

Supplementary Information

for

Lithium compounds as single site catalysts for hydroboration of alkenes and alkynes

Milan Kumar Bisai, Sandeep Yadav, Tamal Das, Kumar Vanka, and Sakya S. Sen*

Contents:

- ❖ General experimental information.
- ❖ Optimization table for hydroboration of styrene catalysed by **1a** and **1b**.
- ❖ General catalytic procedure for the hydroboration of alkene.
- ❖ Analytical data of boronate ester of corresponding alkenes.
- ❖ Optimization table for hydroboration of phenylacetylene catalysed by **1a** and **1b**.
- ❖ General catalytic procedure for the hydroboration of alkyne.
- ❖ Analytical data of boronate ester of corresponding alkyne.
- ❖ General catalytic procedure for the hydroboration of terpene.
- ❖ Analytical data of boronate ester of corresponding terpene.
- ❖ List of unsuccessful substrates for catalytic hydroboration.
- ❖ Competitive experiment for aldehyde/alkyne/alkene hydroboration-selectivity study.
- ❖ Deuterium labelling experiment.
- ❖ Mechanistic investigation.
- ❖ Kinetic Analysis (% of yield vs time (h) plot) for the hydroboration of phenylacetylene and styrene.
- ❖ Representative NMR spectra.
- ❖ Details of the theoretical calculations.
- ❖ References.

General experimental information:

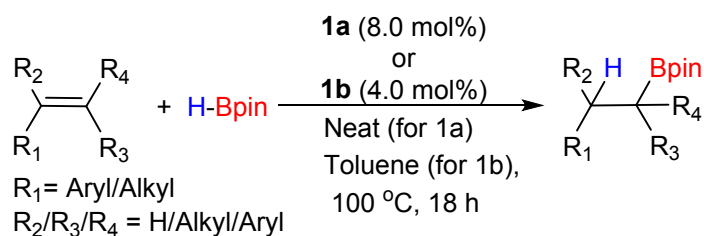
All reactions were carried out under argon atmosphere using Schlenk techniques or inside a MBraun glove box. Catalysts **1a** and **1b** were prepared according to the reported literature.¹⁻² Pinacolborane (HBpin), alkene and alkyne were purchased from Sigma-Aldrich, TCI Chemicals and used without further purification. Phenylacetylene-d₁ and Pinacolborane-d₁ were synthesized according to reported methodology.³⁻⁴ Toluene was collected from SPS and further dried by molecular sieves prior to use. C₆D₆, toluene-d₈, CD₃CN and CDCl₃ were purchased from Sigma-Aldrich, were degassed by three freeze-pump-thaw cycles and stored over molecular sieves. ¹H, ¹³C{¹H} and ¹¹B NMR spectra were recorded on Bruker AV-200 MHz, AV-400 MHz and AV-500 MHz and referenced to the resonances of the internal standard with respect to the solvent used.

Table S1. Optimization table of hydroboration of styrene catalysed by 1a and 1b.

Entry	Catalyst	Catalyst (mol%)	Solvent	Temperature (°C)	Time (h)	NMR Yield (%)
1.	1b	2.0	Toluene	100	24	84
2.	1b	3.0	Toluene	100	24	93
3.	1b	4.0	Toluene	100	24	96
4.	1b	3.0	Toluene	100	20	79
5.	1b	3.0	Toluene	100	18	75
6.	1b	4.0	Toluene	100	18	89
7.	1b	4.0	Toluene	100	15	84
8.	1b	5.0	Toluene	100	12	76
9.	1a	5.0	Acetonitrile	100	24	10
10.	1a	5.0	DMF	100	24	<5

11.	1a	5.0	DMSO	100	24	<5
12.	1a	5.0	1,4-Dioxane	100	24	46
13.	1a	5.0	Toluene	100	18	45
14.	1a	5.0	Neat	100	24	56
15.	1a	8.0	Neat	100	18	92
16.	1a	8.0	Neat	100	12	75

General catalytic procedure for the hydroboration of alkenes:

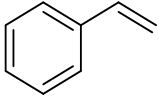
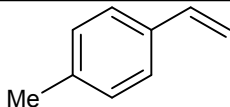
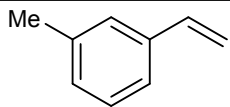
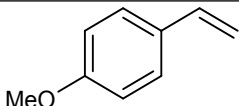
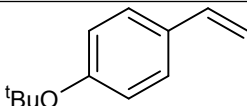
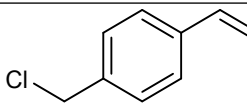
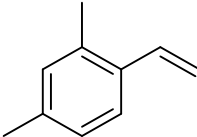
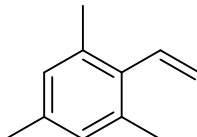
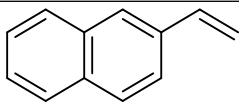


Scheme S1. General catalytic procedure for the hydroboration of alkenes.

Alkene (0.50 mmol), pinacolborane (1.1 equiv, 0.55 mmol), catalyst (8.0 mol% for **1a**, and 4.0 mol% for **1b**) were mixed together in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at 100 °C for 18 h in neat condition or in 0.5 mL toluene solvent for **1a** and **1b**, respectively. Volatiles of the mixture were removed under reduced pressure and mesitylene (0.5 mmol) as an internal standard, was added while making the NMR in appropriate deuterated solvent. The progress of the reaction was monitored by ¹H NMR, which indicated the completion of the reaction by the disappearance of alkene (RCH=CH₂) proton and appearance of a new RCH₂CH₂Bpin resonance.

Upon completion, the reaction mixture was eluted with Et₂O:hexane (2:8) mixture through a short plug of silica and the product was purified by silica gel column chromatography eluted with mostly EtOAc:hexane (02:98) mixture. Hydroboration product of four alkenes, namely **2e**, **2f**, **2g** and **2m** were isolated and in all the cases little discrepancy was observed with the NMR yield.

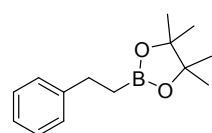
Table S2. Alkene substrate scope with anti Markovnikov: Markovnikov product ratio.

Entry	Substrate	Temperature (°C)	Time (h)	Catalyst 1a/1b (mol%)	NMR Yield (%)	Product	Selectivity
1.		100	18	8.0/4.0	92 ^a /89 ^b	2a	99:1 95:5
2.		100	18	8.0/4.0	97 ^a /96 ^b	2b	99:1 98:2
3.		100	18	8.0/4.0	88 ^a /86 ^b	2c	99:1 98:2
4.		100	18	8.0/4.0	92 ^a /93 ^b	2d	98:2 95:5
5.		100	18	8.0/4.0	81 ^a /85 ^b	2e	98:2 98:2
6.		100	18	8.0/4.0	81 ^a /59 ^b	2f	97:3 98:2
7.		100	18	8.0/4.0	90 ^a /92 ^b	2g	99:1 96:4
8.		100	18	8.0/4.0	65 ^a /62 ^b	2h	99:1 94:6
9.		100	18	8.0/4.0	73 ^a /74 ^b	2i	97:3 95:5

10.		100	18	8.0/4.0	87 ^a /65 ^b	2j	95:5 99:1
11.		100	18	8.0/4.0	58 ^a /51 ^b	2k	99:1 99:1
12.		100	18	8.0/4.0	66 ^a /68 ^b	2l	98:2 99:1
13.		100	18	8.0/4.0	93 ^a /96 ^b	2m	98:2 99:1
14.		100	18	8.0/4.0	92 ^a /64 ^b	2n	100 100
15.		100	18	8.0/4.0	87 ^a /65 ^b	2o	99:1 98:2
16.		100	18	8.0/4.0	69 ^a /66 ^b	2p	99:1 99:1

Analytical data of boronate esters of corresponding alkenes:

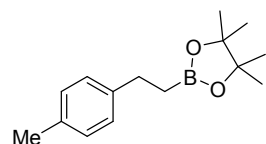
4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2a): ¹H NMR (CDCl₃, 200 MHz, 298 K):



δ 7.29-7.11 (m, 5H, ArH), 2.74 (t, 2H, ArCH₂CH₂), 1.19 (s, 12H, CH₃), 1.14 (t, 2H, ArCH₂CH₂) ppm; ¹³C{¹H} NMR (CDCl₃, 50.28 MHz, 298 K): δ 144.3, 128.2, 128.1, 127.9, 127.7, 125.4, 82.9, 29.9, 24.7 ppm.

The spectroscopic data is consistent with the literature data.⁵

4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (2b): ¹H NMR (CDCl₃, 200

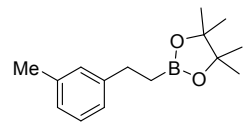


MHz, 298 K): δ 7.08-6.80 (m, 4H, ArH), 2.66 (t, 2H, ArCH₂CH₂), 2.21 (s, 3H, ArCH₃), 1.17-1.12 (s, 14H, CH₃ & ArCH₂CH₂) ppm; ¹³C{¹H} NMR

(CDCl₃, 50.28 MHz, 298 K): δ 141.2, 134.6, 128.7, 127.7, 82.9, 29.4, 24.6, 20.8 ppm.

The spectroscopic data is consistent with the literature data.⁶

4,4,5,5-tetramethyl-2-(3-methylphenethyl)-1,3,2-dioxaborolane (2c): ¹H NMR (CDCl₃, 200

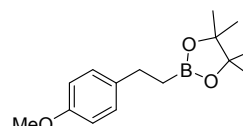


MHz, 298 K): δ 7.17-6.81 (m, 4H, ArH), 2.66 (t, 2H, ArCH₂CH₂), 2.23 (s, 3H, ArCH₃), 1.19-1.13 (s, 14H, CH₃ & ArCH₂CH₂) ppm; ¹³C{¹H} NMR (CDCl₃, 50.28 MHz, 298 K): δ 144.2, 128.7, 128.0, 126.1, 124.9, 82.9, 29.8,

24.7, 21.2 ppm.

The spectroscopic data is consistent with the literature data.⁷

2-(4-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d): ¹H NMR (C₆D₆, 200

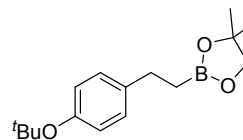


MHz, 298 K): δ 7.25-7.02 (m, 2H, ArH), 6.91-6.77 (m, 2H, ArH), 3.44 (s, 3H, -OMe), 2.86 (t, 2H, ArCH₂CH₂), 1.25 (t, 2H, ArCH₂CH₂), 1.11 (s, 12H, CH₃) ppm; ¹³C{¹H} NMR (C₆D₆, 50.28 MHz, 298 K): δ 158.5, 137.0, 130.6,

129.5, 114.3, 83.2, 55.0, 29.9, 25.2 ppm.

The spectroscopic data is consistent with the literature data.⁵

2-(4-(tert-butoxy)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e): According to

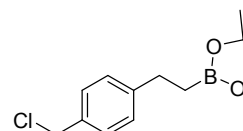


general procedure, 4-*tert*-Butoxystyrene (0.77 mmol, 137 mg), HBpin (0.78 mmol, 100 mg), **1b** (4.0 mol%, 9.0 mg) were reacted. The product was purified by silica gel column chromatography eluted with EtOAc:hexane (02:98) mixture to get the boronate ester **2e** (isolated yield: 181 mg, 76.5%)

as a colorless oil. ¹H NMR (CDCl₃, 200 MHz, 298 K): δ 7.17-7.01 (m, 2H, ArH), 6.82-6.79 (m, 2H, ArH), 2.66 (t, 2H, ArCH₂CH₂), 1.24 (s, 12H, CH₃), 1.18 (t, 2H, ArCH₂CH₂), 1.10 (s, 9H, -*O*Bu) ppm; ¹³C{¹H} NMR (C₆D₆, 50.28 MHz, 298 K): δ 154.2, 139.8, 129.1, 124.8, 124.6, 83.2, 77.7, 30.1, 29.3, 25.3 ppm.

The spectroscopic data is consistent with the literature data.⁷

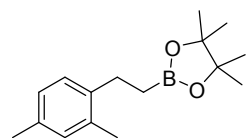
2-(4-(chloromethyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f): According to



general procedure, 4-Vinylbenzyl chloride (0.65 mmol, 100 mg), HBpin (0.65 mmol, 84 mg), **1a** (8.0 mol%, 14.9 mg) were reacted. The product

was purified by silica gel column chromatography eluted with EtOAc:hexane (01:99) mixture to get the boronate ester **2f** (isolated yield: 132 mg, 72.1%) as a colorless oil. ^1H NMR (CDCl_3 , 200 MHz, 298 K): δ 7.19-7.01 (m, 4H, ArH), 4.41 (s, 2H, ArCH₂Cl), 2.68 (t, 2H, ArCH₂CH₂), 1.17-1.13 (s, 14H, CH₃ & ArCH₂CH₂) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 144.5, 134.5, 128.2, 128.1, 82.8, 45.9, 29.5, 24.5 ppm; ^{11}B NMR (CDCl_3 , 128 MHz, 298 K): δ 34.0 ppm; LC-MS: m/z (%) = 245.2 [$\text{M}^+ - \text{Cl}$].

2-(2,4-dimethylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g): According to general

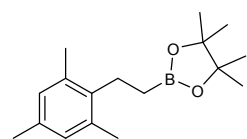


procedure, 2,4-Dimethylstyrene (0.78 mmol, 103mg), HBpin (0.78 mmol, 100 mg), **1a** (8.0 mol%, 17 mg) were reacted. The product was purified by silica gel column chromatography eluted with EtOAc:hexane (01:99) mixture

to get the boronate ester **2g** (isolated yield: 168 mg, 83.1%) as a colorless solid. ^1H NMR (CDCl_3 , 200 MHz, 298 K): δ 7.04-7.00 (d, $^3J_{\text{H-H}} = 8.27$ Hz, 1H, ArH), 6.87 (s, 2H, ArH), 2.63 (t, 2H, ArCH₂CH₂), 2.21 (s, 6H, ArCH₃), 1.16 (s, 12H, CH₃), 1.03 (t, 2H, ArCH₂CH₂) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.56 MHz, 298 K): δ 139.2, 135.2, 134.6, 130.6, 127.8, 126.2, 82.7, 26.6, 24.6, 20.6, 19.0 ppm.

The spectroscopic data is consistent with the literature data.⁵

4,4,5,5-tetramethyl-2-(2,4,6-trimethylphenethyl)-1,3,2-dioxaborolane (2h): ^1H NMR (CDCl_3 ,

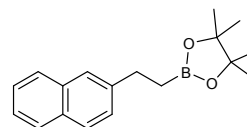


200 MHz, 298 K): δ 6.82 (s, 2H, ArH), 2.71 (t, 2H, ArCH₂CH₂), 2.32 (s, 6H, ArCH₃), 2.29 (s, 3H, ArCH₃), 1.28 (s, 12H, CH₃), 0.99 (t, 2H, ArCH₂CH₂) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.56MHz, 298 K): δ 138.3, 135.3, 135.3,

128.7, 128.4, 82.8, 24.6, 24.6, 20.6, 19.4 ppm.

The spectroscopic data is consistent with the literature data.⁵

4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (2i): ^1H NMR (CDCl_3 ,

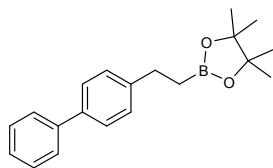


500 MHz, 298 K): δ 7.90-7.84 (m, 3H, ArH), 7.77 (s, 1H, ArH), 7.55-7.48 (m, 3H, ArH), 3.05 (t, 2H, ArCH₂CH₂), 1.36 (t, 2H, ArCH₂CH₂), 1.32 (s, 12H, CH₃) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125.70 MHz, 298 K): δ 141.8, 133.6,

131.8, 127.6, 127.5, 127.3, 127.2, 125.6, 124.8, 83.0, 30.0, 24.7 ppm.

The spectroscopic data is consistent with the literature data.⁷

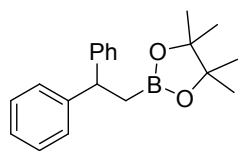
2-(2-([1,1'-biphenyl]-4-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j): ^1H NMR



(C_6D_6 , 200 MHz, 298 K): δ 7.53-7.43 (m, 4H, ArH), 7.30-7.16 (m, 5H, ArH), 2.90 (t, 2H, ArCH₂CH₂), 1.08 (s, 12H, CH₃), 1.04 (t, 2H, ArCH₂CH₂) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.56 MHz, 298 K): δ 137.8, 129.3, 129.2, 127.7, 127.6, 83.3, 30.5, 25.3 ppm.

The spectroscopic data is consistent with the literature data.⁵

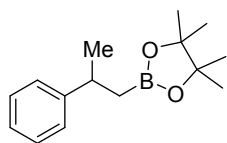
2-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k): ^1H NMR (CDCl_3 , 200



MHz, 298 K): δ 7.32-6.94 (m, 10H, ArH), 4.33 (t, 1H, ArCHPh), 1.25 (s, 12H, CH₃), 1.06 (d, 2H, ArCH(Me)CH₂) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 150.0, 146.7, 141.3, 128.3, 128.1, 125.7, 82.8, 46.4, 31.5, 24.4 ppm.

The spectroscopic data is consistent with the literature data.⁶

4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (2l): ^1H NMR (CDCl_3 , 200 MHz,

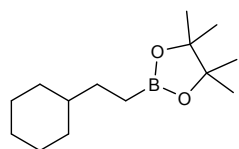


298 K): δ 7.23-7.02 (m, 5H, ArH), 3.10-2.93 (sextet, 1H, ArCHMe), 1.25 (d, 2H, ArCH(Me)CH₂), 1.20-1.08 (br, 14H, CH₃) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 149.0, 128.0, 126.5, 126.5, 82.7, 35.7, 24.7, 24.6, 24.5

ppm.

The spectroscopic data is consistent with the literature data.⁵

2-(2-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m): According to general

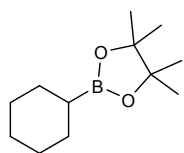


procedure, Vinylcyclohexane (0.78 mmol, 86 mg), HBpin (0.78 mmol, 100 mg), **1b** (4.0 mol%, 9mg) were reacted. The product was purified by silica gel column chromatography eluted with EtOAc:hexane (02:98) mixture to get the boronate ester **2m** (isolated yield: 165 mg, 88.7%) as a colorless liquid. ^1H NMR(CDCl_3 , 200

MHz, 298 K): δ 1.69-1.58 (m, 4H), 1.26-1.14 (m, 17H), 1.14-1.07 (m, 2H), 0.83-0.85 (m, 4H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125.70 MHz, 298 K): δ 82.5, 39.8, 32.9, 31.2, 26.6, 26.3, 24.6 ppm.

The spectroscopic data is consistent with the literature data.⁵

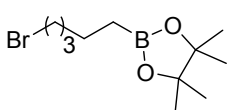
2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n): ^1H NMR (CDCl_3 , 200MHz, 298



K): δ 1.72-1.50 (m, 5H), 1.30-1.19 (m, 17H), 0.93-0.90 (m, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125.70 MHz, 298 K): δ 82.6, 27.9, 27.2, 26.4, 24.6 ppm.

The spectroscopic data is consistent with the literature data.⁸

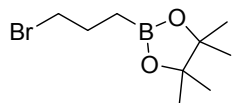
2-(5-bromopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o): ^1H NMR (CDCl_3 , 200 MHz,



298 K): δ 3.30 (t, 2H, CH_2Br), 1.80 (q, 2H, CH_2), 1.37 (br, 4H, CH_2), 1.17 (s, 12H, CH_3), 0.74 (t, 2H, CH_2) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 82.6, 33.4, 32.4, 30.5, 24.5, 23.0 ppm.

The spectroscopic data is consistent with the literature data.⁹

2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p): ^1H NMR (CDCl_3 , 200 MHz,



298 K): δ 3.33 (t, 2H, CH_2Br), 1.90 (q, 2H, CH_2), 1.17 (s, 12H, CH_3), 0.92-0.82 (m, 2H, CH_2) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 82.9, 35.7, 27.3, 24.5 ppm.

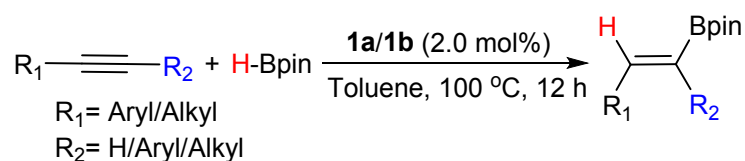
The spectroscopic data is consistent with the literature data.⁵

Table S3. Optimization table of hydroboration of phenylacetylene catalysed by 1a and 1b.

Entry	Catalyst	Catalyst (mol%)	Solvent	Temperature (°C)	Time (h)	NMR Yield (%)
1.	1a	0.5	Toluene	100	18	35
2.	1a	1.0	Toluene	100	18	64
3.	1a	2.0	Toluene	100	12	92
4.	1a	3.0	Toluene	100	12	94
5.	1a	2.0	Toluene	100	10	85
6.	CpLi	2.0	Toluene	100	12	65
7.	1b	0.5	Toluene	100	18	55

8.	1b	1.0	Toluene	100	18	76
9.	1b	2.0	Toluene	100	12	90
10.	1b	3.0	Toluene	100	12	93
11.	1b	3.0	Toluene	80	16	72
12.	1b	2.0	Toluene	100	10	80

General catalytic procedure for the hydroboration of alkynes:

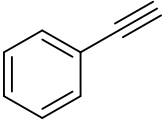
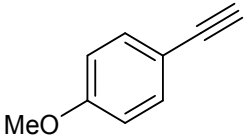
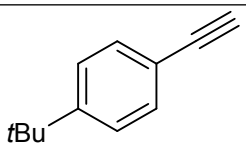
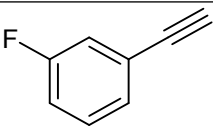
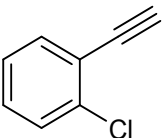
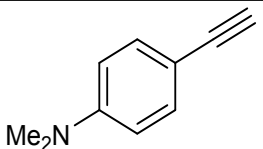
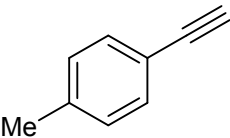
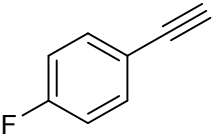


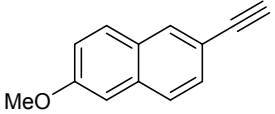
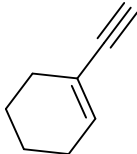
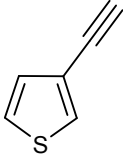
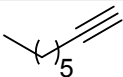
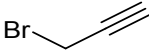

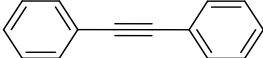
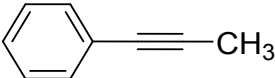
Scheme S2. General catalytic procedure for the hydroboration of alkynes.

Alkyne (0.50 mmol), pinacolborane (1.1 equiv., 0.55 mmol), catalyst (**1a**, 2.0 mol% or **1b**, 2.0 mol%) were charged in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at 100 °C for 12 h after adding 0.5 mL of toluene for **1a** and **1b**. Upon completion of the reaction, the solvent was removed using vacuum in a Schlenk line and mesitylene (0.5 mmol) was added as the internal standard, while making the NMR in appropriate deuterated solvent. The progress of the reaction was monitored by the ¹H NMR spectroscopy, which indicated the completion of the reaction by the disappearance of alkyne (RC≡CH) proton and the appearance of a new CH=CH resonance.

Upon completion, the reaction mixture was eluted with Et₂O:hexane (2:8) mixture through a short plug of silica and the product was purified by silica gel column chromatography eluted with mostly EtOAc:hexane (02:98) mixture. Hydroboration product of four alkynes namely **3b**, **3c**, **3j** and **3l** were isolated and in all these cases little discrepancy was observed with the NMR yield.

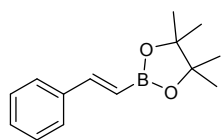
Table S4. Alkyne substrate scope with anti-Markovnikov: Markovnikov product ratio.

Entry	Substrate	Temperature (°C)	Time (h)	Catalyst (mol%)	NMR Yield (%)	Product	Selectivity
1.		100	12	2.0	92 ^a /90 ^b	3a	100:0 100:0
2.		100	12	2.0	96 ^a /84 ^b	3b	100:0 100:0
3.		100	12	2.0	87 ^a /89 ^b	3c	100:0 100:0
4.		100	12	2.0	67 ^a /66 ^b	3d	100:0 100:0
5		100	12	2.0	55 ^a /51 ^b	3e	100:0 100:0
6.		100	12	2.0	84 ^a /86 ^b	3f	100:0 100:0
7.		100	12	2.0	94 ^a /86 ^b	3g	100:0 100:0
8..		100	12	2.0	73 ^a /80 ^b	3h	100:0 100:0

9.		100	12	2.0	88 ^a /90 ^b	3i	100:0 100:0
10.		100	12	2.0	97 ^a /94 ^b	3j	100:0 100:0
11.		100	12	2.0	75 ^a /64 ^b	3k	100:0 100:0
12.		100	12	2.0	81 ^a /84 ^b	3l	100:0 100:0
13.		100	12	2.0	20 ^a /12 ^b	3m	100:0 100:0
14.		100	12	2.0	47 ^a /50 ^b	3n	100:0 100:0
15.		100	12	2.0	53 ^a /57 ^b	3o	100:0 100:0
16.		100	12	2.0	(58+37) ^a / (40+18) ^b	3p	61:39 69:31

Analytical data of boronate esters of corresponding alkynes:

(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (3a): ¹H NMR (CDCl₃, 200 MHz, 298 K):

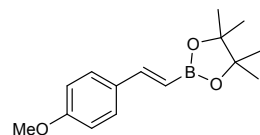


δ 7.44-7.32 (m, 2H, ArH), 7.31-7.22 (m, 4H, ArH and ArCH), 6.17-6.07 (d,

^1H , $^3J_{\text{H-H}} = 18.44$ Hz, ArCHCH), 1.24 (s, 12H, CH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 149.4, 137.4, 128.7, 128.4, 126.9, 83.2, 24.7 ppm; ^{11}B NMR (C_6D_6 , 128 MHz, 298 K): δ 30.5 ppm.

The spectroscopic data is consistent with the literature data.¹⁰

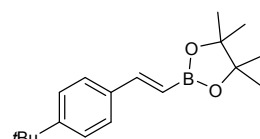
(E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b): According to general



procedure, 4-Ethynylanisole (0.75 mmol, 100 mg), HBpin (0.76 mmol, 97 mg), **1a** (4.0 mol%, 4.3 mg) were reacted. The product was purified by silica gel column chromatography eluted with EtOAc:hexane (02:98) mixture to get the boronate ester **3b** (isolated yield: 170 mg, 86.7%) as a colorless liquid. ^1H NMR (CDCl_3 , 200 MHz, 298 K): δ 7.38-7.26 (m, 3H, ArH), 6.80 (m, 2H, ArH and ArCH), 6.02-5.92 (d, 1H, $^3J_{\text{H-H}} = 18.32$ Hz, ArCHCH), 3.70 (s, 3H, OCH_3), 1.24 (s, 12H, CH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 160.2, 149.0, 130.3, 128.4, 113.9, 83.1, 55.1, 24.7 ppm; ^{11}B NMR (C_6D_6 , 128 MHz, 298 K): δ 30.7 ppm.

The spectroscopic data is consistent with the literature data.¹⁰

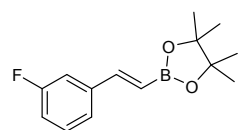
(E)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c): According to



general procedure, 4-*tert*-Butylphenylacetylene (0.77 mmol, 123 mg), HBpin (0.78 mmol, 100 mg), **1a** (4.0 mol%, 4.3 mg) were reacted. The product was purified by silica gel column chromatography eluted with EtOAc:hexane (02:98) mixture to get the boronate ester **3c** (isolated yield: 201 mg, 90.3%) as a pale yellow solid. ^1H NMR (CDCl_3 , 200 MHz, 298 K): δ 7.40-7.25 (m, 5H, ArH and ArCH), 6.14-6.05 (d, 1H, $^3J_{\text{H-H}} = 18.44$ Hz, ArCHCH), 1.25 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.22 (s, 12H, CH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 151.9, 149.3, 134.7, 131.8, 125.3, 125.1, 83.1, 34.5, 31.1, 24.7 ppm.

The spectroscopic data is consistent with the literature data.¹¹

(E)-2-(3-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d): ^1H NMR (CDCl_3 , 200

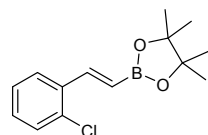


MHz, 298 K): δ 7.36-7.27 (d, 1H, $^3J_{\text{H-H}} = 18.32$ Hz, ArCH), 7.21-7.10 (m, 3H, ArH), 6.97-6.87 (m, 1H, ArH), 6.18-6.09 (d, 1H, $^3J_{\text{H-H}} = 18.32$ Hz, ArCHCH), 1.27 (s, 12H, CH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 165.4,

160.5, 148.0-147.9, 139.9-139.7, 129.9-129.8, 122.9-122.8, 115.7-115.3, 113.4-113.0, 83.3, 24.6 ppm.

The spectroscopic data is consistent with the literature data.¹⁰

(E)-2-(2-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e): ¹H NMR (CDCl₃, 200

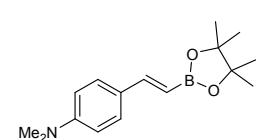


MHz, 298 K): δ 7.80-7.71 (d, 1H, $^3J_{\text{H-H}} = 18.30$ Hz, ArCHCH), 7.55-7.50 (m, 1H, ArH), 7.40-7.02 (m, 3H, ArH), 6.15-6.05 (d, 1H, $^3J_{\text{H-H}} = 18.32$ Hz, ArCHCH), 1.21 (s, 12H, CH₃) ppm; ¹³C{¹H} NMR (CDCl₃, 50.28 MHz, 298

K): δ 144.7, 133.7, 133.6, 129.5, 129.4, 129.0, 126.6, 126.1, 83.1, 24.5 ppm.

The spectroscopic data is consistent with the literature data.¹⁰

(E)-N,N-dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (3f):

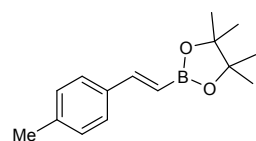


¹H NMR (CDCl₃, 200 MHz, 298 K): δ 7.36-7.32 (m, 3H, ArH and ArCH), 6.60-6.56 (d, 2H, $^3J_{\text{H-H}} = 8.27$ Hz, ArH), 5.94-5.85 (d, 1H, $^3J_{\text{H-H}} = 18.30$ Hz, ArCHCH), 2.87 (s, 6H, -NMe₂), 1.25 (s, 12H, CH₃) ppm; ¹³C{¹H} NMR

(CDCl₃, 50.28 MHz, 298 K): δ 150.8, 149.7, 128.9, 128.3, 125.8, 111.8, 82.8, 40.0, 24.7 ppm.

The spectroscopic data is consistent with the literature data.¹⁰

(E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (3g): ¹H NMR (CDCl₃, 200

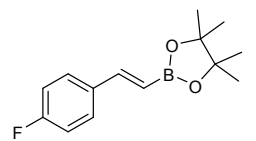


MHz, 298 K): δ 7.37-7.27 (m, 3H, ArH and ArCH), 7.05-7.01 (d, 2H, $^3J_{\text{H-H}} = 7.96$ Hz, ArH), 6.09-6.00 (d, 1H, $^3J_{\text{H-H}} = 18.44$ Hz, ArCHCH), 2.23 (s, 3H, ArCH₃), 1.21 (s, 12H, CH₃) ppm; ¹³C{¹H} NMR (CDCl₃, 50.28 MHz, 298

K): δ 149.4, 138.8, 134.8, 129.2, 126.9, 83.2, 24.7, 21.2 ppm; ¹¹B NMR (C₆D₆, 128 MHz, 298 K): δ 30.73 ppm.

The spectroscopic data is consistent with the literature data.¹⁰

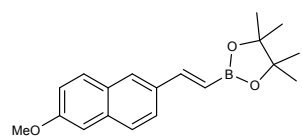
(E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h): ¹H NMR (CDCl₃, 200



MHz, 298 K): δ 7.42-7.29 (m, 3H, ArH and ArCH), 6.99-6.90 (m, 2H, ArH), 6.08-5.99 (d, 1H, $^3J_{\text{H-H}} = 18.44$ Hz, ArCHCH), 1.26 (s, 12H, CH₃) ppm; ¹³C{¹H} NMR (CDCl₃, 50.28 MHz, 298 K): δ 165.5, 160.5, 133.6, 128.6-128.5, 115.6-115.2, 83.2, 24.6 ppm.

The spectroscopic data is consistent with the literature data.¹⁰

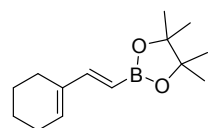
2-(6-methoxynaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i): ¹H NMR



(CDCl₃, 200 MHz, 298 K): δ 7.79-7.54 (m, 5H, ArH and ArCH), 7.16-7.10 (m, 2H, ArH), 6.32-6.23 (d, 1H, ³J_{H-H} = 18.32 Hz, ArCHCH), 3.90 (s, 3H, OCH₃), 1.35 (s, 12H, CH₃) ppm; ¹³C{¹H} NMR (CDCl₃, 50.28 MHz, 298 K): δ 158.1, 149.6, 134.9, 132.9, 129.8, 128.7, 127.7, 127.0, 123.9, 118.9, 105.8, 83.2, 55.1, 24.7 ppm.

The spectroscopic data is consistent with the literature data.¹²

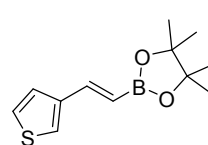
(E)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j): According



to general procedure, 1-Ethynylcyclohexene (0.77 mmol, 82mg), HBpin (0.78 mmol, 100 mg), **1a** (4.0 mol%, 4.3 mg) were reacted. The product was purified by silica gel column chromatography eluted with EtOAc:hexane (03:97) mixture to get the boronate ester **3j** (isolated yield: 170 mg, 94.0%) as a colorless liquid. ¹H NMR (CDCl₃, 200 MHz, 298 K): δ 7.22-7.13 (d, 1H, ³J_{H-H} = 18.30 Hz, RCHCH), 6.05 (s, 1H, Internal-CH), 5.62-5.52 (d, 1H, ³J_{H-H} = 18.19 Hz, RCHCH), 2.27 (br, 4H, -CH₂), 1.74 (br, 4H, -CH₂), 1.38 (s, 12H, CH₃) ppm; ¹³C{¹H} NMR (CDCl₃, 50.28 MHz, 298 K): δ 152.8, 136.8, 133.4, 82.4, 25.8, 24.3, 23.4, 22.1, 22.0, 20.8 ppm.

The spectroscopic data is consistent with the literature data.¹⁰

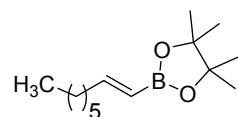
(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (3k): ¹H NMR



(CDCl₃, 200 MHz, 298 K): δ 7.38-7.29(d, 1H, ³J_{H-H} = 18.30 Hz, ArCHCH), 7.21-7.17 (m, 2H, ArCH), 7.13-7.11 (m, 1H, ArCH), 5.94-5.85 (d, 1H, ³J_{H-H} = 18.30 Hz, RCHCH), 1.21 (s, 12H, CH₃) ppm; ¹³C{¹H} NMR (CDCl₃, 50.28 MHz, 298 K): δ 143.0, 141.1, 129.8, 125.9, 124.8, 124.6, 82.9, 24.6 ppm.

The spectroscopic data is consistent with the literature data.¹¹

(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (3l): According to

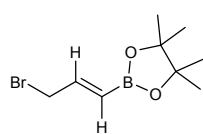


general procedure, 1-octyne (0.78 mmol, 86mg), HBpin (0.78 mmol, 100 mg), **1a** (4.0 mol%, 4.3 mg) were reacted. The product was purified by silica gel column chromatography eluted with EtOAc:hexane (03:97) mixture to get the

boronate ester **3j** (isolated yield: 170 mg, 94.0%) as a colorless liquid. ^1H NMR (CDCl_3 , 200 MHz, 298 K): δ 7.80-7.71 (dt, 1H, $^3J_{\text{H-H}} = 17.86$ Hz, RCHCH), 5.59-5.50 (d, 1H, $^3J_{\text{H-H}} = 18.30$ Hz, RCHCH), 2.30-2.20 (quat, 2H, $-\text{CH}_2$), 1.53 (br, 8H, $-\text{CH}_2$), 1.36 (s, 12H, CH_3), 0.99 (s, 3H, CH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 154.5, 82.7, 35.7, 31.6, 28.8, 28.1, 24.6, 13.9 ppm.

The spectroscopic data is consistent with the literature data.¹³

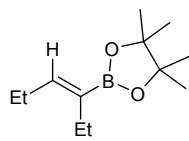
(E)-2-(3-bromoprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m): ^1H NMR



(C_6D_6 , 200 MHz, 298 K): δ 5.88-5.82 (m, 1H, $\text{CH}=\text{CHBpin}$), 5.64-5.55 (d, 1H, $^3J_{\text{H-H}} = 17.53$ Hz, $\text{CH}=\text{CHBpin}$), 3.85-3.82 (d, 2H, $^3J_{\text{H-H}} = 8.49$ Hz, BrCH_2 -), 1.19 (s, 12H, CH_3) ppm.

The spectroscopic data is consistent with the literature data.¹⁴

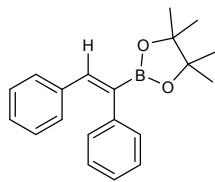
(Z)-2-(hex-3-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n): ^1H NMR (C_6D_6 , 200 MHz,



298 K): δ 6.64-6.57 (t, 1H, EtCH), 2.38-2.28 (m, 4H, CH_2CH_3), 1.12 (s, 12H, CH_3), 1.05 (m, 6H, CH_2CH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 50.28 MHz, 298 K): δ 147.8, 83.3, 25.2, 22.4, 22.1, 15.6, 14.4 ppm.

The spectroscopic data is consistent with the literature data.¹⁵

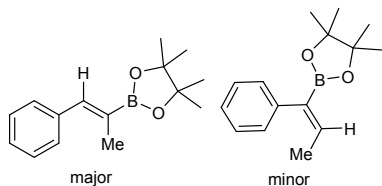
(Z)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o): ^1H NMR (C_6D_6 ,



200MHz, 298 K): δ 7.54 (s, 1H), 7.42-7.31 (m, 4H), 7.25-7.19 (m, 5H), 1.45 (s, 12H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 50.28 MHz, 298 K): δ 143.1, 140.3, 136.8, 131.4, 128.7, 128.1, 128.0, 127.7, 126.1, 83.5, 24.7 ppm.

The spectroscopic data is consistent with the literature data.¹⁰

(Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane and (Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (3p): Major isomer: ^1H NMR



(CDCl_3 , 200 MHz, 298 K): δ 7.64-7.40 (m, 6H, ArCH), 2.28 (s, 3H, CH_2CH_3), 1.53 (s, 12H, CH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.28 MHz, 298 K): δ 142.3, 137.7, 131.3, 129.2, 127.8, 126.9, 83.2, 24.6, 22.4, 15.6 ppm. Minor isomer: ^1H NMR (C_6D_6 , 200

MHz, 298 K): δ 7.64-7.40 (m, 6H, ArCH), 2.03-1.99 (d, 3H, $^3J_{\text{H-H}} = 6.95$ Hz, CHCH_3), 1.49 (s,

12H, CH₃) ppm; ¹³C{¹H} NMR (CDCl₃, 50.28 MHz, 298 K): δ 142.4, 139.6, 128.9, 127.5, 125.6, 83.1, 24.5, 15.7 ppm.

The spectroscopic data is consistent with the literature data.¹⁰

General catalytic procedure for the hydroboration of terpenes:

Terpene (0.50 mmol), pinacolborane (1.1 equiv., 0.55 mmol), catalyst (8.0 mol% for **1a**, and 4.0 mol% for **1b**) were mixed together in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at 100 °C for 18 h in neat condition or in 0.5 mL toluene for **1a** and **1b** respectively. Volatiles of the mixture were removed under reduced pressure and mesitylene (0.5 mmol) was added while making the NMR in appropriate deuterated solvent. The progress of the reaction was monitored by the ¹H NMR spectroscopy, which indicated the completion of the reaction by the disappearance of alkene (RCH=CH₂) proton and the appearance of a new RCH₂CH₂Bpin resonance.

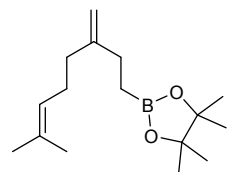
Table S5. Substrate scope for terpenes.

Entry	Substrate	Temperature (°C)	Time (h)	Catalyst (mol%)	NMR Yield (%)	Product
1.		100	18	8.0/4.0	12 ^a /18 ^b	4a
2.		100	18	8.0/4.0	13 ^a /15 ^b	4b
3.		100	18	8.0/4.0	73 ^a /65 ^b (17:1) for 3,4 vs 1,2 HB	4c
4.		100	18	8.0/4.0	61 ^a /63 ^b	4d

Analytical data of boronate esters of corresponding terpenes:

Conversion of R-(+)-Limonene and S-(-)-Limonene to their corresponding hydroboration products was identified by the ^1H NMR spectroscopy using mesitylene as the internal standard. However, their spectra were not assigned because of the overlapping of the peak with the unreacted starting materials.

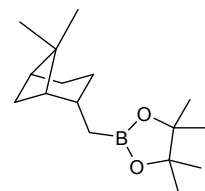
4,4,5,5-tetramethyl-2-(7-methyl-3-methyleneoct-6-en-1-yl)-1,3,2-dioxaborolane (4c):



^1H NMR (C_6D_6 , 200 MHz, 298 K): δ 5.24-5.01 (m, 1H), 4.94 (s, 2H), 2.16-1.94 (m, 6H), 1.63 (s, 3H), 1.55 (s, 3H), 1.16 (s, 12H), 0.88 (t, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 50.28 MHz, 298 K): δ 151.2, 131.3, 124.0, 107.5, 82.4, 36.0, 29.9, 26.6, 25.5, 24.6, 17.4 ppm.

