Dual Photoredox/Cobalt Catalysis Enabled Regiospecific Markovnikov Hydroboration of Unactivated Mono-, Di-, and Trisubstituted Alkenes

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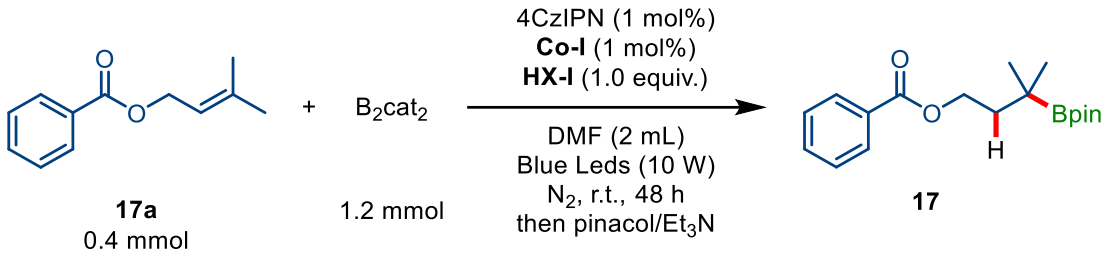
1. General information

Unless otherwise noted, all these reactions were carried out under nitrogen atmosphere. For column chromatography, silica gel (200-300 mesh) was employed. Solvent was freshly distilled prior to use unless otherwise noted. Organic solvents were concentrated under reduced pressure using a rotary evaporator.

Instrumentation. Deuterated solvents were purchased from Cambridge Isotope Laboratories. ^{1}H NMR spectra were recorded on Bruker AVANCE III 400 or Bruker AVANCE III HD 400 with 400 MHz frequencies, and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 or Bruker AVANCE III HD 400 with 101 MHz frequencies. ^{19}F NMR spectra were recorded on a Bruker AVANCE III HD 400 spectrometer with a ^{19}F operating frequency of 376 MHz. Chemical shifts (ppm) were recorded with TMS (tetramethylsilane) as the internal reference standard. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal (TMS δ = 0 for ^{1}H NMR and $CDCl_3$ δ = 77.0 for ^{13}C NMR). Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). Data collection for crystal structure was performed using Mo Kα radiation on a Bruker APEXII diffractometer. HRMS obtained using a Q-TOF instrument equipped with an ESI source. All photochemical reactions were conducted using a blue light-emitting diode (LED) as the visible-light source (440 nm, Kessil LEDs lights).

Materials. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available. Commercial reagents were used without further purification.

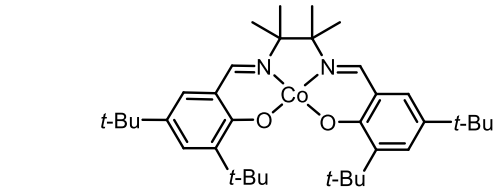
2. The optimization of the reaction[a]



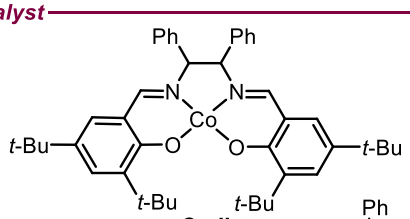
entry	modified conditions	yield of **17**[b]
1	none	66%
2	DCE was used as solvent	0
3	DMSO was used as solvent	0
4	toluene was used as solvent	0
5	CH_3CN was used as solvent	0
6	1,4-dioxane was used as solvent	0
7	**Co-II** instead of **Co-I**	0
8	**Co-III** instead of **Co-I**	0
9	**Co-IV** instead of **Co-I**	0
10	**Co(TPP)** instead of **Co-I**	54%
11	3CzClIPN instead of 4CzIPN	trace
12	Mes-Acr$^+$$ClO_4^-$ instead of 4CzIPN	0
13	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 instead of 4CzIPN	67%
14	Ir(ppy)$_3$ instead of 4CzIPN	44%
15	Ru(bpy)$_3$$Cl_2$·6$H_2O$ instead of 4CzIPN	0
16	4CzIPN (0.5 mol%) + **Co-I** (0.5 mol%)	69%
17	4CzIPN (0.25 mol%) + **Co-I** (0.25 mol%)	55%
18	4CzIPN (0.5 mol%) + **Co-I** (0.5 mol%)	69%[c]
19	**HX-II** instead of **HX-I**	0[d]
20	**HX-III** instead of **HX-I**	0[d]
21	B_2pin_2 instead of B_2cat_2	0[d]
22	$B_2(OH)_2$ instead of B_2cat_2	0[d]
23	No 4CzIPN	0[d]

24	No **Co-I**	0[d]
25	No **HX-I**	0[d]
26	No light	0[d]

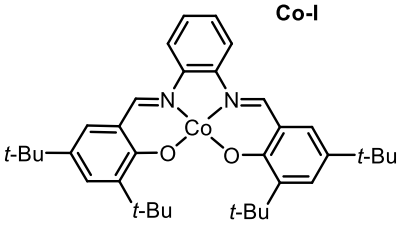
Cobalt catalyst



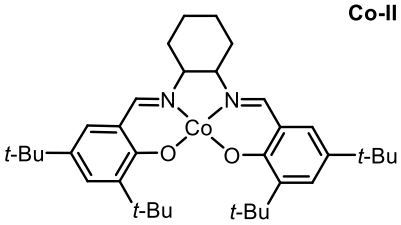
Co-I



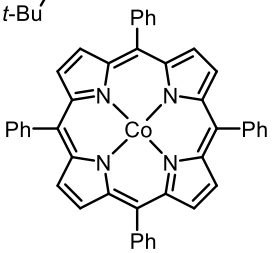
Co-II



Co-III

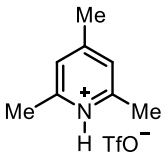


Co-IV

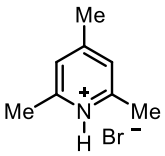


Co(TPP)

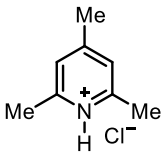
Brønsted acid



HX-I

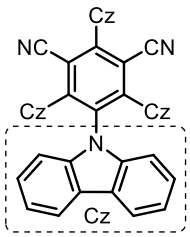


HX-II

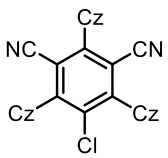


HX-III

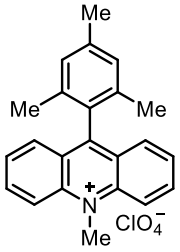
Photoredox catalyst



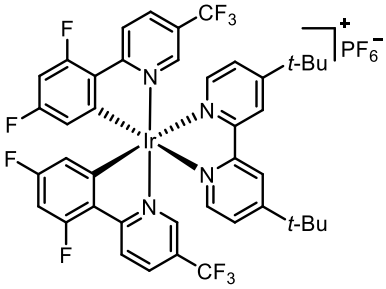
4CzIPN



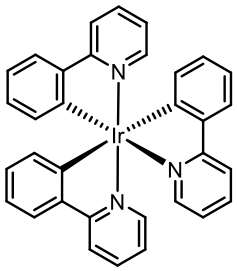
3CzClIPN



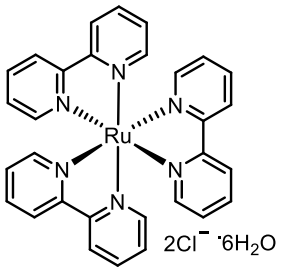
Mes-Acr$^+$ClO$_4^-$



Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$



Ir(ppy)$_3$



Ru(bpy)$_3$Cl$_2$·6H$_2$O

[a]Reaction conditions: **17a** (0.4 mmol), B_2cat_2 (1.2 mmol, 3.0 equiv.), 4CzIPN (1 mol%), **Co-I** (1 mol%), **HX-I** (0.4 mmol, 1.0 equiv.), DMF (2 mL), Blue Leds (10 W), r.t., N_2, 48 h; pinacol (2 mmol, 5.0 equiv.), Et_3N (2.8 mL), 1 h. [b] Isolated yield. [c]15 h. [d]4CzIPN (0.5 mol%) and **Co-I** (0.5 mol%) were employed for 15 h. DMF = *N, N*-Dimethylformamide. DCE = 1, 2-Dichloroethane. DMSO = Dimethyl sulfoxide.

3. Synthesis and characterization of products

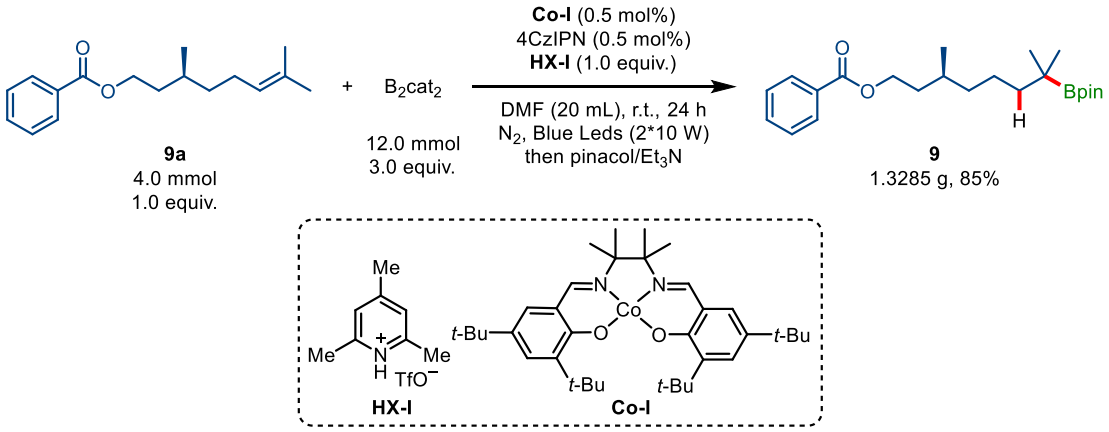
3.1 General Procedures I (GPI)

In an oven-dried 15 mL tube equipped with a stirring bar, unactivated alkenes (0.8 mmol, 1.0 equiv.), bis(catecholato)diboron (B_2cat_2) (2.4 mmol, 3.0 equiv.), collidinium triflate (**HX-I**) (0.8 mmol, 1.0 equiv.), 4CzIPN (0.002 mmol, 0.25 mol%), and **Co-I** (0.002 mmol, 0.25 mol%) were added. The tube was charged with nitrogen (repeated three times), then *N*,*N*-Dimethylformamide (DMF, 4 mL) was injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) for 15 h. Then pinacol (4.0 mmol, 5.0 equiv.) and Et_3N (5.6 mL) were added and stirring was continued for 1 h. After completion, the resulting mixture was quenched with H_2O (30 mL). Then the mixture was extracted with ethyl acetate (30 mL). The organic layer was washed with brine (30 mL × 2), dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products.

3.2 General Procedures II (GPII)

In an oven-dried 15 mL tube equipped with a stirring bar, unactivated alkenes (0.4 mmol, 1.0 equiv.), bis(catecholato)diboron (B_2cat_2) (1.2 mmol, 3.0 equiv.), collidinium triflate (**HX-I**) (0.4 mmol, 1.0 equiv.), 4CzIPN (0.002 mmol, 0.5 mol%), and **Co-I** (0.002 mmol, 0.5 mol%) were added. The tube was charged with nitrogen (repeated three times), then *N*,*N*-Dimethylformamide (DMF, 2 mL) was injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) for 15 h. Then pinacol (2.0 mmol, 5.0 equiv.) and Et_3N (2.8 mL) were added and stirring was continued for 1 h. After completion, the resulting mixture was quenched with H_2O (30 mL). Then the mixture was extracted with ethyl acetate (30 mL). The organic layer was washed with brine (30 mL × 2), dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products.

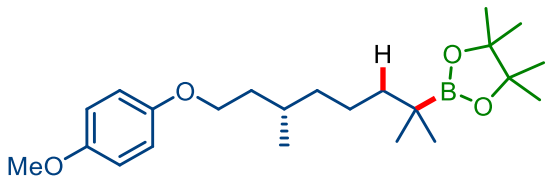
3.3 Gram-scale reaction procedures



In an oven-dried 100 mL tube equipped with a stirring bar, unactivated alkene **48a** (4.0 mmol, 1 equiv.), B_2cat_2 (12.0 mmol, 3.0 equiv.), collidinium triflate (**HX-I**) (4.0 mmol, 1.0 equiv.), 4CzIPN (0.02 mmol, 0.5 mol%), and **Co-I** (0.02 mmol, 0.5 mol%) were added. The tube was charged with nitrogen (repeated three times), then DMF (20.0 mL) was injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 2*10 W) for 24 h. Then pinacol (20.0 mmol, 5.0 equiv.) and Et_3N (28 mL) were added and stirring was continued for 1 h. After completion, the resulting mixture was quenched with H_2O (100 mL). Then the mixture was extracted with ethyl acetate (100 mL). The organic layer was washed with brine (100 mL × 2), dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired product **48** (1.3285 g, 85%).

3.4 Characterization of products

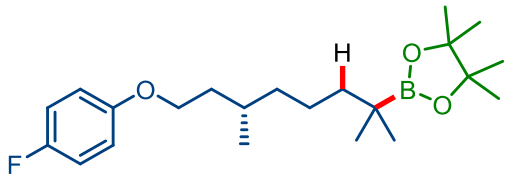
(*S*)-2-(8-(4-methoxyphenoxy)-2,6-dimethyloctan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1)



GP II, 108.4 mg, 69% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 – 6.79 (m, 4H), 3.97 – 3.88 (m, 2H), 3.76 (s, 3H), 1.83 – 1.74 (m, 1H), 1.70 – 1.63 (m, 1H), 1.60 – 1.50 (m, 1H), 1.33 – 1.27 (m, 2H), 1.27 – 1.23 (m, 3H), 1.22 – 1.14 (m, 13H), 0.94 – 0.89 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 153.3, 115.4, 114.6, 82.8, 67.0, 55.7, 41.4, 37.9, 36.3, 29.7, 25.0, 24.9, 24.7, 24.7, 23.8, 19.6. HRMS (ESI-TOF)

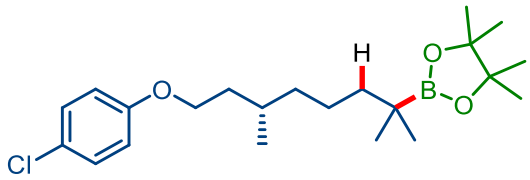
(m/z): Calcd for $C_{23}H_{39}BO_4Na$ ([M + Na]$^+$): 413.2834; found: 413.2832.

(*S*)-2-(8-(4-fluorophenoxy)-2,6-dimethyloctan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2)



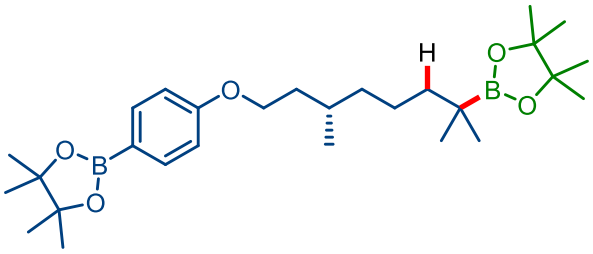
GP II, 135.8 mg, 89% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.92 (m, 2H), 6.85 – 6.79 (m, 2H), 3.97 – 3.90 (m, 2H), 1.84 – 1.74 (m, 1H), 1.70 – 1.64 (m, 1H), 1.60 – 1.51 (m, 1H), 1.34 – 1.29 (m, 2H), 1.28 – 1.23 (m, 4H), 1.22 (s, 12H), 0.92 (d, *J* = 5.4 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (d, *J* = 237.6 Hz), 155.2 (d, *J* = 2.0 Hz), 115.7 (d, *J* = 23.0 Hz), 115.4 (d, *J* = 7.9 Hz), 82.8, 66.9, 41.4, 37.8, 36.2, 29.7, 24.9, 24.9, 24.7, 24.7, 23.7, 19.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.55. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{36}BFO_3Na$ ([M + Na]$^+$): 401.2634; found: 401.2634.

(*S*)-2-(8-(4-chlorophenoxy)-2,6-dimethyloctan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3)



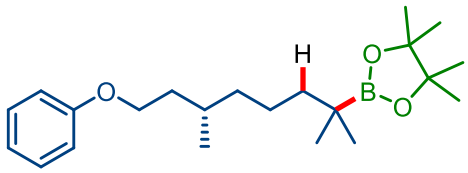
GP II, 132.5 mg, 83% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 6.84 – 6.77 (m, 2H), 3.98 – 3.90 (m, 2H), 1.84 – 1.75 (m, 1H), 1.70 – 1.63 (m, 1H), 1.61 – 1.51 (m, 1H), 1.31 – 1.25 (m, 3H), 1.24 – 1.16 (m, 15H), 0.92 (d, *J* = 4.6 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 129.2, 125.2, 115.7, 82.8, 66.6, 41.4, 37.8, 36.1, 29.7, 24.9, 24.9, 24.7, 24.7, 23.7, 19.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{36}BClO_3Na$ ([M + Na]$^+$): 417.2338; found: 417.2337.

(*S*)-2-(4-((3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)



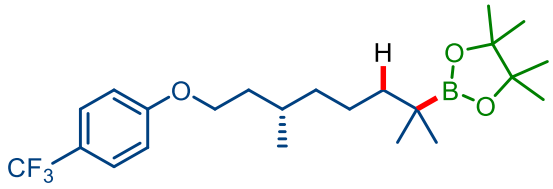
GP II, 127.0 mg, 65% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 6.90 – 6.86 (m, 2H), 4.03 – 3.97 (m, 2H), 1.86 – 1.77 (m, 1H), 1.72 – 1.63 (m, 1H), 1.60 – 1.53 (m, 1H), 1.35 – 1.29 (m, 14H), 1.26 – 1.21 (m, 16H), 0.92 (d, J = 6.6 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 136.4, 113.8, 83.5, 82.8, 66.1, 41.4, 37.8, 36.1, 29.7, 25.0, 24.9, 24.9, 24.7, 24.7, 23.8, 19.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{48}B_2O_5Na$ ($[M + Na]^+$): 509.3580; found: 509.3579.

(*S*)-2-(2,6-dimethyl-8-phenoxyoctan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)



GP II, 113.9 mg, 79% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 6.96 – 6.85 (m, 3H), 4.03 – 3.93 (m, 2H), 1.85 – 1.78 (m, 1H), 1.71 – 1.65 (m, 1H), 1.63 – 1.52 (m, 2H), 1.35 – 1.28 (m, 3H), 1.25 – 1.20 (m, 13H), 1.18 – 1.13 (m, 1H), 0.97 – 0.88 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 129.3, 120.4, 114.5, 82.8, 66.2, 41.4, 37.8, 36.2, 29.7, 25.0, 24.9, 24.7, 24.7, 23.7, 19.6 . HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{37}BO_3Na$ ($[M + Na]^+$): 383.2728; found: 383.2726.

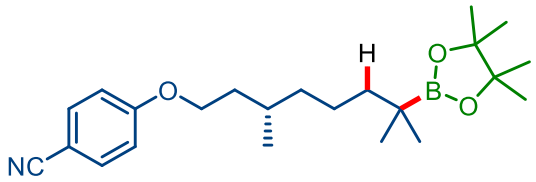
(*S*)-2-(2,6-dimethyl-8-(4-(trifluoromethyl)phenoxy)octan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)



GP II, 121.5 mg, 70% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.5 Hz, 2H), 4.05 – 3.99 (m, 2H), 1.87 – 1.78 (m, 1H), 1.73 –

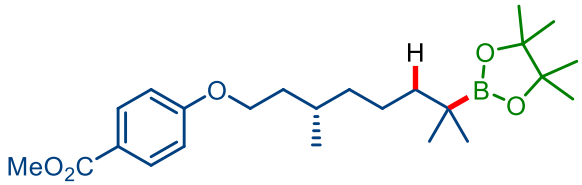
1.65 (m, 1H), 1.64 – 1.58 (m, 1H), 1.35 – 1.30 (m, 2H), 1.28 – 1.23 (m, 4H), 1.22 (s, 12H), 0.95 – 0.90 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 126.8 (q, J = 3.8 Hz), 124.5 (q, J = 271.0 Hz), 122.5 (q, J = 32.7 Hz), 114.4, 82.8, 66.6, 41.4, 37.8, 35.9, 29.7, 24.9, 24.9, 24.7, 24.7, 23.7, 19.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.43. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{36}BF_3O_3Na$ ($[M + Na]^+$): 451.2602; found: 451.2601.

(*S*)-4-((3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)oxy)benzonitrile (7)



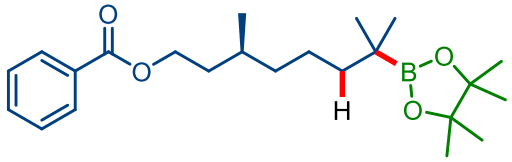
GP II, 104.8 mg, 67% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 6.95 – 6.91 (m, 2H), 4.06 – 3.99 (m, 2H), 1.87 – 1.78 (m, 1H), 1.72 – 1.60 (m, 2H), 1.34 – 1.29 (m, 2H), 1.27 – 1.23 (m, 4H), 1.22 (s, 12H), 0.95 – 0.90 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 133.9, 119.3, 115.2, 103.6, 82.9, 66.8, 41.3, 37.7, 35.8, 29.6, 24.9, 24.9, 24.7, 24.7, 23.7, 19.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{36}BNO_3Na$ ($[M + Na]^+$): 408.2680; found: 408.2679.

methyl (*S*)-4-((3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)-oxy)benzoate (8)



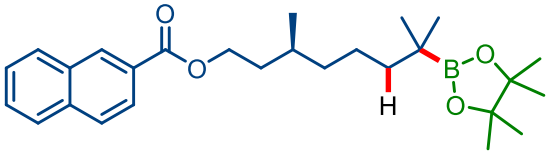
GP II, 110.8 mg, 66% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 6.92 – 6.87 (m, 2H), 4.07 – 3.99 (m, 2H), 3.88 (s, 3H), 1.87 – 1.78 (m, 1H), 1.72 – 1.66 (m, 1H), 1.64 – 1.55 (m, 1H), 1.33 – 1.30 (m, 1H), 1.27 – 1.15 (m, 17H), 0.95 – 0.89 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 162.9, 131.5, 122.2, 114.0, 82.8, 66.5, 51.8, 41.4, 37.7, 36.0, 29.7, 24.9, 24.9, 24.7, 24.6, 23.7, 19.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{39}BO_5Na$ ($[M + Na]^+$): 441.2783; found: 441.2783.

(*S*)-3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl benzoate (9)



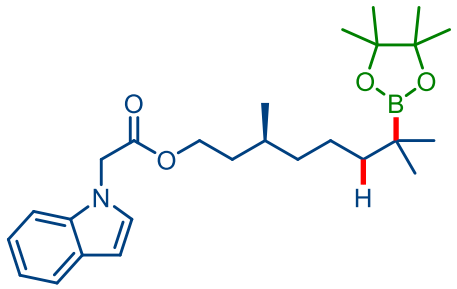
GP II, 123.9 mg, 79% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.57 – 7.51 (m, 1H), 7.46 – 7.40 (m, 2H), 4.40 – 4.30 (m, 2H), 1.85 – 1.76 (m, 1H), 1.70 – 1.61 (m, 1H), 1.61 – 1.52 (m, 1H), 1.36 – 1.28 (m, 2H), 1.28 – 1.24 (m, 3H), 1.23 – 1.18 (m, 13H), 0.95 (d, J = 6.5 Hz, 3H), 0.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.7, 130.5, 129.5, 128.3, 82.8, 63.5, 41.4, 37.7, 35.5, 29.8, 24.9, 24.9, 24.7, 23.7, 19.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{37}BO_4Na$ ($[M + Na]^+$): 411.2677; found: 411.2675.

(S)-3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl 2-naphthoate (**10**)



GP II, 111.5 mg, 63% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.08 – 8.04 (m, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.61 – 7.51 (m, 2H), 4.45 – 4.38 (m, 2H), 1.90 – 1.81 (m, 1H), 1.74 – 1.67 (m, 1H), 1.66 – 1.60 (m, 1H), 1.40 – 1.32 (m, 2H), 1.29 – 1.24 (m, 4H), 1.21 (s, 12H), 0.98 (d, J = 6.5 Hz, 3H), 0.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 135.5, 132.5, 130.9, 129.3, 128.1, 128.1, 127.8, 127.7, 126.5, 125.3, 82.8, 63.8, 41.4, 37.8, 35.6, 29.9, 25.0, 24.9, 24.7, 23.8, 19.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{40}BO_4$ ($[M + H]^+$): 439.3010; found: 439.3010.

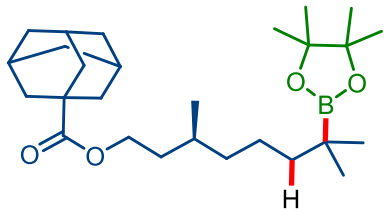
(*S*)-3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl 2-(1*H*-indol-1-yl)acetate (**11**)



GP II, 103.2 mg, 58% yield, brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m,

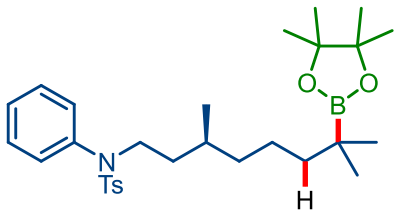
1H), 7.26 – 7.19 (m, 2H), 7.14 – 7.09 (m, 1H), 7.09 – 7.07 (m, 1H), 6.57 – 6.54 (m, 1H), 4.82 (s, 2H), 4.20 – 4.12 (m, 2H), 1.64 – 1.57 (m, 1H), 1.44 – 1.36 (m, 2H), 1.23 – 1.14 (m, 17H), 1.11 – 1.04 (m, 1H), 0.92 (s, 6H), 0.82 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 136.5, 128.6, 128.4, 122.0, 121.1, 119.8, 108.9, 102.5, 82.8, 64.2, 47.9, 41.3, 37.6, 35.4, 29.5, 24.9, 24.9, 24.7, 24.7, 23.6, 19.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{40}BNO_4Na$ ([M + Na]$^+$): 464.2943; found: 464.2941.

(*S*)-3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl adamantane-1-carboxylate (12)



GP II, 128.2 mg, 71% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 – 4.03 (m, 2H), 2.04 – 1.98 (m, 3H), 1.88 (d, J = 2.9 Hz, 6H), 1.76 – 1.59 (m, 8H), 1.58 – 1.50 (m, 1H), 1.44 – 1.37 (m, 1H), 1.22 (s, 17H), 0.91 (s, 6H), 0.89 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 82.8, 62.6, 41.4, 40.7, 38.9, 37.7, 36.5, 35.5, 29.7, 28.0, 24.9, 24.9, 24.7, 23.8, 19.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{47}BO_4Na$ ([M + Na]$^+$): 469.3460; found: 469.3458.

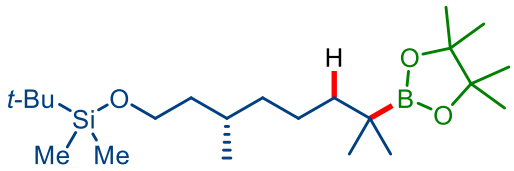
(*S*)-*N*-(3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)-4-methyl-*N*-phenylbenzenesulfonamide (13)



GP II, 166.2 mg, 80% yield, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.24 – 7.18 (m, 3H), 7.15 (d, J = 8.0 Hz, 2H), 6.97 – 6.92 (m, 2H), 3.55 – 3.46 (m, 1H), 3.45 – 3.37 (m, 1H), 2.33 (s, 3H), 1.46 – 1.37 (m, 1H), 1.35 – 1.28 (m, 1H), 1.16 – 1.10 (m, 13H), 1.10 – 1.07 (m, 3H), 1.07 – 1.01 (m, 2H), 0.98 – 0.91 (m, 1H), 0.80 (s, 3H), 0.79 (s, 3H), 0.75 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 139.0, 135.1, 129.2, 128.8, 128.7, 127.6, 127.6, 82.7, 48.5, 41.2, 37.6, 35.1, 29.9,

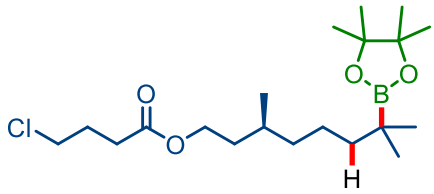
24.8, 24.8, 24.6, 24.6, 23.6, 21.4, 19.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{44}BNO_4SNa$ ([M + Na]$^+$): 536.2976; found: 536.2975.

(*S*)-tert-butyl((3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)oxy)dimethylsilane (**14**)



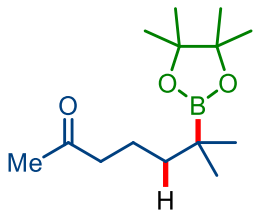
GP II, 130.3 mg, 81% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 – 3.59 (m, 2H), 1.58 – 1.49 (m, 2H), 1.34 – 1.29 (m, 1H), 1.28 – 1.20 (m, 17H), 1.12 – 1.05 (m, 1H), 0.91 (s, 6H), 0.89 (s, 9H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.8, 61.5, 41.5, 40.0, 38.0, 29.4, 26.0, 24.9, 24.9, 24.7, 24.7, 23.8, 19.7, 18.3, -5.2, -5.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{47}BO_3SiNa$ ([M + Na]$^+$): 421.3280; found: 421.3279.

(*S*)-3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl 4-chlorobutanoate (**15**)



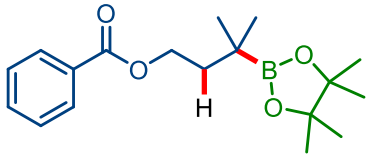
GP II, 120.1 mg, 77% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 – 4.07 (m, 2H), 3.60 (t, *J* = 6.3 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 2.13 – 2.05 (m, 2H), 1.70 – 1.60 (m, 1H), 1.58 – 1.49 (m, 1H), 1.47 – 1.37 (m, 1H), 1.30 – 1.24 (m, 3H), 1.23 – 1.18 (m, 14H), 1.17 – 1.09 (m, 1H), 0.91 (s, 6H), 0.89 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 82.8, 63.2, 44.1, 41.3, 37.7, 35.5, 31.3, 29.7, 27.7, 24.9, 24.9, 24.7, 24.7, 23.7, 19.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{38}BClO_4Na$ ([M + Na]$^+$): 411.2444; found: 411.2443.

6-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-2-one (**16**)



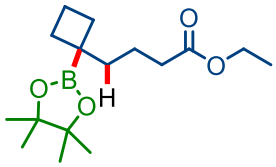
GP II, 37.1 mg, 36% yield, brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (t, *J* = 7.4 Hz, 2H), 2.13 (s, 3H), 1.58 – 1.50 (m, 2H), 1.24 – 1.20 (m, 14H), 0.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 82.9, 44.7, 40.6, 29.7, 24.7, 24.7, 20.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{14}H_{27}BO_3Na$ ($[M + Na]^+$): 277.1945; found: 277.1945.

3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl benzoate (**17**)



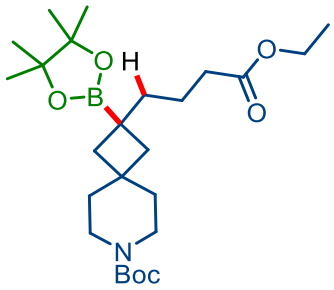
GP II, 88.3 mg, 69% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.56 – 7.51 (m, 1H), 7.45 – 7.40 (m, 2H), 4.36 (t, *J* = 8.0 Hz, 2H), 1.79 (t, *J* = 8.0 Hz, 2H), 1.23 (s, 12H), 1.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 132.7, 130.6, 129.5, 128.2, 83.2, 63.6, 39.0, 25.0, 24.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{27}BO_4Na$ ($[M + Na]^+$): 341.1895; found: 341.1892.

ethyl 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutyl)butanoate (**18**)



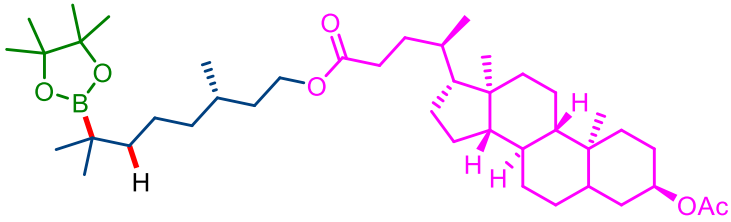
GP II, 103.7 mg, 87% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.1 Hz, 2H), 2.27 (t, *J* = 7.0 Hz, 2H), 2.15 – 2.08 (m, 2H), 1.96 – 1.82 (m, 2H), 1.73 – 1.64 (m, 2H), 1.57 – 1.46 (m, 4H), 1.28 – 1.24 (m, 14H), 1.23 (d, *J* = 1.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 83.0, 60.0, 39.3, 34.9, 30.2, 24.6, 22.3, 18.1, 14.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{29}BO_4Na$ ($[M + Na]^+$): 319.2051; found: 319.2049.

***tert*-butyl 2-(4-ethoxy-4-oxobutyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-azaspiro[3.5]nonane-7-carboxylate** (**19**)



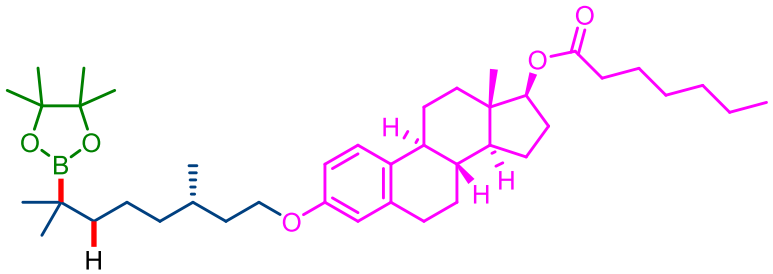
GP II, 154.5 mg, 82% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 5.6 Hz, 2H), 3.25 (t, *J* = 5.6 Hz, 2H), 2.27 (t, *J* = 7.1 Hz, 2H), 2.02 (d, *J* = 12.4 Hz, 2H), 1.60 – 1.55 (m, 2H), 1.53 – 1.49 (m, 4H), 1.44 (s, 12H), 1.27 – 1.23 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 155.0, 83.2, 79.0, 60.1, 41.0, 40.1, 40.0, 37.0, 34.8, 32.8, 28.4, 24.7, 22.3, 14.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{44}BNO_6Na$ ([M + Na]$^+$): 488.3154; found: 488.3154.

(*S*)-3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl (4R)-4-((3*R*, 8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-acetoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (20)



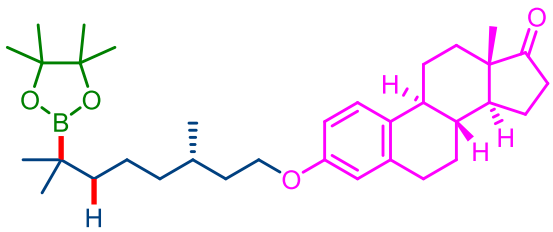
GP II, 191.7 mg, 69% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 – 4.65 (m, 1H), 4.14 – 4.03 (m, 2H), 2.37 – 2.28 (m, 1H), 2.25 – 2.16 (m, 1H), 2.02 (s, 3H), 1.99 – 1.94 (m, 1H), 1.89 – 1.77 (m, 5H), 1.72 – 1.63 (m, 2H), 1.61 – 1.50 (m, 4H), 1.46 – 1.36 (m, 9H), 1.27 – 1.21 (m, 18H), 1.16 – 1.10 (m, 3H), 1.09 – 1.01 (m, 5H), 0.94 – 0.87 (m, 15H), 0.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 170.4, 82.7, 74.2, 62.7, 56.4, 55.9, 42.6, 41.8, 41.3, 40.3, 40.0, 37.6, 35.7, 35.5, 35.2, 34.9, 34.5, 32.1, 31.2, 30.9, 29.6, 28.1, 26.9, 26.5, 26.2, 24.9, 24.8, 24.6, 24.6, 24.1, 23.6, 23.2, 21.3, 20.7, 19.3, 18.2, 11.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{42}H_{73}BO_6Na$ ([M + Na]$^+$): 707.5392; found: 707.5389.

(8*R*,9*S*,13*S*,14*S*,17*S*)-3-(((*S*)-3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl heptanoate (21)



GP II, 213.6 mg, 82% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 1H), 6.72 – 6.65 (m, 1H), 6.62 (d, *J* = 2.7 Hz, 1H), 4.74 – 4.64 (m, 1H), 3.94 (t, *J* = 6.9 Hz, 2H), 2.92 – 2.78 (m, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.21 – 2.17 (m, 1H), 1.90 – 1.83 (m, 2H), 1.80 – 1.72 (m, 2H), 1.70 – 1.64 (m, 2H), 1.60 – 1.50 (m, 3H), 1.49 – 1.41 (m, 4H), 1.39 – 1.36 (m, 2H), 1.34 – 1.27 (m, 10H), 1.26 – 1.24 (m, 2H), 1.22 (s, 13H), 1.17 – 1.13 (m, 1H), 0.93 – 0.87 (m, 12H), 0.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 157.0, 137.8, 132.2, 126.2, 114.4, 112.0, 82.8, 82.4, 66.2, 49.8, 43.8, 43.0, 41.4, 38.6, 37.8, 36.9, 36.3, 34.6, 31.5, 29.8, 29.7, 28.8, 27.6, 27.2, 26.2, 25.1, 25.0, 24.9, 24.7, 24.7, 23.7, 23.3, 22.5, 19.6, 14.0, 12.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{41}H_{67}BO_5Na$ ($[M + Na]^+$): 673.4974; found: 673.4974.

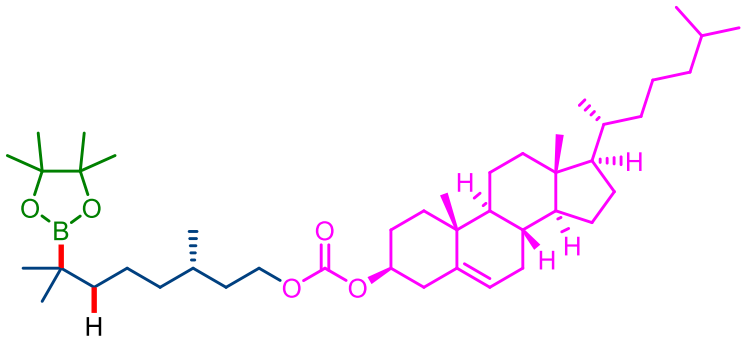
(8*R*,9*S*,13*S*,14*S*)-3-(((*S*)-3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]p-henanthren-17-one (22)



GP II, 131.2 mg, 61% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 1H), 6.73 – 6.68 (m, 1H), 6.63 (d, *J* = 2.7 Hz, 1H), 3.98 – 3.91 (m, 2H), 2.94 – 2.83 (m, 2H), 2.54 – 2.45 (m, 1H), 2.42 – 2.35 (m, 1H), 2.29 – 2.20 (m, 1H), 2.19 – 2.08 (m, 1H), 2.08 – 1.97 (m, 2H), 1.97 – 1.92 (m, 1H), 1.84 – 1.74 (m, 1H), 1.73 – 1.60 (m, 2H), 1.60 – 1.52 (m, 3H), 1.51 – 1.41 (m, 3H), 1.32 – 1.25 (m, 3H), 1.25 – 1.19 (m, 14H), 1.18 – 1.11 (m, 1H), 0.92 (t, *J* = 5.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 157.1, 137.6, 131.7, 126.2, 114.5, 112.1, 82.8, 66.2, 50.4, 48.0, 44.0, 41.4, 38.4, 37.8, 36.3, 35.9, 31.6, 29.7, 29.6, 26.6, 25.9, 24.9, 24.9, 24.7, 24.7, 23.7,

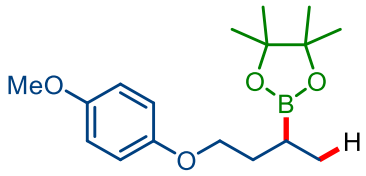
21.6, 19.5, 13.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{34}H_{53}BO_4Na$ ([M + Na]$^+$): 559.3929; found: 559.3928.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,-7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl ((*S*)-3,7-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl) carbonate (23)



GP II, 223.5 mg, 81% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (d, *J* = 5.1 Hz, 1H), 4.51 – 4.42 (m, 1H), 4.18 – 4.11 (m, 2H), 2.45 – 2.32 (m, 2H), 2.04 – 1.92 (m, 3H), 1.90 – 1.79 (m, 2H), 1.74 – 1.64 (m, 2H), 1.60 – 1.53 (m, 3H), 1.50 – 1.42 (m, 4H), 1.38 – 1.32 (m, 3H), 1.30 – 1.26 (m, 3H), 1.26 – 1.21 (m, 16H), 1.19 – 1.15 (m, 2H), 1.14 – 1.07 (m, 5H), 1.03 – 0.95 (m, 6H), 0.93 – 0.85 (m, 19H), 0.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 139.4, 122.8, 82.8, 77.6, 66.3, 56.7, 56.1, 50.0, 42.3, 41.4, 39.7, 39.5, 38.0, 37.7, 36.9, 36.5, 36.2, 35.8, 35.6, 31.9, 31.8, 29.4, 28.2, 28.0, 27.7, 24.9, 24.9, 24.7, 24.7, 24.3, 23.8, 23.7, 22.8, 22.6, 21.0, 19.3, 19.3, 18.7, 11.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{44}H_{77}BO_5Na$ ([M + Na]$^+$): 719.5756; found: 719.5752.

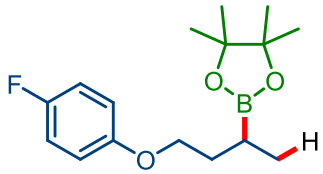
2-(4-(4-methoxyphenoxy)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24)



GP I, 157.6 mg, 64% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.79 (m, 4H), 3.97 – 3.90 (m, 2H), 3.75 (s, 3H), 1.99 – 1.88 (m, 1H), 1.79 – 1.69 (m, 1H),

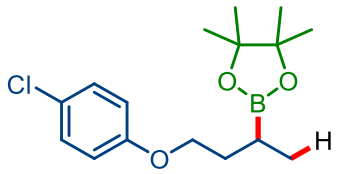
1.23 (s, 13H), 1.04 (d, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 153.4, 115.7, 114.6, 83.0, 68.2, 55.7, 32.6, 24.8, 24.7, 15.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{27}BO_4Na$ ([M + Na]$^+$): 329.1895; found: 329.1896.

2-(4-(4-fluorophenoxy)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25)



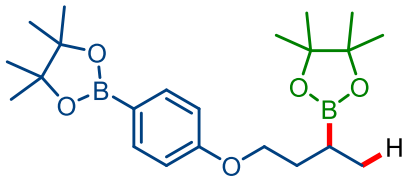
GP I, 178.2 mg, 75% yield, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.91 (m, 2H), 6.86 – 6.81 (m, 2H), 3.98 – 3.91 (m, 2H), 1.99 – 1.89 (m, 1H), 1.80 – 1.70 (m, 1H), 1.26 – 1.20 (m, 13H), 1.04 (d, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (d, J = 237.7 Hz), 155.3 (d, J = 2.0 Hz), 115.7 (d, J = 8.9 Hz), 115.5 (d, J = 6.2 Hz), 83.0, 68.1, 32.4, 24.8, 24.7, 15.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.60. HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{24}BFO_3Na$ ([M + Na]$^+$): 317.1695; found: 317.1707.

2-(4-(4-chlorophenoxy)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26)



GP I, 216.6 mg, 87% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 2H), 6.85 – 6.80 (m, 2H), 3.99 – 3.93 (m, 2H), 1.99 – 1.89 (m, 1H), 1.79 – 1.70 (m, 1H), 1.25 – 1.18 (m, 13H), 1.04 (d, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 129.2, 125.2, 115.9, 83.1, 67.8, 32.3, 24.8, 24.7, 15.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{24}BClO_3Na$ ([M + Na]$^+$): 333.1399; found: 333.1399.

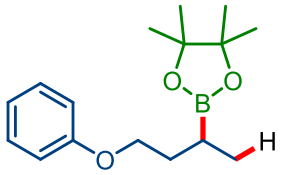
4,5,5-tetramethyl-2-(4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)phenyl)-1,3,2-dioxaborolane (27)



GP I, 237.3 mg, 73% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 6.92 – 6.86 (m, 2H), 4.05 – 3.98 (m, 2H), 2.01 – 1.91 (m, 1H), 1.81 – 1.71 (m,

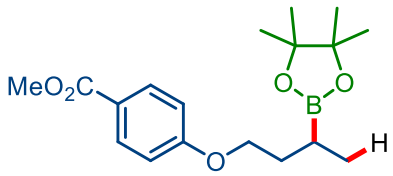
1H), 1.33 (s, 12H), 1.24 – 1.19 (m, 13H), 1.04 (d, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 136.4, 114.0, 83.5, 83.0, 67.1, 32.3, 24.8, 24.8, 24.7, 15.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{36}B_2O_5Na$ ([M + Na]$^+$): 425.2641; found: 425.2641.

4,4,5,5-tetramethyl-2-(4-phenoxybutan-2-yl)-1,3,2-dioxaborolane (28)



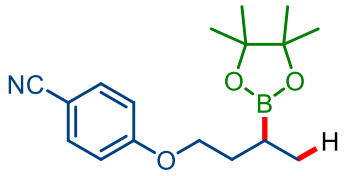
GP I, 192.7 mg, 87% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 6.93 – 6.87 (m, 3H), 4.03 – 3.94 (m, 2H), 2.01 – 1.92 (m, 1H), 1.81 – 1.72 (m, 1H), 1.28 – 1.19 (m, 13H), 1.05 (d, J = 7.5 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 129.3, 120.3, 114.6, 83.0, 67.2, 32.4, 24.8, 24.7, 15.5. . HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{25}BO_3Na$ ([M + Na]$^+$): 299.1789; found: 299.1787.

methyl 4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)benzoate (29)



GP I, 191.6 mg, 71% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 6.94 – 6.89 (m, 2H), 4.08 – 4.02 (m, 2H), 3.87 (s, 3H), 2.02 – 1.93 (m, 1H), 1.83 – 1.74 (m, 1H), 1.24 (s, 13H), 1.05 (d, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 162.9, 131.4, 122.1, 114.1, 83.0, 67.5, 51.7, 32.1, 24.7, 24.6, 15.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{27}BO_5Na$ ([M + Na]$^+$): 357.1844; found: 357.1844.

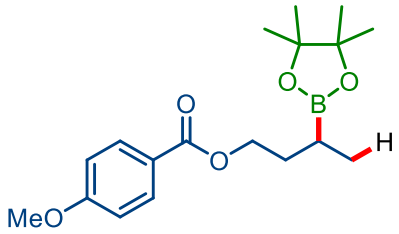
4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)benzonitrile (30)



GP I, 165.0 mg, 68% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 6.97 – 6.93 (m, 2H), 4.09 – 4.02 (m, 2H), 2.02 – 1.92 (m, 1H), 1.82 – 1.73 (m, 1H), 1.24 (s, 13H), 1.05 (d, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 133.9, 119.3, 115.3, 103.5, 83.1, 67.8, 32.0, 24.8, 24.7, 15.5. HRMS (ESI-TOF) (m/z):

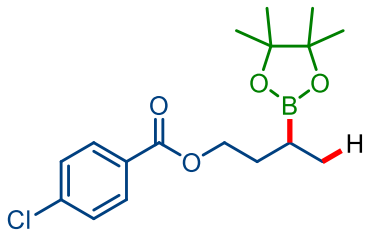
Calcd for $C_{17}H_{24}BNO_3Na$ ([M + Na]$^+$): 324.1741; found: 324.1740.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-methoxybenzoate (31)



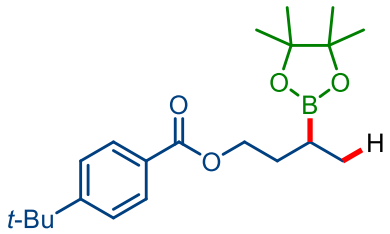
GP I, 234.4 mg, 87% yield, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 6.92 – 6.87 (m, 2H), 4.36 – 4.29 (m, 2H), 3.85 (s, 3H), 1.99 – 1.89 (m, 1H), 1.78 – 1.67 (m, 1H), 1.26 – 1.21 (m, 13H), 1.06 (d, J = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 163.2, 131.5, 123.1, 113.5, 83.1, 64.2, 55.4, 31.8, 24.7, 24.7, 15.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{27}BO_5Na$ ([M + Na]$^+$): 357.1844; found: 357.1842.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-chlorobenzoate (32)



GP I, 223.4 mg, 82% yield, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.42 – 7.37 (m, 2H), 4.39 – 4.32 (m, 2H), 1.99 – 1.89 (m, 1H), 1.79 – 1.69 (m, 1H), 1.26 – 1.19 (m, 13H), 1.06 (d, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 139.1, 130.9, 129.0, 128.6, 83.1, 64.7, 31.7, 24.7, 24.7, 15.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{24}BClO_4Na$ ([M + Na]$^+$): 361.1348; found: 361.1347.

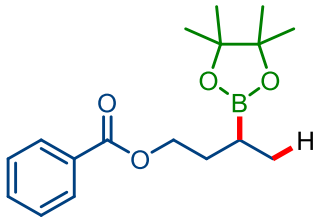
3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-(*tert*-butyl)benzoate (33)



GP I, 246.4 mg, 85% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.46 – 7.42 (m, 2H), 4.37 – 4.31 (m, 2H), 1.99 – 1.89 (m, 1H), 1.78 – 1.68 (m, 1H), 1.33 (s, 9H), 1.26 – 1.21 (m, 13H), 1.05 (d, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz,

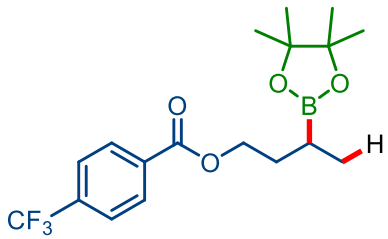
$CDCl_3$*d*) δ 166.7, 156.3, 129.4, 127.8, 125.2, 83.1, 64.3, 35.0, 31.8, 31.1, 24.8, 24.7, 15.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{33}BO_4Na$ ($[M + Na]^+$): 383.2364; found: 383.2362.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl benzoate (**34**)



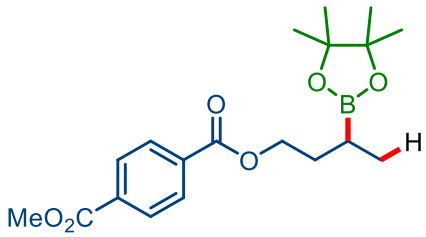
GP I, 218.4 mg, 89% yield, yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 2H), 7.56 – 7.51 (m, 1H), 7.45 – 7.39 (m, 2H), 4.39 – 4.33 (m, 2H), 2.00 – 1.91 (m, 1H), 1.80 – 1.70 (m, 1H), 1.26 – 1.20 (m, 13H), 1.06 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.7, 130.6, 129.5, 128.2, 83.1, 64.5, 31.8, 24.7, 24.7, 15.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{25}BO_4Na$ ($[M + Na]^+$): 327.1738; found: 327.1735.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-(trifluoromethyl)benzoate (**35**)



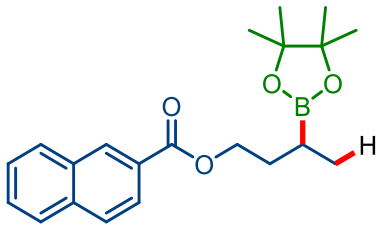
GP I, 215.2 mg, 72% yield, colourless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 2H), 7.72 – 7.67 (m, 2H), 4.42 – 4.37 (m, 2H), 2.01 – 1.91 (m, 1H), 1.81 – 1.71 (m, 1H), 1.26 – 1.24 (m, 13H), 1.06 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 134.2 (q, *J* = 32.6 Hz), 133.8, 130.0, 125.3 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.7 Hz), 83.2, 65.1, 31.7, 24.8, 24.7, 15.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.09. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{24}BF_3O_4Na$ ($[M + Na]^+$): 395.1612; found: 395.1611.

methyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl) terephthalate (**36**)



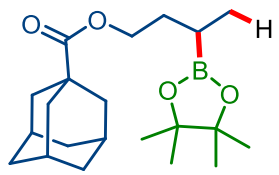
GP I, 232.4 mg, 80% yield, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 4H), 4.41 – 4.36 (m, 2H), 3.94 (s, 3H), 2.02 – 1.92 (m, 1H), 1.81 – 1.71 (m, 1H), 1.27 – 1.22 (m, 13H), 1.06 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.8, 134.3, 133.7, 129.5, 129.4, 83.1, 64.9, 52.3, 31.7, 24.7, 24.6, 15.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{27}BO_6Na$ ($[M + Na]^+$): 385.1793; found: 385.1791.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 2-naphthoate (**37**)



GP I, 244.5 mg, 86% yield, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.09 – 8.04 (m, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.60 – 7.50 (m, 2H), 4.46 – 4.39 (m, 2H), 2.06 – 1.96 (m, 1H), 1.85 – 1.75 (m, 1H), 1.30 – 1.27 (m, 1H), 1.25 (s, 12H), 1.09 (d, *J* = 7.4 Hz, 3H). HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{27}BO_4Na$ ($[M + Na]^+$): 377.1895; found: 377.1894.

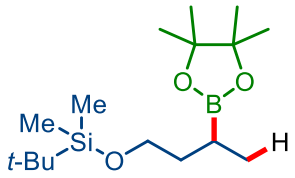
3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl (3r,5r,7r)-adamantane-1-carboxylate (**38**)



GP I, 212.1 mg, 73% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 – 4.04 (m, 2H), 2.03 – 1.97 (m, 3H), 1.88 (d, *J* = 3.0 Hz, 6H), 1.84 – 1.76 (m, 1H), 1.74 – 1.67 (m, 6H), 1.63 – 1.53 (m, 1H), 1.24 (s, 12H), 1.16 – 1.07 (m, 1H), 1.00 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 83.0, 63.5, 40.7, 38.8, 36.5, 31.6, 28.0, 24.8, 24.7, 15.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{21}H_{35}BO_4Na$ ($[M + Na]^+$): 385.2521;

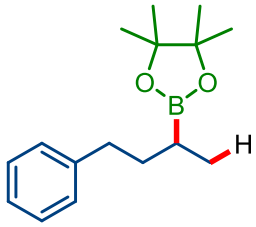
found: 385.2521.

***tert*-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)silane (39)**



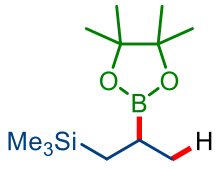
GP I, 153.7 mg, 61% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 – 3.58 (m, 2H), 1.76 – 1.66 (m, 1H), 1.54 – 1.45 (m, 1H), 1.23 (s, 12H), 1.14 – 1.07 (m, 1H), 0.98 (d, J = 7.3 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 82.8, 62.6, 36.1, 26.0, 24.8, 24.7, 18.4, 15.5, -5.2, -5.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{35}BO_3SiNa$ ($[M + Na]^+$): 337.2341; found: 337.2341.

4,4,5,5-tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane (40)



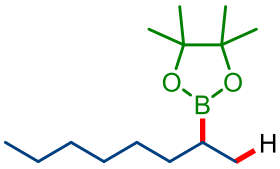
GP I, 177.2 mg, 85% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.20 – 7.13 (m, 3H), 2.65 – 2.59 (m, 2H), 1.83 – 1.73 (m, 1H), 1.63 – 1.53 (m, 1H), 1.25 (s, 12H), 1.11 – 1.04 (m, 1H), 1.02 (d, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 128.4, 128.2, 125.5, 82.8, 35.3, 35.3, 24.8, 24.7, 15.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{25}BO_2Na$ ($[M + Na]^+$): 283.1840; found: 283.1840.

trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (41)



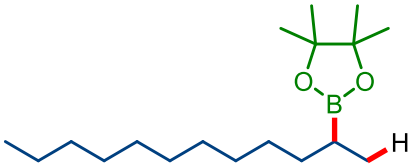
GP I, 118.6 mg, 61% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (s, 12H), 1.06 – 0.98 (m, 1H), 0.94 (d, J = 7.0 Hz, 3H), 0.76 – 0.69 (m, 1H), 0.39 – 0.32 (m, 1H), -0.08 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.8, 24.8, 24.7, 19.9, 19.3, -0.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{12}H_{27}BO_2SiNa$ ($[M + Na]^+$): 265.1766; found: 265.1761.

4,4,5,5-tetramethyl-2-(octan-2-yl)-1,3,2-dioxaborolane (42)



GP I, 143.8 mg, 74% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 – 1.39 (m, 1H), 1.31 – 1.22 (m, 21H), 1.03 – 0.94 (m, 4H), 0.90 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 33.2, 31.9, 29.5, 28.9, 24.7, 24.7, 22.6, 15.5, 14.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{14}H_{30}BO_2$ ($[M + H]^+$): 241.2333; found: 241.2332.

2-(dodecan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (43)

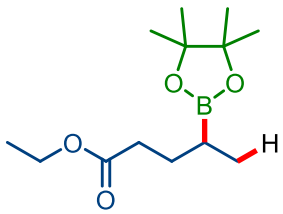


GP I, 211.4 mg, 89% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 – 1.38 (m, 1H), 1.31 – 1.22 (m, 29H), 1.03 – 0.93 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 33.3, 31.9, 29.9, 29.6, 29.4, 29.0, 24.7, 24.7, 22.7, 15.5, 14.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{37}BO_2Na$ ($[M + Na]^+$): 319.2779; found: 319.2779.

