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Electronic Supplementary Information

Chemoselective C(sp)-H Borylation of Terminal Alkynes Catalyzed by a Bis(N-heterocyclicsilylene) Manganese Complex

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1. General Considerations

All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere (argon) glovebox unless otherwise noted. All glassware was stored in a pre-heated at 200 °C oven prior to use. All glassware was cleaned using base (KOH, iPrOH) and acid (HCl (aq)) baths. All reported reaction temperatures correspond to external silicone oil bath temperatures. Room temperature (rt) was approximately 23 °C.

The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[1]

$MnCl_2$ was purchased from Fisher Scientific (99.99%, ultra dry) and dried under high vacuum for 8 h prior to use. Mesitylene, and *N*,*N*′-Di-tert-butylcarbodiimide were dried over CaH_2 degassed by three freeze-pump-thaw cycles and distilled under vacuum prior to use. The terminal alkynes employed in the substrate scope (**1-20**) were purchased from commercial sources (Thermo Fisher Scientific, AmBeed and Sigma Aldrich), dried over lithium aluminum hydride and distilled prior to use. MeLi (1.6 M diethyl ether), $NaHBEt_3$ (1.0 M solution in THF), KO*t*Bu (1.0 M solution in THF), NH_3BH_3 and dmpe were purchased from Sigma Aldrich and used as received. All other reagents were used as received. SiNSi,[2] 2,6-Diamine-*N*,*N*′-diethylpyridine,[2,3] $[Mn(SiNSi)Cl_2]$[4] (**Mn1**), $[Mn(SiNSi)Br_2]$,[5] [Mn(SiNSi)(dmpe)],[5] $[Mn(dmpe)_2Br_2]$,[6] $[Mn(terpy)Cl_2]$,[7] $[Mn(^{iPr}PNP)Cl_2]$[8] and HBDan (Dan = 1,8-diaminonaphthalene)[9] were prepared according to literature procedures. 2,6-Diamine-N,N′-diethylpyridine was distilled under vacuum prior to its use.

DCM-d_2, $CDCl_3$ (Thermo Fisher Scientific) were distilled from CaH_2 under an atmosphere of argon prior to its use and stored over 4 Å molecular sieves. THF-d_8 and Toluene-d_8 (Thermo Fisher Scientific) were distilled from sodium metal under an atmosphere of argon and stored under argon. Benzene-d_6 and DMSO-d_6 were purchased from Thermo Fischer Scientific and used without further purification. D_2O was purchased from Sigma-Aldrich and used without further purification.

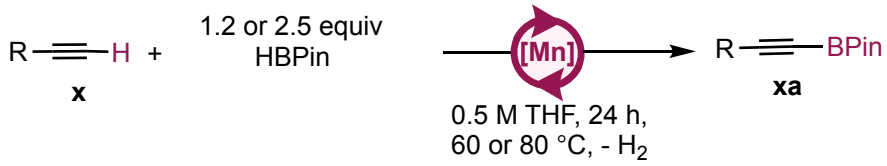
^1H NMR spectra were recorded on either Varian 400 or 500 spectrophotometers operating at 400 MHz, and 500 MHz, respectively. ^{13}C NMR spectra were recorded on Varian 400 or 500 spectrophotometers operating at 101 MHz and 126 MHz, respectively. ^{11}B NMR spectra were recorded on Varian 400 or 500 spectrometers with 128 MHz and 160 MHz frequencies. ^{19}F NMR spectra were recorded on Varian 400 or 500 spectrometers with 376 MHz and 470 MHz frequencies. All ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to $SiMe_4$ using the ^1H (chloroform-*d*: 7.26 ppm; benzene-d_6: 7.16 ppm) and ^{13}C (chloroform-*d*: 77.16 ppm;

benzene-d_6: 128 ppm) chemical shifts of the solvent as a standard. ^{1}H NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent, obsc = obscured), coupling constants (Hz), integration, assignment. ^{13}C NMR data for diamagnetic compounds are reported as follows: chemical shift, number of protons attached to carbon (e. g. CH_2), assignment. QC stands for *quaternary carbon*.

GC analyses were performed using a Shimadzu GC-2014 gas chromatograph equipped with a Shimadzu AOC-20s autosampler and a Shimadzu capillary column (15m x 250μm). The instrument was set to a detector temperature of 250 °C. UHP-grade (99.999%) helium was used as carrier gas and further purified employing a He purifier installed prior to the instrument inlet. The temperature program used for GC analyses was as follows: 60 °C, isothermal 1 min; 15 ºC/min to 250 °C, isothermal 2 min.

Infrared spectroscopy was conducted on a ALPHA II Compact FT-IR Spectrometer spectrometer installed in an argon glovebox.

2. General Catalytic Procedures



Method 1: General Procedure for the C-H borylation of fluorinated aromatic terminal alkynes. In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: **Mn1** (12 mg, 0.015 mmol), terminal alkyne (0.3 mmol), THF (0.5 mL) and HBPin (110 µL, 0.75 mmol for synthesis of alkynylboronate esters or 53 µL, 0.36 mmol for catalyst screening and optimization of the reaction components). The reaction was stirred and heated to 60 °C (for catalyst screening and optimization of the reaction components) or 80 °C (for synthesis of alkynylboronate esters) for 24 h. After this time, the reaction was brought into the glovebox and fluorobenzene (10 µL, 0.106 mmol) was added as an internal standard. The crude reaction mixture was passed through a plug of Whatman filter paper in a Pasteur pipette and then analyzed by GC chromatography and ^{19}F NMR spectroscopy without additional purification.

Method 2: General Procedure for the C-H borylation of other terminal alkynes: In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order: **Mn1** (12.15 g, 0.015 mmol), terminal alkyne (0.3 mmol), THF (0.5 mL) and HBPin (110 µL, 0.75 mmol). The reaction was stirred and heated to 80 °C for 24 h, time after which it was exposed to air and mesitylene (10 µL, 0.07 mmol) was added as an internal standard. The crude reaction mixture was passed through a plug of Whatman filter paper in a Pasteur pipette and then analyzed by GC chromatography and ^{1}H NMR spectroscopy without additional purification.

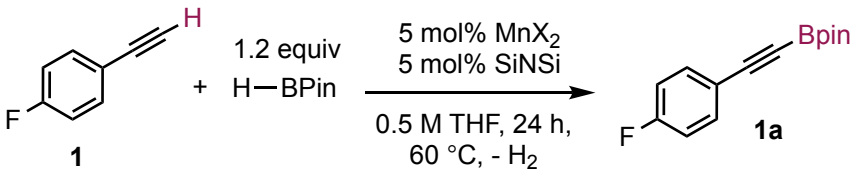
General procedure for isolation of C-H borylated products: After the completion of the reaction, it was exposed to air and volatiles were removed in vacuo. Then, it was brought into the glovebox and hexane was added. The reaction mixture was passed through a plug of Whatman filter paper in a Pasteur pipette and then kept in freezer to precipitate out the product as an amorphous solid. Hexane was decanted the next day and mesitylene was added as an internal standard and isolated product was analyzed by ^{1}H NMR spectroscopy.

3. Optimization of the Catalytic Conditions

3.1 Optimization of the components of the reaction: The optimization of the X-type ligand at the Mn precatalyst afforded the % conversion and % yield reported in Table S1. All the catalytic reactions were conducted following the general catalytic procedure described in Method 1 (60 °C) employing 4-fluorophenylacetylene (34 µL, 0.3 mmol) as the alkyne, [Mn(SiNSi)Br_2] (13 mg, 0.015 mmol) instead of **Mn1**, and HBCat (38 µL, 0.36 mmol) or HBDan (60 mg, 0.36 mmol mmol) instead of HBPin.

Entry	'X' type ligand	Borylating agent	Conversion (%)	Yield (%)
1	Cl (**Mn1**)	HBPin	49	47
2	Cl	HBCat	>99	0
3	Cl	HBDan	23	4
4	Br	HBPin	88	43

Table S1. Optimization of the X-type ligand at Mn and borylating agent.



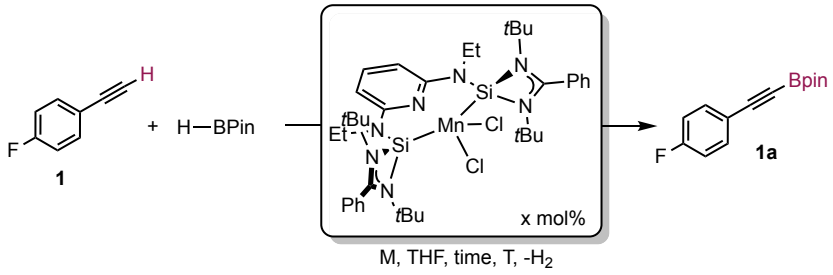
3.2 Evaluation of the catalytic efficiency of *in-situ* formed Mn precatalysts: The catalytic reactions were conducted following the general catalytic procedure Method 1 (1.2 equiv of HBPin and 60 °C) described above employing 4-fluorophenylacetylene (34 µL, 0.3 mmol) as the alkyne and a mixture of MnX_2 (for X = Cl, 2 mg, 0.015 mmol; for X = OAc, 3 mg, 0.015 mmol; for X = OTf, 5 mg, 0.015 mmol) and SiNSi (10 mg, 0.015 mmol) in THF (0.3 mL) freshly generated upon stirring the reagents at room temperature for 1 h.

Entry	X	Conversion (%)	Yield 1a (%)
1	Cl	33	11
2	OAc*	45	<5%
3	OTf	66	<5%

* <5% alkenylboronate ester was detected by ^{19}F NMR spectroscopy.

Table S2. Evaluation of the catalyst efficiency of in-situ formed precatalysts from different MnX_2 salts.

3.3 Optimization of the reaction conditions: The optimization of the reaction conditions afforded the % conversion and % yield reported in Table S2. All the catalytic reactions were conducted following the general Method 1 catalytic procedure described above employing 4-fluorophenylacetylene (34 µL, 0.3 mmol) as the alkyne.



Entry	Molarity of solution	Catalyst loading (mol%)	Equiv of HBPin	T (°C)	Solvent	t (h)	Conversion (%)	Yield 1a (%)
1	0.5	5	0.8	80	THF	24	49	45
2	0.5	5	1.0	80	THF	24	96	74
3	0.5	5	1.2	80	THF	24	83	67
4	0.5	5	1.5	80	THF	24	66	48
5	0.5	5	2.0	80	THF	24	98	88
6	**0.5**	**5**	**2.5**	**80**	**THF**	**24**	**>99**	**>99**
7	0.5	5	3.0	80	THF	24	95	82
8	0.5	5	1.2	r.t.	THF	24	52	<5
9	0.5	5	1.2	r.t.*	THF	24	35	5
10	0.5	5	1.2	40	THF	24	25	9
11	0.5	5	1.2	60	THF	24	49	47
12	0.5	5	1.2	100	THF	24	>99	65

Entry	Molarity of solution	Catalyst loading (mol%)	Equiv of HBPin	T (°C)	Solvent	t (h)	Conversion (%)	Yield 1a (%)
13	0.5	5	1.2	80	FC_6H_5	24	74	44
14[#]	0.5	5	1.2	80	C_6H_6	24	48	36 (10% alkene)
15[#]	0.5	5	1.2	80	Toluene	24	72	31 (7% alkene)
16[#]	0.5	5	1.2	80	Hexane	24	35	22 (13% alkene)
17	0.5	5	1.2	80	2 Me-THF	24	95	63
18	0.5	5	1.2	80	THF	16	85	43
19	0.5	5	2.5	80	THF	72	>99	87
20	0.25	5	1.2	80	THF	24	41	27
21	0.75	5	1.2	80	THF	24	84	77
22	1.00	5	1.2	80	THF	24	92	84
23	0.5	3	1.2	80	THF	24	73	48
24[#]	0.5	3	2.5	80	THF	24	94	61 (9% alkene)
25[#]	0.5	5	2.5	80	neat	24	ND	62 (74% alkene)

(*= reaction was carried out in the presence of blue light)

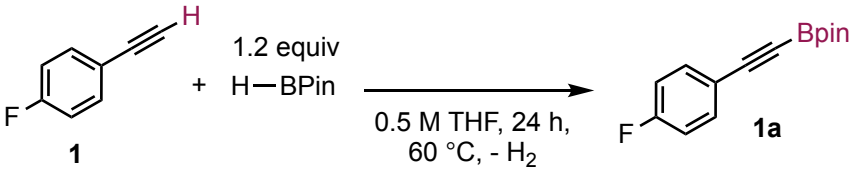
ND : Not determined

([#]= The corresponding alkenylboronate ester **1b** was formed as the side product in these reactions due to the accumulation of H_2 in the reaction medium. When the reaction in entry 14 was carried out in a J. Young NMR tube where the headspace was previously evacuated, the yield of alkenylboronate ester was <5%, supporting the chemoselectivity of the catalytic system in C_6H_6, see section 7.2)

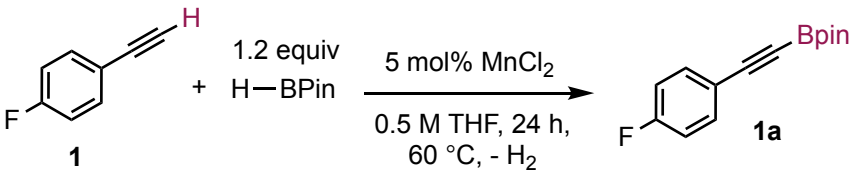
Table S3. Optimization of catalytic conditions.

4. Control Experiments

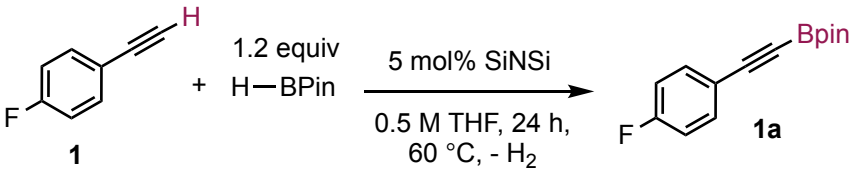
The control experiments were carried out following the general catalytic procedure under the optimized conditions.



4.1 Reaction of 4-fluorophenylacetylene with HBPin. In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and 4-fluorophenylacetylene (34.5 µL, 0.3 mmol), THF (0.52 mL) and HBPin (52 µL, 0.36 mmol) were added. The tube was sealed, and the resulting mixture was stirred at 60 ºC for 24 hours. The reaction was brought into the glovebox and fluorobenzene (10 µL, 0.106 mmol) was added as an internal standard. The crude reaction mixture was passed through a plug of Whatman filter paper in a Pasteur pipette and then analyzed by GC chromatography and ^{19}F NMR spectroscopy without additional purification. Conversion: <5%; Yield: <5%.

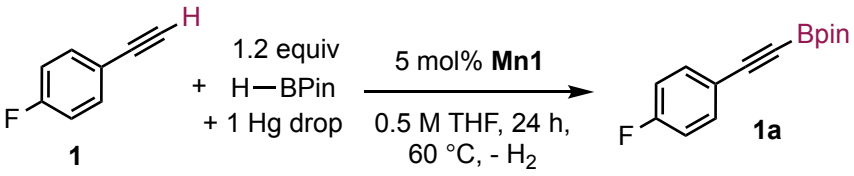


4.2 Reaction of 4-fluoro phenylacetylene with HBPin in the presence of 5 mol% of $MnCl_2$. In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar, 4-fluorophenylacetylene (34.5 µL, 0.3 mmol), THF (0.52 mL), HBPin (52 µL, 0.36 mmol) and $MnCl_2$ (1.89 mg, 0.015 mmol). The tube was sealed, and the resulting mixture was stirred at 60 ºC for 24 hours. The reaction was brought into the glovebox and fluorobenzene (10 µL, 0.106 mmol) was added as an internal standard. The crude reaction mixture was passed through a plug of whatman filter paper in a Pasteur pipette and then analyzed by GC chromatography and NMR spectroscopy without additional purification. Conversion: 17%; Yield: 17%.

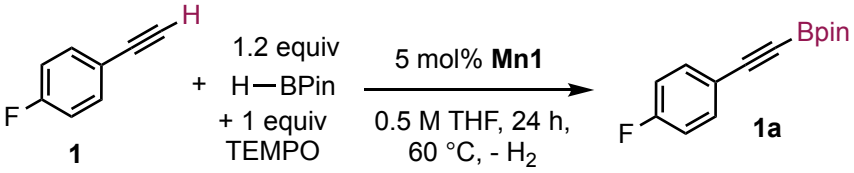


4.3 Reaction of 4- fluorophenylacetylene with HBPin in the presence of 5 mol% of SiNSi. In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar, 4-

fluorophenylacetylene (35 µL, 0.3 mmol), THF (0.52 mL), HBPin (52 µL, 0.36 mmol) and SiNSi (10 mg, 0.015 mmol). The tube was sealed, and the resulting mixture was stirred at 60 ºC for 24 hours. The reaction was brought into the glovebox and fluorobenzene (10 µL, 0.106 mmol) was added as an internal standard. The crude reaction mixture was passed through a plug of whatman filter paper in a Pasteur pipette and then analyzed by GC chromatography and NMR spectroscopy without additional purification. Conversion: <5%; Yield: <5%.

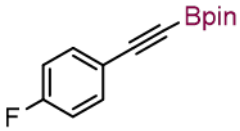


4.4 Catalytic reaction in the presence of a Hg drop. In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order- **Mn1** (12 mg, 0.015 mmol), THF (0.52 mL), 4-Fluorophenylacetylene (33 µL, 0.3 mmol), HBPin (52 µL, 0.36 mmol) and a drop of Hg. The tube was sealed, and the resulting mixture was stirred at 60 ºC for 24 hours. The reaction was brought into the glovebox and the crude reaction mixture was diluted with THF and passed through a plug of silica gel in a Pasteur pipette and then analyzed by ^{19}F NMR spectroscopy without additional purification. Conversion: 91%; Yield: 51%.



4.5 Catalytic reaction in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy). In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order- **Mn1** (12 mg, 0.015 mmol), THF (0.52 mL), 4-Fluorophenylacetylene (33 µL, 0.3 mmol), HBPin (52 µL, 0.36 mmol) and TEMPO (47 µL, 0.3mmol). The tube was sealed, and the resulting mixture was stirred at 60 ºC for 24 hours. The reaction was brought into the glovebox and the crude reaction mixture was diluted with THF and passed through a plug of silica gel in a Pasteur pipette and then analyzed by NMR spectroscopy without additional purification. Conversion: 31%; Yield: 31%.

5. Characterization of alkynylboronate esters



2-((4-Fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a). The compound was prepared according to the general procedure using 4-fluorophenylacetylene (34 µL, 0.3 mmol) as the terminal alkyne. Yield (Crude yield): >99%.

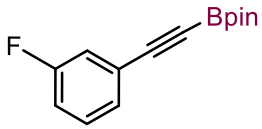
^{1}H NMR (400 MHz, C_6D_6, 23 ºC): δ. 1.01 (12H, s), 6.48 (2H, d), 7.13 (2H, d).

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.71, 84.15, 100.68, 115.92 (d), 118.68 (d), 128.30, 134.72 (d), 162.07, 164.33.

^{11}B NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.40.

^{19}F NMR (400 MHz, C_6D_6, 23 ºC): δ. -109.18.

The spectroscopic data matched that previously reported.[10,11]



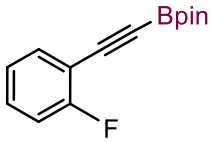
2-((3-Fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a). The compound was prepared according to the general procedure using 3-fluorophenylacetylene (34 µL, 0.3 mmol) as the terminal alkyne. Yield (Crude yield): >99%.

^{1}H NMR (400 MHz, C_6D_6, 23 ºC): δ. 1.03 (12H, s), 6.56- 6.65 (2H,m), 6.97-7.02 (2H,m).

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.69, 24.95, 84.26, 116.61(d), 119.20(d), 124.43(d), 130.15(d), 161.37, 163.82.

^{11}B NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.76.

^{19}F NMR (400 MHz, C_6D_6, 23 ºC): δ. -112.16.



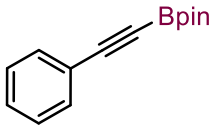
2-((2-Fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a). The compound was prepared according to the general procedure using 2-fluorophenylacetylene (34 µL, 0.3 mmol) as the terminal alkyne. Yield (Crude yield): >99%.

^{1}H NMR (400 MHz, C_6D_6, 23 ºC): δ. 1.01 (12H, s), 6.50-6.54 (1H, t), 6.58- 6.62 (1H, t), 6.68-6.73 (1H, t) (obscured by mesitylene), 7.18-7.22 (1H, s).

$^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.69, 24.94, 84.27, 106.30, 111.28 (d), 115.63 (d), 124.07 (d), 131.12 (d), 134.46, 162.57, 165.09.

^{11}B NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.66.

^{19}F NMR (400 MHz, C_6D_6, 23 ºC): δ. -108.67.



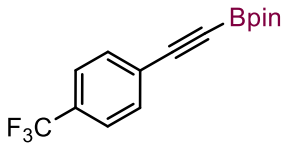
4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (4a). The compound was prepared according to the general procedure using phenylacetylene (33 µL, 0.3 mmol) as the terminal alkyne. Yield (Isolated yield): 88 %.

^1H NMR (500 MHz, C_6D_6, 23 ºC): δ. 1.03 (12H,s), 6.85-6.91 (3H, m), 7.36-7.38 (2H, d).

$^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.73, 84.16, 101.84, 122.70, 128.56, 129.34, 132.67

^{11}B NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.74.

The spectroscopic data matched that previously reported.[10]



4,4,5,5-Tetramethyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane (5a). The compound was prepared according to the general procedure using 1-ethynyl-4-(trifluoromethyl)benzene (49 µL, 0.3 mmol) as the terminal alkyne. Yield (Crude yield): >99% .

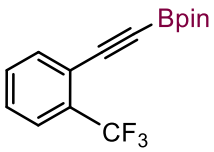
^1H NMR (500 MHz, C_6D_6, 23 ºC): δ. 1.04 (12H, s), 7.02-7.04 (2H, d), 7.14-7.16 (2H, d).

$^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.67, 84.42, 99.87, 125.41 (q), 126.18, 130.64(q), 132.83.

^{11}B NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.32.

^{19}F NMR (400 MHz, C_6D_6, 23 ºC): δ. -62.92.

The spectroscopic data matched that previously reported.[10]



4,4,5,5-Tetramethyl-2-((2-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane (6a). The compound was prepared according to the general procedure using 1-ethynyl-2-(trifluoromethyl)benzene (41 µL, 0.3 mmol) as the terminal alkyne. Yield (Crude yield): 92%.

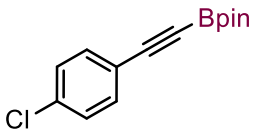
^{1}H NMR (400 MHz, C_6D_6, 23 ºC): δ. 0.98 (12H, s), 6.62-6.71 (2H, m), 7.17-7.19 (1H, d), 7.26-7.28 (1H, d).

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.66, 84.35, 125.91 (q), 128.96, 131.37, 135.17.

^{11}B NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.98.

^{19}F NMR (400 MHz, C_6D_6, 23 ºC): δ. -61.56.

The spectroscopic data matched that previously reported.[12]



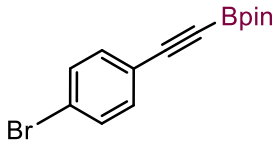
2-((4-Chlorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7a). The compound was prepared according to the general procedure using 1-chloro-4-ethynylbenzene (41 mg, 0.3 mmol) as the terminal alkyne. Yield (Crude yield): 93%.

^{1}H NMR (400 MHz, C_6D_6, 23 ºC): δ. 1.02 (12H,s), 6.75-6.77 (2H,d), 7.03-7.05 (2H,d).

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.69, 84.40, 100.51, 120.90, 127.35, 128.91, 133.89, 135.51.

^{11}B NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.80.

The spectroscopic data matched that previously reported.[11]

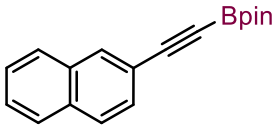


2-((4-Bromophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8a). The compound was prepared according to the general procedure using 1-bromo-4-ethynylbenzene (54 mg, 0.3 mmol) as the terminal alkyne. Yield (Isolated yield): 68%.

^{1}H NMR (400 MHz, C_6D_6, 23 ºC): δ. 1.02 (12H, s), 6.89-6.91 (2H, d), 6.94-6.96 (2H, d).

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.68, 84.22, 100.60, 121.31, 123.87, 131.83, 134.02.

^{11}B NMR (400 MHz,128, C_6D_6, 23 ºC): δ. 24.67.



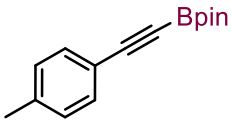
4,4,5,5-tetramethyl-2-[2-(naphthalen-2-yl)ethynyl]-1,3,2-dioxaborolane (9a). The compound was prepared according to the general procedure using 2-ethynyl-naphthalene (45 mg, 0.3 mmol) as the terminal alkyne. Yield (Isolated yield): 92%.

^{1}H NMR (500 MHz, C_6D_6, 23 ºC): δ. 1.06 (12H, s), 7.13-7.17 (2H, m), 7.30-7.33 (1H, m), 7.34-7.36 (1H, m), 7.39-7.43 (2H, m), 7.88 (1H, s).

^{13}C{^{1}H} NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.75, 84.15, 119.97, 126.72, 127.22, 127.82, 128.41, 128.81, 133.25, 133.41, 133.66.

^{11}B NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.83

The spectroscopic data matched that previously reported.[11]



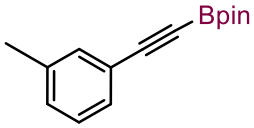
4,4,5,5-Tetramethyl-2-(4-methylphenylethynyl)-1,3,2-dioxaborolane (10a). The compound was prepared according to the general procedure using 4-ethynyltoluene (38 µL, 0.3 mmol) as the terminal alkyne. Yield (Isolated yield): 78%.

^{1}H NMR (400 MHz, C_6D_6, 23 ºC): δ. 1.04 (12H,s), 1.89 (3H,s), 6.69-6.71 (2H, d), 7.32-7.34 (2H, d)

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 23 ºC): δ. 21.30, 24.74, 84.01, 119.78, 129.37, 132.73, 139.50.

^{11}B NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.84.

The spectroscopic data matched that previously reported.[10]



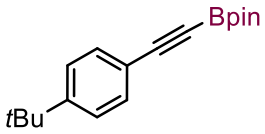
4,4,5,5-Tetramethyl-2-(3-methylphenylethynyl)-1,3,2-dioxaborolane (11a). The compound was prepared according to the general procedure using 3-ethynyltoluene (35 µL, 0.3 mmol) as the terminal alkyne. Yield (Isolated yield): 91%.

^{1}H NMR (500 MHz, C_6D_6, 23 ºC): δ. 1.03 (12 H, s), 1.86 (3H,s), 6.75 (1H,d), 6.82 (1H,t), 7.19 (1H,s), 7.27 (1H,d)

$^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 23 ºC): δ. 20.94, 24.71, 84.04, 102.21, 122.53, 128.49, 129.86, 130.32, 133.40, 138.17

^{11}B NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.69.

The spectroscopic data matched that previously reported.[10]



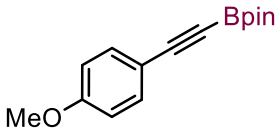
2-((4-*tert*-butylphenyl)ethynyl)-4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (12a). The compound was prepared according to the general procedure using *tert*-butyl phenylacetylene (54 µL, 0.3 mmol) as the terminal alkyne. Yield (Crude yield): 93%.

^1H NMR (500 MHz, C_6D_6, 23 ºC): δ. 1.04 (12H,s), 1.05 (9H,s), 6.98 (2H,d), 7.42 (2H,d).

$^{13}C\{^1H\}$ NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.74, 31.05, 34.71, 84.03, 119.90 125.69, 127.37, 132.67, 152.54.

^{11}B NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.73.

The spectroscopic data matched that previously reported.[10]



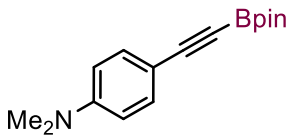
2-((4-Methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13a). The compound was prepared according to the general procedure using 4-ethynylanisole (39 µL, 0.3 mmol) as the terminal alkyne. Yield (Crude yield): 97%.

^1H NMR (400 MHz, C_6D_6, 23 ºC): δ. 1.04 (12H, s), 3.12 (3H,s), 6.43-6.45 (2H, d), 7.33-7.35 (2H, d).

$^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.73, 54.71, 83.95, 114.31, 114.58, 134.42, 160.75.

^{11}B NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.94.

The spectroscopic data matched that previously reported.[10]



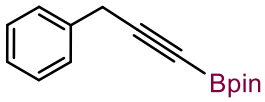
4,4,5,5-Tetramethyl-2-((*p-N,N*-dimethylaniline)ethynyl)-1,3,2-dioxaborolane (14a). The compound was prepared according to the general procedure using 4-ethynyl-N,N-dimethylaniline (44 mg, 0.3 mmol) as the terminal alkyne. Yield (Crude yield): 62%.

^{1}H NMR (400 MHz, C_6D_6, 23 ºC): δ. 1.06 (12H, s), 2.31 (6H, s), 6.18-6.21 (2H, d), 7.42-7.45 (2H, d).

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.80, 39.50, 83.72, 109.39, 111.9, 134.19, 150.82.

^{11}B NMR (400 MHz, C_6D_6, 23 ºC): δ. 25.17.

The spectroscopic data matched that previously reported.[10]



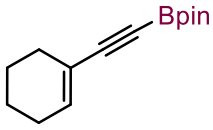
4,4,5,5-Tetramethyl-2-(3-phenylprop-1-yn-1-yl)-1,3,2-dioxaborolane (15a). The compound was prepared according to the general procedure using 3-phenyl-1-propyne (37 µL, 0.3 mmol) as the terminal alkyne. Yield (Isolated yield): 54%.

^{1}H NMR (500 MHz, C_6D_6, 23 ºC): δ.1.03 (12H, s), 3.32 (2H, s), 7.02-7.07 (3H,m), 7.17 (2H,m).

^{13}C{^{1}H} NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.78, 25.91, 83.82, 101.45, 126.88, 128.25, 128.76, 135.28.

^{11}B NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.14.

The spectroscopic data matched that previously reported.[10]



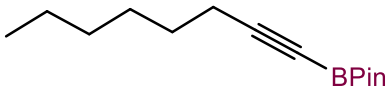
2-[2-(1-cyclohexenyl)ethynyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16a). The compound was prepared according to the general procedure using 1-ethynylcyclohexene (35 µL, 0.3 mmol) as the terminal alkyne. Yield (Crude yield): 71%.

^{1}H NMR (500 MHz, C_6D_6, 23 ºC): δ. 1.01 (12H, s), 1.20 (2H, m), 1.26 (2H, m), 1.69 (2H, m), 2.05 (2H, m), 6.17 (1H, sept.)

^{13}C{^{1}H} NMR (500 MHz, C_6D_6, 23 ºC): δ. 21.51, 22.28, 24.75, 25.80, 28.95, 83.77, 106.28, 120.87, 138.08

^{11}B NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.89.

The spectroscopic data matched that previously reported.[10]



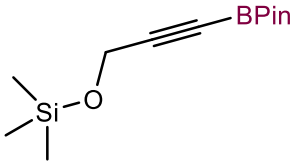
4,4,5,5-Tetramethyl-2-(oct-1yn-1yl)-1,3,2-dioxaborolane (17a). The compound was prepared according to the general procedure using 1-octyne (44 µL, 0.3 mmol) as the terminal alkyne. Yield (Isolated yield): 51%.

^{1}H NMR (500 MHz, C_6D_6, 23 ºC): δ. 0.78 (3H, t), 1.01 (12H, s), 1.02-1.05(2H, m), 1.15-1.21 (4H, m), 1.27-1.31 (2H, m), 1.97 (2H, t).

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 23 ºC): δ. 14.28, 19.72, 22.82, 24.73, 28.48, 28.76, 31.60, 83.61, 106.28.

^{11}B NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.01.

The spectroscopic data matched that previously reported.[12]



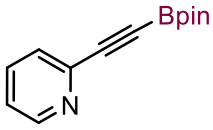
4,4,5,5-Tetramethyl-2-(propargyloxytrimethylsilylethynyl)-1,3,2-dioxaborolane (18a). The compound was prepared according to the general procedure using (propargyloxy)trimethylsilane (46 µL, 0.3 mmol) as the terminal alkyne. Yield (Isolated yield): 50%.

^{1}H NMR (500 MHz, C_6D_6, 23 ºC): δ. 0.08 (9H, s), 0.98 (12h, s), 4.08 (2H, s).

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 23 ºC): δ. -0.43, 24.68, 51.43, 83.98, 106.25.

^{11}B NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.16

The spectroscopic data matched that previously reported.[11]

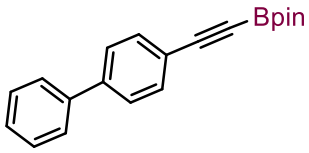


4,4,5,5-Tetramethyl-2-(2-pyridylethynyl)-1,3,2-dioxaborolane (19a). The compound was prepared according to the general procedure using 2-Ethynylpyridine (30 µL, 0.3 mmol) as the terminal alkyne. Yield (Isolated yield): 13%.

^{1}H NMR (400 C_6D_6, 23 ºC): δ. 1.00 (12H, s), 6.48 (1H, t), 6.79 (1H, t), 7.07-7.09 (1H, d), 8.31 (1H, d).

$^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 23 ºC): δ.24.67, 84.33, 101.00, 123.40, 135.58, 143.08, 150.45.

^{11}B NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.80.



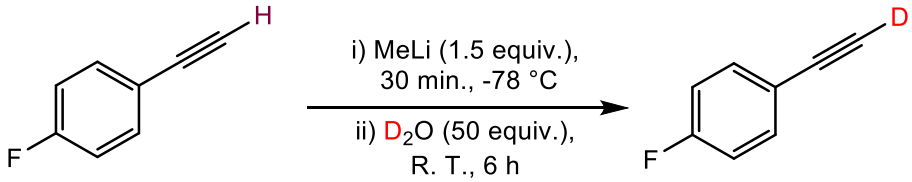
2-((1,1'-biphenyl)-4-ylethynyl)-4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (20a). The compound was prepared according to the general procedure using 4-ethynyl-1,1'-biphenyl (53 mg, 0.3 mmol) as the terminal alkyne. Yield (Isolated yield): 10%.

^1H NMR (500 MHz, C_6D_6, 23 ºC): δ. 1.05 (12H,s), 7.09-7.11 (1H,m), 7.13-7.16 (4H,m) (obscured by C_6D_6), 7.24-7.26 (2H,d), 7.44-7.45 (2H, d).

$^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 23 ºC): δ. 24.75, 24.94, 84.13, 121.51, 127.31, 127.64, 127.95, 129.02, 133.24, 140.47,142.24, 149.83.

^{11}B NMR (500 MHz, C_6D_6, 23 ºC): δ. 24.78.

6. Preparation of 4-fluorophenylacetylene-*d*



4-fluorophenylacetylene-*d* was prepared by dropwise addition of MeLi (3.4 mL of a 1.6 M solution in diethyl ether, 5.39 mmol) to a solution of 4-fluorophenylacetylene (0.55 mL, 4.9 mmol) in diethyl ether (25 mL) at -78 °C. After stirring the contents at -78 °C for 30 min, D_2O (2 mL, 110.8 mmol) was added and the contents were left for stirring at room temperature for 6 hours followed by separation of organic layer. The organic layer was dried using $MgSO_4$ and removal of the solvent in vacuo resulted in the formation of the product with >99 % deuterium incorporation.

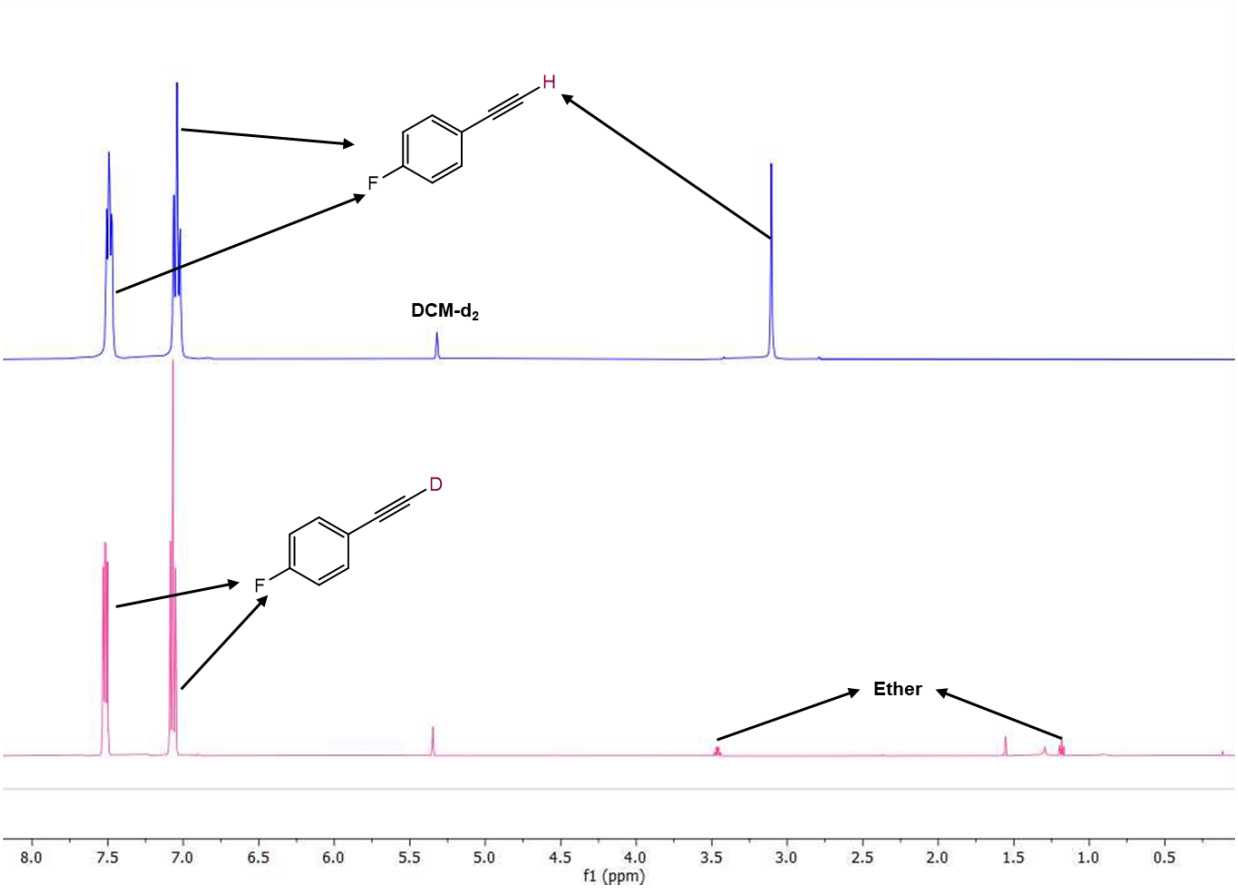
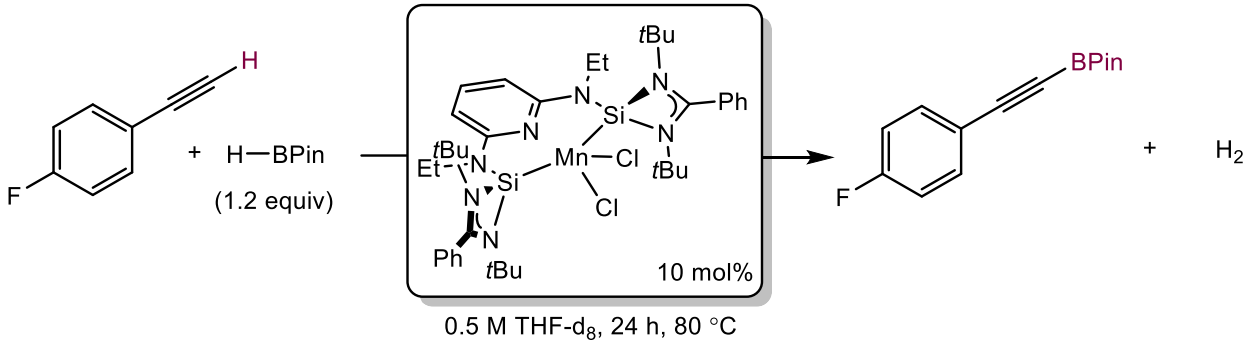


Figure S1: Stacked ^{1}H NMR spectra of 4-fluorophenylacetylene (top) and 4-fluorophenylacetylene-*d* (down) in DCM-d_2. (No signal corresponding to alkynyl proton in 4-fluorophenylacetylene-*d* spectrum)

7. NMR Monitoring of Catalytic and Stoichiometric Reactions.



7.1 NMR monitoring of the C-H borylation of 4-fluorophenylacetylene with HBPin at 80 ºC employing 10 mol% of Mn1 as precatalyst. 4-Fluorophenylacetylene (20 µL, 0.174 mmol) was added to a solution of **Mn1** (14 mg, 0.0174 mmol) in THF-d_8 (0.30 mL) followed by the

addition of HBPin (30 µL, 0.208 mmol) and fluorobenzene (10 µL, 0.106 mmol) as internal standard in a J. Young NMR tube in an argon filled glovebox. The tube was sealed and brought out of the glovebox. The headspace was evacuated by a freeze-pump-thaw cycle. The reaction was monitored by ^{1}H, ^{11}B and ^{19}F NMR spectroscopy at 80 ºC for 24 hours (see Figures S1, S2 and S3). No signals attributable to diamagnetic manganese species were observed in the NMR spectra, however, signals attributable to the C-H borylation product (**1a**) were identified in the ^{11}B and ^{19}F NMR spectra and their intensity grew over time at the expense of those of the starting material. Signals corresponding to H_2 formed as a byproduct were also identified in ^{1}H NMR.

