Iridium-Catalyzed B-H Insertion of Sulfoxonium Ylides and Borane Adducts: A Versatile Platform to α-Boryl Carbonyls.

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1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH$_2$), dichloromethane (CaH$_2$). Anhydrous CF$_3$CH$_2$OH, CH$_3$CN, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR ($^1$H) were recorded at 400 MHz, and Carbon NMR ($^{13}$C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants ($J$) are reported in Hertz (Hz).

High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV$_{254}$ plates. Visualization was accomplished with short wave UV light, or KMnO$_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.
2. Synthesis of substrates 1, 2

The substrates of sulfoxonium ylides 1 were prepared according to the procedure reported by Burtoloso and Aïssa.[1] Borane adduct 2 were prepared following the procedure reported by Zhou.[2] All the characteristic data are consistent with the data reported before.[3]
3. Optimization of Reaction Conditions

Table 1. Catalytic B–H Bond Insertion Reactions: Optimization of Reaction Conditions

Table 1. Catalytic B–H Bond Insertion Reactions: Optimization of Reaction Conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>2</th>
<th>Product</th>
<th>Yield (3b/19d)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>(Cp^]*IrCl_2)</td>
<td>DCM</td>
<td>2a</td>
<td>3aa</td>
<td>36%/17%</td>
</tr>
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<td>2</td>
<td>[Ir(cod)Cl]_2</td>
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<td>2a</td>
<td>3aa</td>
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<td>3</td>
<td>(Cp^]*RhCl_2)</td>
<td>DCM</td>
<td>2a</td>
<td>3aa</td>
<td>15%/8%</td>
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<td>4</td>
<td>Rh_2(OAc)_4</td>
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<td>3aa</td>
<td>Trace/ND</td>
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<tr>
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<td>Cu</td>
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<td>2a</td>
<td>3aa</td>
<td>Trace/ND</td>
</tr>
<tr>
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<td>2a</td>
<td>3aa</td>
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<td>3aa</td>
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<tr>
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<td>3ab</td>
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<td>PhCl</td>
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<td>3ac</td>
<td>Trace/ND</td>
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<tr>
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<td>PhCl</td>
<td>2d</td>
<td>3ad</td>
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</tr>
<tr>
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<td>[Ir(cod)Cl]_2</td>
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<td>2f</td>
<td>3af</td>
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<tr>
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<td>PhCl</td>
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<td>3ag</td>
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<tr>
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<td>-</td>
<td>PhCl</td>
<td>2a</td>
<td>3aa</td>
<td>ND/ND</td>
</tr>
</tbody>
</table>

*aReaction Conditions: 1a (0.2 mmol), 2 (1.5 equiv), catalyst (2.5 mol %), KH_2PO_4 (1.0 equiv), solvent (0.2 M), 55 °C, 12 h. bIsolated yield. cND = not detected. dYield was determined by ^1H NMR using 1-iodo-4-methoxybenzene as internal standard.
4. General procedure and characterization of products

General procedure A

In an oven-dried Schlenk tube under air, a mixture of the substrates 1 (0.2 mmol, 1.0 equiv), trimethylamine-borane 2a (21.9 mg, 0.3 mmol, 1.5 equiv), [Ir(Cod)Cl]₂ (3.4 mg, 0.005 mmol, 2.5 mmol%), KH₂PO₄ (27.2 mg, 0.2 mmol, 1.0 equiv), and PhCl (2.0 mL) was stirred at 55 °C for 1 h - 12 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H₂O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product 3.

Characterization of products

2-(trimethylamine-boranyl)-1-phenylethan-1-one (3aa)

Following the general procedure A, the product 3aa was obtained in 75% yield (28.6 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.23. 

\[ \text{RF (Petroleum ether/EtOAc 3:1): 0.23.} \]

\[ \text{1H NMR (500 MHz, CDCl₃) δ 7.99 (d, J = 7.5 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.3 Hz, 2H), 2.59 (s, 9H), 2.45 (s, 2H), 2.35-1.50 (br, 2H).} \]

\[ \text{13C NMR (126 MHz, CDCl₃) δ 207.9, 138.1, 131.7, 128.7, 128.0, 52.2, 34.2.} \]

\[ \text{11B NMR (128 MHz, CDCl₃) δ -3.53 (t, J = 101.8 Hz).} \]

2-(trimethylamine-boranyl)-1-(4-methoxyphenyl)ethan-1-one (3ba)

Following the general procedure A, the product 3ba was obtained in 66% yield (29.1 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.26.

\[ \text{1H NMR (500 MHz, CDCl₃) δ 7.98 (d, J = 7.5 Hz, 2H), 6.88 (t, J = 7.2 Hz, 2H).} \]
(d, J = 7.5 Hz, 2H), 3.83 (s, 3H), 2.59 (s, 9H), 2.40 (s, 2H), 2.34-1.50 (br, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 206.95, 162.54, 131.16, 130.94, 113.21, 55.43, 52.23, 33.97. \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) -3.42 (t, J = 97.8 Hz).

**2-(trimethylamine-boranyl)-1-(4-(dimethylamino)phenyl)ethan-1-one (3ca)**

![structure](image)

Following the general procedure A, the product **3ca** was obtained in 58% yield (27.2mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 (d, J = 8.9 Hz, 2H), 6.64 (d, J = 8.9 Hz, 2H), 3.01 (s, 3H), 2.60 (s, 9H), 2.38 (s, 2H), 2.23-1.45 (br, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 207.21, 152.85, 130.86, 126.36, 110.60, 52.27, 40.20, 34.09. \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) -3.42 (t, J = 97.8 Hz). ESI-MS: calculated C\(_{13}\)H\(_{24}\)BN\(_2\)O [M+H]\(^+\) 235.1976; Found 235.1975.

**1-([1,1'-biphenyl]-4-yl)-2- trimethylamine-boranelethan-1-one (3da)**

![structure](image)

Following the general procedure A, the product **3da** was obtained in 52% yield (27.7mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.08 (d, J = 8.4 Hz, 2H), 7.68 – 7.54 (m, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 2.63 (s, 9H), 2.50 (s, 2H), 1.98-1.46 (br, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 207.51, 144.33, 140.50, 136.79, 129.31, 128.85, 127.76, 127.25, 126.68, 52.19, 34.36. \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) -3.53 (t, J = 100.9 Hz). ESI-MS: calculated C\(_{17}\)H\(_{22}\)BNONa [M+Na]\(^+\) 290.1687; Found 290.1685.

**2-(trimethylamine-boranyl)-1-(p-tolyl)ethan-1-one (3ea)**
Following the general procedure A, the product 3ea was obtained in 43% yield (17.6mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J= 7.5$ Hz, 1H), 7.19 (d, $J= 14.4$ Hz, 2H), 7.11 (t, $J= 8.2$ Hz, 2H), 2.53 (s, 9H), 2.39 (s, 3H), 2.33 (s, 2H), 2.23-1.39 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 212.42, 140.85, 136.87, 131.34, 129.74, 128.54, 125.22, 52.29, 37.43, 21.12. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -4.02 (t, $J= 99.8$ Hz). ESI-MS: calculated C$_{12}$H$_{20}$BNONa [M+Na]$^+$ 228.1530; Found 228.1527.

