Supplementary information

Photoinduced transition metal-free borylation of aryl halides in aqueous phase

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1. General information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Commercial reagents were purchased from J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, Strem Chemicals, TCI. MeCN, MeOH and Acetone were purchased from Acros Organics and used directly without further purification. Distilled water was degassed by continuous boiling and then backfilled with argon for preservation.

NMR spectra were obtained on a Bruker Avance III600 spectrometer. NMR data were obtained for ^{1}H at 600 MHz, and for ^{13}C at 150 MHz. ^{1}H NMR (600 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal references ($CDCl_3$: δ = 7.26). ^{13}C NMR (150 MHz) chemical shifts were given using $CDCl_3$ as the internal references ($CDCl_3$: δ = 77.16,). GC analysis was performed on Agilent G7820A instrument equipped with an FID detector using nitrogen as the carrier gas. GC-MS analysis was performed on a Thermo Scientific GC1300-ISQ gas chromatography-mass spectrometry. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (300-400 mesh), eluting with petroleum ether and ethyl acetate.

2. General procedure

(A) General procedure for the determination of GC yields

A 15 mL Schlenk tube equipped with a magnetic stirring bar was charged with aryl halides (0.2 mmol), B_2pin_2 (0.4 mmol), K_2HPO_4 (0.3 mmol), 1-methylbenzimidazole (0.04 mmol), H_2O (2 mL). The reaction was irradiated with a 24 W 365 nm LED light bulb for 24 h at room temperature under an argon atmosphere. After completion of the reaction, a slight excess of sodium chloride was added to quench the reaction, and the internal standard *n*-tridecane was added. Then 6 mL ethyl acetate was added to the reaction solution, and the organic phase was analyzed by GC after fully shaking for 1 min.

(B) General procedure for borylation

A 15 mL Schlenk tube equipped with a magnetic stirring bar was charged with aryl halides (0.2 mmol), diboron reagents (0.4 mmol), K_2HPO_4 (0.3 mmol), 1-methylbenzimidazole (0.04 mmol), H_2O (2 mL). The reaction was irradiated with a 24 W 365 nm LED light bulb for 24 h at room temperature under an argon atmosphere. After completion of the reaction, the mixture was extracted

with ethyl acetate (3×4 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (PE: EA= 20:1) to afford the product.

(C) General procedure for hydrophobic substrates

A 15 mL Schlenk tube equipped with a magnetic stirring bar was charged with aryl halides (0.2 mmol), diboron reagents (0.4 mmol), K_2HPO_4 (0.3 mmol), 1-methylbenzimidazole (0.04 mmol), H_2O (2 mL), MeCN (0.2 mL). The reaction was irradiated with a 24 W 365 nm LED light bulb for 24 h at room temperature under an argon atmosphere. After completion of the reaction, the mixture was extracted with ethyl acetate (3×4 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was subjected to silica gel column chromatography (PE: EA= 20:1) to afford the product.

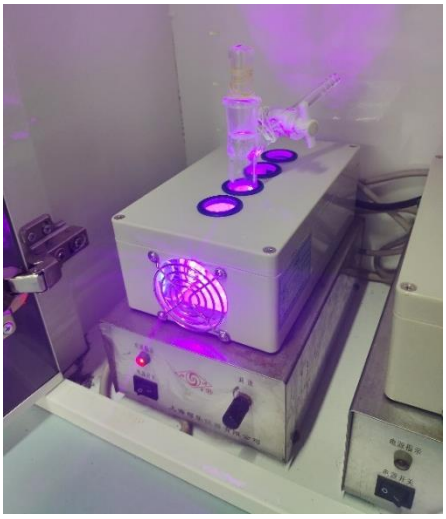
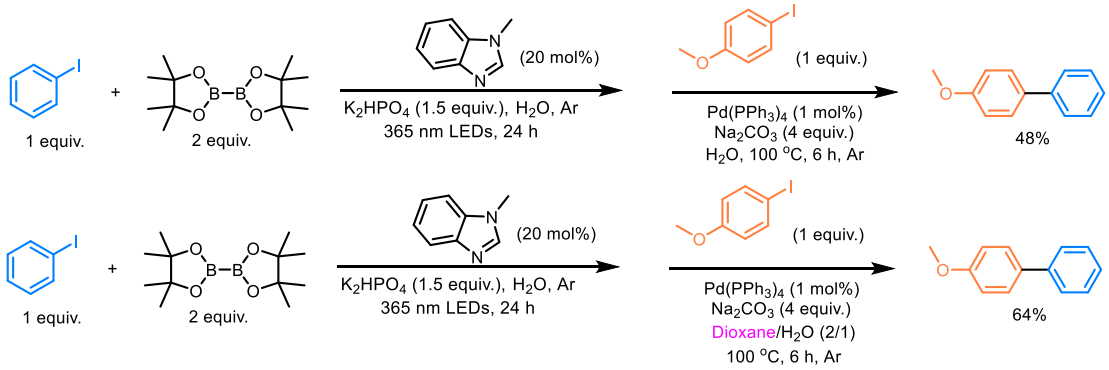


Figure S1. General synthetic equipment

(D) Validation of tandem reaction

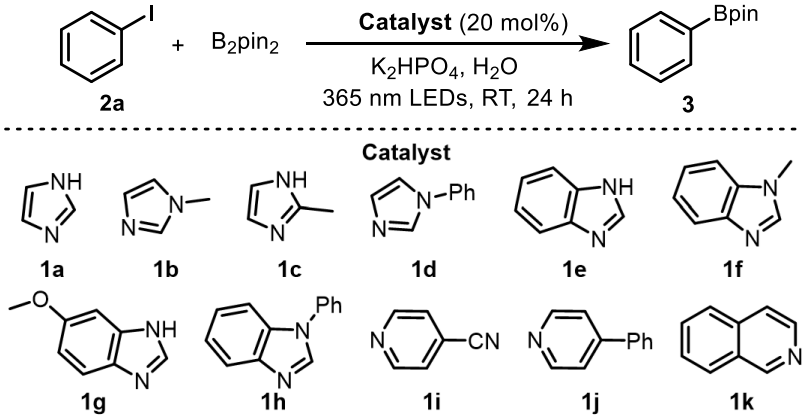


A 15 mL Schlenk tube equipped with a magnetic stirring bar was charged with iodobenzene

(0.2 mmol), B_2pin_2 (0.4 mmol), K_2HPO_4 (0.3 mmol), 1-methylbenzimidazole (0.04 mmol), and H_2O (2 mL). The reaction was irradiated with a 24 W 365 nm LED light bulb for 24 h at room temperature under an argon atmosphere. Then, *p*-methoxyiodobenzene (0.2 mmol), $Pd(PPh_3)_4$ (0.002 mmol), and Na_2CO_3 (0.8 mmol) was added to the reaction mixture. The mixture was stirred at 100 ºC for 6 h. The reaction was extracted with ethyl acetate (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residue was subjected to silica gel column chromatography (petroleum ether) to afford 4-methoxy-1,1'-biphenyl with a yield of 48% (the introduction of additional dioxane as a co-solvent in the second step resulted in an enhanced overall yield of 64%).

3. Condition optimization study

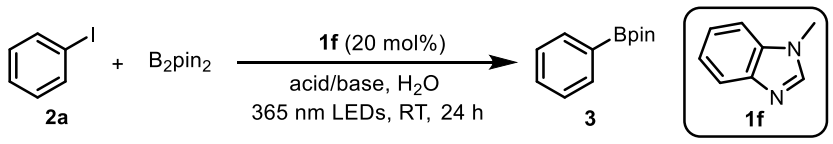
Table S1 Optimization of catalysts in the reaction[a]



Entry	Ph-X	Catalyst	Yield (%)
1	Ph-I(**2a**)	**1a**	26
2	Ph-I	**1b**	28
3	Ph-I	**1c**	68
4	Ph-I	**1d**	84
5	Ph-I	**1e**	82
6	Ph-I	**1f**	95
7	Ph-I	**1i**	trace
8	Ph-I	**1j**	trace
9	Ph-I	**1k**	14
10	Ph-Br (**2b**)	**1c**	trace
11	Ph-Br	**1d**	35
12	Ph-Br	**1e**	54
13	Ph-Br	**1f**	65
14	Ph-Br	**1g**	55
15	Ph-Br	**1h**	52
16	Ph-Cl (**2c**)	**1d**	none
17	Ph-Cl	**1e**	6
18	Ph-Cl	**1f**	8
19	Ph-Cl	**1g**	10
20	Ph-Cl	**1h**	12

[a] General conditions: **2a**, **2b** or **2c** (0.2 mmol), catalyst (0.04 mmol, 20 mol%), K_2HPO_4 (0.3 mmol, 1.5 equiv), B_2pin_2 (0.4 mmol, 2 equiv) in 2 mL of H_2O, 365 nm LEDs for 24 h. The yields were determined by GC using *n*-tridecane as an internal standard.

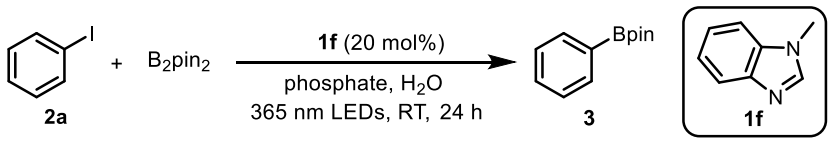
Table S2 Optimization of acid/base in the reaction[a]



Entry	Acid/Base	pH[b]	Yield (%)
1	None	8.40	50
2	$KHSO_4$	1.26	6
3	AcOH	3.68	55
4	KH_2PO_4	5.78	70
5	AcOK	7.48	76
6	$KHCO_3$	8.10	94
7	K_2HPO_4	8.93	95, 70[d], 90[e], 94[f]
8	Na_2HPO_4	8.88	94
9	K_2CO_3	11.85	90
10	K_3PO_4	12.04	90[c]
11	NEt_3	12.45	89[c]
12	KOH	13.46	80[c]

[a] General conditions: **2a** (0.2 mmol), **1f** (0.04 mmol, 20 mol%), acid/base (0.3 mmol, 1.5 equiv), B_2pin_2 (0.4 mmol, 2 equiv) in 2 mL of H_2O, 365nm LEDs for 24 h. The yields were determined by GC using *n*-tridecane as an internal standard. [b] pH value of aqueous phase before reaction. [c] No remaining B_2pin_2. [d] 0.1 mmol K_2HPO_4 (0.5 equiv) [e] 0.2 mmol K_2HPO_4 (1.0 equiv). [f] 0.4 mmol K_2HPO_4 (2.0 equiv).

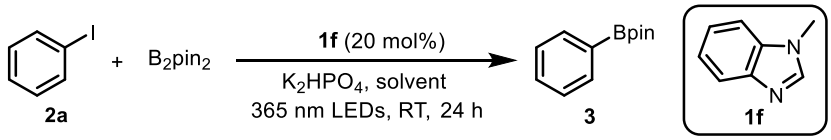
Table S3 Optimization of pH in the reaction[a]



Entry	Base (equiv)	pH[b]	Yield (%)	
			X=I	X=Br
1	KH_2PO_4	5.78	70	20
2	KH_2PO_4/K_2HPO_4	6.78	82	51
3		7.50	90	60
4	K_2HPO_4	8.93	95	65
5	K_2HPO_4 /K_3PO_4	10.66	94	64
6		11.18	91	61
7	K_3PO_4	12.04	90	51

[a] General conditions: **2a** (0.2 mmol), **1f** (0.04 mmol, 20 mol%), phosphate (0.3 mmol, 1.5 equiv), B_2pin_2(0.4 mmol, 2 equiv) in 2 mL of H_2O, 365nm LEDs for 24 h. The yields were determined by GC using *n*-tridecane as an internal standard.

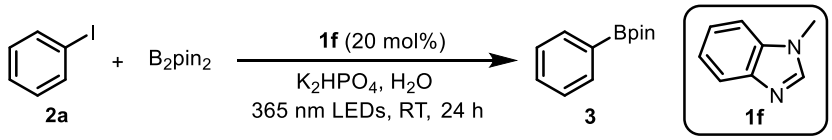
Table S4 Optimization of solvents in the reaction[a]



Entry	Solvent	Yield (%)	
		A：50% aqueous phase	B：Only solvent
1	H_2O	-	95, 78[b], 94[c]
2	ACN	88	8
3	MeOH	90	10
4	THF	43	4
5	DMF	62	4
6	DCM	70	5
7	EtOAc	74	5

[a] General conditions: **2a** (0.2 mmol, 1 equiv), **1f** (0.04 mmol, 20 mol%), K_2HPO_4 (1.5 equiv), B_2pin_2 (2 equiv) in 2 mL of solvent, 365nm LEDs for 24 h. The yields were determined by GC using *n*-tridecane as an internal standard. [b]1 mL water as solvent. [c]3 mL water as solvent.

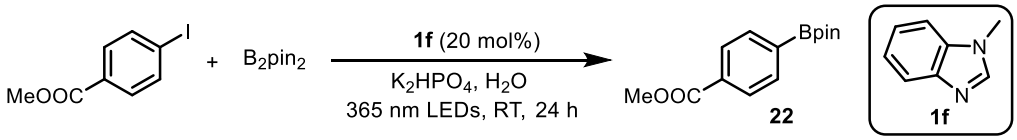
Table S5 Control experiment[a]



Entry	Variation from standard conditions	Yield (%)
1	none	95, 65[b]
2	390 nm LEDs	92, 26[b]
3	420 nm LEDs	84, 12 [b]
4	dark or 85℃	none
5	**1f** (10 mol%)	78
6	**1f** (30 mol%)	94
7	16 h	78
8	32 h	84
9	Air	52

[a] General conditions:**2a** (0.2 mmol, 1 equiv), **1f** (0.04 mmol, 20 mol%), K_2HPO_4 (0.3 mmol, 1.5 equiv), B_2pin_2 (2 equiv) in 2 mL of solvent, 365 nm LEDs. The yields were determined by GC using *n*-tridecane as an internal standard. [b] Bromobenzene as substrate.

Table S6 Optimization of solubilizers in the reaction[a]



Entry	Solubilizer	Yield (%)
1	none	17
2	CTAB	32
3	TBAB	37
4	SDS	33
5	SDBS	10
6	Triton X-100	25
7	Brij L23	18
8	MeCN[b]	90
9	MeOH[b]	88

[a] General conditions: haloarene (0.2 mmol), K_2HPO_4 (0.3 mmol), **1f** (0.04 mmol, 20 mol%), B_2pin_2 (0.4 mmol), solubilizer (0.02 mmol) in 2 mL of H_2O, 60 ℃, 16 h. The yields were determined by GC using *n*-tridecane as an internal standard. [b] 200 μL organic solvent as co-solvent.

4. Gram-scale synthesis

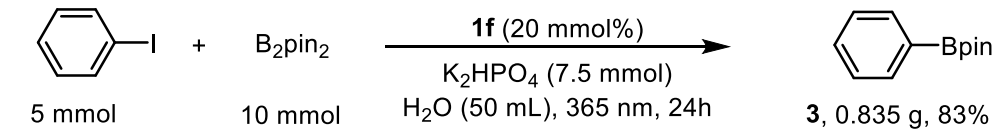
(1) General procedure for gram-scale synthesis

A 100 mL round flask equipped with a magnetic stirring bar was charged with aryl halide (5 mmol), B_2pin_2 (10 mmol), K_2HPO_4 (7.5 mmol), 1-methylbenzimidazole (1 mmol), H_2O (50 mL). The mixture was then stirred at room temperature under nitrogen atmosphere and irradiated with a 20 W 365 nm LEDs light.

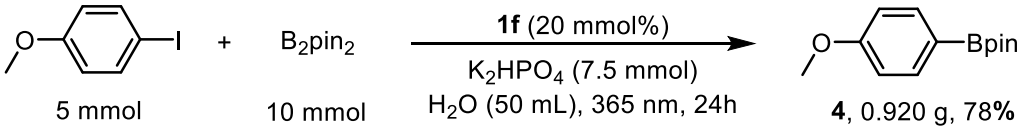
After completion of the reaction, a slightly excessive amount of NaCl was added to the reaction to quench the reaction, and the aqueous phase was extracted with 50 mL ethyl acetate using a separatory funnel. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator. The residual was subjected to silica gel column chromatography (PE: EA= 20:1) to afford the product.

Figure S2. Equipment for gram-scale synthesis.

(2) Gram-scale synthesis of 3

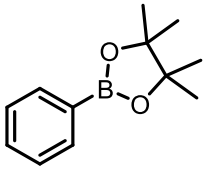


(3) Gram scale synthesis of 4



5. Characterization data of products

4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (3)

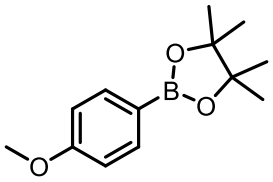


Following general procedure A, **3** was obtained as colorless liquid in 85% yield (33.8 mg) from aryl iodide and 61% yield (24.8 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, J = 6.5 Hz, 2H), 7.48-7.45 (m, 1H), 7.39-7.36 (m, 2H), 1.35 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.9, 131.4, 127.9, 83.9, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

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

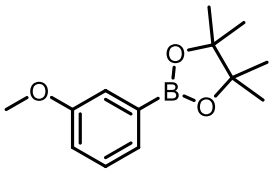


Following general procedure A, **4** was obtained as colorless liquid in 82% yield (38.4 mg) from aryl iodide and 54% yield (25.4 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 136.6, 113.4, 83.7, 55.2, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

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

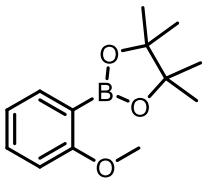


Following general procedure A, **5** was obtained as colorless liquid in 76% yield (35.6 mg) from aryl iodide 50% yield (23.4 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.33(s, 1H), 7.31-7.27 (m, 1H), 7.02-7.00 (m, 1H), 3.84 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 129.0, 127.2, 118.7, 118.0, 83.9, 55.3, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(2-methoxyloxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)



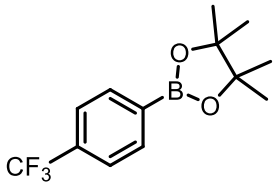
Following general procedure A, **6** was obtained as colorless liquid in n 53% yield (25.0 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.40 (dt, *J* = 8.3, 1.6 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 3.83 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3, 136.8, 132.6, 120.3, 110.6, 83.6, 55.9, 25.0. The carbon

directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (7)



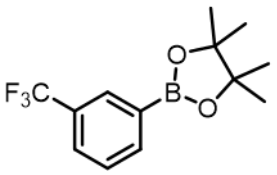
Following general procedure A, **7** was obtained as colorless solid in 76% yield (41.3 mg) from aryl iodide and 33% yield (18.0 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 1.36 (s, 7H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.2, 133.0 (q, J = 31.7 Hz), 124.5 (q, J = 4.5 Hz), 124.3 (q, J = 273.3 Hz), 84.4, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.03.

4,4,5,5-tetramethyl-2-(3-trifluoromethylphenyl)-1,3,2-dioxaborolane (8)



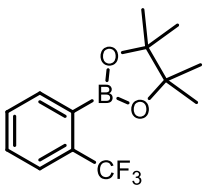
Following general procedure A, **8** was obtained as colorless liquid in 72% yield (39.2 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.97 (d, J = 7.4 Hz, 1H), 7.70 (d, J = 7.9 Hz, 1H), 7.50-7.47 (m, 1H), 1.36 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.1, 131.5 (q, J = 3.0 Hz), 130.2 (q, J = 31.7 Hz), 128.2, 127.9 (q, J = 3.0 Hz), 124.4 (q, J = 273.3 Hz), 84.4, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.61.

4,5,5-tetramethyl-2-(2-(trifluoromethyl)-phenyl)-1,3,2-dioxaborolane (9)



Following general procedure A, **9** was obtained as light yellow liquid in 35% yield (19.1 mg)

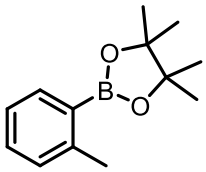
from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.4 Hz, 1H), 7.68–7.64 (m, 1H), 7.53–7.47 (m, 1H), 1.37 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 136.7, 120.6, 120.0, 84.2, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

^{19}F NMR (565 MHz, $CDCl_3$) δ -57.56.

4,4,5,5-tetramethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (10)

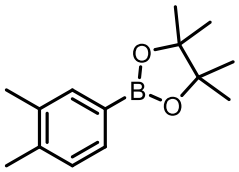


Following general procedure A, **10** was obtained as colorless liquid in 74% yield (32.3 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.7, 1.7 Hz, 1H). 7.36-7.32 (m, 1H), 7.19-7.17 (m, 2H), 2.56 (s, 3H), 1.37 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 136.0, 130.9, 129.9, 124.8, 83.5, 25.0, 22.4. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(3,4-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)

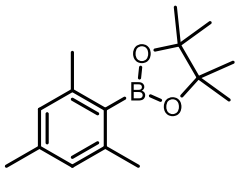


Following general procedure A, **11** was obtained as colorless liquid in 78% yield (36.2 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 1.36 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.3, 136.1, 136.0, 132.5, 129.3, 83.7, 25.1, 25.0, 24.8, 20.1, 19.6. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-mesityl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12)

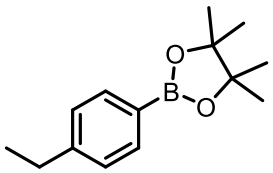


Following general procedure A, **12** was obtained as white solid in 68% yield (33.5 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.78 (s, 2H), 2.38 (s, 6H), 2.25 (s, 3H), 1.38 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 139.5, 128.0, 84.0, 25.5, 22.8, 21.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(4-ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13)

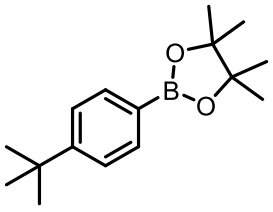


Following general procedure A, **13** was obtained as white solid obtained in 56% yield (26.0 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 2.66 (q, J = 7.6 Hz, 2H), 1.34 (s, 12H), 1.24 (t, J = 7.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 135.0, 127.5, 83.8, 29.3, 25.0, 15.6. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14)

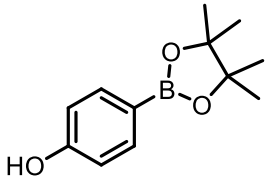


Following general procedure A, **14** was obtained in as colorless liquid 79% yield (41.1 mg) from aryl iodide and 46% yield (23.9 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 1.35 (s, 12H), 1.34 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.6, 134.8, 124.8, 83.7, 35.0, 31.3, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (15)

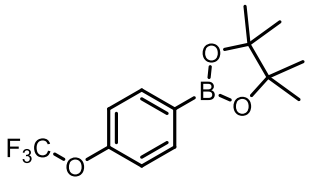


Following general procedure B, **15** was obtained as white solid in 85% yield (37.4 mg) from aryl iodide and 52% yield (22.9 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 5.44 (s, 1H), 1.33 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 136.9, 115.0, 83.8, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (16)



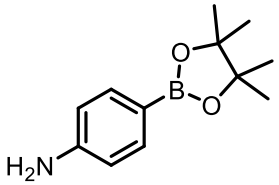
Following general procedure B, **16** was obtained as white solid in 76% yield (43.8 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 1.34 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 136.7, 120.0, 84.23, 25.00. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

^{19}F NMR (565 MHz, $CDCl_3$) δ -57.56.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (17)



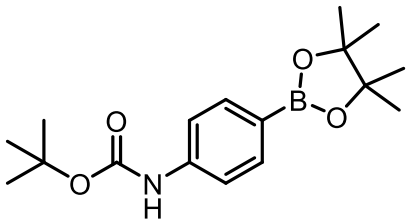
Following general procedure C, **17** was obtained as colorless solid in 85% yield (37.2 mg) from aryl iodide and 50% yield (21.9 mg) from aryl bromide using 10:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, J = 8.5 Hz, 2H), 6.66 (d, J = 8.5 Hz, 2H), 3.83 (s, 2H),

1.32 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 136.5, 114.2, 83.4, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

***N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pivalamide (18)**

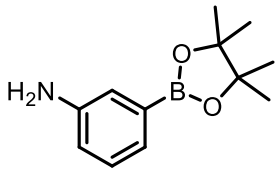


Following general procedure C, **18** was obtained as white solid in 78% yield (47.3 mg) from aryl iodide using 10:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.59 (s, 1H), 1.51 (s, 9H), 1.33 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.6, 141.2, 136.0, 117.4, 83.8, 80.8, 28.5, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (19)

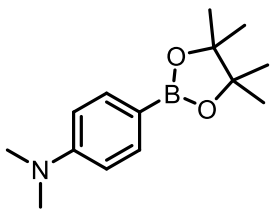


Following general procedure C, **19** was obtained as colorless solid in 81% yield (35.4 mg) from aryl iodide and 49% yield (21.4 mg) from aryl bromide using 10:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.3 Hz, 1H), 7.19-7.16 (m, 1H), 7.14 (d, *J* = 2.6 Hz, 1H), 6.79 (ddd, *J* = 7.8, 2.6, 1.3 Hz, 1H), 3.64 (s, 2H), 1.34 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 128.9, 125.1, 121.3, 118.2, 83.8, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

***N,N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (20)**

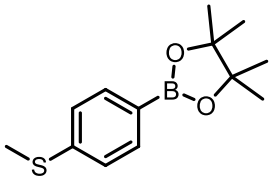


Following general procedure C, **20** was obtained as white solid in 82% yield (40.7 mg) from aryl iodide using 10:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.8 Hz, 1H), 6.69 (d, *J* = 8.9 Hz, 1H), 2.99 (s, 3H), 1.33 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.7, 136.3, 111.4, 83.3, 40.3, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (21)

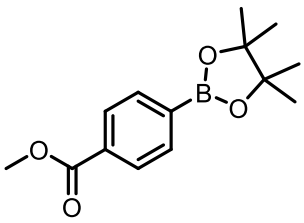


Following general procedure B, **21** was obtained as colorless solid in 72% yield (39.9 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 2.49 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 135.2, 125.1, 83.9, 25.0, 15.2. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (22)

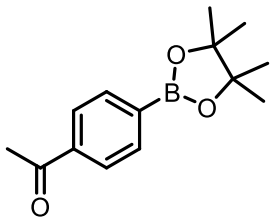


Following general procedure C, **22** was obtained as colorless liquid in 84% yield (44.3 mg) from aryl iodide and 53% yield (27.9 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.5 Hz, 2H), 7.86 (d, *J* = 6.7 Hz, 2H), 3.91 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 134.8, 132.4, 128.7, 84.3, 52.3, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (23)

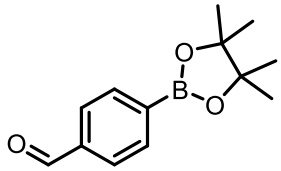


Following general procedure C, **23** was obtained as white solid in 79% yield (38.9 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H). 2.62 (s, 3H), 1.36 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.6, 139.1, 135.1, 127.4, 84.4, 26.9, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (24)

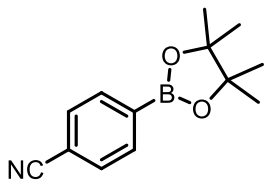


Following general procedure C, **24** was obtained as white solid in 56% yield (25.9 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 1.36 (s, 10H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.8, 138.2, 135.4, 128.8, 84.5, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (25)



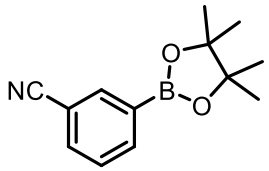
Following general procedure C, **25** was obtained as colorless solid in 67% yield (30.5 mg) from aryl iodide and 41% yield (18.8 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 1.28 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.2, 131.3, 119.0, 114.7, 84.6, 25.0. The carbon directly

attached to the boron atom was not detected due to quadrupolar broadening.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (26)

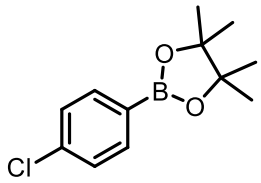


Following general procedure C, **26** was obtained in 63% yield (28.8 mg) from aryl iodide and 56% yield (25.6 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.48-7.46 (m, 1H), 1.35 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 138.6, 134.6, 128.5, 119.0, 112.2, 84.6, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27)

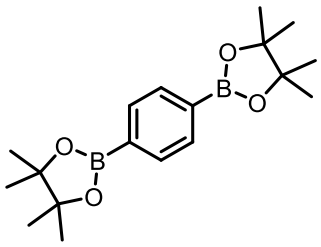


Following general procedure C, **27** was obtained as colorless liquid in 58% yield (27.5 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 1.27 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.7, 136.3, 128.2, 84.2, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (28)



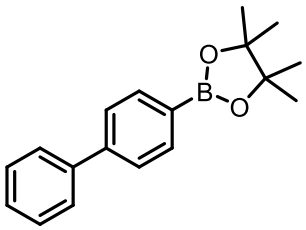
Following general procedure C, **28** was obtained as a colorless liquid in 75% yield (44.8 mg) from aryl iodide.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (s, 4H), 1.35 (s, 24H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.02 84.0, 25.0. The carbon directly attached to the boron

atom was not detected due to quadrupolar broadening.

2-(4-biphenylyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29)

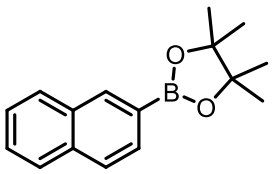


Following general procedure C, **29** was obtained as white solid in 67% yield (37.5 mg) from aryl iodide and 41% yield (22.7 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2H), 7.65 – 7.61 (m, 4H), 7.45-7.44 (m, 2H), 7.37-7.35 (m, 1H), 1.37 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.0, 141.2, 135.4, 128.9, 127.7, 127.4, 126.6, 83.9, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (30)

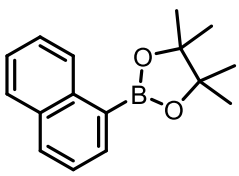


Following general procedure C, **30** was obtained as white solid in 62% yield (31.3 mg) from aryl iodide and 37% yield (18.7 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, J = 8.5 Hz, 1H), 8.10-8.09 (m,1H), 7.95 – 7.93 (m, 1H), 7.85–7.83 (m, 1H), 7.56-7.53 (m, 1H), 7.49-7.47 (m, 2H), 1.44 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 135.7, 133.2, 131.6, 128.4 (2C), 126.4, 125.5, 125.0, 83.8, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (31)

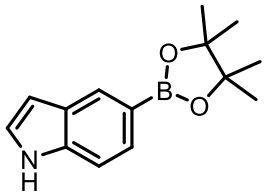


Following general procedure C, **31** was obtained as white solid in 64% yield (32.4 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.5 Hz, 1H), 8.09-8.08 (m, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.53 (m, 1H), 7.49 – 7.47 (m, 2H), 1.43 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.1, 135.8, 133.4, 131.7, 128.6, 128.5, 126.5, 125.6, 125.1, 83.9, 25.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (32)

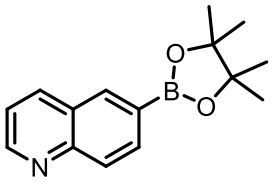


Following general procedure C, **32** was obtained in 56% yield (27.0 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.19 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.19-7.18 (m, 1H), 6.58-6.57 (m, 1H), 1.37 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.0, 128.8, 128.2, 127.8, 124.3, 110.6, 103.3, 83.6, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline (33)

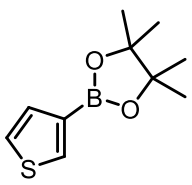


Following general procedure C, **33** was obtained in 32% yield (16.0 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.33 (s, 1H), 8.18 (dd, J = 8.3,1.7 Hz, 1H), 8.07 (s, 2H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 1.38 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 149.8, 136.9, 136.3, 134.4, 128.5, 127.8, 121.3, 84.3, 25.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-tetramethyl-2-(thiophen-3-yl)-1,3,2-dioxaborolane (34)



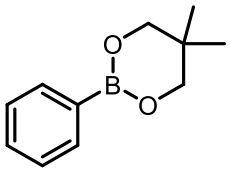
Following general procedure B, **34** was obtained as colorless liquid in 26% yield (10.8 mg) from aryl iodide using 10:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.7 Hz,1H), 7.41 (d, *J* = 4.7 Hz, 1H), 7.35-7.33 (dd, *J* = 4.7, 2.7 Hz, 1H), 1.34 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.4, 131.0, 124.3, 82.6, 23.8.

