Transition-Metal-Free Regioselective Synthesis of Alkylboronates from Arylacetylenes or Vinyl Arenes

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**General information**

All experiments were conducted with a schlenk tube. Flash column chromatography was performed over silica gel (200-300 mesh). $^1$H NMR spectra were recorded on a Bruker AVIII-500M spectrometers, chemical shifts (in ppm) were referenced to CDCl$_3$ ($\delta = 7.26$ ppm) and DMSO-d$_6$ ($\delta = 2.50$ ppm) as internal standards. $^{13}$C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ ($\delta = 77.0$ ppm), DMSO-d$_6$ ($\delta = 39.6$ ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification, and the most starting materials were purchased from Adamas.

**Procedure and characterization data for products**

**General Procedure A for the preparation of arylacetylene from aryl bromides and trimethylsilylacetylene:** An oven-dried schlenk tube was charged with bromo-substrate (1 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (14 mg, 0.02 mmol) and Cul (7.6 mg, 0.04 mmol). The schlenk tube was taken to the glove box and dry THF (1 ml) was added to it. The tube was capped and taken out from the glove box. Triethylamine (216 uL, 1.55 mmol) was injected in it and trimethylsilylacetylene (176 uL, 1.25 mmol) was added to the reaction mixture slowly. The reaction mixture was stirred at room temperature for 24 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel. Terminal alkyne was obtained through hydrolysis of 4-(trimethylsilyl)ethynyl-substrates. The TMS-ethynyl substrates were dissolved in 1.5 ml MeOH and anhydrous K$_2$CO$_3$ (2 eq) were added to it under N$_2$ atmosphere. The reaction mixture was stirred at room temperature for 3 h. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel.$^1$

The following substrates were synthesized using this protocol.

**methyl 4-ethynylbenzoate (3034-86-4, 1k).**$^2$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J = 8.5$ Hz, 2H), 7.53 (d, $J = 8.5$ Hz, 2H), 3.91 (s, 3H), 3.23 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.3, 132.0, 130.1, 129.4, 126.7, 82.7, 80.0, 52.2.

**1-ethynyl-4-(methylsulfonyl)benzene (340771-31-5, 1m).**$^3$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 3.29 (s, 1H), 3.04 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 140.3, 132.9, 127.9, 127.3, 81.7, 81.2, 44.4.

**Synthesis of terminal arylalkyne 4**
Ethyl-1-((4-bromophenyl)sulfonyl)piperidine-2-carboxylate was prepared according to the literature procedure. Ethyl piperidine-2-carboxylate hydrochloride (0.79 g, 5 mmol) and 4-bromobenzenesulfonyl chloride (1.28 g, 5 mmol) were dissolved in 50 mL DMF. Triethylamine (3 eq) was then added dropwise. After stirring for 8 h at room temperature, the residue was suspended in 50 mL of ethyl acetate and washed with 2 M HCl (25 mL*3) and H2O (25 mL). The organic layer was dried over anhydrous Na2SO4, and concentrated in vacuo. The crude reaction mixture was purified on silica gel.

An oven-dried schlenk tube was charged with bromo-substrate (1 mmol), Pd(PPh3)2Cl2 (14 mg, 0.02 mmol) and Cul (7.6 mg, 0.04 mmol). The tube was taken to the glove box and dry THF (1 mL) was added to it. The tube was capped and taken out from the glove box. Triethylamine (216 uL, 1.55 mmol) was injected in it and trimethylsilylacetylene (176 uL, 1.25 mmol) was added to the reaction mixture slowly. The reaction mixture was stirred at room temperature for 24 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel. The internal alkyne was dissolved with anhydrous THF (1 mL), and TBAF (1.5 mL, 1 M in THF) was added. The resulting mixture was stirred at room temperature overnight. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel.