2-(icosan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (44)

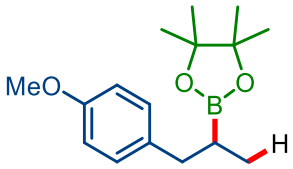
GP I, 258.6 mg, 79% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 – 1.40 (m, 1H), 1.34 – 1.09 (m, 45H), 1.03 – 0.93 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7, 33.3, 31.9, 29.9, 29.7, 29.7, 29.4, 29.0, 24.7, 24.7, 22.7, 15.5, 14.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{53}BO_2Na$ ($[M + Na]^+$): 431.4031; found: 431.4031.

ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (45)



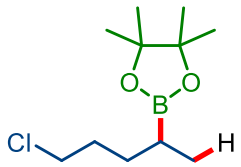
GP I, 134.9 mg, 65% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (q, *J* = 7.1 Hz, 2H), 2.33 (t, *J* = 7.9 Hz, 2H), 1.82 – 1.73 (m, 1H), 1.67 – 1.58 (m, 1H), 1.27 – 1.22 (m, 15H), 1.03 – 0.96 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 83.0, 60.1, 33.7, 28.2, 24.7, 24.7, 15.2, 14.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{25}BO_4Na$ ($[M + Na]^+$): 279.1738; found: 279.1738.

2-(1-(4-methoxyphenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (46)



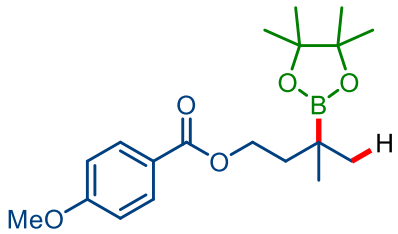
GP I, 167.5 mg, 75% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.09 (m, 2H), 6.82 – 6.78 (m, 2H), 3.78 (s, 3H), 2.78 – 2.71 (m, 1H), 2.52 – 2.45 (m, 1H), 1.36 – 1.28 (m, 1H), 1.19 (s, 6H), 1.18 (s, 6H), 0.95 (d, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 134.4, 129.7, 113.4, 82.9, 55.2, 38.0, 24.7, 24.7, 15.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{25}BO_3Na$ ($[M + Na]^+$): 299.1789; found: 299.1787.

2-(5-chloropentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (47)



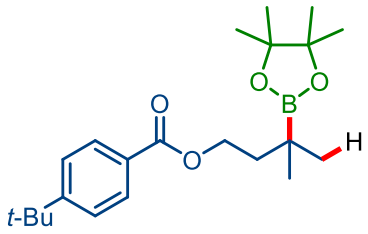
GP I, 110.4 mg, 59% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (t, *J* = 6.9 Hz, 2H), 1.84 – 1.75 (m, 2H), 1.61 – 1.51 (m, 1H), 1.46 – 1.37 (m, 1H), 1.24 (s, 12H), 1.05 – 0.96 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 45.2, 32.0, 30.4, 24.7, 24.7, 15.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{25}BO_4$ ($[M + Na]^+$): 279.1738; found: 279.1738. HRMS (ESI-TOF) (m/z): Calcd for $C_{11}H_{22}BClO_2Na$ ($[M + Na]^+$): 255.1363; found: 255.1361.

3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-methoxybenzoat-e (48)



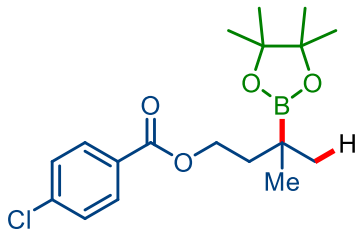
GP I, 239.6 mg, 86% yield, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 6.93 – 6.88 (m, 2H), 4.32 (t, *J* = 8.0 Hz, 2H), 3.85 (s, 3H), 1.77 (t, *J* = 8.0 Hz, 2H), 1.23 (s, 12H), 1.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 163.1, 131.5, 123.1, 113.5, 83.2, 63.3, 55.4, 39.0, 25.1, 24.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{29}BO_5Na$ ($[M + Na]^+$): 371.2000; found: 371.1998.

3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-(*tert*-butyl)benzoate (49)



GP I, 239.6 mg, 80% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.46 – 7.41 (m, 2H), 4.38 – 4.32 (m, 2H), 1.78 (t, *J* = 7.6 Hz, 2H), 1.33 (s, 9H), 1.22 (s, 12H), 1.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 156.2, 129.4, 127.8, 125.2, 83.1, 63.4, 39.0, 35.0, 31.1, 25.0, 24.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{35}BO_4Na$ ($[M + Na]^+$): 397.2521; found: 397.2520.

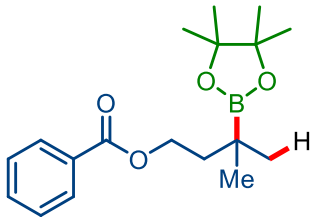
3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-chlorobenzoate (50)



GP I, 229.9 mg, 81% yield, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.41 – 7.37 (m, 2H), 4.36 (t, *J* = 7.7 Hz, 2H), 1.78 (t, *J* = 7.7 Hz, 2H), 1.23 (s, 12H), 1.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 139.1, 130.9, 129.1, 128.5, 83.1, 63.9, 38.9, 25.0, 24.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{26}BClO_4Na$ ([M +

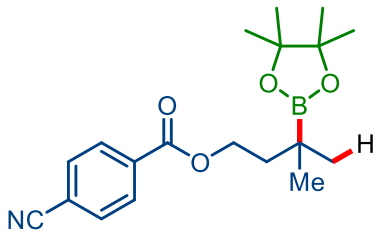
Na]$^+$): 375.1505; found: 375.1505.

3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl benzoate (51)



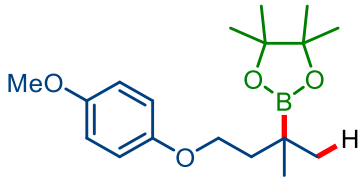
GP I, 203.7 mg, 80% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.56 – 7.51 (m, 1H), 7.45 – 7.40 (m, 2H), 4.36 (t, *J* = 8.0 Hz, 2H), 1.79 (t, *J* = 8.0 Hz, 2H), 1.23 (s, 12H), 1.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 132.7, 130.6, 129.5, 128.2, 83.2, 63.6, 39.0, 25.0, 24.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{27}BO_4Na$ ([M + Na]$^+$): 341.1895; found: 341.1894.

3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-cyanobenzoate (52)



GP I, 148.4 mg, 54% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 2H), 7.75 – 7.71 (m, 2H), 4.40 (t, *J* = 7.6 Hz, 2H), 1.79 (t, *J* = 7.5 Hz, 2H), 1.23 (s, 12H), 1.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 134.4, 132.1, 130.1, 118.0, 116.2, 83.2, 64.5, 38.9, 25.0, 24.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{26}BNO_4Na$ ([M + Na]$^+$): 366.1847; found: 366.1847.

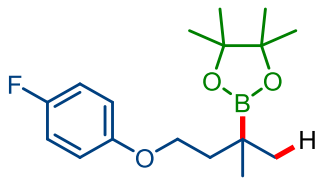
2-(4-(4-methoxyphenoxy)-2-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53)



GP I, 165.5 mg, 64% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.83 (m, 2H), 6.82 – 6.78 (m, 2H), 3.94 (t, *J* = 7.3 Hz, 2H), 3.74 (s, 3H), 1.77 (t, *J* = 7.3 Hz, 2H),

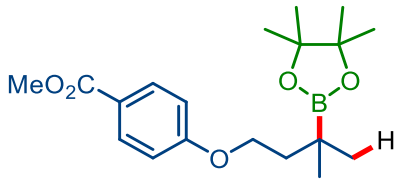
1.22 (s, 12H), 1.01 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 153.3, 115.7, 114.4, 82.9, 67.0, 55.5, 39.8, 25.0, 24.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{29}BO_4Na$ ($[M + Na]^+$): 343.2051; found: 343.2050.

2-(4-(4-fluorophenoxy)-2-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (54)



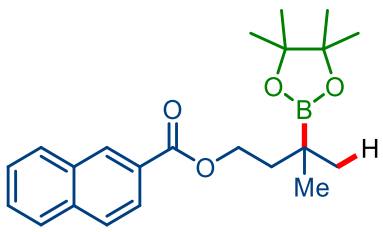
GP I, 166.2 mg, 67% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.91 (m, 2H), 6.88 – 6.81 (m, 2H), 3.96 (t, *J* = 7.3 Hz, 2H), 1.78 (t, *J* = 7.3 Hz, 2H), 1.23 (s, 12H), 1.01 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (d, *J* = 237.7 Hz), 155.3 (d, *J* = 2.1 Hz), 115.7 (d, *J* = 5.4 Hz), 115.6 (d, *J* = 20.3 Hz), 83.1, 67.1, 39.7, 25.1, 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.49. HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{26}BFO_3Na$ ($[M + Na]^+$): 331.1851; found: 331.1851.

methyl 4-(3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)benzoate (55)



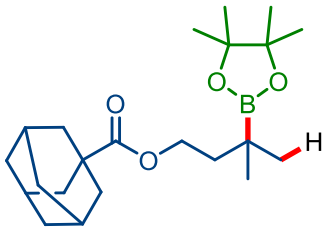
GP I, 241.1 mg, 86% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 6.95 – 6.90 (m, 2H), 4.07 (t, *J* = 7.4 Hz, 2H), 3.87 (s, 3H), 1.80 (t, *J* = 7.4 Hz, 2H), 1.24 (s, 12H), 1.02 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 162.9, 131.4, 122.2, 114.2, 83.1, 66.5, 51.7, 39.4, 25.1, 24.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{19}H_{29}BO_5Na$ ($[M + Na]^+$): 371.2000; found: 371.1998.

3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 2-naphthoate (56)



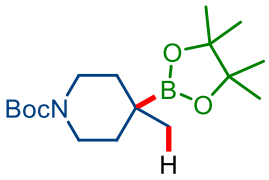
GP I, 190.2 mg, 64% yield, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.09 – 8.03 (m, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.58 – 7.48 (m, 2H), 4.43 (t, *J* = 7.6 Hz, 2H), 1.85 (t, *J* = 7.7 Hz, 2H), 1.22 (s, 12H), 1.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 135.4, 132.4, 130.8, 129.2, 128.0, 127.9, 127.8, 127.6, 126.4, 125.2, 83.1, 63.7, 39.0, 25.0, 24.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{29}BO_4Na$ ($[M + Na]^+$): 391.2051; found: 391.2051.

3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl adamantane-1-carboxylate (57)



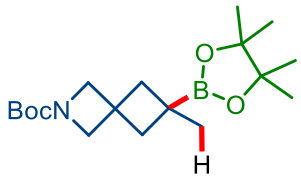
GP I, 223.2 mg, 74% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (t, *J* = 7.7 Hz, 2H), 2.03 – 1.98 (m, 3H), 1.88 (d, *J* = 2.9 Hz, 6H), 1.74 – 1.67 (m, 6H), 1.62 (t, *J* = 7.8 Hz, 2H), 1.23 (s, 12H), 0.97 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 83.1, 62.7, 40.5, 38.9, 38.8, 36.5, 28.0, 25.0, 24.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{37}BO_4Na$ ($[M + Na]^+$): 399.2677; found: 399.2676.

***tert*-butyl 4-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate (58)**



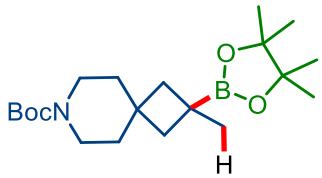
GP I, 211.9 mg, 81% yield, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 2H), 2.76 (t, *J* = 12.9 Hz, 2H), 1.79 (d, *J* = 13.0 Hz, 2H), 1.45 (s, 9H), 1.24 (s, 12H), 1.13 – 1.04 (m, 2H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 83.0, 78.8, 43.3, 35.7, 28.4, 24.9, 24.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{32}BNO_4Na$ ($[M + Na]^+$): 348.2317; found: 348.2316.

***tert*-butyl 6-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-azaspiro[3.3]heptane-2-carboxylate (59)**



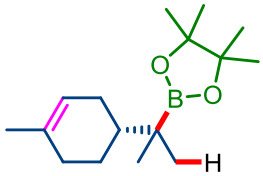
GP I, 165.9 mg, 61% yield, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 2H), 3.80 (s, 2H), 2.38 – 2.33 (m, 2H), 1.82 – 1.78 (m, 2H), 1.43 (s, 9H), 1.23 (s, 12H), 1.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 83.2, 79.0, 42.8, 33.7, 28.4, 24.8, 24.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{18}H_{32}BNO_4Na$ ($[M + Na]^+$): 360.2317; found: 360.2315.

***tert*-butyl 2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-azaspiro-[3.5]nonane-7-carboxylate (60)**



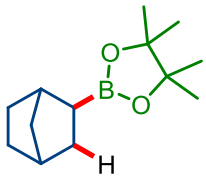
GP I, 233.8 mg, 79% yield, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.32 – 3.24 (m, 4H), 2.10 – 2.04 (m, 2H), 1.52 – 1.47 (m, 5H), 1.46 – 1.42 (m, 10H), 1.24 (s, 12H), 1.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 82.9, 78.7, 41.4, 39.9, 36.7, 32.1, 28.3, 26.4, 24.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{36}BNO_4Na$ ($[M + Na]^+$): 388.2630; found: 388.2630.

(*R*)-4,4,5,5-tetramethyl-2-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)-1,3,2-dioxaborolane (61)



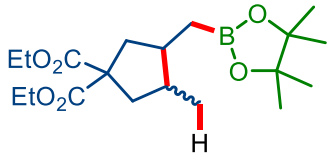
GP I, 114.5 mg, 54% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.34 (m, 1H), 2.02 – 1.87 (m, 3H), 1.86 – 1.77 (m, 1H), 1.75 – 1.69 (m, 1H), 1.63 (s, 3H), 1.46 – 1.37 (m, 1H), 1.26 – 1.19 (m, 13H), 0.91 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 121.3, 82.7, 41.7, 31.4, 27.6, 25.5, 24.7, 24.7, 23.4, 22.0, 21.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{16}H_{29}BO_2Na$ ($[M + Na]^+$): 287.2153; found: 287.2153.

2-((2*S*)-bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (62)



GP I, 132.9 mg, 74% yield, colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 – 2.26 (m, 1H), 2.24 – 2.20 (m, 1H), 1.58 – 1.43 (m, 3H), 1.37 – 1.31 (m, 1H), 1.25 – 1.20 (m, 14H), 1.20 – 1.13 (m, 2H), 0.91 – 0.84 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.8, 38.7, 38.1, 36.6, 32.2, 32.2, 29.3, 24.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{13}H_{23}BO_2Na$ ($[M + Na]^+$): 245.1683; found: 245.1683.

diethyl 3-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclope-ntane-1,1-dicarboxylate (**63**)

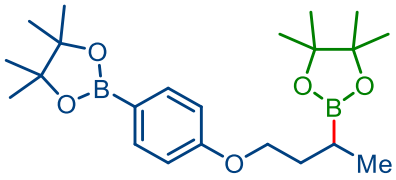


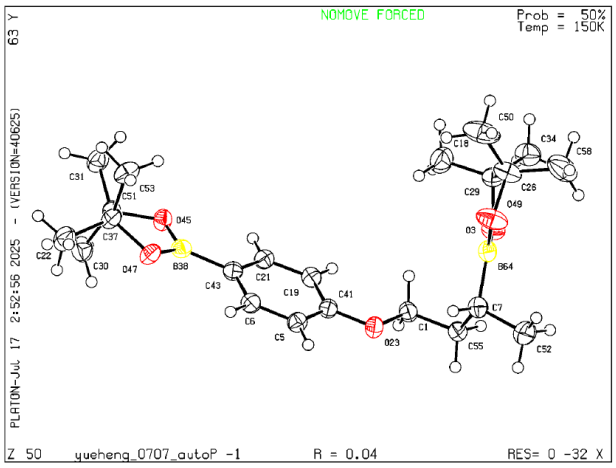
GP I, 261.8 mg, 88% yield, d.r. = 8:1, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 – 4.12 (m, 4H), 2.63 – 2.57 (m, 0.12H), 2.49 (t, *J* = 6.8 Hz, 0.14H), 2.45 – 2.36 (m, 1.79H), 2.28 – 2.11 (m, 2.03H), 2.01 – 1.92 (m, 1.77H), 1.79 – 1.70 (m, 0.23H), 1.30 – 1.16 (m, 19.65H), 0.97 (d, *J* = 6.1 Hz, 0.34H), 0.83 (d, *J* = 6.8 Hz, 2.67H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1 (major), 172.9 (major), 83.0 (minor), 82.9 (major), 61.2 (major), 61.1 (minor), 59.1 (major), 58.2 (minor), 43.0 (minor), 42.5 (minor), 42.3 (minor), 41.1 (major), 40.9 (major), 38.5 (major), 36.8 (major), 24.9 (minor), 24.8 (major), 24.7 (major), 17.3 (minor), 15.1 (major), 14.0 (major). Calcd for $C_{19}H_{34}BO_6$ ($[M + H]^+$): 369.2443; found: 369.2441.

4. X-ray single crystal diffraction data

Sample preparation: A solution of compounds (50 mg) in EtOAc (0.5 mL) was placed in a vial (5 mL). *n*-hexane (1 mL) was added to the solution with a dropper. The single crystal was obtained by slowly evaporating the mixed solvent at room temperature under the aerobic conditions. Data collection for crystal structure was performed using Mo Kα radiation on a Bruker APEXII diffractometer. Thermal ellipsoids are drawn at 50% probability level.

4.1 X-ray single crystal diffraction data of 27 (CCDC 2473444)





Crystal data and structure refinement for **27**

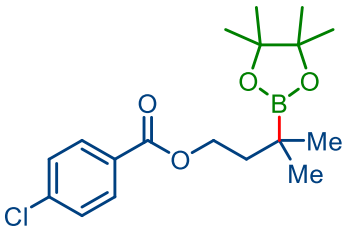
Bond precision:	C-C = 0.0020 A		Wavelength=1.54184
Cell:	a=6.5385(2)	b=12.1674(4)	c=14.9129(4)
	alpha=98.784(2)	beta=92.212(2)	gamma=97.702(2)
Temperature:	150 K		
	Calculated		Reported
Volume	1159.81(6)		1159.81(6)
Space group	P -1		P -1
Hall group	-P 1		-P 1
Moiety formula	C22 H36 B2 O5		C22 H36 B2 O5
Sum formula	C22 H36 B2 O5		C22 H36 B2 O5
Mr	402.13		402.13
Dx,g cm-3	1.151		1.151
Z	2		2
Mu (mm-1)	0.622		0.622
F000	436.0		436.0
F000’	437.27		
h,k,lmax	8, 15, 18		7, 15, 18
Nref	4836		4447
Tmin,Tmax	0.946, 0.957		0.830, 1.000
Tmin’	0.946		

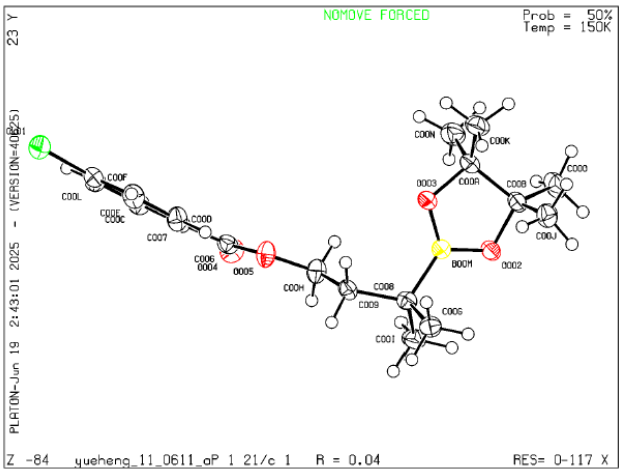
Correction method= # Reported T Limits: Tmin=0.830 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.920	Theta(max)= 75.793
R(reflections)= 0.0445(3813)	wR2(reflections)= 0.1275(4447)
S = 1.050	Npar= 271

4.2 X-ray single crystal diffraction data of 50 (CCDC 2465481)





Crystal data and structure refinement for **50**

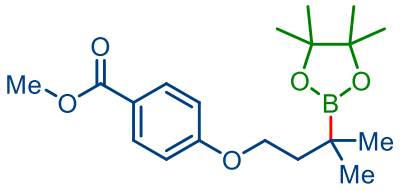
Bond precision:	C-C = 0.0019 A		Wavelength=1.54184
Cell:	a=12.0882(2)	b=15.0961(3)	c=10.6904(2)
	alpha=90	beta=107.296(2)	gamma=90
Temperature:	150 K		
	Calculated		Reported
Volume	1862.62(6)		1862.62(6)
Space group	P 21/c		P 1 21/c 1
Hall group	-P 2ybc		-P 2ybc
Moiety formula	C18 H26 B Cl O4		C18 H26 B Cl O4
Sum formula	C18 H26 B Cl O4		C19 H26 B0.25 Cl O4
Mr	352.65		356.55
Dx,g cm-3	1.258		1.271
Z	4		4
Mu (mm-1)	1.961		1.974
F000	752.0		761.0
F000’	755.52		
h,k,lmax	15, 19, 13		15, 18, 13
Nref	3904		3706
Tmin,Tmax	0.847, 0.888		0.802, 1.000
Tmin’	0.837		

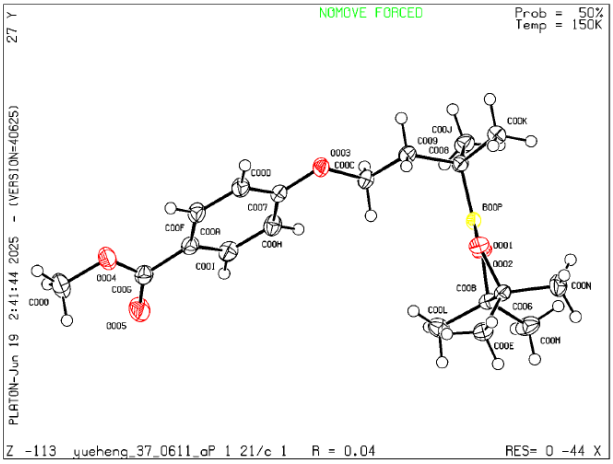
Correction method= # Reported T Limits: Tmin=0.802 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.949	Theta(max)= 76.431
R(reflections)= 0.0351(3355)	wR2(reflections)= 0.0968(3706)
S = 1.080	Npar= 223

4.3 X-ray single crystal diffraction data of 55 (CCDC 2465487)



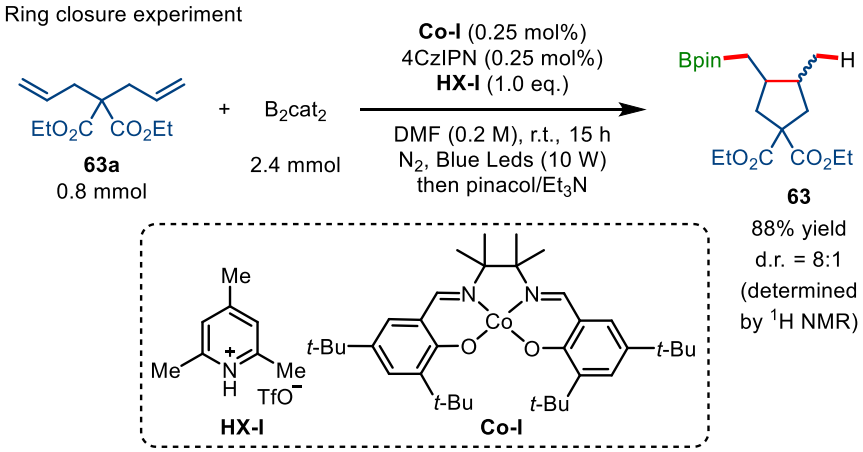


Crystal data and structure refinement for **55**

Bond precision:	C-C = 0.0016 A		Wavelength=1.54184
Cell:	a=13.4652(2)	b=6.1312(1)	c=23.3002(4)
	alpha=90	beta=91.385(2)	gamma=90
Temperature:	150 K		
	Calculated		Reported
Volume	1923.05(5)		1923.05(5)
Space group	P 21/c		P 1 21/c 1
Hall group	-P 2ybc		-P 2ybc
Moiety formula	C19 H29 B O5		C19 H29 B O5
Sum formula	C19 H29 B O5		C19 H29 B O5
Mr	348.23		348.23
Dx,g cm-3	1.203		1.203
Z	4		4
Mu (mm-1)	0.684		0.684
F000	752.0		752.0
F000’	754.31		
h,k,lmax	17, 7, 29		16, 7, 29
Nref	4060		3899
Tmin,Tmax	0.952, 0.966		0.913, 1.000
Tmin’	0.884		
Correction method= # Reported T Limits: Tmin=0.913 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.960		Theta(max)= 76.944	
R(reflections)= 0.0356(3475)		wR2(reflections)= 0.0963(3899)	
S = 1.069		Npar= 233	

5. Mechanism study experiments

5.1 Procedure of ring closure experiment

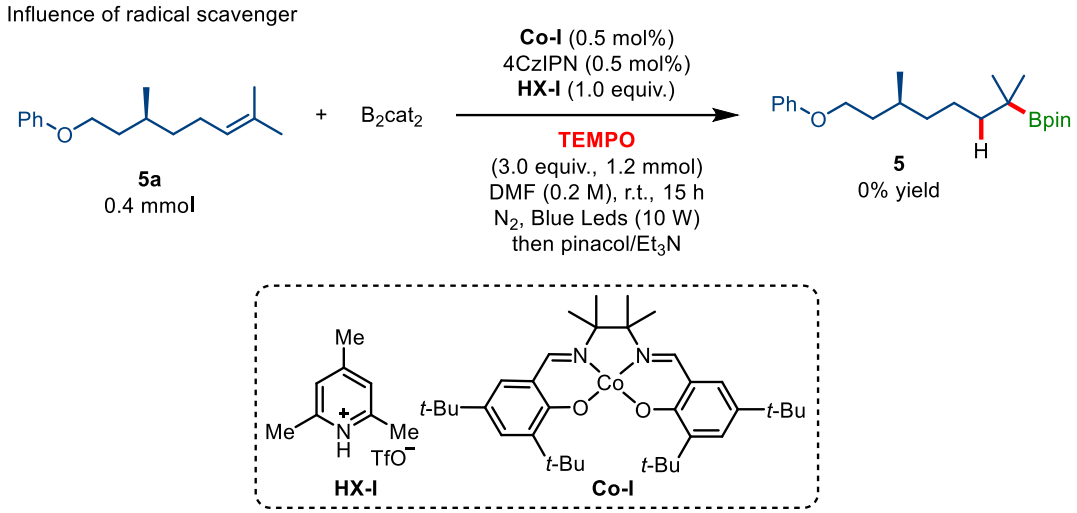


In an oven-dried 15 mL tube equipped with a stirring bar, unactivated alkene **63a** (0.8 mmol, 1.0 equiv.), bis(catecholato)diboron (B_2cat_2) (2.4 mmol, 3.0 equiv.), collidinium triflate (**HX-I**) (0.8 mmol, 1.0 equiv.), 4CzIPN (0.002 mmol, 0.25 mol%), and **Co-I** (0.002 mmol, 0.25 mol%) were added. The tube was charged with nitrogen (repeated three times), then *N*,*N*-Dimethylformamide (DMF, 4 mL) was injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) for 15 h. Then pinacol (4.0 mmol, 5.0 equiv.) and Et_3N (5.6 mL) were added and stirring was continued for 1 h. After completion, the resulting mixture was quenched with H_2O (30 mL). Then the mixture was extracted with ethyl acetate (30 mL). The organic layer was washed with brine (30 mL × 2), dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired products **63** in 88% yield (261.8 mg, d.r. = 8:1). The d.r. value was determined by ^1H NMR.

5.2 Influence of radical scavenger

In an oven-dried 15 mL tube equipped with a stirring bar, unactivated alkene **5a** (0.4 mmol, 1.0 equiv.), bis(catecholato)diboron (B_2cat_2) (1.2 mmol, 3.0 equiv.), collidinium triflate (**HX-I**) (0.4 mmol, 1.0 equiv.), 4CzIPN (0.002 mmol, 0.5 mol%), **Co-I** (0.002 mmol, 0.5 mol%) and TEMPO (0.6 mmol, 3.0 equiv.) were added. The tube was charged with nitrogen (repeated three times), then *N*,*N*-Dimethylformamide (DMF, 2

mL) was injected. The resulting suspension was stirred at room temperature and irradiated with blue LEDs (440 nm, 10 W) for 15 h. Then pinacol (2.0 mmol, 5.0 equiv.) and Et_3N (2.8 mL) were added and stirring was continued for 1 h. After completion, the resulting mixture was monitored by TLC, and no desired product (**5**) was formed.



5.3 UV-Vis absorption experiments

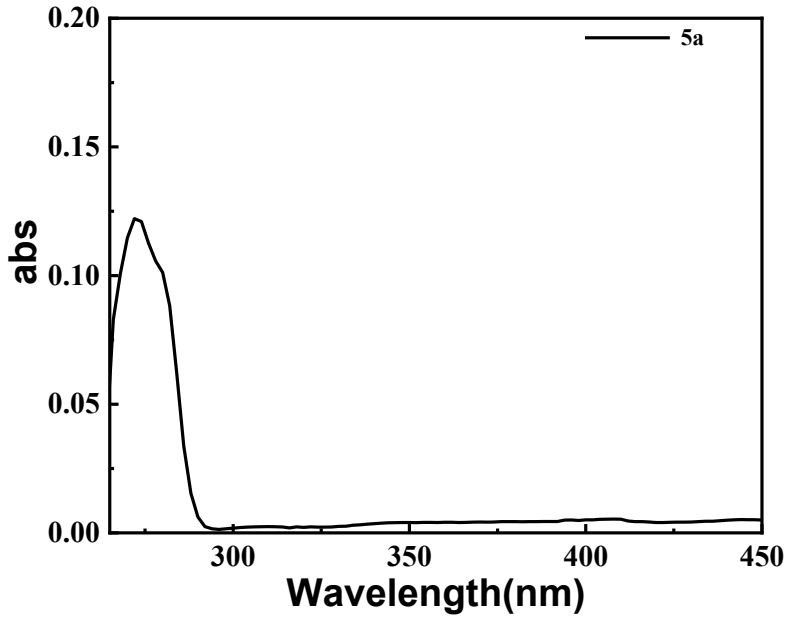


Figure S1 UV-Vis Absorption of **5a** in DMF (Concentration: 0.1 mM)

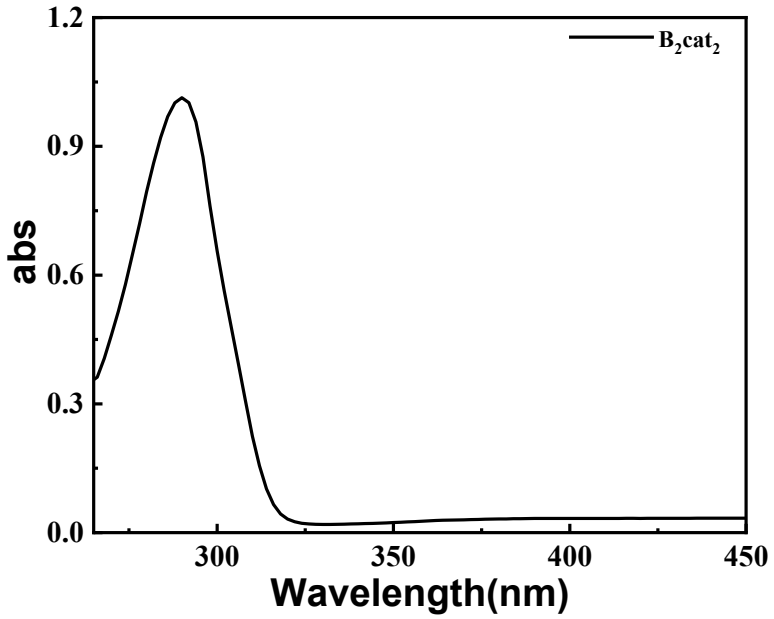


Figure S2 UV-Vis Absorption of B_2cat_2 in DMF (Concentration: 0.1 mM)

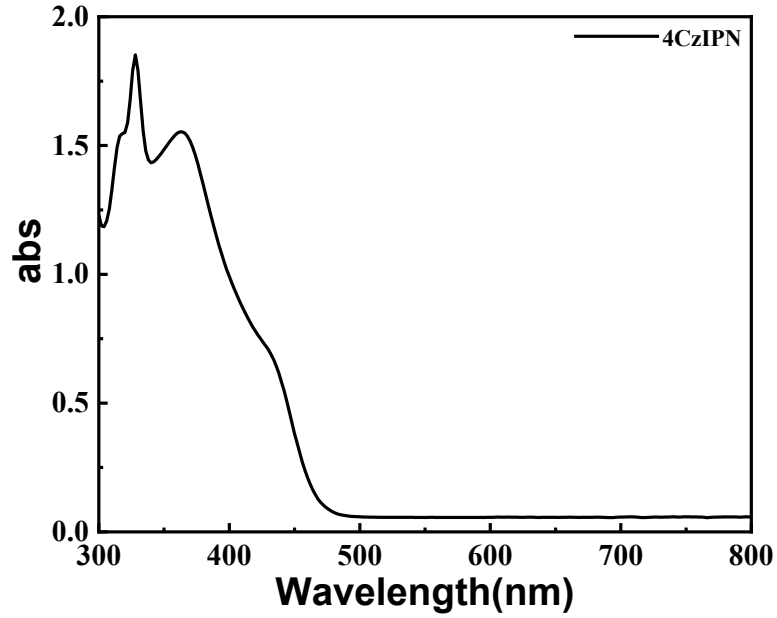


Figure S3 UV-Vis Absorption of 4CzIPN in DMF (Concentration: 0.1 mM)

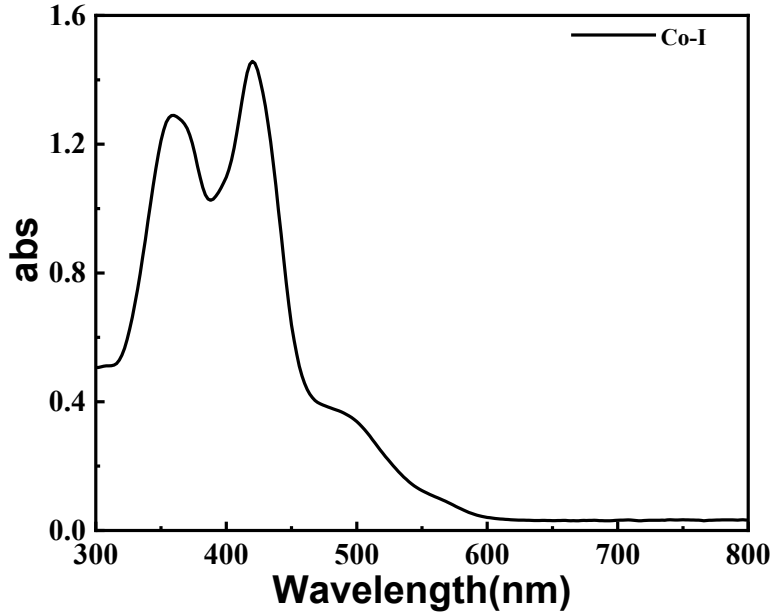


Figure S4 UV-Vis Absorption of **Co-I** in DMF (Concentration: 0.1 mM)

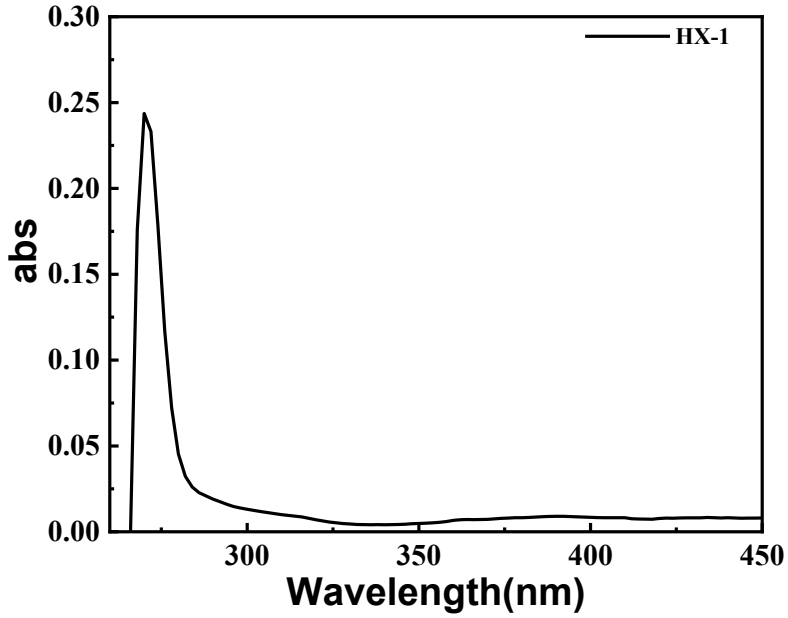


Figure S5 UV-Vis Absorption of collidinium triflate (**HX-I**) in DMF (Concentration: 0.1 mM)

5.4 Stern-Volmer fluorescence quenching experiments

5.4.1 Quenching of 4CzIPN with 5a

Excitation wavelength: 440 nm.

Excitation slit: 5 nm; emission slit: 5 nm.

To a standard solution of 4CzIPN in DMF (0.1 mM) were added different amounts of a solution of **5a** in DMF to afford the final concentrations reported in the figure below.

The fluorescence of the solutions was then measured. DMF was degassed with a stream of nitrogen for 30 min.

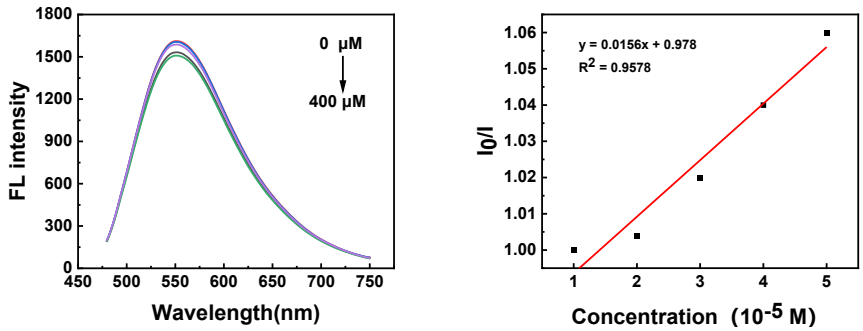


Figure S7 Emission spectra of the 4CzIPN with increasing concentrations of **5a**

5.4.2 Quenching of 4CzIPN with B_2cat_2

Excitation wavelength: 440 nm.

Excitation slit: 5 nm; emission slit: 5 nm.

To a standard solution of 4CzIPN in DMF (0.1 mM) were added different amounts of a solution of B_2cat_2 in DMF to afford the final concentrations reported in the figure below. The fluorescence of the solutions was then measured. DMF was degassed with a stream of nitrogen for 30 min.

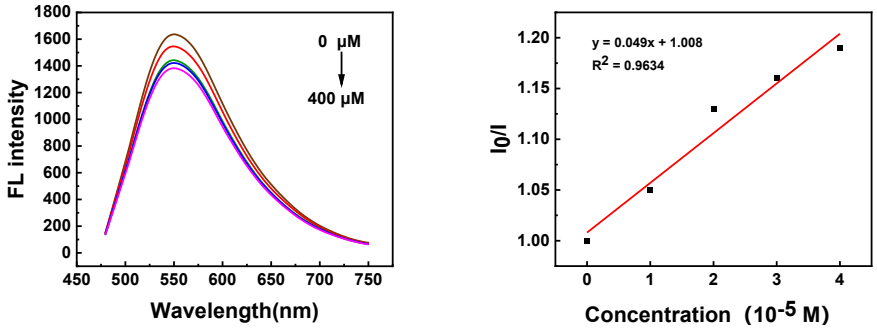


Figure S8 Emission spectra of the 4CzIPN with increasing concentrations of B_2cat_2

5.4.3 Quenching of 4CzIPN with Co-I

Excitation wavelength: 440 nm.

Excitation slit: 5 nm; emission slit: 5 nm.

To a standard solution of 4CzIPN in DMF (0.1 mM) were added different amounts of a solution of **Co-I** in DMF to afford the final concentrations reported in the figure below. The fluorescence of the solutions was then measured. DMF was degassed with a stream of nitrogen for 30 min.

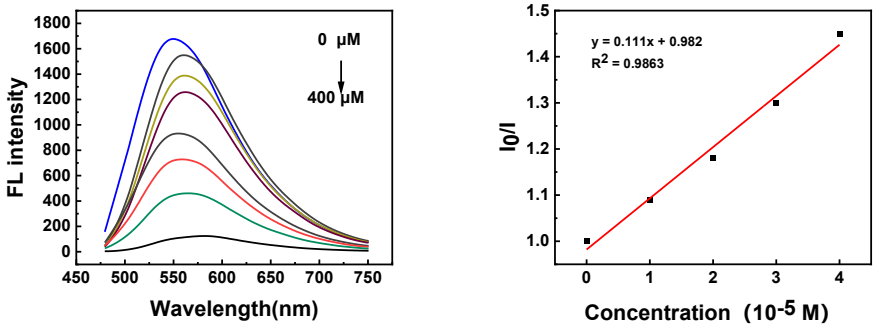


Figure S9 Emission spectra of the 4CzIPN with increasing concentrations of **Co-I**

5.4.4 Quenching of 4CzIPN with HX-I

Excitation wavelength: 440 nm.

Excitation slit: 5 nm; emission slit: 5 nm.

To a standard solution of 4CzIPN in DMF (0.1 mM) were added different amounts of a solution of **HX-I** in DMF to afford the final concentrations reported in the figure below. The fluorescence of the solutions was then measured. DMF was degassed with a stream of nitrogen for 30 min.

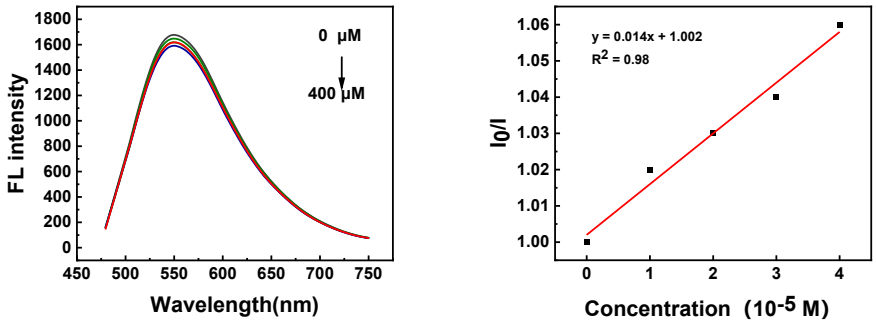
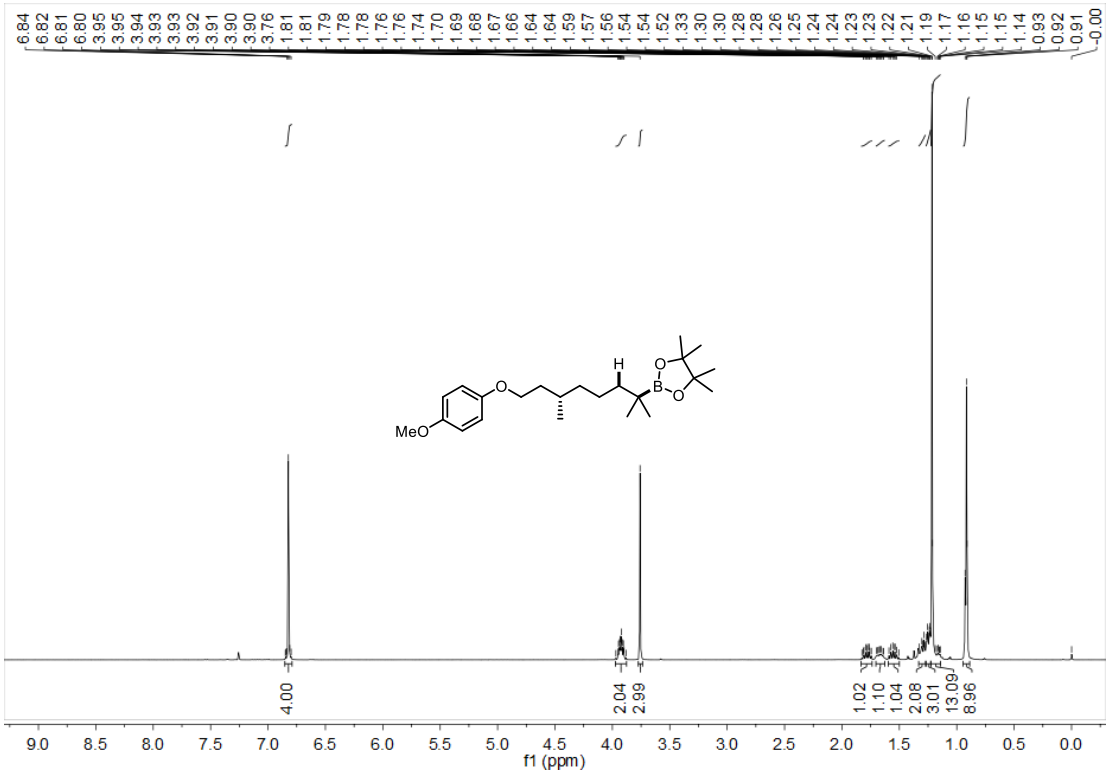


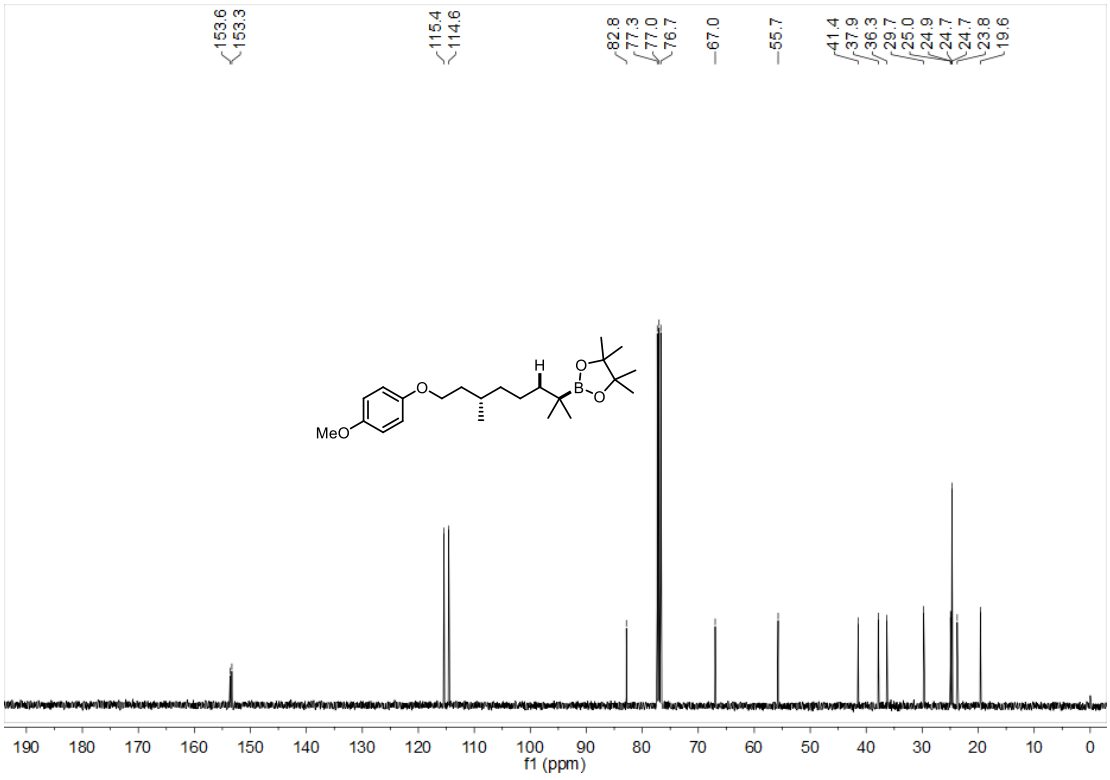
Figure S10 Emission spectra of the 4CzIPN with increasing concentrations of **HX-I**

6. ^{1}H, ^{13}C and ^{19}F NMR spectra of all products

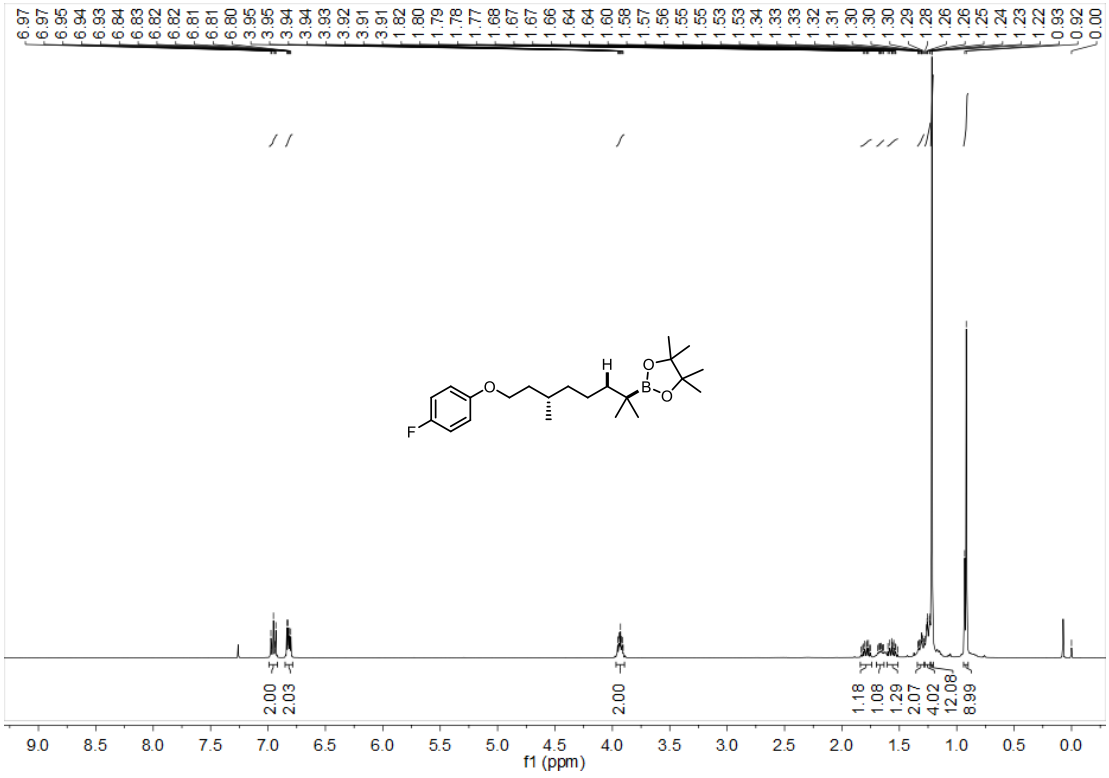
Compound **1** ^{1}H NMR (400 MHz, $CDCl_3$)



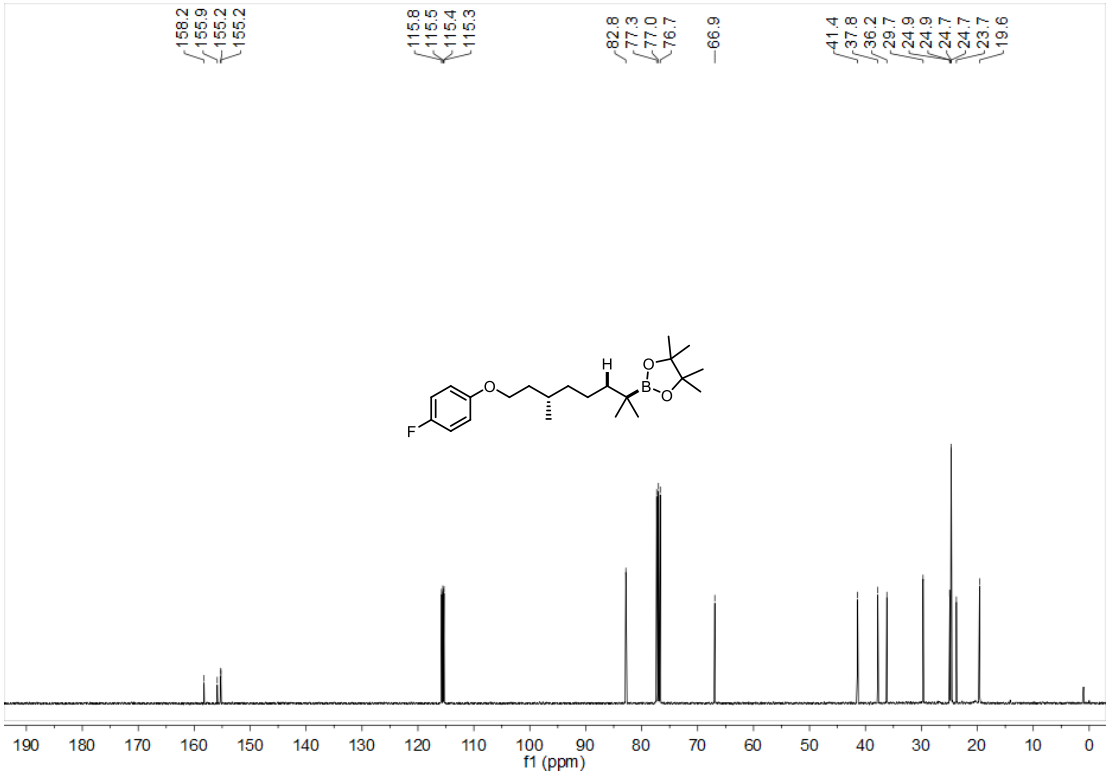
Compound **1** ^{13}C NMR (101 MHz, $CDCl_3$)



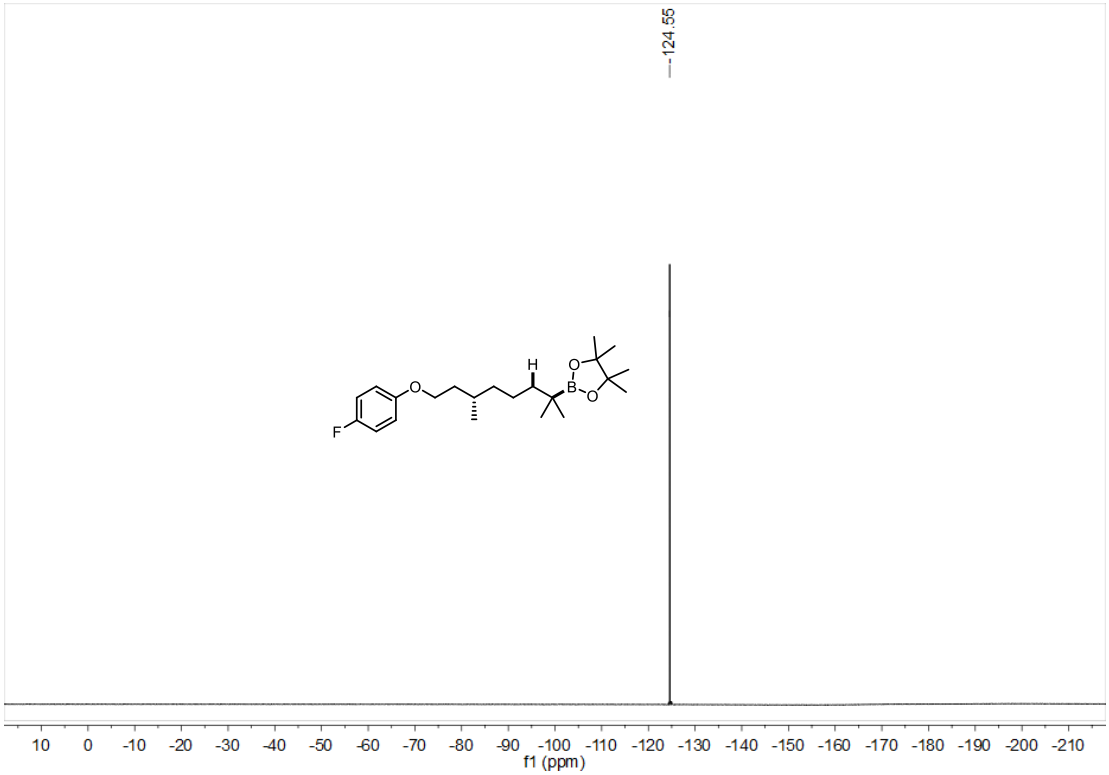
Compound **2** ^{1}H NMR (400 MHz, $CDCl_3$)