**2-(trimethylamine-boranyl)-1-(4-fluorophenyl)ethan-1-one (3fa)**

Following the general procedure A, the product 3fa was obtained in 50% yield (20.8mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.24. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (m, $J= 8.8$, 5.6 Hz, 2H), 7.05 (t, $J= 8.7$ Hz, 2H), 2.60 (s, 9H), 2.42 (s, 2H), 2.33-1.46 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 206.4, 165.1 (d, $J= 252.1$ Hz), 134.5 (d, $J= 2.8$ Hz), 131.3 (d, $J= 9.0$ Hz), 115.0 (d, $J= 21.6$ Hz), 52.2, 34.2. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -3.62 (t, $J= 100.0$ Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -108.37 (s). ESI-MS: calculated C$_{11}$H$_{17}$BFNONa [M+Na]$^+$ 232.1282; Found 232.1266.

**2-(trimethylamine-boranyl)-1-(4-chlorophenyl)ethan-1-one (3ga)**

Following the general procedure A, the product 3ga was obtained in 50% yield (18.2mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.26. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J= 7.1$ Hz, 2H), 7.36 (d, $J= 7.1$ Hz, 2H), 2.60 (s, 9H), 2.42 (s, 2H), 2.30-1.49 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$
2-(trimethylamine-boranyl)-1-(4-bromophenyl)ethan-1-one (3ha)

Following the general procedure A, the product 3ha was obtained in 58% yield (31.2mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.23. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 7.3$ Hz, 2H), 7.52 (d, $J = 7.3$ Hz, 2H), 2.59 (s, 9H), 2.41 (s, 2H), 2.32-1.50 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 206.82, 136.82, 131.36, 130.48, 126.76, 52.27, 34.35. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -3.69 (t, $J = 99.2$ Hz).

2-(trimethylamine-boranyl)-1-(4-iodophenyl)ethan-1-one (3ia)

Following the general procedure A, the product 3ia was obtained in 68% yield (43.2mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.22. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (m, $J = 8.6$ Hz, 4H), 2.59 (s, 9H), 2.40 (s, 2H), 2.31-1.47 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 207.02, 137.39, 130.45, 99.44, 52.27, 34.25. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -3.71 (t, $J = 97.7$ Hz). ESI-MS: calculated C$_{11}$H$_{17}$BiNO$_3$Na [M+Na]$^+$ 340.0340; Found 340.0329.

2-(trimethylamine-boranyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3ja)

Following the general procedure A, the product 3ja was obtained in 45% yield (23.4mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v).
RF (Petroleum ether/EtOAc 3:1): 0.25. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J$ = 8.1 Hz, 2H), 7.65 (d, $J$ = 8.2 Hz, 2H), 2.61 (s, 9H), 2.47 (s, 2H), 2.35-1.46 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 206.61, 140.93 (s), 133.15 (q, $J$ = 32.5 Hz), 129.07, 125.19 (q, $J$ = 3.6 Hz), 124.09 (q, $J$ = 272.5 Hz), 52.30, 34.52. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -3.83 (t, $J$ = 99.5 Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -62.88.

2-(trimethylamine-boranyl)-1-(3-methoxyphenyl)ethan-1-one (3ka)

![Structure of 2-(trimethylamine-boranyl)-1-(3-methoxyphenyl)ethan-1-one (3ka)](image)

Following the general procedure A, the product 3ka was obtained in 70% yield (30.8mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ = 7.7 Hz, 1H), 7.30 (t, $J$ = 7.9 Hz, 1H), 7.01 (dd, $J$ = 8.2, 2.0 Hz, 1H), 3.83 (s, 3H), 2.60 (s, 9H), 2.44 (s, 2H), 2.24-1.47 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 207.69, 159.57, 139.67, 129.07, 121.63, 118.27, 112.96, 55.44, 52.25, 34.52. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -3.54 (t, $J$ = 99.9 Hz). ESI-MS: calculated C$_{12}$H$_{20}$BNO$_2$Na [M+Na]$^+$ 244.1479; Found 244.1469.

2-(trimethylamine-boranyl)-1-(m-tolyl)ethan-1-one (3la)

![Structure of 2-(trimethylamine-boranyl)-1-(m-tolyl)ethan-1-one (3la)](image)

Following the general procedure A, the product 3la was obtained in 62% yield (25.4mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.24. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J$ = 8.1 Hz, 1H), 7.21 (d, $J$ = 5.0 Hz, 1H), 2.53 (s, 4H), 2.38 (s, 1H), 2.31 (s, 1H), 2.18-1.39 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 208.42, 138.20, 137.73, 132.58, 129.19, 128.00, 126.10, 52.26, 34.50, 21.51. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -3.36 (t, $J$ = 139.8 Hz). ESI-MS: calculated C$_{12}$H$_{20}$BNONa [M+Na]$^+$ 228.1530; Found 228.1520.
2-(trimethylamine-boranyl)-1-(3-chlorophenyl)ethan-1-one (3ma)

Following the general procedure A, the product 3ma was obtained in 59% yield (26.6mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.21. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (t, $J$ = 1.8 Hz, 1H), 7.86 (d, $J$ = 9.0 Hz, 1H), 7.43 (d, $J$ = 7.9 Hz, 1H), 7.33 (t, $J$ = 7.8 Hz, 1H), 2.61 (s, 9H), 2.43 (s, 2H), 2.28-1.45 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 206.42, 139.85, 134.40, 131.71, 129.46, 128.86, 126.99, 52.31, 34.56. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -3.78 (t, $J$ = 100.3 Hz). ESI-MS: calculated C$_{11}$H$_{17}$BClNONa [M+Na]$^+$ 248.0984; Found 248.0979.

2-(trimethylamine-boranyl)-1-(o-tolyl)ethan-1-one (3na)

Following the general procedure A, the product 3na was obtained in 54% yield (22.1mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.26. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.59 (d, $J$ = 7.5 Hz, 1H), 7.18 (d, $J$ = 7.6 Hz, 1H), 7.11 (t, $J$ = 8.2 Hz, 2H), 2.53 (s, 9H), 2.39 (s, 3H), 2.33 (s, 2H), 2.21-1.41 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 212.44, 140.83, 136.83, 131.32, 129.73, 128.50, 125.20, 52.25, 37.48, 21.09. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -4.02 (t, $J$ = 99.5 Hz).

