

Supporting Information

P-Directed Borylation of Phenols

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General Remarks

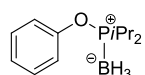
All reactions were performed under N₂ atmosphere except for those run under aqueous conditions. Toluene was distilled over CaH₂ and further dried by storing over activated 3Å molecular sieves in the glovebox. Commercially available NMR grade deuterated solvents (Cambridge Isotope Laboratories), as well as fluorobenzene were not distilled; instead they were simply dried over a large amount of activated 3Å molecular sieves in the glovebox. All other solvents and reagents were used without further purification. Flash column chromatography was performed with 230-400 mesh Whatman Purisil 60 Å silica gel. Preparative TLC used Whatman PK6F 60 Å silica gel plates (1 mm x 20 cm x 20 cm). Analytical TLC used Whatman K6F 60 Å silica gel plates at 0.25 mm thickness. Nuclear magnetic resonance experiments were performed on Varian Inova 500 and Inova 400 spectrometers at the following frequencies: ¹H 500 MHz or 400 MHz; ¹¹B and ¹¹B{¹H} 225 MHz or 128 MHz; ¹³C{¹H} 176 MHz or 101 MHz; ¹⁹F 376 MHz; ³¹P 202 or 162 MHz. All spectra were recorded in CDCl₃, Acetone-*d*₆, or DMSO-*d*₆ and referenced to the ¹H signal of internal Me₄Si according to IUPAC recommendations,¹ using a calibration frequency of 32.083974 for BF₃-OEt₂ (¹¹B), 25.145020 for Me₄Si (¹³C), 94.094011 for CCl₃F (¹⁹F), and 40.480742 for H₃PO₄. Melting points were obtained using a Lab Devices Mel-Temp apparatus and are uncorrected.

General procedure for preparation of phosphinite-borane complexes:²

To a solution of phenol derivative (5.4 mmol) in toluene (10 mL) was added chlorodiisopropylphosphine (0.8 mL, 5.0 mmol). To the resulting solution was added triethylamine (1.0 mL, 7.4 mmol) and the resulting slurry was heated to reflux for 15 h. After cooling to room temperature, the mixture was filtered through a plug of Celite, washing with hexanes (3 x 10 mL) and reducing under vacuum. The residue was taken up in dichloromethane (10 mL) and $\text{BH}_3 \cdot \text{Me}_2\text{S}$ (485 μL , 5.1 mmol) was added dropwise at 0 °C. After stirring 2 h, the solution was filtered through a plug of silica gel, flushing with dichloromethane (30 mL). The filtrate was concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel (95:5 Hexanes:Et₂O) affording the corresponding phosphinite-borane complex **2**.

Phenyl diisopropylphosphinite borane (2a)

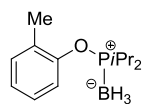
The product was isolated as a colorless oil in 89% yield (1.0 g) after flash on silica gel (95:5 Hexanes:Et₂O)



¹H NMR (400 MHz, CDCl₃): δ 7.32-7.25 (m, 2 H), 7.15-7.08 (m, 3 H), 2.26-2.20 (m, 2 H), 1.33-1.22 (m, 12 H), 0.86-0.11 (br m, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 153.6 (d, J= 6.1 Hz), 129.3, 124.1, 120.8 (d, J= 3.0 Hz), 26.3 (d, J= 36.6 Hz), 16.2 (d, J= 55.3 Hz); ¹¹B NMR (128 MHz, CDCl₃): δ -43 (br m); ³¹P NMR (162 MHz, CDCl₃): δ 143 (br m). HRMS (EI+ 70 eV): m/z calculated for C₁₂H₁₉BOP [M-3H]⁺ 221.1267, found 221.1265.

2-Methylphenyl diisopropylphosphinite borane (2b)

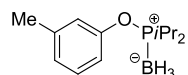
The product was isolated as a colorless oil in 90% yield (1.08 g) after flash on silica gel (95:5 Hexanes:Et₂O)



¹H NMR (400 MHz, CDCl₃): δ 7.37 (dd, J= 3.2 Hz, J= 8.0 Hz, 1H), 7.12 (m, 2 H), 6.97 (td, J= 3.7 Hz, J= 7.4 Hz, 1 H), 2.29-2.23 (m, 5 H), 1.31-1.22 (m, 12 H), 0.99-0.27 (br m, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 152.3 (d, J= 6.8 Hz), 131.1, 128.3 (d, J= 3.9 Hz), 126.7, 123.5, 119.3(d, J= 3.9 Hz), 26.7 (d, J= 37.2 Hz), 16.6 (d, J= 35.2 Hz), 15.9 (d, J= 1.8 Hz); ¹¹B NMR (128 MHz, CDCl₃): δ -42 (br m); ³¹P NMR (202 MHz, CDCl₃): δ 141 (br m). HRMS (EI+ 70 eV): m/z calculated for C₁₃H₂₁BOP [M-3H]⁺ 235.1423, found 235.1422.

