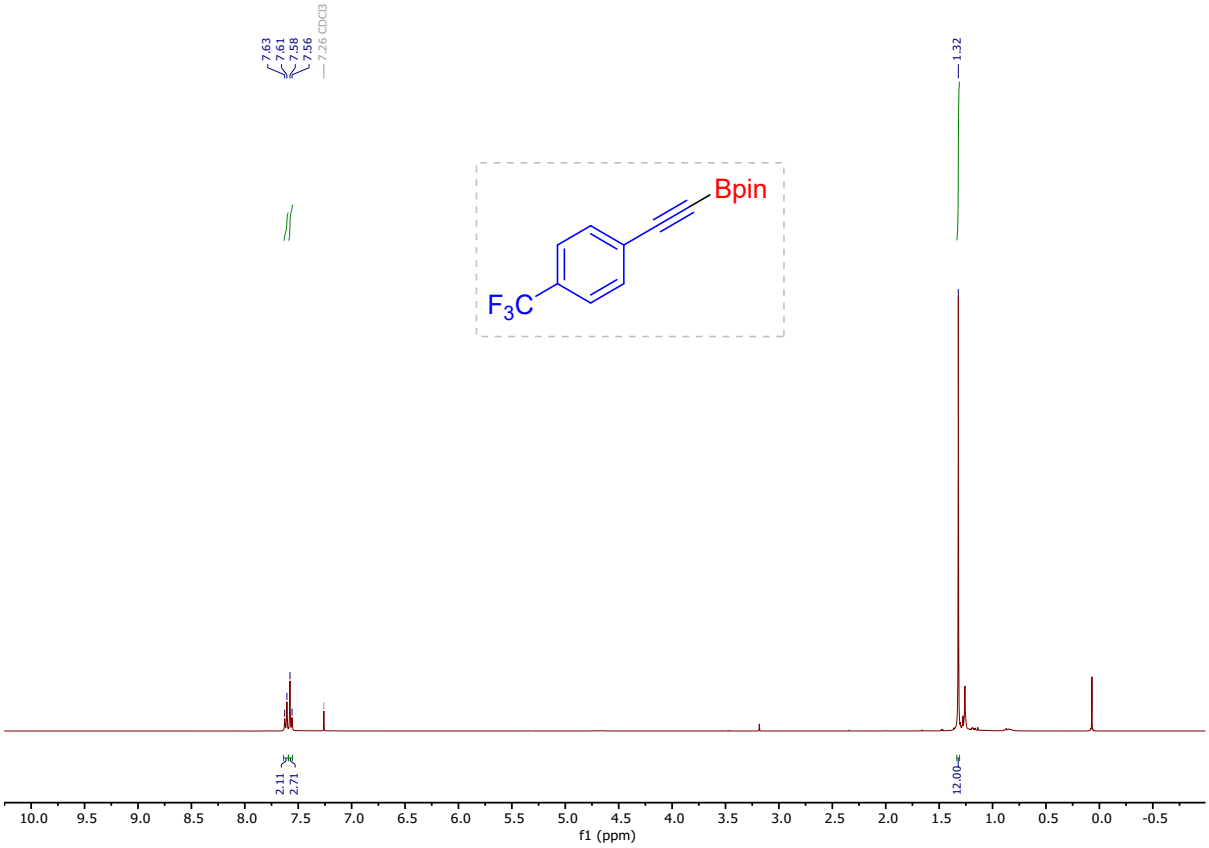


Figure S34: ^{1}H NMR spectrum of the compound **3i** in $CDCl_3$ recorded at 400 MHz

Peak at 1.25 correspond to unidentified impurities.

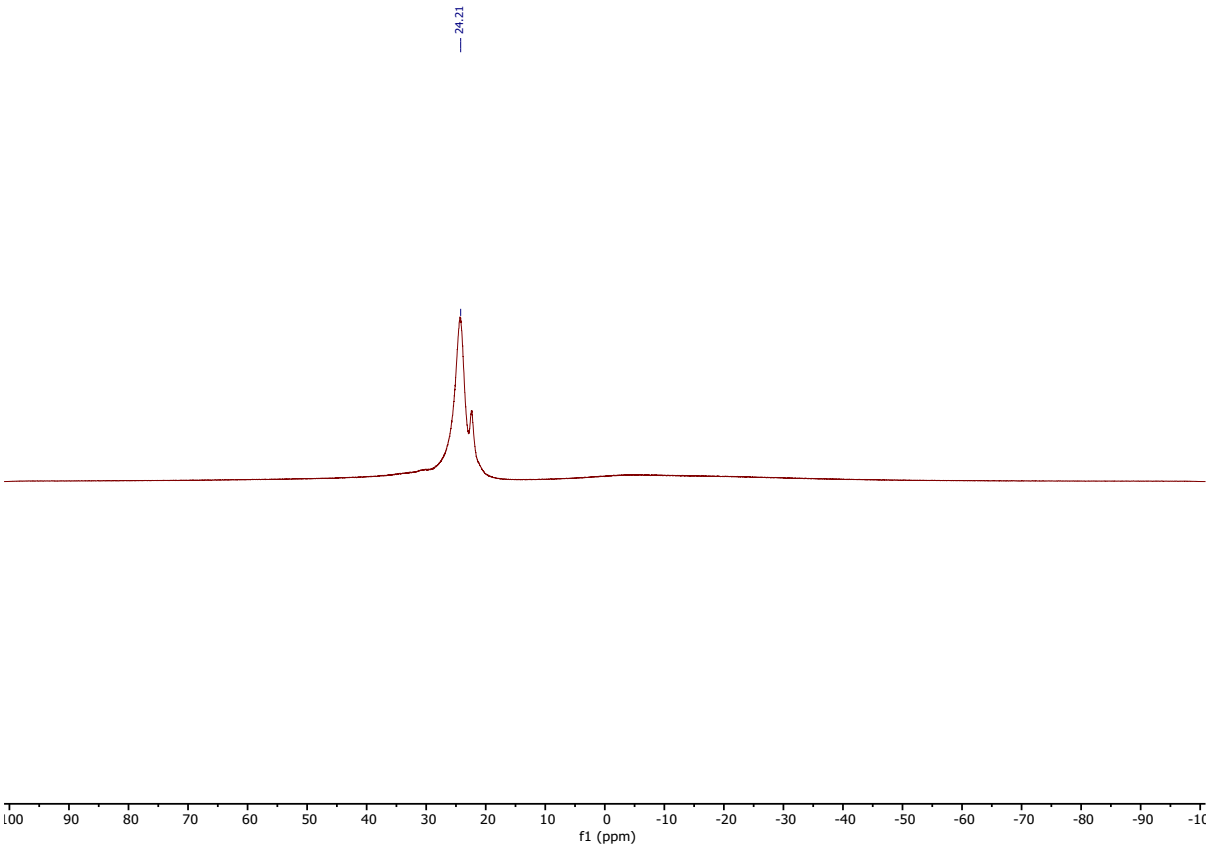


Figure S35: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3i** in $CDCl_3$ recorded at 128.3 MHz

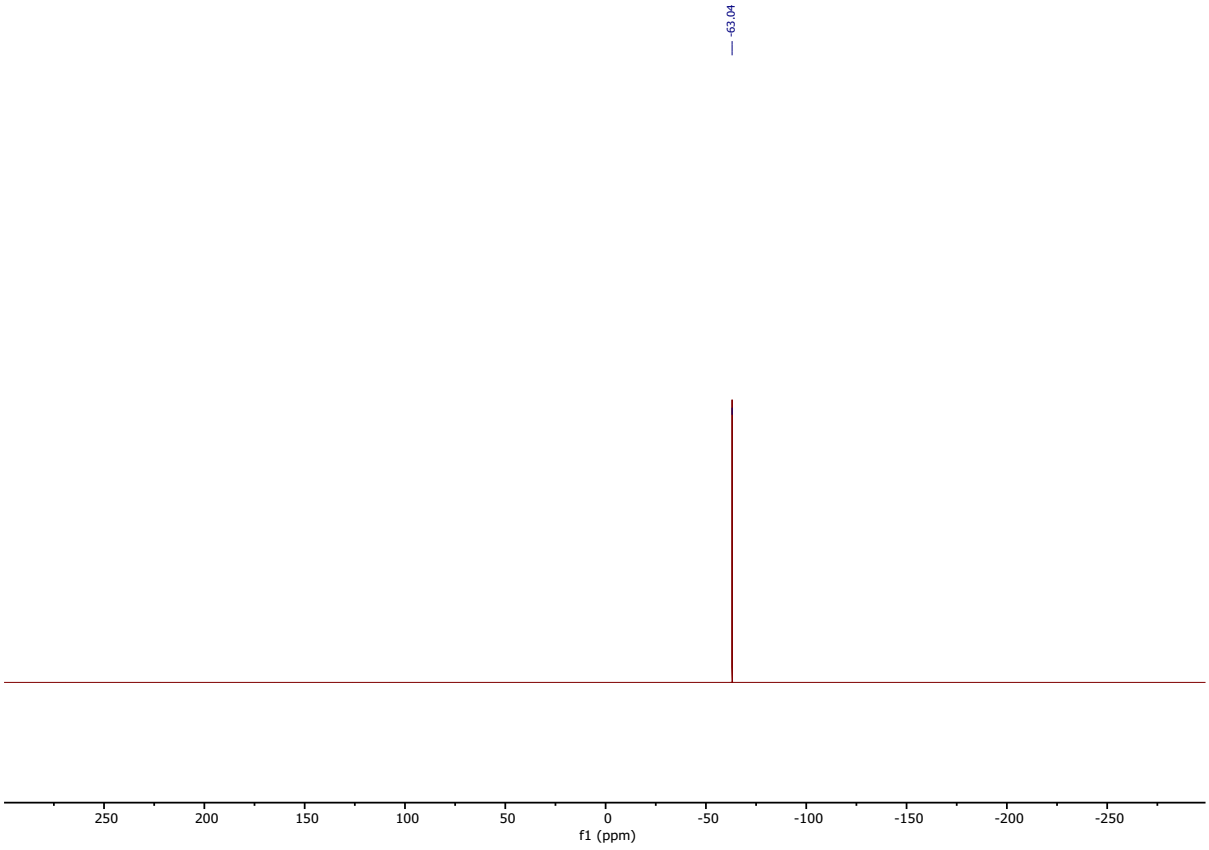


Figure S36: $^{19}F\{^{1}H\}$ NMR spectrum of the compound **3i** in $CDCl_3$ recorded at 376.5 MHz

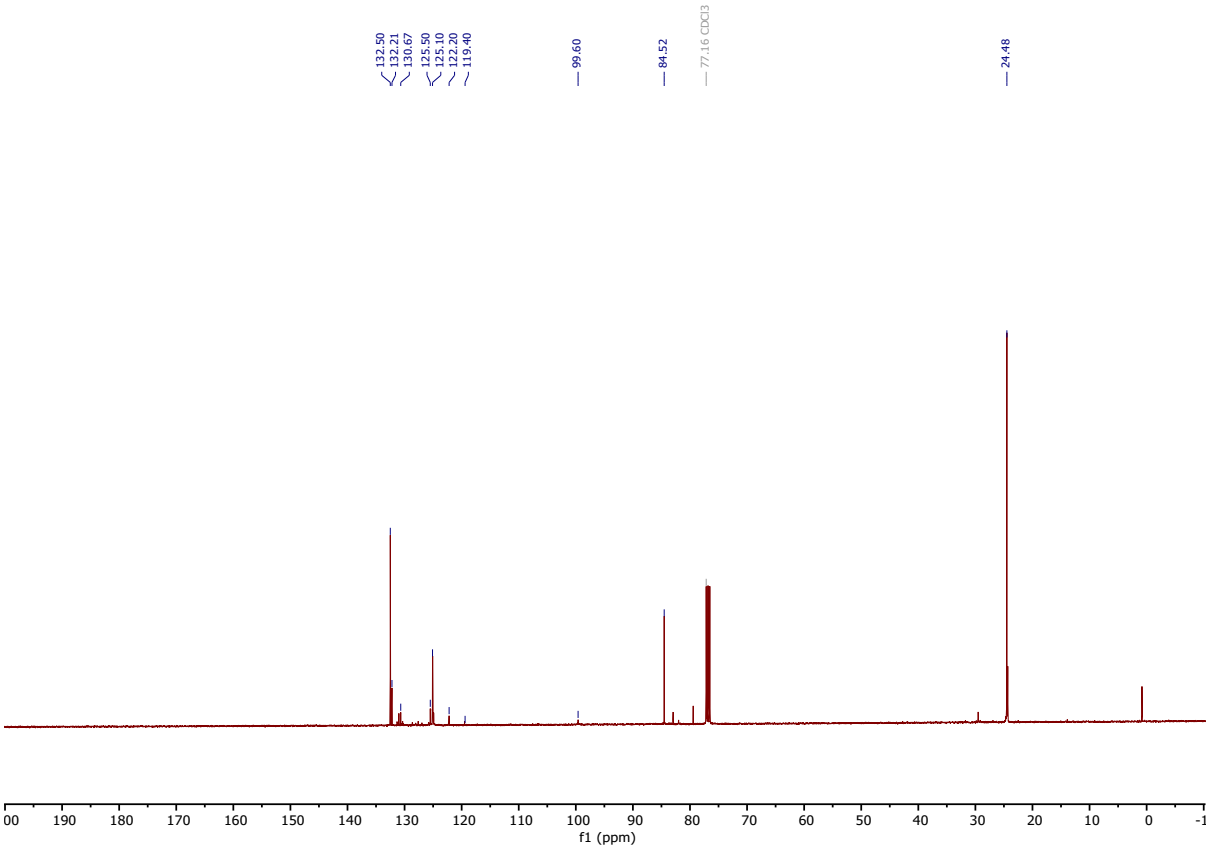


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3i** in $CDCl_3$ recorded at 100.6 MHz

Peak at 82.74 correspond to unidentified impurities

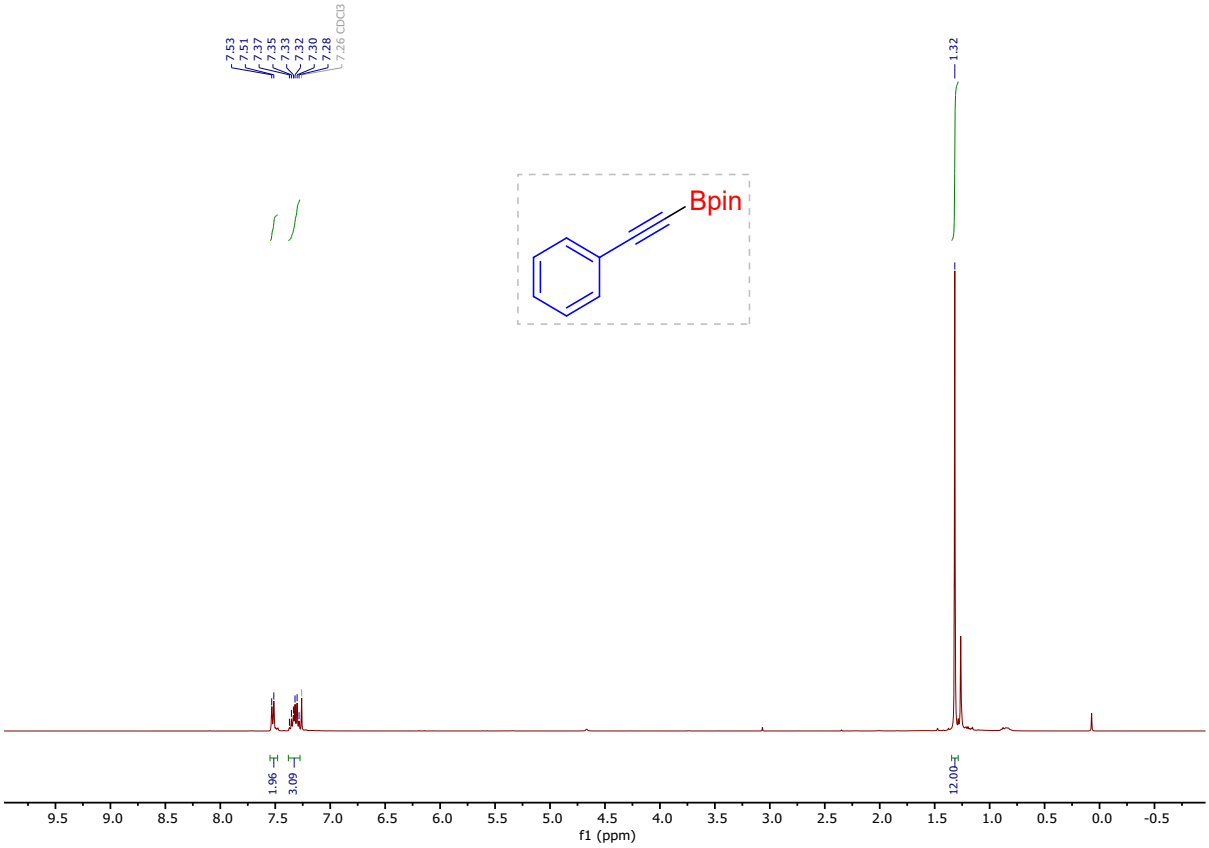


Figure S38: ^{1}H NMR spectrum of the compound **3j** in $CDCl_3$ recorded at 400 MHz

Peak at 1.25 correspond to unidentified impurities.

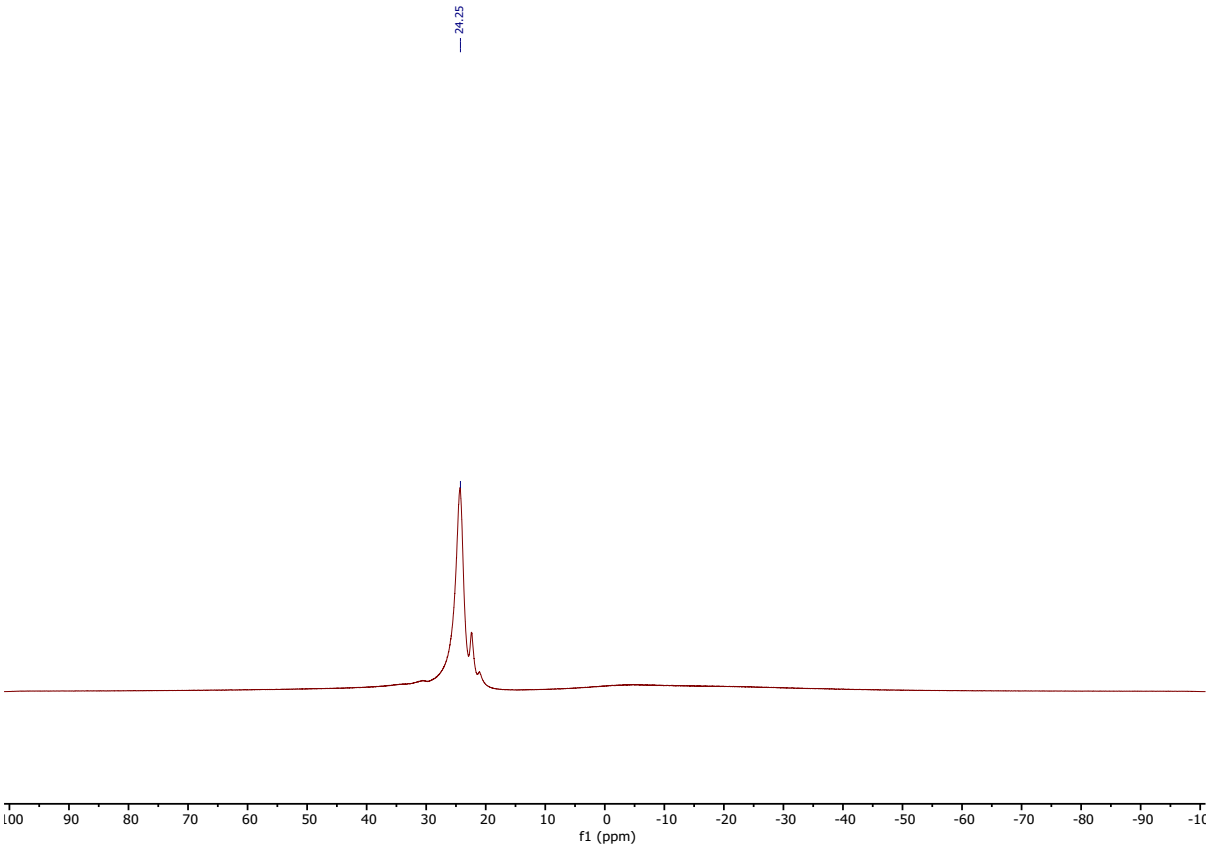


Figure S39: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3j** in $CDCl_3$ recorded at 128.3 MHz

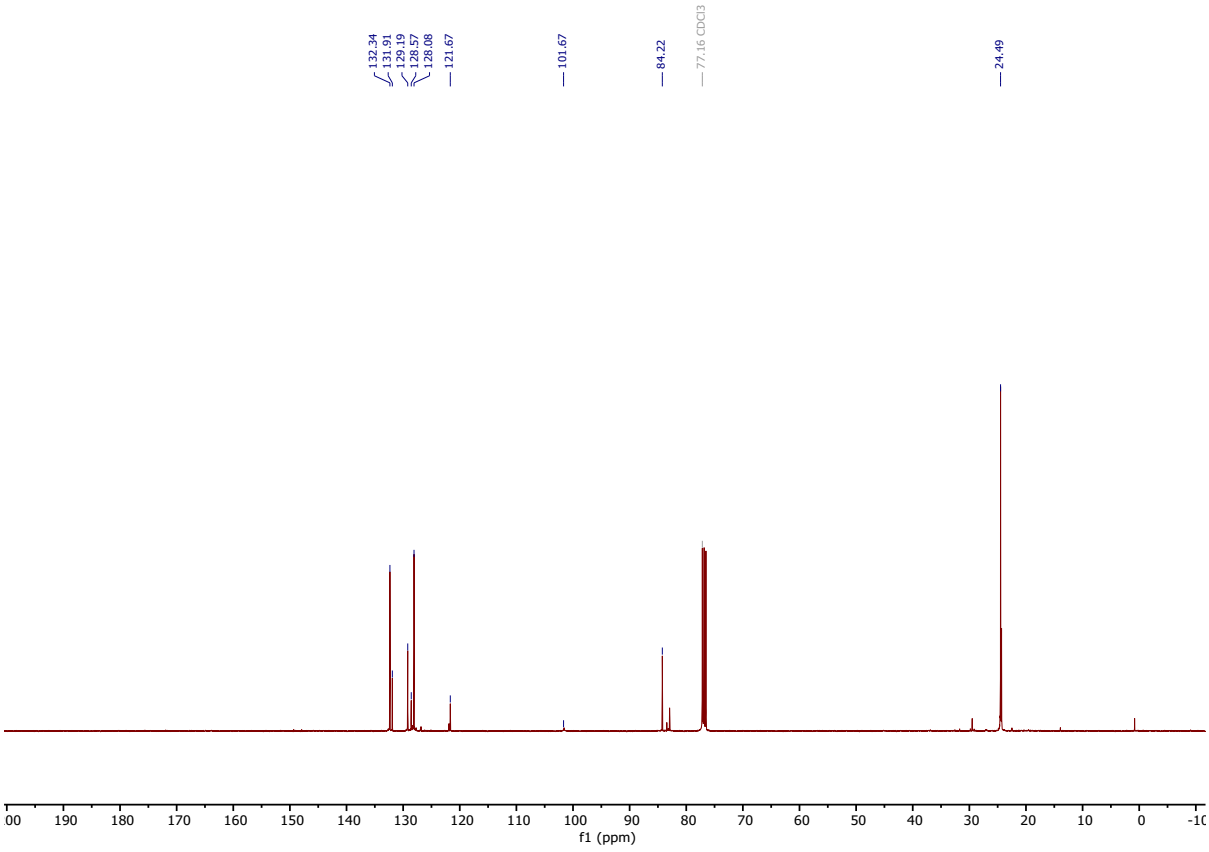


Figure S40: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3j** in $CDCl_3$ recorded at 100.6 MHz Peak at 82.89 correspond to unidentified impurities.