**ethyl 1-((4-ethynylphenyl)sulfonyl)piperidine-2-carboxylate (4).** Light yellow oil, 1H NMR (500 MHz, CDCl3) δ 7.73 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 4.71 (d, J = 5.5 Hz, 1H), 4.05-4.01 (m, 1H), 3.96-3.92 (m, 1H), 3.76 (dd, J = 13.0, 3.0 Hz, 1H), 3.23 (s, 1H), 3.22-3.17 (m, 1H), 2.13 (d, J = 13.5 Hz, 1H), 1.76-1.23 (m, 3H), 1.50 – 1.43 (m, 1H), 1.29 – 1.22 (m, 1H), 1.13 (t, J = 7.0 Hz, 3H). 13C NMR (125 MHz, CDCl3) δ 170.4, 140.0, 132.3, 127.0, 126.3, 82.1, 80.4, 61.1, 55.1, 42.7, 27.8, 24.7, 20.0, 14.0. HRMS (DART, m/z) calcd for [C16H19NO4S + H+] : 327.1106; found: 322.1113.

**General Procedure B** for the preparation of vinyl arenes from aryl bromides and vinyltrifluoroborate: A schlenk tube was charged with vinyltrifluoroborate (134 mg, 1 mmol), PdCl2 (3.5 mg, 0.02 mmol), PPh3 (16 mg, 0.04 mmol), Cs2CO3 (978 mg, 3 eq) and bromo-substrate (1 eq) in THF/H2O (9:1) (2 mL) was heated at 85 ºC under an N2 atmosphere. The reaction mixture was stirred at 85 ºC for 22 h, then cooled to room temperature and diluted with H2O followed by extraction with CH2Cl2. The organic layer was dried over
anhydrous Na₂SO₄, and concentrated in vacuo. The crude reaction mixture was purified on silica gel. The following substrates were synthesized using this protocol.

1-(4-vinylphenyl)propan-1-one (7646-72-2, 3s). Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 6.75 (dd, J = 17.5, 11.0 Hz, 1H), 5.87 (dd, J = 17.5, 0.5 Hz, 1H), 5.38 (d, J = 11.0 Hz, 1H), 2.99 (q, J = 7.2 Hz, 2H), 1.22 (t, J = 7.3 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 200.3, 141.8, 136.0, 135.9, 128.3, 126.3, 116.5, 31.8, 8.3.

ethyl 4-vinylbenzoate (2715-43-7, 2t). Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.86 (d, J = 17.6 Hz, 1H), 5.37 (d, J = 10.9 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 166.4, 141.8, 136.0, 129.8, 129.6, 126.0, 116.3, 60.9, 14.3.

3-vinylquinoline (67752-31-2, 3p). Yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 9.01 (d, J = 2.2 Hz, 1H), 8.16 – 8.00 (m, 2H), 7.79 (d, J = 8.1 Hz, 1H), 7.67 (dd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.58 – 7.47 (m, 1H), 6.86 (dd, J = 17.7, 11.0 Hz, 1H), 5.98 (d, J = 17.7 Hz, 1H), 5.45 (d, J = 11.0 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 149.0, 147.5, 133.7, 132.5, 130.3, 129.3, 129.1, 127.9, 127.8, 126.9, 116.3.

2-methyl-6-vinylquinoline (1365842-17-6, 2o). Yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.98 – 7.94 (m, 2H), 7.82-7.79 (m, 1H), 7.65-7.63 (m, 1H), 7.26 – 7.20 (m, 1H), 6.84 (dd, J = 17.5, 11.0 Hz, 1H), 5.85 (d, J = 17.5 Hz, 1H), 5.34 (d, J = 11.0 Hz, 1H), 2.71 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 158.8, 147.6, 136.2, 136.1, 134.8, 128.7, 126.8, 126.4, 125.5, 122.3, 114.7, 25.2.
(3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-vinylbenzoate. (64448-31-3, 6). A round-bottom flask was charged with 4-bromobenzoyl chloride (720 mg, 1.1 eq), 1,2:3,4-di-O-isopropylpyridine-α-D-galactopyranose (775 mg, 2.98 mmol), Et3N (452 mg, 1.5 eq), and CH2Cl2 (100 mL). The reaction mixture was then filtered, and the filtrate was washed with 1M HCl. The organic layer was dried over anhydrous Na2SO4, and concentrated in vacuo, which was further purified by column chromatography to give a pure alkyl 4-bromobenzoate. The corresponding vinyl arene was prepared by using general procedure B.

