Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Pd-catalyzed Cross-Coupling of 1,1-Diborylalkanes with Aryl Triflates

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I. General Information

a. Materials

All reactions were carried out in oven-dried Schlenk tubes under an argon or nitrogen atmosphere (purity ≥99.999%). Palladium(II) acetate was purchased from Strem Chemicals Inc. as an tan powder and dissolved in 1,4-dioxane for further

application(1.1mg/ml). The following chemicals were purchased as received: Tetrabutylammonium hydroxide（50wt% in water), Trifluoromethanesulfonic anhydride(Energy Chemical), Dibromomethane, PPh_3, bis(pinacolato) diboron(Alfa-Aesar).Other substituted phenols were purchased from Aldrich or TCI America.All other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

b. Analytical Methods

^1H and ^{13}C spectra were recorded either on Bruker Avance 400 or Varian Mercury 400 spectrometer at ambient temperature in $CDCl_3$ unless otherwise noted; Data for ^1H-NMR are reported as follows: chemical shift (δppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed either on Thermo Scientific AS 3000 Series GC-MS System or Agilent 6890N gas chromatograph coupled to an Agilent 5973 inert mass selective detector. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. Elementary Analysis was carried out on Elementar Vario EL III elemental analyzer.

II. Preparation of Substrates

a. Preparation of Aryl Triflates

Aryl Triflates were prepared according to literature procedure.[1]

A flame-dried flask was successively charged with phenol (1.00 g, 10.6 mmol, 1.00 equiv), CH_2Cl_2 (10 mL), and pyridine (1.80 mL, 1.68 g, 21.3 mmol,2.00 equiv) at 0°C.

After dropwise addition of a solution of triflic anhydride (2.15 mL, 3.61 g, 12.8mmol, 1.20 equiv) in CH_2Cl_2 (5 mL), the reaction mixture was stirred at room temperature for 1.5 h and quenched with the addition of Et_2O (15 mL) and aqueous HCl (10%, 5 mL). The reaction mixture was washed successively with aqueous saturated $NaHCO_3$ (10 mL) and brine (10 mL). Drying over $MgSO_4$, evaporation of the solvents under reduced pressure and purification by Kugelrohr distillation afforded the desired product (2.3 g, 95%) as a colorless liquid (b.p.= 95°C, 10 mbar). 1H NMR (400 MHz, CDCl3): δ=7.27–7.30 (m, 2H),7.37–7.50 (m, 3H) ppm. 13C NMR (100 MHz, CDCl3): δ=118.9 (q, JC,F = 320 Hz), 121.5, 128.5,130.4, 149.8 ppm.

b. Preparation of 1,1-Diborylalkanes.

1,1-Diborylakanes were prepared according to literature procedure.[2]

Method A. In air, Cu-catalyst (10 mmol), base (250 mmol), and diboron reagent (220mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF(300 mL), and Dibromomethane (100 mmol) were added via syringe under an argon atmosphere. The reaction mixture was stirred at 40 ^oC for 24 h, and then diluted with EtOAc, filtered through silica gel with copious washings (Et_2O or EtOAc), concentrated, and purified by column chromatography.

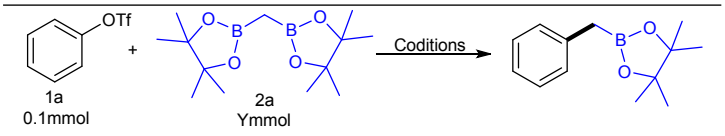
Method B. In air, Cu-catalyst (20 mmol), base (60 mmol), and diboron reagent (44mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF (120 mL), and 1,1-Dibromoethane (20 mmol) were added via syringe under an argon atmosphere.The reaction mixture was stirred at 40 oC for 24 h, and then diluted with EtOAc, filtered through silica gel with copious washings (Et_2O or EtOAc), concentrated, and purified by column chromatography.

Method C.[3] In air, diborylmethane (10 mmol) was added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). THF (30mL), and LDA (11 mmol Acros) were added via syringe under an argon atmosphere at 0 ^oC. The reaction mixture was stirred for 5 min, and then alkyl halide (10 mmol) was added at the same tempurature. The reaction mixture was allowed to warm to room

temperature and stirred for 2 hours. When reaction completed, reaction mixture diluted with Et_2O, and quenched by the NH_4Cl (aq). The organic layer was dried over Na_2SO_4 (s), filtered and concentrated in vacuo and purified by column chromatography.

III. Pd-catalyzed Cross-coupling of 1,1-Diborylalkanes with Phenyl Triflate

Table 1. Various conditions for the reaction of phenyl triflate and diborylmethane[a]



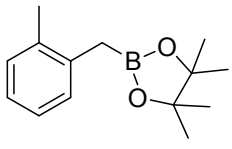
Entry	Y(mmol)	Solvent	Base	Yield（%
1[b]	0.15	H_2O/dioxane	KOH	5

2[b]	0.15	H_2O/dioxane	NaOH	4
3[b]	0.15	H_2O/dioxane	LiOH	20
4[c]	0.15	H_2O/dioxane	TBPOH	65
5	0.15	H_2O/dioxane	TMAOH	50
6	0.15	H_2O/dioxane	TBAOH	85(90)
7	0.15	H_2O/dioxane	TRITON B	54
8	0.15	MeOH/dioxane	TBAOH	trace
9	0.15	H_2O/THF	TBAOH	58
10	0.15	H_2O/DMF	TBAOH	27
11	0.15	H_2O/DMSO	TBAOH	39
12	0.15	H_2O/PhMe	TBAOH	8
13[d]	0.15	H_2O/dioxane	TBAOH	10
14[e]	0.15	H_2O/dioxane	TBAOH	86
15	0.12	H_2O/dioxane	TBAOH	43

[a] Reaction conditions:1a (0.1mmol), 2a (ymmol), $Pd(OAc)_2$ (5mol%), PPh_3 (10mol%), base (3 equiv) in 0.5 mL dioxane at rt under an Ar atmosphere for 3h. The yield was determined by GC using benzophenone as the internal standard (average of two GC runs). [b] The used bases were 8N aqueous solution. [c] Organic bases were 1N aqueous solution or methanol solution. [d] 2equiv TBAOH was used. [e] 4equiv TBAOH was used. TBAOH = Tetrabutylammonium hydroxide. TMAOH = Tetramethylammonium hydroxide. TBPOH = Tetrabutylphosphonium hydroxide. TRITON B = Benzyltrimethylammonium hydroxide. DMF = N,N-dimethylformamide. DMSO = Dimethylsulfoxide. THF = Tetrahydrofuran.

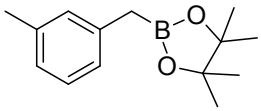
General Procedure for Examples Described in Table 1 and Table 2.

General Procedure A In air, $Pd(OAc)_2$ (1.1mg,0.005mmol), PPh_3 (2.6mg, 0.01mmol), and diborylmethanes (40.2mg, 0.15mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (this process was repeated three times).Dioxane (0.5 mL), 1M TBAOH (0.3ml,0.3mmol) were added in turn by syringe under argon atmosphere at room temperature, and then stirred at rt for 1 min. And aryl triflate (0.1 mmol) was added in turn by syringe under argon atmosphere. The resulting reaction mixture was stirred vigorously at rt over night. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings (Et_2O or EtOAc), concentrated, and purified by column chromatography .



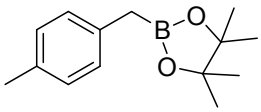
4,4,5,5-tetramethyl-2-(2-methylbenzyl)-1,3,2-dioxaborolane (3b, 17.8mg, 77%yield, CAS: 390381-02-9)[4]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to give colorless oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.15 – 7.00 (m, 4H), 2.26 (s, 3H), 2.25 (s, 2H), 1.22 (s, 12H) ppm.^{13}C NMR (101 MHz, CDCl3) δ 137.49, 135.88, 129.75, 129.43, 125.83, 125.12, 83.33, 24.71, 20.08 ppm.



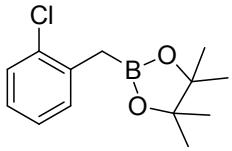
4,4,5,5-tetramethyl-2-(3-methylbenzyl)-1,3,2-dioxaborolane (3c, 17.4mg, 75%yield, CAS: 356570-54-2) [4]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to give colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.6 Hz, 1H), 7.01 – 6.96 (m, 2H), 6.95 – 6.90 (m, 1H), 2.30 (s, 3H), 2.25 (s, 2H), 1.23 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.50, 137.73, 129.90, 128.17, 126.01, 125.64, 83.41, 24.75, 21.45 ppm.



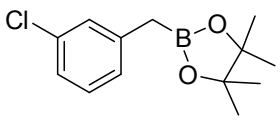
4,4,5,5-tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (3d, 18.5mg, 81% yield, CAS: 356570-52-0) [4]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to give colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.05 (m, 2H), 7.05 – 7.01 (m, 2H), 2.28 (s, 3H), 2.24 (s, 2H), 1.22 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.40, 134.12, 129.02, 128.89, 83.38, 24.77, 21.01 ppm.



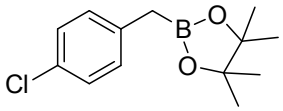
2-(2-chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e, 10.3mg, 41% yield, CAS: 1365565-86-1)[5]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to give colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (td, *J* = 7.6, 1.5 Hz, 1H), 7.22 (td, *J* = 7.5, 1.2 Hz, 1H), 7.14 (td, *J* = 7.4, 1.2 Hz, 1H), 7.08 (td, *J* = 7.6, 1.5 Hz, 1H), 2.38 (s, 2H), 1.24 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.53, 133.87, 130.81, 129.00, 126.67, 126.49, 83.40, 24.72 ppm.



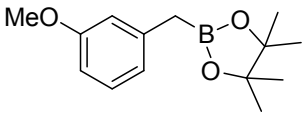
2-(3-chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f, 9.8mg, 39% yield, CAS: 517920 -59-1) [5]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 2.27 (s, 2H), 1.23 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.78, 133.92, 129.41, 129.07, 127.20, 125.08, 83.62, 24.72 ppm.



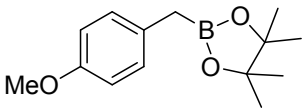
2-(4-chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g, 10.8mg, 43% yield, CAS: 475250-49-8) [5]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 2.25 (s, 2H), 1.23 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.12, 129.54, 129.25, 127.28, 82.53, 23.68 ppm.



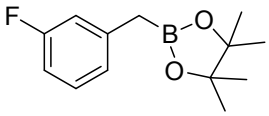
2-(3-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h, 16.3mg, 66% yield, 797762-23-3) [4]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1) to colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.9 Hz, 1H), 6.80 – 6.72 (m, 2H), 6.67 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.77 (s, 3H), 2.27 (s, 2H), 1.23 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.52, 140.35, 129.13, 121.50, 114.59, 110.40, 83.41, 55.03, 24.71 ppm.



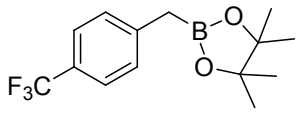
2-(4-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i, 16.4mg, 67% yield, 475250-52-3) [4]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1) to colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 2.22 (s, 2H), 1.23 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.08, 130.48, 129.82, 113.76, 83.37, 55.21, 24.74 ppm.



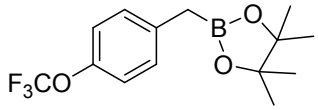
2-(3-fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j, 17.0mg, 72% yield, CAS: 1310048-95-3)[4]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 14.2, 7.8 Hz, 1H), 6.92 (dd, *J* = 16.2, 8.9 Hz, 2H), 6.81 (td, *J* = 8.5, 2.2 Hz, 1H), 2.29 (s, 2H), 1.23 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.86 (d, *J* = 244.4 Hz), 141.26 (d, *J* = 7.8 Hz), 129.51 (d, *J* = 8.5 Hz), 124.68 (d, *J* = 2.6 Hz), 115.84 (d, *J* = 21.0 Hz), 111.74 (d, *J* = 21.0 Hz), 83.58, 24.72 ppm.



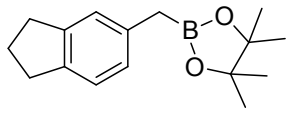
4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)benzyl)-1,3,2-dioxaborolane (3k, 17.1mg, 60% yield, CAS: 475250-46-5)[5]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 2H), 1.23 (s, 12H) ppm. 13C NMR (101 MHz, CDCl3) δ 143.11, 129.17, 127.21 (q, J = 32.3 Hz), 125.15 (q, J = 3.7 Hz), 124.53 (q, J = 271.9 Hz), 83.69, 24.71 ppm.



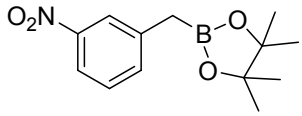
4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)benzyl)-1,3,2-dioxaborolane (3l, 19.0 mg, 63% yield, CAS: 872038-32-9) [5]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1) to colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 2.29 (s, 2H), 1.24 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.79, 137.46, 130.11, 120.83, 120.55 (q, J = 255.0 Hz), 83.61, 24.72 ppm. 146.79, 137.46, 130.11, 124.10, 121.82, 119.27, 116.73, 83.61, 24.72.



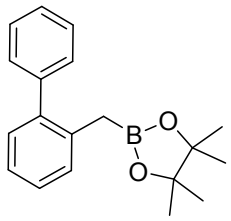
2-((2,3-dihydro-1H-inden-5-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m, 19.1mg, 74% yield):

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 2.85 (dd, *J* = 12.7, 7.1 Hz, 4H), 2.08 – 1.99 (m, 2H), 2.03 (dd, *J* = 14.8, 7.4 Hz, 2H), 1.24 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.36, 140.59, 136.13, 126.70, 125.10, 124.10, 83.37, 32.84, 32.44, 25.51, 24.75 ppm. HRMS (EI) m/z calc. $C_{16}H_{23}BO_2$: 281.1697, found: 281.1704.



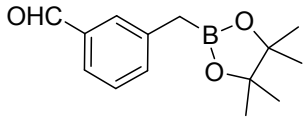
4,4,5,5-tetramethyl-2-(3-nitrobenzyl)-1,3,2-dioxaborolane (3n, 13.7mg, 52% yield):

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 10 : 1) to colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 2.40 (s, 2H), 1.24 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.25, 140.92, 135.33, 128.97, 123.79, 120.19, 83.87, 24.72 ppm.



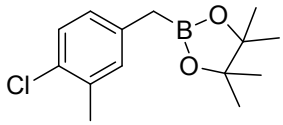
2-([1,1'-biphenyl]-2-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o, 17.9mg, 61% yield, CAS: 792923-26-3)[4]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 7H), 7.20 (dq, *J* = 3.6, 2.8 Hz, 2H), 2.28 (s, 2H), 1.14 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.25, 141.66, 136.55, 130.15, 129.99, 129.51, 128.00, 127.26, 126.68, 125.13, 83.31, 24.73 ppm.



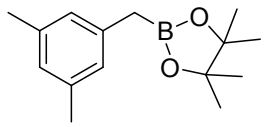
3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzaldehyde (3p, 11.6mg, 47% yield):

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate =10 : 1) to colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.69 (s, 1H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 2.38 (s, 2H), 1.24 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.72, 139.95, 136.50, 135.27, 130.32, 128.88, 126.51, 83.69, 24.72 ppm. HRMS (EI) m/z calc ($M+Na^+$). $C_{14}H_{19}BO_3$: 269.1325, found: 269.1320.



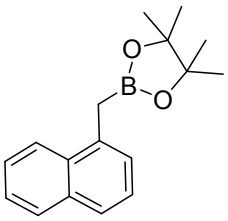
2-(4-chloro-3-methylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q, 18.4mg, 69% yield):

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.1 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.94 (ddd, *J* = 8.1, 2.3, 0.5 Hz, 1H), 2.32 (s, 3H), 2.22 (s, 2H), 1.23 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.14, 135.54, 131.61, 130.77, 128.75, 127.68, 83.52, 24.71, 19.99 ppm. HRMS (EI) m/z calc ($M+Na^+$). $C_{14}H_{20}BClO_2$: 289.1143, found: 289.1149.



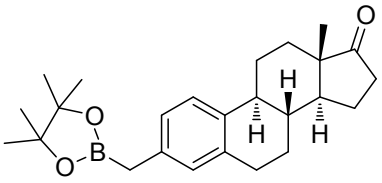
2-(3,5-dimethylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r, 19.4mg, 79% yield，356570 -54-2) [5]:

Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 6.76 (s, 1H), 2.26 (s, 6H), 2.21 (s, 2H), 1.24 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.39, 137.62, 126.87, 126.58, 83.37, 24.72, 21.29 ppm.



4,4,5,5-tetramethyl-2-(naphthalen-1-ylmethyl)-1,3,2-dioxaborolane (3s, 16.6mg, 62%yield, CAS: 475250-57-8)[5]:

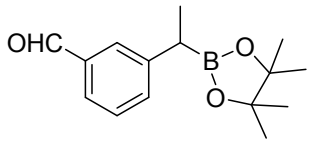
Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1) to colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.36 (q, *J* = 7.3 Hz, 2H), 2.69 (s, 2H), 1.19 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.59, 133.75, 132.43, 128.50, 126.44, 125.76, 125.36, 125.33, 124.51, 83.53, 24.66 ppm.



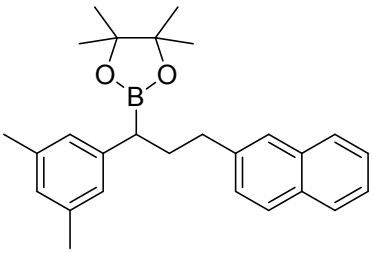
(8R,9S,13S,14S)-13-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (3t, 20.5 mg, 54% yield): Synthesized according to typical procedure and purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.91 (s, 1H), 2.91 – 2.84 (m, 2H), 2.50 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.27 (d, *J* = 10.4 Hz, 1H), 2.23 (s, 2H), 2.15 (dd, *J* = 18.4, 9.3 Hz, 1H), 2.10 – 1.95 (m, 3H), 1.68 – 1.39 (m, 7H), 1.25 (s, 12H), 0.90 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.19, 136.13, 135.88, 129.67, 126.49, 125.25, 83.39, 50.51, 48.03, 44.25, 38.24, 35.88, 31.62, 29.34, 26.60, 25.72, 24.75, 21.59, 13.86 ppm. HRMS (EI) m/z calc ($M+Na^+$). $C_{25}H_{35}BO_3$: 417.2577, found: 417.2578.

Experimental Procedures for Examples Described in Table 3.

General Procedure B In air, $Pd(OAc)_2$(2.2mg, 0.01mmol), PPh_3(5.2mg, 0.02mmol), and 1,1-diborylalkanes (40.2mg, 0.15mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (this process was repeated three times).Dioxane (0.5 mL), 1M TBAOH (0.3ml,0.3mmol) were added in turn by syringe under argon atmosphere at room temperature, and then stirred at rt for 1 min. And aryl triflate (0.1 mmol) was added in turn by syringe under argon atmosphere. The resulting reaction mixture was stirred vigorously at rt over night. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings (Et_2O or EtOAc), concentrated, and purified by column chromatography .

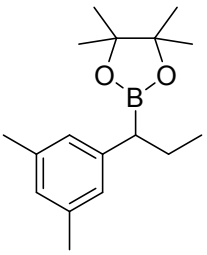


3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzaldehyde (4a, 17.4 mg, 67%yield): Following general procedure B, 1,1-diborylethane and 3-formylphenyl triflates were used; The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a pale colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.74 (s, 1H), 7.67 (dt, *J* = 7.4, 1.3 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 2.54 (q, *J* = 7.5 Hz, 1H), 1.37 (d, *J* = 7.5 Hz, 3H), 1.21 (d, *J* = 4.3 Hz, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.84, 146.15, 136.53, 134.22, 129.05, 128.90, 126.76, 83.56, 24.61, 24.57, 16.76 ppm. HRMS (EI) m/z calc ($M+Na^+$). $C_{14}H_{19}BO_3$: 283.1545, found: 269.1551.



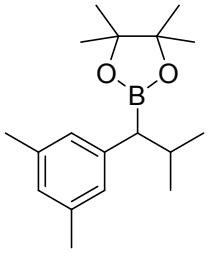
2-(1-(3,5-dimethylphenyl)-3-(naphthalen-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b, 32.4mg, 81% yield):

Following general procedure B, 1,1-diborylnaphthylethyl and 3,5-dimethylphenyl triflates were used; The product was isolated by flash chromatography (20% ethyl acetate/hexane) as a pale colorless oil. ^{1}H NMR (400 MHz, CDCl3) δ 8.06 – 7.99 (m, 1H), 7.81 (td, J = 6.8, 3.7 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.39 – 7.33 (m, 1H), 7.29 (d, J = 6.6 Hz, 1H), 6.88 (s, 2H), 6.80 (s, 1H), 3.11 – 2.95 (m, 2H), 2.41 (dd, J = 14.8, 6.9 Hz, 1H), 2.33 – 2.21 (m, 7H), 2.12 – 2.00 (m, 1H), 1.23 (t, J = 7.1 Hz, 12H) ppm. ^{13}C NMR (101 MHz, CDCl3) δ 142.65, 138.96, 137.64, 133.83, 131.90, 128.59, 127.05, 126.38, 126.24, 125.99, 125.52, 125.27, 124.18, 83.33, 34.04, 32.96, 24.65, 24.64, 21.35 ppm. ($M+Na^+$). $C_{27}H_{33}BO_2$:423.3615, found: 423.3622. HRMS (EI) m/z calc ($M+H^+$). $C_{17}H_{27}BO_2$,found: 275.2181.



2-(1-(3,5-dimethylphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c, 19.6mg, 72%):

Following general procedure B, 2,2'-(propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and 3,5-dimethylphenyl triflates were used; The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a pale colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 2H), 6.77 (s, 1H), 2.27 (s, 6H), 2.14 (t, *J* = 7.9 Hz, 1H), 1.90 – 1.78 (m, 1H), 1.63 (tt, *J* = 14.6, 7.3 Hz, 1H), 1.21 (d, *J* = 7.8 Hz, 12H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.18 (s), 137.51 (s), 126.87 (s), 126.25 (s), 83.18 (s), 25.94 (s), 24.62 (s), 24.61 (s), 21.35 (s), 14.05 (s) ppm. HRMS (EI) m/z calc ($M+H^+$). $C_{18}H_{29}BO_2$,found: 289.2337.



2-(1-(3,5-dimethylphenyl)-2-methylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(4d, 18.7mg, 65%):

Following general procedure B, 2,2'-(2-methylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and 3,5-dimethylphenyl triflates were used; The product was isolated by flash chromatography (10% ethyl acetate/hexane) as a pale white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 2H), 6.76 (s, 1H), 2.26 (s, 6H), 2.07 (tt, *J* = 17.0, 6.5 Hz, 1H), 1.88 (d, *J* = 10.4 Hz, 1H), 1.19 (d, *J* = 7.0 Hz, 12H), 1.02 (d, *J* = 6.5 Hz, 3H), 0.73 (d, *J* = 6.5 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.02 (s), 137.29 (s), 126.96 (s), 126.84 (s), 83.10 (s), 30.94 (s), 24.67 (s), 24.49 (s), 23.17 (s), 22.08 (s), 21.35 (s) ppm.