3-Methylphenyl diisopropylphosphinite borane (2c)

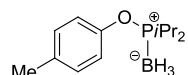
The product was isolated as a colorless oil in 85% yield (1.01 g) after flash on silica gel (95:5 Hexanes:Et₂O)



¹H NMR (400 MHz, CDCl₃): δ 7.18 (t, J= 8.2 Hz, 1 H), 6.94-6.90 (m, 3 H), 2.33 (s, 3H), 2.25-2.20 (m, 2 H), 1.33-1.22 (m, 12 H), 0.84-0.12 (br m, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 153.5 (d, J= 5.8 Hz), 139.5, 128.9, 124.9, 121.4 (d, J= 3.1 Hz), 117.7 (d, J= 3.1 Hz), 26.5 (d, J= 36.6 Hz), 21.4, 16.1 (d, J= 54.5 Hz); ¹¹B NMR (128 MHz, CDCl₃): δ -43 (br m); ³¹P NMR (162 MHz, CDCl₃): δ 143 (br m). HRMS (EI+ 70 eV): m/z calculated for C₁₃H₂₁BOP [M-3H]⁺ 235.1423, found 235.1430.

4-Methylphenyl diisopropylphosphinite borane (2d)

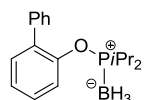
The product was isolated as a colorless oil in 78% yield (932 mg) after flash on silica gel (95:5 Hexanes:Et₂O)



¹H NMR (400 MHz, CDCl₃): δ 7.06 (d, J= 7.6 Hz, 2 H), 7.00 (d, J= 7.6 Hz, 2 H), 2.29 (s, 3 H), 2.23-2.18 (m, 2 H), 1.32-1.21 (m, 12 H), 0.87-0.11 (br m, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 151.3 (d, J= 6.2 Hz), 133.6, 129.8 (d, J= 14.1 Hz), 120.5 (d, J= 3.1 Hz), 26.2 (d, J= 36.9 Hz), 20.7, 16.1 (d, J= 55.6 Hz); ¹¹B NMR (128 MHz, CDCl₃): δ -43 (br m); ³¹P NMR (162 MHz, CDCl₃): δ 143 (br m). HRMS (EI+ 70 eV): m/z calculated for C₁₃H₂₁BOP [M-3H]⁺ 235.1423, found 235.1432.

1,1'-Biphenyl diisopropylphosphinite borane (2e)

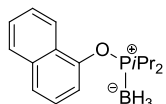
The product was isolated as a white crystals in 87% yield (1.31 g) after flash on silica gel (95:5 Hexanes:Et₂O)



¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, J= 7.8 Hz, 1H), 7.46-7.38 (m, 4 H), 7.35-7.26 (m, 3 H), 7.17 (t, J= 7.5 Hz, 1 H), 1.96-1.90 (m, 2 H), 1.07-0.98 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃): δ 150.6 (d, J= 6.9 Hz), 138.1, 133.5 (d, J= 3.0 Hz), 130.9, 129.8, 128.3, 127.3, 124.1, 121.1 (d, J= 3.0 Hz), 26.6, 26.3, 16.2, 15.6 (d, J= 1.9 Hz); ¹¹B NMR (128 MHz, CDCl₃): δ -42 (br m); ³¹P NMR (162 MHz, CDCl₃): δ 145 (br m). HRMS (EI+ 70 eV): m/z calculated for C₁₈H₂₃BOP [M-3H]⁺ 297.1580, found 297.1587. mp (from Et₂O): 54-55°C.

1-Naphthyl diisopropylphosphinite borane (2f)

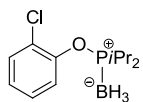
The product was isolated as a white crystals in 95% yield (1.30 g) after flash on silica gel (97:3 Hexanes:Et₂O)



¹H NMR (400 MHz, CDCl₃): δ 8.10 (dd, J= 4.8 Hz, J= 6.3 Hz, 1 H), 7.83 (m, 1H), 7.57 (t, J=7.8 Hz, 2 H), 7.51-7.49 (m, 2 H), 7.38 (t, J= 6.2 Hz, 1 H), 2.41-2.56 (m, 2 H), 1.37-1.27 (m, 12 H), 1.02-0.39 (br m, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 149.5 (d, J= 6.5 Hz), 134.7, 127.9, 126.5 (d, J= 3.8 Hz), 126.3, 125.9, 125.5, 123.5, 121.3, 114.4 (d, J= 4.2 Hz), 26.8 (d, J= 36.6 Hz), 16.2 (d, J= 54.5 Hz); ¹¹B NMR (128 MHz, CDCl₃): δ -42 (br m); ³¹P NMR (162 MHz, CDCl₃): δ 144 (br m). HRMS (EI+ 70 eV): m/z calculated for C₁₆H₂₁BOP [M-3H]⁺ 271.1423, found 271.1427. mp (from Et₂O): 64-65°C.

2-Chlorophenyl diisopropylphosphinite borane (2g)

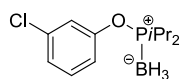
The product was isolated as a colorless oil in 93% yield (1.21 g) after flash on silica gel (95:5 Hexanes:Et₂O)



¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, J= 8.4 Hz, 1H), 7.35 (d, J=7.8 Hz, 2 H), 7.21-7.17 (m, 1 H), 7.03 (d, J= 7.73 Hz, 1 H), 2.34-2.27 (m, 2 H), 0.95-0.23 (m, 12 H), 0.95-0.23 (br m, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 149.7, 130.2, 127.5, 125.0, 124.6, 121.7, 26.6 (d, J= 35.8 Hz), 16.1 (d, J= 51.0 Hz); ¹¹B NMR (128 MHz, CDCl₃): δ -42 (br m); ³¹P NMR (162 MHz, CDCl₃): δ 148 (br m). HRMS (EI+ 70 eV): m/z calculated for C₁₂H₁₈ClBOP [M-3H]⁺ 255.0887, found 255.0885.

