Supporting Information

Cu-Catalyzed Decarboxylative Borylation

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General Experimental

Tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), N,N-dimethylformamide (DMF), and acetonitrile (CH₃CN) were obtained by passing the previously degassed solvents through an activated alumina column. N-hydroxyphthalimide (>98%) was purchased from Alfa Aesar (catalog # A13862). DIC (N,N’-diisopropylcarbodiimide) was purchased from Oakwood. Cu(acac)₂ was purchased from Aldrich (catalog # 51,436-5). MgCl₂ (<200 μm) was purchased from Sigma-Aldrich (lot # MKBX9508V). B₂pin₂ was purchased from Oakwood Chemical (catalog # 019250). LiOH•H₂O was purchased from Sigma-Aldrich and ground to floppy powder prior to use. All the other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous material. TLC was performed on 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent, and cerium ammonium molybdate (CAM) or KMnO₄ and heat as developing agents. NMR spectra were recorded on Bruker DRX-600, DRX-500, and AMX-400 instruments and are calibrated using residual undeuterated solvent (CHCl₃ at 7.26 ppm ¹H NMR, 77.16 ppm ¹³C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Column chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm). High-resolution mass spectra (HRMS) were recorded on Waters LC with G2-XS TOF mass spectrometer by electrospray ionization time of flight reflectron experiments. GCMS (EI) was recorded on Agilent 7820A GC systems and 5975 Series MSD. Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus and are uncorrected.

Handling of Cu Catalysts

All Cu catalysts were handled open to air on the bench top, and the bottles were neither flame dried nor stored under inert atmosphere.
Synthesis of Redox-Active Esters

**General Procedure A**

Redox-active esters were prepared according to the previously reported procedure\(^1\). In short, a round-bottom flask or culture tube equipped with a stir bar was charged with carboxylic acid (1.0 equiv), \(N\)-hydroxy-phthalimide (1.1 equiv) and DMAP (0 – 0.1 equiv). Dichloromethane was added (0.1 – 0.5 M) followed by DIC (1.1 equiv), and the mixture was allowed to stir vigorously for 0.5 – 2 hours. The mixture was filtered (over Celite, SiO\(_2\), or through a fritted funnel) and rinsed with additional \(\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}\). The solvent was removed under reduced pressure, and purification by column chromatography (and recrystallization, if necessary) afforded the corresponding redox-active ester.

Redox-active esters shown below (5, S\(_1\) – S\(_{25}\)) were reported in literature\(^1\)\(^{–}\)\(^8\). Please see these references for characterization as well as graphical supporting information\(^1\)\(^2\) for the synthesis of redox-active esters.

![Figure S1. Known redox-active esters.](image-url)
New redox-active esters synthesized according to **General Procedure A** are listed below.

![Figure S2. New redox-active esters.](image-url)
Optimization Details

All optimization reactions were carried out on 0.1 mmol scale. LiOH•H₂O was grinded to floppy powder prior to use. The crude reaction mixture was analyzed by GC/FID with dodecane as internal standards.

Evaluation of different metals

Table S1. Evaluation of different metals.

| Entry | Conditions | Yield |
|-------|------------|-------|
| 1     | NiCl₂•H₂O, diOMe-bipy (13 mol%), MeLi (1.5 equiv), MgBr₂•Et₂O (1.5 equiv) | 43% |
| 2     | MnBr₂ (5 mol%), TMEDA (20 mol%), EtMgBr (1.5 equiv), DME | 6% |
| 3     | FeBr₂ (10 mol%), MgBr₂•Et₂O (1.5 equiv), tBuLi (1.5 equiv), THF | trace |
| 4     | CuTc/diBu-bipy/Pcy₃ (10/10/10 mol%), tBuOLi (1.5 equiv), THF/NMP | 0 |
| 5     | CuTc/diBu-bipy/PPh₃ (10/10/10 mol%), tBuOLi (1.5 equiv), THF/NMP | 0 |
| 6     | CuI/PPh₃ (10/10 mol%), tBuOLi (1.5 equiv), THF | 0 |
| 7     | CuI/diBu-bipy (10/10 mol%), tBuOLi (1.5 equiv), THF | 11% |
| 8     | CuI/diBu-bipy (10/10 mol%), DMF | 13% |

Evaluation of Cu sources and solvents

Table S2. Evaluation of Cu sources and solvents.

| Entry | Cu [w/ THF/DMF (4/1)] | Yield | Entry | Solvent [w/ Cu(OAc)₂] | Yield |
|-------|------------------------|-------|-------|------------------------|-------|
| 1     | CuCl                   | 12%   | 1     | THF only               | 11%   |
| 2     | CuBr                   | 9%    | 2     | THF/DMA 4/1           | 10%   |
| 3     | CuCN                   | trace | 3     | THF/NMP 4/1           | 11%   |
| 4     | Cu(MeCN)₃PF₆           | 8%    | 4     | THF/NMP 9/1           | 18%   |
| 5     | CuCl₂                  | 11%   | 5     | THF/MeCN 4/1          | 11%   |
| 6     | CuCl₂•H₂O              | 19%   | 6     | dioxane/DMF 4/1       | 24%   |
| 7     | CuBr₂                  | 9%    | 7     | glyme/DMF 4/1         | 20%   |
| 8     | CuF₂                   | 0     | 8     | DMF only              | 5%    |
| 9     | CuSO₄•5H₂O             | Trace |       |                        |       |
| 10    | Cu(OAc)₂               | 19%   |       |                        |       |
### Evaluation of bases

**Table S3. Evaluation of bases.**

| Entry | Base                                      | Yield |
|-------|-------------------------------------------|-------|
| 1     | tBuOLi (1.5 equiv)                        | 25%   |
| 2     | MeOLi (in MeOH, 1.5 equiv)                | <5%   |
| 3     | MeONa                                     | 0     |
| 4     | EtONa                                     | 0     |
| 5     | tBuONa                                    | 0     |
| 6     | tBuOK                                     | 0     |
| 7     | K₂CO₃                                     | 0     |
| 8     | tBuOLi (old bottle, 4.0 equiv), MgBr₂•Et₂O (0.2 equiv) | 40%   |
| 9     | tBuOLi (new bottle, 4.0 equiv), MgBr₂•Et₂O (0.2 equiv) | 29%   |
| 10    | tBuOLi (in THF, 4.0 equiv), MgBr₂•Et₂O (0.2 equiv) | 30%   |
| 11    | LiOH (4.0 equiv), MgBr₂•Et₂O (0.2 equiv)   | 47%   |
| 12    | LiOH•H₂O (4.0 equiv), MgBr₂•Et₂O (0.2 equiv) | 48%   |

### Evaluation of Cu/ligand

**Table S4. Evaluation of Cu/ligand.**

| Entry | Cu/ligand                                      | Yield |
|-------|-----------------------------------------------|-------|
| 1     | Cu(OAc)₂/diBu-bipy/PPh₃ (10/10/10 mol%)       | 35%   |
| 2     | Cu(OAc)₂/diBu-bipy/PCy₃ (10/10/10 mol%)       | 35%   |
| 3     | Cu(OAc)₂/diBu-bipy/PCy₃•HBF₄ (10/10/10 mol%)  | 34%   |
| 4     | Cu(OAc)₂/diBu-bipy/dppe (10/10/10 mol%)       | 19%   |
| 5     | Cu(OAc)₂/dppe (10/10 mol%)                    | 34%   |
| 6     | Cu(OAc)₂/dppe (10/15 mol%)                    | 16%   |
| 7     | Cu(OAc)₂/dppe (10/20 mol%)                    | trace |
| 8     | Cu(acac)₂ (10 mol%)                           | 47%   |
| 9     | L₁, R₁ = R₂ = tBu (10 mol%)                   | 45%   |
| 10    | L₁, R₁ = R₂ = iPr (10 mol%)                   | 35%   |
| 11    | L₁, R₁ = R₂ = Ph (10 mol%)                    | 45%   |
| 12    | L₁, R₁ = R₂ = tBu, Me (10 mol%)               | 48%   |
| 13    | L₁, R₁ = R₂ = CF₃ (10 mol%)                   | 31%   |
| 14    | L₁, R₁ = R₂ = tBu, CF₃ (10 mol%)              | 30%   |
**Evaluation of equivalents and additives**

![Chemical Structure](image)

*Cu/ligands and additives*

**Table S5. Cu/ligands and additives.**

| Entry | Conditions | Yield |
|-------|------------|-------|
| 1     | Cu(OAc)$_2$/diBu-bipy (10/10 mol%) | 62% |
| 2     | Cu(acac)$_2$ (10 mol%) | 51% |
| 3     | Cu(acac)$_2$ (20 mol%) | 62% |
| 4     | Cu(acac)$_2$ (30 mol%) | 63% |
| 5     | Cu(acac)$_2$ (20 mol%), additive H$_2$O (50 μL, 28 equiv) | 59% |
| 6     | Cu(acac)$_2$ (20 mol%), additive tBuOLi (2 equiv) | 60% |
| 7     | Cu(acac)$_2$ (10 mol%), CuCl (10 mol%) | 59% |
| 8     | Cu(acac)$_2$ (10 mol%), Cu(OAc)$_2$ (10 mol%) | 50% |
| 9     | Cu(acac)$_2$ (10 mol%), Cu(ClO$_4$)$_2$•6H$_2$O (10 mol%) | 48% |
| 10    | Cu(acac)$_2$/CuCl/diBu-bipy (10/10/10 mol%) | 59% |
| 11    | Cu(acac)$_2$/Cu(OAc)$_2$/diBu-bipy (10/10/10 mol%) | 59% |

**Magnesium sources**

**Table S6. Magnesium sources.**

| Entry | Instead of MgBr$_2$•Et$_2$O (w/ 20 mol% Cu(acac)$_2$) | Yield |
|-------|-----------------------------------------------------|-------|
| 1     | MgCl$_2$                                             | 61%  |
| 2     | Mg(OTf)$_2$                                          | 19%  |
| 3     | Mg(ClO$_4$)$_2$                                      | 12%  |
| 4     | MgO                                                  | trace|
| 5     | Mg(OAc)$_2$•4H$_2$O                                   | 24%  |

**Final conditions and deviations**

**Table S7. Final conditions and deviations.**

| Entry | With Cu(acac)$_2$ (20 mol%) | Yield |
|-------|------------------------------|-------|
| 1     | LiOH•H$_2$O (15 equiv), MgBr$_2$•Et$_2$O (0.8 equiv) | 69%  |
| 2     | LiOH•H$_2$O (20 equiv), MgBr$_2$•Et$_2$O (0.8 equiv) | 69%  |
| 3     | LiOH•H$_2$O (30 equiv), MgBr$_2$•Et$_2$O (0.8 equiv) | 67%  |
| 4     | LiOH•H$_2$O (15 equiv), MgCl$_2$ (1.5 equiv), dioxane/DMF 4/1 | 69%  |
| 5     | Same as entry 4 with Cu(acac)$_2$ (30 mol%), B$_2$pin$_2$ (3.0 equiv) | 86%  |
| 6     | Same as entry 5, LiOH•H$_2$O not grinded             | 66%  |
Cu-Catalyzed Decarboxylative Borylation of Redox-Active Ester

**General Procedure B**

To a 15 mL culture tube equipped with a stir bar were added redox-active ester (1.0 equiv), B$_2$pin$_2$ (3.0 equiv), LiOH•H$_2$O (15 equiv), Cu(acac)$_2$ (30 mol%) and MgCl$_2$ (1.5 equiv). The tube was evacuated and backfilled with argon for 3 times. Degassed dioxane/DMF (6:1 – 1:2 ratio, 0.14 M) was added and the resulting mixture was stirred under 1000 rpm at RT until dark brown color was observed (typical reaction time < 10 min). The reaction mixture was diluted with Et$_2$O or EtOAc (7 mL for 0.2 mmol scale) and saturated NH$_4$Cl (7 mL for 0.2 mmol scale), and the resulting mixture was shaken vigorously until getting a clear biphasic solution. The organic phase was collected and dried over anhydrous Na$_2$SO$_4$, evaporated and purified by silica gel chromatography to afford the desired product.

**Notes:**

1. LiOH•H$_2$O was grinded to floppy powder prior to use, otherwise lower yield was observed (see entry 6 vs entry 5 in the last optimization table).
2. Substrates 29 and 33 were obtained using MTBE/DMF = 6/1 as solvent.
3. All the primary substrates use dioxane/DMF = 4/1 as solvent.
4. Dioxane/DMF ratio used for secondary substrates varied from 6/1 to 1/2.
5. For cases that the borylation product is close to B$_2$pin$_2$ on TLC and difficult to separate: upon completion, the reaction mixture was diluted with EtOAc and bubbled with air until green color was observed (typically < 3 min). Excess B$_2$pin$_2$ could be consumed this way.
6. For cases that the borylation product is close to phthalimide (PhthH) on TLC and difficult to separate: upon completion, the reaction mixture was diluted with EtOAc and washed with NH$_4$Cl followed by K$_2$CO$_3$ (10% aq). PhthH could be washed away by K$_2$CO$_3$. 
Graphical Supporting Information for General Procedure B

**Cu-Catalyzed Borylation Reaction:**

\[
\begin{array}{c}
\text{MeO}_2\text{C-} \quad \text{5} \\
0.2 \text{ mmol, 1.0 equiv}
\end{array}
\quad +
\begin{array}{c}
\text{MeO}_2\text{C-} \quad \text{B-} \quad \text{Me}_3
\end{array}
\quad \text{3.0 equiv}
\quad \text{Cu(acac)}_2 (30 \text{ mol\%})
\quad \text{LiOH·H}_2\text{O} (15 \text{ equiv})
\quad \text{MgCl}_2 (1.5 \text{ equiv})
\quad \text{dioxane/DMF (4/1, 1.4 mL)}
\quad \rightarrow
\begin{array}{c}
\text{MeO}_2\text{C-} \quad \text{B-} \quad \text{Me}_3
\end{array}
\quad \text{6}
\]

(Left) DMF and dioxane. (Right) Reagents used in this reaction.

(Left) DMF (1 mL). (Center) Dioxane (4 mL). (Right) The mixed solvents were evacuated and backfilled with argon for twice.
(Left) RAE 5 (0.2 mmol, 1.0 equiv). (Center) B$_2$pin$_2$ (3.0 equiv). (Right) LiOH•H$_2$O (15 equiv).

(Left) Cu(acac)$_2$ (30 mol%). (Center) MgCl$_2$ (1.5 equiv). (Right) Put all the five materials into a 15 mL culture tube equipped with a stir bar.
(Left) The tube was evacuated and backfilled with argon for three times. (Right) Dioxane/DMF (4:1, 1.4 mL) was added.

(Above) After addition of solvent, the color change was recorded. The reaction was done (4'08") when dark brown color was observed.
(Left) The crude reaction was diluted with EtOAc (7 mL) and saturated NH₄Cl (7 mL), and the resulting mixture was shaken vigorously until getting a clear biphasic solution. (Right) TLC after stained with KMnO₄ (line 1: crude reaction mixture; line 2: co-spot; line 3: authentic product).
Removal of B$_2$pin$_2$ and Phthalimide:

(Lef) After completion of borylation. (Center) Reaction mixture was diluted with EtOAc and bubbled with air. (Right) After ~3 min, the mixture color changed to green.

