Electronic supplementary information for

Synthesis and characterization of rare-earth metallate amido complexes bearing 2-amidate-functionalized indolyl ligand and their application in the hydroboration of esters with pinacolborane

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Table S1. Summary of crystal and refinement data for complexes **1a-1d.**

	1a (Y)	**1b** (Nd)	**1c** (Sm)	**1d** (Gd)
Formula	$C_{97}H_{152}ClY_3LiN_9O_7Si_6$	$C_{97}H_{152}ClNd_3LiN_9O_7Si_6$	$C_{97}H_{152}ClSm_3LiN_9O_7Si_6$	$C_{97}H_{152}ClGd_3LiN_9O_7Si_6$
FW	2033.93	2199.92	2218.25	2238.95
T(K)	298.15	298.15	298.15	298.15
λ(Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a(Å)	19.816(2)	19.8695(14)	19.8895(16)	19.8493(16)
b(Å)	20.172(2)	20.1675(14)	20.3112(17)	20.2615(17)
c(Å)	21.517(2)	21.5072(15)	21.6747(18	21.6207(18)
α(deg)	67.6430(10)	68.2219(10)	67.0740(10)	67.2240(10)
β(deg)	83.979(2)	84.2175(10)	83.8230(10)	83.7930(10)
γ(deg)	61.6610(10)	61.4812(9)	61.8000(10)	61.7530(10)
v(Å^3)	6970.8(12)	7001.2(9)	7075.6(10)	7032.3(10)
Z	2	2	2	2
$D_{calcd(mg/m^3)}$	0.969	1.044	1.041	1.057
μ(mm^{-1})	1.350	1.207	1.339	1.509
F(000)	2148	2274	2286	2298
θrange(deg)	1.028-27.816	1.024-25.000	1.025-27.476	1.026-27.551
Reflections collected/unique	81971/31977	69464/24635	83569/31916	83693/31936
R(int)	0.0984	0.1055	0.0642	0.1177
Goodness-of-fit on F^2	0.956	0.963	0.995	0.938
R_1,wR_2[$I>2\sigma(I)$]	0.0774, 0.1811	0.0705, 0.1612	0.0587, 0.1378	0.0701, 0.1509
R_1,wR_2(all data)	0.1939, 0.2275	0.1627, 0.2029	0.1265, 0.1675	0.1749, 0.1922
Laegest diff.peak and hole(e. Å^{-3})	0.784 and -0.505	1.012 and -0.502	2.063 and -0.642	1.407 and -0.523

Table S2. Summary of crystal and refinement data for complexes **1e-1g.**

	1e (Dy)	**1f** (Er)	**1g** (Yb)
Formula	$C_{97}H_{152}ClDy_3LiN_9O_7Si_6$	$C_{97}H_{152}ClEr_3LiN_9O_7Si_6$	$C_{97}H_{152}ClYb_3LiN_9O_7Si_6$
FW	2254.70	2268.98	2286.32
T(K)	298.15	298.15	298.15
λ(Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a(Å)	19.827(3)	19.7581(15)	19.7356(17)
b(Å)	20.177(3)	20.0890(15)	20.0788(18)
c(Å)	21.529(3)	21.4239(16)	21.4057(19)
α(deg)	67.638(2)	67.9980(10)	68.0020(10)
β(deg)	83.935(2)	84.0600(10)	84.0650(10)
γ(deg)	61.667(2)	61.6270(10)	61.6860(10)
v(Å^3)	6981.1(18)	6908.1(9)	6895.2(11)
Z	2	2	2
$D_{calcd(mg/m^3)}$	1.073	1.091	1.101
μ(mm^{-1})	1.700	1.918	2.131
F(000)	2310	2322	2334
*θ*range(deg)	1.027- 27.565	1.029-27.475	1.030-27.437
Reflections collected/unique	81915/ 31769	81890/31261	81666/31109
R(int)	0.0905	0.0773	0.0749
Goodness-of-fit on F^2	1.017	1.007	1.022
R_1,wR_2[$I>2\sigma(I)$]	0.0787, 0.1770	0.0641, 0.1405	0.0687, 0.1591
R_1,wR_2(all data)	0.1751, 0.2199	0.1425, 0.1763	0.1491, 0.1959
Laegest diff.peak and hole(e. Å^{-3})	2.804 and -1.036	2.851 and -0.982	2.827 and -0.980

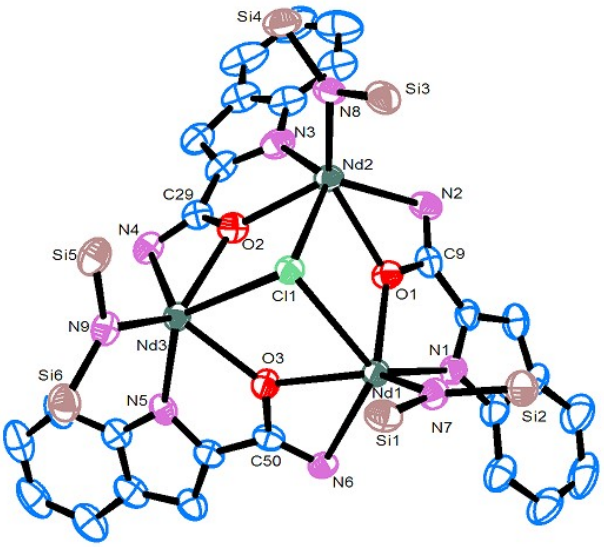

Figure S1. Molecular structure of complex **1b** with the probability ellipsoids drawn at the 25% level. Hydrogen atoms, 2,6-diisopropylphenyl groups on the N2, N4, N6 atoms, methyl groups on the Si atoms, and $Li(THF)_4^+$ are omitted for clarity.

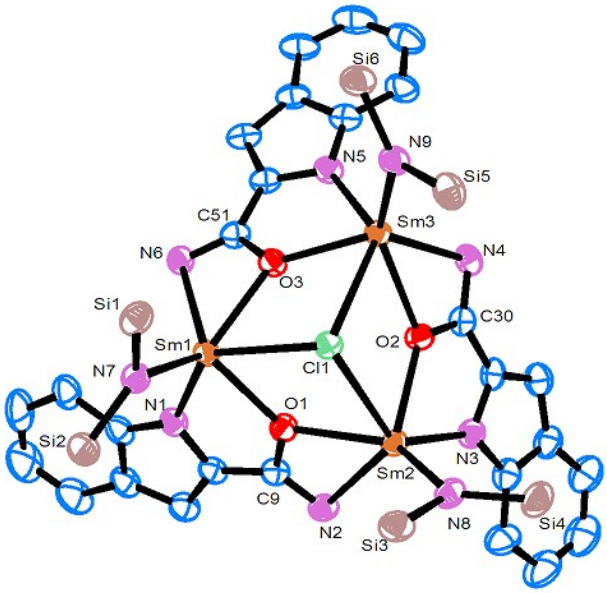

Figure S2. Molecular structure of complex **1c** with the probability ellipsoids drawn at the 25% level. Hydrogen atoms, 2,6-diisopropylphenyl groups on the N2, N4, N6 atoms, methyl groups on the Si atoms, and $Li(THF)_4^+$ are omitted for clarity.

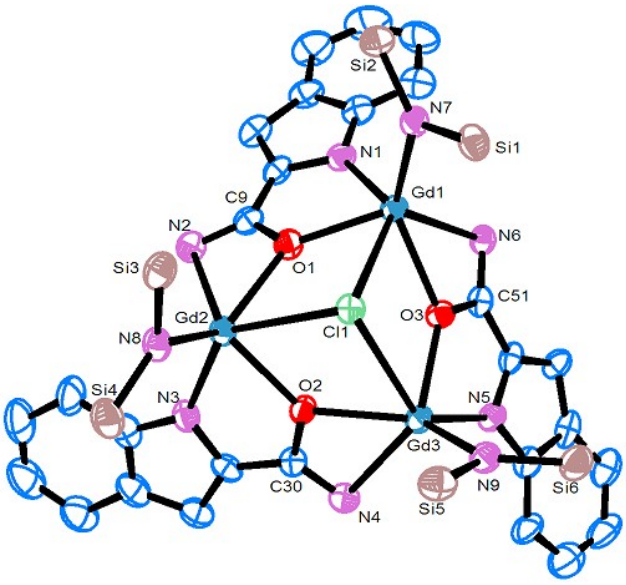

Figure S3. Molecular structure of complex **1d** with the probability ellipsoids drawn at the 25% level. Hydrogen atoms, 2,6-diisopropylphenyl groups on the N2, N4, N6 atoms, methyl groups on the Si atoms, and $Li(THF)_4^+$ are omitted for clarity.

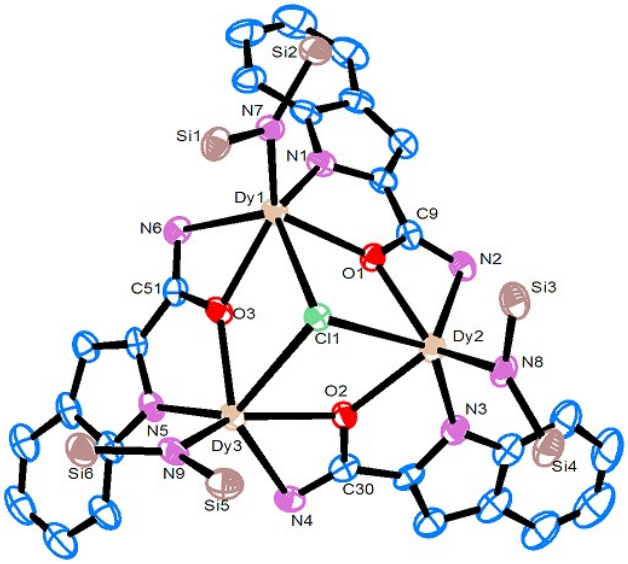

Figure S4. Molecular structure of complex **1e** with the probability ellipsoids drawn at the 25% level. Hydrogen atoms, 2,6-diisopropylphenyl groups on the N2, N4, N6 atoms, methyl groups on the Si atoms, and $Li(THF)_4^+$ are omitted for clarity.

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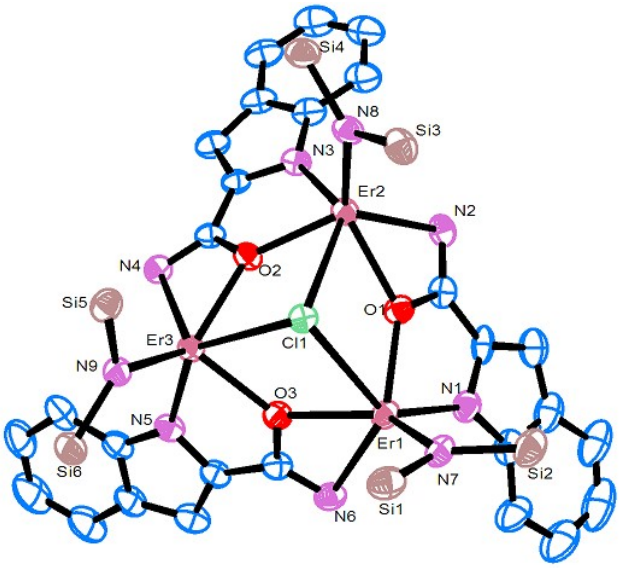


Figure S5. Molecular structure of complex **1f** with the probability ellipsoids drawn at the 25% level. Hydrogen atoms, 2,6-diisopropylphenyl groups on the N2, N4, N6 atoms, methyl groups on the Si atoms, and $Li(THF)_4^+$ are omitted for clarity.

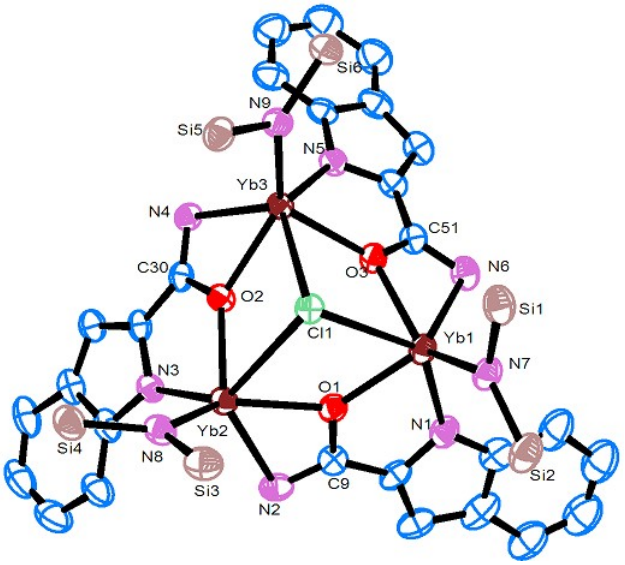


Figure S6. Molecular structure of complex **1g** with the probability ellipsoids drawn at the 25% level. Hydrogen atoms, 2,6-diisopropylphenyl groups on the N2, N4, N6 atoms, methyl groups on the Si atoms, and $Li(THF)_4^+$ are omitted for clarity.

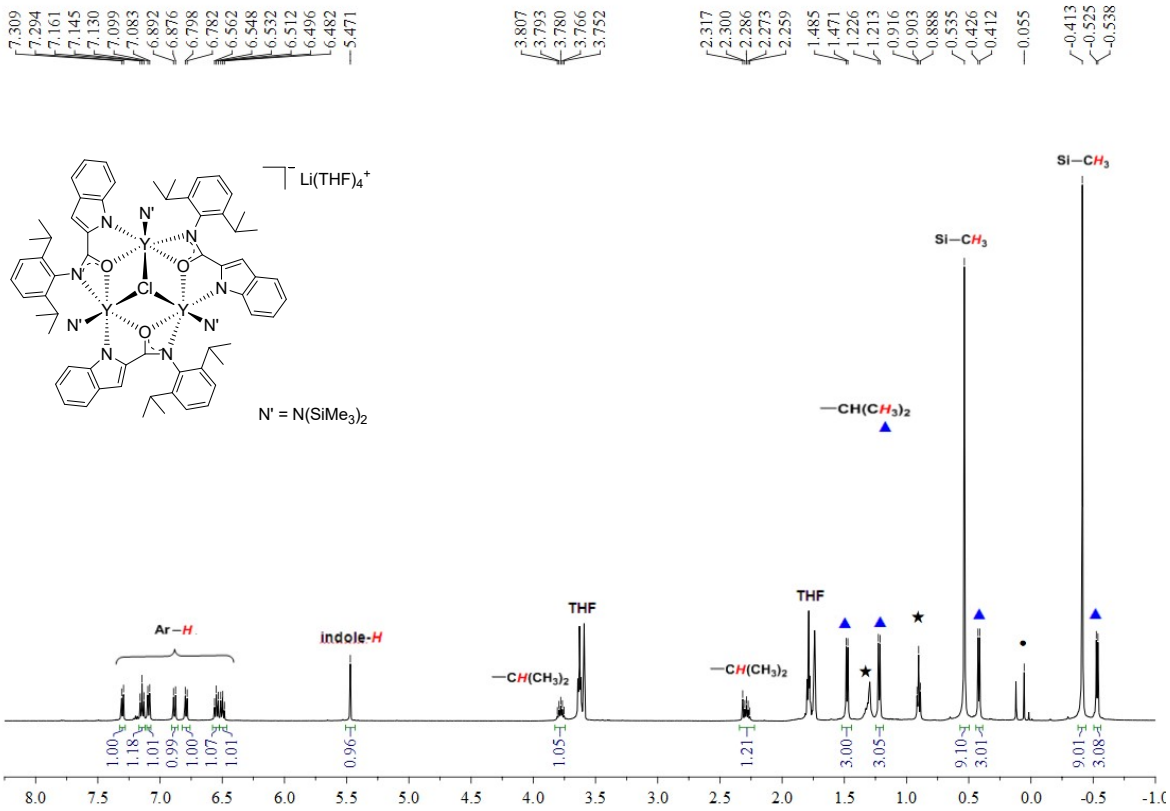


Figure S7. ^{1}H NMR spectrum (500 MHz, THF-d_8, 298 K) of complex **1a** (★ *n*-hexane, ● $HNSiMe_3$).

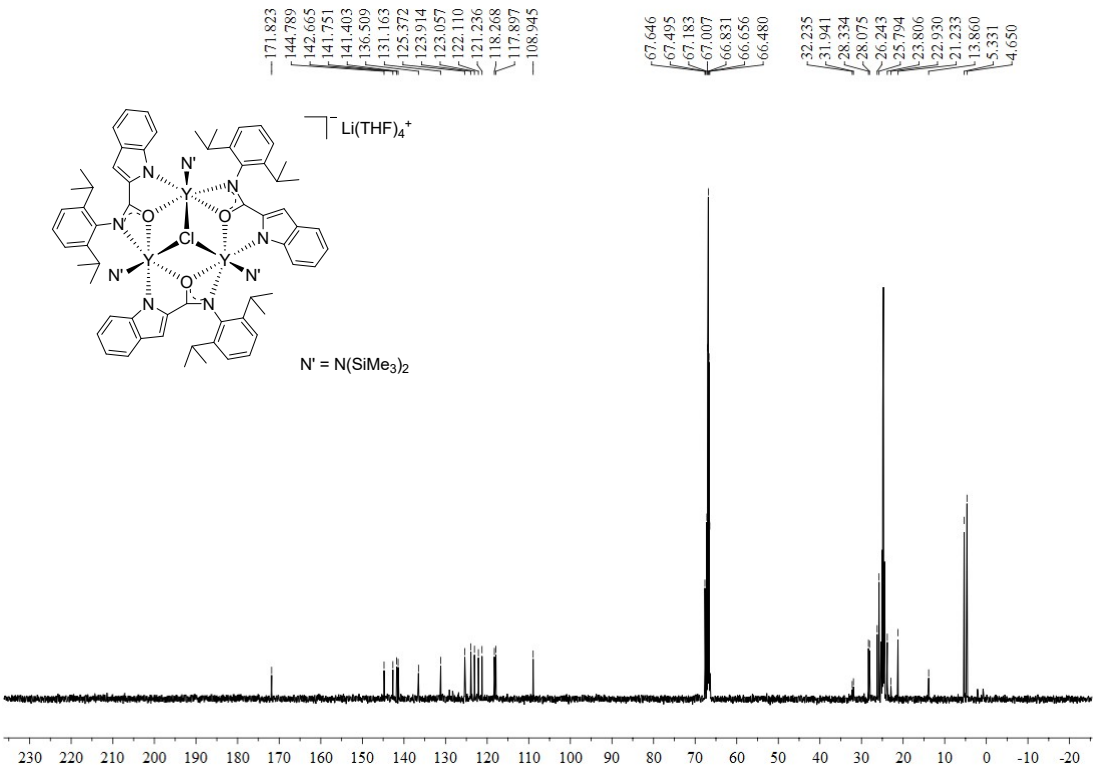


Figure S8. ^{13}C NMR spectrum (125 MHz, THF-d_8, 298 K) of complex **1a**.

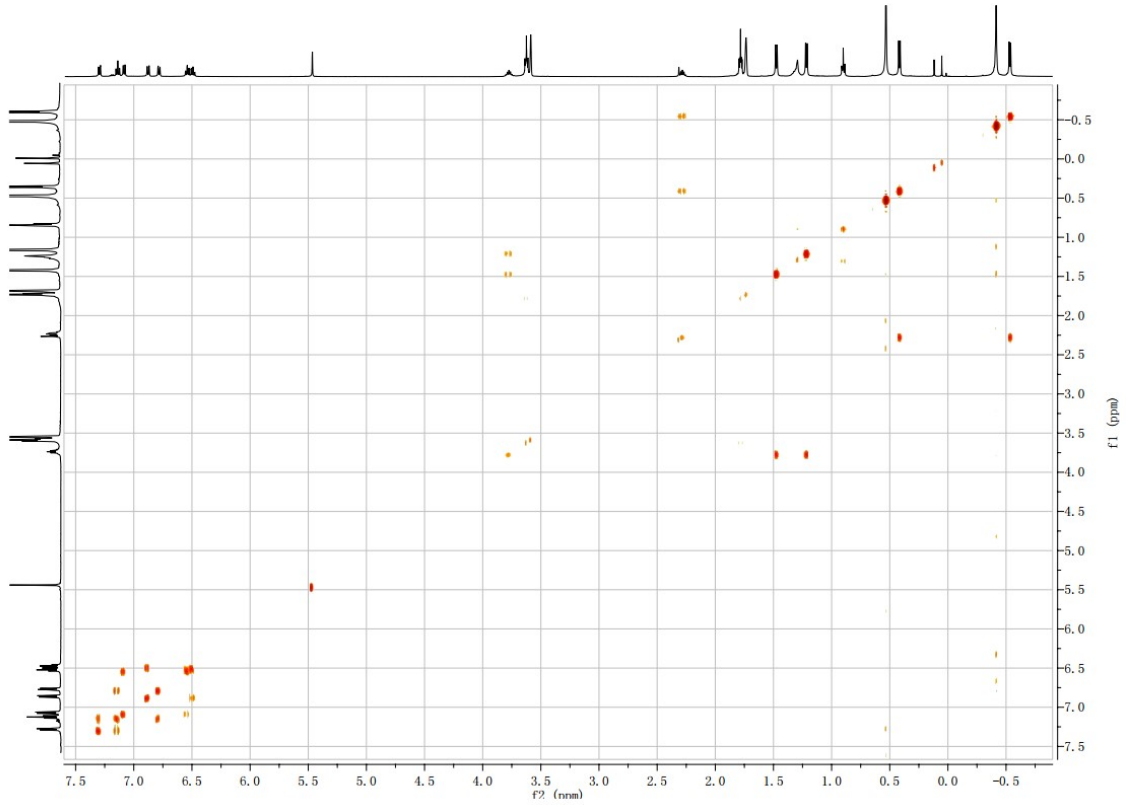


Figure S9. 2D NMR COSY spectrum (500 MHz, THF-d_8, 298 K) of complex **1a**.

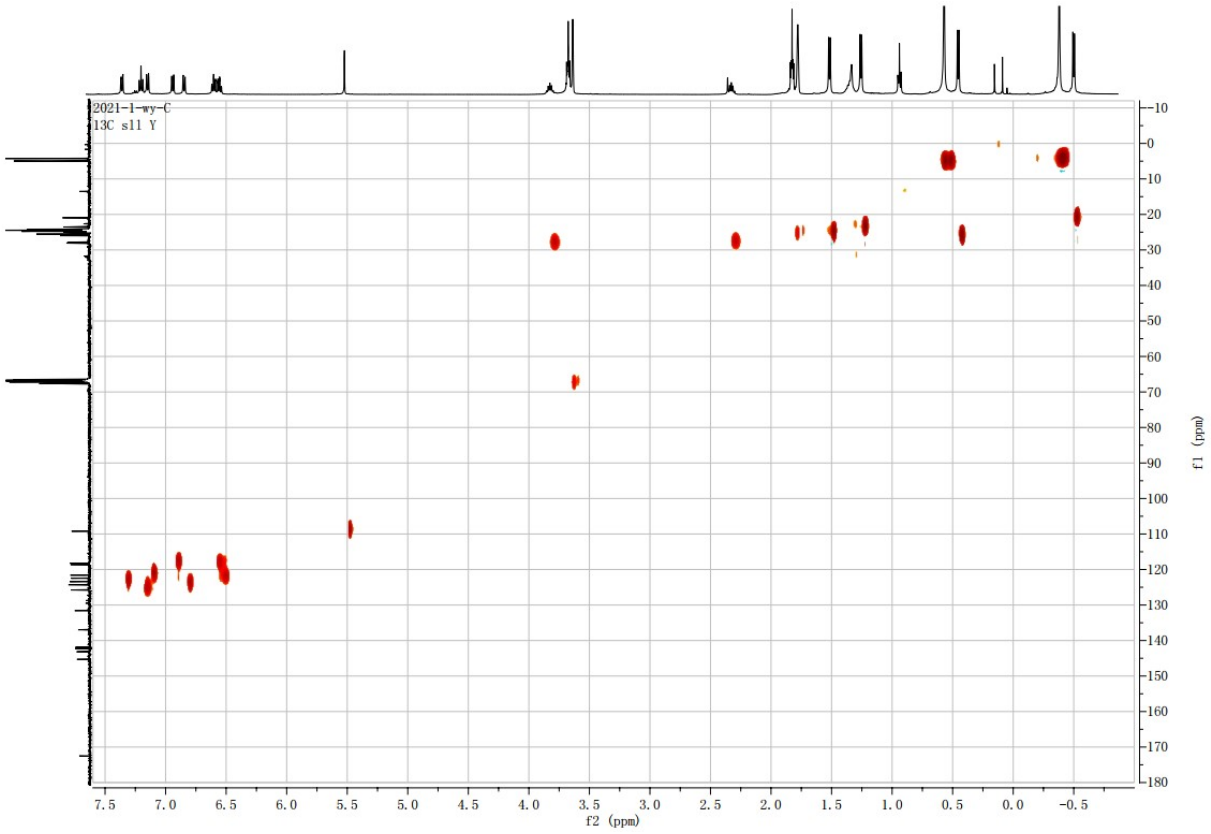


Figure S10. 2D NMR HSQC spectrum (500 MHz, THF-d_8, 298 K) of complex **1a**.

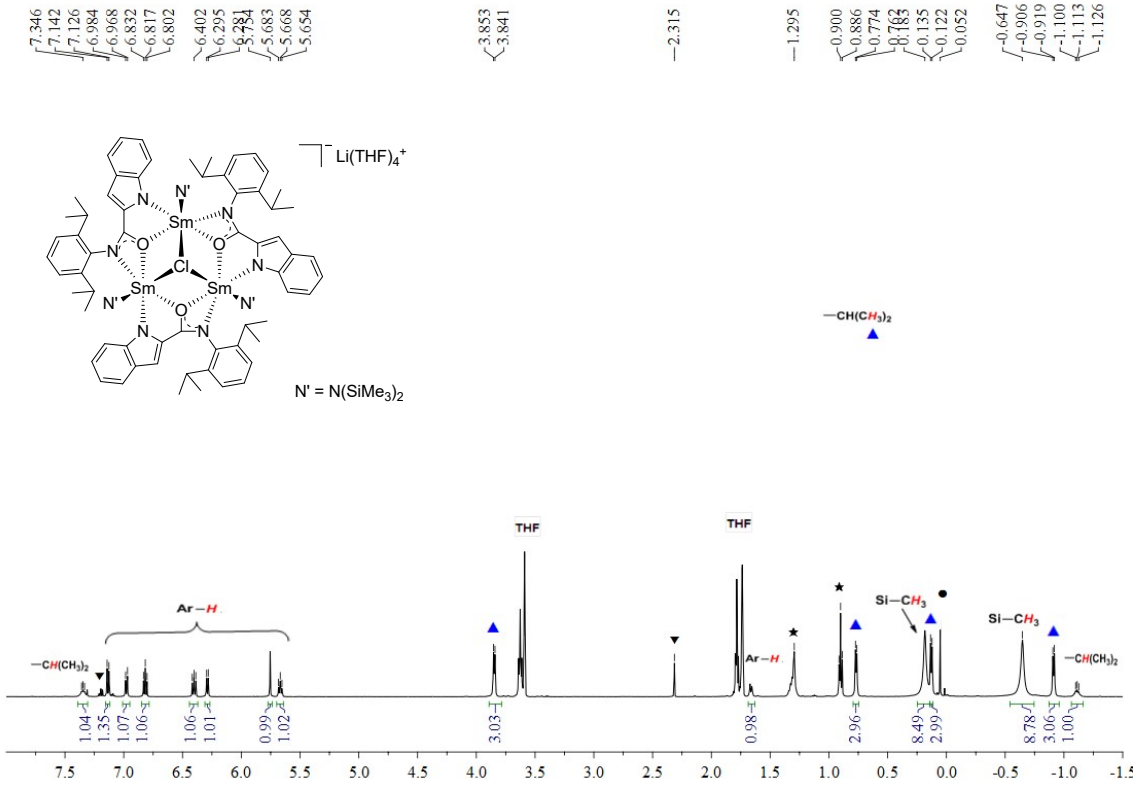


Figure S11. ^{1}H NMR spectrum (500 MHz, THF-d_8, 298 K) of complex **1c** (▼ toluene, ★ *n*-hexane, ● $HNSiMe_3$).

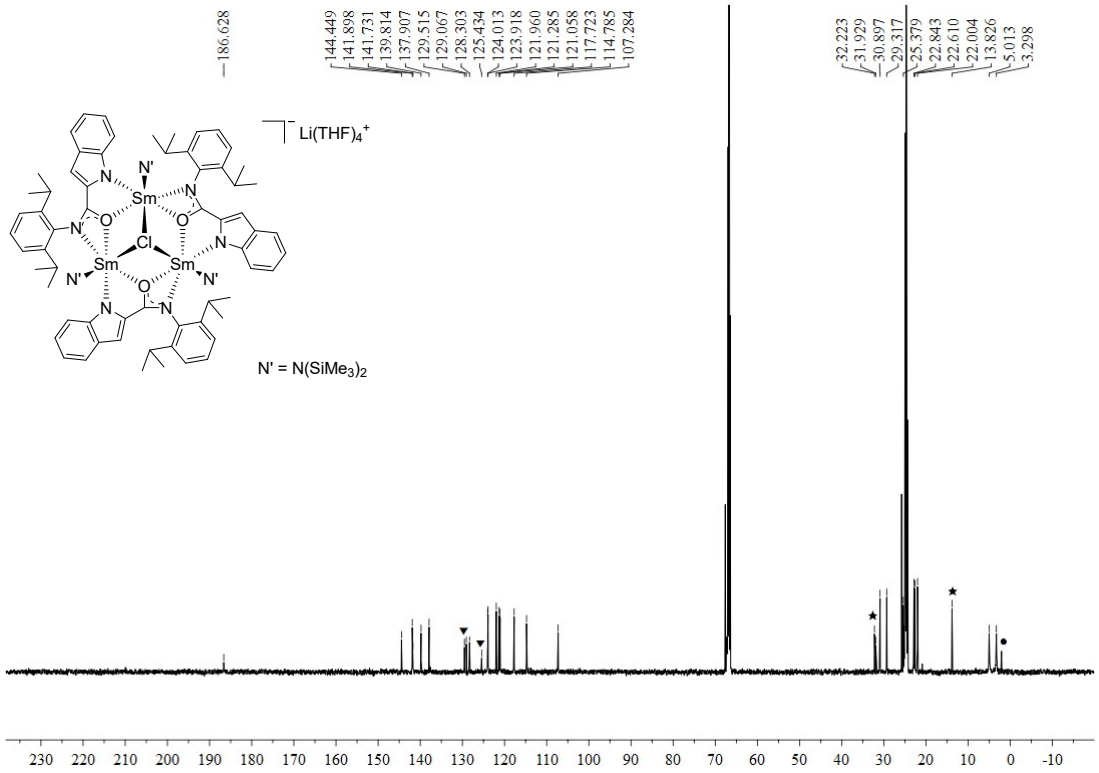


Figure S12. ^{13}C NMR spectrum (125 MHz, THF-d_8, 298 K) of complex **1c** (▼ toluene, ★ *n*-hexane, ● $HNSiMe_3$).

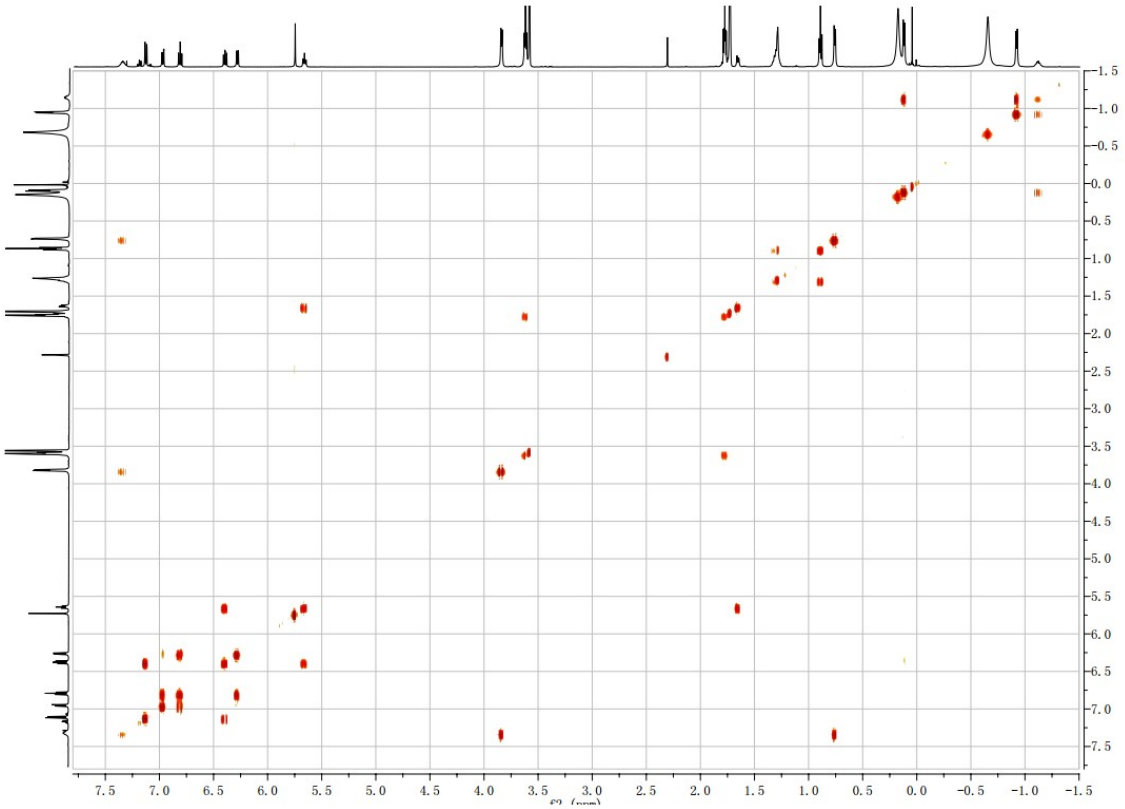


Figure S13. 2D NMR COSY spectrum (500 MHz, THF-d_8, 298 K) of complex **1c**.

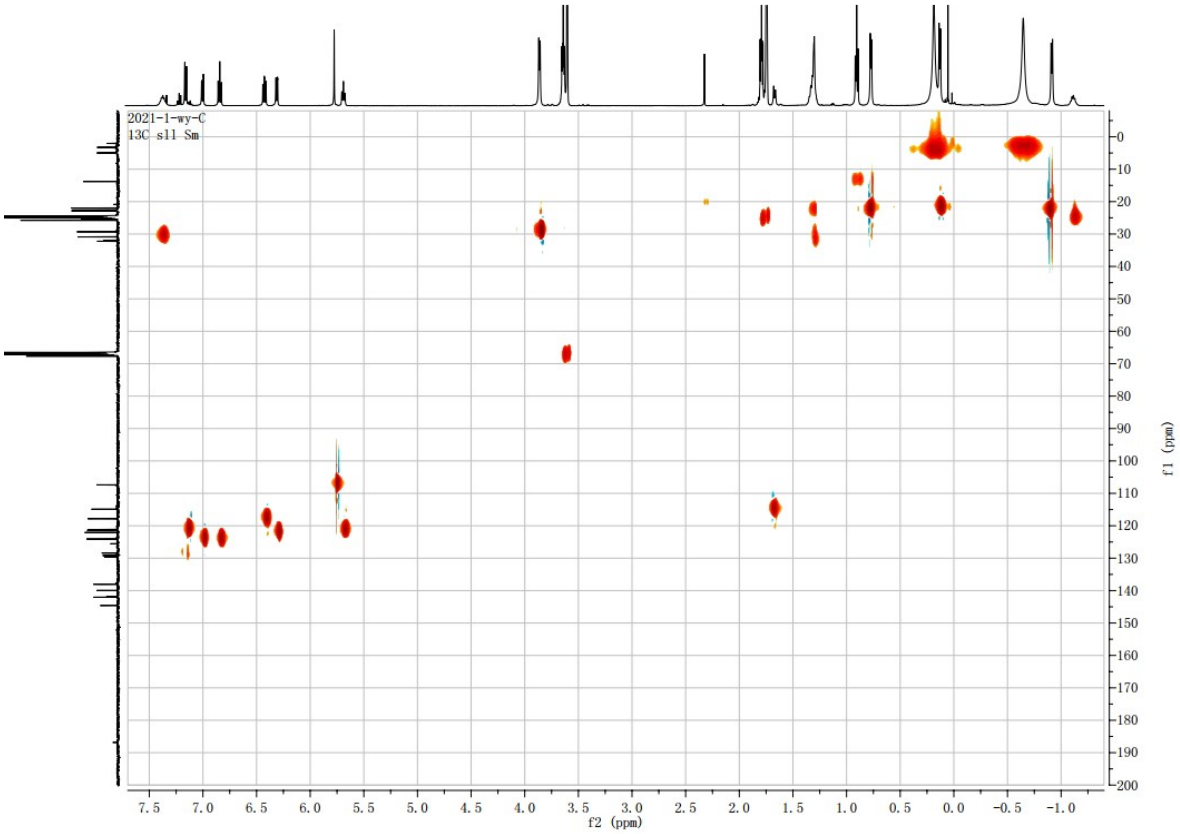
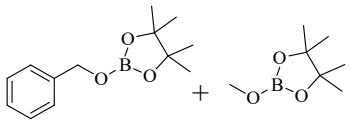
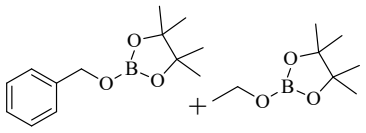


Figure S14. 2D NMR HSQC spectrum (500 MHz, THF-d_8, 298 K) of complex **1c**.

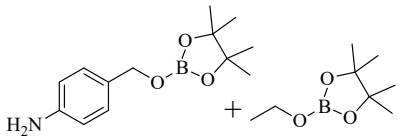
Characterization of ester hydroboration products

1) 

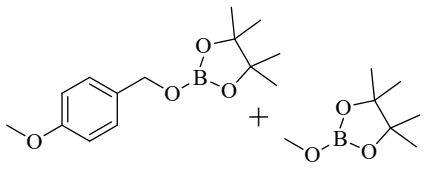
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.32 (d, 2H, J = 10.00 Hz, *Ph*CH_2O*B*pin), 7.13-7.04 (m, 3H, *Ph*CH_2O*B*pin), 4.96 (s, 2H, PhC*H*$_2$O*B*pin), 3.51 (s, 3H, C*H*$_3$OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 140.1, 128.6, 127.6, 127.1, 82.7, 67.0, 52.4, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.06 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (PhCH_2O*B*pin/MeO*B*pin).

2) 

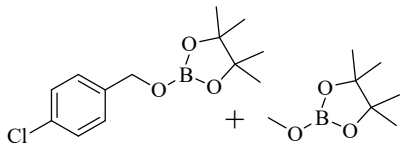
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.32 (d, 2H, J = 10.00 Hz, *Ph*CH_2O*B*pin), 7.13-7.04 (m, 3H, *Ph*CH_2O*B*pin), 4.96 (s, 2H, PhC*H*$_2$O*B*pin), 3.92 (q, 2H, J = 5.00 Hz, CH_3C*H*$_2$OBpin), 1.11 (t, 3H, J = 10.00, C*H*$_3$$CH_2$OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 140.1, 128.6, 127.6, 127.1, 82.7, 67.0, 60.7, 24.7, 17.5. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 1.02-1.07 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.6 (PhCH_2O*B*pin/EtO*B*pin).

3) 

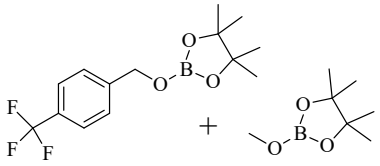
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.27 (d, 2H, J = 10.00 Hz, 4-NH_2*Ph*CH_2OBpin), 7.04 (d, 2H, J = 5.00 Hz, 4-NH_2*Ph*CH_2OBpin), 4.90 (s, 2H, 4-NH_2PhC*H*$_2$OBpin), 3.92 (q, 2H, J = 5.00 Hz, CH_3C*H*$_2$OBpin), 1.11 (t, 3H, J = 10.00, C*H*$_3$$CH_2$OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 143.4,131.7, 128.6, 117.9, 82.7, 67.0, 60.7, 24.7, 17.5. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 1.02-1.09 ppm. ^{11}B NMR NMR (160 MHz, C_6D_6, 298 K): δ 24.2 (NH_2PhCH_2O*B*pin), 22.6 (EtO*B*pin).

4) 

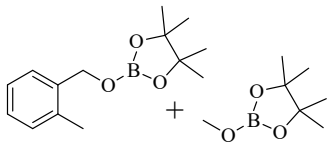
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.28 (d, 2H, J = 10.00 Hz, 4-CH_3ONH_2*Ph*CH_2OBpin), 6.76 (d, 2H, J = 10.00 Hz, 4-CH_3ONH_2*Ph*CH_2OBpin), 4.96 (s, 2H, 4-CH_3ON*H*$_2$PhCH_2OBpin), 3.27 (s, 3H, 4-C*H*$_3$ONH_2PhCH_2OBpin), 3.51 (s, 3H, C*H*$_3$OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 159.7, 132.2, 128.9, 114.1, 82.7, 66.8, 54.8, 52.4, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.05 ppm. ^{11}B NMR (160 MHz, C_6D_6): 22.7 (4-MeOPhCH_2O*B*pin/MeO*B*pin).

5) 

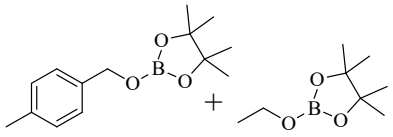
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.06 (d, 2H, J = 10.00 Hz, 4-Cl*Ph*CH_2OBpin), 6.99 (d, 2H, J = 10.00 Hz, 4-Cl*Ph*CH_2OBpin), 4.76 (s, 2H, 4-ClPhC*H*$_2$OBpin), 3.51 (s, 3H, C*H*$_3$OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 138.4, 133.4, 128.7, 128.4, 82.9, 66.1, 52.4, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 1.03-1.04 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (Cl-4-PhCH$_2$O*B*pin/MeO*B*pin).

6) 

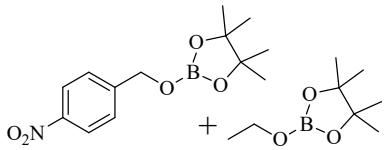
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.29 (d, 2H, J = 5.00 Hz, 4-CF$_3$*Ph*CH_2OBpin), 7.07 (d, 2H, J = 10.00 Hz, 4-CF$_3$*Ph*CH_2OBpin), 4.79 (s, 2H, 4-CF$_3$PhC*H*$_2$OBpin), 3.51 (s, 3H, C*H*$_3$OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 143.9, 129.8, 129.5, 125.5, 125.4, 83.0, 82.5, 66.0, 52.4, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.05 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (CF$_3$-4-PhCH$_2$O*B*pin/MeO*B*pin).

7) 

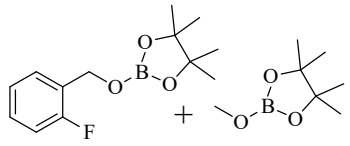
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.56 (d, 1H, J = 5.00 Hz, 2-CH$_3$*Ph*CH_2OBpin), 7.09-7.05 (m, 2H, 2-CH$_3$*Ph*CH_2OBpin), 6.95(d, 1H, J = 10.00 Hz, 2-CH$_3$*Ph*CH_2OBpin), 4.98 (s, 2H, 2-CH$_3$PhC*H*$_2$OBpin), 3.51 (s, 3H, C*H*$_3$OBpin), 2.07 (s, 3H, 2-C*H*$_3$PhCH$_2$OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 137.9,135.8, 130.3, 127.7, 127.5, 126.2, 82.7, 82.5, 65.3, 52.4, 24.9, 18.6.
The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.06 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (CH$_3$-2-PhCH$_2$O*B*pin/MeO*B*pin).

