Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary data for:

$B(C_6F_5)_3$ Mediated Arene Hydrogenation/ Transannulation of *para*-Methoxyanilines

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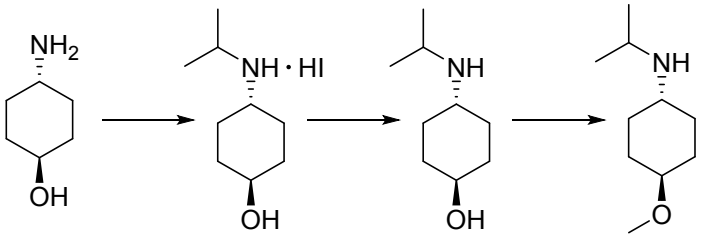
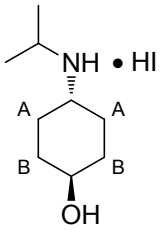
General considerations

Manipulations were performed under an atmosphere of dry, oxygen-free N_2 by means of standard Schlenk or glovebox techniques (MBraun). Tris(pentafluorophenyl)borane was purchased from Boulder Scientific and used without purification. Anilines, amines and other reagents were purchased from Alfa Aesar, Sigma Aldrich and TCI. Et_4NCl was purchased from Aldrich and dried under vacuum for several days. 2-Iodopropane, iodomethane, and potassium bis(trimehtylsilyl)amide were purchased from Sigma Aldrich. Toluene-d_8, dichloromethane-d_2 and bromobenzene-d_5 were purchased from Cambridge Isotope Laboratories, degassed and stored over 4 Å molecular sieves in the glovebox for 8 h prior to use. Toluene, pentane, diethyl ether and tetrahydrofuran were collected from a Grubbs-type column system manufactured by Innovative Technology. Nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance III 400 MHz or an Agilent DD2 500 spectrometer. Spectra were referenced to residual solvent of C_6D_5Br (^1H = 7.28 ppm for *meta* proton; ^{13}C = 122.4 ppm for *ipso* carbon) and CD_2Cl_2 (^1H = 5.32 ppm; ^{13}C = 53.84 ppm) Chemical Shifts (δ) are reported in ppm and the absolute values of the coupling constants (*J*) are in Hz. NMR assignments are supported by additional 2D and DEPT-135 experiments. High Resolution Mass Spectroscopy was obtained using JMS T100-LC AccuTOF DART with ion source Direct Analysis in Real Time (DART), Ionsense Inc., Saugus, MA. Elemental analyses (C, H, N) were performed in house employing a Perkin Elmer 2400 Series II CHNS Analyzer. H_2 (grade 5.0) was purchased from Linde and dried through a Nanochem WeldAssure purifier column prior to use. X-ray crystallography was performed in house.

SECTION 1 – SYNTHESIS OF COMPOUNDS FOR MECHANISTIC STUDIES

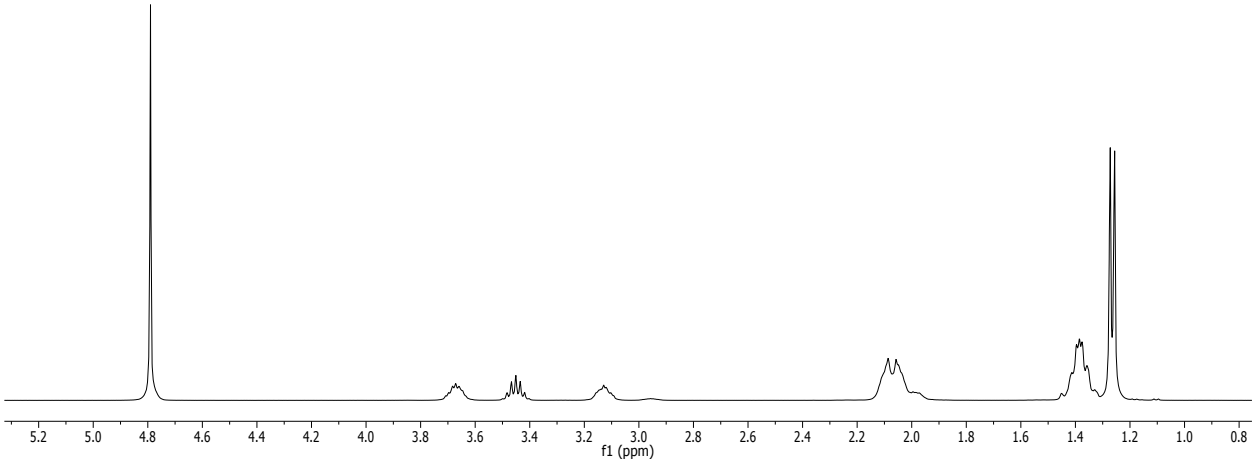


Synthesis of *trans*-4-NH(*i*Pr)C_6H_{10}OH • HI

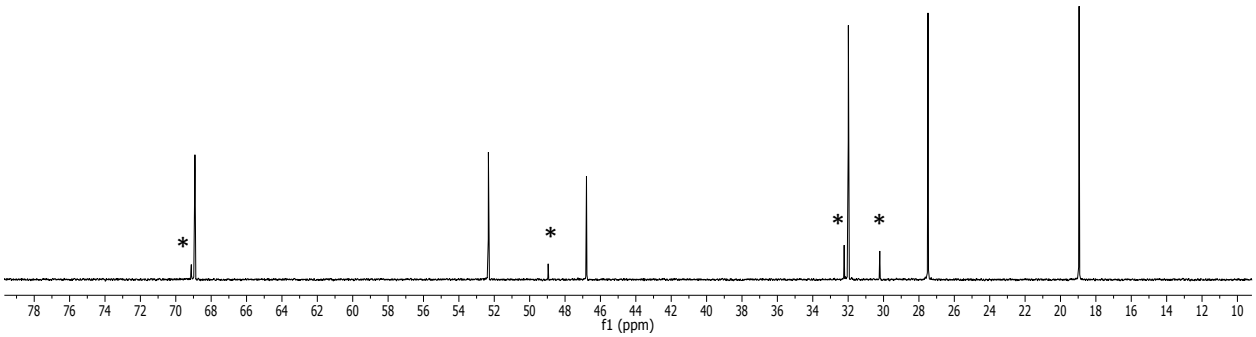


In the glovebox, a thick-walled Schlenk bomb was charged with *trans*-4-aminocyclohexanol (2.00 g, 0.017 mol). To the flask, 2-iodopropane (17.4 mL, 0.17 mol) was added in one shot and the reaction vessel was sealed and heated at 80 °C for 8 h. The excess 2-iodopropane was pumped off and the crude off-white solid was washed with diethyl ether (2 × 10 mL) and filtered. The product was collected as a white solid in 27 % yield.

^{1}H NMR (400 MHz, D_2O): δ 3.67 (tt, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, $^{Cy}CHOH$), 3.45 (m, $^3J_{HH}$ = 6.5 Hz, 1H, ^{i}Pr), 3.13 (tt, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, $^{Cy}CHNH$), 2.09 (m, 2H, $^BCH_2$), 2.05 (m, 2H, $^ACH_2$), 1.41 (m, 2H, $^BCH_2$), 1.36 (m, 2H, $^ACH_2$), 1.20 (d, $^3J_{HH}$ = 6.5 Hz, ^{i}Pr); **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): δ 68.9 ($^{Cy}CHOH$), 52.3 ($^{Cy}CHNH$), 46.8 (^{i}Pr), 32.0 ($^ACH_2$), 27.5 ($^BCH_2$), 19.0 (^{i}Pr).

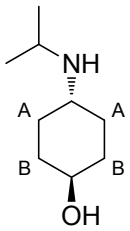


^{1}H NMR (400 MHz, D_2O)



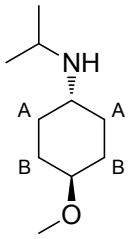
^{13}C{^{1}H} NMR (101 MHz, D_2O) (* Starting material *trans*-4-aminocyclohexanol)

Synthesis of *trans*-4-NH(*i*Pr)C_6H_{10}OH



In the glovebox, a Schlenk tube was charged with *trans*-4-NH(*i*Pr)C_6H_{10}OH • HI (1.823 g, 6.38 mmol) and diethyl ether (40 mL). To the slurry, potassium *tert*-butoxide (0.716 g, 6.38 mmol) was added in small portions. The reaction was allowed to mix at room temperature for 8 h. The solution was decanted and the solid was washed with diethyl ether (2 × 3 mL). The solvent from the collected filtrate was pumped off and the product was obtained as a white solid in 98 % yield.

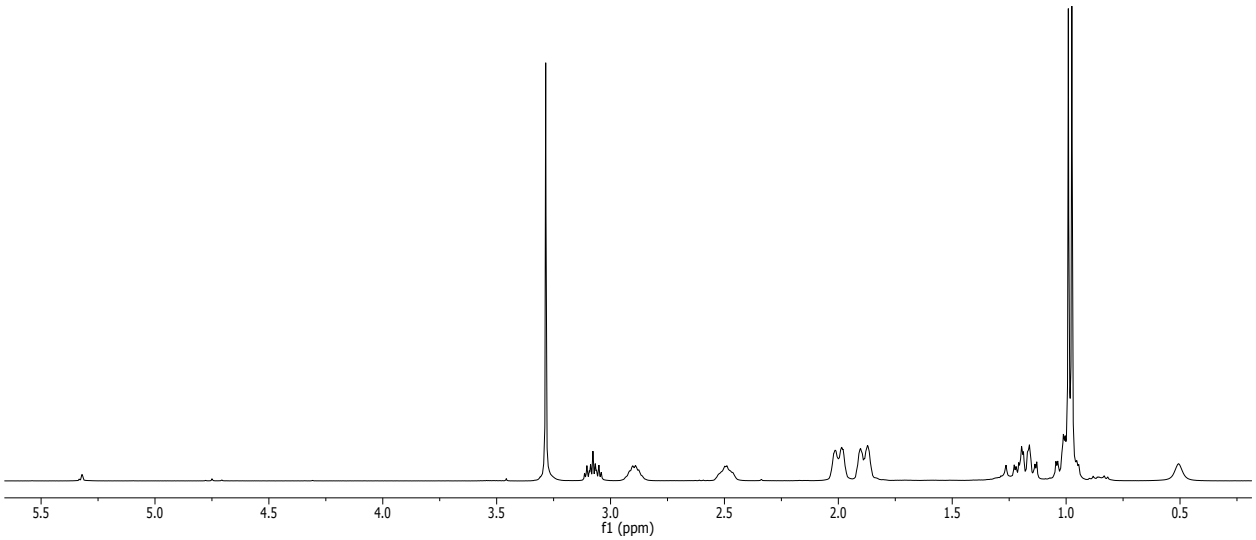
Synthesis of *trans*-4-NH(*i*Pr)$C_6H_{10}OCH_3$



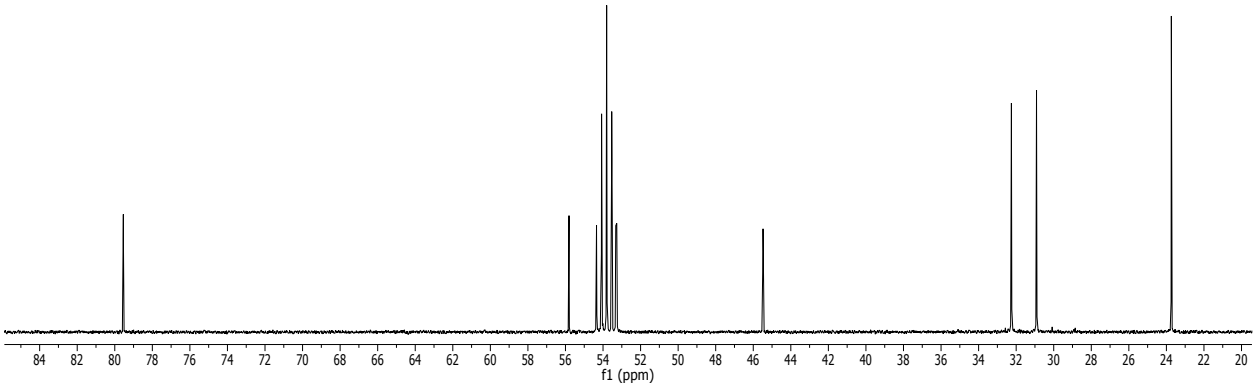
Part 1: In the glovebox, a 4 dram vial was charged with *trans*-4-NH(*i*Pr)C_6H_{10}OH (0.600 g, 3.82 mmol) and tetrahydrofuran (15 mL). The slurry was cooled down to -30 °C in a brass well and potassium bis(trimehtylsilyl)amide (0.800 g, 4.01 mmol) was added in small portions. The reaction mixture was allowed to slowly warm up to room temperature and mix for 3 h.

Part 2: The mixture was cooled down to -30 °C and iodomethane (0.24 mL, 3.82 mmol) was added dropwise. The reaction temperature was maintained at -30 °C for 8 h and warmed up to room temperature for 3 h. The solvent was pumped off and the crude mixture was washed with pentane (10 mL) and filtered through Celite. The solvent from the collected filtrate was pumped off to yield the product as a pale yellow oil in 20 % yield.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.28 (s, 3H, OCH_3), 3.08 (tt, $^3J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 4.1 Hz, 1H, $^{Cy}CHOCH_3$), 2.89 (m, $^3J_{HH}$ = 6.2 Hz, 1H, *i*Pr), 2.49 (tt, $^3J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 4.1 Hz, 1H, $^{Cy}CHNH$), 2.00 (dm, $^3J_{HH}$ = 11.2 Hz, 2H, $^BCH_2$), 1.88 (dm, $^3J_{HH}$ = 12.1 Hz, 2H, $^ACH_2$), 1.18 (m, 2H, $^BCH_2$), 1.00 (m, 2H, $^ACH_2$), 0.98 (d, $^3J_{HH}$ = 6.2 Hz, *i*Pr); **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): δ 79.54 ($^{Cy}CHOCH_3$), 55.8 (OCH_3), 52.9 ($^{Cy}CHNH$), 45.1 (*i*Pr), 32.1 ($^ACH_2$), 30.7 ($^BCH_2$), 23.3 (*i*Pr). HRMS-ESI$^+$ *m/z* [M+H]$^+$ **calc** for $C_{10}H_{22}NO$: 172.17014, **found** 172.17029.

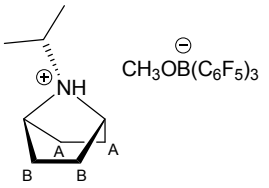


^{1}H NMR (400 MHz, CD_2Cl_2)



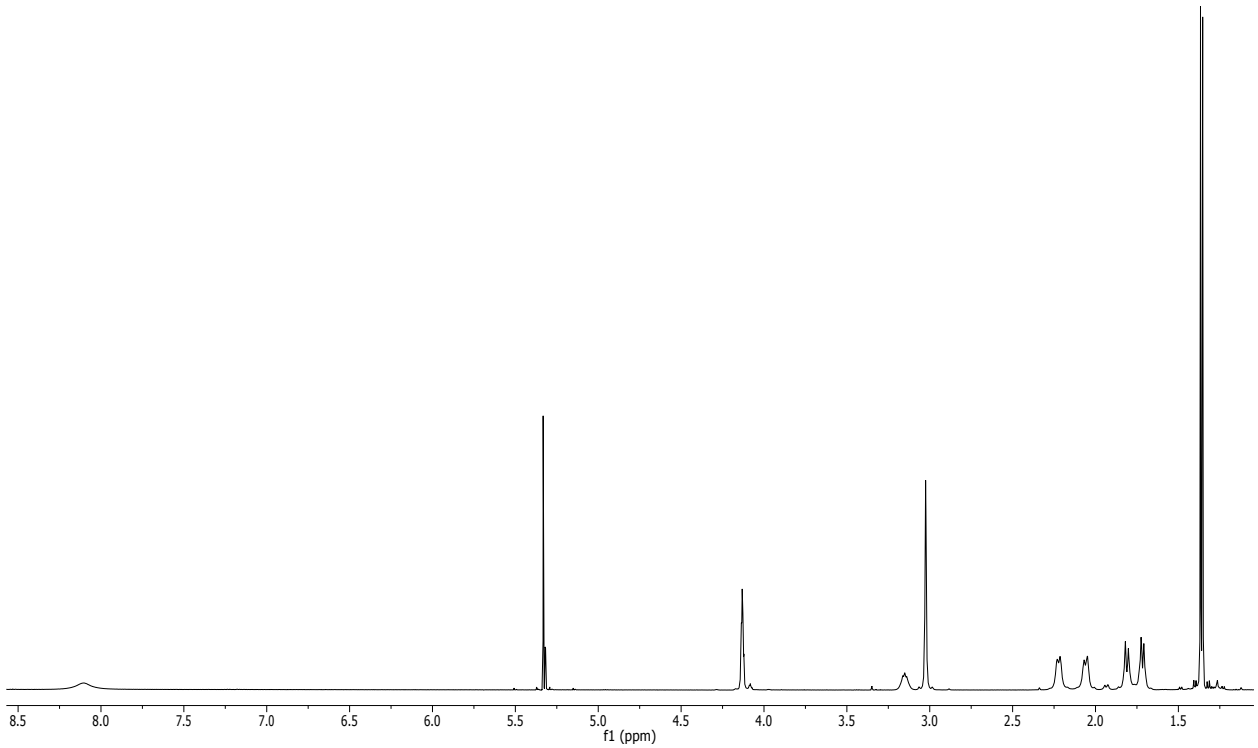
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2)

Synthesis of $[C_6H_{10}NHCH(^iPr)][CH_3OB(C_6F_5)_3]$ (1a) from *trans*-4-NH(^{i}Pr)$C_6H_{10}OCH_3$

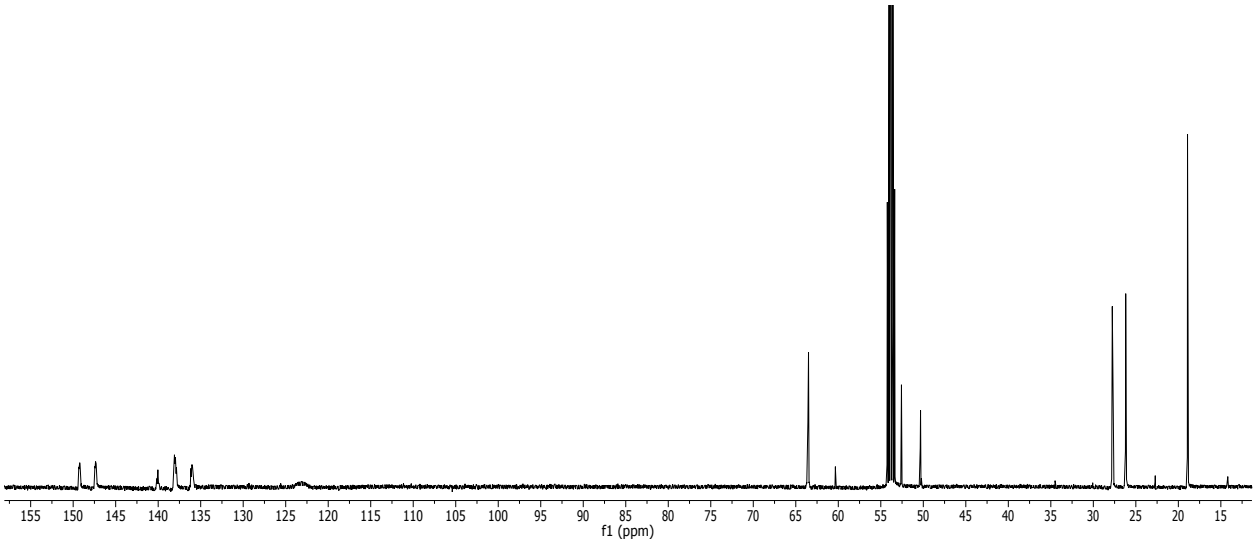


In the glovebox, a Schlenk tube (25 mL) was charged with *trans*-4-NH(^{i}Pr)$C_6H_{10}OCH_3$ (25.3 mg, 0.148 mmol) in toluene (0.5 mL) and $B(C_6F_5)$ (75.8 mg, 0.148 mmol) dissolved in toluene (0.5 mL) was added at once. The Schlenk was sealed and heated at 110 °C for 2h and the solvent was removed under vacuum. The crude solid was washed with pentane (1 × 2 mL) to yield the product as a white solid in 98 % yield. Crystals suitable for X-ray diffraction were obtained from a layered solution of dichloromethane/pentane at -30 °C over 48 h.

