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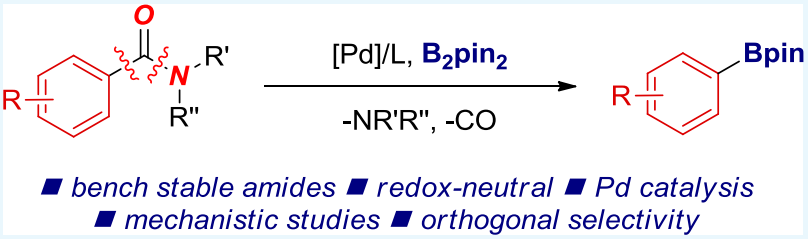
Decarbonylative Borylation of Amides by Palladium Catalysis

Shicheng Shi and Michal Szostak*

Department of Chemistry, Rutgers University—Newark, 73 Warren Street, Newark, New Jersey 07102, United States

Supporting Information



ABSTRACT: The development of transition-metal-catalyzed borylation reactions is of significant importance for the fields of organic synthesis and medicinal chemistry because of the versatility of organoboron functional groups. Herein, we report the direct decarbonylative borylation of amides by highly selective carbon−nitrogen bond cleavage by palladium catalysis. The approach capitalizes on the ground-state destabilization of the amide bond in *N*-acyl glutarimides to achieve Pd-catalyzed insertion into the amide N−C bond and decarbonylation (deamidation). Mechanistic studies and the utility of this methodology in orthogonal sequential cross-couplings of robust, bench-stable amides are reported.

1. INTRODUCTION

Transition-metal-catalyzed cross-coupling of amides has recently emerged as a powerful platform for the functionalization of the traditionally inert amide bond ($n_N \rightarrow \pi^*_{C=O}$ donation, barrier to rotation in planar amides of 15−20 kcal/mol).[1−3] The capacity of the amide bond to support selective insertion of a transition metal into the N−C bond by ground-state destabilization[4] enables an array of new approaches for the synthesis of important motifs in organic synthesis.[5] In this context, there are two general pathways for metal-catalyzed cross-coupling of amides (Figure 1): (i) direct acyl coupling and (ii) decarbonylative cross-coupling, involving formation of the acyl metal complex and CO extrusion to afford aryl-metal intermediates[6] fulfilling the criteria of classical metal-catalyzed cross-coupling reactions.[3]

Unfortunately, although great progress has been made in acyl cross-couplings of the amide bond,[7] the corresponding decarbonylative manifold remains much less developed.[8−15] In particular, palladium-catalyzed decarbonylative cross-couplings have remained a challenging goal, with very few examples of such reactions (cf. Ni) reported to date.[14] The versatility of Pd catalysis,[16] including the broad industrial use of Pd-catalyzed processes,[17] makes this approach attractive in decarbonylative amide bond cross-coupling.

Herein, we report the direct decarbonylative borylation of amides by highly selective carbon−nitrogen bond cleavage by palladium catalysis (Figure 2).[18] The method represents a rare example of using less nucleophilic Pd (cf. Ni) to promote efficient metal insertion into the amide N−C bond and decarbonylation.[6] The method capitalizes on the ground-state destabilization of the amide bond in *N*-acyl glutarimides[4] to achieve high selectivity of the decarbonylation. Mechanistic studies and the utility of this methodology in orthogonal sequential cross-couplings of robust, bench-stable amides are reported. This user-friendly methodology can be used for the construction of the organoboron functional group from bench-stable amides using commercially available and air-stable reagents.[19]

The reaction is fundamentally different from decarbonylative borylation of carboxylic acids reported by our group:[18f] (1) the present study addresses activation of a N−C versus O−C bond; (2) the underlying activation principle hinges upon amide bond twist and geometric distortion of the amide bond[2b,4] (cf. steric-control of regioselectivity and reversible insertion); (3) the catalyst system radically differs in the use of a mono- versus bidentate phosphine ligand; (4) amides can be prepared from fundamentally different precursors than carboxylic acids, including primary amides. Principally, the method constitutes the first example of Pd-catalyzed synthesis of aryl boronates from amides, and as such represents a potentially significant advance in the construction of C−B bonds by N−C decarbonylative coupling akin to the classic Miyaura borylation of aryl halides and pseudohalides.[20] Given the prevalence of amides in organic synthesis and medicinal chemistry, potential future applications range from Pd-catalyzed functionalization of biomolecules to the synthesis of specialty and bulk chemicals.