The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (36)

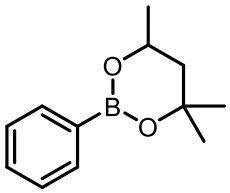


Following general procedure B, **36** was obtained as colorless liquid in 85% yield (32.3 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.44-7.42 (m, 1H), 7.37-7.35 (m, 2H), 3.78 (s, 3H), 1.03 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.9, 130.8, 127.7, 72.5, 32.0, 22.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,6-trimethyl-2-phenyl-1,3,2-dioxaborinane (37)

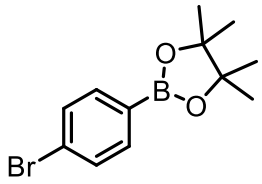


Following general procedure B, **37** was obtained as colorless liquid in 80% yield (32.6 mg) from aryl bromide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 6.6 Hz, 2H), 7.42-7.40 (m, 1H), 7.36-7.33 (m, 2H), 4.36 (m, 1H), 1.87 (dd, *J* = 13.9, 3.0 Hz, 1H), 1.63–1.59 (m, 1H), 1.39 (s, 3H), 1.38 (s, 3H), 1.36 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.9, 130.5, 127.6, 71.1, 65.1, 46.2, 31.4, 28.3, 23.4. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)

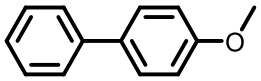


Following general procedure B, **38** was obtained as colorless liquid in 74% yield (42.0 mg) from aryl iodide using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 1.34 (s, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.5, 131.1, 126.4, 84.2, 25.0.

4-methoxy-1,1'-biphenyl



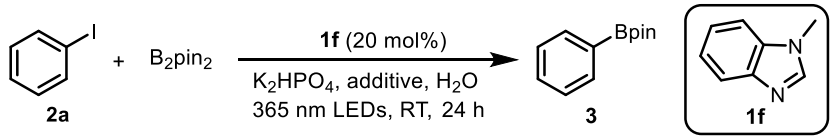
Following general procedure D, 4-methoxy-1,1'-biphenyl was obtained as white solid in 48% yield (17.7 mg) using petroleum ether as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 4H), 7.46 – 7.40 (m, 2H), 7.35 – 7.29 (m, 1H), 7.02 – 6.97 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 140.9, 133.8, 128.8, 128.2, 126.8, 126.7, 114.2, 55.4.

6. Preliminary mechanistic study

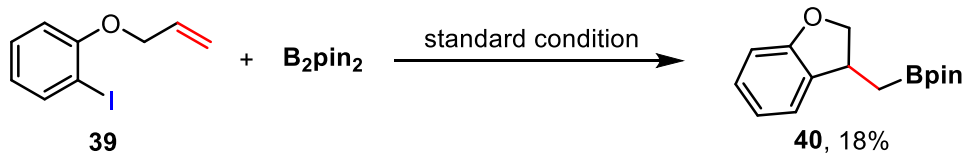
(1) Radical scavenging experiment



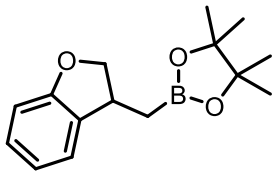
Entry	Additive	Yield (%)
1	TEMPO (0.5 equiv)	67
2	TEMPO (1.0 equiv)	28
3	TEMPO (1.5 equiv)	trace

Experimental procedure: To a 10 mL Schlenk tube charged with **2a** (0.2 mmol), B_2pin_2 (0.4 mmol), K_2HPO_4 (0.3 mmol), 1-methylbenzimidazole (0.04 mmol), TEMPO (0.5-1.5 equiv) was added 2 mL deaerated water under argon. The reaction was irradiated with a 24 W 365 nm LED light bulb for 24 h at room temperature under argon. After the reaction was completed, a slight excess of sodium chloride was added to quench the reaction, and the internal standard n-tridecane was added. Then 6 mL ethyl acetate was added to the reaction solution, and the organic phase was analyzed by GC after fully shaking for 1 min.

(2) Radical clock experiment



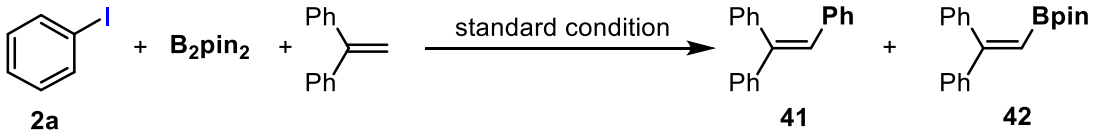
Experimental procedure: Following general procedure B, product **40** was obtained as a colorless liquid in 18% yield (9.3 mg) from 1-(allyloxy)-2-iodobenzene (**39**, 52.0 mg) using 50:1 petroleum ether/EtOAc as eluent.



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.84 (td, *J* = 7.4, 1.0 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 4.70 (t, *J* = 8.8 Hz, 1H), 4.20 – 3.92 (m, 1H), 3.75 – 3.44 (m, 1H), 1.33 (dd, *J* = 16.1, 5.9 Hz, 1H), 1.26 (s, 6H), 1.24 (s, 6H), 1.10 (dd, *J* = 16.1, 8.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 132.8, 128.0, 124.1, 120.4, 109.5, 83.6, 78.8, 37.8, 25.0, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

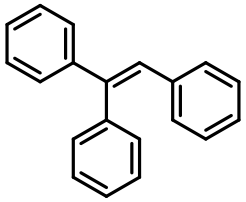
(3) Radical capturing experiment



2a **41** **42**

Entry	Sub.	B_2pin_2	Solvent	*hv*	41	42
1	√	√	H_2O	√	22%	trace
2	×	√	H_2O	√	×	trace
3	×	√	MeCN	√	×	none
4	×	√	50% MeCN aqueous phase	√	×	trace
5	√	×	H_2O	√	none	×
6	×	√	H_2O	×	×	none
7	√	√	H_2O	×	none	none

Experimental procedure: To a 10 mL Schlenk tube charged with **2a** (0.2 mmol), B_2pin_2 (0.4 mmol), K_2HPO_4 (0.3 mmol), 1-methylbenzimidazole (0.04 mmol), 1,1-diphenylethylene (0.3 mmol) was added 2 mL solvent under argon. Experimental procedure: To a 10 mL Schlenk tube charged with **2a** (0.2 mmol), B_2pin_2 (0.4 mmol), K_2HPO_4 (0.3 mmol), 1-methylbenzimidazole (0.04 mmol), TEMPO (0.5-1.5 equiv) was added 2 mL deaerated water under argon. The reaction was irradiated with a 24 W 365 nm LED light bulb for 24 h at room temperature under argon. After completion of the reaction, a slight excess of sodium chloride was added to quench the reaction, and the internal standard *n*-tridecane was added. Then 6 mL ethyl acetate was added to the reaction solution, and the organic phase was analyzed by GC-MS after fully shaking for 1 min. The product was determined by NMR and HRMS.

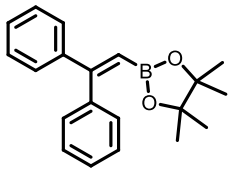


Following general procedure B, **41** was obtained as a light yellow solid in 22% yield (11.2 mg) using 20:1 petroleum ether/EtOAc as eluent.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 8H), 7.24 – 7.21 (m, 2H), 7.17 – 7.10 (m, 3H),

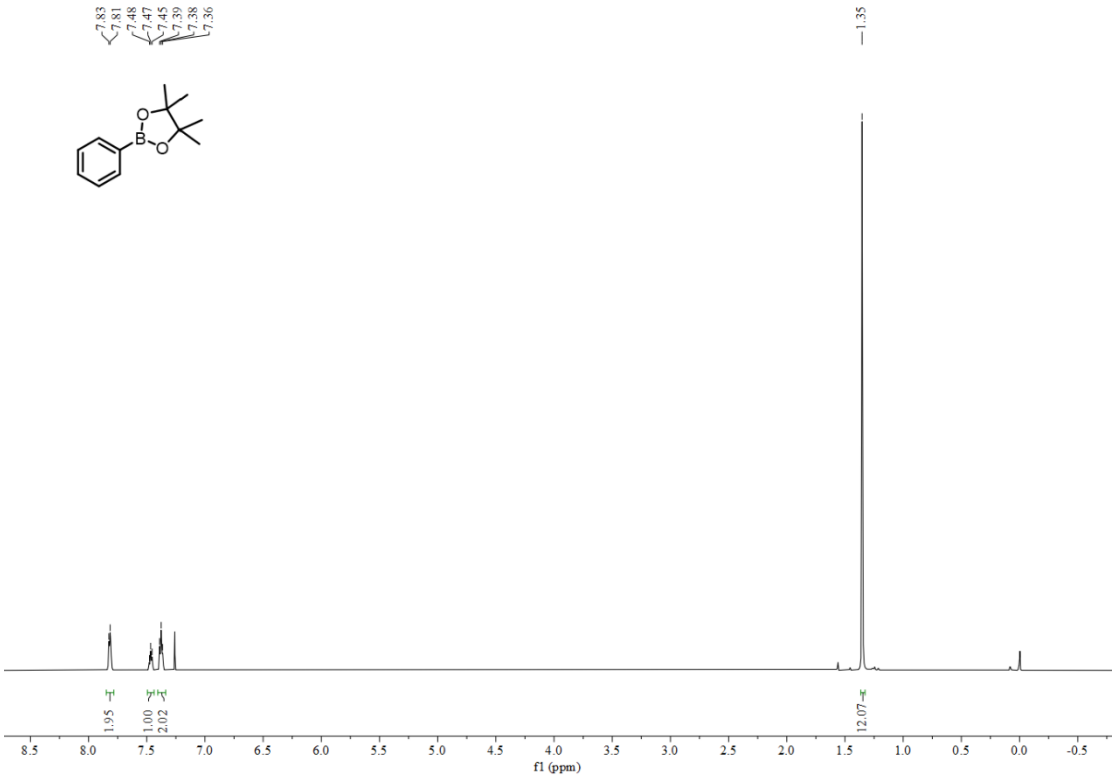
7.06 – 7.03 (m, 2H), 6.98 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.6, 142.7, 140.5, 137.5, 130.5, 129.7, 128.8, 128.3, 128.1, 127.7, 127.6, 127.5, 126.8.

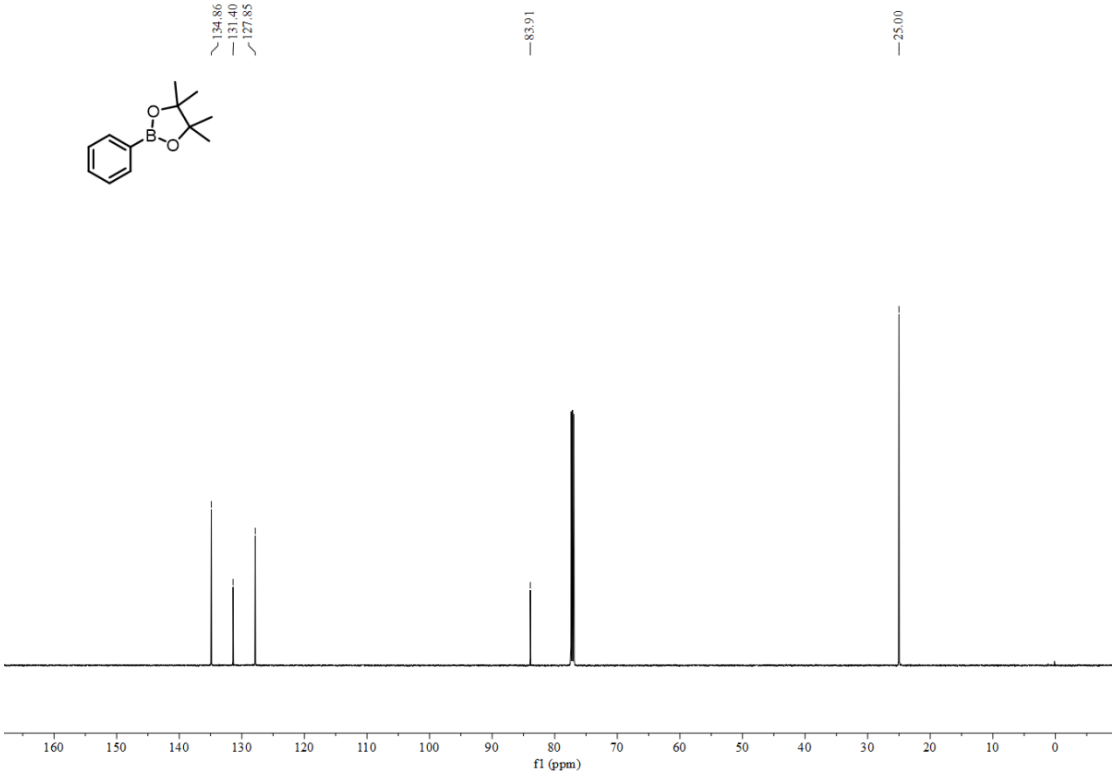


HRMS (ESI) calcd. for $C_{20}H_{23}BO_2$ $[M+H]^+$: 307.1827; found: 307.1882.