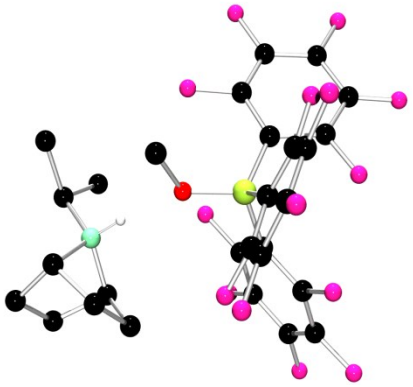
^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.10 (s, 1H, NH), 4.13 (m, 2H, CH_2CH), 3.15 (m, $^3J_{HH}$ = 6.6 Hz, 1H, ^{i}Pr), 3.02 (s, 3H, $BOCH_3$), 2.22 (dm, $^1J_{HH}$ = 9.3 Hz, 2H, $^ACH_2$), 2.05 (dm, $^1J_{HH}$ = 10.0 Hz, 2H, $^BCH_2$), 1.81 (dm, $^1J_{HH}$ = 10.0Hz, 2H, $^BCH_2$), 1.72 (dm, $^1J_{HH}$ = 9.3 Hz, 2H, $^ACH_2$), 1.36 (d, $^3J_{HH}$ = 6.6 Hz, ^{i}Pr); **^{19}F NMR** (377 MHz, CD_2Cl_2): δ 135.1 (br, 2F, *o*-C_6F_5), -162.0 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-C_6F_5), -166.4 (m, 2F, *m*-C_6F_5);); **^{11}B NMR** (128 MHz, CD_2Cl_2): δ -2.42 (s, $BOCH_3$); **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ 148.2 (dm, $^1J_{CF}$ = 241 Hz, C_6F_5), 138.8 (dm, $^1J_{CF}$ = 262 Hz, C_6F_5), 137.0 (dm, $^1J_{CF}$ = 252 Hz, C_6F_5), 123.1 (br s, *ipso*-C_6F_5), 63.4 (CH_2CH), 52.2 ($BOCH_3$), 50.2 (^{i}Pr), 27.4 ($^ACH_2$), 25.8 ($^BCH_2$). Elemental analysis **calcd** (%) for $C_{28}H_{21}BF_{15}N \cdot \frac{1}{2} CH_2Cl_2$: C 47.17; H 3.06; N 1.93; **found**: 46.74; H 3.27; N 1.99. HRMS-DART *m/z* [M] **calc** for $C_9H_{18}N^+$: 140.1, **found** 140.1.



^{1}H NMR (500 MHz, CD_2Cl_2)

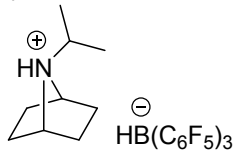


$^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2)



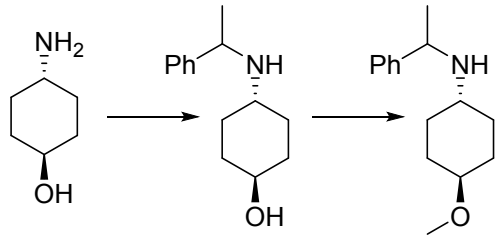
Molecular structure of **$[C_6H_{10}NHCH(^{i}Pr)][CH_3OB(C_6F_5)_3]$**

Synthesis of $[C_6H_{10}NHiPr][HB(C_6F_5)_3]$ (1)

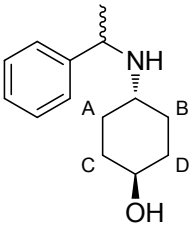


Method 1: In the glovebox, compound *trans*-4-NH(^{i}Pr)$C_6H_{10}OCH_3$ (25 mg, 0.15 mmol) and $B(C_6F_5)_3$ (76 mg, 0.15 mmol) were dissolved in d_8-toluene (0.4 mL) and added into a Teflon capped J-Young tube. The tube was degassed once through a freeze-pump-thaw cycle on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction was found to be complete after 12 h at 110 °C. The solvent was pumped off and the residue was washed with pentane (2 mL). The product was collected in 62 % yield.

Method 2: In the glovebox, compound $[C_6H_{10}NHCH(^iPr)][CH_3OB(C_6F_5)_3]$ (**1a**) (20 mg, 0.029 mmol) was dissolved in d_8-toluene (0.4 mL) and added into a Teflon capped J-Young tube. The tube was degassed once through a freeze-pump-thaw cycle on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction was found to be complete after 12 h at 110 °C.

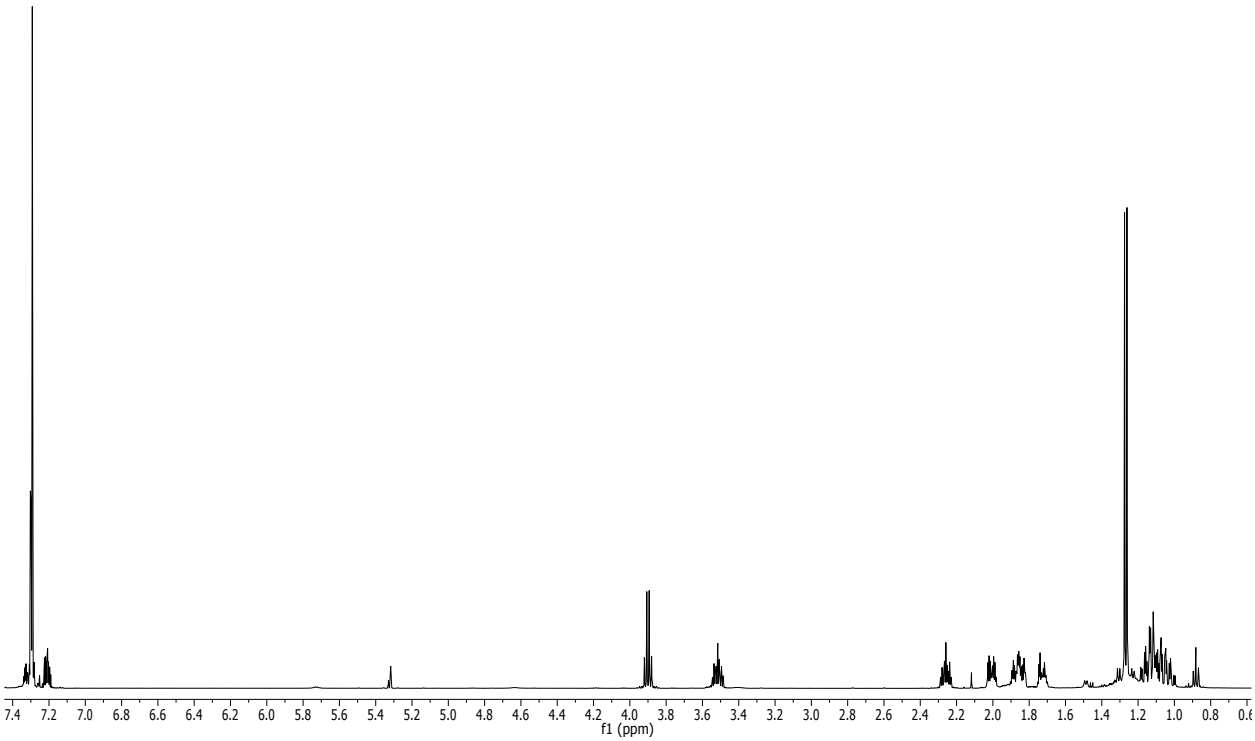


Synthesis of *trans*-4-NH(CH(CH$_3$)Ph)C$_6$H$_{10}$OH

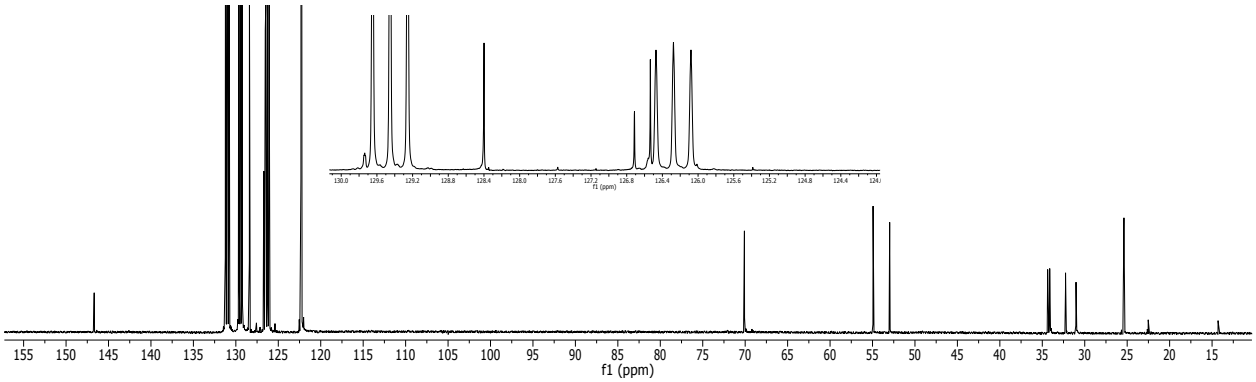


In the glovebox, a thick-walled Schlenk bomb was charged with a solution of *trans*-4-aminocyclohexanol (3.00 g, 0.026 mol) in dimethylformamide (50 mL). To the flask, (1-bromoethyl)benzene (9.62 g, 0.052 mol) and potassium carbonate (8.98 g, 0.065 mol) were added. The reaction mixture was stirred at room temperature for 16 h. The reaction mixture was filtered through a frit and the filtrate was extracted with dichloromethane and brine. The dichloromethane was dried over magnesium sulfate and the evaporated to yield a brown oil that was triturated with pentane (5 × 10 mL) to yield a pale-pink solid. The solid was dissolved in dichloromethane and layered with pentane for 16 h at -30 °C. The product was isolated as a white powder in 10 % yield.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.30-7.21 (m, 5H, Ph), 3.89 (q, $^3J_{HH}$ = 6.6 Hz, 1H, (C*H*(CH$_3$)Ph), 3.52 (tt, J_{HH} = 10.3 Hz, $^3J_{HH}$ = 4.0 Hz, ^{Cy}C*H*OH), 2.26 (tt, J_{HH} = 10.3 Hz, $^3J_{HH}$ = 4.0 Hz, ^{Cy}C*H*N), 2.01 (dm, $^2J_{HH}$ = 12.6 Hz, 1H, ^{A}CH$_2$), 1.88 (m, 1H, ^{C}CH$_2$), 1.84 (m, 1H, ^{D}CH$_2$), 1.74 (dm, $^2J_{HH}$ = 12.6 Hz, ^{B}CH$_2$), 1.27 (d, $^3J_{HH}$ = 6.6 Hz, CH$_3$), 1.24 (br s, 1H, OH), 1.17-1.07 (m, 3H, ^{B,C,D}CH$_2$), 1.05 (dm, $^2J_{HH}$ = 12.6 Hz, ^{A}CH$_2$); **^{13}C{^{1}H} NMR** (125 MHz, C_6D_5Br): δ 146.7 (*ipso*-Ph), 128.4 (*m*-Ph), 126.7 (*p*-Ph), 126.5 (*o*-Ph), 70.1 (^{Cy}*C*HOH), 54.9 ((*C*H(CH$_3$)Ph), 53.0 (^{Cy}*C*HN), 34.4 (^{D}CH$_2$), 34.1 (^{C}CH$_2$), 32.3 (^{B}CH$_2$), 31.0 (^{A}CH$_2$), 25.4 (CH$_3$).

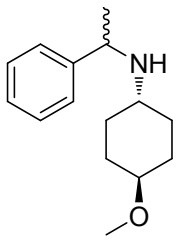


^{1}H NMR (500 MHz, CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_5Br)

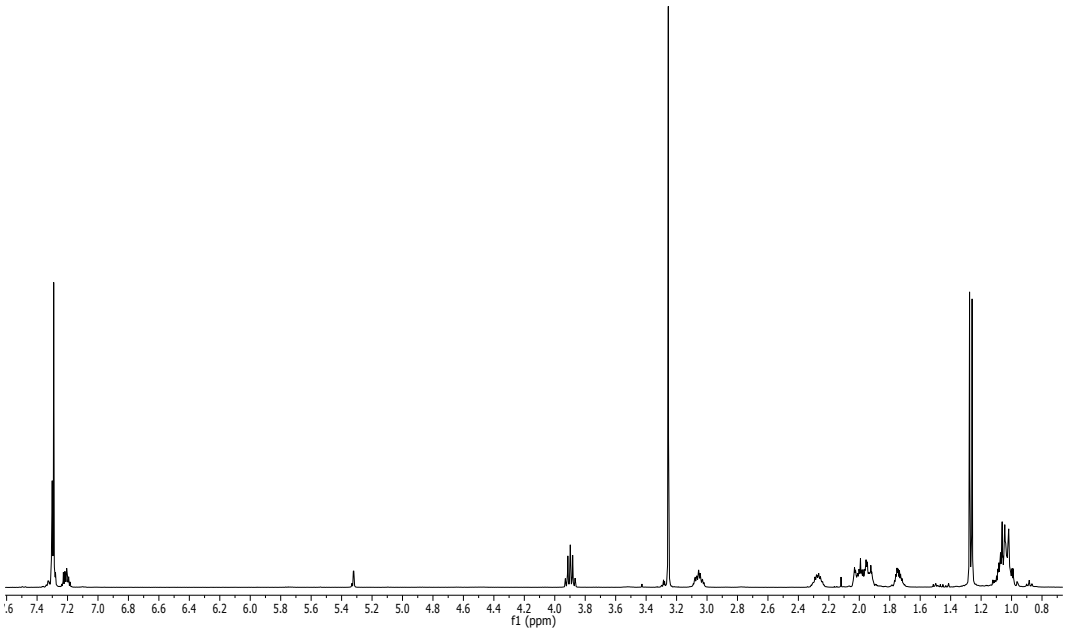
Synthesis of *trans*-4-NH(CH(CH$_3$)Ph)C$_6$H$_{10}$OCH$_3$



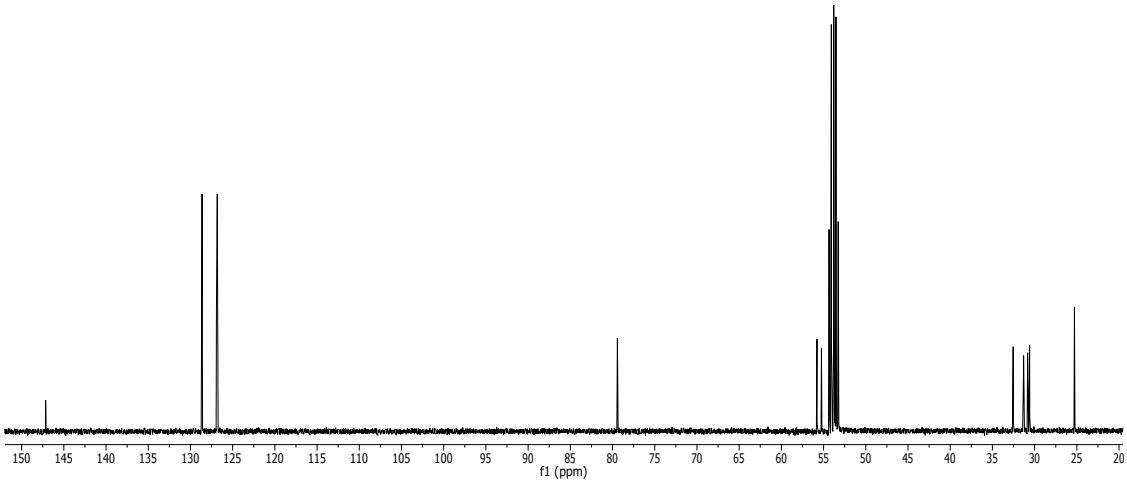
Part 1: In the glovebox, a 4 dram vial was charged with *trans*-4-NH(CH(CH$_3$)Ph)C$_6$H$_{10}$OH (0.100 g, 0.460 mmol) and tetrahydrofuran (10 mL). The slurry was cooled down to -30 °C in a brass well and potassium bis(trimehtylsilyl)amide (0.091 g, 0.460 mmol) was added in small portions. The reaction mixture was allowed to slowly warm up to room temperature and mix for 3 h. The colourless mixture gradually became light brown in colour.

Part 2: The mixture was cooled down to -30 °C and iodomethane (29 µL, 0.46 mmol) was added dropwise. The reaction was slowly warmed up to room temperature and stirred for 8 h. The solvent was pumped off and the crude mixture was washed with pentane (10 mL) and filtered through Celite. The solvent from the collected filtrate was pumped off to yield the product as a pale yellow oil in 93 % yield.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.29-7.12 (m, 5H, Ph), 3.84 (q, 1H, $^{3}J_{HH}$ = 6.6 Hz, C*H*(CH$_3$)Ph), 3.19 (s, 3H, OCH$_3$), 3.00 (tt, $^{2}J_{HH}$ = 10.3 Hz, $^{3}J_{HH}$ = 4.0 Hz, 1H, ^{Cy}C*H*OCH$_3$), 2.22 (tt, $^{2}J_{HH}$ = 10.3 Hz, $^{3}J_{HH}$ = 4.0 Hz, 1H, ^{Cy}C*H*N), 1.97-1.86 (m, 3H, ^{Cy}CH$_2$), 1.68 (m, 1H, ^{Cy}CH$_2$), 1.21 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, CH(C*H*$_3$)Ph), 1.11-0.86 (m, 4H, ^{Cy}CH$_2$); **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): δ 147.2 (*ipso*-Ph), 128.6 (*m*-Ph), 126.9 (*p*-Ph), 126.8 (*o*-Ph), 79.4 (^{Cy}*C*HOCH$_3$), 55.8 (O*C*H$_3$), 55.2 (^{Cy}*C*HN), 53.6 (*C*H(CH$_3$)Ph), 32.5 (^{Cy}CH$_2$), 31.3 (^{Cy}CH$_2$), 30.8 (^{Cy}CH$_2$), 30.6 (^{Cy}CH$_2$), 25.3 (CH(*C*H$_3$)Ph).

