Supporting Information

Synthesis of 2-BMIDA indoles via heteroannulation: Applications in drug scaffold and natural product synthesis

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1. General Experimental Details

1.1 Purification of Solvents & Reagents

Dry DMSO was obtained by standing DMSO over activated alumina overnight before filtration then distilling over CaH$_2$ under vacuum and storing over activated 4 Å molecular sieves under a blanket of N$_2$. Dry DMF was obtained by stirring over 4 Å molecular sieves overnight before distilling over fresh 4 Å molecular sieves under vacuum and storing over activated 4 Å molecular sieves under N$_2$. Dry THF was obtained from a PureSolv SPS-400-5 solvent purification system. DCM, MeCN, Et$_2$O, EtOAc, and hexane for purification purposes were used as obtained from suppliers without further purification. NaOAc was heated to melting under vacuum, then allowed to cool to room temperature, backfilled with N$_2$, and stored in a capped vial under N$_2$. LiCl was placed in a vacuum oven kept at 60 °C for at least 24 hours prior to use. B(OMe)$_3$ was distilled over CaH$_2$ and stored over activated 4 Å molecular sieves under N$_2$. All other reagents and solvents were obtained from commercial suppliers and were used without further purification unless otherwise stated. Purification was carried out according to standard laboratory methods.

1.2 Experimental Details

Reactions were carried out using conventional glassware (preparation of intermediates) or in capped 5 or 20 mL microwave vials. Microwave vials were oven-dried (150 °C) and cooled to room temperature under vacuum and backfilled with N$_2$ prior to use. Reaction mixtures were prepared in a microwave vial before being capped with a septum and purged using N$_2$/vacuum (three cycles). Reactions were carried out at elevated temperatures in a sand bath atop a temperature-regulated hotplate/stirrer. Cooling to 0 °C was achieved using an ice/water bath. Cooling to −78 °C was achieved using a dry ice/acetone bath.

1.3 Purification of Products

Thin layer chromatography was carried out using Merck silica plates coated with fluorescent indicator UV254. These were analysed under 254 nm UV light and/or developed using potassium permanganate or vanillin solution. Normal phase flash chromatography was carried out using ZEOprep 60 HYD 40-63 μm silica gel.

1.4 Analysis of Products

Fourier Transformed Infra-Red (FTIR) spectra were obtained on a Shimadzu IRAffinity-1 machine. $^1$H and $^{13}$C NMR spectra were obtained on either a Bruker AV 400 at 400 MHz and 101 MHz, respectively, or Bruker DRX 500 at 500 MHz and 126 MHz, respectively. $^{19}$F NMR spectra were obtained on a Bruker AV 400 spectrometer at 376 MHz. $^{11}$B NMR spectra were obtained on a Bruker AV 300 spectrometer at 96 MHz. Chemical shifts are reported in ppm and coupling constants are reported in Hz with CDCl$_3$ referenced at 7.26 (1H) and 77.16 ppm (13C), DMSO-$d_6$ referenced at 2.50 (1H) and 39.5 (13C), acetone-$d_6$ referenced at 2.05 (1H) and 28.9 and 206.3 ppm (13C), and MeCN-$d_3$ referenced at 1.94 (1H) and 1.3 and 118.3 ppm (13C). $^{11}$B NMR spectra are referenced to BF$_3$·Et$_2$O.

High-resolution mass spectra were obtained through analysis at the University of St Andrews with a Thermo Exactive Orbitrap mass spectrometer. NMR conversions for optimisation studies were carried out by adding a known standard (0.05 M 1,4-dinitrobenzene in DMSO-$d_6$) to the crude reaction mixture. Note: (i) BMIDA products were typically poorly soluble in most NMR solvents; (ii) Restricted rotation was observed for BMIDA products, within $^{13}$C NMR in particular.

2. General Experimental Procedures

General Procedure A:
For example, synthesis of Compound 3
An oven-dried 5 mL microwave vial was charged with Pd(dppf)Cl₂ (7.3 mg, 10 µmol, 5 mol%), propyne boronic acid MIDA ester (39.0 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N₂ before DMSO (2 mL, 0.1 M) was added via syringe. The mixture was then stirred at 80 °C for 18 hours. The vial was allowed to cool to room temperature, decapped, and diluted with EtOAc (10 mL). The mixture was then washed with 10% aqueous LiCl solution (2 x 5 mL). The organic extract was dried over Na₂SO₄, filtered, and concentrated to give a residue that was purified by flash column chromatography (silica gel, 5–20% MeCN in DCM) to give the product as an off-white solid (48 mg, 84%).

**General procedure B:**
For example, synthesis of Compound S1

An oven-dried 20 mL microwave vial was charged with CuI (19.0 mg, 0.1 mmol, 10 mol%), Pd(dppf)Cl₂ (36.6 mg, 50 µmol, 5 mol%), 4-iodobiphenyl (336 mg, 1.20 mmol, 1.20 equiv.), and ethynyl boronic acid MIDA ester (181 mg, 1.0 mmol, 1.0 equiv.). The vial was capped and purged with N₂ before Et₃N (418 µL, 3.0 mmol, 3.0 equiv.) and DMF (5.0 mL, 0.2 M) were added via syringe. The mixture was stirred at room temperature for 18 hours before being decapped and diluted with EtOAc (50 mL). The mixture was then washed with 10% aqueous LiCl solution (2 x 25 mL). The organic extract was dried over Na₂SO₄, filtered, and concentrated to give a residue that was purified by flash column chromatography (silica gel, 5–20% MeCN in DCM) to give the product as a brown solid (241 mg, 72%).

**General procedure C:**
For example, synthesis of Compound 38

To a flame-dried 250 mL round bottom flask, ((but-3-yn-1-ylxy)methyl)benzene (6.63 g, 41.4 mmol, 1.0 equiv.) was dissolved in THF (124 mL, 0.33 M) and cooled to 0 °C. To this solution was added EtMgBr (22.6 mL, 49.7 mmol, 2.2 M in Et₂O, 1.2 equiv.) dropwise and the resulting suspension was stirred at 0 °C for 10 minutes before the ice bath was removed and stirring was continued for a further 30 minutes.

In a separate, flame-dried 500 mL round bottom flask, B(OMe)₃ (9.23 mL, 82.8 mmol, 2.0 equiv.) was dissolved in THF (100 mL, 0.82 M) and cooled to −78 °C. To this cold solution was added, via cannula, the above Grignard suspension over approximately 10 minutes. After complete addition, the reaction mixture was stirred at −78 °C for one hour before removing the dry ice/acetone bath and stirring for a further two hours as it warmed to room temperature. The flask was unstoppered and N-methyliminodiacetic acid (12.2 g, 82.8 mmol, 2.0 equiv.) was added followed by DMSO (50 mL). The flask was placed on a rotary evaporator with the water bath set at 60 °C to remove the majority of the volatiles. The flask contents were then distilled under high vacuum (<0.5 mbar, 80 °C) to remove remaining DMSO to leave a gum-like residue. To this was added 1:1 brine/H₂O (300 mL) and this was extracted with 3:2 EtOAc/acetone (2 x 300 mL). The organic layers were combined, washed with water (50 mL), dried over Na₂SO₄, filtered, and concentrated to a residue that was purified by flash column chromatography (silica gel, 0–25% MeCN in DCM) to give an off-white solid which was then triturated from EtOAc and hexane to give the product as a fluffy white solid (7.80 g, 60%).

**General procedure D:**
For example, synthesis of Compound 31

In a separate, flame-dried 500 mL round bottom flask, B(OMe)₃ (9.23 mL, 82.8 mmol, 2.0 equiv.) was dissolved in THF (100 mL, 0.82 M) and cooled to −78 °C. To this cold solution was added, via cannula, the above Grignard suspension over approximately 10 minutes. After complete addition, the reaction mixture was stirred at −78 °C for one hour before removing the dry ice/acetone bath and stirring for a further two hours as it warmed to room temperature. The flask was unstoppered and N-methyliminodiacetic acid (12.2 g, 82.8 mmol, 2.0 equiv.) was added followed by DMSO (50 mL). The flask was placed on a rotary evaporator with the water bath set at 60 °C to remove the majority of the volatiles. The flask contents were then distilled under high vacuum (<0.5 mbar, 80 °C) to remove remaining DMSO to leave a gum-like residue. To this was added 1:1 brine/H₂O (300 mL) and this was extracted with 3:2 EtOAc/acetone (2 x 300 mL). The organic layers were combined, washed with water (50 mL), dried over Na₂SO₄, filtered, and concentrated to a residue that was purified by flash column chromatography (silica gel, 0–25% MeCN in DCM) to give an off-white solid which was then triturated from EtOAc and hexane to give the product as a fluffy white solid (7.80 g, 60%).
An oven-dried 5 mL microwave vial was charged with Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), (phenylethynyl)boronic acid MIDA ester (51.4 mg, 0.2 mmol, 1.0 equiv.), N-(6-iodobenzo[d][1,3]dioxol-5-yl)acetamide (73.2 mg, 0.24 mmol, 1.2 equiv.), LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N$_2$ before DMF (2 mL, 0.1 M) was added via syringe. The mixture was then stirred at 65 °C for 48 hours. The vial was allowed to cool to room temperature, decapped, and diluted with EtOAc (10 mL). The mixture was then washed with 10% aqueous LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated to give a residue that was purified by flash column chromatography (silica gel, 8–30% MeCN in DCM) to give the product as a light brown solid (48 mg, 55%).

**General procedure E:**

For example, synthesis of Compound S2

![Chemical structure](image)

A 100 mL round bottom flask was charged with 2-iodo-3-nitrotoluen (2.63 g, 10.0 mmol, 1.0 equiv.), iron powder (4.05 g, 62.0 mmol, 6.20 equiv.), and EtOH (30 mL). The mixture was stirred vigorously while conc. HCl (37%, 0.99 mL, 12.0 mmol, 1.2 equiv.) was added dropwise. The mixture was then heated to reflux for 3 h. The mixture was allowed to cool to room temperature then diluted with EtOAc (50 mL). The mixture was filtered through a pad of celite, washing the cake with H$_2$O (50 mL). The biphasic mixture was separated, the organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated to give a residue that was purified by flash column chromatography (silica gel, 5–10% Et$_2$O in petrol) to give the product as a light pink solid (2.12 g, 91%).

3. Reaction Optimisation Data

### 3.1 Alkyl Alkynes

#### 3.1.1 Solvent

| Entry | Solvent | Yield (%) |
|-------|---------|-----------|
| 1     | DMF     | 69        |
| 2     | THF     | 0         |
| 3     | MeCN    | <5        |
| 4     | Dioxane | 0         |
| 5     | Toluene | 0         |
| 6     | Sulpholane | 0     |
| 7     | DMSO    | 76        |
3.1.2 Temperature

Reactions were carried out according to General Procedure A using Pd(OAc)$_2$ (2.2 mg, 10 µmol, 5 mol%), propyne BMIDA (39.0 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N$_2$ prior to addition of DMSO (2 mL, 0.1 M) via syringe. The reaction was stirred at X ºC for 18 h, then allowed to cool to room temperature and decapped. The reaction mixture was diluted with EtOAc (10 mL) and washed with 10% aqueous LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated. 1,4-Dinitrobenzene in DMSO-$d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.

Table S2

| Entry | Temp. (ºC) | Yield (%) |
|-------|------------|-----------|
| 1     | RT         | trace     |
| 2     | 40         | 5         |
| 3     | 60         | 42        |
| 4     | 100        | 50        |

3.1.3 Time

Reactions were carried out according to General Procedure A using Pd(OAc)$_2$ (2.2 mg, 10 µmol, 5 mol%), propyne BMIDA (39.0 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N$_2$ prior to addition of DMSO (2 mL, 0.1 M) via syringe. The reaction was stirred at 80 ºC for X h, then allowed to cool to room temperature and decapped. The reaction mixture was diluted with EtOAc (10 mL) and washed with 10% aqueous LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated. 1,4-Dinitrobenzene in DMSO-$d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.

Table S3

| Entry | Time (h) | Yield (%) |
|-------|----------|-----------|
| 1     | 2        | 49        |
| 2     | 4        | 62        |
| 3     | 6        | 65        |
| 4     | 8        | 72        |
| 5     | 24       | 73        |
3.1.4 Stoichiometry

Reactions were carried out according to General Procedure A using Pd(OAc)$_2$ (2.2 mg, 10 µmol, 5 mol%), propyne BMIDA (X equiv.), 2-iodoaniline (Y equiv.), LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N$_2$ prior to addition of DMSO (2 mL, 0.1 M) via syringe. The reaction was stirred at 80 °C for 18 h, then allowed to cool to room temperature and decapped. The reaction mixture was diluted with EtOAc (10 mL) and washed with 10% aqueous LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated. 1,4-Dinitrobenzene in DMSO-$d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.

Table S4

| Entry | X:Y (h) | Yield (%) |
|-------|---------|-----------|
| 1     | 1.5:1   | 77        |
| 2     | 2.0:1   | 74        |
| 3     | 1:1.2   | 76        |
| 4     | 1:1.5   | 72        |
| 5     | 1:2.0   | 73        |

3.1.5 Concentration

Reactions were carried out according to General Procedure A using Pd(OAc)$_2$ (2.2 mg, 10 µmol, 5 mol%), propyne BMIDA (39.0 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N$_2$ prior to addition of DMSO (X M) via syringe. The reaction was stirred at 80 °C for 18 h, then allowed to cool to room temperature and decapped. The reaction mixture was diluted with EtOAc (10 mL) and washed with 10% aqueous LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated. 1,4-Dinitrobenzene in DMSO-$d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.

Table S5

| Entry | Concentration (M) | Yield (%) |
|-------|-------------------|-----------|
| 1     | 0.05              | 66        |
| 2     | 0.1               | 72        |
| 3     | 0.2               | 67        |
| 4     | 0.5               | 55        |

3.1.6 Base

Reactions were carried out according to General Procedure A using Pd(OAc)$_2$ (5 mol%), propyne BMIDA (5 mol%), LiCl (2 equiv), NaOAc (2.5 equiv), DMF (0.1 M) at 80 °C for 18 h. The vial was capped and purged with N$_2$ prior to addition of DMSO (0.1 M) via syringe. The reaction was stirred at 80 °C for 18 h, then allowed to cool to room temperature and decapped. The reaction mixture was diluted with EtOAc (10 mL) and washed with 10% aqueous LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated. 1,4-Dinitrobenzene in DMSO-$d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.
Reactions were carried out according to General Procedure A using Pd(OAc)$_2$ (2.2 mg, 10 µmol, 5 mol%), propyne BMIDA (39.0 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.), and base (0.5 mmol, 2.5 equiv.). The vial was capped and purged with N$_2$ prior to addition of DMSO (2 mL, 0.1 M) via syringe. The reaction was stirred at 80 °C for 18 h, then allowed to cool to room temperature and decapped. The reaction mixture was diluted with EtOAc (10 mL) and washed with 10% aqueous LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated. 1,4-Dinitrobenzene in DMSO-$d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.

Table S6

| Entry | Base          | Yield (%) |
|-------|---------------|-----------|
| 1     | KOAc (49.1 mg) | 78        |
| 2     | LiOAc (33.0 mg) | 77        |
| 3     | K$_3$PO$_4$ (106.2 mg) | 17        |
| 4     | K$_2$CO$_3$ (69.1 mg) | <5        |
| 5     | Et$_3$N (70.0 µL) | 71        |

3.1.7 Salt

Reactions were carried out according to General Procedure A using Pd(OAc)$_2$ (2.2 mg, 10 µmol, 5 mol%), propyne BMIDA (39.0 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), salt (0.4 mmol, 2.0 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N$_2$ prior to addition of DMSO (2 mL, 0.1 M) via syringe. The reaction was stirred at 80 °C for 18 h, then allowed to cool to room temperature and decapped. The reaction mixture was diluted with EtOAc (10 mL) and washed with 10% aq. LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated. 1,4-Dinitrobenzene in DMSO-$d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.

Table S7

| Entry | Salt           | Yield (%) |
|-------|----------------|-----------|
| 1     | LiF (10.4 mg)  | 77        |
| 2     | NaCl (23.4 mg) | 77        |
| 3     | KCl (29.8 mg)  | 82        |
| 4     | TBACl hydrate (111.2 mg) | 56        |

3.1.8 Salt/base Stoichiometry

Reactions were carried out according to General Procedure A using Pd(OAc)$_2$ (2.2 mg, 10 µmol, 5 mol%), propyne BMIDA (39.0 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), LiCl (X equiv.), and NaOAc (Y equiv.). The vial was capped and purged with N$_2$ prior to addition of DMSO (2 mL, 0.1 M) via syringe. The reaction was stirred at 80 °C for 18 h, then allowed to cool to room temperature and decapped. The reaction mixture was diluted with EtOAc (10 mL) and washed with 10% aq. LiCl solution (2 x 5 mL).
5 mL). The organic extract was dried over Na₂SO₄, filtered, and concentrated. 1,4-Dinitrobenzene in DMSO-
$^d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.

