Supporting Information for

Nitrile hydroboration reactions catalysed by simple nickel salts, bis(acetylacetonato)nickel(II) and its derivatives

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Experimental Details and Compound Characterization Data

General considerations

Unless otherwise noted, all manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glove box. Benzene, toluene, hexane, and THF were purified by a solvent purification system (MBraun SPS-800 or Glass Contour Ultimate Solvent System). Other solvents (1,2-dichloroethane, benzene-d_6) were dried over CaH_2 or sodium benzophenone ketyl and distilled. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Catecholborane was purchased from Sigma-Aldrich Ltd. and purified by distillation. ^{1}H, ^{11}B, and ^{13}C{^{1}H} NMR spectra (^{1}H, 400 MHz; ^{11}B, 128 MHz; ^{13}C, 101 MHz) were recorded using a Bruker AVANCE 600 spectrometer. Chemical shifts are reported in δ (ppm) and are referenced to the residual solvent signals for ^{1}H and ^{13}C, and to boron trifluoride diethyl ether complex ($BF_3{\cdot}OEt_2$, 0.0 ppm) as an external reference for ^{11}B.

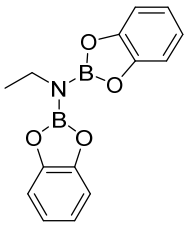
Catalytic Hydroborations

A typical procedure (Table 2, entry 1) is as follows. All reactions were carried out under nitrogen atmosphere. To a stirred solution of bis(2,2,6,6-tetramethyl-3,5-heptanedionato)nickel(II) (**3**) (0.001 mmol) in benzene (0.5 mL), was added benzonitrile (20.6 mg, 0.20 mmol) at 25 °C. After the mixture was stirred for 1 min, catecholborane (52.8 mg, 0.44 mmol) was added, and then the solution was stirred at room temperature for 18 hours. $PhSiMe_3$ (13.1 mg, 0.087 mmol) as an internal standard was added to the reaction mixture, and ^{1}H NMR was measured to determine the NMR yield of $PhCH_2N(Bcat)_2$ (>99%). The resulting solution was then diluted by benzene (30 mL) and filtered to remove precipitates. The filtrate was concentrated to dryness to give analytically pure $PhCH_2N(Bcat)_2$ (65.9 mg, 0.19 mmol, 93%).

Compound Characterization Data

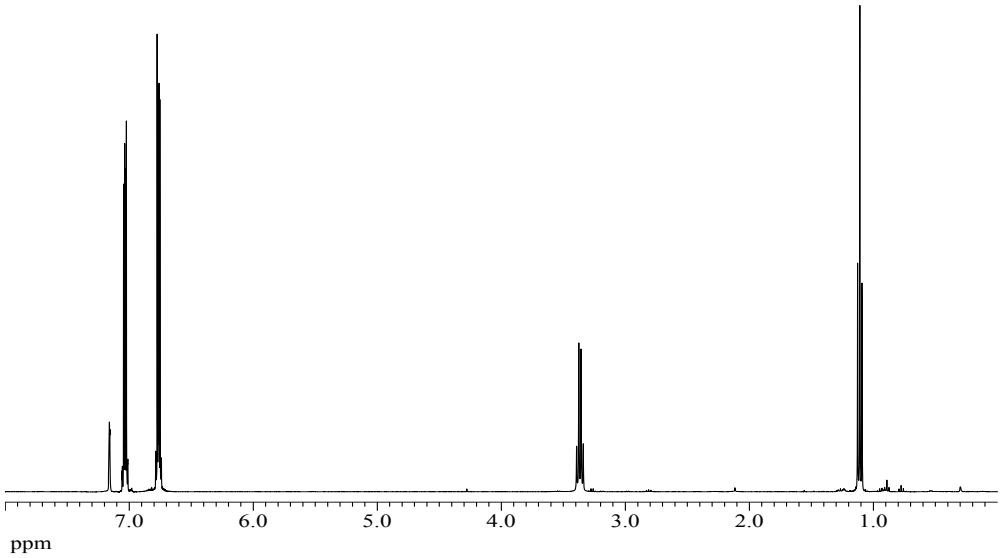
The final product was characterized by ^{1}H, ^{13}C{^{1}H} and ^{11}B{^{1}H} NMR due to the instability of the hydroborated products under air. $CH_3CH_2N(Bcat)_2$ and $PhCH_2N(Bcat)_2$ were identified by comparing their ^{1}H, ^{11}B, and ^{13}C{^{1}H} NMR data with those previously reported.[1]

$CH_3CH_2(Bcat)_2$

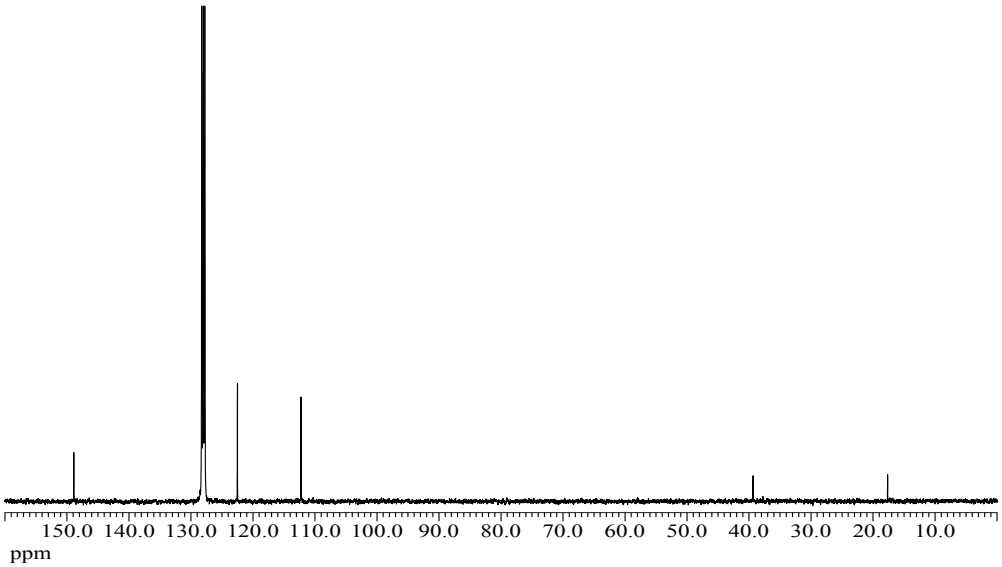


^{1}H NMR (C_6D_6, 25 °C): 7.03 (m, 4H, B*cat*), 6.76 (m, 4H, B*cat*), 3.34 (q, 2H, CH_2N, J = 7.2 Hz), 1.11 (t, 3H, CH_3, J = 7.2 Hz). ^{11}B NMR (C_6D_6, 25 °C): 26.8 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.9, 122.5, 112.3, 39.4, 17.7.

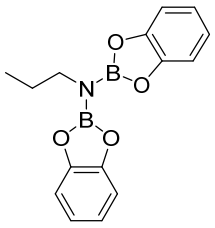
^{1}H NMR:



^{13}C{^{1}H} NMR:

