Supporting Information

Bis-dianionic β-ketoiminato octalithium complex as a universal catalyst for hydroboration with broad scope

Yu Zheng,[a] Xu Zhu,[b] Xiaojuan Xu,[b] Shuai Zhou,[b] Wenguang Lu,[a] and Mingqiang Xue[b*]

[a]Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, College of Chemical Engineering, Nanjing Forestry University, Nanjing, 210037, People's Republic of China.

[b]Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. E-mail: xuemingqiang@suda.edu.cn

Contents

I. General Experimental Information

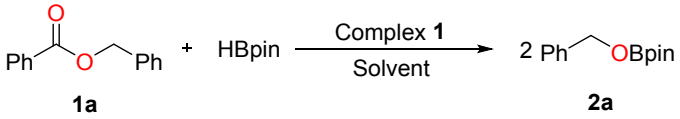
All manipulations were implemented by the Schlenk techniques under a dry argon atmosphere or in a glovebox under nitrogen atmosphere. Solvents of THF, toluene, ^{n}hexane, and 1,4-dioxane were dried and free of oxygen by refluxing over sodium/benzophenone and distilled prior to use. Pinacolborane (HBPin) was purchased from Bide and used without further purification. $CDCl_3$ and DMSO-d_6 were purchased from TCI and stored over activated 4Å molecular sieves. The liquid reagent used in the experiment is added calcium hydride to remove water. The solid reagent used in the experiment is drained under a vacuum pump and then flushed into the argon gas protection seal for backup. Mesitylene was used for the clarification of the yield of hydroboration products. ^{1}H and $^{13}C\{^{1}H\}$ spectra were recorded on Bruker AV–400 MHz, 101 MHz, respectively, and referenced to the resonances of the solvent used. Chemical shifts of the hydroboration products were reported as parts per million in δ scale using a residual solvent. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and coupling constant (J, Hz). The yields of hydroboration products were determined by ^{1}H NMR analysis calculating the integral area of the product characteristic hydrogen and mesitylene.

II. General Catalytic Procedure for Hydroboration

The catalytic reaction was carried out in a glovebox by selecting a 5 mL reaction bottle in which water and oxygen have been removed in advance; the catalyst complex **1** (1.5 mol%), ester (1 mmol), pinacol borane (2.2 mmol), THF (200 μL), were added to the bottle in turn, and the reaction mixture was stirred at 60 ^{o}C for 2 hrs. After the reaction was complete, mesitylene (1 mmol) was added to the reaction bottle as the internal standard, and the reaction process was monitored by ^{1}H NMR. We determined the yield by judging the newly generated methylene and its ratio to the internal target on the spectrum. The procedure for other unsaturated substrates including aldehydes, ketones, imines, nitriles, carbonates, and amides was similar to that of esters. For aldehydes and ketones, the amount of catalyst and borane, solvent, reaction temperature, and time are respectively: complex **1** (0.01 mol%), HBPin (1.2 eq), neat, 25 ^{o}C, 10 min; for imines, complex **1** (1 mol%), HBPin (1.2 eq), THF (200 μL), 60 ^{o}C, 2 hrs; for nitriles and carbonates, complex **1** (1 mol%), HBPin (2.2 eq or 3.3 eq), THF (200 μL), 60 ^{o}C, 2 hrs**;** for amides, complex **1** (5 mol%), HBPin (3 eq), THF (200 μL), 80 ^{o}C, 24 hrs.

III. Optimized Conditions

Table S1 Optimized Conditions of the Catalytic Hydroboration of Esters.[a]

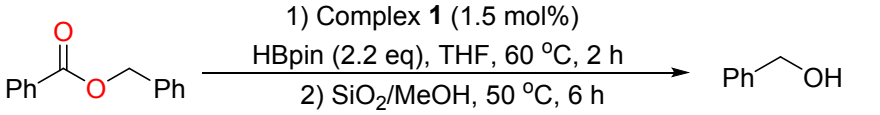


1a **2a**

Entry	Cat. (mol%)	Sol.	HBpin (eq)	Temp (°C)	Yield (%)[b]
1	1	THF	2.1	30	89
2	none	neat	2.1	30	0
3	1	THF	2.0	30	85
4	1	THF	2.2	30	91
5	1	THF	2.3	30	91
6	1	THF	2.2	40	92
7	1	THF	2.2	60	94
8	1	THF	2.2	80	92
9	1	1,4-dioxane	2.2	60	53
10	1	*n*hexane	2.2	60	79
11	1	toluene	2.2	60	64
12	1	neat	2.2	60	80
13	***1.5***	***THF***	***2.2***	***60***	***96***
14	2	THF	2.2	60	96

[a]Reaction conditions: benzyl benzoate **1a** (1.0 mmol), HBpin, complex **1** and solvent (0.2 mL), 2 h. [b]Yield is based on ^{1}H NMR (400 MHz) with mesitylene as an internal standard. THF = tetrahydrofuran.

IV. General Procedure for Gram-Scale Reaction

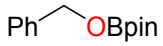


1a, 15 mmol **10a**, 2.77 g, 85%

The catalytic reaction was carried out in a glovebox at a 5 mL reaction bottle in which water and oxygen have been removed in advance. The catalyst complex **1** (1.5 mol%), benzyl benzoate (15 mmol), pinacol borane (2.2 eq), and THF (1 mL) were added to the bottle in turn, and the reaction mixture was stirred at 60 °C for 2 h. After the reaction was complete, the bottle with reaction mixture was exposed to air and was hydrolyzed with silica gel and methanol at 50 °C for 6 h. Then the mixed solution was extracted with diethyl ether (30 mL×3). The combined organic fractions were dried over Na_2SO_4 and the purification was carried out by column chromatography on

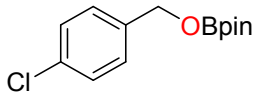
silica gel eluting with ethyl acetate and petroleum ether (EA/PE = 1: 5) to afford pure alcohol products.

V. Analytical Data of Hydroborated Products



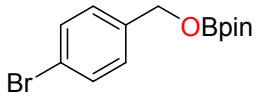
2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)[S1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.23 (m, 10H, Ar*H*), 4.92 (s, 4H, OCH_2), 1.26 (s, 24H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7 (Ar*C*), 128.3 (Ar*C*H), 127.4 (Ar*C*H), 126.9 (Ar*C*H), 83.0 (OB*pin*), 66.7 (O*C*H$_2$), 24.6 (*C*H$_3$, OB*pin*).



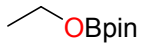
2-((4-Chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)[S2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 8H, Ar*H*), 4.88 (s, 4H, OCH_2), 1.26 (s, 24H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2 (Ar*C*), 130.6 (Ar*C*H), 125.9 (Ar*C*H), 125.6 (Ar*C*), 80.6 (OB*pin*), 63.5 (O*C*H$_2$), 22.1 (*C*H$_3$, OB*pin*).



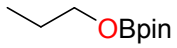
2-((4-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)[S3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 4H, Ar*H*), 7.22 (d, *J* = 8.5 Hz, 4H, Ar*H*), 4.87 (s, 4H, OCH_2), 1.26 (s, 24H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 (Ar*C*), 131.4 (Ar*C*H), 128.4 (Ar*C*H), 121.2 (Ar*C*), 83.0 (OB*pin*), 65.9 (O*C*H$_2$), 24.6 (*C*H$_3$, OB*pin*).



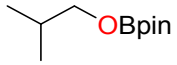
2-Ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)[S4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (q, *J* = 7.0 Hz, 2H, C*H*$_2$), 1.25 (s, 12H, OB*pin*), 1.22 (t, *J* = 7.0 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6 (OB*pin*), 60.6 (O*C*H$_2$), 24.6 (*C*H$_3$, OB*pin*), 17.2 (*C*H$_3$).



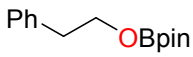
4,4,5,5-Tetramethyl-2-propoxy-1,3,2-dioxaborolane (2e)[S6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (t, *J* = 6.6 Hz, 2H, CH$_2$C*H*$_2$OBpin), 1.58 (m, 2H, CH$_3$C*H*$_2$CH$_2$), 1.24 (s, 12H, OB*pin*), 0.90 (t, *J* = 7.4 Hz, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6 (OB*pin*), 66.5 (O*C*H$_2$CH$_2$), 24.7 (OCH$_2$*C*H$_2$), 24.6 (*C*H$_3$, OB*pin*), 10.1 (*C*H$_3$).



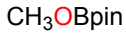
2-Isobutoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f) [S4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (d, *J* = 6.5 Hz, 2H, C*H*$_2$OBpin), 1.81–1.75 (m, 1H, C*H*(CH$_3$)$_2$), 1.24 (s, 12H, OB*pin*), 0.89 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6 (OB*pin*), 71.4 (O*C*H$_2$), 29.8 (*C*(CH$_3$)$_2$), 24.6 (*C*H$_3$, OB*pin*), 18.7 (*C*H$_3$).



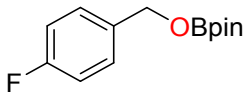
4,4,5,5-Tetramethyl-2-phenethoxy-1,3,2-dioxaborolane (2g)[S5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.16 (m, 5H, ArC*H*), 4.05 (t, *J* = 7.0 Hz, 2H, OC*H*$_2$), 2.87 (t, *J* = 6.9 Hz, 2H, ArC*H*$_2$), 1.18 (s, 12H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5 (Ar*C*), 129.1 (Ar*C*H), 128.3 (Ar*C*H), 126.2 (Ar*C*H), 82.6 (CH$_3$CH$_2$OB*pin*), 65.7 (O*C*H$_2$), 38.1 (*C*H$_2$CH$_2$OBpin), 24.5 (*C*H$_3$, OB*pin*).



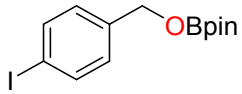
2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h)[S5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59 (s, 3H, C*H*$_3$OBpin), 1.24 (s, 12H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7 (OB*pin*), 52.6 (O*C*H$_3$), 24.6 (*C*H$_3$, OB*pin*).



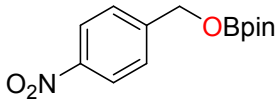
2-((4-Fluorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i)[S6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 2H, ArC*H*), 7.00 (t, *J* = 8.7 Hz, 2H, ArC*H*), 4.87 (s, 2H, OCH_2), 1.25 (s, 12H, OB*pin*).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.1 Hz, Ar*C*-F), 135.0 (d, *J* = 3.0 Hz, Ar*C*-OCH_2), 128.6 (d, *J* = 8.1 Hz, Ar*C*H), 115.0 (d, *J* = 21.4 Hz, Ar*C*), 83.0 (OB*pin*), 66.0 (O*C*H_2), 24.5 (*C*H_3, OB*pin*).



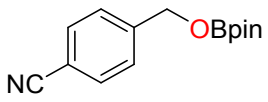
2-((4-Iodobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)[S7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (m, 2H, ArC*H*), 7.21 (d, *J* = 8.5 Hz, 2H, ArC*H*), 4.86 (s, 2H, OCH_2), 1.25 (s, 12H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2 (Ar*C*), 131.3 (Ar*C*H), 128.4 (Ar*C*H), 121.2 (Ar*C*), 82.8 (OB*pin*), 66.0 (O*C*H_2), 24.6 (*C*H_3, OB*pin*).



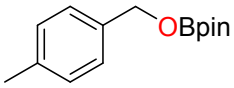
4,4,5,5-Tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (2k)[S7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H, ArC*H*), 7.49 (d, *J* = 8.9 Hz, 2H, ArC*H*), 5.01 (s, 2H, OCH_2), 1.24 (s, 12H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3 (Ar*C*), 146.6 (Ar*C*), 126.8 (Ar*C*H), 123.6 (Ar*C*H), 82.8 (OB*pin*), 65.6 (OCH_2), 24.6 (CH_3, OB*pin*).



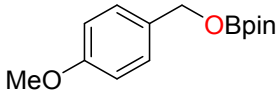
4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (2l)[S7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H, ArC*H*), 7.42 (d, *J* = 8.1 Hz, 2H, ArC*H*), 4.95 (s, 2H, OCH_2), 1.24 (s, 12H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6 (Ar*C*), 132.1 (Ar*C*H),126.8 (Ar*C*H), 118.8 (Ar*C*), 111.1 (Ar*C*), 82.7 (OB*pin*), 65.7 (O*C*H_2), 24.6 (*C*H_3, OB*pin*).



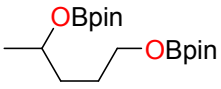
4,4,5,5-Tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (2m)[S7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H, ArC*H*), 7.16 (d, *J* = 7.9 Hz, 2H, ArC*H*), 4.80 (s, 2H, OCH_2), 2.24 (s, 3H, ArCH_3), 1.17 (d, *J* = 1.7 Hz, 12H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0 (*Ar*CH_3) , 136.3 (Ar*C*), 129.0 (Ar*C*H), 126.9 (Ar*C*H), 82.9 (OB*pin*), 66.6 (O*C*H_2), 21.2 (Ar*C*H_3), 24.6 (*C*H_3, OB*pin*) .



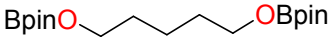
2-((4-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)[S7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 8.7, 2.5 Hz, 2H), 6.76 (dd, *J* = 8.8, 2.6 Hz, 2H), 4.74 (s, 2H), 3.68 (s, 3H), 1.16 (d, *J* = 2.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (Ar*C*), 131.3 (Ar*C*), 128.3 (Ar*C*H), 113.4 (Ar*C*H), 82.6 (OB*pin*), 66.2 (CH_2OB*pin*), 54.9 (*O*CH_3), 24.4 (*C*H_3, OB*pin*).



4,4,5,5-Tetramethyl-2-((4-((4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)oxy)pentyl)oxy) -1,3,2- dioxaborolane (2o)[S8]

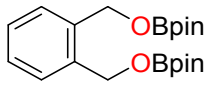
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (m, 1H, CH_3C*H*), 3.93–3.79 (m, 2H, OCH_2), 1.71–1.59 (m, 2H, CH_2), 1.49–1.44 (m, 2H, CH_2), 1.26–1.23 (m, 24H, OB*pin*), 1.18 (d, *J* = 6.2 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6 (OB*pin*), 82.5 (OB*pin*), 70.6 (CH_3*C*HOBpin), 64.8 (CH_2*C*H_2OBpin), 34.1 (*C*H_2), 27.5 (*C*H_2), 24.6 (*C*H_3, OB*pin*), 24.6 (*C*H_3, OB*pin*), 22.6 (*C*H_3CH).



1,5-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)pentane (2p)[S8]

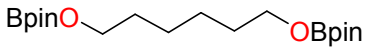
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (t, *J* = 6.6 Hz, 4H, OCH_2), 1.58 (dt, *J* = 14.6, 6.8 Hz, 4H, CH_2), 1.43–1.36 (m, 2H, CH_2), 1.24 (s, 24H, OB*pin*). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 82.6 (OB*pin*), 64.8 (*C*H_2OBpin), 31.1 (*C*H_2CH$_2$OBpin), 24.6 (*C*H_3, OB*pin*), 21.2 (*C*H_2CH$_2$CH$_2$OBpin).



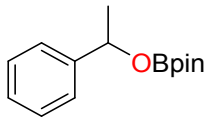
1,2-Bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (2q)[S8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 5.5, 3.5 Hz, 2H, ArC*H*), 7.29–7.24 (m, 2H, ArC*H*), 4.98 (s, 4H, OCH_2), 1.25 (s, 24H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ136.4 (*C*-CH$_2$, Ar*C*), 127.2 (Ar*C*H), 126.9 (Ar*C*H), 82.9 (OB*pin*), 64.1 (*C*H$_2$, O*C*H$_2$), 24.6 (*C*H$_3$, OB*pin*).



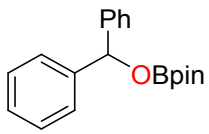
1,6-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)hexane (2r)[S9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (t, *J* = 6.5 Hz, 4H, CH_2OBpin), 1.54 (q, *J* = 6.3 Hz, 4H, CH_2), 1.34 (dt, *J* = 7.3, 3.7 Hz, 4H, CH_2), 1.23 (s, 24H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6 (OB*pin*), 64.8 (O*C*H$_2$), 31.4 (*C*H$_2$), 25.3 (*C*H$_2$), 24.6 (*C*H$_3$, OB*pin*).



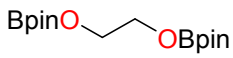
4,4,5,5-Tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (2s)[S10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 17.4, 7.2 Hz, 4H, Ar*H*), 7.15 (t, *J* = 7.1 Hz, 1H, Ar*H*), 5.16 (q, *J* = 6.4 Hz, 1H, C*H*OBPin), 1.41 (d, *J* = 6.5 Hz, 3H, CH_3CHOBPin), 1.14 (d, *J* = 12.0 Hz, 12H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6 (Ar*C*), 128.2 (Ar*C*H), 127.1 (Ar*C*H), 125.3 (Ar*C*H), 82.7 (OB*pin*), 72.6 (*C*HOBPin), 25.4 (*C*H$_3$CHOBPin), 24.6 (*C*H$_3$, OB*pin*), 24.5 (*C*H$_3$, OB*pin*).



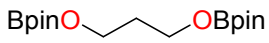
2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2t)[S10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 4H, Ar*H*), 7.20–7.15 (m, 4H, Ar*H*), 7.12–7.09 (m, 2H, Ar*H*), 6.09 (s, 1H, C*H*OBPin), 1.08 (s, 12H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2 (Ar*C*), 128.3 (Ar*C*H), 127.3 (Ar*C*H), 126.5 (Ar*C*H), 83.0 (OB*pin*), 77.9 (*C*HOBPin), 24.5 (*C*H_3, OB*pin*).



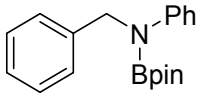
1,2-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethane (2u)[S11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 4H, OCH_2), 1.17 (d, J = 1.3 Hz, 24H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.5 (OB*pin*), 64.9 (O*C*H_2), 24.4 (*C*H_3, OB*pin*).



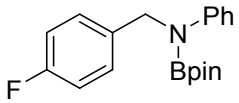
1,3-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)propane (2v)[S11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (t, J = 6.2 Hz, 4H, OCH_2), 1.87–1.81 (m, 2H, OCH$_2$CH_2), 1.20-1.16 (m, 24H, OB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.7 (OB*pin*), 61.4 (O*C*H_2), 33.2 (OCH$_2$*C*H_2), 24.5 (*C*H_3, OB*pin*).



***N*-Benzyl-4,4,5,5-tetramethyl-*N*-phenyl-1,3,2-dioxaborolan-2-amine (5a)**[S12]

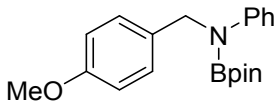
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–6.98 (m, 10H, Ar*H*), 4.59 (s, 2H, CH_2NBPin), 1.19 (s, 12H, NB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3 (Ar*C*), 140.5 (Ar*C*), 128.5 (Ar*C*H), 128.3 (Ar*C*H), 126.4 (Ar*C*H), 121.3 (Ar*C*H), 120.5 (Ar*C*H), 82.9 (NB*pin*), 51.2 (*C*H$_2$NBPin), 24.6 (*C*H_3, NB*pin*).



***N*-(4-Fluorobenzyl)-4,4,5,5-tetramethyl-*N*-phenyl-1,3,2-dioxaborolan-2-amine (5b)**[S12]

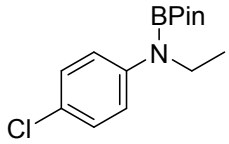
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08–6.96 (m, 6H, Ar*H*), 6.79–6.68 (m, 3H, Ar*H*), 4.50 (s, 2H, CH_2NB*pin*), 1.13 (s, 12H, NB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9

(Ar*C*-F), 160.4 (Ar*C*-F), 146.0 (Ar*C*), 136.2 (Ar*C*), 128.5(Ar*C*H), 128.0 (Ar*C*H), 126.9 (Ar*C*H), 121.4 (Ar*C*H), 120.7 (Ar*C*H), 115.2 (Ar*C*H), 114.9 (Ar*C*H), 82.9 (NB*pin*), 50.4 (CH$_2$NBPin), 24.5 (CH$_3$, NB*pin*).



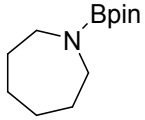
_N_-(4-Methoxybenzyl)-4,4,5,5-tetramethyl-_N_-phenyl-1,3,2-dioxaborolan-2-amine (5c)[S12]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13–7.02 (m, 7H, Ar*H*), 6.69 (d, *J* = 8.7 Hz, 2H, Ar*H*), 4.52 (s, 2H, CH_2NBPin), 3.61 (s, 3H, OCH_3), 1.18 (s, 12H, NB*pin*). ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.3 (Ar*C*), 146.3 (Ar*C*), 132.5 (Ar*C*), 128.5 (Ar*C*H), 127.6 (Ar*C*H), 121.3 (Ar*C*H), 120.7 (Ar*C*H), 113.8 (Ar*C*H), 82.9 (NB*pin*) , 55.1 (OCH$_3$), 50.6 (CH$_2$NBPin), 24.6 (CH$_3$, NB*pin*).



_N_-(4-Chlorophenyl)-_N_-ethyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (5d)[S13]

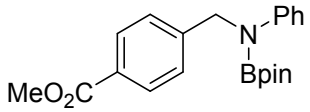
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.06 (d, *J* = 8.8 Hz, 2H, ArH), 6.54 (d, *J* = 8.4 Hz, 2H, Ar*H*), 3.04–2.95 (m, 2H, NCH_2CH$_3$), 1.16 (s, 12H, NB*Pin*), 0.93 (d, 3H, NCH$_2$CH_3). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.3 (Ar*C*-Cl), 128.9 (Ar*C*), 119.0 (Ar*C*H), 113.6 (Ar*C*H), 81.7 (NB*pin*), 37.7 (NCH_2CH_3), 24.9 (CH$_3$, NB*pin*), 14.6 (NCH$_2$$CH_3$).



1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)azepane (5e)[S13]

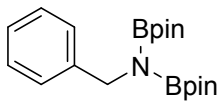
^{1}H NMR (400 MHz, DMSO-d_6) δ 2.86–2.80 (m, 4H), 1.62 (br, 4H), 1.55 (br, 4H), 1.15 (s, 12H, NB*pin*). ^{13}C NMR (101 MHz, DMSO-d_6) δ 81.63 (NB*pin*), 46.78

(CH_2NBPin), 31.00 (CH_2CH_2-R), 27.13 (CH_2CH_2-R), 24.86 (CH_3, NB*pin*), 24.76 (CH_3, NB*pin*).



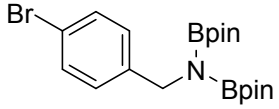
Methyl 4-((phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)amino)methyl)benzoate (5f)[S12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H, Ar*H*), 7.87 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.46–7.28 (m, 4H, Ar*H*), 7.14 (dd, *J* = 37.6, 7.3 Hz, 3H, Ar*H*), 4.93 (d, *J* = 34.2 Hz, 2H, CH_2NBPin), 3.58 (s, 3H, COOCH_3), 1.25-1.24 (m, 12H, NB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.00, 152.03, 147.83, 129.87, 126.12, 125.92, 125.10, 125.05, 121.96, 116.79, 79.74, 56.60, 20.55.



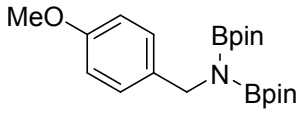
***N*-Benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (7a)**[S14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.4 Hz, 2H, Ar*H*), 7.15 (t, *J* = 7.4 Hz, 2H, Ar*H*), 7.06 (t, *J* = 7.1 Hz, 1H, Ar*H*), 4.15 (s, 2H, CH_2), 1.11 (s, 24H, NB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1 (Ar*C*), 127.8 (Ar*C*H), 127.5 (Ar*C*H), 126.1 (Ar*C*H), 82.3 (NB*pin*), 47.3 (CH_2), 24.5 (CH_3, NB*pin*).



***N*-(4-Bromobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (7b)**[S14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.18 (d, *J* = 8.4 Hz, 2H, Ar*H*), 4.16 (s, 2H, CH_2), 1.19 (s, 24H, NB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1 (Ar*C*), 130.8 (Ar*C*), 129.3 (Ar*C*H) , 119.8 (Ar*C*H) , 82.4 (Nb*pin*), 46.7 (CH_2), 24.5 (CH_3, NB*pin*).