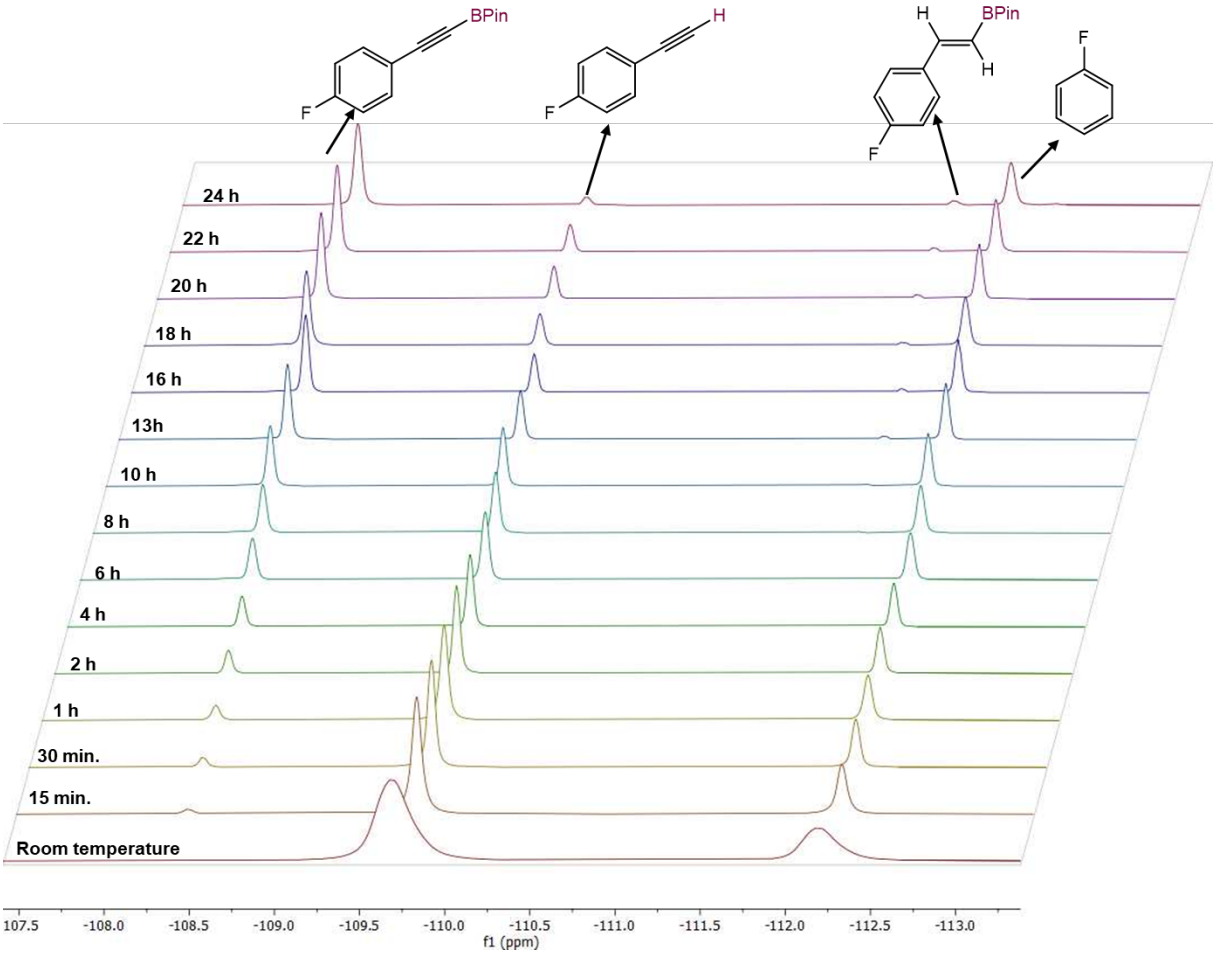


Figure S2: ^{19}F NMR spectra of catalytic reaction in THF-d_8 at 80 ºC, using fluorobenzene as internal standard.

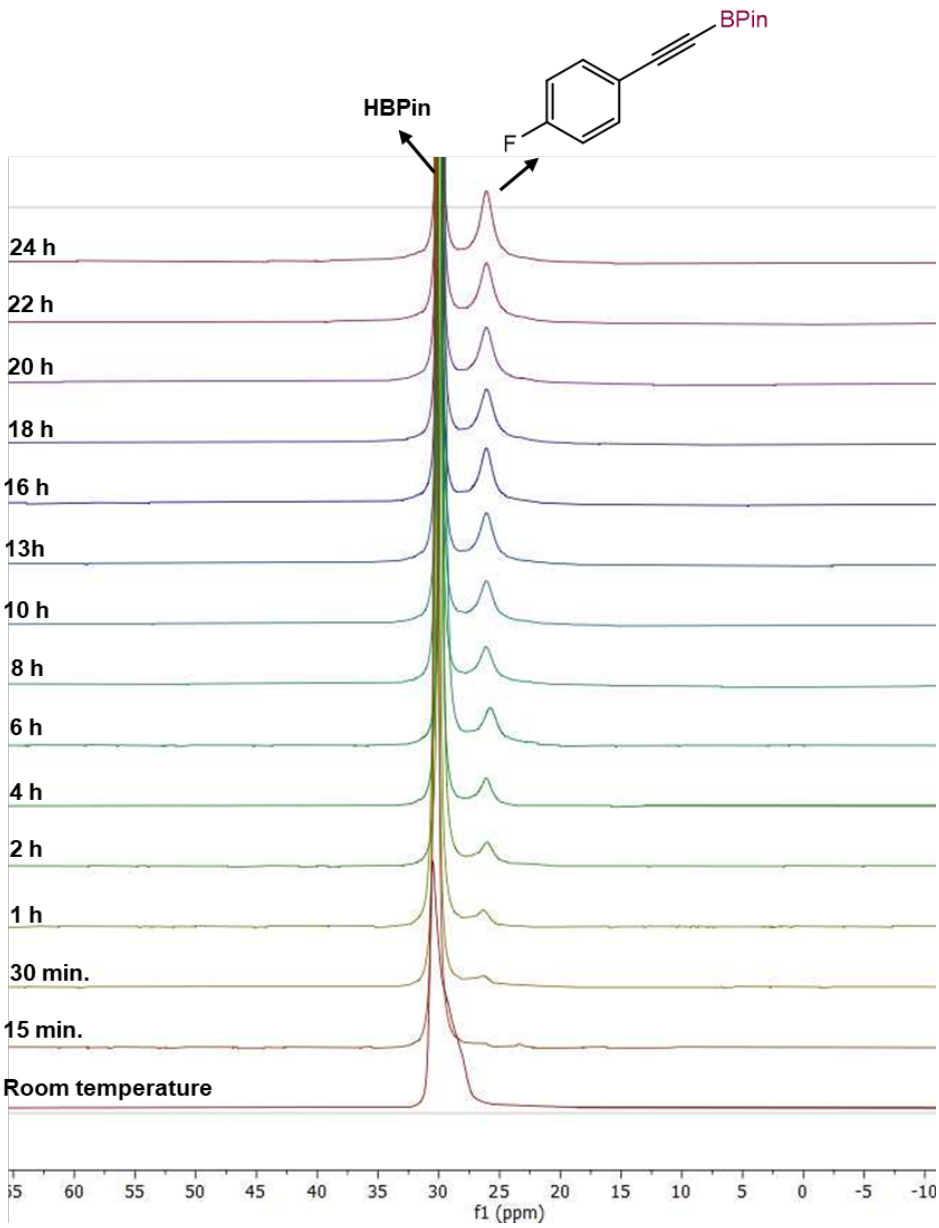


Figure S3: ^{11}B NMR spectra of catalytic reaction in THF-d_8 at 80 ºC, using fluorobenzene as internal standard.

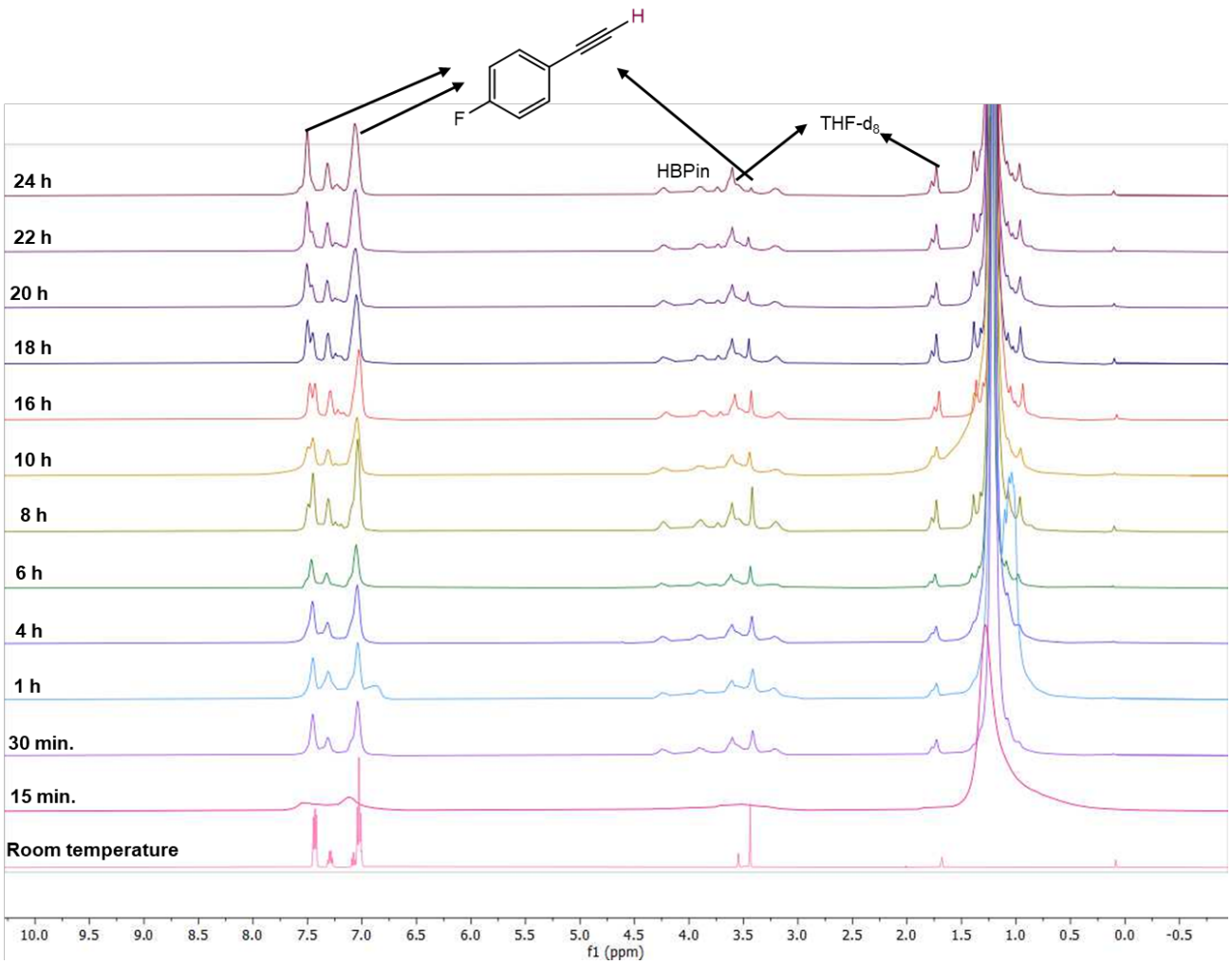


Figure S4: ^{1}H NMR spectra of catalytic reaction in THF-d_8 at 80 ºC.

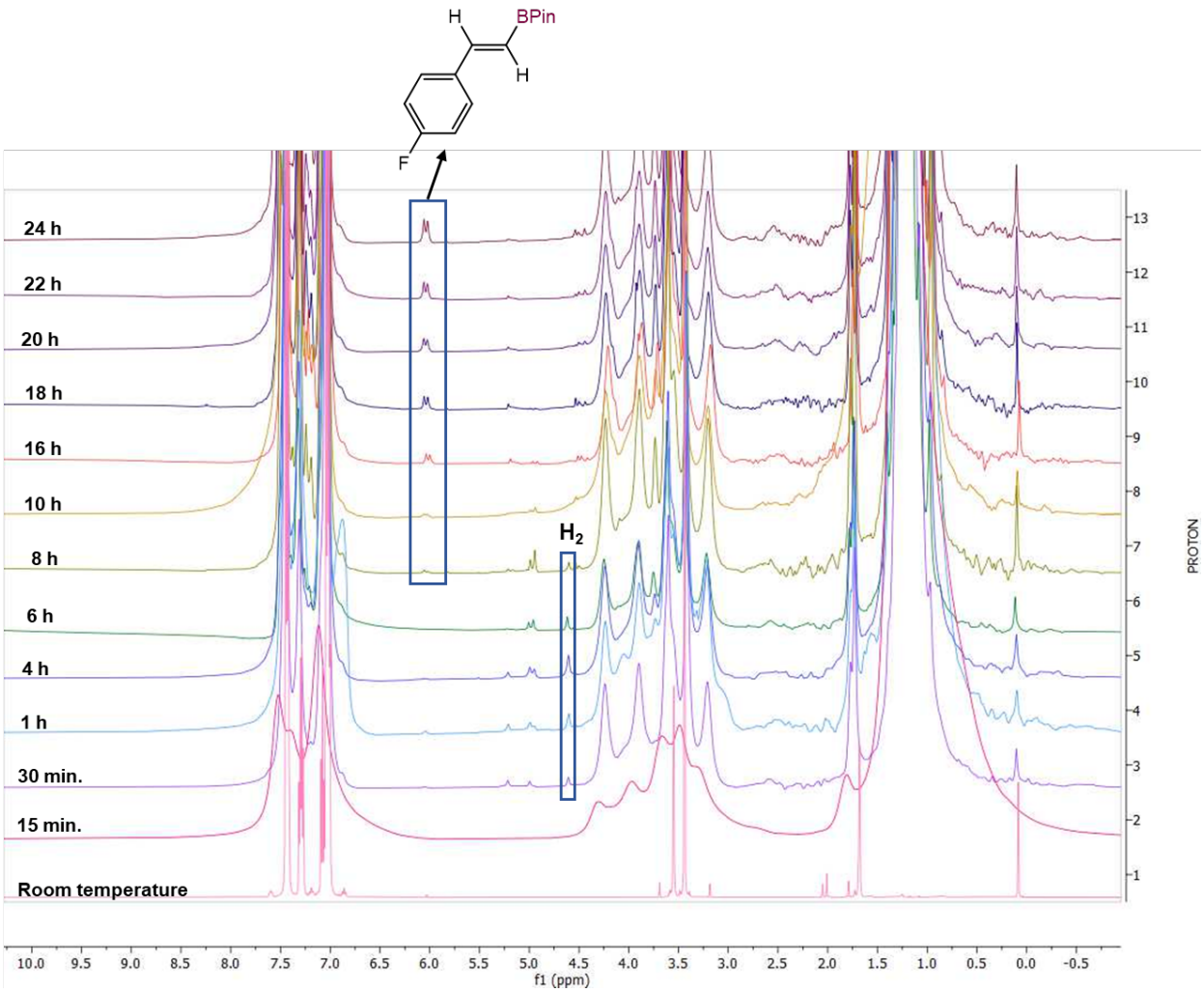
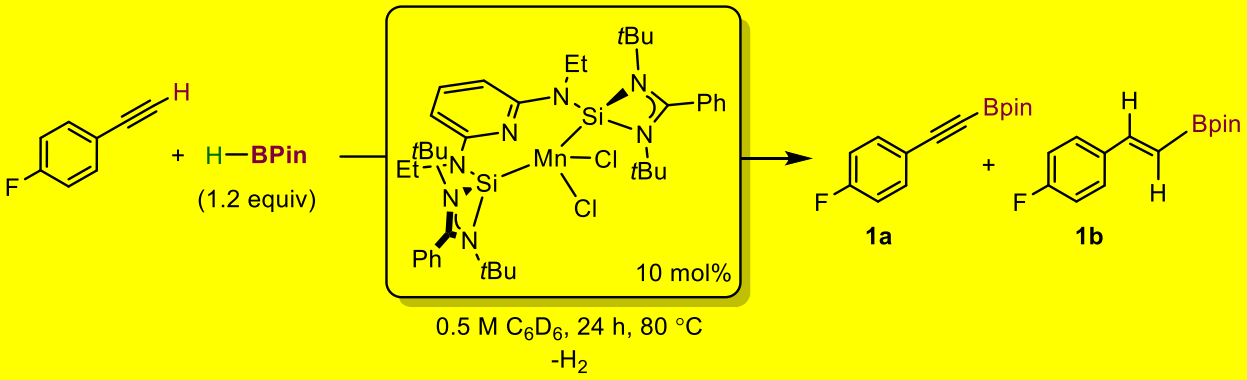


Figure S5: ^{1}H NMR spectra of catalytic reaction in THF-d_8 at 80 ºC, highlighting H_2 and alkene formation.

Note: The peak attributable to H_2 grows in the spectra taken from 30 min to 8 hours, consistent with the formation of H_2 during catalytic turnover. After this time the J. Young NMR tube was kept in the freezer overnight to stop the catalytic reaction due to the inability of monitoring overnight. Therefore, the H_2 already formed was lost and no signal can be attributed to H_2 after this time.



7.2 NMR monitoring of the C-H borylation of 4-fluorophenylacetylene with HBPin at 80 ºC employing 10 mol% of Mn1 as precatalyst in C_6D_6

4-Fluorophenylacetylene (20 µL, 0.174 mmol) was added to a solution of **Mn1** (14 mg, 0.0174 mmol) in C_6D_6 (0.30 mL) followed by the addition of HBPin (30 µL, 0.208 mmol) and fluorobenzene (10 µL, 0.106 mmol) as internal standard in a J. Young NMR tube in an argon filled glovebox. The tube was sealed and brought out of the glovebox. The headspace was evacuated by a freeze-pump-thaw cycle. The reaction was monitored by ^{1}H, ^{11}B and ^{19}F NMR spectroscopy at 80 ºC for 24 hours (see Figures S6, S7 and S8). No signals attributable to diamagnetic manganese species were observed in the NMR spectra, however, signals attributable to the C-H borylation product (**1a**) were identified in the ^{11}B and ^{19}F NMR spectra and their intensity grew over time at the expense of those of the starting material.

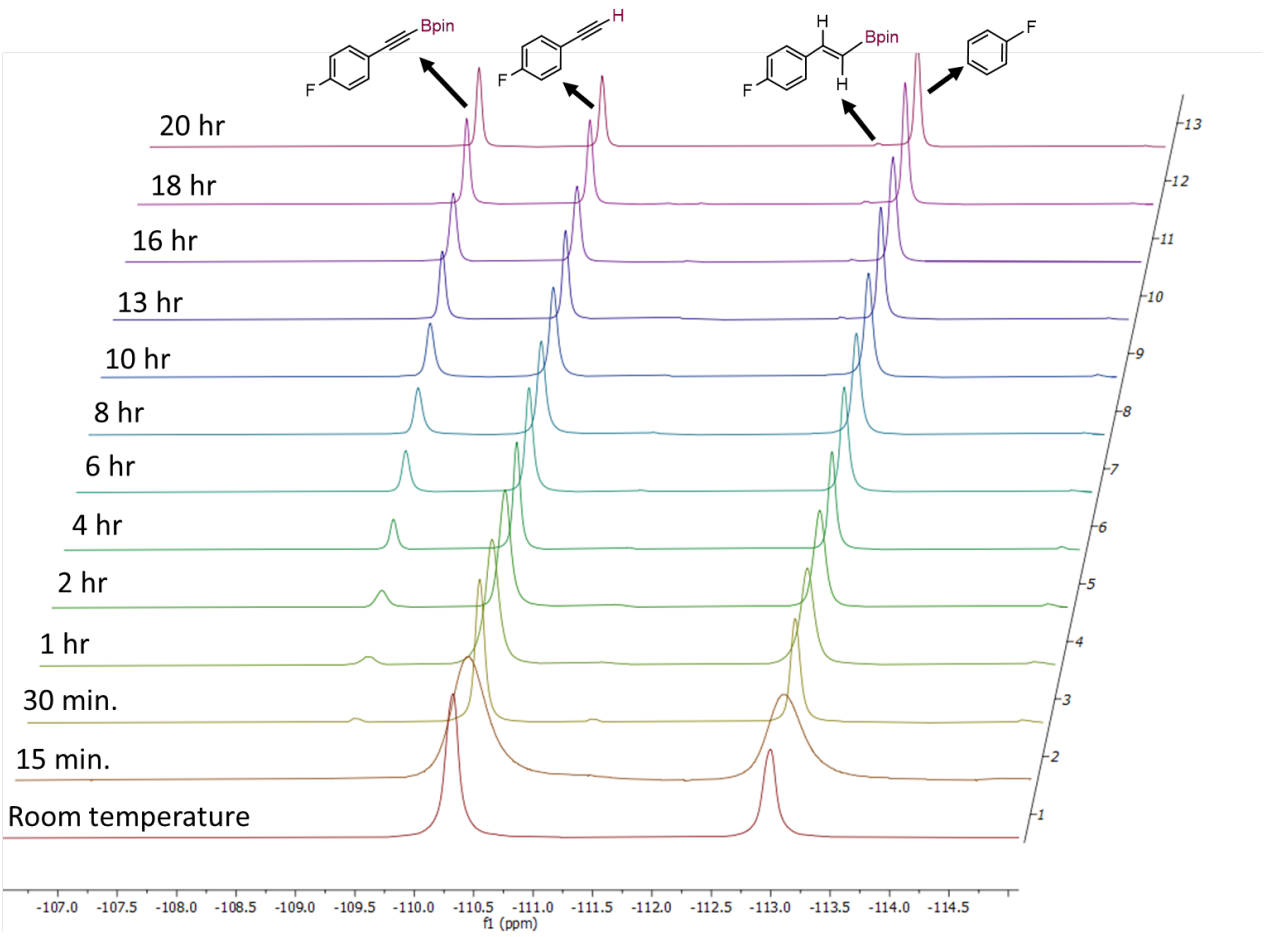


Figure S6: ^{19}F NMR spectra of catalytic reaction in C_6D_6 at 80 ºC.

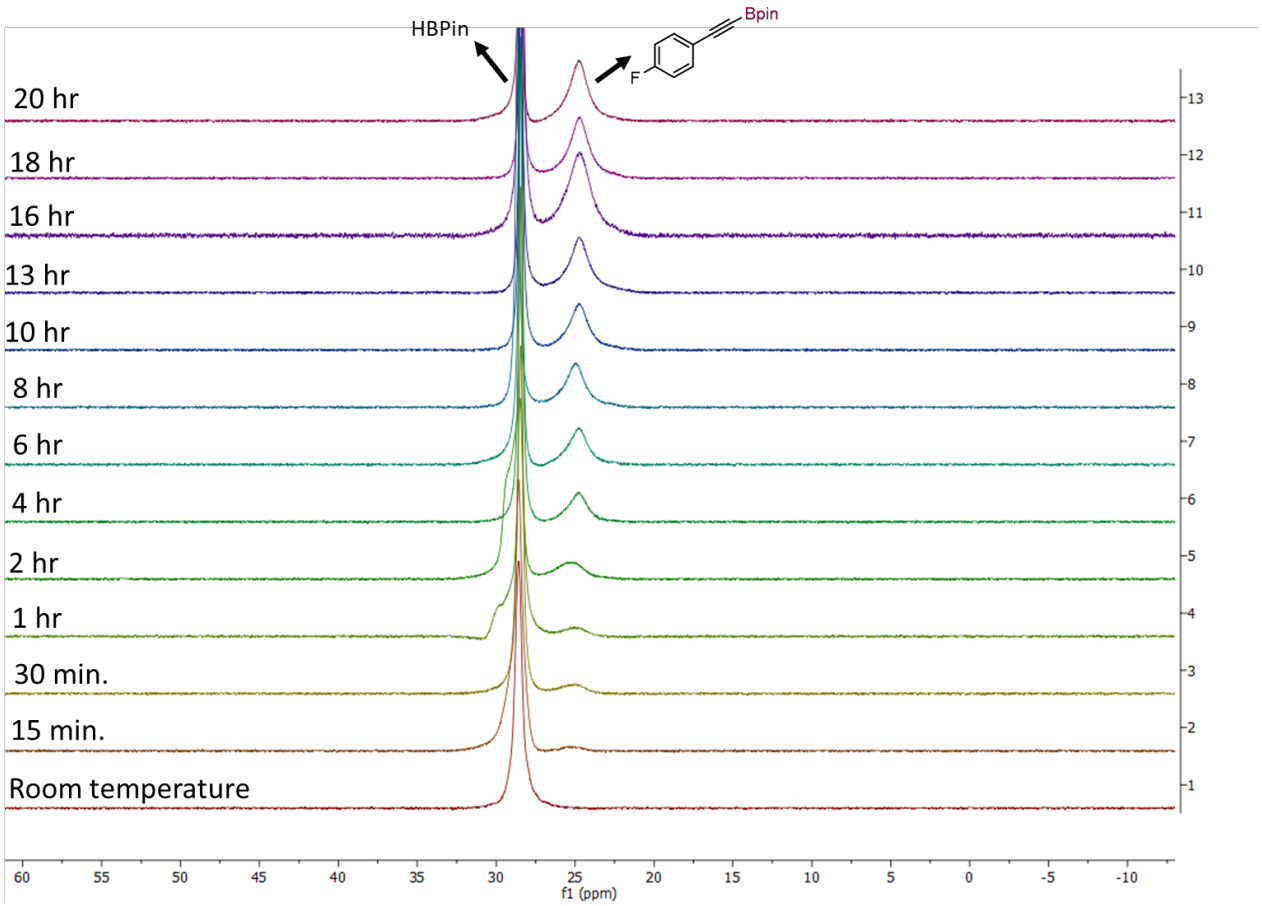


Figure S7: ^{11}B NMR spectra of catalytic reaction in C_6D_6 at 80 ºC.

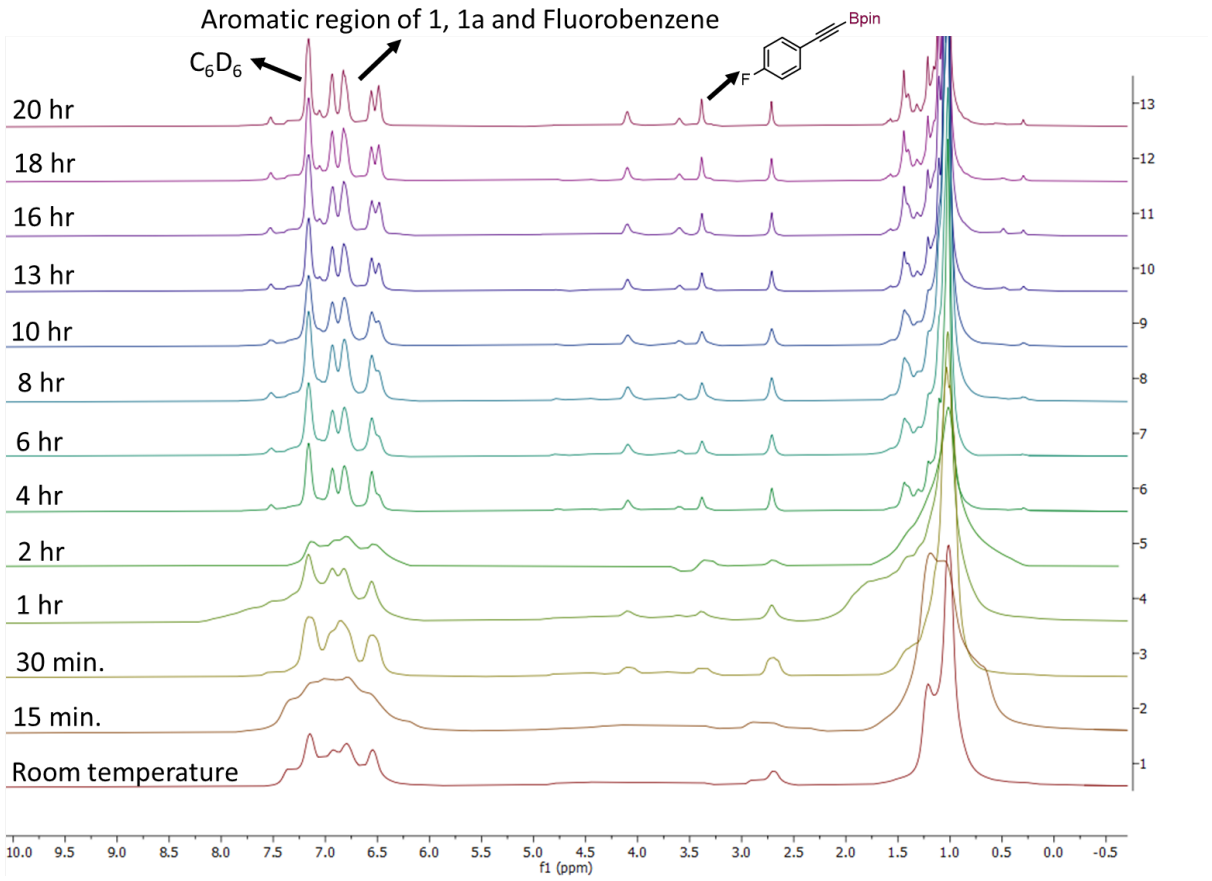


Figure S8: ^{1}H NMR spectra of catalytic reaction in C_6D_6 at 80 ºC.

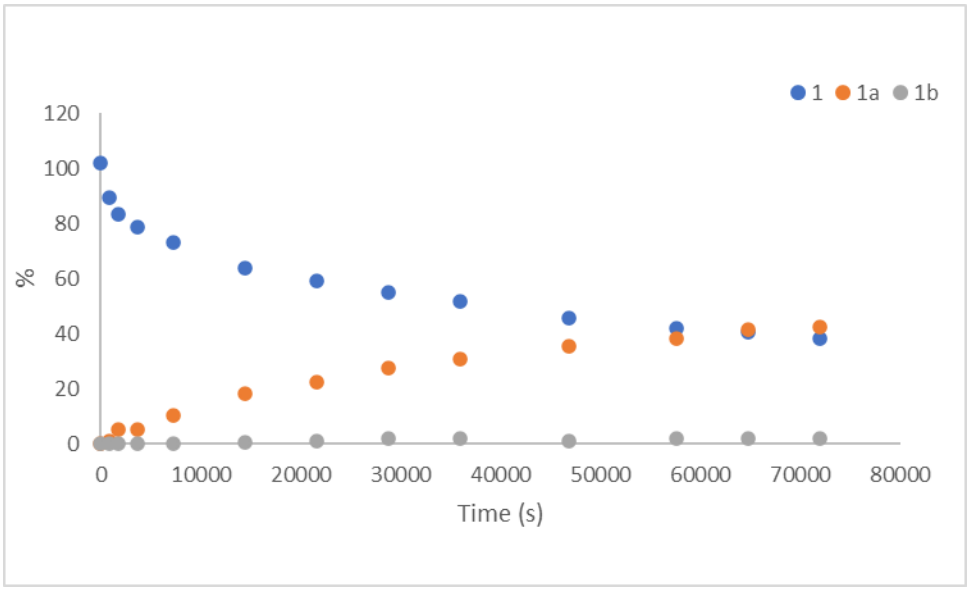
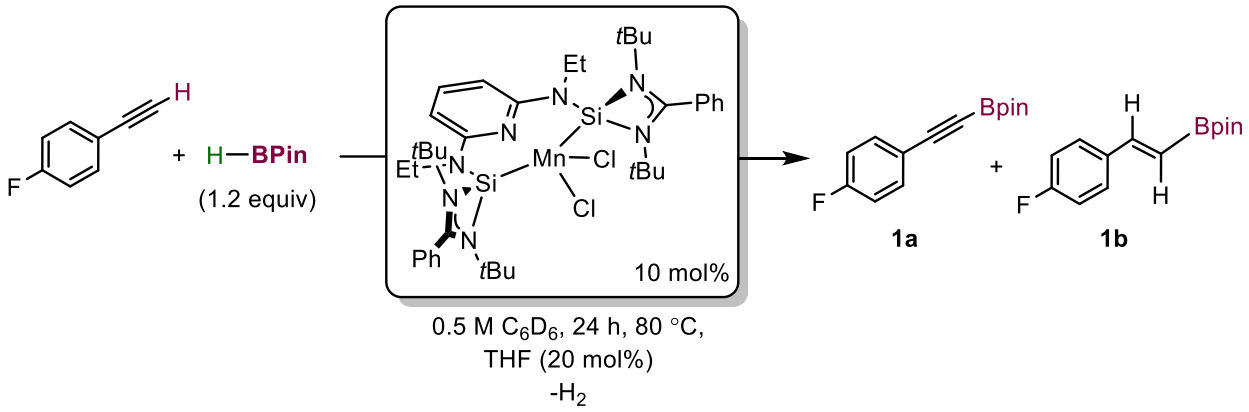


Figure S9: Quantitative reaction profile for the catalytic reaction in C_6D_6 at 80 ºC.



7.3 NMR monitoring of the C-H borylation of 4-fluorophenylacetylene with HBPin at 80 ºC employing 10 mol% of Mn1 as precatalyst in C_6D_6 / 20 mol% of THF

4-Fluorophenylacetylene (20 µL, 0.174 mmol) was added to a solution of **Mn1** (14 mg, 0.0174 mmol) in C_6D_6 (0.30 mL) followed by the addition of HBPin (30 µL, 0.208 mmol), THF (3 µL 0.0348 mmol) and fluorobenzene (10 µL, 0.106 mmol) as internal standard in a J. Young NMR tube in an argon filled glovebox. The tube was sealed and brought out of the glovebox. The headspace was evacuated by a freeze-pump-thaw cycle. The reaction was monitored by ^{1}H, ^{11}B and ^{19}F NMR spectroscopy at 80 ºC for 24 hours (see Figures S10, S11 and S12). No signals attributable to diamagnetic manganese species were observed in the NMR spectra, however, signals attributable to the C-H borylation product (**1a**) were identified in the ^{11}B and ^{19}F NMR spectra and their intensity grew over time at the expense of those of the starting material.

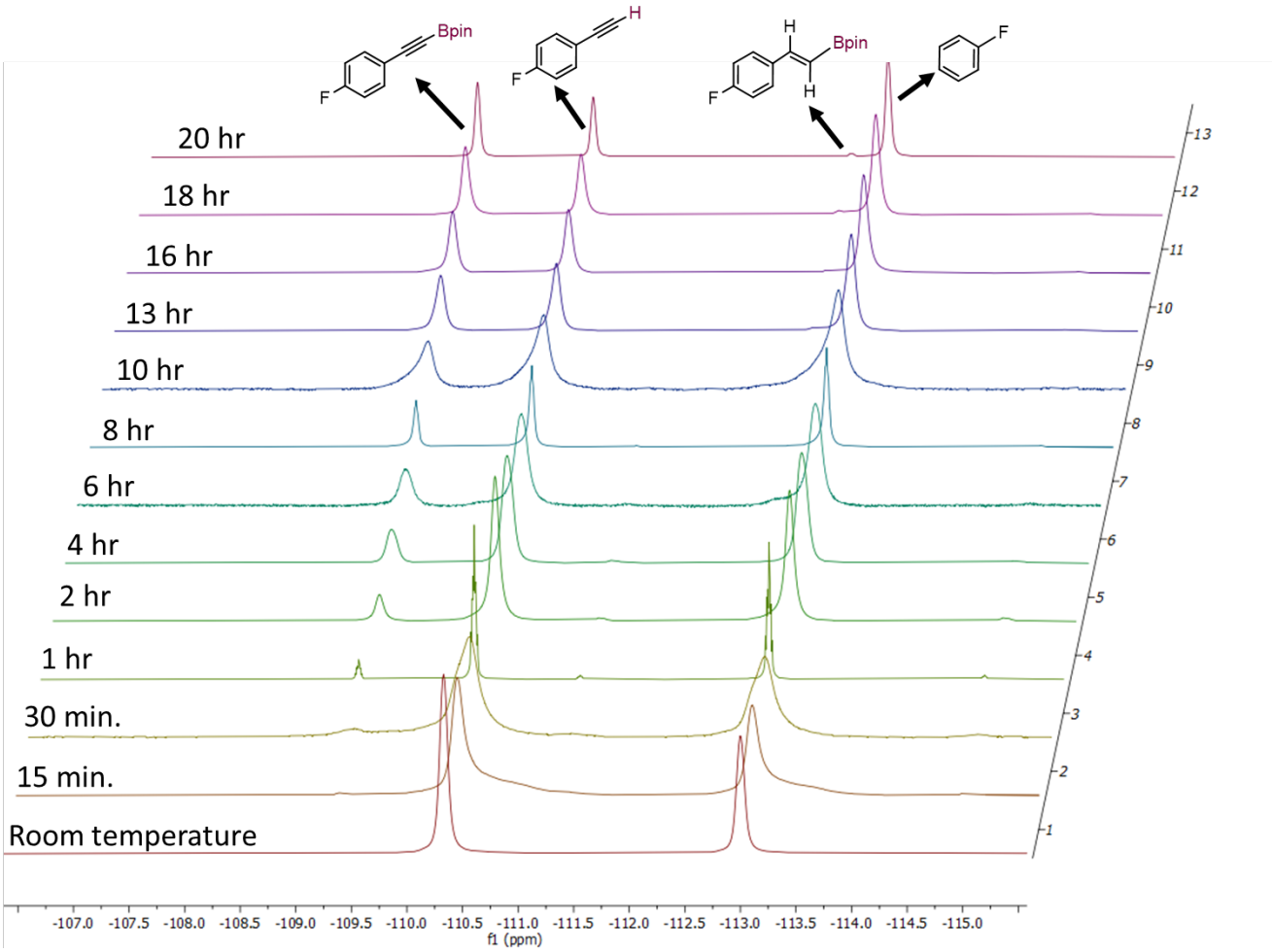


Figure S10: ^{19}F NMR spectra of catalytic reaction in C_6D_6 at 80 ºC.

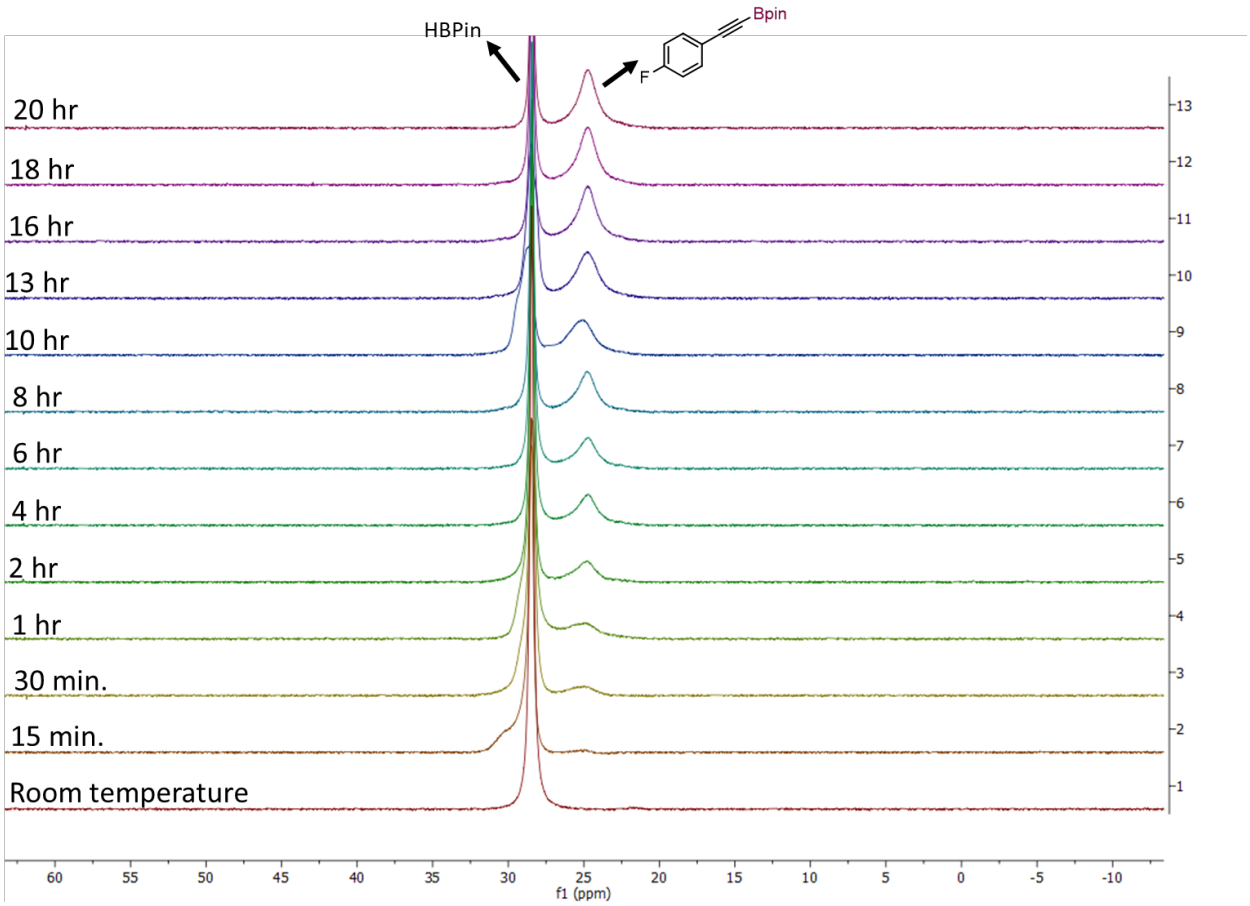


Figure S11: ^{11}B NMR spectra of catalytic reaction in C_6D_6 / 20 mol% of THF at 80 ºC.

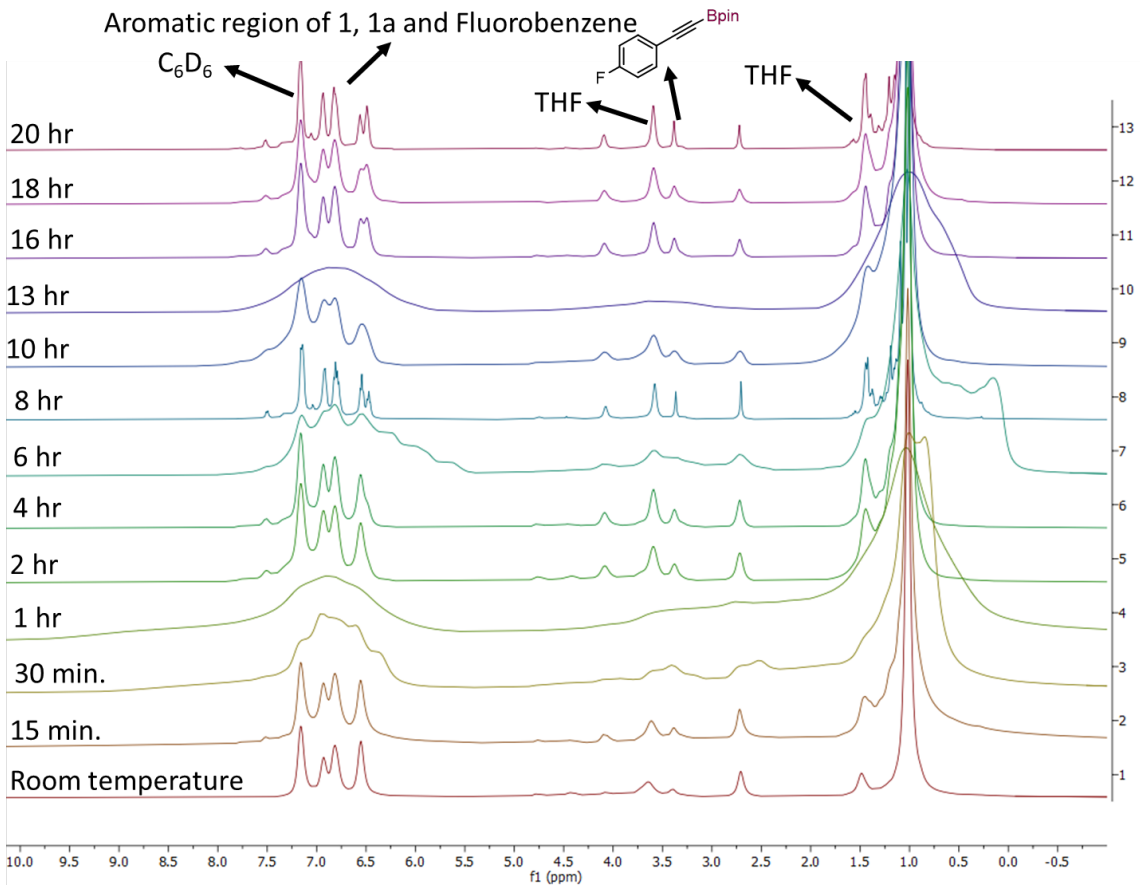


Figure S12: ^{1}H NMR spectra of catalytic reaction in C_6D_6 / 20 mol% of THF at 80 ºC.