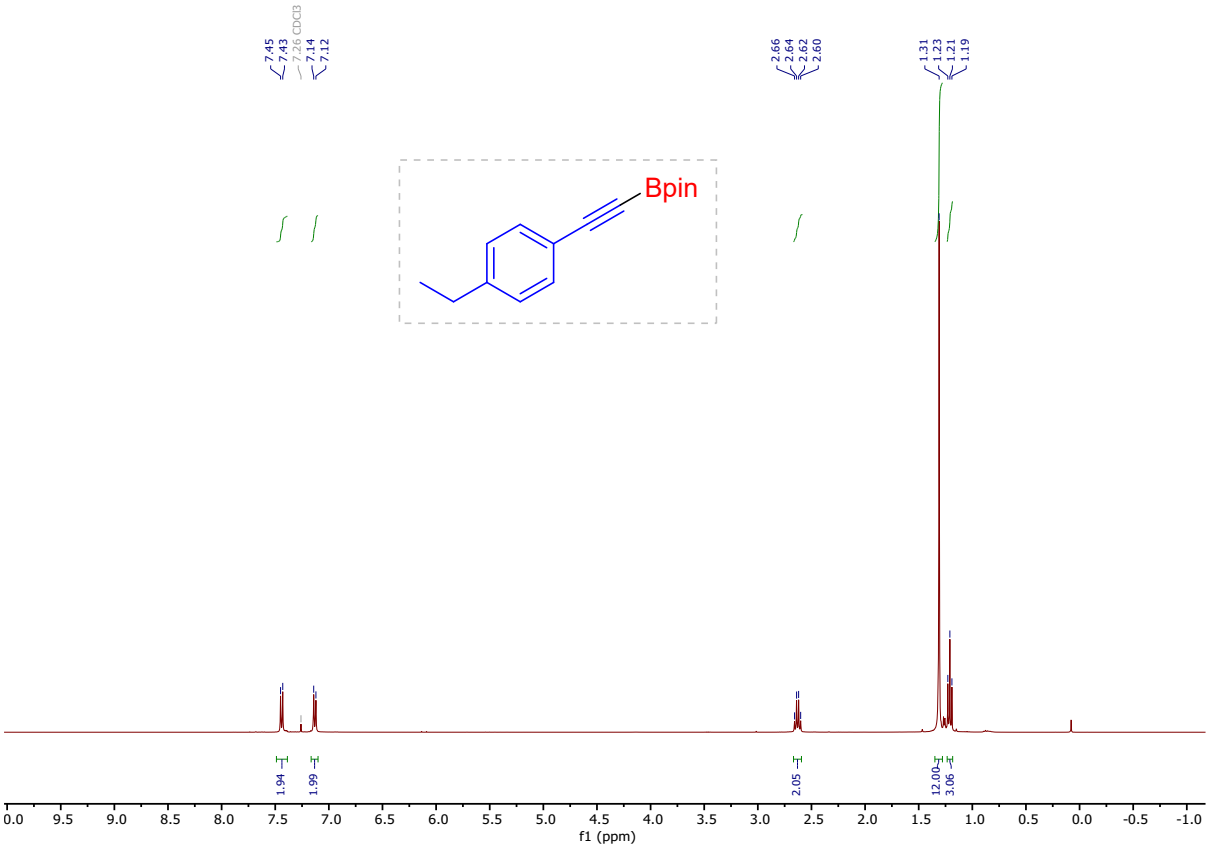


Figure S41: ^{1}H NMR spectrum of the compound **3k** in $CDCl_3$ recorded at 400 MHz

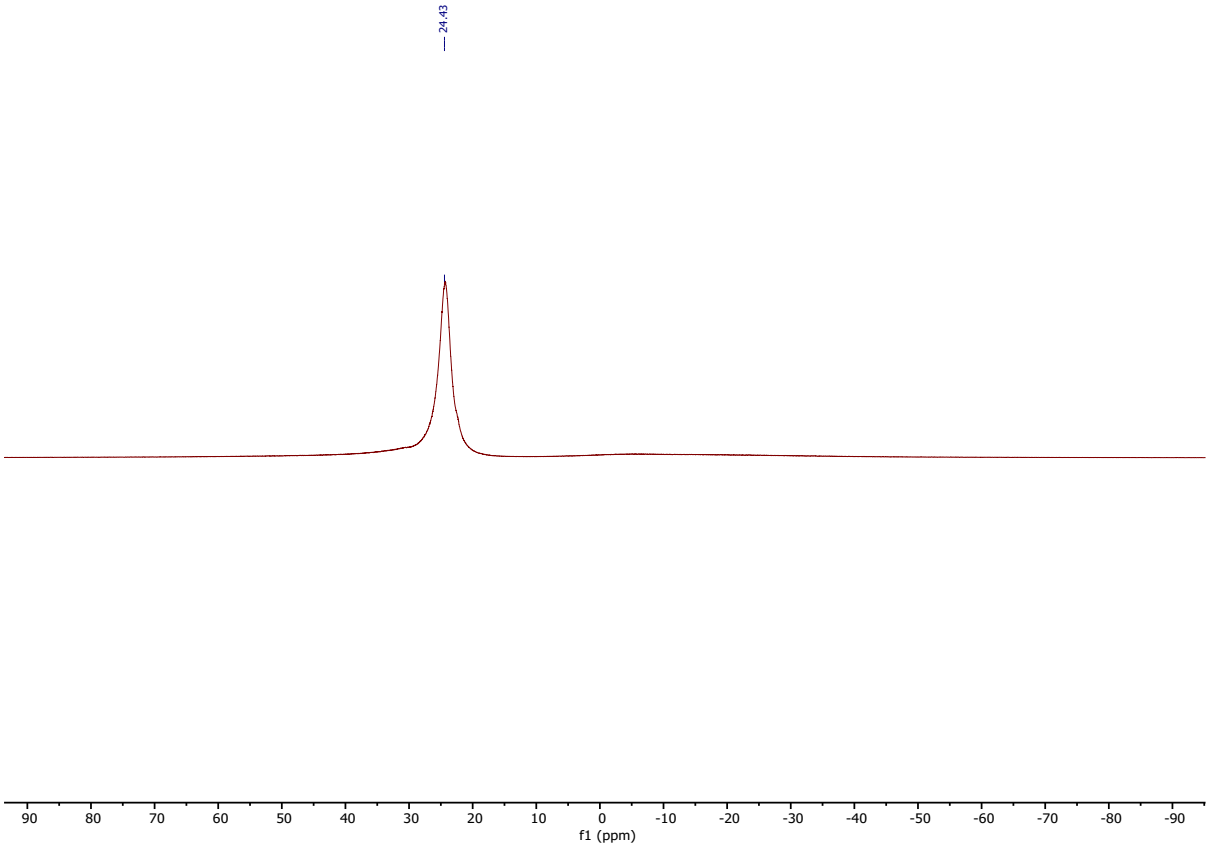


Figure S42: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3k** in $CDCl_3$ recorded at 128.3 MHz

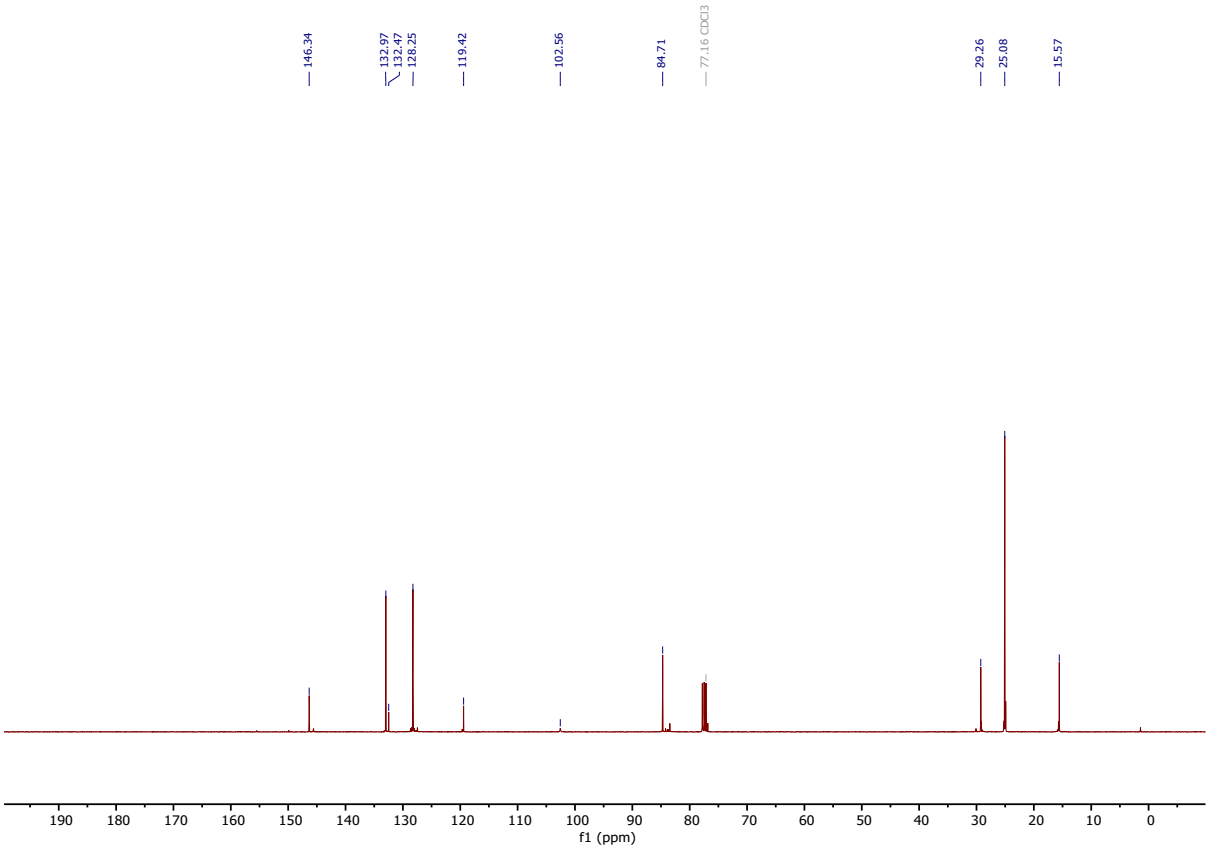


Figure S43: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3k** in $CDCl_3$ recorded at 100.6 MHz

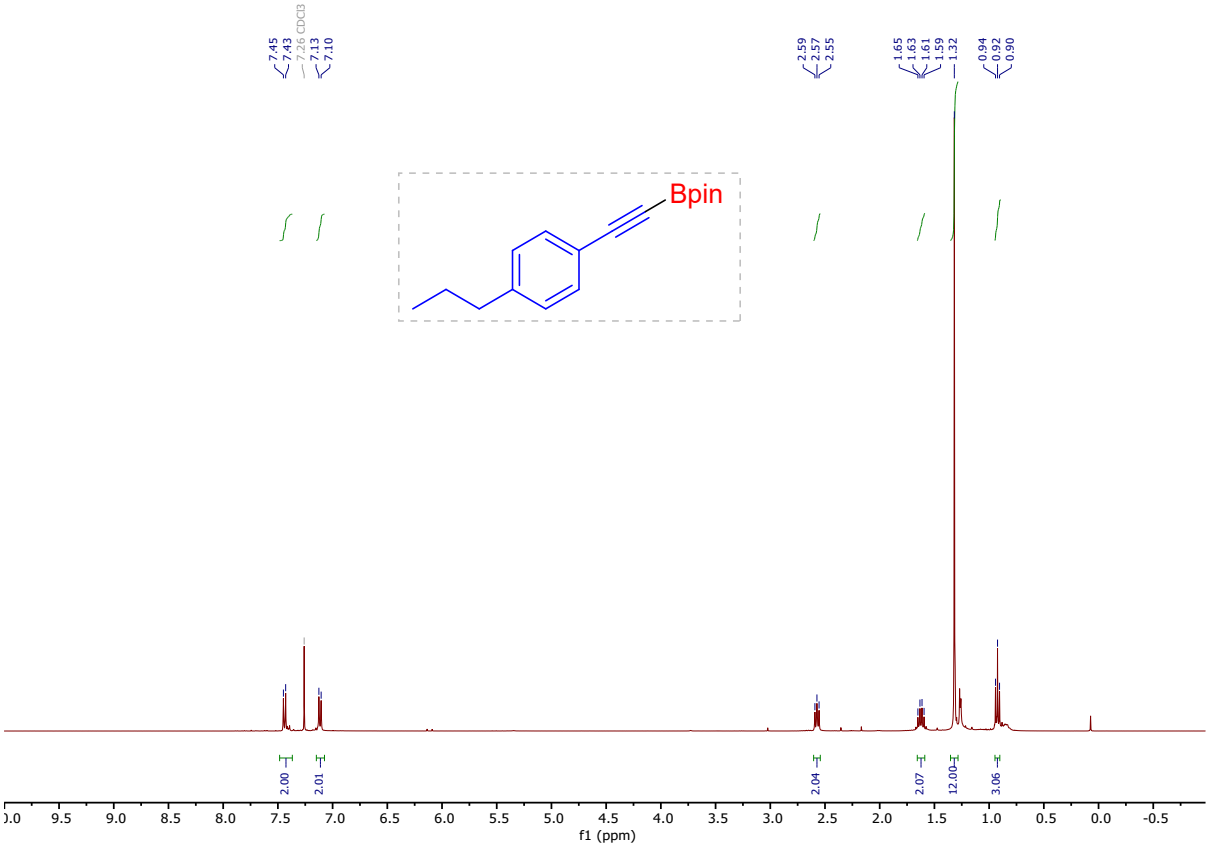


Figure S44: ^{1}H NMR spectrum of the compound **3l** in $CDCl_3$ recorded at 400 MHz

Peak at 1.27 correspond to unidentified impurities.

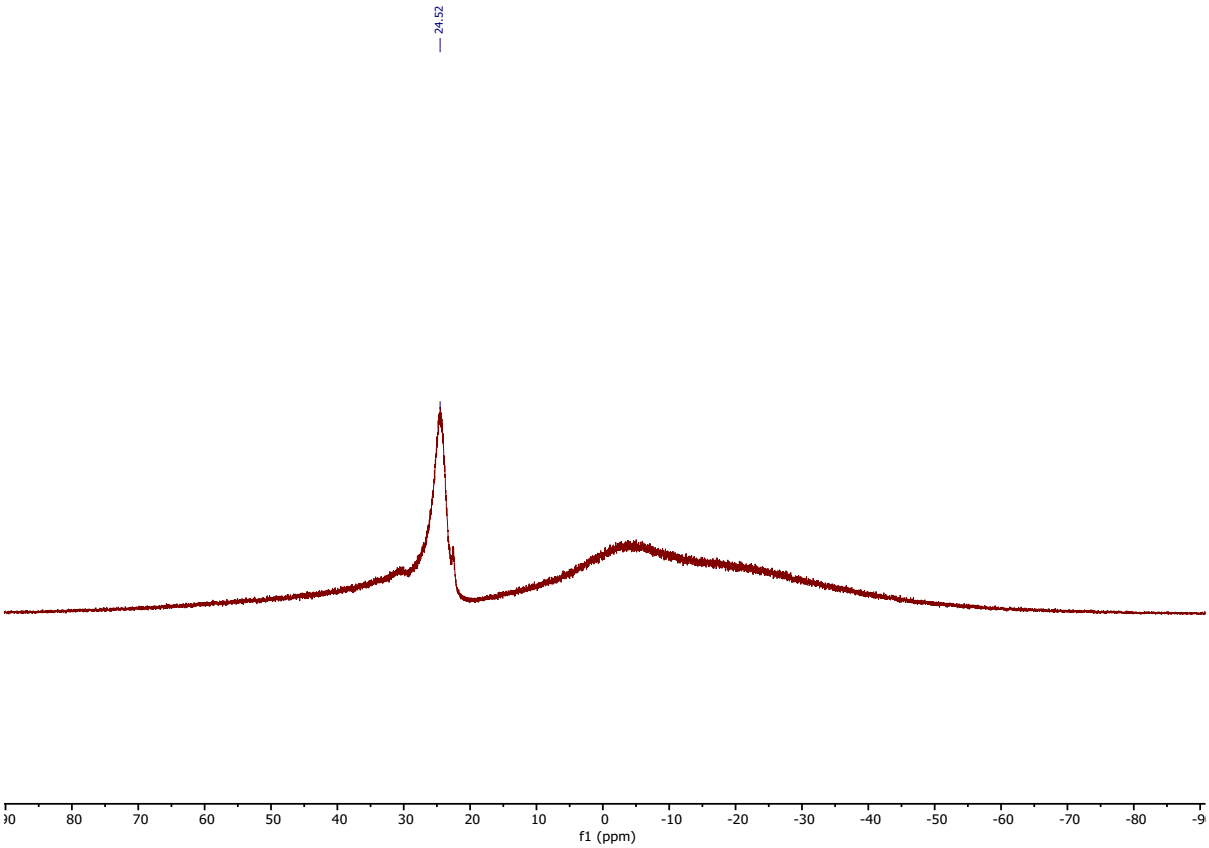


Figure S45: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3l** in $CDCl_3$ recorded at 128.3 MHz

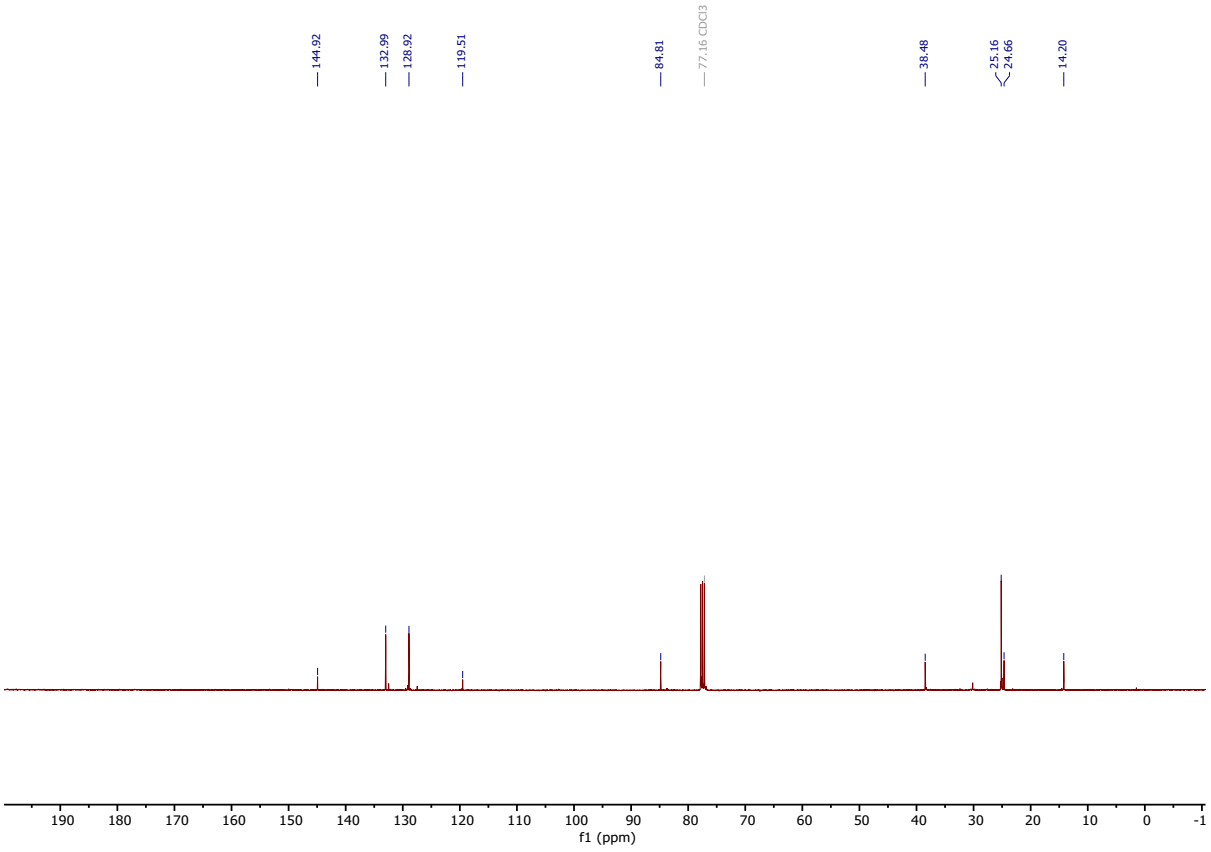


Figure S46: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3l** in $CDCl_3$ recorded at 100.6 MHz

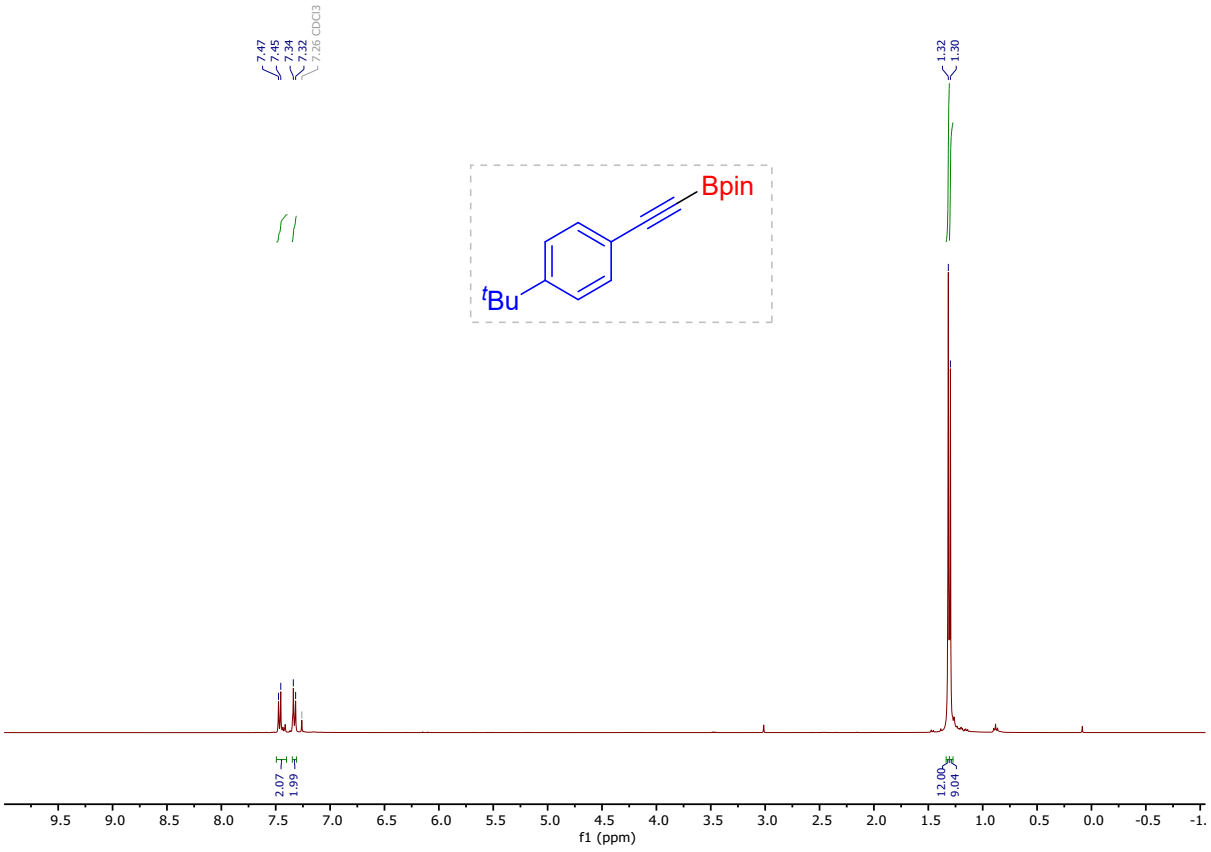


Figure S47: ^{1}H NMR spectrum of the compound **3m** in $CDCl_3$ recorded at 400 MHz

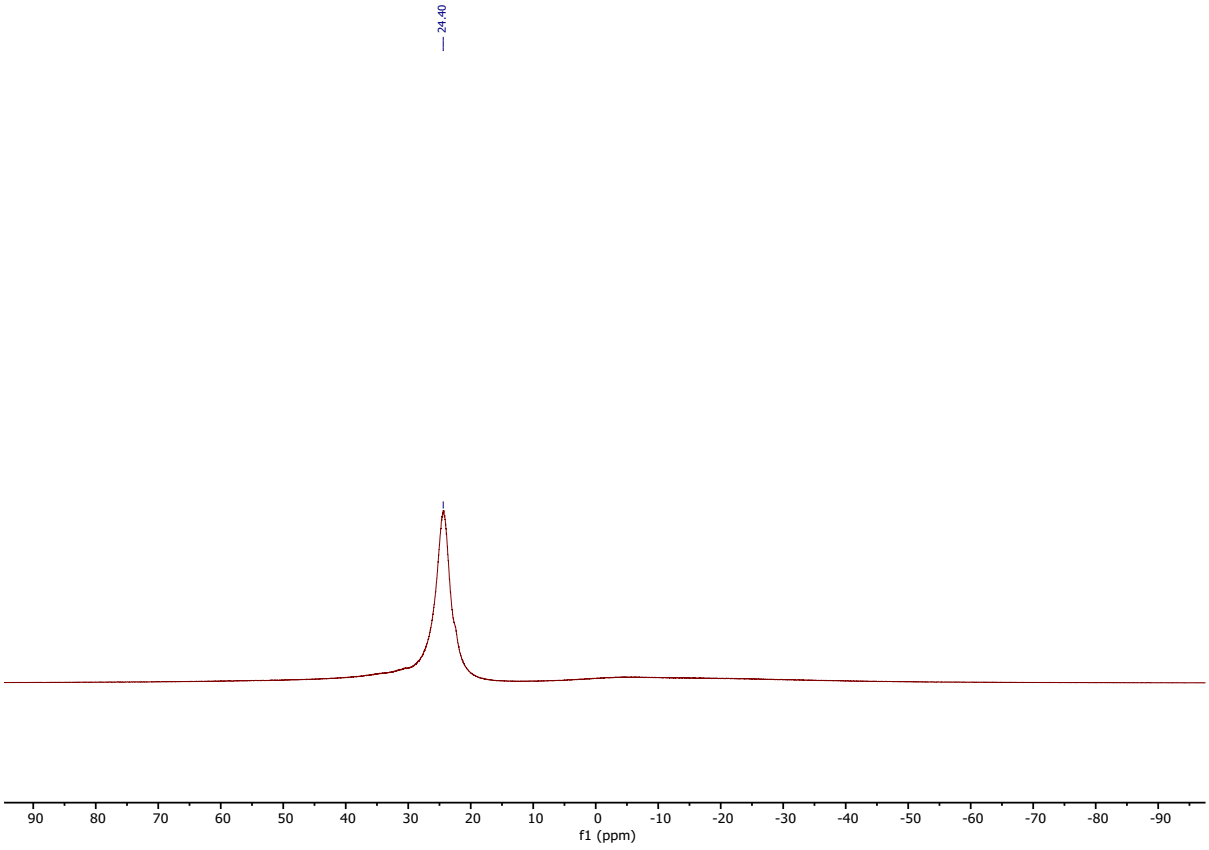


Figure S48: $^{11}B\{^1H\}$ NMR spectrum of the compound **3m** in $CDCl_3$ recorded at 128.3 MHz