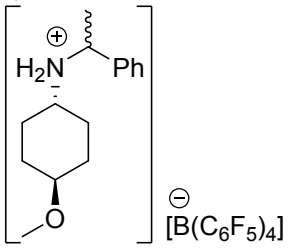


^{1}H NMR (400 MHz, CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2)

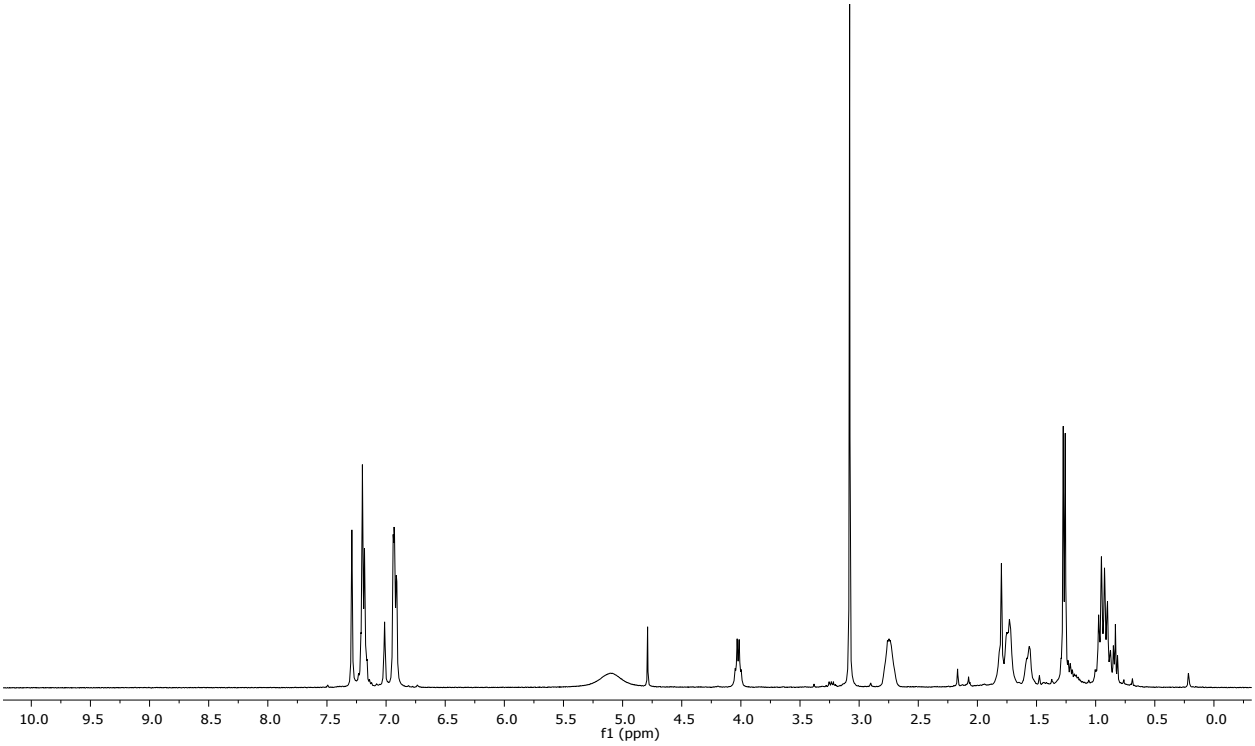
Synthesis of [*trans*-4-$NH_2(CH(CH_3)Ph)C_6H_{10}OCH_3$][$B(C_6F_5)_4$] (8a)



Part 1: In a Schlenk tube, *trans*-4-$NH(CH(CH_3)Ph)C_6H_{10}OCH_3$ (16 mg, 0.068 mmol) was dissolved in pentane (2 mL) and hydrogen chloride (68 µL, 0.27 mmol, 4.0 M in 1,4-dioxane) was added dropwise. White precipitate was immediately formed. The pentane was decanted and the solid was washed with pentane (2 × 1 mL) and dried *in vacuo* to yield *trans*-4-$NH(CH(CH_3)Ph)C_6H_{10}OCH_3$ • HCl in 89 %.

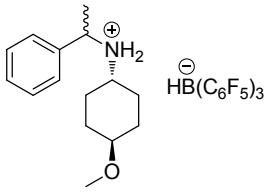
Part 2: In the glovebox, a 4 dram vial was charged with *trans*-4-$NH(CH(CH_3)Ph)C_6H_{10}OCH_3$ • HCl (6.1 mg, 0.026 mmol) in dichloromethane (8 mL) and $K^+ B(C_6F_5)_4^-$ (16.2 mg, 0.026 mmol) was added at once. The reaction was allowed to stir for 16 h at room temperature. The mixture was filtered through Celite and the solvent of the filtrate was removed under vacuum. The product was obtained as a white solid in 88 % yield.

^{1}H NMR (400 MHz, C_6D_5Br): δ 7.19 (m, 2H, *m*-Ph), 6.90 (m, 3H, *o*,*p*-Ph), 5.10 (br s, 2H, NH_2), 4.02 (q, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*(CH_3)Ph), 3.10 (s, 3H, OCH_3), 2.72 (m, 2H, ^{Cy}C*H*OCH_3, ^{Cy}C*H*N), 1.74 (m, 3H, $^{Cy}CH_2$), 1.56 (m, 1H, $^{Cy}CH_2$), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(C*H*$_3$)Ph, 0.93 - 0.84 (m, 4H, $^{Cy}CH_2$); **^{19}F NMR** (377 MHz, C_6D_5Br): δ -131.8 (m, 2F, *o*-C_6F_5), -161.0 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -165.3 (m, 2F, *m*-C_6F_5); **^{11}B NMR** (128 MHz, C_6D_5Br): δ -16.4;



^{1}H NMR (400 MHz, C_6D_5Br)

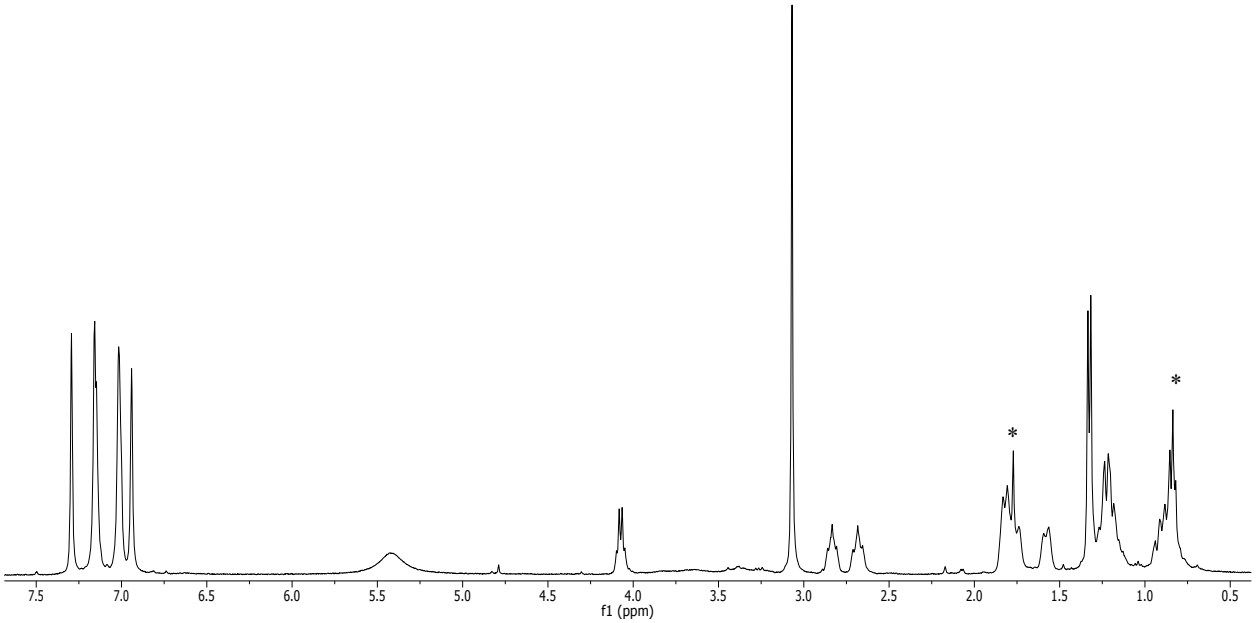
Synthesis of [*trans*-4-$NH_2(CH(CH_3)Ph)C_6H_{10}OCH_3$][$HB(C_6F_5)_3$] (8b)



Part 1: In a Schlenk tube, *trans*-4-$NH(CH(CH_3)Ph)C_6H_{10}OCH_3$ (16 mg, 0.068 mmol) was dissolved in pentane (2 mL) and hydrogen chloride (68 µL, 0.27 mmol, 4.0 M in 1,4-dioxane) was added dropwise. White precipitate was immediately formed. The pentane was decanted and the solid was washed with pentane (2 × 1 mL) and dried *in vacuo* to yield *trans*-4-$NH(CH(CH_3)Ph)C_6H_{10}OCH_3$ • HCl in 89 %.

Part 2: In the glovebox, a 4 dram vial was charged with *trans*-4-$NH(CH(CH_3)Ph)C_6H_{10}OCH_3$ • HCl (9.3 mg, 0.034 mmol) in dichloromethane (8 mL) and $Na{\cdot}HB(C_6F_5)_3$ (18.5 mg, 0.034 mmol) was added at once. The reaction was allowed to stir for 16 h at room temperature. The mixture was filtered through Celite and the solvent of the filtrate was removed under vacuum. The product was obtained as a white solid in 76 % yield.

^{1}H NMR (400 MHz, C_6D_5Br): δ 7.16 (m, 3H, Ph), 7.02 (m, 2H, Ph), 5.46 (br, 2H, NH_2), 4.07 (q, $^3J_{HH}$ = 6.8 Hz, C*H*(CH_3)Ph), 3.47 (br q, $^1J_{BH}$ = 78 Hz, 1H, HB), 3.07 (s, 3H, OCH_3), 2.83 (tt, $^3J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 4.6 Hz, 1H, ^{Cy}C*H*OCH_3), 2.68 (tt, $^3J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 3.9 Hz, 1H, ^{Cy}C*H*N), 1.83 (m, 3H, $^{Cy}CH_2$), 1.56 (dm, $^3J_{HH}$ = 12.8 Hz, 1H, $^{Cy}CH_2$), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)Ph, 1.21 (m, 2H, $^{Cy}CH_2$), 0.84 (m, 2H, $^{Cy}CH_2$); **^{19}F NMR** (377 MHz, C_6D_5Br): δ -133.4 (m, 2F, *o*-C_6F_5), -160.4 (t, 1F, $^3J_{FF}$ = 22 Hz, *p*-C_6F_5), -164.3 (m, 2F, *m*-C_6F_5); **^{11}B NMR** (128 MHz, C_6D_5Br): δ -23.8 (d, $^1J_{BH}$ = 78 Hz, HB);

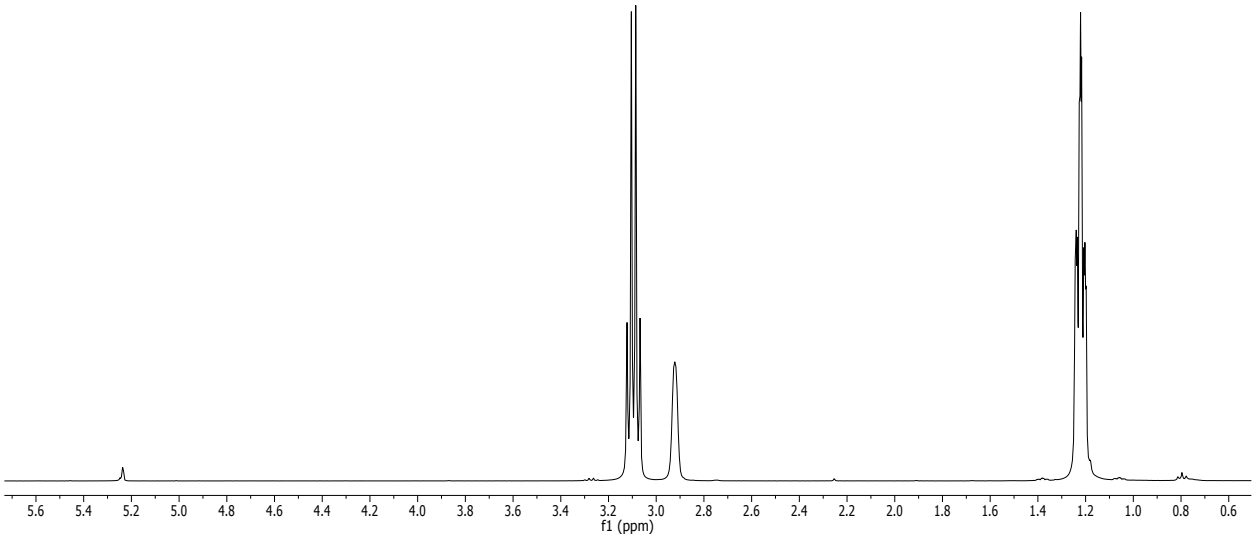


^{1}H NMR (400 MHz, C_6D_5Br) (* pentane)

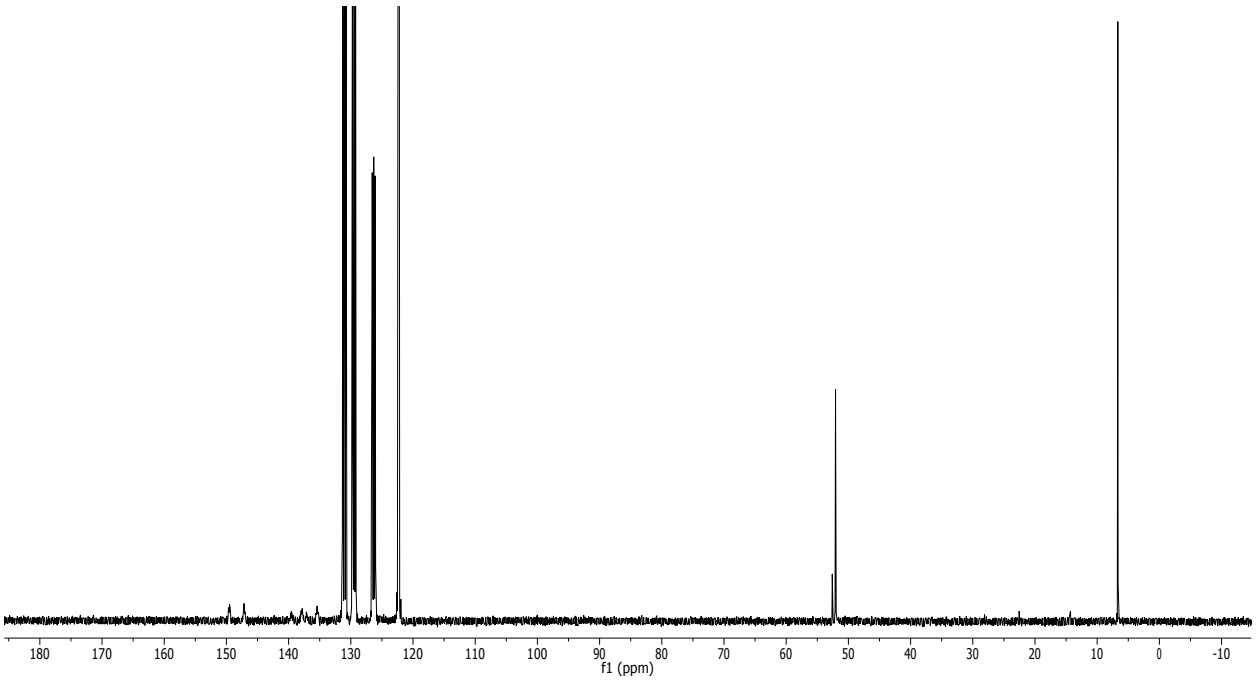
Synthesis of $[N(CH_2CH_3)_4][CH_3OB(C_6F_5)_3]$

In the glovebox, a 4 dram vial was charged with $Na{\cdot}CH_3OB(C_6F_5)_3$ (0.175 g, 0.308 mmol) and $N(CH_2CH_3)_4{\cdot}Cl$ (51.0 mg, 0.308 mmol) in dichloromethane (15 mL). The reaction was stirred at room temperature for 12 h and the mixture was filtered through Celite. The solvent was removed under vacuum and the product was obtained as a white solid in 88 % yield. EA failed over several attempts.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.10 (q, $^3J_{HH}$ = 7.3 Hz, 8 H, CH_2), 2.98 (s, 3H, $BOCH_3$), 1.22 (t, $^3J_{HH}$ = 7.3 Hz, 12H, CH_3); **^{19}F NMR** (377 MHz, CD_2Cl_2): δ -133.0 (m, 2F, *o*-C_6F_5), -161.7 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), -165.5 (m, 2F, *m*-C_6F_5); **^{11}B NMR** (128 MHz, CD_2Cl_2): δ -2.17 (s, $BOCH_3$); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_5Br): δ 148.3 (dm, $^1J_{CF}$ = 236 Hz, C_6F_5), 138.3 (dm, $^1J_{CF}$ = 250 Hz, C_6F_5), 136.6 (dm, $^1J_{CF}$ = 241 Hz, C_6F_5), 52.6 ($BOCH_3$), 52.0 (CH_2), 6.63 (CH_3).