8) 

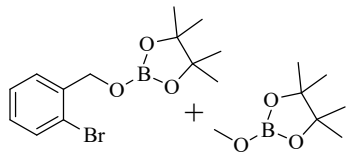
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.28 (d, 2H, J = 10.00 Hz, 4-CH$_3$*Ph*CH_2OBpin), 6.97 (d, 2H, J = 10.00 Hz, 4-CH$_3$*Ph*CH_2OBpin), 4.99 (s, 2H, 4-CH$_3$PhC*H*$_2$OBpin), 3.93 (q, 2H, J = 5.00, CH$_3$C*H*$_2$O*B*pin), 2.08 (s, 3H, 4-C*H*$_3$PhCH$_2$OBpin), 1.12 (t, 3H, J = 10.00, C*H*$_3$CH$_2$O*B*pin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 137.2, 137.0, 129.3, 127.3, 82.7, 66.9, 60.7, 24.9, 17.5. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.05 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.6 (CH$_3$-4-PhCH$_2$O*B*pin/MeO*B*pin).

9) 

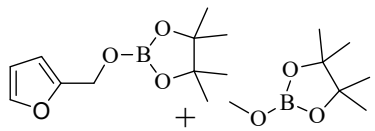
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.78 (d, 2H, J = 10.00 Hz, 4-NO_2-*Ph*CH_2OBpin), 6.89 (d, 2H, J = 5.00 Hz, 4-NO_2-*Ph*CH_2OBpin), 4.68 (s, 2H, 4-NO_2PhC*H*$_2$OBpin), 3.92 (q, 2H, J = 10.00, CH_3CH_2O*B*pin), 1.12 (t, 3H, J = 10.00 Hz, C*H*$_3$$CH_2O$*B*pin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 147.6, 146.5,126.7, 123.6, 83.1, 82.4, 65.6, 60,7, 24.7, 17.5. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 1.03-1.09 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.6 (NO_2-4-PhCH_2O*B*pin/EtO*B*pin).

10) 

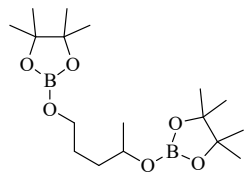
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.43-7.46 (m, 1H, 2-F*Ph*CH_2OBpin), 6.83-6.72 (m, 3H, 2-F*Ph*CH_2OBpin), 5.11 (s, 2H, 2-FPhC*H*$_2$OBpin), 3.51 (s, 3H, C*H*$_3$OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 161.6, 159.7, 129.2, 124.3, 115.3, 115.1, 82.9, 82.5, 61.0, 52.4, 24.9, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.04 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (F-2-PhCH_2O*B*pin/MeO*B*pin).

11) 

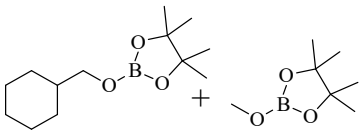
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.58 (d, 1H, J = 10.00 Hz, 2-Br*Ph*CH_2OBpin), 7.56 (d, 1H, J = 10.00 Hz, 2-Br*Ph*CH_2OBpin), 6.93 (d, 1H, J = 10.00 Hz, 2-Br*Ph*CH_2OBpin), 6.66 (d, 1H, J = 5.00 Hz, 2-Br*Ph*CH_2OBpin), 5.14 (s, 2H, 2-BrPhC*H*$_2$OBpin), 3.51 (s, 3H, C*H*$_3$OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 139.0, 132.5, 128.8, 127.6, 121.8, 83.0, 82.5, 66.6, 52.4, 24.9,24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 1.01-1.04 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (Br-2-PhCH_2O*B*pin/MeO*B*pin).

12) 

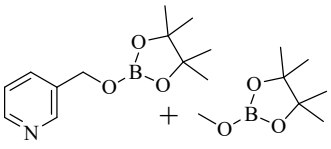
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.04 (s, 1H, C*H*), 6.14 (d, 1H, J = 5.00 Hz, C*H*), 6.01(m, 1H, C*H*), 4.86 (s, 2H, C*H*$_2$), 3.51 (s, 3H, C*H*$_3$OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 153.4, 142.6, 110.5, 108.5, 82.8, 82.5, 59.4, 52.4, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.06 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (RCH_2O*B*pin/MeO*B*pin).

13) 

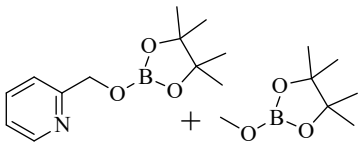
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 4.34 (m, 1H, C*H*), 3.96-3.93 (m, 2H, C*H*$_2$), 1.67-1.47 (m, 4H, C*H*$_2$), 1.15 (d, 3H, J = 5.00 Hz, C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 82.4, 82.2, 70.7, 65.0, 34.7, 28.2, 24.7, 22.9. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.06 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (pin*B*$O(CH_2)_3CH(CH_3)O$*B*pin).

14) 

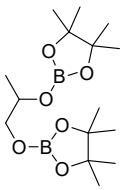
^{1}H NMR (500 MHz, C_6D_6): δ 3.80 (d, J = 6.0 Hz, 2H, CyCH_2OBpin), 3.51 (s, 3H, CH_3OBpin), 1.74-1.72 (m, 2H, *Cy*CH_2OBpin), 1.63-1.60 (m, 3H, *Cy*CH_2OBpin), 1.55-1.53 (m, 2H, *Cy*CH_2OBpin), 0.94-0.89 (m, 4H, *Cy*CH_2OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 82.5, 52.4, 70.6, 39.9, 29.7, 26.9, 26.2, 24.8. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.08 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.5 (CyCH_2O*B*pin/MeO*B*pin).

15) 

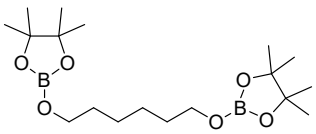
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.68 (s, 1H, 3-*Py*CH_2OBpin), 8.43 (s, 1H, 3-*Py*CH_2OBpin), 7.31 (s, 1H, 3-*Py*CH_2OBpin), 6.67 (s, 1H, 3-*Py*CH_2OBpin), 4.70 (d, 2H, J = 15.00 Hz, 3-PyCH_2OBpin), 3.51 (s, 3H, CH_3OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 149.1, 135.1, 134.3, 129.6, 123.3, 83.0, 82.5, 64.6, 52.3, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.06 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (PyCH_2O*B*pin/MeO*B*pin).

16) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.41 (d, 1H, J = 5.00 Hz, 2-*Py*CH_2OBpin), 7.28 (d, 1H, J = 10.00 Hz, 2-*Py*CH_2OBpin), 7.03 (d, 1H, J = 10.00 Hz, 2-*Py*CH_2OBpin), 6.55 (t, 1H, J = 5.00 Hz, 2-*Py*CH_2OBpin), 5.26 (s, 2H, 2-PyCH_2OBpin), 3.51 (s, 3H, CH_3OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 160.0, 148.6, 136.5, 122.1, 119.9, 83.2, 82.7, 82.5, 67.8, 52.4, 24.9, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.07 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (PyCH_2O*B*pin/MeO*B*pin).

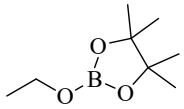
17) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 4.55 (s, 1H, CH_3C*H*OBpin), 3.90 (d, 2H, J = 10.00 Hz, CH_2 OBpin), 1.63 (m, 3H, CH_3CHOBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 82.6, 82.4, 70.9, 69.7, 24.7, 24.8, 18.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 1.01-1.12 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.6 (pin*B*OCH_2CH(CH_3)O*B*pin).

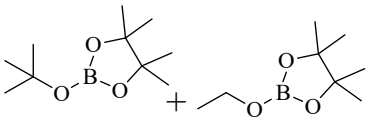
18) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 3.90 (t, 4H, J = 7.50 Hz, CH_2), 1.50-1.47 (m, 4H, CH_2), 1.24-1.22 (m, 4H, CH_2). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 82.4, 65.0, 32.0, 25.7, 24.8. The

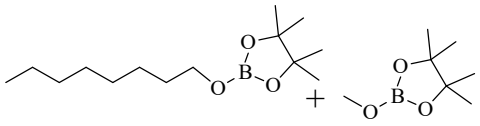
methyl peaks of -OBpin in ^{1}H NMR are in the region 1.07 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.6 (pin*B*OC_2H_{12}O*B*pin).

19) 

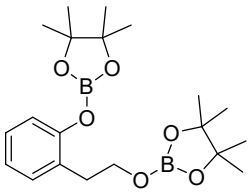
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 3.93 (q, 2H, J = 5.00 Hz, CH_3CH_2OBpin), 1.12 (t, 3H, J = 10.00 Hz, CH_3CH_2OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 82.4, 60,7, 24.7, 17.5. The methyl peaks of -OBpin in ^{1}H NMR are in the 1.10 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.6 (EtO*B*pin).

20) 

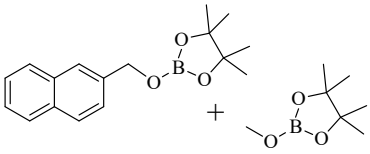
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 3.92 (q, 2H, J = 5.00 Hz, CH_3CH_2OBpin), 1.12 (t, 3H, J = 10.00 Hz, CH_3CH_2OBpin), 1.01(s, 9H, $(CH_3)_3$COBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 82.3, 81.7, 73.5, 60.7, 30.2, 24.7, 17.5. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 1.01-1.05 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.6 (EtO*B*pin), 21.7 (^{t}BuO*B*pin).

21) 

^{1}H (500 MHz, C_6D_6, 298 K): δ 3.92 (t, 2H, J = 7.50 Hz, CH_2), 3.49 (s, 3H, CH_3OBpin), 1.56-1.51, (m, 2H, CH_2), 1.30-1.22 (m, 10H, CH_2), 0.86 (t, J = 7.00 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 83.1, 82.5, 65.1, 52.4, 32.2, 32.1, 29.7, 25.0, 24.8, 23.1, 14.3. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 1.00-1.07 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.6 (C_8H_{17}O*B*pin/MeO*B*pin).

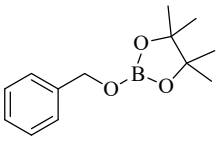
22) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.28 (d, 1H, J = 10.00 Hz, PhC*H*), 7.11 (d, 1H, J = 10.00 Hz, PhC*H*), 6.99 (d, 1H, J = 5.00 Hz, PhC*H*), 6.82 (d, 1H, J = 5.00 Hz, PHC*H*), 4.26 (t, 2H, J = 7.50, CH_2), 3.07 (t, 2H, J = 7.50, CH_2). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 152.7, 131.4, 129.2, 127.6, 123.5, 120.3, 83.3, 83.2, 82.3, 64.8, 33.2, 24.9, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.05 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.2 (pin*B*OPhC_2H_4O*B*pin).

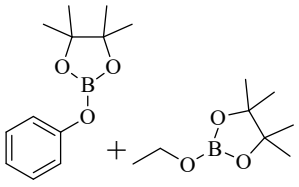
23) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.79 (s, 1H, PhC*H*), 7.61-7.58 (m, 3H, PhC*H*), 7.40 (d, 1H, J = 10.00 Hz, PhC*H*), 7.24-7.22 (m, 2H, PhC*H*), 5.11 (s, 2H, CH_2), 3.51 (s, 3H, CH_3OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 133.9, 133.4, 128.4, 126.3, 125.9, 125.7, 125.3, 83.2, 83.8, 67.0,

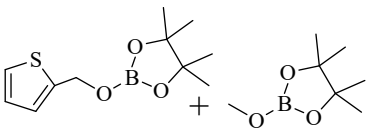
52.4, 24.9. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.05 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (Ph_2CH_2OBpin/MeO*B*pin).

24) 

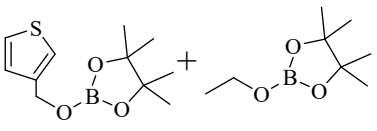
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.32 (d, 2H, J = 10.00 Hz, PhC*H*), 7.13-7.04 (m, 3H, PhC*H*), 4.97 (s, 2H, CH_2). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 140.0, 128.6, 127.6, 127.1, 83.2, 82.7, 67.0, 24.9, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are in the 1.03 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 ($PhCH_2OBpin$).

25) 

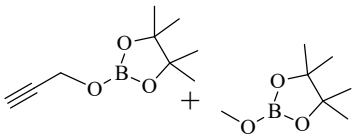
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.20-7.05 (m, 4H, PhC*H*), 6.84 (t, 2H, J = 7.50 Hz, PhC*H*), 3.89 (q, 2H, J = 7.50, CH_2), 1.11 (t, 3H, J = 10.00, CH_3). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 154.4, 129.6, 123.3, 120.1, 82.4, 82.3, 60.7, 24.9, 17.5. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 1.01-1.06 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.4 (PhO*B*pin/MeO*B*pin).

26) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 6.84-6.82 (m, 2H, C*H*), 6.66 (m, 1H, C*H*), 5.02 (s, 2H, CH_2), 3.51 (s, 3H, CH_3OBpin). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 142.8, 126.8, 126.1, 125.7, 82.9, 82.5, 61.8, 52.4, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.04 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (RCH_2OBpin/MeO*B*pin).

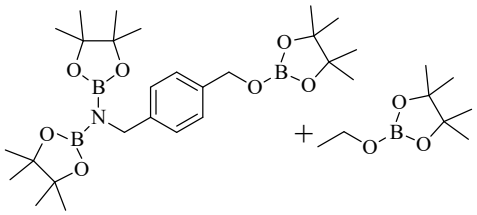
27) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 6.96 (s, 1H, C*H*), 6.93(d, 1H, J = 5.0 Hz, C*H*), 6.84(t, 1H, J = 5.00 Hz, C*H*), 4.89 (s, 2H, CH_2), 3.93 (d, 3H, J = 7.50 Hz, CH_2), 1.12 (t, 3H, J = 5.00 Hz, CH_3). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 141.2, 127.0, 126.0, 122.1, 82.7, 82.4, 62.7, 60.7, 24.9, 17.5. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.05 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.5 (RCH_2OBpin/EtO*B*pin).

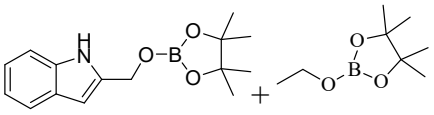
28) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 4.37 (s, 2H, CH_2), 3.51 (s, 3H, CH_3OBpin), 2.01 (s, 1H, C*H*). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 83.1, 82.5, 79.8, 73.8, 53.0, 52.4, 24.9, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 1.00-1.06 ppm. ^{11}B NMR (160 MHz,

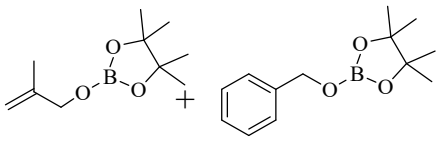
C_6D_6, 298 K): δ 22.7 (MeO*B*pin), 21.8 (CHCCH$_2$O*B*pin).

29) 

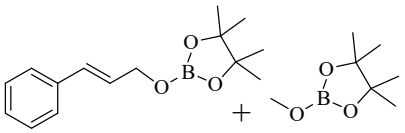
^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.58 (d, 2H, J = 8.0 Hz , PhC*H*), 7.39 (d, 2H, J = 8.0 Hz , PhC*H*), 5.01 (s, 2H, CH_2), 4.86 (s, 2H, CH_2), 3.93 (q, 3H, J = 7.5 Hz, CH_2), 1.12 (t, 3H, J = 5.00 Hz, CH_3). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 143.0, 138.1 127.4, 127.1, 82.7, 82.4, 82.4, 67.0, 60.7, 47.7, 24.9, 24.7, 17.5. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.05 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.6 ((pinB)$_2$NCH$_2$C$_6$H$_4$CH$_2$OBpin/ EtOBpin).

30) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.39 (d, 1H, J = 7.5 Hz , indole-C*H*), 7.58 (d, 1H, J = 7.5 Hz , indole-C*H*), 7.30 (d, 1H, J = 7.0 Hz , indole-C*H*), 7.20 (t, 1H, J = 6.5 Hz , indole-C*H*), 6.91(s, 1H, indole-C*H*), 5.52 (s, 2H, CH_2), 3.92 (q, 2H, CH_2), 1.11 (t, 3H, J = 5.00 Hz, CH_3). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 142.7, 141.6, 131.4, 123.1, 122.0, 120.6, 115.5, 107.3, 83.9, 82.8, 82.4, 62.1, 60.7, 24.7, 24.5, 17.5. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.96-1.06 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 27.9 (indole-CH$_2$O*B*pin), 22.6 (EtO*B*pin).

31) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.33 (d, 2H, J = 10.0 Hz, PhC*H*), 7.13 (t, 2H, J = 7.5 Hz, PhC*H*), 7.07 (d, 1H, J = 10.0 Hz, PhC*H*), 5.18 (s, 1H, C*H*), 4.97 (s, 2H, CH_2), 4.83 (s, 1H, C*H*), 4.35 (s, 2H, CH_2), 1.56 (s, 3H, CH_3). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 143.3, 140.0, 128.6, 127.6, 127.3, 110.1, 82.7, 82.6, 68.4, 66.9, 24.7, 19.0. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.05 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (PhCH$_2$O*B*pin/H$_2$C=CHMeCH$_2$O*B*pin).

32) 

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.19 (d, 2H, J = 10.0 Hz, PhC*H*), 7.00-7.10 (t, J = 7.5 Hz, 2H, PhC*H*), 7.00-7.03 (m, 1H, PhC*H*), 6.64 (d, 1H, J = 15.0 Hz, C*H*), 6.15-6.21 (m, 1H, C*H*), 4.56 (d, 2H, J = 5.0 Hz, CH_2). ^{13}C NMR (125 MHz, C_6D_6, 298 K): δ 137.3, 130.9, 128.8, 127.7, 127.5, 126.8, 82.7, 82.5, 65.5, 52.4, 24.7. The methyl peaks of -OBpin in ^{1}H NMR are overlapping in the region 0.99-1.06 ppm. ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ 22.7 (PhC$_3$H$_4$O*B*pin/MeO*B*pin).

NMR data of ester hydroboration products

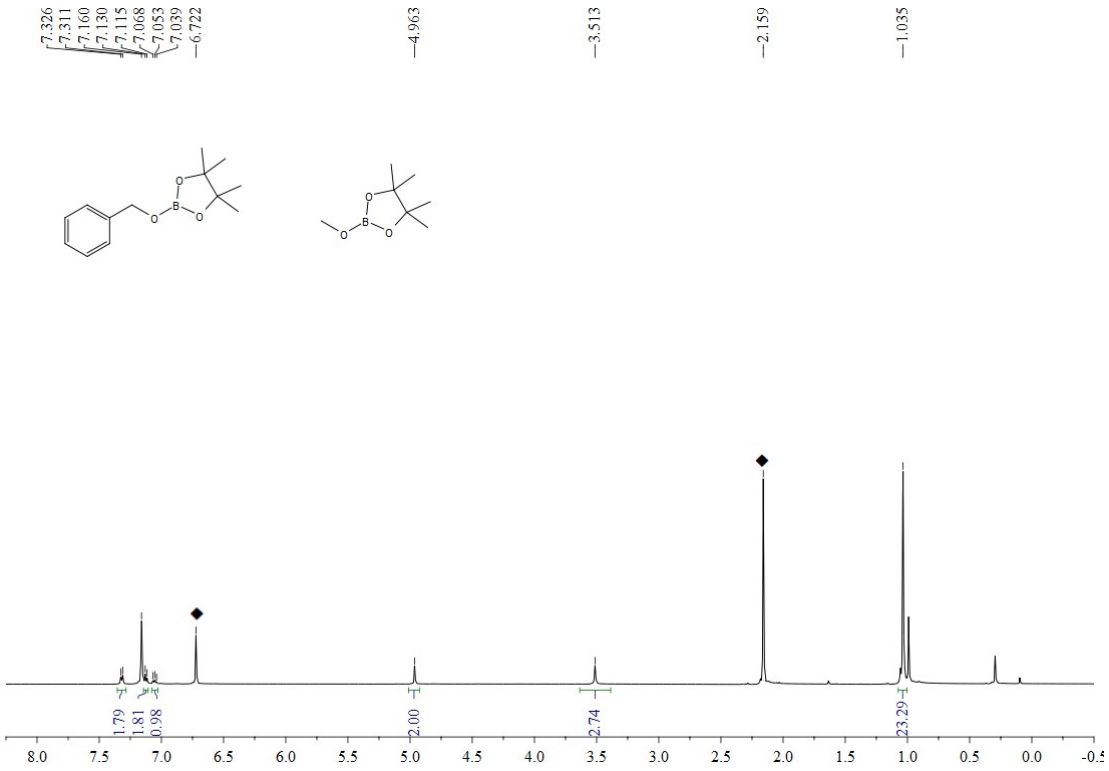


Figure S16. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $PhCH_2OBpin$/MeOBpin (◆ represents mesitylene)

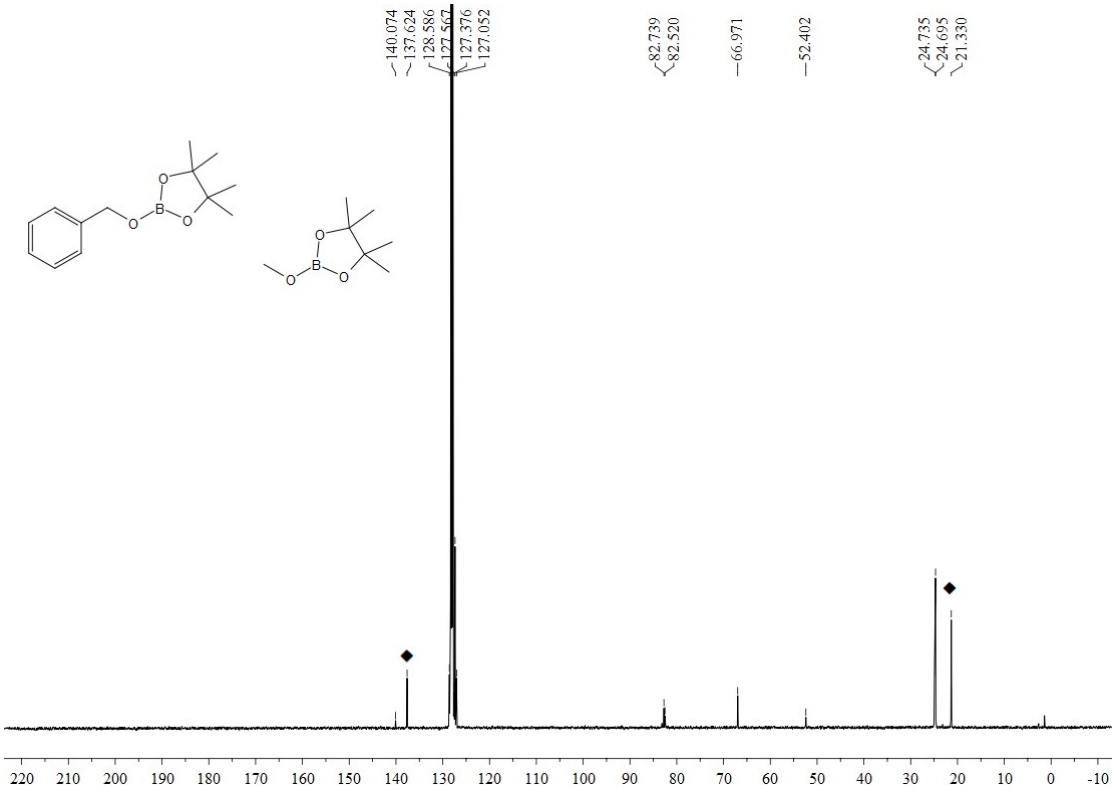


Figure S17. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $PhCH_2OBpin$/MeOBpin (◆ represents

mesitylene).

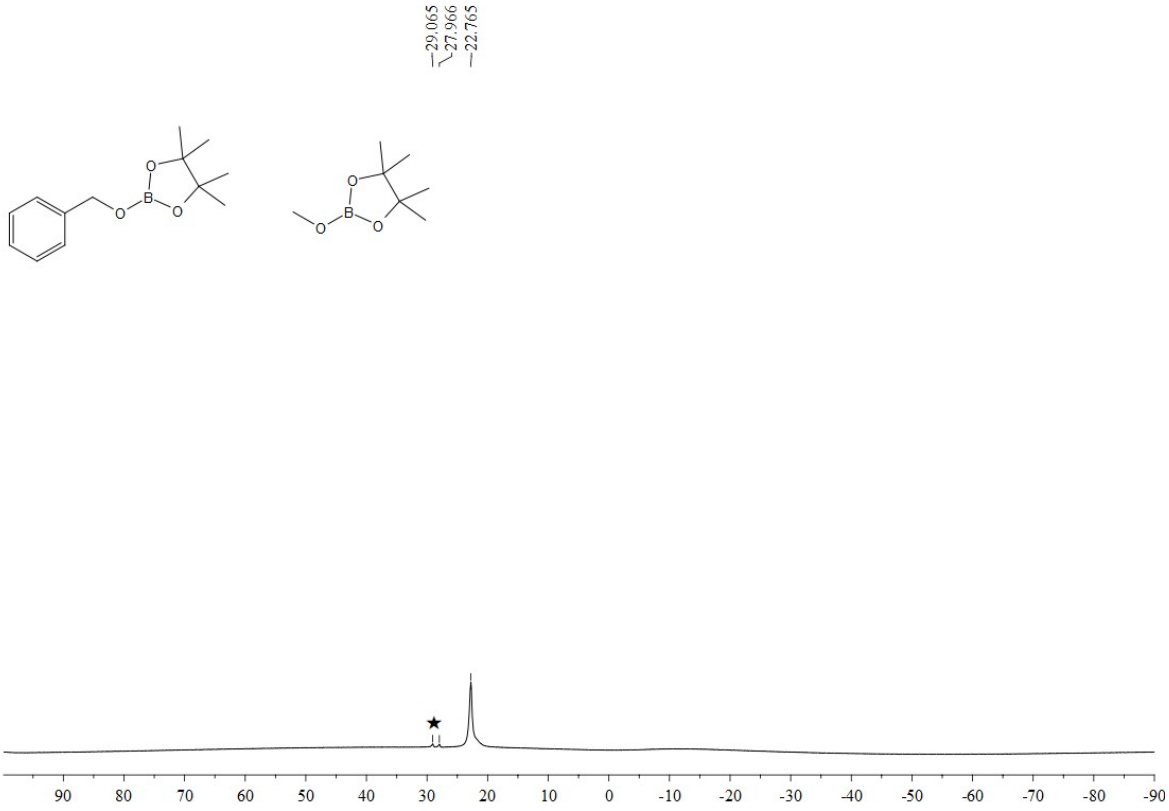


Figure S18. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $PhCH_2OBpin$/MeOBpin (★ indicates excess HBpin).

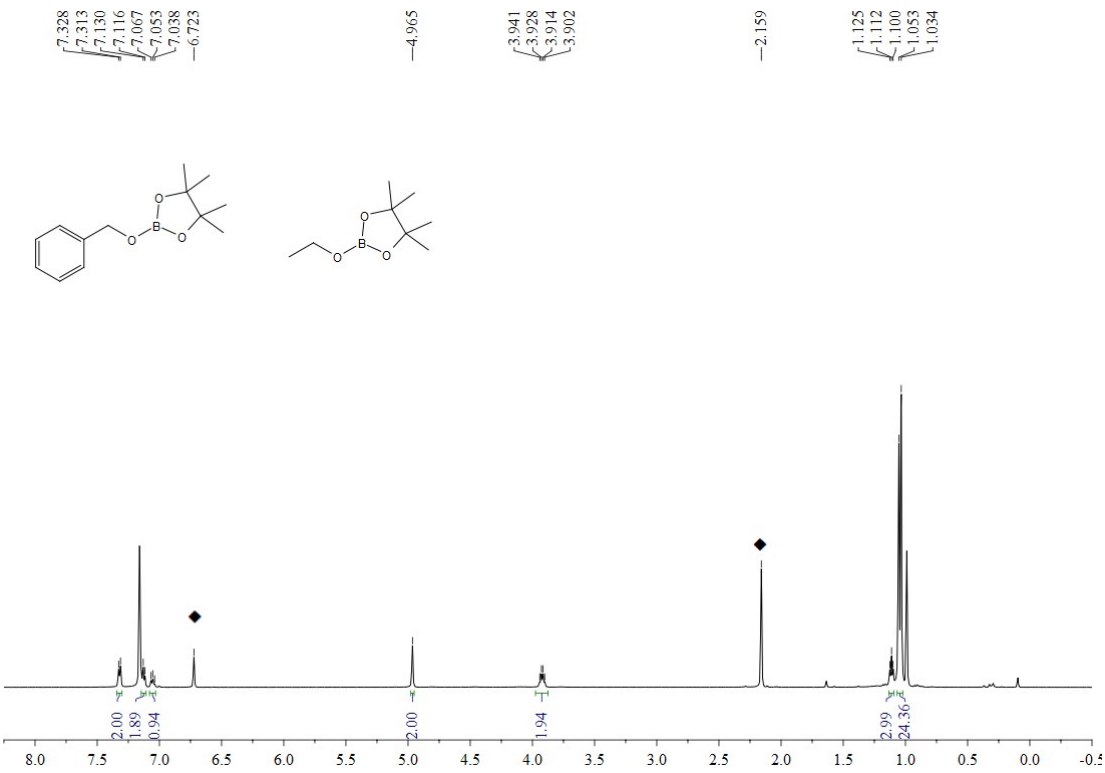


Figure S19. ^1H NMR spectrum (500 MHz, C_6D_6) of $PhCH_2OBpin$/EtOBpin (◆ represents

mesitylene)

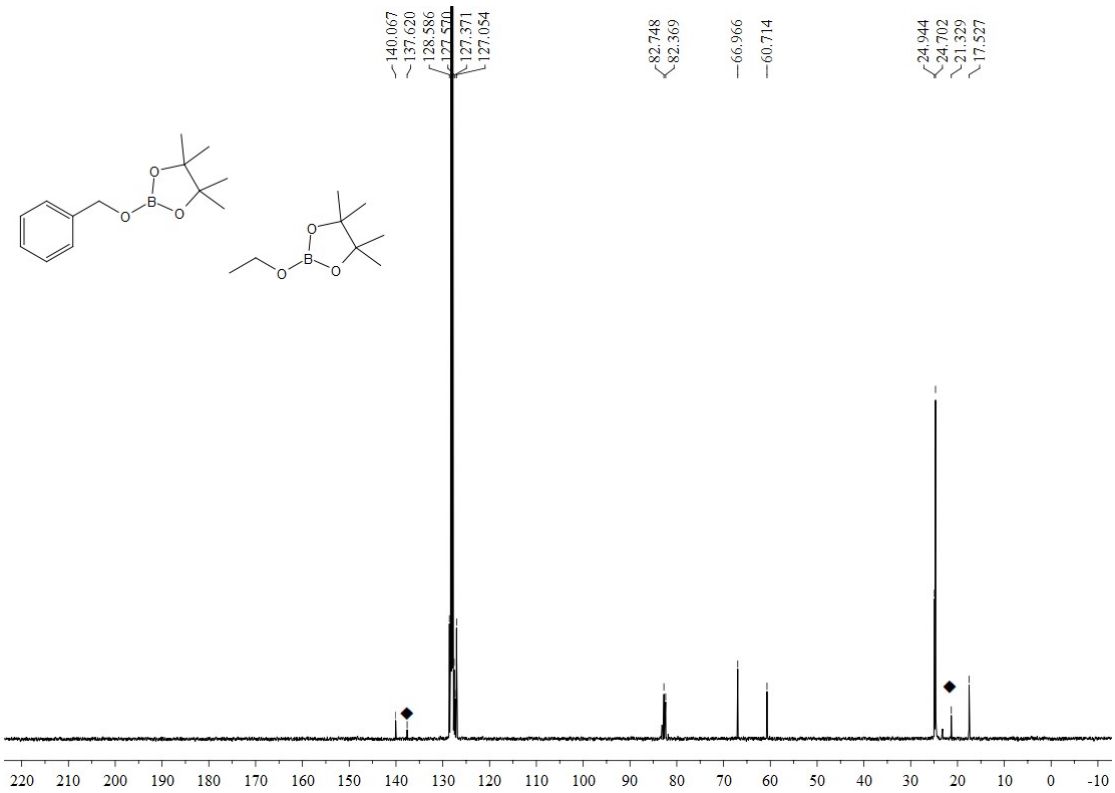


Figure S20. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $PhCH_2OBpin/EtOBpin$ (◆ represents mesitylene)

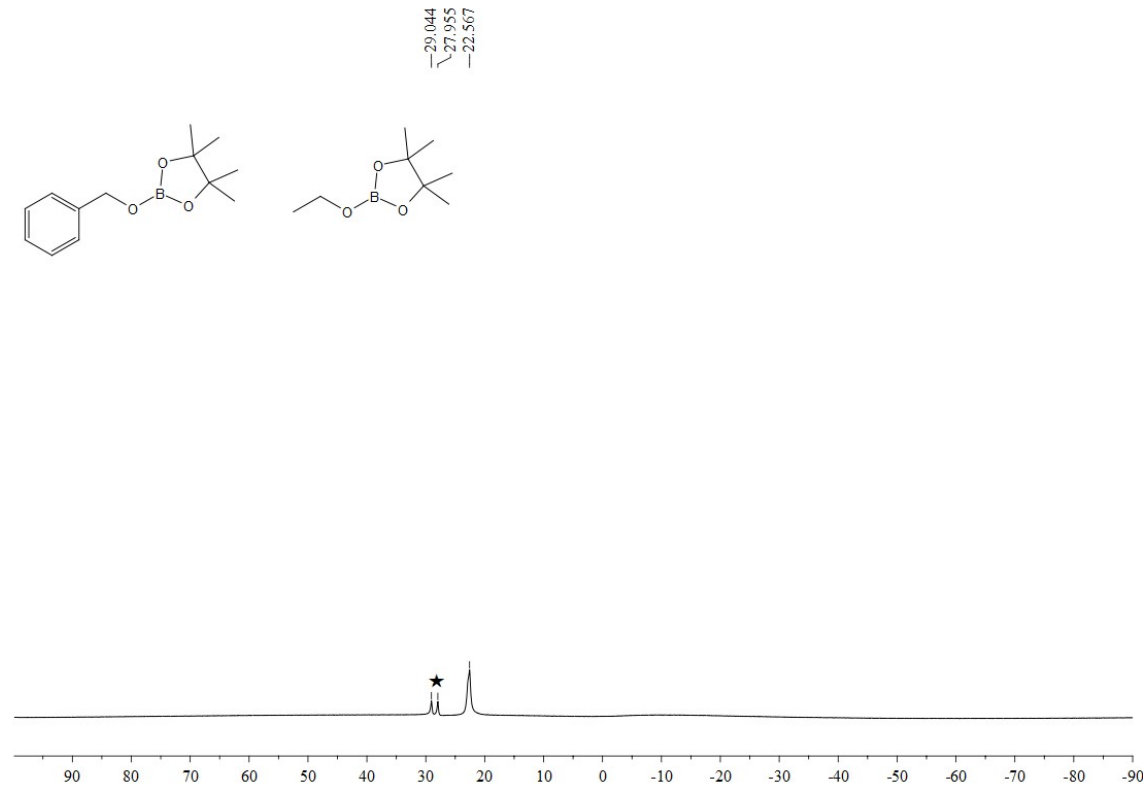


Figure S21. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $PhCH_2OBpin/EtOBpin$ (★ represents HBpin).

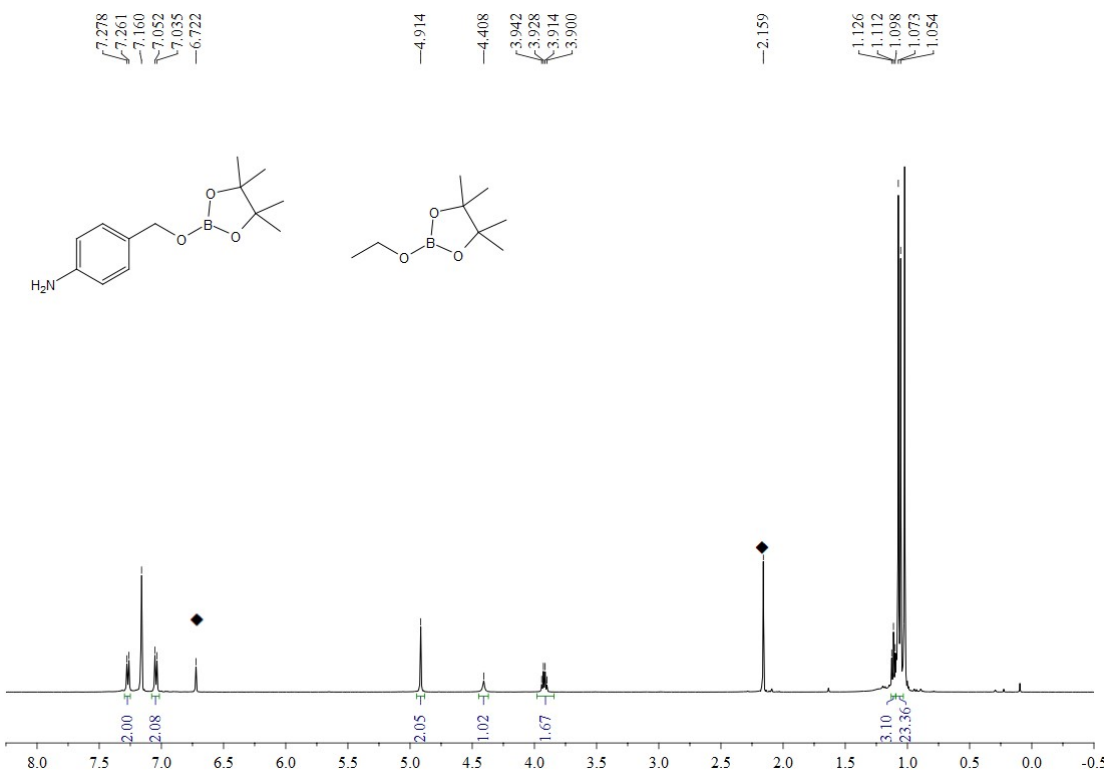


Figure S22. ^{1}H NMR spectrum (500 MHz, C_6D_6) of NH_2PhCH_2OBpin/EtOBpin (◆ represents mesitylene)

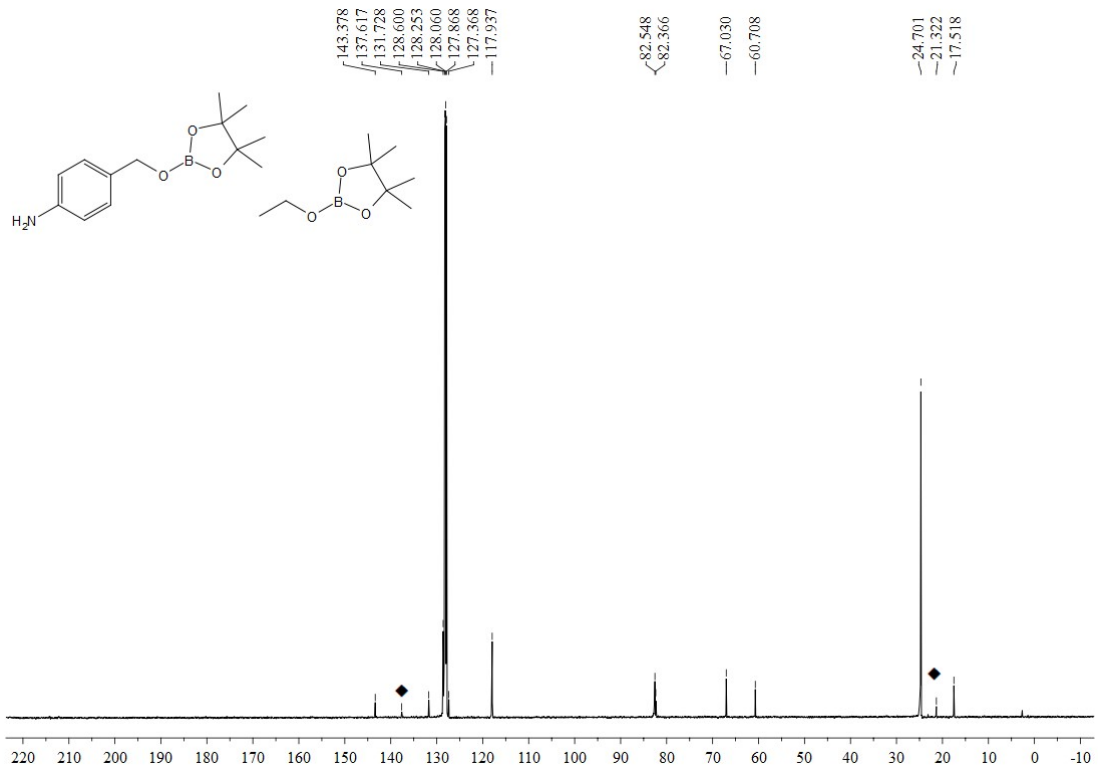


Figure S23. ^{13}C NMR spectrum (125 MHz, C_6D_6) of NH_2PhCH_2OBpin/EtOBpin (◆ represents mesitylene).

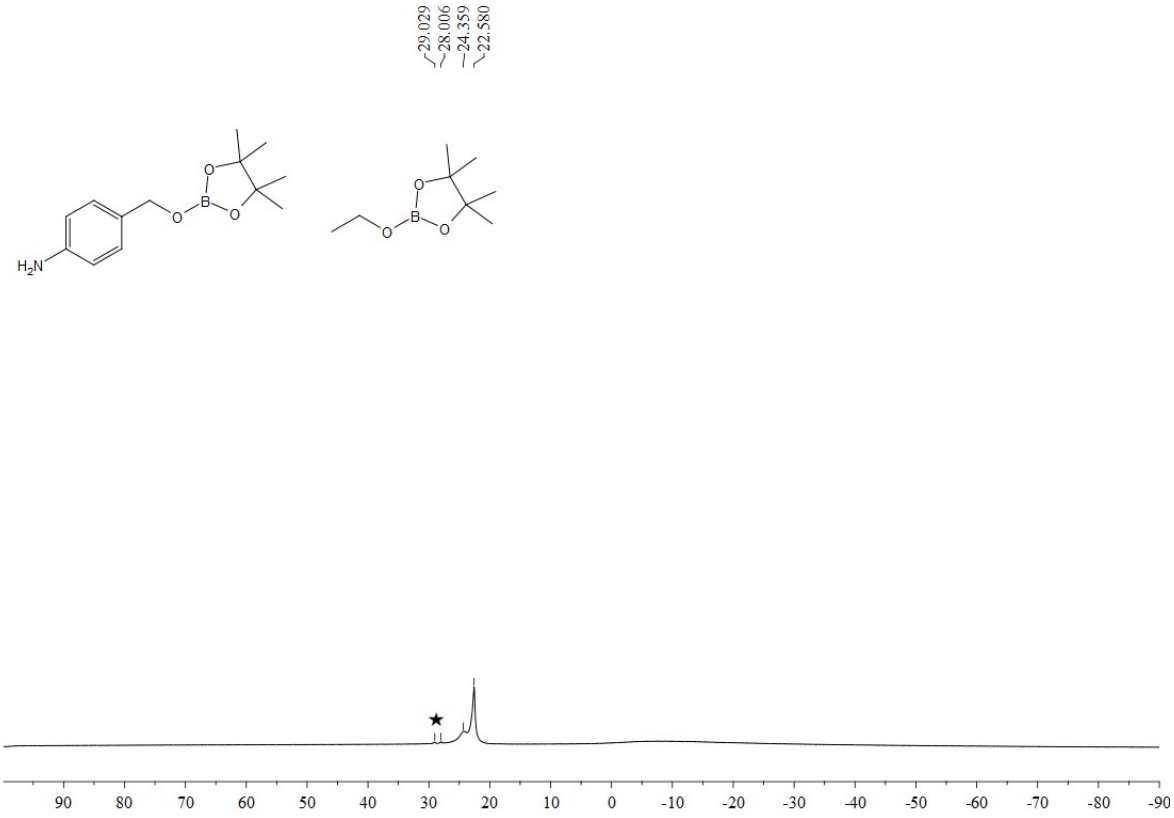


Figure S24. ^{11}B NMR spectrum (128 MHz, C_6D_6) of NH_2PhCH_2OBpin/EtOBpin (★ represents HBpin).