The spectroscopic data is consistent with the literature data.¹⁶

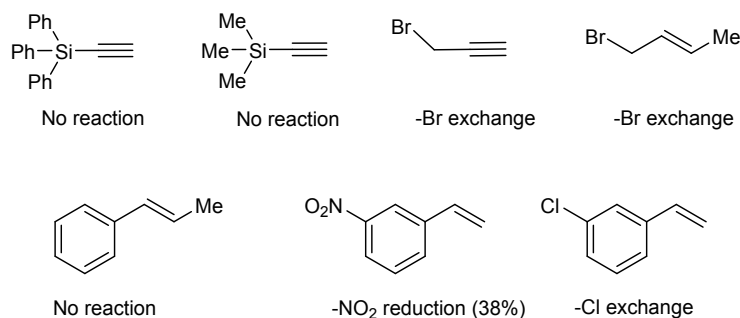
2-(((1S,2S,5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-



dioxaborolane (4d): The ^1H NMR spectrum was not assigned since the proton resonances of **4d** overlap with the other diastereomer and unreacted starting materials. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 50.28 MHz, 298 K): δ 82.6, 48.7, 40.5, 40.3, 38.7, 31.5, 26.8, 26.0, 24.7, 24.7, 23.4, 20.1 ppm.

The spectroscopic data is consistent with the literature data.¹⁶

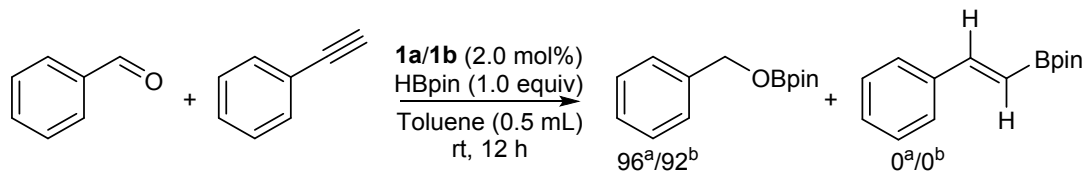
List of unsuccessful substrates for catalytic hydroboration:



Competitive experiment for aldehyde/alkyne/alkene hydroboration-selectivity study:

Selective hydroboration of benzaldehyde over phenylacetylene in presence of 1 equiv.

HBpin:



Scheme S3. Selective hydroboration of PhCHO over PhC≡CH in presence of 1 equiv. HBpin.

Benzaldehyde (53 mg, 0.50 mmol), Phenylacetylene (51 mg, 0.50 mmol), pinacolborane (64 mg, 0.50 mmol), catalyst (2.0 mol% for **1a** or 2.0 mol% for **1b**) were charged in a Schlenk tube inside the glove box. The reaction mixture was stirred for 12 hat room temperature after the addition of 0.50 mL toluene. Upon completion of the reaction, volatiles of the mixture were removed under reduced pressure. The progress of the reaction was monitored by ¹H NMR after addition of mesitylene (0.50mmol) as an internal standard in CDCl₃. A sharp resonance at δ = 4.84 ppm indicates for the formation of hydroboration product from benzaldehyde.

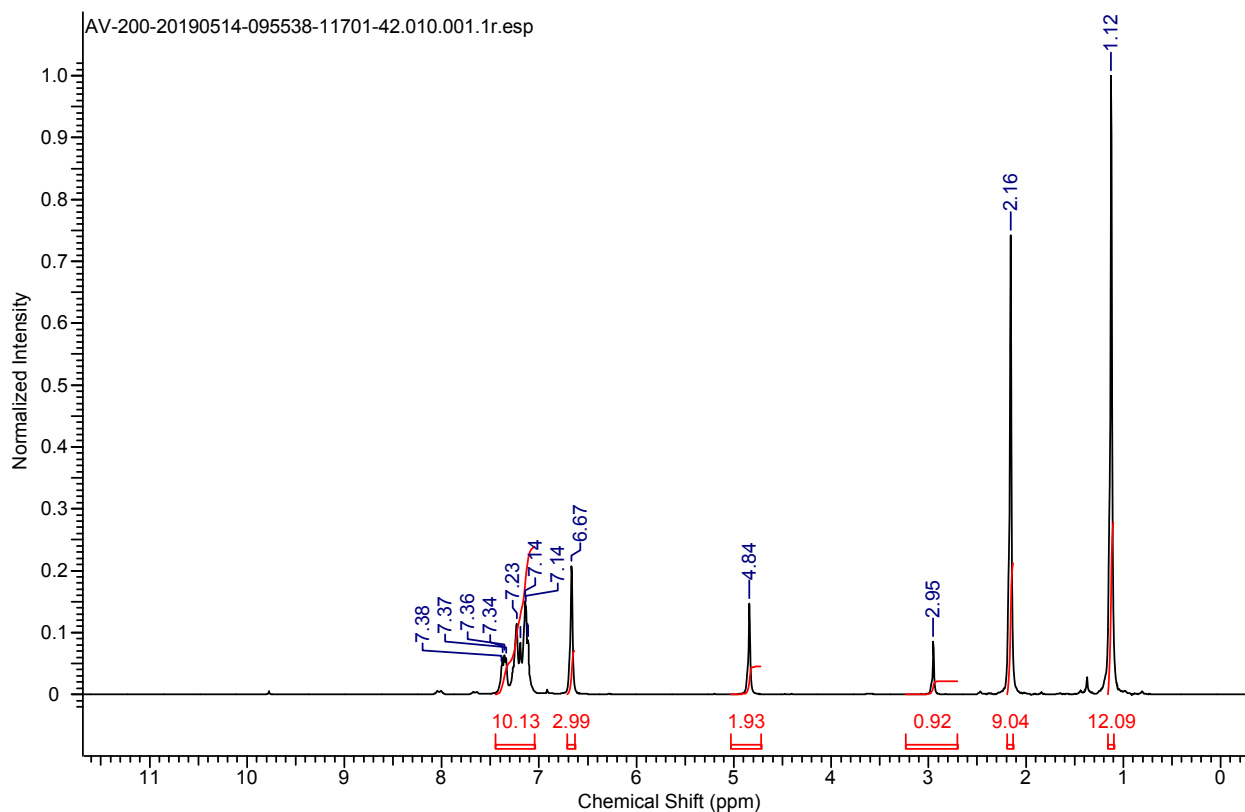
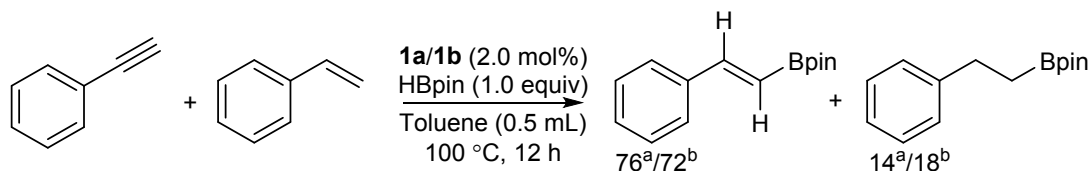


Figure S1. ^1H NMR spectrum of the reaction of PhCHO and PhC \equiv CH in presence of 1 equiv. HBpin(CDCl $_3$, 200 MHz, 298 K).

Selective hydroboration of phenylacetylene over styrene in presence of 1 equiv. HBpin:



Scheme S4. Selective hydroboration of phenylacetylene over styrene in presence of 1 equiv. HBpin

Phenylacetylene (51 mg, 0.50 mmol), styrene (52 mg, 0.50 mmol), pinacolborane (64 mg, 0.50 mmol), catalyst (2.0 mol% for **1a** or 2.0 mol% for **1b**) were charged in a Schlenk tube inside the glove box. The reaction mixture was stirred for 12 hat 100 °C after addition of 0.50 mL toluene. Upon completion of the reaction, volatiles of the mixture were removed under reduced pressure. The progress of the reaction was monitored by ^1H NMR after addition of mesitylene (0.50 mmol) as an internal standard in CDCl $_3$. Formation of the hydroboration product was identified

from the doublet resonance at $\delta = 6.14$ ppm for alkyne and triplet resonance at $\delta = 2.70$ ppm for alkene.

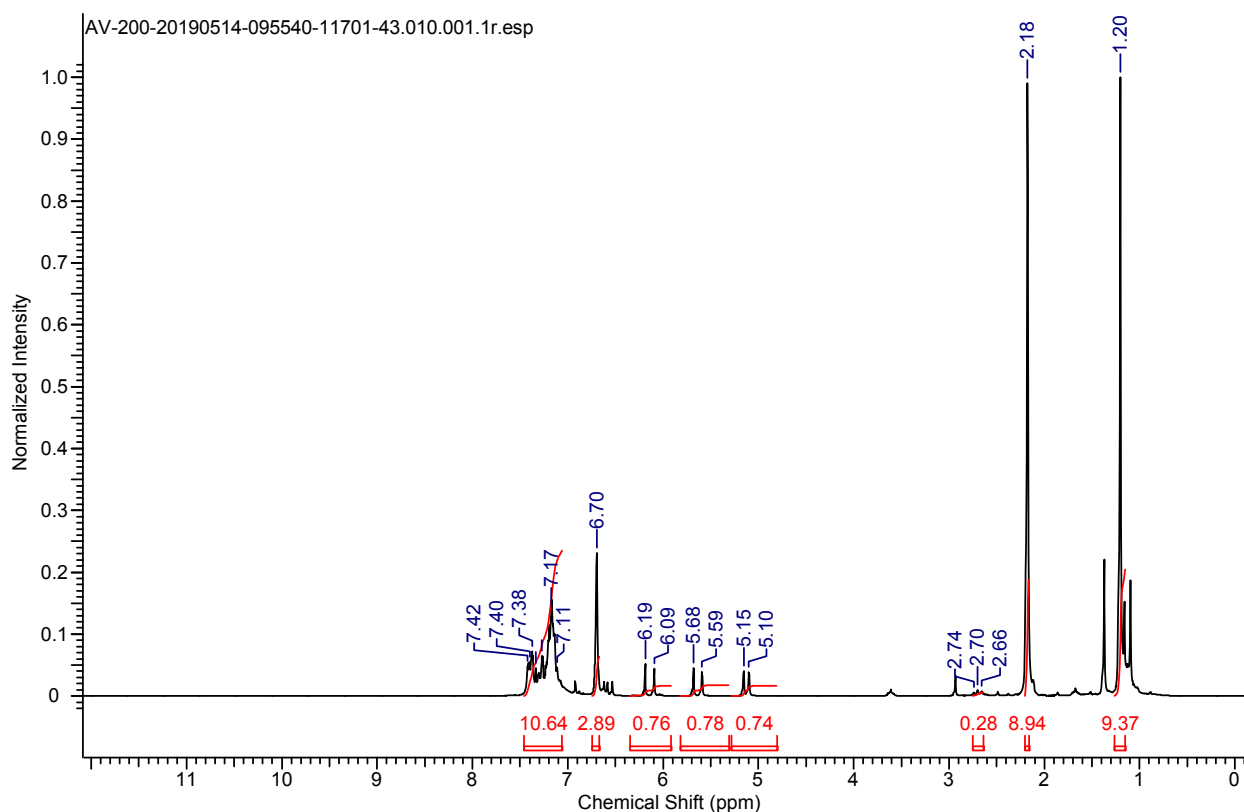
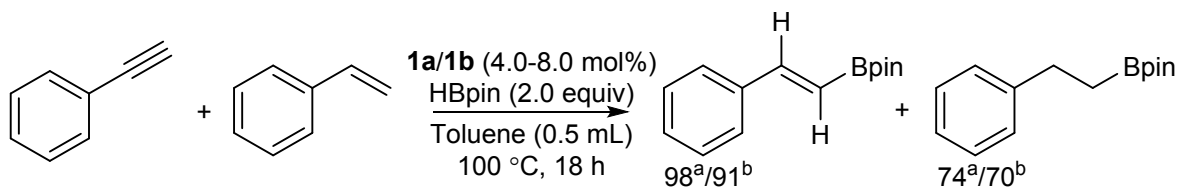


Figure S2. ^1H NMR spectrum of the reaction of $\text{PhC}\equiv\text{CH}$ and $\text{PhCH}=\text{CH}_2$ in presence of 1 equiv. $\text{HBpin}(\text{CDCl}_3, 200 \text{ MHz}, 298 \text{ K})$.

Hydroboration of phenylacetylene and styrene in presence of 2 equiv. HBpin :



Scheme S5. Selective hydroboration of phenylacetylene and styrene in presence of 2 equivs. HBpin

Phenylacetylene (51 mg, 0.50 mmol), styrene (52 mg, 0.50 mmol), pinacolborane (128 mg, 1.00 mmol), catalyst (8.0 mol% for **1a** or 4.0 mol% for **1b**) were mixed together in a Schlenk tube inside the glove box. The reaction mixture was heated at 100 °C for 18 h after addition of 0.50 mL toluene. Upon completion of the reaction, volatiles of the mixture were removed under reduced

pressure. The progress of the reaction was monitored by ^1H NMR after addition of mesitylene (0.5 mmol) as an internal standard in CDCl_3 . Formation of the hydroboration product was identified from the doublet resonance at $\delta = 6.14$ ppm for alkyne and triplet resonance at $\delta = 2.70$ ppm for alkene.

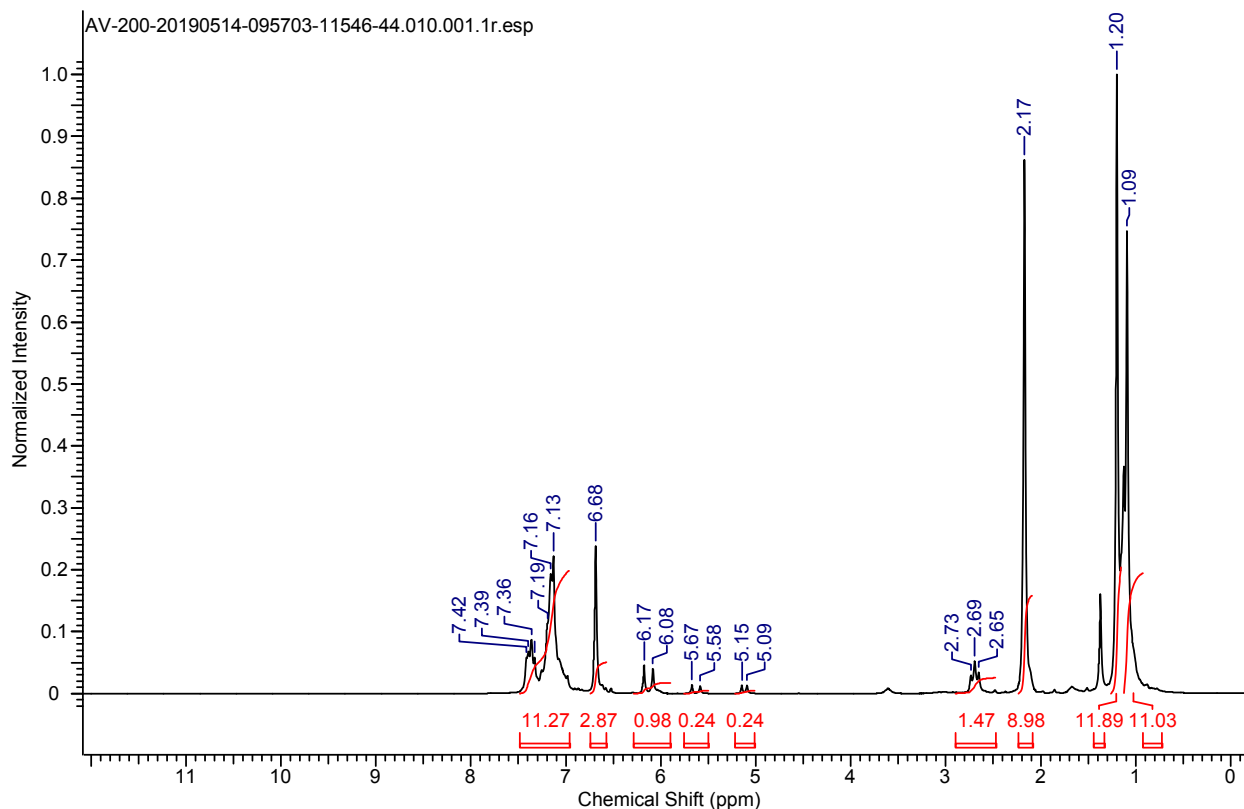
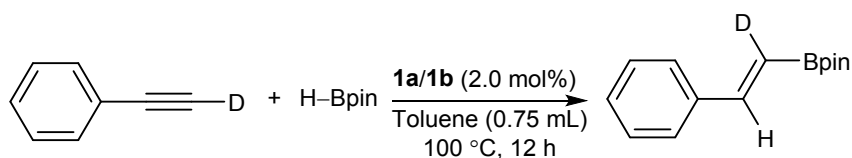


Figure S3. ^1H NMR spectrum of the reaction of $\text{PhC}\equiv\text{CH}$ and $\text{PhCH}=\text{CH}_2$ in presence of 2 equiv. HBpin (CDCl_3 , 200 MHz, 298 K).

Deuterium labeling experiments:



Scheme S6. Deuterium labeling experiment with $\text{PhC}\equiv\text{CD}$ with HBpin.

Phenylacetylene- d_1 (51.5 mg, 0.50 mmol), pinacolborane (75 mg, 0.59 mmol), catalyst (2.0 mol% for **1a** or 2.0 mol% for **1b**) and 0.75 mL toluene were charged in a screw cap NMR tube inside the glove box. The reaction mixture was heated at 100 $^\circ\text{C}$ for 12 h before the volatiles of the mixture were removed under reduced pressure. The progress of the reaction was monitored by the ^2H NMR.

After dissolving in CDCl₃, the spectrum shows a peak at $\delta = 6.18$ ppm (Figure S4), which indicates a *cis* orientation of deuterium and phenyl group.

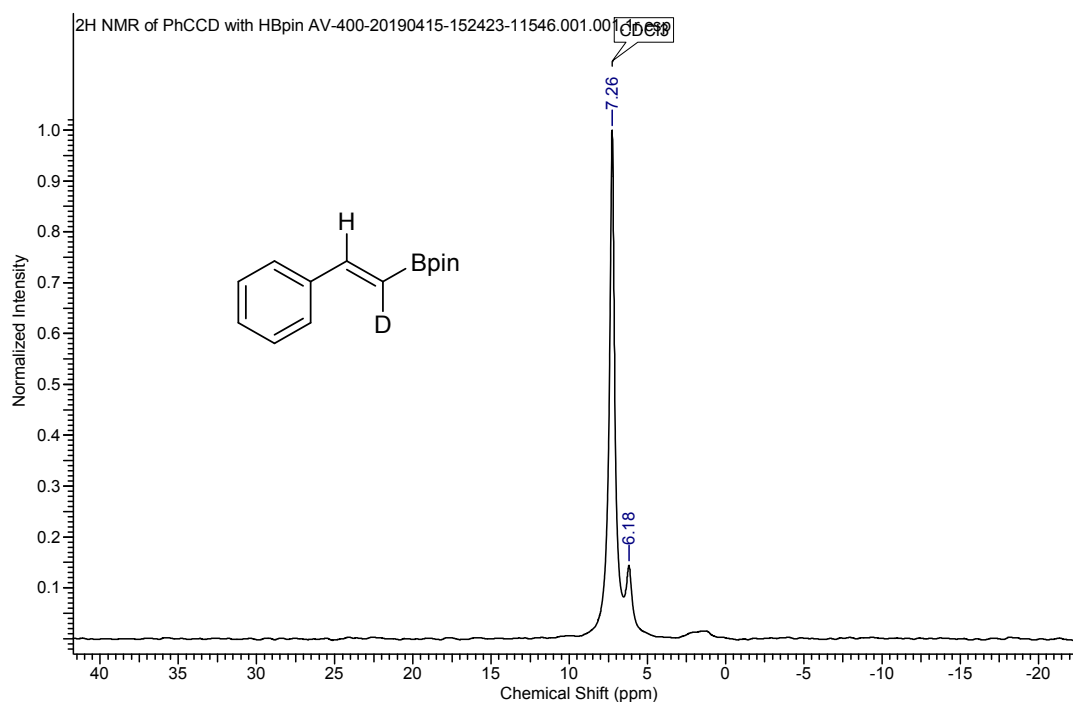
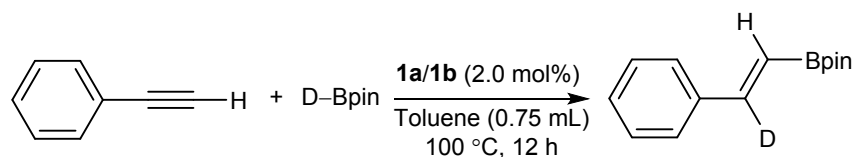


Figure S4. ²H NMR spectrum of the reaction of PhC≡CD with HBpin in presence of **1a** (CDCl₃, 61.42 MHz, 298 K).



Scheme S7. Deuterium labeling experiment with PhC≡CH with DBpin.

Phenylacetylene (31 mg, 0.30 mmol), pinacolborane-d₁ (42 mg, 0.32 mmol in 0.75 mL toluene), catalyst (2.0 mol% for **1a** or 2.0 mol% for **1b**) were charged in a screw cap NMR tube inside the glove box. The reaction mixture was heated at 100 °C for 12 h before the volatiles of the mixture were removed under reduced pressure. The progress of the reaction was monitored by ²H NMR after dissolving in CD₃CN, which indicated the peak at $\delta = 7.28$ ppm (Figure S5), due to the *cis* orientation of deuterium and Bpin unit.

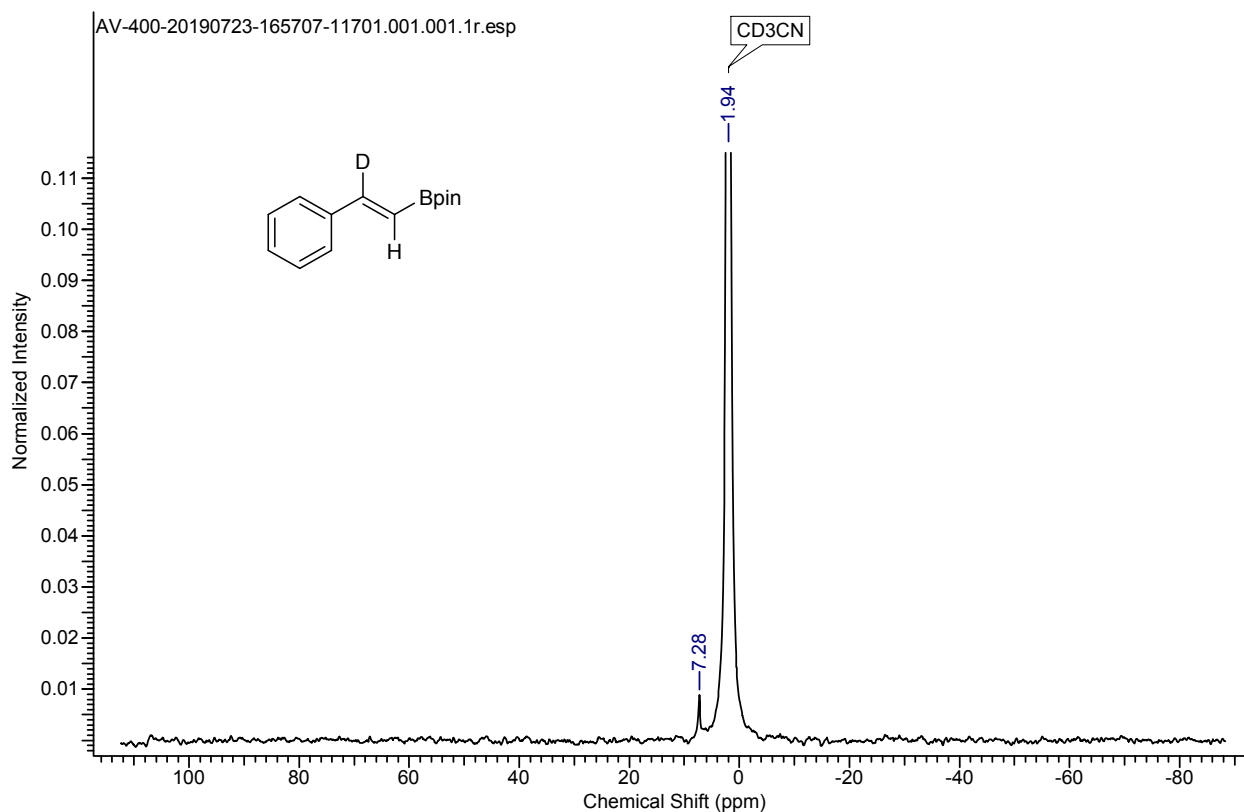
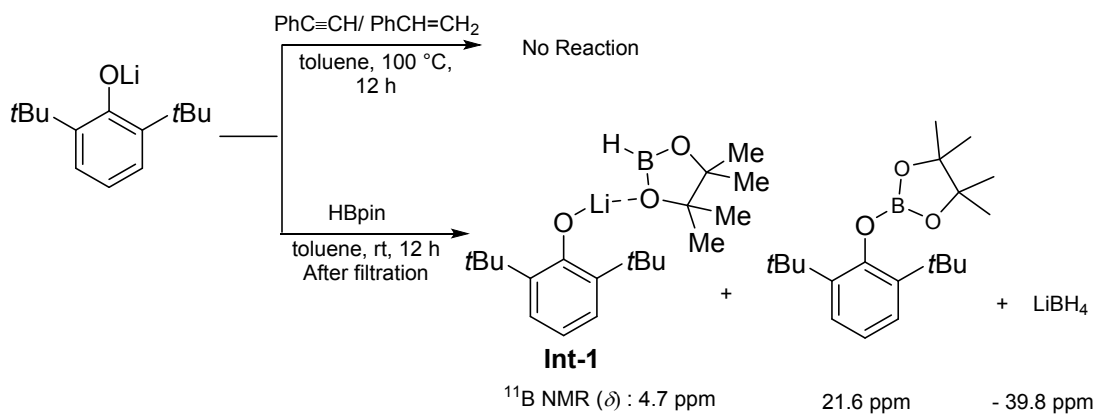


Figure S5. ²H NMR spectrum of the reaction of PhC≡CH with DBpin in presence of **1a** (CD₃CN, 61.42 MHz, 298 K).

Mechanistic investigation:

Stoichiometric reaction of catalyst **1a** and HBpin:



Scheme S8. Stoichiometric reaction of **1a** with phenylacetylene or styrene and HBpin:.

A solution of HBpin (135mg, 1.05 mmol) in toluene (5 mL) was added drop by drop to the toluene solution (10 mL) of **1a** (300mg, 1.05 mmol) at room temperature. The reaction mixture was stirred for overnight. After addition of HBpin, the solution was clear up to 3-4 h and after that a white ppt started to form. The reaction mixture was subjected for characterization. Yield (0.192 g, 55 %), ^1H NMR (C_6D_6 , 200 MHz, 298 K): δ 7.22 (d, $^3J_{\text{H-H}} = 7.83$ Hz, 2H, ArH), 6.92 (t, 1H, ArH), 1.52 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.06 (s, 12H, CH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8 , 100.56 MHz, 298 K): δ 152.1 (*Ph*), 141.1 (*Ph*), 125.9 (*Ph*), 123.2 (*Ph*), 83.3 ($\text{C}(\text{CH}_3)_2$), 35.4 ($\text{C}(\text{CH}_3)_3$), 31.8 ($\text{C}(\text{CH}_3)_3$), 31.6(CH_3) ppm; ^{11}B NMR (toluene- d_8 , 128 MHz, 298 K): δ 86.9 (s), 21.7 (s), 4.6 (s), -25.7 (quatrate), -39.9 (quintet), 29.1-27.8 (d, for unreacted HBpin) ppm. Upon filtration and evaporation of solvent, the filtrate part shows only three peaks at δ 4.6 (s), 21.7 (s), and -39.9 (quintet) in the ^{11}B NMR spectrum.

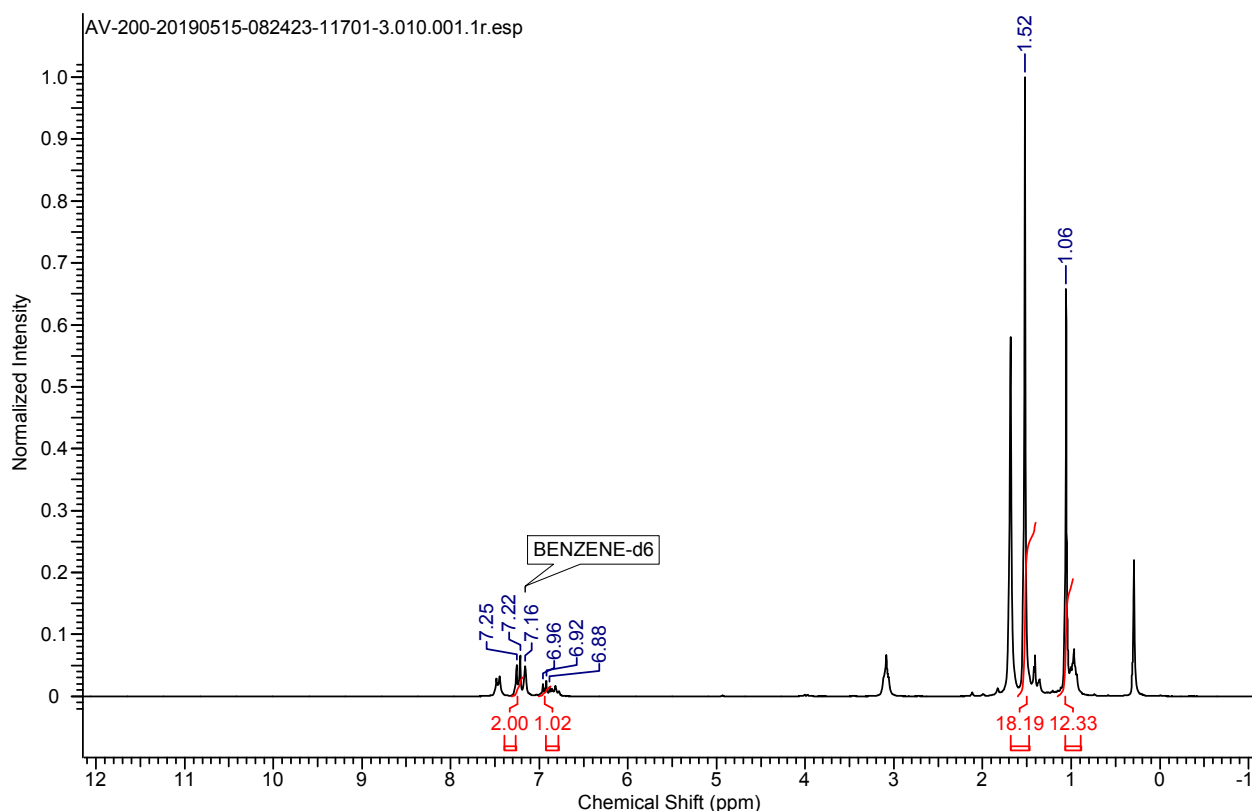


Figure S6. ^1H NMR spectrum of the reaction of **1a** with HBpin (C_6D_6 , 200 MHz, 298 K).

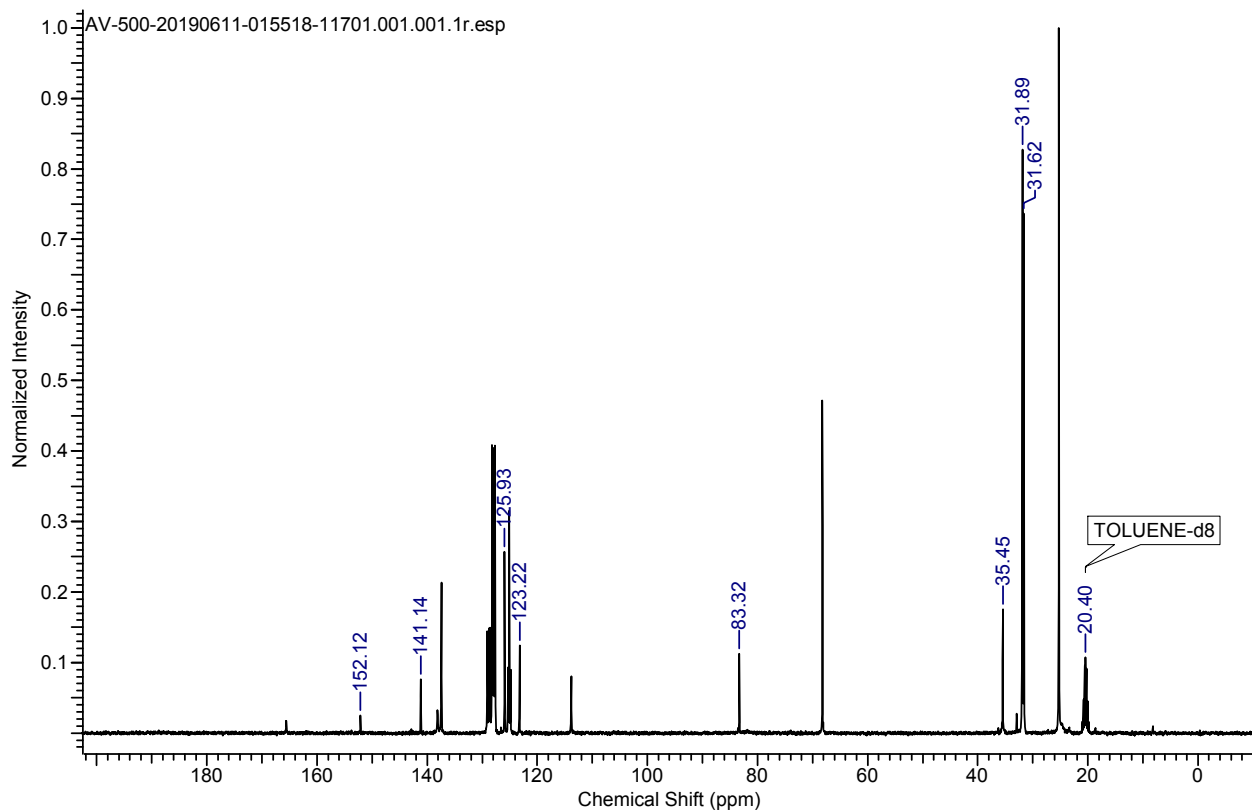


Figure S7. ^{13}C NMR spectrum of the reaction of **1a** with HBpin (C_7D_8 , 100.56 MHz, 298 K).

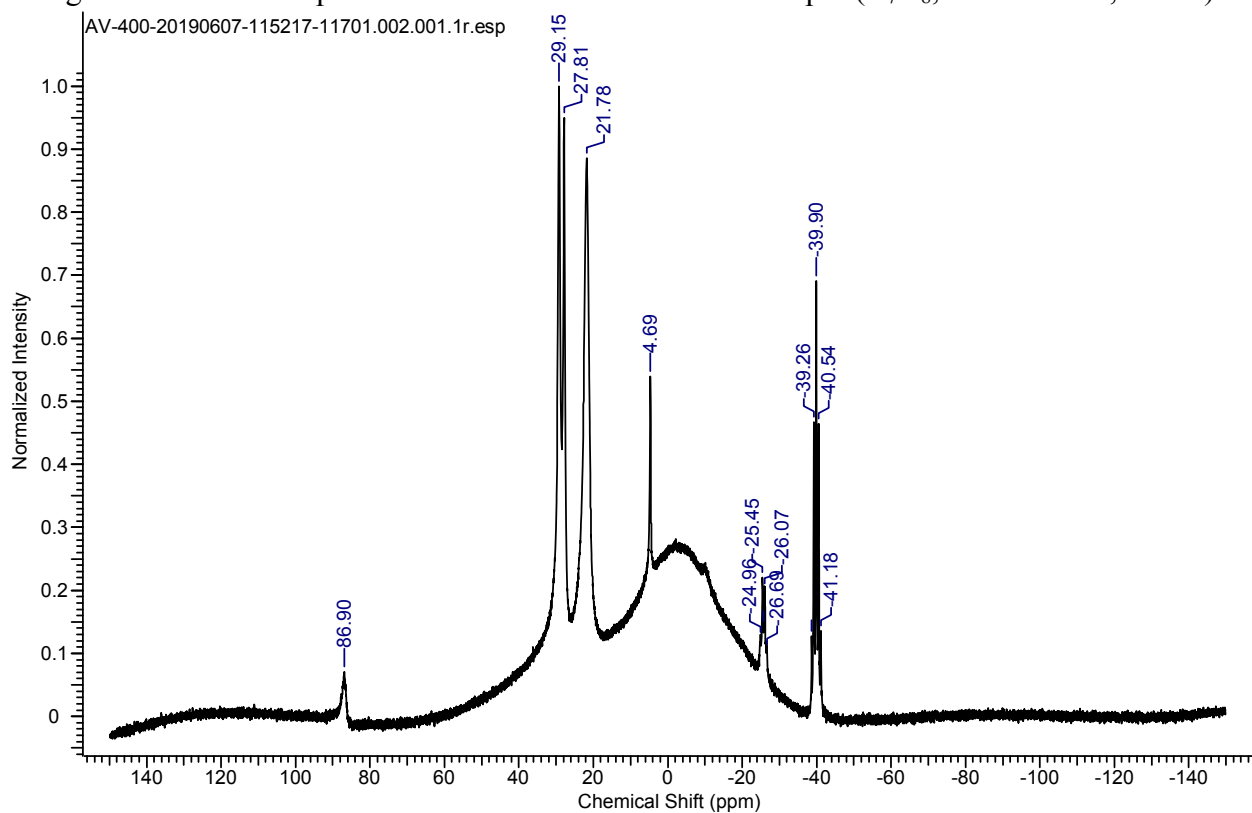


Figure S8. ^{11}B NMR spectrum of the reaction of **1a** with HBpin (C_7D_8 , 100.56 MHz, 298 K).

Stoichiometric reaction of 1a with phenylacetylene or styrene:

No reaction was observed when an equimolar amount of **1a** was treated separately with phenylacetylene or styrene in toluene or benzene solvent at room temperature. Further heating at 100 °C overnight does not indicate any appreciable changes in the ¹H NMR spectra.

Kinetic analysis:**Hydroboration of styrene:**

Styrene (52 mg, 0.50 mmol) and HBpin (64 mg, 0.50 mmol) were added to the catalysts (**1a**, 8.0 mol% or **1b**, 4.0 mol%), at room temperature and then heated at 100 °C for 18 h. Different set of reactions were stopped at fixed intervals and the yield was determined by ¹H NMR of the crude reaction mixture using with the addition of 0.50 mmol mesitylene as an internal standard in CDCl₃.

Entry	Catalyst	Time (h)	% Yield
1.	1a/1b	0.5	28 ^a /19 ^b
2.	1a/1b	1	36 ^a /25 ^b
3.	1a/1b	3	43 ^a /40 ^b
4.	1a/1b	6	58 ^a /57 ^b
5.	1a/1b	9	67 ^a /69 ^b
6.	1a/1b	12	75 ^a /75 ^b
7.	1a/1b	15	83 ^a /84 ^b
8.	1a/1b	18	92 ^a /89 ^b

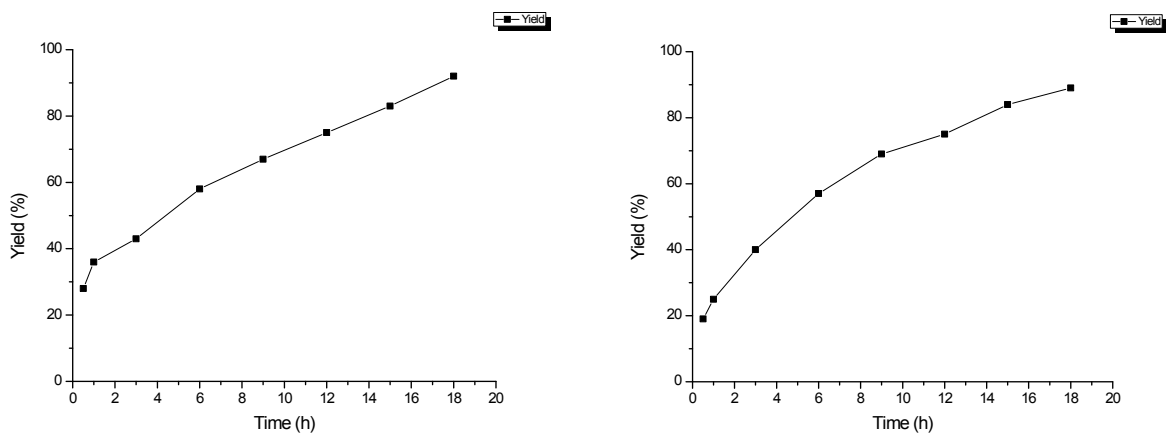


Figure S9: Yield (%) vs time (h) plot for HB of Styrene with **1a**(left)and **1b**(right).

Hydroboration of phenylacetylene:

Phenylacetylene (51 mg, 0.50 mmol) and HBpin (64 mg, 0.50 mmol) were added to the catalysts (**1a**, 2.0 mol% or **1b**, 2.0 mol%), at room temperature and then heated at 100 °C for 12 h. Different set of reactions were stopped at fixed intervals and the yield was determined by ¹H NMR of the crude reaction mixture using with the addition of 0.50 mmol mesitylene as an internal standard in CDCl₃.

Entry	Catalyst	Time (h)	% Yield
1.	1a/1b	0.5	37 ^a /44 ^b
2.	1a/1b	1	46 ^a /50 ^b
3.	1a/1b	3	56 ^a /54 ^b
4.	1a/1b	6	65 ^a /62 ^b
5.	1a/1b	9	71 ^a /69 ^b
6.	1a/1b	12	79 ^a /74 ^b
7.	1a/1b	15	85 ^a /80 ^b
8.	1a/1b	18	92 ^a /90 ^b

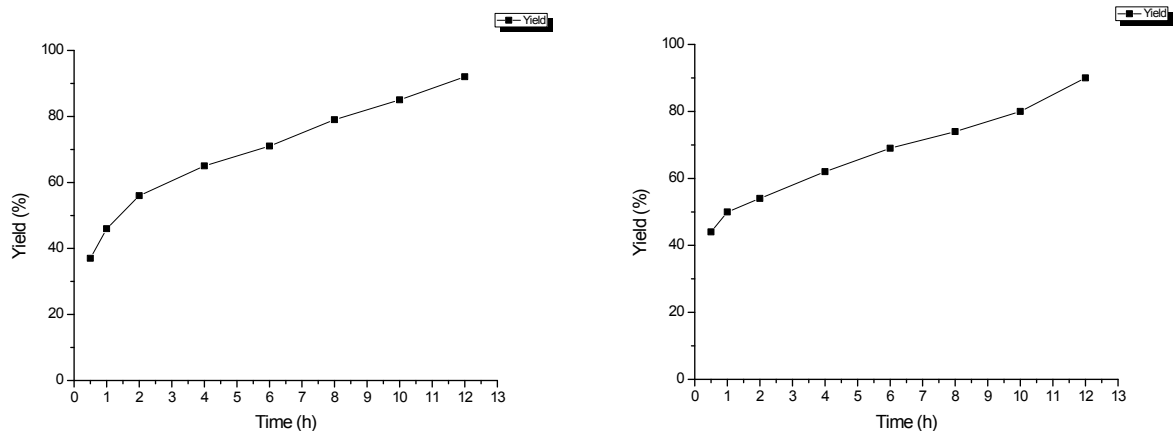


Figure S10: Yield (%) vs time (h) plot for HB of Phenylacetylene with **1a**(left)and **1b**(right).