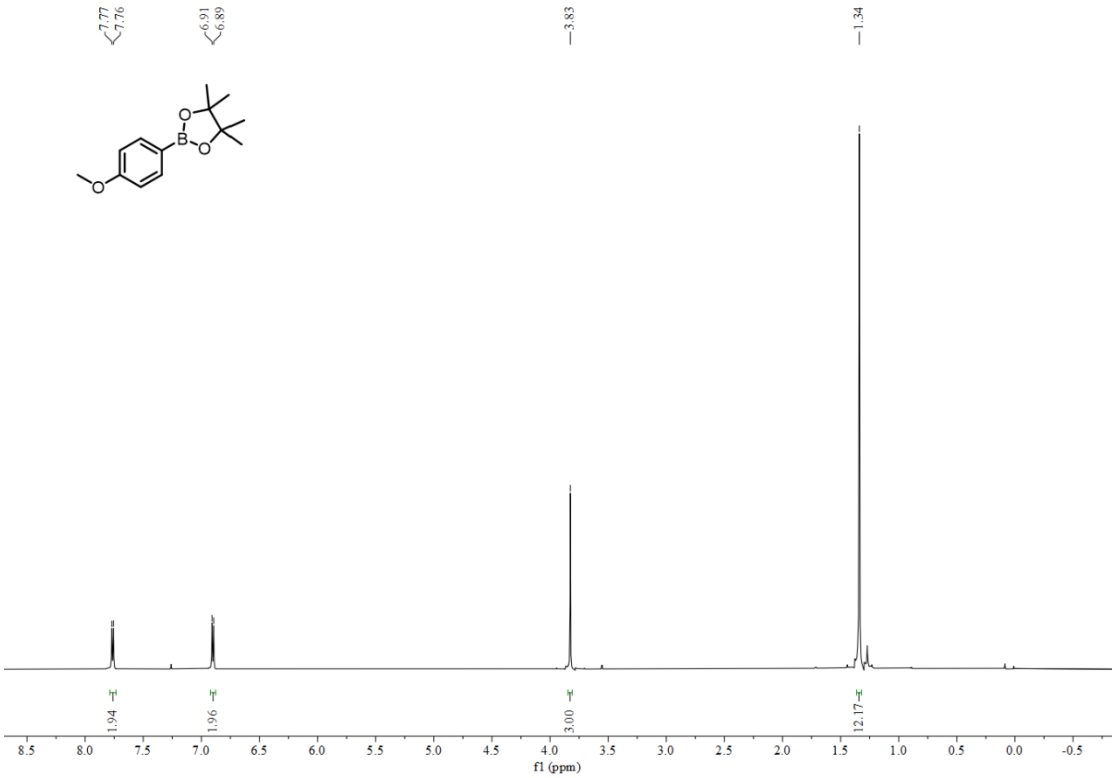
7. NMR Spectra



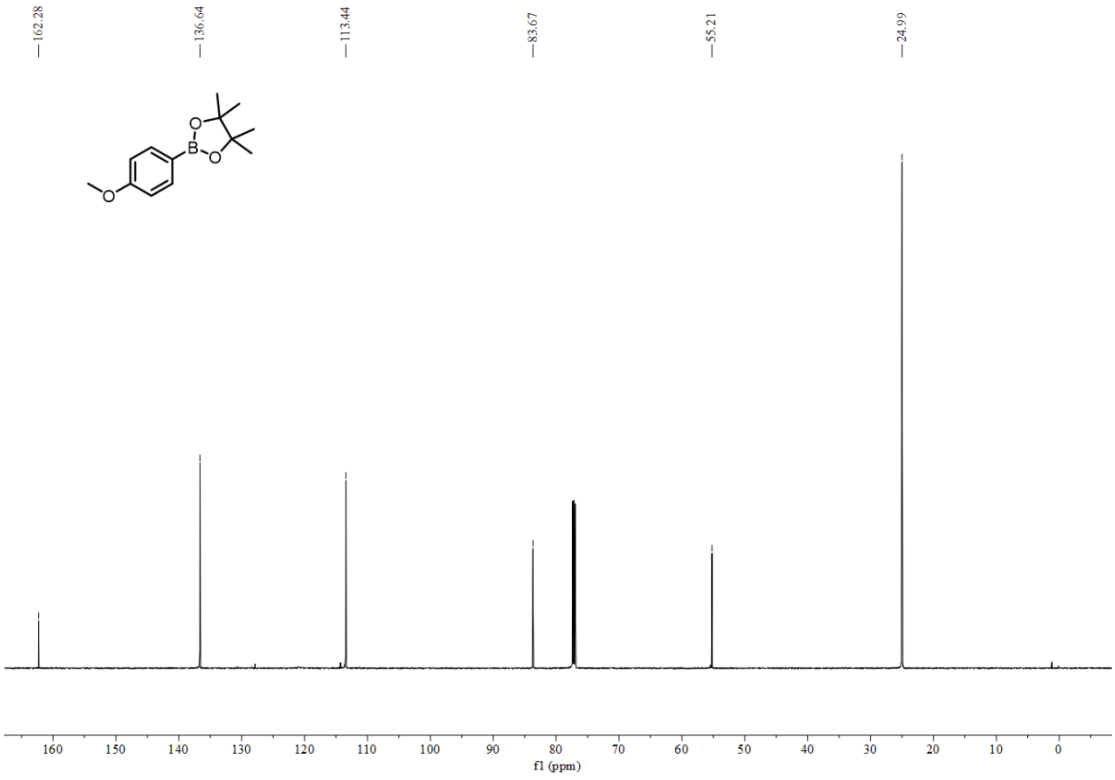
^{1}H NMR spectrum of compound **3**



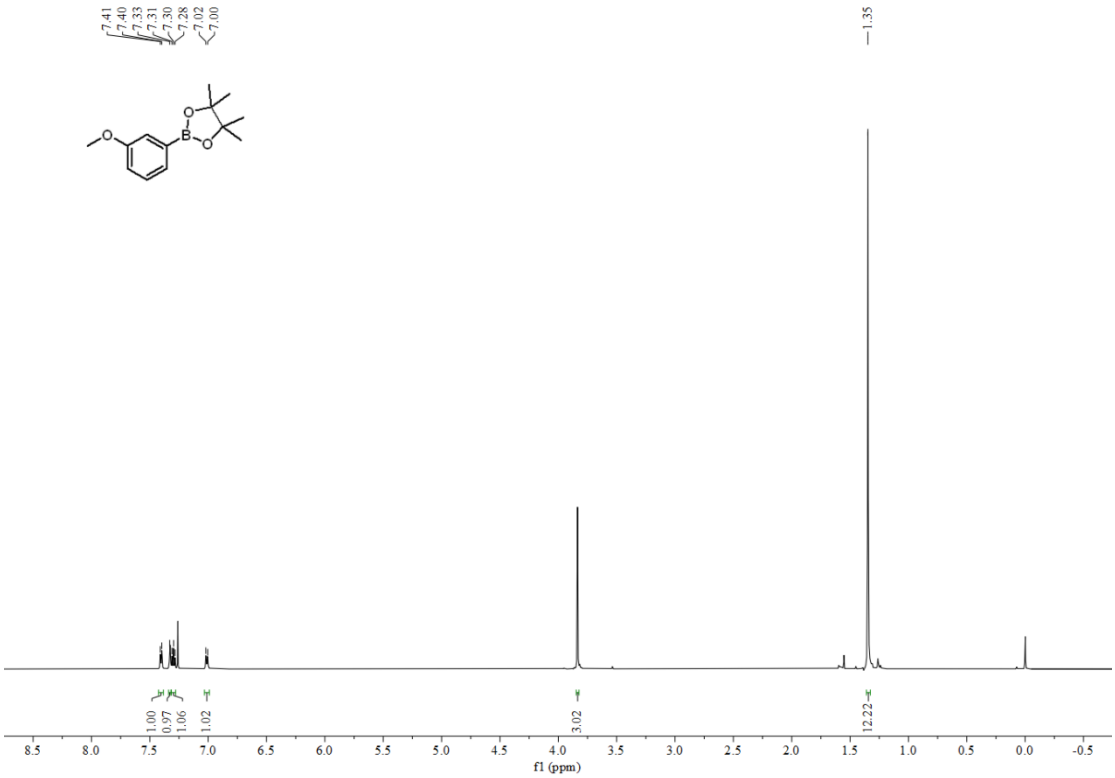
^{13}C NMR spectrum of compound **3**



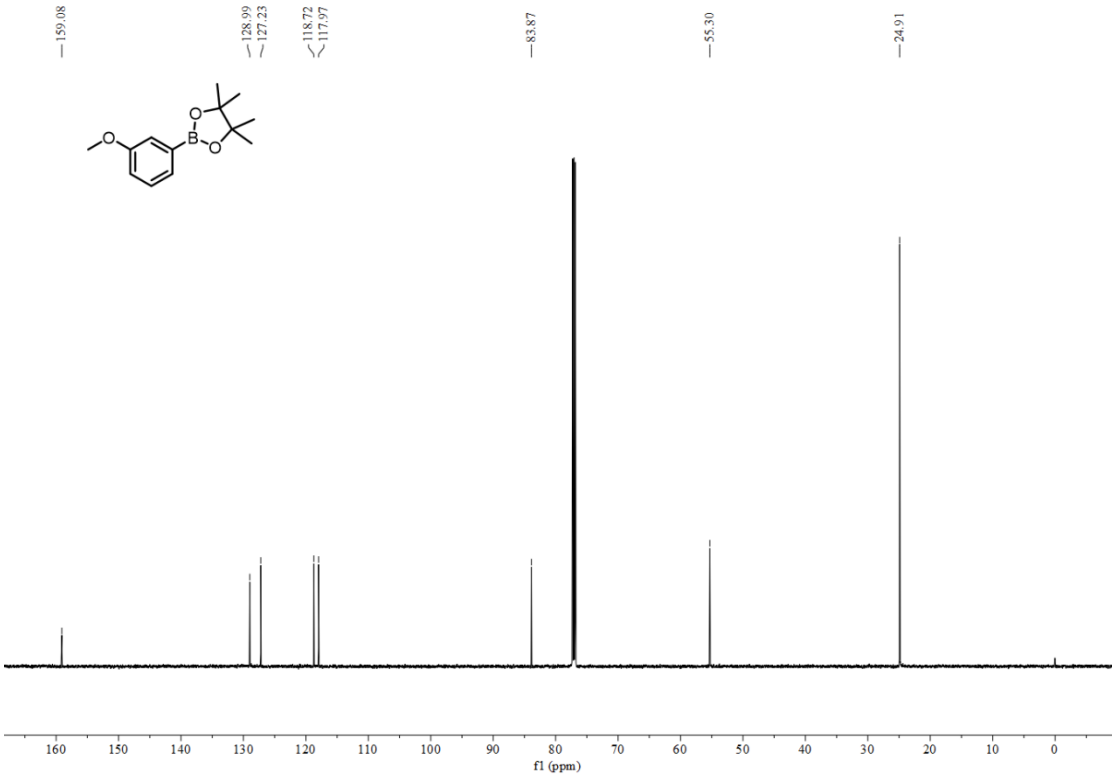
^{1}H NMR spectrum of compound **4**



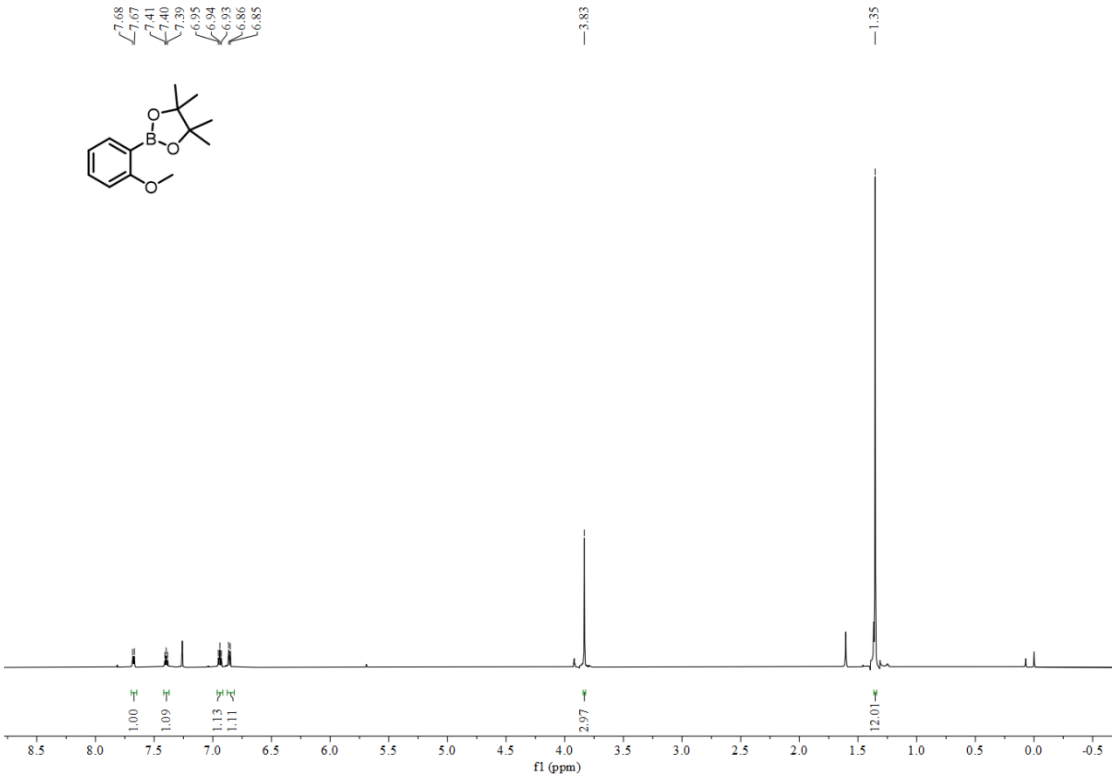
^{13}C NMR spectrum of compound **4**



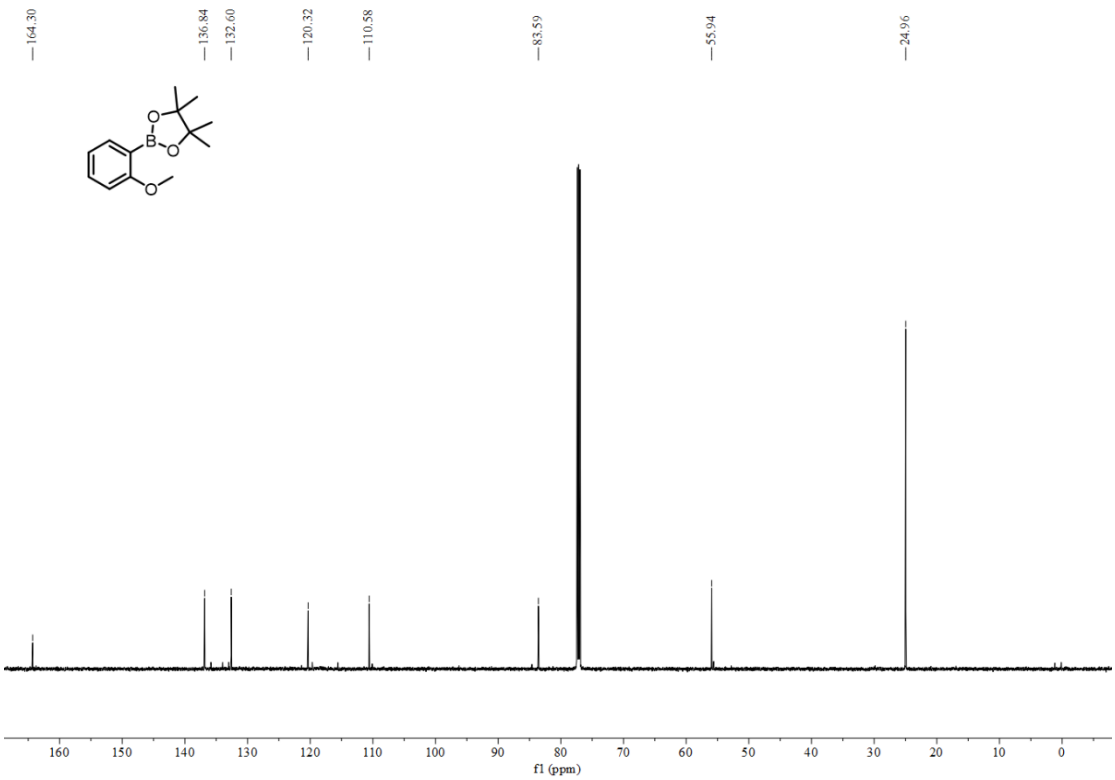
^{1}H NMR spectrum of compound **5**



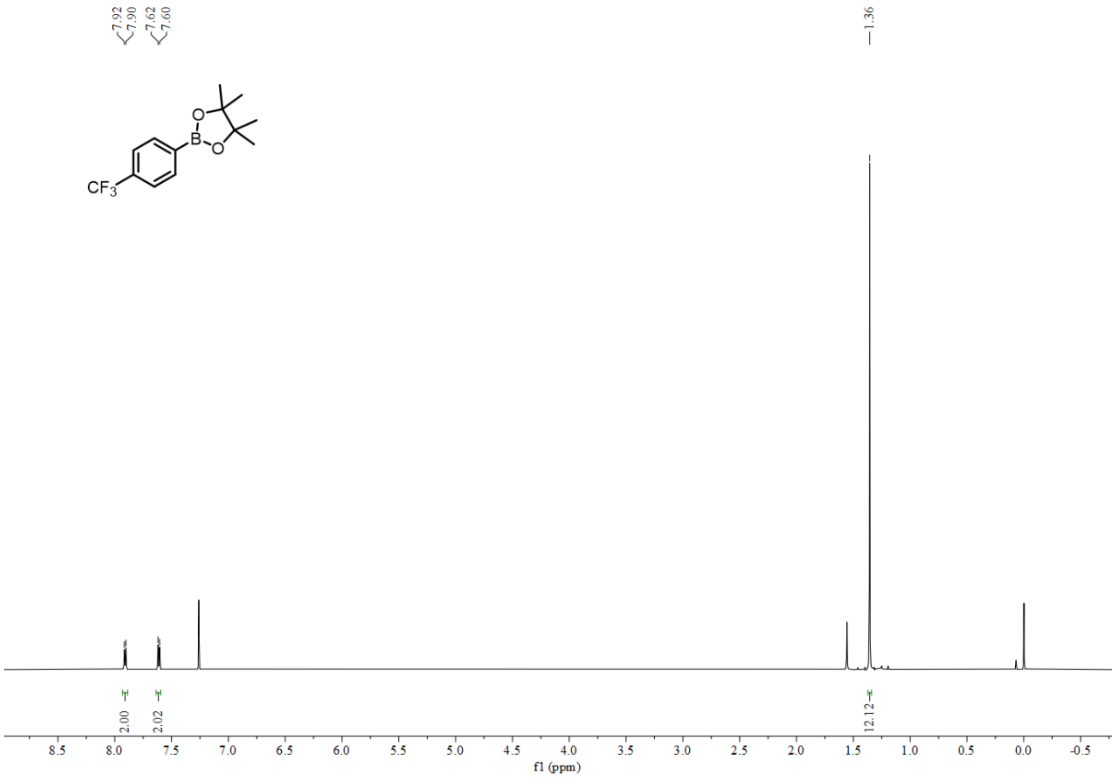
^{13}C NMR spectrum of compound **5**



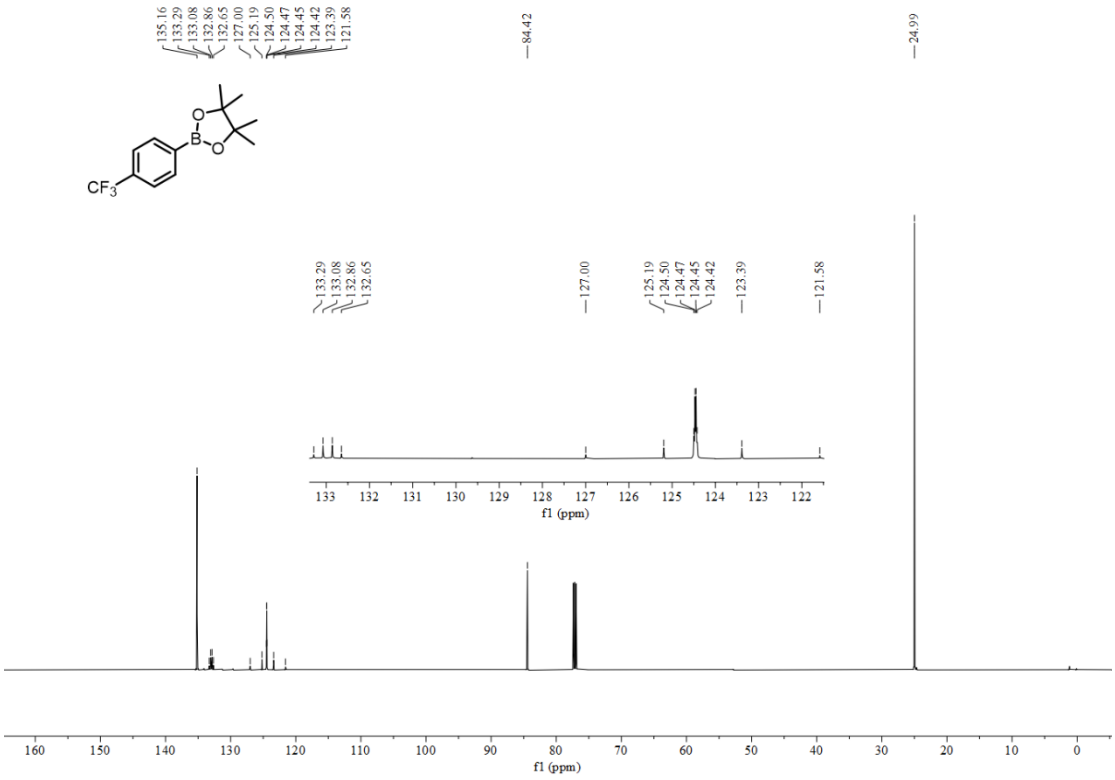
^{1}H NMR spectrum of compound **6**



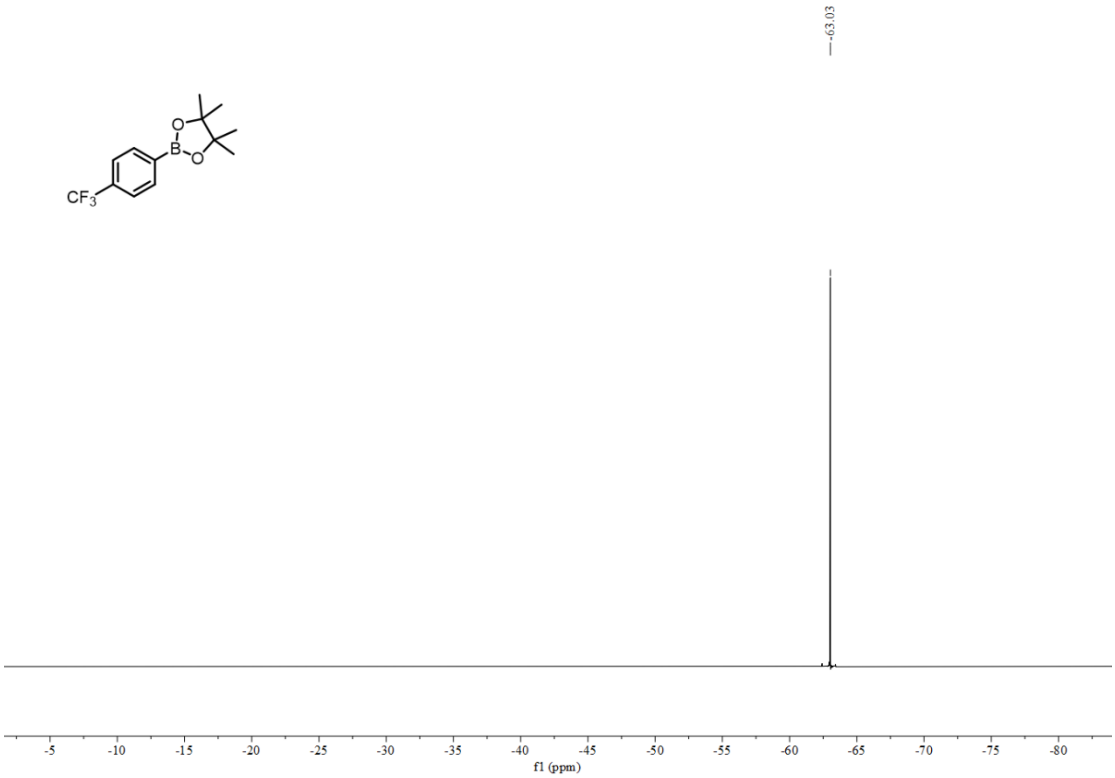
^{13}C NMR spectrum of compound **6**



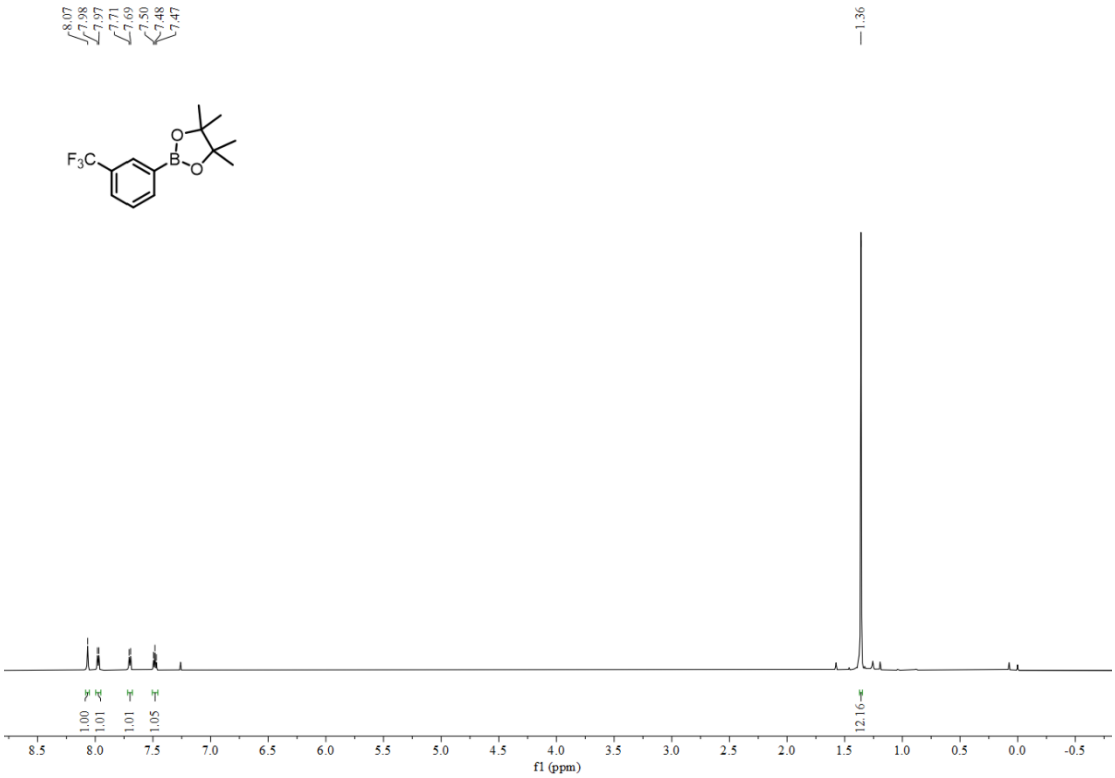
^{1}H NMR spectrum of compound **7**



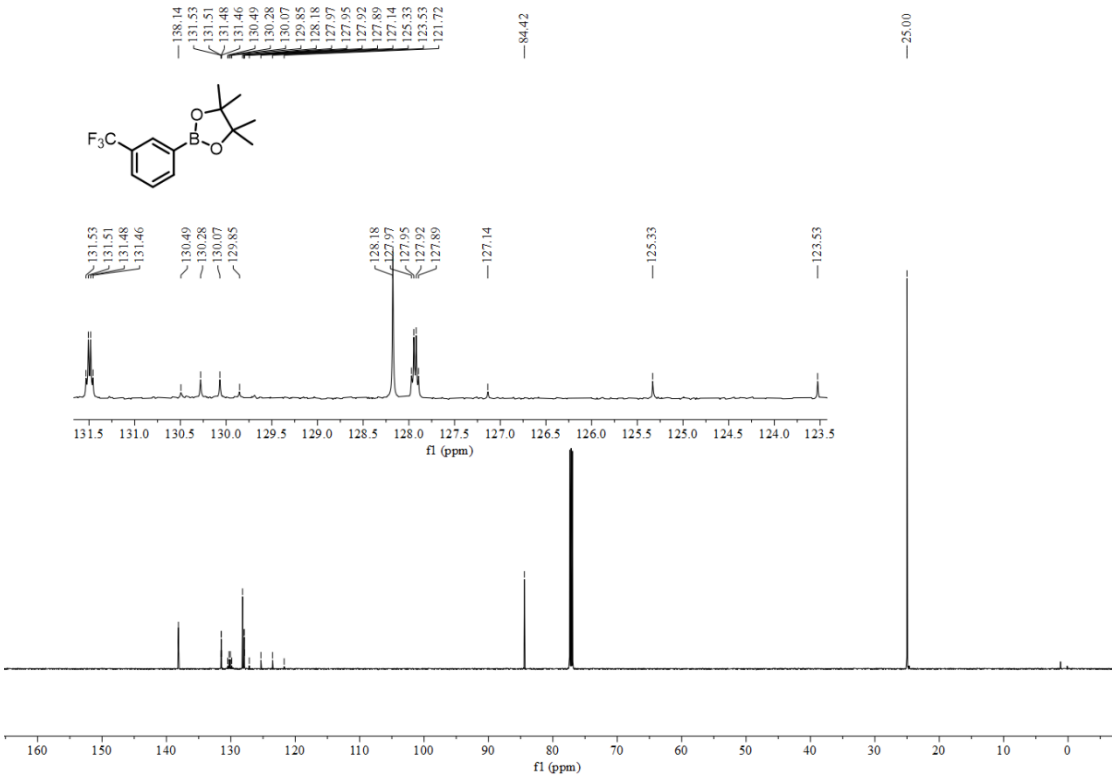
^{13}C NMR spectrum of compound **7**



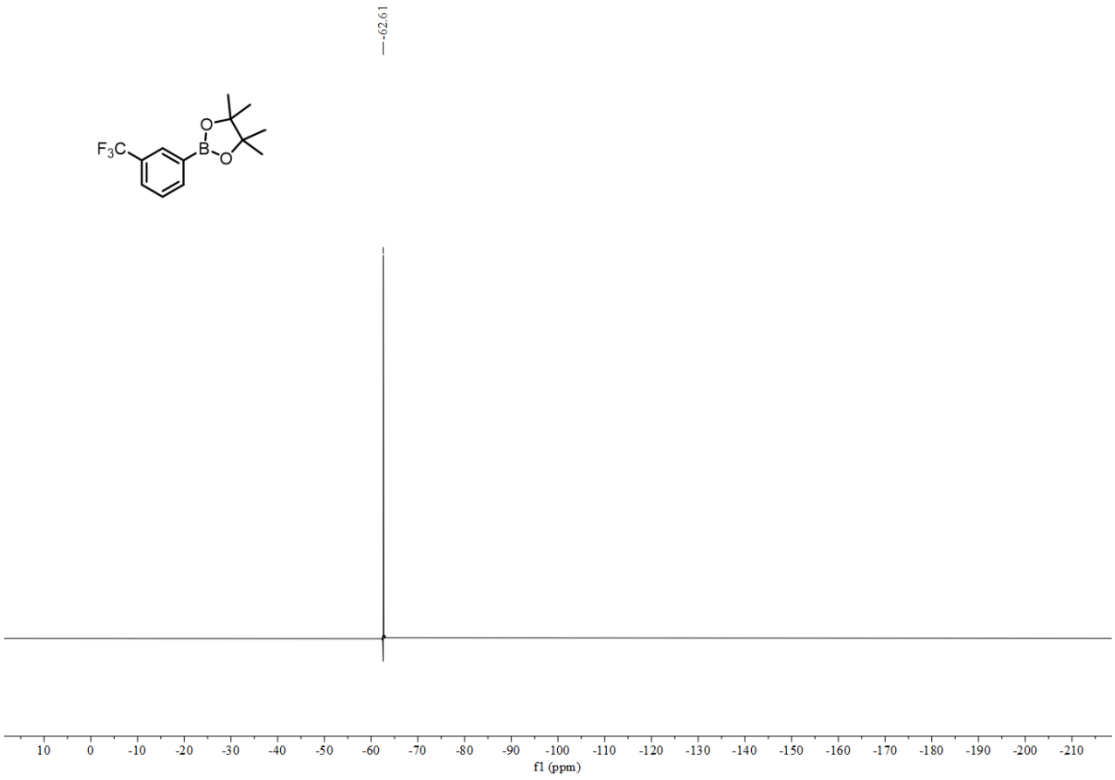
^{19}F NMR spectrum of compound **7**



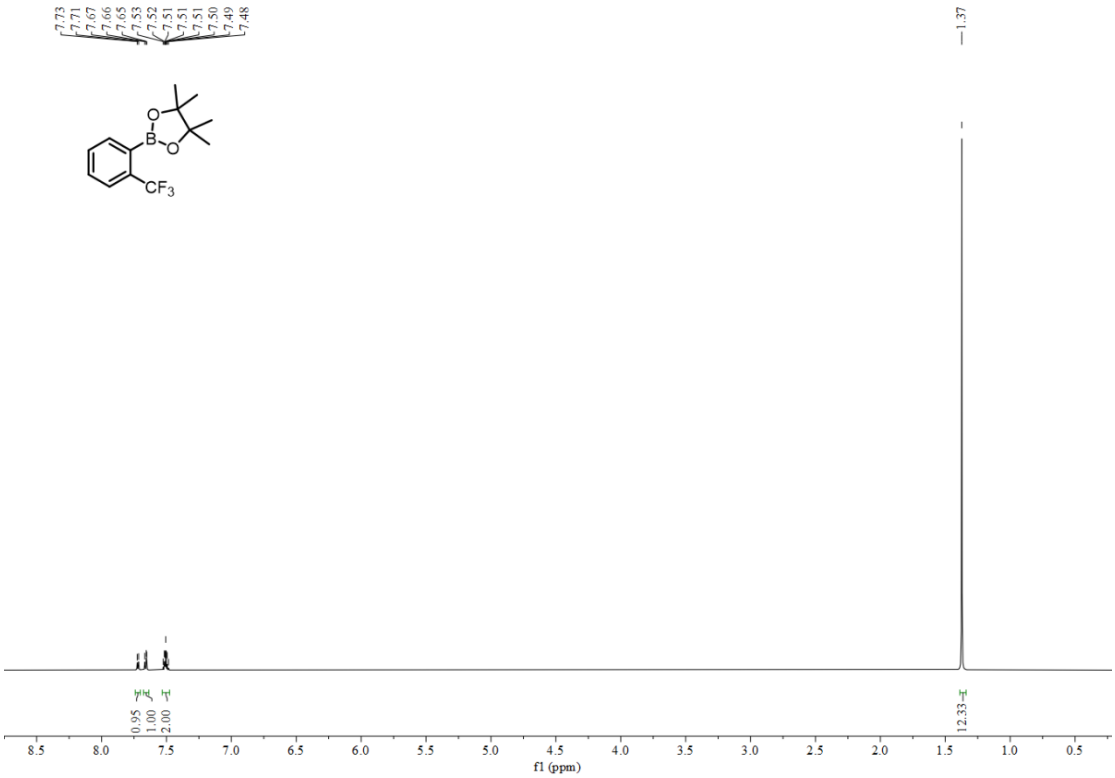
^{1}H NMR spectrum of compound **8**



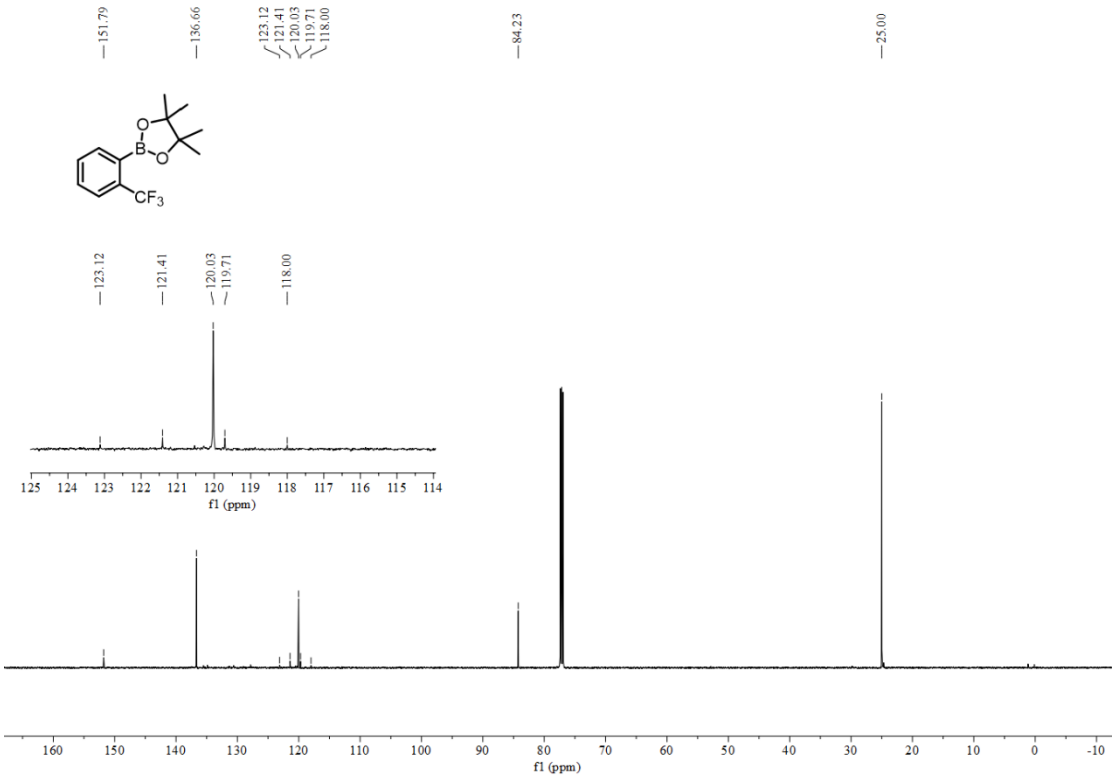