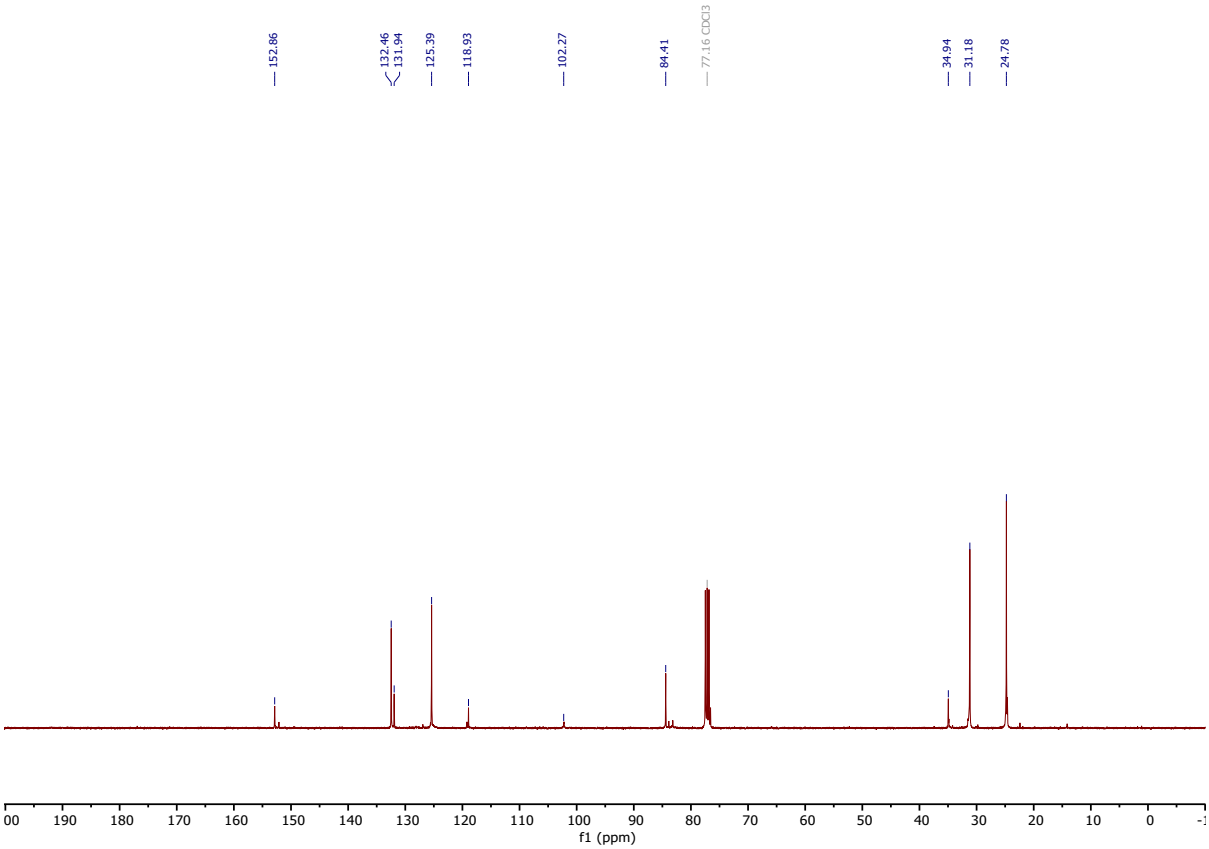


Figure S49: $^{13}C\{^1H\}$ NMR spectrum of the compound **3m** in $CDCl_3$ recorded at 100.6 MHz

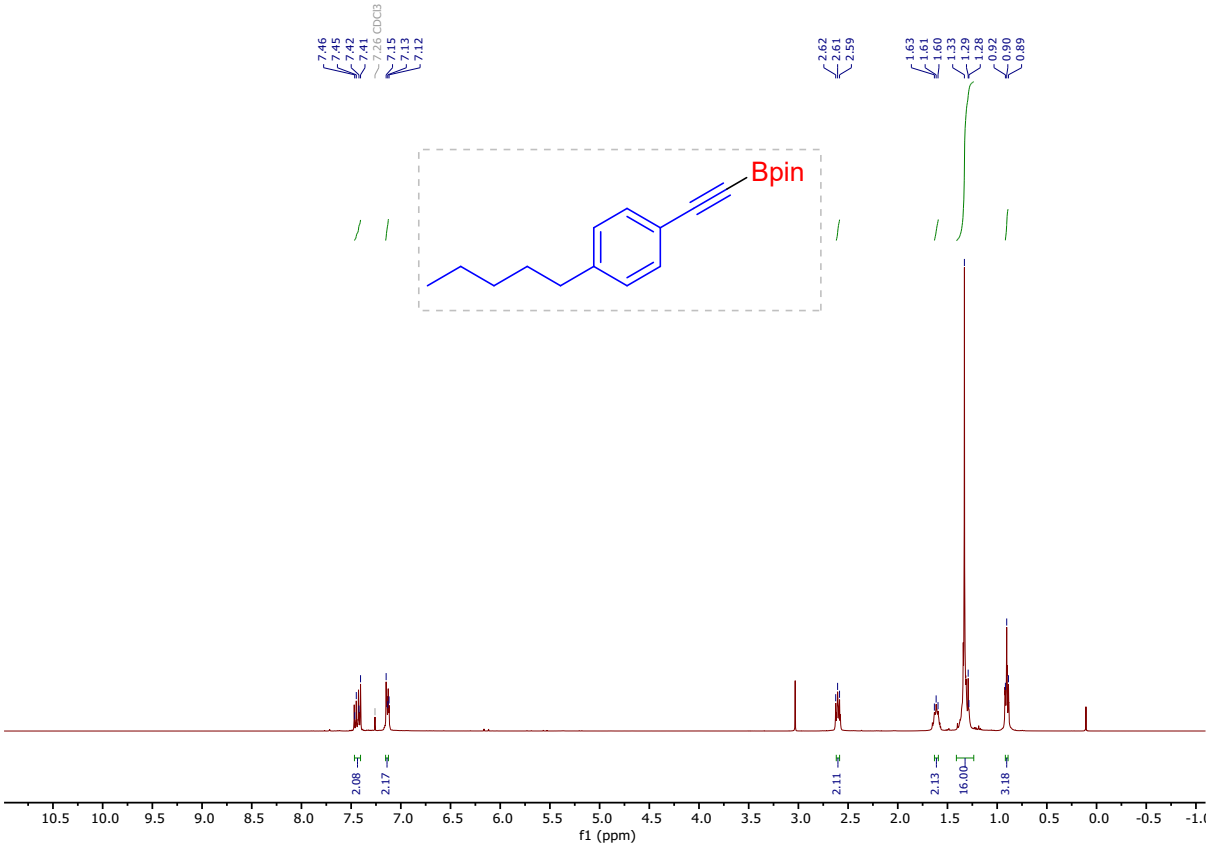


Figure S50: ^{1}H NMR spectrum of the compound **3n** in $CDCl_3$ recorded at 400 MHz

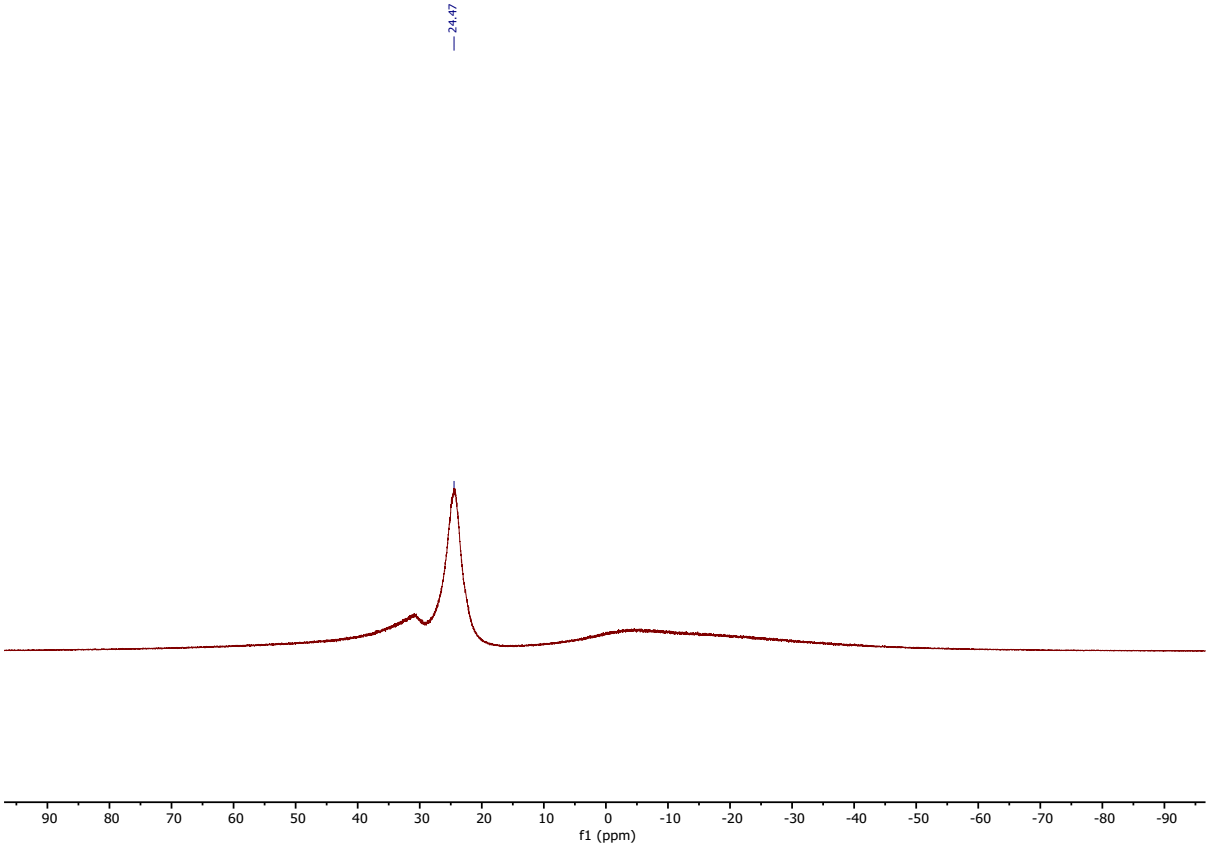


Figure S51: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3n** in $CDCl_3$ recorded at 128.3 MHz

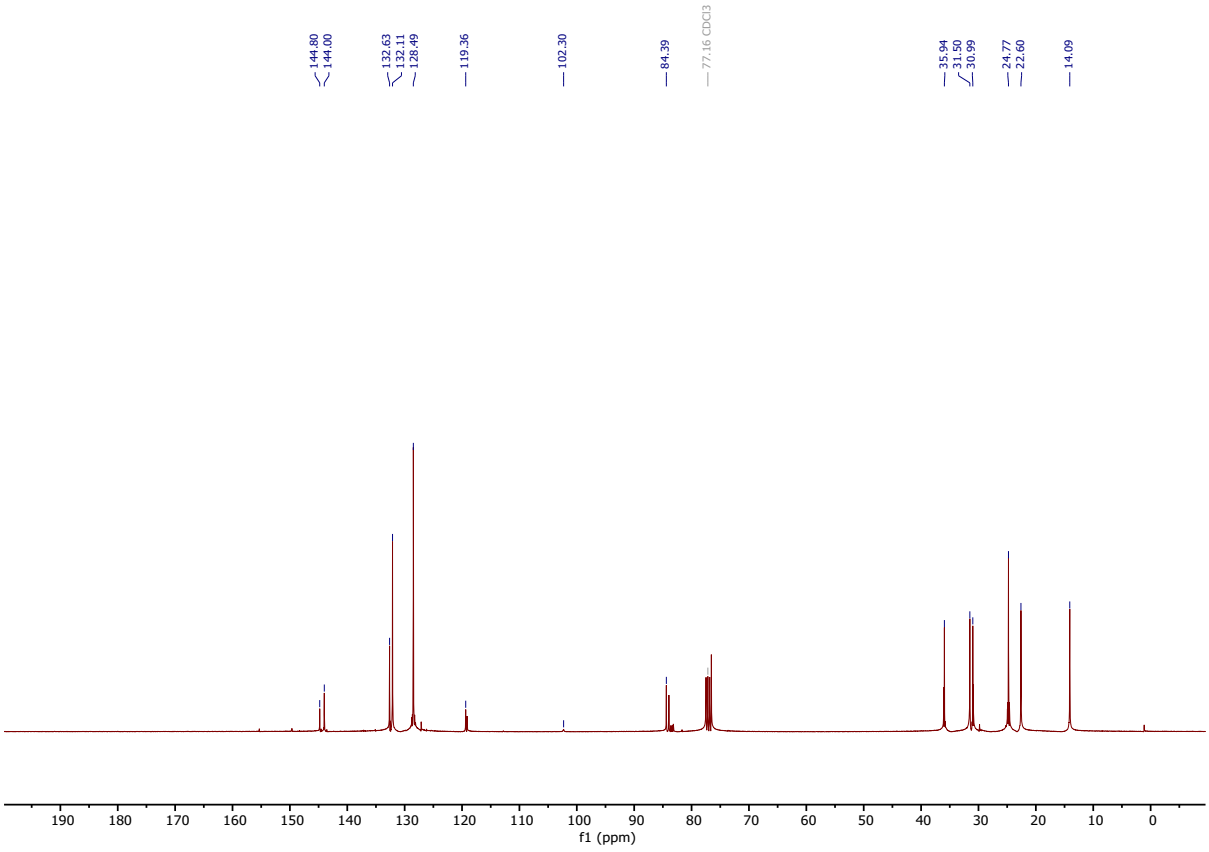


Figure S52: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3n** in $CDCl_3$ recorded at 100.6 MHz Peak at 83.4 correspond to unidentified impurities

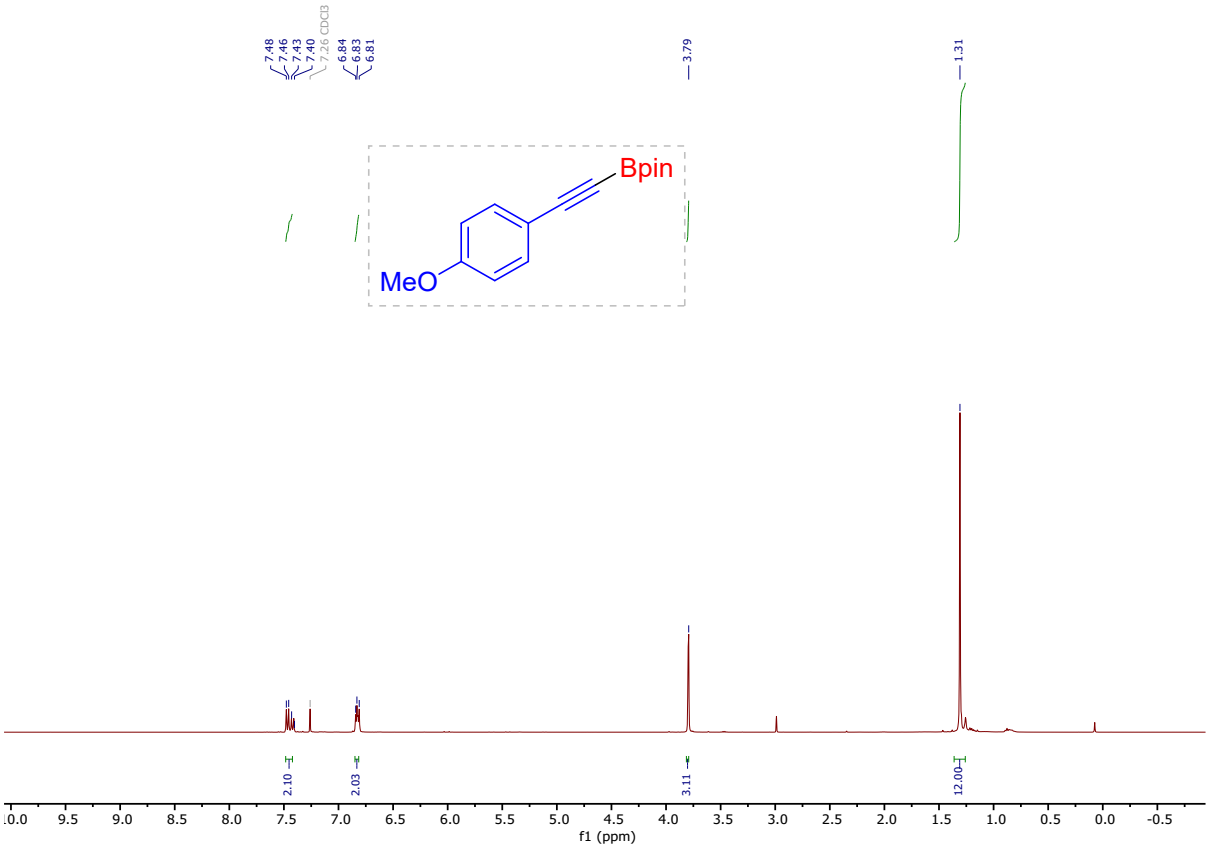


Figure S53: ^{1}H NMR spectrum of the compound **3o** in $CDCl_3$ recorded at 400 MHz

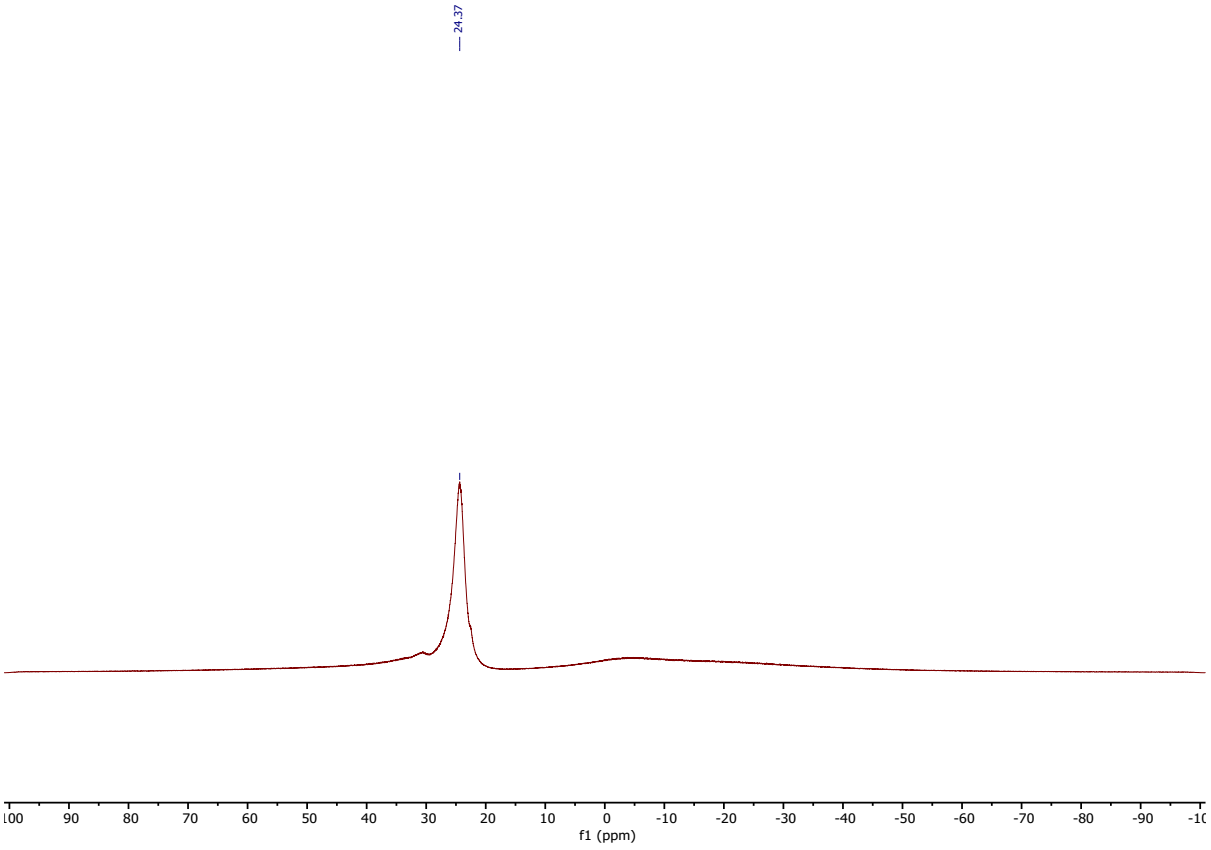


Figure S54: $^{11}B\{^1H\}$ NMR spectrum of the compound **3o** in $CDCl_3$ recorded at 128.3 MHz

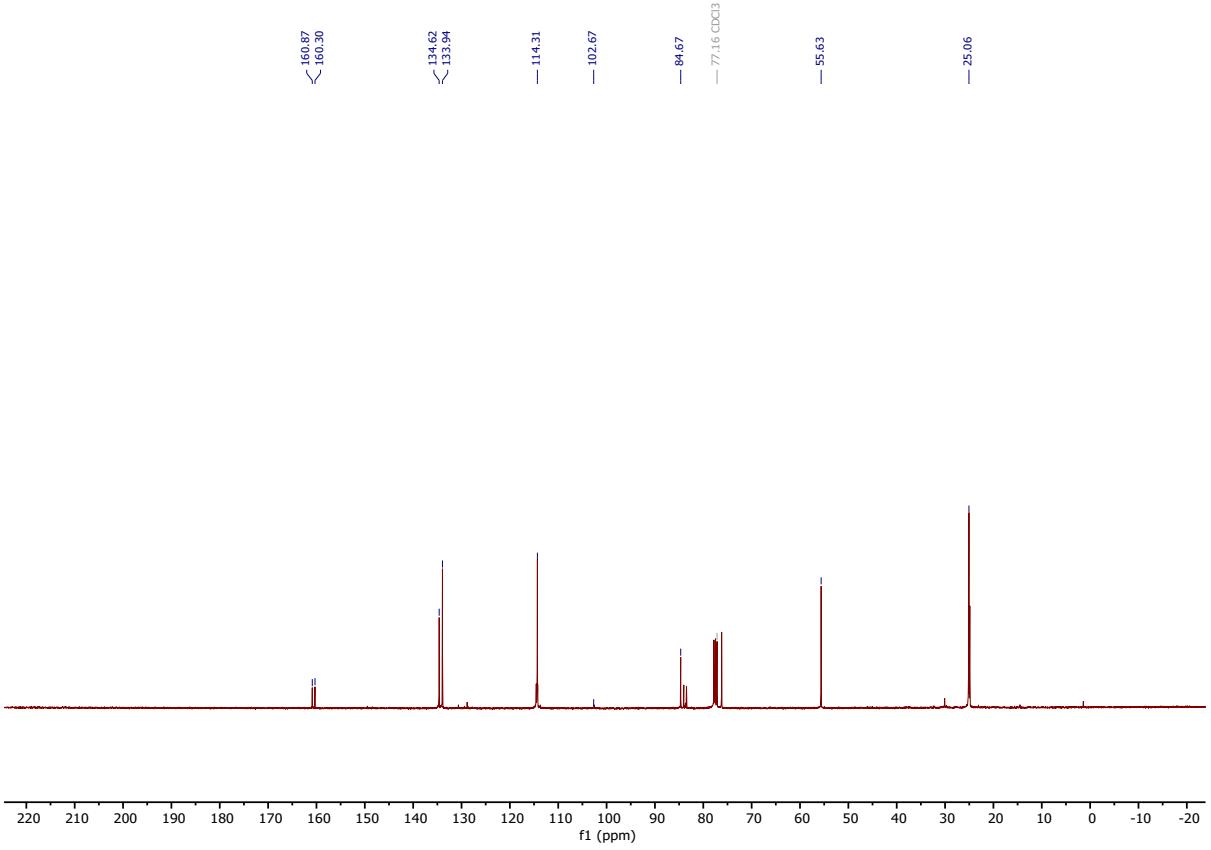


Figure S55: $^{13}C\{^1H\}$ NMR spectrum of the compound **3o** in $CDCl_3$ recorded at 100.6 MHz

Peak at 83.82 and 82.31 correspond to unidentified impurities.

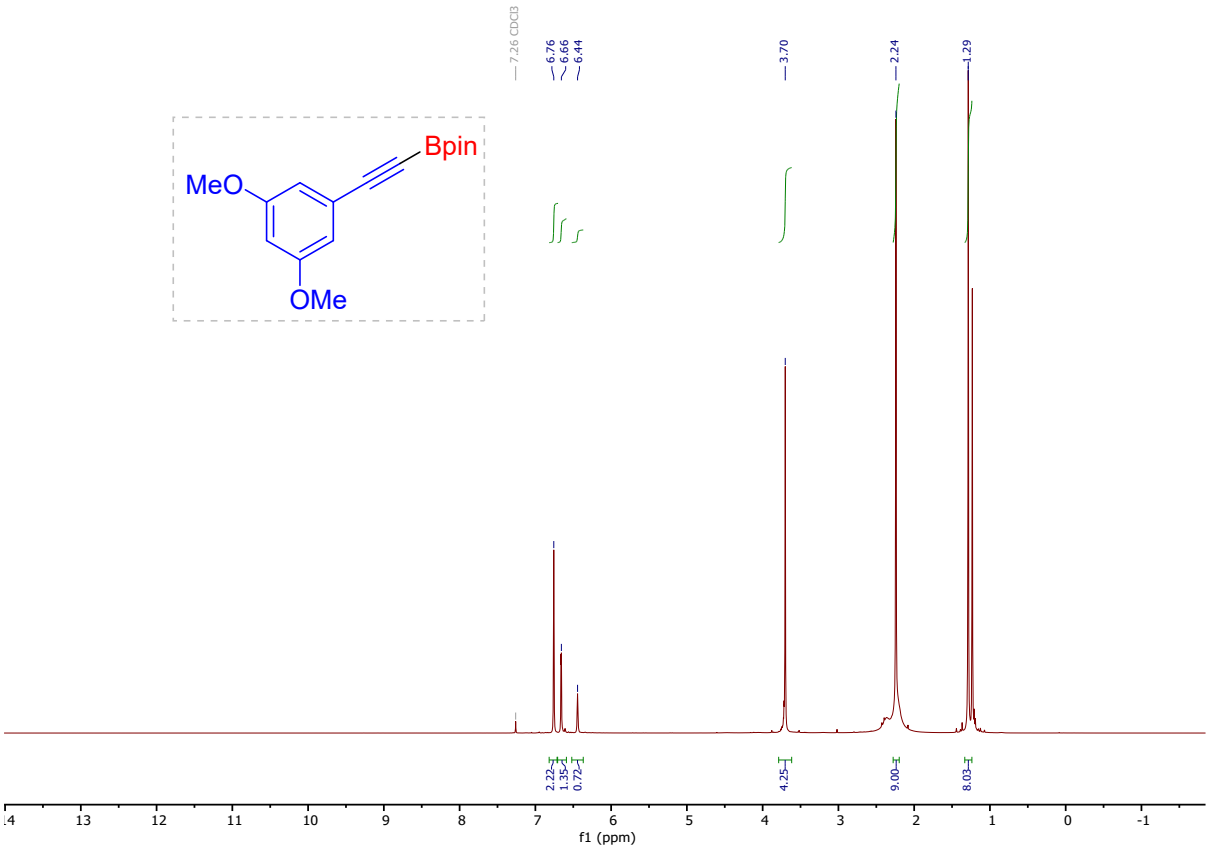


Figure S56: ^{1}H NMR spectrum of the compound **3p** in $CDCl_3$ recorded at 400 MHz. Peaks at 2.24 and 6.76 ppm correspond to internal standard (mesitylene). Peak at 1.23 correspond to unidentified impurities.