Representative NMR Spectra

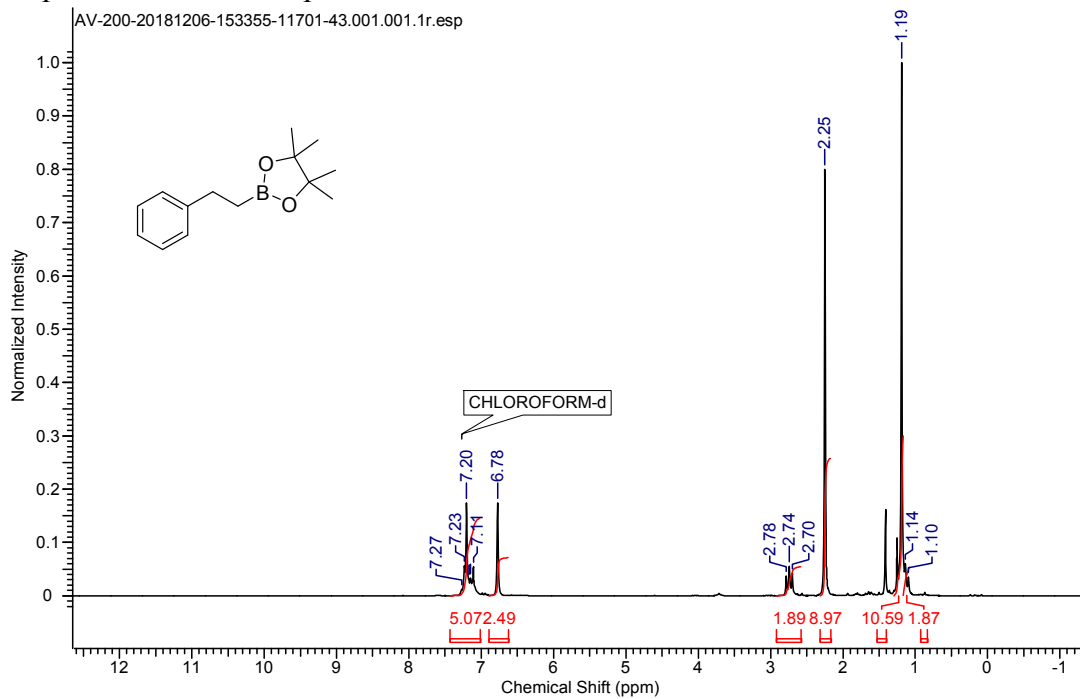


Figure S11. ¹H NMR Spectrum of **2a** (CDCl₃, 200 MHz, 298 K).

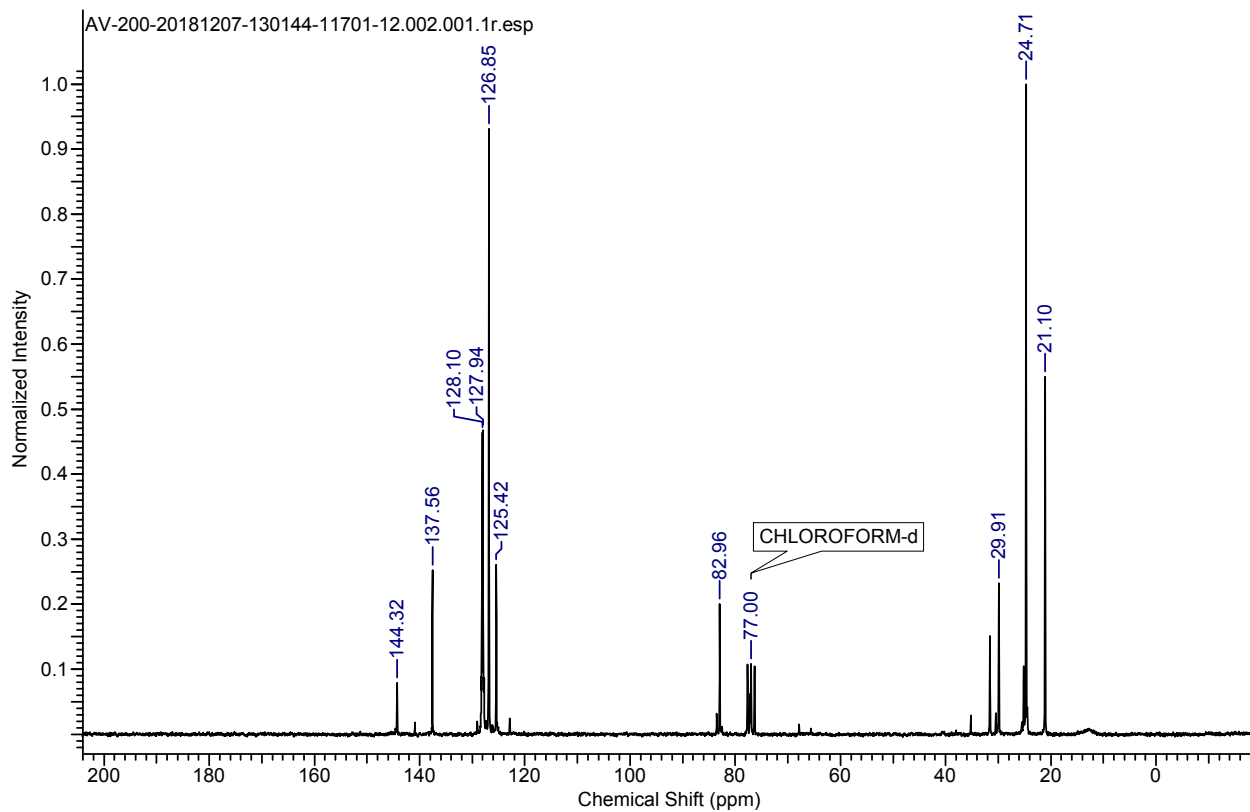


Figure S12. ^{13}C NMR spectrum of **2a** (CDCl_3 , 50.28 MHz, 298 K).

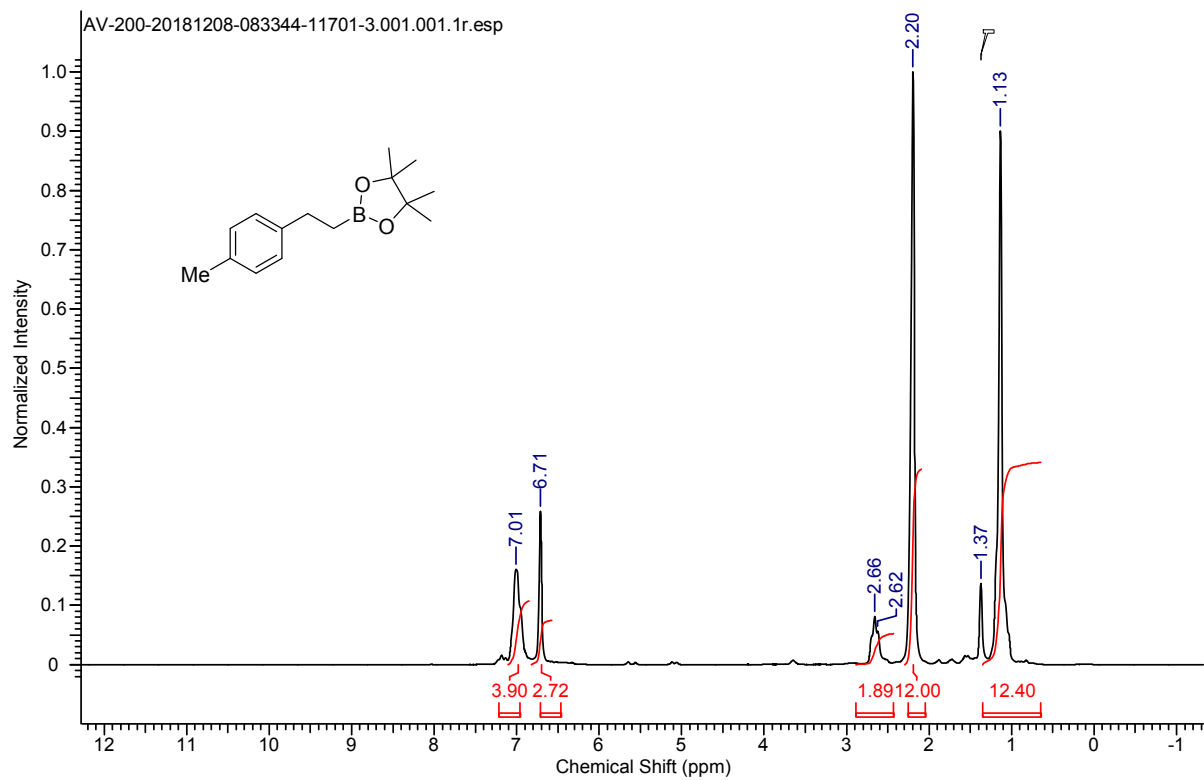


Figure S13. ^1H NMR Spectrum of **2b** (CDCl_3 , 200 MHz, 298 K).

Fig

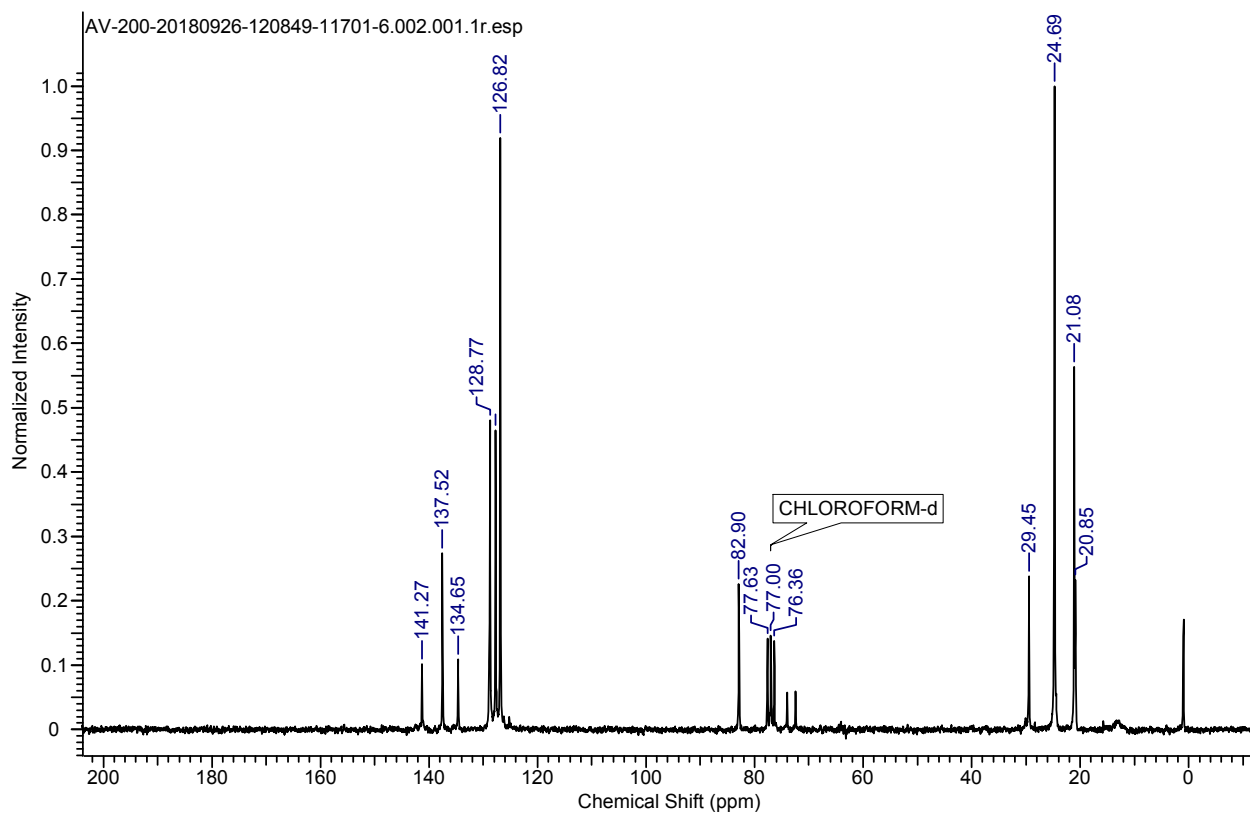


Figure S14. ^{13}C NMR spectrum of **2b** (CDCl_3 , 50.28 MHz, 298 K).

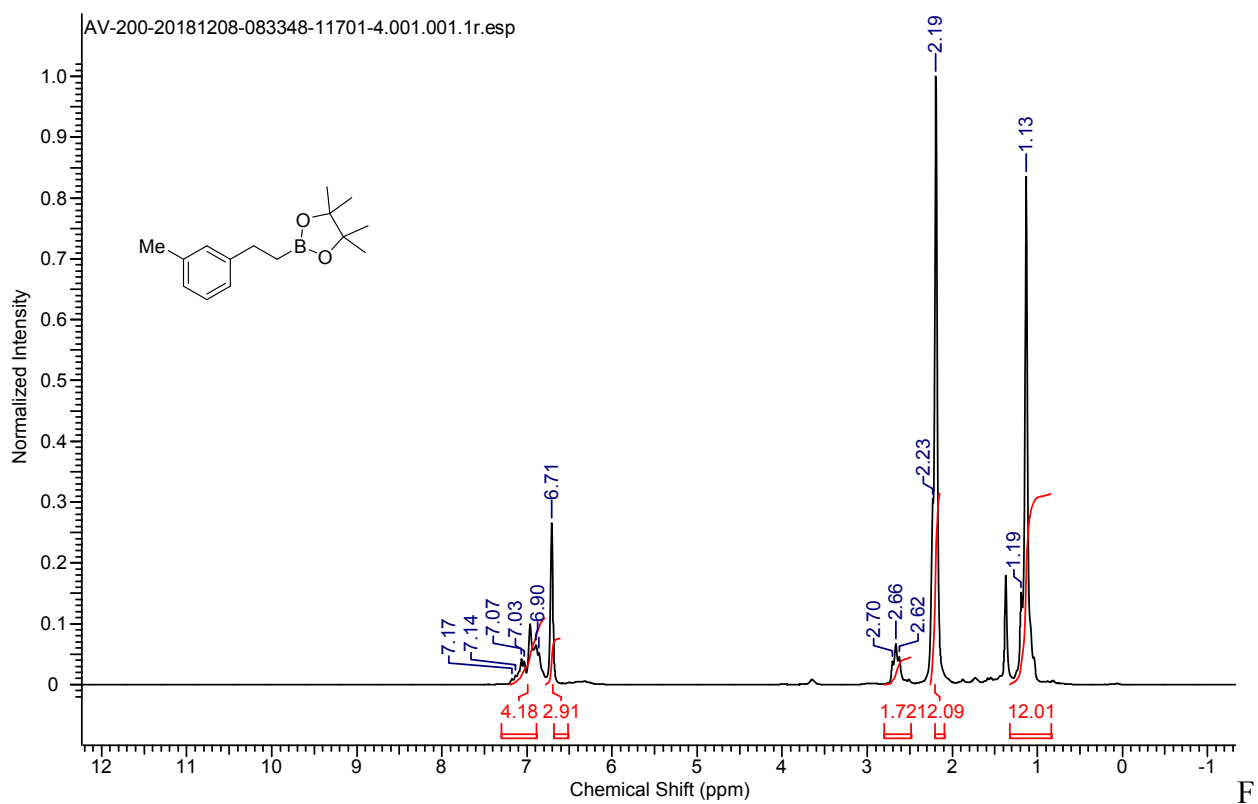


Figure S15. ^1H NMR Spectrum of **2c** (CDCl_3 , 200 MHz, 298 K).

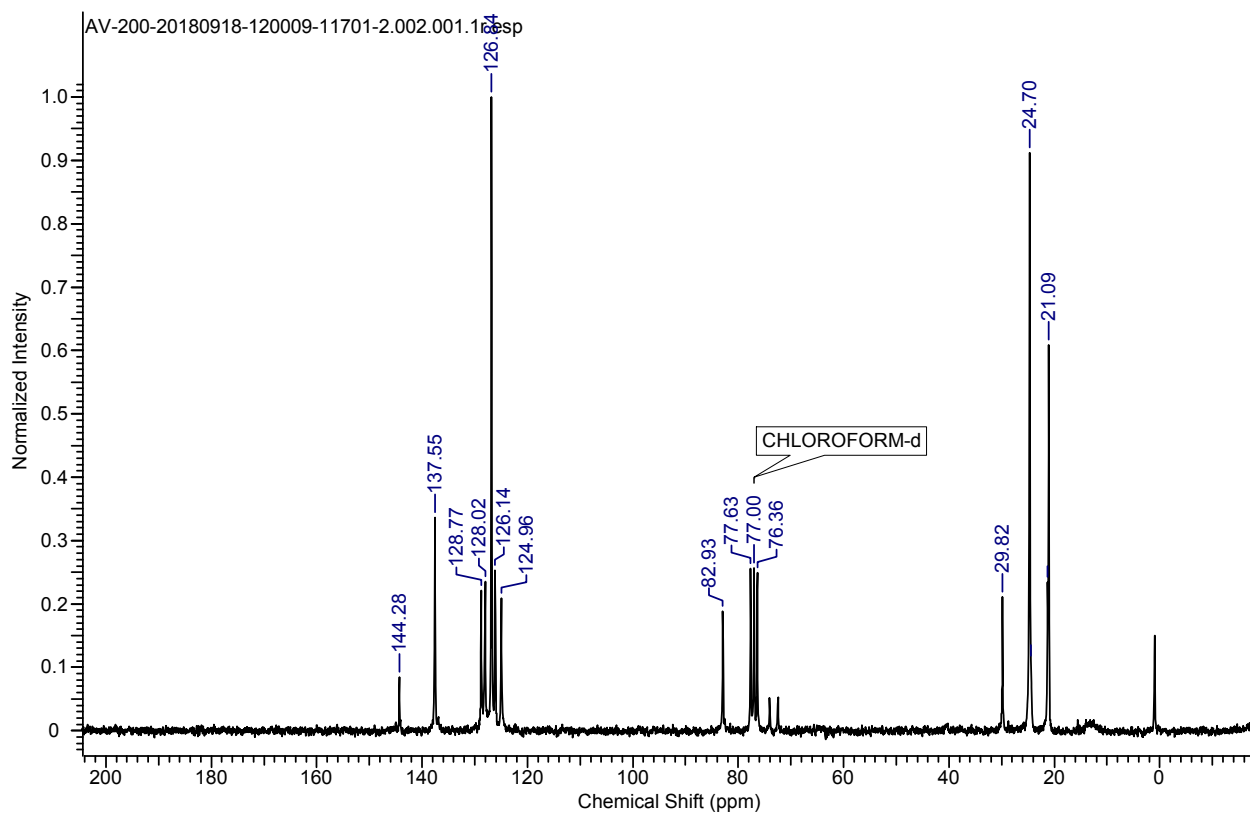


Figure S16. ^{13}C NMR spectrum of **2c** (CDCl_3 , 50.28 MHz, 298 K).

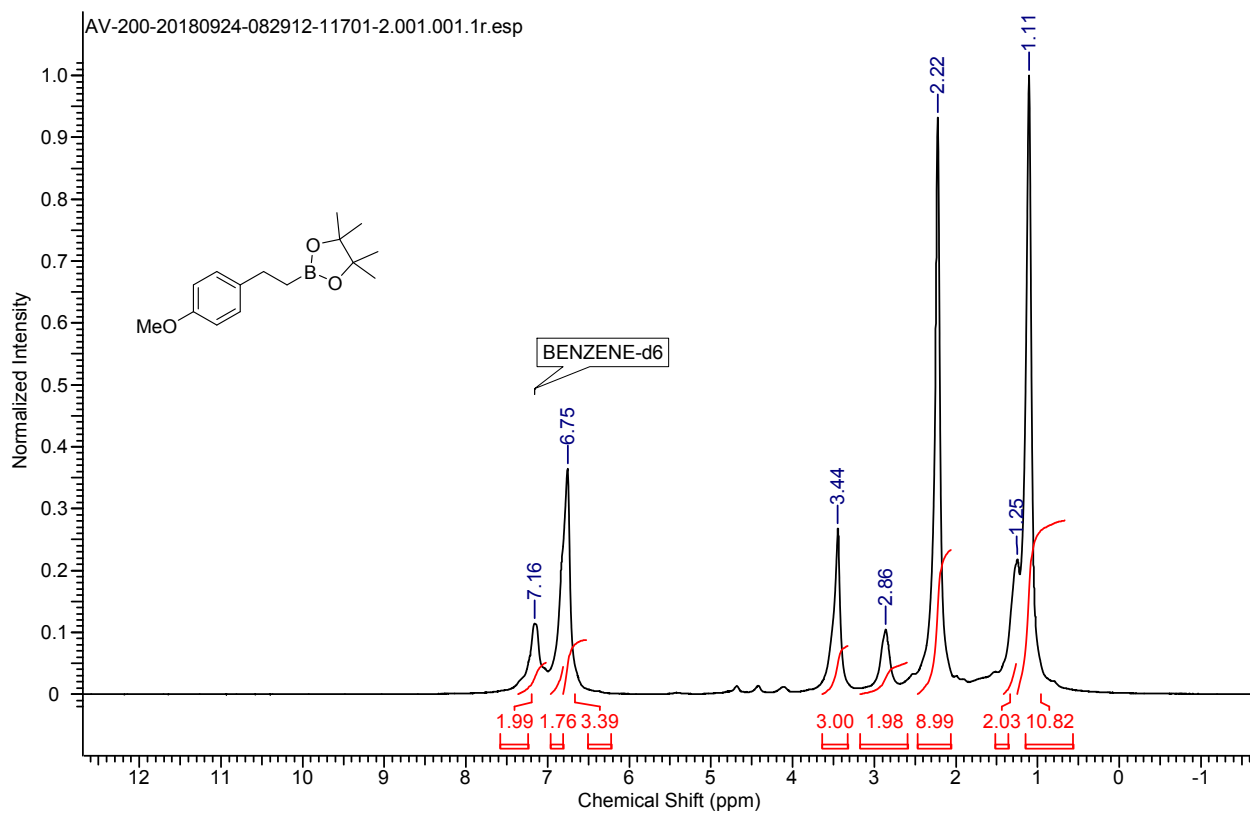


Figure S17. ^1H NMR Spectrum of **2d** (C_6D_6 , 200 MHz, 298 K).

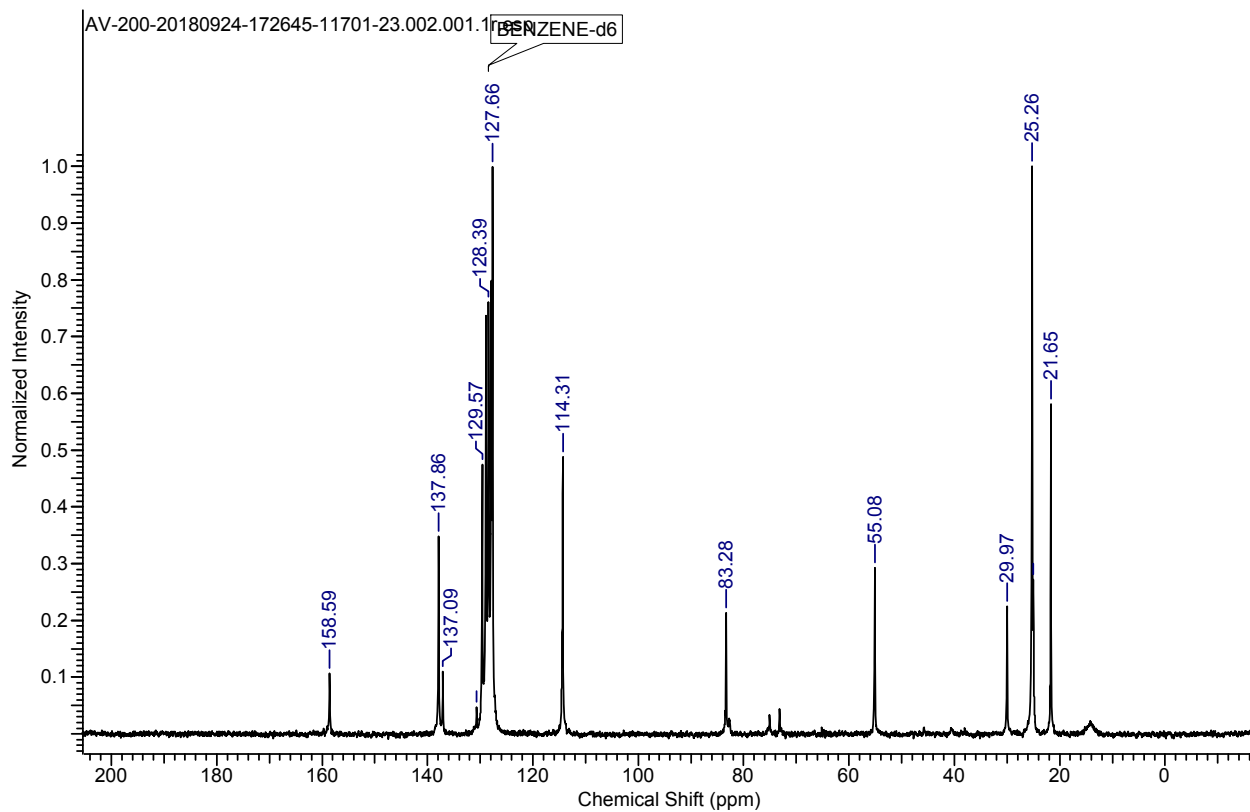


Figure S18. ^{13}C NMR spectrum of **2d** (C_6D_6 , 50.28 MHz, 298 K).

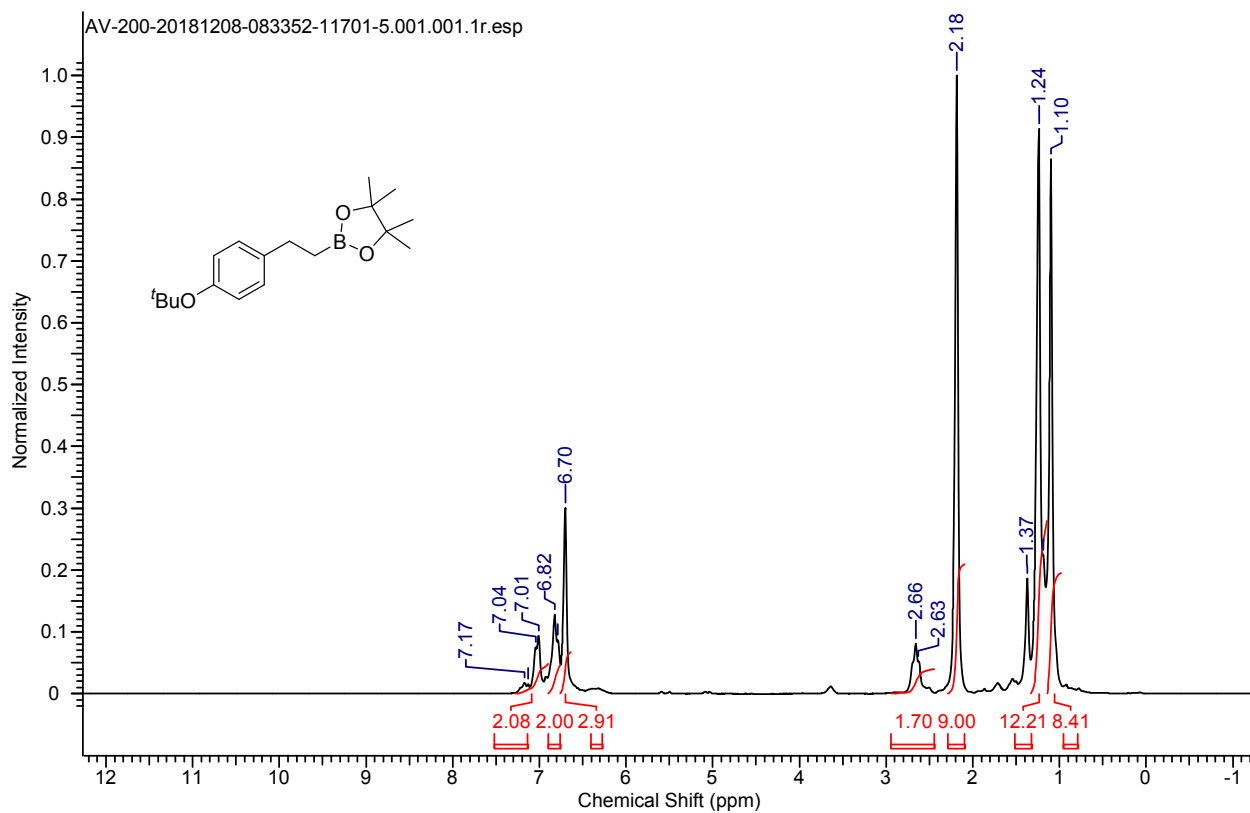


Figure S19. ^1H NMR Spectrum of **2e** (CDCl_3 , 200 MHz, 298 K).

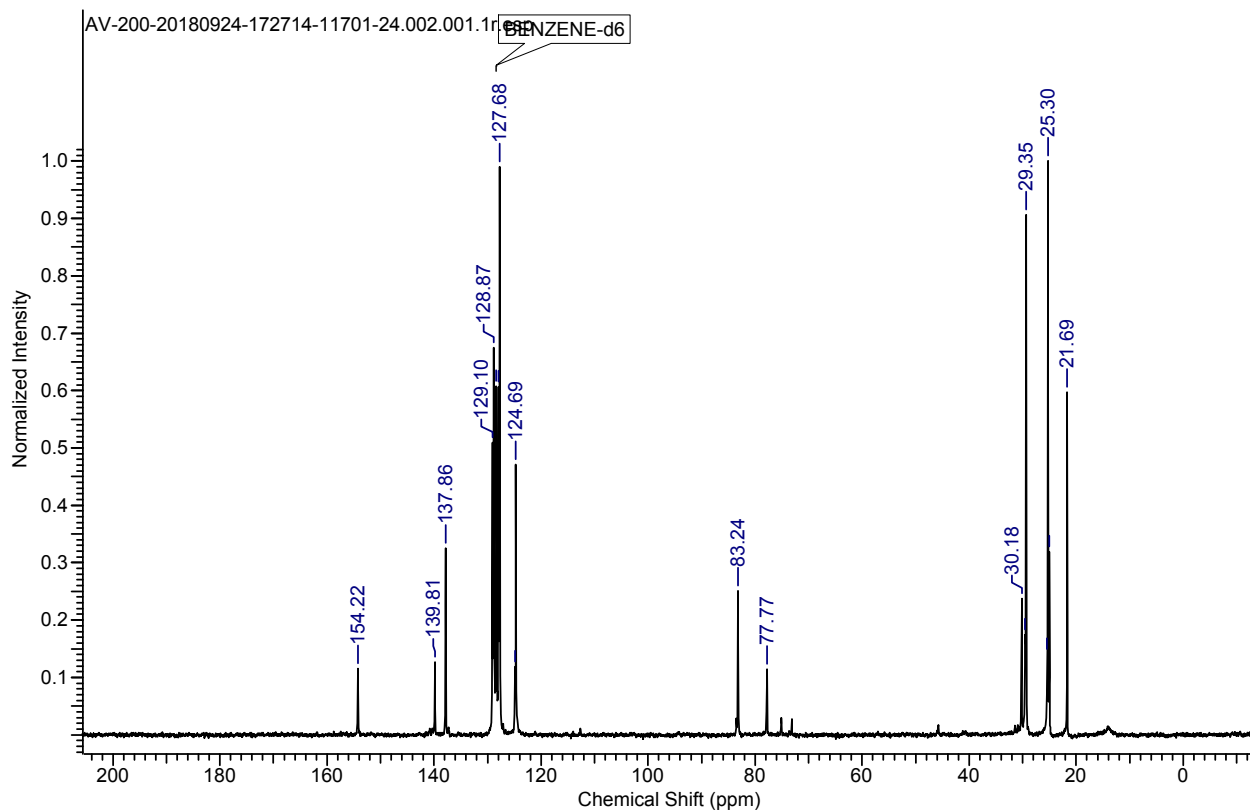


Figure S20. ^{13}C NMR spectrum of **2e** (C_6D_6 , 50.28 MHz, 298 K).

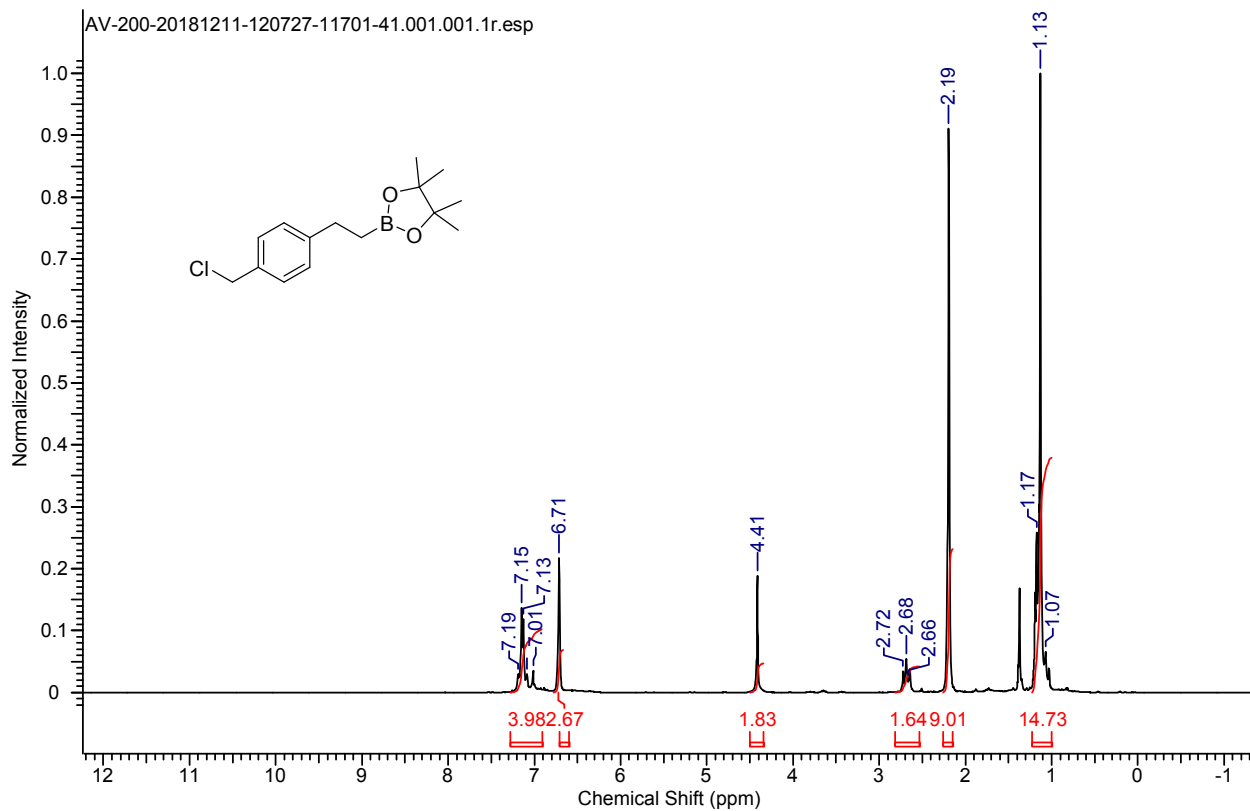


Figure S21. ^1H NMR Spectrum of **2f** (CDCl_3 , 200 MHz, 298 K).

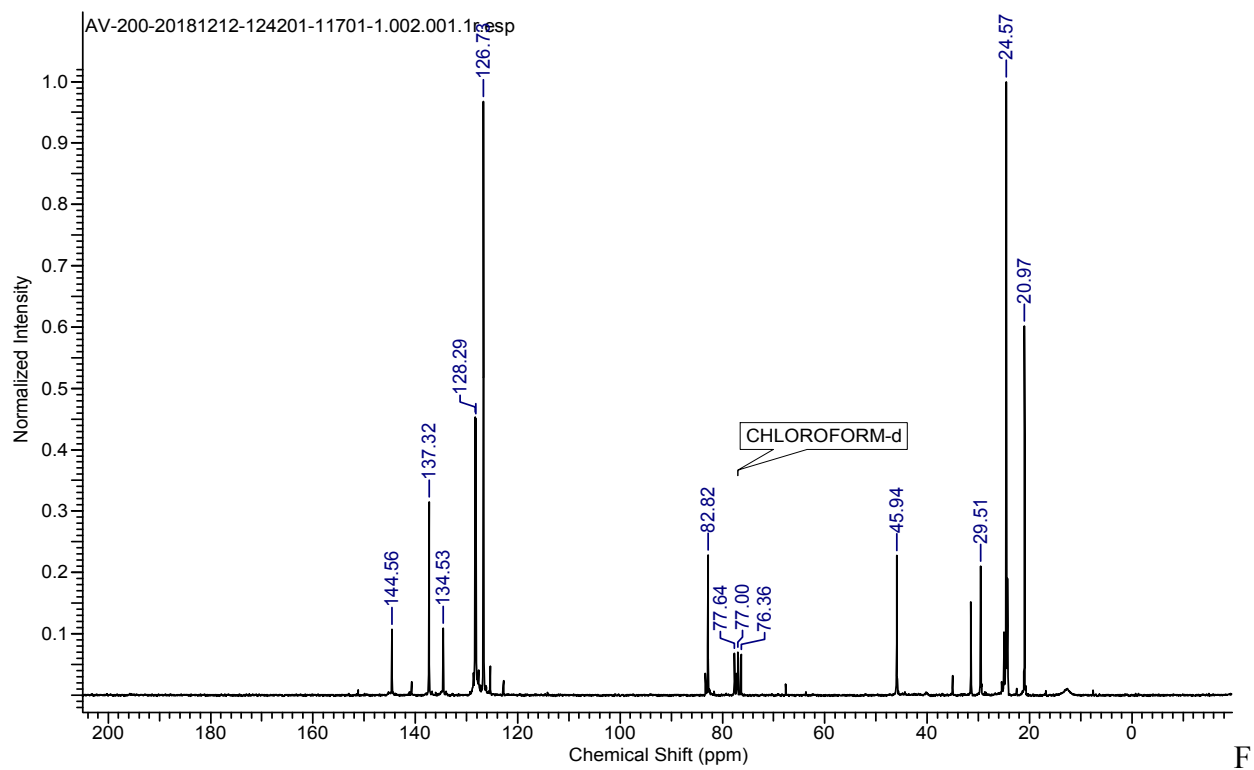


figure S22. ^{13}C NMR spectrum of **2f** (CDCl_3 , 50.28 MHz, 298 K).

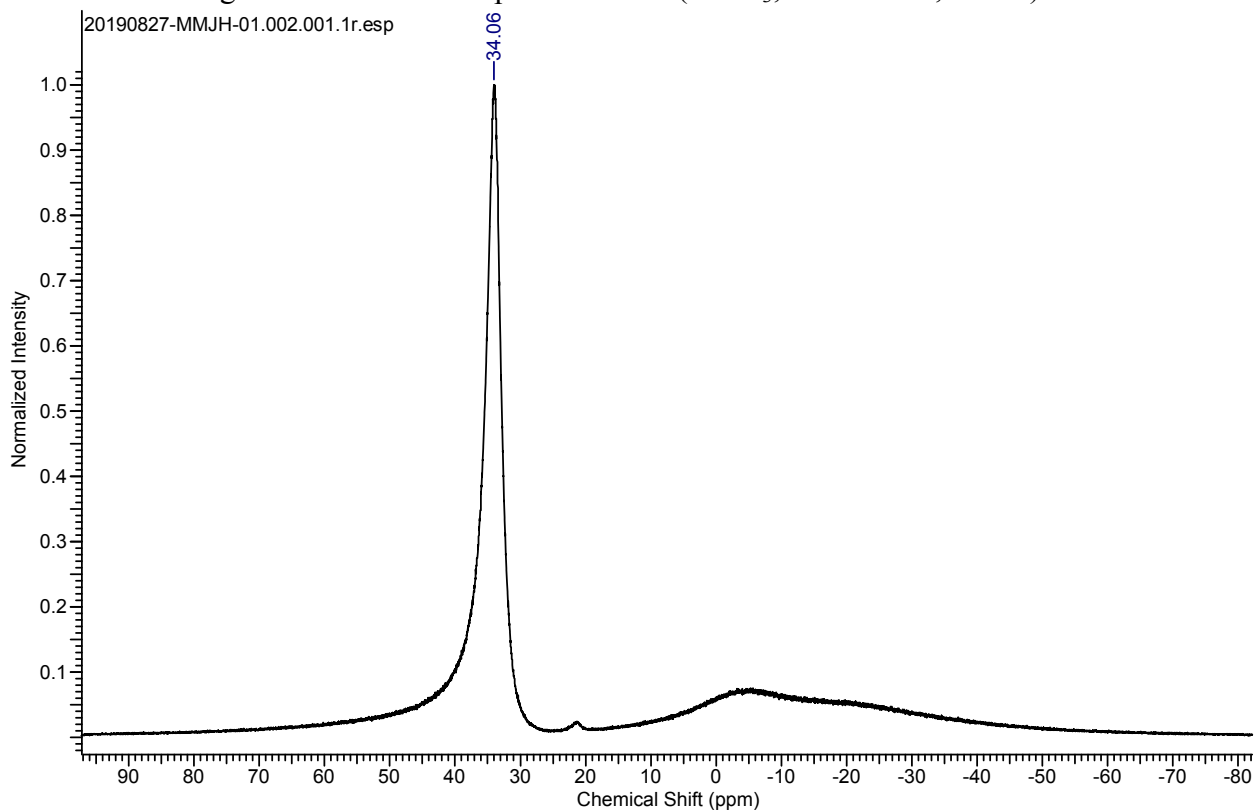


Figure S23. ^{13}C NMR spectrum of **2f** (CDCl_3 , 128.4 MHz, 298 K).