^{13}C NMR spectrum of compound **8**



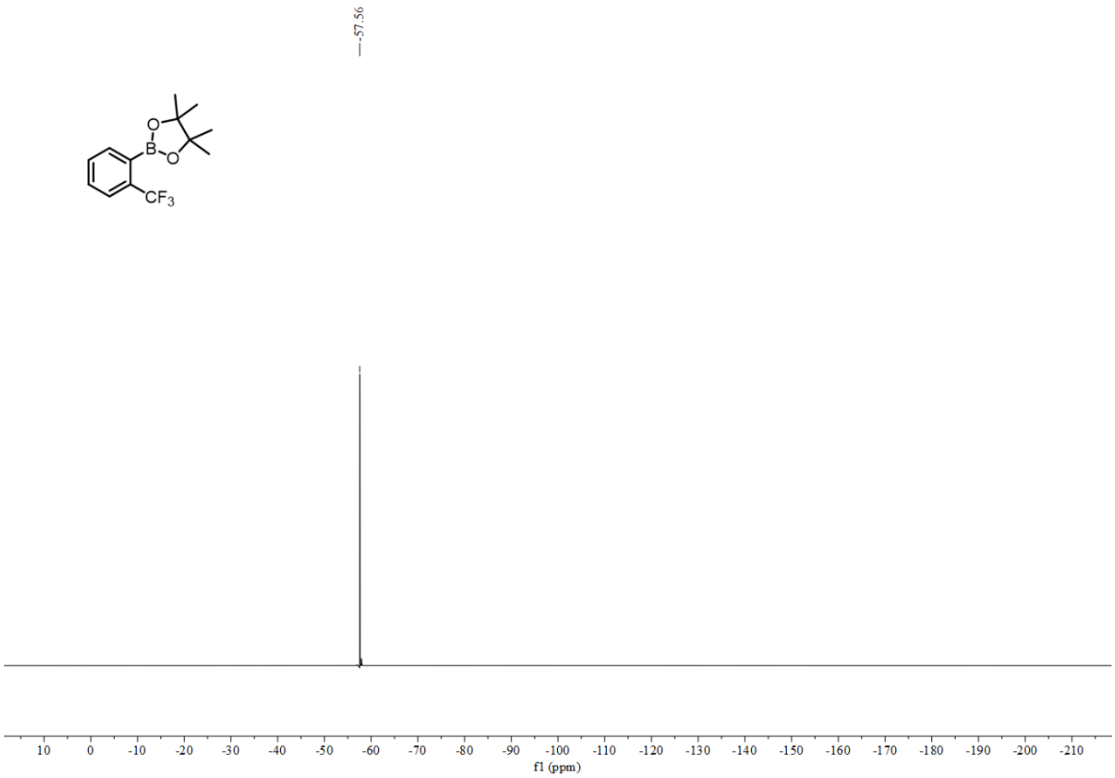
^{19}F NMR spectrum of compound **8**



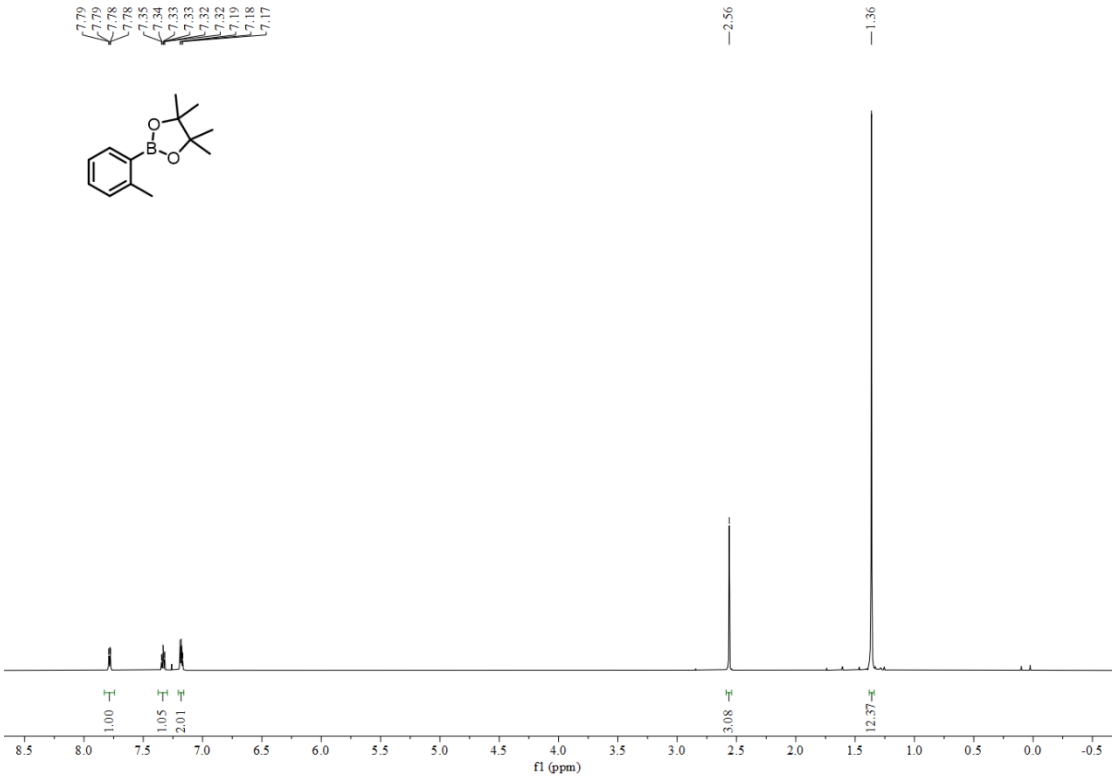
^{1}H NMR spectrum of compound **9**



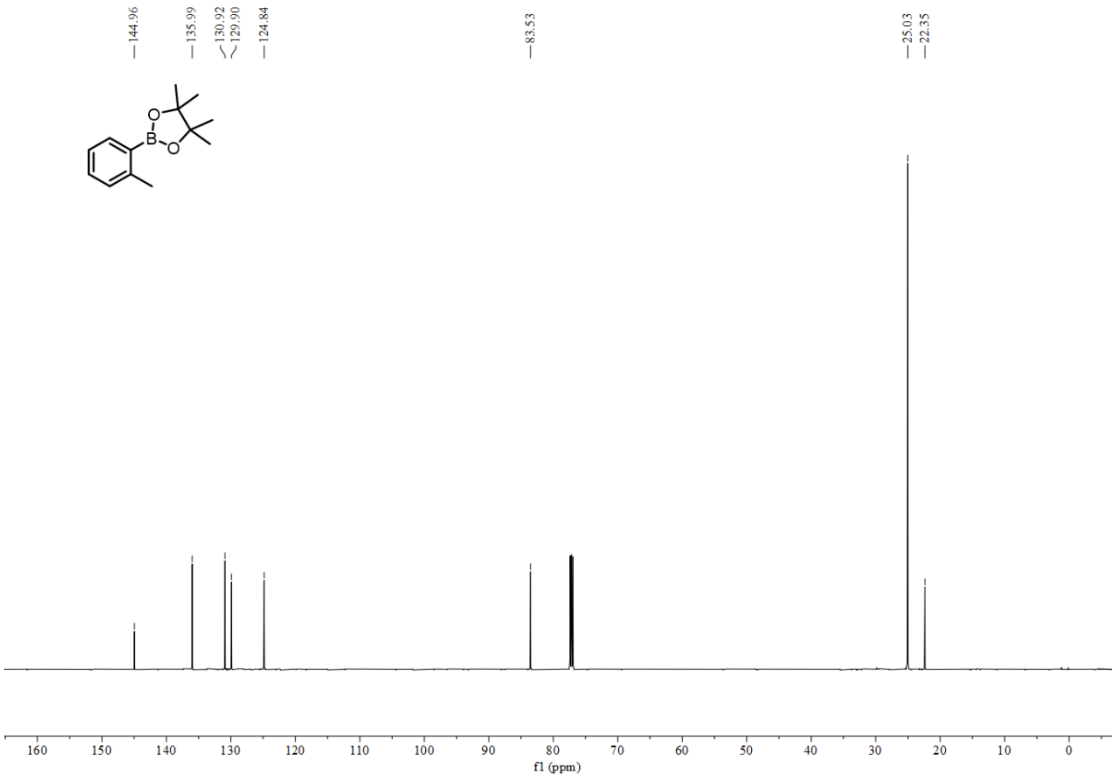
^{13}C NMR spectrum of compound **9**



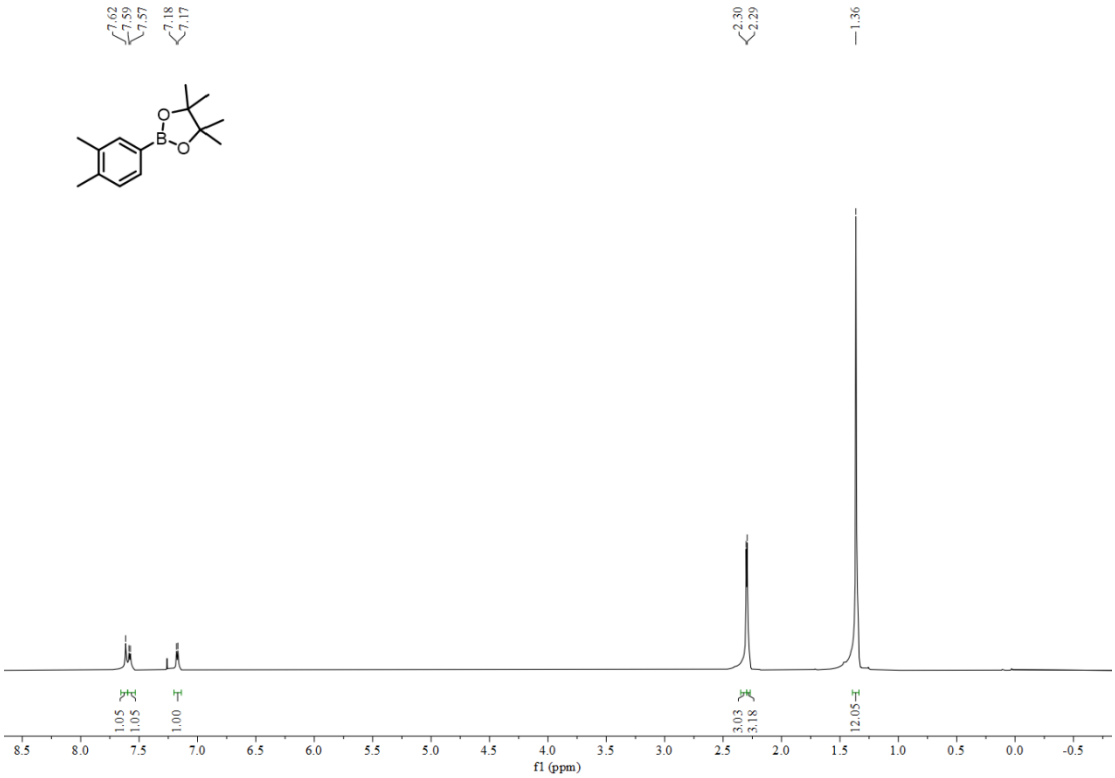
^{19}F NMR spectrum of compound **9**



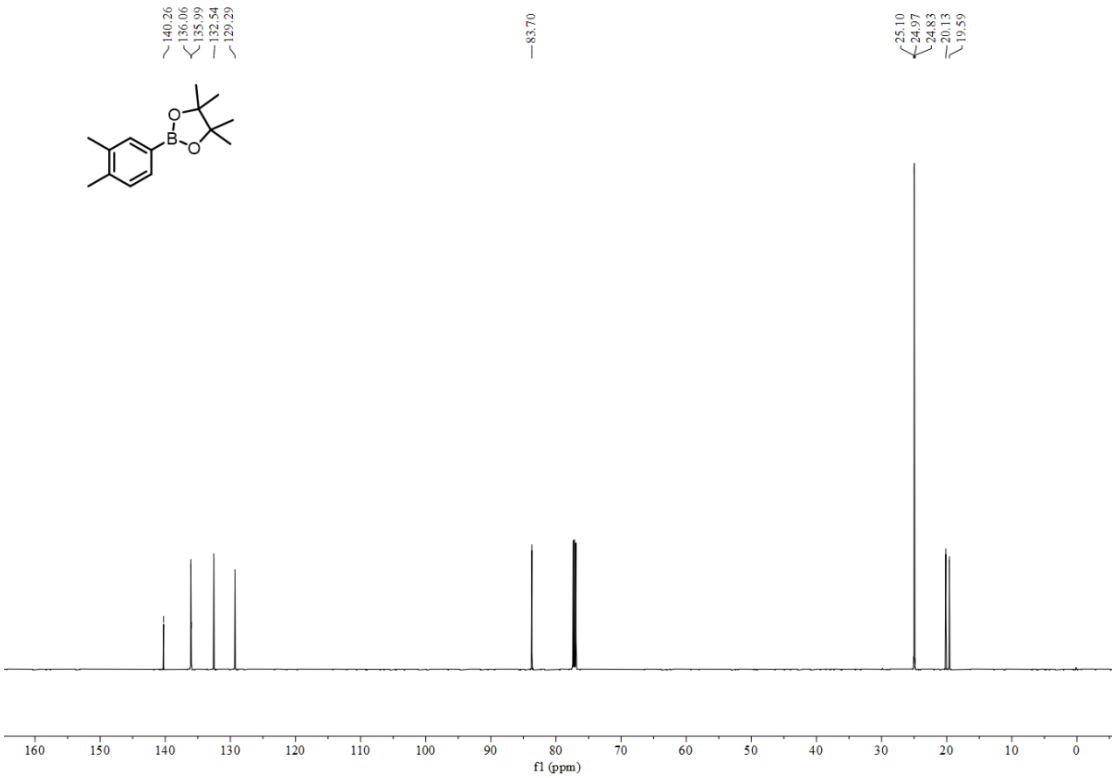
^{1}H NMR spectrum of compound **10**



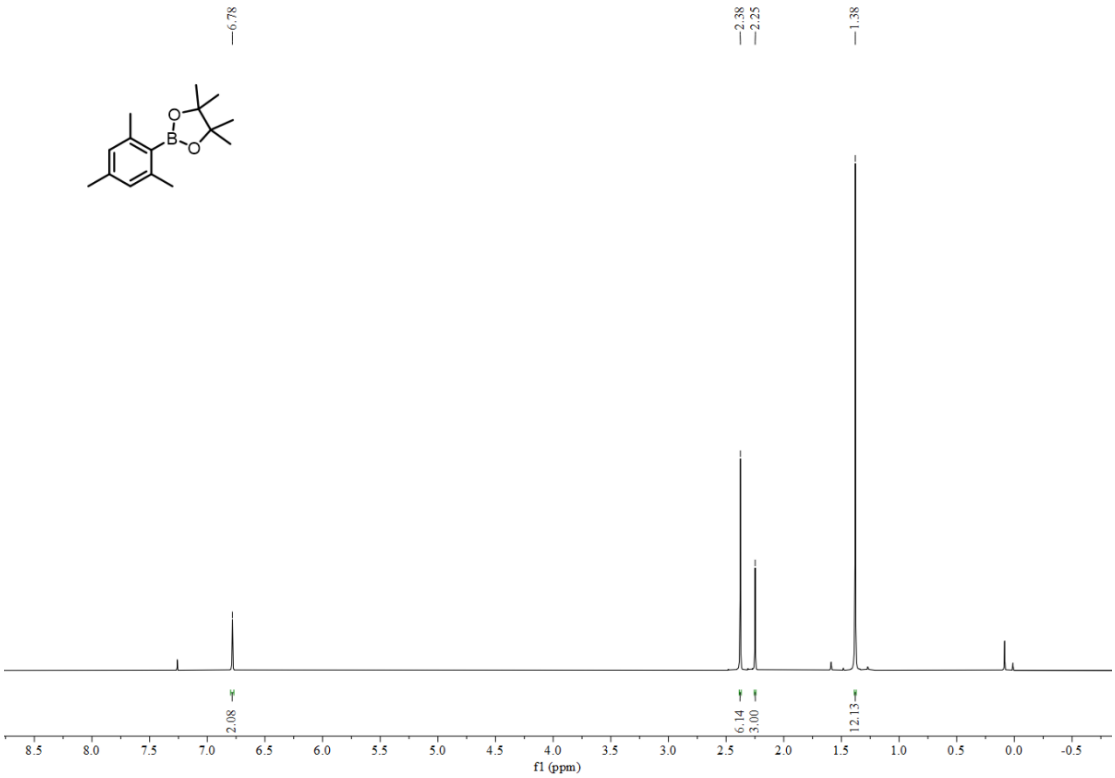
^{13}C NMR spectrum of compound **10**



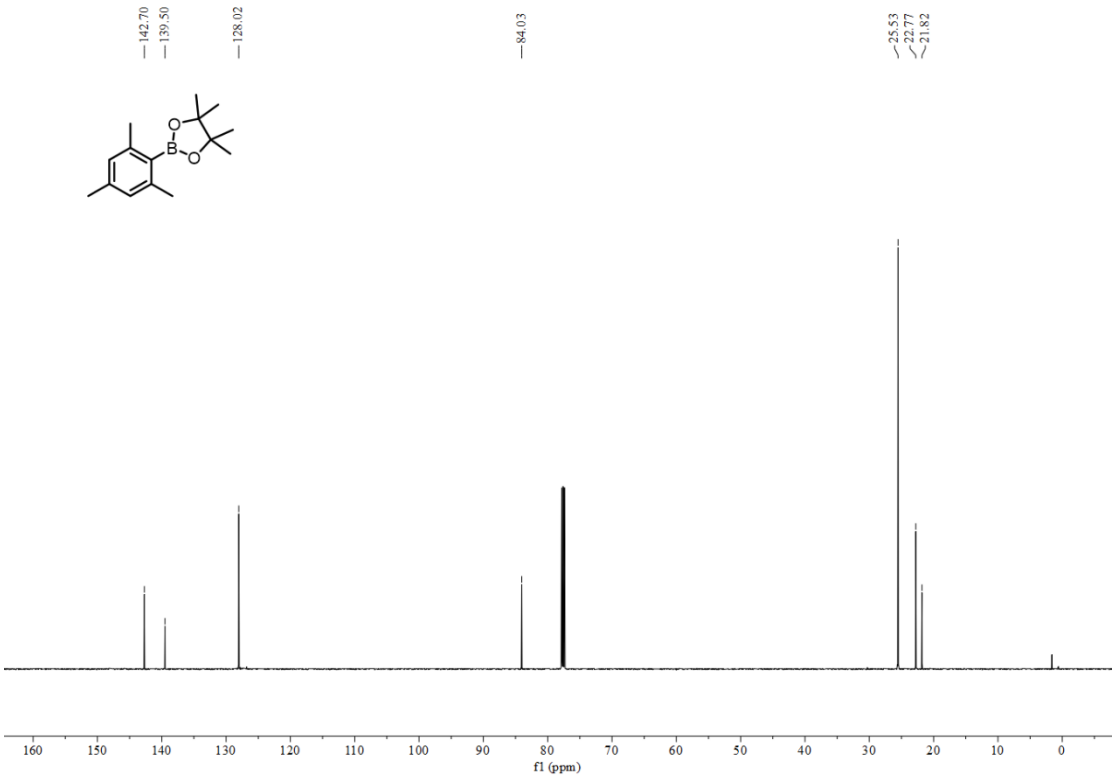
^{1}H NMR spectrum of compound **11**



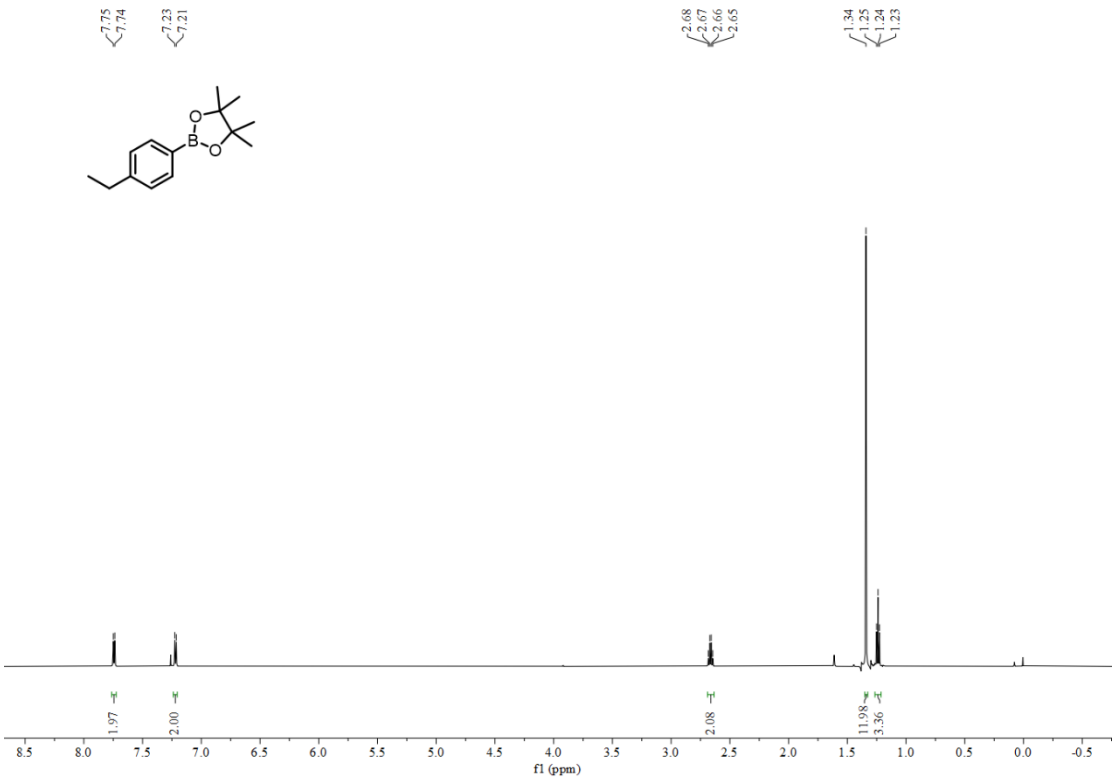
^{13}C NMR spectrum of compound **11**



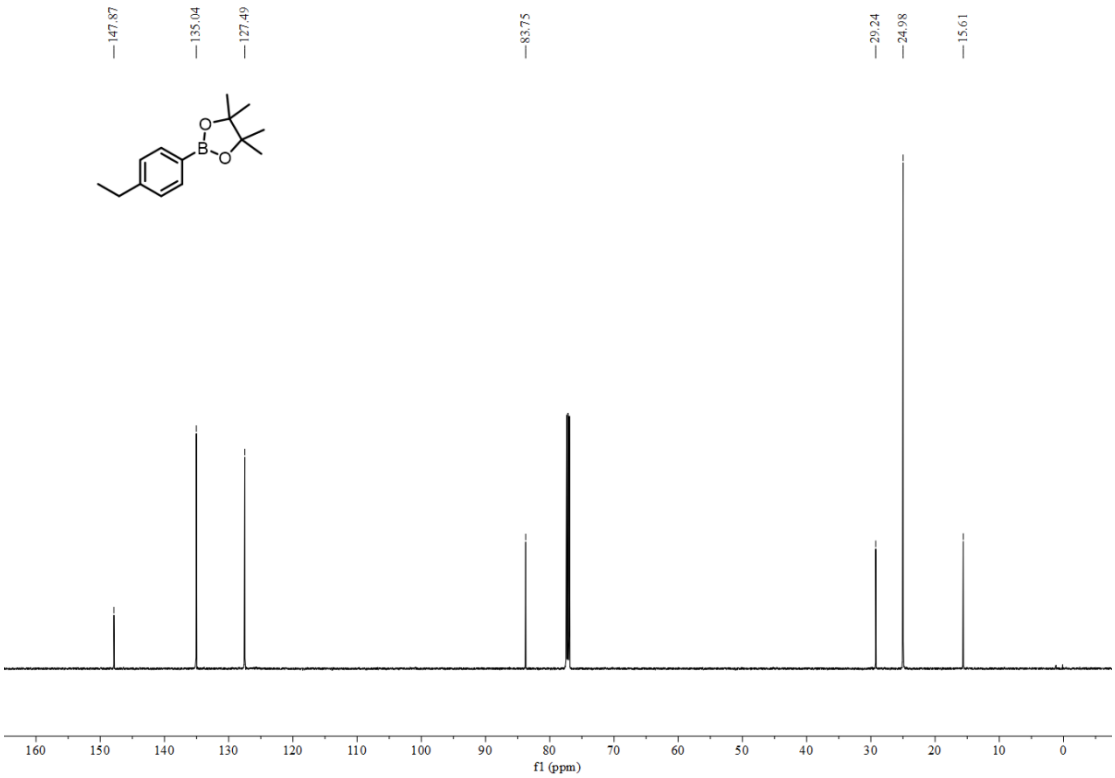
^{1}H NMR spectrum of compound **12**



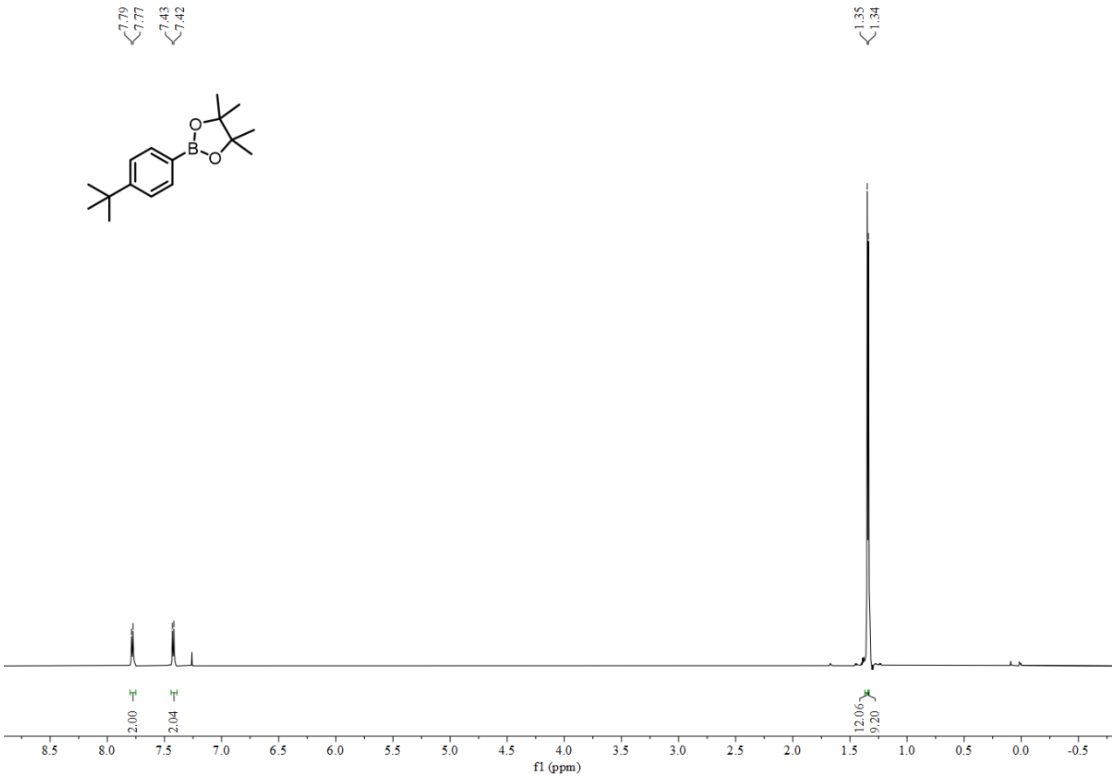
^{13}C NMR spectrum of compound **12**



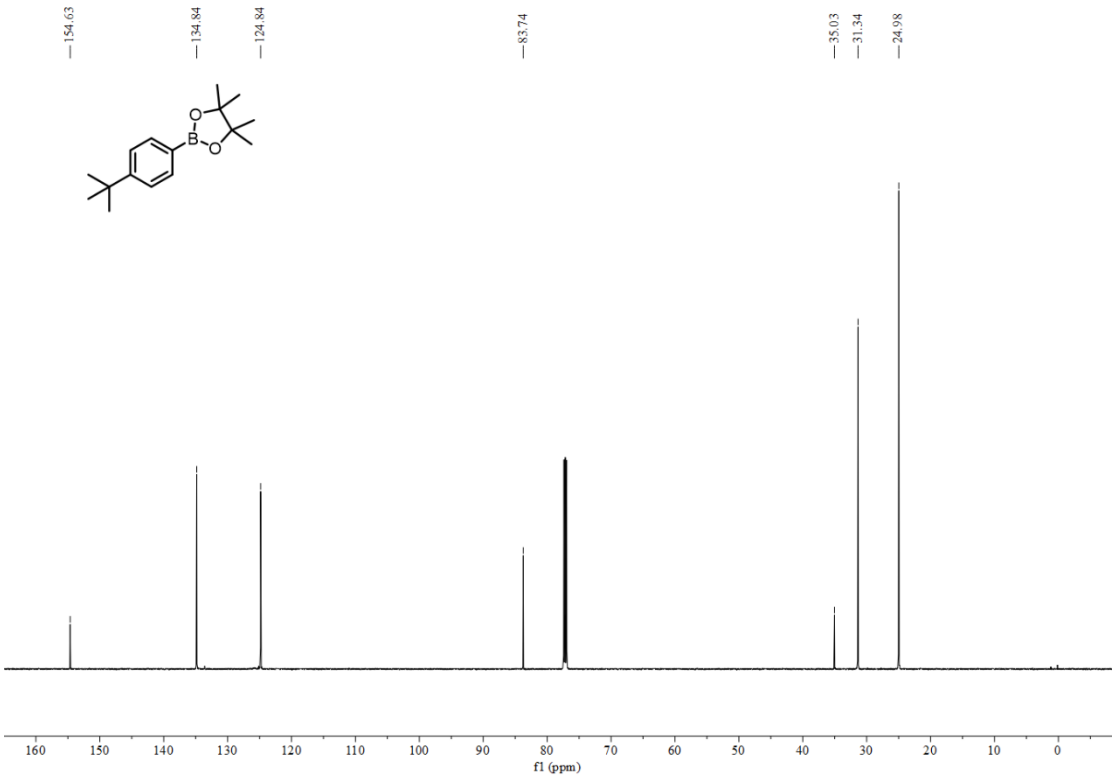
^{1}H NMR spectrum of compound **13**



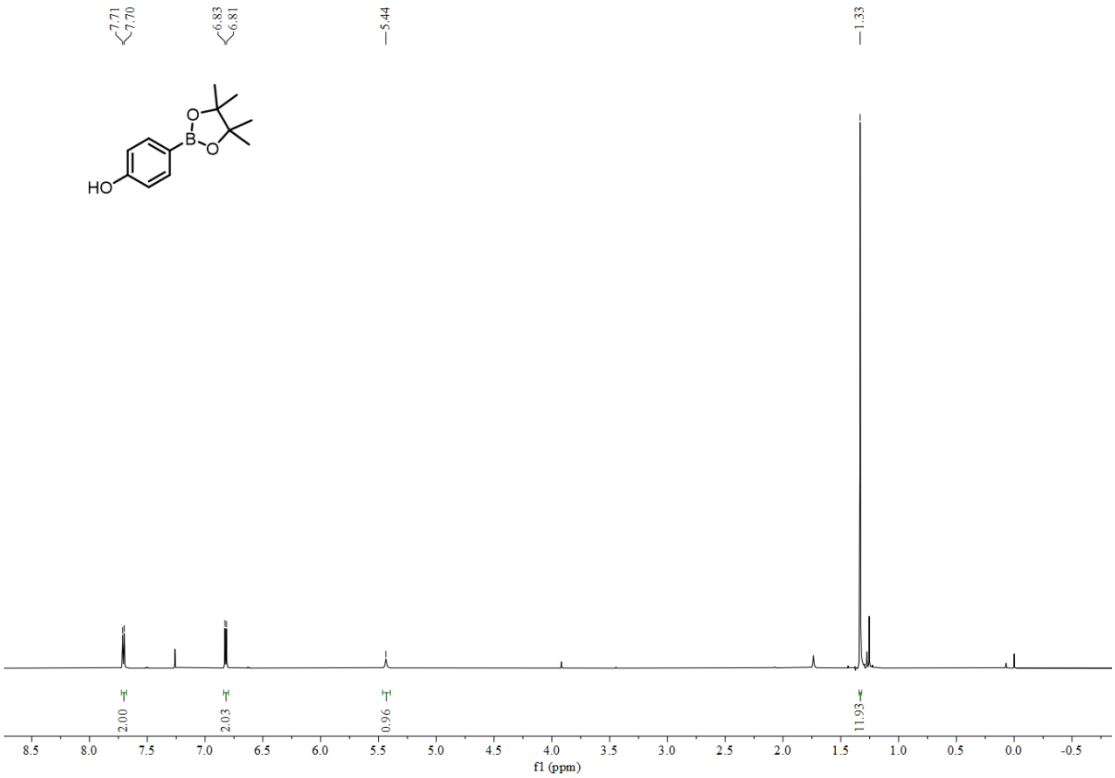
^{13}C NMR spectrum of compound **13**



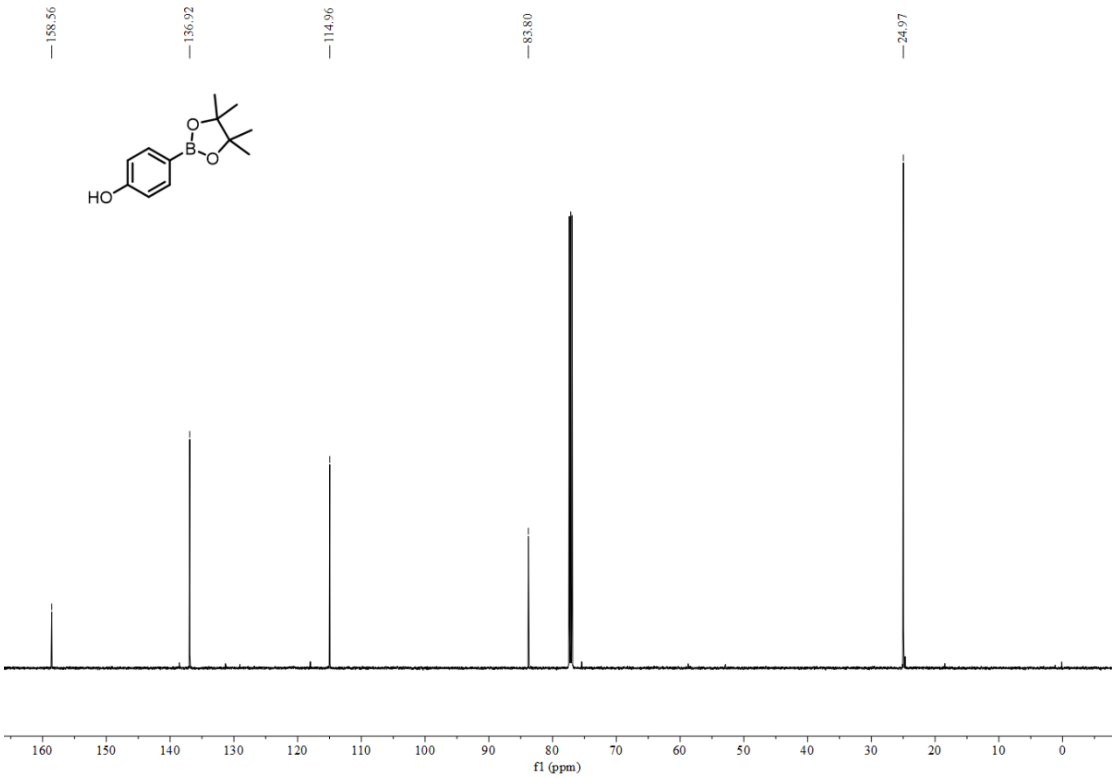
^{1}H NMR spectrum of compound **14**