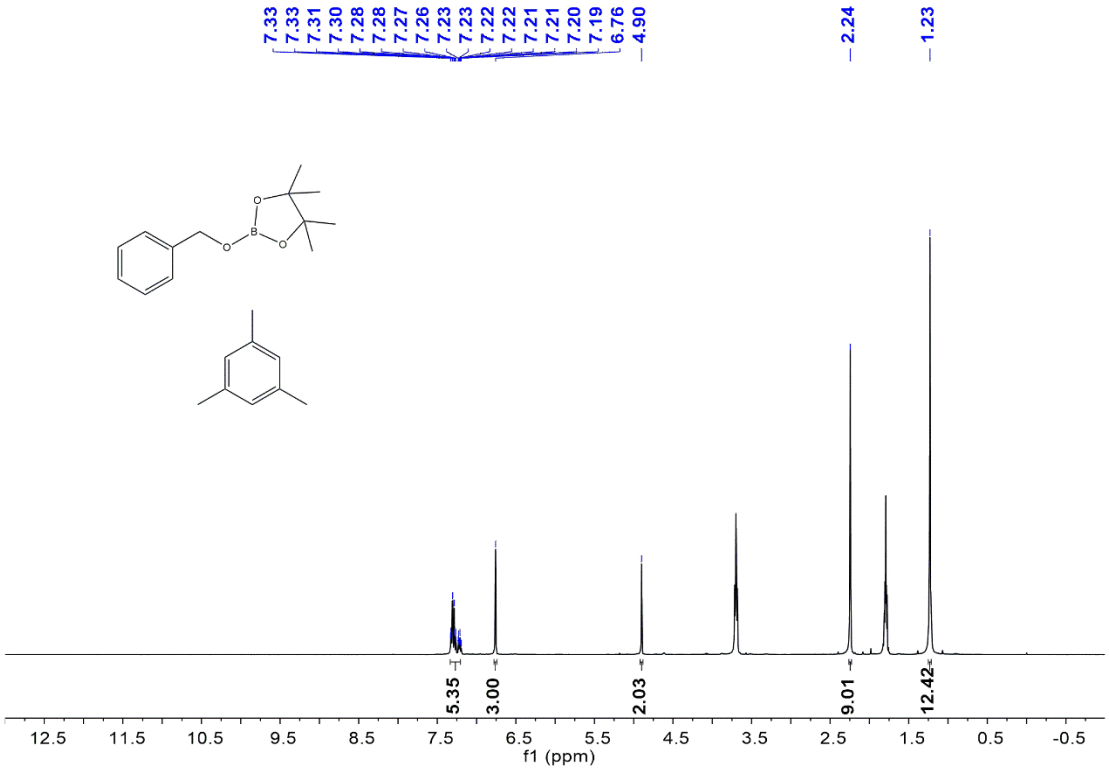


_N_-(4-Methoxybenzyl)-4,4,5,5-tetramethyl-_N_-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (7c)[S14]

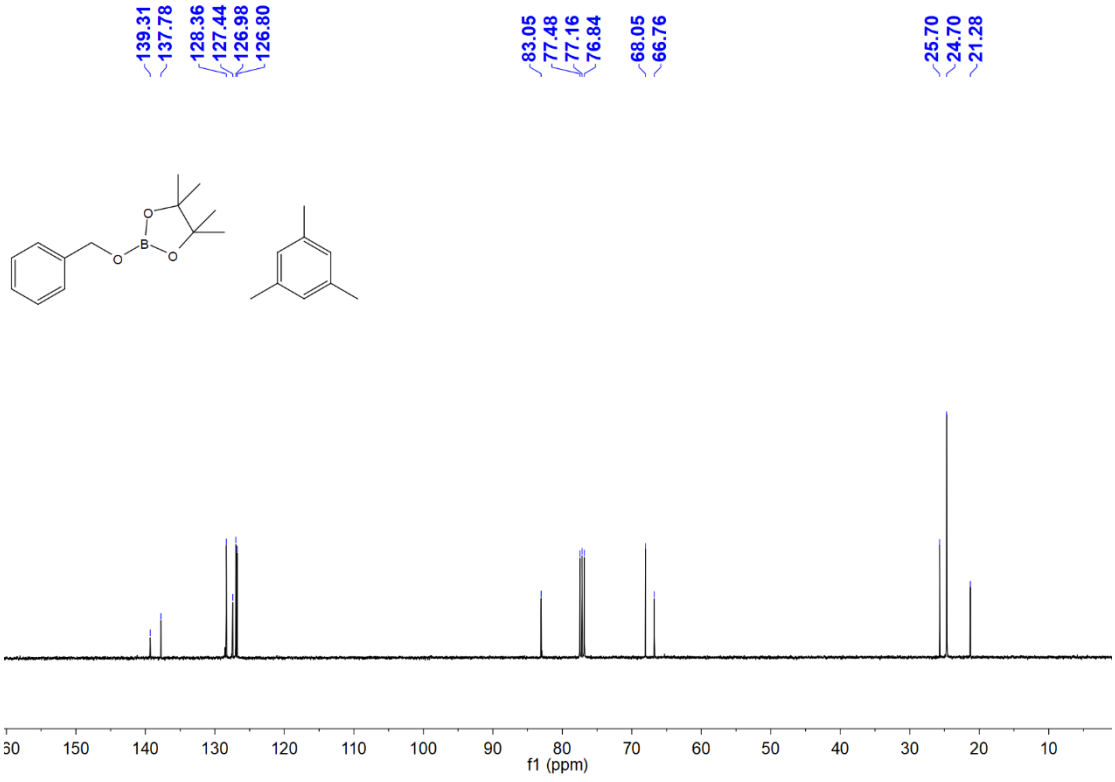
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 123.2 Hz, 2H, Ar*H*), 6.84 (d, *J* = 32.2 Hz, 2H, Ar*H*), 3.78 (s, 2H, C*H*$_2$NBPin), 3.71 (s, 3H, OC*H*$_3$), 1.15 (s, 24H, NB*pin*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (Ar*C*), 133.9 (Ar*C*), 129.0 (Ar*C*H), 114.8 (Ar*C*H), 114.1 (Ar*C*H), 82.3 (NB*pin*), 55.5 (O*C*H$_3$), 44.9 (*C*H$_2$NBPin), 24.6 (*C*H$_3$, NB*pin*).

VI. NMR Spectra

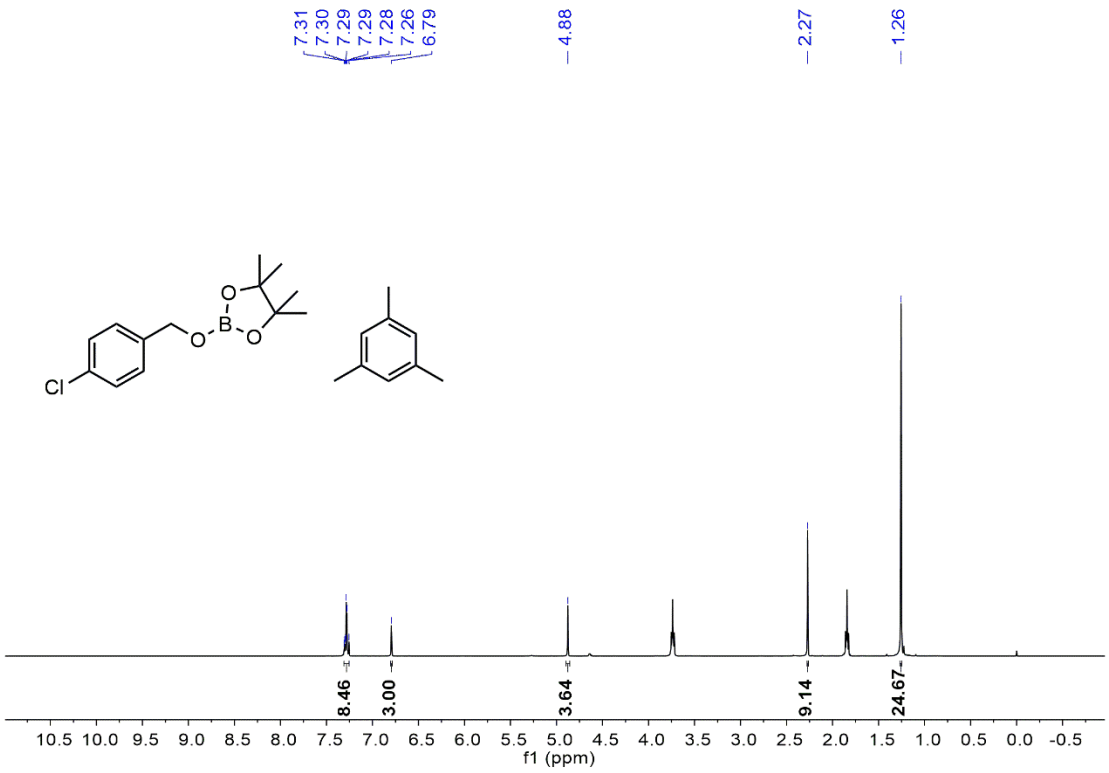
^{1}H NMR spectrum of product **2a** (400 MHZ, $CDCl_3$)



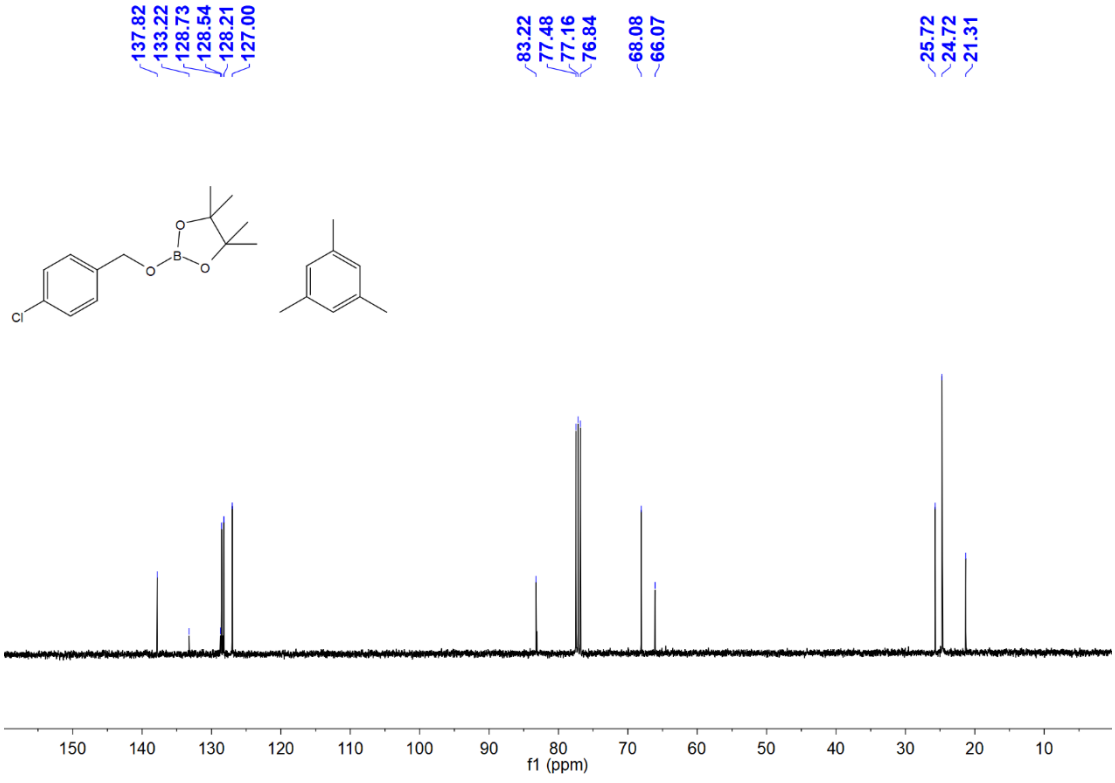
^{13}C NMR spectrum of product **2a** (101 MHZ, $CDCl_3$)



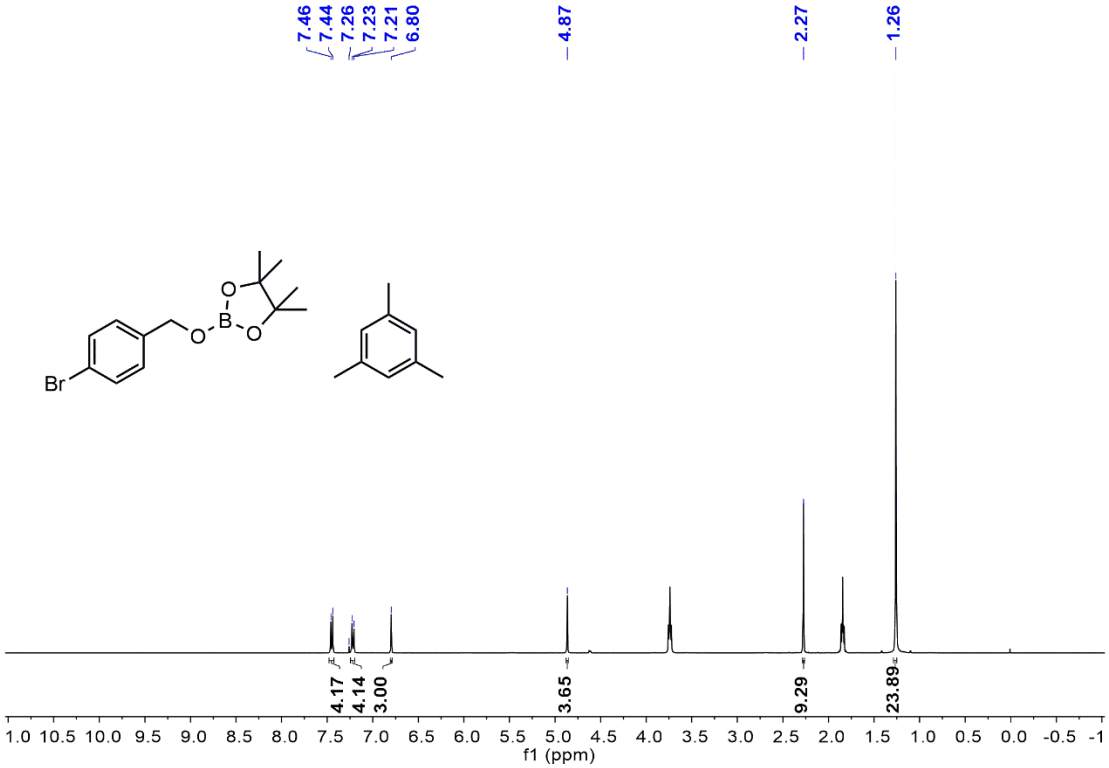
^{1}H NMR spectrum of product **2b** (400 MHZ, $CDCl_3$)



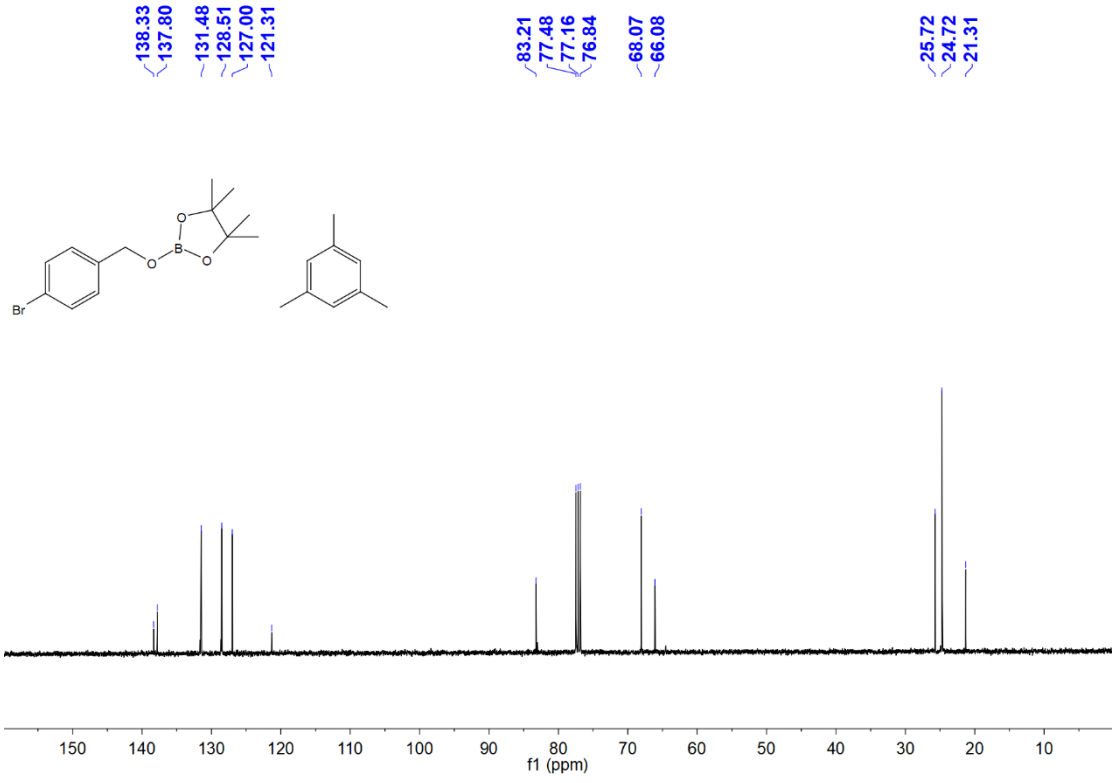
^{13}C NMR spectrum of product **2b** (101 MHZ, $CDCl_3$)



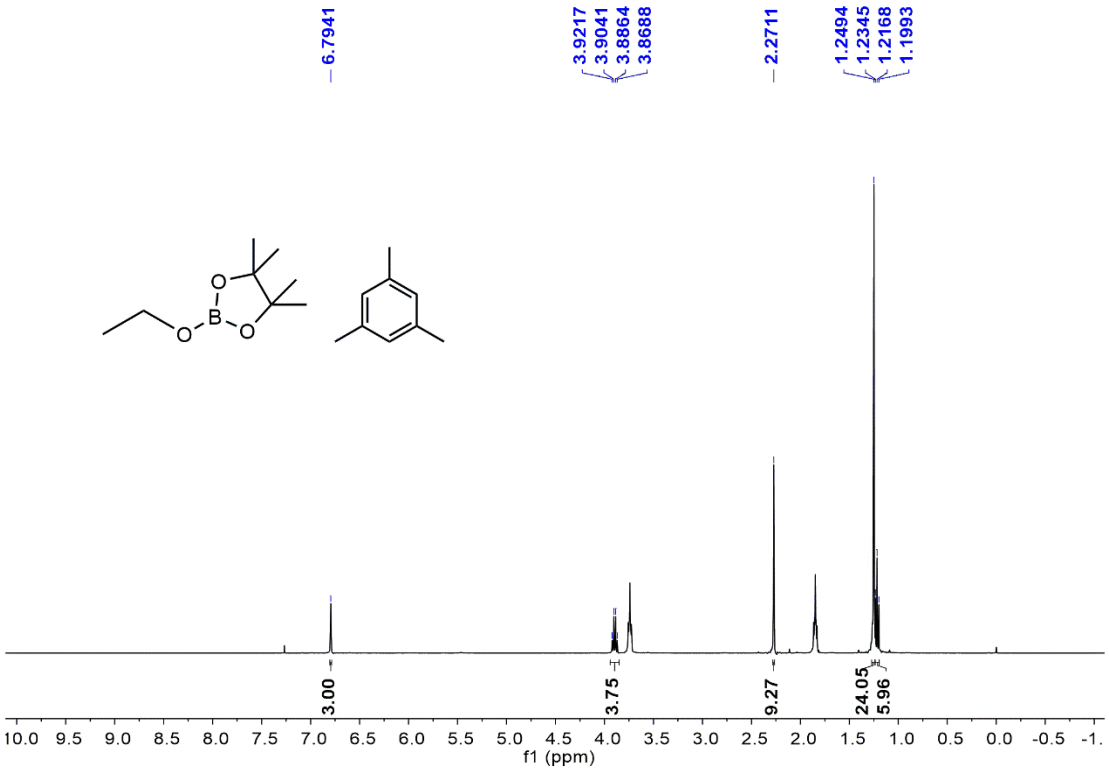
^{1}H NMR spectrum of product **2c** (400 MHZ, $CDCl_3$)



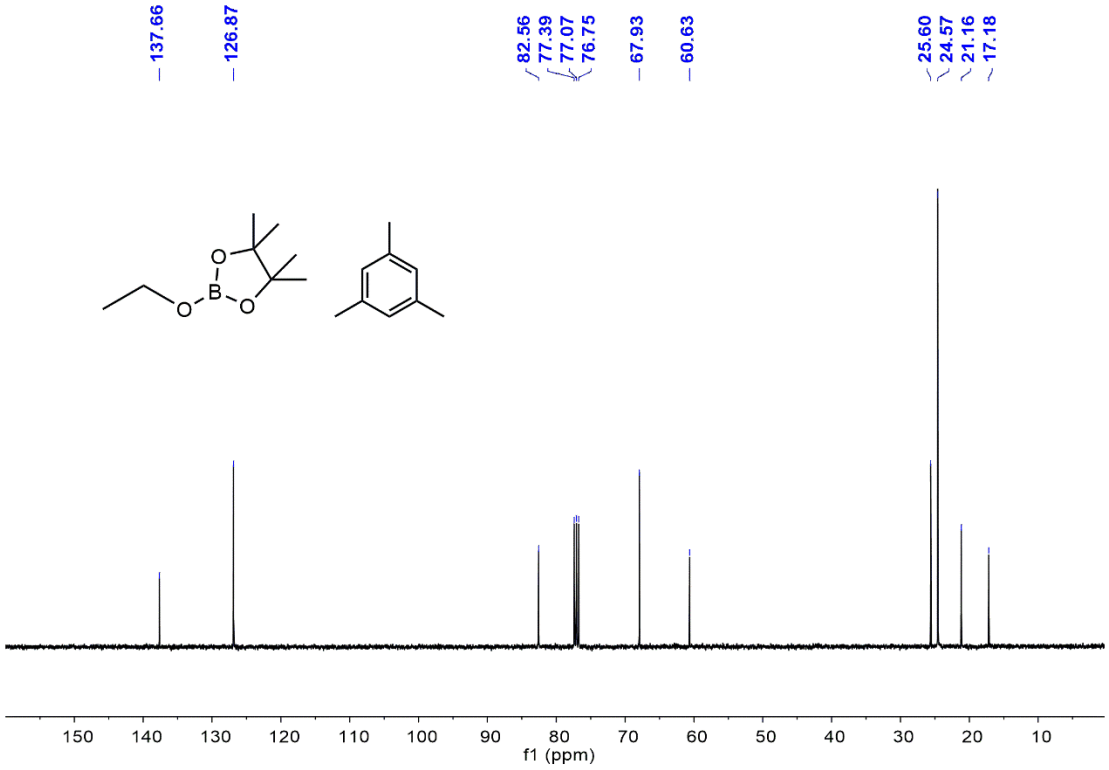
^{13}C NMR spectrum of product **2c** (101 MHZ, $CDCl_3$)



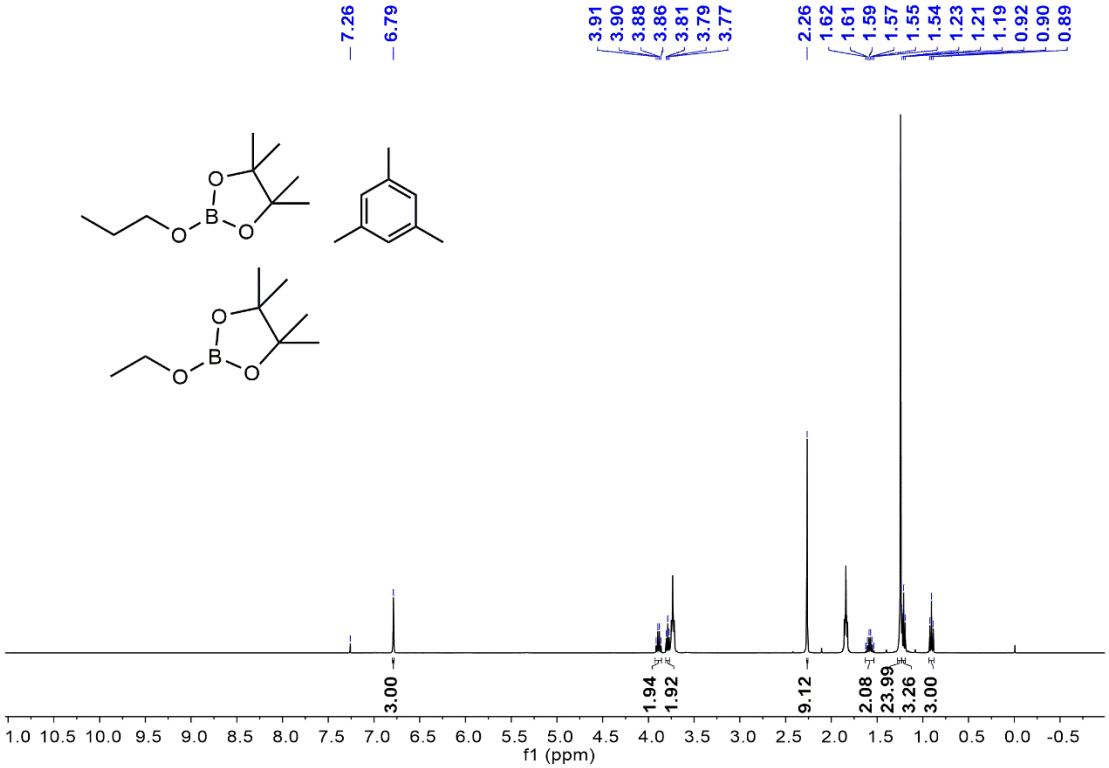
^{1}H NMR spectrum of product **2d** (400 MHZ, $CDCl_3$)



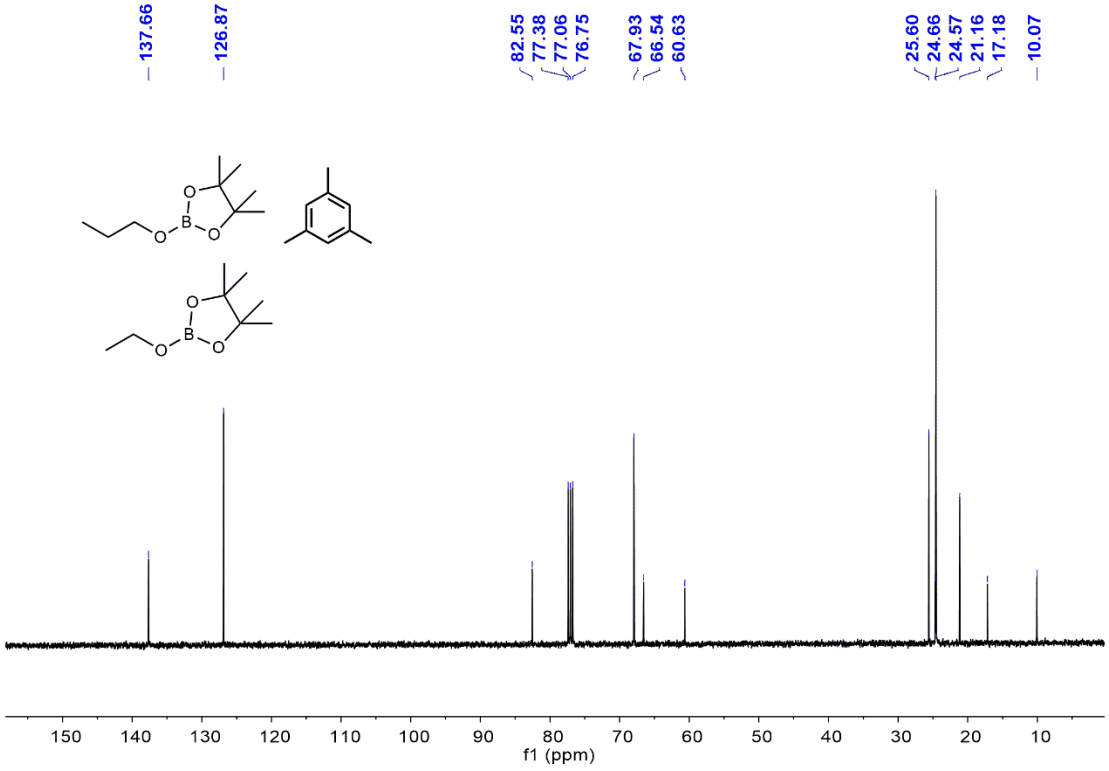
^{13}C NMR spectrum of product **2d** (101 MHZ, $CDCl_3$)