Experimental Procedures for Examples Described in Scheme 3.

General Procedure C In air, $Pd(OAc)_2$(2.2mg, 0.01mmol), PPh_3(5.2mg, 0.02mmol), and diborylmethanes (40.2mg, 0.15mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (this process was repeated three times).Dioxane (0.5 mL), 1M TBAOH (0.3ml,0.3mmol) were added in turn by syringe under argon atmosphere at room temperature, and then stirred at rt for 1 min. And 4-bromophenyl triflate (0.1 mmol) was added in turn by syringe under argon atmosphere. The resulting reaction mixture was stirred vigorously at rt over night. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings (Et_2O or EtOAc), concentrated, and purified by column chromatography .

IV. References

[1] L. J. Goossen, C. Linder, N. Rodríguez, P. P. Lange. *Chem. Eur. J.* **2009**, *15*, 9336–9349.

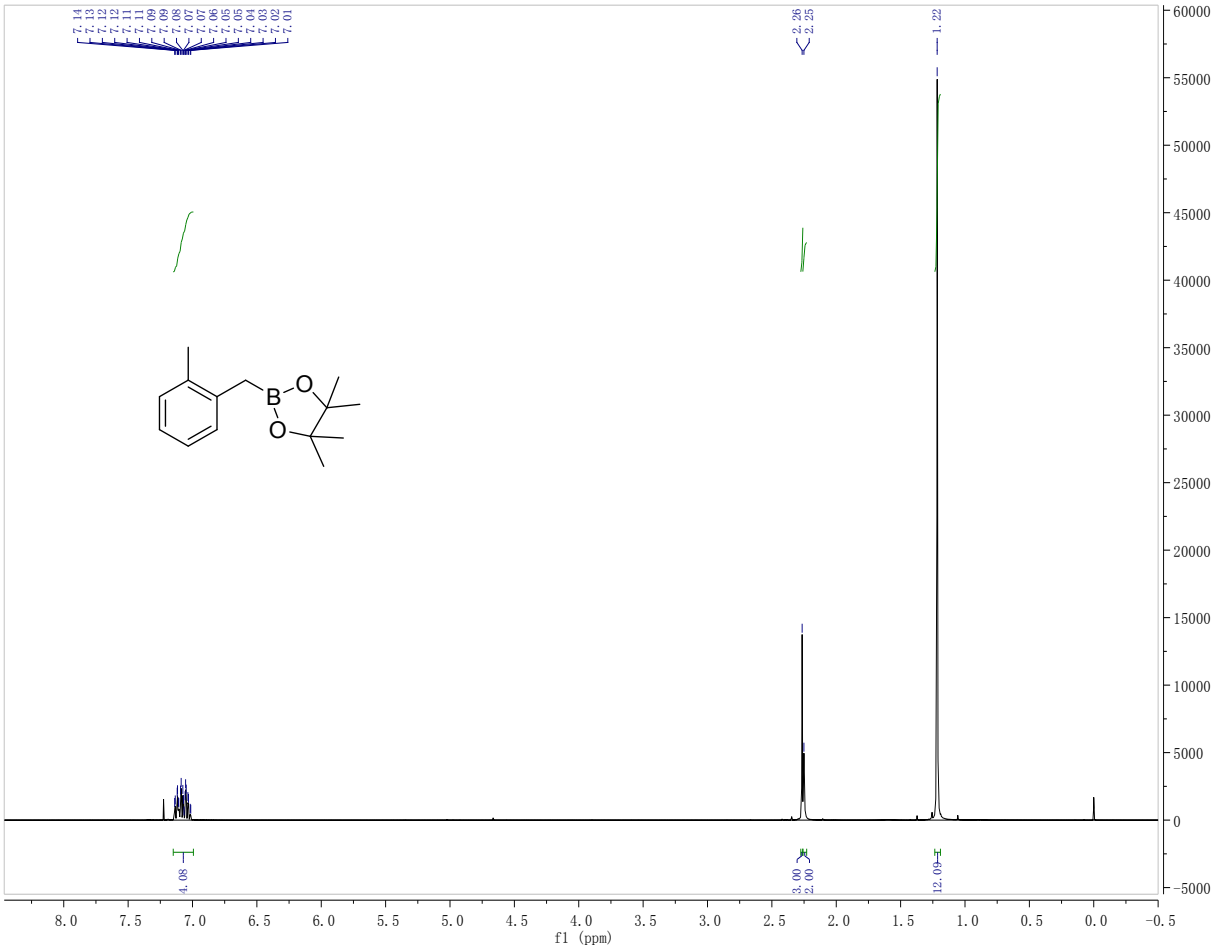
[2] Zhang, Zhen-Qi; Yang, Chu-Ting; Liang, Lu-Jun. *Org. Lett.* **2014**,16, 6342.

[3] Matteson, D. S, Moody, R. J. *Organometallics*.**1982**,1,20.

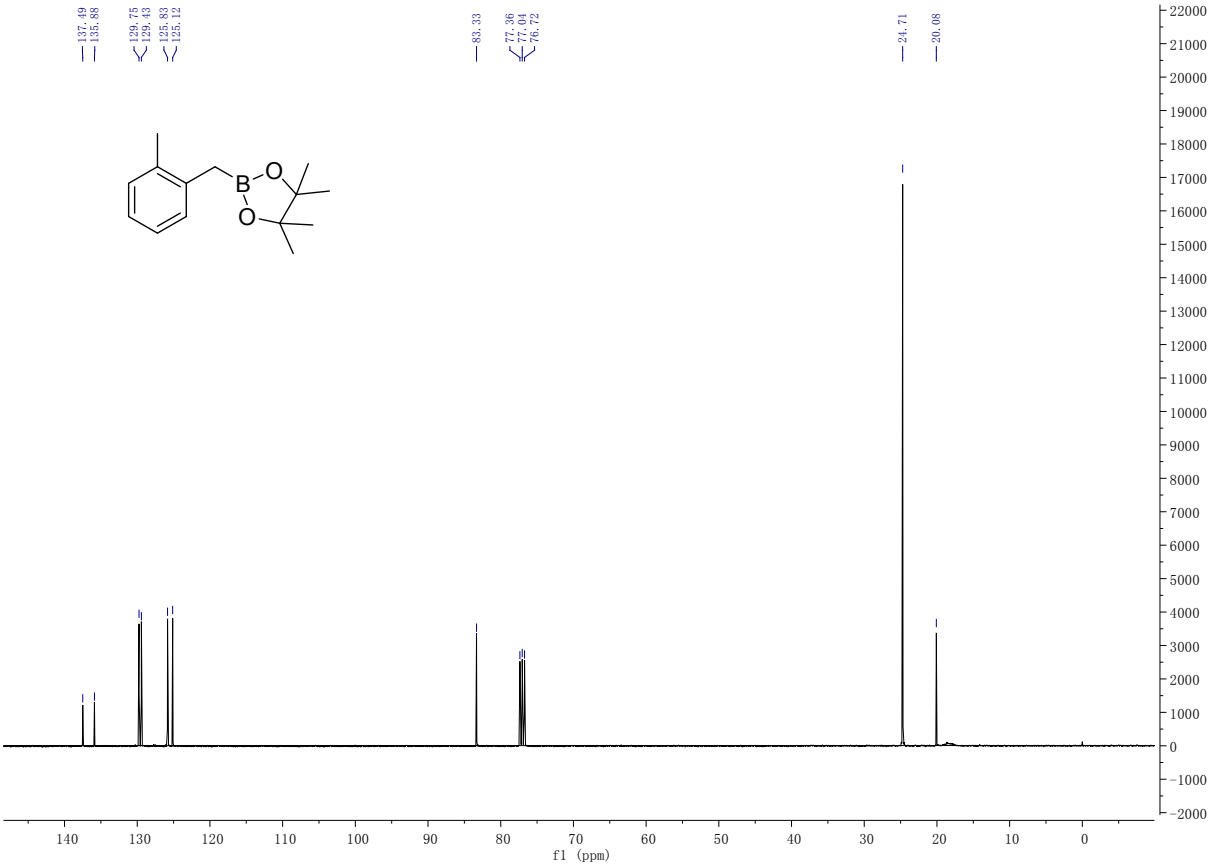
[4] Endo, K.; Ohkubo, T.; Shibata. T. *Org. Lett.* **2011**, 13, 3368.

[5] Matthew A. Larsen, Conner V. Wilson, John F. Hartwig. *J. Am. Chem. Soc.* **2015**, *137*, 8633.