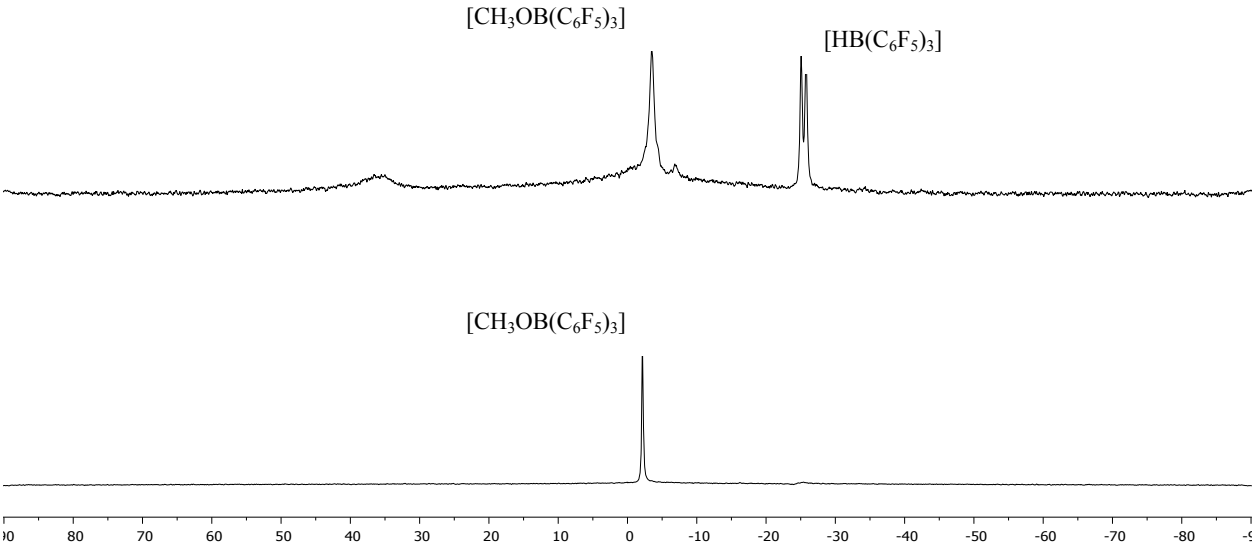
^{1}H NMR (400 MHz, CD_2Cl_2)



^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br)

$$[NEt_4][CH_3OB(C_6F_5)_3] \xrightarrow[110\ ^\circ C,\ H_2]{(5\ mol\%)\ B(C_6F_5)_3} [NEt_4][HB(C_6F_5)_3] + CH_3OH$$

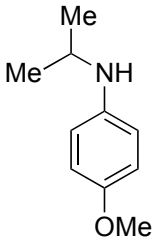
^{11}B NMR showing H_2-activation between $[CH_3OB(C_6F_5)_3]$ anion and $B(C_6F_5)_3$ showing emergence of $[HB(C_6F_5)_3]$ after heating at 110 °C for 30 min. Bottom spectrum is of starting material $[NEt_4][CH_3OB(C_6F_5)_3]$. Top spectrum heating at 110 °C for 30 min.



^{11}B NMR (128 MHz, C_6D_5Br)

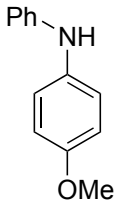
SECTION 2 – SYNTHESIS OF STARTING MATERIAL ANILINES

Synthesis of 4-methoxy-*N*-*iso*-propylaniline



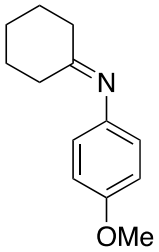
Following a modified literature procedure,[1] *p*-anisidine (2.2 g, 18 mmol) was dissolved in 30 mL acetone. The solution was stirred over ~20 g of 4 Å molecular sieves for 24 h. The solution was filtered and the acetone was removed *in vacuo*, yielding the imine as an orange oil (3.0 g, >99% yield). The imine was then redissolved in 30 mL of methanol and cooled to 0 °C in an ice bath. $NaBH_4$ (2.1 g, 55 mmol) was added portionwise to the solution; upon complete addition the solution was allowed to slowly warm to room temperature. The reaction was quenched with 2M NaOH, and the product was extracted into 100 mL DCM. The organic layer was separated and washed with 100 mL brine, dried over Na_2SO_4, filtered and the solvent was removed *in vacuo* yielding a yellow oil. The material was purified by flash column chromatography (5% EtOAc in hexanes) yielding the product as a pale yellow oil, isolated in 82% yield (2.5 g). NMR data is consistent with reported values.[2]

Synthesis of 4-methoxy-*N*-phenylaniline



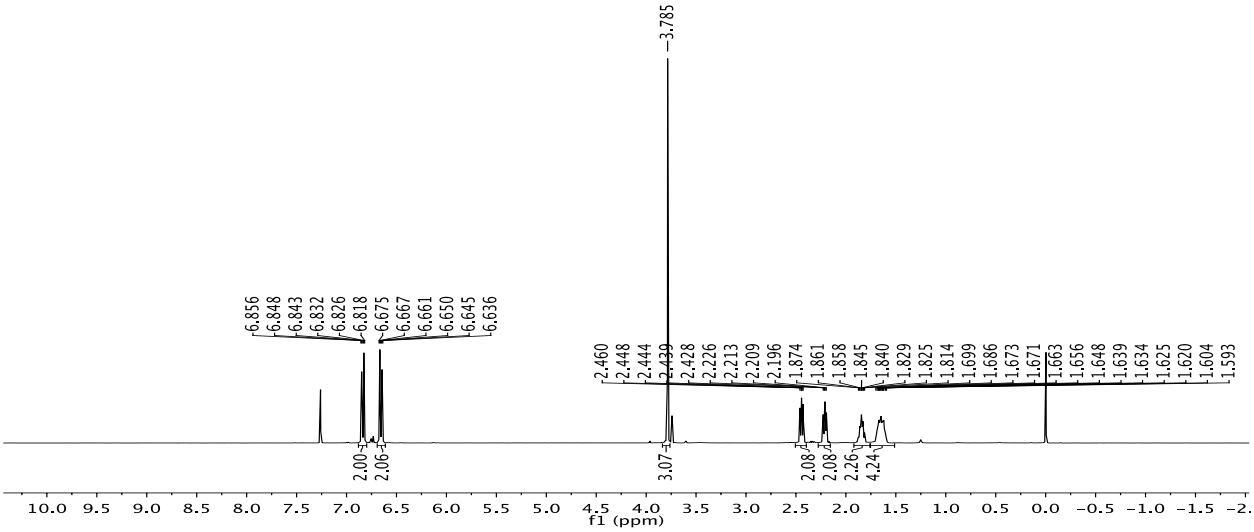
Following a literature procedure,[3] in a glovebox Pd_2dba_3 (28 mg, 0.03 mmol) was dissolved in 2 mL toluene. The solution was transferred to a vial containing *rac*-BINAP (56 mg, 0.09 mmol). This catalyst mixture was transferred to a 100 mL Schlenk bomb, followed by NaO*t*-Bu (1.614 g, 16.8 mmol) and another 28 mL of toluene. 4-bromoanisole (1.50 mL, 12 mmol) and aniline (1.3 mL, 14.4 mmol) were then added to the reaction mixture. The bomb was sealed and heated to 100 ºC for 24 h. The reaction mixture was then filtered over celite in EtOAc. The filtrate was washed with distilled water, dried over Na_2SO_4, and filtered. The solvent was removed *in vacuo* yielding a green-yellow solid. The material was purified by flash column chromatography (5% EtOAc in hexanes) recovering a yellow solid in 50% yield (1.2 g). NMR data is consistent with reported values.[3]

Synthesis of *N*-(4-methoxyphenyl)cyclohexanimine



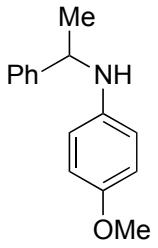
Following a literature procedure,[4] *p*-anisidine (6.16 g, 50 mmol) was transferred to a 250 mL round bottom flask equipped with a stir bar. 100 mL of toluene was added to the flask, followed by cyclohexanone (5.2 mL, 50 mmol). The resulting mixture was refluxed for 12 h, during which time the water was removed azeotropically using a Dean-Stark apparatus. The reaction was cooled to rt and all volatiles were removed *in vacuo*. The desired product was isolated as an orange oil in 60% yield (6.13 g, 30 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86-6.82 (m, 2H, ArH), 6.68-6.64 9m, 2H, ArH), 3.78 (s, 3H, OMe), 2.46-2.43 (m, 2H, Cy), 2.23-2.20 (m, 2H, Cy), 1.87-1.81 (m, 2H, Cy), 1.70-1.59 (m, 4H, Cy).



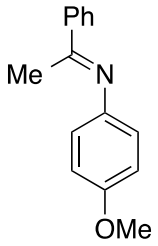
^{1}H NMR (400 MHz, $CDCl_3$)

Synthesis of 4-methoxy-*N*-(1-phenylethyl)aniline



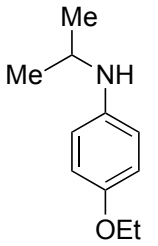
Following a literature procedure,[5] 4-aminoanisole (2.95 g, 24 mmol) was dissolved in 12 mL dry toluene and quantitatively transferred to a flame-dried 100 mL round bottom flask equipped with a magnetic stir bar. 2.3 mL (20 mmol) acetophenone was added to the vessel, followed by ~ 3 g of activated 4 Å molecular sieves. The reaction was heated to reflux for 16 h. Once all of the acetophenone was consumed (determined by TLC analysis) the reaction was filtered and the solvent was removed *in vacuo* yielding an orange oil. The oil was dissolved in 22 mL dry THF and 2.5 g (21 mmol) benzoic acid was added to the solution. $NaBH_4$ (832 mg, 22 mmol) was added portionwise to the reaction at room temperature, and the reaction stirred for 24 h. After completion the reaction was quenched with sat. $NaHCO_3$ and extracted into Et_2O. The organic layer was removed, dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. Flash column chromatography (5% EtOAc in hexanes) recovered the pure product in 50% yield (2.3 g). NMR data is consistent with reported values.[6]

Synthesis of *N*-(4-methoxyphenyl)-1-phenylethan-1-imine



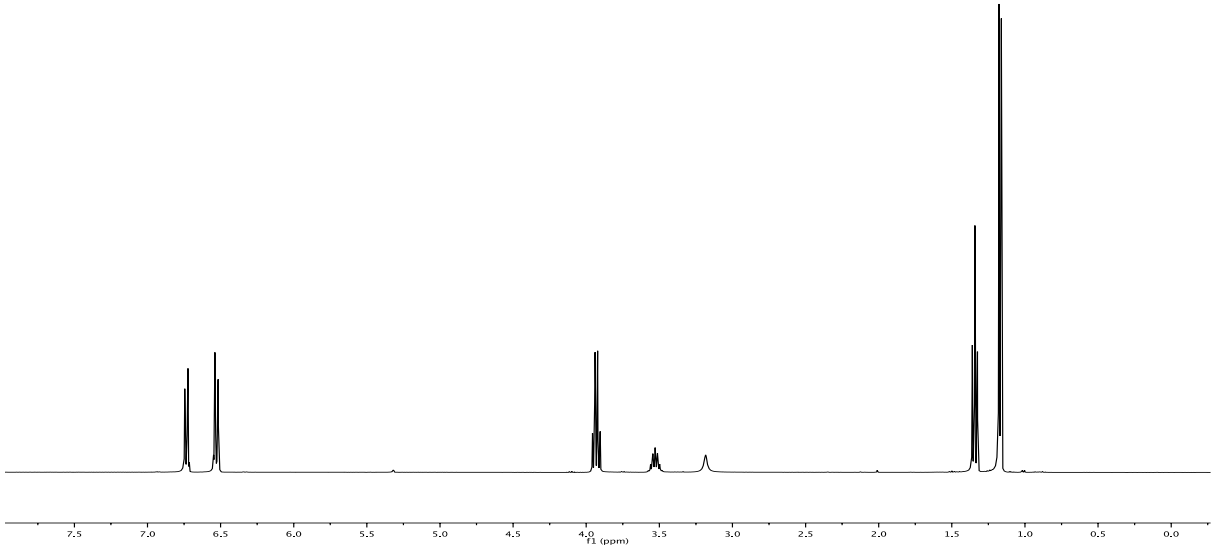
Following a modified literature procedure,[7] *p*-anisidine (3.08 g, 25 mmol) was transferred to a flame-dried round bottom flask equipped with a magnetic stir bar and ~5 g of activated 4Å molecular sieves. 10 mL of diethyl ether was added to the flask, followed by acetophenone (2.9 mL, 25 mmol). The reaction was stirred vigorously under N_2 for 24 h, afterwhich the reaction was filtered to remove the sieves and any precipitate. The filtrate was concentrated *in vacuo* to reveal faint yellow crystals, which were obtained in 45% yield (2.52 g, 11 mmol). NMR data is consistent with reported values.[7]

Synthesis of 4-ethoxy-*N*-*iso*-propylaniline

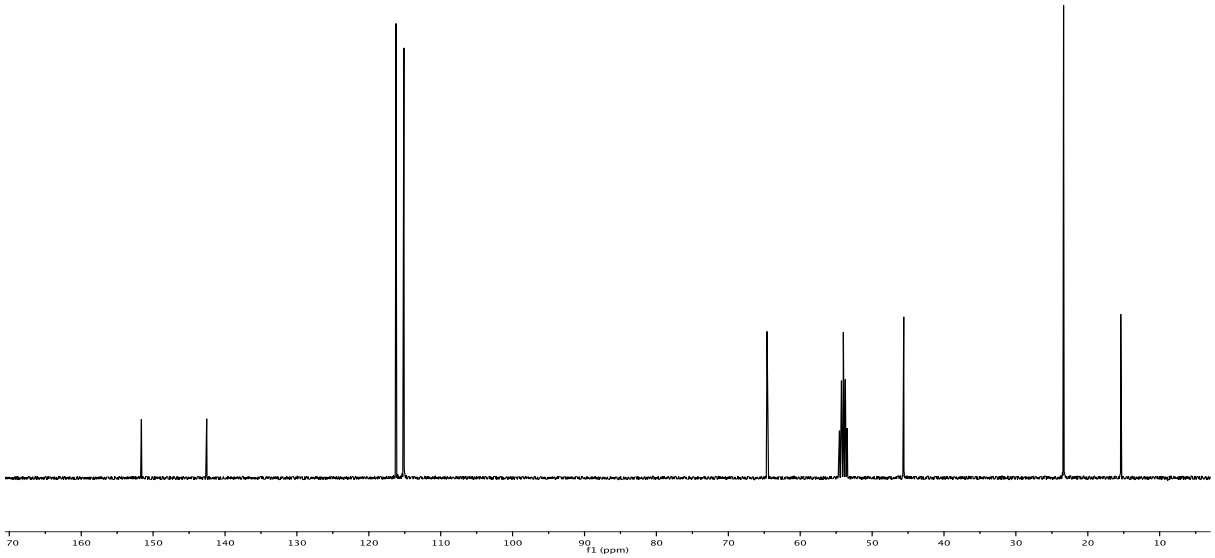


Following a literature procedure,[8] 4.9 mL (36 mmol) of 4-ethoxyaniline was added to a 250 mL round bottom flask and was treated with 19 mL (55 mmol) acetone, 10 g (73 mmol) $NaOAc{\cdot}3H_2O$, 31 mL (547 mmol) glacial acetic acid, 90 mL distilled H_2O and 22 mL 95% EtOH. The reaction stirred at room temperature for 30 min, followed by slow addition of 6.9 g (182 mmol) $NaBH_4$. The reaction stirred for 24 h at room temperature. After monitoring the reaction by TLC the reaction was extracted into 100 mL EtOAc and washed with 2x100 mL distilled water. The organic layer was separated, dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. Flash column chromatography (20% EtOAc in hexanes) resulted in pure material isolated as a red oil in 41% yield (2.9 g).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.75-6.71 (m, 2H, ArH), 6.55-6.51 (m, 2H, ArH), 3.93 (q, $^3J_{H\text{-}H}$ = 7.0 Hz, 2H, OEt), 3.53 (septet, $^3J_{H\text{-}H}$ = 6.3 Hz, 1H, N-*i*Pr), 3.18 (br s, 1H, NH), 1.34 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 3H, OEt), 1.17 (d, $^3J_{H\text{-}H}$ = 6.3 Hz, 6H, N-*i*-Pr); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 151.6 (4° Ar), 142.6 (4° Ar), 116.2 (Ar), 115.1 (Ar), 64.6 (OCH_2), 45.6 (N-CH), 23.4 (*i*-Pr), 15.4 (OEt); Elemental analysis calcd (%) for $C_{11}H_{17}NO$: C 73.70; H 9.56; N 7.81; Found: C 73.68; H 9.32; N 7.75.

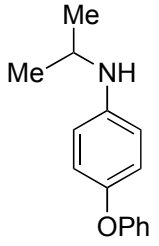


^{1}H NMR (400 MHz, CD_2Cl_2)



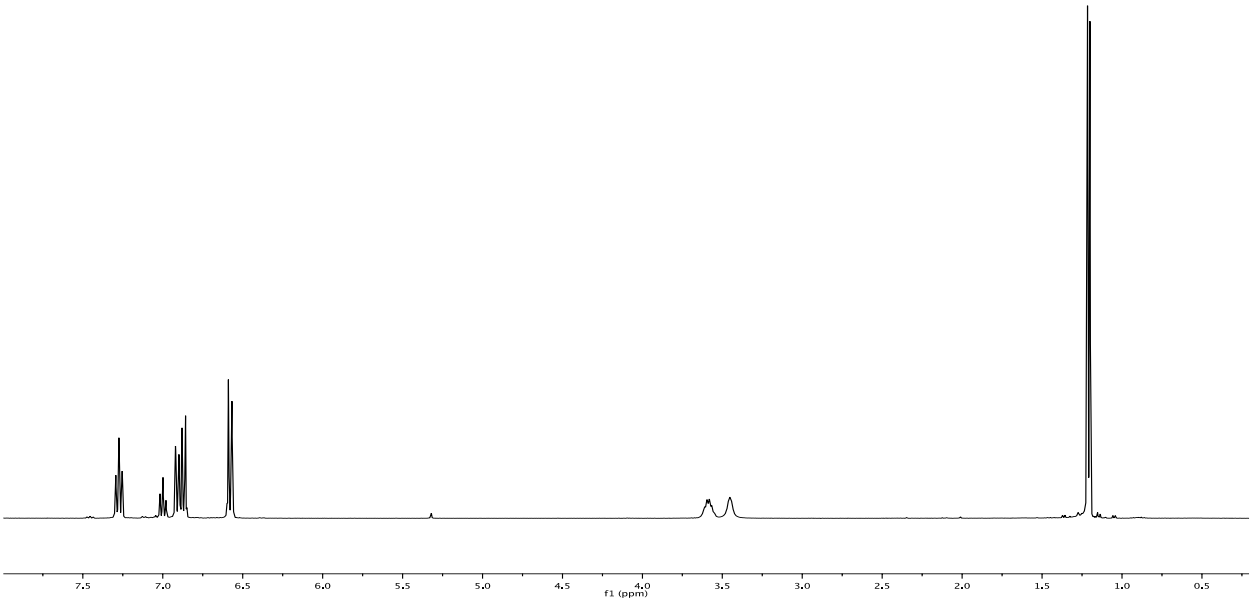
^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2)