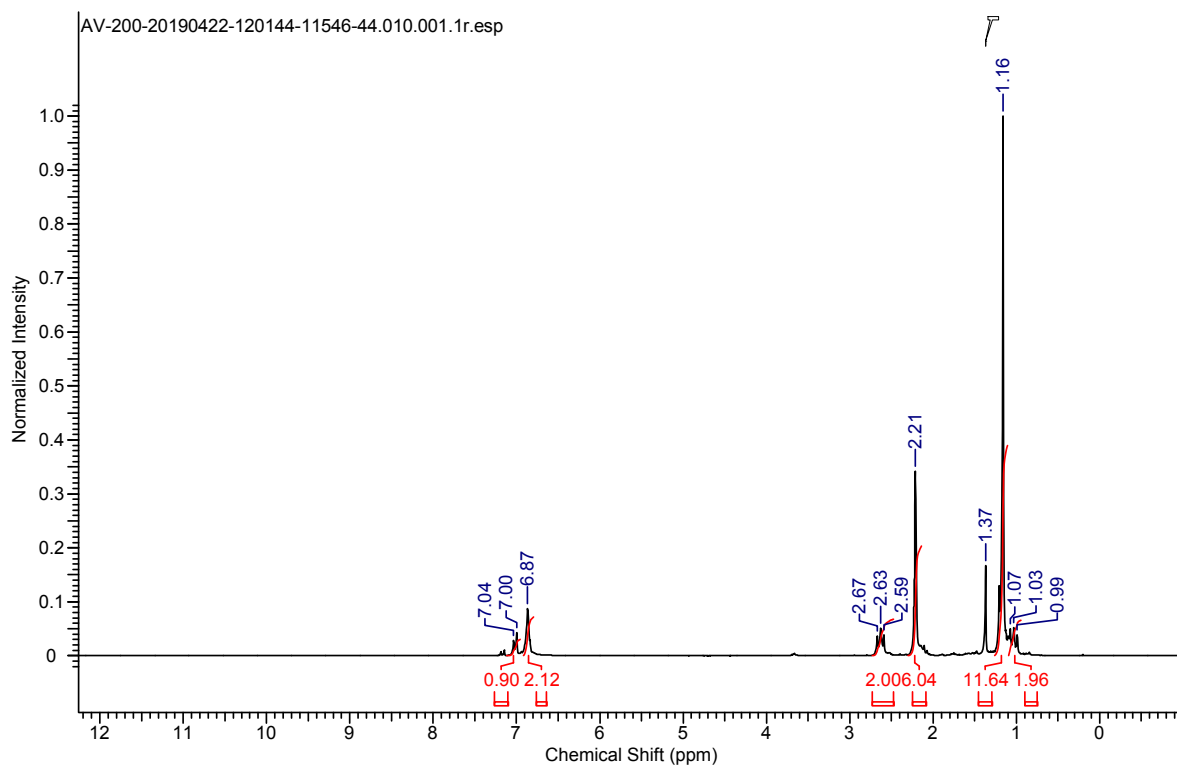


Figure S24. ^1H NMR Spectrum of **2g** (CDCl_3 , 200 MHz, 298 K).

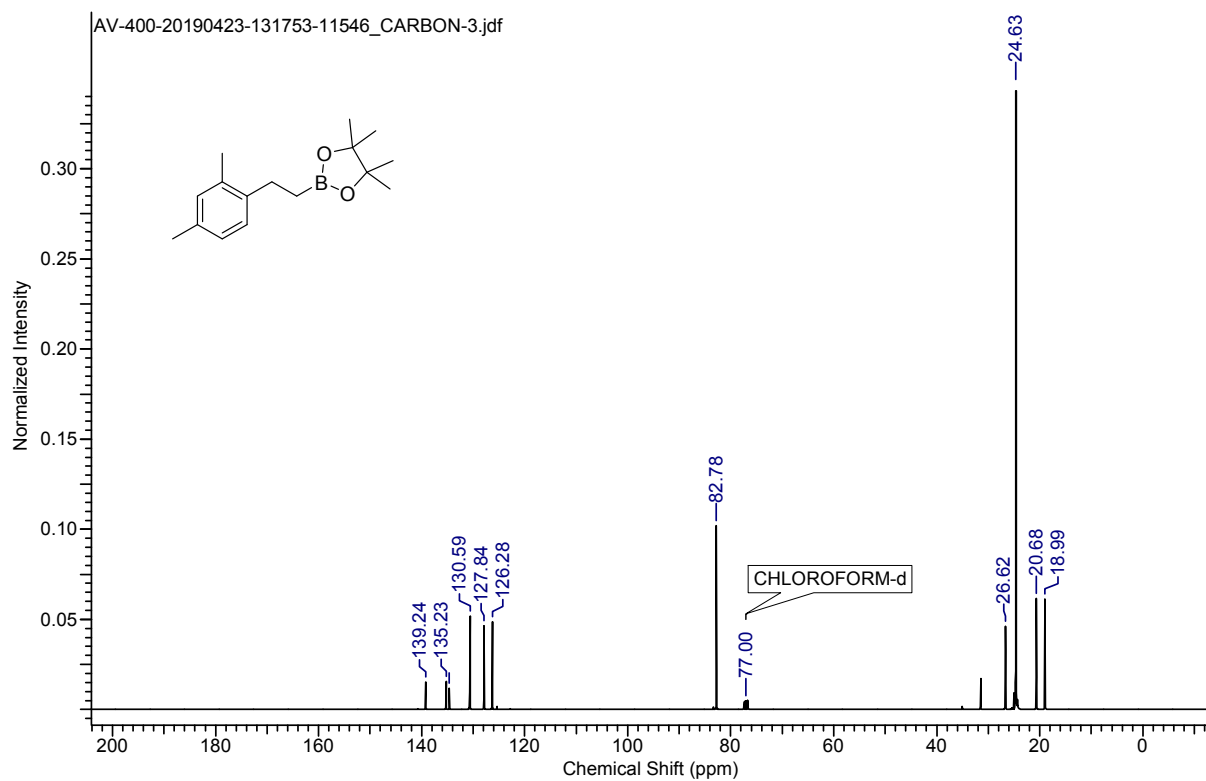
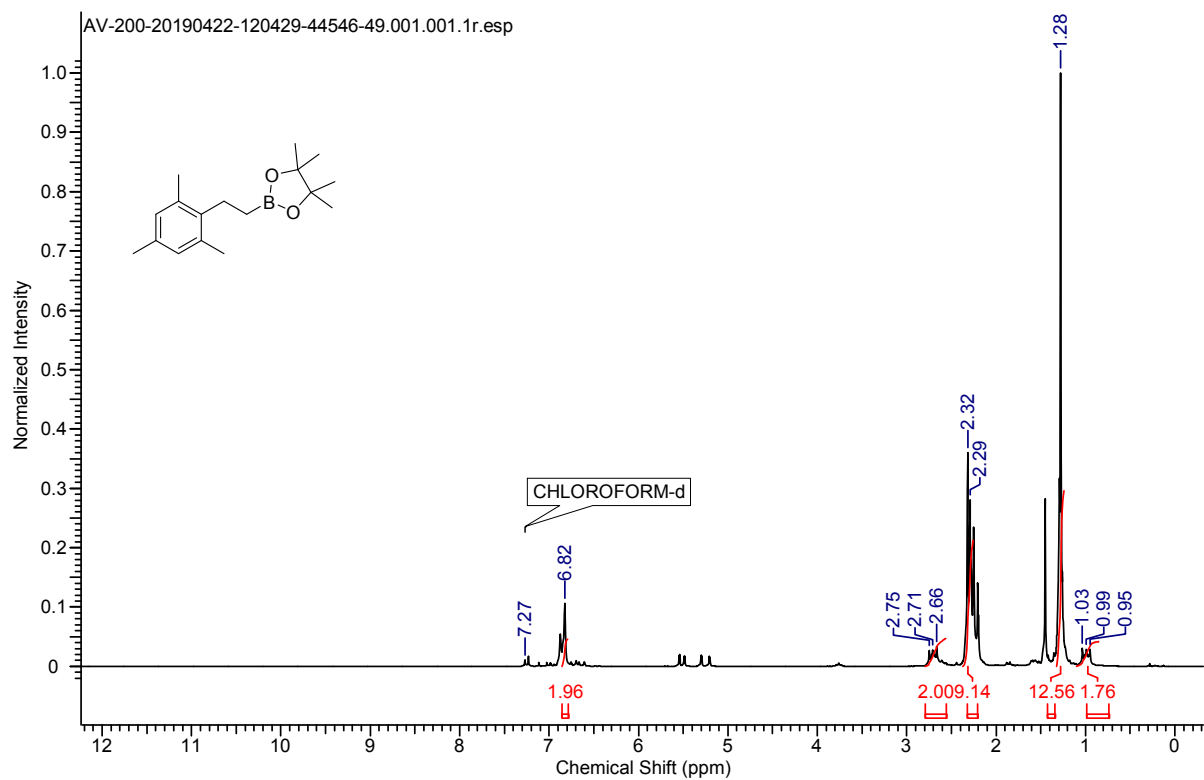


Figure S25. ^{13}C NMR spectrum of **2g** (CDCl_3 , 100.56 MHz, 298 K).



Fig

Figure S26. ^1H NMR Spectrum of **2h** (CDCl_3 , 200 MHz, 298 K).

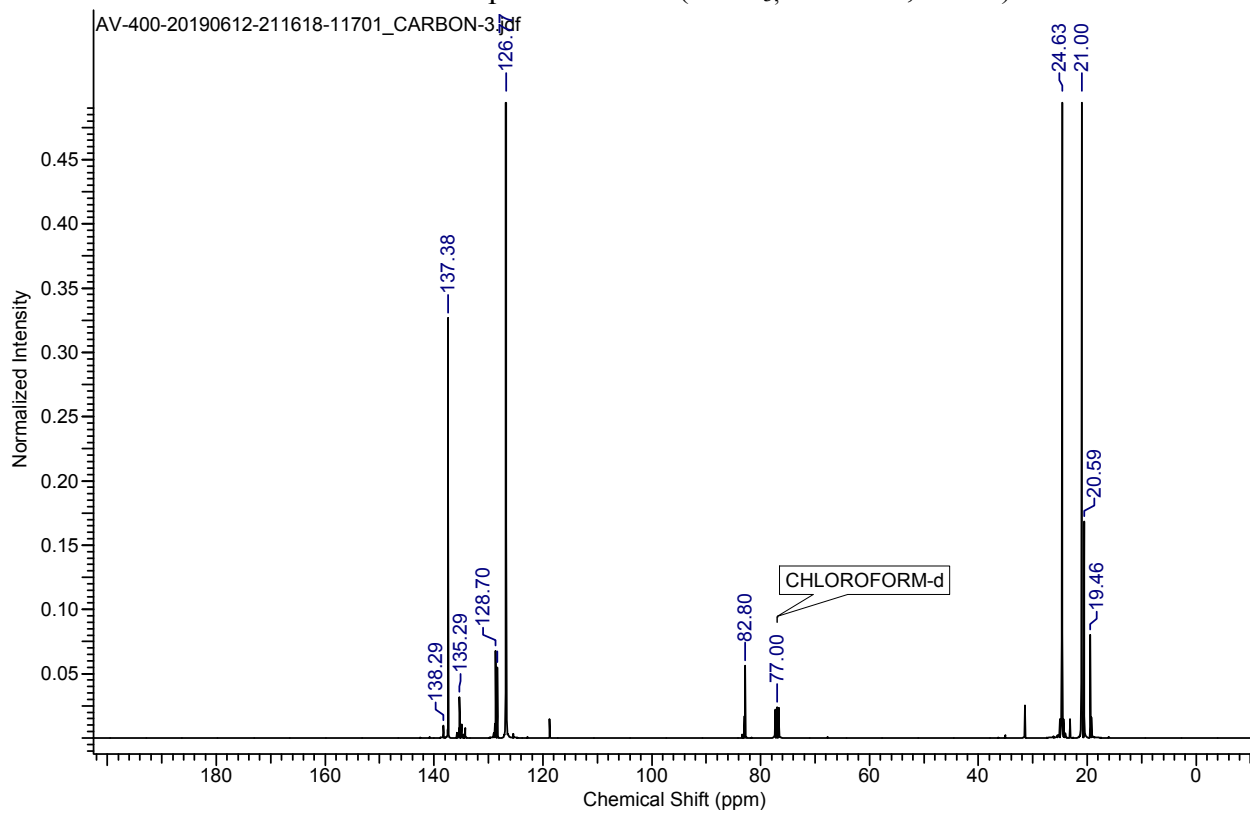
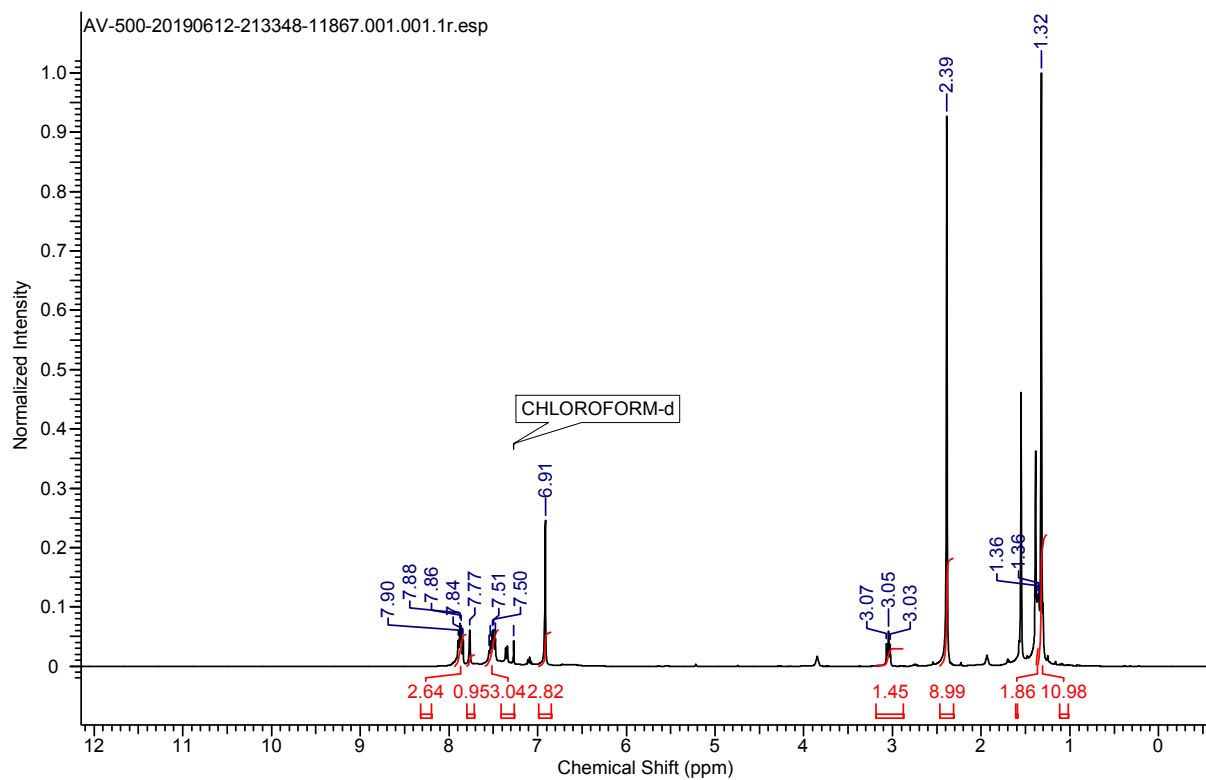


Figure S27. ^{13}C NMR spectrum of **2h** (CDCl_3 , 100.56 MHz, 298 K).



Fig

Figure S28. ^1H NMR Spectrum of **2i** (CDCl_3 , 500 MHz, 298 K).

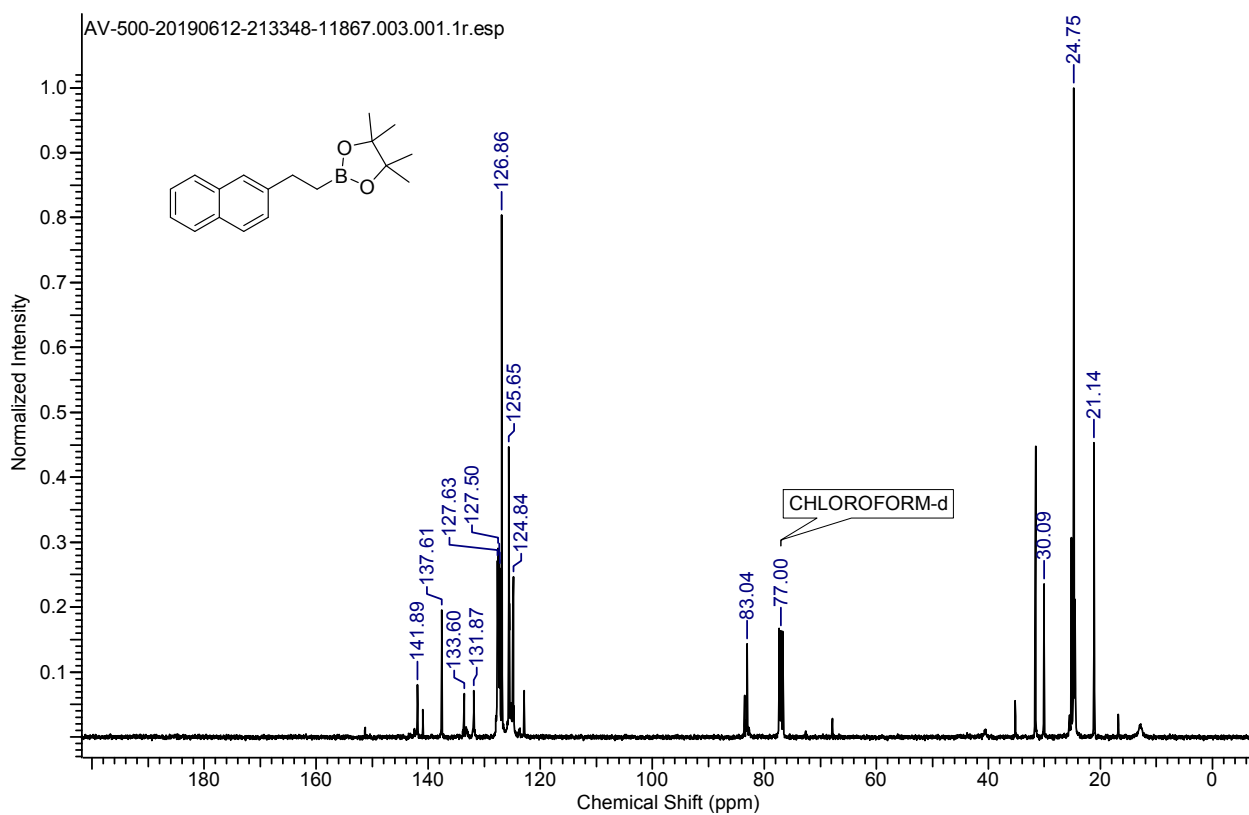


Figure S29. ^{13}C NMR spectrum of **2i** (CDCl_3 , 125.70 MHz, 298 K).

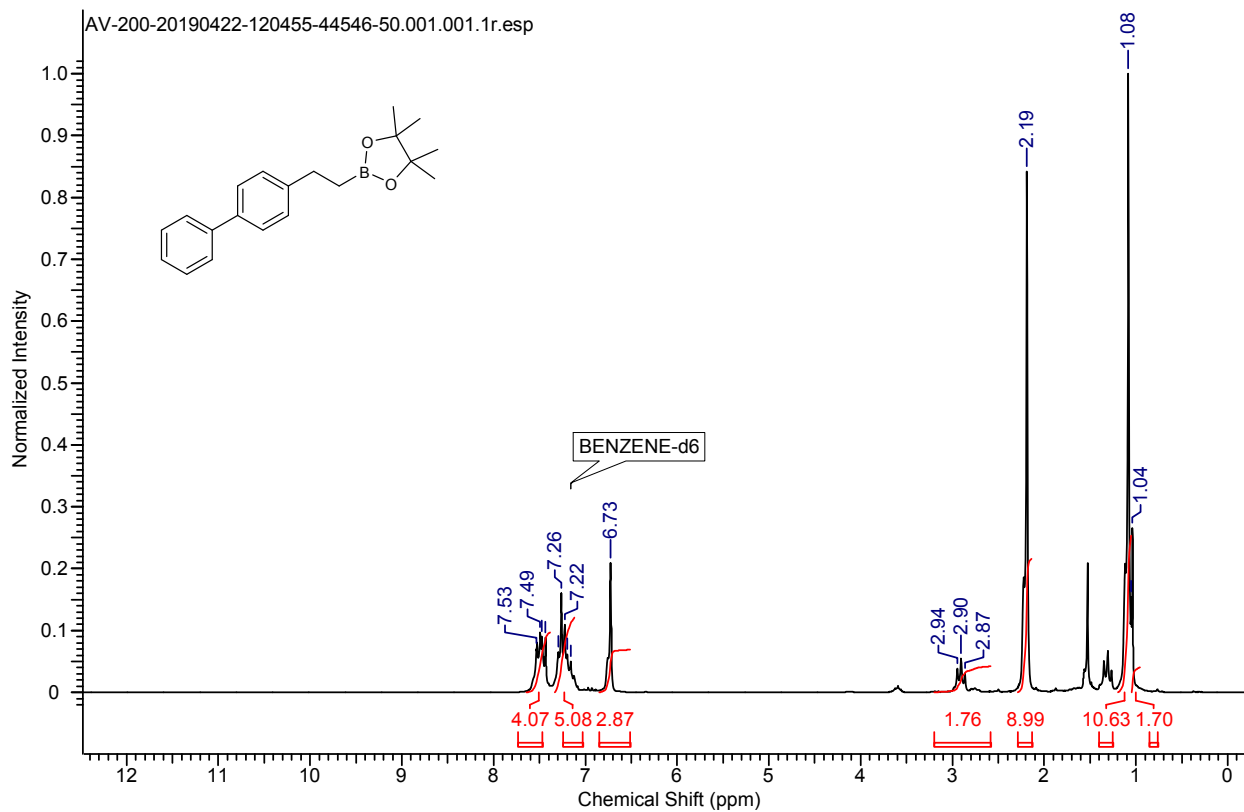


Figure S30. ^1H NMR Spectrum of **2j** (C_6D_6 , 200 MHz, 298 K).

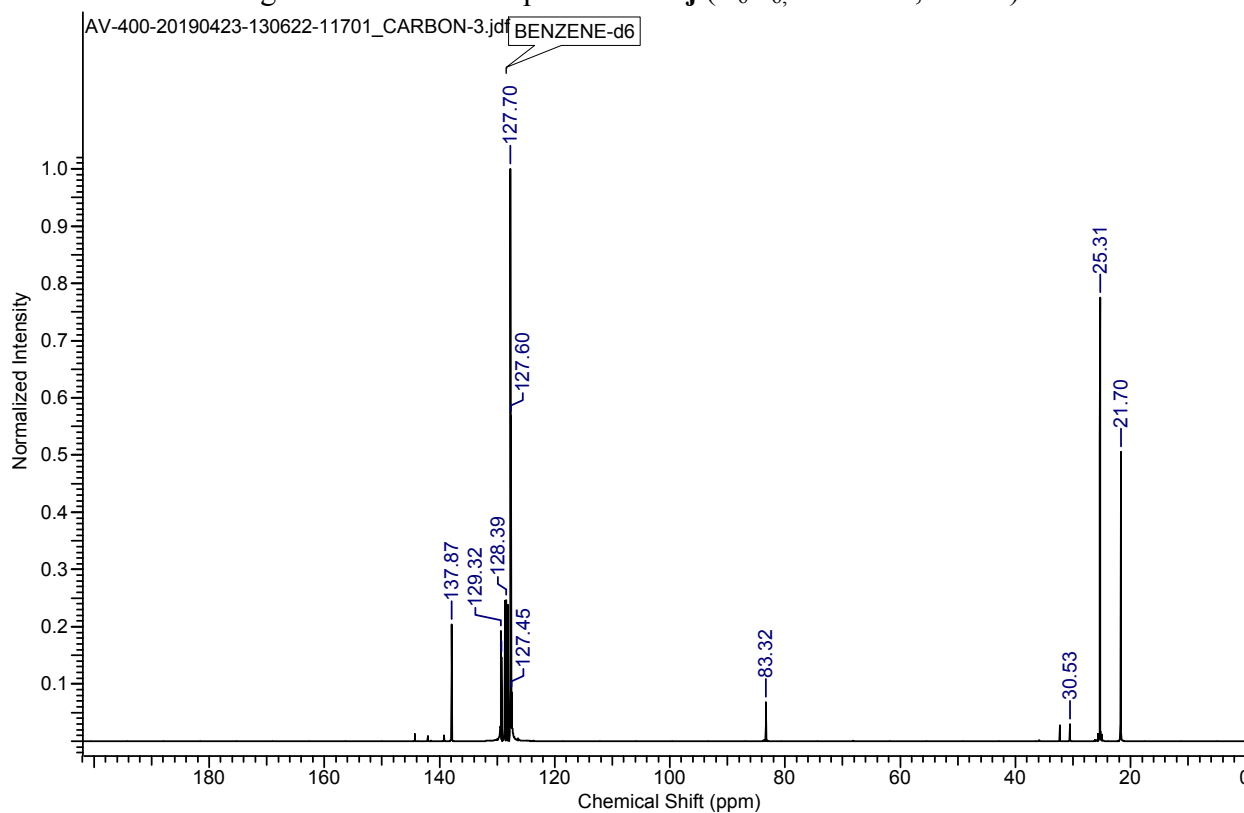


Figure S31. ^{13}C NMR spectrum of **2j** (C_6D_6 , 100.56 MHz, 298 K).

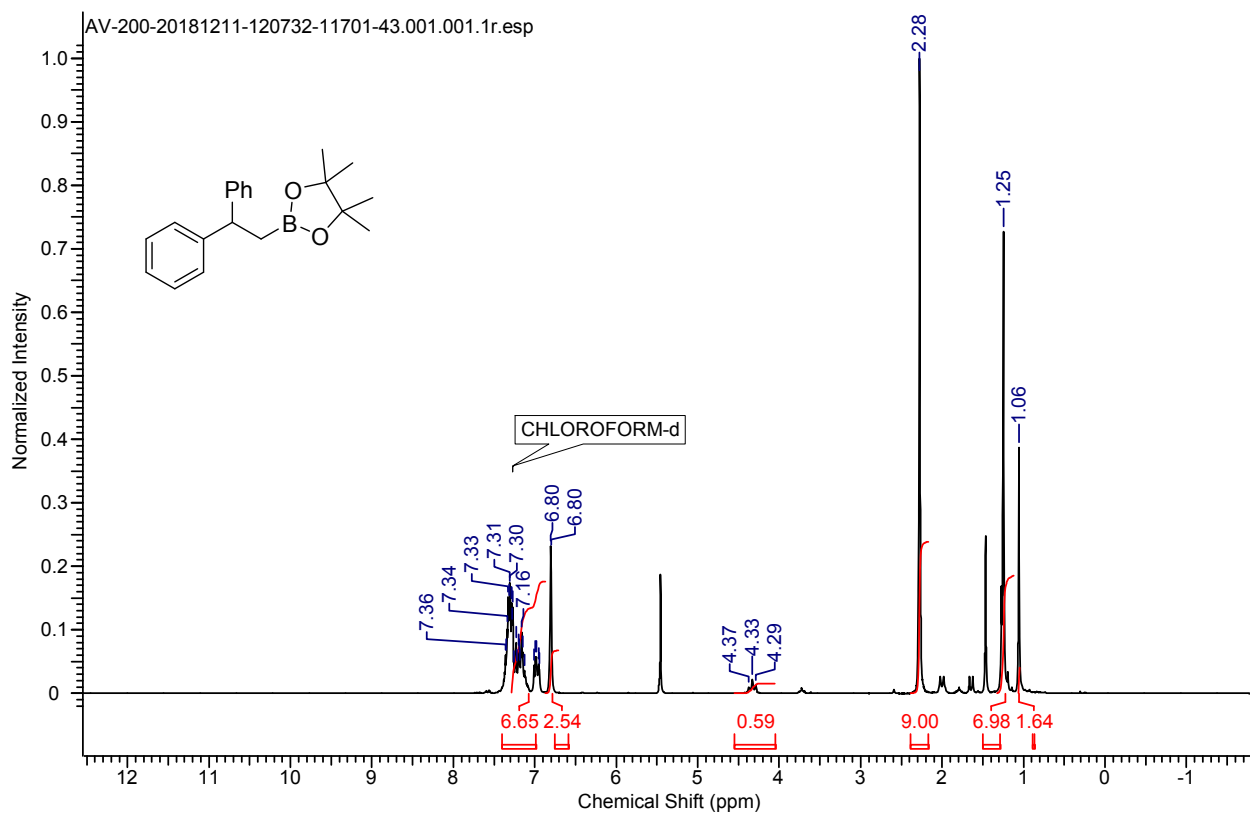


Figure S32. ^1H NMR Spectrum of **2k** (CDCl_3 , 200 MHz, 298 K).

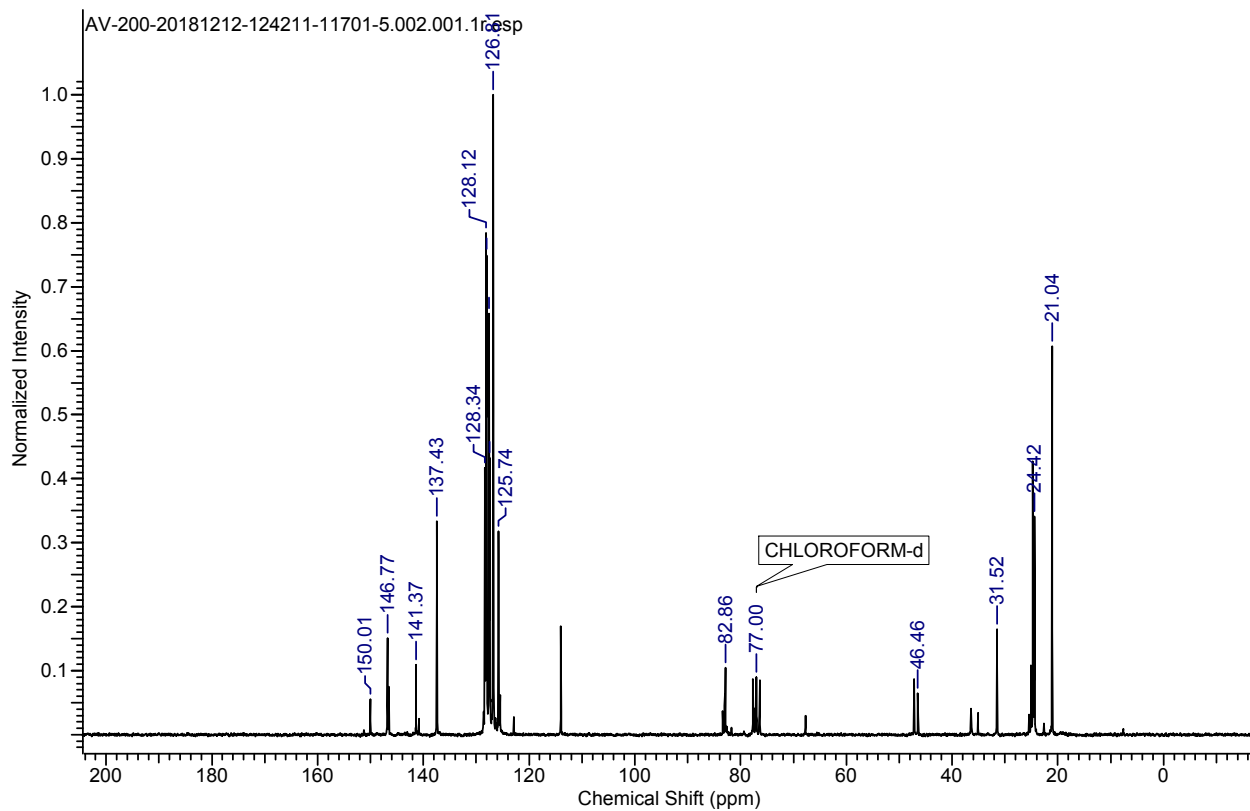


Figure S33. ^{13}C NMR spectrum of **2k** (CDCl_3 , 50.28 MHz, 298 K).

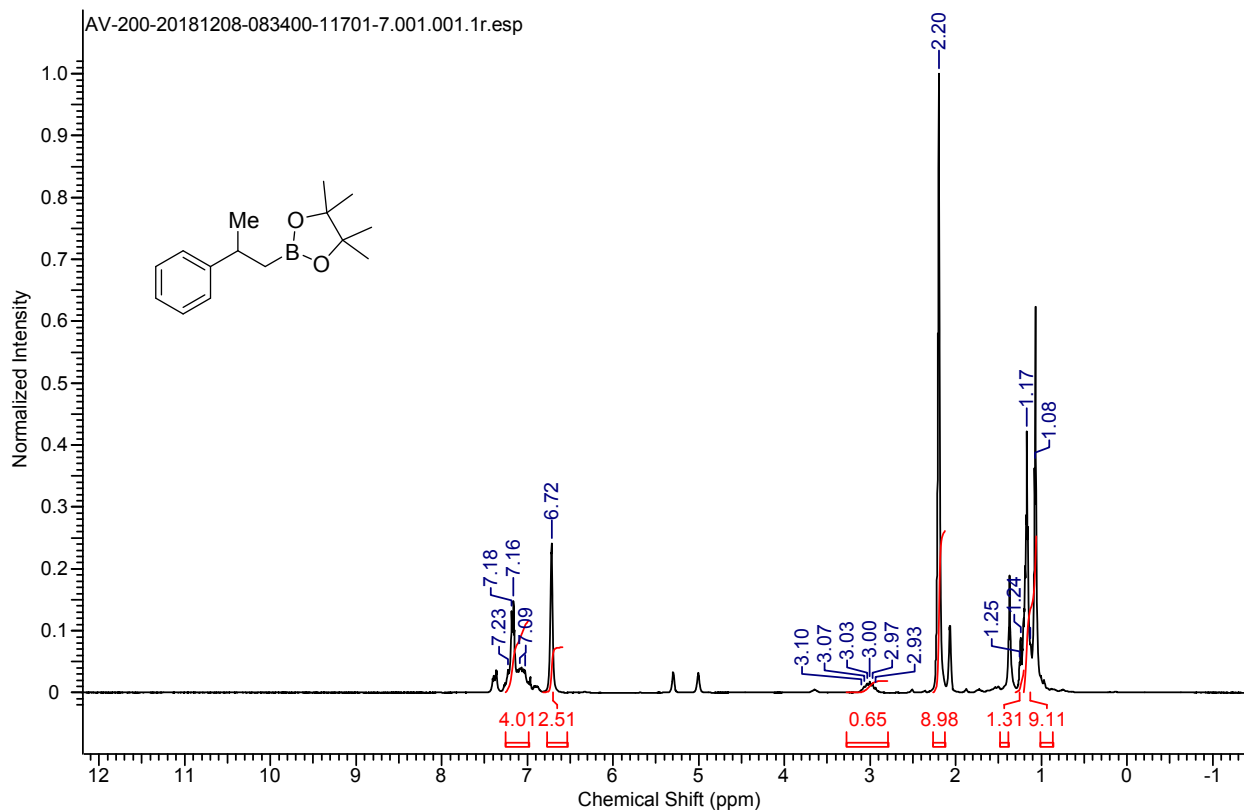


Figure S34. ^1H NMR Spectrum of **2I** (CDCl_3 , 200 MHz, 298 K).