3-Chlorophenyl diisopropylphosphinite borane (2h)

The product was isolated as a colorless oil in 84% yield (1.09 g) after flash on silica gel (95:5 Hexanes:Et₂O)

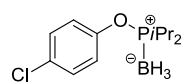


¹H NMR (400 MHz, CDCl₃): δ 7.20 (d, J= 8.1 Hz, 1H), 7.11-7.04 (m, 3 H), 2.24-2.19 (m, 2 H), 1.31-1.20 (m, 12 H), 0.82-0.11 (br m, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 154.7, 134.9, 130.5, 124.9, 121.7, 119.6, 26.7 (d, J= 36.2 Hz), 16.5 (d, J= 54.1 Hz);

^{11}B NMR (128 MHz, CDCl_3): δ -46 (br m); ^{31}P NMR (162 MHz, CDCl_3): δ 149 (br m). HRMS (EI+ 70 eV): m/z calculated for $\text{C}_{12}\text{H}_{18}\text{ClBOP} [\text{M}-3\text{H}]^+$ 255.0887, found 255.0885.

4-Chlorophenyl diisopropylphosphinite borane (2i)

The product was isolated as a colorless oil in 92% yield (1.19 g) after flash on silica gel (95:5 Hexanes:Et₂O)



^1H NMR (400 MHz, CDCl_3): δ 7.25 (d, J = 9.0 Hz, 1H), 7.06 (d, J = 9.0 Hz, 2 H), 2.25-2.20 (m, 2 H), 1.32-1.21 (m, 12 H), 0.92-0.20 (br m, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.7 (d, J = 6.3 Hz), 129.8, 129.7 (d, J = 7.8 Hz), 122.6 (d, J = 3.1 Hz), 26.8 (d, J = 36.2 Hz), 16.5 (d, J = 54.5 Hz); ^{11}B NMR (128 MHz, CDCl_3): δ -43 (br m); ^{31}P NMR (162 MHz, CDCl_3): δ 146 (br m). HRMS (EI+ 70 eV): m/z calculated for $\text{C}_{12}\text{H}_{18}\text{ClBOP} [\text{M}-3\text{H}]^+$ 255.0887, found 255.0877.

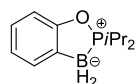
General procedure for borylation reaction:

A dry 12 mL thick-walled Schlenk tube fitted with a teflon stopper was charged with a mixture of phosphinite-borane complex **2** (200 μmol), dissolved in fluorobenzene (2 mL) and Tf_2NH (52 mg, 180 μmol) was then added. The tube was sealed and heated at 140 $^\circ\text{C}$ (bath) for 16h. The reaction mixture was quenched by adding $n\text{-Bu}_4\text{NBH}_4$ (~30 mg) in solution in dichloromethane (1 mL). The mixture was then filtered through a short plug of silica, eluting with CH_2Cl_2 . The products were isolated by preparative TLC (95:5 Hexanes:Et₂O).

Compounds **6a-g** were named according to ChemDraw nomenclature. For molecules **6a-g**, the carbon *ipso* to boron was not detected due to the quadrupolar relaxation mechanism of the ^{11}B nucleus.

2,2-Diisopropyl-2,3-dihydrobenzo[d][1,2,3]oxaphosphaborol-2-ium-3-uide (6a)

The product was isolated as a colorless oil in 80% yield after preparative TLC (95:5 Hexanes:Et₂O)

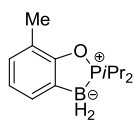


^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, J = 7.0 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1 H), 6.93 (t, J = 7.2 Hz, 1 H), 6.85 (d, J = 7.8 Hz, 1 H), 2.38-2.29 (m, 2 H), 1.36-1.26 (br m, 2

H), 1.27-1.10 (m, 12 H); ^{13}C NMR (100 MHz, CDCl_3): δ 161.0 (d, $J= 12.4$ Hz), 133.6 (d, $J= 19.1$ Hz), 126.3, 122.7, 112.0 (d, $J= 9.5$ Hz), 24.4 (d, $J= 30.5$ Hz), 15.8 (d, $J= 1.9$ Hz); ^{11}B NMR (128 MHz, CDCl_3): δ -31 (br m); ^{31}P NMR (162 MHz, CDCl_3): δ 141 (br m). HRMS (ES⁺): m/z calculated for $\text{C}_{12}\text{H}_{21}\text{BOP}$ $[\text{M}+\text{H}]^+$ 223.1418, found 223.1424.

2,2-Diisopropyl-7-methyl-2,3-dihydrobenzo[d][1,2,3]oxaphosphaborol-2-ium-3-uide (6b)

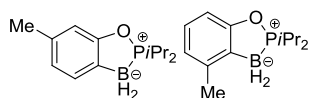
The product was isolated as a colorless oil in 84% yield after preparative TLC (95:5 Hexanes:Et₂O)



^1H NMR (400 MHz, CDCl_3): δ 7.25 (m, 1H), 6.85 (m, 2 H), 2.36-2.31 (m, 2 H), 2.21 (s, 3 H), 2.34-1.43 (br m, 2 H), 1.26-1.18 (m, 12 H); ^{13}C NMR (125 MHz, CDCl_3): δ 159.4 (d, $J= 12.7$ Hz), 130.8 (d, $J= 19.6$ Hz), 127.5, 122.4, 121.4 (d, $J= 8.8$ Hz), 24.3 (d, $J= 31.3$ Hz), 15.6 (d, $J= 70.2$ Hz), 15.4; ^{11}B (128 MHz, CDCl_3) NMR : δ -31 (br m); ^{31}P NMR (162 MHz, CDCl_3): δ 137 (br m). HRMS (ES⁺): m/z calculated for $\text{C}_{13}\text{H}_{23}\text{BOP}$ $[\text{M}+\text{H}]^+$ 237.1574, found 237.1583.