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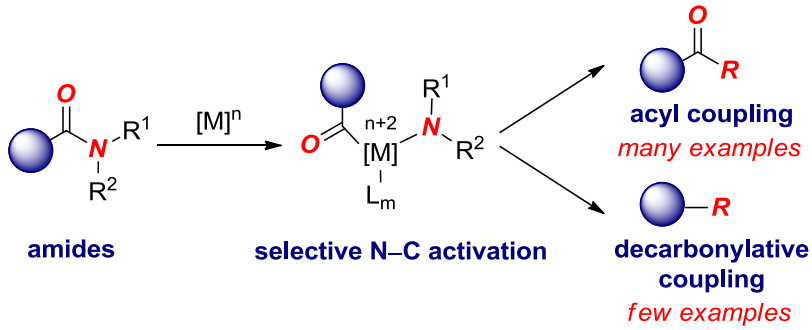


Figure 1. Acyl and decarbonylative cross-coupling of amides.

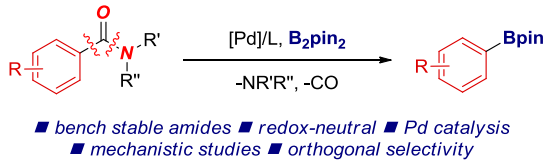


Figure 2. Palladium-catalyzed redox-neutral decarbonylative borylation of amides (this study).

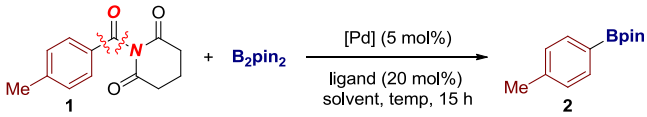
2. RESULTS AND DISCUSSION

Drawing from our studies in the decarbonylative cross-coupling of amides,[6a,9a,14b,c] we envisioned that Pd-catalyzed decarbonylative borylation of rotationally inverted *N*-acyl glutarimides could be achieved by applying a catalyst system that would favor decarbonylation. We commenced our studies by investigating the cross-coupling of electronically unbiased 1-(4-toluoyl)-*N*-glutarimide with bis(pinacolato)diboron as the boron source (Table 1).[20]

Although initial attempts were unsuccessful, after very extensive survey of the reaction conditions, we identified a catalyst system that provided a significant improvement in the cross-coupling, furnishing the desired decarbonylative borylation product in 77% yield (Table 1, entries 1−28). Several optimization results are worth noting. The choice of the phosphane ligand had a significant effect on the cross-coupling (entries 1−11). We identified PCy_3 as the preferred ligand for this transformation, presumably because of facile activation of the N−C bond to form the acyl-metal intermediate. In the evaluation of different bases, Na_2CO_3 proved optimal (entries 12−17). Various Pd catalysts were tested, and $Pd(TFA)_2$ showed the best activity (entries 18−24). Further improvement of the reaction efficiency was achieved by careful adjustment of the reagent stoichiometry (entries 25−28), presumably to match decarbonylation with the transmetalation step. Importantly, the reaction proceeds with a complete selectivity for N−C(O) acyl bond decarbonylation, with products corresponding to the acyl coupling and unselective cleavage of the endocyclic C−O bonds not observed. Furthermore, as an important synthetic advantage, the method utilizes commercially available, bench-stable reagents and does not require preparation of the activated boron source or co-catalytic metal additives.[9b,f] Furthermore, we note that the cross-coupling of *N*-benzoylsuccinimide proceeds in an unoptimized 45% yield.[8c,d] At this stage of reaction development, other amides have not been tested.

