Supporting Information for

Imidazolin-2-iminato ligand supported organozinc complex as Catalyst for Hydroboration of Organic Nitriles.

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X-ray crystallographic analyses: Single crystals of complexes **1a, 1b** and **1c** were grown from a concentrated solution of toluene in an argon-filled atmosphere at -35 °C. However, single crystals of **4d** was obtained from a solution of ethanol at -35 °C. A crystal of suitable dimensions of complexes **1a**, **1b**, and **1c** was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. The crystals of **4d** was measured at 298 K. All measurements were made on an Rigaku Supernova X-calibur Eos CCD detector with graphite monochromatic Cu-Kα (1.54184 Å) radiation. The data for the complexes **1a** and **1c** are not satisfactory and R factors are very high. Thus only figure of **1c** (Fig FS1) is used for comparison only. Crystal data and structure refinement parameters of complexes **1b** and **4d** are summarized in Table TS1. The structures were solved by direct methods (SIR2004)[1] and refined on F^2 by full-matrix least-squares methods, using SHELXL-97.[2] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecules of **1b** and **4d**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1945309 (**1b**), 1945343 (**4d**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Table TS1. Crystallography table of metal complexes **1b** and **4d.**

Crystal Parameters	**1b**	**4d**
CCDC No.	1945309	1945343
Empirical formula	$C_{46}H_{58}N_6Zn_2$	$C_8H_{12}ClNS$
Formula weight	825.76	189.70
T (K)	293(2) K	293(2) K
λ (Å)	1.54184 A	1.54184 A
Crystal system	Monoclinic	Triclinic
Space group	$P\,2_1/n$	*P* -1
a(Å)	10.3684(3)	4.3870(3)
b (Å)	18.0523(6)	5.6906(3)
c(Å)	11.7948(4)	19.2566(14)
α (°)	90.00	86.981(5)
β (°)	93.385(3)	85.060(6)
γ (°)	90.00	85.181(5)
V(Å^3)	2203.82(12)	476.76(5)
Z	2	2
D_{calc} g cm^{-3}	1.244	1.321
μ (mm^{-1})	1.615	5.080
F(000)	872	200
Theta range for data collection	4.483 to 71.273 deg	2.305 to 69.941 deg.
Limiting indices	-12<=h<=11, -18<=k<=21, -14<=l<=9	-5<=h<=5, -4<=k<=6, -23<=l<=23
Reflections collected / unique	8719 / 4166 [R(int) = 0.0279]	3213 / 1786 [R(int) = 0.0256]
Completeness to theta	99.1 %	99.8 %
Absorption correction	multi-scan	multi-scan
Max. and min. transmission	1.00000 and 0.80551	1.00000 and 0.25201
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4166 / 0 / 252	1786 / 0 / 102
Goodness-of-fit on F^2	1.069	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1140	R1 = 0.0449, wR2 = 0.1253
R indices (all data)	R1 = 0.0551, wR2 = 0.1287	R1 = 0.0499, wR2 = 0.1328

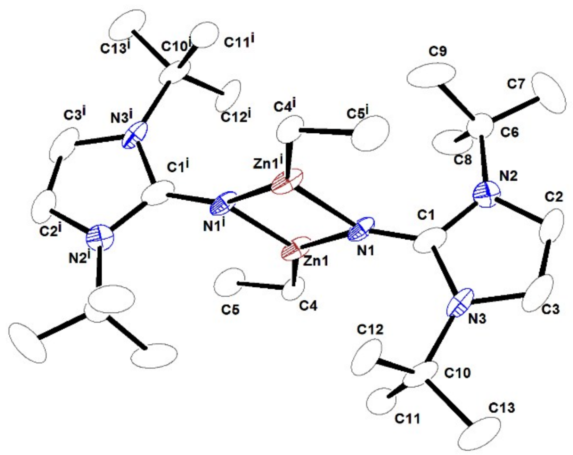


Figure FS1. Molecular solid-state structure of [{(Im^{tBu}N)Zn(CH_2CH_3)}$_2$] (**1c**). Selected bond lengths (Å) and angles (°) are: Zn1-N1 1.974(2), Zn1^{i}-N1 1.976(2), Zn1-C22 1.965(3), N1-C1 1.276(3), C1-N2 1.396(3), C1-N3 1.401(3), Zn1-N1-C1 133.53(19), C1-N1-Zn1^{i} 132.48(18), Zn1-N1-Zn1^{i} 93.98(9), C22-Zn1-N1 136.68(11), C22-Zn1-N1^{i} 133.48(10), N1-Zn1-N1^{i} 86.02(9).

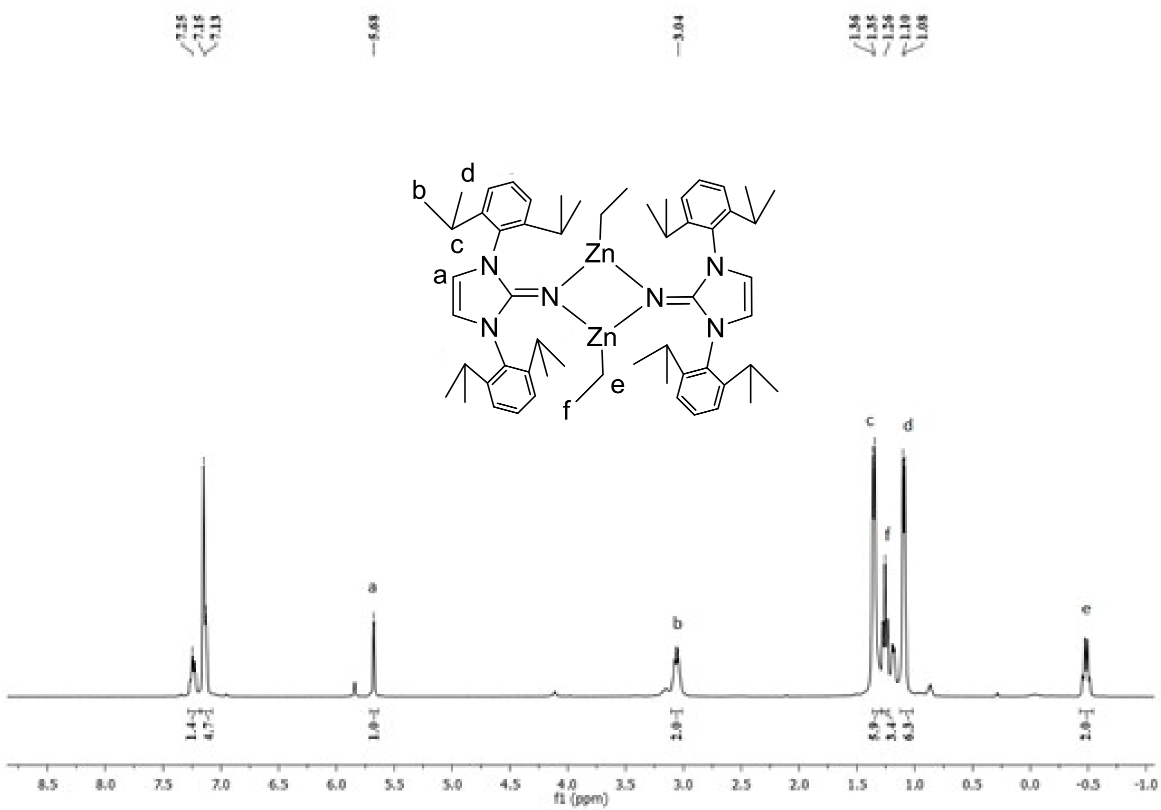


Figure FS2. ^{1}H NMR spectra of complex **1a**.

Figure FS3. ^{13}C NMR spectra of complex **1a**.

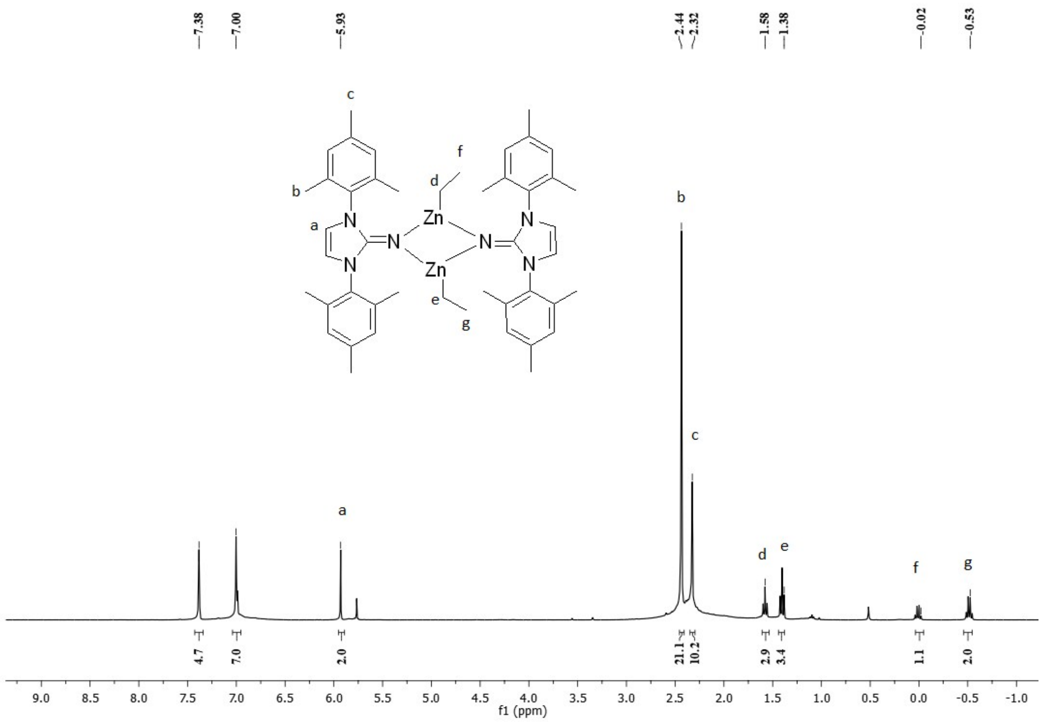


Figure FS4. ^{1}H NMR spectra of complex **1b**.

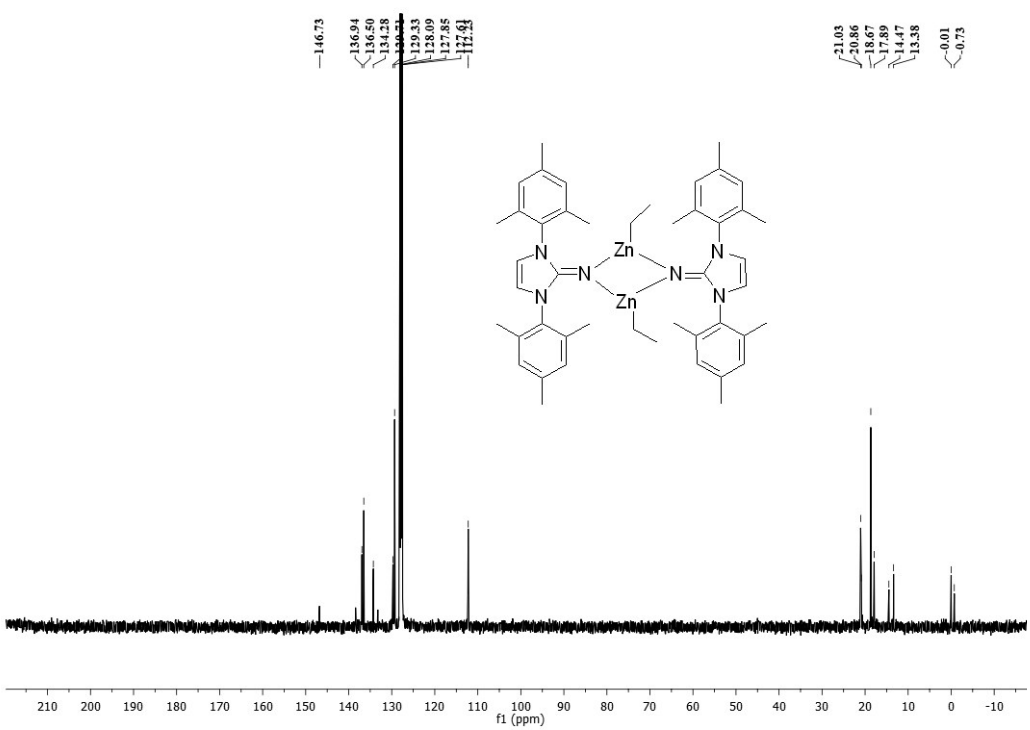


Figure FS5. ^{13}C NMR spectra of complex **1b**.

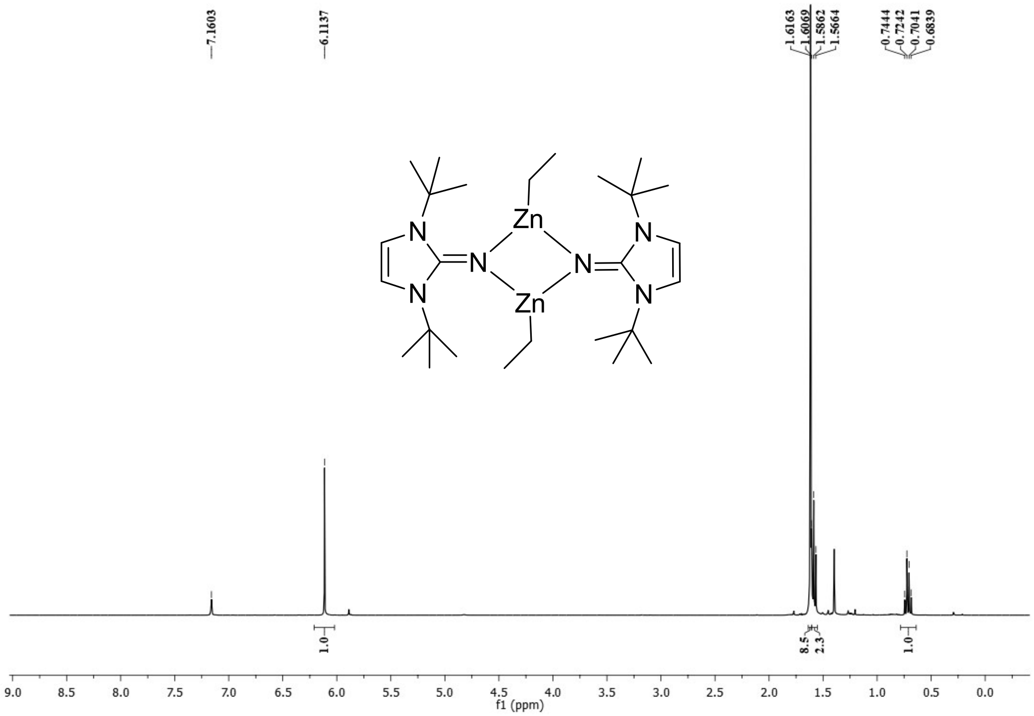


Figure FS6. ^{1}H NMR spectra of complex **1c.**

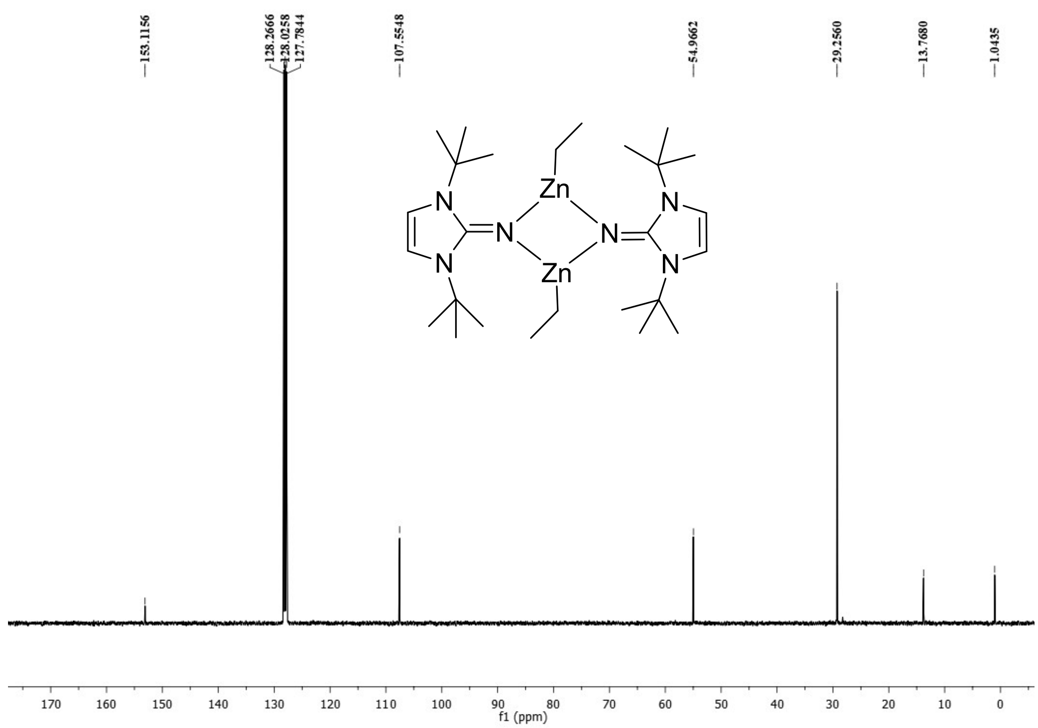
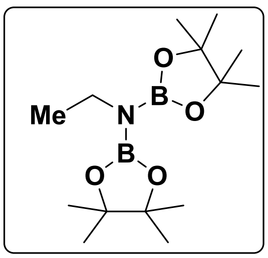


Figure FS7. ^{13}C NMR spectra of complex **1c.**

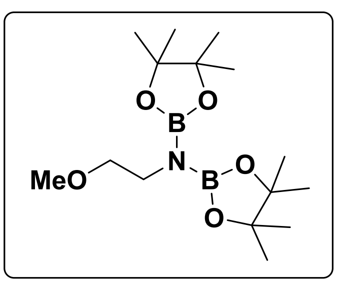
General procedure for Catalytic Hydroboration of Organic Nitriles by Imidazolin-2-iminato zinc Complex as Catalyst.

Inside the glove box, organic nitrile (0.97 mmol, 1 equiv.) was added drop-wise into the reaction mixture of respective pinacolborane (1.93948 mmol, 2.0 equiv.), and **1c** (2.8 mg, 0.0048 mmol, 0.5 mol% in a 25 mL dry Schlenk flask. The colourless reaction mixture was kept in the room temperature or heated to 40 - 60 °C depending upon the nature of nitriles. After 12 hours of stirring, the progress of the reaction was monitored by using ^{1}H NMR spectroscopy using hexamethylbenzene (5 mol%) as an internal standard. Once the reaction was completed, the excess of pinacolborane was evaporated under reduced pressure to obtained desired product and the products were characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy.

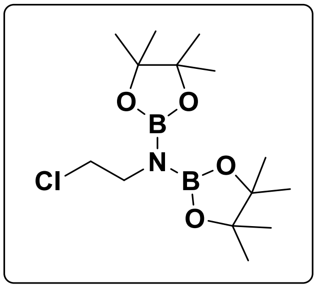
Characterization Data:



N-ethyl-dioxaborolan-2-amine (2a).
Yield (282.2 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.04 (q, J = 7.04 Hz, 2H), 1.19 (s, 24H), 0.99 (t, J = 7 Hz, 3H), ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ_C 81.9, 38.5, 24.8, 18.6, ppm. ^{11}B(^{1}H) NMR (128 MHz, $CDCl_3$) δ_B 25.7 ppm. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $[C_{14}H_{29}B_2NO_4]^+$ 298.2361; found 298.2355.

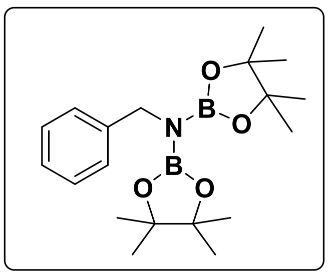


N-(2-methoxyethyl)- dioxaborolan-2-amine (2b).
Yield (310.5 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.65 (s, 3H), 3.53 (t, J = 6 Hz, 2H), 3.19 (t, J = 6.8 Hz, 2H), 1.18 (S, 24H) ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 82.4, 58.5, 45.4, 24.5 ppm. ^{11}B(^{1}H) NMR (128 MHz, $CDCl_3$) δ_B 25.8 ppm. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $[C_{14}H_{28}B_2NClO_4]^+$ 331.1893; found 331.1845.



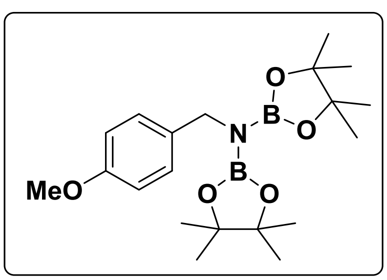
N-(2-chloroethyl)- dioxaborolan-2-amine (2c).

Yield (300 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.43 (t, *J* = 6.48 Hz, 2H), 1.21 (s, 24H), 3.32 (m, *J* = 6.8 Hz, 2H), $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 82.4, 58.5, 45.4, 24.5, ppm. $^{11}B(^{1}H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.6 ppm. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $[C_{14}H_{28}B_2NClO_4]^+$ 331.1893; found 331.1845.



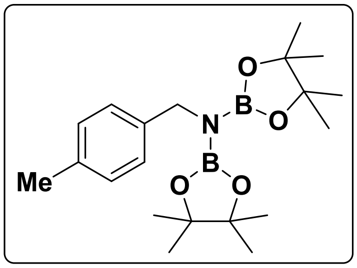
N-(benzyl)- dioxaborolan-2-amine (2d).

Yield (330.4 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38 (m, 2H), 7.22 – 7.21 (m, 2H), 7.16 – 7.12 (m, 2H), 4.22 (s, 2H), 1.18 (s, 24H), $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 143.0, 127.7, 127.4, 126.0, 82.2, 47.2, 24.5, ppm. $^{11}B(^{1}H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.7 ppm. HRMS (ESI) m/z calcd for $C_7H_{10}N$ (fragment): (M+H-C12H24B2NO4) + : 108.0813, found: 108.0798.



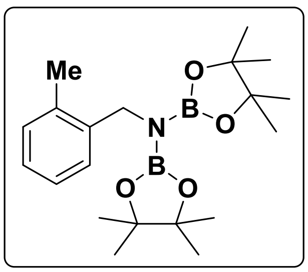
N-(4-methoxybenzyl-dioxaborolan-2-amine (2e).

Yield (365.6 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.23 (dd, *J* = 2.2, 7.7 Hz, 2H), 6.76 (dd, *J* = 2.2, 7.7 Hz, 2H), 4.14 (s, 2H), 3.75 (s, 3H), 1.19 (s, 24H), $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 158.0, 135.4, 128.6, 113.1, 82.2, 55.15, 46.5, 24.5 ppm. $^{11}B(^{1}H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.7 ppm. HRMS (EI) m/z calcd for C_8H_9O (fragment): $(M-C_{12}H_{24}B_2NO_4)$ + : 121.0653, found: 121.0658.



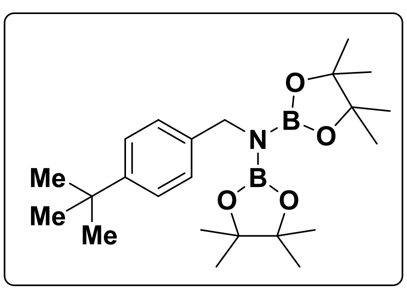
N-(4-methylbenzyl)- dioxaborolan-2-amine (2f).

Yield (346.9 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.10 - 7.08 (d, *J* = 8 Hz, 2H), 6.92 - 6.90 (d, *J* = 8 Hz, 2H), 4.08 (s, 2H), 2.16 (s, 3H), 1.06 (s, 24H), ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 140.0, 135.3, 128.4, 127.4, 82.2, 46.9, 24.5, 21.05 ppm. ^{11}B(^{1}H) NMR (128 MHz, $CDCl_3$) δ_B 26.4 ppm. HRMS (ESI) m/z calcd for C_8H_9 (fragment): $(MC_{12}H_{24}B_2NO_4)$ + : 105.0704, found: 105.0721.



N-(2-methylbenzyl)- dioxaborolan-2-amine (2g).

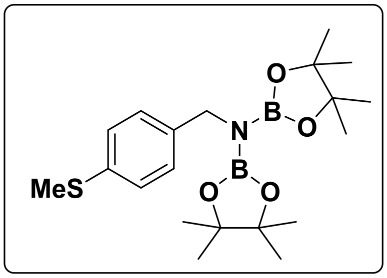
Yield (346.9 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43 - 7.41 (m, 1H), 7.34 - 7.30 (m, 1H), 7.17 - 7.09 (m, 2H), 4.11 (s, 2H), 2.38 (s, 3H), 1.13 (s, 24H), ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 141.6, 132.6, 132.3,130.2 126.2, 117.8, 112.6, 82.2, 44.7, 24.5, 18.9 ppm. ^{11}B(^{1}H) NMR (128 MHz, $CDCl_3$) δ_B 25.68 ppm. HRMS (ESI) m/z calcd for C_8H_9 (fragment): $(M-C_{12}H_{24}B_2NO_4)$ + : 105.0704, found: 105.0706.



N-(4-(tert-butyl)benzyl-dioxaborolan-2-amine (2h).

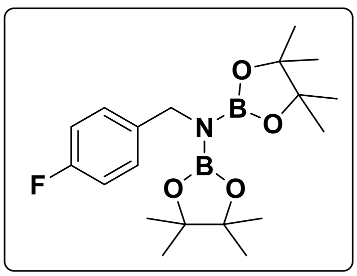
Yield (394 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.25 (m, 4H), 4.19 (s, 2H), 1.29 (s, 9H), 1.19 (s, 24H), ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ_C 148.0, 140.0, 127.3, 124.6, 82.2, 46.8, 34.3, 31.4 24.5 ppm.

$^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.9 ppm. HRMS (EI) m/z calcd for $C_{11}H_{15}$ (fragment): (M-$C_{12}H_{24}B_2NO_4$) + : 147.1174, found: 147.1165.



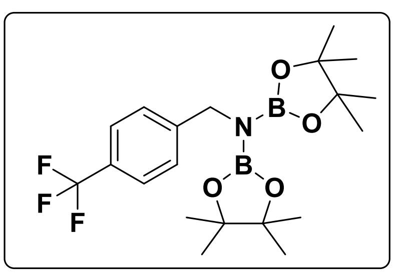
N-(4-(methylthio)benzyl) dioxaborolan-2-amine (2i).

Yield (380.6 mg, 97%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.15 - 7.13 (d, J = 8.2 Hz, 2H), 7.06 - 7.04 (d, J = 8.0 Hz 2H), 4.08 (s, 2H), 2.32 (s, 3H), 1.09 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 146.1, 132.0, 125.4, 118.8,107.5, 83.1, 24.8, 14.5 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.3 ppm.



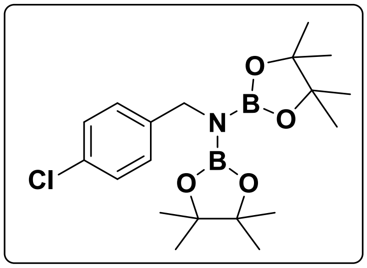
N-(4-fluorobenzyl-dioxaborolan-2-amine (2j).

Yield (358.0 mg, 98%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.28 - 7.24 (m, 2H), 6.90 (m, 2H), 4.16 (s, 2H), 1.19 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 162.7, 138.8, 129.2, 129.1, 114.5, 114.3, 83.2, 46.5, 24.5 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.6 ppm. HRMS (EI) m/z calcd for C_7H_6F (fragment): (M-$C_{12}H_{24}B_2NO_4$) + : 109.0454, found: 109.0486



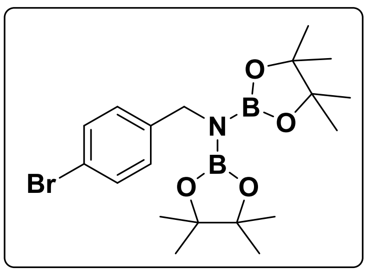
N-(4-(trifluoromethyl)benzyl)- dioxaborolan-2-amine (2k).

Yield (405.4 mg, 98%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.49 (d, J = 7.96 Hz, 2H), 7.39 (d, J = 7.96 Hz, 2H), 4.26 (s, 2H), 1.18 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 147.0, 132.7, 127.6, 124.7, 82.5, 46.9, 24.5 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.8 ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$) δ_F -58.66 ppm. HRMS (EI) m/z calcd for $C_8H_6F_3$ (fragment): $(M-C_{12}H_{24}B_2NO_4)$ + : 159.0422, found: 159.0415.



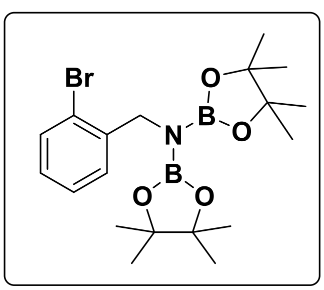
N-(4-chlorobenzyl-dioxaborolan-2-amine (2l).

Yield (369.3 mg, 97%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.22 (m, 4H), 4.17 (s, 2H), 1.18 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 141.5, 133.3, 129.7, 128.9, 82.4, 46.6, 24.4 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.6 ppm. HRMS (EI) m/z calcd for C_7H_6Cl (fragment): $(M-C_{12}H_{24}B_2NO_4)$ + : 125.0158, found: 125.0148.



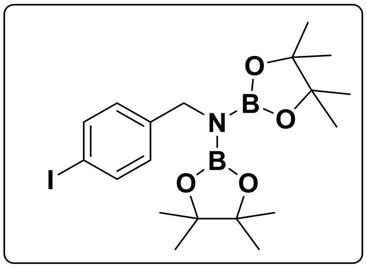
N-(4-bromobenzyl-dioxaborolan-2-amine (2m).

Yield (402.2 mg, 95%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.35 (d, J = 8.44 Hz, 2H), 7.17 (d, J = 8.44 Hz, 2H), 4.15 (s, 2H), 1.18 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 142.0, 130.8, 129.2, 119.8, 82.4, 46.6, 24.4 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.9 ppm. HRMS (EI) m/z calcd for C_7H_6Br (fragment): $(M-C_{12}H_{24}B_2NO_4)$ + : 168.9653, found: 168.9646.



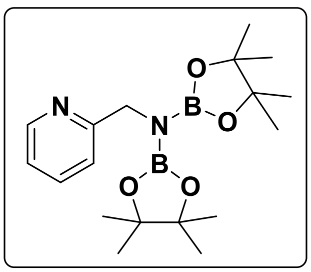
N-(2-bromobenzyl-dioxaborolan-2-amine (2n).

Yield (406.5 mg, 96%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.43 - 7.41 (d, J = 8.04 Hz, 1H), 7.20 - 7.18 (m, 2H), 7.00 - 6.97 (m, 1H), 4.26 (s, 2H), 1.21 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 141.3, 132.0, 127.3,127.01,126.8, 122.6, 82.4, 47.5, 24.4 ppm. $^{11}B(^{1}H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.9 ppm. HRMS (EI) m/z calcd for C_7H_6Br (fragment): $(M-C_{12}H_{24}B_2NO_4)$ + : 168.9653, found: 168.9646.



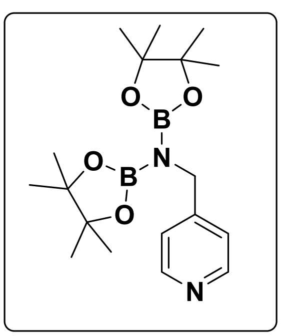
N-(4-Iodobenzyl-dioxaborolan-2-amine (2o).

Yield (440.8 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.47 - 7.45 (d, J = 8.2 Hz, 2H), 6.98 - 6.96 (d, J = 8.2 Hz, 2H), 4.05 (s, 2H), 1.15 (s, 24H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 142.7, 136.7, 129.5, 91.2, 83.0 82.4, 46.6, 24.4 ppm. $^{11}B(^{1}H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.9 ppm.



N-(Pyridine-2-ylmethyl) dioxaborolan-2-amine (2p).

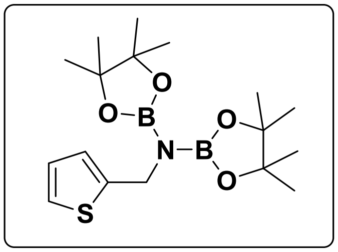
Yield (334.8 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.32-8.31 (d, J = 4.84 Hz, 1H), 7.52 - 7.47 (m, 1H), 7.09 – 7.07 (d, J = 7.9 Hz, 1H), 7.00 - 6.97 (m, 1H), 4.25 (s, 2H), 1.01 (s, 24H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 161.3, 146.2, 137.0, 121.3,127.5,119.8, 81.6, 49.1, 24.4 ppm. $^{11}B(^{1}H)$ NMR (128 MHz, $CDCl_3$) δ_B 24.01 ppm.



N-(Pyridine-4-ylmethyl) dioxaborolan-2-amine (2q).

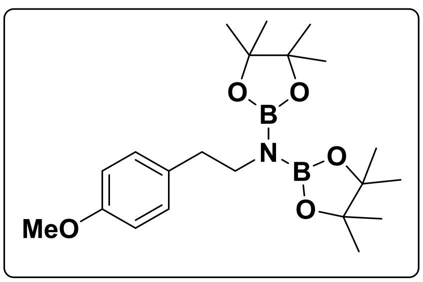
Yield (338.3 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.61 - 8.59 (d, J = 4.76 Hz, 1H), 8.12 - 8.11 (d, J = 4.72 Hz, 1H), 7.18 – 7.14 (m, 1H), 6.42 - 6.41 (d, J = 4.76 Hz, 1H), 4.40 (s, 2H), 0.99 (s, 24H). $^{13}C\{^{1}H\}$

NMR (100 MHz, $CDCl_3$): δ_C 161.3, 146.2, 137.0, 121.3, 119.8, 82.9, 81.6, 49.1, 28.3, 24.4 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 24.01 ppm. HRMS (EI) m/z calcd for C_7H_6Br (fragment): $(M-C_{12}H_{24}B_2NO_4)$ + : 168.9653, found: 168.9646



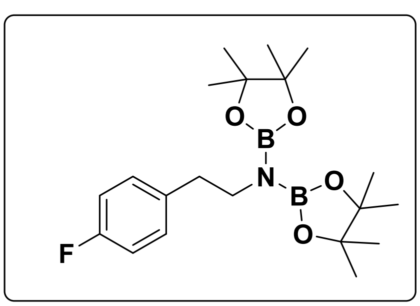
N-(thiophen-2-ylmethyl)-1,3,2-dioxaborolan-2-amine (2r).

Yield (336.0 mg, 95%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.12 - 7.11 (m, 1H), 6.90 (m, 1H), 6.89 (m, 1H) 4.40 (s, 2H) 1.22 (s, 24H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 146.7, 126.1, 124.5, 123.5, 82.4, 42.1, 24.5 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.8 ppm. HRMS (EI) m/z calcd for C_5H_5SNa: $(M-C_{12}H_{24}B_2O_4+Na)$ + : 120.0010, found: 120.0035.



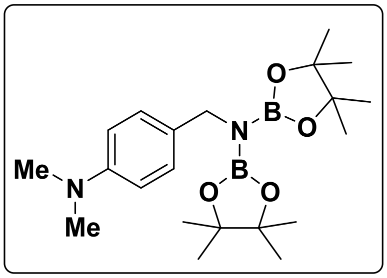
N-(4-Metoxy phenethyl) dioxaborolan-2-amine (2s).