2-(trimethylamine-boranyl)-1-(3-fluoro-4-methylphenyl)ethan-1-one (3oa)

Following the general procedure A, the product 3oa was obtained in 64% yield (28.4mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.28. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (dd, $J$ = 18.7, 9.9 Hz, 2H), 7.19 (t, $J$ = 7.7 Hz, 1H), 2.60 (s, 9H), 2.39 (s, 2H), 2.29 (s, 3H), 2.18-1.44 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 206.42, 139.85, 134.40, 131.71, 129.46, 128.86, 126.99, 52.31, 34.56. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -3.78 (t, $J$ = 100.3 Hz). ESI-MS: calculated C$_{11}$H$_{17}$BClNONa [M+Na]$^+$ 248.0984; Found 248.0979.
MHz, CDCl$_3$ δ 206.52, 161.19 (d, J = 244.9 Hz), 138.07 (d, J = 6.2 Hz), 131.04 (d, J = 4.7 Hz), 129.05 (d, J = 17.5 Hz), 124.38 (d, J = 3.1 Hz), 115.09 (d, J = 22.9 Hz), 52.26, 34.50, 14.79. $^{11}$BNMR (128 MHz, CDCl$_3$) δ -3.62 (t, J = 100.2 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -117.75. ESI-MS: calculated C$_{12}$H$_{19}$BFNONa [M+Na]$^+$ 246.1436; Found 246.1433.

2-(trimethylamine-boranyl)-1-(3,5-dimethylphenyl)ethan-1-one (3pa)

Following the general procedure A, the product 3pa was obtained in 69% yield (30.2mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (s, 2H), 7.10 (s, 1H), 2.60 (s, 9H), 2.43 (s, 2H), 2.34 (s, 6H), 2.11-1.47 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 208.69, 138.31, 137.57, 133.47, 126.56, 52.27, 34.36, 21.41. $^{11}$BNMR (128 MHz, CDCl$_3$) δ -3.54 (t, J = 99.0 Hz). ESI-MS: calculated C$_{13}$H$_{22}$BNONa [M+Na]$^+$ 242.1687; Found 242.1683.

2-(trimethylamine-boranyl)-1-(naphthalen-2-yl)ethan-1-one (3qa)

Following the general procedure A, the product 3qa was obtained in 64% yield (30.9mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.28. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.54 (s, 1H), 8.07 (d, J = 1.6 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 8.5 Hz, 2H), 7.62 – 7.43 (m, 2H), 2.61 (s, 9H), 2.58 (s, 2H), 2.37-1.46 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 208.10, 135.48, 135.23, 132.83, 130.03, 129.70, 127.72, 127.68, 126.24, 125.19, 52.28, 34.61. $^{11}$BNMR (128 MHz, CDCl$_3$) δ -3.44 (t, J = 98.4 Hz).

2-(trimethylamine-boranyl)-1-(1-methyl-1H-indol-2-yl)ethan-1-one (3ra)
Following the general procedure A, the product 3ra was obtained in 65% yield (32.0mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J = 8.0$ Hz, 1H), 7.39 – 7.27 (m, 3H), 7.11 (t, $J = 7.9$ Hz, 1H), 4.06 (s, 3H), 2.63 (s, 9H), 2.43 (s, 2H), 2.25-1.47 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 202.33, 139.64, 136.40, 126.22, 124.67, 122.68, 120.12, 110.66, 110.22, 52.26, 35.93, 32.21. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -2.92 (t, $J = 98.1$ Hz). ESI-MS: calculated C$_{14}$H$_{21}$BN$_2$ONa [M+Na]$^+$ 267.1639; Found 267.1633.

2-(trimethylamine-boranyl)-1-(1-methyl-1H-pyrrol-2-yl)ethan-1-one (3sa)

Following the general procedure A, the product 3sa was obtained in 58% yield (22.0mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.25. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.94 (dd, $J = 4.0, 1.7$ Hz, 1H), 6.74 – 6.57 (m, 1H), 6.06 (dd, $J = 3.9, 2.5$ Hz, 1H), 3.91 (s, 3H), 2.61 (s, 9H), 2.23 (s, 2H), 2.11-1.45 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 199.61, 131.79, 129.17, 118.74, 107.12, 52.23, 37.71, 34.92. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -2.80 (t, $J = 99.5$ Hz). ESI-MS: calculated C$_{10}$H$_{18}$BN$_2$ONa [M+Na]$^+$ 217.1483; Found 217.1479.

2-(trimethylamine-boranyl)-1-(thiophen-2-yl)ethan-1-one (3ta)

Following the general procedure A, the product 3ta was obtained in 41% yield (16.1mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.22. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (dd, $J = 3.7, 1.1$ Hz, 1H), 7.49 (dd, $J = 5.0, 1.1$ Hz, 1H), 7.06 (dd, $J = 4.9, 3.7$ Hz, 1H), 2.62 (s, 9H), 2.39 (s, 2H), 2.32-
1.47 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 201.17, 145.94, 131.69, 131.59, 127.77, 52.33, 35.58. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -3.27 (t, $J = 101.3$ Hz).

1-(trimethylamine-boranyl)-4-phenylbutan-2-one (5aa)

Following the general procedure A, the product 5aa was obtained in 83% yield (36.4mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 1:1): 0.23. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.13 (m, 5H), 2.96 – 2.85 (m, 2H), 2.83 – 2.74 (m, 2H), 2.54 (s, 9H), 1.96 (s, 2H), 2.39-1.38 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 217.65, 142.29, 128.59, 128.34, 125.76, 52.21, 43.48, 38.72, 30.57. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -4.12 (t, $J = 98.9$ Hz). ESI-MS: calculated C$_{13}$H$_{22}$BNONa [M+Na]$^+$ 242.1687; Found 242.1680.

1-trimethylamine-boranylnonan-2-one (5ba)

Following the general procedure A, the product 5ba was obtained in 74% yield (31.5mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.56 (s, 9H), 2.44 – 2.34 (m, 2H), 1.92 (s, 2H), 1.56 – 1.44 (m, 2H), 1.25 (s, 8H), 0.85 (t, $J = 6.8$ Hz, 3H), 2.24-1.55 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 219.36, 52.16, 42.20, 38.62, 31.90, 29.60, 29.31, 24.75, 22.76, 14.21. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -4.04 (t, $J = 98.0$ Hz). ESI-MS: calculated C$_{12}$H$_{28}$BNONa [M+Na]$^+$ 236.2152; Found 236.2152.

1-(trimethylamine-boranyl)-3,3-dimethylbutan-2-one (5ca)
Following the general procedure A, the product 5ca was obtained in 43% yield (14.8mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.25. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.59 (s, 9H), 1.98 (s, 2H), 1.13 (s, 9H), 2.23-1.39 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 52.21, 44.16, 32.44, 27.56. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -4.12 (t, $J = 99.5$ Hz). ESI-MS: calculated C$_9$H$_{22}$BNONa [M+Na]$^+$ 194.1687; Found 194.1685.

2-(trimethylamine-boranyl)-1-cyclopropylethan-1-one (5da)

Following the general procedure A, the product 5da was obtained in 83% yield (25.8mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.22. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.57 (s, 9H), 2.05 (s, 3H), 0.94 – 0.79 (m, 2H), 0.71 (m, $J = 6.7$, 3.4 Hz, 2H), 2.24-1.46 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 218.51, 52.29, 39.45, 20.09, 9.80. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -4.18 (t, $J = 100.7$ Hz).