Table S8

| Entry | LiCl:NaOAc (equiv.) | Yield (%) |
|-------|---------------------|-----------|
| 1     | 2:3 (17.0: 49.2 mg) | 82        |
| 2     | 2:1 (17.0: 16.4 mg) | 79        |
| 3     | 2:0.5 (17.0: 8.2 mg)| 45        |
| 4     | 2:0 (17.0 mg)       | 7         |
| 5     | 3:2.5 (25.4 mg: 41 mg) | 78    |
| 6     | 1:2.5 (8.5 mg: 41 mg)| 83        |
| 7     | 0.5:2.5 (4.2: 41 mg)| 83        |
| 8     | 0:2.5 (41 mg)       | 66        |

3.1.9 Pd Catalyst

Reactions were carried out according to General Procedure A using Pd catalyst (10 µmol, 5 mol%), propyne
BMIDA (39.0 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), LiCl (17.0 mg, 0.4
mmol, 2.0 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N₂
prior to addition of DMSO (2 mL, 0.1 M) via syringe. The reaction was stirred at 80 °C for 18 h, then allowed
to cool to room temperature and decapped. The reaction mixture was diluted with EtOAc (10 mL) and washed
with 10% aq. LiCl solution (2 x 5 mL). The organic extract was dried over Na₂SO₄, filtered, and concentrated.
1,4-Dinitrobenzene in DMSO-$^d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed
by $^1$H NMR.

Table S9

| Entry | Pd catalyst | Yield (%) |
|-------|-------------|-----------|
| 1     | PdCl₂(1.8 mg)| 85        |
| 2     | Pd(dppf)Cl₂(7.3 mg)| 87    |
| 3     | Pd(PPh₃)₄(11.6 mg)| 10    |
| 4     | [Pd(allyl)Cl]₂(1.8 mg)| 84    |
| 5     | Pd(MeCN)₂Cl₂(2.6 mg)| 85    |
| 6     | Pd(PPh₃)₂Cl₂(7.0 mg)| 62    |

3.2 Aryl Alkynes

3.2.1 NaOAc/Temperature

Reactions were carried out according to General Procedure D using Pd(dppf)Cl₂ (1.8 mg, 10 µmol, 5 mol%),
(phenylethynyl)boronic acid MIDA ester (51.4 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol,
1.2 equiv.), and NaOAc (X equiv.). The vial was capped and purged with N₂ before DMSO (2 mL, 0.1 M) was
added via syringe. The mixture was then stirred at Y °C for 18 hours. The vial was allowed to cool to room
temperature, and decapped. The mixture was diluted with EtOAc (10 mL) and washed with 10% aq. LiCl
solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated. 1,4-Dinitrobenzene in DMSO-$d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.

Table S10

| Entry | NaOAc (equiv.) | Temp. (°C) | Yield (%) | Remaining 2b (%) |
|-------|----------------|------------|-----------|-----------------|
| 1     | 1.2 (20 mg)    | 80         | 14        | 65              |
| 2     | 2.5 (41 mg)    | 80         | 16        | 58              |
| 3     | 1.2 (20 mg)    | 100        | 37        | 25              |
| 4     | 2.5 (41 mg)    | 100        | 35        | 24              |
| 5     | 1.2 (20 mg)    | 120        | 41        | 5               |
| 6     | 2.5 (41 mg)    | 120        | 30        | 7               |
| 7     | 1.2 (20 mg)    | 140        | 37        | 8               |
| 8     | 2.5 (41 mg)    | 140        | 14        | 2               |

3.2.2 Temperature/Time

Reactions were carried out according to General Procedure D using Pd(dppf)Cl$_2$ (1.8 mg, 10 µmol, 5 mol%), (phenylethynyl)boronic acid MIDA ester (51.4 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N$_2$ before DMSO (2 mL, 0.1 M) was added via syringe. The mixture was then stirred at X °C for Y hours. The vial was allowed to cool to room temperature, and decapped. The mixture was diluted with EtOAc (10 mL) and washed with 10% aq. LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated.

Table S11

| Entry | Temp. (°C) | Time (h) | Yield (%) | Remaining 2b (%) |
|-------|------------|----------|-----------|-----------------|
| 1     | 80         | 48       | 23        | 45              |
| 2     | 80         | 72       | 25        | 38              |
| 3     | 100        | 48       | 39        | 12              |
| 4     | 100        | 72       | 25        | 12              |

3.2.3 Pd Catalyst

Reactions were carried out according to General Procedure D using Pd catalyst (10 µmol, 5 mol%), (phenylethynyl)boronic acid MIDA ester (51.4 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N$_2$ before DMSO (2 mL, 0.1 M) was added via syringe. The mixture was then stirred at 80 °C for 18 hours. The vial was allowed to cool to room temperature and decapped. The mixture was diluted with EtOAc (10 mL) and washed with 10% aq. LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated.
1,4-Dinitrobenzene in DMSO-$d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.

Table S12

| Entry | Catalyst | Yield (%) | Remaining 2b (%) |
|-------|----------|-----------|------------------|
| 1     | PdCl$_2$ (1.8 mg) | 34        | 30               |
| 2     | [Pd(allyl)Cl]$_2$ (1.8 mg) | 47        | 32               |
| 3     | Pd(MeCN)$_2$Cl$_2$ (2.6 mg) | 29        | 43               |

3.2.4 Aniline/Anilide with LiCl

Reactions were carried out according to General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), (phenylethynyl)boronic acid MIDA ester (51.4 mg, 0.2 mmol, 1.0 equiv.), aniline/anilide (0.24 mmol, 1.2 equiv.), LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). The vial was capped and purged with N$_2$ before solvent (2 mL, 0.1 M) was added via syringe. The mixture was then stirred at X °C for Y hours. The vial was allowed to cool to room temperature and decapped. The mixture was diluted with EtOAc (10 mL) and washed with 10% aq. LiCl solution (2 x 5 mL). The organic extract was dried over Na$_2$SO$_4$, filtered, and concentrated. 1,4-Dinitrobenzene in DMSO-$d_6$ (0.05 M, 1 mL) was added to the crude product and an aliquot was analysed by $^1$H NMR.

Table S13

| Entry | R | Solvent | Temp. (°C) | Time (h) | Yield (%) | Remaining 2b (%) |
|-------|---|---------|------------|----------|-----------|------------------|
| 1     | H (1a) | DMF     | 65         | 24       | 38        | 44               |
| 2     | Ac (1b) | DMF     | 65         | 24       | 55        | 20               |
| 3     | Ac (1b) | DMF     | 65         | 48       | 60$^a$   | 20               |
| 4     | Ts (S27) | DMF     | 65         | 48       | n.d.     | 72               |
| 5     | Ac (1b) | DMSO    | 80         | 18       | 11        | 52               |

$^a$Isolated yield.

4. Characterization Data

4.1 Synthesis of Starting Materials and Intermediates

Compound S1

Prepared according to General Procedure B using Pd(dppf)Cl$_2$ (36.6 mg, 50 µmol, 5 mol%) 4-iodobiphenyl (336 mg, 1.20 mmol, 1.20 equiv.) CuI (19.0 mg, 100 µmol, 10 mol%), acetylene boronic acid MIDA ester (181 mg, 1.0 mmol, 1.0 equiv.), and Et$_3$N (418 µL, 3.0 mmol, 3.0 equiv.). Stirred at 50 °C for 17 h. Flash column chromatography (5–20% MeCN in DCM) gave the product as a brown solid (241 mg, 72%).

$^1$H NMR (500 MHz, Acetone-$d_6$): δ 7.72 – 7.64 (m, 4H), 7.62 – 7.53 (m, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.35 (m, 1H), 4.35 (d, J = 17.0 Hz, 2H), 4.20 (d, J = 16.9 Hz, 2H), 3.35 (s, 3H).

$^{13}$C NMR (126 MHz, Acetone-$d_6$): δ 168.6, 142.0, 140.8, 133.1, 129.8, 128.7, 127.7, 127.7, 122.9, 62.4, 48.5. The carbon bearing boron was not observed.
$^{11}$B NMR (96 MHz, Acetone-$d_6$): $\delta$ 6.5.

$\nu_{\text{max}}$(solid): 3024, 2191, 1765, 1483, 1288, 1254, 1020, 1005 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+Na]$^+$ Calcd for C$_{19}$H$_{16}$BNaO$_4$ 356.1070; Found 356.1067.

**Compound S2**

![Structure](image)

Prepared according to General procedure E using 2-iodo-3-nitrotoluene (2.63 g, 10.0 mmol, 1.0 equiv.), iron powder (4.05 g, 62.0 mmol, 6.20 equiv.), and conc. HCl (37%, 0.99 mL, 12.0 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 5–10% Et$_2$O in petrol) gave the product as a light pink solid (2.12 g, 91%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.03 – 7.00 (m, 1H), 6.65 (dd, $J = 7.3$, 1.6 Hz, 1H), 6.58 (dd, $J = 7.9$, 1.5 Hz, 1H), 4.09 (br s, 2H), 2.43 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 147.2, 142.5, 128.6, 119.7, 112.0, 91.7, 29.4.

Spectral data in agreement with literature values.

**Compound S3**

![Structure](image)

Prepared according to General Procedure C using cyclopropylacetylene (2.54 mL, 30 mmol, 1.0 equiv.), EtMgBr (3.0 M in Et$_2$O, 12 mL, 36.0 mmol 1.2 equiv.), B(OMe)$_3$ (6.69 mL, 60 mmol, 2.0 equiv.), and $N$-methyliminodiacetic acid (8.83 g, 60.0 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 10–30% MeCN in DCM) gave the product as a white solid (3.83 g, 58%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 4.20 (d, $J = 17.1$ Hz, 2H), 4.01 (d, $J = 17.1$ Hz, 2H), 2.92 (s, 3H), 1.36 – 1.29 (m, 1H), 0.82 – 0.73 (m, 2H), 0.63 – 0.61 (m, 2H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 168.8, 104.6, 61.3, 47.7, 8.2, –0.2. The carbon bearing boron was not observed.

$^{11}$B NMR (160 MHz, DMSO-$d_6$): $\delta$ 5.8.

$\nu_{\text{max}}$(solid): 3013, 2369, 2205, 1765, 1464, 1450, 1422 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+Na]$^+$ Calcd for C$_{10}$H$_{12}$BNaNO$_4$ 244.0757; Found 244.0753.

**Compound S4**

![Structure](image)

Prepared according to General Procedure C using 1-pentyne (0.99 mL, 10 mmol, 1.0 equiv.), EtMgBr (3.0 M in Et$_2$O, 4 mL, 12 mmol, 1.2 equiv.), B(OMe)$_3$ (2.23 mL, 20 mmol, 2.0 equiv.), and $N$-methyliminodiacetic acid (2.95 g, 20 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 10–30% MeCN in DCM) gave the product as a white solid (1.10 g, 49%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.09 – 4.00 (m, 2H), 3.79 (d, $J = 16.8$ Hz, 2H), 3.08 (s, 3H), 2.20 (t, $J = 7.1$ Hz, 2H), 1.57 – 1.50 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 168.1, 103.9, 61.3, 48.0, 22.0, 21.5, 13.7. The carbon bearing boron was not observed.

$^{11}$B NMR (160 MHz, CDCl$_3$): $\delta$ 6.3.

$\nu_{\text{max}}$(solid): 3019, 2189, 1767, 1514, 1464, 1450, 1422 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+H]$^+$ Calcd for C$_{10}$H$_{15}$BNaO$_4$ 224.1094; Found 224.1088.

**Compound S5**

![Structure](image)
Prepared according to General Procedure C using tert-butyl(dimethyl)silyl chloride (5.11 g, 30.0 mmol 1.0 equiv.), EtMgBr (3.08 M in Et₂O, 11.7 mL, 36.0 mmol, 1.2 equiv.), B(OEt)₃ (6.69 mL, 60.0 mmol, 2.0 equiv.), and N-methylimidodiacetic acid (8.83 g, 60.0 mmol, 2.0 equiv.). Flash column chromatography (silica gel 10–30% MeCN in DCMe) gave the product as a white solid (2.47 g, 25%).

1H NMR (500 MHz, DMSO-d₆): δ 8.32 (s, 2H), 4.23 (d, J = 17.2 Hz, 2H), 4.07 (d, J = 17.2 Hz, 2H), 2.97 (s, 3H), 0.86 (s, 9H), 0.09 (s, 6H).

Spectral data in agreement with literature values.

**Compound S6**

A mixture of benzocaine (826 mg, 5.00 mmol, 1.00 equiv.), potassium periodate (1.15 g, 5.00 mmol, 1.00 equiv.), NaCl (584 mg, 10.0 mmol, 2.00 equiv.) and KI (830 mg, 5.00 mmol, 1.00 equiv.) was stirred vigorously in AcOH/H₂O (9:1, 10 mL) at room temperature for 24 h. EtOAc (25 mL) was then added, and the layers were separated. The organic extract was washed successively with brine (10 mL), sat. aq. Na₂S₂O₅ (10 mL), and sat. aq. NaHCO₃ (10 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated to a residue that was purified by flash column chromatography (silica gel, 10–30% Et₂O in hexane) to afford the product as a white solid (1.26 g, 87%).

1H NMR (500 MHz, CDCl₃): δ 8.33 (d, J = 1.9 Hz, 1H), 7.82 (dd, J = 8.4, 1.9 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 4.52 (s, 2H), 4.31 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H).

13C NMR (126 MHz, CDCl₃): δ 165.5, 150.7, 141.1, 131.3, 121.7, 113.2, 82.3, 60.8, 14.5.

Spectral data in agreement with literature values.³

**Compound S7**

Prepared according to General procedure E using 2-iodo-5-fluoronitrobenzene (1.33 g, 5.00 mmol, 1.0 equiv.), iron powder (2.03 g, 31.0 mmol, 6.20 equiv.), and conc. HCl (37%, 493 µL, 12.0 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 2–4% Et₂O in petrol) gave the product as a pale yellow solid (902 mg, 76%).

1H NMR (500 MHz, CDCl₃): δ 7.56 – 7.53 (m, 1H), 6.48 – 6.45 (m, 1H), 6.28 – 6.24 (m, 1H), 4.19 (br s, 2H).

13C NMR (126 MHz, CDCl₃): δ 164.1 (d, J = 244.8 Hz), 148.2 (d, J = 11.0 Hz), 139.8 (d, J = 9.6 Hz), 107.3 (d, J = 22.2 Hz), 101.7 (d, J = 25.6 Hz), 77.1 (d, J = 2.6 Hz).

19F NMR (470 MHz, CDCl₃): δ −113.4.

Spectral data in agreement with literature values.⁴

**Compound S8**

A mixture of 2,3-dimethoxyaniline (157 mg, 1.02 mmol, 1.00 equiv.) in Et₂O (6.8 mL, 0.15 M) and sat. aq. Na₂CO₃ (2 mL) was stirred vigorously in the dark at room temperature. A solution of ICl (271 mg, 1.67 mmol, 1.63 equiv.) in Et₂O (2 mL) was added in one portion and the mixture was stirred for 3 h at room temperature. The layers were separated, and the organic extract was washed successively with sat. aq. Na₂S₂O₅ (10 mL) and sat. aq. NaHCO₃ (10 mL). The organic extract was dried over Na₂SO₄, filtered, and concentrated to a residue...
that was purified by flash column chromatography (silica gel, 2.5–5% acetone in hexane) to give the product as a pale yellow oil which solidified on standing (146 mg, 51%).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.30 (d, $J = 8.8$ Hz, 1H), 6.18 (d, $J = 8.8$ Hz, 1H), 4.25 (s, 2H), 3.83 (s, 3H), 3.82 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 153.2, 141.7, 135.4, 133.2, 104.3, 74.0, 60.0, 56.0.

Spectral data in agreement with literature values.$^5$

**Compound S9**

Prepared according to General Procedure C with 1,7-octadiyne (1.33 mL, 10.0 mmol, 1.0 equiv.), EtMgBr (2.85 M in Et$_2$O, 8.42 mL, 2.4 equiv.), B(OMe)$_3$ (4.46 mL, 40.0 mmol, 2.0 equiv.), and N-methyliminodiacetic acid (5.89 g, 40.0 mmol, 4.0 equiv.). Flash column chromatography (silica gel 10–60% MeCN in DCM) gave the product as a white solid (448 mg, 11%).

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 4.23 (d, $J = 17.2$ Hz, 4H), 4.03 (d, $J = 17.1$ Hz, 4H), 2.95 (s, 6H), 2.27–2.21 (m, 4H), 1.56–1.54 (m, 4H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$): δ 168.7, 101.3, 61.3, 47.7, 27.2, 18.3.

The carbon bearing boron is not observed due to quadrupolar relaxation.

$^{11}$B NMR (96 MHz, DMSO-d$_6$): δ 6.3.

$\nu_{\text{max}}$ (solid): 1749, 1454, 1339, 1290, 1167, 1140, 1022, 1005 cm$^{-1}$.

HRMS (ESI) $m/z$: [M–H]$^-$ Calcd for C$_{18}$H$_{21}$B$_2$N$_2$O$_8$ 415.1490; Found 415.1490.