With the optimal conditions for cross-coupling, the scope of the reaction was briefly investigated (Table 2). We were pleased to find that the reaction readily tolerates unbiased

Table 1. Optimization of Pd-Catalyzed Decarbonylative Borylation of Amides[a]



entry	catalyst	ligand	base	yield[b] (%)
1	$Pd(OAc)_2$	PPh_3	Na_2CO_3	15
2	$Pd(OAc)_2$	$P(4\text{-MeO-}C_6H_4)_3$	Na_2CO_3	27
3	$Pd(OAc)_2$	$P(4\text{-}CF_3\text{-}C_6H_4)_3$	Na_2CO_3	12
4	$Pd(OAc)_2$	$PCyPh_2$	Na_2CO_3	24
5	$Pd(OAc)_2$	PCy_2Ph	Na_2CO_3	28
6	$Pd(OAc)_2$	PCy_3HBF_4	Na_2CO_3	49
7	$Pd(OAc)_2$	Dppb	Na_2CO_3	5
8	$Pd(OAc)_2$	Dppp	Na_2CO_3	25
9	$Pd(OAc)_2$	$P\textit{n}\text{-}Bu_3HBF_4$	Na_2CO_3	<5
10	$Pd(OAc)_2$	Xphos	Na_2CO_3	<5
11	$Pd(OAc)_2$	SPhos	Na_2CO_3	<5
12	$Pd(OAc)_2$	PCy_3HBF_4	NaOAc	44
13	$Pd(OAc)_2$	PCy_3HBF_4	KOAc	15
14	$Pd(OAc)_2$	PCy_3HBF_4	K_2CO_3	36
15	$Pd(OAc)_2$	PCy_3HBF_4	K_3PO_4	34
16	$Pd(OAc)_2$	PCy_3HBF_4	Li_2CO_3	20
17	$Pd(OAc)_2$	PCy_3HBF_4	NaO*t*-Bu	16
18	$Pd(CH_3CN)_2Cl_2$	PCy_3HBF_4	Na_2CO_3	55
19	$Pd(PPh_3)_2Cl_2$	PCy_3HBF_4	Na_2CO_3	52
20	$Pd(acac)_2$	PCy_3HBF_4	Na_2CO_3	47
21	$Pd(TFA)_2$	PCy_3HBF_4	Na_2CO_3	64
22	$Pd(dba)_2$	PCy_3HBF_4	Na_2CO_3	58
23	$Pd_2(dba)_3$	PCy_3HBF_4	Na_2CO_3	56
24	PEPPSI-IPr	PCy_3HBF_4	Na_2CO_3	<5
25[c]	$Pd(TFA)_2$	PCy_3HBF_4	Na_2CO_3	58
26[d]	$Pd(TFA)_2$	PCy_3HBF_4	Na_2CO_3	69
27[e]	$Pd(TFA)_2$	PCy_3HBF_4	Na_2CO_3	60
28[f]	$Pd(TFA)_2$	PCy_3HBF_4	Na_2CO_3	77

[a]Conditions: amide (1.0 equiv), B_2pin_2 (2.0 equiv), [Pd] (5 mol %), ligand (20 mol %),base (2.0 equiv), dioxane(0.25 M), 150 °C, and 15 h. [b]GC/^{1}H NMR yields. [c]B_2pin_2 (1.2 equiv). [d]Na_2CO_3 (1.0 equiv). [e]Na_2CO_3 (0.5 equiv). [f]B_2pin_2 (1.2 equiv), Na_2CO_3 (1.0 equiv). See the Supporting Information for details.

neutral (entries 1−2), electron-withdrawing (entry 3), and electron-donating (entry 4) arenes, affording the desired organoboranes in 61−71% yields. In contrast, Ni-catalyzed cross-couplings are often limited to the use of conjugated π-systems to favor insertion/decarbonylation.[6b,9c] Electron-donating oxygen heterocycles that are important in medicinal chemistry applications such as dioxolane (entry 5) are well

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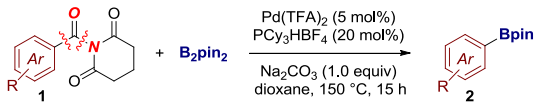
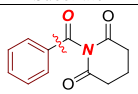
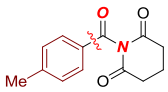
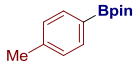
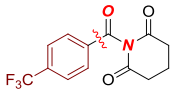
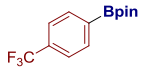
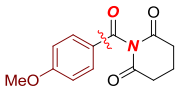
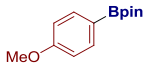
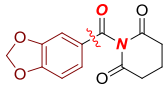
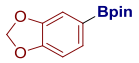
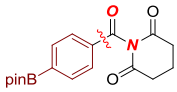
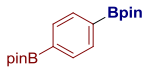
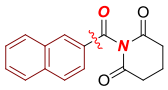
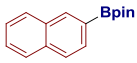
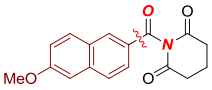
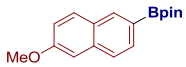
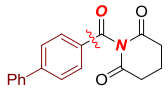
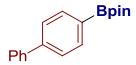
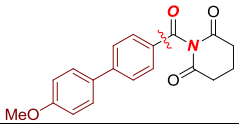
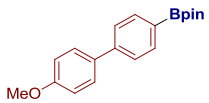
Table 2. Pd-Catalyzed Decarbonylative Borylation of Amides[a]