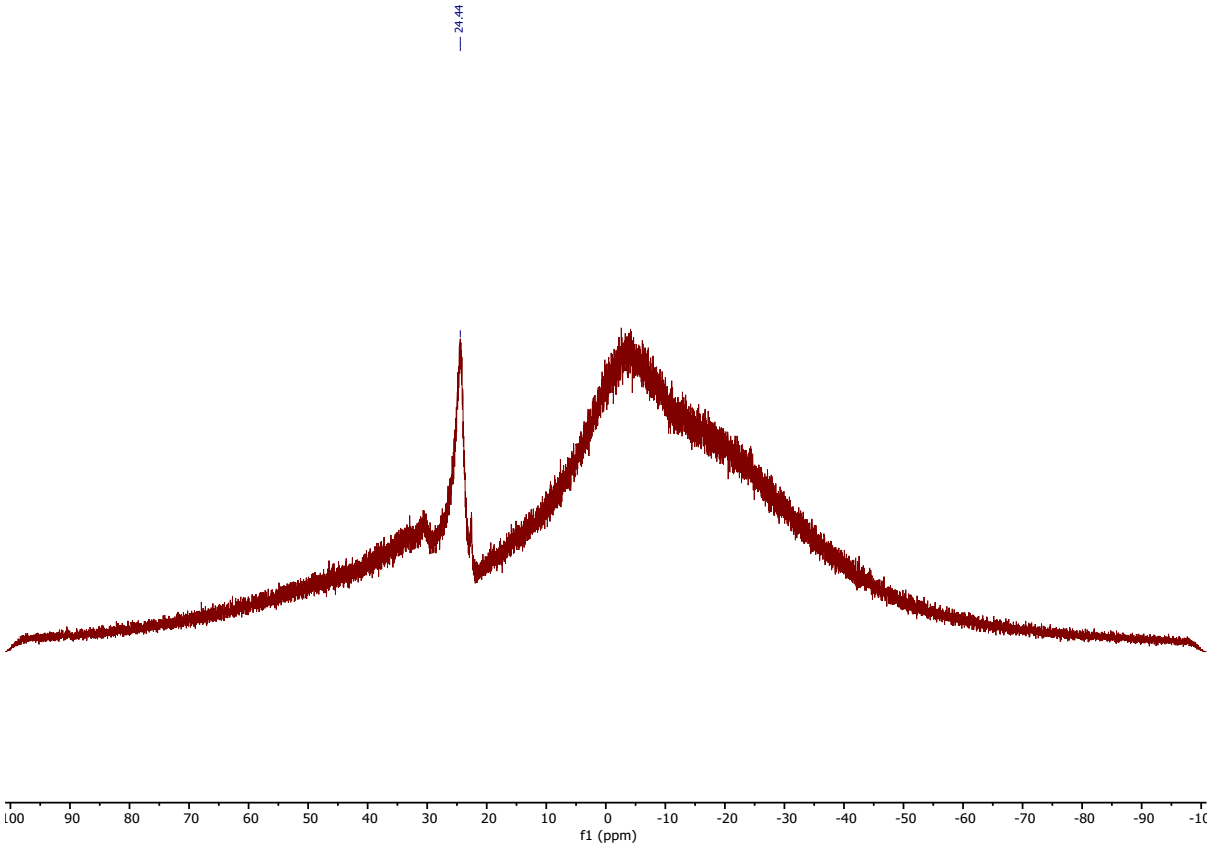


Figure S57: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3p** in $CDCl_3$ recorded at 128.3 MHz.

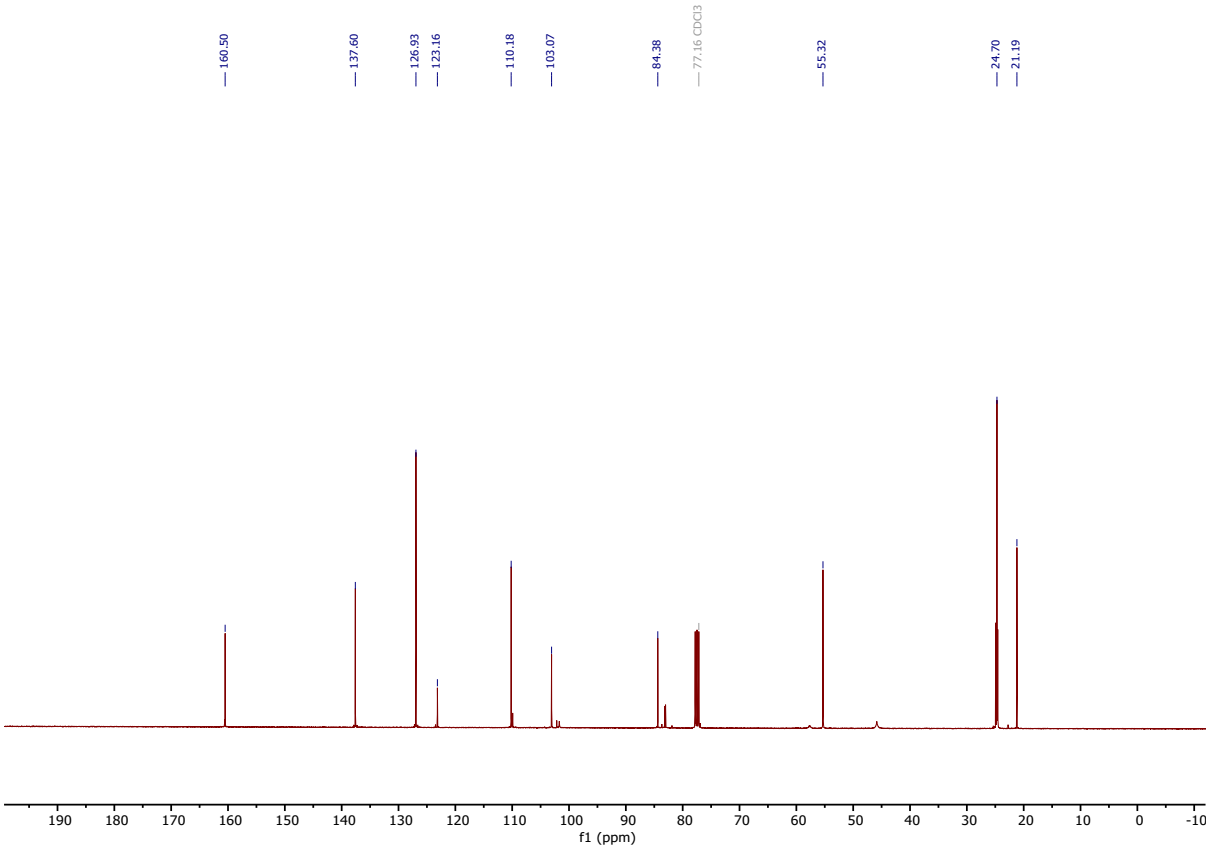


Figure S58: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3p** in $CDCl_3$ recorded at 100.6 MHz Peaks at 21.19, 126.93 and 137.60 ppm correspond to internal standard (mesitylene), Peak at 83.11 correspond to unidentified impurities.

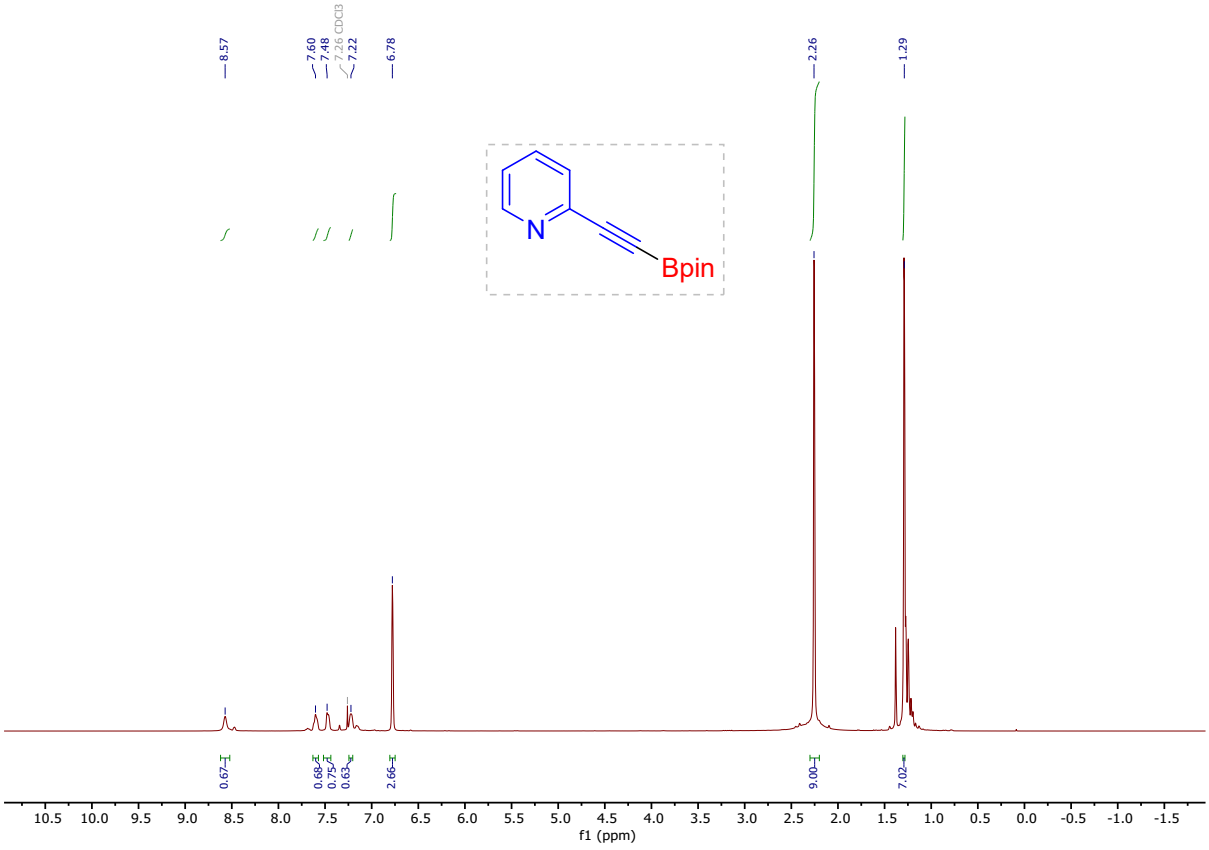


Figure S59: ^{1}H NMR spectrum of the compound **3q** in $CDCl_3$ recorded at 400 MHz. Peaks at 2.26 and 6.78 ppm correspond to internal standard (mesitylene). Peak at 1.38 and 1.24 correspond to unidentified impurities.

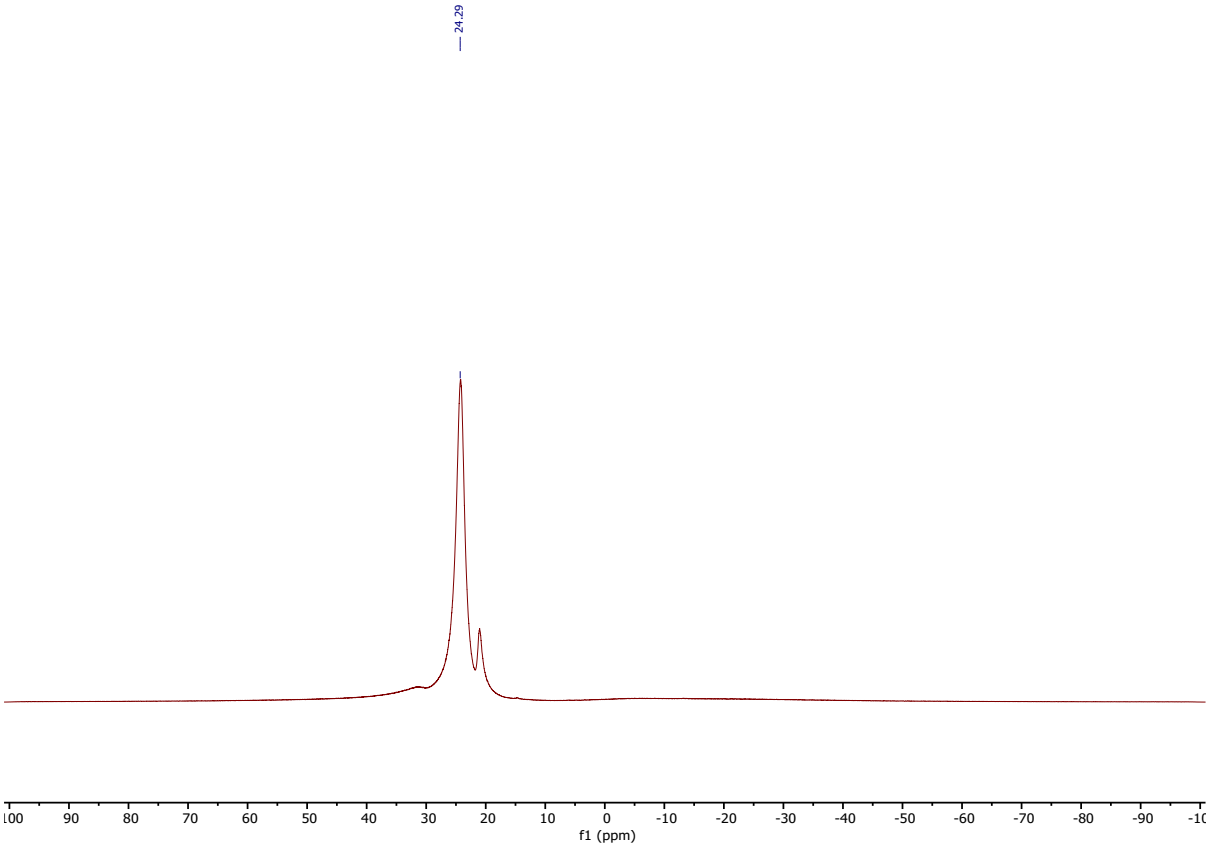


Figure S60: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3q** in $CDCl_3$ recorded at 128.3 MHz.

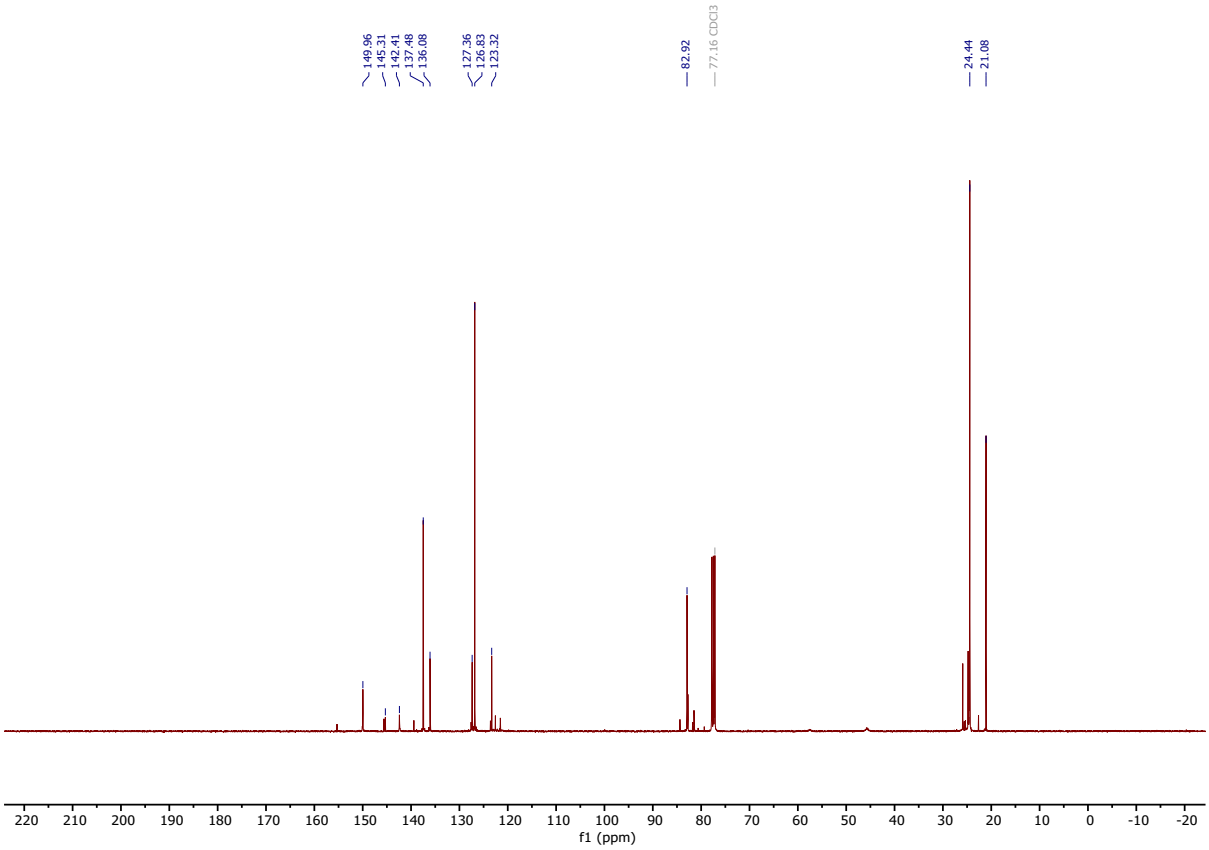


Figure S61: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3q** in $CDCl_3$ recorded at 100.6 MHz Peaks at 21.08, 126.83 and 137.48 ppm correspond to internal standard (mesitylene). Peak at 25.8, 155.28, 122.62, 121.67 correspond to unidentified impurities.

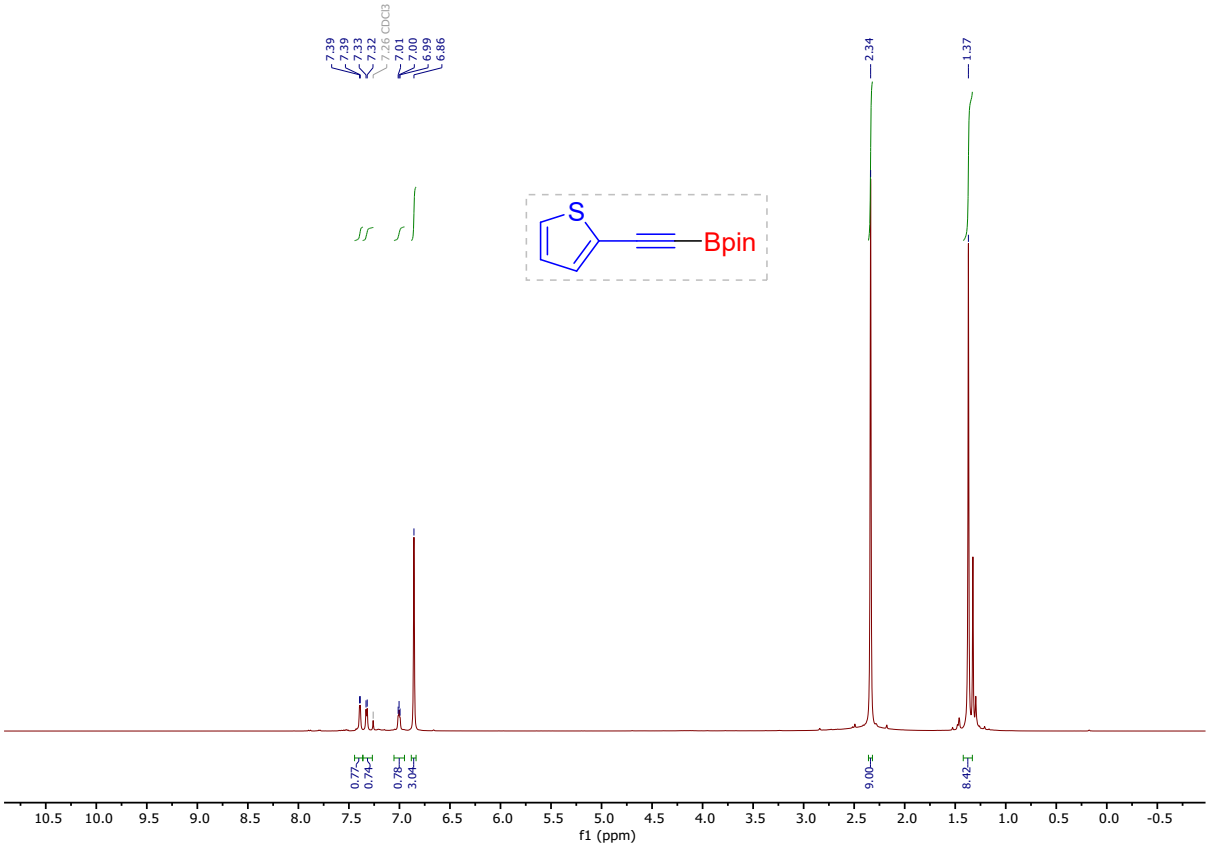


Figure S62: ^{1}H NMR spectrum of the compound **3r** in $CDCl_3$ recorded at 400 MHz. Peaks at 2.34 and 6.86 ppm correspond to internal standard (mesitylene). Peak at 1.32 and 1.29 correspond to unidentified impurities.

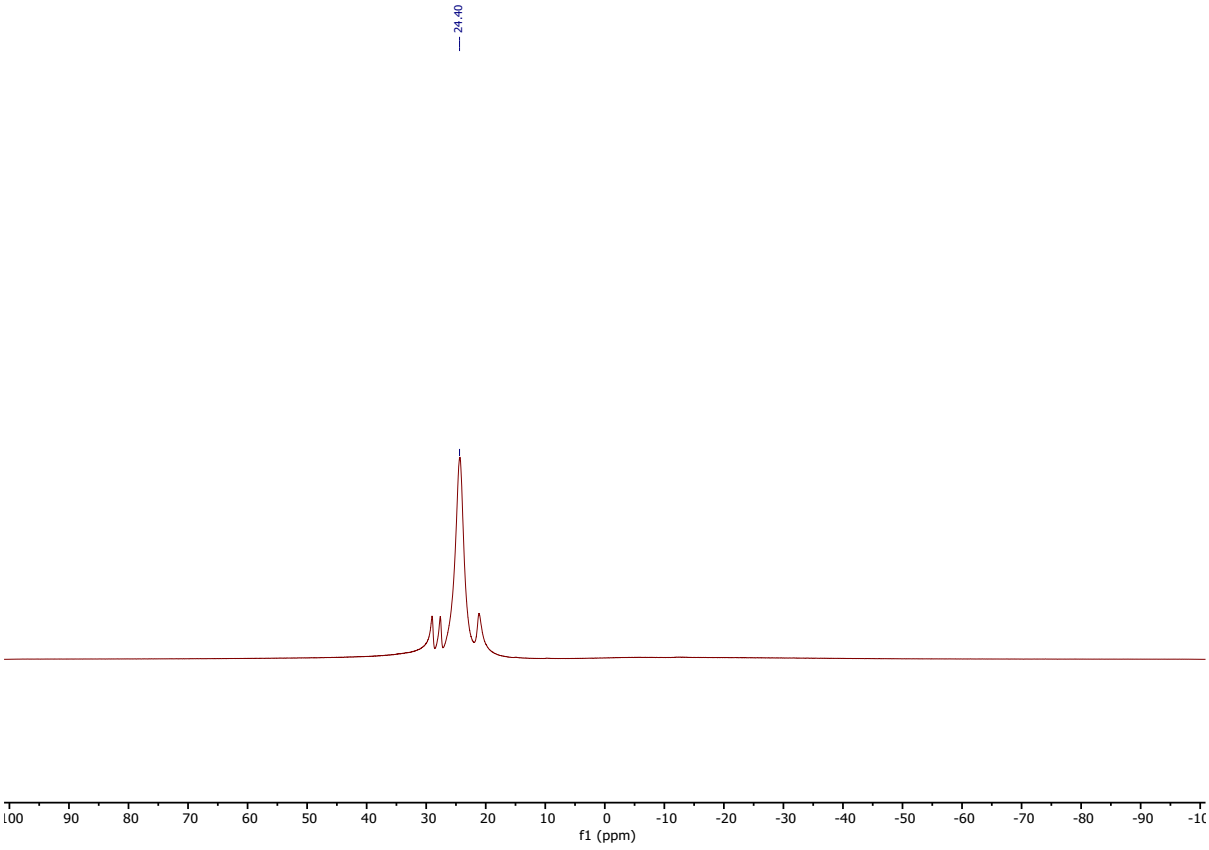


Figure S63: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3r** in $CDCl_3$ recorded at 128.3 MHz.

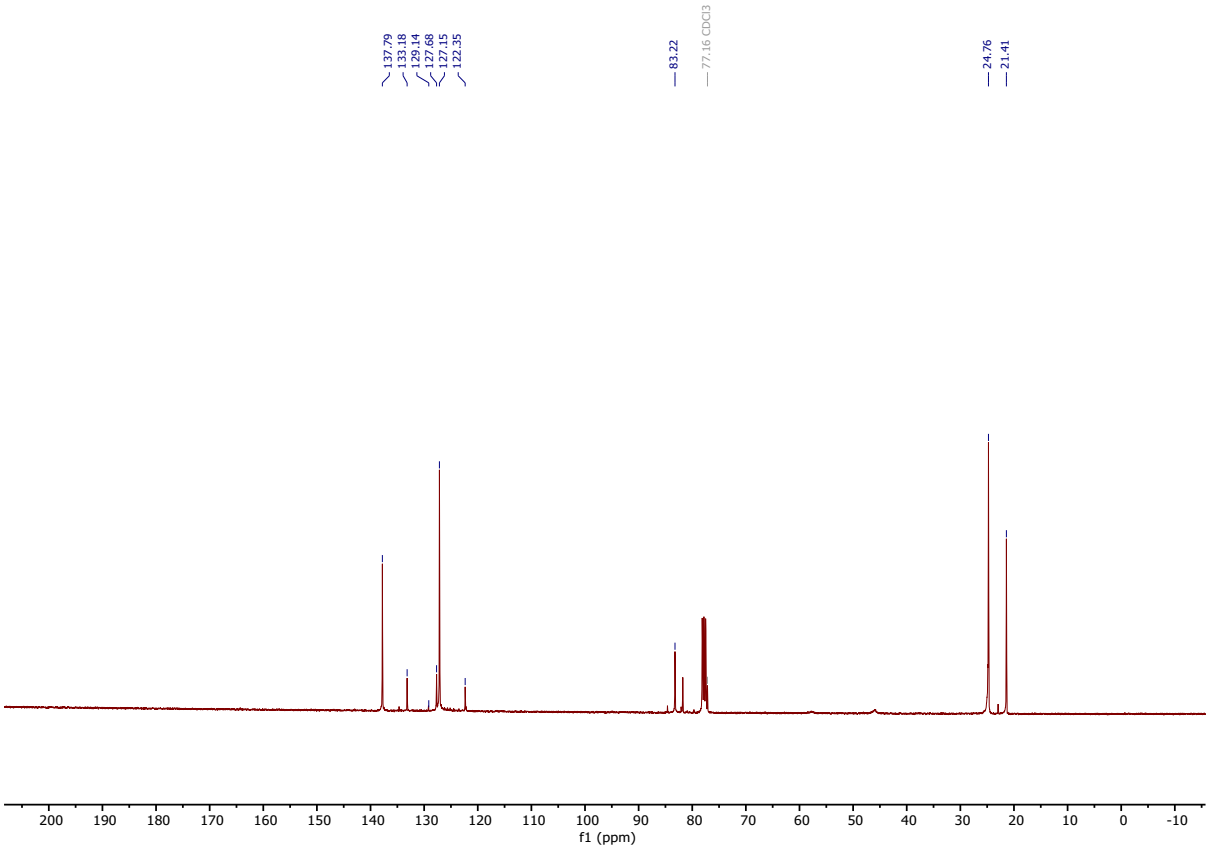


Figure S64: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3r** in $CDCl_3$ recorded at 100.6 MHz
Peaks at 21.41, 127.15 and 137.79 ppm correspond to internal standard (mesitylene)
Peak at 82.31 correspond to unidentified impurities.