**Compound S10**

A slurry of NaH (60% dispersion in mineral oil, 3.0 g, 75 mmol, 1.5 equiv.) in THF (100 mL, 0.36 M) and DMF (40 mL, 0.36 M) was cooled to 0 °C and stirred. To this was added 3-butyln-1-ol (3.50 g, 50 mmol, 1.0 equiv.) dropwise via syringe. The reaction mixture was then stirred at 0 °C for 30 min before allowing to warm to room temperature where it was stirred for 30 min. The mixture was then cooled to 0 °C prior to addition of benzyl bromide (8.9 mL, 75 mmol, 1.5 equiv.). The reaction mass was then allowed to warm to room temperature and stirred for a further 4 h before being quenched with saturated aq. NH$_4$Cl (20 mL). The layers were separated, and the aqueous layer was extracted with Et$_2$O (2 x 250 mL). The combined organics were then washed with water, dried over Na$_2$SO$_4$, filtered, and concentrated to give a residue that was purified by flash column chromatography (silica gel, 0–10% Et$_2$O in hexane) to give the product as a colourless oil (8.19 g, >99%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.38–7.32 (m, 4H), 7.32–7.26 (m, 1H), 4.57 (s, 2H), 3.61 (t, $J = 6.9$ Hz, 2H), 2.51 (td, $J = 6.9, 2.7$ Hz, 2H), 2.00 (t, $J = 2.7$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 138.1, 128.5, 127.8, 127.8, 81.4, 73.1, 69.5, 68.2, 20.0. Spectral data in agreement with literature values.$^6$

**Compound S11**

Prepared using General Procedure C using phenyl propargyl ether (1.59 g, 12 mmol, 1 equiv.), EtMgBr (3.05 M in Et$_2$O, 4.72 mL, 14.4 mmol, 1.2 equiv.), B(OMe)$_3$ (2.68 mL, 24 mmol, 2 equiv.), and N-methyliminodiacetic acid (3.53 g, 24 mmol, 2 equiv.). Flash column chromatography (silica gel, 0–10% MeCN in DCM) gave the product as an off-white solid (1.05 g, 30%).

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 7.33–7.28 (m, 2H), 7.00–6.95 (m, 3H), 4.82 (s, 2H), 4.26 (d, $J = 17.2$ Hz, 2H), 4.05 (d, $J = 17.1$ Hz, 2H), 2.91 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$): δ 168.6, 157.3, 129.5, 121.2, 114.9, 95.5, 61.5, 55.9, 47.8. The carbon bearing boron was not observed.
$^{11}$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 6.1.

$\nu_{\text{max}}$ (solid): 3215, 1768, 1492, 1134, 1028, 752, 688 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+Na]$^+$ Calcd for C$_{14}$H$_{14}$BNO$_5$Na 310.0863; Found 310.0851.

**Compound S12**

A solution of 4-amino-3-iodobenzyl alcohol (400 mg, 1.61 mmol, 1.0 equiv.) and imidazole (153 mg, 2.24 mmol, 1.40 equiv.) in DCM (4.9 mL, 0.33 M) was treated with tert-butyldimethylsilyl chloride (290 mg, 1.93 mmol, 1.20 equiv.). The reaction mixture was stirred at room temperature for 24 h then filtered through a plug of silica, eluting with EtOAc/hexane (1/1, 100 mL). The filtrate was concentrated to give the product as a brown oil (570 mg, 98%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.60 (dd, $J$ = 1.9, 0.9 Hz, 1H), 7.12 – 7.06 (m, 1H), 6.71 (d, $J$ = 8.1 Hz, 1H), 4.58 (d, $J$ = 0.9 Hz, 2H), 4.04 (br s, 2H), 0.93 (s, 9H), 0.09 (s, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 145.8, 137.1, 133.3, 127.8, 114.6, 84.1, 64.2, 26.1, 18.5, −5.0.

Spectral data in agreement with literature values.

**Compound S13**

Prepared according to General Procedure B using 4-iodoanisole (155 mg, 663 µmol, 1.2 equiv.), Pd(dppf)Cl$_2$ (20.2 mg, 27.6 µmol, 5 mol%), CuI (10.5 mg, 55.3 µmol, 0.1 equiv.), acetylene boronic acid MIDA ester (100 mg, 553 µmol, 1 equiv.), and Et$_3$N (0.231 mL, 1.66 mmol, 3 equiv.). Flash column chromatography (5–30% MeCN in DCM) gave the product as a light brown solid (115 mg, 72%).

$^1$H NMR (500 MHz, CD$_2$CN): $\delta$ 7.42 (d, $J$ = 8.7 Hz, 2H), 6.94 (d, $J$ = 8.8 Hz, 2H), 4.30 (d, $J$ = 17.2 Hz, 2H), 4.12 (d, $J$ = 17.1 Hz, 2H), 3.77 (s, 3H), 3.05 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$CN): $\delta$ 168.7, 159.1, 129.8, 124.0, 123.5, 116.3, 115.4, 99.3, 61.5, 55.2, 47.9.

The carbon bearing boron was not observed.

$^1$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 6.5.

$\nu_{\text{max}}$ (solid): 2183, 1749, 1574, 1464, 1290, 1005 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+H]$^+$ Calcd for C$_{14}$H$_{13}$BNO$_5$ 288.1043; Found 288.1039.

**Compound S14**

Prepared according to General Procedure B using 3-iodoanisole (155 mg, 663 µmol, 1.2 equiv.), Pd(dppf)Cl$_2$ (20.2 mg, 27.6 µmol, 5 mol%), CuI (10.5 mg, 55.3 µmol, 10 mol%), acetylene boronic acid MIDA ester (100 mg, 553 µmol, 1 equiv.), and Et$_3$N (0.231 mL, 1.66 mmol, 3 equiv.). Flash column chromatography (5–30% MeCN in DCM) gave the product as a white solid (92 mg, 57%).

$^1$H NMR (500 MHz, CD$_2$CN): $\delta$ 7.32 – 7.27 (m, 1H), 7.10 – 6.94 (m, 3H), 4.32 (d, $J$ = 17.2 Hz, 2H), 4.14 (d, $J$ = 17.2 Hz, 2H), 3.76 (s, 3H), 3.06 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_2$CN): $\delta$ 168.7, 159.1, 129.8, 124.0, 123.5, 116.3, 115.4, 99.3, 61.5, 55.2, 47.9. The carbon bearing boron was not observed.

$^1$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 6.3.

$\nu_{\text{max}}$ (solid): 3013, 2197, 1767, 1574, 1464, 1290, 1202, 1018 cm$^{-1}$.

HRMS (ESI) $m/z$: [M–H] Calcd for C$_{14}$H$_{13}$BNO$_5$ 286.0892; Found 286.0891.
Prepared according to General Procedure B using Pd(PPh₃)₂Cl₂ (35.1 mg, 0.05 mmol, 5 mol%), acetylene boronic acid MIDA ester (181.0 mg, 1 mmol, 1.0 equiv.), 2-iodothiophene (133 µL, 1.2 mmol, 1.2 equiv.), CuI (19.1 mg, 0.1 mmol, 10 mol%), and Et₃N (420 µL, 3.0 mmol, 3.0 equiv.). Flash column chromatography (silica gel, 5–25% MeCN in DCM) gave the product as a beige solid (516 mg, 76%).

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₁H₁₀BNNaO₅S 286.0321; Found 286.0317.

**Compound S16**

Prepared using General Procedure B using 4-fluoriodobenzene (444 mg, 2 mmol, 1 equiv.), Pd(PPh₃)₂Cl₂ (70.2 mg, 0.1 µmol, 5 mol%), CuI (38.1 mg, 0.2 mmol, 10 mol%), acetylene boronic acid MIDA ester (434 mg, 2.40 mmol, 1.2 equiv.), and Et₃N (0.84 mL, 6 mmol, 3 equiv.). After work-up, the crude material was triturated with EtO to afford the product as an off-white solid (522 mg, 95%).

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₃H₁₀BFNO₂Na 298.0657; Found 298.0655.

**Compound S17**

Prepared according to General Procedure B using 4-iodonitrobenzene (388 mg, 1.56 mmol, 1.20 equiv.), Pd(dppf)Cl₂ (47.6 mg, 65.0 µmol, 5 mol%), CuI (24.8 mg, 130 µmol, 10 mol%), acetylene boronic acid MIDA ester (235 mg, 1.30 mmol, 1 equiv.), and Et₃N (0.544 mL, 3.90 mmol, 3 equiv.). Flash column chromatography (5–30% MeCN in DCM) gave the product as a yellow solid (323 mg, 82%).

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₃H₁₁BFNO₂Na 325.0603; Found 325.0608.

**Compound S18**

Prepared using General Procedure B using 5-iodo-N-acyl-indole (570 mg, 2 mmol, 1 equiv.), Pd(PPh₃)₂Cl₂ (70.2 mg, 0.1 µmol, 5 mol%), CuI (38.1 mg, 0.2 mmol, 10 mol%), acetylene boronic acid MIDA ester (434 mg, 2.40 mmol, 1.2 equiv.), and Et₃N (0.84 mL, 6 mmol, 3 equiv.). Flash column chromatography (silica gel, 20% MeCN in DCM) gave the product as a beige solid (516 mg, 76%).
1H NMR (400 MHz, DMSO-d6): δ 8.31 (d, J = 8.6 Hz, 1H), 7.92 (d, J = 3.8 Hz, 1H), 7.78 (dd, J = 1.6, 0.7 Hz, 1H), 7.43 (dd, J = 8.6, 1.7 Hz, 1H), 6.75 (dd, J = 3.8, 0.7 Hz, 1H), 4.32 (d, J = 17.2 Hz, 2H), 4.15 (d, J = 17.1 Hz, 2H), 3.09 (s, 3H), 2.65 (s, 3H).

13C NMR (126 MHz, DMSO-d6): δ 169.7, 168.8, 134.6, 130.3, 128.5, 128.0, 124.4, 117.3, 116.0, 107.9, 100.1, 61.5, 47.9, 23.8. The carbon bearing boron was not observed.

B NMR (96 MHz, DMSO-d6): δ 7.2.

υmax (solid): 1776, 1755, 1712, 1463, 1217, 1022, 894, 715 cm⁻¹.

HRMS (ESI) m/z [M+Na]⁺ Calcd for C₁₇H₁₅BN₂O₃Na 361.0972; Found 361.0957.

**Compound S19**

To a mixture of 4-fluoro-2-iodoaniline (237 mg, 1.00 mmol, 1.00 equiv.) and Et₃N (307 µL, 2.2 mmol, 2.2 equiv.) in DCM (5 mL, 0.2 M) was added Ac₂O (113 µL, 1.2 mmol, 1.2 equiv.) dropwise. The mixture was heated to reflux for 24 h then cooled to room temperature. The mixture was treated with sat. aq. NaHCO₃ (10 mL) and the layers were separated. The aqueous layer was extracted with DCM (10 mL). The combined organic extracts were dried over Na₂SO₄, filtered, and concentrated to a residue that was purified by flash column chromatography (silica gel, 30–50% EtOAc in hexane) to afford the product as a beige solid (241 mg, 89%).

1H NMR (400 MHz, CDCl₃): δ 8.09 (dd, J = 9.1, 5.5 Hz, 1H), 7.50 (dd, J = 7.7, 2.9 Hz, 1H), 7.26 (br s, 1H), 7.08 (dd, J = 9.1, 7.8, 2.9 Hz, 1H), 2.23 (s, 3H).

13C NMR (126 MHz, CDCl₃): δ 168.4, 158.8 (d, J = 48.9 Hz), 134.9 (d, J = 3.1 Hz), 125.5 (d, J = 24.8 Hz), 123.3 (d, J = 7.9 Hz), 116.2 (d, J = 21.7 Hz), 89.9 (d, J = 8.3 Hz), 24.8.

19F NMR (471 MHz, CDCl₃): δ –116.1.

Spectral data in agreement with literature values.⁸

**Compound S20**

A solution of 4-methyl-2-iodoaniline (1.17 g, 5.00 mmol, 1.00 equiv.) and Et₃N (767 µL, 5.50 mmol, 1.10 equiv.) in DCM (16.7 mL, 0.33 M) was cooled to 0 °C. AcCl (945 µL, 13.0 mmol, 2.60 equiv.) was added dropwise and the mixture was allowed to warm to room temperature and stir for 68 h. Methanol (10 mL) was added and the mixture was stirred for 10 min before water (20 mL) was added. The layers were separated, and the aqueous layer was extracted with DCM (20 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated to give a residue that was purified by flash column chromatography (silica gel, 20–40% EtOAc in hexanes) to give the product as a pale yellow solid (1.03 g, 75%).

1H NMR (500 MHz, CDCl₃): δ 8.02 (d, J = 8.3 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.32 (br s, 1H), 7.16 – 7.12 (m, 1H), 2.28 (s, 3H), 2.23 (s, 3H).

13C NMR (126 MHz, CDCl₃): δ 168.3, 139.1, 136.2, 135.9, 130.1, 122.1, 90.3, 24.9, 20.5.

Spectral data in agreement with literature values.⁹

**Compound S21**

To a mixture of 2-fluoro-5-iodoaniline (510 mg, 2.15 mmol, 1.00 equiv.) and Et₃N (330 µL, 2.37 mmol, 1.10 equiv.) in DCM (7.2 mL, 0.3 M) at 0 °C, was added AcCl (406 µL, 5.59 mmol, 2.60 equiv.) dropwise. The mixture was allowed to warm to room temperature and stir for 66 hours. MeOH (10 mL) was then added, followed by H₂O (20 mL). The layers were separated, and the aqueous layer extracted with DCM (20 mL). The combined organic extracts were dried over Na₂SO₄, filtered, and concentrated to give a residue that was purified...
by flash column chromatography (silica gel, 10–30% EtOAc in hexane) to give the product as a white solid (349 mg, 58%).

\[ \text{H NMR (500 MHz, CDCl}_3\text{): } \delta 8.17 - 8.15 (m, 1H), 7.72 - 7.69 (m, 1H), 7.47 (br s, 1H), 6.65 - 6.62 (m, 1H), 2.25 (s, 3H). \]

\[ \text{C NMR (126 MHz, CDCl}_3\text{): } \delta 168.4, 163.4 (d, \text{ }^3J = 246.4 \text{ Hz}), 139.6 (d, \text{ }^3J = 11.7 \text{ Hz}), 139.2 (d, \text{ }^3J = 8.9 \text{ Hz}), 113.1 (d, \text{ }^2J = 22.7 \text{ Hz}), 109.3 (d, \text{ }^2J = 28.4 \text{ Hz}), 81.9, 25.1. \]

\[ \text{F NMR (471 MHz, CDCl}_3\text{): } \delta -110.5. \]

Spectral data in agreement with literature values.

**Compound S22**

\[
\text{HNAC} \quad \begin{array}{c}
\text{O} \\
\text{I} \\
\text{NHAc}
\end{array}
\]

To a solution of benzo[d][1,3]dioxol-5-amine (960 mg, 7.00 mmol, 1.0 equiv.) in 1,4-dioxane (10 mL, 0.07 M) at 0 °C, was added acetic anhydride (79.4 µL, 8.40 mmol, 1.2 equiv.). The resulting mixture was allowed to warm to room temperature and stirred for 3 h. MeOH was then added and the resulting mixture stirred at room temperature for 10 min, then concentrated to give a residue that was purified by flash column chromatography (silica gel, 30–50%) EtOAc in petroleum ether to give the product as a grey/brown solid (1.11 g, 89%).

\[ \text{H NMR (500 MHz, CDCl}_3\text{): } \delta 7.21 (d, \text{ }^1J = 1.9 \text{ Hz, 1H}), 7.11 (br s, 1H), 6.77 - 6.71 (m, 2H), 5.95 (s, 2H), 2.15 (s, 3H). \]

\[ \text{C NMR (126 MHz, CDCl}_3\text{): } \delta 168.3, 147.9, 144.4, 132.1, 113.3, 108.2, 103.1, 101.4, 24.6. \]

Spectral data in agreement with literature values.

**Compound S23**

\[
\text{HNAC} \quad \begin{array}{c}
\text{O} \\
\text{I} \\
\text{NHAc}
\end{array}
\]

To a mixture of 3,4-(methylenedioxy)acetanilide (1.12 g, 6.23 mmol, 1.1 equiv.) and AcOH (971 µL, 17.0 mmol, 3.0 equiv.) in DCM (13.5 mL, 0.42 M) at room temperature was added a solution of ICl in DCM (919 mg, 5.66 mmol, 1.0 equiv., 0.57 M) via syringe. After 24 h, sat. aq. Na₂S₂O₅ was added, and the layers were separated. The aqueous layer was extracted with DCM (10 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated to give a residue that was purified by flash column chromatography (silica gel, 20–30% EtOAc in petrol) to give the product as a white solid (500 mg, 29%).

\[ \text{H NMR (500 MHz, DMSO-d}_6\text{): } \delta 9.37 (s, 1H), 7.37 (s, 1H), 6.95 (s, 1H), 6.06 (s, 2H), 2.00 (s, 3H). \]

\[ \text{C NMR (126 MHz, DMSO-d}_6\text{): } \delta 168.5, 147.9, 146.3, 133.7, 116.9, 108.6, 102.1, 86.0, 23.1. \]

υ\text{max (solid): } 3244, 1645, 1533, 1476, 1234 \text{ cm}^{-1}.