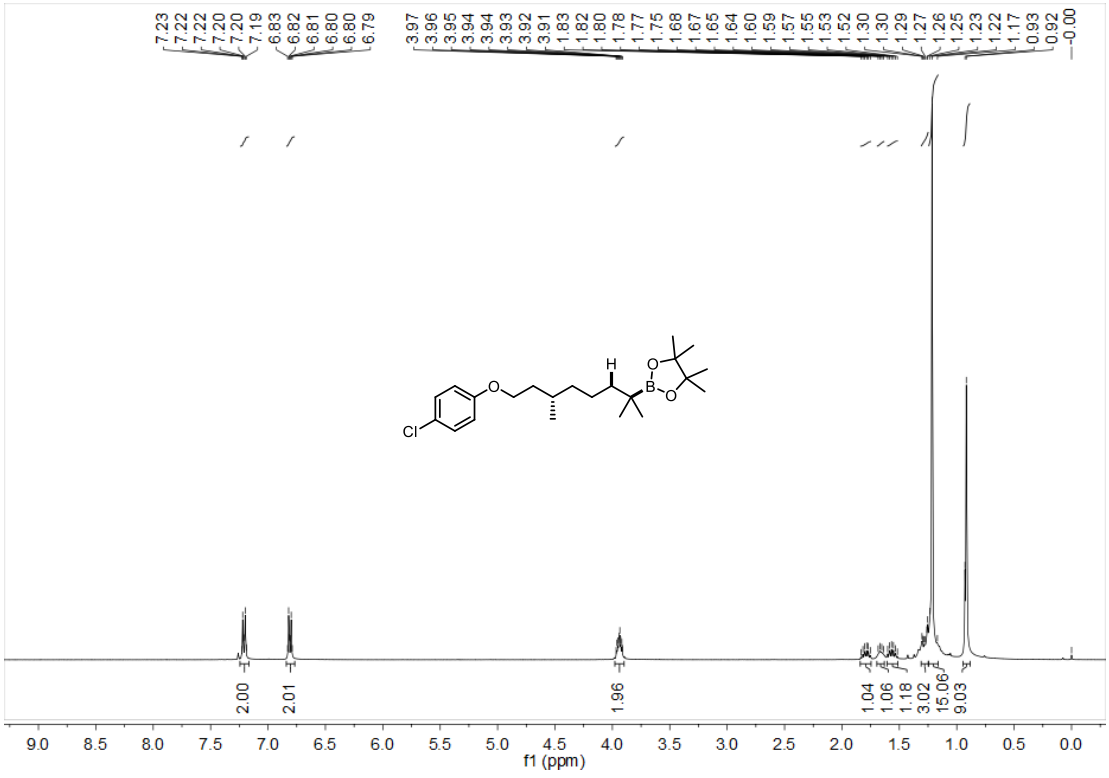
Compound **2** ^{13}C NMR (101 MHz, $CDCl_3$)



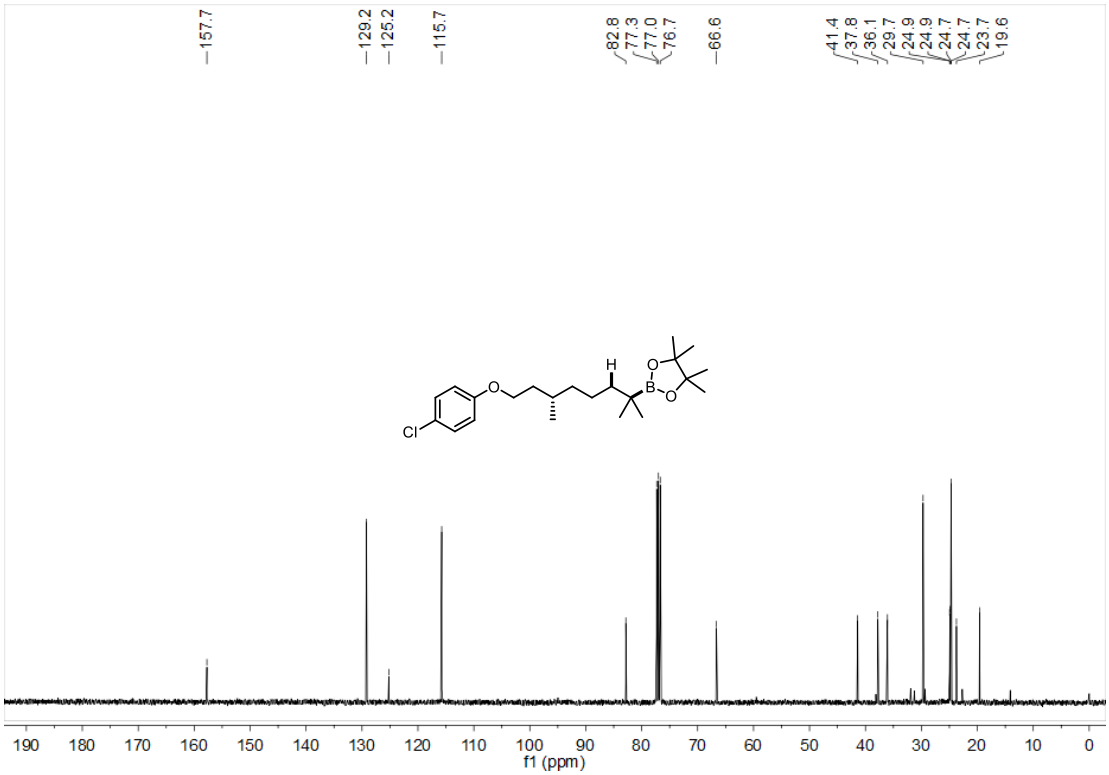
Compound **2** ^{19}F NMR (376 MHz, $CDCl_3$)



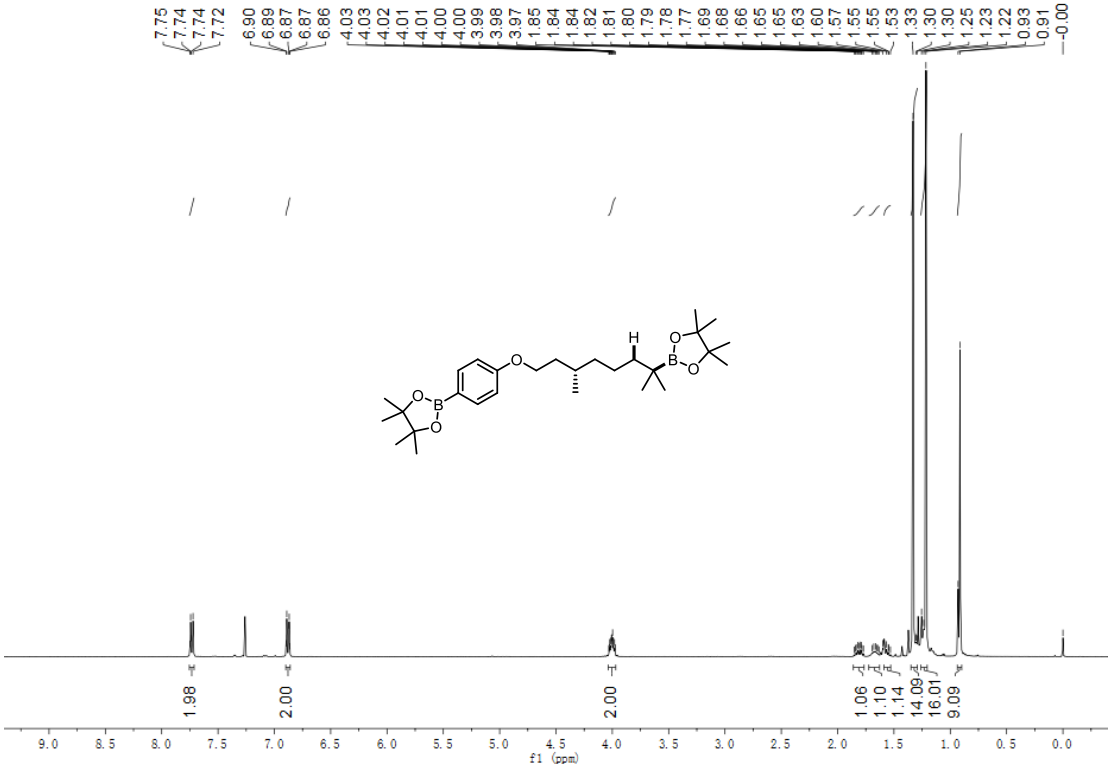
Compound **3** ^{1}H NMR (400 MHz, $CDCl_3$)



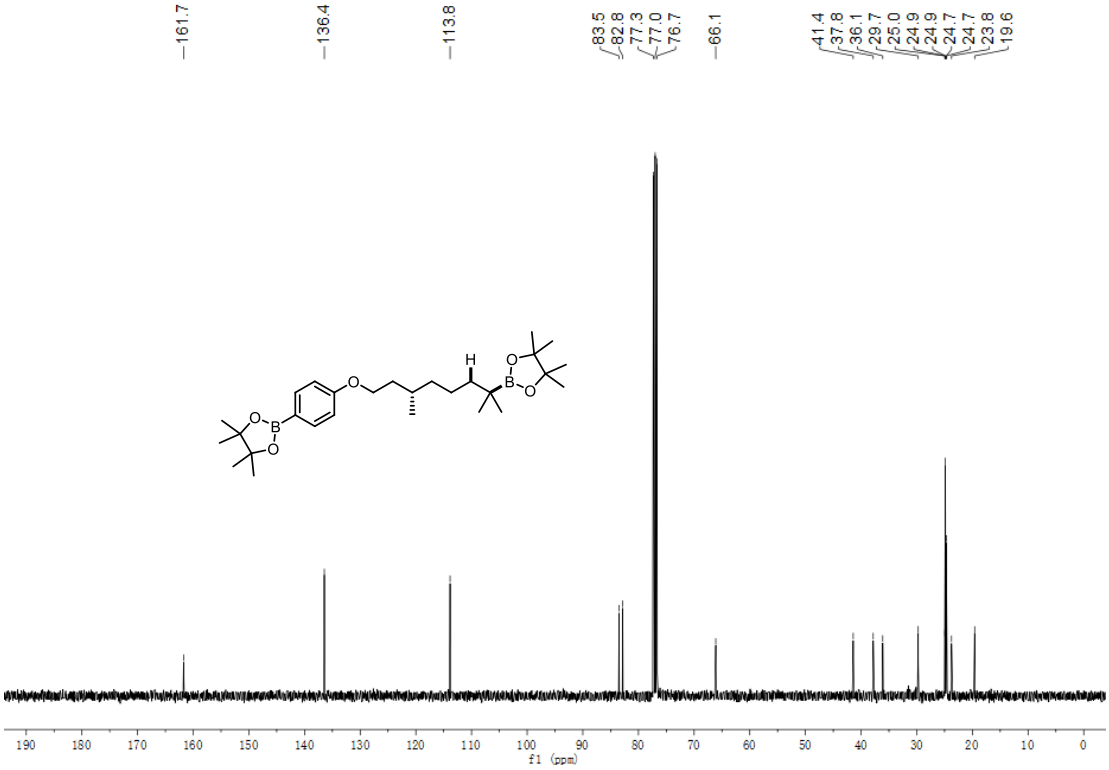
Compound **3** ^{13}C NMR (101 MHz, $CDCl_3$)



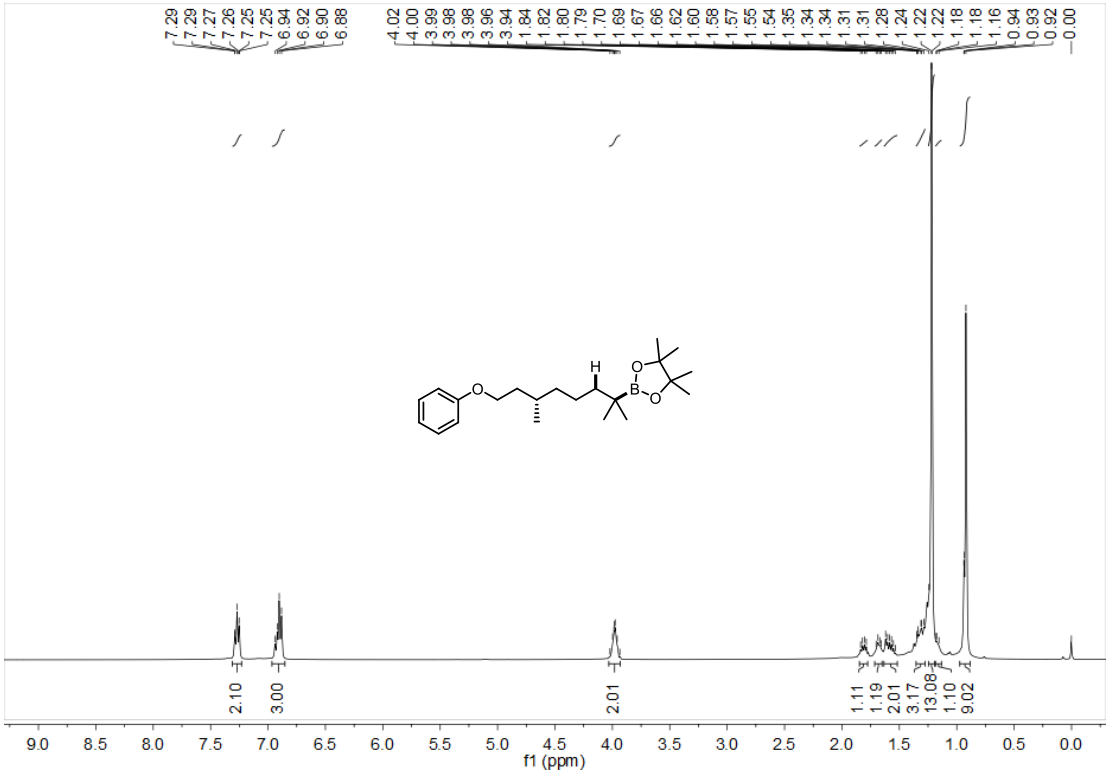
Compound **4** ^{1}H NMR (400 MHz, $CDCl_3$)



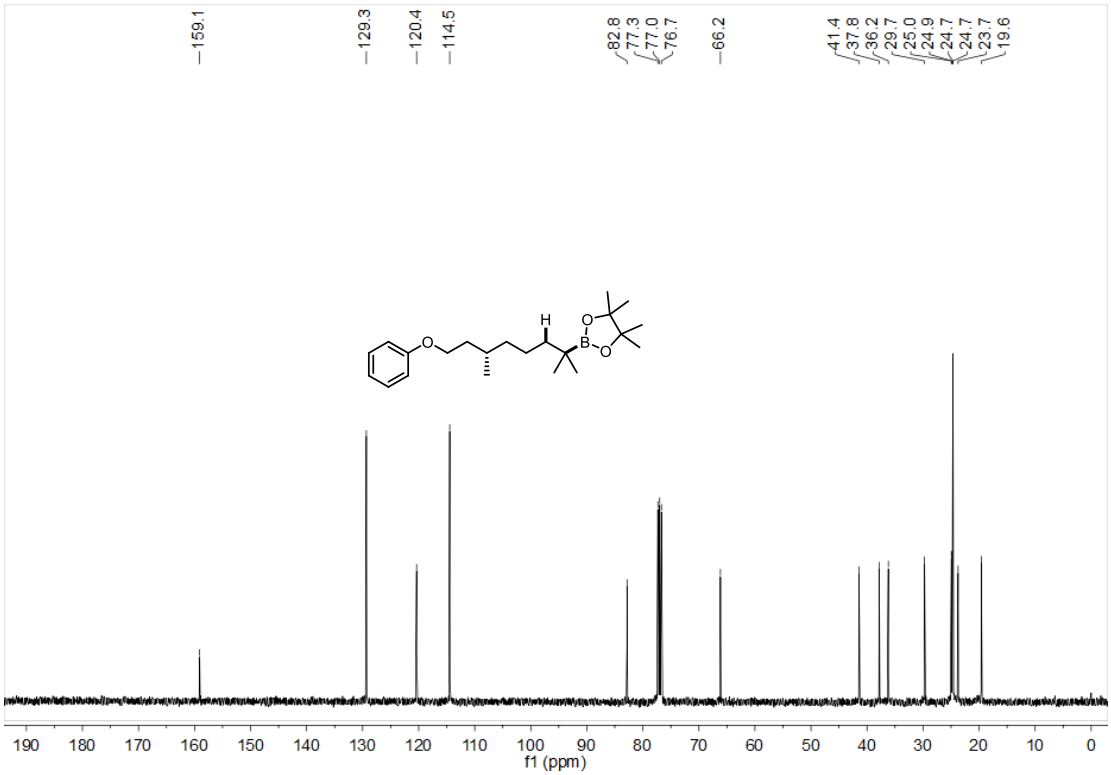
Compound **4** ^{13}C NMR (101 MHz, $CDCl_3$)



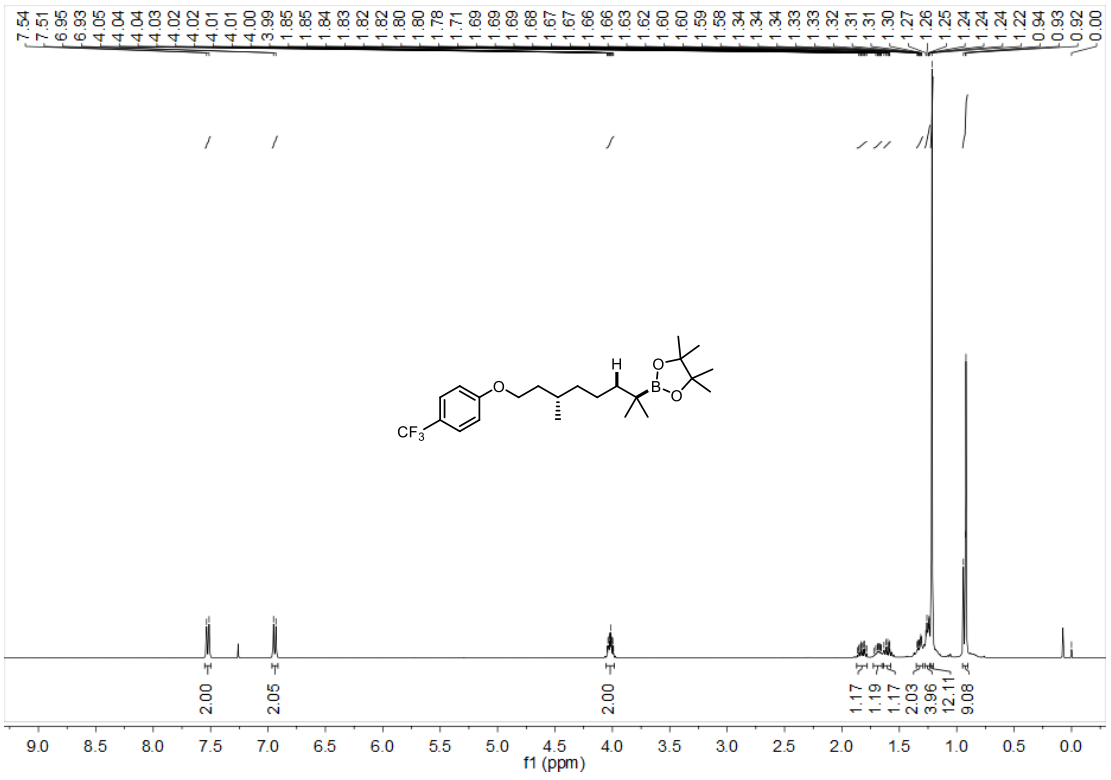
Compound **5** ^{1}H NMR (400 MHz, $CDCl_3$)



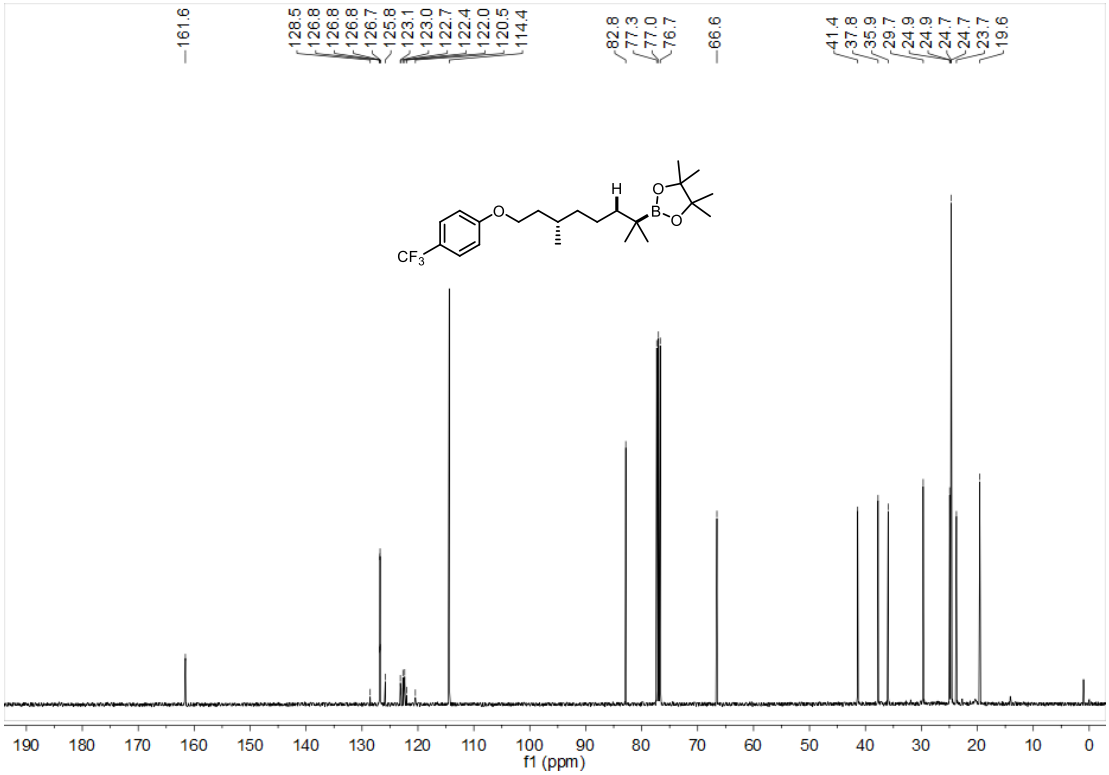
Compound **5** ^{13}C NMR (101 MHz, $CDCl_3$)



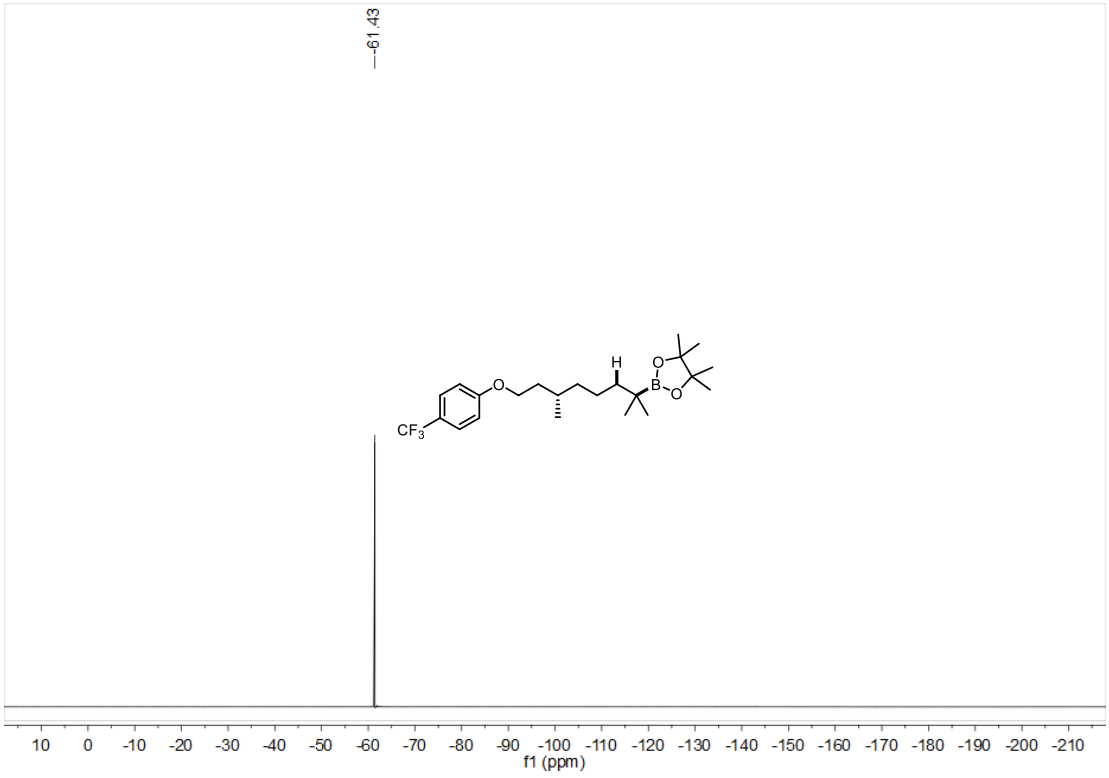
Compound **6** ^{1}H NMR (400 MHz, $CDCl_3$)



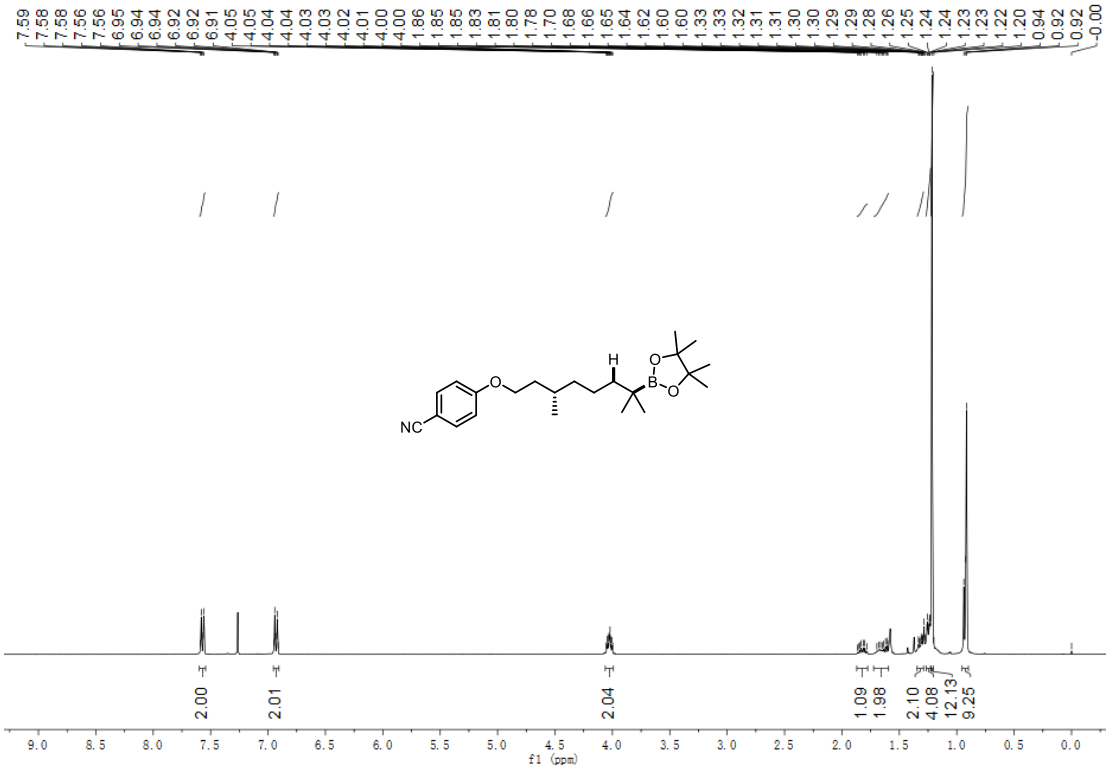
Compound **6** ^{13}C NMR (101 MHz, $CDCl_3$)



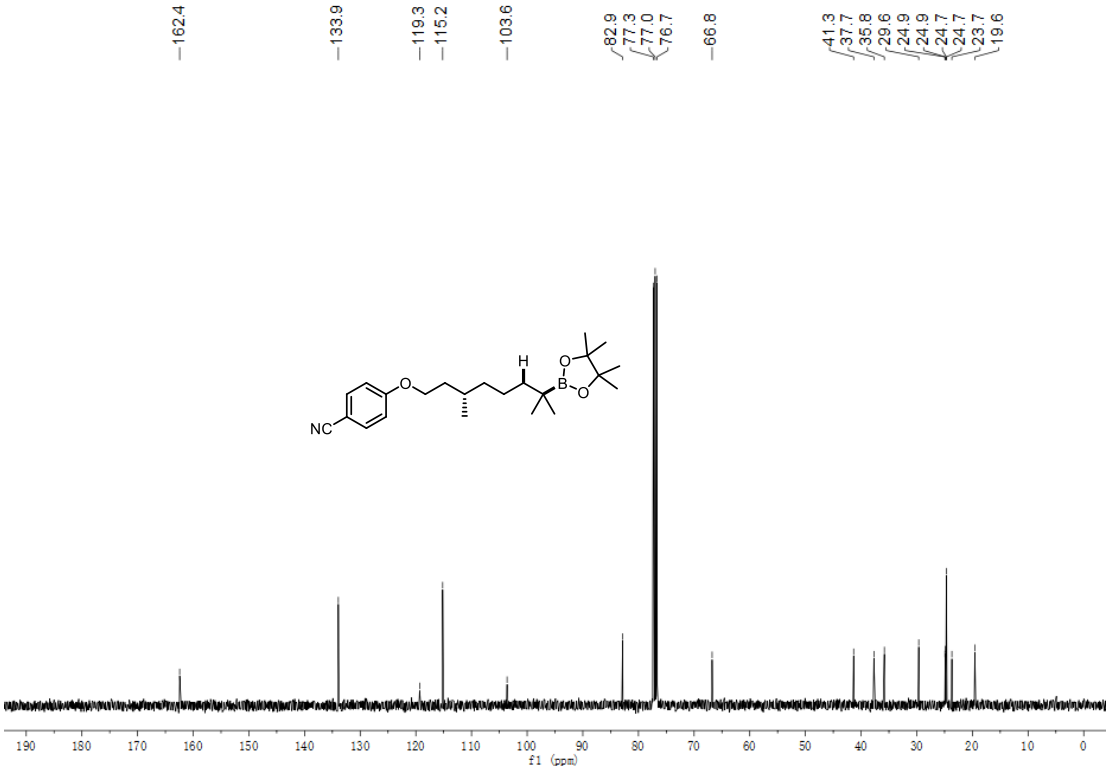
Compound **6** ^{19}F NMR (376 MHz, $CDCl_3$)



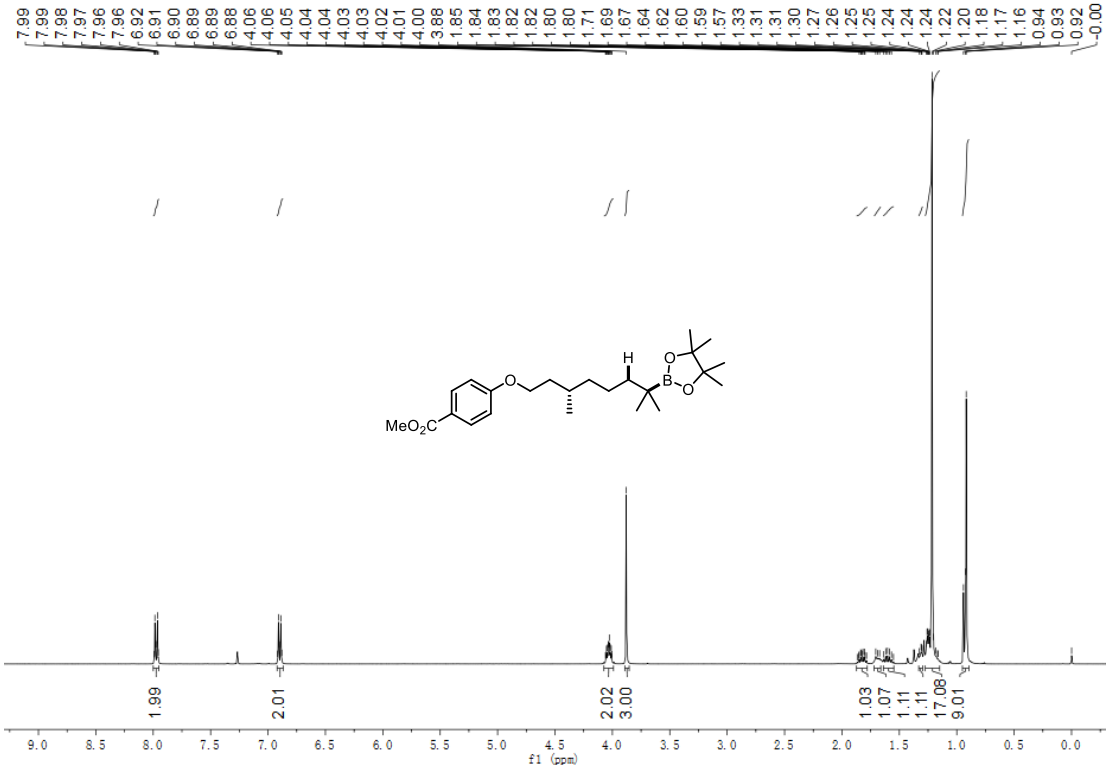
Compound **7** ^{1}H NMR (400 MHz, $CDCl_3$)



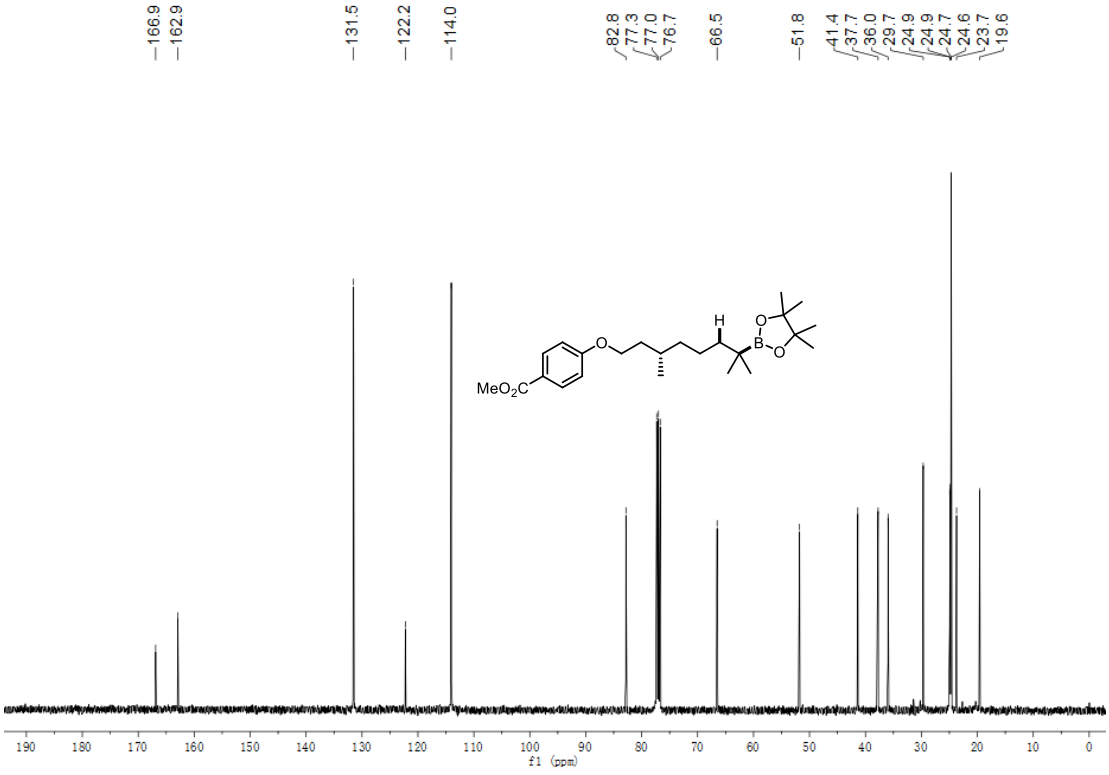
Compound **7** ^{13}C NMR (101 MHz, $CDCl_3$)



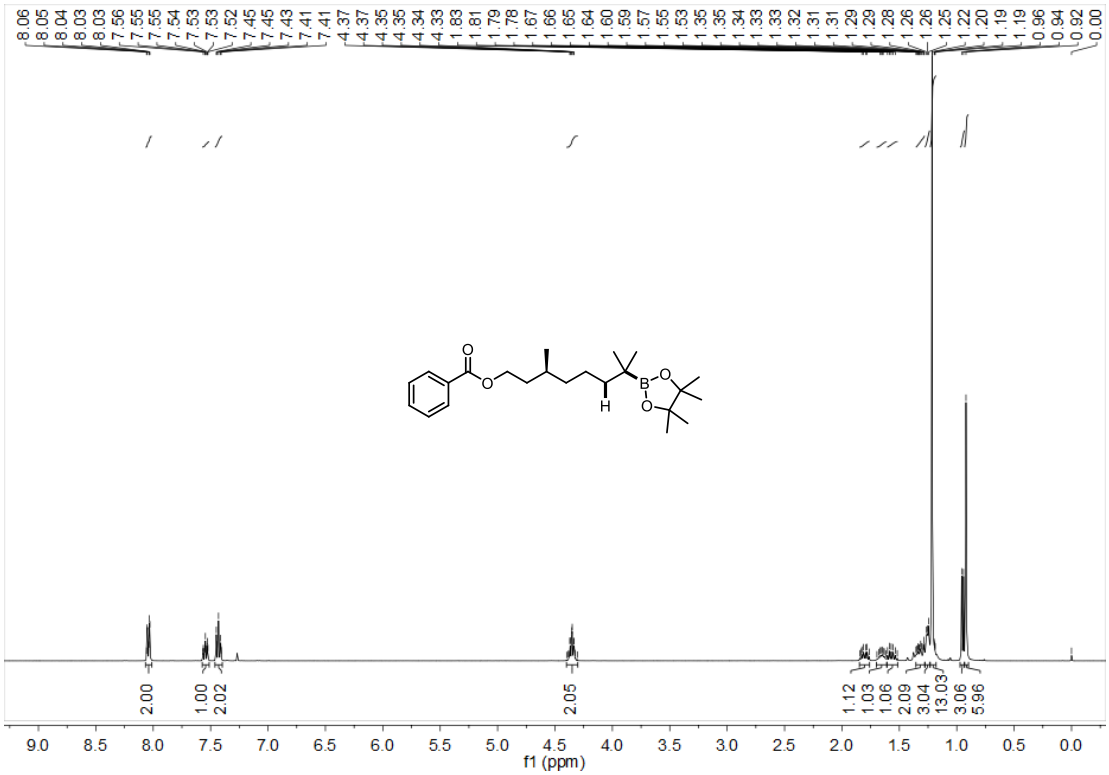
Compound **8** ^{1}H NMR (400 MHz, $CDCl_3$)



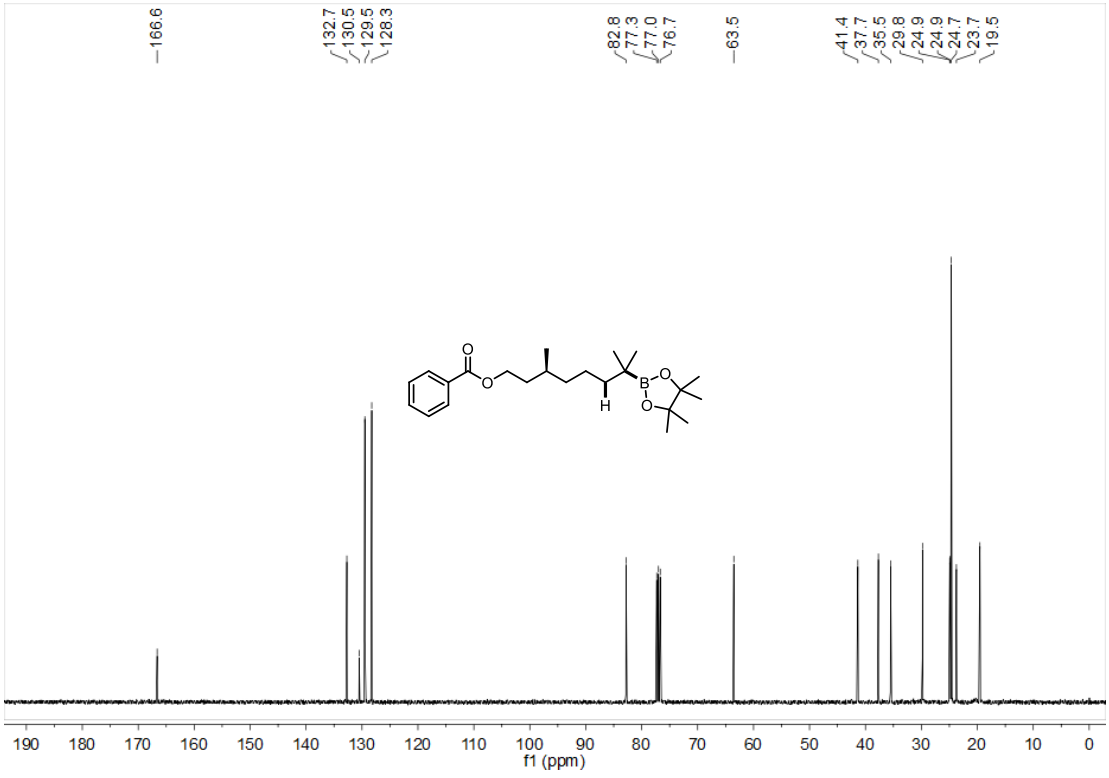
Compound **8** ^{13}C NMR (101 MHz, $CDCl_3$)



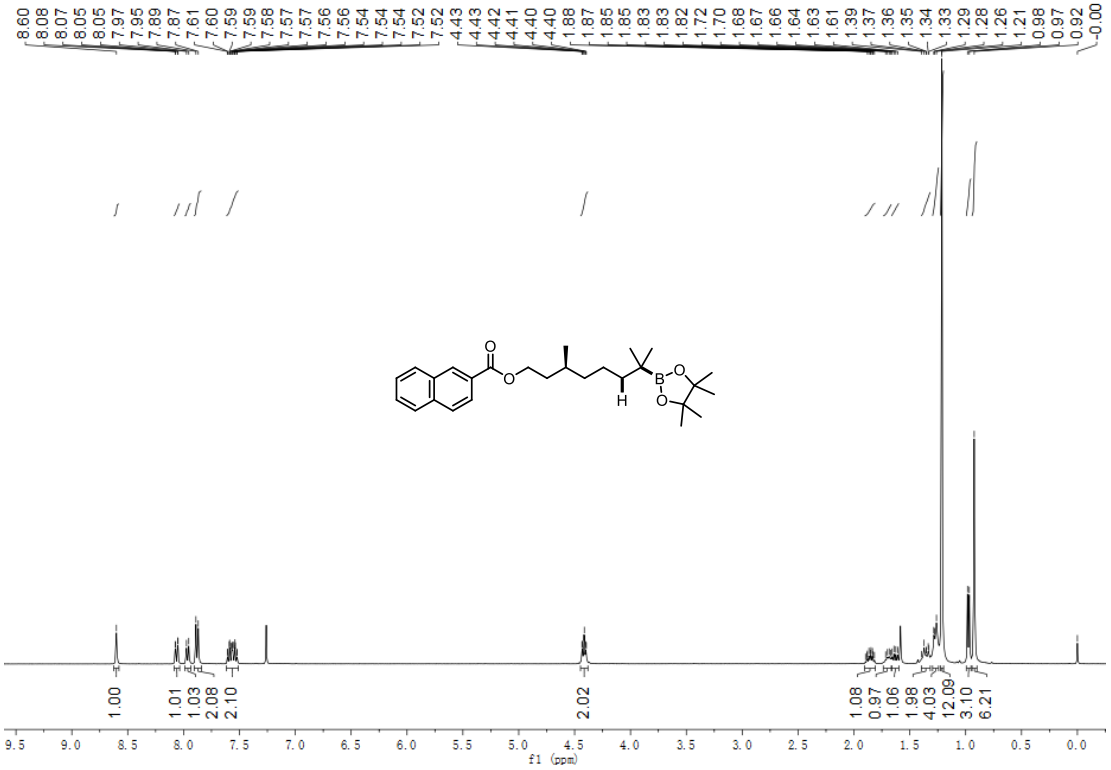
Compound **9** ^{1}H NMR (400 MHz, $CDCl_3$)



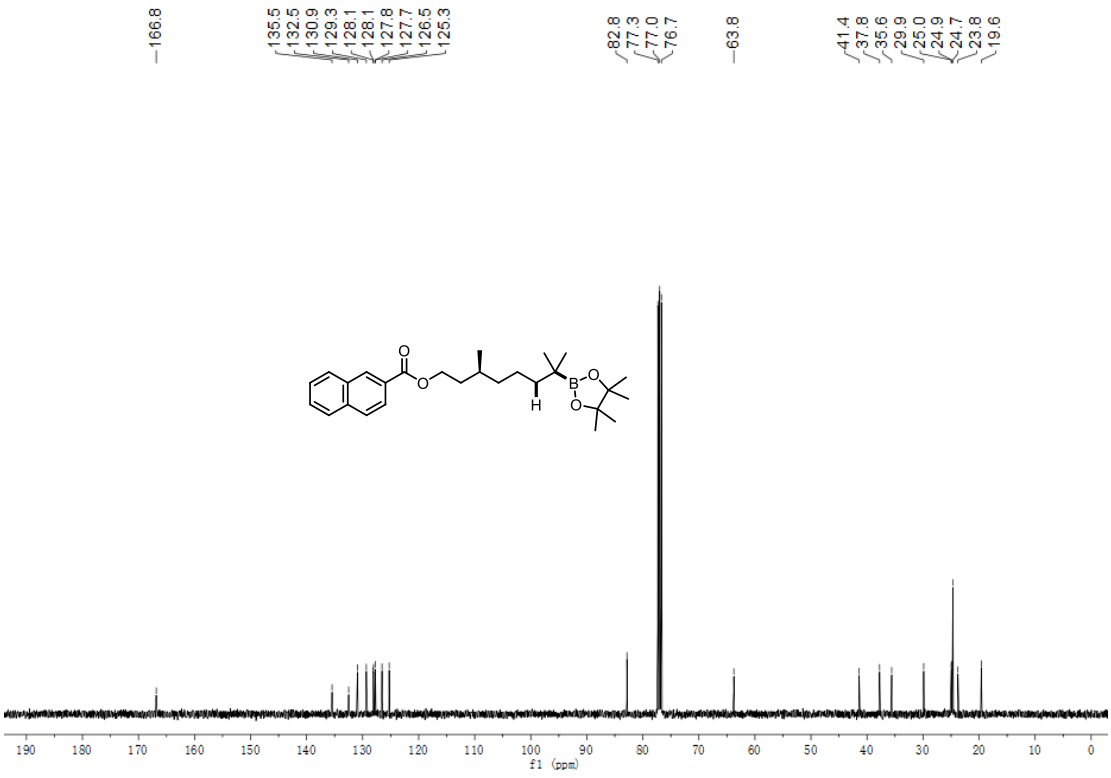
Compound **9** ^{13}C NMR (101 MHz, $CDCl_3$)



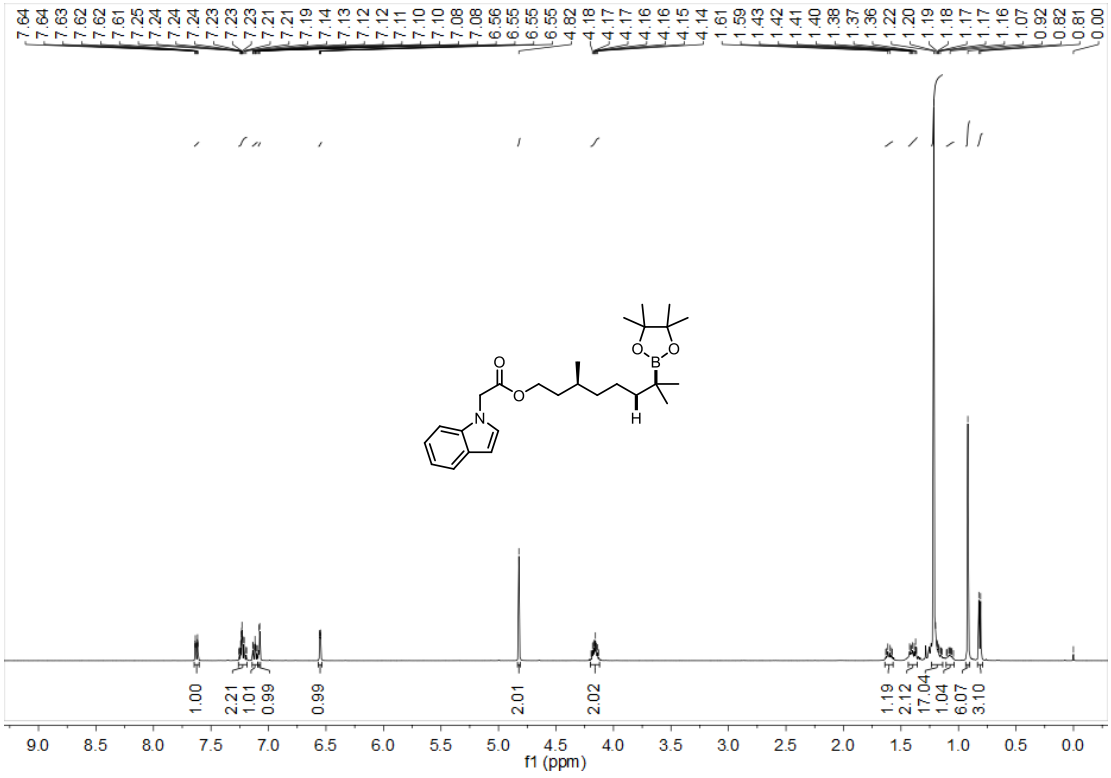
Compound **10** ^{1}H NMR (400 MHz, $CDCl_3$)



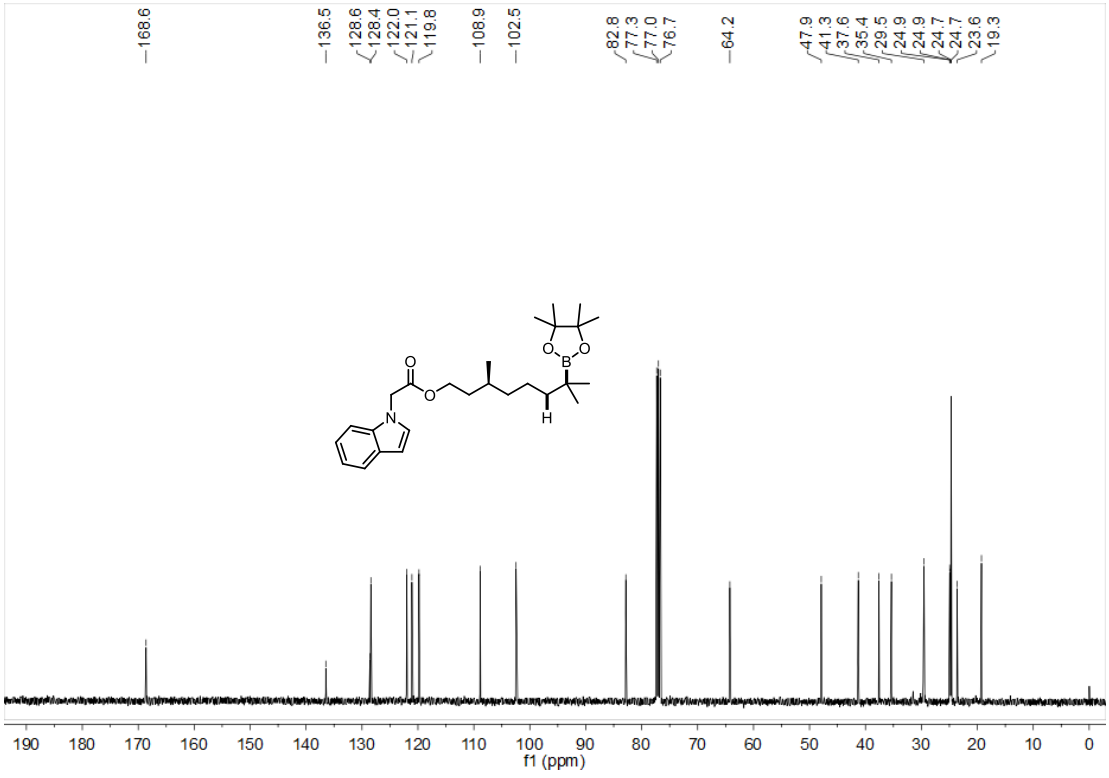
Compound **10** ^{13}C NMR (101 MHz, $CDCl_3$)



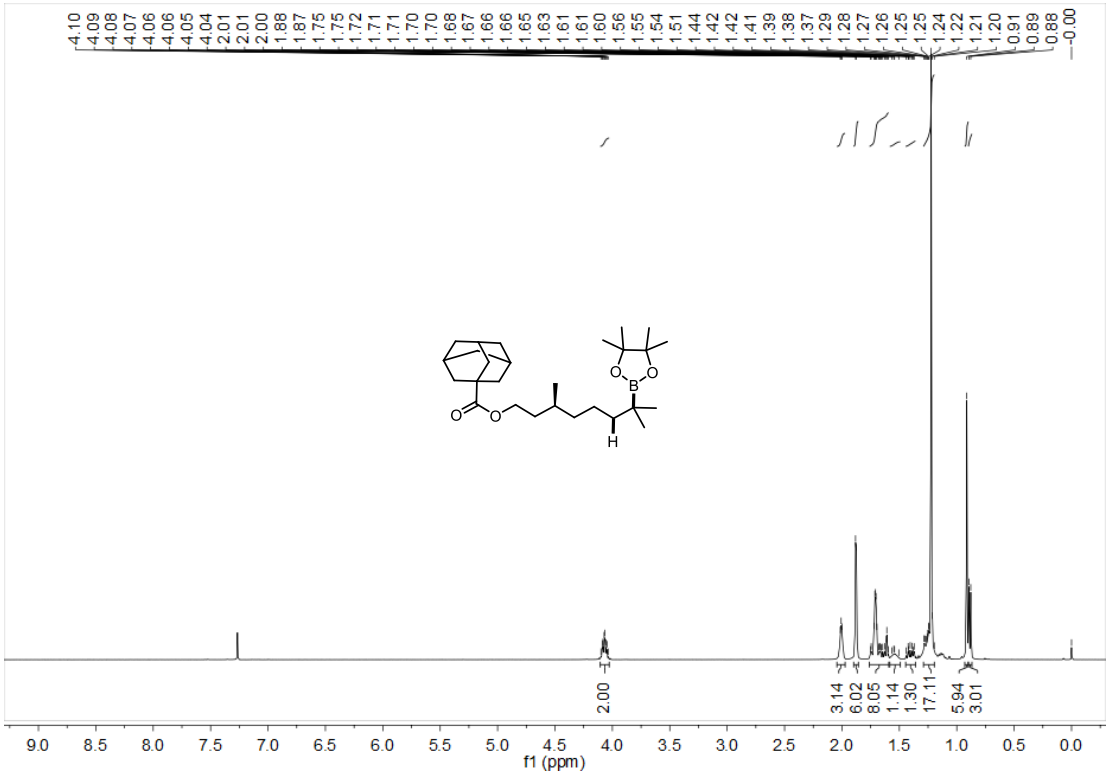
Compound **11** ^{1}H NMR (400 MHz, $CDCl_3$)



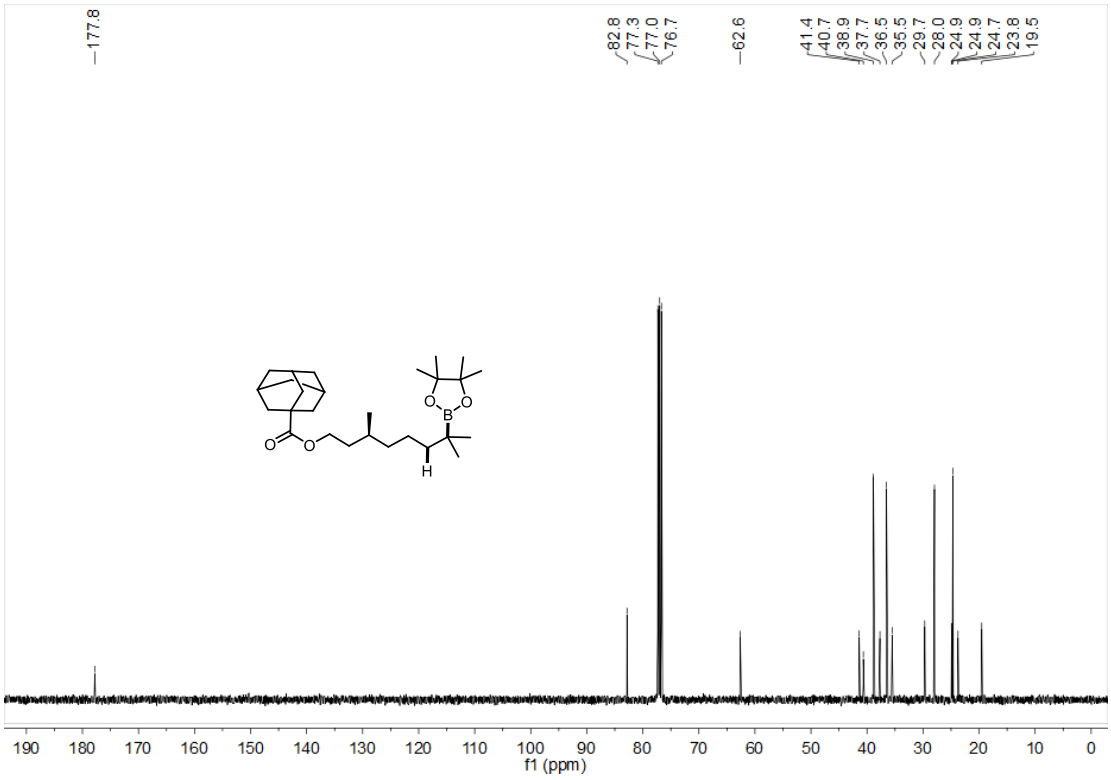
Compound **11** ^{13}C NMR (101 MHz, $CDCl_3$)