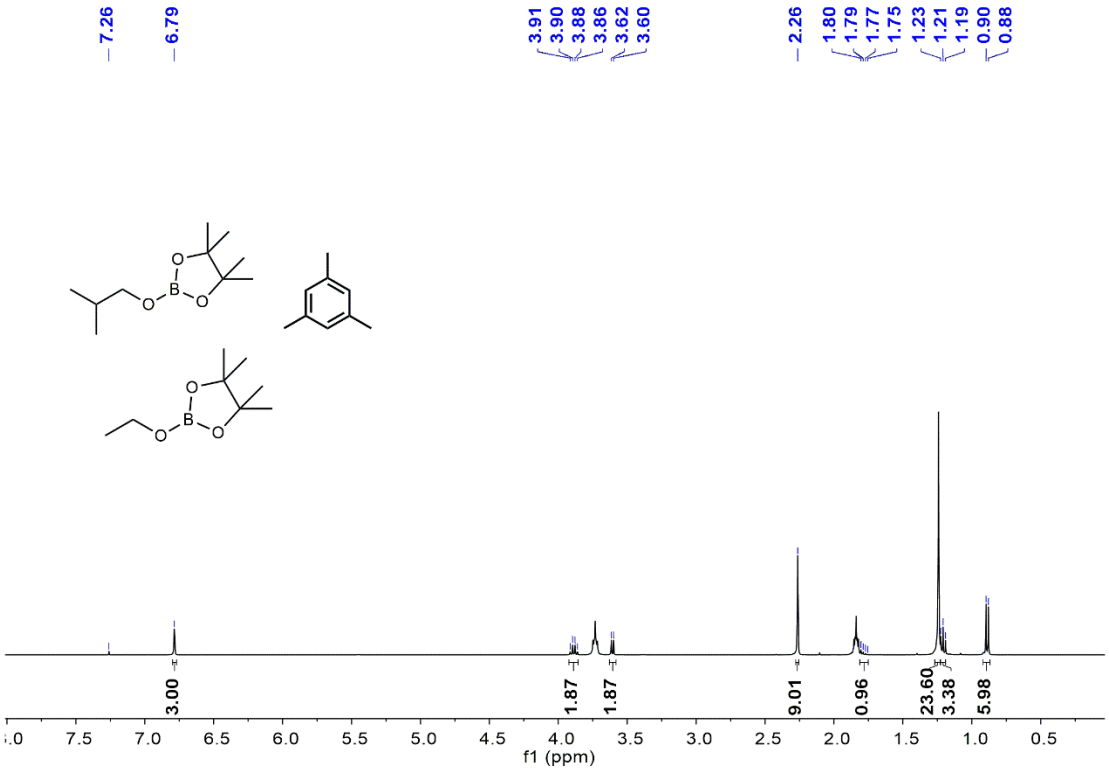
^{1}H NMR spectrum of product **2d**, **2e** (400 MHZ, $CDCl_3$)



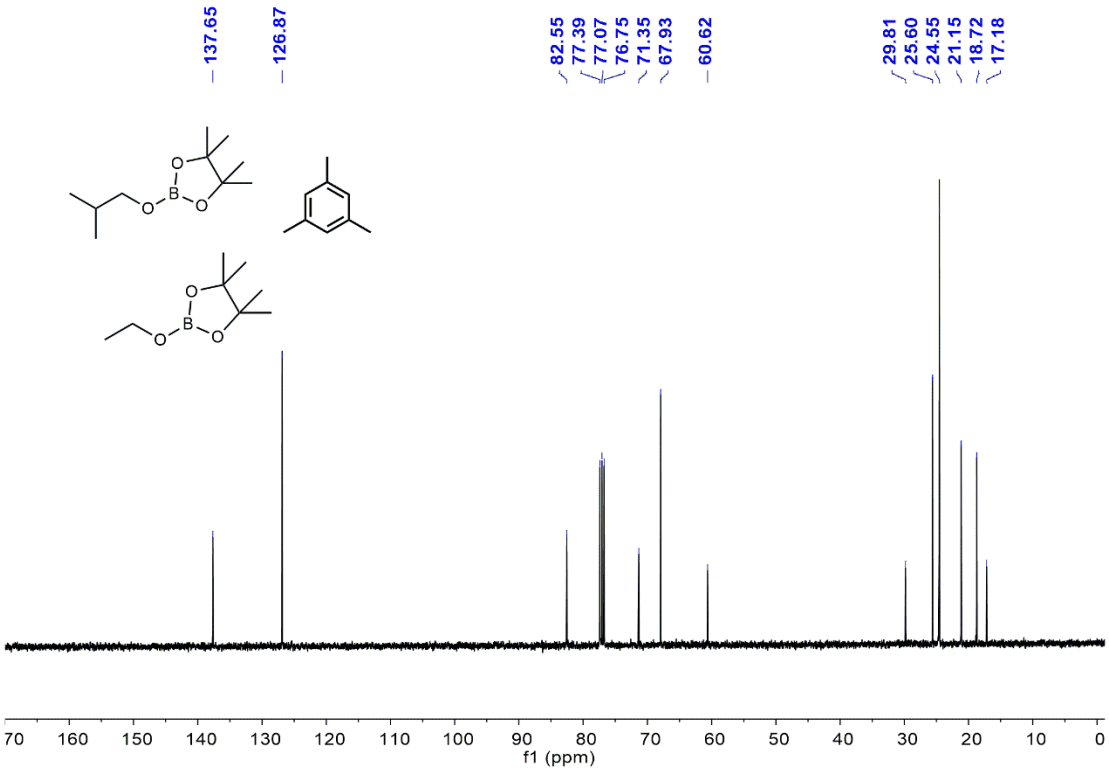
^{13}C NMR spectrum of product **2d**, **2e** (101 MHZ, $CDCl_3$)



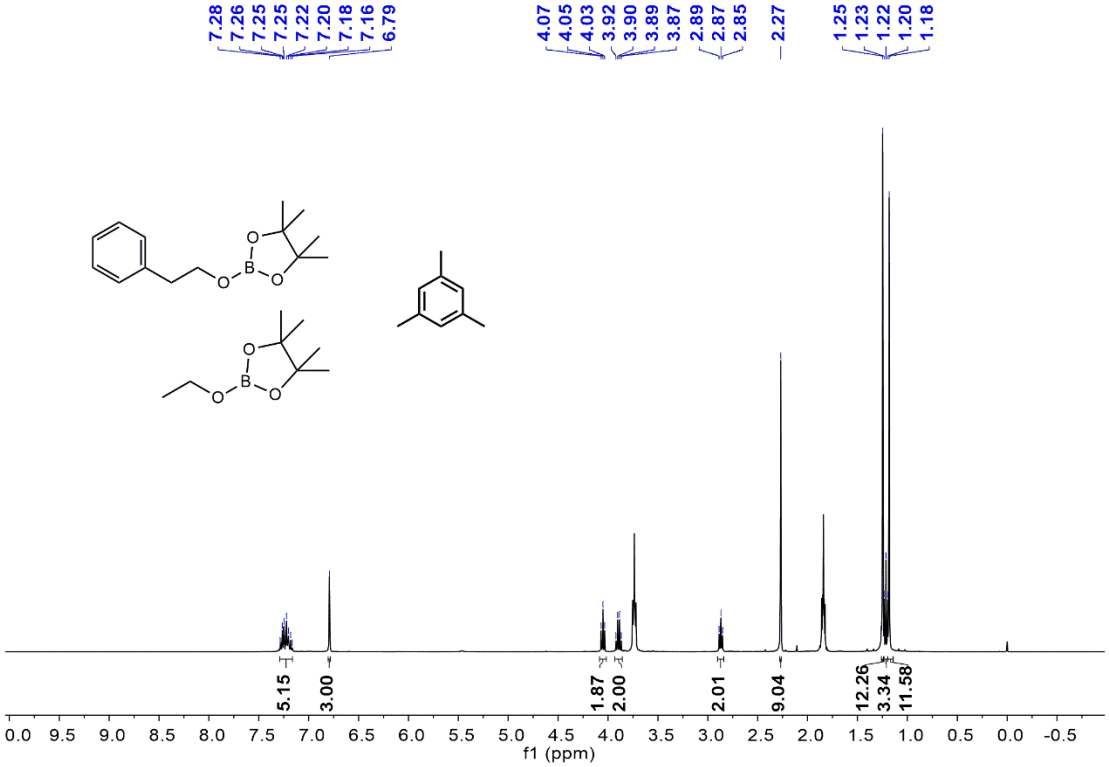
^{1}H NMR spectrum of product **2d**, **2f** (400 MHZ, $CDCl_3$)



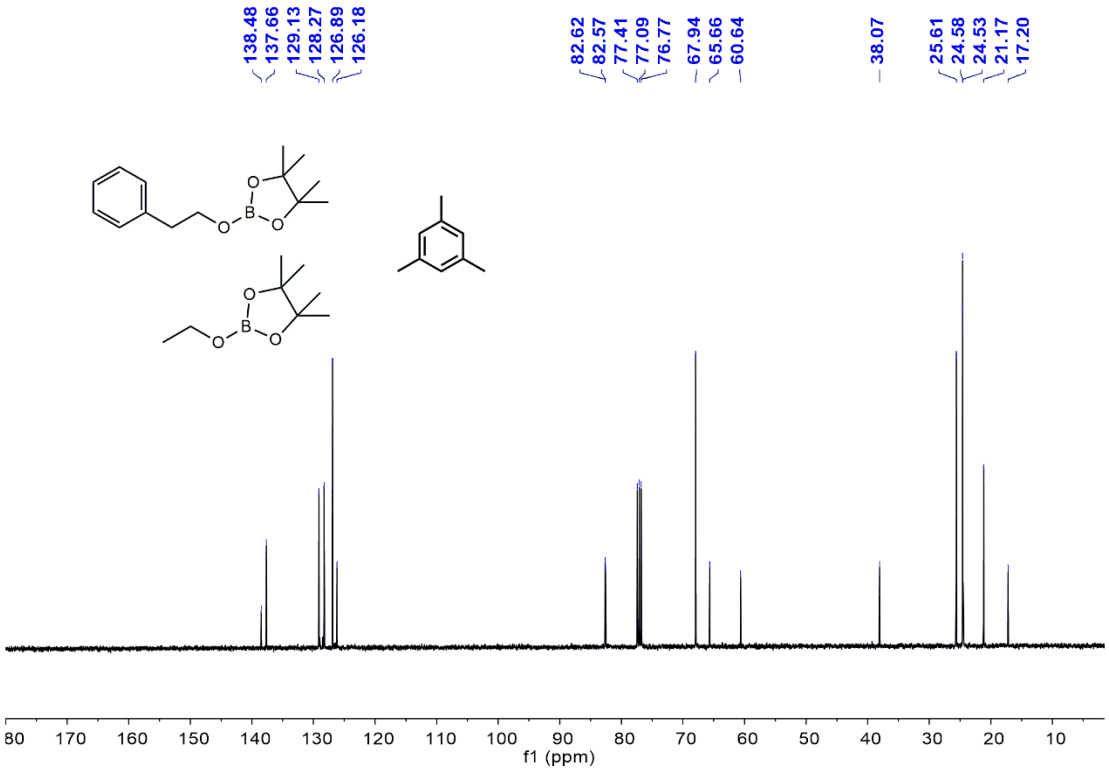
^{13}C NMR spectrum of product **2d**, **2f** (101 MHZ, $CDCl_3$)



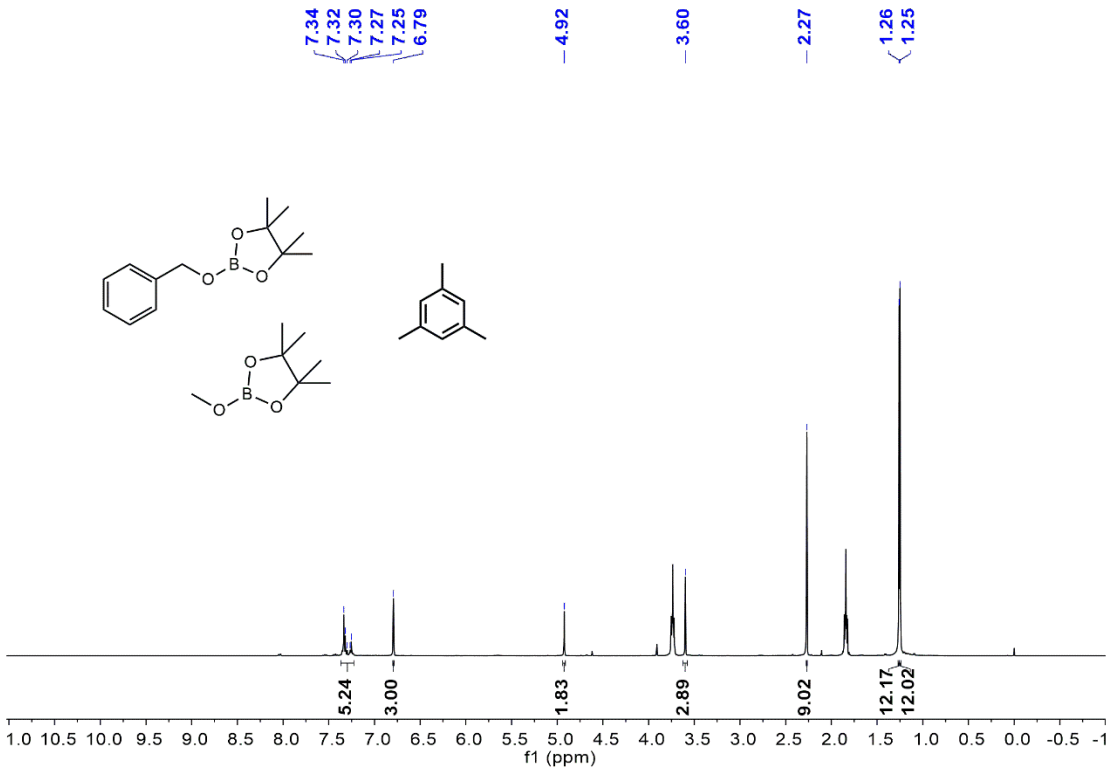
^{1}H NMR spectrum of product **2g**, **2d** (400 MHZ, $CDCl_3$)



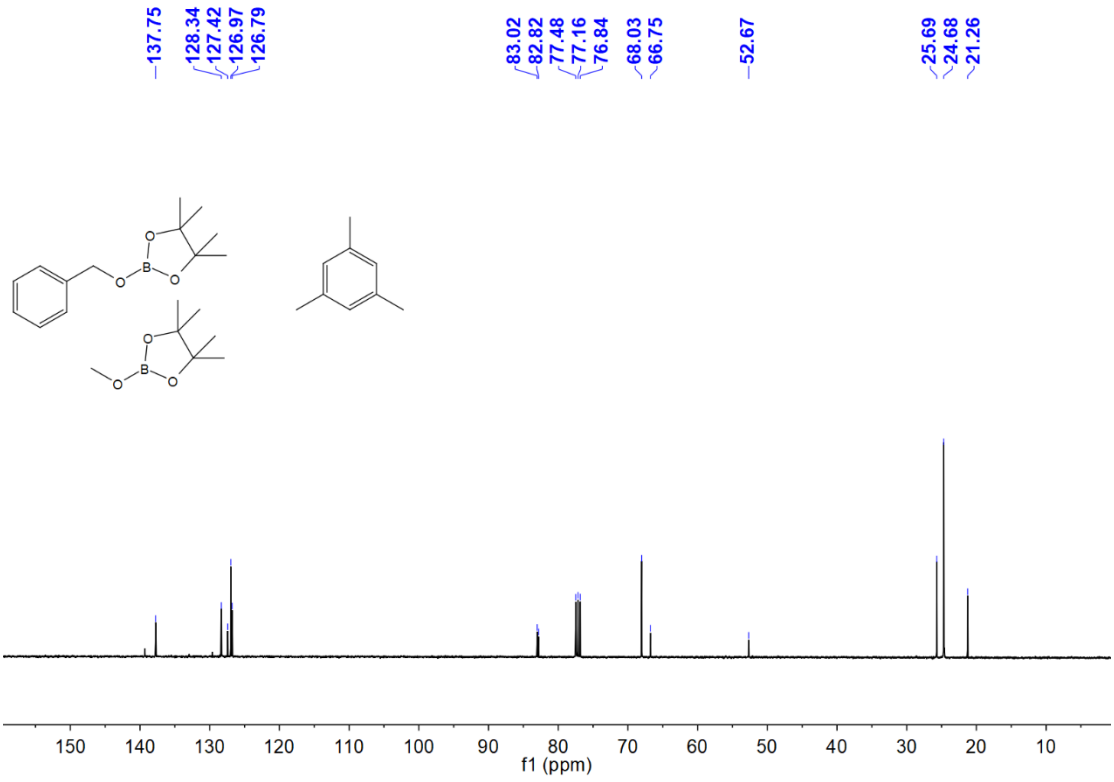
^{13}C NMR spectrum of product **2g**, **2d** (101 MHZ, $CDCl_3$)



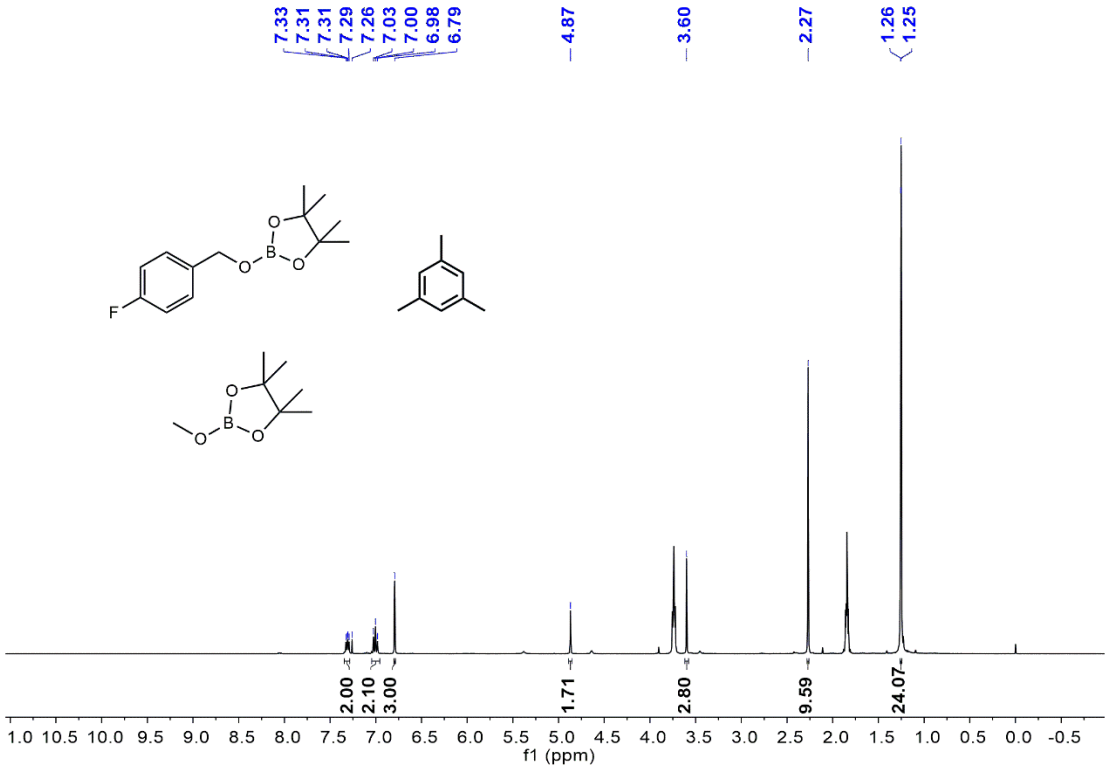
^{1}H NMR spectrum of product **2a**, **2h** (400 MHZ, $CDCl_3$)



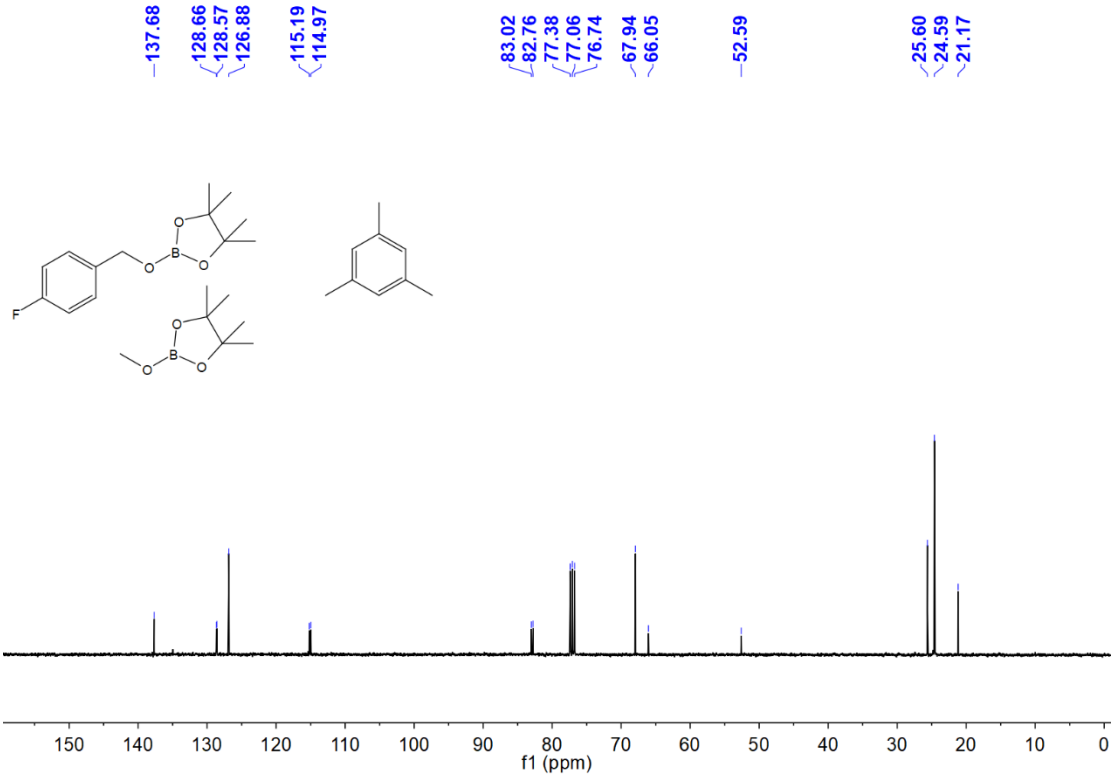
^{13}C NMR spectrum of product **2a**, **2h** (101 MHZ, $CDCl_3$)



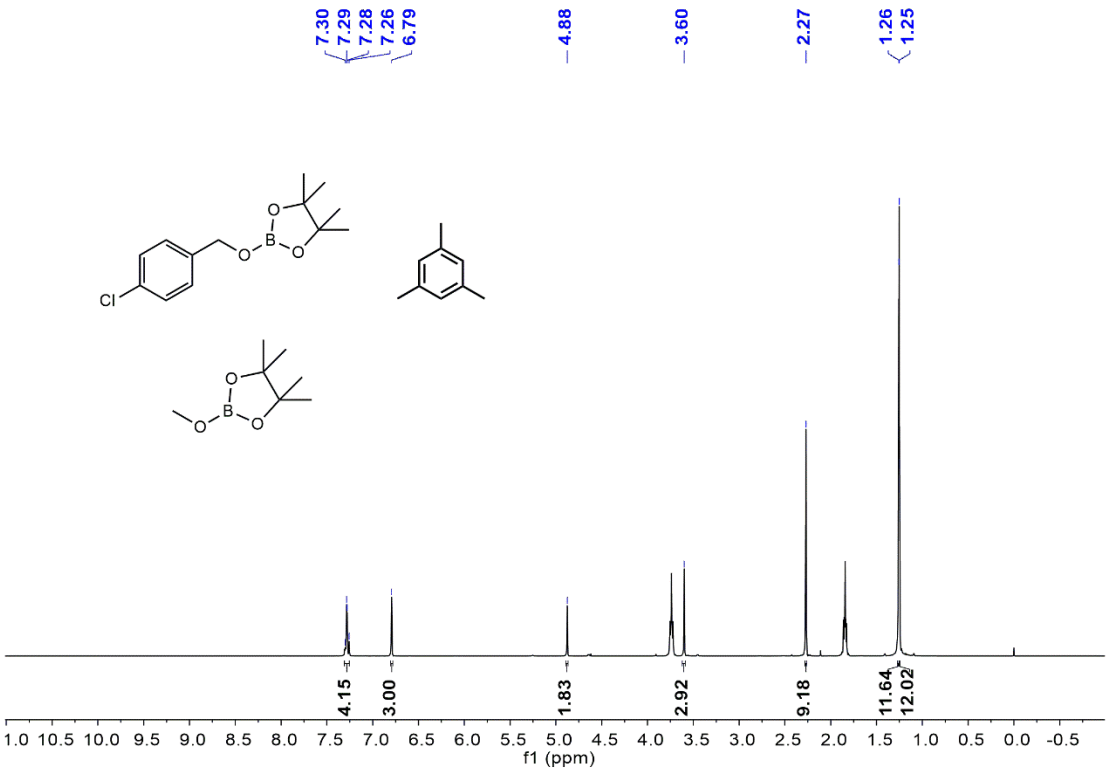
^{1}H NMR spectrum of product **2i**, **2h** (400 MHZ, $CDCl_3$)



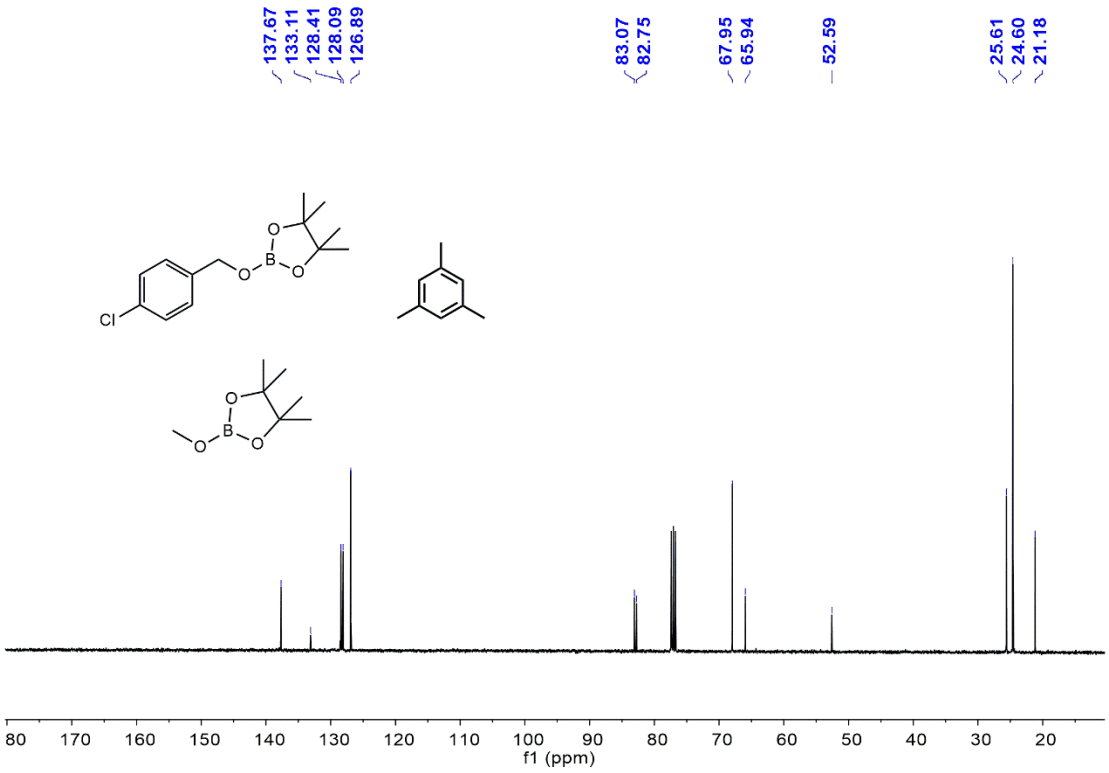
^{13}C NMR spectrum of product **2i**, **2h** (101 MHZ, $CDCl_3$)