Yield (378.7 mg, 97%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.09 (m, 2H), 6.89 (m, 2H), 3.74 (s, 3H), 3.25 (t, J = 7.0 Hz, 2H), 2.65 (t, J = 7.0 Hz, 3H), 1.17 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 157.7, 131.9, 130.1, 129.0,114.4,113.5, 82.0, 55.2, 45.3, 38.4, 24.4 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.2 ppm. HRMS (EI) m/z calcd for $C_9H_{11}O$ (fragment): $(M-C_{12}H_{24}B_2NO_4)$ + : 136.0810, found: 136.0816.



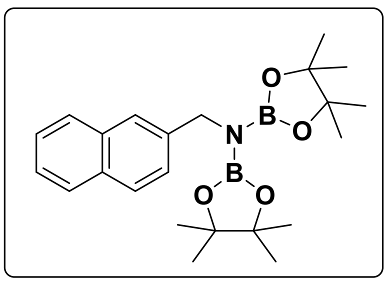
N-(4-Flouro phenethyl) dioxaborolan-2-amine (2t).

Yield (358.9 mg, 98%). [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.12 (d, J = 8 Hz 2H), 6.92 (d, J = 8 Hz, 2H), 3.25 (t, J = 6.96 Hz, 2H), 2.65 (t, J = 6.96 Hz, 3H), 1.16 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 162.5, 136.0, 130.6, 116.2, 116.0, 114.8, 82.0, 45.1, 38.4, 24.8 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.2 ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$) δ_F -58.66 ppm HRMS (EI) m/z calcd for C_8H_8F (fragment): (M-$C_{12}H_{24}B_2NO_4$) + : 123.0610, found: 123.0617.



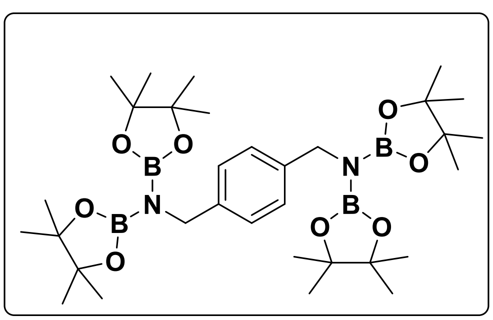
N-(4-(methylthio)benzyl) dioxaborolan-2-amine (2u).

Yield (385.6 mg, 99%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.10 - 7.08 (d, J = 6.6 Hz, 2H), 6.52 - 6.51 (d, J = 6.5 Hz, 2H), 4.01 (s, 2H), 2.76 (s, 6H), 1.09 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 148.2, 130.6, 127.6, 111.3, 82.0, 80.7, 45.5, 39.7, 24.8 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.3 ppm.



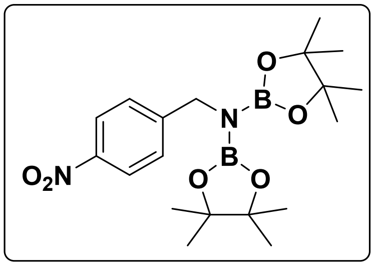
N-(napthalen - 2 - ylmethyl) dioxaborolan-2-amine (2v).

Yield (388.3 mg, 98%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.79 - 7.72 (d, J = 8 Hz, 2H), 7.75 - 7.72 (d, J = 8.8 Hz, 2H), 7.48 - 7.45 (d, J = 8 Hz, 1H), 7.42 - 7.39 (m, 2H), 4.42 (s, 2H), 1.09 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 139.5, 132.4, 131.3, 126.6, 126.5,126.3, 123.9, 82.1, 81.3, 46.3, 24.8 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 21.1 ppm.



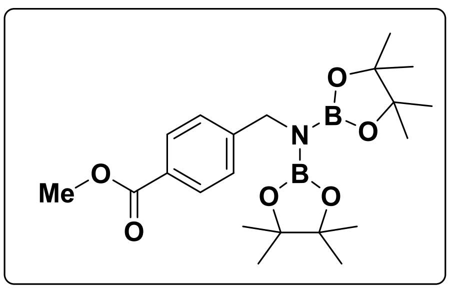
N,N-(1,4-(phenylenebis(methylene) dioxaborolan-2-amine (2w).

Yield (582.9 mg, 94%). [1]H NMR (400 MHz, $CDCl_3$): δ_H 7.11 (s, 2H), 4.12 (s, 2H), 1.13 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 140.6, 132.4, 126.8, 83.0, 82.1, 81.3, 46.3, 24.8 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 21.1 ppm.



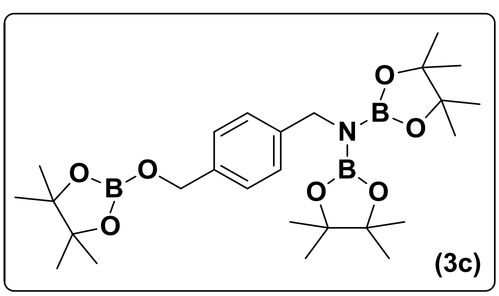
N-(4-(nitro)benzyl) dioxaborolan-2-amine (3a).

Yield (380.3 mg, 94%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.22 (m, 4H), 4.17 (s, 2H), 1.18 (s, 24H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 141.5, 133.3, 129.7, 128.9, 82.4, 46.6, 24.4 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.6 ppm. HRMS (EI) m/z calcd for C_7H_6Cl (fragment): $(M-C_{12}H_{24}B_2NO_4)$ + : 125.0158, found: 125.0148.

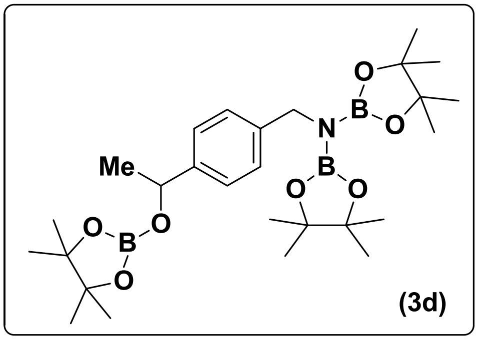


N-{B(OCMe$_2$)$_2$} – 4-(methylbenzoate)methanamine (3b).

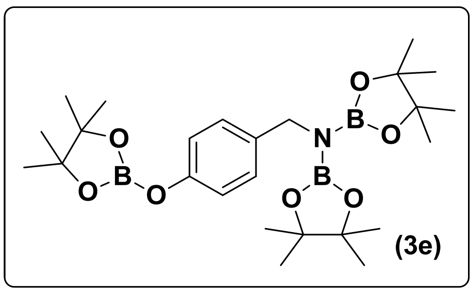
Yield (392.6 mg, 94%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.92 (d, *J* = 8 Hz, 2H), 7.35 (d, *J* = 8 Hz, 2H), 4.27 (s, 2H), 3.88 (s, 3H), 1.18 (s, 24H), $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 167.0,148.4, 130.0, 129.2, 128.0, 127.2, 82.4, 51.8, 47.1, 24.4 ppm. $^{11}B(^1H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.6 ppm. HRMS (ESI) m/z calcd for $C_9H_{20}O_2$: $(M-C_{12}H_{24}B_2NO_4)$ + : 160.1463, found: 160.1478.



Yield (395.1 mg, 96%). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.26 - 7.24 (d, *J* = 8 Hz, 2H), 7.21 - 7.19 (d, *J* = 8 Hz, 2H), 4.85 (s, 2H), 4.19 (s, 2H), 1.17 (s, 24H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ_C 142.1, 136.9, 127.3, 126.3, 83.0, 82.6, 82.4, 81.7, 66.5, 46.8, 24.4 ppm. $^{11}B(^{1}H)$ NMR (128 MHz, $CDCl_3$) δ_B 22.4 ppm.



Yield (387.8 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 - 7.60 (m, 1H), 7.47 - 7.45 (m, 1H), 7.24 - 7.23 (m, 1H), 7.05 - 7.04 (m, 4H), 5.26 (q, J = 8 Hz, 3H), 4.19 (s, 2H), 3.93 (s, 2H), 1.17 (s, 24H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 149.8,142.3, 127.3, 124.8, 118.8, 82.6, 82.2,72.5, 46.8, 24.8, 24.4 ppm. $^{11}B(^{1}H)$ NMR (128 MHz, $CDCl_3$) δ_B 22.4 ppm.



N-(dioxaborolan-2-yl)oxy)benzyl) -dioxaborolan-2-amine.

Yield (379.4 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.20 (d, J = 6.5 Hz, 2H), 6.94 (d, J = 6.5 Hz, 2H), 4.15 (s, 2H), 1.31 (s, 12H), 1.18 (s, 24H) $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ_C 151.7, 137.8, 128.5,120.5, 118.7, 83.3, 82.4, 46.3, 24.5 ppm. $^{11}B(^{1}H)$ NMR (128 MHz, $CDCl_3$) δ_B 25.8, 21.0 ppm. HRMS (ESI) m/z calcd for $C_{13}H_{19}BO_3$: $(M-C_{12}H_{24}B_2NO_4)$ + : 234.1427, found: 234.1450.

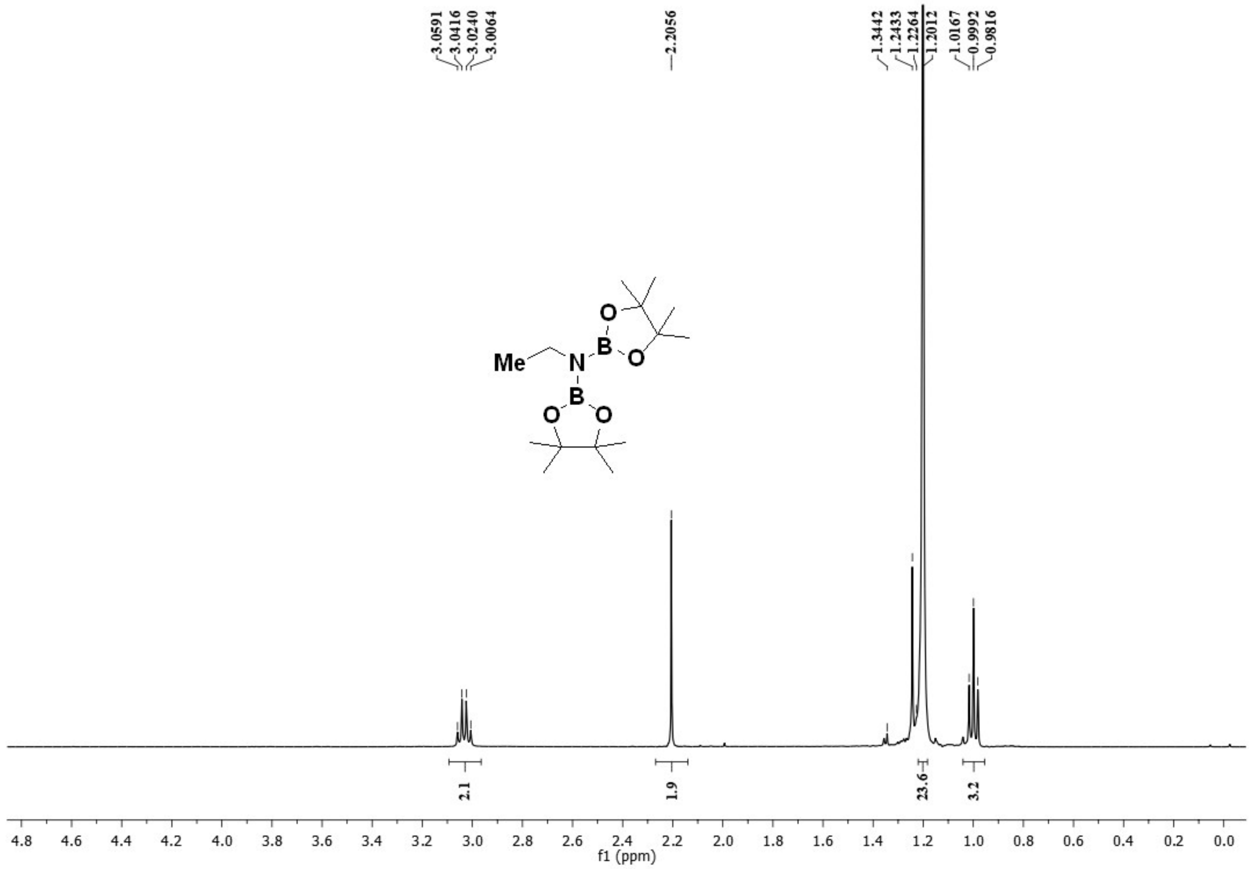


Figure FS8. ^{1}H NMR spectra of complex **2a**.

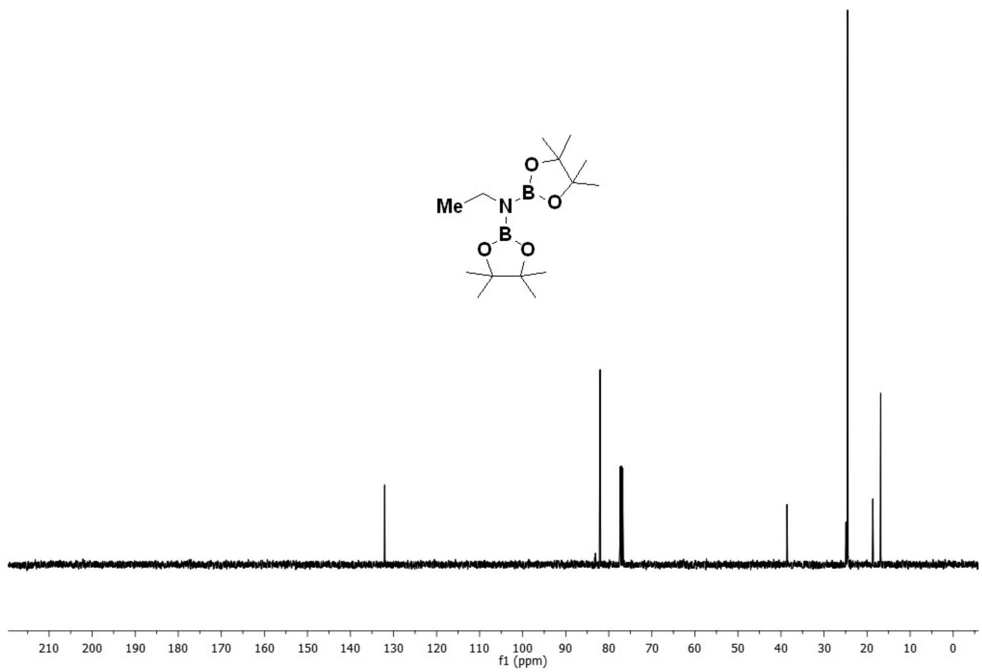


Figure FS9. ^{13}C NMR spectra of complex **2a**.

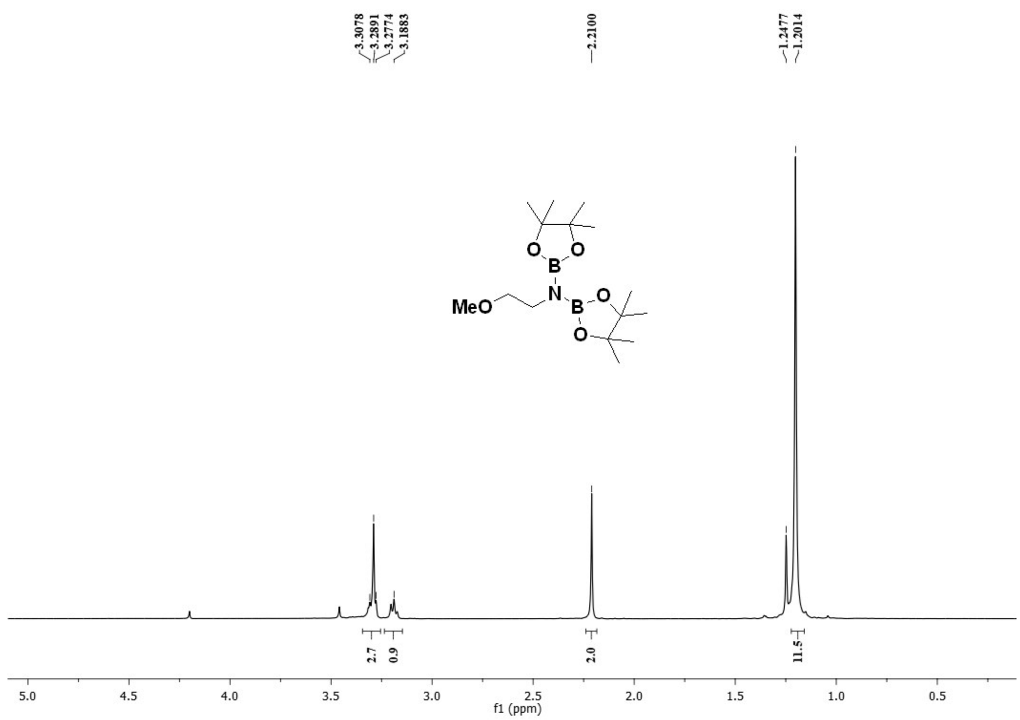


Figure FS10. ^{1}H NMR spectra of complex **2b**.

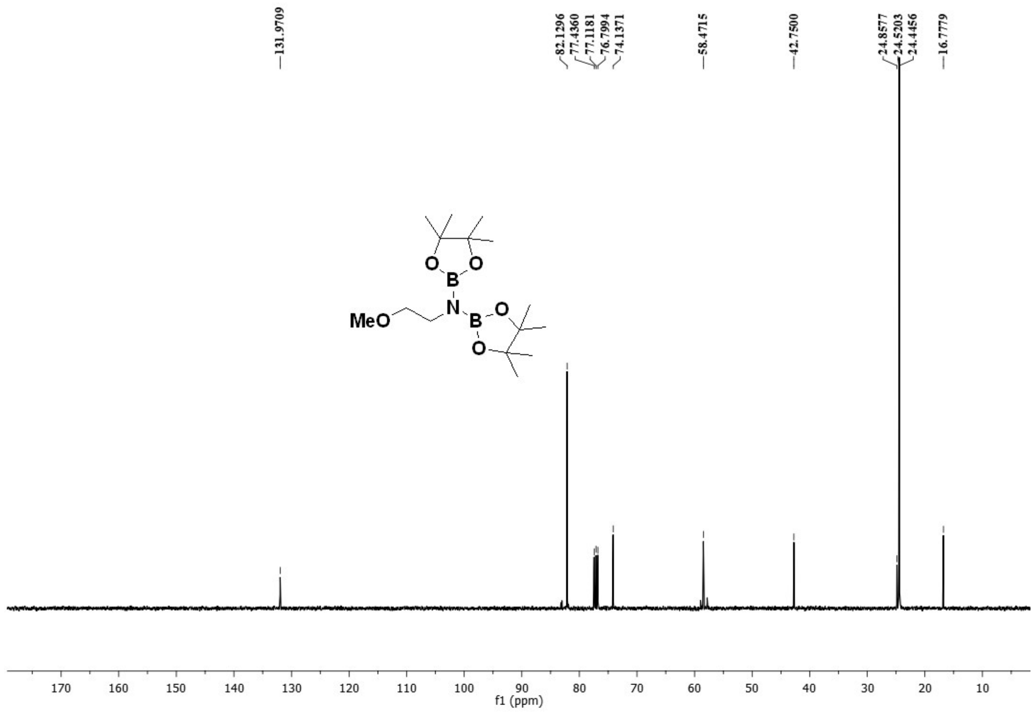


Figure FS11. ^{13}C NMR spectra of complex **2b**.