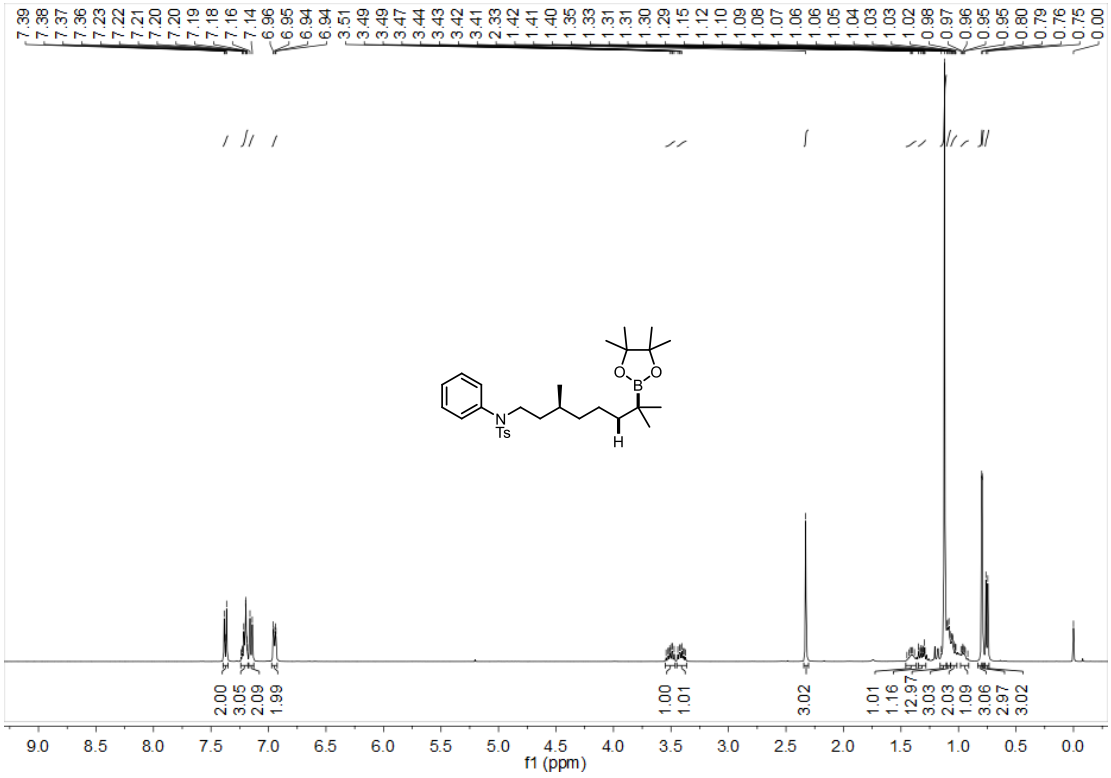
Compound **12** ^{1}H NMR (400 MHz, $CDCl_3$)



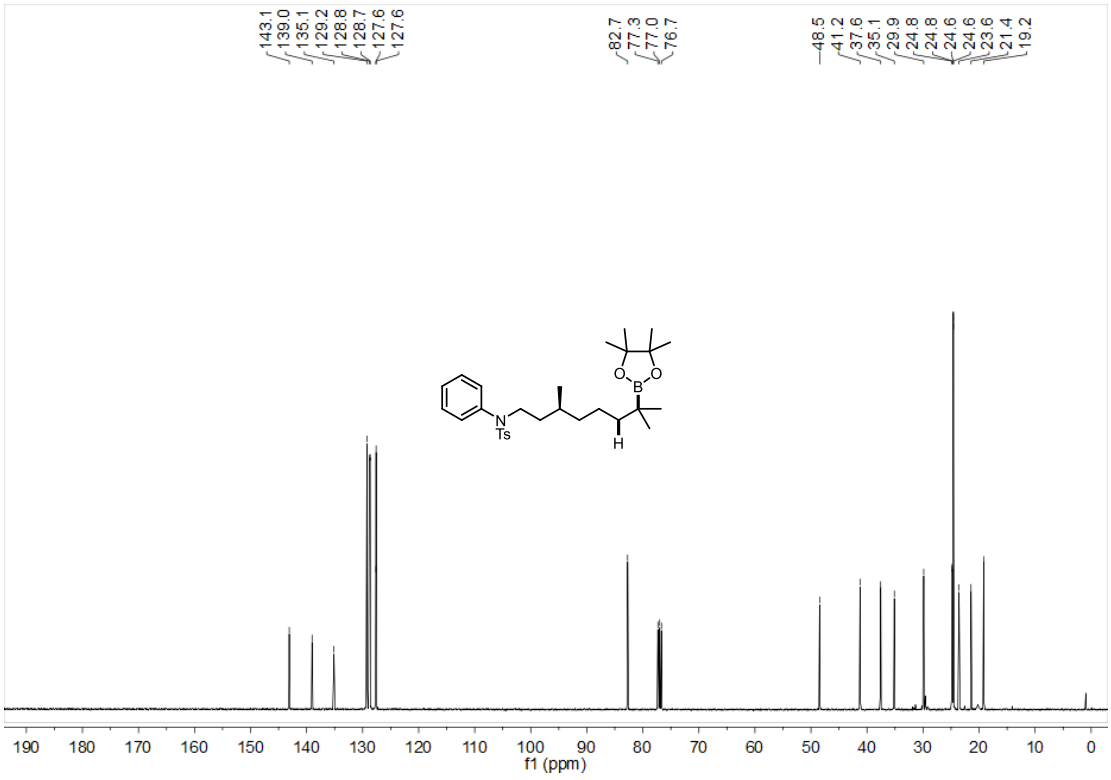
Compound **12** ^{13}C NMR (101 MHz, $CDCl_3$)



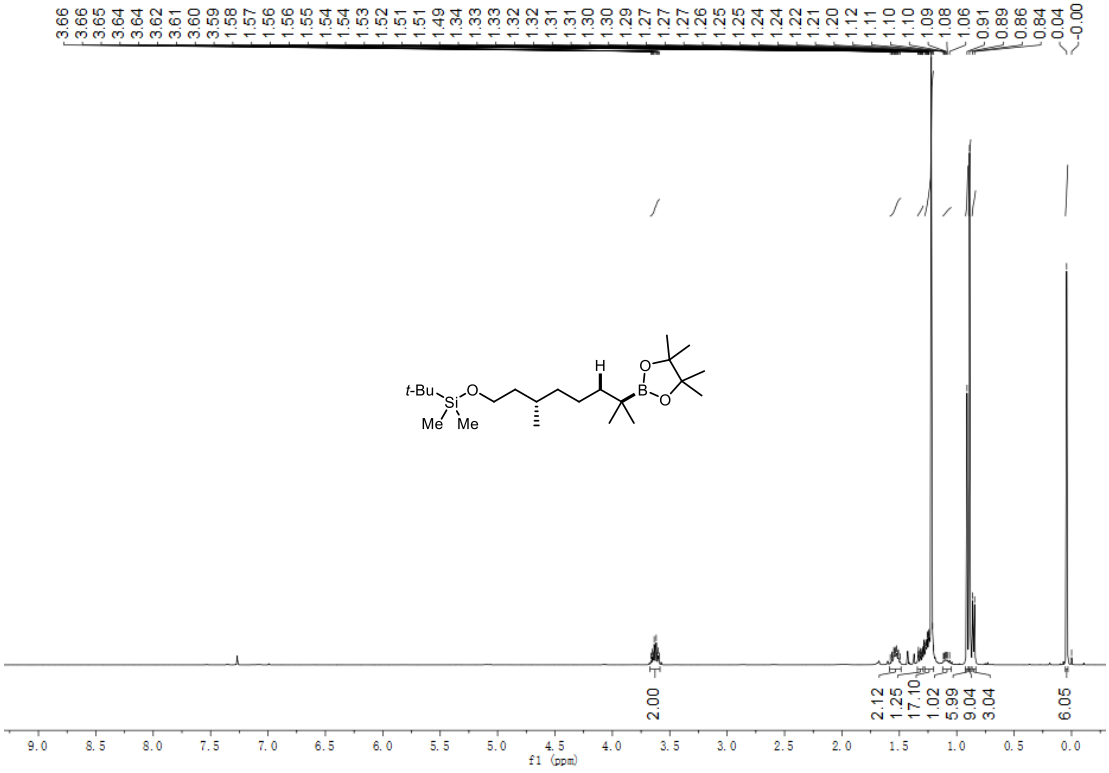
Compound **13** ^{1}H NMR (400 MHz, $CDCl_3$)



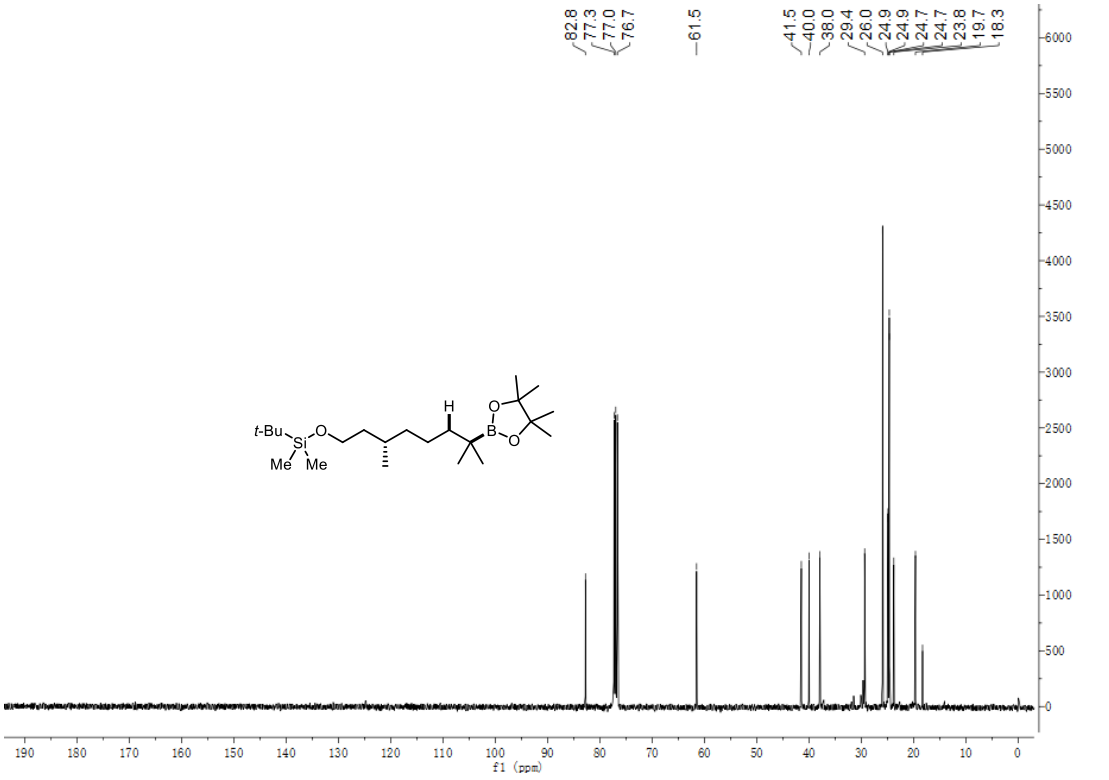
Compound **13** ^{13}C NMR (101 MHz, $CDCl_3$)



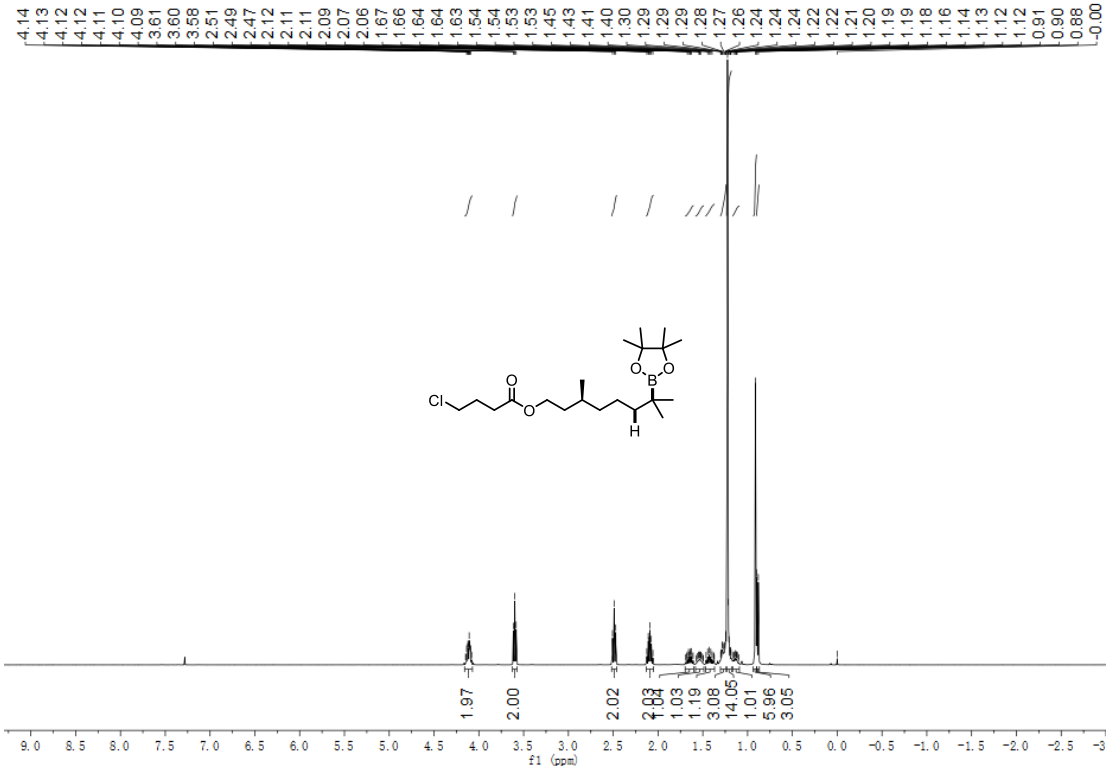
Compound **14** ^{1}H NMR (400 MHz, $CDCl_3$)



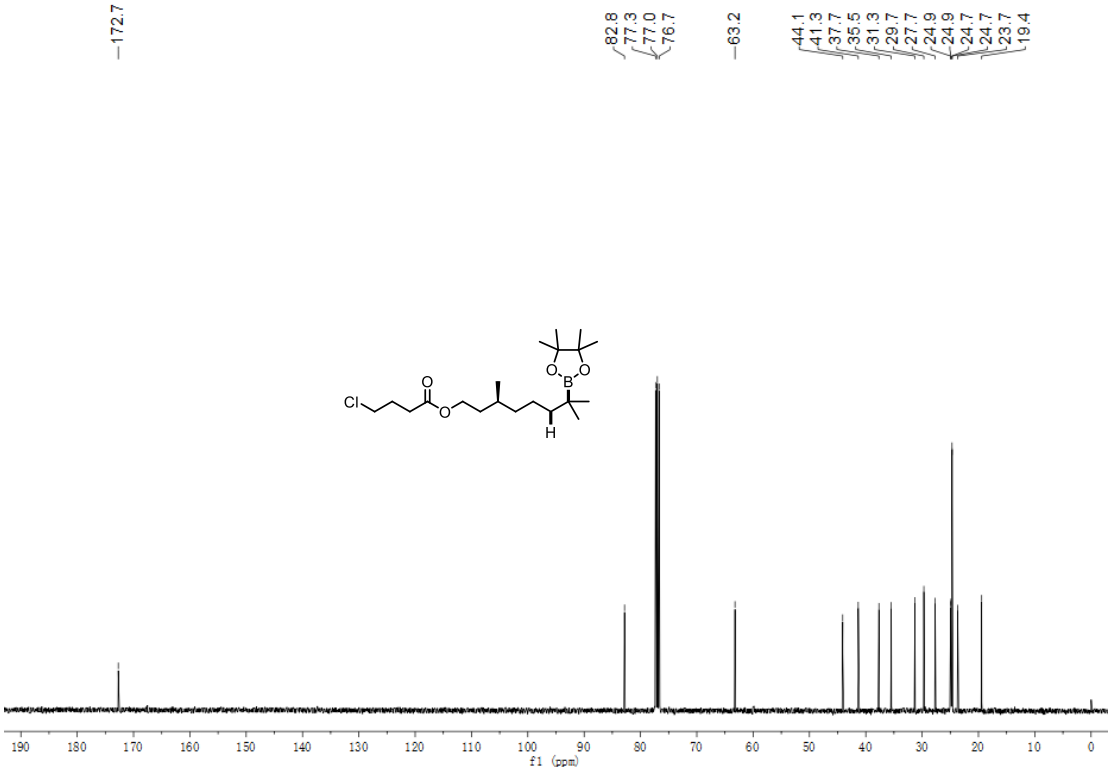
Compound **14** ^{13}C NMR (101 MHz, $CDCl_3$)



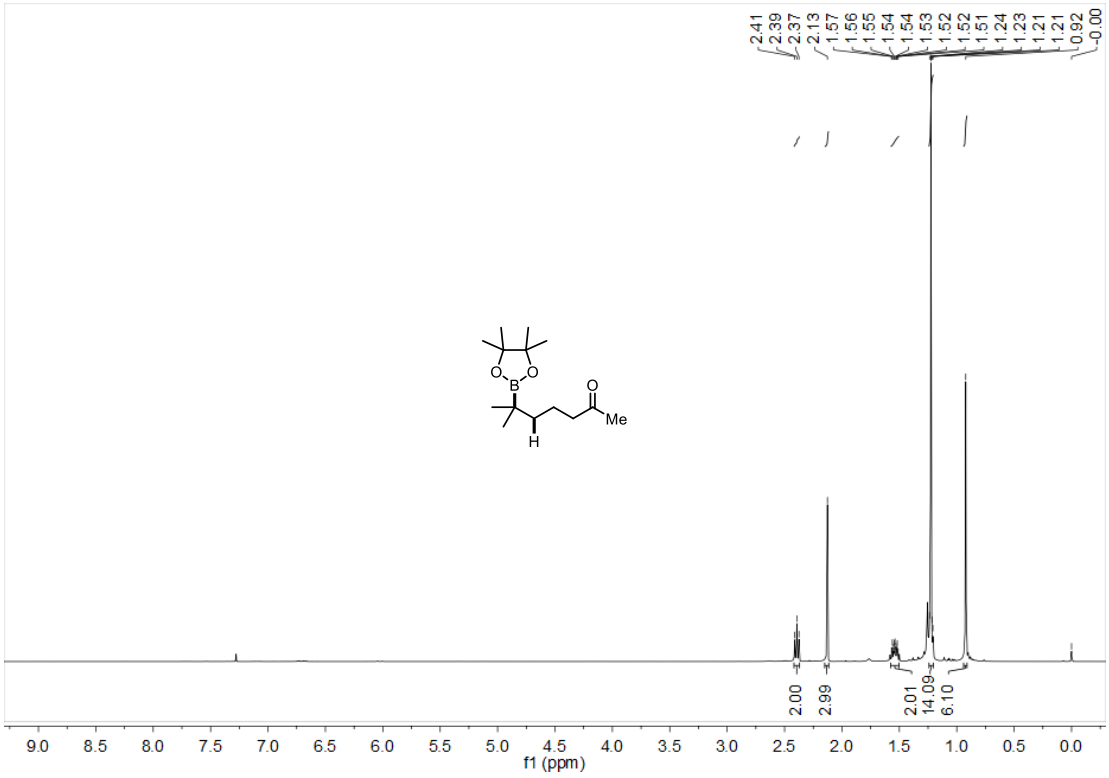
Compound **15** ^{1}H NMR (400 MHz, $CDCl_3$)



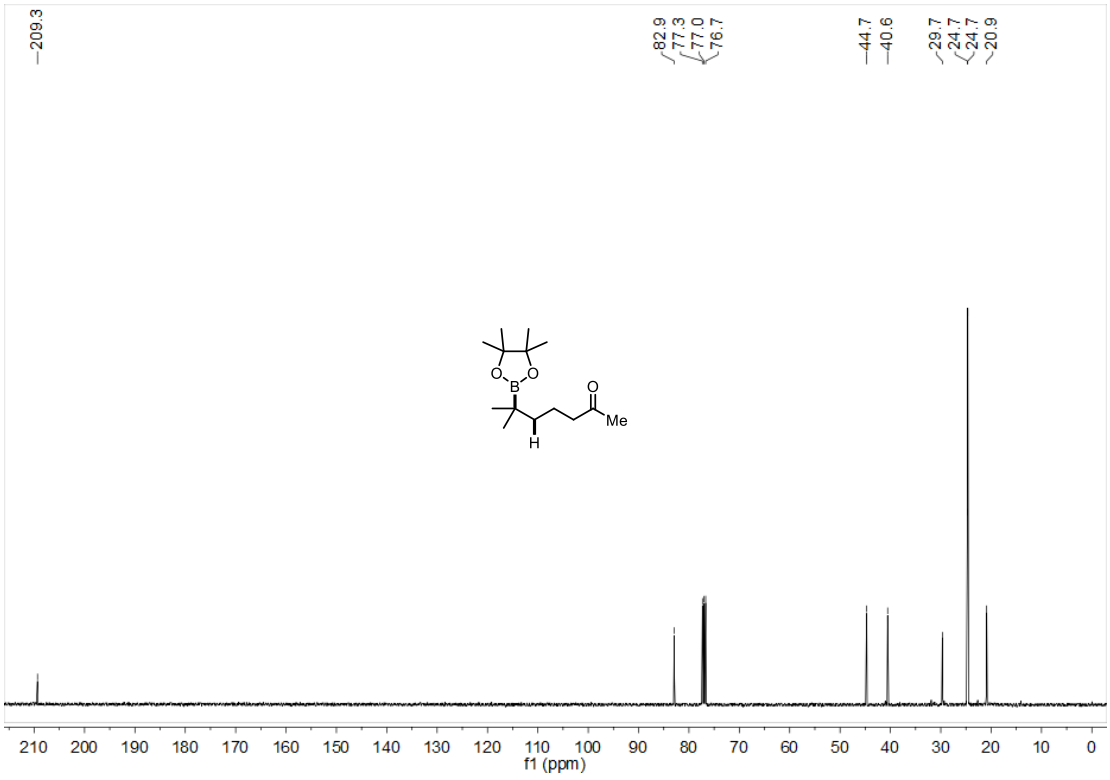
Compound **15** ^{13}C NMR (101 MHz, $CDCl_3$)



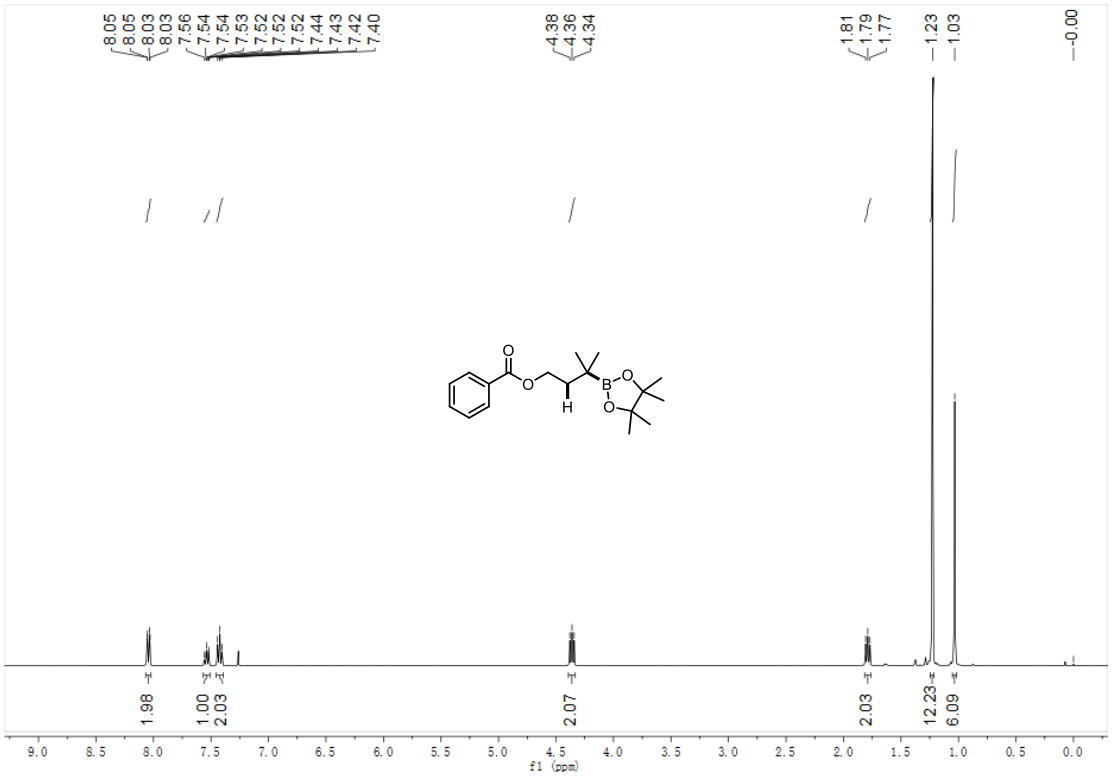
Compound **16** ^{1}H NMR (400 MHz, $CDCl_3$)



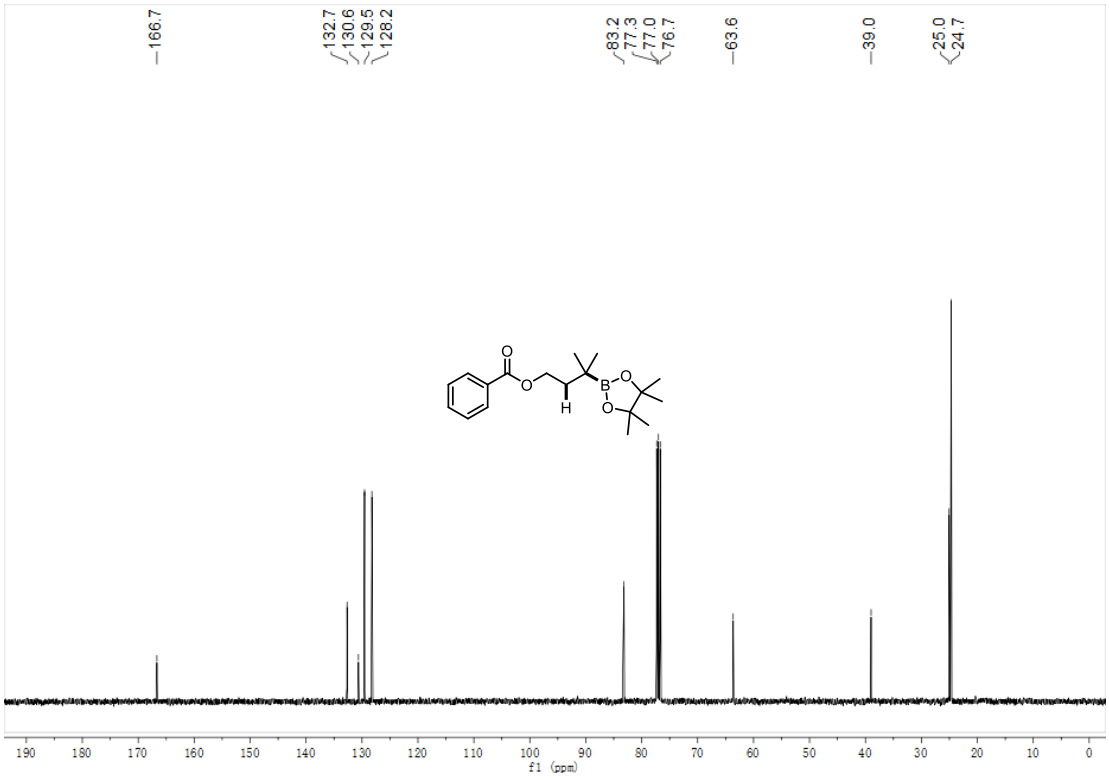
Compound **16** ^{13}C NMR (101 MHz, $CDCl_3$)



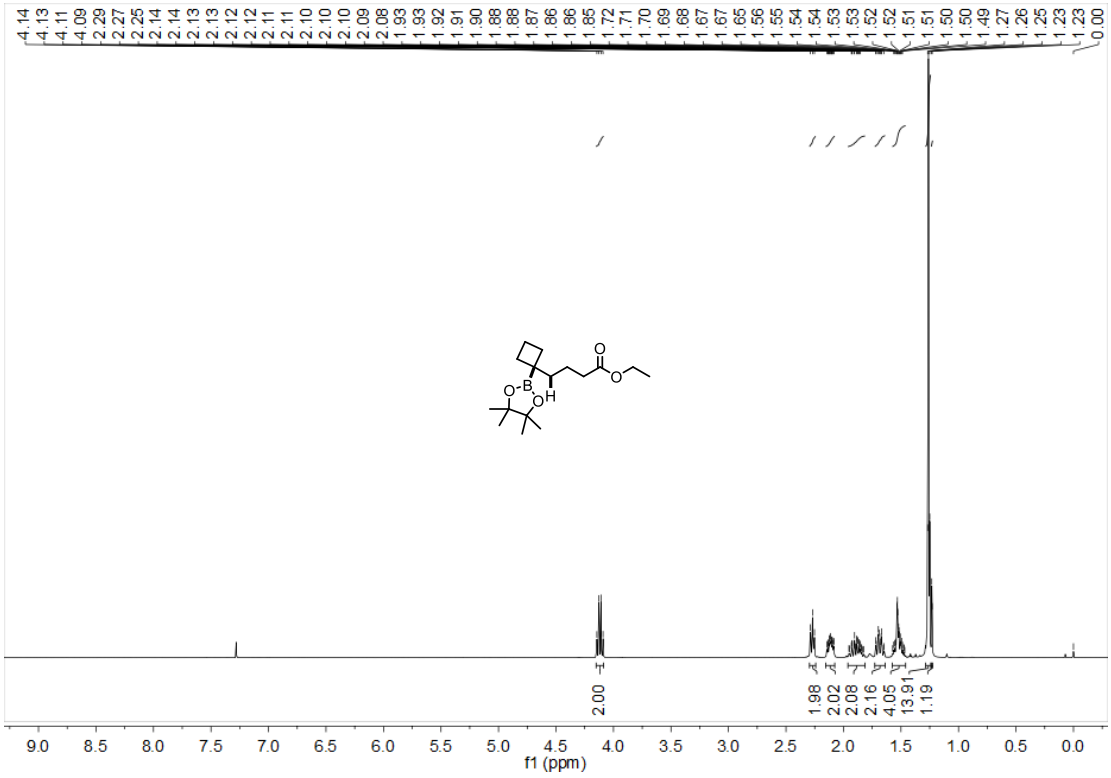
Compound **17** ^{1}H NMR (400 MHz, $CDCl_3$)



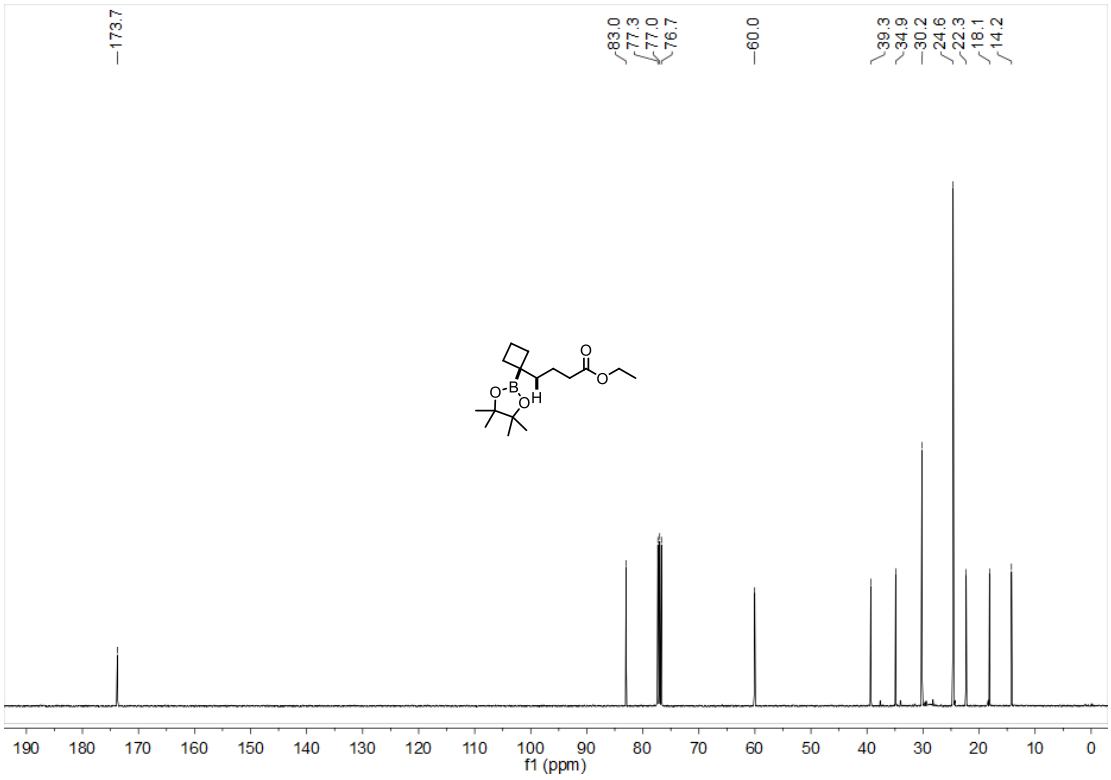
Compound **17** ^{13}C NMR (101 MHz, $CDCl_3$)



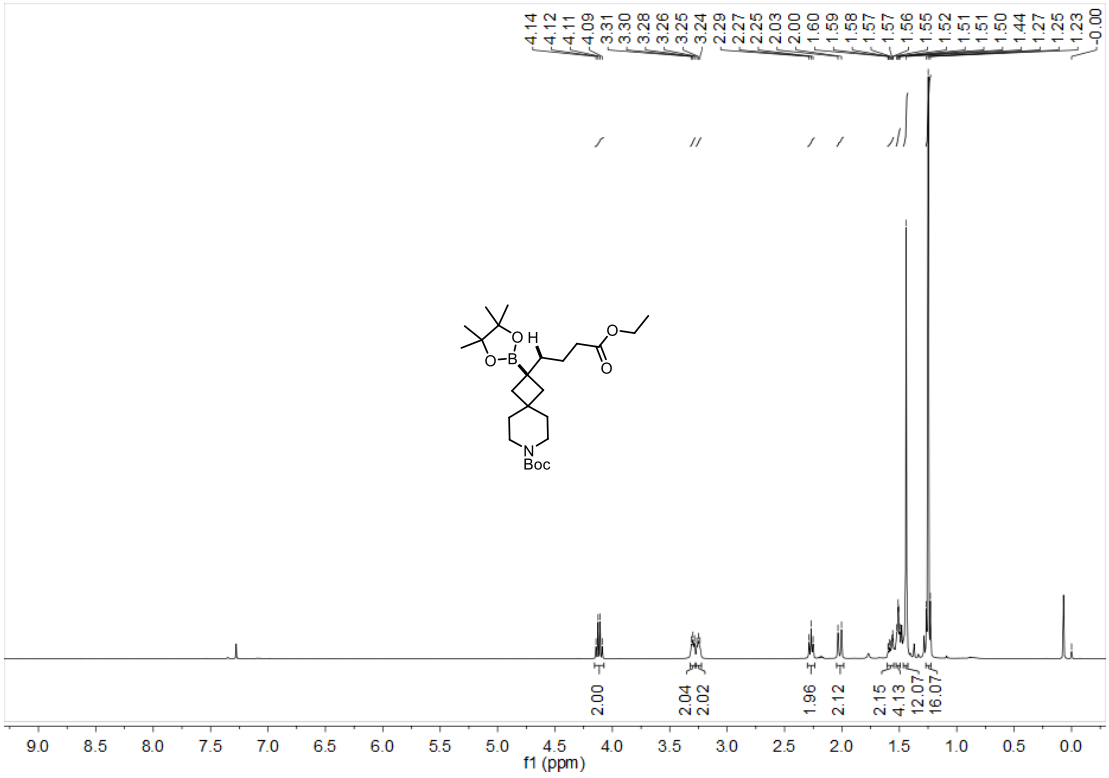
Compound **18** ^{1}H NMR (400 MHz, $CDCl_3$)



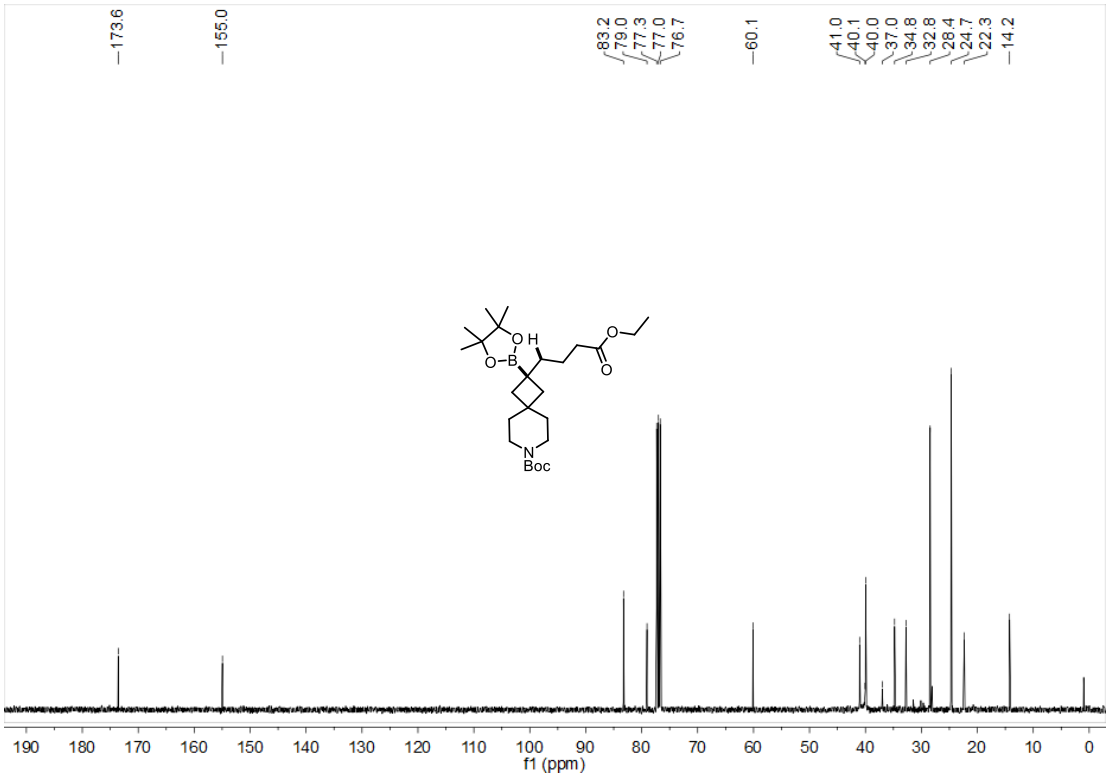
Compound **18** ^{13}C NMR (101 MHz, $CDCl_3$)



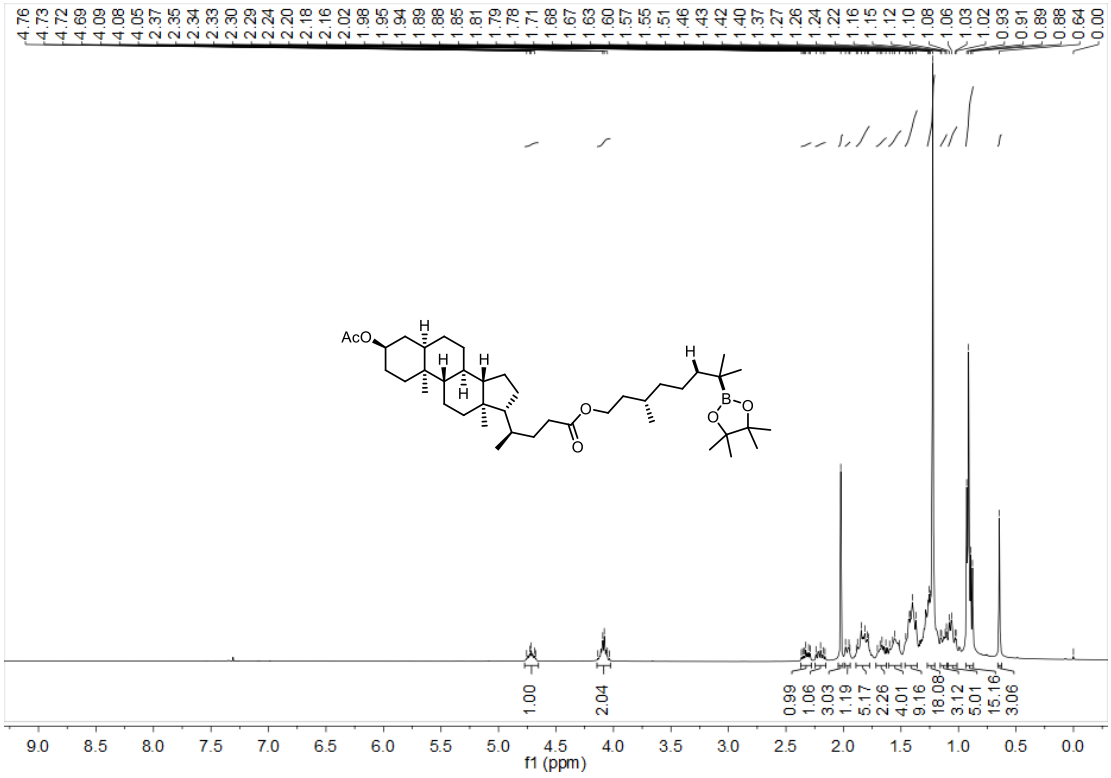
Compound **19** ^{1}H NMR (400 MHz, $CDCl_3$)



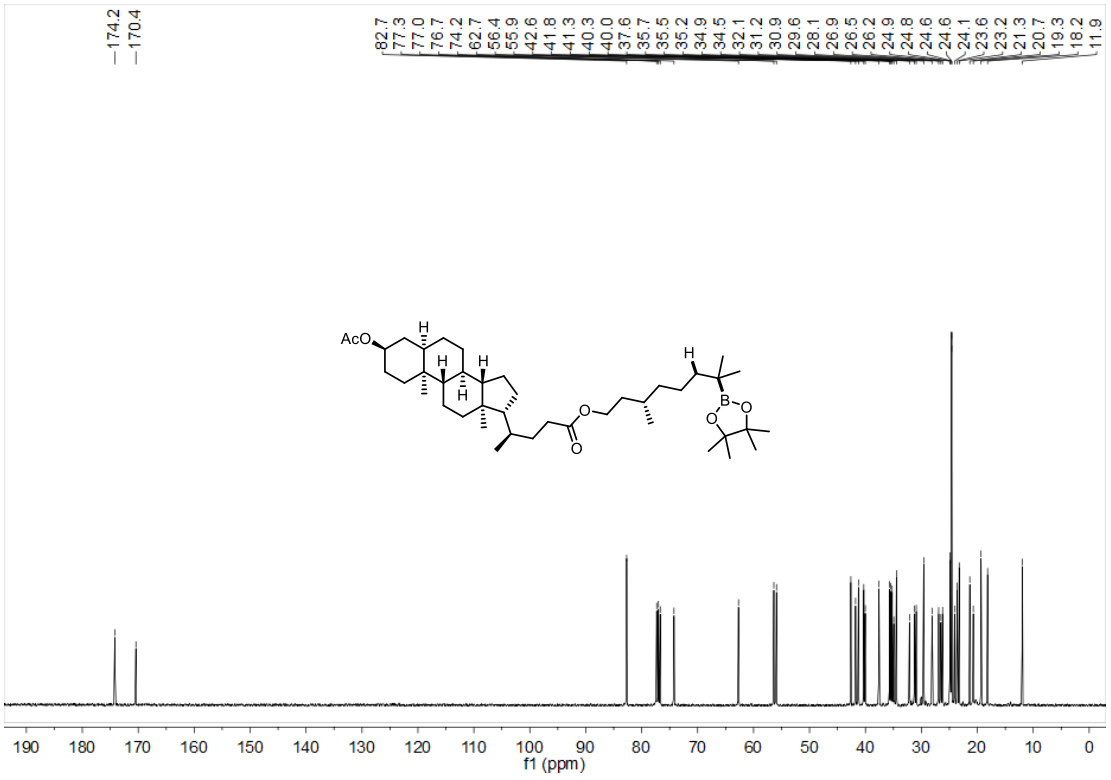
Compound **19** ^{13}C NMR (101 MHz, $CDCl_3$)



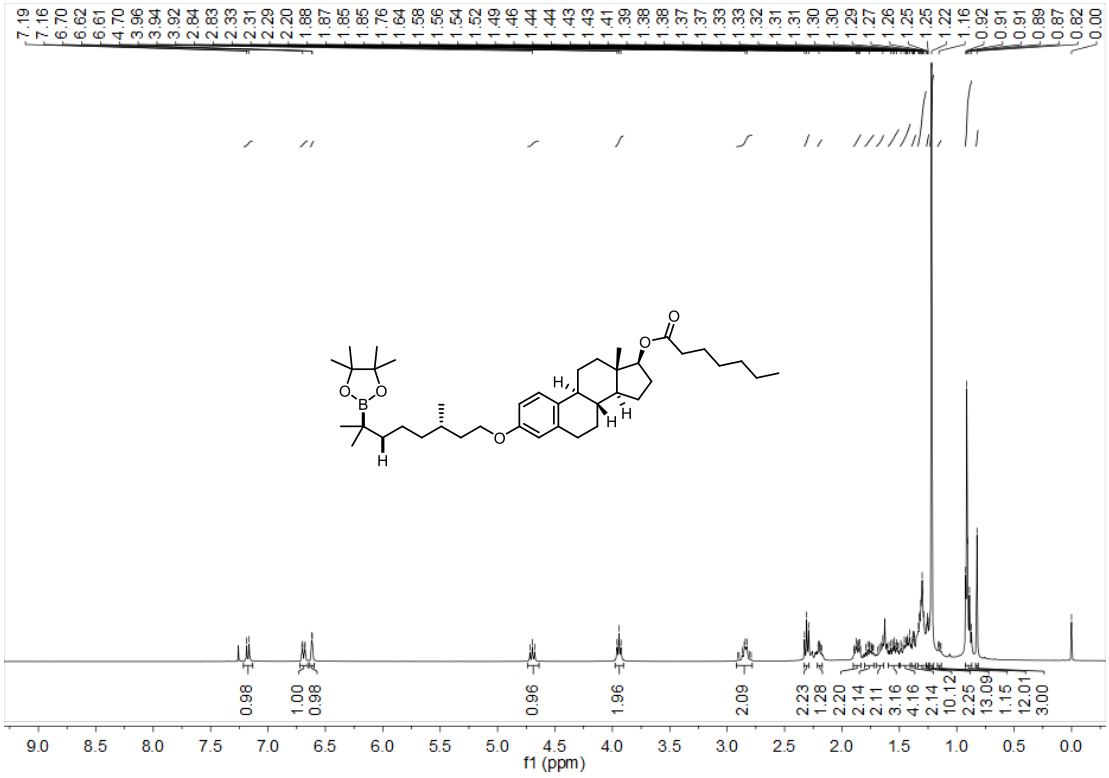
Compound **20** ^{1}H NMR (400 MHz, $CDCl_3$)



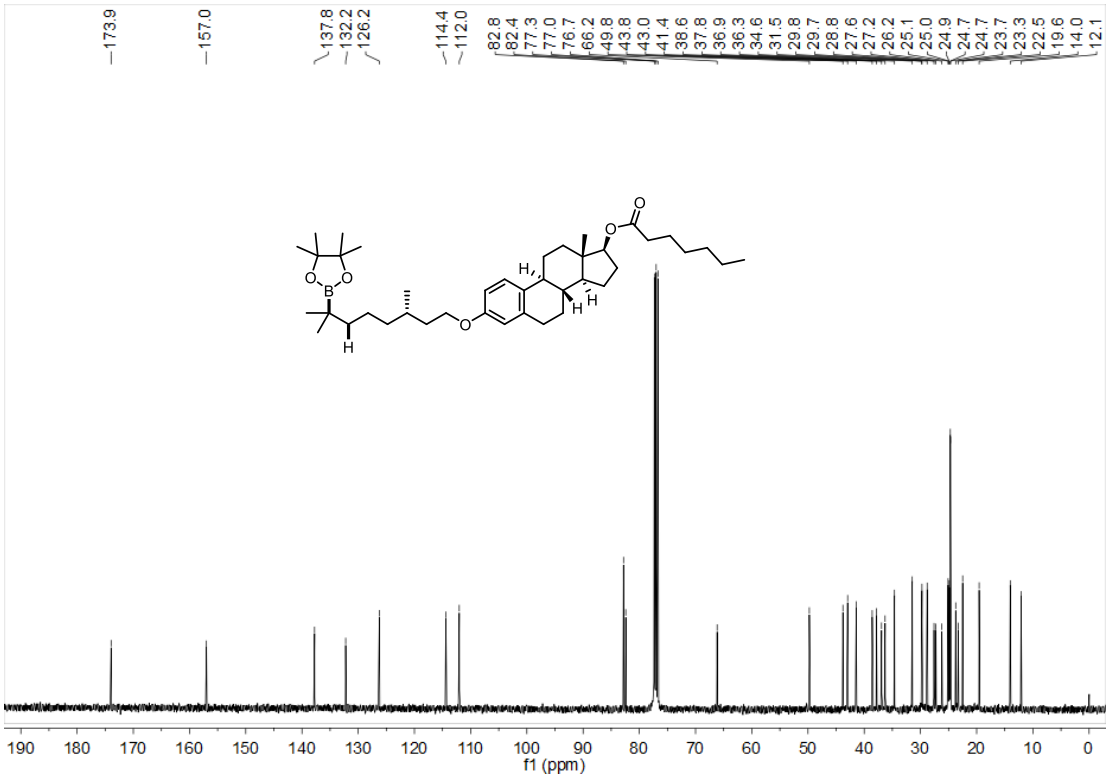
Compound **20** ^{13}C NMR (101 MHz, $CDCl_3$)



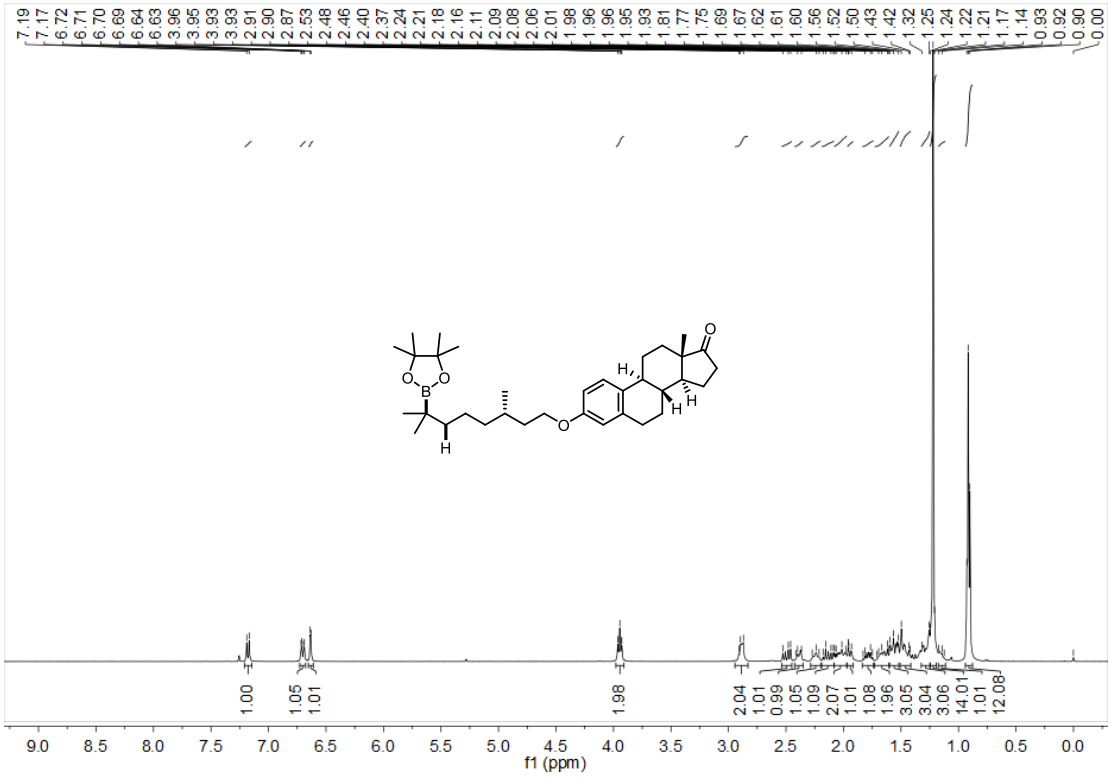
Compound **21** ^{1}H NMR (400 MHz, $CDCl_3$)



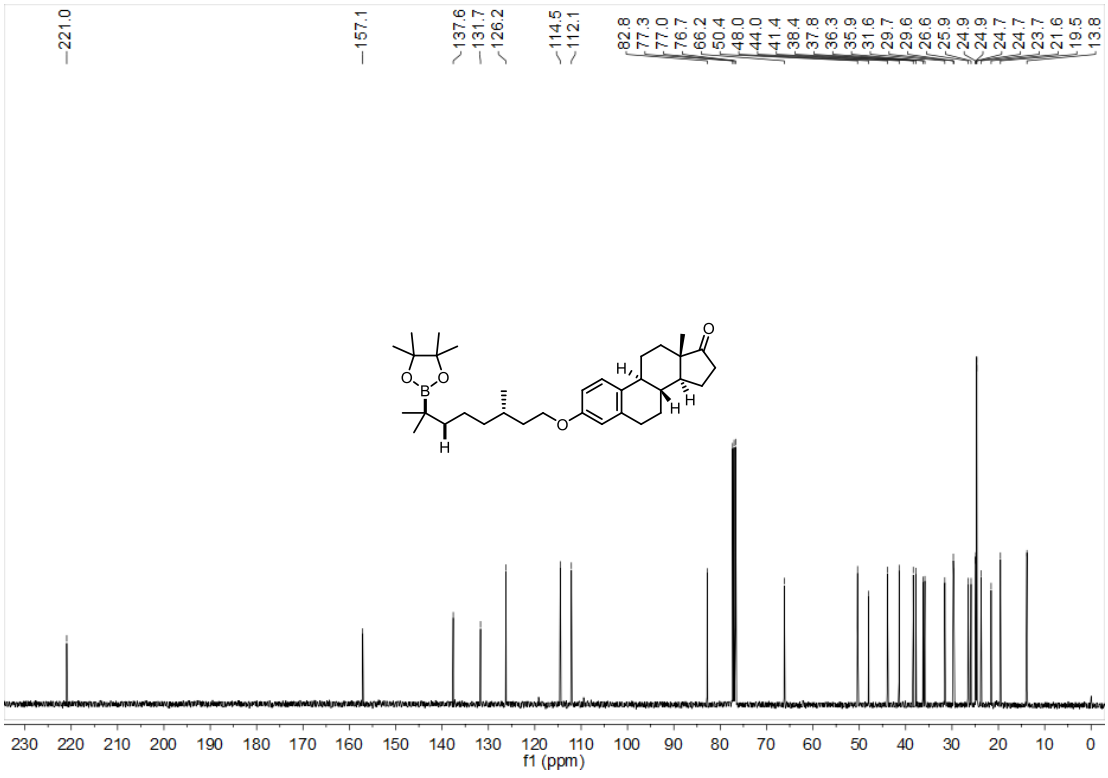
Compound **21** ^{13}C NMR (101 MHz, $CDCl_3$)



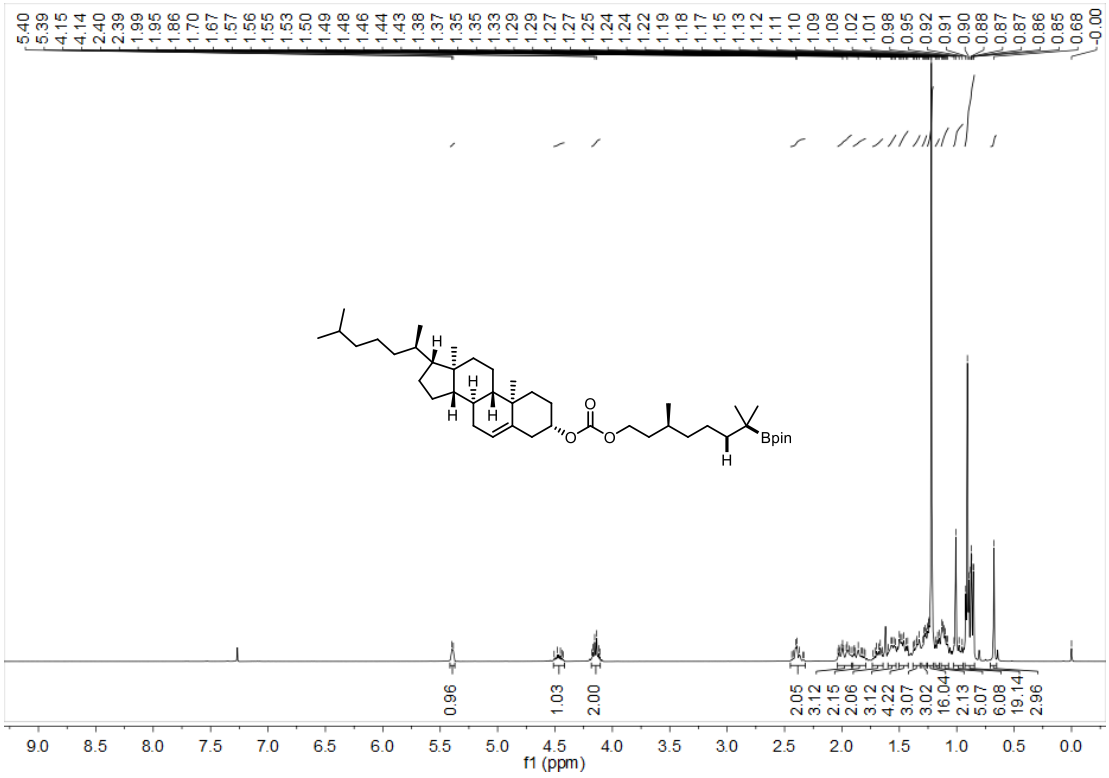
Compound **22** ^{1}H NMR (400 MHz, $CDCl_3$)