2,2-Diisopropyl-6-methyl-2,3-dihydrobenzo[d][1,2,3]oxaphosphaborol-2-ium-3-uide (6c), 2,2-Diisopropyl-4-methyl-2,3-dihydrobenzo[d][1,2,3]oxaphosphaborol-2-ium-3-uide(6c')

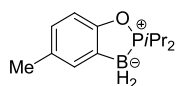
The product was obtained as a mixture of régioisomères in 84% yield (1:1 ratio) after preparative TLC (95:5 Hexanes:Et₂O)



^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 7.1$ Hz, 1H), 6.96 (t, $J = 7.7$ Hz, 1H), 6.82-6.75 (m, 2H), 6.70 (d, $J = 7.1$ Hz, 2H), 2.39-2.21 (m, 10H), 2.34-1.43 (br m, 4H), 1.30-1.14 (m, 24H). ; ^{11}B (128 MHz, CDCl_3) NMR : δ -31 (br m); ^{31}P NMR (162 MHz, CDCl_3): δ 141 (br m).

2,2-Diisopropyl-5-methyl-2,3-dihydrobenzo[d][1,2,3]oxaphosphaborol-2-ium-3-uide (6d)

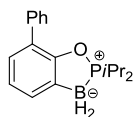
The product was isolated as a colorless oil in 72% yield after preparative TLC (95:5 Hexanes:Et₂O)



^1H NMR (400 MHz, CDCl_3): δ 7.25 (s, 1H), 6.83 (d, J = 7.8 Hz, 1 H), 6.75 (d, J = 7.8 Hz, 1 H), 2.35-2.24 (m, 5 H), 2.21 (s, 1 H), 2.34-1.46 (br m, 2 H), 1.27-1.18 (m, 12 H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.0 (d, J = 12.5 Hz), 134.0 (d, J = 18.7 Hz), 131.6, 126.6, 111.4 (d, J = 8.9 Hz), 24.2 (d, J = 30.7 Hz), 20.8, 15.3 (d, J = 2.7 Hz); ^{11}B NMR (128 MHz, CDCl_3): δ -31 (br m); ^{31}P NMR (162 MHz, CDCl_3): δ 141 (br m). HRMS (ES⁺): m/z calculated for $\text{C}_{13}\text{H}_{23}\text{BOP}$ $[\text{M}+\text{H}]^+$ 237.1574, found 237.1581.

2,2-Diisopropyl-7-phenyl-2,3-dihydrobenzo[d][1,2,3]oxaphosphaborol-2-ium-3-uide (6e)

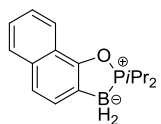
The product was isolated as a colorless oil in 78% yield after preparative TLC (95:5 Hexanes:Et₂O)



^1H NMR (400 MHz, CDCl_3): δ 7.50 (d, J = 7.4 Hz, 2H); 7.43-7.38 (m, 4 H), 7.32-7.28 (m, 1 H), 7.11 (d, J = 7.4 Hz, 1 H), 7.02 (t, J = 7.3 Hz, 1 H), 2.36-2.30 (m, 2 H), 1.26-1.19 (m, 12 H); ^{13}C NMR (100 MHz, CDCl_3): δ 157.3 (d, J = 12.7 Hz), 138.6, 132.7 (d, J = 19.1 Hz), 128.9, 127.9, 128.3, 127.3, 126.7, 125.9 (d, J = 8.6 Hz), 122.9, 24.2 (d, J = 30.7 Hz), 15.5 (d, J = 2.7 Hz), 15.4 (d, J = 4.3 Hz); ^{11}B NMR (128 MHz, CDCl_3): δ -31 (br m); ^{31}P NMR (162 MHz, CDCl_3): δ 141 (br m). HRMS (ES⁺): m/z calculated for $\text{C}_{18}\text{H}_{25}\text{BOP}$ $[\text{M}+\text{H}]^+$ 299.1731, found 299.1745.

2,2-Diisopropyl-2,3-dihydronaphtho[2,1-d][1,2,3]oxaphosphaborol-2-ium-3-uide (6f)

The product was isolated as a orange solid in 66% yield after preparative TLC (95:5 Hexanes:Et₂O)

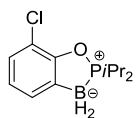


^1H NMR (400 MHz, CDCl_3): δ 7.97 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.47-7.36 (m, 3 H), 2.44-2.38 (m, 2 H), 2.34-1.63 (br m, 2 H), 1.30-1.20 (m, 12 H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.0 (d, J =12.9 Hz), 133.3, 131.0 (d, J = 19.1 Hz), 127.7, 125.4, 124.6, 122.1 (d, J = 8.6 Hz), 121.8 (d, J = 1.9 Hz), 120.8, 24.3 (d, J = 30.5 Hz), 15.8 (d, J = 7.6 Hz); ^{11}B NMR (128 MHz, CDCl_3): δ -30 (br m); ^{31}P NMR (162 MHz,

CDCl₃): δ 142 (br m). HRMS (ES⁺): m/z calculated for C₁₆H₂₃BOP [M+H]⁺ 273.1574, found 273.1584. mp(from Et₂O): 115-116°C.