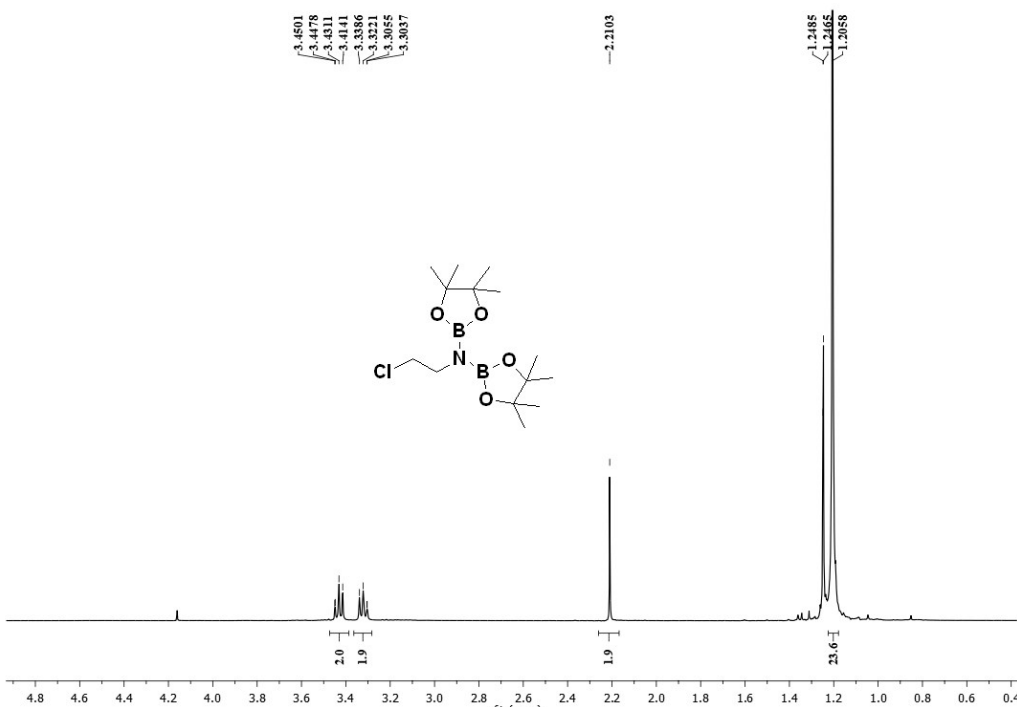


Figure FS12. ^{1}H NMR spectra of complex **2c.**

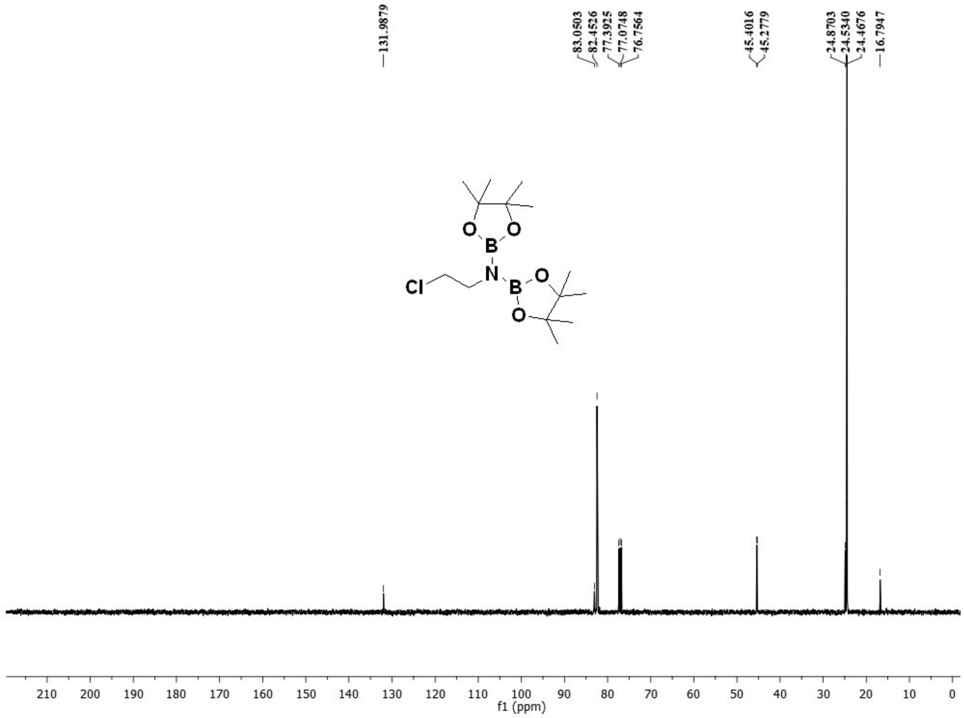


Figure FS13. ^{13}C NMR spectra of complex **2c.**

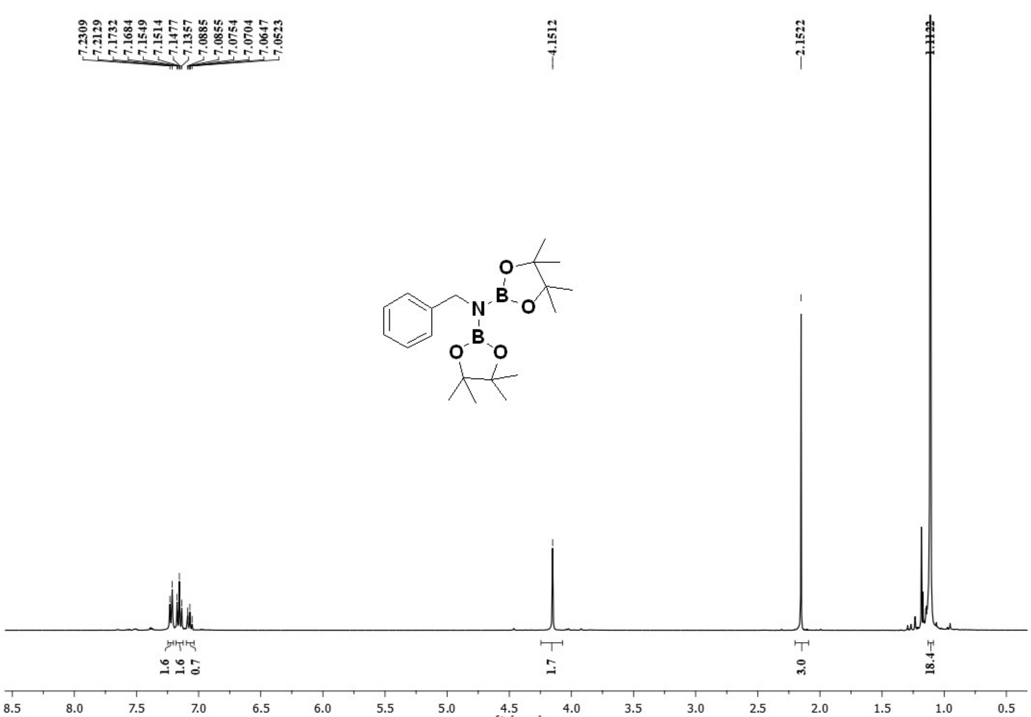


Figure FS14. ^{1}H NMR spectra of complex **2d.**

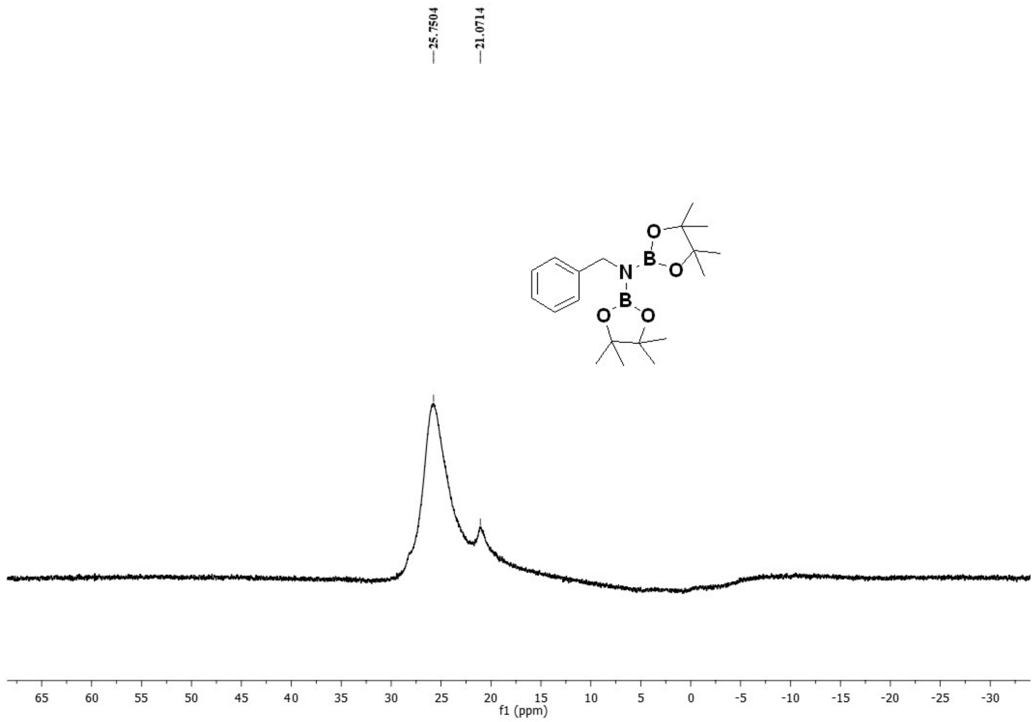


Figure FS15. ^{11}B NMR spectra of complex **2d.**

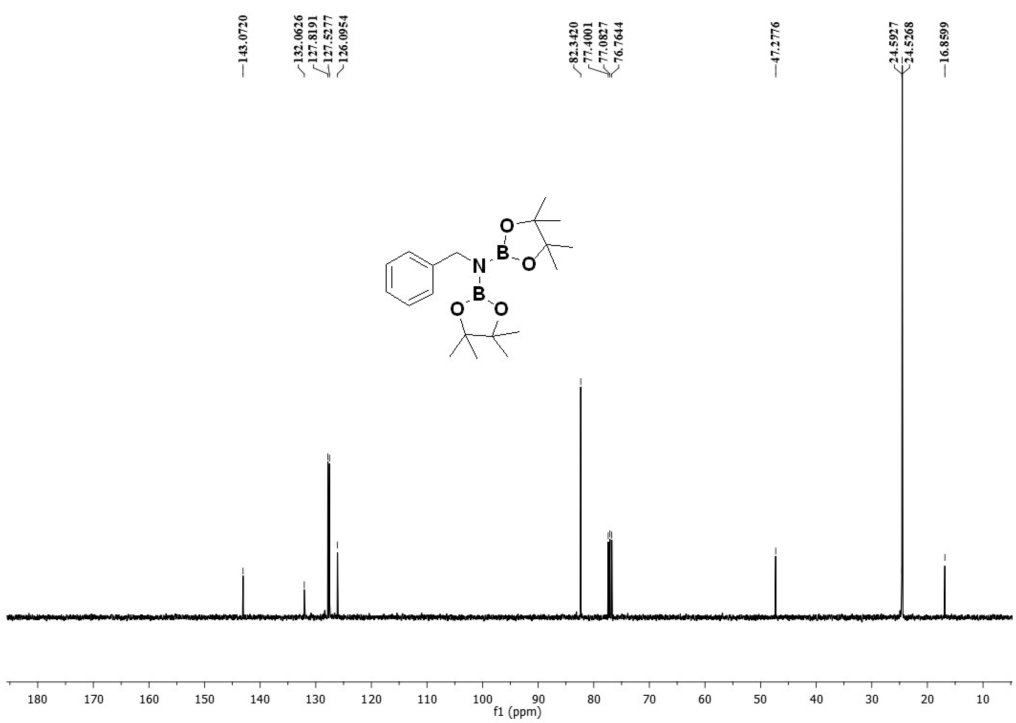


Figure FS16. ^{13}C NMR spectra of complex **2d.**

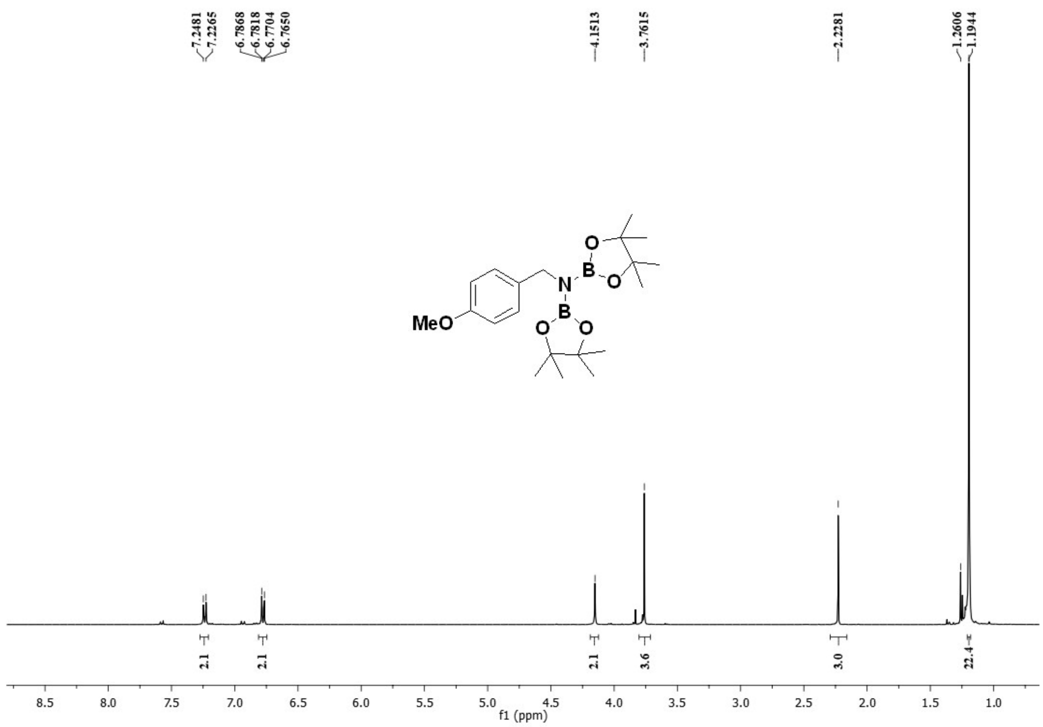


Figure FS17. ^{1}H NMR spectra of complex **2e.**

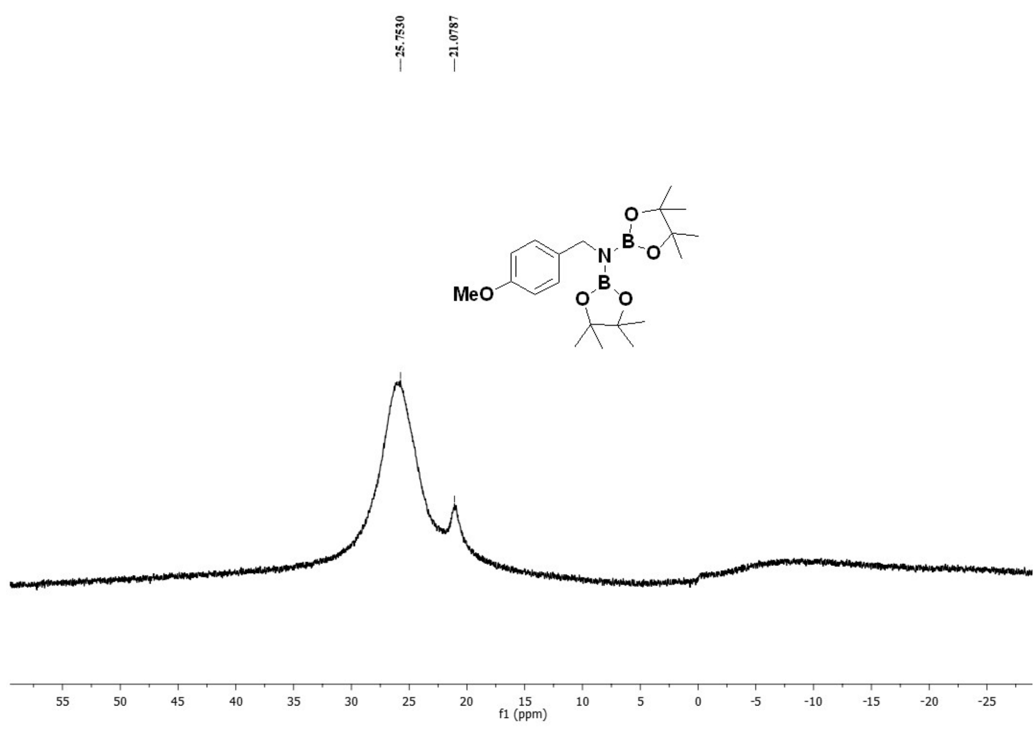


Figure FS18. ^{11}B NMR spectra of complex **2e.**

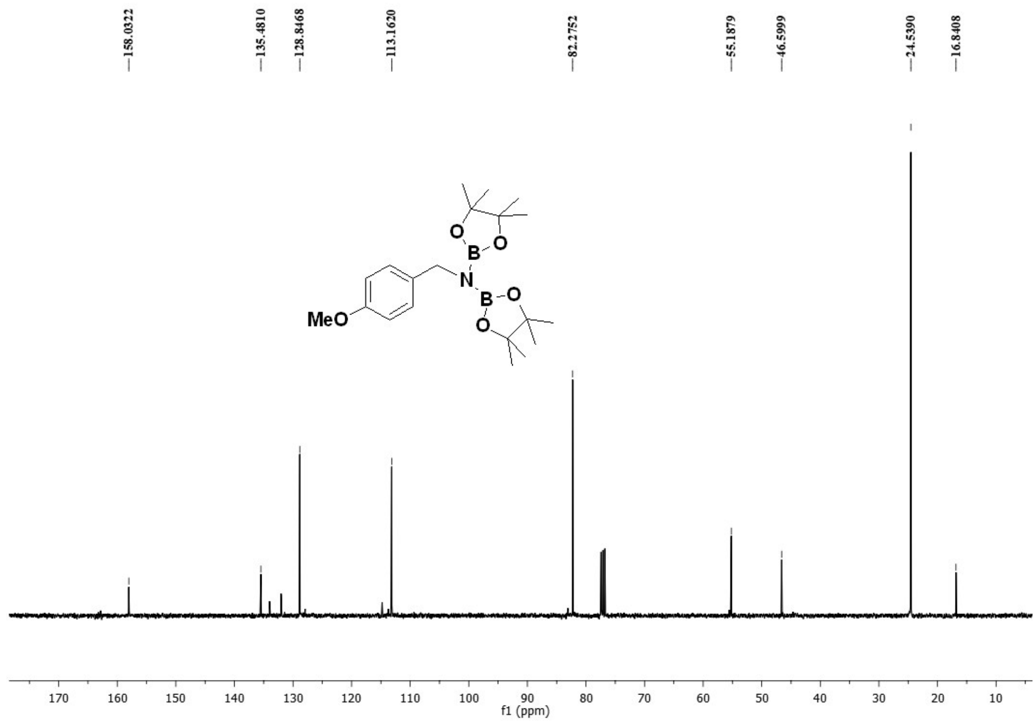


Figure FS19. ^{13}C NMR spectra of complex **2e.**

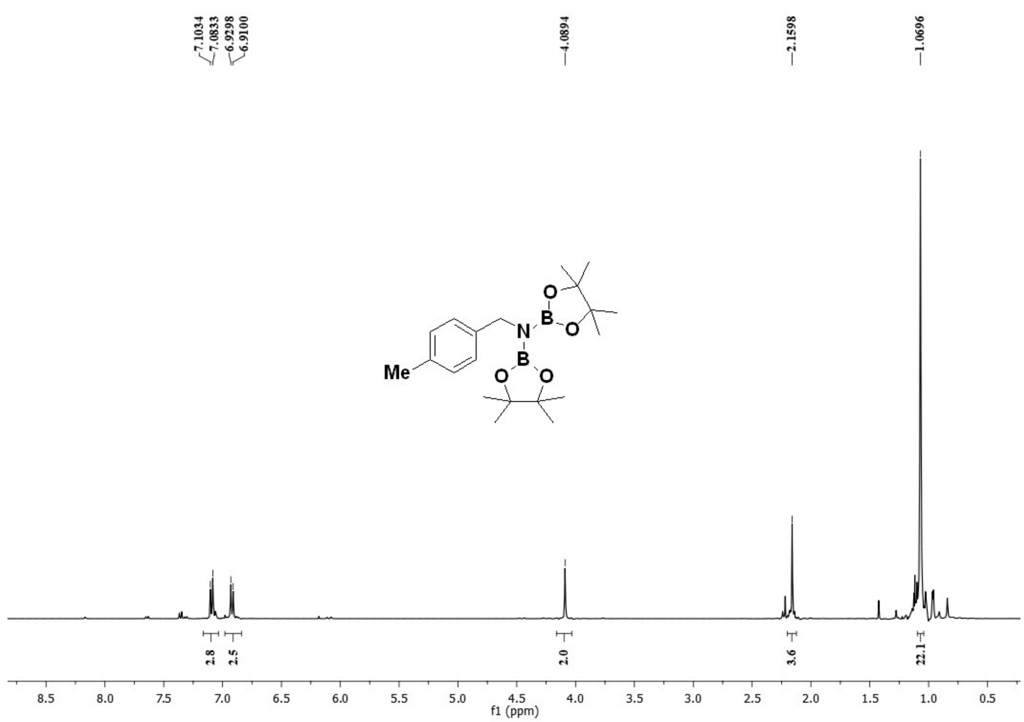


Figure FS20. ^{1}H NMR spectra of complex **2f.**

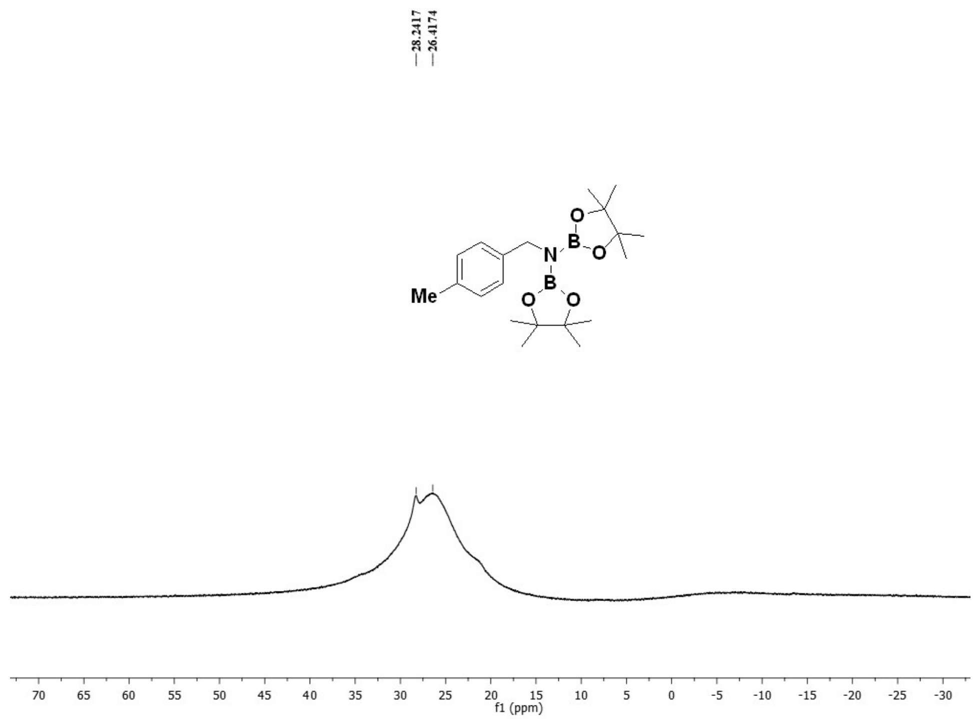


Figure FS21. ^{11}B NMR spectra of complex **2f.**

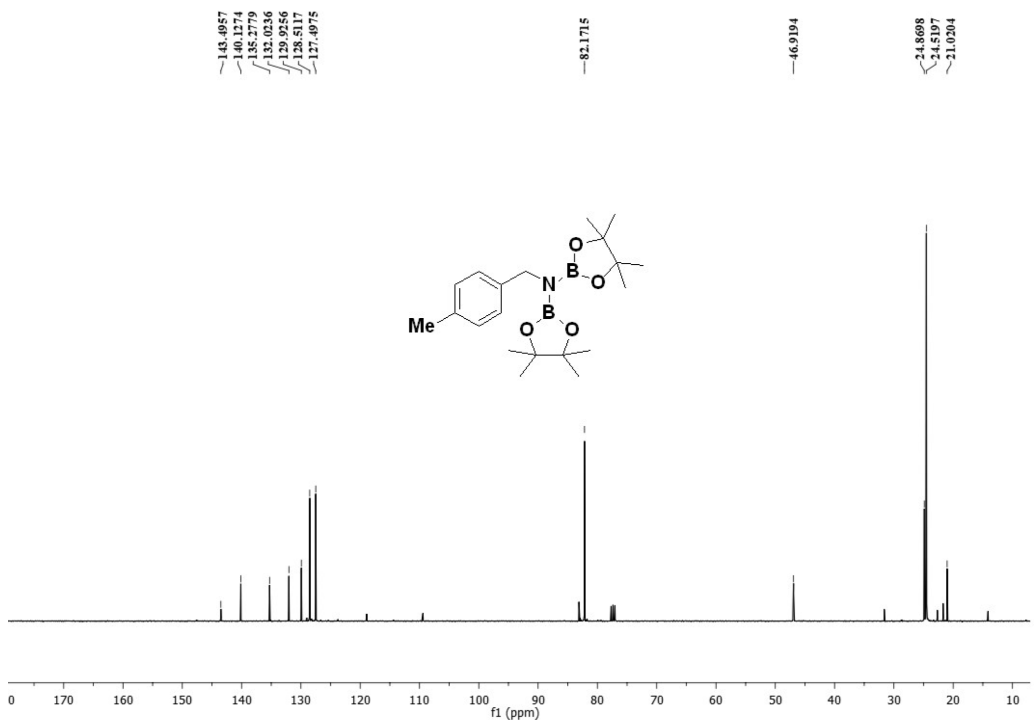


Figure FS22. ^{13}C NMR spectra of complex **2f.**

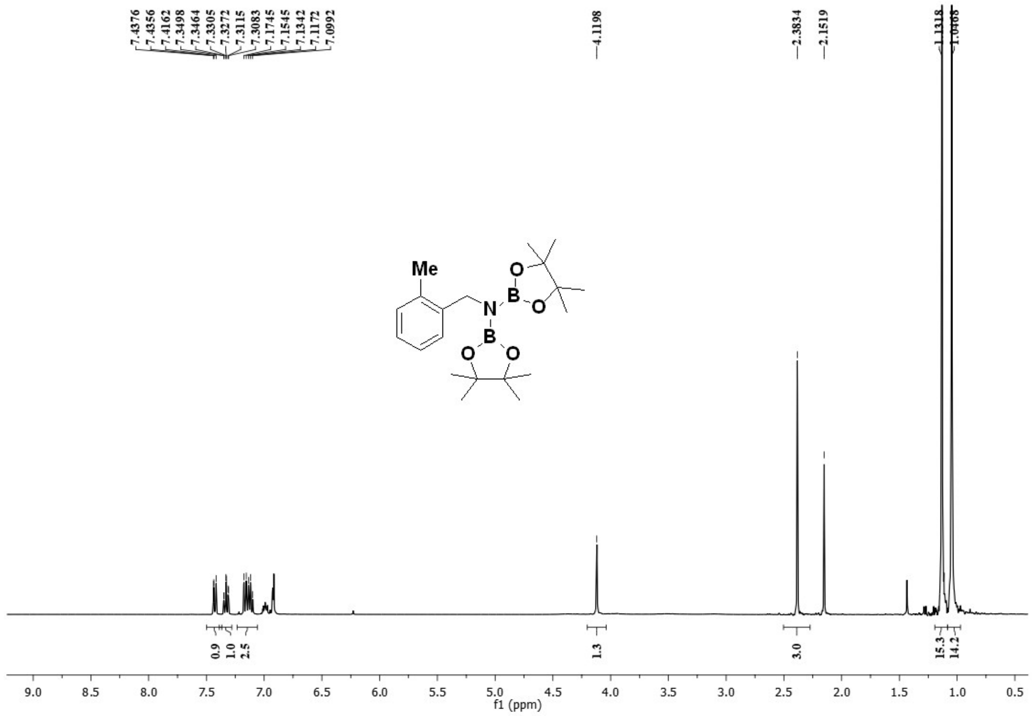


Figure FS23. ^{1}H NMR spectra of complex **2g.**

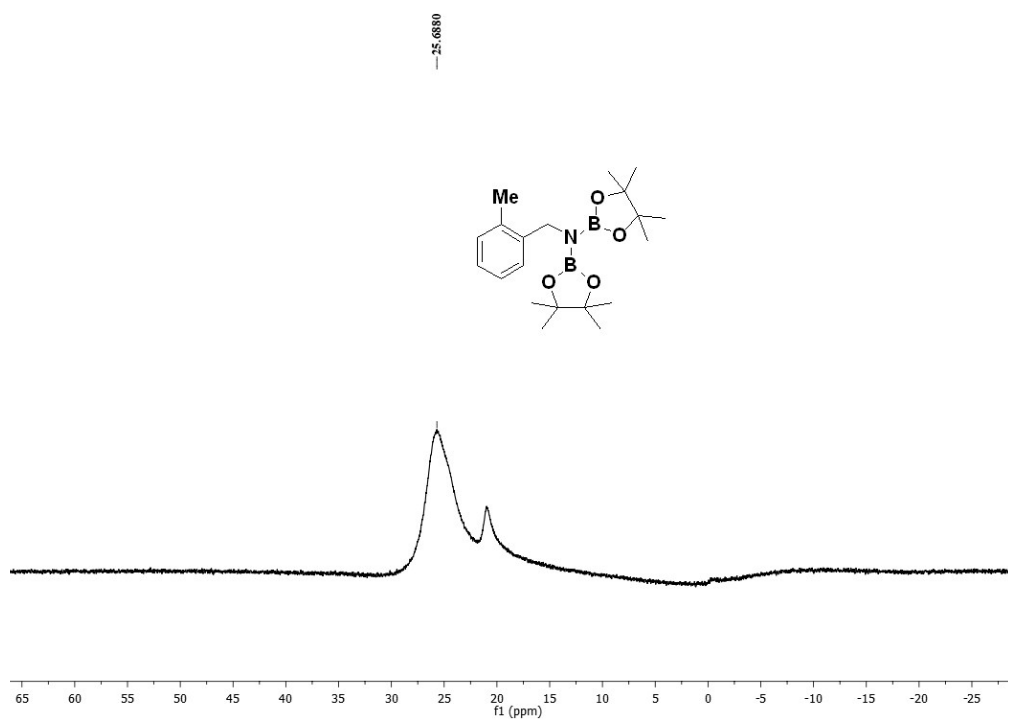


Figure FS24. ^{11}B NMR spectra of complex **2g.**

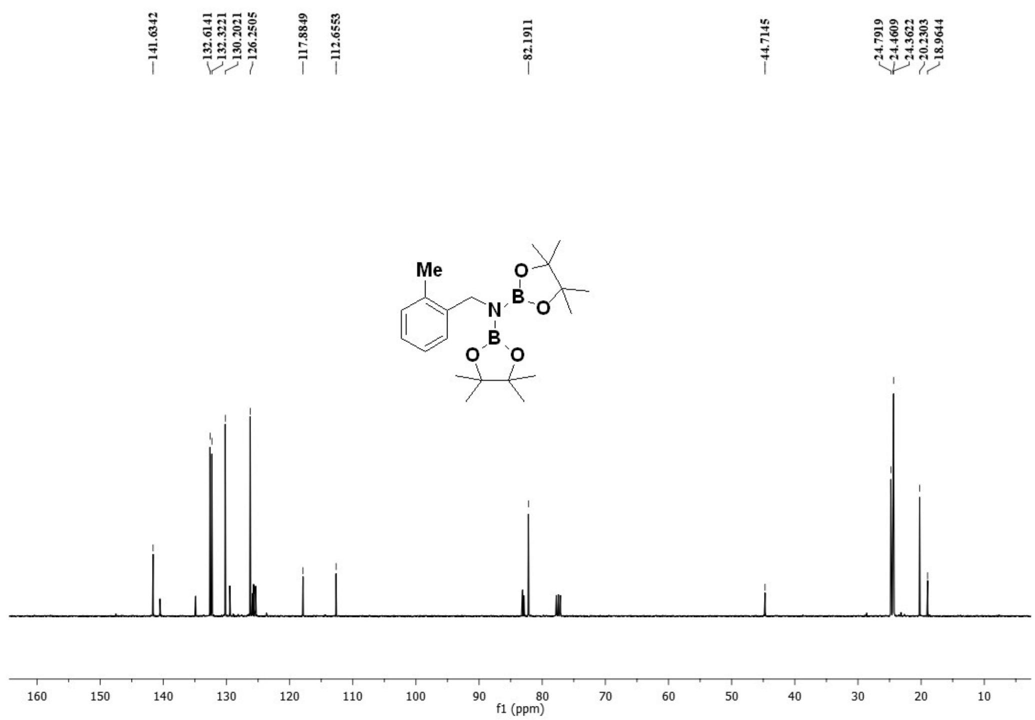


Figure FS25. ^{13}C NMR spectra of complex **2g.**

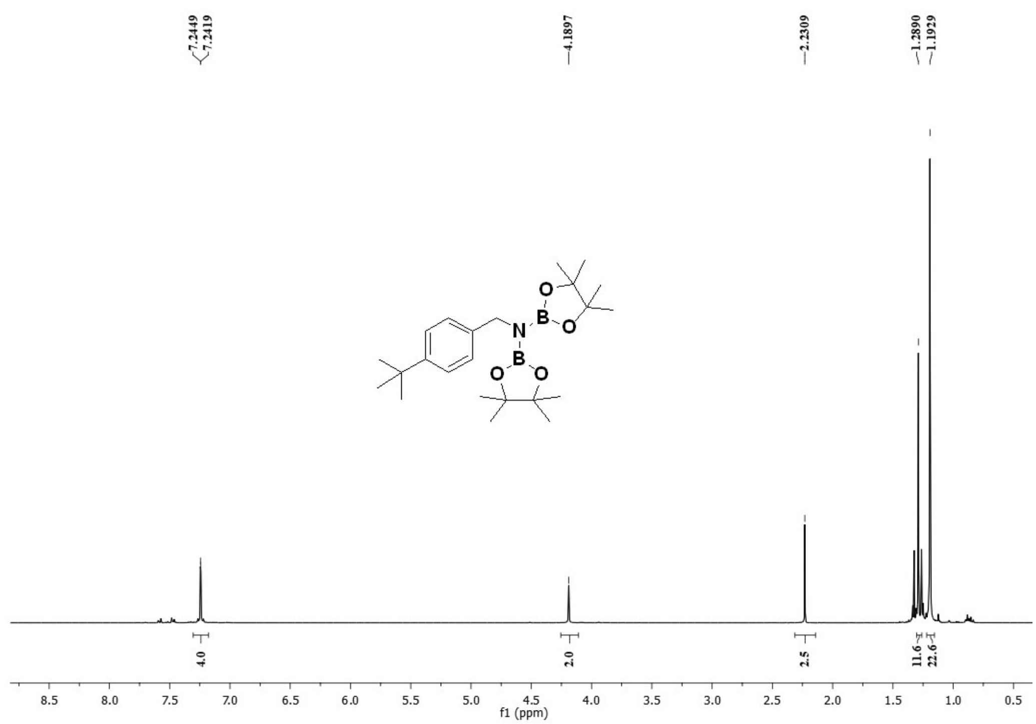


Figure FS26. ^{1}H NMR spectra of complex **2h.**

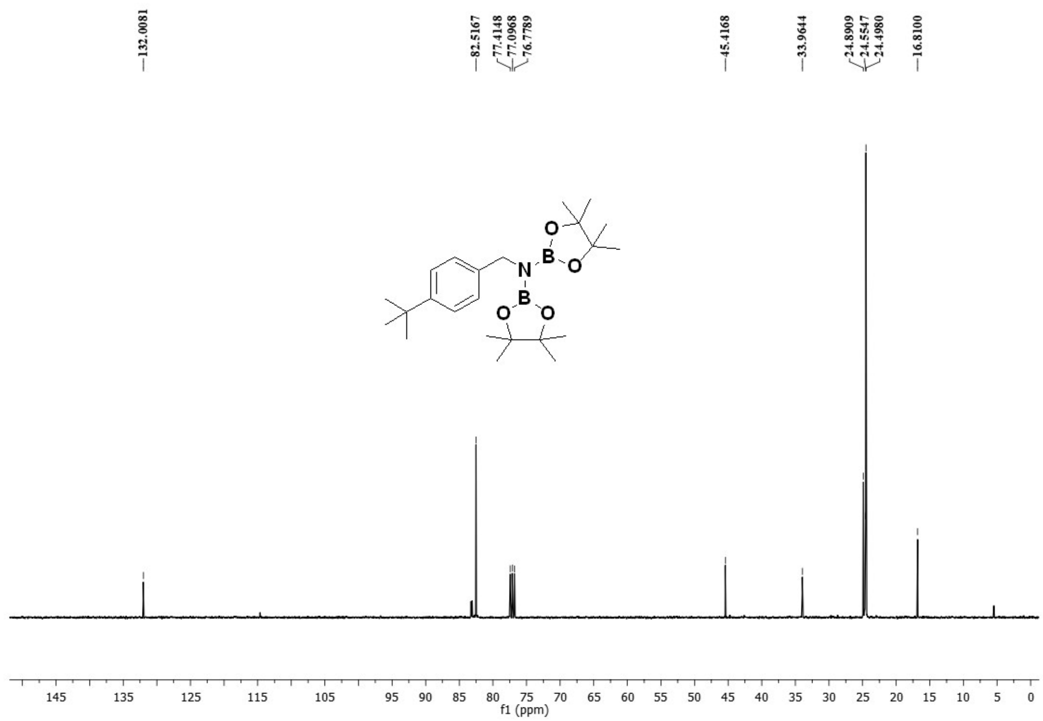


Figure FS27. ^{13}C NMR spectra of complex **2h.**

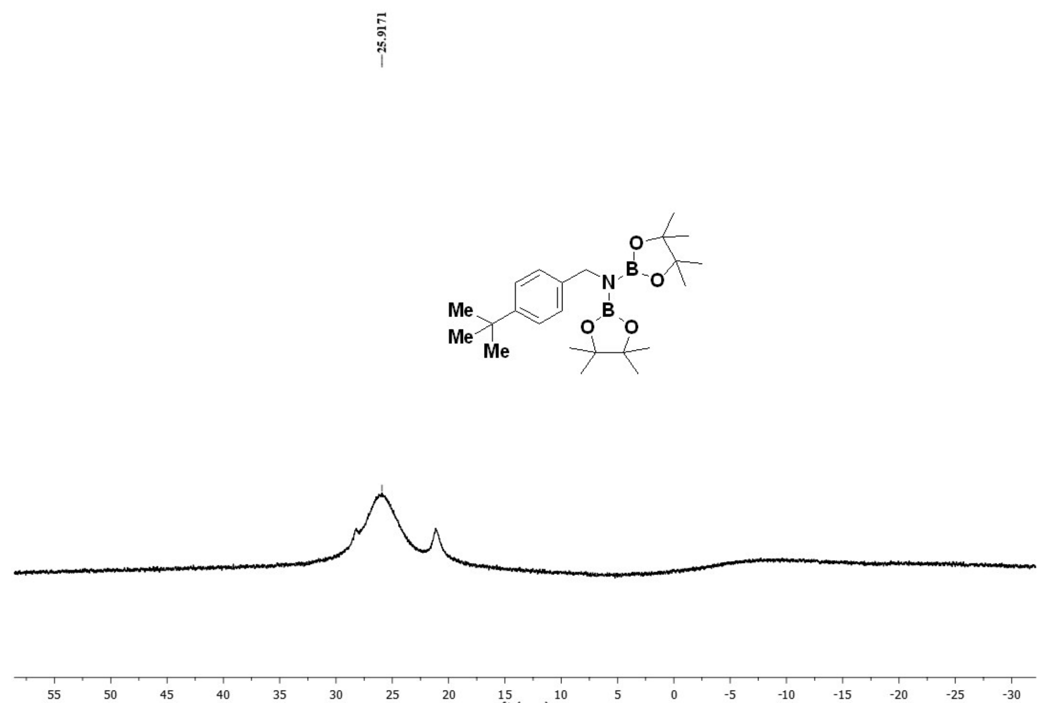


Figure FS28. ^{11}B NMR spectra of complex **2h.**

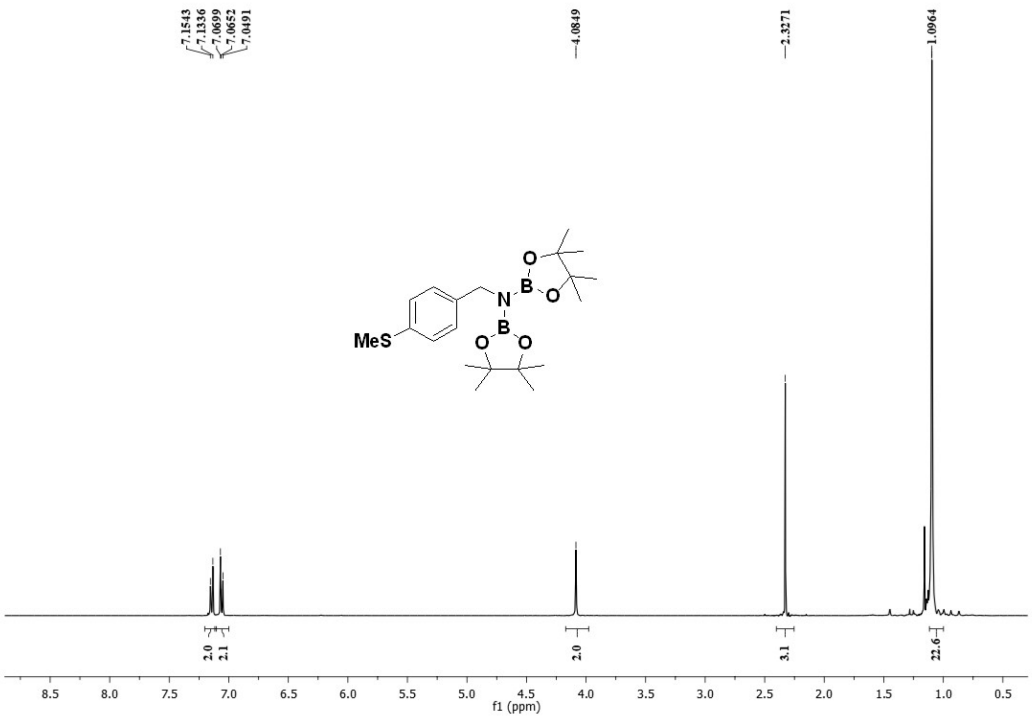


Figure FS29. [1]H NMR spectra of complex **2i.**

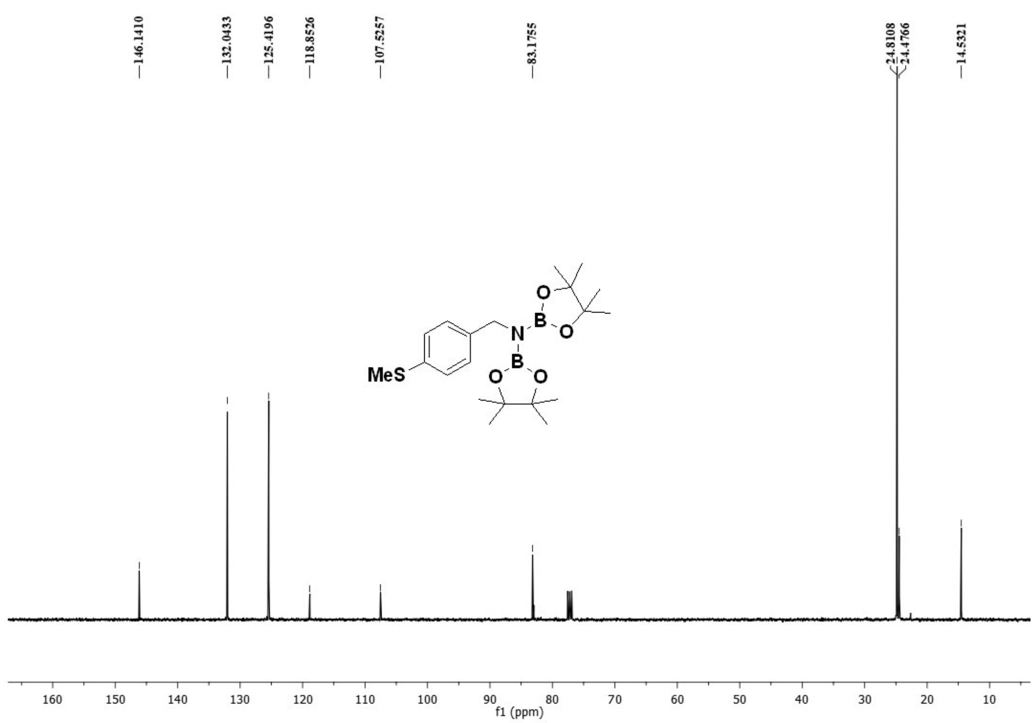


Figure FS30. [13]C NMR spectra of complex **2i.**

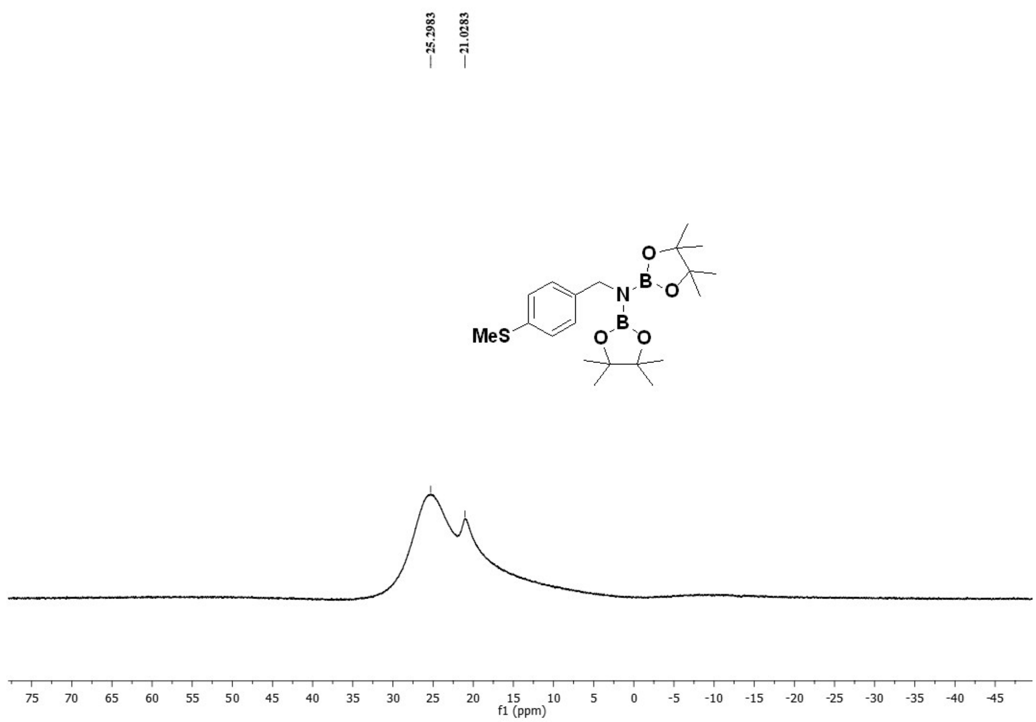


Figure FS31. ^{11}B NMR spectra of complex **2i.**

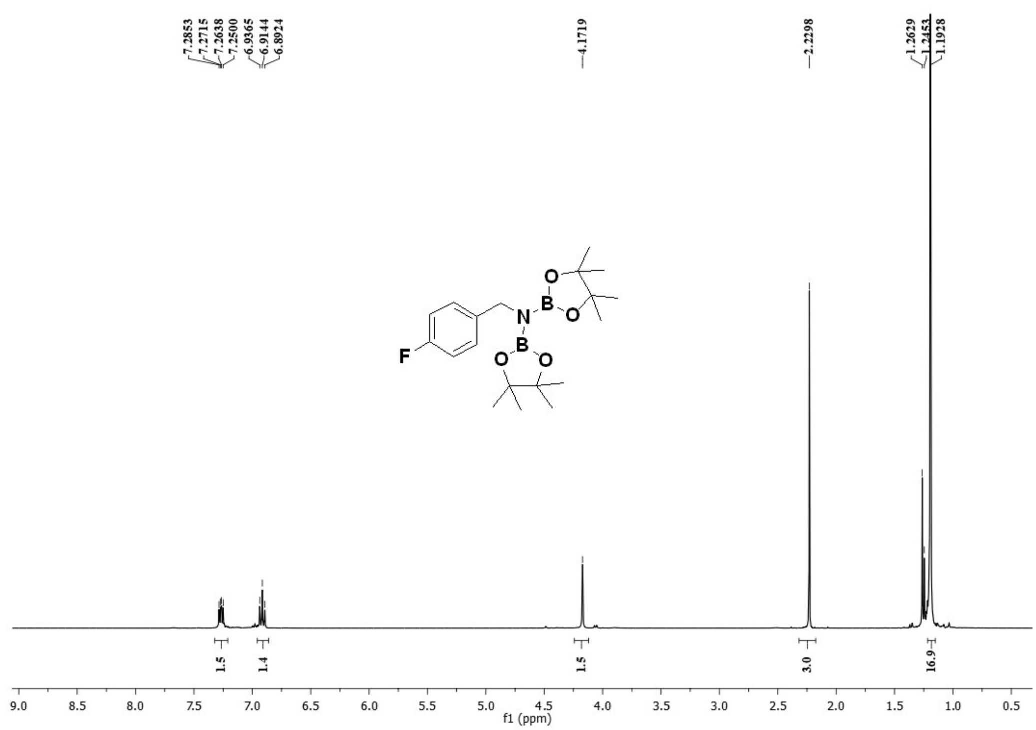


Figure FS32. ^{1}H NMR spectra of complex **2j.**

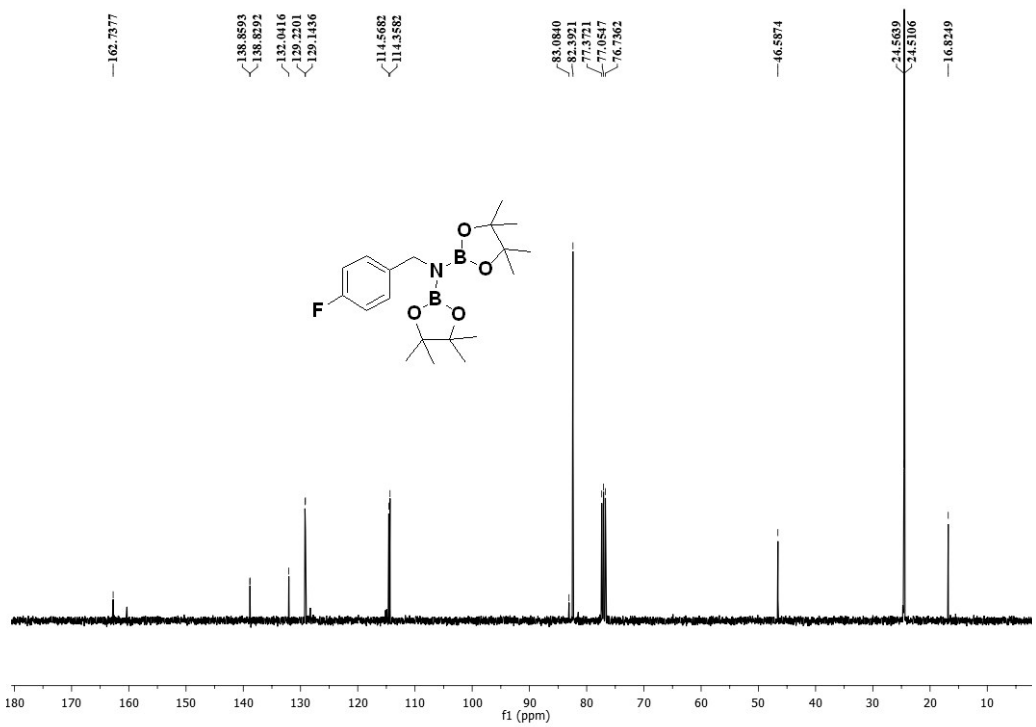