1H NMR (500 MHz, CDCl3) δ 7.99 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 6.73 (dd, J = 17.5, 11.0 Hz, 1H), 5.84 (d, J = 17.5 Hz, 1H), 5.55 (d, J = 5.0 Hz, 1H), 5.36 (d, J = 11.0 Hz, 1H), 4.64 (dd, J = 8.0, 2.0 Hz, 1H), 4.51 (dd, J = 11.5, 4.5 Hz, 1H), 4.41 (dd, J = 11.5, 7.5 Hz, 1H), 4.34 – 4.30 (m, 2H), 4.18-4.15 (m, 1H), 1.50 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 166.1, 141.9, 135.9, 129.9, 129.1, 126.0, 116.4, 109.6, 108.7, 96.2, 71.1, 70.7, 70.5, 66.1, 63.8, 25.9, 25.9, 24.9, 24.4.

(35,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-5-methylhexan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-vinylbenzoate (111252-11-0, 8). A round-bottom flask was charged with 4-bromobenzoyl chloride (720 mg, 1.1 eq), cholestanol (1.16 g, 2.98 mmol), Et3N (452 mg, 1.5 eq), and CH2Cl2 (100 mL). The reaction mixture was then filtered, and the filtrate was washed with 1M HCl. The organic layer was dried over anhydrous Na2SO4, and concentrated in vacuo, which was further purified by column chromatography to give a pure alkyl 4-bromobenzoate. The corresponding vinyl arene was prepared by using general procedure B. 1H NMR (500 MHz, CDCl3) δ 8.00 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 6.75 (dd, J = 17.5, 11.0 Hz, 1H), 5.86 (d, J = 17.5 Hz, 1H), 5.42 (d, J = 4.0 Hz, 1H), 5.37 (d, J = 11.0 Hz, 1H), 4.87-4.83 (m, 1H), 2.47 (d, J = 7.5 Hz, 2H), 2.04 – 1.97 (m, 3H), 1.94-1.89 (m, 1H), 1.86 – 1.82 (m, 1H), 1.75 – 1.72 (m, 1H), 1.58 – 1.46 (m, 5H), 1.28 – 1.09 (m, 13H), 1.07-0.97 (m, 7H), 0.95 (d, J = 6.5 Hz, 3H), 0.88 (d, J = 2.5 Hz, 3H), 0.86 (d, J = 2.5 Hz, 3H), 0.69 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 165.7, 141.7, 139.7, 136.1, 129.9, 129.8, 126.0, 122.7, 116.3, 74.5, 56.7, 56.1, 50.1, 42.32 (s), 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 29.7, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.9.

General Procedure C for the preparation of alkylboronates from terminal arylacetylenes and B3Pin2: In air, a 25 mL schlenk tube was charged with B3Pin2 (152 mg, 3 eq) and Cs2CO3 (260 mg, 4 eq). The flask was evacuated and filled with nitrogen for three cycles. CH3CN (3 mL), arylalkyne (0.2 mmol) and CH3OH (40 uL, 5 eq) were added. The reaction was allowed to stir at 70 °C for 4 or 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (petroleum ether: ethyl acetate = 50:1) to afford the desired product.
Table S1 Condition screening.

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<th>solvent</th>
<th>yield (%)</th>
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<td>11</td>
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<td>3</td>
<td>Nat-BuO (2.5 eq)</td>
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<td>dioxane</td>
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</tr>
<tr>
<td>4</td>
<td>Na$_2$CO$_3$ (2.5 eq)</td>
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<td>dioxane</td>
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<tr>
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<td>CsF (2.5 eq)</td>
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<td>dioxane</td>
<td>59</td>
</tr>
<tr>
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<td>dioxane</td>
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</tr>
<tr>
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<td>MeOH (5 eq)</td>
<td>dioxane</td>
<td>99(89)</td>
</tr>
<tr>
<td>8</td>
<td>Cs$_2$CO$_3$ (2.5 eq)</td>
<td>MeOH (3 eq)</td>
<td>dioxane</td>
<td>89</td>
</tr>
<tr>
<td>9</td>
<td>Cs$_2$CO$_3$ (2.0 eq)</td>
<td>MeOH (5 eq)</td>
<td>dioxane</td>
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</tr>
<tr>
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<td>Cs$_2$CO$_3$ (2.5 eq)</td>
<td>MeOH (5 eq)</td>
<td>THF</td>
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</tr>
<tr>
<td>11</td>
<td>Cs$_2$CO$_3$ (2.5 eq)</td>
<td>MeOH (5 eq)</td>
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<tr>
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<td>Cs$_2$CO$_3$ (2.5 eq)</td>
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<td>MeOH</td>
<td>61</td>
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</tbody>
</table>

condition: 1) styrene (0.2 mmol), B$_2$pin$_2$ (1.5 eq), solvent (2 mL), 100 °C, 12 h, N$_2$