7-Chloro-2,2-diisopropyl-2,3-dihydrobenzo[d][1,2,3]oxaphosphaborol-2-ium-3-uide
(6g)

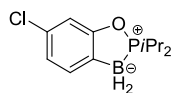
The product was isolated as a colorless oil in 56% after preparative TLC (95:5 Hexanes:Et₂O)



¹H NMR (400 MHz, CDCl₃): δ 7.28 (d, J= 7.0 Hz, 1H), 7.04 (d, J= 7.8 Hz, 1H), 6.85 (d, J= 7.5 Hz, 1H), 2.42-2.36 (m, 2 H), 2.34-1.63 (br m, 2 H), 1.29-1.20 (m, 12 H); ¹³C NMR (100 MHz, CDCl₃): δ 156.4 (d, J= 14.7 Hz), 132.0 (d, J= 18.6 Hz), 127.1, 123.9, 24.8 (d, J= 30.3 Hz), 15.8 (d, J= 12.7 Hz); ¹¹B NMR (128 MHz, CDCl₃): δ -33 (br m); ³¹P NMR (162 MHz, CDCl₃): δ 144 (br m). HRMS (ES⁺): m/z calculated for C₁₂H₂₀BClOP [M+H]⁺ 257.1028 found 257.1034.

6-Chloro-2,2-diisopropyl-2,3-dihydrobenzo[d][1,2,3]oxaphosphaborol-2-ium-3-uide
(6h)

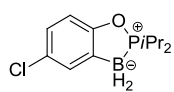
The product was isolated as a colorless oil in 41% yield after preparative TLC (95:5 Hexanes:Et₂O)



¹H NMR (400 MHz, CDCl₃): δ 7.32 (d, J= 7.7 Hz, 1H), 6.91 (dd, J= 7.7 Hz, J= 1.7 Hz, 1H), 6.86 (d, J= 1.7 Hz, 1H), 2.38-2.29 (m, 2 H), 2.10-1.60 (br m, 2 H), 1.26-1.18 (m, 12 H); ¹³C NMR (125 MHz, CDCl₃): δ 161.4 (d, J=12.9 Hz), 134.0 (d, J= 18.6 Hz), 131.1, 122.7, 112.6 (d, J= 9.1 Hz), 24.4 (d, J= 30.2 Hz), 15.4 (d, J= 12.7 Hz); ¹¹B NMR (128 MHz, CDCl₃): δ -31 (br m); ³¹P NMR (162 MHz, CDCl₃): δ 145 (br m). HRMS (ES⁺): m/z calculated for C₁₂H₂₀BClOP [M+H]⁺ 257.1028 found 257.1029.

5-Chloro-2,2-diisopropyl-2,3-dihydrobenzo[d][1,2,3]oxaphosphaborol-2-ium-3-uide
(6i)

The product was isolated as a colorless oil in 56% yield after preparative TLC (95:5 Hexanes:Et₂O)



¹H NMR (400 MHz, CDCl₃): δ 7.36 (s, 1H), 6.97 (d, J= 8.3 Hz, 1 H), 6.76 (d, J= 8.3 Hz, 1 H), 2.38-2.29 (m, 2 H), 2.16-1.62 (br m, 2 H), 1.26-1.17 (m, 12 H); ¹³C NMR

(100 MHz, CDCl₃): δ 159.9 (d, J= 12.7 Hz), 133.4, 132.7 (d, J= 19.6 Hz), 126.4, 113.3 (d, J= 8.8 Hz), 24.7 (d, J= 31.3 Hz), 15.8 (d, J= 6.8 Hz); ¹¹B NMR (128 MHz, CDCl₃) : δ -31 (br m); ³¹P NMR (162 MHz, CDCl₃): δ 143 (br m). HRMS (ES+): m/z calculated for C₁₂H₂₀BClOP [M+H]⁺ 257.1028 found 257.1028.

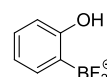
General procedure for preparation of trifluoroborate salts by borylation reaction:

A dry 12 mL thick-walled Schlenk tube fitted with a teflon stopper was charged with a mixture of phosphine borane (500 μ mol), dissolved in toluene (4 mL) and Tf₂NH (130 mg, 460 μ mol) was then added. The tube was sealed and heated at 140 °C (bath) for 16h. After cooling at 0 °C MeOH (4 mL) was added, followed by KHF₂ (4.5 M in H₂O, 1.25 mL, 5 mmol). The slurry was stirred 2 h, at room temperature before concentration to dryness. The resulting solid was taken up in hot acetone and insoluble materials were removed by filtration, washing with acetone (3 x 5 mL). The filtrate was concentrated under reduced pressure, and the white powder was recrystallized in a minimal amount of MeOH (~3 mL). The desired product was isolated by filtration, and washed with cold MeOH (chilled in dry ice acetone 3 x 1 mL) and Et₂O (3 x 1 mL).

For molecules **10a-g**, carbon *ipso* to boron were not detected due to the quadrupolar relaxation mechanism of ¹¹B nucleus.

Potassium (2-hydroxyphenyl)trifluoroborate (10a)

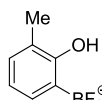
The product was isolated as a white solid in 75% yield (68 mg).