(Lef) TLC (hexane:CH$_2$Cl$_2$:EtOAc 6:1:1) under UV (line 1: crude reaction mixture immediately after completion; line 2: co-spot of line 1 and 3; line 3: crude reaction mixture after bubbling with air). (Center) The same TLC after CAM stein. (Right) TLC (hexane:EtOAc 2:1) after washing with K$_2$CO$_3$ (10% aq). Line 1: PhthH authentic sample; line 2: co-spot of line 1 and 3; line 3: crude reaction mixture before washing with K$_2$CO$_3$ (10% aq); line 4: co-spot of line 3 and 5; line 5: crude reaction mixture after washing with K$_2$CO$_3$ (10% aq).
One-pot Cu-Catalyzed Decarboxylative Borylation from Carboxylic Acid

General Procedure C

To a 15 mL culture tube equipped with a stir bar were added carboxylic acid (0.2 mmol, 1.0 equiv) and NHPI (1.0 equiv). The tube was evacuated and backfilled with argon for three times followed by addition of CH$_2$Cl$_2$ (2 mL, 0.1 M) and DIC (1.0 equiv). The resulting mixture was stirred under 1000 rpm at RT for 2 h before removal of the solvent by rotavapor. Then B$_2$pin$_2$ (3.0 equiv), LiOH•H$_2$O (15 equiv), Cu(acac)$_2$ (30 mol%) and MgCl$_2$ (1.5 equiv) were added and the tube was evacuated and backfilled with argon for three times. Degassed dioxane/DMF (4:1, 1.4 mL, 0.14 M) was added and the resulting mixture was stirred at RT until dark brown color was observed (typical reaction time < 15 min). The reaction mixture was diluted with EtOAc and saturated NH$_4$Cl, and the resulting mixture was shaken vigorously until getting a clear biphasic solution. The organic phase was collected and dried over anhydrous Na$_2$SO$_4$, evaporated and purified by silica gel chromatography to afford the desired product.

This one-pot procedure was demonstrated with 4 examples:
Graphical Supporting Information for General Procedure C

(Left) N-Hydroxyphthalimide and 5-Phenylvaleric acid (Sigma-Aldrich). (Center) 5-Phenylvaleric acid (0.2 mmol). (Right) N-Hydroxyphthalimide (1.0 equiv).

(Left) Add the acid and NHPI to a 15 mL culture tube. (Center) CH₂Cl₂ (2 mL). (Right) The tube was evacuated and backfilled with argon for three times and CH₂Cl₂ was added.
(Left) Add DIC (1.0 equiv). (Center) After stirring at RT for 2h. (Right) CH₂Cl₂ was removed by rotavapor.

(Left) After removal of CH₂Cl₂. (Center) Reagents used for decarboxylative borylation. (Right) B₂pin₂ (3.0 equiv).
(Left) Cu(acac)$_2$ (30 mol%). (Center) MgCl$_2$ (1.5 equiv). (Right) LiOH•H$_2$O (15 equiv).

(Left) Add the four materials to the tube and the tube was evacuated and backfilled with argon for three times. (Center) Add solvent (dioxane/DMF = 4/1, 1.4 mL) to the tube. (Right) 10 mins after addition of solvent, the color changed to dark brown, which indicated the completion of the borylation reaction.
(Left) Quench the reaction with saturated NH₄Cl (aq) and EtOAc. (Center) Transfer the crude reaction mixture to a separation funnel. (Right) Organic phase was collected and dried over anhydrous Na₂SO₄.

(Left) Crude TLC (right top spot is the product). (Center) Purification by flash column chromatography (silica gel). (Right) TLC after column.
(Left) Weight of empty vial. (Center) Weight of vial with product (29.5 mg, 57% yield).
Gram-Scale Cu-Catalyzed Decarboxylative Borylation of Redox-Active Ester

General Procedure D

To a 50 mL flask equipped with a stir bar were added redox-active ester 5 (1.07 g, 3.5 mmol), B<sub>2</sub>pin<sub>2</sub> (1.33 g, 1.5 equiv), LiOH•H<sub>2</sub>O (2.21 g, 15 equiv), Cu(acac)<sub>2</sub> (183 mg, 20 mol%) and MgCl<sub>2</sub> (499 mg, 1.5 equiv). The flask was evacuated and backfilled with argon for three times. Degassed dioxane/DMF (4/1, 17.5 mL) was added at once and the resulting mixture was stirred under 1000 rpm at RT until the reaction color turned dark brown (typically < 10 min). The reaction mixture was diluted with Et<sub>2</sub>O (50 mL) and washed with saturated NH<sub>4</sub>Cl (30 mL), K<sub>2</sub>CO<sub>3</sub> (10% aq, 30 mL) and brine (30 mL) successively. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporated and purified by flash column chromatography (silica gel, hexanes to 100:1 CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O) to afford 466 mg (55%) of the borylation product 6.

Notes:
LiOH•H<sub>2</sub>O was grinded to floppy powder prior to use.

This procedure was also demonstrated on 2.5 mmol scale (1.19 g) with redox-active ester 45, Cu(acac)<sub>2</sub> (20 mol%) and B<sub>2</sub>pin<sub>2</sub> (1.5 equiv). Purification by flash column chromatography (silica, 20:1 hexanes:Et<sub>2</sub>O) afforded 622 mg (60%) of the borylation product 2.
Graphical Supporting Information for General Procedure D

(Left) Reagents for this reaction. (Center) RAE 5 (1.07 g, 3.5 mmol). (Right) B$_2$pin$_2$ (1.33 g, 1.5 equiv).

(Left) Cu(acac)$_2$ (183 mg, 20 mol%). (Center) MgCl$_2$ (499 mg, 1.5 equiv). (Right) LiOH•H$_2$O (2.21 g, 15 equiv).

(Left) Dioxane (1 L sealed bottle, Acros). (Center) Prepare the solvent, DMF (4 mL), dioxane (16 mL). (Right) Premix the solvent in a 25 mL scintillation vial.
(Left) Evacuate the flask and backfill with argon for three times. (Center left) After addition of solvent (17.5 mL). (Center Right) 5 min after addition. (Right) 6 min.

(Left) 6.5 min. (Center left) 7 min. (Center right) 7.5 min. (Right) 8 min.
(Left) Quench the reaction by adding 10 mL NH₄Cl (aq) and 10 mL Et₂O. (Center) Transfer to a separation funnel. (Right) The organic phase was dried over anhydrous Na₂SO₄.
Troubleshooting: Frequently Asked Questions

Question 1:
Do I need to run the reaction in glovebox?

Answer:
We do not set up or run the reaction in glovebox. A glovebox is not necessary for this reaction. We do evacuate the air from the tube via vacuum manifold though.

Question 2:
How sensitive is this reaction to water and air?

Answer:
Addition of ~30 equivalents of H₂O resulted in <5% drop in yield. Running the reaction under air without inert atmosphere resulted in ~20% drop in yield.

Question 3:
Why do you need 15 equivalents of LiOH•H₂O?

Answer:
The solubility of LiOH•H₂O in organic solvent is limited. So 15 equivalents is necessary to increase the actually effective amounts of LiOH•H₂O.

Question 4:
Can I use LiOH instead of LiOH•H₂O?

Answer:
LiOH resulted in similar yield (within 5% difference) as long as LiOH was also grinded to floppy powder prior to use.

Question 5:
Is MgCl₂ essential for this reaction?

Answer:
Without MgCl₂, the yield dropped to <20%. However, instead of MgCl₂, many other metal salts also proved to be effective, such as MgBr•Et₂O, LiCl, FeCl₃•6H₂O, CoCl₂, NiCl₂•6H₂O, CrCl₃, MnCl₂•4H₂O, ZrCl₄ (control studies showed no product formation in the absence of Cu). We chose MgCl₂ because it’s cheap, environment friendly and easy to handle.

Question 6:
How do I purify my products?
Answer:
The pinacol alkylboronate esters are not stable on preparative TLC due to possible oxidation of C–B bond or hydrolytic cleavage of pinacol esters. In all cases shown in this paper, we purify the products by flash column chromatography with gradient elution. For products that were very unstable on silica gel, deactivated silica gel (35 wt% H₂O) could be used as suggested in reference 5.
Two major impurities, namely B₂pin₂ and phthalimide (PhthH), could be removed by methods shown below:
a. Upon completion, the reaction mixture was diluted with EtOAc and bubbled with air. Observing of green color (typically < 2 min) indicated complete consumption of excess B₂pin₂.
b. Upon completion, the reaction mixture was diluted with EtOAc and washed with NH₄Cl followed by K₂CO₃ (10% aq) for three times. PhthH could be washed away by K₂CO₃.

Question 7:
Are the Bpin products volatile?
Answer:
Most of products reported in this study are not volatile except the radical clock products 43 and 44. You can use pentane and Et₂O for workup and column chromatography and keep the temperature of rotavapor water bath below 30 °C.

Question 8:
Sometimes emulsion formed during the workup. What should I do?
Answer:
After addition of NH₄Cl solution, shake the reaction tube vigorously until getting a clear biphasic solution. Intermittent introduce of air (oxygen) could help break the metal aggregates. If lighter color was observed but emulsion still existed, add more H₂O or brine and shake again.

Question 9:
I’m working on small scales, and the general procedure requires relatively high concentration (0.14 M). Can I dilute the reaction?
Answer:
The reaction can be diluted to 0.07 M by the addition of more solvent, thus diluting all reaction components, obtaining essentially the same yield, although the reaction will take a little longer to completion. Further dilution will cause decrease in yield.

Question 10:
Is this reaction exothermic? Does that affect the yield?
The reaction became exothermic when brown color was observed. We didn’t observe any appreciable ill effect to the yield though.

**Question 11:**
Dose longer reaction time cause decrease in yield?

**Answer:**
We left the reaction running overnight sometimes and no significant decrease of yield was observed.

**Question 12:**
Does the base-sensitive group survive under current base conditions?

**Answer:**
Base-sensitive functional groups such as ketone, ester, lactone, amide, free phenol, epoxide and carbamates such as Boc and Fmoc are all tolerated in this method.

**Question 13:**
How’s the color changing during the transformation and which color indicates the completion of this reaction?

**Answer:**
Color change of this reaction was recorded graphically. The observation of dark brown color (4’08’’) indicated the completion of the reaction.

**Question 14:**
What's the limitation of current copper-catalyzed decarboxylative borylation?

**Answer:**
Substrates containing alkyl or aryl halogens (Br or I) gave lower yields due to competing
protodehalogenation and borylation of halogens. Tertiary and amino acid substrates are in general not working well in this method. Please see ‘Unsuccessful or Challenging Substrates’ section for the problematic examples we’ve tried.

**Question 15:**
Could external ligand on copper improve the yield?

**Answer:**
We’ve screened common nitrogen, phosphine and acac-type ligands and no appreciable improvement was observed.

**Question 16:**
Is a rigorous stirring rate required to maintain high yields? Does it have any effect on the yield?

**Answer:**
Rigorous stirring rate is not necessary. Stirring control experiments have been done under stir rates of 200, 400, 600, 800, 1000 and 1200 rpm on substrate 11. All entries gave essentially the same yield of product (<5% difference).

**Question 17:**
This is a heterogeneous reaction. Does the yield drop in a larger scale?

**Answer:**
We obtained similar yield when scaling up the reaction to 1 gram scale. Larger scale was not tested. We believe that it is very important to use well-grinded powder of LiOH•H₂O, MgCl₂ and Cu(acac)₂ for scale up.
Experimental Procedures and Characterization Data for Redox-Active Esters

Compound S26

![Chemical Structure of Compound S26](image)

*1,3-dioxoisooindolin-2-yl 3-(2-fluorophenyl)propanoate*

Following General Procedure A on 1.0 mmol scale with 3-(2-fluorophenyl)propionic acid. Purification by flash column chromatography (silica, 8:1 hexanes:EtOAc) afforded 246 mg (79%) of the title compound S26.

**Physical State**: white solid.

**m.p.**: 102 – 104 ºC.

Rf = 0.45 (4:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): δ 7.89 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.79 (dd, $J = 5.4, 3.1$ Hz, 2H), 7.28 (t, $J = 7.6, 1$H), 7.26 – 7.21 (m, 1H), 7.11 (td, $J = 7.5, 1.3$ Hz, 1H), 7.08 – 7.03 (m, 1H), 3.13 (t, $J = 7.7$ Hz, 2H), 3.05 – 2.97 (m, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 168.9, 162.0, 161.3 (d, $J = 245.6$ Hz), 134.9, 130.9 (d, $J = 4.4$ Hz), 129.1, 128.8 (d, $J = 8.2$ Hz), 126.1 (d, $J = 15.4$ Hz), 124.4 (d, $J = 3.6$ Hz), 124.1, 115.6 (d, $J = 21.9$ Hz), 31.3 (d, $J = 1.7$ Hz), 24.5 (d, $J = 2.8$ Hz) ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -118.6 ppm.

HRMS (ESI-TOF): calc’d for C$_{17}$H$_{13}$FNO$_4$ [M+H]$^+$ 314.0823; found 314.0829.

Compound S27

![Chemical Structure of Compound S27](image)

*tert-butyl 3-(2-((1,3-dioxoisooindolin-2-yl)oxy)-2-oxoethyl)azetidine-1-carboxylate*

Following General Procedure A on 2.0 mmol scale with 2-(1-(tert-butoxycarbonyl)azetidin-3-yl)acetic acid. Purification by flash column chromatography (silica, 3:1 hexanes:EtOAc) afforded 540 mg (75%) of the title compound S27.

**Physical State**: white amorphous solid.

Rf = 0.25 (3:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): δ 7.86 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.78 (dd, $J = 5.5, 3.1$ Hz, 2H), 4.14 (t, $J = 8.2$ Hz, 2H), 3.71 (dd, $J = 8.9, 4.7$ Hz, 2H), 3.04 – 2.95 (m, 3H), 1.42 (s, 9H) ppm.
$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 167.9, 161.8, 156.3, 135.0, 128.9, 124.1, 79.7, 54.0, 35.4, 28.5, 25.1 ppm.

HRMS (ESI-TOF): calc’d for C$_{18}$H$_{21}$N$_2$O$_6$ [M+H]$^+$ 361.1394; found 361.1393.

Compound S28

1,3-dioxoisindolin-2-yl 3-((tert-butoxycarbonyl)amino)-3-methylbutanoate

Following General Procedure A on 1.0 mmol scale with 3-((tert-butoxycarbonyl)amino)-3-methylbutanoic acid. Purification by flash column chromatography (silica, 4:1 hexanes:EtOAc) afforded 297 mg (82%) of the title compound S28.

Physical State: white solid.

m.p.: 103 – 105 ºC.

$R_f = 0.30$ (4:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.87 (dd, $J = 5.4, 3.1$ Hz, 2H), 7.77 (dd, $J = 5.5, 3.0$ Hz, 2H), 4.79 (s, 1H), 3.13 (s, 2H), 1.46 (s, 6H), 1.40 (s, 9H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 167.1, 162.0, 154.7, 134.9, 129.0, 124.0, 79.4, 51.3, 40.4, 28.5, 27.8 ppm.

