Supporting Information

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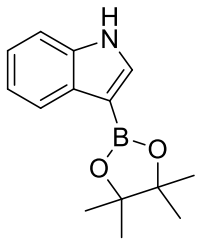
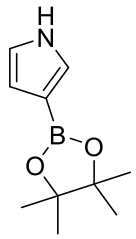
General Methods. All reactions were conducted in a nitrogen filled glove-box. THF was distilled from sodium benzophenone solutions. All other solvents were used as received from Sigma-Aldrich (Sure/Seal^{TM}) and were stored in the glovebox. All other commercially available materials were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-300 (300.11 and 75.47 MHz respectively), Varian VXR-500 or Varian Unity-500-Plus spectrometer (499.74 and 125.67 MHz respectively) and referenced to residual solvent signals. ^{11}B spectra were recorded on Varian VXR-500 or Varian Inova-300 operating at 160.41 and 96.29 MHz respectively, and were referenced to neat $BF_3{\cdot}Et_2O$ as the external standard. Elemental analyses were performed at Michigan State University using a Perkin Elmer Series II 2400 CHNS/O Analyzer. Melting points were measured on a MEL-TEMP® capillary melting apparatus and are uncorrected.

5, 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-indole (5)



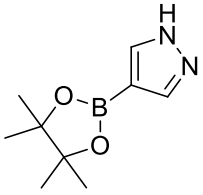
In a nitrogen filled glovebox, 117 mg indole (1 mmol) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 2.0 equiv HBpin (290 µL) and 1.0 equiv NEt_3 (140 µL) was added and the reaction vessel was sealed and heated at 80 °C for 10 min. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added and the reaction vessel was sealed and heated at 80 °C for 4 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using $MeOH/H_2O$ to afford a white solid (139 mg, 57% isolated yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (br s, 1H), 8.08 (dd, J = 7.3, 2.4 Hz, 2H), 7.65 (d, J = 2.4 Hz, 1H), 7.40 (dd, J = 7.4, 1.9 Hz, 1H), 7.23-7.18 (m, 2H), 1.37 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.0, 133.5, 131.9, 122.8, 83.0, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s).[1]

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (6)



In a nitrogen filled glovebox, 69 µL pyrrole (1 mmol) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 3.0 equiv HBpin (435 µL) and 1.0 equiv NEt_3 (140 µL) was added and the reaction vessel was sealed and stirred at room temperature for 12 h. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added and the reaction vessel was sealed and heated at 80 °C for 4 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the residue was crystallized from the residue using $MeOH/H_2O$ to afford a white solid (185 mg, 76% isolated yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (br s, 1H), 7.24 (d, 2H), 6.85 (dd, J = 4.4, 2.5 Hz, 1H), 6.57 (d, J = 1.4 Hz, 1H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 127.0, 118.5, 113.8, 83.0, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 29 (br s).[1,2]

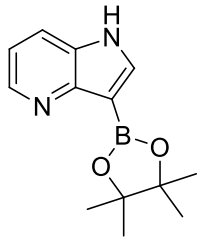
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-pyrazole (7)



In a nitrogen filled glovebox, 68 mg pyrazole (1 mmol) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%), 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) and 2.0 equiv HBPin (290 µL) were added and the reaction vessel was sealed and heated at 80 °C for 4 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Removal of the solvent under reduced pressure gave the product as a white solid (171 mg, 88% isolated yield); ^{1}H NMR (500 MHz,

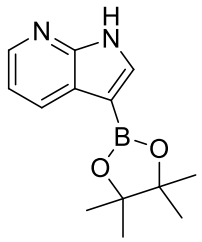
$CDCl_3$) δ 7.90 (s, 1H), 7.81 (s, 1H), 4.75 (br s, 1H), 1.35 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.9, 83.8, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s).[1]

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-4-azaindole (8)



In a nitrogen filled glovebox, 188 mg 4-azaindole (1 mmol) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 0.25 μmol $[Ir(OMe)COD]_2$ (0.25 mol%), 1.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) and 2.0 equiv HBPin (290 μL) were added and the reaction vessel was sealed and heated at 80 °C for 4 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Removal of the solvent under reduced pressure gave the product as a white solid (202 mg, 83% isolated yield); ^1H NMR (500 MHz, DMSO-d_6) δ 11.39 (br s, 1H), 8.51 (s, 1H), 7.97 (s, 1H), 7.71 (dd, J = 5.9, 3.0 Hz, 1H), 6.54 (s, 1H), 1.30 (s, 12H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 148.5, 148.0, 131.3, 128.3, 124.8, 102.2, 84.0, 25.1; HRMS (ESI) m/z calcd for $C_{13}H17BN_2O_2$ $[M + H]^+$ 245.1461, found 245.1456.

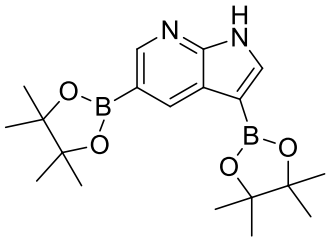
3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-7-azaindole (9)



In a nitrogen filled glovebox, 188 mg 7-azaindole (1 mmol) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 0.25 μmol $[Ir(OMe)COD]_2$ (0.25 mol%), 1.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) and 2.0 equiv HBPin (290 μL) were added and the reaction vessel was sealed and heated at 80 °C for 4 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under

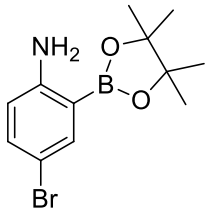
reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (185 mg, 76% isolated yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.36 (br s, 1H), 8.32 (m, 2H), 7.84 (s, 1H), 7.14 (dd, *J* = 7.3, 4.9 Hz, 1H), 1.37 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 142.5, 134.8, 130.9, 124.4, 116.5, 83.0, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 29 (br s).

3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-7-azaindole (10)



In a nitrogen filled glovebox, 188 mg 7-azaindole (1 mmol) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 0.25 μmol $[Ir(OMe)COD]_2$ (0.25 mol%), 1.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) and 2.0 equiv B_2Pin_2 (508 mg) were added and the reaction vessel was sealed and heated at 80 °C for 4 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (332 mg, 91% isolated yield); mp: 209-210 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.7 (s, 1H), 8.73 (d, *J* = 1.5 Hz, 1H), 8.68 (d, *J* = 1.5 Hz, 1H), 7.83 (s, 1H), 1.40 (s, 12H), 1.38 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 149.3, 137.6, 134.9, 123.4, 83.8, 83.1, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31; HRMS (ESI) m/z calcd for $C_{19}H_{28}B_2N_2O_4$ $[M + H]^+$ 371.2320, found 371.2509.

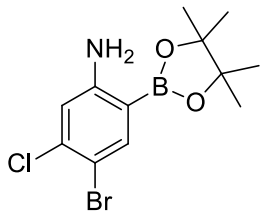
4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine (11a)



In a nitrogen filled glovebox, 170 mg 4-bromoaniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 μL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 μmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added followed by an

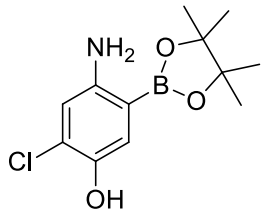
additional 1.5 equiv HBPin (218 μL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (246 mg, 88% yield); mp: 101-102 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.62 (d, *J* = 2.5 Hz, 1H), 7.27 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.53 (d, J = 8.3 Hz, 1H), 4.85 (br s, 2H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 152.5, 138.5, 135.0, 116.5, 108.1, 83.9, 24.6; ^{11}B NMR (160 MHz, CD_2Cl_2) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{17}BBrNO_2$ $[M + H]^+$ 298.0614, found 298.0609.

4-bromo-5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine (11b)



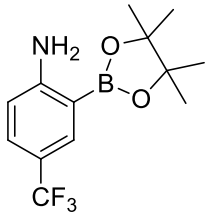
In a nitrogen filled glovebox, 206 mg 4-bromo-3-chloroaniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 μL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 μmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added followed by an additional 1.5 equiv HBPin (218 μL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (305 mg, 92% yield); mp: 79-81 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.70 (s, 1H), 4.80 (br s, 2H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 141.0, 138.0, 116.0, 108.4, 84.0, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{17}BBrClNO_2$ $[M + H]^+$ 332.0224, found 332.0222.

4-amino-2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-phenol (11c)



In a nitrogen filled glovebox, 109 mg 4-aminophenol (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 4.0 equiv HBPin (580 μL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 μmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using DCM/hexanes to afford a white solid (170 mg, 63% isolated yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, H), 6.61 (s, 1H), 4.84 (br s, 1H), 4.40 (br s, 2H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 142.8, 124.5, 123.1, 115.0, 83.8, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{17}BClNO_3$ $[M + H]^+$ 270.1068, found 270.1066.

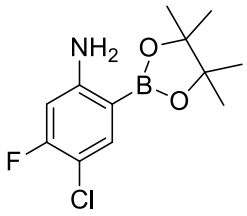
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-4-(trifluoromethyl)-benzenamine (11d)



In a nitrogen filled glovebox, 161 mg of 4-(trifluoromethyl)aniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBpin (218 μL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 μmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added followed by an additional 1.5 equiv HBpin (218 μL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed

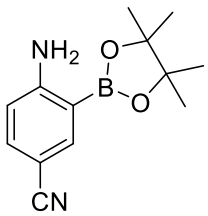
with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (250 mg, 87% yield); mp: 110-113 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.42 (dd, *J* = 8.3, 2.0, 1H), 6.61 (d, J = 8.4 Hz, 1H), 5.05 (br s, 2H), 1.35 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 129.5, 124,7, 120.2 (q, 270.8), 113.9 (q, 32,5), 109.4, 79.2, 20.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{17}BF3NO_2$ $[M + H]^+$ 288.1385, found 288.1389.[3]

4-chloro-5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine (11e)



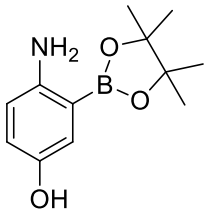
In a nitrogen filled glovebox, 145 mg 4-chloro-3-fluoroaniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added followed by an additional 1.5 equiv HBPin (218 µL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. 8% of the isomer where borylation occurred ortho to F was observed by ^{1}H NMR, but it was not isolated. The 2-borylated product isolated was isolated by recrystallization from MeOH/H_2O, which gave a white solid (244 mg, 90% isolated yield); mp: 95-96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 9.3 Hz, 1H), 6.36 (d, *J* = 11.2 Hz, 1H), 4.84 (br s, 2H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9 (d, *J* = 249.8 Hz), 154.0 (d, *J* = 10.5 Hz), 138.4 (d, *J* = 2.9 Hz), 125.5, 102.4 (d, *J* = 23.9 Hz), 83.9, 24.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ 110.9 (t, *J* = 10 Hz); ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{16}BClFNO_2$ $[M + H]^+$ 272.1025, found 272.1019.

4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (11f)



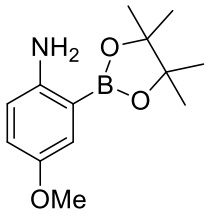
In a nitrogen filled glovebox, 118 mg 4-aminobenzonitrile (1.0 mmol, 1.0 equiv) was dissolved in 1 mL *n*-hexane in a 15 mL pressure tube containing a magnetic stir bar. 2.0 equiv HBPin (290 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 1.5 µmol $[Ir(OMe)COD]_2$ (1.5 mol%) and 3.0 µmol $N^4,N^4,N^{4'},N^{4'}$-tetramethyl-[2,2'-bipyridine]-4,4'-diamine (3.0 mol%) were added and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (146 mg, 60% isolated yield, (83% assay yield by ^{1}H NMR); mp: 96-97 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.0 Hz, 1H), 7.43 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.57 (d, *J* = 8.8 Hz, 1H), 5.27 (br s, 2H), 1.37 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 141.9, 135.9, 120.2, 114.5, 99.0, 84.2, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{17}BN_2O_2$ $[M + H]^+$ 245.1464, found 245.1594.

4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-phenol (11g)



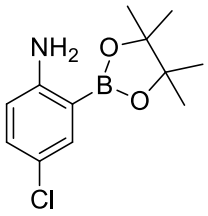
In a nitrogen filled glovebox, 109 mg 4-aminophenol (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 4.0 equiv HBPin (580 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, the residue was dissolved in DCM, and the solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL DCM. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using DCM/hexanes to afford a white solid (165 mg, 70% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 2.9 Hz, 1H), 6.78 (dd, *J* = 8.3, 3.0 Hz, 1H), 6.53 (d, J = 8.3 Hz, 1H), 4.44 (br s, 3H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 147.0, 121.9, 120.6, 116.5, 83.7, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{18}BNO_3$ $[M + H]^+$ 236.1414, found 236.1413.

4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine (11h)



In a nitrogen filled glovebox, 115 µL *p*-anisidine (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added followed by an additional 1.5 equiv HBPin (218 µL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE to give a pale red solid (157 mg, 63% yield); mp: 73-74 °C; ^{1}H NMR (500 MHz, C_6D_6) δ 7.60 (d, *J* = 2.9 Hz, 1H), 6.94 (dd, *J* = 8.3, 2.9 Hz, 1H), 6.53 (d, J = 8.8 Hz, 1H), 4.31 (br s, 2H), 3.37 (s, 3H), 1.03 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 133.9, 120.6, 119.6, 116.5, 83.8, 56.0, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{20}BNO_3$ $[M + H]^+$ 250.1617, found 250.1616.

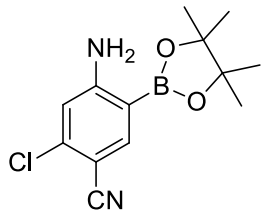
4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine (11i)



In a nitrogen filled glovebox, 128 mg 4-chloroaniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added followed by an additional 1.5 equiv HBPin (218 µL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the

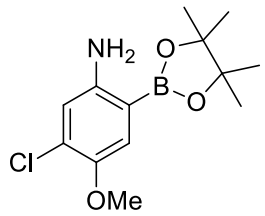
residue using MeOH/H_2O to afford a white solid (236 mg, 93% yield); mp: 91-93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.5 Hz, 1H), 7.14 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.53 (d, J = 8.8 Hz, 1H), 4.69 (br s, 2H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 135.8, 132.4, 121.6, 116.2, 83.9, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{17}BClNO_2$ $[M + H]^+$ 254.1119, found 254.1116.

4-amino-2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzonitrile (11j)



In a nitrogen filled glovebox, 152 mg 4-amino-2-2chlorobenzonitrile (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added followed by an additional 1.5 equiv HBPin (218 µL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (250 mg, 90% isolated yield); mp: 123-125 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 6.61 (s, 1H), 5.32 (br s, 2H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 143.37, 140.4, 117.3, 114.5, 100.1, 84.4, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{16}BClN_2O_2$ $[M + H]^+$ 279.1072, found 279.1068.