**General Procedure D for the preparation of alkylboronates from vinyl arenes and B$_2$Pin:** In air, a 25 mL schlenk tube was charged with B$_2$pin$_2$ (76 mg, 1.5 eq) and Cs$_2$CO$_3$ (162 mg, 2.5 eq). The flask was evacuated and filled with nitrogen for three cycles. Dioxane (2 mL), vinyl arene (0.2 mmol) and CH$_3$OH (40 uL, 5 eq) were added. The reaction was allowed to stir at 100 °C for 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (petroleum ether: ethyl acetate = 50:1) to afford the desired product.

**4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (165904-22-3, 2a).** Colorless oil, $^1$H NMR (500 MHz, CDCl$_3$) δ 7.28 – 7.21 (m, 4H), 7.17-7.14 (m, 1H), 2.75 (t, J = 8.0 Hz, 2H), 1.22 (s, 12H), 1.15 (t, J = 8.0 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 144.4, 128.1, 128.0, 125.46 (s), 83.1, 29.9, 24.8.
4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (444094-87-5, 2b).\(^9\)
Colorless oil, \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.12 (d, \(J = 8.0\) Hz, 2H), 7.08 (d, \(J = 8.0\) Hz, 2H), 2.72 (t, \(J = 8.0\) Hz, 2H), 2.31 (s, 3H), 1.24 (s, 12H), 1.13 (t, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 141.3, 134.8, 128.8, 127.8, 83.0, 29.5, 24.8, 20.9.

2-(4-ethylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c).
Colorless oil, \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.15 (d, \(J = 8.0\) Hz, 2H), 7.10 (d, \(J = 8.0\) Hz, 2H), 2.72 (t, \(J = 8.0\) Hz, 2H), 2.62 (q, \(J = 7.5\) Hz, 2H), 1.23 (s, 12H), 1.14 (t, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 141.6, 141.3, 127.9, 127.6, 83.0, 29.5, 28.4, 24.8, 15.7.
HRMS (EI, m/z) calcd for [C\(_{16}\)H\(_{25}\)BO\(_2\)]: 260.1948; found: 260.1950.

2-(4-(tert-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1073355-22-2, 2d).\(^{10}\)
Colorless oil, \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.30 (d, \(J = 8.0\) Hz, 2H), 7.16 (d, \(J = 8.0\) Hz, 2H), 2.73 (t, \(J = 8.0\) Hz, 2H), 1.31 (s, 9H), 1.23 (s, 12H), 1.15 (t, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 148.2, 141.3, 127.6, 125.0, 83.0, 34.3, 31.4, 29.3, 24.8.

2-(4-chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (444094-88-6, 2e).\(^9\)
Light yellow oil, \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.21 (d, \(J = 8.5\) Hz, 2H), 7.13 (d, \(J = 8.5\) Hz, 2H), 2.71 (t, \(J = 8.0\) Hz, 2H), 1.21 (s, 12H), 1.11 (t, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 142.8, 131.1, 129.3, 128.2, 83.2, 29.3, 24.8.
2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (748801-42-5, 2f). Light yellow oil, \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.36\) (d, \(J = 8.5\) Hz, 2H), 7.08 (d, \(J = 8.5\) Hz, 2H), 2.69 (t, \(J = 8.0\) Hz, 2H), 1.21 (s, 12H), 1.11 (t, \(J = 8.0\) Hz, 2H). \(^1\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 143.3, 131.1, 129.9, 119.1, 83.2, 29.4, 24.8\).

![Structure of 2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane](image)

2-(4-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1065498-70-5, 2g). Light yellow oil, \(^1H\) NMR (500 MHz, CDCl\(_3\), ppm) 7.17-7.14 (m, 2H), 6.95-6.91 (m, 2H), 2.71 (t, \(J = 8.0\) Hz, 2H), 1.21 (s, 12H), 1.11 (t, \(J = 8.0\) Hz).