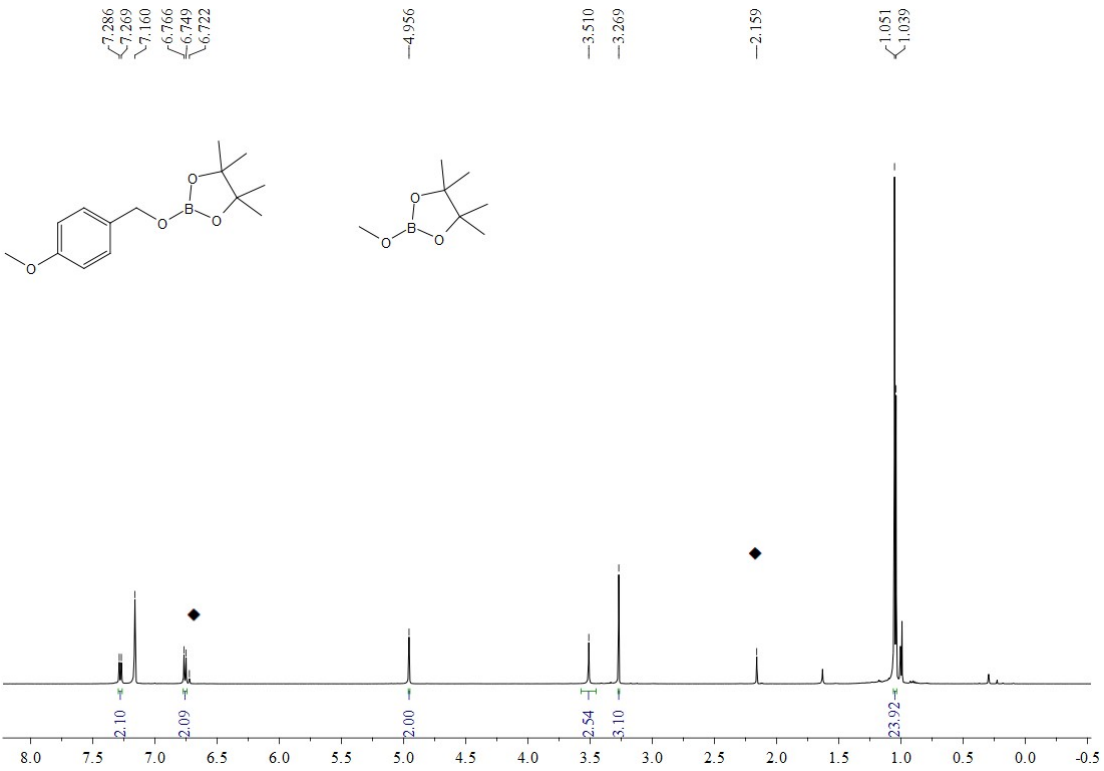


Figure S25. ^{1}H NMR spectrum (500 MHz, C_6D_6) of CH_3OPhCH_2OBpin/MeOBpin (◆ represents mesitylene)

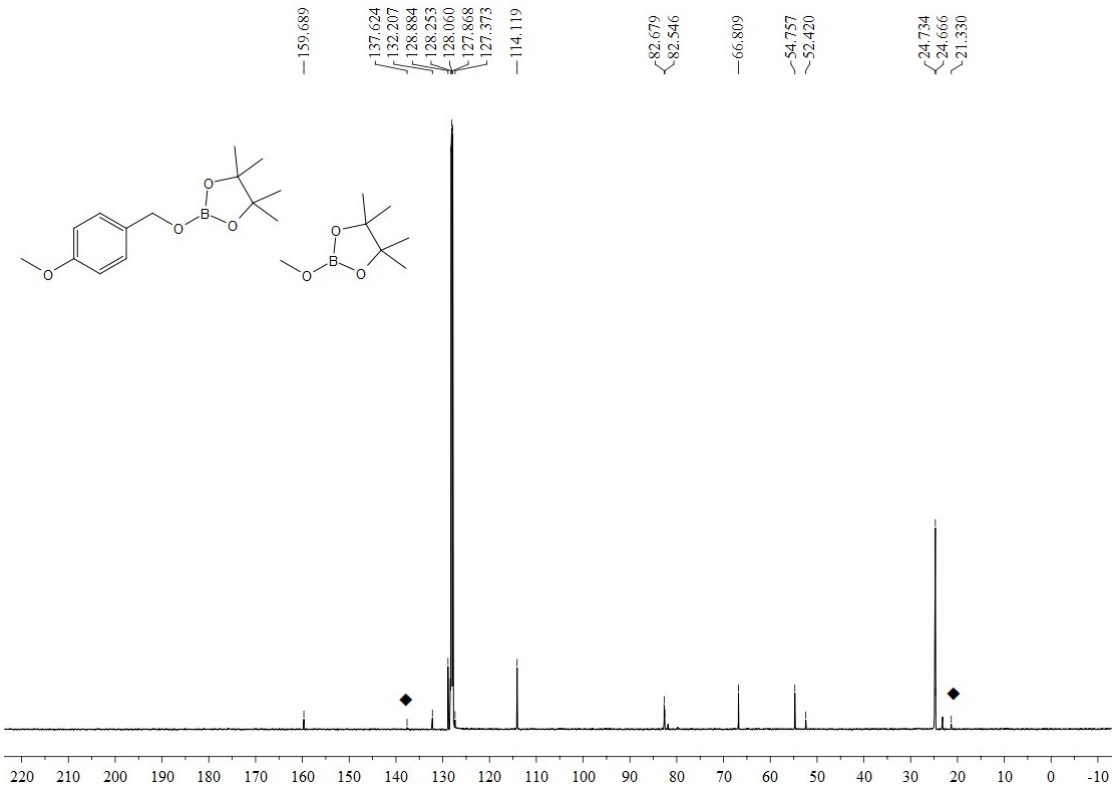


Figure S26. ^{13}C NMR spectrum (125 MHz, C_6D_6) of CH_3OPhCH_2OBpin/MeOBpin (◆ represents mesitylene)

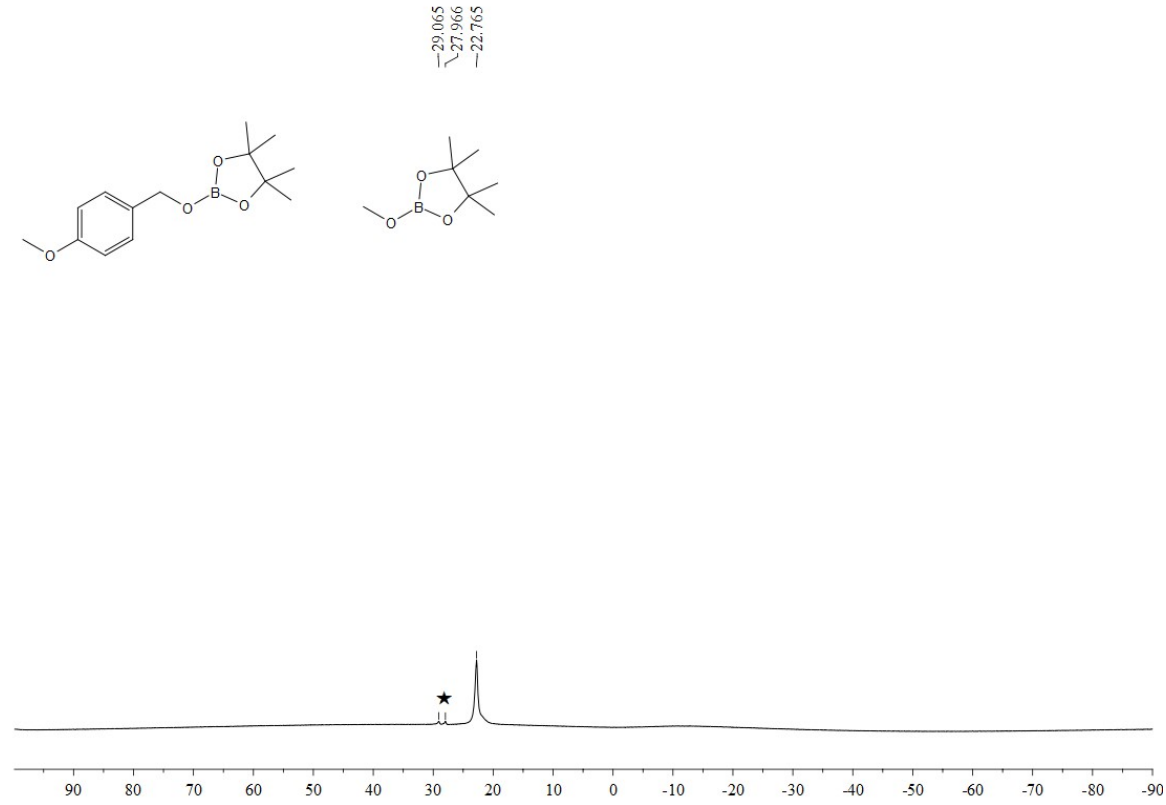


Figure S27. ^{11}B NMR spectrum (128 MHz, C_6D_6) of CH_3OPhCH_2OBpin/MeOBpin (★ represents HBpin).

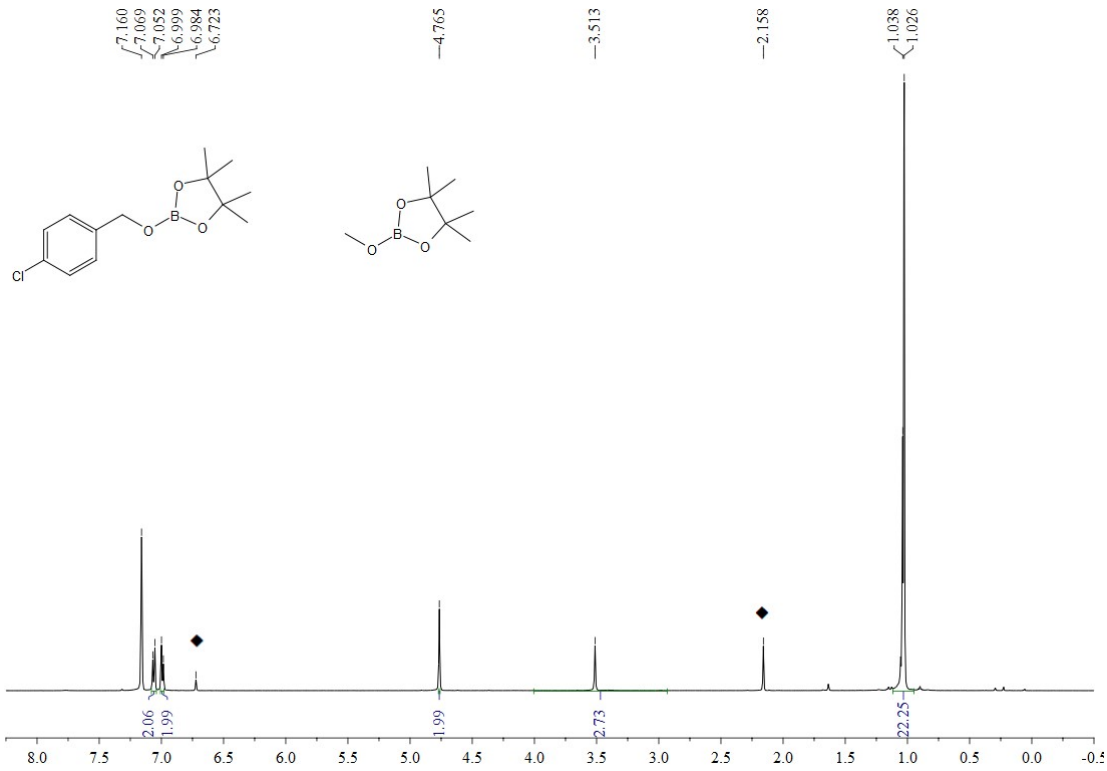


Figure S28. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $ClPhCH_2OBpin$/MeOBpin (◆ represents mesitylene).

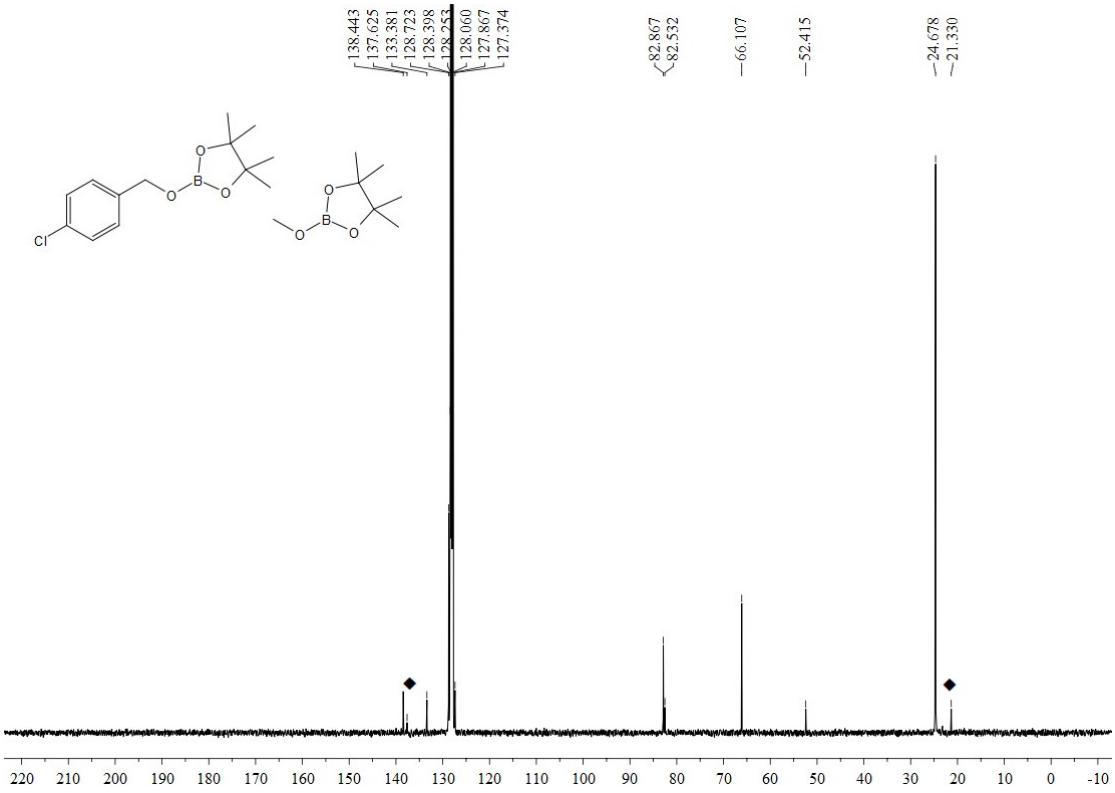


Figure S29. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $ClPhCH_2OBpin$/MeOBpin (◆ represents mesitylene).

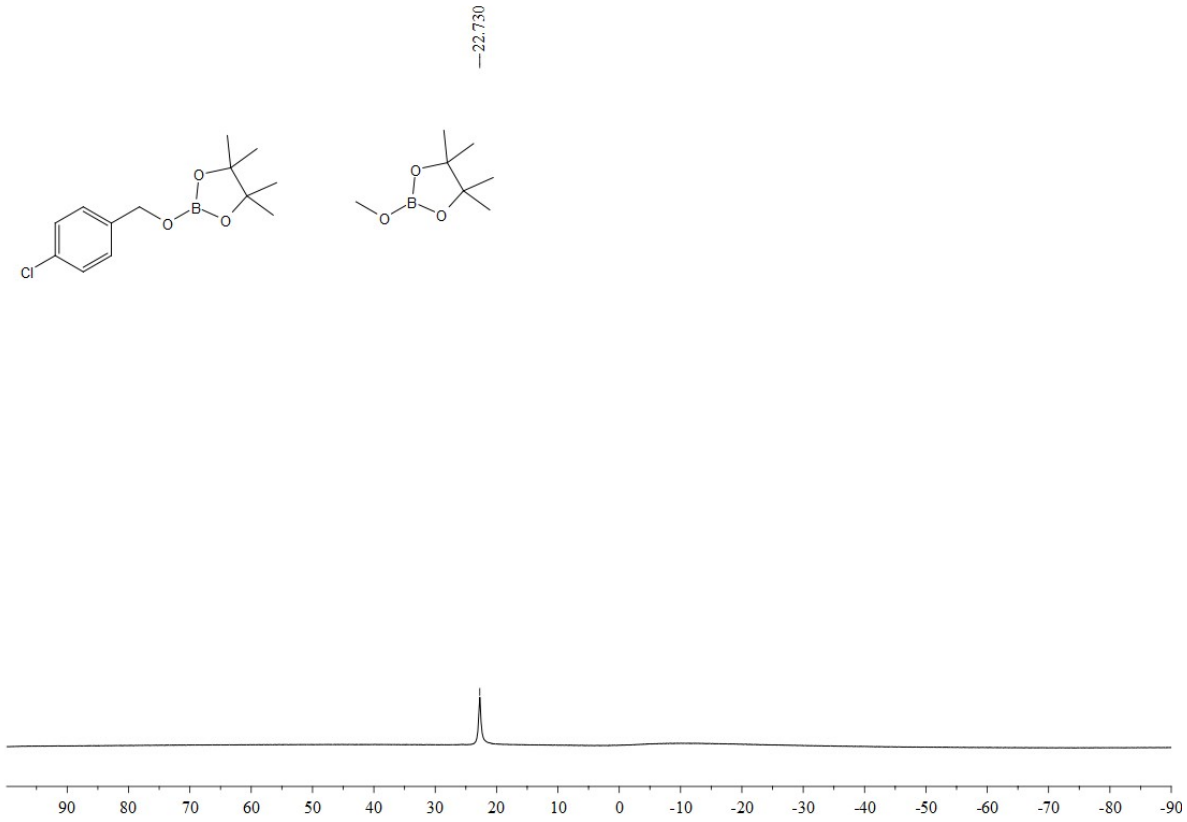


Figure S30. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $ClPhCH_2OBpin$/MeOBpin (★ represents HBpin).

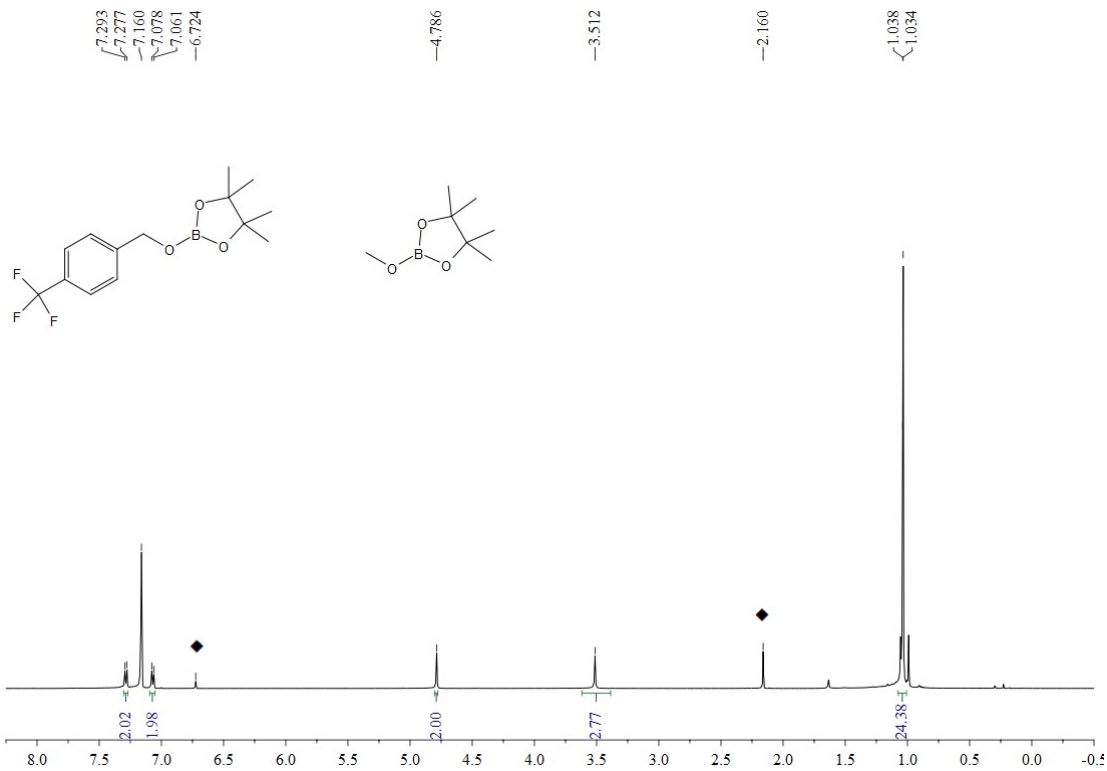


Figure S31. ^1H NMR spectrum (500 MHz, C_6D_6) of CF_3PhCH_2OBpin/MeOBpin (◆ represents

mesitylene)

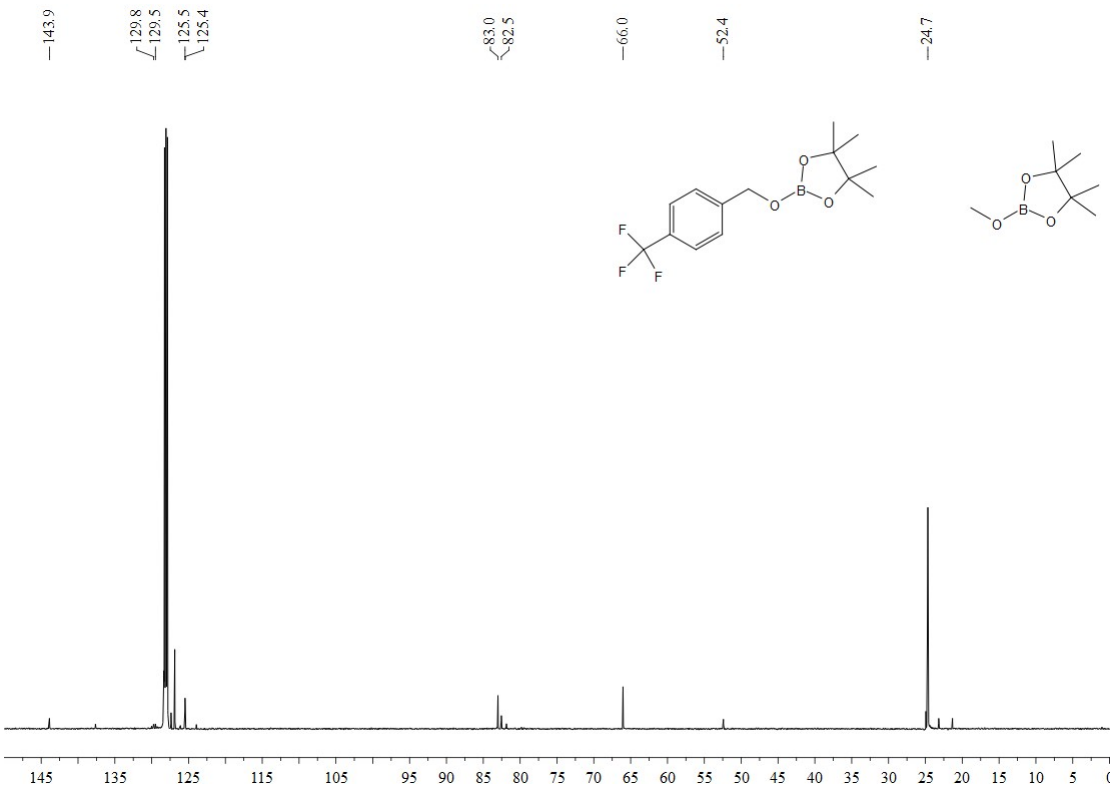


Figure S32. ^{13}C NMR spectrum (125 MHz, C_6D_6) of CF_3PhCH_2OBpin/MeOBpin (◆ represents mesitylene)

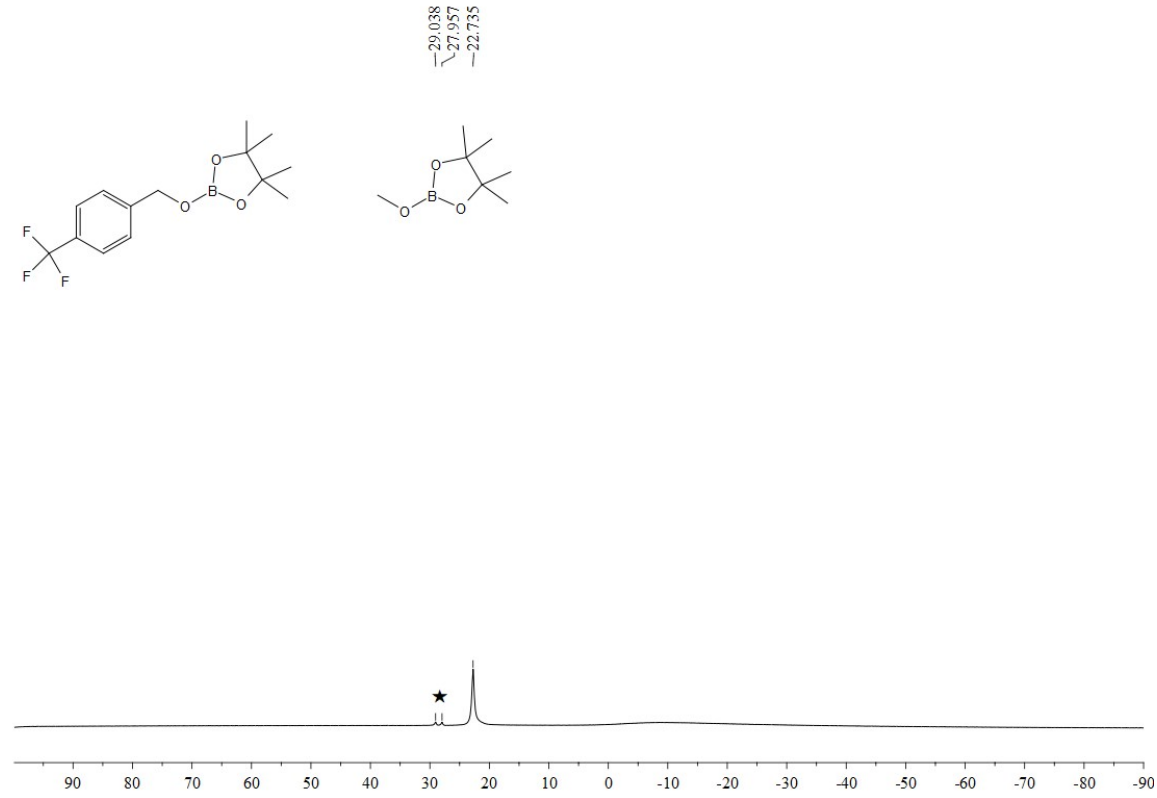


Figure S33. ^{11}B NMR spectrum (128 MHz, C_6D_6) of CF_3PhCH_2OBpin/MeOBpin (★ represents HBpin).

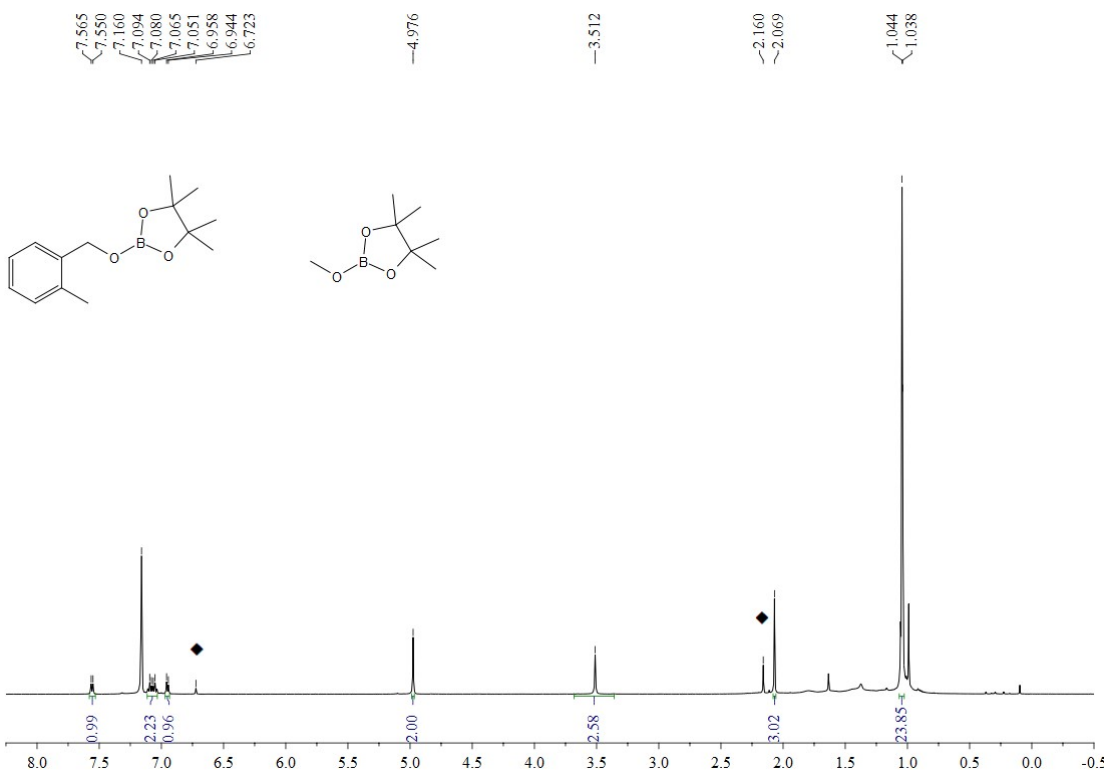


Figure S34. ^{1}H NMR spectrum (500 MHz, C_6D_6) of CH_3PhCH_2OBpin/MeOBpin. (◆ represents mesitylene)

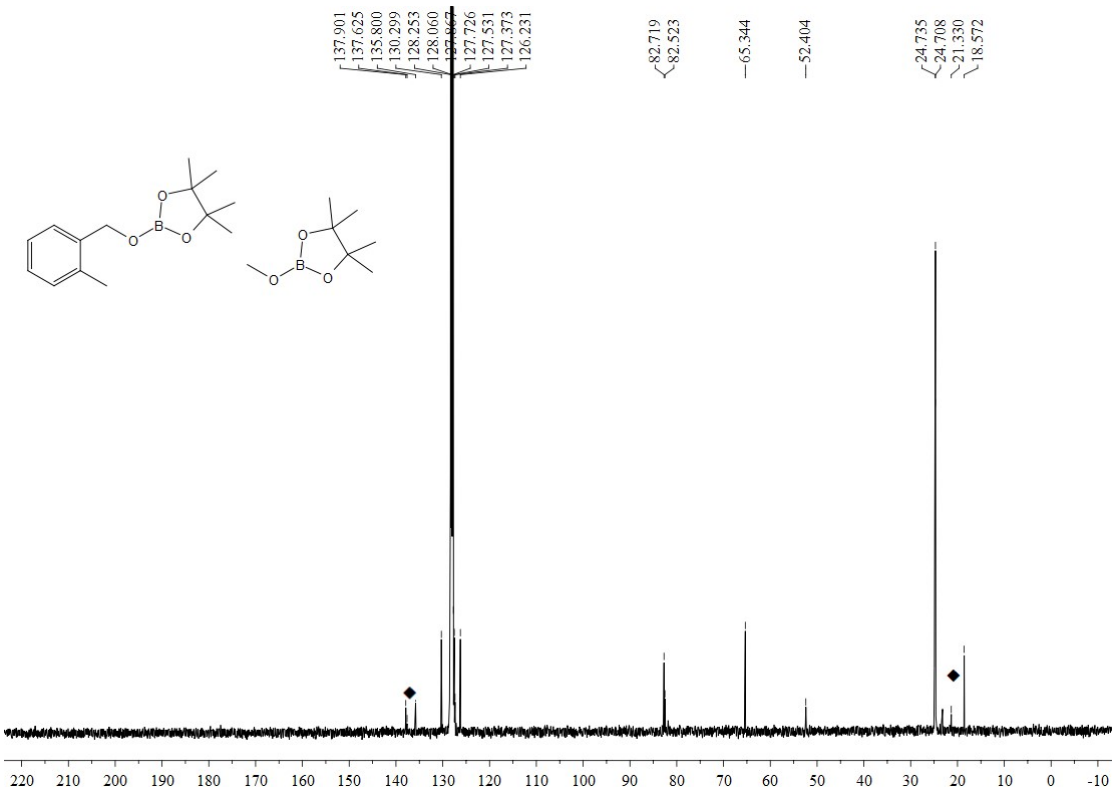


Figure S35. ^{13}C NMR spectrum (125 MHz, C_6D_6) of CH_3PhCH_2OBpin/MeOBpin. (◆ represents mesitylene).

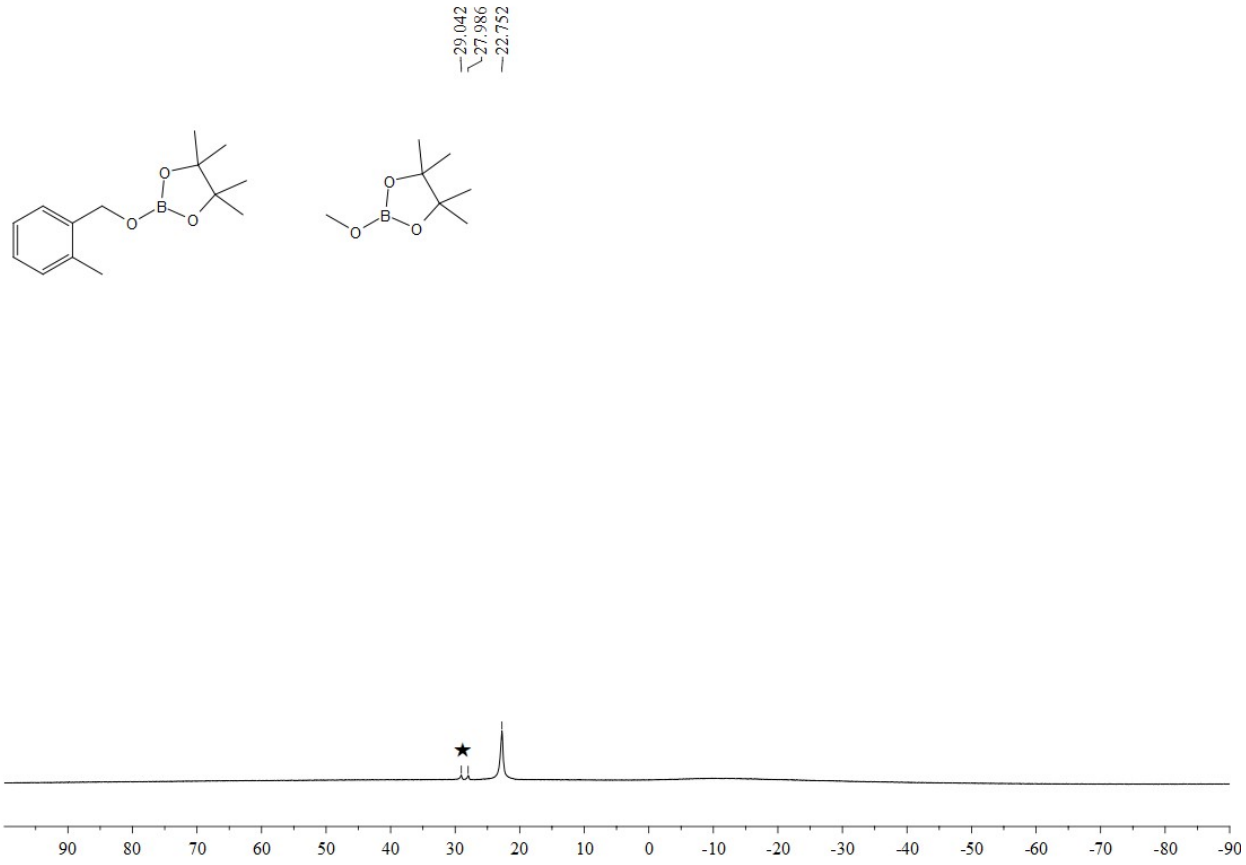


Figure S36. ^{11}B NMR spectrum (128 MHz, C_6D_6) of CH_3PhCH_2OBpin/MeOBpin (★ represents HBpin).

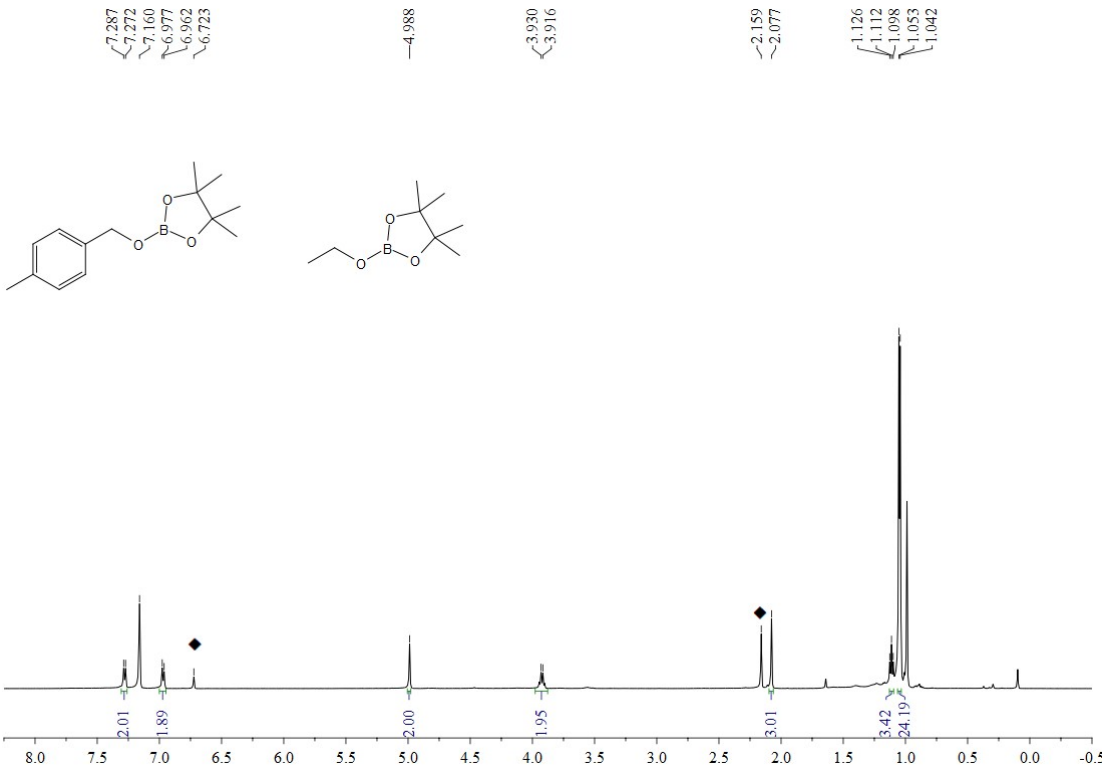


Figure S37. ^{1}H NMR spectrum (500 MHz, C_6D_6) of CH_3PhCH_2OBpin/EtOBpin (◆ represents

mesitylene)

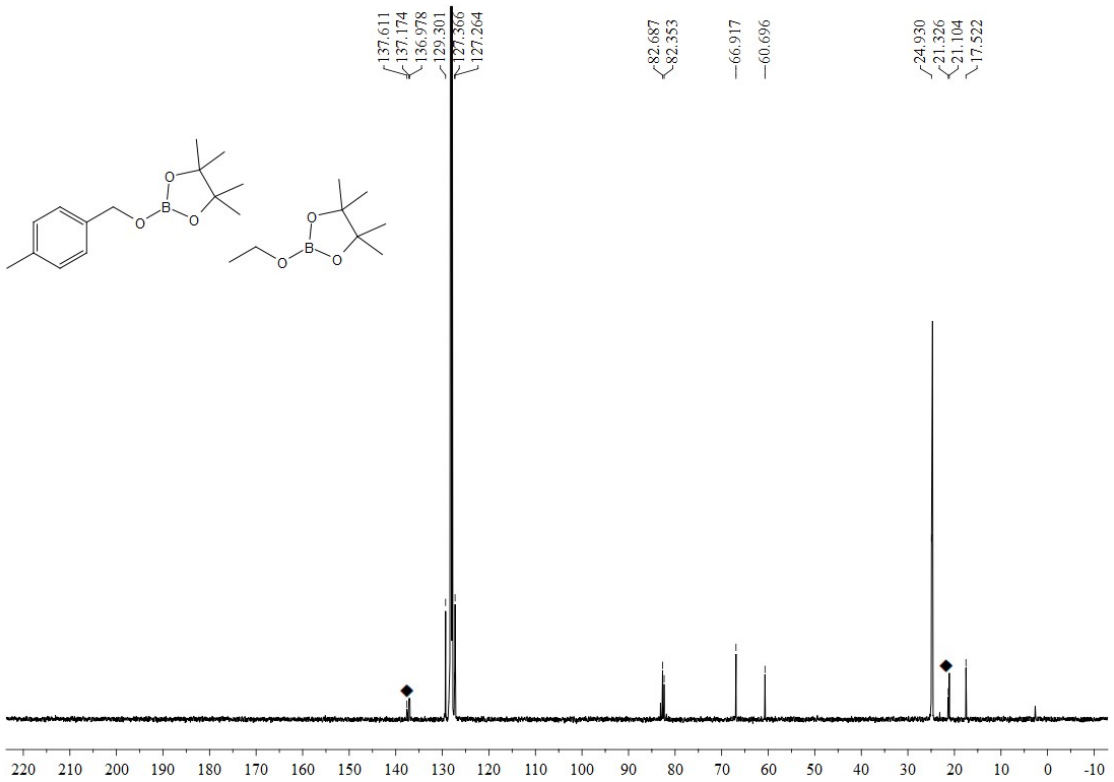


Figure S38. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $CH_3PhCH_2OBpin/EtOBpin$ (◆ represents mesitylene)

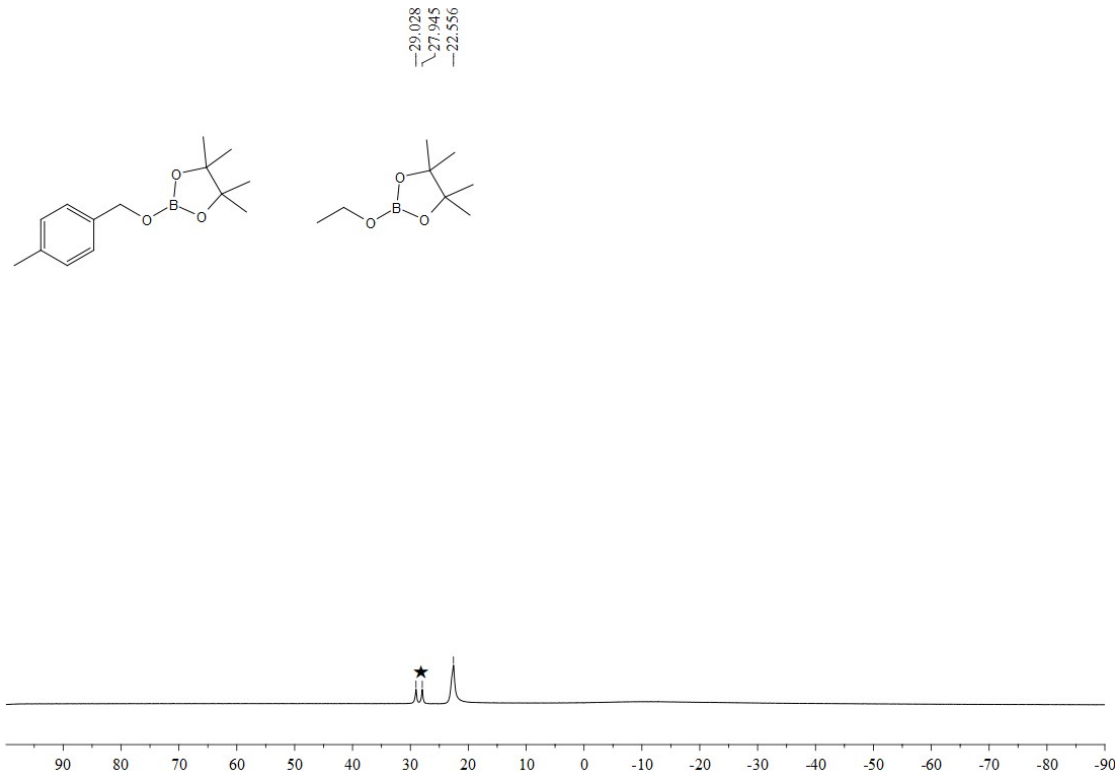


Figure S39. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $CH_3PhCH_2OBpin/MeOBpin$ (★ represents HBpin).