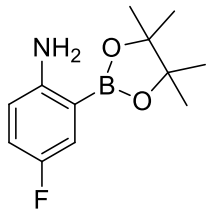
5-chloro-4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine (11k)



In a nitrogen filled glovebox, 154 mg 3-chloro-4-methoxyaniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 µL) was added

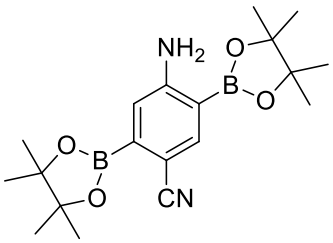
and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 μmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added followed by an additional 1.5 equiv HBPin (218 μL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Removal of the solvent under reduced pressure gave the product as a white solid (210 mg, 74% isolated yield); mp: 133-134 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.67 (s, 1H), 4.49 (br s, 2H), 3.84 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 146.8, 127.6, 119.9, 116.9, 83.8, 57.0, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{19}BClNO_3$ $[M + H]^+$ 284.1225, found 284.1220.

4-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine (11l)



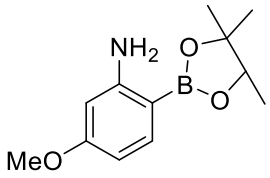
In a nitrogen filled glovebox, 95 μL 4-fluoroaniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL *n*-hexane in a 15 mL pressure tube containing a magnetic stir bar. 2.0 equiv HBPin (290 μL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 1.5 μmol $[Ir(OMe)COD]_2$ (1.5 mol%) and 3.0 μmol N^4,N^4,$N^{4'}$,$N^{4'}$-tetramethyl-[2,2'-bipyridine]-4,4'-diamine (3.0 mol%) were added and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. The residue was purified by recrystallization from DCM/hexanes and the solvent was collected on a cold frit as a solid, which gave a yellow oil upon warming to room temperature (102 mg, 43% isolated yield (74% assay yield by ^{1}H NMR)); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.20 (dd, J = 9.3, 3.0 Hz, 1H), 6.91 (td, J = 17.1, 8.8, 3.5 Hz, 1H), 6.54 (q, J = 4.4 Hz, 1H), 4.46 (br s, 2 H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 155.9 (d J = 276.2 Hz), 150.1, 121.2 (d, J = 20 Hz), 119.4 (d, J = 23 Hz), 115.7 (d, J = 6.7 Hz), 84.0, 24.6; ^{19}F NMR (470 MHz, CD_2Cl_2) δ 130.2 (td, J = 21.6, 13.2, 5.0 Hz); ^{11}B NMR (160 MHz, CD_2Cl_2) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{17}BFNO_2$ $[M + H]^+$ 238.1417, found 238.1540.

4-amino-2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzonitrile (11m)



In a nitrogen filled glovebox, 118 mg of 4-aminobenzonitrile (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBpin (218 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added followed by an additional 1.5 equiv HBpin (218 µL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using $MeOH/H_2O$ to afford a white solid (329 mg, 89% isolated yield); mp: 175-180 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 6.97 (s, 1H), 5.15 (br, s, 2H), 1.36 (s, 12H) 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ155.3, 143.0, 121.3, 120.2, 103.5, 84.6, 84.1, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.7 (br s), 22.3 (s); HRMS (ESI) m/z calcd for $C_{19}H_{28}B_2N_2O_4$ $[M + H]^+$ 371.2313, found 371.2314.

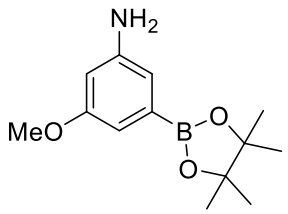
5-methoxy-2-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)aniline (11n)



In a nitrogen filled glovebox, 123 mg of 3-methoxyaniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 2.5 µmol $[Ir(OMe)COD]_2$ (2.5 mol%) and 5.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (5.0 mol%) were added followed by an additional 1.5 equiv HBPin (218 µL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Purified by column chromatography; hexane: EtOAc (70: 30), yielding a red gel (91.0 mg,

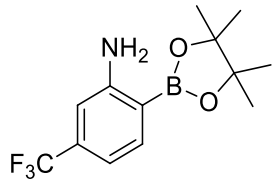
26% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 1H), 6.27 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.11 (d, *J* = 2.4 Hz, 1H), 4.76 (br s, 2H), 3.76 (s, 3H), 1.32 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ163.6, 155.4, 138.4, 103.7, 99.4, 83.2, 54.9, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{20}BNO_3$ $[M + H]^+$ 250.1617, found 250.1626

3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (11n´)



Chromatagraphy of the mixture above gave this isomer as a red solid (163.8 mg, 47%); mp: 90-93 °C; ^{1}H NMR (500 MHz, CD_3CN) δ 6.61 (d, *J* = 1.4 Hz, 1H), 6.54 (d, *J* = 1.9 Hz, 1H), 6.39 (t, *J* = 2.6, 1.9 Hz, 1H), 4.15 (br s, 2H), 3.73 (s, 3H), 1.32 (s, 12H); ^{13}C NMR (125 MHz, CD_3CN) δ163.3, 146.7, 114.5, 109.1, 104.9, 83.7, 55.2, 24.8; ^{11}B NMR (160 MHz, CD_3CN) δ 31 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{20}BNO_3$ $[M + H]^+$ 250.1617, found 250.1620.

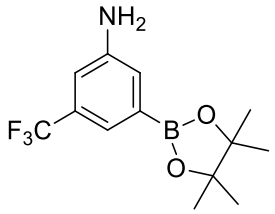
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-5-(trifluoromethyl)-benzenamine (11o)



In a nitrogen filled glovebox, 124 µL 3-(trifluoromethyl)aniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 2.5 µmol $[Ir(OMe)COD]_2$ (2.5 mol%) and 5.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (5.0 mol%) were added followed by an additional 1.5 equiv HBPin (218 µL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. The product was purified by column chromatography; heptane: MTBE (90: 10), affording a white solid (153 mg, 53% yield); mp: 64-65 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.80 (s, 1H), 4.92 (br s, 2H), 1.35 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 137.4, 134.4 (q, *J* = 31.5 Hz), 125.2 (q, *J* = 272.8 Hz), 112.8 (q, *J* = 3.8 Hz), 110.9 (q, *J* = 3.8 Hz),

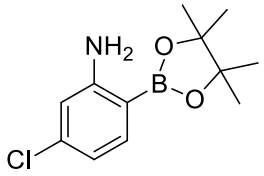
84.0, 24.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ 63.6; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{17}BF_3NO_2$ $[M + H]^+$ 288.1383, found 288.1378.[3]

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-5-(trifluoromethyl)-benzenamine (11o´)



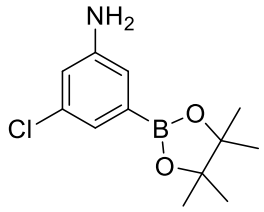
Chromatagraphy of the mixture above gave this isomer as a white solid (62 mg, 22% yield); mp: 61-62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.26 (s, 1H), 6.96 (s, 1H), 3.82 (br s, 2H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 131.2 (q, J = 31.5 Hz), 125.3 (q, J = 272.7 Hz), 124.1, 121.1 (q, J = 3.8 Hz), 113.8 (q, J = 3.8 Hz), 84.2, 24.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ 62.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{17}BF_3NO_2$ $[M + H]^+$ 288.1383, found 288.1376.

5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine (11p)



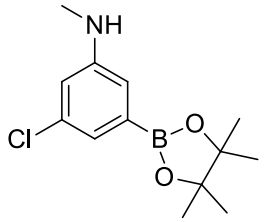
In a nitrogen filled glovebox, 106 µL 3-(chloro)aniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 2.5 µmol $[Ir(OMe)COD]_2$ (2.5 mol%) and 5.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (5.0 mol%) were added followed by an additional 1.5 equiv HBPin (218 µL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Purified by column chromatography; heptane: MTBE (90:10), affording a white solid (105 mg, 42% yield); mp: 64-65 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 7.8 Hz, 1H), 6.63 (dd, J = 7.8, 1.9 Hz, 1H), 6.58 (d, J = 2.0 Hz, 1H), 4.80 (br s, 2H), 1.35 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 138.6, 138.0, 117.1, 114.2, 83.6, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{17}BClNO_2$ $[M + H]^+$ 254.1121, found 254.1129.

3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (11p´)



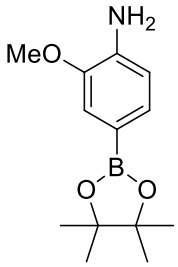
Chromatagraphy of the mixture above gave this isomer as a yellow solid (43 mg, 17% yield); mp: 54-55 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 1.0 Hz, 1H), 6.98 (d, *J* = 1.9 Hz, 1H) 6.76 (dd, *J* = 1.9, 1.0 Hz, 1H), 3.70 (br s, 2H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 146.3, 124.4, 119.2, 115.4, 84.0, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{17}BClNO_2$ $[M + H]^+$ 254.1121, found 254.1134.

N-methyl-3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine (12)



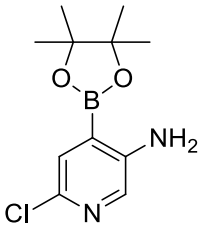
In a nitrogen filled glovebox, 122 µL 3-chloro-*N*-methylaniline (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 2.0 equiv HBPin (290 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) was added and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (230 mg, 86% isolated yield); mp: 75-76 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.66 (t, *J* = 2.4, 2.0 Hz, 1H), 3.77 (br s, 1H), 2.82 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.9, 122.9, 117.0, 114.4, 84.0, 30.6, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{19}BClNO_2$ $[M + H]^+$ 268.1276, found 268.1270.

2-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine (13)



In a nitrogen filled glovebox, 113 µL *o*-anisidine (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBPin (218 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 µmol $[Ir(OMe)COD]_2$ (0.25 mol%) and 1.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%) were added followed by an additional 1.5 equiv HBPin (218 µL) and the reaction vessel was sealed and heated at 80 °C for 16h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using $MeOH/H_2O$ to afford a white solid (152 mg, 61% isolated yield); mp: 68-70 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.20 (d, *J* = 1.5 Hz, 1H), 6.71 (d, J = 7.5 Hz, 1H), 4.08 (br s, 2H), 3.89 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 139.3, 128.8, 115.9, 114.1, 83.3, 55.5, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31 (br s); HRMS (ESI) m/z calcd for $C_{13}H_{20}BNO_3$ $[M + H]^+$ 250.1614, found 250.1612.

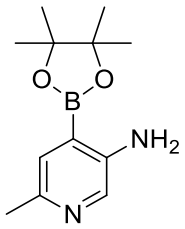
5-amino-2-chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-pyridine (14a)



In a nitrogen filled glovebox, 128 mg 6-chloropyridin-3-amine (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.2 equiv HBPin (173 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 1.5 µmol $[Ir(OMe)COD]_2$ (1.5 mol%), 3.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (3.0 mol%) and 0.5 equiv B_2Pin_2 (127 mg) were added and the reaction vessel was sealed and heated at 80 °C for 8 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL

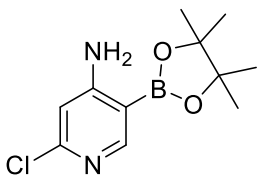
MeOH. The volatiles were then removed under reduced pressure, the residue was dissolved in DCM, and the solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL DCM. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using DCM/hexanes to afford a white solid (224 mg, 88% isolated yield); mp: 116-117 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.41 (s, 1H), 4.68 (br s, 2H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 138.7, 136.8, 129.4, 84.6, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{11}H_{16}BClN_2O_2$ $[M + H]^+$ 255.1016, found 255.0990.

5-amino-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-2-methyl pyridine (14b)



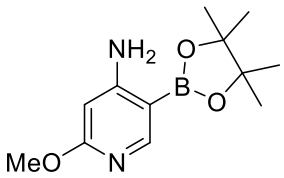
In a nitrogen filled glovebox, 108 mg 6-methylpyridin-3-amine (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.2 equiv HBPin (173 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 1.5 µmol $[Ir(OMe)COD]_2$ (1.5 mol%), 3.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (3.0 mol%) and 0.5 equiv B_2Pin_2 (127 mg) were added and the reaction vessel was sealed and heated at 80 °C for 8 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using EtOAc/hexanes to afford a white solid (152 mg, 63% isolated yield); mp: 68-70 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.95 (s, H), 7.23 (s, 1H), 4.55 (br s, 2H), 2.37 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 146.2, 145.6, 136.7, 128.2, 84.2, 24.7, 22.5; ^{11}B NMR (160 MHz, CD_2Cl_2) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{19}BN_2O_2$ $[M + H]^+$ 235.1620, found 235.1387.

2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-4-amine (14c)



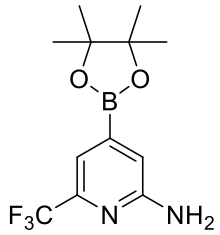
In a nitrogen filled glovebox, 128 mg 2-chloropyridin-4-amine (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.2 equiv HBPin (173 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 1.5 µmol $[Ir(OMe)COD]_2$ (1.5 mol%), 3.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (3.0 mol%) and 0.5 equiv B_2Pin_2 (127 mg) were added and the reaction vessel was sealed and heated at 80 °C for 8 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, the residue was dissolved in DCM, and the solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL DCM. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (249 mg, 98% isolated yield); mp: 170-171 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 6.46 (s, 1H), 5.29 (br s, 2H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 157.5, 154.8, 107.7, 84.1, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{11}H_{16}BClN_2O_2$ $[M + H]^+$ 255.1074, found 255.1206.