Entry	Substrate	2	Product	Yield (%)
1		2a		68
2		2b		61
3		2c		66
4		2d		71
5		2e		76
6		2f		68
7		2g		60
8		2h		67
9		2i		63
10		2j		72

[a]Conditions: amide (1.0 equiv), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), Na_2CO_3 (1.0 equiv), dioxane (0.25 M), 150 °C, and 15 h. Isolated yields. See the Supporting Information for full details.

tolerated. Furthermore, amides containing Bpin bonds are also competent substrates (entry 6), resulting in formal double borylation by exploiting orthogonal electrophilicity of aryl halide and amide functional groups. Notably, conjugated arenes that are typically prone to reduction under decarbonylative conditions also delivered the corresponding borylated products in good yields (entries 7−8). Finally, the method could be applied to biaryl amides to generate the desired conjugated adducts, containing synthetically useful C−B handle for further cross-coupling functionalization (entries 9−10, vide infra).

While the method establishes an important precedent in the Pd-catalyzed borylation by selective N−C bond cleavage of amides, several limitations should be noted. (1) At the present stage, the method is not compatible with heteroaromatic amides (<20% yield) and ortho-substituted amides (<5% yield). (2) Aliphatic amides undergo decarbonylation/β-hydride elimination to give olefins. This is in agreement with a recent report by Shi and co-workers on Ni-catalyzed *retro*-hydroamidocarbonylation of aliphatic amides.[9g,h] (3) In general, halogens are not compatible with the decarbonylative cross-coupling manifold of amides. We further note that primary and secondary amides are unreactive under the present conditions, while *N*-methoxy amides undergo decomposition by the N−O cleavage pathway. Meta-substituted amides have not been tested because they are not at the conjugating position. Studies to address these limitations and the design of more selective catalyst systems are currently underway.

To gain insight into the reaction mechanism, intermolecular competition experiments were conducted (Scheme 1). To this end, intermolecular competition experiments with 4-substituted amides revealed that electron-deficient amides react preferentially, consistent with facility of metal insertion (Scheme 1A).[4] Further competition experiments established that conjugated π-systems such as naphthalene couple preferentially (Scheme 1B). Furthermore, competition experiments established that π-conjugated arenes react preferentially over biaryls (Scheme 1C).[6b]

Overall, the mechanistic studies highlight that (i) electrophilicity of the amide bond and (ii) capacity of the acyl-metal intermediate to influence the relative reactivity of amides in this decarbonylative (deamidative) cross-coupling.

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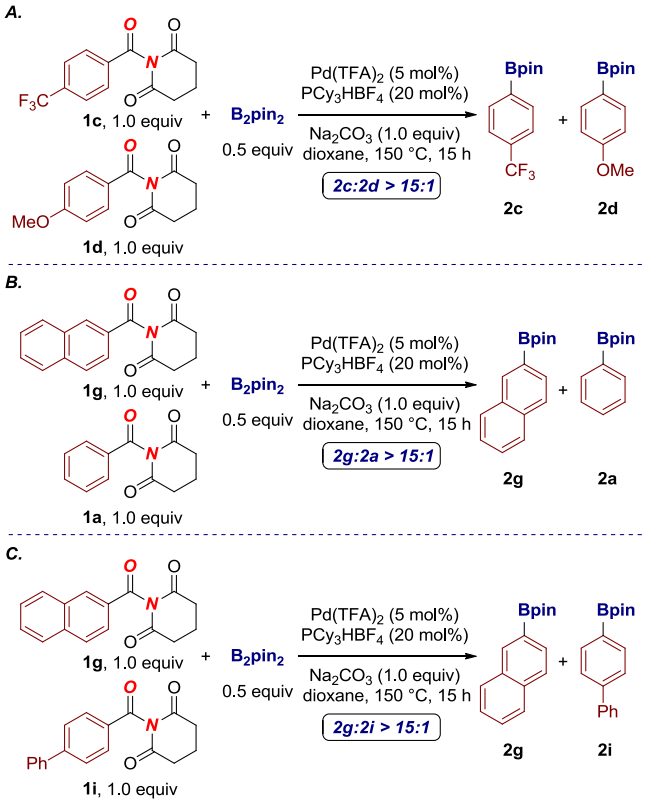
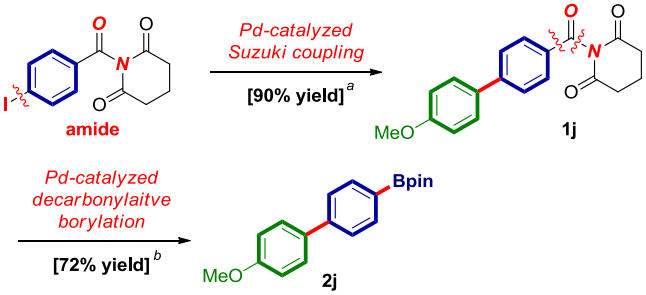
Scheme 1. Intermolecular Competition Experiments in Decarbonylative Borylation of Amides