2-(trimethylamine-boranyl)-1-cyclobutylethan-1-one (5ea)

Following the general procedure A, the product 5ea was obtained in 72% yield (24.4mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.59 (s, 9H), 2.22 (m, $J = 17.8$, 9.0, 2.3 Hz, 2H), 2.12 – 2.02 (m, 2H), 1.98 – 1.85 (m, 3H), 1.82 – 1.69 (m, 2H), 2.35-1.37 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 52.27, 44.91, 35.99, 25.20, 17.85. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -4.25 (t, $J = 99.9$ Hz). ESI-MS: calculated C$_9$H$_{20}$BNONa [M+Na]$^+$ 192.1530; Found 192.1527.

2-(trimethylamine-boranyl)-1-cyclohexylethan-1-one (5fa)
Following the general procedure A, the product 5fa was obtained in 84% yield (33.1mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.28. 1H NMR (400 MHz, CDCl3) δ 2.55 (s, 9H), 1.93 (s, 2H), 1.75 (dd, J = 18.0, 10.9 Hz, 4H), 1.62 (d, J = 10.0 Hz, 1H), 1.36 – 1.12 (m, 6H), 2.32-1.38 (br, 2H). 13C NMR (101 MHz, CDCl3) δ 52.28, 49.83, 36.82, 29.30, 26.21, 26.11. 11B NMR (128 MHz, CDCl3) δ -4.35 (t, J = 99.3 Hz).

1-((3r,5r,7r)-adamantan-1-yl)-2-trimethylamine-boranylethan-1-one (5ga)

Following the general procedure A, the product 5ga was obtained in 62% yield (31.0mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. 1H NMR (400 MHz, CDCl3) δ 2.58 (s, 9H), 1.97 (d, J = 14.0 Hz, 5H), 1.85 (s, 6H), 1.68 (s, 6H), 2.28-1.43 (br, 2H). 13C NMR (101 MHz, CDCl3) δ 52.24, 46.35, 39.19, 37.01, 32.27, 28.52. 11B NMR (128 MHz, CDCl3) δ -4.32 (t, J = 99.2 Hz). ESI-MS: calculated C15H28BNONa [M+Na]+ 272.2156; Found 272.2151.

methyl 6-((trimethylamine-boranyl)-5-oxohexanoate (5ha)

Following the general procedure A, the product 5ha was obtained in 51% yield (21.9mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.28. 1H NMR (400 MHz, CDCl3) δ 3.65 (s, 3H), 2.56 (s, 9H), 2.48 (t, J = 7.3 Hz, 2H), 2.31 (t, J = 7.5 Hz, 2H), 1.92 (s, 2H), 1.85 (m, J = 14.7, 7.5 Hz, 2H), 2.49-1.35 (br, 2H). 13C NMR (101 MHz, CDCl3) δ 217.69, 174.15, 52.29, 51.55, 40.87, 38.74, 33.71, 19.80. 11B NMR (128 MHz, CDCl3) δ -4.10 (t, J = 99.0 Hz). ESI-MS: calculated C10H22BN03Na [M+Na]+ 238.1585; Found 238.1578.
2-(4-(trimethylamine-boranyl)-3-oxobutyl)isoindoline-1,3-dione (5ia)

Following the general procedure A, the product 5ia was obtained in 68% yield (39.9mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). RF (Petroleum ether/EtOAc 1:1): 0.28. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.84 – 7.75 (m, 2H), 7.73 – 7.64 (m, 2H), 3.89 (t, \(J = 7.5\) Hz, 2H), 2.86 (s, 2H), 2.53 (s, 9H), 1.92 (s, 2H), 2.24-1.37 (br, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 215.37, 168.27, 133.87, 132.32, 123.17, 52.19, 39.79, 38.67, 33.89. \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) -4.21 (t, \(J = 97.5\) Hz). ESI-MS: calculated C\(_{15}\)H\(_{21}\)BN\(_2\)O\(_3\)Na [M+Na]\(^+\) 311.1537; Found 311.1533.

benzyl 4-(2-(trimethylamine-boranylacetyl)piperidine-1-carboxylate (5ja)

Following the general procedure A, the product 5ja was obtained in 70% yield (46.5mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.25. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.27 (m, 5H), 5.10 (s, 2H), 4.16 (s, 2H), 2.81 (t, \(J = 11.1\) Hz, 2H), 2.64 (m, \(J = 11.5, 9.4, 3.6\) Hz, 1H), 2.56 (s, 9H), 1.95 (s, 2H), 1.77 (s, 2H), 1.54 (m, \(J = 16.3, 12.5, 4.2\) Hz, 2H), 2.31-1.35 (br, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 219.36, 155.32, 137.04, 128.54, 127.97, 127.87, 67.04, 52.26, 47.36, 43.88, 36.62, 28.22. \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) -3.77, -4.47, -5.19. ESI-MS: calculated C\(_{18}\)H\(_{29}\)BN\(_2\)O\(_3\)Na [M+Na]\(^+\) 355.2163; Found 355.2159.

1-(trimethylamine-boranyl)-3-(naphthalen-2-yloxy)propan-2-one (5ka)
Following the general procedure A, the product **5ka** was obtained in 47% yield (25.5mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.26. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.78 – 7.66 (m, 1H), 7.45 – 7.38 (m, 1H), 7.35 – 7.28 (m, 1H), 7.25 – 7.20 (m, 1H), 7.12 (d, $J = 2.4$ Hz, 1H), 4.77 (s, 1H), 2.60 (s, 3H), 2.08 (s, 1H), 2.48-1.49 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 212.56, 156.45, 134.58, 129.54, 129.26, 127.72, 126.91, 126.41, 123.79, 119.02, 107.32, 71.97, 52.31, 34.45. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -4.15 (t, $J = 96.9$ Hz). ESI-MS: calculated C$_{16}$H$_{22}$BNO$_2$Na [M+Na]$^+$ 294.1636; Found 294.1631.

1-(trimethylamine-boranyl)-3-(4-chloro-2-methylphenoxy)propan-2-one (5la)

Following the general procedure A, the product **5la** was obtained in 55% yield (29.6mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.10 (d, $J = 2.4$ Hz, 1H), 7.04 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.63 (d, $J = 8.7$ Hz, 1H), 4.59 (s, 2H), 2.59 (s, 10H), 2.24 (d, $J = 19.0$ Hz, 4H), 2.04 (s, 3H), 2.31-1.39 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 212.81, 155.42, 130.58, 129.01, 126.34, 125.42, 112.67, 72.48, 52.31, 34.29, 16.40. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -4.23 (t, $J = 100.1$ Hz). ESI-MS: calculated C$_{13}$H$_{21}$BClNO$_2$Na [M+Na]$^+$ 292.1246; Found 292.1244.

propyl 2-(trimethylamine-boranyl)-2-phenylacetate (7aa)

Following the general procedure A, the product **7aa** was obtained in 50% yield (24.8mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc :1): 0.26. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, $J = 7.4$ Hz, 2H), 7.30 – 7.23 (m, 2H), 7.12 (t, $J = 7.3$ Hz, 1H), 4.00 (q, $J = 5.4$ Hz, 2H), 3.26 (s, 1H), 2.55 (s, 9H), 1.65 (dt, $J = 14.0, 7.0$ Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H), 2.44-1.55 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ
propyl 2-(trimethylamine-boranyl)-2-(4-chlorophenyl)acetate (7ba)