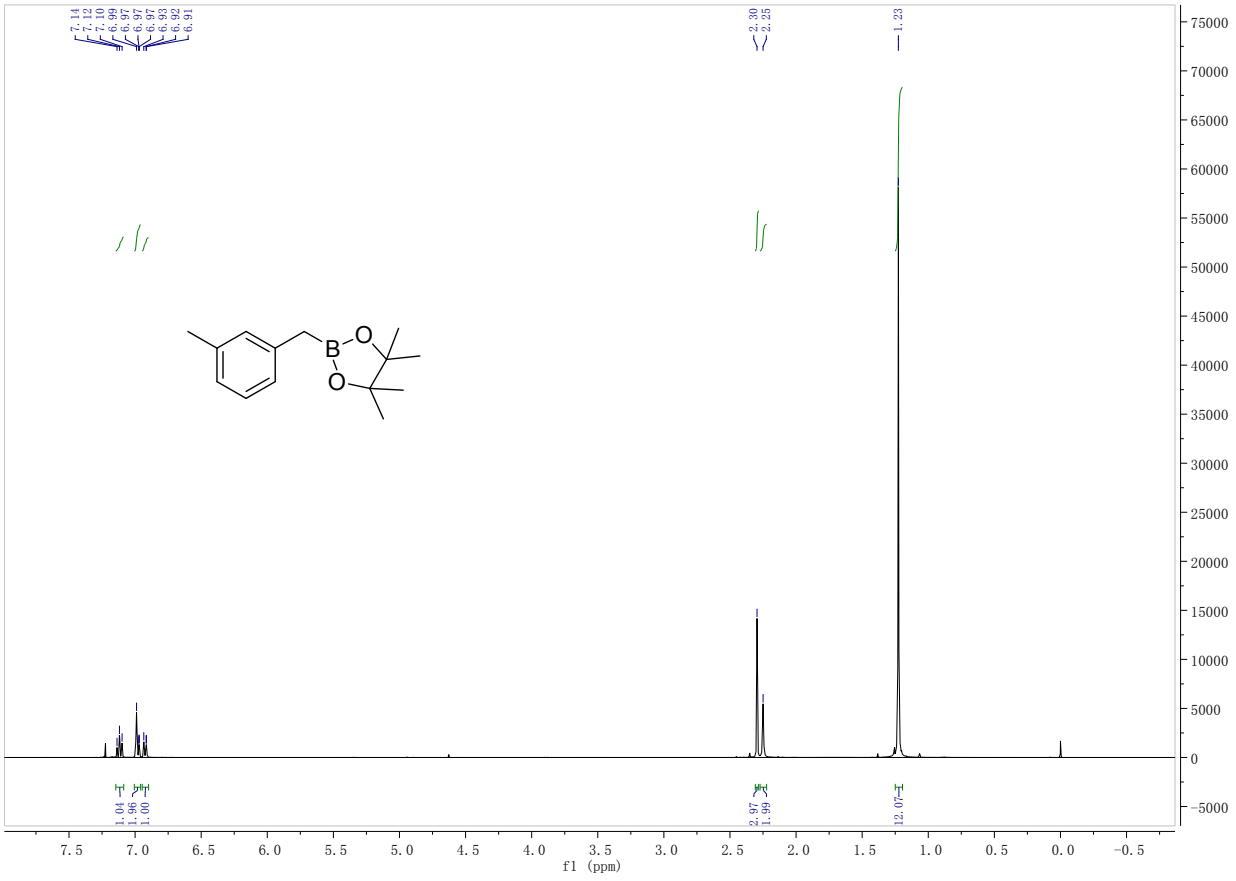
V. NMR Spectra



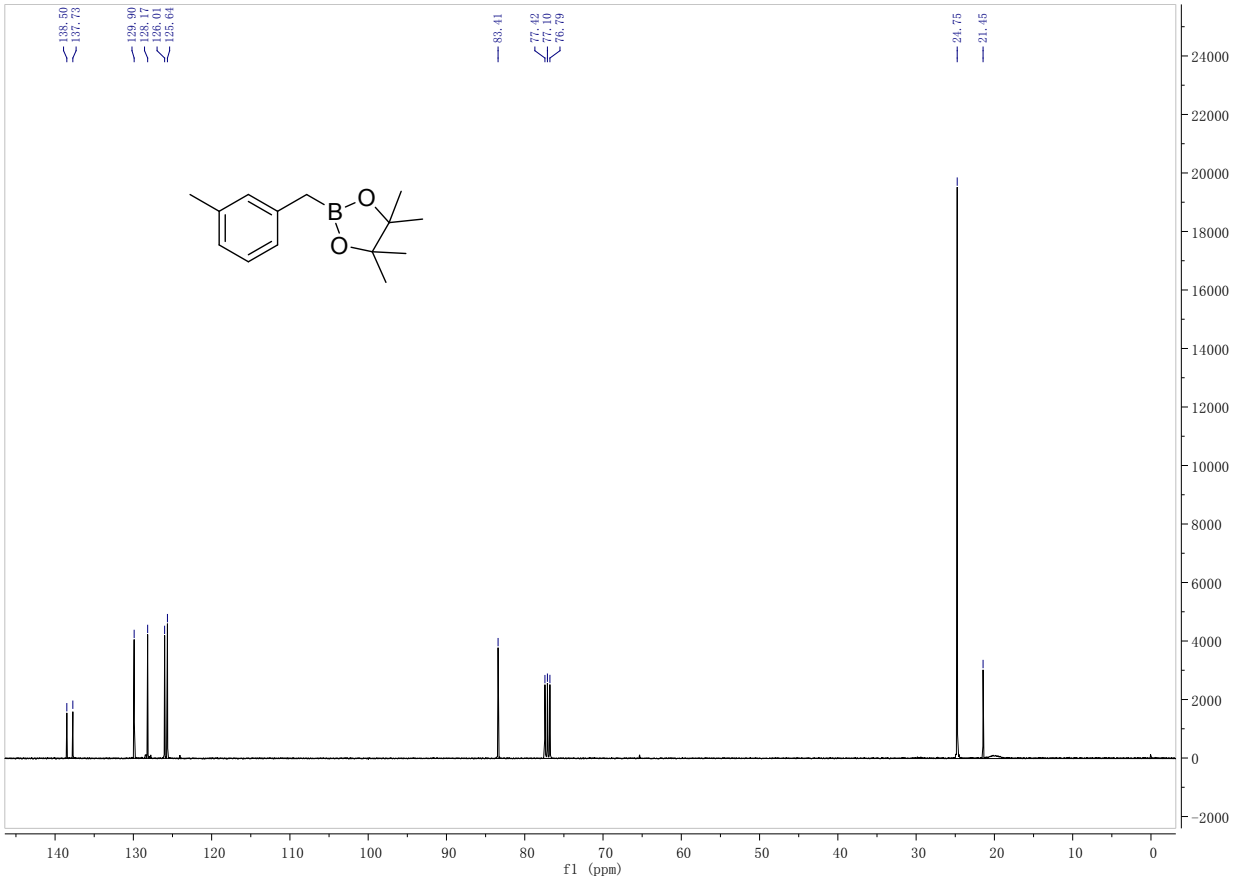
^{1}H NMR spectra for 3b



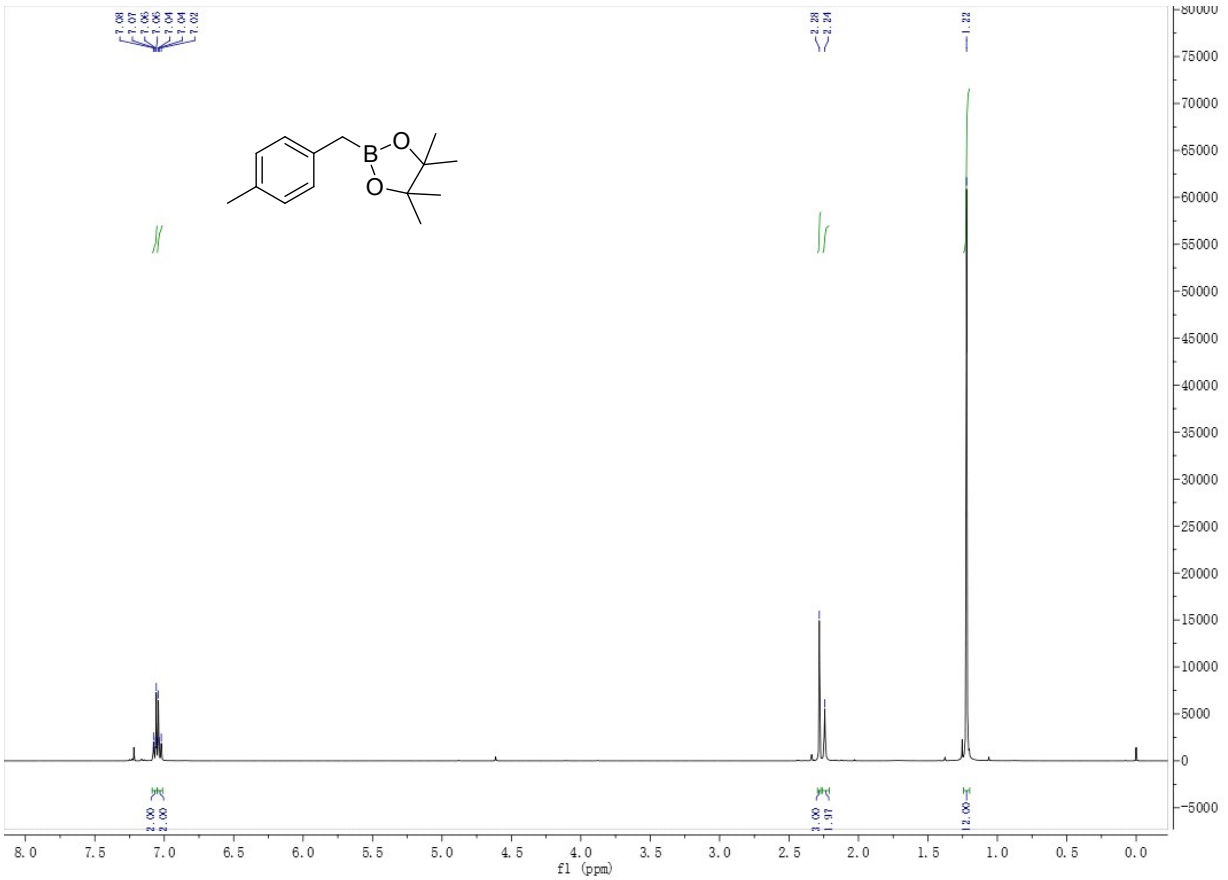
^{13}C NMR spectra for 3b



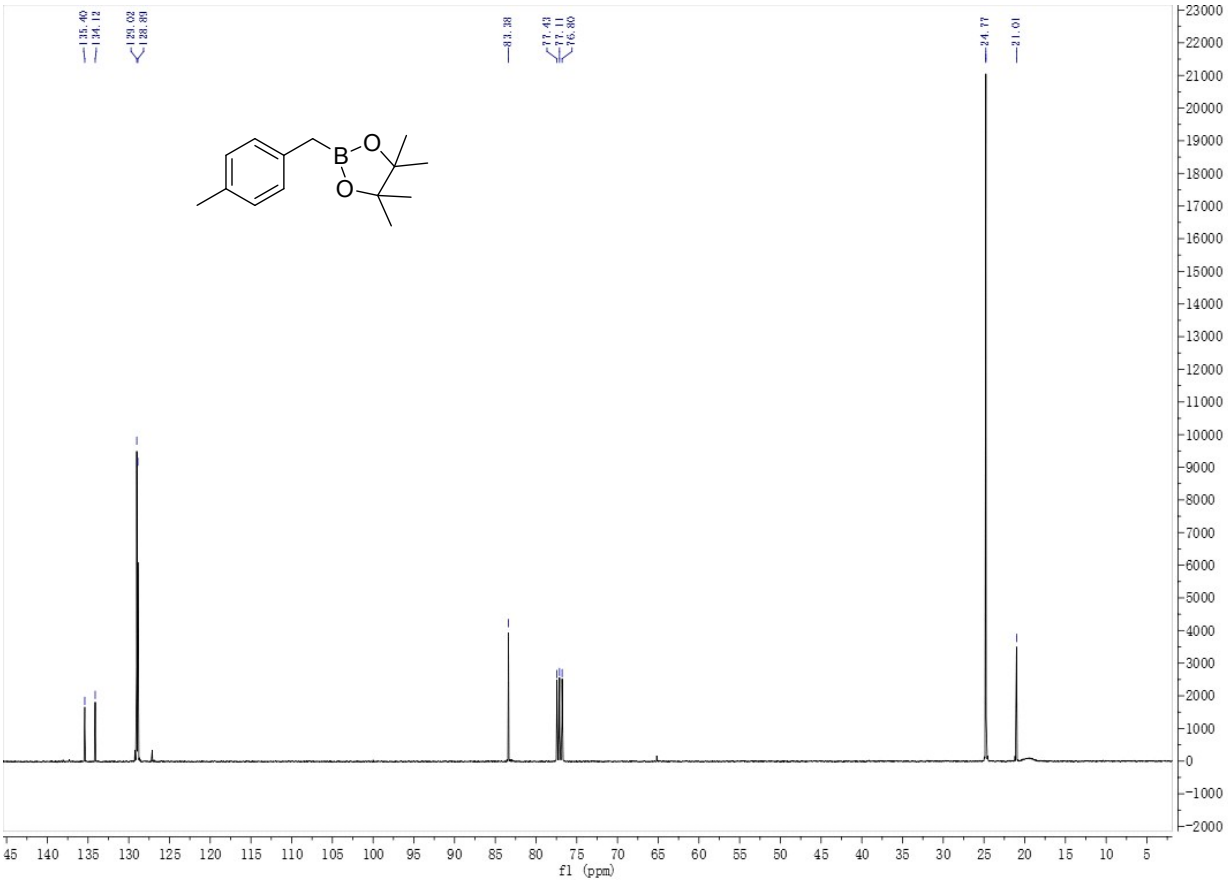
^{1}H NMR spectra for 3c



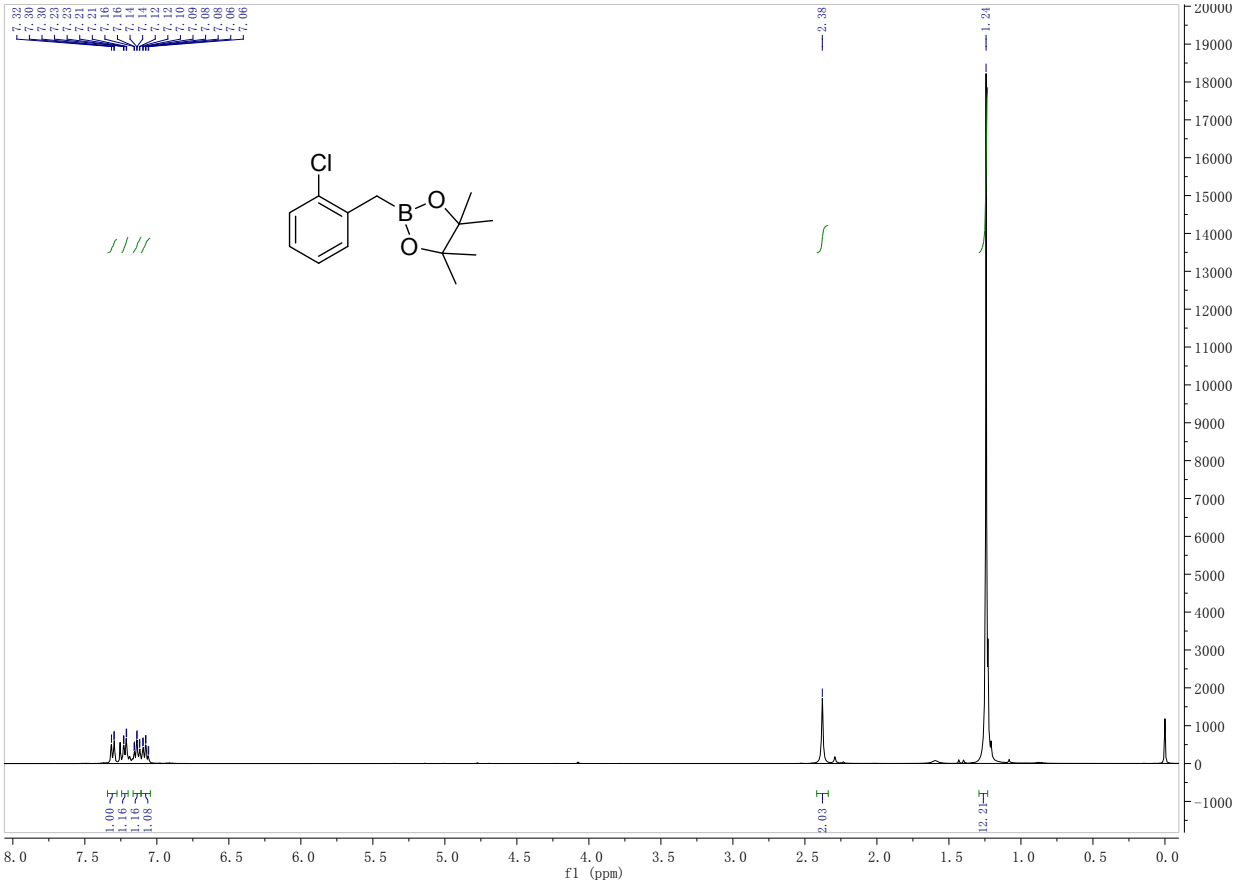
^{13}C NMR spectra for 3c



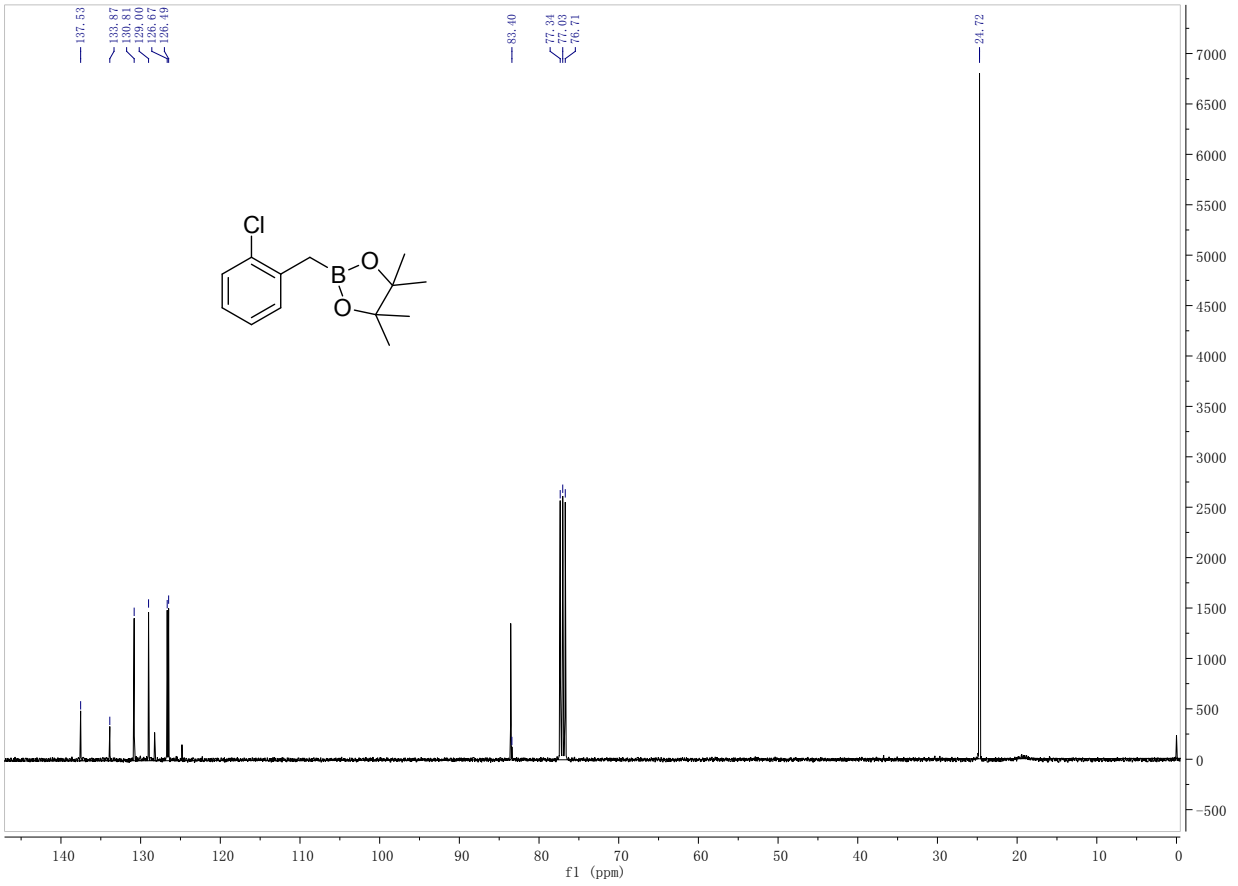
^{1}H NMR spectra for 3d



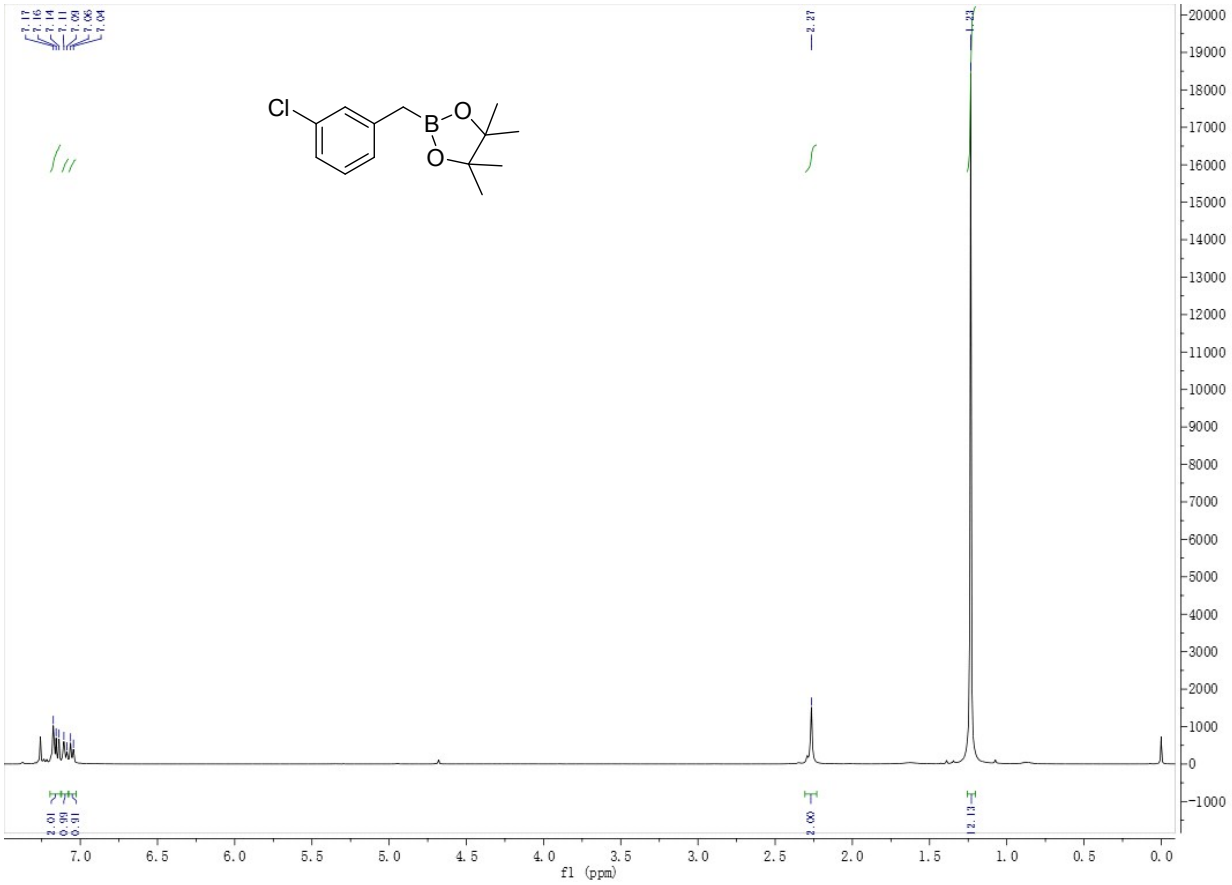
^{13}C NMR spectra for 3d



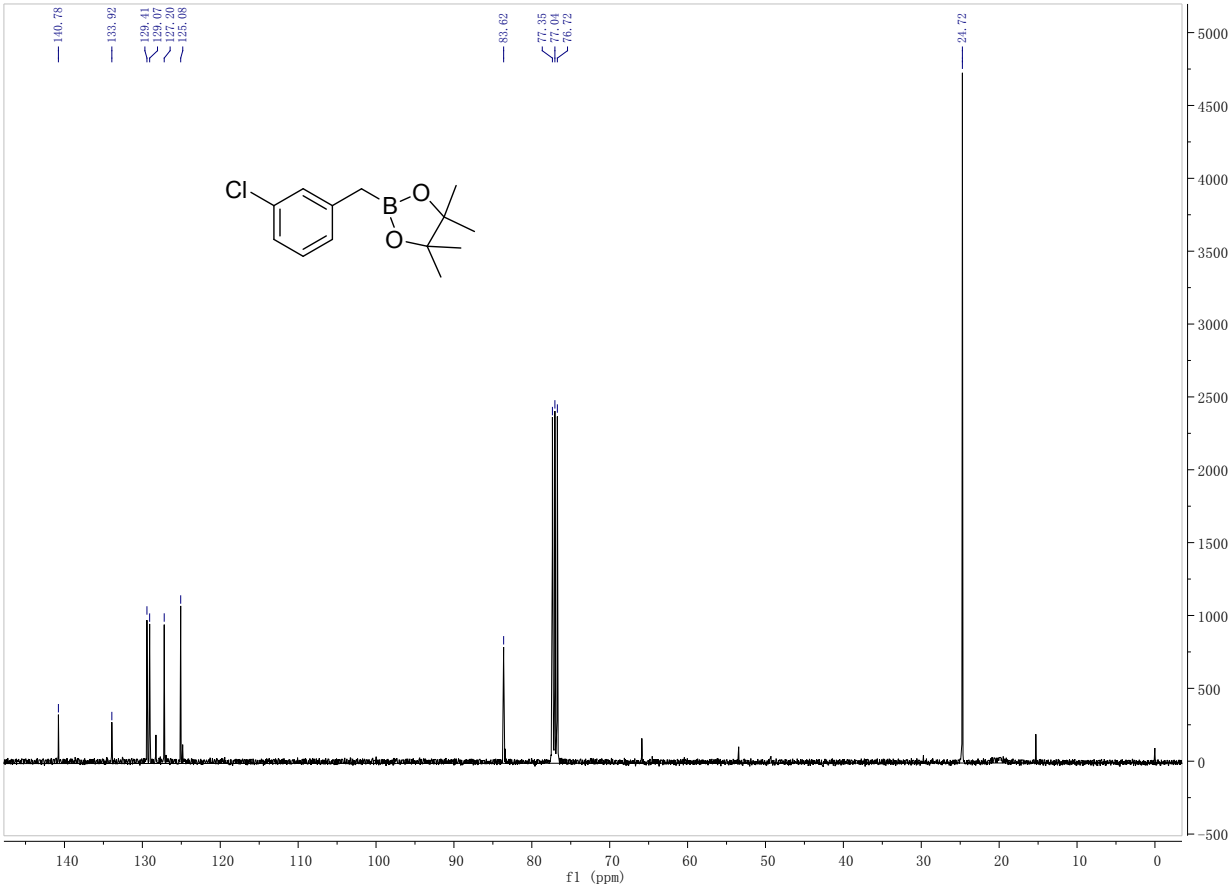
^{1}H NMR spectra for 3e