HRMS (ESI-TOF): calc’d for C$_{18}$H$_{22}$N$_2$O$_6$Na [M+Na]$^+$ 385.1370; found 385.1375.

Compound S29

1,3-dioxoisindolin-2-yl 3-(4-acetylphenyl)propanoate

Following General Procedure A on 1.0 mmol scale with 3-(4-acetylphenyl)propanoic acid. Purification by flash column chromatography (silica, 3:1 hexanes:EtOAc) afforded 239 mg (71%) of the title compound S29.

Physical State: white solid.

m.p.: 159 – 160 ºC.

$R_f = 0.20$ (4:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.93 (d, $J = 8.3$ Hz, 2H), 7.89 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.80 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.36 (d, $J = 8.3$ Hz, 2H), 3.16 (t, $J = 7.7$ Hz, 2H), 3.01 (t, $J = 7.7$ Hz, 2H), 2.59 (s, 3H) ppm.
\( ^{13}\text{C} \) NMR (151 MHz, CDCl\(_3\)): \( \delta \) 197.9, 168.7, 162.0, 144.8, 135.9, 135.0, 129.0, 129.0, 128.7, 124.2, 32.3, 30.6, 26.8 ppm.

HRMS (ESI-TOF): calc’d for C\(_{19}\)H\(_{16}\)NO\(_5\) [M+H]\(^{+}\) 338.1023; found 338.1028.

**Compound S30**

\[ \text{1,3-dioxoisindolin-2-yl 3-(3,4,5-trimethoxyphenyl)propanoate} \]

Following General Procedure A on 1.0 mmol scale with 3-(3,4,5-trimethoxyphenyl)propanoic acid. Purification by flash column chromatography (silica, 6:1 hexane:EtOAc) afforded 327 mg (85%) of the title compound S30.

**Physical State**: light yellow solid.

m.p.: 124 – 126 °C.

\( R_f = 0.4 \) (4:1 hexanes:EtOAc).

\( ^1\text{H} \) NMR (600 MHz, CDCl\(_3\)): \( \delta \) 7.91 – 7.86 (m, 2H), 7.82 – 7.77 (m, 2H), 6.47 (d, \( J = 1.8 \) Hz, 2H), 3.87 (d, \( J = 2.8 \) Hz, 6H), 3.83 (d, \( J = 2.8 \) Hz, 3H), 3.07 – 3.02 (ddd, \( J = 9.9, 5.5, 2.3 \) Hz, 2H), 3.00 – 2.96 (m, 2H) ppm.

\( ^{13}\text{C} \) NMR (151 MHz, CDCl\(_3\)): \( \delta \) 169.0, 162.0, 153.5, 136.8, 135.1, 134.9, 129.03, 129.02, 124.1, 105.3, 61.0, 56.3, 33.0, 31.1 ppm.

HRMS (ESI-TOF): calc’d for C\(_{20}\)H\(_{20}\)NO\(_7\) [M+H]\(^{+}\) 386.1234; found 386.1234.

**Compound S31**

\[ \text{1-(tert-butyl) 3-(1,3-dioxoisindolin-2-yl) piperidine-1,3-dicarboxylate} \]

Following General Procedure A on 5.0 mmol scale with 1-(tert-butoxycarbonyl)piperidine-3-carboxylic acid. Purification by flash column chromatography (silica, 2:1 hexanes:EtOAc) afforded 1.42 g (76%) of the title compound S31.

**Physical State**: white solid.

m.p.: 135 – 137 °C.

\( R_f = 0.30 \) (1:1 hexanes:EtOAc).

\( ^1\text{H} \) NMR (600 MHz, CDCl\(_3\)): \( \delta \) 7.88 (dd, \( J = 5.5, 3.1 \) Hz, 2H), 7.78 (dd, \( J = 5.5, 3.1 \) Hz, 2H), 4.51 – 4.14 (m, 1H), 3.95 (d, \( J = 13.3 \) Hz, 1H), 3.29 – 3.02 (m, 1H), 2.94 – 2.80 (m, 2H), 2.33 – 2.19 (m, 1H).
1.88 – 1.72 (m, 2H), 1.61 – 1.50 (m, 1H), 1.47 (s, 9H) ppm.

\[ ^{13}\text{C NMR (151 MHz, CDCl}_3\] : \( \delta 169.6, 161.9, 154.6, 134.9, 129.0, 124.1, 80.2, 45.4 \) (br), 43.5 (br), 39.2, 28.5, 27.6, 24.1 (br) ppm.

HRMS (ESI-TOF): calc’d for C\textsubscript{19}H\textsubscript{23}N\textsubscript{2}O\textsubscript{6} \[ [\text{M+H}]^+ \text{ 375.1551; found 375.1546.}\]

**Compound S32**

\[ \text{1,3-dioxoisouindolin-2-yl 3-((t\text{ert}-butoxy carbonyl)amino)-2-methylpropanoate} \]

Following General Procedure A on 2.0 mmol scale with 3-((t\text{ert}-butoxy carbonyl)amino)-2-methylpropanoic acid. Purification by flash column chromatography (silica, 4:1 hexanes:EtOAc) afforded 501 mg (72%) of the title compound S32.

**Physical State**: white solid.

**m.p.**: 77 – 80 °C.

\( R_f = 0.25 \) (4:1 hexanes:EtOAc).

\[ ^{1}\text{H NMR (600 MHz, CDCl}_3\] : \( \delta 7.87 \) (dd, \( J = 5.5, 3.1 \) Hz, 2H), 7.78 (dd, \( J = 5.5, 3.1 \) Hz, 2H), 5.27 (t, \( J = 6.5 \) Hz, 1H), 3.57 – 3.52 (m, 1H), 3.37 – 3.32 (m, 1H), 3.12 – 3.08 (m, 1H), 1.43 (s, 9H), 1.34 (d, \( J = 7.1 \) Hz, 3H) ppm.

\[ ^{13}\text{C NMR (151 MHz, CDCl}_3\] : \( \delta 171.7, 162.1, 156.2, 135.0, 129.0, 124.2, 79.7, 43.5, 38.5, 28.5, 14.3 \) ppm.

HRMS (ESI-TOF): calc’d for C\textsubscript{17}H\textsubscript{21}N\textsubscript{2}O\textsubscript{6} \[ [\text{M+H}]^+ \text{ 349.1394; found 349.1392.}\]

**Compound S33**

Following General Procedure A on 6.0 mmol scale with 4-(4-methoxyphenyl)-2-methylbutanoic acid. Purification by flash column chromatography (silica, 6:1 hexanes:EtOAc) afforded 1.80 g (85%) of the title compound S33.

**Physical State**: white solid.

**m.p.**: 54 – 55 °C.

\( R_f = 0.40 \) (4:1 hexanes:EtOAc).

\[ ^{1}\text{H NMR (600 MHz, CDCl}_3\] : \( \delta 7.89 \) (dd, \( J = 5.5, 3.1 \) Hz, 2H), 7.79 (dd, \( J = 5.5, 3.1 \) Hz, 2H), 7.18 (d, \( J = 8.6 \) Hz, 2H), 6.85 (d, \( J = 8.6 \) Hz, 2H), 3.79 (s, 3H), 2.89 – 2.81 (m, 1H), 2.80 – 2.67 (m, 2H), 2.17 – 2.09 (m, 1H), 1.92 – 1.84 (m, 1H), 1.38 (d, \( J = 7.0 \) Hz, 3H) ppm.
13C NMR (151 MHz, CDCl3): δ 172.8, 162.2, 158.1, 134.9, 133.3, 129.6, 129.1, 124.1, 124.0, 114.1, 55.4, 36.6, 35.9, 32.2, 17.2 ppm.
HRMS (ESI-TOF): calc’d for C20H20NO5 [M+H]+ 354.1336; found 354.1325.

Compound S34

1,3-dioxoisindolin-2-yl heptadecanoate

Following General Procedure A on 1.5 mmol scale with heptadecanoic acid. Purification by flash column chromatography (silica, 8:1 hexanes:EtOAc) afforded 433 mg of the title compound S34 (70%).

Physical State: white fluffy solid.
m.p.: 62 – 63 ºC.
Rf = 0.51 (4:1 hexanes:EtOAc).
1H NMR (600 MHz, CDCl3): δ 7.91 (dd, J = 5.5, 3.1 Hz, 2H), 7.81 (dd, J = 5.5, 3.1 Hz, 2H), 2.68 (t, J = 7.5 Hz, 2H), 1.81 (p, J = 7.5 Hz, 2H), 1.52 – 1.40 (m, 2H), 1.40 – 1.24 (m, 24H), 0.90 (t, J = 7.0 Hz, 3H) ppm.
13C NMR (151 MHz, CDCl3): δ 169.7, 162.0, 134.7, 129.0, 123.9, 31.9, 31.0, 29.71, 29.70, 29.69, 29.68, 29.67, 29.64, 29.58, 29.39, 29.37, 29.31, 28.8, 24.7, 22.7, 14.1 ppm.
HRMS (ESI-TOF): calc’d for C25H38NO4 [M+H]+ 416.2795; found 416.2787.

Compound 45

Following General Procedure A on 10.0 mmol scale with 4. Purification by flash column chromatography (silica, 8:1 hexanes:EtOAc) afforded 4.25 g of the title compound 45 (89%).

Physical State: white solid.
m.p.: 69 – 70 ºC.
Rf = 0.54 (3:1 hexanes:EtOAc).
1H NMR (600 MHz, CDCl3): δ 7.88 (dd, J = 5.5, 3.1 Hz, 2H), 7.78 (dd, J = 5.5, 3.0 Hz, 2H), 4.22 (tdd, J = 6.9, 5.6, 4.2 Hz, 1H), 2.85 – 2.66 (m, 2H), 2.47 (dd, J = 14.9, 5.7 Hz, 1H), 2.35 (dd, J = 14.9, 6.9 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.97 – 1.89 (m, 1H), 1.45 (s, 9H), 0.90 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H) ppm.
$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 170.3, 169.8, 162.0, 134.9, 129.1, 124.1, 80.9, 67.9, 43.7, 31.8, 28.3, 26.7, 26.0, 18.1, -4.5, -4.6 ppm.

HRMS (ESI-TOF): calc’d for C$_{24}$H$_{36}$NO$_7$Si [M+H]$^+$ 478.2254; found 478.2256.
Experimental Procedures and Characterization Data for Borylation Products

**Compound 2**

![Structure of Compound 2]

*Tert-butyl* 3-(((tert-butyldimethylsilyl)oxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate

Following General Procedure B on 0.1 mmol scale with redox-active ester 45, Cu(acac)$_2$ (20 mol%) and B$_2$pin$_2$ (1.5 equiv) in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:Et$_2$O) afforded 26.6 mg (64%) of the title compound 2.

**Physical State:** colorless oil.

$R_f$ = 0.54 (8:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 4.04 (p, $J = 5.9$ Hz, 1H), 2.33 (dd, $J = 6.1$, 2.0 Hz, 2H), 1.66 – 1.56 (m, 2H), 1.44 (s, 9H), 1.24 (s, 12H), 0.87 (s, 9H), 0.78 (ddd, $J = 11.6$, 9.6, 6.4 Hz, 2H), 0.07 (s, 3H), 0.05 (s, 3H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 171.3, 83.1, 80.3, 70.8, 43.6, 31.6, 28.3, 26.7, 25.0, 18.2, -4.3, -4.5 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

**HRMS (ESI-TOF):** calc’d for C$_{21}$H$_{43}$BNaO$_5$Si [$M+Na]^+$ 437.2865; found 437.2874.

**Compound 6**

![Structure of Compound 6]

Following General Procedure B on 0.2 mmol scale with redox-active ester 5 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, hexanes to 100:1 CH$_2$Cl$_2$:Et$_2$O) afforded 36.8 mg (76%) of the title compound 6.

Following General Procedure B on 0.1 mmol scale with redox-active ester 5, Cu(acac)$_2$ (20 mol%) and B$_2$pin$_2$ (1.5 equiv) in dioxane/DMF (4:1). Purification by flash column chromatography (silica, hexanes to 100:1 CH$_2$Cl$_2$:Et$_2$O) afforded 14.3 mg (59%) of the title compound 6.

**Physical state:** colorless oil.

$R_f$ = 0.55 (silica gel, 6:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 3.65 (s, 3H), 2.30 (t, $J = 7.6$ Hz, 2H), 1.66 – 1.59 (m, 2H), 1.46 – 1.40 (m, 2H), 1.23 (s, 12H), 0.78 (t, $J = 7.9$ Hz, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 174.4, 83.1, 51.6, 34.1, 27.7, 25.0, 23.8, 11.1 (br, C–B) ppm.
Spectroscopic data are in accordance with that reported in the literature.5

Compound 11

Following General Procedure B on 0.2 mmol scale with redox-active ester S1 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:EtO) afforded 36.5 mg (70%) of the title compound 11.

Physical state: colorless oil. 

\[ R_f = 0.50 \text{ (silica gel, 12:1 hexanes:EtOAc).} \]

\[ ^1H \text{ NMR (600 MHz, CDCl}_3\): } \delta 7.28 – 7.25 (m, 2H), 7.18 – 7.15 (m, 3H), 2.61 (t, \( J = 7.8 \text{ Hz}, 2H\)), 1.66 – 1.61 (m, 2H), 1.50 – 1.45 (m, 2H), 1.24 (s, 12H), 0.82 (t, \( J = 7.8 \text{ Hz}, 2H\)) ppm. \]

\[ ^{13}C \text{ NMR (151 MHz, CDCl}_3\): } \delta 143.1, 128.5, 128.3, 125.6, 83.0, 35.9, 34.3, 25.0, 23.9 11.3 (br, C–B) ppm. \]

Spectroscopic data are in accordance with that reported in the literature.5

Compound 12

\[ 4,4,5,5\text{-tetramethyl-2-phenethyl-1,3,2-dioxaborolane} \]

Following General Procedure B on 0.2 mmol scale with redox-active ester S2 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:EtO) afforded 33.3 mg (72%) of the title compound 12.

Physical State: colorless oil.

\[ R_f = 0.50 \text{ (silica gel, 12:1 hexanes:EtOAc).} \]

\[ ^1H \text{ NMR (600 MHz, CDCl}_3\): } \delta 7.28 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 7.18 – 7.10 (m, 1H), 2.75 (t, \( J = 8.2 \text{ Hz}, 2H\)), 1.22 (s, 12H), 1.15 (t, \( J = 8.3 \text{ Hz}, 2H\)) ppm. \]

\[ ^{13}C \text{ NMR (151 MHz, CDCl}_3\): } \delta 144.5, 128.3, 128.1, 125.6, 83.2, 30.1, 25.0, 13.2 (br, C–B) ppm. \]

Spectroscopic data are in accordance with that reported in the literature.6
Compound 13

2-(2-fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Following General Procedure B on 0.2 mmol scale with redox-active ester S26 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:Et2O) afforded 30.2 mg (60%) of the title compound 13.