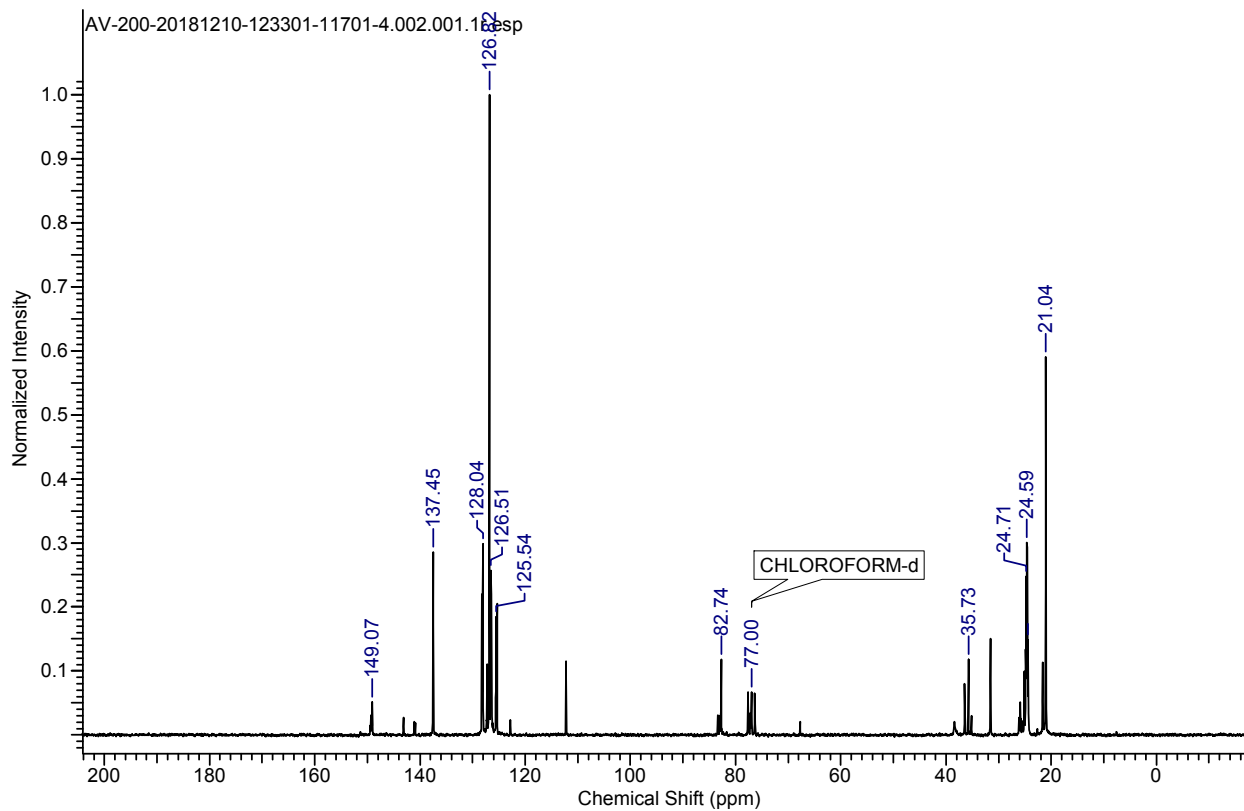
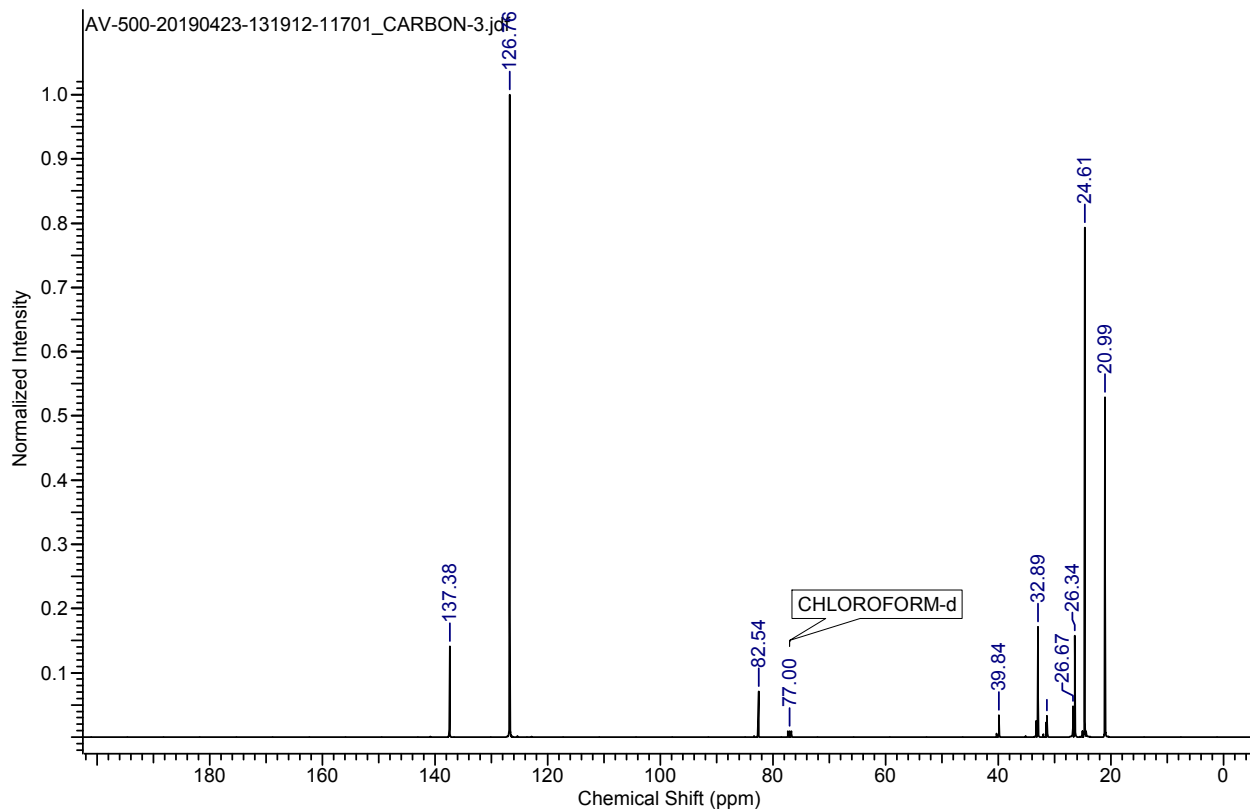
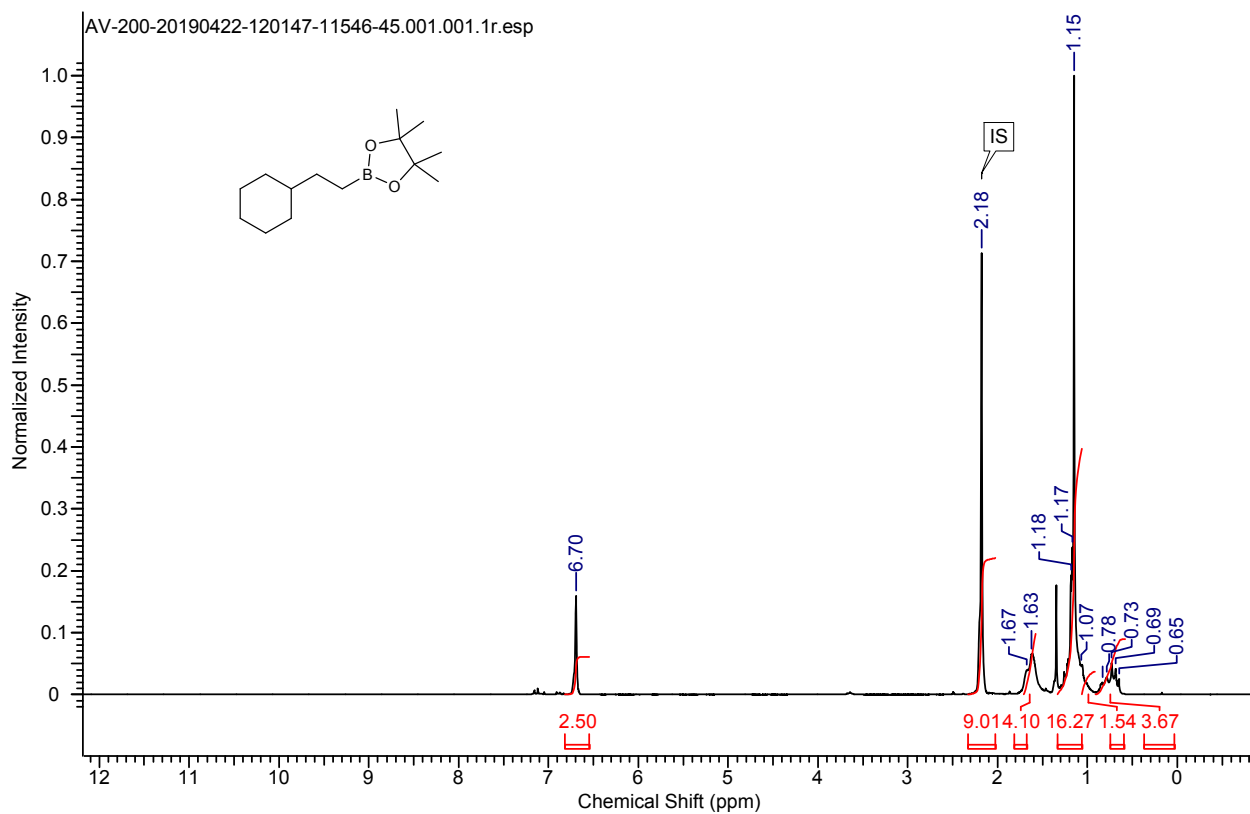
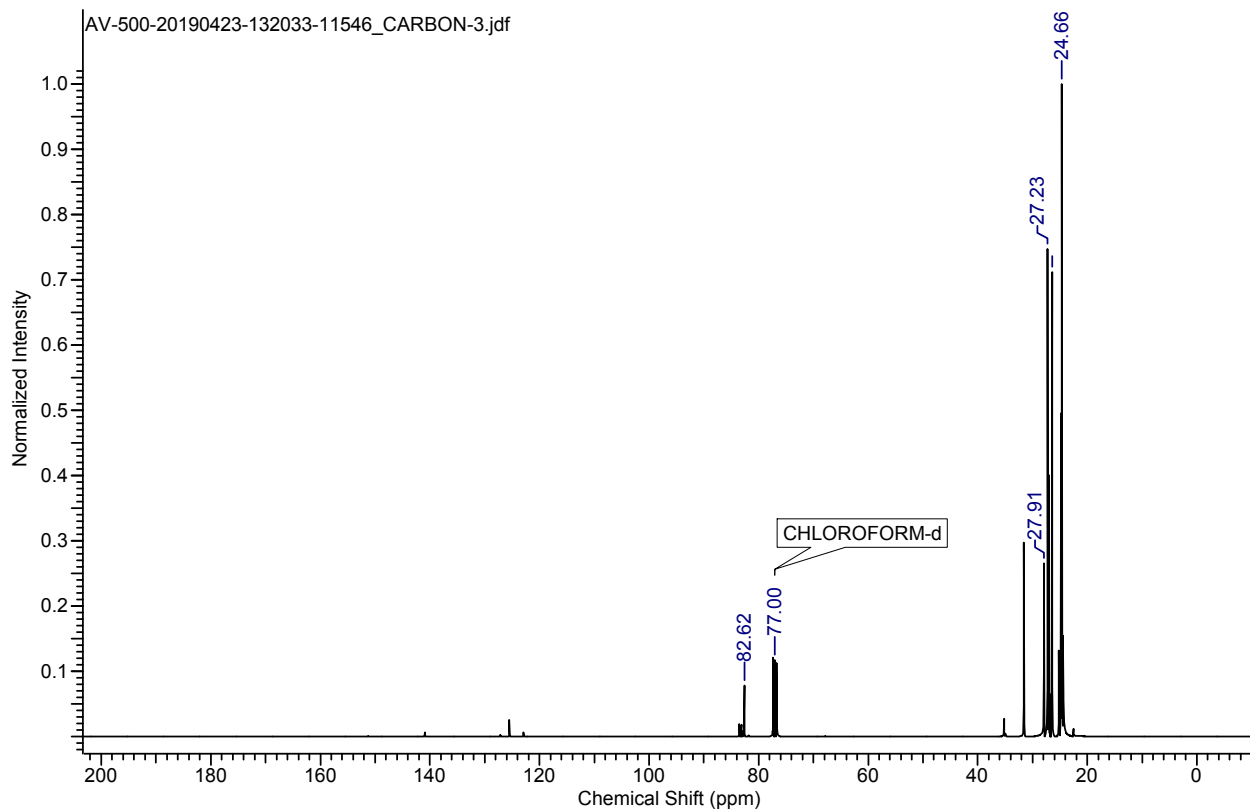
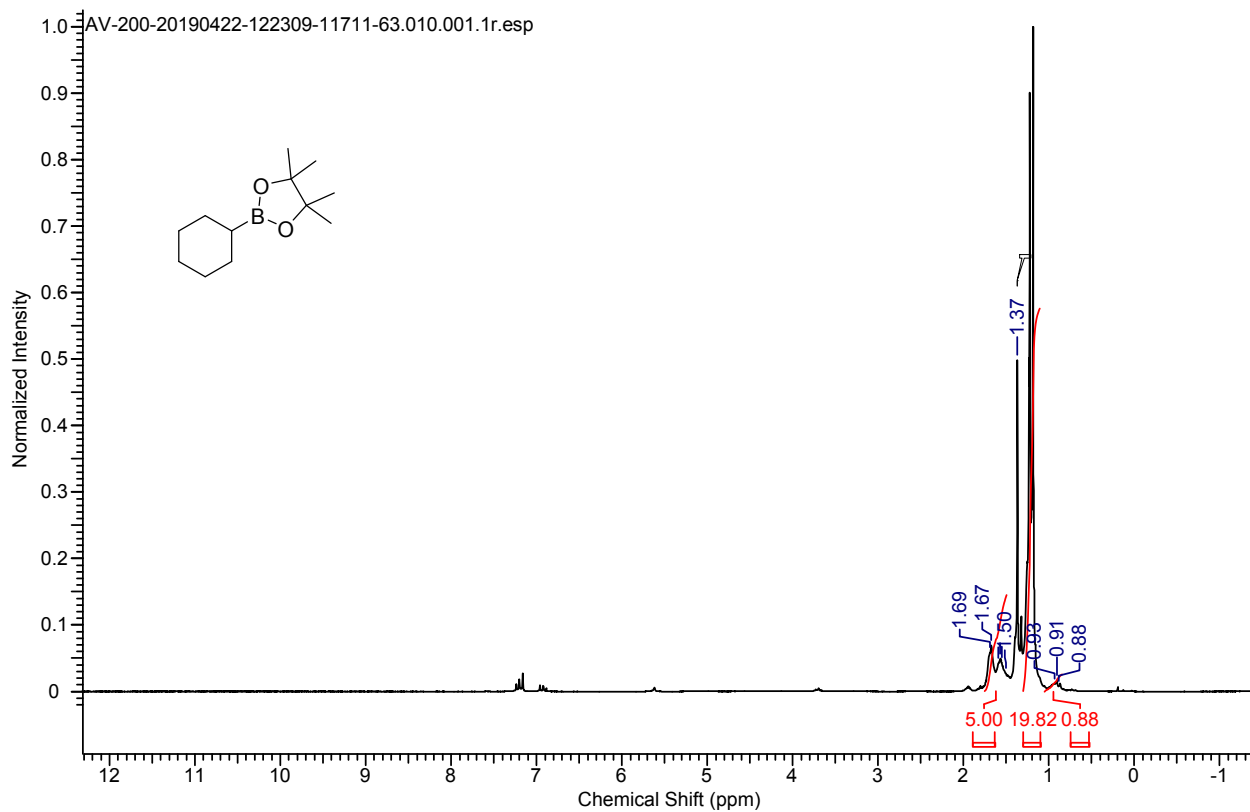


Figure S35. ^{13}C NMR spectrum of **2I** (CDCl_3 , 50.28 MHz, 298 K).





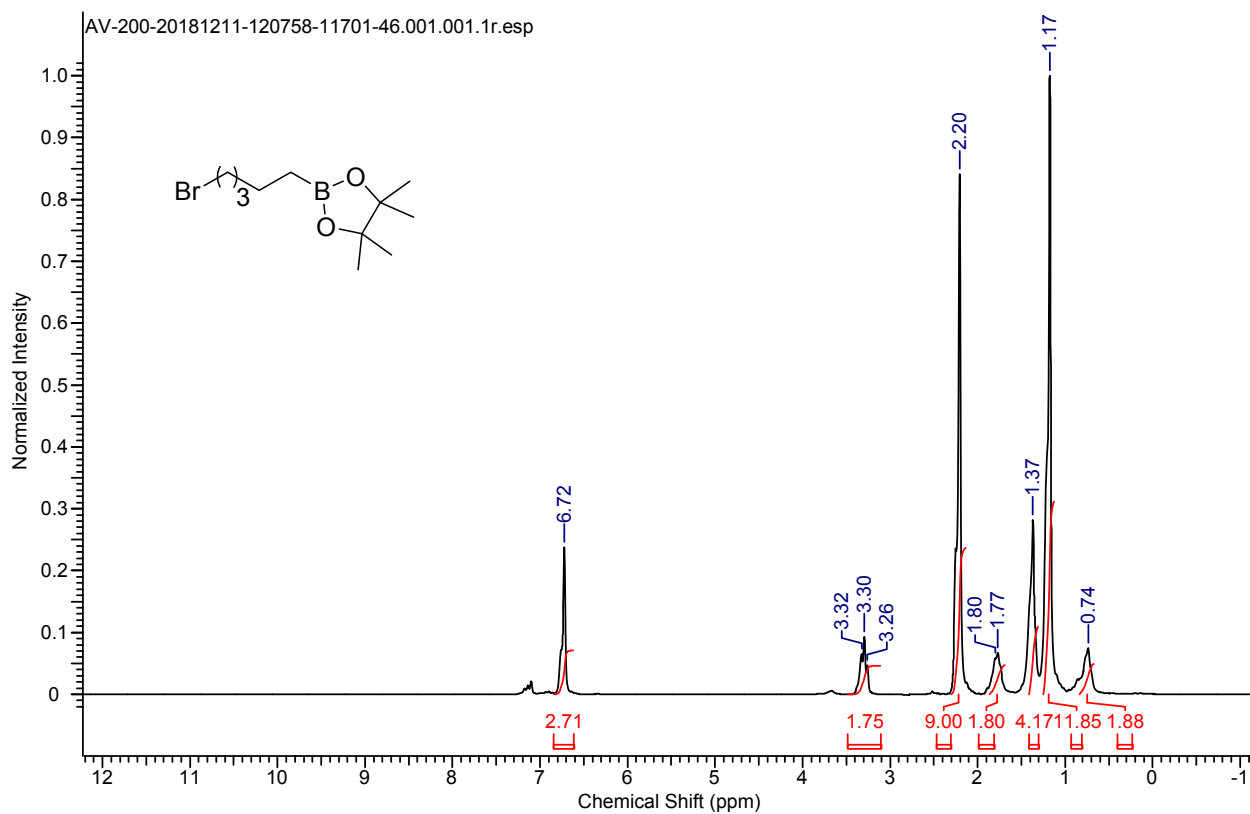


Figure S40. ^1H NMR Spectrum of **2o** (CDCl_3 , 200 MHz, 298 K).

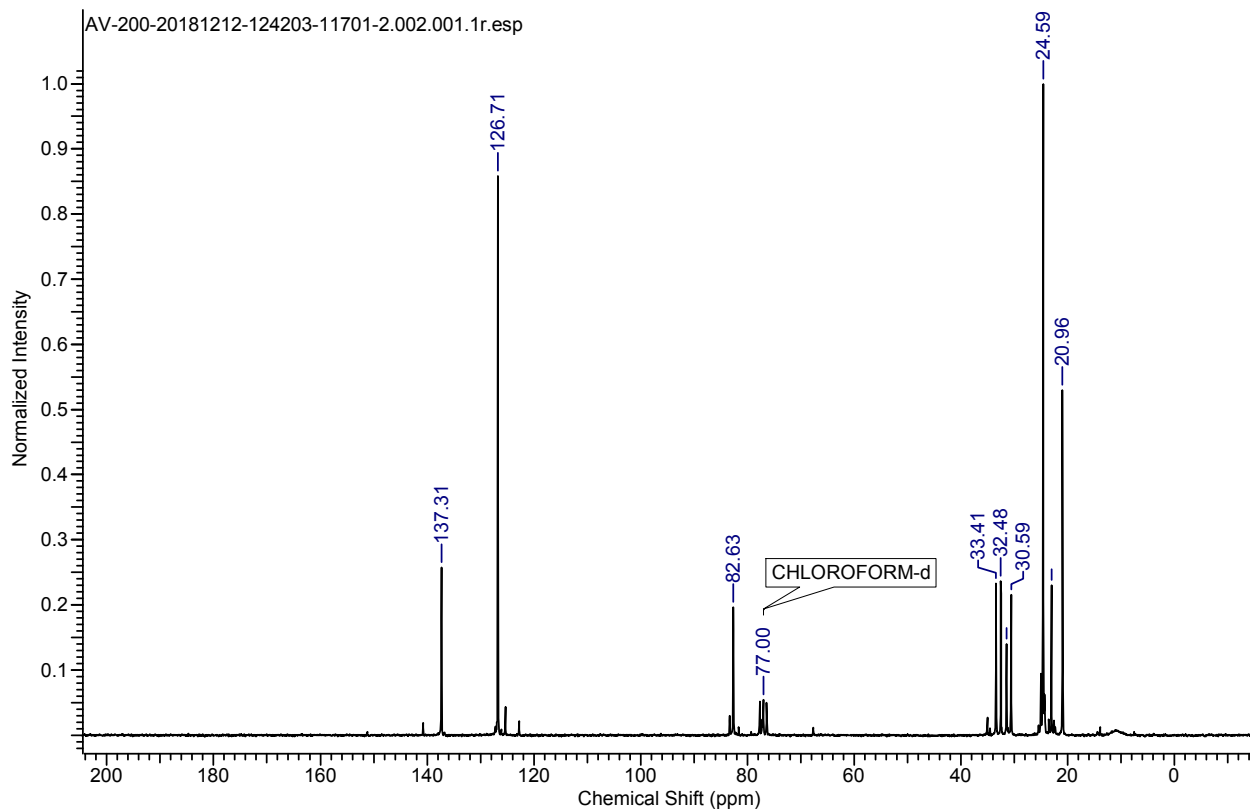


Figure S41. ^{13}C NMR spectrum of **2o** (CDCl_3 , 50.28 MHz, 298 K)

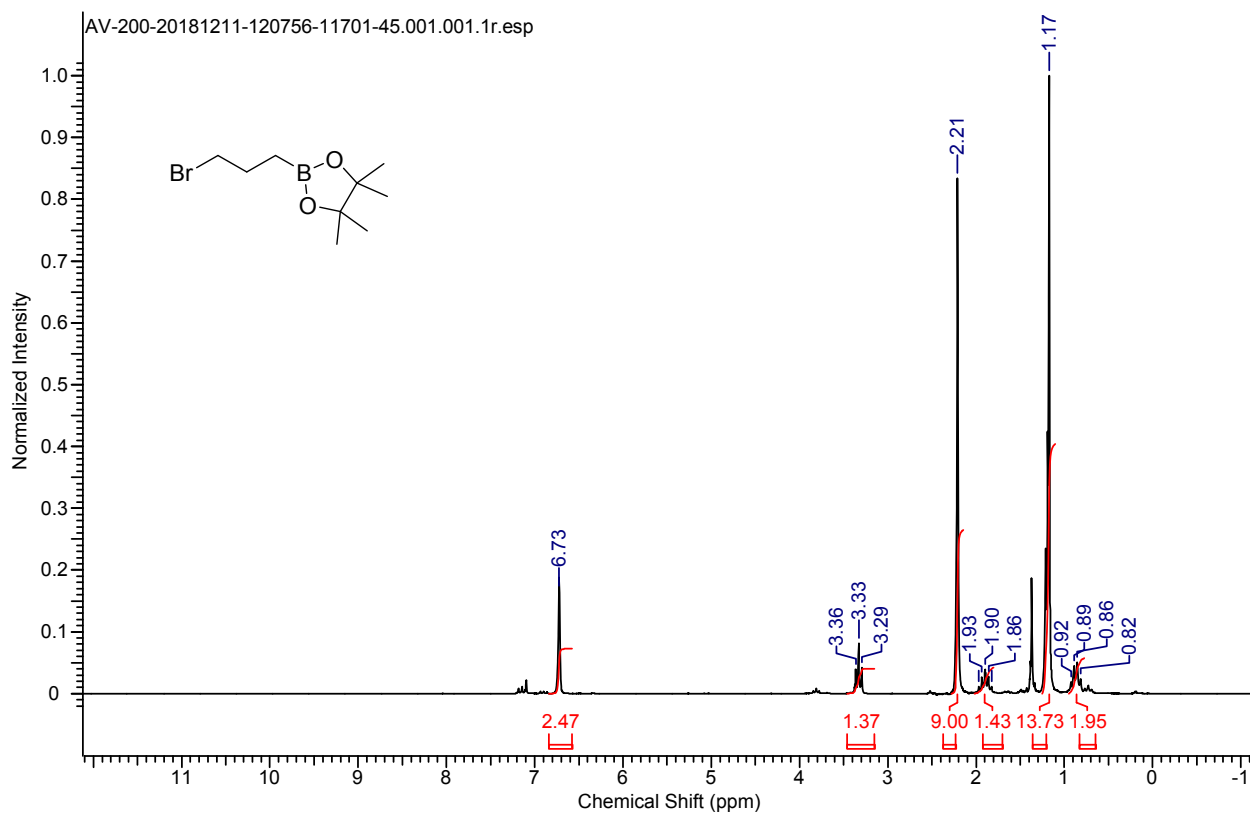


Figure S42. ^1H NMR Spectrum of **2p** (CDCl_3 , 200 MHz, 298 K).

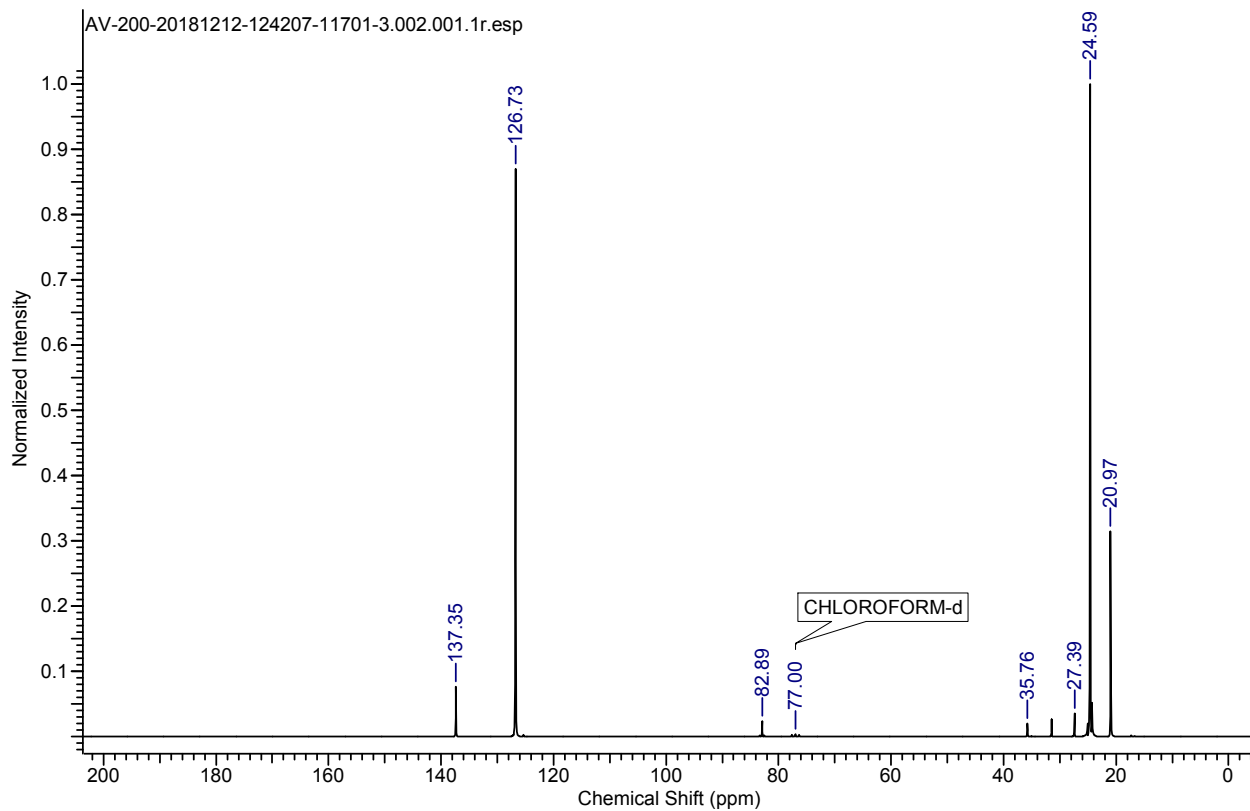


Figure S43. ^{13}C NMR spectrum of **2p** (CDCl_3 , 50.28 MHz, 298 K).

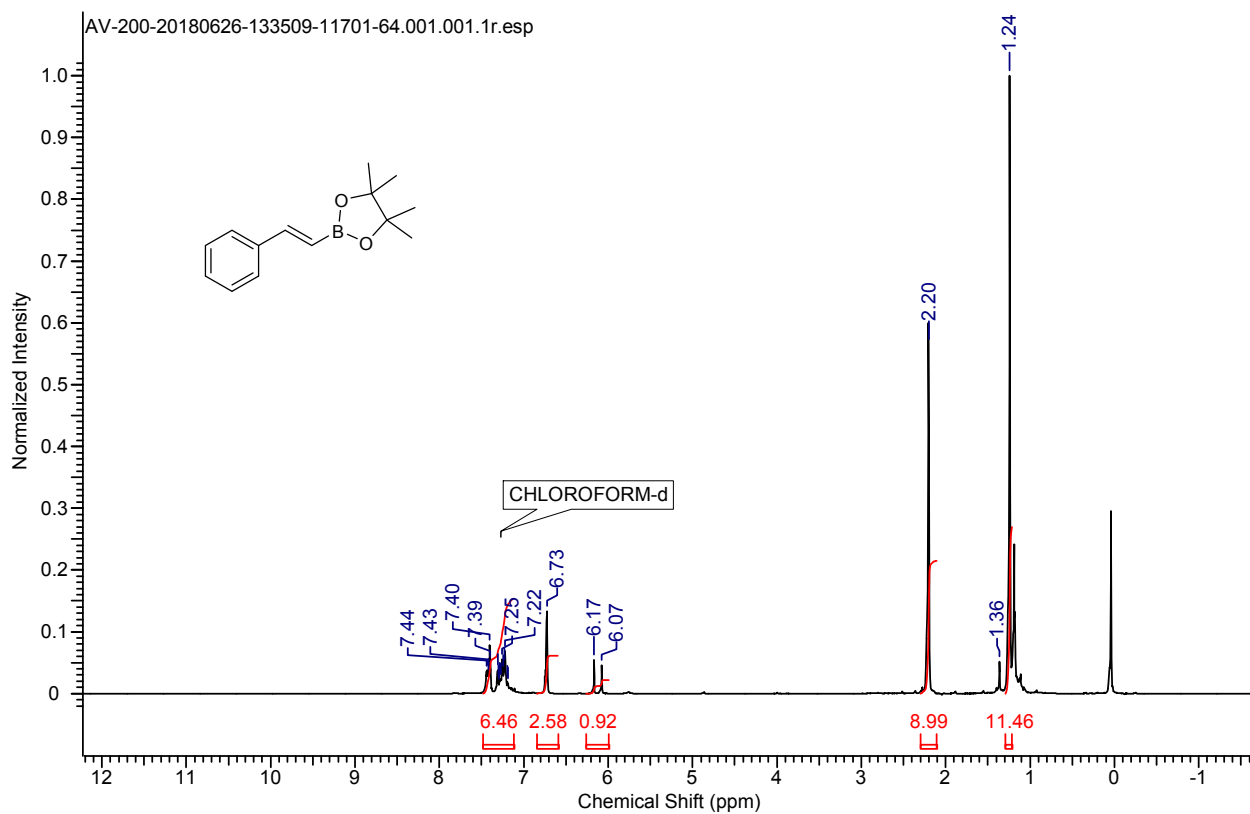


Figure S44. ^1H NMR Spectrum of **3a** (CDCl_3 , 200 MHz, 298 K).

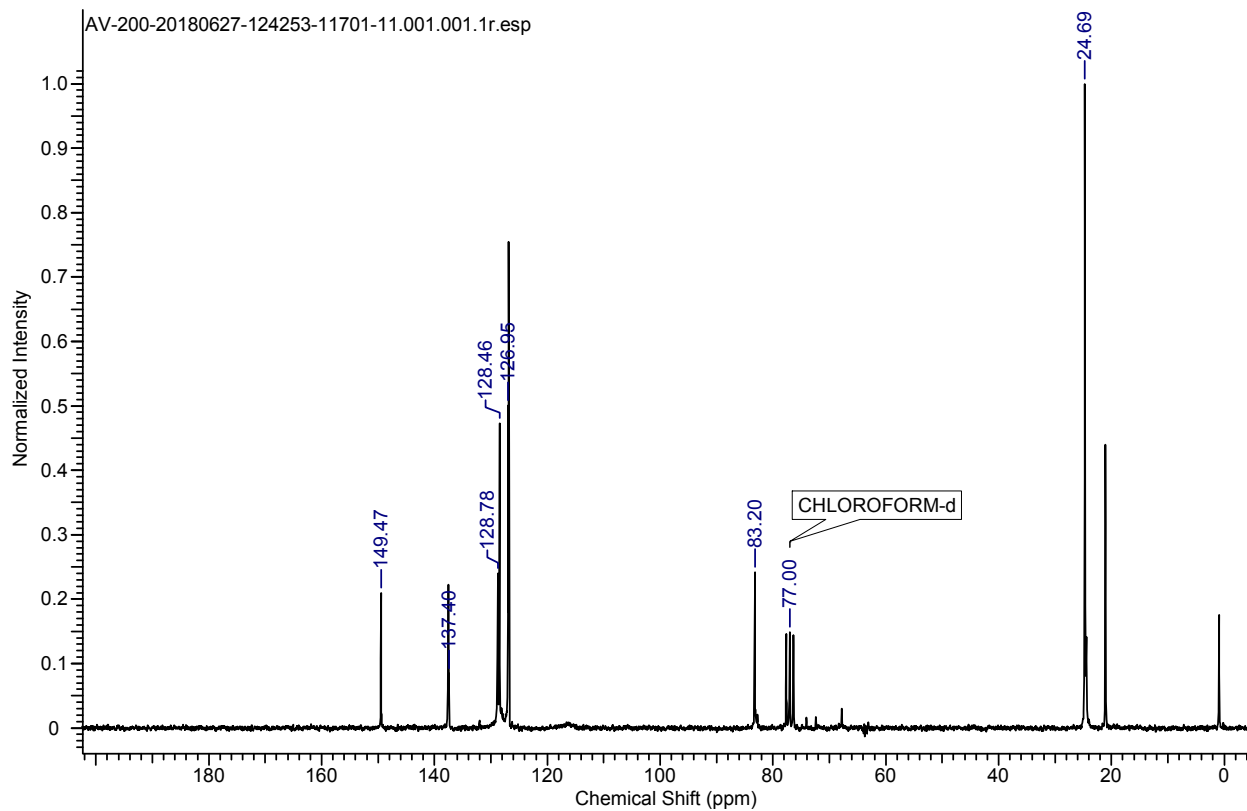


Figure S45. ^{13}C NMR spectrum of **3a** (CDCl_3 , 50.28 MHz, 298 K).

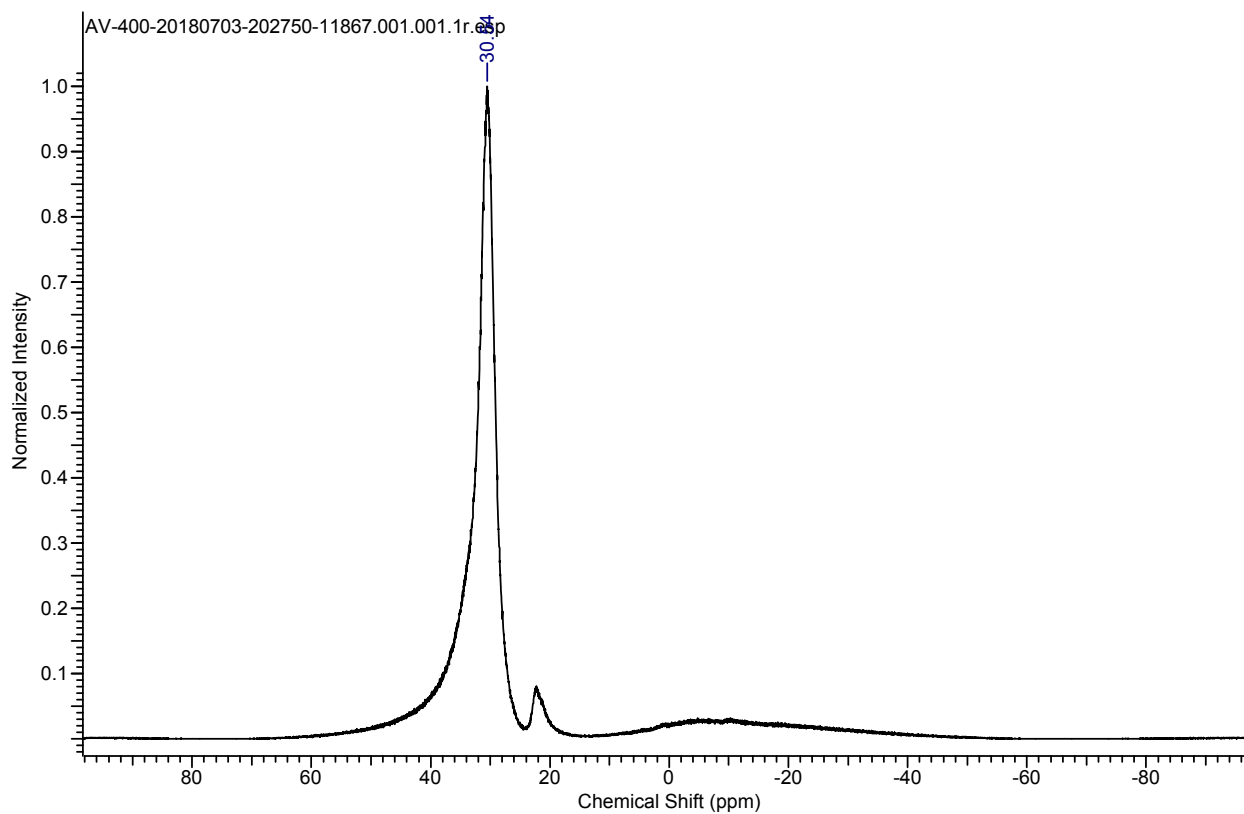


Figure S46. ^{11}B NMR spectrum of **3a** (C_6D_6 , 128 MHz, 298 K).

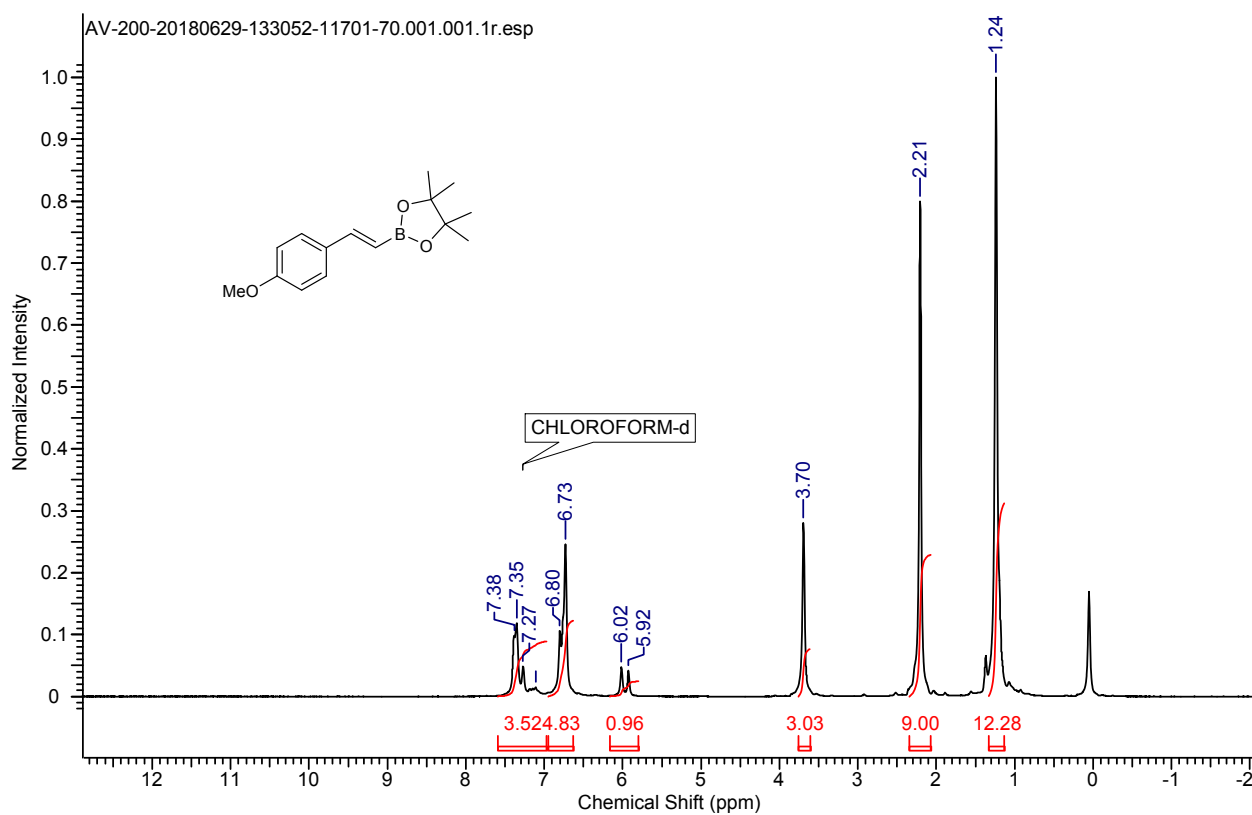


Figure S47. ^1H NMR Spectrum of **3b** (CDCl_3 , 200 MHz, 298 K).

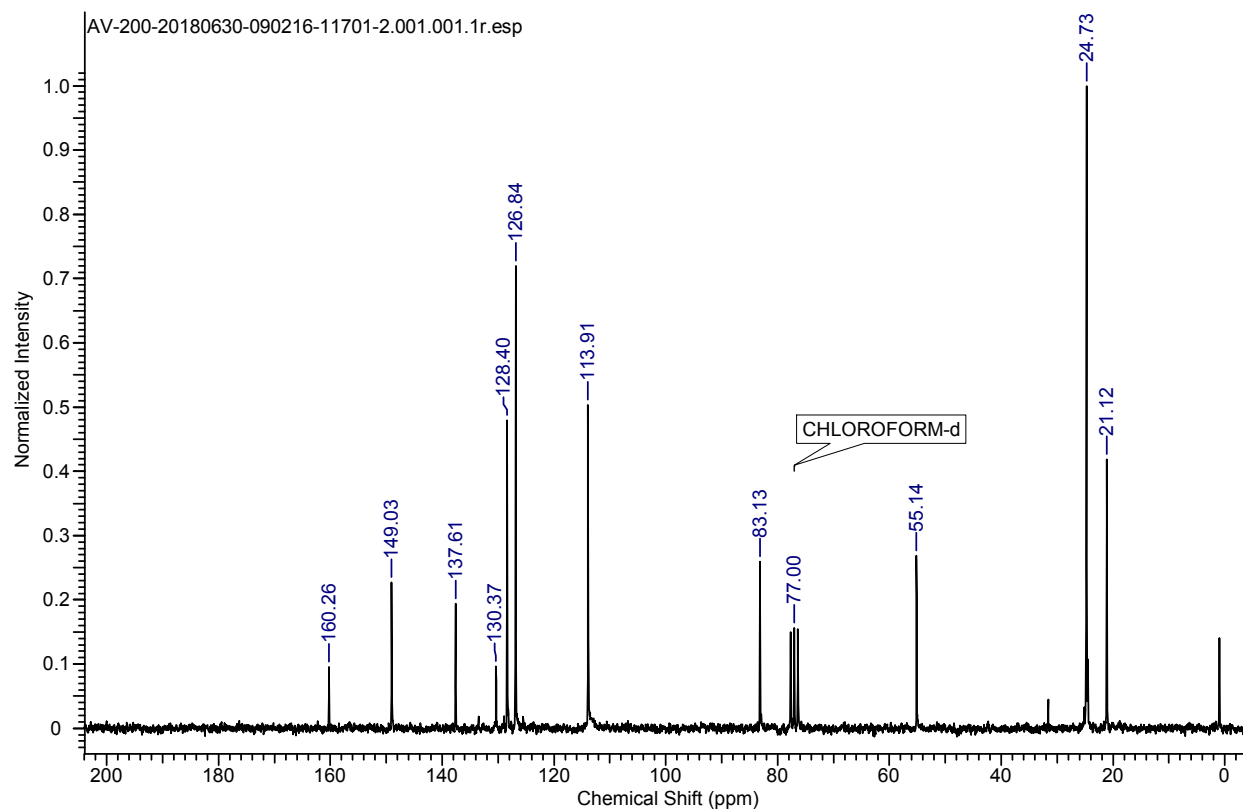


Figure S48. ^{13}C NMR spectrum of **3b** (CDCl_3 , 50.28 MHz, 298 K).

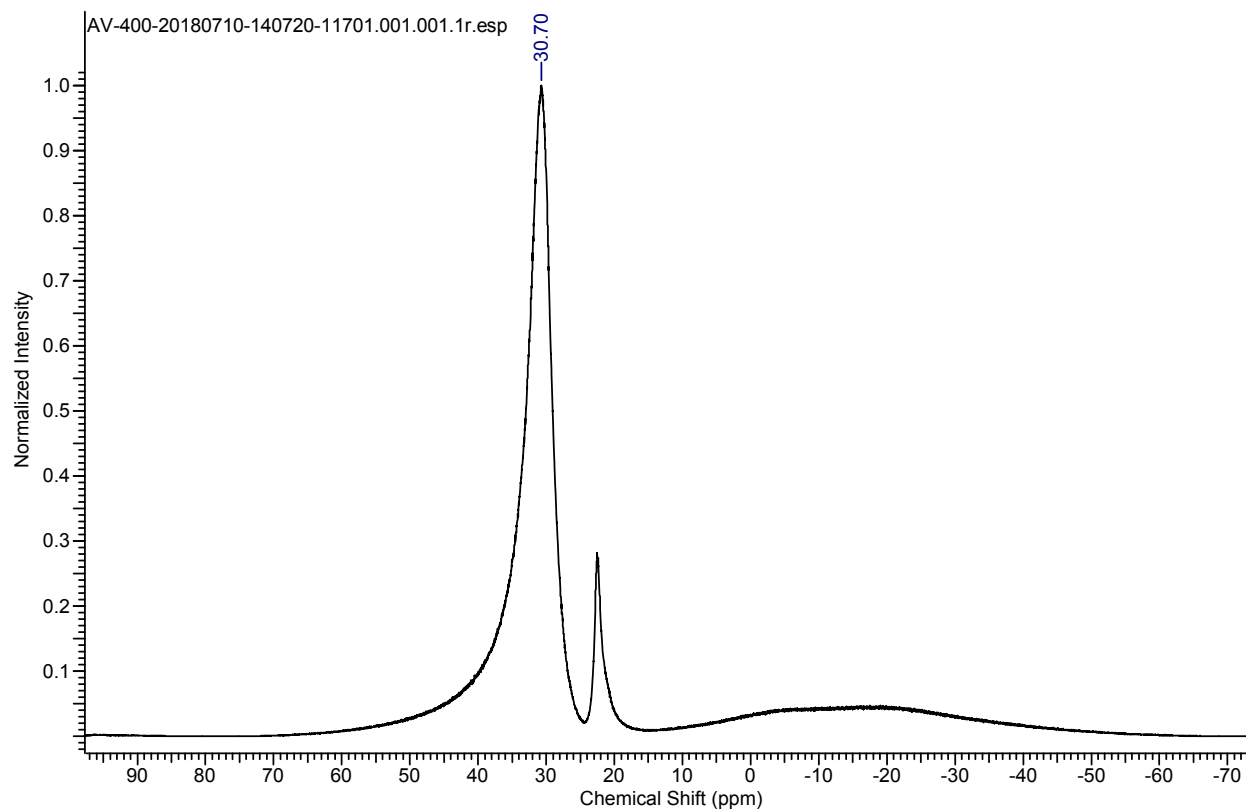


Figure S49. ^{11}B NMR spectrum of **3b** (C_6D_6 , 128 MHz, 298 K).