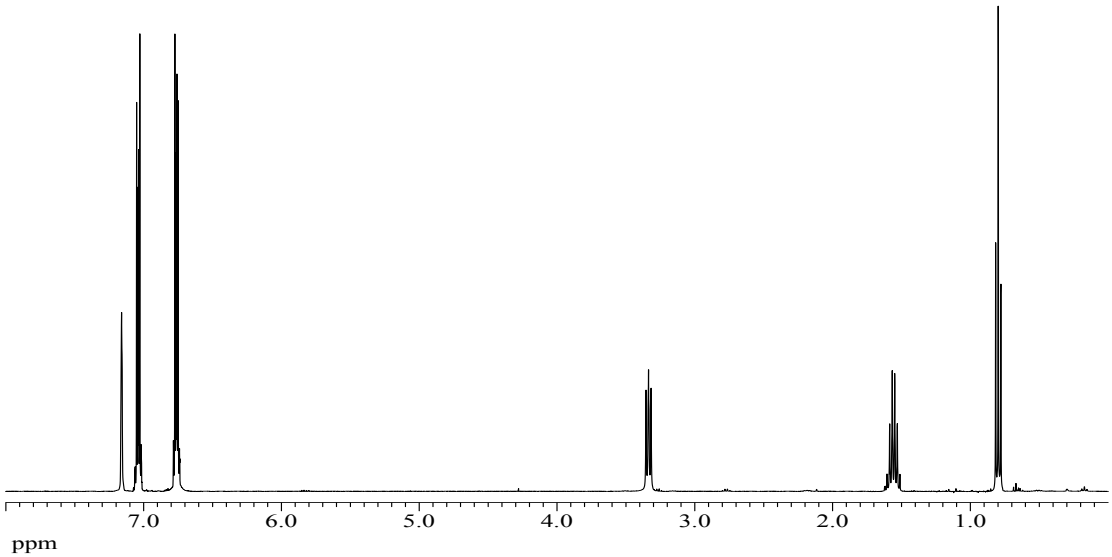


$CH_3CH_2CH_2N(Bcat)_2$

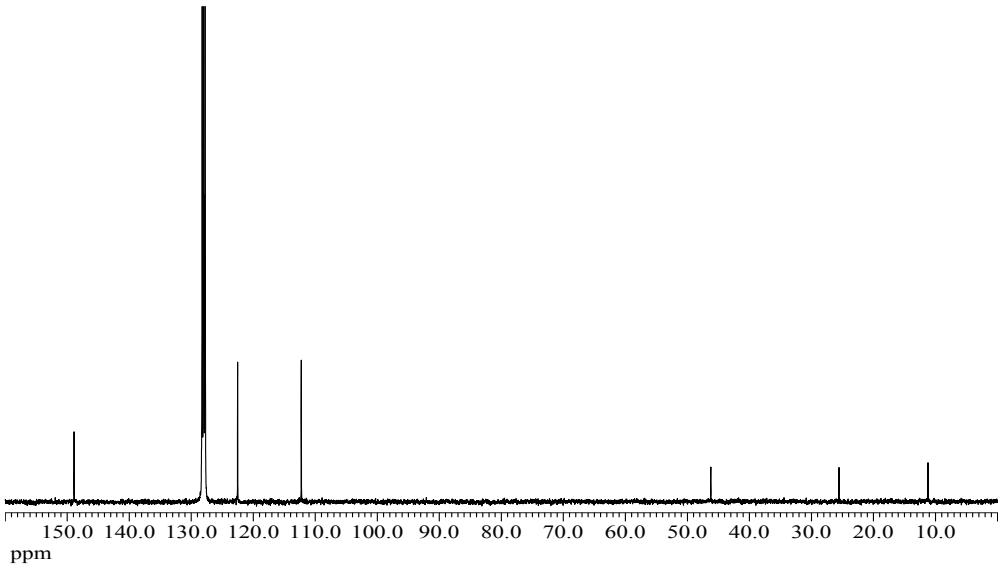


^{1}H NMR (C_6D_6, 25 °C): 7.04 (m, 4H, B*cat*), 6.76 (m, 4H, B*cat*), 3.34 (t, 2H, CH_2N, J = 7.6 Hz), 1.56 (m, 2H, NCH_2-CH_2-CH_3), 0.80 (t, 3H, CH_3, J = 7.2 Hz). ^{11}B NMR (C_6D_6, 25 °C): 27.0 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.9, 122.5, 112.3, 46.2, 25.6, 11.2.

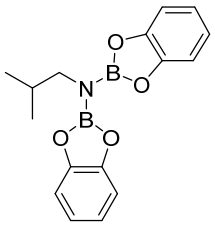
^{1}H NMR:



^{13}C{^{1}H} NMR:

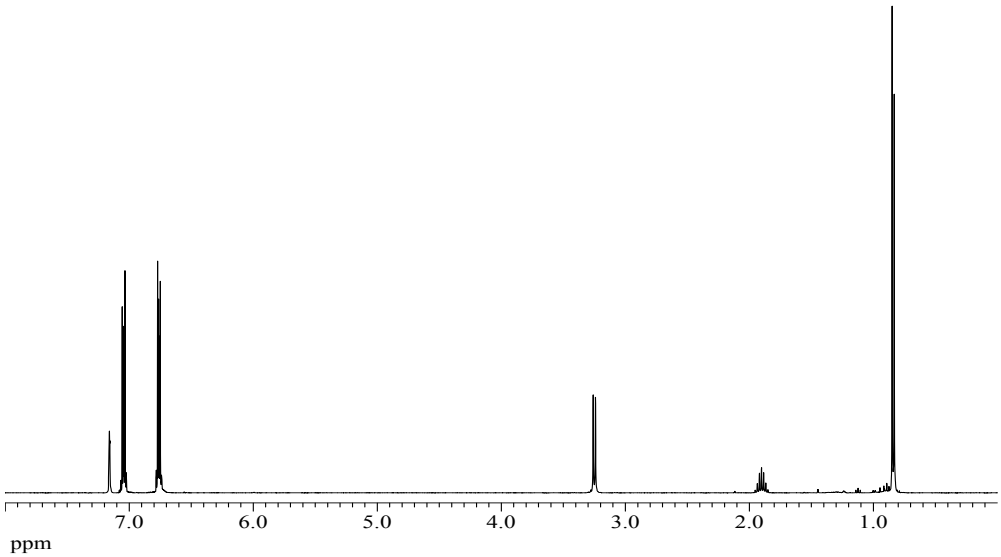


$^{i}PrCH_2N(Bcat)_2$

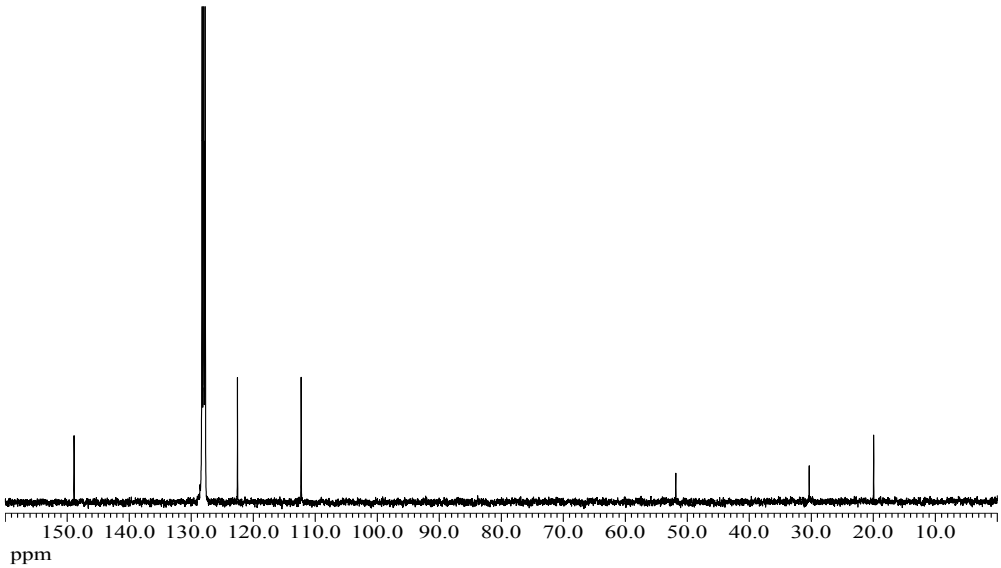


^{1}H NMR (C_6D_6, 25 °C): 7.05 (m, 4H, B*cat*), 6.76 (m, 4H, B*cat*), 3.25 (d, 2H, CH_2N, J = 7.6 Hz), 1.90 (m, 1H, $(CH_3)_2CH$), 0.84 (d, 6H, CH_3, J = 6.4 Hz). ^{11}B NMR (C_6D_6, 25 °C): 26.9 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.9, 122.6, 112.3, 51.9, 30.4, 20.0.

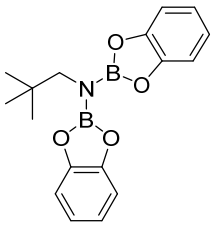
^{1}H NMR:



^{13}C{^{1}H} NMR:

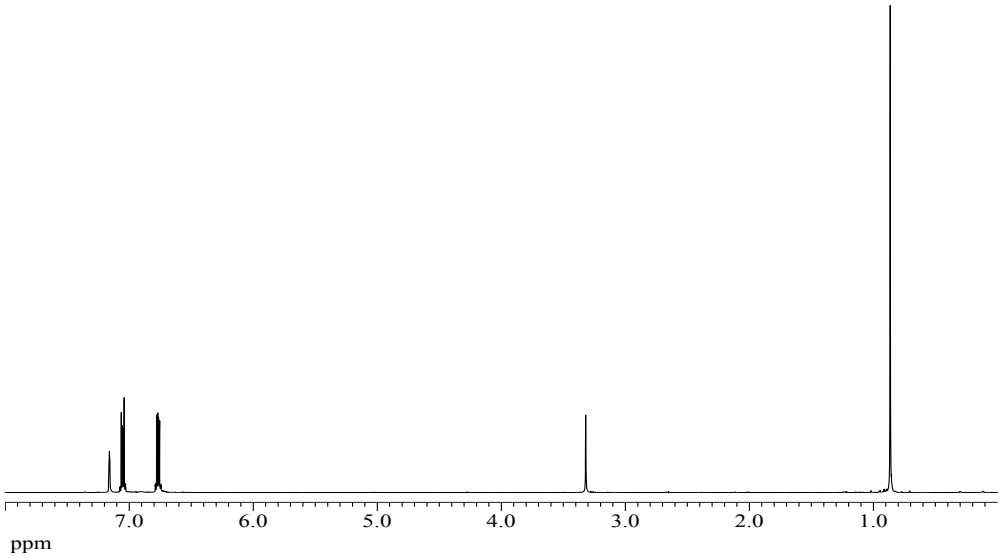


^{t}BuCH$_2$N(Bcat)$_2$

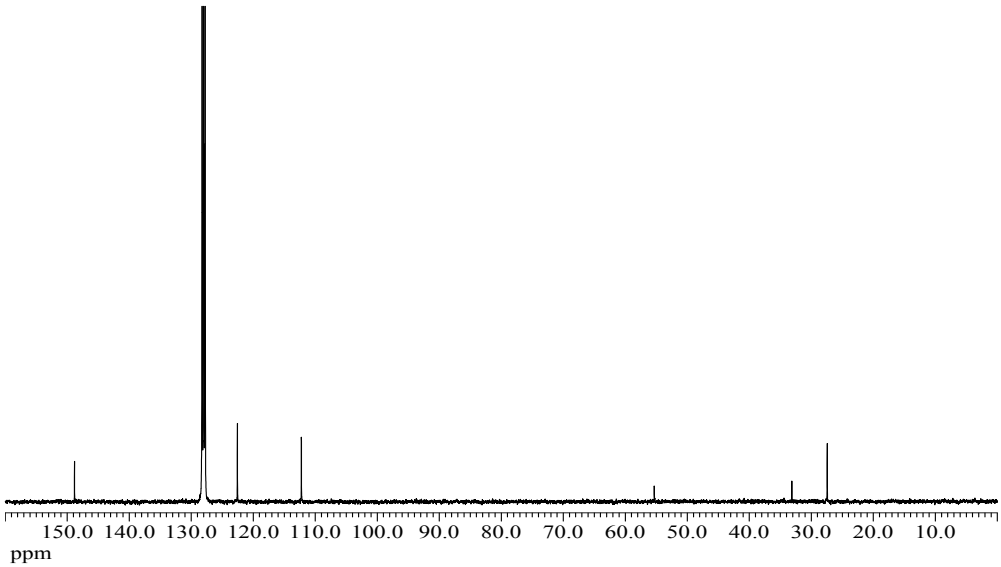


^{1}H NMR (C_6D_6, 25 °C): 7.05 (m, 4H, B*cat*), 6.77 (m, 4H, B*cat*), 3.32 (s, 2H, C*H*$_2$N), 0.86 (s, 9H, C*H*$_3$). ^{11}B NMR (C_6D_6, 25 °C): 27.0 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.8, 122.6, 112.2, 55.3, 33.2, 27.4.