![Structure of 2-(4-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane](image)

2-(3-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1600527-27-2, 2h). Colorless oil, \(^1H\) NMR (500 MHz, CDCl\(_3\), ppm) 7.29-7.22 (m, 1H), 6.99-6.97 (m, 1H), 1.22 (s, 12H), 1.13 (t, \(J = 8.0\) Hz).

![Structure of 2-(3-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane](image)

4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenethyl)-1,3,2-dioxaborolane (1360649-56-4, 2i). Light yellow oil, \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.51\) (d, \(J = 8.0\) Hz, 2H), 7.32 (d, \(J = 8.0\) Hz, 2H), 2.80 (t, \(J = 8.0\) Hz, 2H), 1.21 (s, 12H), 1.15 (t, \(J = 8.0\) Hz, 2H). \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 148.5, 128.3, 125.1\) (q, \(J = 3.8\) Hz), 83.2, 29.8, 24.8, 12.6.

![Structure of 4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenethyl)-1,3,2-dioxaborolane](image)

1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)phenylethan-1-one (2j), Colorless oil, \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.86\) (d, \(J = 8.5\) Hz, 2H), 7.30 (d, \(J = 8.5\) Hz, 2H), 7.29 (t, \(J = 8.0\) Hz, 2H), 2.57 (s, 3H), 1.21 (s, 12H), 1.15 (t, \(J = 8.0\) Hz, 2H). \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 148.5, 128.3, 125.1\) (q, \(J = 3.8\) Hz), 83.2, 29.8, 24.8, 12.6.
MHz, CDCl₃) δ 198.0, 150.3, 134.8, 128.4, 128.2, 83.2, 30.0, 26.5, 24.8. HRMS (EI, m/z) calcd for [C16H23BO3 + Na⁺]: 297.1638; found: 297.1644.

**Methyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborol-2-yl)ethyl)benzoate (1375536-90-5, 2k).** Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 2.79 (t, J = 8.0 Hz, 2H), 1.20 (s, 12H), 1.14 (t, J = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 167.2, 149.9, 129.5, 128.0, 127.5, 83.2, 51.9, 30.0, 24.7.

**4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborol-2-yl)ethyl)benzonitrile (1375536-88-1, 2l).** White solid, ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.54 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.79 (t, J = 8.0 Hz, 2H), 1.20 (s, 12H), 1.13 (t, J = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃, ppm) δ 150.0, 132.0, 128.8, 119.2, 109.3, 83.3, 30.1, 24.8

**4,4,5,5-tetramethyl-2-(4-(methylsulfonyl)phenethyl)-1,3,2-dioxaborolane (2m).** Light yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 3.01 (s, 3H), 2.81 (t, J = 8.0 Hz, 2H), 1.26 (t, J = 8.0 Hz, 2H), 1.24 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 151.0, 137.7, 128.9, 127.28 (s), 83.3, 44.5, 29.9, 24.7. HRMS (ESI, m/z) calcd for [C15H24BO4S + H⁺]: 311.1488; found: 311.1488.

**4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (807611-10-5, 2n).** Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.81 – 7.76 (m, 3H), 7.67 (s, 1H), 7.46 – 7.38 (m, 3H), 2.94 (t, J = 8.0 Hz, 2H), 1.26 (t, J = 8.0 Hz, 2H), 1.24 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 141.9, 133.6, 131.9, 127.6, 127.5, 127.4, 125.7, 125.6, 124.9, 83.1, 30.1, 24.8.
4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)ethyl)-1,3,2-dioxaborolane (1361022-77-6, 2o). Light yellow, ¹H NMR (500 MHz, CDCl₃) δ 7.08 (dd, J = 5.5, 1.5 Hz, 1H), 6.88 (dd, J = 5.5, 3.5 Hz, 1H), 6.80 – 6.79 (m, 1H), 2.96 (t, J = 8.0 Hz, 2H), 1.23-1.22 (m, 15H). ¹³C NMR (125 MHz, CDCl₃) δ 147.7 126.5, 123.4, 122.6, 83.2, 24.8, 24.3.