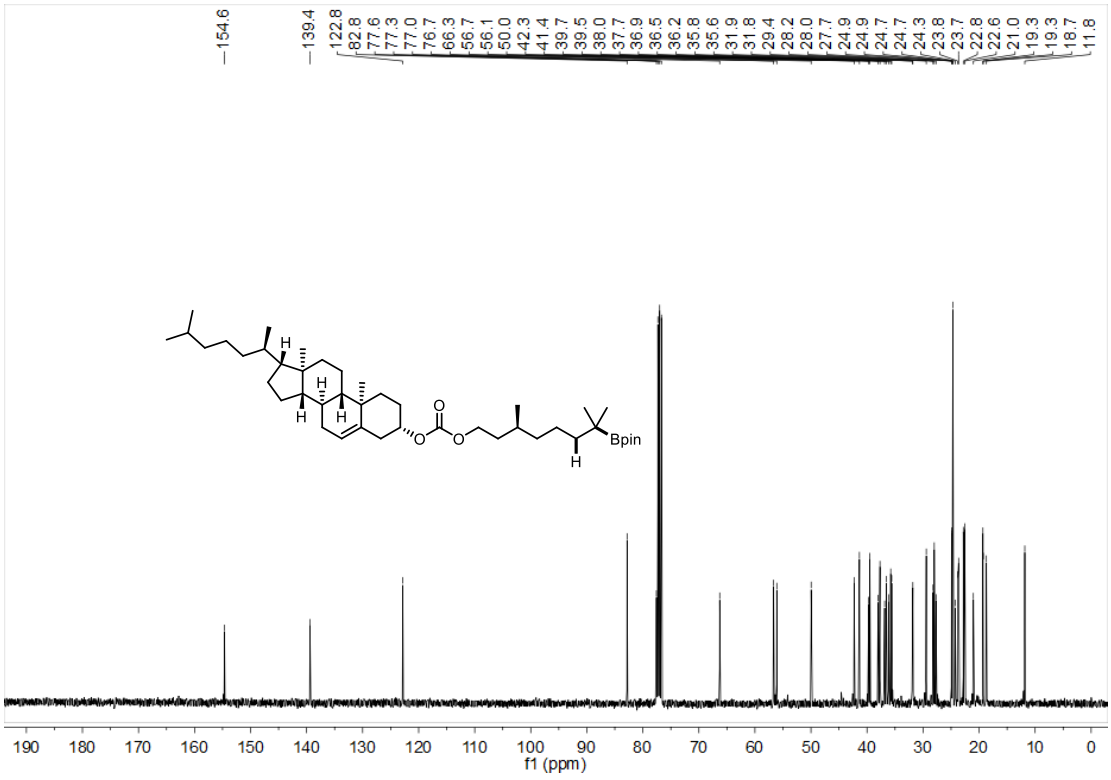
Compound **22** ^{13}C NMR (101 MHz, $CDCl_3$)



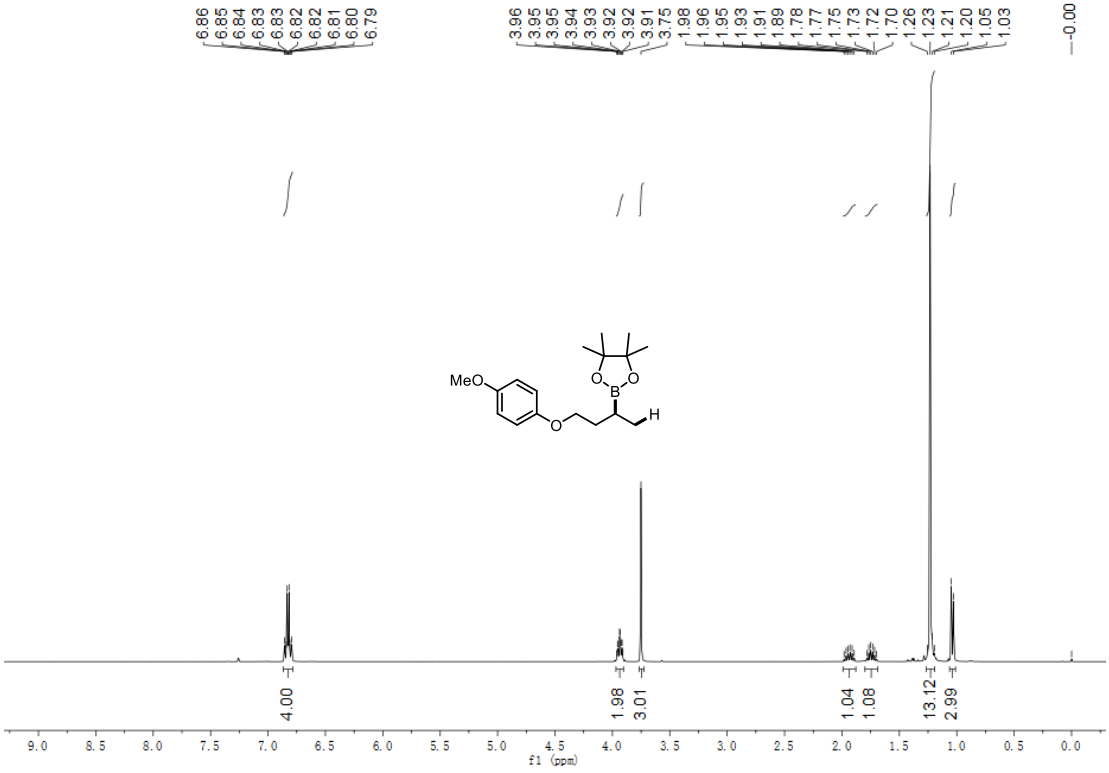
Compound **23** ^{1}H NMR (400 MHz, $CDCl_3$)



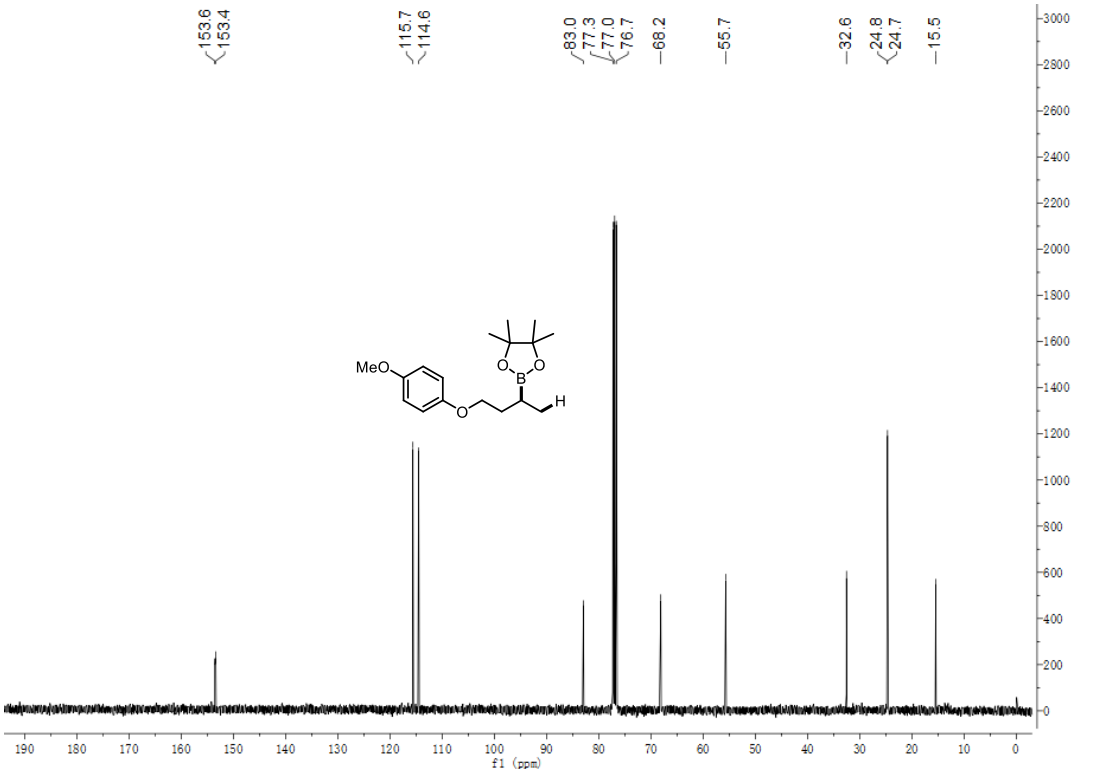
Compound **23** ^{13}C NMR (101 MHz, $CDCl_3$)



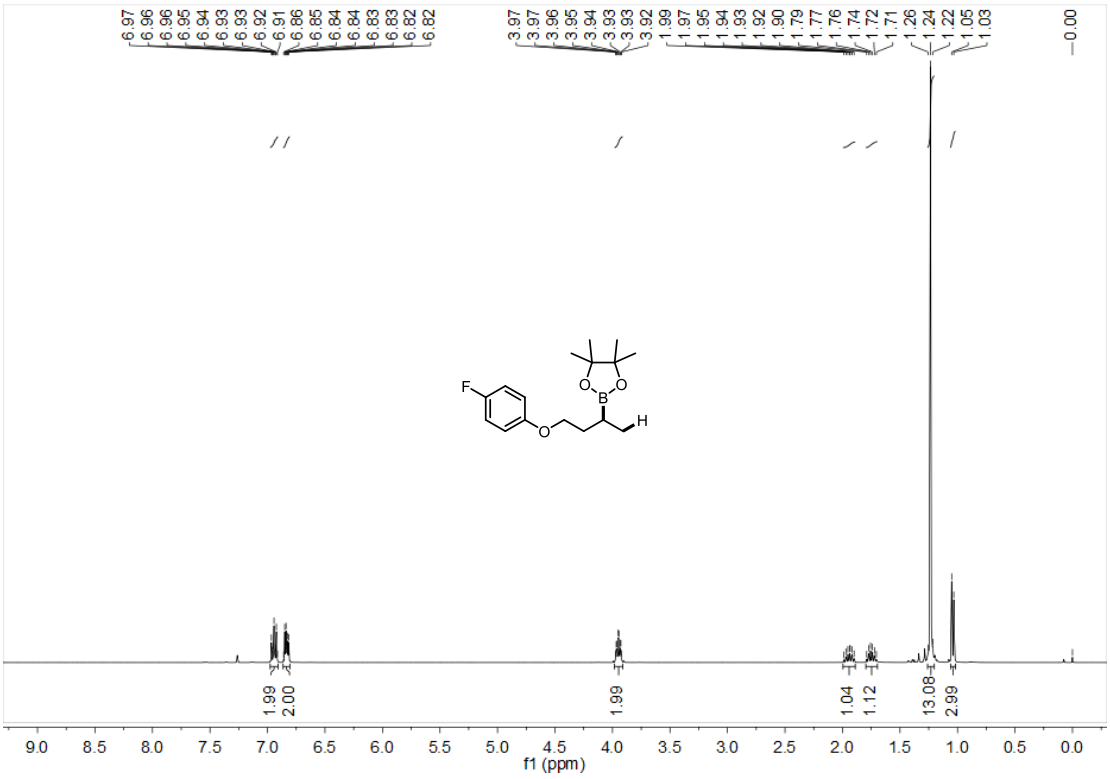
Compound **24** ^{1}H NMR (400 MHz, $CDCl_3$)



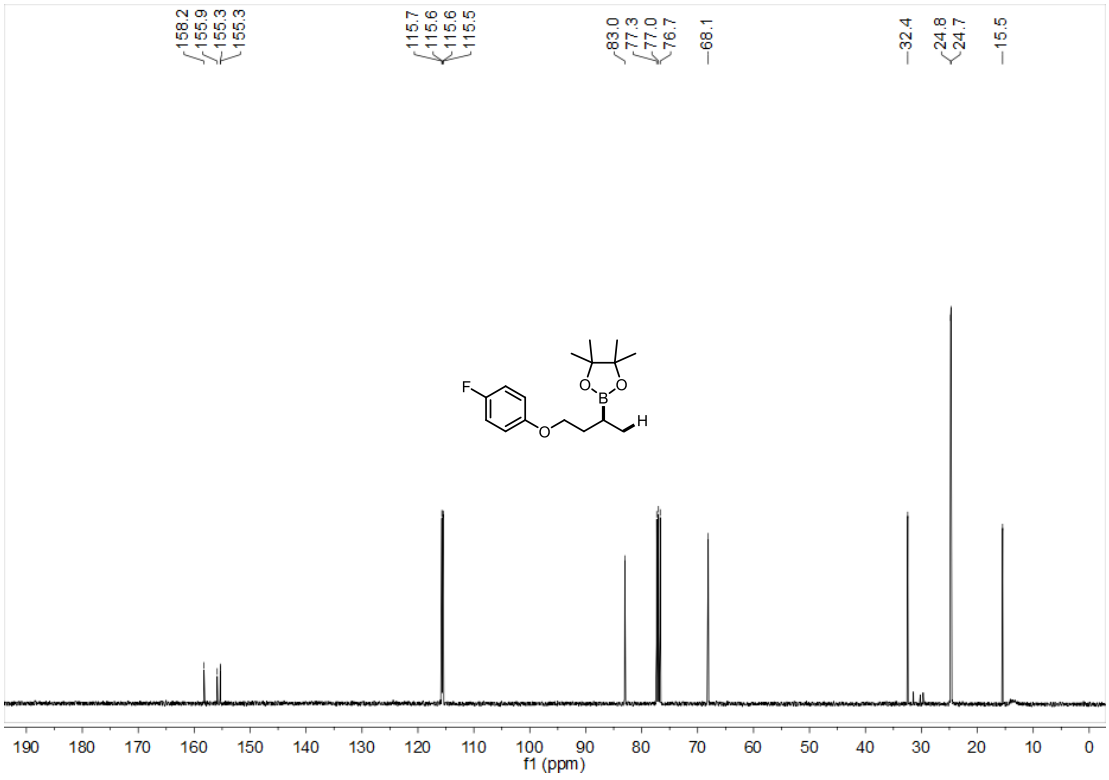
Compound **24** ^{13}C NMR (101 MHz, $CDCl_3$)



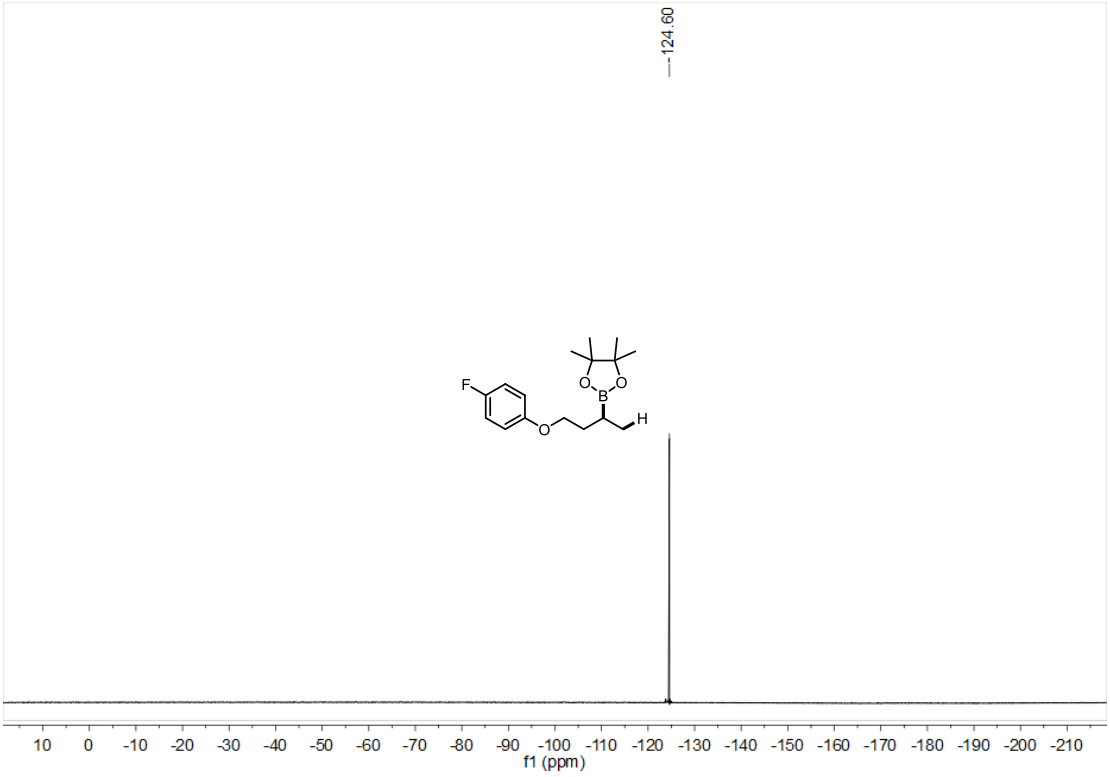
Compound **25** ^{1}H NMR (400 MHz, $CDCl_3$)



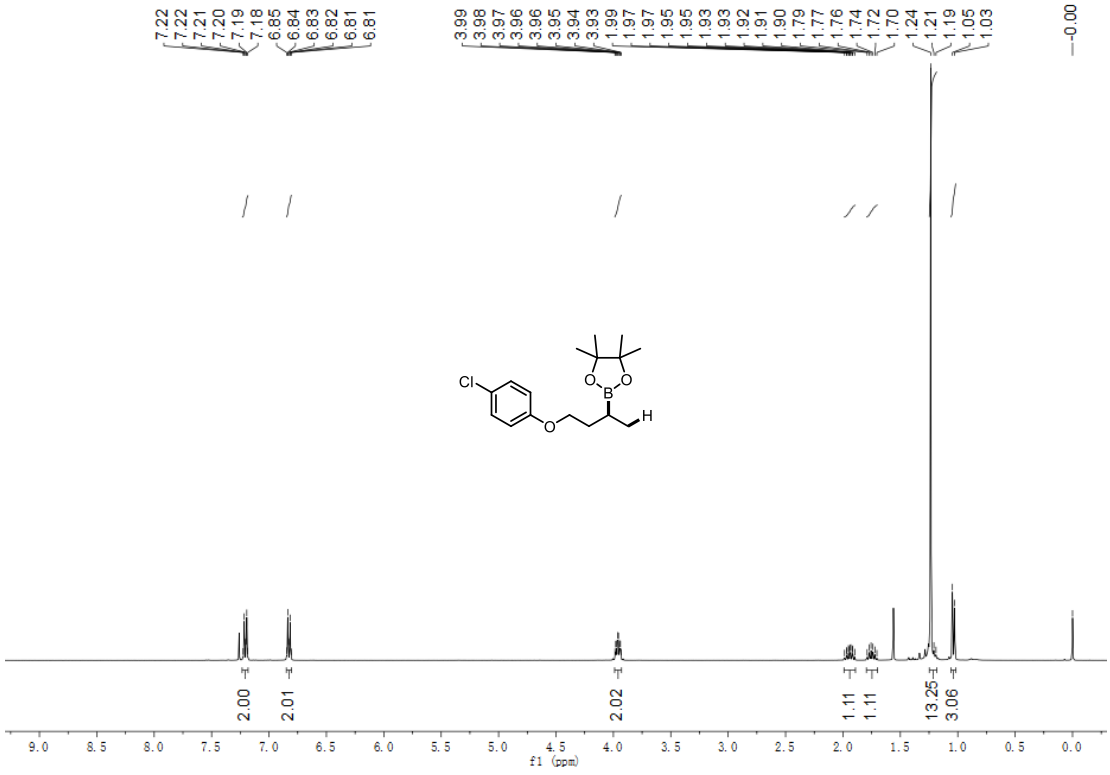
Compound **25** ^{13}C NMR (101 MHz, $CDCl_3$)



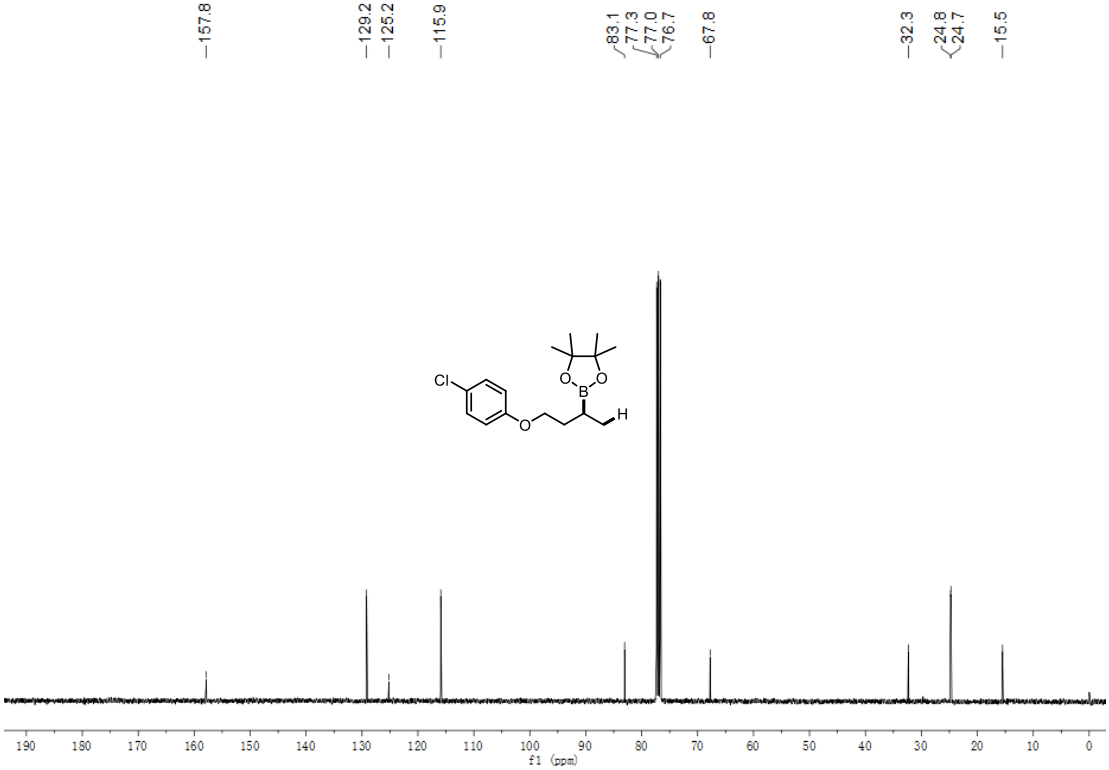
Compound **25** ^{19}F NMR (376 MHz, $CDCl_3$)



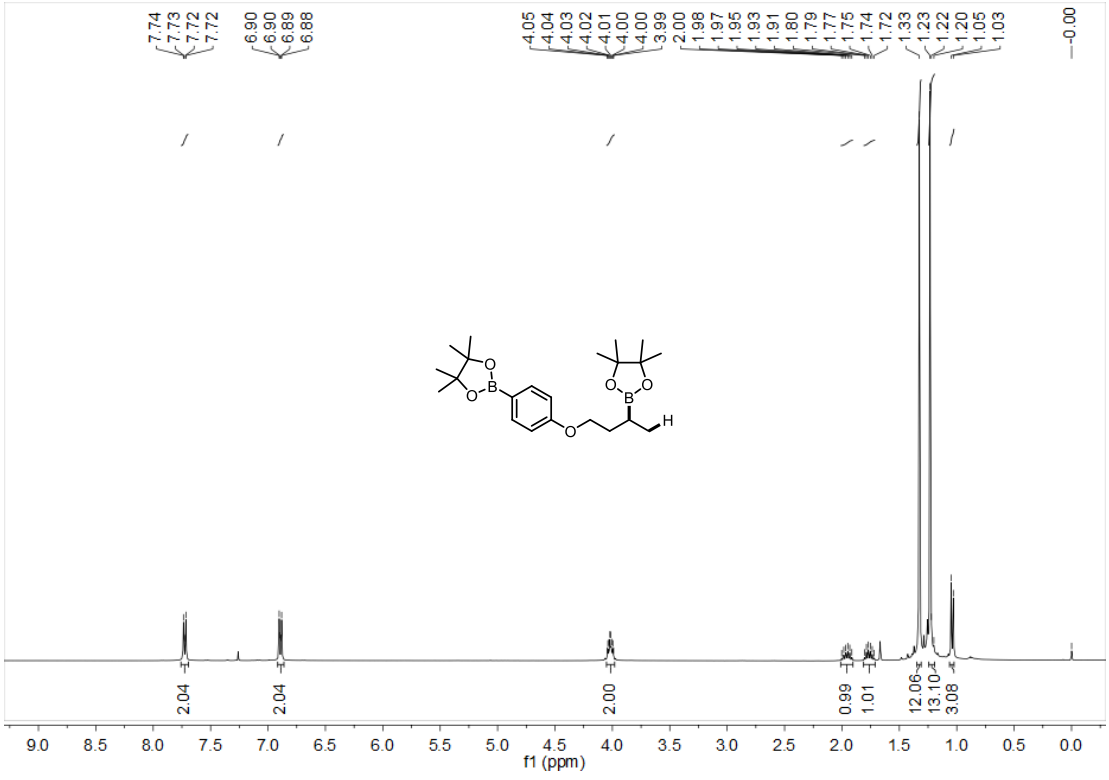
Compound **26** ^{1}H NMR (400 MHz, $CDCl_3$)



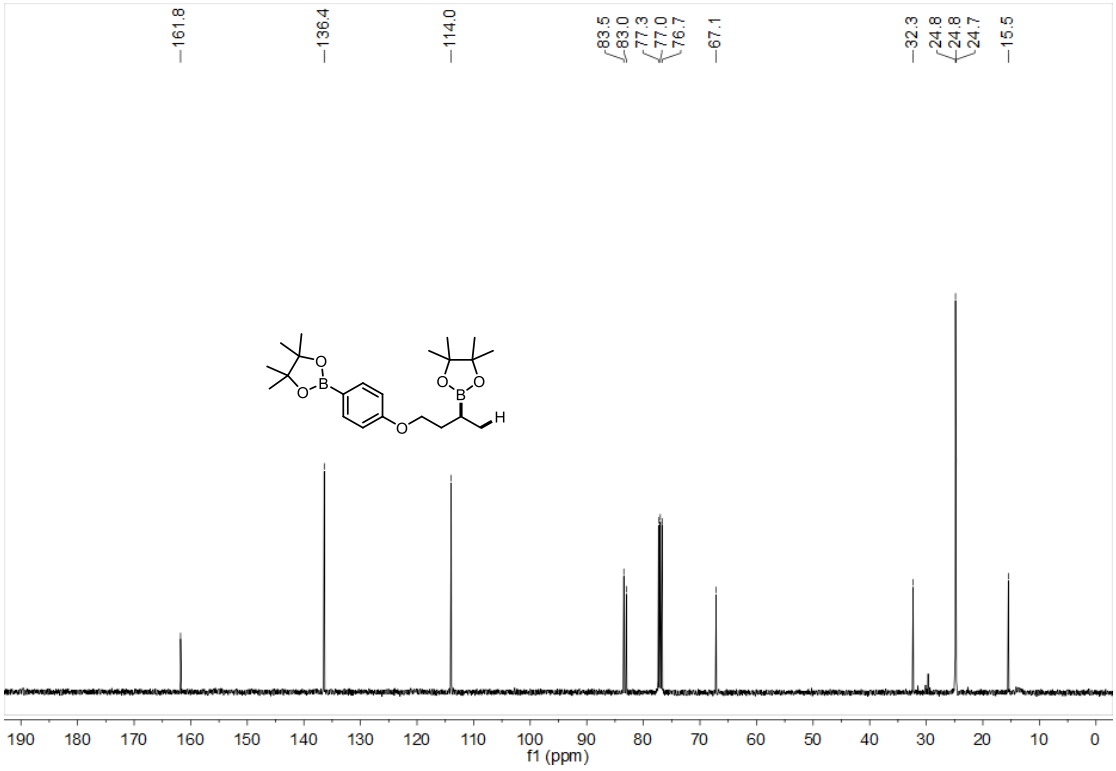
Compound **26** ^{13}C NMR (101 MHz, $CDCl_3$)



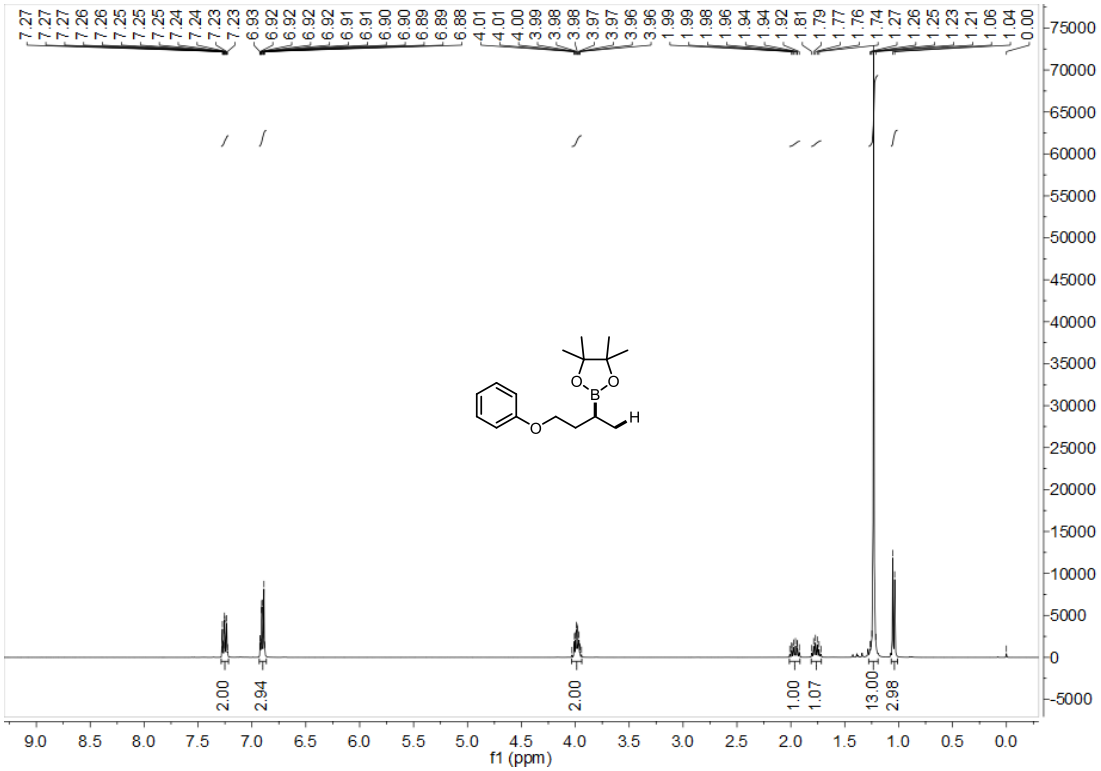
Compound **27** ^{1}H NMR (400 MHz, $CDCl_3$)



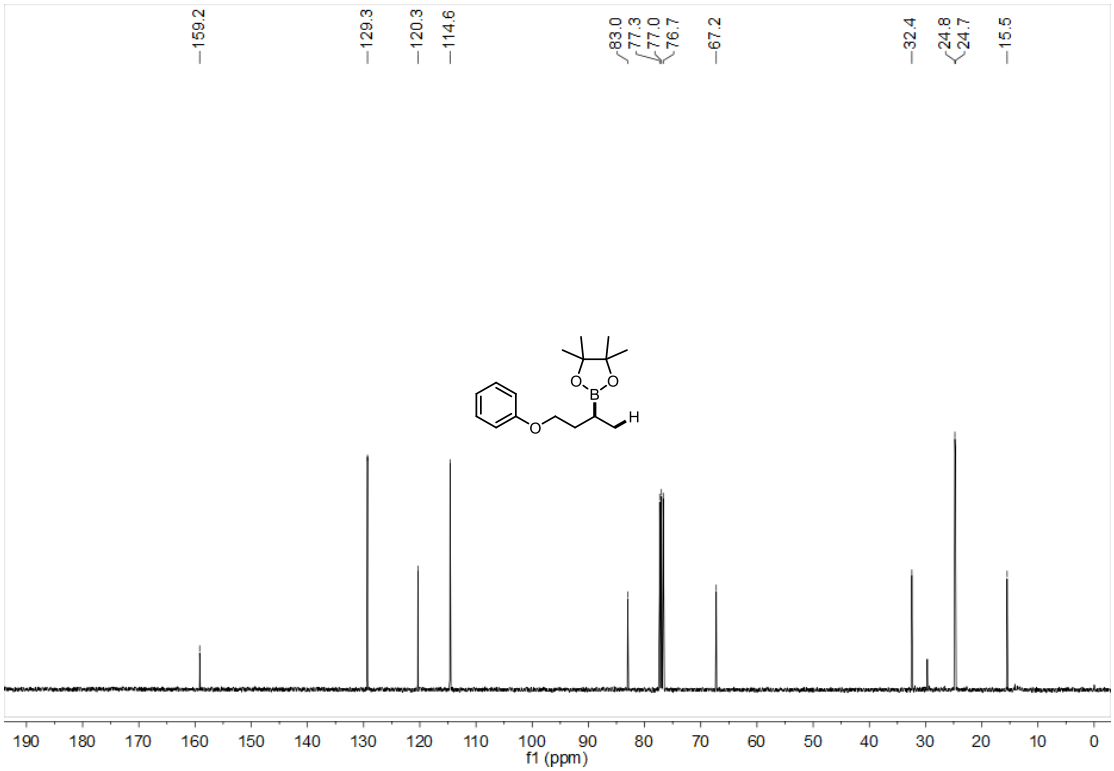
Compound **27** ^{13}C NMR (101 MHz, $CDCl_3$)



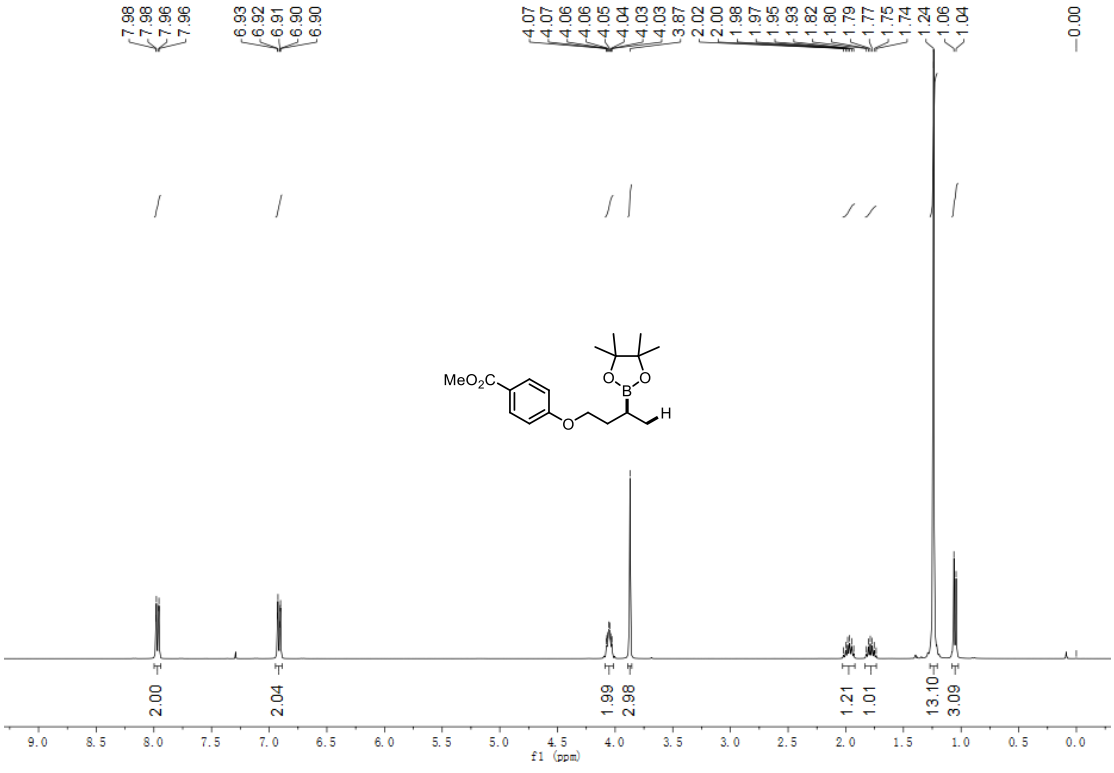
Compound **28** ^{1}H NMR (400 MHz, $CDCl_3$)



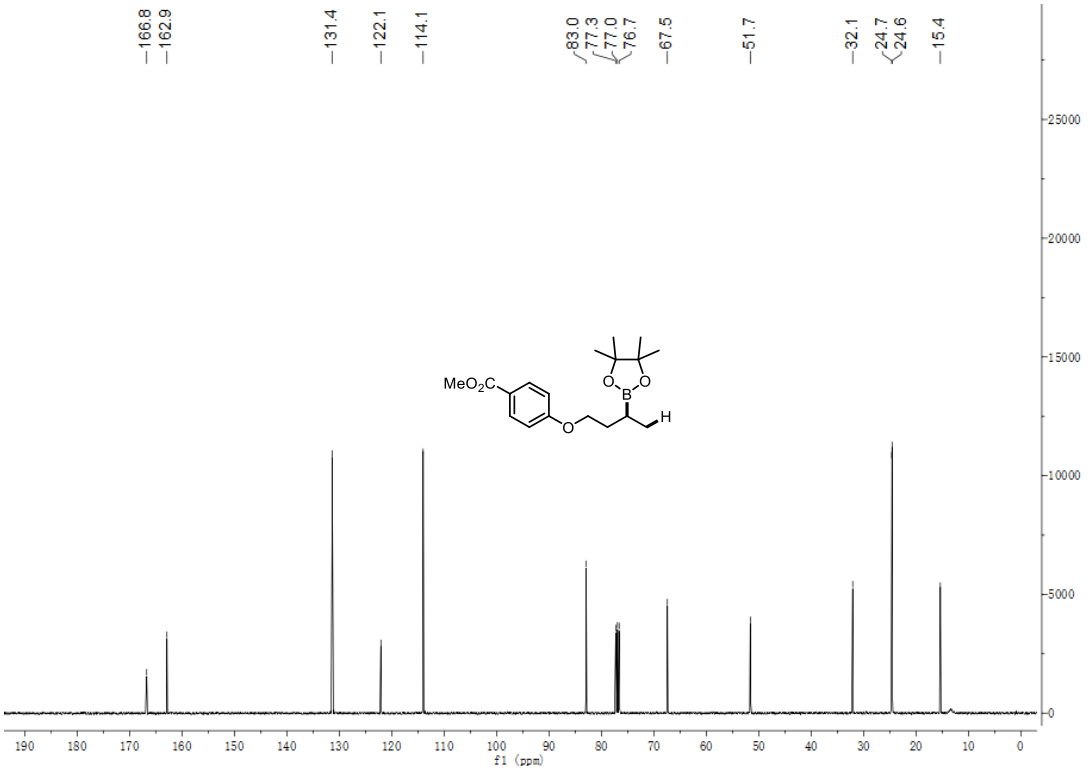
Compound **28** ^{13}C NMR (101 MHz, $CDCl_3$)



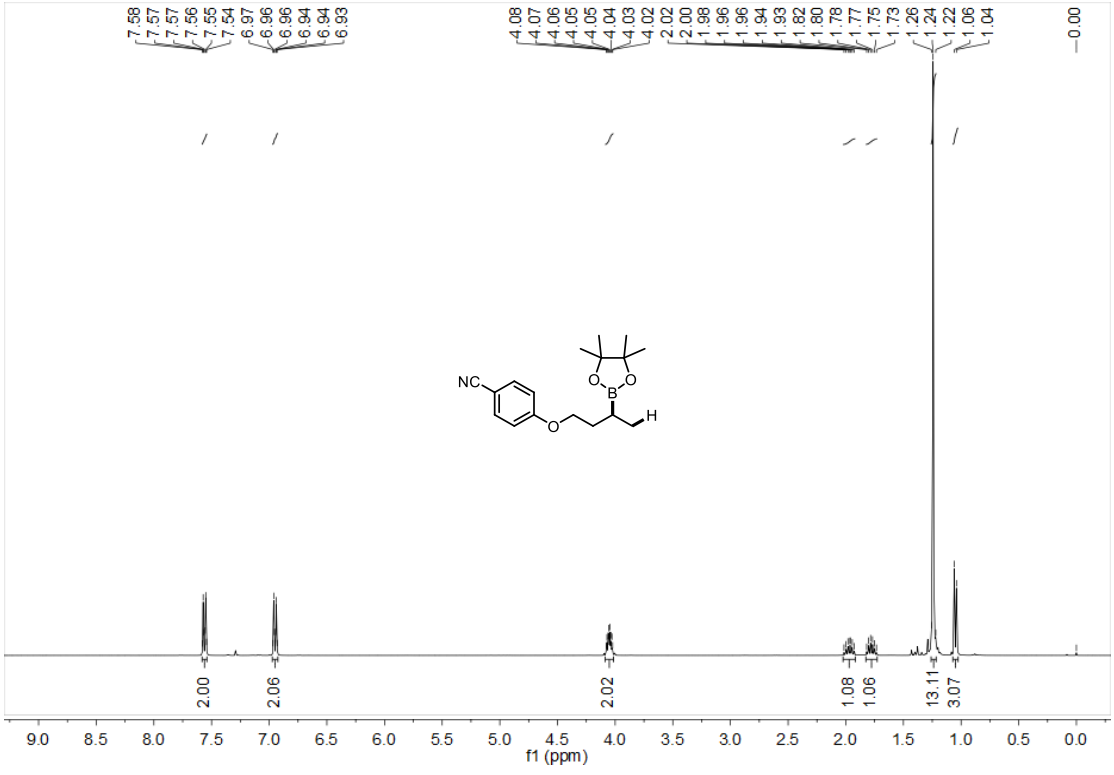
Compound **29** ^{1}H NMR (400 MHz, $CDCl_3$)



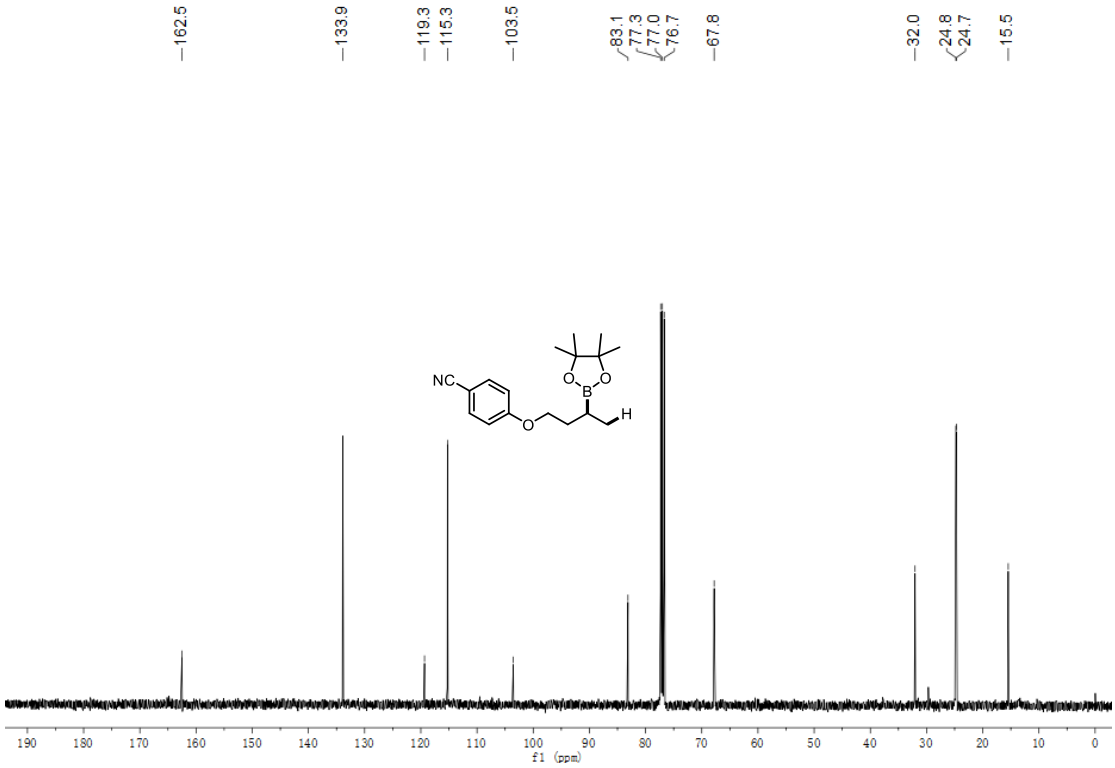
Compound **29** ^{13}C NMR (101 MHz, $CDCl_3$)



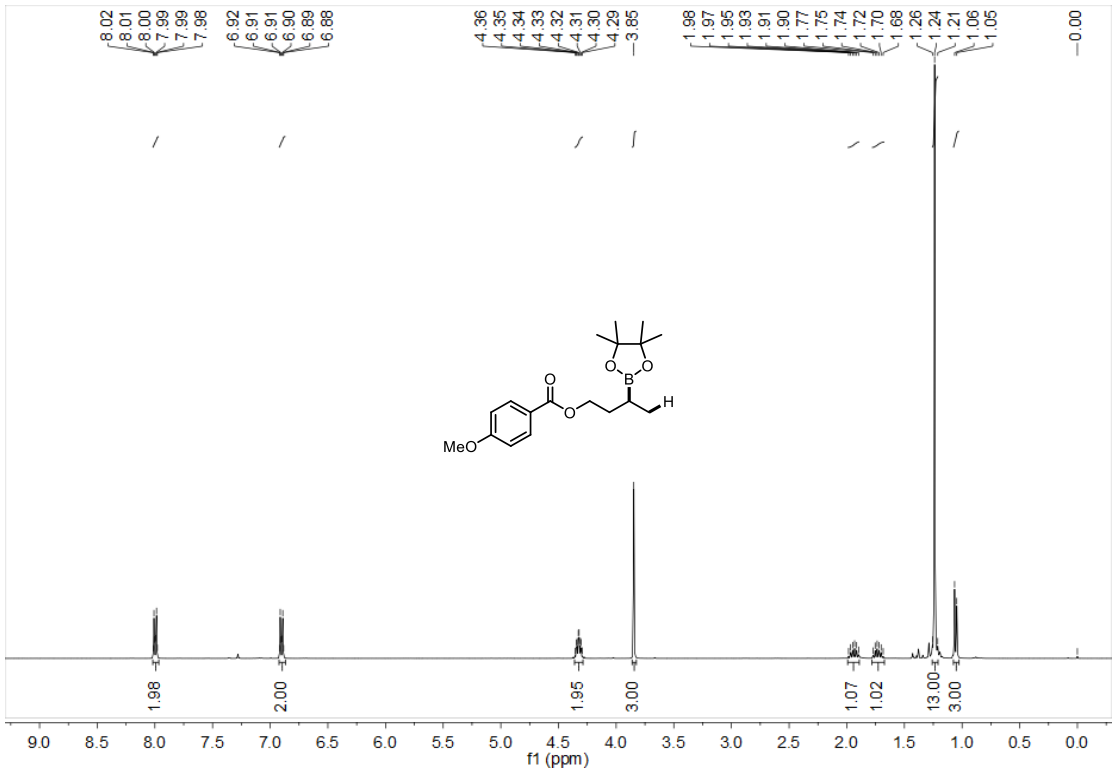
Compound **30** ^{1}H NMR (400 MHz, $CDCl_3$)



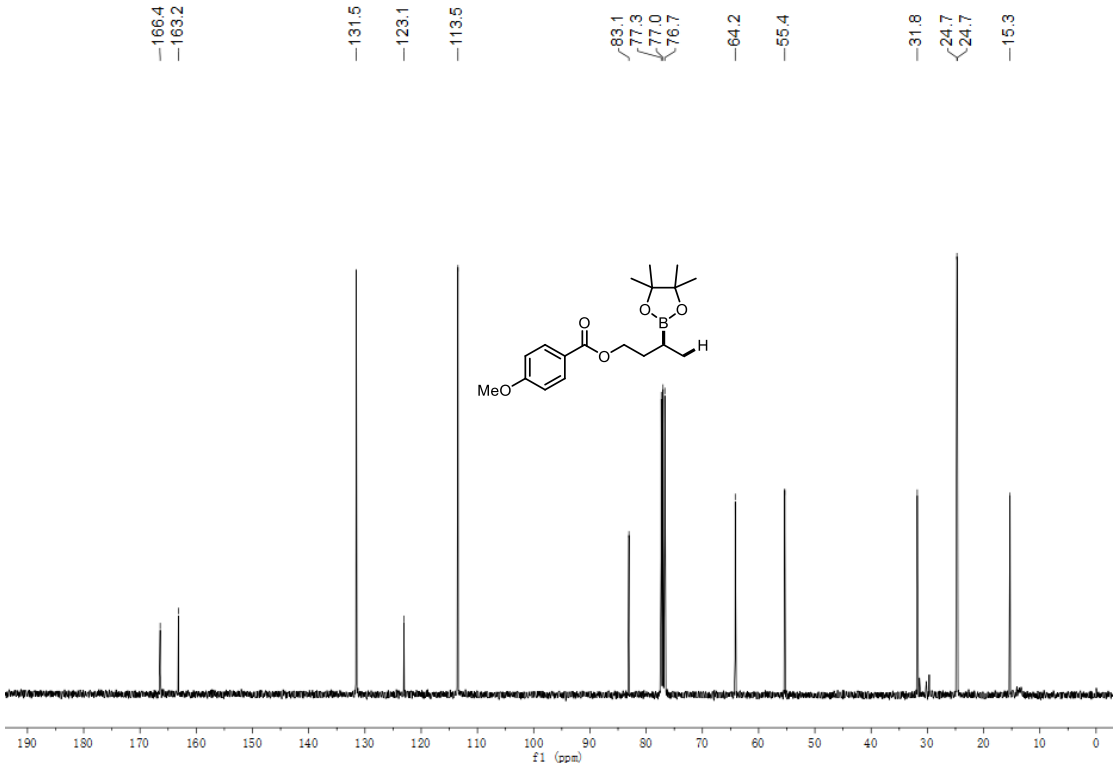
Compound **30** ^{13}C NMR (101 MHz, $CDCl_3$)



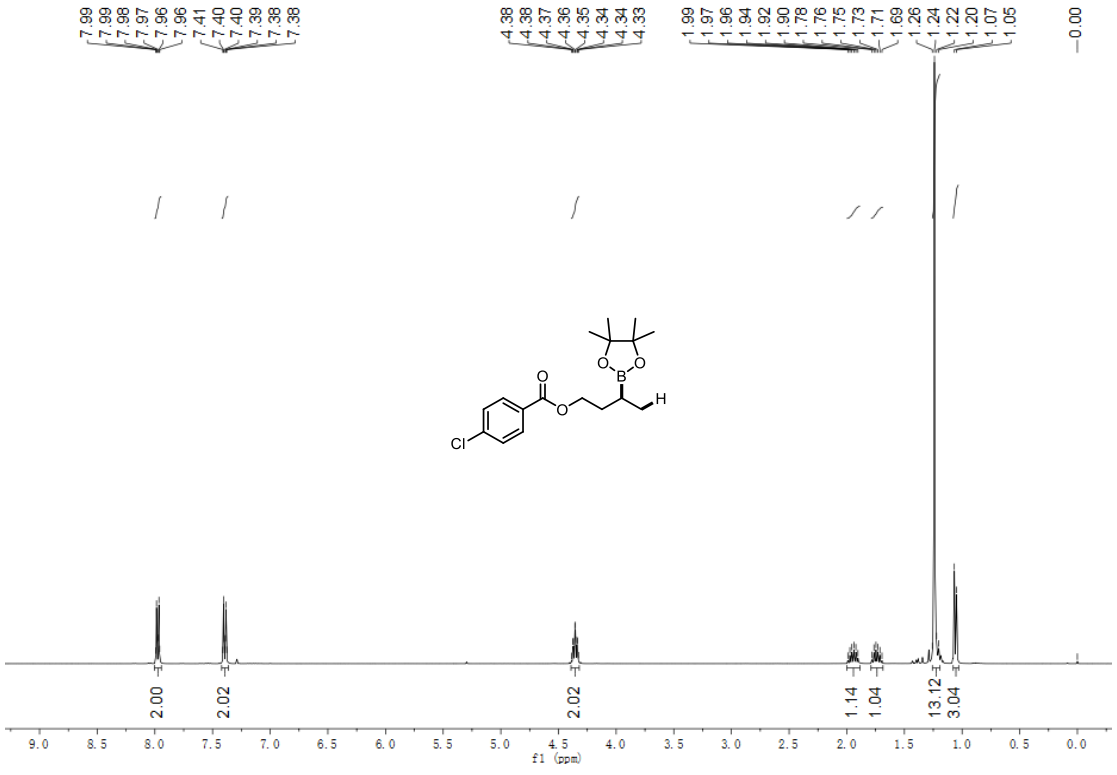
Compound **31** ^{1}H NMR (400 MHz, $CDCl_3$)



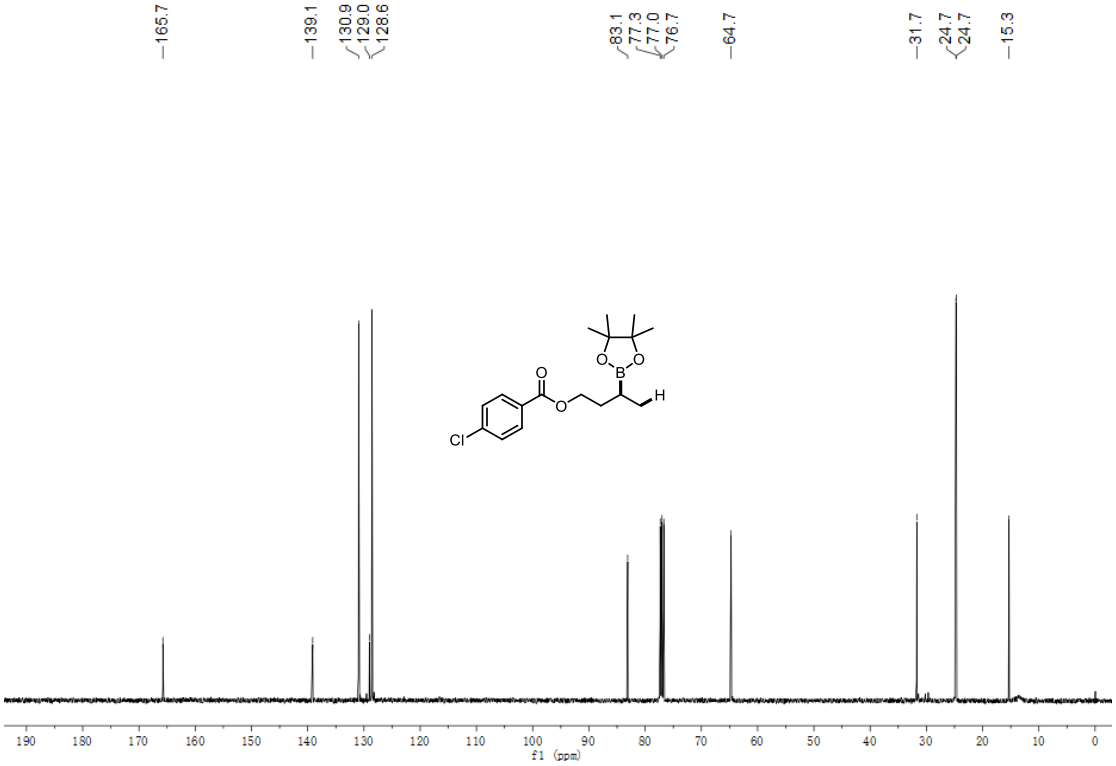
Compound **31** ^{13}C NMR (101 MHz, $CDCl_3$)