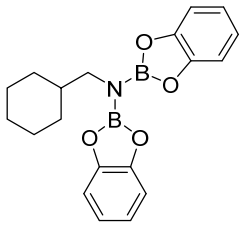
^{1}H NMR:



^{13}C{^{1}H} NMR:

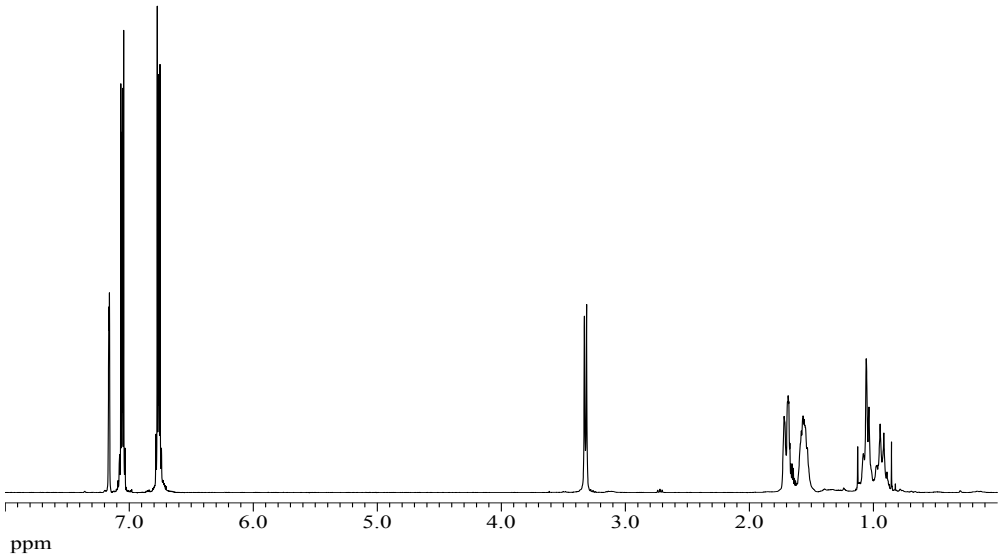


$CyCH_2N(Bcat)_2$

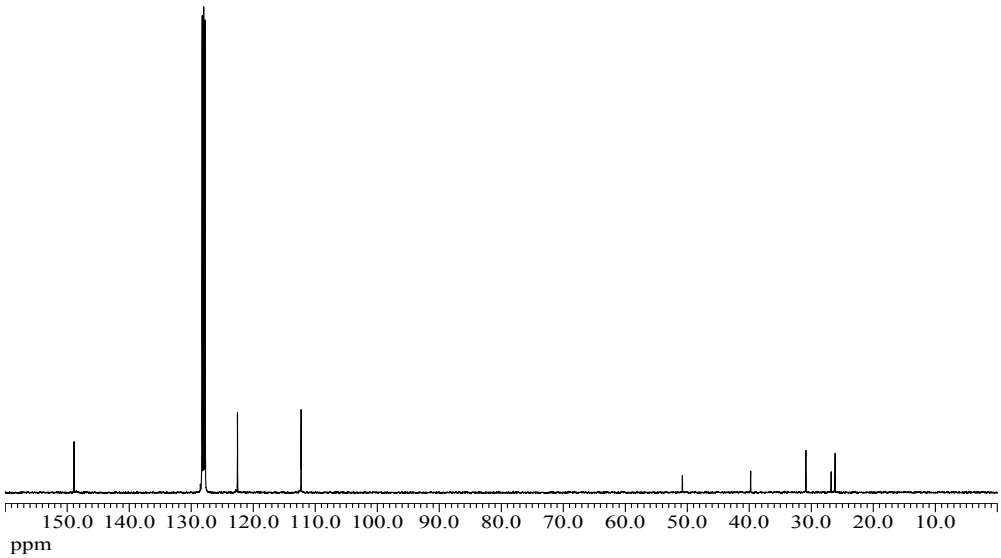


^{1}H NMR (C_6D_6, 25 °C): 7.06 (m, 4H, B*cat*), 6.76 (m, 4H, B*cat*), 3.32 (d, 2H, CH_2N, J = 7.2 Hz), 1.63 (m, 6H, Cy-*H*), 0.99 (m, 5H, Cy-*H*). ^{11}B NMR (C_6D_6, 25 °C): 26.9 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.9, 122.55, 112.3, 50.8, 39.8, 30.9, 26.8, 26.2.

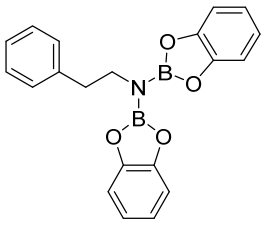
^{1}H NMR:



^{13}C{^{1}H} NMR:

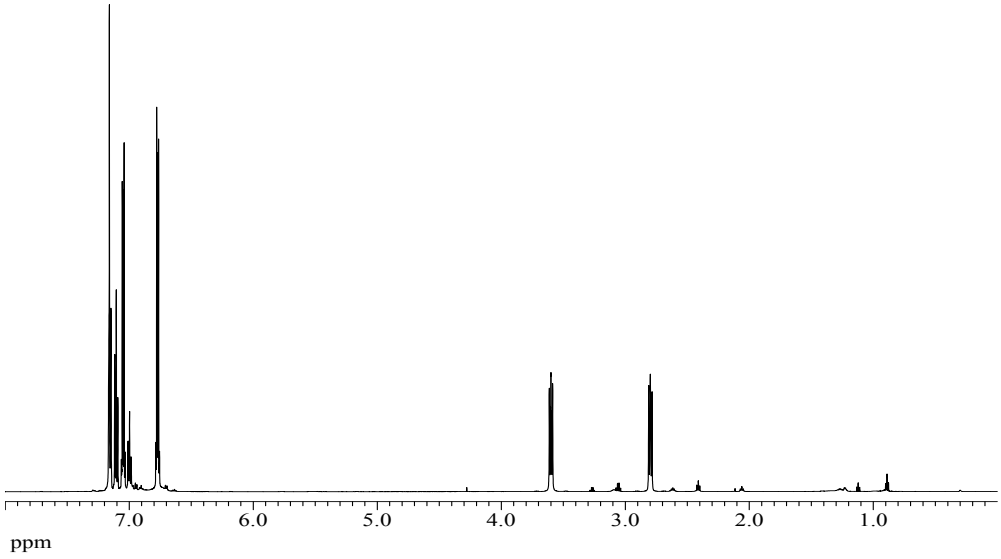


$PhCH_2CH_2N(Bcat)_2$

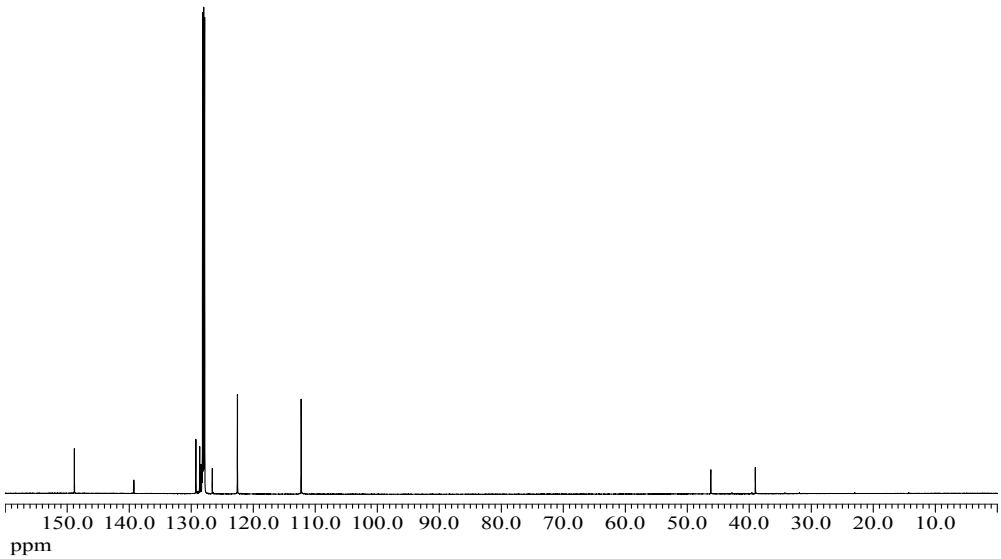


^{1}H NMR (C_6D_6, 25 °C): 7.15 (d, 2H, *J* = 7.2 Hz, Ar-*H*), 7.10 (t, 2H, *J* = 7.2 Hz, Ar-*H*), 7.05 (m, 4H, B*cat*), 7.00 (t, 1H, *J* = 7.2 Hz, Ar-*H*), 6.77 (m, 4H, B*cat*), 3.60 (t, 2H, *J* = 7.6 Hz, C*H*$_2$N), 2.80 (t, 2H, *J* = 7.6 Hz, PhC*H*$_2$). ^{11}B NMR (C_6D_6, 25 °C): 27.0 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.8, 139.3, 129.3, 128.7, 128.5, 128.3, 122.6, 112.3, 46.2, 39.0.