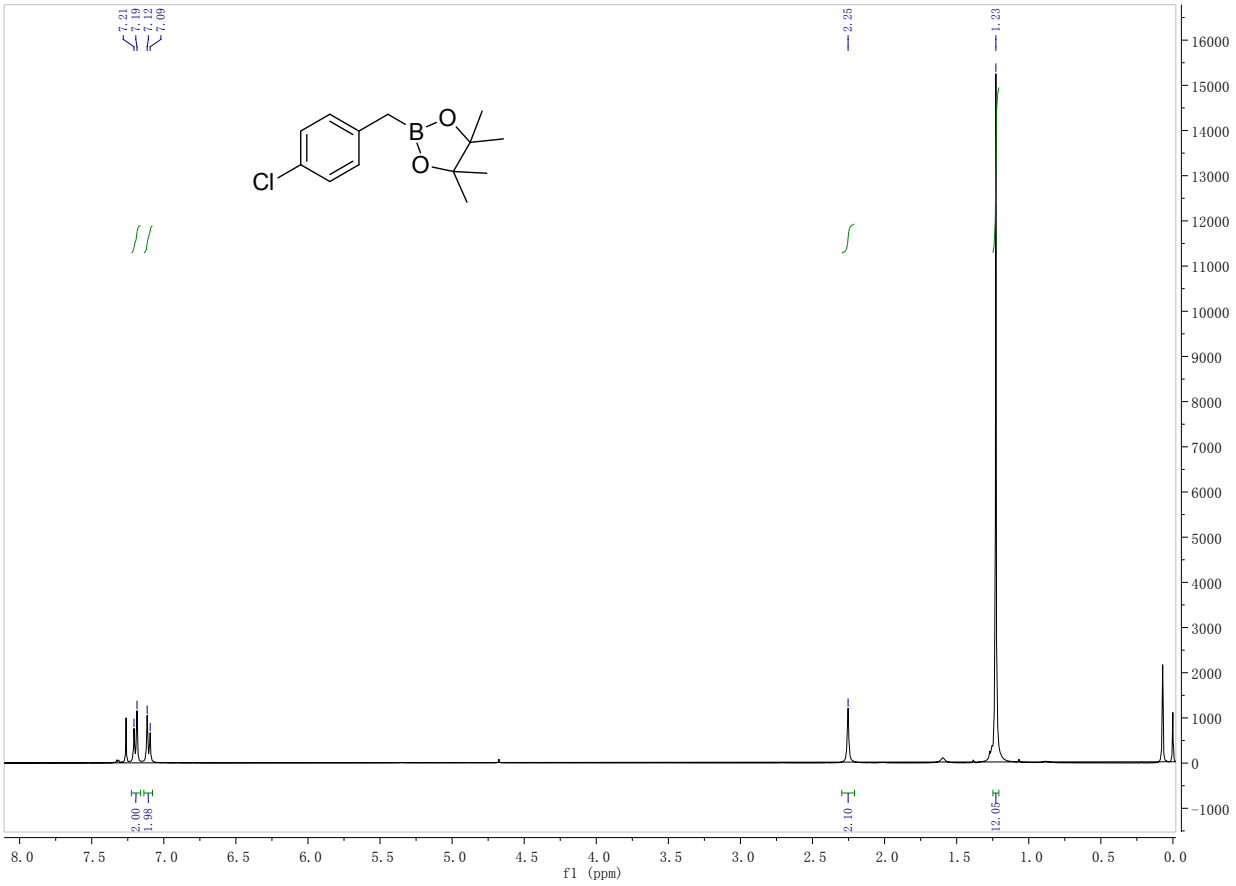
^{13}C NMR spectra for 3e



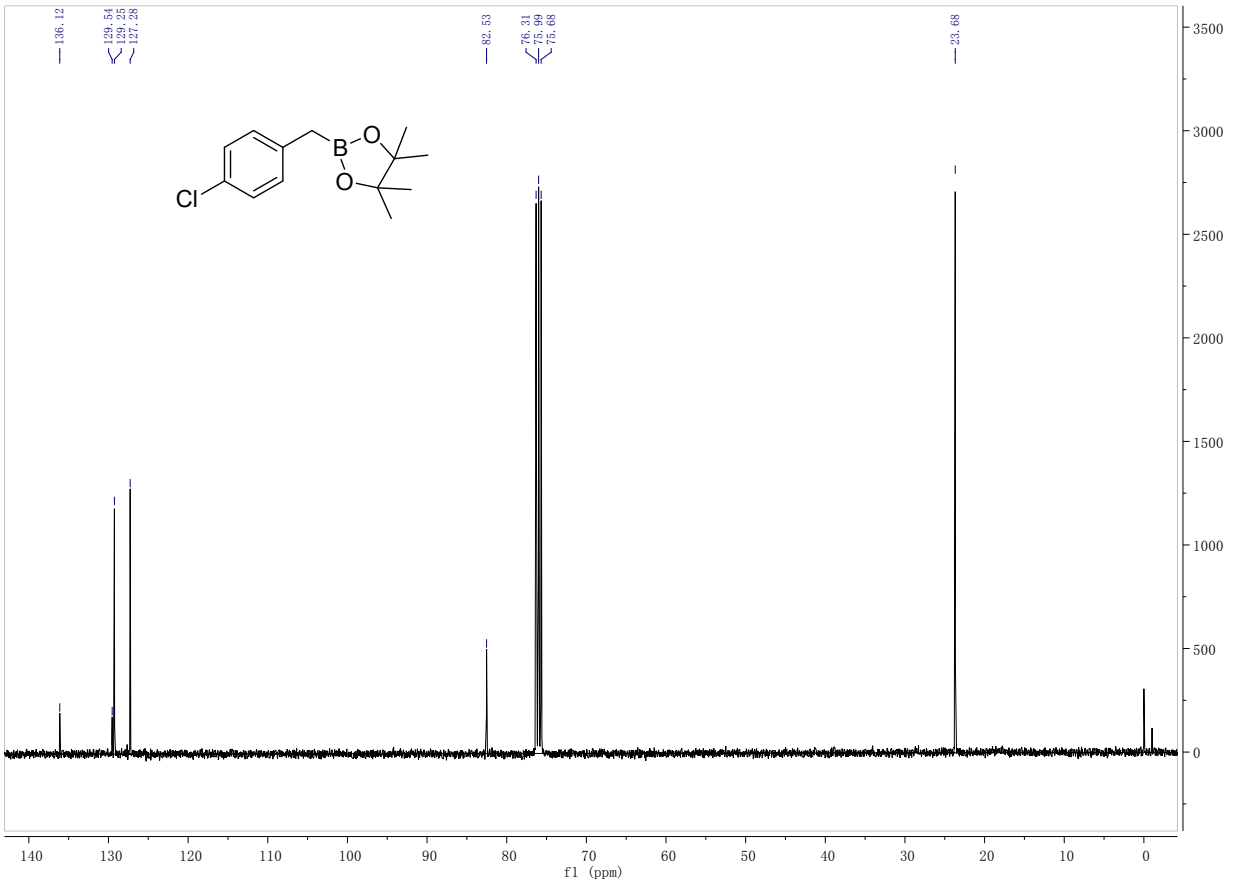
^{1}H NMR spectra for 3f



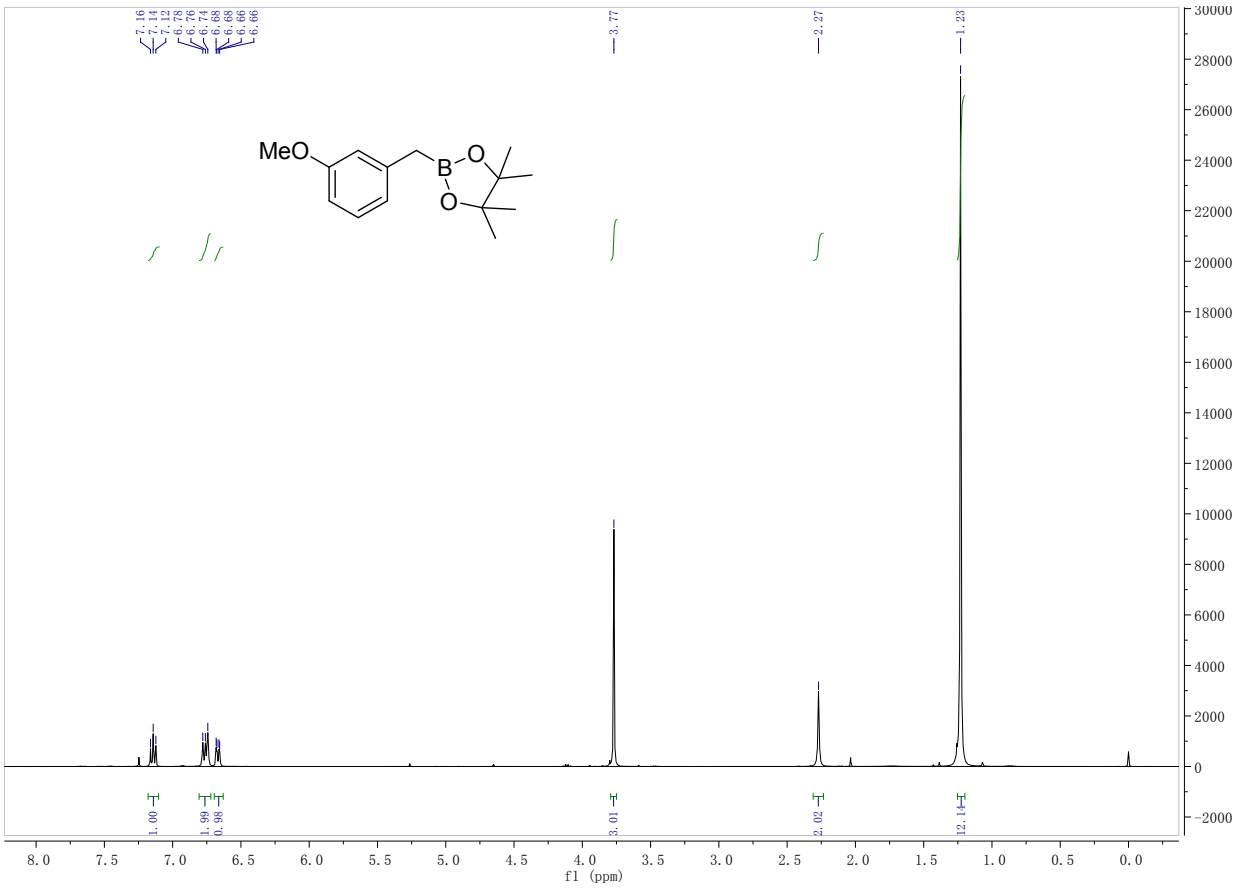
^{13}C NMR spectra for 3f



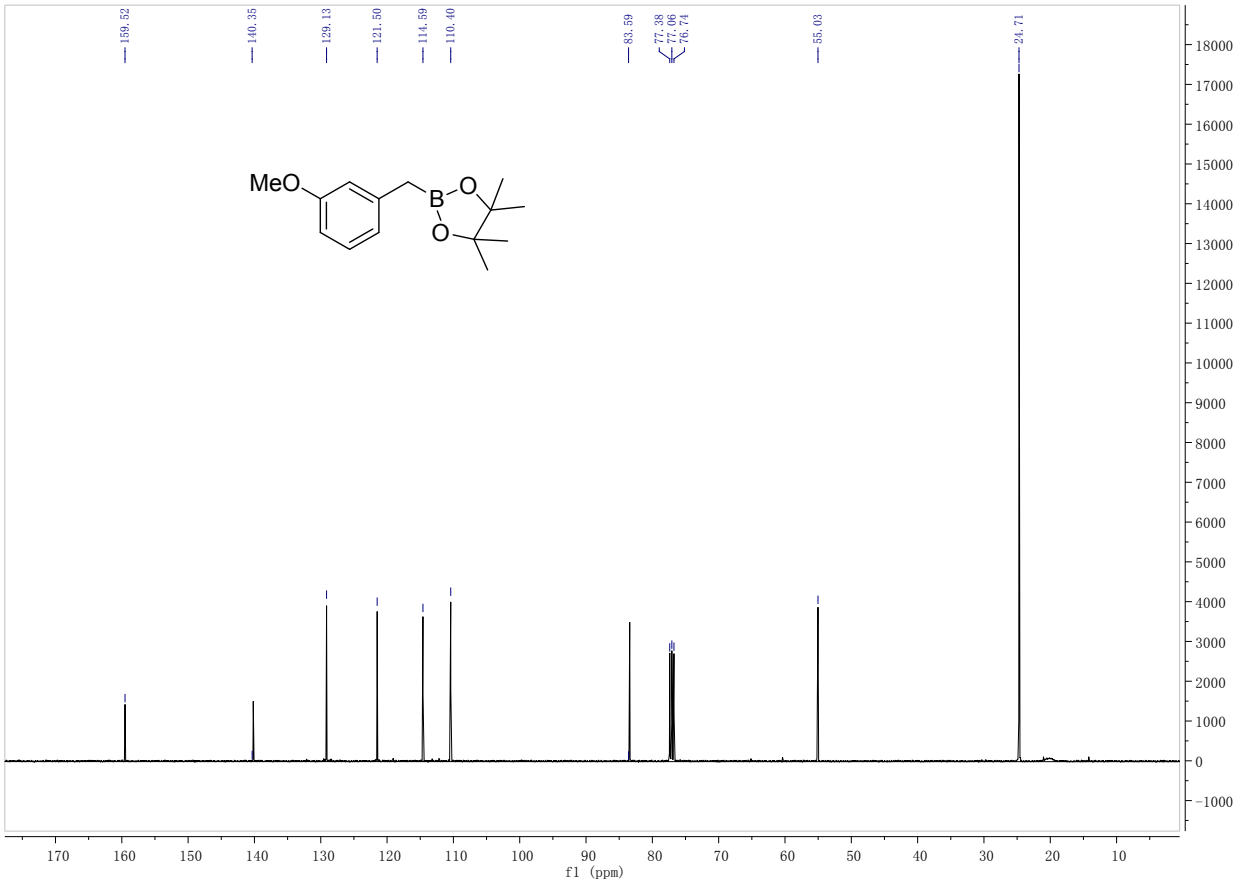
^{1}H NMR spectra for 3g



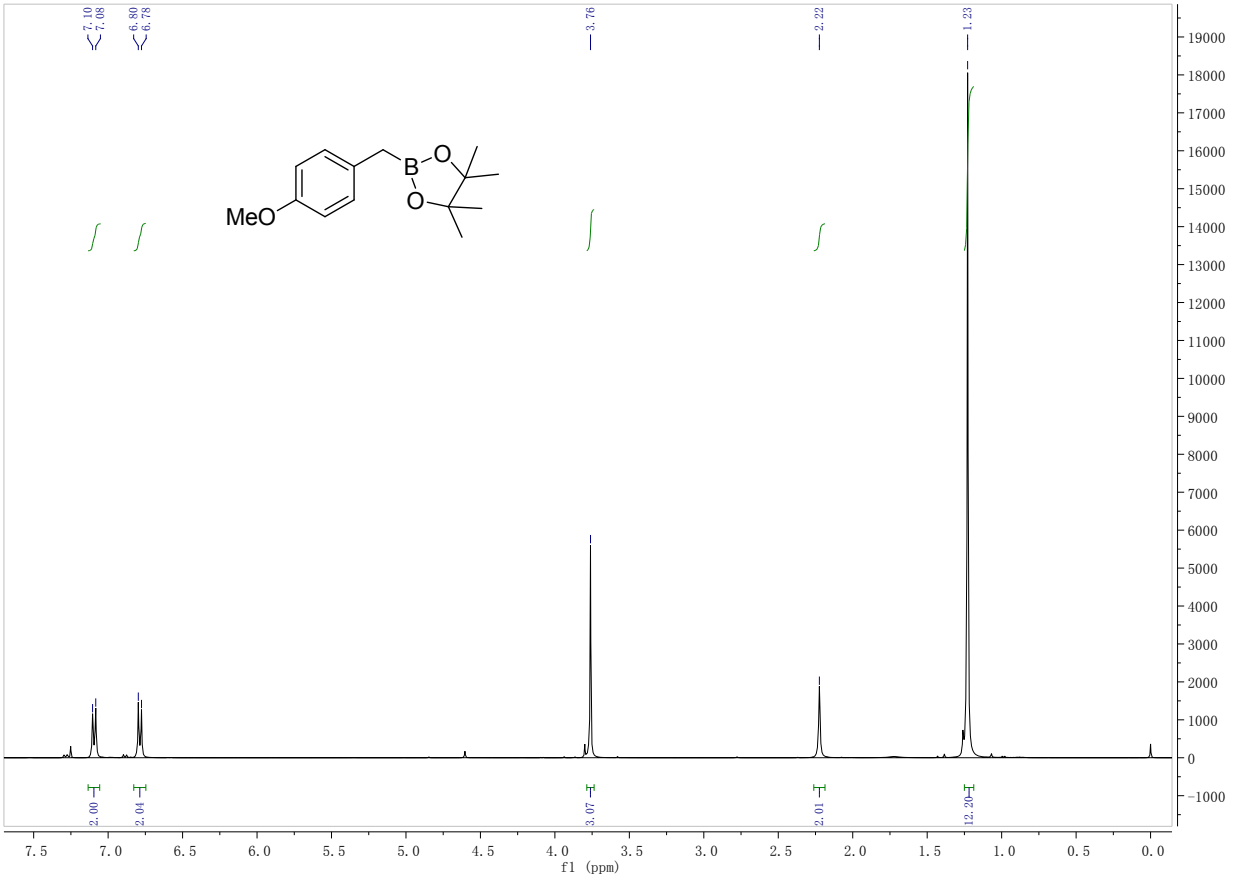
^{13}C NMR spectra for 3g



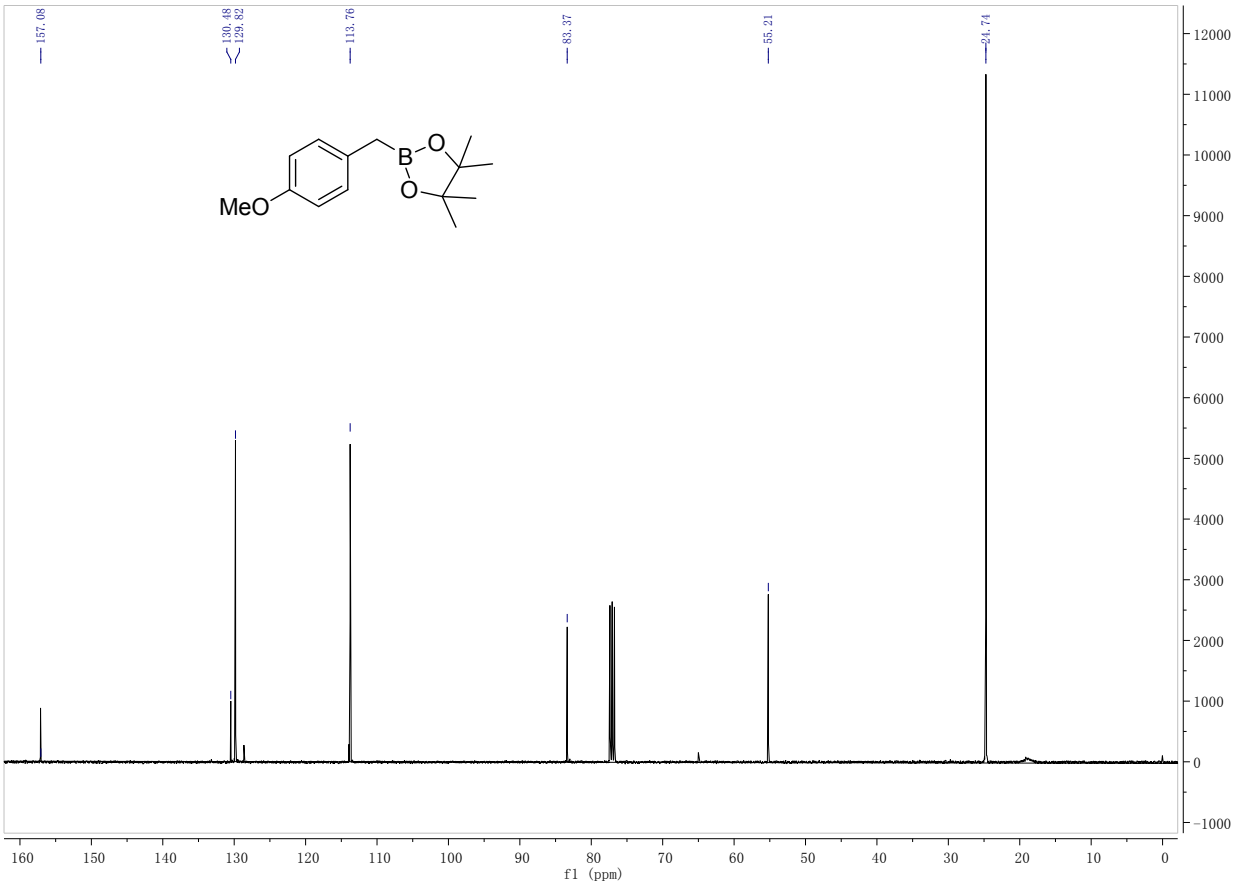
^{1}H NMR spectra for 3h



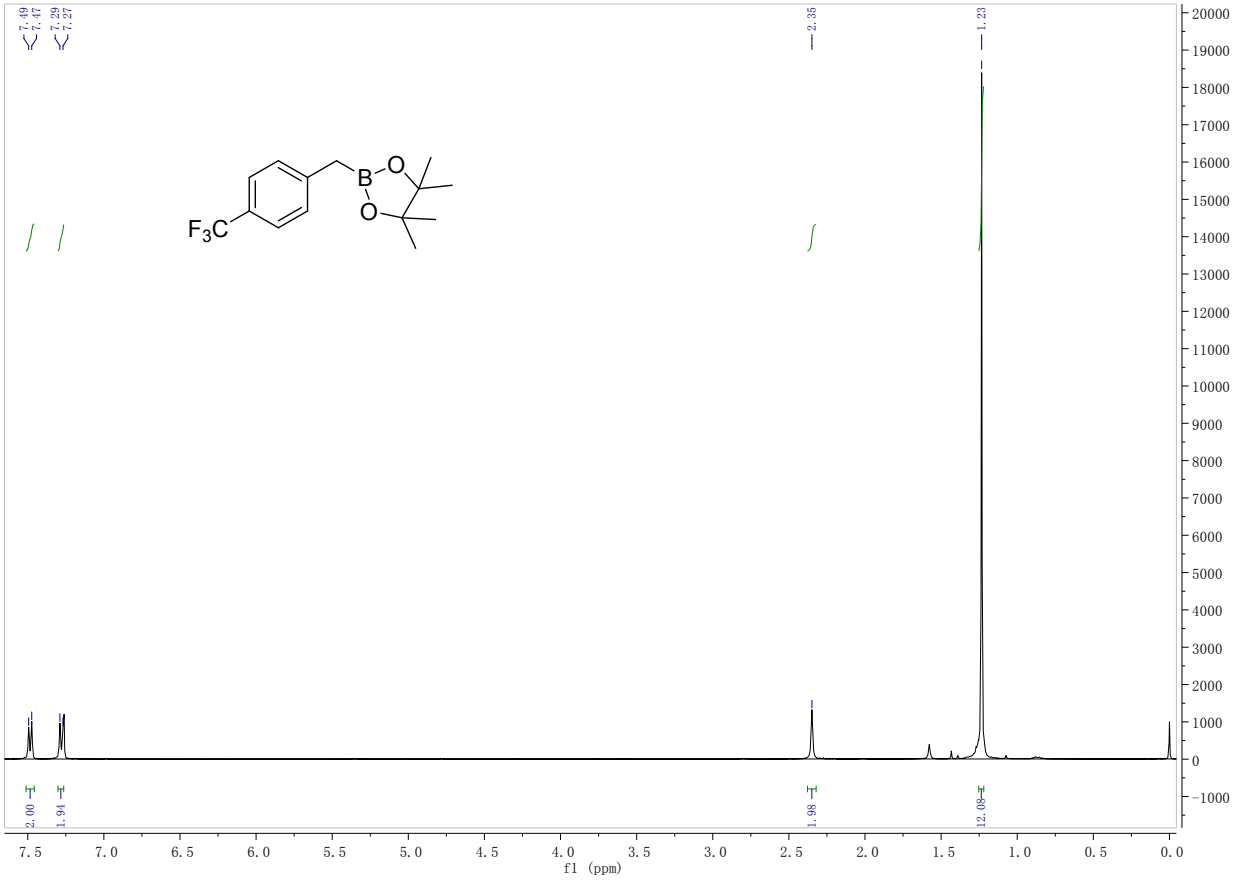
^{13}C NMR spectra for 3h



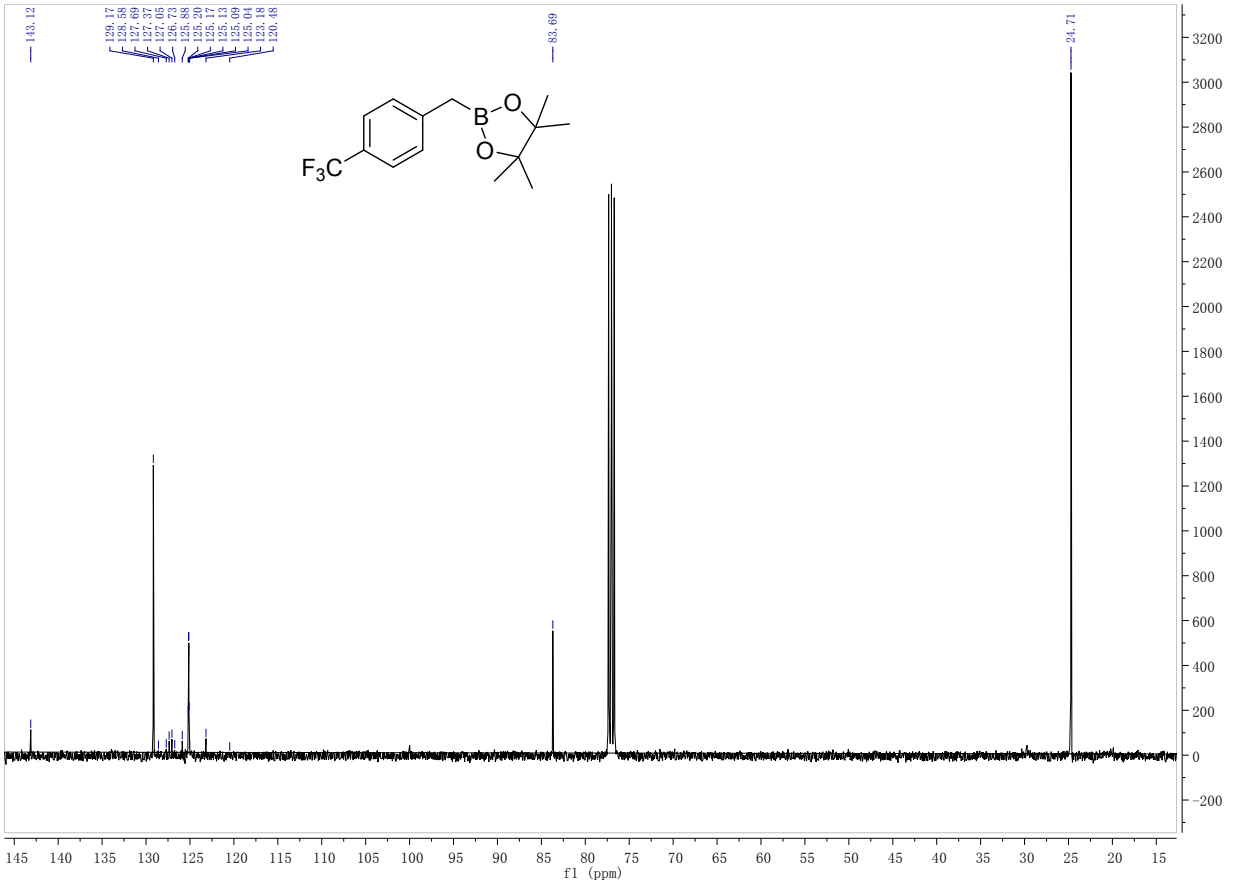
^{1}H NMR spectra for 3i