Figure FS33. ^{13}C NMR spectra of complex **2j.**

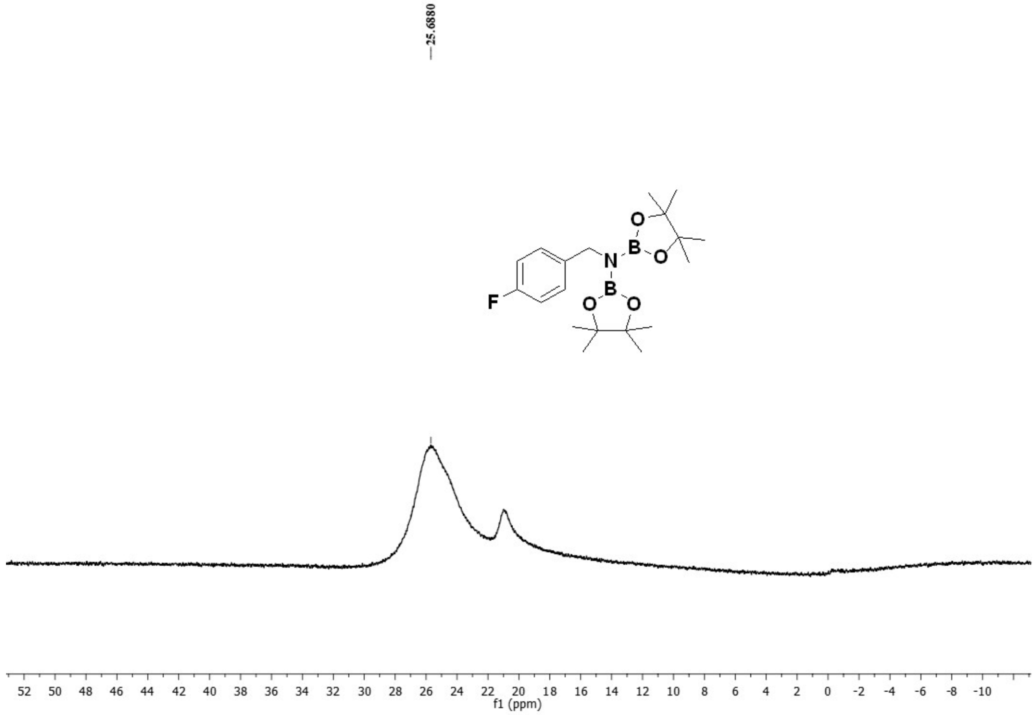


Figure FS34. ^{11}B NMR spectra of complex **2j.**

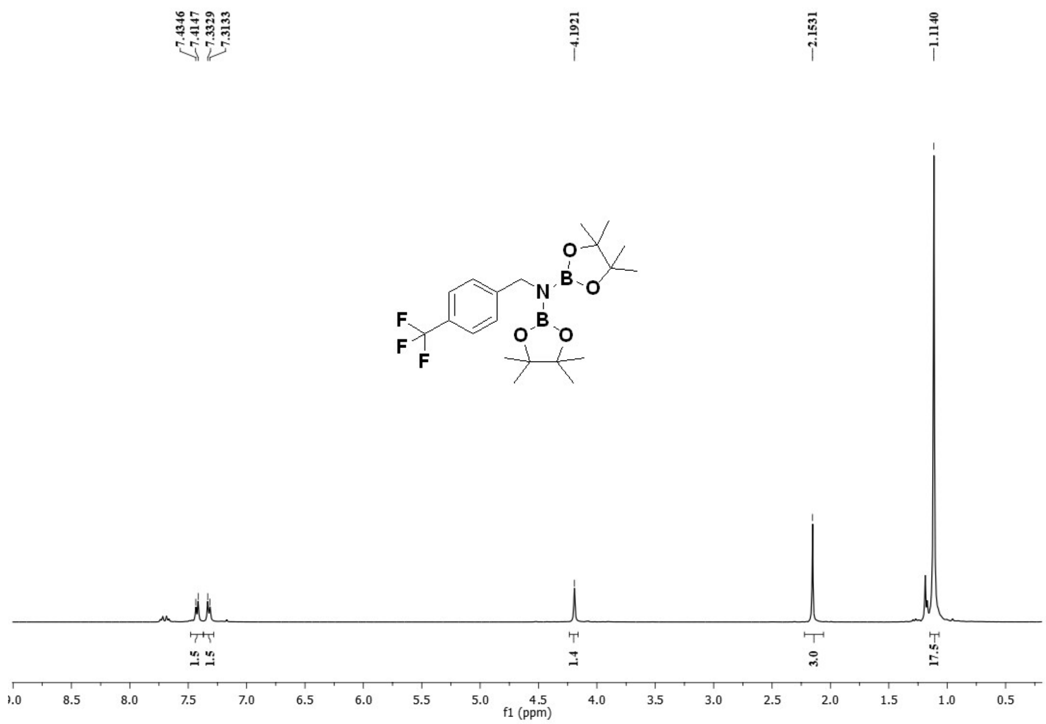


Figure FS35. ^{1}H NMR spectra of complex **2k.**

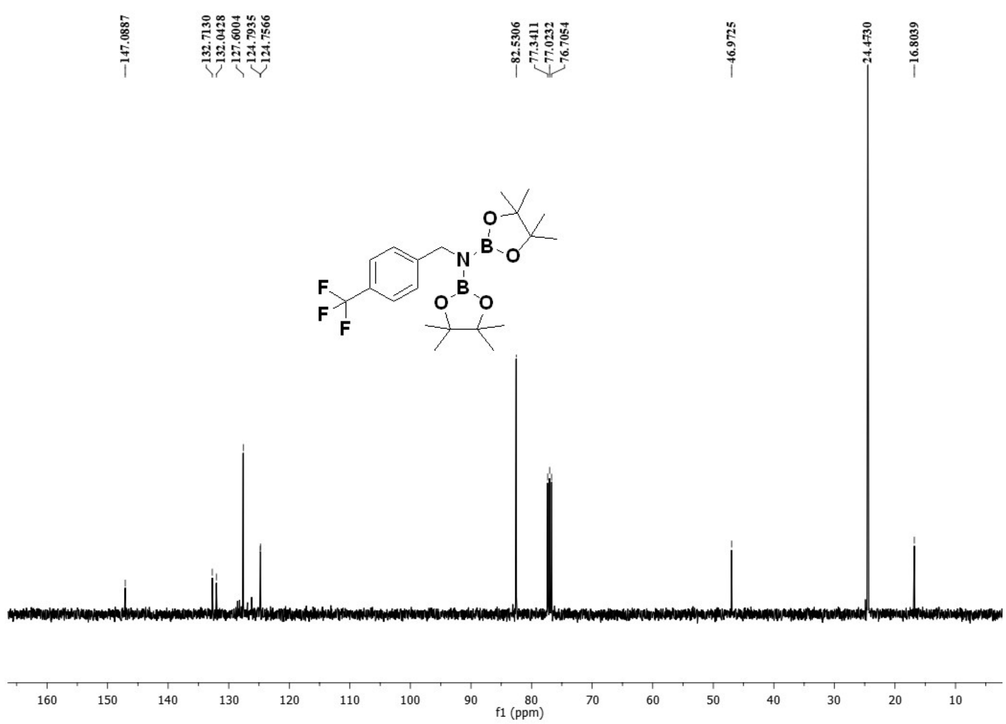


Figure FS36. ^{13}C NMR spectra of complex **2j.**

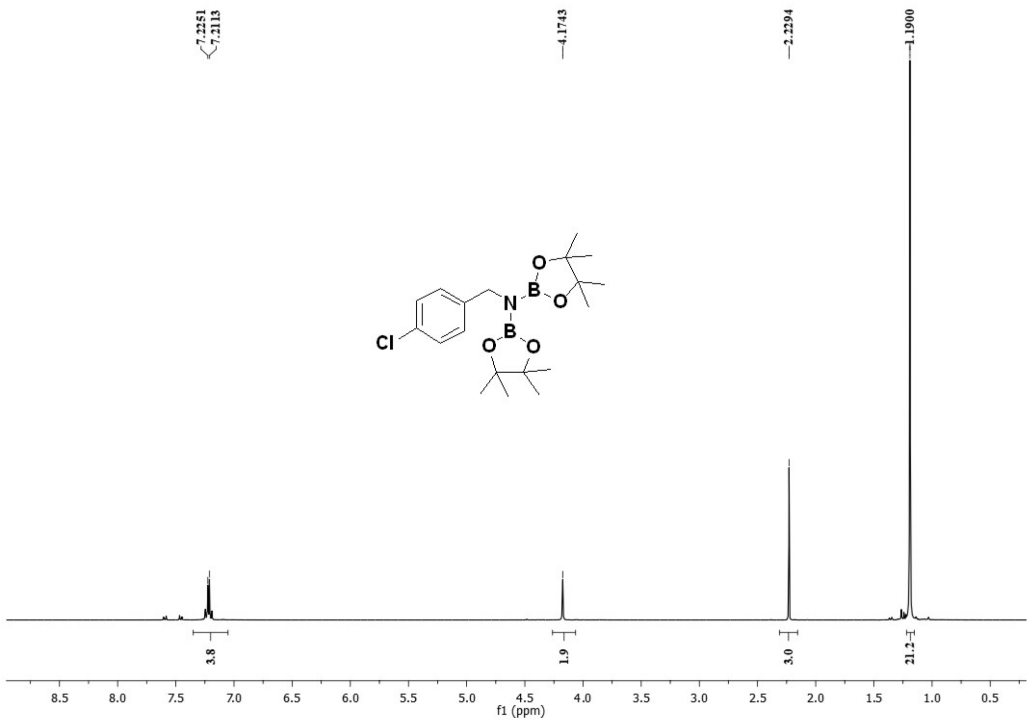


Figure FS37. ^{1}H NMR spectra of complex **2l.**

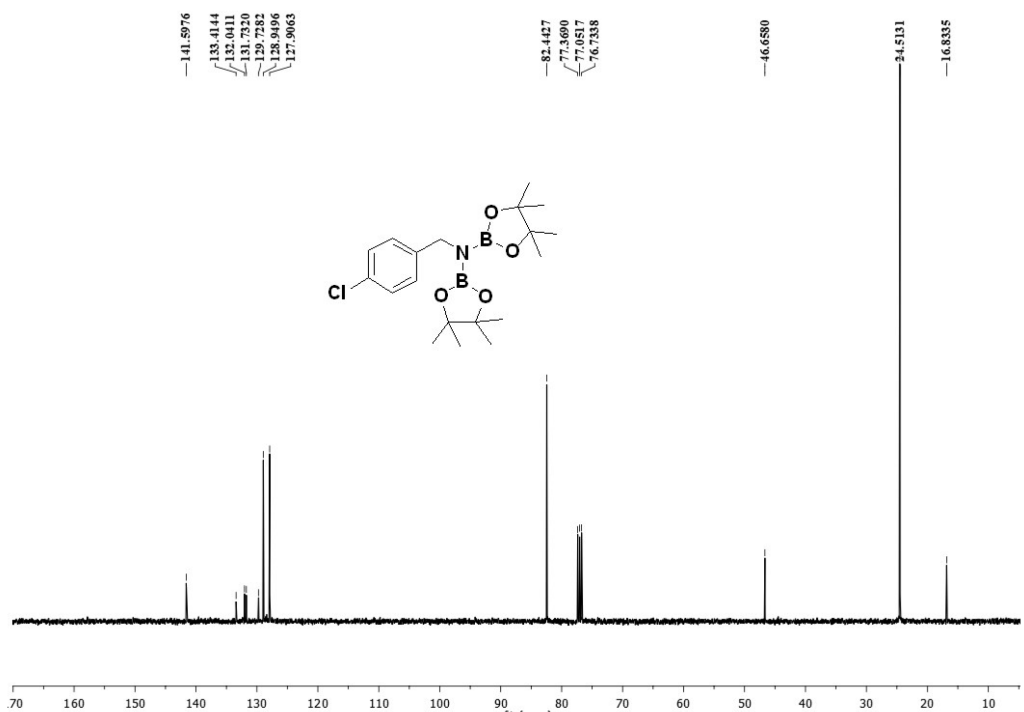


Figure FS38. ^{13}C NMR spectra of complex **2l.**

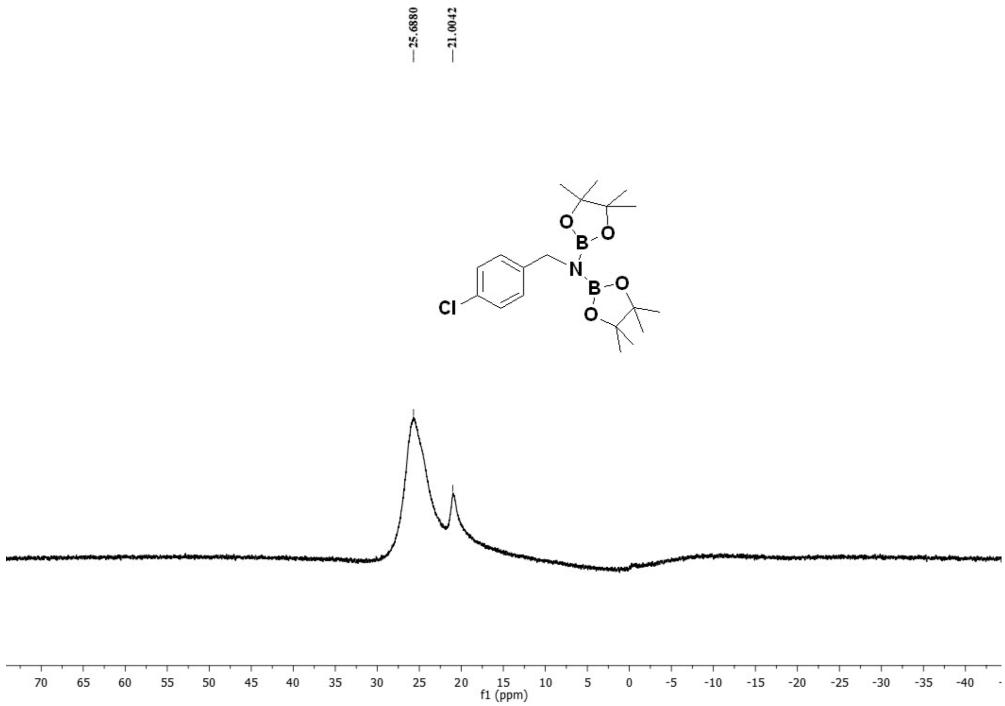


Figure FS39. ^{11}B NMR spectra of complex **2l.**

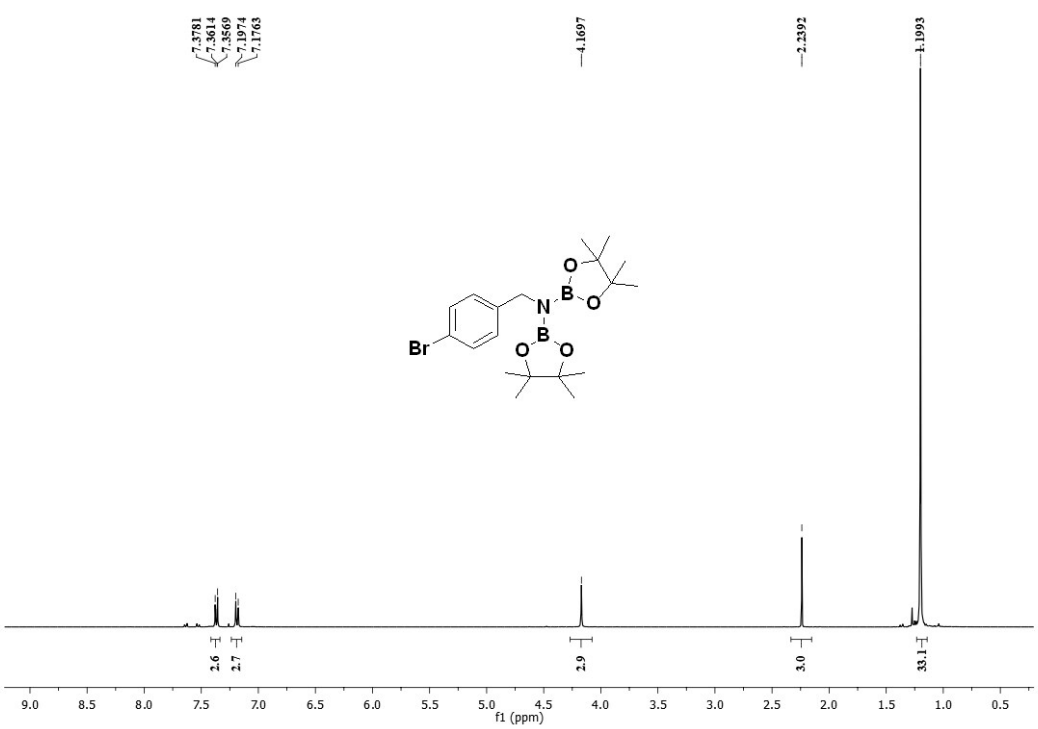


Figure FS40. ^{1}H NMR spectra of complex **2m.**

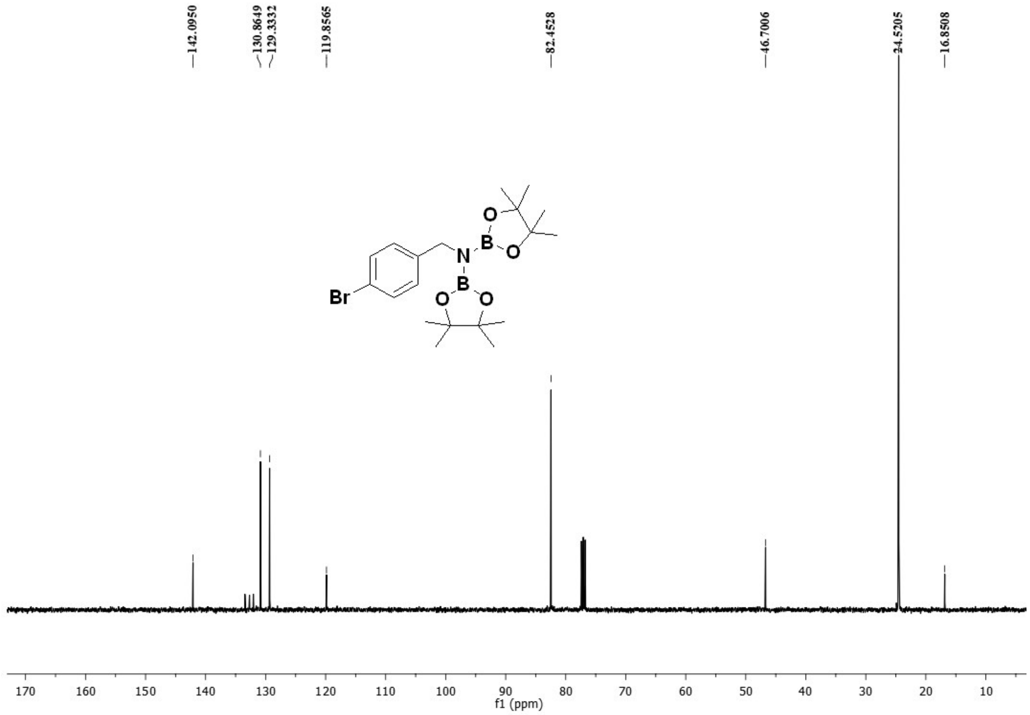


Figure FS41. ^{13}C NMR spectra of complex **2m.**

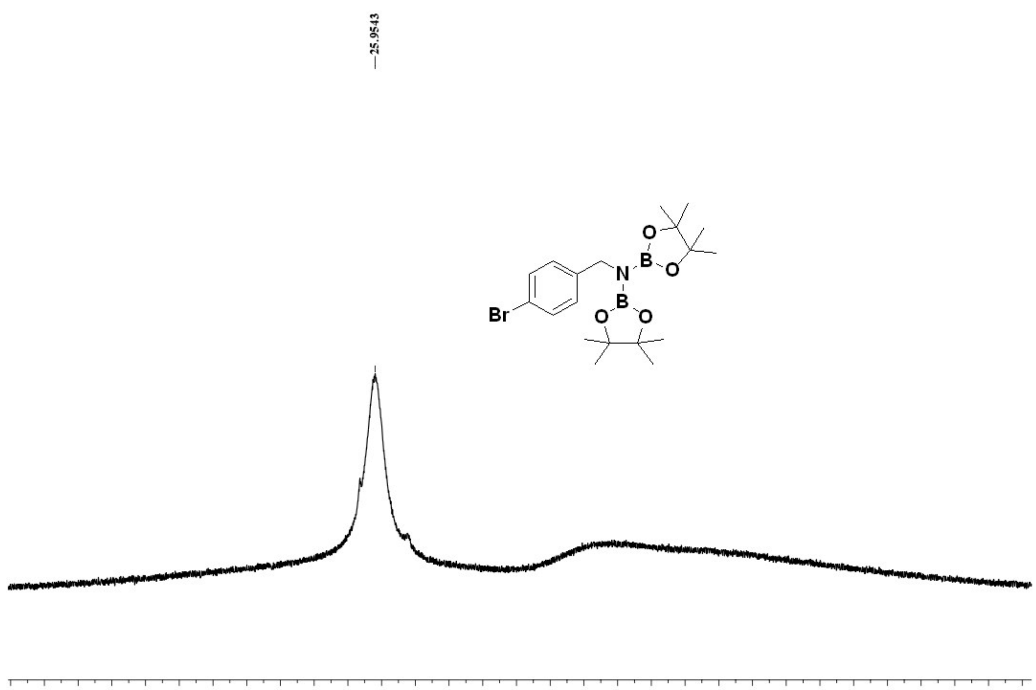


Figure FS42. ^{11}B NMR spectra of complex **2m.**

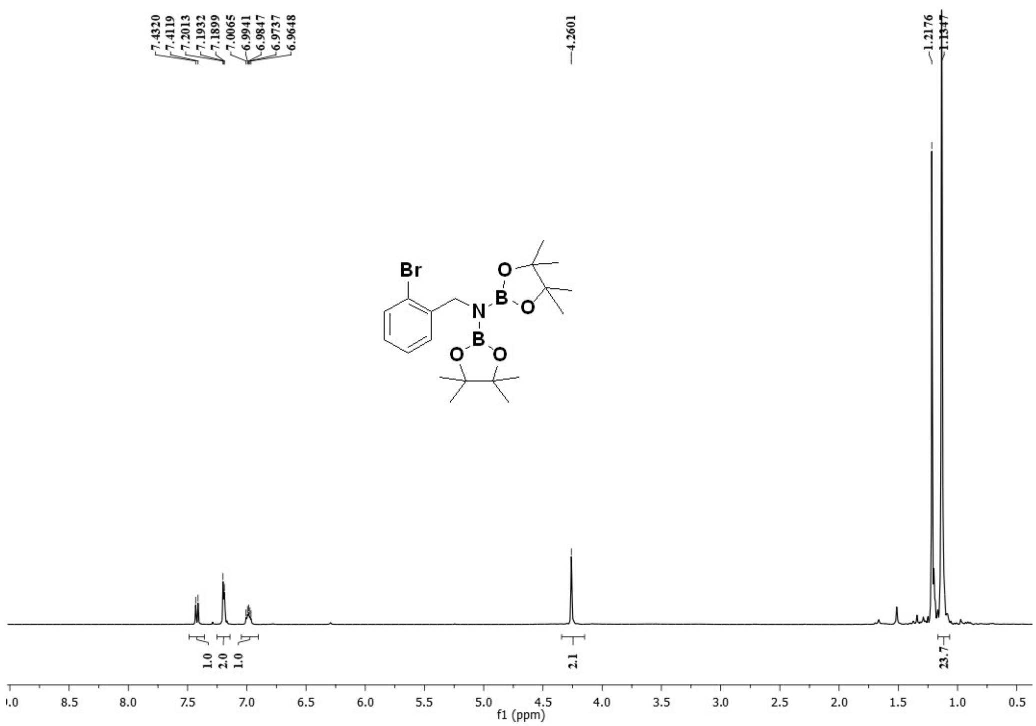


Figure FS43. ^{1}H NMR spectra of complex **2n.**

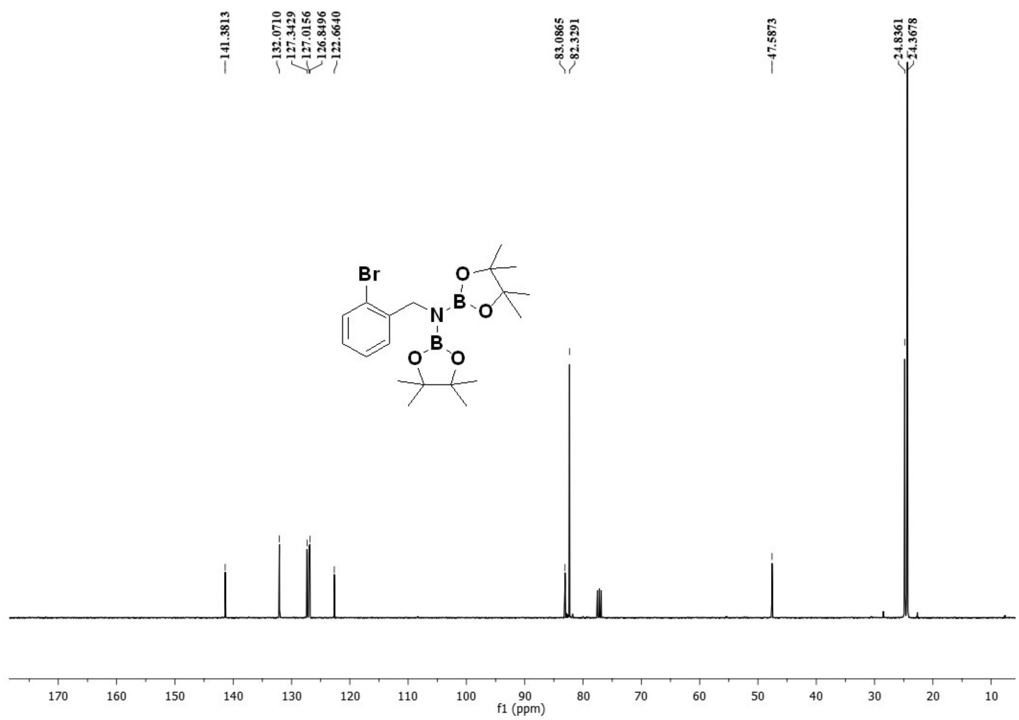


Figure FS44. ^{13}C NMR spectra of complex **2n.**

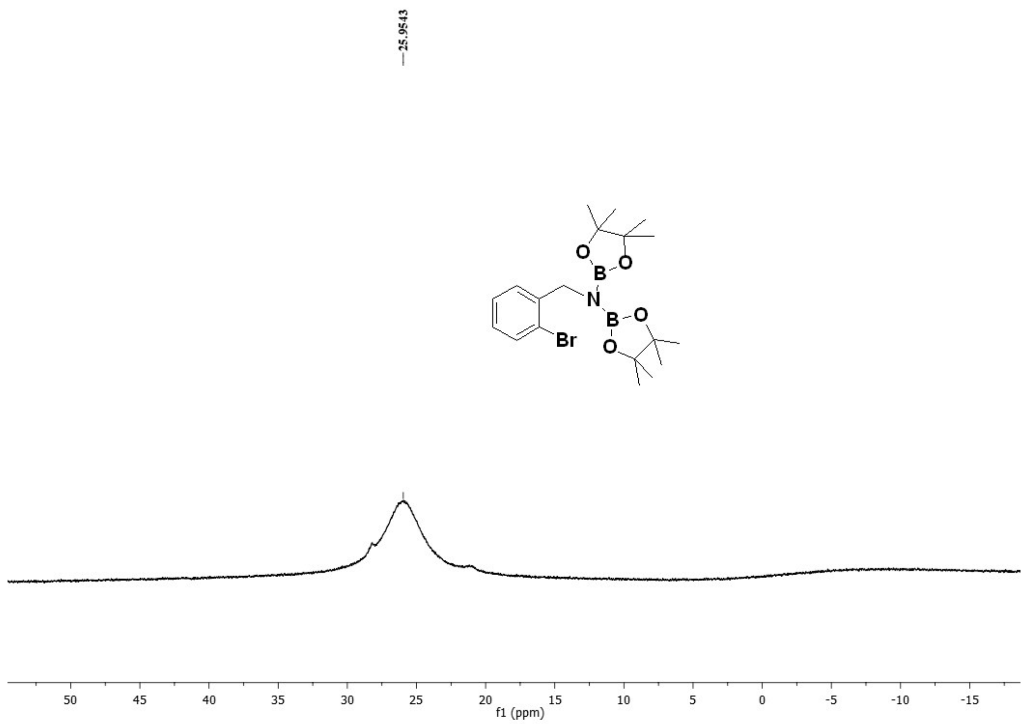


Figure FS45. ^{11}B NMR spectra of complex **2n.**

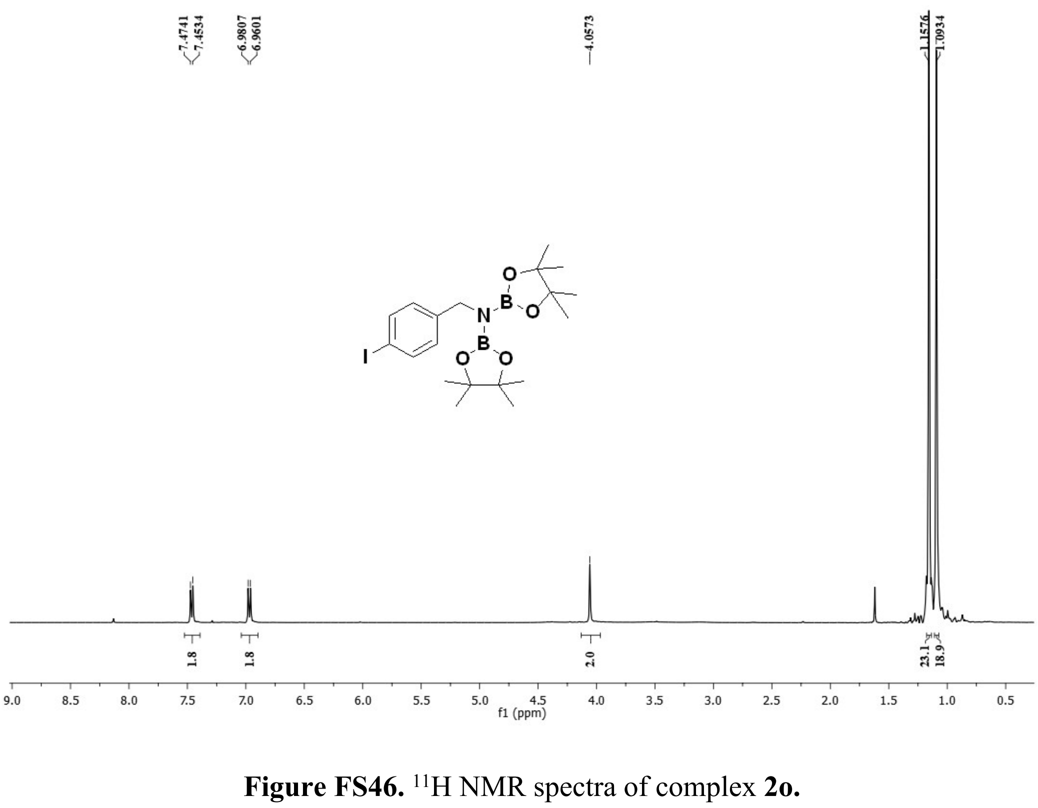


Figure FS46. ^{11}H NMR spectra of complex **2o.**

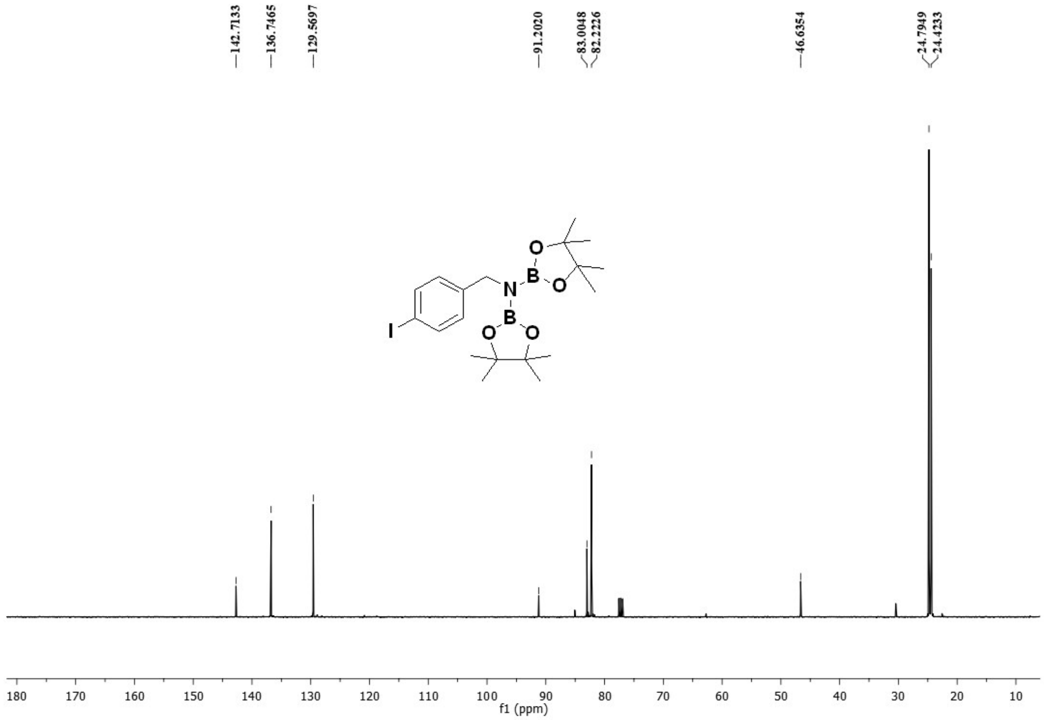


Figure FS47. ^{13}C NMR spectra of complex **2o.**

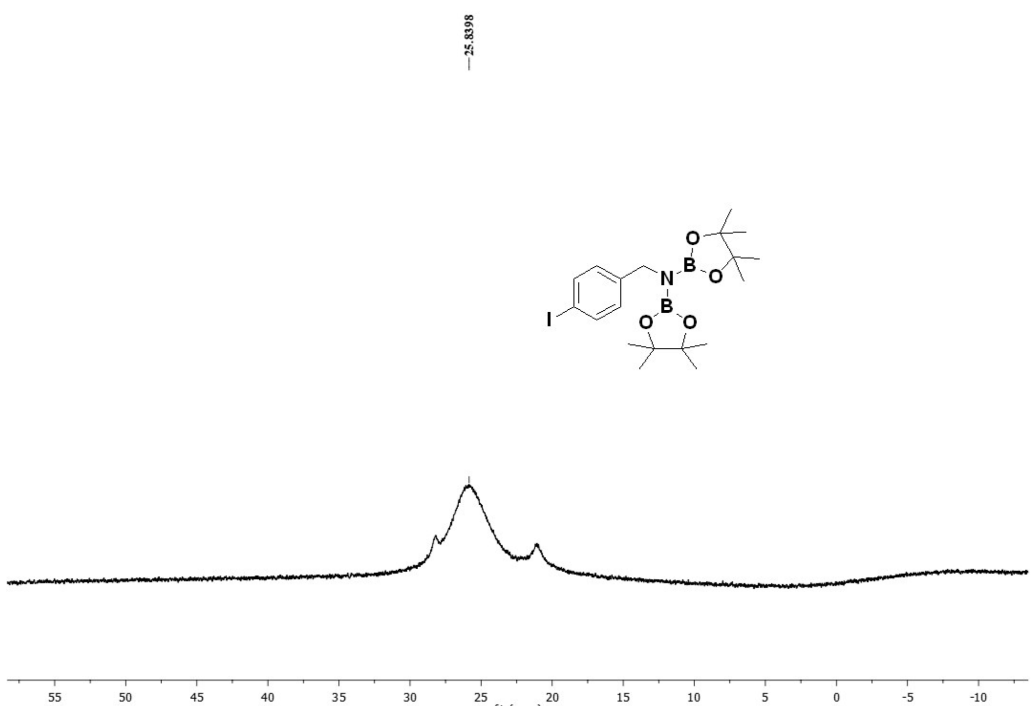


Figure FS48. ^{11}B NMR spectra of complex **2o.**

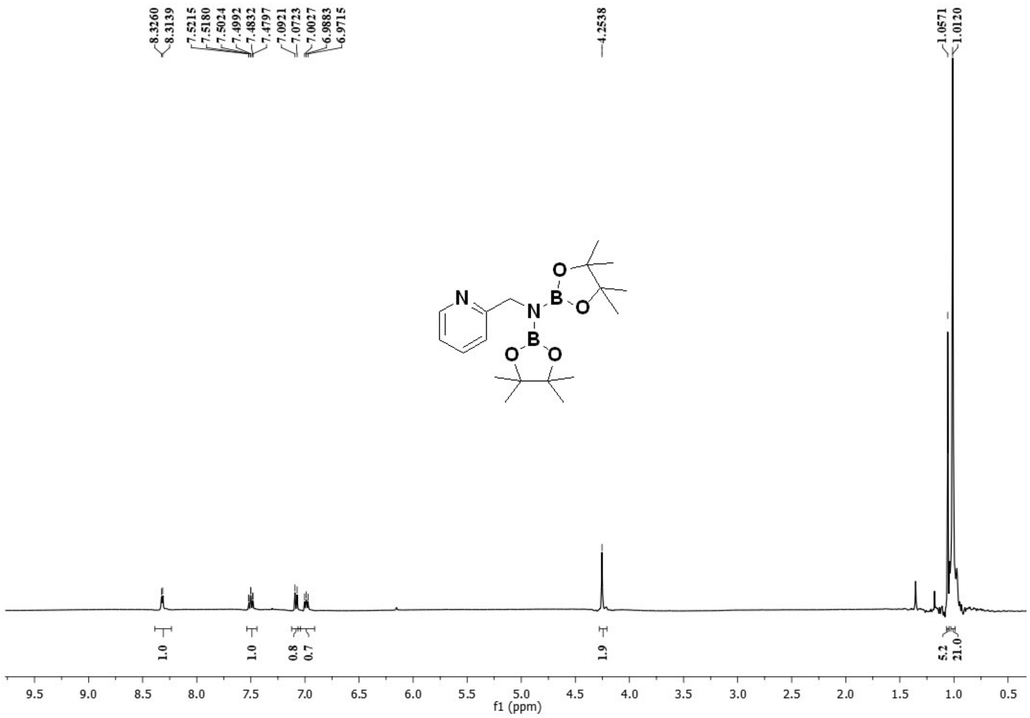


Figure FS49. ^{1}H NMR spectra of complex **2p.**

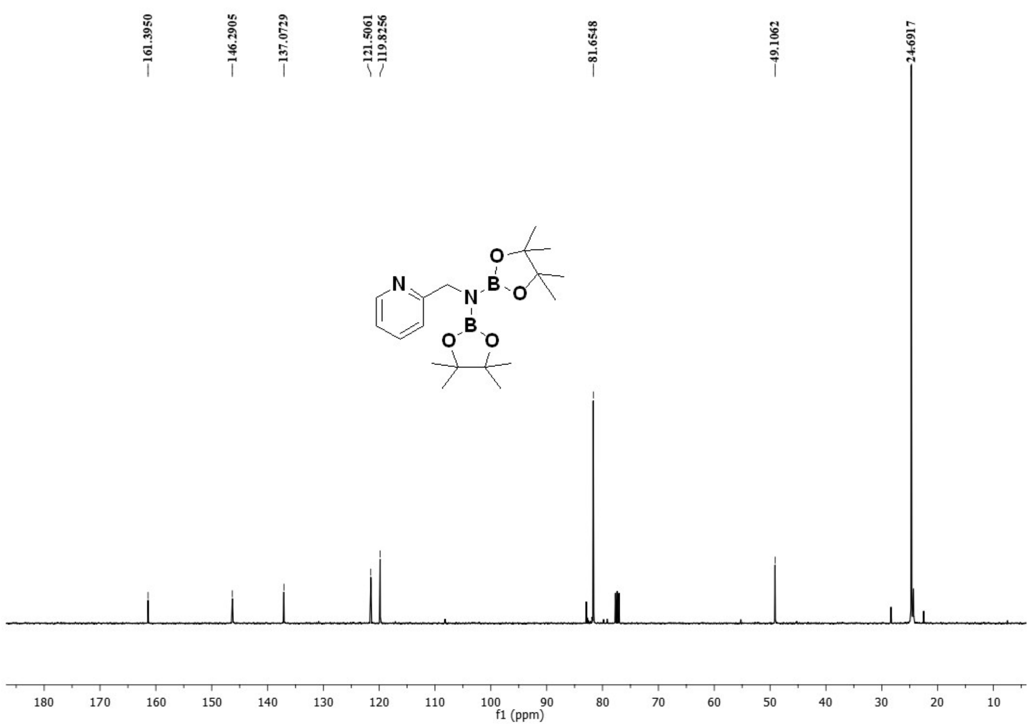


Figure FS50. ^{13}C NMR spectra of complex **2p.**

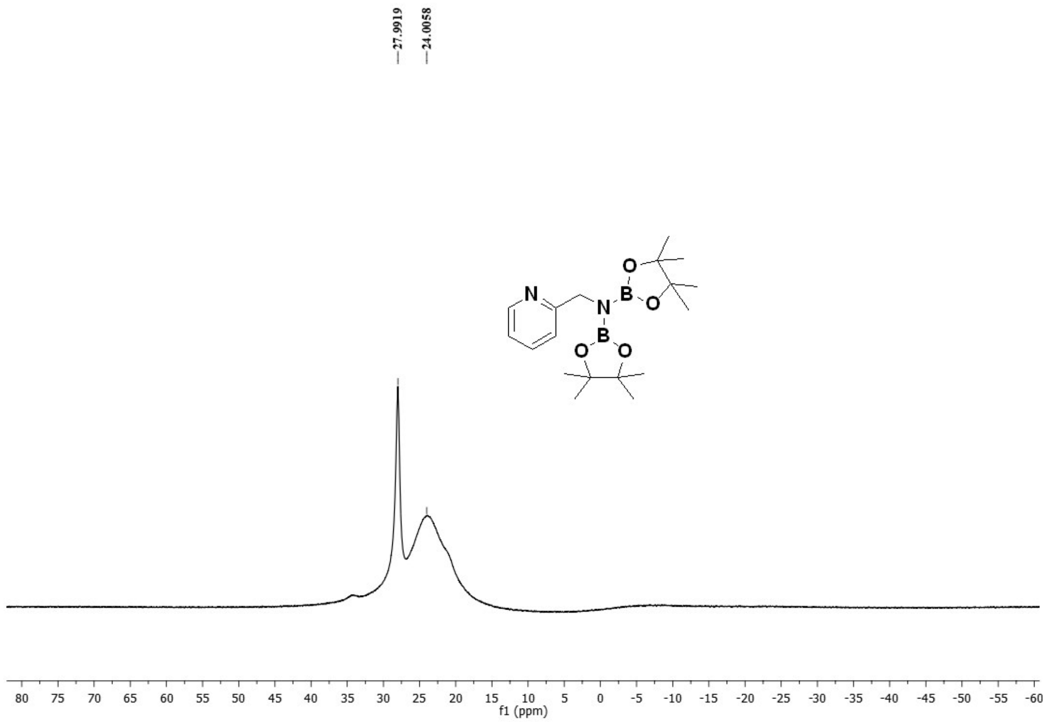


Figure FS51. ^{11}B NMR spectra of complex **2p.**

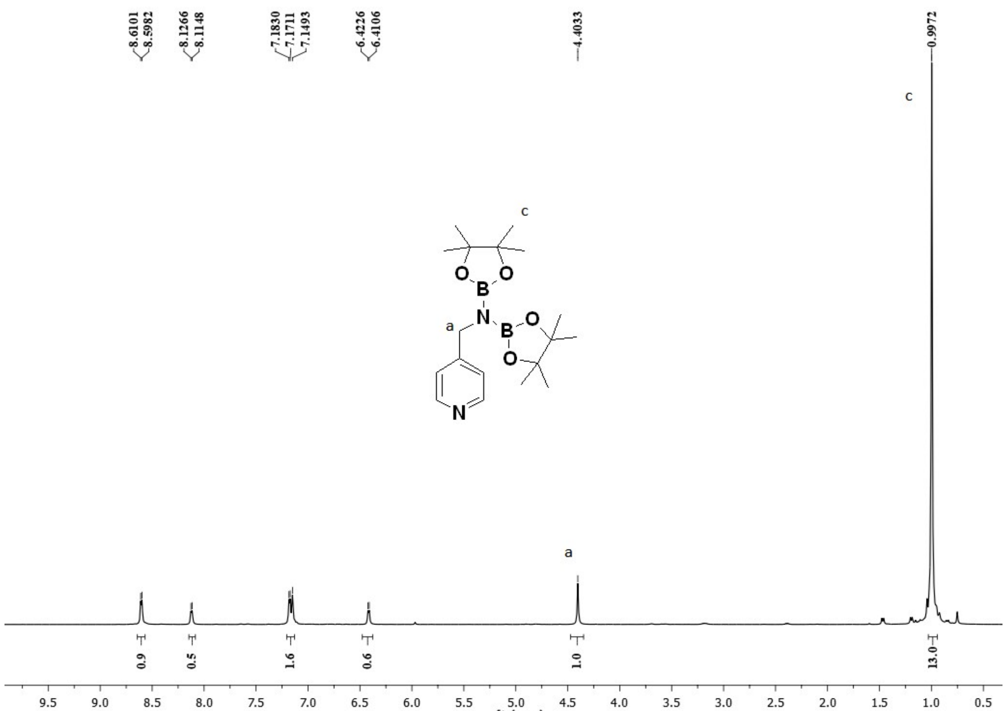


Figure FS52. ^{1}H NMR spectra of complex **2q.**

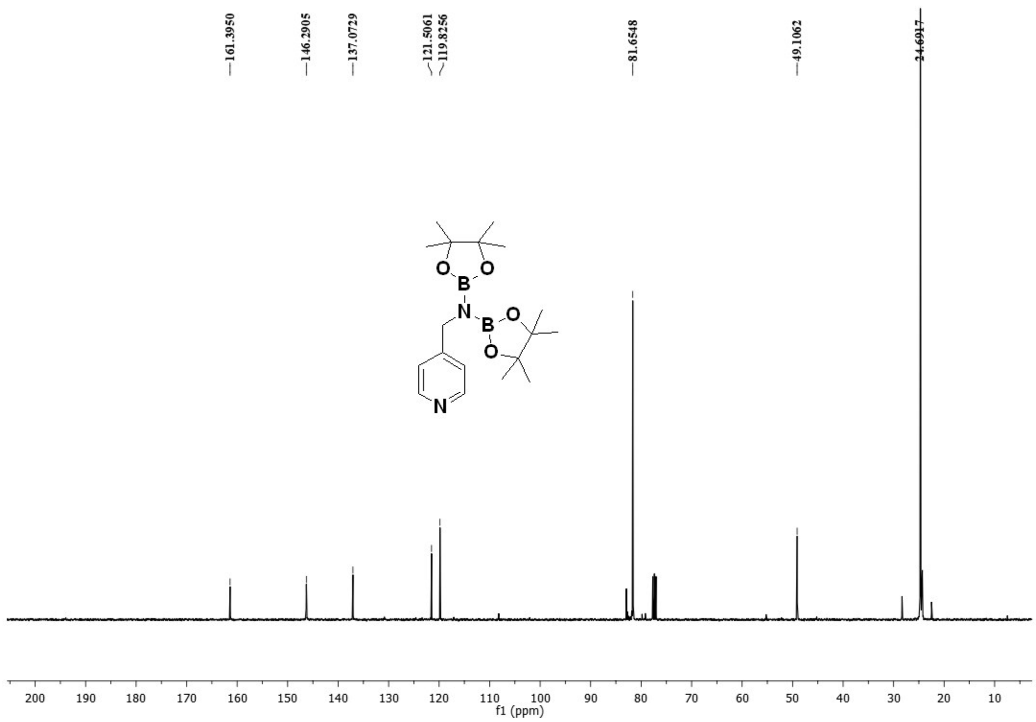


Figure FS53. ^{13}C NMR spectra of complex **2q.**

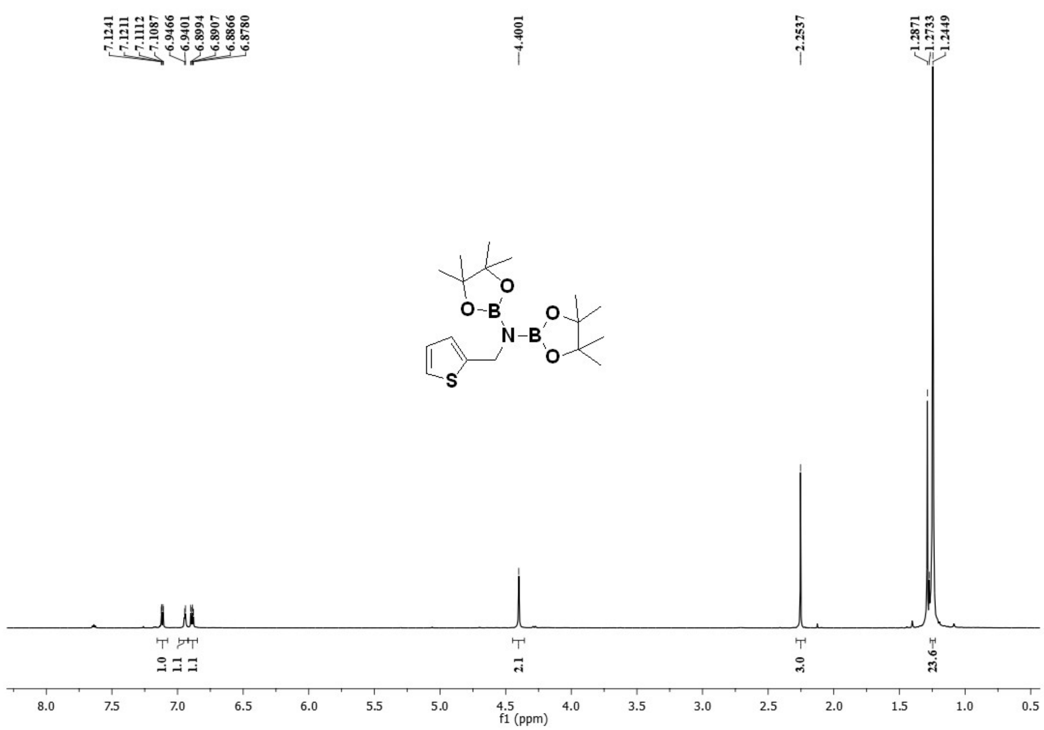


Figure FS54. ^{1}H NMR spectra of complex **2r.**