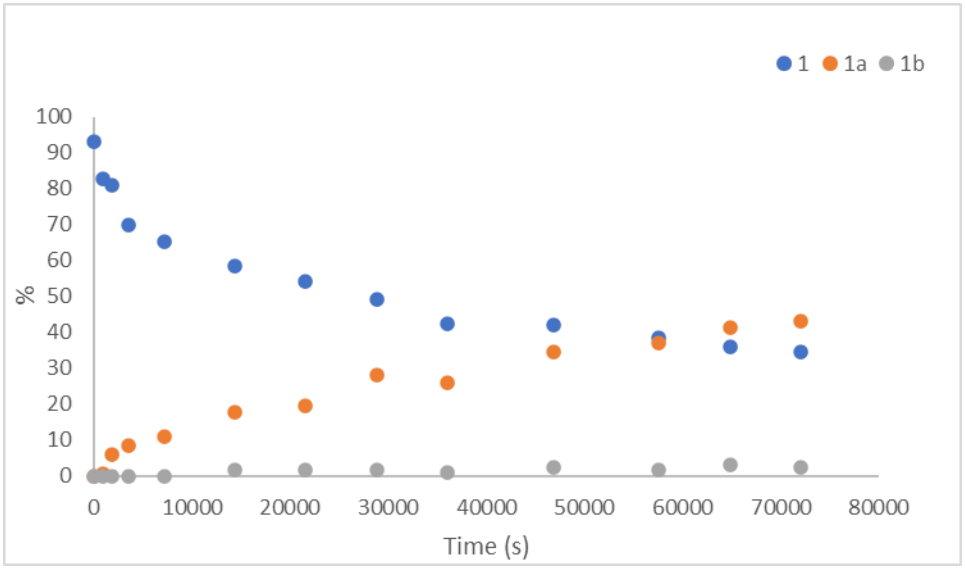
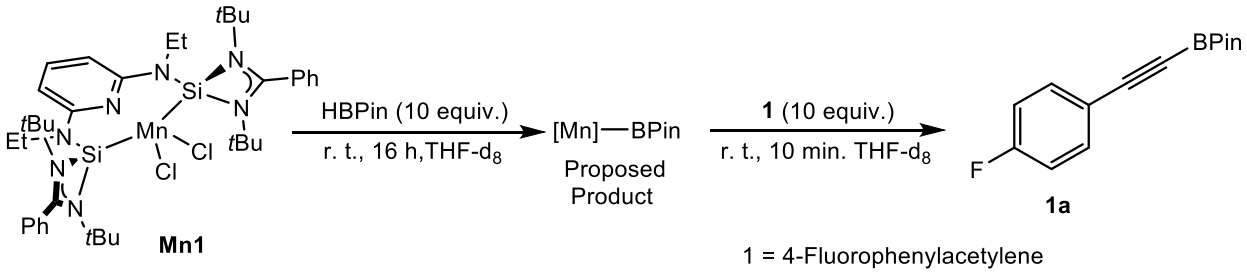


Figure S13: Quantitative reaction profile for the catalytic reaction in C_6D_6 / 20 mol% of THF at 80 ºC.



7.4 NMR monitoring of the reaction of Mn1 with HBPin at room temperature followed by addition of 4-fluorophenylacetylene. HBPin (35 µL, 0.24 mmol) was added to a solution of **Mn1** (20 mg, 0.024 mmol) in THF-d_8 (0.35 mL) in a J. Young NMR tube in an argon filled glovebox. The tube was sealed and brought out of the glovebox. The reaction was monitored by ^{1}H and ^{11}B NMR spectroscopy at room temperature for 16 hours. After this time, the tube was brought into the glovebox, 4-fluorophenylacetylene (27 µL, 0.24 mmol) was added at room temperature and the ^{1}H, ^{11}B and ^{19}F NMR spectra were registered at room temperature after 10 min. The resulting mixture was heated up to 80 ºC for 1.5 hours and the reaction was monitored by ^{1}H, ^{19}F and ^{11}B NMR spectroscopy.

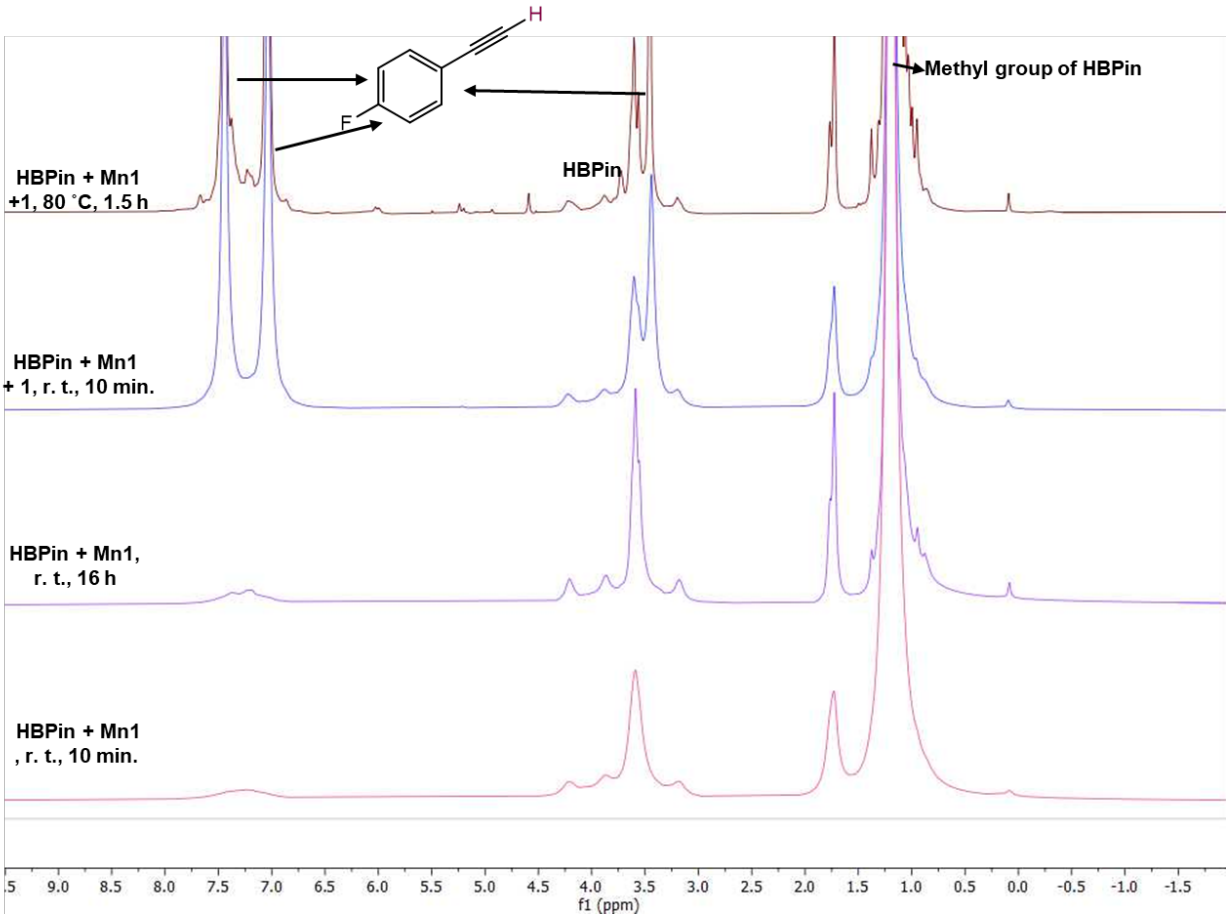


Figure S14: ^{1}H NMR spectra of stoichiometric reaction of **Mn1** with HBPin in THF-d_8 followed by addition of **1**.

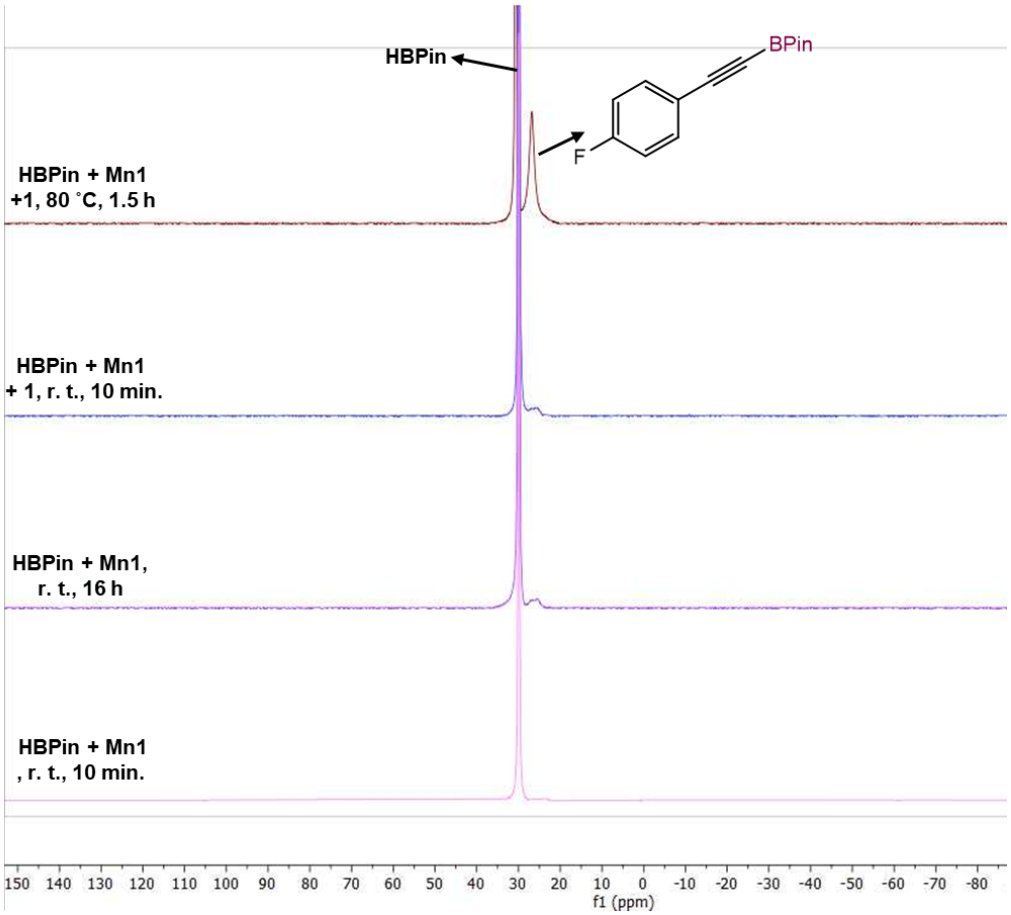


Figure S15: ^{11}B NMR spectra of stoichiometric reaction of **Mn1** with HBPin in THF-d_8, followed by addition of **1**.

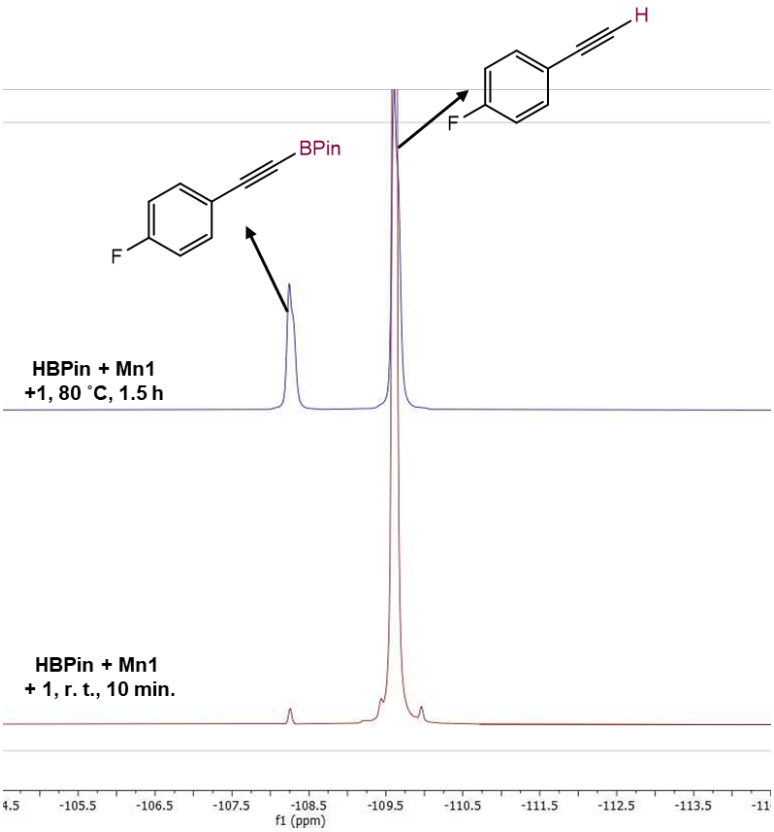
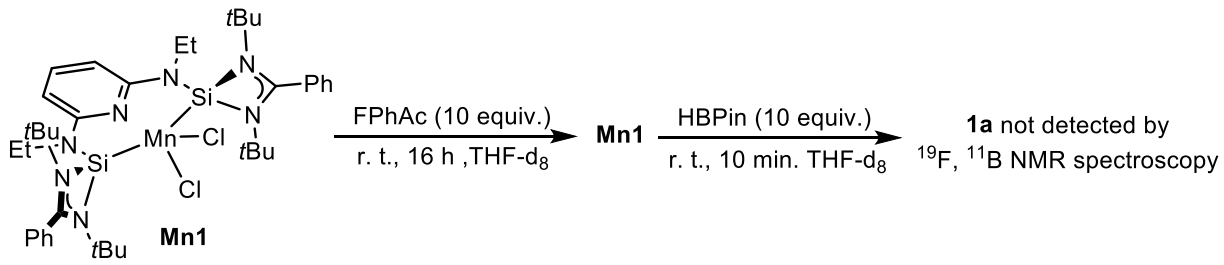


Figure S16: ^{19}F NMR spectra of stoichiometric reaction of Mn1 with HBPin in THF-D_8, followed by addition of of **1**.



FPhAc = 4-Fluorophenylacetylene

7.5 NMR monitoring of the reaction of Mn1 with 4-fluorophenylacetylene at room temperature followed by addition of HBPin. 4-fluorophenylacetylene (27 µL, 0.24 mmol) was added to a solution of **Mn1** (20 mg, 0.024 mmol) in THF-d_8 (0.35 mL) in a J. Young NMR tube in an argon filled glovebox. The tube was sealed and brought out of the glovebox. The reaction was monitored by ^{1}H, ^{11}B and ^{19}F NMR spectroscopy at room temperature for 16 hours. After this time the tube was brought into the glovebox, HBPin (35 µL, 0.24 mmol) was added at room temperature and the ^{1}H, ^{11}B and ^{19}F NMR spectra were registered at room temperature. The

resulting mixture was heated up to 80 ºC for 1.5 hours and the reaction was monitored by ^{1}H, ^{19}F and ^{11}B NMR spectroscopy.

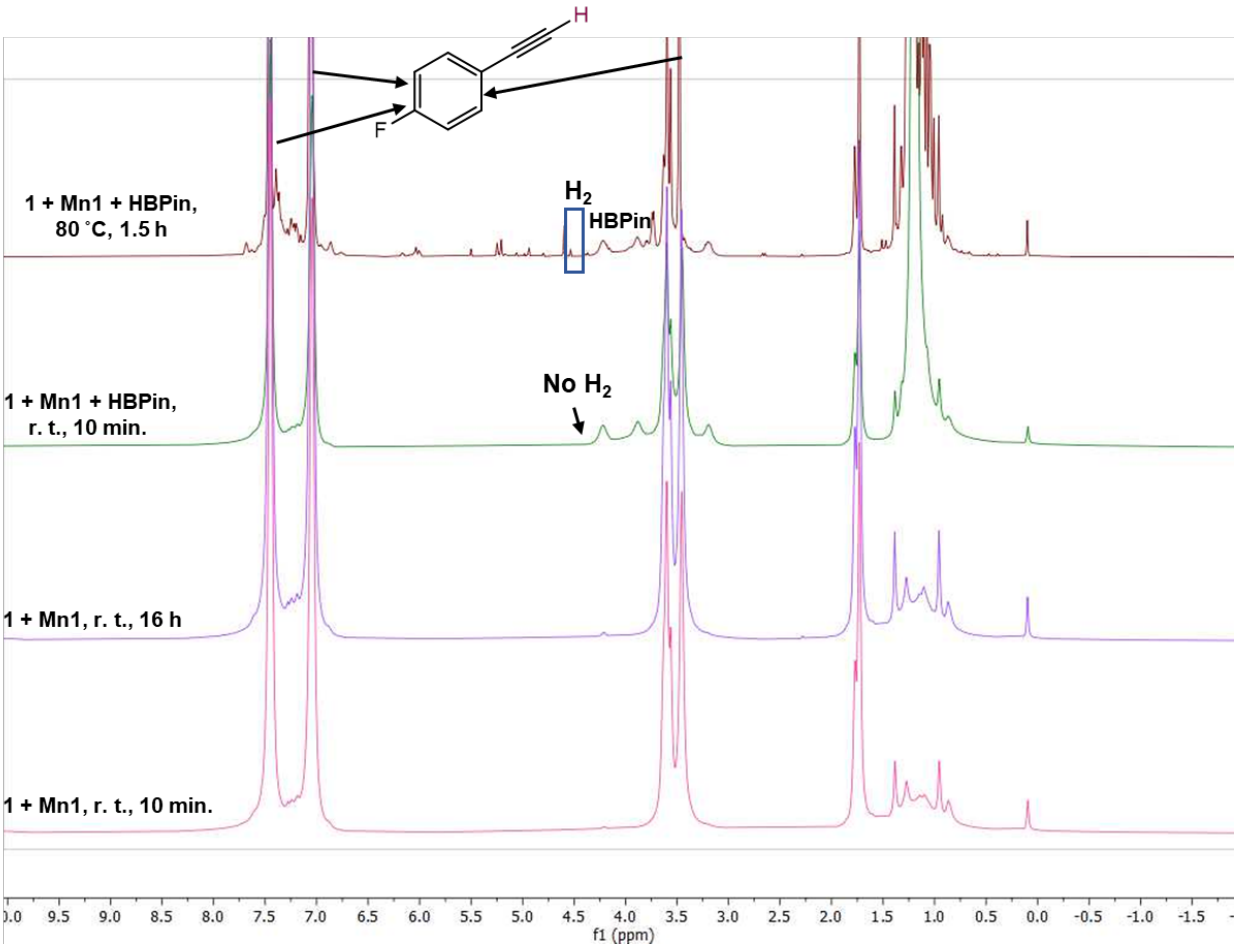


Figure S17: ^{1}H NMR spectra of stoichiometric reaction of Mn1with 4-fluorophenylacetylene in THF-d_8, followed by addition of HBPin.

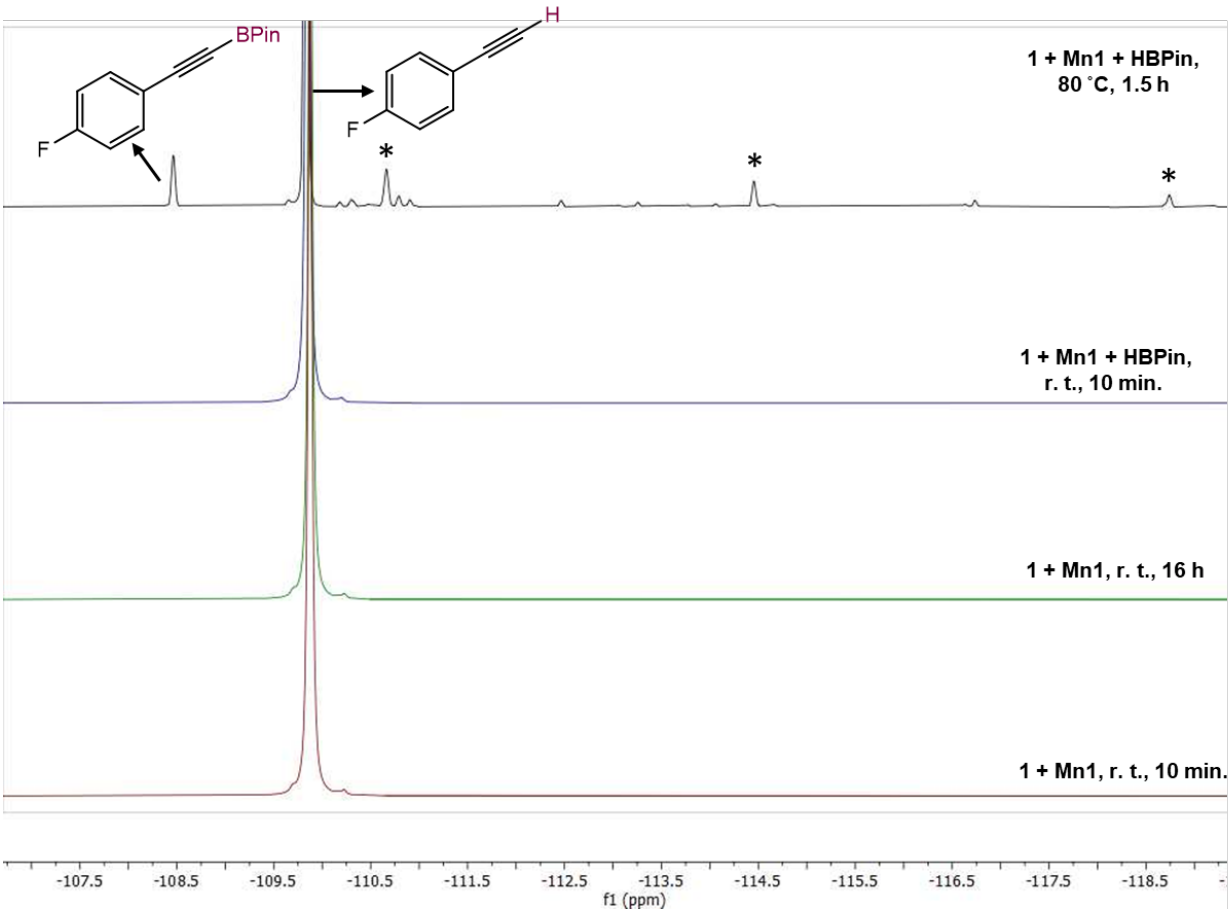


Figure S18: ^{19}F NMR spectra of stoichiometric reaction of Mn1with 4-fluorophenylacetylene in THF-d_8, followed by addition of HBPin. (* = unidentified products)

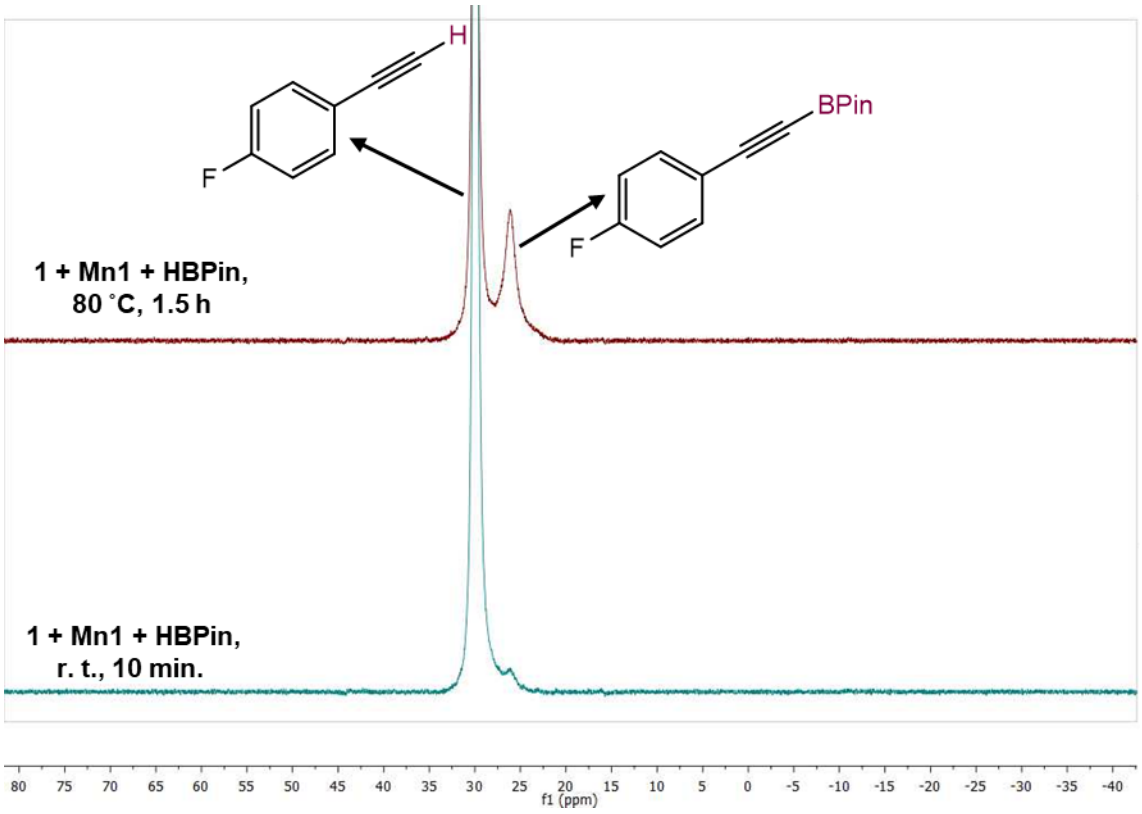


Figure S19: ^{11}B NMR spectra of stoichiometric reaction of Mn1 with 4-fluorophenylacetylene in THF-d_8, followed by addition of HBPin.

8. Stoichiometric Reactions of Mn1.

8.1 Reaction of Mn1 with HBPin to yield Mn5.

In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar, **Mn1** (70 mg, 0.087 mmol), THF (2.5 mL) and HBPin (125 µL, 0.87 mmol). The reaction mixture was stirred for 16 h at room temperature. After the completion of the reaction, the reaction mixture was passed through a plug of Whatman filter paper in a Pasteur pipette and solvent was removed under vacuo to obtain orange oil. The product was extracted in hexane and solvent was removed under vacuum to obtain orange oil which was then analyzed by IR spectroscopy.

IR spectra of the stoichiometric reaction of Mn1 and HBPin:

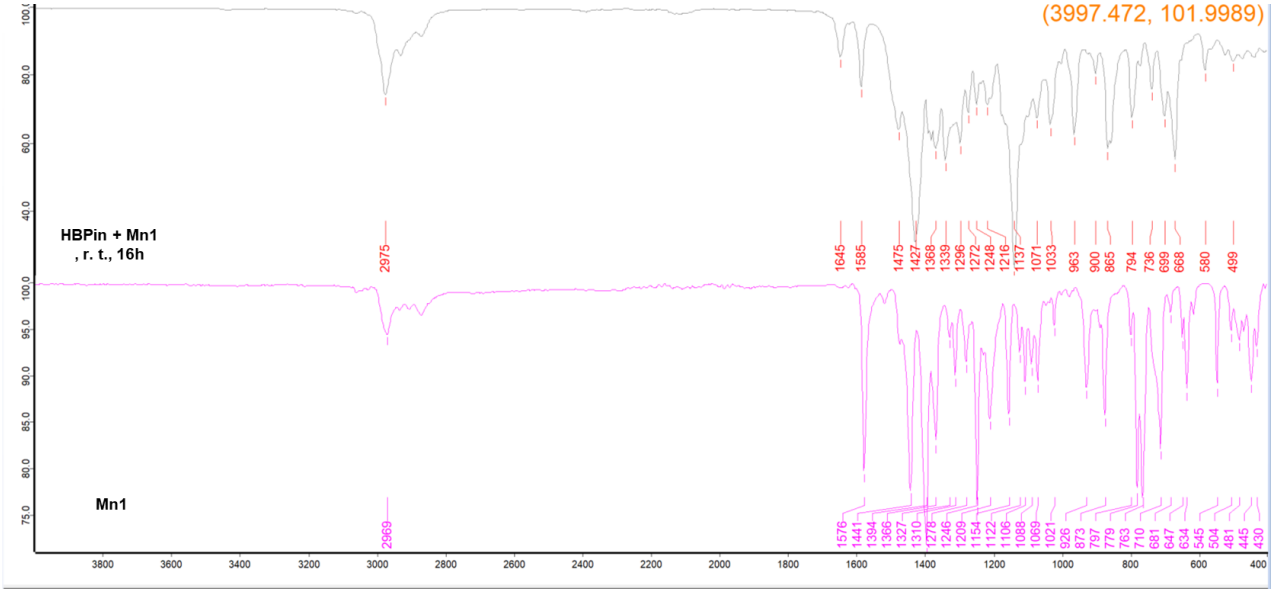


Figure S20: Stacked IR spectra of isolated product (top) and **Mn1**(bottom) and obtained from reaction 8.1.

IR of Reaction 8.1 (isolated product): 499(w), 580(w), 668(m), 699(w), 736(w), 794(w), 865(m), 900(w), 963(m), 1033(w), 1071(w), 1137(s), 1216(w), 1248(w), 1272(w), 1296(m), 1339(m), 1368(m), 1427(s), 1475(w), 1585(w), 1645(w), 2975(w).

IR of **Mn1**: 430(w), 445(m), 481(w), 504(w), 545(m), 634(m), 647(w), 681(s), 710(s), 763(s), 779(w), 797(m), 873(m), 926(m), 1021(w), 1069(w), 1088(w), 1106(w), 1122(w), 1154(m), 1209(m), 1246(s), 1278(w), 1310(w), 1327(w), 1366(m), 1394(s), 1441(s), 1576(s), 2969(w).

The spectroscopic data matched that of previously reported.[4]

8.2 NMR monitoring of the reaction of Mn1 with HBPin at room temperature for detecting formation of ClBPin:

In an argon-filled glovebox, a scintillation vial was charged with a solution of Mn1 (20 mg, 0.025 mmol) in 0.35ml THF-d_8. To this solution HBPin (7.25 µL, 0.05 mmol) was added and the contents were stirred until a clear solution was formed and then transferred to a J. Young NMR tube. The reaction was monitored by ^{1}H, ^{11}B and ^{13}C NMR spectroscopy at room temperature for 48 hours.

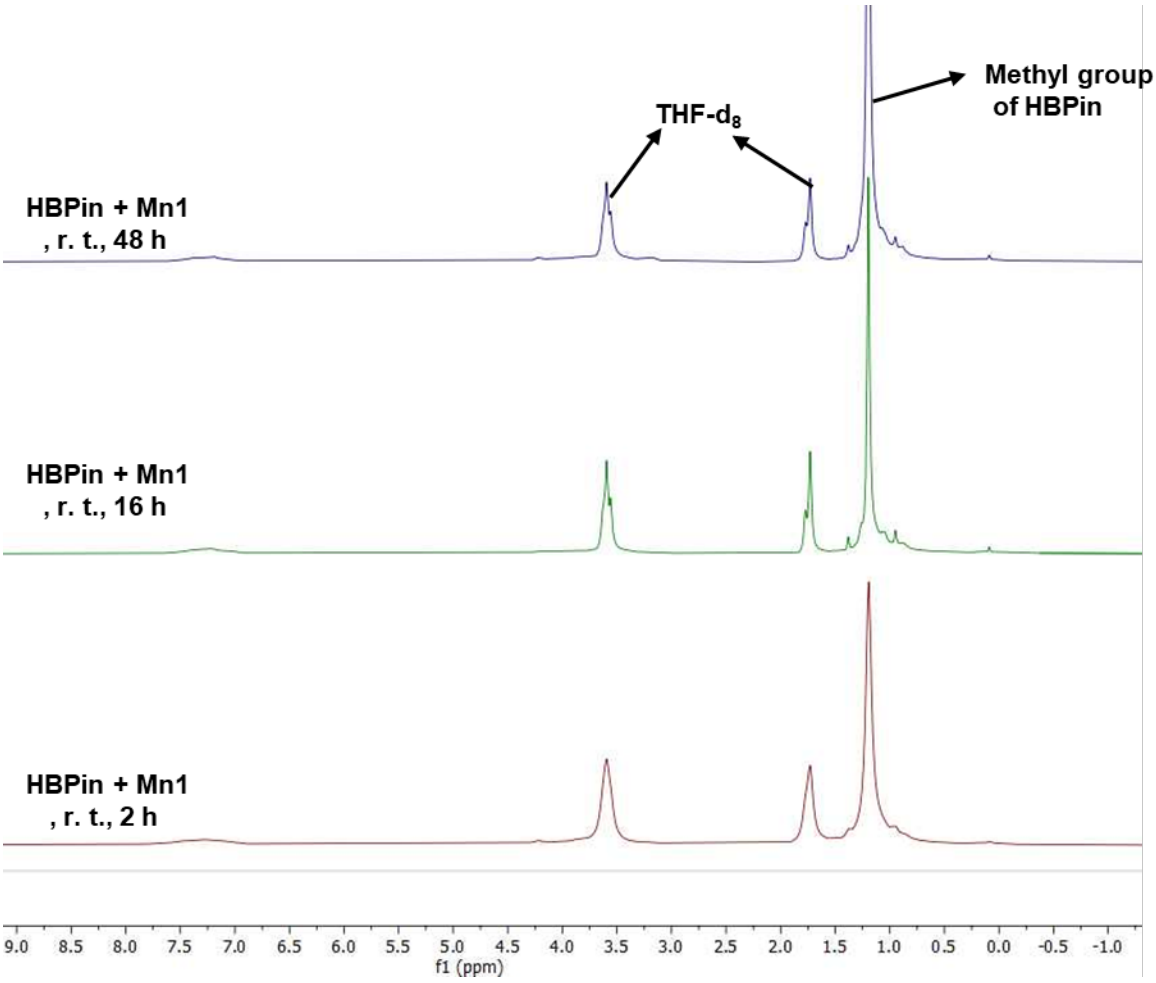


Figure S21: ^{1}H NMR spectra of reaction of **Mn1** with HBPin in THF-d_8.

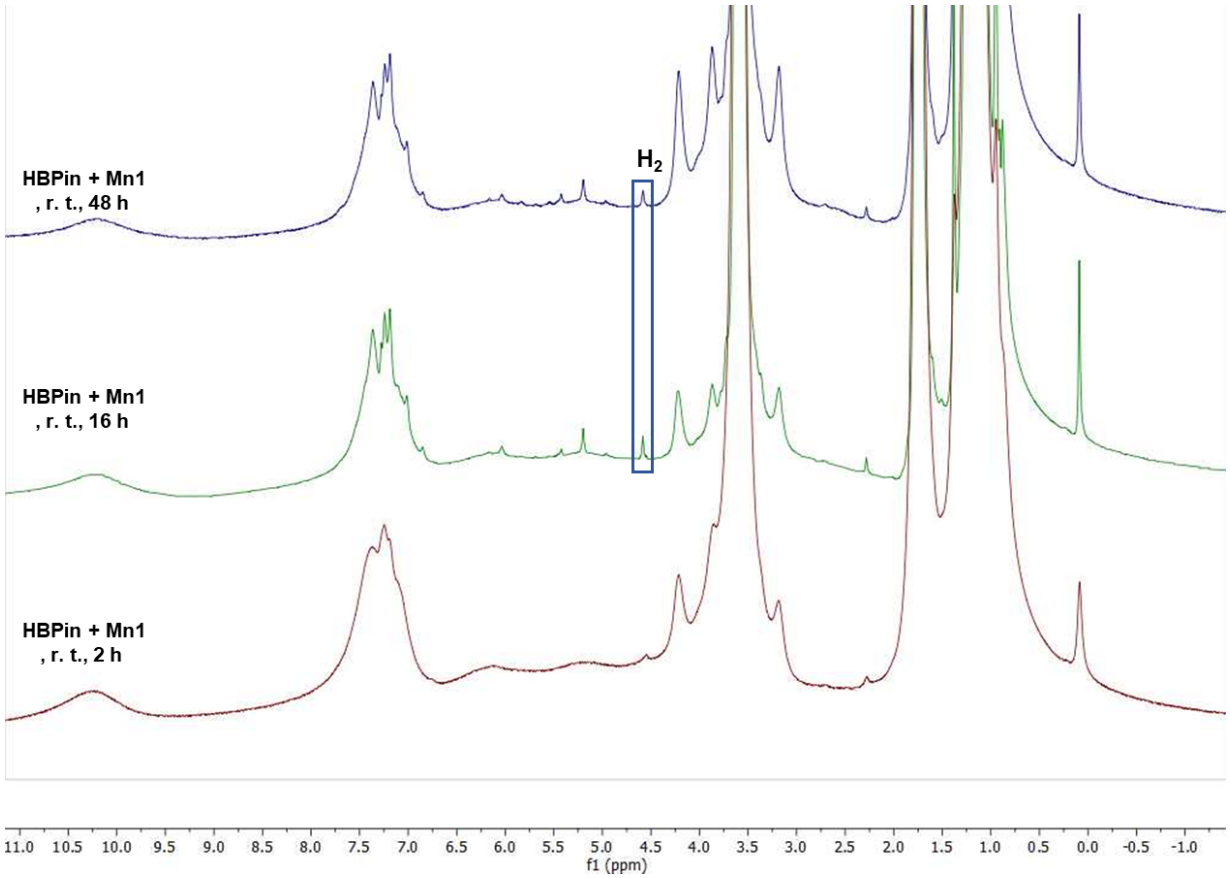


Figure S22: ^{1}H NMR spectra of reaction of **Mn1** with HBPin in THF-d_8, highlighting the formation of H_2. H_2 is formed due to formation of B_2Pin_2 from HBPin, in the presence of **Mn1** (also confirmed from GC).

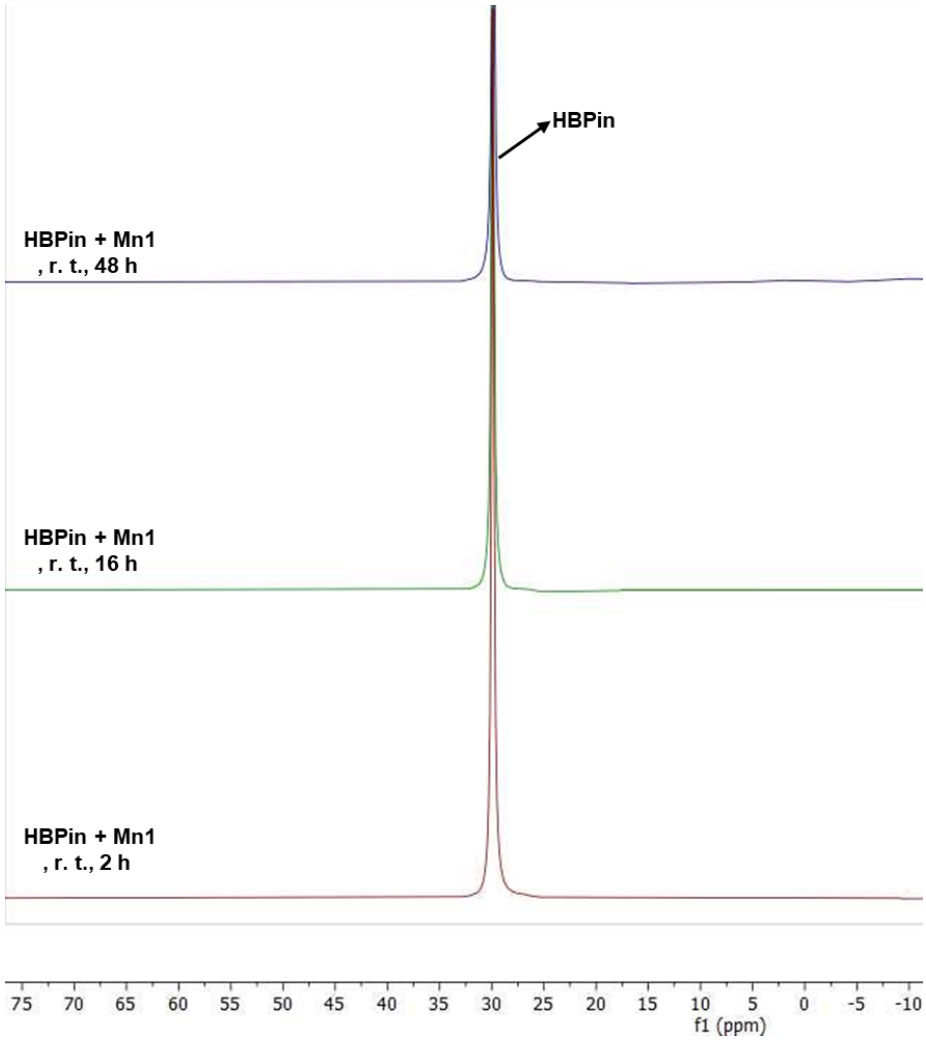


Figure S23: ^{11}B NMR spectra of reaction of **Mn1** with HBPin in THF-d_8.