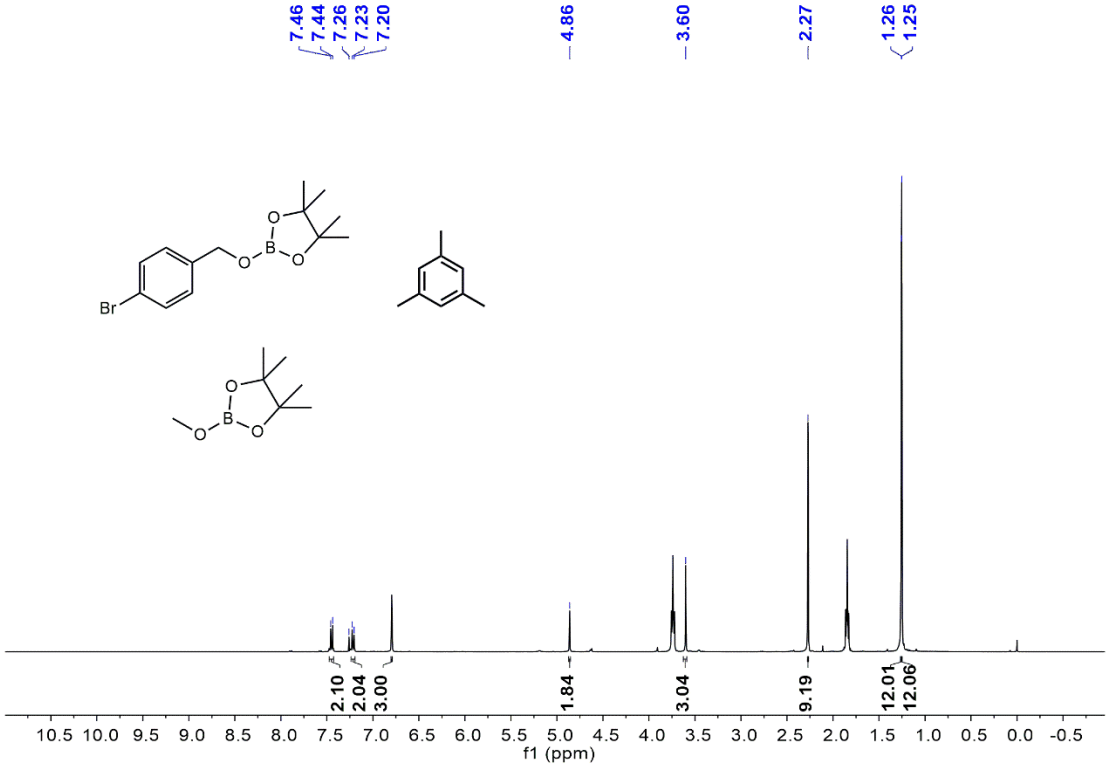
^{1}H NMR spectrum of product **2b**, **2h** (400 MHZ, $CDCl_3$)



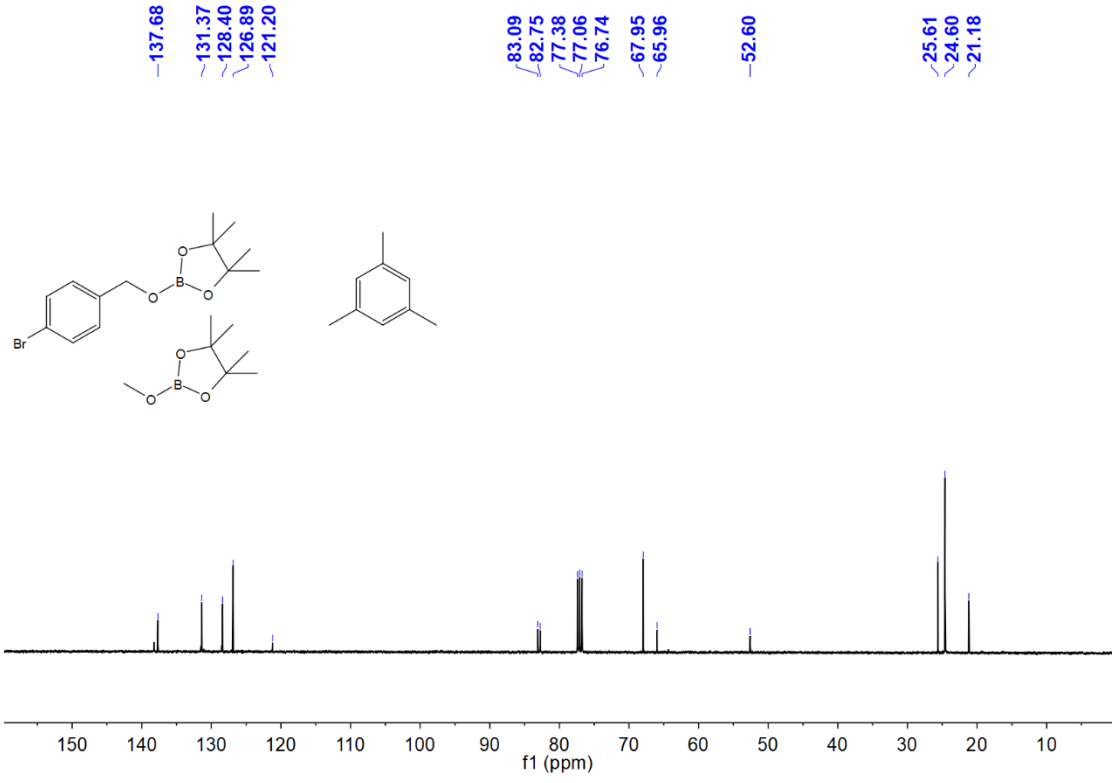
^{13}C NMR spectrum of product **2b**, **2h** (101 MHZ, $CDCl_3$)



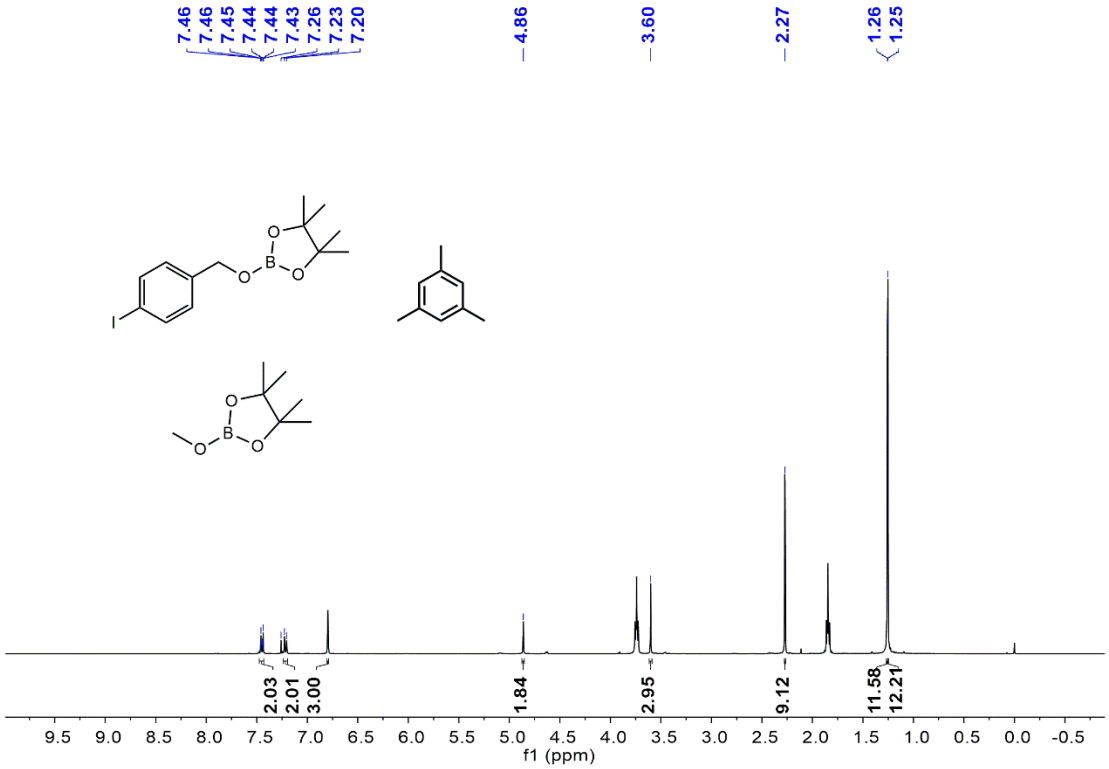
^{1}H NMR spectrum of product **2c**, **2h** (400 MHZ, $CDCl_3$)



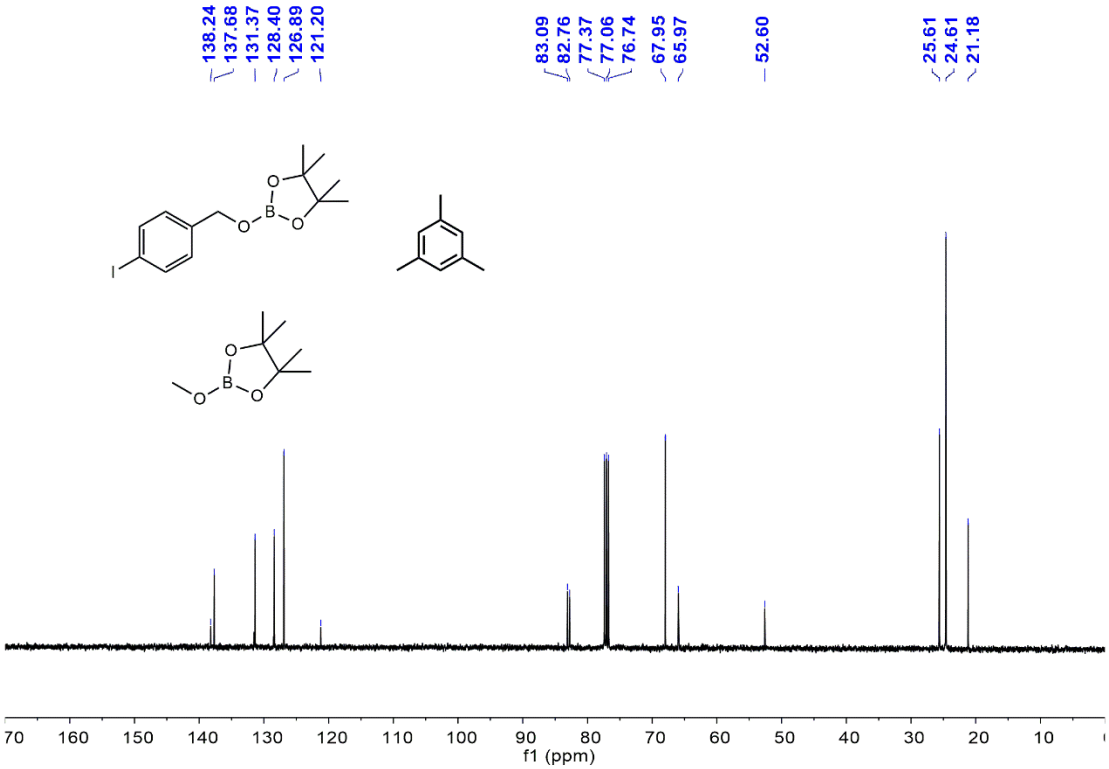
^{13}C NMR spectrum of product **2c**, **2h** (101 MHZ, $CDCl_3$)



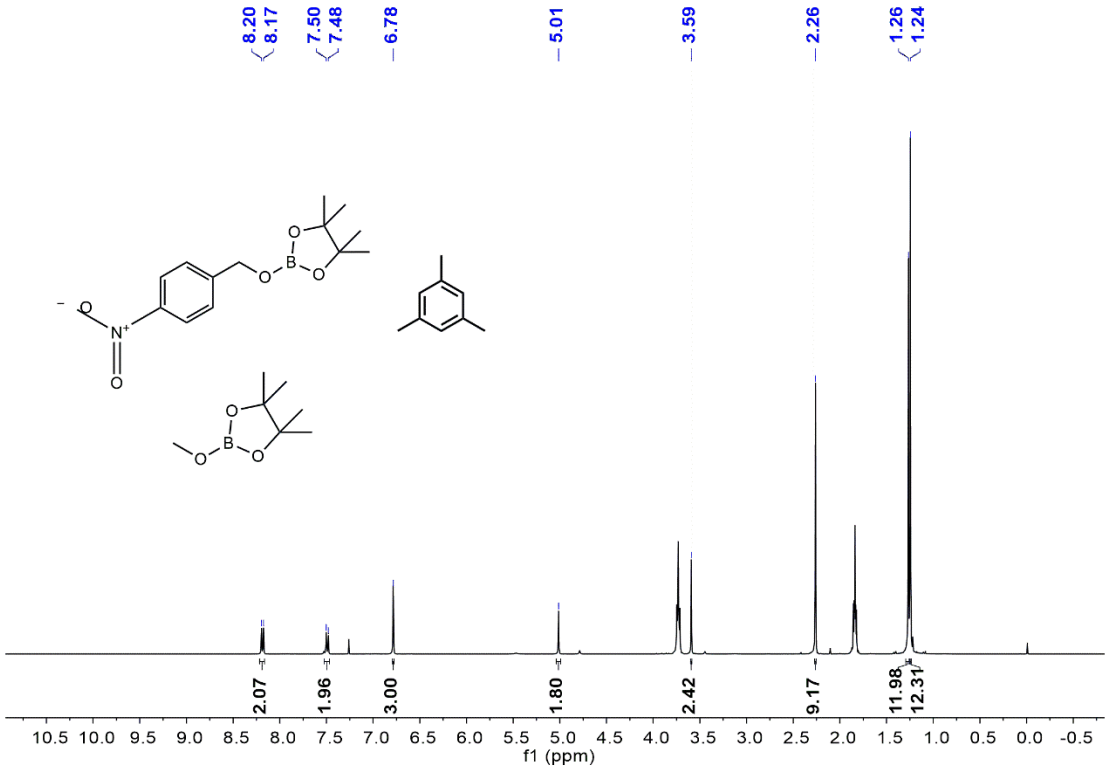
^{1}H NMR spectrum of product **2j**, **2h** (400 MHZ, $CDCl_3$)



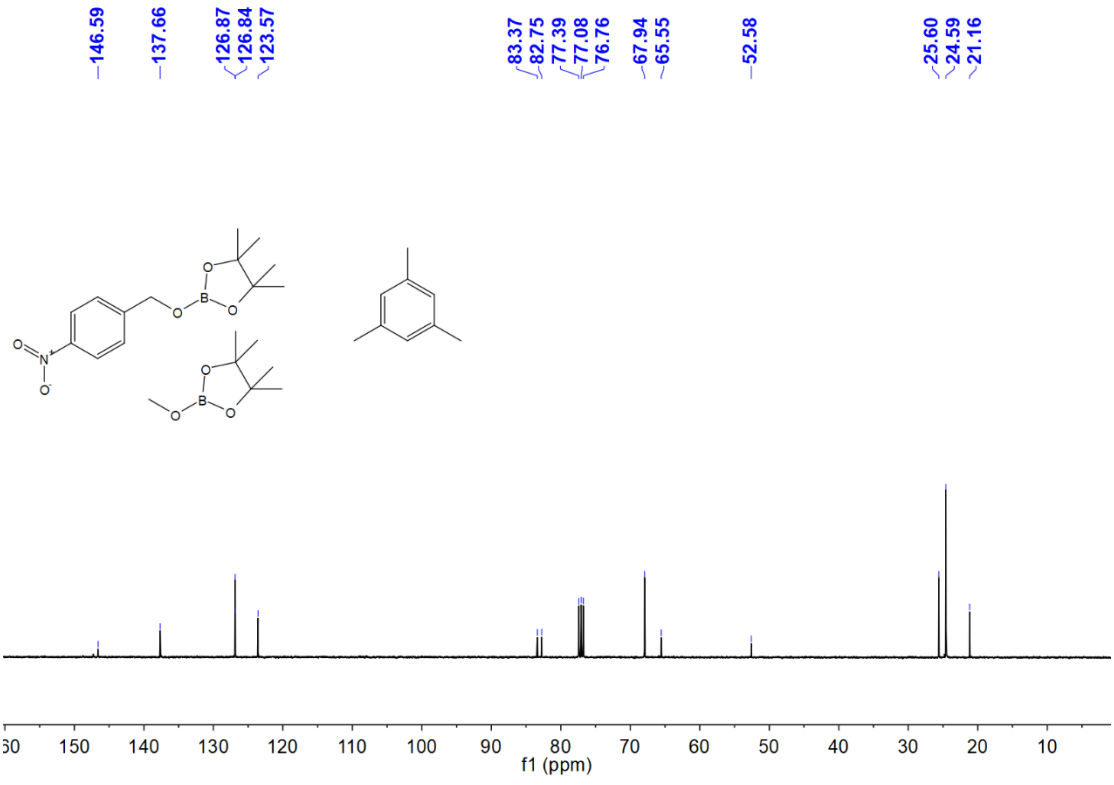
^{13}C NMR spectrum of product **2j**, **2h** (101 MHZ, $CDCl_3$)



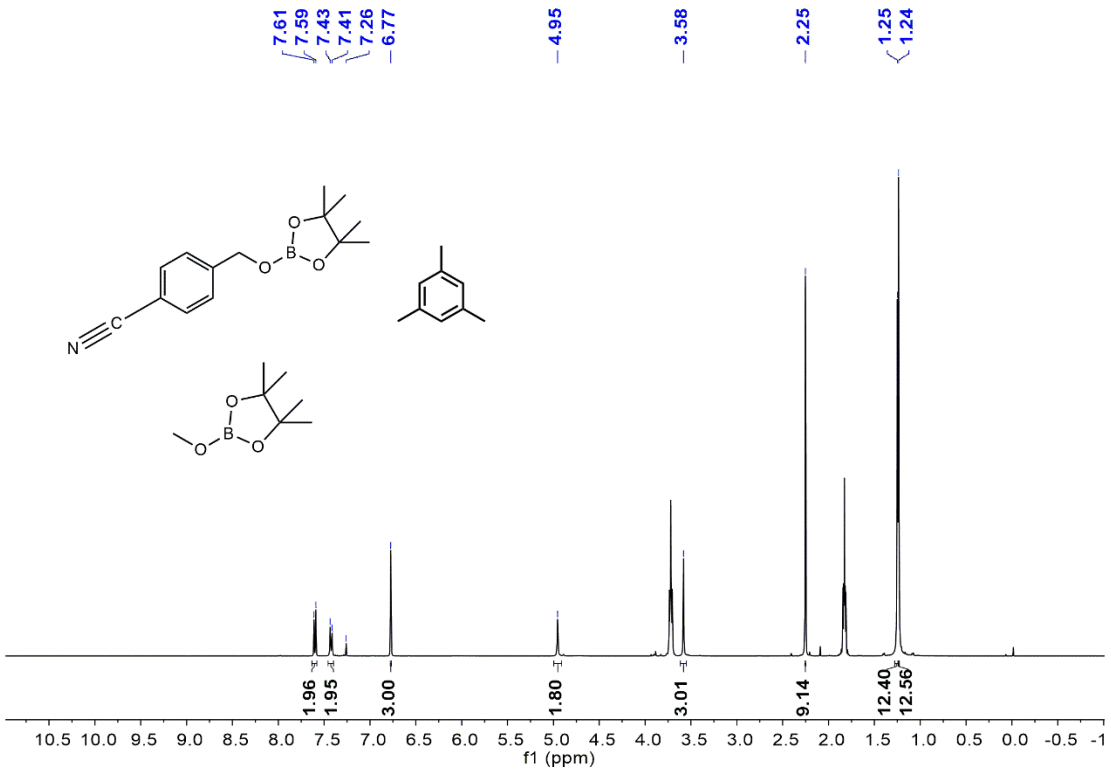
^{1}H NMR spectrum of product **2k**, **2h** (400 MHZ, $CDCl_3$)



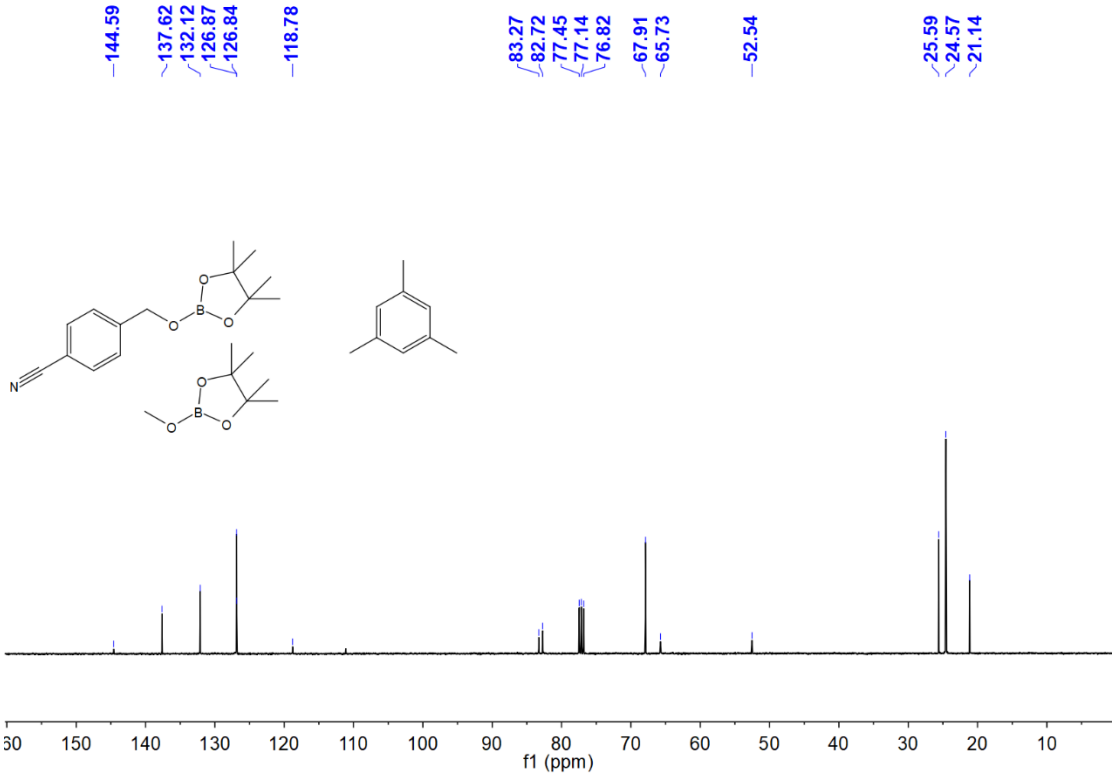
^{13}C NMR spectrum of product **2k**, **2h** (101 MHZ, $CDCl_3$)



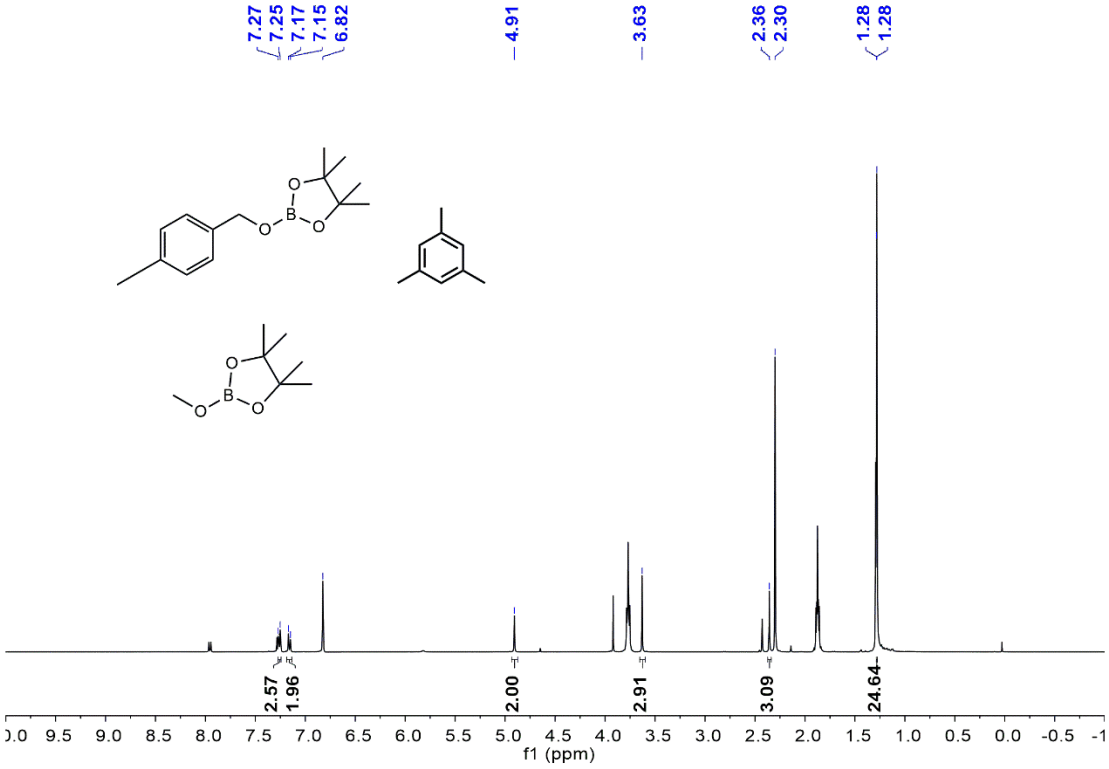
^{1}H NMR spectrum of product **2l**, **2h** (400 MHZ, $CDCl_3$)