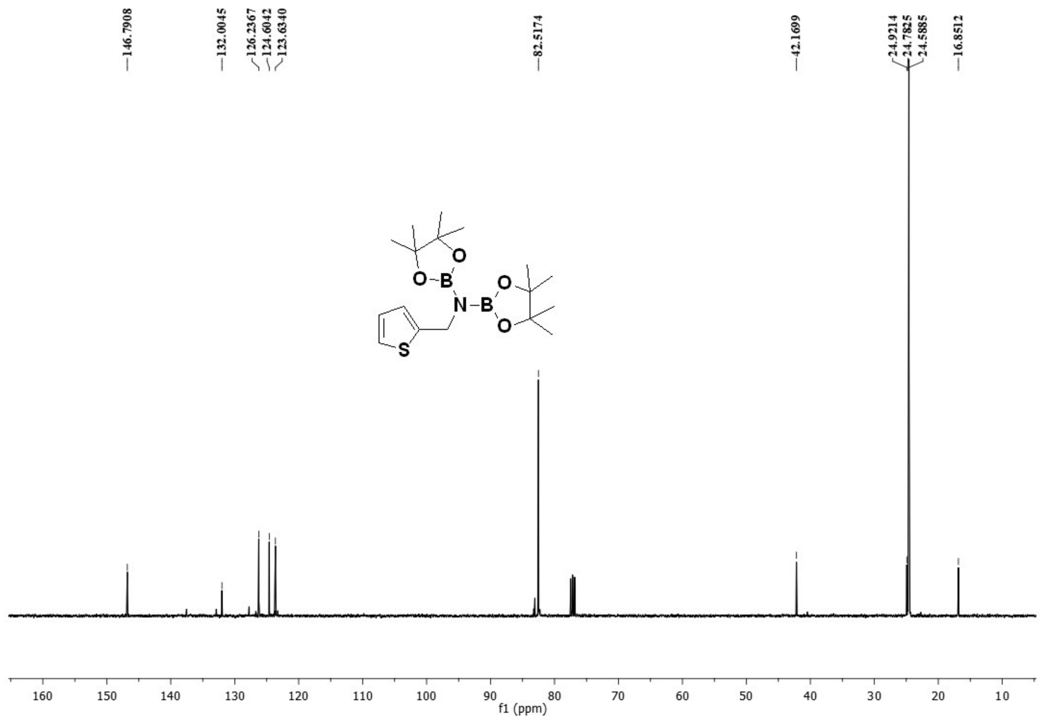


Figure FS55. ^{13}C NMR spectra of complex **2r.**

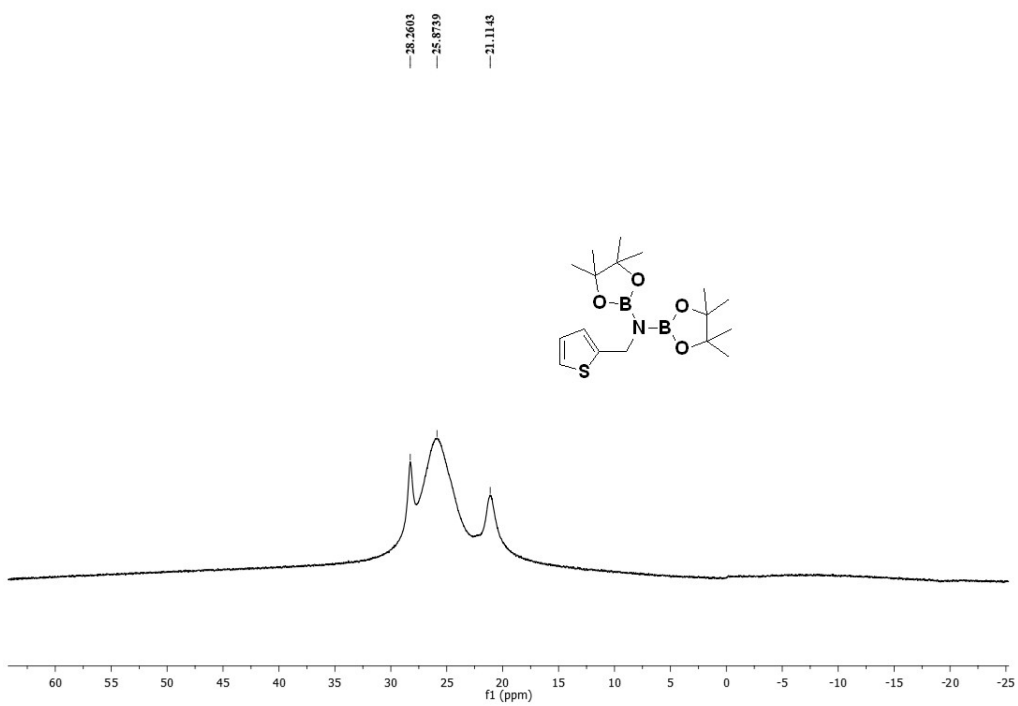


Figure FS56. ^{11}B NMR spectra of complex **2r.**

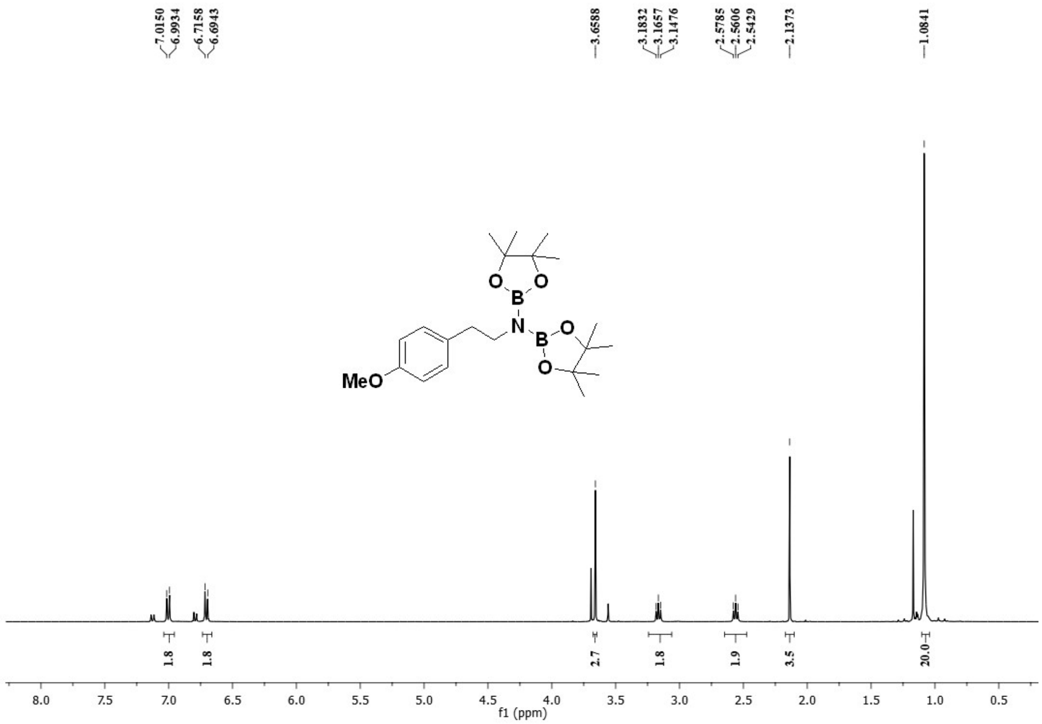


Figure FS57. ^{13}C NMR spectra of complex **2s.**

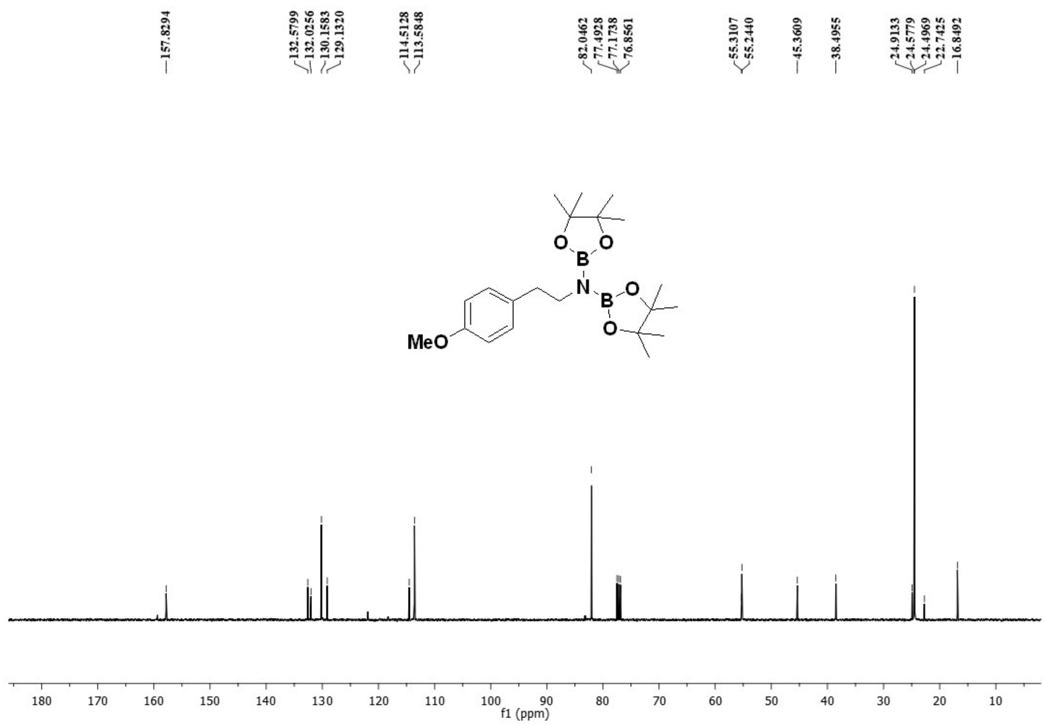


Figure FS58. ^{13}C NMR spectra of complex **2s.**

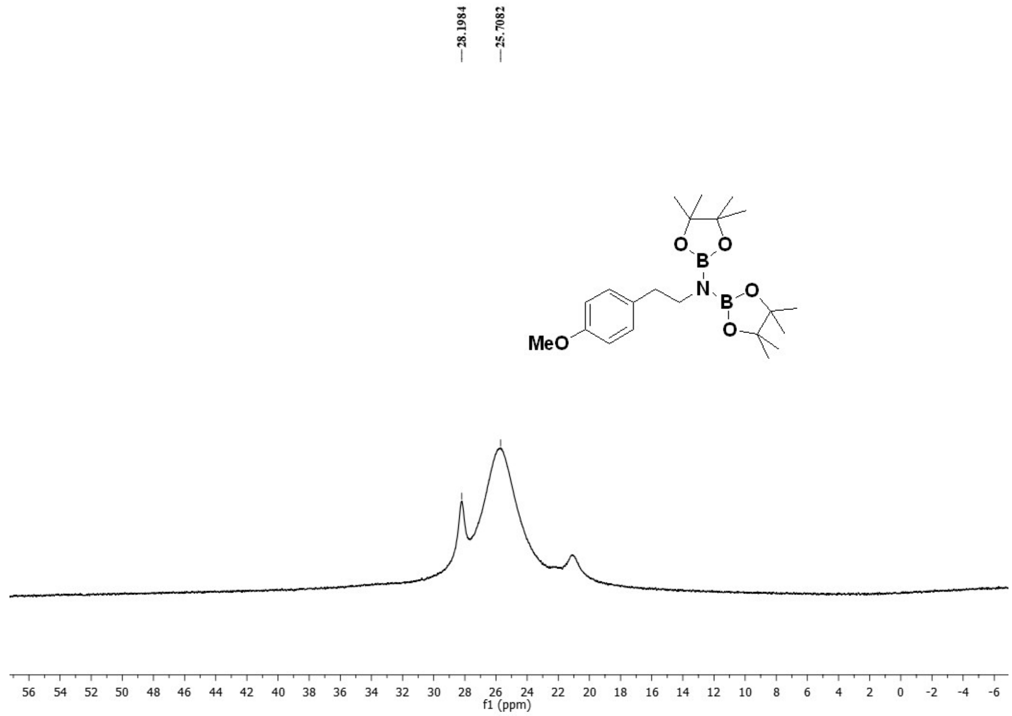


Figure FS59. ^{11}B NMR spectra of complex **2s.**

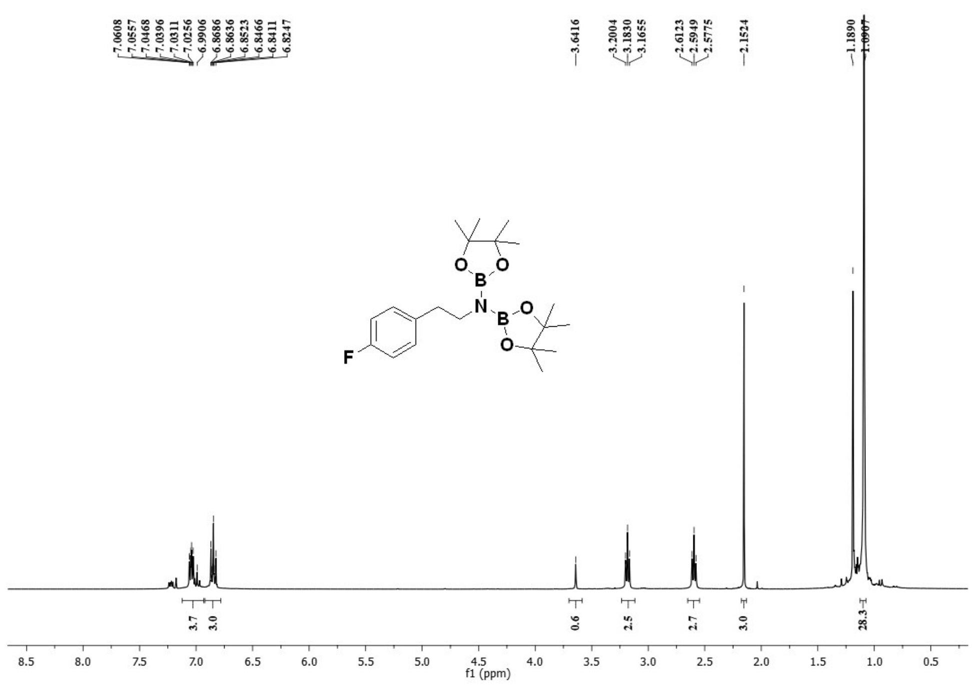


Figure FS60. ^{1}H NMR spectra of complex **2s.**

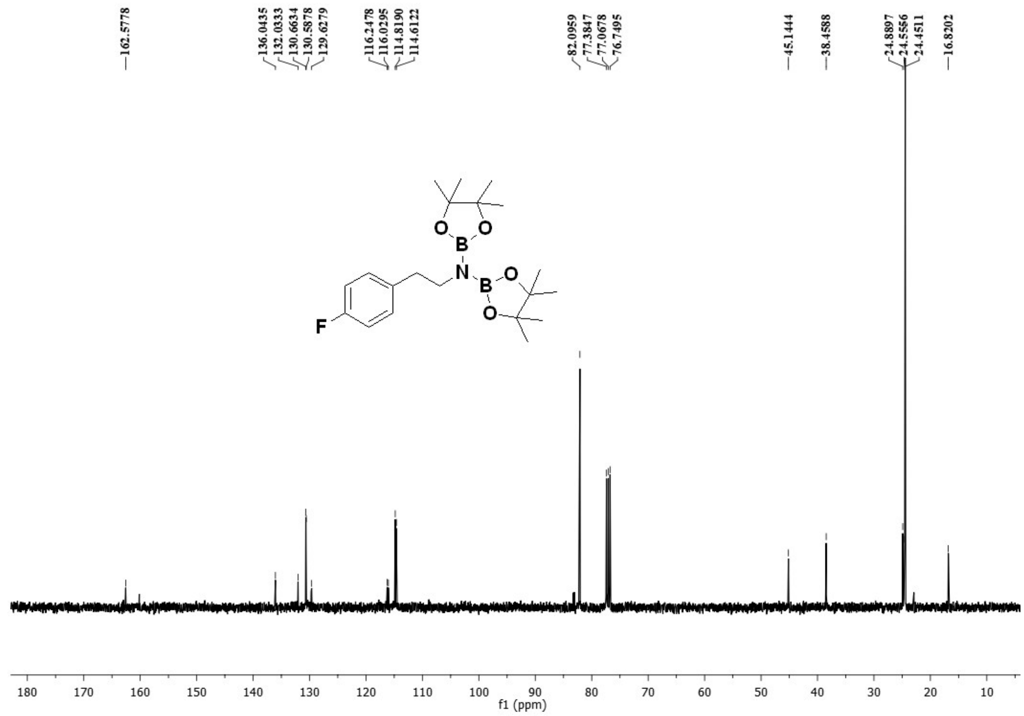


Figure FS61. ^{13}C NMR spectra of complex **2s.**

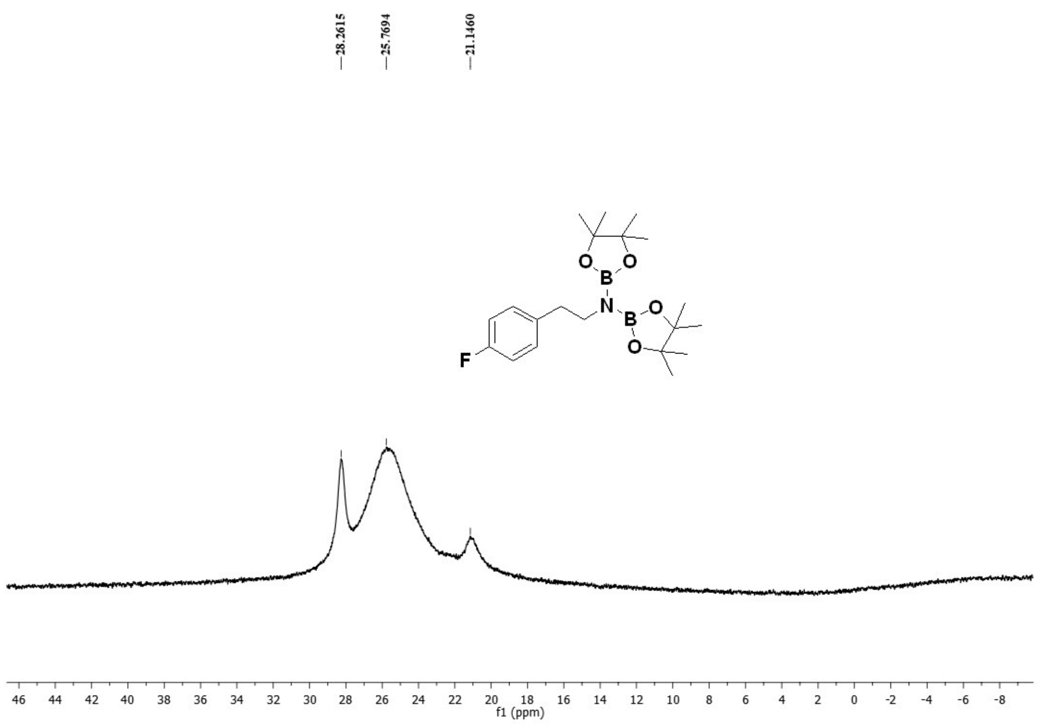


Figure FS62. ^{11}B NMR spectra of complex **2s.**

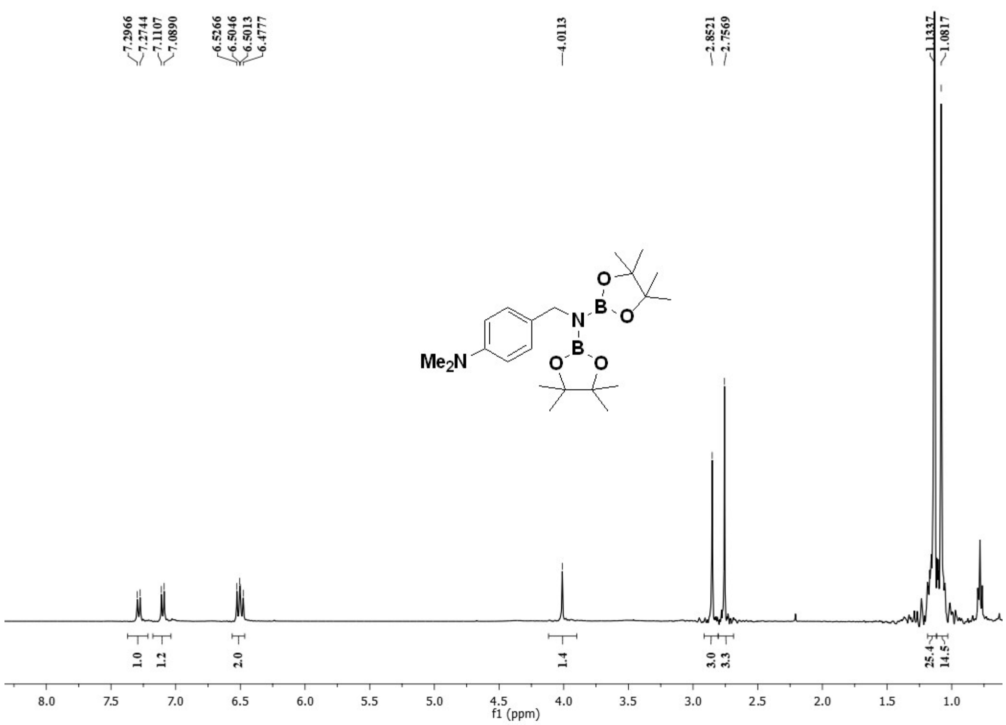


Figure FS63. ^{1}H NMR spectra of complex **2u.**

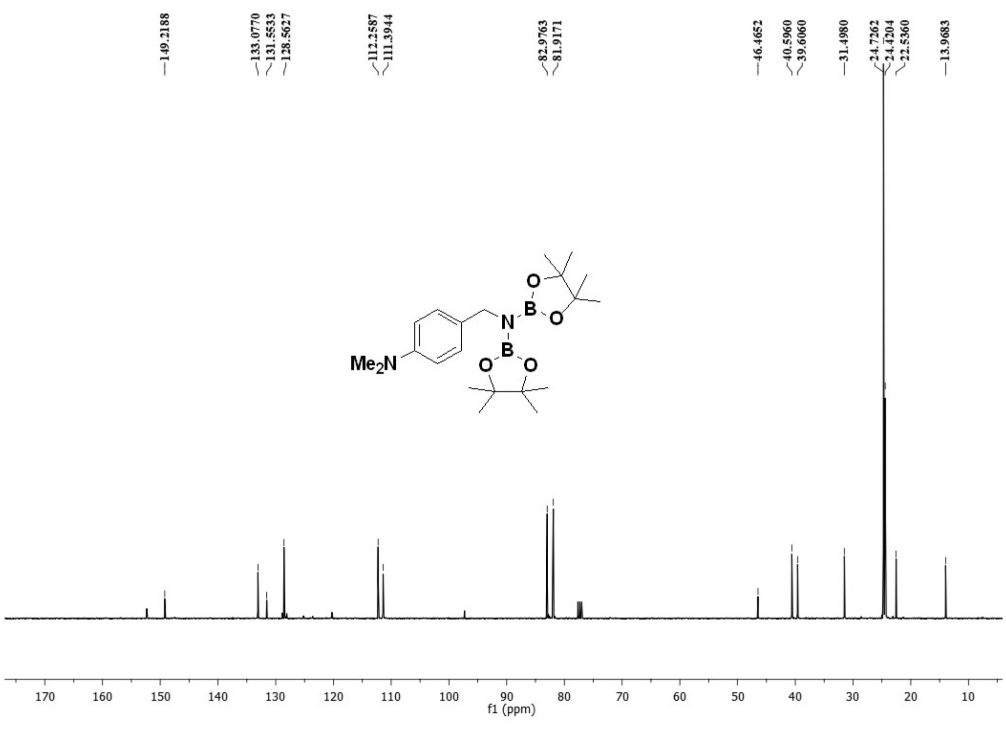


Figure FS64. ^{13}C NMR spectra of complex **2u.**

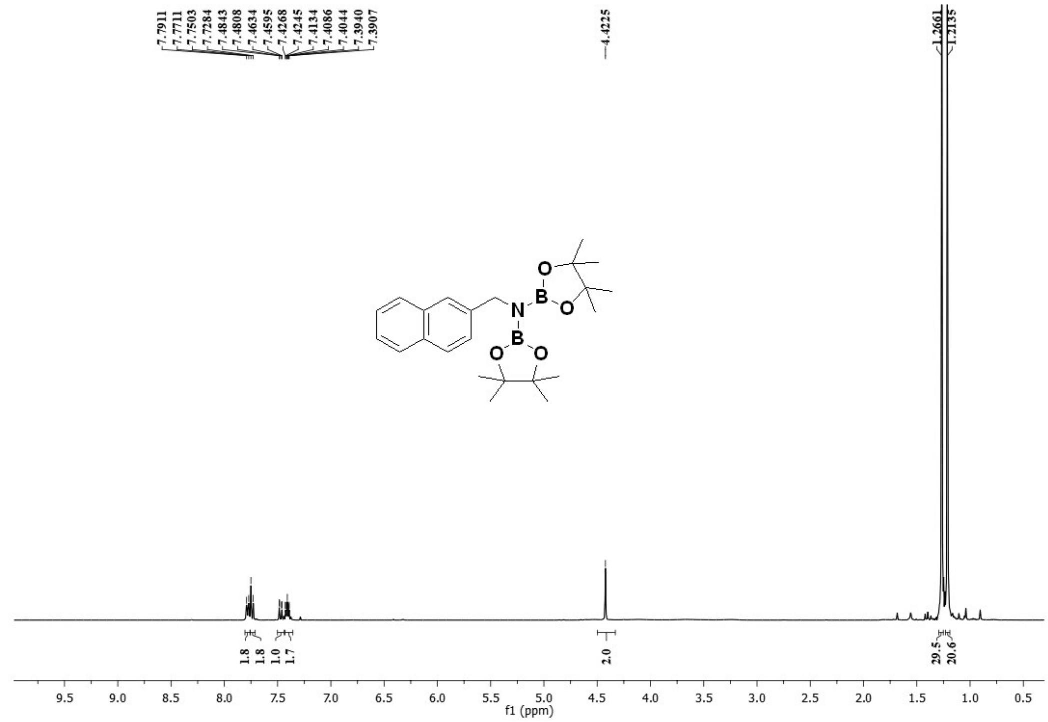


Figure FS65. ^{1}H NMR spectra of complex **2v.**

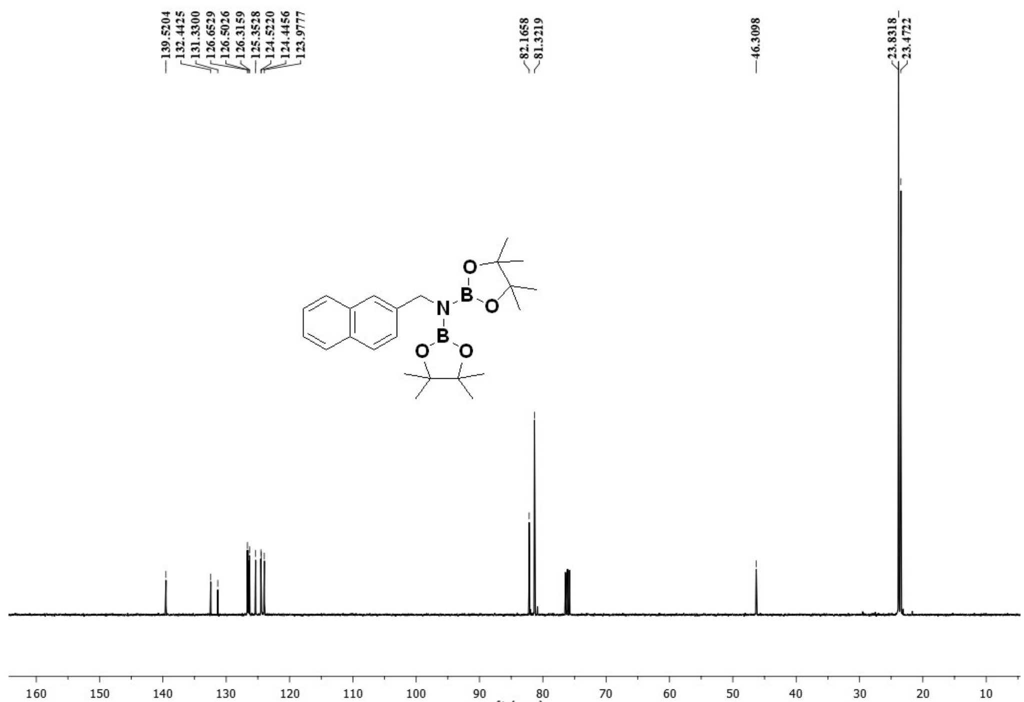


Figure FS66. ^{13}C NMR spectra of complex **2v.**

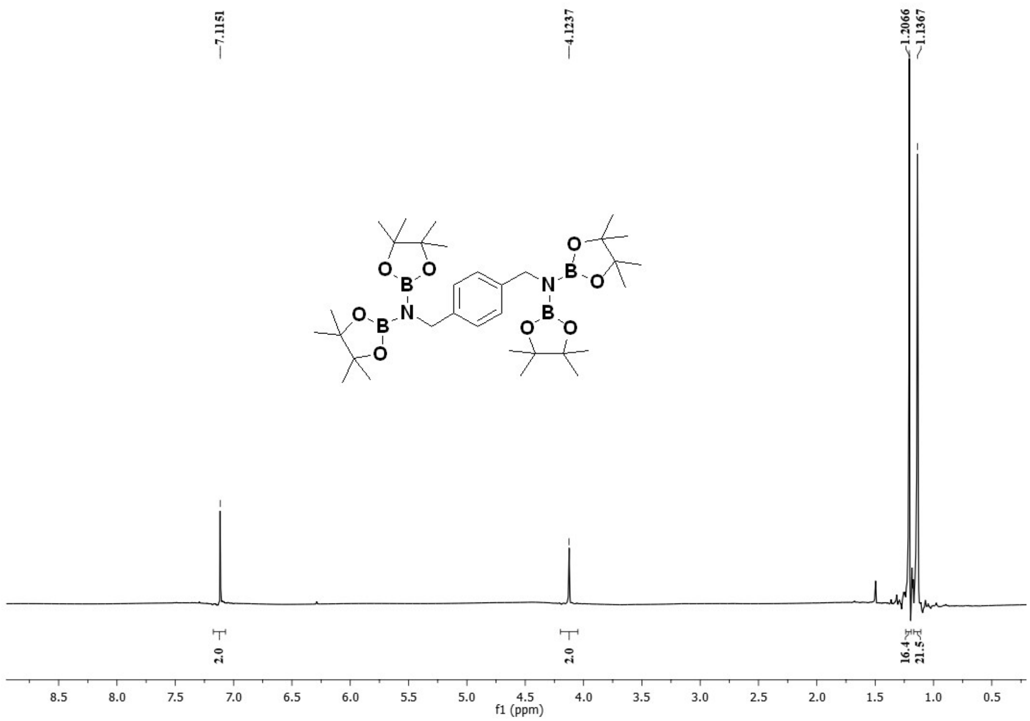


Figure FS67. ^{1}H NMR spectra of complex **2w.**

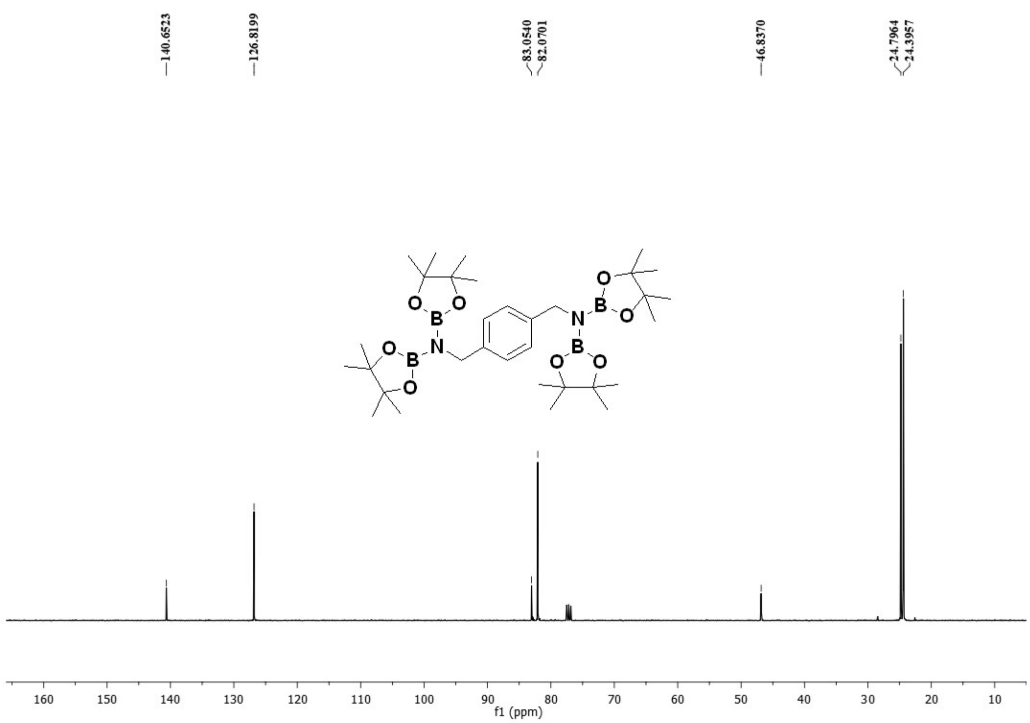


Figure FS68. ^{13}C NMR spectra of complex **2w.**

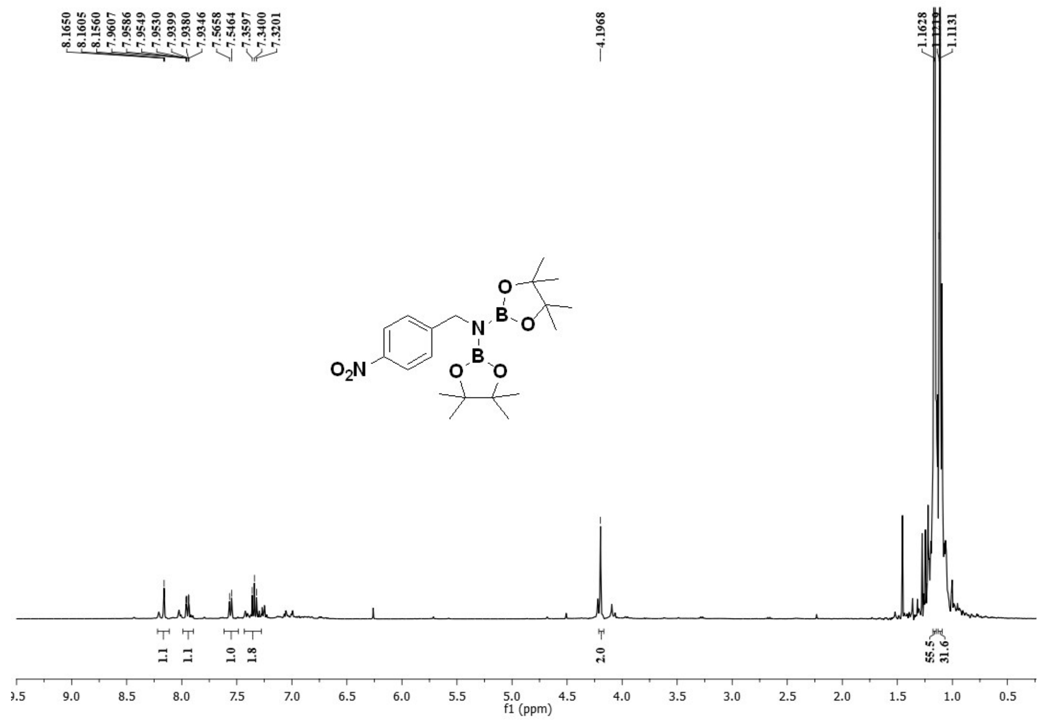


Figure FS69. ^{1}H NMR spectra of complex **3a.**

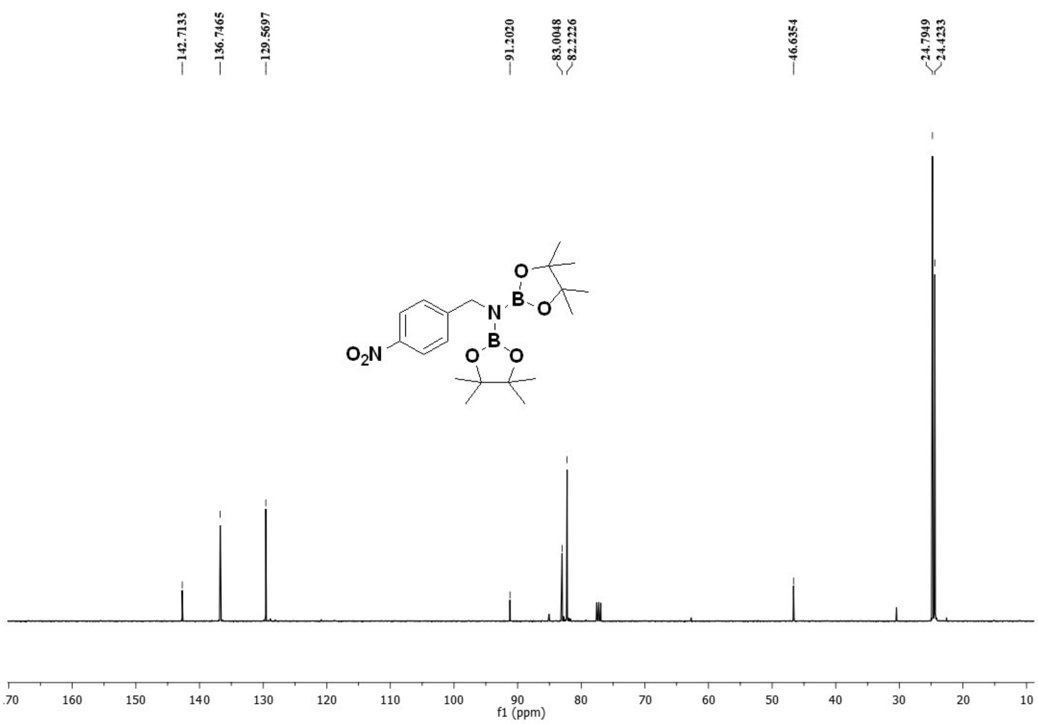


Figure FS70. ^{13}C NMR spectra of complex **3a.**

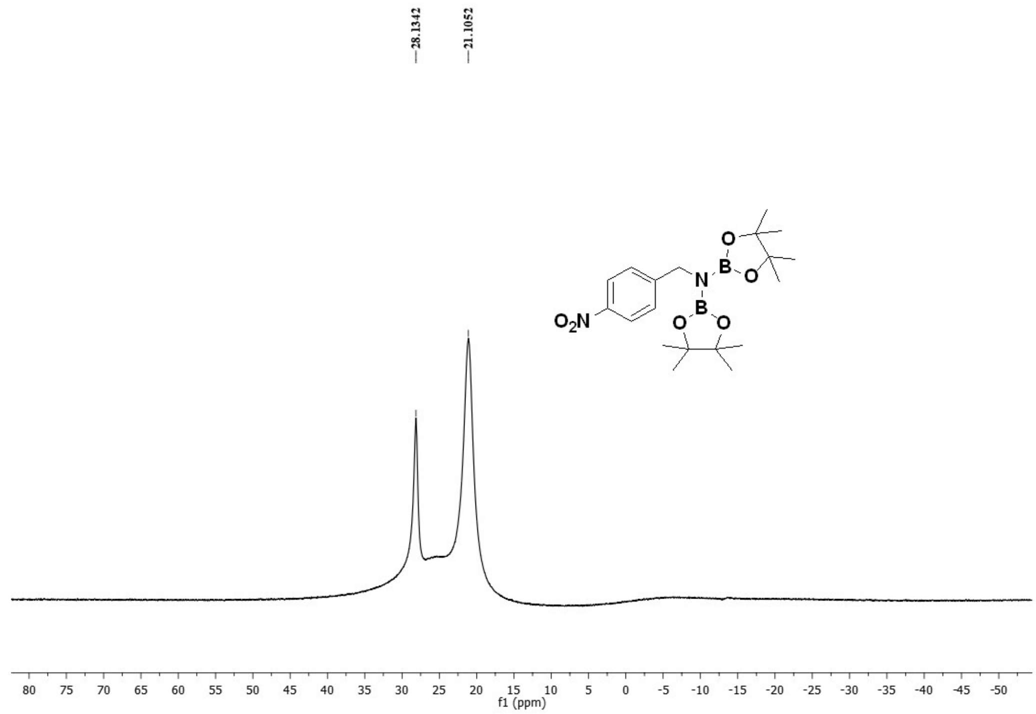


Figure FS71. ^{11}B NMR spectra of complex **3a.**

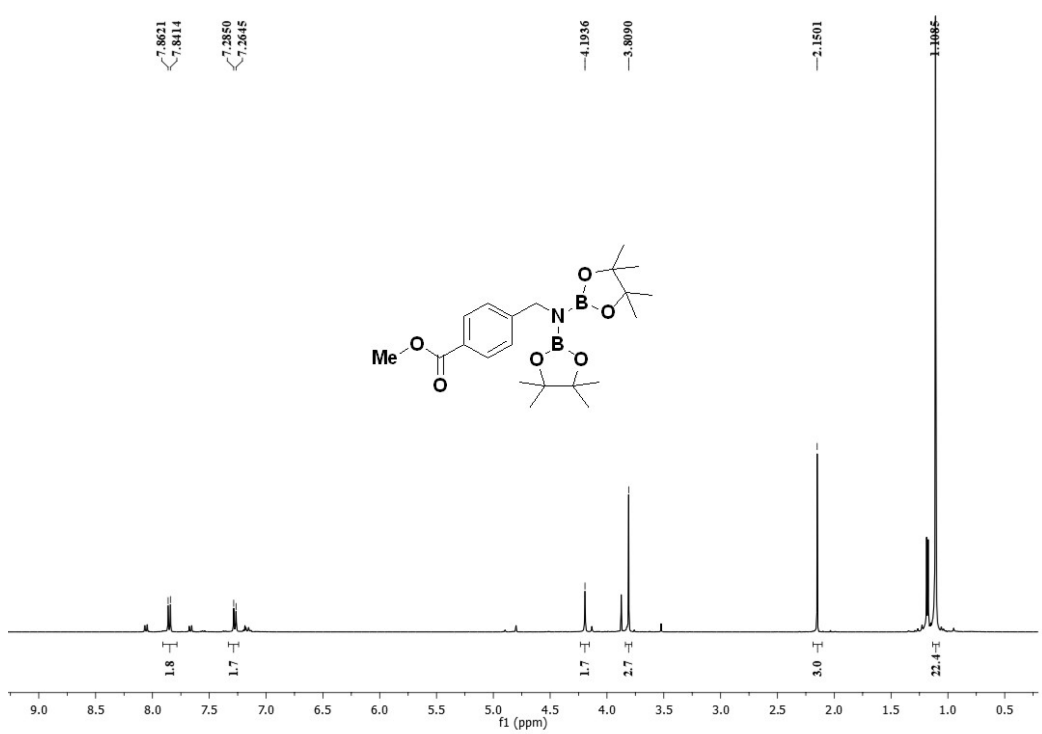


Figure FS72. ^{1}H NMR spectra of complex **3b.**

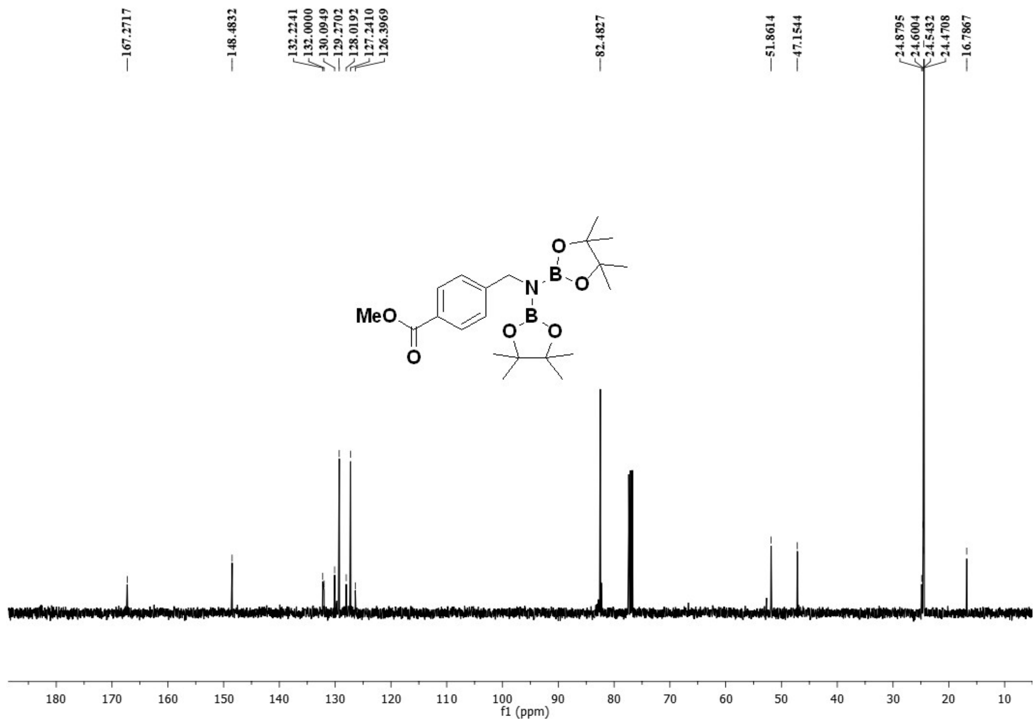


Figure FS73. ^{13}CNMR spectra of complex **3b.**

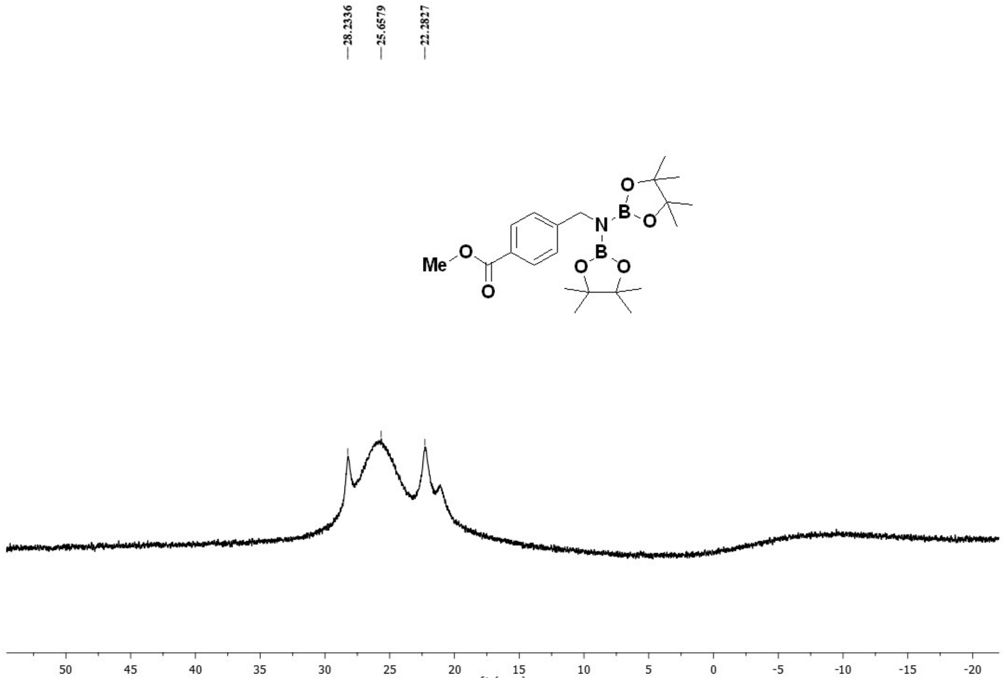


Figure FS73. ^{11}BNMR spectra of complex **3b.**

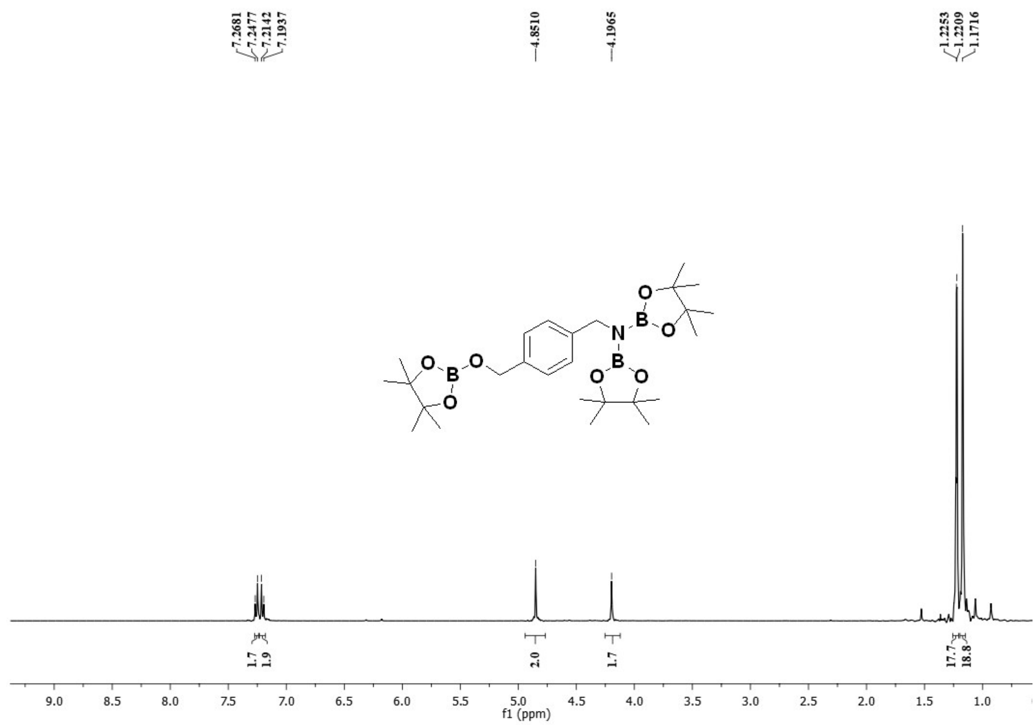


Figure FS74. ^{1}H NMR spectra of complex **3c.**

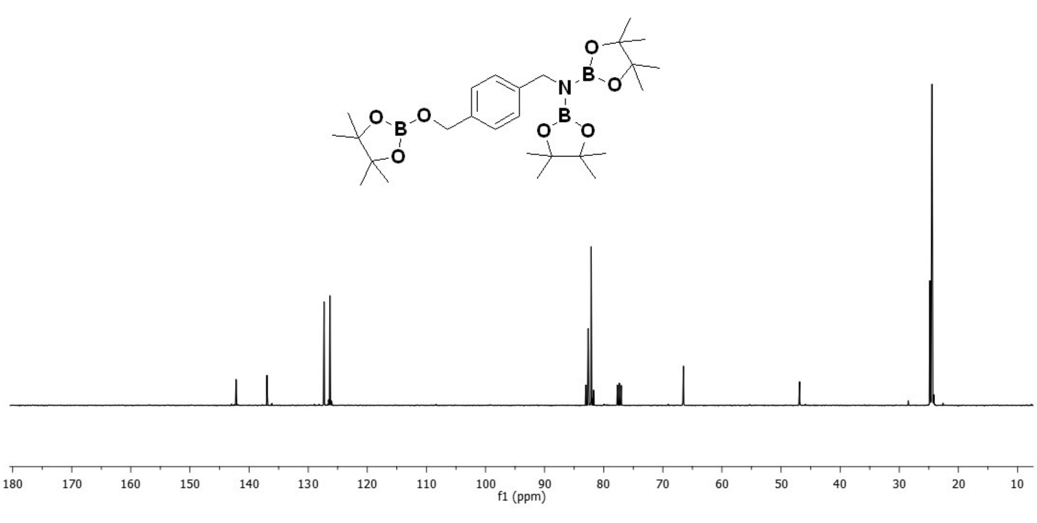


Figure FS75. ^{13}C NMR spectra of complex **3c.**