Physical State: colorless oil.

\[ R_f = 0.51 \] (silica gel, 12:1 hexanes:EtOAc).

\[^1\mathrm{H} \text{ NMR} \ (600 \ \mathrm{MHz}, \ \text{CDCl}_3): \delta \ 7.23 \ (t, J = 7.7 \ \mathrm{Hz}, \ 1\mathrm{H}), \ 7.16 - 7.10 \ (m, \ 1\mathrm{H}), \ 7.03 \ (t, J = 7.5 \ \mathrm{Hz}, \ 1\mathrm{H}), \ 7.00 - 6.91 \ (m, \ 1\mathrm{H}), \ 2.77 \ (t, J = 8.2 \ \mathrm{Hz}, \ 2\mathrm{H}), \ 1.22 \ (s, \ 12\mathrm{H}), \ 1.14 \ (t, J = 8.2 \ \mathrm{Hz}, \ 2\mathrm{H}) \ \mathrm{ppm}. \]

\[^{13}\mathrm{C} \text{ NMR} \ (151 \ \mathrm{MHz}, \ \text{CDCl}_3): \delta \ 161.2 \ (d, J = 244.6 \ \mathrm{Hz}), \ 131.3 \ (d, J = 15.9 \ \mathrm{Hz}), \ 130.2 \ (d, J = 5.2 \ \mathrm{Hz}), \ 127.3 \ (d, J = 8.2 \ \mathrm{Hz}), \ 123.9 \ (d, J = 3.5 \ \mathrm{Hz}), \ 115.2 \ (d, J = 22.3 \ \mathrm{Hz}), \ 25.0, \ 23.3 \ (d, J = 3.0 \ \mathrm{Hz}), \ 11.8 \ (\text{br, C–B}) \ \mathrm{ppm}. \]

\[^{19}\mathrm{F} \text{ NMR} \ (376 \ \mathrm{MHz}, \ \text{CDCl}_3): \delta \ -119.1. \]

Spectroscopic data are in accordance with that reported in the literature.\(^9\)

Compound 14

\[ \text{tert-butyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate} \]

Following General Procedure B on 0.2 mmol scale with redox-active ester S3 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:acetone) afforded 31.4 mg (55%) of the title compound 14.

Physical State: colorless oil.

\[ R_f = 0.54 \] (8:1 hexanes:EtOAc).

\[^1\mathrm{H} \text{ NMR} \ (600 \ \mathrm{MHz}, \ \text{CDCl}_3): \delta \ 4.73 \ (\text{br s, 0.86H}), \ 4.38 \ (\text{br s, 0.14H}), \ 3.17 - 2.95 \ (m, \ 2\mathrm{H}), \ 1.63 - 1.53 \ (m, \ 2\mathrm{H}), \ 1.42 \ (s, \ 9\mathrm{H}), \ 1.24 \ (s, \ 12\mathrm{H}), \ 0.78 \ (t, J = 7.7 \ \mathrm{Hz}, \ 2\mathrm{H}) \ \mathrm{ppm}. \]

\[^{13}\mathrm{C} \text{ NMR} \ (151 \ \mathrm{MHz}, \ \text{CDCl}_3): \delta \ 156.1, \ 83.3, \ 79.0, \ 42.8, \ 28.6, \ 25.0, \ 24.3, \ 8.6 \ (\text{br, C–B}) \ \mathrm{ppm}. \]

HRMS (ESI-TOF): calc’d for C\(_{14}\)H\(_{28}\)BNNaO\(_4\) [M+Na]\(^+\) 308.2004; found 308.2015.
Compound 15

4,4,5,5-tetramethyl-2-(4-(oxiran-2-yl)butyl)-1,3,2-dioxaborolane

Following General Procedure B on 0.2 mmol scale with redox-active ester S4 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 15:1 hexanes:EtOAc) afforded 31.0 mg (69%) of the title compound 15.

Physical State: colorless oil.

Rf = 0.4 (10:1 hexanes:EtOAc).

1H NMR (600 MHz, CDCl3): δ 2.92 – 2.88 (m, 1H), 2.75 – 2.71 (m, 1H), 2.45 (dd, J = 5.1, 2.7 Hz, 1H), 1.58 – 1.40 (m, 6H), 1.24 (s, 12H), 0.81 – 0.77 (m, 2H) ppm.

13C NMR (151 MHz, CDCl3): δ 83.1, 52.5, 47.3, 32.4, 28.7, 25.0, 24.0, 11.4 (br, C–B) ppm.

HRMS (ESI-TOF): calc’d for C12H24BO3 [M+H]+ 227.1813; found: 227.1815.

Compound 16

tert-butyl 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)azetidine-1-carboxylate

Following General Procedure B on 0.144 mmol scale with redox-active ester S27 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 10:1 hexanes: EtOAc) afforded 24.0 mg (56%) of the title compound 16.

Physical State: colorless oil.

Rf = 0.2 (10:1 hexanes:EtOAc).

1H NMR (600 MHz, CDCl3): δ 4.05 – 3.98 (m, 2H), 3.51 (dd, J = 8.5, 5.7 Hz, 2H), 2.70 – 2.65 (m, 1H), 1.43 (s, 9H), 1.22 (s, 12H), 1.10 (d, J = 7.9 Hz, 2H) ppm.

13C NMR (151 MHz, CDCl3): δ 156.6, 83.4, 79.1, 56.6 (br), 28.6, 25.3, 24.9 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

HRMS (ESI-TOF): calc’d for C15H28BNO4Na [M+Na]+ 320.2004; found: 320.2010.

Compound 17

3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)pyridine
Following General Procedure B on 0.2 mmol scale with redox-active ester S5 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 10:1 hexanes:acetone) afforded 18.6 mg (40%) of the title compound 17.

Physical State: colorless oil.

$R_f = 0.48$ (4:1 hexanes:acetone).

$^1$H NMR (600 MHz, CDCl$_3$): δ 8.48 (s, 1H), 8.41 (d, $J = 4.8$ Hz, 1H), 7.55 (dt, $J = 7.8, 1.9$ Hz, 1H), 7.20 (dd, $J = 7.8, 4.8$ Hz, 1H), 2.75 (t, $J = 8.0$ Hz, 2H), 1.21 (s, 12H), 1.14 (t, $J = 8.0$ Hz, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 149.6, 146.9, 139.8, 135.9, 123.4, 83.4, 27.3, 25.0 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.$^6$

Compound 18

![Compound 18](image)

tert-butyl (2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)carbamate

Following General Procedure B on 0.2 mmol scale with redox-active ester S28 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 15:1 hexanes: EtOAc) afforded 42.1 mg (70%) of the title compound 18.

Physical State: colorless oil.

$R_f = 0.4$ (10:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): δ 4.75 (s, 1H), 1.41 (s, 9H), 1.34 (s, 6H), 1.23 (s, 2H), 1.22 (s, 12H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 154.8, 83.2, 78.4, 51.6, 29.3, 28.6, 26.3 (br, C–B), 24.9 ppm.

HRMS (ESI-TOF): calc’d for C$_{15}$H$_{30}$BNO$_4$Na [M+Na]$^+$ 322.2160; found 322.2172.

Compound 19

![Compound 19](image)

1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one

Following General Procedure B on 0.2 mmol scale with redox-active ester S29 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 15:1 hexanes: EtOAc) afforded 35.1 mg (64%) of the title compound 19.
**Compound 20**

4,4,5,5-tetramethyl-2-(3,4,5-trimethoxyphenethyl)-1,3,2-dioxaborolane

Following General Procedure B on 0.2 mmol scale with redox-active ester S30 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 15:1 hexanes:Et2O) afforded 41.9 mg (65%) of the title compound 20.

**Physical State**: white solid.

**m.p.**: 45 – 47 ºC.

**Rf** = 0.50 (silica gel, 6:1 hexanes:EtOAc).

**1H NMR (600 MHz, CDCl3)**: δ 6.45 (s, 2H), 3.84 (s, 6H), 3.81 (s, 3H), 2.70 – 2.67 (m, 2H), 1.22 (s, 12H), 1.16 – 1.12 (m, 2H) ppm.

**13C NMR (151 MHz, CDCl3)**: δ 153.1, 140.4, 136.0, 105.0, 83.3, 61.0, 56.1, 30.5, 25.0, 13.2 (br, C–B) ppm.

**HRMS (ESI-TOF)**: calc’d for C17H27BNaO5 [M+Na]+ 345.1844; found 345.1854.

**Compound 21**

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylpiperidine

Following General Procedure B on 0.2 mmol scale with redox-active ester S6 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 5:1 hexanes: EtOAc) afforded 48.2 mg (66%) of the title compound 21.

**Physical State**: white solid.
m.p.: 102 – 104 °C.

$R_f = 0.2$ (4:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.62 (d, $J$ = 8.0 Hz, 2H), 7.30 (d, $J$ = 8.0 Hz, 2H), 3.36 (dt, $J$ = 10.3, 4.3 Hz, 2H), 2.51 (td, $J$ = 9.9, 3.1 Hz, 2H), 2.41 (s, 3H), 1.76 – 1.70 (m, 2H), 1.67 – 1.59 (m, 2H), 1.15 (s, 12H), 0.89 (tt, $J$ = 10.2, 4.0 Hz, 1H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 143.3, 133.2, 129.6, 127.9, 83.4, 47.2, 26.6, 24.8, 21.6, 18.9 (br, C–B) ppm.

HRMS (ESI-TOF): calc’d for C$_{18}$H$_{29}$BN$_4$S $[M+H]^+$ 366.1905; found 366.1919.

**Compound 22**

**tert-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate**

Following General Procedure B on 0.2 mmol scale with redox-active ester S7 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 5:2:1 hexanes:CH$_2$Cl$_2$:EtOAc) afforded 42.5 mg (68%) of the title compound 22.

**Physical State:** colorless oil.

$R_f = 0.46$ (4:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 3.89 – 3.65 (m, 2H), 3.01 – 2.84 (m, 2H), 1.66 – 1.57 (m, 2H), 1.51 – 1.44 (m, 2H), 1.44 (s, 9H), 1.22 (s, 12H), 1.09 (tt, $J$ = 10.5, 3.6 Hz, 1H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 155.0, 83.3, 79.1, 45.5 (br), 44.5 (br), 28.6, 27.1, 24.9, 20.0 (br, C–B) ppm.

Spectroscopic data are in accordance with that reported in the literature.$^6$

**Compound 23**

**2-(4,4-difluorocyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**

Following General Procedure B on 0.1 mmol scale with redox-active ester S8 in dioxane/DMF (6:1). Purification by flash column chromatography (silica, 20:1 hexanes: EtOAc) afforded 18.5 mg (75%) of the title compound 23.

**Physical state:** colorless oil.
\( R_f = 0.45 \) (silica gel, 9:1 hexanes:EtOAc).

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta \) 2.02 – 1.91 (m, 2H), 1.83 – 1.75 (m, 2H), 1.75 – 1.55 (m, 4H), 1.22 (s, 12H), 1.02 – 0.92 (m, 1H) ppm.

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \( \delta \) 123.9 (t, \( J = 240.5 \) Hz), 83.4, 34.5 (t, \( J = 23.3 \) Hz), 24.9, 24.4 (t, \( J = 4.9 \) Hz) 19.9 (br, C–B) ppm.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -91.8 (d, \( J = 235.5 \) Hz), -99.0 (d, \( J = 235.4 \) Hz).

Spectroscopic data are in accordance with that reported in the literature.\(^5\)

**Compound 24**

\[ 4,4,5,5\text{-tetramethyl-2-(tetrahydro-2H-pyran-4-yl)-1,3,2-dioxaborolane} \]

Following General Procedure B on 0.1 mmol scale with redox-active ester S9 in dioxane/DMF (6:1). Purification by flash column chromatography (silica, 15:1 hexanes:EtOAc) afforded 13.9 mg (66%) of the title compound 24.

**Physical state:** colorless oil.

\( R_f = 0.4 \) (silica gel, 10:1 hexanes:EtOAc).

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta \) 3.83 (dt, \( J = 11.2, 4.0 \) Hz, 2H), 3.49 – 3.44 (m, 2H), 1.64 – 1.59 (m, 4H), 1.24 (s, 12H), 1.22 – 1.18 (m, 1H) ppm.

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \( \delta \) 83.3, 69.0, 27.8, 24.9 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.\(^6\)

**Compound 25**

\[ \text{tert-butyl (R)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate} \]

Following General Procedure B on 0.2 mmol scale with redox-active ester S31 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 5:2:1 hexanes:CH\(_2\)Cl\(_2\):EtOAc) afforded 38.6 mg (62%) of the title compound 25.

**Physical State:** colorless oil.

\( R_f = 0.46 \) (4:1 hexanes:EtOAc).
\[ {^1}H \text{ NMR (600 MHz, CDCl}_3\text{): } \delta 3.96 \text{ – } 3.77 (m, 2H), 3.01 \text{ – } 2.82 (m, 2H), 1.84 \text{ – } 1.73 (m, 1H), 1.45 (s, 9H), 1.44 \text{ – } 1.39 (m, 2H), 1.22 (s, 12H), 1.16 \text{ – } 1.10 (m, 2H) \text{ ppm.} \]

\[ {^{13}}C \text{ NMR (151 MHz, CDCl}_3\text{): } \delta 155.0, 83.3, 79.2, 45.8 (\text{br}), 44.7 (\text{br}), 28.7, 26.21, 26.17, 24.93, 24.86, 22.0 (\text{br}, \text{C–B}) \text{ ppm.} \]

HRMS (ESI-TOF): calcd for C_{16}H_{30}BNNaO_{4} [M+Na]^+ 334.2160; found 334.2167.

Compound 26

\[
\text{BocHN}
\]

\[ \text{tert-butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate} \]

Following General Procedure B on 0.1 mmol scale with redox-active ester S32 in dioxane/DMF (6:1). Purification by flash column chromatography (silica, 10:1 hexanes: EtOAc) afforded 16.0 mg (56%) of the title compound 26.

Physical State: colorless oil.

\[ R_f = 0.4 \text{ (10:1 hexanes:EIOAc).} \]

\[ {^1}H \text{ NMR (600 MHz, CDCl}_3\text{): } \delta 4.78 (\text{br s, 1H}), 3.21 \text{ – } 3.04 (m, 2H), 1.42 (s, 9H), 1.24 \text{ – } 1.19 (m, 1H), 1.22 (s, 12H), 0.96 (d, } J = 7.6 \text{ Hz, 3H) ppm.} \]

\[ {^{13}}C \text{ NMR (151 MHz, CDCl}_3\text{): } \delta 156.2, 83.4, 78.9, 43.6, 28.6, 24.9, 24.8, 18.4 (\text{br, C–B}), 13.2 \text{ ppm.} \]

HRMS (ESI-TOF): calcd for C_{14}H_{28}BNO_{4}Na [M+Na]^+ 308.2004; found 308.2016.

Compound 27

\[
\text{Me}
\]

\[ \text{2-(bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane} \]

Following General Procedure B on 0.1 mmol scale with redox-active ester S10 in dioxane/DMF (6:1). Purification by flash column chromatography (silica, 25:1 hexanes:EIOAc) afforded 13.1 mg (59%) of the title compound 27 with 10:1 \text{dr} as determined by crude \text{H NMR}.