¹H NMR (400 MHz, Acetone-*d*₆) : δ 7.49-7.33 (br m, 1H), 7.27 (d, J= 6.7 Hz, 1 H), 6.91 (m, 1 H), 6.61 (t, J= 7.2 Hz, 1 H), 6.53 (d, J= 7.9 Hz, 1 H); ¹³C NMR (125 MHz, Acetone-*d*₆): δ 159.9, 133.2, 127.0, 118.3, 113.4; ¹¹B NMR (128 MHz, Acetone-*d*₆) : δ 9 (br m); ¹⁹F NMR (376 MHz, Acetone-*d*₆): δ -137 (br m). HRMS (ESI-): m/z calculated for C₆H₅BF₃O [M-K]⁻ 161.0391, found 161.0392.

Potassium (2-hydroxy-3-methylphenyl)trifluoroborate (10b)

The product was isolated as a white solid in 88% yield (86 mg).

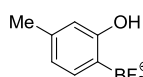


^1H NMR (400 MHz, Acetone- d_6): δ 7.56 (q, J = 11.3 Hz, 1 H), 7.18 (d, J = 6.8 Hz, 1 H), 6.85 (d, J =7.2 Hz, 1 H), 6.59 (t, J = 7.2 Hz, 1 H), 2.16 (s, 3 H); ^{13}C NMR (125 MHz, Acetone- d_6): δ 158.1, 131.1, 130.9, 128.5, 121.5, 118.3, 15.6; ^{11}B NMR (128 MHz, Acetone- d_6): δ 3 (br m); ^{19}F NMR (376 MHz, Acetone- d_6): δ -135 (br m). HRMS (ESI-): m/z calculated for $\text{C}_7\text{H}_7\text{BF}_3\text{O}$ [M-K] $^-$ 175.0548, found 175.0544.

The spectral data were in accordance with those reported in the literature.³

Potassium (2-hydroxy-4-methylphenyl)trifluoroborate (10c)

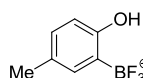
The product was isolated as a white solid in 39% yield (58 mg).



^1H NMR (400 MHz, Acetone- d_6): δ 7.24 (q, J = 9.9 Hz, 1 H), 7.14 (d, J = 7.2 Hz, 1 H), 6.44 (d, J =7.2 Hz, 1 H), 6.38 (s, 1 H), 2.15 (s, 3 H); ^{13}C NMR (125 MHz, Acetone- d_6): δ 160.1, 136.0, 133.2, 119.1, 114.1, 20.3; ^{11}B NMR (128 MHz, Acetone- d_6): δ 4 (br m); ^{19}F NMR (376 MHz, Acetone- d_6): δ -137 (br m). HRMS (ESI-): m/z calculated for $\text{C}_7\text{H}_7\text{BF}_3\text{O}$ [M-K] $^-$ 175.0548, found 175.0551.

Potassium (2-hydroxy-5-methylphenyl)trifluoroborate (10d)

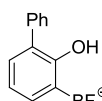
The product was isolated as a white solid in 94% yield (91 mg).



^1H NMR (400 MHz, Acetone- d_6): δ 7.22 (q, J = 10.7 Hz, 1 H), 7.05 (m, 1 H), 6.69 (dd, J =8.2 Hz, J = 2.1 Hz, 1 H), 6.39 (d, J = 7.9 Hz, 1 H), 2.07 (s, 3 H); ^{13}C NMR (125 MHz, dms- d_6): δ 157.6, 134.0, 129.7, 126.3, 113.4, 20.9; ^{11}B NMR (128 MHz, Acetone- d_6): δ 9 (br m); ^{19}F NMR (376 MHz, Acetone- d_6): δ -137 (br m). HRMS (ESI-): m/z calculated for $\text{C}_7\text{H}_7\text{BF}_3\text{O}$ [M-K] $^-$ 175.0548, found 175.0550.

Potassium (2-hydroxy-[1,1'-biphenyl]-3-yl)trifluoroborate (10e)

The product was isolated as a white solid in 57% yield (58 mg).



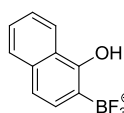
^1H NMR (400 MHz, Acetone- d_6): δ 7.68 (q, J = 11.7 Hz, 1 H), 7.57 (d, J = 7.9 Hz, 2 H), 7.32 (m, 3 H), 7.21 (t, J = 7.4 Hz, 1 H), 7.03 (dd, J = 7.4 Hz, J = 1.7 Hz, 1 H), 6.73 (t, J = 7.3 Hz, 1 H); ^{13}C NMR (125 MHz, Methanol- d_4): δ 157.3, 141.7, 133.7, 130.5, 130.2, 128.7, 128.2, 127.1, 120.5; ^{11}B NMR (128 MHz, Acetone- d_6): δ 3 (br m); ^{19}F NMR (376 MHz,

Acetone- d_6): δ -136 (br m). HRMS (ESI-): m/z calculated for $C_{12}H_9BF_3O$ $[M-K]^-$ 237.0704, found 237.0714.

The spectral data were in accordance with those reported in the literature.³

Potassium (1-hydroxynaphthalen-2-yl)trifluoroborate (10f)

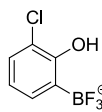
The product was isolated as an orange solid in 56% yield (64 mg).



1H NMR (400 MHz, Acetone- d_6): δ 8.49-8.19 (br s, 1 H), 8.11 (m, 1H), 7.63 (m, 1 H), 7.46 (d, J = 7.9 Hz, 3 H), 7.26 (m, 2 H), 7.15 (d, J = 7.4 Hz, 1 H); ^{13}C NMR (125 MHz, Acetone- d_6): δ 154.7, 134.2, 131.8, 131.7, 129.9, 124.4, 123.2, 122.0, 117.2; ^{11}B NMR (128 MHz, Acetone- d_6): δ 4 (br m); ^{19}F NMR (376 MHz, Acetone- d_6): δ -135 (br m). HRMS (ESI-): m/z calculated for $C_{10}H_7BF_3O$ $[M-K]^-$ 211.0548, found 211.0552.

