One-Pot Synthesis of Aryl Boronic Acids and Aryl Trifluoroborates by Ir-Catalyzed Borylation of Arènes

Supporting Information

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General Experimental Information and Reagent Information: Borylations of arenes were conducted in sealed vessels. \([\text{Ir}(\text{COD})\text{Cl}]_2\) and \([\text{Ir}(\text{COD})(\text{OMe})]_2\) were prepared according to literature procedure.\(^1\) Conversion of aryl boronic esters to either arylboronic acids or aryltrifluoroborates were conducted under ambient atmosphere. All arenes, \(\text{B}_2\text{pin}_2\), \(\text{NaIO}_4\), and \(\text{KHF}_2\) were bought from commercial sources and were used without further purification. Borylations were performed using THF that was degassed by purging with nitrogen for 45 min and then dried with a solvent purification system using a 1 m column containing activated alumina. For the conversion of arylboronic esters to arylboronic acids and potassium aryltrifluoroborates, ACS grade THF was purchased from Aldrich and was used without further purification.

GC-MS data were obtained on an Agilient 6890-N GC system containing an Alltech EC-1 capillary column and an Agilient 5973 mass selective detector. \(^1\)H-NMR, \(^{13}\)C-NMR, \(^{11}\)B-NMR, and \(^{19}\)F-NMR spectra were obtained on a 400 MHz or 500MHz Varian Unities.

Conversion of 1-methoxy-3-trifluoromethylbenzene to potassium (3-methoxy-5-trifluoromethylphenyl)trifluoroborate. In a glove box, 1-methoxy-3-trifluoromethylbenzene (0.72 mL, 5.0 mmol), \(\text{B}_2\text{pin}_2\), (0.893 g, 3.52 mmol), \([\text{Ir}(\text{COD})(\text{OMe})]_2\) (3.3 mg, 5.0 µmol), dtbpy (2.5 mg, 10.0 µmol), and THF (5.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then \(\text{H}_2\text{O}\) (3.0 mL) and \(\text{KHF}_2\) (2.30 g, 28.5 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum to yield a mixture of potassium aryltrifluoroborate and pinacol. The crude product was rinsed with hexanes and heated at 60 °C under vacuum (6 mtorr) to remove pinacol. Purified product was recovered in 85% yield as a white solid. \(^1\)H NMR (500 MHz, acetone-\(d_6\)) \(\delta\)7.36 (s, 1 H), \(\delta\)7.25 (s, 1 H), \(\delta\)6.83 (s, 1 H), \(\delta\)3.77 (s, 3 H). \(^{11}\)B NMR (600 MHz, acetone-\(d_6\)): \(\delta\)3.73 (q, J=155 Hz). \(^{19}\)F NMR (600 MHz, acetone-\(d_6\)): \(\delta\)-63.4 (s), \(\delta\)-144.8 (q, J=44 Hz). \(^{13}\)C NMR (500 MHz, acetone-\(d_6\)): \(\delta\)160.5, \(\delta\)109.8, \(\delta\)98.5, \(\delta\)54.9.