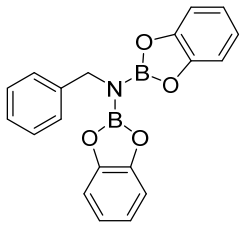
^{1}H NMR:



^{13}C{^{1}H} NMR:

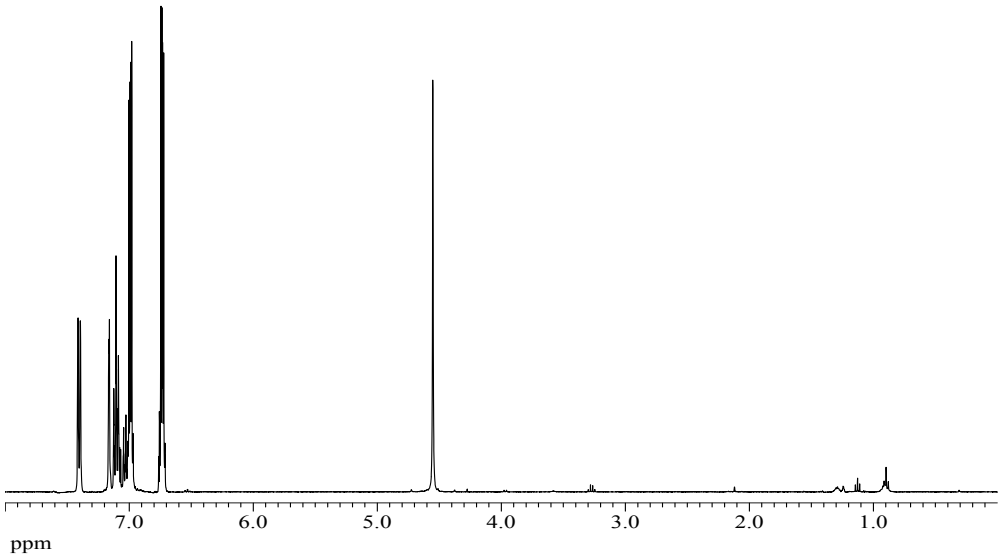


$PhCH_2N(Bcat)_2$

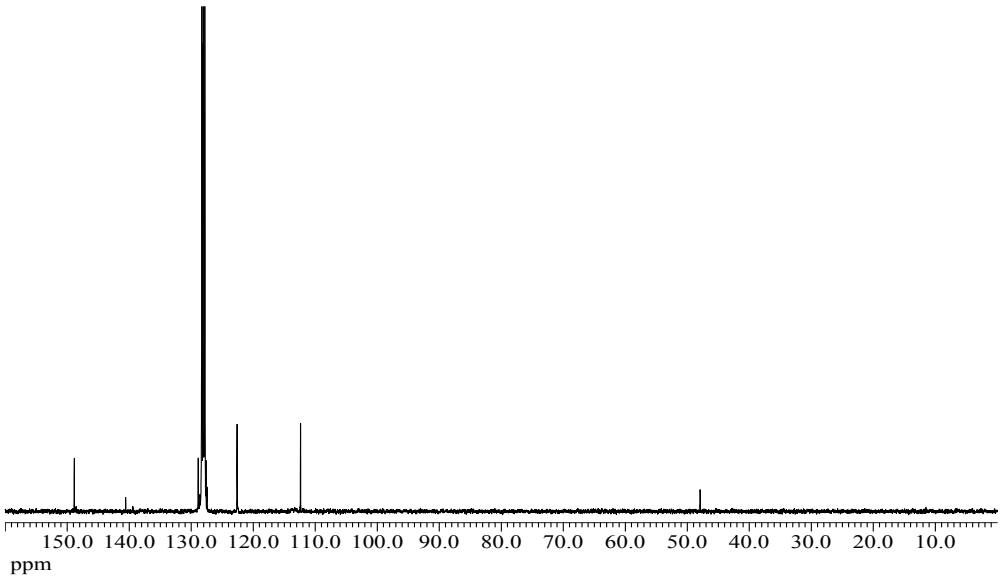


^{1}H NMR (C_6D_6, 25 °C): 7.40 (d, 2H, *J* = 7.2 Hz, Ar-*H*), 7.11 (t, 2H, *J* = 7.6 Hz, Ar-*H*), 7.05 (m, 1H, Ar-*H*), 6.99 (m, 4H, B*cat*), 6.73 (m, 4H, B*cat*), 4.55 (s, 2H, CH_2N). ^{11}B NMR (C_6D_6, 25 °C): 27.2 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.8, 140.6, 139.4, 128.8, 127.4, 122.6, 112.3, 47.9.

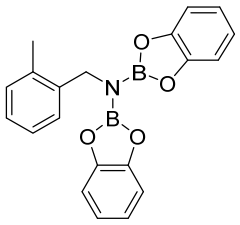
^{1}H NMR:



^{13}C{^{1}H} NMR:

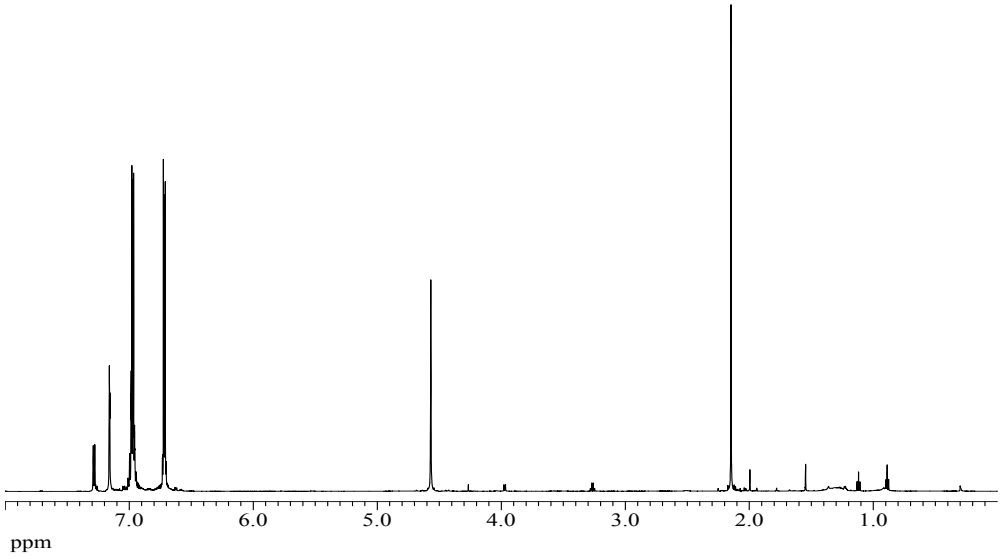


(o-tolyl)$CH_2N(Bcat)_2$

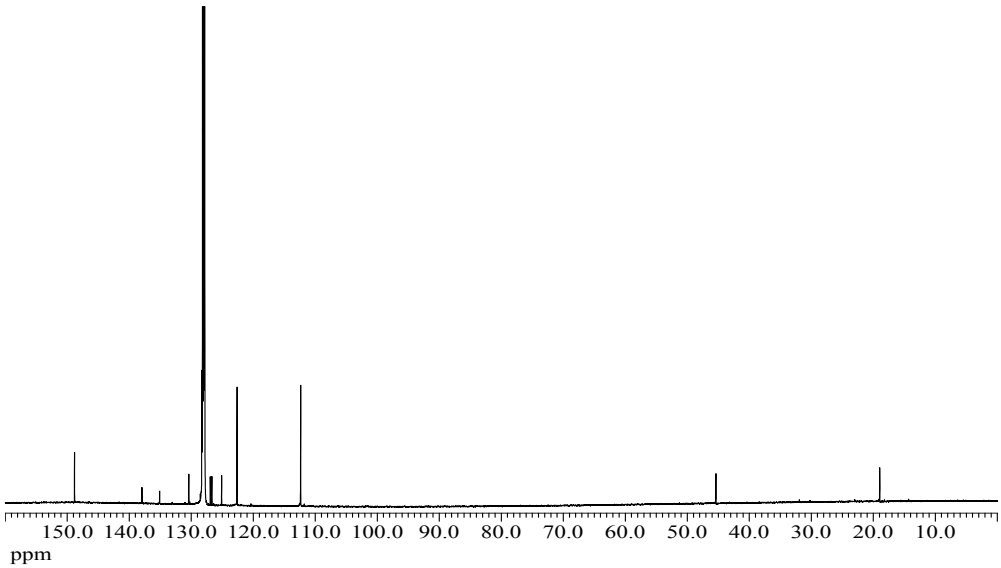


^{1}H NMR (C_6D_6, 25 °C): δ 7.28 (d, 2H, J = 8.0 Hz, Ar-*H*), 6.98 (m, 6H, Ar-*H* and B*cat*), 6.88 (d, 1H, J = 7.6 Hz, Ar-*H*), 6.72 (m, 4H, B*cat*), 4.57 (s, 2H, CH_2N), 2.15 (s, 3H, CH_3). ^{11}B NMR (C_6D_6, 25 °C): δ 27.1 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 148.8, 138.0, 135.1, 130.4, 128.3, 126.9, 126.7, 125.1, 122.6, 112.4, 45.38, 19.0.