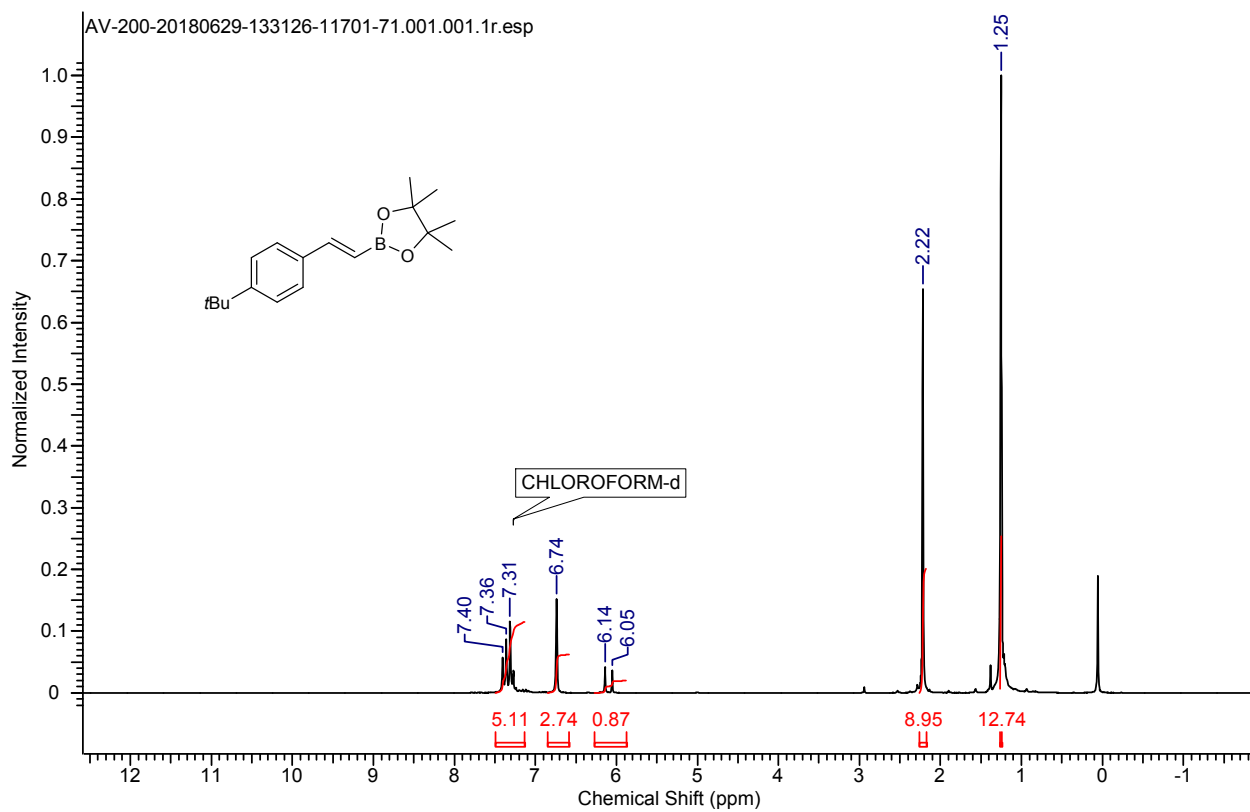


Figure S50. ^1H NMR Spectrum of **3c** (CDCl_3 , 200 MHz, 298 K).

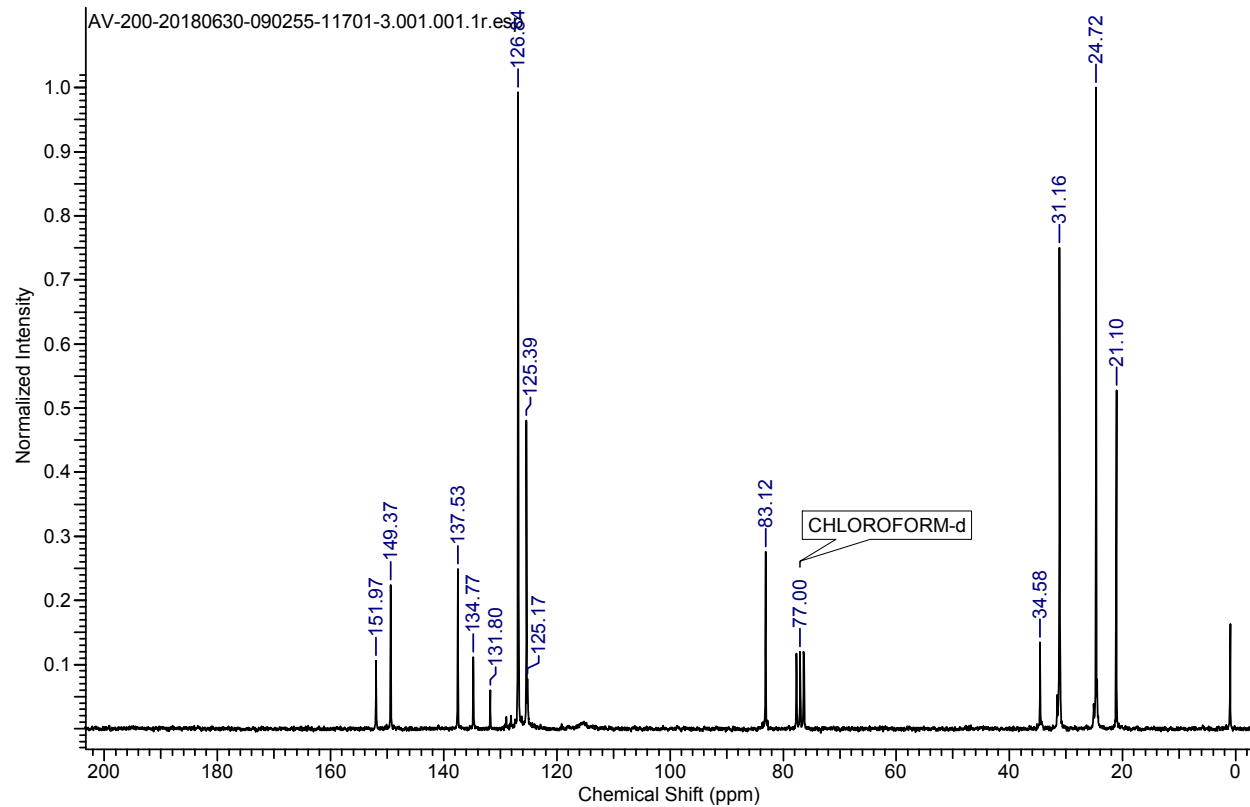


Figure S51. ^{13}C NMR spectrum of **3c** (CDCl_3 , 50.28 MHz, 298 K).

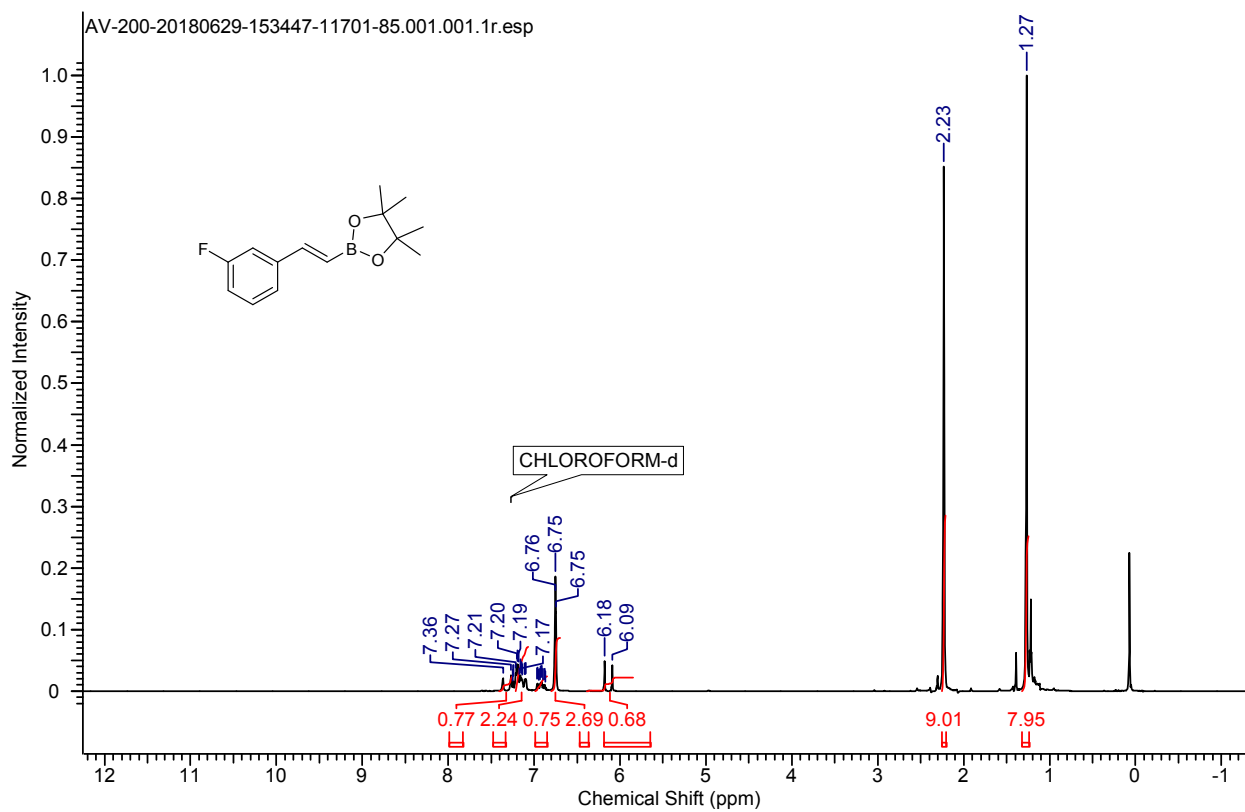


Figure S52. ^1H NMR Spectrum of **3d** (CDCl_3 , 200 MHz, 298 K).

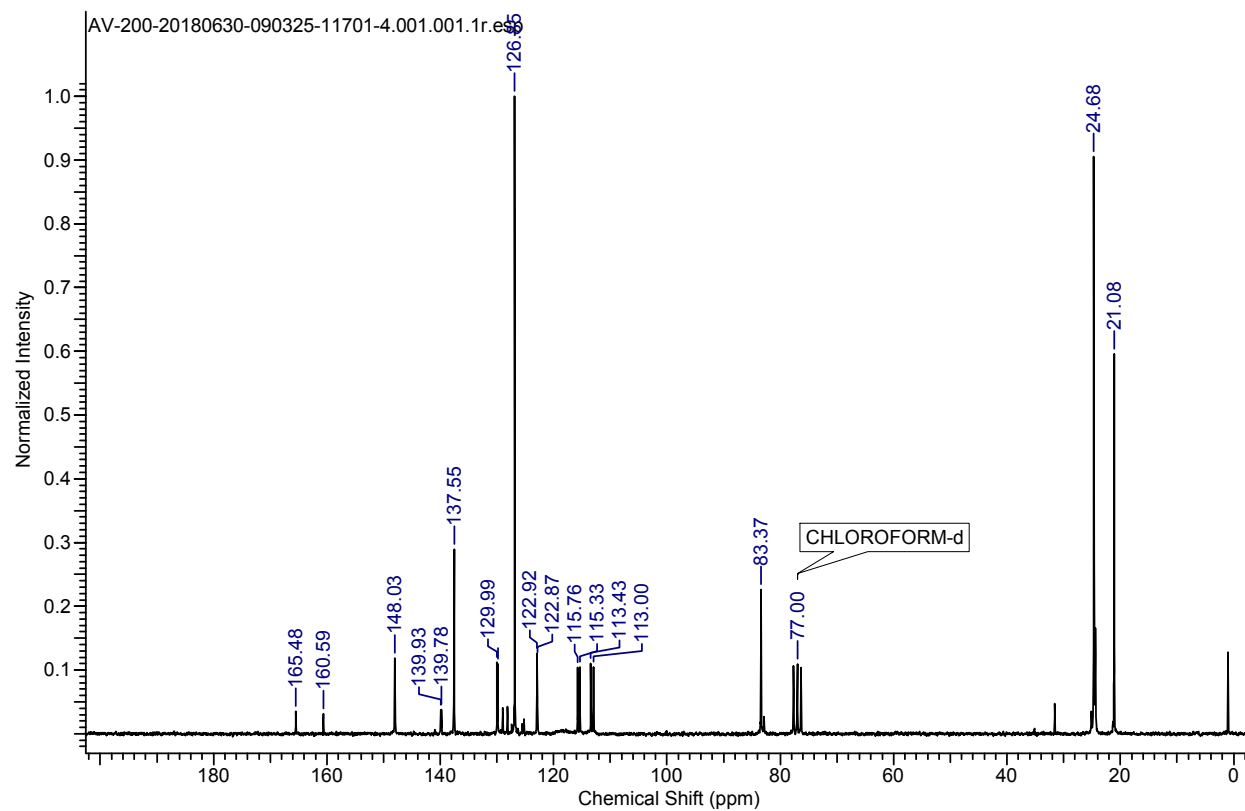


Figure S53. ^{13}C NMR spectrum of **3d** (CDCl_3 , 50.28 MHz, 298 K).

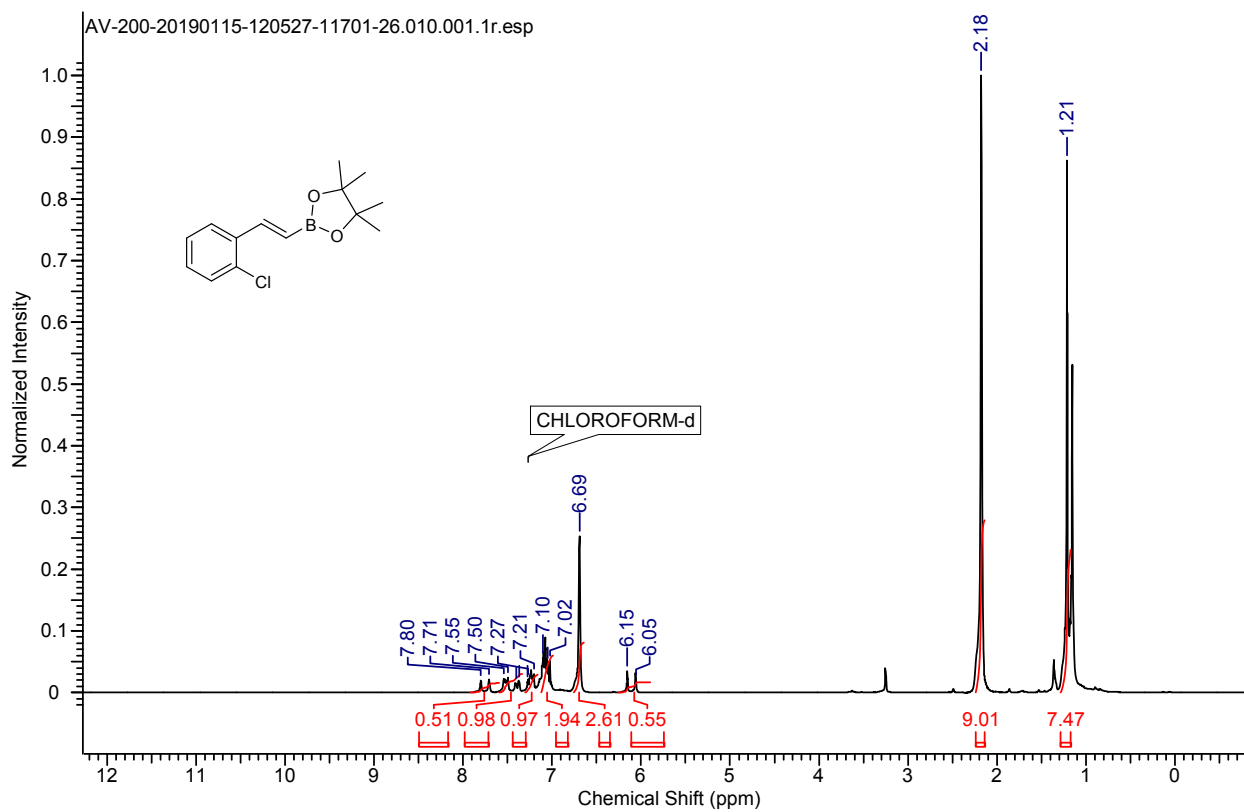


Figure S54. ^1H NMR Spectrum of **3e** (CDCl_3 , 200 MHz, 298 K).

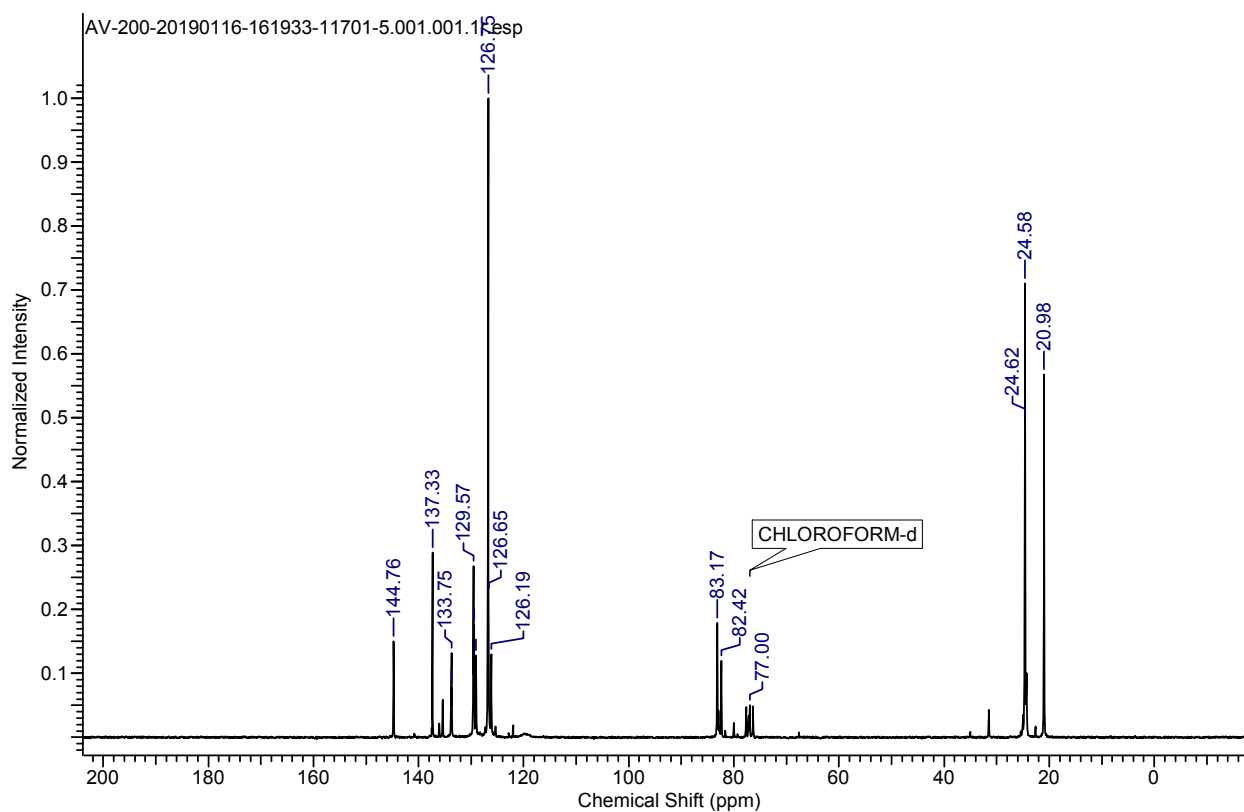


Figure S55. ^{13}C NMR spectrum of **3e** (CDCl_3 , 50.28 MHz, 298 K).

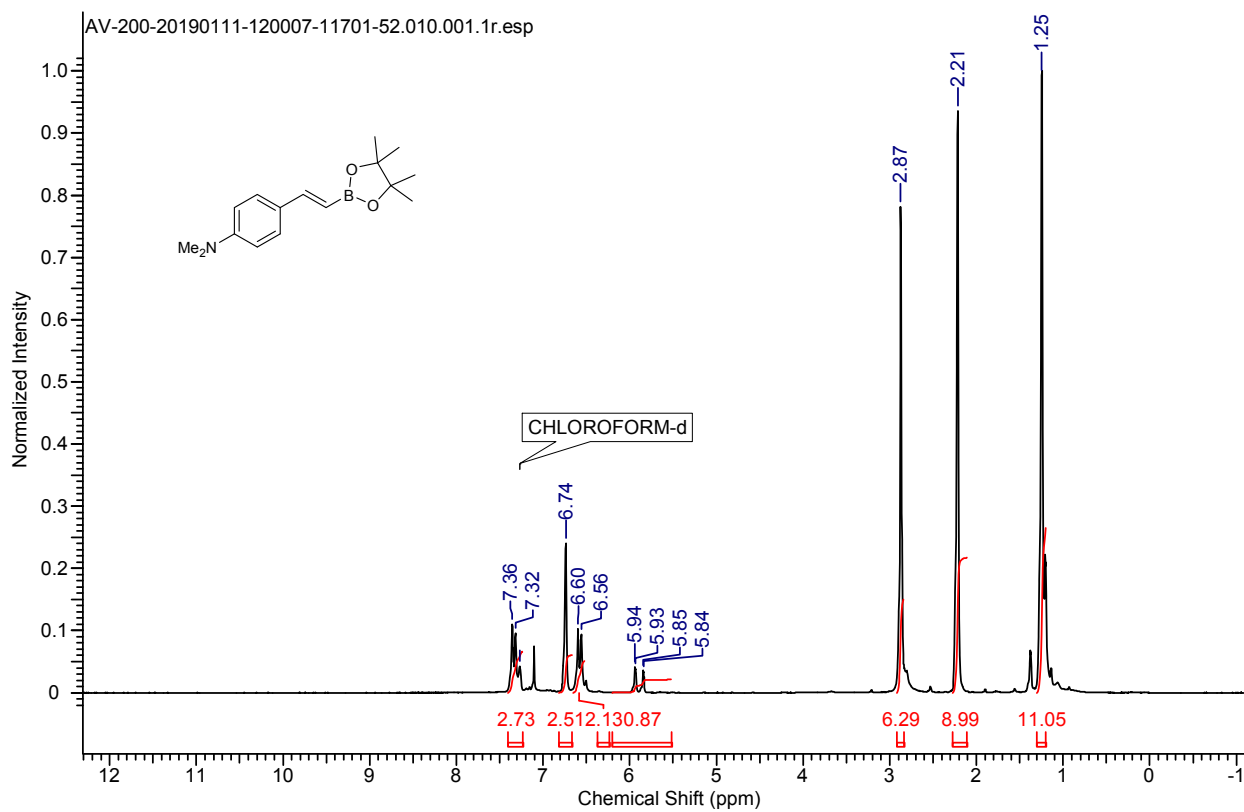


Figure S56. ^1H NMR Spectrum of **3f** (CDCl_3 , 200 MHz, 298 K).

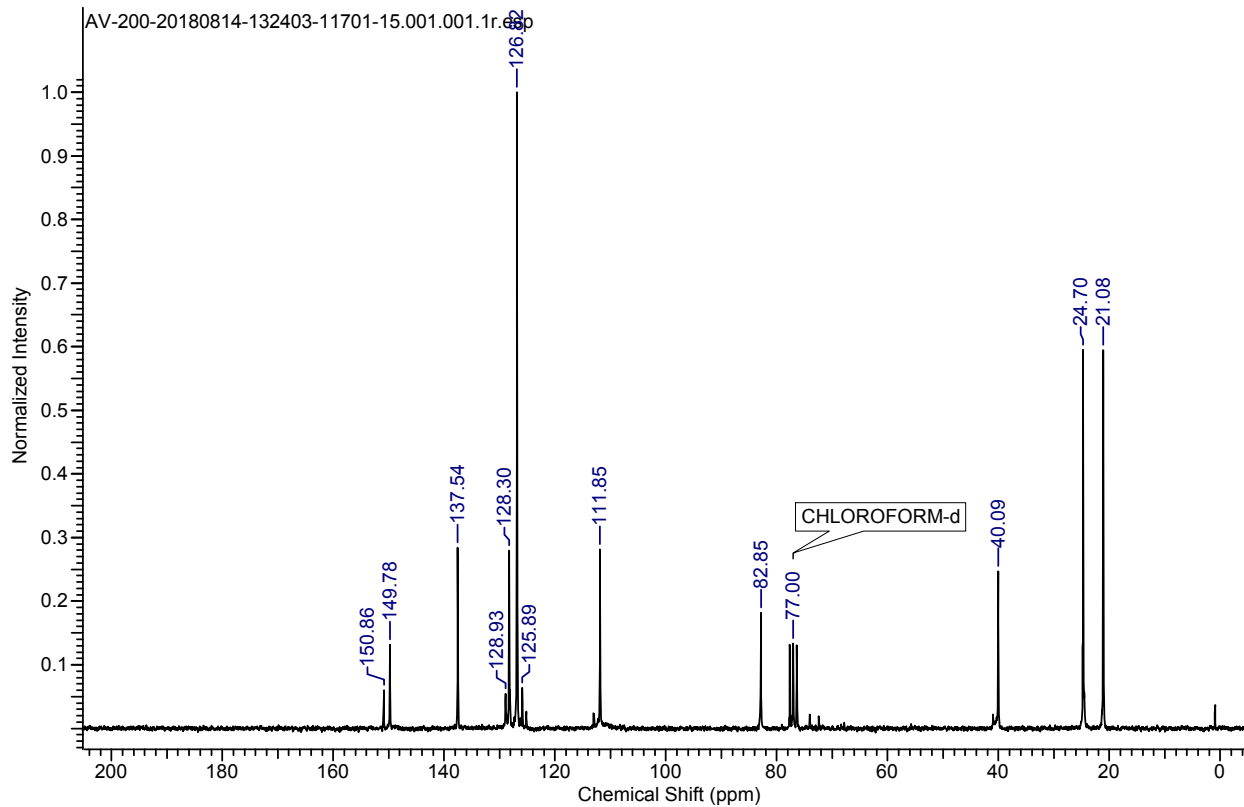


Figure S57. ^{13}C NMR spectrum of **3f** (CDCl_3 , 50.28 MHz, 298 K).

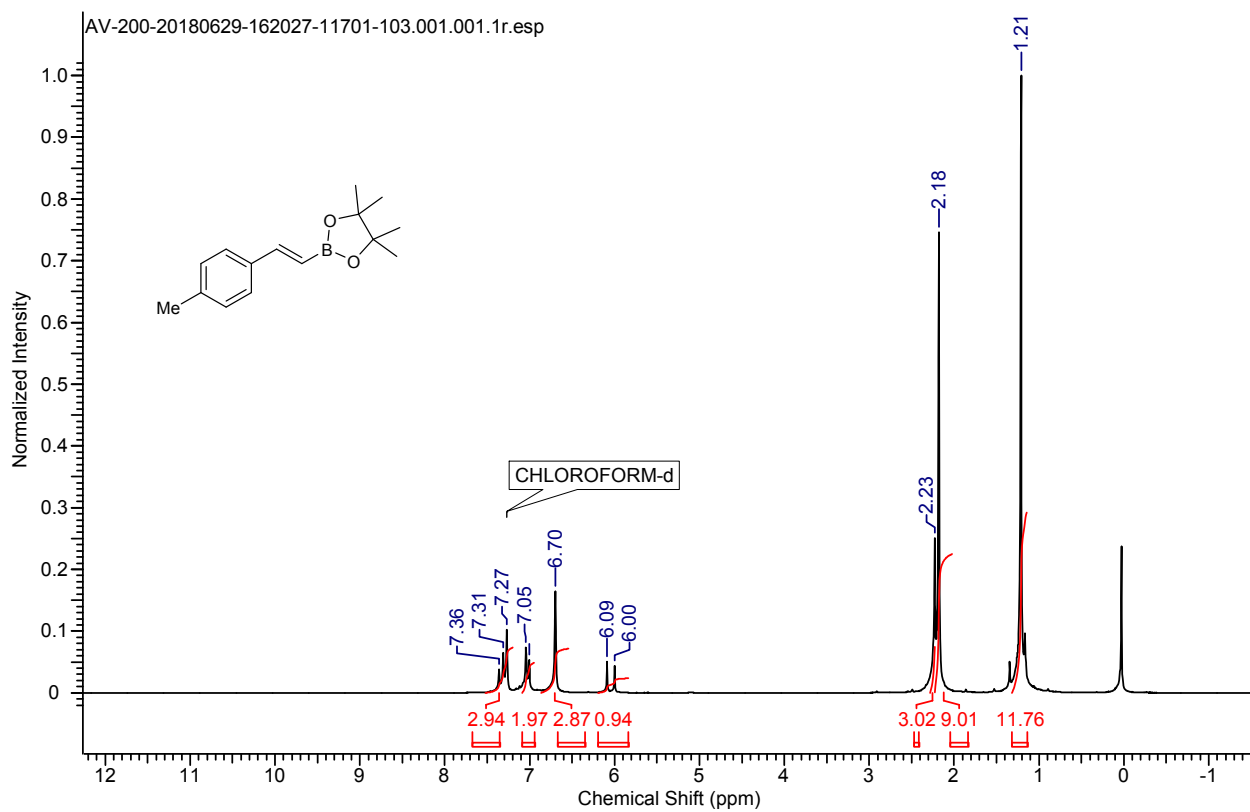


Figure S58. ^1H NMR Spectrum of **3g** (CDCl_3 , 200 MHz, 298 K).

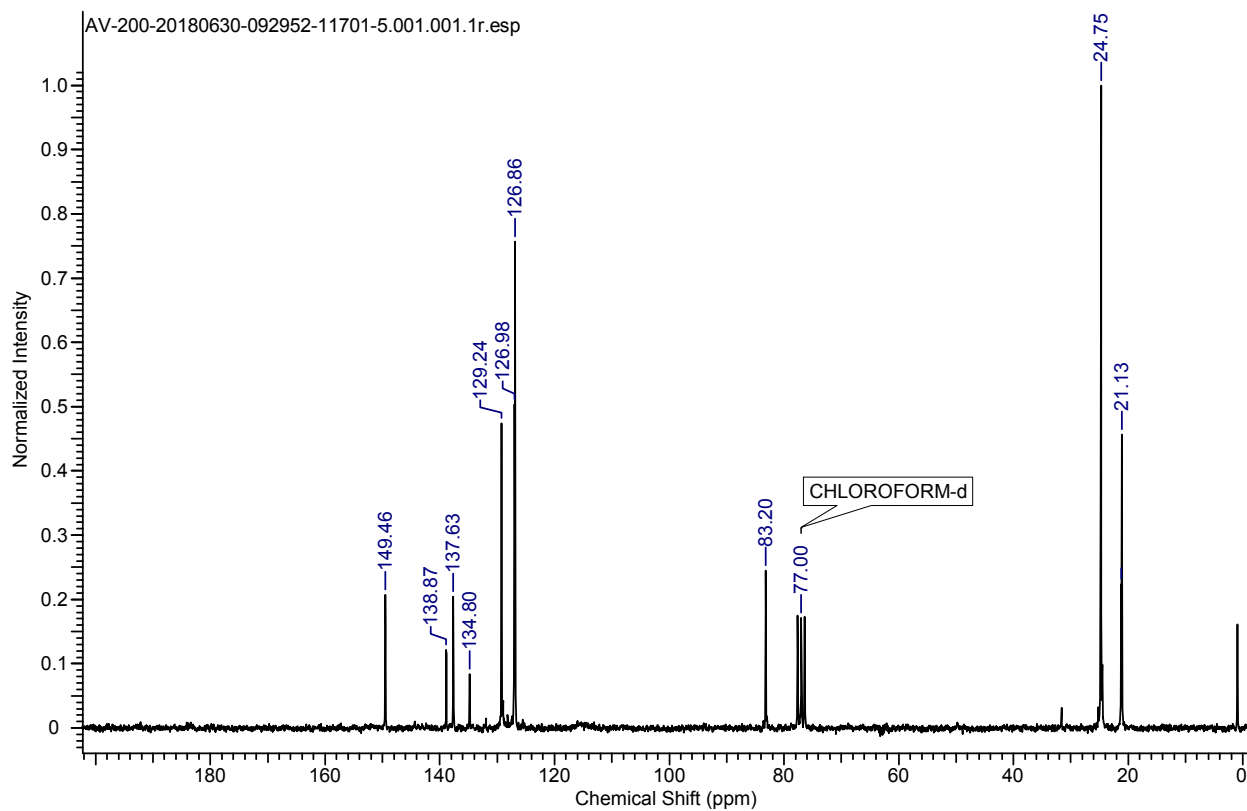


Figure S59. ^{13}C NMR spectrum of **3g** (CDCl_3 , 50.28 MHz, 298 K).

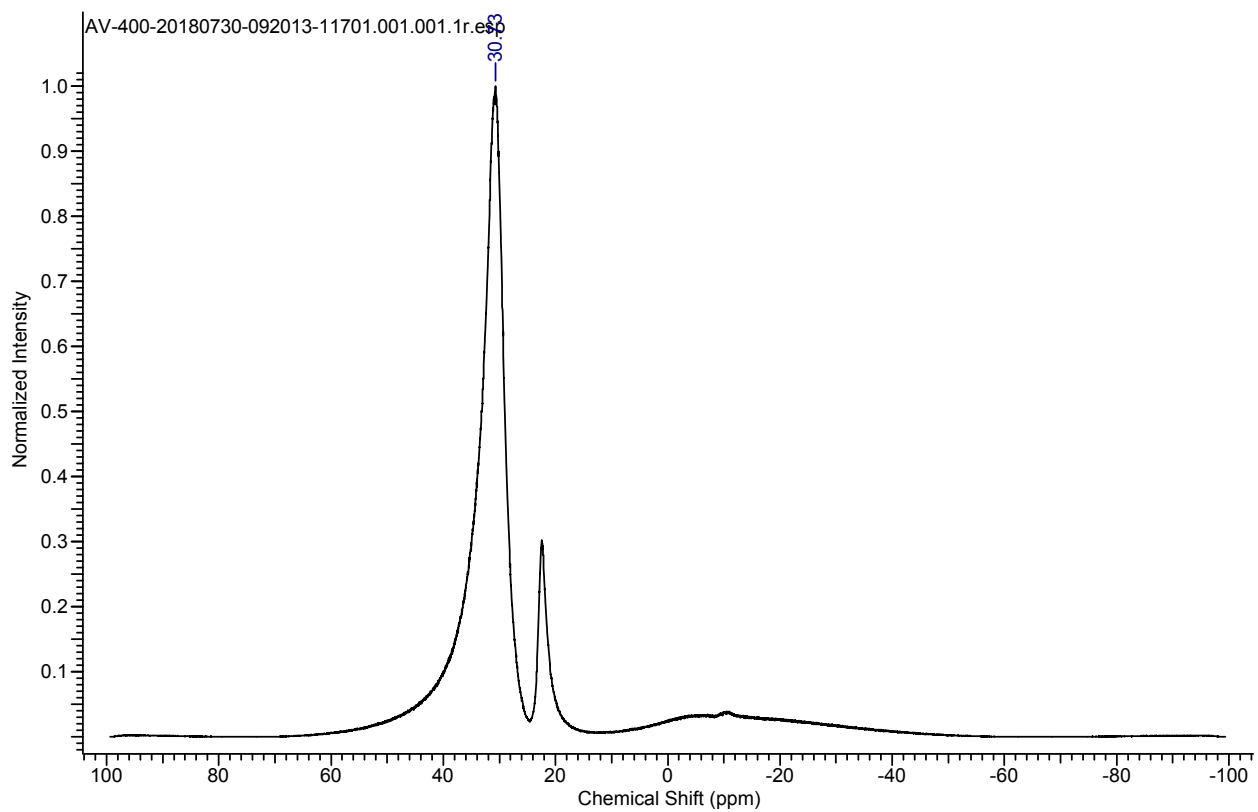


Figure S60. ^{11}B NMR spectrum of **3g** (C_6D_6 , 128 MHz, 298 K).

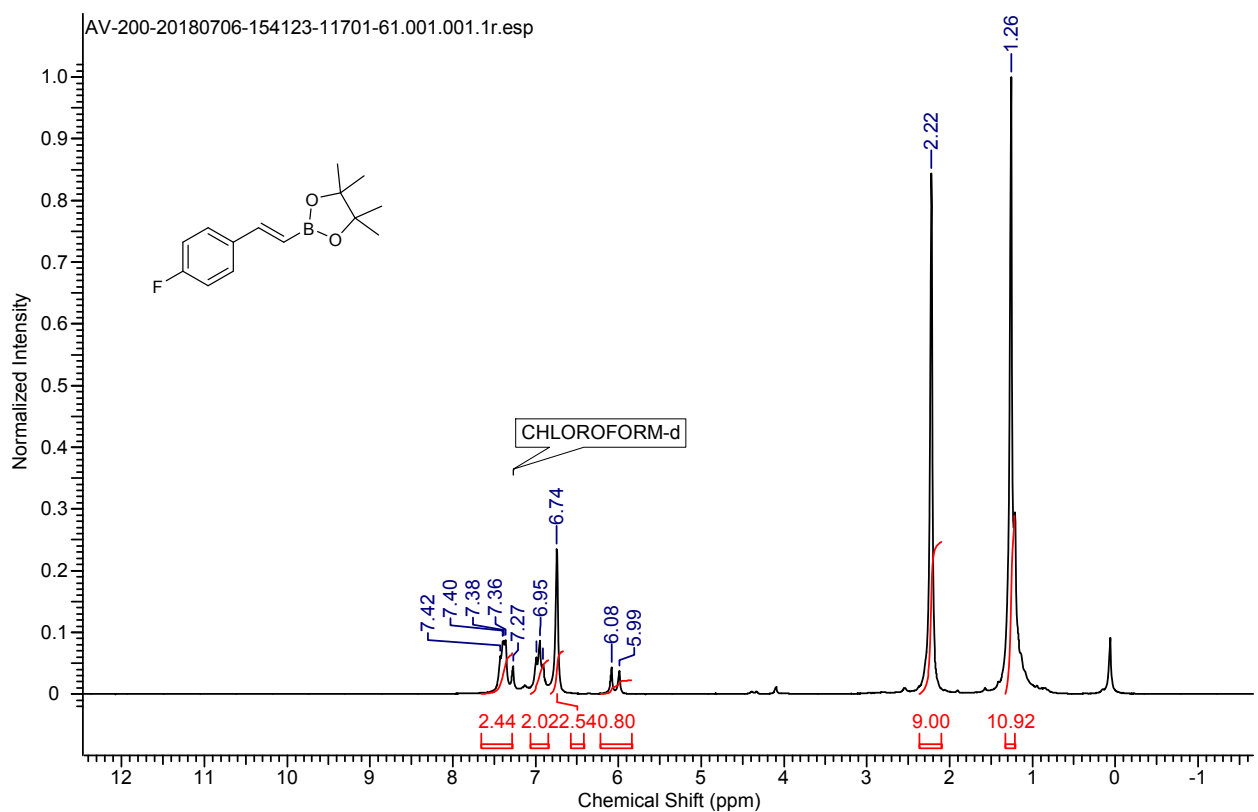


Figure S61. ^1H NMR Spectrum of **3h** (CDCl_3 , 200 MHz, 298 K).

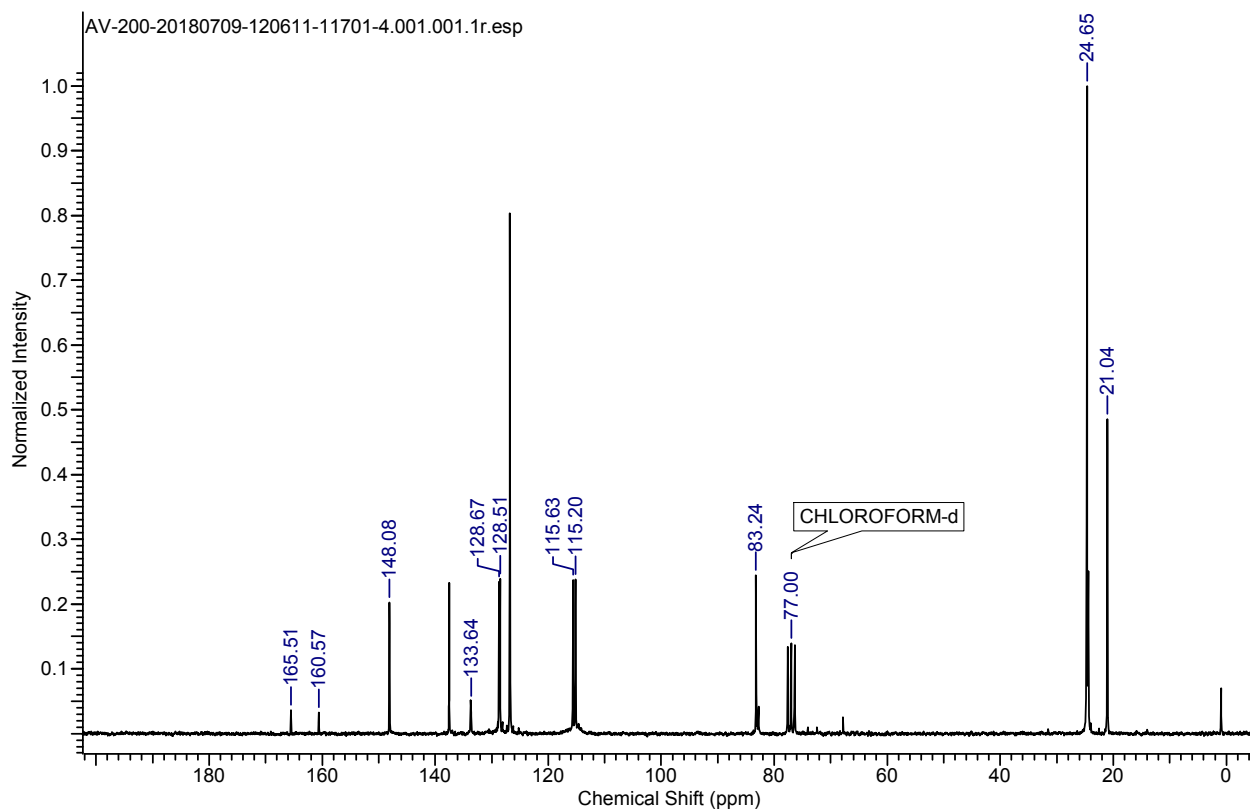


Figure S62. ^{13}C NMR spectrum of **3h** (CDCl_3 , 50.28 MHz, 298 K).