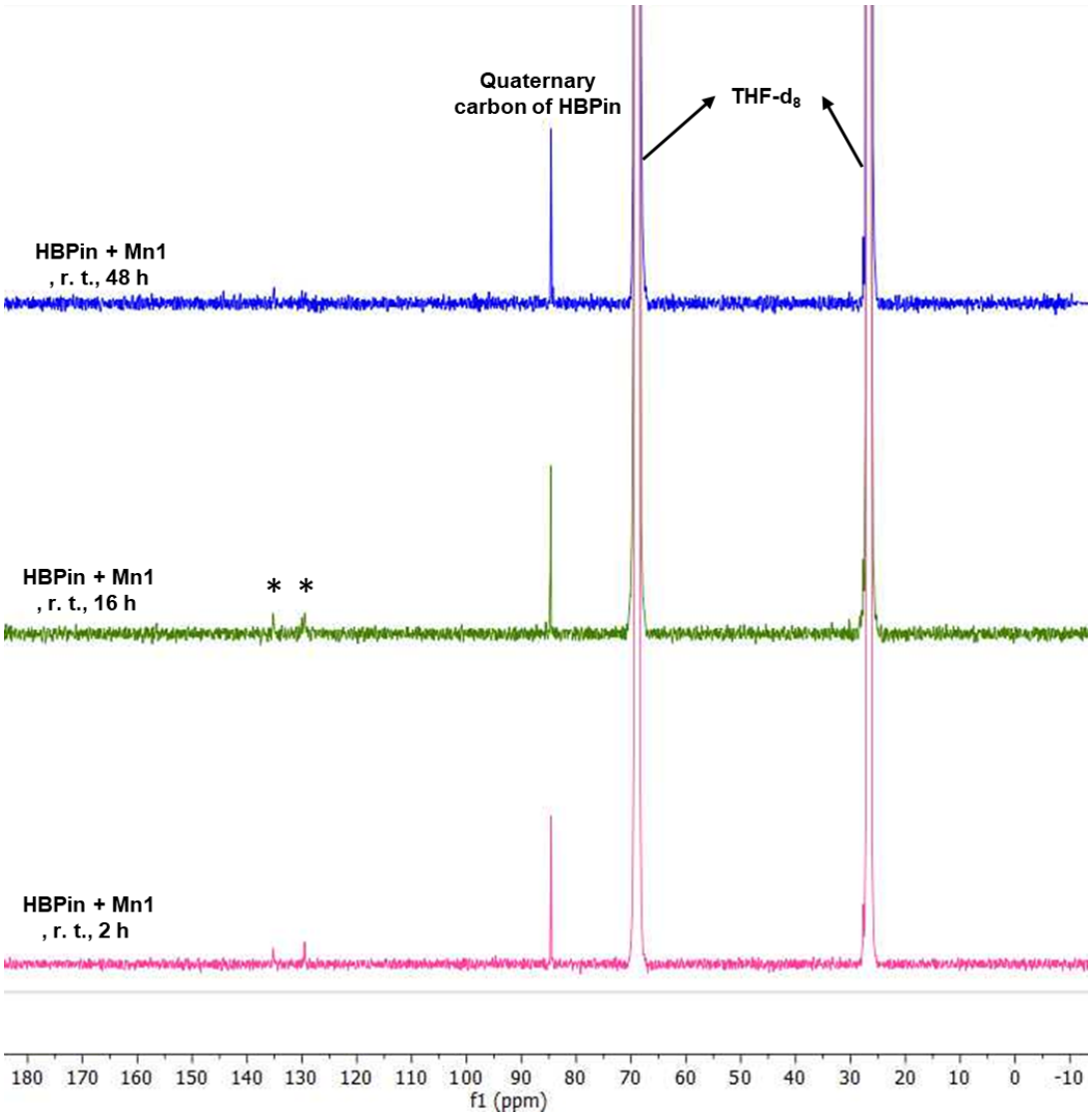


Figure S24: ^{13}C NMR spectra of reaction of **Mn1** with HBPin in THF-d_8. (* = unidentified products).

Note: No formation of ClBPin was detected.

8.3 Reaction of Mn5 with CCl_4. In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar, crude **Mn5** (obtained starting from 100 mg, 0.123 mmol of **Mn1** and 18 µL, 0.12 mmol of HBPin), THF (1.0 mL) and CCl_4 (20 µL, 0.206 mmol). The tube was sealed, and the resulting mixture was stirred at r.t. for 30 minutes. The resulting solution was exposed to air, passed through a plug of Celite in a Pasteur pipette and analyzed by ^1H NMR spectroscopy.

8.4 Reaction of Mn1 with 1 at room temperature. In an argon filled glove box, a 20 mL scintillation vial was charged with a magnetic stir bar, **Mn1** (50 mg, 0.062 mmol), THF (1.5 mL)

and 4-fluorophenylacetylene (71 µL, 0.62 mmol). The reaction mixture was stirred for 16 hours at room temperature. After the completion of the reaction, the reaction mixture was passed through a plug of Whatman filter paper in a Pasteur pipette, layered with hexane and kept in the freezer. After 4 days, the precipitated yellow solid from the reaction was separated.

IR spectra of the stoichiometric reaction 8.4 and comparison to Mn1.

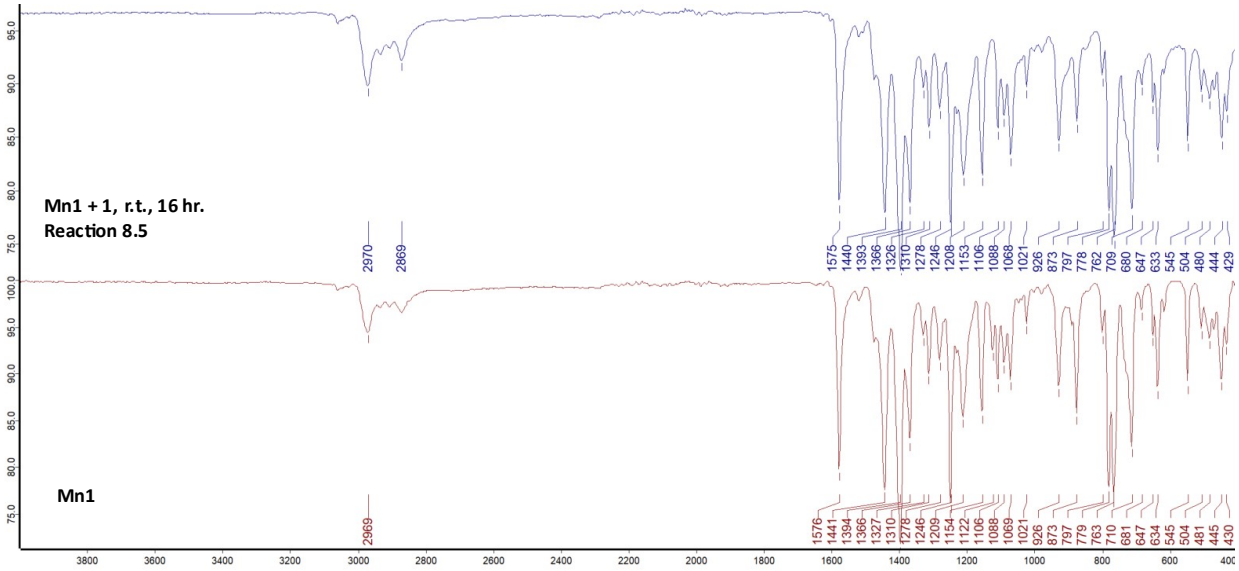


Figure S25: Stacked IR spectra of **Mn1** and isolated solid (bottom) from reaction 8.4 (top).

IR of **Mn1**: 430(w), 445(m), 481(w), 504(w), 545(m),634(m), 647(w), 681(m), 710(s), 763(s), 779(s), 797(w), 873(m), 926(m), 1021(w), 1069(m), 1088(m), 1106(m), 1122(w), 1154(m), 1209(m), 1246(s), 1278(w), 1310(m), 1327(m), 1366(m), 1394(s), 1441(s), 1576(s), 2869(w), 2969(m).

The spectroscopic data matched that previously reported.[4]

IR of Reaction 8.4 (isolated solid): 429(w), 444(m), 480(w), 504(w), 545(m), 633(m), 647(w), 680(w), 709(s), 762(s), 778(s), 797(w), 873(m), 926(m), 1021(w), 1068(m), 1088(m), 1106(m), 1153(m), 1208(m), 1246(s), 1278(m), 1310(m), 1326(w), 1366(s), 1393(s), 1440(s), 1575(s), 2869(w), 2970(m).

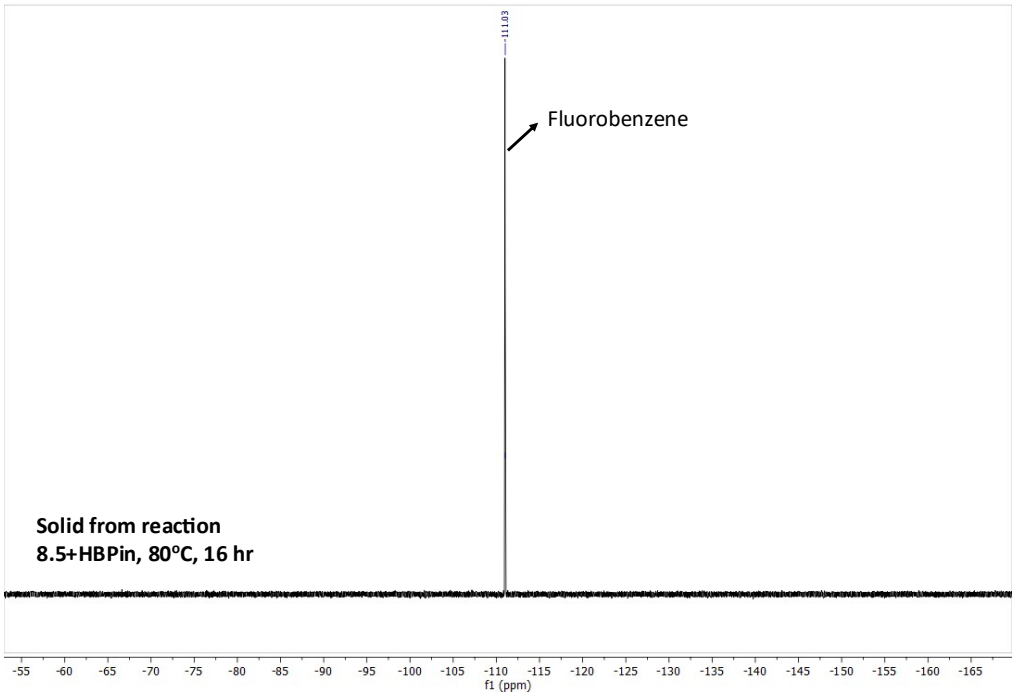
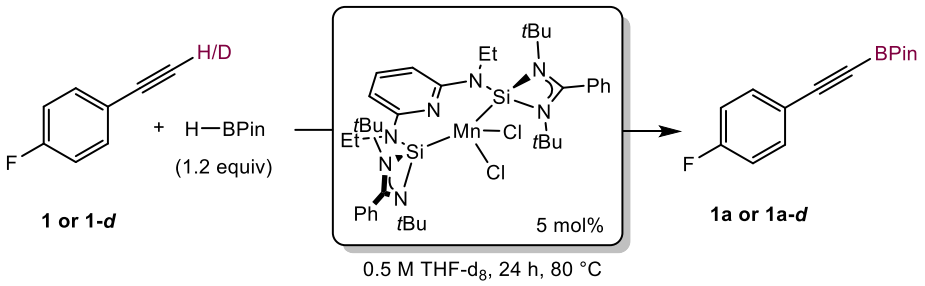


Figure S26: ^{19}F NMR spectrum of solid from reaction 8.4 with HBPin

Peak at -111.03 ppm corresponds to internal standard (fluorobenzene).

9. Kinetic Isotope Effect (KIE) determination



KIE Determination for the C-H borylation of 4-fluorophenylacetylene and 4-fluorophenylacetylene-*d* using Mn1 as the Catalyst (2 Separate Vessels)

In an argon-filled glovebox, a scintillation vial was charged with a solution of **Mn1** (7 mg, 0.008 mmol) in 0.35 mL THF-d_8. To this solution, 4-fluorophenylacetylene (20 µL, 0.174 mmol), fluorobenzene (10 µL, 0.106 mmol) as the internal standard and HBPin (30 µL, 0.208 mmol) were added in the same order. The contents were stirred until a clear solution was formed and then transferred to a J. Young NMR tube. The tube was sealed and brought out of the glovebox. The headspace was evacuated by a freeze-pump-thaw cycle. A separate scintillation vial was charged with a solution of **Mn1** (7.03 mg, 0.008 mmol) in 0.35ml THF-d_8. To this solution, 4-

fluorophenylacetylene-*d* (19.1 µL, 0.174 mmol), fluorobenzene (10 µL, 0.106 mmol) as the internal standard and HBPin (30 µL, 0.208 mmol) were added in the same order. The contents were stirred until a clear solution was formed and then transferred to a J. Young NMR tube. The tube was sealed and brought out of the glovebox. The headspace was evacuated by a freeze-pump-thaw cycle. The reactions were monitored by ^{19}F NMR spectroscopy at 80 ºC. Integration of the signal for the internal standard, the starting material, and the product by ^{19}F NMR spectroscopy afforded the quantitative data reported in Table S3. The KIE was determined using the initial rates method (up to 10% yield). The rates of the reactions, $rate_H$ and $rate_D$, correspond to the rates of formation of product **1a** (2-((4-Fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) using 4-fluorophenylacetylene and 4-fluorophenylacetylene-*d* as substrates respectively. The overall KIE was calculated by taking the average of the ratios of $rate_H$ and $rate_D$ for all the three runs (Table S3).

Run	$Rate_H$ (Ms^{-1})	$Rate_D$ (Ms^{-1})	KIE (K_H/K_D)
1	8×10^{-9}	7×10^{-9}	1.14
2	7×10^{-9}	6×10^{-9}	1.16
3	8×10^{-9}	7×10^{-9}	1.14
KIE = 1.15			

Table S4. KIE values for the C-H activation of 4-fluorophenylacetylene and 4-fluorophenylacetylene-*d* using HBPin, catalyzed by **Mn1** in THF-d_8 at 80 °C, using fluorobenzene as internal standard.

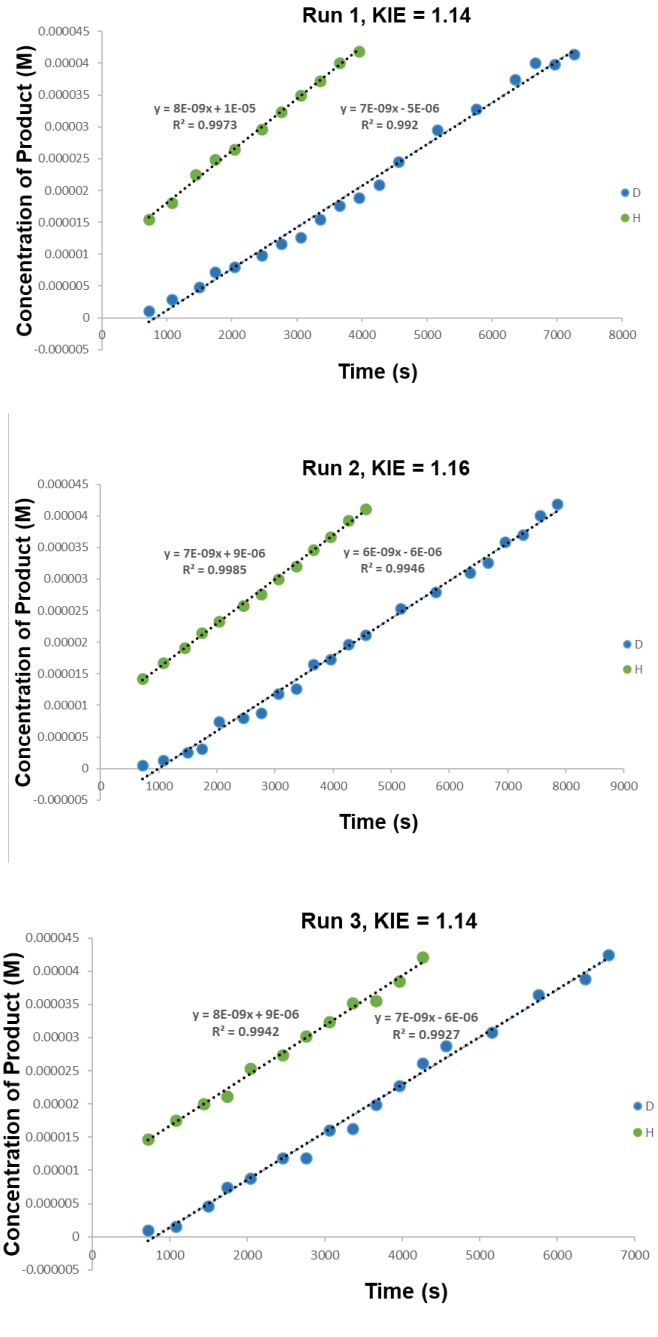
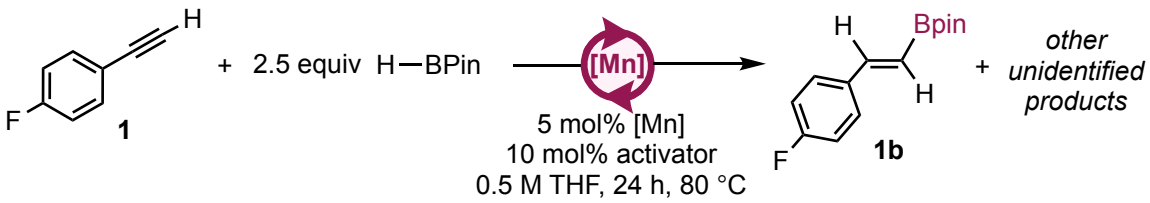


Figure S27: Plots of concentration of 2-((4-Fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (M) vs. time (s) using 4-fluorophenylacetylene and 4-fluorophenylacetylene-*d* as substrates for runs 1-3 using **Mn1** as the precatalyst.

10. Reaction of 1 with HBPin employing different Mn active species as catalysts

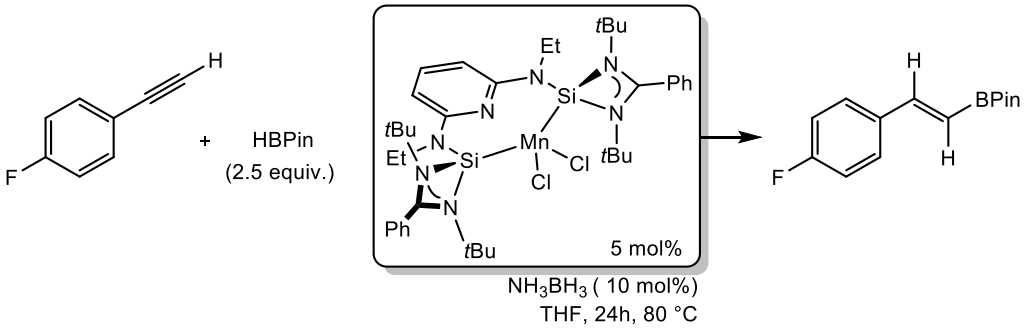


Entry	[Mn]	Activator (10 mol%)	Conversion (%)	Yield 1b (%)
1	**Mn1**	NH_3BH_3	>99	8
2	**Mn1**	NH_3BH_3 (Preactivation)	>99	50
3	**Mn1**	KO*t*Bu	>99	9
4	**Mn1**	$NaHBEt_3$	>99	N. D.
5	**Mn1**	$NaHBEt_3$ (Preactivation)	>99	N. D.
6	[Mn(SiNSi)(dmpe)]	None	>99	17

Table S5. Conversion and yields for the reaction of **1** with HBPin catalyzed by different Mn active species.

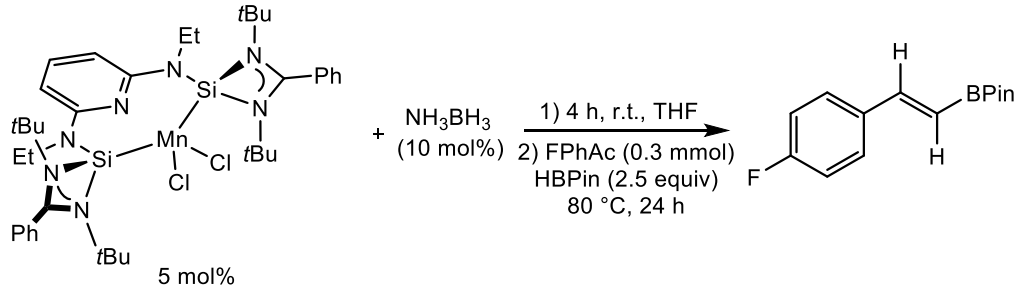
*Note: In none of the reactions the alkynylboronate ester **1a** was detected by ^{19}F NMR spectroscopy. Other unidentified products were formed and account for the observed 99% conversion of the starting material. N. D. = Not detected.*

10.1 Reaction of 1 with HBPin employing Mn1 *in-situ* activated with NH_3BH_3



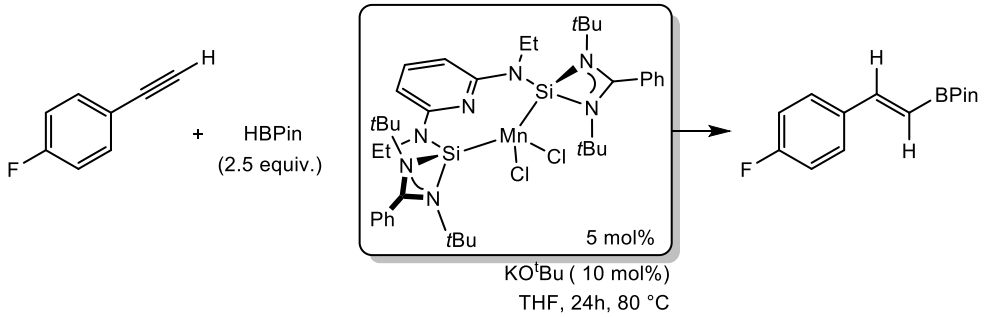
In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order- **Mn1** (12 mg, 0.015 mmol), THF (0.46 mL), 4-Fluorophenylacetylene (34 µL, 0.3 mmol), HBPin (108 µL, 0.75 mmol) and NH_3BH_3 (0.93 mg, 0.030 mmol). The tube was sealed, and the resulting mixture was stirred at 80 ºC for 24 hours. The reaction was brought into the glovebox and the crude reaction mixture was diluted with THF and passed through a plug of silica gel in a Pasteur pipette and then analyzed by ^{19}F NMR spectroscopy without additional purification. Conversion: >99%; Yield (**1b**): 8%.

10.2 Reaction of 1 with HBPin employing Mn1 preactivated with NH_3BH_3



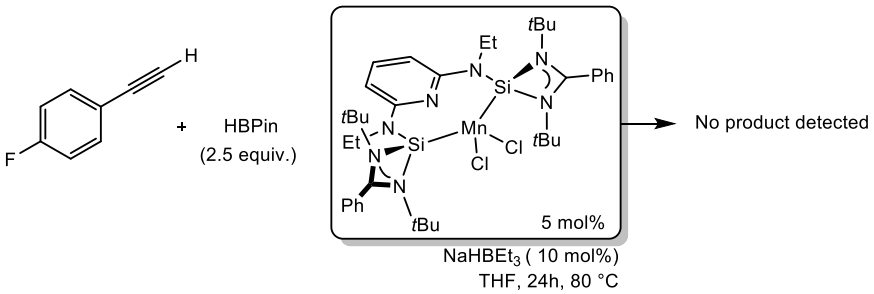
In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar, **Mn1** (12 mg, 0.015 mmol), THF (0.46 mL) and NH_3BH_3 (0.93 mg, 0.030 mmol). The contents were stirred at room temperature for 4 h followed by the addition of 4-Fluorophenylacetylene (33 µL, 0.3 mmol) and HBPin (108 µL, 0.36 mmol). The tube was sealed, and the resulting mixture was stirred at 80 ºC for 24 hours. The reaction was brought into the glovebox and the crude reaction mixture was diluted with THF and passed through a plug of silica gel in a Pasteur pipette and then analyzed by ^{19}F NMR spectroscopy without additional purification. Conversion: >99%; Yield (**1b**): 50%.

10.3 Reaction of 1 with HBPin employing Mn1 *in-situ* activated with KO*t*Bu



In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order- **Mn1** (12 mg, 0.015 mmol), THF (0.43 mL), 4-Fluorophenylacetylene (34 µL, 0.3 mmol), HBPin (108 µL, 0.75 mmol) and KO*t*Bu (30 µL of a 1 M solution in THF, 0.030 mmol). The tube was sealed, and the resulting mixture was stirred at 80 ºC for 24 hours. The reaction was brought into the glovebox and the crude reaction mixture was diluted with THF and passed through a plug of silica gel in a Pasteur pipette and then analyzed by ^{19}F NMR spectroscopy without additional purification. Conversion: >99%; Yield (**1b**): 9%.

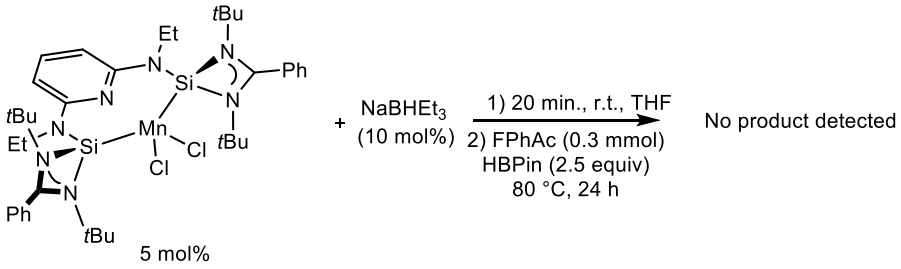
10.4 Reaction of 1 with HBPin employing Mn1 *in-situ* activated with NaHBEt$_3$



In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar and the reagents in the following order- **Mn1** (12 mg, 0.015 mmol), THF (0.43 mL), 4-Fluorophenylacetylene (33 µL, 0.3 mmol), HBPin (108 µL, 0.36 mmol) and NaBHEt$_3$ (30 µL of a 1 M solution in THF, 0.030 mmol). The tube was sealed, and the resulting mixture was stirred at 80 ºC for 24 hours. The reaction was brought into the glovebox and the crude reaction mixture was diluted with THF and passed through a plug of silica gel in a Pasteur pipette and then

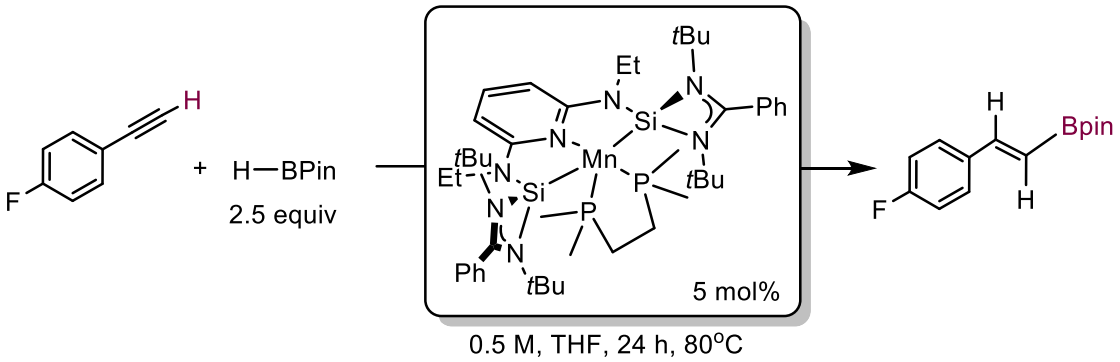
analyzed by ^{19}F NMR spectroscopy without additional purification. Conversion: >99%; Yield (**1b**): Not detected.

10.5 Reaction of 1 with HBPin employing Mn1 preactivated with $NaHBEt_3$



In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar, **Mn1** (12 mg, 0.015 mmol), THF (0.43 mL) and $NaBHEt_3$ (30 µL of a 1 M solution in THF, 0.030 mmol). The contents were stirred at room temperature for 20 min. followed by the addition of 4-Fluorophenylacetylene (33 µL, 0.3 mmol) and HBPin (108 µL, 0.36 mmol). The tube was sealed, and the resulting mixture was stirred at 80 ºC for 24 hours. The reaction was brought into the glovebox and the crude reaction mixture was diluted with THF and passed through a plug of silica gel in a Pasteur pipette and then analyzed by ^{19}F NMR spectroscopy without additional purification. Conversion: >99%; Yield (**1b**): Not detected.

10.6 Reaction of 1 with HBPin employing 5 mol% of [Mn(SiNSi)(dmpe)] as precatalyst



In an argon-filled glovebox a J. Young flask was charged with a magnetic stir bar, 4-fluorophenylacetylene (34 µL, 0.3 mmol), THF (0.52 mL), HBPin (108 µL, 0.75 mmol) and [Mn(SiNSi)(dmpe)] (13 mg, 0.015 mmol). The tube was sealed, and the resulting mixture was stirred at 80 ºC for 24 hours. The reaction was brought into the glovebox and fluorobenzene (10 µL, 0.106 mmol) was added as an internal standard. The crude reaction mixture was passed

through a plug of whatman filter paper in a Pasteur pipette and then analyzed by GC chromatography and NMR spectroscopy without additional purification. Conversion: >99%; Yield (**1b**): 17%.

11. Spectroscopic Data

NMR spectra of alkynylboronate esters

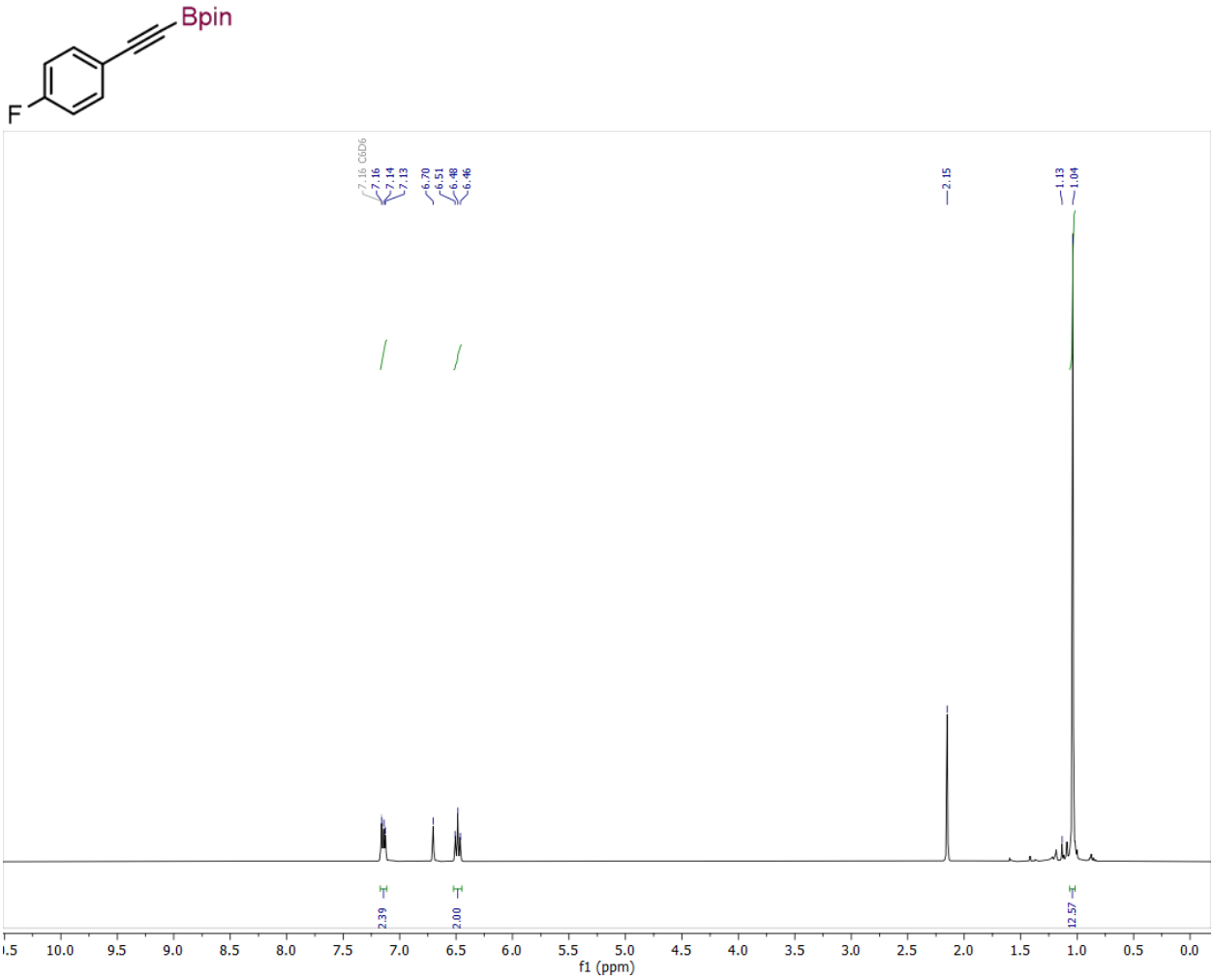


Figure S28: ^{1}H NMR (C_6D_6, 400MHz) of 2-((4-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

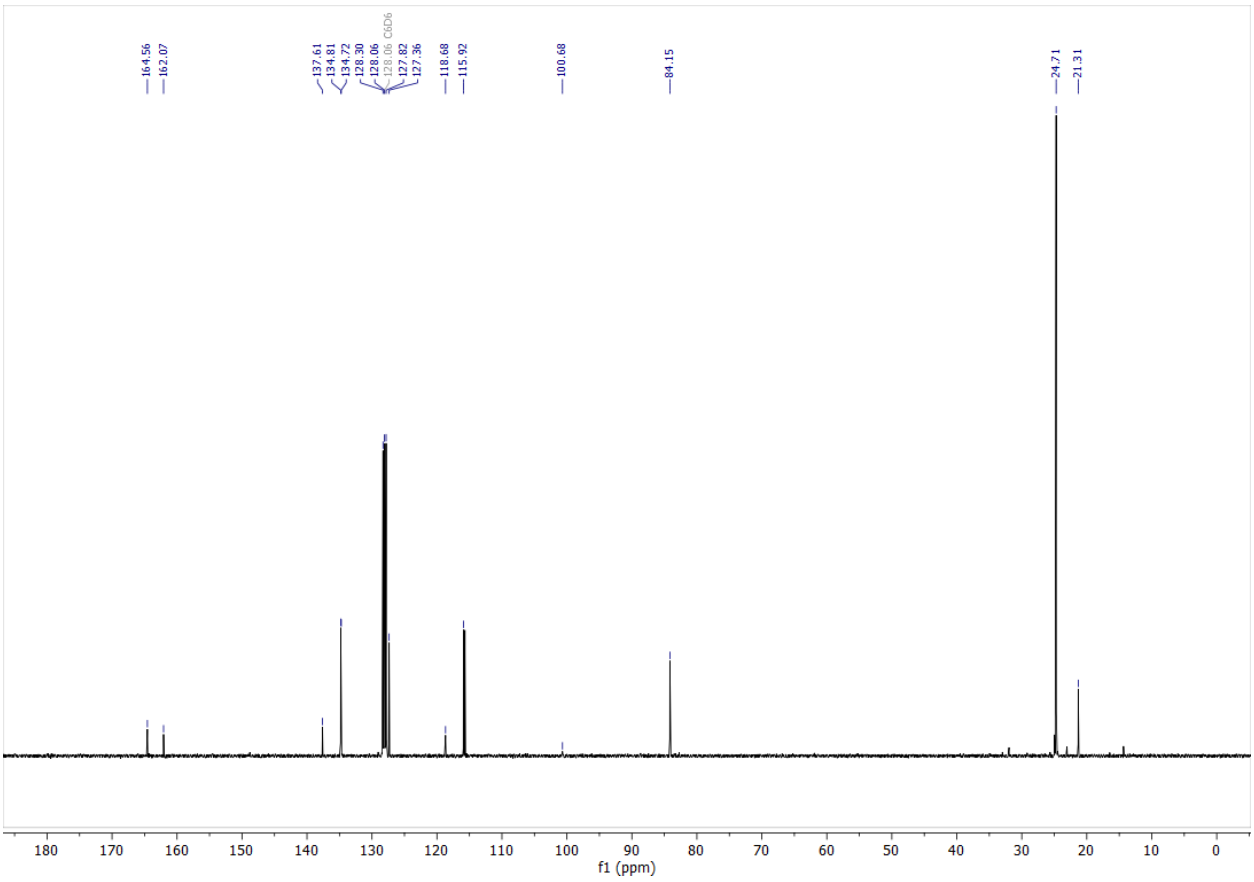


Figure 29: ^{13}C NMR (C_6D_6, 400MHz) of 2-((4-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.31, 127.36 and 137.61 ppm correspond to internal standard (mesitylene).

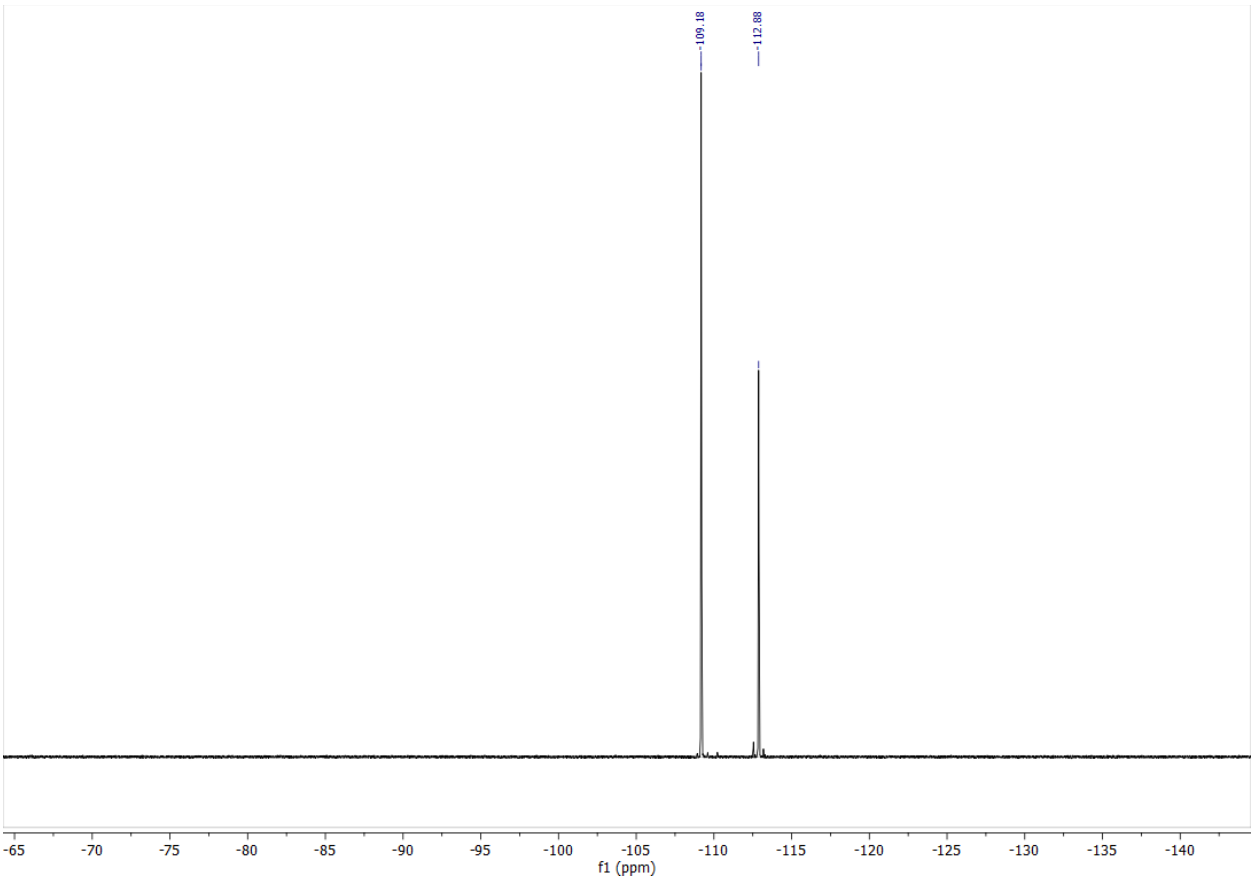


Figure S30: ^{19}F NMR(C_6D_6, 400MHz) of 2-((4-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peak at -112.98 ppm corresponds to internal standard (fluorobenzene).

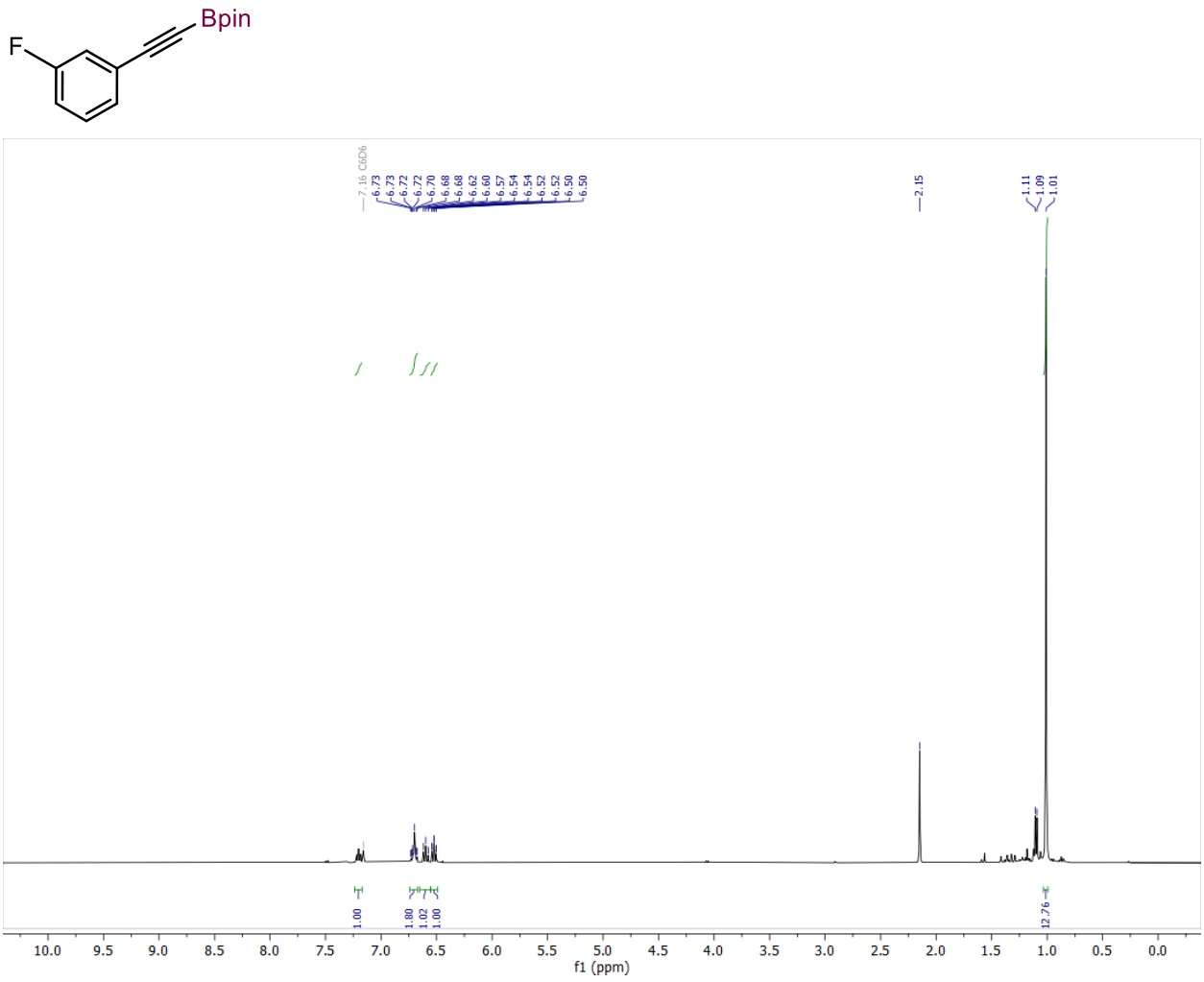


Figure S31: ^{1}H NMR (C_6D_6, 400MHz) of 2-((3-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

Peaks at 1.09 and 1.11 correspond to unidentified impurities.