2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-4-amine (14d)



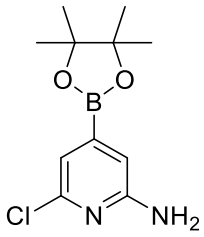
In a nitrogen filled glovebox, 124 mg 2-methoxypyridin-4-amine (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.2 equiv HBPin (173 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 1.5 µmol $[Ir(OMe)COD]_2$ (1.5 mol%), 3.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (3.0 mol%) and 0.5 equiv B_2Pin_2 (127 mg) were added and the reaction vessel was sealed and heated at 80 °C for 8 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, the residue was dissolved in DCM, and the solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL DCM. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (150 mg, 60% isolated yield); mp: 91-94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 5.83 (s, 1H), 5.10 (br s, 2H), 3.89 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 156.3, 148.5, 92.0, 83.5, 53.3, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{19}BN_2O_3$ $[M + H]^+$ 251.1569, found 251.1700.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)pyridin-2-amine (14e)



In a nitrogen filled glovebox, 162 mg 6-(trifluoromethyl)pyridin-2-amine (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.2 equiv HBPin (173 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 1.5 µmol $[Ir(OMe)COD]_2$ (1.5 mol%), 3.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (3.0 mol%) and 0.5 equiv B_2Pin_2 (127 mg) were added and the reaction vessel was sealed and heated at 80 °C for 8 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, the residue was dissolved in DCM, and the solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL DCM. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using $MeOH/H_2O$ to afford a white solid (282 mg, 98% isolated yield); mp: 97-98 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.03 (s, 1H), 4.74 (br s, 2H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 145.9 (q, J = 33 Hz), 122.8 (q, J = 273 Hz), 117.8, 114.5 (q, J = 3 Hz), 84.7, 24.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ 68.5; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{12}H_{16}BF_3N_2O_2$ $[M + H]^+$ 289.1337, found 289.1680.

6-chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-amine (14f)



In a nitrogen filled glovebox, 128 mg 6-chloropyridin-2-amine (1.0 mmol, 1.0 equiv) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.2 equiv HBPin (173 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 1.5 µmol $[Ir(OMe)COD]_2$ (1.5 mol%), 3.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (3.0 mol%) and 0.5 equiv B_2Pin_2 (127 mg) were added and the reaction vessel was sealed and heated at 80 °C for 8 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL

MeOH. The volatiles were then removed under reduced pressure, the residue was dissolved in DCM, and the solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL DCM. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using MeOH/H_2O to afford a white solid (170 mg, 67% isolated yield); mp: 160-163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.75 (s, 1H), 4.54 (br s, 2H), 1.34 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 149.4, 117.8, 112.0, 84.6, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s); HRMS (ESI) m/z calcd for $C_{11}H_{16}BClN_2O_2$ $[M + H]^+$ 255.1074, found 255.1205.

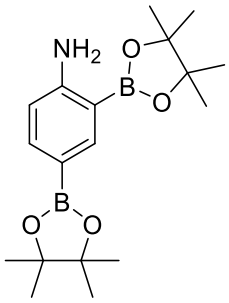
Borylation of Aniline. In a nitrogen filled glovebox, 91 μL aniline (1 mmol) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBpin (218 μL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 1.5 μmol $[Ir(OMe)COD]_2$ (1.5 mol%), 3.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (3.0 mol%) and 24 mg dodecahydrotriphenylene (0.10 mmol) were added and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure and the product assay yields were determined by ^{1}H NMR.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 8.4 Hz, 2H), 3.83 (br, s, 2H), 1.32 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 136.5, 114.0, 83.2, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30 (br s).

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.01 (t, J = 7.8, 7.3 Hz, 1H), 6.98 (s, J =1.5 Hz, 1H), 6.81 (d, J = 7.3 Hz, 1H), 6.65 (dd, J = 8.3, 1.5 Hz, 1H), 5.07 (br, s, 2H), 1.25 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 128.7, 124.9, 121.1, 117.9, 83.6, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31 (br s).

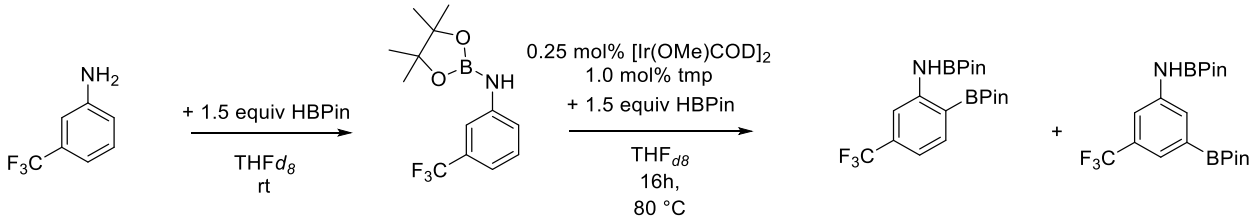
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.3, 1.5 Hz, 1H), 7.24 (dt, J = 8.8, 8.3, 2.0 Hz, 1H), 6.68 (td, J = 8.3, 7.3, 1.0 Hz, 1H), 6.61 (d, J = 8.3 Hz, 1H), 4.73 (br, s, 2H), 1.35 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 135.7, 132.7, 116.8, 114.7, 83.4, 24.9; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31 (br s)

Independent Synthesis of 2,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline



In a nitrogen filled glovebox, 219 mg 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (1 mmol) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 2.2 equiv HBpin (319 µL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 1.5 µmol $[Ir(OMe)COD]_2$ (1.5 mol%), 3.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (3.0 mol%) and were added and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. The volatiles were then removed under reduced pressure, and the residue was dissolved in MTBE. The solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL MTBE. Volatiles were removed under reduced pressure, and the product was crystallized from the residue using $MeOH/H_2O$ to afford a red solid (242 mg, 70% isolated yield); mp: 152-157 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, *J* = 1.4 Hz, 1H), 7.67 (dd, *J* = 15, 8.3Hz, 1H), 6.62 (d, *J* = 7.8 1H) 5.30 (br, s, 2H), 1.33 (s, 24H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 144.4, 139.4, 113,8, 83.4, 83.1, 24.9, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31 (br s); HRMS (ESI) m/z calcd for $C_{18}H_{29}B_2NO_4$ $[M + H]^+$ 346.2368, found 346.2547.

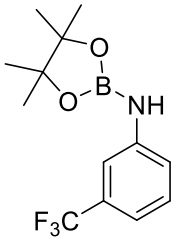
In Situ generation and borylation of 4,4,5,5-tetramethyl-N-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolan-2-amine



In a nitrogen filled glovebox, 62 µL 3-(trifluoromethyl)aniline (0.5 mmol) and 21 mg 1,4-bis(trifluoromethyl)-benzene (0.1 mmol) was dissolved in 1 mL THF_{d8} and transferred to a screw cap NMR tube. 109 µL HBpin (0.75 mmol) was added via micro pipette and the tube was loosely sealed. After 30 min, the cap was firmly tightened and ^{1}H and ^{19}F NMR were recorded. The NMR tube was returned to the glove box and 1.7 mg $[Ir(OMe)COD]_2$ (0.25 mol%), 2.4 mg 3,4,7,8-tetramethyl-1,10-

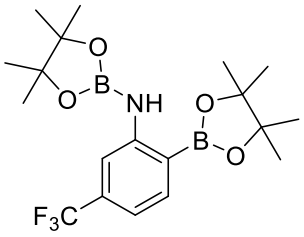
phenanthroline (1.0 mol%) and an additional 109 μL HBPin (0.75 mmol 1.5 equiv HBpin (218 μL) was added and the reaction vessel was sealed and heated at 80 °C for 16 h.

^{1}H and ^{19}F NMR of 4,4,5,5-tetramethyl-N-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolan-2-amine.



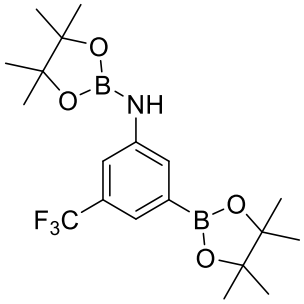
^{1}H NMR (500 MHz, THF_{d8}) δ 7.39 (s, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.24 (t, *J* = 8.3, 7.8 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.32 (br s, 1H), 1.27 (s, 12H); ^{19}F NMR (470 MHz, THF-d_8) δ 63.6 (s).

^{1}H and ^{19}F NMR of 4,4,5,5-tetramethyl-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)phenyl)-1,3,2-dioxaborolan-2-amine



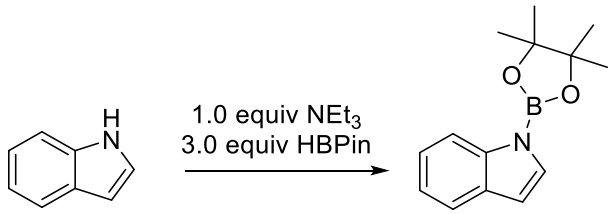
^{1}H NMR (500 MHz, THF_{d8}) δ 7.96 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.88 (s, 1H), 1.35 (s, 12H), 1.29 (s, 12H); ^{19}F NMR (470 MHz, THF-d_8) δ 64.1 (s).

^{1}H and ^{19}F NMR of 4,4,5,5-tetramethyl-N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)phenyl)-1,3,2-dioxaborolan-2-amine

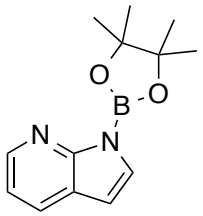


^{1}H NMR (500 MHz, THF-d_8) δ 7.67 (s, 1H), 7.57 (s, 1H), 7.42 (s, 1H), 6.26 (s, 1H), 1.31 (s, 12H), 1.27 (s, 12H); ^{19}F NMR (470 MHz, THF-d_8) δ 63.4 (s).

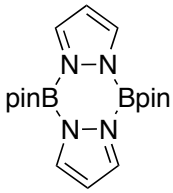
In Situ generation of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (3)



In a nitrogen filled glovebox 117 mg indole (1 mmol) was dissolved in 1 mL C_6D_6 in a screw cap NMR tube. 2.0 equiv HBpin (290 µL) and 1.0 equiv NEt_3 (140 µL) was added and the tube was sealed and heated at 80 °C for 30 min. Quantitative conversion was observed by NMR. ^{1}H NMR (500 MHz, C_6D_6) δ 8.24 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.25 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.15 (dd, *J* = 7.8, 6.8 Hz, 1H), 0.96 (s, 12H)); ^{11}B NMR (160 MHz, C_6D_6) δ 24 (br s).



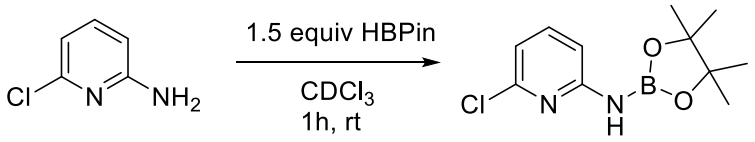
***N*-Borylation of 7-azaindole.** In a nitrogen filled glovebox, 10 mg 7-azaindole (0.085 mmol) was dissolved in THF-d_8 in a NMR pressure tube. $[Ir(OMe)COD]_2$ (2.5 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (5.0 mol%) and 2.0 equiv B_2Pin_2 were added and the reaction vessel was sealed and heated at 80 °C for 1.5 hours, and N-borylated 7-azaindole was obtained. ^{1}H NMR (500 MHz, THF-d_8) δ 8.34 (dd, *J* = 2, 4.9 Hz, 1H), 7.91 (dd, *J* = 1.9, 7.8 Hz, 1H), 7.53 (d, *J* = 3.9 Hz, 1H), 7.13 (dd, *J* = 4.4, 7.8 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 1.46 (s, 12H); Following the addition of 0.1 ml methanol, the nitrogen-boron bond was cleaved, regenerating 7-azaindole.



***N*-Borylation of pyrazole.** In a nitrogen filled glovebox, 68 mg pyrazole (1 mmol) was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar and 1.0 equiv HBPin was added and the reaction vessel was sealed and heated at 80 °C for 7 hours. The N-borylated compound was the major species in solution. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.0 Hz, 2 H), 6.28 (t, *J* = 2.5 Hz, 1H), 1.29

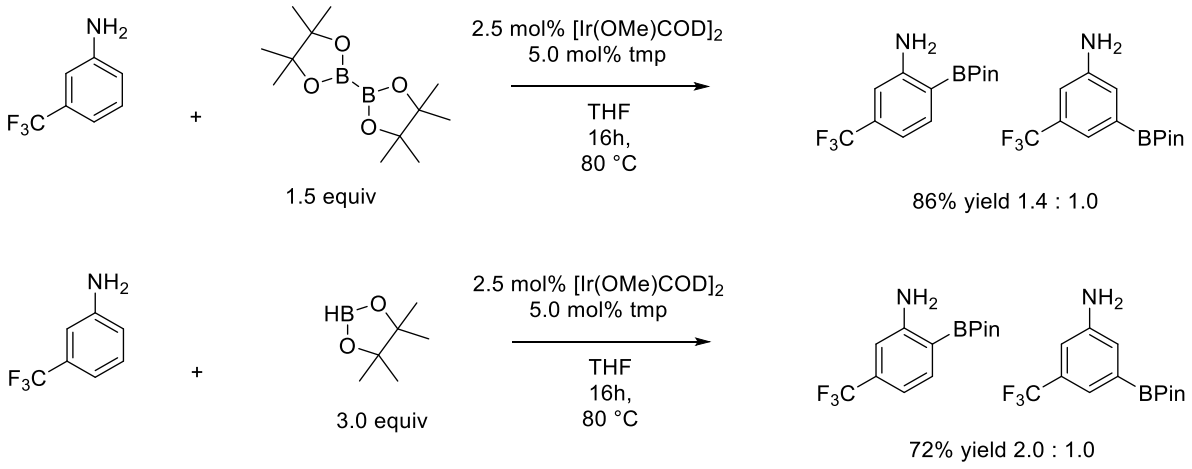
(s, 6H), 1.21 (s, 6H); ^{11}B NMR (160 MHz, $CDCl_3$) δ 5.0 (s). The ^{1}H NMR data are similar to those reported for a related pyrazbole complex with catecholate groups in place of the pinacolates.[4] Following the addition of 0.4 ml methanol, the nitrogen-boron bond was cleaved, regenerating the starting pyrazole.

In Situ generation of 6-chloro-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-amine



In a nitrogen filled glovebox 128 mg 6-chloropyridin-2-amine (1 mmol) was dissolved in 1 mL $CDCl_3$ in a screw cap NMR tube. 1.5 equiv HBpin (218 µL) was added and the tube was sealed and kept at room temperature for 1h. Quantitative conversion was observed by NMR. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, J = 7.8, 7.3 Hz, 1H), 7.24 (d, J = 8.3 Hz, 1H), 6.72 (d, J = 7.3 Hz, 1H), 5.55 (s, 1H), 1.26 (s, 12H); ^{11}B NMR (160 MHz, $CDCl_3$) δ 24 (br s).

Borane Effect on Regioselectivity of borylation of 3-(trifluoromethyl)aniline.



In a nitrogen filled glovebox, 124 µL 3-(trifluoromethyl)aniline (1.0 mmol, 1.0 equiv) and 48 mg dodecahydrotriphenylene (0.20 mmol, 0.2 equiv) internal standard was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 2.5 µmol $[Ir(OMe)COD]_2$ (2.5 mol%) and 5.0 µmol 3,4,7,8-tetramethyl-1,10-phenanthroline (5.0 mol%) were added followed by an additional 1.5 equiv B_2pin_2 (381 mg) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. Volatiles were removed and isomer ratios were determined by ^{1}H NMR (*ortho : meta;* 1.4 : 1.0).