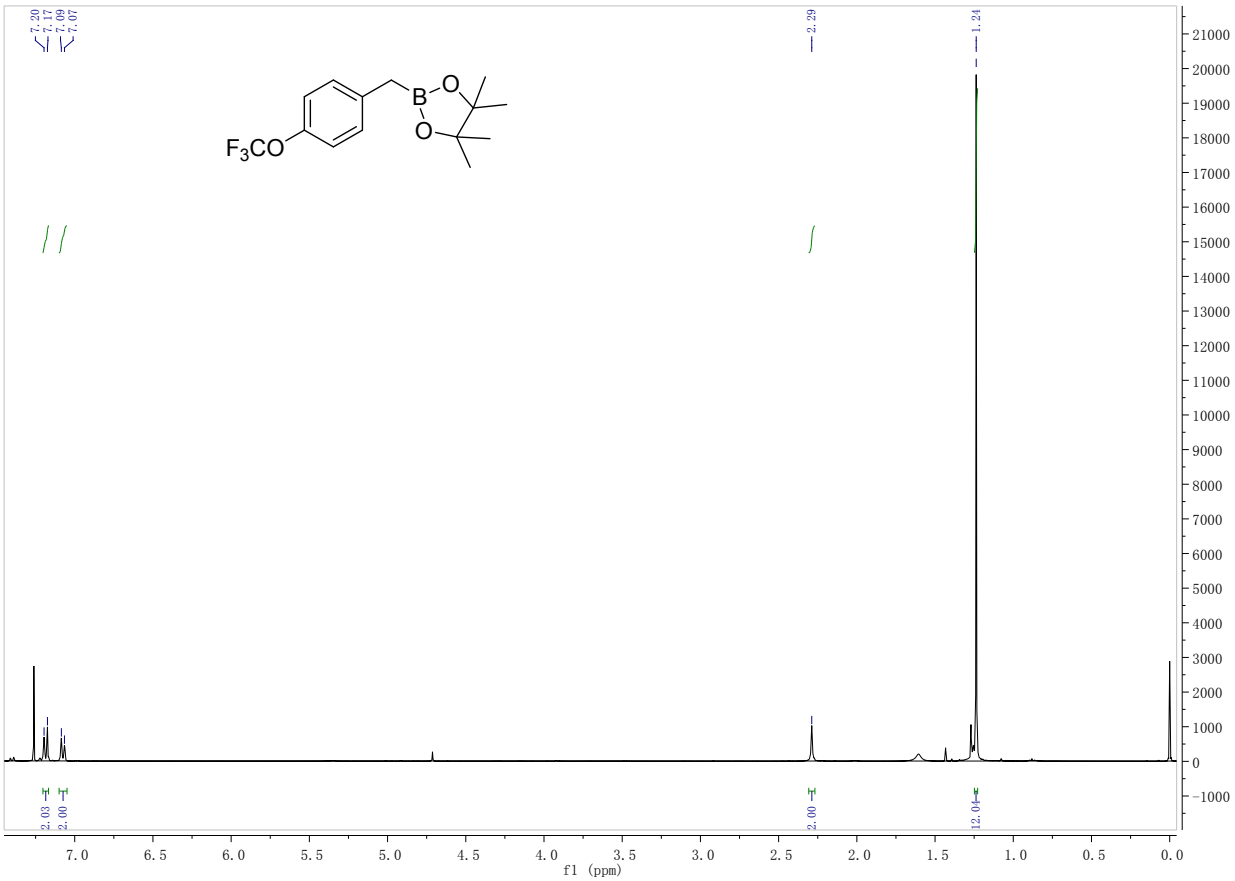
^{13}C NMR spectra for 3i



^{1}H NMR spectra for 3j



^{13}C NMR spectra for 3j



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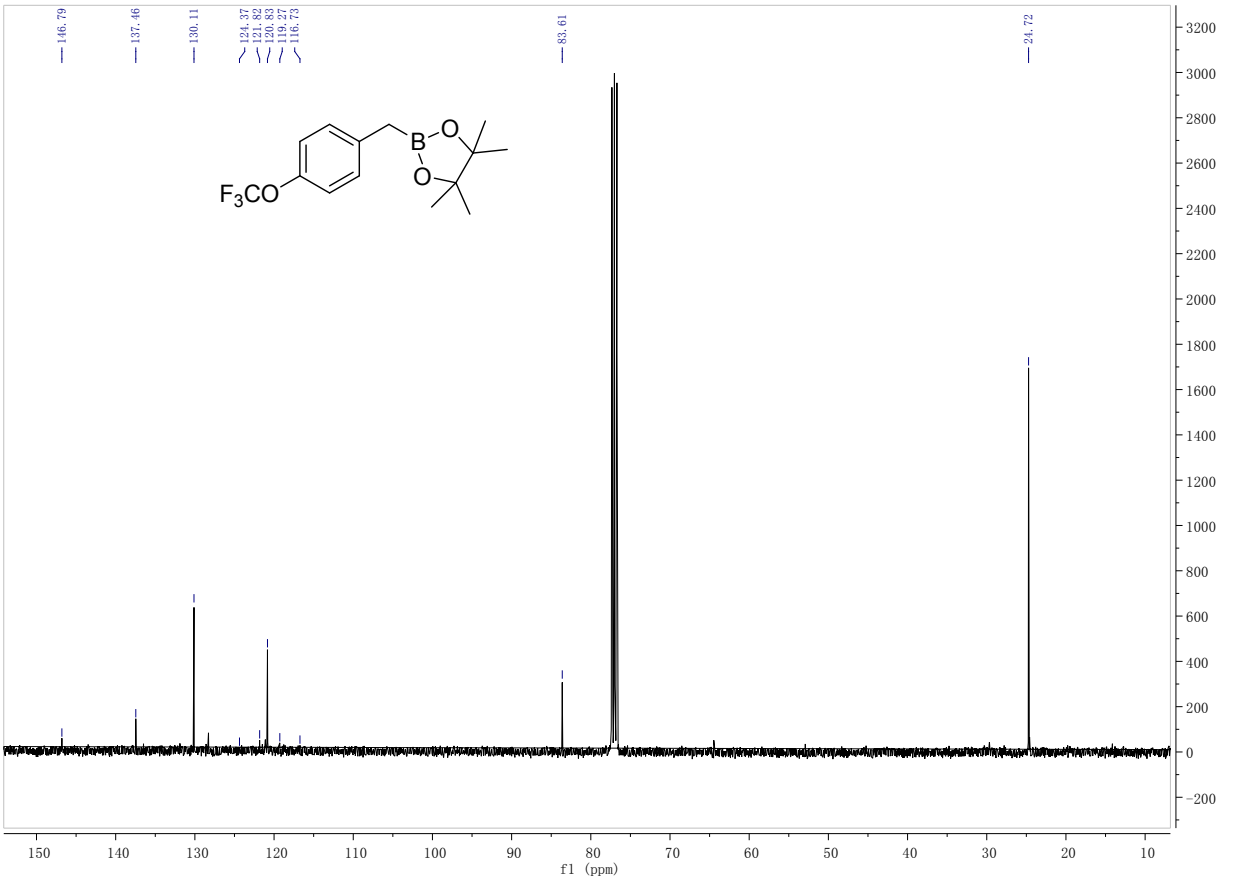
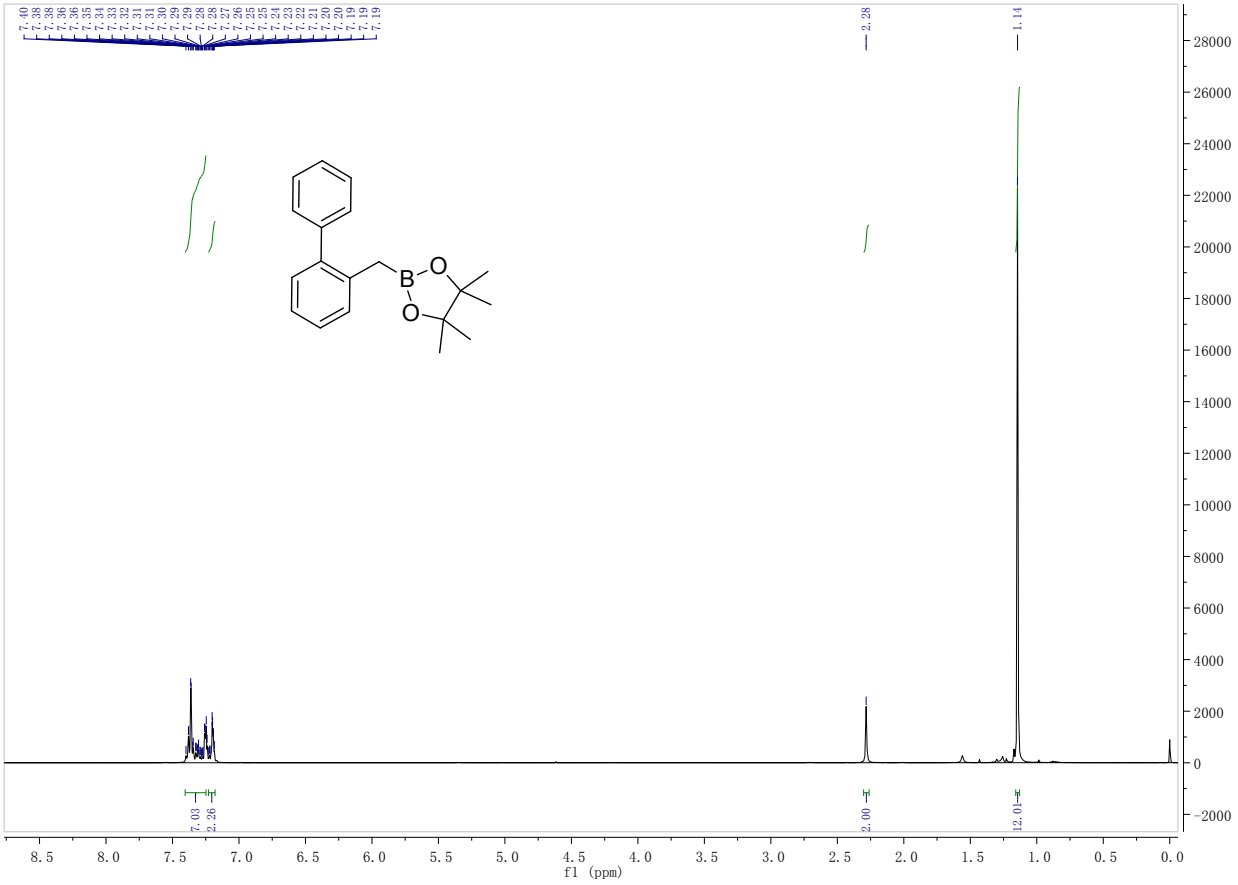
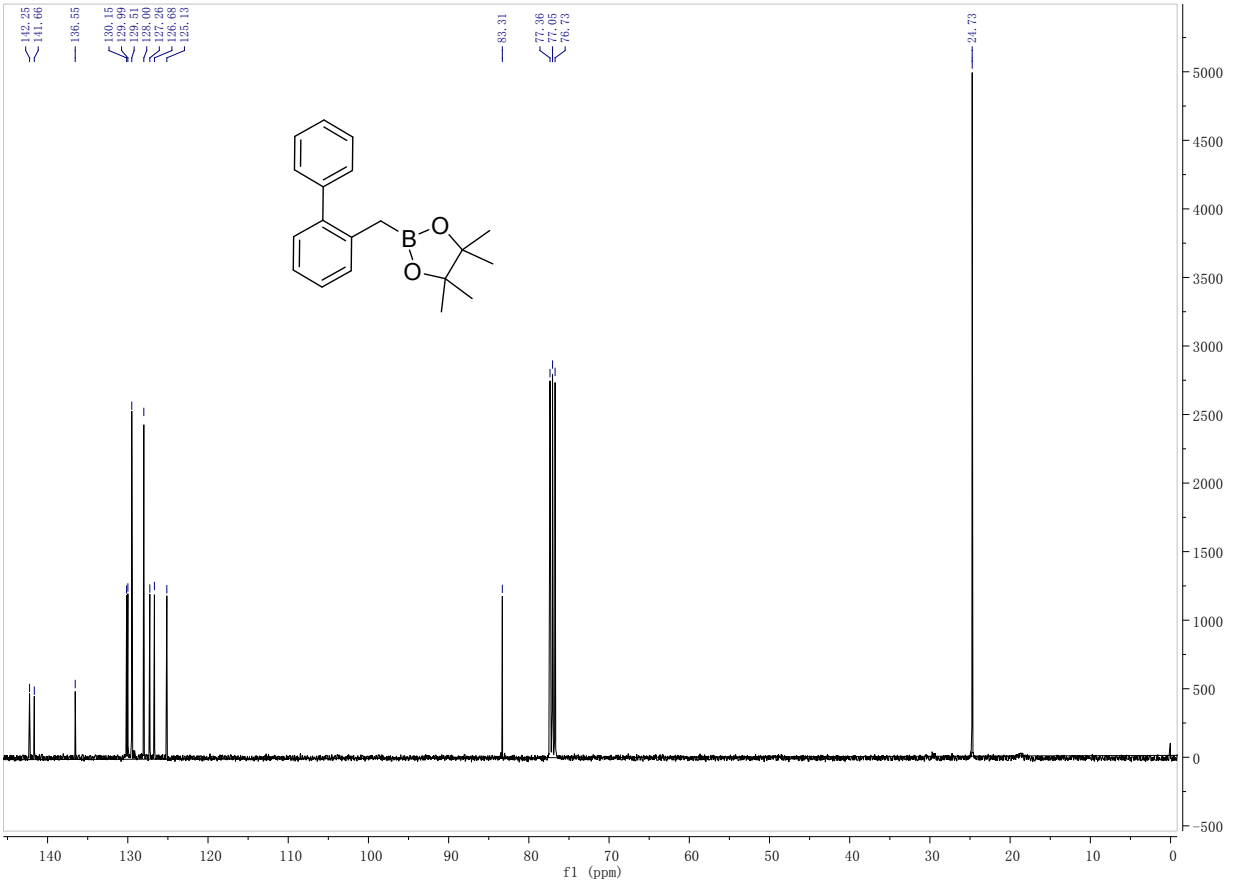


^{13}C NMR spectra for 3k



^{1}H NMR spectra for 3l



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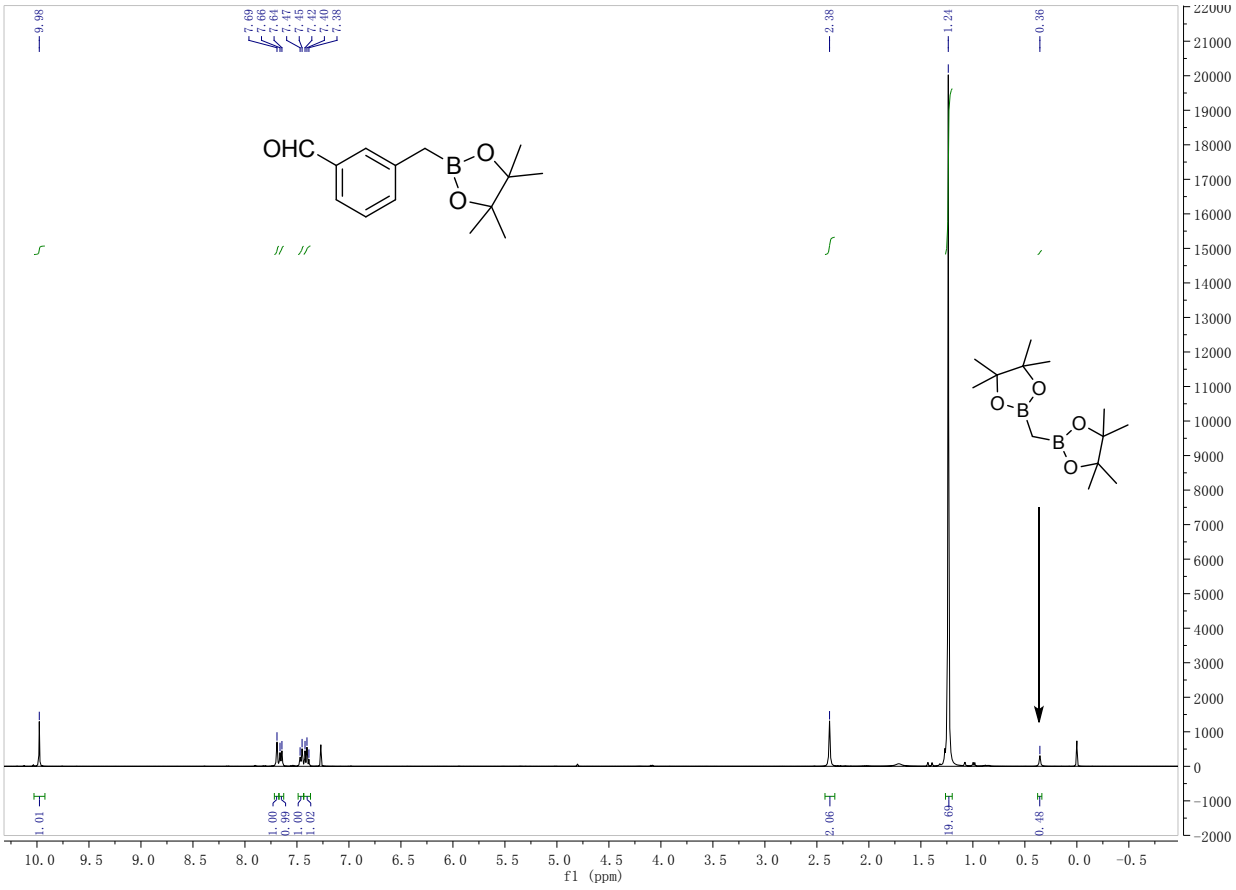
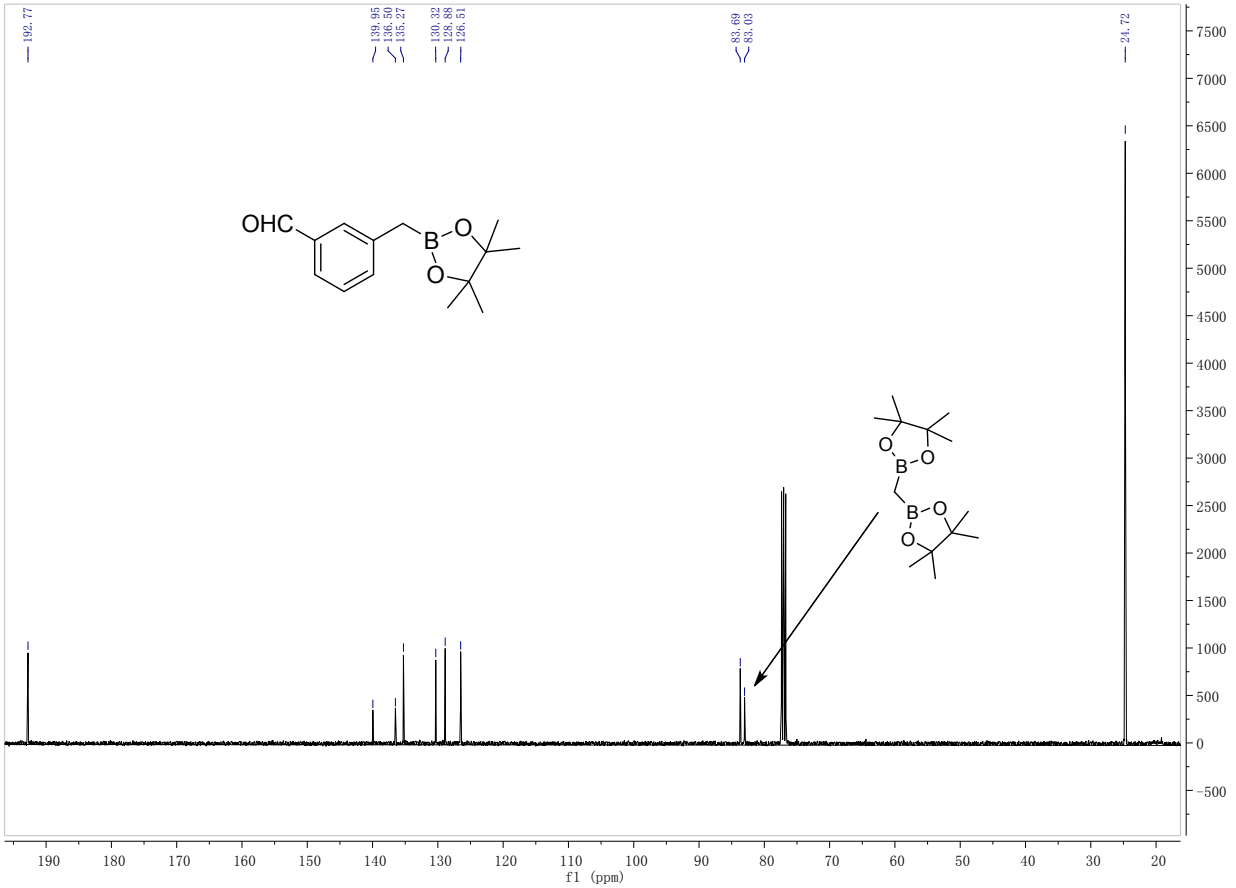
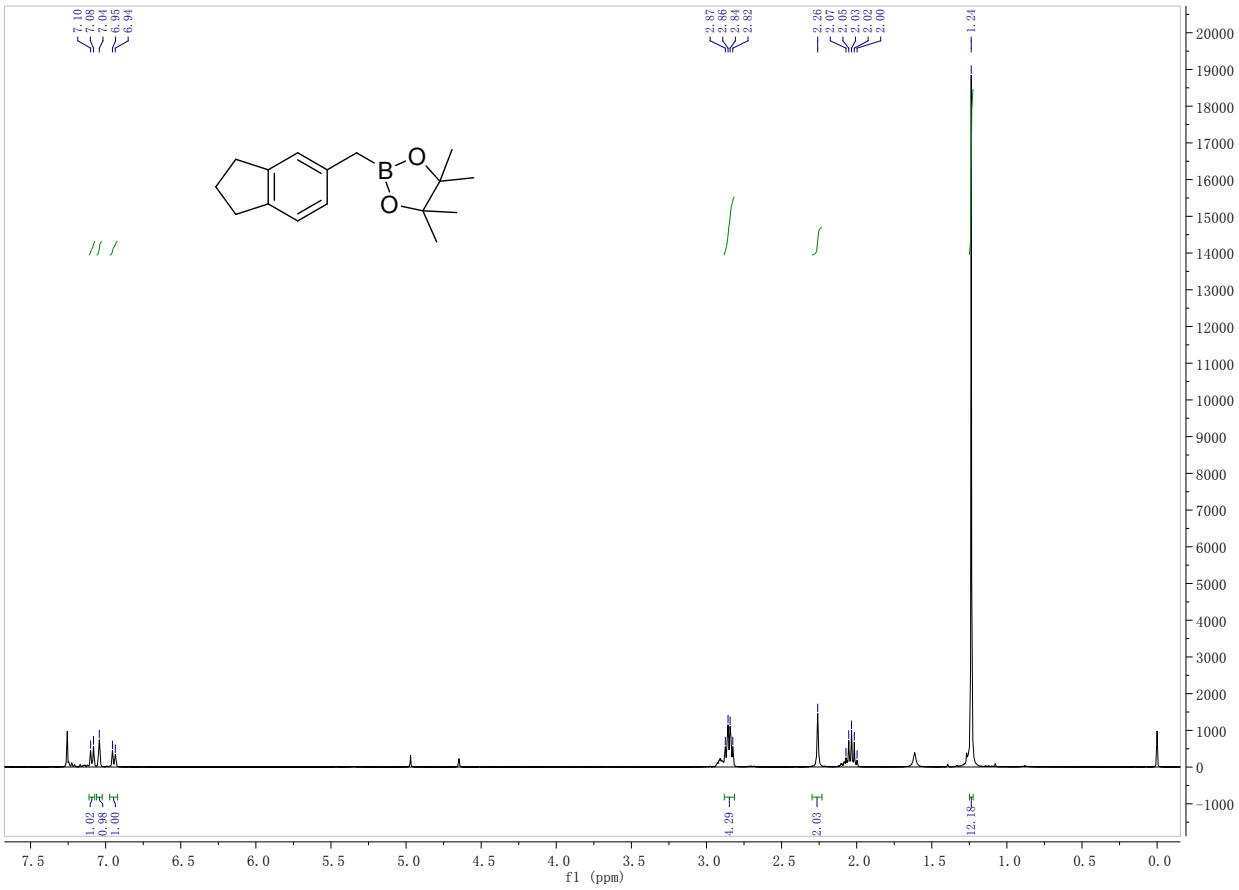