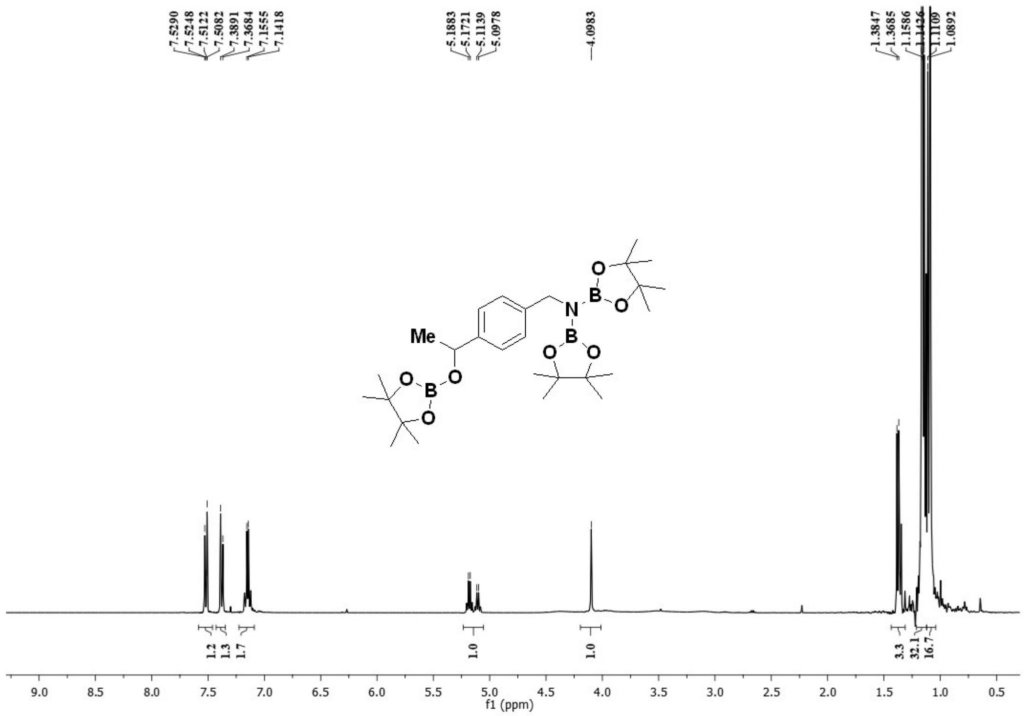


Figure FS76. ^{1}H NMR spectra of complex **3d.**

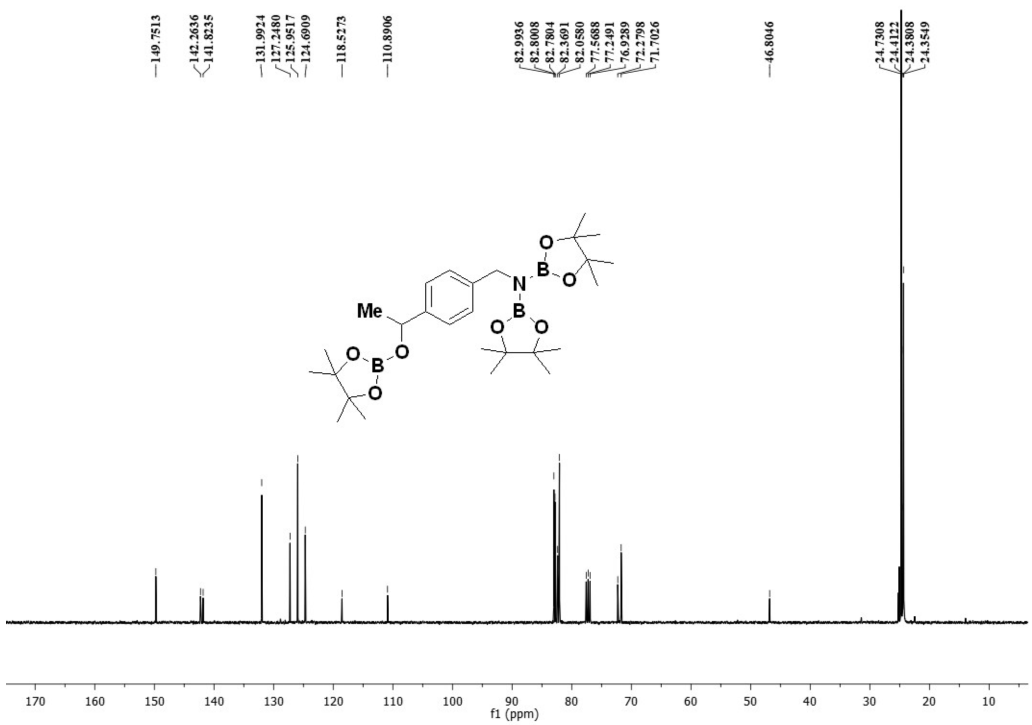


Figure FS77. ^{13}C NMR spectra of complex **3d.**

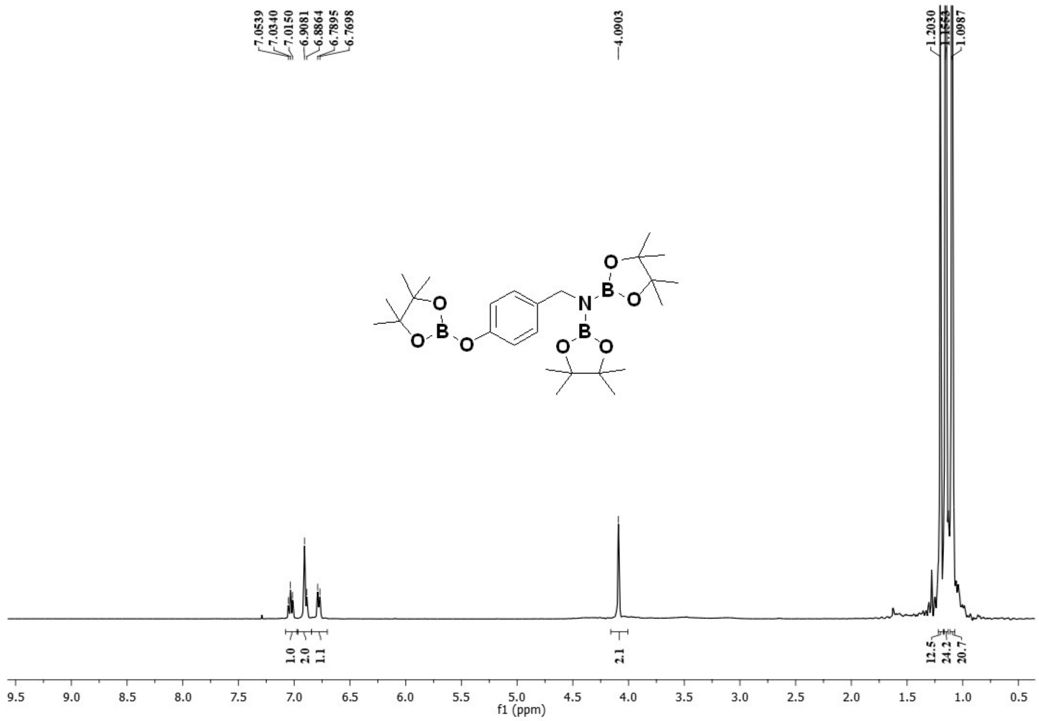


Figure FS78. ^{1}H NMR spectra of complex **3e.**

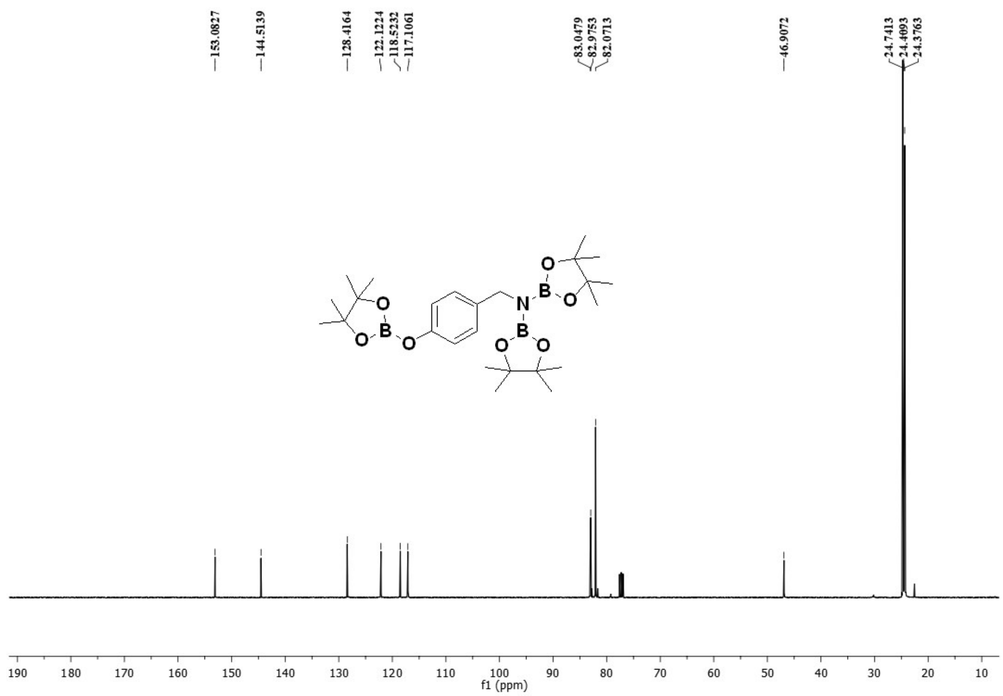
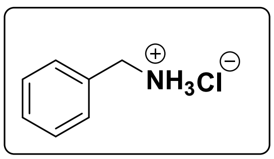


Figure FS79. ^{13}C NMR spectra of complex **3e.**

General procedure for hydrolysis of boronate esters.

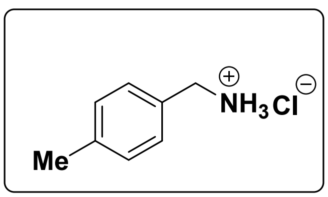
Inside the glove box, organic nitrile (0.96974 mmol, 1 equiv.) was added drop-wise into the reaction mixture of respective pinacolborane (1.93948 mmol, 2 equiv.), and (**1c**) 2 mg (0.0048 mmol) 0.5 mol% in a 25 mL dry Schlenk flask. The colorless reaction mixture was kept in the room temperature or heated to 40-60 °C depends on nature of nucleophiles. After 12 h of stirring. the reaction mixture was quench by 4N aqueous HCl and washed with dichloromethane (DCM) 2-3 times. The aqueous part was evaporated to obtain a colorless product. The products were characterized by ^{1}H, ^{13}C, and DEPT NMR spectroscopy.

Characterization Data: (reduction of organic nitrile to amines).



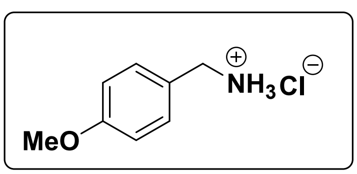
Phenylmethanaminium Chloride (4a).

Isolated Yield (104.0 mg, 75%). ^{1}H NMR (400 MHz, D_2O): δ_H 7.41 (s, 5H), 4.12 (s, 2H), $^{13}C\{^{1}H\}$ NMR (100 MHz, D_2O): δ_C 139.2, 129.6, 129.4, 126.6, 42.7 ppm.



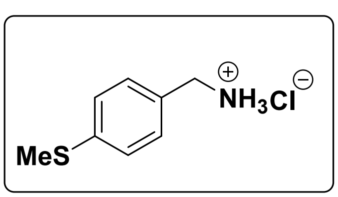
(*p*-tolylmethanaminim Chloride (4b).

Isolated Yield (115.7 mg, 76%). ^{1}H NMR (400 MHz, D_2O): δ_H 7.28 - 7.26 (s, 4H), 4.13 (s, 2H), 2.29 (s, 3H), $^{13}C\{^{1}H\}$ NMR (100 MHz, D_2O): δ_C 136.4, 130.2, 129.3, 126.0, 125.9, 83.8, 75.6, 42.7, 23.7 ppm.



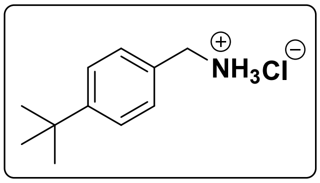
(4-Methoxyphenyl)methanaminim Chloride (4c).

Isolated Yield (132.5 mg, 79%). ^{1}H NMR (400 MHz, D_2O): δ_H 7.37 - 7.35 (d, J = 8.1 Hz, 2H), 7.00 - 6.99 (d, J = 8.1 Hz, 2H), 4.08 (s, 2H), 3.79 (s, 3H, OMe), $^{13}C\{^{1}H\}$ NMR (100 MHz, D_2O): δ_C 159.2, 130.6, 125.42, 114.6, 55.5, 43.6, 23.8 ppm.