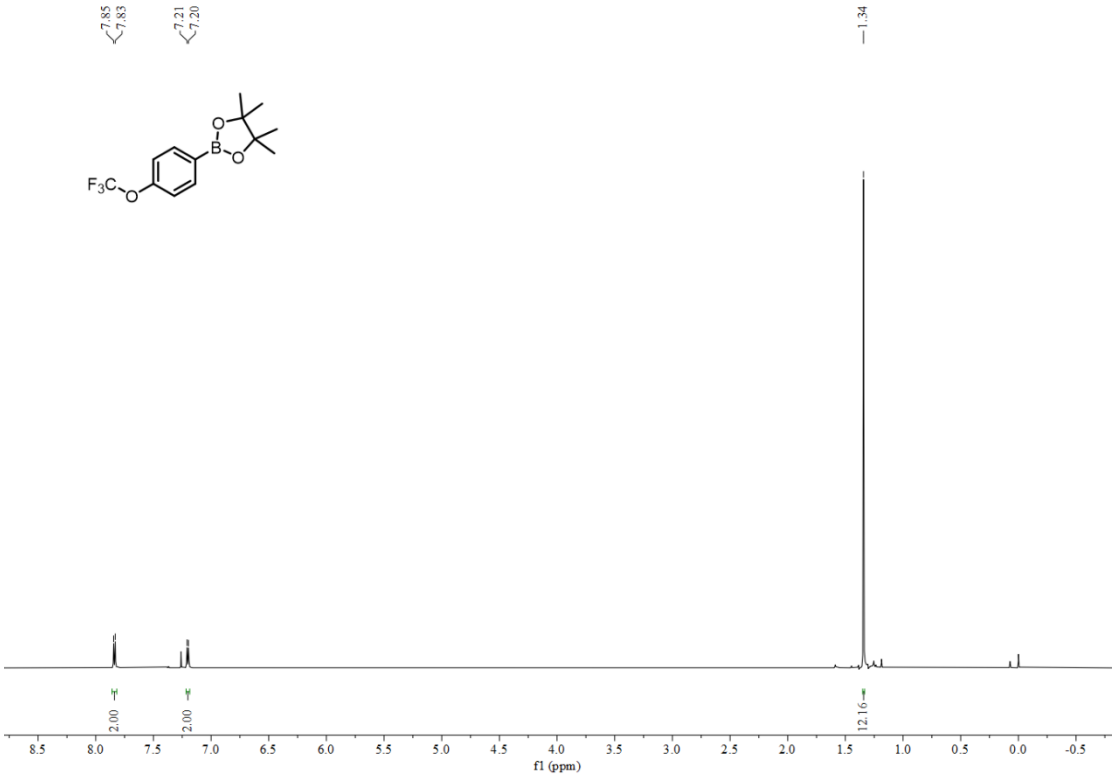
^{13}C NMR spectrum of compound **14**



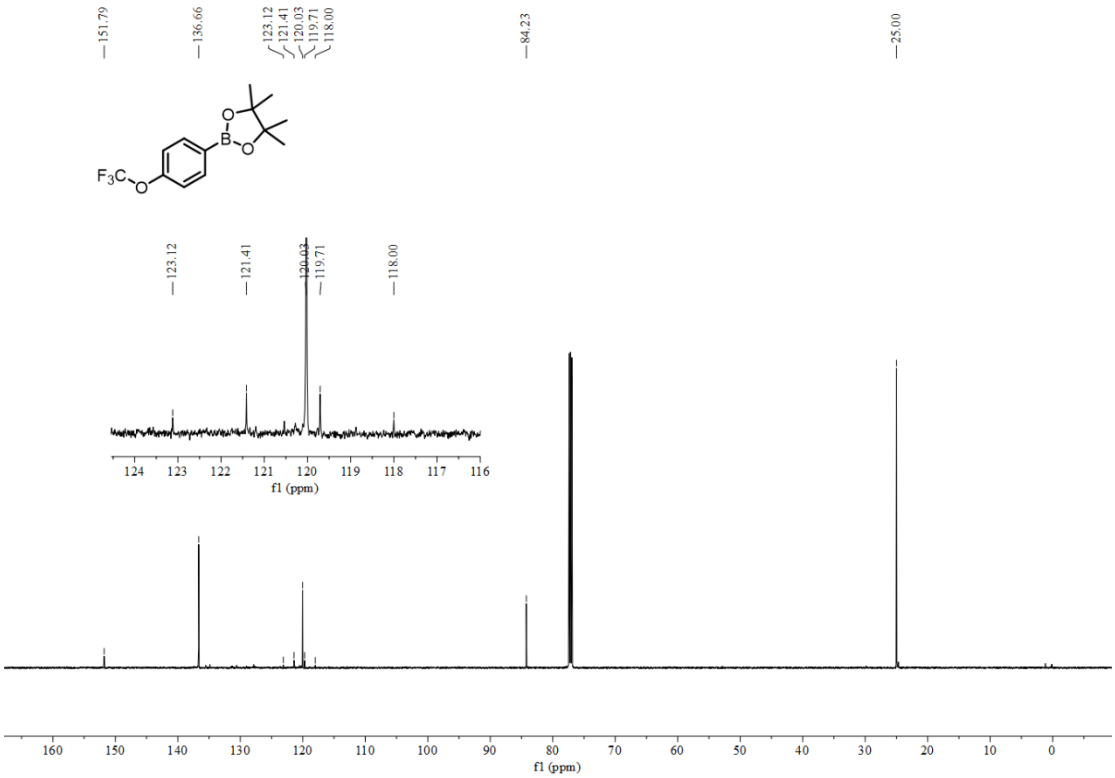
^{1}H NMR spectrum of compound **15**



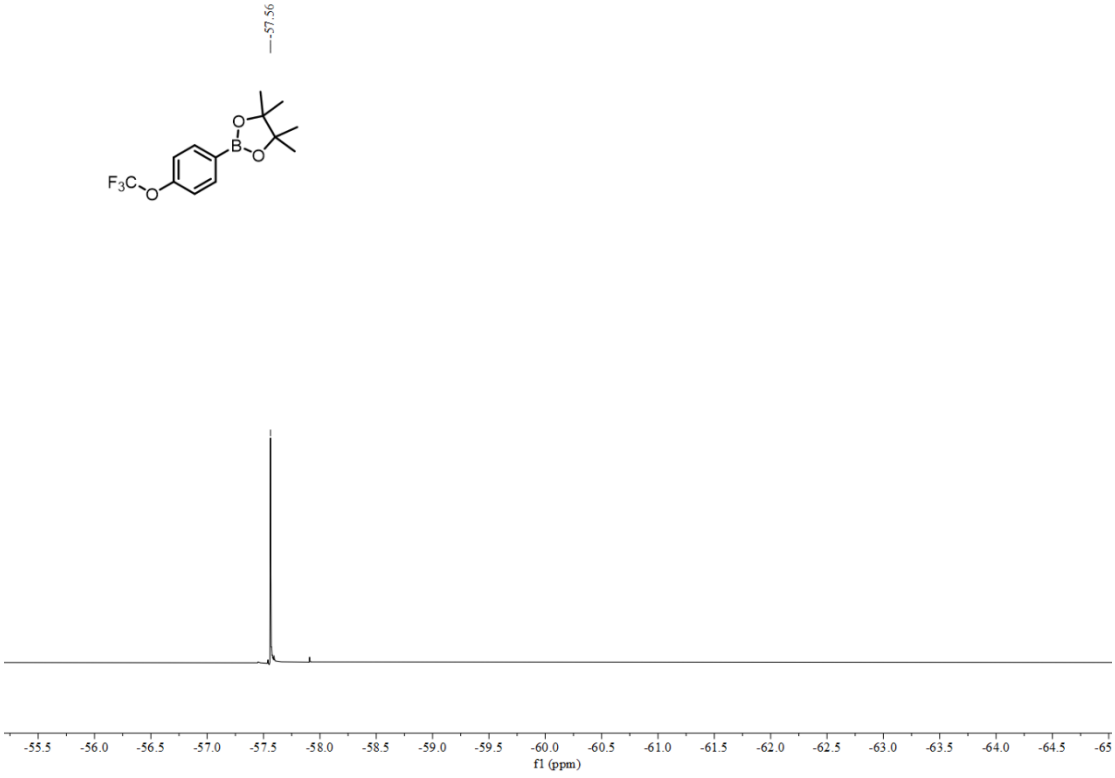
^{13}C NMR spectrum of compound **15**



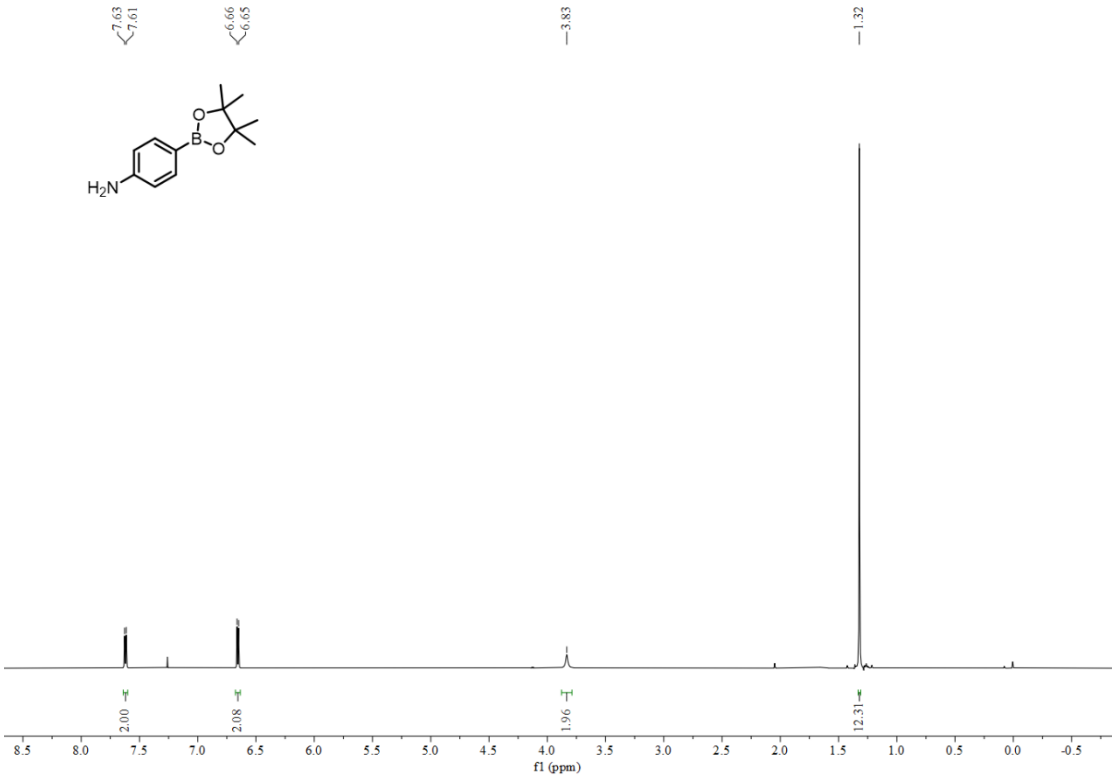
^{1}H NMR spectrum of compound **16**



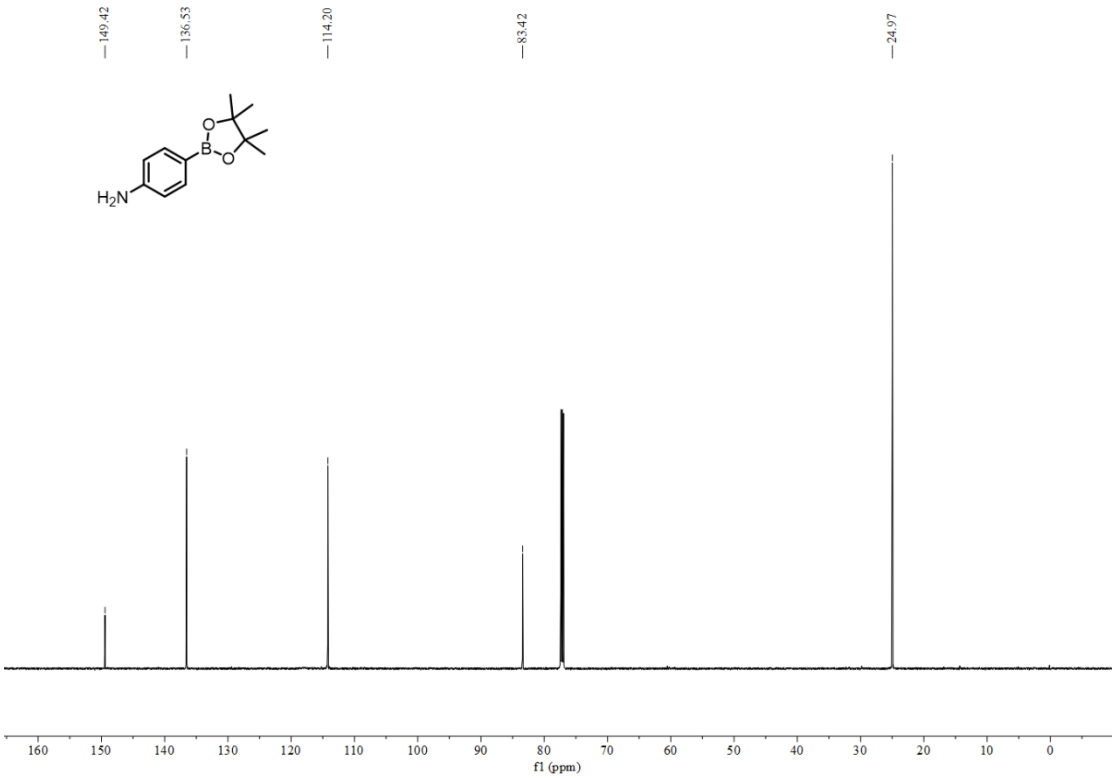
^{13}C NMR spectrum of compound **16**



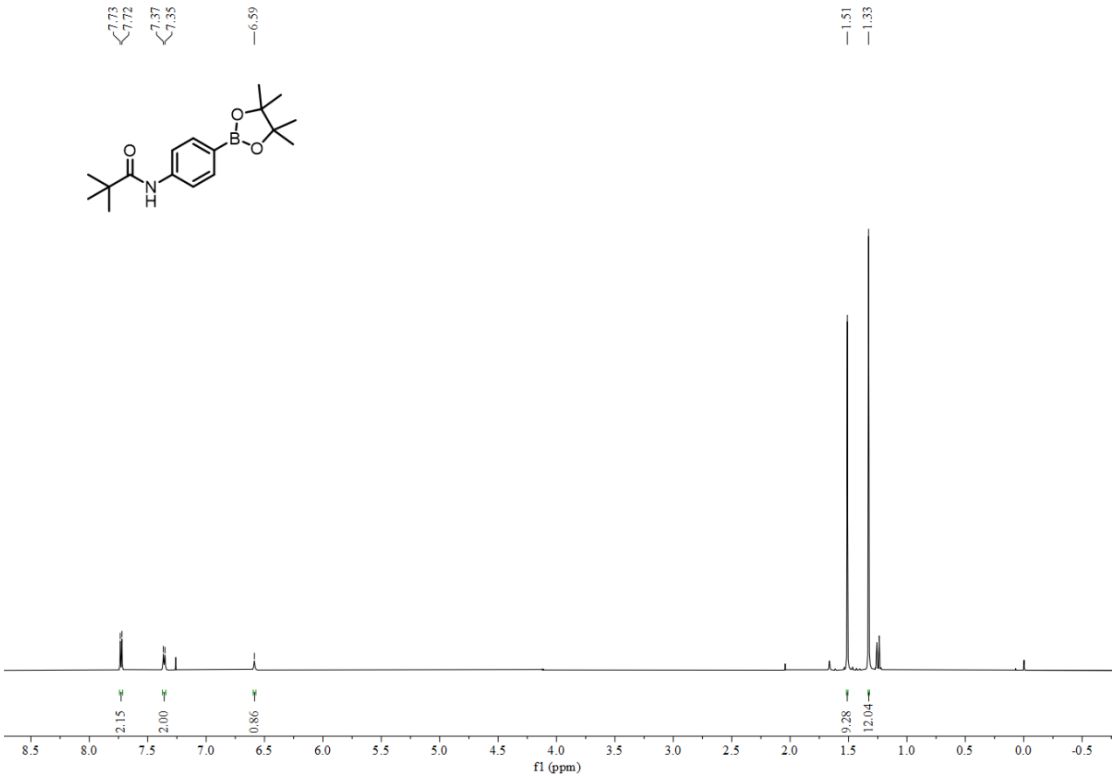
^{19}F NMR spectrum of compound **16**



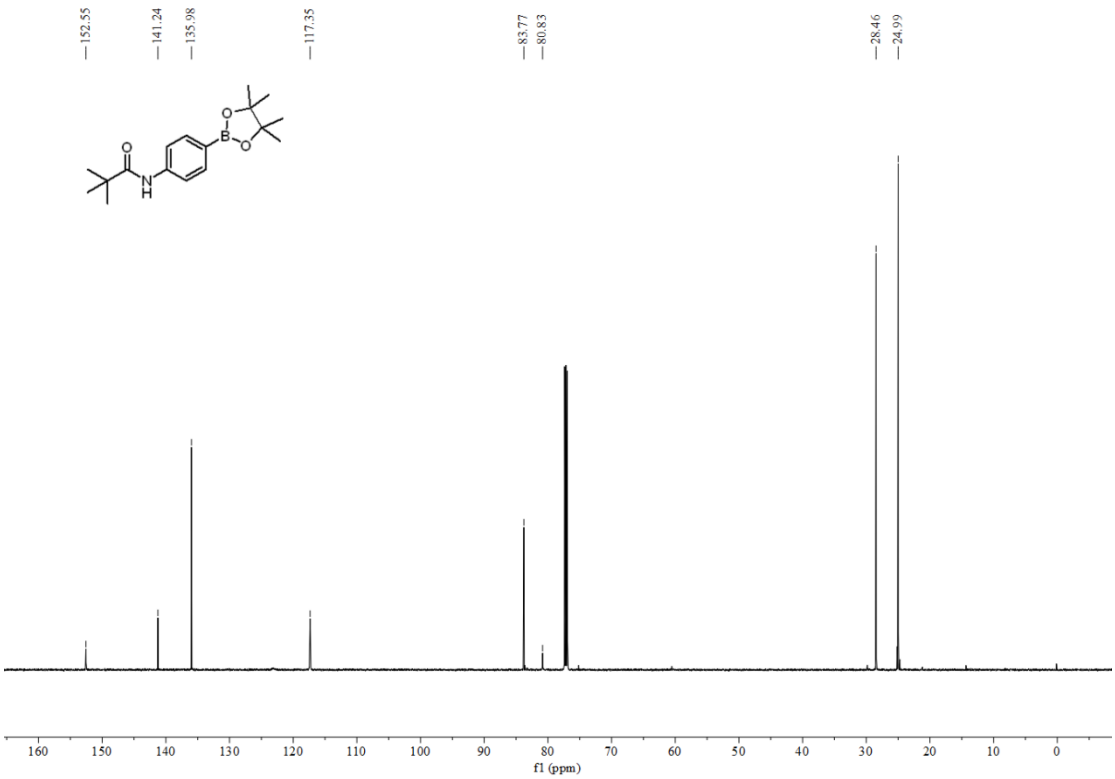
^{1}H NMR spectrum of compound **17**



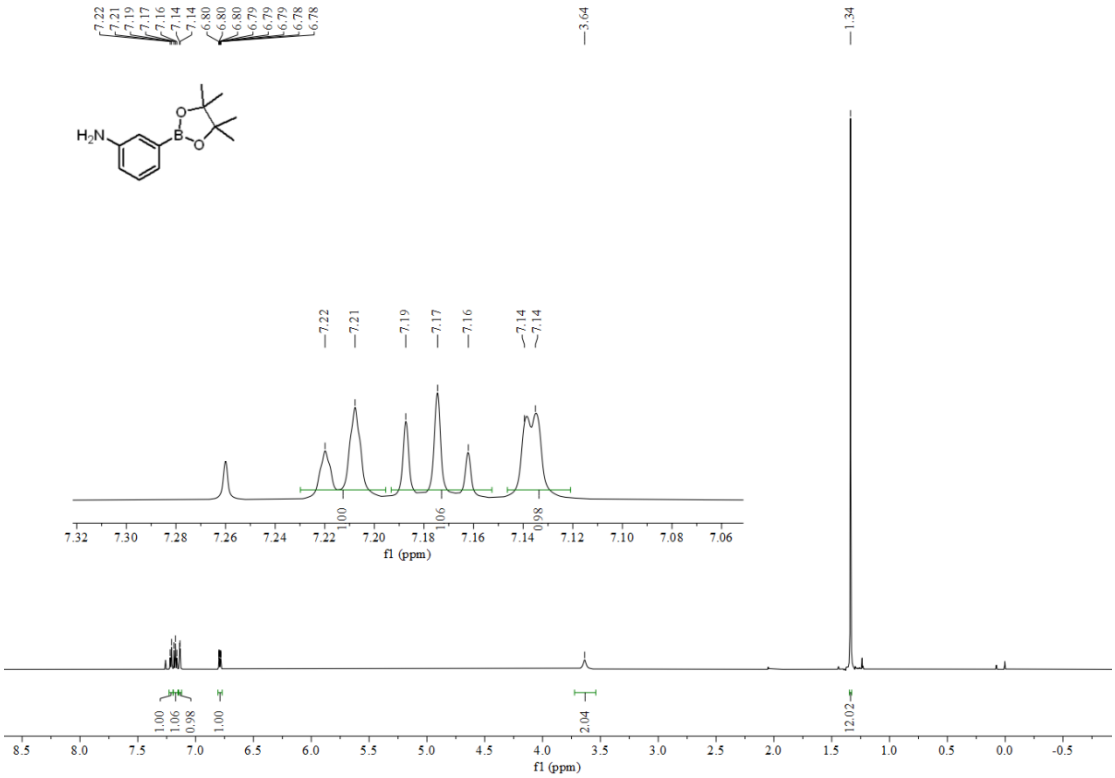
^{13}C NMR spectrum of compound **17**



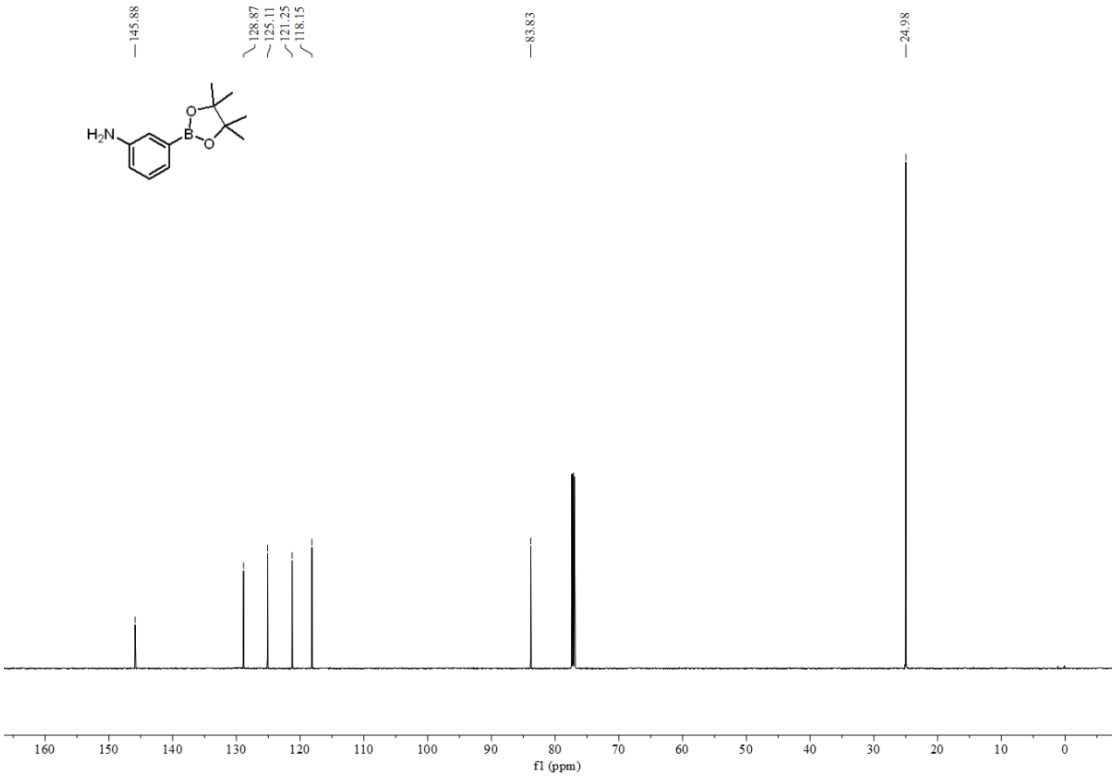
^{1}H NMR spectrum of compound **18**



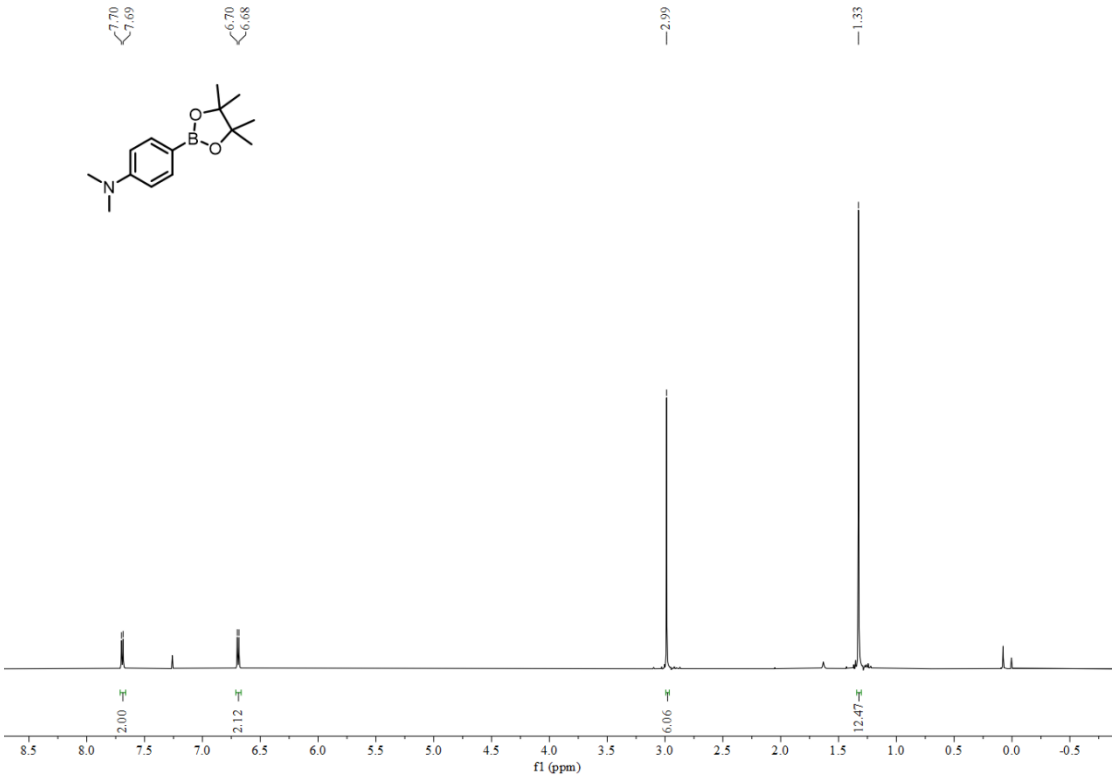
^{13}C NMR spectrum of compound **18**



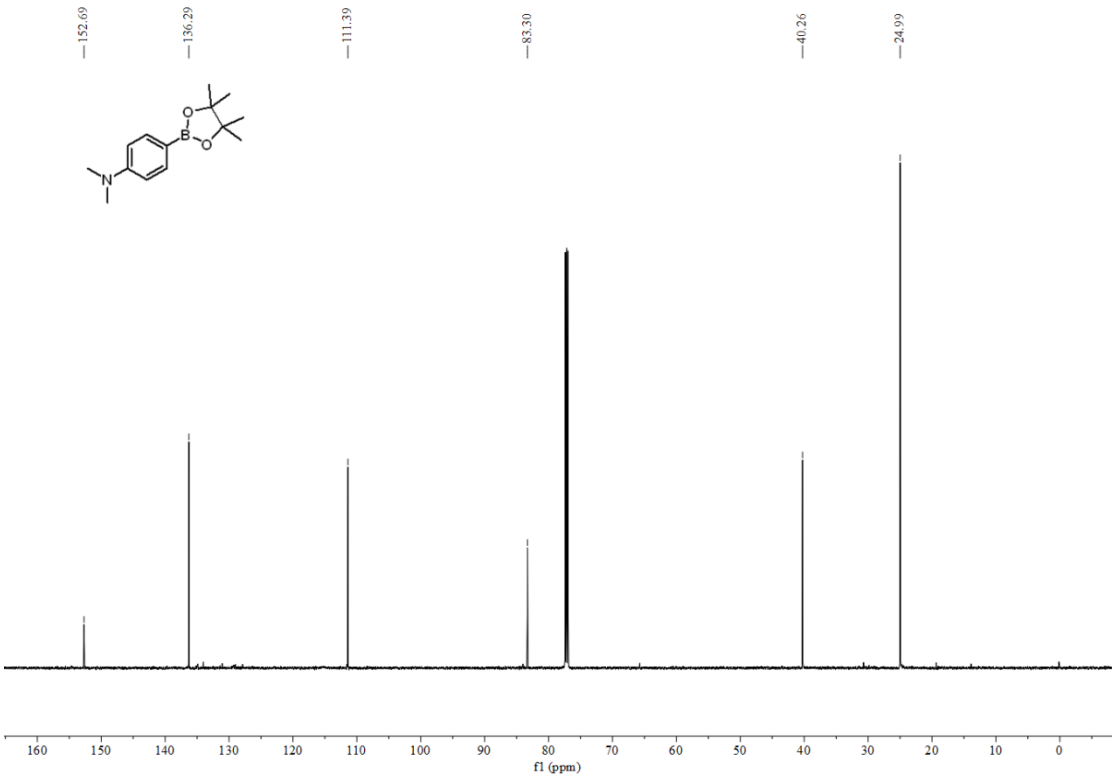
^{1}H NMR spectrum of compound **19**



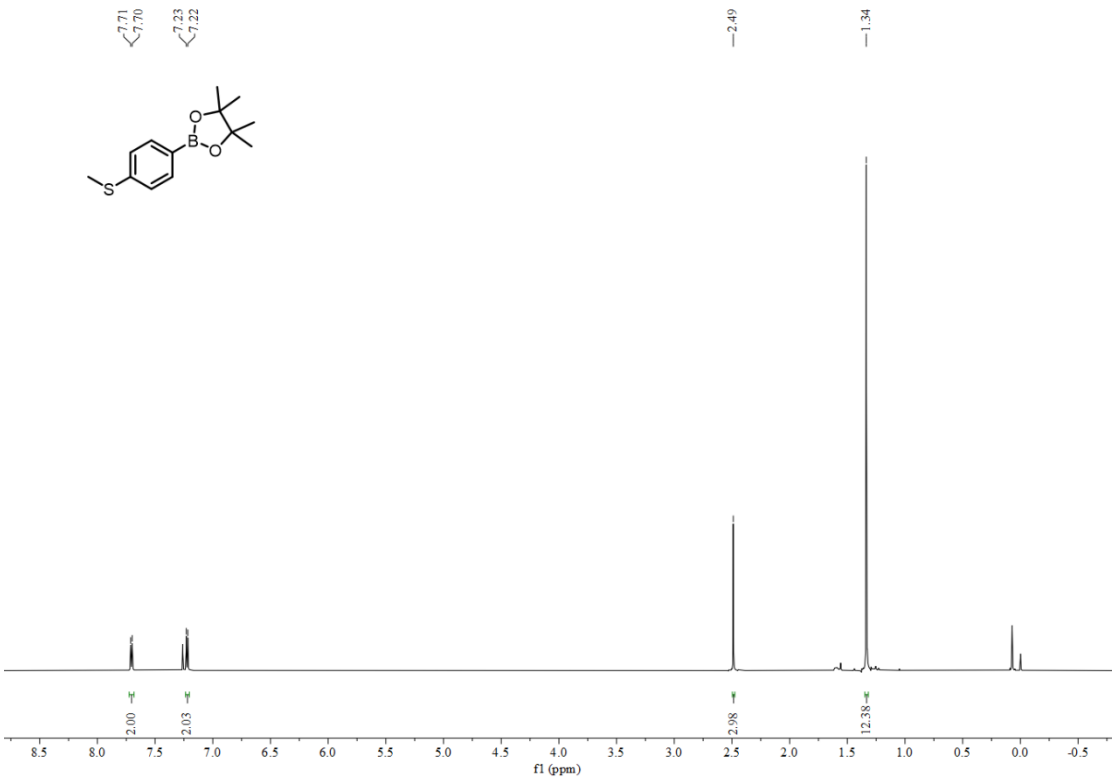
^{13}C NMR spectrum of compound **19**



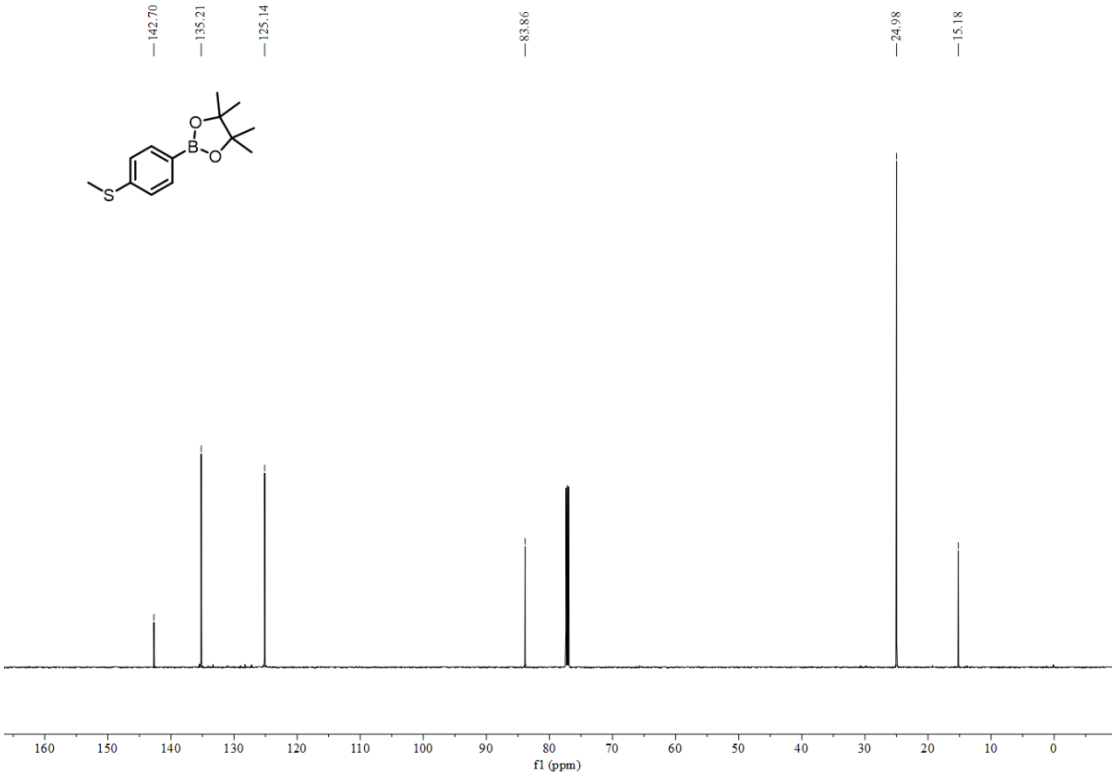
^{1}H NMR spectrum of compound **20**