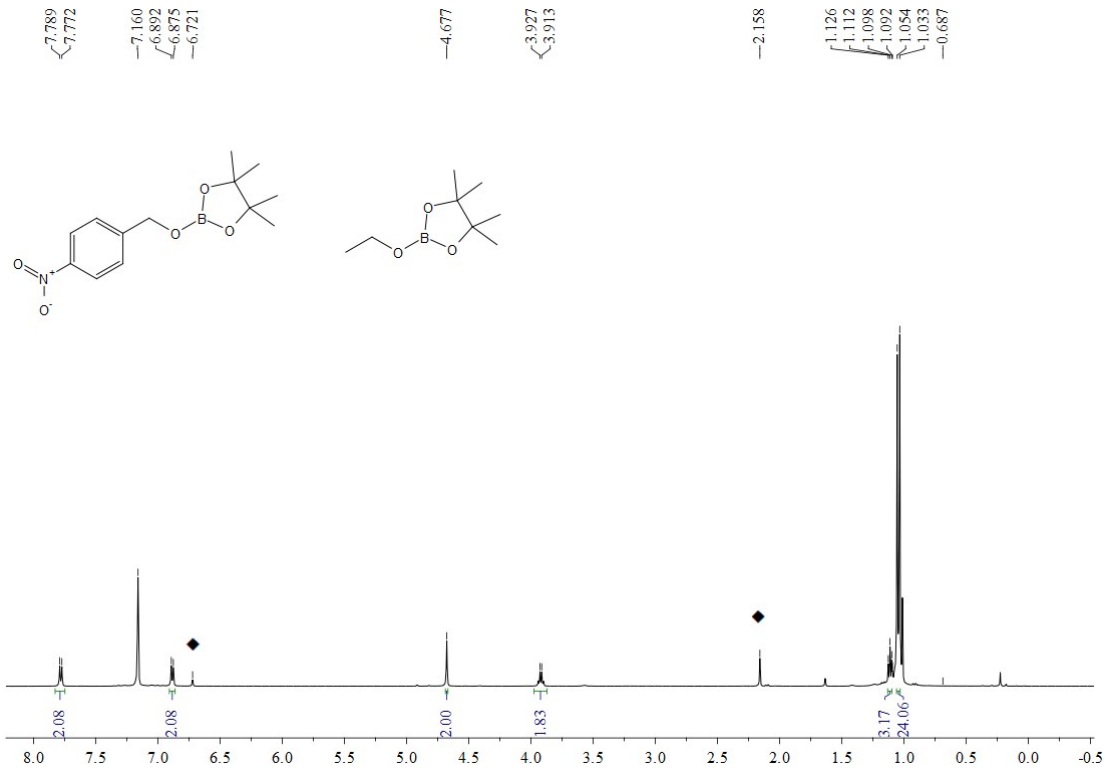


Figure S40. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $NO_2PhCH_2OBpin/EtOBpin$ (◆ represents mesitylene)

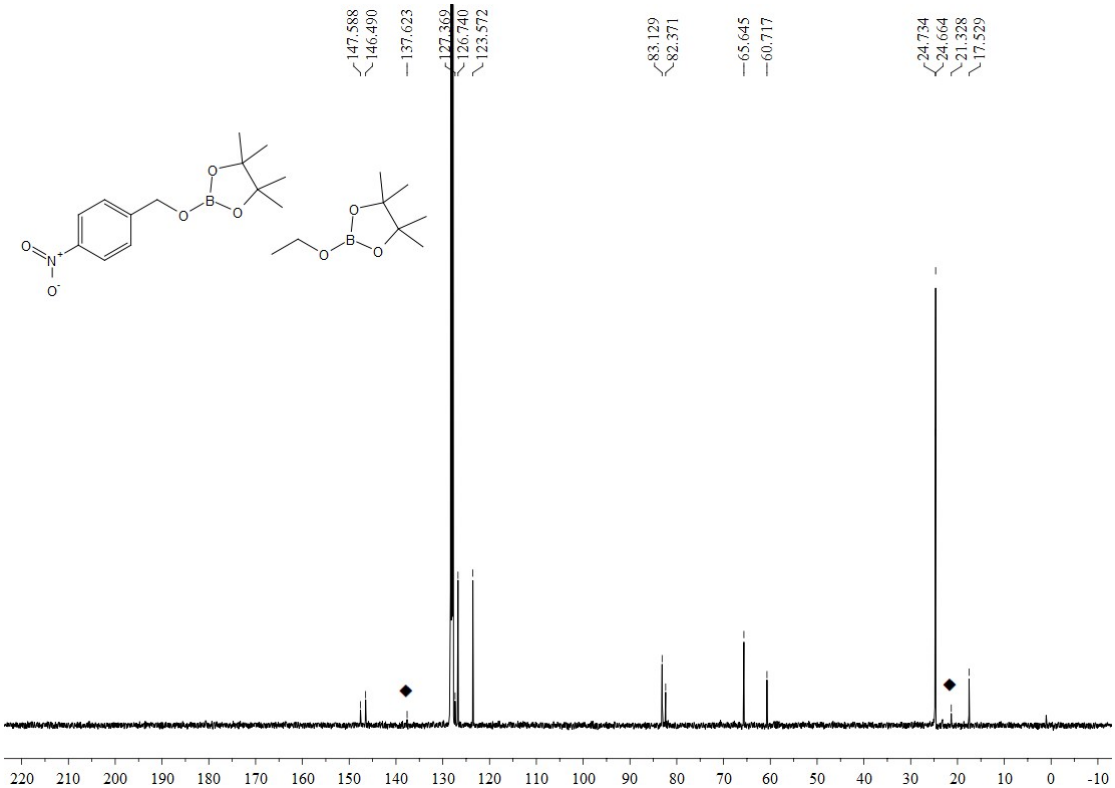


Figure S41. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $NO_2PhCH_2OBpin/EtOBpin$. (◆ represents mesitylene).

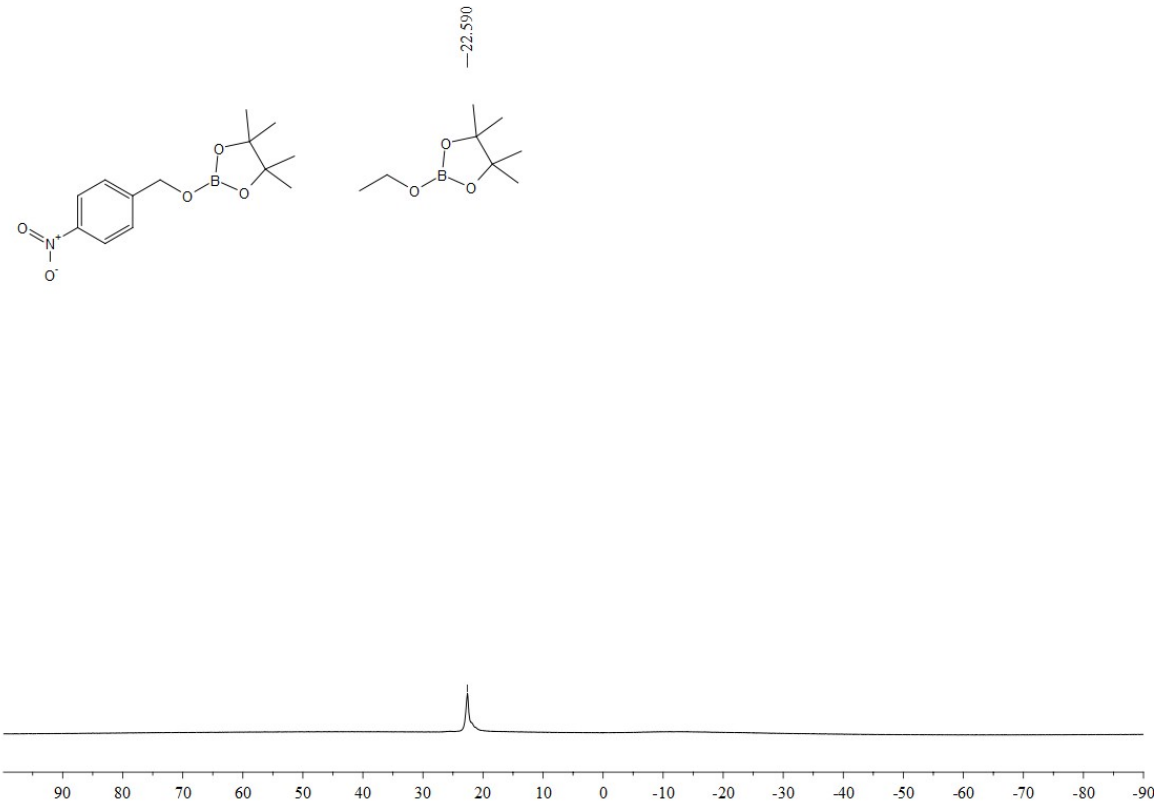


Figure S42. ^{11}B NMR spectrum (128 MHz, C_6D_6) of NO_2PhCH_2OBpin/EtOBpin (★ represents HBpin).

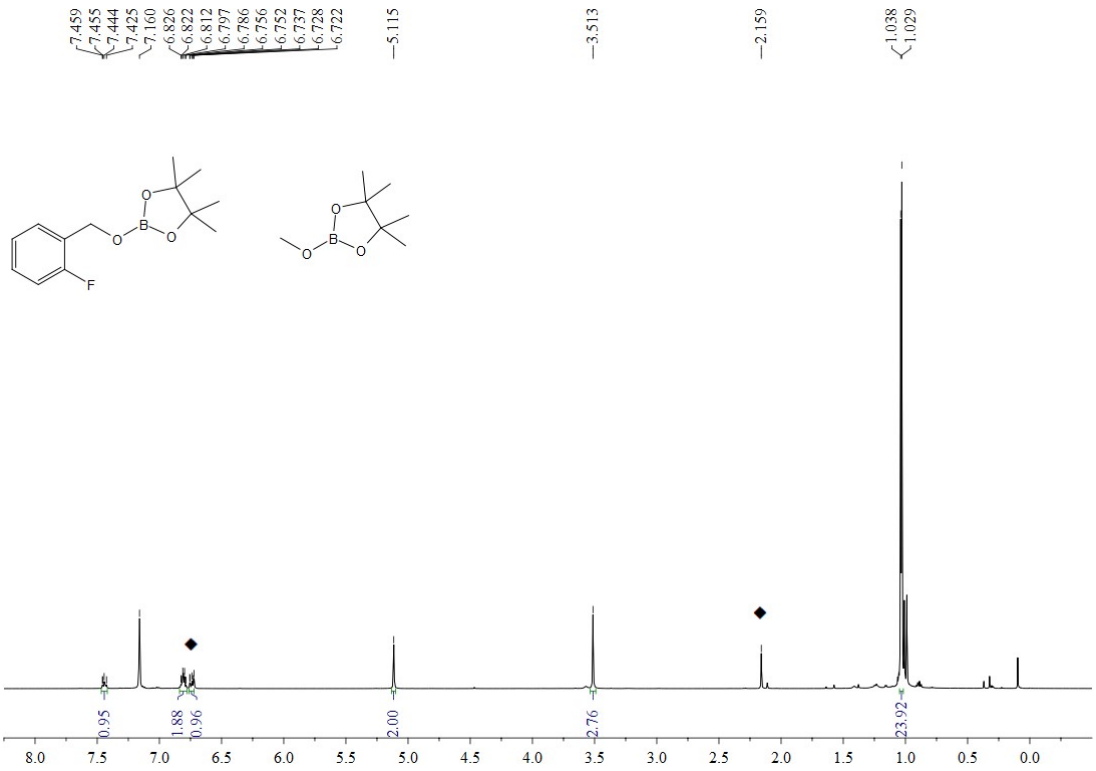


Figure S43. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $FPhCH_2OBpin$/MeOBpin (◆ represents mesitylene)

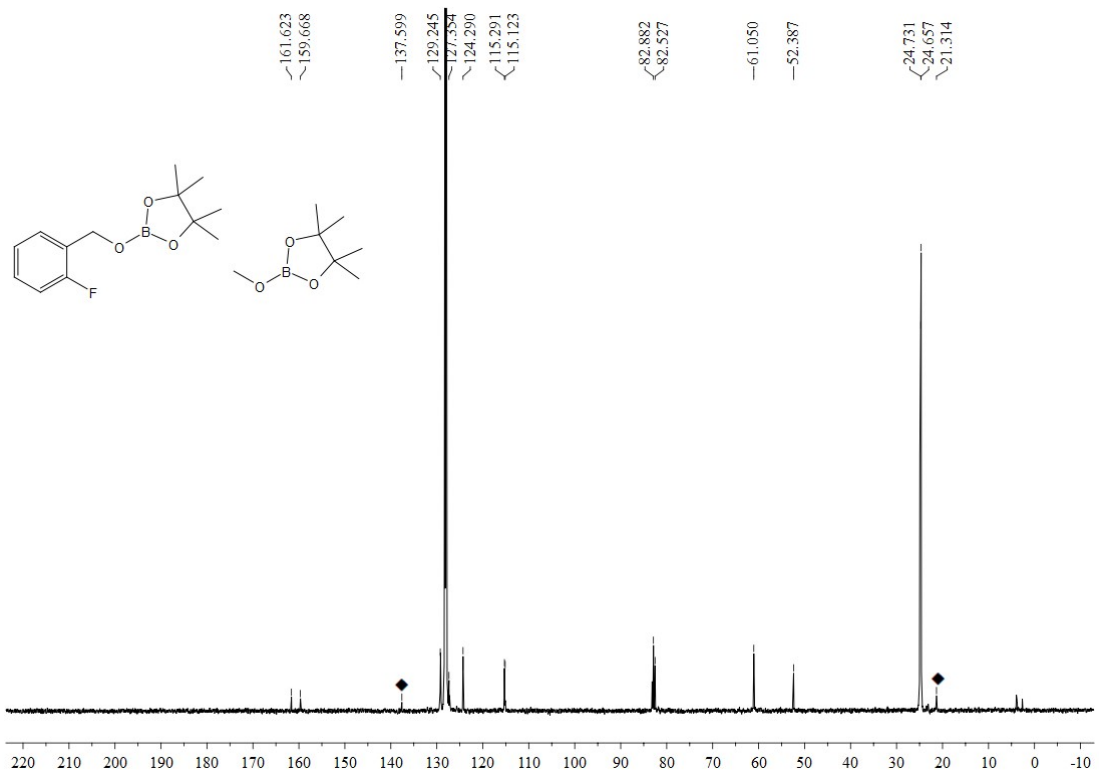


Figure S44. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $FPhCH_2OBpin$/MeOBpin (◆ represents mesitylene).

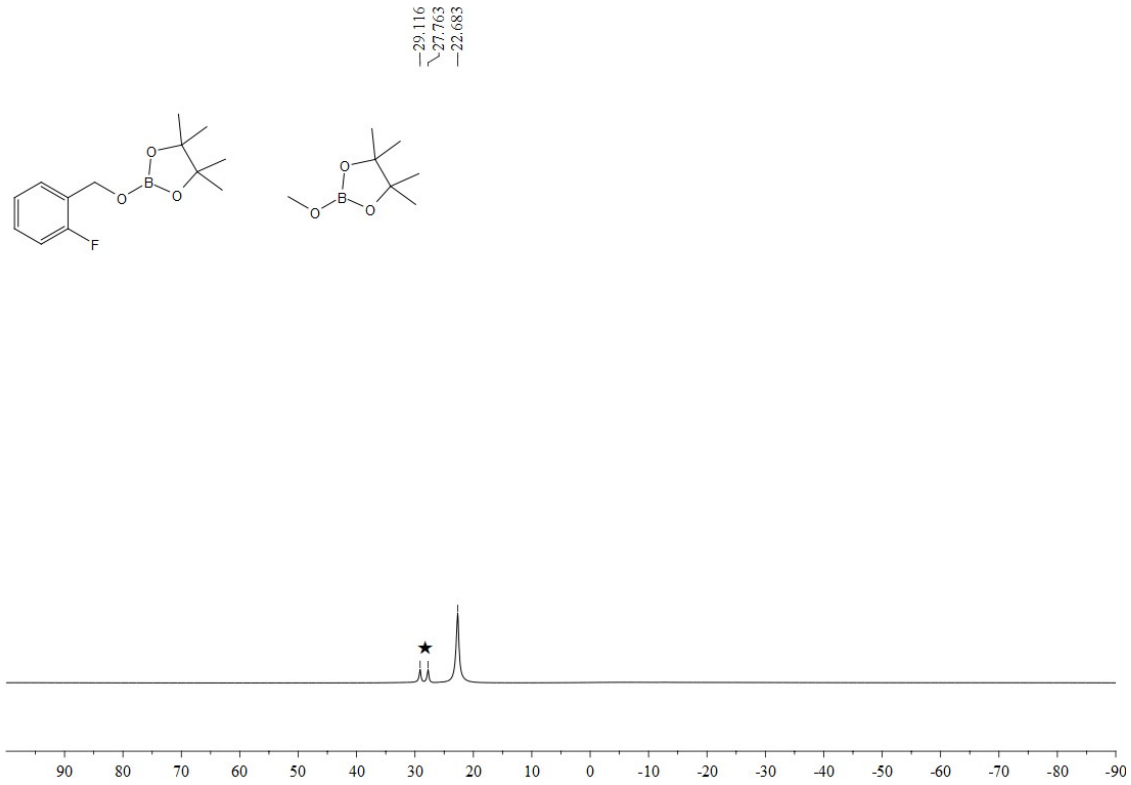


Figure S45. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $FPhCH_2OBpin$/MeOBpin (★ represents HBpin).

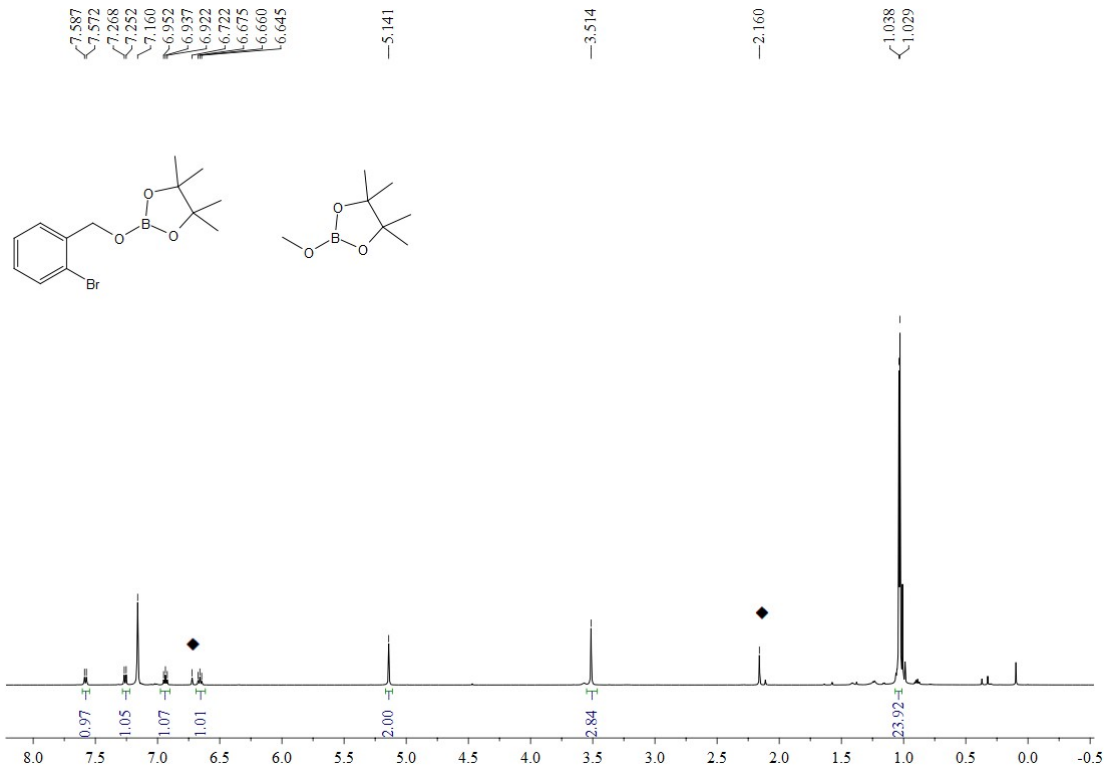


Figure S46. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $BrPhCH_2OBpin$/MeOBpin (◆ represents mesitylene)

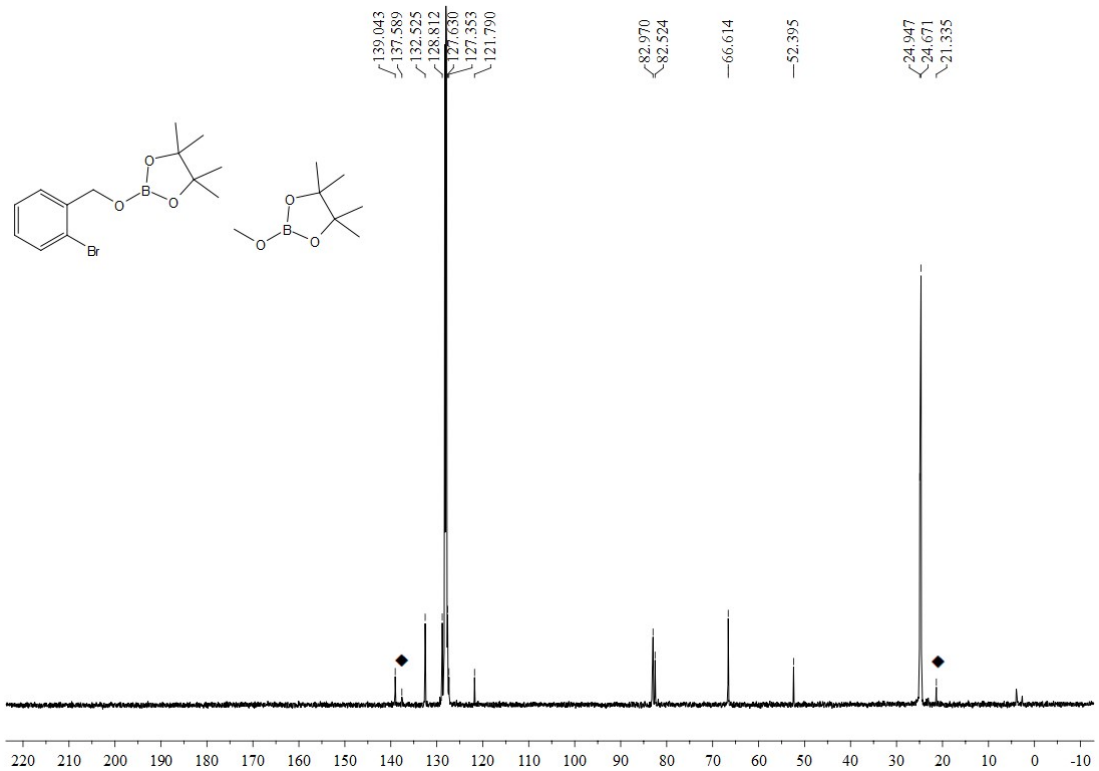


Figure S47. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $BrPhCH_2OBpin$/MeOBpin (◆ represents mesitylene).

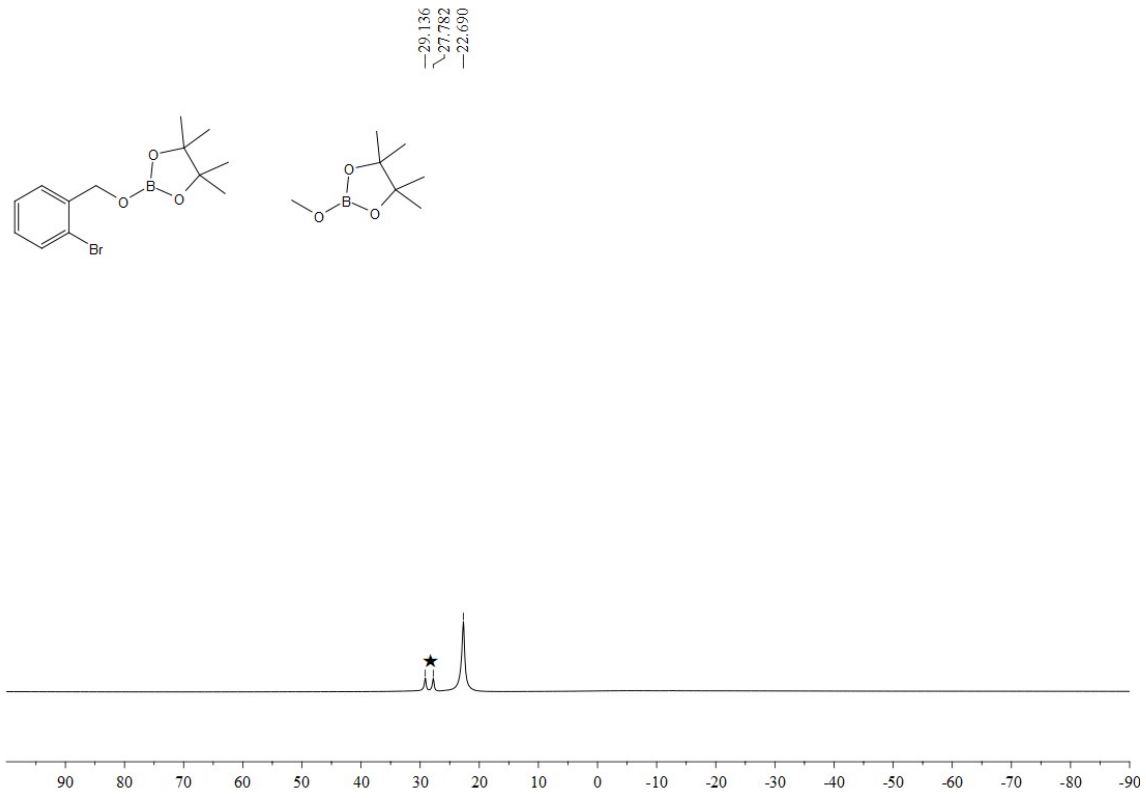


Figure S48. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $BrPhCH_2OBpin$/MeOBpin (★ represents HBpin).

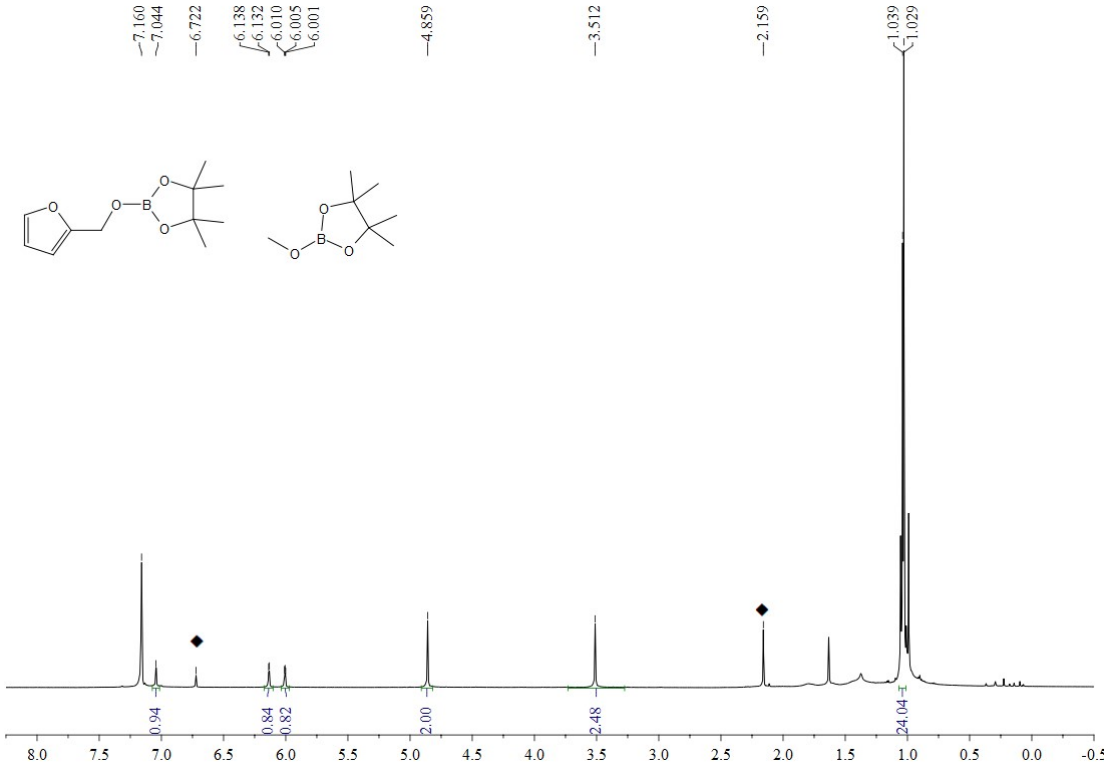


Figure S49. ^{1}H NMR spectrum (500 MHz, C_6D_6) of 2-furan-CH_2O*B*pin/MeO*B*pin (◆ represents mesitylene)

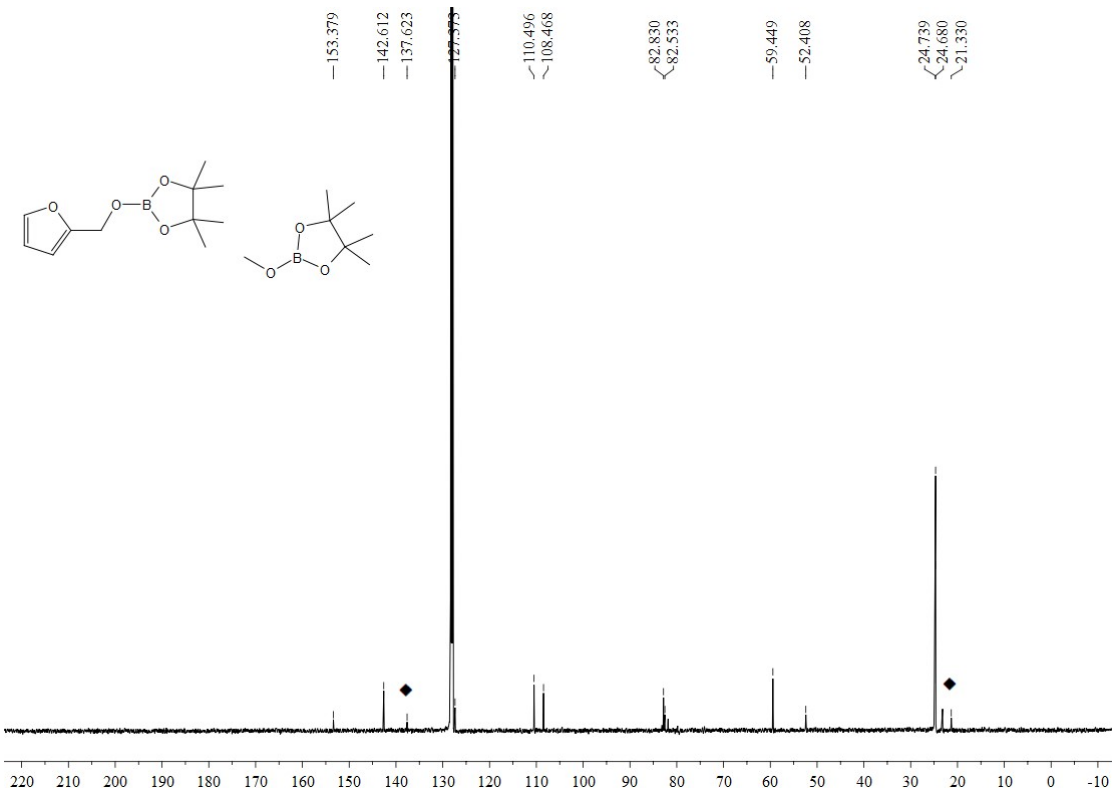


Figure S50. ^{13}C NMR spectrum (125 MHz, C_6D_6) of 2-furan-CH_2O*B*pin/MeO*B*pin (◆ represents mesitylene).

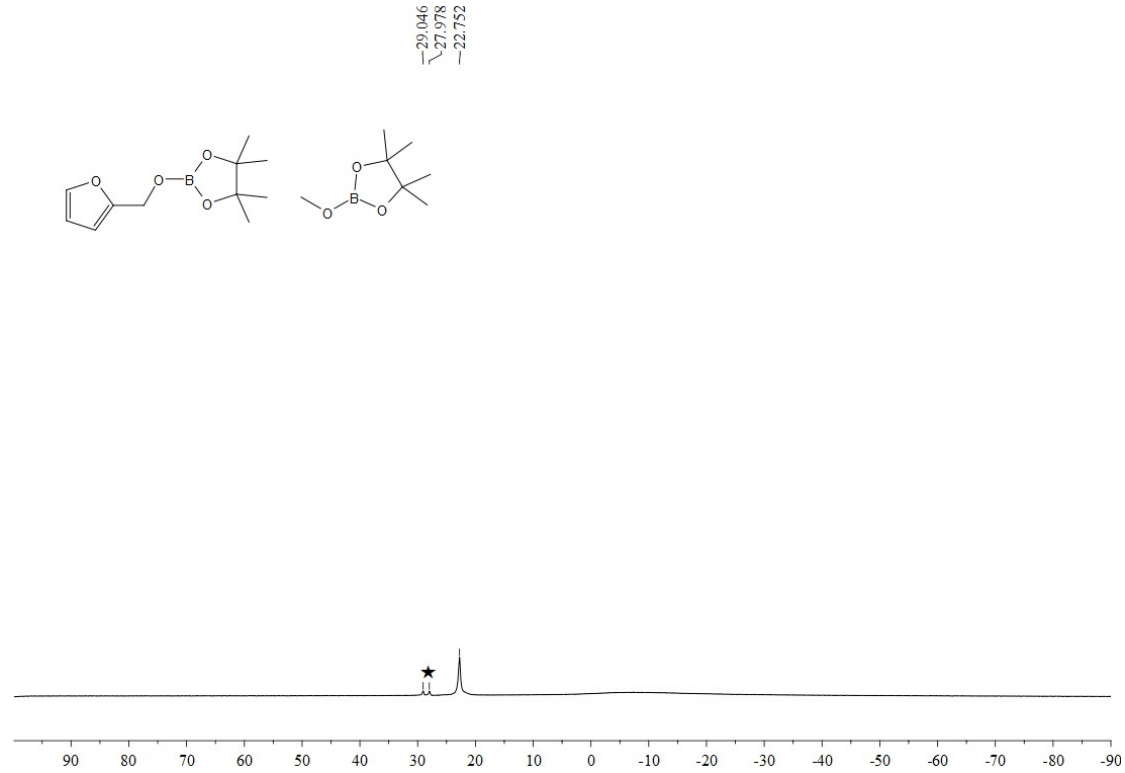


Figure S51. ^{11}B NMR spectrum (128 MHz, C_6D_6) of 2-furan-CH_2O*B*pin/MeO*B*pin (★ represents HBpin).

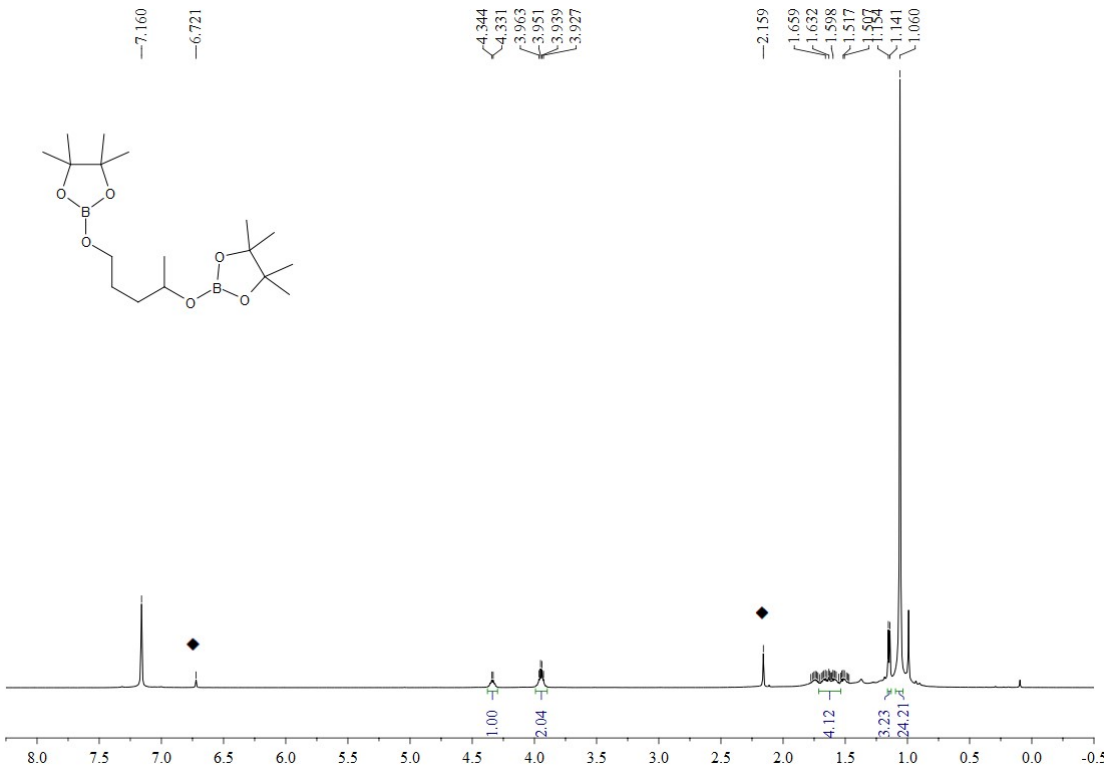


Figure S52. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $BpinO(CH_2)_3CMeOBpin$ (◆ represents mesitylene)

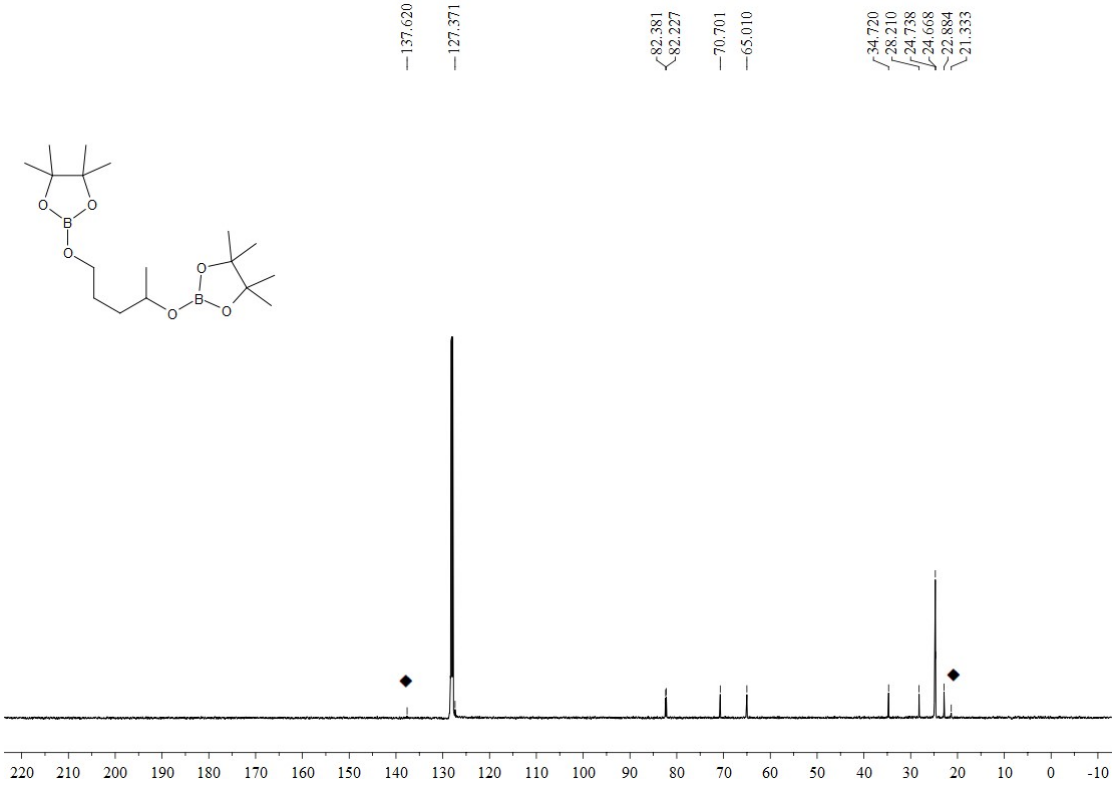


Figure S53. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $BpinO(CH_2)_3CMeOBpin$ (◆ represents mesitylene).

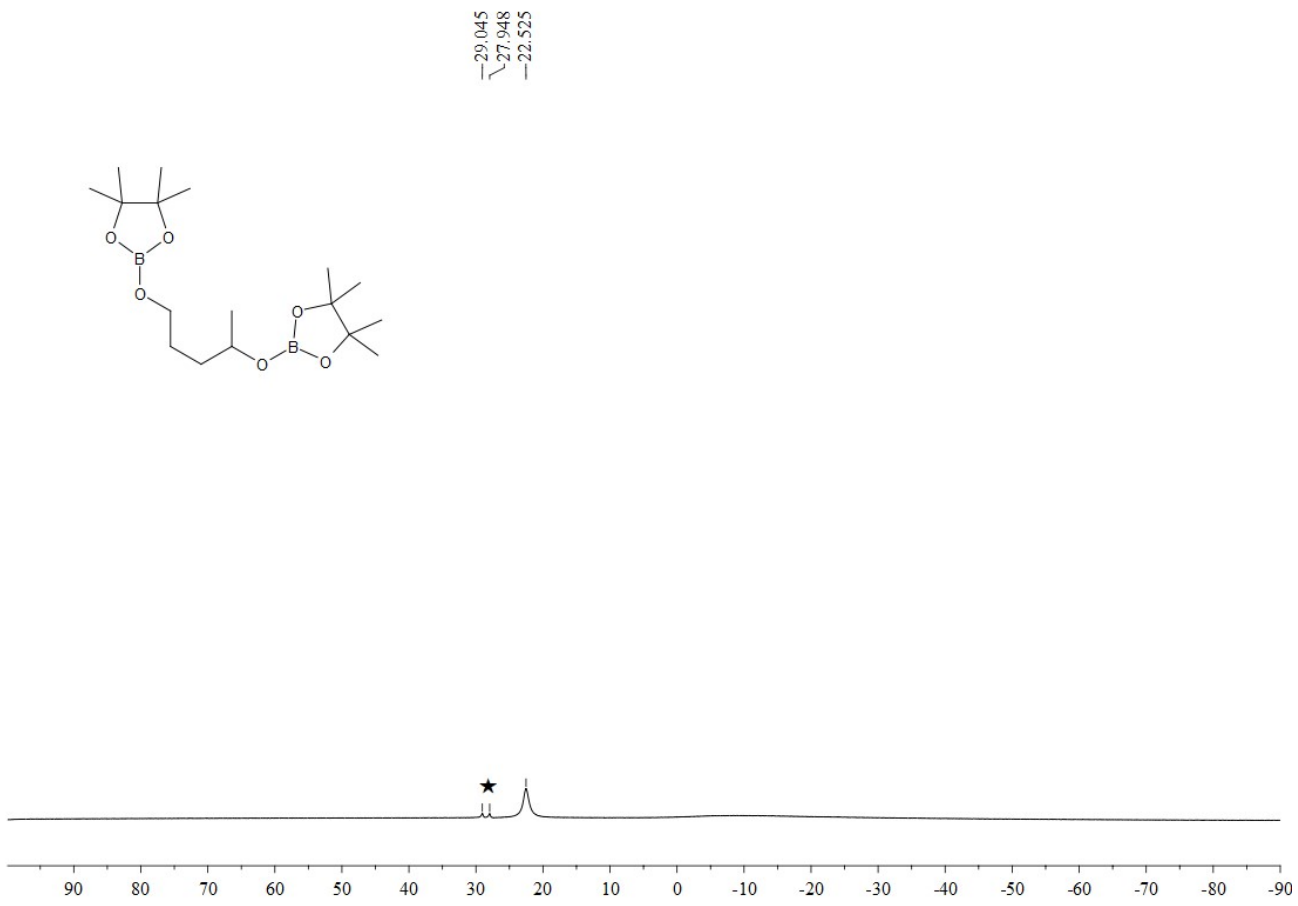


Figure S54. ^{11}B NMR spectrum (128 MHz, C_6D_6) of pinBO$(CH_2)_3$CMeOBpin (★ represents HBpin).