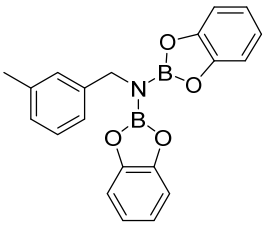
^{1}H NMR:



^{13}C{^{1}H} NMR:

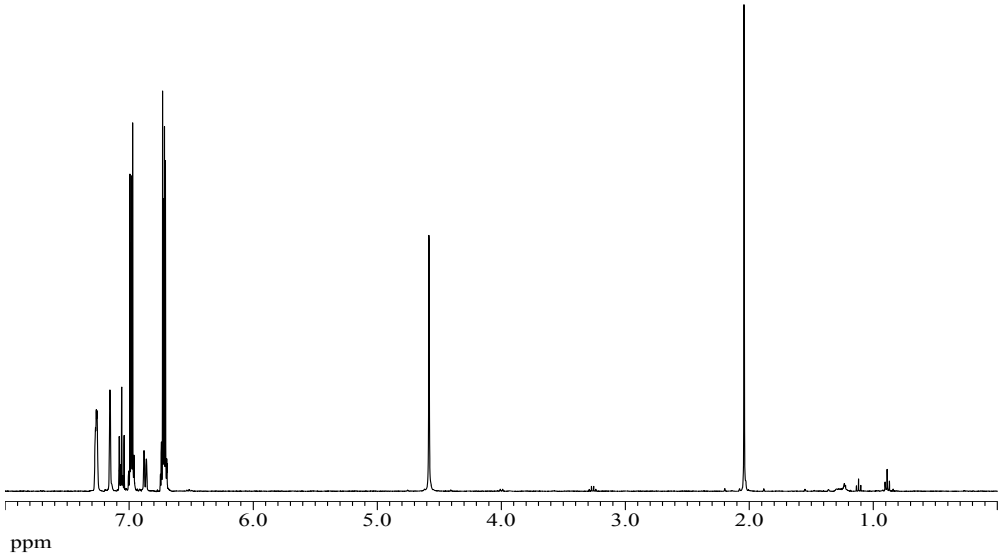


(m-tolyl)CH_2N(Bcat)$_2$

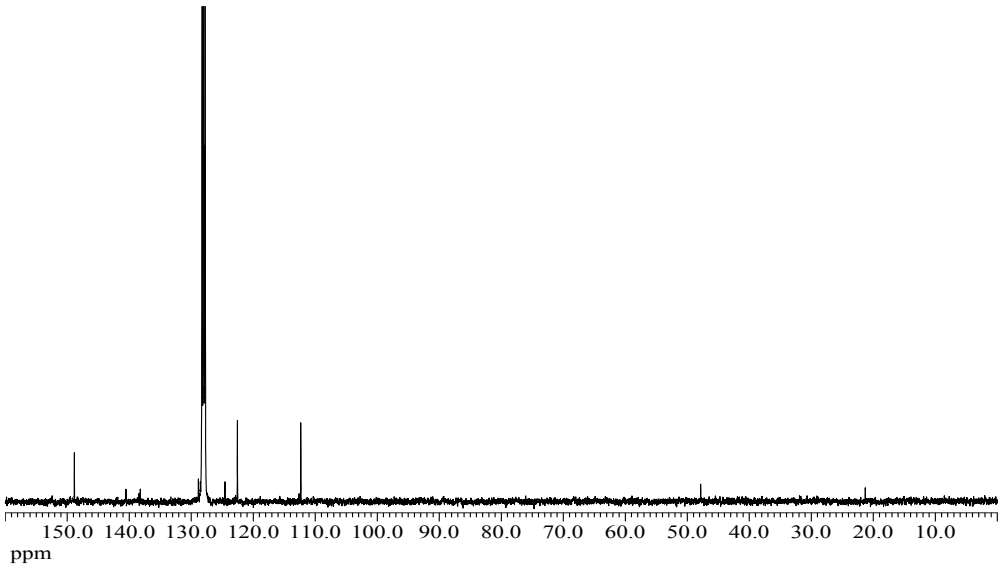


^{1}H NMR (C_6D_6, 25 °C): δ 7.27 (m, 2H, Ar-*H*), 7.11 (m, 1H, Ar-*H*), 6.99 (m, 4H, B*cat*), 6.88 (d, 1H, J = 7.6 Hz, Ar-*H*), 6.72 (m, 4H, B*cat*), 4.59 (s, 2H, CH_2N), 2.05 (s, 3H, CH_3). ^{11}B NMR (C_6D_6, 25 °C): δ 27.0 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 148.8, 140.5, 138.2, 128.9, 127.9, 124.6, 122.6, 112.3, 47.9, 21.3.

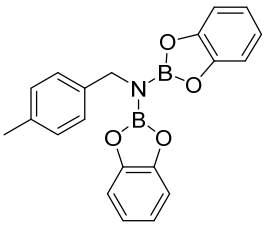
^{1}H NMR:



^{13}C{^{1}H} NMR:

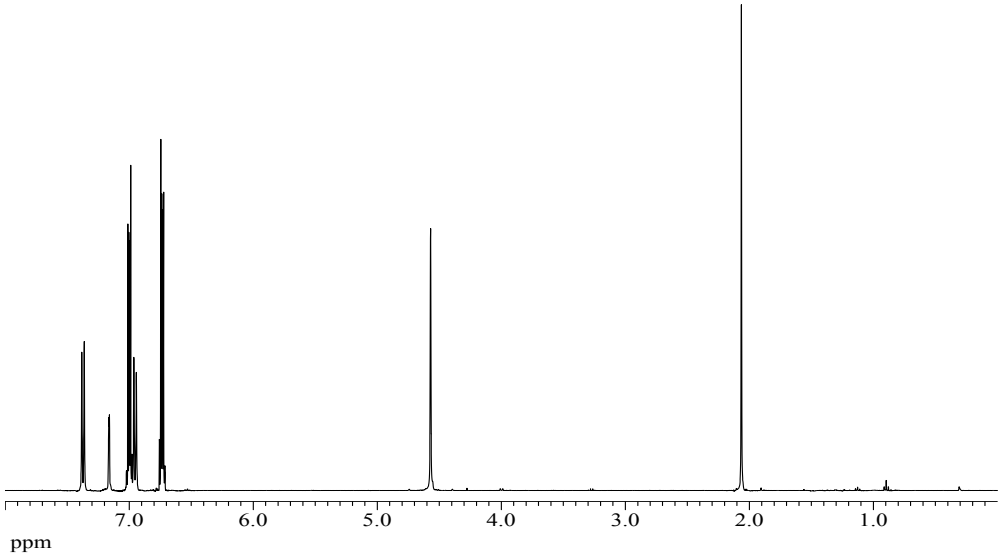


(p-tolyl)CH_2N(Bcat)$_2$

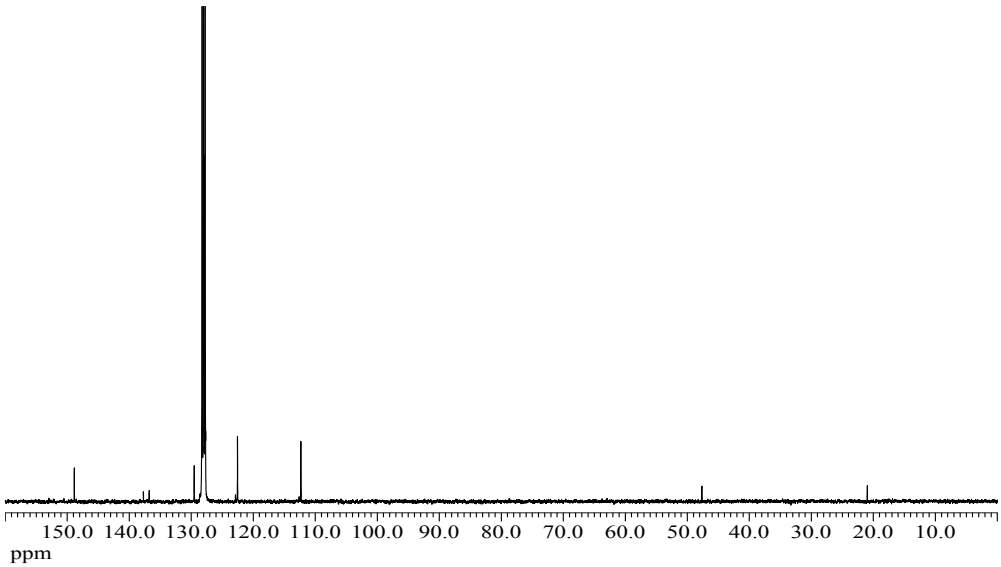


^{1}H NMR (C_6D_6, 25 °C): 7.37 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 7.00 (m, 4H, B*cat*), 6.95 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 6.72 (m, 4H, B*cat*), 4.57 (s, 2H, CH_2N), 2.06 (s, 3H, CH_3). ^{11}B NMR (C_6D_6, 25 °C): 27.1 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.9, 137.7, 136.8, 129.5, 122.5, 112.3, 47.7, 21.0.

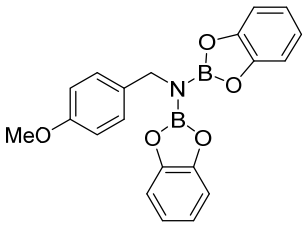
^{1}H NMR:



^{13}C{^{1}H} NMR:

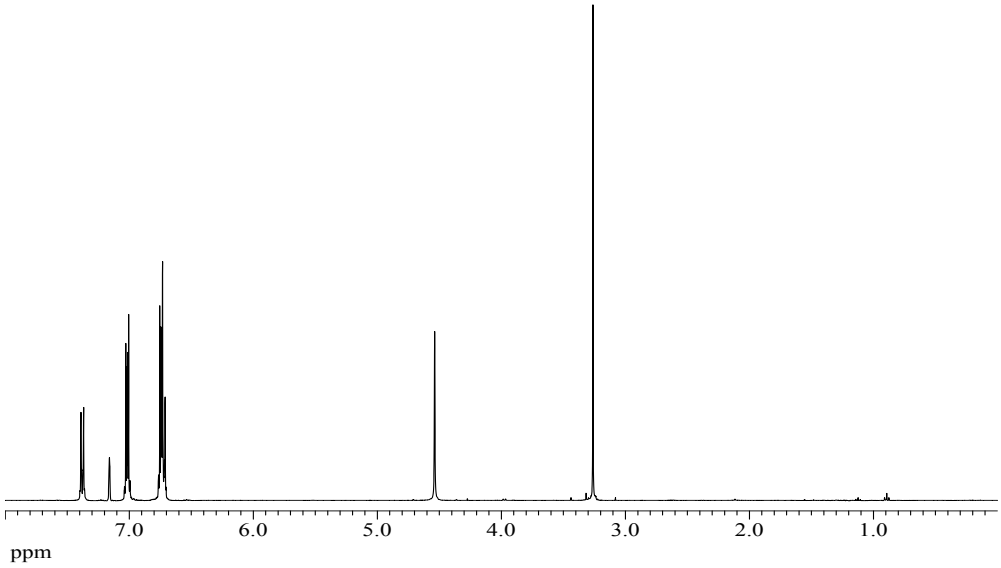


(p-MeOC$_6$H$_4$)CH$_2$N(Bcat)$_2$

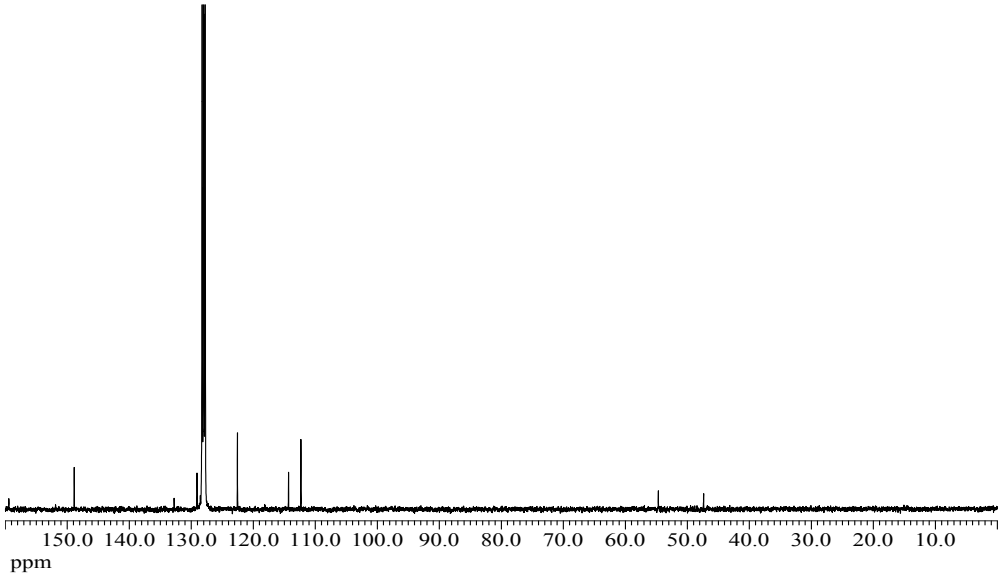


^{1}H NMR (C_6D_6, 25 °C): 7.38 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.02 (m, 4H, B*cat*), 6.73 (m, 6H, Ar-*H* and B*cat*), 4.54 (s, 2H, C*H*$_2$N), 3.26 (s, 3H, OC*H*$_3$). ^{11}B NMR (C_6D_6, 25 °C): 27.2 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 159.4, 148.9, 132.8, 136.8, 129.1, 122.6, 114.2, 112.3, 54.8, 47.4.

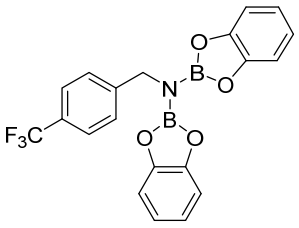
^{1}H NMR:



^{13}C{^{1}H} NMR:

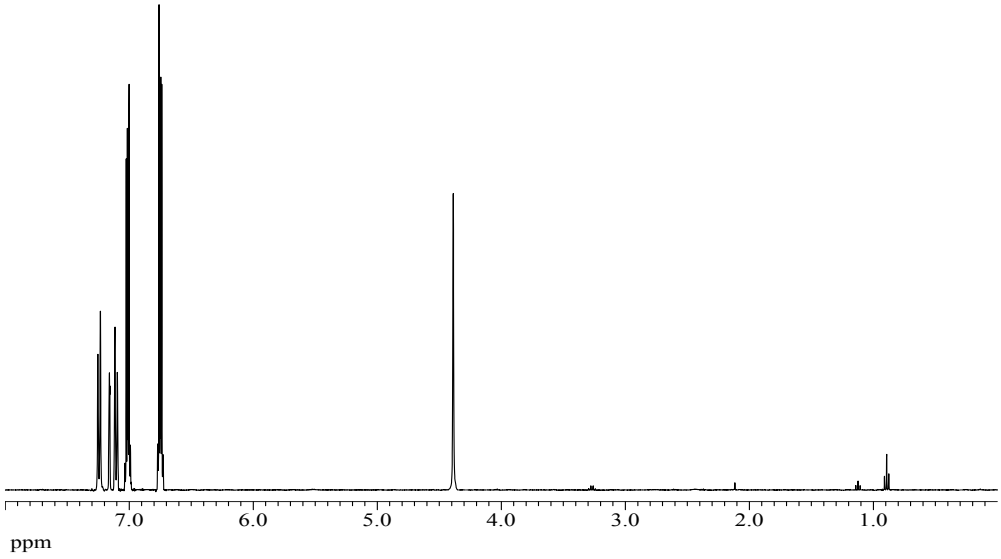


(p-$F_3CC_6H_4$)CH_2N(Bcat)$_2$

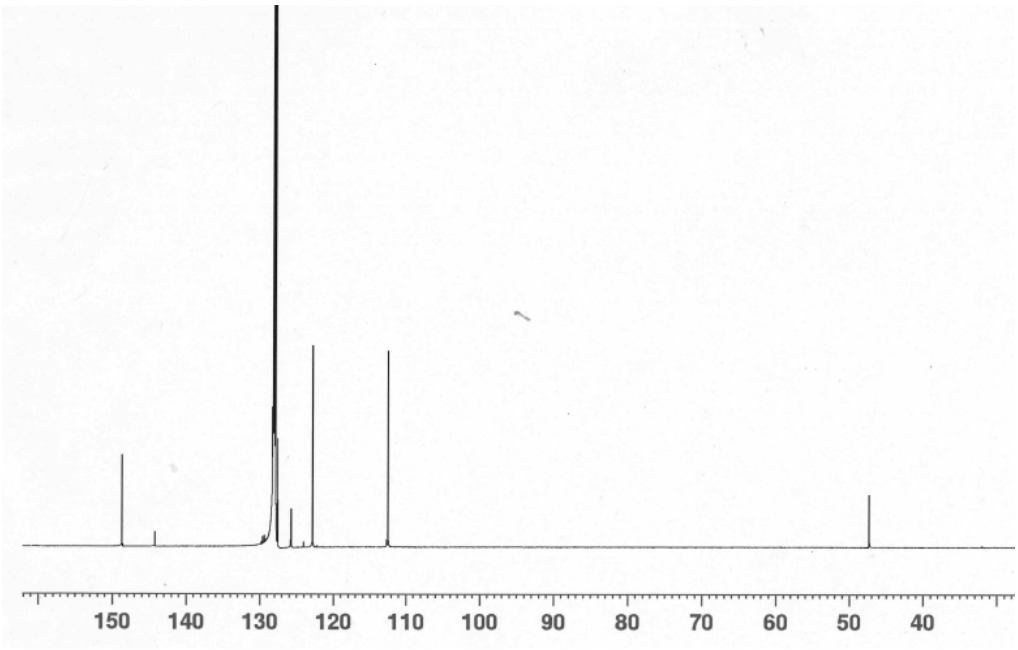


^{1}H NMR (C_6D_6, 25 °C): 7.24 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 7.11 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 7.01 (m, 4H, B*cat*), 6.75 (m, 4H, B*cat*), 4.39 (s, 2H, CH_2N). ^{11}B NMR (C_6D_6, 25 °C): 26.8 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.7, 144.2, 136.8, 129.5, 125.8, 127.5, 122.8, 112.4, 47.3.

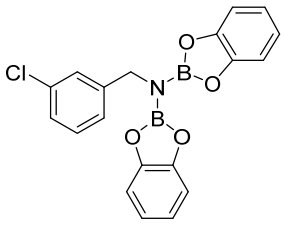
^{1}H NMR:



^{13}C{^{1}H} NMR:

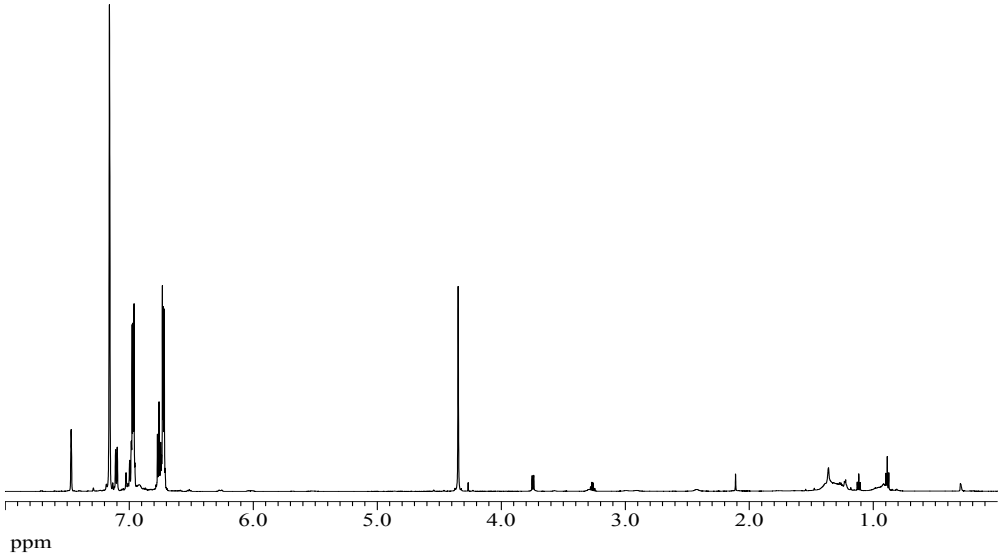


(m-ClC$_6$H$_4$)CH$_2$N(Bcat)$_2$

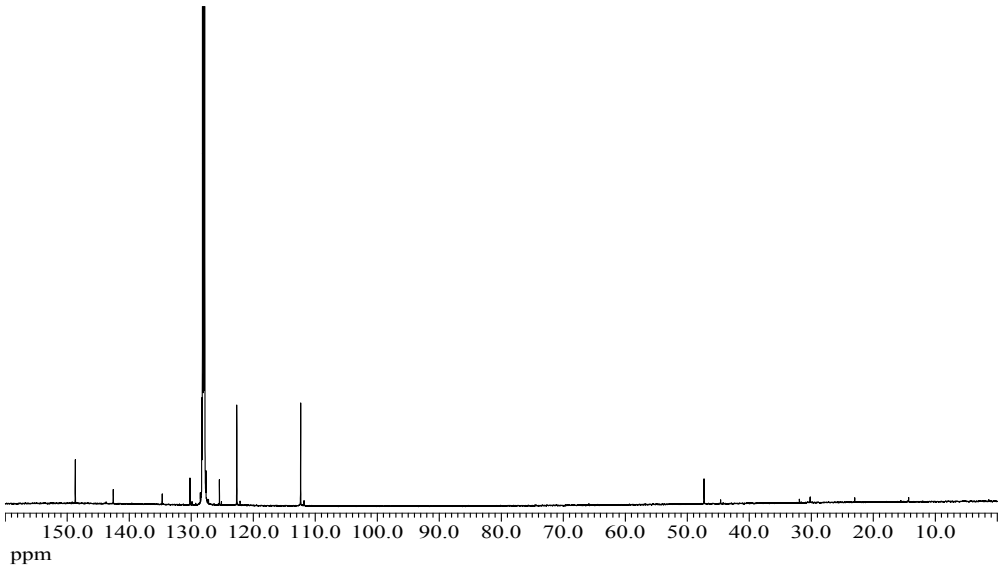


^{1}H NMR (C_6D_6, 25 °C): 7.47 (s, 1H, Ar-*H*), 7.10 (d, 1H, *J* = 8.0 Hz, Ar-*H*), 6.98 (m, 5H, Ar-*H* and B*cat*), 6.74 (m, 5H, Ar-*H* and B*cat*), 4.35 (s, 2H, C*H*$_2$N). ^{11}B NMR (C_6D_6, 25 °C): 26.9 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.7, 142.6, 134.7, 130.2, 128.3, 125.5, 122.7, 112.4, 47.3.

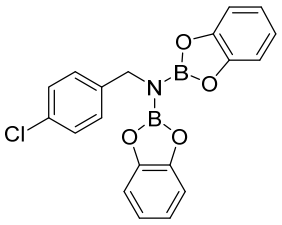
^{1}H NMR:



^{13}C{^{1}H} NMR:

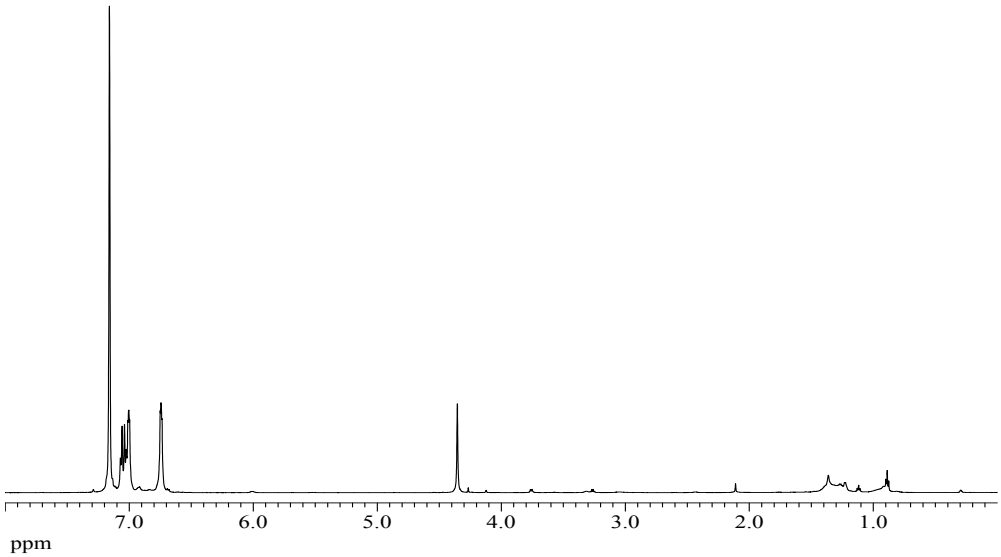


(p-ClC$_6$H$_4$)CH$_2$N(Bcat)$_2$

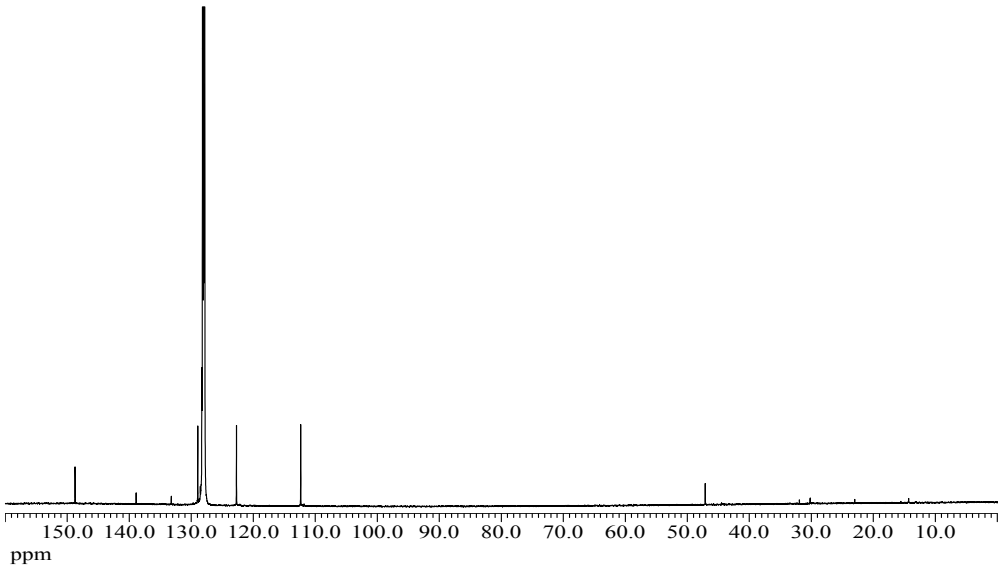


^{1}H NMR (C_6D_6, 25 °C): 7.04 (m, 8H, Ar-*H* and B*cat*), 6.74 (m, 4H, B*cat*), 4.35 (s, 2H, CH_2N). ^{11}B NMR (C_6D_6, 25 °C): 26.9 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.7, 138.9, 133.2, 129.0, 128.3, 122.7, 112.4, 47.1.

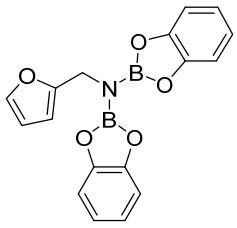
^{1}H NMR:



^{13}C{^{1}H} NMR:

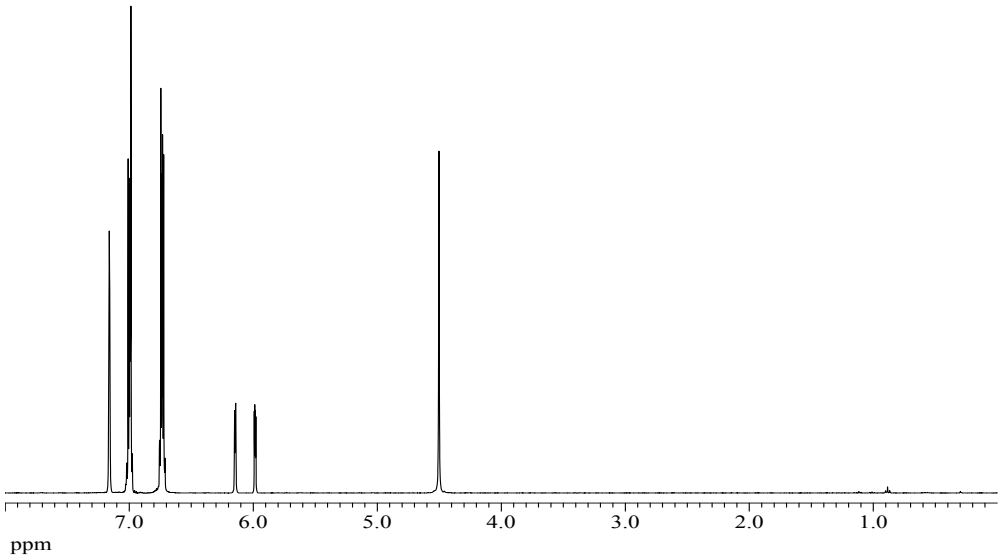


(2-furyl)$CH_2N(Bcat)_2$

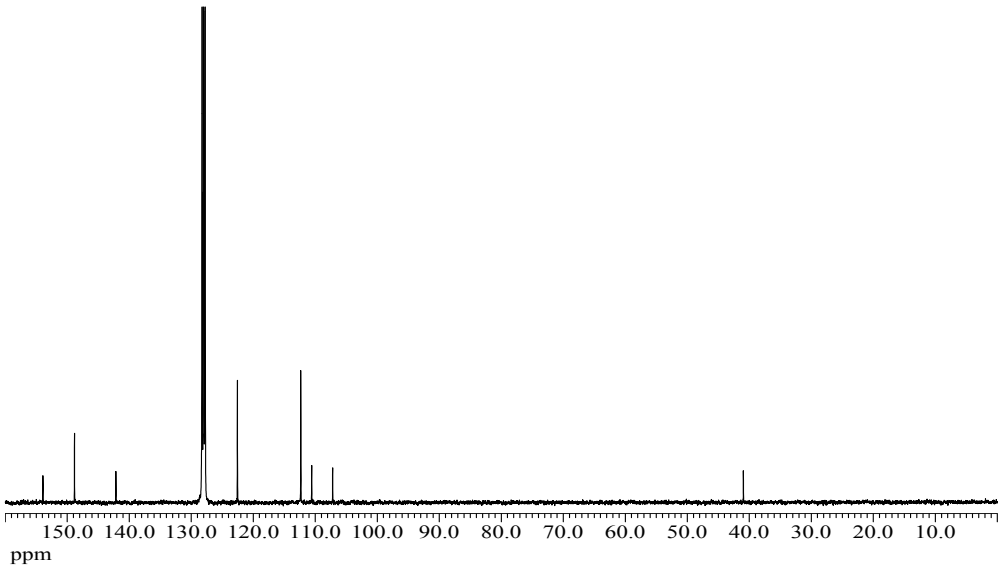


^{1}H NMR (C_6D_6, 25 °C): 7.00 (m, 5H, furyl-*H* and B*cat*), 6.73 (m, 4H, B*cat*), 6.15 (d, 1H, *J* = 3.2 Hz, furyl-*H*), 5.98 (m, 1H, furyl-*H*), 4.50 (s, 2H, CH_2N). ^{11}B NMR (C_6D_6, 25 °C): 27.0 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 159.9, 148.8, 142.2, 122.6, 112.3, 110.6, 107.2, 41.0.