Conversion of 1,3-(trifluoromethyl)benzene to potassium (3-methoxy-5-trifluoromethylphenyl)trifluoroborate. In a glove box, 1,3-(trifluoromethyl)benzene (0.78 mL, 5.0 mmol), \(\text{B}_2\text{pin}_2\), (0.886 g, 3.94 mmol), \([\text{Ir}(\text{COD})(\text{OMe})]_2\) (3.3 mg, 5.0 µmol), dtbpy (2.9 mg, 10.1 µmol), and THF (5.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then \(\text{H}_2\text{O}\) (3.0 mL) and \(\text{KHF}_2\) (2.22 g, 28.5 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum to yield a mixture of potassium aryltrifluoroborate and pinacol. The crude product was rinsed with hexanes and heated at 60 °C under vacuum (6 mtorr) to remove pinacol. Purified product was recovered in 82% yield as a white solid. \(^1\)H NMR (500 MHz, acetone-\(d_6\)) \(\delta\)8.01 (s, 2 H), \(\delta\)7.67 (s, 1 H),...
Conversion of 1,3-dichlorobenzene to potassium (3,5-dichlorophenyl)trifluoroborate. In a glove box, 1,3-dichlorobenzene (0.57 mL, 5.0 mmol), B
2
pin
2
(0.915 g, 3.60 mmol), [Ir(COD)(OMe)]
2
(3.6 mg, 5.8 µmol), dtbpy (3.3 mg, 12 µmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then H
2
O (3.0 mL) and KHF
2
(2.23 g, 28.5 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum to yield a mixture of potassium aryltrifluoroborate and pinacol. The crude product was rinsed with hexanes and heated at 60 °C under vacuum (6 mtorr) to remove pinacol. Purified product was recovered in 66% yield as a white solid. 

\[ ^1H\text{NMR (500 MHz, acetone-}d_6\text{): } \delta 7.34 (s, 1 H), \delta 7.05 (s, 2 H). \]

\[ ^11B\text{NMR (500 MHz, acetone-}d_6\text{): } \delta 3.47 . \]

\[ ^13C\text{NMR (500 MHz, acetone-}d_6\text{): } \delta 133.8, \delta 130.7, \delta 125.3. \]

\[ ^19F\text{NMR (500 MHz, acetone-}d_6\text{): } \delta -143.3. \]

Conversion of 1-methoxycarbonyl-3-methylbenzene to potassium (3-methoxycarbonyl-5-methylphenyl)trifluoroborates. In a glove box, 1-methoxycarbonyl-3-methylbenzene (0.71 mL, 5.0 mmol), B
2
pin
2
(0.887 g, 3.50 mmol), [Ir(COD)(OMe)]
2
(3.2 mg, 4.8 µmol), dtbpy (2.7 mg, 10 µmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then H
2
O (3.0 mL) and KHF
2
(2.26 g, 28.5 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum to yield a mixture of aryltrifluoroborate and pinacol. The crude product was rinsed with hexanes and heated at 60 °C under vacuum (6 mtorr) to remove pinacol. Purified product was recovered in 75% yield as a white solid.

\[ ^1H\text{NMR (500 MHz, acetone-}d_6\text{): } \delta 7.99 (s, 1 H), \delta 7.50 (s, 2 H), \delta 3.77 (s, 3 H), \delta 2.26 (s, 3 H). \]

\[ ^11B\text{NMR (500 MHz, acetone-}d_6\text{): } \delta 3.59. \]

\[ ^13C\text{NMR (500 MHz, acetone-}d_6\text{): } \delta 138.36, \delta 135.84, \delta 131.09, \delta 127.50, \delta 51.54, \delta 21.38. \]

\[ ^19F\text{NMR (500 MHz, acetone-}d_6\text{): } \delta -142.4. \]

Conversion of 1,3-dibromobenzene to potassium (3,5-dibromophenyl)trifluoroborate. In a glove box, 1,3-dibromobenzene (0.60 mL, 5.0 mmol), B
2
pin
2
(0.927 g, 3.70 mmol), [Ir(COD)(OMe)]
2
(3.6 mg, 5.8 µmol), dtbpy (3.3 mg, 12 µmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then H
2
O (3.0 mL) and KHF
2
(2.26 g, 28.5 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum to yield a mixture of aryltrifluoroborate and pinacol. The crude product was rinsed with hexanes and heated at 60 °C under vacuum (6 mtorr) to remove pinacol. Clean product was recovered in 75% yield as a white solid.