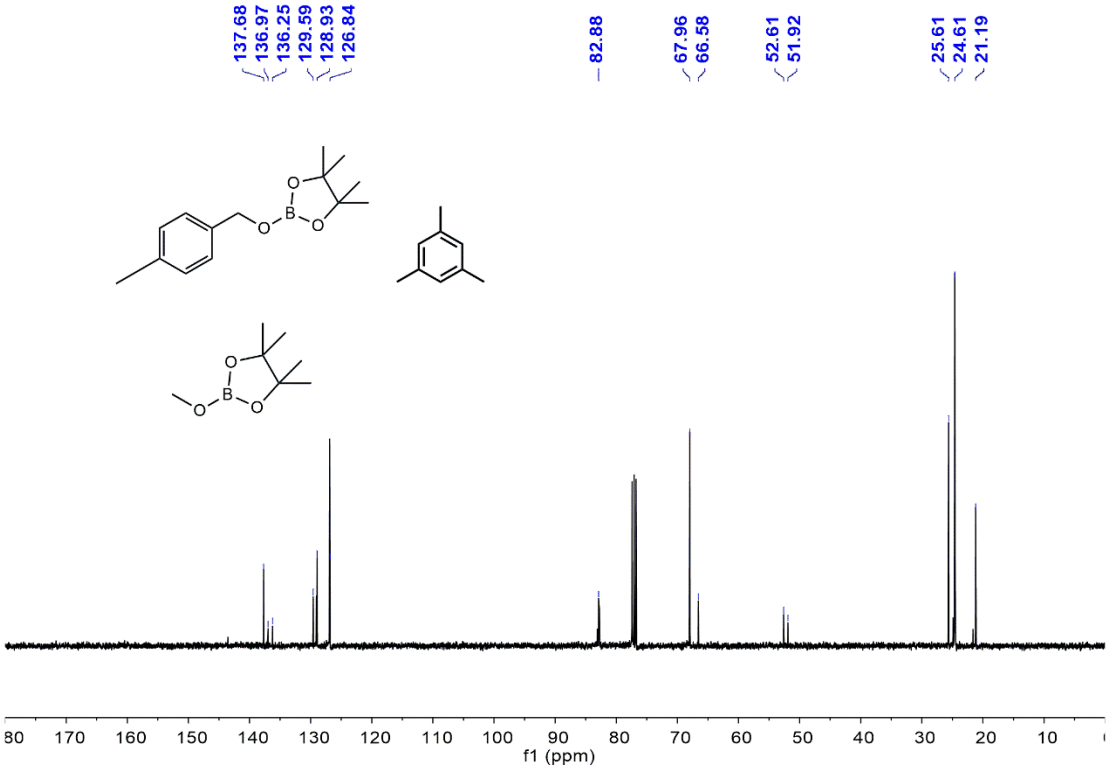
^{13}C NMR spectrum of product **2l**, **2h** (101 MHZ, $CDCl_3$)



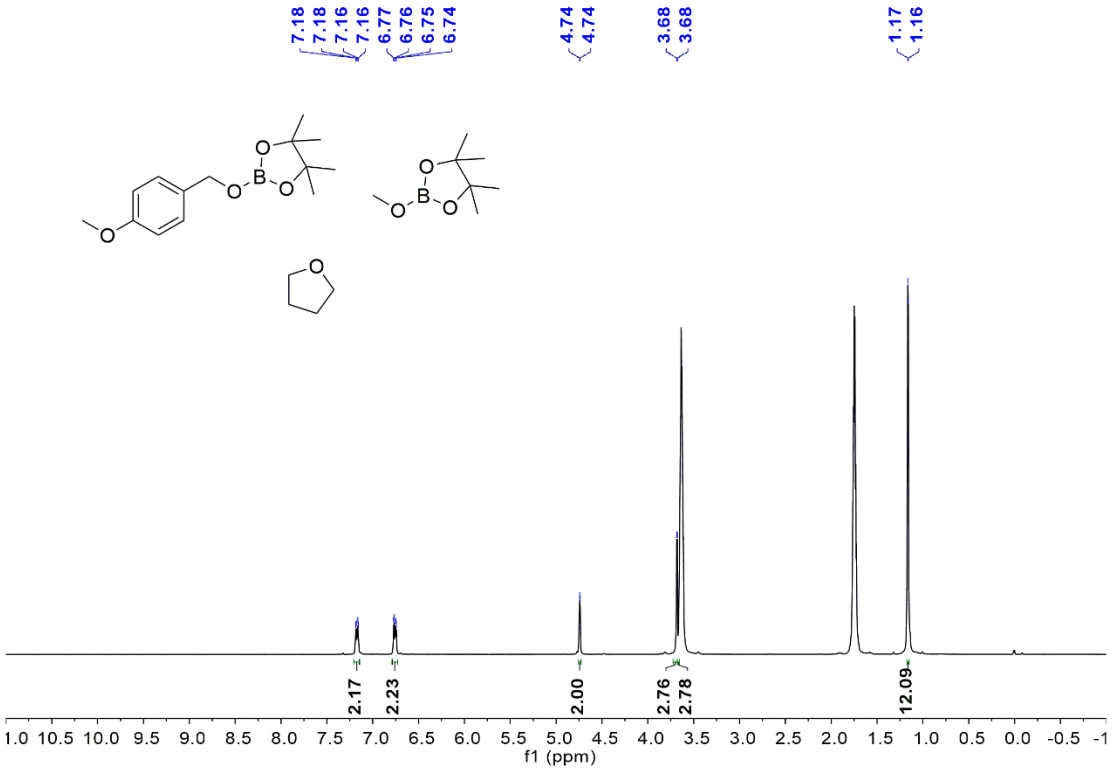
^{1}H NMR spectrum of product **2m**, **2h** (400 MHZ, $CDCl_3$)



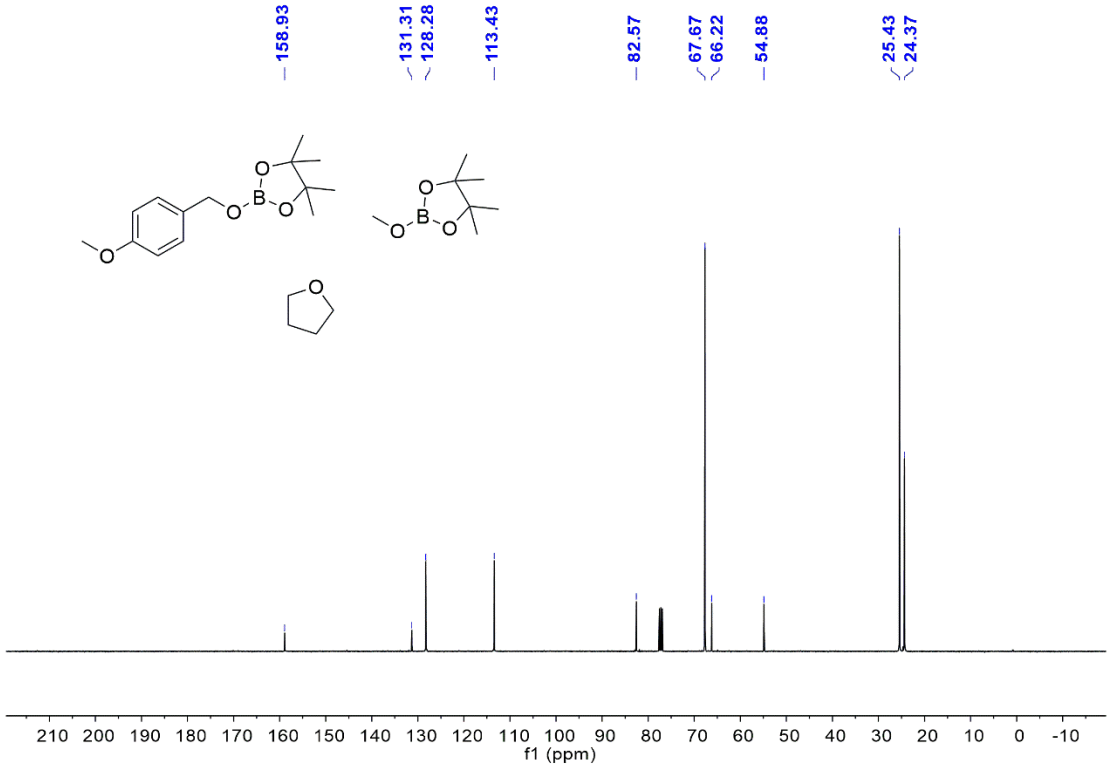
^{13}C NMR spectrum of product **2m**, **2h** (101 MHZ, $CDCl_3$)



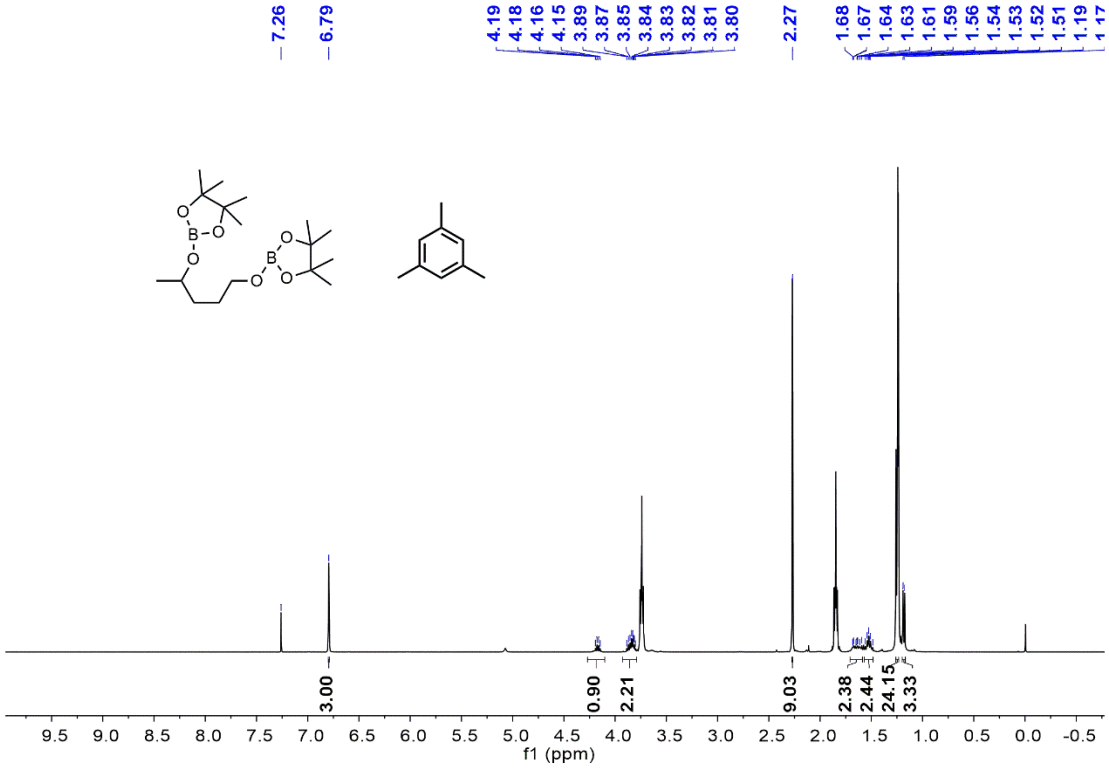
^{1}H NMR spectrum of product **2n**, **2h** (400 MHZ, $CDCl_3$)



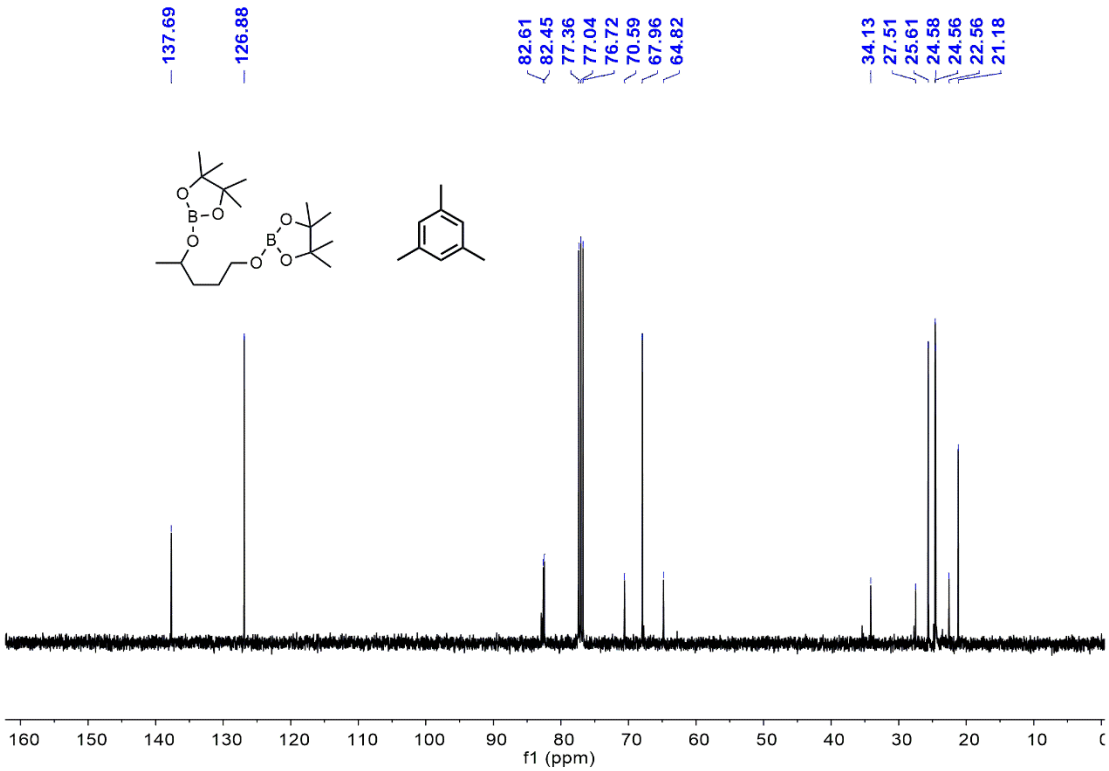
^{13}C NMR spectrum of product **2n**, **2h** (101 MHZ, $CDCl_3$)



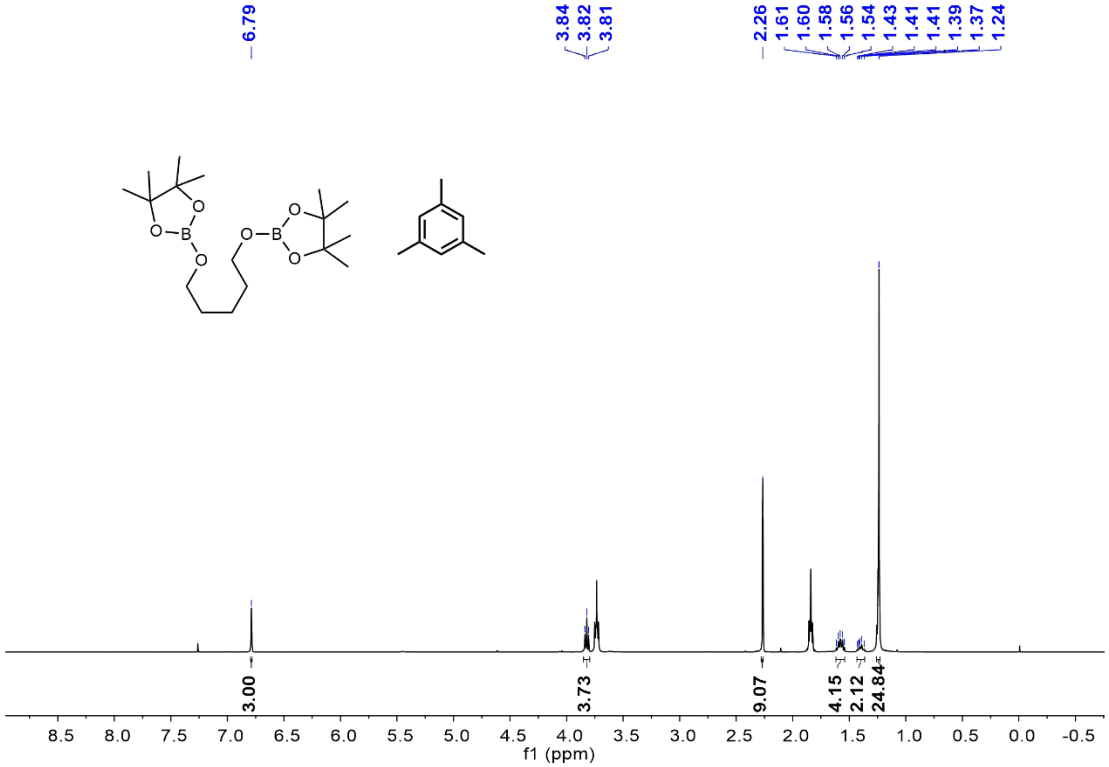
^{1}H NMR spectrum of product **2o** (400 MHZ, $CDCl_3$)



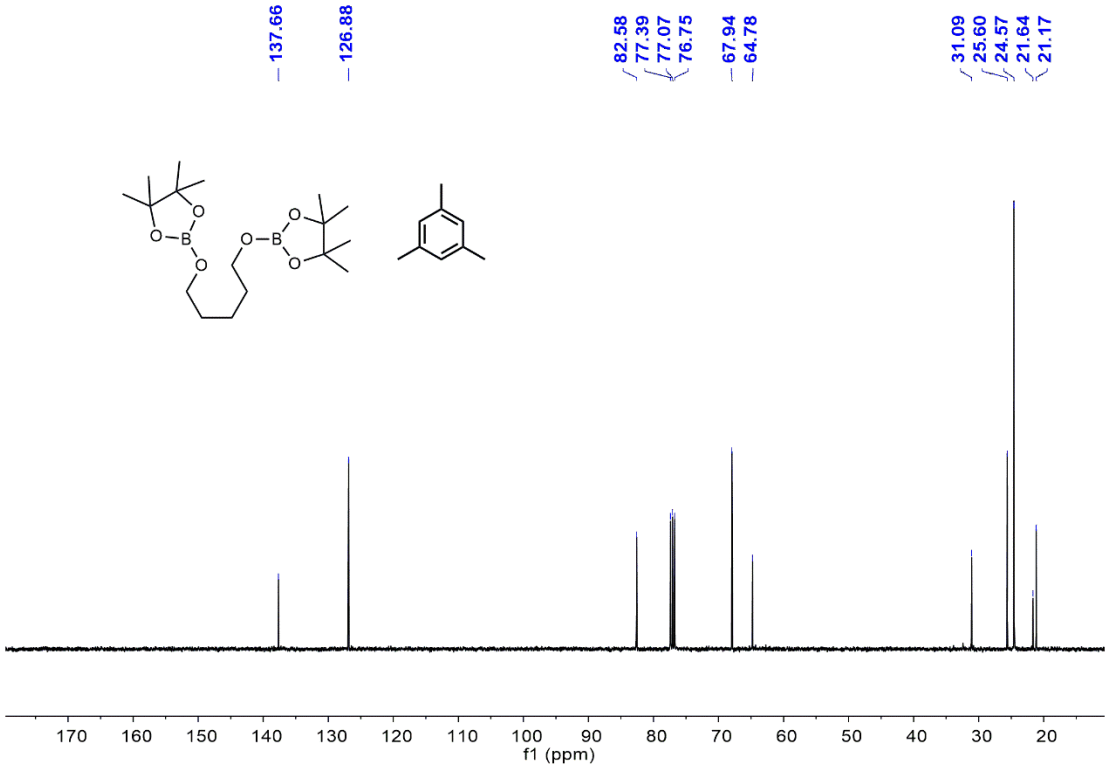
^{13}C NMR spectrum of product **2o** (101 MHZ, $CDCl_3$)



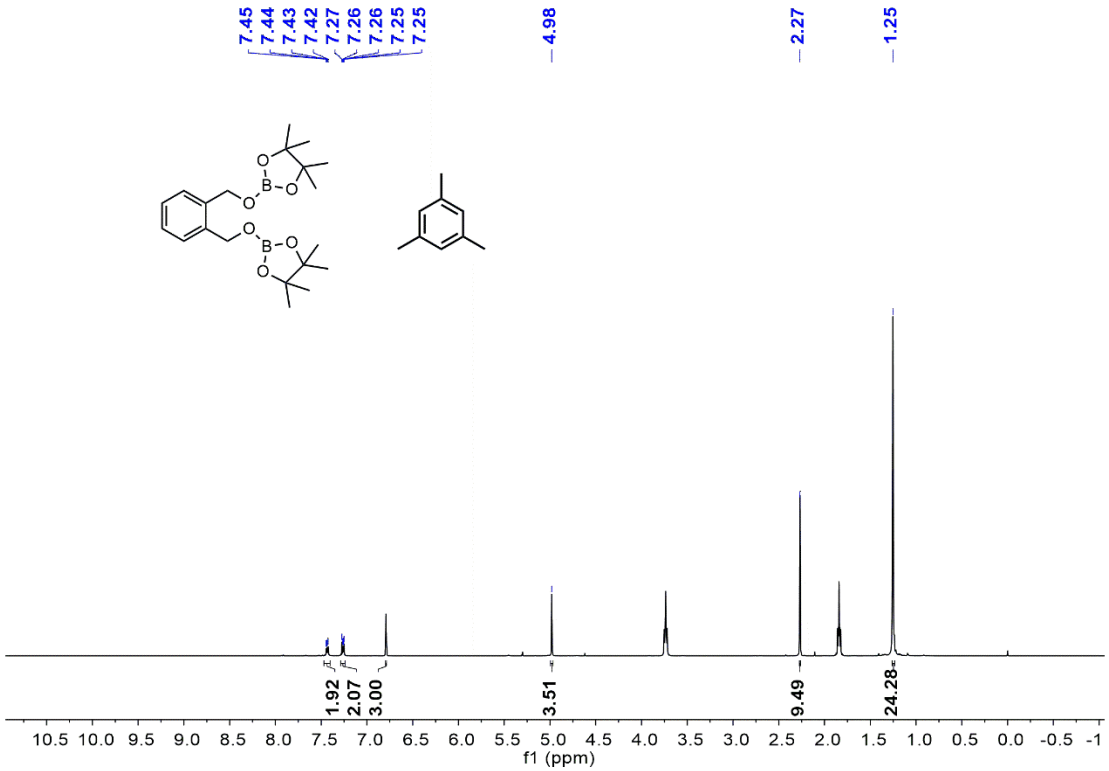
^{1}H NMR spectrum of product **2p** (400 MHZ, $CDCl_3$)



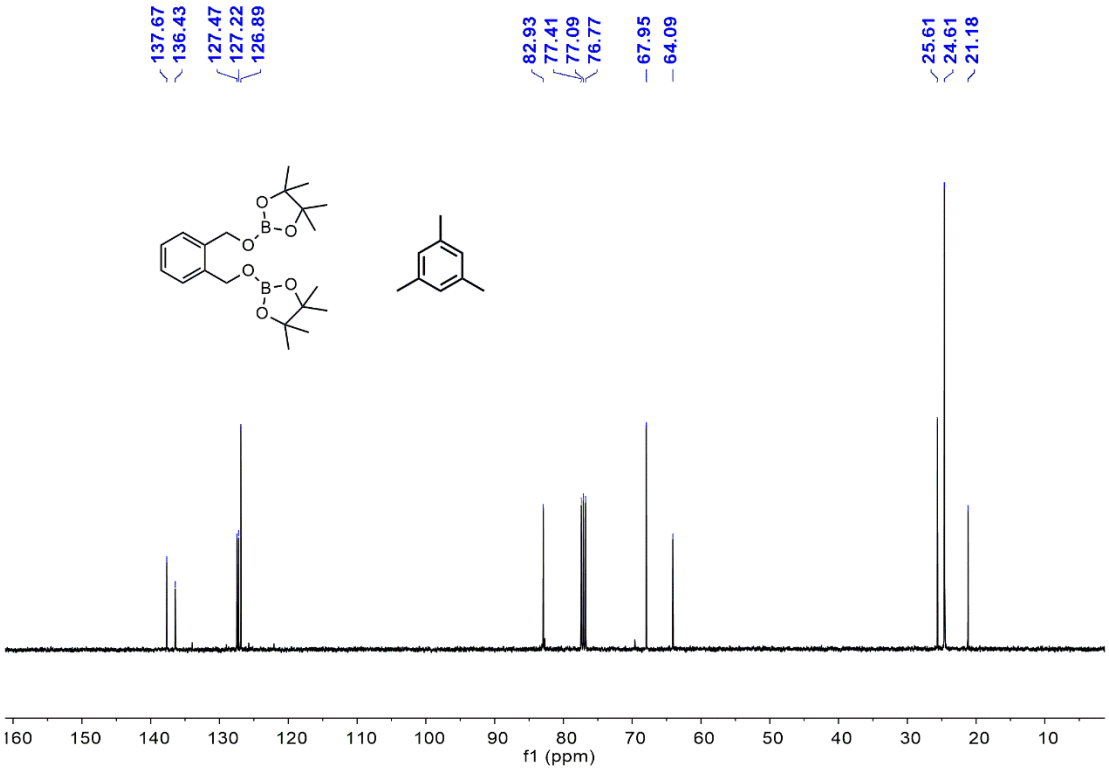
^{13}C NMR spectrum of product **2p** (101 MHZ, $CDCl_3$)