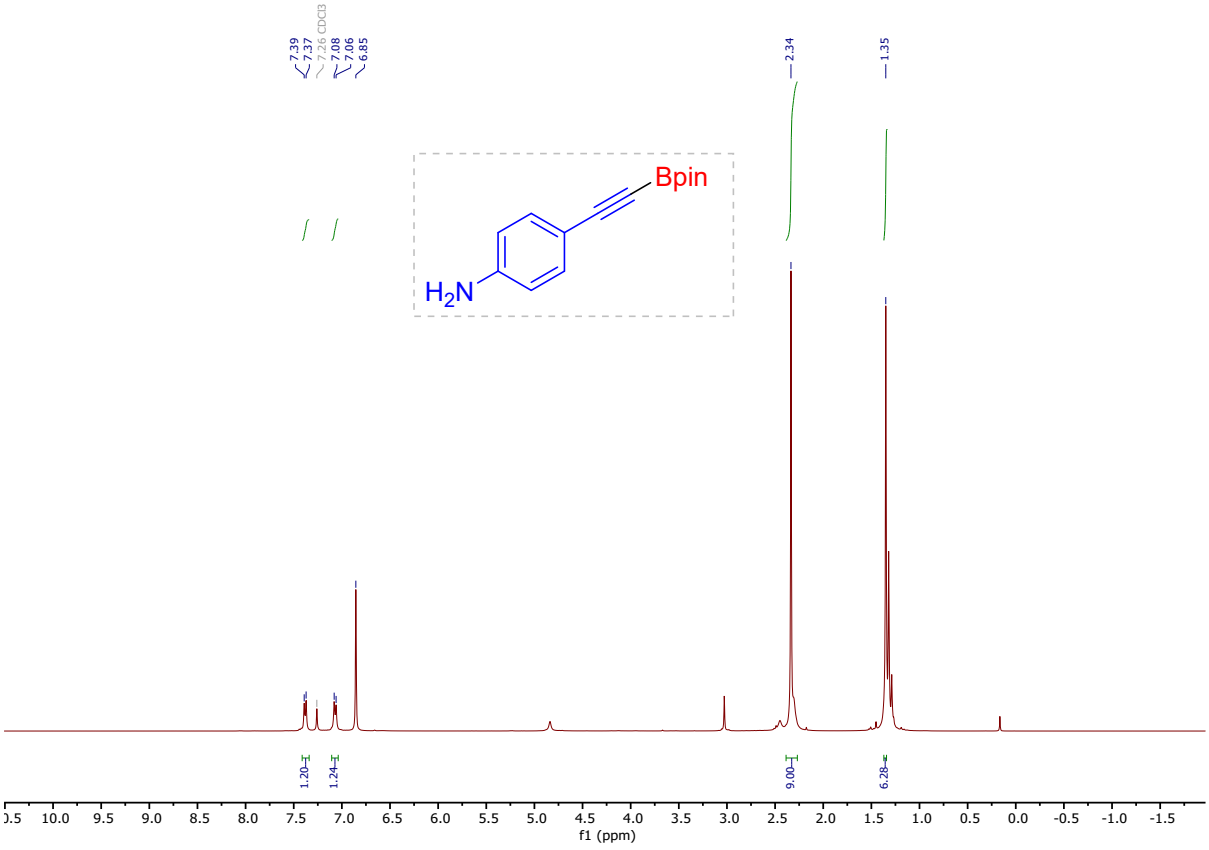


Figure S65: ^{1}H NMR spectrum of the compound **3s** in $CDCl_3$ recorded at 400 MHz. Peaks at 2.34 and 6.85 ppm correspond to internal standard (mesitylene). Peak at 1.32 and 1.28 correspond to unidentified impurities.

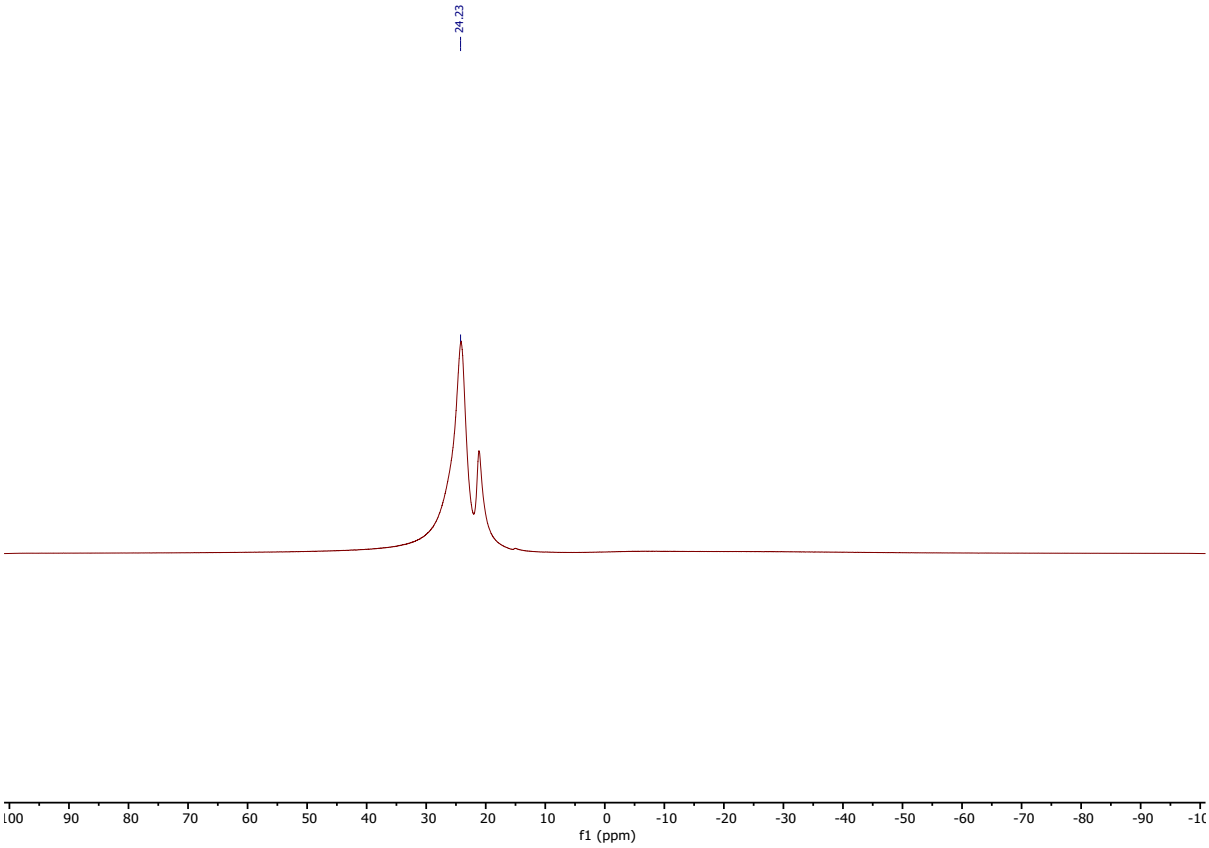


Figure S66: $^{11}B\{^{1}H\}$ NMR spectrum of the compound **3s** in $CDCl_3$ recorded at 128.3 MHz

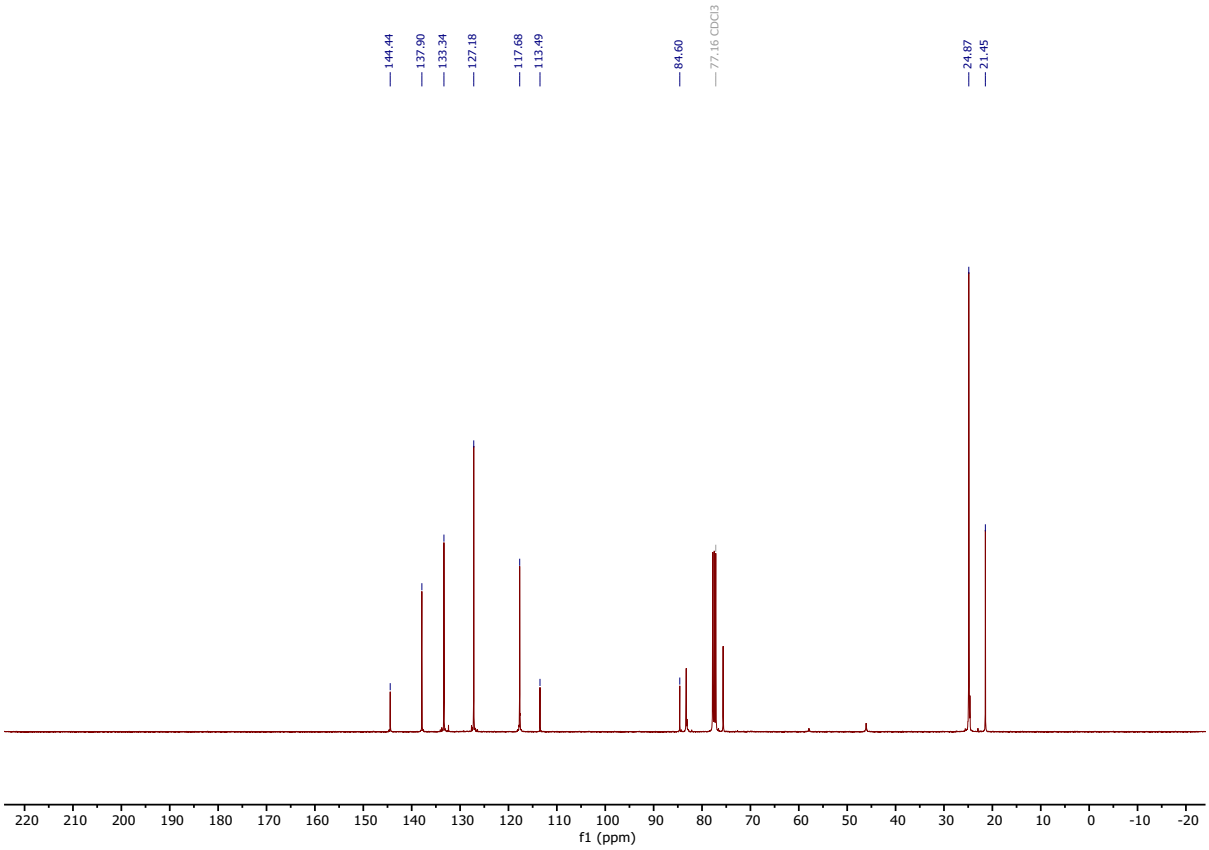


Figure S67: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3s** in $CDCl_3$ recorded at 100.6 MHz. Peaks at 21.45, 127.18 and 137.90 ppm correspond to internal standard (mesitylene). Peak at 83.1 and 75.64 correspond to unidentified impurities.

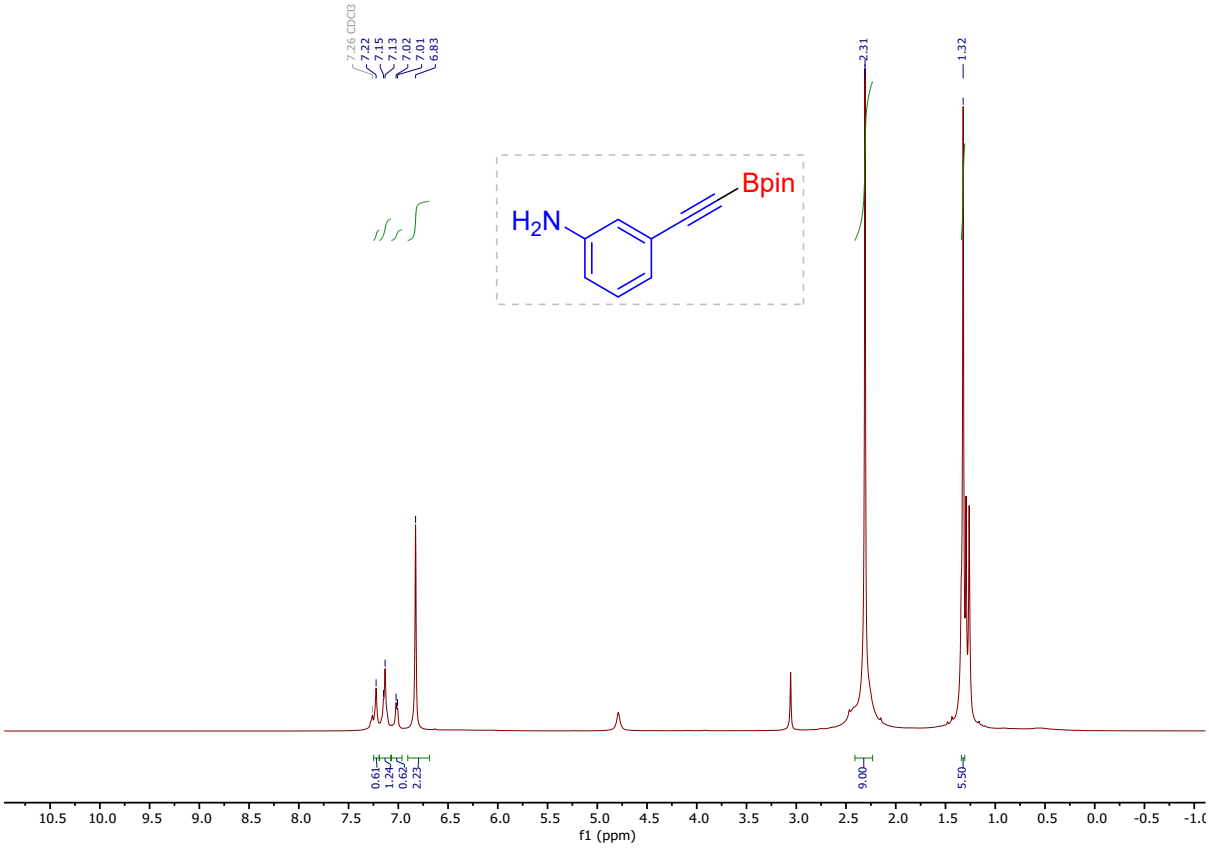


Figure S68: ^{1}H NMR spectrum of the compound **3t** in $CDCl_3$ recorded at 400 MHz. Peaks at 2.31 and 6.85 ppm correspond to internal standard (mesitylene). Peak at 1.29 and 1.26 correspond to unidentified impurities.

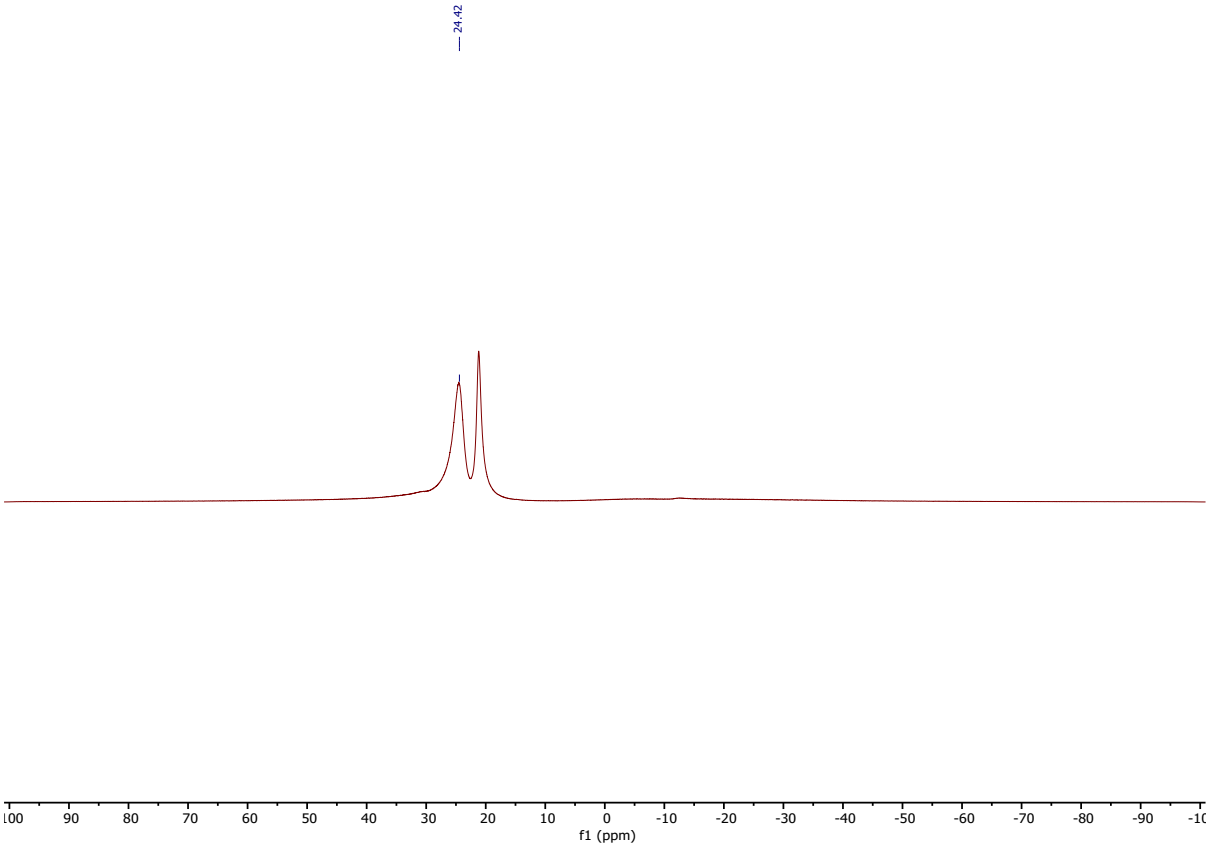


Figure S69: $^{11}B\{^1H\}$ NMR spectrum of the compound **3t** in $CDCl_3$ recorded at 128.3 MHz

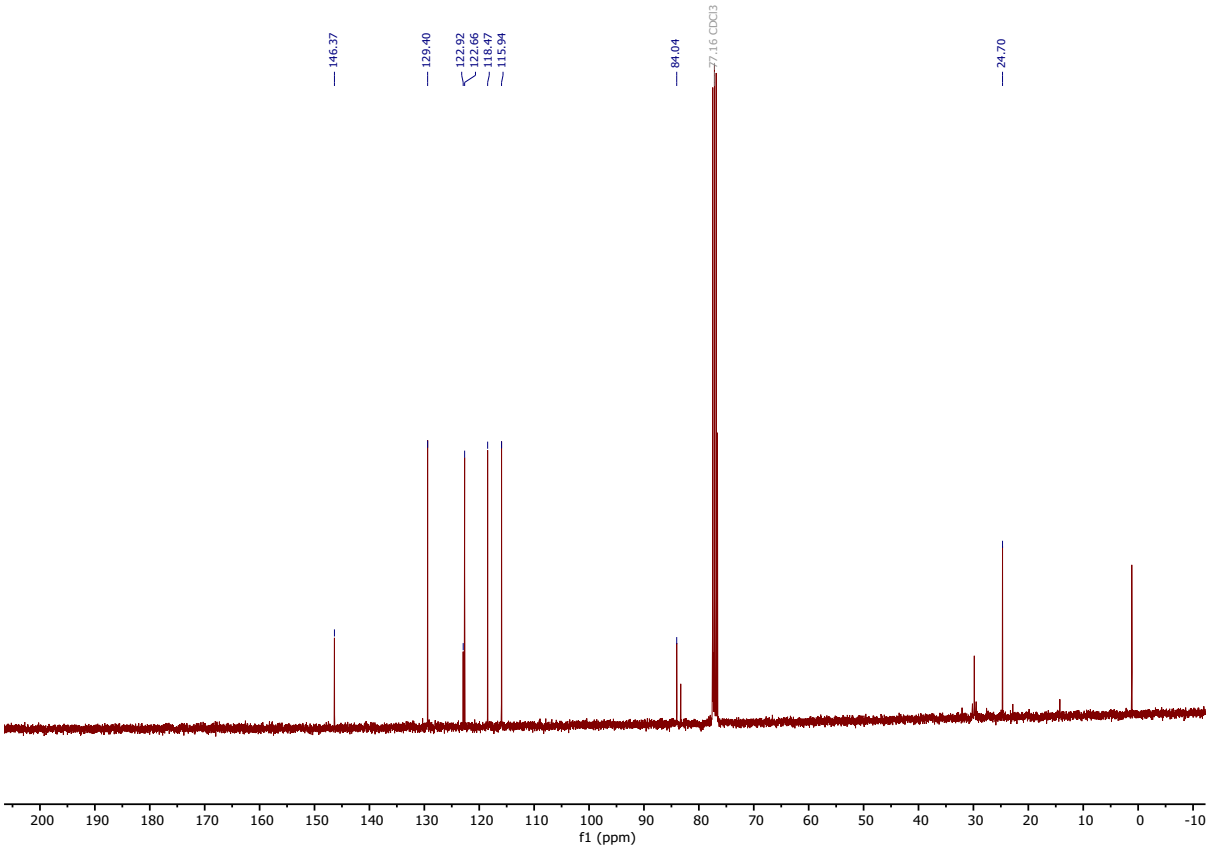


Figure S70: $^{13}C\{^1H\}$ NMR spectrum of the compound **3t** in $CDCl_3$ recorded at 100.6 MHz

Peak at 82.9 and 29.61 correspond to unidentified impurities.

❖ **NMR Spectra of Control Reactions**

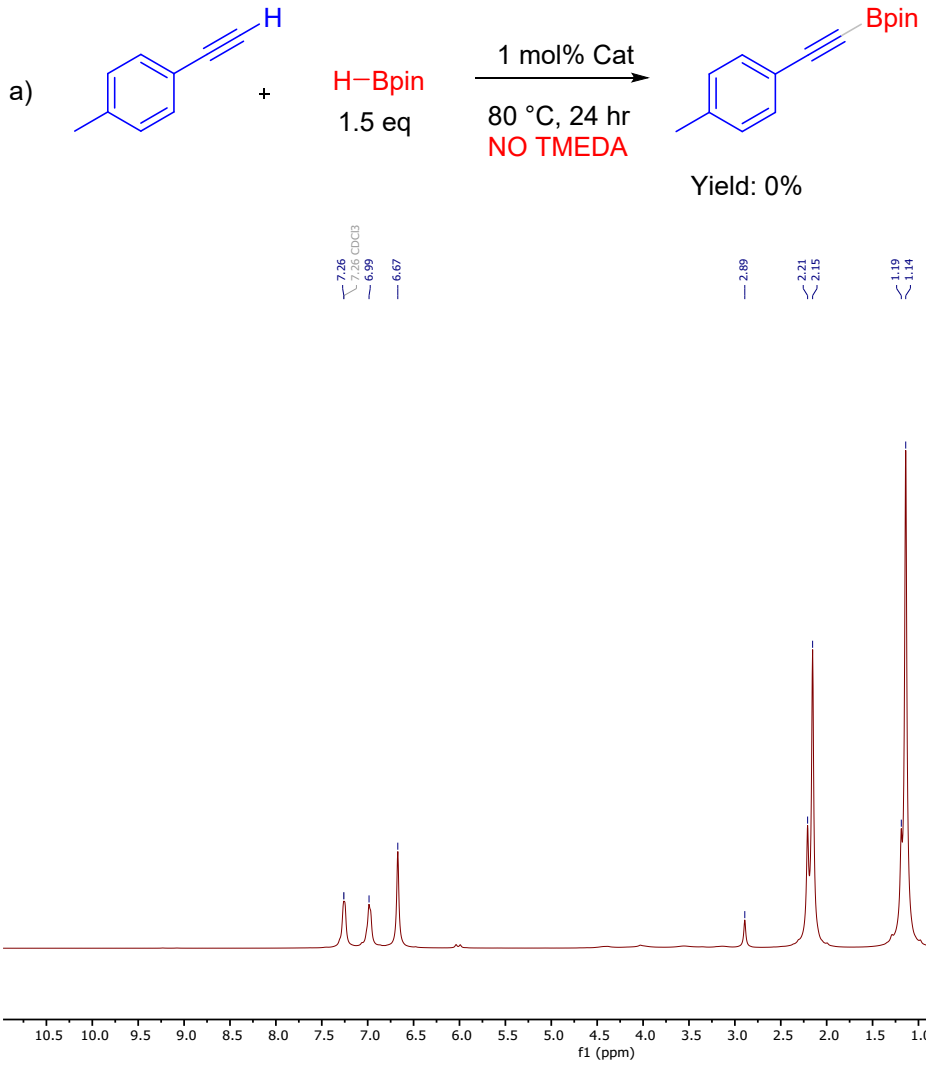


Figure S71: ^{1}H NMR spectrum in $CDCl_3$ recorded at 400 MHz

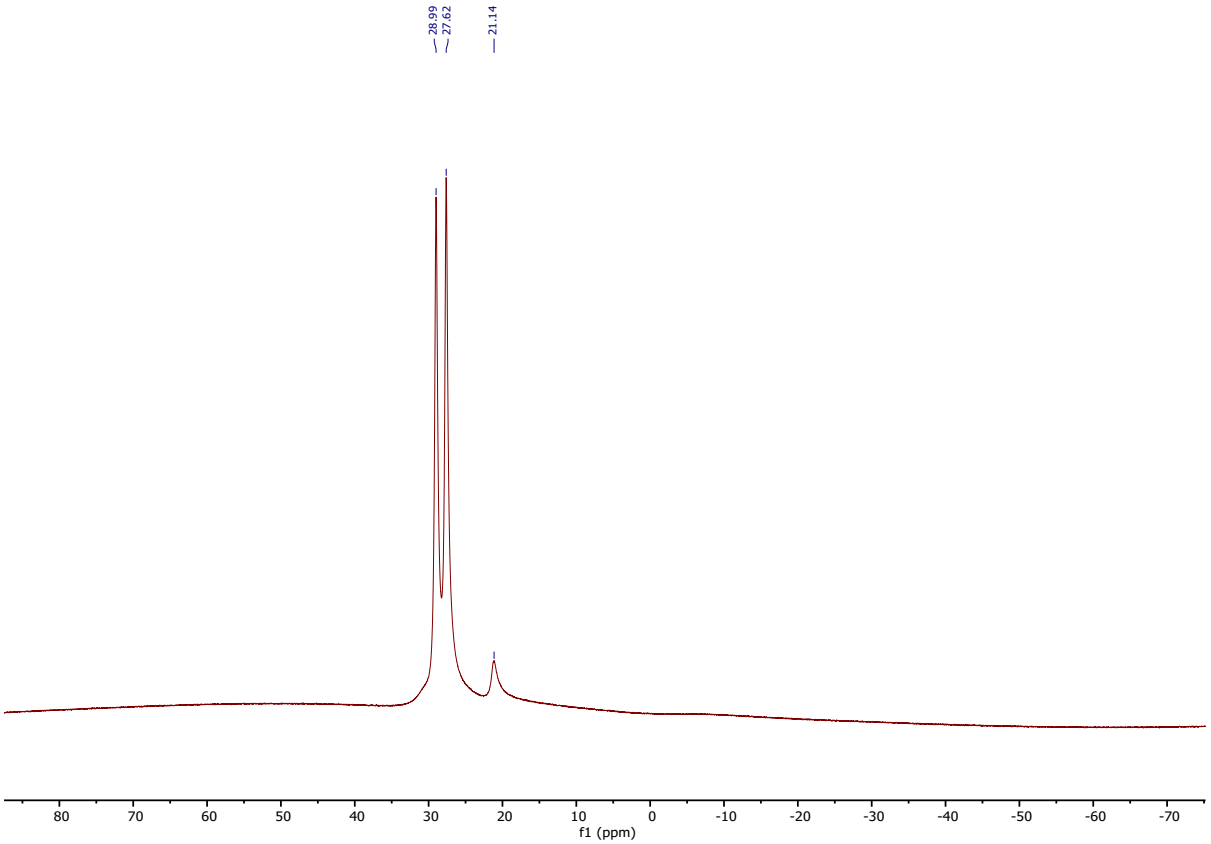


Figure S72: $^{11}B\{^{1}H\}$ NMR spectrum in $CDCl_3$ recorded at 128.3 MHz.