Synthesis of 4-phenoxy-*N-iso*-propylaniline

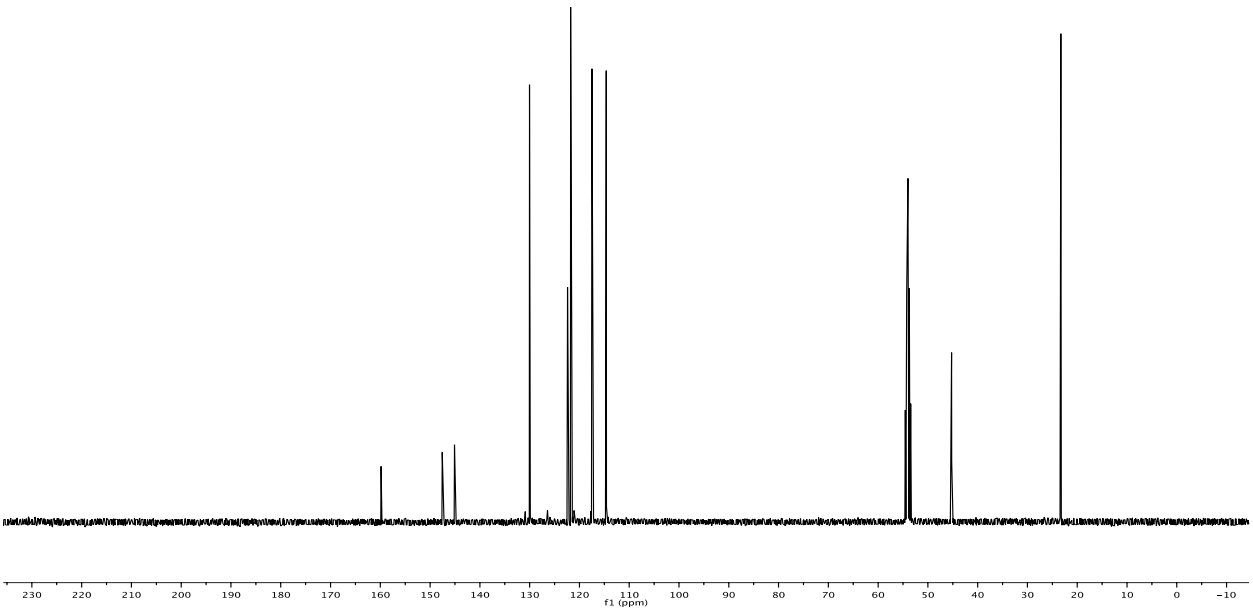


Prepared in an analogous fashion to 4-ethoxy-*N-iso*-propylaniline, 1.85 g (10 mmol) 4-phenoxyanilne was added to a 250 mL round bottom flash and was treated with 5 mL (70 mmol) acetone, 2.7 g (20 mmol) $NaOAc{\cdot}3H_2O$, 8.6 mL (150 mmol) glacial acetic acid, 25 mL distilled H_2O and 6 mL 95% EtOH. The reaction stirred at room temperature for 30 min, followed by slow addition of 1.9 g (50 mmol) $NaBH_4$. After the reaction was complete (determined by TLC analysis) the reaction was quenched with sat. $NaHCO_3$ and

extracted into EtOAc. The organic layer was washed with 2x50 mL distilled water and then separated. It was subsequently dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. Flash column chromatography (100% hexanes to 10% EtOAc in hexanes) recovered the material as a white solid in 65% yield (1.5 g).
^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.28 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, *m*-OPh), 7.02-6.98 (m, 1H, *p*-OPh), 6.92-6.85 (m, 4H, *o*-OPh and N-Ar), 6.58 (d, $^3J_{H\text{-}H}$ = 8.8 Hz, 2H, N-Ar), 3.63-3.55 (m, 1H, *i*-Pr), 3.45 (br s, 1H, NH), 1.21 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 6H, *i*-Pr); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 159.8 (4° Ar), 147.6 (4° Ar), 145.1 (4° Ar), 130.0 (*m*-OPh), 122.4 (*p*-OPh), 121.8 (N-Ar), 117.5 (*p*-OPh), 114.6 (N-Ar), 45.2 (N-*i*-Pr), 23.3 (*i*-Pr); Elemental analysis calcd (%) for $C_{15}H_{17}NO$: C 79.26; H 7.54; N 6.16; Found: C 79.59; H 7.47; N 6.20.



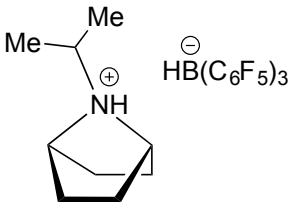
^{1}H NMR (400 MHz, CD_2Cl_2)



^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2)

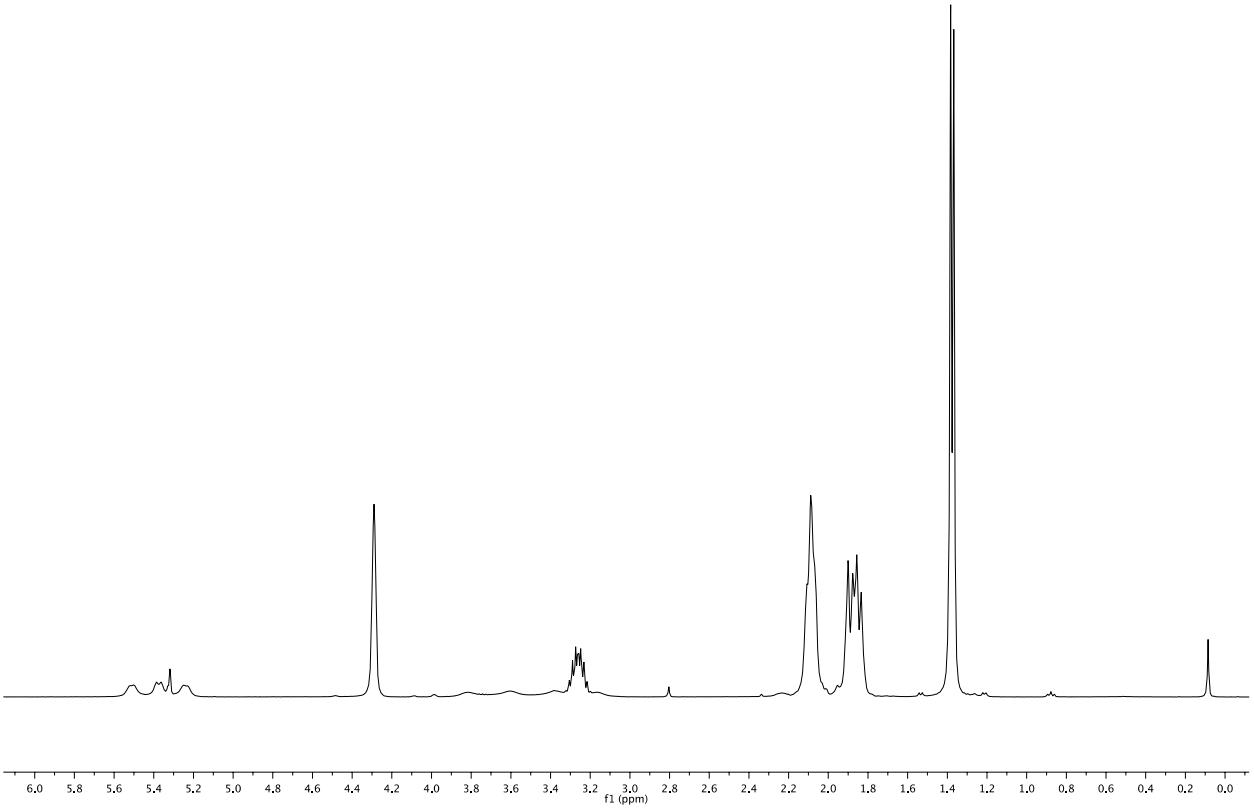
SECTION 3 – ARENE HYDROGENATION AND INTRAMOLECULAR RING CLOSURE REACTIONS

Synthesis of $[C_6H_{10}NHiPr][HB(C_6F_5)_3]$ (1)

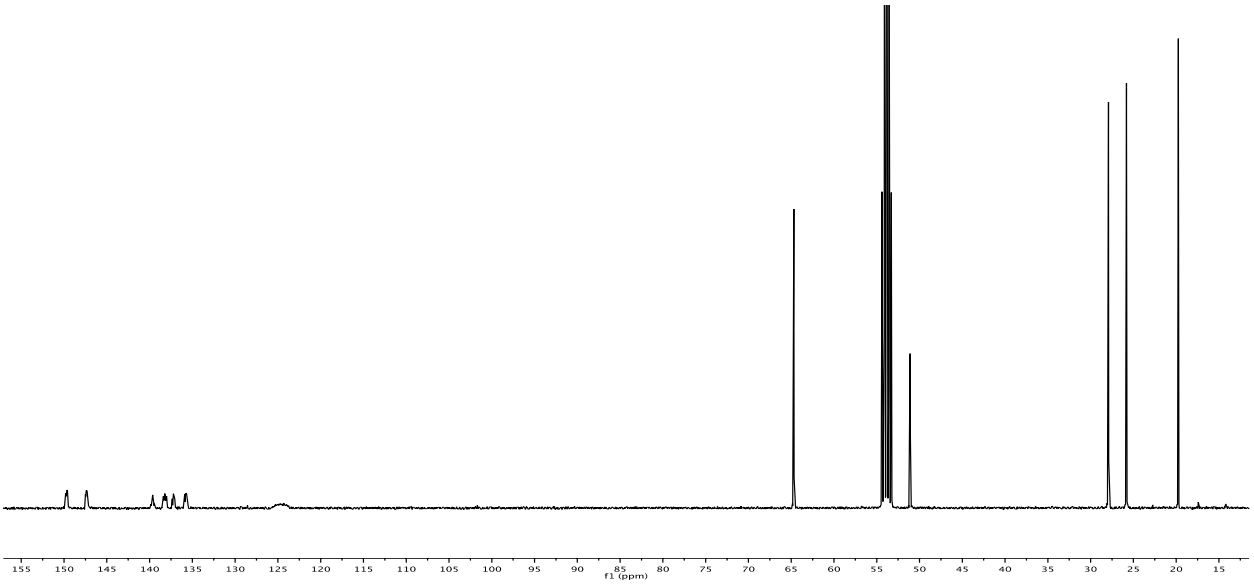


In the glovebox, a Schlenk bomb (50 mL) was charged with a solution of 4-methoxy-*N*-*iso*-propylaniline (83 mg, 0.50 mmol) and $B(C_6F_5)$ (358 mg, 0.70 mmol) dissolved in toluene (4 mL). The Schlenk bomb was degassed three times through freeze-pump-thaw cycles on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction bomb was placed in a 115 °C oil bath for 48 h. The toluene was then removed under reduced pressure resulting in crude pale yellow oil. The oil was washed with pentane (3 × 2 mL) affording the product as a white powder. Compound **1** was dried under vacuum and the product was isolated in 87% yield (285 mg, 0.44 mmol). Crystals suitable for X-ray diffraction were obtained from a layered solution of dichloromethane/pentane at -30 °C over 48 h.

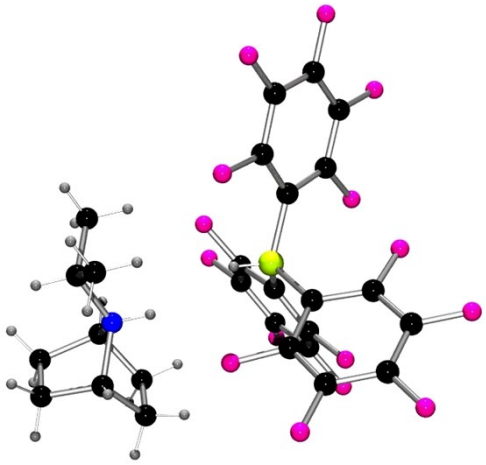
^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ 5.38 (br m, 1H, NH), 4.29 (br s, 2H, bridgehead H), 3.49 (br m, $^1J_{B-H}$ = 88 Hz, BH), 3.38-3.16 (m, 1H, N-*i*Pr), 2.11-2.06 (m, 4H, Cy), 1.91-1.83 (m, 4H, Cy), 1.38 (d, $^3J_{H-H}$ = 6 Hz, 6H, *i*Pr); **^{19}F NMR** (377 MHz, CD_2Cl_2, 298K): δ -134.2 (d, $^3J_{F-F}$ = 21 Hz, 2F, *o*-C_6F_5), -163.6 (t, $^3J_{F-F}$ = 21 Hz, 1F, *p*-C_6F_5), -166.8 - -167.0 (m, 2F, *m*-C_6F_5); **^{11}B NMR** (128 MHz, CD_2Cl_2, 298K): δ -24.8 (d, $^1J_{B-H}$ = 88 Hz, HB); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2, 298K): δ 148.5 (dm, $^1J_{C-F}$ ~ 234 Hz, CF), 138.4 (dm, $^1J_{C-F}$ ~ 243 Hz, CF), 137.0 (dm, $^1J_{C-F}$ ~ 247 Hz, CF), 124.6 (br, *i*-C_6F_5), 64.7 (bridgehead), 51.1 (N-*i*Pr), 27.9, 25.8, 19.7 (*i*Pr). Elemental analysis calcd (%) for $C_{27}H_{19}BF_{15}N$: C 49.64; H 2.93; N 2.14; Found: C 49.30; H 3.03; N 2.20.



^{1}H NMR (400 MHz, CD_2Cl_2)

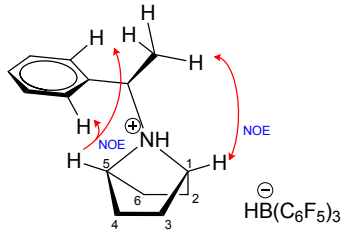


$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2)



Molecular Structure of **[$C_6H_{10}NHiPr$][$HB(C_6F_5)_3$]**

Synthesis of $[C_6H_{10}NHCH(CH_3)Ph][HB(C_6F_5)_3]$ (2)

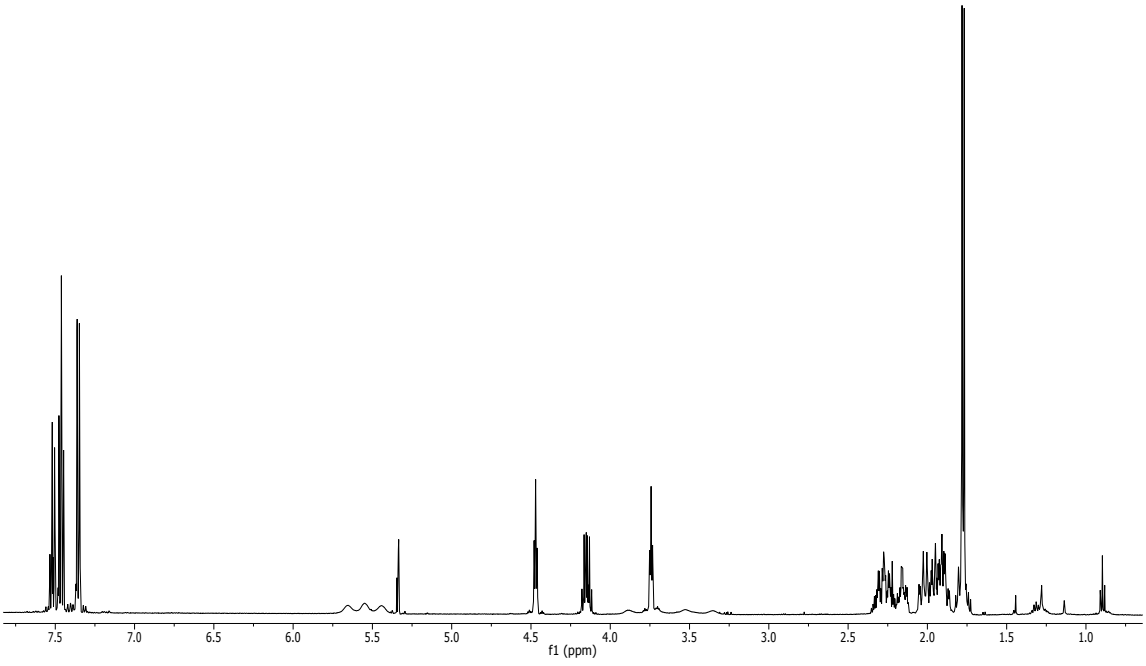


Method 1: In the glovebox, a Schlenk bomb (50 mL) was charged with a solution of 4-methoxy-*N*-(1-phenylethyl)aniline (114 mg, 0.50 mmol) and $B(C_6F_5)$ (358 mg, 0.7 mmol) dissolved in toluene (4 mL). The Schlenk bomb was degassed three times through freeze-pump-thaw cycles on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction bomb was placed in a 115 °C oil bath for 48 hours. The toluene was then removed under reduced pressure resulting in a crude pale yellow oil. The oil was washed with pentane (2 × 10 mL) and the remaining material was purified via crystallization by slow diffusion of pentane into DCM. Crystals were extracted from the mother liquor and dried under vacuum. The product was isolated in 51% yield (182 mg, 0.25 mmol). Crystals suitable for X-ray diffraction were obtained from a layered solution of dichloromethane/pentane at -30 °C over 48 h.

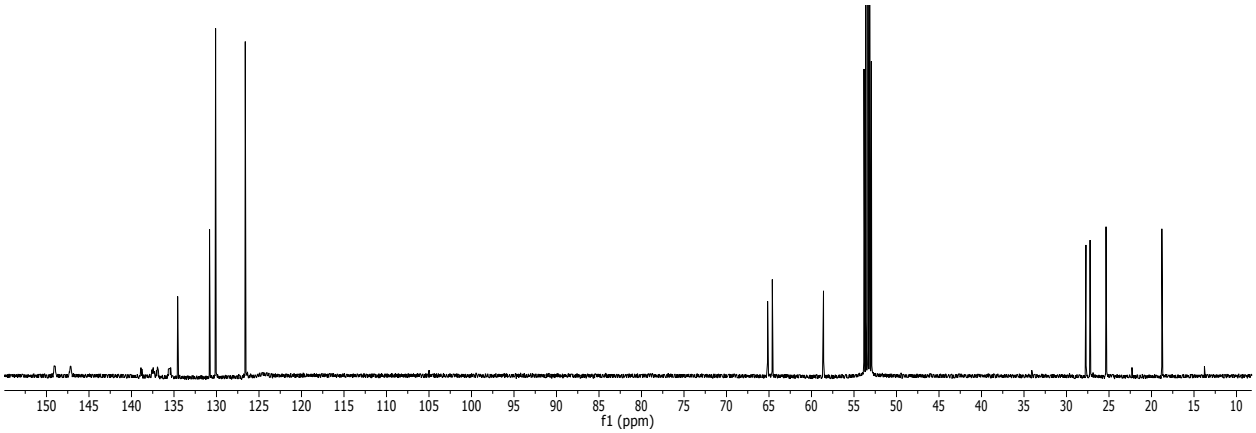
Method 2: In the glovebox, a Schlenk bomb (50 mL) was charged with a solution of 4-methoxy-*N*-(1-phenylethylidene)aniline (113 mg, 0.5 mmol) and $B(C_6F_5)$ (358 mg, 0.7 mmol) dissolved in toluene (4 mL). The Schlenk bomb was degassed three times through freeze-pump-thaw cycles on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction bomb was placed in a 115 °C oil bath for 48 h. The toluene was then removed under reduced pressure resulting in crude pale yellow oil. The oil was washed with pentane (2 × 10 mL) affording the product as a white powder. Compound **2** was dried under vacuum and the product was isolated in 63% yield (225 mg, 0.31 mmol). Crystals suitable for X-ray diffraction were obtained from a layered solution of dichloromethane/pentane at -30 °C over 48 h.