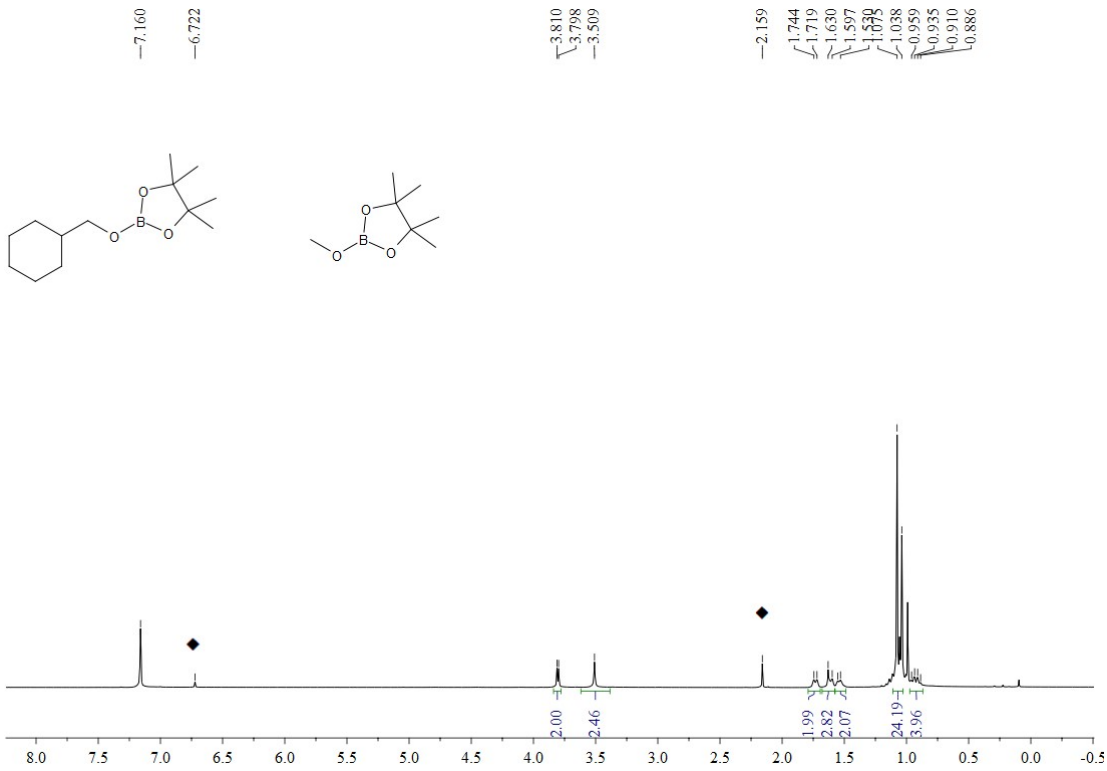


Figure S55. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $CyCH_2OBpin$/MeOBpin (◆ represents

mesitylene)

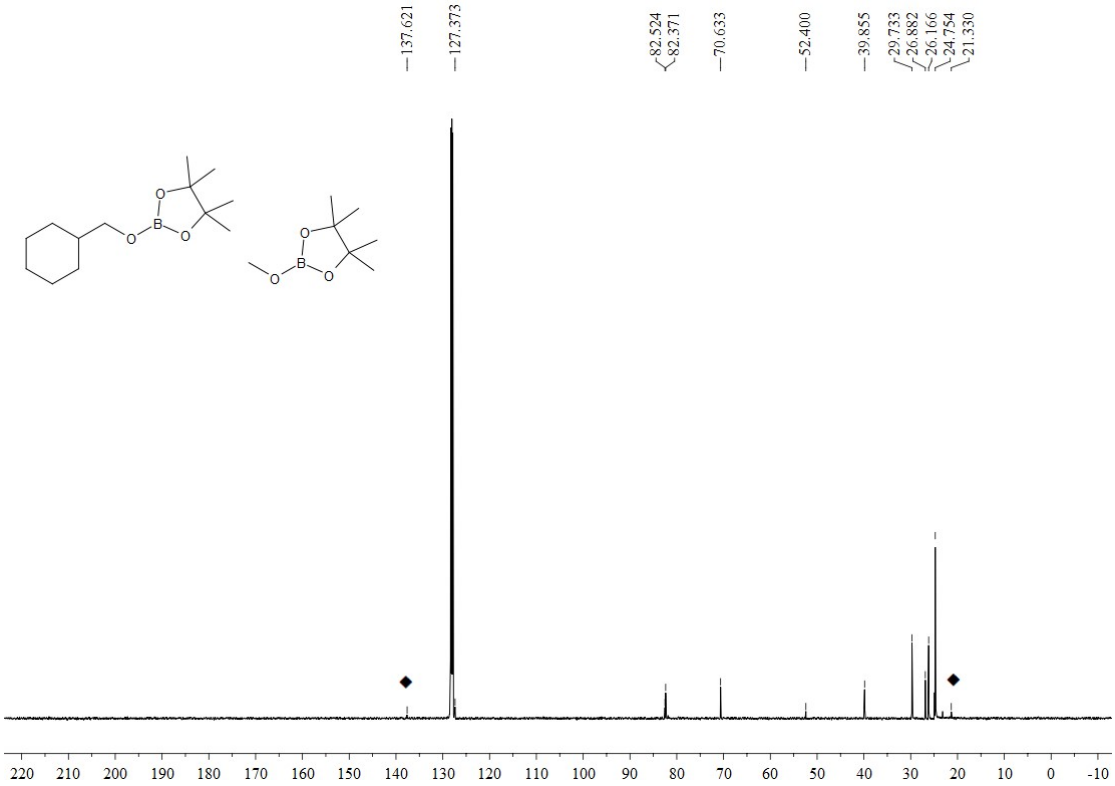


Figure S56. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $CyCH_2OBpin/MeOBpin$ (◆ represents mesitylene).

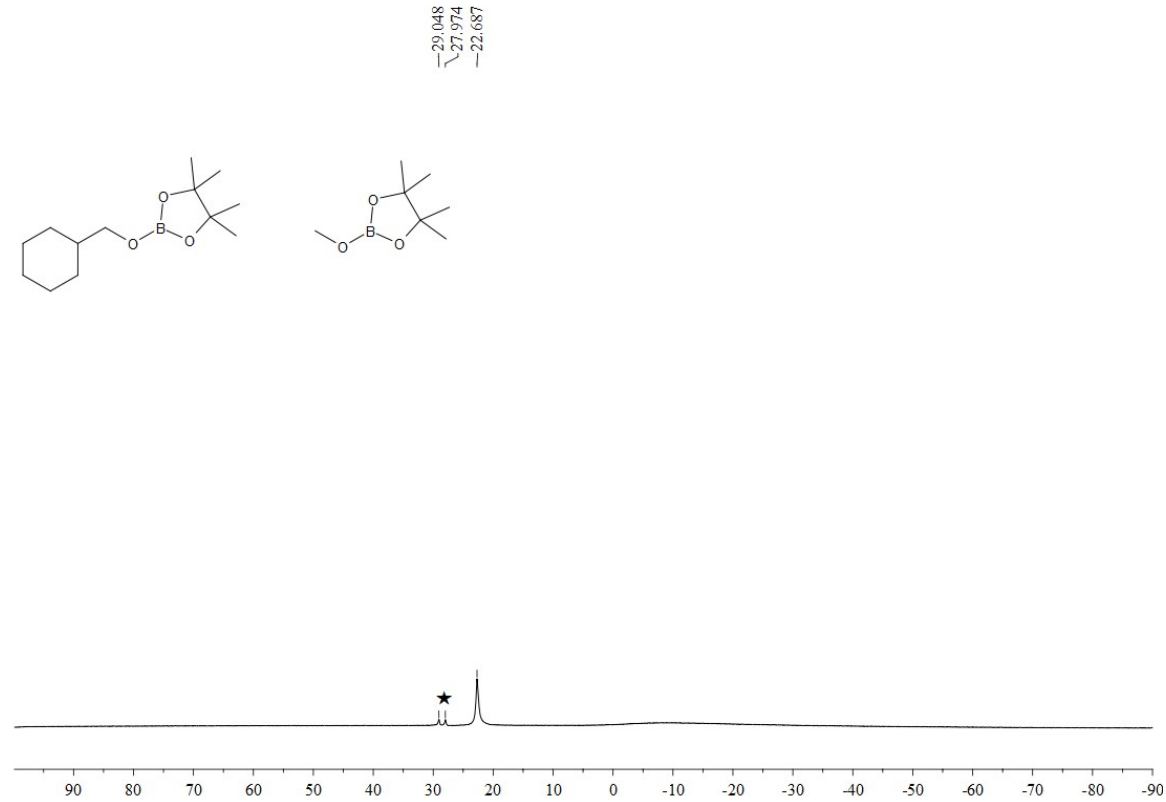


Figure S57. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $pinBO(CH_2)_3CMeOBpin$ (★ represents HBpin).

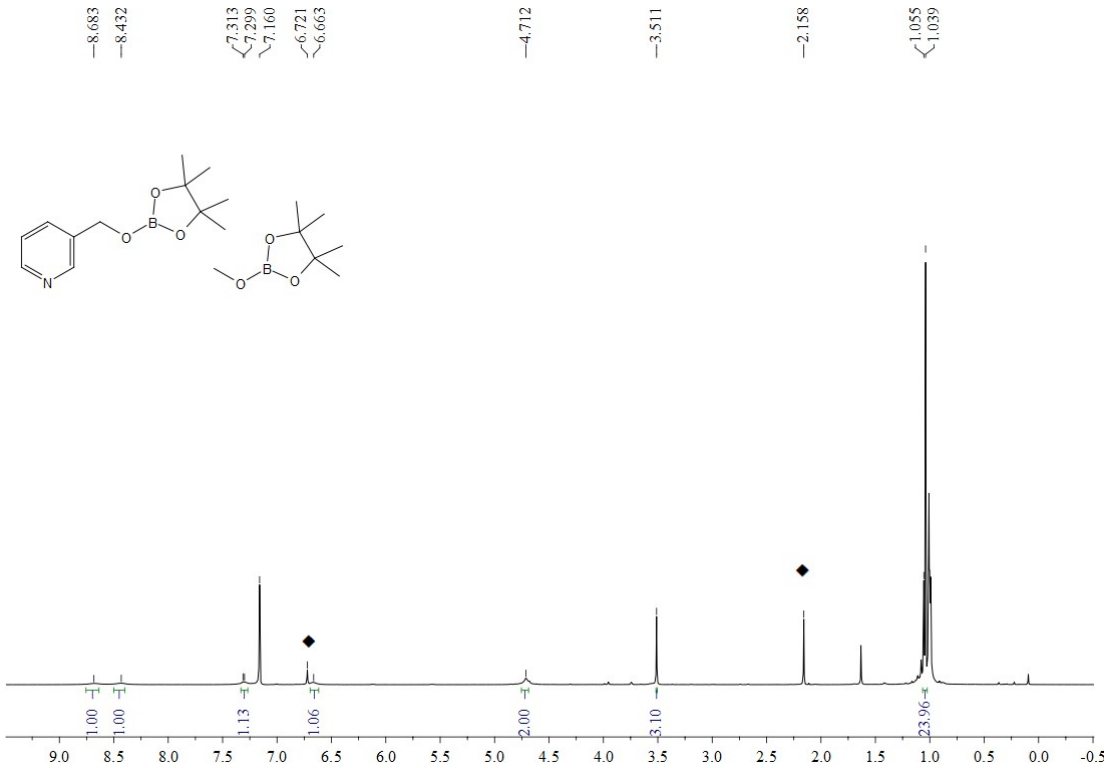


Figure S58. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $PyCH_2OBpin$/MeOBpin (◆ represents mesitylene)

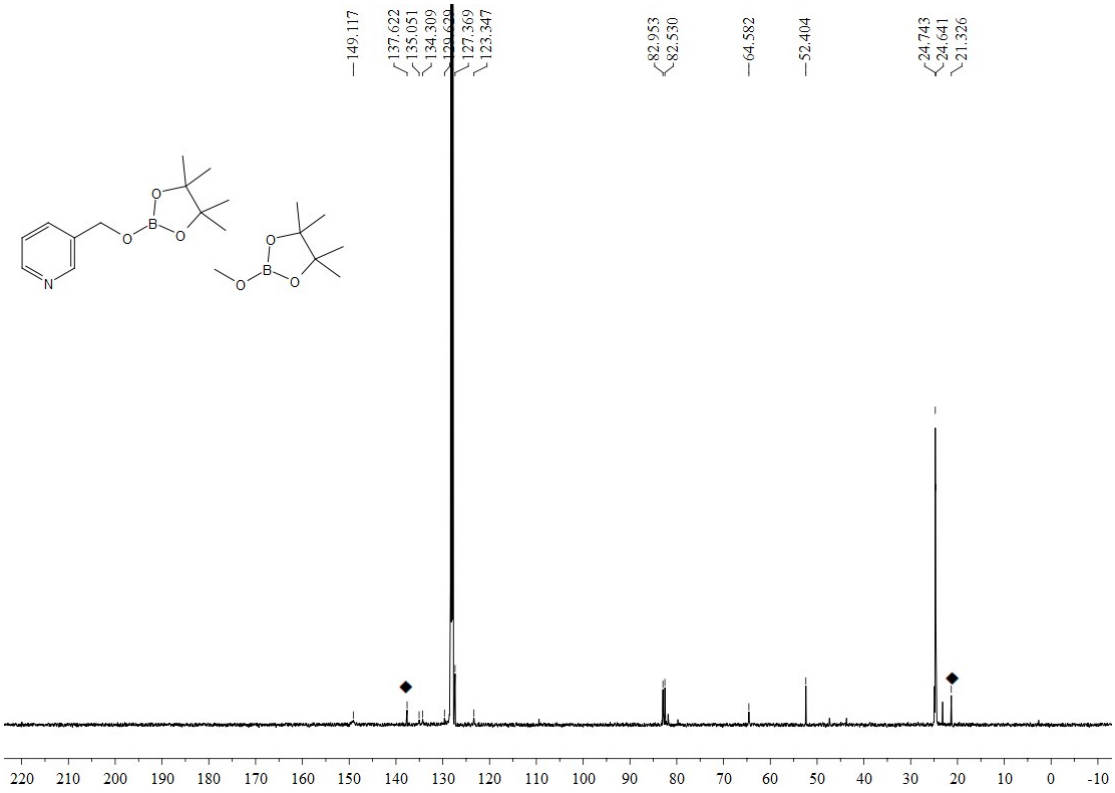


Figure S59. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $PyCH_2OBpin$/MeOBpin (◆ represents mesitylene).

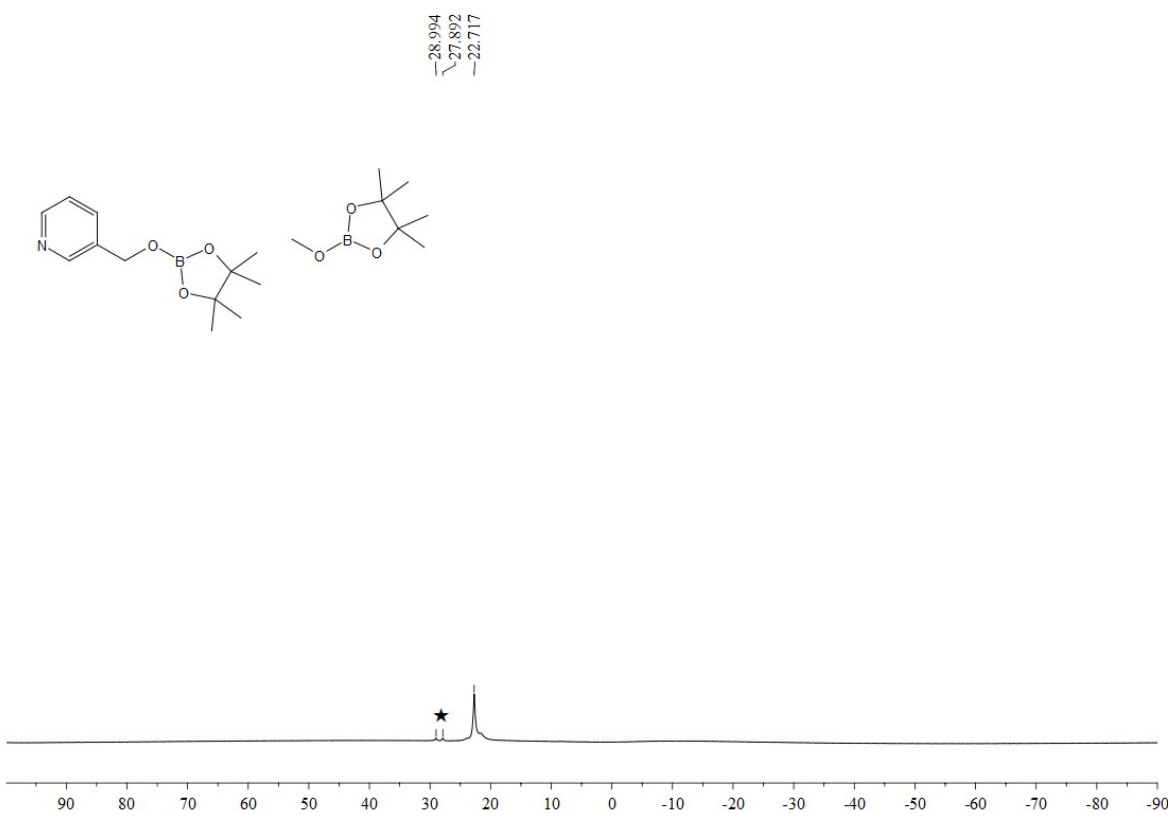


Figure S60. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $PyCH_2OBpin/MeOBpin$ (★ represents HBpin).

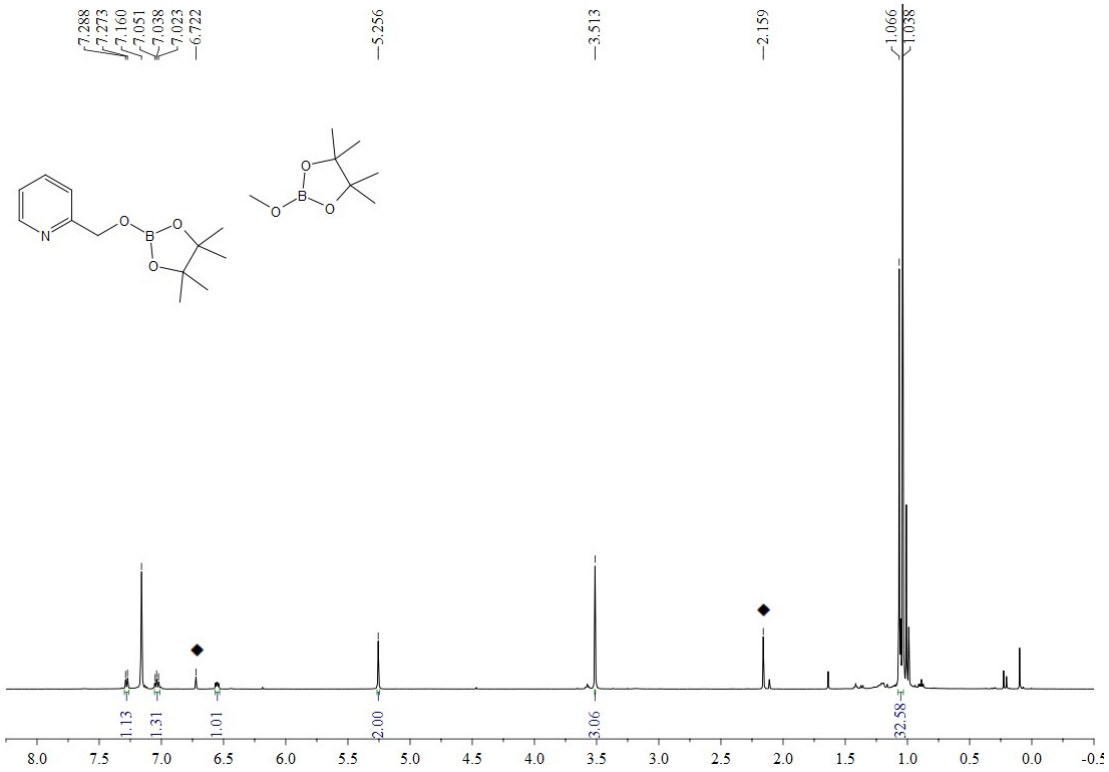


Figure S61. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $PyCH_2OBpin/MeOBpin$ (◆ represents mesitylene)

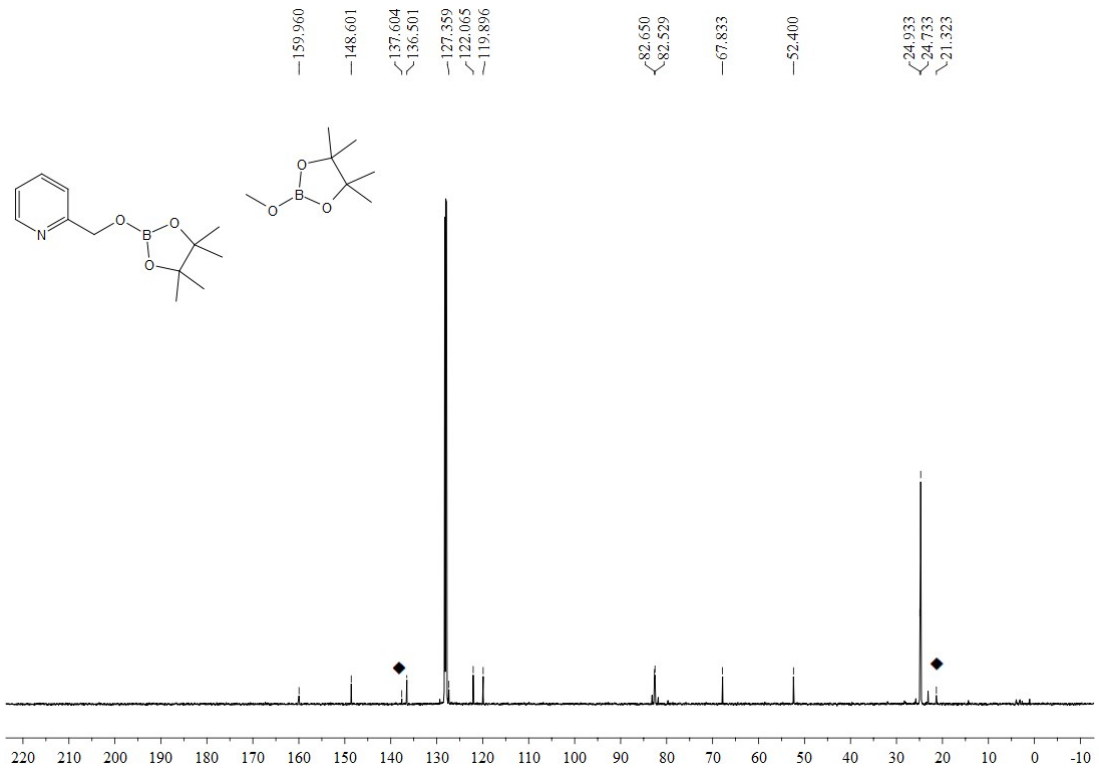


Figure S62. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $PyCH_2OBpin/MeOBpin$ (◆ represents mesitylene).

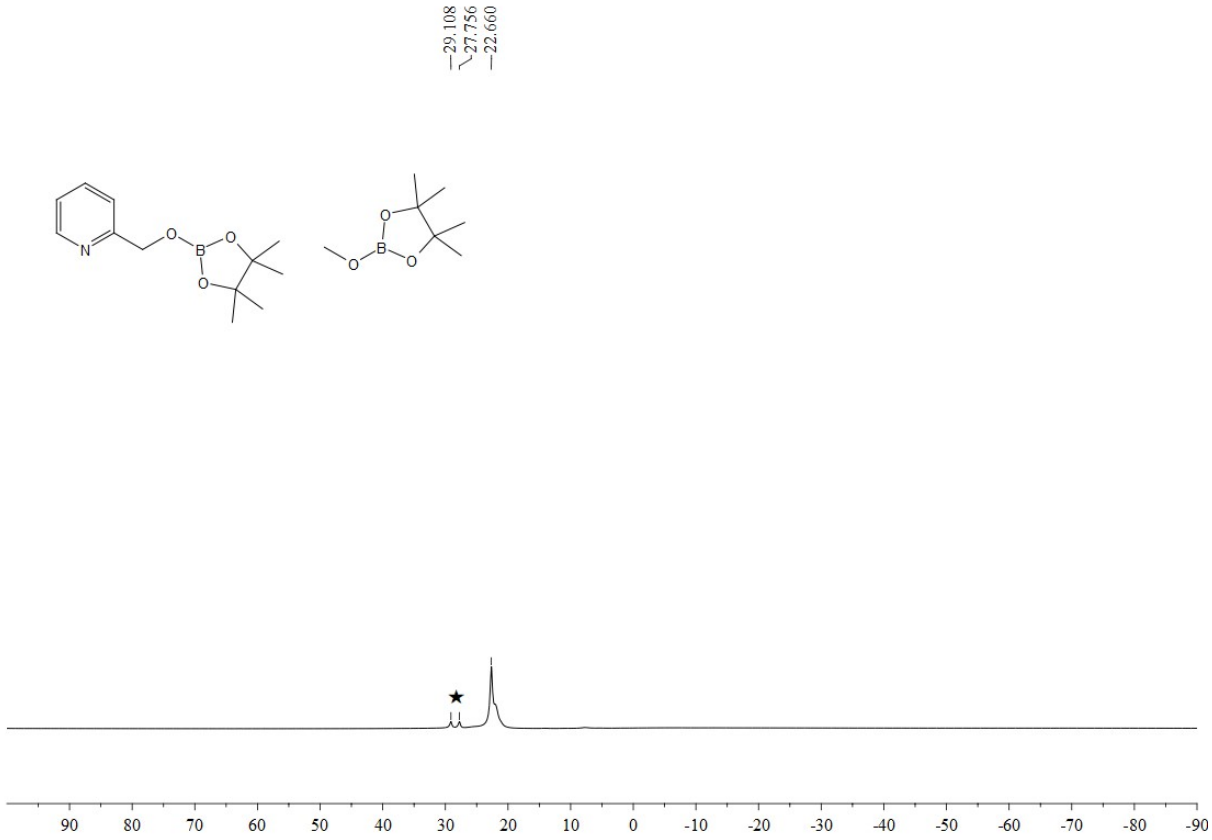


Figure S63. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $PyCH_2OBpin/MeOBpin$ (★ represents HBpin).

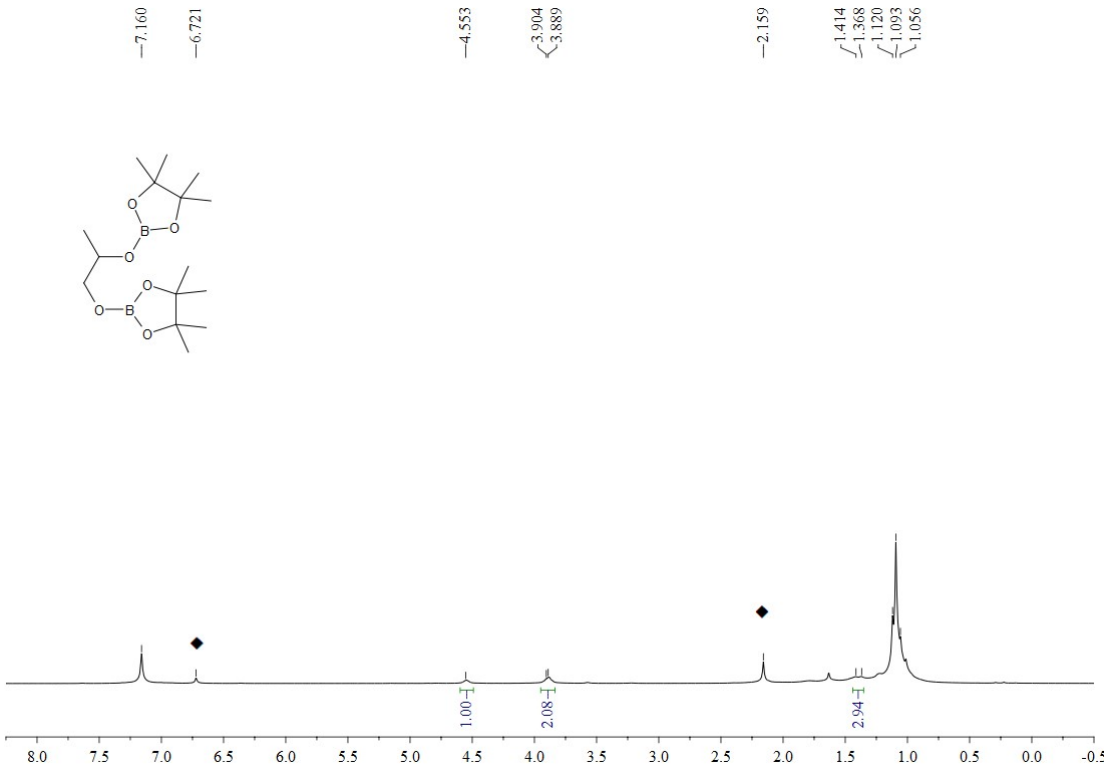


Figure S64. ^{1}H NMR spectrum (500 MHz, C_6D_6) of pinBOCH$_2$CMeOBpin (◆ represents mesitylene)

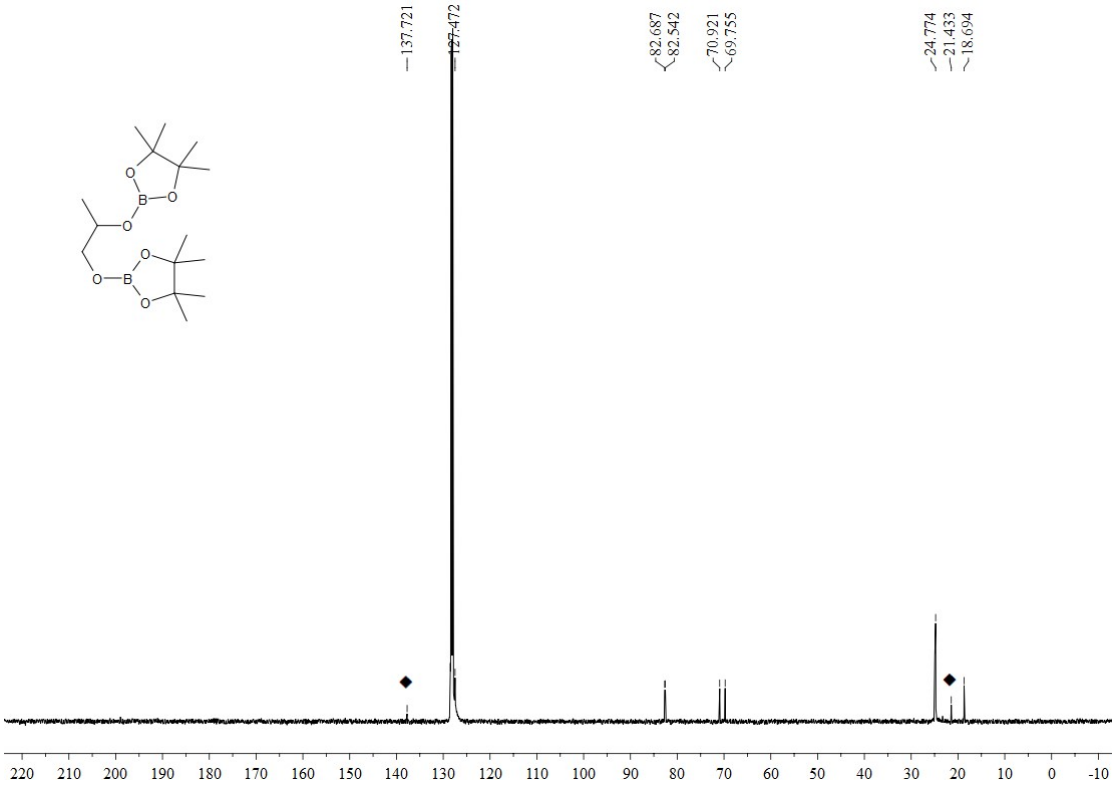


Figure S65. ^{13}C NMR spectrum (125 MHz, C_6D_6) of pinBOCH$_2$CMeOBpin (◆ represents mesitylene).

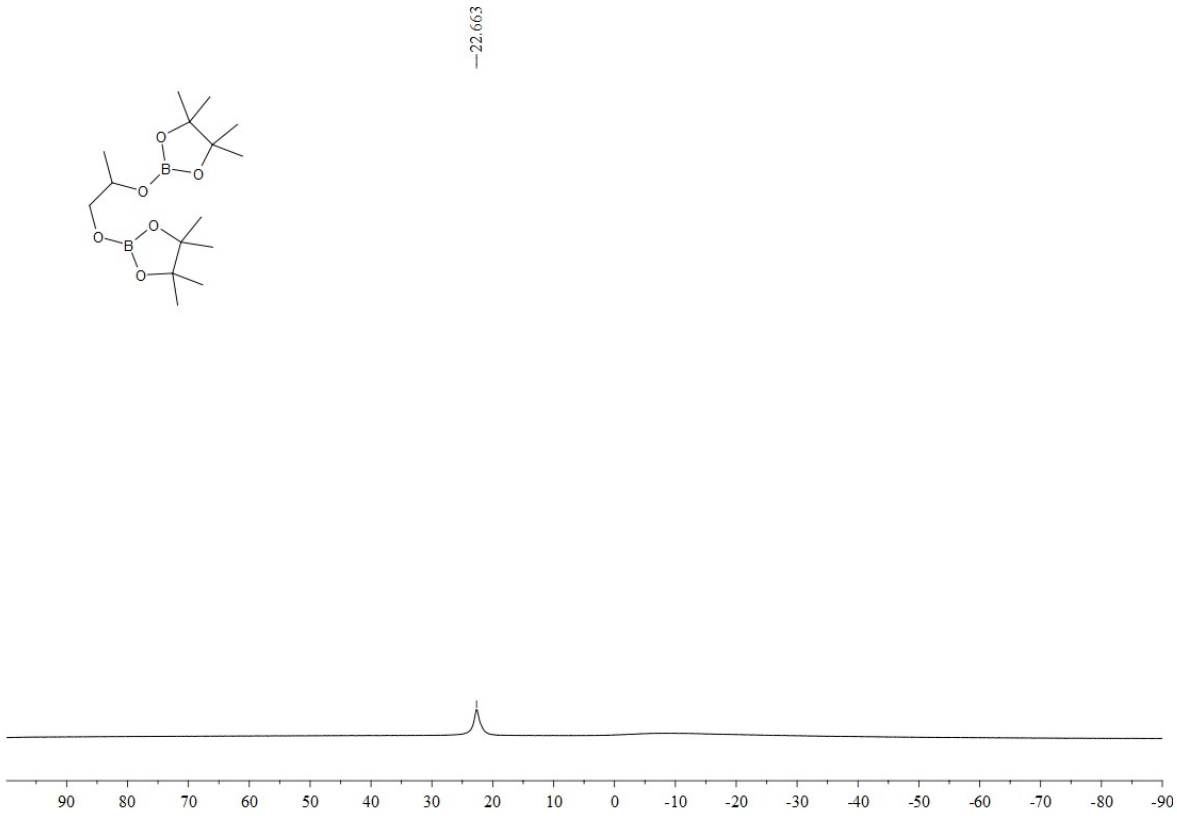


Figure S66. ^{11}B NMR spectrum (128 MHz, C_6D_6) of pinBOCH$_2$CMeOBpin (★ represents HBpin).

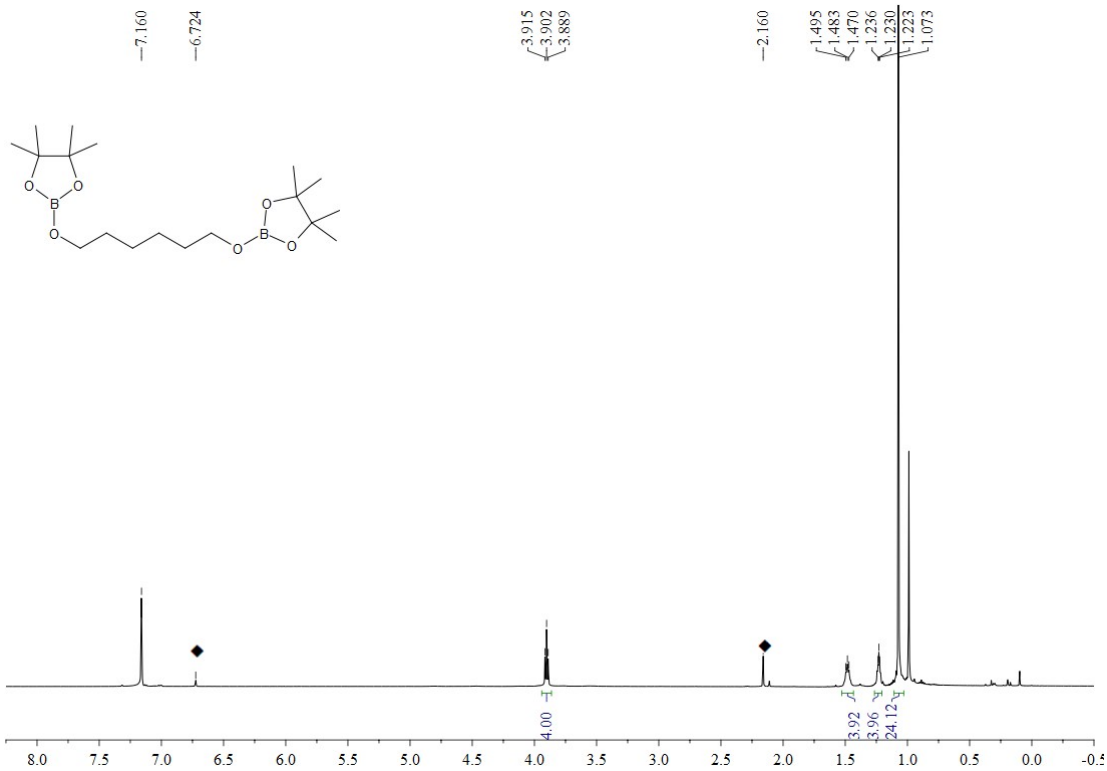


Figure S67. ^{1}H NMR spectrum (500 MHz, C_6D_6) of pinBOC$_6$H$_{12}$OBpin (◆ represents mesitylene)

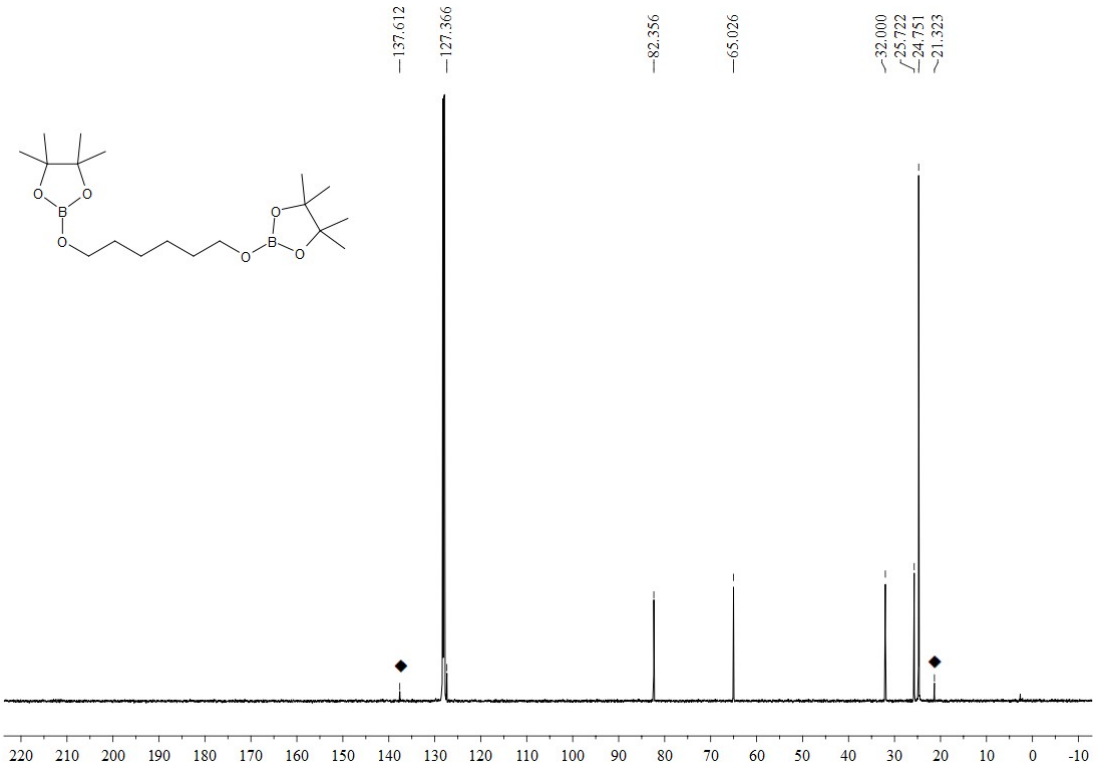


Figure S68. ^{13}C NMR spectrum (125 MHz, C_6D_6) of pin$BOC_6H_{12}OB$pin (◆ represents mesitylene).

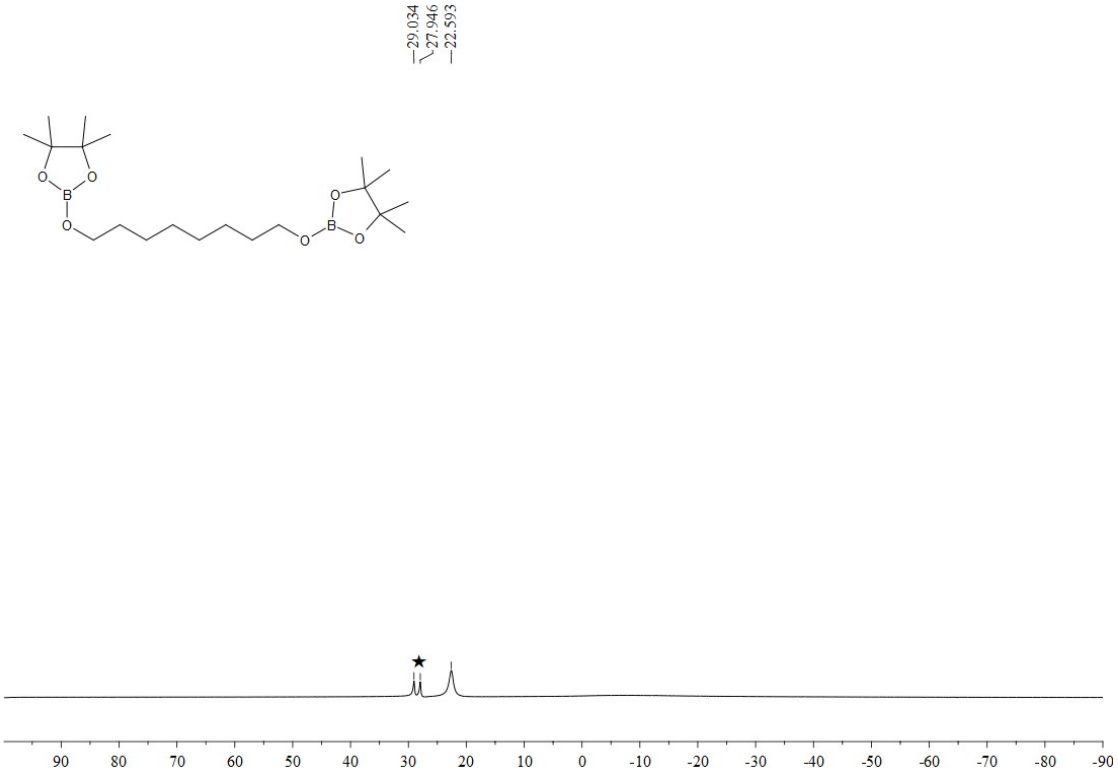


Figure S69. ^{11}B NMR spectrum (128 MHz, C_6D_6) of pin$BOC_6H_{12}OB$pin (★ represents HBpin).