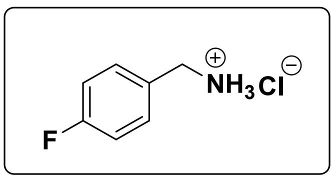
(4-(methylthio)phenyl)methanaminim Chloride (4d).

Isolated Yield (144.7 mg, 79%). ^{1}H NMR (400 MHz, D_2O): δ_H 7.35 (m, 4H), 4.07 (s, 2H), 2.44 (s, 3H), ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_C 139.2, 129.6, 129.4, 126.6, 42.7, 14.4 ppm.



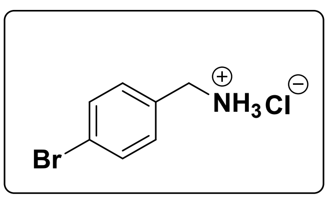
(4-(tert-butyl)Phenyl) methanaminium Chloride (4e).

Isolated Yield (150.5 mg, 78%). ^{1}H NMR (400 MHz, D_2O): δ_H 7.53-7.51 (d, *J* = 8.2 Hz, 2H), 7.38 - 7.36 (d, *J* = 8.1 Hz, 2H), 4.11 (s, 2H), 1.26 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_C 131.2, 130.8, 129.4, 129.0, 75.6, 40.4, 28.8, 18.0 ppm.



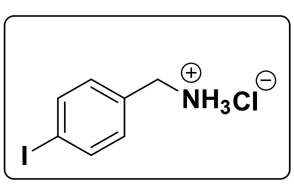
(4-MethoxyPhenyl)methanaminim Chloride (4f).

Isolated Yield (106.1 mg, 68%). ^{1}H NMR (400 MHz, D_2O): δ_H 7.74 - 7.72 (d, *J* = 8.1 Hz, 2H), 7.57 - 7.55 (d, *J* = 8.1 Hz, 2H), 4.22 (s, 2H), 3.79. ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_C 131.10,131.0, 116.0,115.8, 75.6, 42.4, 23.7 ppm.



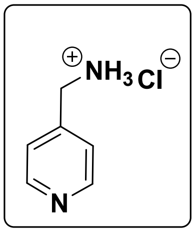
(4-(bromo)phenyl)methanaminim Chloride (4g).

Isolated Yield (150.6 mg, 70%). ^{1}H NMR (400 MHz, D_2O): δ_H 7.56 - 7.54 (d, *J* = 8.1 Hz, 2H), 7.29 - 7.27 (d, *J* = 8.1 Hz, 2H), 4.08 (s, 2H), ^{13}C{^{1}H} NMR (100 MHz, D_2O): δ_C 149.2, 129.2, 128.8, 69.3, 43.1, 23.7 ppm.



(4-iodophenyl)methaminium Chloride (4h).

Isolated Yield (187.8 mg, 72%). [1]H NMR (400 MHz, DMSO-d_6): δ_H 8.52 (s, 2H), 7.53 - 7.51 (d, J = 8.2 Hz, 2H), 7.32 - 7.30 (d, J = 8.1 Hz, 2H), 3.96 (s, 2H), [13]C{[1]H} NMR (100 MHz, DMSO-d_6): δ_C 137.26, 133.7, 131.2, 94.7, 41.6 ppm.



(pyridine-4-ylmethanaminim Chloride (4i).

Isolated Yield (99.1 mg, 71%). [1]H NMR (400 MHz, DMSO-d_6): δ_H 8.62 (s, 2H), 8.02 - 7.96 (s, 1H), 7.94 -7.89 (m, 1H), 7.67 - 7.65 (d, J = 8.1 Hz, 1H), 7.55 - 7.53 (d, J = 8.1 Hz, 1H), 4.19 (s, 2H), [13]C{[1]H} NMR (100 MHz, DMSO-d_6): δ_C 132.5, 132.5, 131.4, 128.1, 127.9, 127.7,127.6, 48.5, 42.3 ppm.