Following the general procedure A, the product 7ba was obtained in 56% yield (31.9mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.24. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 3.96 (m, $J = 10.7, 5.4$ Hz, 2H), 3.19 (s, 1H), 2.52 (s, 9H), 1.72 – 1.51 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H), 2.41-1.36 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.07, 142.45, 130.60, 130.54, 127.94, 65.62, 52.55, 46.08, 22.27, 10.67. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 2.32 – -6.55 (m). ESI-MS: calculated C$_{14}$H$_{24}$BNO$_2$Na [M+Na]$^+$ 272.1792; Found 272.1790.

propyl 2-(trimethylamine-boranyl)-2-(4-cyanophenyl)acetate (7ca)

Following the general procedure A, the product 7ca was obtained in 46% yield (25.2mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 – 7.38 (m, 4H), 4.13 – 3.82 (m, 2H), 3.28 (s, 1H), 2.55 (s, 9H), 1.74 – 1.46 (m, 2H), 0.99 – 0.74 (m, 3H), 2.53-1.37 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.37, 150.10, 131.67, 129.84, 119.74, 108.38, 65.84, 52.52, 47.39, 22.22, 10.67. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 4.12 – -7.51 (m). ESI-MS: calculated C$_{15}$H$_{25}$BN$_2$O$_2$Na [M+Na]$^+$ 297.1745; Found 297.1745.
propyl 2-(trimethylamine-boranyl)-2-(4-(trifluoromethyl)phenyl)acetate (7da)

Following the general procedure A, the product 7da was obtained in 43% yield (27.3mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.24. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, $J = 8.3$ Hz, 2H), 7.48 (d, $J = 8.3$ Hz, 2H), 3.99 (m, $J = 12.5$, 6.5 Hz, 2H), 3.29 (s, 1H), 2.55 (s, 9H), 1.70 – 1.53 (m, 4H), 0.92 (t, $J = 7.4$ Hz, 3H), 2.39-1.40 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.78, 148.30, 129.39, 127.09 (q, $J = 32.0$ Hz), 124.78 (q, $J = 271.3$ Hz), 124.75 (q, $J = 3.7$ Hz), 65.74, 52.54, 46.85, 22.26, 10.68. $^{11}$B NMR (128 MHz, CDCl$_3$) δ 6.57 – -5.93 (m). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.10. ESI-MS: calculated C$_{15}$H$_{23}$BF$_3$NO$_2$Na [M+Na]$^+$ 340.1666; Found 340.1662.

propyl 2-(trimethylamine-boranyl)-2-(4-(trifluoromethoxy)phenyl)acetate (7ea)

Following the general procedure A, the product 7ea was obtained in 38% yield (25.3mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.26. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, $J = 7.5$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 3.97 (m, $J = 11.6$, 5.2 Hz, 2H), 3.23 (s, 1H), 2.54 (s, 9H), 1.69 – 1.53 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H), 2.42-1.44 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.18, 146.82, 142.70, 130.30, 120.70 (q, $J = 256.1$ Hz), 120.42, 65.66, 52.52, 45.84, 22.25, 10.66. $^{11}$B NMR (128 MHz, CDCl$_3$) δ 4.12 – -5.70 (m). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -57.86. ESI-MS: calculated C$_{15}$H$_{23}$BF$_3$NO$_3$Na [M+Na]$^+$ 356.1615; Found 356.1611.

propyl 2-(4-acetylphenyl)-2- trimethylamine-boranylacetate (7fa)
Following the general procedure A, the product 7fa was obtained in 35% yield (20.4mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.22. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 8.3$ Hz, 2H), 7.52 (d, $J = 8.3$ Hz, 2H), 4.11 – 3.75 (m, 2H), 3.31 (s, 1H), 2.55 (s, 3H), 2.53 (s, 9H), 1.63 (m, $J = 14.2$, 7.1 Hz, 2H), 0.92 (t, $J = 7.4$ Hz, 3H), 2.39-1.36 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.26, 177.60, 150.30, 134.18, 129.28, 128.16, 65.72, 52.53, 47.15, 26.62, 22.25, 10.67. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 3.89 – -5.52 (m). ESI-MS: calculated C$_{16}$H$_{26}$BNO$_3$Na $[M+Na]^+$ 314.1898; Found 314.1891.

**propyl 2-(trimethylamine-boranyl)-2-(3-bromophenyl)acetate (7ga)**

Following the general procedure A, the product 7ga was obtained in 38% yield (25.0mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.26. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.59 (s, 1H), 7.36 (d, $J = 7.7$ Hz, 1H), 7.22 (d, $J = 7.8$ Hz, 1H), 7.10 (t, $J = 7.8$ Hz, 1H), 4.04 – 3.80 (m, 2H), 3.18 (s, 1H), 2.54 (s, 9H), 1.70 – 1.51 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 3H), 2.42-1.45 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 177.86, 146.37, 132.19, 129.39, 127.97, 121.99, 65.68, 52.55, 46.46, 22.25, 10.68. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 2.08 – -3.94 (m). ESI-MS: calculated C$_{14}$H$_{23}$BBrNO$_2$Na $[M+Na]^+$ 350.0897; Found 350.0896.

**propyl 2-(trimethylamine-boranyl)-2-(3,5-difluorophenyl)acetate (7ha)**
Following the general procedure A, the product 7ha was obtained in 41% yield (23.4mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.24. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.97 (d, \(J = 8.6\) Hz, 2H), 6.53 (m, \(J = 9.0, 1.8\) Hz, 1H), 3.98 (q, \(J = 5.4\) Hz, 2H), 3.20 (s, 1H), 2.55 (s, 9H), 1.63 (m, \(J = 7.1\) Hz, 1H), 0.92 (t, \(J = 7.3\) Hz, 3H), 2.42-1.45 (br, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 177.42, 162.69 (dd, \(J = 245.7, 13.3\) Hz), 148.04 (t, \(J = 9.4\) Hz), 111.85 (dd, \(J = 19.3, 5.6\) Hz), 100.21 (t, \(J = 25.5\) Hz), 65.78, 52.53, 46.30 (d, \(J = 103.0\) Hz), 22.23, 10.66. \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) -6.39. ESI-MS: calculated C\(_{14}\)H\(_{22}\)BF\(_2\)NO\(_2\)Na [M+Na]\(^+\) 308.1604; Found 308.1603.

(S)-1-(trimethylamine-boranyl)-3-(6-methoxynaphthalen-2-yl)butan-2-one (8)

Following the general procedure A, the product 8 was obtained in 80% yield (47.9mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.25. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.74 – 7.63 (m, 3H), 7.40 (d, \(J = 9.4\) Hz, 1H), 7.14 – 7.07 (m, 2H), 4.18 (q, \(J = 6.9\) Hz, 1H), 3.89 (s, 3H), 2.52 (s, 9H), 2.05 (s, 2H), 1.42 (d, \(J = 7.0\) Hz, 3H), 2.26-1.49 (br, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 218.07, 157.44, 138.18, 133.47, 129.29, 129.22, 127.19, 126.97, 126.46, 118.74, 105.74, 55.39, 52.23, 51.00, 37.44, 18.50. \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \(\delta\) -1.72 – -8.38 (m). ESI-MS: calculated C\(_{18}\)H\(_{26}\)BNO\(_2\)Na [M+Na]\(^+\) 322.1949; Found 322.1948.