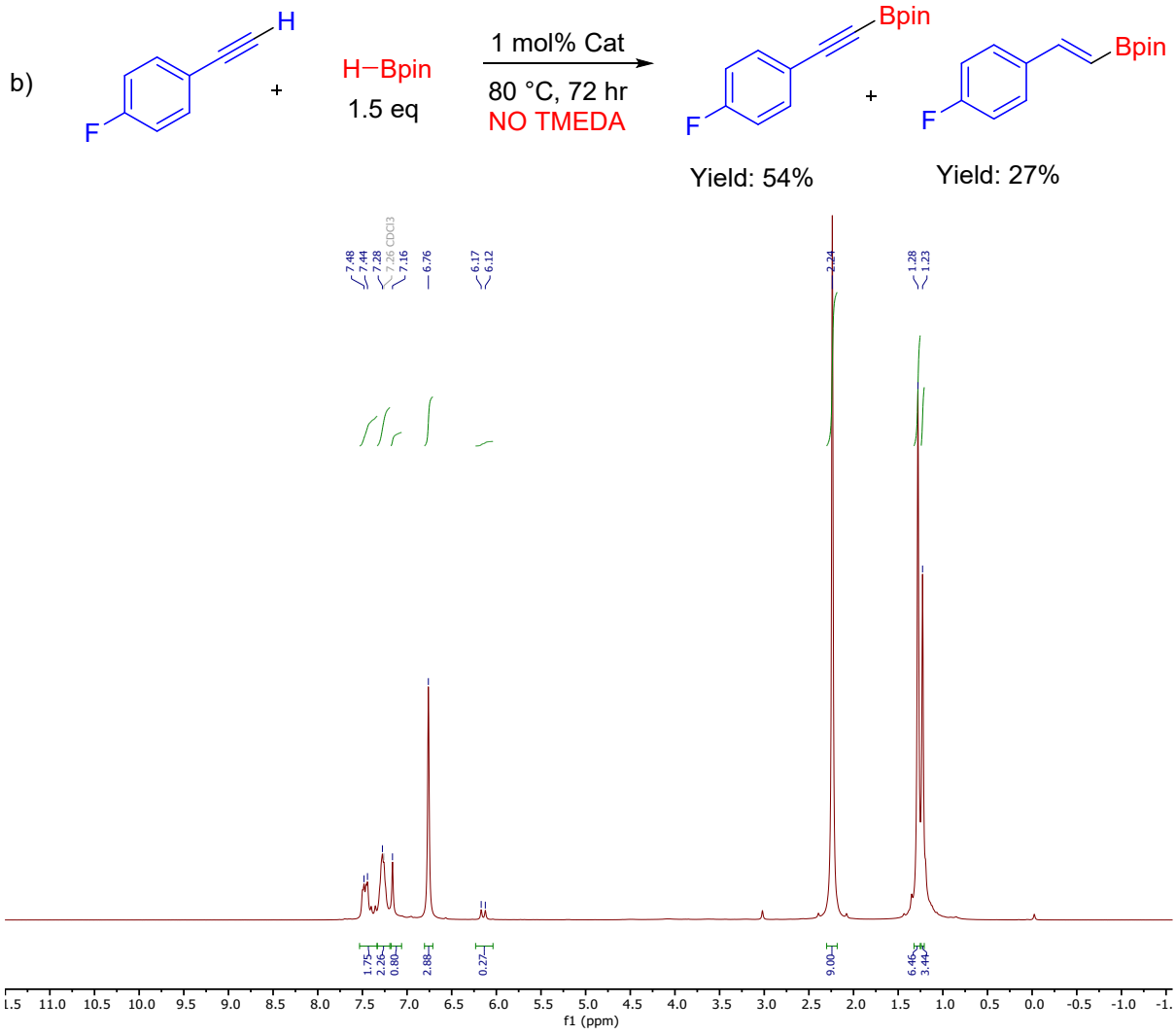


Figure S73: ^{1}H NMR spectrum in $CDCl_3$ recorded at 400 MHz

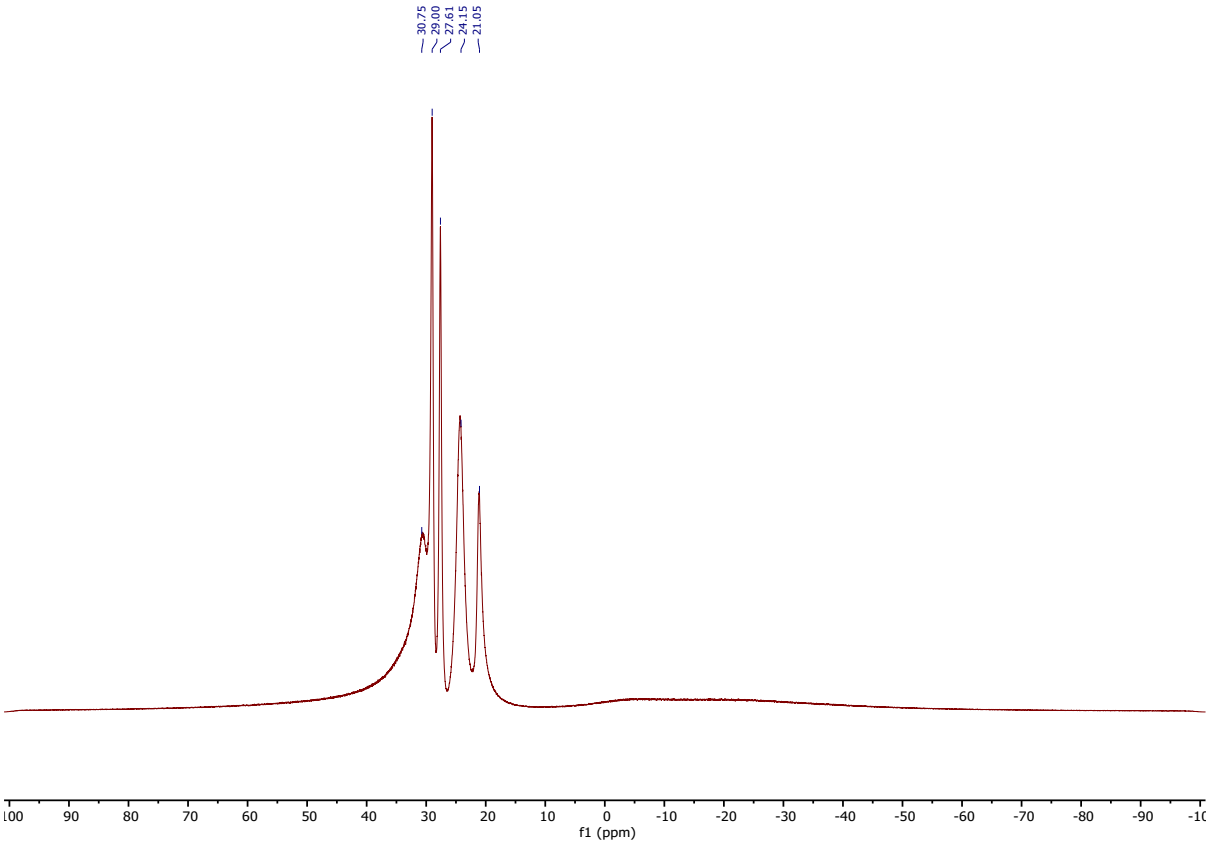


Figure S74: $^{11}B\{^{1}H\}$ NMR spectrum in $CDCl_3$ recorded at 128.3 MHz.