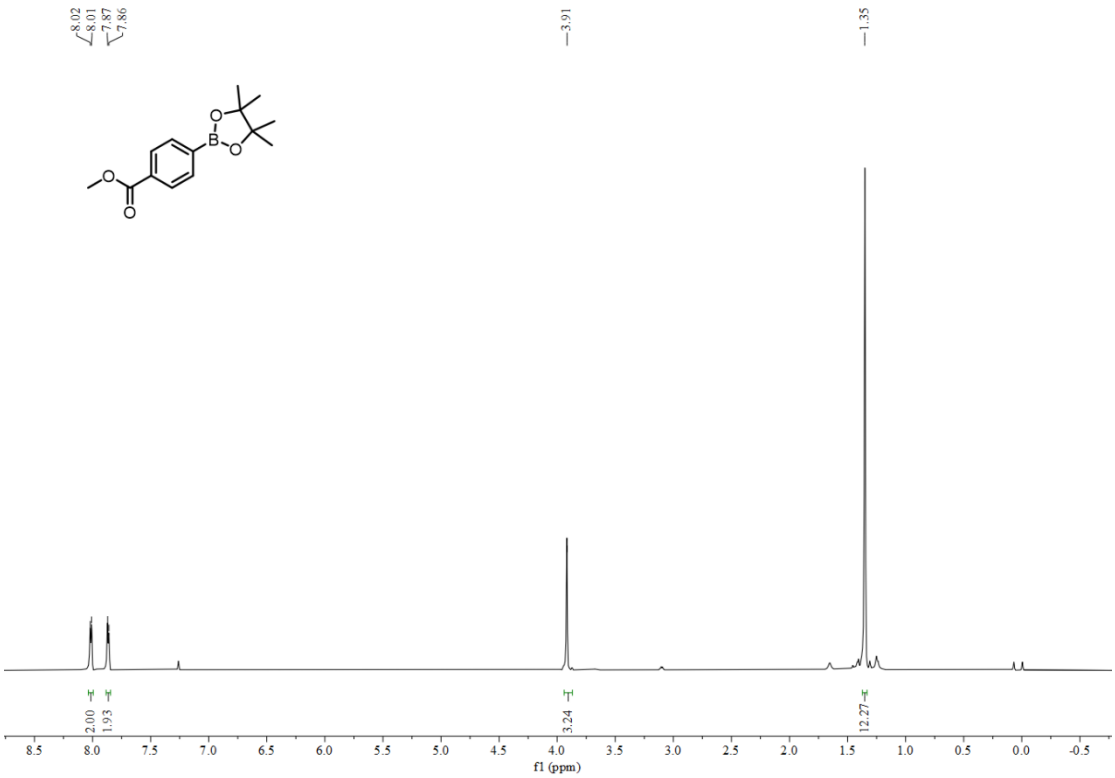
^{13}C NMR spectrum of compound **20**



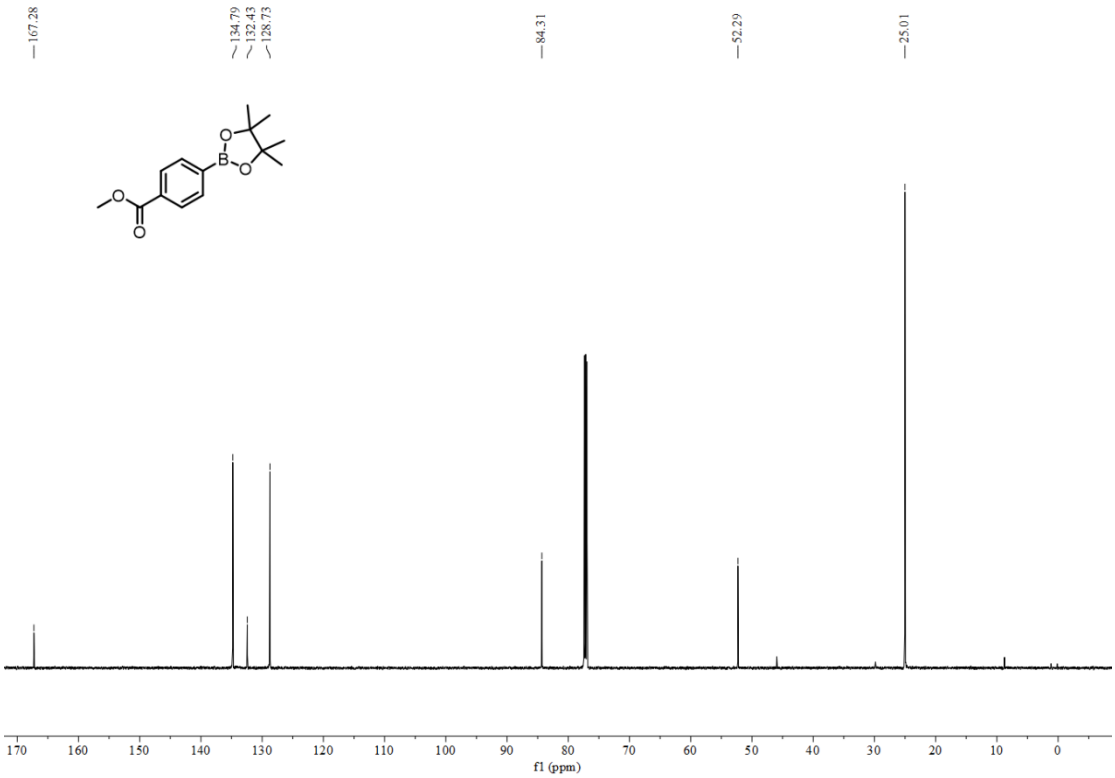
^{1}H NMR spectrum of compound **21**



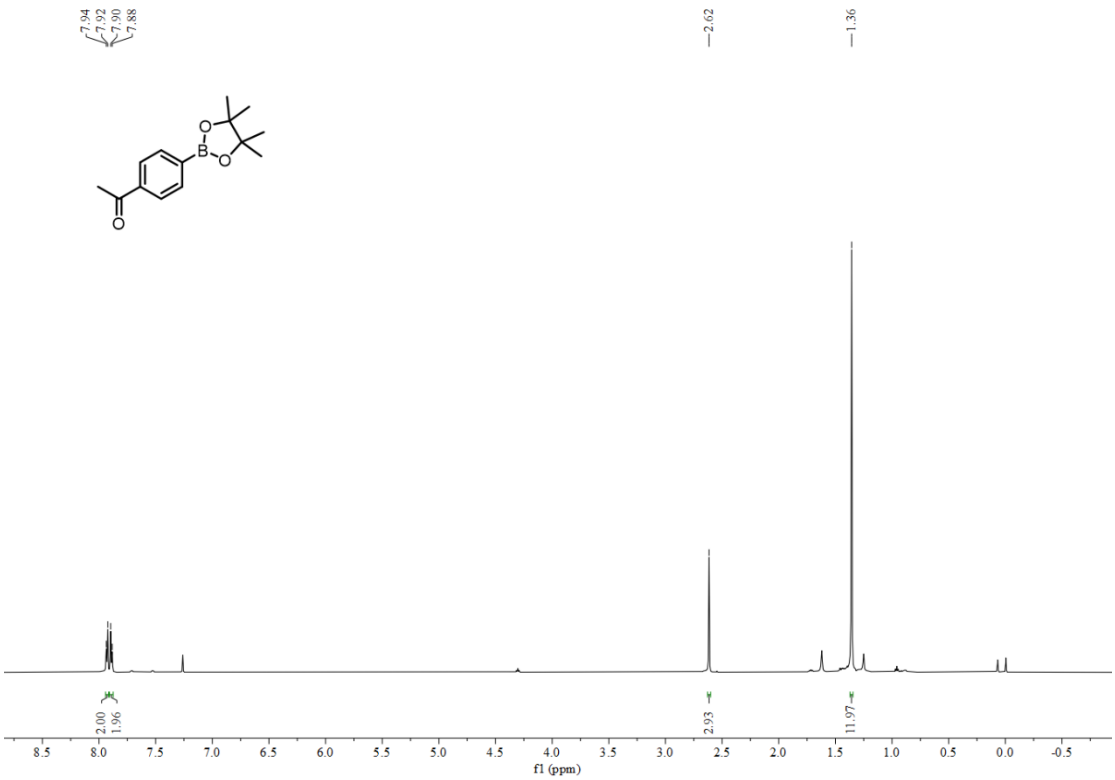
^{13}C NMR spectrum of compound **21**



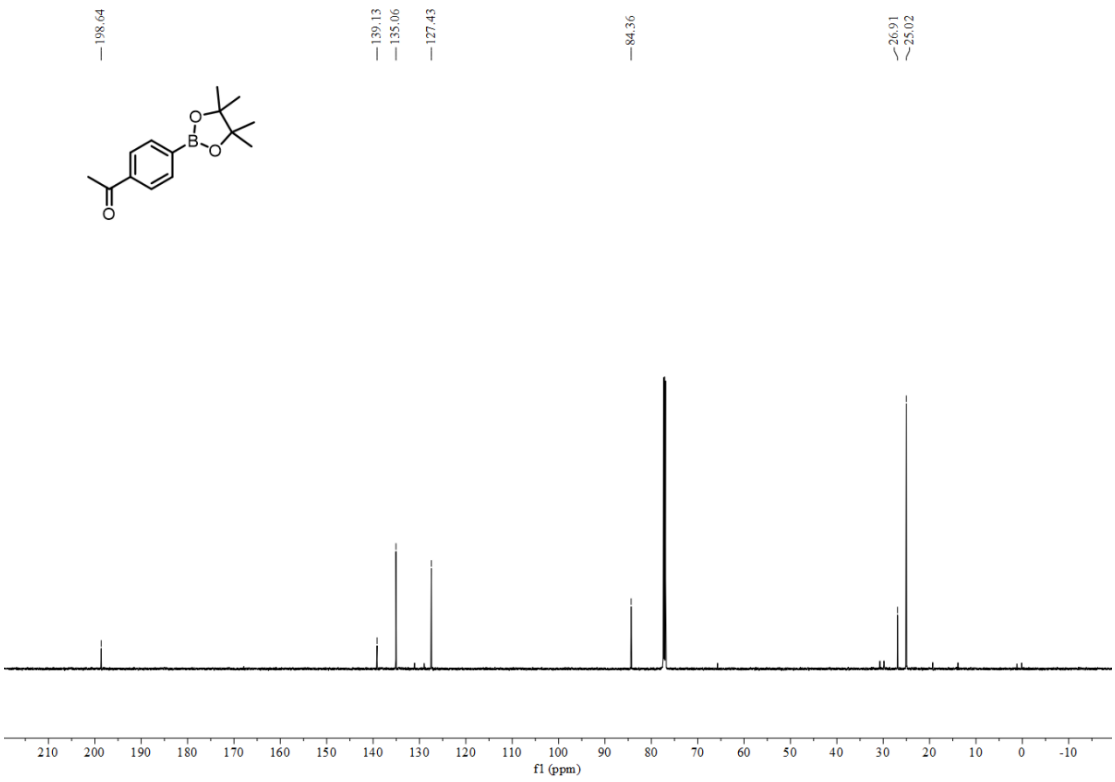
^{1}H NMR spectrum of compound **22**



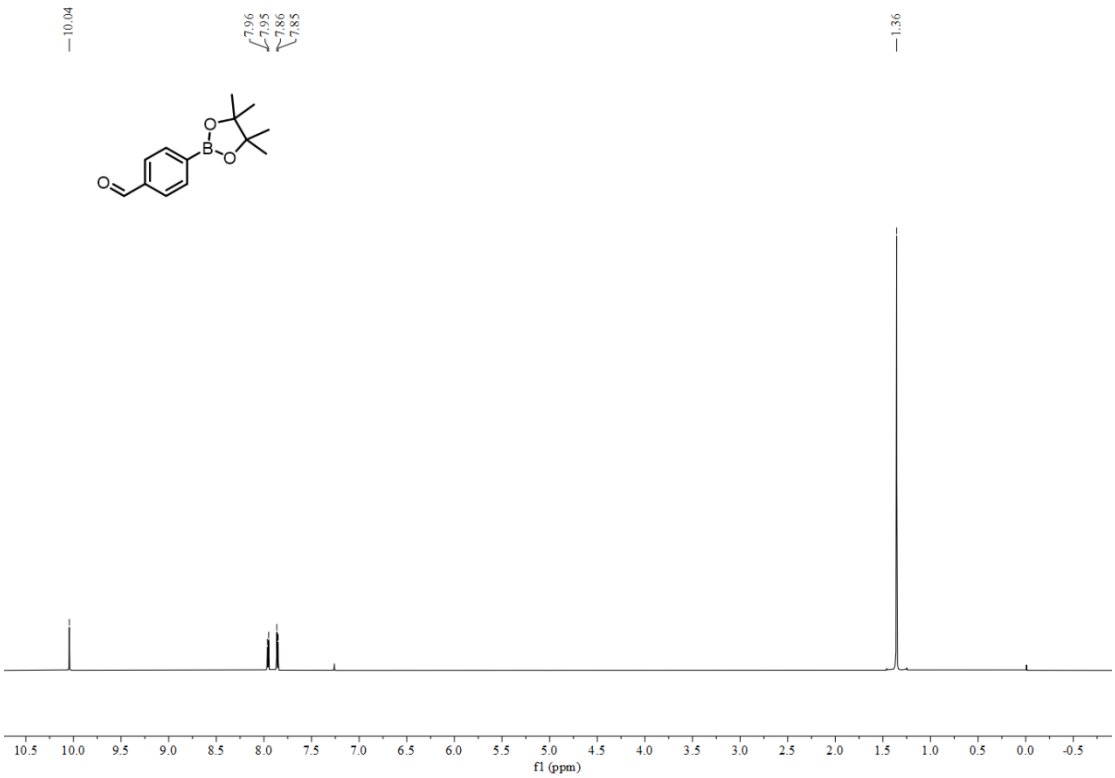
^{13}C NMR spectrum of compound **22**



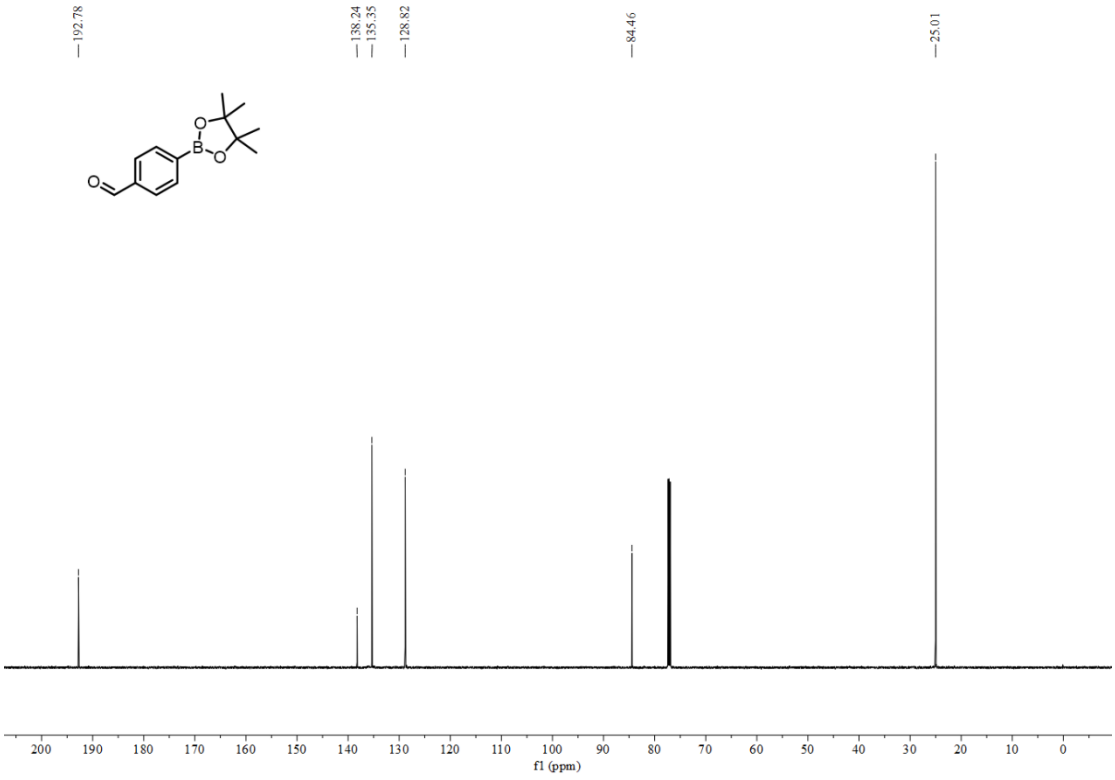
^{1}H NMR spectrum of compound **23**



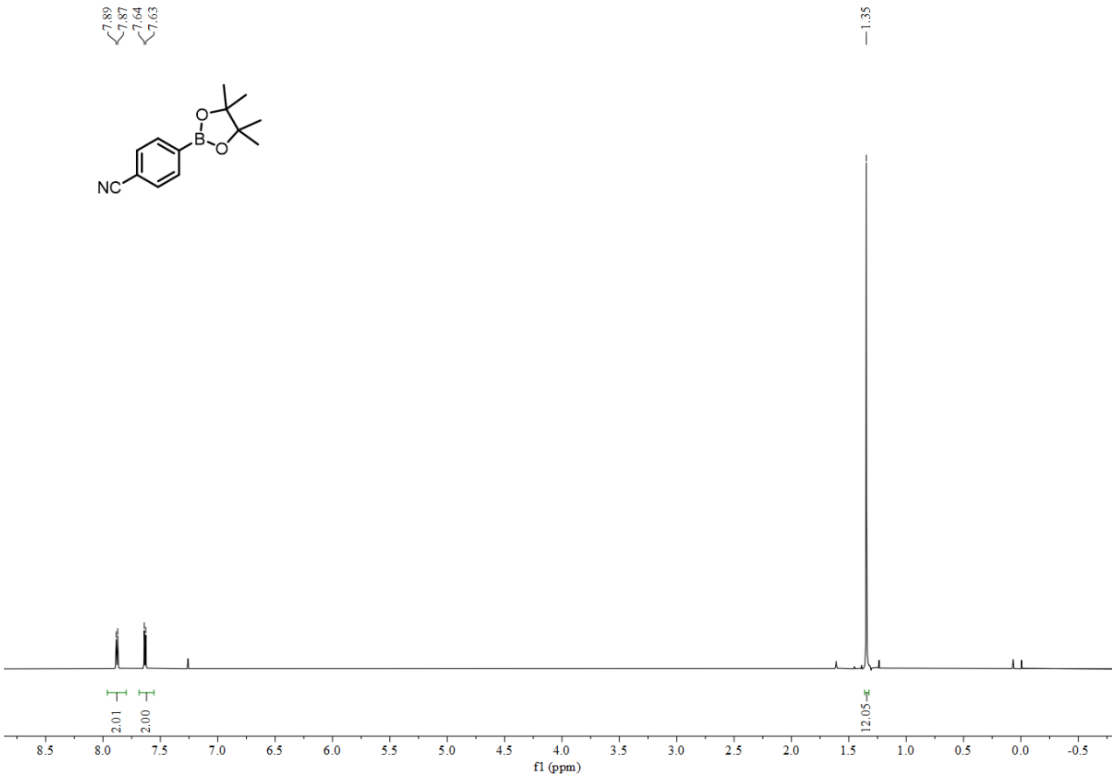
^{13}C NMR spectrum of compound **23**



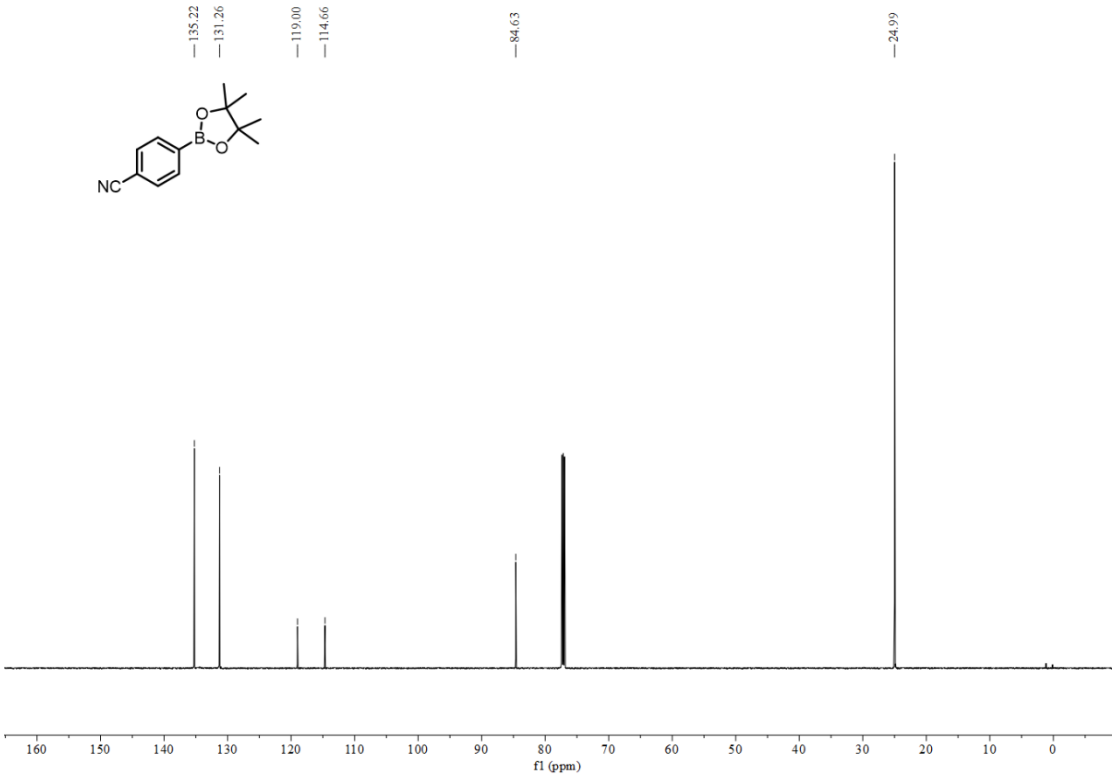
^{1}H NMR spectrum of compound **24**



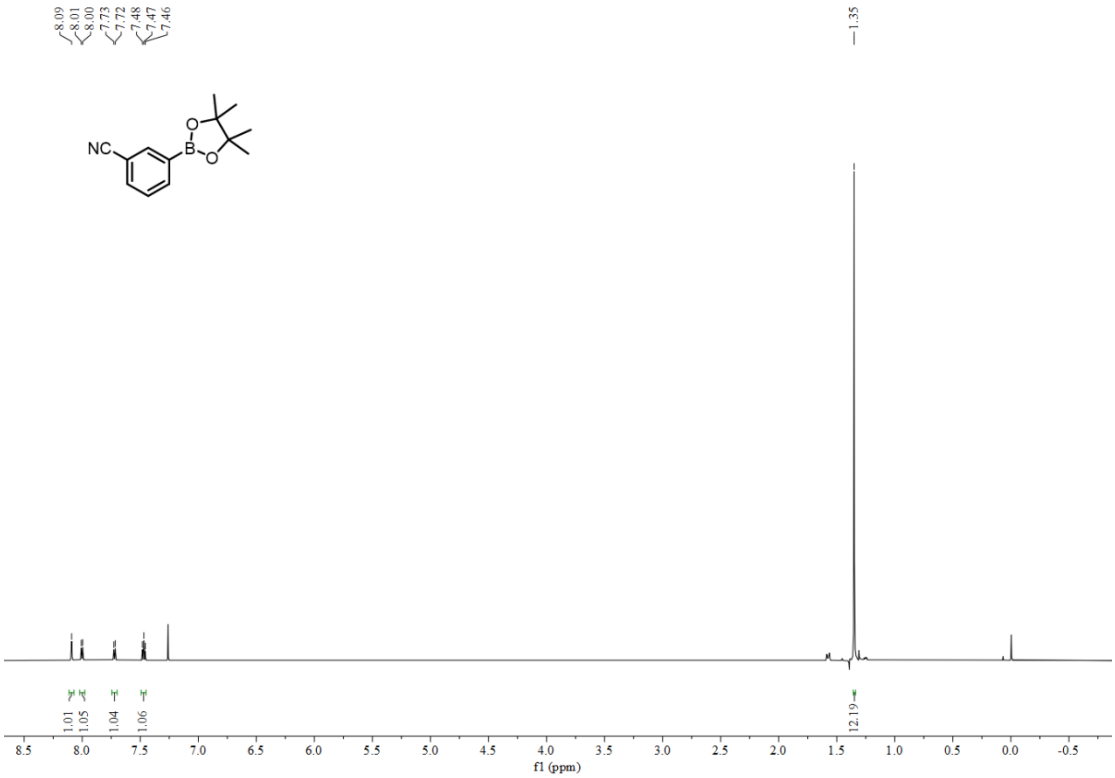
^{13}C NMR spectrum of compound **24**



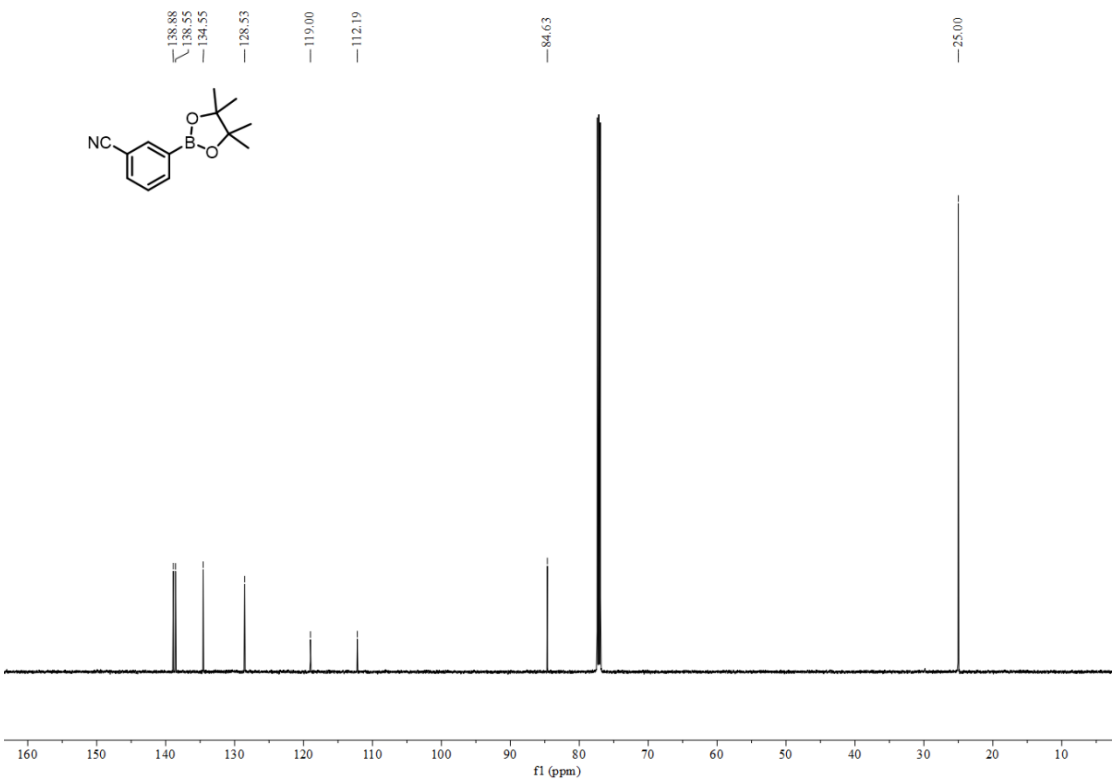
^{1}H NMR spectrum of compound **25**



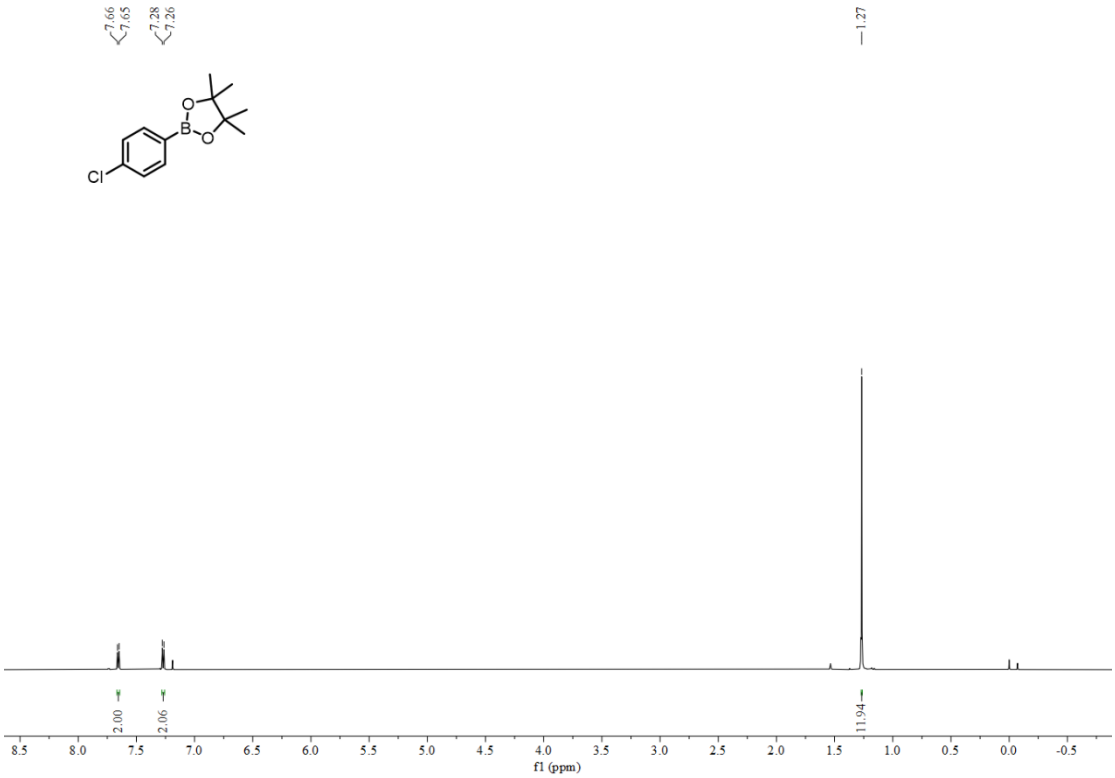
^{13}C NMR spectrum of compound **25**



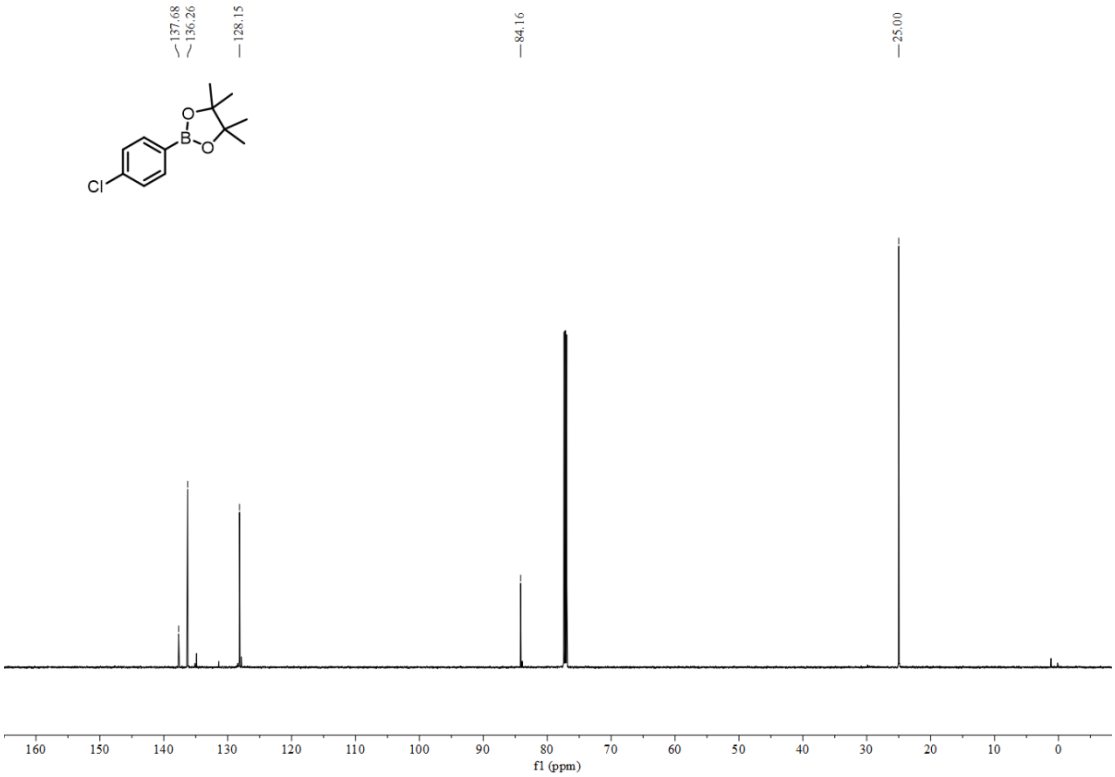
^{1}H NMR spectrum of compound **26**



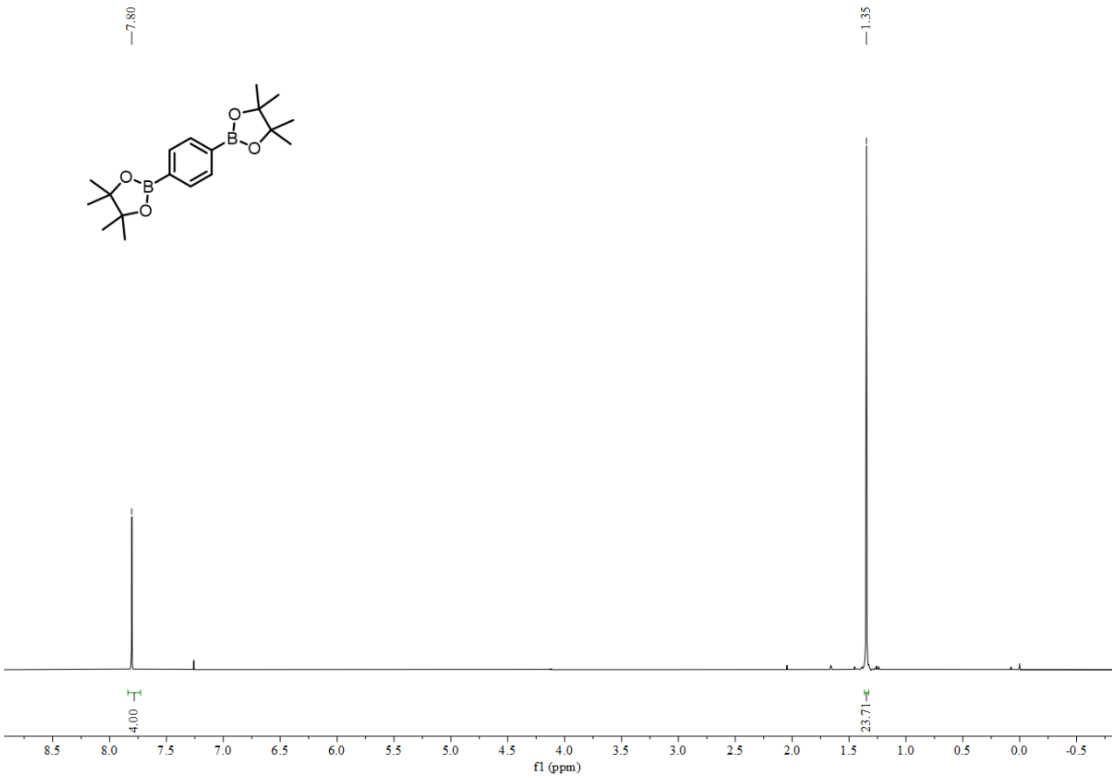
^{13}C NMR spectrum of compound **26**



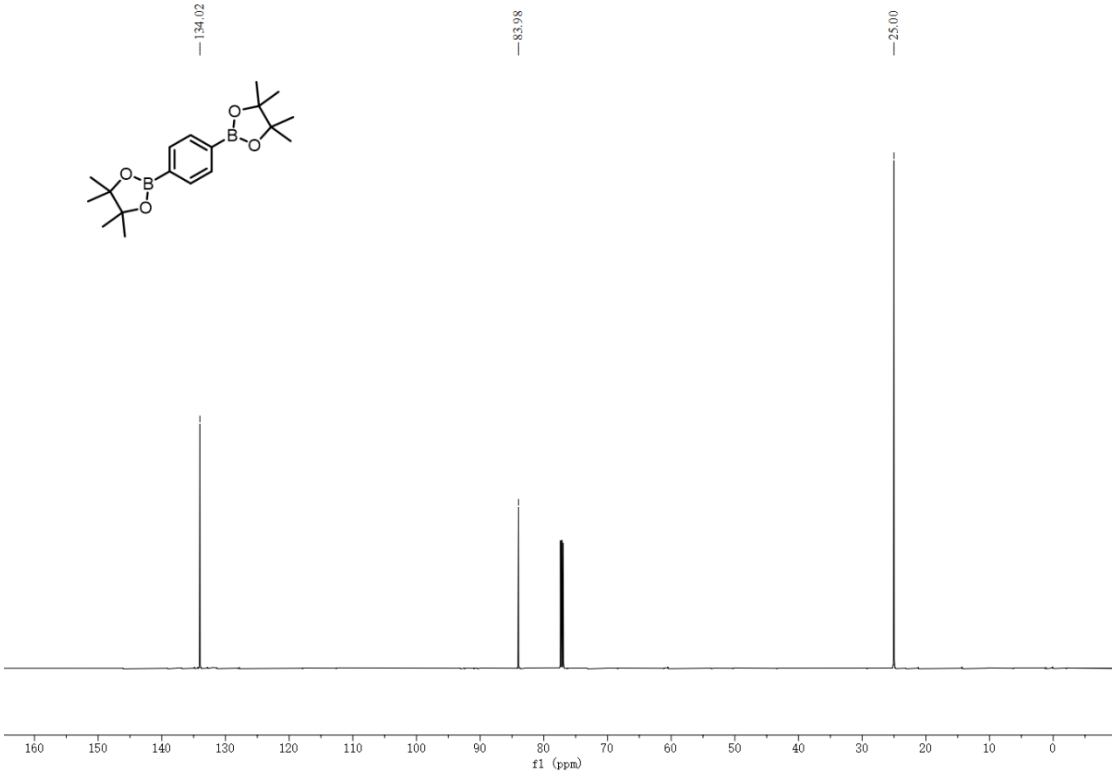