HRMS (ESI) m/z: [M+Na]\text{]}^+ Calcd for C₉H₈INaO₃ 327.9447; Found 327.9429.

**Compound S24**

\[
\text{NHAc} \quad \begin{array}{c}
\text{O} \\
\text{I} \\
\text{NH}_2
\end{array}
\]

A mixture of S23 (458 mg, 1.50 mmol, 1.0 equiv.) and NaOH pellets (3.00 g, 75.0 mmol, 55 equiv.) in EtOH/H₂O (4.4/1, 75 mL, 0.02 M) was refluxed for 4 h. The reaction mixture was concentrated to give a crude residue, which was treated with water (10 mL) and extracted with DCM (5 x 10 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated to give the product as a beige solid (360 mg, >99%).

\[ \text{H NMR (500 MHz, CDCl}_3\text{): } \delta 7.05 (s, 1H), 6.38 (s, 1H), 5.88 (s, 2H), 3.85 (br s, 2H). \]

\[ \text{C NMR (126 MHz, CDCl}_3\text{): } \delta 149.3, 141.8, 141.3, 117.4, 101.3, 97.0, 70.9. \]

υ\text{max (solid): } 3304, 1645, 1533, 1476, 1234 \text{ cm}^{-1}.

HRMS (ESI) m/z: [M+H]\text{]}^+ Calcd for C₇H₇INO₂ 263.9521; Found 263.9509.
Compound S25

Prepared according to General Procedure C using 1-ethynylcyclohexene (3.19 mL, 30 mmol, 1.0 equiv.), EtMgBr (3.0 M in Et2O, 12 mL, 36 mmol, 1.2 equiv.), B(OH)3 (6.69 mL, 60 mmol, 2.0 equiv.), and N-methyliminodiacetic acid (8.83 g, 60 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 10–30% MeCN in DCM) gave the product as a white solid (4.99 g, 64%).

1H NMR (500 MHz, DMSO-d6): δ 6.16 – 6.07 (m, 1H), 4.24 (d, J = 17.2 Hz, 2H), 4.06 (d, J = 17.1 Hz, 2H), 2.96 (s, 3H), 2.07 – 2.04 (m, 4H), 1.60 – 1.47 (m, 4H).

13C NMR (126 MHz, DMSO-d6): δ 167.8, 135.3, 120.8, 102.0, 61.4, 47.5, 28.8, 25.2, 22.0, 21.3. The carbon bearing boron was not observed.

11B NMR (160 MHz, DMSO-d6): δ 6.4.

υmax (solid): 2361, 2343, 1761, 1749, 1734, 1558, 1506, 1456 cm⁻¹.

HRMS (ESI) m/z: [M+Na]+ Calcd for C13H16BNaNO2 284.1070; Found 284.1058.

Compound S26

Prepared using General Procedure B using cycloheptenyl triflate (244 mg, 1 mmol, 1 equiv.), Pd(PPh3)2Cl2 (35.1 mg, 50 µmol, 5 mol%), CuI (19 mg, 0.1 mmol, 10 mol%), ethynyl boronic acid MIDA ester (217 mg, 1.20 mmol, 1.2 equiv.), Et3N (0.42 mL, 3 mmol, 3 equiv.). Flash column chromatography (silica gel, 0–10% MeCN in DCM) gave the product as a white solid (165 mg, 60%).

1H NMR (500 MHz, DMSO-d6): δ 6.29 (t, J = 6.7 Hz, 1H), 4.24 (d, J = 17.1 Hz, 2H), 4.06 (d, J = 17.1 Hz, 2H), 2.96 (s, 3H), 2.31 – 2.23 (m, 2H), 2.20 – 2.10 (m, 2H), 1.74 – 1.64 (m, 2H), 1.55 – 1.39 (m, 4H).

13C NMR (126 MHz, DMSO-d6): δ 168.7, 140.6, 126.4, 103.2, 61.4, 47.7, 33.5, 31.4, 28.5, 26.1. The carbon bearing boron was not observed.

11B NMR (96 MHz, DMSO-d6): δ 7.1.

υmax (solid): 1766, 1290, 1236, 1022, 1002, 956, 858 cm⁻¹.

HRMS (ESI) m/z: [M+Na]+ Calcd for C14H18BNO4Na 298.1221; Found 298.1214.

Compound S27

Prepared according to General Procedure B using Pd(dppf)Cl2 (73.2 mg, 0.10 mmol, 5 mol%), tert-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-carboxylate (795 mg, 1.20 mmol, 1.20 equiv.), CuI (38.1 mg, 0.20 mmol, 10 mol%), acetylene boronic acid MIDA ester (181 mg, 1.0 mmol, 1.0 equiv.), and Et3N (836 µL, 3.0 mmol, 3.0 equiv.). Stirred at 50 °C for 16 h. Flash column chromatography (5–20% MeCN in DCM) followed by trituration from acetone with Et2O to give the product as a pale yellow solid (235 mg, 65%).

1H NMR (500 MHz, DMSO-d6): δ 6.11 (br s, 1H), 4.27 (d, J = 17.2 Hz, 2H), 4.07 (d, J = 17.1 Hz, 2H), 3.89 (br s, 2H), 3.39 (t, J = 5.7 Hz, 2H), 2.97 (s, 3H), 2.17 – 2.14 (m, 2H), 1.40 (s, 9H).

13C NMR (126 MHz, DMSO-d6): δ 168.7, 153.8, 132.1, 118.6, 99.8, 79.1, 61.4, 47.8, 43.3, 42.8, 28.5, 28.1.

11B NMR (96 MHz, DMSO-d6): δ 7.3.

υmax (solid): 3976, 2374, 2191, 1769, 1695, 1288, 1024 cm⁻¹.

HRMS (ESI) m/z: [M+Na]+ Calcd for C14H18BNO4Na 298.1212; Found 298.1214.

Compound S28
Tosyl chloride (0.92 g, 4.80 mmol, 1.05 equiv.) was added in one portion to a solution of 2-iodoaniline (1.00 g, 4.57 mmol, 1.00 equiv.) in pyridine (10 mL). The reaction mixture was stirred at room temperature for 3 h before addition of H₂O (20 mL). The mixture was extracted with DCM (3 x 20 mL). The combined organic extracts were then washed with aqueous CuSO₄ solution (2 x 20 mL), dried over Na₂SO₄, filtered, and concentrated to a residue that was purified by flash column chromatography (silica gel, 10–20% EtOAc in hexane) to give the product as a pale yellow solid (1.54 g, 90%).

**1H NMR (500 MHz, CDCl₃):** δ 7.68 – 7.59 (m, 4H), 7.30 (ddd, J = 8.4, 7.3, 1.4 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.83 (ddd, J = 8.0, 7.4, 1.5 Hz, 1H), 6.79 (br s, 1H), 2.38 (s, 3H).

**13C NMR (126 MHz, CDCl₃):** δ 144.4, 139.2, 137.6, 136.0, 129.8, 129.6, 127.6, 127.0, 122.6, 92.5, 21.7.

Spectral data in agreement with literature.

### 4.2 Products from Table 1, Scheme 2, and Scheme 3

#### Compound 1b

A solution of 2-iodoaniline (21.9 g, 100 mmol, 1.00 equiv.) and Et₃N (30.7 mL, 220 mmol, 2.20 equiv.) in DCM (250 mL) was cooled to 0 °C. Ac₂O (11.3 mL, 120 mmol, 1.20 equiv.) was added. The reaction mixture was then warmed to a gentle reflux for 18 h. The mixture was allowed to cool to room temperature before addition of sat. aq. NaHCO₃ (200 mL). The layers were separated, and the aqueous layer was extracted with DCM (2 x 100 mL). The combined organic extracts were then dried over Na₂SO₄, filtered, and concentrated to a residue that was purified by flash column chromatography (silica gel, 20–80% EtOAc in hexane) to give the product as a white solid (23.1 g, 88%).

**1H NMR (500 MHz, CDCl₃):** δ 8.21 (d, J = 8.2 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.41 (br s, 1H), 7.34 (ddd, J = 8.5, 7.5, 1.5 Hz, 1H), 6.86 – 6.83 (t, J = 7.4 Hz, 1H), 2.24 (s, 3H).

**13C NMR (126 MHz, CDCl₃):** δ 168.3, 138.9, 138.3, 129.4, 126.1, 122.2, 90.1, 25.0.

Spectral data in agreement with literature values.

#### Compound 2b

Prepared according to General Procedure C using phenylacetylene (5.11 g, 50 mmol, 1.0 equiv.), EtMgBr (3.28 M in Et₂O, 18.3 mL, 60 mmol, 1.2 equiv.), B(OMe)₃ (11.1 mL, 100 mmol, 2.0 equiv.), and N-methyliminodiacetic acid (14.7 g, 100 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 0–30% MeCN in DCM) gave the product as a pale yellow solid (7.82 g, 61%).

**1H NMR (500 MHz, DMSO-d₆):** δ 7.54 – 7.43 (m, 2H), 7.43 – 7.34 (m, 3H), 4.30 (d, J = 17.2 Hz, 2H), 4.13 (d, J = 17.2 Hz, 2H), 3.06 (s, 3H).

**13C NMR (126 MHz, DMSO-d₆):** δ 168.8, 131.6, 128.9, 128.7, 122.4, 99.5, 61.5, 47.9. The carbon bearing boron was not observed.

**11B NMR (96 MHz, DMSO-d₆):** δ 6.2.

Spectral data in agreement with literature values.

#### Compound 3

Prepared according to General Procedure A using Pd(dppf)Cl₂ (7.3 mg, 0.01 mmol, 5 mol%), propyne boronic acid MIDA ester (39.0 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the product as a tan solid (48.0 mg, 84%).
$^1$H NMR (400 MHz, Acetone-$d_6$): $\delta$ 9.87 (br s, 1H), 7.52 (dd, $J$ = 8.0, 1.3 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.08 (ddd, $J$ = 8.0, 7.0, 1.2 Hz, 1H), 7.02 – 6.96 (m, 1H), 4.38 (d, $J$ = 17.1 Hz, 2H), 4.15 (d, $J$ = 17.1 Hz, 2H), 2.82 (s, 3H), 2.37 (s, 3H).

$^{13}$C NMR (101 MHz, Acetone-$d_6$): $\delta$ 169.2, 139.0, 130.7, 122.4, 119.2, 119.0, 118.1, 111.9, 62.8, 48.0, 9.9. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, Acetone-$d_6$): $\delta$ 10.7.

$\nu_{\text{max}}$ (solid): 3366, 1771, 1749, 1539, 1458, 1333, 1294, 1244, 1211, 1138 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+H]$^+$ Calcd for C$_{14}$H$_{16}$BN$_2$O$_4$ 287.1203; Found 287.1197.

**Compound 4**

![Structure of Compound 4](image)

Prepared according to General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), phenylethynylboronic acid MIDA ester (51.4 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.), LiCl (17.0 mg, 0.4 mmol, 2 equiv.), and N-(2-iodophenyl)acetamide (62.6 mg, 0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the product as a light brown solid (47 mg, 60%).

$^1$H NMR (500 MHz, CD$_3$CN): $\delta$ 7.81 (d, $J$ = 8.5 Hz, 1H), 7.47 – 7.33 (m, 4H), 7.32 – 7.16 (m, 4H), 4.28 – 4.21 (m, 1H), 3.99 (d, $J$ = 17.1 Hz, 3H), 3.20 (s, 3H), 2.85 (s, 3H).

$^{13}$C NMR (126 MHz, CD$_3$CN): $\delta$ 173.0, 137.7, 136.8, 136.2, 133.1, 132.2, 130.2, 129.2, 128.0, 126.2, 123.7, 121.2, 115.1, 66.3, 51.6, 27.7. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, CD$_3$CN): $\delta$ 10.9.

$\nu_{\text{max}}$ (film): 2922, 1740, 1686, 1310, 1030, 1012, 748 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+Na]$^+$ Calcd for C$_{23}$H$_{19}$BN$_2$NaN$_2$O$_5$ 413.1285; Found 413.1288.

**Compound 5**

![Structure of Compound 5](image)

Prepared according to General Procedure A using Pd(dppf)Cl$_2$ (7.3 mg, 0.01 mmol, 5 mol%), S$_3$ (44.2 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). Flash column chromatography (silica gel, 0–35% MeCN in DCM) gave the product as a tan solid (57 mg, 91%).

$^1$H NMR (400 MHz, Acetone-$d_6$): $\delta$ 9.88 (br s, 1H), 7.65 – 7.63 (m, 1H), 7.39 – 7.37 (m, 1H), 7.05 (ddd, $J$ = 8.1, 6.9, 1.2 Hz, 1H), 6.95 (ddd, $J$ = 8.0, 6.9, 1.1 Hz, 1H), 4.39 (d, $J$ = 17.0 Hz, 2H), 4.18 (d, $J$ = 17.0 Hz, 2H), 2.87 (s, 3H), 1.98 (tt, $J$ = 8.3, 5.5 Hz, 1H), 0.91 – 0.83 (m, 4H).

$^{13}$C NMR (126 MHz, Acetone-$d_6$): $\delta$ 169.2, 138.7, 129.8, 123.6, 122.2, 120.3, 119.1, 112.3, 63.0, 48.1, 8.1, 6.6. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, Acetone-$d_6$): $\delta$ 10.6.

$\nu_{\text{max}}$ (solid): 1761, 1740, 1686, 1310, 1030, 1012, 748 cm$^{-1}$.

HRMS (ESI) $m/z$: [M–H]$^-$ Calcd for C$_{16}$H$_{16}$BN$_2$O$_4$ 311.1209; Found 311.1212.

**Compound 6**

![Structure of Compound 6](image)

"S20"
Prepared according to General Procedure A using Pd(dppf)Cl$_2$ (7.3 mg, 0.01 mmol, 5 mol%), S4 (44.6 mg, 0.2 mmol, 1.0 equiv.), 2-iodoaniline (52.6 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). Flash column chromatography (silica gel, 0–35% MeCN in DCM) gave the product as a tan solid (59 mg, 94%).

$^1$H NMR (500 MHz, CD$_3$CN): δ 9.05 (br s, 1H), 7.59 – 7.57 (m, 1H), 7.36 – 7.34 (m, 1H), 7.11 (ddd, $J =$ 8.2, 6.9, 1.2 Hz, 1H), 7.00 (ddd, $J =$ 8.0, 6.9, 1.0 Hz, 1H), 4.10 (d, $J =$ 17.2 Hz, 2H), 3.92 (d, $J =$ 17.2 Hz, 2H), 2.74 – 2.69 (m, 2H), 2.59 (s, 3H), 1.67 – 1.59 (m, 2H), 0.95 (t, $J =$ 7.4 Hz, 3H).

$^{13}$C NMR (126 MHz, CD$_3$CN): δ 169.3, 138.9, 130.0, 124.3, 122.8, 119.8, 119.3, 112.0, 62.9, 48.4, 28.2, 26.1, 14.6. The carbon bearing boron was not observed.

υ$_{\text{max}}$ (solid): 3360, 2953, 2361, 1765, 1744, 1541, 1454, 1292, 1034, 1009 cm$^{-1}$.

HRMS (ESI) m/z: [M–H] Calcd for C$_{16}$H$_{18}$BN$_2$O$_4$: 313.1365; Found 313.1368.

**Compound 7**

Prepared according to General Procedure A using Pd(dppf)Cl$_2$ (7.3 mg, 0.01 mmol, 5 mol%), S5 (65.0 mg, 0.2 mmol, 1.0 equiv.), 2,3-dimethoxy-6-iodoaniline (67.0 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). Flash column chromatography (silica gel, 5–30% MeCN in DCM) gave the product as a light pink solid (40.0 mg, 42%).

$^1$H NMR (500 MHz, Acetone-d$_6$): δ 9.96 (br s, 1H), 7.30 (d, $J =$ 8.6 Hz, 1H), 6.87 (d, $J =$ 8.6 Hz, 1H), 4.95 (s, 2H), 4.36 (d, $J =$ 16.8 Hz, 2H), 4.16 (d, $J =$ 16.8 Hz, 2H), 3.88 (app d, 6H), 2.89 (s, 3H), 0.91 (s, 9H), 0.15 (s, 6H).

$^{13}$C NMR (126 MHz, Acetone-d$_6$): δ 169.2, 148.1, 135.7, 133.0, 126.8, 123.0, 114.2, 109.5, 62.9, 60.8, 57.8, 57.2, 48.3, 26.5, 19.1, −5.0. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, Acetone-d$_6$): δ 10.5.

υ$_{\text{max}}$ (solid): 3310, 2930, 1765, 1517, 1449, 1248, 1088, 1045, 999 cm$^{-1}$.

HRMS (ESI) m/z: [M+Na]$^+$ Calcd for C$_{24}$H$_{33}$BNaN$_2$O$_7$: 499.2048; Found 499.2034.

**Compound 8**

Prepared according to General Procedure A using Pd(dppf)Cl$_2$ (7.3 mg, 10 µmol, 5 mol%), propyne boronic acid MIDA ester (39.0 mg, 0.2 mmol, 1.0 equiv.), 2-iodobenzocaine (52.6 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). Flash column chromatography (silica gel, 5–30% MeCN in DCM) gave the product as an off-white solid (72 mg, 71%).