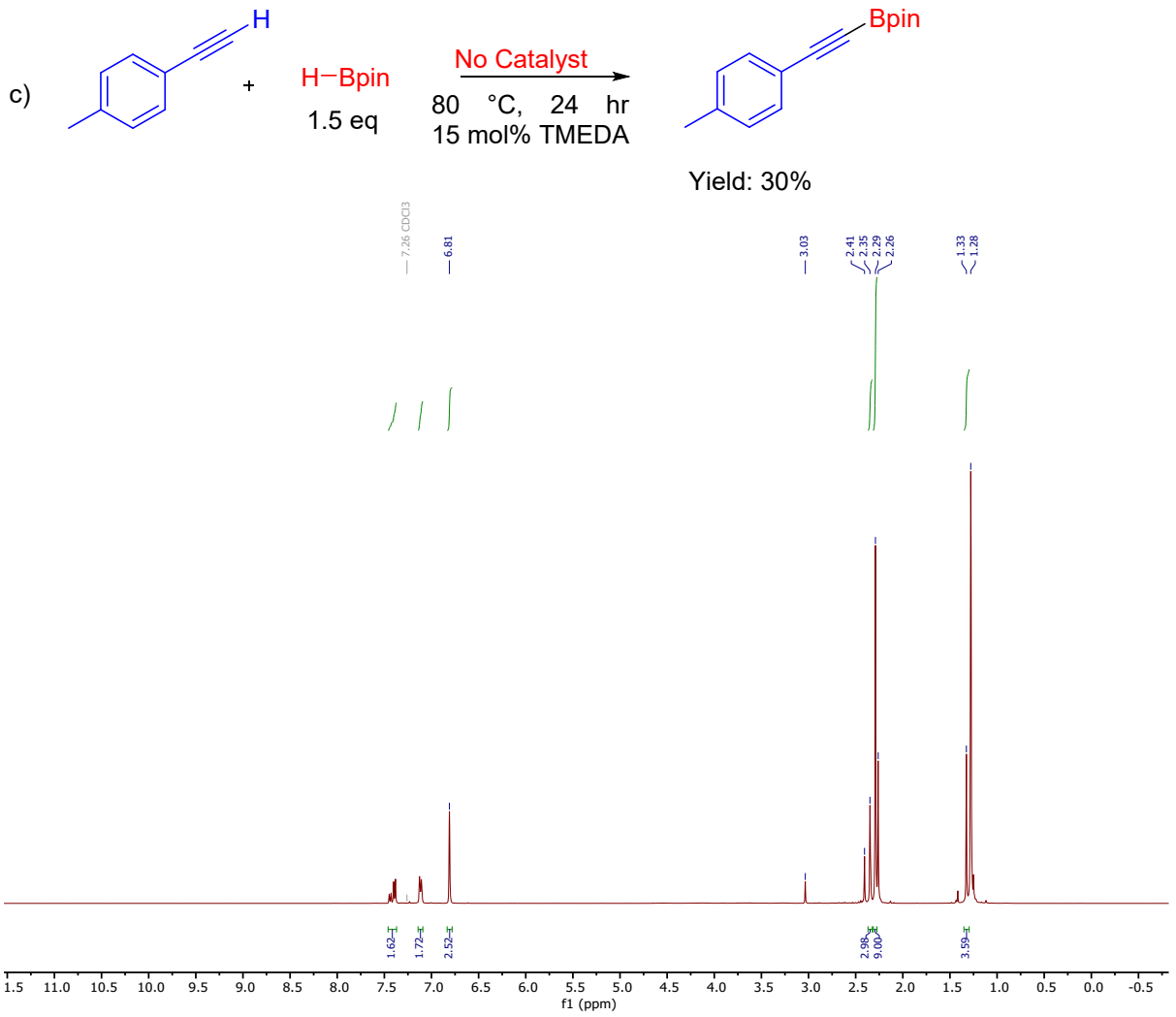


Figure S75: ^{1}H NMR spectrum in $CDCl_3$ recorded at 400 MHz

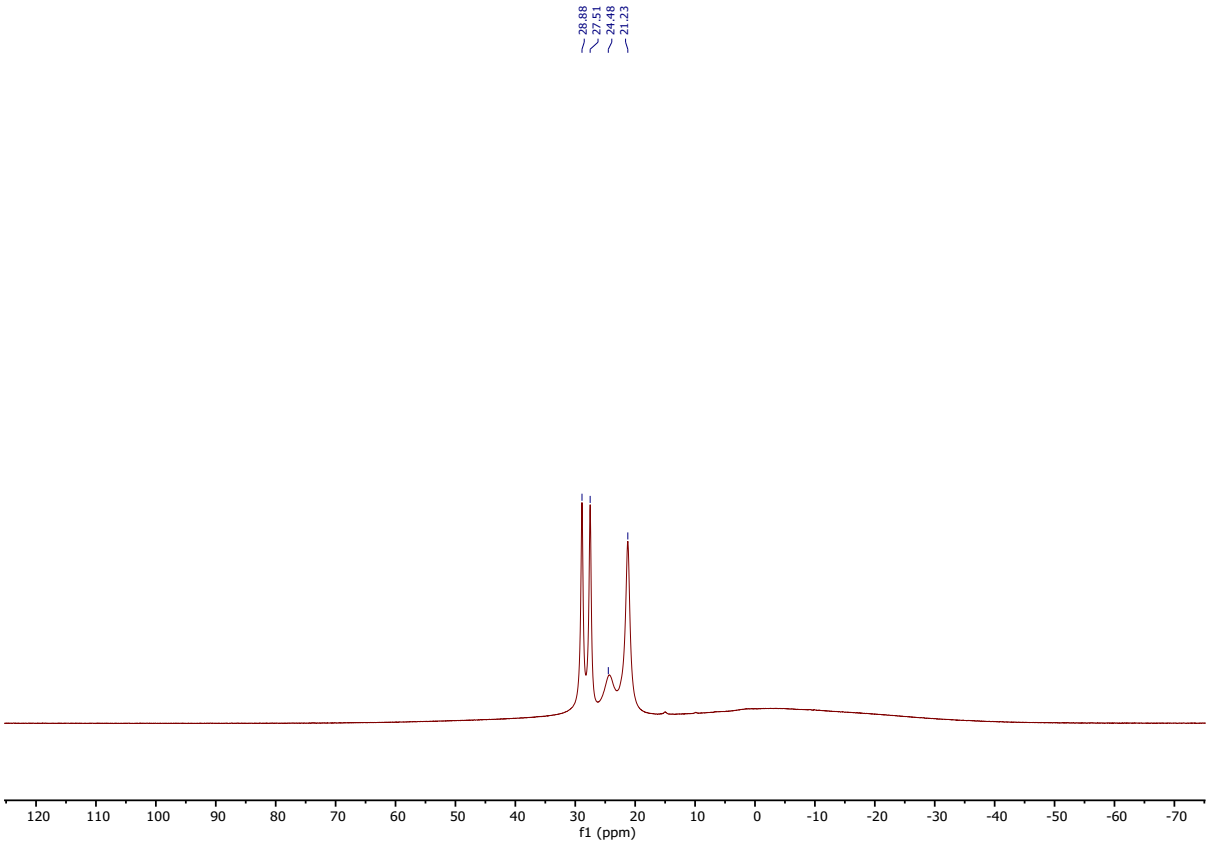


Figure S76: $^{11}B\{^{1}H\}$ NMR spectrum in $CDCl_3$ recorded at 128.3 MHz

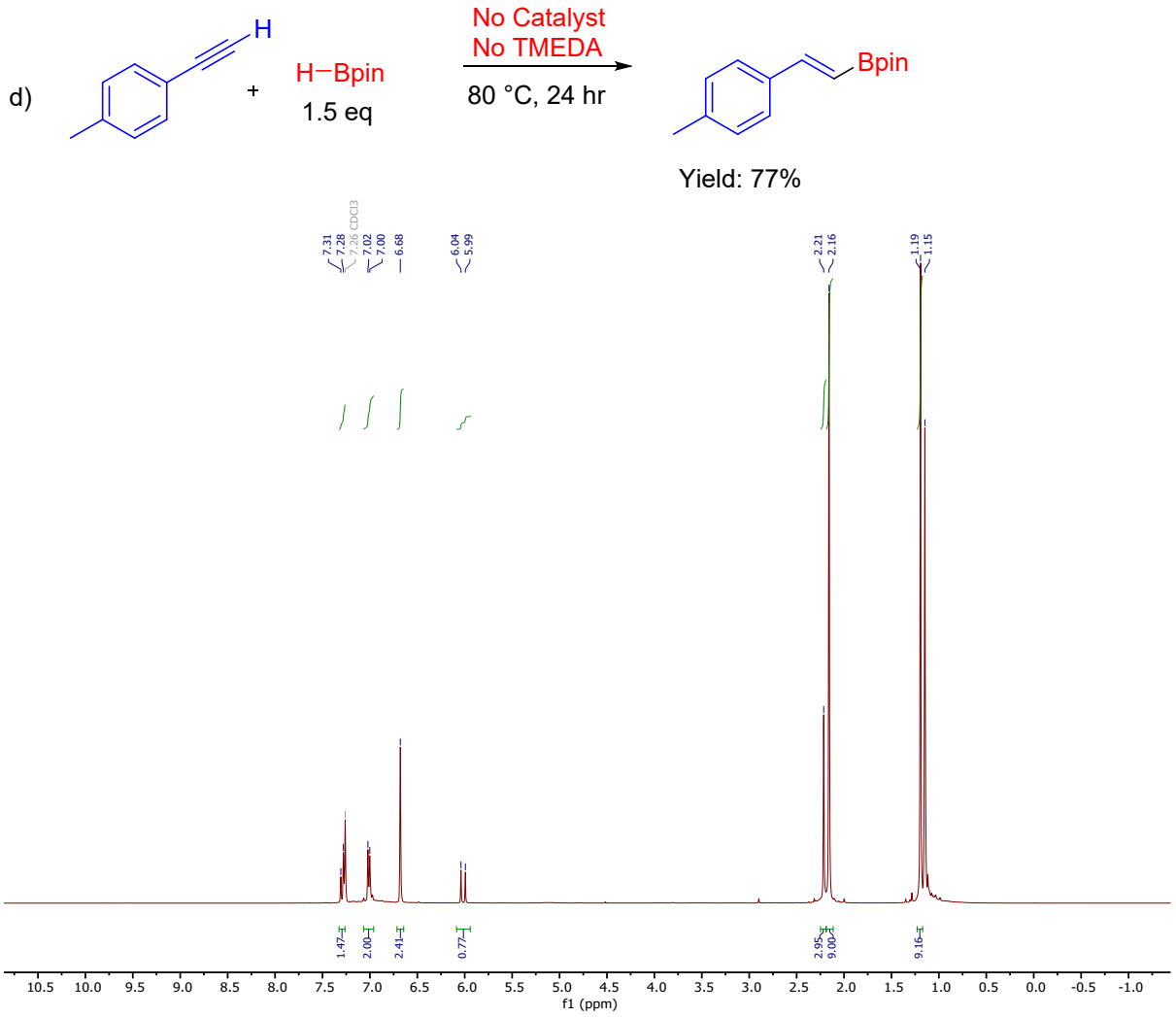


Figure S77: ^{1}H NMR spectrum in $CDCl_3$ recorded at 400 MHz

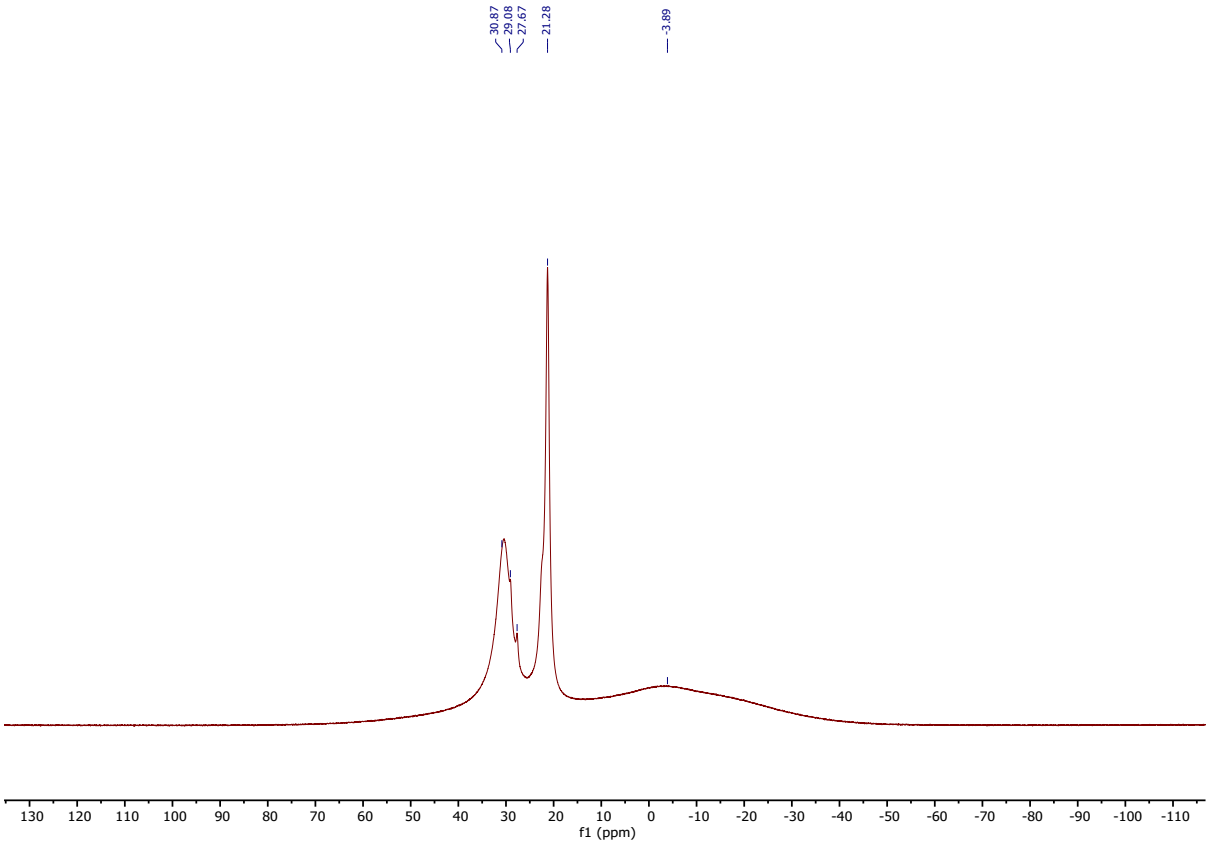


Figure S78: $^{11}B\{^{1}H\}$ NMR spectrum in $CDCl_3$ recorded at 128.3 MHz

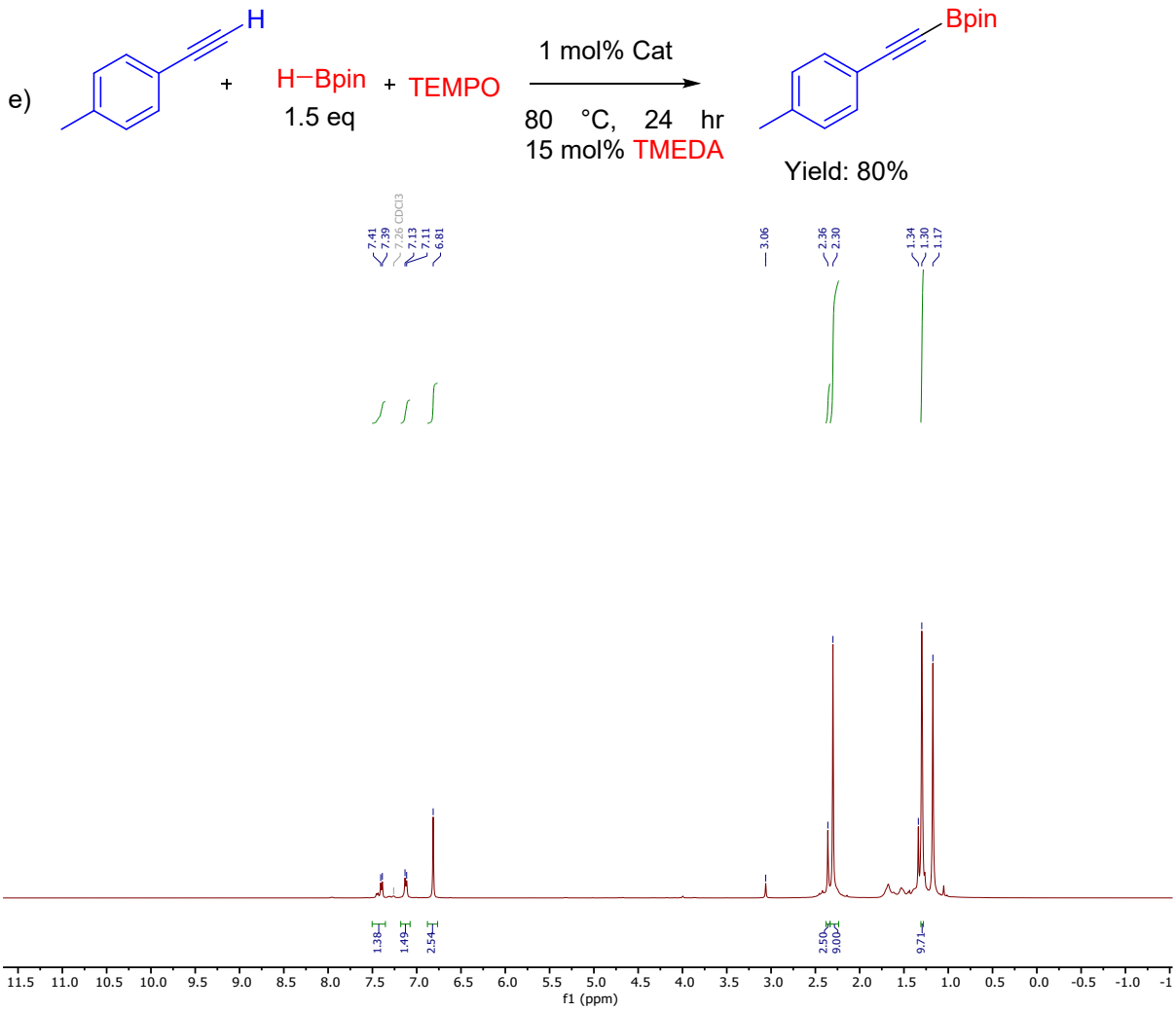


Figure S79: ^{1}H NMR spectrum in $CDCl_3$ recorded at 400 MHz

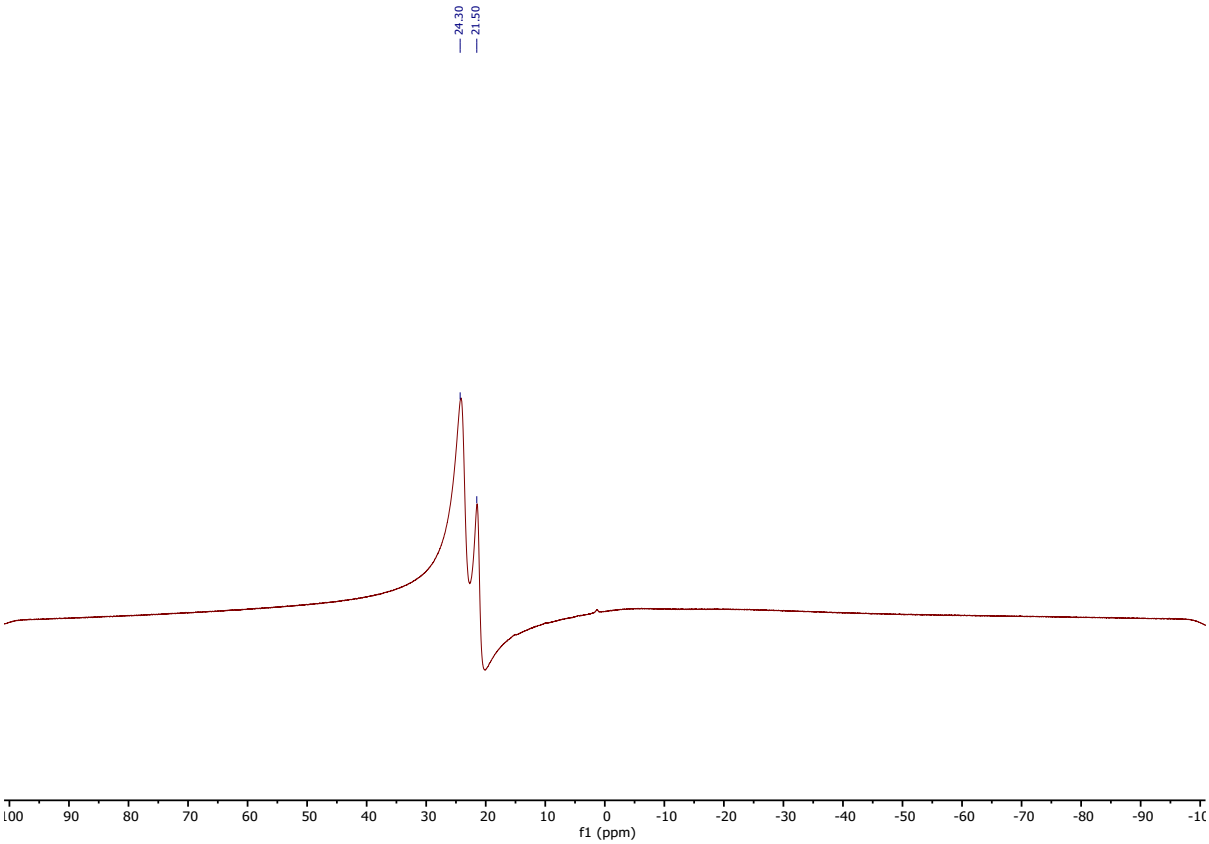


Figure S80: $^{11}B\{^{1}H\}$ NMR spectrum in $CDCl_3$ recorded at 128.3 MHz.

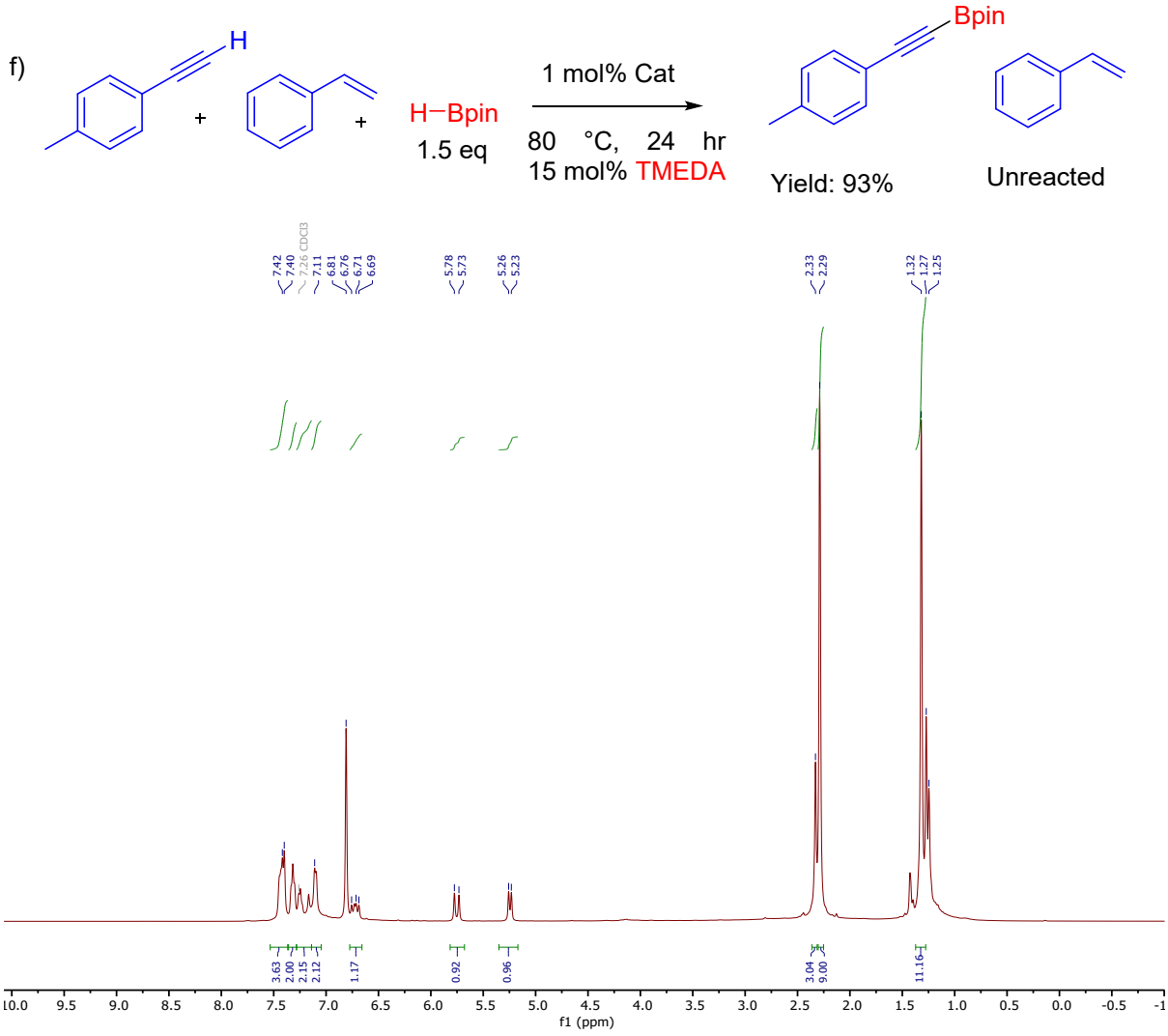


Figure S81: ^{1}H NMR spectrum in $CDCl_3$ recorded at 400 MHz

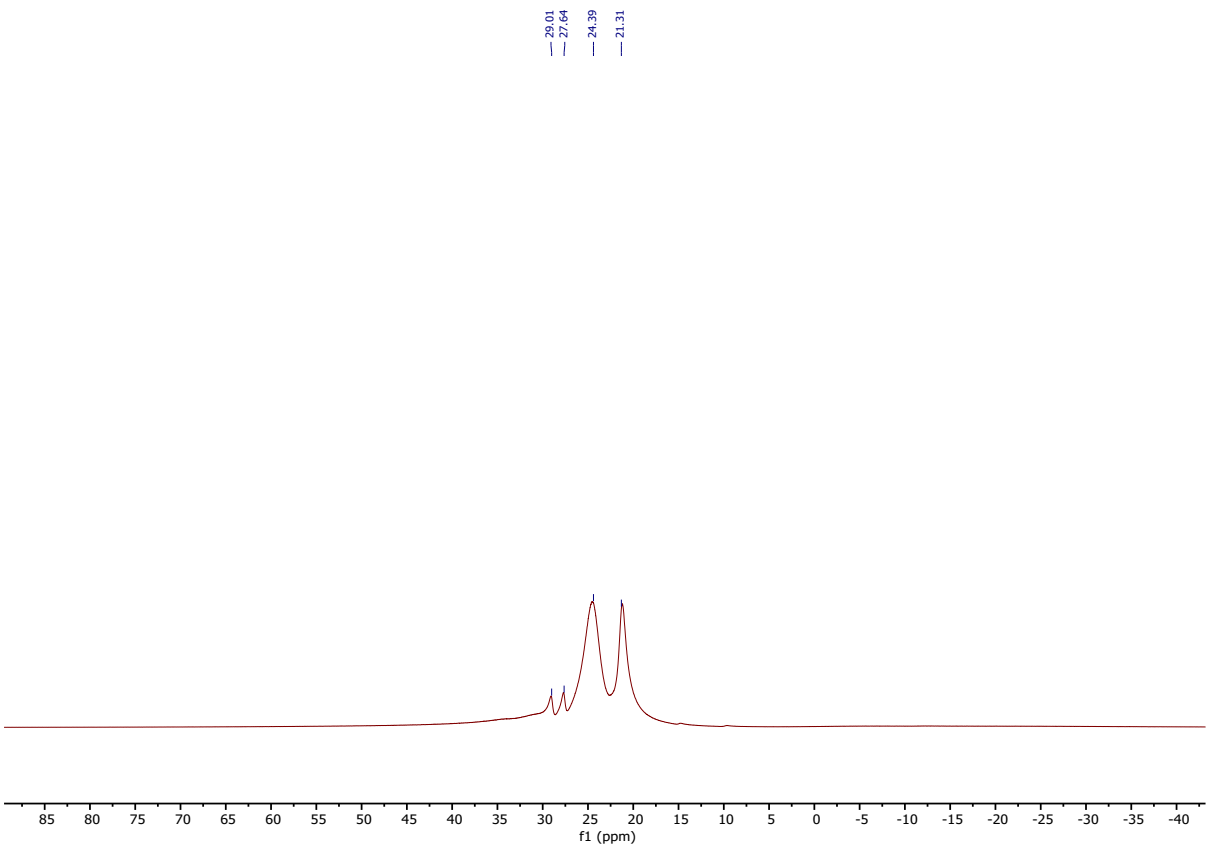


Figure S82: $^{11}B\{^{1}H\}$ NMR spectrum in $CDCl_3$ recorded at 128.3 MHz

Computational methods:

For our computational investigations, we employed density functional theory (DFT) in conjunction with Turbomole 7.5.1 software.[8] The Perdew-Burke-Ernzerhof (PBE) functional[9] with dispersion correction (DFT-D3)[10] was utilized to accurately describe the molecular systems, and the def2-SVP basis set[11] was applied for the calculations. To efficiently handle electronic Coulomb interactions, the resolution of identity (RI)[12] approximation, along with the multipole-accelerated resolution of identity (MARIJ)[13] approach, was employed. Solvent effects were incorporated using the Conductor-like Screening Model (COSMO)[14], with HBpin (ε = 2.48)[15] as the explicit solvent. Frequency calculations were conducted at all stationary points to confirm their nature as local minima. Gibbs free energy (ΔG) values, which account for zero-point energy corrections, internal energy, and entropic contributions from frequency calculations on the optimized structures, were reported. The absence of imaginary frequencies confirmed the identification of minima, while a single imaginary frequency indicated a transition state. Additionally, Intrinsic Reaction Coordinate (IRC)[16] calculations were performed for all transition states to validate their structures and ensure accurate determination of the reactant and product geometries.

Discarded mechanism

To investigate the process, various pathways were examined using thermodynamic analysis, as illustrated in the figure. To simplify the calculations, the ferrocene moiety was excluded from the computational models. As depicted in the figure, none of the proposed pathways were found to be thermodynamically favorable, and the process could not be achieved at 80°C. The most suitable pathway for borylation is detailed in the main manuscript.

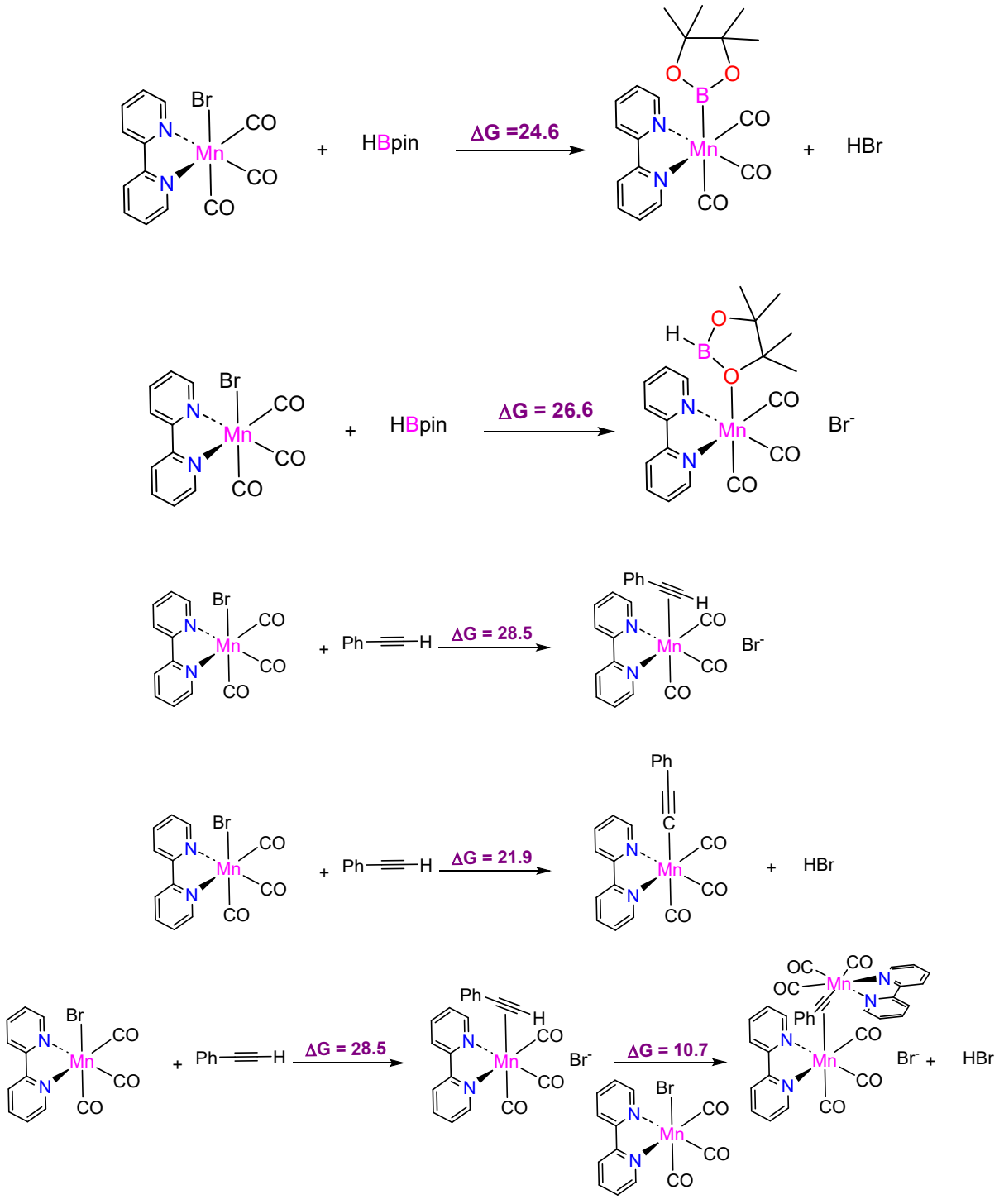


Figure S83. Thermodynamics of various pathways for borylation of alkyne. The free energies (ΔG) and is calculated at PBE-D3/Def2- SVP level of theory (ε = 2.48). The values are in kcal/mol.

Coordinates:

Catalyst

Br	-0.9650956	-1.7866032	3.0760713
Fe	-0.0211077	0.0585963	-4.2728937
Mn	-0.7990484	0.5530256	2.1227341
O	-0.5753134	3.2137325	0.8780718
O	-3.3598667	0.0178292	0.7478453
O	-2.2592356	1.5361911	4.4990116
N	1.0549758	0.6193672	3.0037140
N	0.3667648	-0.2629074	0.6503168
C	1.3158514	1.1017481	4.2365255
H	0.4685035	1.5420007	4.7803245
C	2.5867320	1.0473467	4.8168135
H	2.7391991	1.4546232	5.8261434
C	3.6381083	0.4663860	4.0904885
H	4.6505600	0.4026752	4.5156448
C	3.3750812	-0.0332796	2.8122808
H	4.1766438	-0.4955035	2.2208054
C	2.0710006	0.0543489	2.2870859
C	1.6878625	-0.4205987	0.9543883
C	2.5746231	-0.9772158	0.0130212
H	3.6339858	-1.1159890	0.2672607
C	2.1099416	-1.3427671	-1.2497238
H	2.8062127	-1.7691665	-1.9852114
C	0.7462882	-1.1547869	-1.5765987
C	-0.0800330	-0.6278977	-0.5604865
H	-1.1518566	-0.4783130	-0.7436118
C	-0.6609560	2.1669365	1.3959208
C	-2.3528483	0.2302503	1.2988771
C	-1.6852656	1.1485108	3.5600291
C	-0.0605011	1.8737577	-3.3300691
H	-0.2913518	2.0439735	-2.2694404
C	-1.0090901	1.8501712	-4.4110126
H	-2.0936582	1.9904863	-4.3187507
C	-0.2917930	1.5756644	-5.6272630
H	-0.7338377	1.4693112	-6.6261919
C	1.1010927	1.4283303	-5.2995931
H	1.9080695	1.1925971	-6.0050918
C	1.2448347	1.6115665	-3.8793993
H	2.1813189	1.5435110	-3.3100313
C	0.1995010	-1.4309612	-2.9071355
C	0.9682527	-1.7114431	-4.1045982
H	2.0554161	-1.8452973	-4.1619330
C	0.0630879	-1.7598260	-5.2172464
H	0.3425431	-1.9348013	-6.2637709
C	-1.2642975	-1.5067454	-4.7280240
H	-2.1779625	-1.4559878	-5.3333770
C	-1.1891830	-1.2966414	-3.3109789
H	-2.0413945	-1.0756631	-2.6567210

Int_1

Mn	0.7539924	0.8604076	1.7981597
O	3.4530645	0.5995200	0.6570012
O	0.1372757	3.1207230	0.0048196
O	1.6594621	2.6448654	3.9740555
N	0.9161385	-0.9717486	2.9469518
N	0.0549772	-0.6398668	0.4663930
C	1.2997438	-1.0379145	4.2371541
H	1.5698426	-0.0865619	4.7180242
C	1.3533725	-2.2427043	4.9456413
H	1.6697498	-2.2422965	5.9979352
C	0.9936862	-3.4266410	4.2835704
H	1.0191790	-4.3940350	4.8065617
C	0.5939944	-3.3604683	2.9457087
H	0.2967414	-4.2727961	2.4119263
C	0.5607020	-2.1131465	2.2905198
C	0.1300529	-1.9348863	0.8947442
C	-0.2027635	-2.9890752	0.0259902
H	-0.1282601	-4.0297374	0.3677093

C	-0.6377741	-2.7131935	-1.2724298
H	-0.9045087	-3.5344386	-1.9532714
C	-0.7616822	-1.3734105	-1.6940471
C	-0.3969970	-0.3765383	-0.7643062
H	-0.4423953	0.6799279	-1.0592367
C	2.3907323	0.7114702	1.1297574
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C	1.2971528	1.9531050	3.1074139
Br	-1.7193504	1.0107208	2.7617394
B	-2.9849905	-0.3104508	1.6197892
H	-2.9335093	0.1110196	0.4666165
H	-4.0617610	-0.1223071	2.1829428
H	-2.5156467	-1.4339406	1.7854768
C	-1.2119757	-0.9811954	-3.0323369
C	-0.9606077	-1.6849985	-4.2722666
C	-1.9209202	0.2426008	-3.3593063
Fe	-0.1296036	0.1807039	-4.3059452
C	-1.5155209	-0.9068451	-5.3453683
H	-0.4159266	-2.6320660	-4.3742227
C	-2.1120214	0.2756857	-4.7820044
H	-2.2757006	0.9895045	-2.6379452
C	0.9637070	1.7526038	-3.5873037
C	1.8556336	-0.0679386	-4.7380353
C	1.2261788	0.8003672	-5.6988092
H	-1.4719419	-1.1606975	-6.4119666
H	-2.6126920	1.0761430	-5.3410496
C	1.6942743	0.5215323	-3.4362739
C	0.6739333	1.9246726	-4.9880626
H	0.6748723	2.4371196	-2.7783381
H	2.3557959	-1.0198299	-4.9565766
H	1.1609466	0.6263699	-6.7804357
H	2.0484760	0.0968374	-2.4869573
H	0.1163345	2.7587740	-5.4329006

TS1

Mn	-0.9530192	0.5202405	1.1683853
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O	-0.3273351	1.1719343	3.9901933
N	0.8267849	-0.4167962	0.7383170
N	-1.1833030	0.0924729	-0.8386693
C	1.7931241	-0.6859163	1.6422407
H	1.6070216	-0.3564778	2.6732720
C	2.9718367	-1.3584779	1.3078032
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C	3.1555738	-1.7809190	-0.0178425
H	4.0660282	-2.3211723	-0.3160677
C	2.1577070	-1.5077920	-0.9573007
H	2.2689250	-1.8350360	-1.9994455
C	0.9977138	-0.8182546	-0.5545434
C	-0.1081202	-0.4751406	-1.4564783
C	-0.1082418	-0.6760147	-2.8482465
H	0.7614760	-1.1311527	-3.3409591
C	-1.2158727	-0.2863664	-3.6060005
H	-1.2209123	-0.4350790	-4.6955162
C	-2.3345102	0.2850099	-2.9616558
C	-2.2558863	0.4345021	-1.5610053
H	-3.0940979	0.8904110	-1.0175967
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C	-0.5859326	0.8568753	2.8995170
Br	-1.1516137	-2.0529607	2.9018083
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H	-2.6734752	-1.1715843	0.8273932
H	-3.0638611	-3.1204112	1.2448630
H	-1.3307663	-2.6135180	0.2220999
C	-3.5239851	0.7613477	-3.6742135
C	-3.5542736	1.3611974	-4.9916849
C	-4.8722231	0.8149451	-3.1380451
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C	-4.9049922	1.7675037	-5.2646054
H	-2.6898567	1.5054653	-5.6519036
C	-5.7166108	1.4251589	-4.1267674
H	-5.1932236	0.4267856	-2.1628466
C	-4.1367803	3.6912576	-1.7958708

C	-3.0584461	4.3663725	-3.7482208
C	-4.4575350	4.6783524	-3.8828462
H	-5.2528798	2.2714206	-6.1752343
H	-6.7925422	1.6123665	-4.0209643
C	-2.8616657	3.7596697	-2.4595947
C	-5.1242801	4.2609401	-2.6764844
H	-4.3254208	3.2745697	-0.7974994
H	-2.2803887	4.5468699	-4.5007013
H	-4.9350399	5.1364394	-4.7583590
H	-1.9068273	3.3952879	-2.0570454
H	-6.1987951	4.3456780	-2.4702274