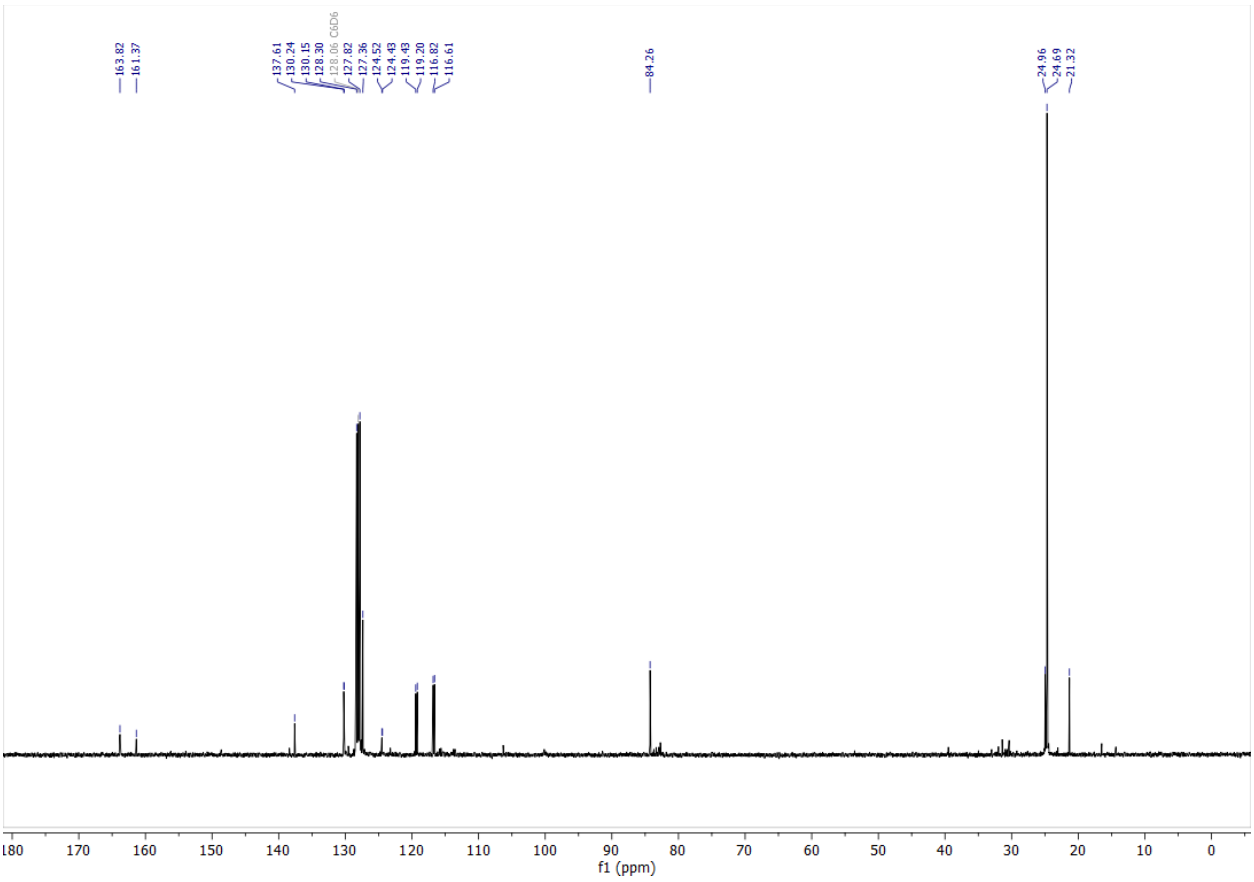


Figure S32: ^{13}C NMR (C_6D_6, 400MHz) of 2-((3-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.32, 127.36 and 137.61 ppm correspond to internal standard (mesitylene).

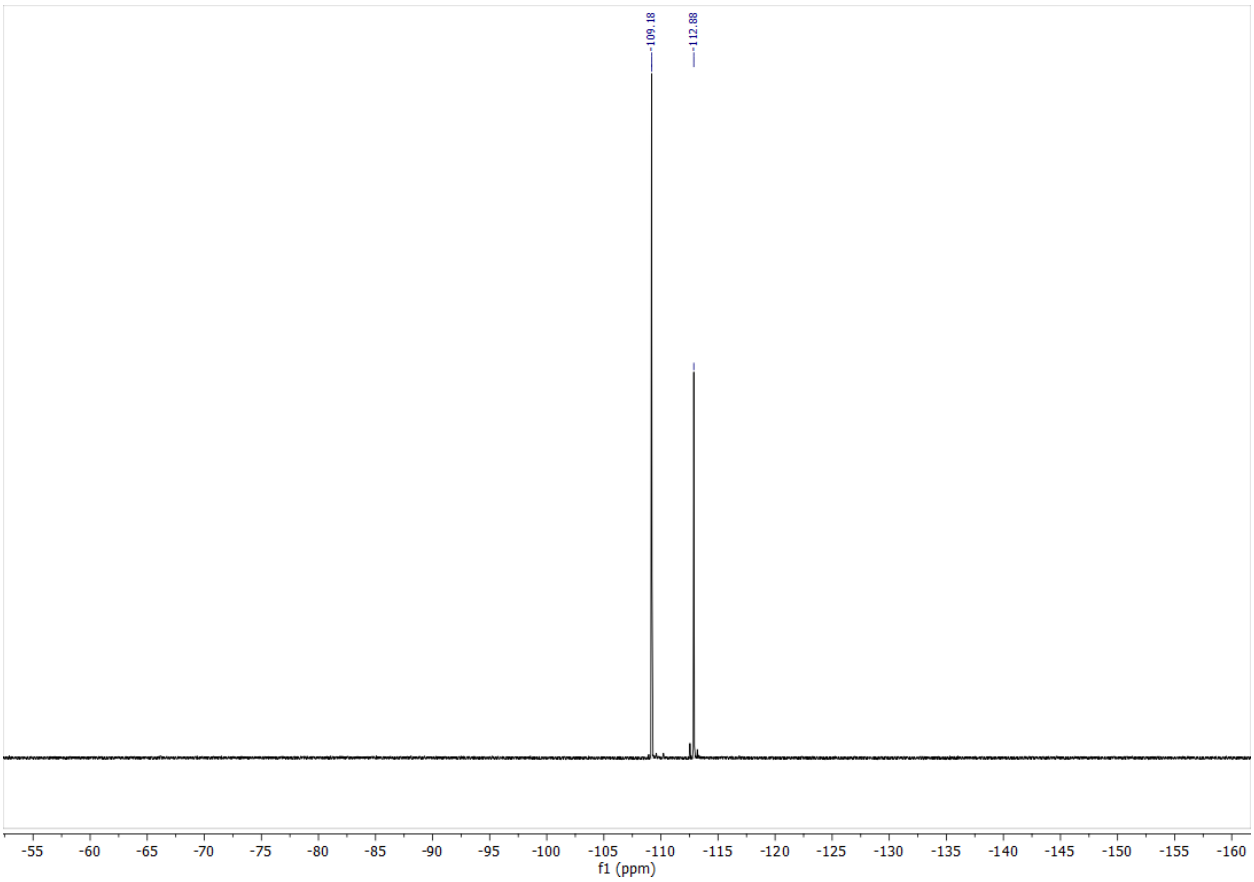


Figure S33: ^{19}F NMR (C_6D_6, 400MHz) of 2-((3-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peak at -112.88 ppm corresponds to internal standard (fluorobenzene).

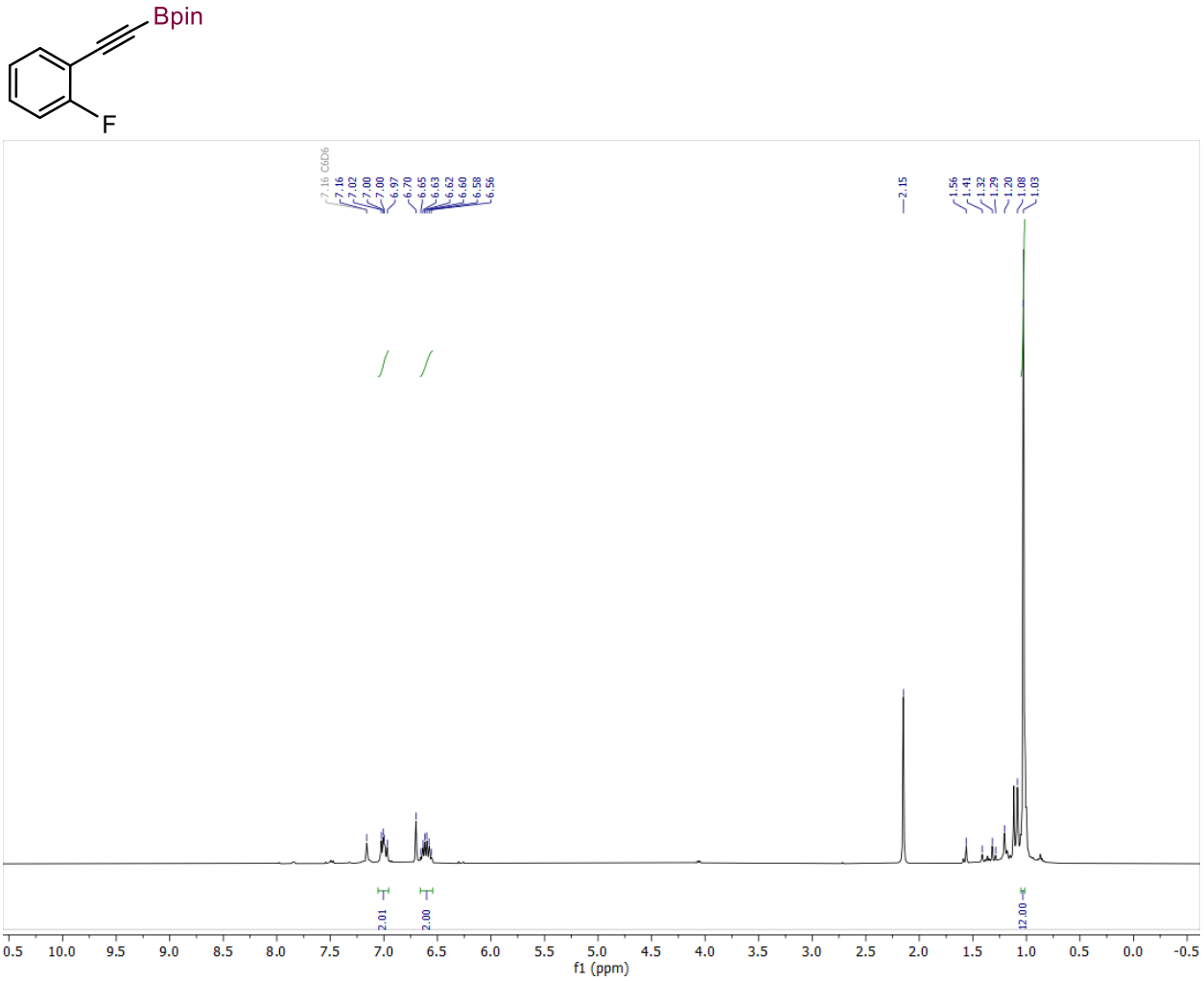


Figure S34: ^{1}H NMR (C_6D_6, 400MHz) of 2-((2-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

Peaks at 1.08, 1.20, 1.28, 1.29, 1.32, 1.41, 1.56 correspond to unidentified impurities.

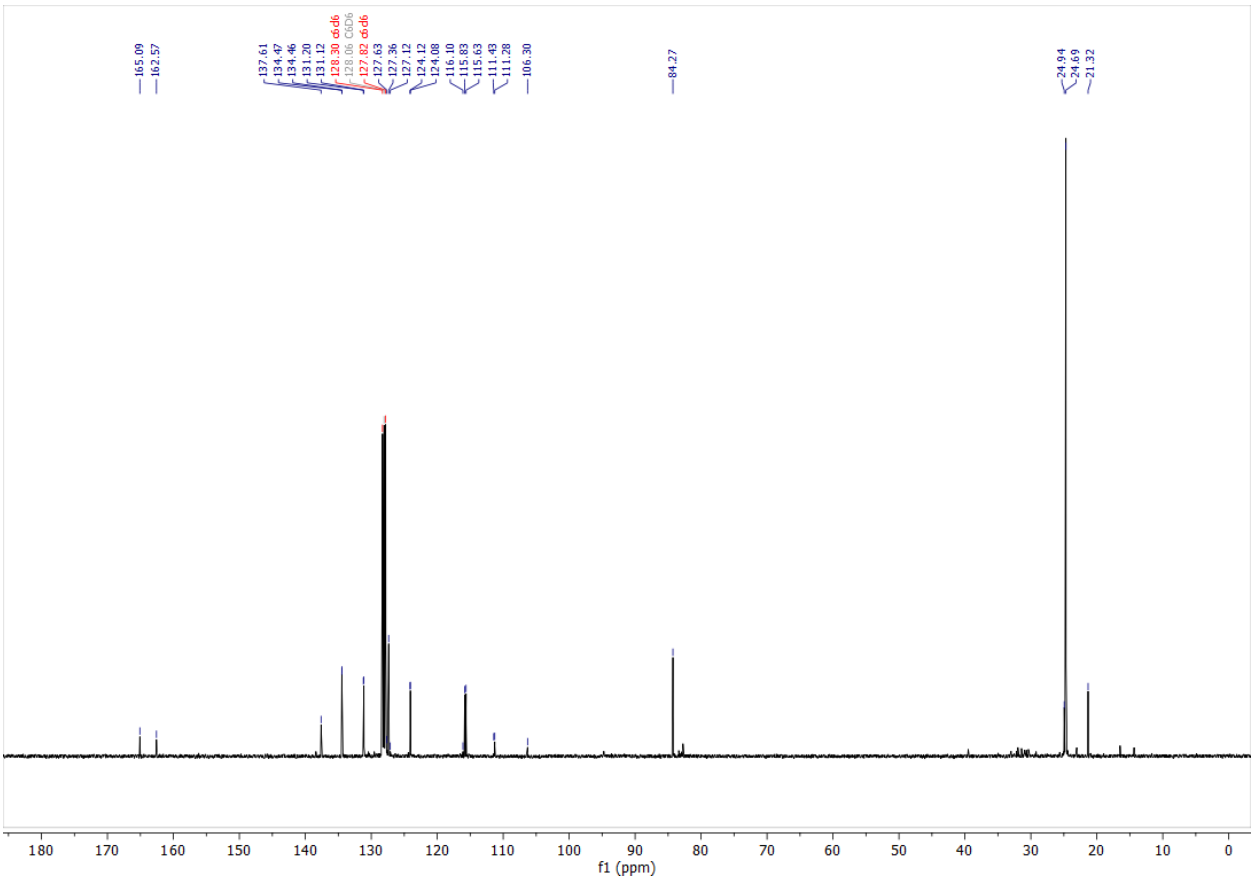


Figure S35: ^{13}C NMR (C_6D_6, 400MHz) of 2-((2-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.32, 127.36 and 137.61 ppm correspond to internal standard (mesitylene).

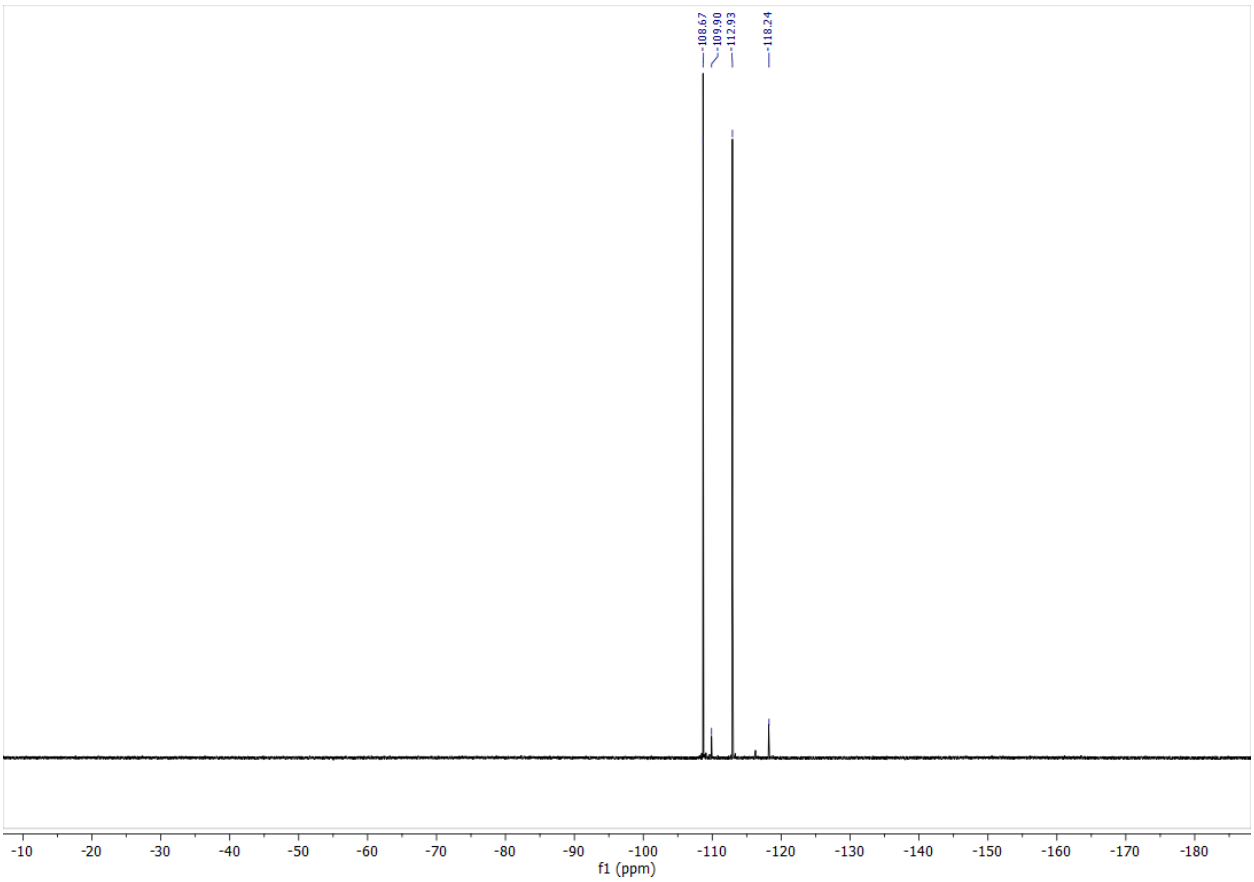


Figure S36: ^{19}F NMR (C_6D_6, 400MHz) of 2-((2-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peak at -112.93 ppm corresponds to internal standard (fluorobenzene).

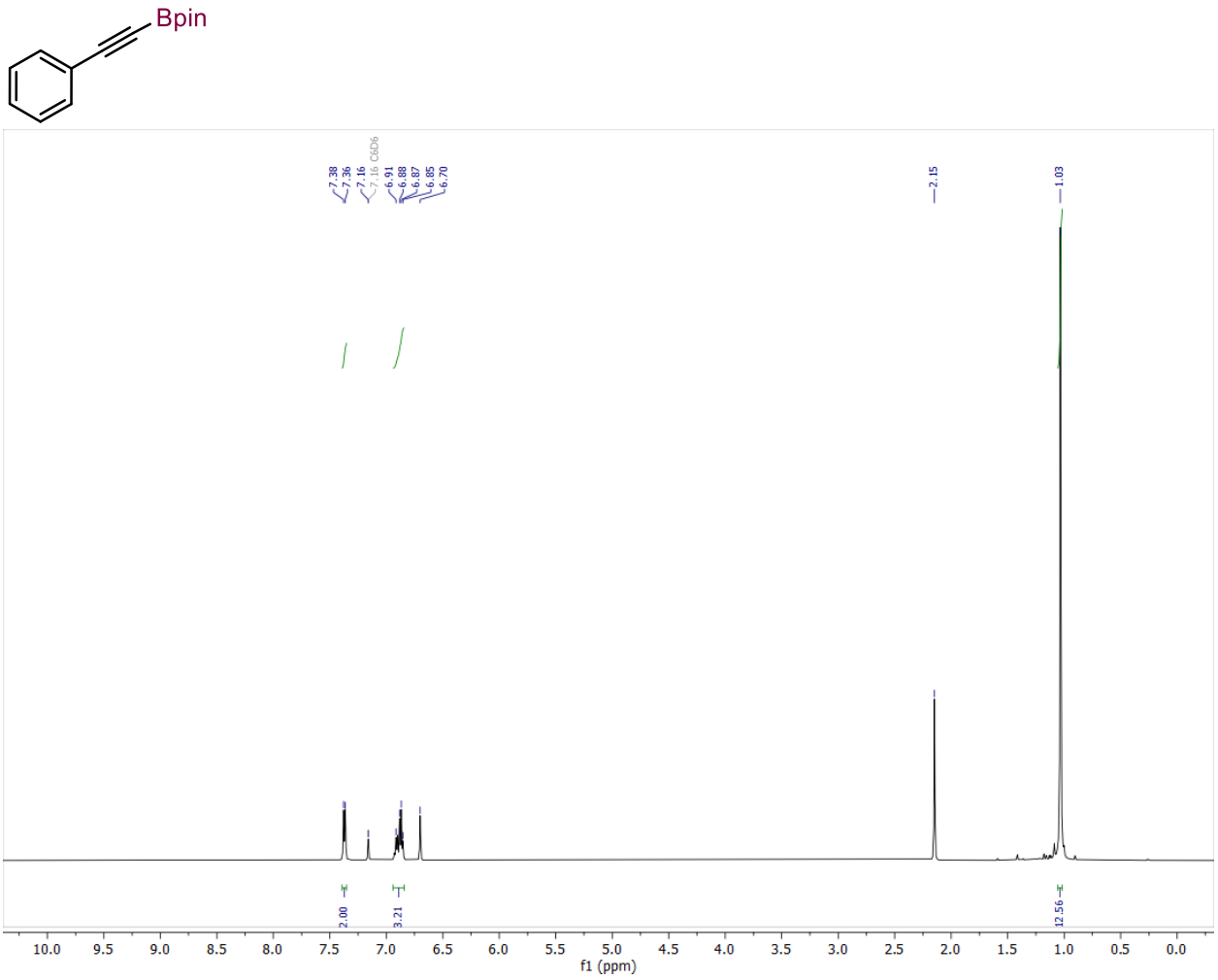


Figure S37: ^{1}H NMR (C_6D_6, 500MHz) of 4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

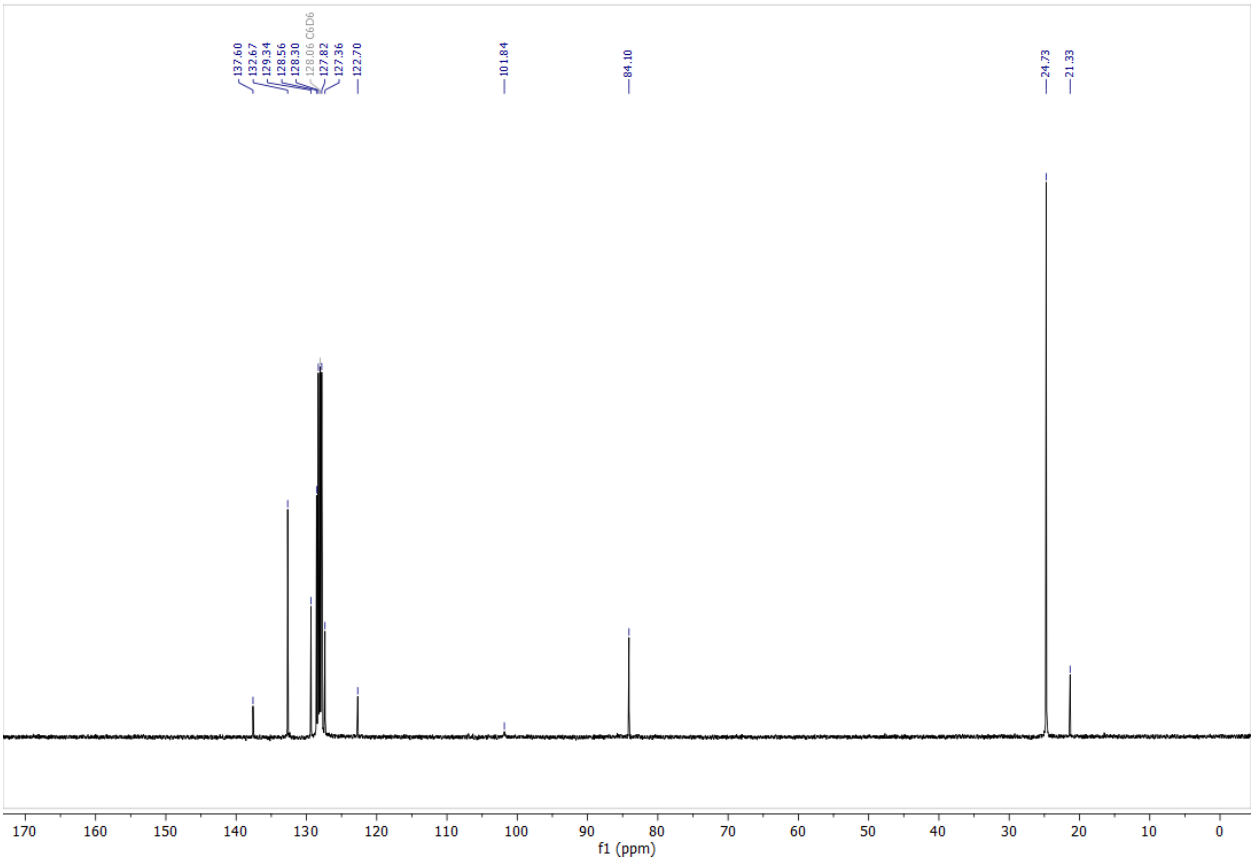


Figure S38: ^{13}C NMR (C_6D_6, 400MHz) of 4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane

Peaks at 21.33, 127.36 and 137.60 ppm correspond to internal standard (mesitylene).

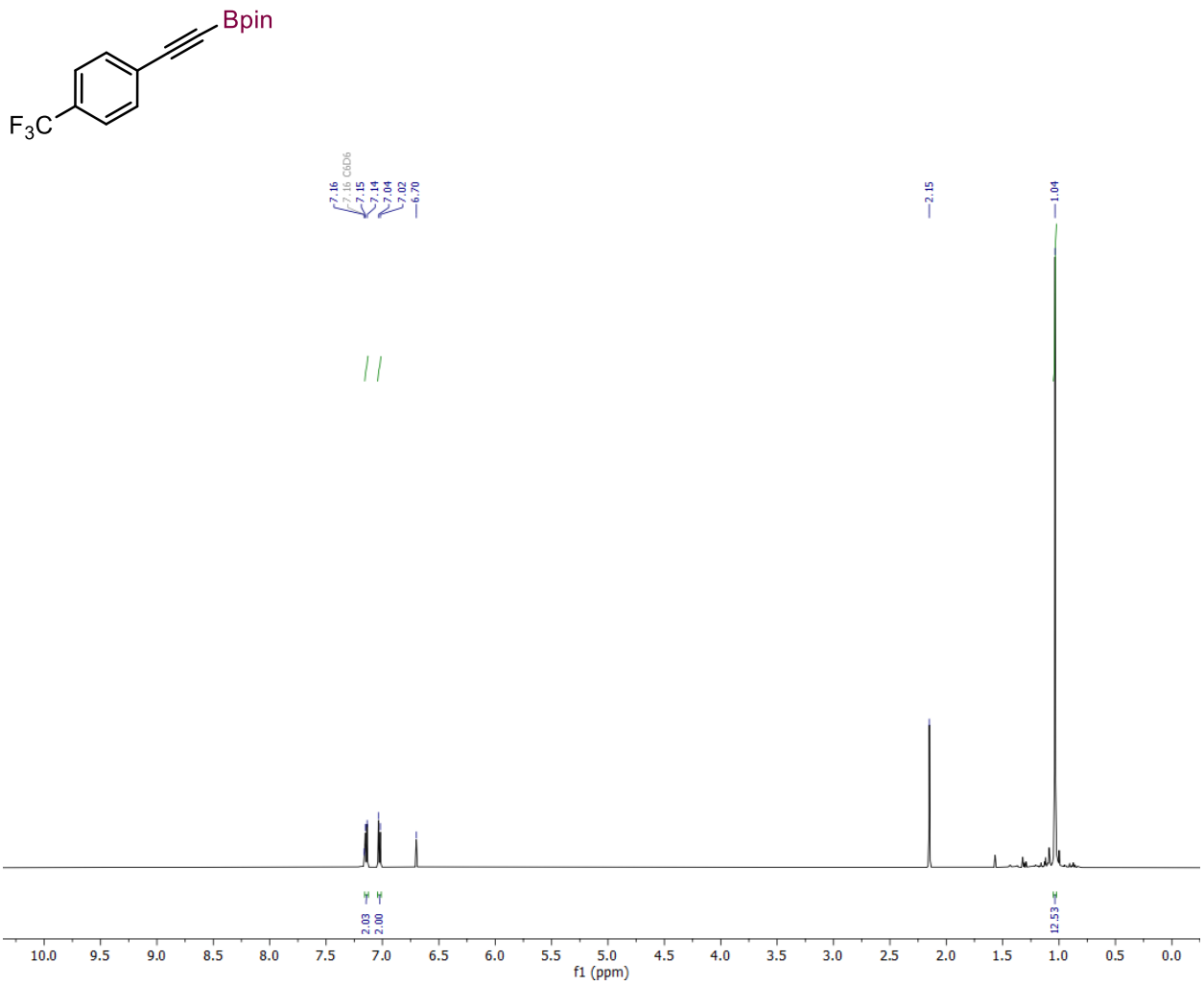


Figure S39: ^{1}H NMR (C_6D_6, 500MHz) of 4,4,5,5-tetramethyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

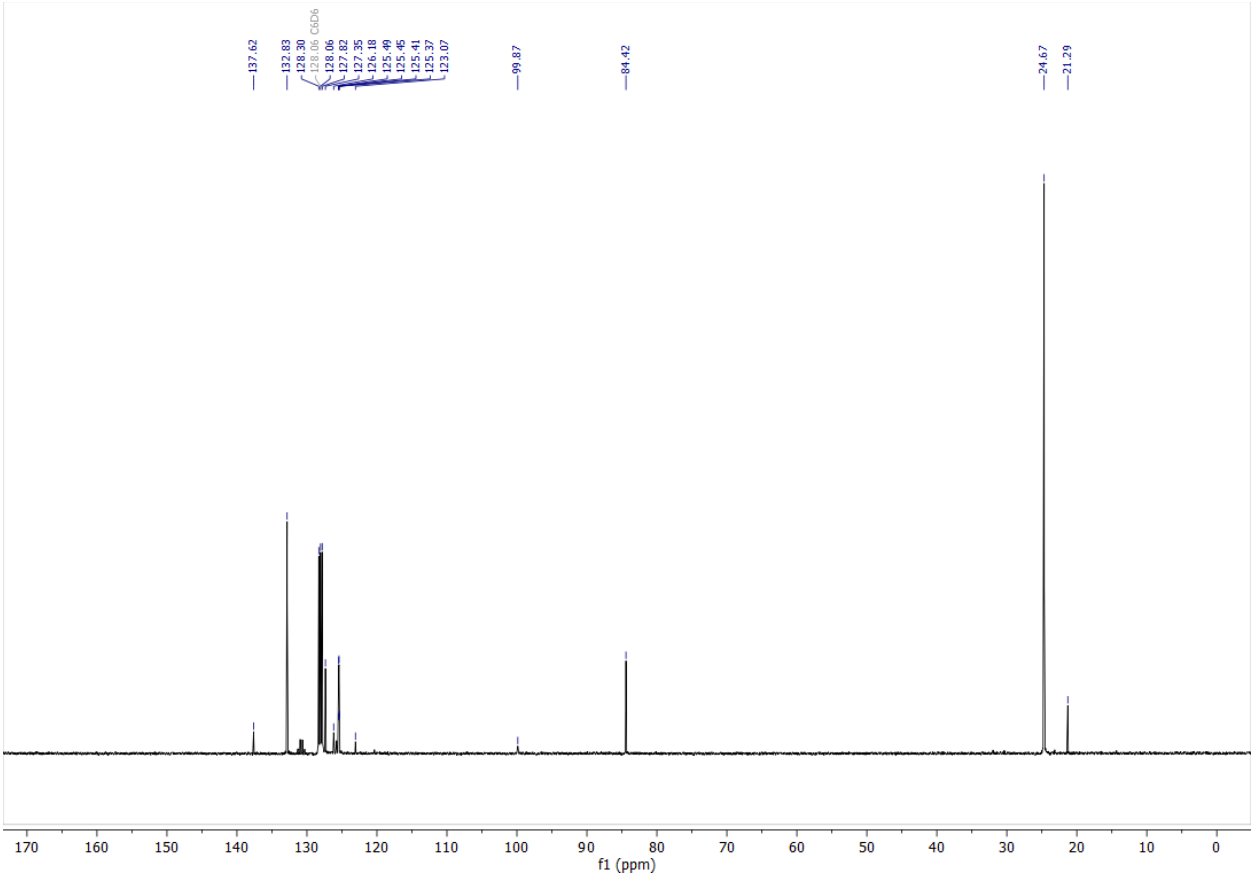


Figure S40: ^{13}C NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane

Peaks at 21.29, 127.35 and 137.62 ppm correspond to internal standard (mesitylene).

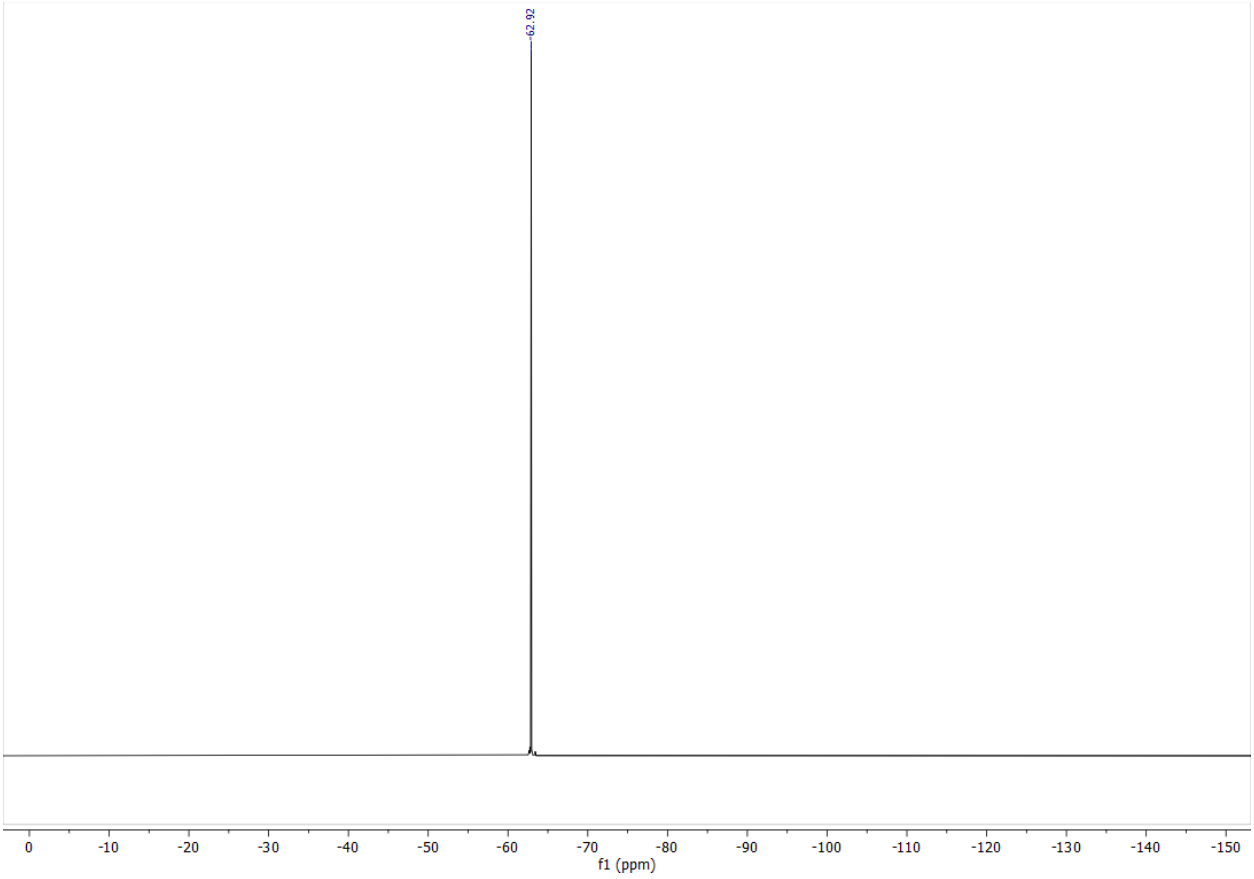
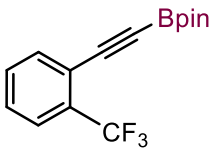


Figure S41: ^{19}F NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane



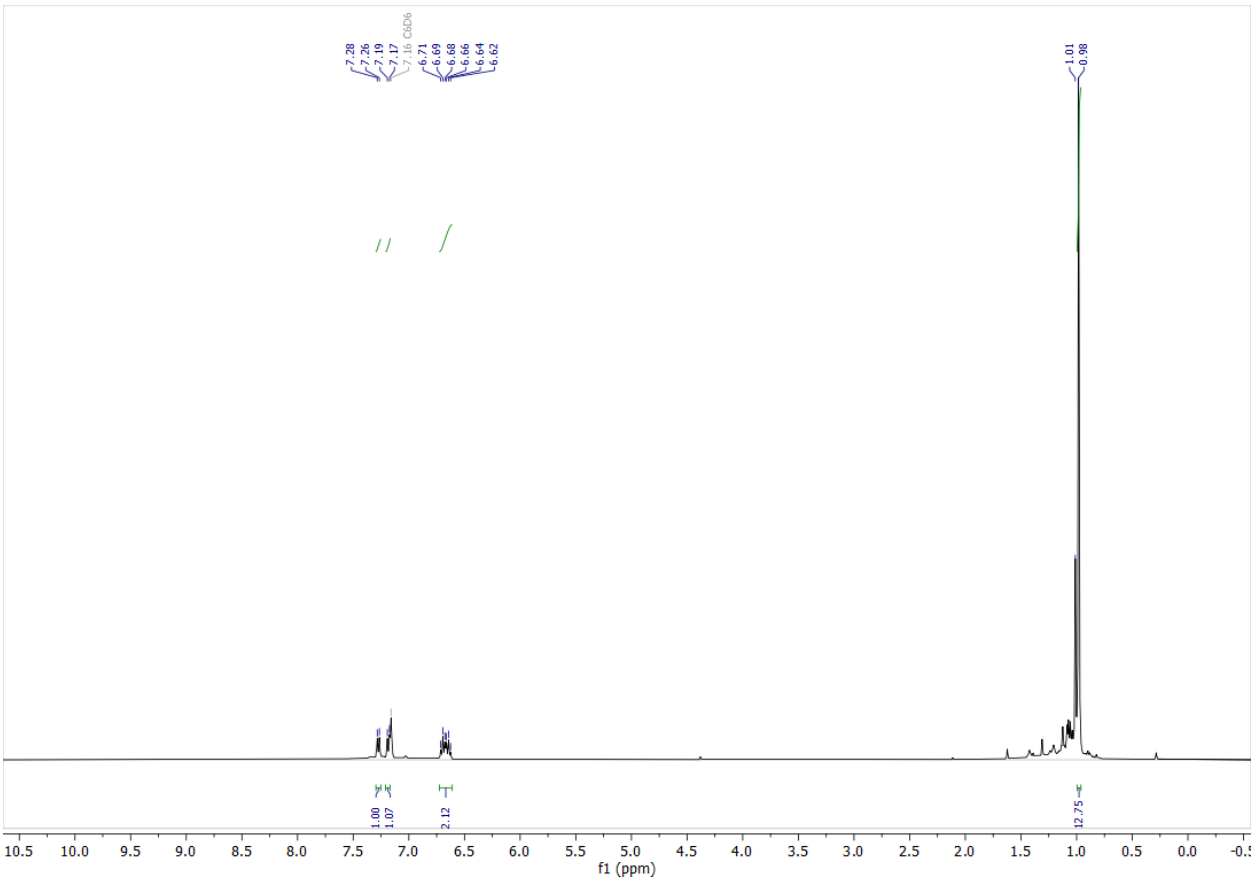


Figure S42: ^{1}H NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-((2-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane

Peak at 1.01 corresponds to unidentified impurity.