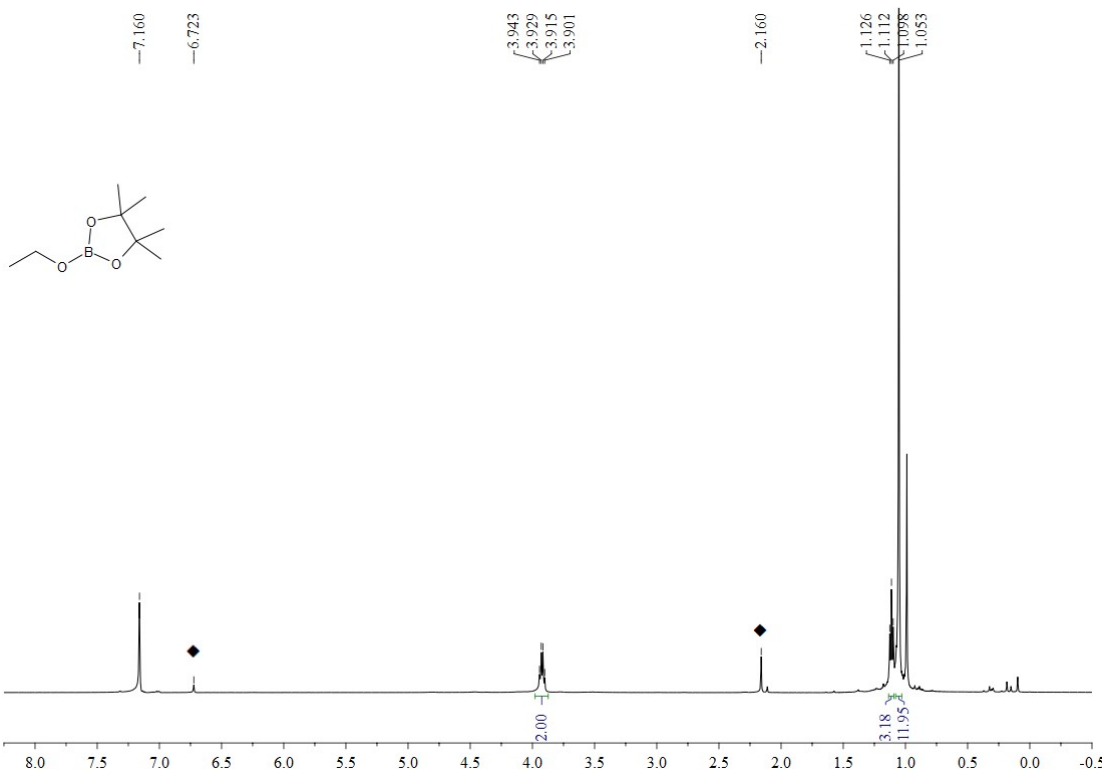


Figure S70. ^{1}H NMR spectrum (500 MHz, C_6D_6) of EtOBpin (◆ represents mesitylene)

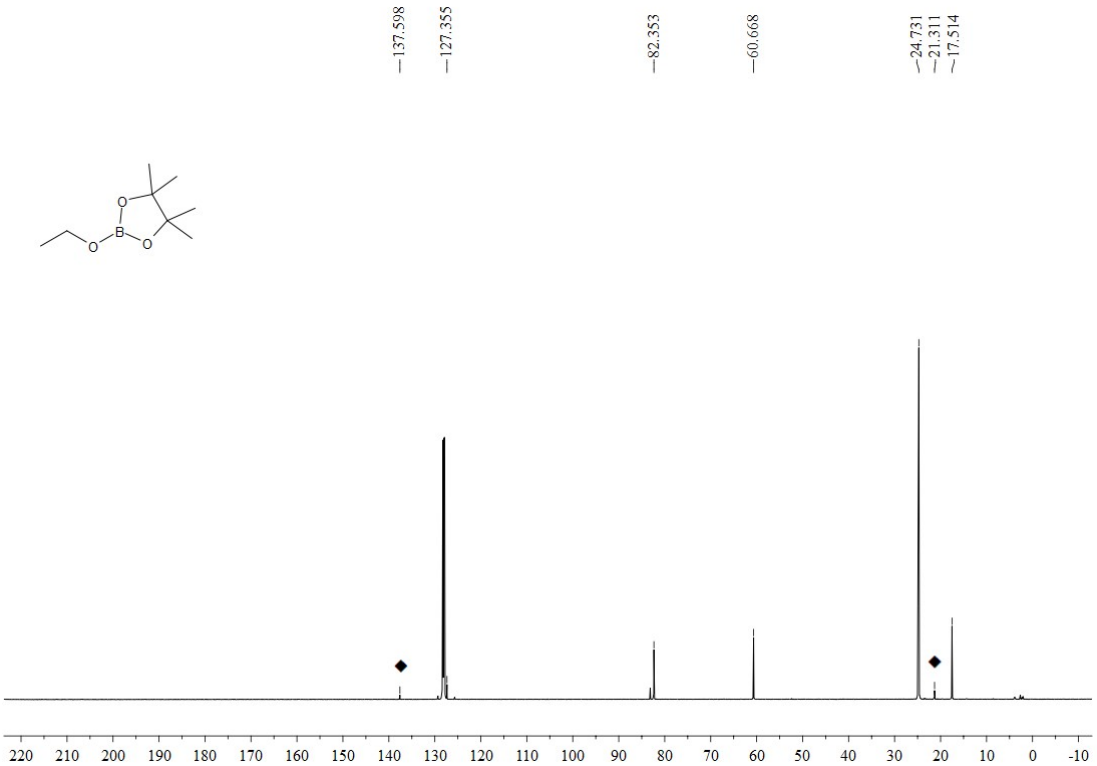


Figure S71. ^{13}C NMR spectrum (125 MHz, C_6D_6) of EtOBpin (◆ represents mesitylene)

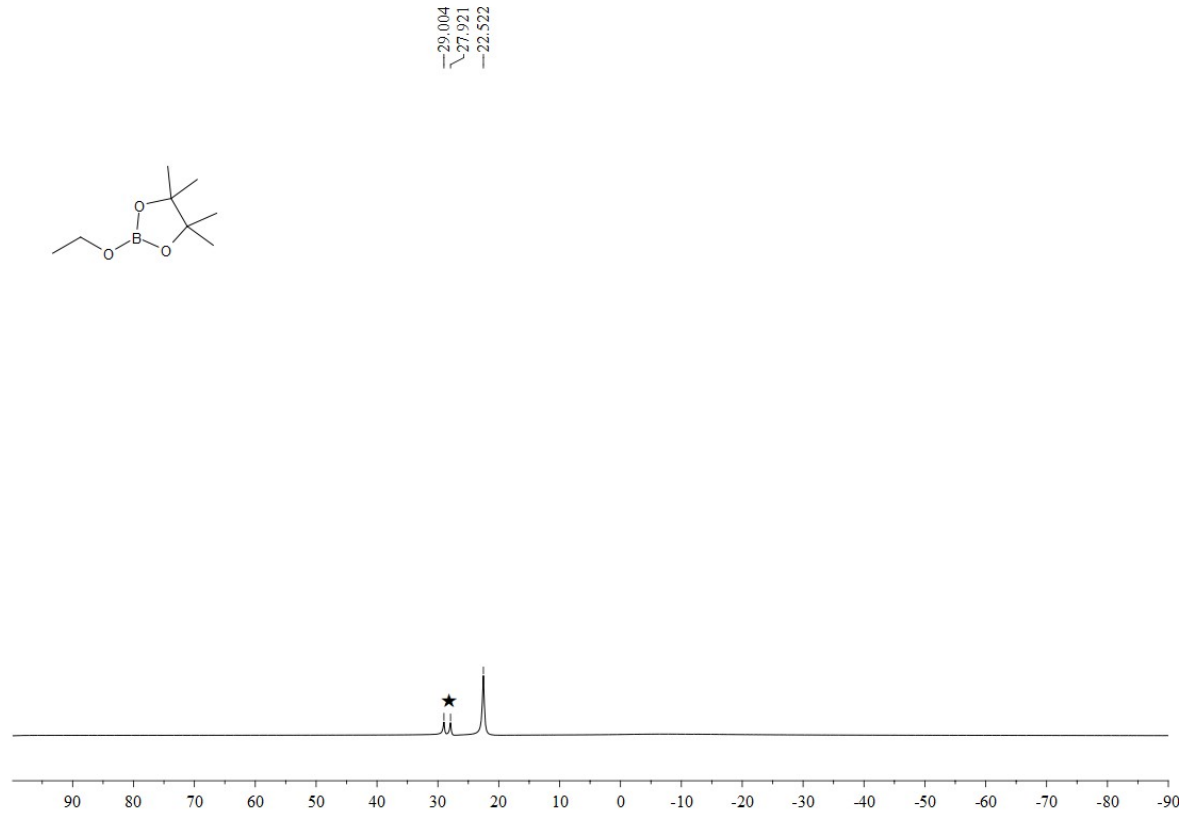


Figure S72. ^{11}B NMR spectrum (128 MHz, C_6D_6) of EtOBpin (★ represents HBpin).

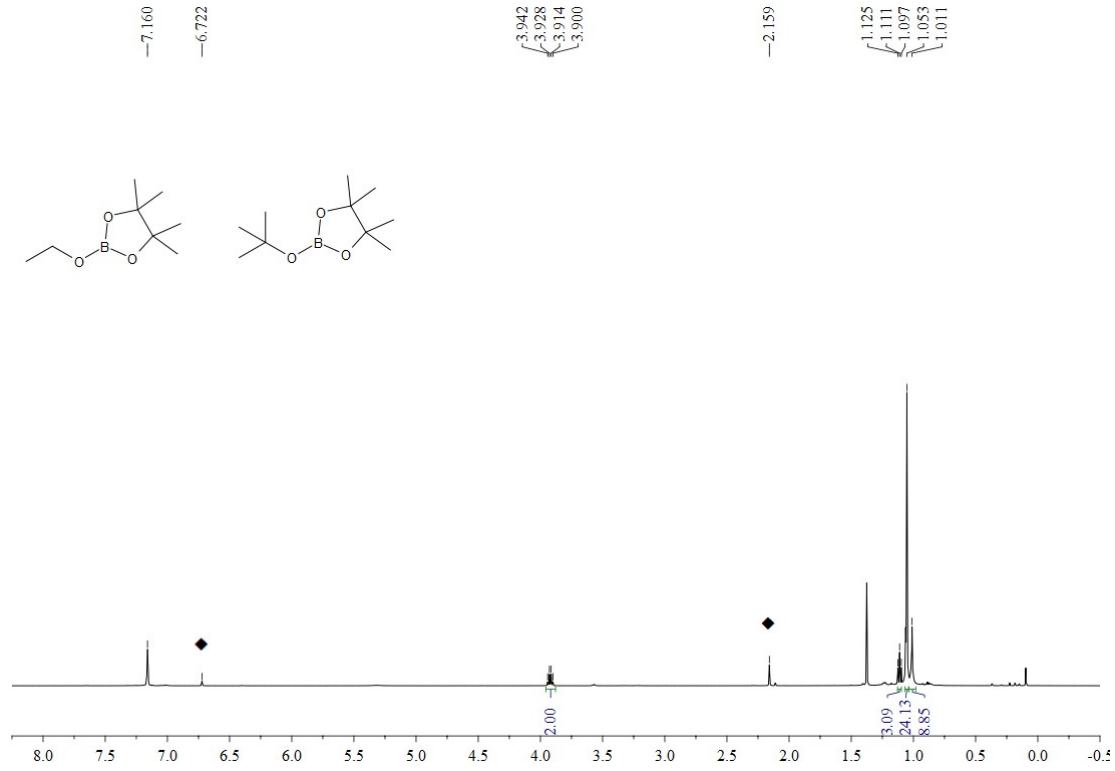


Figure S73. ^{1}H NMR spectrum (500 MHz, C_6D_6) of EtOBpin/ ^{t}BuOBpin (◆ represents mesitylene)

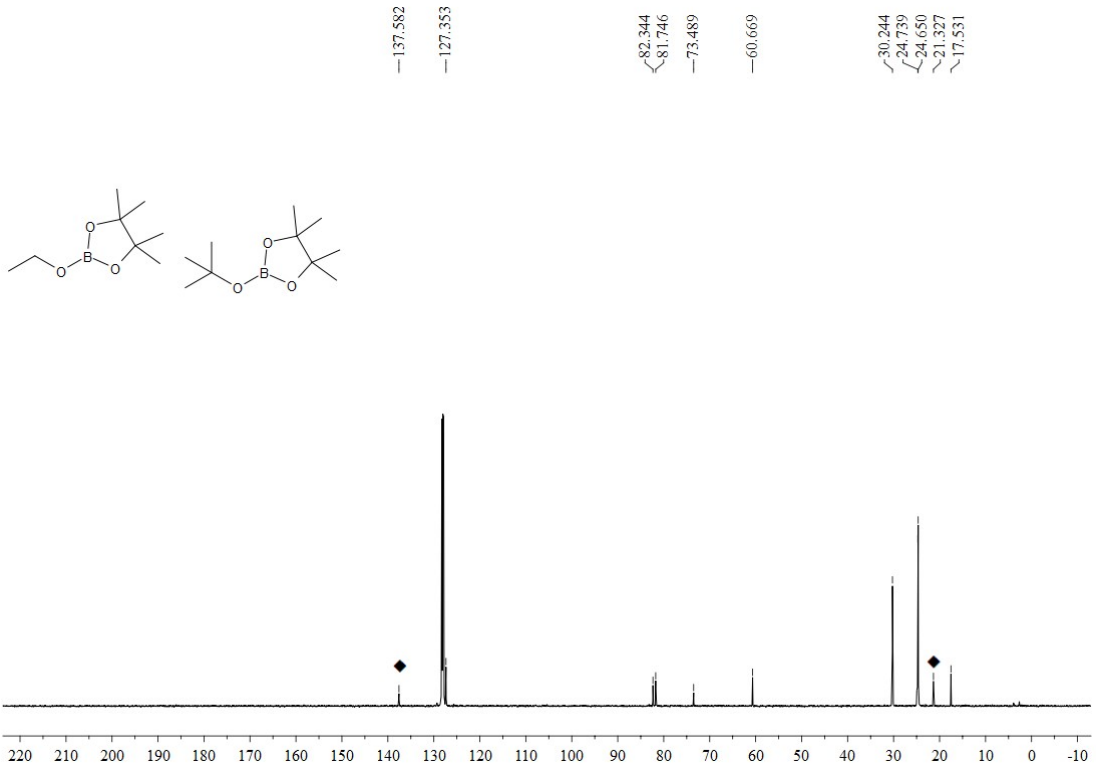


Figure S74. ^{13}C NMR spectrum (125 MHz, C_6D_6) of EtOBpin/ ^{t}BuOBpin (◆ represents mesitylene).

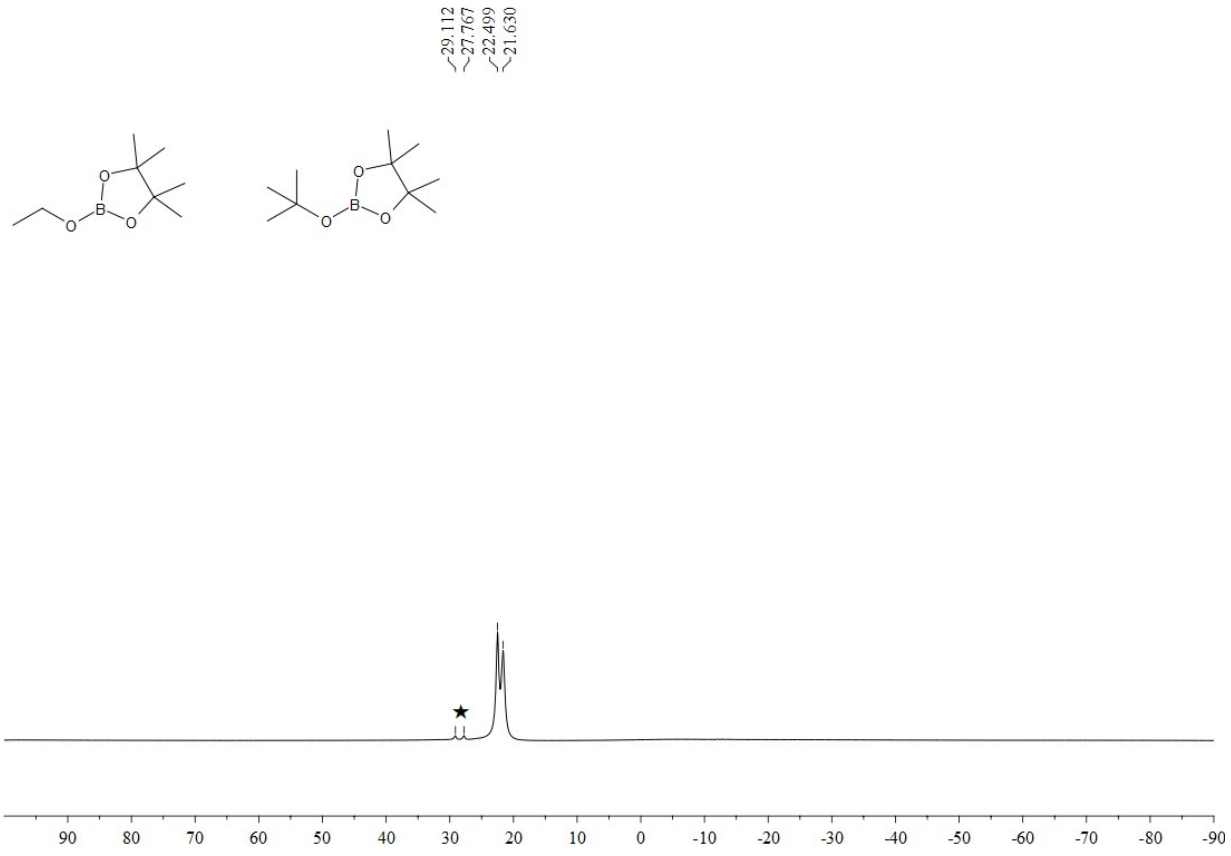


Figure S75. ^{11}B NMR spectrum (128 MHz, C_6D_6) of EtOBpin/ ^{t}BuOBpin (★ represents HBpin).

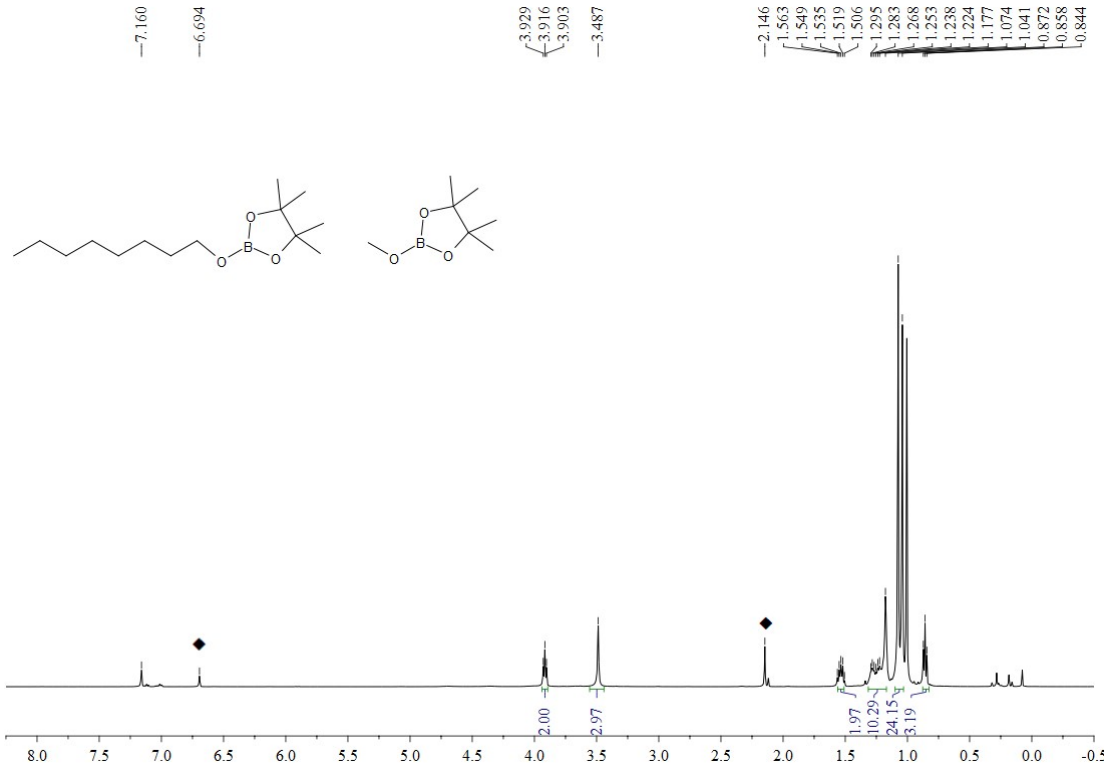


Figure S76. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $C_8H_{17}OBpin$/MeOBpin (◆ represents mesitylene)

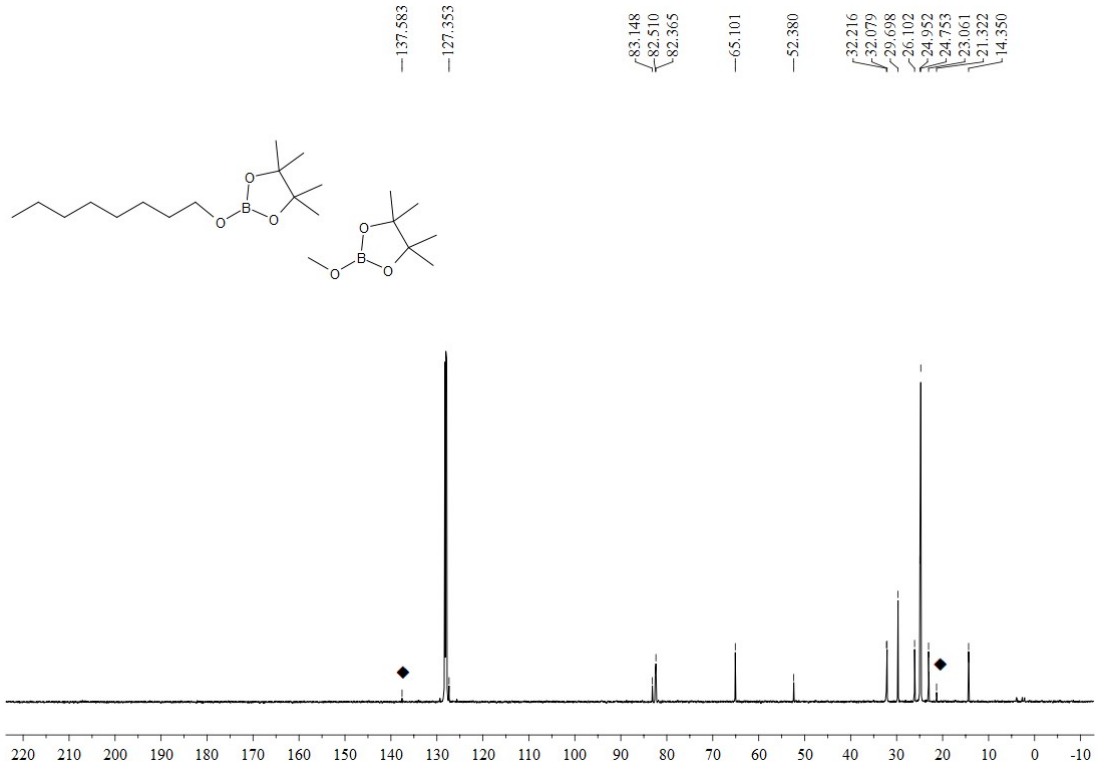


Figure S77. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $C_8H_{17}OBpin$/MeOBpin (◆ represents mesitylene).

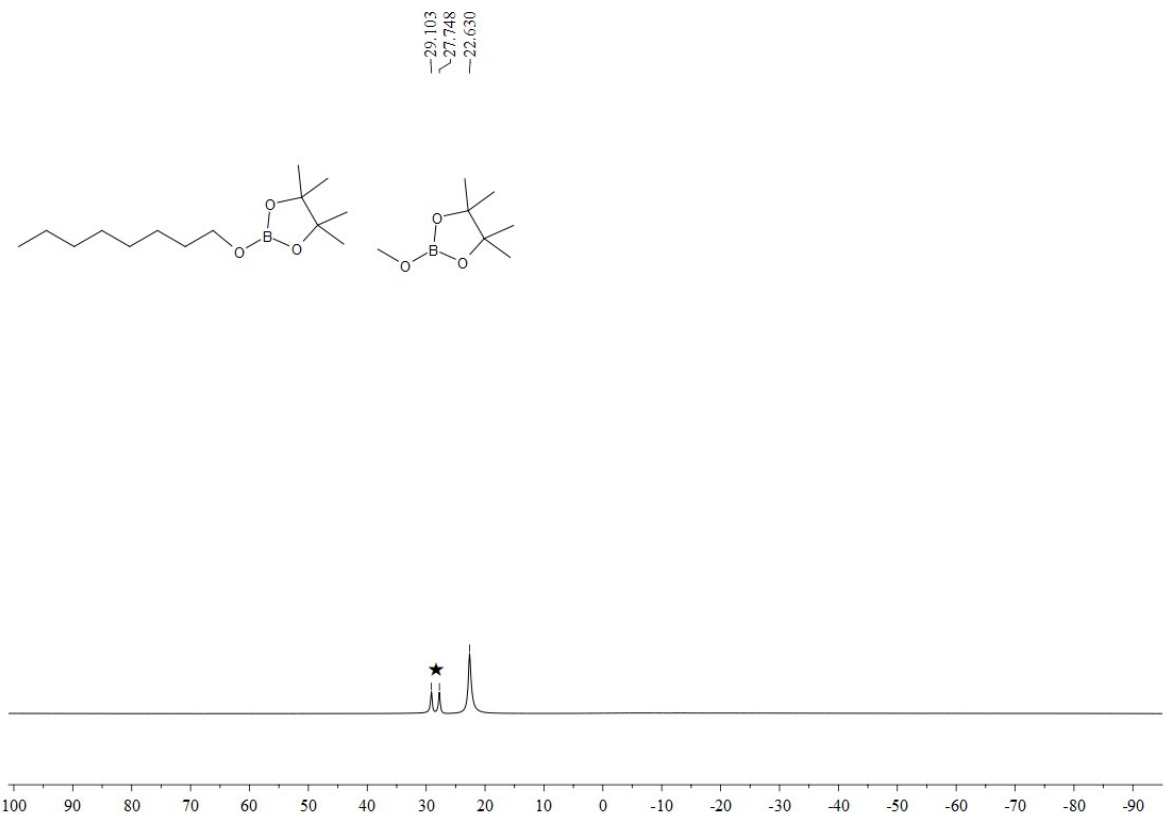


Figure S78. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $C_8H_{17}OBpin$/MeOBpin (★ represents HBpin).

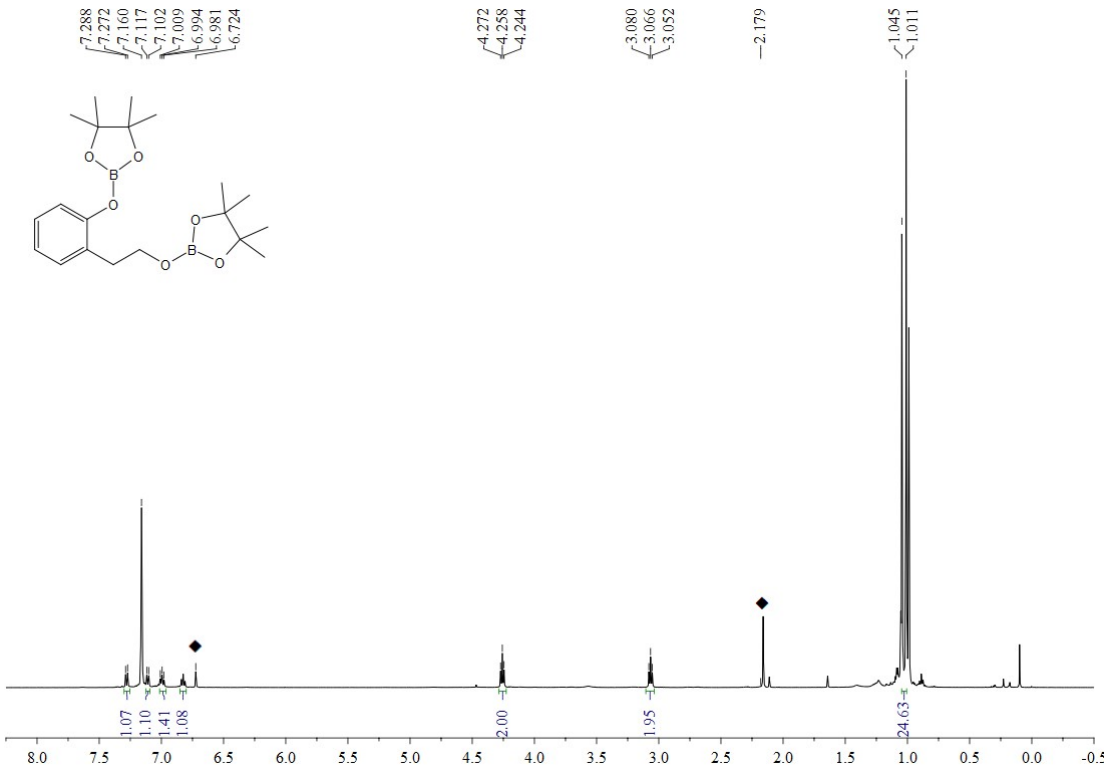


Figure S79. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $pinBOPhCH_2CH_2OBpin$ (◆ represents mesitylene)

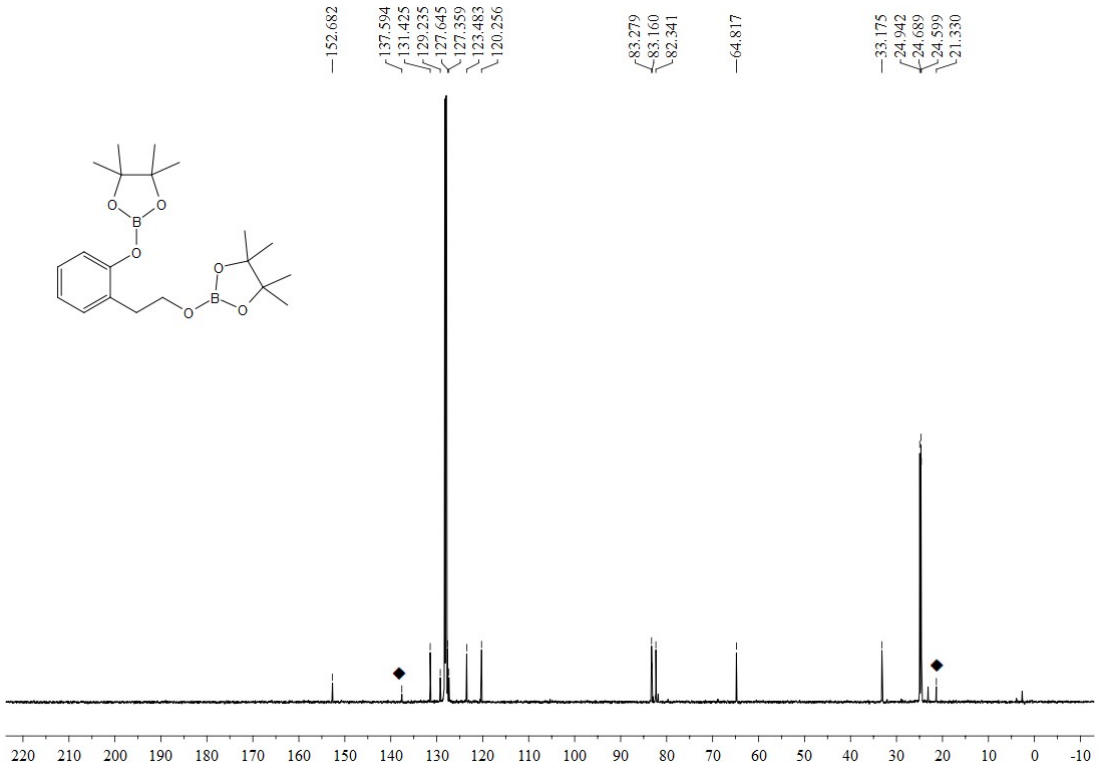


Figure S80. ^{13}C NMR spectrum (125 MHz, C_6D_6) of pinBOPhCH_2CH_2OBpin (◆ represents mesitylene).

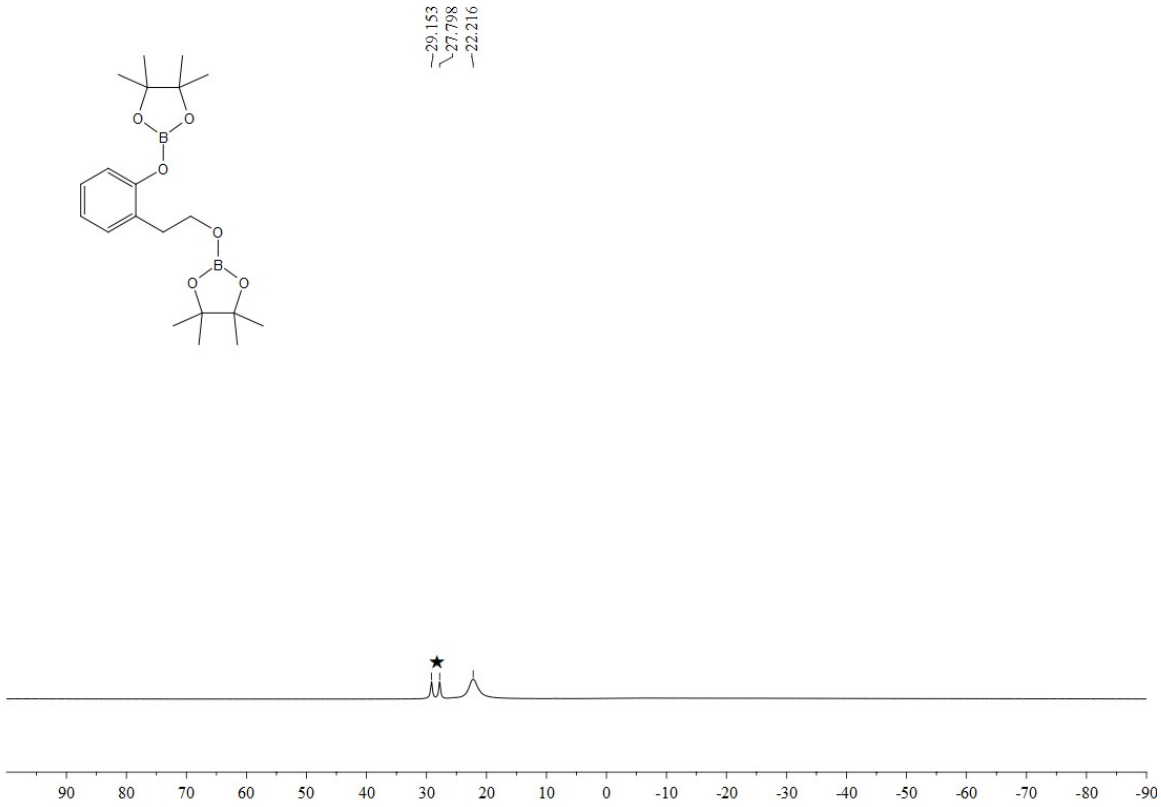


Figure S81. ^{11}B NMR spectrum (128 MHz, C_6D_6) of pinBOPhCH_2CH_2OBpin (★ represents HBpin).

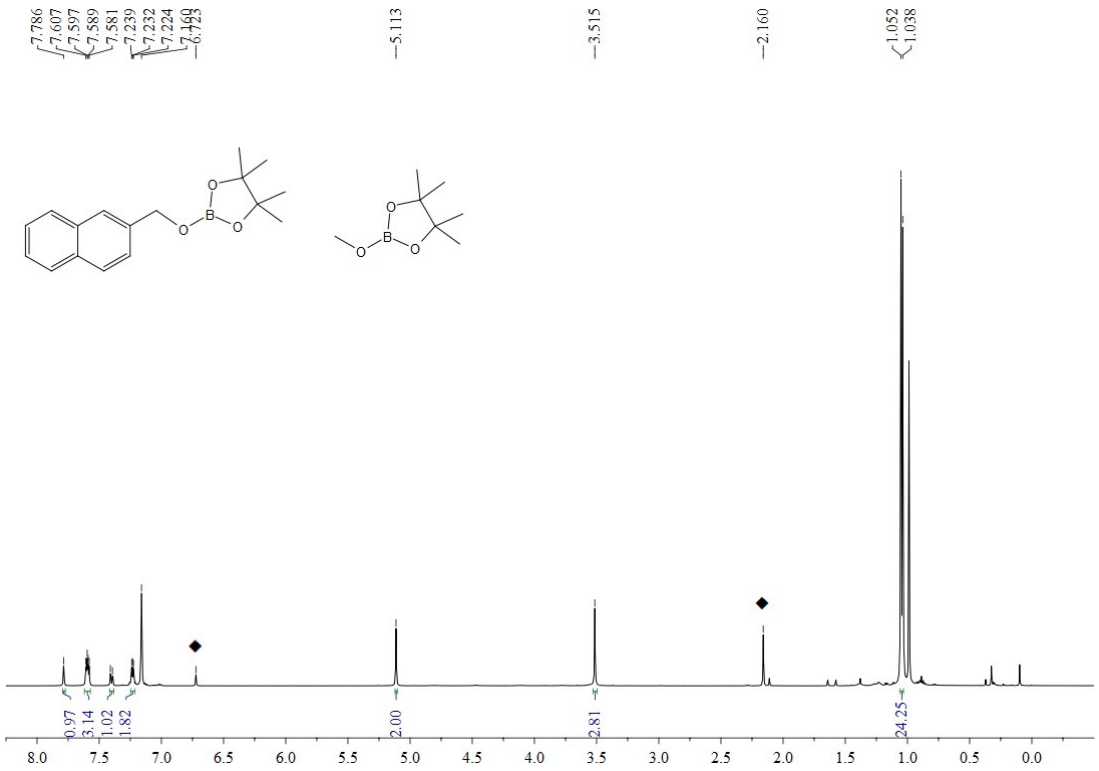


Figure S82. ^{1}H NMR spectrum (500 MHz, C_6D_6) of naphthyl-CH_2OBpin/MeOBpin (◆ represents mesitylene)

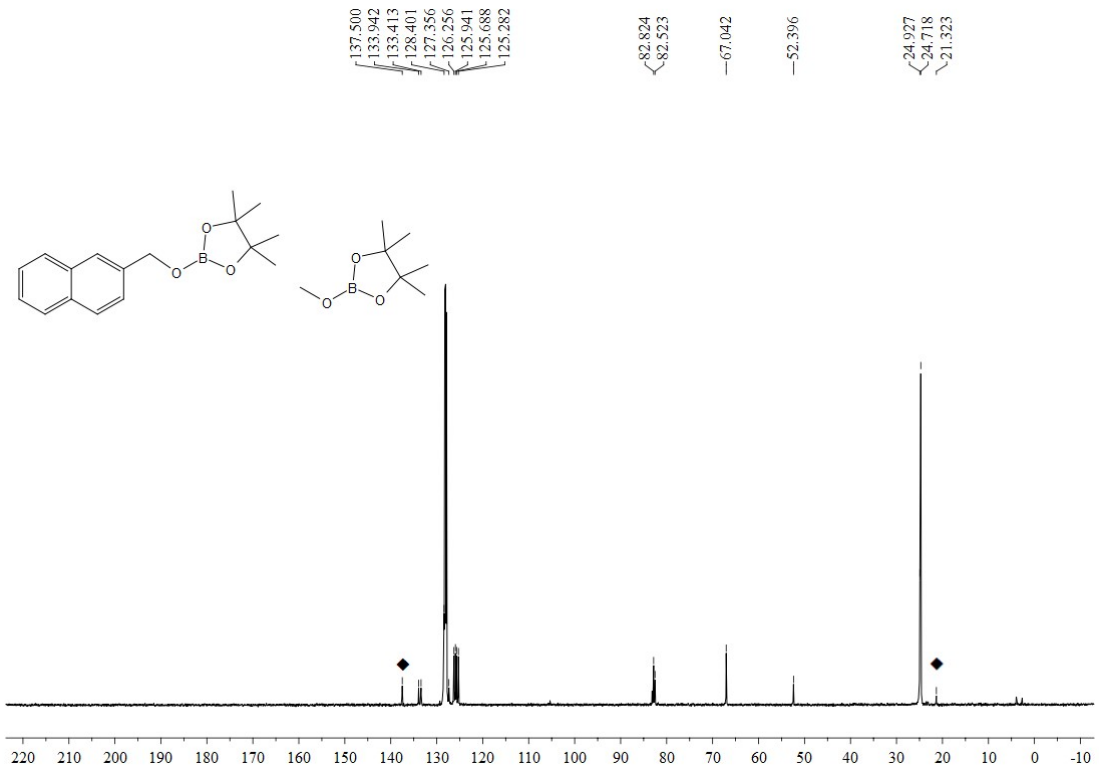


Figure S83. ^{13}C NMR spectrum (125 MHz, C_6D_6) of naphthyl-CH_2OBpin/MeOBpin (◆ represents mesitylene).

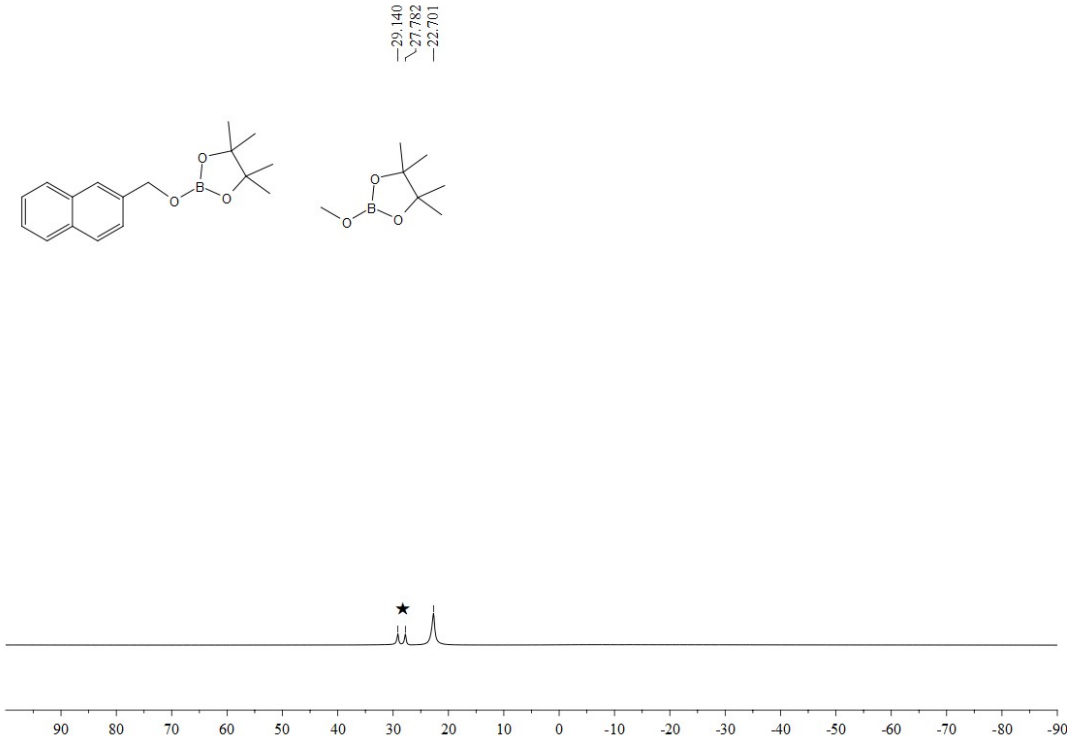


Figure S84. ^{11}B NMR spectrum (128 MHz, C_6D_6) of naphthyl-CH_2OBpin/MeOBpin (★ represents HBpin).