In a nitrogen filled glovebox, 124 μL 3-(trifluoromethyl)aniline (1.0 mmol, 1.0 equiv) and 48 mg dodecahydrotriphenylene (0.20 mmol, 0.2 equiv) internal standard was dissolved in 1 mL THF in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBpin (218 μL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 2.5 μmol $[Ir(OMe)COD]_2$ (2.5 mol%) and 5.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (5.0 mol%) were added followed by an additional 1.5 equiv HBpin (218 μL) and the reaction vessel was sealed and heated at 80 °C for 16h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL MeOH. Volatiles were removed and isomer ratios were determined by ^{1}H NMR (*ortho : meta;* 2.0 : 1.0).

General Procedures for Screening Iridium Catalyzed C-H Borylation Conditions with Varying Ligands, Borane and Solvent. All reactions were conducted in a nitrogen filled glove-box. Reactions for high through-put screening were conducted in 8 × 30 mm borosilicate glass shell vials arranged in 96 well metal blocks (Symyx) with magnetic stirring. Materials were dispensed to the vials whenever possible as solutions in the reaction solvent, otherwise in suitable solvents (in which the material was soluble in) via micro pippetters followed by evaporation of the solvent in vacuuo in a Genevac^{TM} centrifugal evaporator in the glove box. The reactions were heated via the metal 96 well blocks after sealing with a perfluoroelastomeric backed metal top plate screwed to the metal block. Analysis was accomplished by reversed phase HPLC (Zorbax Eclipse Plus C18, 1.8 micron, 4.6 × 50 mm column eluted with 0.1% aq H_3PO_4 and acetonitrile) using an internal standard such as dodecahydrotriphenylene to facilitate quantitative HPLC solution assay yield determination or ^{1}H NMR relative to internal standard.

Borane and Solvent Effects Screen on Borylation of 3-chloroaniline. In a nitrogen filled glove box, a 50 μL of 0.01 M stock solutions of $[Ir(OMe)COD]_2$ in THF were added to a 1 mL reaction vial containing a magnetic stir bar. 50 μL of a 0.02 M stock solution of dtbpy (1.0 μmol) or tmphen (1.0 μmol) in DCM was added to reaction vials containing $[Ir(OMe)COD]_2$. Volatiles were removed under reduced pressure. The reaction vials were then subjected to one set of three following conditions using stock solutions made up in THF, cyclohexane, N,N-diisopropylethylamine, or NMP:

1) 100 μL of a solution of 22 μmol B_2pin_2 (0.22 M) in the reaction solvent was added via micropipette.

2) 100 μL of a solution of 44 μmol B_2pin_2 (0.44 M) in the reaction solvent was added via micropipette.

3) 100 μL of a solution containing 22 μmol HBpin (0.22 M) and 22 μmol B_2pin_2 (0.22 M) in the reaction solvent was added via micropipette.

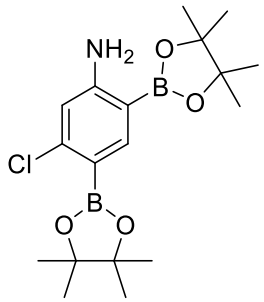
Then, 100 μL of a 0.2 M stock solution containing 3-chloroaniline (20 μmol) and 2.0 μmol dodecahydrotriphenylene internal standard in reaction solvent was added to the reaction mixture. The

reaction vessel was then sealed and the reaction mixture stirred at 80 °C for 8 h. The reaction was then cooled to room temperature and quenched by exposure to atmospheric O_2 and dilution with MeOH. Volatiles were removed and assay yields were determined by ^{1}H NMR.

Table S1. Borane and Solvent Effects on Borylation of 3-chloroaniline.

entry	ligand	solvent.	equiv borane	yield (%)	*ortho* (**11p**, %)	*meta* (**11p´**, %)	*dibo-rylated* (%)	**11p** + *diborylated:* **11p´**
1	tmphen	THF	1.1 B_2pin_2	77	35	32	10	1.4:1.0
2	tmphen	Cyclohexane	1.1 B_2pin_2	79	51	23	5	2.4:1.0
3	tmphen	Hünig's Base	1.1 B_2pin_2	71	45	25	1	1.8:1.0
4	tmphen	NMP	1.1 B_2pin_2	24	8	16	1	1.0:1.8
5	tmphen	THF	2.2 B_2pin_2	99	21	58	21	1.0:1.4
6	tmphen	Cyclohexane	2.2 B_2pin_2	99	29	38	32	1.6:1.0
7	tmphen	Hünig's Base	2.2 B_2pin_2	99	32	50	18	1.0:1.0
8	tmphen	NMP	2.2 B_2pin_2	74	22	45	8	1.0:1.5
9	tmphen	THF	1.1 B_2pin_2/1.1 HBpin	99	31	43	25	1.3:1.0
10	tmphen	Cyclohexane	1.1 B_2pin_2/1.1 HBpin	99	39	26	34	2.8:1.0
11	tmphen	Hünig's Base	1.1 B_2pin_2/1.1 HBpin	99	40	27	31	2.6:1.0
12	tmphen	NMP	1.1 B_2pin_2/1.1 HBpin	96	31	56	8	1.0:1.4
13	dtbpy	THF	1.1 B_2pin_2	67	23	43	1	1.0:1.8
14	dtbpy	Cyclohexane	1.1 B_2pin_2	58	31	27	0	1.2:1.0
15	dtbpy	Hünig's Base	1.1 B_2pin_2	34	18	16	0	1.1:1.0
16	dtbpy	NMP	1.1 B_2pin_2	38	11	27	0	1.0:2.6
17	dtbpy	THF	2.2 B_2pin_2	99	18	71	10	1.0:2.5
18	dtbpy	Cyclohexane	2.2 B_2pin_2	99	31	65	3	1.0:2.0
19	dtbpy	Hünig's Base	2.2 B_2pin_2	99	33	65	2	1.0:1.9
20	dtbpy	NMP	2.2 B_2pin_2	84	17	65	2	1.0:3.3
21	dtbpy	THF	1.1 B_2pin_2/1.1 HBpin	95	36	57	2	1.0:1.5
22	dtbpy	Cyclohexane	1.1 B_2pin_2/1.1 HBpin	74	36	37	1	1.0:1.0
23	dtbpy	Hünig's Base	1.1 B_2pin_2/1.1 HBpin	71	39	33	0	1.2:1.0
24	dtbpy	NMP	1.1 B_2pin_2/1.1 HBpin	77	19	56	2	1.0:2.6

^{1}H and ^{13}C NMR of 5-chloro-2,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline



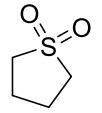
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 6.56 (s, 1H), 4.97 (br s, 2H), 1.34 (s, 12H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 146.3, 144.6, 114.9, 83.6, 83.4, 24.9, 24.8.

Polar Solvent Screen with 3-(trifluoromethyl)aniline. In a nitrogen filled glove box, 1 mmol 3-(trifluoromethyl)aniline was dissolved in 1 mL NMP, DMA or 1.26 g sulfolane in a 15 mL pressure tube containing a magnetic stir bar. 1.5 equiv HBpin (218 μL) was added and the reaction vessel was sealed and stirred at room temperature for 1 h. 0.25 μmol $[Ir(OMe)COD]_2$ (0.25 mol%), 1.0 μmol 3,4,7,8-tetramethyl-1,10-phenanthroline (1.0 mol%), and 100 μmol dodecahydrotriphenylene (24 mg) internal standard and an additional 1.5 mmol HBpin (218 μL) and the reaction vessel was sealed and heated at 80 °C for 16 h. The reaction mixture was allowed to return to room temperature and the reaction mixture was exposed to air and diluted with 5 mL H_2O. The residue was extracted with DCM and dried under reduced pressure. The residue was dissolved in MTBE, and the solution was passed through a short SiO_2 plug, which was washed with ~ 75 mL of MTBE. Removal of the solvent under reduced pressure afforded the product.

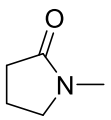
Table S2. Solvent Screen for 3-(trifluoromethyl)anilines.

entry	solvent	yield (%)	*ortho* (%)	*meta* (%)	*ortho : meta*
1	Sulfolane	0	--	--	NA
2	NMP	89	27	62	1.0:2.3
3	DMA	36	10	26	1.0:2.6

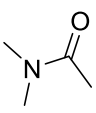
Solvent Key for Table S2.



Sulfolane



NMP



DMA

Ligand Effects Screen on Borylation of 3-(trifluoromethyl)aniline. Reaction was conducted in 8 × 30 mm borosilicate glass shell vials arranged in 24 well metal blocks (Symyx) with magnetic stirring. In a nitrogen filled glove box, a 50 μL of 0.01 M stock solutions of $[Ir(OMe)COD]_2$ (0.5 μmol) in THF were added to a 1 mL reaction vial containing a magnetic stir bar. 50 μL of a 0.02 M stock solution of ligand (1.0 μmol) in THF was added to reaction vials containing $[Ir(OMe)COD]_2$. 50 μL of a solution of 30 μmol B_2pin_2 (0.6 M) in THF was added via micropipette. Finally, 50 μL of a 0.2 M stock solution containing 3-(trifluoromethyl)aniline (20 μmol) and 2.0 μmol dodecahydrotriphenylene internal standard in THF was added to the reaction mixture. The reaction vessel was then sealed and stirred at 80 °C for 16 h. The reaction was then cooled to room temperature and quenched by exposure to atmospheric O_2 and dilution with MeOH. Volatiles were removed and assay yields were determined by ^{1}H NMR.

Table S3. Ligand Effects on Borylation of 3-(trifluoromethyl)anilines.

entry	ligand	yield (%)	*ortho* (%)	*meta* (%)	*ortho : meta*
1	dtbpy	80	42	38	1.1 : 1.0
2	dmabpy	86	53	33	1.6 : 1.0
3	phen	73	30	42	1.0 : 1.4
4	tmphen	86	50	36	1.4 : 1.0
5	diim	17	8	8	1.0 : 1.0
6	box	10	6	4	1.5 : 1.0

Ligand Key for Table S3.

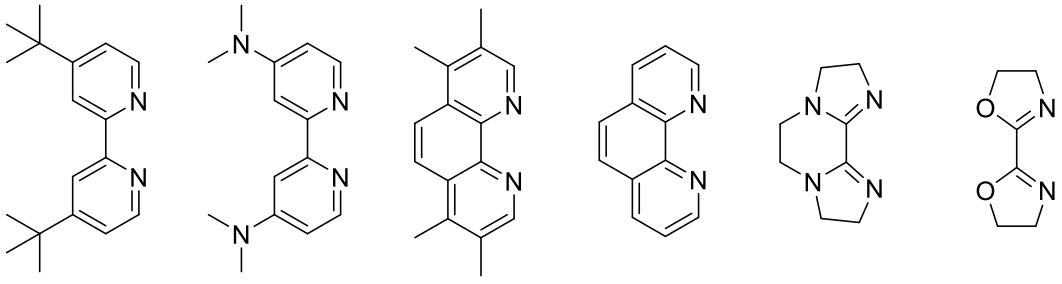
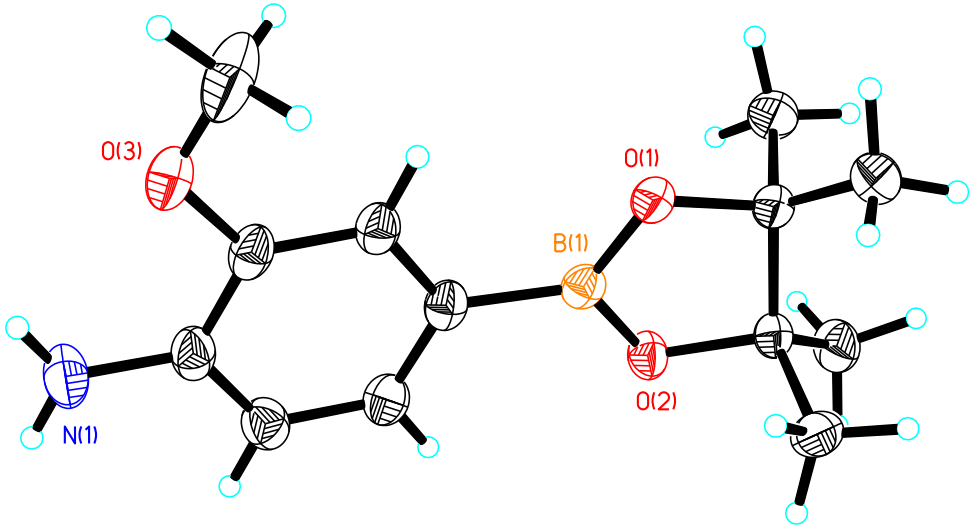


Figure S1. 2-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine. The following are 50% thermal ellipsoidal drawings of the molecule in the asymmetric cell with various amount of labeling.



Crystal structure determination of 2-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine. Crystal Data. $C_{13}H_{20}BNO_3$, M = 249.11, orthorhombic, a = 7.76150(10) Å, b = 9.78630(10) Å, c = 17.9222(2) Å, V = 1371.31(3) Å^3, T = 173(2) K, space group $P2_12_12_1$ (# 19), Z = 4, μ(Cu Kα) = 0.678 mm^{-1}, 9806 reflections measured, 2457 unique (R_{int} = 0.0258) which were used in all calculations. The final wR_2 was 0.0842 (all data) an R_1 was 0.0319 (>2σ(I)).

References

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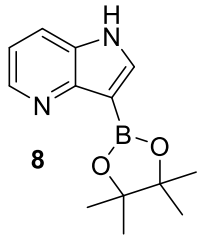
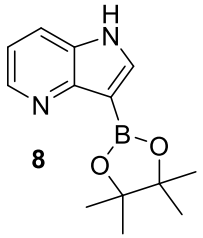
4) S. Trofimenko, *J. Am. Chem. Soc.* **1967**, *89*, 4948-4952.