Potassium (3-chloro-2-hydroxyphenyl)trifluoroborate (10g)

The product was isolated as a white solid in 61% yield (65 mg).

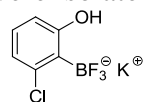
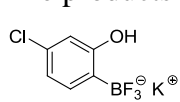


1H NMR (400 MHz, Acetone- d_6): δ 8.04-7.86 (br s, 1 H), 7.18 (d, J = 6.6 Hz, 1 H), 6.98 (m, 1 H), 6.59 (t, J = 7.4 Hz, 1 H); ^{13}C NMR (125 MHz, Acetone- d_6): δ 155.2, 131.8, 127.5, 119.6, 118.1; ^{11}B NMR (128 MHz, Acetone- d_6): δ 3 (br m); ^{19}F NMR (376 MHz, Acetone- d_6): δ -136 (br m). HRMS (ESI-): m/z calculated for $C_6H_4BClF_3O$ $[M-K]^-$ 195.0001, found 195.0005.

The spectral data were in accordance with those reported in the literature.³

Potassium (4-chloro-2-hydroxyphenyl)trifluoroborate and potassium (6-chloro-2-hydroxyphenyl)trifluoroborate (10h and 10h')

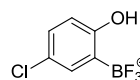
The products were isolated as a white solid in 61% yield in a 1.3:1 mixture.



1H NMR (400 MHz, acetone) δ 8.79 – 8.54 (m, 1H), 7.77 (q, J = 10.9 Hz, 1H), 7.28 (s, 1H), 6.91 (t, J = 7.9 Hz, 1H), 6.68 (m, 2H), 6.59 (s, 1H), 6.51 (d, J = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, dmsO) δ 161.5, 160.9, 138.9, 134.6, 131.2, 128.3, 120.4, 118.6, 113.7, 113.0. ^{11}B NMR (128 MHz, Acetone- d_6): δ 3 (br m); ^{19}F NMR (376 MHz, Acetone- d_6): δ -133 (br m), -137 (br m). $C_6H_4BClF_3O$ $[M-K]^-$ 195.0001, found 195.0008.

Potassium (5-chloro-2-hydroxyphenyl)trifluoroborate (10i)

The product was isolated as a white solid in 34% yield (36 mg).



^1H NMR (400 MHz, Acetone- d_6): δ 7.54-7.49 (br s, 1 H), 7.19 (s, 1 H), 6.88 (dd, $J=8.5$ Hz, $J=3.1$, 1 H), 6.50 (dd, $J=8.5$ Hz, $J=3.1$, 1 H); ^{13}C NMR (125 MHz, DMSO- d_6): δ 158.7, 132.8, 127.0, 122.9, 115.8; ^{11}B NMR (128 MHz, Acetone- d_6): δ 3 (br m). ^{19}F NMR (376 MHz, Acetone- d_6): δ -136 (br m). HRMS (ESI-): m/z calculated for $\text{C}_6\text{H}_4\text{BClF}_3\text{O}$ [M-K] 195.0001, found 195.0005.

General procedure for Suzuki coupling:⁴

Following the procedure of Saito,³ a 5mL flask fused with a condenser was charged with trifluoroborate salt, K_2CO_3 (2 equivalents) and $\text{Pd}(\text{PPh}_3)_4$ (5 mol%). The flask was evacuated and back-filled with nitrogen (this was repeated two additional times). Degassed toluene, ethanol and water (3:1:1, 1.25M, sonicated under nitrogen for 10 min) were added followed by iodobenzene (1.5 equivalents). After refluxing for 13 h, the organic layer was separated and the aqueous layer was acidified with 10% HCl and extracted with AcOEt. The combined organic solution was dried over MgSO_4 and concentrated. The residue was purified by flash chromatography on silica gel (9:1 hexanes:Et₂O).

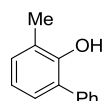
For compounds **11a**,⁵ **11b**,⁵ **11c**,⁵ **11d**,⁵ **11e**,⁵ **11f**⁵ and **11i**⁶ identity with the literature sample was established by comparison of NMR data.

2-Phenylphenol (11a)

The product was isolated as a white solid in 89% yield.

2-Methyl-6-phenylphenol (11b)

The product was isolated as a yellow oil in 91% yield.

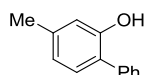


^1H NMR (400 MHz, CDCl_3): δ 7.51-7.39 (m, 5 H), 7.13 (d, $J=7.4$ Hz, 1 H), 7.08 (dd, $J=7.6$ Hz, $J=1.2$ Hz, 1 H), 6.89 (t, $J=7.6$ Hz, 1 H), 5.21 (s, 1 H), 2.31 (s, 3 H); ^{13}C NMR (125 MHz, CDCl_3): δ 150.7, 137.5, 130.7, 129.5, 129.3, 128.0, 127.9, 127.8, 124.8,

120.4, 16.4; HRMS (EI+ 70 eV): m/z calculated for C₁₃H₁₂O [M]⁺ 184.0888, found 184.0880.

3-Methyl-6-phenylphenol (11c)

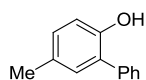
The product was isolated as a colorless oil in 74% yield.