Physical state: colorless oil.

\[ R_f = 0.38 \text{ (silica gel, 19:1 hexanes:EIOAc).} \]

\[ {^1}H \text{ NMR (600 MHz, CDCl}_3\text{): } \delta 2.38 \text{ – } 2.17 (m, 2H), 1.57 \text{ – } 1.42 (m, 3H), 1.38 \text{ – } 1.31 (m, 1H), 1.26 \text{ – } 1.12 (m, 18H), 0.91 \text{ – } 0.81 (m, 1H) \text{ ppm. (mixture of exo and endo isomers)} \]

\[ {^{13}}C \text{ NMR (151 MHz, CDCl}_3\text{): } \delta 82.9, 38.9, 38.3, 36.8, 32.4, 32.3, 29.4, 24.9 \text{ ppm (exo); } 83.0, 41.1, 39.1, 37.2, 32.0, 30.0, 28.0, 25.1, 25.0 \text{ ppm (endo). The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.} \]
Spectroscopic data are in accordance with that reported in the literature.5

**Compound 28**

(R)-2-(4-(4-methoxyphenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Following General Procedure B on 0.2 mmol scale with redox-active ester S33 in dioxane/DMF (2:1). Purification by flash column chromatography (silica, 15:1 hexanes:Et₂O) afforded 37.8 mg (65%) of the title compound 28.

**Physical State**: colorless oil.

$R_f = 0.47$ (12:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl₃): δ 7.17 – 7.04 (m, 2H), 6.88 – 6.74 (m, 2H), 3.78 (s, 3H), 2.56 (ddd, $J = 9.6, 6.5, 2.9$ Hz, 2H), 1.82 – 1.68 (m, 1H), 1.63 – 1.48 (m, 1H), 1.25 (s, 12H), 1.01 (d, $J = 7.0$ Hz, 3H) ppm.

$^{13}$C NMR (151 MHz, CDCl₃): δ 157.7, 135.3, 129.4, 113.8, 83.0, 55.4, 35.7, 34.5, 24.94, 24.90, 15.6 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

**GCMS (EI)**: m/z (%) 290 (21), 121 (100).

**Compound 29**

4,4,5,5-tetramethyl-2-(2-phenylcyclopropyl)-1,3,2-dioxaborolane

Following General Procedure B on 0.2 mmol scale with redox-active ester S11 in MTBE/DMF (6:1). Purification by flash column chromatography (silica, 20:1 hexanes:Et₂O) afforded 20.5 mg (42%) of the title compound 29 with >20:1 dr as determined by $^1$H NMR.

**Physical State**: colorless oil.

$R_f = 0.48$ (silica gel, 9:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl₃): δ 7.26 – 7.22 (m, 2H), 7.15 – 7.11 (m, 1H), 7.10 – 7.06 (m, 2H), 2.11 (dt, $J = 8.1, 5.4$ Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.16 (ddd, $J = 8.1, 6.8, 3.7$ Hz, 1H), 1.01 (ddd, $J = 9.9, 5.3, 3.7$ Hz, 1H), 0.31 (ddd, $J = 9.8, 6.8, 5.5$ Hz, 1H) ppm.

$^{13}$C NMR (151 MHz, CDCl₃): δ 143.5, 128.4, 125.8, 125.7, 83.3, 24.9, 24.8, 22.0, 15.2 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.5
Compound 30

(R)-2-(heptan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Following General Procedure B on 0.2 mmol scale with redox-active ester S12 in dioxane/DMF (1:2). Purification by flash column chromatography (silica, 20:1 hexanes:Et2O) afforded 31.0 mg (69%) of the title compound 30.

Physical state: colorless oil.

Rf = 0.52 (silica gel, 12:1 EtOAc:hexanes).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 1.46 – 1.20 (m, 8H), 1.24 (s, 12H), 0.90 – 0.86 (m, 7H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 82.9, 31.7, 31.0, 25.0, 24.96, 24.94, 24.4, 23.1, 14.3, 13.9 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.$^5$

Compound 31

4,4,5,5-tetramethyl-2-(1-phenylcyclopropyl)-1,3,2-dioxaborolane

Following General Procedure B on 0.2 mmol scale with redox-active ester S13 in dioxane/DMF (2:1). Purification by flash column chromatography (silica, 20:1 hexanes:Et2O) afforded 41.7 mg (85%) of the title compound 31.

Physical State: white solid.

m.p.: 46 – 47 °C.

Rf = 0.54 (8:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.31 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 7.17 – 7.13 (m, 1H), 1.24 (s, 12H), 1.15 – 1.12 (m, 2H), 0.97 – 0.91 (m, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 144.9, 129.0, 128.1, 125.3, 83.4, 24.7, 13.5 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.$^6$

Compound 32
2-(1-(4-chlorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Following General Procedure B on 0.2 mmol scale with redox-active ester S14 in dioxane/DMF (2:1). Purification by flash column chromatography (silica, 50:1 hexanes:Et2O) afforded 43.8 mg (76%) of the title compound 32.

Physical State: white solid.

m.p.: 83 – 85 °C.

$R_f = 0.50$ (silica gel, 12:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl3): $\delta$ 7.19 (s, 4H), 1.21 (s, 12H), 1.11 (dd, $J = 6.0, 3.6$ Hz, 2H), 0.87 (dd, $J = 6.0$ Hz, 3.6 Hz, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl3): $\delta$ 143.5, 131.0, 130.5, 128.2, 83.6, 24.7, 13.6 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.5

Compound 33

2-(1-(4-iodophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Following General Procedure B on 0.2 mmol scale with redox-active ester S15 in MTBE/DMF (6:1). Purification by flash column chromatography (silica, 100:1 hexanes:Et2O) afforded 28.0 mg (38%) of the title compound 33.

Physical State: white solid.

m.p.: 90 – 91 ºC.

$R_f = 0.50$ (8:1 hexanes:Et2O).

$^1$H NMR (600 MHz, CDCl3): $\delta$ 7.56 (d, $J = 8.4$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 2H), 1.23 (s, 12H), 1.15 – 1.12 (m, 2H), 0.90 – 0.87 (m, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl3): $\delta$ 144.2, 136.5, 130.7, 89.9, 83.0, 24.1, 13.0 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

GCMS (EI): m/z (%) 370 (40), 143 (61), 101 (100).

Compound 34

$N,N$-bis(2-chloroethyl)-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)aniline

Following General Procedure B on 0.225 mmol scale with redox-active ester S16 in dioxane/DMF
(4:1). Purification by flash column chromatography (silica, 20:1 hexanes:EtOAc) afforded 49 mg (57%) of the title compound 34.

**Physical State**: colorless oil. 

\( R_f = 0.30 \) (silica gel, 20:1 hexanes:EtOAc).

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta \) 7.07 (d, \( J = 8.6 \) Hz, 2H), 6.62 (d, \( J = 8.7 \) Hz, 2H), 3.69 (t, \( J = 6.9 \) Hz, 4H), 3.63 – 3.60 (m, 4H), 2.54 – 2.50 (m, 2H), 1.68 (p, \( J = 7.6 \) Hz, 2H), 1.24 (s, 12H), 0.81 (t, \( J = 7.9 \) Hz, 2H) ppm.

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \( \delta \) 144.1, 132.2, 129.9, 112.2, 83.0, 53.8, 40.7, 37.5, 26.5, 25.0, 11.00 (br, C–B) ppm.

Spectroscopic data are in accordance with that reported in the literature.\(^5\)

**Compound 35**

![Structure of Compound 35](image)

1-(1,1'-biphenyl-4-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one

Following General Procedure B on 0.2 mmol scale with redox-active ester S17 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 12:1 hexanes:Et\(_2\)O) afforded 30.2 mg (45%) of the title compound 35.

**Physical State**: white solid.

\( \text{m.p.: } 92 – 94 ^\circ\text{C.} \)

\( R_f = 0.44 \) (6:1 hexanes:EtOAc).

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta \) 8.05 (d, \( J = 8.5 \) Hz, 2H), 7.70 – 7.64 (m, 2H), 7.64 – 7.60 (m, 2H), 7.50 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H), 3.19 (t, \( J = 7.0 \) Hz, 2H), 1.27 (s, 12H), 1.10 (t, \( J = 7.0 \) Hz, 2H) ppm.

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \( \delta \) 200.3, 145.6, 140.2, 135.8, 129.1, 128.7, 128.3, 127.4, 127.3, 83.3, 33.9, 24.9 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.\(^6\)

**Compound 36**

![Structure of Compound 36](image)
1-(2-(((4R,6S)-2,2-dimethyl-6-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1,3-dioxan-4-yl)ethyl)-5-(4-fluorophenyl)-2-isopropyl-N,4-diphenyl-1H-pyrrole-3-carboxamide

Following General Procedure B on 0.025 mmol scale with redox-active ester S20 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 6:1 hexanes:EtOAc) afforded 9.0 mg (52%) of the title compound 36.

Physical State: white foam.

$R_f = 0.52$ (silica gel, 4:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): δ 7.22 – 7.12 (m, 9H), 7.10 – 7.03 (m, 2H), 7.02 – 6.94 (m, 3H), 6.85 (br s, 1H), 4.09 – 4.02 (m, 1H), 4.01 – 3.95 (m, 1H), 3.86 – 3.79 (m, 1H), 3.70 – 3.64 (m, 1H), 3.62 – 3.53 (m, 1H), 1.69 – 1.63 (m, 2H), 1.53 (d, $J = 7.1$ Hz, 3H), 1.52 (d, $J = 7.1$ Hz, 3H), 1.36 – 1.32 (m, 1H), 1.34 (s, 3H), 1.29 (s, 3H), 1.23 (s, 12H), 1.08 – 1.00 (m, 2H), 0.96 (dd, $J = 15.2$, 7.9 Hz, 1H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 165.0, 162.4 (d, $J = 247.6$ Hz), 141.7, 138.6, 134.8, 133.3 (d, $J = 8.1$ Hz), 130.7, 128.9, 128.8, 128.5, 128.4 (d, $J = 3.6$ Hz), 126.7, 123.6, 121.9, 119.7, 115.43 (d, $J = 21.4$ Hz), 115.37, 98.6, 83.3, 66.73, 66.68, 41.0, 38.4, 38.3, 30.3, 26.2, 24.91, 24.87, 21.9, 21.7, 20.0 ppm.

The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -114.1 ppm.

$[\alpha]_D^{20} = +3.9$ (c 1.0, CHCl$_3$).

Spectroscopic data are in accordance with that reported in the literature.$^5$

Compound 37

(E)-7-hydroxy-5-methoxy-4-methyl-6-(3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-1-yl)isobenzofuran-1(3H)-one

Following General Procedure B on 0.2 mmol scale with redox-active ester S18 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, hexanes to 7:6:1 hexanes:CH$_2$Cl$_2$:EtOAc) afforded 54.6 mg (68%) of the title compound 37.

Physical State: white solid.

m.p.: 122 – 124 °C.

$R_f = 0.40$ (silica gel, 2:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): δ 7.65 (s, 1H), 5.22 – 5.19 (m, 1H), 5.19 (s, 2H), 3.75 (s, 3H), 3.37 (d, $J = 6.6$ Hz, 2H), 2.14 (s, 3H), 2.09 (t, $J = 7.8$ Hz, 2H), 1.78 (s, 3H), 1.18 (s, 12H), 0.86 (t, $J = 7.8$ Hz, 2H) ppm.
\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 173.1, 163.9, 153.9, 143.9, 137.9, 122.8, 120.6, 116.8, 106.4, 83.0, 70.2, 61.1, 33.6, 24.9, 22.7, 16.3, 11.7, 9.8 (br, C–B) ppm.

Spectroscopic data are in accordance with that reported in the literature.\(^5\)

**Compound 38**

\((5S,8R,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)dodecahydro-3H-cyclopenta[al]phenanthrene-3,7,12(2H,4H)-trione\)

Following General Procedure B on 0.2 mmol scale with redox-active ester S21 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 5:1 to 2:1 hexanes:EtOAc) afforded 66.9 mg (69%) of the title compound 38.

**Physical State:** white solid.

m.p.: 230 – 232 °C.

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 2.94 – 2.79 (m, 3H), 2.36 – 2.16 (m, 6H), 2.16 – 2.07 (m, 2H), 2.06 – 1.92 (m, 4H), 1.83 (td, \(J = 11.4, 7.1\) Hz, 1H), 1.63 – 1.54 (m, 2H), 1.39 (s, 3H), 1.34 – 1.13 (m, 16 H), 1.05 (s, 3H), 0.87 – 0.78 (m, 4H), 0.69 – 0.61 (m, 1H) ppm.

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 212.1, 209.2, 208.9, 83.0, 57.1, 51.9, 49.2, 47.0, 45.8, 45.7, 45.1, 42.9, 38.8, 38.2, 36.6, 36.1, 35.4, 29.4, 27.8, 25.4, 25.0, 24.9, 22.1, 18.6, 12.0, 8.1 (br, C–B) ppm.

\([\alpha]_{D}^{20} = +11.3\) (c 1.0, CHCl\(_3\)).

Spectroscopic data are in accordance with that reported in the literature.\(^5\)

**Compound 39**

tert-butyl ((1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclohexyl)methyl)carbamate

Following General Procedure B on 0.123 mmol scale with redox-active ester S19 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 15:1 hexanes:EtOAc) afforded 36.0 mg (83%) of the title compound 39.

**Physical State:** white solid.

m.p.: 92 – 96 °C.

\(R_f = 0.28\) (silica gel, 20:1 hexanes:EtOAc).
\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 5.32 (br s, 1H), 3.12 – 3.00 (m, 2H), 1.52 – 1.41 (m, 4H), 1.43 (s, 9H), 1.38 – 1.34 (m, 2H), 1.33 – 1.28 (m, 4H), 1.25 (s, 12H), 0.80 (s, 2H) ppm.
\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 156.5, 83.4, 78.7, 50.0, 36.7, 36.3, 28.6, 26.4, 25.0, 21.9 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. Spectroscopic data are in accordance with that reported in the literature.5

**Compound 40**

![Image of Compound 40]

4,4,5,5-tetramethyl-2-((4Z,7Z,10Z,13Z)-nonadeca-4,7,10,13-tetraen-1-yl)-1,3,2-dioxaborolane

Following General Procedure B on 0.2 mmol scale with redox-active ester S23 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:Et\(_2\)O) afforded 27.0 mg (35%) of the title compound 40.

**Physical State:** colorless oil. 
\(R_f = 0.52\) (12:1 hexanes:EtOAc).

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 5.49 – 5.26 (m, 8H), 2.88 – 2.77 (m, 6H), 2.12 – 1.99 (m, 4H), 1.48 (p, \(J = 7.7\) Hz, 2H), 1.39 – 1.26 (m, 6H), 1.24 (s, 12H), 0.89 (t, \(J = 6.9\) Hz, 3H), 0.80 (t, \(J = 7.9\) Hz, 2H) ppm.