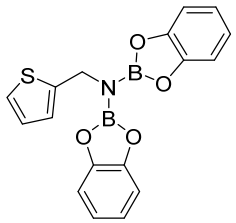
^{1}H NMR:



^{13}C{^{1}H} NMR:

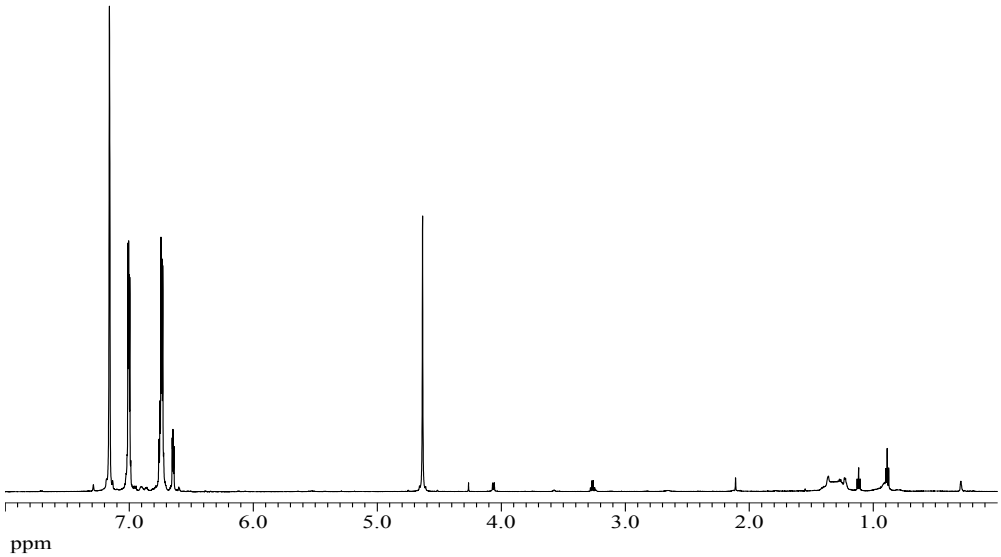


(2-thienyl)CH_2N(Bcat)$_2$

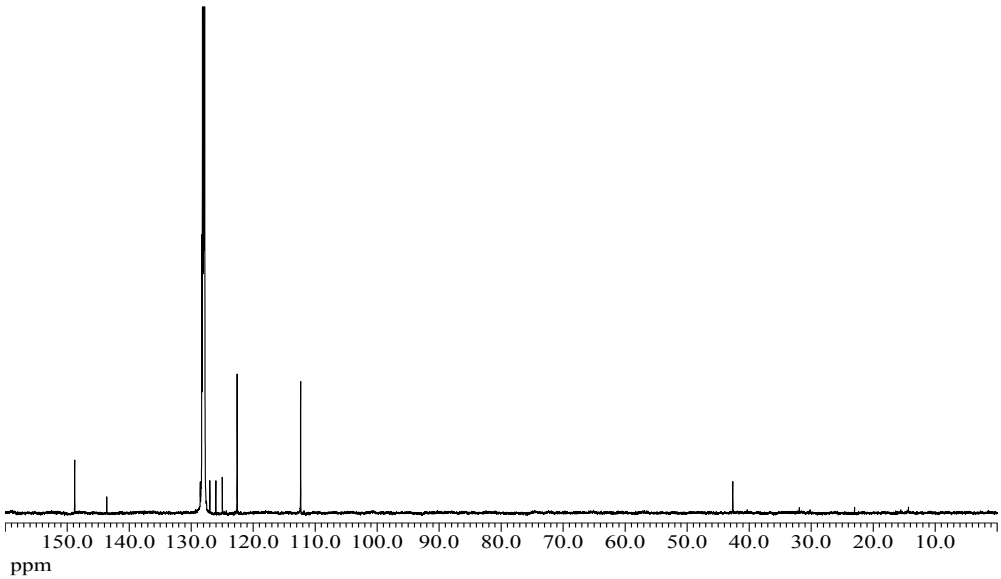


^{1}H NMR (C_6D_6, 25 °C): 7.00 (m, 4H, B*cat*), 6.74 (m, 6H, thienyl-*H* and B*cat*), 6.65 (m, 1H, thienyl-*H*), 4.63 (s, 2H, CH_2N). ^{11}B NMR (C_6D_6, 25 ^{o}C): 26.8 (bs, *B*cat). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 148.8, 143.6, 127.0, 126.0, 125.0, 122.6, 112.4, 42.7.

^{1}H NMR:



^{13}C{^{1}H} NMR:



Reaction of 3 with HBcat. A J-young NMR tube was charged with a C_6D_6 solution (0.4 mL) of **3** (5.0 mg, 0.012 mmol) and HBcat (5.5 mg, 0.046 mmol). After 15 min at room temperature, formation of black precipitate was observed. Formation of [*t*BuCOCHC(*t*Bu)O–κO,κO′]Bcat was supported by both ^{1}H and $^{11}B\{^{1}H\}$ NMR although all the signals appeared as significantly broad signals due to the existence of paramagnetic nickel species. In addition, formation of several unidentified products, which exhibit broad signals as δ 28.9, 23.3, 18.7 ppm in the ^{11}B NMR spectrum, was also confirmed. After filtration, slow evaporation of the filtrate afforded single crystals of [*t*BuCOCHC(*t*Bu)O–κO,κO′]Bcat.

[*t*BuCOCHC(*t*Bu)O–κO,κO′]Bcat: ^{1}H NMR (C_6D_6, 25 °C): 7.11 (dd, 2H, J = 5.4, 3.6 Hz, B*cat*), 6.84 (dd, 2H, J = 5.4, 3.6 Hz, B*cat*), 5.82 (s, 1H, CH), 0.84 (s, 18H, *t*Bu). ^{11}B NMR (C_6D_6, 25 °C): 9.7 (bs, *B*cat). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 25 °C): 201.3, 151.9, 120.1, 110.2, 92.9, 39.5, 26.9.

Single-crystal X-ray diffraction studies. The single crystal X-ray diffraction measurements of [*t*BuCOCHC(*t*Bu)O–κO,κO']Bcat was performed under a cold nitrogen stream on a Rigaku XtaLAB P200 diffractometer with a Pilatus 200K detector using multi-layer mirrore monochromated Mo Kα radiation. The determination of crystal systems and unit cell parameters and data processing were performed with the *CrystalClear* program package. The data sets were corrected for Lorentz and polarzation effects and absorption. The structure was solved by direct methods using SIR97 program,[2] and refined by full-matrix least squares calculations on F^2 for all reflections (SHELXL-97)[3]. The structure was not fully refined due to the bad quality of the crystal and the final R values remain 0.1208 (R_1) and 0.2771 (wR_2).

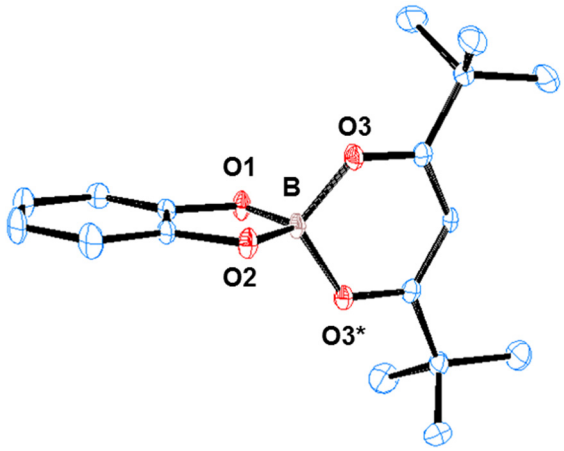


Figure 1. Molecular structure of [*t*BuCOCHC(*t*Bu)O–κO,κO′]Bcat with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): B–O1 1.463(3), B–O2 1.452(3), B–O3 1.490(2), O1–B–O2 107.1(2), O3–B–O3* 108.9(2).

Table S1. Crystal data and details of the crystal structure determination for *t*BuCOCHC(*t*Bu)OBcat.

formula	$C_{17}H_{23}O_4B$	Z	4
fw	302.17	D_{calcd} (g/cm^3)	1.200
T (K)	93(2)	$R1$, $wR2$ [$I > 2\sigma(I)$]	0.1208, 0.2771
cryst system	Orthorhombic	$R1$, $wR2$ (all data)	0.1386, 0.2945
space group	*P*bnm (#62)	GOF	1.371
a (Å)	9.246(3)		
b (Å)	12.853(4)		
c (Å)	14.074(4)		
α (deg)	90		
β (deg)	90		
γ (deg)	90		
V (Å^3)	1672.5(9)		

References

1) A. Y. Khalimon, P. Farha, L. G. Kuzmina and G. I. Nikonov, *Chem. Commun.*, **2012**, *48*, 455.
2) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115.
3) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.