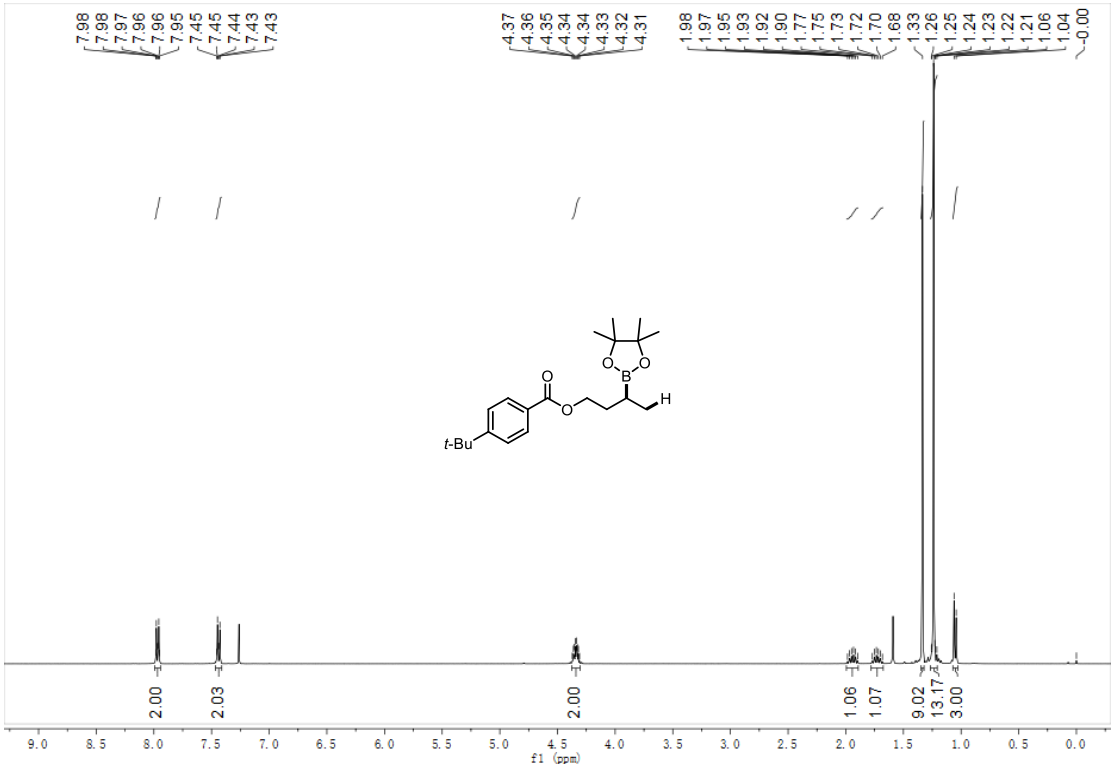
Compound **32** ^{1}H NMR (400 MHz, $CDCl_3$)



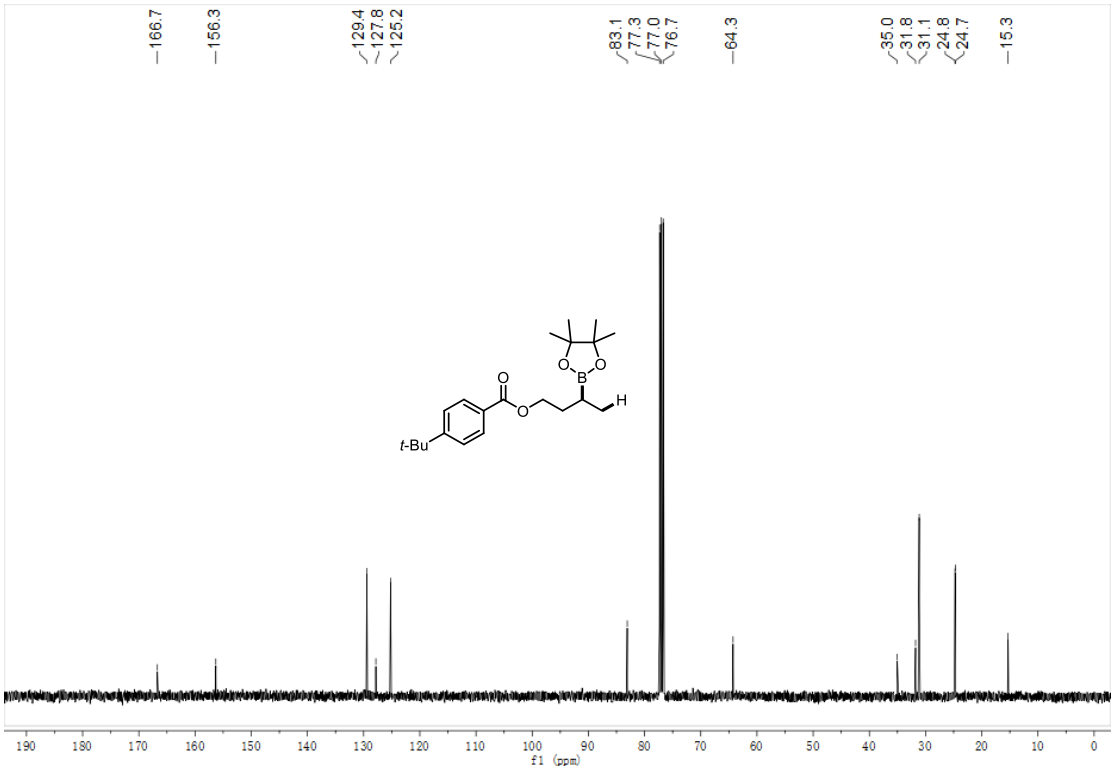
Compound **32** ^{13}C NMR (101 MHz, $CDCl_3$)



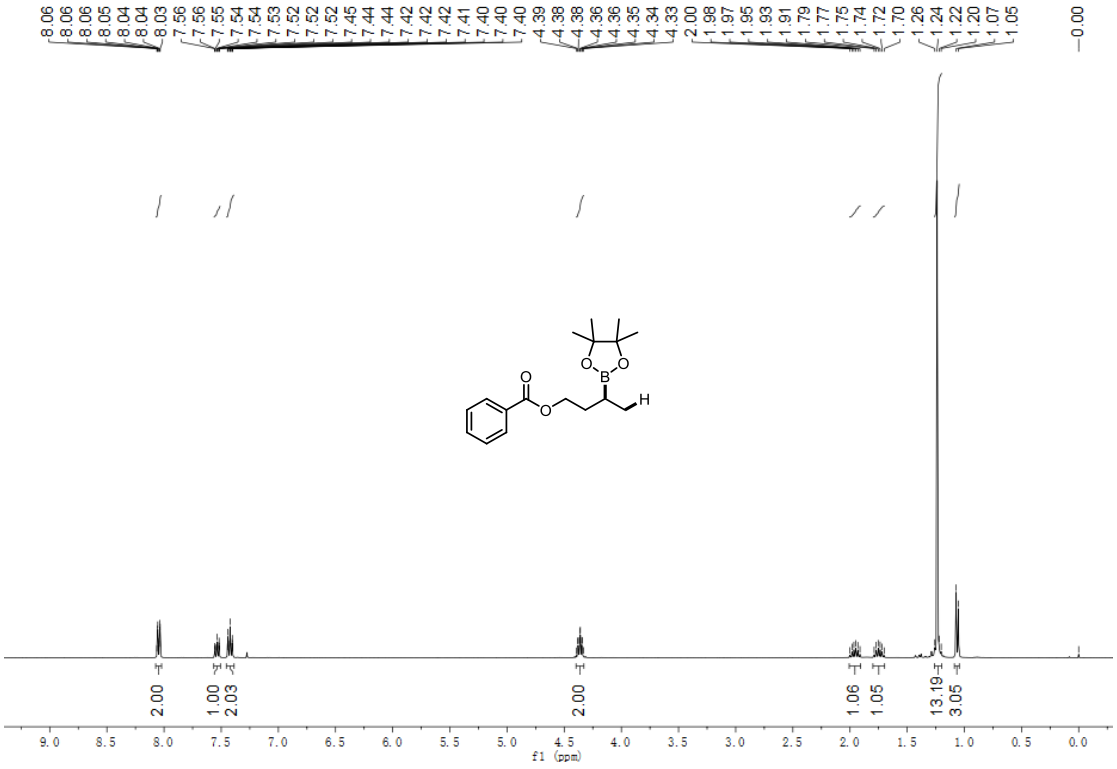
Compound **33** ^{1}H NMR (400 MHz, $CDCl_3$)



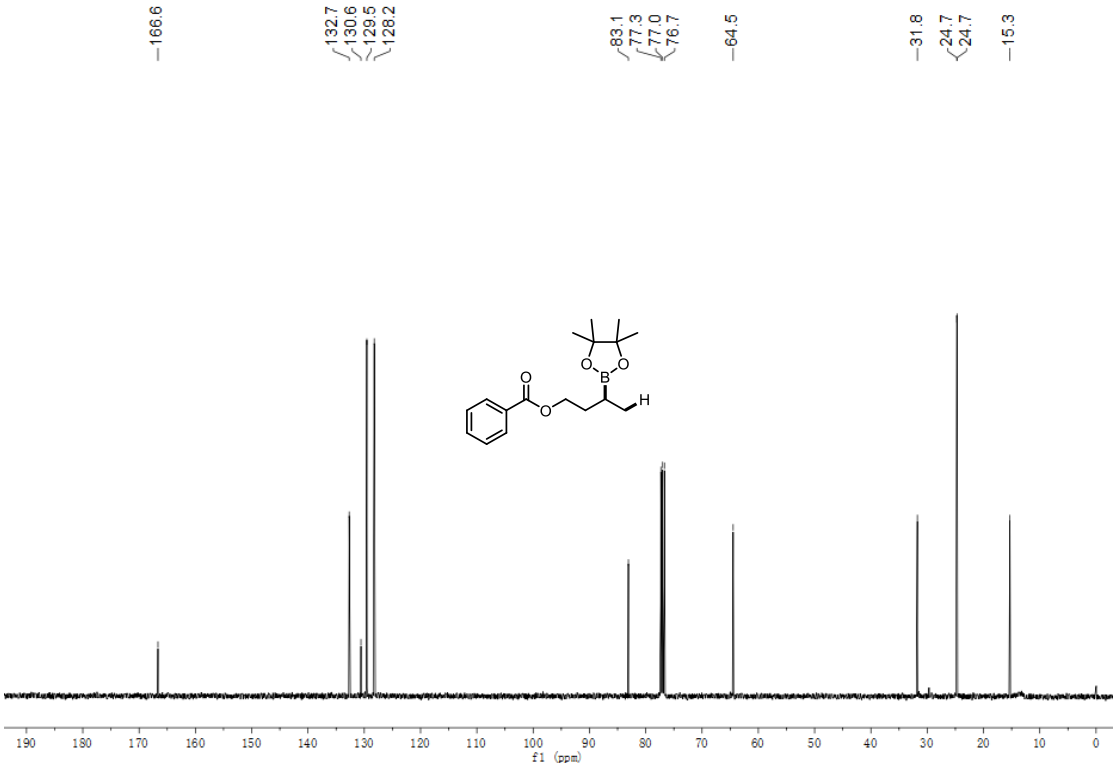
Compound **33** ^{13}C NMR (101 MHz, $CDCl_3$)



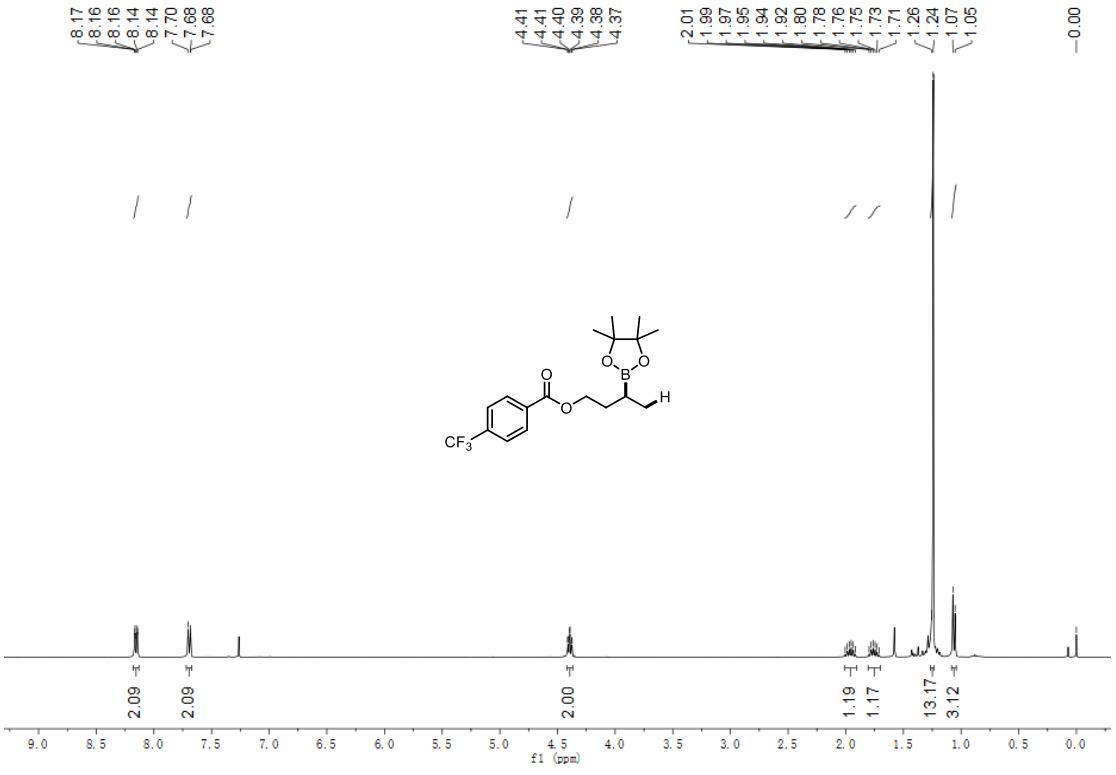
Compound **34** ^{1}H NMR (400 MHz, $CDCl_3$)



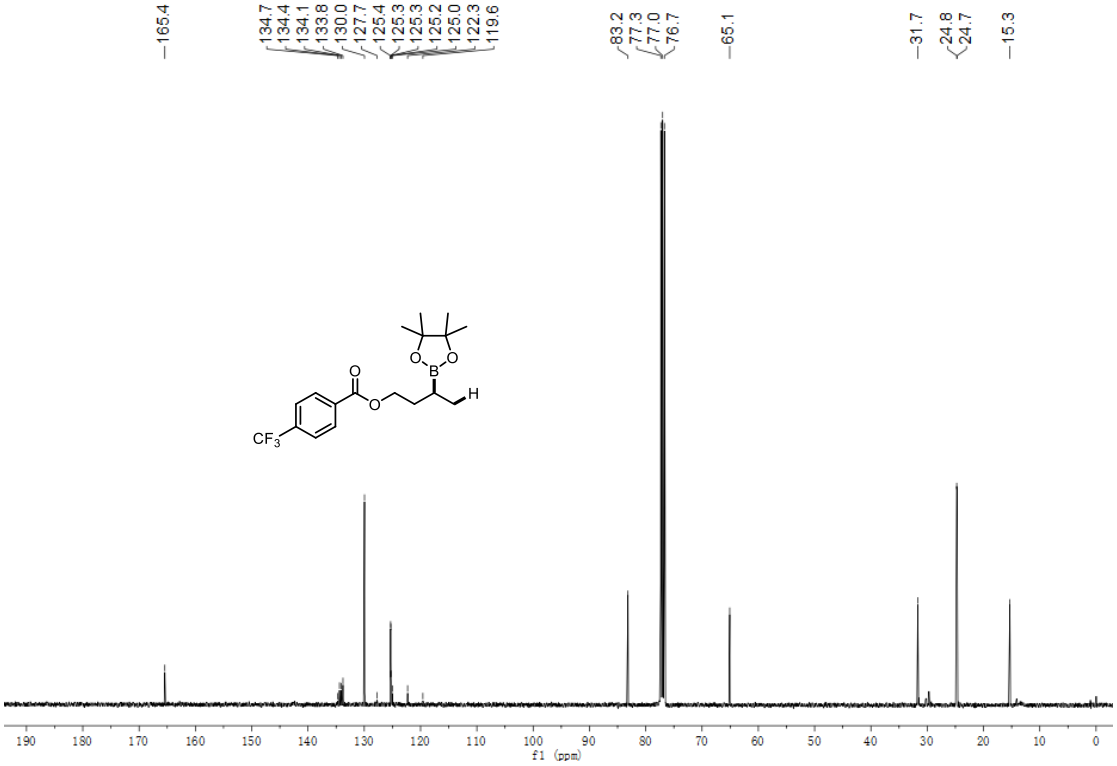
Compound **34** ^{13}C NMR (101 MHz, $CDCl_3$)



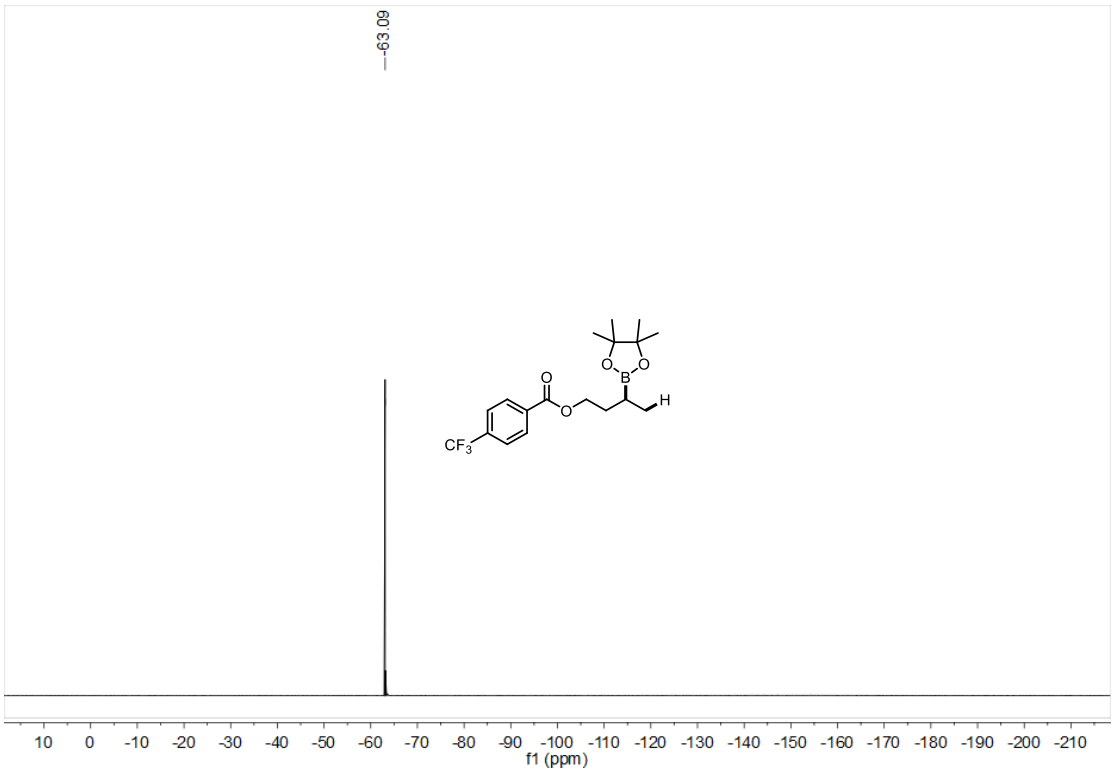
Compound **35** ^{1}H NMR (400 MHz, $CDCl_3$)



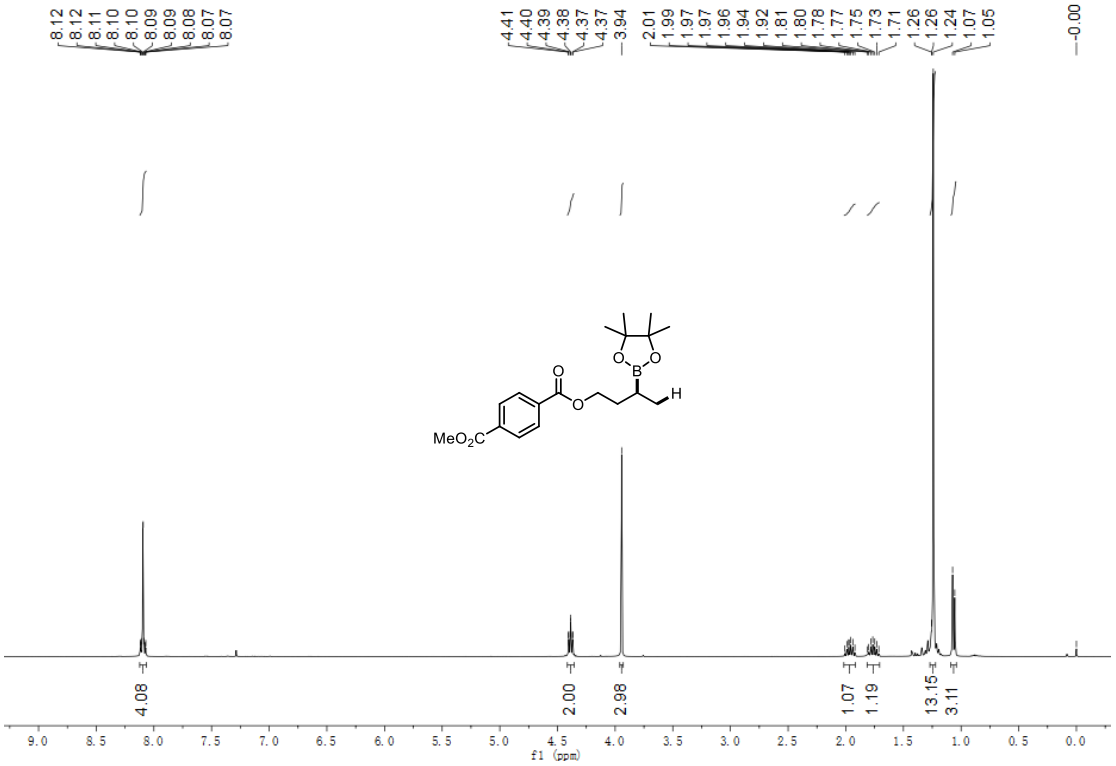
Compound **35** ^{13}C NMR (101 MHz, $CDCl_3$)



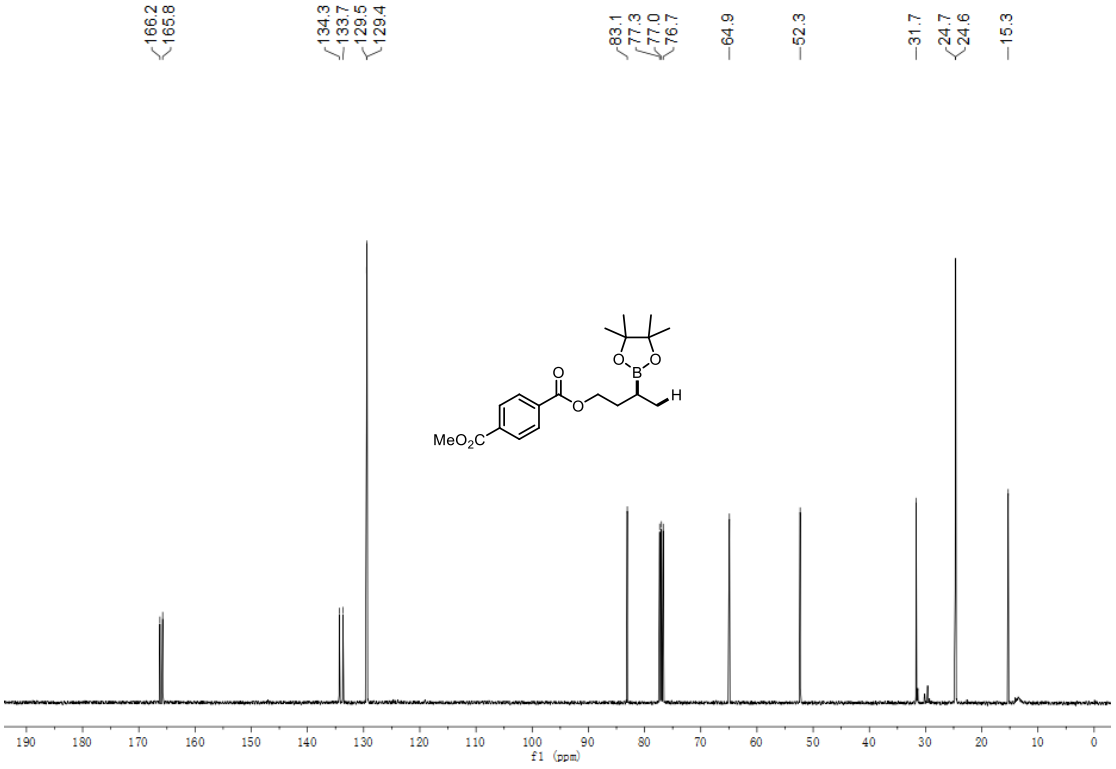
Compound **35** ^{19}F NMR (376 MHz, $CDCl_3$)



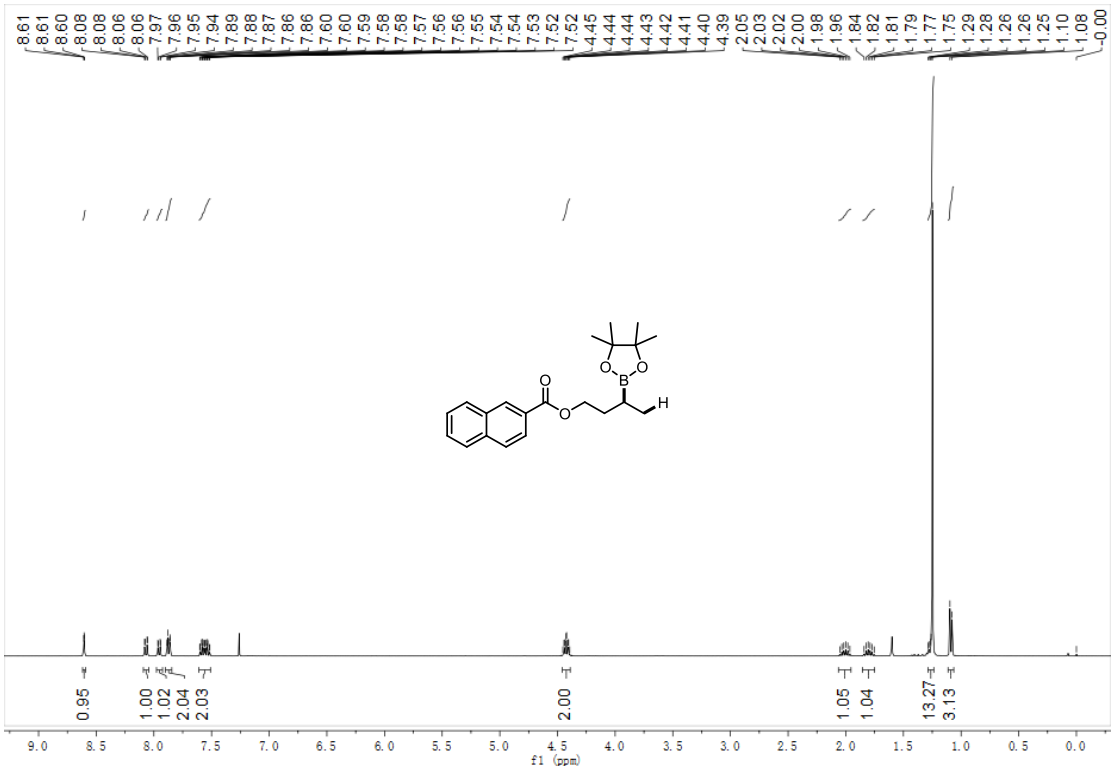
Compound **36** ^{1}H NMR (400 MHz, $CDCl_3$)



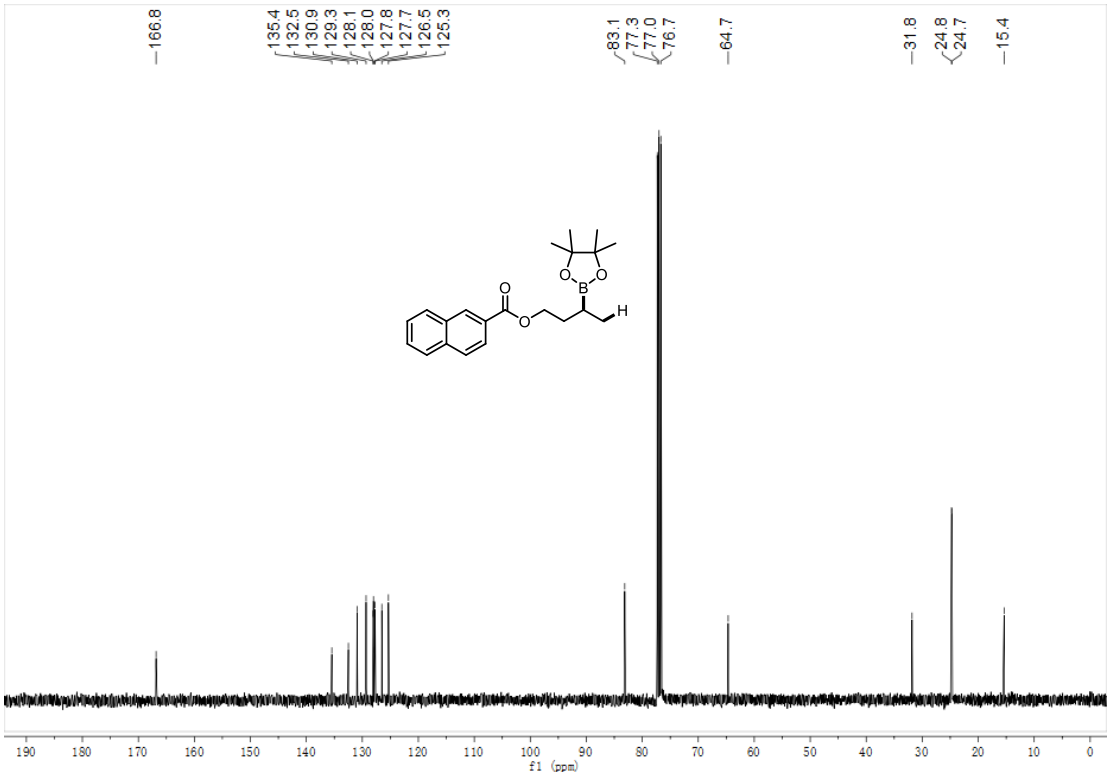
Compound **36** ^{13}C NMR (101 MHz, $CDCl_3$)



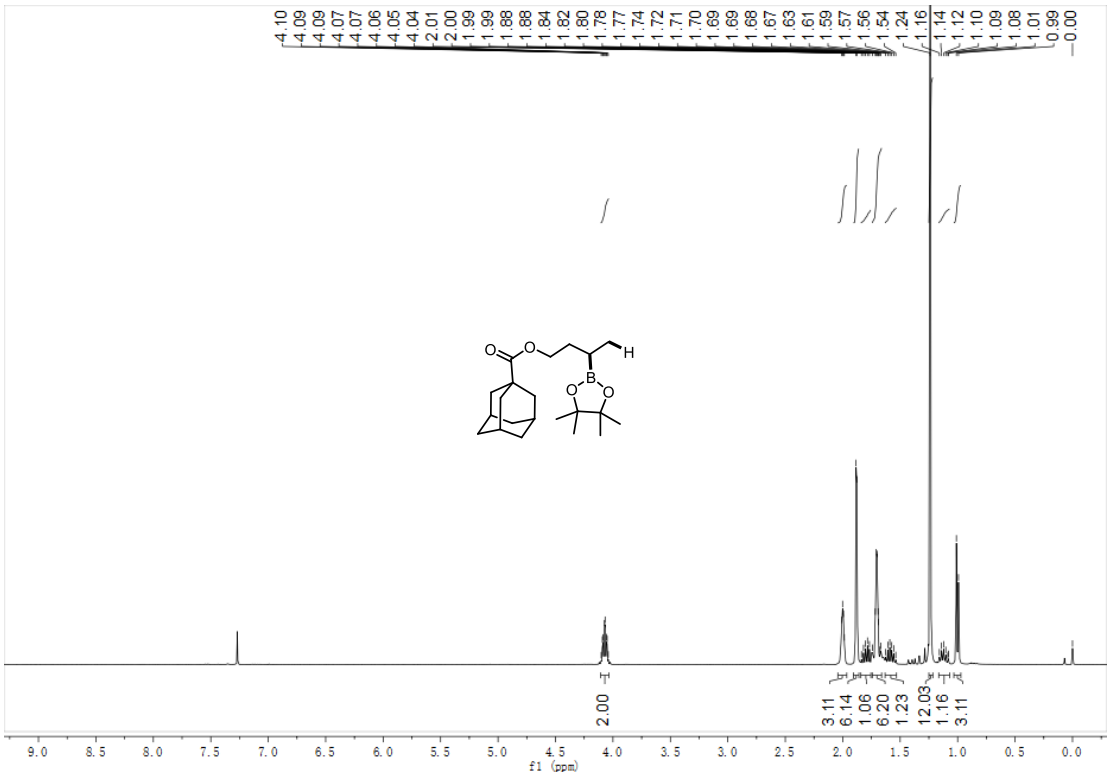
Compound **37** ^{1}H NMR (400 MHz, $CDCl_3$)



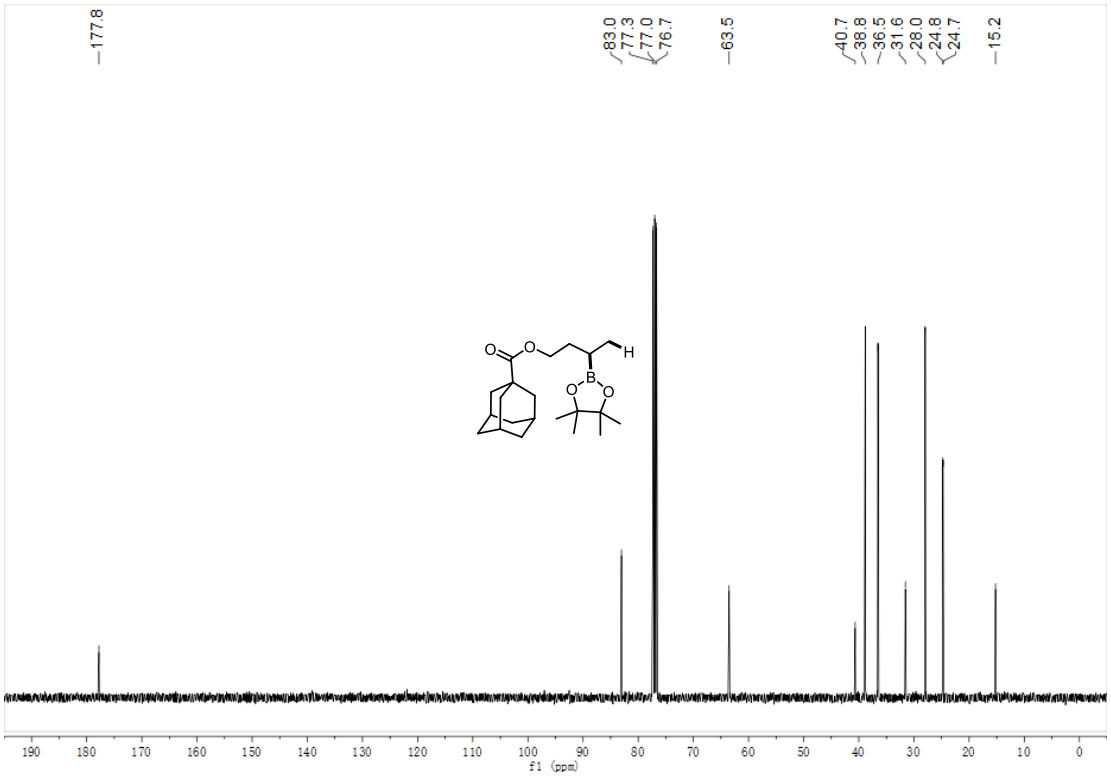
Compound **37** ^{13}C NMR (101 MHz, $CDCl_3$)



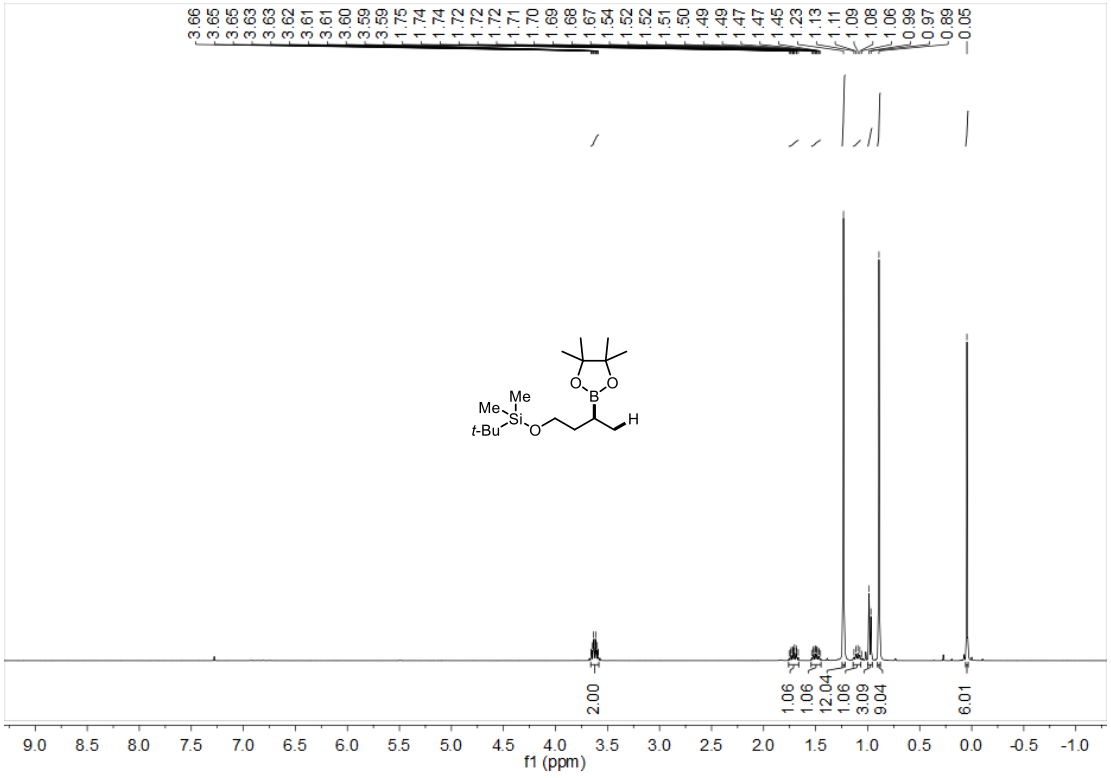
Compound **38** ^{1}H NMR (400 MHz, $CDCl_3$)



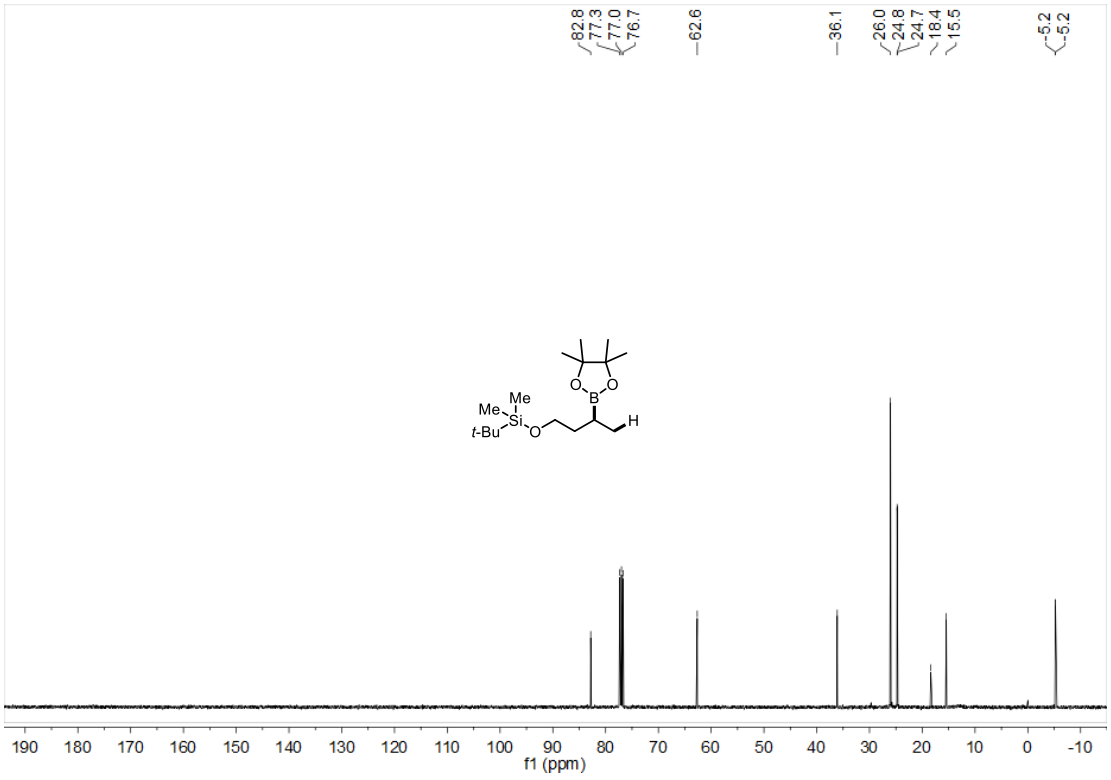
Compound **38** ^{13}C NMR (101 MHz, $CDCl_3$)



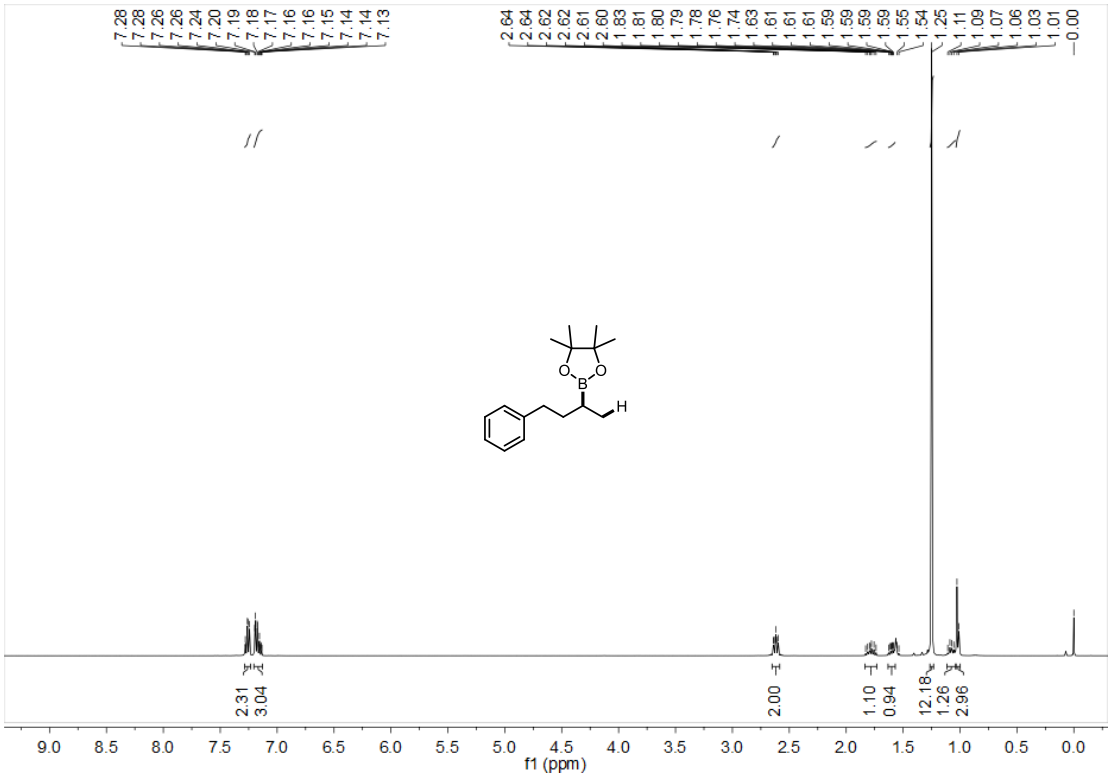
Compound **39** ^{1}H NMR (400 MHz, $CDCl_3$)



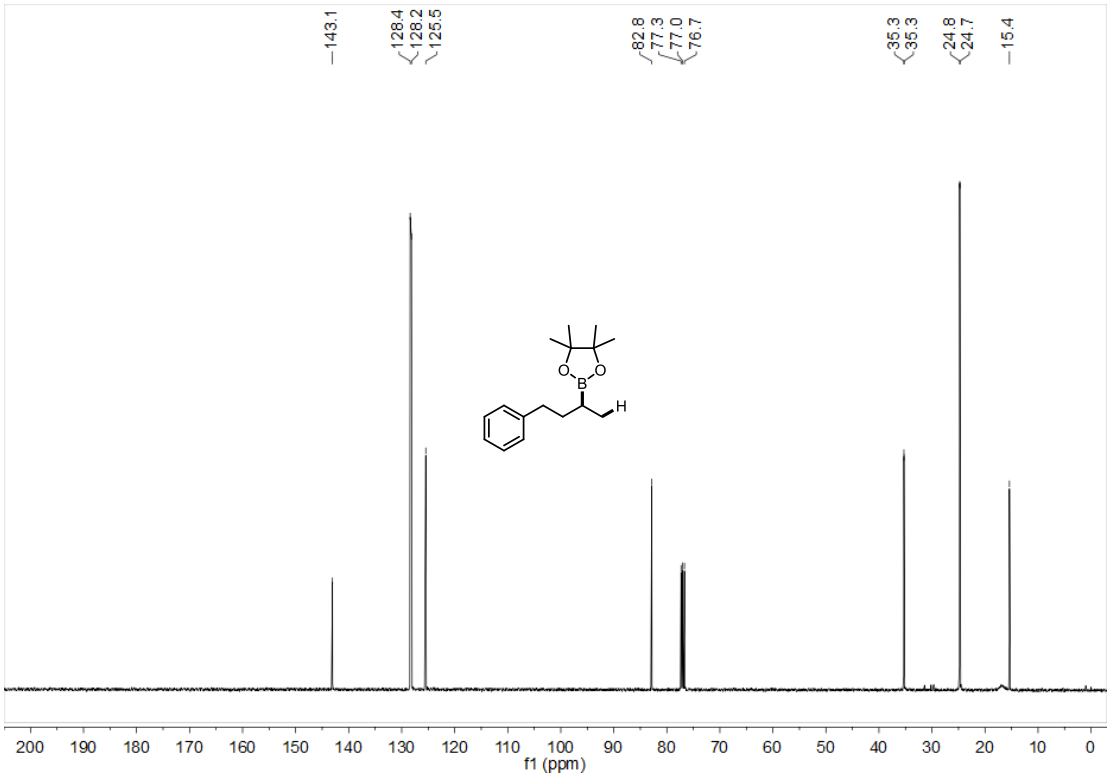
Compound **39** ^{13}C NMR (101 MHz, $CDCl_3$)



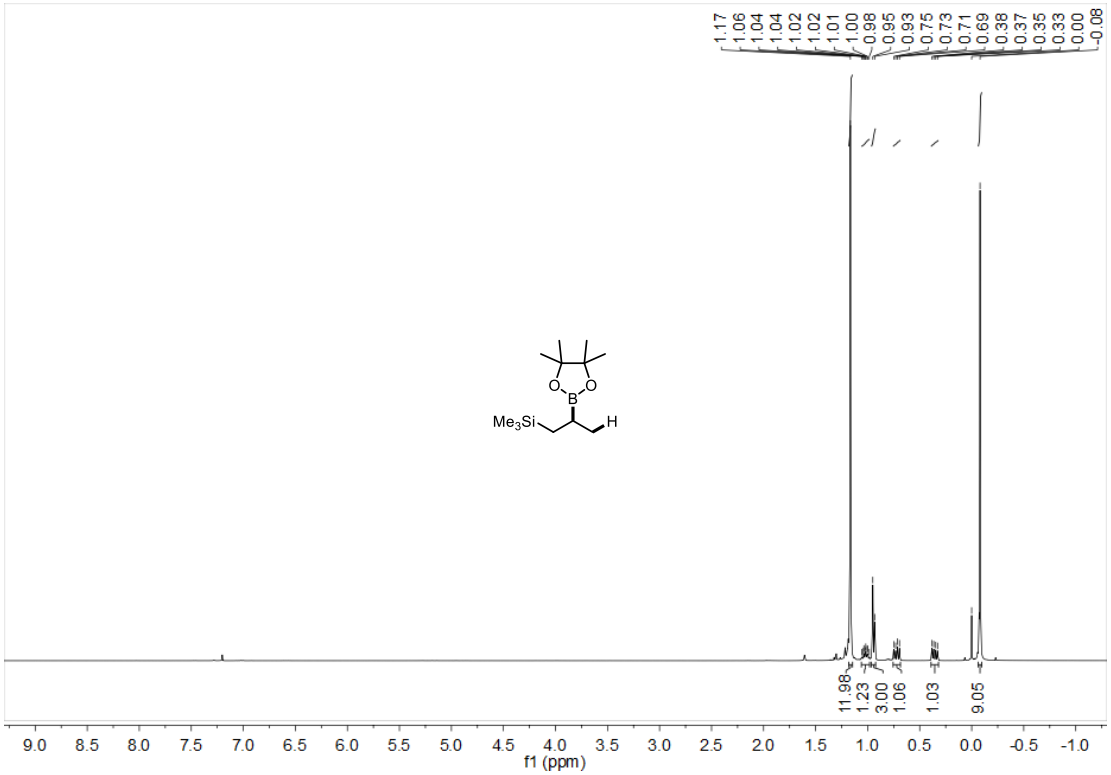
Compound **40** ^{1}H NMR (400 MHz, $CDCl_3$)



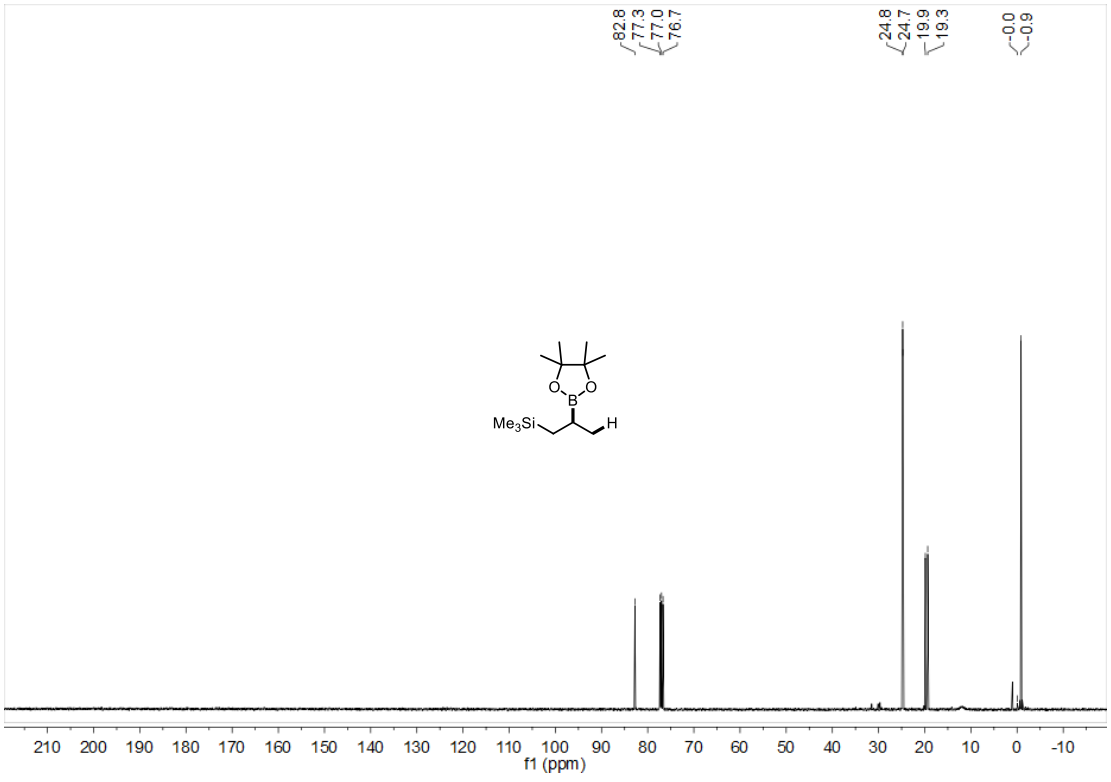
Compound **40** ^{13}C NMR (101 MHz, $CDCl_3$)



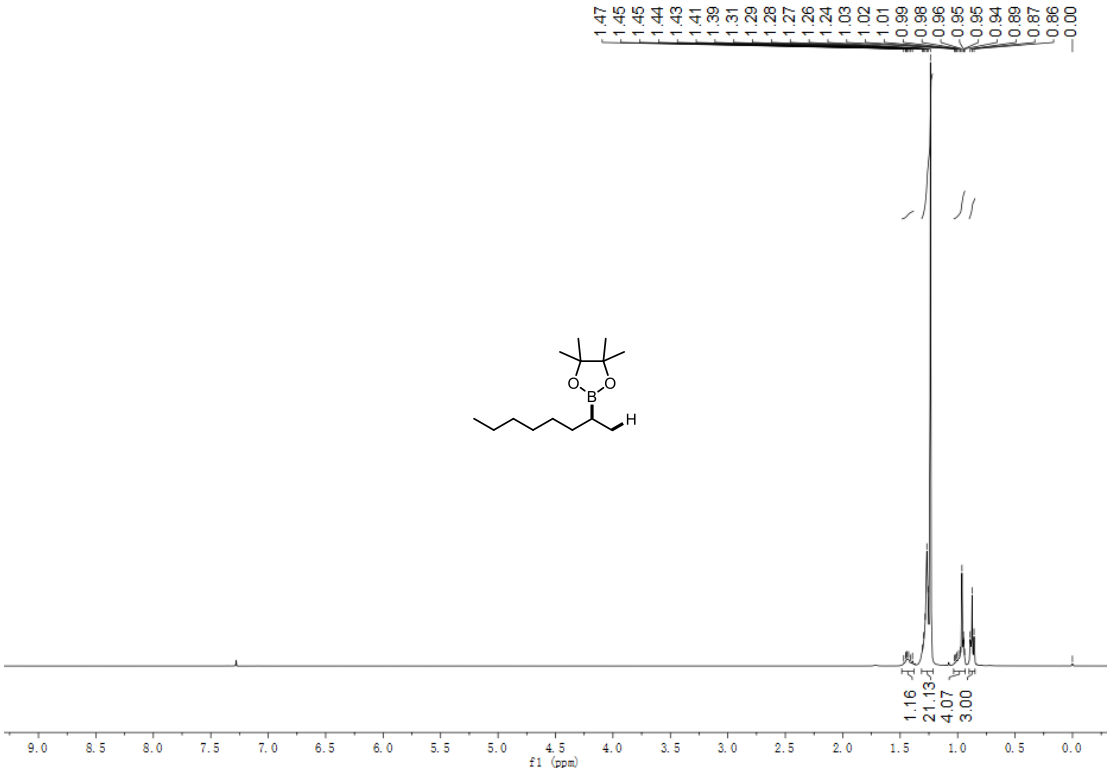
Compound **41** ^{1}H NMR (400 MHz, $CDCl_3$)



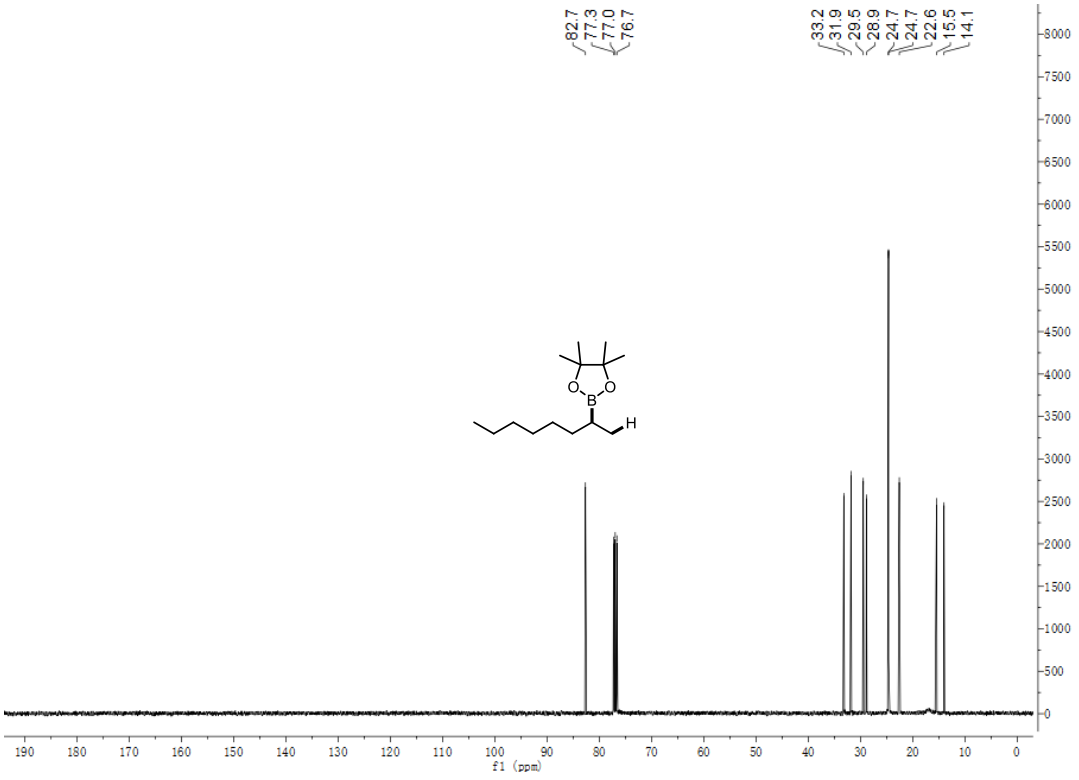
Compound **41** ^{13}C NMR (101 MHz, $CDCl_3$)