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 130.6, 130.3, 128.7, 128.6, 128.1, 128.0, 127.7, 83.0, 31.7, 30.0, 29.5, 27.4, 25.8, 25.0, 24.2, 22.7, 14.2, 11.0 (br, C–B) ppm. 
Spectroscopic data are in accordance with that reported in the literature.6

**Compound 41**

![Image of Compound 41]

tert-butyl \((R)-2-(((9H-fluoren-9-yl)methoxy)carbonyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate

Following General Procedure B on 0.2 mmol scale with redox-active ester S22 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 8:1 hexanes:EtOAc) afforded 43.3 mg (43%) of the title compound 41.

**Physical state:** white foam.
$R_f = 0.49$ (silica gel, 4:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.76 (d, $J = 7.5$ Hz, 2H), 7.61 (d, $J = 7.5$ Hz, 2H), 7.39 (t, $J = 7.4$ Hz, 2H), 7.31 (t, $J = 7.4$ Hz, 2H), 5.54 (d, $J = 8.2$ Hz, 0.87H), 5.23 (br s, 0.13H), 4.44 – 4.30 (m, 2H), 4.26 – 4.07 (m, 2H), 2.00 – 1.86 (m, 1H), 1.86 – 1.72 (m, 1H), 1.47 (s, 9H), 1.23 (s, 12H), 0.91 – 0.72 (m, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 171.9, 156.2, 144.2, 144.1, 141.41, 141.42, 127.8, 127.2, 125.3, 120.1, 83.5, 81.9, 67.0, 56.0, 47.4, 28.2, 27.0, 25.0, 24.9, 6.9 (br, C–B) ppm;

$\left[\alpha\right]_{D}^{20} = +0.75$ (c 0.66, CHCl$_3$).

Spectroscopic data are in accordance with that reported in the literature.$^5$

**Compound 42**

![2-hexadecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane](image)

Following General Procedure B on 0.2 mmol scale with redox-active ester S34 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:Et$_2$O) afforded 54.2 mg (77%) of the title compound 42.

**Physical State**: colorless oil.

$R_f = 0.47$ (10:1 hexanes:Et$_2$O).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.43 – 1.34 (m, 2H), 1.34 – 1.17 (m, 38H), 0.88 (t, $J = 7.0$ Hz, 3H), 0.76 (t, $J = 7.8$ Hz, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 82.9, 32.6, 32.1, 29.9, 29.82, 29.81, 29.75, 29.6, 29.5, 24.9, 24.2, 22.8, 14.3, 11.4 (br, C–B) ppm.

GCMS (EI): m/z (%) 352 (0.2), 337 (39), 129 (100).

**Compound 48**

![2-(but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane](image)

Following General Procedure B on 0.2 mmol scale with redox-active ester S24 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 pentane:Et$_2$O) afforded 17.1 mg (47%) of the title compound 48.

**Physical State**: colorless oil.

$R_f = 0.47$ (19:1 pentane:Et$_2$O).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 5.88 (ddt, $J = 17.2$, 10.2, 6.2 Hz, 1H), 4.99 (dq, $J = 17.1$, 1.8 Hz, 1H), 4.90 (ddt, $J = 10.2$, 2.0, 1.3 Hz, 1H), 2.17 (tdd, $J = 7.8$, 6.3, 1.5 Hz, 2H), 1.24 (s, 12H), 0.88 (t, $J = 7.9$ Hz,
2H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 140.8, 113.3, 83.2, 28.1, 25.0 ppm. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.$^6$

**Mixture 49**

Following General Procedure B on 0.2 mmol scale with redox-active ester S25 in dioxane/DMF (4:1). Purification by flash column chromatography (silica, 20:1 hexanes:Et$_2$O) afforded an inseparable mixture 49 (23.5 mg, 56%) containing cyclized and noncyclized products in 3.6:1 ratio.

**Physical State**: colorless oil.

$R_f$ = 0.52 (12:1 hexanes:EtOAc).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 5.80 (ddt, $J$ = 16.9, 10.2, 6.6 Hz, 0.22H), 4.98 (dq, $J$ = 17.1, 1.7 Hz, 0.22H), 4.91 (ddt, $J$ = 10.2, 2.4, 1.2 Hz, 0.22H), 2.04 (tdd, $J$ = 6.7, 5.3, 1.4 Hz, 0.44H), 1.95 (tt, $J$ = 8.9, 7.3 Hz, 0.78H), 1.83 – 1.72 (m, 1.56H), 1.65 – 1.55 (m, 1.56H), 1.54 – 1.45 (m, 1.56H), 1.44 – 1.35 (m, 0.88H), 1.24 (s, 12H), 1.11 – 0.99 (m, 1.56H), 0.83 (d, $J$ = 7.5 Hz, 1.56H), 0.77 (t, $J$ = 7.5 Hz, 0.44H) ppm. (Data in red color belong to cyclized product)

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 139.3, 114.2, 83.01, 82.95, 36.3, 35.2, 33.7, 31.8, 25.3, 25.0, 23.7 ppm. (Data in red color belong to cyclized product). The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Spectroscopic data are in accordance with that reported in the literature.$^6$
X-ray information for compound 35 can be obtained free of charge from The Cambridge Crystallographic Data center with number CCDC 1862648.

Table 1. Crystal data and structure refinement for Baran676.

| Description                | Value          |
|----------------------------|----------------|
| Report date                | 2018-07-30     |
| Identification code        | jie4-065-3     |
| Empirical formula          | C21 H25 B O3   |
| Molecular formula          | C21 H25 B O3   |
| Formula weight             | 336.22         |
| Temperature                | 100.0 K        |
| Wavelength                 | 1.54178 Å      |
| Crystal system             | Triclinic      |
| Space group                | P-1            |
|                           | S57            |
| Property                                      | Value                                           |
|----------------------------------------------|-------------------------------------------------|
| Unit cell dimensions                         | $a = 5.9378(3)$ Å, $\alpha = 72.769(2)^\circ$ |
|                                              | $b = 14.5346(7)$ Å, $\beta = 89.933(3)^\circ$  |
|                                              | $c = 21.5395(11)$ Å, $\gamma = 89.866(3)^\circ$|
| Volume                                       | 1775.50(15) Å³                                   |
| Z                                            | 4                                               |
| Density (calculated)                         | 1.258 Mg/m³                                      |
| Absorption coefficient                       | 0.644 mm⁻¹                                       |
| F(000)                                       | 720                                             |
| Crystal size                                 | 0.276 x 0.043 x 0.038 mm³                        |
| Crystal color, habit                         | Colorless Needle                                 |
| Theta range for data collection              | 2.147 to 68.490°                                 |
| Index ranges                                 | $-6 \leq h \leq 7$, $-17 \leq k \leq 17$, $-25 \leq l \leq 25$ |
| Reflections collected                        | 54888                                           |
| Independent reflections                      | 6407 [R(int) = 0.0352, R(sigma) = 0.0168]        |
| Completeness to theta = 68.000°              | 98.5 %                                          |
| Absorption correction                        | Semi-empirical from equivalents                 |
| Max. and min. transmission                   | 0.3201 and 0.2347                                |
| Refinement method                            | Full-matrix least-squares on F²                 |
| Data / restraints / parameters               | 6407 / 0 / 459                                   |
| Goodness-of-fit on F²                         | 1.041                                           |
| Final R indices [I>2sigma(I)]                | $R_1 = 0.0370, \text{wR}^2 = 0.0892$             |
| R indices (all data)                         | $R_1 = 0.0421, \text{wR}^2 = 0.0920$             |
| Extinction coefficient                       | n/a                                             |
| Largest diff. peak and hole                  | 0.315 and -0.215 e Å⁻³                           |

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Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2 x 10^3$) for Baran676. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|   | x    | y    | z    | U(eq) |
|---|------|------|------|-------|
| O(1) | 6747(2) | 3260(1) | 2323(1) | 28(1) |
| O(2) | 9735(2) | 5206(1) | 1642(1) | 25(1) |
| O(3) | 7806(2) | 4692(1) | 889(1)  | 25(1) |
| C(1) | 10682(2) | 3494(1) | 1611(1) | 24(1) |
| C(2) | 10733(2) | 3062(1) | 2351(1) | 23(1) |
| C(3) | 8410(2)  | 2946(1) | 2650(1) | 22(1) |
| C(4) | 8177(2)  | 2432(1) | 3359(1) | 21(1) |
| C(5) | 6151(2)  | 1974(1) | 3597(1) | 23(1) |
| C(6) | 5890(2)  | 1490(1) | 4250(1) | 22(1) |
| C(7) | 7639(2)  | 1463(1) | 4690(1) | 21(1) |
| C(8) | 9656(2)  | 1923(1) | 4448(1) | 22(1) |
| C(9) | 9936(2)  | 2393(1) | 3793(1) | 22(1) |
| C(10)| 7398(2)  | 954(1)  | 5394(1) | 21(1) |
| C(11)| 5420(2)  | 1015(1) | 5731(1) | 24(1) |
| C(12)| 5235(3)  | 553(1)  | 6392(1) | 26(1) |
| C(13)| 7020(3)  | 14(1)   | 6731(1) | 27(1) |
| C(14)| 8987(2)  | -56(1)  | 6400(1) | 26(1) |
| C(15)| 9177(2)  | 408(1)  | 5740(1) | 23(1) |
| C(16)| 8048(2)  | 5948(1) | 1376(1) | 25(1) |
| C(17)| 7283(2)  | 5716(1) | 744(1)  | 24(1) |
| C(18)| 6190(3)  | 5797(1) | 1886(1) | 30(1) |
| C(19)| 9150(3)  | 6927(1) | 1264(1) | 33(1) |
| C(20)| 4790(2)  | 5858(1) | 599(1)  | 31(1) |
| C(21)| 8635(3)  | 6231(1) | 143(1)  | 32(1) |
| B(1) | 9340(3)  | 4466(1) | 1383(1) | 23(1) |
| O(1')| 2152(2)  | 1721(1) | 7630(1) | 25(1) |
| O(2')| 5095(2)  | -151(1) | 8297(1) | 26(1) |
| O(3')| 3991(2)  | 363(1)  | 9041(1) | 27(1) |
| C(1')| 6014(3)  | 1560(1) | 8344(1) | 26(1) |
| C(2')| 6067(2)  | 2045(1) | 7608(1) | 25(1) |
| C(3')| 3756(2)  | 2126(1) | 7309(1) | 24(1) |
| C(4')| 3456(2)  | 2667(1) | 6606(1) | 22(1) |
| C(5')| 1404(2)  | 2589(1) | 6307(1) | 23(1) |
|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| C(6') | 1078(2) | 3038(1) | 5654(1) | 23(1) |
| C(7') | 2801(2) | 3579(1) | 5269(1) | 21(1) |
| C(8') | 4833(2) | 3666(1) | 5571(1) | 23(1) |
| C(9') | 5162(2) | 3220(1) | 6229(1) | 23(1) |
| C(10') | 2503(2) | 4040(1) | 4561(1) | 22(1) |
| C(11') | 510(2) | 4514(1) | 4311(1) | 24(1) |
| C(12') | 250(2) | 4946(1) | 3649(1) | 26(1) |
| C(13') | 1966(2) | 4903(1) | 3221(1) | 26(1) |
| C(14') | 3954(2) | 4423(1) | 3463(1) | 25(1) |
| C(15') | 4224(2) | 4001(1) | 4126(1) | 23(1) |
| C(16') | 3417(2) | -899(1) | 8561(1) | 26(1) |
| C(17') | 2582(2) | -658(1) | 9186(1) | 26(1) |
| C(18') | 1614(3) | -773(1) | 8041(1) | 32(1) |
| C(19') | 4567(3) | -1871(1) | 8684(1) | 34(1) |
| C(20') | 88(3) | -807(1) | 9321(1) | 35(1) |
| C(21') | 3902(3) | -1170(1) | 9797(1) | 34(1) |
| B(1') | 4652(3) | 592(1) | 8553(1) | 24(1) |

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Table 3. Bond lengths [Å] and angles [°] for Baran676.

| Bond                  | Distance [Å]   |
|-----------------------|----------------|
| O(1)-C(3)             | 1.2201(16)     |
| O(2)-C(16)            | 1.4585(16)     |
| O(2)-B(1)             | 1.3701(19)     |
| O(3)-C(17)            | 1.4608(16)     |
| O(3)-B(1)             | 1.3651(18)     |
| C(1)-C(2)             | 1.5316(18)     |
| C(1)-B(1)             | 1.568(2)       |
| C(2)-C(3)             | 1.510(2)       |
| C(3)-C(4)             | 1.4943(18)     |
| C(4)-C(5)             | 1.398(2)       |
| C(4)-C(9)             | 1.3918(19)     |
| C(5)-C(6)             | 1.3825(19)     |
| C(6)-C(7)             | 1.3989(19)     |
| C(7)-C(8)             | 1.396(2)       |
| C(7)-C(10)            | 1.4839(18)     |
| C(8)-C(9)             | 1.3831(19)     |
| C(10)-C(11)           | 1.397(2)       |
| C(10)-C(15)           | 1.3961(19)     |
| C(11)-C(12)           | 1.387(2)       |
| C(12)-C(13)           | 1.388(2)       |
| C(13)-C(14)           | 1.387(2)       |
| C(14)-C(15)           | 1.3859(19)     |
| C(16)-C(17)           | 1.565(2)       |
| C(16)-C(18)           | 1.525(2)       |
| C(16)-C(19)           | 1.520(2)       |
| C(17)-C(20)           | 1.514(2)       |
| C(17)-C(21)           | 1.5179(19)     |
| O(1')-C(3')           | 1.2215(17)     |
| O(2')-C(16')          | 1.4619(17)     |
| O(2')-B(1')           | 1.3743(19)     |
| O(3')-C(17')          | 1.4554(17)     |
| O(3')-B(1')           | 1.3672(19)     |
| C(1')-C(2')           | 1.5334(18)     |
| C(1')-B(1')           | 1.571(2)       |
| C(2')-C(3')           | 1.506(2)       |
| C(3')-C(4')           | 1.4959(18)     |
| Bond                        | Length (Å) |
|-----------------------------|------------|
| C(4')-C(5')                | 1.399(2)   |
| C(4')-C(9')                | 1.395(2)   |
| C(5')-C(6')                | 1.3789(19) |
| C(6')-C(7')                | 1.4022(19) |
| C(7')-C(8')                | 1.3953(19) |
| C(7')-C(10')               | 1.4842(18) |
| C(8')-C(9')                | 1.3854(19) |
| C(10')-C(11')              | 1.3944(19) |
| C(10')-C(15')              | 1.398(2)   |
| C(11')-C(12')              | 1.3855(19) |
| C(12')-C(13')              | 1.387(2)   |
| C(13')-C(14')              | 1.391(2)   |
| C(14')-C(15')              | 1.3850(19) |
| C(16')-C(17')              | 1.568(2)   |
| C(16')-C(18')              | 1.5207(19) |
| C(16')-C(19')              | 1.518(2)   |
| C(17')-C(20')              | 1.513(2)   |
| C(17')-C(21')              | 1.524(2)   |