Int_2

Mn	0.4648322	0.7245232	1.6891439
O	3.1904760	0.6864826	0.5471605
O	-0.2741942	2.9891265	-0.0576471
O	1.2356479	2.5746885	3.8657428
N	0.7230042	-0.9760435	2.7934635
N	-0.1303884	-0.6962074	0.3497324
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C	1.2144277	-2.2100447	4.8064224
H	1.5120111	-2.1775643	5.8635215
C	0.9442447	-3.4195910	4.1529623
H	1.0295967	-4.3794430	4.6831245
C	0.5513641	-3.3863457	2.8102365
H	0.3163786	-4.3171729	2.2770885
C	0.4435392	-2.1487451	2.1507903
C	0.0129660	-1.9934830	0.7580204
C	-0.2377927	-3.0532734	-0.1313042
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C	-0.6401605	-2.7844951	-1.4413640
H	-0.8367607	-3.6096905	-2.1409932
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C	2.1233496	0.6915370	1.0192820
C	0.0199671	2.1031065	0.6445277
C	0.9333096	1.8462390	3.0087654
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H	-3.0021458	0.9955936	2.2926003
H	-2.0878935	-0.8685775	2.2205779
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C	-1.9226594	0.1341721	-3.5966117
Fe	-0.0798709	0.1212249	-4.4357426
C	-1.3677078	-1.0160013	-5.5460905
H	-0.2758983	-2.7000120	-4.4986072
C	-2.0313430	0.1516511	-5.0287675
H	-2.3378052	0.8799700	-2.9069244
C	0.9166951	1.7298365	-3.6611596
C	1.9344735	-0.0591357	-4.7549259
C	1.3305879	0.7860579	-5.7520258
H	-1.2537413	-1.2759925	-6.6059602
H	-2.5208919	0.9328835	-5.6238230
C	1.6805467	0.5256215	-3.4657850
C	0.7001884	1.8907316	-5.0764739
H	0.5587831	2.4039890	-2.8712972
H	2.4796576	-0.9927421	-4.9424312
H	1.3332905	0.6098483	-6.8353215
H	1.9975339	0.1160620	-2.4968908
H	0.1397251	2.7043508	-5.5544464

Cat_H

Fe	0.8641848	4.3945576	1.8292043
Mn	-0.3452538	4.7787730	8.0938229
O	-0.6141672	7.4330362	6.7549518
O	-2.5437512	3.4616071	6.6420090
O	-2.1331563	5.3457100	10.3705862
N	1.3513590	5.0920175	9.1666256
N	1.0691323	4.1459173	6.7810036
C	1.4073885	5.5983303	10.4225904
H	0.4469835	5.8798980	10.8760373
C	2.6014690	5.7590491	11.1278263

H	2.5746334	6.1764726	12.1443248
C	3.8108246	5.3814603	10.5181060
H	4.7698354	5.4903155	11.0452948
C	3.7672812	4.8649364	9.2215439
H	4.6925221	4.5608955	8.7131311
C	2.5278403	4.7321908	8.5623706
C	2.3699086	4.2246952	7.2018010
C	3.4271440	3.8643494	6.3433579
H	4.4653029	3.9214271	6.6976589
C	3.1578270	3.4484455	5.0409255
H	3.9821562	3.1685563	4.3702838
C	1.8160056	3.3889059	4.5929773
C	0.8172505	3.7353960	5.5241764
H	-0.2404424	3.7087691	5.2316842
C	-0.4776484	6.4098692	7.3085965
C	-1.6848224	4.0204898	7.2105531
C	-1.4311508	5.1406881	9.4551406
C	0.5088937	6.1657662	2.7971408
H	0.4438190	6.3054044	3.8850375
C	-0.5851020	5.8414435	1.9229152
H	-1.6284780	5.6894994	2.2273712
C	-0.0665622	5.7240637	0.5853790
H	-0.6466388	5.4665591	-0.3099814
C	1.3502138	5.9745073	0.6337508
H	2.0392464	5.9441299	-0.2201322
C	1.7068467	6.2450320	2.0029816
H	2.7156469	6.4607712	2.3776968
C	1.4544688	3.0275583	3.2183166
C	2.3457453	3.0212586	2.0743897
H	3.4207995	3.2387601	2.0912470
C	1.5731390	2.7131087	0.9039728
H	1.9590810	2.6529115	-0.1212300
C	0.2043952	2.5313731	1.3053597
H	-0.6381579	2.3019749	0.6411644
C	0.1211478	2.7311926	2.7247028
H	-0.7934234	2.6562423	3.3258258
H	-0.3468786	3.3052783	8.7123824

int_3

Mn	1.6632058	-0.5929600	-1.7093896
O	3.6547488	1.3476813	-0.6233044
O	2.1929198	-2.6672150	0.3128235
O	3.4412838	-1.9192162	-3.6531855
N	0.7880535	0.6074071	-3.1007756
N	0.1237353	0.1879930	-0.6462508
C	1.1867196	0.7388108	-4.3876666
H	2.0670671	0.1529955	-4.6868650
C	0.5318652	1.5597802	-5.3078638
H	0.9078939	1.6200233	-6.3390643
C	-0.5963453	2.2872735	-4.8925825
H	-1.1408578	2.9377704	-5.5924556
C	-1.0159420	2.1607045	-3.5676604
H	-1.8996880	2.7045968	-3.2077890
C	-0.3071062	1.3181364	-2.6885045
C	-0.6560966	1.1156775	-1.2844124
C	-1.6741826	1.8019686	-0.5958990
H	-2.2876799	2.5430324	-1.1248184
C	-1.9064568	1.5366659	0.7537680
H	-2.7055021	2.0615599	1.2965653
C	-1.1227253	0.5589835	1.4061488
C	-0.1267366	-0.0812434	0.6468401
H	0.5220030	-0.8251153	1.1267290
C	2.8611722	0.6158832	-1.0767324
C	2.0168718	-1.8345887	-0.4957471
C	2.7592650	-1.3771015	-2.8697104
H	0.6773726	-1.7388678	-2.2221382
C	-1.5711952	-1.3649255	-5.1750084
C	-2.1712315	-1.2374216	-4.1128664
H	-1.0339538	-1.4841651	-6.1059770
C	-2.8723304	-1.0899306	-2.8743740
C	-2.4259551	-1.7671922	-1.7105487
C	-4.0211108	-0.2623072	-2.7898965
C	-3.1188541	-1.6229790	-0.5019075
H	-1.5165286	-2.3825721	-1.7675002

C	-4.7031941	-0.1219382	-1.5740694
H	-4.3688540	0.2662031	-3.6900810
C	-4.2573844	-0.8026291	-0.4279765
H	-2.7598617	-2.1484649	0.3962101
H	-5.5931067	0.5240347	-1.5206084
H	-4.7928021	-0.6879512	0.5269537
C	-1.2916642	0.1992626	2.8202787
Fe	0.1922405	0.2330041	4.2130703
C	-1.6368348	1.0905164	3.9073720
C	-1.0729525	-1.1176779	3.3904077
C	1.5264589	1.7625577	4.4715380
C	1.8567734	1.0003421	3.2975031
C	1.5451107	0.8694697	5.6010355
C	-1.2921232	-1.0313588	4.8079020
C	-1.6340483	0.3301103	5.1272589
H	-1.8352250	2.1659603	3.8160648
H	-0.8042166	-2.0217320	2.8287312
H	1.2870575	2.8332039	4.4979088
H	1.9111483	1.3849097	2.2702414
C	2.0786635	-0.3642353	3.6964584
C	1.8855173	-0.4456677	5.1219343
H	1.3222302	1.1391902	6.6413690
H	-1.1972732	-1.8587787	5.5223677
H	-1.8372472	0.7244117	6.1310453
H	2.3386787	-1.1969048	3.0292001
H	1.9676793	-1.3538736	5.7323883

Int_4

Mn	-1.0001105	0.3247226	-0.8241771
O	-2.9971572	2.4471213	-0.3038488
O	-0.5840841	1.5254871	-3.4664403
O	-3.4922153	-1.2670022	-0.6492581
N	-0.9585687	-0.4010951	1.1685038
N	0.4749104	1.4592769	0.0456776
C	-1.6890408	-1.4320272	1.6420911
H	-2.4430652	-1.8254954	0.9413218
C	-1.5425641	-1.9281423	2.9430428
H	-2.1682396	-2.7692440	3.2747978
C	-0.6009806	-1.3322513	3.7969654
H	-0.4577608	-1.6964116	4.8252723
C	0.1589420	-0.2645230	3.3129843
H	0.9146952	0.2142427	3.9502449
C	-0.0349046	0.1792393	1.9888745
C	0.7396554	1.2606631	1.3713109
C	1.6946616	2.0484353	2.0423187
H	1.8916678	1.8820904	3.1099596
C	2.3944311	3.0397822	1.3518124
H	3.1470440	3.6526885	1.8685003
C	2.1400042	3.2290109	-0.0238267
C	1.1672749	2.4008094	-0.6157695
H	0.9169247	2.5386349	-1.6755670
C	-2.2107677	1.5990536	-0.4883249
C	-0.7745280	1.0155064	-2.4185100
C	-2.7273731	-0.6180080	-1.3490105
H	-3.0042801	-0.4880382	-2.4424038
C	0.5382693	-1.2106987	-1.1040759
C	-0.5746051	-1.5675086	-1.6104011
H	-1.0994634	-2.3111561	-2.2175527
C	1.8684565	-1.1541332	-0.5794053
C	2.8661836	-0.3500424	-1.1950107
C	2.1945690	-1.8317610	0.6261035
C	4.1361467	-0.2274806	-0.6201078
H	2.6214526	0.1812543	-2.1267887
C	3.4701391	-1.7036954	1.1914066
H	1.4281614	-2.4529350	1.1130276
C	4.4447081	-0.8985406	0.5773734
H	4.8929708	0.4060712	-1.1082400
H	3.7035085	-2.2363594	2.1266076
H	5.4431403	-0.7947922	1.0289133
C	2.8157661	4.2432113	-0.8422010
Fe	1.8584527	5.6843050	-1.9145293
C	3.2415555	5.5592629	-0.4155920
C	3.1078795	4.1299659	-2.2601055
C	0.3369882	6.8653563	-1.2243532
C	-0.1381692	5.5323483	-1.4815181

C	0.8750575	7.3890747	-2.4530026
C	3.7165127	5.3590481	-2.6882836
C	3.7930750	6.2419260	-1.5538360
H	3.1336571	5.9718946	0.5957317
H	2.9128427	3.2504408	-2.8869358
H	0.3082534	7.3846461	-0.2579993
H	-0.5902070	4.8529130	-0.7460218
C	0.1068000	5.2266246	-2.8661503
C	0.7333050	6.3761650	-3.4673397
H	1.3297330	8.3788172	-2.5884947
H	4.0471310	5.5884436	-3.7090267
H	4.1849431	7.2668265	-1.5605689
H	-0.1330121	4.2792836	-3.3678702
H	1.0609367	6.4587728	-4.5114112

TS2

Mn	-1.9346607	1.3112117	0.2521040
O	-3.1795716	3.9743061	-0.0190724
O	-2.9497539	0.4697106	-2.3865252
O	-4.6159003	0.8588090	1.4922687
N	-0.9941706	1.7595027	2.0118884
N	-0.1037639	1.8750453	-0.4271402
C	-1.5619087	1.7328478	3.2377913
H	-2.6328711	1.4868808	3.2719583
C	-0.8466164	1.9978799	4.4092342
H	-1.3627029	1.9598828	5.3789457
C	0.5209740	2.3046970	4.3141653
H	1.1163000	2.5165510	5.2144497
C	1.1134789	2.3414073	3.0491449
H	2.1786850	2.5872262	2.9414935
C	0.3333801	2.0681288	1.9075980
C	0.8442309	2.0874411	0.5348149
C	2.1972296	2.2685511	0.1864161
H	2.9501628	2.4272035	0.9703652
C	2.5862225	2.2122062	-1.1493076
H	3.6443321	2.3359486	-1.4175382
C	1.6111246	1.9862979	-2.1498803
C	0.2766434	1.8408647	-1.7184583
H	-0.5213648	1.6444741	-2.4458930
C	-2.6884042	2.9163823	0.1009294
C	-2.5652652	0.8035878	-1.3297137
C	-3.5161764	0.6359756	1.1089313
H	-3.1780230	-0.8947704	1.4841127
C	-0.0291061	-1.1071079	0.0892447
C	-1.1360185	-0.6279628	0.4438899
H	-2.2433484	-1.0222328	1.0871773
C	1.2562642	-1.4110212	-0.4307632
C	1.4343691	-1.5457296	-1.8370043
C	2.4032470	-1.4531802	0.4099243
C	2.7165119	-1.6826130	-2.3797244
H	0.5493988	-1.5076820	-2.4891755
C	3.6797123	-1.6051919	-0.1421108
H	2.2691627	-1.3456151	1.4965424
C	3.8420118	-1.7111389	-1.5362488
H	2.8418887	-1.7583560	-3.4706014
H	4.5606188	-1.6319686	0.5176913
H	4.8496388	-1.8186456	-1.9665442
C	1.9518966	1.8681493	-3.5704253
Fe	2.2998102	3.4181789	-4.8403394
C	3.2898107	1.7956307	-4.1269111
C	1.0231201	1.8464478	-4.6856136
C	3.3911178	5.0541747	-4.2906315
C	2.0638056	5.1241179	-3.7388755
C	3.2720010	4.9775497	-5.7245070
C	1.7823076	1.7504472	-5.9007443
C	3.1786655	1.7184104	-5.5564734
H	4.2269324	1.7852643	-3.5574557
H	-0.0701385	1.9078730	-4.6223170
H	4.3282471	5.0476358	-3.7194238
H	1.8098394	5.1579632	-2.6710191
C	1.1237147	5.0873250	-4.8272361
C	1.8705387	4.9986148	-6.0556741
H	4.1027021	4.9016199	-6.4376792
H	1.3659250	1.7283421	-6.9155451
H	4.0173911	1.6620582	-6.2618126

H	0.0303125	5.1054142	-4.7346673
H	1.4454056	4.9397122	-7.0657700

Int_5

Mn	-1.1627887	0.6395923	-0.8262336
O	-3.6767348	2.2460586	-0.7893992
O	-0.3714848	1.6539177	-3.4807013
O	-2.4073158	-1.7454792	-2.0433155
N	-1.3319439	-0.0363973	1.1121937
N	-0.2083877	2.1348084	0.2088912
C	-1.9274321	-1.1879078	1.4859719
H	-2.4257110	-1.7619659	0.6923226
C	-1.9160378	-1.6537301	2.8044227
H	-2.4173015	-2.6008750	3.0485029
C	-1.2541570	-0.8971884	3.7845193
H	-1.2171367	-1.2354640	4.8304805
C	-0.6382491	0.2982003	3.4049605
H	-0.1093227	0.9108733	4.1472633
C	-0.6915267	0.7109754	2.0586093
C	-0.0966167	1.9530521	1.5569688
C	0.5196950	2.9314655	2.3601577
H	0.6153842	2.7758930	3.4432414
C	0.9976534	4.1070010	1.7819944
H	1.4754121	4.8717558	2.4104138
C	0.8638433	4.3054821	0.3881662
C	0.2651400	3.2594986	-0.3460724
H	0.1395442	3.3516947	-1.4328129
C	-2.7068914	1.5935006	-0.7841038
C	-0.7060970	1.2504074	-2.4364511
C	-1.9227895	-0.7957967	-1.5665588
C	1.6457838	-0.9244645	-0.7817048
C	0.5576185	-0.3269922	-0.8366291
C	2.8950356	-1.6094764	-0.6946151
C	3.6276036	-1.9580310	-1.8628909
C	3.4477315	-1.9669342	0.5666514
C	4.8524120	-2.6315277	-1.7697167
H	3.2141029	-1.6891151	-2.8465769
C	4.6727970	-2.6409483	0.6515405
H	2.8918605	-1.7038497	1.4795372
C	5.3834434	-2.9779133	-0.5143825
H	5.4005256	-2.8907031	-2.6893379
H	5.0792939	-2.9078101	1.6399799
H	6.3458886	-3.5079243	-0.4454588
C	1.2736827	5.5411991	-0.2837311
Fe	-0.0716147	6.9467141	-0.8837639
C	1.5356765	6.8149468	0.3576640
C	1.3488133	5.7581702	-1.7176009
C	-1.7675475	6.9838276	0.2513195
C	-1.9465730	6.1200019	-0.8866727
C	-1.4565575	8.3020350	-0.2370785
C	1.6698723	7.1384854	-1.9432163
C	1.7822751	7.7899817	-0.6665951
H	1.5226340	7.0109989	1.4367819
H	1.2020282	5.0024949	-2.4991019
H	-1.8405528	6.6844945	1.3047416
H	-2.1809852	5.0473389	-0.8517927
C	-1.7401890	6.9013576	-2.0756040
C	-1.4390824	8.2501061	-1.6750713
H	-1.2458066	9.1858427	0.3784946
H	1.7849207	7.6159940	-2.9242089
H	1.9935884	8.8540538	-0.5019696
H	-1.7808954	6.5273735	-3.1064146
H	-1.2096521	9.0858433	-2.3482404

TS3

Mn	-1.5543256	-0.9150508	-0.4519434
O	-3.9778180	0.7811538	-0.4555994
O	-0.5929100	0.2463708	-2.9871143
O	-3.1066792	-3.0121944	-1.8430341
N	-1.8223224	-1.7101729	1.4166166
N	-0.6878459	0.5220003	0.7375640
C	-2.2483873	-2.9657746	1.6708331
H	-2.4284650	-3.6057893	0.7954166
C	-2.4352543	-3.4466286	2.9713925
H	-2.7893183	-4.4762346	3.1217236
C	-2.1669305	-2.5968879	4.0569090

H	-2.3173227	-2.9374795	5.0920073
C	-1.6831381	-1.3114807	3.7988677
H	-1.4278473	-0.6347207	4.6254706
C	-1.5028379	-0.8949150	2.4656288
C	-0.9095297	0.3902253	2.0789232
C	-0.5486140	1.4174426	2.9698818
H	-0.7472896	1.3106014	4.0447755
C	0.0621459	2.5764295	2.4839690
H	0.3433294	3.3876349	3.1712671
C	0.3462483	2.6831930	1.1057013
C	-0.0535469	1.6105184	0.2826638
H	0.1207876	1.6650069	-0.7999948
C	-3.0372954	0.0852033	-0.4346128
C	-0.9987486	-0.2197057	-1.9953896
C	-2.4466621	-2.2136235	-1.3095055
H	-0.2917724	-2.6750024	-2.7698069
C	1.2086870	-1.6924009	0.3844172
C	0.3059503	-1.9201002	-0.4578478
C	2.0221377	-1.2862217	1.4770006
C	2.8815148	-0.1572002	1.3698556
C	1.8487550	-1.8848077	2.7577305
C	3.5035205	0.3753515	2.5050552
H	3.0199394	0.3102053	0.3837529
C	2.4750619	-1.3451948	3.8872434
H	1.1834776	-2.7566471	2.8478528
C	3.2967485	-0.2091222	3.7682276
H	4.1462564	1.2638777	2.4076816
H	2.3125127	-1.8059663	4.8741695
H	3.7761739	0.2216848	4.6608341
C	1.0039598	3.8522310	0.5073194
Fe	0.3600339	4.8707354	-1.1362533
C	0.7663867	5.2419075	0.8332815
C	1.9887768	3.8148213	-0.5581171
C	-1.5418359	5.5416947	-1.4876742
C	-1.4708418	4.1168402	-1.6678375
C	-0.6073062	6.1511157	-2.3975160
C	2.3587277	5.1685898	-0.8669097
C	1.6001450	6.0477254	-0.0160437
H	0.0492634	5.6111570	1.5774150
H	2.3954944	2.9062503	-1.0209625
H	-2.1853284	6.0692496	-0.7723066
H	-2.0514375	3.3670534	-1.1135008
C	-0.4926238	3.8416086	-2.6870863
C	0.0418878	5.1004350	-3.1375558
H	-0.4106819	7.2263292	-2.4971657
H	3.0820301	5.4760271	-1.6326881
H	1.6344355	7.1443428	-0.0294552
H	-0.2059819	2.8476934	-3.0546866
H	0.8197636	5.2341442	-3.9001605
B	0.3038361	-3.3809827	-1.9717781
O	-0.3407708	-4.4331119	-1.2768417
O	1.6016407	-3.7624697	-2.3554708
C	0.4797629	-5.6123882	-1.3796140
C	1.9166043	-5.0349633	-1.7545991
C	0.4374660	-6.3732066	-0.0524053
C	-0.1361426	-6.4788601	-2.4924037
C	2.8157829	-4.7809186	-0.5358730
C	2.6770203	-5.8659511	-2.7934068
H	-0.5924096	-6.7360522	0.1387333
H	1.1113237	-7.2538961	-0.0779722
H	0.7325022	-5.7245083	0.7930135
H	0.3857979	-7.4494145	-2.6115210
H	-1.1950187	-6.6800038	-2.2344393
H	-0.1229021	-5.9462200	-3.4632945
H	3.1706860	-5.7259506	-0.0786255
H	3.7004120	-4.2017450	-0.8682170
H	2.2917144	-4.1844550	0.2350798
H	3.6506414	-5.3846314	-3.0150976
H	2.8760242	-6.8918687	-2.4227788
H	2.1147173	-5.9350544	-3.7431652

Int_6

Mn	-0.8967567	0.3074445	-1.1737860
O	-2.7906278	2.5496743	-0.8124576
O	-0.0371292	1.5475572	-3.6929178

O	-3.5454299	-0.9697912	-1.3009419
N	-1.1640444	-0.5695538	0.7045622
N	0.4176747	1.3578953	-0.0061217
C	-1.8667274	-1.6944168	0.9525651
H	-2.3570650	-2.1545323	0.0870656
C	-1.9942129	-2.2383214	2.2364332
H	-2.5797543	-3.1579104	2.3772628
C	-1.3689304	-1.5931664	3.3142354
H	-1.4538743	-1.9882930	4.3375668
C	-0.6153214	-0.4425098	3.0602966
H	-0.0873963	0.0691244	3.8764427
C	-0.5153013	0.0403555	1.7404579
C	0.3302440	1.1718429	1.3461730
C	1.0388950	2.0021624	2.2337088
H	0.9422381	1.8569330	3.3182797
C	1.8653963	3.0116907	1.7345682
H	2.4239704	3.6641021	2.4214881
C	1.9949433	3.1699891	0.3373424
C	1.2425144	2.3033835	-0.4802059
H	1.2818496	2.4152257	-1.5710920
C	-2.0556932	1.6446555	-0.9303716
C	-0.4181893	1.0374426	-2.6990832
C	-2.6321447	-0.4391955	-1.9234438
H	-2.7585026	-0.3209408	-3.0430915
C	0.7463132	-1.1005196	-1.4576644
C	-0.2902322	-1.6743768	-1.9164615
C	2.1082426	-0.8069463	-1.1124539
C	2.9448086	-0.1212508	-2.0326963
C	2.6178786	-1.1108705	0.1763728
C	4.2500519	0.2388657	-1.6716356
H	2.5484259	0.1310924	-3.0273224
C	3.9218432	-0.7379293	0.5286173
H	1.9736716	-1.6376133	0.8959802
C	4.7437332	-0.0613191	-0.3897635
H	4.8885495	0.7645323	-2.3986788
H	4.3012310	-0.9794521	1.5336123
H	5.7662255	0.2317612	-0.1072735
C	2.8320155	4.2007468	-0.2874423
Fe	2.1290092	5.6018276	-1.5866991
C	3.0848185	5.5343093	0.2161410
C	3.4814860	4.0930080	-1.5807109
C	0.4441496	6.7312445	-1.3155240
C	0.0925145	5.3826177	-1.6698971
C	1.2583214	7.2704677	-2.3740767
C	4.1339412	5.3430699	-1.8556435
C	3.8853239	6.2330880	-0.7520421
H	2.7024530	5.9471097	1.1581984
H	3.4915150	3.1982186	-2.2153178
H	0.1546656	7.2512332	-0.3933556
H	-0.5107903	4.6907593	-1.0662388
C	0.6886661	5.0826884	-2.9447878
C	1.4097714	6.2513388	-3.3807286
H	1.7009141	8.2744260	-2.4005221
H	4.7073900	5.5804287	-2.7606201
H	4.2281092	7.2724541	-0.6721944
H	0.6107916	4.1279384	-3.4819951
H	1.9863862	6.3427421	-4.3099799
B	-1.1754814	-2.7768694	-2.5091934
O	-1.7311183	-2.7018008	-3.7664406
O	-1.5334583	-3.9072741	-1.8058153
C	-2.3934383	-3.9767050	-4.0304330
C	-2.5753569	-4.5907249	-2.5744521
C	-3.6997223	-3.6916757	-4.7669577
C	-1.4409114	-4.7851892	-4.9198591
C	-3.9156434	-4.2316703	-1.9223455
C	-2.3278852	-6.0948688	-2.4820384
H	-3.4796538	-3.2540034	-5.7606023
H	-4.2740301	-4.6267143	-4.9224501
H	-4.3303979	-2.9757076	-4.2090829
H	-1.8879619	-5.7503104	-5.2280711
H	-1.2182889	-4.1972043	-5.8317173
H	-0.4818998	-4.9893126	-4.4040202
H	-4.7581130	-4.7549164	-2.4152645
H	-3.8893872	-4.5471349	-0.8602884

H	-4.1004804	-3.1404324	-1.9457149		H	-3.0544742	-6.6492198	-3.1091538
H	-2.4575659	-6.4276979	-1.4333048		H	-1.3050911	-6.3664236	-2.801961

❖ **Crystallographic Data:**

Single-crystal X-ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. All the data were collected at 100(2) K using graphite-monochromated MoK_α radiation (λ_α = 0.71073 Å). The frames were indexed, integrated, and scaled by using the SMART and SAINT software packages[17] and the data were corrected for absorption by using the SADABS program.[18] The structures were solved and refined with the SHELX suite of programs.[19] All the hydrogen atoms were included in the final stages of the refinement and were refined with a typical riding model. Structure solution and refinement details for compound **1** is provided in the table below. Pertinent crystallographic data for compound **1** is summarized in Table 4. The crystallographic figures used in this manuscript were generated using Diamond 3.1e software.[20]

	1
Empirical formula	C_{23} H_{16} Br Fe Mn N_2 O_3, C H_2 Cl_2
Formula Weight	644.00
Crystal System	triclinic
Space Group	*P*-1
a (Å)	9.6556(12)
b (Å)	10.7004(12)
c (Å)	13.2591(16)
α (deg)	112.6020(10)
β (deg)	91.100(2)
γ (deg)	109.359(3)
V (Å^3)	1176.2(2)
Z	2
ρ_{calcd} (g cm$^{-3)}$	1.818
μ (mm^{-1})	3.110
F(000)	640
Reflections	

Collected	43888
Independent	5964
Observed [I>2σ(I)]	4205
No. of variables	307
GooF	1.025
R_{int}	0.1165
Final R indices [I > 2σ(I)][a]	R1 = 0.0465 wR2 = 0.0963
R indices (all data)[a]	R1 = 0.0841 wR2 = 0.1104

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$

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