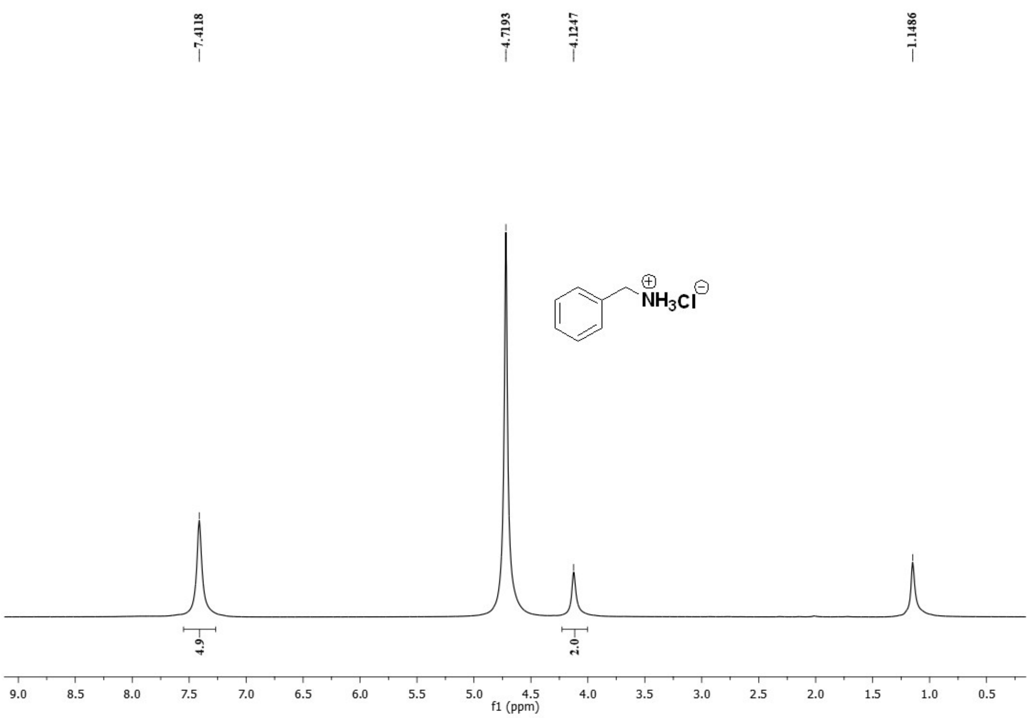


Figure FS80. [1]H NMR spectra of complex **4a.**

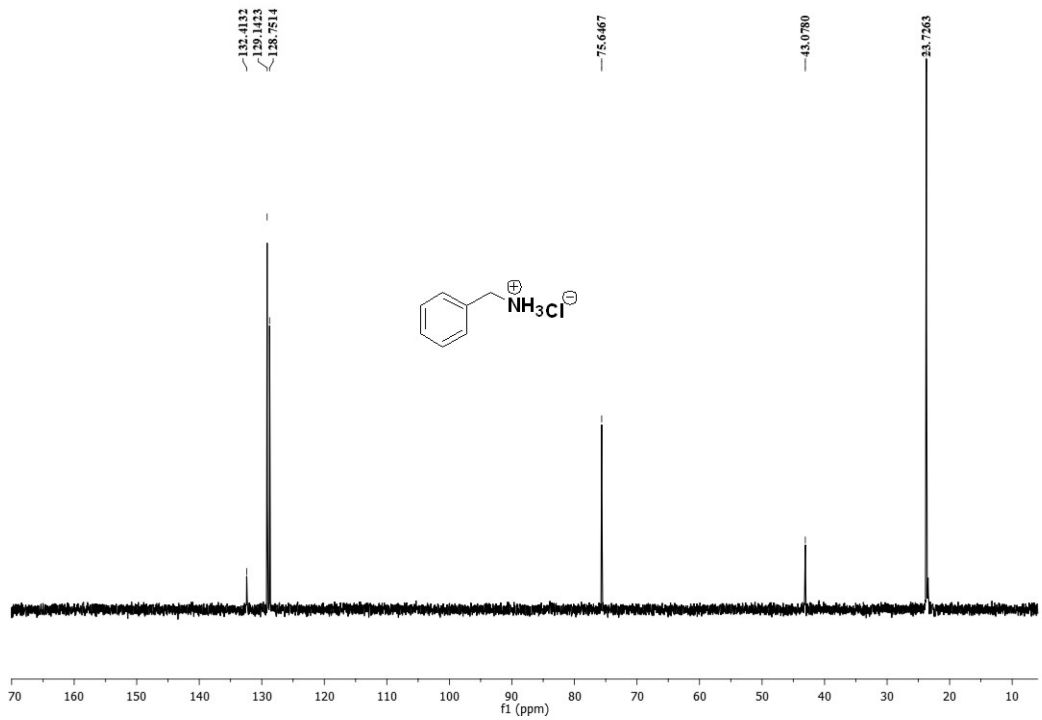


Figure FS81. ^{13}C NMR spectra of complex **4a.**

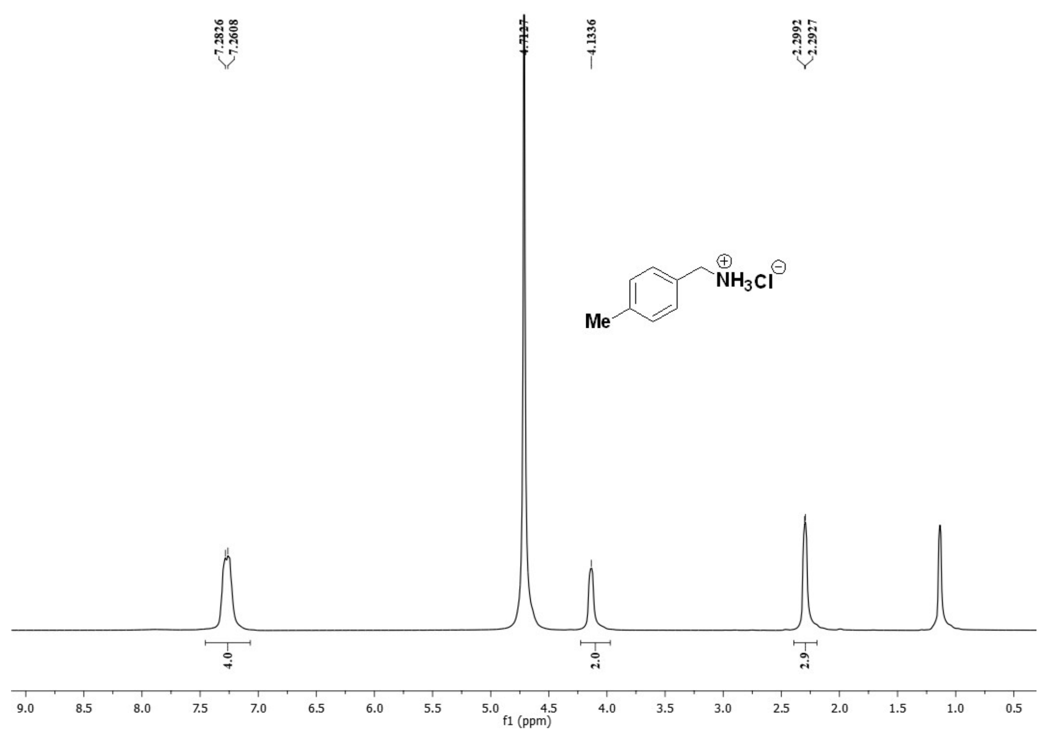


Figure FS82. ^{1}H NMR spectra of complex **4b.**

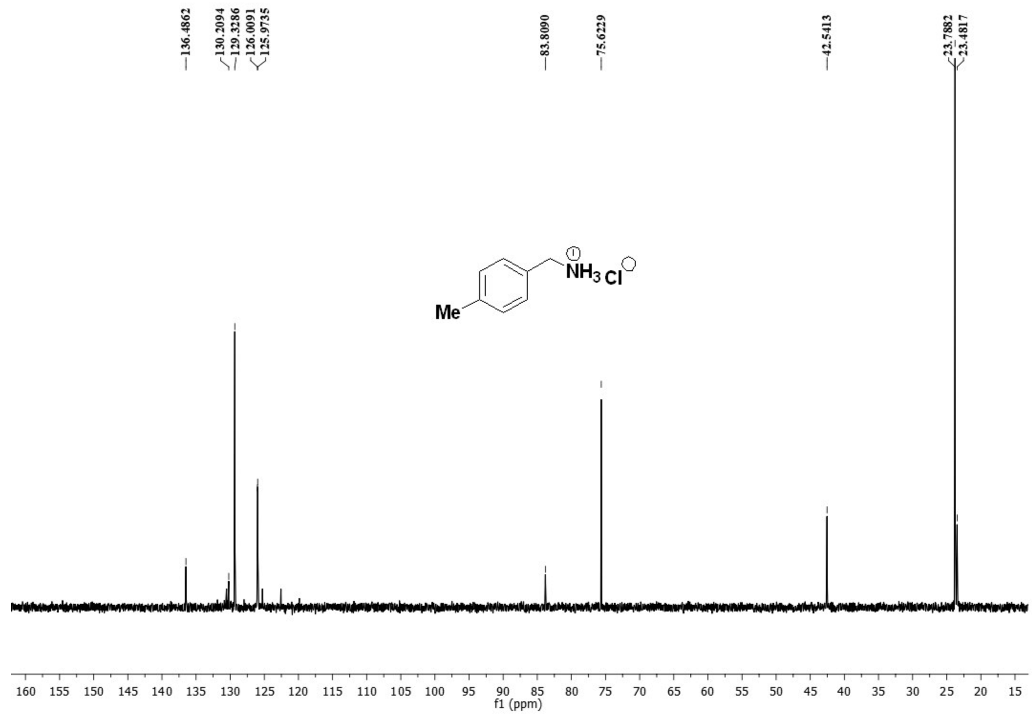


Figure FS83. ^{13}C NMR spectra of complex **4b.**

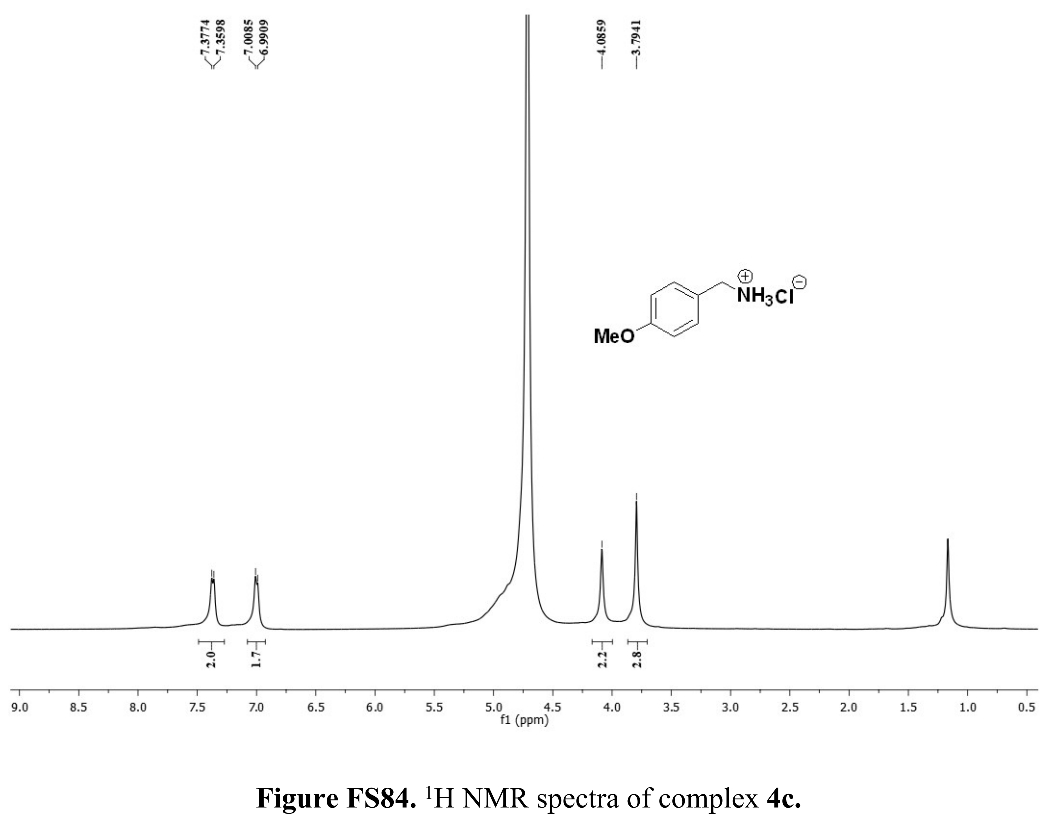


Figure FS84. ^{1}H NMR spectra of complex **4c.**

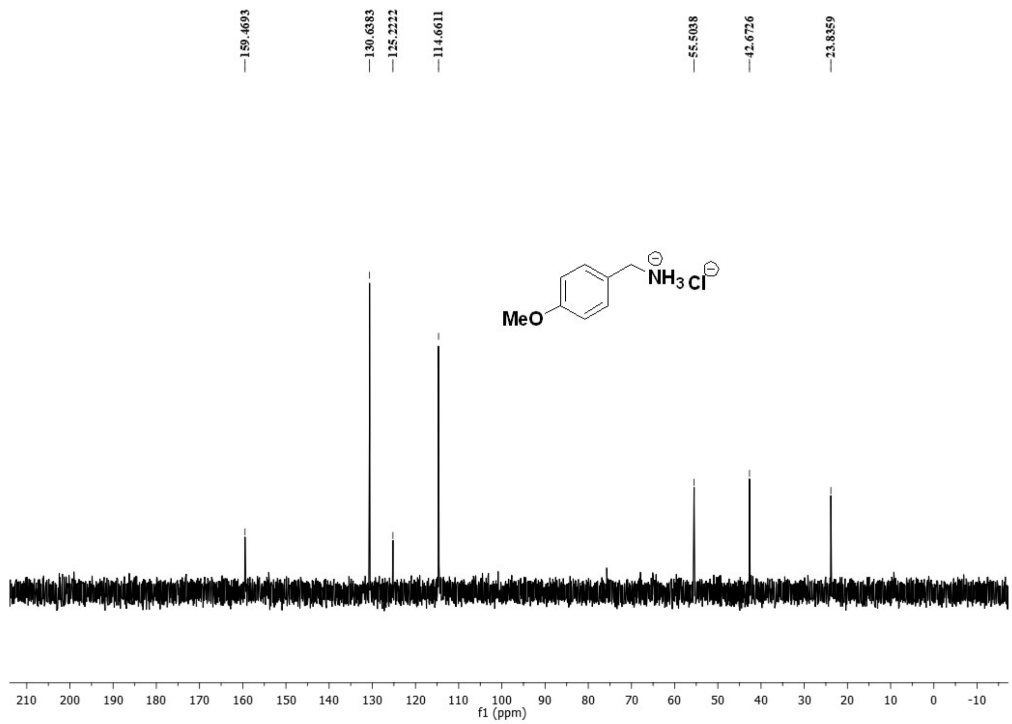


Figure FS85. ^{13}C NMR spectra of complex **4c.**

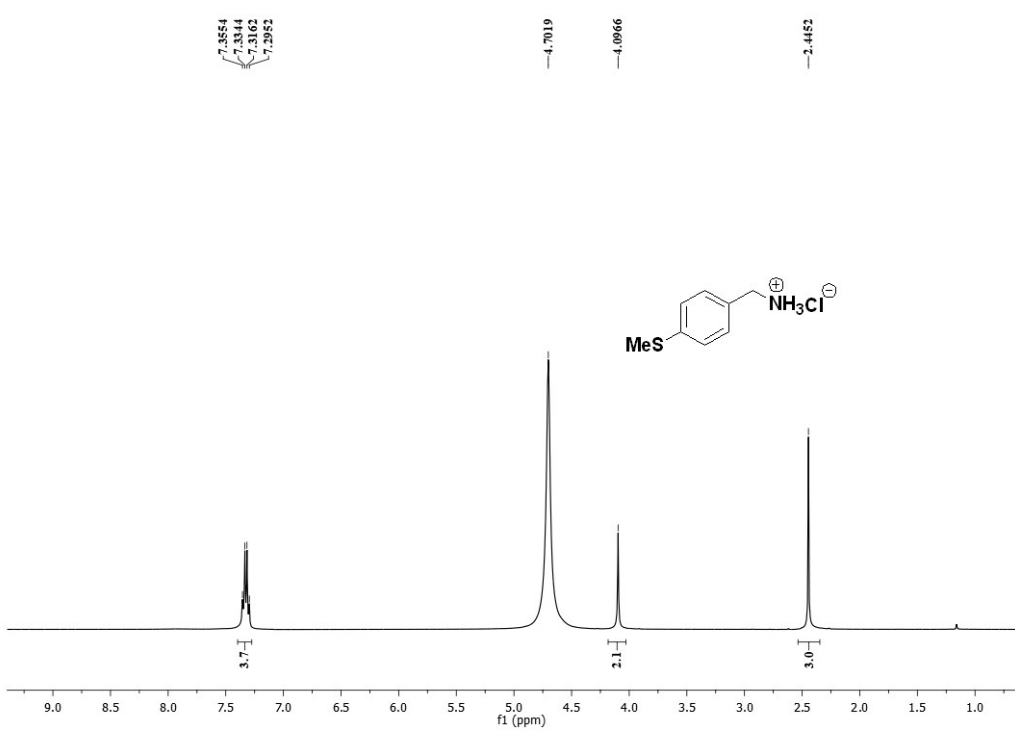


Figure FS86. ^{1}H NMR spectra of complex **4d.**

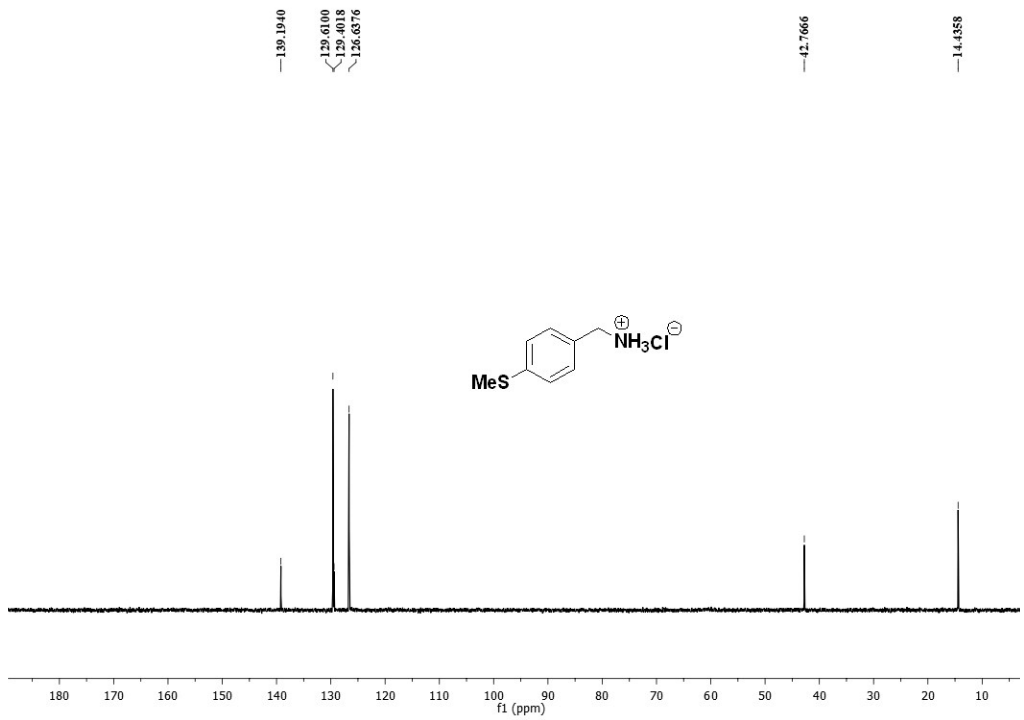


Figure FS87. ^{13}C NMR spectra of complex **4d.**

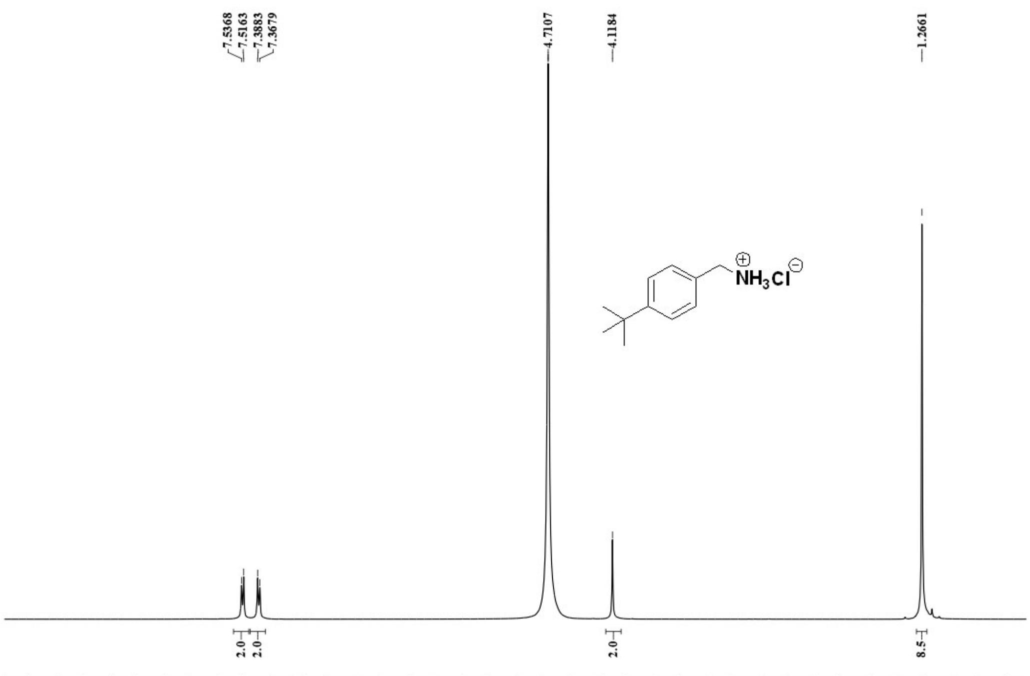


Figure FS88. ^{1}H NMR spectra of complex **4e.**

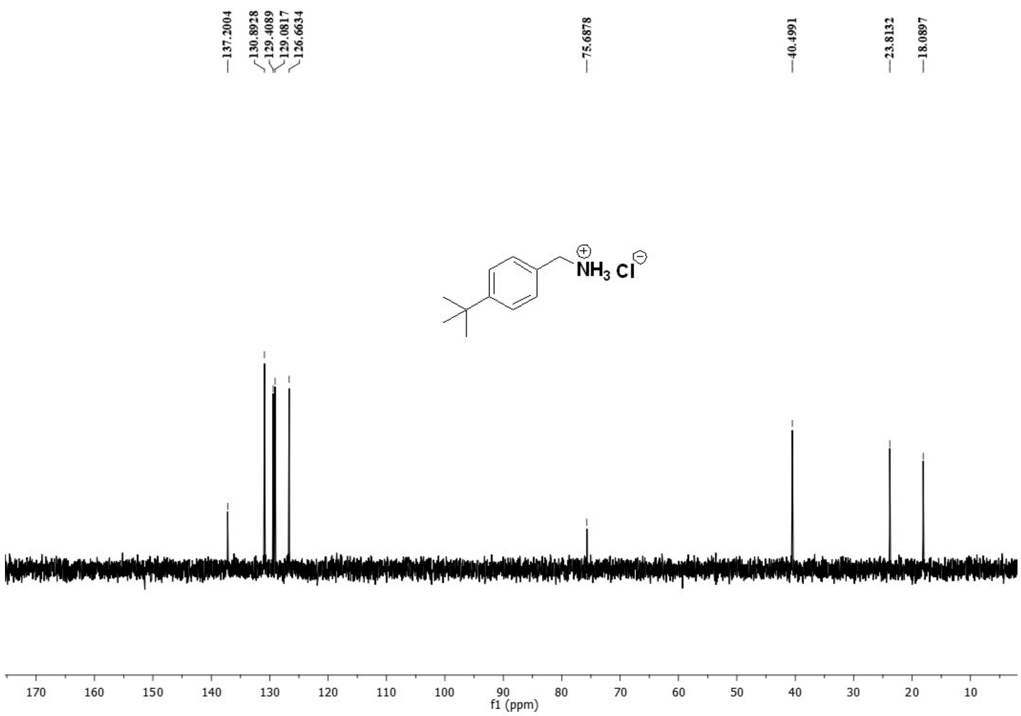


Figure FS89. ^{13}C NMR spectra of complex **4e.**

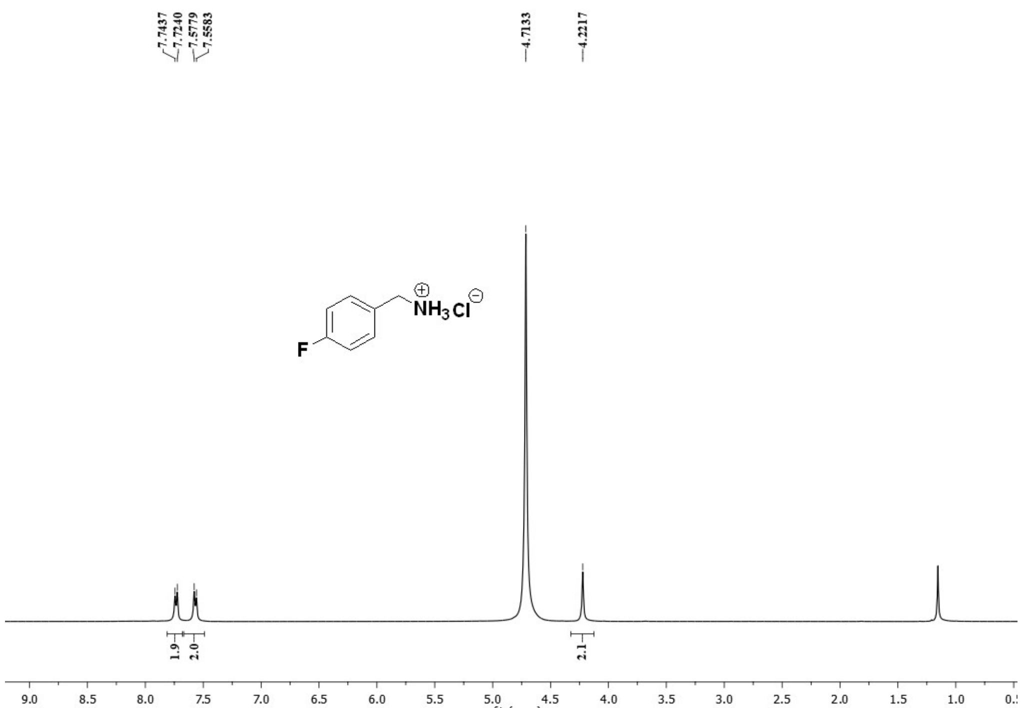


Figure FS90. ^{1}H NMR spectra of complex **4f.**

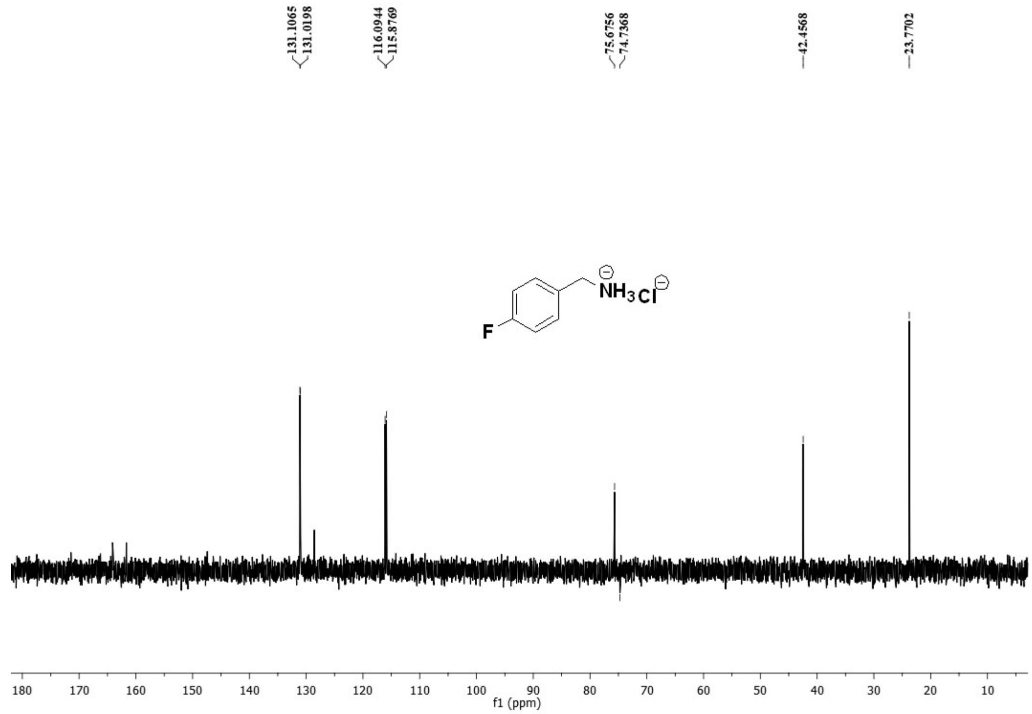


Figure FS91. ^{13}C NMR spectra of complex **4f.**

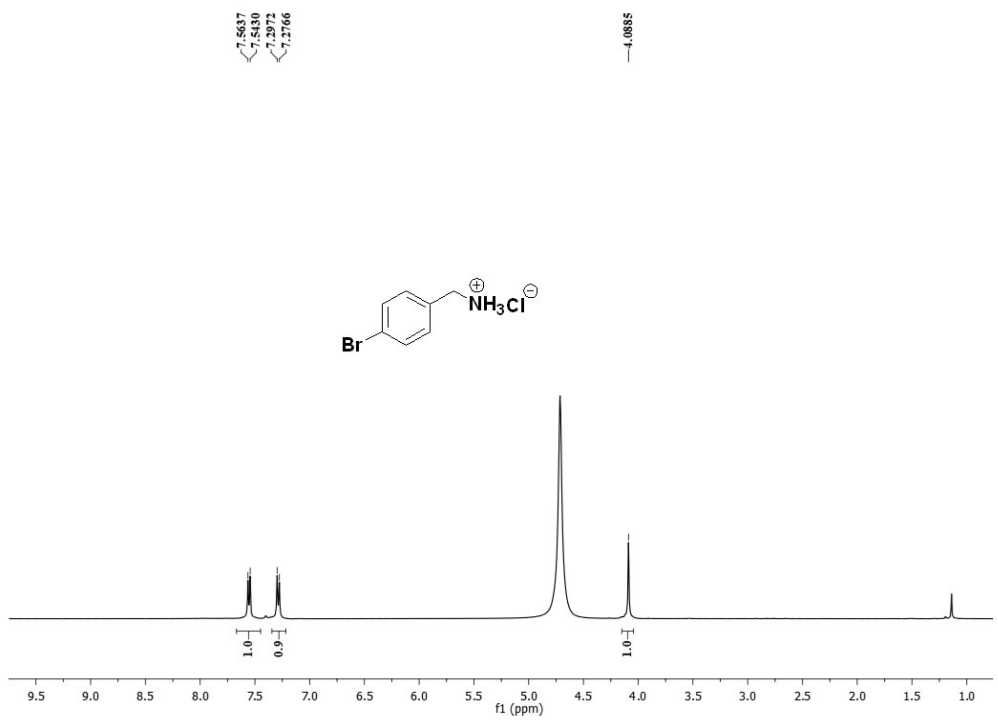


Figure FS92. ^{1}H NMR spectra of complex **4g.**

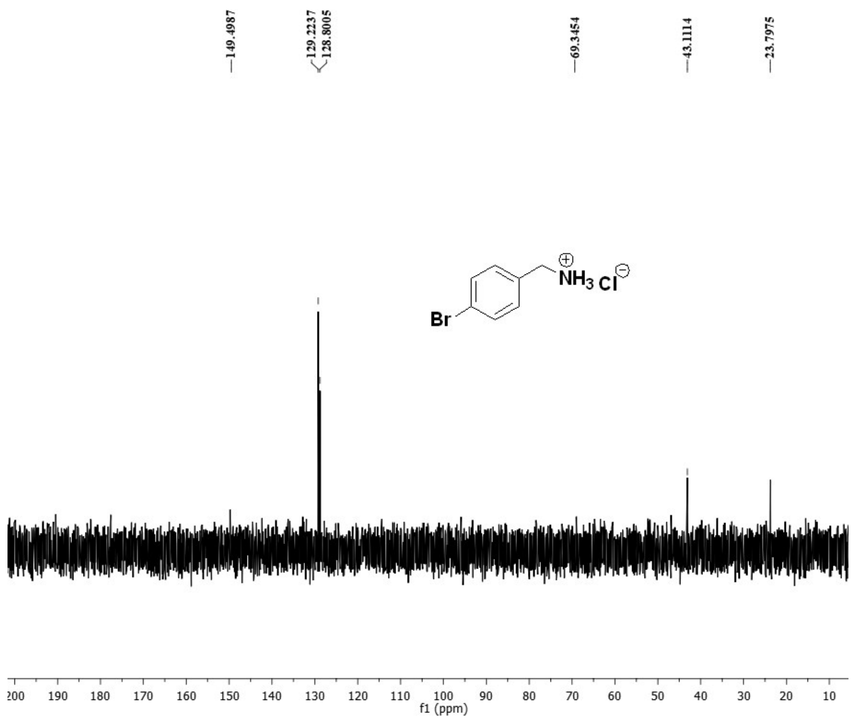


Figure FS93. ^{13}C NMR spectra of complex **4g.**

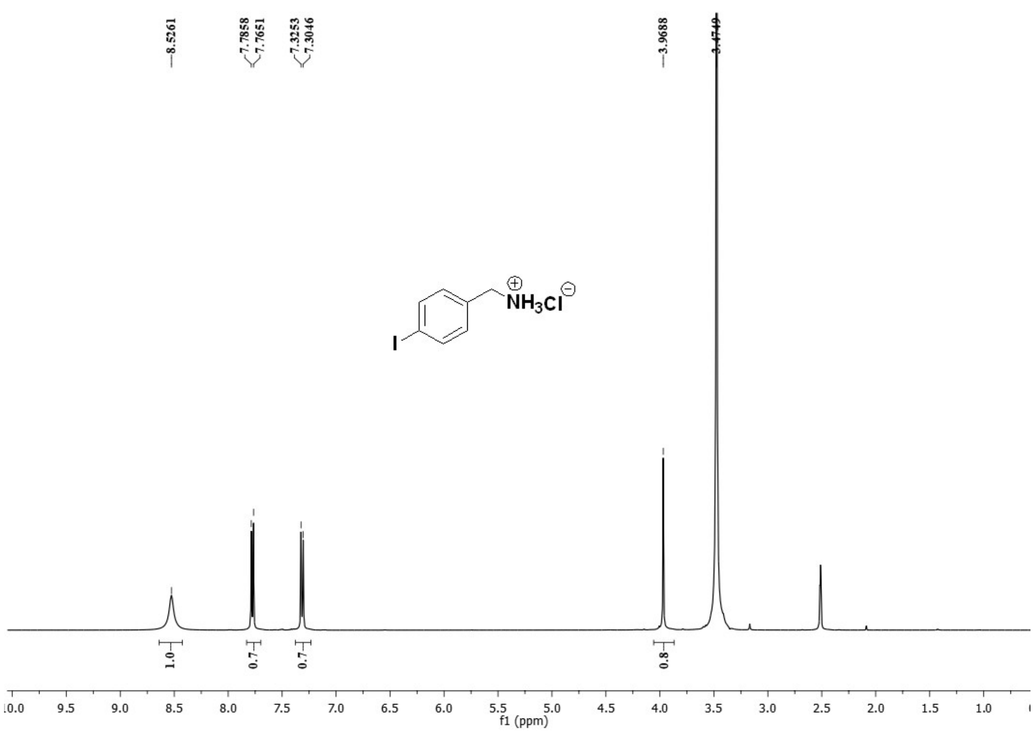


Figure FS94. ^{1}H NMR spectra of complex **4h.**

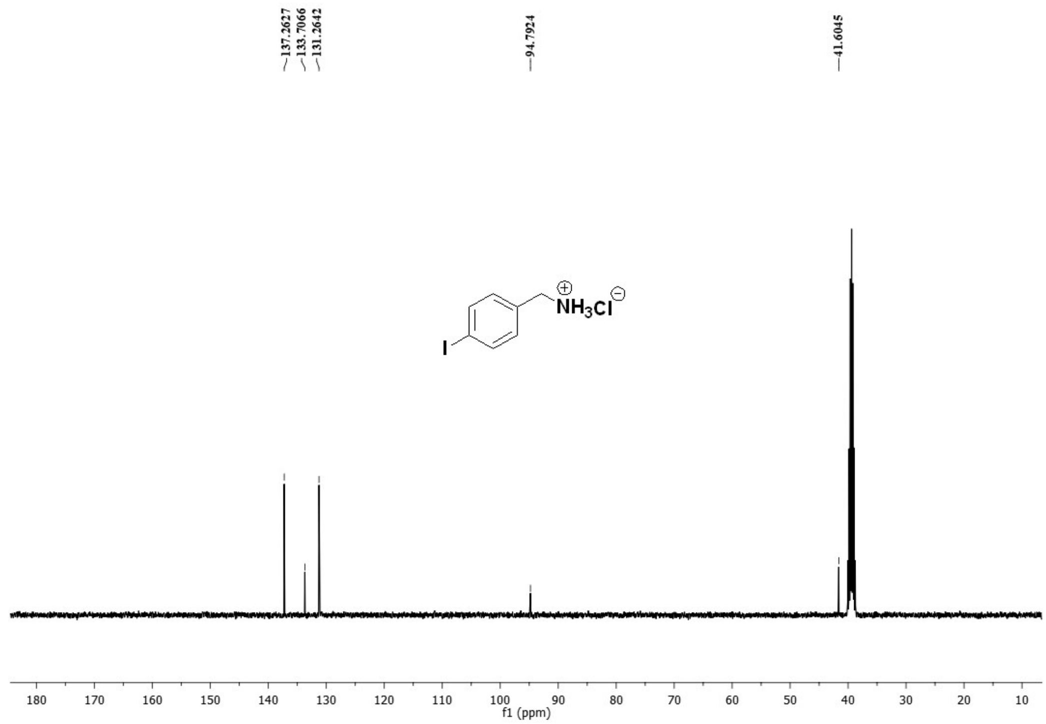


Figure FS95. ^{13}C NMR spectra of complex **4h.**

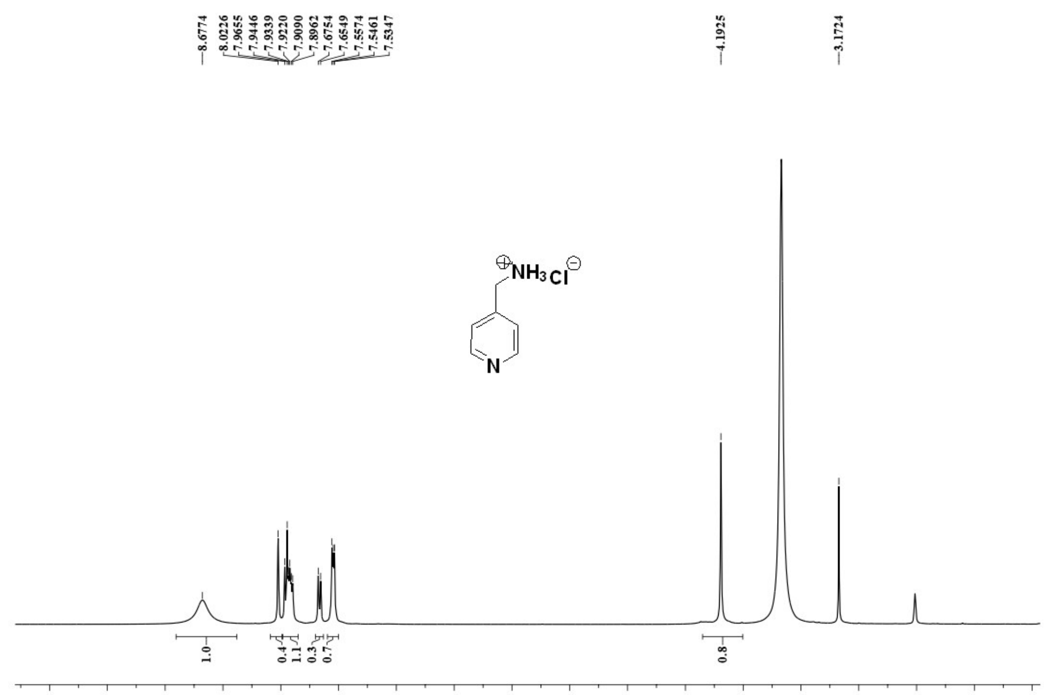


Figure FS96. ^{1}H NMR spectra of complex **4i.**

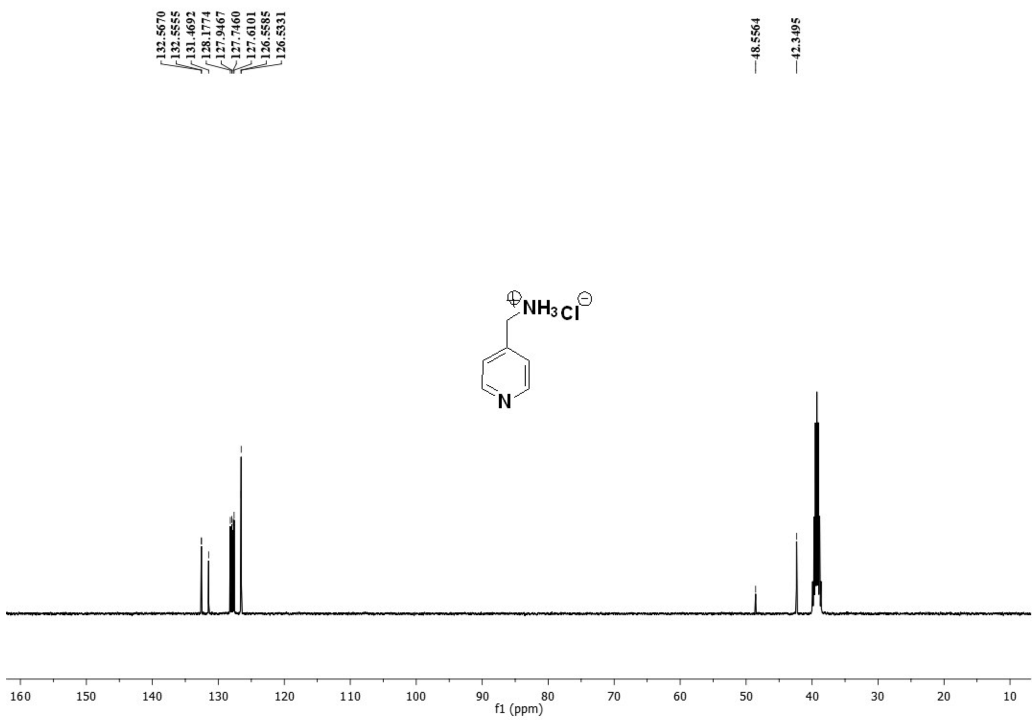


Figure FS97. ^{13}C NMR spectra of complex **4i.**

Kinetic studies

Typical NMR-Scale Reaction for determine Kinetic Study by ^{1}H-NMR Arrays.

In a glove box, the respective amount of complex **1c** (0.0015, 0.002, 0.0025, 0.0030, 0.0035 M), 2-chloroacetonitrile (0.5 M), HBpin (1.0 M), and the internal standard, hexamethylbenzene (8 mg, 0.05 M), was added in a vial and after that $CDCl_3$ (1 mL) was added to these reaction mixture. From this stock solution finally 0.5 mL aliquot were taken out and it was added to rubber septum-sealed NMR tube, wrapped with paraxfilm, and removed from the box. The solution was set in the NMR tube at 25^{o}C. After that the tube was shaken and reinserted into the instrument again and scanning was begun. Single (^{1}H NMR) scans were collected at regular intervals. Substrate and/or product concentrations were determined relative to the intensity of the internal standard resonance plotted verses time. Like this varying wide range of concentration of $ClCH_2CN$ (0.3-0.7 M), HBpin (0.9-1.3 M) rate of the hydroboration reaction determined with respect to each substrate.

Kinetic Analysis. Kinetic analysis of the NMR-scale reactions described above was carried out by collecting multiple (>10) data points early in the reaction (<20% conversion). Under these conditions, the reaction can be approximated as pseudo-zero-order with respect to the substrate concentrations. The product concentration was measured from the area of the methylene peak (4.14) ppm of

$MeOC_6H_4CH_2N(Bpin)_2$ also from the area of methoxy peak (3.85) and (3.77) of starting material as well as products standardized to the methyl peak area of the C_6Me_6 as internal standard (2.22).

General Procedure for Kinetic NMR Experiments.

As expected, plots of ln[$ClCH_2CN$]/ln[$ClCH_2CN$]$_0$ vs. time for a wide range of catalyst [Im^{t}BuEt_2Zn(**1c**)] are linear (Figure FS98, Table S2). A plot of $\boldsymbol{k}_{\mathbf{obs}}$ vs. [{Im^{tBu}NZnEt}$_2$(**1c**)] (Figure FS99, Table S3) is also linear, with slope 1 which indicate the rate law of the reaction follow first order dependence with respect to catalyst [{Im^{tBu}NZnEt}$_2$(**1c**)]. Same experiment also conducted varying wide range of concentration of $ClCH_2CN$ (0.3 - 0.7 M) and HBpin (0.9 - 1.3 M) which were also linear and follows first order dependence with respect to [$ClCH_2CN$] and HBpin (Figure FS100, Table S4, Figure FS101, Table S5).

Table TS2. Table for formation rates of $ClCH_2CH_2N(Bpin)_2$ at various time.

S.No	[$ClCH_2CN$]/cat	Time (h:m)	Conversion[a]	[$ClCH_2CN$]^t	ln([$ClCH_2CN$]$_t$/ [$ClCH_2CN$]$_0$)
1	100/0.3	00.00	0	0	0
2	100/0.3	01.00	23%	0.385	-.261
3	100/0.3	02.00	35%	0.325	-.430
4	100/0.3	03.00	44%	0.28	-.579
5	100/0.3	04.00	52%	0.24	-.734
6	100/0.3	05.00	61%	0.195	-0.942
7	100/0.3	06.00	70%	0.15	-1.20
8	100/0.3	07.00	73%	0.135	-1.31
			0	0	0
10	100/0.4	00.00	25%	0.375	-0.287
11	100/0.4	01.00	42%	0.29	-0.544
12	100/0.4	02.00	55%	0.225	-0.798
13	100/0.4	03.00	67%	0.165	-1.11
14	100/0.4	04.00	75%	0.125	-1.38
15	100/0.4	05.00	81%	0.095	-1.66
16	100/0.4	06.00	88%	0.06	-2.12
17	100/0.4	07.00	0	0	0
			27.5	0.362	-0.322
19	100/0.5	00.00	46	0.27	-0.616
20	100/0.5	01.00	62.5	0.1875	-0.975
21	100/0.5	02.00	70	0.15	-1.20
22	100/0.5	03.00	80	0.10	-1.61
23	100/0.5	04.00	87	0.065	-2.04
24	100/0.5	05.00	91	0.045	-2.41
25	100/0.5	06.00	0	0	0
26	100/0.5	07.00	29%	0.355	-0.342
			48%	0.26	-0.654
28	100/0.6	00.00	64%	0.18	-1.02
29	100/0.6	01.00	74%	0.13	-1.35
30	100/0.6	02.00	84%	0.08	-1.83
31	100/0.6	03.00	89.5%	0.0525	-2.25
32	100/0.6	04.00	93%	0.035	-2.66
33	100/0.6	05.00	0	0	0
34	100/0.6	06.00	49%	0.255	-.673
35	100/0.6	07.00	64%	0.18	-1.02
			79%	0.105	-1.56
37	100/0.7	00.00	87%	0.065	-2.04
38	100/0.7	01.00	92%	0.04	-2.52
39	100/0.7	02.00	95%	0.025	-2.99
40	100/0.7	03.00	97%	0.015	-3.51
41	100/0.7	04.00	0	0	0
42	100/0.7	05.00	23%	0.385	-.261
43	100/0.7	06.00	35%	0.325	-.430
44	100/0.7	07.00	44%	0.28	-.579

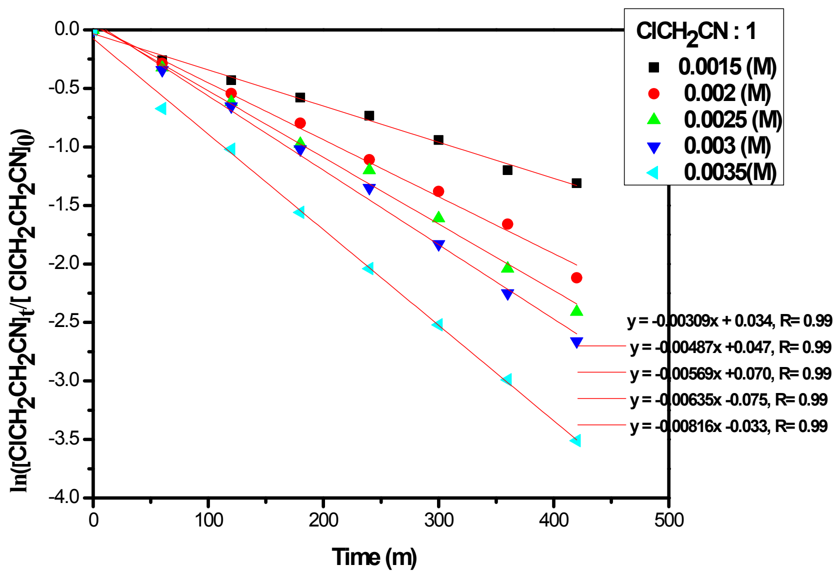


Figure FS98. Plots of ln[$ClCH_2CN$] versus time for the Zinc complex (**1c**) catalysed reaction of $ClCH_2CN$ and HBpin at 25°C in $CDCl_3$ (0.4 ML).

Table TS3. Table for formation rates of $ClCH_2\mathit{CH}_2N(Bpin)_2$ vs [{Im^{tBu}NZnEt}$_2$(**1c**)] for the reaction of [$ClCH_2CN$] with [HBpin] in presence of catalyst [{Im^{tBu}NZnEt}$_2$(**1c**)]. Reaction conditions: [HBpin] = 1 M and [$ClCH_2CN$] = 0.5 M, [{Im^{tBu}NZnEt}$_2$(**1c**)] = [0.0015M to 0.0035 M] in $CDCl_3$ (0.5 mL).

S.NO.	[Im^{t}BuEt$_2$Zn(**1c**)]	k_{obs}
1	0.0015	0.0032
2	0.0020	0.0047
3	0.0025	0.00569
4	0.0030	0.00635
5	0.0035	0.00816

S.NO.	[{Im^{tBu}NZnEt}$_2$(**1c**)]	lnk_{obs}
1	-4.199	-5.71
2	-3.91	-5.35

3	-3.68	-5.17
4	-3.50	-5.06
5	-3.35	-4.81

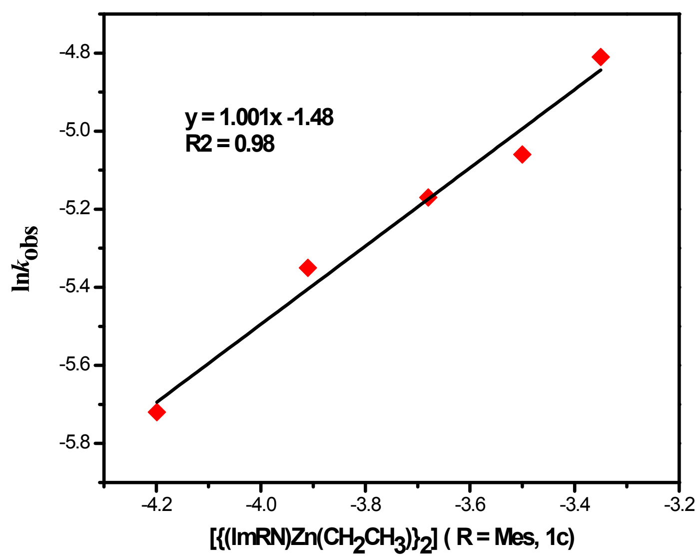


Figure FS99. Kinetics plots of k_{obs} vs [{Im^{tBu}NZnEt}$_2$(**1c**)] for the reaction of [$ClCH_2CN$] with [HBpin] in presence of catalyst (**1c**) [{Im^{tBu}NZnEt}$_2$(**1c**)]. Reaction conditions: [HBpin] = 1 M and [$ClCH_2CN$] = 0.5 M, [{Im^{tBu}NZnEt}$_2$(**1c**)] = [0.0015 M to 0.0035 M] in $CDCl_3$ (0.4 mL).

Table TS4. Table for Formation rates of $ClCH_2CH_2N(Bpin)_2$ versus the ratios of $ClCH_2CN$ / HBpin in $CDCl_3$ at 298 K, indicating a linear dependence. Conditions: [{Im^{tBu}NZnEt}$_2$(**1c**)] = 0.0025(M), [HBpin] = 1 M and [$ClCH_2CN$] [0.3 M to 0.7 M] in $CDCl_3$ (0.4 mL).

mL).

S.NO.	**[$ClCH_2CN$]**	$\boldsymbol{k_{obs}}$
1	0.3	0.009
2	0.4	0.0151

3	0.5	0.0185
4	0.6	0.0215
5	0.7	0.0259

S.NO.	ln[$ClCH_2CN$]	lnk_{obs}
1	-1.203	-4.71
2	-0.916	-4.19
3	-0.693	-3.98
4	-0.511	-3.84
5	-0.356	-3.65

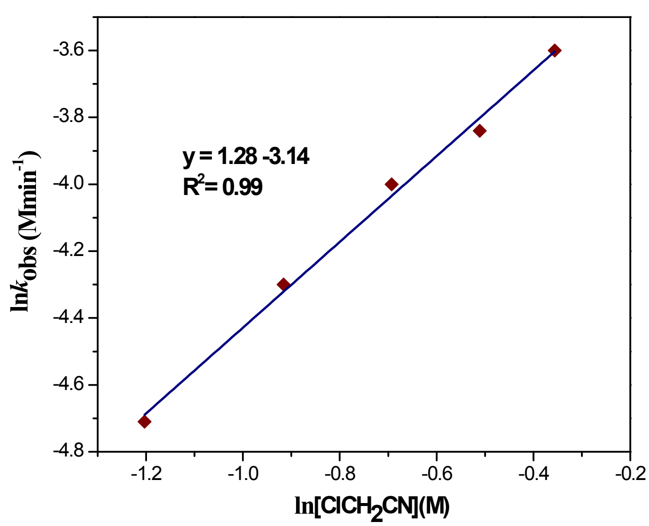


Figure FS100. Kinetics plots of k_{obs} vs [$ClCH_2CN$] for the reaction of [$ClCH_2CN$] with [HBpin] in presence of catalyst (**1c**) [{Im^{tBu}NZnEt}$_2$(**1c**)]. Reaction conditions: [{Im^{tBu}NZnEt}$_2$(**1c**)] = 0.0025(M), [HBpin] = 1 M and [$ClCH_2CN$] [0.3 M to 0.7 M] in $CDCl_3$ (0.4 mL).

Table TS5. Table for Formation rates of $ClCH_2CH_2N(Bpin)_2$ versus the ratios of $ClCH_2CN$ / HBpin in $CDCl_3$ at 298 K, indicating a linear dependence. Conditions: [{Im[tBu]NZnEt}$_2$(**1c**)] = 0.0025 M, [$ClCH_2CN$] = 0.5 (M) and [HBpin] [0.9 M to 1.3 M] in $CDCl_3$ (0.4 mL).

S.NO.	[HBpin]	k_{obs}
1	0.9	0.002045
2	1.0	0.00339
3	1.1	0.00457
4	1.2	0.00707
5	1.3	0.0107

S.NO.	ln[HBpin]	$ln\ k_{obs}$
1	-0.105	-6.1923
2	0	-5.687
3	0.095	-5.38
4	0.182	-4.95
5	0.262	-4.53

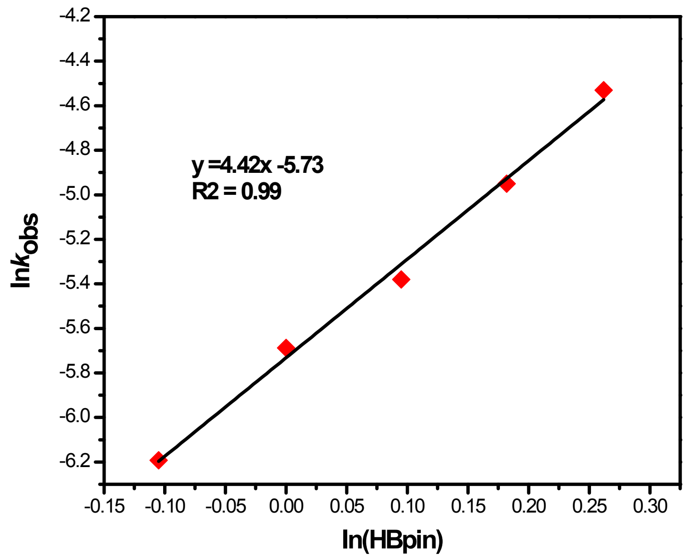


Figure FS101. Kinetics plots of k_{obs} vs [HBpin] for the reaction of [$ClCH_2CN$] with [HBpin] in presence of catalyst (**1c**) [$\{Im^{tBu}NZnEt\}_2$(**1c**)]. Reaction conditions: [$\{Im^{tBu}NZnEt\}_2$(**1c**)] = 0.0025(M), [$OMeC_6H_4CN$] = 0.5 M and [HBpin] = 0.9 M to 1.3 M] in $CDCl_3$ (0.4 mL).

Reference.

1. (a) A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* 1993, **26** 343-350; (b) M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 2005, **38**, 381-388.
2. G. M. Sheldrick, SHELXTLVersion 2014/7. http://shelx.uni-ac.gwdg.de/SHELX/index.php.