1-(trimethylamine-boranyl)-4-(4,5-diphenyloxazol-2-yl)butan-2-one (9)
Following the general procedure A, the product 9 was obtained in 52% yield (37.7mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.26. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 – 7.60 (m, 2H), 7.59 – 7.54 (m, 2H), 7.33 (m, $J = 10.7$, 9.1, 4.4, 2.7 Hz, 6H), 3.17 – 3.02 (m, 4H), 2.55 (s, 9H), 2.02 (s, 2H), 2.44-1.42 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 215.80, 163.52, 145.18, 135.16, 132.87, 129.36, 128.68, 128.60, 128.35, 128.08, 128.02, 126.58, 52.29, 38.58, 23.03, 19.29. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -0.38 – -7.74 (m). ESI-MS: calculated C$_{22}$H$_{27}$BN$_2$O$_2$Na [M+Na]$^+$ 385.2058; Found 385.2054.

4-(2-trimethylamine-boranylacetyl)-N,N-dipropylbenzenesulfonamide (10)

Following the general procedure A, the product 10 was obtained in 48% yield (34.0mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.07 (d, $J = 8.1$ Hz, 2H), 7.80 (d, $J = 8.1$ Hz, 2H), 3.16 – 2.98 (m, 4H), 2.60 (s, 9H), 2.45 (s, 2H), 1.53 (dd, $J = 15.1$, 7.5 Hz, 4H), 0.85 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 206.44, 142.62, 141.06, 129.26, 126.87, 52.25, 50.18, 34.68, 22.15, 11.27. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -1.29 – -6.60 (m). ESI-MS: calculated C$_{17}$H$_{31}$BN$_2$O$_3$SNa [M+Na]$^+$ 377.2041; Found 377.2039.

1-(trimethylamine-boranyl)-3-(4-isobutylphenyl)butan-2-one (11)

Following the general procedure A, the product 11 was obtained in 70% yield (40.0mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF
(Petroleum ether/EtOAc 4:1): 0.25. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.18 (d, $J = 7.4$ Hz, 2H), 7.05 (d, $J = 7.5$ Hz, 2H), 4.01 (q, $J = 6.9$ Hz, 1H), 2.52 (s, 9H), 2.42 (d, $J = 7.1$ Hz, 2H), 2.03 (s, 1H), 1.87 – 1.79 (m, 1H), 1.77 (s, 1H), 1.33 (d, $J = 6.9$ Hz, 3H), 0.88 (d, $J = 6.6$ Hz, 6H), 2.32-1.47 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 218.29, 140.02, 139.78, 129.23, 127.83, 52.21, 50.68, 45.16, 37.36, 30.28, 22.50, 18.38. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -4.23 (t, $J = 96.6$ Hz). ESI-MS: calculated C$_{17}$H$_{30}$BNONa [M+Na]$^+$ 298.2313; Found 298.2311.

(8S,9S,10R,13S,14S,17S)-17-(2-trimethylamine-boranylacetyl)-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (12)

Following the general procedure A, the product 12 was obtained in 65% yield (50.1mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.24. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.04 (s, 1H), 5.38 (s, 1H), 2.80 (t, $J = 9.0$ Hz, 1H), 2.55 (s, 9H), 2.48 (d, $J = 12.4$ Hz, 1H), 2.30 (m, $J = 18.1$, 5.1 Hz, 1H), 2.21 – 2.10 (m, 2H), 2.02 (m, $J = 16.4$, 6.5 Hz, 2H), 1.92 – 1.80 (m, 2H), 1.73 – 1.54 (m, 5H), 1.41 (d, $J = 9.0$ Hz, 2H), 1.34 – 1.13 (m, 5H), 0.94 (s, 3H), 0.66 (s, 3H), 2.22-1.50 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.64, 130.35, 127.14, 124.29, 61.05, 57.15, 52.31, 48.10, 44.06, 40.08, 38.89, 34.93, 34.64, 31.88, 31.79, 30.80, 29.82, 24.71, 23.87, 21.31, 19.00, 13.70. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 2.31 – -11.95 (m). ESI-MS: calculated C$_{24}$H$_{40}$BNO$_2$Na [M+Na]$^+$ 408.3044; Found 408.3066.

2-(3-trimethylamine-boranyl-2-oxopropyl)dibenzo[b,e]oxepin-11(6H)-one (13)

Following the general procedure A, the product 13 was obtained in 45% yield (30.4mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.24. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 2.1$ Hz, 1H), 7.91 – 7.84 (m, 1H), 7.53 (td, $J = 7.4$, 1.2 Hz, 1H), 7.45 (td, $J = 7.6$, 1.0 Hz, 1H), 7.36 (dd, $J = 12.9$, 4.6
Hz, 2H), 6.99 (d, J = 8.4 Hz, 1H), 5.16 (s, 2H), 3.76 (s, 2H), 2.58 (s, 9H), 2.00 (s, 2H), 2.43-1.47 (br, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 215.22, 191.16, 160.12, 140.69, 137.20, 135.87, 132.71, 132.62, 130.42, 129.58, 129.25, 127.84, 125.18, 120.72, 73.73, 52.33, 47.73, 38.05. $^{11}$B NMR (128 MHz, CDCl$_3$) δ -4.22 (t, J = 97.5 Hz). ESI-MS: calculated C$_{20}$H$_{24}$BNO$_3$Na [M+Na]$^+$ 360.1741; Found 360.1743.

Propyl 2-trimethylamine-boranyl-2-((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)acetate (14)

Following the general procedure A, the product 14 was obtained in 46% yield (39.2mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). RF (Petroleum ether/EtOAc 3:1): 0.26. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.22 (d, J = 12.4 Hz, 1H), 7.14 (t, J = 7.3 Hz, 2H), 4.03 – 3.84 (m, 2H), 3.16 (s, 1H), 2.89 (d, J = 3.8 Hz, 2H), 2.60 (s, 1H), 2.55 (s, 9H), 2.48 (dd, J = 19.0, 8.7 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.25 (t, J = 9.3 Hz, 1H), 2.17 – 2.05 (m, 1H), 1.95 (dd, J = 25.2, 11.3 Hz, 2H), 1.77 (s, 1H), 1.69 – 1.53 (m, 4H), 1.53 – 1.46 (m, 2H), 1.44 – 1.35 (m, 1H), 0.93 (t, J = 7.3 Hz, 3H), 0.88 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.77, 141.06, 141.00, 136.06, 136.04, 135.71, 135.63, 129.57, 129.53, 126.69, 126.59, 124.84, 124.71, 65.44, 52.45, 52.16, 50.66, 48.15, 45.97, 44.41, 38.36, 38.33, 36.00, 31.74, 29.61, 29.55, 26.83, 26.81, 25.77, 25.75, 22.23, 21.69, 13.97, 10.70. $^{11}$B NMR (128 MHz, CDCl$_3$) δ 4.12–2.36 (m). ESI-MS: calculated C$_{26}$H$_{40}$BNO$_3$Na [M+Na]$^+$ 448.2993; Found 448.2989.