\[ ^1H\text{NMR (500 MHz, acetone-}d_6\text{): } \delta 7.99 (s, 1 H), \delta 7.50 (s, 2 H), \delta 3.77 (s, 3 H), \delta 2.26 (s, 3 H). \]

\[ ^11B\text{NMR (500 MHz, acetone-}d_6\text{): } \delta 3.59. \]

\[ ^13C\text{NMR (500 MHz, acetone-}d_6\text{): } \delta 138.36, \delta 135.84, \delta 131.09, \delta 127.50, \delta 51.54, \delta 21.38. \]

\[ ^19F\text{NMR (500 MHz, acetone-}d_6\text{): } \delta -142.4. \]
mmol), B\textsubscript{2}pin\textsubscript{2}, (0.900 g, 3.54 mmol), [Ir(COD)(OMe)]\textsubscript{2} (3.2 mg, 4.8 \mu mol), dtbpy (3.5 mg, 13 \mu mol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then H\textsubscript{2}O (3.0 mL) and KHF\textsubscript{2} (2.21 g, 28.3 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum to yield a mixture of aryltrifluoroborate and pinacol. The crude product was rinsed with hexanes and heated at 60 °C under vacuum (6 mtorr) to remove pinacol. Purified product was recovered in 72% yield as a white solid.

1\textsuperscript{H} NMR (500 MHz, acetone-\textsubscript{d}6) \(\delta\) 7.52 (s, 2 H), \(\delta\) 7.36 (s, 1 H).

11\textsuperscript{B} NMR (500 MHz, acetone-\textsubscript{d}6): \(\delta\) 3.11 (q, J=165 Hz).

13\textsuperscript{C} NMR (600 MHz, acetone-\textsubscript{d}6): \(\delta\) 134.1, \(\delta\) 130.7, \(\delta\) 122.4.

19\textsuperscript{F} NMR (500 MHz, acetone-\textsubscript{d}6): \(\delta\) 143.4 (q, J=59 Hz).

Conversion of 1,3-dimethoxybenzene to potassium (3,5-dimethoxyphenyl)trifluoroborate

In a glove box, 1,3-dimethoxybenzene (0.66 mL, 5.0 mmol), B\textsubscript{2}pin\textsubscript{2}, (0.892 g, 3.51 mmol), [Ir(COD)(OMe)]\textsubscript{2} (3.6 mg, 5.5 \mu mol), dtbpy (3.5 mg, 13 \mu mol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then H\textsubscript{2}O (3.0 mL) and KHF\textsubscript{2} (2.28 g, 29.1 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum to yield a mixture of aryltrifluoroborate and pinacol. The crude product was rinsed with hexanes and heated at 60 °C under vacuum (6 mtorr) to remove pinacol. Purified product was recovered in 93% yield as a white solid.

1\textsuperscript{H} NMR (500 MHz, acetone-\textsubscript{d}6) \(\delta\) 6.64 (s, 2 H), \(\delta\) 6.12 (s, 1 H), \(\delta\) 3.66 (s, 6 H).

11\textsuperscript{B} NMR (500 MHz, acetone-\textsubscript{d}6): \(\delta\) 4.10 (q, J=XX Hz).

13\textsuperscript{C} NMR (500 MHz, acetone-\textsubscript{d}6): \(\delta\) 160.56, \(\delta\) 109.76, \(\delta\) 98.54, \(\delta\) 54.95.

19\textsuperscript{F} NMR (500 MHz, acetone-\textsubscript{d}6): \(\delta\) 142.1.

Conversion of 1-chloro-3-trifluoromethylbenzene to potassium (3-chloro-5-trifluoromethylphenyl)trifluoroborate