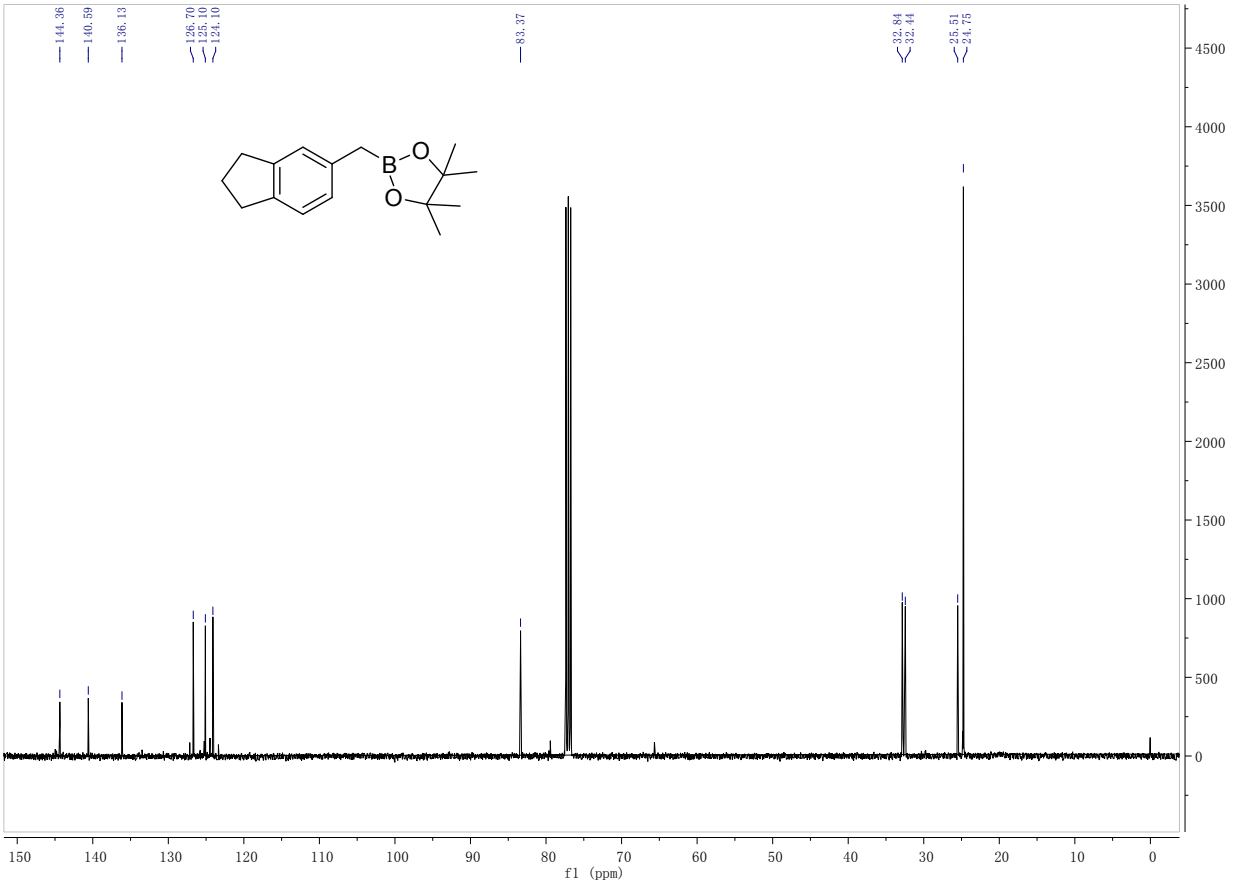
^{1}H NMR spectra for 3m



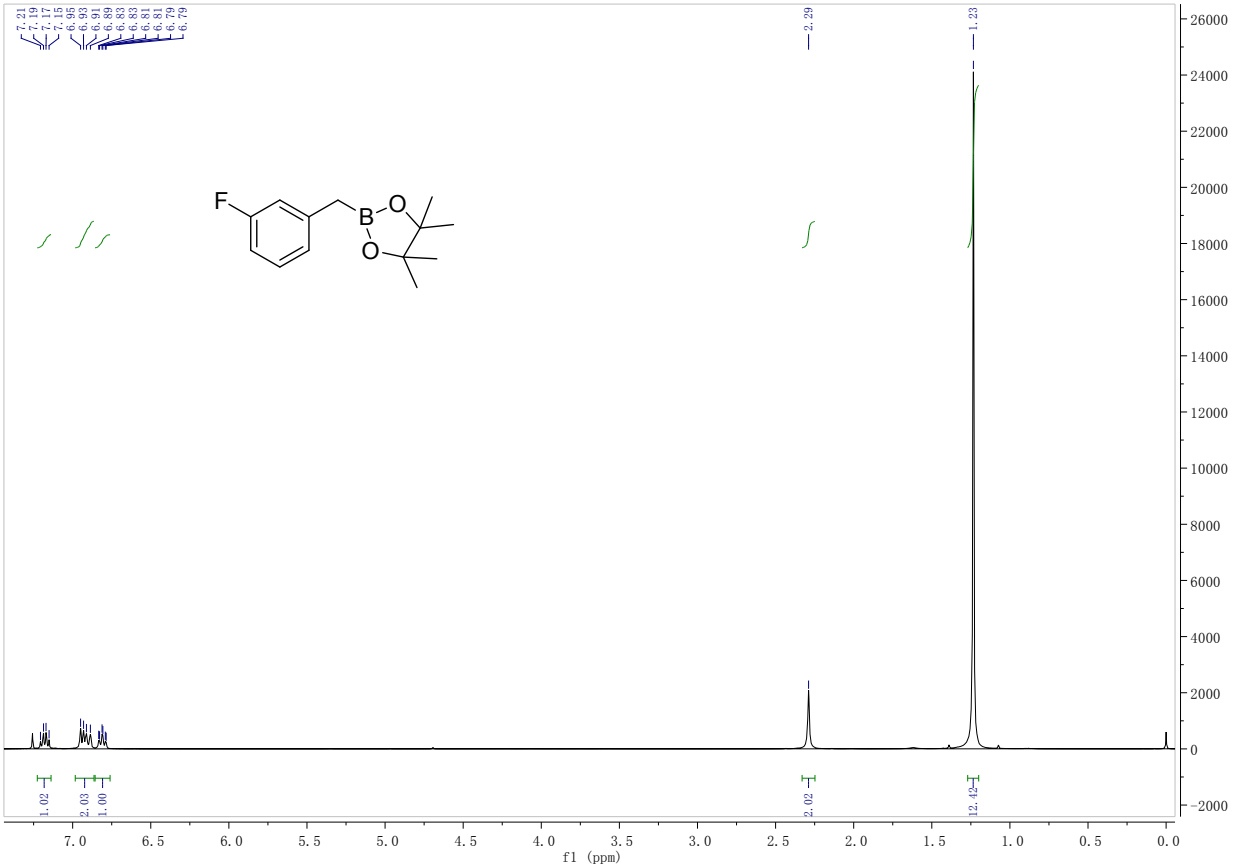
^{13}C NMR spectra for 3m



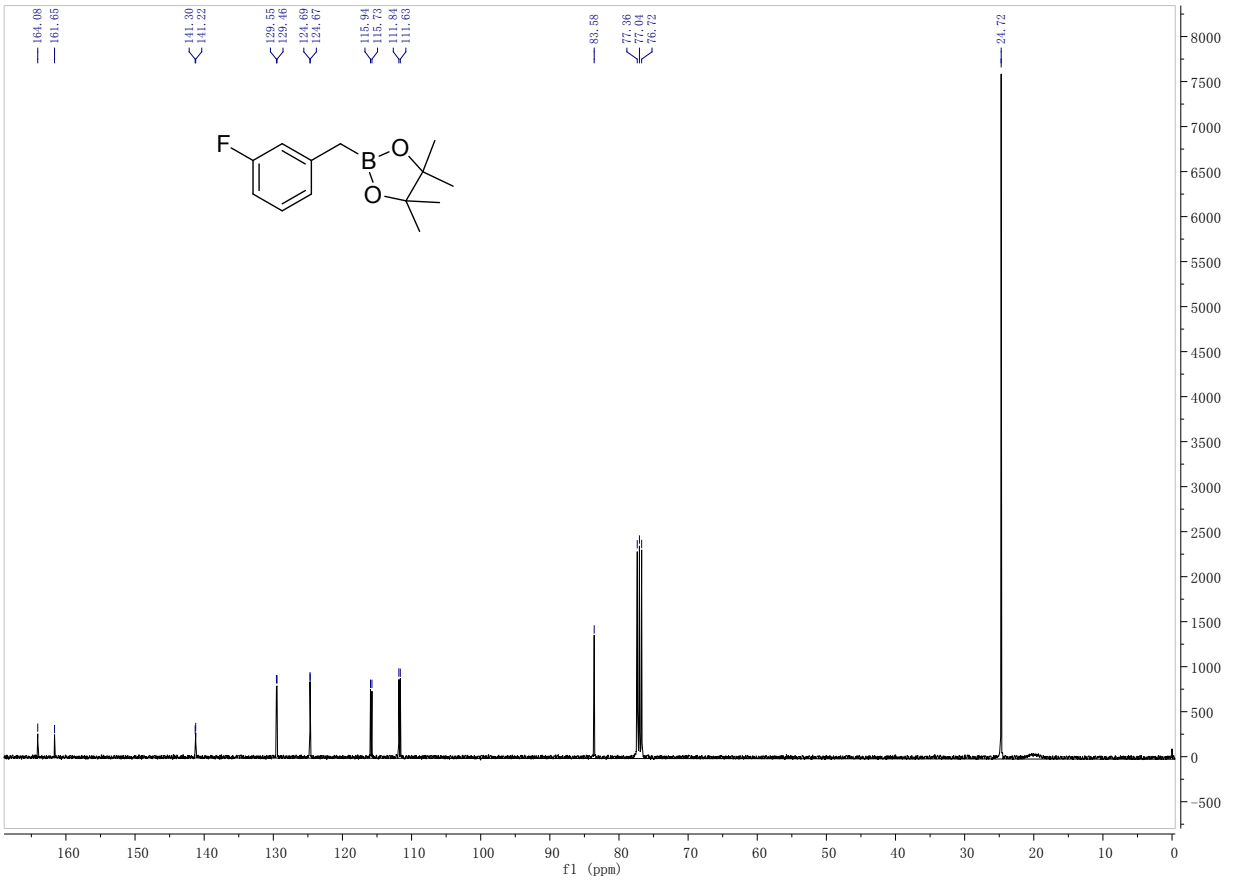
^{1}H NMR spectra for 3n



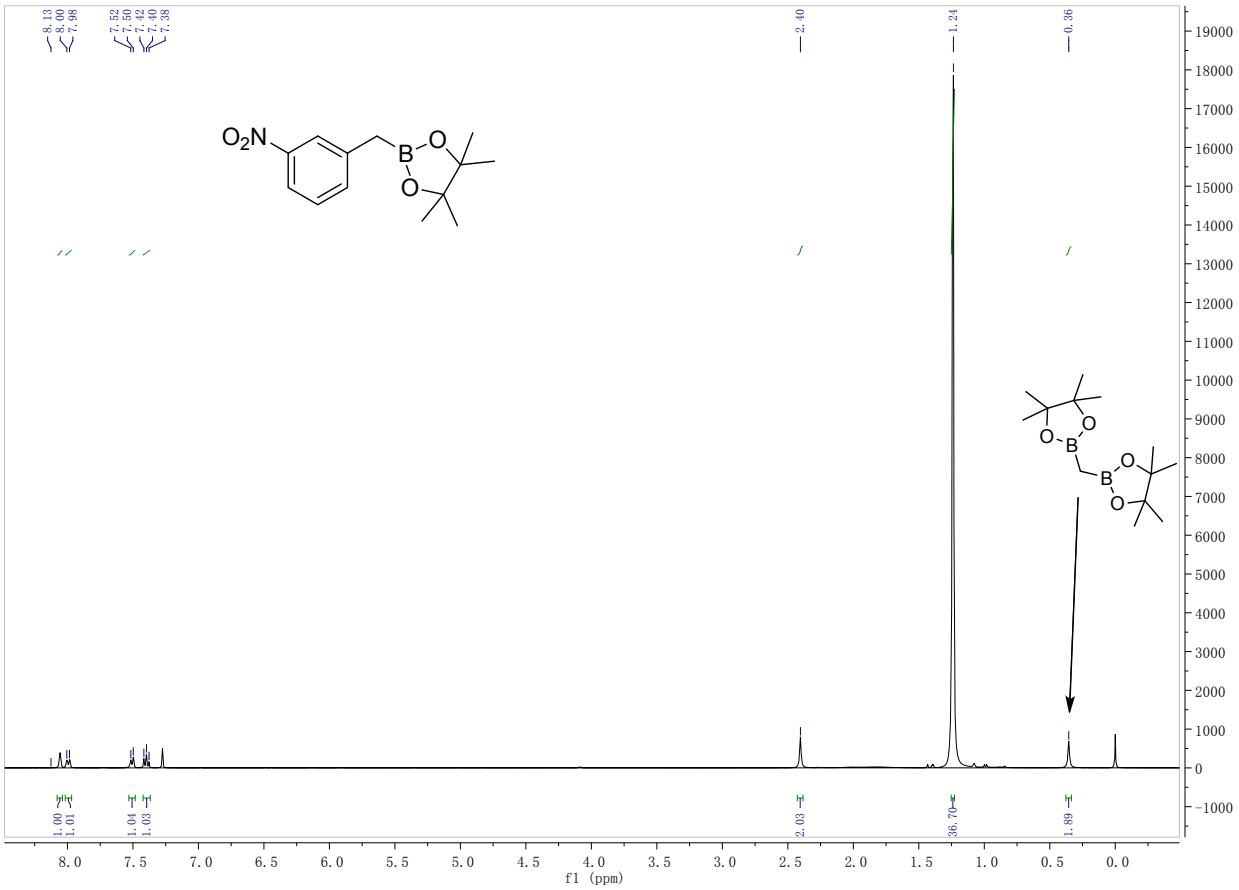
^{13}C NMR spectra for 3n



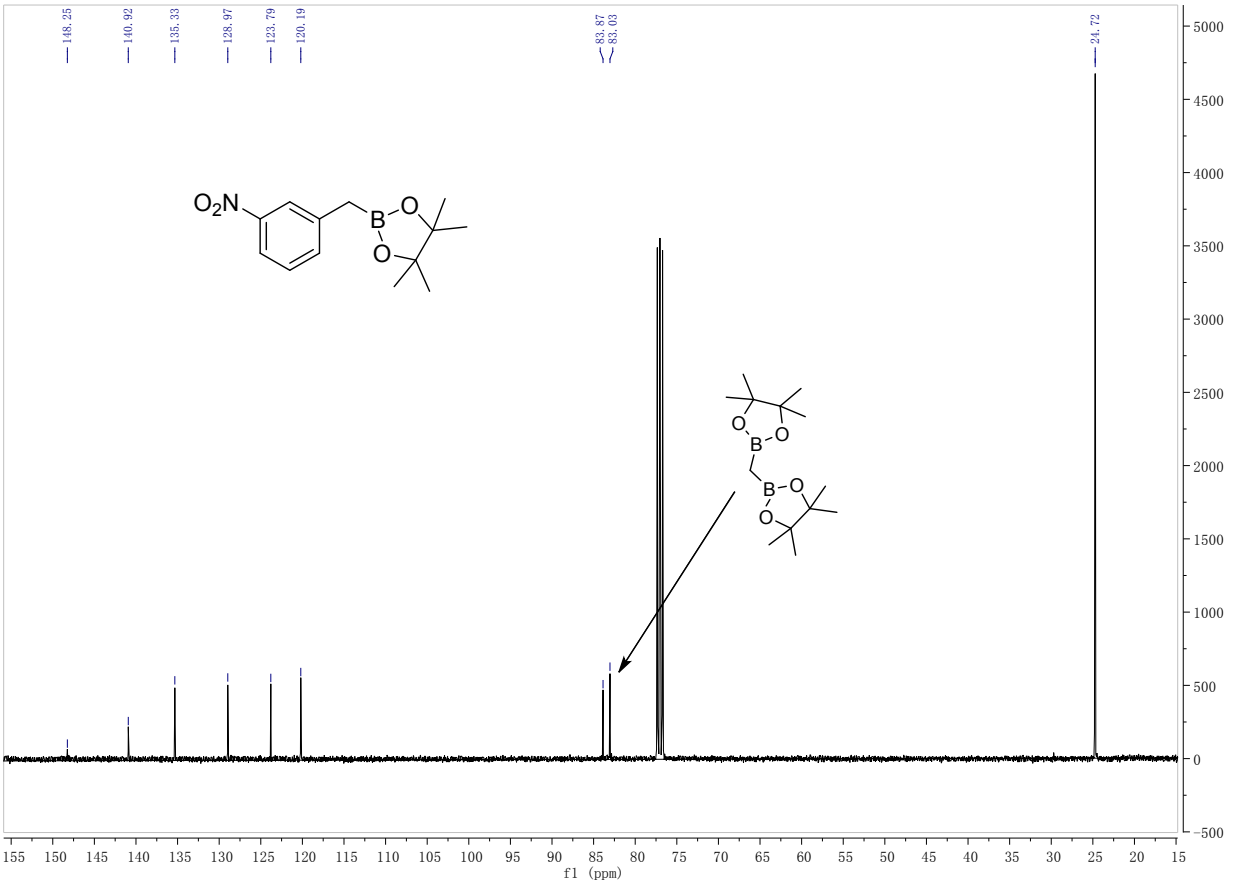
^{1}H NMR spectra for 3o



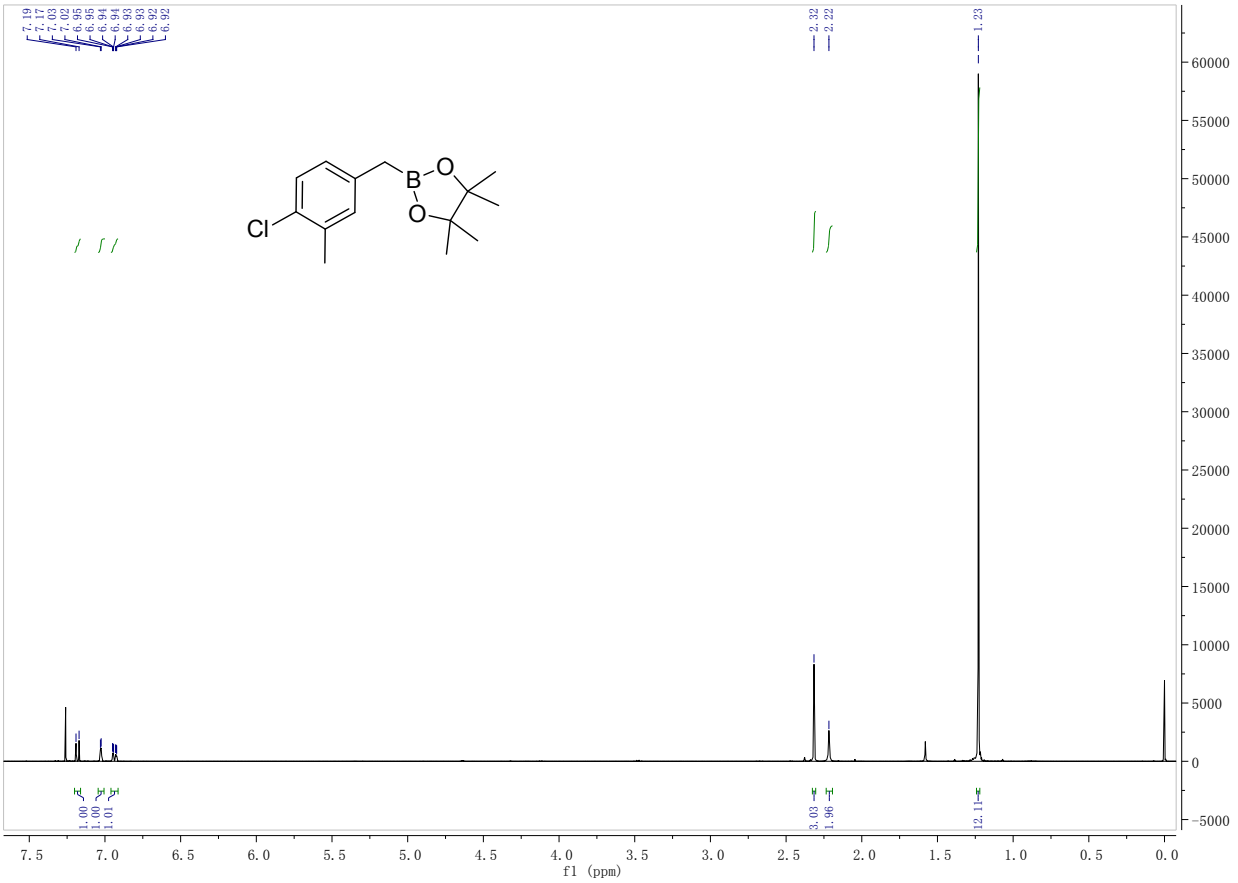
^{13}C NMR spectra for 3o



^{1}H NMR spectra for 3p

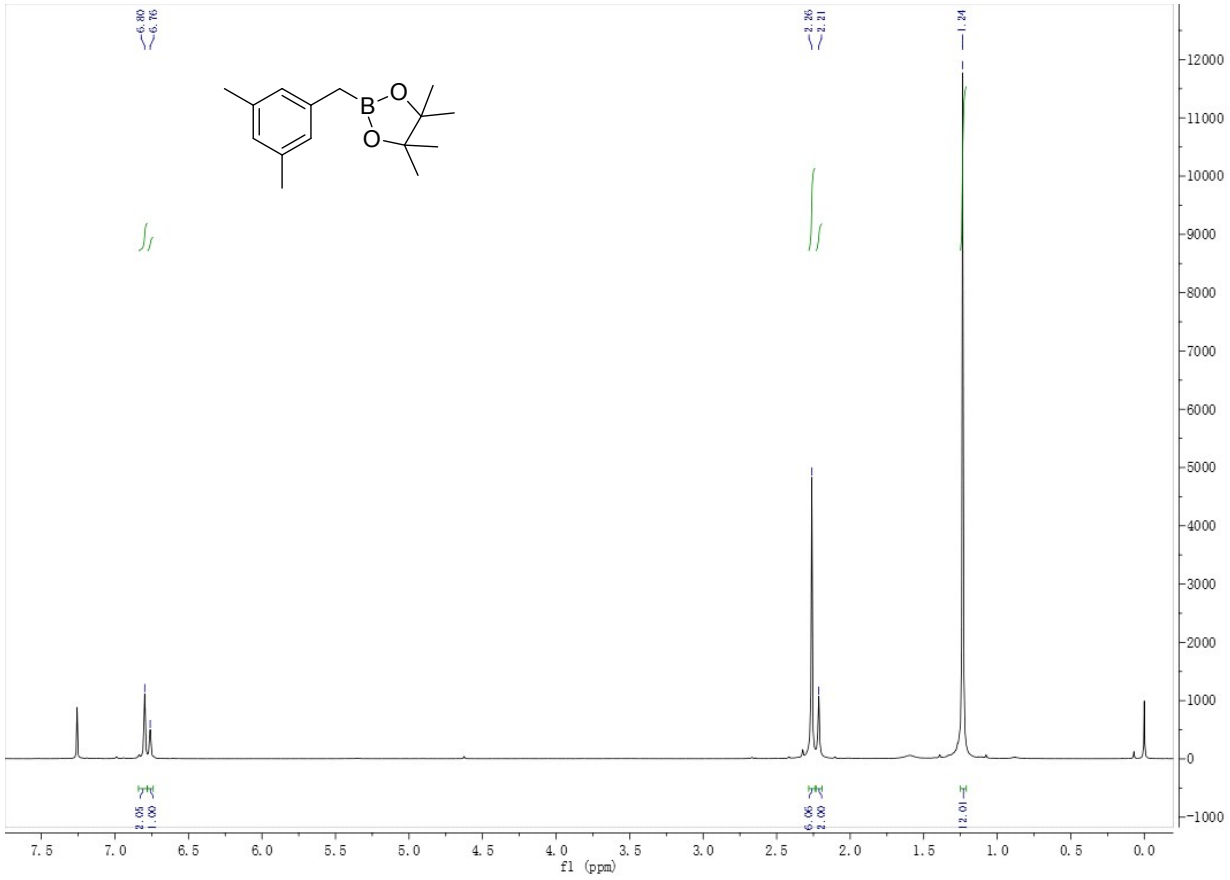