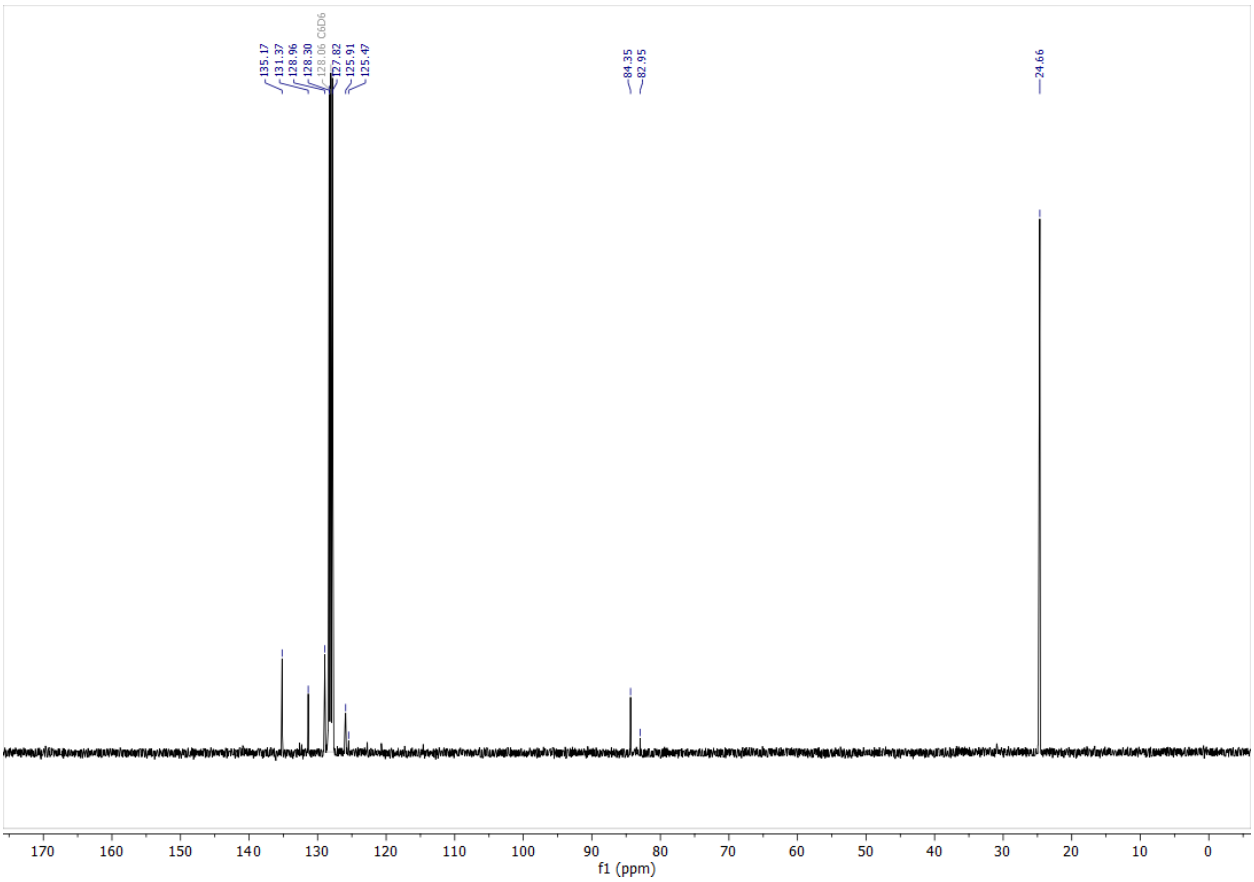


Figure S43: ^{13}C NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-((2-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane

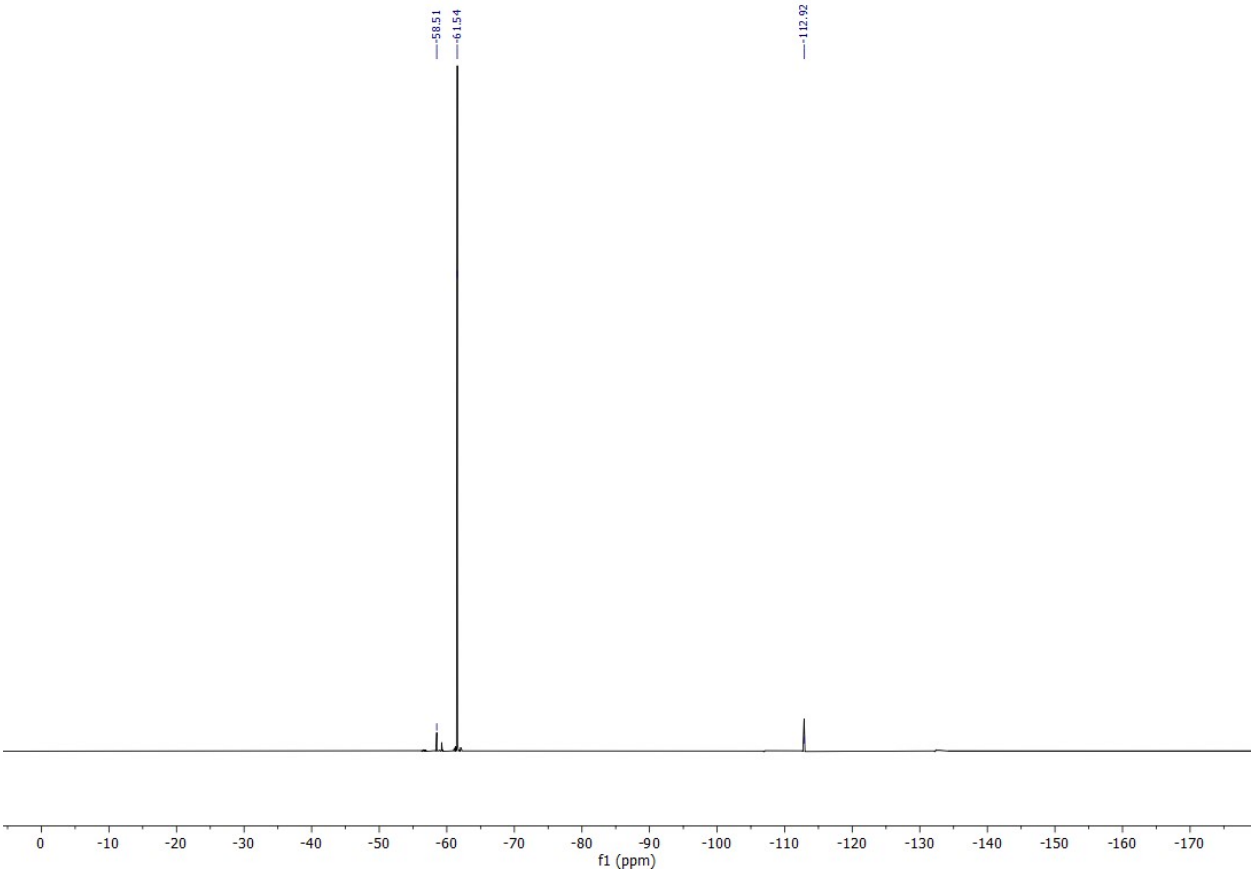
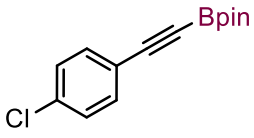


Figure S44: ^{19}F NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-((2-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane

Peak at -112.92 corresponds to internal standard.

Peak at -58.51 corresponds to unidentified impurity.



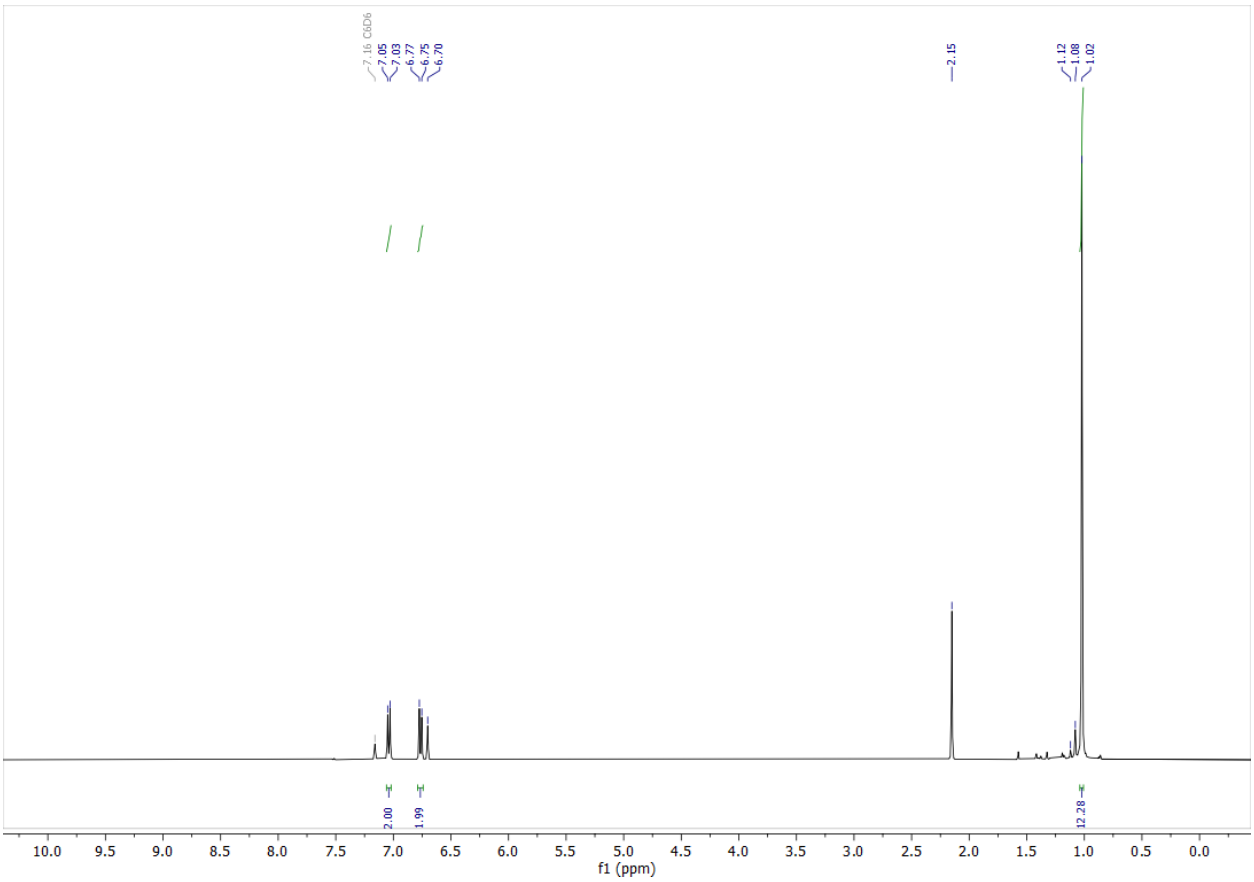


Figure S45: ^{1}H NMR (C_6D_6, 400MHz) of 2-((4-chlorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

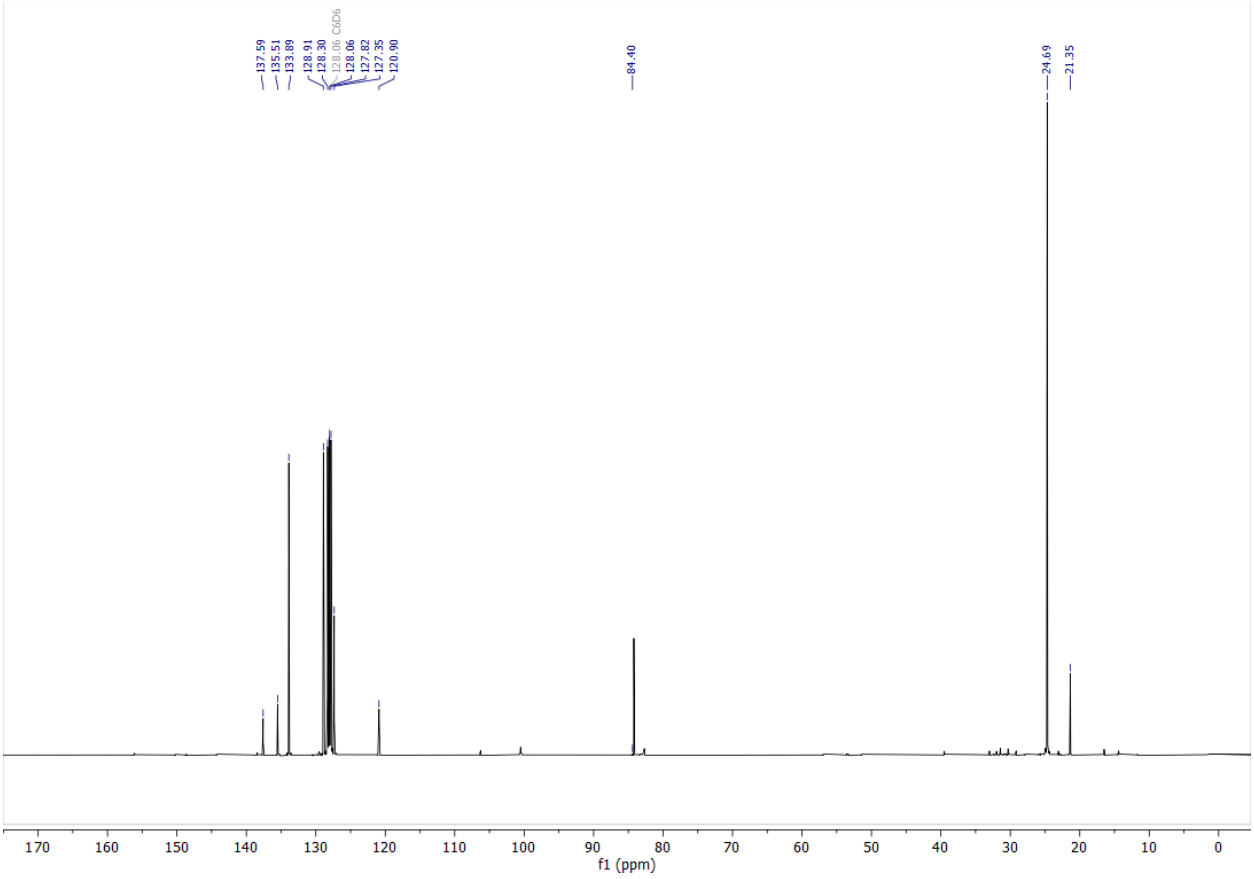
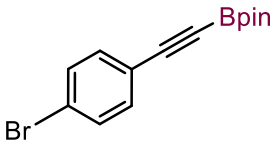


Figure S46: ^{13}C NMR(C_6D_6, 400MHz) of 2-((4-chlorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.35, 127.35 and 137.59 ppm correspond to internal standard (mesitylene).



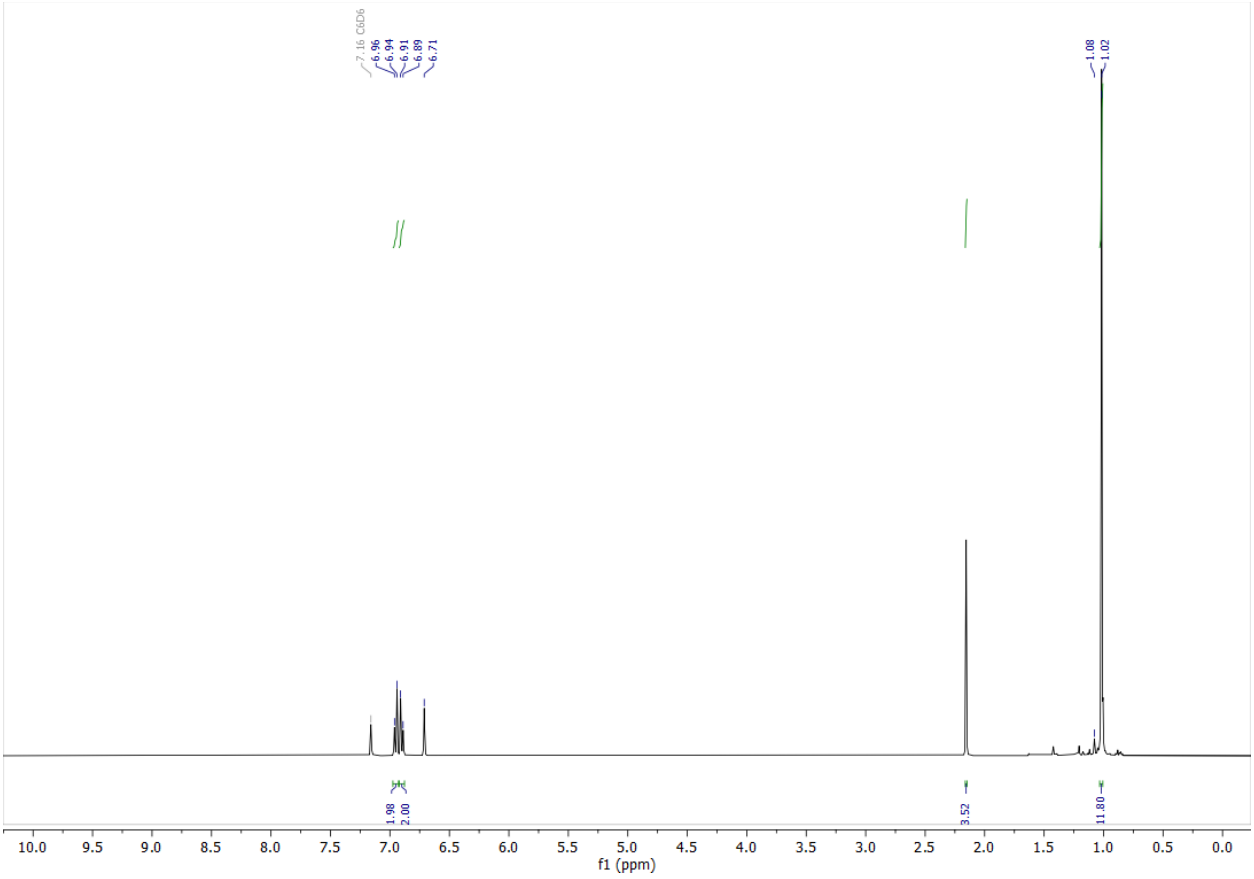


Figure S47: ^{1}H NMR (C_6D_6, 400MHz) of 2-((4-bromophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

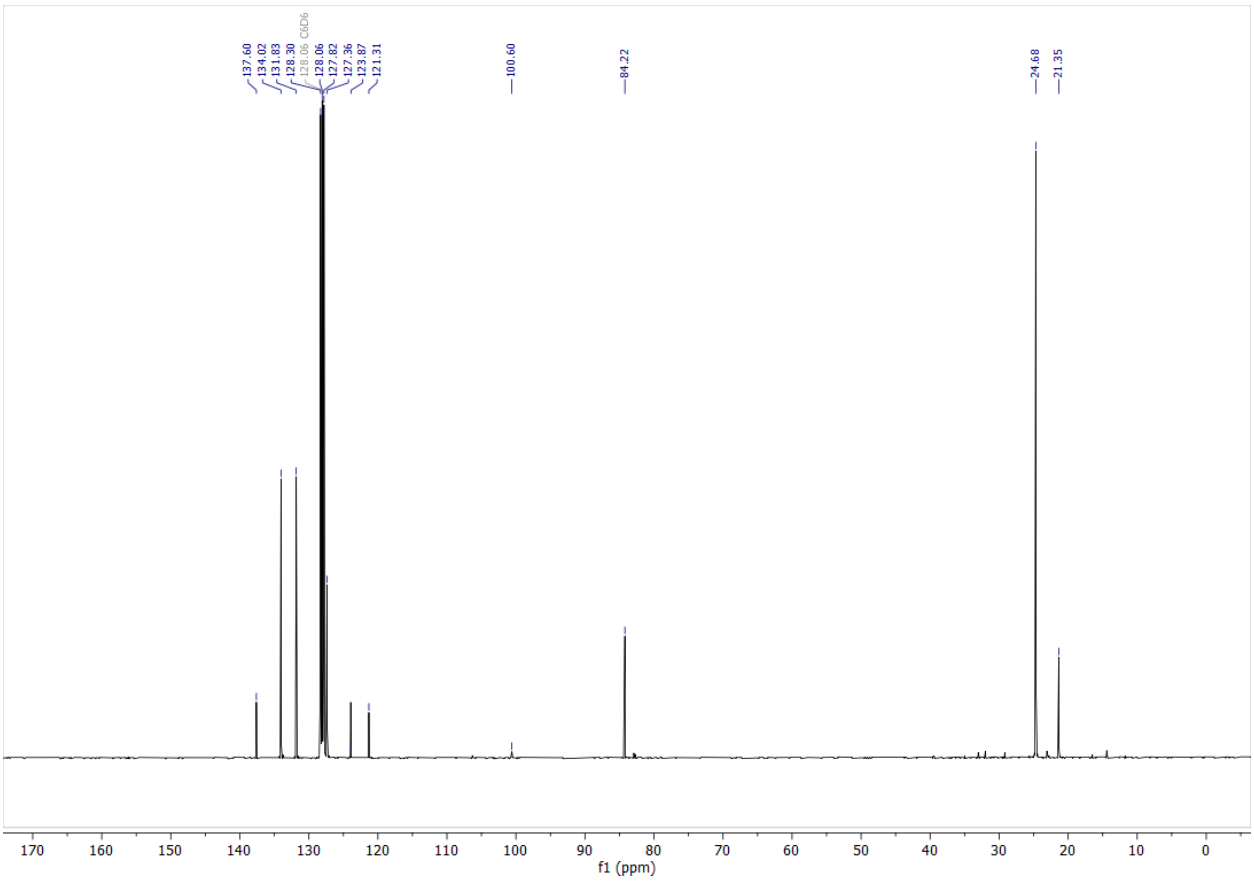
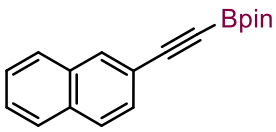


Figure S48: ^{13}C NMR (C_6D_6, 400MHz) of 2-((4-bromophenyl)ethynyl) 4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.35, 127.36 and 137.60 ppm correspond to internal standard (mesitylene).



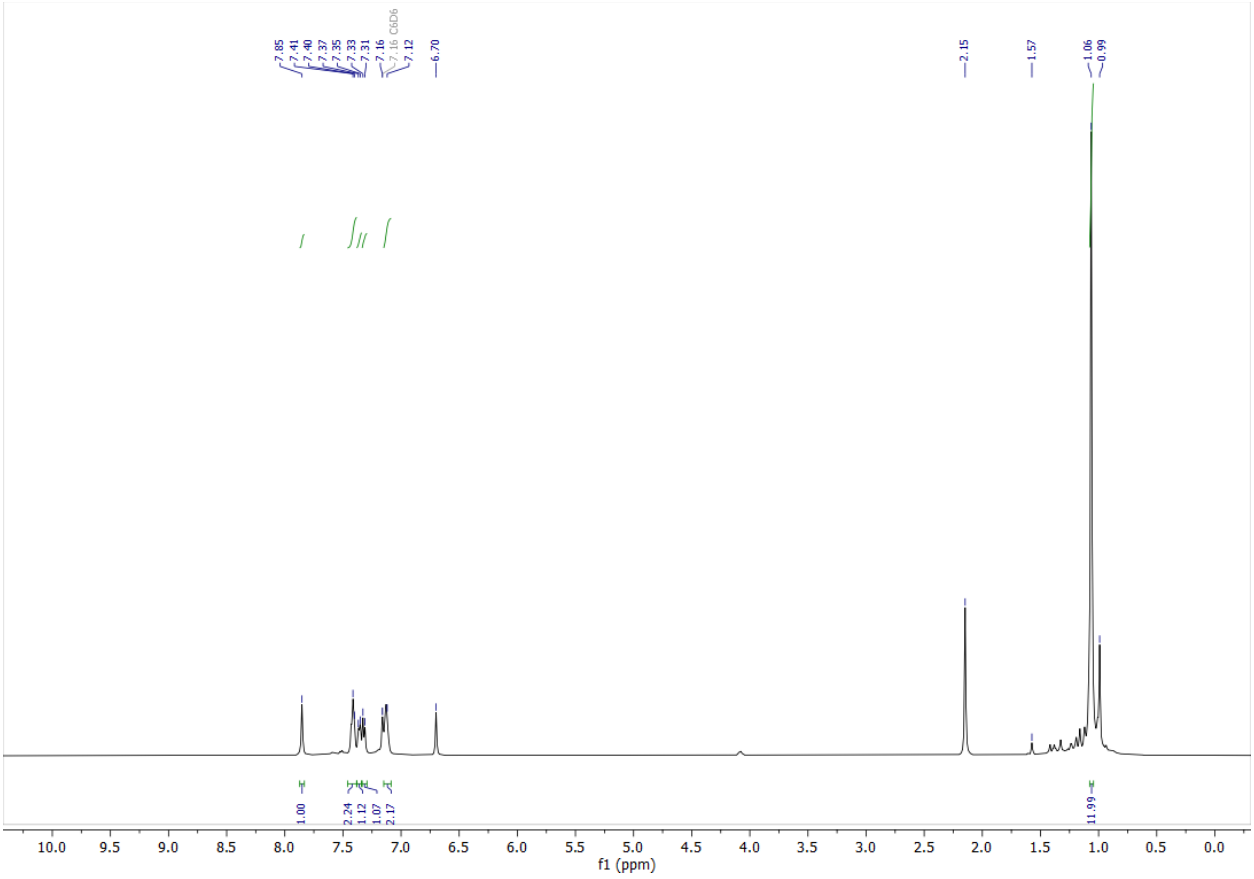


Figure S49: ^{1}H NMR (C_6D_6, 500MHz) of 4,4,5,5-tetramethyl-2-[2-(naphthalen-2-yl)ethynyl]-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

Peaks at 0.99 and 1.57 correspond to unidentified impurities.

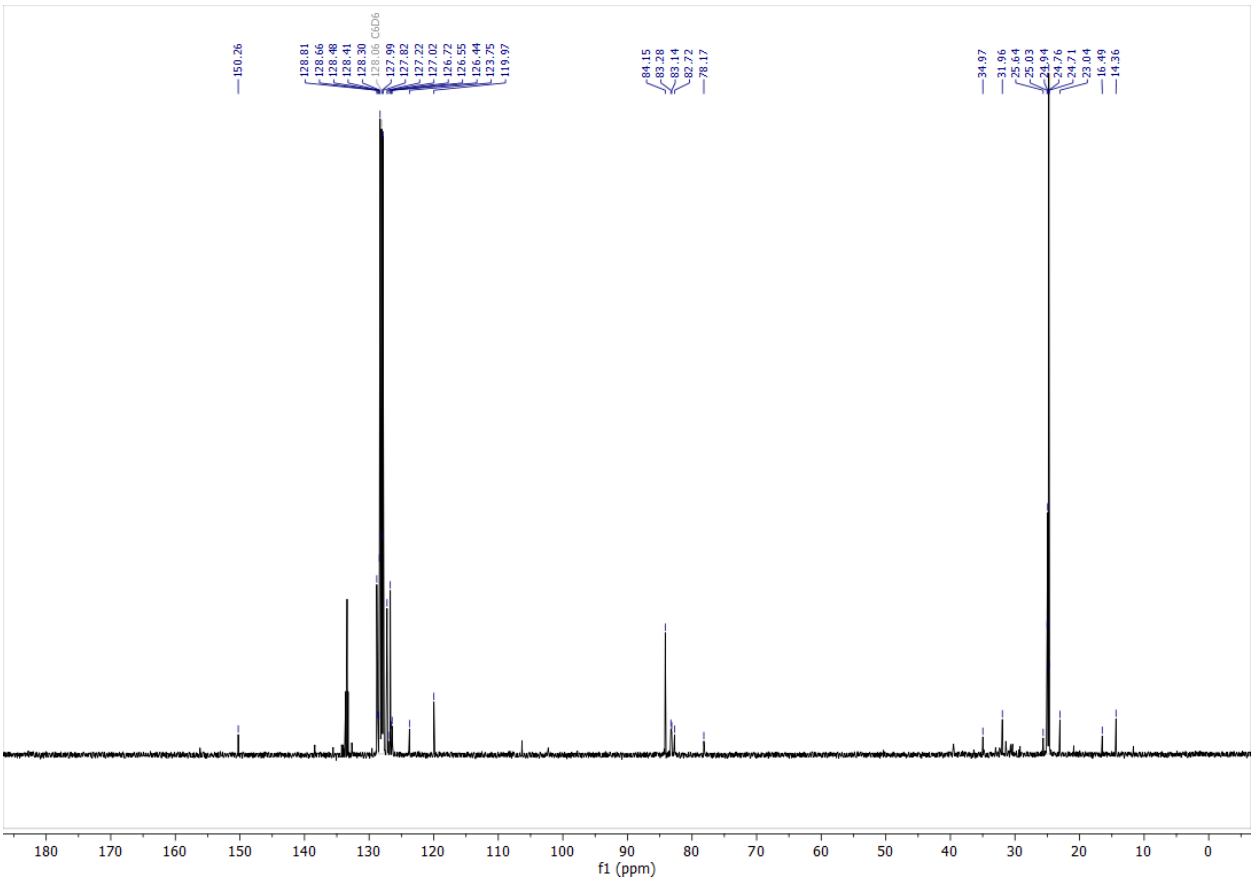
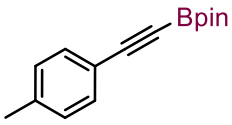


Figure S50: ^{13}C NMR (C_6D_6, 500MHz) of 4,4,5,5-tetramethyl-2-[2-(naphthalen-2-yl)ethynyl]-1,3,2-dioxaborolane

Peaks at 14.36, 16.49, 23.04, 24.94, 25.03, 82.72, 83.28, 83.14 and 123.75 correspond to unidentified impurities.



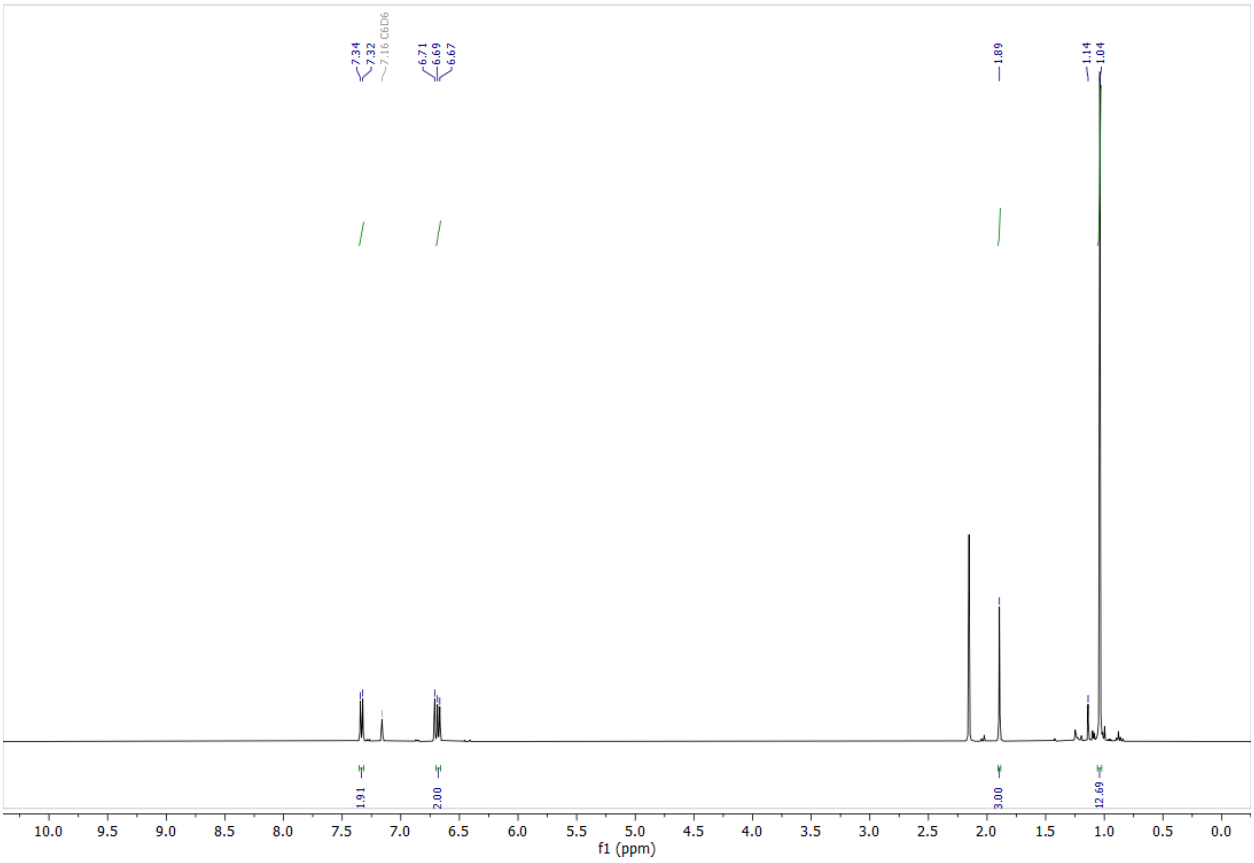


Figure S51: ^{1}H NMR (C_6D_6, 400MHz) of 2-((4-methylphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

Peak at 1.14 corresponds to unidentified impurity.

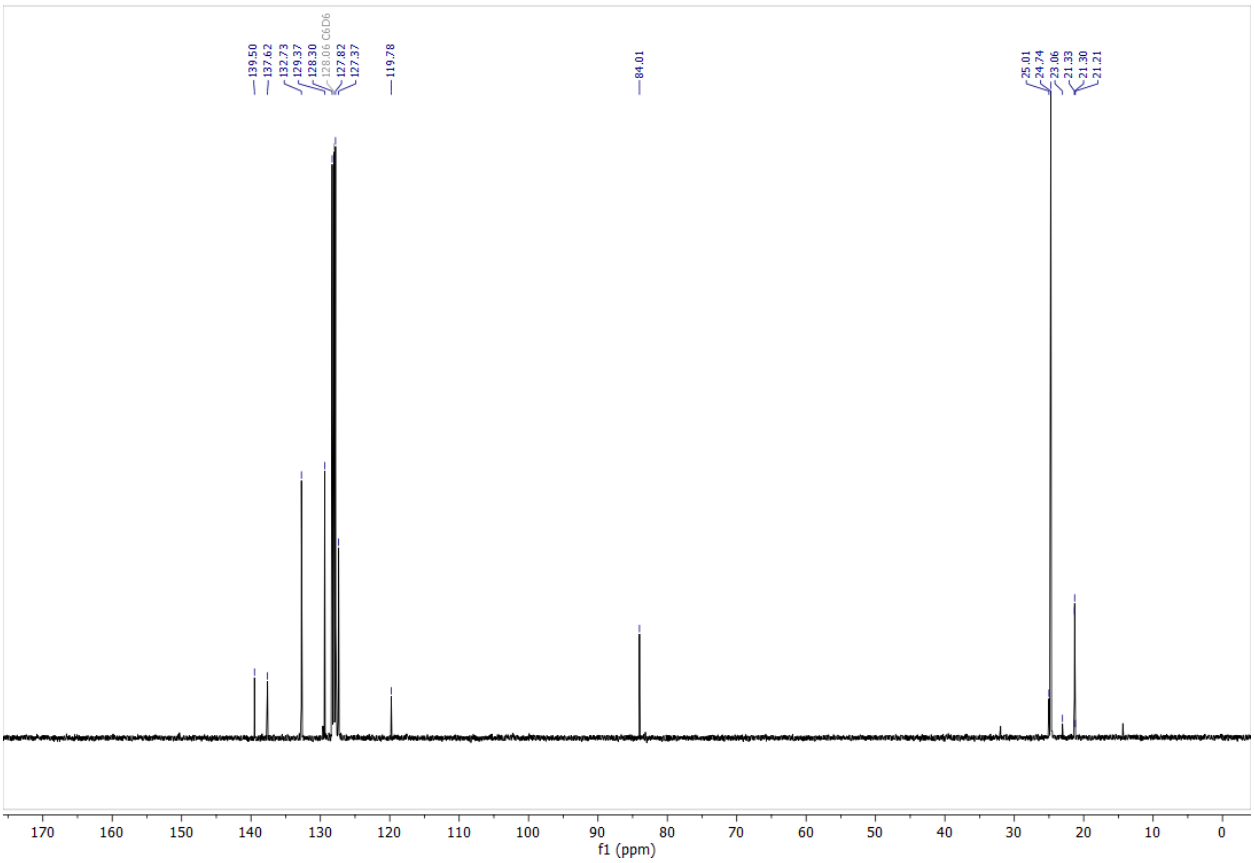
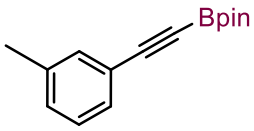


Figure S52: ^{13}C NMR (C_6D_6, 400MHz) of 2-((4-methylphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.33, 127.37 and 137.62 ppm correspond to internal standard (mesitylene).



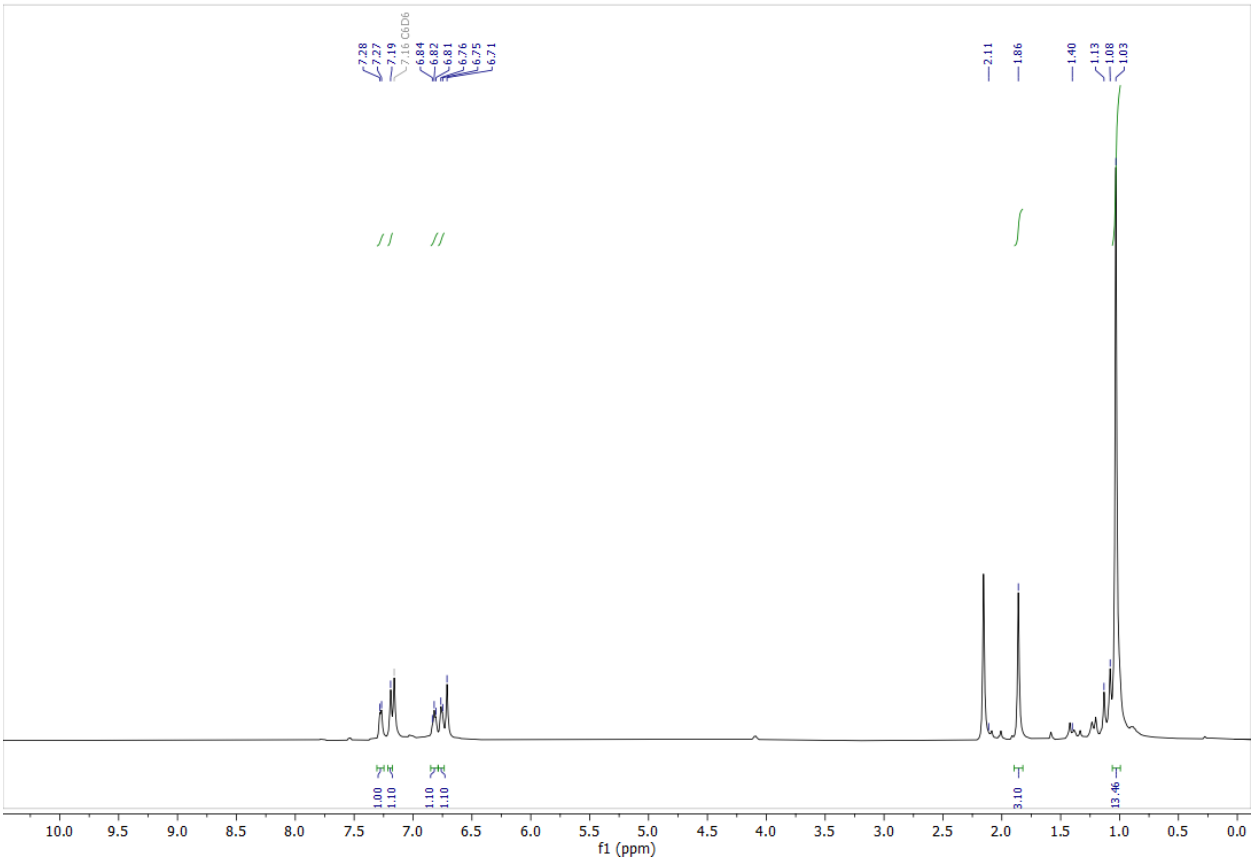


Figure S53: ^{1}H NMR (C_6D_6, 500MHz) of 2-((3-methylphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.11 and 6.71 ppm correspond to internal standard (mesitylene).

Peaks at 1.08 and 1.13 correspond to unidentified impurities.

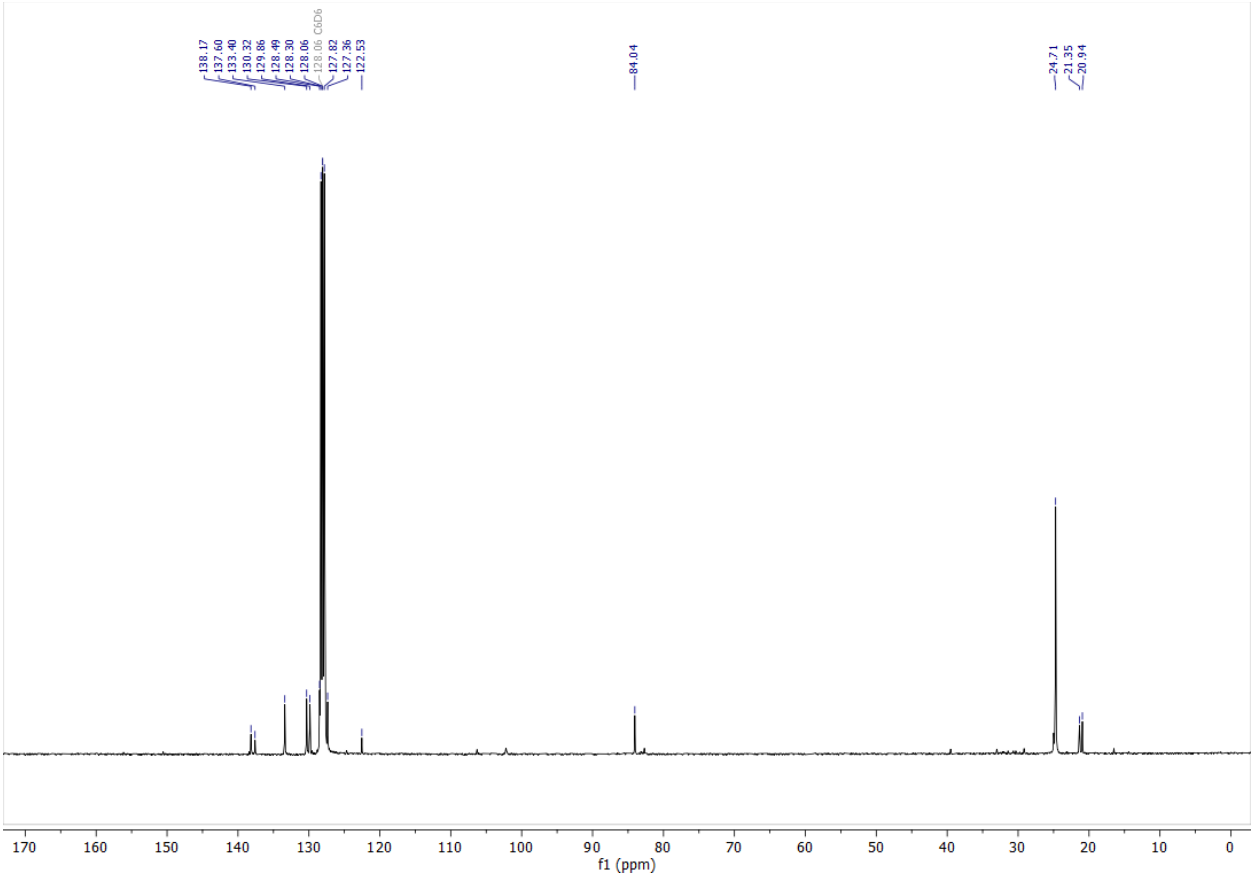
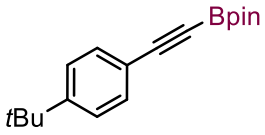


Figure S54: ^{13}C NMR (C_6D_6, 400MHz) of 2-((3-methylphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.35, 127.36 and 137.60 ppm correspond to internal standard (mesitylene).