| Bond                        | Angle (°)  |
|-----------------------------|------------|
| B(1)-O(2)-C(16)            | 107.44(11) |
| B(1)-O(3)-C(17)            | 107.51(11) |
| C(2)-C(1)-B(1)             | 112.89(11) |
| C(3)-C(2)-C(1)             | 112.70(11) |
| O(1)-C(3)-C(2)             | 121.10(12) |
| O(1)-C(3)-C(4)             | 120.25(13) |
| C(4)-C(3)-C(2)             | 118.65(11) |
| C(5)-C(4)-C(3)             | 119.62(12) |
| C(9)-C(4)-C(3)             | 121.64(12) |
| C(9)-C(4)-C(5)             | 118.74(12) |
| C(6)-C(5)-C(4)             | 120.85(13) |
| C(5)-C(6)-C(7)             | 120.65(13) |
| C(6)-C(7)-C(10)            | 121.72(12) |
| C(8)-C(7)-C(6)             | 118.05(12) |
| C(8)-C(7)-C(10)            | 120.22(12) |
| C(9)-C(8)-C(7)             | 121.44(12) |
| C(8)-C(9)-C(4)             | 120.24(13) |
| C(11)-C(10)-C(7)           | 121.57(12) |
| C(15)-C(10)-C(7)           | 120.31(12) |
C(15)-C(10)-C(11) 118.12(12)
C(12)-C(11)-C(10) 120.94(13)
C(11)-C(12)-C(13) 120.32(13)
C(14)-C(13)-C(12) 119.23(13)
C(15)-C(14)-C(13) 120.50(13)
C(14)-C(15)-C(10) 120.88(13)
O(2)-C(16)-C(17) 102.48(10)
O(2)-C(16)-C(18) 106.32(11)
O(2)-C(16)-C(19) 108.36(12)
C(18)-C(16)-C(17) 113.14(12)
C(19)-C(16)-C(17) 114.87(12)
C(19)-C(16)-C(18) 110.86(12)
O(3)-C(17)-C(16) 102.79(10)
O(3)-C(17)-C(20) 108.51(12)
O(3)-C(17)-C(21) 110.86(12)
C(20)-C(17)-C(16) 114.43(12)
C(20)-C(17)-C(21) 111.77(12)
C(21)-C(17)-C(16) 114.11(12)
O(2)-B(1)-C(1) 121.86(13)
O(3)-B(1)-O(2) 113.43(12)
O(3)-B(1)-C(1) 124.57(13)
B(1')-O(2')-C(16') 107.28(11)
B(1')-O(3')-C(17') 107.88(11)
C(2')-C(1')-B(1') 113.91(12)
C(2')-C(1')-C(3') 112.17(12)
O(1')-C(3')-C(2') 120.40(12)
O(1')-C(3')-C(4') 120.04(13)
C(4')-C(3')-C(2') 119.49(12)
C(5')-C(4')-C(3') 118.61(12)
C(9')-C(4')-C(3') 122.83(12)
C(9')-C(4')-C(5') 118.52(12)
C(6')-C(5')-C(4') 120.87(13)
C(5')-C(6')-C(7') 120.89(13)
C(6')-C(7')-C(10') 121.56(12)
C(8')-C(7')-C(6') 117.99(12)
C(8')-C(7')-C(10') 120.45(12)
C(9')-C(8')-C(7') 121.26(13)
C(8')-C(9')-C(4') 120.46(13)
| Bond                  | Distance (Å) |
|-----------------------|--------------|
| C(11')-C(10')-C(7')  | 121.26(12)   |
| C(11')-C(10')-C(15') | 118.26(12)   |
| C(15')-C(10')-C(7')  | 120.48(12)   |
| C(12')-C(11')-C(10') | 120.90(13)   |
| C(11')-C(12')-C(13') | 120.42(13)   |
| C(12')-C(13')-C(14') | 119.26(13)   |
| C(15')-C(14')-C(13') | 120.30(13)   |
| C(14')-C(15')-C(10') | 120.85(13)   |
| O(2')-C(16')-C(17')  | 102.65(11)   |
| O(2')-C(16')-C(18')  | 106.34(11)   |
| O(2')-C(16')-C(19')  | 107.97(12)   |
| C(18')-C(16')-C(17') | 113.66(12)   |
| C(19')-C(16')-C(17') | 115.04(12)   |
| C(19')-C(16')-C(18') | 110.36(12)   |
| O(3')-C(17')-C(16')  | 102.91(11)   |
| O(3')-C(17')-C(20')  | 108.95(12)   |
| O(3')-C(17')-C(21')  | 106.46(11)   |
| C(20')-C(17')-C(16') | 114.67(12)   |
| C(20')-C(17')-C(21') | 109.38(12)   |
| C(21')-C(17')-C(16') | 113.87(12)   |
| O(2')-B(1')-C(1')   | 122.05(13)   |
| O(3')-B(1')-O(2')   | 113.32(13)   |
| O(3')-B(1')-C(1')   | 124.34(13)   |
Table 4. Anisotropic displacement parameters (Å$^2$ x 10$^3$) for Baran676. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^*^2 U^{11} + \ldots + 2hk a^* b^* U^{12}]$

| atom | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{23}$    | $U^{13}$    | $U^{12}$   |
|------|------------|------------|------------|-------------|-------------|------------|
| O(1) | 25(1)      | 31(1)      | 24(1)      | -4(1)       | -4(1)       | 4(1)       |
| O(2) | 26(1)      | 23(1)      | 25(1)      | -6(1)       | -2(1)       | 3(1)       |
| O(3) | 28(1)      | 24(1)      | 22(1)      | -6(1)       | -2(1)       | 5(1)       |
| C(1) | 25(1)      | 24(1)      | 22(1)      | -6(1)       | 1(1)        | 2(1)       |
| C(2) | 24(1)      | 23(1)      | 22(1)      | -6(1)       | -2(1)       | 3(1)       |
| C(3) | 26(1)      | 18(1)      | 23(1)      | -8(1)       | -3(1)       | 2(1)       |
| C(4) | 23(1)      | 18(1)      | 23(1)      | -8(1)       | -1(1)       | 3(1)       |
| C(5) | 22(1)      | 22(1)      | 26(1)      | -8(1)       | -4(1)       | 3(1)       |
| C(6) | 20(1)      | 21(1)      | 26(1)      | -7(1)       | 0(1)        | 1(1)       |
| C(7) | 23(1)      | 18(1)      | 23(1)      | -7(1)       | -1(1)       | 2(1)       |
| C(8) | 22(1)      | 22(1)      | 23(1)      | -8(1)       | -4(1)       | 3(1)       |
| C(9) | 21(1)      | 20(1)      | 25(1)      | -7(1)       | 0(1)        | 0(1)       |
| C(10)| 23(1)      | 17(1)      | 24(1)      | -8(1)       | 0(1)        | -1(1)      |
| C(11)| 25(1)      | 20(1)      | 27(1)      | -7(1)       | -1(1)       | 2(1)       |
| C(12)| 29(1)      | 23(1)      | 27(1)      | -9(1)       | 5(1)        | -1(1)      |
| C(13)| 37(1)      | 22(1)      | 22(1)      | -6(1)       | 0(1)        | -2(1)      |
| C(14)| 29(1)      | 23(1)      | 26(1)      | -6(1)       | -6(1)       | 3(1)       |
| C(15)| 23(1)      | 22(1)      | 25(1)      | -8(1)       | 0(1)        | 1(1)       |
| C(16)| 26(1)      | 22(1)      | 26(1)      | -4(1)       | 2(1)        | 4(1)       |
| C(17)| 24(1)      | 22(1)      | 24(1)      | -3(1)       | 2(1)        | 4(1)       |
| C(18)| 36(1)      | 26(1)      | 27(1)      | -6(1)       | 6(1)        | 3(1)       |
| C(19)| 35(1)      | 25(1)      | 38(1)      | -9(1)       | 6(1)        | -1(1)      |
| C(20)| 26(1)      | 32(1)      | 33(1)      | -5(1)       | -1(1)       | 4(1)       |
| C(21)| 30(1)      | 35(1)      | 25(1)      | -1(1)       | 3(1)        | 5(1)       |
| B(1) | 21(1)      | 26(1)      | 20(1)      | -4(1)       | 4(1)        | -1(1)      |
| O(1')| 29(1)      | 33(1)      | 25(1)      | -2(1)       | 2(1)        | -3(1)      |
| O(2')| 29(1)      | 24(1)      | 26(1)      | -7(1)       | 0(1)        | -2(1)      |
| O(3')| 32(1)      | 23(1)      | 25(1)      | -6(1)       | 0(1)        | -2(1)      |
| C(1')| 30(1)      | 26(1)      | 24(1)      | -7(1)       | -3(1)       | -1(1)      |
| C(2')| 28(1)      | 24(1)      | 23(1)      | -5(1)       | 0(1)        | -1(1)      |
| C(3')| 30(1)      | 18(1)      | 23(1)      | -7(1)       | 2(1)        | 1(1)       |
| C(4')| 25(1)      | 19(1)      | 23(1)      | -8(1)       | 1(1)        | 2(1)       |
| C(5')| 22(1)      | 22(1)      | 26(1)      | -7(1)       | 4(1)        | 0(1)       |
|     | C(6') | C(7') | C(8') | C(9') | C(10') | C(11') | C(12') | C(13') | C(14') | C(15') | C(16') | C(17') | C(18') | C(19') | C(20') | C(21') | B(1') |
|-----|-------|-------|-------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|
|     | 21(1) | 23(1) | 26(1) | -9(1) | 0(1)   | 2(1)   | 24(1)  | 18(1)  | 23(1)  | -7(1)  | 1(1)   | 2(1)   | 24(1)  | 20(1)  | 24(1)  | -6(1)  | 3(1)  |
|     | 23(1) | 18(1) | 24(1) | -8(1) | -1(1)  | 0(1)   | 23(1)  | 21(1)  | 24(1)  | -8(1)  | -1(1)  | -2(1)  | 23(1)  | 21(1)  | 24(1)  | -9(1)  | 4(1)  |
|     | 24(1) | 27(1) | 22(1) | -5(1) | -2(1)  | -4(1)  | 28(1)  | 24(1)  | 24(1)  | -9(1)  | 4(1)   | -4(1)  | 34(1)  | 21(1)  | 22(1)  | -5(1)  | -4(1) |
|     | 34(1) | 22(1) | 21(1) | 24(1) | -9(1)  | 4(1)   | 22(1)  | 21(1)  | 25(1)  | -8(1)  | -1(1)  | -1(1)  | 27(1)  | 23(1)  | 27(1)  | -5(1)  | -3(1) |
|     | 29(1) | 22(1) | 26(1) | -4(1) | -2(1)  | -3(1)  | 22(1)  | 22(1)  | 26(1)  | -4(1)  | -2(1)  | -3(1)  | 37(1)  | 28(1)  | 30(1)  | -6(1)  | -9(1) |
|     | 30(1) | 35(1) | 37(1) | -8(1) | -1(1)  | -3(1)  | 37(1)  | 35(1)  | 26(1)  | -3(1)  | -5(1)  | -3(1)  | 36(1)  | 35(1)  | 26(1)  | -3(1)  | -5(1) |
|     | 36(1) | 26(1) | 21(1) | -5(1) | -6(1)  | 4(1)   | 26(1)  | 26(1)  | 21(1)  | -5(1)  | -6(1)  | 4(1)   | 26(1)  | 26(1)  | 21(1)  | -5(1)  | -6(1) |
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2x 10^{-3}) for Baran676.

|      | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| H(1A)| 9986 | 3024 | 1417 | 28    |
| H(1B)| 12247| 3606 | 1447 | 28    |
| H(2A)| 11480| 2424 | 2462 | 28    |
| H(2B)| 11639| 3483 | 2540 | 28    |
| H(5) | 4937 | 1995 | 3306 | 27    |
| H(6) | 4510 | 1173 | 4402 | 27    |
| H(8) | 10863| 1913 | 4739 | 27    |
| H(9) | 11335| 2690 | 3638 | 26    |
| H(11)| 4183 | 1379 | 5505 | 29    |
| H(12)| 3879 | 604  | 6615 | 31    |
| H(13)| 6896 | -302 | 7184 | 32    |
| H(14)| 10214| -426 | 6627 | 32    |
| H(15)| 10536| 354  | 5520 | 28    |
| H(18A)| 5529 | 5156 | 1958 | 45    |
| H(18B)| 5021 | 6289 | 1733 | 45    |
| H(18C)| 6825 | 5848 | 2294 | 45    |
| H(19A)| 9556 | 7016 | 1683 | 49    |
| H(19B)| 8094 | 7434 | 1037 | 49    |
| H(19C)| 10509| 6962 | 1000 | 49    |
| H(20A)| 4454 | 5715 | 191  | 47    |
| H(20B)| 4375 | 6527 | 557  | 47    |
| H(20C)| 3927 | 5424 | 954  | 47    |
| H(21A)| 10247| 6140 | 241  | 47    |
| H(21B)| 8275 | 6920 | 13   | 47    |
| H(21C)| 8256 | 5964 | 211  | 47    |
| H(1'A)| 5341 | 2013 | 8557 | 32    |
| H(1'B)| 7581 | 1429 | 8503 | 32    |
| H(2'A)| 6722 | 2697 | 7519 | 30    |
| H(2'B)| 7051 | 1668 | 7402 | 30    |
| H(5') | 219  | 2221 | 6558 | 28    |
| H(6') | -333 | 2980 | 5461 | 27    |
| H(8') | 6013 | 4039 | 5322 | 27    |
|   |   |   |   |   |
|---|---|---|---|---|
| H(9') | 6559 | 3291 | 6424 | 27 |
| H(11') | -687 | 4541 | 4598 | 28 |
| H(12') | -1112 | 5274 | 3488 | 31 |
| H(13') | 1786 | 5199 | 2767 | 31 |
| H(14') | 5133 | 4384 | 3173 | 30 |
| H(15') | 5595 | 3680 | 4286 | 27 |
| H(18D) | 938 | -131 | 7951 | 48 |
| H(18E) | 446 | -1263 | 8195 | 48 |
| H(18F) | 2294 | -843 | 7643 | 48 |
| H(19D) | 5023 | -1962 | 8269 | 51 |
| H(19E) | 3520 | -2383 | 8907 | 51 |
| H(19F) | 5900 | -1894 | 8956 | 51 |
| H(20D) | -290 | -644 | 9719 | 52 |
| H(20E) | -295 | -1482 | 9376 | 52 |
| H(21D) | 5519 | -1080 | 9709 | 51 |
| H(21E) | 3549 | -1860 | 9928 | 51 |
| H(21F) | 3485 | -901 | 10148 | 51 |
Unsuccessful or Challenging Substrates