^{13}C NMR spectra for 3p

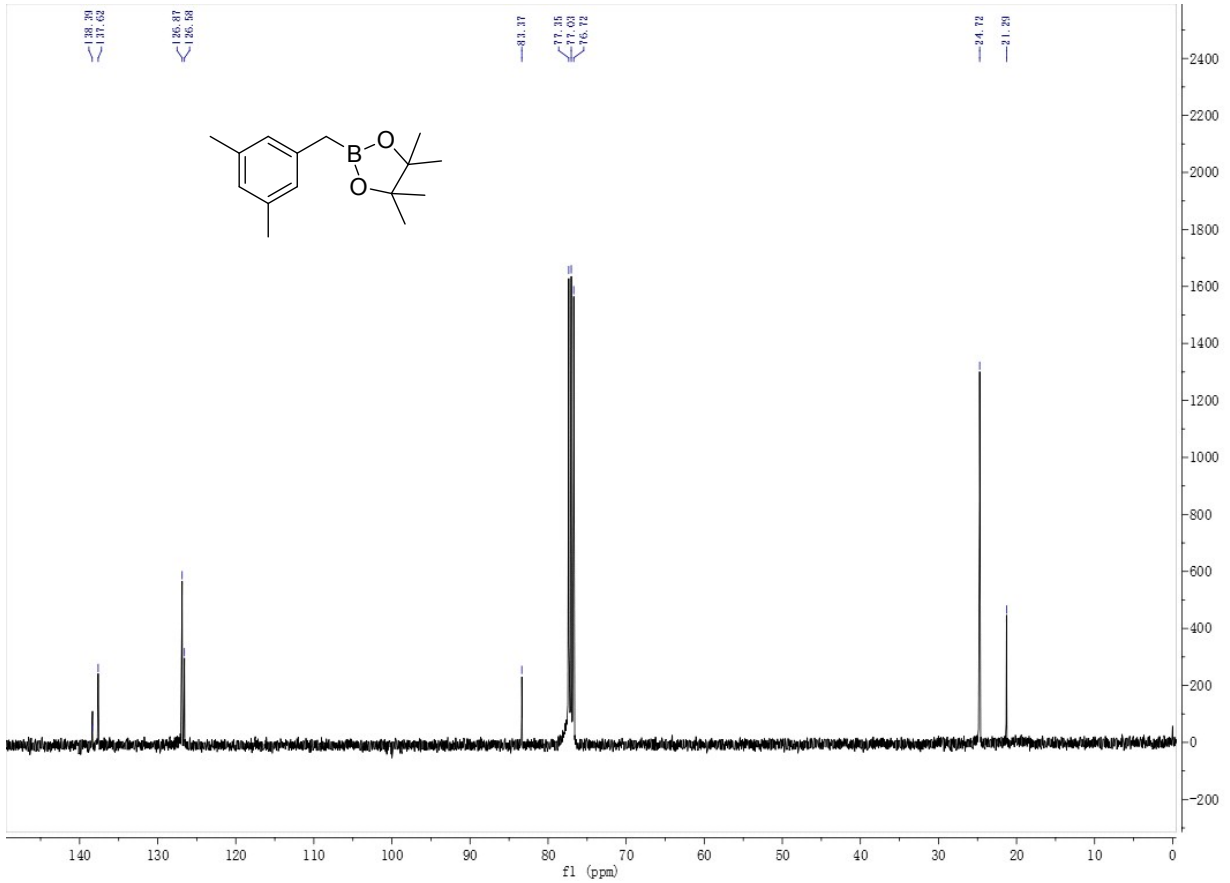


^{1}H NMR spectra for 3q

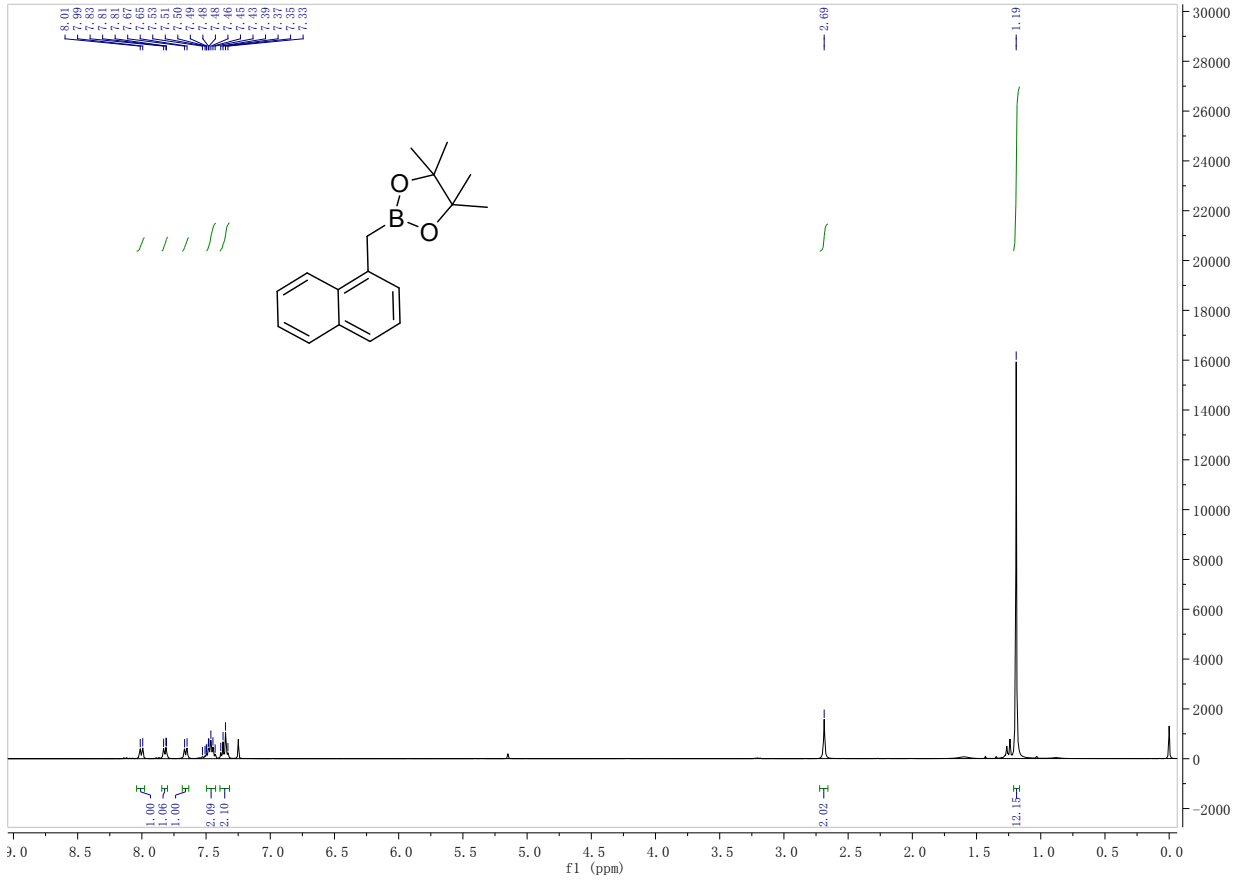
^{13}C NMR spectra for 3q



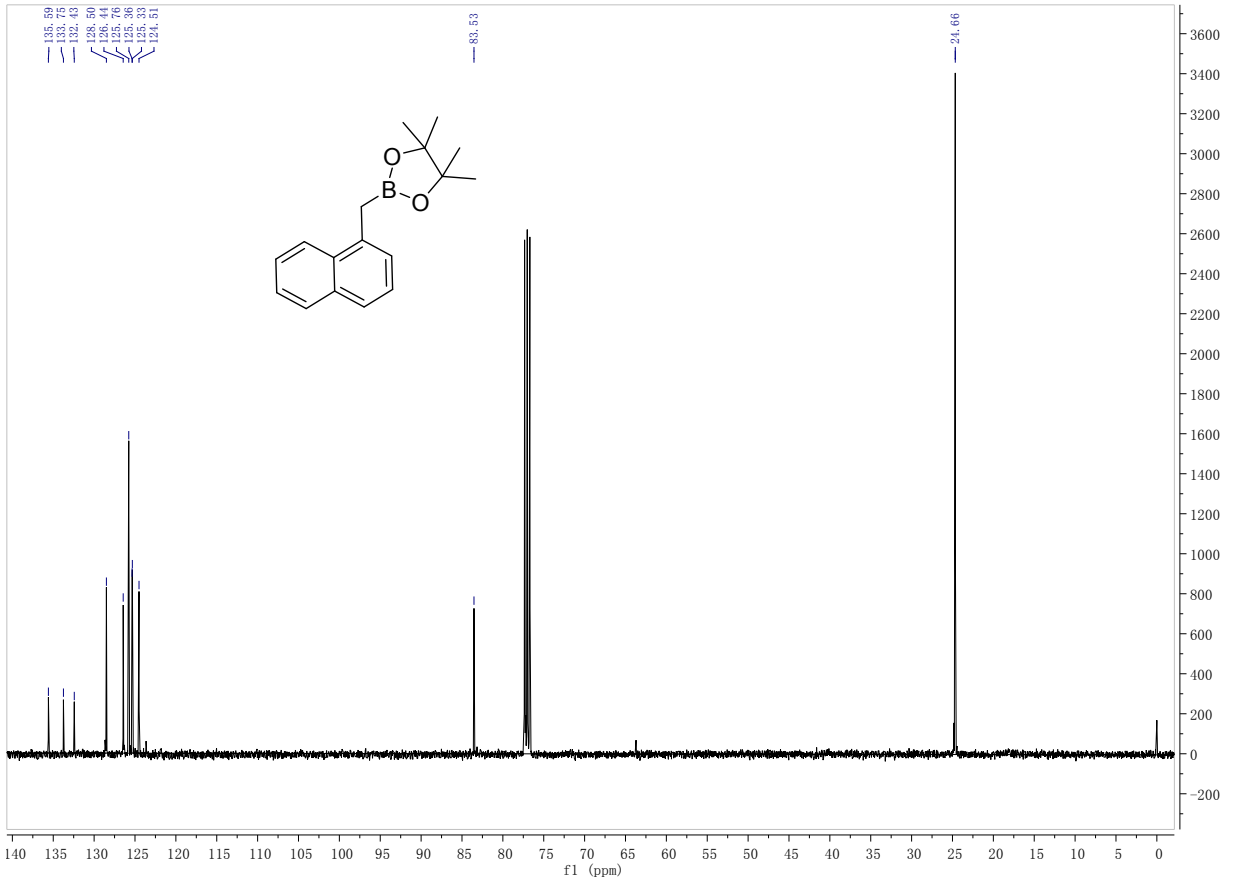
^{1}H NMR spectra for 3r



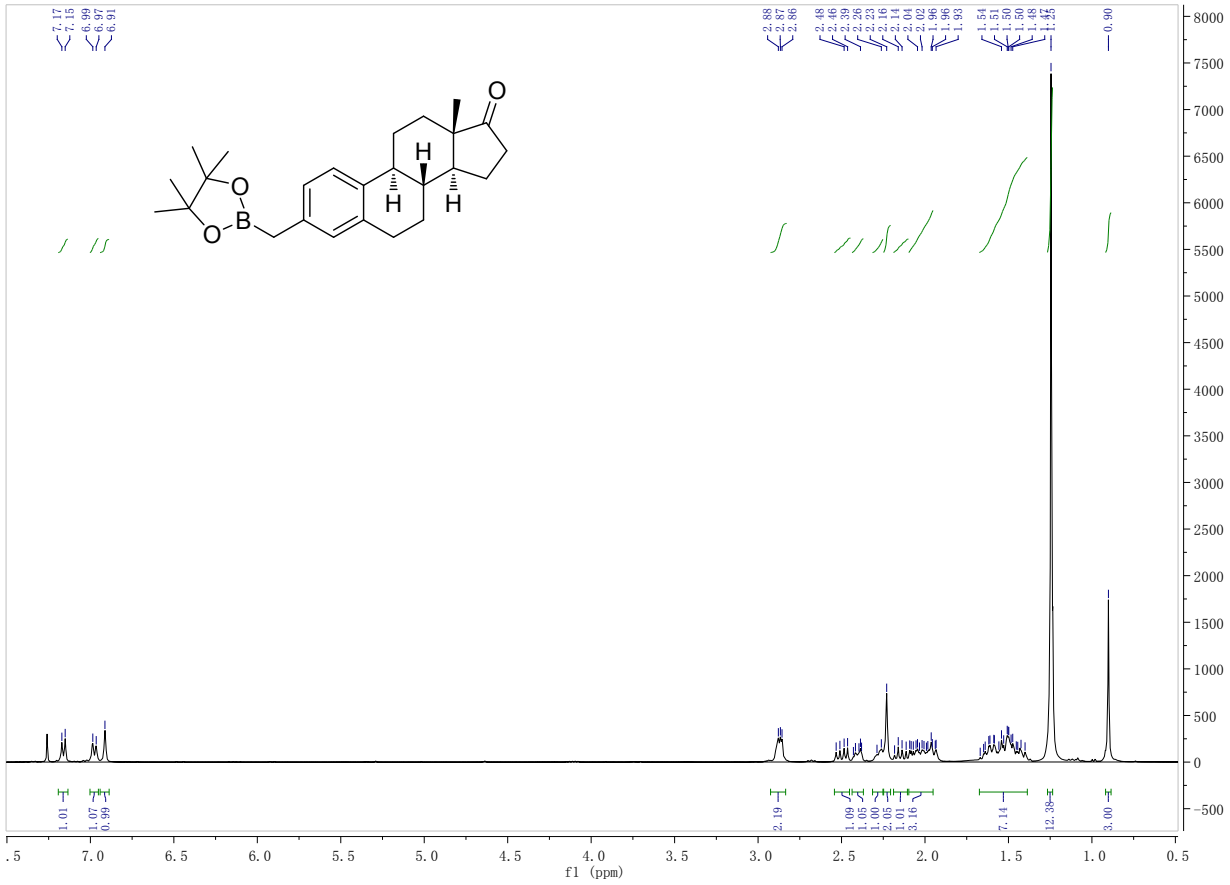
^{13}C NMR spectra for 3r



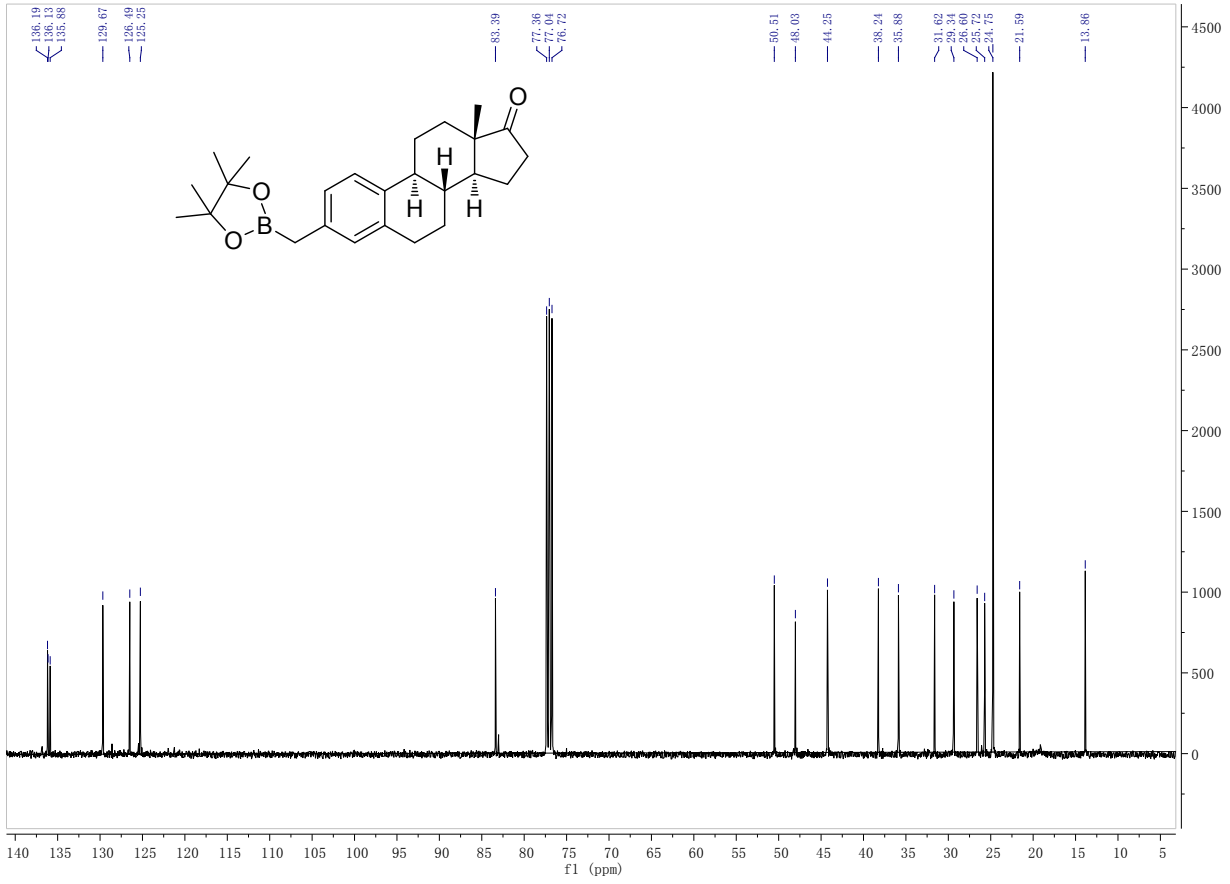
^{1}H NMR spectra for 3s



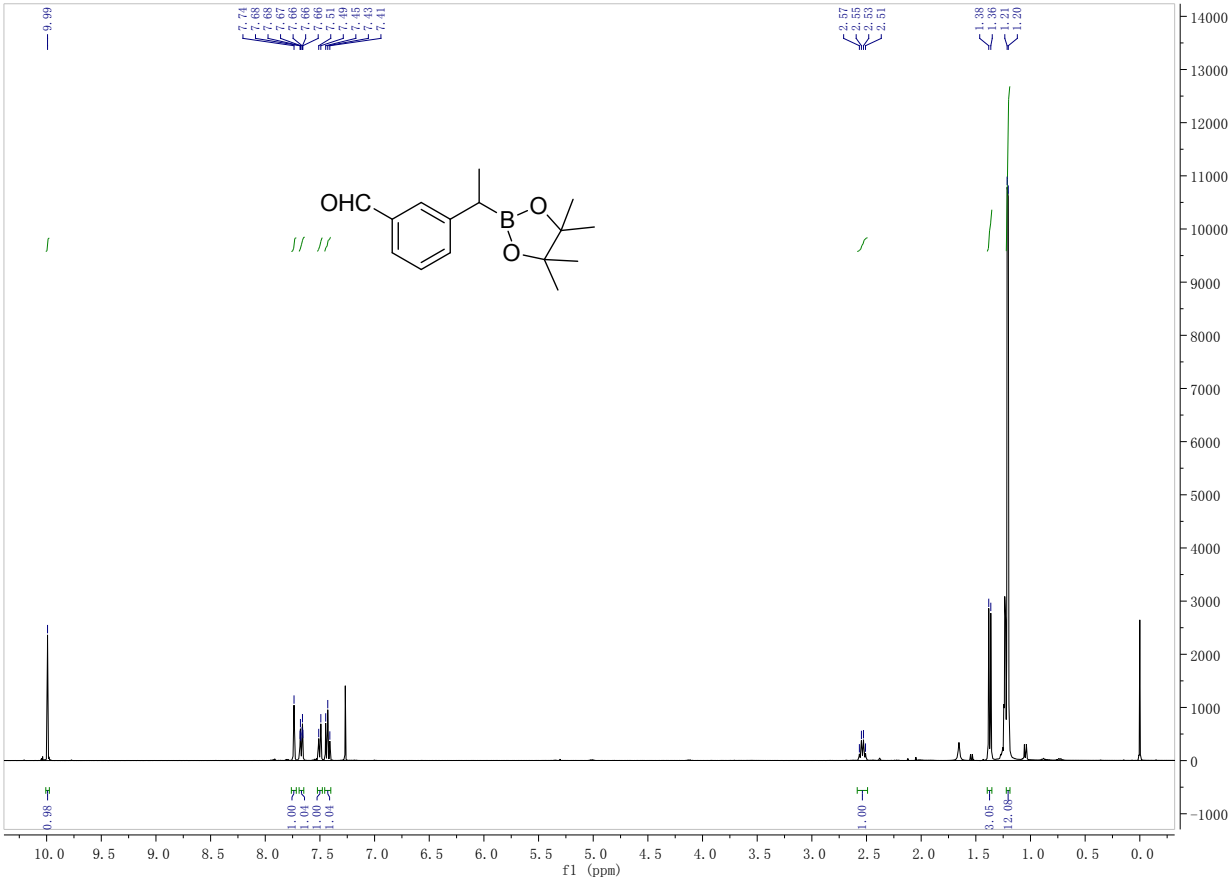
^{13}C NMR spectra for 3s



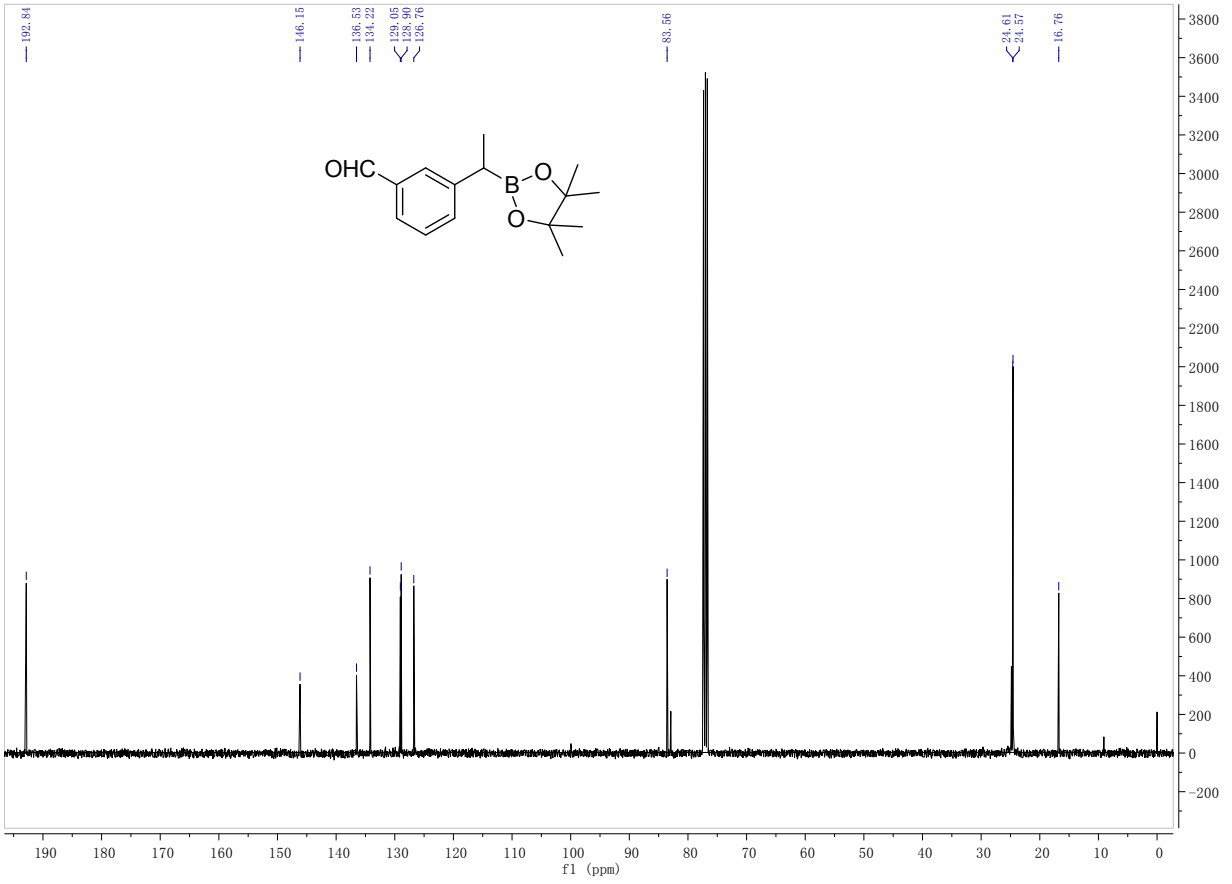
^{1}H NMR spectra for 3t