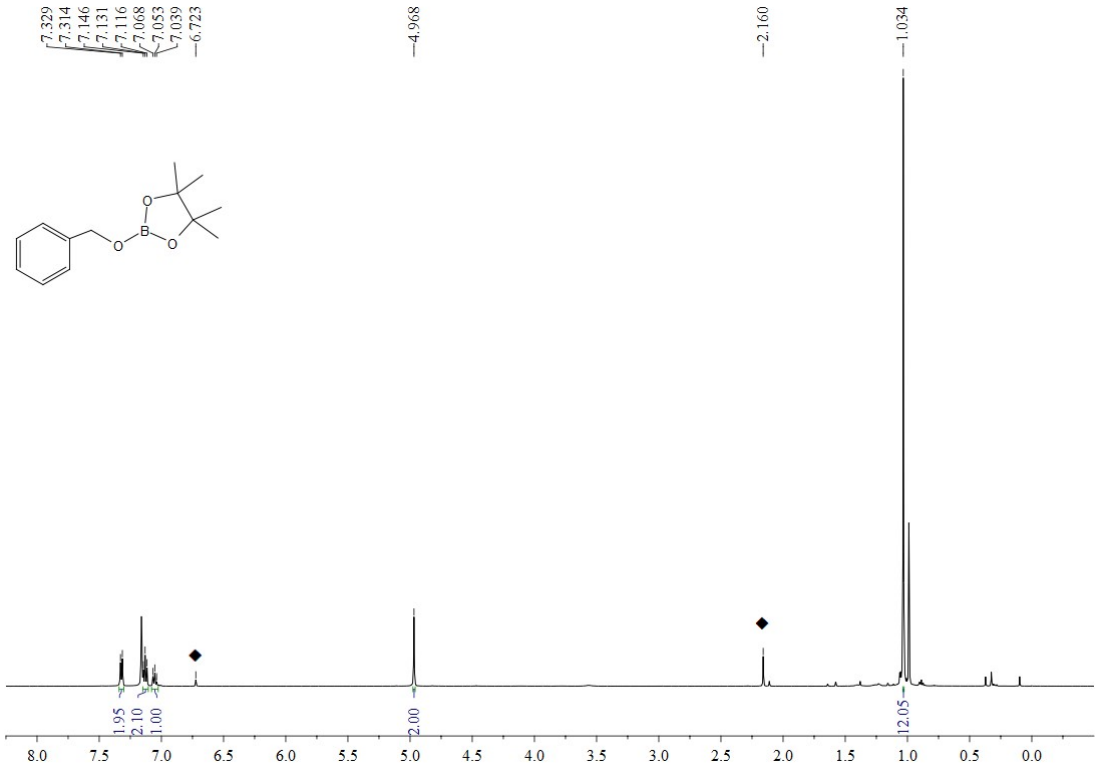


Figure S85. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $PhCH_2OBpin$ (◆ represents mesitylene)

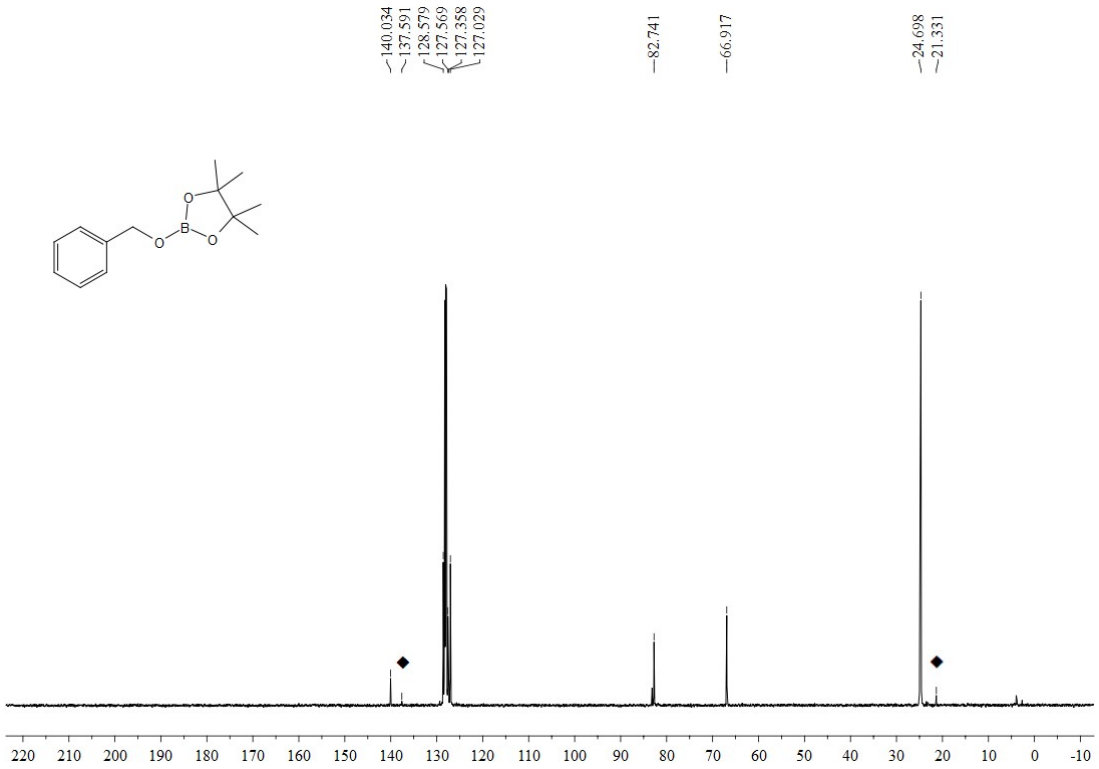


Figure S86. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $PhCH_2OBpin$ (◆ represents mesitylene).

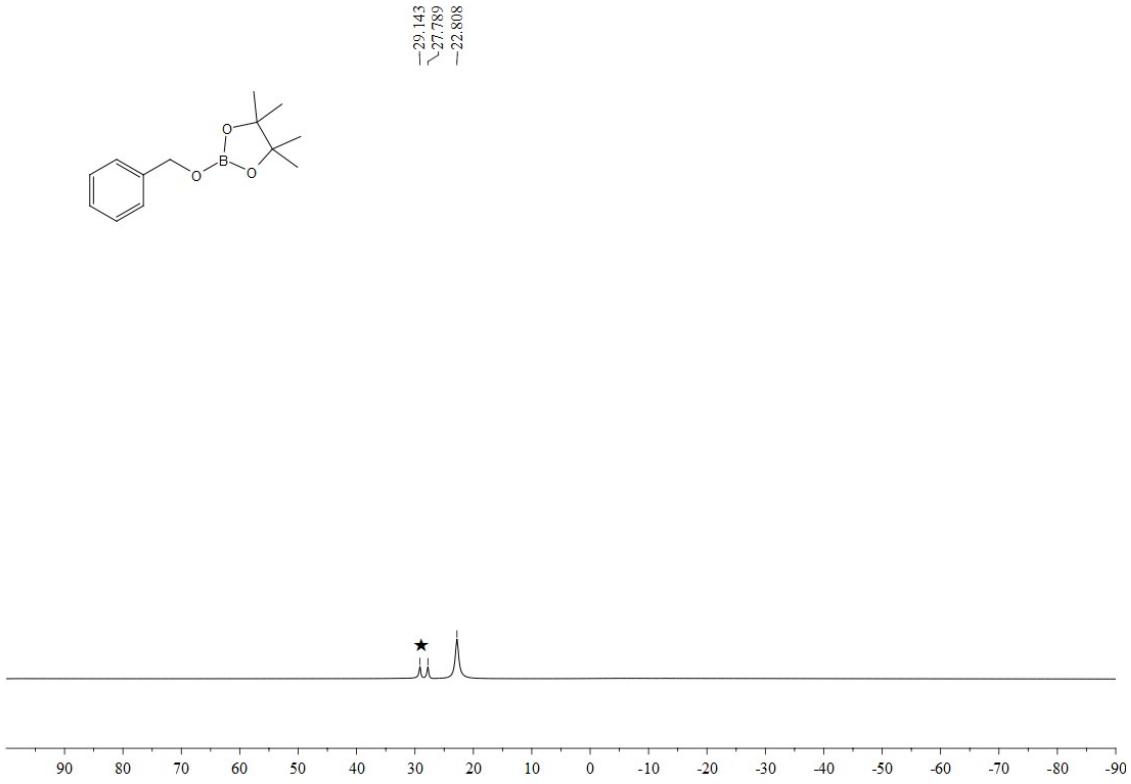


Figure S87. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $PhCH_2OBpin$ (★ represents HBpin).

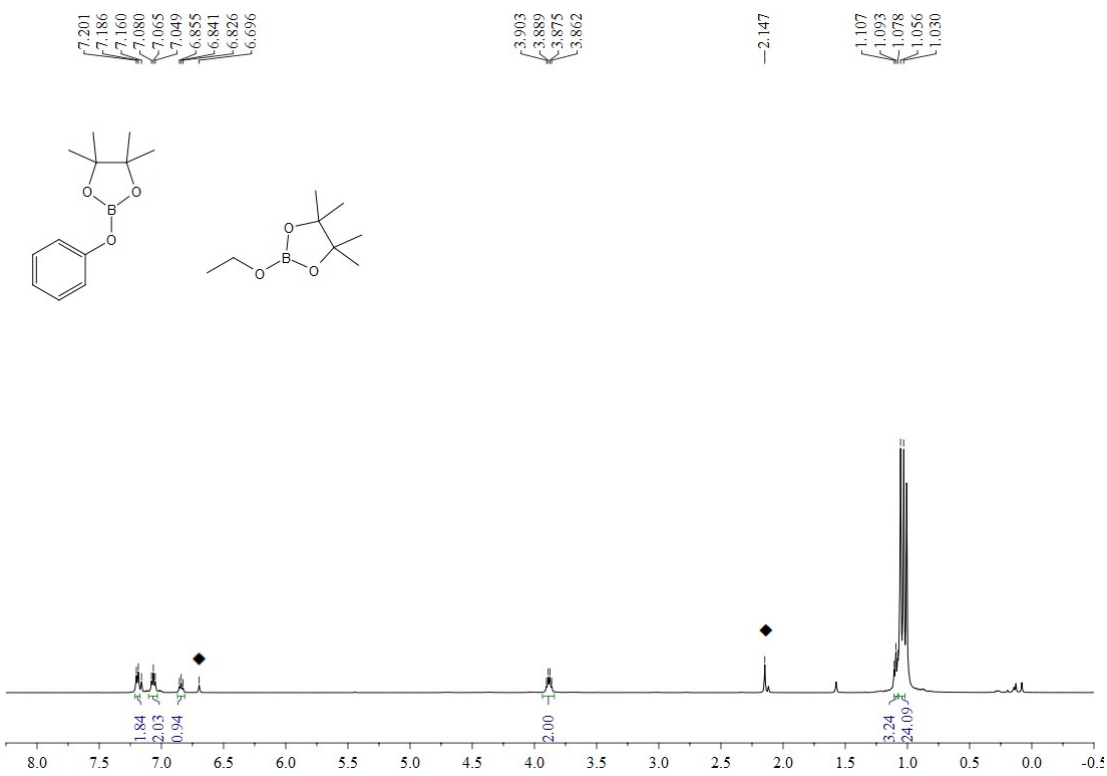


Figure S88. ^{1}H NMR spectrum (500 MHz, C_6D_6) of PhOBpin/EtOBpin (◆ represents mesitylene)

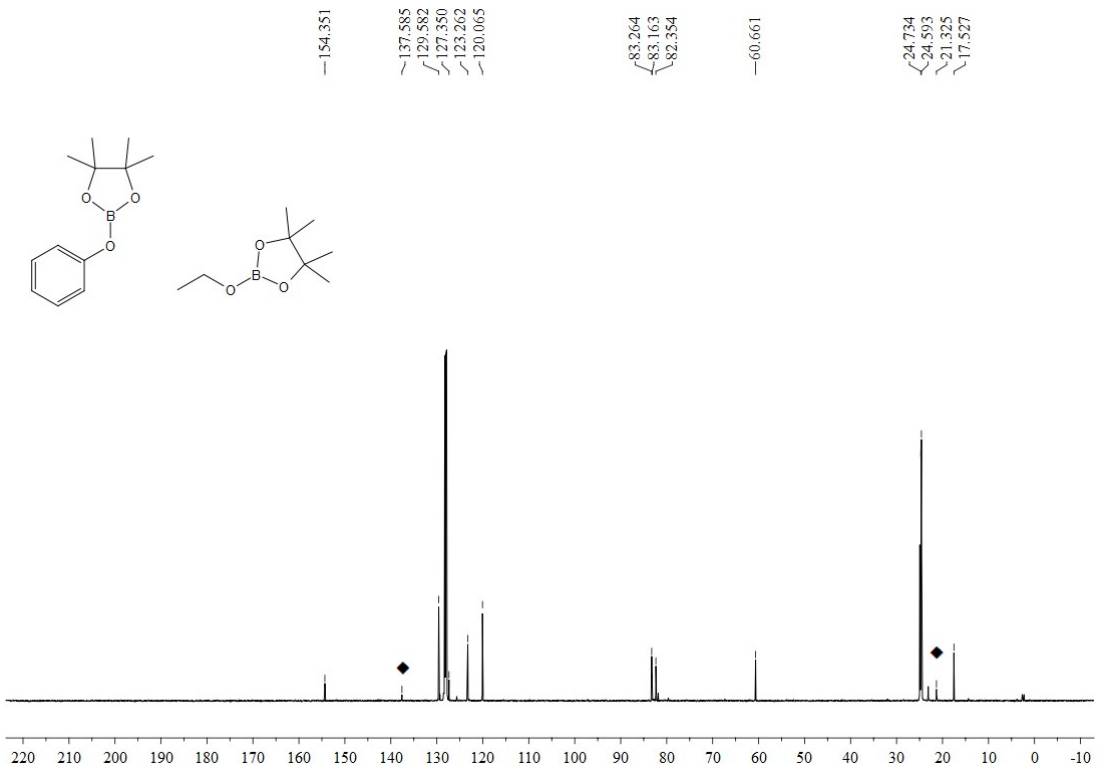


Figure S89. ^{13}C NMR spectrum (125 MHz, C_6D_6) of PhOBpin/EtOBpin (◆ represents mesitylene).

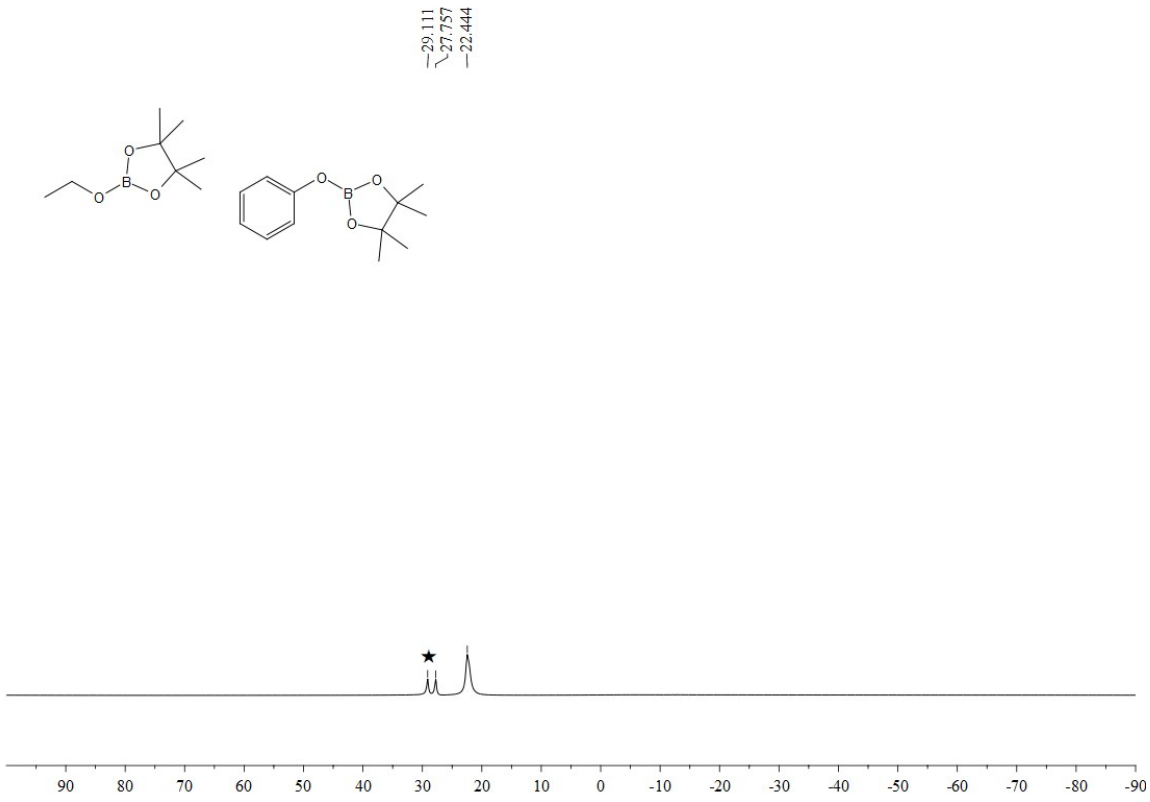


Figure S90. ^{11}B NMR spectrum (128 MHz, C_6D_6) ofEtOBpin /PhOBpin (★ represents HBpin).

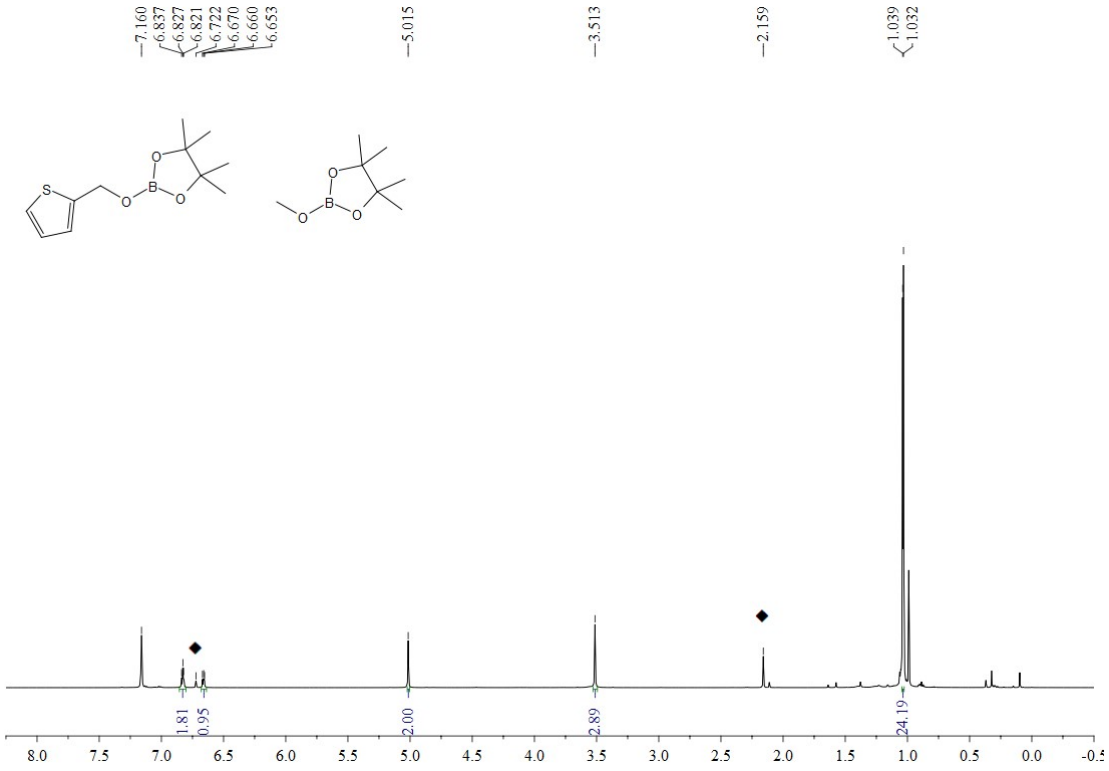


Figure S91. ^{1}H NMR spectrum (500 MHz, C_6D_6) of 2-thienyl-CH_2OBpin/MeOBpin (◆ represents mesitylene).

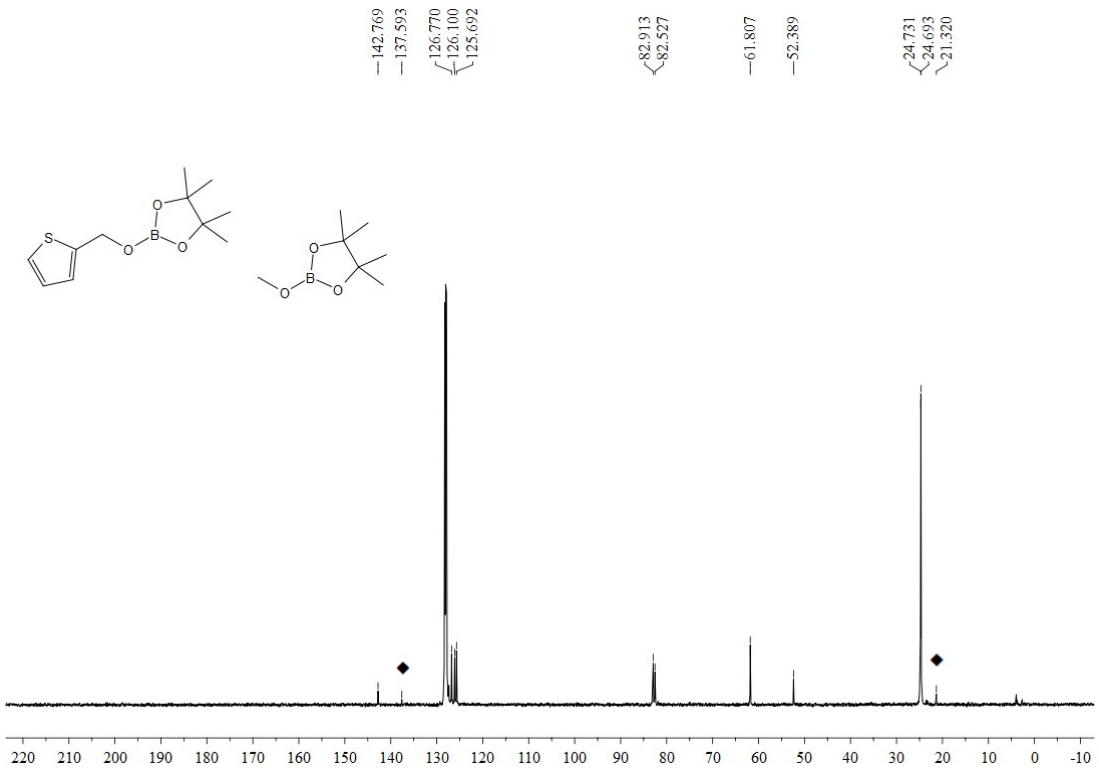


Figure S92. ^{13}C NMR spectrum (125 MHz, C_6D_6) of 2-thienyl-CH_2OBpin/MeOBpin (◆ represents mesitylene)

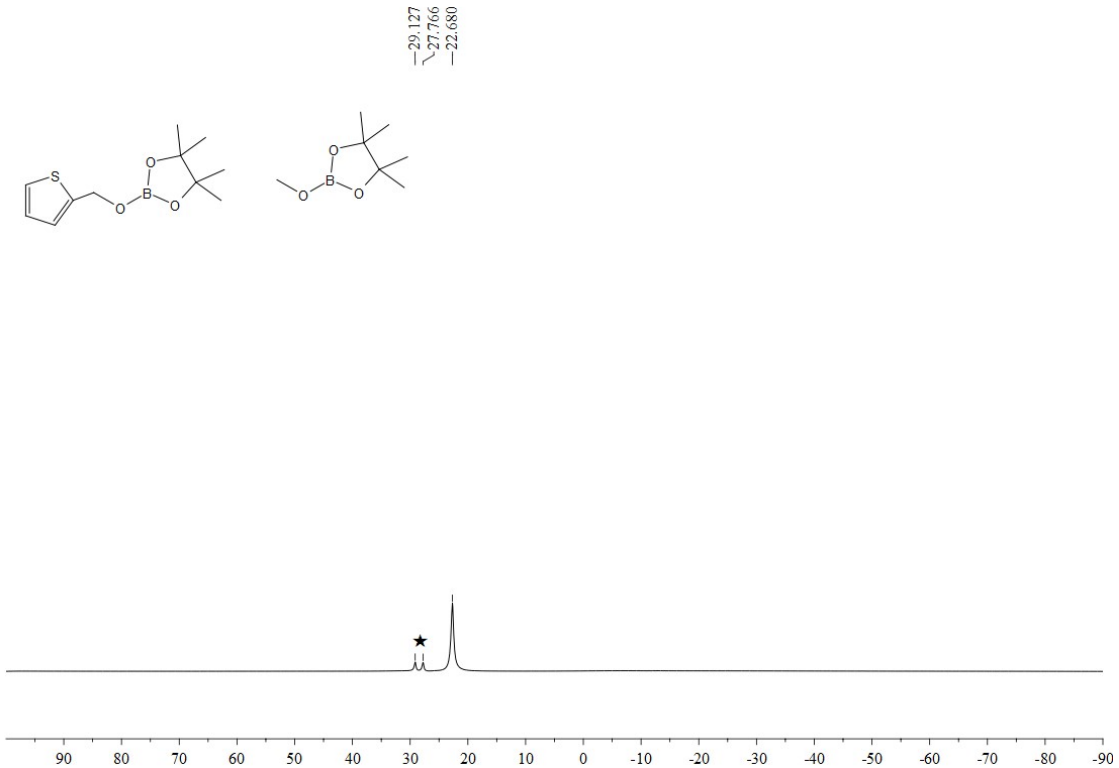


Figure S93. ^{11}B NMR spectrum (128 MHz, C_6D_6) of 2-thienyl-CH_2OBpin/MeOBpin (★ represents HBpin).

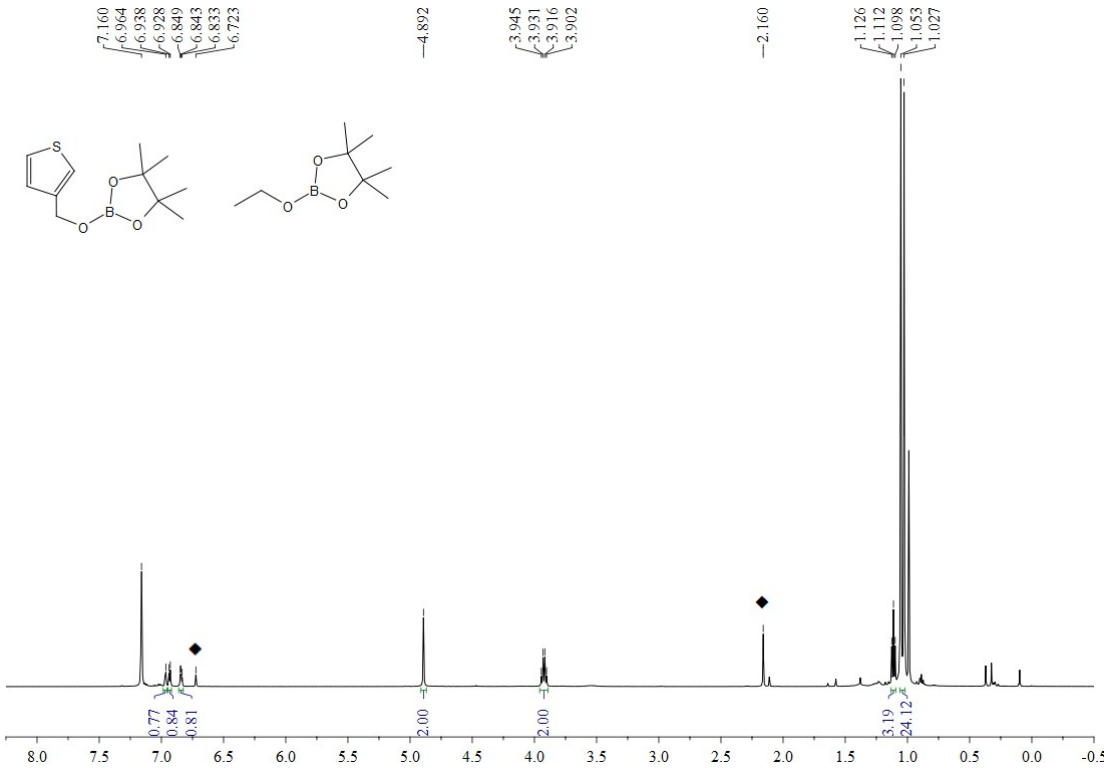


Figure S94. ^{1}H NMR spectrum (500 MHz, C_6D_6) of 3-thienyl-CH_2OBpin/EtOBpin (◆ represents mesitylene).

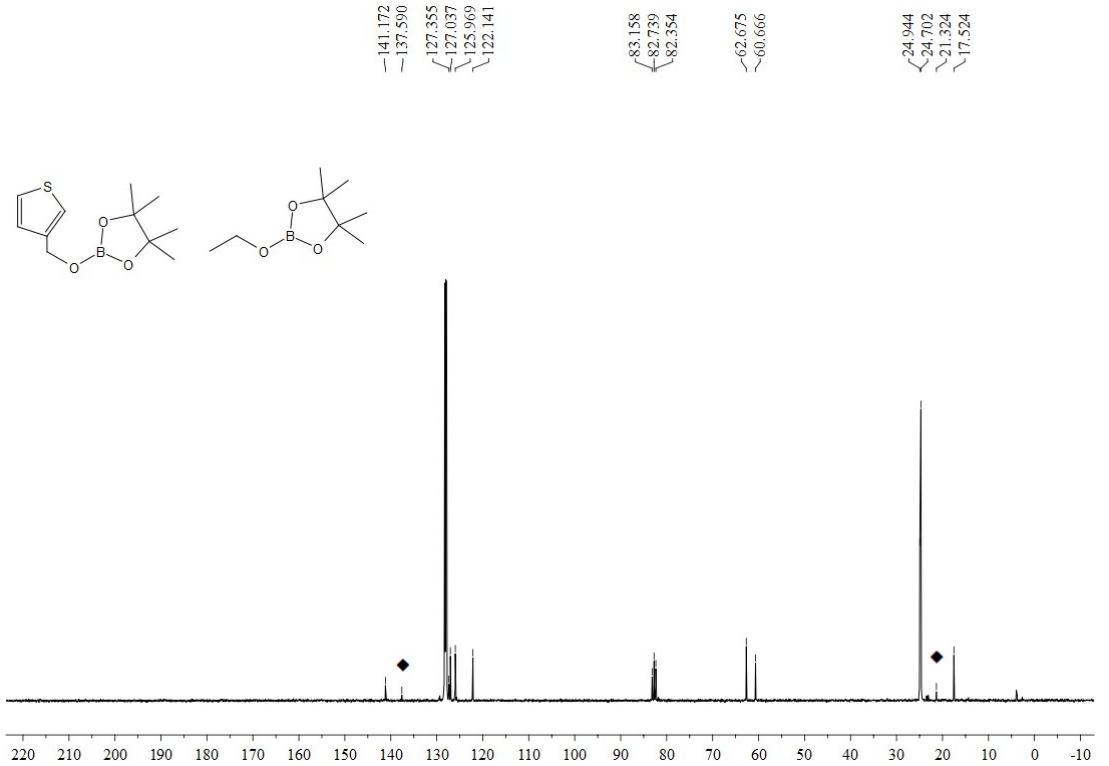


Figure S95. ^{13}C NMR spectrum (125 MHz, C_6D_6) of 3-thienyl-CH_2OBpin/EtOBpin. (◆ represents mesitylene).

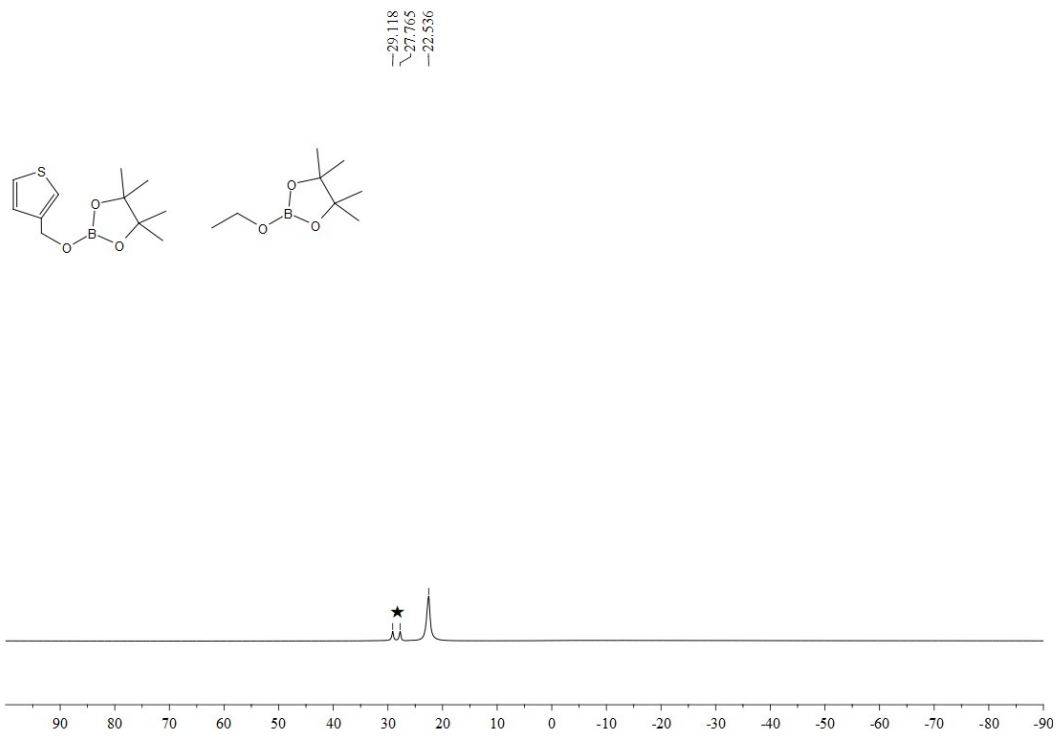


Figure S96. ^{11}B NMR spectrum (128 MHz, C_6D_6) of 3-thienyl-CH_2OBpin/EtOBpin (★ represents HBpin).

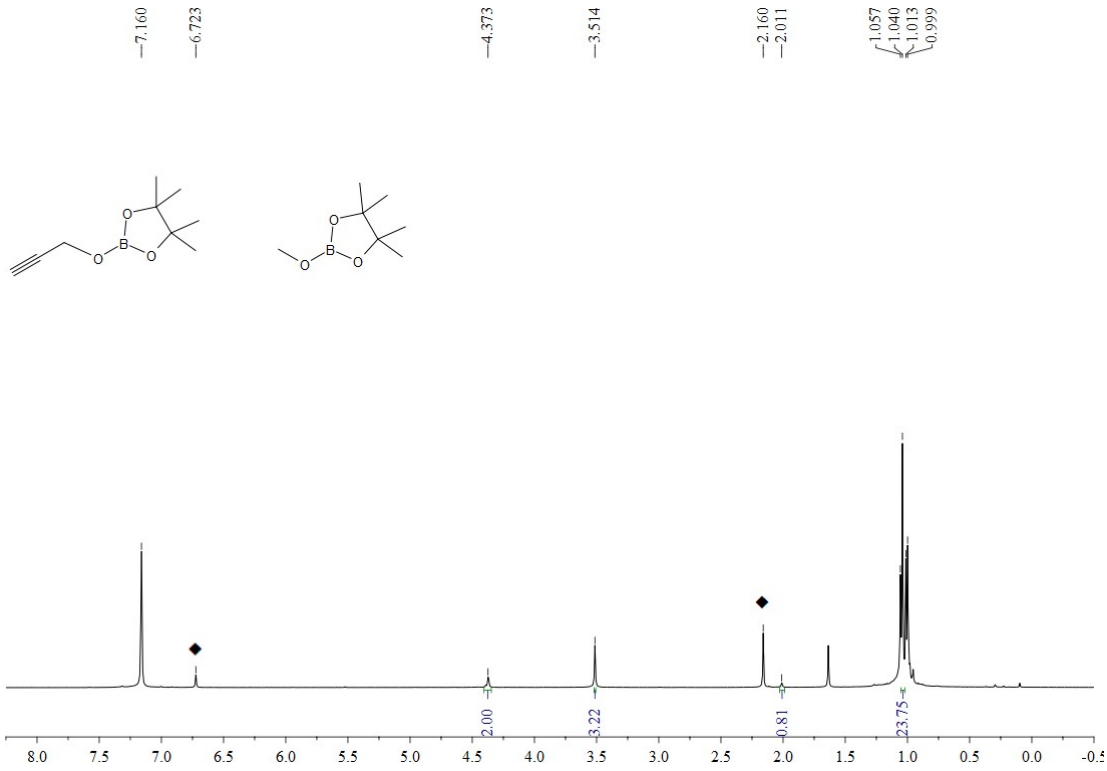


Figure S97. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $HCCCH_2OBpin$/MeOBpin (◆ represents mesitylene).

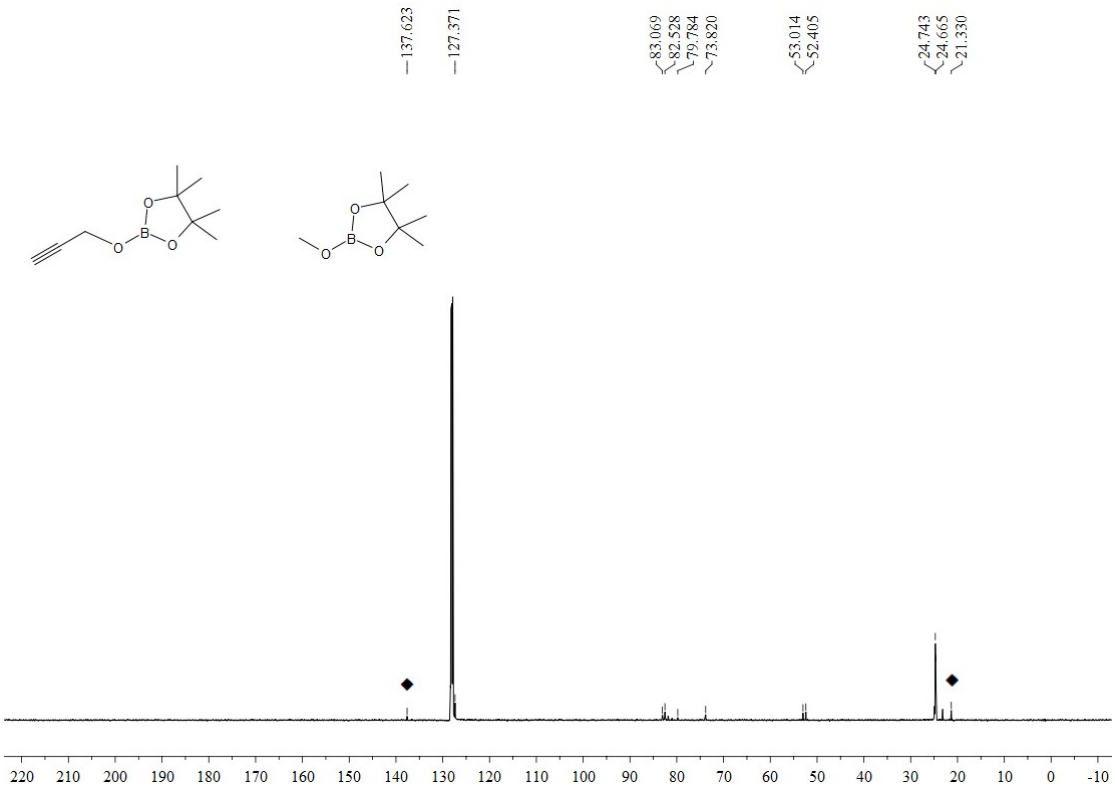


Figure S98. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $HCCCH_2OBpin$/MeOBpin (◆ represents mesitylene).

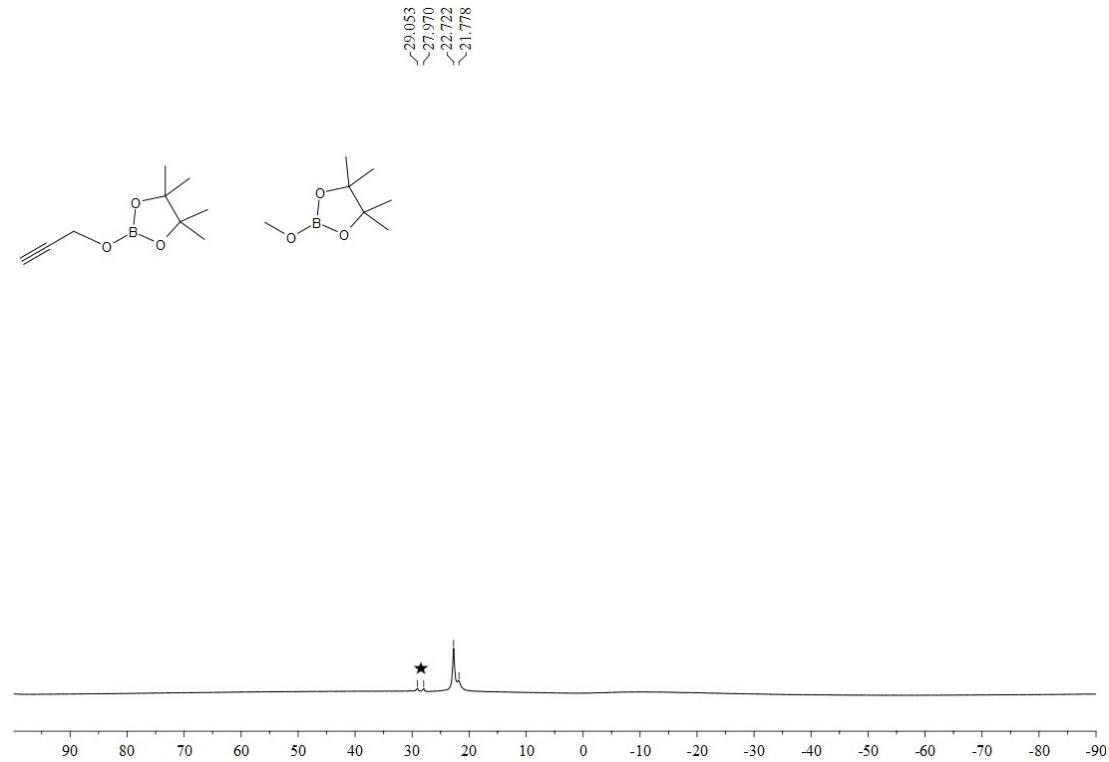


Figure S99. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $HCCCH_2OBpin$/MeOBpin (★ represents HBpin).