3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)quinolone (2p). Yellow solid, ¹H NMR (500 MHz, CDCl₃) δ 8.81 (d, J = 2.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 1.5 Hz, 1H), 7.74 (dd, J = 8.0, 1.5 Hz, 1H), 7.64-7.61 (m, 1H), 7.51-7.47 (m, 1H), 2.93 (t, J = 8.0 Hz, 2H), 1.24 (t, J = 8.0 Hz, 2H), 1.19 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 152.1, 146.6, 136.9, 133.6, 129.0, 128.4, 127.3, 126.4, 83.3, 27.3, 24.8. HRMS (EI, m/z) calcd for [C₁₇H₂₂BNO₂ + H⁺]: 284.1822; found: 289.1865.

2-methyl-6-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)quinolone (2q). White solid, ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.95 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.56-7.55 (m, 2H), 7.22 (d, J = 8.5 Hz, 1H), 2.91 (t, J = 8.0 Hz, 2H), 2.71 (s, 3H), 1.22 (t, J = 8.0 Hz). ¹³C NMR (125 MHz, CDCl₃, ppm) δ 157.9, 146.5, 141.8, 135.7, 130.8, 128.2, 126.4, 125.2, 121.8, 83.1, 29.8, 25.2, 24.8. HRMS (EI, m/z) calcd for [C₁₈H₂₄BNO₂ + H⁺]: 298.1978; found: 298.1978.

2-(2-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1700308-87-7, 2r). Colorless oil, ¹H NMR (500 MHz, CDCl₃, ppm) 7.24-7.21(m, 1H), 7.15-7.11(m, 1H), 7.04-7.01(m, 1H), 6.99-6.95(m, 1H), 2.77 (t, J = 8.0 Hz, 2H), 1.22 (s, 12H), 1.14 (t, J = 8.0 Hz). ¹³C NMR (125 MHz, CDCl₃, ppm) 161.0 (d, J = 243.7 Hz), 131.1 (d, J = 16.3 Hz), 130.0 (d, J = 5.0 Hz), 123.7 (d, J = 3.7 Hz), 115.0(d, J = 21.3 Hz), 83.1, 24.8, 23.1 (d, J = 1.3 Hz).
1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)propan-1-one (2s).
Colorless oil, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.5$ Hz, 2H), 7.28(d, $J = 8.5$ Hz, 2H), 2.97 (q, $J = 7.3$ Hz, 2H), 2.78 (t, $J = 8.0$ Hz, 2H), 1.21 (s, 12H), 1.20(t, $J = 7.5$ Hz, 2H), 1.14 (t, $J = 8.0$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 200.6, 150.0, 134.52 (s), 128.2, 128.1, 83.2, 31.6, 30.0, 24.8, 8.3. HRMS (EI, m/z) calcd for [C$_{17}$H$_{25}$BO$_3$ + H$^+$]: 289.1975; found: 289.1975.

ethyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (2t). Colorless oil, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 4.35 (q, $J = 7.0$ Hz, 2H), 2.79 (t, $J = 8.0$ Hz, 2H), 1.37 (t, $J = 7.0$ Hz, 3H), 1.14 (t, $J = 8.0$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.8, 149.8, 129.5, 127.9, 127.8, 83.2, 60.7, 30.0, 24.8, 14.3. HRMS (EI, m/z) calcd for [C$_{17}$H$_{25}$BO$_4$ + H$^+$]: 327.1744; found: 327.1774.

2-(2,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1609554-12-2, 2u).$^{14}$
Colorless oil, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.28-7.23 (m, 8H), 7.15-7.12 (m, 2H), 4.28 (t, $J = 8.5$ Hz, 1H), 1.60 (d, $J = 8.5$ Hz, 2H), 1.05 (s, 12H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 146.6, 128.2, 127.6, 125.9, 83.1, 46.5, 24.6.