Method 3: In the glovebox, compound *trans*-4-$NH(CH(CH_3)Ph)C_6H_{10}OCH_3$ (8 mg, 0.034 mmol) and $B(C_6F_5)_3$ (17 mg, 0.034 mmol) were dissolved in d_8-toluene (0.4 mL) and added into a Teflon capped J-Young tube. The tube was degassed once through a freeze-pump-thaw cycle on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction was found to be complete after 12 h at 110 °C. The solvent was pumped off and the residue was washed with pentane (2 mL). The product was collected in 33 % yield.

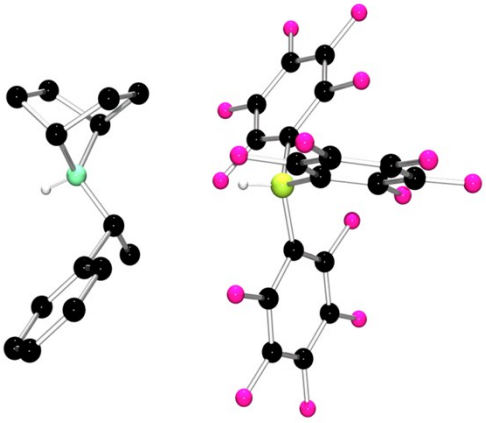
^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.52 (tm, 1H, $^3J_{HH}$ = 7.7 Hz, *p*-Ph), 7.46 (tm, 2H, $^3J_{HH}$ = 7.7 Hz, *m*-Ph), 7.35 (dm, 2H, $^3J_{HH}$ = 7.7 Hz, *o*-Ph), 5.55 (br m, 1H, NH), 4.47 (dd, 1H, $^3J_{HH}$ = 9.5 Hz, 4.8 Hz, H_1), 4.15 (dq, 1H, $^3J_{HH}$ = 10.2 Hz, 6.8 Hz, C*H*(CH_3)Ph), 3.74 (dd, 1H, $^3J_{HH}$ = 9.5 Hz, 4.8 Hz, H_5), 3.63 (br q, 1H, $^1J_{BH}$ = 83 Hz, BH), 2.29 (m, 1H, H_3), 2.23 (m, 1H, H_4), 2.15 (m, 1H, H_2), 2.01 (m, 1H, H_3), 1.96 (m, 1H, H_6), 1.90 (m, 1H, H_2), 1.88 (m, 1H, H_4), 1.77 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.76 (m, 1H, H_6); **^{19}F NMR** (377 MHz, CD_2Cl_2): δ -130.4 (m, 2F, *o*-C_6F_5), -163.8 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -167.0 (m, 2F, *m*-C_6F_5); **^{11}B NMR** (128 MHz, CD_2Cl_2): δ -24.9 (d, $^1J_{BH}$ = 83 Hz, BH), **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ 148.2 (dm, $^1J_{CF}$ = 236 Hz, C_6F_5), 137.8 (dm, $^1J_{CF}$ = 245 Hz, C_6F_5), 136.4 (dm, $^1J_{CF}$ = 249 Hz, C_6F_5), 134.6 (*ipso*-Ph), 130.8 (*p*-Ph), 130.1 (*m*-Ph), 126.6 (*o*-Ph), 124.6 (*ipso*- C_6F_5), 65.2 (C_5), 64.7 (C_1), 58.6 (*C*H(CH_3)Ph), 27.7 (C_2), 27.3 (C_6), 25.4 (C_3, C_4), 18.8 (CH_3);. Elemental analysis calcd (%) for $C_{32}H_{21}BF_{15}N$: C 53.73; H 2.96; N 1.96; Found: 53.84; H 3.21; N 2.00



^{1}H NMR (500 MHz, CD_2Cl_2)

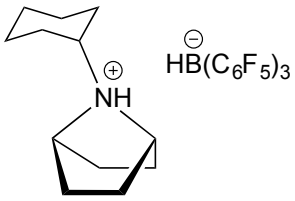


$^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2)



Molecular structure of **$[C_6H_{10}NHCH(CH_3)Ph][HB(C_6F_5)_3]$**

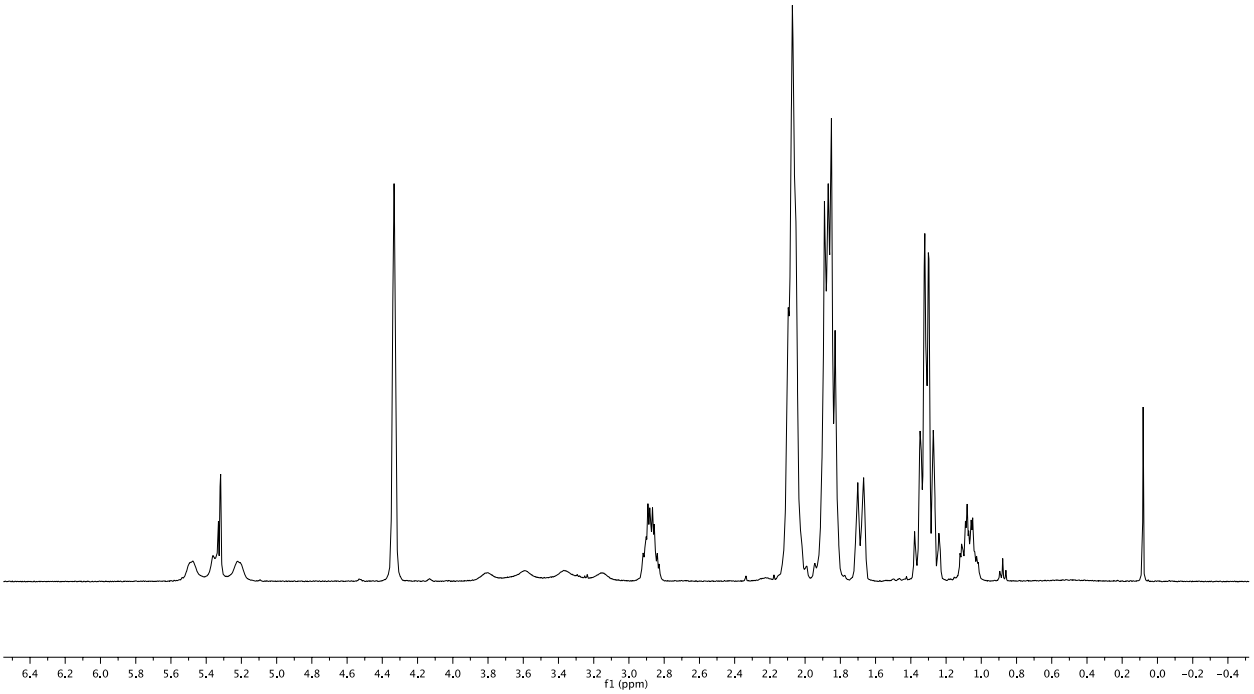
Synthesis of $[C_6H_{10}NHCy][HB(C_6F_5)_3]$ (3)



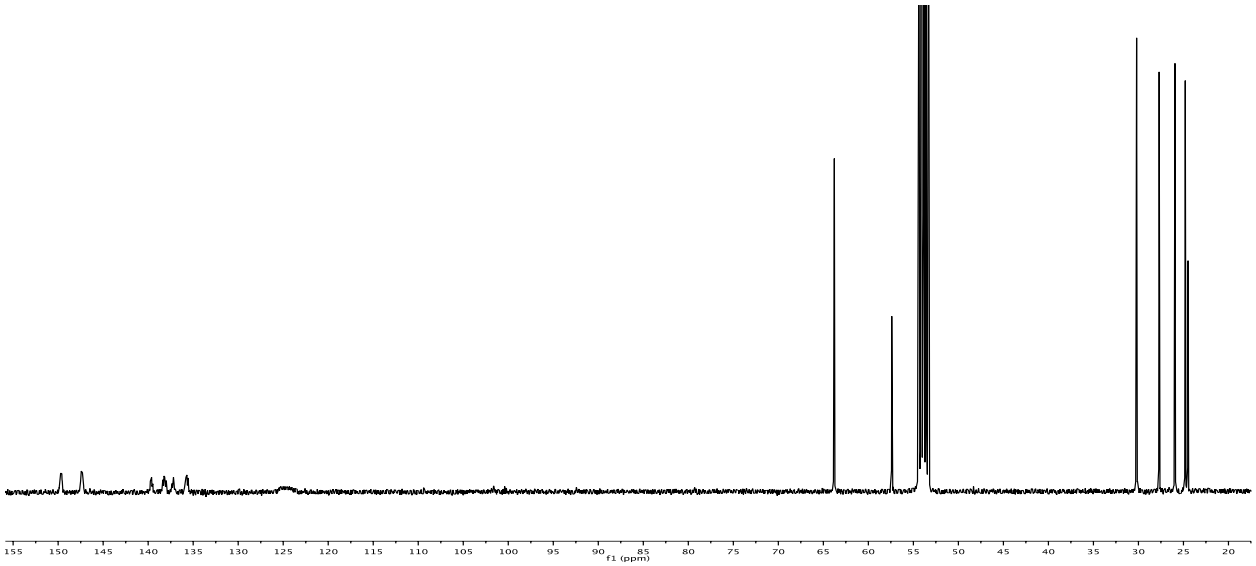
Method 1: In a glovebox, a Schlenk bomb (50 mL) was charged with a solution of 4-methoxy-*N*-phenylaniline (100 mg, 0.50 mmol) and $B(C_6F_5)$ (256 mg, 0.50 mmol) dissolved in toluene (4 mL). The Schlenk bomb was degassed three times through freeze-pump-thaw cycles on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction bomb was placed in a 115 °C oil bath for 48 h. The toluene was then removed under reduced pressure resulting in a yellow-green oil. The oil was washed with pentane (2 × 10 mL) and the resulting material was recrystallized via slow diffusion of pentane into dichloromethane, yielding compound **3** in 36% yield (125 mg, 0.18 mmol). Crystals suitable for X-ray diffraction were obtained from a layered solution of dichloromethane/pentane at -30 °C over 48 h.

Method 2: In a glovebox, a Schlenk bomb (50 mL) was charged with a solution of *N*-(4-methoxyphenyl)cyclohexanimine (102 mg, 0.50 mmol) and $B(C_6F_5)$ (358 mg, 0.70 mmol) dissolved in toluene (4 mL). The Schlenk bomb was degassed three times through freeze-pump-thaw cycles on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction bomb was placed in a 115 °C oil bath for 48 h. The toluene was then removed under reduced pressure resulting in a yellow oil. The oil was washed with pentane (2 × 10 mL) affording the crude product as an off-white oil. The material was recrystallized via slow diffusion of pentane into dichloromethane, yielding compound **3** in 56% yield (194 mg, 0.28 mmol). Crystals suitable for X-ray diffraction were obtained from a layered solution of dichloromethane/pentane at -30 °C over 48 h.

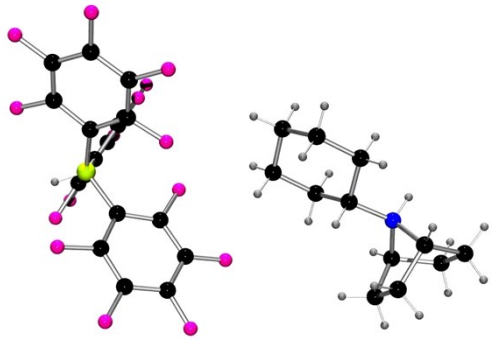
^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ 5.35 (br m, 1H, NH), 4.33 (br s, 2H, bridgehead H), 3.47 (br m, $^1J_{B\text{-}H}$ = 88 Hz, BH), 2.93-2.83 (m, 1H, N-Cy), 2.10-2.05 (m, 6H), 1.89-1.83 (m, 6H), 1.68 (dt, $^2J_{H\text{-}H}$ = 13.2 Hz, $^3J_{H\text{-}H}$ = 3.2 Hz, 1H), 1.38-1.23 (m, 4H), 1.12-1.02 (m, 1H); **^{19}F NMR** (377 MHz, CD_2Cl_2, 298K): δ -134.2 (d, $^3J_{F\text{-}F}$ = 23 Hz, 2F, *o*-C_6F_5), -163.6 (t, $^3J_{F\text{-}F}$ = 20 Hz, 1F, *p*-C_6F_5), -166.9 - -167.0 (m, 2F, *m*-C_6F_5); **^{11}B NMR** (128 MHz, CD_2Cl_2, 298K): δ -24.8 (d, $^1J_{B\text{-}H}$ = 89 Hz, HB); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2, 298K): δ 148.5 (dm, $^1J_{C\text{-}F}$ ~ 234 Hz, CF), 138.4 (dm, $^1J_{C\text{-}F}$ ~ 243 Hz, CF), 137.0 (dm, $^1J_{C\text{-}F}$ ~ 246 Hz, CF), 124.6 (br, *i*-C_6F_5), 63.8 (bridgehead), 57.4 (N-Cy), 30.2, 27.7, 25.9, 24.8, 24.5. Elemental analysis calcd (%) for $C_{30}H_{23}BF_{15}N$: C 51.97; H 3.34; N 2.02; Found: C 51.56; H 3.42; N 2.30.



^{1}H NMR (400 MHz, CD_2Cl_2)



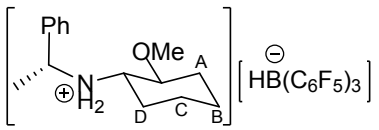
$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2)



Molecular Structure of **$[C_6H_{10}NHCy][HB(C_6F_5)_3]$**

SECTION 4 – REACTIONS 4 - 7

Synthesis of [2-$OCH_3C_6H_{10}NH_2CH(CH_3)Ph$][$HB(C_6F_5)_3$] (4)

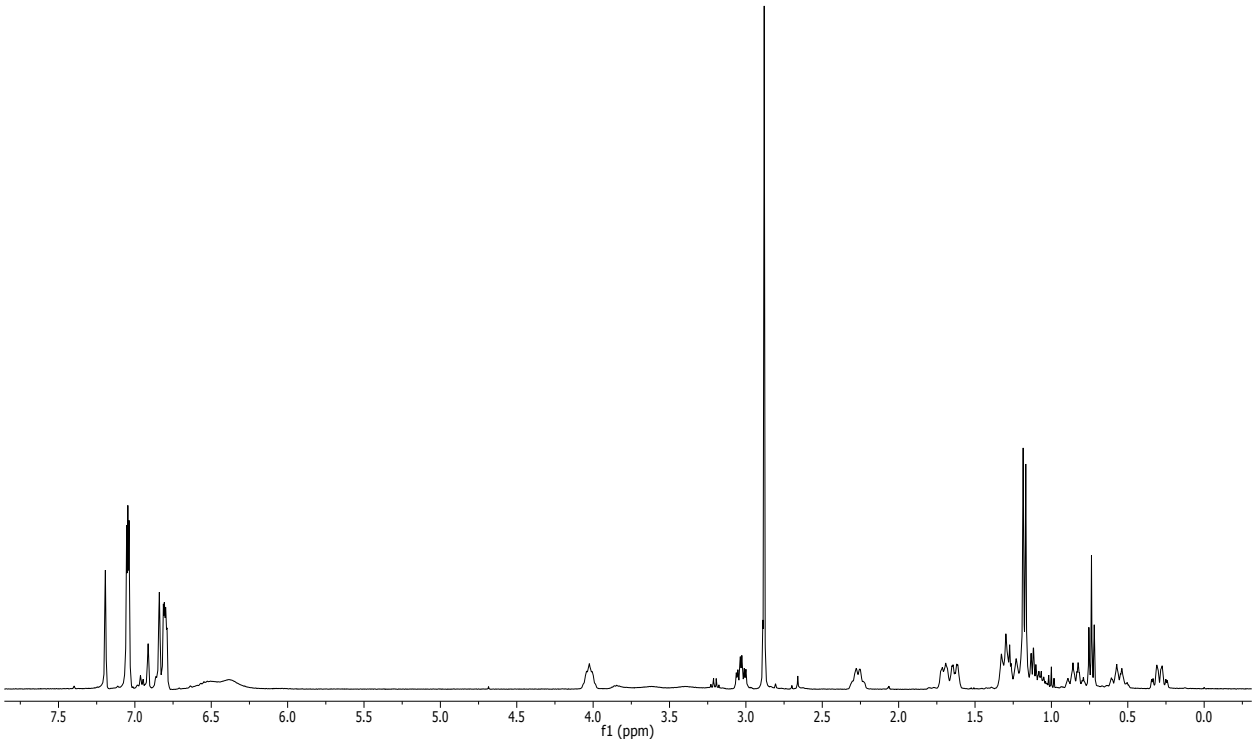


In the glovebox, a Schlenk bomb (50 mL) was charged with a solution of 2-methoxy-*N*-(1-phenylethyl)aniline (168 mg, 0.74 mmol) and $B(C_6F_5)$ (379 mg, 0.74 mmol) dissolved in toluene (5 mL). The Schlenk bomb was degassed once through a freeze-pump-thaw cycle on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction bomb was placed in a 115 °C oil bath for 40 h. The toluene was then removed under reduced pressure resulting in a white powder. The material was washed with pentane (3 × 2 mL) affording compound **4** as a white solid in 92% yield.