In a glove box, 1-chloro-3-trifluoromethylbenzene (0.72 mL, 5.0 mmol), B\textsubscript{2}pin\textsubscript{2}, (0.893 g, 3.52 mmol), [Ir(COD)(OMe)]\textsubscript{2} (3.3 mg, 5.0 \mu mol), dtbpy (2.5 mg, 9.3 \mu mol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then H\textsubscript{2}O (3.0 mL) and KHF\textsubscript{2} (2.28 g, 29.1 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum to yield a mixture of aryltrifluoroborate and pinacol. The crude product was rinsed with hexanes and heated at 60 °C under vacuum (6 mtorr) to remove pinacol. Clean product
was recovered in 91% yield as a white solid. $^1$H NMR (500 MHz, acetone-$d_6$): δ 7.02 (s, 1 H), δ 6.95 (s, 1 H), δ 6.60 (s, 1 H). $^1$B NMR (300 MHz, acetone-$d_6$): δ 8.36 (q, J=78 Hz). $^{13}$C NMR (500 MHz, acetone-$d_6$): δ 160.43, δ 133.29, δ 124.65, δ 116.05, δ 111.64, δ 55.29. $^{19}$F NMR (500 MHz, acetone-$d_6$): δ 142.7.

**Conversion of 1-chloro-3-methylbenzene to potassium (3-chloro-5-trifluoromethylphenyl)trifluoroborate.** In a glove box, 1-chloro-3-methylbenzene (0.59 mL, 5.0 mmol), B$_2$pin$_2$, (0.895 g, 3.52 mmol), [Ir(COD)(OMe)]$_2$ (3.1 mg, 5.0 µmol), dtbpy (3.0 mg, 11.2 µmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then H$_2$O (3.0 mL) and KHF$_2$ (2.28 g, 29.2 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum to yield a mixture of aryl boronic acid and pinacol. The crude product was rinsed with hexanes and heated at 60 °C under vacuum (6 mtorr) to remove pinacol. Clean product was recovered in 97% yield as a white solid. $^1$H NMR (400 MHz, acetone-$d_6$): δ 7.32 (s, 1 H), δ 7.19 (s, 1 H), δ 6.86 (s, 1 H), δ 2.22 (s, 3 H). $^{11}$B NMR (300 MHz, acetone-$d_6$): δ 8.35 (q, J=155 Hz). $^{13}$C NMR (500 MHz, acetone-$d_6$): δ 138.2, δ 132.0, δ 131.6, δ 129.3, δ 126.2, δ 21.2. $^{19}$F NMR (600 MHz, acetone-$d_6$): δ 142.8 (q, J= 62 Hz).

**Conversion of m-xylilyboronic ester to potassium (3,5-dimethylphenyl)trifluoroborate.** In a glove box, m-xylene (0.29 mL, 2.0 mmol), B$_2$pin$_2$, (0.364 g, 1.43 mmol), HBpin (30 µL, 0.02 mmol), [Ir(COD)(OMe)]$_2$ (16.2 mg, 24.4 µmol), dtbpy (1.0 mg, 66.3 µmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then H$_2$O (3.0 mL) and KHF$_2$ (0.860 g, 11.0 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum to yield a mixture of aryltrifluoroborate and pinacol. The crude product was rinsed with hexanes and heated at 60 °C under vacuum (6 mtorr) to remove pinacol. Clean product was recovered in 61% yield as a white solid. $^1$H NMR (500 MHz, acetone-$d_6$): δ 7.06 (s, 2 H), δ 6.62 (s, 1 H), δ 6.16 (s, 6 H). $^{13}$C NMR (500 MHz, acetone-$d_6$): δ 135.2, δ 130.5, δ 127.3. $^{11}$B NMR (500 MHz, acetone-$d_6$): δ 4.36. $^{19}$F NMR (500 MHz, acetone-$d_6$): δ141.7 (q, J= 74 Hz).
Conversion of 2-benzofuran to potassium (2-benzofuranyl)trifluoroborate.
In a glove box, 2-benzofuran (0.54 mL, 2.0 mmol), HBpin, (0.07 mL, 0.500 mmol), [Ir(COD)(OMe)]₂ (31.4 mg, 0.047 mmol), dtbpy (29.1 mg, 0.108 mmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then H₂O (3.0 mL) and KHF₂ (2.18 g, 27.9 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum and the crude product mixture was heated to 60 °C under vacuum (6 mtorr) to remove pinacol. The product was recovered in 78% yield as a white solid. ¹H NMR (500 MHz, acetone-d₆) δ 7.42 (d, J= 2Hz, 1 H), δ 7.41 (d, J= 2 Hz, 1 H), δ 7.03 (m, 2 H), δ 6.52 (s, 1H). ¹¹B NMR (500 MHz, acetone-d₆): δ 2.59 (q, J=156 Hz). ¹³C NMR (600 MHz, acetone-d₆): δ 122.3, δ 121.8, δ 120.6, δ 111.2, δ 110.6. ¹⁹F NMR (600 MHz, acetone-d₆): δ 142.2 (q, J= 55 Hz).