Ethyl-1-((4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)sulfonyl)piperidine-2-carboxylate (5). Colorless oil, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 4.70 (d, $J = 5.0$ Hz, 1H), 4.06 – 3.99 (m, 1H), 3.94-3.88 (m, 1H), 3.75– 3.72 (m, 1H), 3.24-3.18 (m, 1H), 2.78 (t, $J = 8.0$ Hz, 2H), 2.10 (dd, $J = 13.5, 1.5$ Hz,
1H), 1.75 – 1.61 (m, 3H), 1.51 – 1.41 (m, 1H), 1.33 – 1.24 (m, 1H), 1.21 (s, 12H), 1.14 – 1.11 (m, 5H). 13C NMR (125 MHz, CDCl3) δ 170.7, 149.4, 137.2, 128.4, 127.3, 83.3, 61.0, 55.0, 42.5, 29.8, 27.8, 24.8, 24.7, 20.0, 14.0. HRMS (ESI, m/z) calcd for [C22H34BNO6S + H+]: 452.2278; found: 452.2276.

((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis[1,3]dioxolo[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (7). Colorless oil, 1H NMR (500 MHz, CDCl3) δ 7.94 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 5.55 (d, J = 5.0 Hz, 1H), 4.64 (dd, J = 8.0, 2.5 Hz, 1H), 4.51 (dd, J = 11.5, 5.0 Hz, 1H), 4.39 (dd, J = 11.5, 7.5 Hz, 1H), 4.34 – 4.31 (m, 2H), 4.18-4.15 (m, 1H), 2.75 (t, J = 8.0 Hz, 2H), 1.50 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.21 (s, 12H), 1.14 (t, J = 8.0 Hz, 2H). 13C NMR (125 MHz, CDCl3) δ 166.5, 150.0, 129.7, 128.0, 127.4, 109.6, 108.8, 96.3, 83.2, 71.1, 70.7, 70.5, 66.1, 63.6, 30.0, 26.0, 25.9, 25.0, 24.8, 24.5. HRMS (ESI, m/z) calcd for [C27H39BO9 + H+]: 519.2765; found: 519.2761.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-4-methylpentan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (9). White solid, 1H NMR (500 MHz, CDCl3) δ 7.93 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 5.41 (d, J = 3.5 Hz, 1H), 4.86-4.81 (m, 1H), 2.79 (m, J = 8.0 Hz, 2H), 2.45 (d, J = 7.5 Hz, 2H), 2.03-1.96 (m, 3H), 1.92 – 1.82 (m, 2H), 1.80 – 1.70 (m, 1H), 1.64-1.24 (m, 12H), 1.21 (s, 12H), 1.16-1.09 (m, 7H), 1.06 (s, 3H), 1.04-0.97 (m, 4H), 0.92 (d, J = 7.0 Hz, 3H), 0.87 (d, J = 2.0 Hz, 3H), 0.86 (d, J = 2.0 Hz, 3H), 0.69 (s, 3H). 13C NMR (125 MHz, CDCl3) δ 166.1, 149.7, 139.7, 129.5 128.2, 127.9, 122.6, 83.2, 74.3, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 30.0, 28.2, 28.0, 27.9, 24.8, 24.3, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 11.9. HRMS (ESI, m/z) calcd for [C42H65BO4 + Na+]: 667.4874; found: 667.4870.

1,2-diphenylethane (103-29-7, 10). White solid, 1H NMR (500 MHz, CDCl3) δ 7.32-7.28 (m, 4H), 7.23-7.20 (m, 6H), 2.95 (s, 4H). 13C NMR (125 MHz, CDCl3) δ 141.8, 128.4, 128.3, 125.9, 37.9.
trifluoro(phenethyl)-l4-borane, potassium salt (329976-74-1,11).\textsuperscript{16} White solid, \textsuperscript{1}H NMR (500 MHz, DMSO) δ 7.20 – 7.12 (m, 4H), 7.06-7.03 (m, 1H), 2.42 (s, 2H), 0.30 (s, 2H). \textsuperscript{13}C NMR (125 MHz, DMSO) δ 148.1, 127.9, 127.7, 124.4, 32.2. \textsuperscript{19}F NMR (471 MHz, DMSO) δ -137.8.

2-phenylethan-1-ol (60-12-8,12).\textsuperscript{17} Colorless oil, \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.34 – 7.31 (m, 2H), 7.26 – 7.23 (m, 3H), 3.84 (t, J = 6.5 Hz, 2H), 2.87 (t, J = 6.5 Hz, 2H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ 138.5, 129.0, 128.5, 126.4, 63.6, 39.1.