^{1}H NMR spectrum of compound **27**



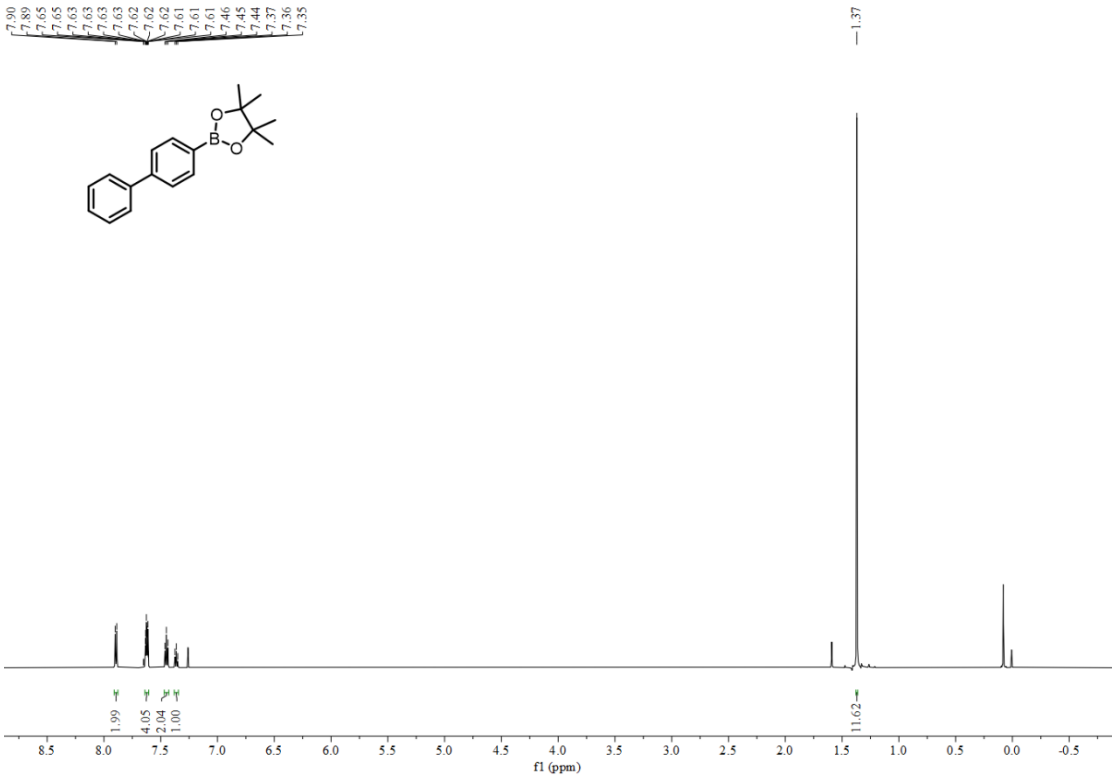
^{13}C NMR spectrum of compound **27**



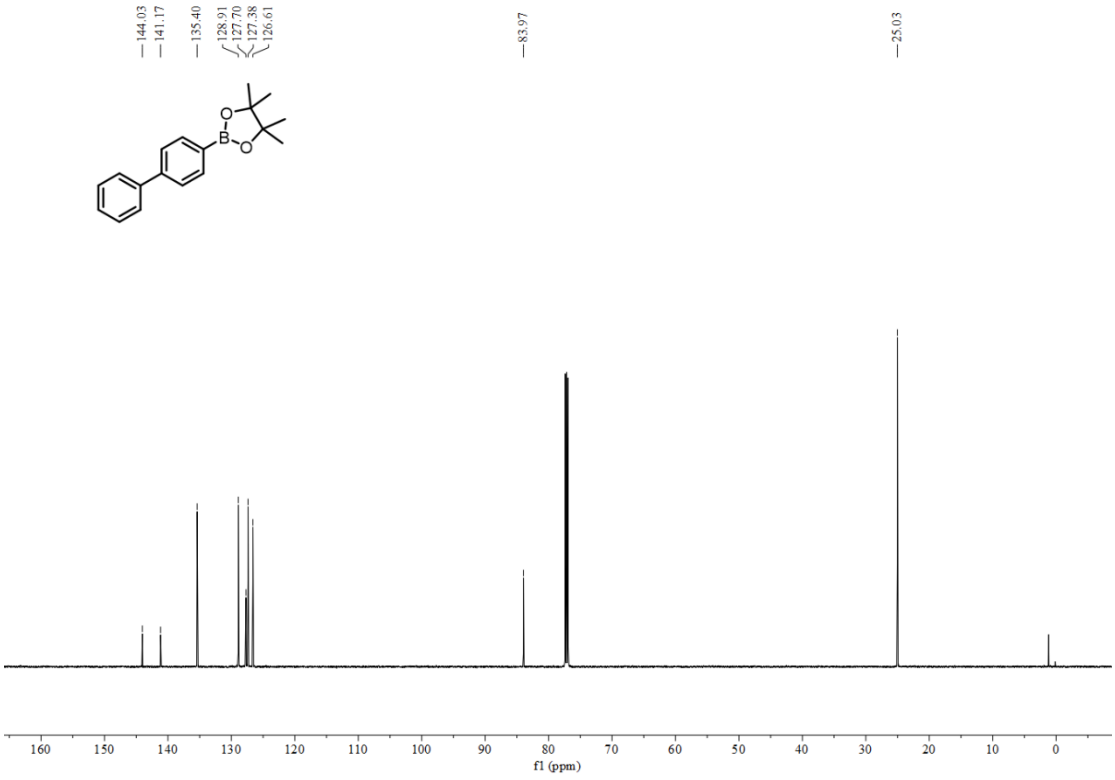
^{1}H NMR spectrum of compound **28**



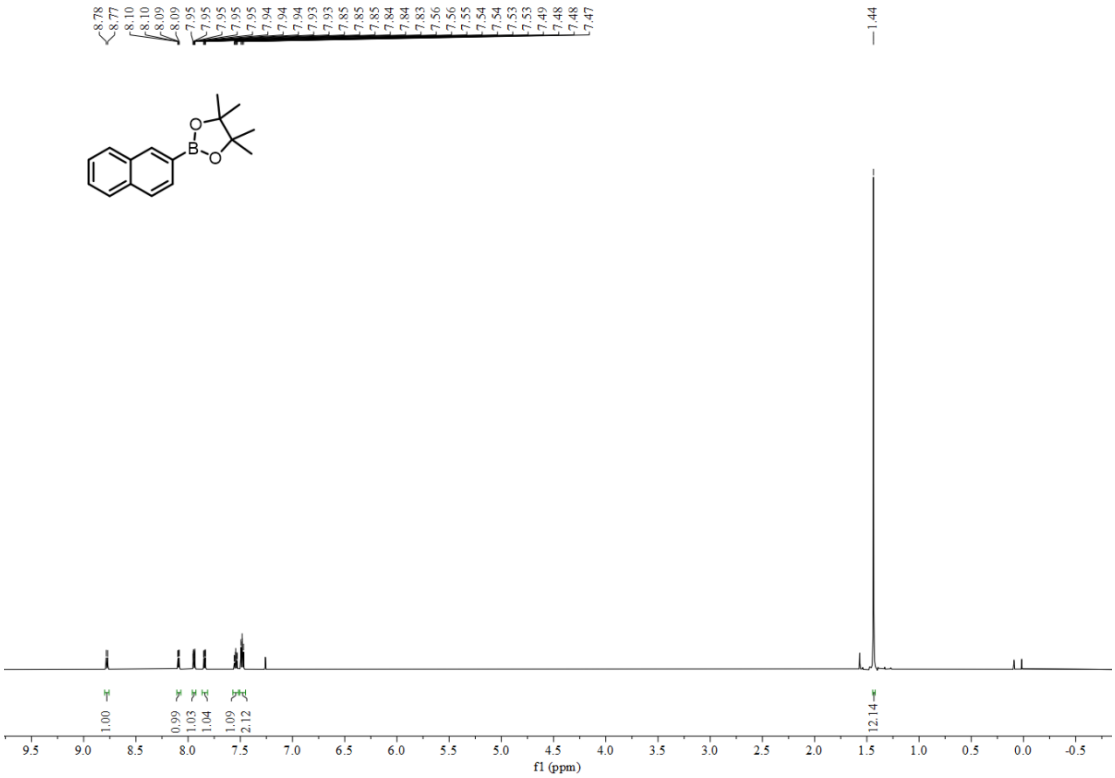
^{13}C NMR spectrum of compound **28**



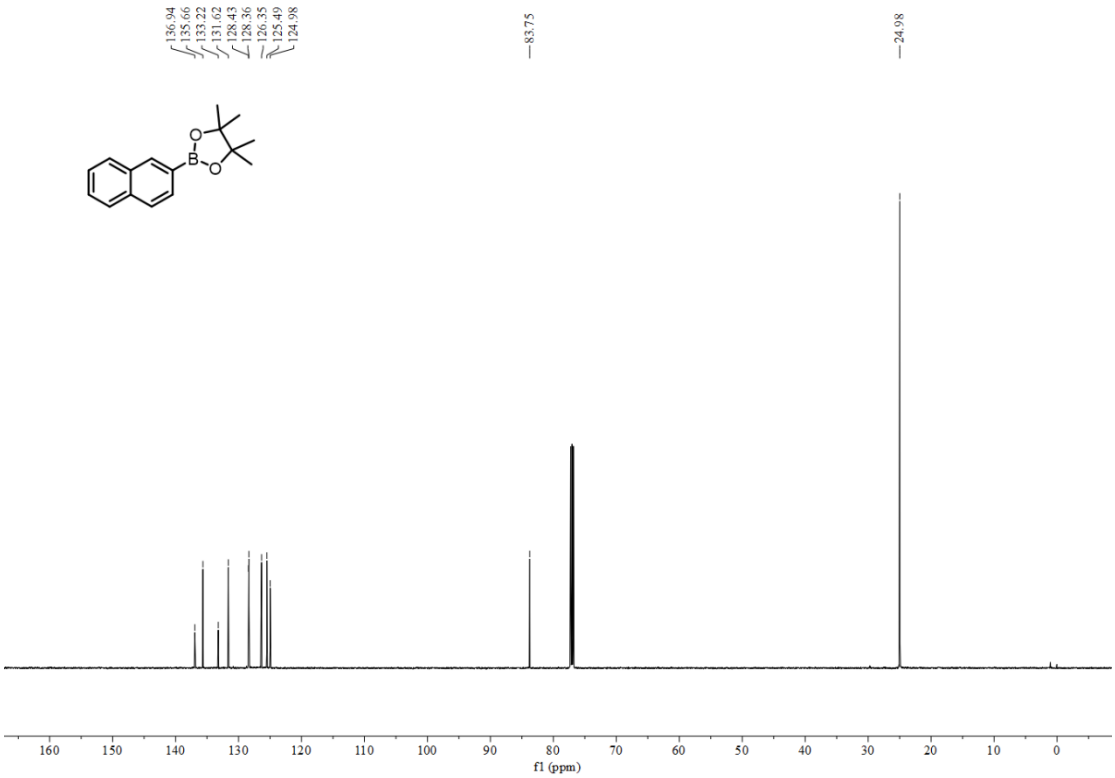
^{1}H NMR spectrum of compound **29**



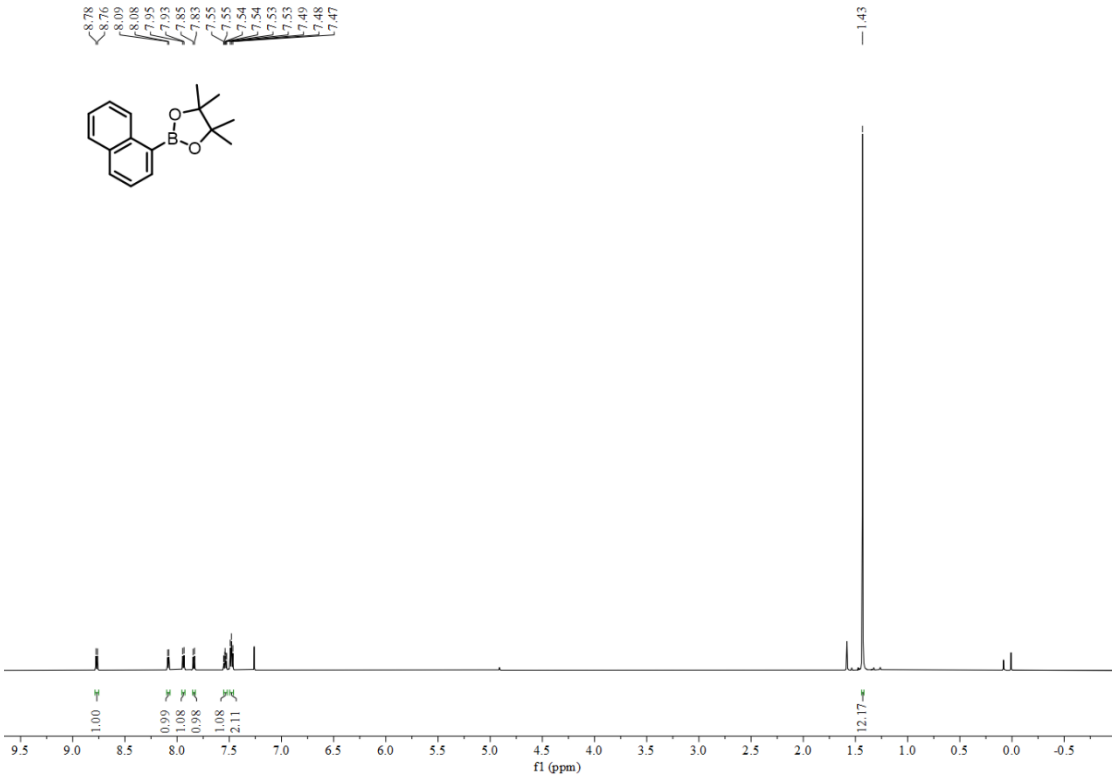
^{13}C NMR spectrum of compound **29**



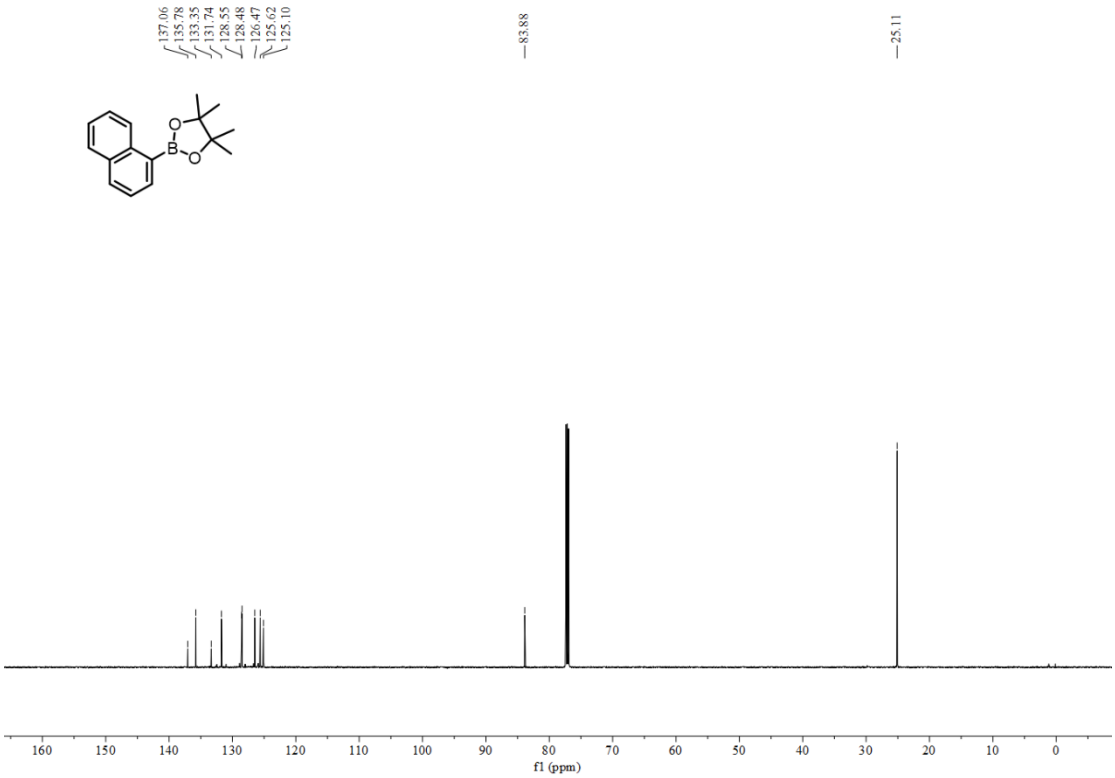
^{1}H NMR spectrum of compound **30**



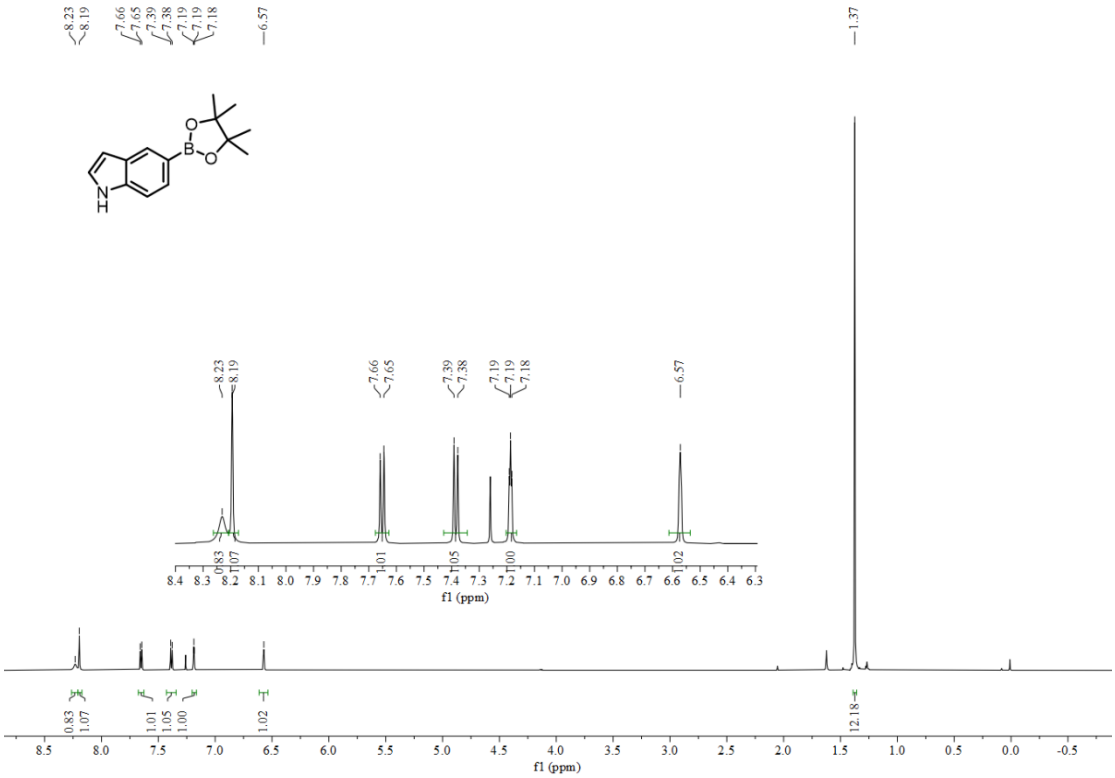
^{13}C NMR spectrum of compound **30**



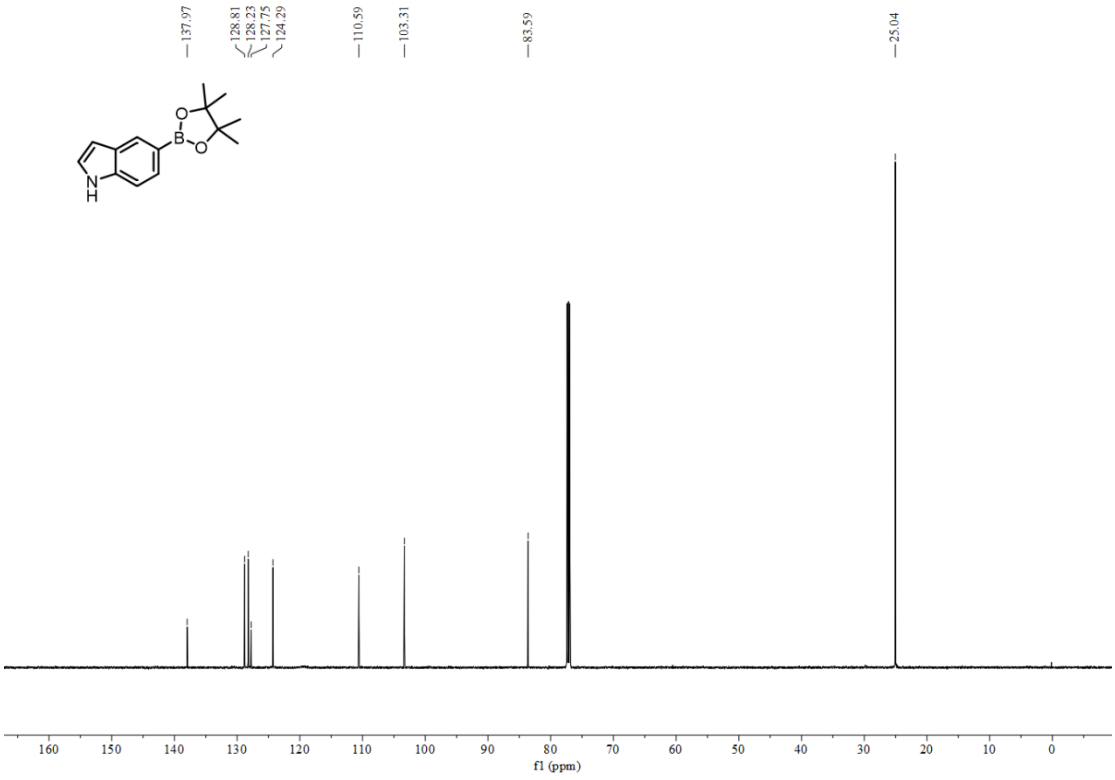
^{1}H NMR spectrum of compound **31**



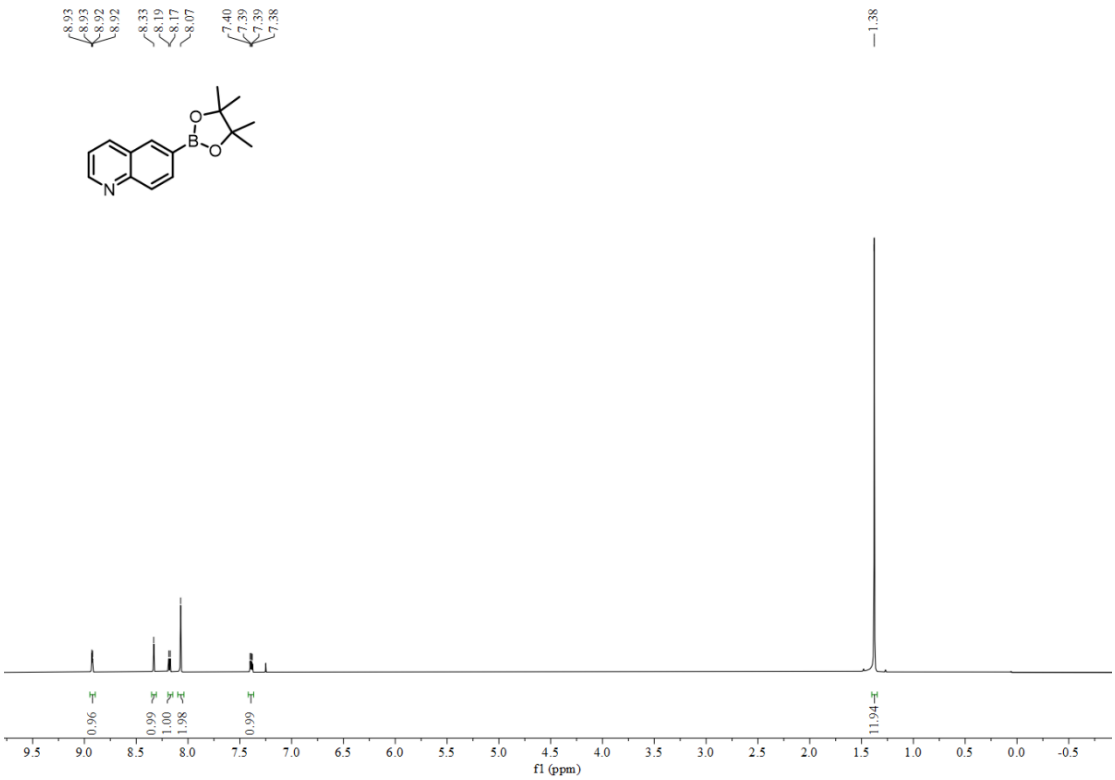
^{13}C NMR spectrum of compound **31**



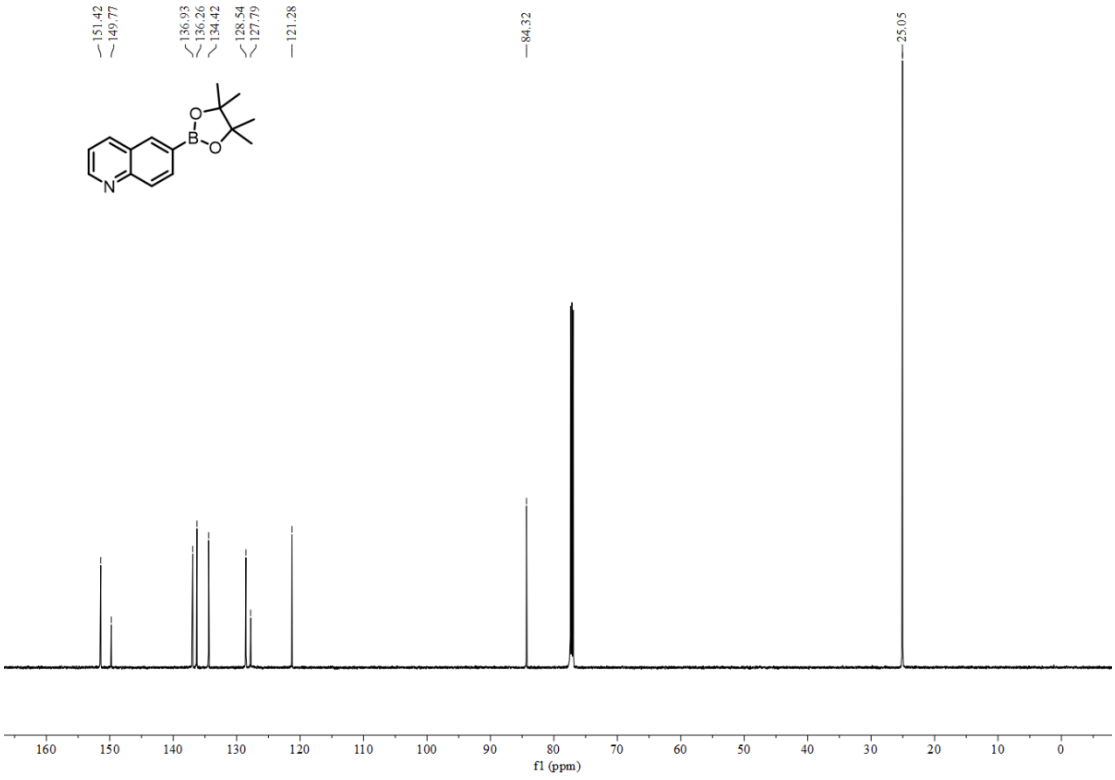
^{1}H NMR spectrum of compound **32**



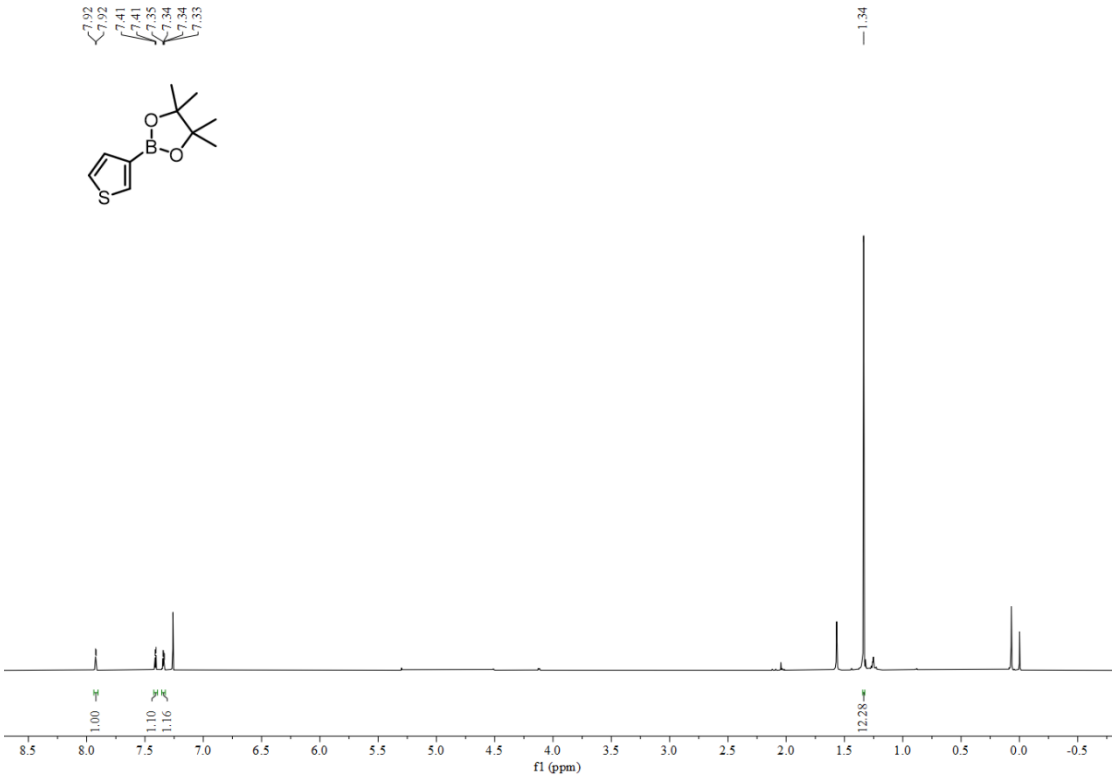
^{13}C NMR spectrum of compound **32**



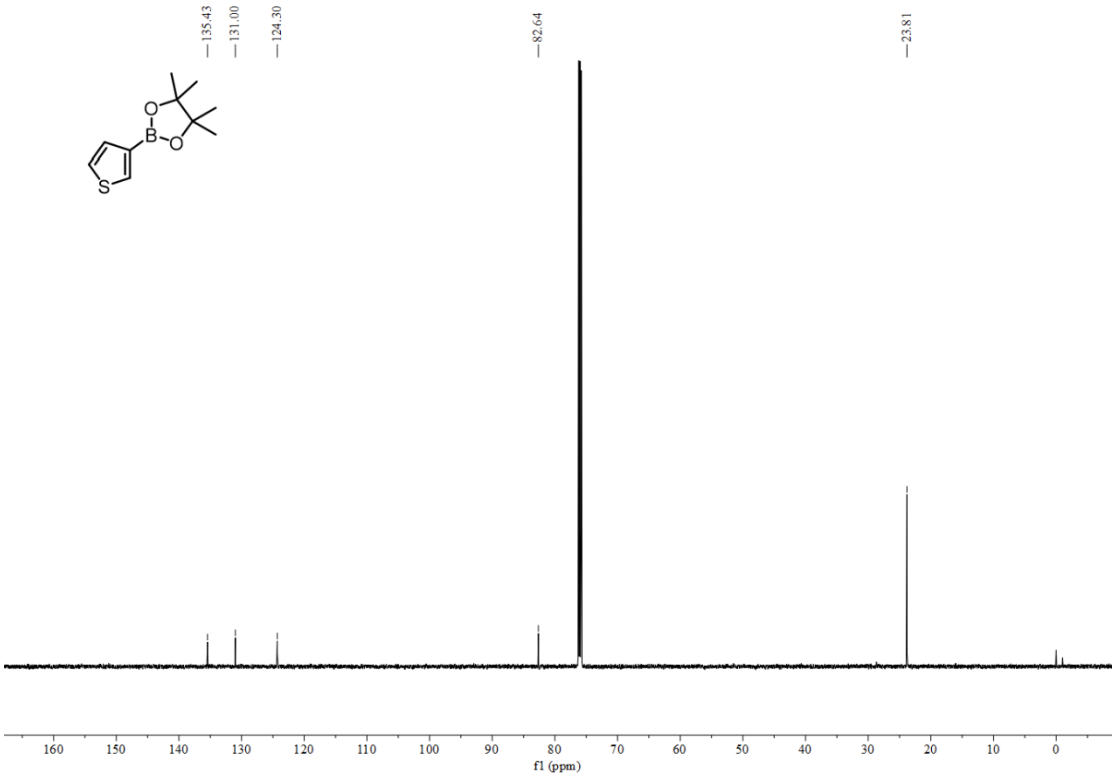
^{1}H NMR spectrum of compound **33**



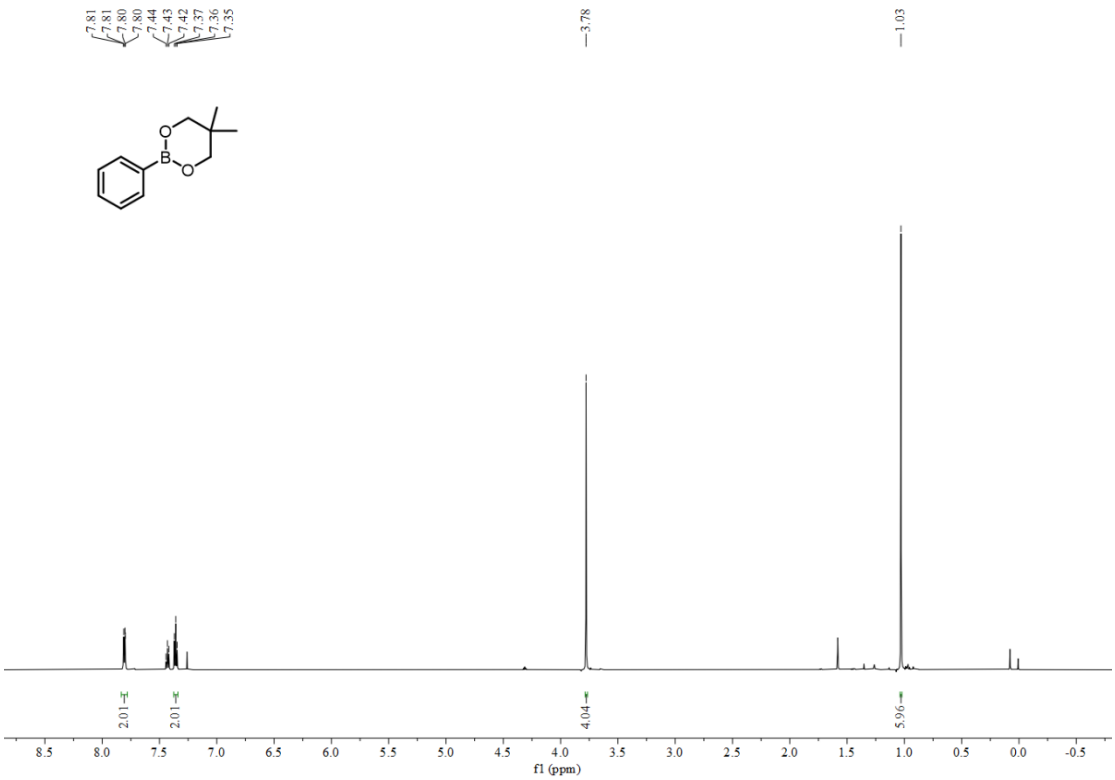