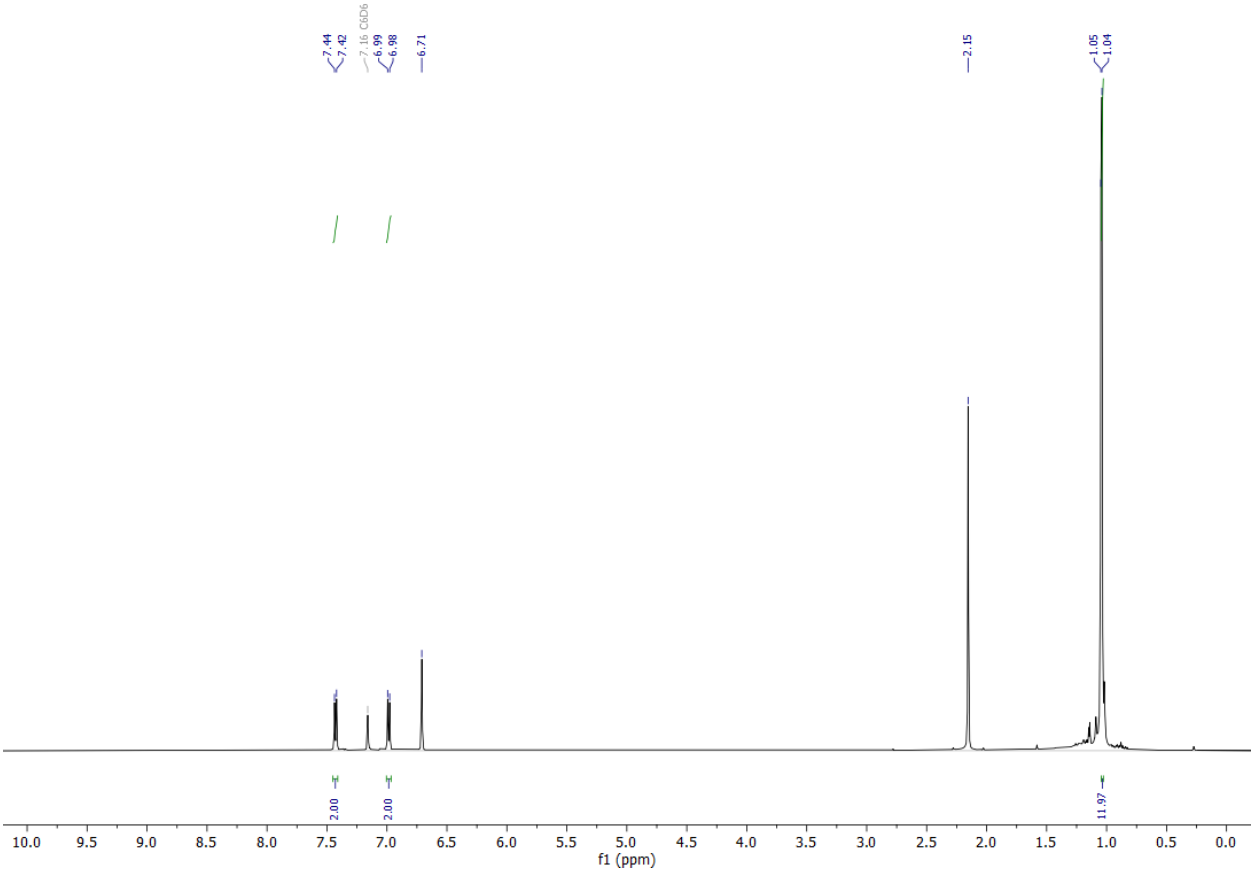


Figure S55: ^{1}H NMR (C_6D_6, 500MHz) of 2-((4-*tert*-butylphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.15 and 6.71 ppm correspond to internal standard (mesitylene).

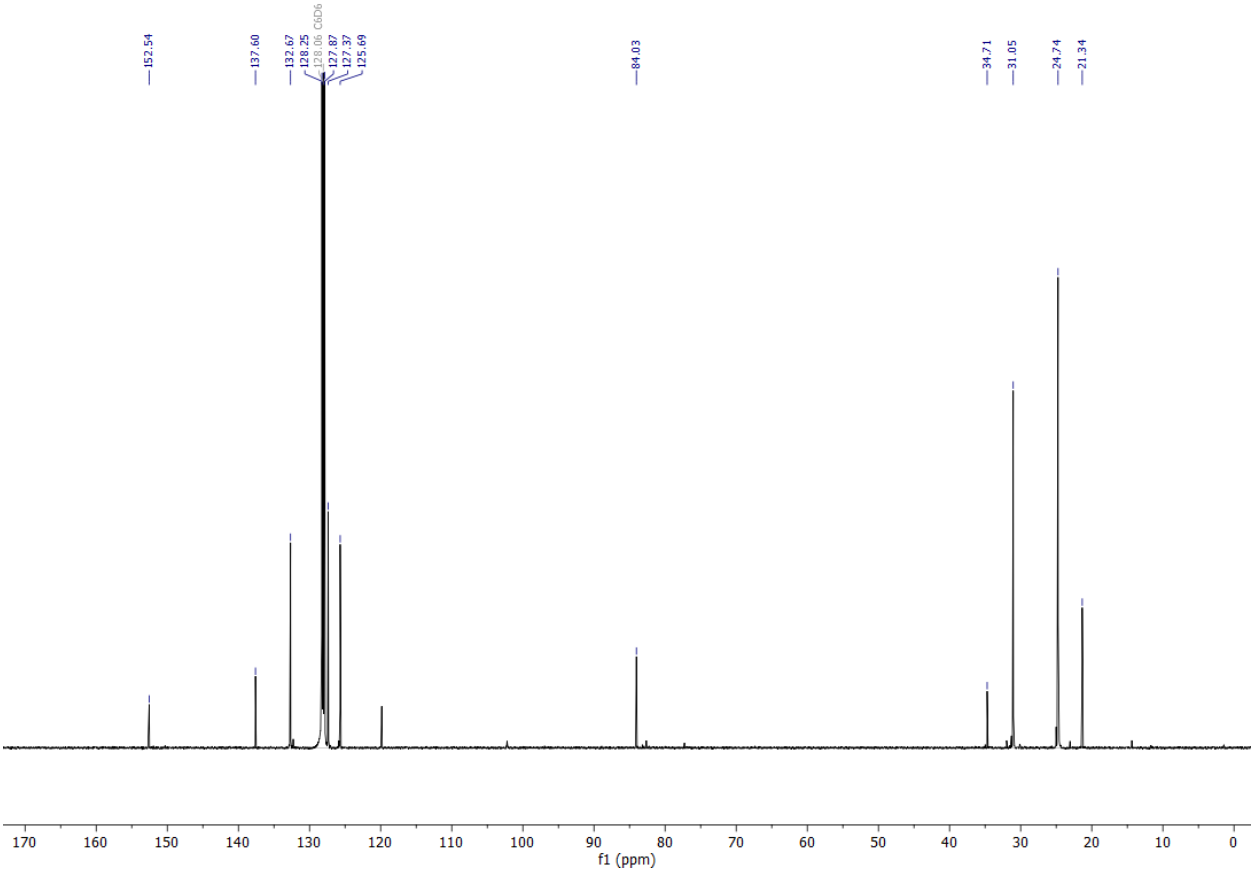
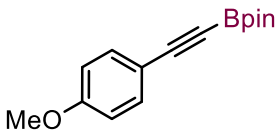


Figure S56: ^{13}C NMR(C_6D_6, 500MHz) of 2-((4-*tert*-butylphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.35, 127.36 and 137.60 ppm correspond to internal standard (mesitylene).



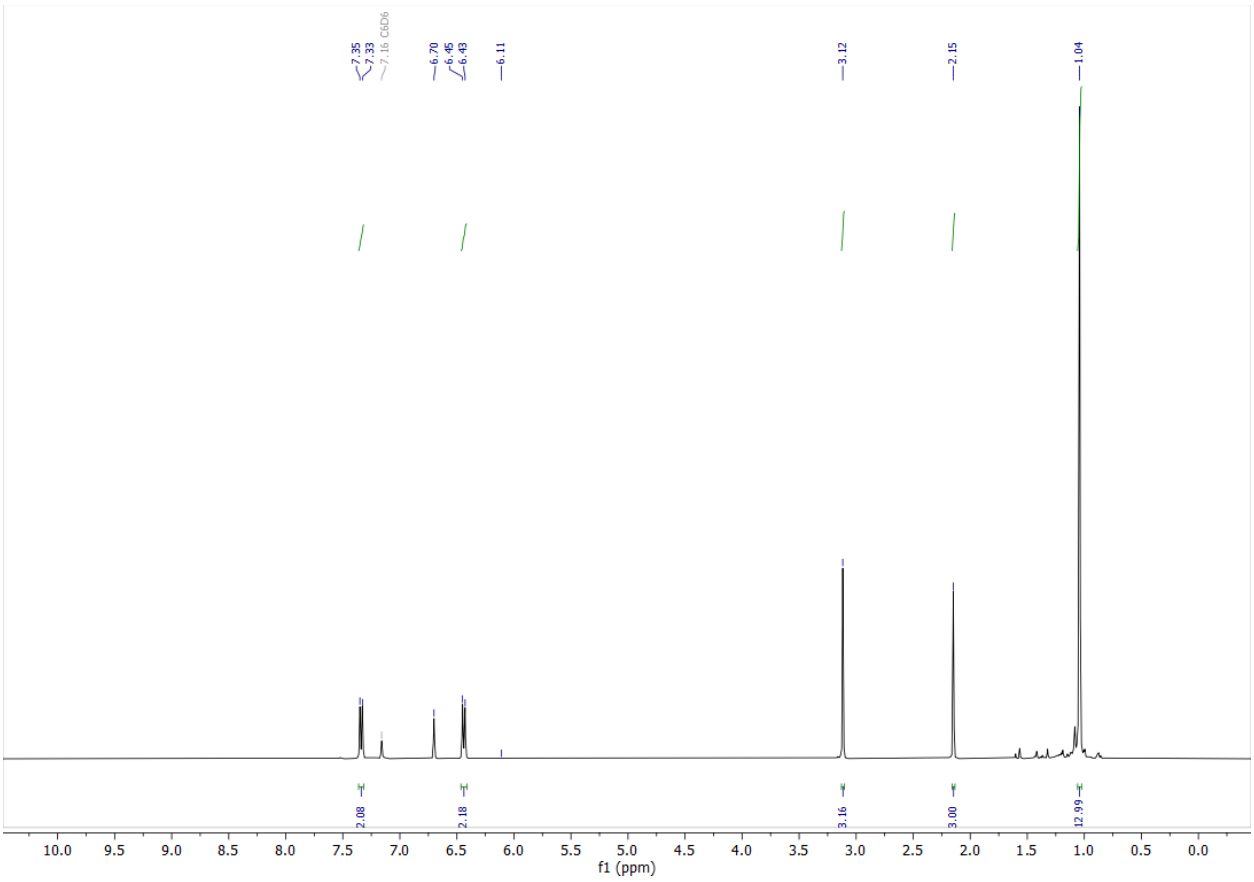


Figure S57: ^{1}H NMR (C_6D_6, 400MHz) of 2-((4-methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

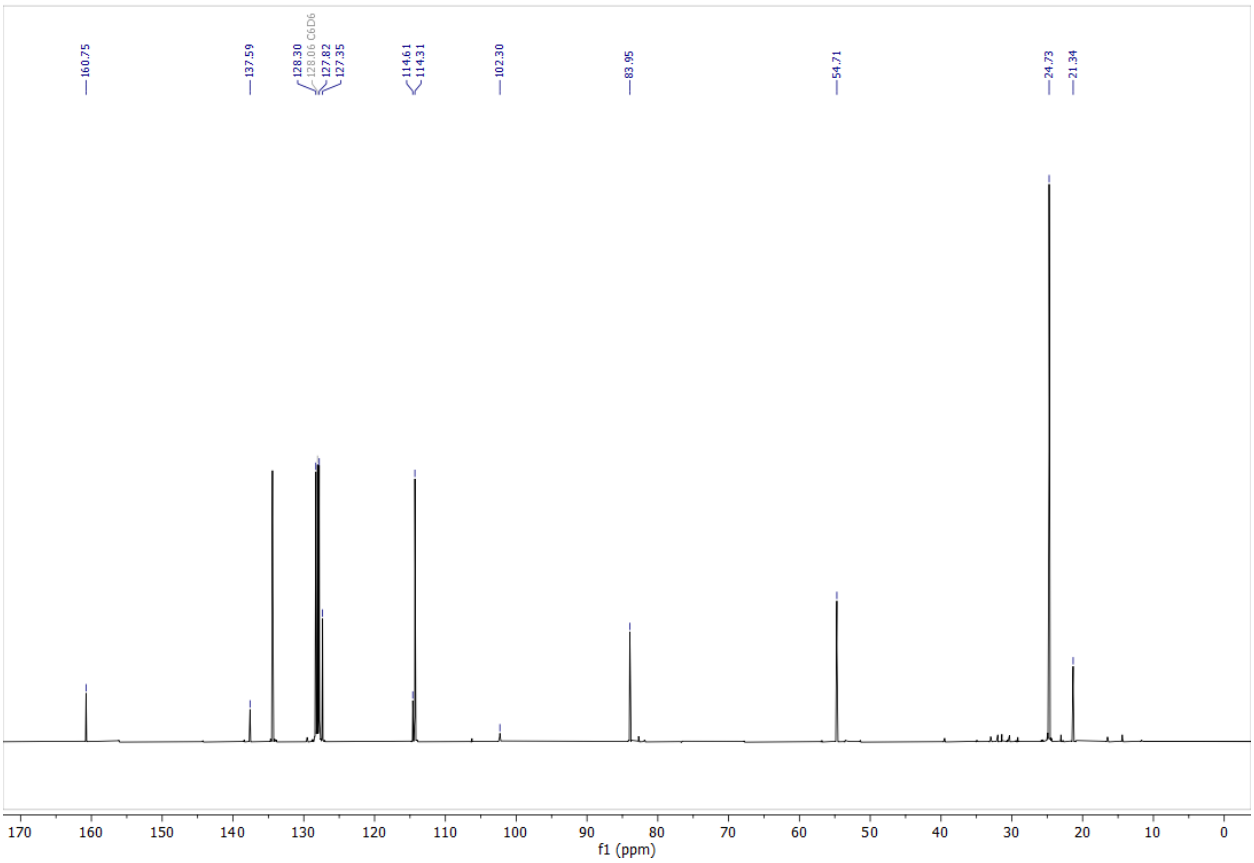
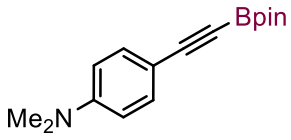


Figure S58: ^{13}C NMR (C_6D_6, 400MHz) of 2-((4-methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.34, 127.35 and 137.59 ppm correspond to internal standard (mesitylene).



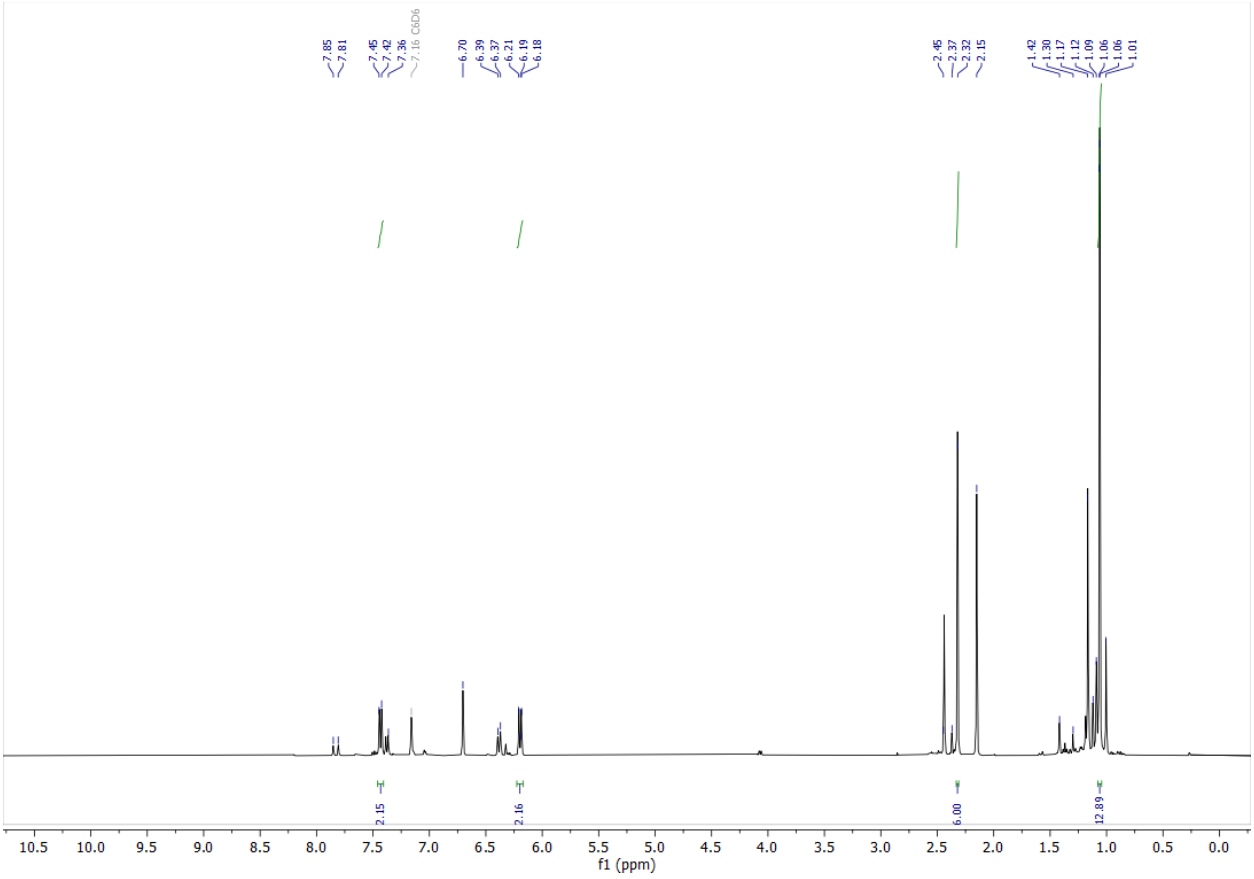


Figure S59: ^{1}H NMR (C_6D_6, 400MHz) of 2-((*p*-N,N dimethylaniline)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

Peaks at 1.09, 1.12, 1.17, 2.45, 6.37, 6.39, 7.36, 7.81 and 7.85 correspond to unidentified impurities.

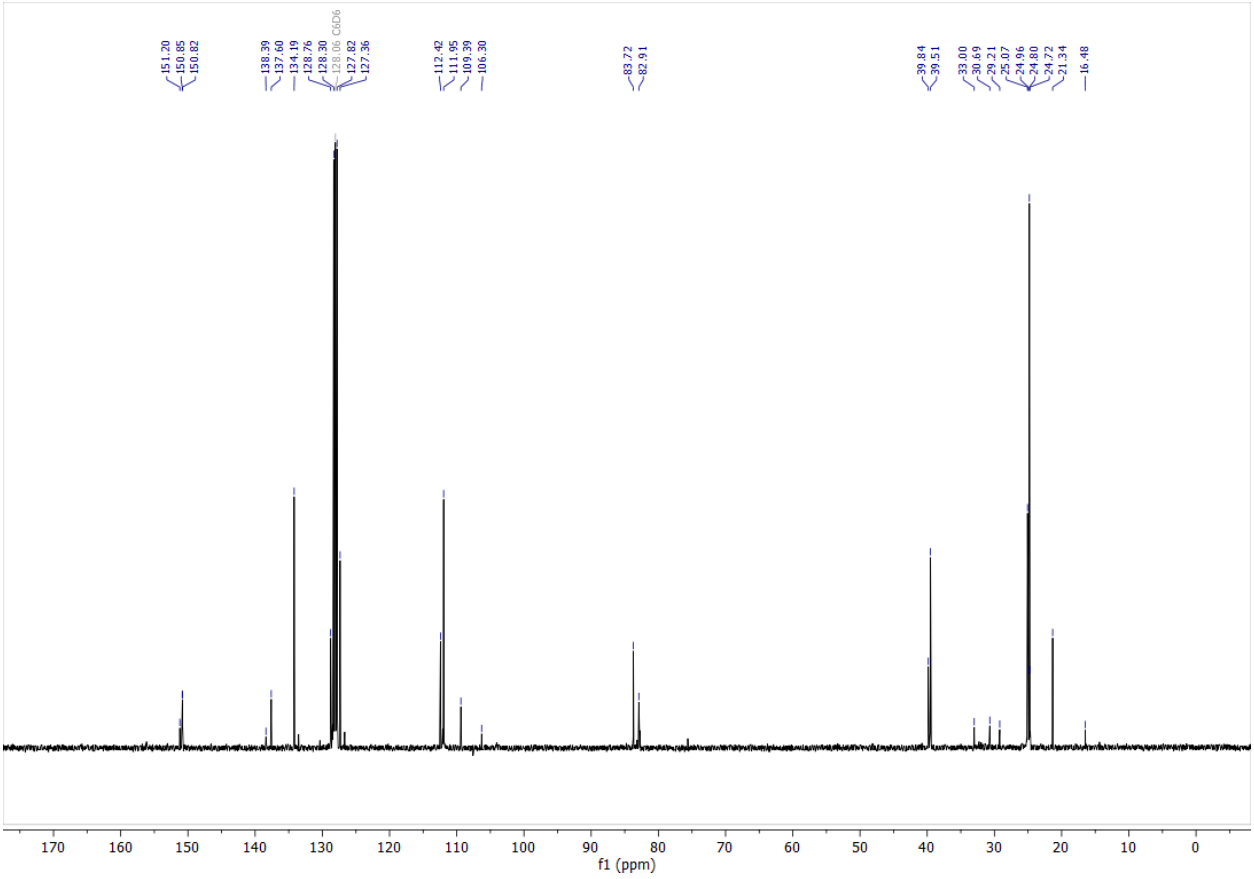
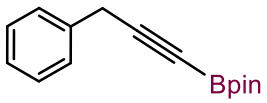


Figure S60: ^{13}C NMR (C_6D_6, 400MHz) of 2-((*p*-N,N dimethylaniline)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.34, 127.36 and 137.60 ppm correspond to internal standard (mesitylene).

Peaks at 24.72, 24.96, 25.07, 39.84, 82.91, 112.42, 128.76, 137.60 and 151.20 correspond to unidentified impurities.



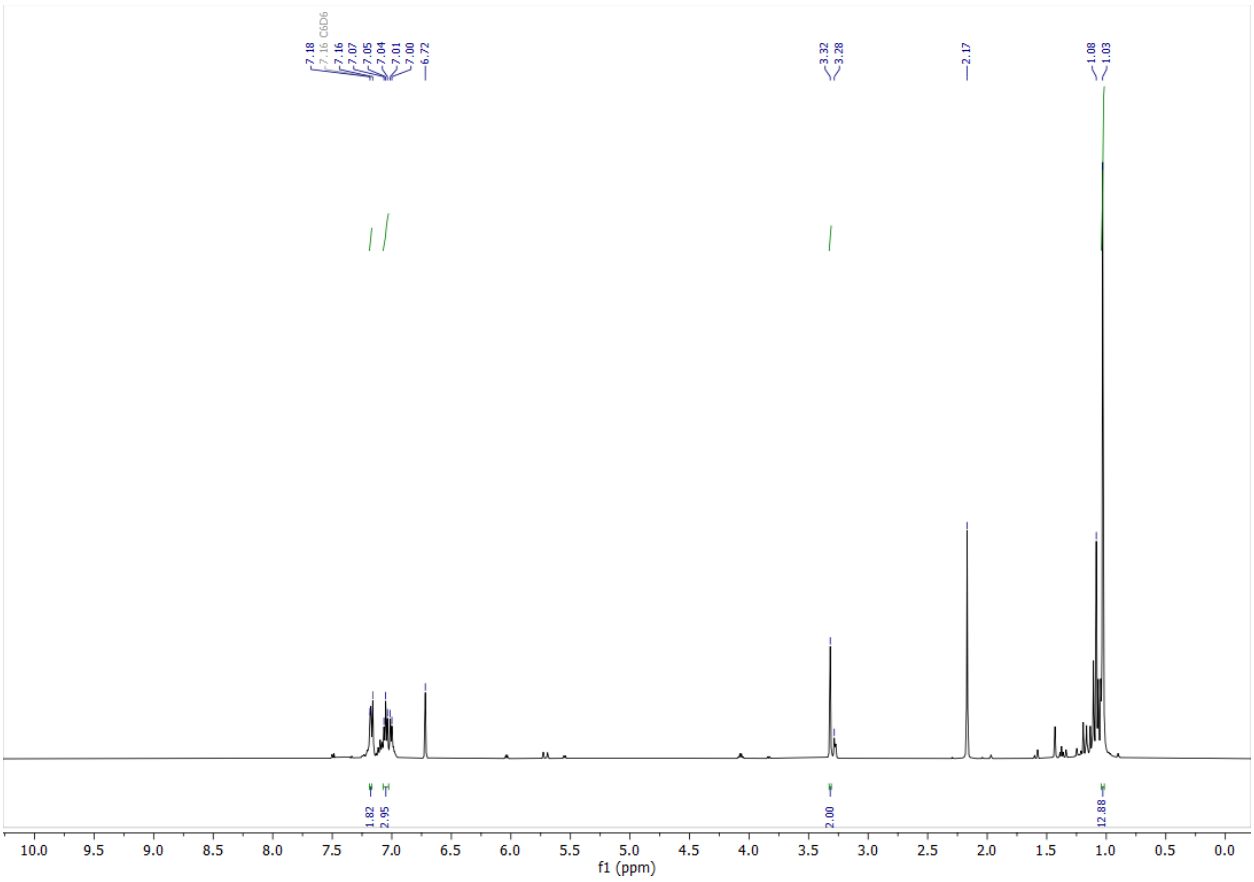


Figure S61: ^{1}H NMR (C_6D_6, 500MHz) of 4,4,5,5-tetramethyl-2-((3-phenylprop-1-yn-1-yl))-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

Peaks at 1.07, 1.08, 1.11, 3.28, 7.00 and 7.01 correspond to unidentified impurities.

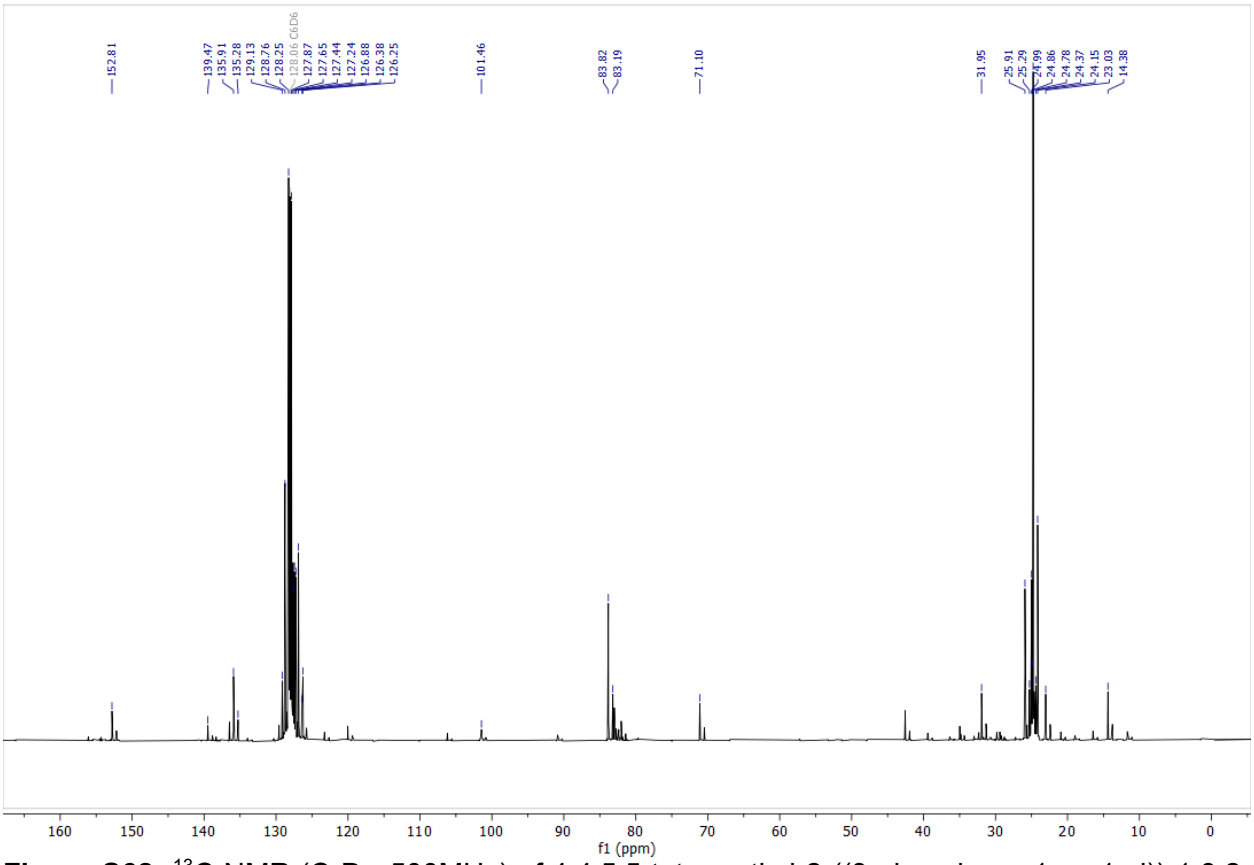
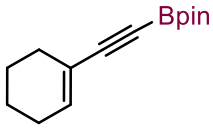


Figure S62: ^{13}C NMR (C_6D_6, 500MHz) of 4,4,5,5-tetramethyl-2-((3-phenylprop-1-yn-1-yl))-1,3,2-dioxaborolane

Peaks at 14.38, 23.03, 24.15, 24.37, 24.78, 24.86, 24.99, 25.29, 31.95, 71.10, 83.19, 126.25, 126.38, 127.24, 127.44, 127.65, 129.13 and 152.81 correspond to unidentified impurities.



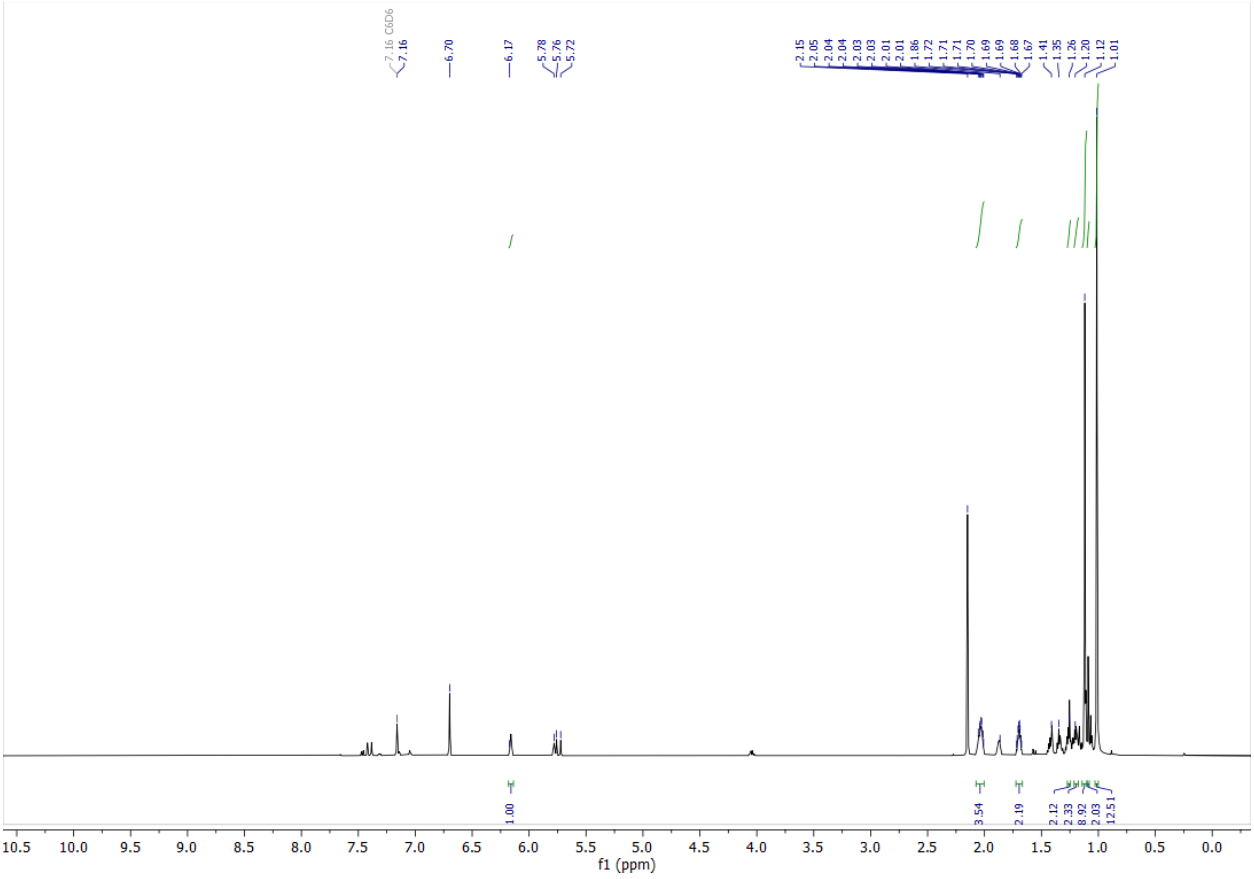


Figure S63: ^{1}H NMR (C_6D_6, 500MHz) of 2-[2-(1-cyclohexenyl)ethynyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

Peaks at 1.12, 1.35, 1.41, 5.72, 5.76 and 5.78 correspond to unidentified impurities.

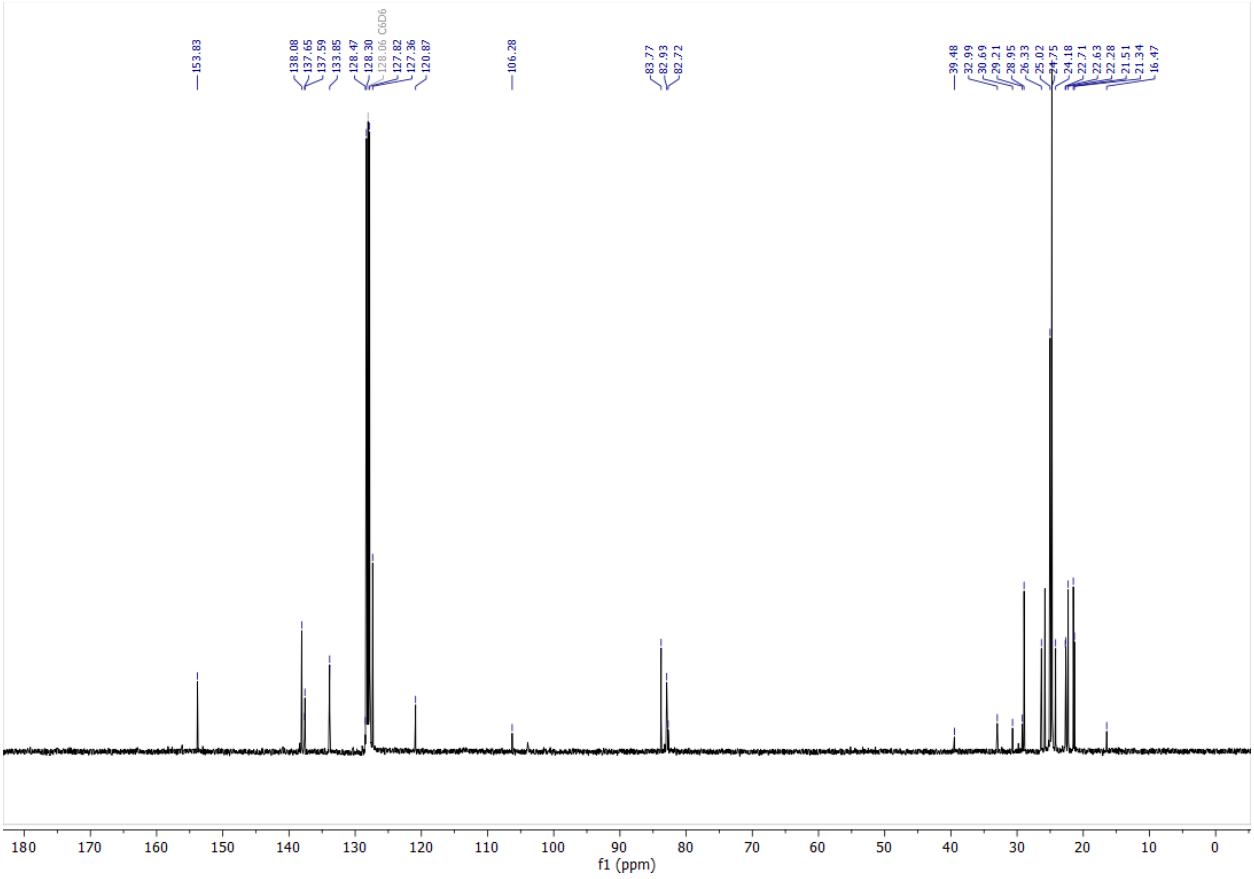
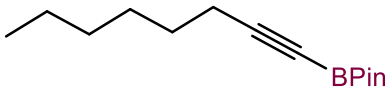


Figure S64: ^{13}C NMR (C_6D_6, 400MHz) of 2-[2-(1-cyclohexenyl)ethynyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Peaks at 21.34, 127.36 and 137.65 ppm correspond to internal standard (mesitylene).

Peaks at 22.63, 22.71, 24.18, 26.33, 29.21, 82.93, 133.85 and 153.83 correspond to unidentified impurities.