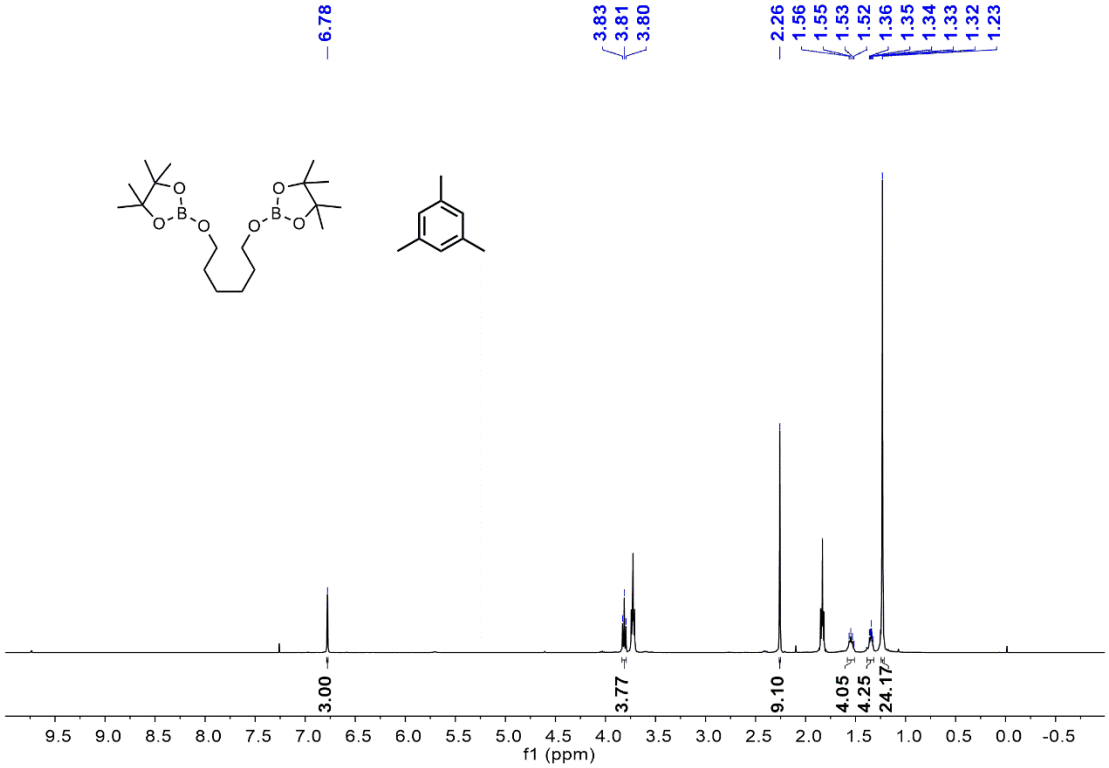
^{1}H NMR spectrum of product **2q** (400 MHZ, $CDCl_3$)



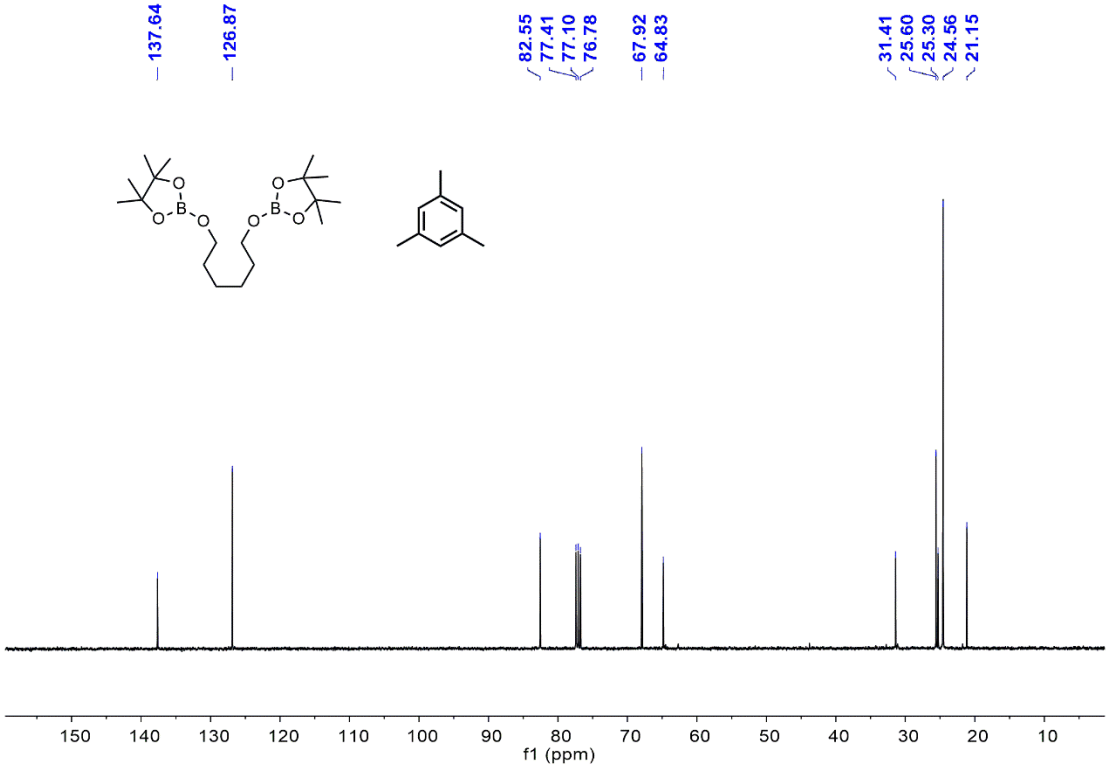
^{13}C NMR spectrum of product **2q** (101 MHZ, $CDCl_3$)



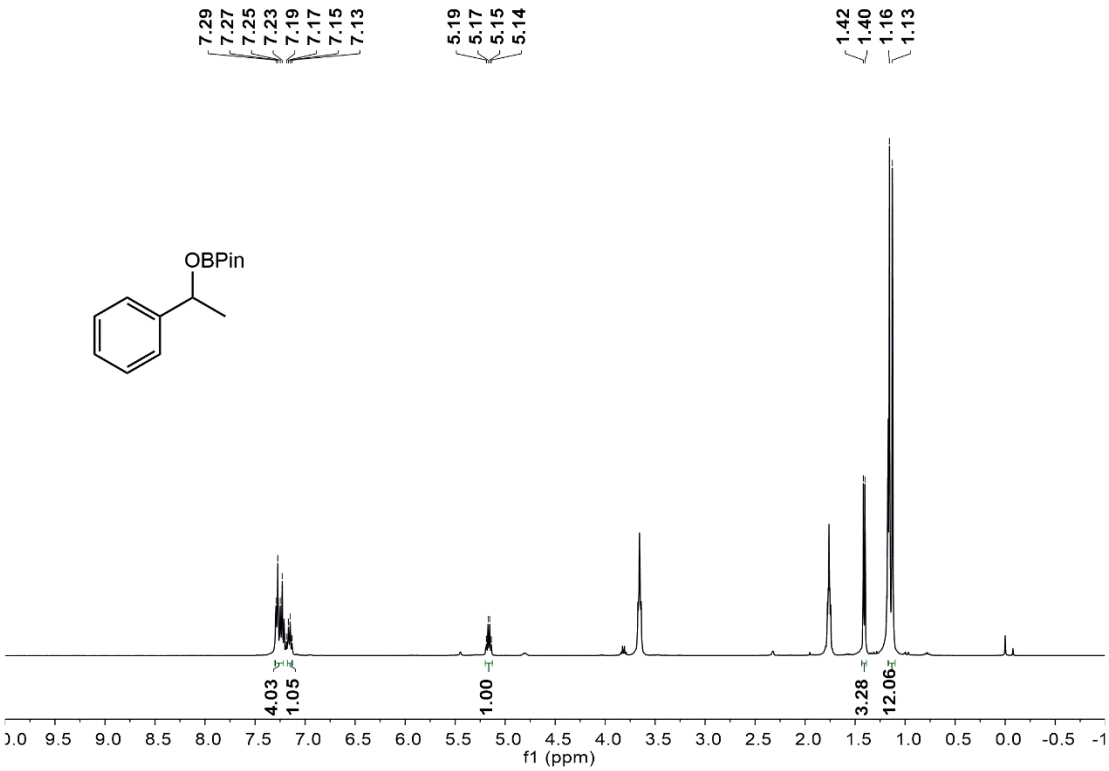
^{1}H NMR spectrum of product **2r** (400 MHZ, $CDCl_3$)



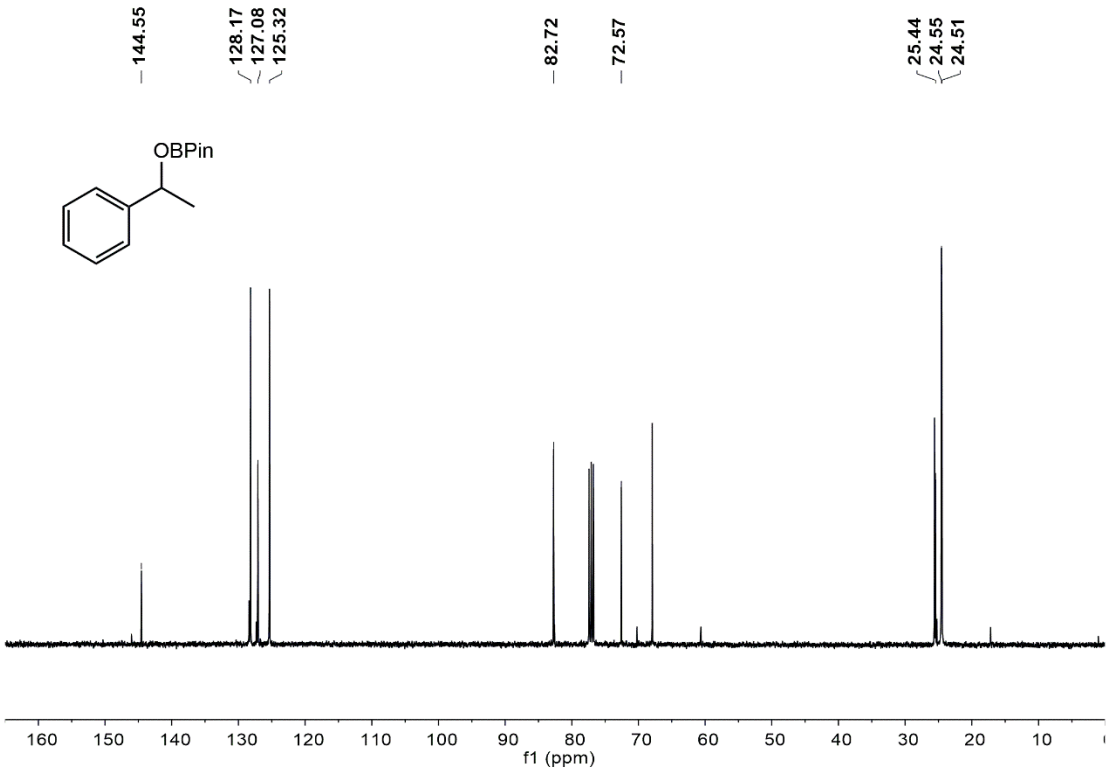
^{13}C NMR spectrum of product **2r** (101 MHZ, $CDCl_3$)



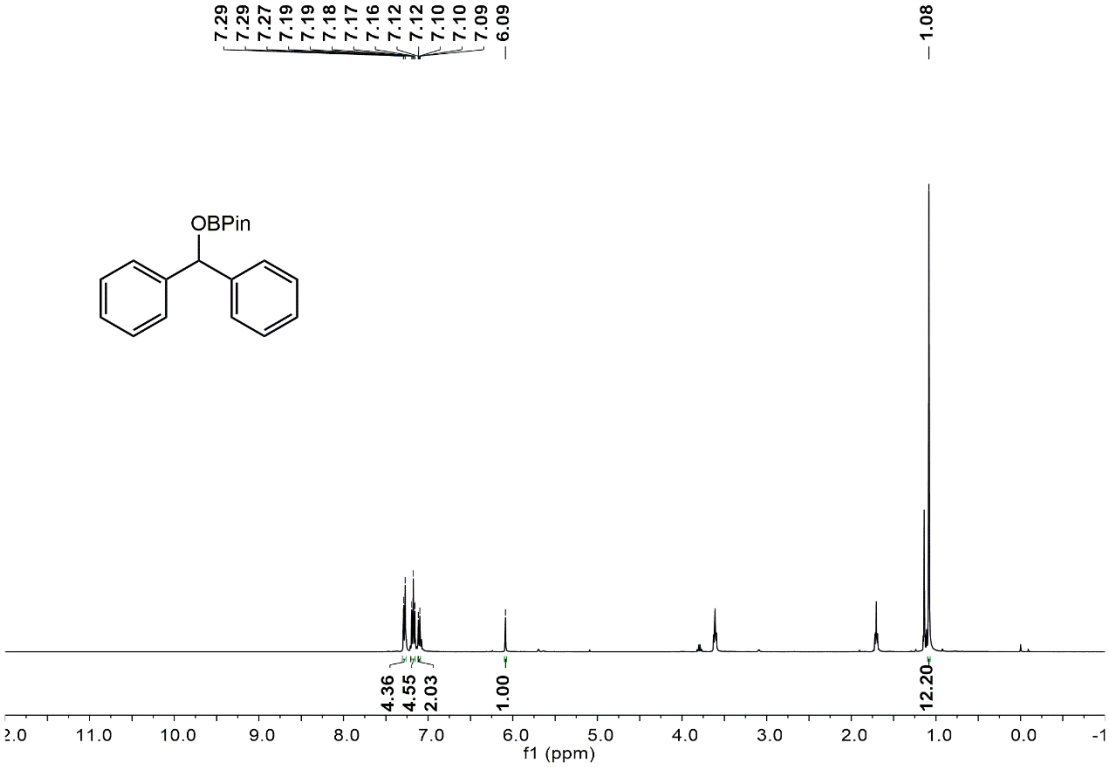
^{1}H NMR spectrum of product **2s** (400 MHZ, $CDCl_3$)



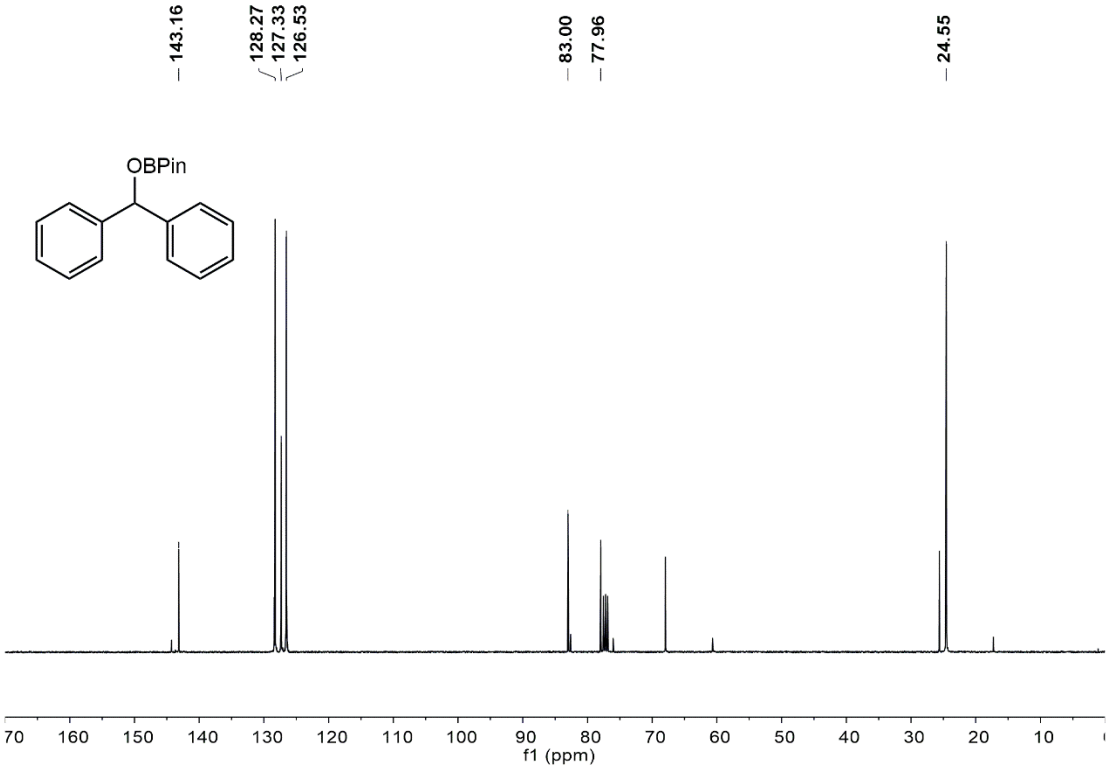
^{13}C NMR spectrum of product **2s** (101 MHZ, $CDCl_3$)\



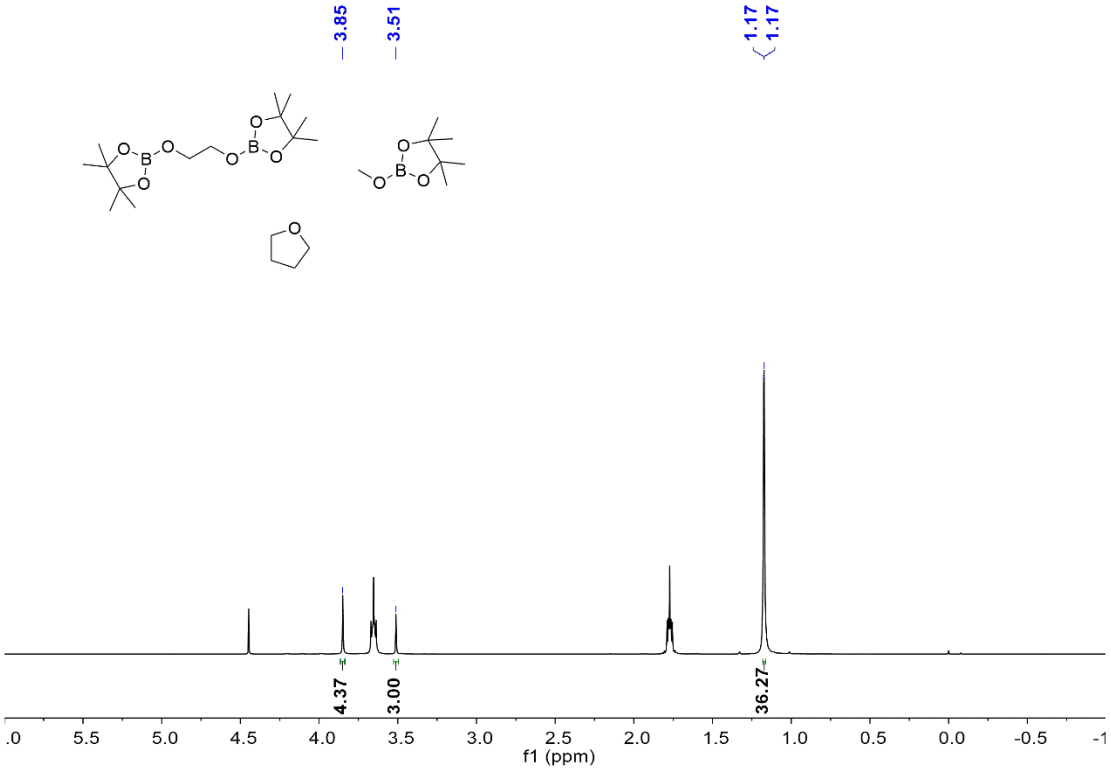
^{1}H NMR spectrum of product **2t** (400 MHZ, $CDCl_3$)



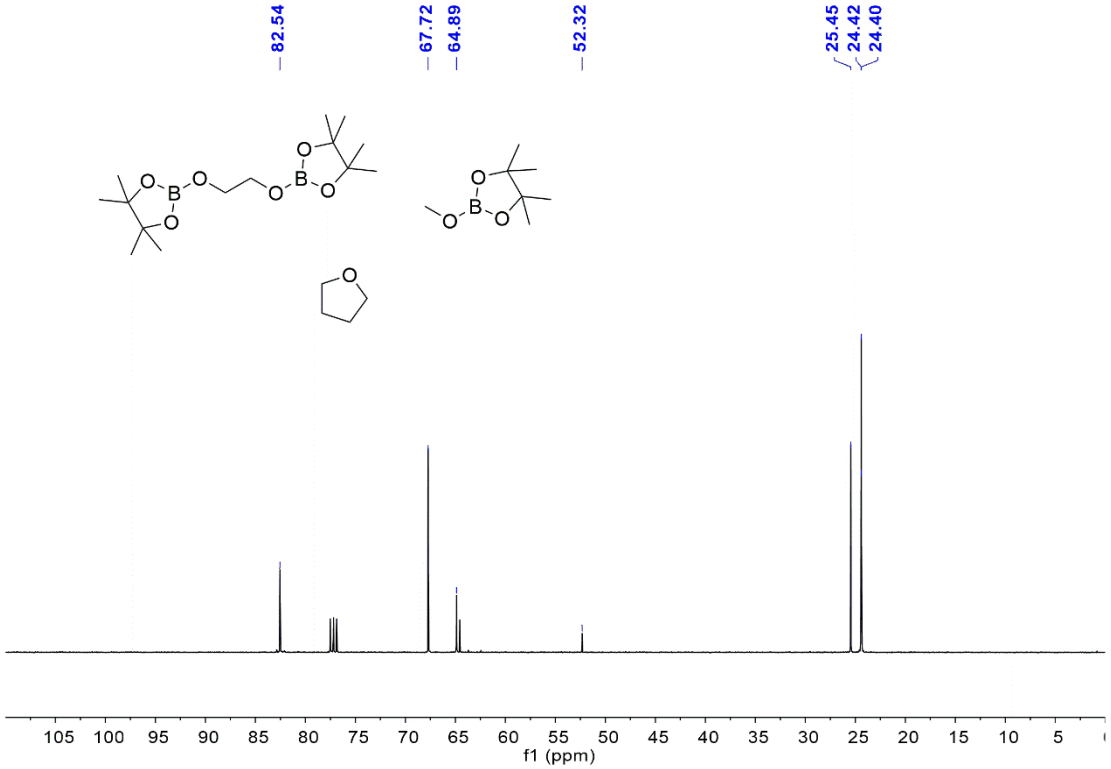
^{13}C NMR spectrum of product **2t** (101 MHZ, $CDCl_3$)



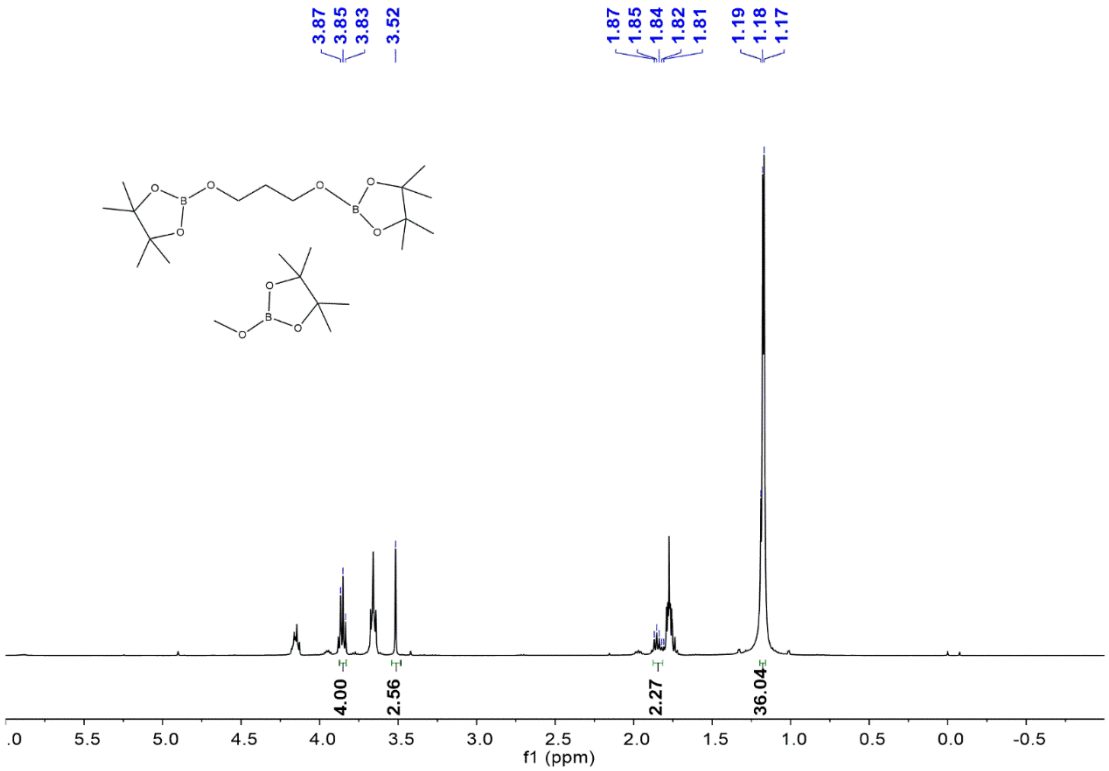
^{1}H NMR spectrum of product **2u**, **2h** (400 MHZ, $CDCl_3$)



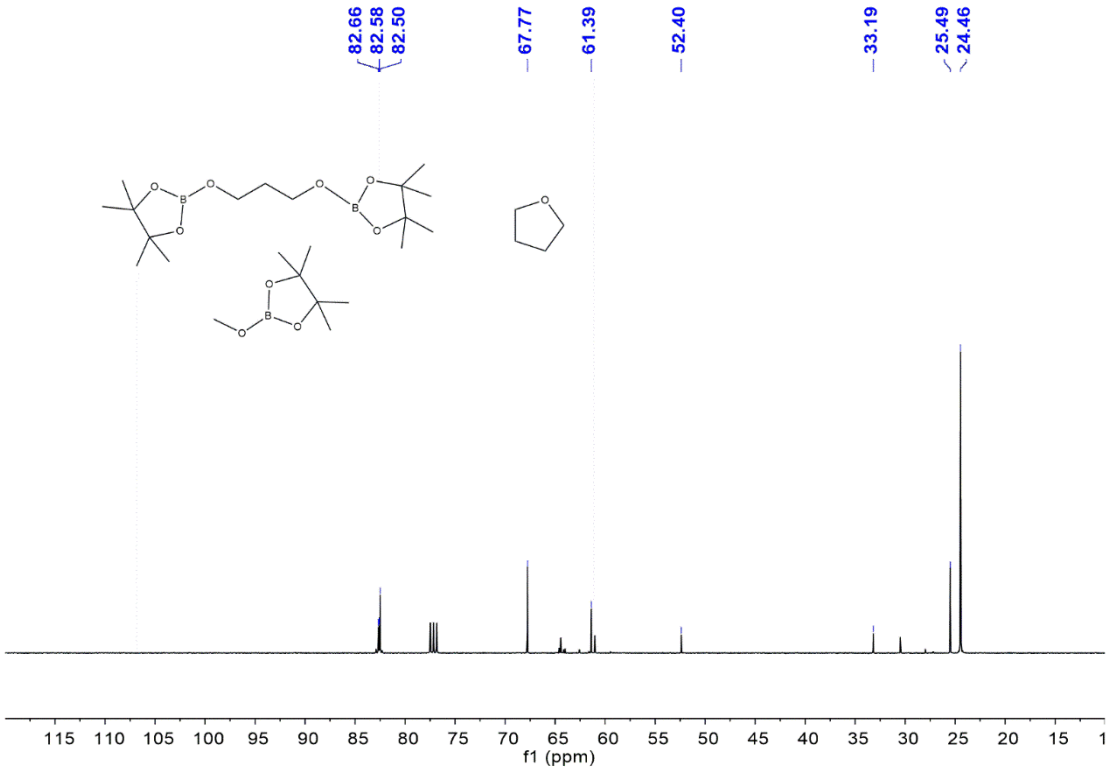
^{13}C NMR spectrum of product **2u**, **2h** (101 MHZ, $CDCl_3$)