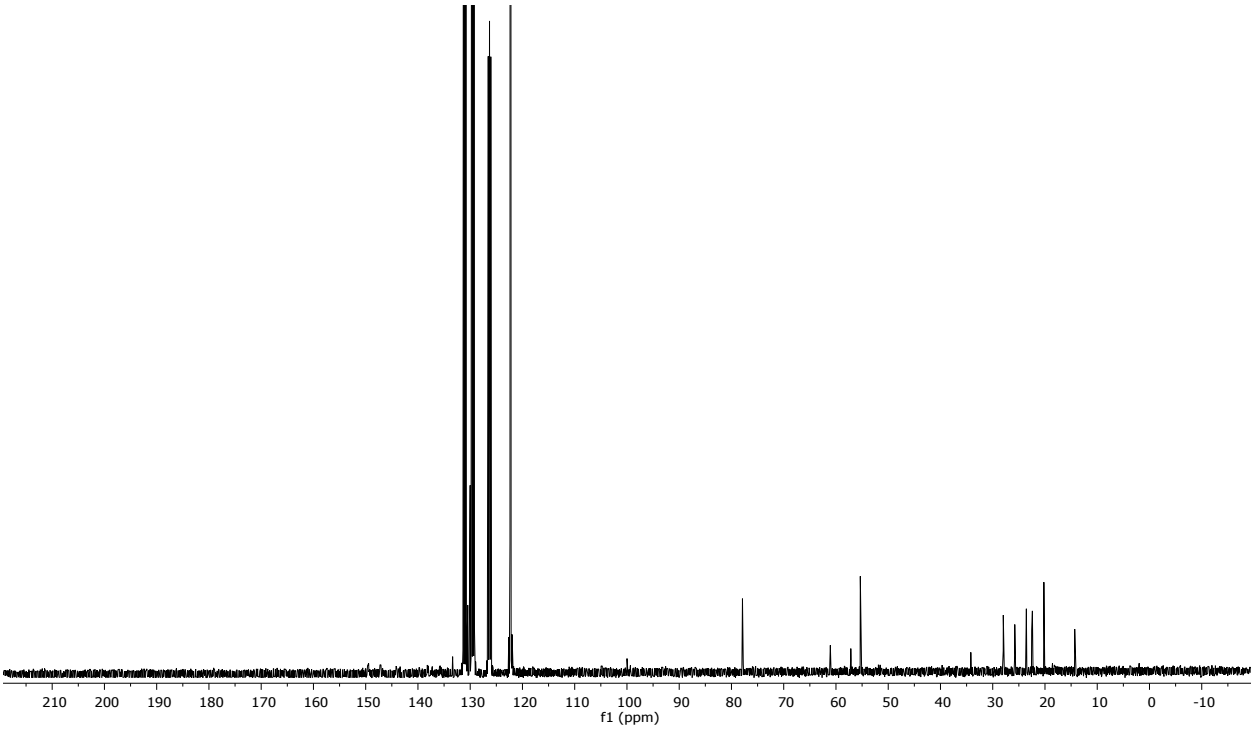
^{1}H NMR (400 MHz, C_6D_5Br): δ 7.16 (m, 3H, *m*,*p*-Ph), 6.91 (m, 2H, *o*-Ph), 6.55 (br s, 2H, NH_2), 4.13 (q, 1H, $^3J_{HH}$ = 6.4 Hz, C*H*(Me)Ph), 3.65 (br q, 1H, $^1J_{BH}$ = 92 Hz, BH), 3.13 (ddd, 1H, $^3J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 4.3 Hz, C*H*OMe), 2.98 (s, 3H, OMe), 2.37 (td, 1H, $^3J_{HH}$ = 10.7 Hz, CH_2CHNH_2), 1.80 (m, 1H, $^DCH_2$), 1.73 (dm, $^3J_{HH}$ = 13.6 Hz, 1H, $^ACH_2$), 1.40 (m, 2H, $^{D,C}CH_2$), 1.28 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH(*Me*)Ph), 1.20 (m, 1H, $^BCH_2$), 0.95 (pseudo qt, J_{HH} = 13.6 Hz, $^3J_{HH}$ = 3.1 Hz, $^BCH_2$), 0.66 (pseudo qt, J_{HH} = 13.6 Hz, $^3J_{HH}$ = 3.1 Hz, $^CCH_2$), 0.39 (pseudo qd, J_{HH} = 13.6 Hz, $^3J_{HH}$ = 3.1 Hz, $^ACH_2$); **^{19}F NMR** (377 MHz, C_6D_5Br, 298K): δ -134.1 (m, 2F, *o*-C_6F_5), -163.4 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -166.7 (m, 2F, *m*-C_6F_5); **^{11}B NMR** (128 MHz, C_6D_5Br, 298K): δ -24.6 (d, $^1J_{BH}$ = 92 Hz, BH); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_5Br, 298K): δ 148.4 (dm, $^1J_{CF}$ = 235 Hz, C_6F_5), 138.1 (dm, $^1J_{CF}$ = 246 Hz, C_6F_5), 136.7 (dm, $^1J_{CF}$ = 247 Hz, C_6F_5), 133.4 (*ipso*-Ph), 130.4 (*p*-Ph), 129.9 (*m*-Ph), 126.4 (*o*-Ph), 123.9 (*ipso*-C_6F_5), 77.8 (*C*HOMe), 61.1 (CH_2CHNH_2), 57.1 (*C*H(Me)Ph), 55.4 (OMe), 27.9 ($^ACH_2$), 25.7 ($^DCH_2$), 23.6 ($^CCH_2$), 22.4 ($^BCH_2$), 20.2 (Me). Elemental analysis **calcd** (%) for $C_{33}H_{25}BF_{15}NO$: C 53.03; H 3.37; N 1.87; **Found**: 52.88; H 3.57; N 1.90

Ratio of isomers = 1:1, determined by ^{1}H NMR

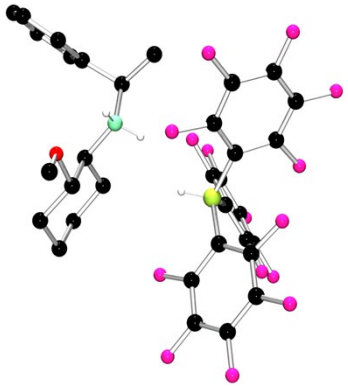
The *trans* isomer has been isolated and characterized.



^{1}H NMR (400 MHz, C_6D_5Br)

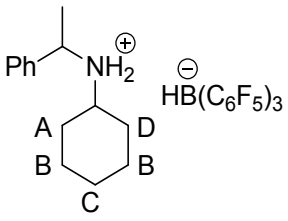


$^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_5Br)



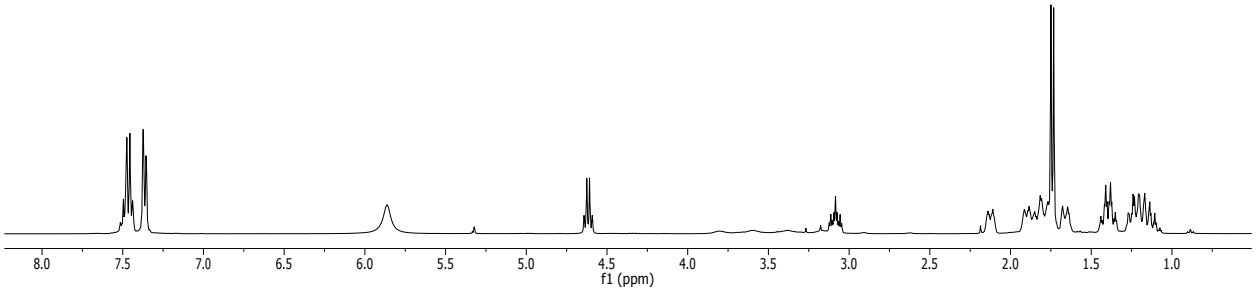
Molecular structure of **[2-$OCH_3C_6H_{10}NH_2CH(CH_3)Ph$][$HB(C_6F_5)_3$]**

Synthesis of $[C_6H_{11}NH_2CH(CH_3)Ph][HB(C_6F_5)_3]$ (5)

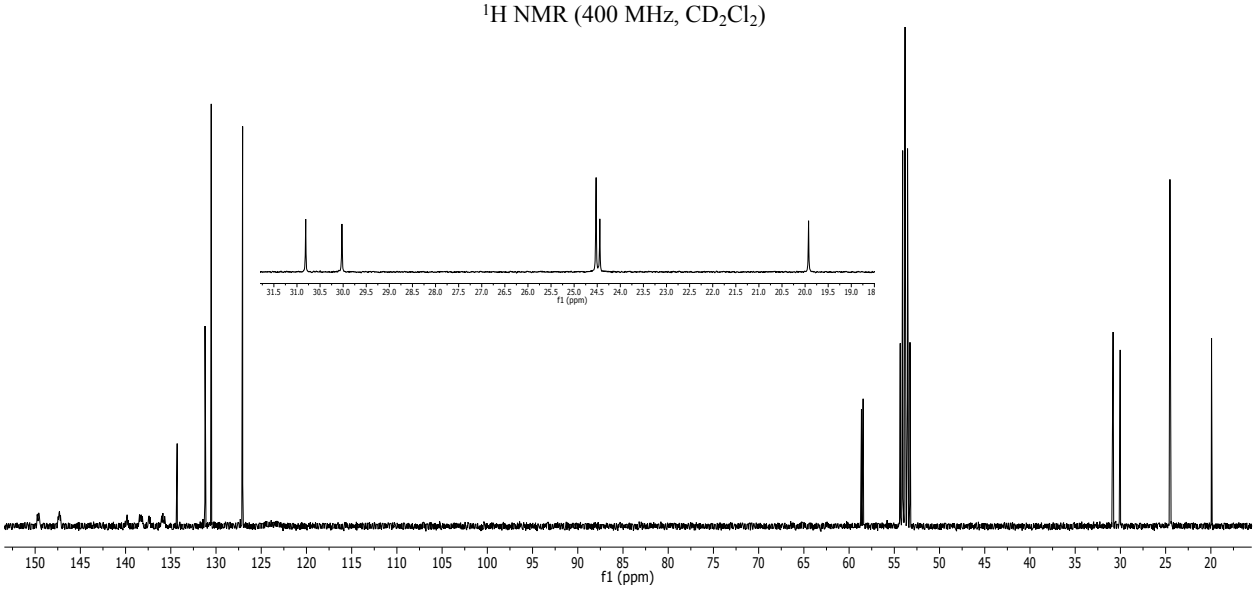


In the glovebox, a Schlenk bomb (50 mL) was charged with a solution of 3-methoxy-*N*-(1-phenylethyl)aniline (168 mg, 0.74 mmol) and $B(C_6F_5)$ (379 mg, 0.74 mmol) dissolved in toluene (5 mL). The Schlenk bomb was degassed once through a freeze-pump-thaw cycle on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction bomb was placed in a 115 °C oil bath for 40 h. The toluene was then removed under reduced pressure resulting in a white powder. The material was washed with pentane (3 × 2 mL) affording compound **5** as a white solid in 67% yield.

^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ 7.56-7.48 (m, 3H, *m*,*p*-Ph), 7.41 (d, 2H, $^3J_{HH}$ = 7.4, *o*-Ph), 5.43 (br, 2H, NH_2), 4.65 (q, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*(Me)Ph), 3.54 (br q, 1H, $^1J_{BH}$ = 85 Hz, BH), 3.11 (tt, 1H, $^3J_{HH}$ = 11.5 Hz, 3.9 Hz, CH_2CHNH_2), 2.17 (dm, 1H, $^3J_{HH}$ = 11.5 Hz, ^{A}CH$_2$), 1.95 (dm, 1H, $^3J_{HH}$ = 11.5 Hz, ^{D}CH$_2$), 1.91-1.80 (m, 2H ^{B}CH$_2$), 1.78 (d, 3H, $^3J_{HH}$ = 6.8 Hz, Me), 1.73-1.66 (m, 1H, ^{C}CH$_2$), 1.49-1.36 (m, 2H, ^{A,D}CH$_2$), 1.34-1.12 (m, 3H, ^{B,C}CH$_2$); **^{19}F NMR** (377 MHz, CD_2Cl_2, 298K): δ -134.1 (m, 2F, *o*-C_6F_5), -162.9 (t, 1F, $^3J_{FF}$ = 20.1 Hz, *p*-C_6F_5), -166.4 (m, 2F, *m*-C_6F_5); **^{11}B NMR** (128 MHz, CD_2Cl_2, 298K): δ -24.2 (d, $^1J_{BH}$ = 85 Hz, BH); **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2, 298K): δ 148.5 (dm, $^1J_{CF}$ = 236 Hz, C_6F_5), 138.5 (dm, $^1J_{CF}$ = 243 Hz, C_6F_5), 137.0 (dm, $^1J_{CF}$ = 245 Hz, C_6F_5), 134.3 (*ipso*-Ph), 131.2 (*p*-Ph), 130.5 (*m*-Ph), 127.1 (*o*-Ph), 123.7 (*ipso*-C_6F_5), 58.7 (CH_2CHNH_2), 58.4 (*C*H(Me)Ph), 30.8 (^{D}CH$_2$), 30.6 (^{A}CH$_2$), 24.5 (^{B}CH$_2$), 24.4 (^{C}CH$_2$), 19.9 (Me). Elemental analysis **calcd** (%) for $C_{32}H_{23}BF_{15}N$: C 53.58; H 3.23; N 1.95; **Found**: 53.73; H 3.56; N 2.09.

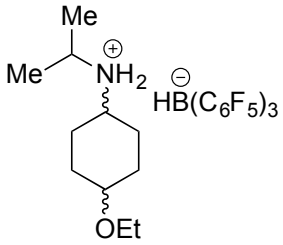


^{1}H NMR (400 MHz, CD_2Cl_2)



^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2)

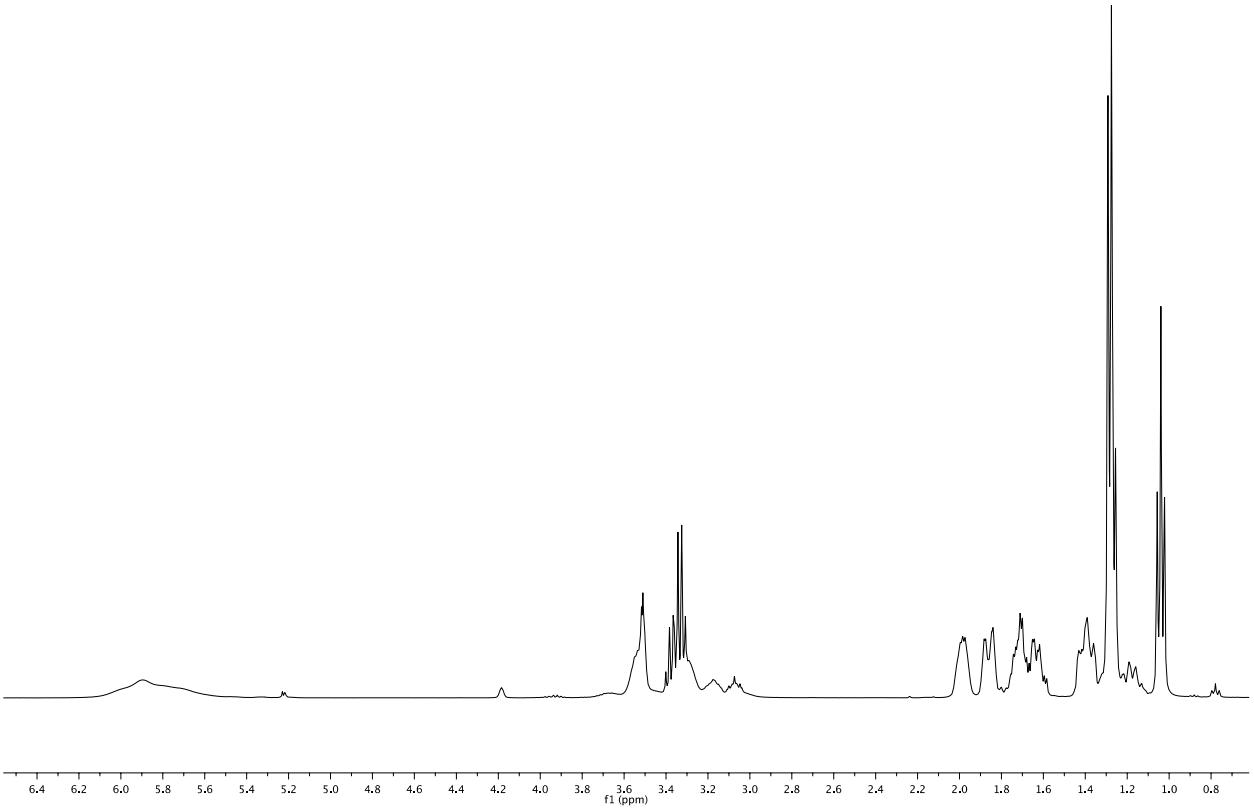
Synthesis of [iPrNH$_2$C$_6$H$_{10}$OEt][HB(C$_6$F$_5$)$_3$] (6)



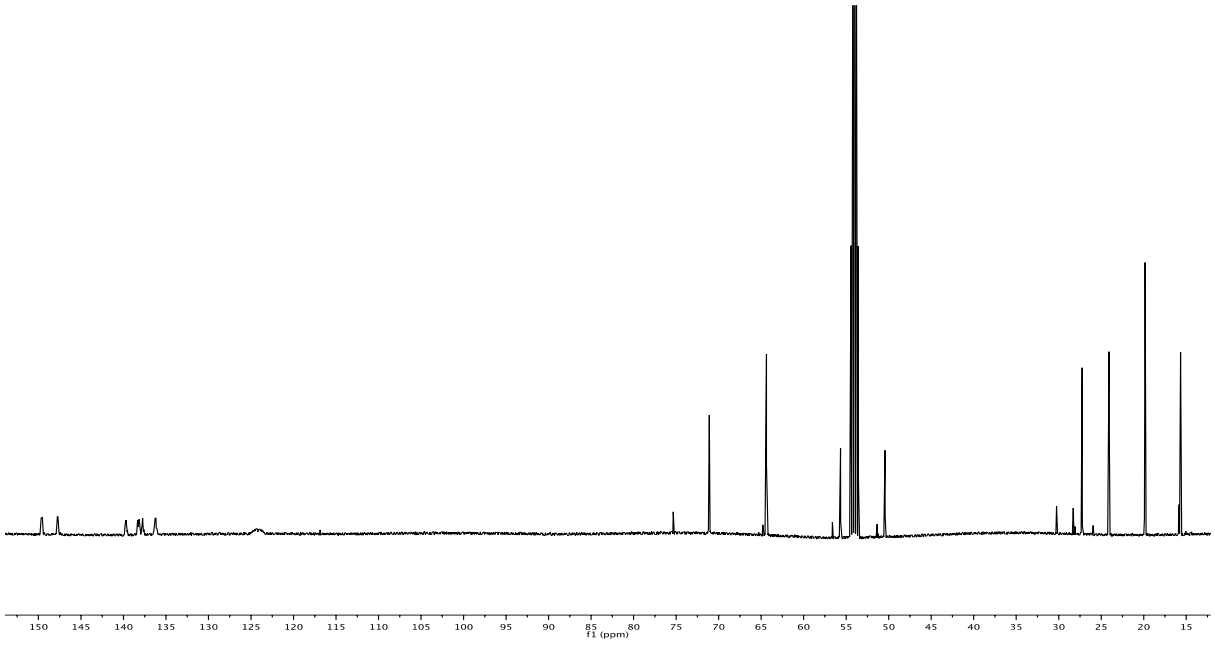
In the glovebox, a Schlenk bomb (50 mL) was charged with a solution of 4-ethoxy-*N*-*iso*-propylaniline (90 mg, 0.50 mmol) and B(C$_6$F$_5$) (269 mg, 0.52 mmol) dissolved in toluene (1 mL). The Schlenk bomb was degassed three through a freeze-pump-thaw cycle on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction bomb was placed in a 115 °C oil bath for 96 h. The toluene was then removed under reduced pressure resulting in a yellow oil. The oil was washed with pentane (3 × 2 mL) affording the product as a yellow oil. The material was recrystallized via slow diffusion of pentane into dichloromethane, yielding compound **6** in 82% yield (287 mg, 0.41 mmol).