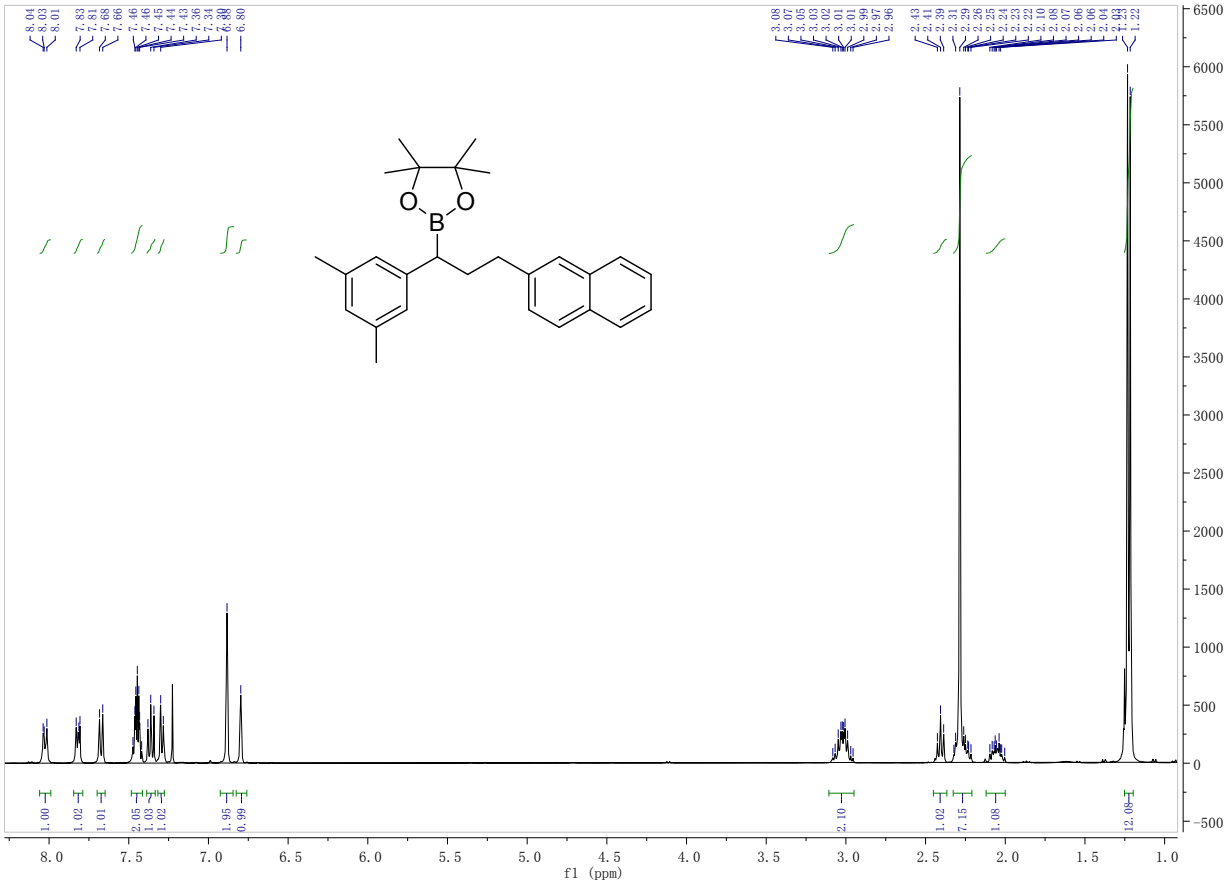
^{13}C NMR spectra for 3t



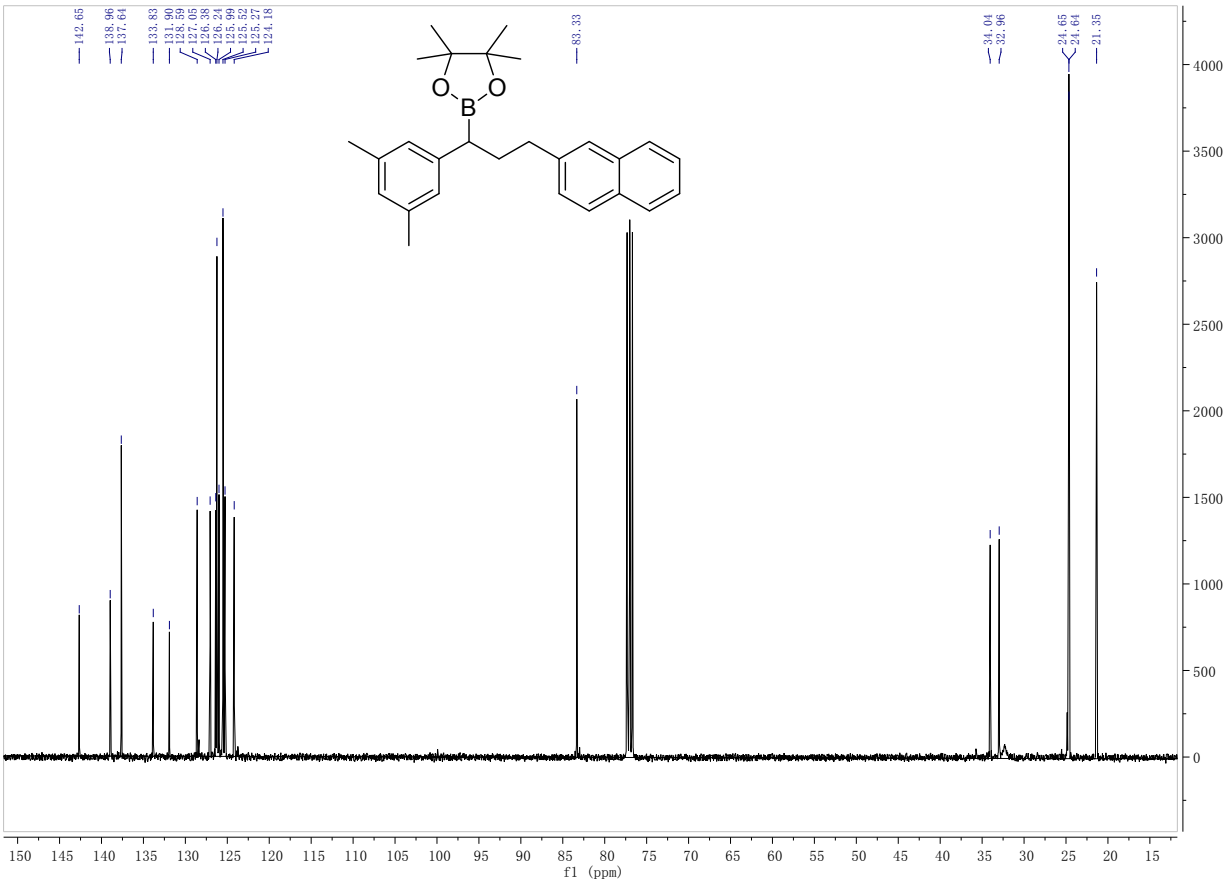
^{1}H NMR spectra for 4a



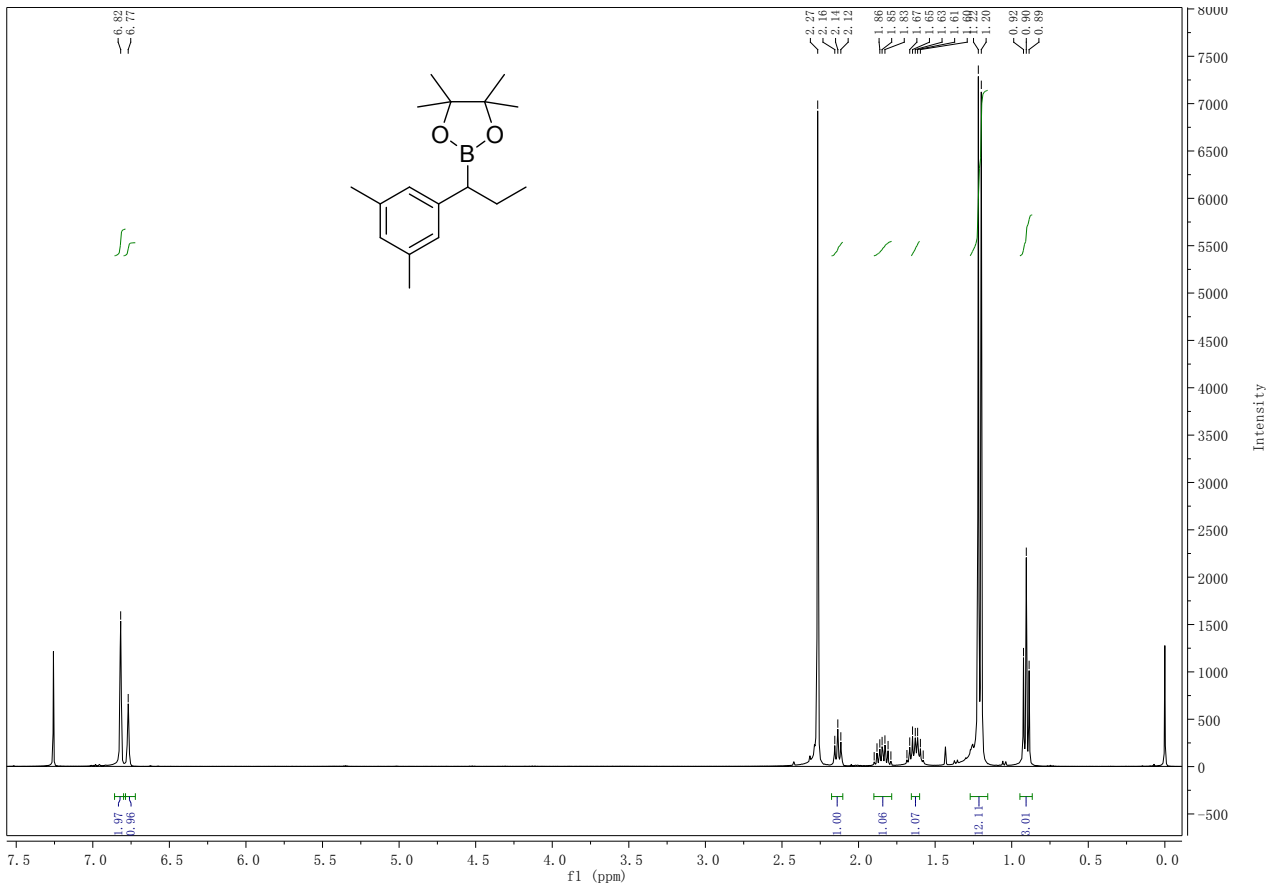
^{13}C NMR spectra for 4a



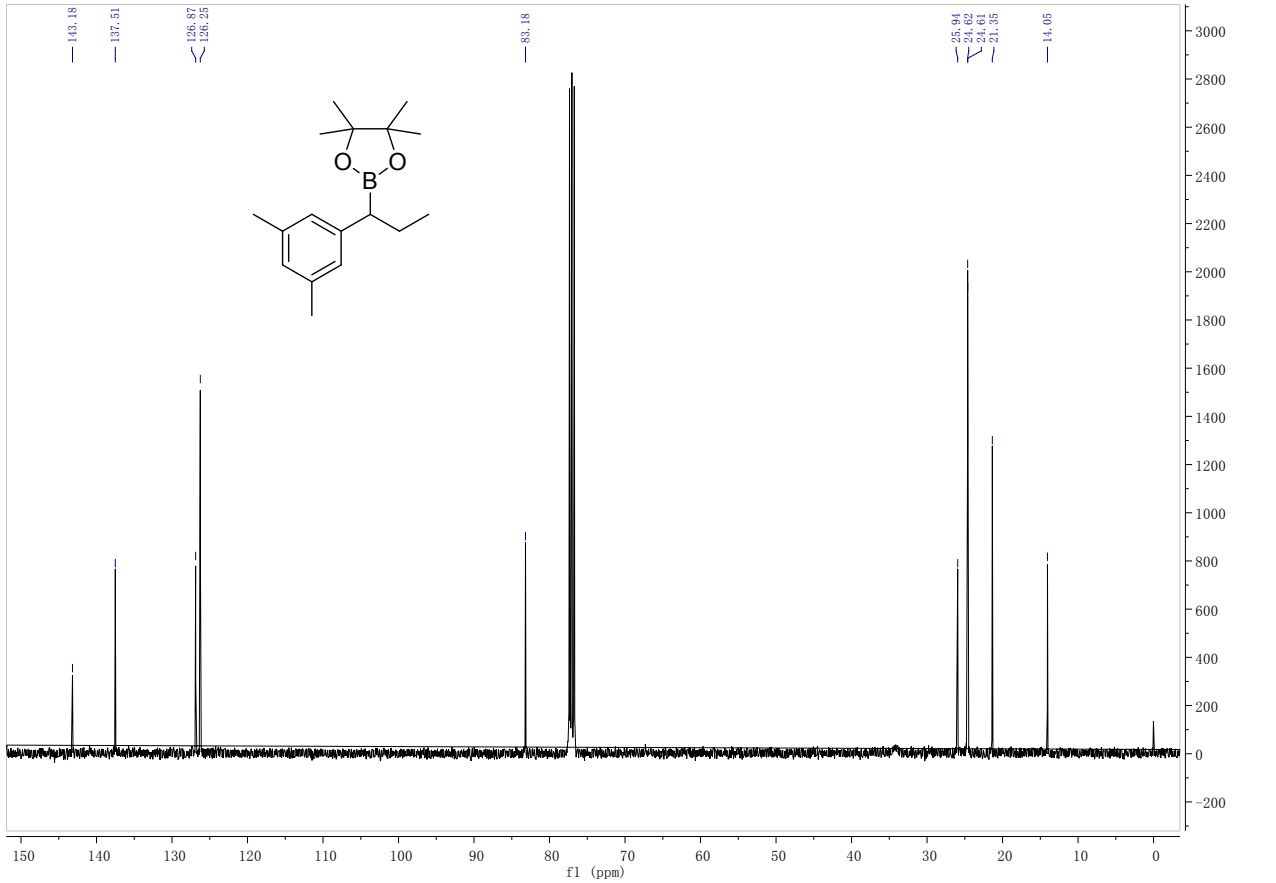
^{1}H NMR spectra for 4b



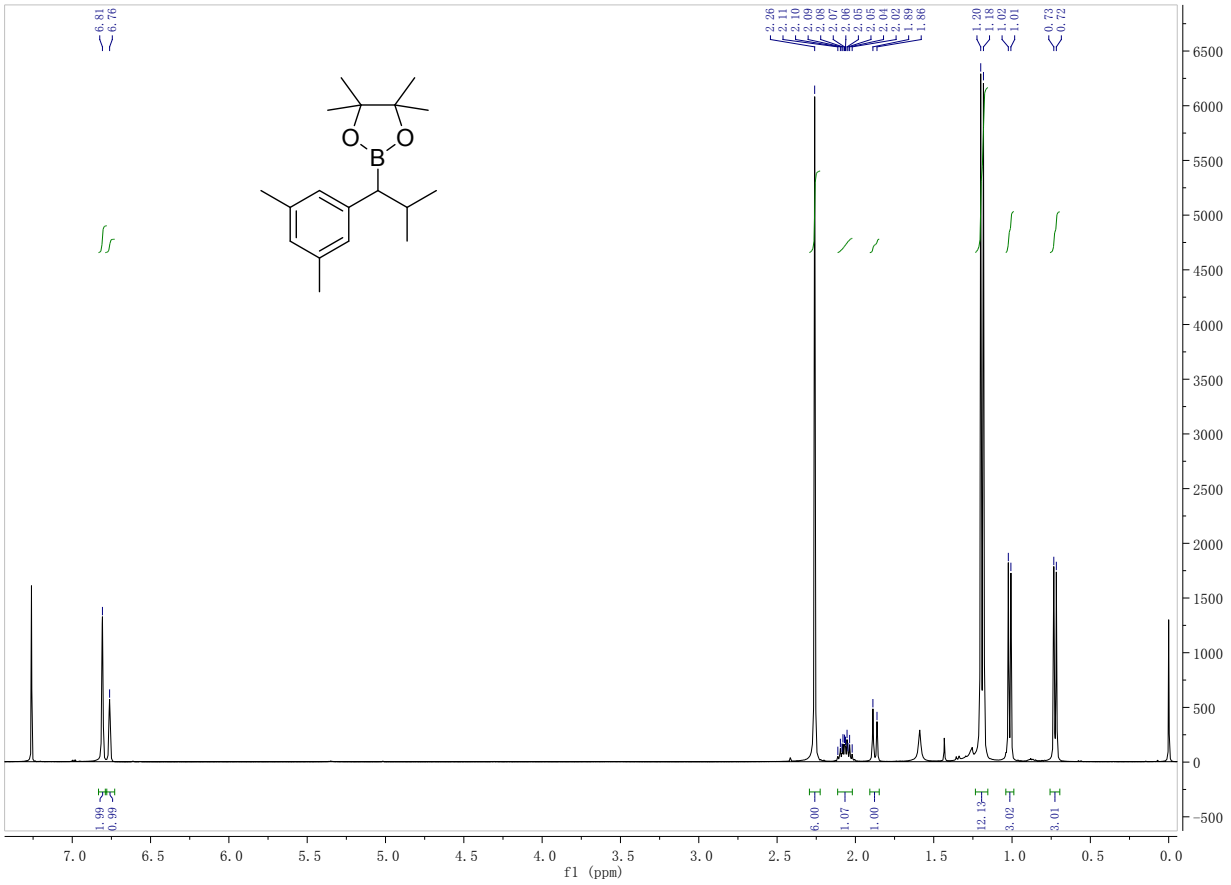
^{13}C NMR spectra for 4b



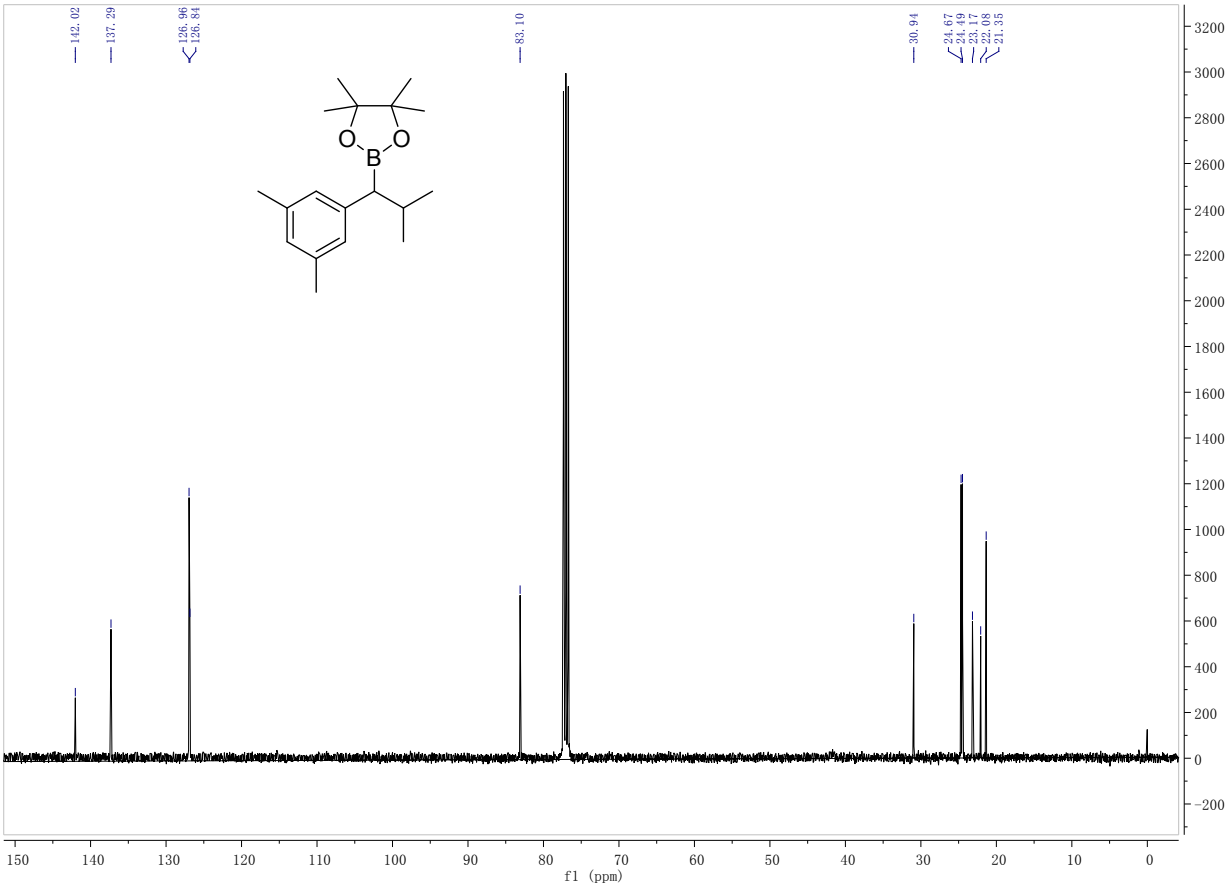
^{1}H NMR spectra for 4c



^{13}C NMR spectra for 4c



^{1}H NMR spectra for 4d



^{13}C NMR spectra for 4d