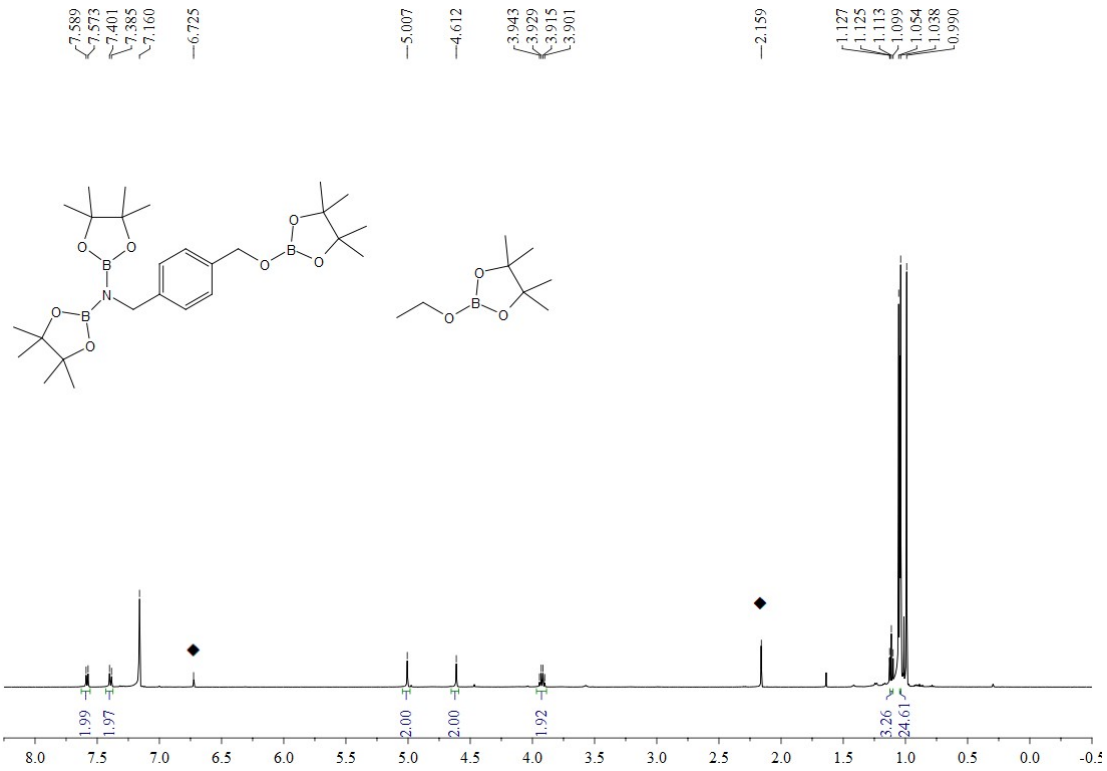


Figure S100. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $(pinB)_2NCH_2C_6H_4CH_2OBpin$/EtOBpin (◆ represents mesitylene)

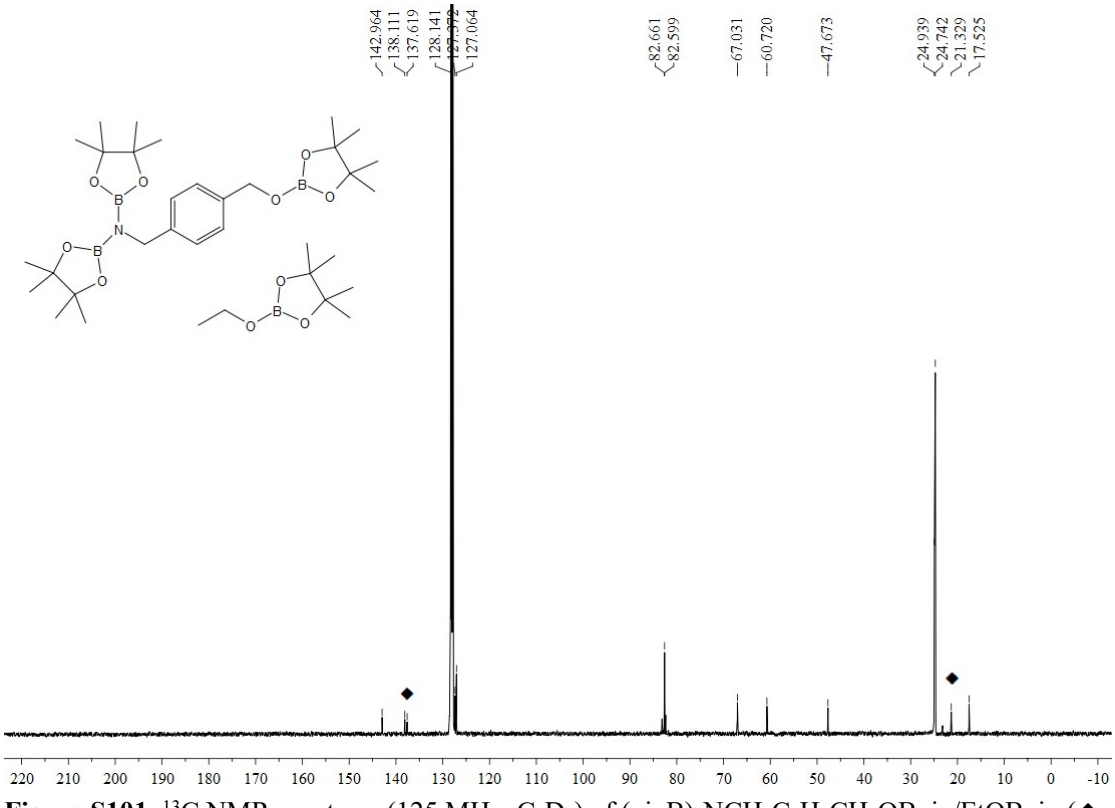


Figure S101. ^{13}C NMR spectrum (125 MHz, C_6D_6) of $(pinB)_2NCH_2C_6H_4CH_2OBpin$/EtOBpin (◆ represents mesitylene).

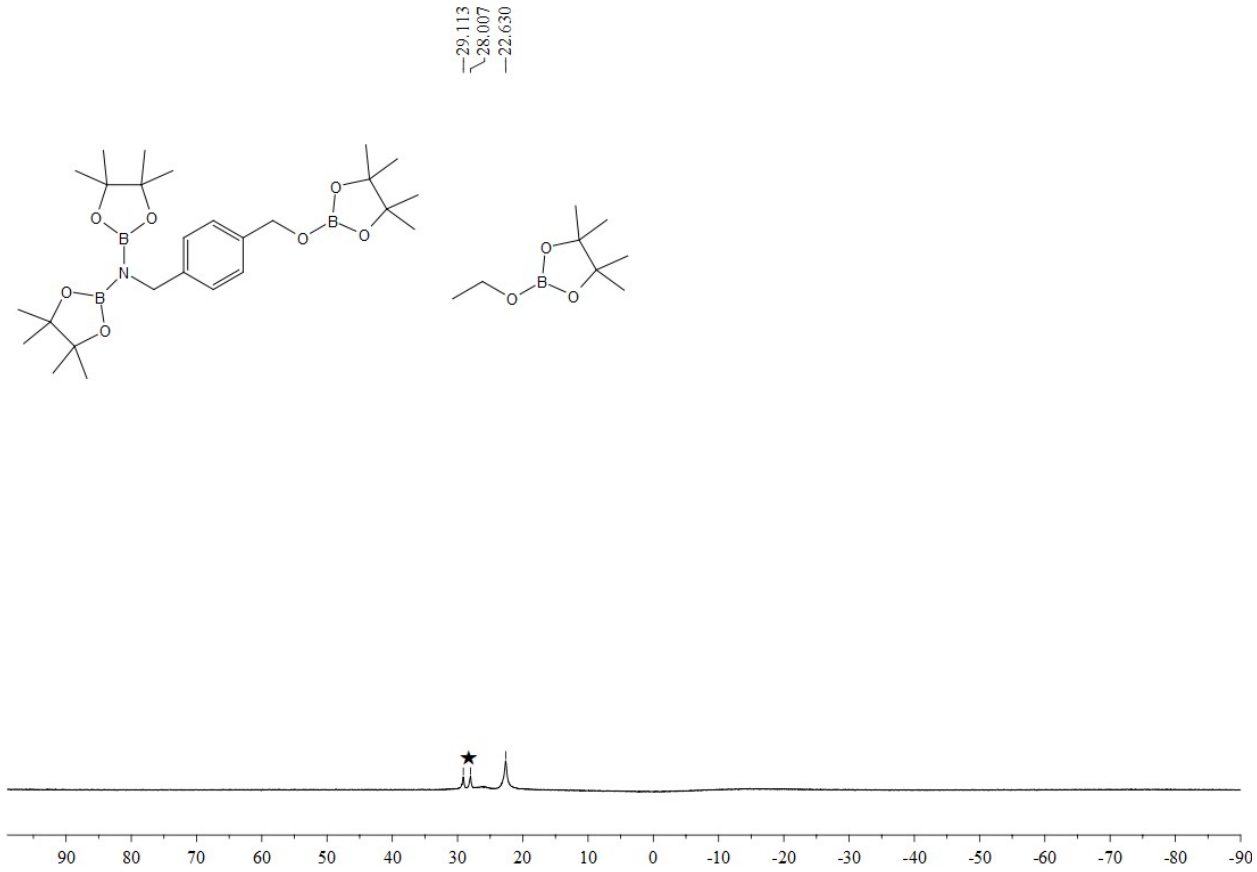


Figure S102. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $(pinB)_2NCH_2C_6H_4CH_2OBpin/EtOBpin$ (★ represents HBpin).

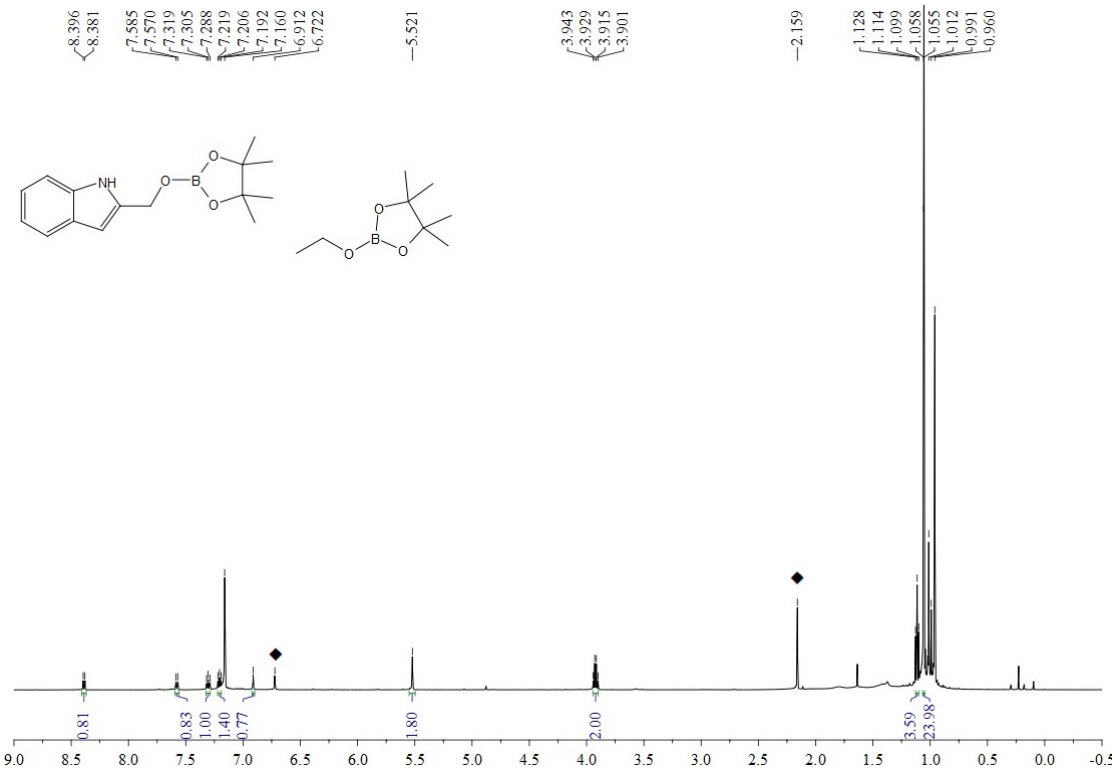


Figure S103. ^1H NMR spectrum (500 MHz, C_6D_6) of 2-indolyl-$CH_2OBpin/EtOBpin$. (◆

represents mesitylene).

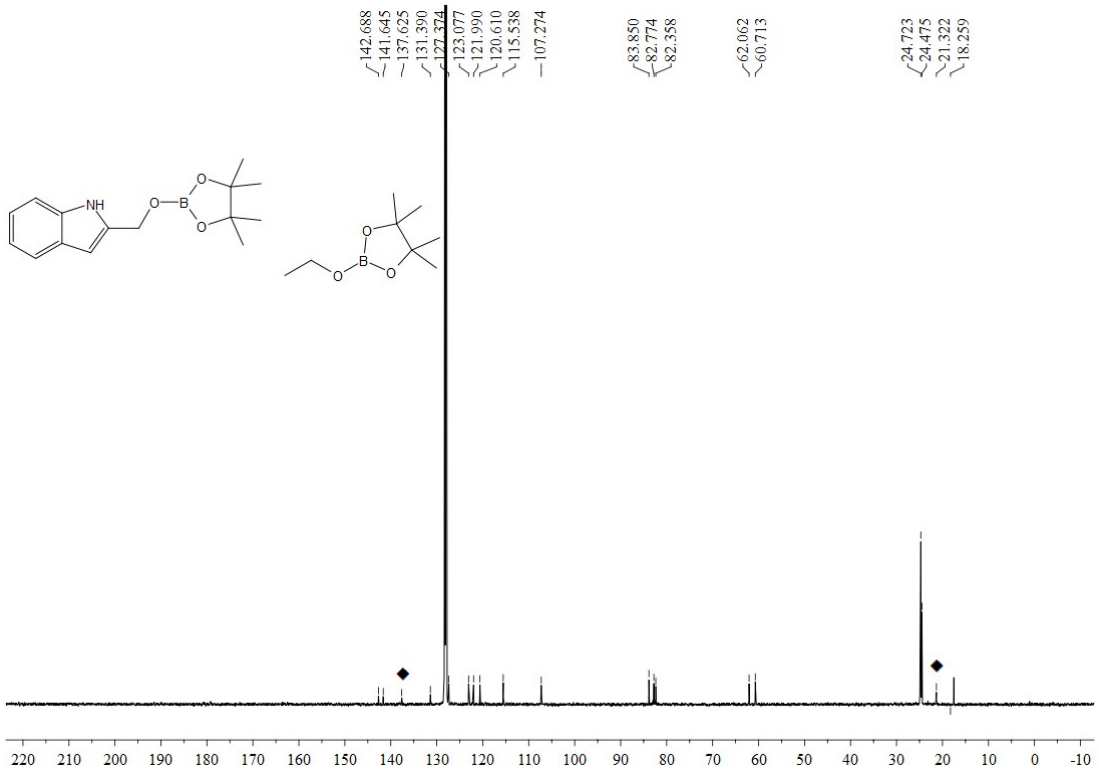


Figure S104. ^{13}C NMR spectrum (125 MHz, C_6D_6) of 2-indolyl-CH_2OBpin/EtOBpin. (◆ represents mesitylene).

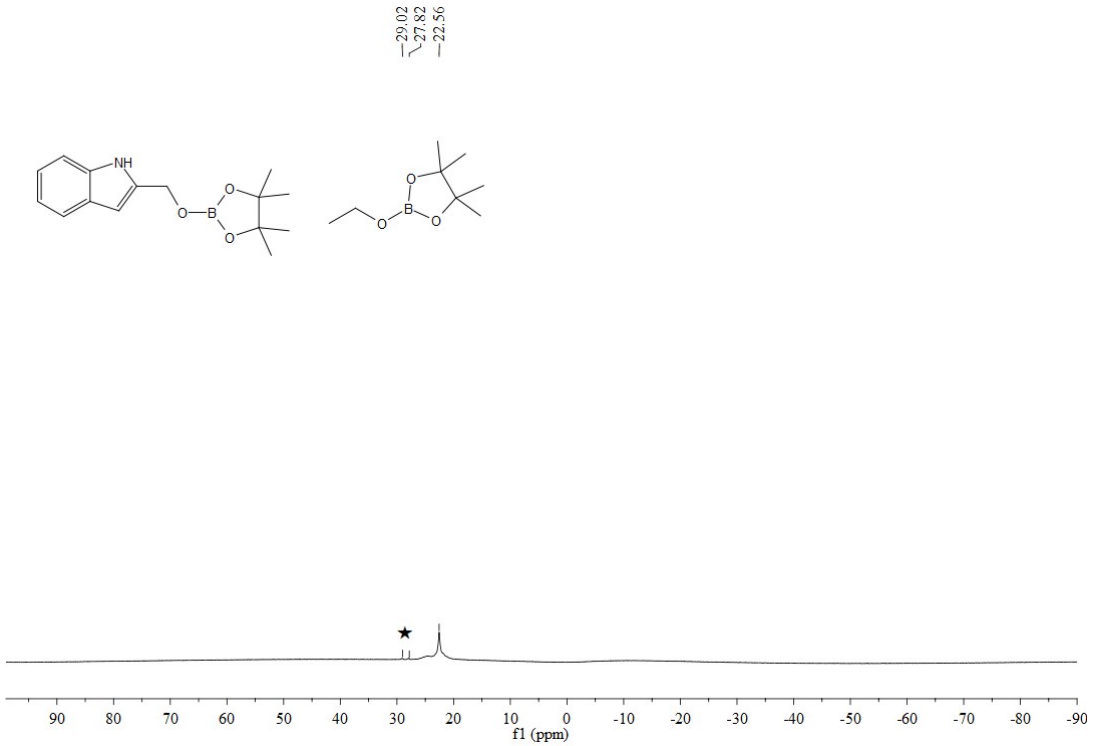


Figure S105. ^{11}B NMR spectrum (128 MHz, C_6D_6) of 2-indolyl-CH_2OBpin/EtOBpin. (★ represents HBpin).

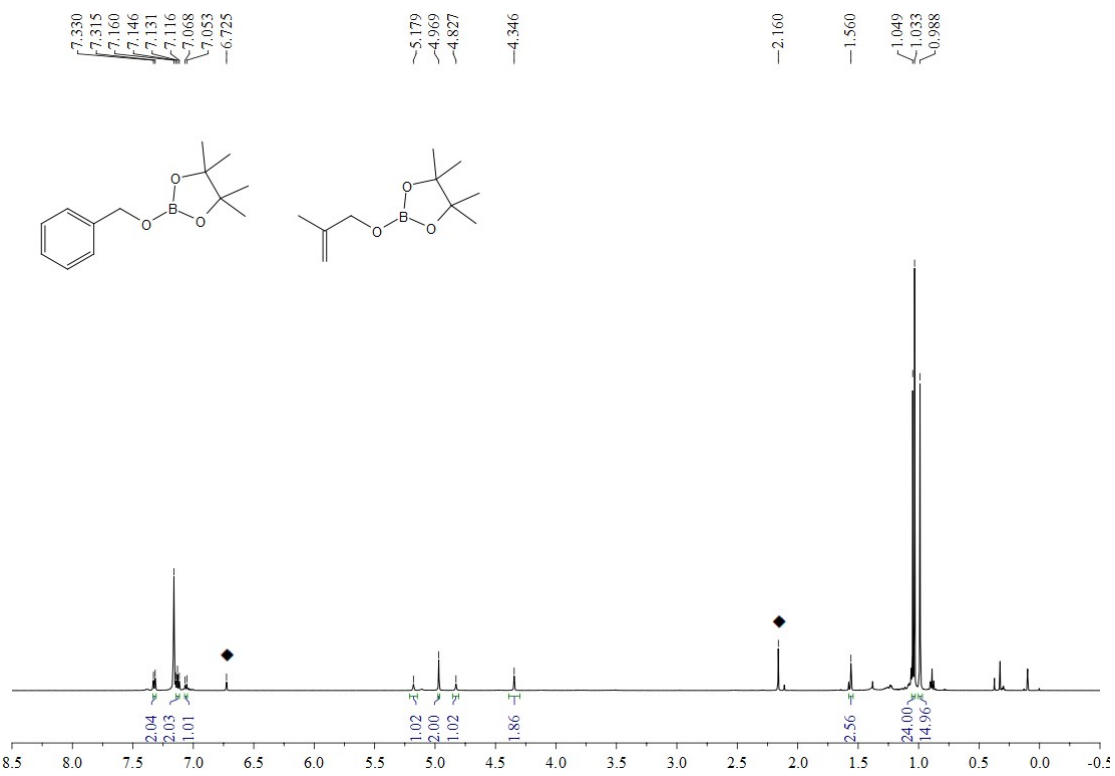


Figure S106. ^{1}H NMR spectrum (500 MHz, C_6D_6) of CH=CMeCH$_2$OBpin/PhCH$_2$OBpin (◆ represents mesitylene)

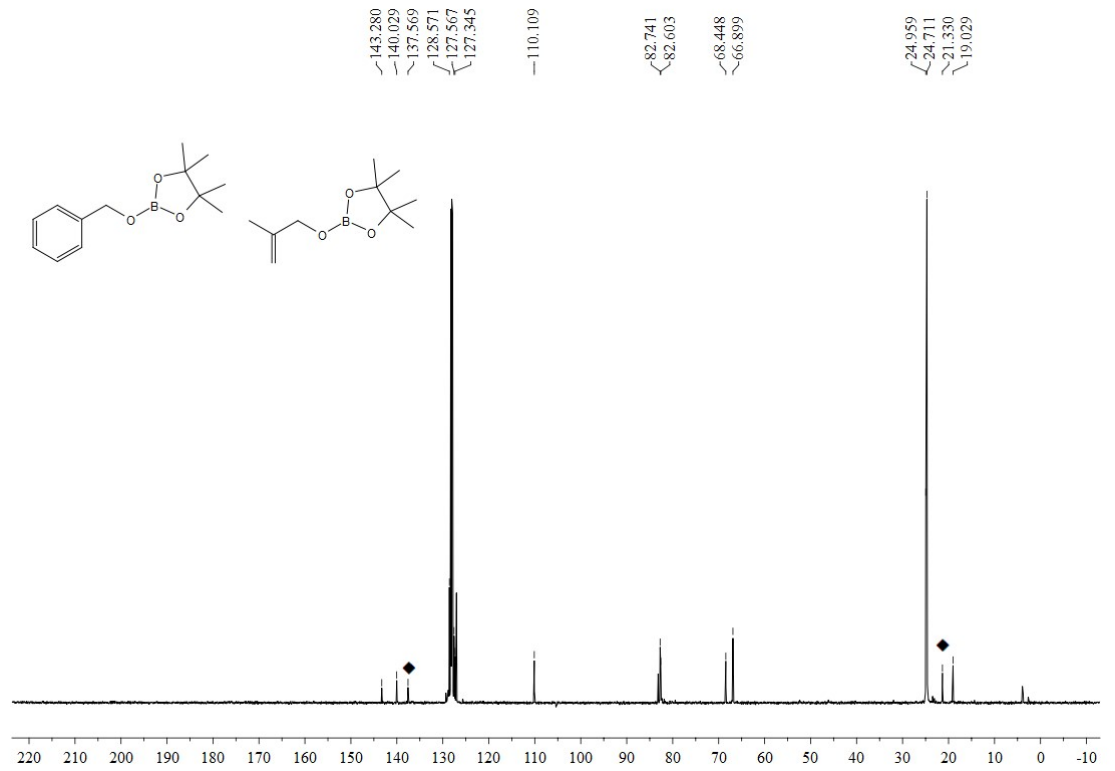


Figure S107. ^{13}C NMR spectrum (125 MHz, C_6D_6) of CH=CMeCH$_2$OBpin/PhCH$_2$OBpin (◆ represents mesitylene).

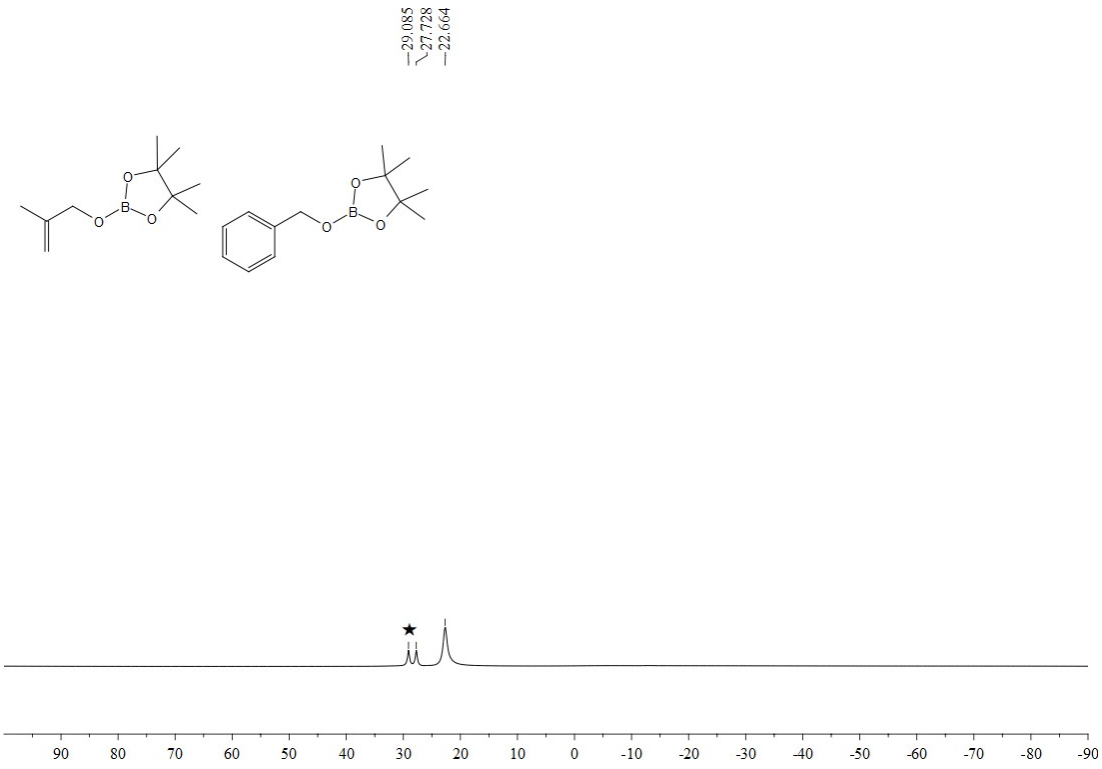


Figure S108. ^{11}B NMR spectrum (128 MHz, C_6D_6) of CH=CMeCH$_2$OBpin/PhCH$_2$OBpin (★ represents HBpin).

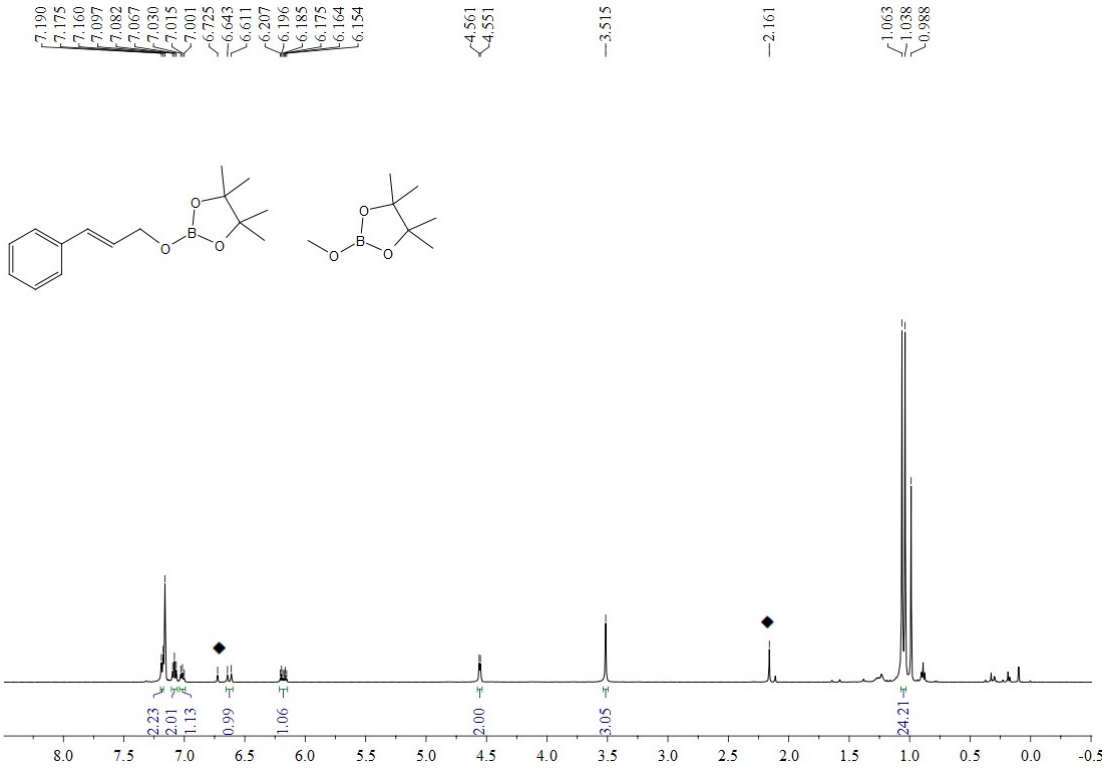


Figure S109. ^{1}H NMR spectrum (500 MHz, C_6D_6) of PhC=CHCH$_2$O*B*pin/MeO*B*pin (◆ represents mesitylene)

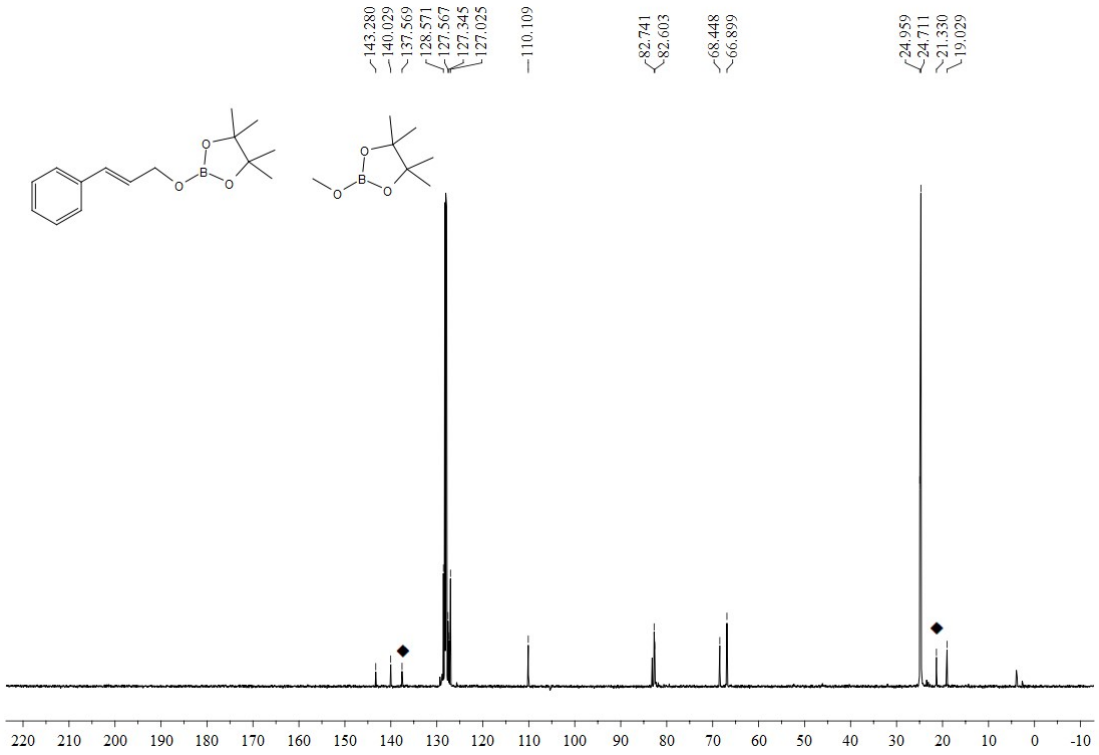


Figure S200. ^{13}C NMR spectrum (125 MHz, C_6D_6) of PhC=CHCH$_2$O*B*pin/MeO*B*pin (◆ represents mesitylene).

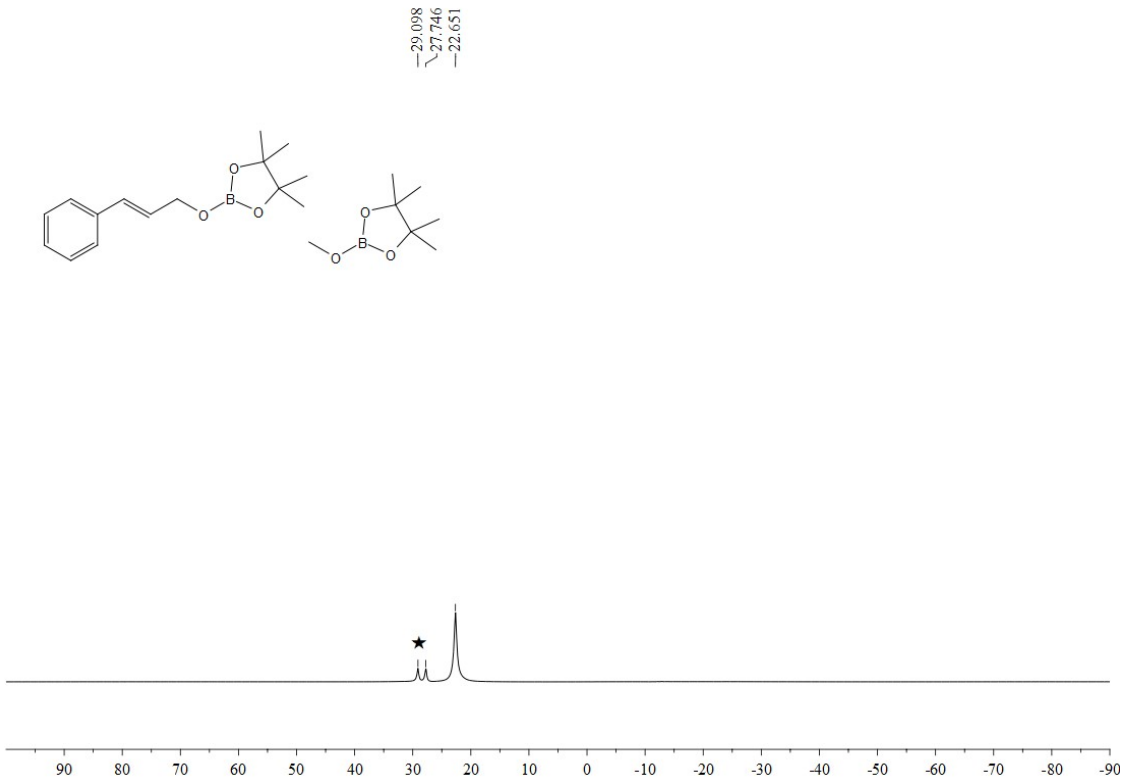


Figure S201. ^{11}B NMR spectrum (128 MHz, C_6D_6) of PhC=CHCH$_2$O*B*pin/MeO*B*pin (★ represents HBpin).

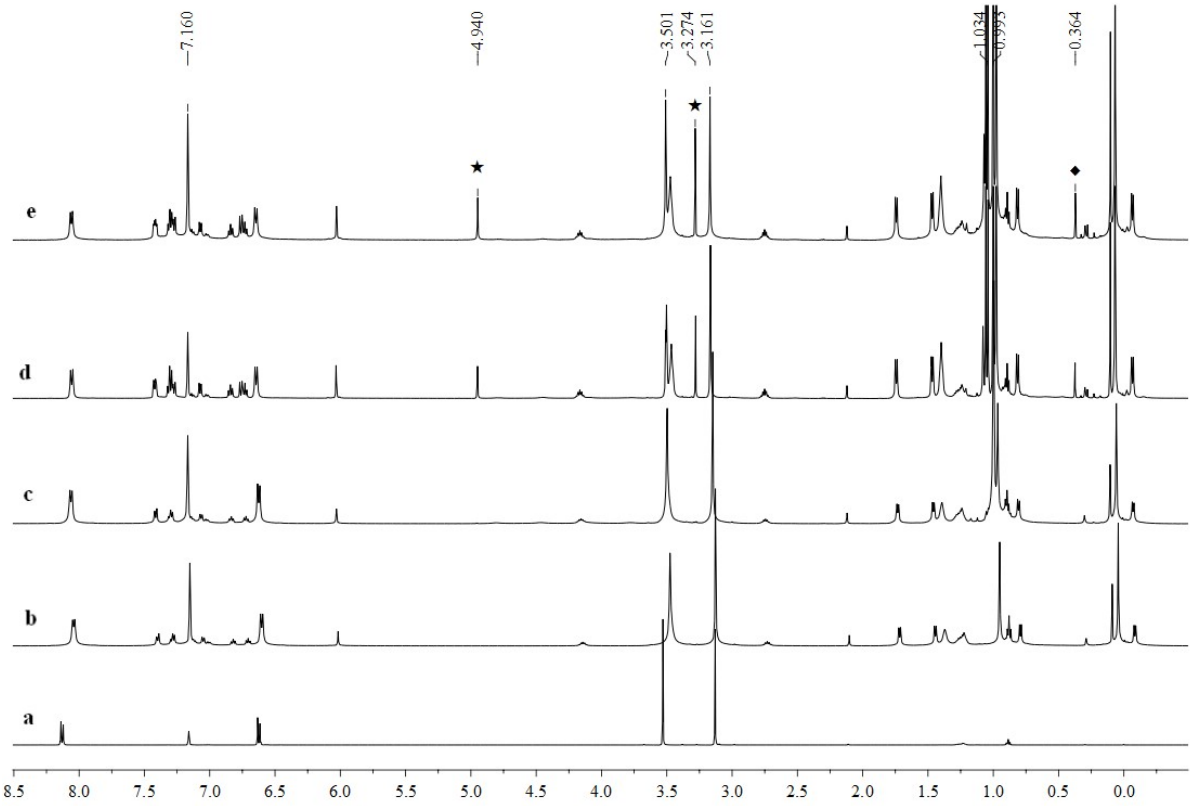


Figure S202. ^{1}H NMR stack spectra plot of stoichiometric reaction in C_6D_6. (a) 4-MeOPhCOOMe, (b) **1a** + 4-MeOPhCOOMe (1:3), (c) 4-MeOPhCOOMe + **1a** + HBpin (1:3:3), (d) 4-MeOPhCOOMe + **1a** + HBpin (1:3:3 at 80 °C for 2.0 h), (e) 4-MeOPhCOOMe + **1a** + HBpin (1:3:3 at 80 °C for 3.5 h, ★ = 4-MeOPhCH_2OBpin/CH_3OBpin), ◆ = [(CH_3)$_3$Si]$_2$N-Bpin).

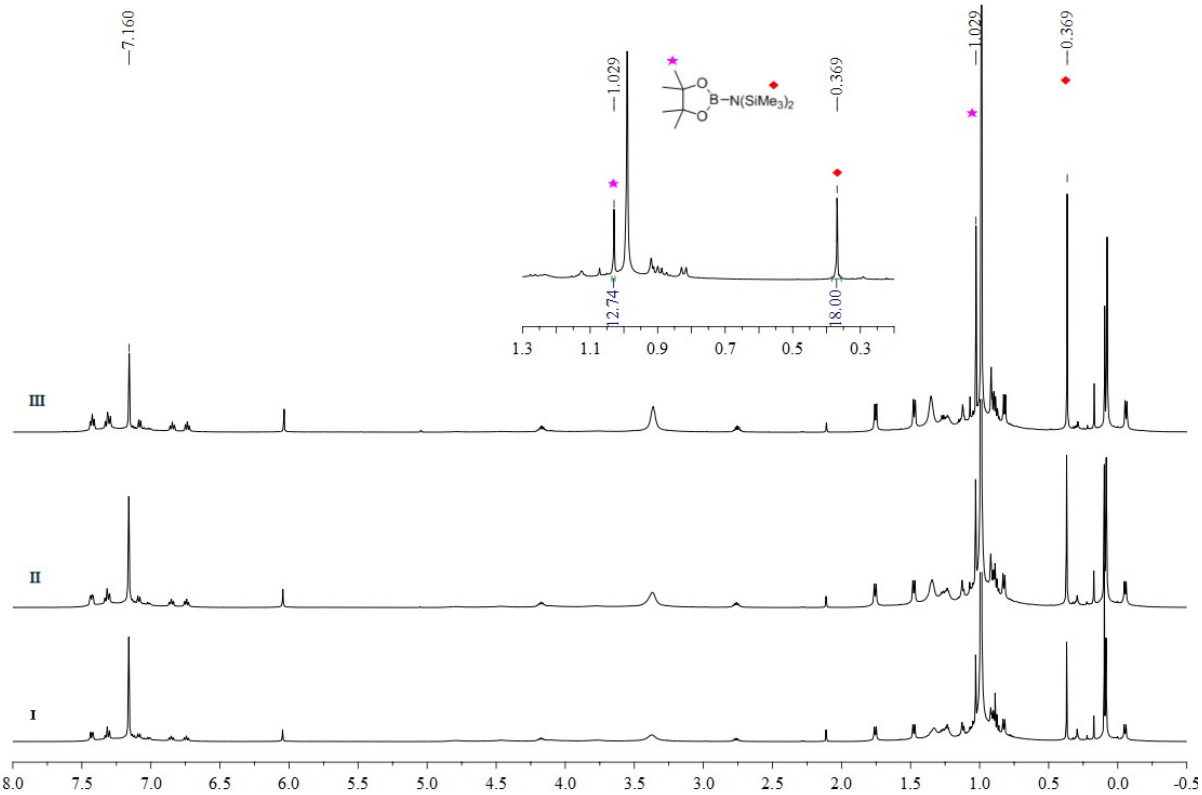


Figure S203. ^{1}H NMR spectrum (500 MHz, C_6D_6) of complex **1a** with HBpin (**I**: **1a** + 6 HBpin at 80 °C for 1.5 h; **II**: 4 h, **III**: 20 h.

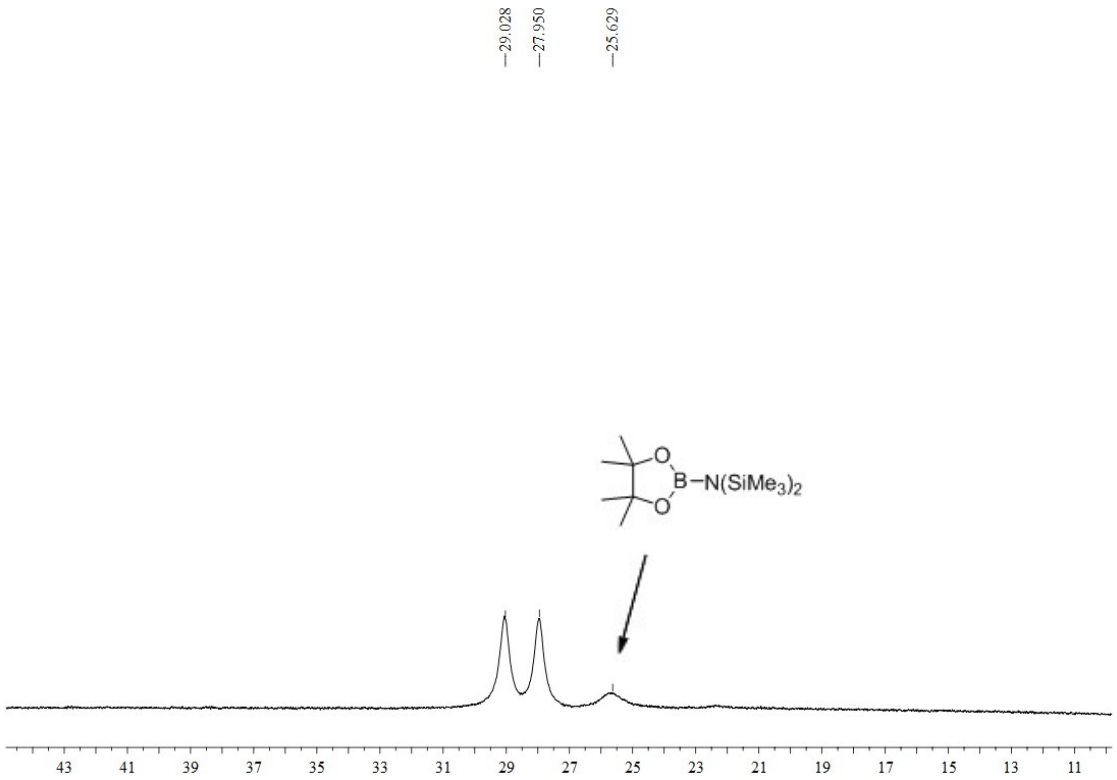


Figure S204. ^{11}B NMR spectrum (128 MHz, C_6D_6) of complex **1a** with HBpin (1:6) at 80 °C for 20 h.