2-(1-methylpyrrolidine-boranyl)-1-phenylethan-1-one (3ad)

Following the general procedure A, the product 3ad was obtained in 62% yield (26.9mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v).
RF (Petroleum ether/EtOAc 4:1): 0.24. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J$ = 7.4 Hz, 1H), 7.46 (t, $J$ = 6.9 Hz, 1H), 7.39 (t, $J$ = 7.2 Hz, 1H), 3.14 (s, 1H), 2.83 (s, 1H), 2.63 (s, 2H), 2.47 (s, 1H), 1.96 (dd, $J$ = 21.8, 6.5 Hz, 2H), 2.37-1.53 (br, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 208.23, 138.18, 131.75, 128.75, 128.10, 61.55, 47.94, 34.62, 22.59. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ -4.76 (t, $J$ = 98.7 Hz). ESI-MS: calculated C$_{13}$H$_{20}$BNONa [M+Na]$^+$ 240.1530; Found 240.1528.
5. Synthetic application of the product 3aa

4.1 Synthesis of (R)-2-(3-(6-methoxynaphthalen-2-yl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

\[
\begin{align*}
\text{MeO} & \quad \text{H} & \quad \text{H} & \quad \text{NMe}_3 \\
\text{8} & & & \\
\text{1)} \text{BH}_3 \cdot \text{THF}, \text{THF, reflux, 2h} & \quad \text{MeO} & \quad \text{H} & \quad \text{Bpin} \\
\text{2)} \text{HCl, pinacol, CH}_3\text{CN, rt, 2h} & & & \\
\text{15} & & & \\
\end{align*}
\]

To a solution of 8 (149.7 mg, 0.5 mmol) in anhydrous THF (10.0 ml) was slowly added a solution of BH$_3$·THF (1.5 mL, 1.0M) at 0 °C. The reaction mixture was warm to reflux and stirred under nitrogen atmosphere for 2 hours. The solvent was removed under vacuo, followed by adding 10.0 mL of MeOH, and the mixture was heated to refluxed for 1 hour. After evaporation under vacuo, the residue was dissolved in 10.0 mL MeCN, HCl (1.3 mL, 1.0 M in water) and pinacol (118.2 mg, 1.0 mmol) were then added. The reaction mixture was stirred under nitrogen atmosphere for 2 hours at room temperature and quenched with saturated NaHCO$_3$ aqueous. The reaction mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 20:1) to give 15 (115.7 mg, 0.34 mmol) in 68% yield as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (dd, $J$ = 8.4, 2.9 Hz, 2H), 7.55 (s, 1H), 7.33 (dd, $J$ = 8.5, 1.7 Hz, 1H), 7.17 – 7.09 (m, 2H), 3.91 (s, 3H), 2.79 (dd, $J$ = 14.0, 7.0 Hz, 1H), 1.83 – 1.72 (m, 2H), 1.34 (d, $J$ = 6.9 Hz, 3H), 1.23 (s, 12H), 0.82 – 0.68 (m, 2H). $^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.19, 142.80, 133.25, 129.22, 129.13, 126.76, 126.63, 125.30, 118.55, 105.74, 82.97, 55.37, 42.19, 32.78, 24.92, 21.80. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 33.77 (s). ESI-MS: calculated C$_{21}$H$_{29}$BNO$_3$Na [M+Na]$^+$ 363.2102; Found 363.2115.

4.2 Synthesis of (R)-difluoro(3-(6-methoxynaphthalen-2-yl)butyl)borane, potassium salt

\[
\begin{align*}
\text{MeO} & \quad \text{Bpin} \\
\text{15} & & & \\
\text{KHF}_2, \text{MeOH, rt, 0.5 h} & \quad \text{MeO} & \quad \text{BF}_2\text{K} \\
\text{16} & & & \\
\end{align*}
\]
To a solution of pinacol ester 15 (68.1 mg, 0.2 mmol) in methanol (1.0 mL) was added 4.5 M KHF$_2$(aq) (35.9 mg, 0.46 mmol) The resulting mixture was stirred for 1h, and concentrated to dryness. The residue, a white solid, was extracted with hot acetone (2×10), and the combined filtered extracts were concentrated to a volume of ca. 2.0 mL. Ether (10 mL) was added and the resultant precipitate was collected and dried to afford the title compound 16 (57.2 mg, 95%) as a white solid.

$^1$H NMR (400 MHz, DMSO) $\delta$ 7.69 (dd, $J = 15.9$, 8.7 Hz, 2H), 7.50 (s, 1H), 7.27 (d, $J = 8.4$ Hz, 1H), 7.21 (d, $J = 2.2$ Hz, 1H), 7.07 (dd, $J = 8.9$, 2.5 Hz, 1H), 3.83 (s, 3H), 2.60 (dd, $J = 13.8$, 6.9 Hz, 1H), 1.52 – 1.31 (m, 2H), 1.18 (d, $J = 6.9$ Hz, 3H), 0.03 – -0.38 (m, 2H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 156.90, 144.85, 133.02, 129.26, 129.08, 127.21, 126.64, 124.89, 118.50, 106.15, 55.55, 42.59, 35.44, 22.39. $^{11}$B NMR (128 MHz, DMSO) $\delta$ 5.86. $^{19}$F NMR (376 MHz, DMSO) $\delta$ -136.91.

4.3 Synthesis of (R)-3-(6-methoxynaphthalen-2-yl)butan-1-ol

To a solution of pinacol ester 15 (68.1 mg, 0.2 mmol) in aqueous THF (1.0 ml 1:1(v/v)) was added Sodium perborate tetrahydrate (92.3 mg, 0.6 mmol) The resulting mixture was stirred for 12 h at room temperature. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over Na$_2$SO$_4$ and concentrated in vacuo. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 8 : 1) to give 17 (40.1 mg, 87%) as a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (dd, $J = 8.5$, 4.2 Hz, 2H), 7.57 (s, 1H), 7.34 (dd, $J = 8.5$, 1.7 Hz, 1H), 7.17 – 7.11 (m, 2H), 3.92 (s, 3H), 3.58 (m, $J = 10.6$, 6.6 Hz, 2H), 3.03 (dd, $J = 14.4$, 7.2 Hz, 1H), 1.93 (q, $J = 7.0$ Hz, 2H), 1.46 (s, 1H), 1.35 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.38, 142.07, 133.37, 129.22, 129.14, 127.12, 126.18, 125.17, 118.83, 105.80, 61.36, 55.42, 41.03, 36.51, 22.61. ESI-MS: calculated C$_{15}$H$_{18}$O$_2$Na [M+Na]$^+$ 253.1199; Found 253.1195.