Conversion of 2-benzothiophene to potassium (2-benzothiophenyl)trifluoroborate.
In a glove box, 2-benzothiophene (0.23 mL, 2.0 mmol), HBpin (3.0 µL, 0.20 mmol), [Ir(COD)(OMe)]₂ (13.4 mg, 0.020 mmol), dtbpy (11.3 mg, 0.042 mmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to room temperature, and then H₂O (3.0 mL) and KHF₂ (2.22 g, 28.4 mmol) were added. The reaction mixture was stirred for 5 h at room temperature. The solvent mixture was removed under vacuum, and the resulting mixture was extracted into acetone. The acetone solution was then reduced under vacuum and the crude product mixture was heated to 60 °C under vacuum (6 mtorr) to remove pinacol. The product was recovered in 45% yield as a light tan solid. ¹H NMR (500 MHz, acetone-d₆) δ 7.42 (d, J= 2Hz, 1 H), δ 7.41 (d, J= 2 Hz, 1 H), δ 7.03 (m, 2 H), δ 6.52 (s, 1H). ¹¹B NMR (500 MHz, acetone-d₆): δ 2.59 (q, J=156 Hz). ¹³C NMR (600 MHz, acetone-d₆): δ 122.3, δ 121.8, δ 120.6, δ 111.2, δ 110.6. ¹⁹F NMR (600 MHz, acetone-d₆): δ 142.2 (q, J= 55 Hz).

Conversion of m-xylene to 3,5-dimethylphenyl boronic acid.
In a glove box, m-xylene (1.28 mL, 10.0 mmol), B₂pin₂, (2.16 g, 8.50 mmol), HBpin (30 µL, 0.02 mmol), [Ir(COD)(OMe)]₂ (16.2 mg, 24.4 µmol), dtbpy (1.0 mg, 66 µmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction solution was allowed to cool to room temperature. After cooling, half of the solution was transferred to a 50 mL round bottom flask and was diluted with 4.0 mL H₂O. NaIO₄ (3.21 g, 15.0 mmol) was then added. After stirring the reaction mixture for 15 min, 10 mL 1M HCl (aq) was added to the reaction mixture and allowed to stir for 4 h. The resulting mixture was extracted with EtOAc (3 x 25 mL), and the organic layers were combined, washed with H₂O (10 mL), and finally washed with brine (2 x 20 mL). The organic layer was dried over MgSO₄. After filtering, the organic solvent was removed.
under vacuum and a yellow solid was obtained. The crude boronic acid was washed with hexanes and 54% yield was obtained. \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}CN) \(\delta\) 7.33 (\textit{s}, 2 H), \(\delta\) 7.05 (\textit{s}, 1 H) \(\delta\) 3.45 (\textit{s}, 6 H). \textsuperscript{13}C NMR (500 MHz, acetone-\textit{d}_6): \(\delta\) 137.6, \(\delta\) 132.6, \(\delta\) 132.3, \(\delta\) 20.9. \textsuperscript{11}B NMR (500 MHz, CD\textsubscript{3}CN): \(\delta\) 29.49 (bs).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1}
\caption{Conversion of 1,3-dichlorobenzene to 3,5-dichlorophenyl boronic acid.}
\end{figure}