1. Alkyl or aryl bromide

2. Benzylic

3. Tertiary

4. Amino acids

Figure S4. Unsuccessful or challenging substrates.
### Cost Calculations

#### Price and Vendor of Reagents

Table S8. Price and vendor of reagents

| Reagents          | CAS No       | Mw/Conc. | Vender      | Price listed ($) | Price/mol ($)       |
|-------------------|--------------|----------|-------------|------------------|---------------------|
| B<sub>2</sub>pin<sub>2</sub> | 73183-34-3  | 253.9    | Combi-Blocks | 360/1 kg         | 91.4                |
| B<sub>2</sub>cat<sub>2</sub> | 13826-27-2  | 237.8    | Combi-Blocks | 480/100 g        | 1141.4              |
| B<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> | 1630-79-1   | 197.9    | Combi-Blocks | 599/500 g        | 237.1               |
| Catechol          | 120-80-9     | 110.1    | Sigma-Aldrich | 292/5 kg         | 6.4                 |
| B<sub>2</sub>cat<sub>2</sub> |             | 72% yield (2.2 eq catechol)<sup>10</sup> |             |                   | 348.9               |
| LiOH•H<sub>2</sub>O | 1310-66-3   | 42.0     | Sigma-Aldrich | 215/2 kg         | 4.5                 |
| Cu(acac)<sub>2</sub> | 13395-16-9  | 261.8    | Combi-Blocks | 250/1 kg         | 65.5                |
| MgCl<sub>2</sub>   | 7786-30-3   | 95.2     | Sigma-Aldrich | 164/5 kg         | 3.1                 |
| NiCl<sub>2</sub>•H<sub>2</sub>O | 7791-20-0 | 237.7    | Sigma-Aldrich | 350/2 kg         | 41.6                |
| diMeObipy         | 17217-57-1  | 216.2    | Combi-Blocks | 360/25 g         | 3113.3              |
| MeLi              | 917-54-4    | 1.6 M in Et<sub>2</sub>O Sigma-Aldrich | 1410/8 L | 110.2             |
| MgBr<sub>2</sub>•Et<sub>2</sub>O | 29858-07-9 | 258.2    | Sigma-Aldrich | 135.3/100 g      | 349.3               |
| Pinacol           | 76-09-5     | 118.2    | Combi-Blocks | 250/1 kg         | 29.6                |
| Ir[(ppy)<sub>2</sub>dtbpy]PF<sub>6</sub> | 676525-77-2 | 914.0 | Sigma-Aldrich | 160/250 mg       | 584960              |
| IrCl<sub>3</sub>•xH<sub>2</sub>O | 14996-61-3 | >316.6   | Sigma-Aldrich | 1250/25 g        | 15830               |
| 2-phenylpyridine  | 1008-89-5   | 155.2    | Combi-Blocks | 900/1 kg         | 139.7               |
| tBubipy           | 72914-19-3  | 268.4    | Oakwood      | 210/25 g         | 2254.6              |
| NH<sub>4</sub>PF<sub>6</sub> | 16941-11-0 | 163.0    | Oakwood      | 395/2.5 kg       | 25.8                |
| Ir[(ppy)<sub>2</sub>dtbpy]PF<sub>6</sub> | 1. 95% (2.5 eq PPy)<sup>11</sup>, 2. 92% (2.5 eq tBubipy, 10 eq NH<sub>4</sub>PF<sub>6</sub>)<sup>12</sup> | 24918.8 |                   |                   |

<sup>10</sup> Equilibrium yield is given.

<sup>11</sup> Yield is given in parentheses.

<sup>12</sup> Yield is given in parentheses.
### Cost Comparison

**Table S9.** Cost comparison.

| Reagents       | Price/mol ($) | Ni  | hv  | PET | Cu  |
|----------------|---------------|-----|-----|-----|-----|
| $\text{B}_2\text{pin}_2$ | 91.4          | 3.3 eq |     | 4 eq | 1.5 eq |
| $\text{B}_2\text{cat}_2$ | 1141.4$^a$   | 1.25 eq$^a$ |     |     |     |
| $\text{B}_2\text{cat}_2$ | 348.9$^b$    | 1.25 eq$^b$ |     |     |     |
| LiOH$\cdot$H$_2$O | 4.5           |     |     |     |     |
| Cu(acac)$_2$     | 65.5          |     |     | 0.2 eq |     |
| MgCl$_2$        | 3.1           |     |     |     | 1.5 eq |
| NiCl$_2$$\cdot$H$_2$O | 41.6      | 0.1 eq |     |     |     |
| $\text{diMeObipy}$ | 3113.3       | 0.13 eq |     |     |     |
| MeLi            | 110.2         |     |     | 3.0 eq |     |
| MgBr$_2$$\cdot$Et$_2$O | 349.3       | 1.5 eq |     |     |     |
| Pinacol         | 29.6          |     | 4 eq |     |     |
| Ir[(ppy)$_2$dtpbpy]PF$_6$ | 584960$^a$ | 0.01 eq$^a$ |     |     |     |
| Ir[(ppy)$_2$dtpbpy]PF$_6$ | 24918.8$^b$ |     |     | 0.01 eq$^b$ |     |
| **Cost/mol ($)** | **1565**     | **1545$^a$** | **555$^b$$** | **6215$^a$$** | **615$^b$$** | **222** |

$^a$: Cost calculated based on price from commercial sources.

$^b$: Cost calculated based on price of self-made reagents.
Kinetic Studies

General Method for Kinetic Studies

To a dry 1 dram vial equipped with a magnetic stir bar and a screw cap with septum was added 5-phenylvaleric NHPI ester (16.2 mg, 0.05 mmol), LiOH•H₂O (31.5 mg, 0.75 mmol), MgCl₂ (anhydrous, 15.2 mg, 0.075 mmol) and B₂pin₂ (19 mg, 0.075 mmol). The screw joint of the vial was Teflon taped, the vial was closed and the atmosphere exchanged by 3 cycles of vacuum/N₂. The vial was placed in a 27 °C oil bath (stir speed 1000 rpm) and at time = 0, 0.35 mL of a mixed solution of Cu(acac)₂ (0.01 mmol) and 4,4’-di-tert-butylbiphenyl (0.005 mmol) was added. The mixture of Cu(acac)₂ (0.0286 M) and internal standard (0.0144 M) was prepared inert in a volumetric flask using a dry and inert solvent mixture of 1,4-dioxane and DMF (4:1). Aliquots (~20 μL) were removed from the reaction at the indicated times and directly injected into 0.4 mL MeCN in a filter vial without any further quench and subjected to analysis.

Analysis

All samples were analyzed using a Waters I-Class (SM-FTN) instrument with Waters PDA diode array detector and Waters QDa mass spectrometer, equipped with a Waters Cortecs C18 column (2.1x55 mm, 1.6 micron). The analysis was taking place at 35 °C using a gradient based on (A) 0.1% formic acid in water and (B) acetonitrile (10-99% B over 2.5 minutes, hold at 99% B for 0.2 minutes).

Retention times for relevant species: RAE (S1) 1.836 minutes (detection wavelength 298 nm), product (11) 2.143 minutes (detection wavelength 228 nm), 5-phenylvaleric acid 1.211 minutes (detection wavelength 228 nm), 4,4’-di-tert-butyl biphenyl 2.614 minutes (detection wavelength 228 nm). Analyte concentrations were calculated against 4,4’-di-tert-butyl biphenyl as internal standard, and all analytes were calibrated separately using a series of six calibration solutions of different concentration with the highest concentration of the series being 5 mM.
Results

**Figure S5.** Time course of the borylation reaction under standard conditions: 140 mM RAE, 1.5 equiv B$_2$pin$_2$, 20 mol% Cu(acac)$_2$, 1.5 equiv MgCl$_2$, 15 equiv LiOH•H$_2$O.

**Figure S6.** Time course of the borylation reaction with varying concentrations of reactants/reagents (cf Fig 3A in main article). Standard conditions: 140 mM RAE, 1.5 equiv B$_2$pin$_2$, 20 mol% Cu(acac)$_2$, 1.5 equiv MgCl$_2$, 15 equiv LiOH•H$_2$O. Low MgCl$_2$ = 28 mM (0.2 equiv)
Figure S7. Yield of the borylation reaction after 4 minutes when one reaction component at a time has been removed or, in the case of Cu, exchanged (20 mol% Cu(acac)₂ for 20 mol% Cul). Standard conditions: 140 mM RAE, 1.5 equiv B₂Pin₂, 20 mol% Cu(acac)₂, 1.5 equiv MgCl₂, 15 equiv LiOH·H₂O. Where applicable, [LiCl] = 210 mM (1.5 equiv) and [H₂O] = 2100 mM (15 equiv).
Figure S8. Time course data for the borylation reaction when one reaction component at a time has been removed or, in the case of Cu, exchanged (20 mol% Cu(acac)$_2$ for 20 mol% Cul). Standard conditions: 140 mM RAE, 1.5 equiv B$_2$pin$_2$, 20 mol% Cu(acac)$_2$, 1.5 equiv MgCl$_2$, 15 equiv LiOH•H$_2$O. Where applicable, [LiCl] = 210 mM (1.5 equiv) and [H$_2$O] = 2100 mM (15 equiv). For the no B$_2$pin$_2$ experiment, [RAE] = 70 mM.
**Figure S9.** Time course data for the borylation reaction when one reaction component at a time has been removed or, in the case of Cu, exchanged (20 mol% Cu(acac)$_2$ for 20 mol% Cul). Standard conditions: 140 mM RAE, 1.5 equiv B$_2$pin$_2$, 20 mol% Cu(acac)$_2$, 1.5 equiv MgCl$_2$, 15 equiv LiOH•H$_2$O. Where applicable, [LiCl] = 210 mM (1.5 equiv) and [H$_2$O] = 2100 mM (15 equiv). For the no B$_2$pin$_2$ experiment, [RAE] = 70 mM.

**Equations derived from Eq. 3 in the main article:**

\[
\frac{d[\text{product}]}{d[\text{RAE}]} = \frac{1}{1 + \frac{k_r}{K} \cdot TON} \tag{S1}
\]

\[
TON = \frac{[\text{RAE}]}{[\text{Cu}]} \tag{S2}
\]

\[
\text{mol\%} = \frac{1}{TON} \cdot 100 \tag{S3}
\]
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NMR Spectra

Compound S26 $^1$H NMR

[Diagram of NMR spectrum with peaks at various ppm values]
Compound S26 $^{13}$C NMR
Compound S26 $^{19}$F NMR
Compound S27 $^1$H NMR
Compound S27 $^{13}$C NMR
Compound S28 $^1$H NMR
Compound S28 $^{13}$C NMR
Compound S29 $^1$H NMR

![NMR spectrum of Compound S29](image)

- Chemical shift values: 7.92, 7.88, 7.80, 7.37, 3.16, 3.01, 2.59

- Molecular structure of Compound S29

- Integration peaks at 1.99 ppm, 2.04 ppm, 2.03 ppm, 1.99 ppm, 2.04 ppm, 2.03 ppm
Compound S29 $^{13}$C NMR
Compound S30 $^1$H NMR
Compound S30 $^{13}$C NMR

![Chemical Structure](image)

- 168.99
- 162.01
- 153.50
- 134.02
- 135.11
- 136.63
- 124.13
- 115.32
- 60.06
- 56.25
- 33.64
- 31.07

f1 (ppm)
Compound S31 $^1$H NMR
Compound S31 $^{13}$C NMR

$^{13}$C NMR spectrum showing chemical shifts at various ppm values. The spectrum includes a structure labeled with Boc.
Compound S32 $^1$H NMR
Compound S32 $^{13}$C NMR
Compound S33 $^1$H NMR
Compound S33 $^{13}$C NMR

![Carbon NMR spectrum of compound S33](image-url)
Compound S34 $^1$H NMR
Compound S34 $^{13}$C NMR

![Compound Structure Image]
Compound 45 $^1$H NMR

$^1$H NMR spectrum of Compound 45 with peaks at various ppm values.
Compound 45 $^{13}$C NMR

![NMR spectrum of Compound 45](image)
Compound 2 $^1$H NMR
Compound 2 $^{13}$C NMR
Compound 6 $^1$H NMR
Compound 6 $^{13}$C NMR

[Spectrum image with chemical structure and peaks labeled with frequencies]
Compound 11 $^1$H NMR
Compound 11 $^{13}$C NMR
Compound 12 $^1$H NMR
Compound 12 $^{13}$C NMR
Compound 13 $^1$H NMR
Compound 13 $^{13}$C NMR
Compound 13 $^{19}$F NMR
Compound 14 $^1$H NMR

S110
Compound 14 $^{13}$C NMR
Compound 15 $^1$H NMR
Compound 15 $^{13}$C NMR
Compound 16 \( ^1H \) NMR
Compound 16 $^{13}$C NMR
Compound 17 $^1$H NMR
Compound 17 $^{13}$C NMR
Compound 18 $^1$H NMR
Compound 18 $^{13}$C NMR
Compound 19 $^1$H NMR
Compound 19 $^{13}$C NMR
Compound 20 $^1$H NMR
Compound 21 $^1$H NMR
Compound 21 $^{13}$C NMR
Compound 22 $^1$H NMR
Compound 23 $^1$H NMR
Compound 23 $^{13}$C NMR
Compound 24 $^1$H NMR
Compound 24 $^{13}$C NMR
Compound 25 $^1$H NMR
Compound 25 $^{13}$C NMR
Compound 26 $^1$H NMR
Compound 26 $^{13}$C NMR
Compound 27 $^1$H NMR
Compound 27 $^{13}$C NMR
Compound 28 $^1$H NMR
Compound 28 $^{13}$C NMR
Compound 29 $^1$H NMR
Compound 29 $^{13}$C NMR
Compound 30 $^1$H NMR
Compound 30 $^{13}$C NMR
Compound 31 $^1$H NMR
Compound 31 $^{13}$C NMR

![Compound 31 $^{13}$C NMR spectrum](image)
Compound 32 $^1$H NMR
Compound 32 $^{13}$C NMR
Compound 33 $^1$H NMR
Compound 33 $^{13}$C NMR

$I$-aryl boronic ester with Me substituents

- 144.21
- 136.49
- 130.66
- 89.85
- 83.02
- 24.13
- 12.97

f1 (ppm): 90, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0
Compound 34 $^1$H NMR

S151
Compound 34 $^{13}$C NMR
Compound 35 $^1$H NMR
Compound 35 $^{13}$C NMR

![Chemical Structure](image)

| Chemical Shift (ppm) | Intensity |
|----------------------|-----------|
| 141.37               |            |
| 140.69               |            |
| 139.82               |            |
| 130.06               |            |
| 129.27               |            |
| 128.45               |            |
| 127.27               |            |
| 92.26                |            |
| 33.87                |            |
| 24.94                |            |

S154
Compound 36 $^1$H NMR
Compound 36 $^{13}$C NMR
Compound 36 $^{19}\text{F}$ NMR
Compound 37 $^1$H NMR
Compound 37 $^{13}$C NMR

![Compound 37 $^{13}$C NMR spectrum]
Compound 38 $^1$H NMR
Compound 38 $^{13}$C NMR
Compound 39 $^1$H NMR
Compound 39 $^{13}$C NMR
Compound 40 $^1$H NMR
Compound 40 $^{13}$C NMR
Compound 41 $^1$H NMR
Compound 42 $^{13}$C NMR

![Compound 42 $^{13}$C NMR spectrum](image)
Compound 48 $^1$H NMR
Compound 48 $^{13}$C NMR

![Carbon-13 NMR spectrum of compound 48](image)
Mixture 49 $^1$H NMR

3:1 mixture
Mixture 49 $^{13}$C NMR

3.6 : 1 mixture