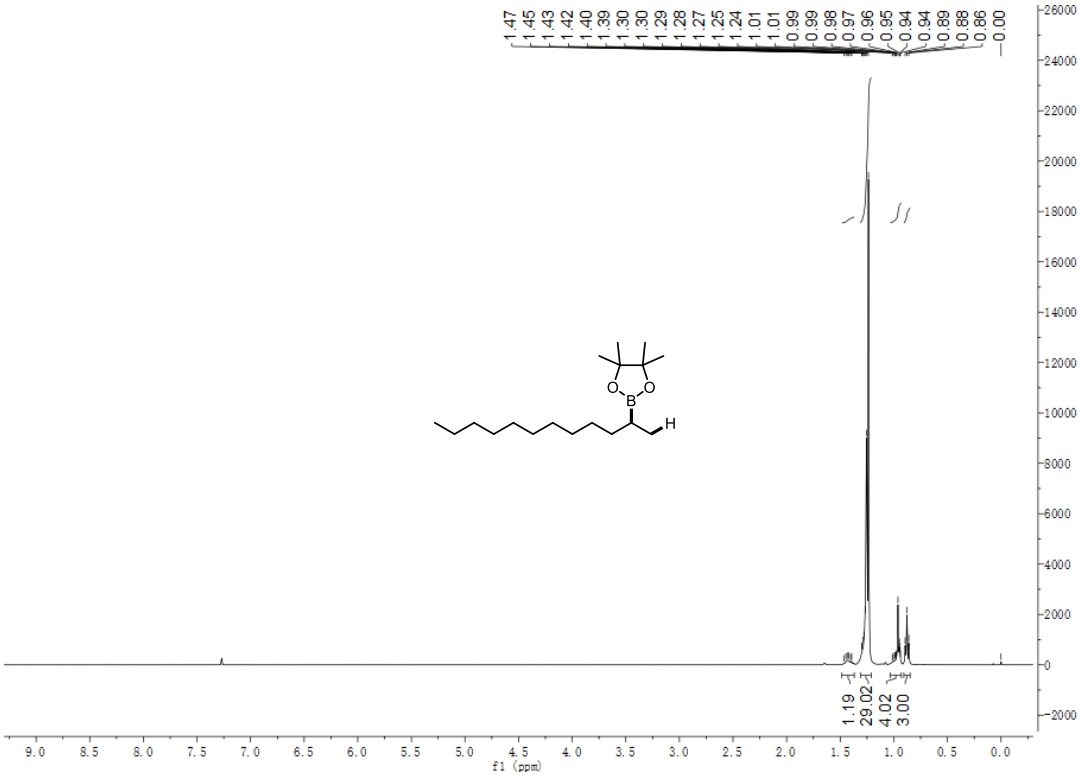
Compound **42** ^{1}H NMR (400 MHz, $CDCl_3$)



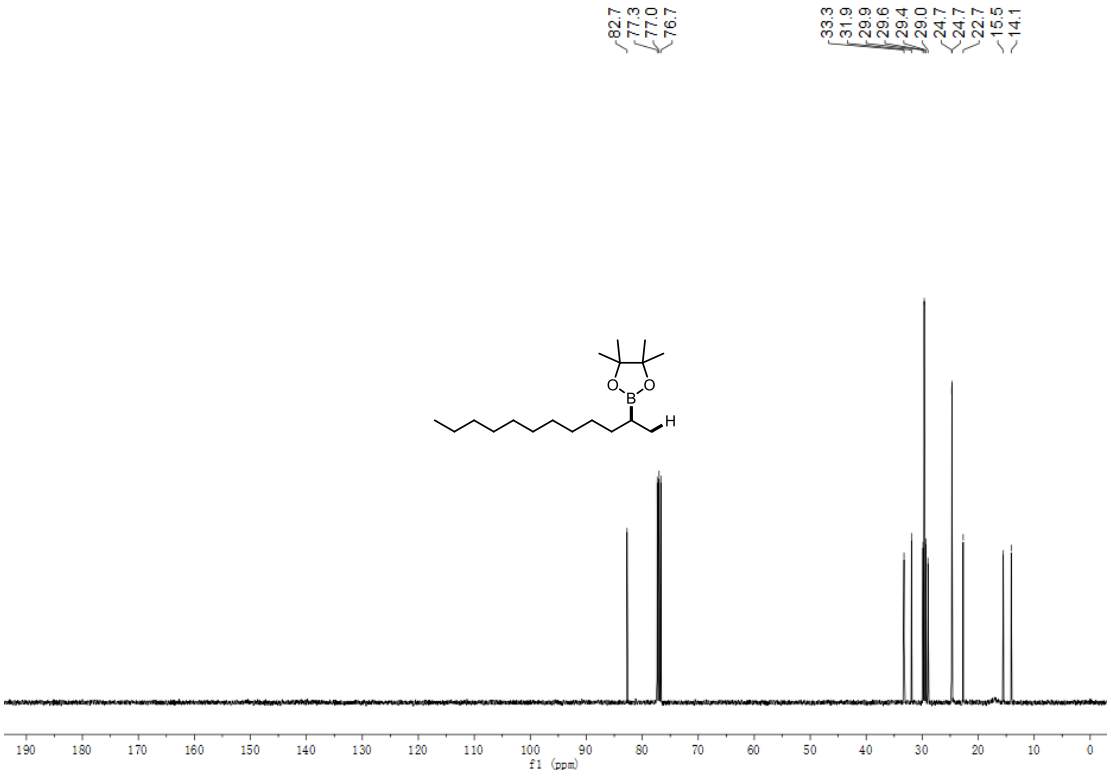
Compound **42** ^{13}C NMR (101 MHz, $CDCl_3$)



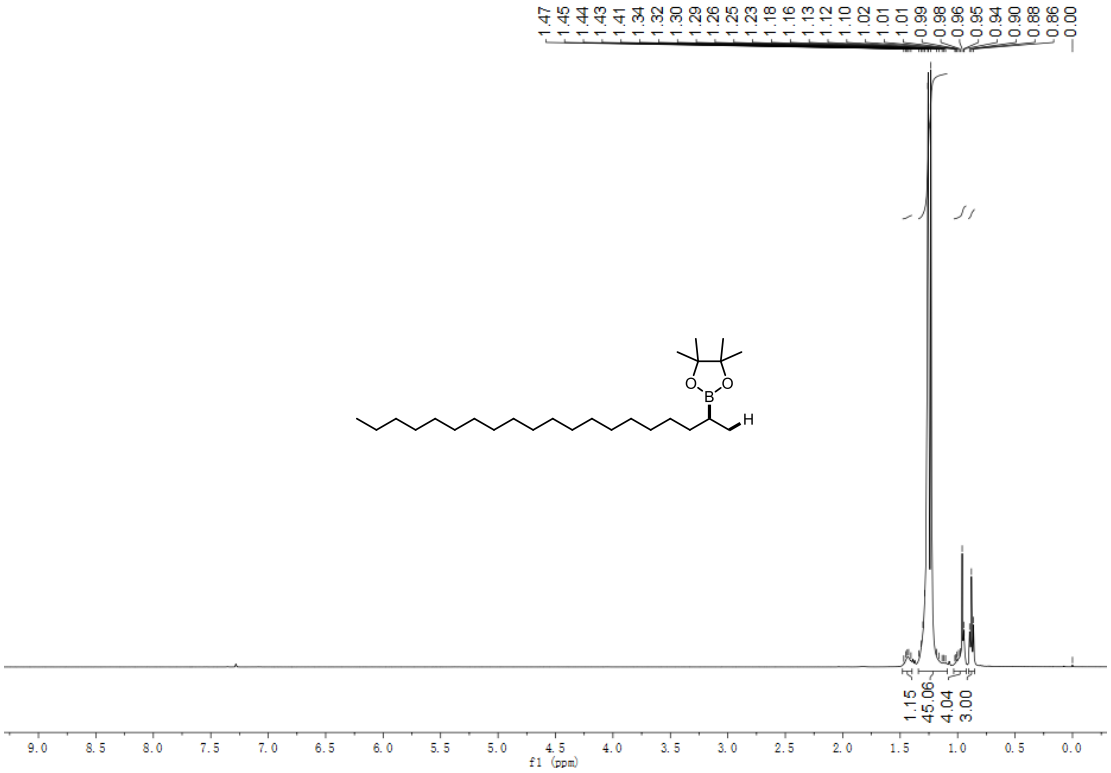
Compound **43** ^{1}H NMR (400 MHz, $CDCl_3$)



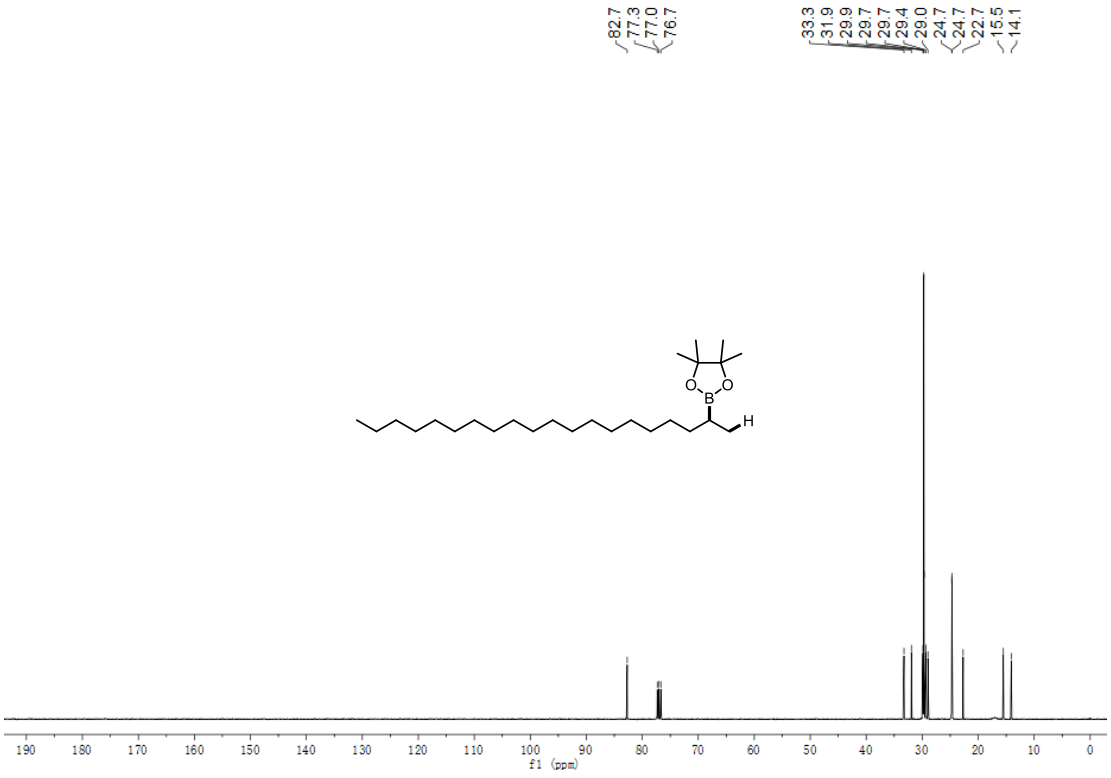
Compound **43** ^{13}C NMR (101 MHz, $CDCl_3$)



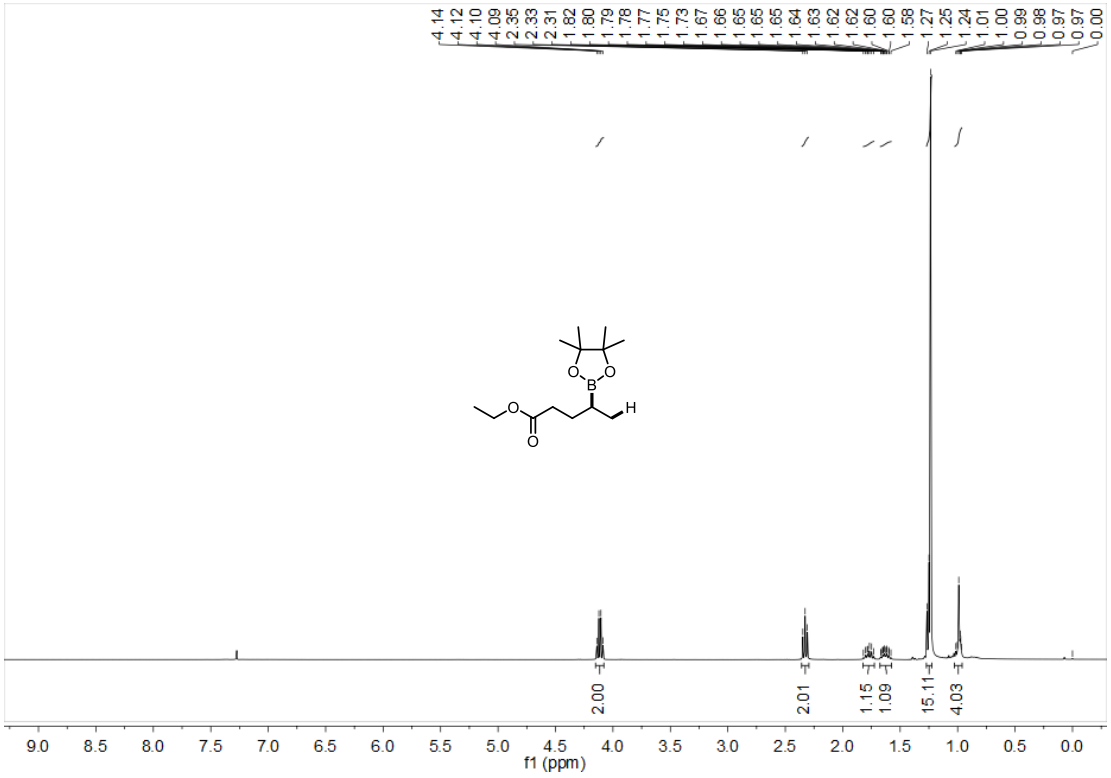
Compound **44** ^{1}H NMR (400 MHz, $CDCl_3$)



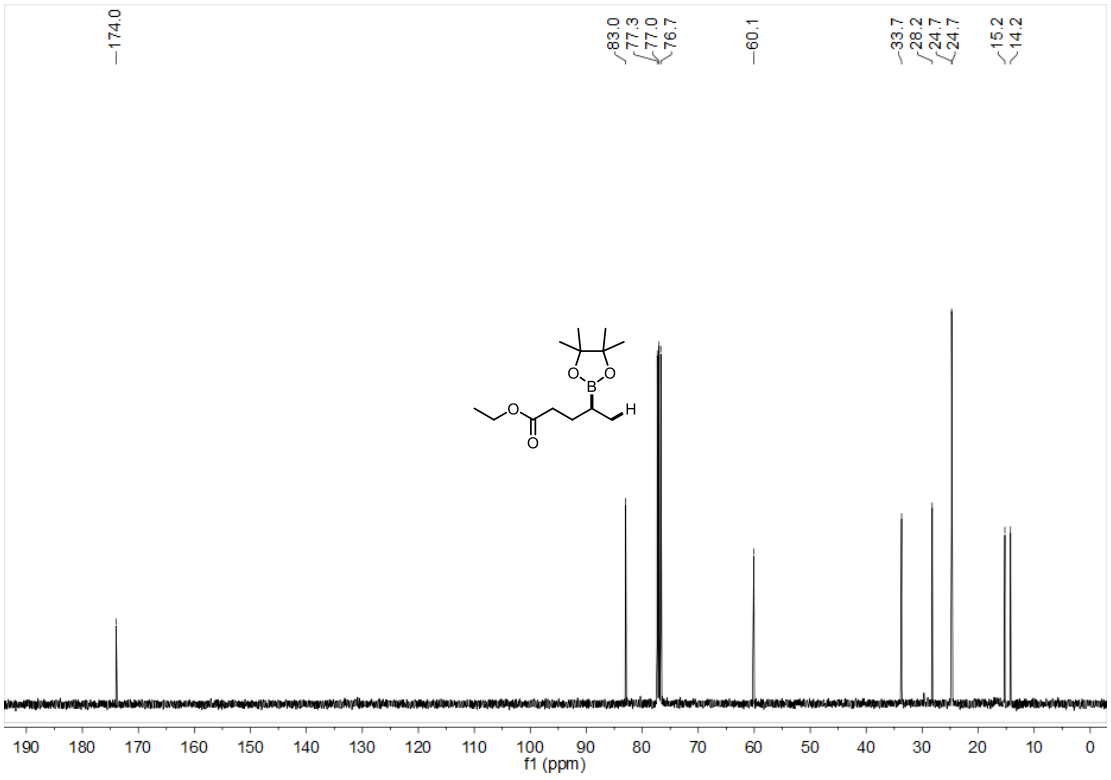
Compound **44** ^{13}C NMR (101 MHz, $CDCl_3$)



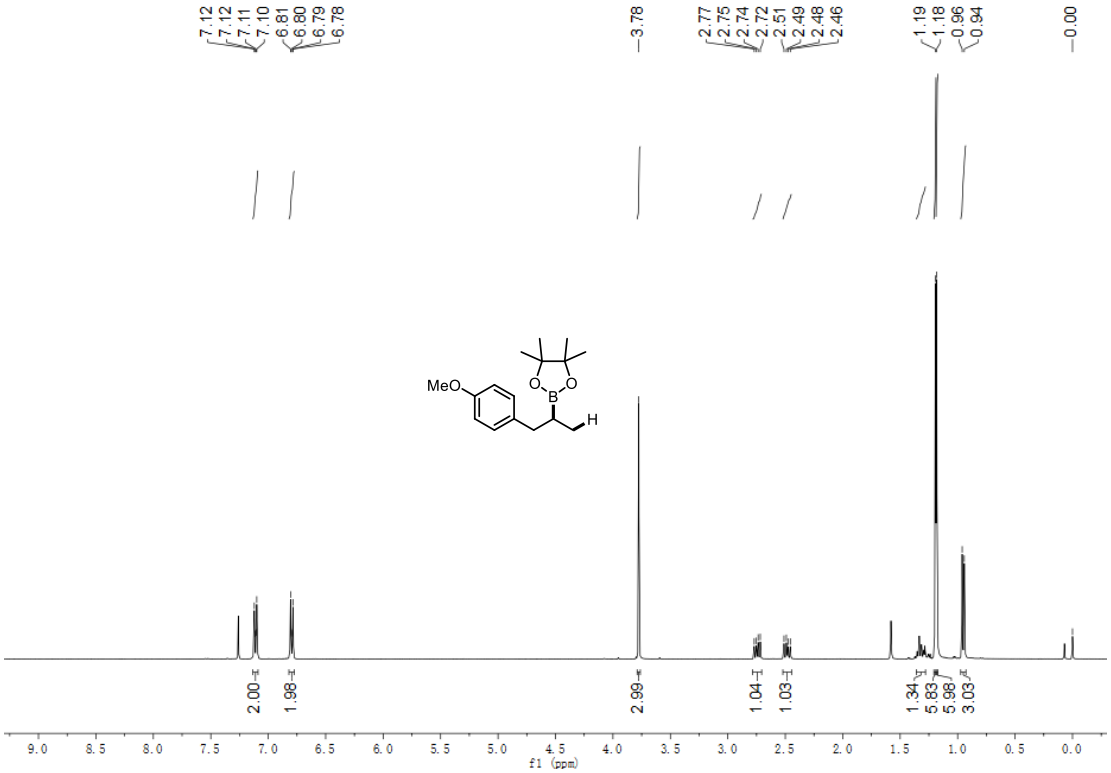
Compound **45** ^{1}H NMR (400 MHz, $CDCl_3$)



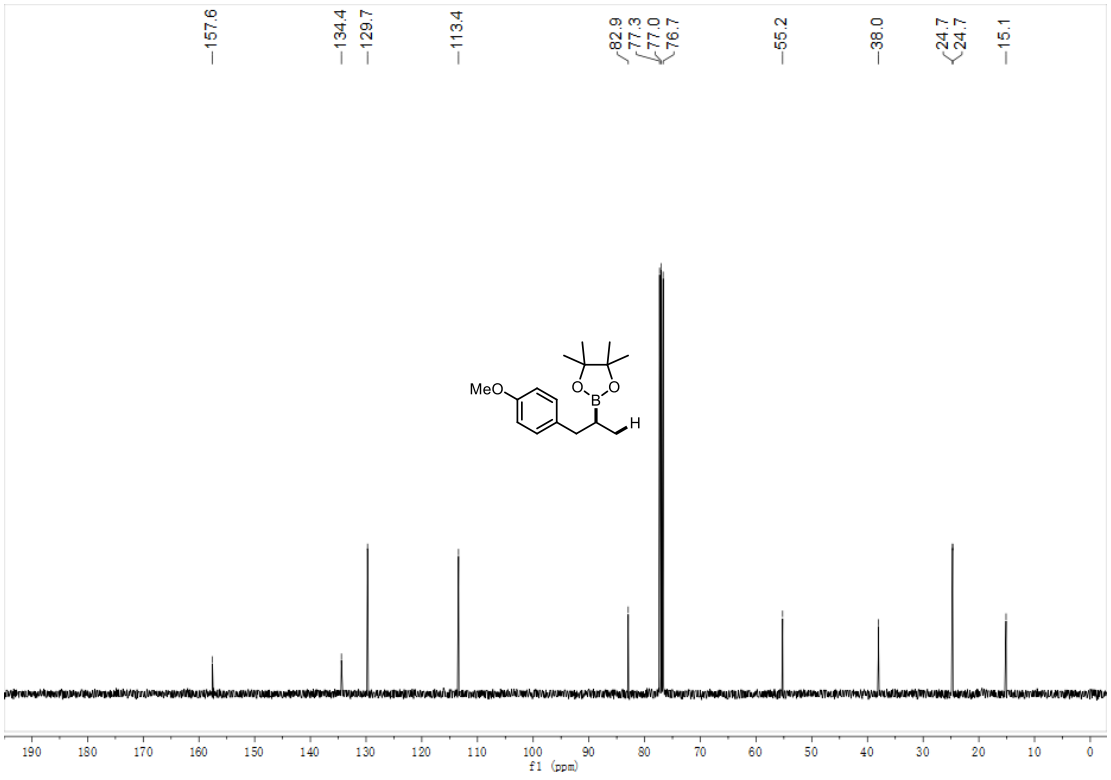
Compound **45** ^{13}C NMR (101 MHz, $CDCl_3$)



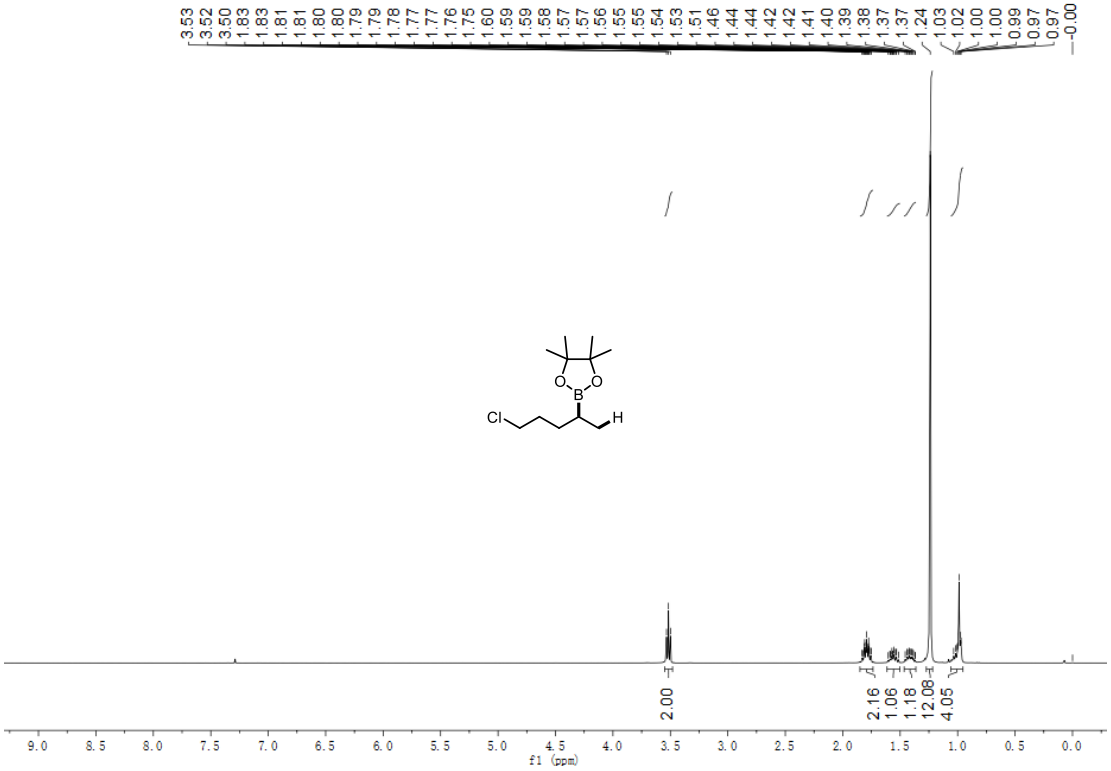
Compound **46** ^{1}H NMR (400 MHz, $CDCl_3$)



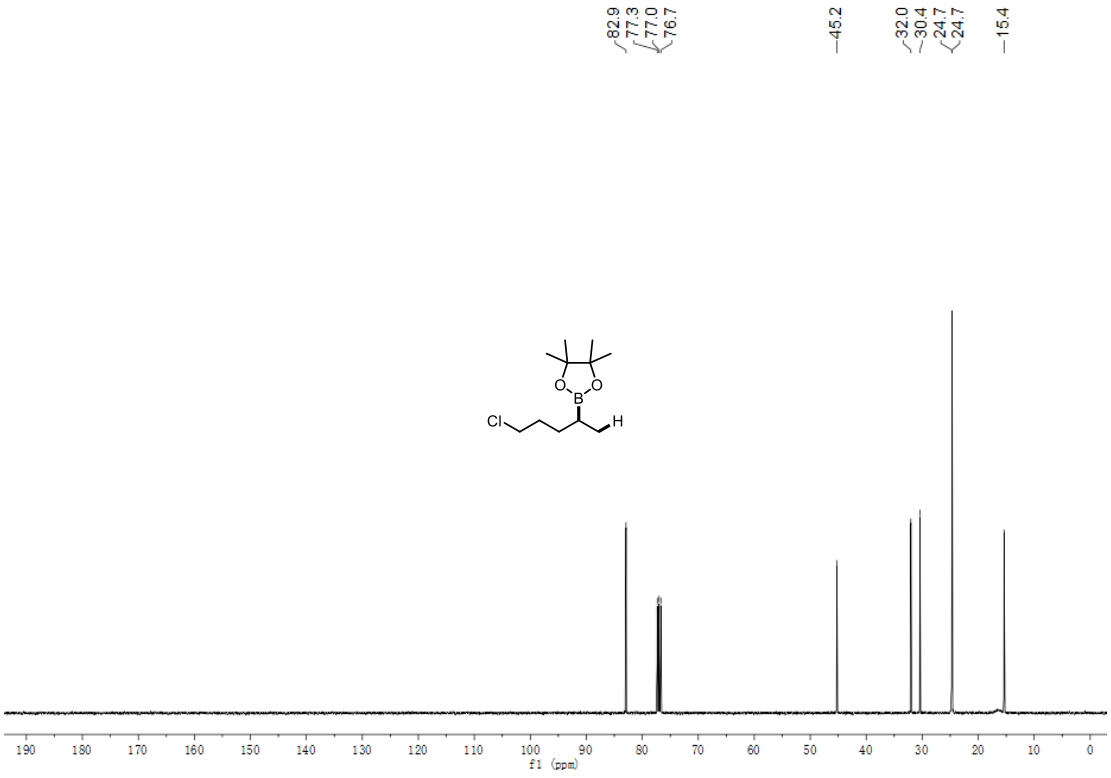
Compound **46** ^{13}C NMR (101 MHz, $CDCl_3$)



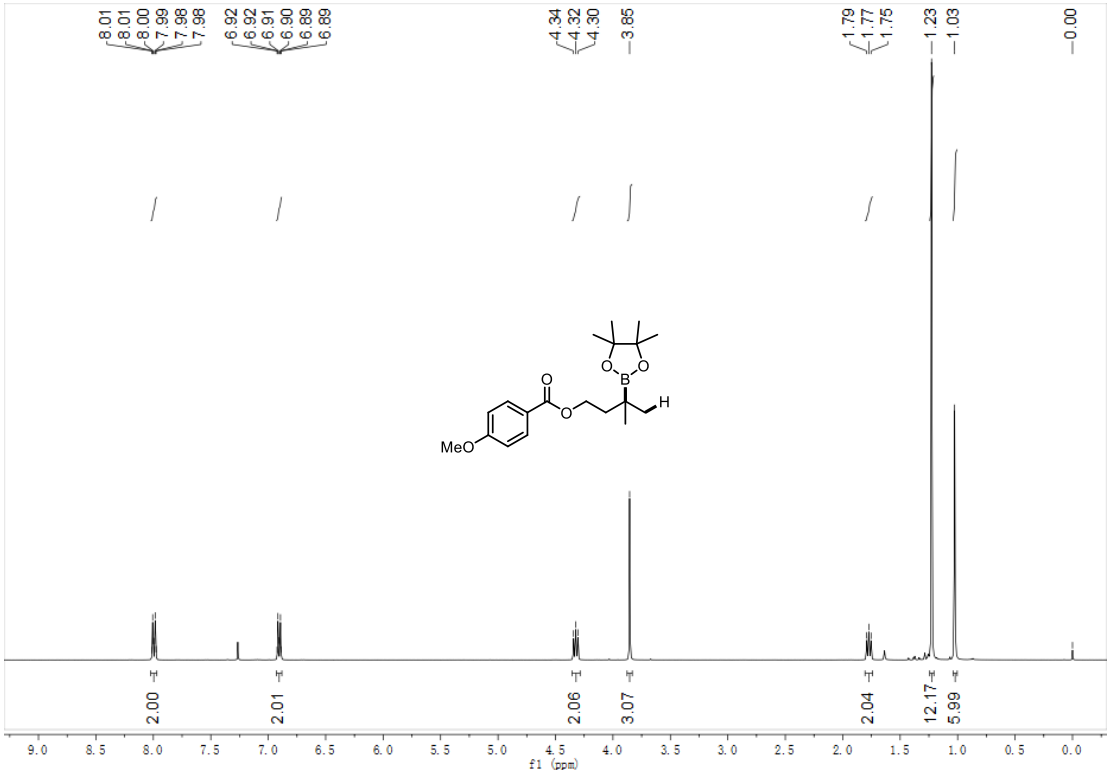
Compound **47** ^{1}H NMR (400 MHz, $CDCl_3$)



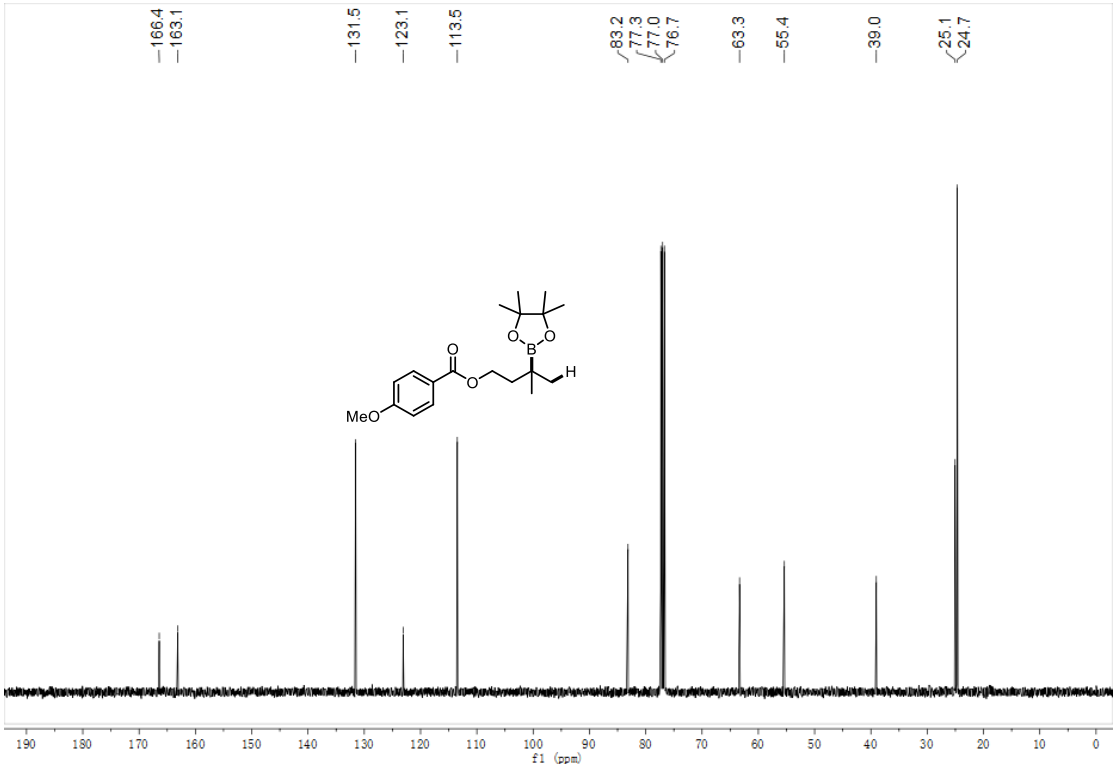
Compound **47** ^{13}C NMR (101 MHz, $CDCl_3$)



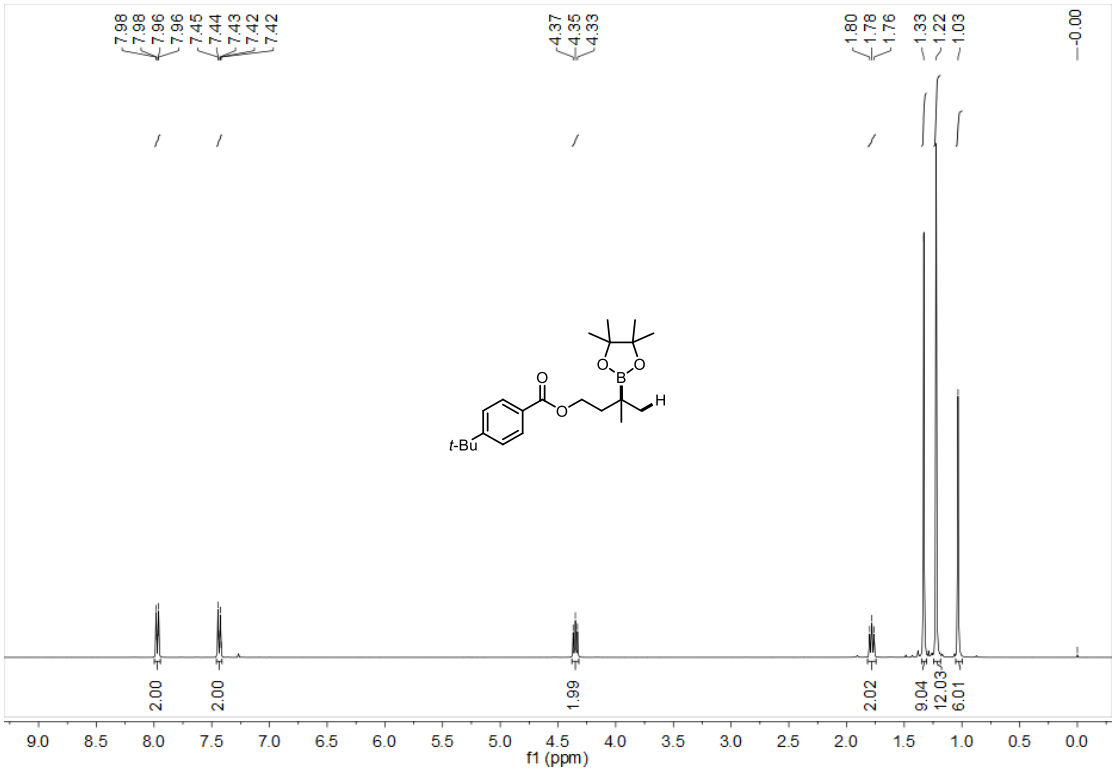
Compound **48** ^{1}H NMR (400 MHz, $CDCl_3$)



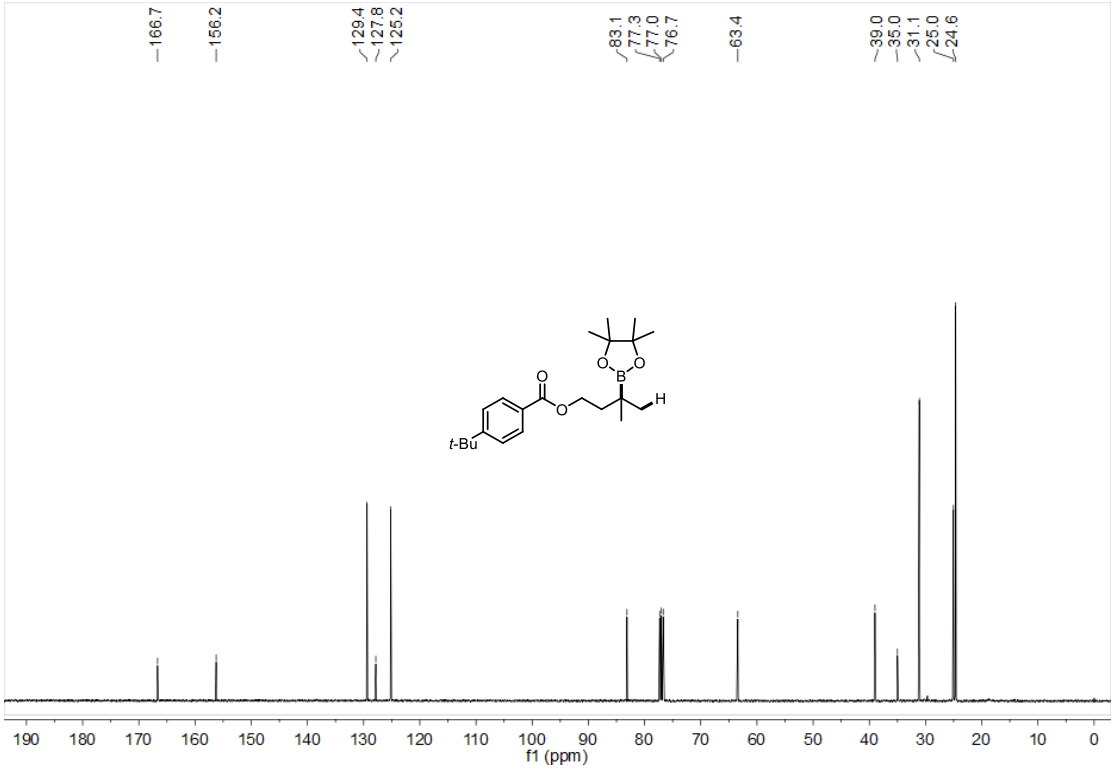
Compound **48** ^{13}C NMR (101 MHz, $CDCl_3$)



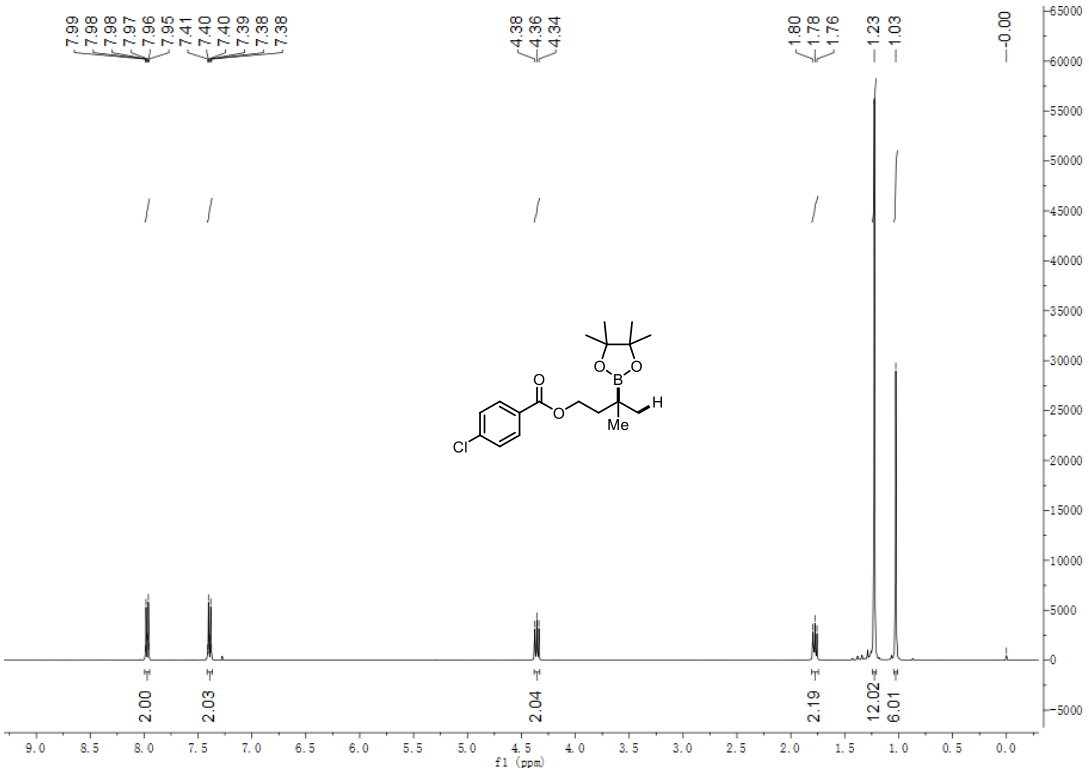
Compound **49** ^{1}H NMR (400 MHz, $CDCl_3$)



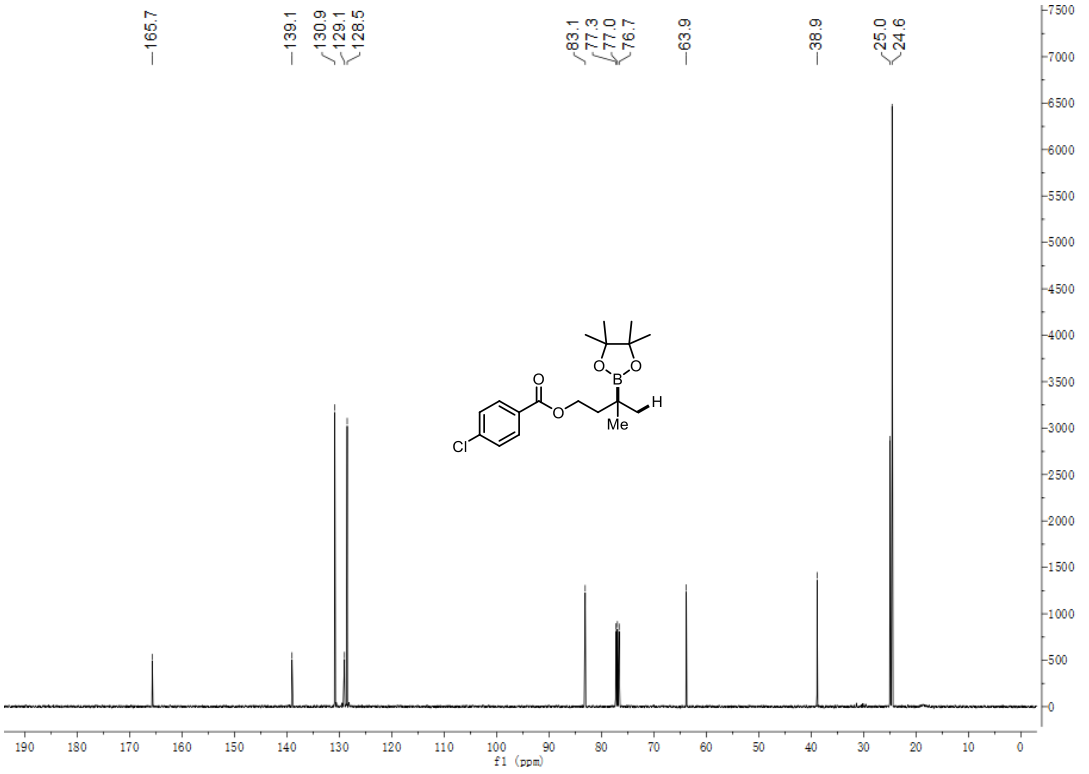
Compound **49** ^{13}C NMR (101 MHz, $CDCl_3$)



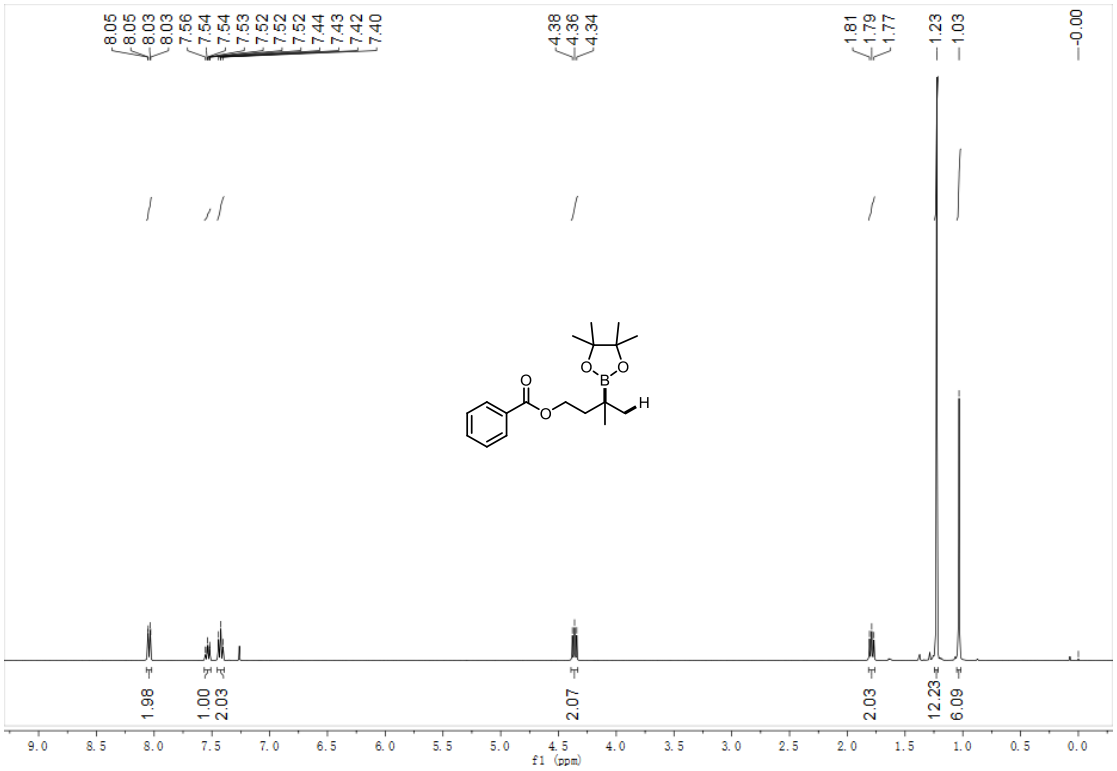
Compound **50** ^{1}H NMR (400 MHz, $CDCl_3$)



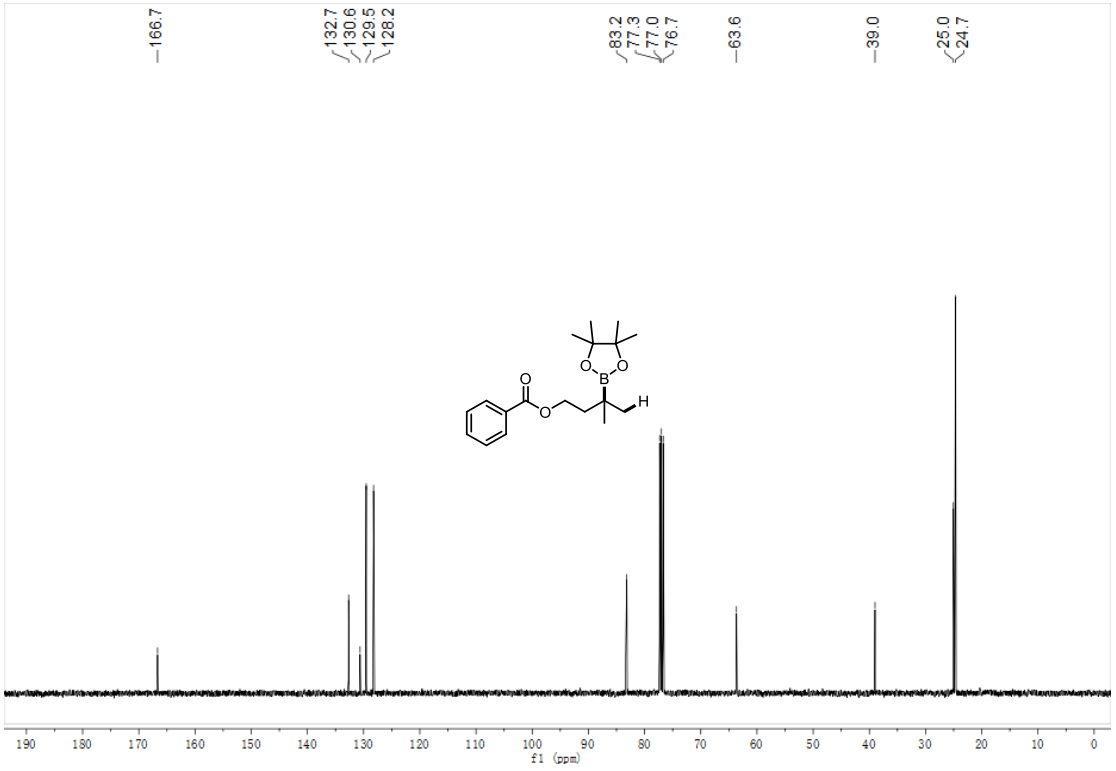
Compound **50** ^{13}C NMR (101 MHz, $CDCl_3$)



Compound **51** ^{1}H NMR (400 MHz, $CDCl_3$)

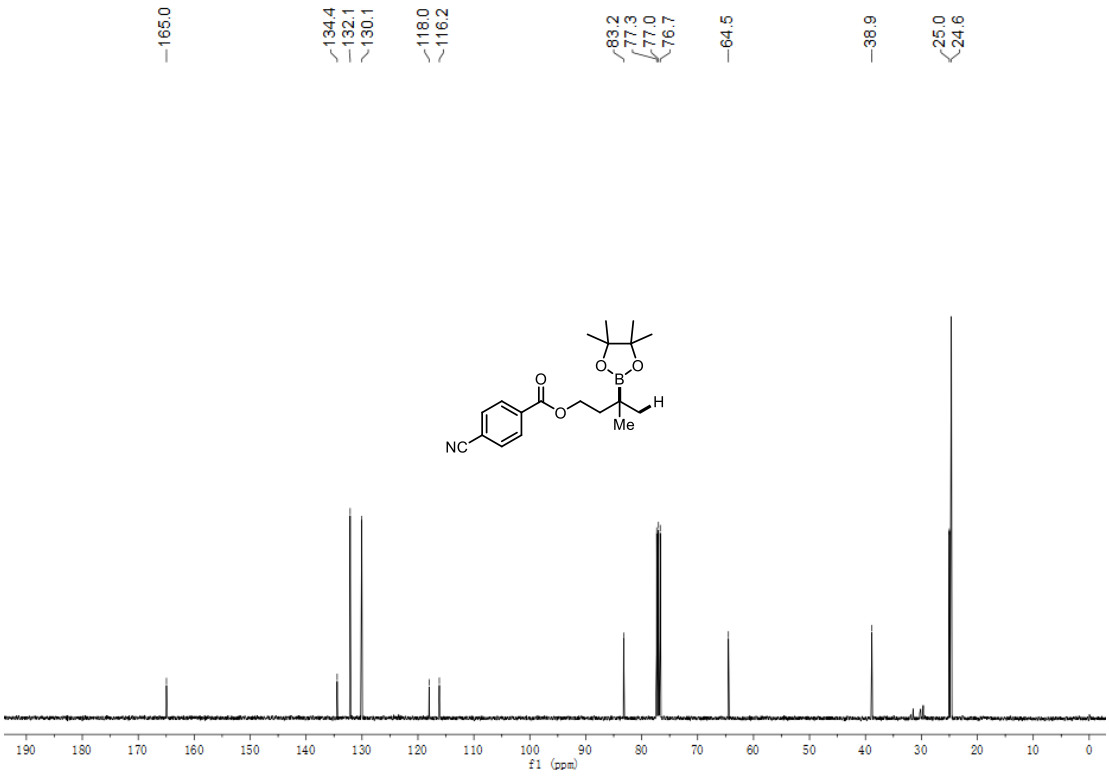


Compound **51** ^{13}C NMR (101 MHz, $CDCl_3$)

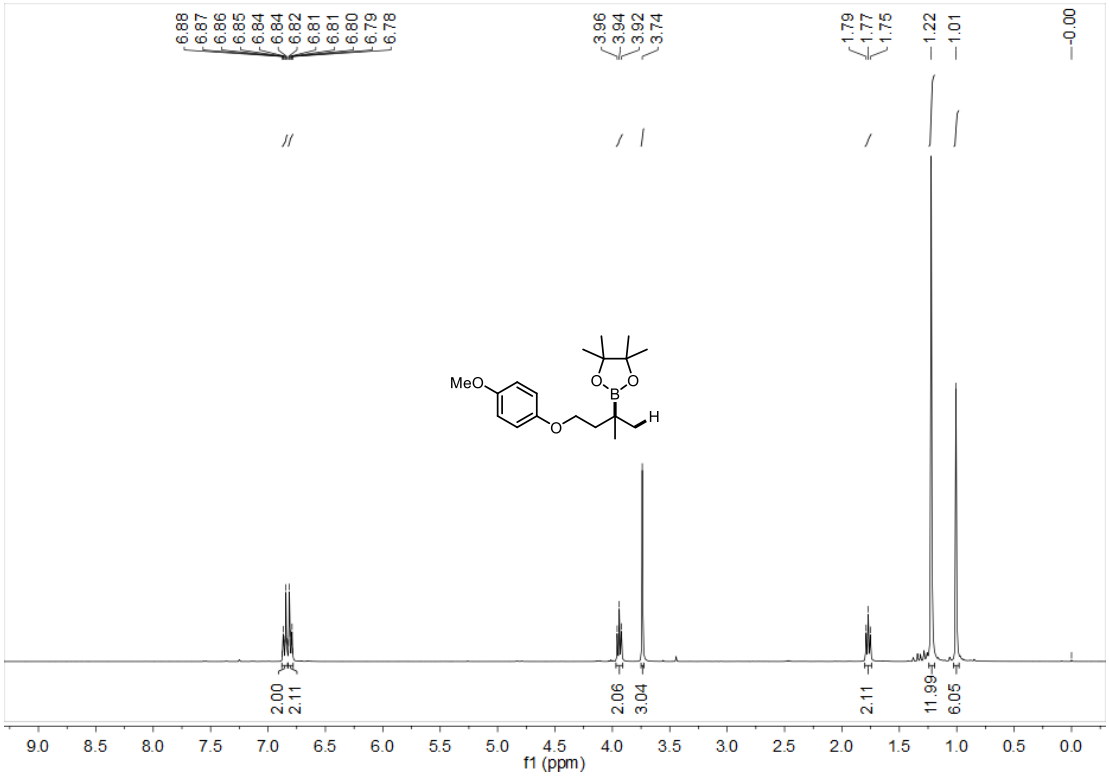


Compound **52** ^{1}H NMR (400 MHz, $CDCl_3$)