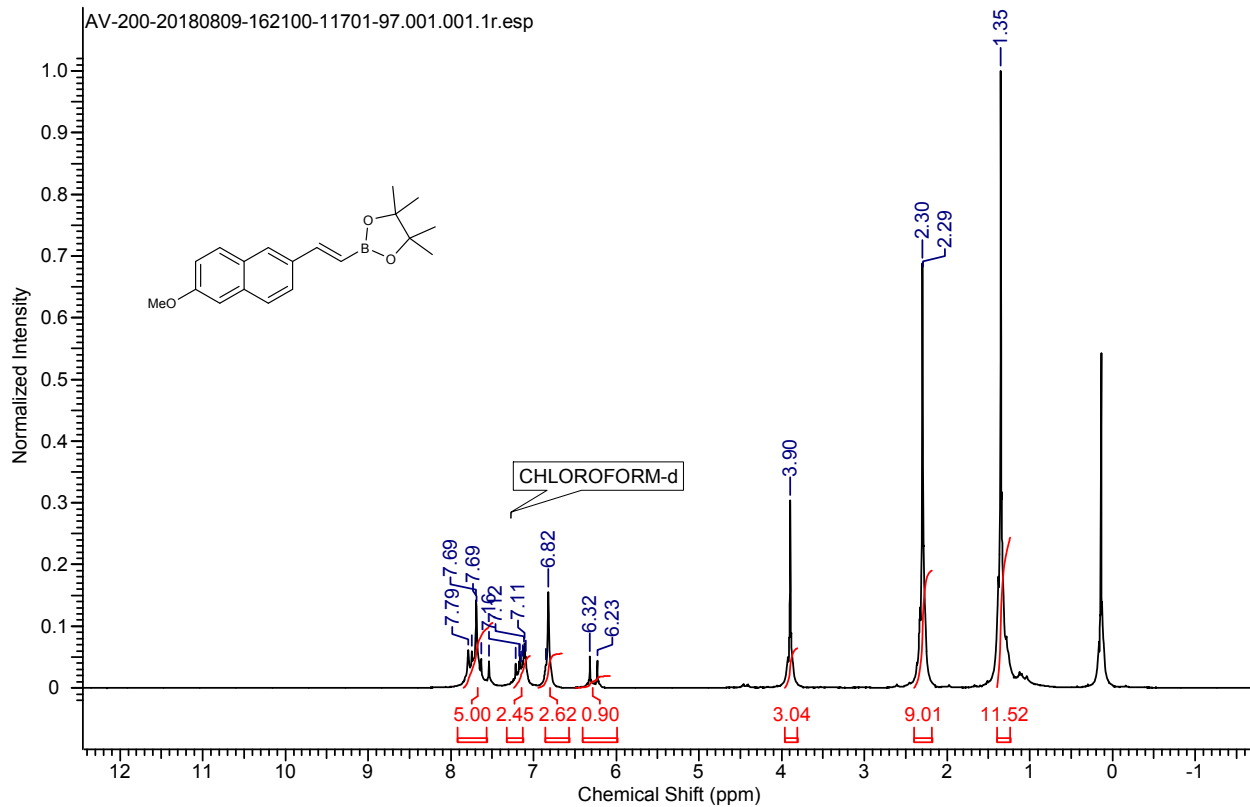


Figure S63. ^{13}C NMR spectrum of **3i** (CDCl_3 , 50.28 MHz, 298 K).

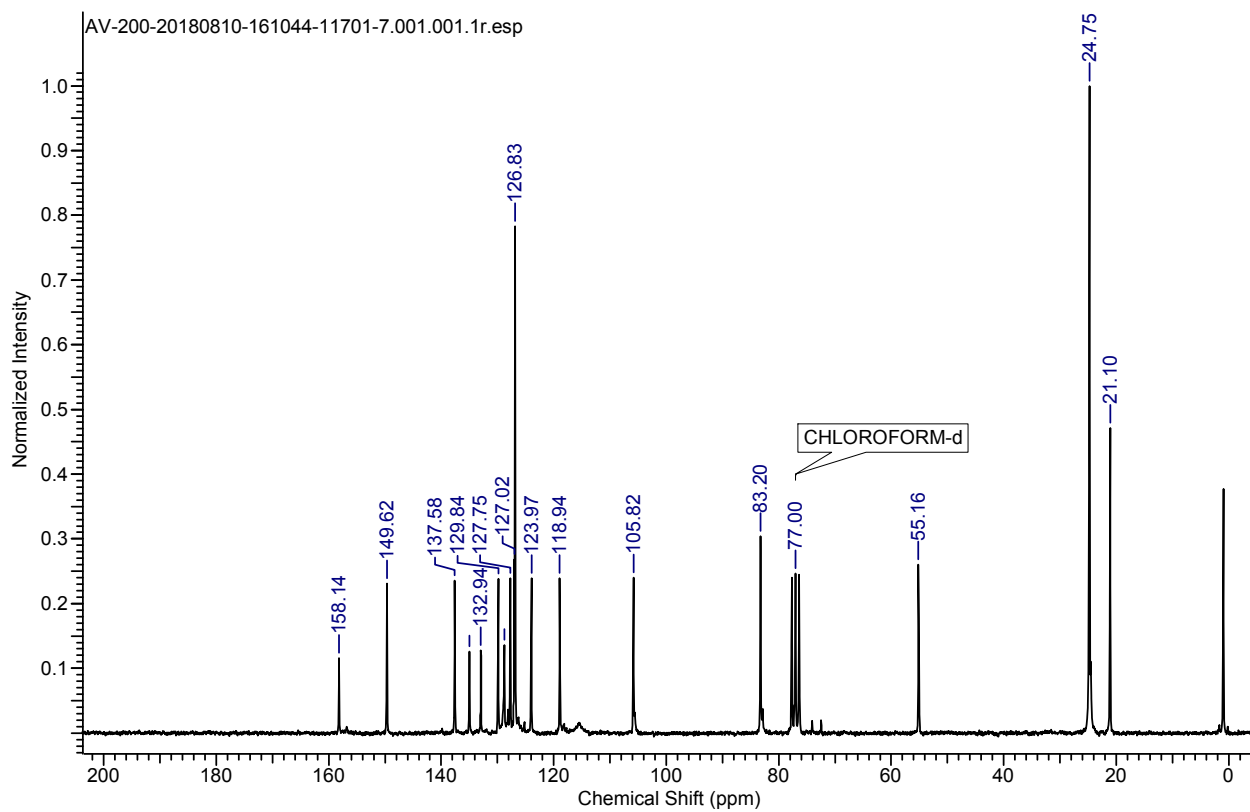


Figure S64. ^{13}C NMR Spectrum of **3i** (CDCl_3 , 200 MHz, 298 K).

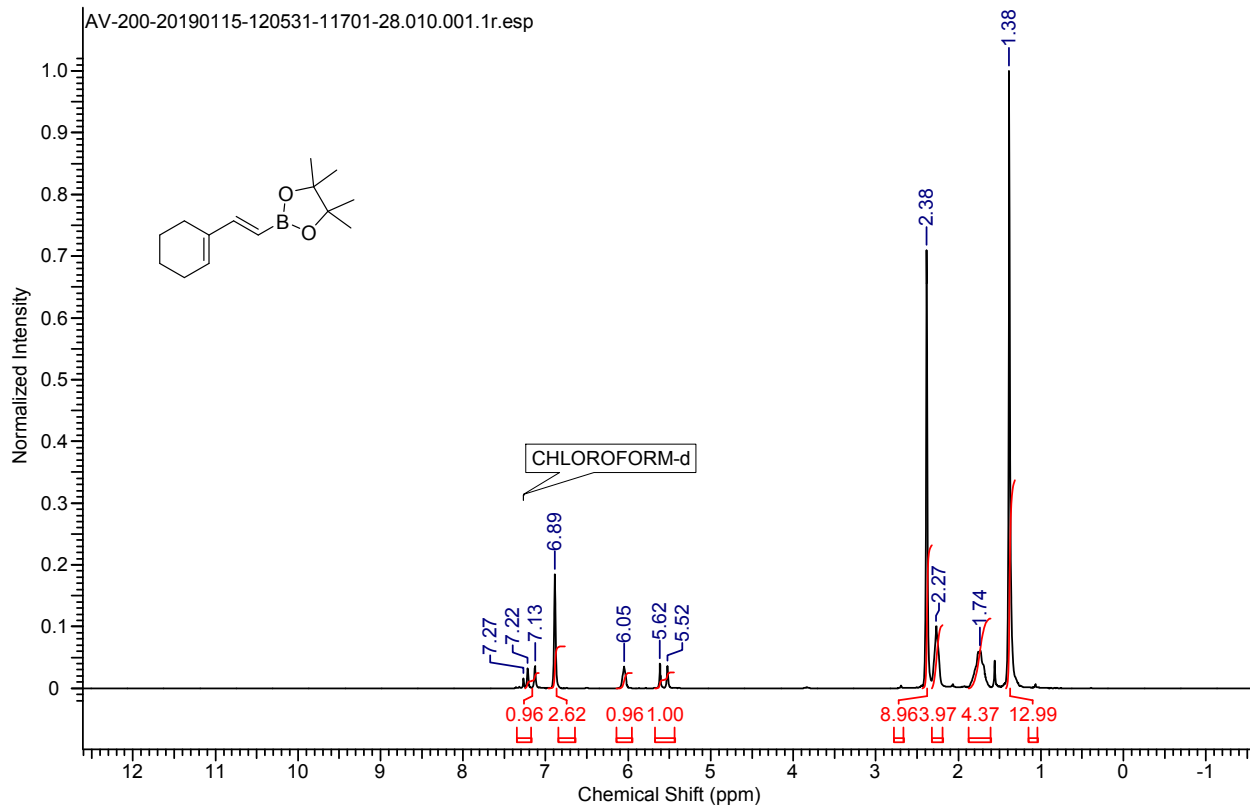


Figure S65. ^1H NMR Spectrum of **3j** (CDCl_3 , 200 MHz, 298 K).

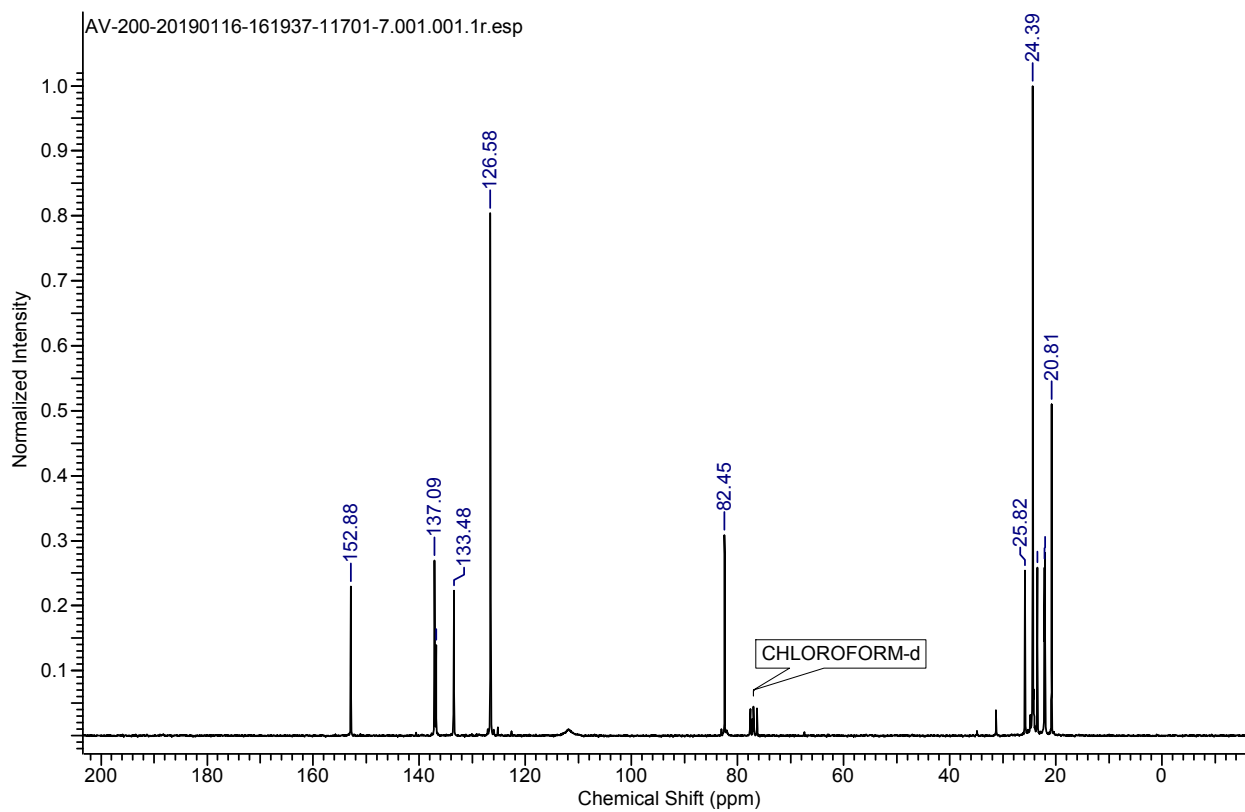


Figure S66. ^{13}C NMR spectrum of **3j** (CDCl_3 , 50.28 MHz, 298 K).

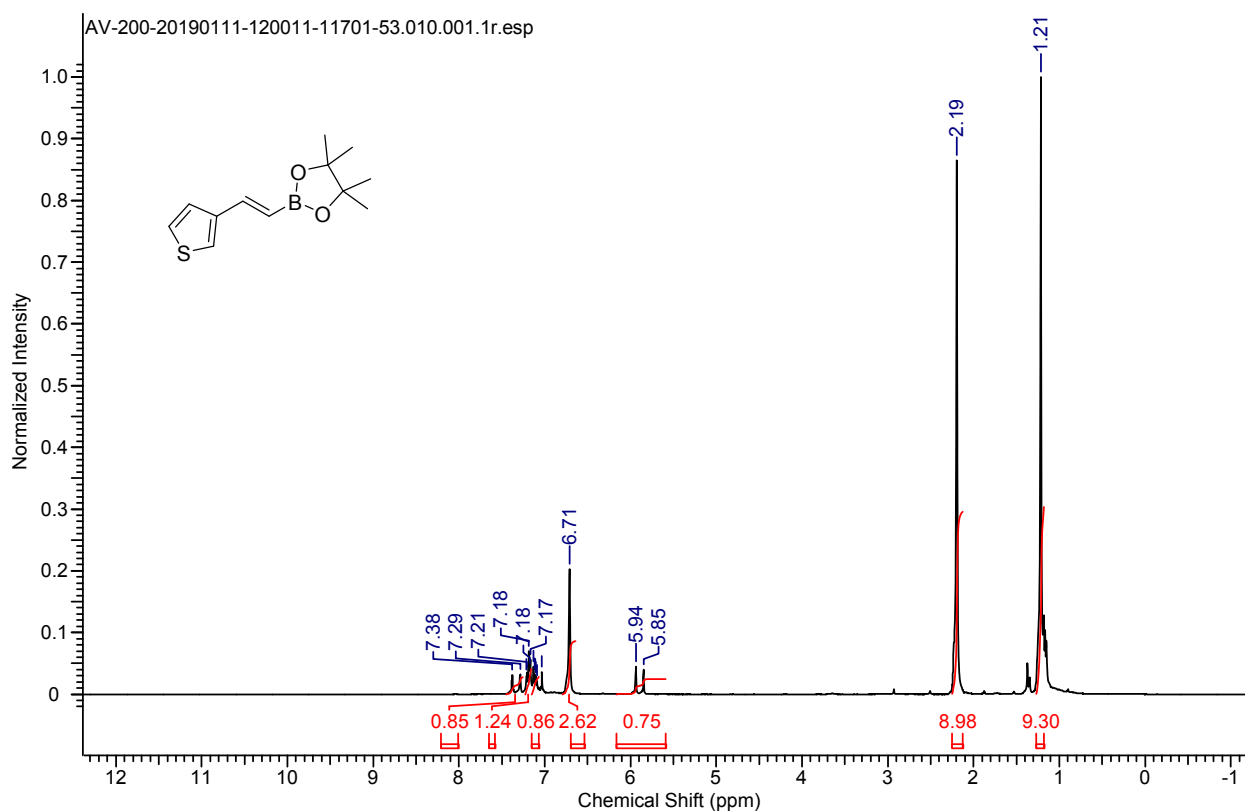


Figure S67. ^1H NMR Spectrum of **3k** (CDCl_3 , 200 MHz, 298 K).

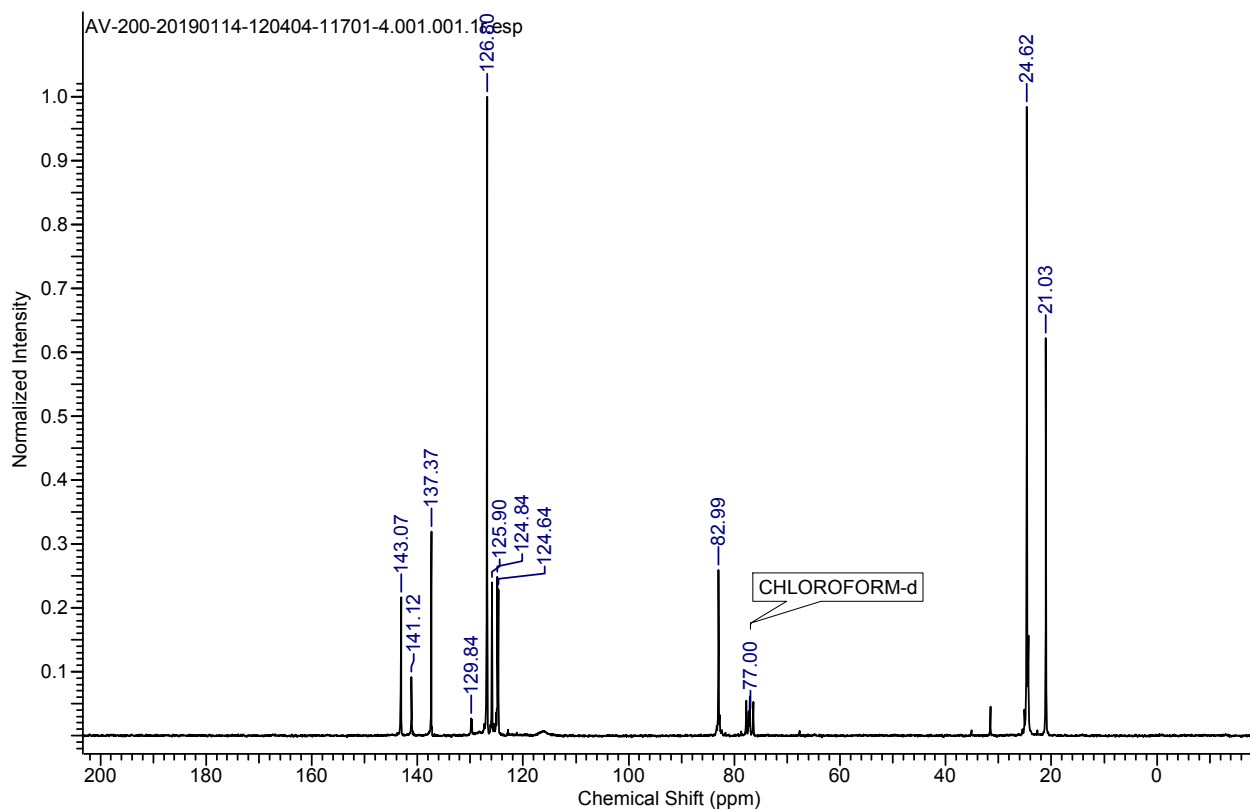


Figure S68. ^{13}C NMR spectrum of **3k** (CDCl_3 , 50.28 MHz, 298 K).

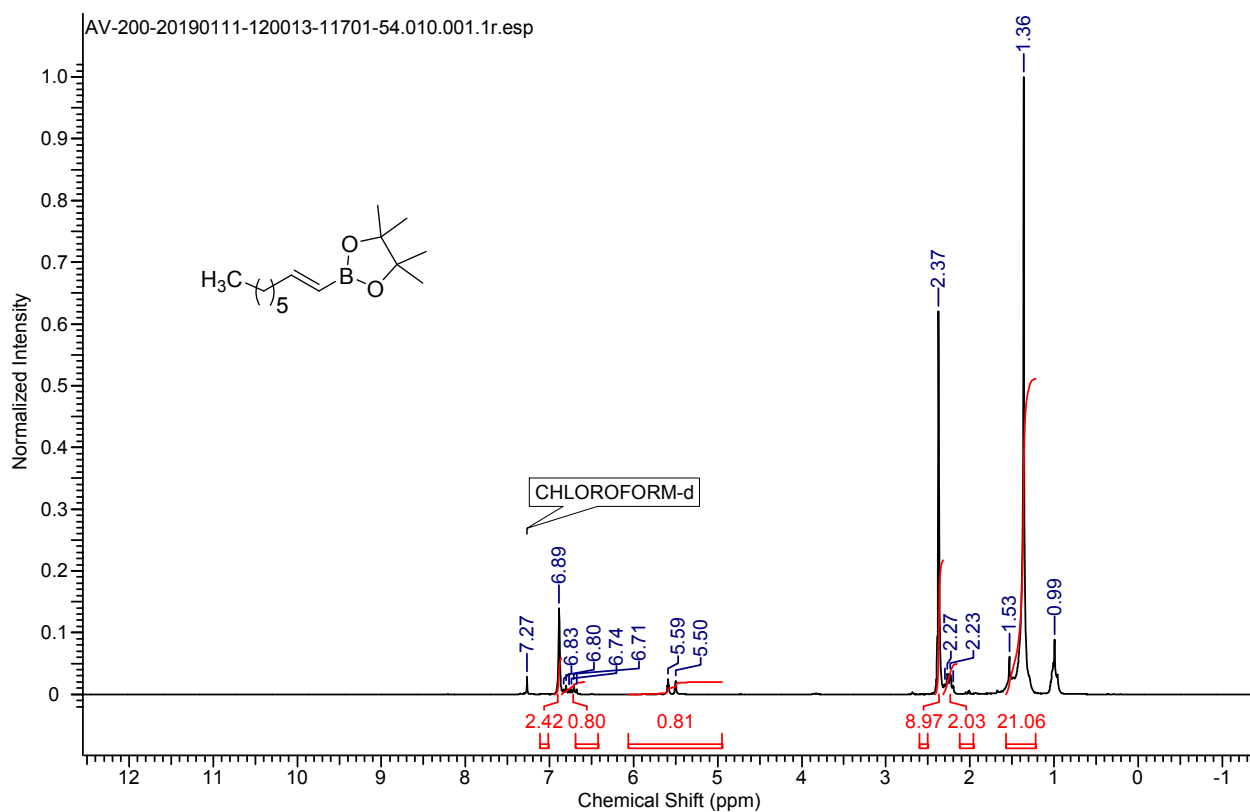


Figure S69. ^1H NMR Spectrum of **3l** (CDCl_3 , 200 MHz, 298 K).

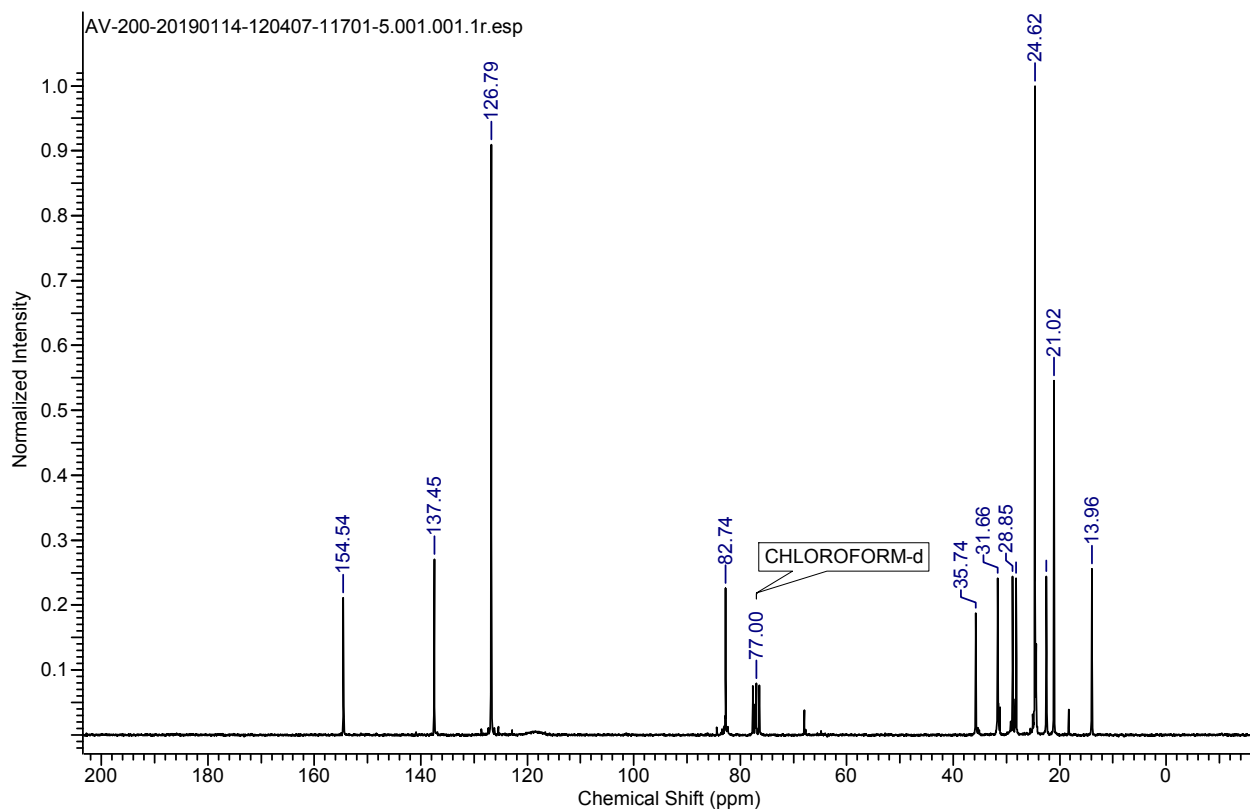


Figure S70. ^{13}C NMR spectrum of **3I** (CDCl_3 , 50.28 MHz, 298 K).

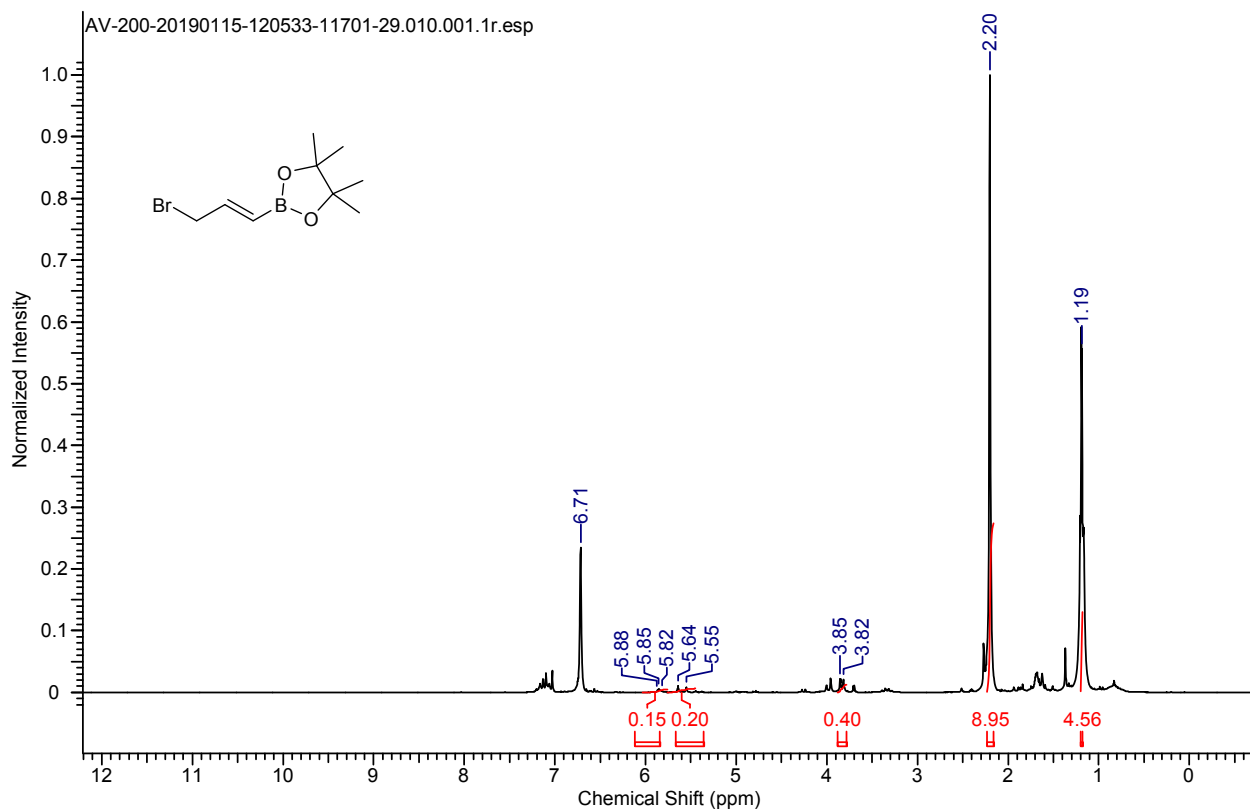
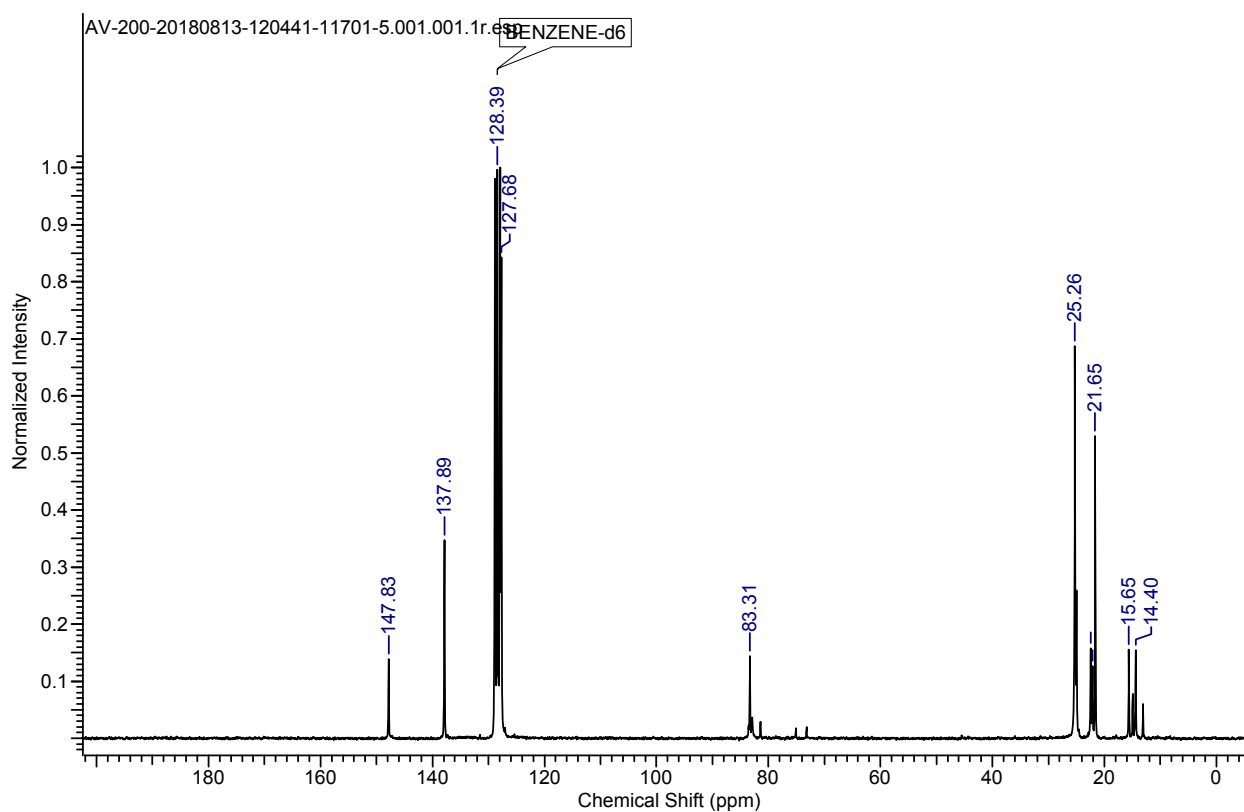
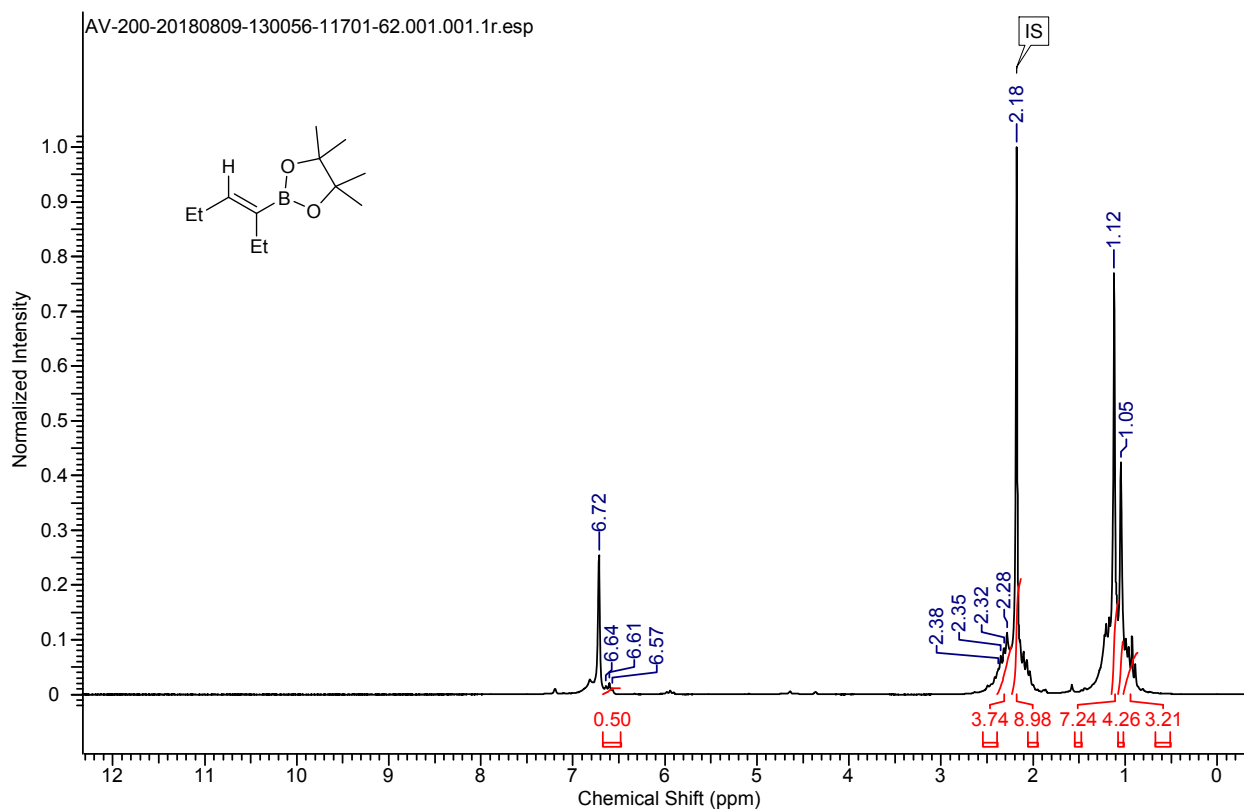


Figure S71. ^1H NMR Spectrum of **3m** (C_6D_6 , 200 MHz, 298 K).



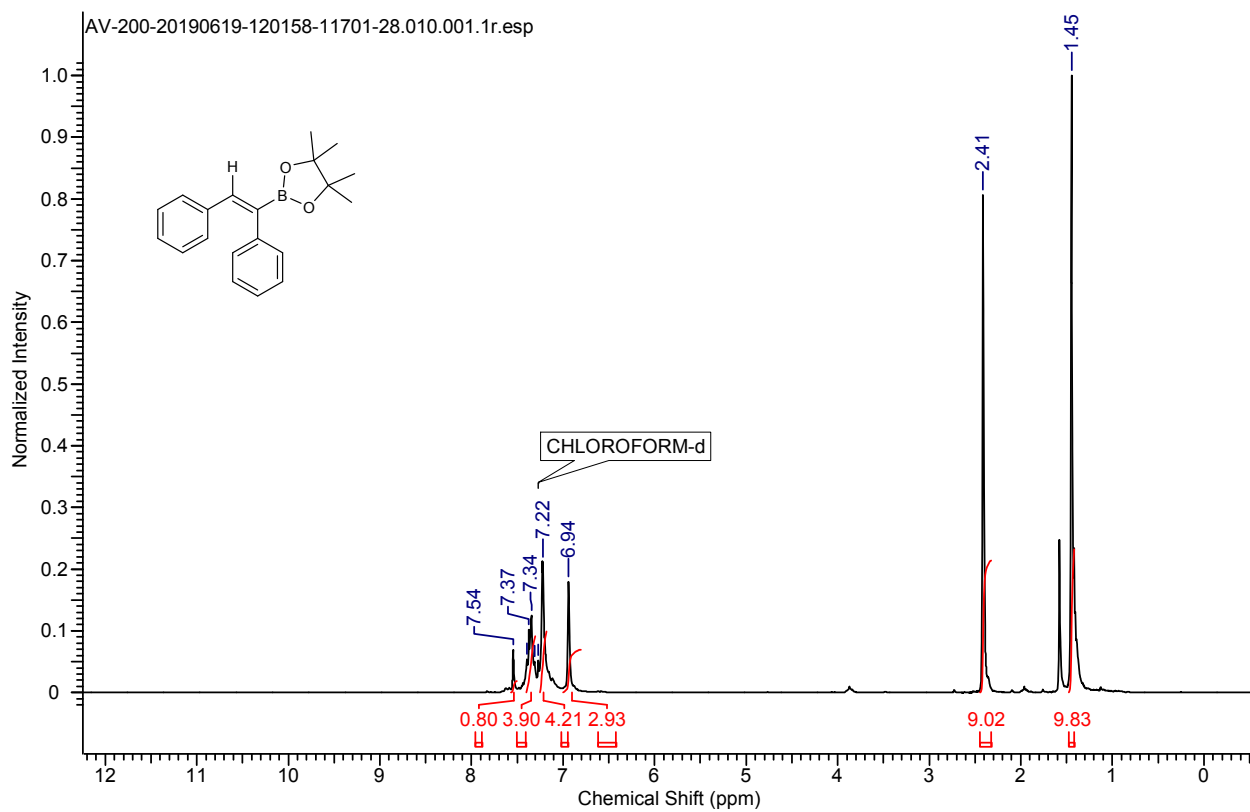


Figure S74. ^1H NMR Spectrum of **3o** (CDCl_3 , 200 MHz, 298 K).

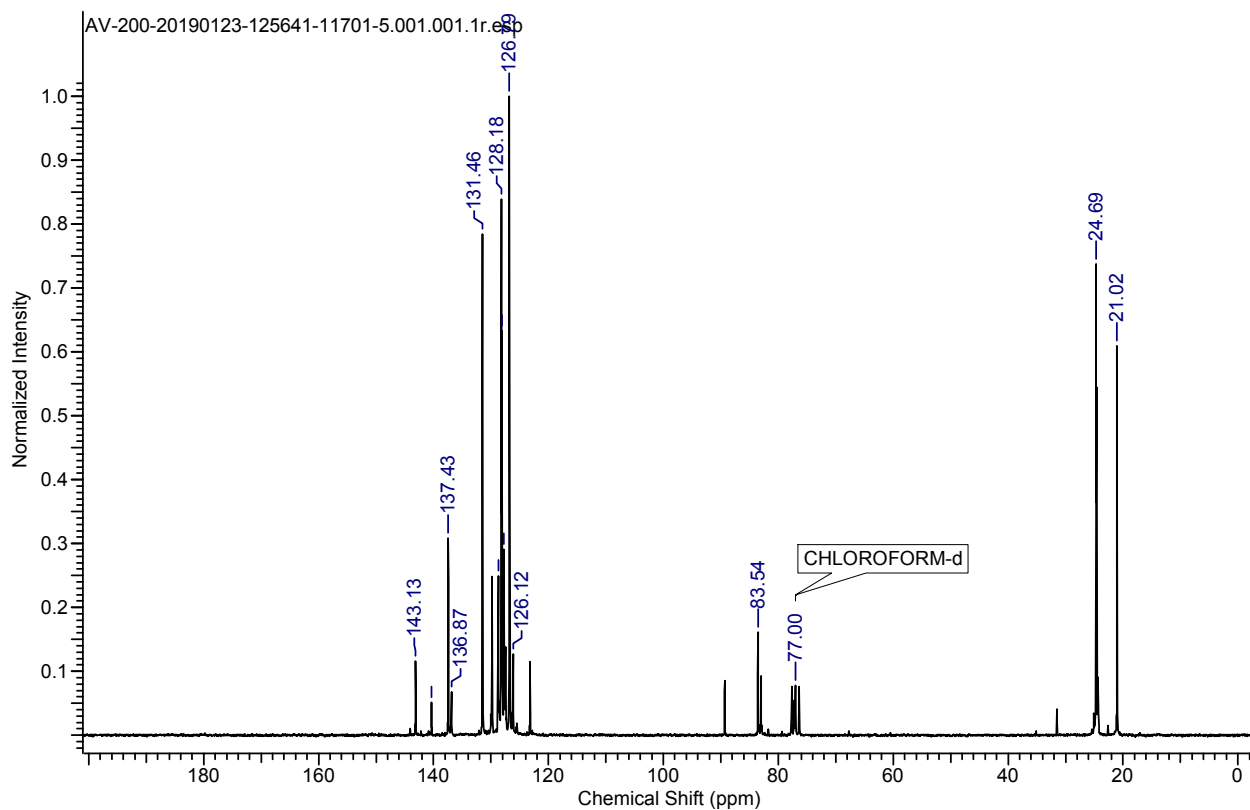


Figure S75. ^{13}C NMR spectrum of **3o** (CDCl_3 , 200 MHz, 298 K).