^{13}C NMR spectrum of compound **33**



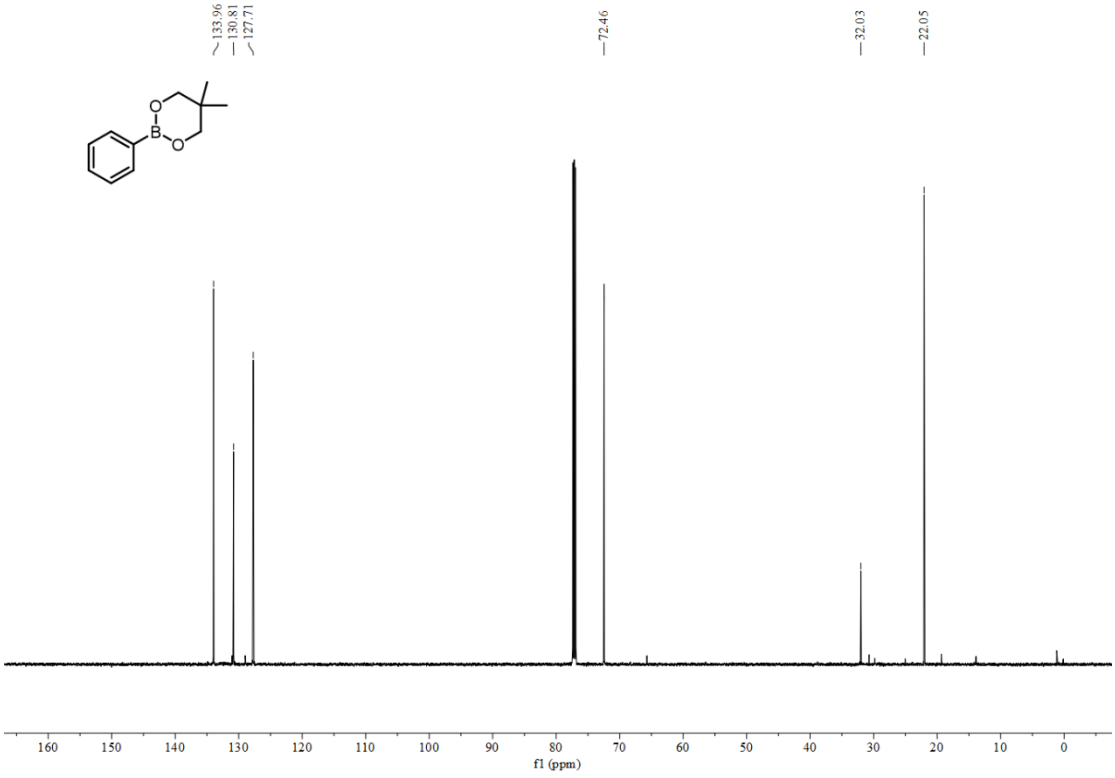
^{1}H NMR spectrum of compound **34**



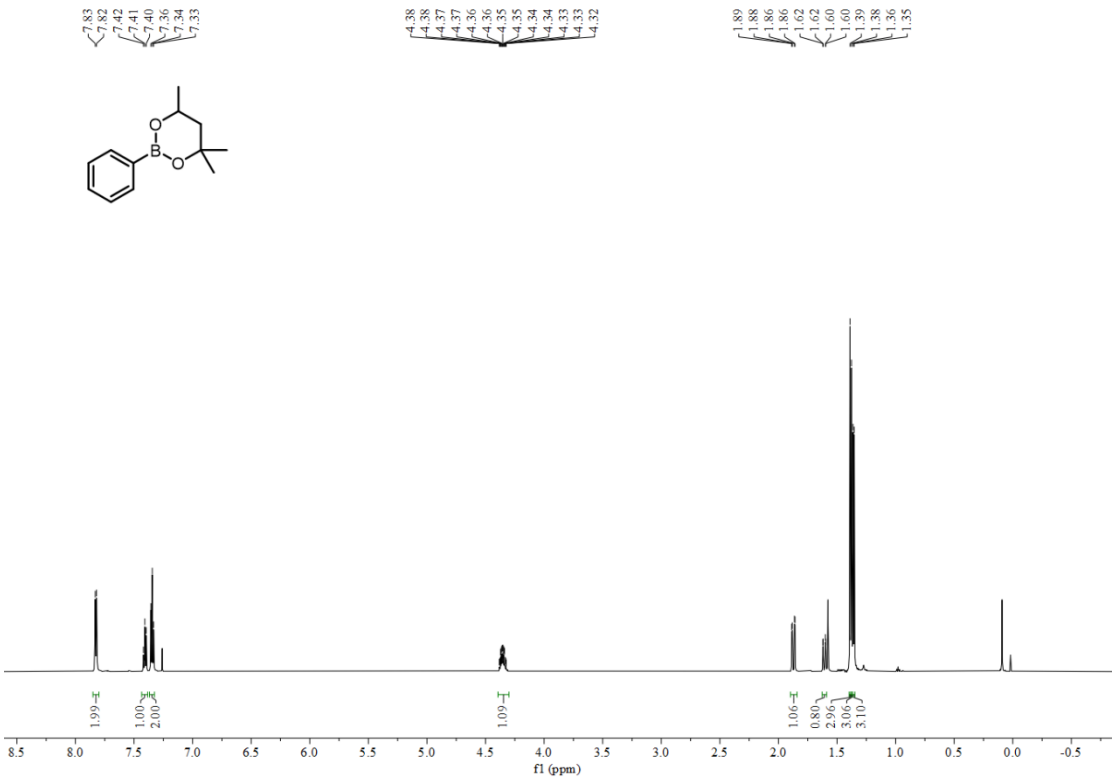
^{13}C NMR spectrum of compound **34**



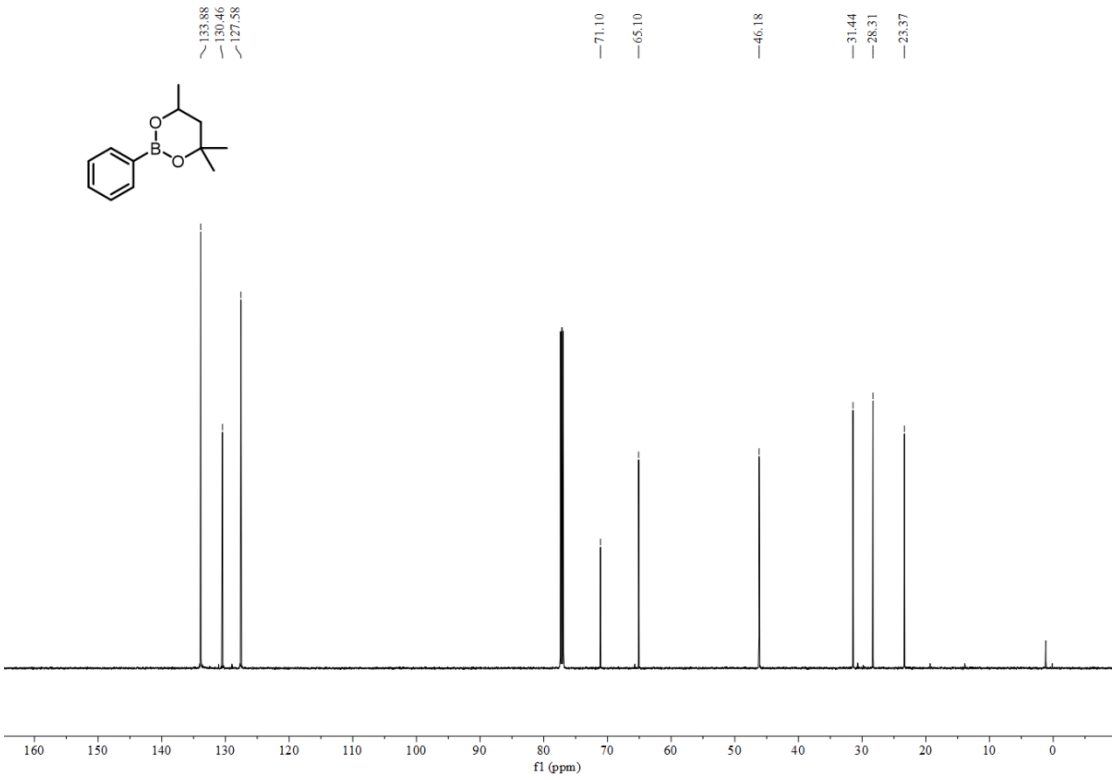
^{1}H NMR spectrum of compound **36**



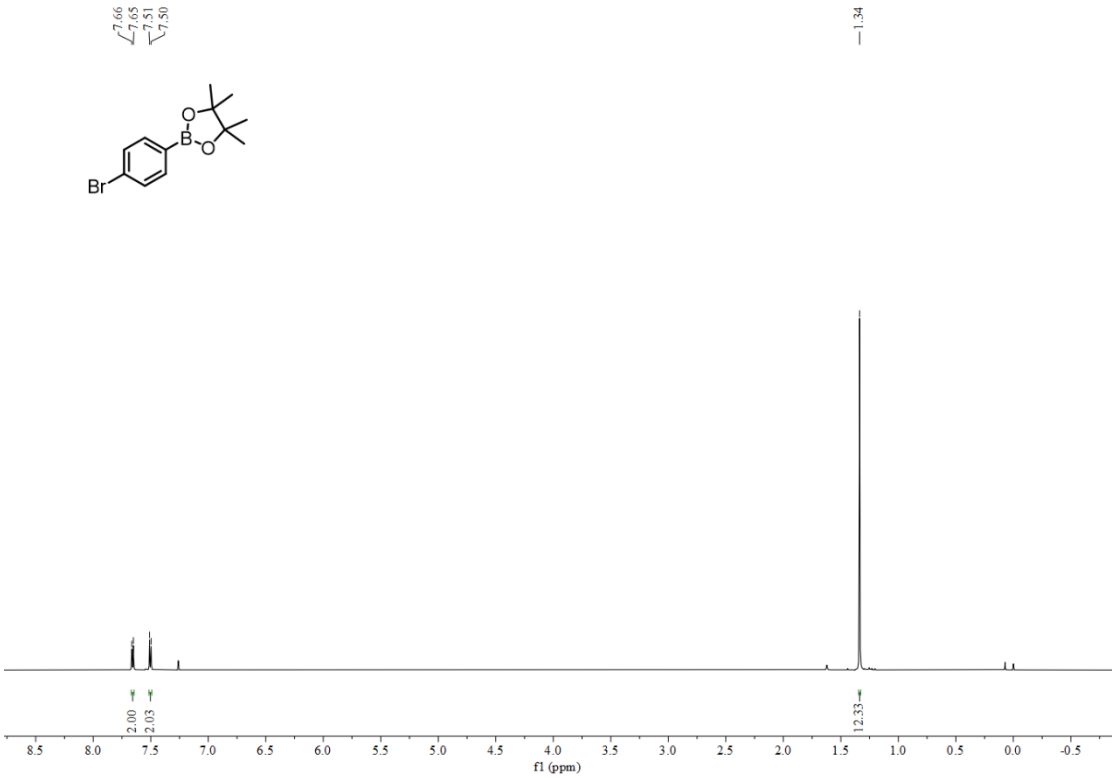
^{13}C NMR spectrum of compound **36**



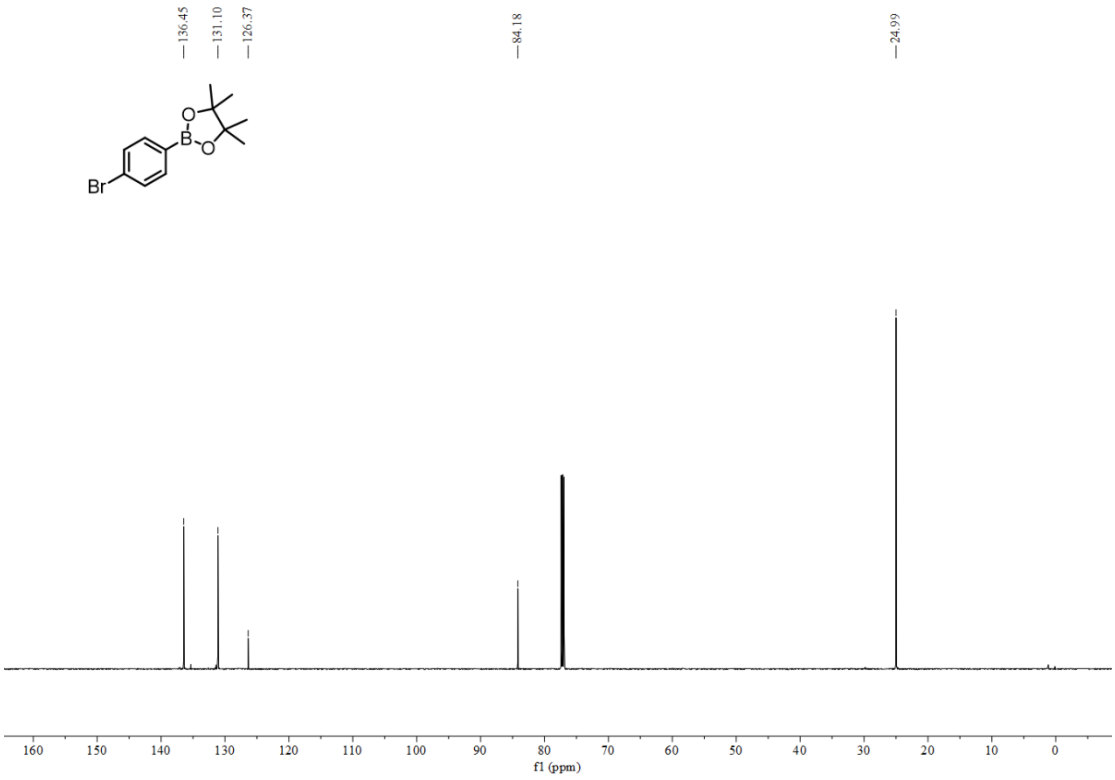
^{1}H NMR spectrum of compound **37**



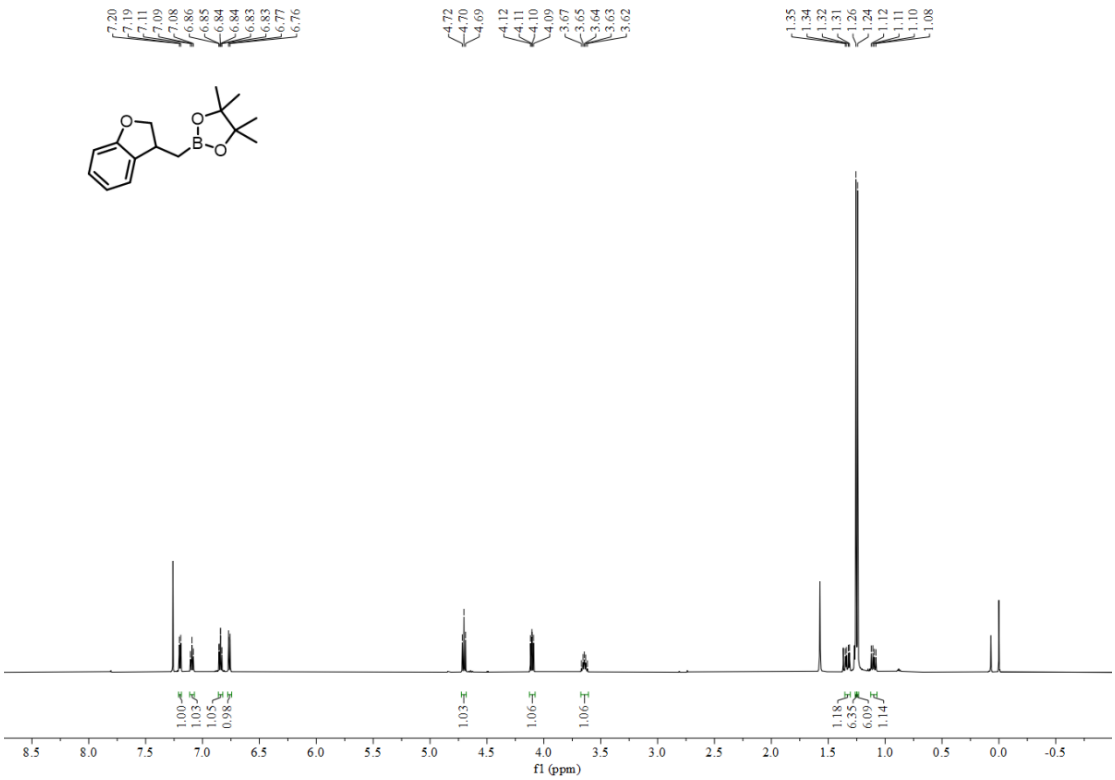
^{13}C NMR spectrum of compound **37**



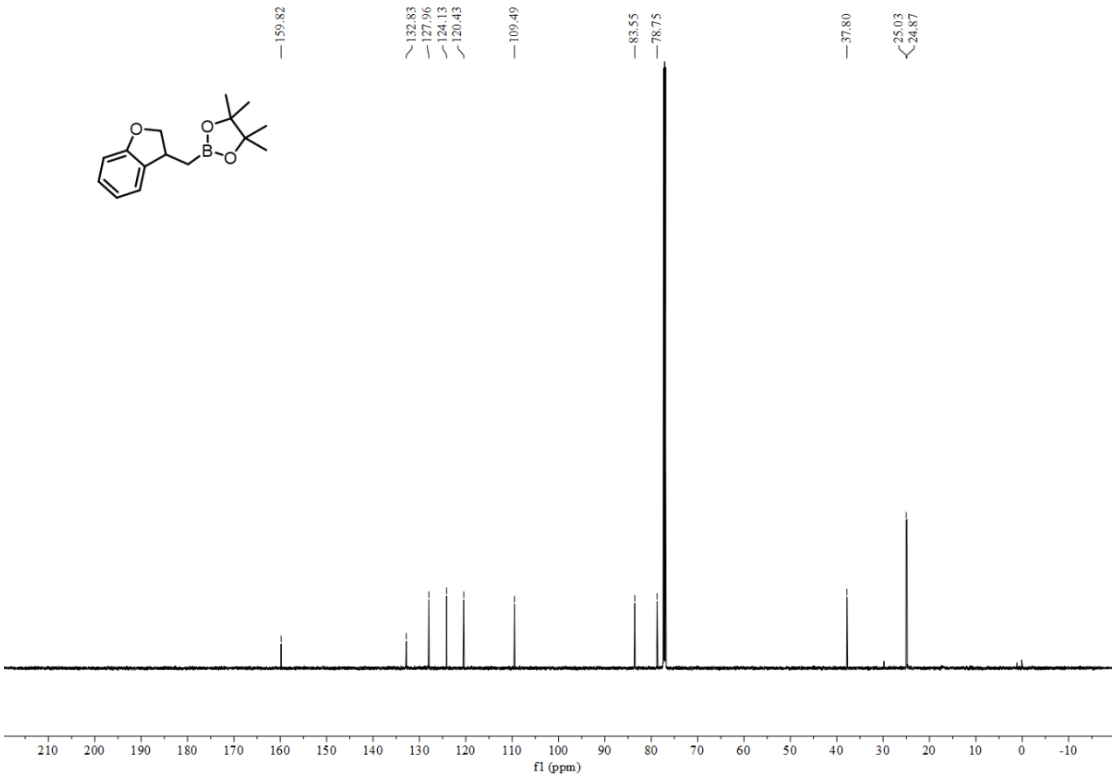
^{1}H NMR spectrum of compound **38**



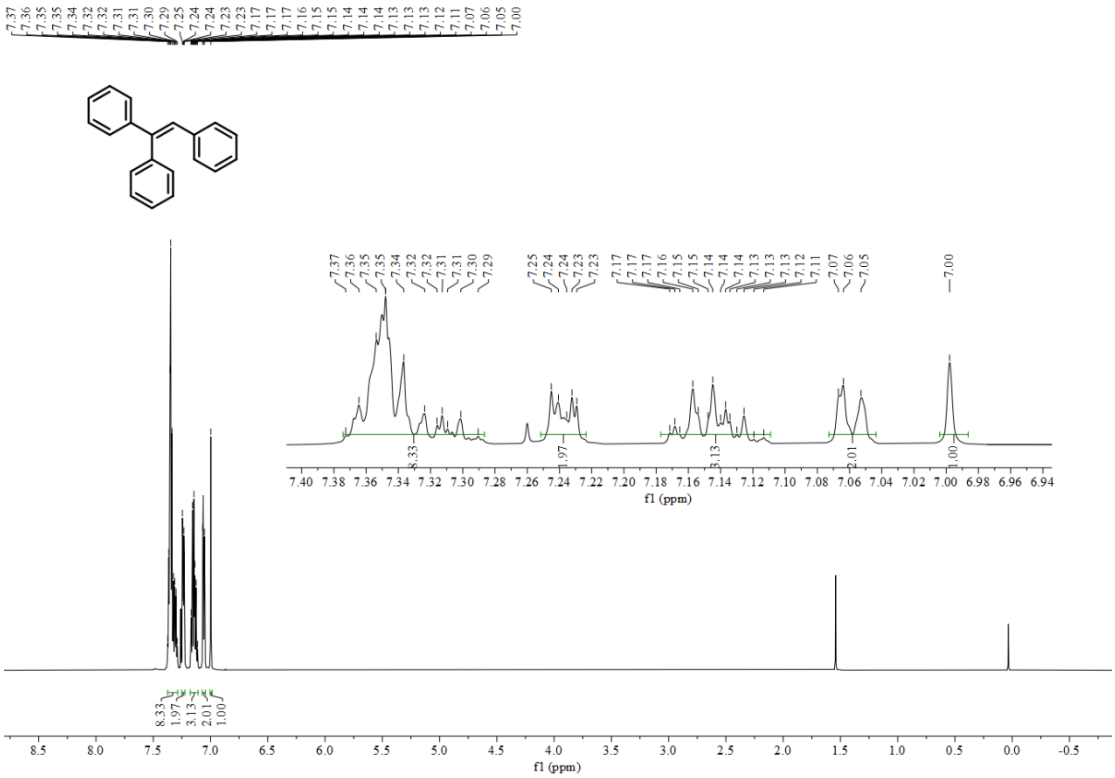
^{13}C NMR spectrum of compound **38**



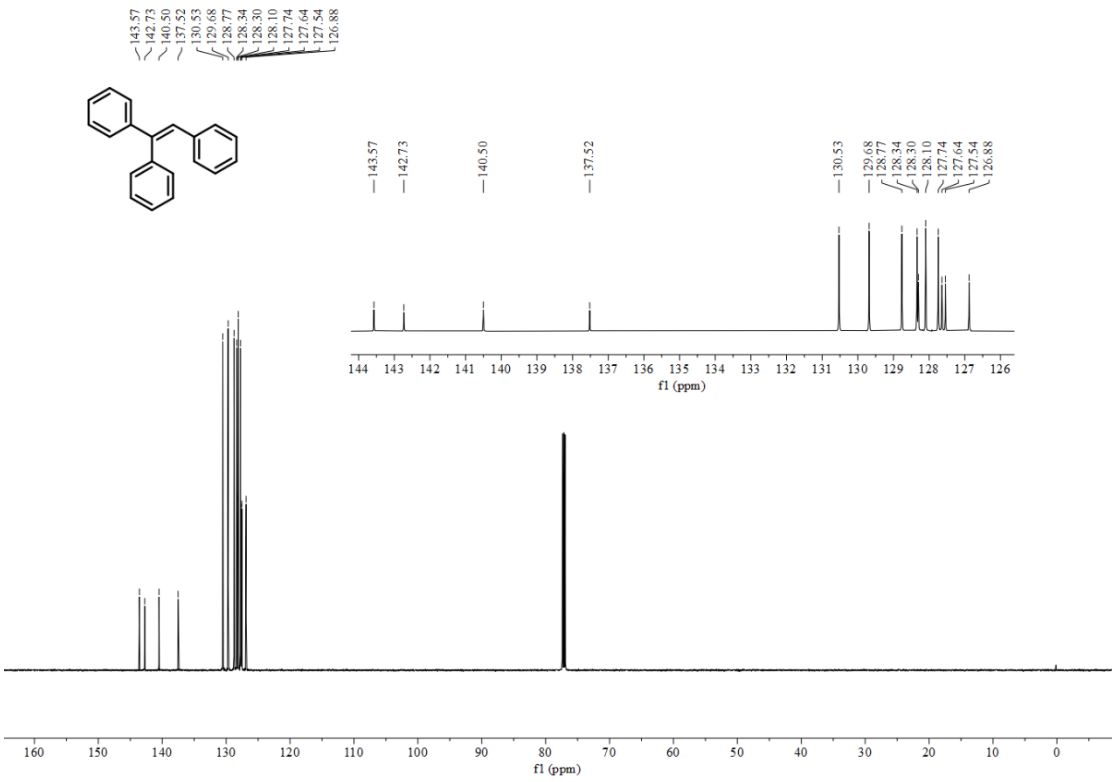
^{1}H NMR spectrum of compound **40**



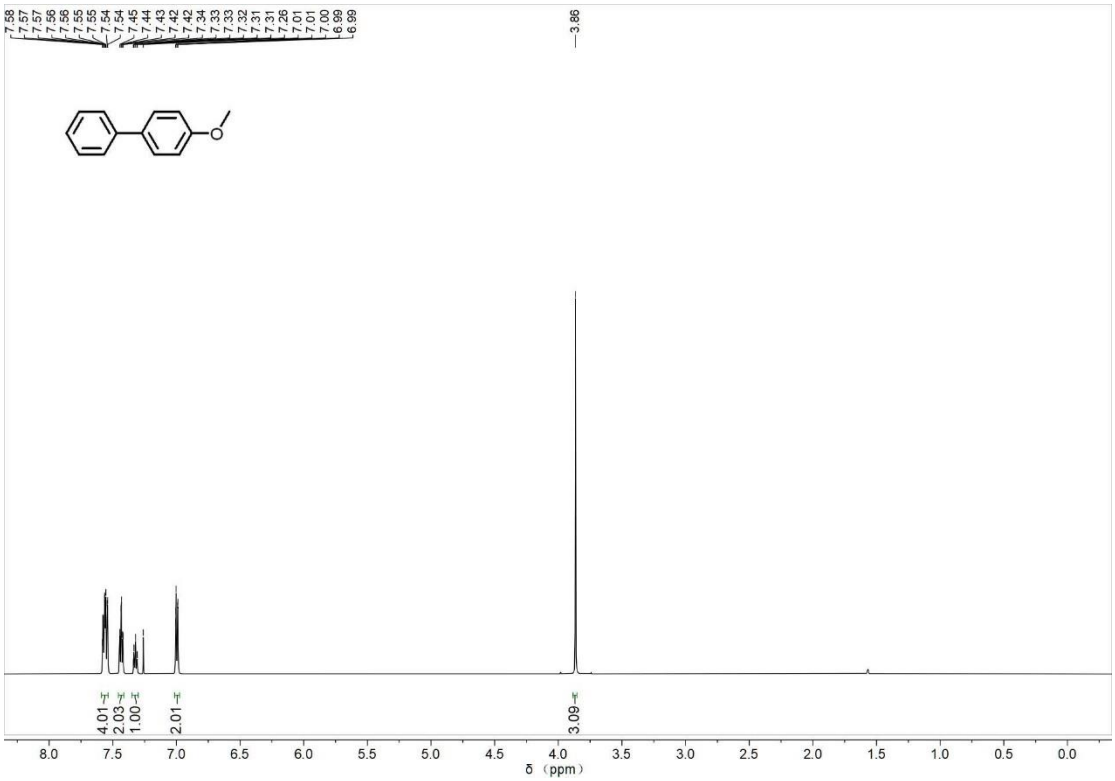
^{13}C NMR spectrum of compound **40**



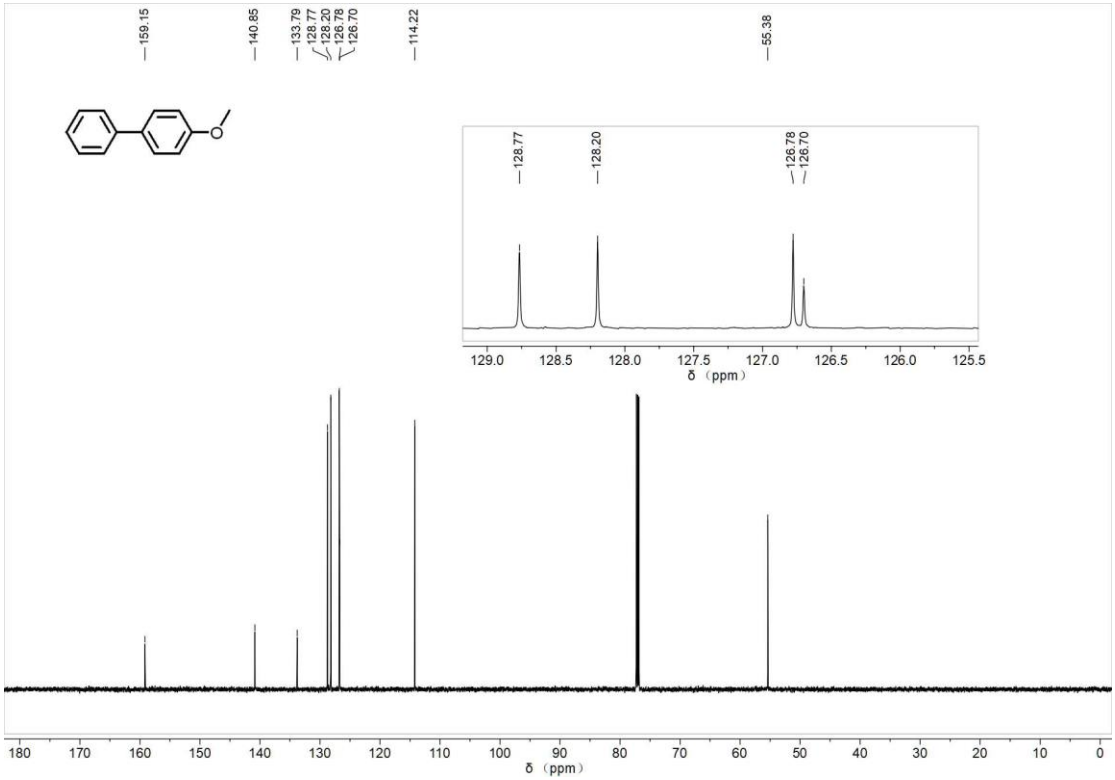
^{1}H NMR spectrum of compound **41**



^{13}C NMR spectrum of compound **41**



^{1}H NMR spectrum of **4-methoxy-1,1'-biphenyl**



^{13}C NMR spectrum of **4-methoxy-1,1'-biphenyl**