$^1$H NMR (500 MHz, DMSO-d$_6$): δ 10.99 (s, 1H), 8.19 – 8.15 (m, 1H), 7.69 (dd, $J =$ 8.5, 1.6 Hz, 1H), 7.39 (d, $J =$ 8.5 Hz, 1H), 4.39 (d, $J =$ 17.3 Hz, 2H), 4.30 (q, $J =$ 7.1 Hz, 2H), 4.12 (d, $J =$ 17.3 Hz, 2H), 2.57 (s, 3H), 2.31 (s, 3H), 1.33 (t, $J =$ 7.1 Hz, 3H).

$^{13}$C NMR (126 MHz, DMSO-d$_6$): δ 169.2, 166.9, 140.1, 128.8, 122.2, 120.9, 119.6, 118.2, 111.1, 61.8, 60.0, 47.4, 14.4, 9.4. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, DMSO-d$_6$): δ 12.9.

υ$_{\text{max}}$ (solid): 1767, 1694, 1449, 1250, 1099, 1034, 1001 cm$^{-1}$.

HRMS (ESI) m/z: [M+Na]$^+$ Calcd for C$_{19}$H$_{19}$BNaN$_2$O$_6$: 381.1234; Found 381.1222.

**Compound 9**
Prepared using General Procedure A using Pd(dppf)Cl₂ (7.3 mg, 0.01 mmol, 5 mol%), S₇ (67.0 mg, 0.24 mmol, 1.2 equiv.) and NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.). Flash column chromatography (silica gel, 5–30% MeCN in DCM) gave the product as a tan solid (45.0 mg, 65%).

1H NMR (500 MHz, Acetone-d₆): δ 9.66 (br s, 1H), 7.17 (d, J = 8.5 Hz, 1H), 6.82 (d, J = 8.6 Hz, 1H), 4.35 (d, J = 17.1 Hz, 2H), 4.13 (d, J = 17.1 Hz, 2H), 3.86 (app d, 6H), 2.89 (s, 3H), 2.31 (s, 3H).

13C NMR (126 MHz, Acetone-d₆): δ 169.3, 148.2, 135.5, 133.3, 128.0, 118.9, 114.2, 108.8, 62.9, 60.7, 57.9, 48.1, 10.0. The carbon bearing boron was not observed.

HRMS (ESI) m/z: [M–H] Calcd for C₁₄H₁₃BF₃O₄ 303.0958; Found 303.0959.

**Compound 11**

Prepared according to General Procedure A using Pd(dppf)Cl₂ (7.3 mg, 0.01 mmol, 5 mol%), propyne boronic acid MIDA ester (39.0 mg, 0.2 mmol, 1.0 equiv.), S₇ (56.9 mg, 0.24 mmol, 1.2 equiv.) and NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the product as a light brown powder (62 mg, >99%).

1H NMR (500 MHz, Acetone-d₆): δ 9.98 (br s, 1H), 7.49 (dd, J = 8.6, 5.4 Hz, 1H), 7.07 (dd, J = 10.1, 2.3 Hz, 1H), 6.80 (ddd, J = 9.8, 8.6, 2.3 Hz, 1H), 4.39 (d, J = 17.1 Hz, 2H), 4.16 (d, J = 17.2 Hz, 2H), 2.85 (s, 3H), 2.35 (s, 3H).

13C NMR (126 MHz, Acetone-d₆): δ 169.1, 148.2, 135.5, 133.3, 128.0, 118.9, 114.2, 108.8, 62.9, 60.7, 57.9, 48.1, 10.0. The carbon bearing boron was not observed.

F NMR (471 MHz, Acetone-d₆): δ –123.7.

11B NMR (96 MHz, Acetone-d₆): δ 10.5.

υₘₐₓ (solid): 2953, 1763, 1456, 1288, 1209, 1032 cm⁻¹.

HRMS (ESI) m/z: [M–H] Calcd for C₁₃H₁₂BF₂O₄ 301.1526; Found 301.1525.
$^{11}$B NMR (96 MHz, Acetone-$d_6$): $\delta$ 10.7.

$\nu_{\text{max}}$(solid): 3383, 2932, 1757, 1294, 1217 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+Na]$^+$ Calcd for C$_{18}$H$_{19}$BNaN$_2$O$_6$ 369.1234; Found 369.1228.

**Compound 12**

\[
\begin{align*}
\text{MeO} & \quad \text{O} \\
\text{N} & \quad \text{BMIDA} \\
\end{align*}
\]

Prepared according to General Procedure A using $\text{Pd(dppf)}Cl_2$ (7.3 mg, 0.01 mmol, 5 mol%), $\text{S3}$ (44.2 mg, 0.2 mmol, 1.0 equiv.), $\text{S8}$ (67.0 mg, 0.24 mmol, 1.2 equiv.) and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). Flash column chromatography (silica gel, 5–30% MeCN in DCM) gave the product as a light pink solid (60.0 mg, 81%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 10.30 (s, 1H), 7.21 (d, $J = 8.7$ Hz, 1H), 6.74 (d, $J = 8.7$ Hz, 1H), 4.34 (d, $J = 17.3$ Hz, 2H), 4.06 (d, $J = 17.3$ Hz, 2H), 3.81 (d, $J = 13.1$ Hz, 6H), 2.65 (s, 3H), 1.88 (tt, $J = 8.5$, 5.4 Hz, 1H), 0.81 – 0.75 (m, 2H), 0.68 (dt, $J = 5.5$, 2.8 Hz, 2H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 169.4, 146.4, 134.2, 131.8, 125.2, 122.9, 114.2, 107.5, 62.4, 60.4, 57.2, 47.8, 7.3, 6.0. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 10.6.

$\nu_{\text{max}}$(solid): 3374, 2963, 1748, 1450, 1246 cm$^{-1}$.

HRMS (EI) $m/z$: [M]$^+$ Calcd for C$_{18}$H$_{21}$BN$_2$O$_6$ 372.1493; Found 372.1491.

**Compound 13**

\[
\begin{align*}
\text{MeO} & \quad \text{O} \\
\text{N} & \quad \text{BMIDA} \\
\end{align*}
\]

Prepared using General Procedure A using $\text{Pd(dppf)}Cl_2$ (14.6 mg, 20 µmol, 10 mol%), $\text{S9}$ (83.2 mg, 0.2 mmol, 1.0 equiv.), NaOAc (82.0 mg, 1.0 mmol, 5.0 equiv.), and 2-iodoaniline (105 mg, 0.48 mmol, 2.4 equiv.). Flash column chromatography (silica gel, 5–50% MeCN in DCM) gave the product as a brown solid (89.0 mg, 74%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 9.86 (s, 2H), 7.60 – 7.58 (m, 2H), 7.35 – 7.33 (m, 2H), 7.06 (ddd, $J = 8.1$, 6.9, 1.2 Hz, 2H), 6.96 (ddd, $J = 7.9$, 6.9, 1.0 Hz, 2H), 4.33 (d, $J = 17.2$ Hz, 4H), 4.06 (d, $J = 17.2$ Hz, 4H), 2.92 – 2.89 (m, 4H), 2.76 (s, 6H), 1.78 (p, $J = 3.8$ Hz, 4H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 169.3, 139.1, 130.2, 124.6, 122.4, 119.8, 119.0, 112.0, 63.0, 48.4, 33.8, 26.0. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 10.8.

$\nu_{\text{max}}$(solid): 3374, 2963, 1748, 1450, 1246 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+H]$^+$ Calcd for C$_{32}$H$_{32}$B$_2$Na$_4$O$_8$ 621.2304; Found 621.2286.

**Compound 14**

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{N} & \quad \text{BMIDA} \\
\end{align*}
\]

Prepared according to General Procedure A using $\text{Pd(dppf)}Cl_2$ (7.3 mg, 0.01 mmol, 5 mol%), propyne boronic acid MIDA ester (39.0 mg, 0.2 mmol, 1.0 equiv.), $\text{S2}$ (55.9 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg,
0.5 mmol, 2.5 equiv.). Flash column chromatography (silica gel, 5–30% MeCN in DCM) gave the product as a beige solid (47 mg, 78%).

\textsuperscript{1}H NMR (500 MHz, Acetone-\textit{d}_{6}): \( \delta \) 9.77 (br s, 1H), 7.19 – 7.17 (m, 1H), 6.90 (dd, \( J = 8.2, 7.0 \) Hz, 1H), 6.67 – 6.65 (m, 1H), 4.37 (d, \( J = 17.1 \) Hz, 2H), 4.14 (d, \( J = 17.1 \) Hz, 2H), 2.83 (s, 3H), 2.68 (s, 3H), 2.57 (s, 3H).

\textsuperscript{13}C NMR (126 MHz, Acetone-\textit{d}_{6}): \( \delta \) 169.2, 139.4, 131.4, 129.1, 122.4, 120.8, 119.2, 110.2, 62.9, 48.0, 20.9, 13.1. The carbon bearing boron was not observed.

\textsuperscript{11}B NMR (96 MHz, Acetone-\textit{d}_{6}): \( \delta \) 10.8.

\( \nu_{\text{max}} \) (solid): 3381, 2918, 1757, 1456, 1327, 1211, 1030, 993 cm\(^{-1}\).

HRMS (ESI) \( m/z \): [M–H] Calcd for C\(_{15}\)H\(_{15}\)BN\(_2\)O\(_4\) 299.1209; Found 299.1210.

**Compound 15**

![Diagram of Compound 15]

Prepared according to General Procedure A using Pd(dppf)Cl\(_2\) (22.0 mg, 0.03 mmol, 5 mol%), S\(_3\) (133 mg, 0.6 mmol, 1.0 equiv.), 4-amino-3-iodobenzotri fluoride (207 mg, 0.72 mmol, 1.2 equiv.), and NaOAc (123 mg, 1.5 mmol, 2.5 equiv.). Analysis of the reaction mixture by \textsuperscript{1}H NMR indicated 63% conversion to the desired product. Flash column chromatography (silica gel, 1–5% IPA in DCM) gave the product as a brown solid (90.0 mg, 39%).

\textsuperscript{1}H NMR (500 MHz, Acetone-\textit{d}_{6}): \( \delta \) 10.36 (s, 1H), 7.99 (dd, \( J = 1.9, 1.0 \) Hz, 1H), 7.57 (d, \( J = 8.5 \) Hz, 1H), 7.35 (dd, \( J = 8.6, 1.8 \) Hz, 1H), 4.44 (d, \( J = 17.1 \) Hz, 2H), 4.23 (d, \( J = 17.0 \) Hz, 2H), 2.91 (s, 3H), 2.00 (tt, \( J = 8.4, 5.3 \) Hz, 1H), 0.99 – 0.91 (m, 2H), 0.88 – 0.80 (m, 2H).

\textsuperscript{13}C NMR (126 MHz, Acetone-\textit{d}_{6}): \( \delta \) 169.0, 139.9, 129.3, 126.8 (d, \( ^1J = 270.3 \) Hz), 124.6, 120.9 (q, \( ^2J = 31.1 \) Hz), 118.6 (q, \( ^3J = 3.6 \) Hz), 117.7 (q, \( ^3J = 4.2 \) Hz), 112.9, 63.1, 48.2, 7.6, 6.7. The carbon bearing boron was not observed.

\textsuperscript{19}F NMR (376 MHz, Acetone-\textit{d}_{6}): \( \delta \) –60.4.

\textsuperscript{11}B NMR (96 MHz, Acetone-\textit{d}_{6}): \( \delta \) 10.4.

\( \nu_{\text{max}} \) (solid): 1767, 1744, 1456, 1331, 1296, 1049, 1034 cm\(^{-1}\).

HRMS (ESI) \( m/z \): [M+Na]\(^+\) Calcd for C\(_{15}\)H\(_{16}\)BF\(_3\)Na\(_2\)O\(_4\) 403.1053; Found 403.1044.

**Compound 16**

![Diagram of Compound 16]

Prepared according to General Procedure A using Pd(dppf)Cl\(_2\) (7.3 mg, 0.01 mmol, 5 mol%), S\(_4\) (44.6 mg, 0.2 mmol, 1.0 equiv.), S\(_8\) (67.0 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). Flash column chromatography (silica gel, 5–30% MeCN in DCM) gave the product as a light pink solid (63 mg, 84%).

\textsuperscript{1}H NMR (500 MHz, Acetone-\textit{d}_{6}): \( \delta \) 9.68 (br s, 1H), 7.21 (dd, \( J = 8.6, 0.7 \) Hz, 1H), 6.80 (d, \( J = 8.6 \) Hz, 1H), 4.37 (d, \( J = 17.0 \) Hz, 2H), 4.13 (d, \( J = 17.1 \) Hz, 2H), 3.86 (app d, 6H), 2.92 (s, 3H), 2.77 – 2.70 (m, 2H), 1.69 – 1.59 (m, 2H), 0.95 (t, \( J = 7.3 \) Hz, 3H).

\textsuperscript{13}C NMR (126 MHz, Acetone-\textit{d}_{6}): \( \delta \) 169.2, 148.1, 135.6, 133.5, 127.4, 124.8, 114.6, 108.8, 63.1, 60.7, 57.9, 48.4, 28.3, 26.2, 14.7. The carbon bearing boron was not observed.

\textsuperscript{11}B NMR (96 MHz, Acetone-\textit{d}_{6}): \( \delta \) 10.7.

\( \nu_{\text{max}} \) (solid): 3389, 2957, 1748, 1450, 1246, 1213, 1028, 1009 cm\(^{-1}\).

HRMS (EI) \( m/z \): [M]\(^+\) Calcd for (C\(_{18}\)H\(_{23}\)BN\(_2\)O\(_6\)) 374.1649; Found 374.1643.
**Compound 17**

Prepared according to General Procedure A using Pd(dppf)Cl₂ (7.3 mg, 0.01 mmol, 5 mol%), S8 (63.0 mg, 0.24 mmol, 1.2 equiv.), and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the product as a light brown solid (71.0 mg, 76%).

1H NMR (500 MHz, Acetone-d₆): δ 9.73 (br s, 1H), 7.33 – 7.23 (m, 5H), 7.22 (d, J = 8.6 Hz, 1H), 6.81 (d, J = 8.6 Hz, 1H), 4.45 (s, 2H), 4.15 (d, J = 17.0 Hz, 2H), 4.02 (d, J = 17.0 Hz, 2H), 3.87 (app d, 6H), 3.77 (t, J = 6.2 Hz, 2H), 3.11 (t, J = 6.2 Hz, 2H), 2.75 (s, 3H).

13C NMR (126 MHz, Acetone-d₆): δ 169.4, 148.2, 139.4, 135.6, 133.5, 129.1, 129.1, 128.4, 127.0, 121.2, 114.5, 108.9, 73.6, 71.9, 63.1, 60.7, 57.9, 48.1, 26.7.

The carbon bearing boron was not observed.

11B NMR (96 MHz, Acetone-d₆): δ 10.7.

υₘₐₓ (solid): 3374, 1771, 1744, 1310, 1217, 1024 cm⁻¹.

HRMS (ESI) m/z: [M+Na⁺] Calcd for C₂₆H₂₇BN₂O₇ 489.1809; Found 489.1802.

**Compound 18**

Prepared according to General Procedure A using Pd(dppf)Cl₂ (7.3 mg, 0.01 mmol, 5 mol%), propyne boronic acid MIDA ester (39.0 mg, 0.2 mmol, 1.0 equiv.), 4-amino-3-iodotoluene (55.9 mg, 0.24 mmol, 1.2 equiv.) and NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.). Flash column chromatography (silica gel, 5–30% MeCN in DCM) gave the product as a beige solid (54 mg, 90%).

1H NMR (500 MHz, Acetone-d₆): δ 9.73 (br s, 1H), 7.30 (dd, J = 1.7, 0.8 Hz, 1H), 7.25 (dd, J = 8.2, 0.7 Hz, 1H), 6.92 (dd, J = 8.4, 1.6 Hz, 1H), 4.37 (d, J = 17.1 Hz, 2H), 4.13 (d, J = 17.0 Hz, 2H), 2.81 (s, 3H), 2.40 (s, 3H), 2.34 (s, 3H).

13C NMR (126 MHz, Acetone-d₆): δ 169.2, 137.4, 131.0, 127.7, 124.1, 118.9, 117.6, 111.7, 62.8, 48.0, 21.6, 9.9. The carbon bearing boron was not observed.

11B NMR (96 MHz, Acetone-d₆): δ 10.7.

υₘₐₓ (solid): 3414, 2924, 1759, 1456, 1288, 1215, 1030 cm⁻¹.

HRMS (ESI) m/z: [M+Na⁺] Calcd for C₁₇H₁₇BN₂O₄ 323.1179; Found 323.1172.

**Compound 19**

Prepared using General Procedure D using Pd(OAc)₂ (4.5 mg, 20 µmol, 10 mol%), S11 (57.4 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.), LiCl (17.0 mg, 0.4 mmol, 2 equiv.), and 1b (62.6 mg, 0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the product as an off-white solid (57 mg, 68%).