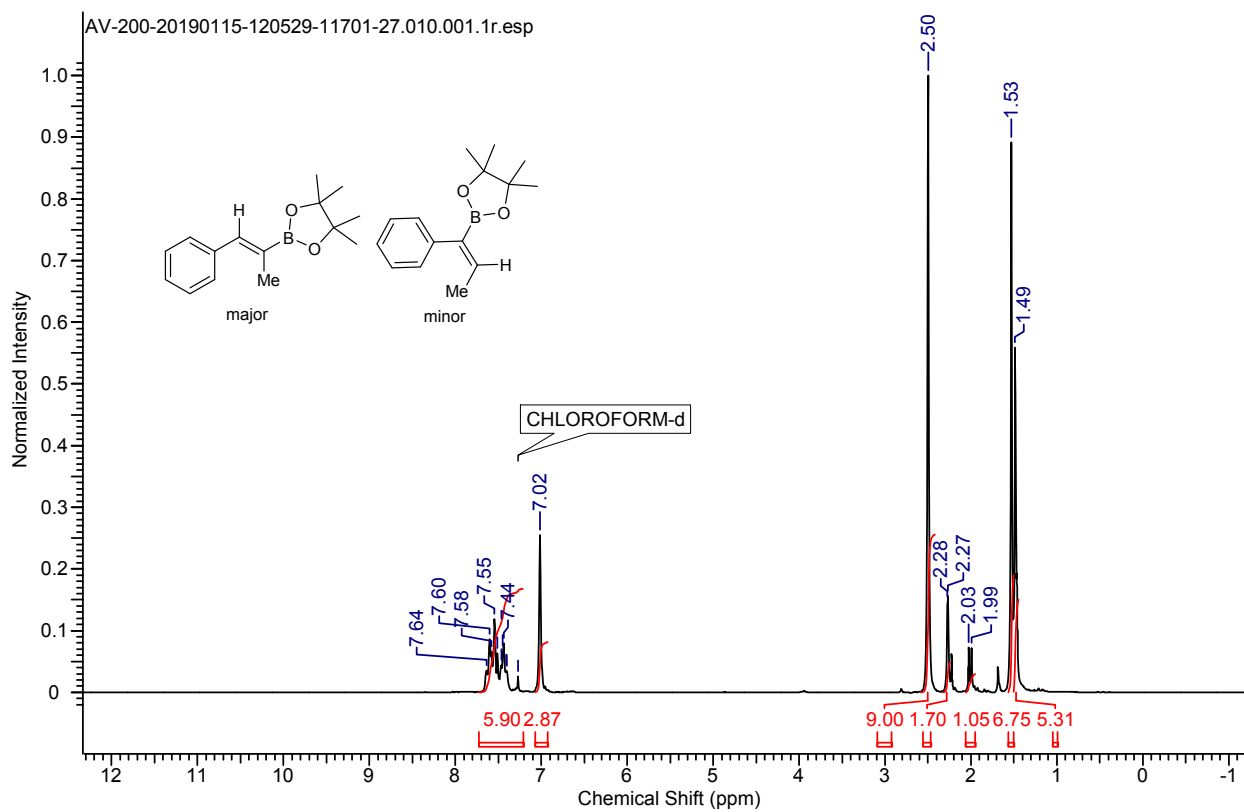


Figure S76. ^1H NMR Spectrum of **3p** (CDCl_3 , 200 MHz, 298 K).

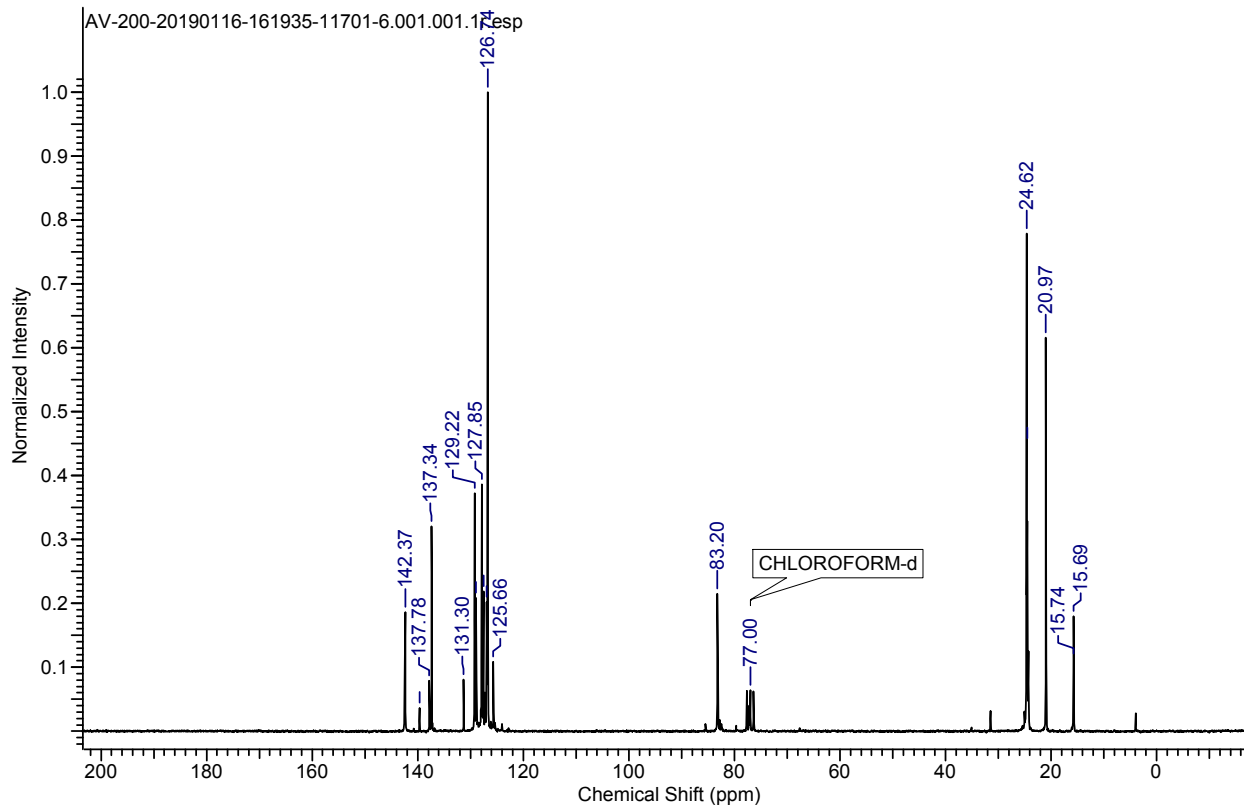


Figure S77. ^{13}C NMR spectrum of **3p** (CDCl_3 , 50.28 MHz, 298 K).

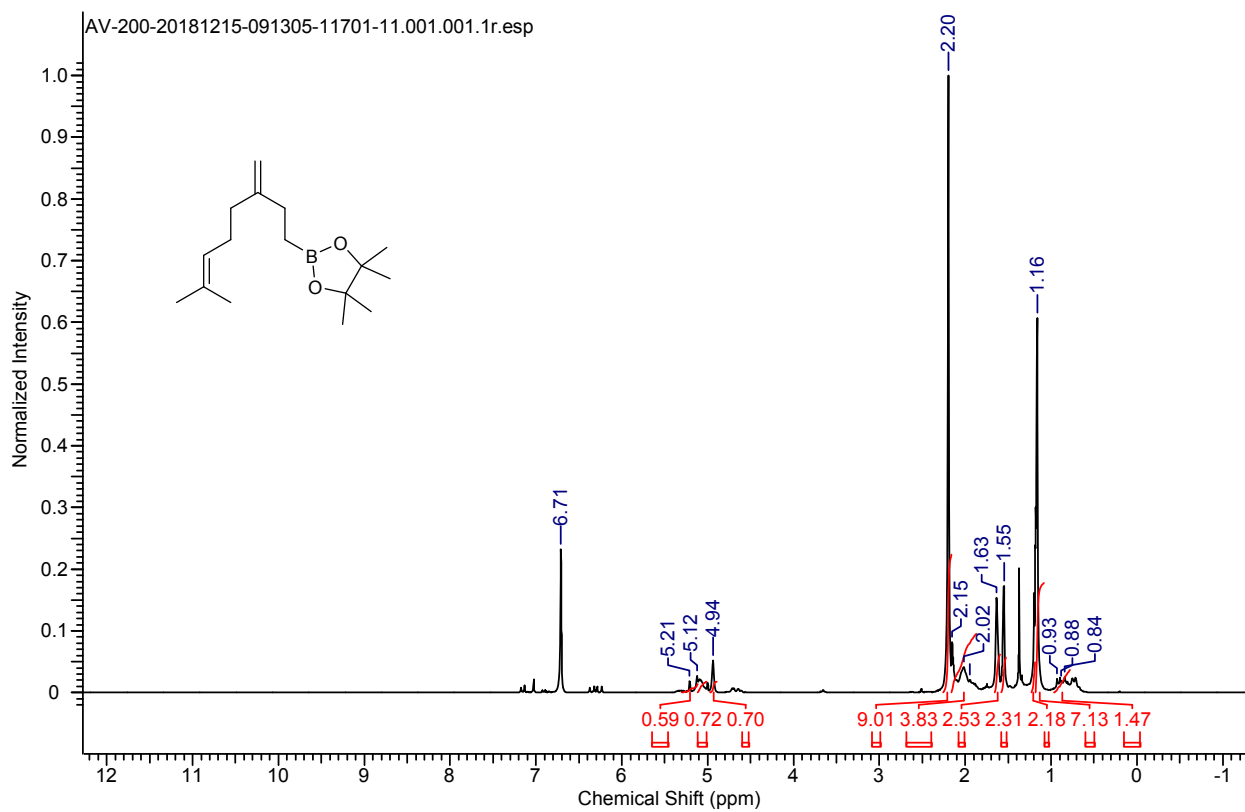


Figure S78. ¹H NMR Spectrum of **4c** (CDCl₃, 200 MHz, 298 K).

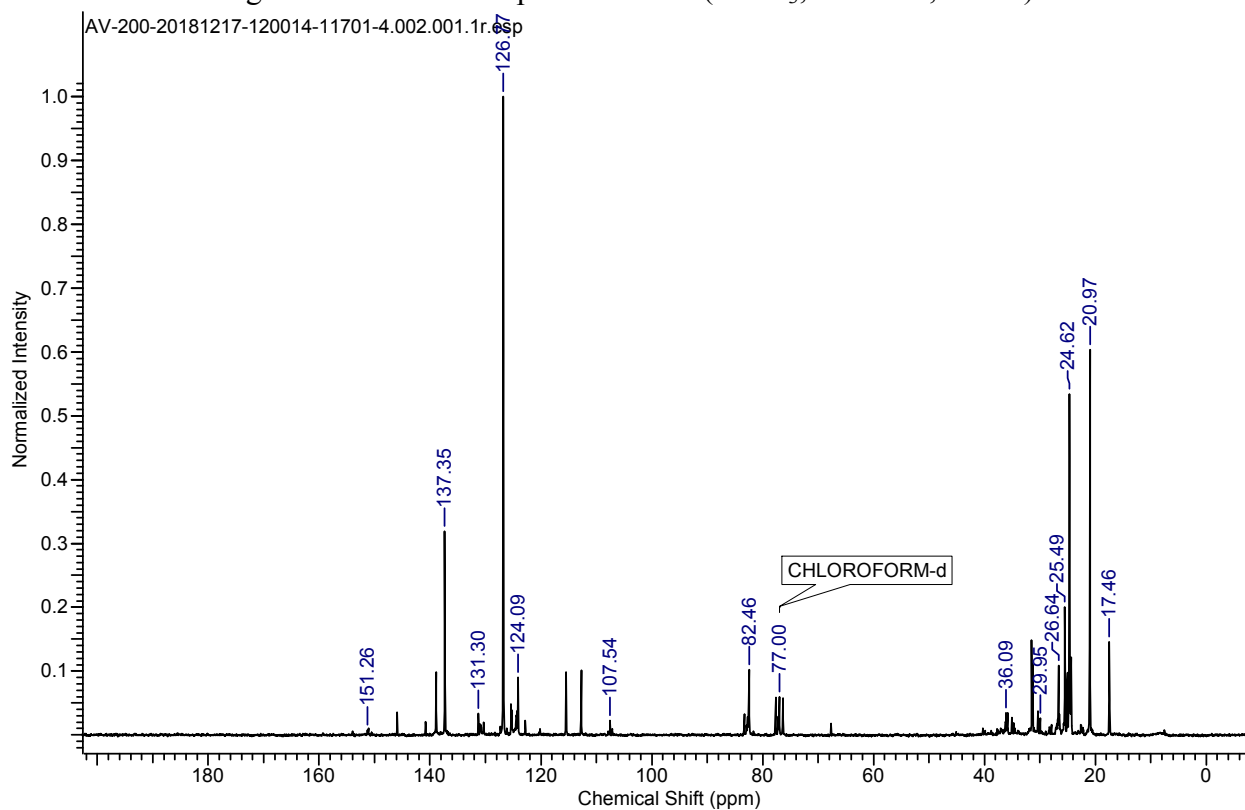


Figure S79. ¹³C NMR spectrum of **4c** (CDCl₃, 50.28 MHz, 298 K).

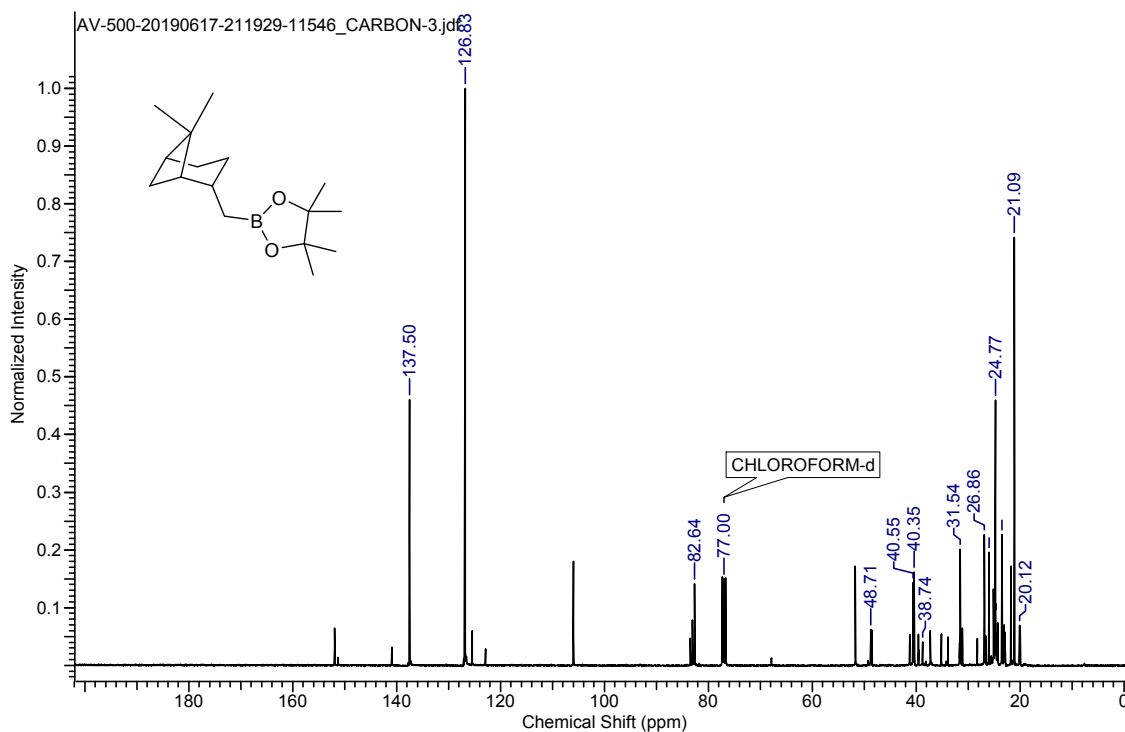
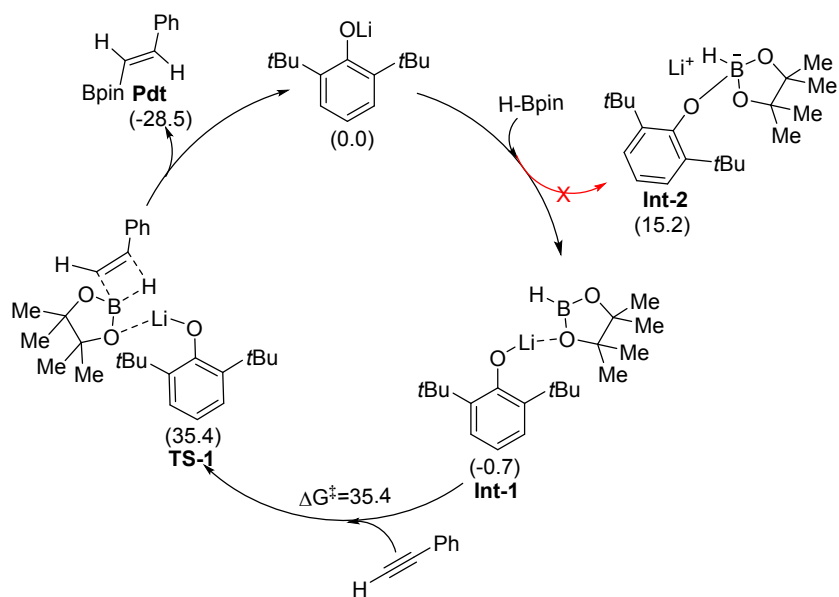


Figure S80. ^{13}C NMR spectrum of **4d** (CDCl_3 , 50.28 MHz, 298 K).

Details of DFT calculations:

All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 7.1 suite of programs,¹⁶ using the PBE functional.¹⁷ The TZVP¹⁸ basis set has been employed. The resolution of identity (RI),¹⁹ along with the multipole accelerated resolution of identity (marij)²⁰ approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent correction were incorporated with optimization calculations using the COSMO model,²¹ with toluene ($\epsilon = 2.38$) as the solvent. The values reported are ΔG values, with zero-point energy corrections, internal energy and entropic contributions included through frequency calculations on the optimized minima with the temperature taken to be 298.15 K. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition state structures.



Scheme S9. The catalytic cycle and reaction mechanism for the alkyne hydroboration by catalyst **1a**, calculated at the PBE/TZVP level of theory with DFT. The relative free energy (ΔG) for each species are shown within the parenthesis of the catalytic cycle. ΔG^\ddagger represent the Gibbs free energy of activation respectively. All values are in kcal/mol.

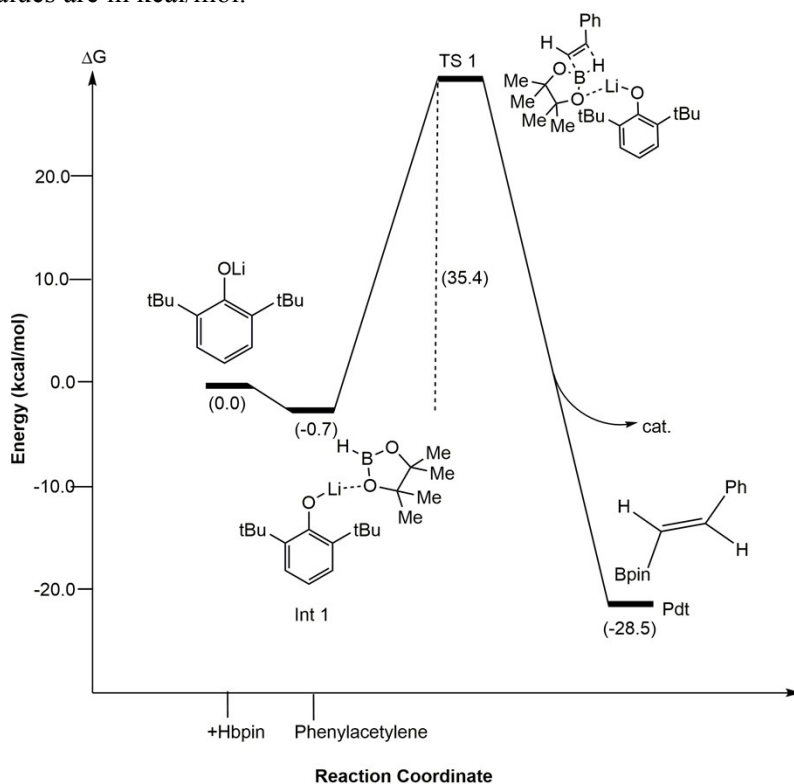
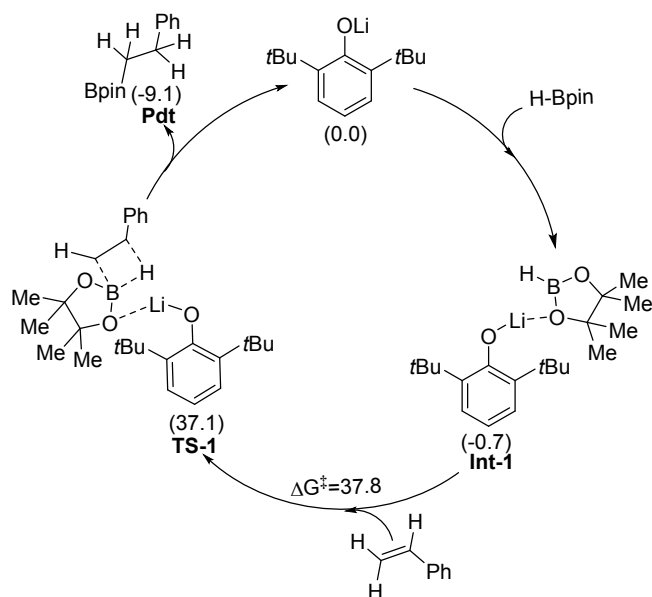


Figure S81. The reaction energy profile diagram for the catalytic alkyne hydroboration by catalyst **1a**. The values (in kcal/mol) have been calculated at the PBE/TZVP level of theory with DFT.



Scheme S10. The catalytic cycle and reaction mechanism for the alkyne hydroboration by catalyst **1a**, calculated at the PBE/TZVP level of theory with DFT. The relative free energy (ΔG) for each species are shown within the parenthesis of the catalytic cycle. ΔG^\ddagger represent the Gibbs free energy of activation respectively. All values are in kcal/mol.

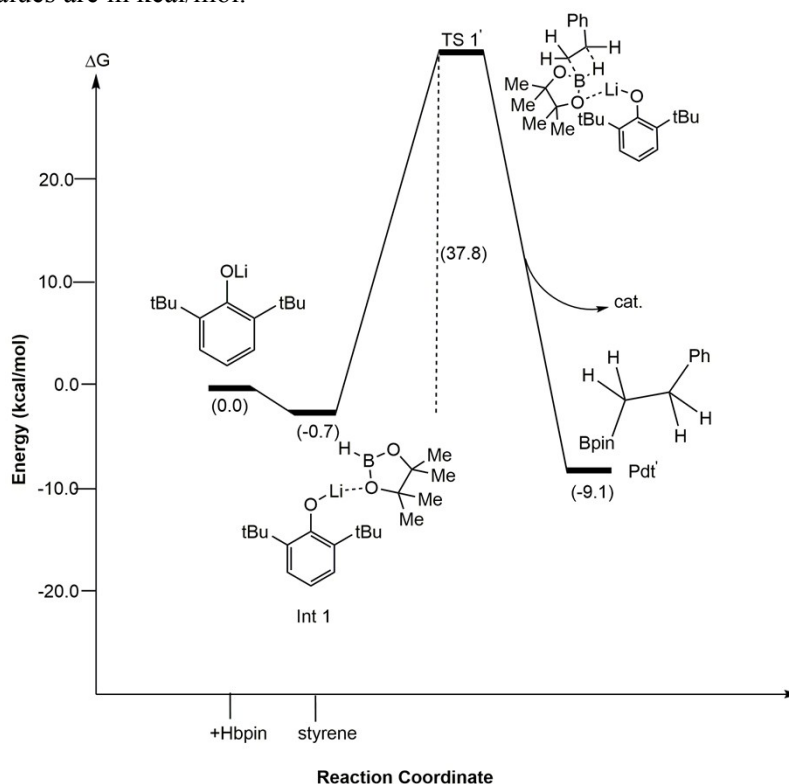


Figure S82. The reaction energy profile diagram for the catalytic alkyne hydroboration by catalyst **1a**. The values (in kcal/mol) have been calculated at the PBE/TZVP level of theory with DFT.

References:

1. T. J. Boyle, D. M. Pedrotty, T. M. Alam, S. C. Vick, M. A. Rodriguez, *Inorg. Chem.*, 2000, **39**, 5133-5146.
2. J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, C. Smart, *J. Organometal. Chem.*, 1971, **27**, 241-249.
3. D. G. Kohler, S. N. Gockel, J. L. Kennemur, P. J. Waller, K. L. Hull, *Nat. Chem.*, 2018, **10**, 333-340.
4. M. Tobisu, K. Nakamura, N. Chatani, *J. Am. Chem. Soc.*, 2014, **136**, 5587-5590.
5. A. Bismuto, M. J. Cowley and S. P. Thomas, *ACS Catal.*, 2018, **8**, 2001–2005.
6. Y. Liu, Y. Zhou, H. Wang and J. Qu, *RSC Adv.*, 2015, **5**, 73705–73713.
7. L. Zhang, Z. Zuo, X. Leng and Z. Huang, *Angew. Chem. Int. Ed.*, 2014, **53**, 2696–2700.
8. P. K. Verma, A. S. Sethulekshmi and K. Geetharani, *Org. Lett.*, 2018, **20**, 7840–7845.
9. F. Li, X. Bai, Y. Cai, H. Li, S.-Q. Zhang, F.-H. Liu, X. Hong, Y. Xu and S.-L. Shi, *Org. Process Res. Dev.*, 2019, **23**, 1703–1708.
10. M. Magre, B. Maity, A. Falconnet, L. Cavallo and M. Rueping, *Angew. Chem. Int. Ed.*, 2019, **58**, 7025–7029.
11. M. Fleige, J. Möbus, T. v. Stein, F. Glorius and D. W. Stephan, *Chem. Commun.*, 2016, **52**, 10830–10833.
12. R. Mamidala, V. K. Pandey and A. Rit, *Chem. Commun.*, 2019, **55**, 989-992.
13. J. R. Lawson, L. C. Wilkins and R. L. Melen, *Chem. Eur. J.*, 2017, **23**, 10997–11000.
14. S. Mandal, P. K. Verma and K. Geetharani, *Chem. Commun.*, 2018, **54**, 13690-13693.
15. M. D. Greenhalgh and S. P. Thomas, *Chem. Commun.*, 2013, **49**, 11230–11232.
16. R. Ahlrichs, M. Bar, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165–169.
17. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
18. S. Ansgar, H. Christian, A. Reinhart, *J. Chem. Phys.*, 1994, **100**, 5829–5835.
19. K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283–289.
20. M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.*, 2003, **118**, 9136-9148.
21. A. Klamt, G. Schuurmann, *J. Chem. Soc., Perkin Trans.*, 1993, 799–805.

PBE/TZVP optimized geometries for all the compounds and transition states

Alkene

C	-0.580797	2.963512	-1.544213
C	0.450149	2.651540	-2.346709
H	0.352961	1.970081	-3.194631
C	-1.964829	2.477016	-1.636953
C	-2.374269	1.489675	-2.556680
C	-2.936140	3.014601	-0.769579
C	-3.700795	1.065891	-2.608309
H	-1.645116	1.042886	-3.235327
C	-4.265981	2.591704	-0.820796
H	-2.638924	3.779035	-0.047023
C	-4.655075	1.614976	-1.741384
H	-3.994523	0.298024	-3.327019
H	-5.000021	3.025839	-0.138943
H	-5.693400	1.280740	-1.784304
H	-0.400013	3.665137	-0.722381
H	1.439134	3.078496	-2.176518

Alkyne

C	-0.559587	2.520346	-1.776038
C	0.639401	2.724804	-1.780369
H	1.696149	2.903836	-1.783486
C	-1.963158	2.271144	-1.764959
C	-2.569228	1.542133	-2.810465
C	-2.765495	2.743123	-0.704027
C	-3.940832	1.290575	-2.788526
H	-1.951990	1.175689	-3.632001
C	-4.136216	2.486123	-0.691630
H	-2.300591	3.307878	0.105326
C	-4.728298	1.758796	-1.730507
H	-4.397781	0.723733	-3.602201
H	-4.746254	2.854883	0.135398
H	-5.801420	1.558739	-1.716516

HBpin

C	-2.385032	-0.548218	-0.040641
C	-0.810668	-0.544753	0.029229
O	-2.690084	0.845887	-0.448060
O	-0.507005	0.879191	0.315240
B	-1.599123	1.605301	-0.096725
H	-1.600670	2.801805	-0.145520

C	-3.052654	-0.754083	1.319255
H	-4.130005	-0.561912	1.222218
H	-2.917585	-1.785762	1.672278
H	-2.646104	-0.067650	2.075591
C	-2.973667	-1.493766	-1.076484
H	-2.699138	-2.532412	-0.841022
H	-4.070136	-1.420342	-1.062960
H	-2.621854	-1.259643	-2.088705
C	-0.219451	-1.396941	1.142520
H	-0.490693	-2.453041	0.998056
H	0.876964	-1.322368	1.121814
H	-0.571338	-1.077295	2.130911
C	-0.143078	-0.865898	-1.308181
H	0.933512	-0.662136	-1.227729
H	-0.274443	-1.924559	-1.570756
H	-0.552213	-0.248403	-2.120497

Catalyst 1a

Li	6.322742	13.925952	0.417046
O	4.726484	13.347082	0.665172
C	3.509305	12.892784	0.860581
C	2.694398	13.411950	1.934236
C	1.416069	12.875585	2.134639
C	0.898789	11.864755	1.321455
C	1.674077	11.381492	0.265128
C	2.960854	11.868648	0.002350
C	3.218104	14.542018	2.842878
C	4.474084	14.071470	3.611879
C	3.773502	11.323336	-1.189995
C	2.998941	10.265624	-1.999283
C	2.184347	14.980004	3.898099
C	3.547075	15.792691	1.994905
C	4.113598	12.472886	-2.167212
C	5.069576	10.645529	-0.689321
H	0.795077	13.253496	2.948373
H	-0.100848	11.463667	1.504139
H	1.253278	10.601213	-0.370746
H	2.611921	15.793511	4.504525
H	1.918763	14.159662	4.581849
H	1.260485	15.360135	3.435982
H	4.268574	15.553753	1.204710
H	3.965230	16.588754	2.632423
H	2.633017	16.182483	1.520738
H	5.251421	13.724443	2.920341
H	4.219451	13.240833	4.287714

H	4.880927	14.894536	4.221593
H	3.190693	12.897360	-2.591755
H	4.731774	12.098021	-2.999464
H	4.655724	13.277189	-1.654851
H	5.669871	11.340761	-0.089994
H	5.673910	10.295219	-1.542370
H	4.827237	9.773386	-0.062627
H	2.749795	9.382058	-1.392294
H	3.624144	9.926853	-2.840001
H	2.066212	10.670865	-2.419942

Int 1

C	-0.755767	-3.508899	-0.980590
C	-0.872232	-2.337063	-0.144000
C	-1.279719	-2.502670	1.232638
C	-1.561314	-3.790808	1.706267
C	-1.456753	-4.920944	0.891995
C	-1.054805	-4.764224	-0.436820
O	-0.610949	-1.145176	-0.627477
Li	-0.373397	0.495554	-1.066820
C	-1.400584	-1.283026	2.169069
C	-2.464255	-0.297974	1.630791
C	-0.302956	-3.378670	-2.449080
C	1.114890	-2.763542	-2.509159
C	-0.030170	-0.577515	2.297434
C	-1.836545	-1.671494	3.594793
C	-0.234272	-4.738506	-3.170594
C	-1.298880	-2.498678	-3.239290
O	0.699921	2.040036	-0.640864
C	2.193450	2.147259	-0.748694
C	2.799921	0.770939	-0.530365
B	0.258865	3.226241	-0.063069
O	1.265924	4.005045	0.425500
C	2.511713	3.197323	0.375673
C	2.673354	2.571026	1.760279
C	3.673842	4.125678	0.058450
C	2.477578	2.655855	-2.159663
H	-1.871800	-3.927163	2.743106
H	-1.684303	-5.912921	1.289022
H	-0.973486	-5.655304	-1.061020
H	-1.899753	-0.762030	4.212015
H	-1.116367	-2.351409	4.075136
H	-2.826718	-2.152089	3.606573
H	-2.242347	0.002886	0.599347
H	-2.509268	0.603823	2.262611

H	-3.458564	-0.770577	1.637319
H	0.356043	-0.288280	1.312963
H	0.703576	-1.250517	2.767562
H	-0.117384	0.324999	2.924687
H	-2.294607	-2.968425	-3.255476
H	-0.960680	-2.380455	-4.281932
H	-1.391857	-1.507224	-2.780318
H	1.137579	-1.793177	-1.998827
H	1.430478	-2.625380	-3.556303
H	1.841638	-3.429187	-2.018072
H	0.481966	-5.424308	-2.692473
H	0.099628	-4.579098	-4.207581
H	-1.215459	-5.235381	-3.208517
H	-0.900099	3.510609	-0.007089
H	3.559461	2.717166	-2.337660
H	2.050950	1.956826	-2.892383
H	2.037192	3.648521	-2.329069
H	3.820744	4.826242	0.891449
H	4.599761	3.545669	-0.065760
H	3.496123	4.704632	-0.855797
H	2.529788	0.098364	-1.357821
H	3.896288	0.847667	-0.514161
H	2.468865	0.314456	0.409825
H	3.613825	2.008399	1.829979
H	2.693502	3.370970	2.512873
H	1.840525	1.894526	1.999088

TS1 (alkyne)

C	-4.763592	5.965753	-2.256503
C	-3.566403	6.210644	-2.938331
C	-2.365523	5.692873	-2.459970
C	-2.359917	4.919042	-1.279066
C	-3.562104	4.674687	-0.598435
C	-4.757046	5.198150	-1.088093
C	-1.077941	4.407870	-0.869947
C	0.146722	4.144417	-0.857454
B	-0.503052	3.286902	0.522871
O	0.164574	3.630492	1.755309
C	0.990484	2.492262	2.117356
C	2.376689	2.647875	1.477208
O	-0.292351	1.846179	0.254643
C	0.191445	1.277436	1.517362
C	1.030193	0.045547	1.202130
C	-1.030183	0.898799	2.358905
C	1.113587	2.464771	3.636882

H	-1.721448	3.572536	0.598300
H	1.502152	-0.338001	2.118073
H	0.395222	-0.758060	0.798819
H	1.817059	0.266362	0.470391
H	2.779885	3.633683	1.747043
H	3.075902	1.879017	1.835999
H	2.326757	2.579856	0.381426
H	-1.660180	0.200678	1.789166
H	-0.732115	0.403896	3.293464
H	-1.630362	1.784617	2.609102
H	1.631215	1.553169	3.970790
H	1.698064	3.332106	3.974577
H	0.127903	2.509478	4.115656
H	1.172650	4.160547	-1.184283
H	-1.432203	5.873382	-2.994535
H	-3.554732	4.068244	0.309338
H	-3.566982	6.803854	-3.854088
H	-5.688876	4.998565	-0.557253
H	-5.702303	6.369150	-2.639637
C	-2.785117	0.208603	-4.737072
C	-1.982698	-0.384251	-3.696397
C	-1.719869	-1.802100	-3.736996
C	-2.237343	-2.556465	-4.797141
C	-3.002998	-1.978506	-5.810954
C	-3.268650	-0.608350	-5.765829
O	-1.501613	0.358243	-2.723139
Li	-0.797894	0.974772	-1.307646
C	-0.888243	-2.475982	-2.626487
C	-1.590368	-2.301182	-1.258982
C	-3.114667	1.714332	-4.705698
C	-1.814458	2.550046	-4.761473
C	0.538851	-1.880291	-2.589227
C	-0.725512	-3.992721	-2.844339
C	-3.982571	2.153399	-5.900412
C	-3.908151	2.054117	-3.422972
H	-2.044159	-3.629176	-4.842014
H	-3.392983	-2.590872	-6.626817
H	-3.875026	-0.172900	-6.561335
H	-0.126650	-4.414063	-2.021930
H	-0.203201	-4.217803	-3.786335
H	-1.694504	-4.513625	-2.852178
H	-1.807358	-1.245452	-1.049699
H	-0.965461	-2.708206	-0.446308
H	-2.549032	-2.841177	-1.253368
H	0.514769	-0.787024	-2.499147
H	1.075005	-2.124011	-3.519098

H	1.112108	-2.298380	-1.745011
H	-4.862092	1.505152	-3.409143
H	-4.131189	3.132184	-3.383608
H	-3.338351	1.778676	-2.527454
H	-1.151329	2.290903	-3.927919
H	-2.051723	3.625293	-4.710513
H	-1.278853	2.360650	-5.704681
H	-3.478287	1.978169	-6.863130
H	-4.184317	3.233297	-5.821551
H	-4.952717	1.633983	-5.917669

TS 1[‡](alkene)

C	-3.818801	-0.287866	-5.247292
C	-3.293261	0.580361	-4.284184
C	-2.386486	0.059099	-3.291996
C	-2.059190	-1.347962	-3.331313
C	-2.620023	-2.159076	-4.324584
C	-3.494715	-1.646239	-5.282535
C	-3.680342	2.070357	-4.272226
C	-4.371255	2.415831	-2.933025
O	-1.871755	0.848599	-2.366694
Li	-0.826708	0.517449	-0.969186
C	-1.110991	-1.943499	-2.274807
C	-0.856573	-3.450774	-2.466129
C	-1.748027	-1.799915	-0.862696
C	0.286273	-1.265866	-2.366396
C	-2.416631	2.938939	-4.471382
C	-4.667150	2.438491	-5.395617
O	-0.100607	1.607404	0.347630
C	0.279631	1.322485	1.733189
C	-0.997236	1.098204	2.547840
B	-0.368319	3.067171	0.320817
O	0.222647	3.673776	1.495634
C	1.026106	2.650445	2.129037
C	1.050361	2.923195	3.629326
C	2.448046	2.707053	1.553611
C	1.151996	0.073545	1.739604
C	0.182100	3.737555	-1.183847
C	-1.184543	4.103348	-1.137233
C	-1.726700	5.419445	-0.765546
C	-0.917680	6.447635	-0.249229
C	-1.474555	7.687648	0.057901
C	-2.840607	7.917065	-0.148536
C	-3.653150	6.899447	-0.659374
C	-3.100215	5.655264	-0.959939

H	-1.629268	3.260037	0.366201
H	1.575099	-0.091822	2.740950
H	0.552915	-0.813611	1.484540
H	1.976618	0.156481	1.020261
H	2.832762	3.729586	1.672962
H	3.128840	2.019607	2.076106
H	2.452985	2.459631	0.482656
H	-1.580256	0.282834	2.094404
H	-0.767420	0.813589	3.584057
H	-1.619795	2.003296	2.563852
H	1.559320	2.111055	4.169230
H	1.596334	3.857062	3.823875
H	0.034271	3.033039	4.028522
H	0.949784	4.484304	-0.985003
H	0.144502	6.272999	-0.072550
H	-3.730633	4.853651	-1.350517
H	-0.842294	8.480788	0.460643
H	-4.718237	7.075030	-0.819824
H	-3.271543	8.890961	0.091574
H	-2.376043	-3.222071	-4.358672
H	-3.922053	-2.297510	-6.047702
H	-4.507558	0.098175	-6.000080
H	-0.170831	-3.808331	-1.681962
H	-0.391637	-3.663023	-3.439891
H	-1.785331	-4.034413	-2.390339
H	-2.239321	-0.827570	-0.696083
H	-1.013436	-1.997062	-0.063491
H	-2.554456	-2.538277	-0.749657
H	0.235147	-0.176208	-2.521031
H	0.819000	-1.649938	-3.248061
H	0.907378	-1.493456	-1.483755
H	-5.299150	1.834057	-2.822355
H	-4.640980	3.485118	-2.909448
H	-3.717491	2.180324	-2.083729
H	-1.645297	2.673783	-3.738590
H	-2.661378	4.009781	-4.371436
H	-2.001993	2.779998	-5.479049
H	-4.245954	2.244452	-6.393574
H	-4.897337	3.513658	-5.335268
H	-5.616551	1.888652	-5.307048
H	0.453511	2.940994	-1.879267
H	-1.884890	3.430695	-1.642932

Pdt (Alkyne)

C	-1.660721	-0.638160	0.845728
---	-----------	-----------	----------

H	-0.970417	0.057117	0.351616
C	-2.400444	-0.165208	1.876624
H	-3.084255	-0.842312	2.401208
C	-1.649366	-1.996698	0.295381
C	-2.534552	-3.008919	0.723600
C	-0.711660	-2.317384	-0.707853
C	-2.475152	-4.287918	0.174689
H	-3.279786	-2.788602	1.490111
C	-0.648901	-3.599830	-1.255832
H	-0.021747	-1.543327	-1.053625
C	-1.531068	-4.591349	-0.816289
H	-3.170200	-5.057129	0.517878
H	0.089469	-3.825570	-2.027765
H	-1.487836	-5.595106	-1.243338
C	-2.819613	3.222561	3.505304
C	-1.531139	3.439647	2.625563
B	-2.310465	1.298830	2.361502
O	-2.965096	1.759685	3.493907
O	-1.570607	2.282817	1.721506
C	-2.693338	3.689589	4.948887
H	-2.505905	4.772983	4.987224
H	-3.629674	3.486101	5.487032
H	-1.878343	3.173216	5.470256
C	-4.087302	3.792765	2.863772
H	-4.961844	3.431373	3.421818
H	-4.089516	4.891540	2.888864
H	-4.186690	3.463754	1.819479
C	-0.230352	3.328845	3.425728
H	0.614180	3.284627	2.724297
H	-0.088502	4.197100	4.084615
H	-0.215590	2.416205	4.038019
C	-1.535545	4.711794	1.789306
H	-1.591201	5.599116	2.437345
H	-0.606134	4.773542	1.205756
H	-2.381391	4.733478	1.091119

Pdt²⁺ (Alkene)

C	-1.526170	-0.548622	0.735314
H	-0.486298	-0.318158	1.023341
C	-2.459271	-0.197371	1.898112
H	-2.279466	-0.865127	2.759642
C	-1.570911	-1.977984	0.227759
C	-2.476527	-2.933777	0.709604
C	-0.667000	-2.373826	-0.775278
C	-2.480284	-4.241548	0.207474

H	-3.190611	-2.662215	1.488817
C	-0.666202	-3.675011	-1.279189
H	0.048837	-1.643664	-1.164031
C	-1.576634	-4.618772	-0.787765
H	-3.194430	-4.968597	0.600775
H	0.048423	-3.955830	-2.056232
H	-1.578631	-5.638527	-1.178097
C	-2.833493	3.221856	3.529824
C	-1.547129	3.427888	2.645746
B	-2.338691	1.286557	2.399454
O	-2.980775	1.758605	3.532702
O	-1.587516	2.255978	1.758973
C	-2.705477	3.702069	4.968797
H	-2.510630	4.784376	4.996898
H	-3.644386	3.510779	5.506810
H	-1.895350	3.184735	5.496832
C	-4.100759	3.789989	2.885623
H	-4.974739	3.439801	3.451668
H	-4.097016	4.888963	2.897249
H	-4.207010	3.449940	1.845382
C	-0.243269	3.328792	3.441912
H	0.597995	3.266742	2.737926
H	-0.094982	4.210034	4.081971
H	-0.228839	2.429366	4.073415
C	-1.552864	4.687340	1.790699
H	-1.596965	5.583876	2.426775
H	-0.628995	4.735244	1.197662
H	-2.405137	4.704741	1.100520
H	-1.737292	0.126973	-0.111627
H	-3.513415	-0.376950	1.618584