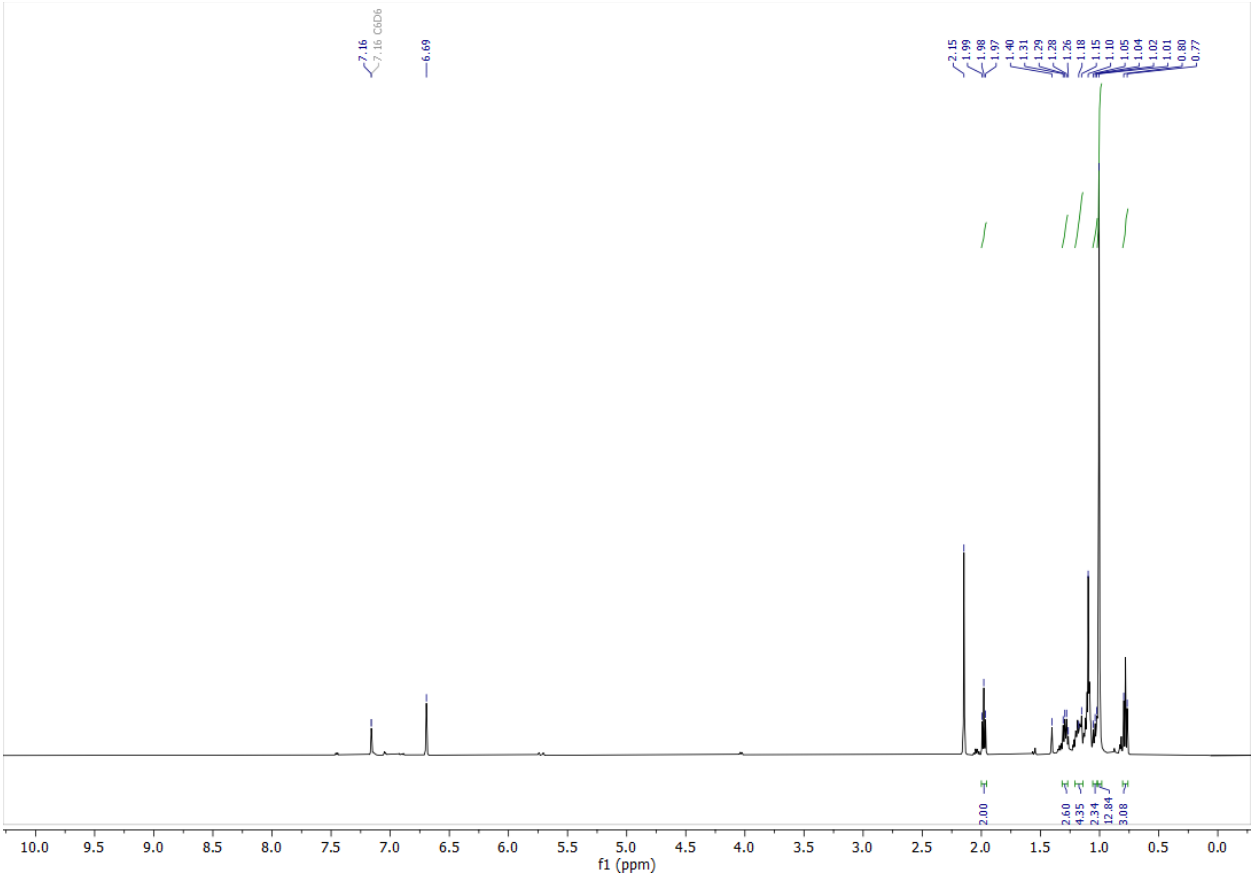


Figure S65: ^{1}H NMR (C_6D_6, 500MHz) of 4,4,5,5-tetramethyl-2-(oct-1yn-1yl)-1,3,2-dioxaborolane Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

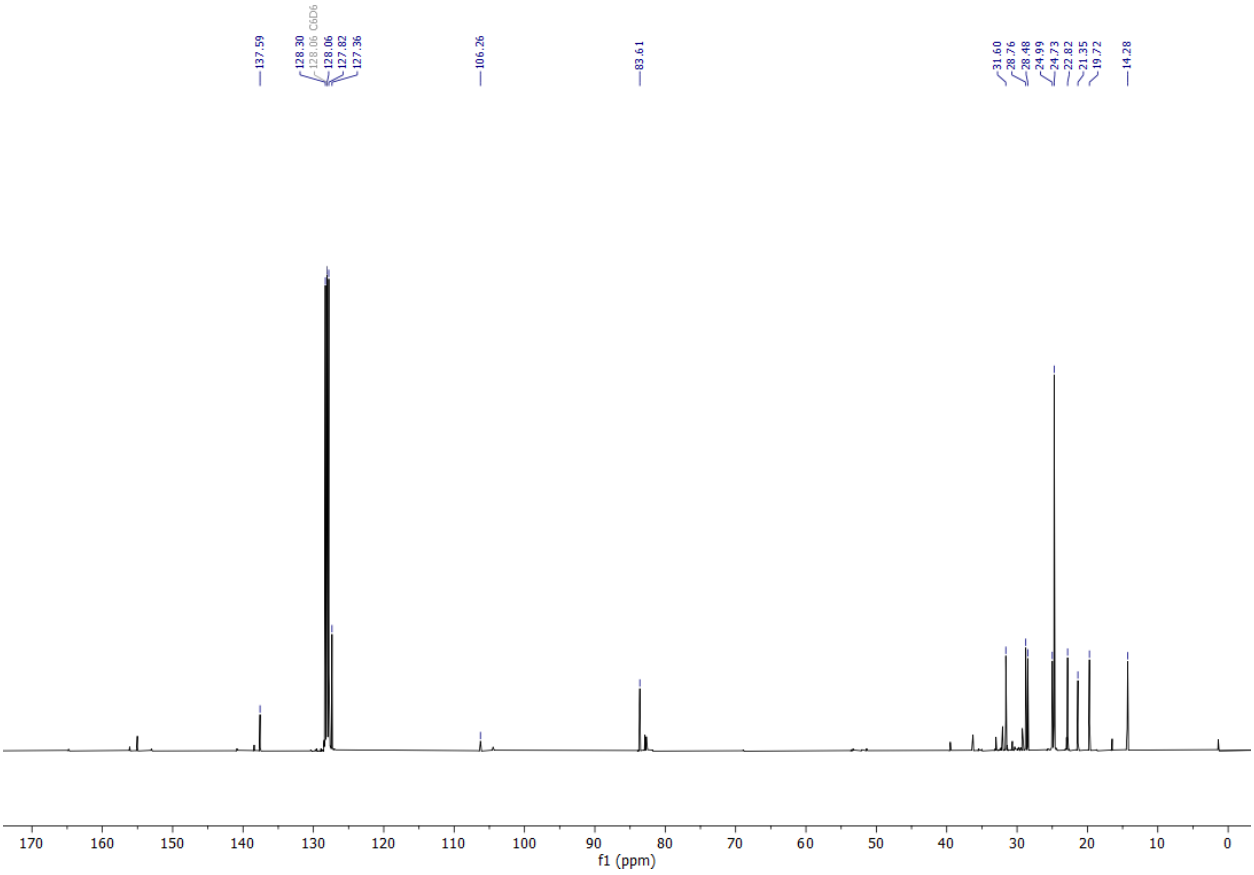
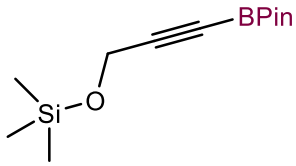


Figure S66: ^{13}C NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-(oct-1yn-1yl)-1,3,2-dioxaborolane

Peaks at 21.35, 127.36 and 137.59 ppm correspond to internal standard (mesitylene).

Peaks at 19.72, 24.99, 82.69 and 82.89 correspond to unidentified impurities.



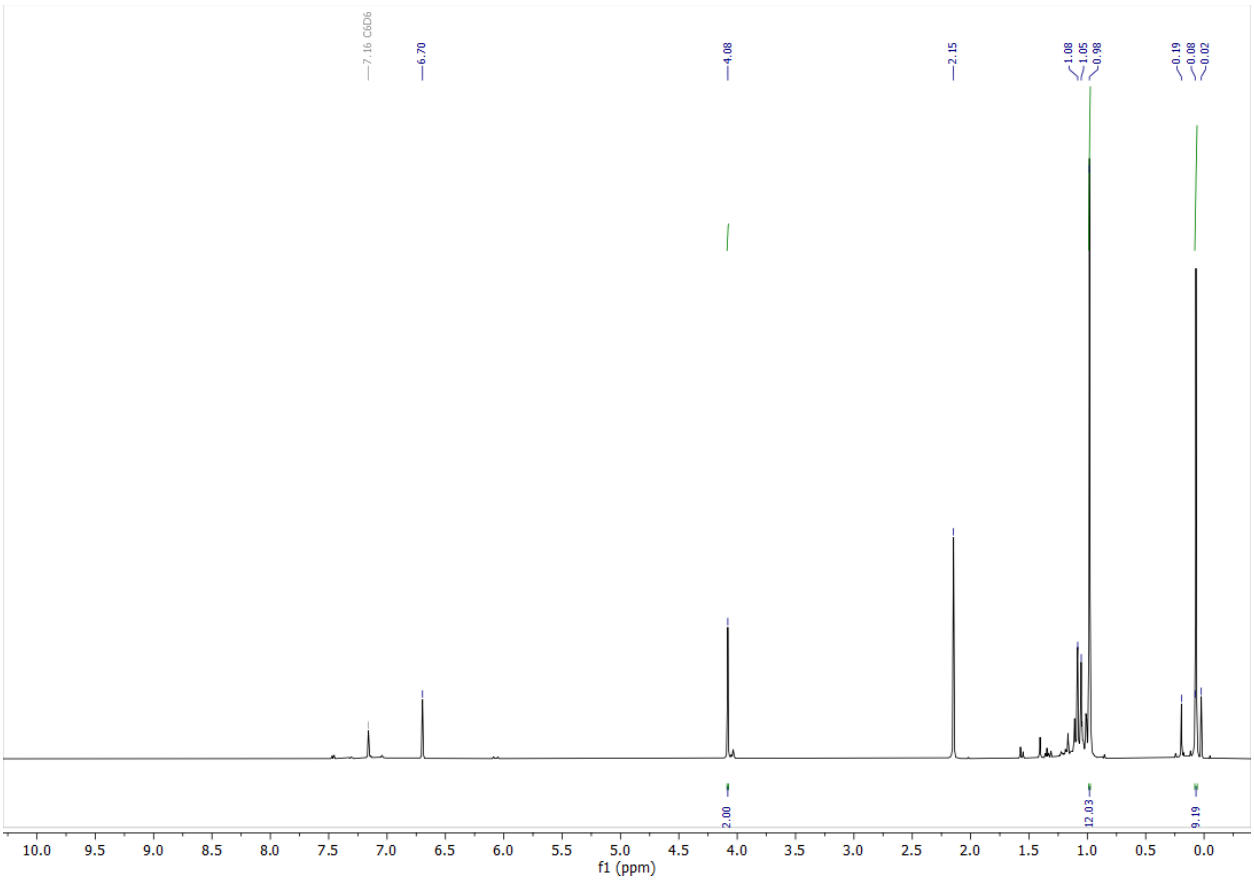


Figure S67: ^{1}H NMR (C_6D_6, 500MHz) of 4,4,5,5-Tetramethyl-2-(propargyloxytrimethylsilylethynyl)-1,3,2-dioxaborolane

Peaks at 2.15 and 6.70 ppm correspond to internal standard (mesitylene).

Peaks at 0.02, 0.19, 1.05 and 1.08 correspond to unidentified impurities.

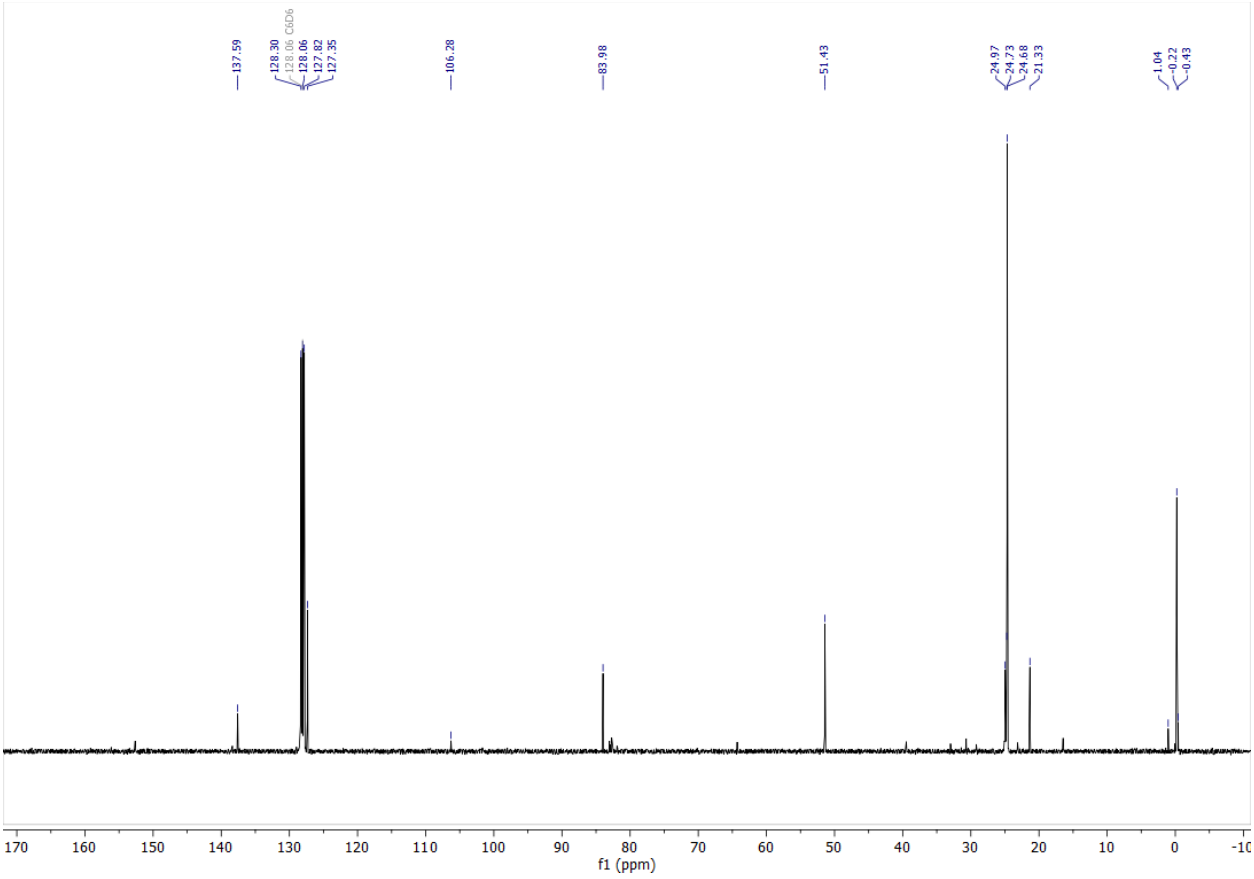
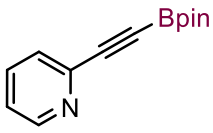


Figure S68: ^{13}C NMR (C_6D_6, 400MHz) of 4,4,5,5-Tetramethyl-2-(propargyloxytrimethylsilylethynyl)-1,3,2-dioxaborolane

Peaks at 21.33, 127.35 and 137.59 ppm correspond to internal standard (mesitylene).

Peaks at 0.22, 1.04, 24.97 and 106.28 correspond to unidentified impurities.



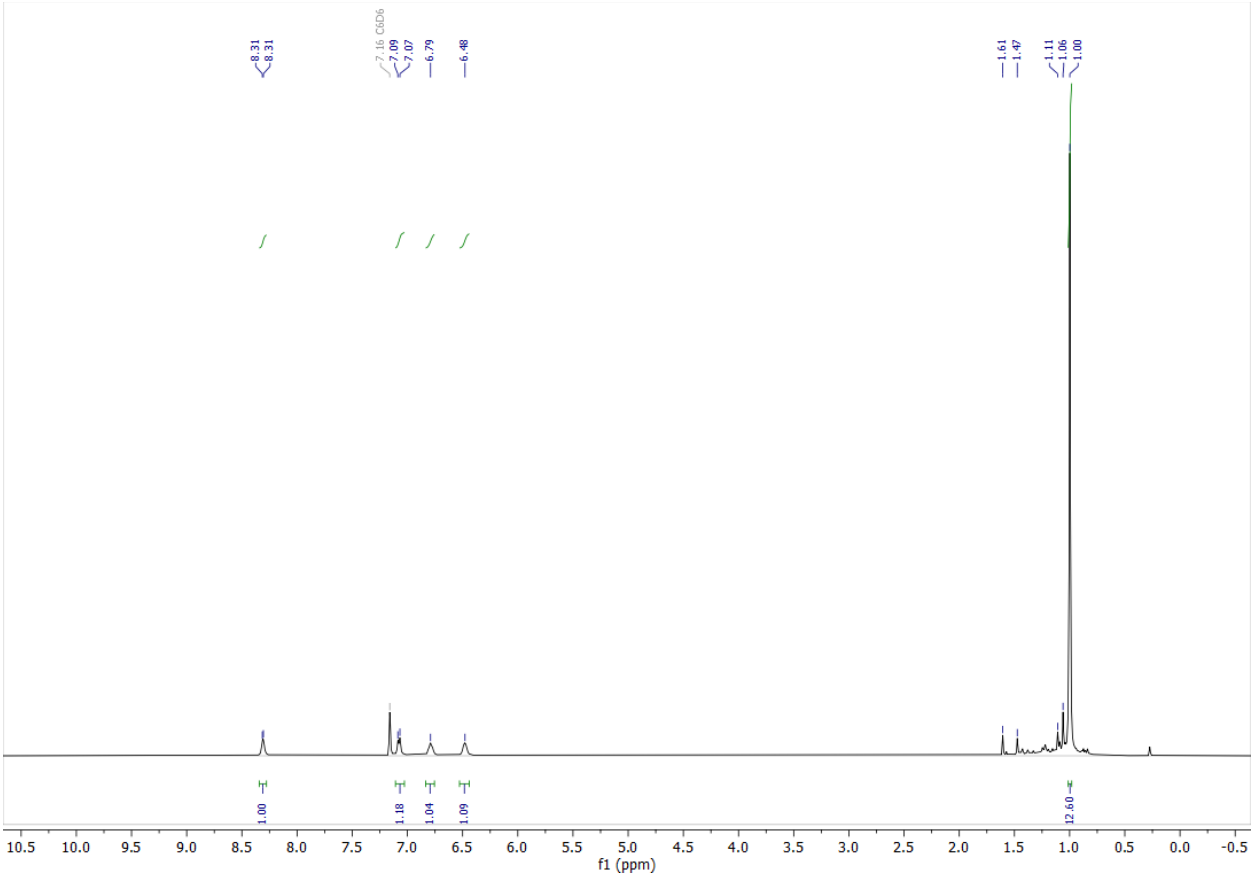


Figure S69: ^{1}H NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-(2-pyridylethynyl)-1,3,2-dioxaborolane

Peaks at 1.06, 1.11, 1.47 and 1.61 correspond to unidentified impurities.

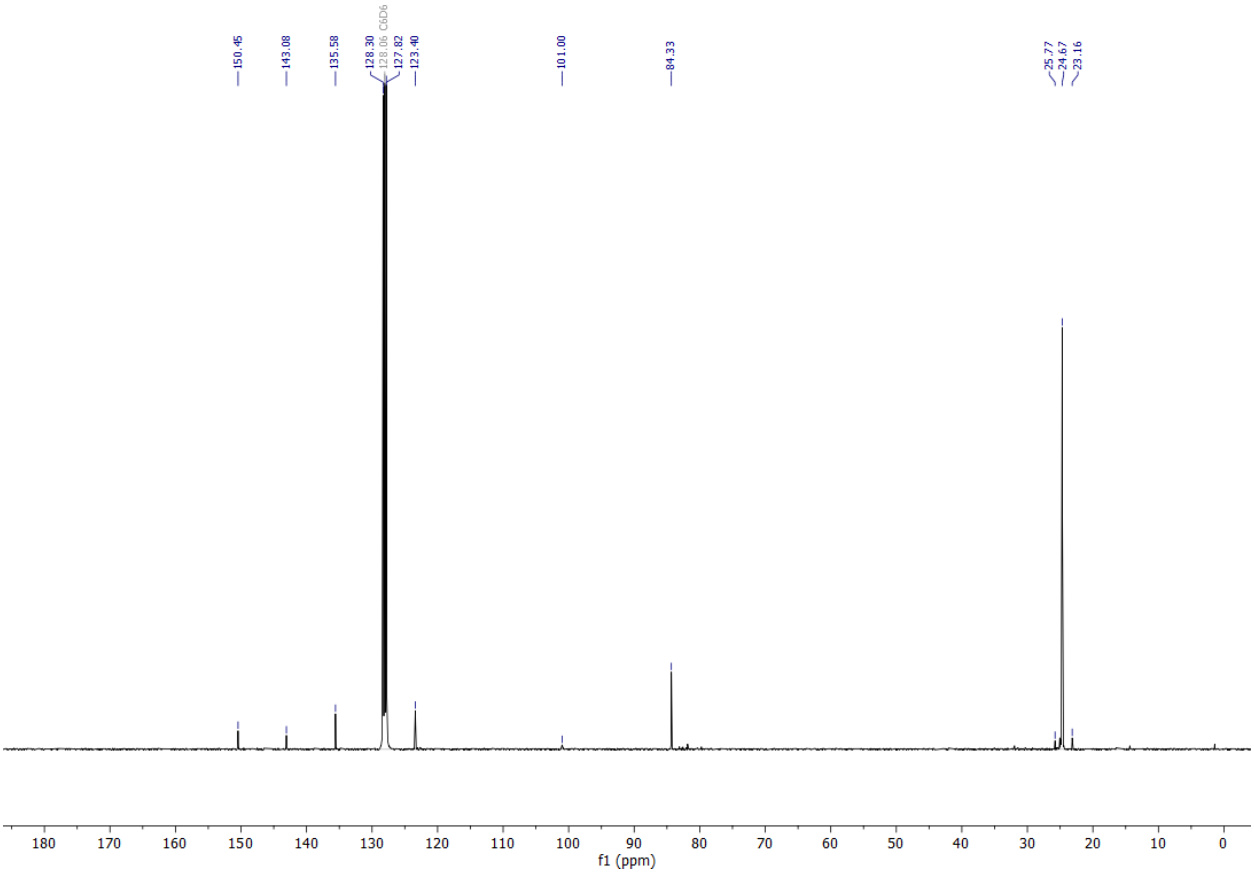


Figure S70: ^{13}C NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-(2-pyridylethynyl)-1,3,2-dioxaborolane

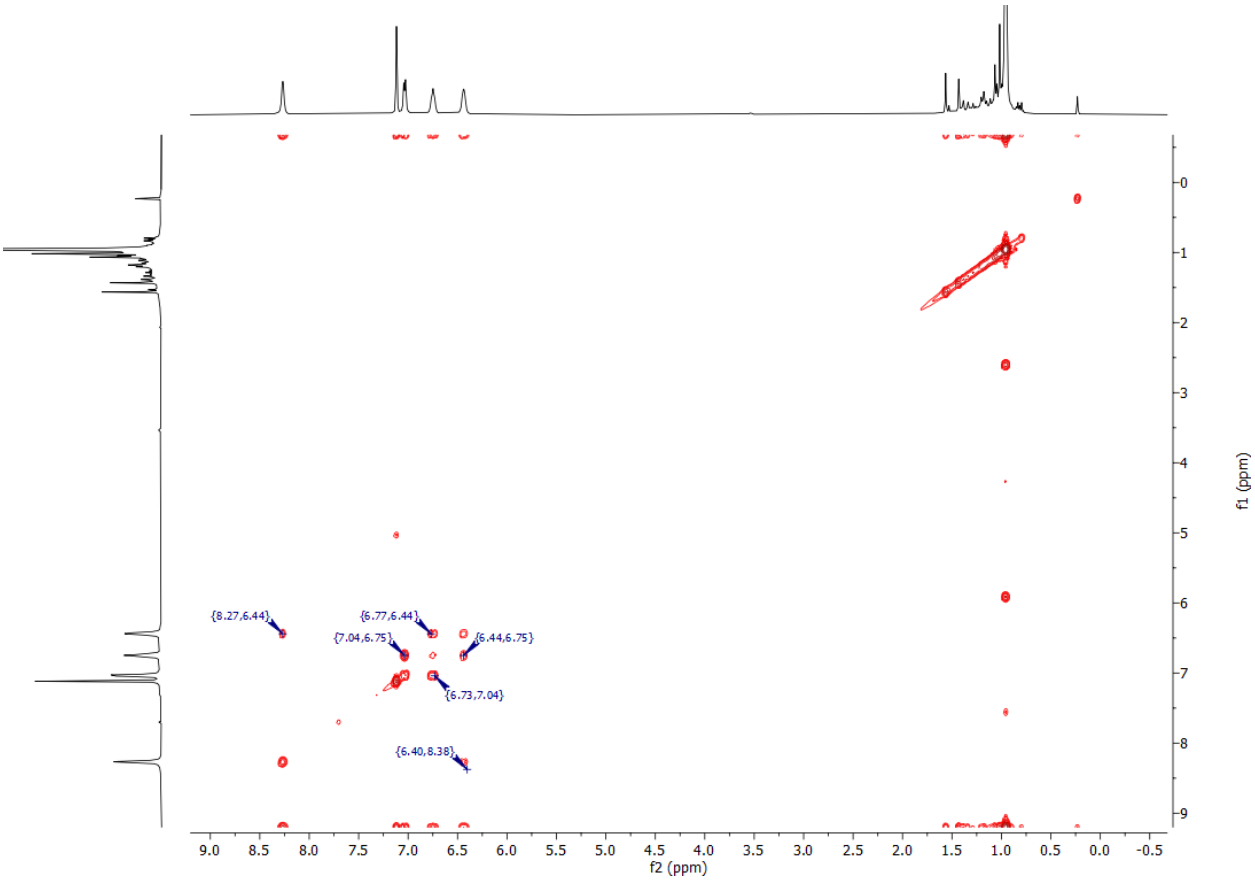


Figure S71: COSY NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-(2-pyridylethynyl)-1,3,2-dioxaborolane

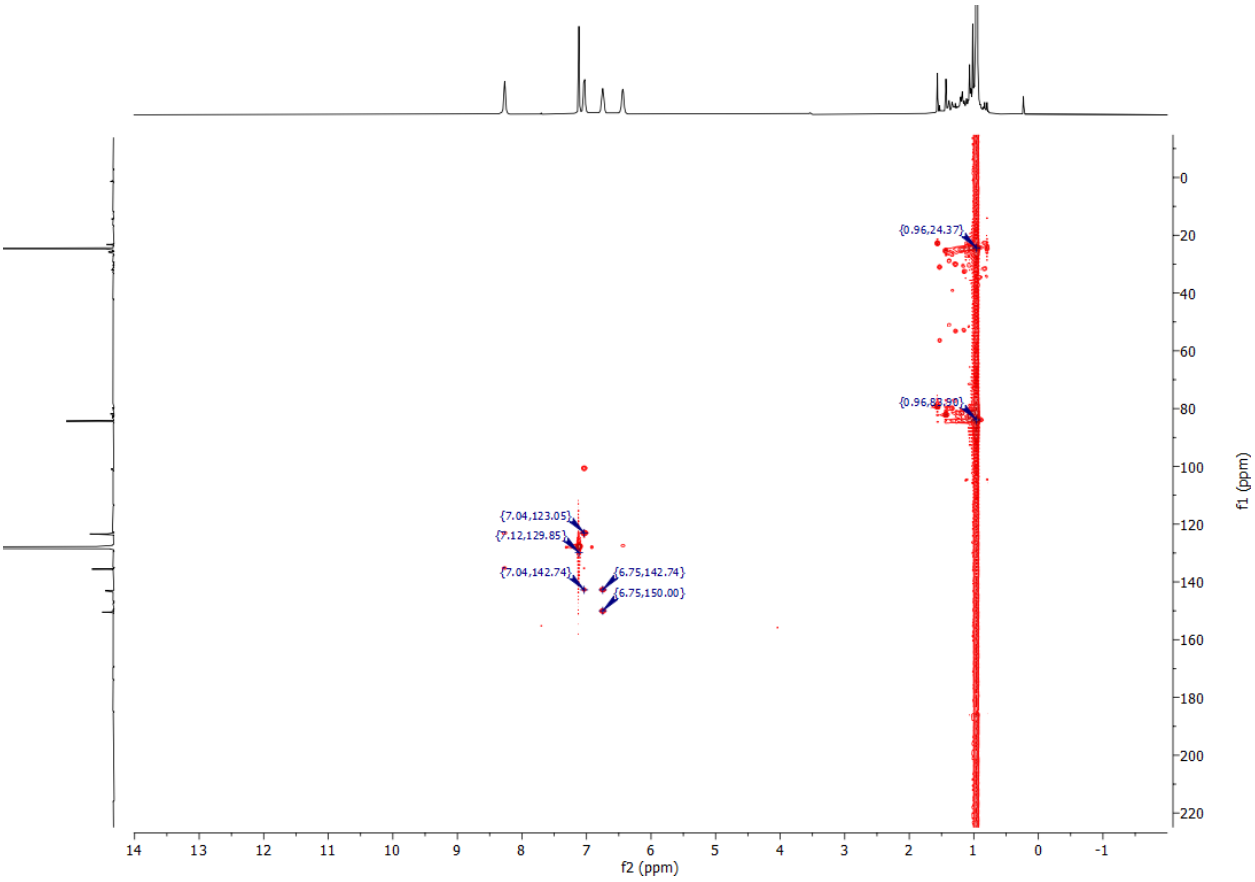


Figure S72: gHMBC NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-(2-pyridylethynyl)-1,3,2-dioxaborolane

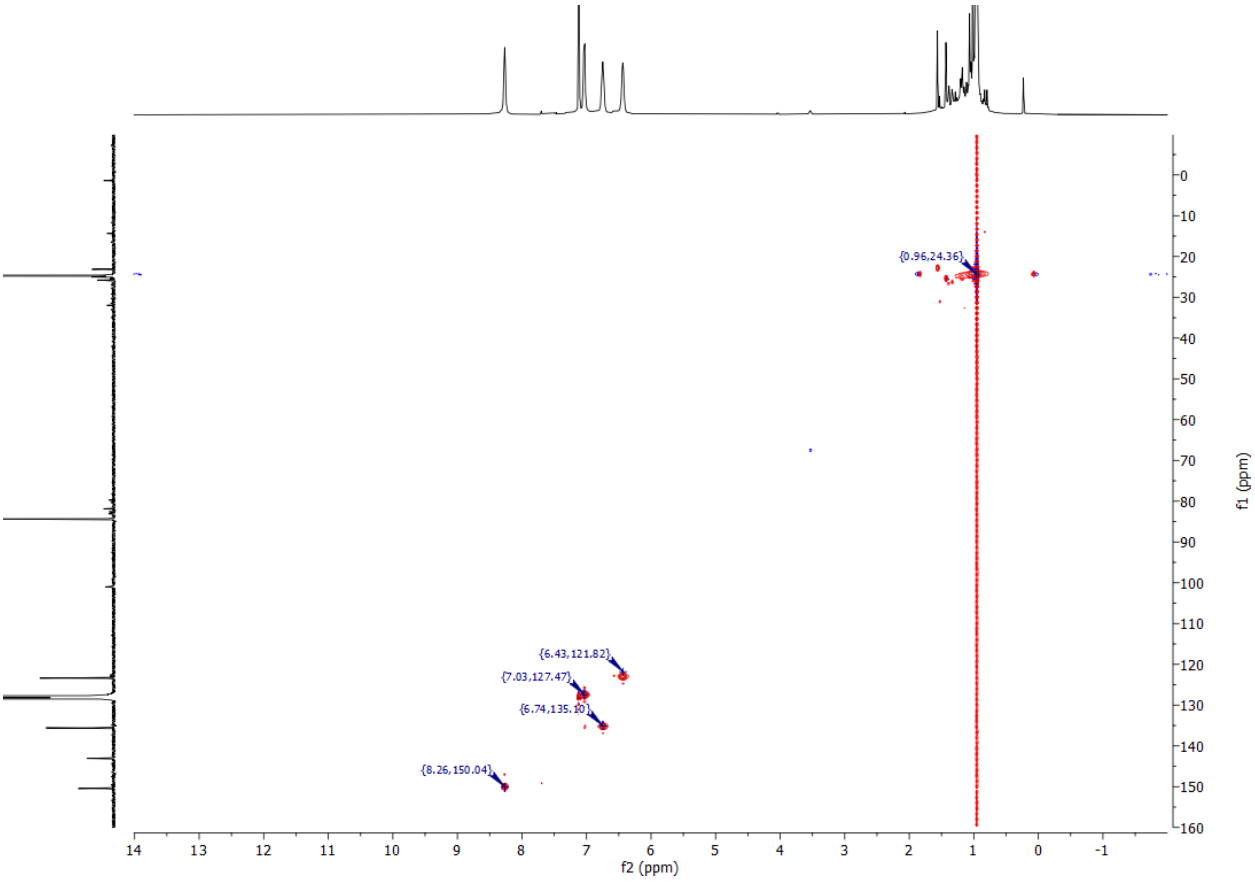


Figure S73: gHSQC NMR (C_6D_6, 400MHz) of 4,4,5,5-tetramethyl-2-(2-pyridylethynyl)-1,3,2-dioxaborolane

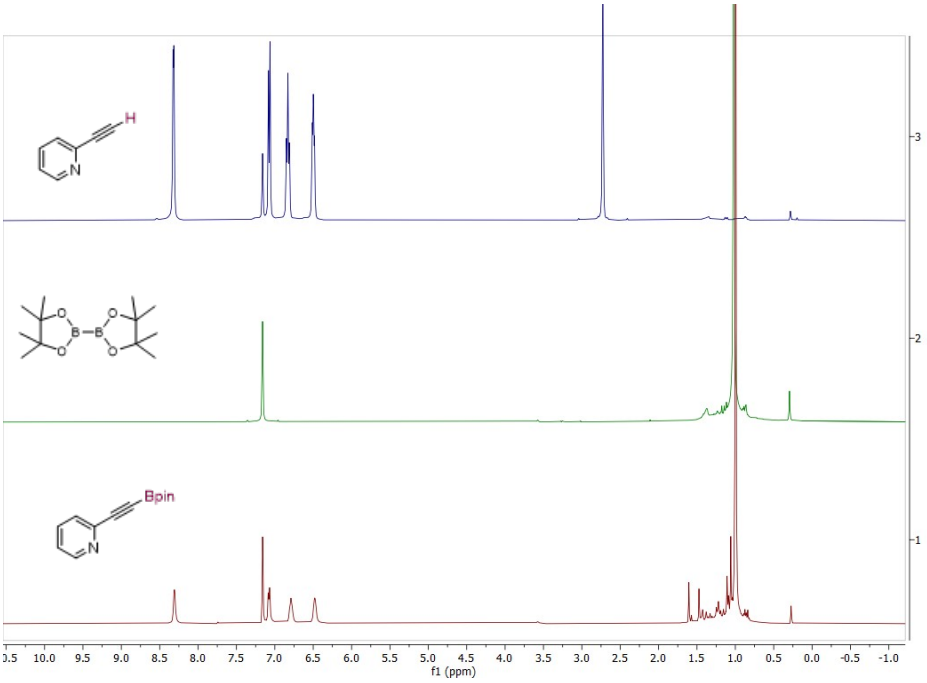


Figure S74: Stacked ^{1}H NMR (C_6D_6, 400MHz) of 2- ethynyl pyridine (top), bis(pinacolato)diboron (center) and 4,4,5,5-tetramethyl-2-(2-pyridylethynyl)-1,3,2-dioxaborolane (bottom).

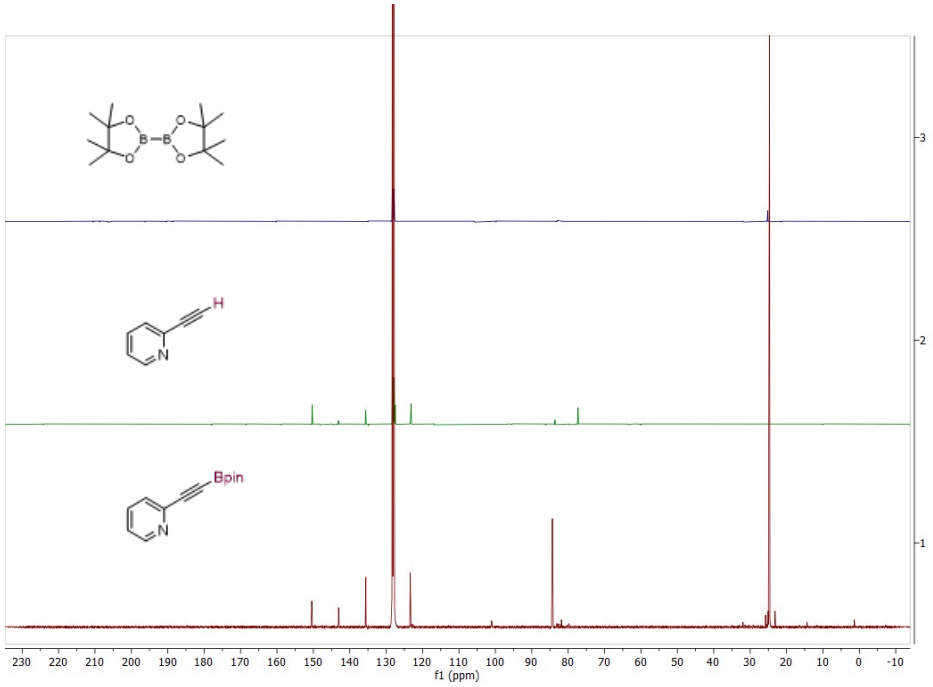


Figure S75: Stacked ^{13}C NMR(C_6D_6, 400MHz) of bis(pinacolato)diboron (top), 2-ethynyl pyridine (center) and 4,4,5,5-tetramethyl-2-(2-pyridylethynyl)-1,3,2-dioxaborolane (bottom).

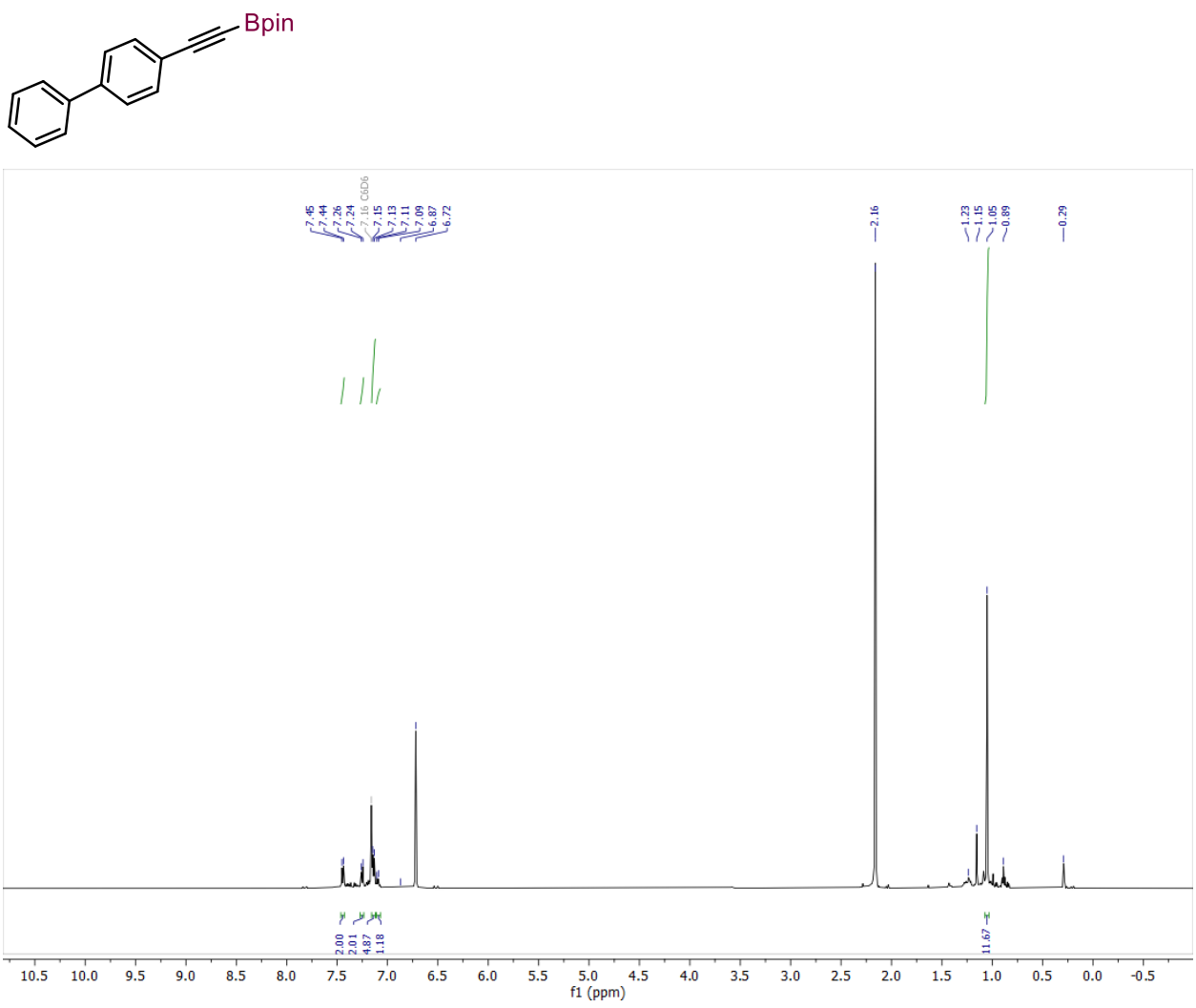


Figure S76: ^{1}H NMR (C_6D_6, 500MHz) of 2-((1,1'-biphenyl)-4-ylethynyl)-4,4,5,5-Tetramethyl-1,3,2-dioxaborolane

Peaks at 2.16 and 6.72 ppm correspond to internal standard (mesitylene).

Peaks at 0.29, 0.89, 1.15 and 1.23 ppm correspond to unidentified impurities.

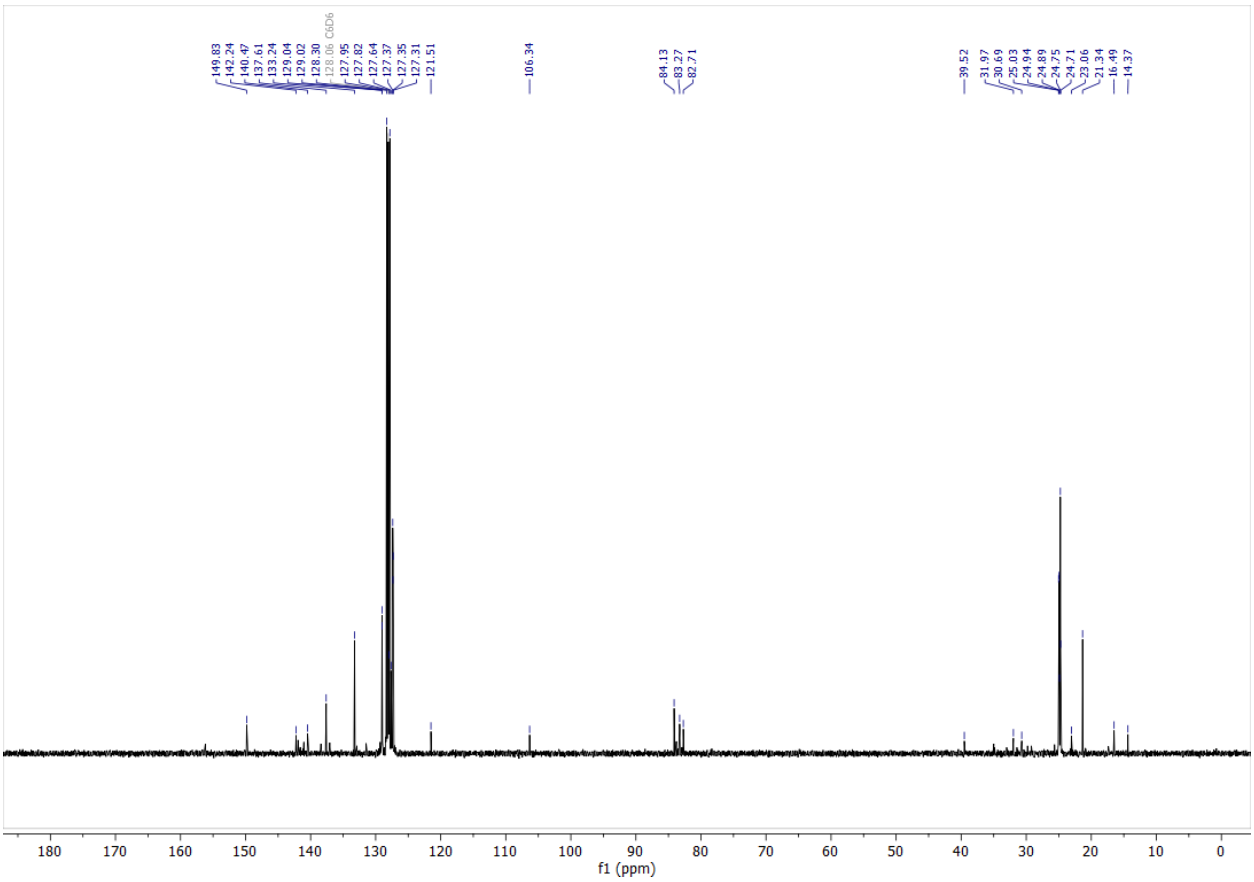


Figure S77: ^{13}C NMR (C_6D_6, 400MHz) 2-((1,1'-biphenyl)-4-ylethynyl)-4,4,5,5-Tetramethyl-1,3,2-dioxaborolane

Peaks at 21.34, 127.31 and 137.61 ppm correspond to internal standard (mesitylene).

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