Conversion of 1,3-dichlorobenzene to 3,5-dichlorophenyl boronic acid. In a glove box, 1,3-dichlorobenzene (1.14 mL, 10.0 mmol), B\textsubscript{2}pin\textsubscript{2}, (2.18 g, 8.60 mmol), [Ir(COD)(OMe)]\textsubscript{2} (6.2 mg, 9.4 \textmu mol), dtbpy (6.0 mg, 24 \textmu mol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction solution was allowed to cool to room temperature. After cooling, half of the solution was transferred to a 50 mL round bottom flask and was diluted with 4.0 mL H\textsubscript{2}O. NaIO\textsubscript{4} (3.20 g, 14.9 mmol) was then added. After stirring the reaction mixture for 15 min, 10 mL 1M HCl (aq) was added to the reaction mixture and allowed to stir for 4h. The resulting mixture was extracted with EtOAc (3 x 25 mL), and the organic layers were combined, washed with H\textsubscript{2}O (10 mL), and finally washed with brine (2 x 20 mL). The organic layer was dried over MgSO\textsubscript{4}. After filtering, the organic solvent was removed under vacuum and a yellow solid was obtained. The crude boronic acid was washed with hexanes and 94% yield was obtained. \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}CN) \(\delta\) 7.69 (\textit{s}, 2 H), \(\delta\) 7.52 (\textit{s}, 1 H), \(\delta\) 3.63 (\textit{s}, 2 H). \textsuperscript{13}C NMR (500MHz, CD\textsubscript{3}CN): \(\delta\) 135.1, \(\delta\) 133.0, \(\delta\) 130.7. \textsuperscript{11}B NMR (500 MHz, CD\textsubscript{3}CN): \(\delta\) 28.1 (bs).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure2}
\caption{Conversion of 1-methoxy-3-trifluoromethylbenzene to 3-methoxy-5-trifluoromethylphenyl boronic acid.}
\end{figure}

Conversion of 1-methoxy-3-trifluoromethylbenzene to 3-methoxy-5-trifluoromethylphenyl boronic acid. In a glove box, 1-methoxy-3-trifluoromethylbenzene (1.45 mL, 10.00 mmol), B\textsubscript{2}pin\textsubscript{2}, (2.23 g, 8.78 mmol), [Ir(COD)(OMe)]\textsubscript{2} (6.4 mg, 10 \textmu mol), dtbpy (5.7 mg, 21 \textmu mol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction solution was allowed to cool to room temperature. After cooling, half of the solution was transferred to a 50 mL round bottom flask and was diluted with 4.0 mL H\textsubscript{2}O. NaIO\textsubscript{4} (3.17 g, 14.8 mmol) was added. After stirring the reaction mixture for 15 min, 10.0 mL 1M HCl (aq) was added to the reaction mixture and allowed to stir for 4h. The resulting mixture was extracted with EtOAc (3 x 25 mL), and the organic layers were combined, washed with H\textsubscript{2}O (10 mL), and finally washed with brine (2 x 20 mL). The organic layer was dried over MgSO\textsubscript{4}. After filtering, the organic solvent was removed under vacuum and a yellow solid was obtained. The crude boronic acid was washed with hexanes and 85% yield was obtained. \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}CN) \(\delta\) 7.60 (\textit{s}, 2 H), \(\delta\) 7.51 (\textit{s}, 1 H) \(\delta\) 7.51 (\textit{s}, 1 H) \(\delta\) 3.80 (\textit{s}, 2 H). \textsuperscript{13}C NMR (500MHz, CD\textsubscript{3}CN): \(\delta\) 135.1, \(\delta\) 133.0, \(\delta\) 130.7. \textsuperscript{11}B NMR (500 MHz, CD\textsubscript{3}CN): \(\delta\) 28.7 (bs).
Conversion of 1-methoxycarbonyl-3-methylbenzene to 3-methoxycarbonyl-5-methylphenyl boronic acid. In a glove box, 1-methoxycarbonyl-3-methylbenzene (1.42 mL, 10.0 mmol), B$_2$pin$_2$, (2.16 g, 8.52 mmol), [Ir(COD)(OMe)]$_2$ (6.4 mg, 9.6 µmol), dtbpy (5.4 mg, 20 µmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction solution was allowed to cool to room temperature. After cooling, half of the solution was transferred to a 50 mL round bottom flask and was diluted with 4.0 mL H$_2$O. NaIO$_4$ (3.17 g, 14.8 mmol) was added. After stirring the reaction mixture for 15 min, 10.0 mL 1M HCl (aq) was added to the reaction mixture and allowed to stir for 4h. The resulting mixture was extracted with EtOAc (3 x 25 mL), and the organic layers were combined, washed with H$_2$O (10 mL), and finally washed with brine (2 x 20 mL). The organic layer was dried over MgSO$_4$. After filtering, the organic solvent was removed under vacuum and a yellow solid was obtained. The crude boronic acid was washed with hexanes and 85% yield was obtained. $^1$H NMR (500 MHz, CD$_3$CN) δ 7.60 (s, 2 H), δ 7.51 (s, 1 H), δ 3.82 (s, 3H), δ 3.48 (s, 3H). $^{13}$C NMR (500MHz, CD$_3$CN): δ 167.9, δ 138.5, δ 132.9, δ 132.5, δ 130.4, δ 52.4, δ 21.1. $^{11}$B NMR (500 MHz, CD$_3$CN): δ 28.9 (bs).