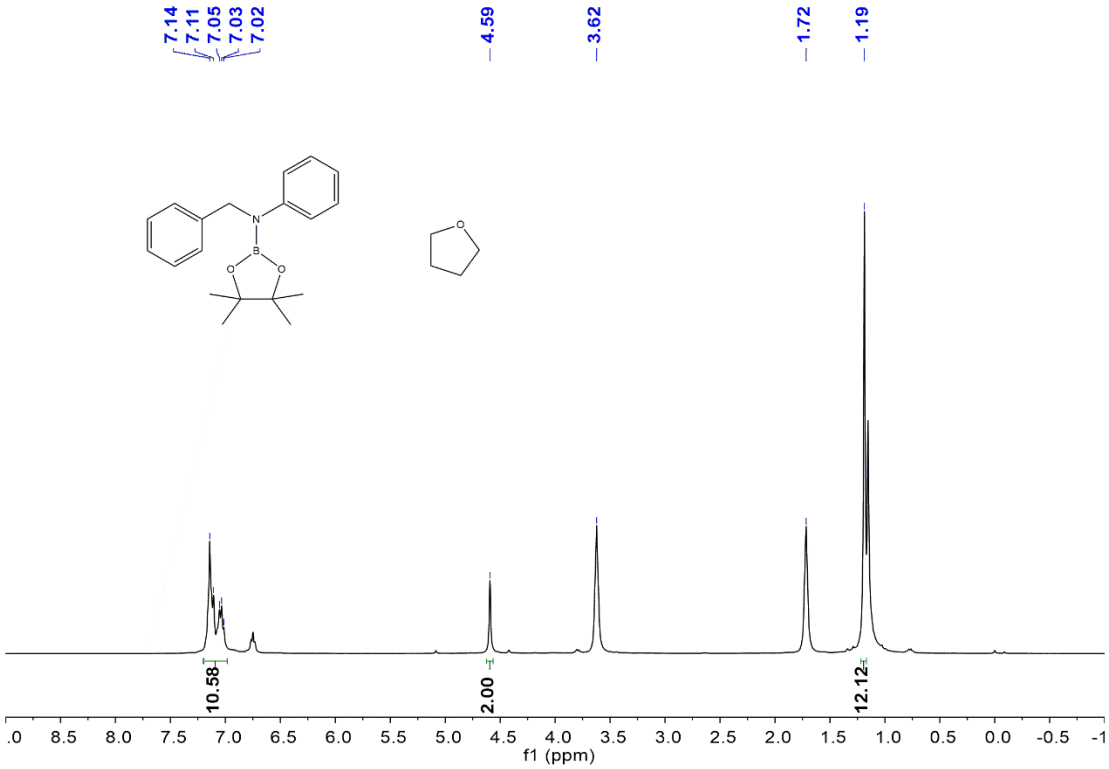
^{1}H NMR spectrum of product **2v**, **2h** (400 MHZ, $CDCl_3$)



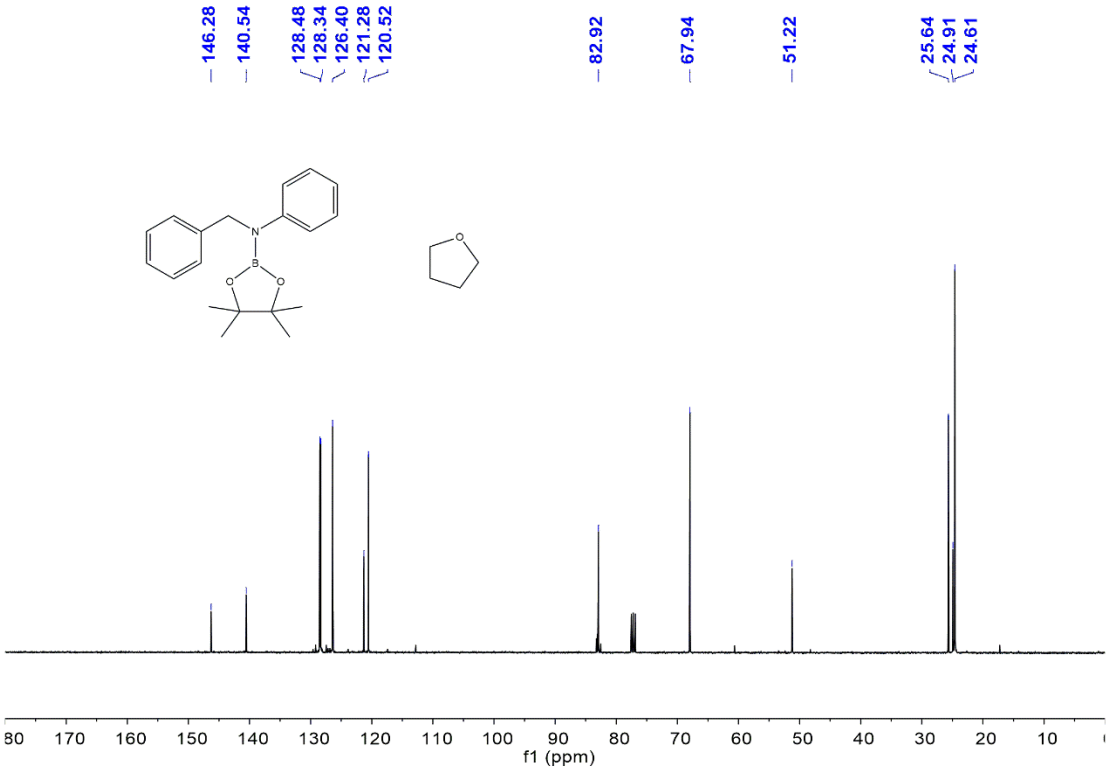
^{13}C NMR spectrum of product **2v**, **2h** (101 MHZ, $CDCl_3$)



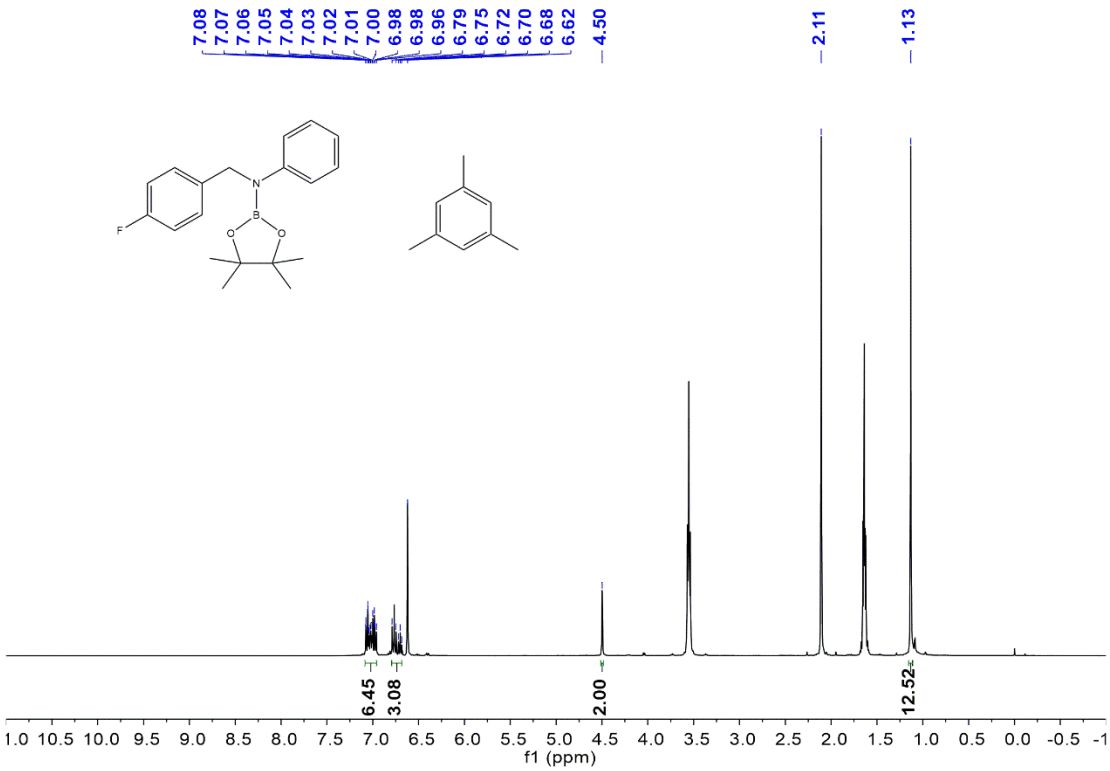
^{1}H NMR spectrum of product **5a** (400 MHZ, $CDCl_3$)



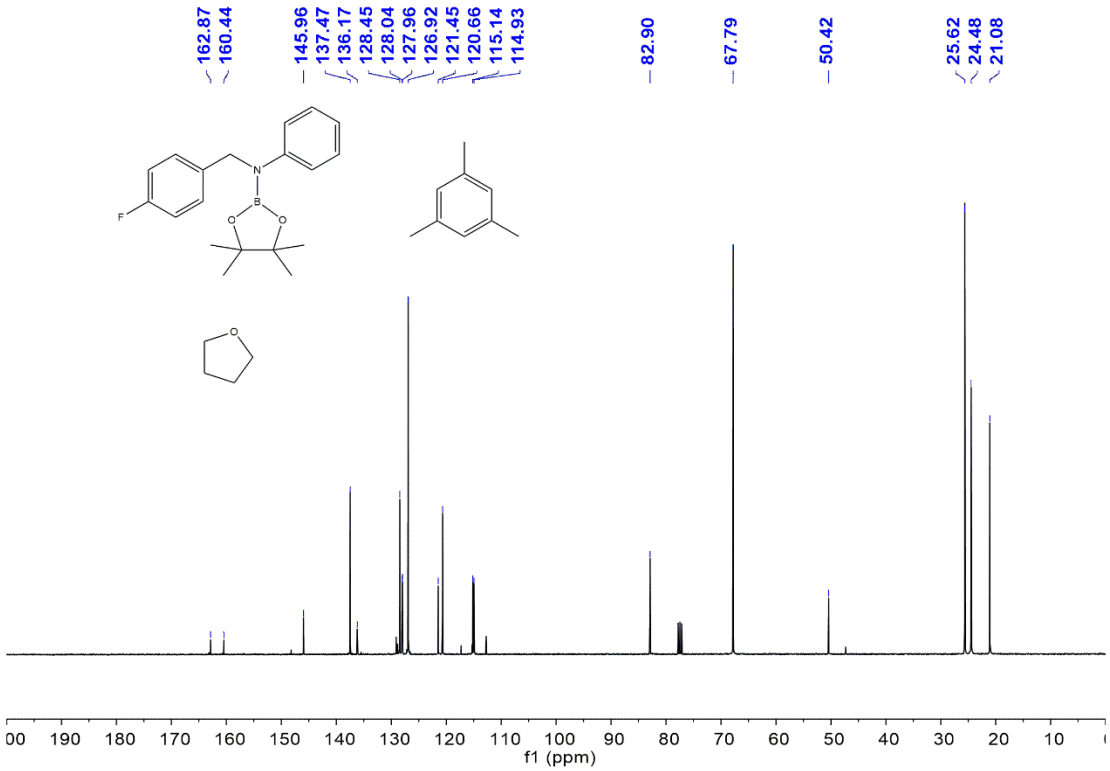
^{13}C NMR spectrum of product **5a** (101 MHZ, $CDCl_3$)



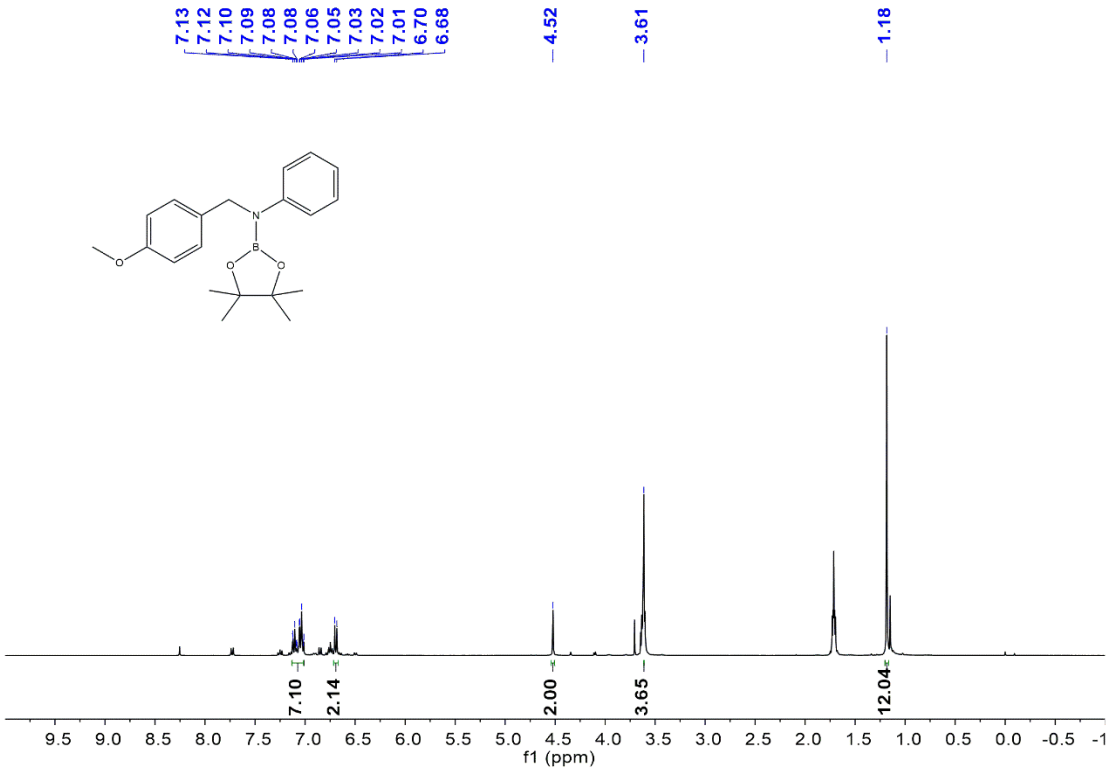
^{1}H NMR spectrum of product **5b** (400 MHZ, $CDCl_3$)



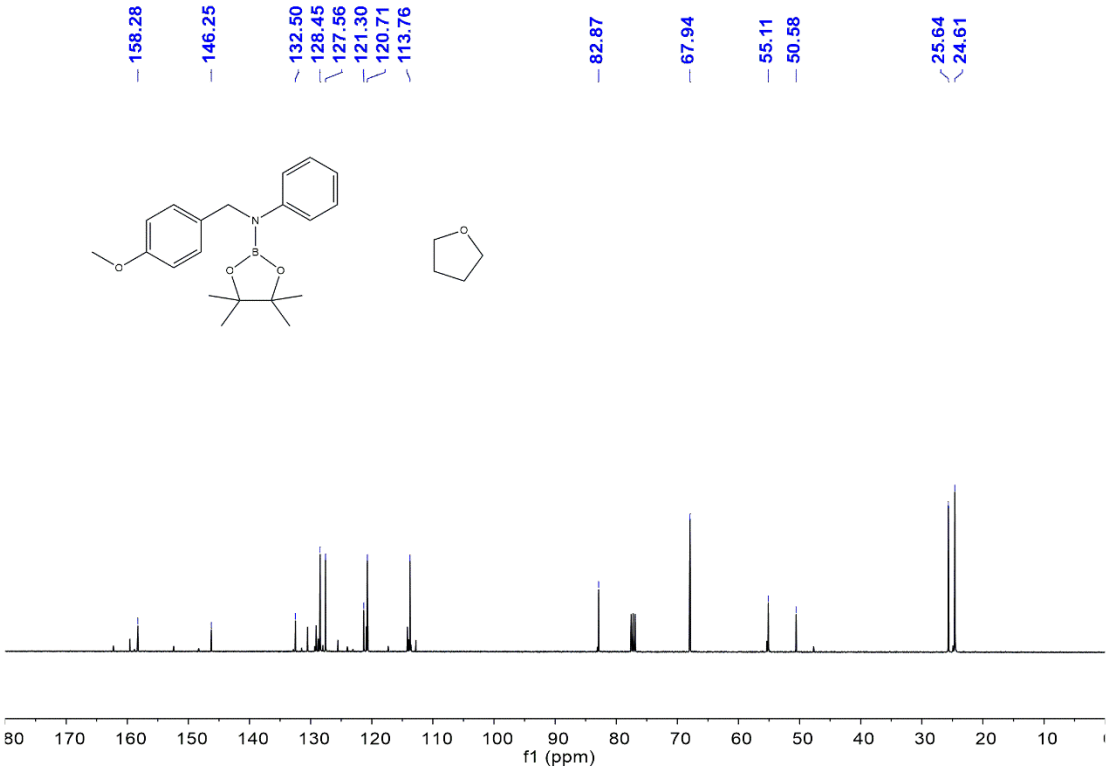
^{13}C NMR spectrum of product **5b** (101 MHZ, $CDCl_3$)



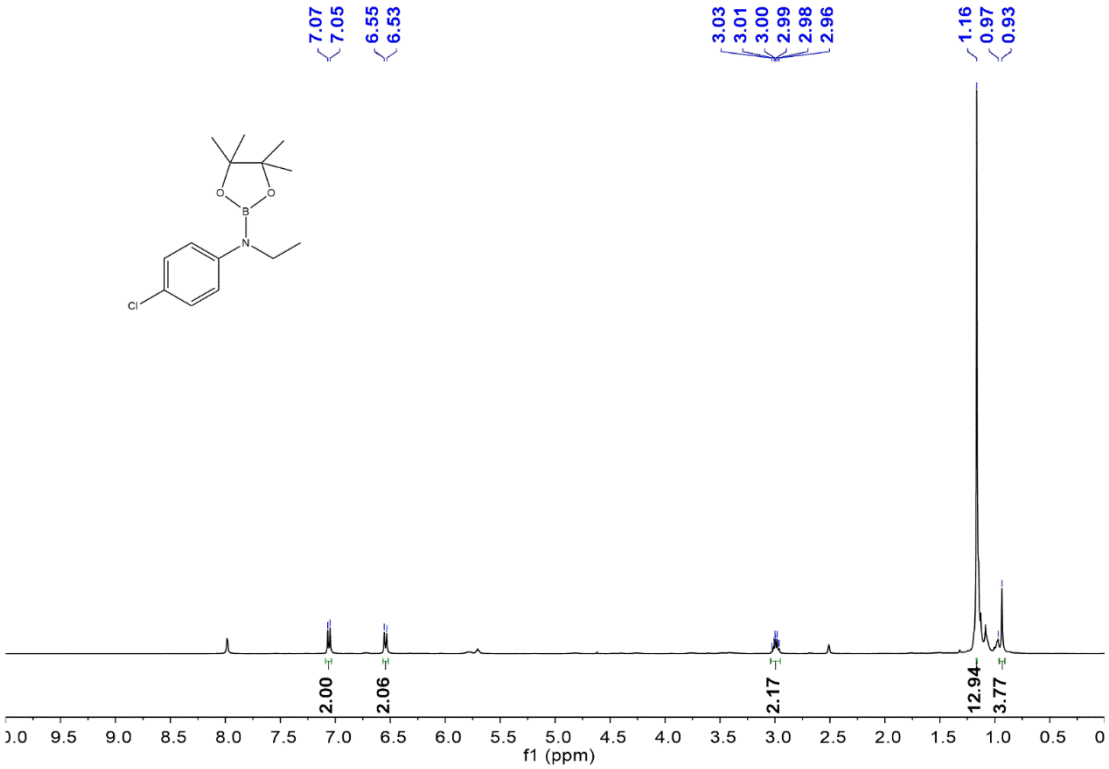
^{1}H NMR spectrum of product **5c** (400 MHZ, $CDCl_3$)



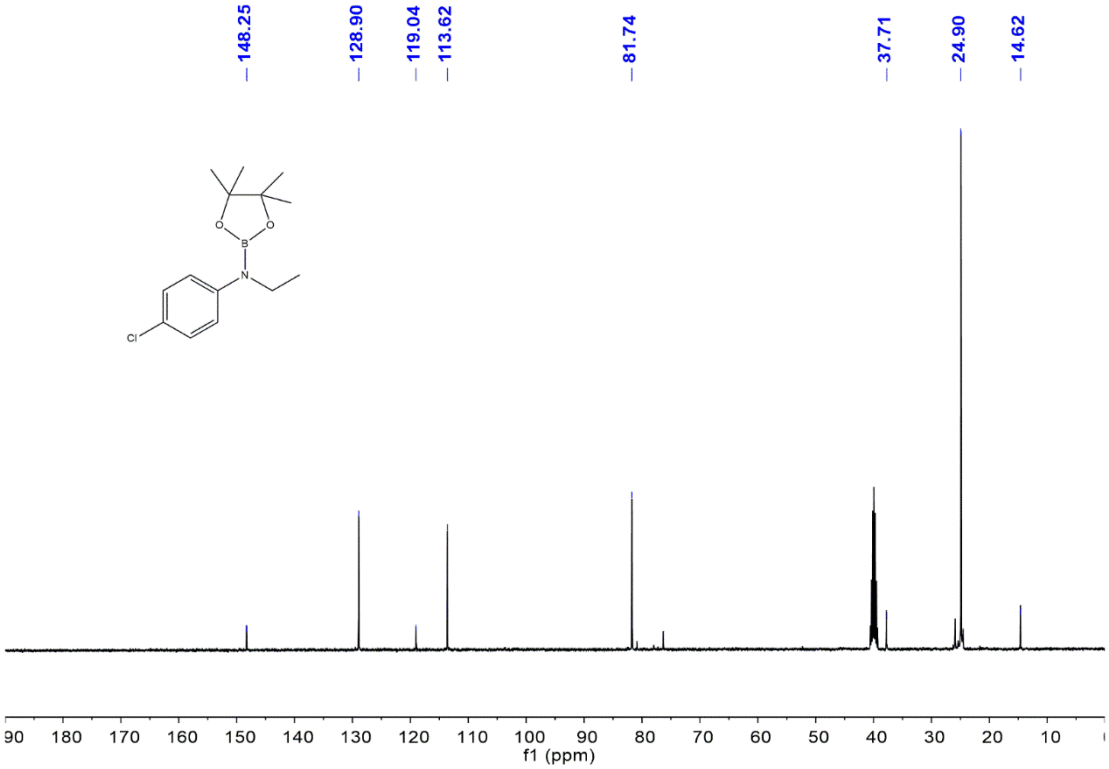
^{13}C NMR spectrum of product **5c** (101 MHZ, $CDCl_3$)



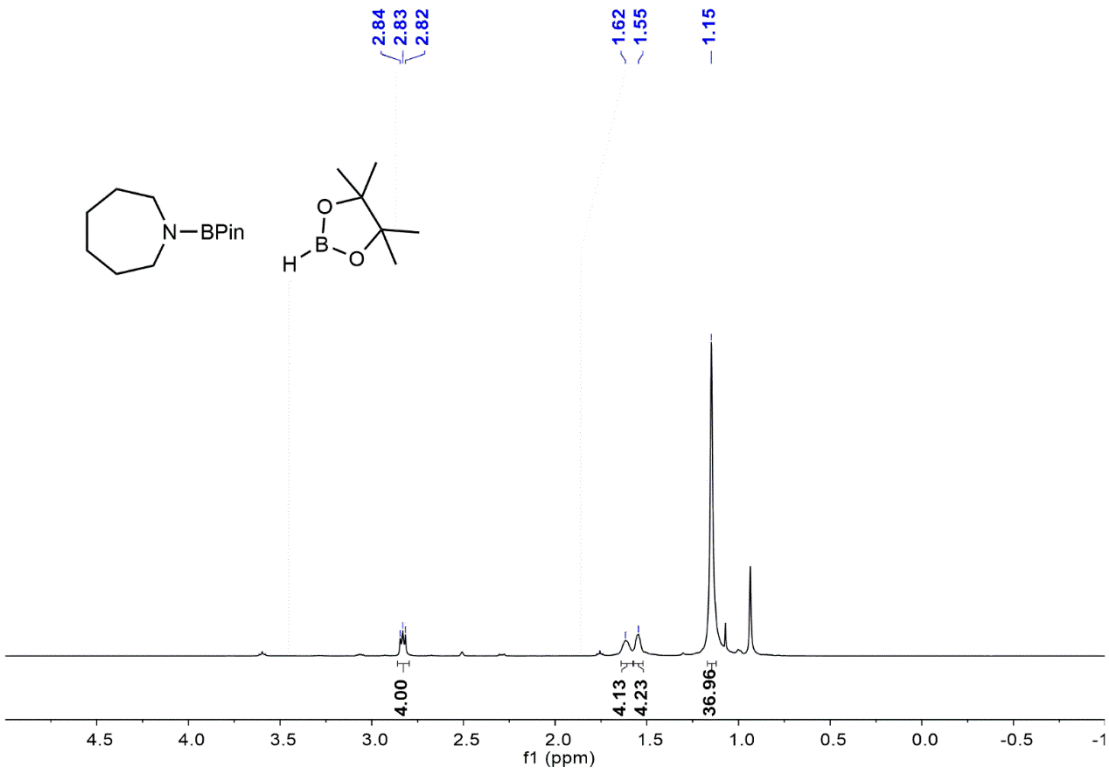
[1]H NMR spectrum of product **5d** (400 MHZ, DMSO-d_6)