^{1}H NMR (500 MHz, DMSO-d_6) 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-4-azaindole

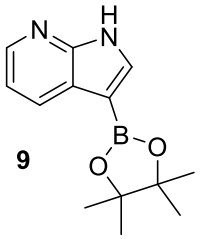


8

^{13}C NMR (125 MHz, DMSO-d_6) 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-4-azaindole

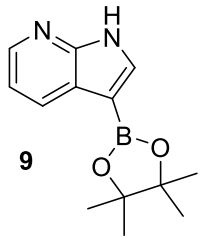


^{1}H NMR (500 MHz, $CDCl_3$) 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-7-azaindole



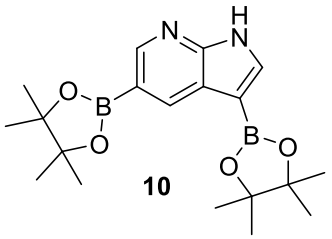
9

^{13}C NMR (125 MHz, $CDCl_3$) 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-7-azaindole

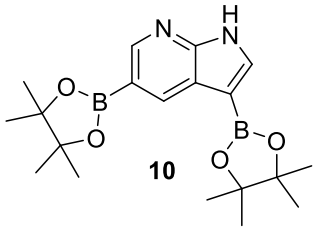


9

^{1}H NMR (500 MHz, $CDCl_3$) 3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-7-azaindole

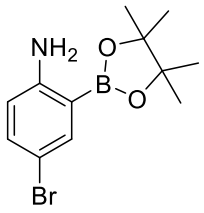


^{13}C NMR (125 MHz, $CDCl_3$) 3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-7-azaindole



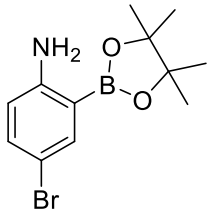
10

^{1}H NMR (500 MHz, CD_2Cl_2) 4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine



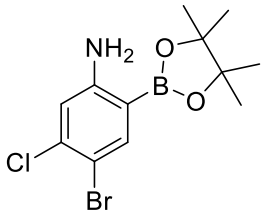
11a

^{13}C NMR (125 MHz, CD_2Cl_2) 4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine



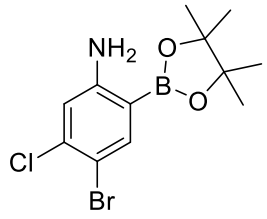
11a

^{1}H NMR (500 MHz, $CDCl_3$) 4-bromo-5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine



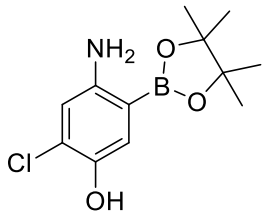
11b

^{13}C NMR (125 MHz, $CDCl_3$) 4-bromo-5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine



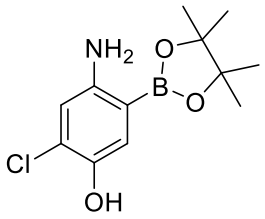
11b

^{1}H NMR (500 MHz, $CDCl_3$) 4-amino-2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-phenol



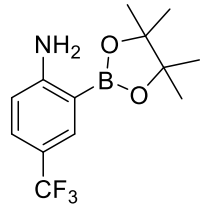
11c

^{13}C NMR (125 MHz, $CDCl_3$) 4-amino-2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-phenol



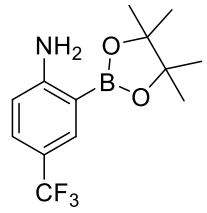
11c

^{1}H NMR (500 MHz, $CDCl_3$) 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-4-(trifluoromethyl)-benzenamine



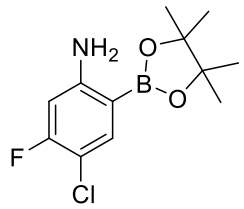
11d

^{13}C NMR (125 MHz, $CDCl_3$) 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-4-(trifluoromethyl)-benzenamine



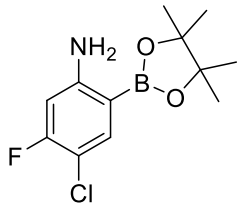
11d

^{1}H NMR (500 MHz, $CDCl_3$) 4-chloro-5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine



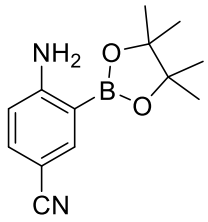
11e

^{13}C NMR (125 MHz, $CDCl_3$) 4-chloro-5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine



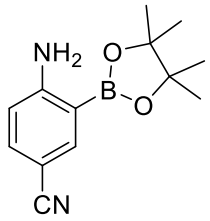
11e

^{1}H NMR (500 MHz, $CDCl_3$) 4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile



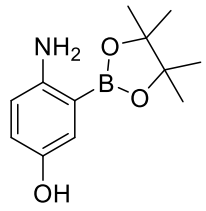
11f

^{13}C NMR (125 MHz, $CDCl_3$) 4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile



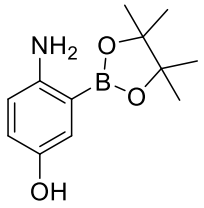
11f

^{1}H NMR (500 MHz, $CDCl_3$) 4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-phenol



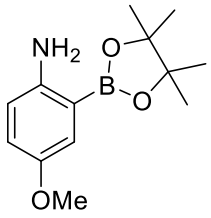
11g

^{13}C NMR (125 MHz, $CDCl_3$) 4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-phenol



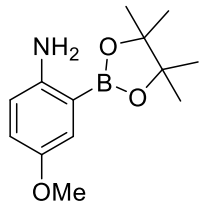
11g

^{1}H NMR (500 MHz, C_6D_6) 4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine



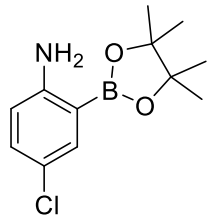
11h

^{13}C NMR (125 MHz, $CDCl_3$) 4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine



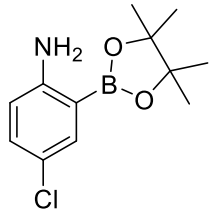
11h

^{1}H NMR (500 MHz, $CDCl_3$) 4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine



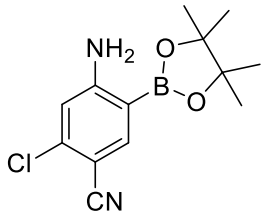
11i

^{13}C NMR (125 MHz, $CDCl_3$) 4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine



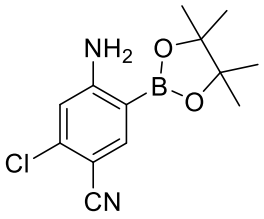
11i

^{1}H NMR (500 MHz, $CDCl_3$) 4-amino-2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzonitrile



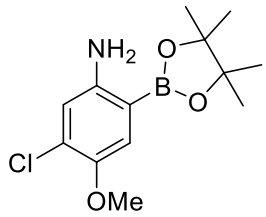
11j

^{13}C NMR (125 MHz, $CDCl_3$) 4-amino-2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzonitrile



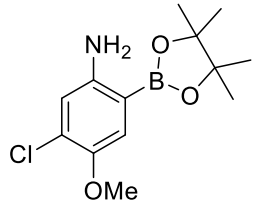
11j

^{1}H NMR (500 MHz, $CDCl_3$) 5-chloro-4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine



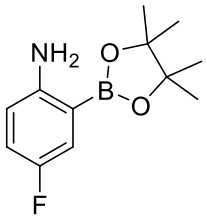
11k

^{13}C NMR (125 MHz, $CDCl_3$) 5-chloro-4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine



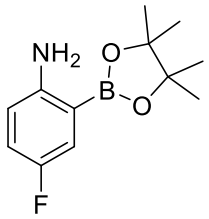
11k

^{1}H NMR (500 MHz, CD_2Cl_2) 4-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine



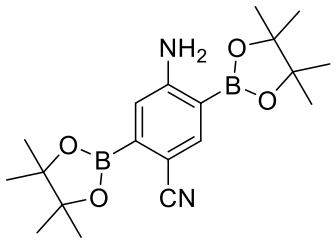
11l

^{13}C NMR (125 MHz, CD_2Cl_2) 4-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzamine



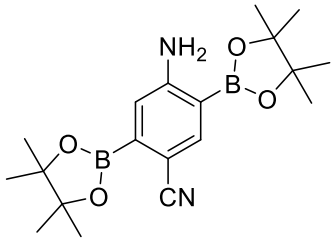
11l

^{1}H NMR (500 MHz, $CDCl_3$) 4-amino-2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzonitrile



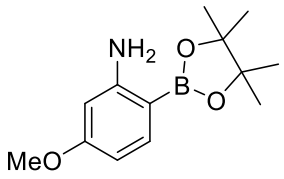
11m

^{13}C NMR (125 MHz, $CDCl_3$) 4-amino-2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzonitrile



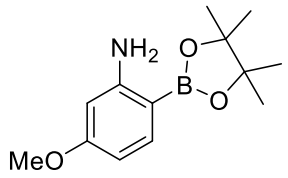
11m

^{1}H NMR (500 MHz, $CDCl_3$) 5-methoxy-2-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)aniline

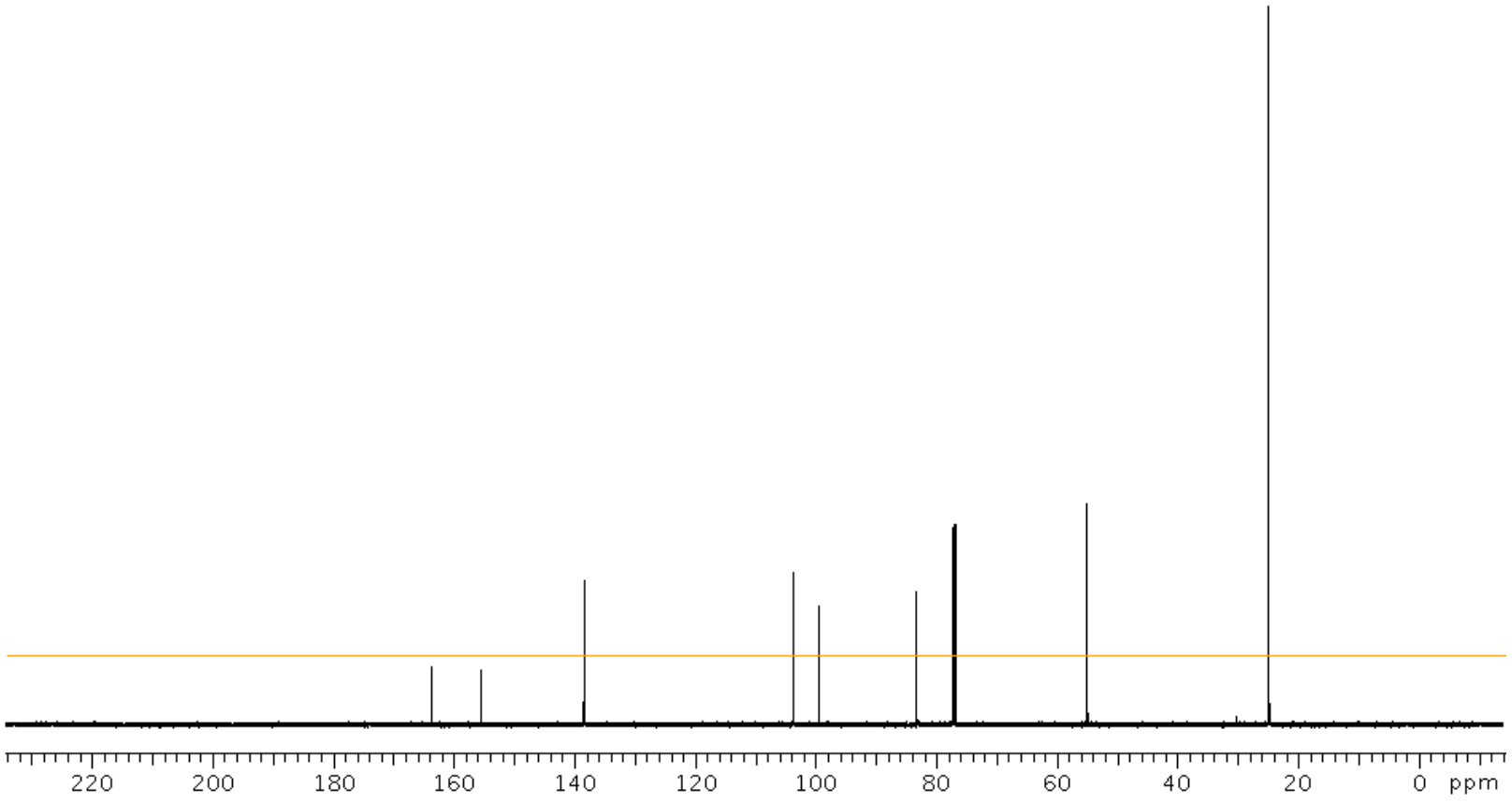


11n

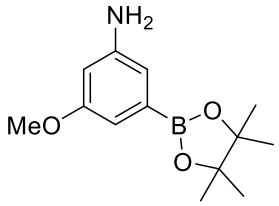
^{13}C NMR (125 MHz, $CDCl_3$) 5-methoxy-2-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)aniline



11n

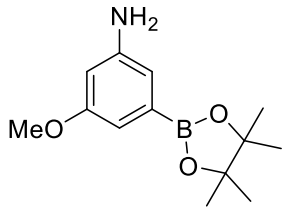


^{1}H NMR (500 MHz, CD_3CN) 3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline



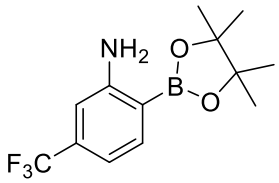
11n'

^{13}C NMR (125 MHz, CD_3CN) 3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline



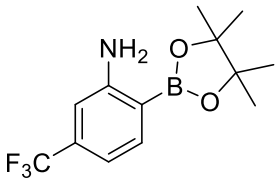
11n'

^{1}H NMR (500 MHz, $CDCl_3$) 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-5-(trifluoromethyl)-benzenamine



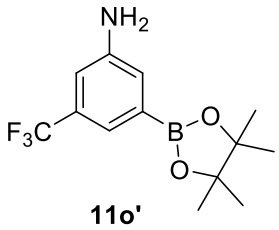
11o

^{13}C NMR (125 MHz, $CDCl_3$) 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-5-(trifluoromethyl)-benzenamine



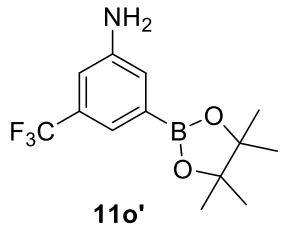
11o

^{1}H NMR (500 MHz, $CDCl_3$) 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-5-(trifluoromethyl)-benzenamine



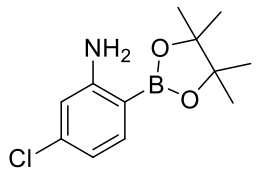
11o'

^{13}C NMR (125 MHz, $CDCl_3$) 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-5-(trifluoromethyl)-benzenamine



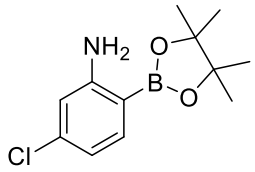
11o'