1H NMR (500 MHz, DMSO-d₆): δ 7.88 – 7.77 (m, 2H), 7.39 (ddd, J = 8.5, 7.1, 1.4 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.04 – 7.01 (m, 2H), 6.96 – 6.91 (m, 1H), 5.31 (s, 2H), 4.50 (d, J = 17.8 Hz, 1H), 4.37 – 4.22 (m, 2H), 4.03 (d, J = 17.7 Hz, 1H), 3.03 (s, 3H), 2.85 (s, 3H).

13C NMR (126 MHz, DMSO-d₆): δ 171.2, 169.8, 168.6, 158.5, 136.1, 130.2, 129.5, 127.4, 125.0, 122.6, 120.7, 119.3, 114.4, 114.2, 65.3, 64.9, 61.2, 50.0, 27.1. The carbon bearing boron was not observed.
$^{11}$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 10.9.

$\nu_{\text{max}}$(solid): 1776, 1757, 1691, 1315, 1301, 1209, 1041, 873, 754 cm$^{-1}$.

HRMS (ESI) m/z: [M+Na]$^+$ Calcd for C$_{24}$H$_{21}$BNaN$_2$O$_6$ 443.1385; Found 443.1373.

**Compound 20**

Prepared using General Procedure A using Pd(dppf)Cl$_2$ (7.3 mg, 10 µmol, 5 mol%), S$_3$ (44.2 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.) and S$_1$ (87.2 mg, 0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 5–30% MeCN in DCM) gave the product as a light brown solid (51 mg, 56%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 10.54 (s, 1H), 7.50 (s, 1H), 7.28 (d, $J$ = 8.3 Hz, 1H), 6.95 (dd, $J$ = 8.4, 1.6 Hz, 1H), 4.73 (s, 2H), 4.37 (d, $J$ = 17.3 Hz, 2H), 4.10 (d, $J$ = 17.3 Hz, 2H), 2.58 (s, 3H), 1.91 (tt, $J$ = 8.5, 5.4 Hz, 1H), 0.91 (s, 9H), 0.82 – 0.79 (m, 2H), 0.76 – 0.73 (m, 2H), 0.07 (s, 6H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 169.2, 136.8, 130.6, 127.7, 121.9, 120.2, 116.8, 111.3, 65.3, 62.0, 47.5, 25.9, 18.1, 7.4, 6.0, –5.1.

$^{11}$B NMR (96 MHz, DMSO): $\delta$ 11.4.

$\nu_{\text{max}}$(solid): 2923, 2361, 1771, 1456, 1339, 1292, 1250, 1132, 835 cm$^{-1}$.

HRMS (ESI) m/z: [M–H]$^-$ Calcd for C$_{23}$H$_{32}$BN$_2$O$_5$Si 455.2179; Found 455.2186.

**Compound 21**

Prepared using General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), S$_3$ (57.4 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.), LiCl (17.0 mg, 0.4 mmol, 2 equiv.), and 1b (62.6 mg, 0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the product as an off-white solid (63 mg, 75%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.84 (dd, $J$ = 8.6, 0.8 Hz, 1H), 7.38 (ddd, $J$ = 8.5, 6.9, 1.5 Hz, 1H), 7.28 – 7.11 (m, 4H), 6.96 (d, $J$ = 8.1 Hz, 2H), 4.30 (d, $J$ = 17.1 Hz, 2H), 4.15 (s, 2H), 3.78 (s, 3H), 3.15 (s, 3H), 2.85 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 172.3, 170.3, 168.4, 158.6, 144.8, 136.7, 134.6, 132.2, 130.7, 127.8, 125.6, 123.1, 120.5, 114.7, 114.3, 65.3, 55.5, 50.8, 27.6. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 10.5.

$\nu_{\text{max}}$(solid): 1766, 1755, 1689, 1319, 1029, 754 cm$^{-1}$.

HRMS (ESI) m/z: [M+Na]$^+$ Calcd for C$_{24}$H$_{21}$BNaN$_2$O$_6$ 443.1385; Found 443.1372.

**Compound 22**

Prepared using General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), S$_3$ (57.4 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.), LiCl (17.0 mg, 0.4 mmol, 2 equiv.), and 1b (62.6 mg,
0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the product as a beige solid (50 mg, 60%).

\[ ^1H \text{ NMR (500 MHz, DMSO-d}_6\]: δ 7.85 (d, \( J = 8.4 \text{ Hz}, 1H \)), 7.40 – 7.37 (m, 1H), 7.30 (br s, 1H), 7.24 – 7.19 (m, 2H), 6.93 – 6.86 (m, 1H), 6.83 – 6.80 (m, 2H), 4.32 (d, \( J = 17.4 \text{ Hz}, 2H \)), 4.24 – 4.03 (m, 2H), 3.77 (s, 3H), 3.20 – 3.07 (s, 3H), 2.86 (s, 3H).

\[ ^13C \text{ NMR (126 MHz, DMSO-d}_6\]: δ 171.9, 169.8, 167.9, 159.0, 136.7, 136.3, 134.2, 131.6, 131.5, 129.4, 125.2, 122.7, 120.1, 114.6, 114.3, 112.7, 64.9, 64.7, 55.0, 50.4, 27.2. The carbon bearing boron was not observed.

\[ ^1B \text{ NMR (96 MHz, DMSO-d}_6\]: δ 12.0.

\( \nu_{\text{max}} \) (solid): 1759, 1685, 1373, 1311, 1251, 1215, 1042, 1001, 746, 704 cm\(^{-1}\).

HRMS (ESI) \( m/z \): [M+Na\(^+\)] Calcd for C\(_{23}\)H\(_{21}\)BNaN\(_2\)O\(_6\) 443.1385; found 443.1366.

**Compound 23**

Prepared using General Procedure D using Pd(OAc)\(_2\) (4.5 mg, 20 μmol, 10 mol%), S15 (52.6 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.), LiCl (17.0 mg, 0.4 mmol, 2 equiv.), and 1b (62.6 mg, 0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 10–15% MeCN in DCM) afforded the product as a brown film, with subsequent trituration with Et\(_2\)O giving the product as a brown solid (35 mg, 44%).

\[ ^1H \text{ NMR (500 MHz, DMSO-d}_6\]: δ 7.85 (d, \( J = 8.5 \text{ Hz}, 1H \)), 7.57 (dd, \( J = 5.1, 1.2 \text{ Hz}, 1H \)), 7.42 – 7.36 (m, 2H), 7.26 (t, \( J = 7.5 \text{ Hz}, 1H \)), 7.13 – 7.07 (m, 2H), 4.37 (d, \( J = 17.6 \text{ Hz}, 2H \)), 4.22 (d, \( J = 17.7 \text{ Hz}, 2H \)), 3.16 (s, 3H), 2.86 (s, 3H).

\[ ^13C \text{ NMR (126 MHz, DMSO-d}_6\]: δ 172.2, 169.6, 168.3, 136.2, 135.4, 131.3, 127.6, 127.1, 126.3, 126.2, 125.5, 122.9, 119.9, 114.2, 65.1, 64.8, 50.5, 27.1. The carbon bearing boron was not observed.

\[ ^1B \text{ NMR (96 MHz, DMSO-d}_6\]: δ 10.4.

\( \nu_{\text{max}} \) (film): 1716, 1683, 1298, 1034, 1004, 750 cm\(^{-1}\).

HRMS (ESI) \( m/z \): [M+Na\(^+\)] Calcd for C\(_{23}\)H\(_{21}\)BFNaN\(_2\)O\(_6\)S 419.0843; Found 419.0836.

**Compound 24**

Prepared using General Procedure D using Pd(OAc)\(_2\) (4.5 mg, 20 μmol, 10 mol%), S16 (55.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.), LiCl (17.0 mg, 0.4 mmol, 2 equiv.), and 1b (62.6 mg, 0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the product as a brown solid (28 mg, 34%).

\[ ^1H \text{ NMR (500 MHz, DMSO-d}_6\]: δ 7.86 (d, \( J = 8.6 \text{ Hz}, 1H \)), 7.40 (ddd, \( J = 8.5, 7.0, 1.4 \text{ Hz}, 1H \)), 7.32 – 7.27 (m, 2H), 7.25 – 7.21 (m, 2H), 7.20 – 7.11 (m, 2H), 4.31 (d, \( J = 17.4 \text{ Hz}, 2H \)), 4.25 – 4.08 (m, 2H), 3.14 (s, 3H), 2.86 (s, 3H).

\[ ^13C \text{ NMR (126 MHz, DMSO-d}_6\]: δ 171.8, 169.8, 168.0, 161.3 (d, \( J = 242.8 \text{ Hz} \)), 136.2, 133.3, 131.7 (d, \( J = 3.1 \text{ Hz} \)), 131.5, 131.1, 125.3, 122.8, 119.9, 115.2 (d, \( J = 21.2 \text{ Hz} \)), 114.4, 65.2, 64.6, 50.4, 27.1. The carbon bearing boron was not observed.

\[ ^19F \text{ NMR (471 MHz, DMSO-d}_6\]: δ –115.9.

\[ ^1B \text{ NMR (96 MHz, DMSO-d}_6\]: δ 11.1.

\( \nu_{\text{max}} \) (solid): 1745, 1601, 1333, 1199, 1041, 904, 879 cm\(^{-1}\).

HRMS (ESI) \( m/z \): [M+Na\(^+\)] Calcd for C\(_{23}\)H\(_{18}\)BFNaN\(_2\)O\(_6\)S 431.1185; Found 431.1178.
Compound 25

Prepared using General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), S17 (60.4 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.), LiCl (17.0 mg, 0.4 mmol, 2 equiv.), and 1b (62.6 mg, 0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the product as an off-white solid (38 mg, 44%).

$^1$H NMR (500 MHz, DMSO-$d_6$): δ 8.38 – 8.13 (m, 2H), 7.90 (d, $J = 8.5$ Hz, 1H), 7.57 (d, $J = 8.3$ Hz, 2H), 7.45 – 7.42 (m, 1H), 7.28 – 7.25 (m, 1H), 7.18 (d, $J = 7.9$ Hz, 1H), 4.40 – 4.29 (m, 2H), 4.26 – 4.20 (m, 2H), 3.18 (s, 3H), 2.89 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): δ 171.9, 169.7, 168.1, 146.3, 143.5, 136.3, 132.2, 130.7, 130.6, 125.5, 123.5, 119.7, 114.6, 65.4, 64.7, 50.4, 27.1.

The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, DMSO-$d_6$): δ 11.4.

$\nu$$_{max}$ (film): 1759, 1685, 1514, 1350, 1311, 1037, 750 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+Na]$^+$ Calcd for C$_{23}$H$_{18}$BNaN$_3$O$_7$ 458.1130; Found 458.1117.

Compound 26

Prepared using General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), S18 (67.6 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.), LiCl (17.0 mg, 0.4 mmol, 2 equiv.), and 1b (62.6 mg, 0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 10–30% MeCN in DCM) gave the product as a colourless solid (42 mg, 52%).

$^1$H NMR (500 MHz, DMSO-$d_6$): δ 8.35 (d, $J = 8.4$ Hz, 1H), 7.90 – 7.83 (m, 2H), 7.52 (br s, 1H), 7.39 (ddd, $J = 8.5, 6.8, 1.6$ Hz, 1H), 7.25 – 7.14 (m, 3H), 6.78 (br s, 1H), 4.34 – 4.10 (m, 4H), 3.20 (s, 3H), 2.87 (s, 3H), 2.68 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): δ 171.9, 169.7, 168.1, 146.3, 134.5, 134.0, 131.8, 130.5, 130.4, 127.4, 126.0, 125.2, 122.7, 121.3, 120.1, 115.8, 114.3, 108.6, 65.2, 64.6, 50.5, 27.2, 23.8. The carbon bearing boron was not observed. Due to poor solubility the BMIDA carbonyl signals were not visible.

$^{11}$B NMR (96 MHz, DMSO-$d_6$): δ 10.4.

$\nu$$_{max}$ (solid): 1761, 1693, 1460, 1369, 1325, 1199, 933, 873, 744, 725, 611 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+Na]$^+$ Calcd for C$_{27}$H$_{22}$BNaN$_3$O$_6$ 494.1494; Found 494.1482.

Compound 27

Prepared according to General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), 2b (51.4 mg, 0.2 mmol, 1.0 equiv.), S19 (67.0 mg, 0.24 mmol, 1.2 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.), and LiCl.
(17.0 mg, 0.4 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 6–30% MeCN in DCM) gave the product as a brown solid (26 mg, 32%).

1H NMR (500 MHz, DMSO-d6): δ 7.88 (dd, J = 9.2, 4.1 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.34 – 7.32 (m, 1H), 7.27 – 7.22 (m, 3H), 6.82 (dd, J = 8.8, 2.7 Hz, 1H), 4.31 (d, J = 17.4 Hz, 2H), 4.26 – 4.05 (m, 2H), 3.16 (s, 3H), 2.86 (s, 3H).

13C NMR (126 MHz, DMSO-d6): δ 171.7, 169.7, 167.8, 158.5 (d, 1J = 238.3 Hz), 134.8, 133.9, 132.8, 132.6 (d, 3J = 3.8 Hz), 129.0, 128.4, 127.1, 115.9 (d, 3J = 9.2 Hz), 112.8 (d, 2J = 25.1 Hz), 104.8 (d, 2J = 23.4 Hz), 65.0, 64.6, 50.4, 27.0. The carbon bearing boron was not observed.

19F NMR (376 MHz, DMSO-d6): δ –120.9.

11B NMR (96 MHz, DMSO-d6): δ 9.1.

υ_max (solid): 1749, 1709, 1269, 1304, 1121, 1043 cm⁻¹.

HRMS (ESI) m/z: [M+Na]+ Calcd for C23H19BFNaN₂O₅ 431.1191; Found 431.1176.

**Compound 28**

![Compound 28](image)

Prepared according to General Procedure D using Pd(OAc)₂ (4.5 mg, 20 µmol, 10 mol%), 2b (51.4 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.) and LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 6–30% MeCN in DCM) gave the product as a light brown solid (41 mg, 51%).

1H NMR (500 MHz, DMSO-d6): δ 7.73 (d, J = 8.6 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.34 – 7.30 (m, 1H), 7.25 – 7.23 (m, 2H), 7.20 (dd, J = 8.8, 1.8 Hz, 1H), 6.94 – 6.90 (m, 1H), 4.29 (d, J = 17.2 Hz, 2H), 4.21 – 4.04 (m, 2H), 3.14 (s, 3H), 2.83 (s, 3H), 2.32 (s, 3H).

13C NMR (126 MHz, DMSO-d6): δ 171.5, 169.8, 167.8, 135.4, 134.6, 134.3, 131.9, 131.7, 129.1, 128.3, 126.9, 126.5, 119.7, 114.1, 65.1, 64.6, 50.4, 27.1, 20.7. The carbon bearing boron was not observed.

11B NMR (96 MHz, DMSO-d6): δ 9.5.

υ_max (solid): 1746, 1697, 1449, 1310, 1038 cm⁻¹.

HRMS (ESI) m/z: [M+Na]+ Calcd for C24H22BFNaN₂O₅ 427.1441; Found 427.1432.

**Compound 29**

![Compound 29](image)

Prepared according to General Procedure D using Pd(OAc)₂ (4.5 mg, 20 µmol, 10 mol%), 2b (51.4 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.) and LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 6–30% MeCN in DCM) gave the title product as a dark brown solid (48 mg, 59%).

1H NMR (500 MHz, DMSO-d6): δ 7.70 (dd, J = 11.1, 2.1 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.35 – 7.31 (m, 1H), 7.26 (d, J = 7.4 Hz, 2H), 7.15 – 7.08 (m, 2H), 4.30 (d, J = 17.3 Hz, 2H), 4.25 – 4.02 (m, 2H), 3.15 (s, 3H), 2.86 (s, 3H).

13C NMR (126 MHz, DMSO-d6): δ 171.9, 169.8, 167.8, 160.6 (d, 1J = 238.8 Hz), 136.3 (d, 3J = 12.1 Hz), 134.9, 133.9, 129.1, 128.4, 128.1, 127.1, 121.0 (d, 3J = 10.3 Hz), 110.8 (d, 2J = 24.3 Hz), 101.8 (d, 2J = 28.6 Hz), 65.0, 64.7, 50.4, 26.9. The carbon bearing boron was not observed.

19F NMR (376 MHz, DMSO-d6): δ –116.3.

11B NMR (96 MHz, DMSO-d6): δ 10.7.
υ_{max} (solid): 1769, 1715, 1479, 1314, 1152, 1061 cm^{-1}.

HRMS (ESI) m/z: [M+Na]^+ Calcd for C_{23}H_{18}BFNaN_{2}O_{5} 431.1191; Found 431.1174.