Conversion of 1-chloro-3-trifluoromethylbenzene to 3-chloro-5-trifluoromethylphenyl boronic acid. In a glove box, 1-chloro-3-trifluoromethylbenzene (1.23 mL, 10.0 mmol), B$_2$pin$_2$, (2.23 g, 8.79 mmol), [Ir(COD)(OMe)]$_2$ (6.8 mg, 10 µmol), dtbpy (7.0 mg, 26 µmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction solution was allowed to cool to room temperature. After cooling, half of the solution was transferred to a 50 mL round bottom flask and was diluted with 4.0 mL H$_2$O. NaIO$_4$ (3.23 g, 15.1 mmol) was added. After stirring the reaction mixture for 15 min, 10.0 mL 1M HCl (aq) was added to the reaction mixture and allowed to stir for 4h. The resulting mixture was extracted with EtOAc (3 x 25 mL), and the organic layers were combined, washed with H$_2$O (10 mL), and finally washed with brine (2 x 20 mL). The organic layer was dried over MgSO$_4$. After filtering, the organic solvent was removed under vacuum and a yellow solid was obtained. The crude boronic acid was washed with hexanes and 90% yield was obtained. $^1$H NMR (500 MHz, CD$_3$CN) δ 7.98 (s, 1 H), δ 7.26 (s, 1 H), δ 7.04 (s, 1 H), δ 3.81 (s, 3 H). $^{13}$C NMR (500MHz, CD$_3$CN): δ 160.5, δ 109.8, δ 98.5, δ 54.9. $^{11}$B NMR (500 MHz, CD$_3$CN): δ 28.6 (bs).
Conversion of 1-chloro-3-methylbenzene to 3-chloro-5-trifluoromethylphenyl boronic acid. In a glove box, 1-chloro-3-methylbenzene (1.18 mL, 10.0 mmol), B$_2$pin$_2$, (2.16 g, 8.51 mmol), [Ir(COD)(OMe)]$_2$ (6.7 mg, 10 nL mol), dtbpy (5.6 mg, 21 µmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction solution was allowed to cool to room temperature. After cooling, half of the solution was transferred to a 50 mL round bottom flask and was diluted with 4.0 mL H$_2$O. NaIO$_4$ (3.16 g, 14.8 mmol) was added. After stirring the reaction mixture for 15 min, 10.0 mL 1M HCl (aq) was added to the reaction mixture and allowed to stir for 4h. The resulting mixture was extracted with EtOAc (3 x 25 mL), and the organic layers were combined, washed with H$_2$O (10 mL), and finally washed with brine (2 x 20 mL). The organic layer was dried over MgSO$_4$. After filtering, the organic solvent was removed under vacuum and a yellow solid was obtained. The crude boronic acid was washed with hexanes and 89% yield was obtained. $^1$H NMR (500 MHz, CD$_3$CN) δ 7.98 (s, 1 H), δ 7.26 (s, 1 H), δ 7.04 (s, 1 H), δ 3.81 (s, 3 H). $^{13}$C NMR (500 MHz, CD$_3$CN): δ 140.5, δ 134.0, δ 133.9, δ 131.6, δ 131.4, δ 21.0. $^{11}$B NMR (500 MHz, CD$_3$CN): δ 28.6 (bs).