^{1}H NMR (500 MHz, $CDCl_3$) 5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine



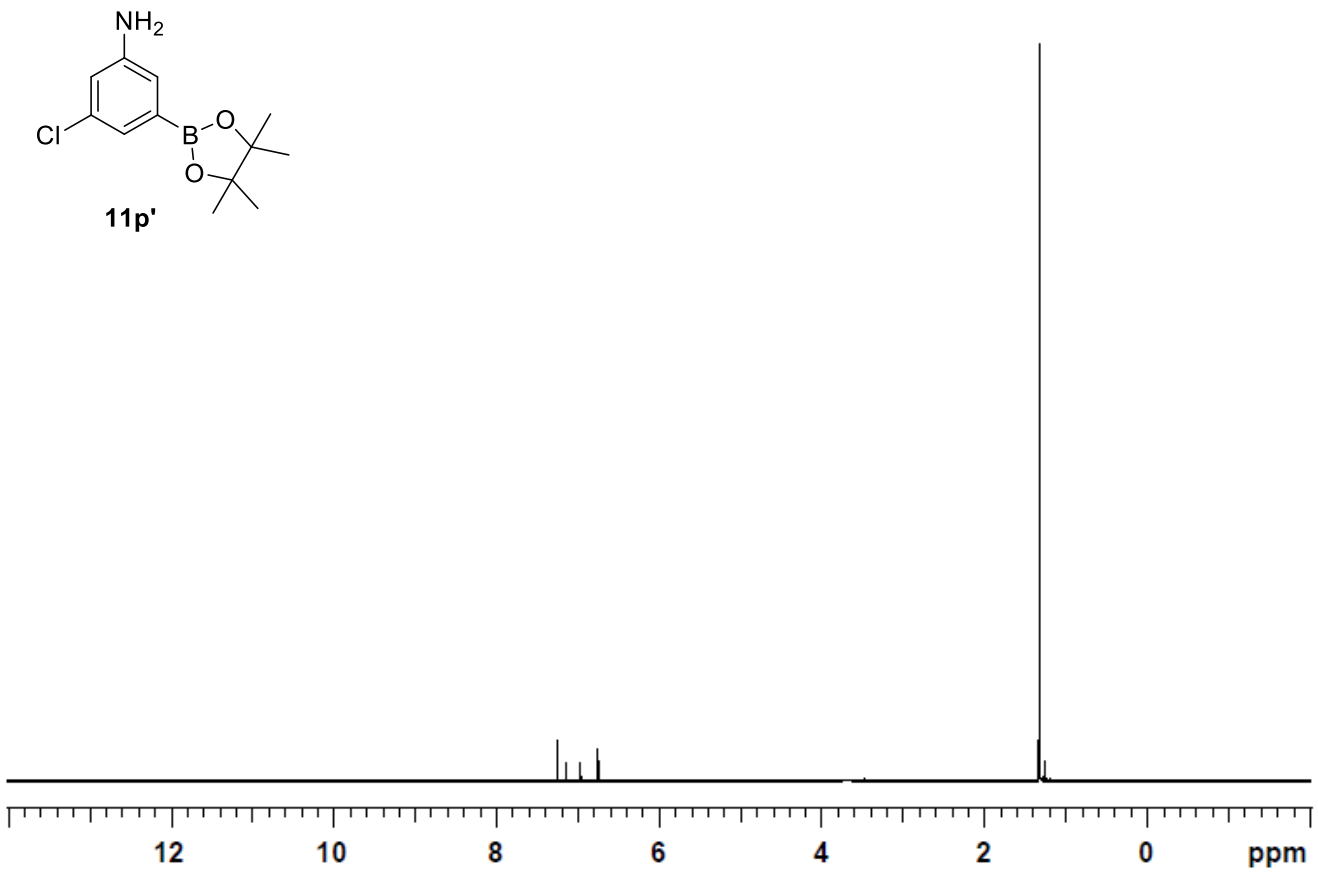
11p

^{13}C NMR (125 MHz, $CDCl_3$) 5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine

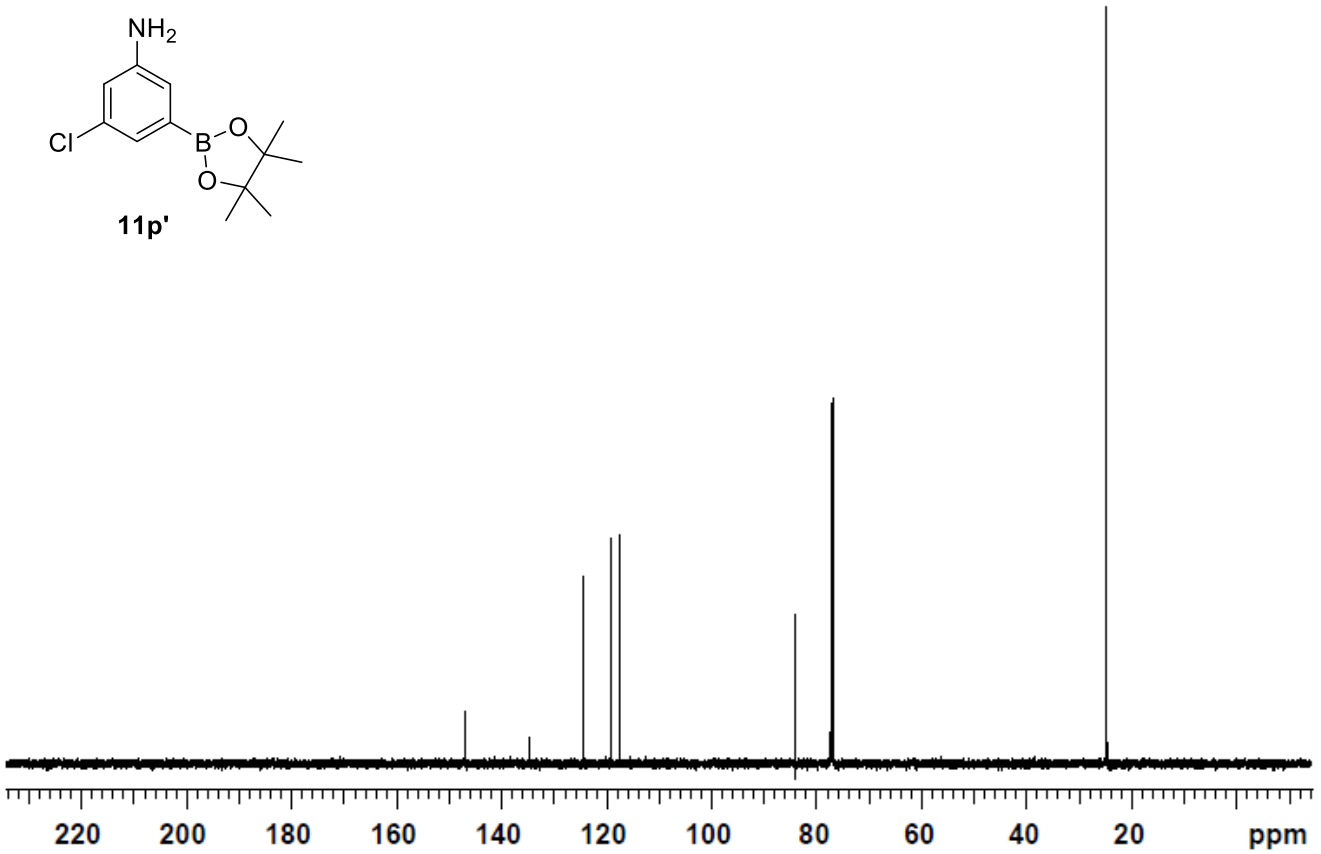


11p

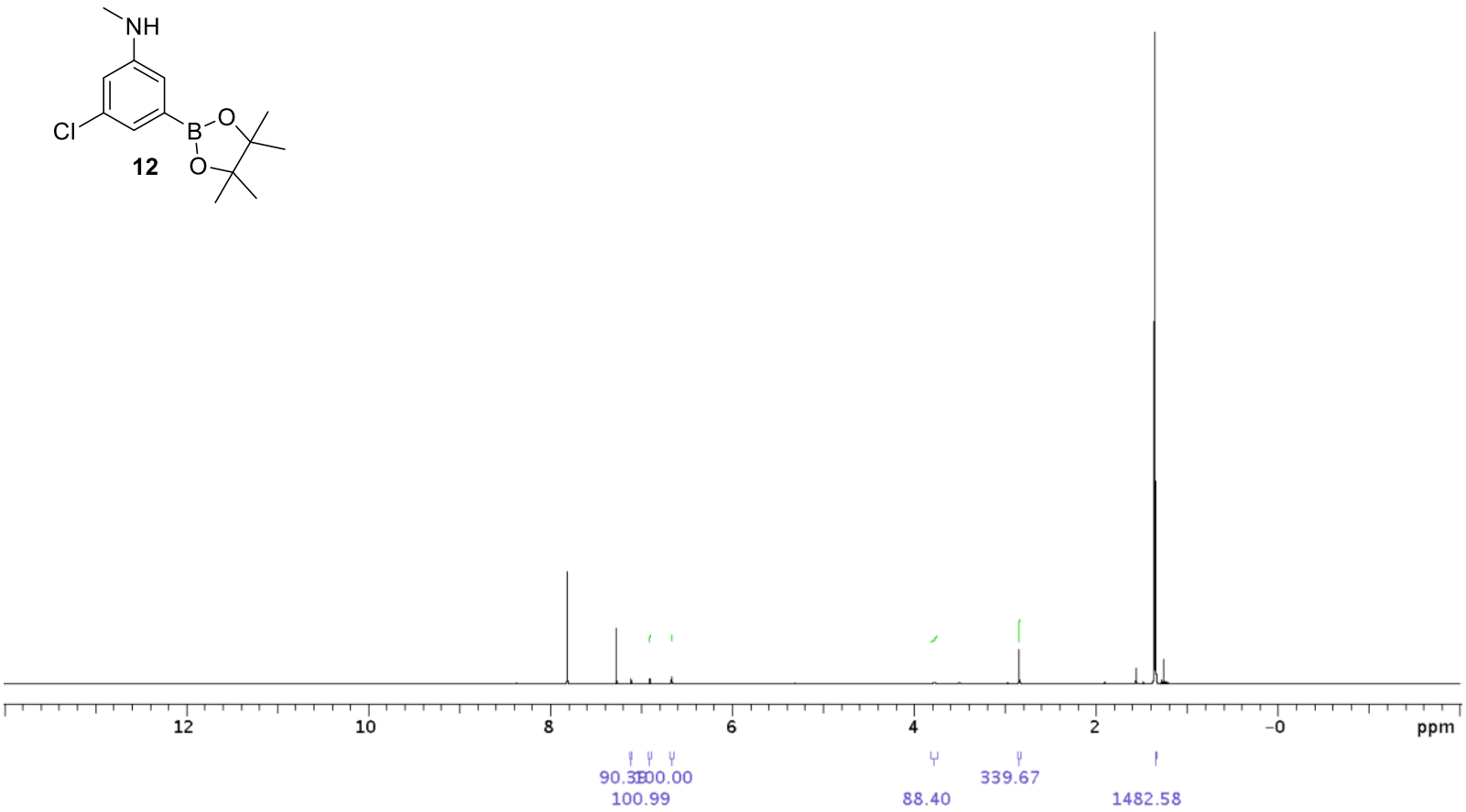
^{1}H NMR (500 MHz, $CDCl_3$) 3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline



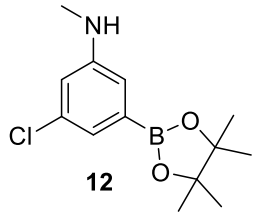
^{13}C NMR (125 MHz, $CDCl_3$) 3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline



^{1}H NMR (500 MHz, $CDCl_3$) N-methyl-3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine

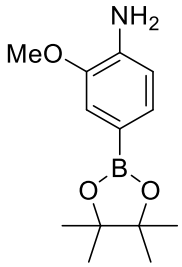


^{13}C NMR (125 MHz, $CDCl_3$) N-methyl-3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine



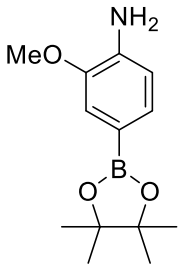
12

^{1}H NMR (500 MHz, $CDCl_3$) 2-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine



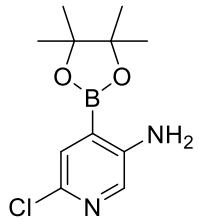
13

^{13}C NMR (125 MHz, $CDCl_3$) 2-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-benzenamine



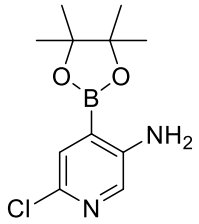
13

^{1}H NMR (500 MHz, $CDCl_3$) 5-amino-2-chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-pyridine



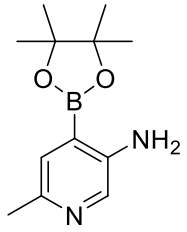
14a

^{13}C NMR (125 MHz, $CDCl_3$) 5-amino-2-chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-pyridine



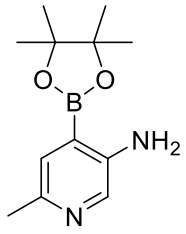
14a

^{1}H NMR (500 MHz, CD_2Cl_2) 5-amino-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-2-methyl pyridine