**Compound 30**

 Prepared according to General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), S1 (66.6 mg, 0.2 mmol, 1.0 equiv.), S20 (66.0 mg, 0.24 mmol, 1.2 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.) and LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 6–30% MeCN in DCM) gave the title product as a light brown solid (45 mg, 47%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.75 (d, $J = 8.6$ Hz, 1H), 7.74 – 7.66 (m, 4H), 7.52 – 7.49 (m, 2H), 7.42 – 7.30 (m, 3H), 7.22 (dd, $J = 8.7$, 1.8 Hz, 1H), 7.04 – 7.00 (m, 1H), 4.31 (d, $J = 17.4$ Hz, 2H), 4.27 – 4.11 (m, 2H), 3.18 (s, 3H), 2.85 (s, 3H), 2.34 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 171.6, 169.8, 167.9, 140.0, 138.4, 134.7, 134.7, 133.9, 131.8, 131.7, 129.7, 129.0, 127.4, 126.5, 119.7, 114.2, 65.2, 64.7, 50.5, 27.1, 20.7. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 11.2.

υ_{max} (solid): 1749, 1709, 1269, 1304, 1121, 1043 cm^{-1}.

HRMS (ESI) m/z: [M+Na]^+ Calcd for C$_{30}$H$_{25}$BFNaN$_2$O$_5$ 503.1754; Found 503.1744.

**Compound 31**

 Prepared according to General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), 2b (51.4 mg, 0.2 mmol, 1.0 equiv.), S23 (73.2 mg, 0.24 mmol, 1.2 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.) and LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 8–30% MeCN in DCM) gave the title product as a light brown solid (48 mg, 55%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.75 (s, 1H), 7.43 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.23 – 7.22 (m, 2H), 6.48 (s, 1H), 6.05 (s, 2H), 4.27 (d, $J = 17.3$ Hz, 2H), 4.17 – 4.05 (m, 2H), 3.14 (s, 3H), 2.80 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 171.9, 169.7, 167.8, 146.8, 144.2, 135.4, 134.3, 131.1, 129.0, 128.3, 126.9, 125.7, 101.4, 98.1, 96.1, 65.0, 64.6, 50.4, 26.9. The carbon bearing boron was not observed. Due to poor solubility the BMIDA carbonyl signals were weak – these were confirmed by 2D NMR.

$^{11}$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 11.2.

υ_{max} (solid): 2363, 1773, 1749, 1707, 1476, 1348, 1310, 1169, 1024 cm^{-1}.

HRMS (ESI) m/z: [M+Na]^+ Calcd for C$_{24}$H$_{23}$BNaN$_2$O$_5$ 503.1754; Found 503.1744.

**Compound 32**

 Prepared using General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), S25 (52.2 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.), LiCl (17.0 mg, 0.4 mmol, 2 equiv.), and 1b (62.6 mg,
0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the title product as a brown solid (58 mg, 74%).

1H NMR (500 MHz, DMSO-<d>): δ 7.77 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.34 (ddd, J = 8.5, 7.1, 1.4 Hz, 1H), 7.25 – 7.22 (m, 1H), 5.57 – 5.51 (m, 1H), 4.43 – 4.35 (m, 2H), 4.19 (d, J = 17.3 Hz, 1H), 4.09 (d, J = 17.7 Hz, 1H), 3.00 (s, 3H), 2.79 (s, 3H), 2.23 (br s, 2H), 2.06 (br s, 2H), 1.83 (br s, 1H), 1.69 (br s, 2H), 1.64 – 1.62 (m, 1H).

13C NMR (126 MHz, DMSO-<d>): δ 171.2, 169.9, 168.6, 136.7, 136.3, 133.9, 130.8, 125.3, 124.8, 122.4, 119.9, 114.3, 64.8, 64.5, 50.5, 29.6, 27.0, 25.1, 22.1, 21.3. The carbon bearing boron was not observed.

11B NMR (96 MHz, DMSO-<d>): δ 11.3.

νmax (solid): 1755, 1695, 1309, 1035, 1010, 744 cm⁻¹.

HRMS (ESI) m/z: [M+Na⁺] Calcd for C₂₅H₂₃BN₂Na₂O₅ 417.1592; Found 417.1582.

**Compound 33**

Prepared using General Procedure D using Pd(OAc)₂ (4.5 mg, 20 µmol, 10 mol%), S26 (55.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.50 equiv.), LiCl (17.0 mg, 0.4 mmol, 2 equiv.), and 1b (62.6 mg, 0.24 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 5–20% MeCN in DCM) gave the title product as an off-white solid (45 mg, 55%).

1H NMR (500 MHz, DMSO-<d>): δ 7.77 (d, J = 8.5 Hz, 1H), 7.44 (br d, J = 7.7 Hz, 1H), 7.34 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.28 – 7.23 (m, 1H), 5.66 (t, J = 6.1 Hz, 1H), 4.44 – 4.33 (m, 2H), 4.19 (d, J = 17.3 Hz, 1H), 4.05 (br d, J = 17.7 Hz, 1H), 2.99 (s, 3H), 2.79 (s, 3H), 2.64 – 2.53 (m, 1H), 2.30 – 2.21 (m, 1H), 2.21 – 2.12 (m, 2H), 1.95 – 1.79 (m, 2H), 1.77 – 1.60 (m, 3H), 1.52 – 1.41 (m, 1H).

13C NMR (126 MHz, DMSO-<d>): δ 171.3, 169.9, 168.7, 139.9, 138.8, 136.3, 130.8, 130.4, 124.9, 122.5, 120.2, 114.3, 64.8, 64.6, 50.4, 34.7, 31.6, 28.5, 27.0, 26.5. The carbon bearing boron was not observed.

11B NMR (96 MHz, DMSO-<d>): δ 12.4.

νmax (solid): 1755, 1695, 1446, 1307, 1201, 1018, 877, 744 cm⁻¹.

HRMS (ESI) m/z: [M+Na⁺] Calcd for C₂₄H₂₅BN₂Na₂O₅ 431.1749; Found 431.1736.

**Compound 34**

Prepared using General Procedure D using Pd(OAc)₂ (4.5 mg, 20 µmol, 10 mol%), S25 (52.2 mg, 0.2 mmol, 1.0 equiv.), S23 (73.2 mg, 0.24 mmol, 1.2 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.), and LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 8–30% MeCN in DCM) gave the title product as a light brown solid (61 mg, 70%).

1H NMR (500 MHz, DMSO-<d>): δ 7.36 (s, 1H), 6.78 (s, 1H), 6.05 (d, J = 5.5 Hz, 2H), 5.53 – 5.46 (m, 1H), 4.40 – 4.32 (m, 2H), 4.16 (d, J = 17.3 Hz, 1H), 4.12 – 3.97 (m, 1H), 2.97 (s, 3H), 2.73 (s, 3H), 2.18 (br s, 2H), 2.03 (br s, 2H), 1.80 (br s, 1H), 1.73 – 1.56 (m, 3H).

13C NMR (126 MHz, DMSO-<d>): δ 171.1, 169.8, 168.6, 146.4, 143.9, 136.7, 134.0, 131.0, 125.3, 124.9, 101.3, 98.2, 96.1, 64.7, 64.4, 50.5, 29.4, 26.7, 25.1, 22.1, 21.3. The carbon bearing boron was not observed.

11B NMR (96 MHz, DMSO-<d>): δ 10.6.

νmax (solid): 1759, 1686, 1337, 1300, 1173, 1032 cm⁻¹.

HRMS (ESI) m/z: [M+H⁺] Calcd for C₂₂H₂₃BN₂O₇ 439.1677; Found 439.1664.
**Compound 35**

Prepared according to General Procedure D using Pd(OAc)$_2$ (4.5 mg, 20 µmol, 10 mol%), S27 (72.4 mg, 0.2 mmol, 1.0 equiv.), 1b (62.7 mg, 0.24 mmol, 1.2 equiv.), NaOAc (41.0 mg, 0.5 mmol, 2.5 equiv.) and LiCl (17.0 mg, 0.4 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 6–30% MeCN in DCM) gave the product as a brown solid (82 mg, 83%).

$^1$H NMR (500 MHz, DMSO-$d_6$): δ 7.82 – 7.77 (m, 1H), 7.40 – 7.34 (m, 2H), 7.26 – 7.22 (m, 1H), 5.59 (br s, 1H), 4.44 (d, $J = 17.8$ Hz, 1H), 4.37 (d, $J = 17.3$ Hz, 1H), 4.22 – 4.18 (m, 2H), 4.07 – 3.95 (m, 1H), 3.80 – 3.65 (m, 2H), 3.60 – 3.51 (m, 1H), 3.01 (s, 3H), 2.81 (s, 3H), 2.47 – 2.34 (m, 1H), 1.46 (s, 9H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): δ 171.3, 169.9, 169.0, 154.2, 136.3, 135.1, 132.2, 130.4, 125.0, 122.6, 119.8, 114.4, 78.6, 65.0, 64.6, 50.5, 43.6, 43.0, 39.8, 29.7, 28.2, 27.0. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, DMSO-$d_6$): δ 11.1.

$\nu_{\text{max}}$ (solid): 1763, 1695, 1676, 1283, 1026 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+H]$^+$ Calcd for C$_{25}$H$_{31}$BN$_3$O$_7$ 496.2255; Found 496.2238.

**Compound 37**

To a flame dried 10 mL microwave vial was added 4 (45 mg, 0.115 mmol, 1 equiv.), 4-bromobenzenesulfonamide (27.2 mg, 0.115 mmol, 1 equiv.), Cs$_2$CO$_3$ (113 mg, 0.346 mmol, 3 equiv.), and Pd(PPh$_3$)$_2$Cl$_2$ (4.05 mg, 5.7 µmol, 5 mol%). The vial was capped and purged with N$_2$ before adding THF (1.15 mL, 0.1 M) and H$_2$O (31 µL, 1.73 mmol, 15 equiv.). The reaction mixture was then heated to 65 ºC for 24 h. The reaction mixture was allowed to cool to room temperature and diluted with EtOAc (10 mL), washed with H$_2$O (10 mL), and brine (10 mL), before being dried over Na$_2$SO$_4$ and concentrated. The crude mixture was taken up in THF/H$_2$O (4/1, 1 mL, 0.1 M), LiOH pellets (6.9 mg, 0.288 mmol, 2.5 equiv.) were added, and the mixture was stirred at room temperature for 5 h. The reaction mixture was diluted with EtOAc (10 mL), washed with H$_2$O (10 mL), and brine (10 mL), before being dried over Na$_2$SO$_4$ and concentrated to a residue that was purified by flash column chromatography (silica gel, 20–40% EtOAc in hexanes) to afford the product as a white solid (25 mg, 62%).

$^1$H NMR (400 MHz, DMSO-$d_6$): δ 11.72 (s, 1H), 7.80 – 7.75 (m, 2H), 7.61 – 7.56 (m, 2H), 7.51 – 7.46 (m, 2H), 7.46 – 7.41 (m, 2H), 7.39 (br s, 2H), 7.36 – 7.31 (m, 3H), 7.21 (ddd, $J = 8.3$, 7.0, 1.1 Hz, 1H), 7.07 (ddd, $J = 8.0$, 7.0, 1.0 Hz, 1H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): δ 142.6, 136.4, 135.8, 134.8, 132.5, 129.9, 128.9, 128.4, 127.9, 126.5, 125.9, 122.8, 120.1, 118.9, 114.8, 111.7.

$\nu_{\text{max}}$ (solid): 3286, 3147, 1598, 1325, 1163, 1026 cm$^{-1}$.

HRMS (ESI) $m/z$: [M–H]$^-$ Calcd for C$_{20}$H$_{15}$N$_2$O$_2$S 347.0860; Found 347.0860.

**Compound 38**

Prepared according to General Procedure C using S10 (6.63 g, 41.4 mmol, 1.0 equiv.), THF (124 mL), EtMgBr (22.6 mL, 49.7 mmol, 2.2 M in Et$_2$O, 1.2 equiv.), B(OMe)$_3$ (9.23 mL, 82.8 mmol, 2.0 equiv.), THF (100 mL), and N-methyliminodiacetic acid (12.2 g, 82.8 mmol, 2.0 equiv.). Flash column chromatography (silica gel, 0–
25% MeCN in DCM) gave an off-white solid which was triturated from EtOAc and hexane to give the product as a fluffy white solid (7.80 g, 60%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.37 – 7.26 (m, 5H), 4.52 (s, 2H), 3.85 (d, $J = 16.5$ Hz, 2H), 3.68 (d, $J = 16.5$ Hz, 2H), 3.61 (t, $J = 6.7$ Hz, 2H), 2.96 (s, 3H), 2.55 (t, $J = 6.7$ Hz, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 167.1, 138.1, 128.6, 128.0, 127.9, 100.7, 73.1, 68.2, 61.5, 47.7, 21.0. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 6.2.

$\nu$$_{max}$ (solid): 3017, 2866, 2208, 1763, 1462, 1329, 1275, 1167 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+Na]$^+$ Calcd for C$_{16}$H$_{18}$BNNaO$_3$ 338.1176; Found 338.1164.

**Compound 39**

Prepared using General Procedure A using Pd(dppf)Cl$_2$ (707 mg, 966 µmol, 5 mol%), NaOAc (3.96 g, 48.3 mmol, 2.5 equiv.) and 2-iodoaniline (5.08 g, 23.2 mmol, 1.2 equiv.). Flash column chromatography (silica gel, 6–30% MeCN in DCM) gave the product as a brown solid (7.08 g, 90%).

$^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 10.63 (s, 1H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.36 – 7.23 (m, 6H), 7.07 – 7.04 (m, 1H), 6.95 – 6.92 (m, 1H), 4.44 (s, 2H), 4.29 (d, $J = 17.2$ Hz, 2H), 3.97 (d, $J = 17.3$ Hz, 2H), 3.63 (t, $J = 6.7$ Hz, 2H), 3.05 (t, $J = 6.7$ Hz, 2H), 2.50 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ 169.2, 138.4, 137.8, 128.4, 128.2, 127.8, 127.5, 121.3, 118.5, 118.4, 118.0, 111.3, 71.9, 70.9, 61.9, 47.5, 25.4. The carbon bearing boron was not observed.

$^{11}$B NMR (96 MHz, DMSO-$d_6$): $\delta$ 10.6.

$\nu$$_{max}$ (solid): 3352, 1769, 1746, 1234, 1221, 1038, 997 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+Na]$^+$ Calcd for C$_{24}$H$_{23}$BNaN$_2$O$_5$ 429.1598; Found 429.1590.

**Compound 40**

a) **Compound S29.** A flame-dried round-bottom flask was charged with $i$-Pr$_2$NH (9.95 mL, 71.0 mmol, 1.30 equiv.) and THF (250 mL, 0.28 M) and cooled to 0 °C. To the stirred solution was added $n$-BuLi (2.43 M in hexanes, 27.0 mL, 65.6 mmol, 1.20 equiv.) via syringe, and the solution was stirred at 0 °C for 30 min. A solution of 1-benzyl-2-piperidinone (10.3 g, 54.6 mmol, 1.0 equiv.) in THF (100 mL, 0.54 M) was added, resulting in a bright yellow coloured solution. This was stirred at 0 °C for 10 min before being allowed to warm to room temperature where it was stirred for a further 30 min. The mixture was then cooled to –78 °C. Ethyl iodide (5.71 mL, 71.0 mmol, 1.30 equiv.) was added via syringe over several minutes and the reaction mixture was stirred at this temperature for a further 30 min before being allowed to warm to room temperature and stir for 1 h. Sat. aq. NH$_4$Cl (100 mL) was added, and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organics were dried over Na$_2$SO$_4$, filtered, and concentrated to a residue that was purified by flash column chromatography (10–30% EtOAc in hexane) to give the product as a colourless oil (11.56 g, 97%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.34 – 7.31 (m, 2H), 7.29 – 7.22 (m, 3H), 4.63 – 4.57 (m, 2H), 3.20 (dd, $J = 7.3$, 4.9 Hz, 2H), 2.35 – 2.29 (m, 1H), 2.05 – 1.97 (m, 1H), 1.96 – 1.91 (m, 1H), 1.88 – 1.82 (m, 1H), 1.74 – 1.67 (m, 1H), 1.66 – 1.53 (m, 2H), 0.98 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 172.8, 137.6, 128.6, 128.0, 127.3, 50.3, 47.5, 43.0, 25.9, 25.0, 21.7, 11.6. Spectral data in agreement with literature values.$^{15}$

S33
b) **Compound S30** A flame-dried round-bottom flask was charged with \( i-\text{Pr}_2\text{NH} \) (2.80 mL, 12 mmol, 1.20 equiv.) and THF (30 mL, 0.04 M), and cooled to 0 °C. To the stirred solution was added \( n\)-BuLi (2.3 M in hexanes, 5.17 mL, 11.9 mmol, 1.19 equiv.) \( \text{via} \) syringe, and the solution was stirred at 0 °C for 30 min. A solution of **S29** (2.17 g, 10.0 mmol, 1.0 equiv.) in THF (20 mL, 0.5 M) was then added \( \text{via} \) cannula. The mixture was stirred for 1 h at 0 °C before being cooled to −78 °C. A solution of ethyl formate (1.05 mL, 13 mmol, 1.3 equiv.) in THF (10 mL) was then added \( \text{via} \) syringe then the reaction mixture was allowed to warm to room temperature and stir overnight. The mixture was quenched with sat. aq. NH₄Cl (20 mL) and extracted with EtOAc (2 x 50 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated to a residue that was purified by flash column chromatography (silica gel, 10–20% ethyl acetate in hexane) to give the product as a colourless oil (1.50 g, 61%).