^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ 5.98 (br s, 2H, NH_2), 3.83-3.14 (m, 6H, BH, N-*i*Pr, N-Cy, O-Cy, O-CH_2), 2.11-2.06 (m, 2H, Cy), 1.98-1.94 (m, 2H, Cy), 1.85-1.68 (m, 2H, Cy), 1.54-1.45 (m, 2H, Cy), 1.38 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 6H, *i*Pr), 1.1.4 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 3H, Et); **^{19}F NMR** (377 MHz, CD_2Cl_2, 298K): δ -134.2 (d, $^3J_{F\text{-}F}$ = 23 Hz, 2F, *o*-C_6F_5), -163.0 (t, $^3J_{F\text{-}F}$ = 20 Hz, 1F, *p*-C_6F_5), -166.5 (td, $^3J_{F\text{-}F}$ = 22, 7 Hz, 2F, *m*-C_6F_5); **^{11}B NMR** (128 MHz, CD_2Cl_2, 298K): δ -24.4 (d, $^1J_{B\text{-}H}$ = 85 Hz, HB); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2, 298K): δ 148.5 (dm, $^1J_{C\text{-}F}$ ~ 233 Hz, CF), 138.6 (dm, $^1J_{C\text{-}F}$ ~ 243 Hz, CF), 137.1 (dm, $^1J_{C\text{-}F}$ ~ 245 Hz, CF), 124.2 (br, *i*-C_6F_5), 75.1 (B), 70.9 (A), 64.3 (A), 64.2 (B), 56.7 (B), 55.5 (A), 51.4 (B), 50.4 (A), 30.1 (B), 28.2 (B), 27.0 (A), 23.9 (A), 19.8 (B), 19.8 (A), 15.7 (CH_3 of Et, isomer B), 15.5 (CH_3 of Et, isomer A). Elemental analysis calcd (%) for $C_{29}H_{25}BF_{15}NO$: C 49.81; H 3.60; N 2.00; Found: C 49.99; H 3.42; N 2.17.

Ratio of isomers = 3:1

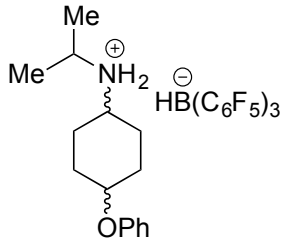


^{1}H NMR (400 MHz, CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2)

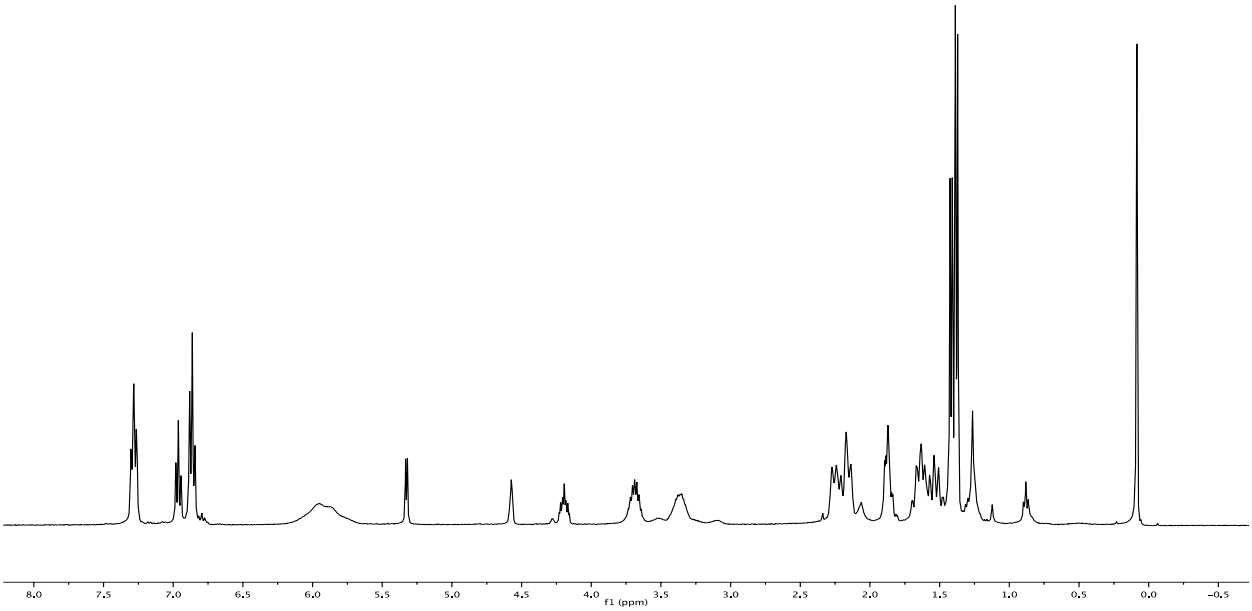
Synthesis of [iPrNH$_2$C$_6$H$_{10}$OPh][HB(C$_6$F$_5$)$_3$] (7)



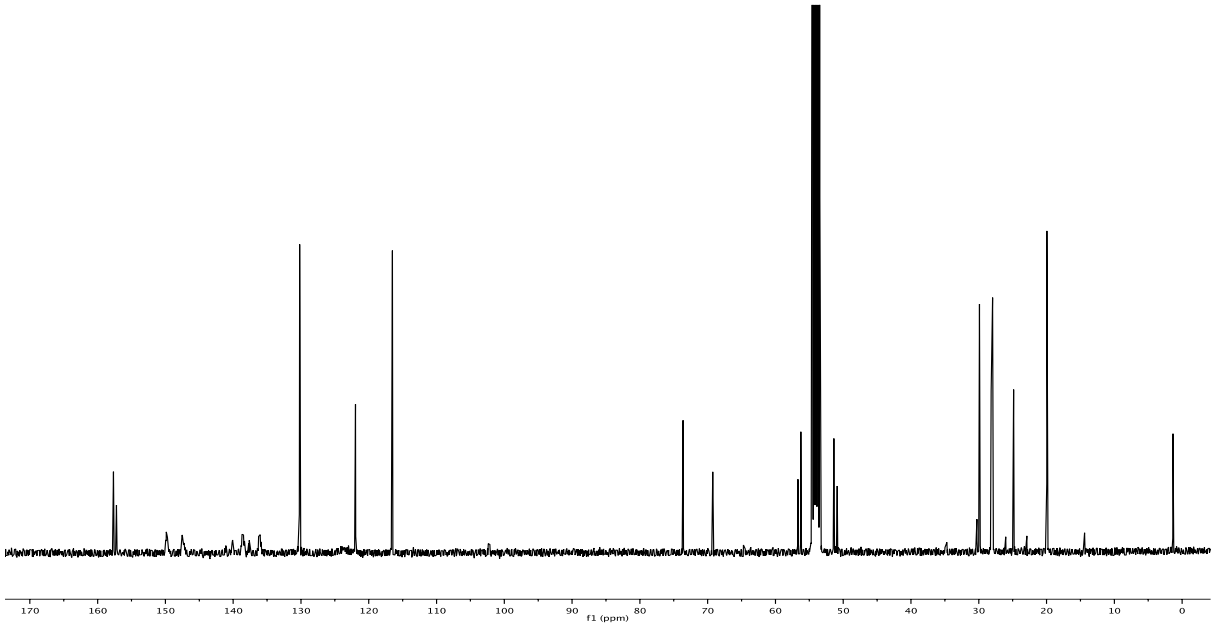
In the glovebox, a Schlenk bomb (50 mL) was charged with a solution of 4-phenoxy-*N*-*iso*-propylaniline (114 mg, 0.50 mmol) and B(C_6F_5) (269 mg, 0.52 mmol) dissolved in toluene (1 mL). The Schlenk bomb was degassed three through a freeze-pump-thaw cycle on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction bomb was placed in a 115 °C oil bath for 4 days. The toluene was then removed under reduced pressure resulting in a white powder. The material was washed with pentane (3 × 2 mL) affording compound **7** as a white solid in 48% yield.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.30-7.26 (m, 2H, *m*-Ph), 6.96 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Ph), 6.88-6.84 (m, 2H, *o*-Ph), 5.93 (br s, 2H, NH_2), 4.59-4.56 (m, 0.4H, O-CH), 4.23-4.16 (m, 0.6H, O-CH), 3.74-3.10 (m, 3H, N-*i*-Pr, N-CH, BH), 2.27-2.06 (m, 3H, Cy), 1.90-1.81 (m, 2H, Cy), 1.70-1.48 (m, 3H, Cy), 1.42-1.37 (m, 6H, *i*-Pr); **^{19}F NMR** (377 MHz, CD_2Cl_2, 298K): δ -134.24 (d, *J* = 23 Hz, 2F, *o*-C_6F_5), -162.57 (t, *J* = 20 Hz, 1F, *p*-C_6F_5), -166.23 (td, *J* = 24, 8 Hz, 2F, *m*-C_6F_5); **^{11}B NMR** (128 MHz, CD_2Cl_2, 298K): δ -24.2 (d, $^1J_{B-H}$ = 85 Hz, HB); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2, 298 K): δ 157.7 (O-Ph), 157.2 O-Ph), 148.6 (dm, $^1J_{C-F}$ ~ 234 Hz, CF), 138.9 (dm, $^1J_{C-F}$ ~ 245 Hz, CF), 137.3 (dm, $^1J_{C-F}$ ~ 250 Hz, CF), 130.2 (*m*-Ph), 130.2 (*m*-Ph), 123.9 (br, *i*-C_6F_5), 122.0 (*p*-Ph), 121.9 (*p*-Ph), 116.5 (*o*-Ph), 116.5 (*o*-Ph), 73.6 (O-CH), 69.2 (O-CH), 56.7 (N-*i*-Pr), 56.2 (N-*i*-Pr), 51.4 (N-CH), 50.9 (N-CH), 29.9 (Cy), 28.2 (Cy), 28.0 (Cy), 24.8 (Cy), 20.0 (*i*-Pr), 19.9 (*i*-Pr). Elemental analysis calcd (%) for $C_{33}H_{25}BF_{15}NO$: C 53.03; H 3.37; N 1.87; Found: C 52.54; H 3.73; N 1.84.

Ratio of isomers = 1:1.4



^{1}H NMR (400 MHz, CD_2Cl_2)



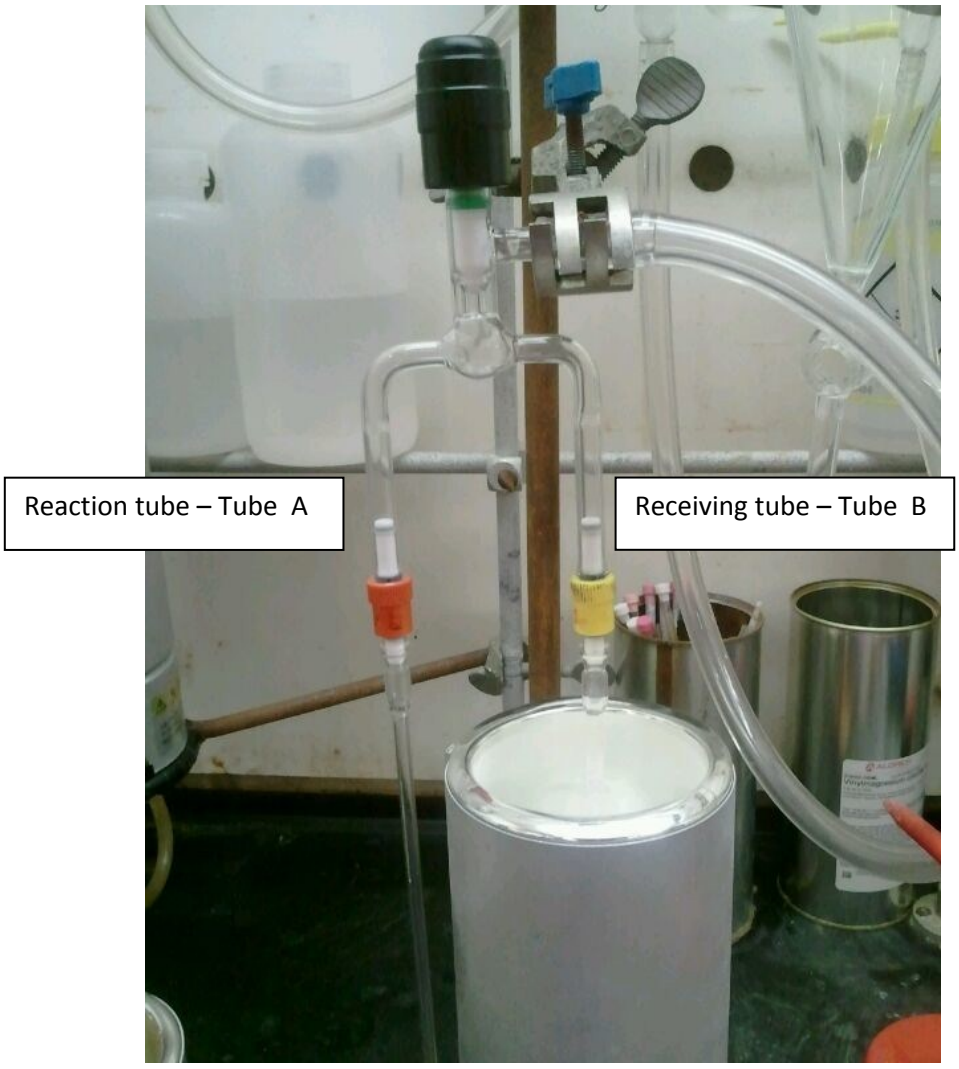
$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2)

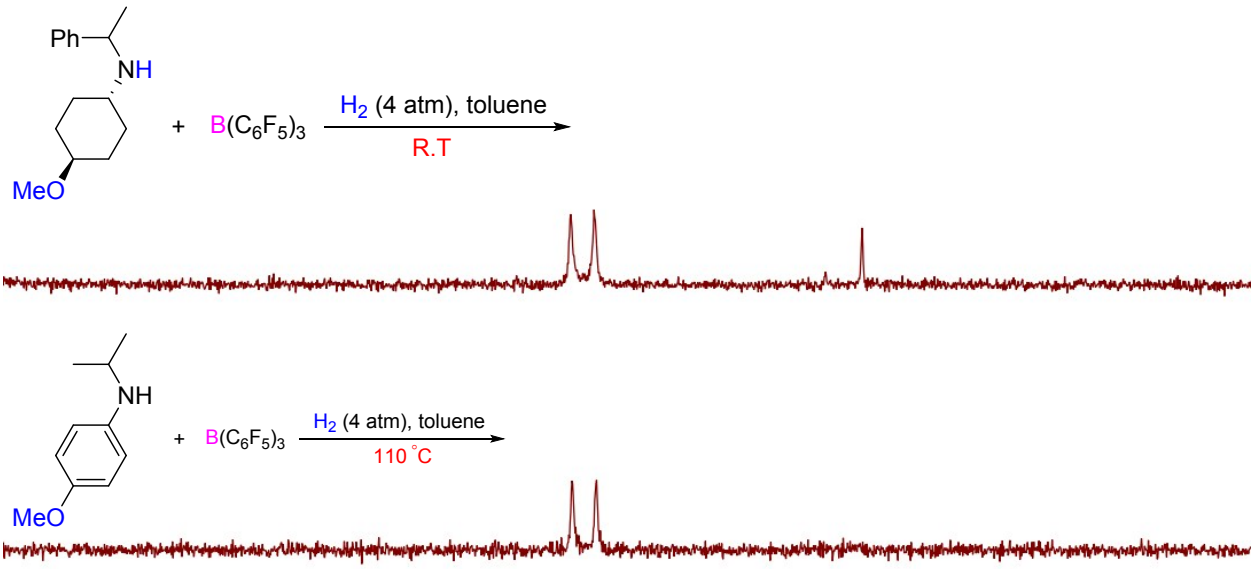
SECTION 5 – NMR EVIDENCE FOR METHANOL

Two separate reactions were carried through to spectroscopically the evidence methanol product,.
Experiment 1: In the glovebox, a J-Young tube was charged with a solution of 4-methoxy-*N*-*iso*-propylaniline (10 mg, 0.06 mmol) and $B(C_6F_5)$ (30.7 mg, 0.06 mmol) dissolved in d_8-toluene (0.5 mL). The J-Young tube was degassed three times through freeze-pump-thaw cycles on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The J-Young tube was placed in a 110 °C oil bath for 24 h. The J-Young tube was then degassed once to remove unreacted H_2.

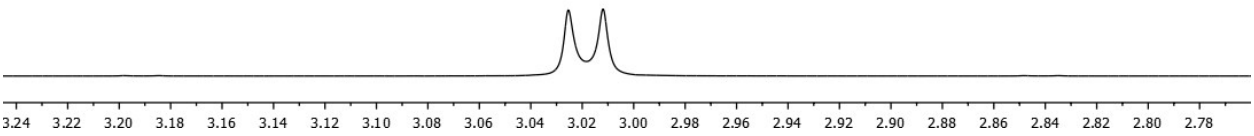
Experiment 2: : In the glovebox, a J-Young tube was charged with a solution of *trans*-4-$NH(CH(CH_3)Ph)C_6H_{10}OCH_3$ (14 mg, 0.06 mmol) and $B(C_6F_5)$ (30.7 mg, 0.06 mmol) dissolved in d_8-toluene (0.5 mL). The J-Young tube was degassed three times through freeze-pump-thaw cycles on the vacuum/H_2 line and filled with H_2 (4 atm) at -196 ºC. The reaction bomb was left at R.T for 3 days. After the reaction, the J-Young tube was degassed once to remove unreacted H_2.

Methanol transfer: The reaction tube (tube A) was attached to a T-shaped joint with an empty J-Young tube (tube B) sealed under vacuum. With both tubes attached and sealed, the headspace in the T-joint was evacuated. Tube B was placed in liquid nitrogen for 5 minutes and tube A was slowly opened to allow the volatiles to transfer over and condense in tube B. After complete transfer of the volatiles, ^1H NMR spectra showed evidence of methanol (middle spectrum).





MeOH in d_8-tol - control



^{1}H NMR (400 MHz, d_8-Tol)

REFERENCES

(1) Weber, L.; Eickhoff, D.; Kahlert, J.; Böhling, L.; Brockhinke, A.; Stammler, H.-G.; Neumann, B.; Fox, M. a. *Dalton Trans.* **2012**, *41*, 10328–10346.

(2) Wahba, A. E.; Hamann, M. T. *J. Org. Chem.* **2012**, *77*, 4578–4585.

(3) MacNeil, S. L.; Wilson, B. J.; Snieckus, V. *Org. Lett.* **2006**, *8*, 1133–1136.

(4) Anand, N.; Shah, B. A.; Kapoor, M.; Parshad, R.; Sharma, R. L.; Hundal, M. S.; Pannu, A. P. S.; Bharatam, P. V; Taneja, S. C. *J. Org. Chem.* **2011**, *76*, 5999–6006.

(5) Lai, P.-S.; Dubland, J. a.; Sarwar, M. G.; Chudzinski, M. G.; Taylor, M. S. *Tetrahedron* **2011**, *67*, 7586–7592.

(6) Wang, C.; Pettman, A.; Basca, J.; Xiao, J. *Angew. Chem. Int. Ed. Engl.* **2010**, *49*, 7548–7552.

(7) Pirovano, V.; Facoetti, D.; Acqua, M. D.; Fontana, E. Della; Abbiati, G.; Rossi, E.; Farmaceutiche, S.; Generale, C.; Marchesini, A.; Venezian, V. *Org. Lett.* **2013**, *15*, 3812–3815.

(8) Schellenberg, K. A. *J. Org. Chem.* **1963**, *28*, 3259–3261.