4.4 Synthesis of (R)-2-(hex-5-en-2-yl)-6-methoxynaphthalene
A stirred solution of boronic ester 15 (0.2 mmol) in THF (0.5 mL) and DMSO (0.5 mL) was cooled to 0 °C and a solution of Grignard reagent (0.3 mmol) was added dropwise [N.B. upon addition of the Grignard reagent a white precipitate was observed]. The resulting mixture was stirred at room temperature for 30 min and then cooled to 0 °C. A suspension of NaOMe (30 wt% in MeOH, 32.4 mg, 0.6 mmol) in was added in a single portion, followed by dropwise addition of a solution of I₂ (0.5 M in MeOH, 0.48 mL, 0.24 mmol). The resulting mixture was stirred at 0 °C for 30 min and then saturated aqueous sodium thiosulfate and dichloromethane were added. The organic phase was separated and the aqueous phase was extracted twice with dichloromethane. The combined organic extracts were washed with water twice, dried over anhydrous Na₂SO₄. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 100 : 1) to give 18 (38.4 mg, 80%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 8.4 Hz, 2H), 7.56 (s, 1H), 7.34 (dd, J = 8.4, 1.6 Hz, 1H), 7.19 – 7.09 (m, 2H), 5.83 (m J = 16.9, 10.2, 6.6 Hz, 1H), 5.10 – 4.85 (m, 2H), 3.93 (s, 3H), 2.99 – 2.74 (m, 1H), 2.22 – 1.88 (m, 2H), 1.89 – 1.63 (m, 2H), 1.35 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.32, 142.68, 138.98, 133.31, 129.25, 129.16, 126.95, 126.41, 125.24, 118.73, 114.52, 105.81, 55.43, 39.40, 37.59, 32.03, 22.44.

4.5 One-Pot Sequence

To a solution of the carboxylic acid (5.0 mmol, 1.0 equiv) in dry CH₂Cl₂ (30 mL) at 0 °C under N₂ was added dropwise of (COCl)₂ (0.85 mL, 10 mmol, 2 equiv) followed by a catalytic amount of dry DMF (2 drops). The reaction was allowed to stir at room temperature until completion (typically 3 h). The solvent was then removed under reduce pressure to afford the corresponding crude acid chloride.
In a 100 mL flame-dried round bottom flask attached to a reflux condenser, under argon atmosphere, 1.68 g of potassium tert-butoxide (15.0 mmol, 3.0 equiv) and 15.0 mL of anhydrous THF were added. Then, 2.20 g of trimethylsulfoxonium iodide (10.0 mmol; 2.0 equiv) was added in one portion. The suspension was heated at reflux for 2 hours. After this time, the mixture was cooled at 0 °C, followed by slow addition of the crude acid chloride diluted with anhydrous THF. The reaction mixture temperature was naturally increased to room temperature and this mixture stirred for additional 3 hours. Then, the solvent was removed on a rotary evaporator.

trimethylamine-borane 2a (547.5 mg, 7.5 mmol, 1.5 equiv), [Ir(cod)Cl]₂ (83.9 mg, 0.125 mmol, 2.5 mmol%), KH₂PO₄ (680.5 mg, 5.0 mmol, 1.0 equiv), and PhCl (25 mL) was stirred at 55 °C for 12 h. The reaction mixture was then diluted with DCM (10 mL) and washed with H₂O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 4:1) to give 3aa (0.4 g, 42%) and 3ka (0.46 g, 42%).

4.6 Gram-Scale Synthesis

In an oven-dried Schlenk tube under air, a mixture of the substrates 1k (5.0 mmol, 1.0 equiv), trimethylamine-borane 2a (547.5 mg, 7.5 mmol, 1.5 equiv), [Ir(cod)Cl]₂ (83.9 mg, 0.125 mmol, 2.5 mmol%), KH₂PO₄ (680.5 mg, 5.0 mmol, 1.0 equiv), and PhCl (25.0 mL) was stirred at 55 °C for 12 h. The reaction mixture was then diluted with DCM (50 mL) and washed with H₂O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 4:1) to give 3ka (0.67 g, 61%).
In an oven-dried Schlenk tube under air, a mixture of the substrates 1u (5.0 mmol, 1.0 equiv), trimethylamine-borane 2a (547.5 mg, 7.5 mmol, 1.5 equiv), [Ir(cod)Cl]₂ (83.9 mg, 0.125 mmol, 2.5 mmol%), KH₂PO₄ (680.5 mg, 5.0 mmol, 1.0 equiv), and PhCl (25.0 mL) was stirred at 55 °C for 12 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H₂O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give 8 (1.0 g, 67%).
6. Mechanistic experiments

In an oven-dried Schlenk tube under air, a mixture of the substrates 1a (0.2 mmol, 1.0 equiv), trimethylamine-borane 2a (21.9 mg, 0.3 mmol, 1.5 equiv), [Ir(cod)Cl]2 (3.4 mg, 0.005 mmol, 2.5 mmol%), KH2PO4 (27.2 mg, 0.2 mmol, 1.0 equiv), TEMPO (156.3 mg, 0.4 mmol, 2.0 equiv) and PhCl (2.0 mL) was stirred at 55 °C for 1 h - 12 h. The reaction mixture was then diluted with DCM (10 mL) and washed with H2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na2SO4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product 3aa as a yellow liquid (28.2 mg, 74%).

In an oven-dried Schlenk tube under air, a mixture of the substrates 1a (0.2 mmol, 1.0 equiv), trimethylamine-borane 2a (21.9 mg, 0.3 mmol, 1.5 equiv), [Ir(cod)Cl]2 (3.4 mg, 0.005 mmol, 2.5 mmol%), KH2PO4 (27.2 mg, 0.2 mmol, 1.0 equiv), BHT (220.4 mg, 0.4 mmol, 2.0 equiv) and PhCl (2.0 mL) was stirred at 55 °C for 1 h - 12 h. The reaction mixture was then diluted with DCM (10 mL) and washed with H2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na2SO4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product 3aa as a yellow liquid (26.7 mg, 70%).
In an oven-dried Schlenk tube under air, a mixture of the substrates 1a (0.2 mmol, 1.0 equiv), 1-methylpyrrolidine-boranyl 2d-D3 (30.6 mg, 0.3 mmol, 1.5 equiv), [Ir(cod)Cl]2 (3.4 mg, 0.005 mmol, 2.5 mmol%), KH2PO4 (27.2 mg, 0.2 mmol, 1.0 equiv) and PhCl (2.0 mL) was stirred at 55 °C for 1 h - 12 h. The reaction mixture was then diluted with DCM (10 mL) and washed with H2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na2SO4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product as a white solid (22.9 mg, 52%). 1H NMR (400 MHz, CDCl3) δ 8.01 (d, J = 7.1 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.3 Hz, 2H), 3.19 – 3.07 (m, 2H), 2.89 – 2.74 (m, 2H), 2.62 (s, 3H), 2.44 (s, 1H), 2.05 – 1.86 (m, 4H), 2.37-1.52 (br, 2H). 13C NMR (126 MHz, CDCl3) δ 208.23, 138.18, 131.75, 128.75, 128.10, 61.55, 47.94, 34.62, 22.59. 11B NMR (128 MHz, CDCl3) δ -4.76 (t, J = 98.7 Hz)
7. NMR Spectra for New Compounds
8. Reference