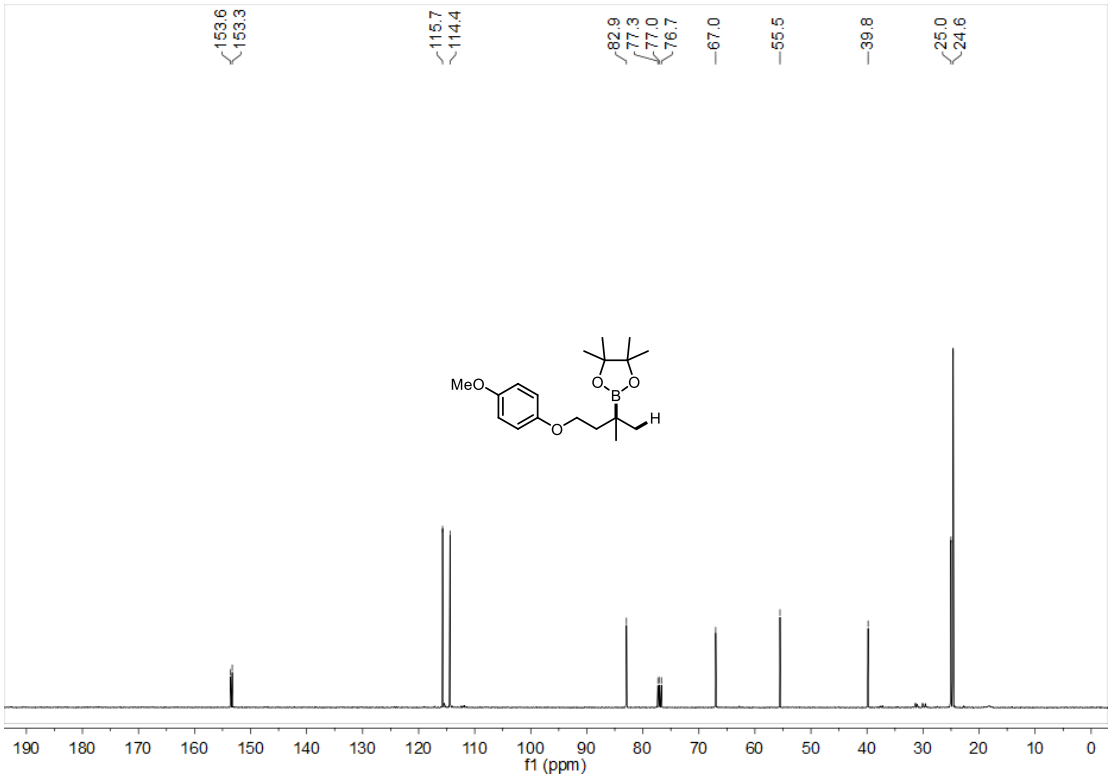
Compound **52** ^{13}C NMR (101 MHz, $CDCl_3$)



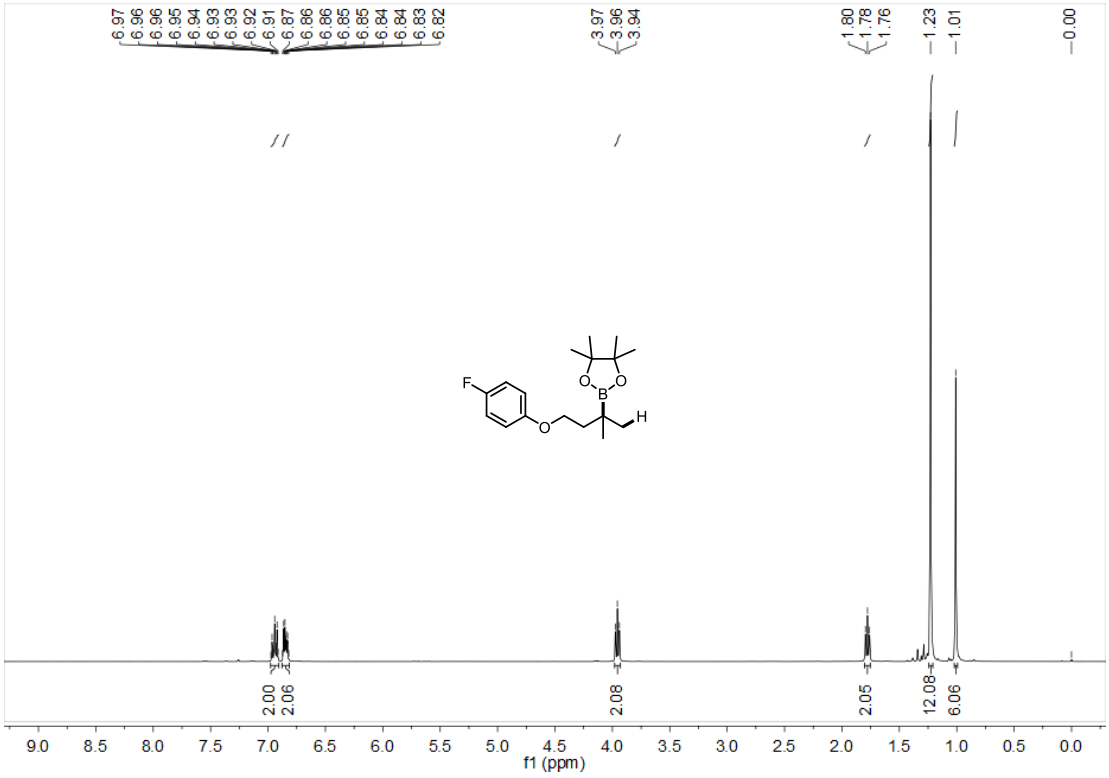
Compound **53** ^{1}H NMR (400 MHz, $CDCl_3$)



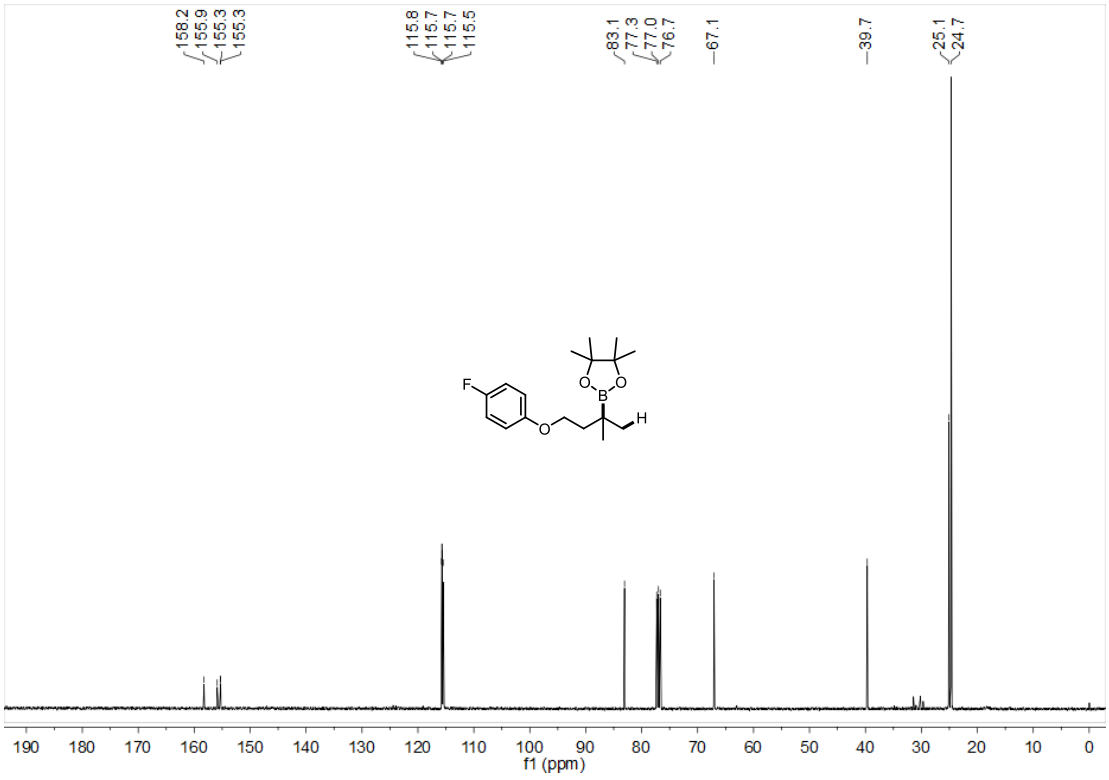
Compound **53** ^{13}C NMR (101 MHz, $CDCl_3$)



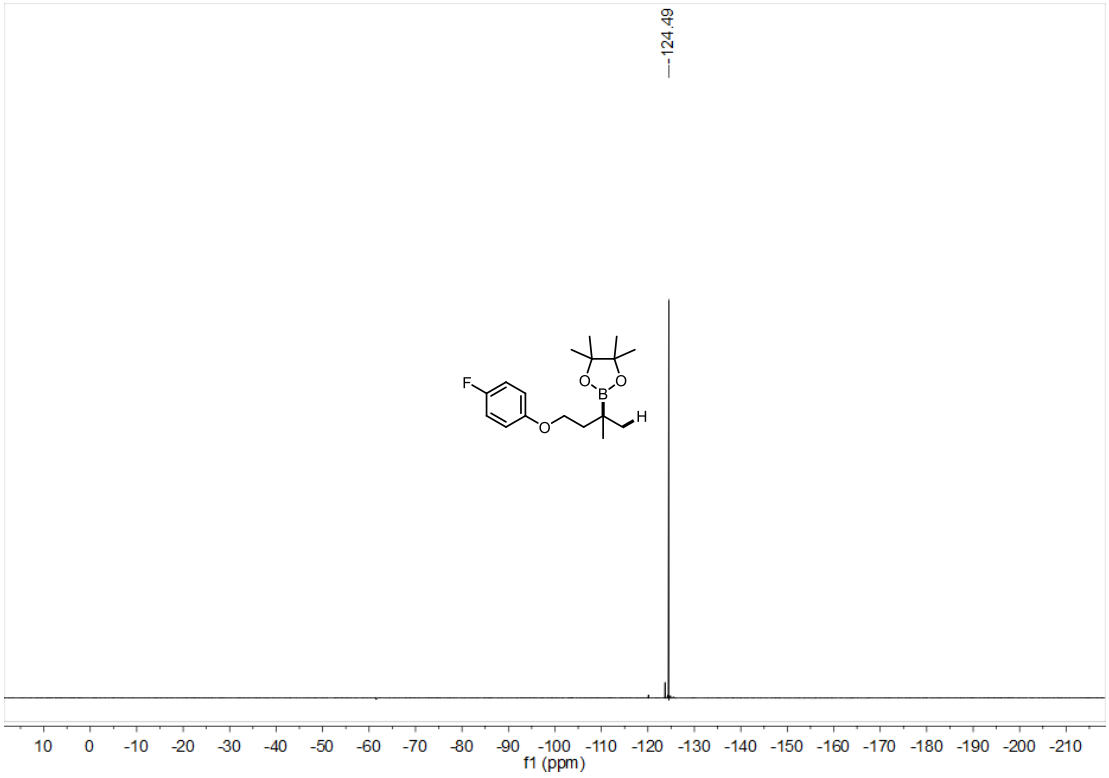
Compound **54** ^{1}H NMR (400 MHz, $CDCl_3$)



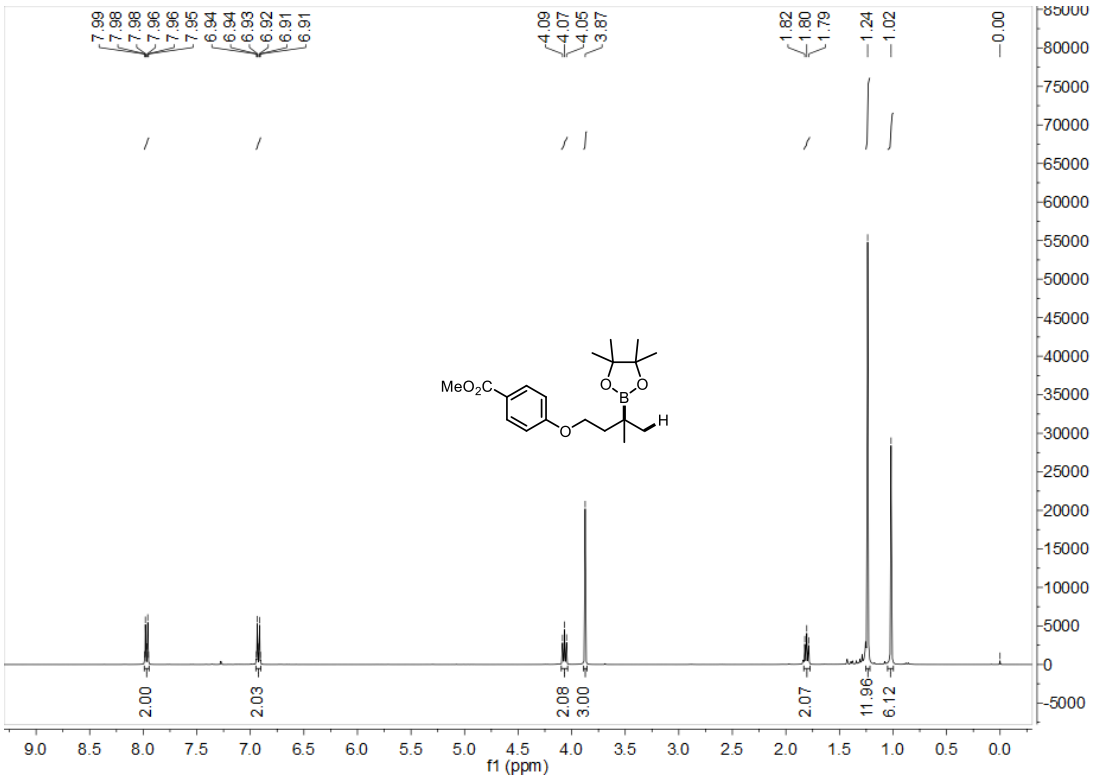
Compound **54** ^{13}C NMR (101 MHz, $CDCl_3$)



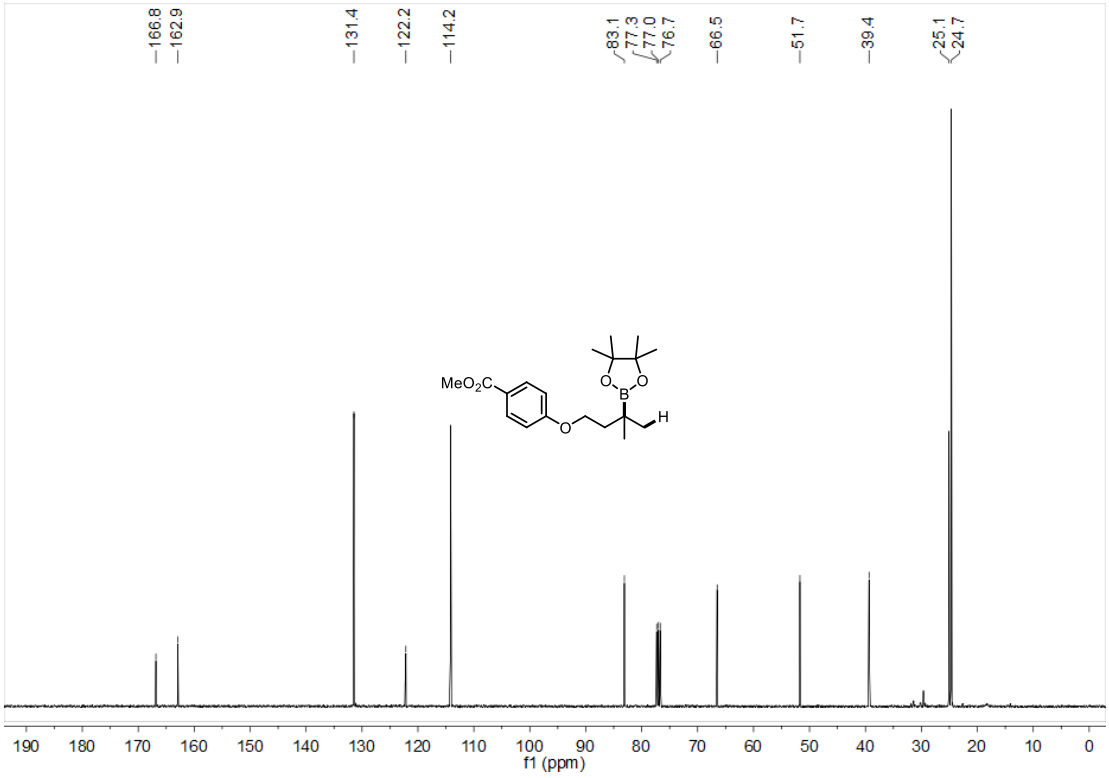
Compound **54** ^{19}F NMR (376 MHz, $CDCl_3$)



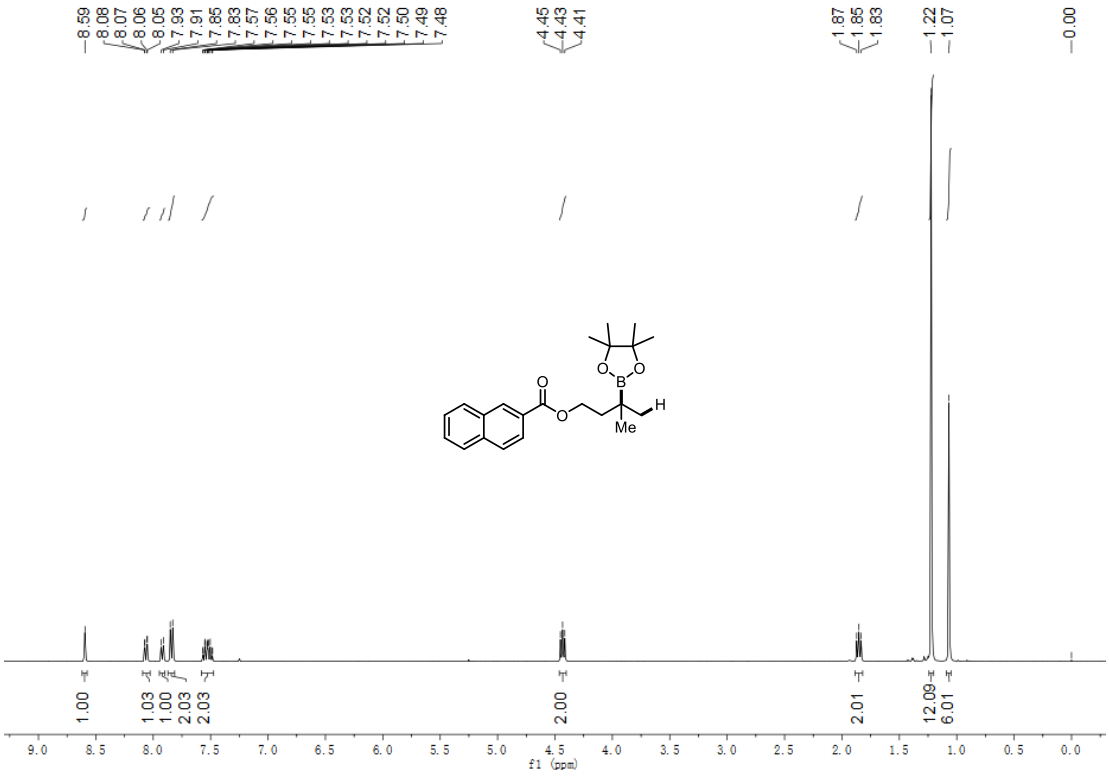
Compound **55** ^{1}H NMR (400 MHz, $CDCl_3$)



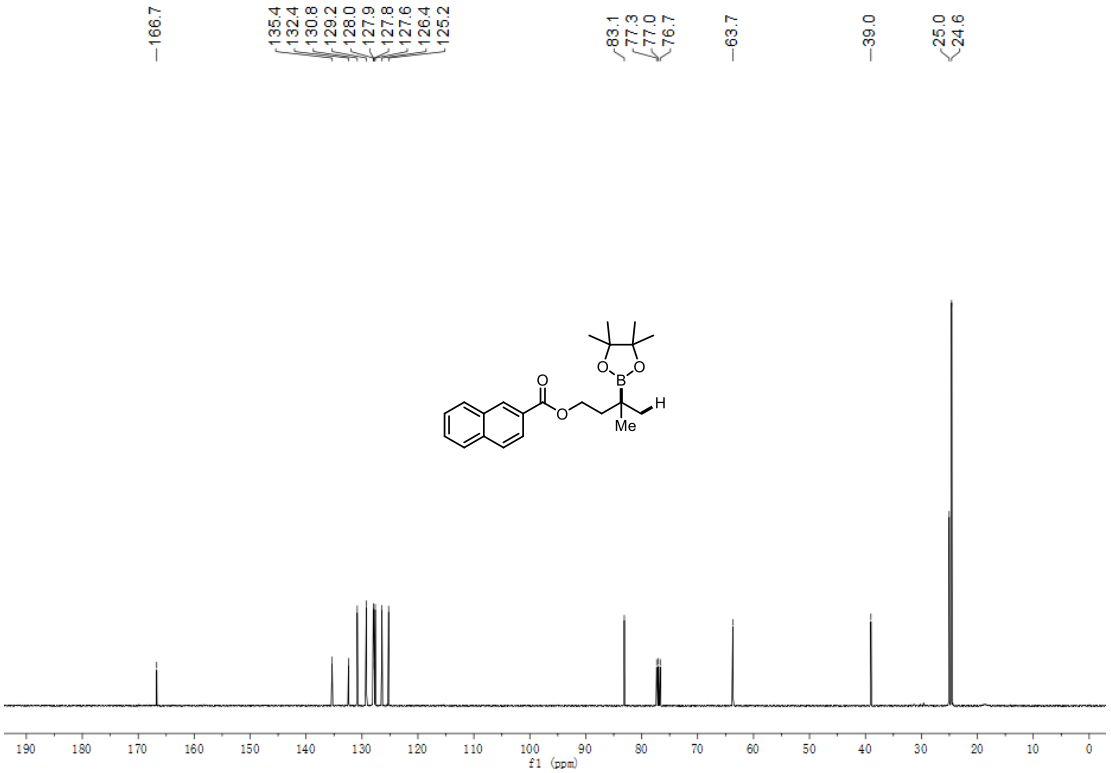
Compound **55** ^{13}C NMR (101 MHz, $CDCl_3$)



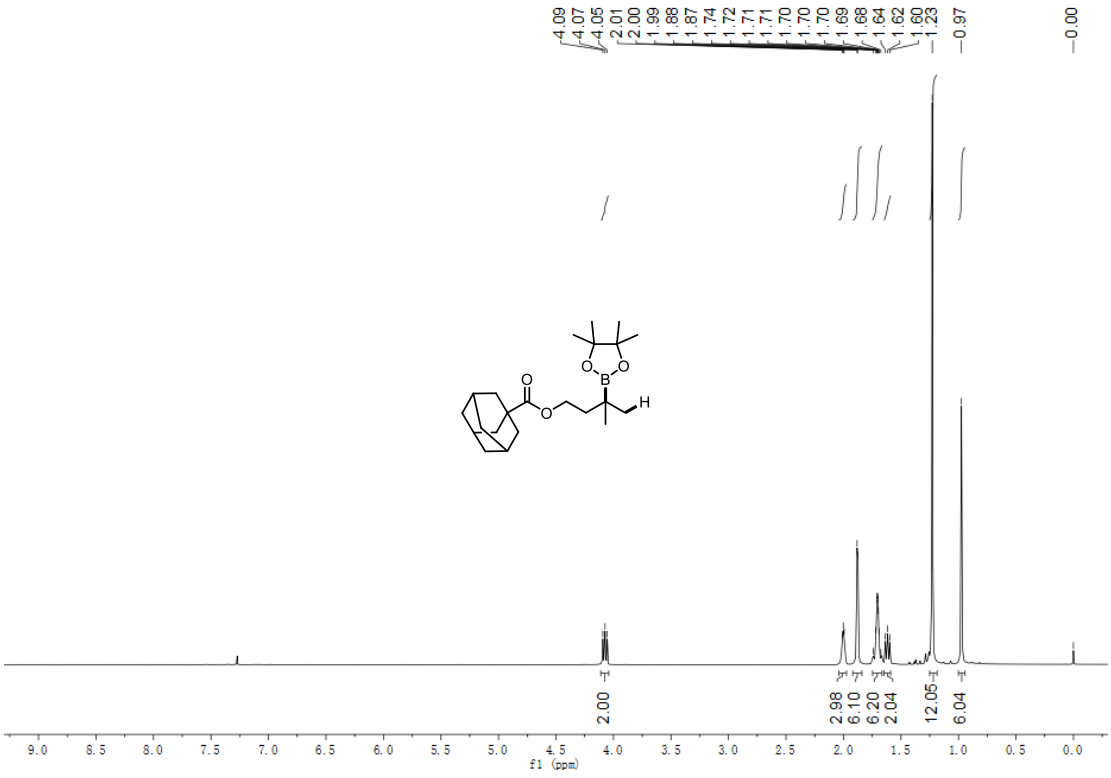
Compound **56** ^{1}H NMR (400 MHz, $CDCl_3$)



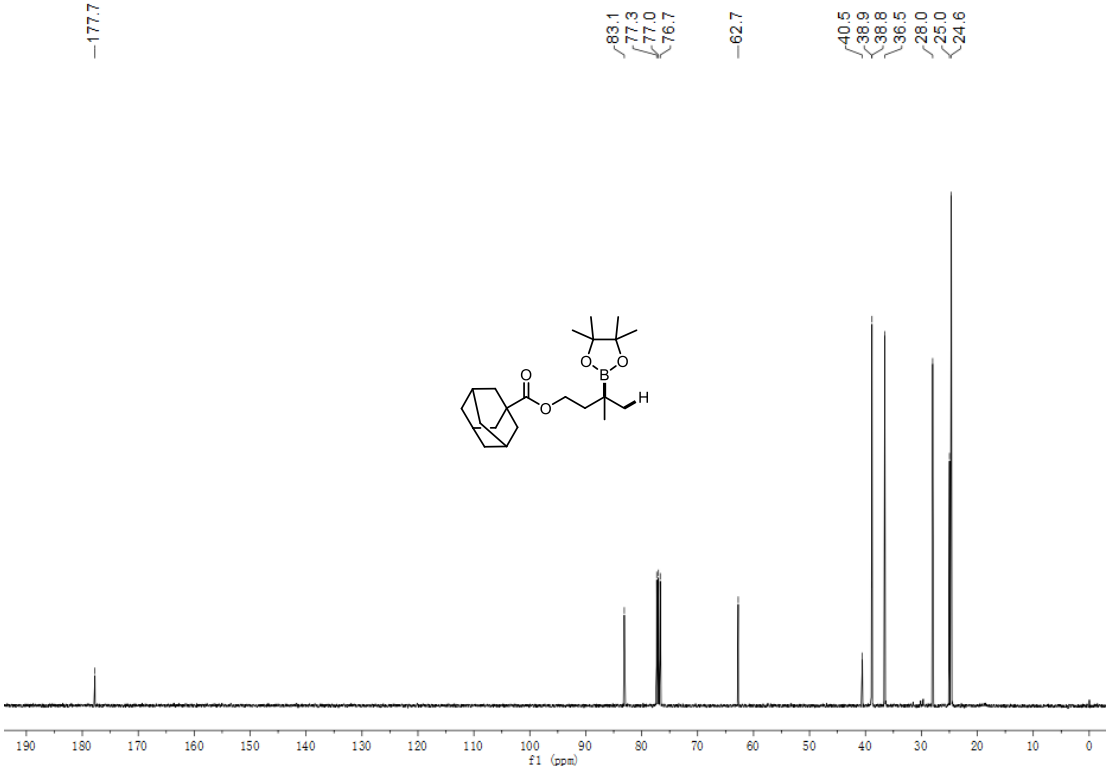
Compound **56** ^{13}C NMR (101 MHz, $CDCl_3$)



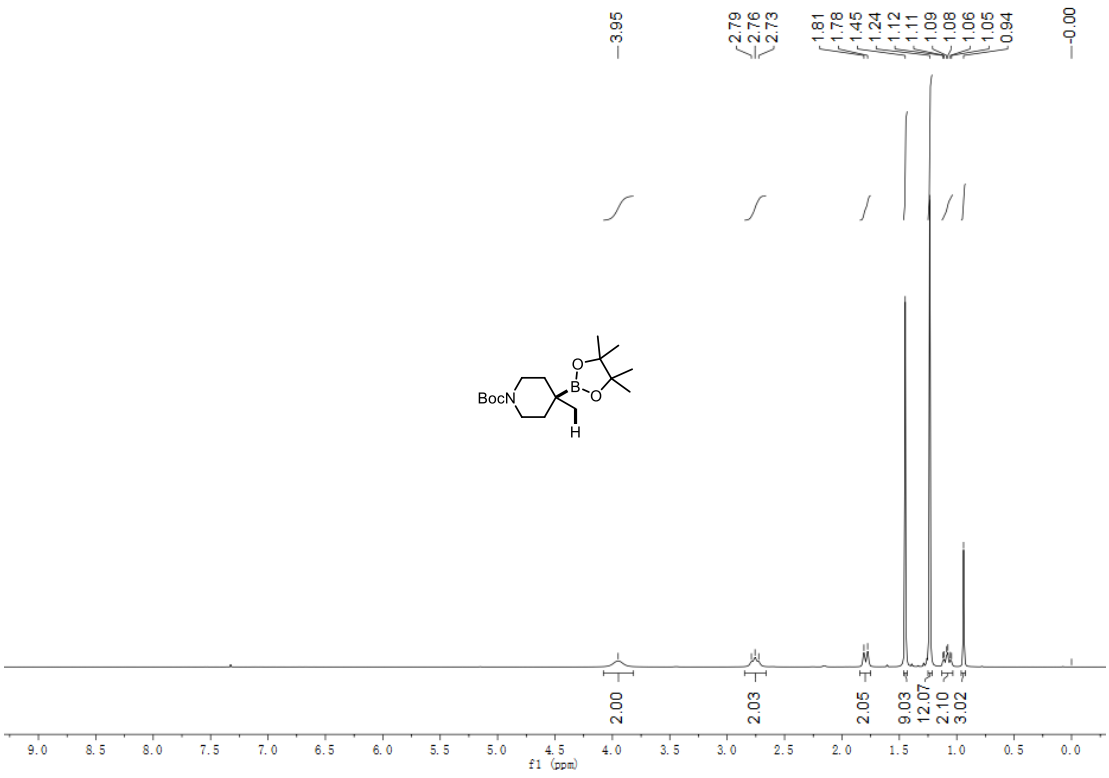
Compound **57** ^{1}H NMR (400 MHz, $CDCl_3$)



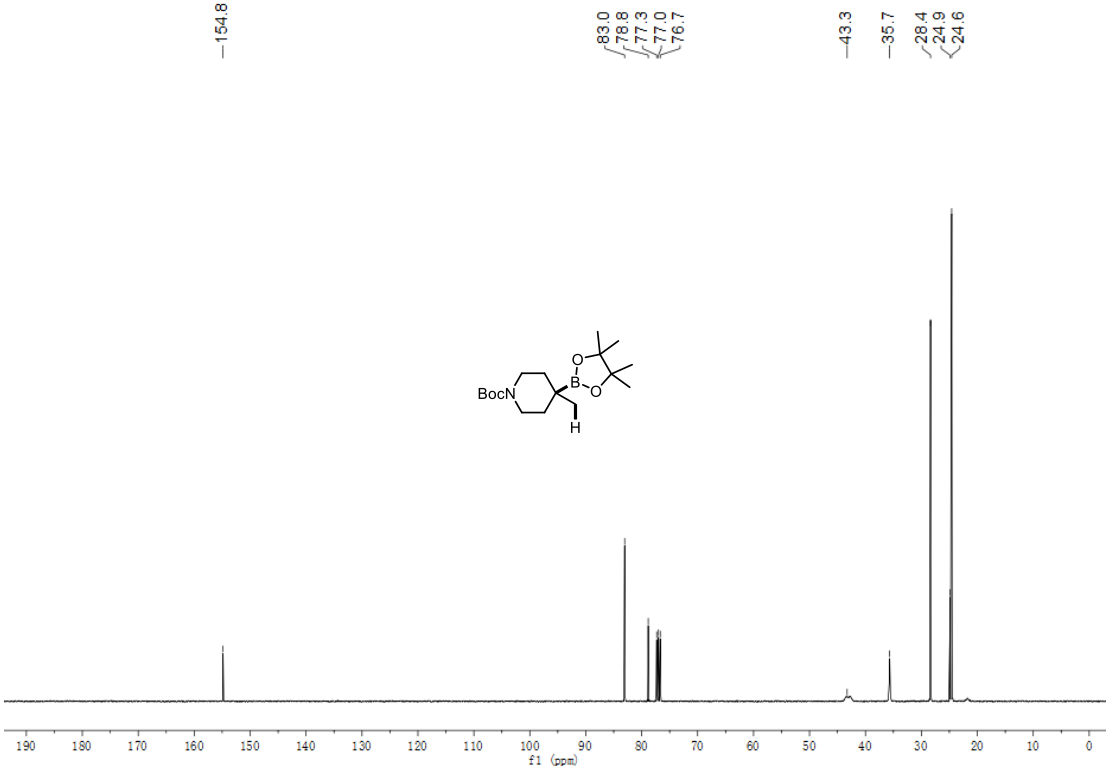
Compound **57** ^{13}C NMR (101 MHz, $CDCl_3$)



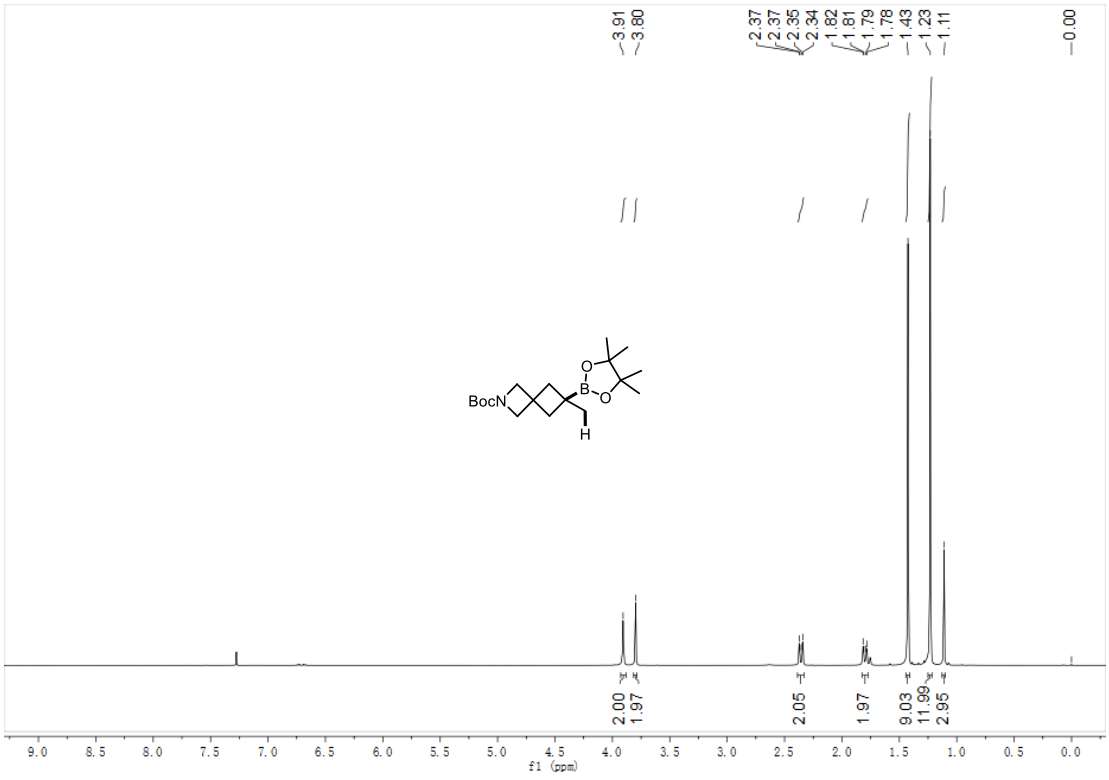
Compound **58** ^{1}H NMR (400 MHz, $CDCl_3$)



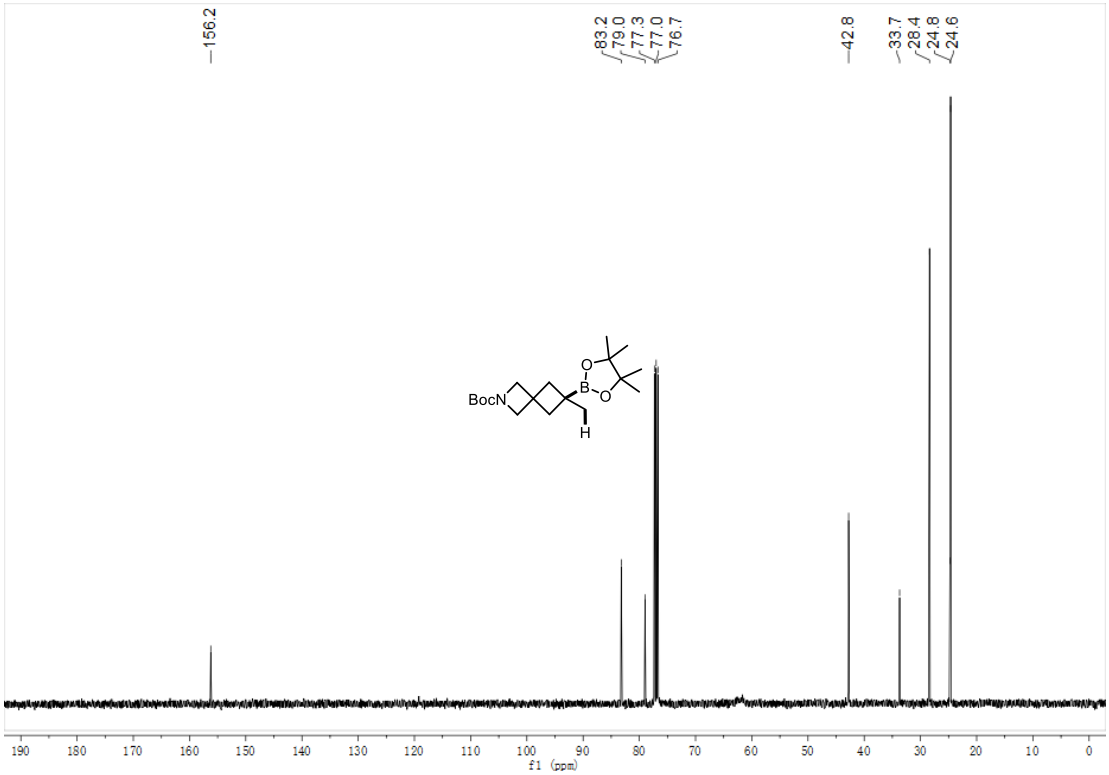
Compound **58** ^{13}C NMR (101 MHz, $CDCl_3$)



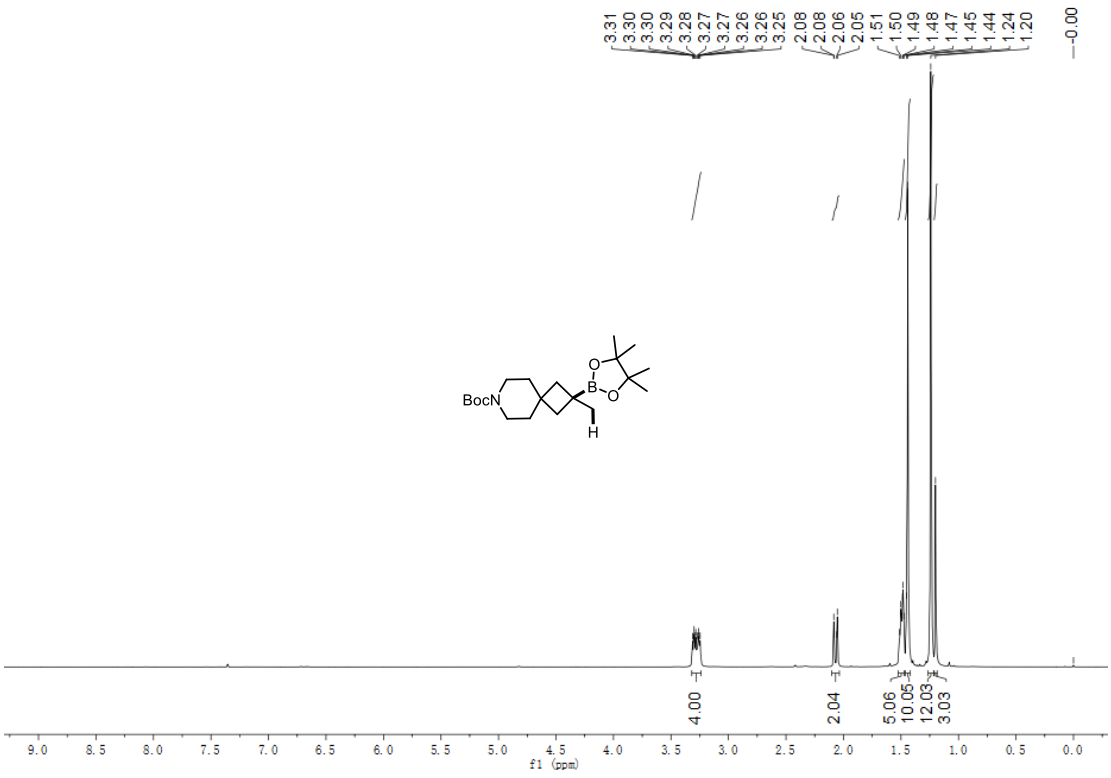
Compound **59** ^{1}H NMR (400 MHz, $CDCl_3$)



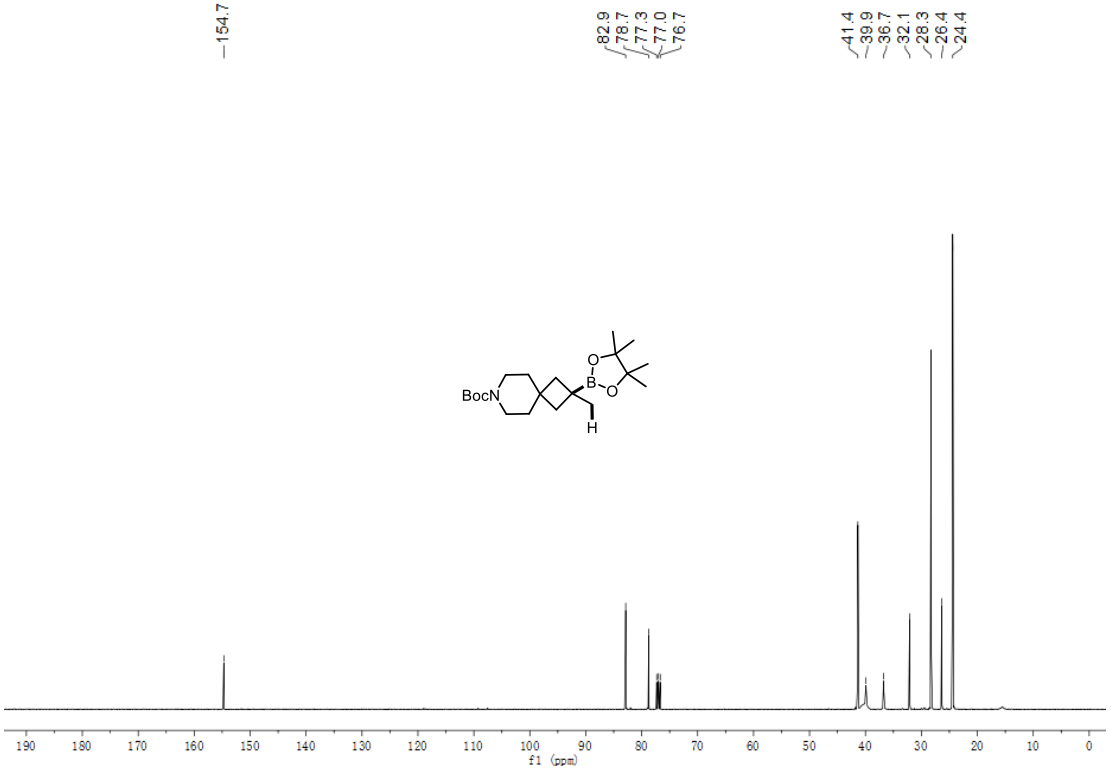
Compound **59** ^{13}C NMR (101 MHz, $CDCl_3$)



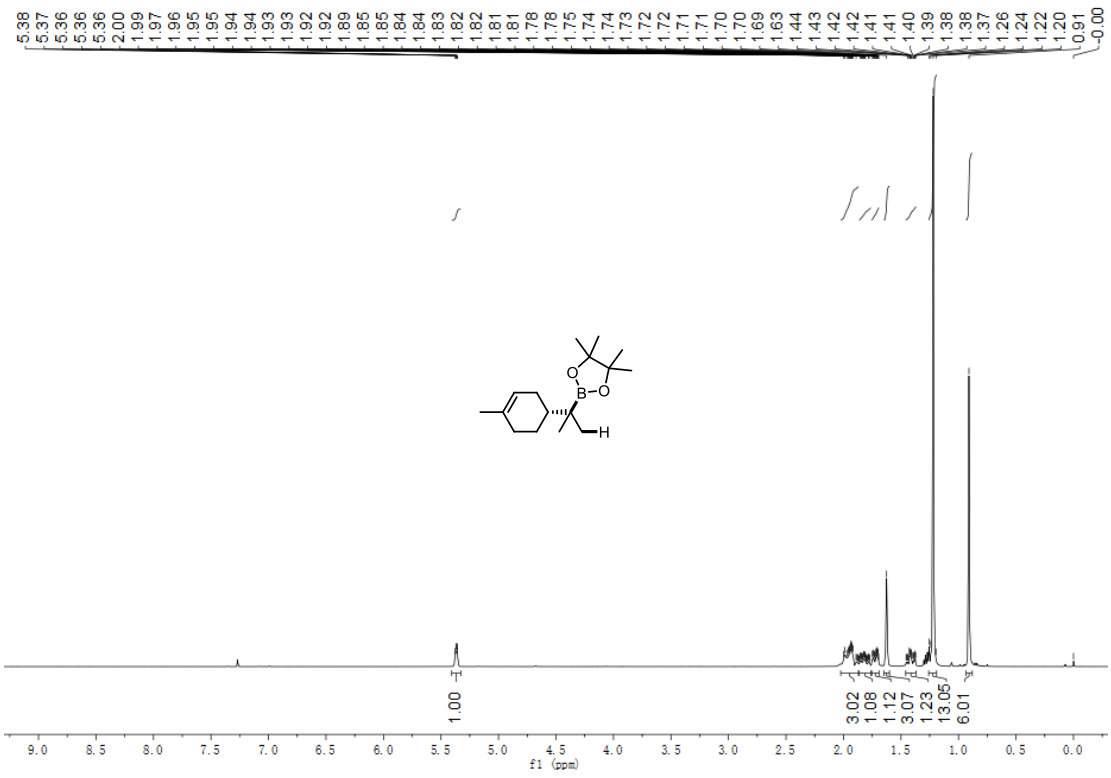
Compound **60** ^{1}H NMR (400 MHz, $CDCl_3$)



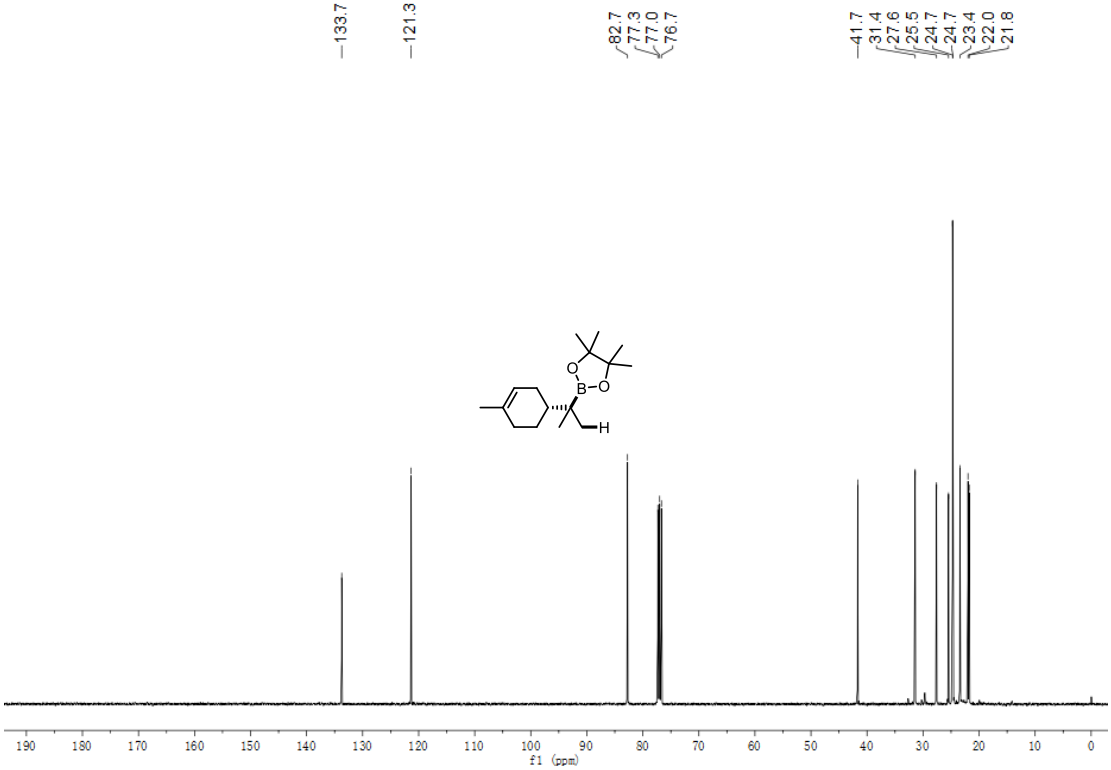
Compound **60** ^{13}C NMR (101 MHz, $CDCl_3$)



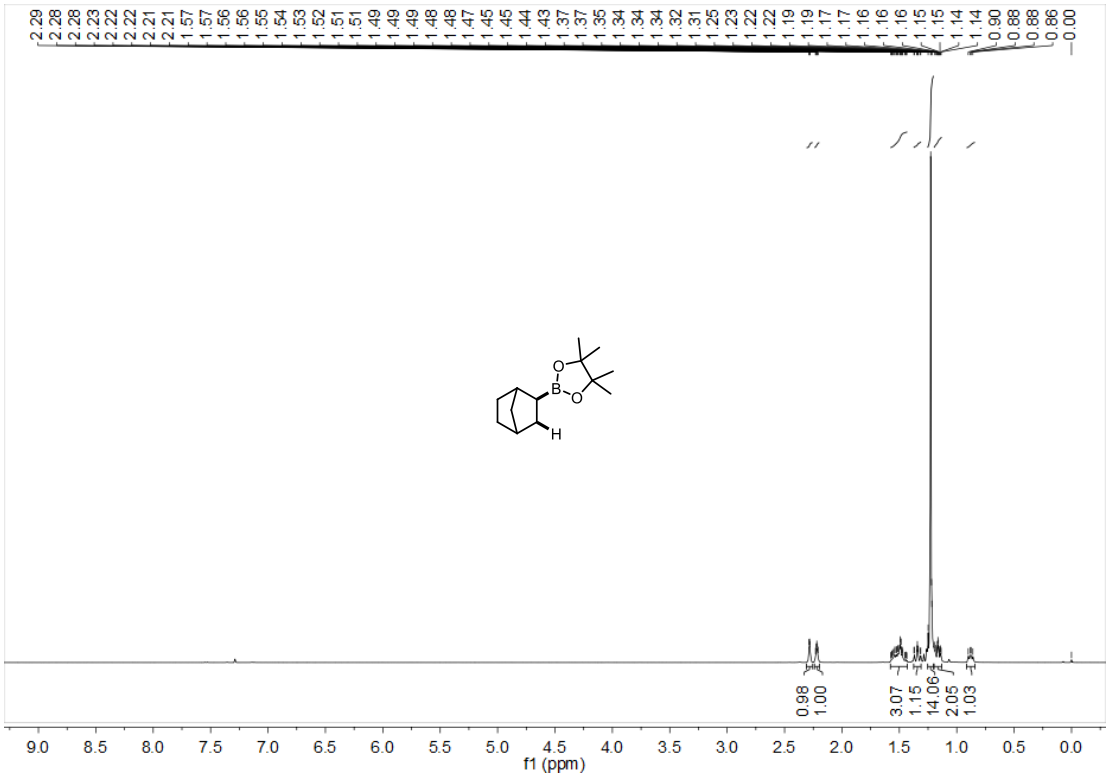
Compound **61** ^{1}H NMR (400 MHz, $CDCl_3$)



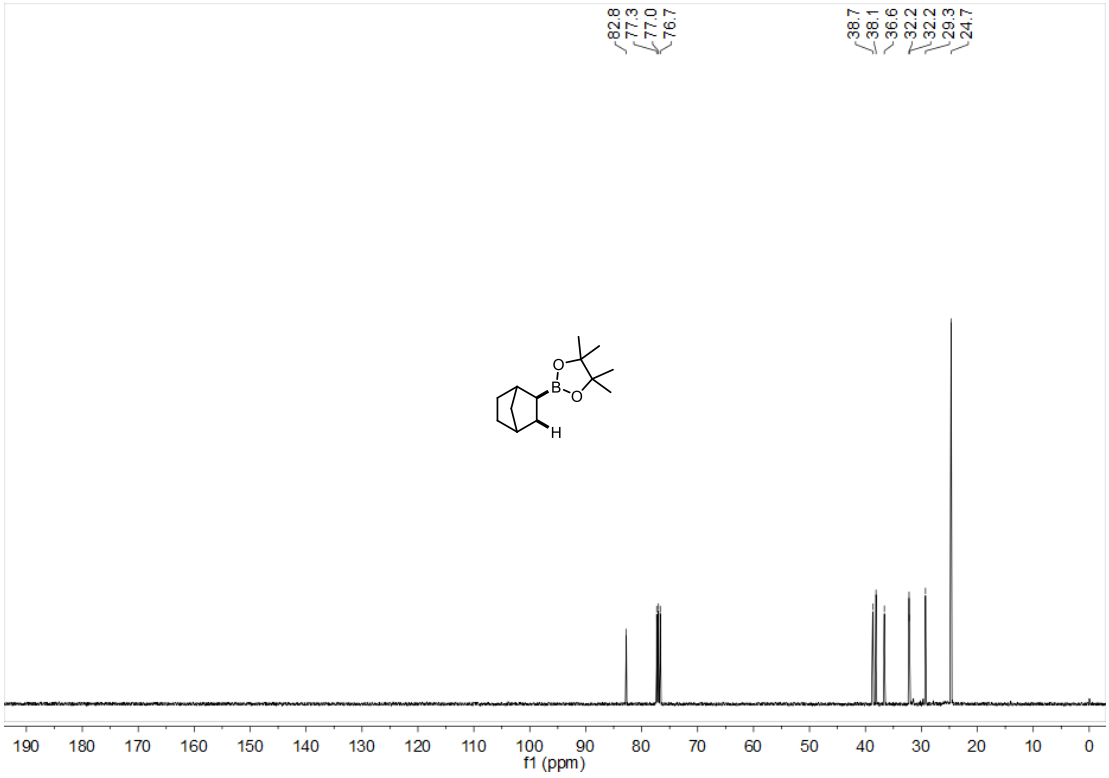
Compound **61** ^{13}C NMR (101 MHz, $CDCl_3$)



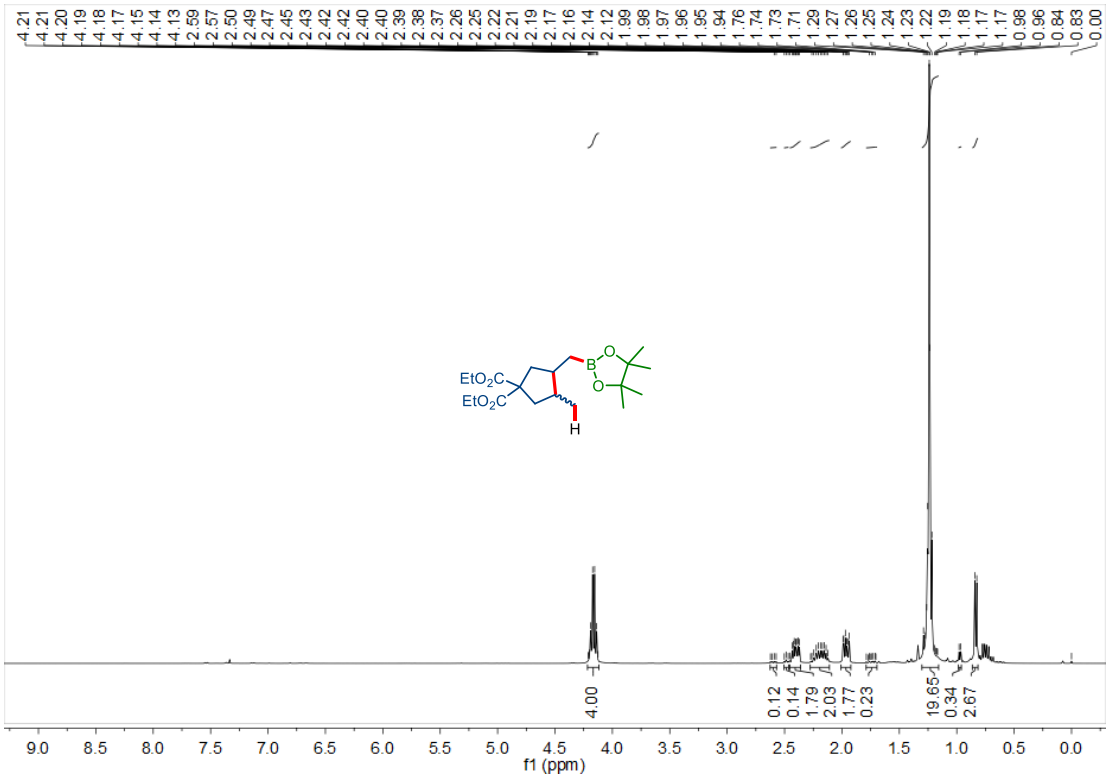
Compound **62** ^{1}H NMR (400 MHz, $CDCl_3$)



Compound **62** ^{13}C NMR (101 MHz, $CDCl_3$)



Compound **63** ^{1}H NMR (400 MHz, $CDCl_3$)



Compound **63** ^{13}C NMR (101 MHz, $CDCl_3$)