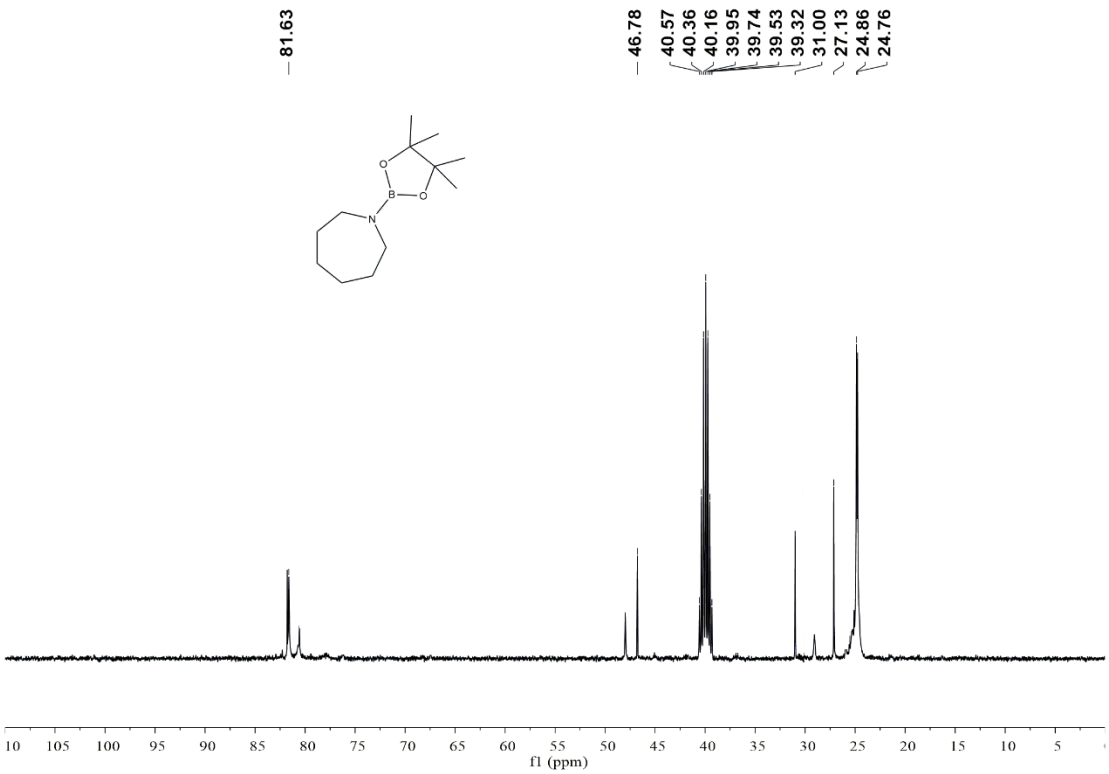
[13]C NMR spectrum of product **5d** (101 MHZ, DMSO-d_6)



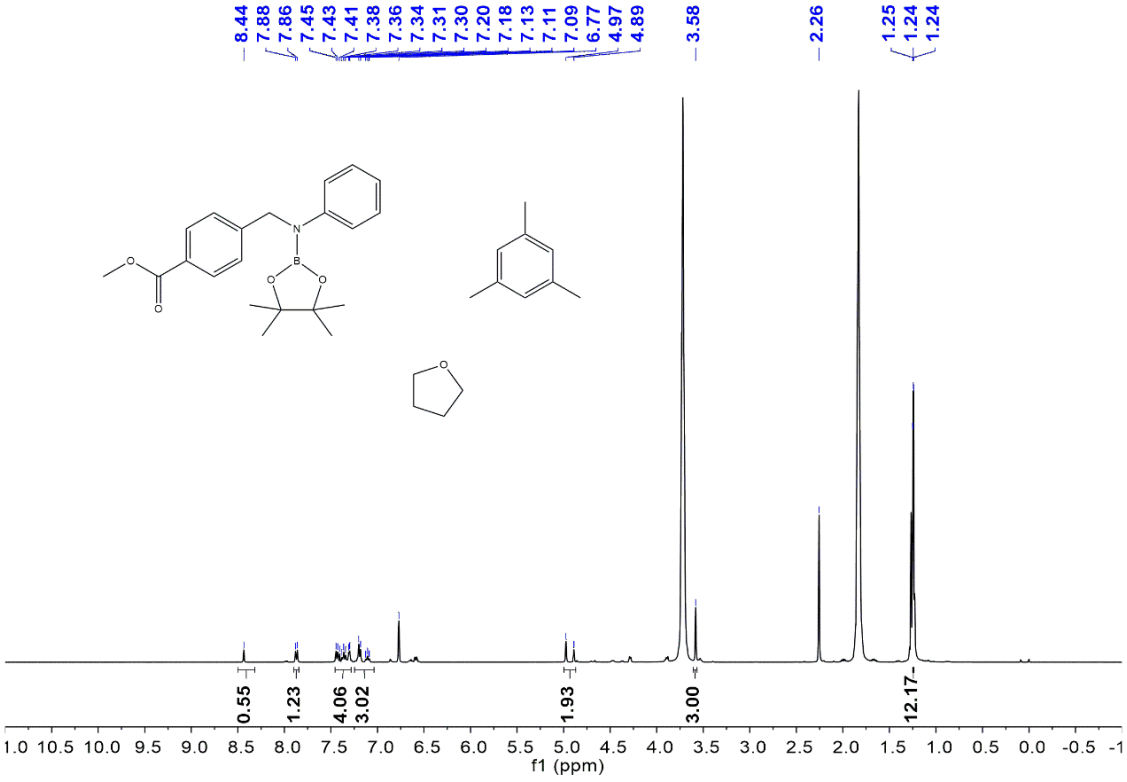
^{1}H NMR spectrum of product **5e** (400 MHZ, DMSO-d_6)



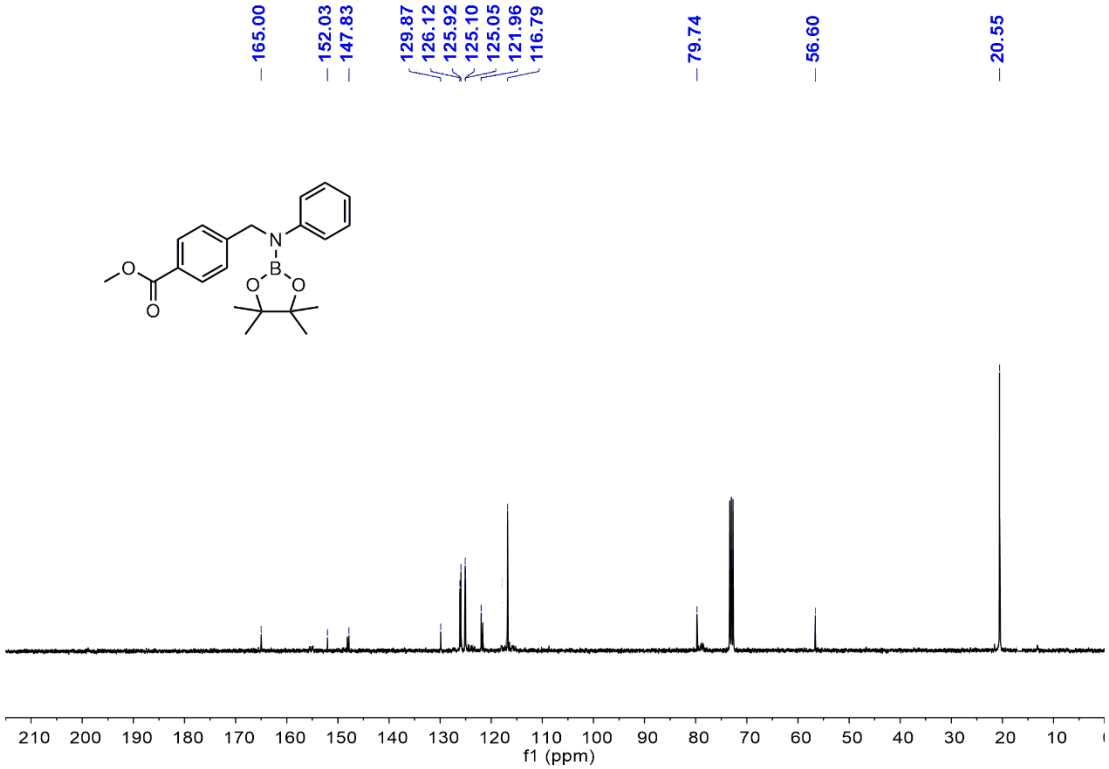
^{13}C NMR spectrum of product **5e** (101 MHZ, $CDCl_3$)



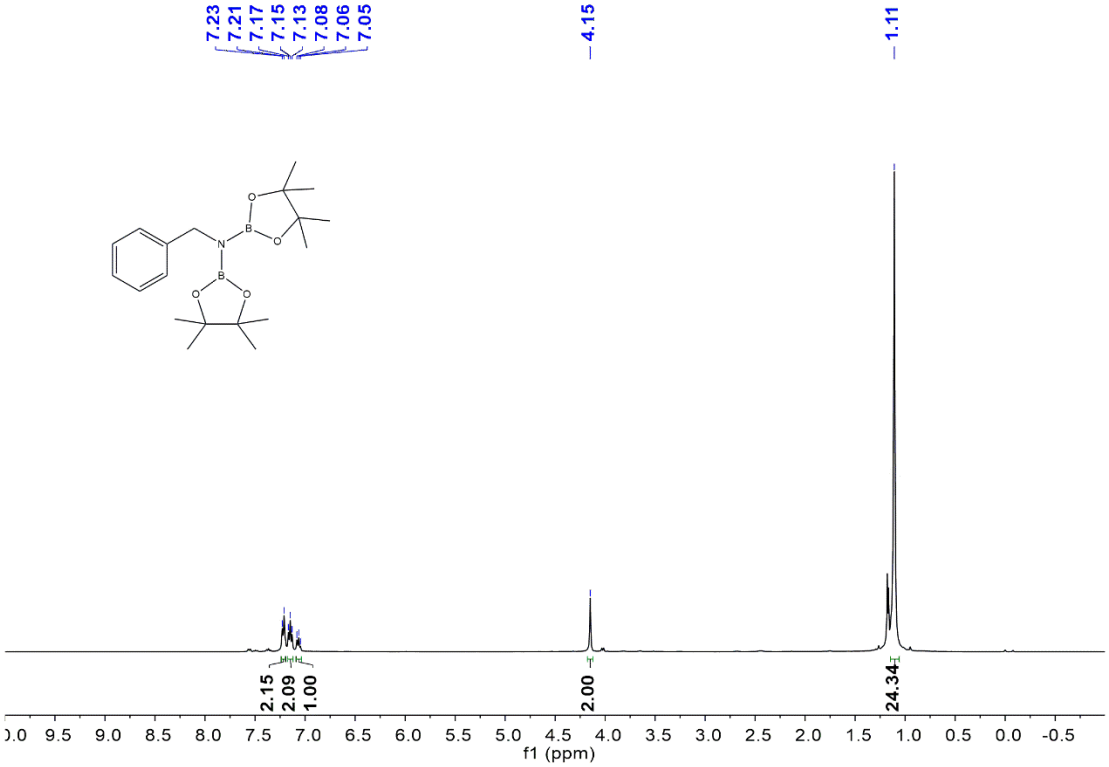
^{1}H NMR spectrum of product **5f** (400 MHZ, $CDCl_3$)



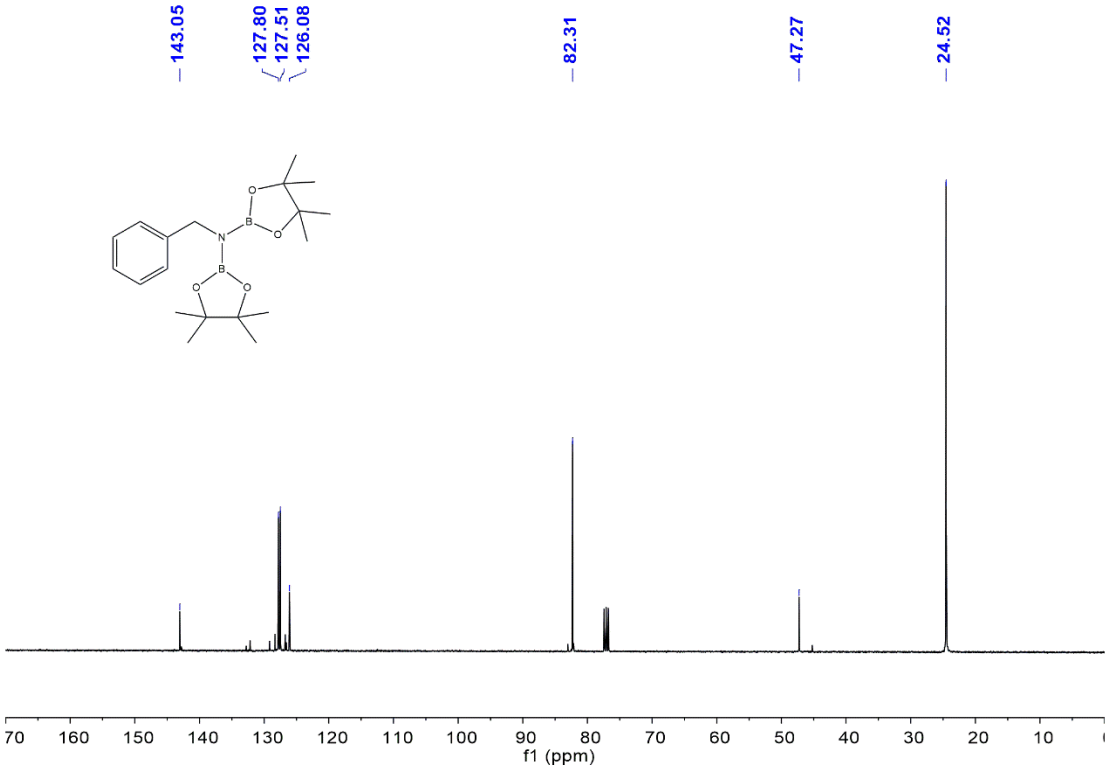
^{13}C NMR spectrum of product **5f** (101 MHZ, $CDCl_3$)



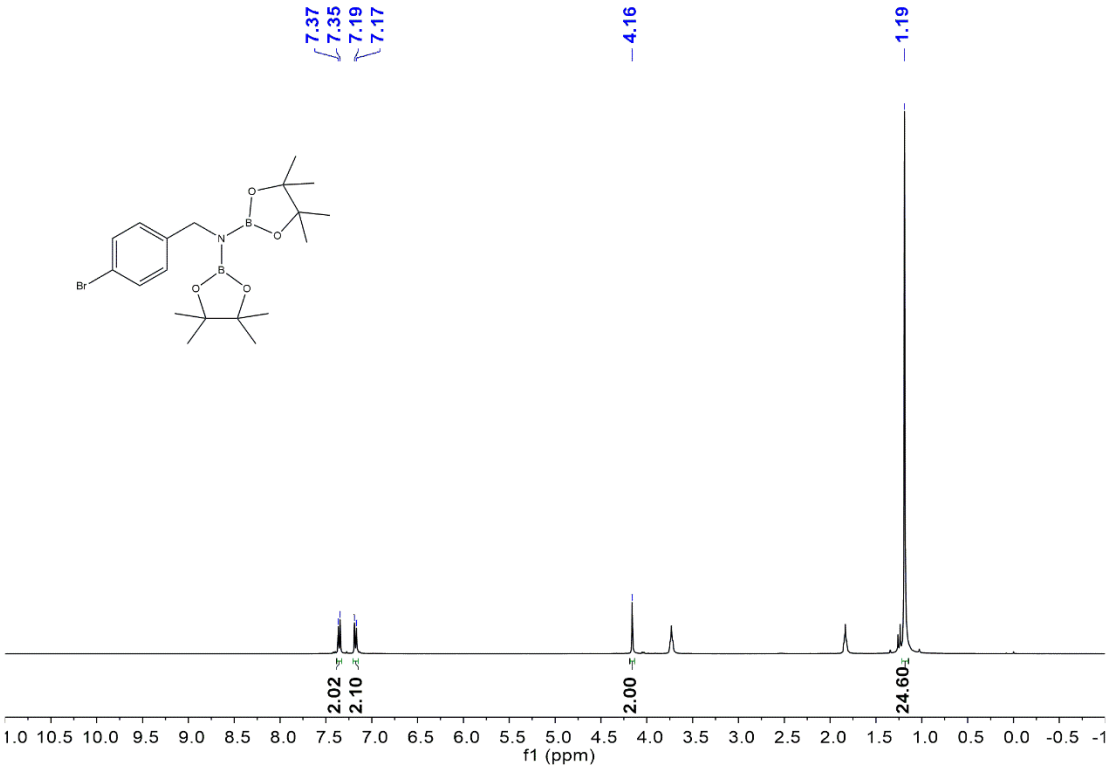
^{1}H NMR spectrum of product **7a** (400 MHZ, $CDCl_3$)



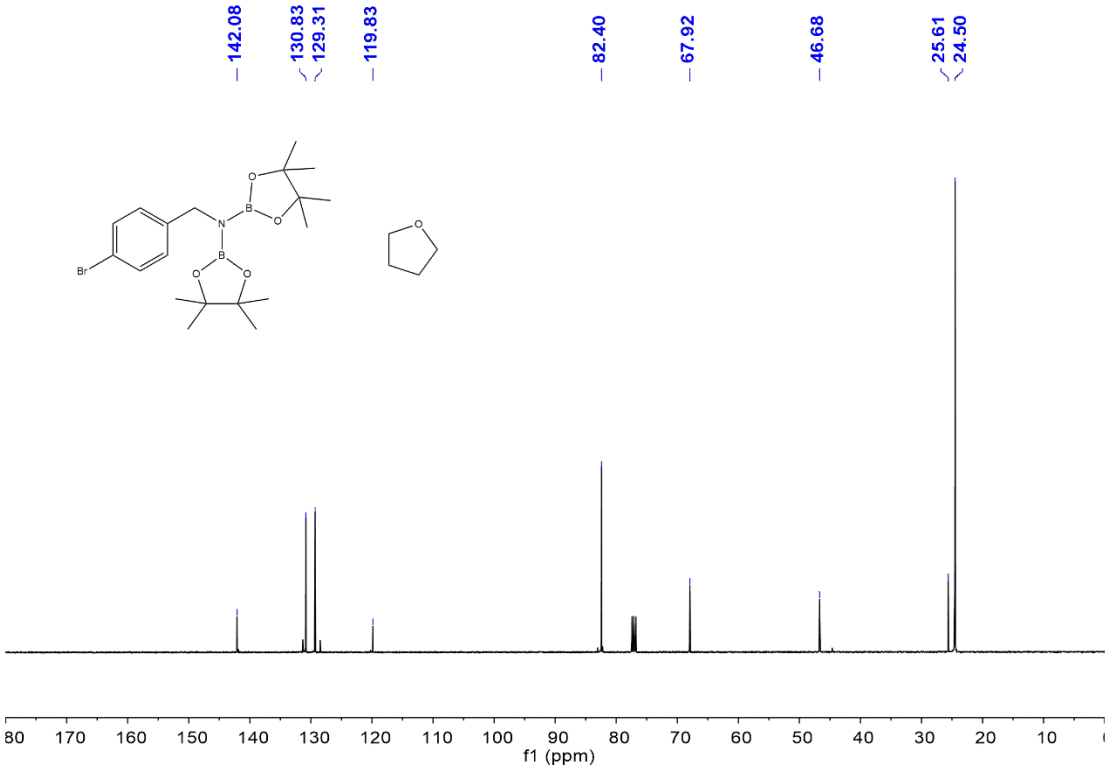
^{13}C NMR spectrum of product **7a** (101 MHZ, $CDCl_3$)



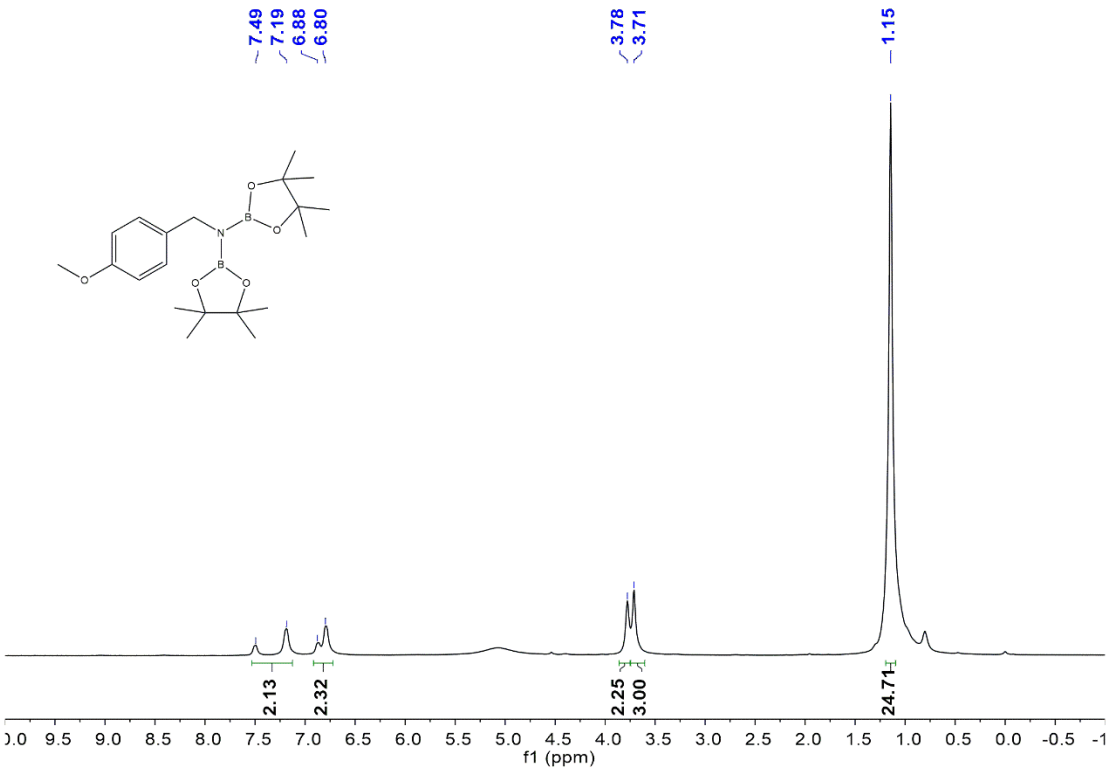
^{1}H NMR spectrum of product **7b** (400 MHZ, $CDCl_3$)



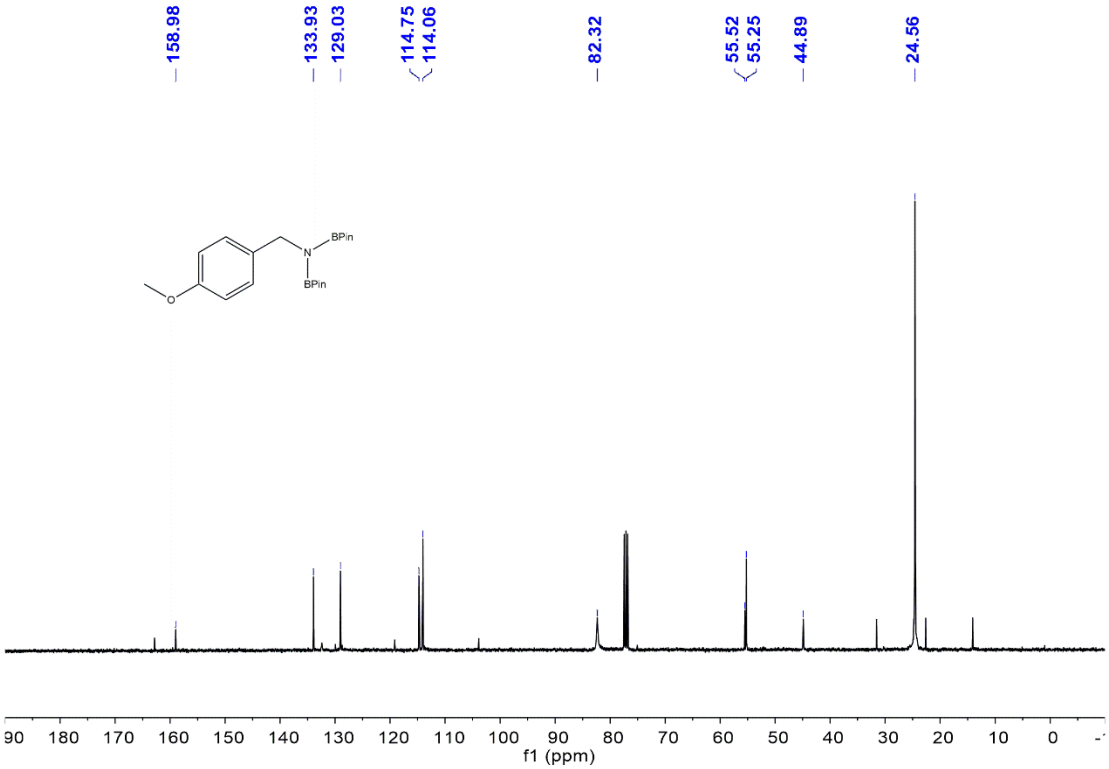
^{13}C NMR spectrum of product **7b** (101 MHZ, $CDCl_3$)



^{1}H NMR spectrum of product **7c** (400 MHZ, $CDCl_3$)



^{13}C NMR spectrum of product **7c** (101 MHZ, $CDCl_3$)



VII. References

S1. X. Xu, D. Yan, Z. Zhu, Z. Kang, Y. Yao, Q. Shen, M. Xue, *ACS Omega* **2019**, *4*, 6775–6783.

S2. K. M. Sharma, M. Ansari, P. Mahawar, G. Rajaraman, S. Nagendran, *Dalton Trans*. **2019**, *48*, 664–672.

S3. S. Chen, D. Yan, M. Xue, Y. Hong, Y. Yao, Q. Shen, *Org. Lett*. **2017**, *19*, 3382–3385.

S4. C. J. Barger, A. Motta, L. V. Weidner, L. T. Lohr, J. T. Marks, *ACS Catal.* **2019**, *9*, 9015–9024.

S5. K. M. Barman, K. Das, B. Maji, *J. Org. Chem*. **2019**, *84*, 1570–1579.

S6. Z. Zhu, X. Wu, X. Xu, Z. Wu, M. Xue, Y. Yao, Q. Shen, X. Bao, *J. Org. Chem*. **2018**, *83*, 10677–10683.

S7. A. Harinath, J. Bhattacharjee, T. K. Panda, *Chem. Commun*. **2019**, *55*, 1386–1389.

S8. M. K. Barman, A. Baishya, S. Nembenna, *Dalton Trans*. **2017**, *46*, 4152–4156.

S9. M. Kobylarski, C. J.Berthet, T. Cantat, *Chem. Commun*. **2022**, *58*, 2830–2833.

S10. H. Zeng, J. Wu, S. Li, C. Hui, A. Ta, S. Y. Cheng, S. Zheng, G. Zhang, *Org. Lett*. **2019**, *21*, 401–406.

S11. X. Xu, Z. Kang, D. Yan, M. Xue, *Chin. J. Chem.* **2019**, *37*, 1142-1146.

S12. D. Yan, X. Wu, J. Xiao, Z. Zhu, X. Xu, X. Bao, Y. Yao, Q. Shen, M. Xue, *Org. Chem. Front*.,**2019**, *6*, 648–653.

S13. M. K. Bisai, K. Gour, T. Das, K. Vank, S. S. Sen, *Dalton.Trans.* **2021**, *50*, 2354–2358.

S14. A. Harinath, J. Bhattacharjee, T. K. Panda, *Adv. Synth. Catal*. **2019**, *361*, 850–857.