¹H NMR (400 MHz, CDCl₃): δ 7.49-7.43 (m, 4 H), 7.39-7.35 (m, 1 H), 7.13 (d, J= 8.1 Hz, 1 H), 6.82-6.80 (m, 2 H), 5.16 (s, 1 H), 2.35 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 152.2, 139.4, 137.1, 130.0, 129.2, 127.6, 125.2, 121.7, 116.4, 21.2; HRMS (EI+ 70 eV): m/z calculated for C₁₃H₁₂O [M]⁺ 184.0888, found 184.0881.

4-Methyl-6-phenylphenol (11d)

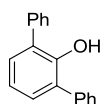
The product was isolated as a white solid in 84% yield.



¹H NMR (400 MHz, CDCl₃): δ 7.49-7.44 (m, 4 H), 7.41-7.37 (m, 1 H), 7.08-7.07 (m, 2 H), 6.91-6.88 (m, 1 H), 5.14 (s, 1 H), 2.33 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 150.3, 137.5, 130.9, 130.1, 129.8, 129.3, 129.2, 128.0, 127.9, 115.8, 20.7; HRMS (EI+ 70 eV): m/z calculated for C₁₃H₁₂O [M]⁺ 184.0888, found 184.0879. mp(from Et₂O): 68-69°C.

2,6-Diphenylphenol (11e)

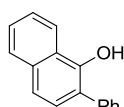
The product was isolated as a white solid in 80% yield.



¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, J= 7.1 Hz, 4 H), 7.46 (t, J= 7.7 Hz, 4 H), 7.37 (t, J= 7.3 Hz, 2 H), 7.27 (d, J= 7.6 Hz, 2 H), 7.05 (t, J= 7.6 Hz, 1 H), 5.39 (s, 1 H); ¹³C NMR (125 MHz, CDCl₃): δ 149.3, 137.6, 130.0, 129.4, 128.9, 128.8, 127.7, 120.7; HRMS (EI+ 70 eV): m/z calculated for C₁₈H₁₄O [M]⁺ 246.1045, found 246.1039. mp(from Et₂O): 101-102°C.

2-Phenyl-naphthalen-1-ol (11f)

The product was isolated as an orange solid in 68% yield.

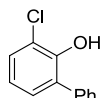


¹H NMR (400 MHz, CDCl₃): δ 8.34-8.27 (m, 1 H), 7.82-7.80 (m, 1H), 7.53-7.47 (m, 7 H), 7.44-7.39 (m, 1H), 7.35 (d, J= 8.4 Hz, 1H), 5.83 (s, 1 H); ¹³C NMR (125 MHz, CDCl₃): δ 147.9, 137.6, 134.4, 129.8, 129.5, 128.1, 127.8, 127.7, 126.7, 125.7, 124.5, 122.6,

121.4, 120.4 ; HRMS (EI+ 70 eV): m/z calculated for C₁₆H₁₂O [M]⁺ 220.0888, found 220.0880. mp(from Et₂O): 64-65°C.

2-Chloro-6-phenylphenol (11g)

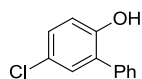
The product was isolated as a white solid in 89% yield.



¹H NMR (400 MHz, CDCl₃) : δ 7.53 (d, J= 7.6 Hz, 2 H), 7.44 (t, j= 7.6 Hz, 2 H), 7.37 (td, J= 7.3 Hz, J= 1.2 Hz, 1 H), 7.31 (d, J= 7.6 Hz, 1 H), 7.21 (d, J= 7.6 Hz, 1 H), 6.91 (t, J= 7.6 Hz, 1 H), 5.69 (s, 1 H) ; ¹³C NMR (125 MHz, CDCl₃): δ 148.6, 137.2, 129.8, 129.6, 129.3, 128.7, 128.5, 127.9, 121.3, 120.8 ; HRMS (EI+ 70 eV): m/z calculated for C₁₂H₉ClO [M]⁺ 204.0342, found 204.0343. mp(from Et₂O): 74-75°C.

4-Chloro-6-phenylphenol (11i)

The product was isolated as a colorless oil in 86% yield.



¹H NMR (400 MHz, CDCl₃) : δ 7.50-7.47 (m, 2 H), 7.44-7.39 (m, 3 H), 7.22-7.19 (m, 2 H), 6.91 (d, J= 8.6 Hz, 1 H), 5.21 (s, 1 H) ; ¹³C NMR (125 MHz, CDCl₃): δ 151.3, 136.0, 129.9, 129.7, 129.7, 129.1, 129.0, 128.6, 125.7, 117.4 ; HRMS (EI+ 70 eV): m/z calculated for C₁₂H₉ClO [M]⁺ 204.0342, found 204.0333.

References:

- (1) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, *73*, 1795.
- (2) Bedford, R. B.; Hazelwood, S. L.; Horton, P. N.; Hursthouse, M. B. *Dalton Trans.* **2003**, 4164.
- (3) Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 7534.
- (4) Makino, T.; Yamasaki, R.; Saito, S. *Synthesis* **2008**, *6*, 859.
- (5) Ackermann, L.; Kapdi, A. R.; Fenner, S.; Kornhaaß, C.; Schulzke, C. *Chem. Eur. J.* **2011**, *17*, 2965.

(6) Oi, S.; Watanabe, S. I.; Fukita, S.; Inoue, Y. *Tetrahedron Lett.* **2003**, 44, 8665.