Conversion of 1,3-(trifluoromethyl)benzene to potassium (3,5-trifluoromethyl phenyl)trifluoroborate. In a glove box, 1,3-(trifluoromethyl)benzene (1.55 mL, 10.0 mmol), B$_2$pin$_2$, (3.17 g, 14.8 mmol), [Ir(COD)(OMe)]$_2$ (6.1 mg, 9.2 µmol), dtbpy (5.3 mg, 20 µmol), and THF (10.0 mL) were combined. The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction solution was allowed to cool to room temperature. After cooling, half of the solution was transferred to a 50 mL round bottom flask and was diluted with 4.0 mL H$_2$O. NaIO$_4$ (3.17 g, 14.8 mmol) was added. After stirring the reaction mixture for 15 min, 10.0 mL 1M HCl (aq) was added to the reaction mixture and allowed to stir for 4 h. The resulting mixture was extracted with EtOAc (3 x 25 mL), and the organic layers were combined, washed with H$_2$O (10 mL), and finally washed with brine (2 x 20 mL). The organic layer was dried over MgSO$_4$. After filtering, the organic solvent was removed under vacuum and a yellow solid was obtained. The crude boronic acid was washed with hexanes and 81% yield was obtained. $^1$H NMR (500 MHz, CD$_3$CN) δ 7.98 (s, 1 H), δ 7.26 (s, 1 H), δ 7.04 (s, 1 H), δ 3.81 (s, 3 H). $^{11}$B NMR (500 MHz, CD$_3$CN): δ 28.6 (bs).

REFERENCES
Table 2, Entry 1
Table 2, Entry 2

\[
\text{Cl} \quad \text{Cl} \\
\begin{array}{c}
\text{Cl} \\
\text{B(OH)}_2
\end{array}
\]

* data 55556
  sample time 11 min, 35 sec
Table 2, Entry 3
Table 2, Entry 5
Table 2, Entry 6
Table 2, Entry 7

\[
\begin{align*}
\text{MeO} & \quad \text{B(OH)}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{MeO} & \quad \text{B(OH)}_2 \\
\end{align*}
\]
Table 3, Entry 1
Table 3, Entry 2
Table 3, Entry 3
Table 3, Entry 4
Table 3, Entry 5
Table 3, Entry 6
Table 3, Entry 7
Table 3, Entry 8
Table 3, Entry 9
Table 3, Entry 11

![Chemical Structure Image](image-url)

**Chemical Details**
- Chemical formula: [Chemical Structure]
- **Spectral Data**
  - Time: 1'586 sec
  - Temperature: 30165 K
  - Resolution: 0.0400 THz
- **Comments**
  - **C33**: 335.64011615
  - **2H**: 099.70070515
- **NMR Setting**
  - **Frequency**: 1.0 Hz
  - **Time**: 12 min, 16 sec

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**Notes**

- Additional spectral data may be included in the paper for a comprehensive understanding of the chemical properties.

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**Acknowledgments**

- Acknowledgements for the support and collaboration in this research can be found in the paper.

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**References**

- Further reading and references related to the chemical structure and its applications can be found in the paper.