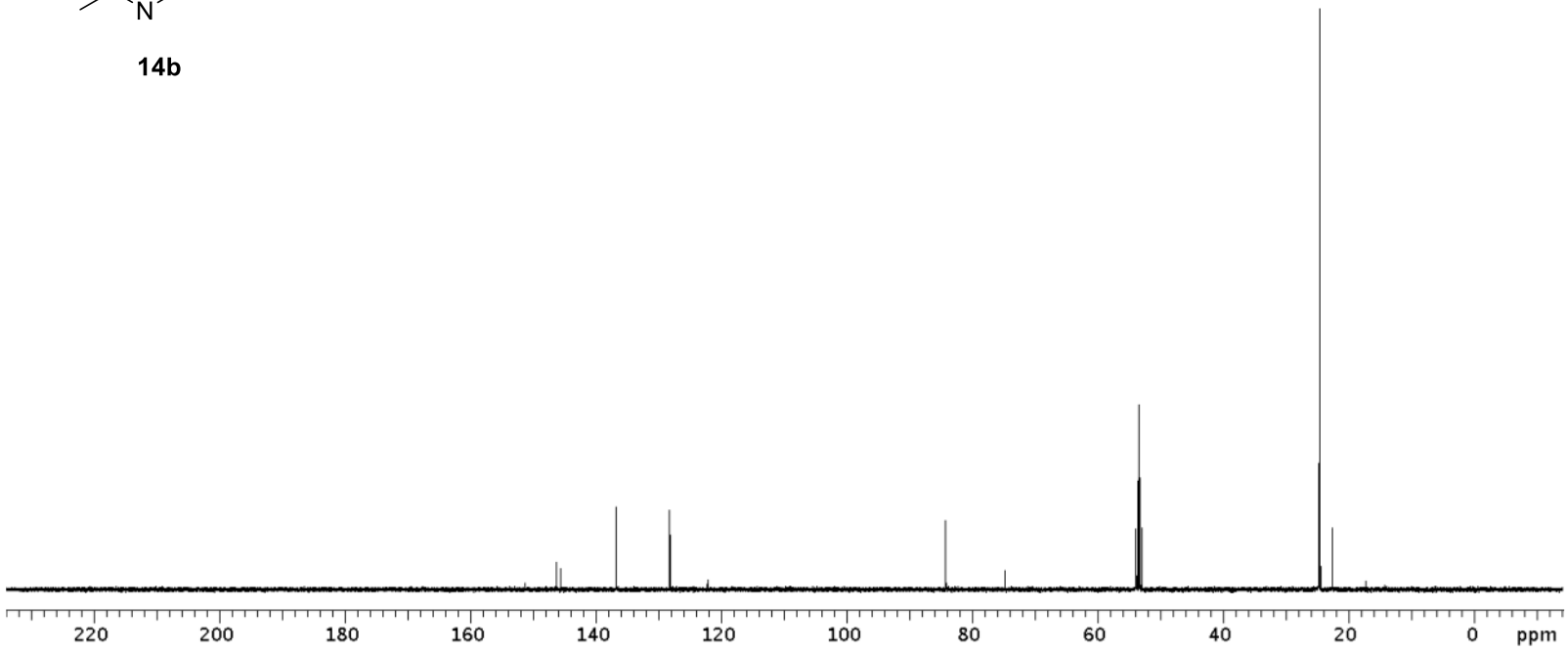


14b

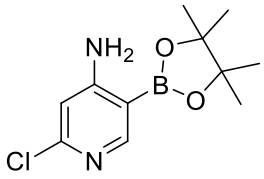
^{13}C NMR (125 MHz, CD_2Cl_2) 5-amino-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-2-methyl pyridine



14b

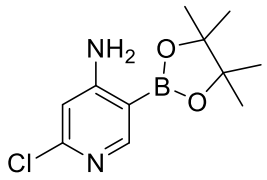


^{1}H NMR (500 MHz, $CDCl_3$) 2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-4-amine



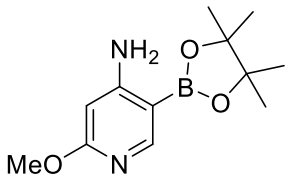
14c

^{13}C NMR (125 MHz, $CDCl_3$) 2-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-4-amine



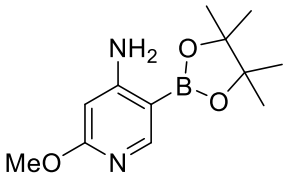
14c

^{1}H NMR (500 MHz, $CDCl_3$) 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-4-amine



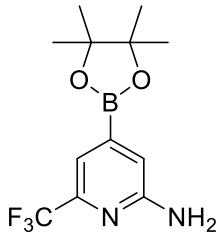
14d

^{13}C NMR (125 MHz, $CDCl_3$) 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-4-amine



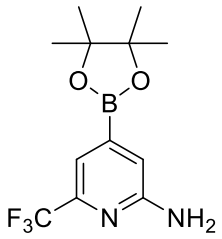
14d

^{1}H NMR (500 MHz, $CDCl_3$) 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)pyridin-2-amine

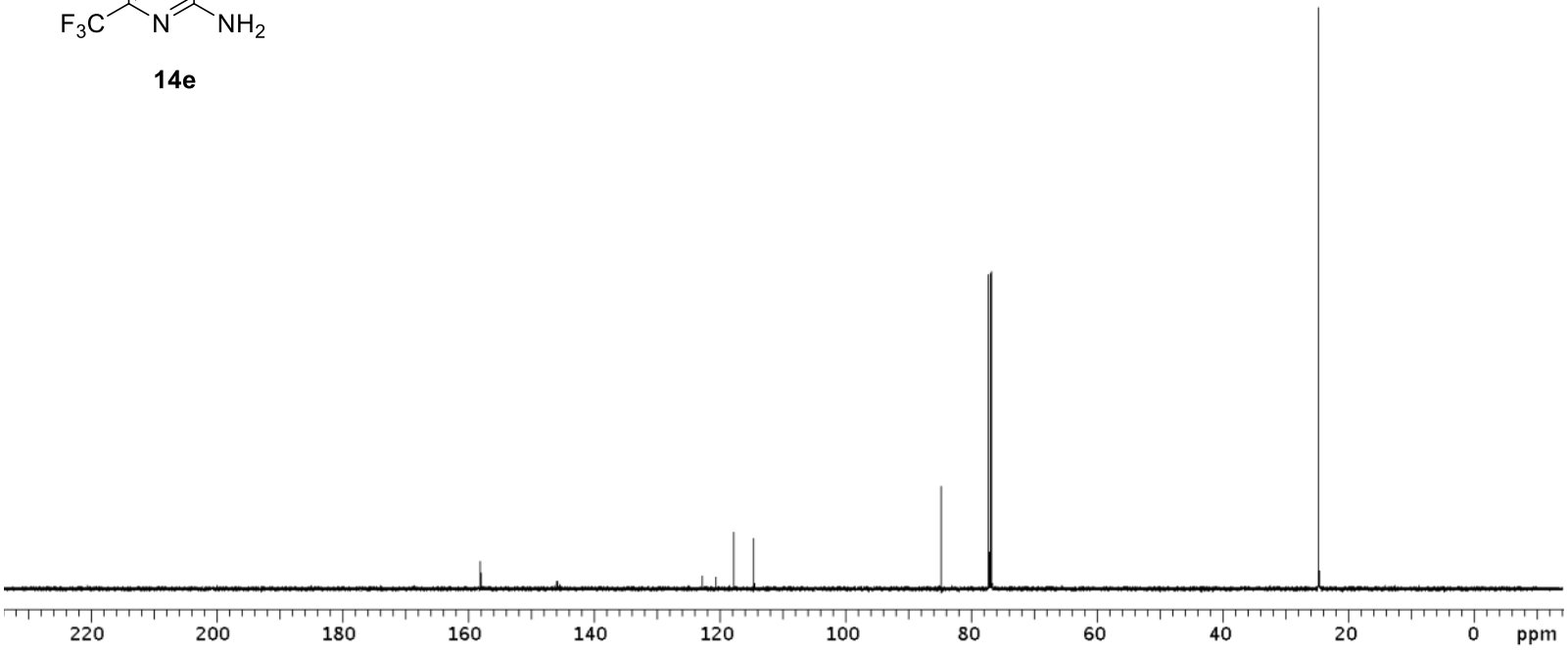


14e

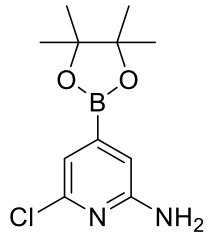
^{13}C NMR (125 MHz, $CDCl_3$) 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)pyridin-2-amine



14e

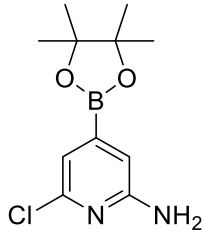


^{1}H NMR (500 MHz, $CDCl_3$) 6-chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-amine



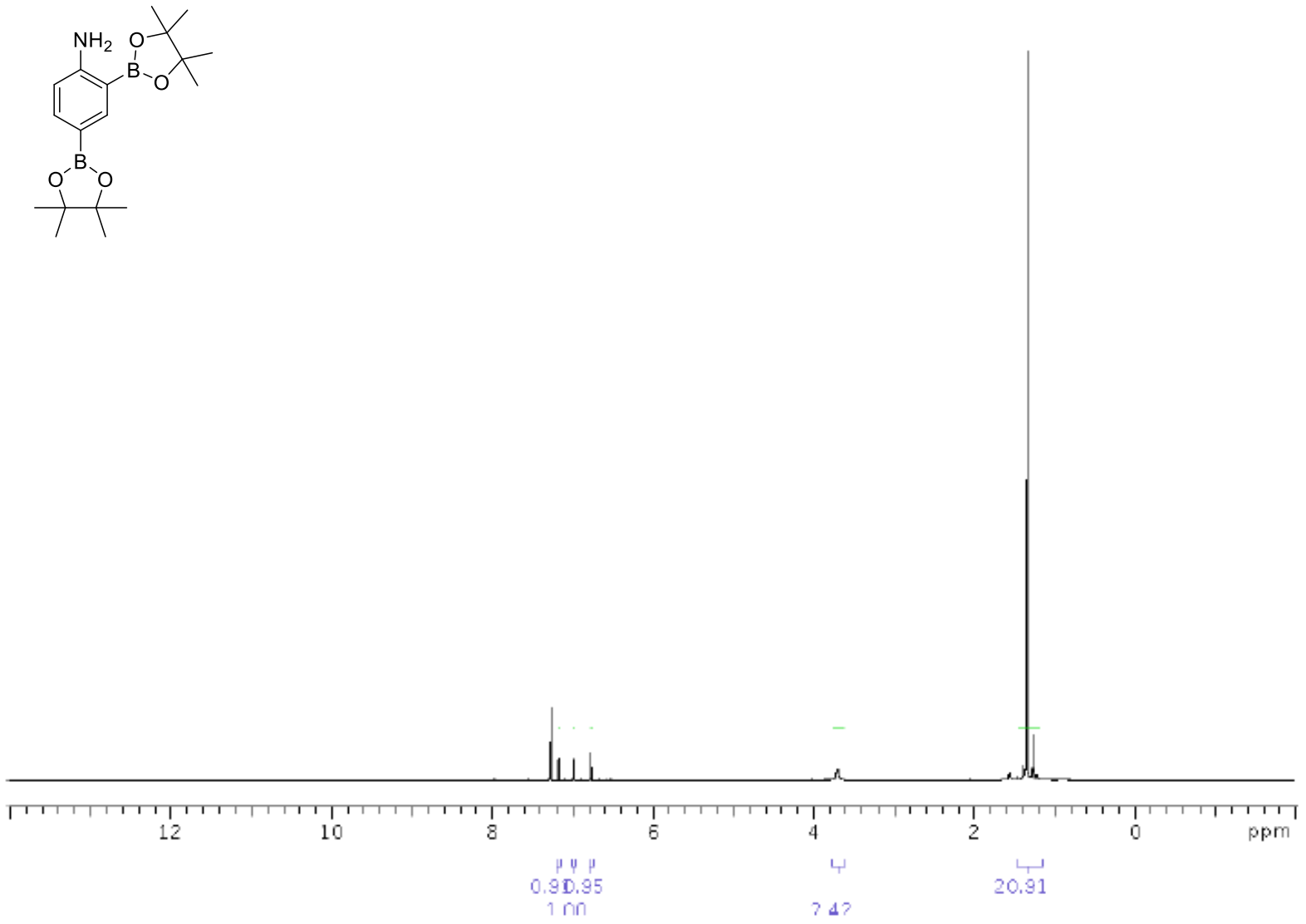
14f

^{13}C NMR (125 MHz, $CDCl_3$) 6-chloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-amine

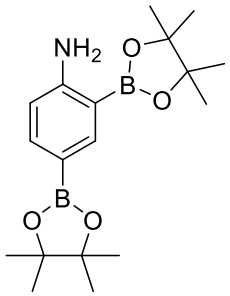


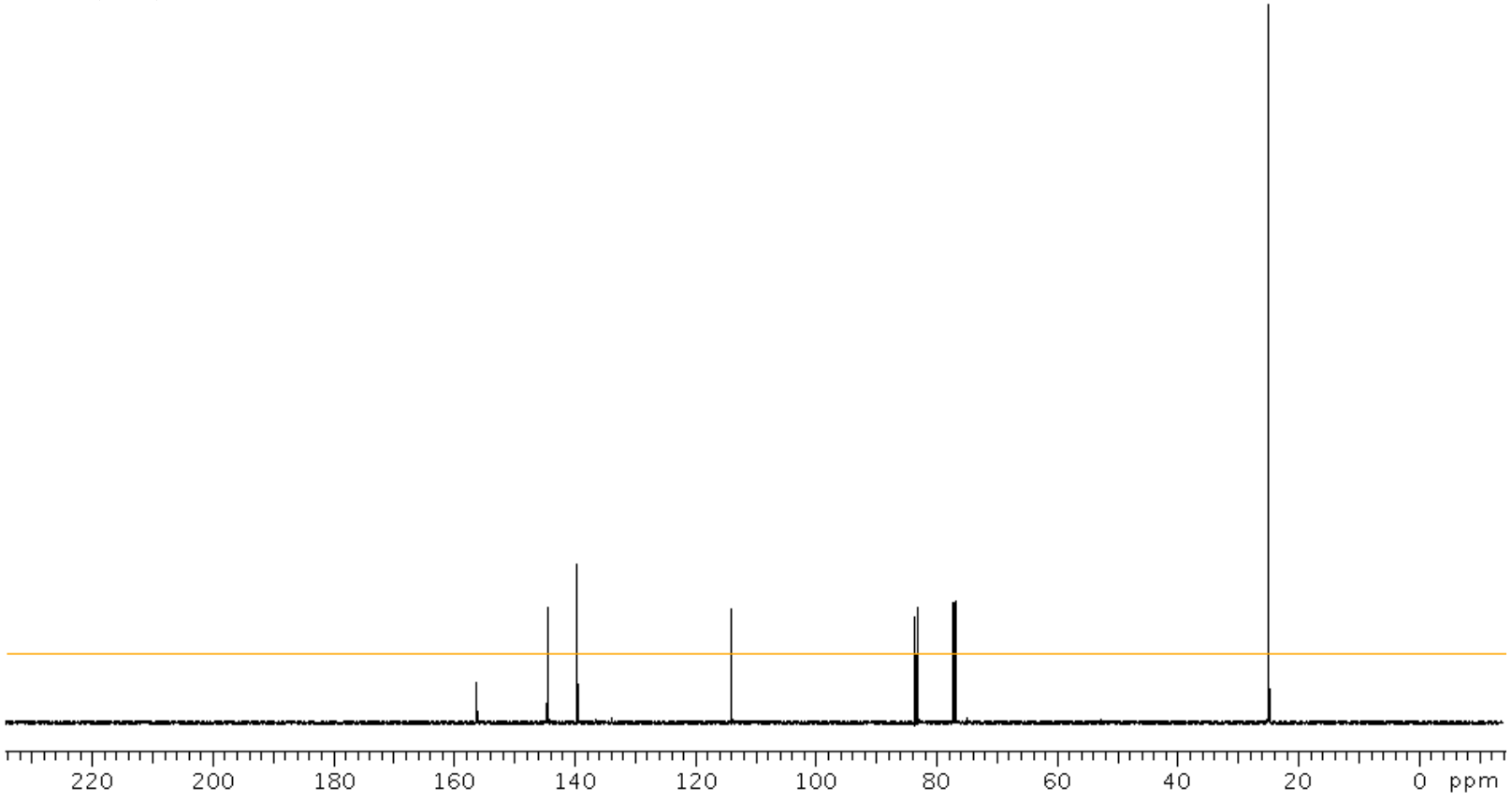
14f

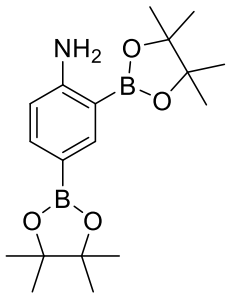
^{1}H NMR (500 MHz, $CDCl_3$) 2,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline

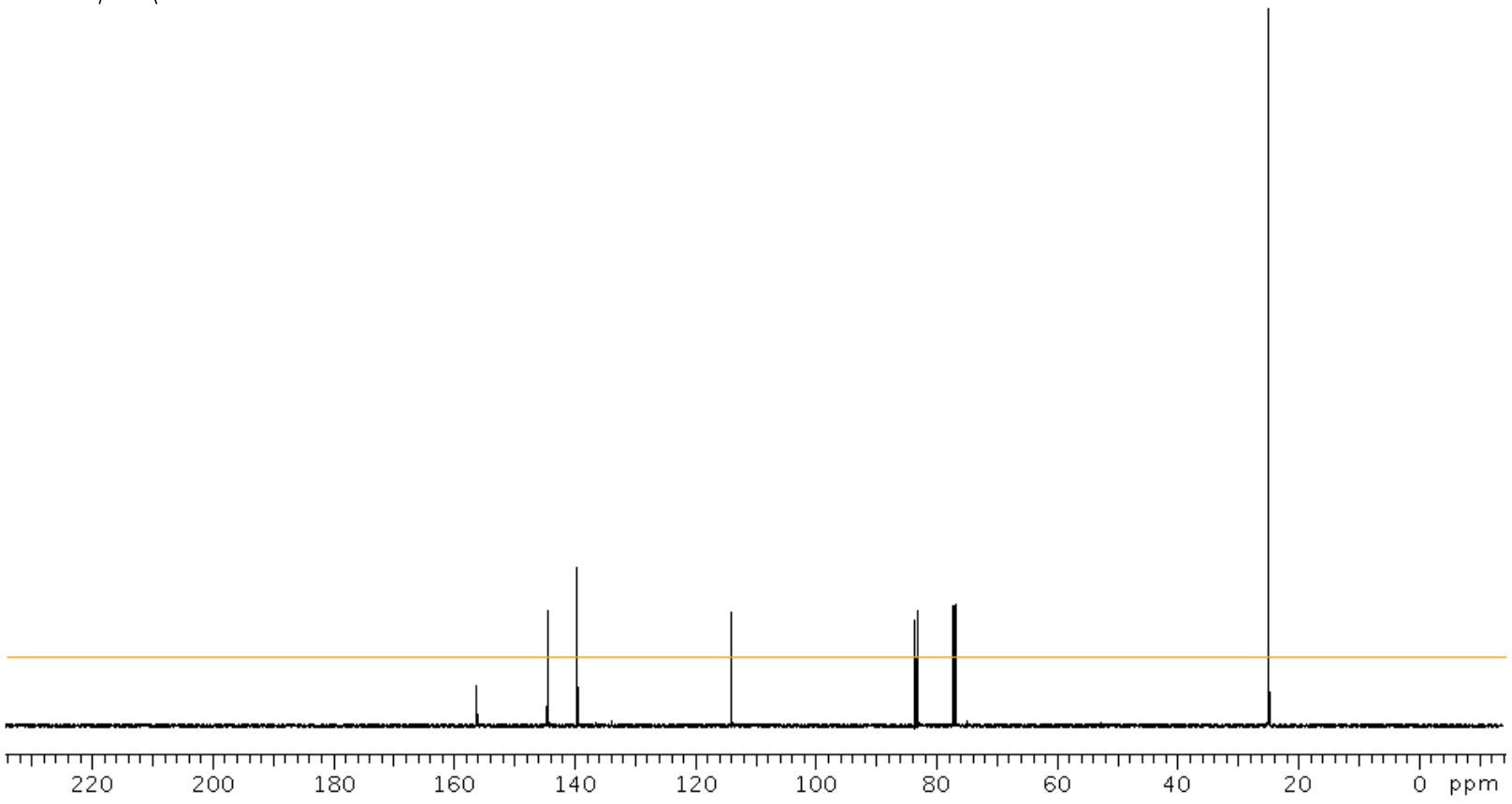


^{13}C NMR (125 MHz, $CDCl_3$) 2,4-**bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline**






NH2
O
B
O
B
O
O


220
200
180
160
140
120
100
80
60
40
20
0
ppm

Theoretical Methods

The structures and energies for all stationary points were obtained using Gaussian 09.[i] Vibrational frequency analyses were carried out on all stationary points.

2-Bpinindole

RB3LYP/6-311++G(d,p)

0,1

C,-1.57486359,1.26862889,0.14214053
C,-0.72095691,0.18960044,0.03060143
C,-2.91720985,0.78005832,0.08522949
N,-1.49894003,-0.95940219,-0.09375587
C,-2.83141429,-0.63347599,-0.06587538
C,-4.18737258,1.38262874,0.14425201
H,-1.11725856,-1.8857746,-0.19535045
C,-3.97171704,-1.44066568,-0.15844139
C,-5.31521705,0.58488971,0.05296044
H,-4.27929632,2.45725456,0.25913248
H,-3.89436392,-2.51633012,-0.27356005
C,-5.20698863,-0.81475744,-0.09726624
H,-6.29977747,1.03653552,0.09673475
H,-6.10952872,-1.41161228,-0.16629405
H,-1.26179968,2.29564931,0.25217036
B,0.81446807,0.12030139,0.02412893
O,1.49209269,-1.06430735,-0.15749239
O,1.64771486,1.19583399,0.19132233
C, .906436,-0.80861987,0.10523646
C,3.00569291,0.7536261,-0.11233703
C,3.28076057,1.15049297,-1.5667127
H,3.13615692,2.22783547,-1.66954403
H,4.30500335,0.91135195,-1.86284392
H,2.59392996,0.6516048,-2.25355349
C, 3.96859999,1.47754155,0.82307302
H,4.99288462,1.12340296,0.67558007
H, 3.94705346,2.54846814,0.60979204
H,3.69691582,1.33696153,1.86894169
C, 3.73636686,-1.6517051,-0.85713396
H,4.80278845,-1.44218745,-0.73508387
H,3.57478464,-2.71126356,-0.64638887
H,3.46112649,-1.46807371,-1.89537792
C,3.17081529,-1.23998361,1.55169768
H,2.89713803,-2.29141534,1.66236107
H,4.22518994,-1.13063551,1.81641896

H,2.5732425,-0.65923035,2.25732594
Zero-point correction= 0.300216 (Hartree/Particle)
Thermal correction to Energy= 0.316678
Thermal correction to Enthalpy= 0.317622
Thermal correction to Gibbs Free Energy= 0.256740
Sum of electronic and zero-point Energies= -774.424229
Sum of electronic and thermal Energies= -774.407767
Sum of electronic and thermal Enthalpies= -774.406822
Sum of electronic and thermal Free Energies= -774.467705

N-Bpinindole
RB3LYP/6-311++G(d,p)
0,1
C,2.6540926477,-2.1657637622,-0.1448805939
C,1.2964055254,-2.0975448963,-0.1437455496
C,3.1506162812,-0.8159346229,-0.0496525255
N,0.8691016553,-0.7659234809,-0.0546563081
C,2.0194146977,0.0353767677,0.0051742709
C,4.4355869565,-0.2576502937,-0.0028853702
C,2.1446569491,1.4214769789,0.1069151173
C,4.5646497371,1.1210814793,0.0975528384
H,5.3133364168,-0.89349041,-0.0436019699
H,1.2710867144,2.0579473081,0.1512303614
C,3.4306229647,1.9499044434,0.1518571025
H,5.5520134028,1.5675692948,0.1355097654
H,3.5594678906,3.0235632216,0.231279007
H,3.2414298721,-3.0691788442,-0.2053379355
H,0.5609701004,-2.8839538281,-0.2002116303
B,-0.5102727649,-0.3644733225,-0.0355011653
O,-1.5329444588,-1.2733165296,-0.1433517341
O,-0.9333854143,0.9326953322,0.0933042474
C,-2.7712509466,-0.5604060057,0.1607355523
C,-2.3757306508,0.938589933,-0.1495749029
C,-3.8816082431,-1.1313198955,-0.7143599025
H,-4.0589796561,-2.1743807824,-0.4433696799
H,-4.8142228914,-0.580097977,-0.5649233867
H,-3.6201277043,-1.0967887971,-1.7715597189
C,-3.0769215452,-0.814557881,1.6405808685
H,-4.024044296,-0.358179641,1.9374987207
H,-3.1476783133,-1.8915524573,1.8057486164
H,-2.28642554,-0.424717738,2.285337866
C,-3.0109898953,1.9791418747,0.7658197308
H,-2.6582592022,2.9745917233,0.4874501923
H,-4.1000856646,1.9670691441,0.6679485908

H,-2.7516651906,1.8089067175,1.8103034153
C,-2.5760675405,1.3269178428,-1.617838336
H,-3.6365542789,1.4081071116,-1.8674365936
H,-2.1059059273,2.2963330606,-1.794786928
H,-2.1156704476,0.6002815518,-2.2905865825

Zero-point correction= 0.300362 (Hartree/Particle)
Thermal correction to Energy= 0.316559
Thermal correction to Enthalpy= 0.317503
Thermal correction to Gibbs Free Energy= 0.257462
Sum of electronic and zero-point Energies= -774.442396
Sum of electronic and thermal Energies= -774.426199
Sum of electronic and thermal Enthalpies= -774.425254
Sum of electronic and thermal Free Energies= -774.485295

2-Bpinpyrrole
RB3LYP/6-311++G(d,p)
0,1

C,-4.01275159,-0.71941641,-0.12730315
C,-4.13968119,0.63922521,0.10184355
C,-2.83050773,1.16904189,0.19615092
C,-1.92233734,0.12971291,0.02424783
N,-2.68192213,-1.01343824,-0.17130681
H,-2.28667159,-1.9270853,-0.32627657
H,-4.76284362,-1.4830134,-0.25999407
H,-5.06995663,1.17871031,0.18966574
H,-2.56147247,2.1995 7913,0.37072601
B,-0.39338408,0.09264956,0.02102239
O,0.31473742,-1.06371951,-0.23804327
O,0.42178718,1.17016638,0.26794253
C,1.71878348,-0.79750964,0.056196
C,1.7871299,0.77688159,-0.0573935
C,1.98104361,-1.31617089,1.47472443
H,1.72988679,-2.37831393,1.51473347
H,3.03046152,-1.20101128,1.75646846
H,1.36442168,-0.79508383,2.21002742
C,2.73289856,1.45700221,0.92742343
H,3.76525375,1.1372008,0.75887086
H,2.68697674,2.53917705,0.78693673
H,2.46315513,1.24003774,1.96061426
C,2.57702445,-1.55812093,-0.94942837
H,3.63693582,-1.3292419,-0.8064396
H,2.44165283,-2.63264978,-0.806325

H,2.30319484,-1.31697382,-1.97615843
C,2.06279857,1.2724532,-1.48180727
H,1.90097788,2.35181571,-1.51530696
H,3.0922597,1.06914052,-1.78687595
H,1.38754172,0.80836201,-2.20374786

Zero-point correction= 0.253664 (Hartree/Particle)
Thermal correction to Energy= 0.267483
Thermal correction to Enthalpy= 0.268427
Thermal correction to Gibbs Free Energy= 0.213872
Sum of electronic and zero-point Energies= -620.788950
Sum of electronic and thermal Energies= -620.775131
Sum of electronic and thermal Enthalpies= -620.774187
Sum of electronic and thermal Free Energies= -620.828742

N-Bpinpyrrole
RB3LYP/6-311++G(d,p)
0,1

C,2.6874951,-1.10948725,-0.18756521
C,3.99309839,-0.70640187,-0.11972379
C,3.99314332,0.7063521,0.11955974
C,2.68756511,1.10944593,0.18784121
N,1.86857589,0.00003536,-0.00003184
H,2.25358026,-2.08179494,-0.35276876
H,4.85769411,-1.34311482,-0.22805511
H,4.85778002,1.34303908,0.22771297
H,2.25371667,2.08174948,0.35324931
B,0.42877526,0.00007521,-0.00006303
O,-0.31600878,1.1197891,0.25765409
O,-0.31599632,-1.1197064,-0.25770575
C,-1.70454421,0.78889708,-0.05720446
C,-1.7044718,-0.78892409,0.05717317
C,-2.6076473,-1.51017099,-0.93695786
H,-2.51659566,-2.58930721,-0.79545338
H,-3.65422413,-1.23521365,-0.77857974
H,-2.33755202,-1.2807857,-1.96727528
C,-1.96804774,-1.29521545,1.47915789
H,-3.00775859,-1.13573321,1.77447987
H,-1.76089183,-2.36664855,1.51611004
H,-1.32087669,-0.80092686,2.20684771
C,-2.60762543,1.51011721,0.9369919
H,-2.51665839,2.58925943,0.79546613
H,-3.65419397,1.23508935,0.77869389

H,-2.33743331,1.28077016,1.96729443
C,-1.96808867,1.2952183,-1.47916229
H,-3.00758099,1.13489095,-1.77480249
H,-1.7618422,2.36683363,-1.51586741
H,-1.32029058,0.80162195,-2.20676275

Zero-point correction= 0.253396 (Hartree/Particle)
Thermal correction to Energy= 0.267071
Thermal correction to Enthalpy= 0.268015
Thermal correction to Gibbs Free Energy= 0.213928
Sum of electronic and zero-point Energies= -620.804365
Sum of electronic and thermal Energies= -620.790690
Sum of electronic and thermal Enthalpies= -620.789746
Sum of electronic and thermal Free Energies= -620.843834

(i) Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,

M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.