1H NMR (500 MHz, CDCl₃): \( 8 7.92 \) (s, 1H), 7.34 – 7.31 (m, 2H), 7.29 – 7.25 (m, 1H), 7.24 – 7.19 (m, 2H), 4.67 (d, \( J = 14.6 \) Hz, 1H), 4.55 (d, \( J = 14.6 \) Hz, 1H), 3.24 – 3.12 (m, 2H), 2.30 – 2.22 (m, 1H), 2.10 – 2.02 (m, 1H), 1.90 – 1.79 (m, 1H), 1.79 – 1.75 (m, 1H), 1.69 – 1.57 (m, 2H), 0.89 (t, \( J = 7.5 \) Hz, 3H).

13C NMR (126 MHz, CDCl₃): \( 1 \delta 202.1, 169.0, 137.0, 128.8, 128.1, 127.6, 59.5, 50.8, 47.7, 27.9, 24.5, 20.4, 8.5. \)

\( \nu_{\text{max}} \) (solid): 2967, 2940, 1724, 1489, 1452, 1352, 1265, 1200, 1169 cm⁻¹.

HRMS (ESI) m/z: [M+H⁺] Calcd for C₁₆H₂₆NO₂ 246.1494; Found 246.1484.

c) **Compound 40.** A slurry of iodomethylphosphonium iodide (6.76 g, 12.8 mmol, 1.40 equiv.) in THF (2.17 g, 10.0 mmol, 1.0 equiv.) in THF (20 mL, 0.04 M) was cooled to 0 °C prior to addition of NaHMDS (0.85 M in THF, 13.9 mL, 11.8 mmol, 1.30 equiv.). A solution of iodomethylphosphonium iodide (6.76 g, 12.8 mmol, 1.40 equiv.) in THF (57 mL, 0.22 M) was cooled to 0 °C prior to addition of NaHMDS (0.85 M in THF, 13.9 mL, 11.8 mmol, 1.30 equiv.) dropwise \( \text{via} \) syringe. The deep yellow suspension was stirred at 0 °C for 10 min before being cooled to −78 °C and stirred for a further 30 min. A solution of **S30** (2.23 g, 9.11 mmol, 1.0 equiv.) was added as a solution in THF (3.5 mL) dropwise \( \text{via} \) syringe. The reaction mixture was stirred at −78 °C for 3 h before being quenched with sat. aq. NH₄Cl (50 mL) then allowed to warm to room temperature. The mixture was then extracted with EtOAc (3 x 100 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated prior to purification by flash column chromatography (silica gel, 5–30% EtOAc in hexane) to give the product as a light, yellow oil (3.07 g, 91%).

1H NMR (500 MHz, CDCl₃): \( 8 7.34 – 7.24 \) (m, 5H), 6.69 (d, \( J = 8.3 \) Hz, 1H), 6.35 (d, \( J = 8.2 \) Hz, 1H), 5.03 (d, \( J = 14.5 \) Hz, 1H), 4.17 (d, \( J = 14.5 \) Hz, 1H), 3.36 – 3.31 (m, 1H), 3.25 – 3.20 (m, 1H), 2.27 – 2.22 (m, 1H), 2.02 – 1.86 (m, 3H), 1.84 – 1.78 (m, 2H), 0.97 (t, \( J = 7.4 \) Hz, 3H).

13C NMR (126 MHz, CDCl₃): \( 1 \delta 171.9, 144.4, 137.4, 128.6, 128.5, 127.4, 78.8, 50.9, 50.1, 47.6, 31.5, 29.2, 19.6, 9.1. \)

\( \nu_{\text{max}} \) (neat): 2936, 1632, 1487, 1294, 1194, 696 cm⁻¹.

HRMS (ESI) m/z: [M+Na⁺] Calcd for C₁₆H₂₅INNaO 392.0487; Found 392.0470.

**Compound 41**

![Compound 41](image)

To an oven-dried 100 mL round bottom flask was added **41** (1.74 g, 4.71 mmol, 1.0 equiv.), Pd(dpdpf)Cl₂ (165 mg, 236 μmol, 5 mol%), Cs₂CO₃ (4.61 g, 14.1 mmol, 3.0 equiv.), and **40** (2.87 g, 7.07 mmol, 1.50 equiv.). The flask was purged with N₂ prior to the addition of THF (47 mL, 0.1 M) and H₂O (1.27 mL, 70.7 mmol, 15.0 equiv.). The mixture was then heated to 65 °C and stirred for 20 h. The reaction was allowed to cool to room temperature before brine (25 mL) was added and the mixture was extracted with EtOAc (3 x 25 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated to a residue that was purified by flash...
column chromatography (5–20% EtOAc in hexane) to give the product as a yellow oil (2.07 g, 89%). Product isomerises on standing to a mixture of E/Z isomers. Used immediately in the next step.

1H NMR (500 MHz, CDCl3): δ 12.38 (s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.38 – 7.29 (m, 8H), 7.27 - 7.21 (m, 2H), 7.18 (dd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.07 (dd, J = 7.9, 7.0, 1.0 Hz, 1H), 6.74 (d, J = 13.2 Hz, 1H), 5.42 (d, J = 13.2 Hz, 1H), 4.75 – 4.63 (m, 2H), 4.57 (s, 2H), 3.73 – 3.65 (m, 2H), 3.34 – 3.17 (m, 3H), 3.16 – 3.10 (m, 1H), 2.16 – 1.96 (m, 3H), 1.96 – 1.82 (m, 3H), 0.78 (t, J = 7.4 Hz, 3H).

13C NMR* (126 MHz, CDCl3): δ 173.3, 138.6, 137.5, 136.3, 132.9, 132.5, 130.6, 128.8, 128.4, 128.1, 127.8, 127.6, 122.8, 122.1, 119.5, 118.8, 117.8, 111.6, 110.7, 73.1, 70.9, 50.8, 49.0, 47.9, 32.5, 28.5, 25.1, 19.5, 8.7.

HRMS (ESI) m/z: [M+H]+ Calcd for C35H37N2O2: 493.2855; Found: 493.2852.

*aData for the major isomer reported.

**Compound 42**

![a] Compound S31. A mixture of 41 (526 mg, 1.07 mmol, 1 equiv.) and Pd/C (10 wt%, 114 mg, 107 μmol, 10 mol%) in EtOAc (11 mL, 0.1 M) was stirred vigorously as it was sparged with a balloon of H2. The reaction mixture was then stirred at room temperature under balloon pressure of H2 for 3.5 h. The reaction mixture was then filtered through a plug of celite, and the cake washed with MeOH (3 x 10 mL). The filtrate was concentrated to a residue that was purified by flash column chromatography (silica gel, 10–30% EtOAc in hexane) to give the product as a light pink oil (527 mg, 89%).

1H NMR (400 MHz, CDCl3): δ 8.46 (s, 1H), 7.53 – 7.48 (m, 1H), 7.38 – 7.24 (m, 12H), 7.16 – 7.05 (m, 2H), 4.70 (d, J = 14.5 Hz, 1H), 4.57 (d, J = 12.6 Hz, 3H), 3.69 (t, J = 7.5 Hz, 2H), 3.24 (t, J = 5.6 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H), 2.91 (dd, J = 14.4, 10.3, 6.7 Hz, 1H), 2.55 (dd, J = 14.4, 10.2, 4.2 Hz, 1H), 2.14 (dd, J = 14.2, 10.3, 4.3 Hz, 1H), 1.88 – 1.62 (m, 6H), 0.90 (t, J = 7.5 Hz, 3H).

13C NMR (126 MHz, CDCl3): δ 175.1, 138.6, 137.4, 136.7, 135.4, 128.7, 128.4, 128.3, 127.9, 127.7, 127.5, 127.4, 120.9, 118.8, 117.9, 110.6, 107.2, 73.0, 71.0, 50.7, 47.8, 45.8, 38.3, 31.7, 28.9, 25.0, 21.6, 19.6, 8.5.

υmax (solid): 3277, 2936, 1609, 1452, 1096, 737, 696 cm⁻¹.

HRMS (ESI) m/z: [M+H]+ Calcd for C33H39N2O2: 495.3012; Found: 495.2997.

b) Compound S32. A solution of S31 (143 mg, 0.29 mmol, 1.00 equiv.) in THF (6.1 mL, 0.05 M) was cooled to −78 °C and DIBAL-H (1 M in THF, 1.45 mL, 1.45 mmol, 5.0 equiv.) was added dropwise over 5 minutes. After complete addition, the reaction mixture was allowed to warm to room temperature, stirred for 1 h. The mixture was quenched with sat. aq. Rochelle’s salt (10 mL) then stirred overnight at room temperature. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organics were dried over Na2SO4, filtered, and concentrated to a residue that was purified by flash column chromatography (silica gel, 5–40% EtOAc in hexane) to give the product as a colourless gum (76 mg, 55%).

1H NMR (500 MHz, CDCl3): δ 8.59 (s, 1H), 7.49 (dd, J = 7.8, 1.2 Hz, 1H), 7.33 – 7.27 (m, 7H), 7.26 – 7.22 (m, 4H), 7.10 (dd, J = 8.1, 7.1, 1.3 Hz, 1H), 7.05 (dd, J = 8.1, 7.1, 1.2 Hz, 1H), 4.67 (d, J = 14.6 Hz, 1H), 4.56 – 4.53 (m, 3H), 3.72 – 3.60 (m, 2H), 3.23 – 3.21 (m, 2H), 3.03 (t, J = 7.6 Hz, 2H), 2.91 – 2.85 (m, 1H), 2.54 – 2.48 (m, 1H), 2.15 – 2.10 (m, 1H), 1.85 – 1.71 (m, 5H), 1.70 – 1.65 (m, 2H), 0.87 (t, J = 7.5 Hz, 3H).

13C NMR (126 MHz, CDCl3): δ 175.3, 138.7, 137.6, 136.9, 135.6, 128.8, 128.5, 128.5, 128.1, 127.8, 127.6, 127.5, 121.0, 119.0, 118.1, 110.7, 107.3, 73.1, 71.1, 50.8, 48.0, 45.9, 38.4, 31.8, 29.0, 25.2, 21.7, 19.7, 8.6.

υmax (solid): 3734, 3628, 2922, 2851, 2361, 1458, 1096, 735 cm⁻¹.

HRMS (ESI) m/z: [M+H]+ Calcd for C33H39N2O: 479.3062; Found: 479.3053.
c) **Compound 42.** A mixture of S30 (73.0 mg, 0.15 mmol, 1.00 equiv.) and Pd(OH)$_2$ (20 wt.% on carbon, 128 mg, 0.18 mmol, 1.20 equiv.) in AcOH/EtOH (2/1, 7.6 mL, 0.02 M) was sparged with a balloon of H$_2$. The mixture was then stirred at room temperature under balloon pressure of H$_2$ for 3 h. The reaction mixture was then filtered through a plug of celite, and the cake washed with MeOH (3 x 10 mL). The filtrate was concentrated to a residue that was purified by flash column chromatography (silica gel, 2–5% MeOH in DCM) to give the product as a pale yellow residue (19.0 mg, 42%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.51 (d, $J = 7.6$ Hz, 1H), 7.31 – 7.27 (m, 1H), 7.14 (ddd, $J = 8.1, 7.0, 1.2$ Hz, 1H), 7.08 (ddd, $J = 8.0, 7.1, 1.1$ Hz, 1H), 4.79 (s, 1H), 3.83 (t, $J = 6.4$ Hz, 2H), 3.08 – 3.00 (m, 2H), 2.97 – 2.90 (m, 2H), 2.87 – 2.77 (m, 2H), 2.51 (td, $J = 13.1, 6.7$ Hz, 1H), 1.91 – 1.87 (m, 3H), 1.76 – 1.66 (m, 1H), 1.59 (dq, $J = 15.0, 7.6$ Hz, 1H), 1.55 – 1.44 (m, 3H), 1.22 – 1.17 (m, 1H), 0.88 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 135.5, 132.9, 129.2, 120.7, 119.7, 118.2, 108.4, 106.2, 71.6, 62.7, 45.7, 35.2, 34.1, 28.8, 27.8, 21.7, 21.6, 18.7, 7.2.

$\nu_{\text{max}}$ (solid): 3303, 2926, 2853, 1460, 1308, 1043, 737 cm$^{-1}$.

HRMS (ESI) $m/z$: [M+H]$^+$ Caled for C$_{19}$H$_{27}$N$_2$O$_2$ 299.2123; Found 299.2110.

Spectral data in agreement with literature values.$^{15}$

5. **X-Ray Crystallography Data**

CCDC 2133112 (Compound 3) and 2149746 (Compound 4) contain the supplementary crystallographic data for this study. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

**Compound 3**

X-ray quality crystals isolated by liquid-liquid diffusion at room temperature by dissolving the sample in MeCN and layering with Et$_2$O.

**Table 1 Crystal data and structure refinement for 3**

| Identification code | 3 |
|---------------------|---|
| Empirical formula   | C$_{14}$H$_{15}$BN$_2$O$_4$ |
| Formula weight      | 286.09 |
| Temperature/K       | 125 |
| Crystal system      | monoclinic |
| Space group         | P2$_1$/c |
| $a/\text{Å}$        | 8.91842(12) |
| $b/\text{Å}$        | 11.69930(14) |
| $c/\text{Å}$        | 13.55730(17) |
| $\alpha/$°          | 90.0000 |
| $\beta/$°           | 103.0910(14) |
\(\gamma^\circ\) 90.0000

Volume/Å\(^3\) 1377.80(3)

Z 4

\(\rho\)\(_{\text{calc}}\) g/cm\(^3\) 1.379

\(\mu\) mm\(^-1\) 0.836

F(000) 600.0

Crystal size/Å\(^3\) 0.180 \times 0.120 \times 0.030

Radiation Cu K\(\alpha\) (\(\lambda = 1.54184\))

2\(\Theta\) range for data collection/\(^\circ\) 10.102 to 151.238

Index ranges -11 \(\leq h \leq 11\), -14 \(\leq k \leq 14\), -16 \(\leq l \leq 16\)

Reflections collected 14684

Independent reflections 2771 [\(R_{\text{int}} = 0.0189\), \(R_{\sigma} = 0.0082\)]

Data/restraints/parameters 2771/1/196

Goodness-of-fit on \(F^2\) 1.055

Final R indexes [\(I \geq 2\sigma (I)\)] \(R_1 = 0.0409\), \(wR_2 = 0.1072\)

Final R indexes [all data] \(R_1 = 0.0413\), \(wR_2 = 0.1081\)

Largest diff. peak/hole / e Å\(^{-3}\) 0.35/-0.22
Compound 4

X-ray quality crystals isolated by liquid-liquid diffusion at room temperature by dissolving the sample in MeCN and layering with Et$_2$O.

Table 1 Crystal data and structure refinement for 4

| Identification code | 4             |
|---------------------|---------------|
| Empirical formula   | C$_{21}$H$_{19}$BN$_2$O$_5$ |
| Formula weight      | 390.20        |
| Temperature/K       | 173           |
| Crystal system      | monoclinic    |
| Space group         | P2$_1$/c       |
| a/Å                 | 14.7636(15)   |
| b/Å                 | 12.0831(12)   |
| c/Å                 | 10.7076(11)   |
| α/°                 | 90.0000       |
\( \beta \, ^\circ \quad 97.887(2) \)

\( \gamma \, ^\circ \quad 90.000 \)

Volume/Å\(^3\) 1892.1(3)

\( Z \quad 4 \)

\( \rho_{\text{calc}} \, \text{g/cm}^3 \quad 1.370 \)

\( \mu/\text{mm}^\text{-1} \quad 0.097 \)

\( F(000) \quad 816.0 \)

Crystal size/mm\(^3\) 0.100 \( \times \) 0.100 \( \times \) 0.020

Radiation Mo K\(\alpha \) (\(\lambda = 0.71075\))

2\(\Theta\) range for data collection/\(^\circ\) 5.562 to 50.718

Index ranges -17 \( \leq h \leq 17 \), -14 \( \leq k \leq 14 \), -12 \( \leq l \leq 12 \)

Reflections collected 35689

Independent reflections 3469 [\( R_{\text{int}} = 0.1314 \), \( R_{\text{sigma}} = 0.0503 \)]

Data/restraints/parameters 3469/0/264

Goodness-of-fit on \( F^2 \) 1.053

Final R indexes [\( I \geq 2\sigma (I) \)] \( R_1 = 0.0525 \), \( wR_2 = 0.1332 \)

Final R indexes [all data] \( R_1 = 0.0590 \), \( wR_2 = 0.1415 \)

Largest diff. peak/hole / e Å\(^{-3} \) 0.39/-0.23
6. BMIDA Volume Calculation

Maximum Tolman cone angle measured mathematically to be 152.04° from SCXRD of compound 3 (assuming perfect free rotation, constraining C–B to 2.28 Å and r_{vdw}(H) = 1.1 Å. Cf. calculated Θ_{max(Ph)} = 129° in gas phase iodobenzene I-C(Ph) = 2.113 Å). We attempted to model exact cone angle and solid angle using the methods described by Aggarwal and coworkers using the scripts developed by Allen and coworkers using the program Mathematica; however, the software was unable to calculate a real value for either cone angle or solid angle.

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