\textsuperscript{(E)}-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (78782-27-1, 13).\textsuperscript{18} Colorless oil, \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.49 (d, J = 7.0 Hz, 2H), 7.40 (d, J = 18.5 Hz, 1H), 7.35 – 7.27 (m, 3H), 6.17 (d, J = 18.5 Hz, 1H), 1.32 (s, 12H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ 149.5, 137.4, 128.9, 128.5, 127.0, 83.3, 24.8.

2,2'-(1-phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (189885-64-1, 15).\textsuperscript{20} white solid, \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.22 (d, J = 4.5 Hz, 4H), 7.12 – 7.07 (m, 1H), 2.52 (dd, J = 11.0, 6.0 Hz, 1H), 1.38 (dd, J = 16.0, 11.0 Hz, 1H), 1.20 (s, 12H), 1.19 (s, 6H), 1.17 (s, 6H), 1.11 (dd, J = 16.0, 5.5 Hz, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ 145.3, 128.1, 127.9, 124.9, 83.2, 83.0, 24.9, 24.7, 24.6, 24.4.

2,2'-(3-phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1172611-59-4,19).\textsuperscript{21} Colorless oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.24-7.18 (m, 4H),
7.14-7.11 (m, 1H), 2.79 (dd, J = 13.0, 7.0 Hz, 1H), 2.60 (dd, J = 13.5, 8.5 Hz, 1H), 1.49 (s, 1H), 1.22 (s, 2H), 1.19 (s, 6H), 1.16 (s, 6H), 0.82 (d, J = 7.5Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 142.3, 129.1, 127.9, 125.4, 82.9, 82.8, 39.5, 24.9, 24.8, 24.7.

**Trace Transition Metal Analysis/Exclusion**

In order to rule out the possibility of the trace amount of transition metal in the reaction mixture, three different strategies have been performed:

1) 99.99% purity of Cs$_2$CO$_3$ was used in the two standard conditions and the results were listed below:

$$
\text{B}_2\text{pin}_2 + \text{Cs}_2\text{CO}_3 (99.99\%, 4 \text{ eq}) \text{ MeOH (5 eq)} \rightarrow \text{MeCN,70°C, 4h} \rightarrow 3\text{aa} \quad \text{GC yield: 95%}
$$

As we can see, with high purity of Cs$_2$CO$_3$, desired product 3aa were obtained in very high GC yields, which are consistent to the results listed in the manuscript with regular Cs$_2$CO$_3$. So we have reasons to believe that this IS a transition-metal FREE reaction.

2) On the other hand, since copper salt was widely used as a catalyst in the borylation of unsaturated compounds, 2 mol% of Cu(OAc)$_2$ was added as a catalyst in the standard condition of styrene, the desired product 3aa was obtained in 95% in GC, which is consistent to the result without copper catalyst in our manuscript, therefore once again it suggested that the transformation in our manuscript is a transition-metal free reaction.

$$
\text{B}_2\text{pin}_2 + \text{Cs}_2\text{CO}_3 (99.99\%, 2.5 \text{ eq}) \text{ MeOH (5 eq)} \rightarrow \text{dioxane,100°C, 12h} \rightarrow 3\text{aa} \quad \text{GC yield: 99%}
$$

3) ICP-MS was used to analyze trace metal in B$_2$pin$_2$ and Cs$_2$CO$_3$ and the results were listed below:

B$_2$pin$_2$ (152.4 mg, 0.6 mmol) include 27Al (1.8 ug), 56Fe(8.0 ug), 60Ni(0.2 ug), 63Cu(0.35 ug), Zn(1.4 ug), 195Pt(0.0 ug), 208Pb(0.06 ug);

Cs$_2$CO$_3$ (259.2 mg, 0.8 mmol) include 27Al (0.7 ug), 56Fe(0.9 ug), 60Ni(0.05 ug), 63Cu(0.12 ug), Zn(0.5 ug), 195Pt(0.0 ug), 208Pb(0.04 ug)

From all the above three strategies, it indicates that this is a transition metal-free methods and base/MeOH combination play key role for the success of the reaction.
References

Spectroscopic data

![Spectroscopic data](image)