In recent years, orthogonal cross-couplings have been an area of significant interest due to permitting versatile disconnections in organic synthesis.[21] An attractive feature of the present methodology is the enabling nature for orthogonal cross-couplings (Scheme 2). As shown in Scheme 2, the amide bond in *N*-acyl glutarimides displays orthogonal electrophilic reactivity to the traditional Pd-catalyzed cross-couplings.[3,19,20] The amide group is not reactive toward Pd(0)-orthogonal Suzuki–Miyaura cross-coupling reactions, highlighting a powerful opportunity for sequential Pd-catalyzed C(sp^2)–C(sp^2) cross-coupling/Pd-catalyzed decarbonylative cross-coupling in organic synthesis.

Scheme 2. Orthogonal Cross-Coupling/Decarbonylative Borylation of Amides by Pd-Catalysis[a]



[a]Conditions: (a) $Pd(OAc)_2$, 4-MeO-C_6H_4-$B(OH)_2$, Na_2CO_3, EtOH:H_2O, 23 °C. (b) B_2pin_2, $Pd(TFA)_2$, PCy_3HBF_4, Na_2CO_3, dioxane, and 150 °C.

3. CONCLUSIONS

In summary, we have documented the first palladium-catalyzed decarbonylative borylation of amides by selective carbon–nitrogen cleavage for the synthesis of versatile organoboranes. The method exploits the ground-state destabilization of the amide bond in *N*-acyl glutarimides to achieve Pd-catalyzed insertion into the amide N–C bond and decarbonylation. Although the yields are good to modest, the reaction is synthetically useful because it employs commercially available and air-stable reagents. Furthermore, the method sets an important precedent for decarbonylative borylation of amides using versatile Pd-catalysis. Moreover, the potential of the amide N–C bond disconnection has been demonstrated in orthogonal cross-couplings using palladium. Additional studies directed at decarbonylative cross-coupling of amide electrophiles, including extension to other nucleophiles, as well as structural mechanistic investigations and studies on the development of improved reaction conditions and catalyst systems are in progress in our laboratory and will be reported in due course.

4. EXPERIMENTAL SECTION

4.1. General Methods. All compounds reported in the manuscript are commercially available or have been previously described in literature unless indicated otherwise. All experiments involving palladium were performed using standard Schlenk techniques under an argon or a nitrogen atmosphere unless stated otherwise. All amides were prepared by standard methods.[14c] ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Experimental Section for characterization purposes. ^{1}H NMR, ^{13}C NMR and HRMS data are reported for all new compounds. All products have been previously reported, unless stated otherwise. Spectroscopic data matched literature values. General methods have been published.[14c]

4.2. Synthesis of Starting Materials. Amides **1a–1j** have been reported.[14c] The synthesis of amide **1j** by Suzuki–Miyaura cross-coupling of 1-(4-iodobenzoyl)piperidine-2,6-dione has been published.[14c]

4.3. General Procedure for Decarbonylative Borylation of Amides. An oven-dried vial equipped with a stir bar was charged with an amide substrate (neat, 1.0 equiv), B_2pin_2 (1.2 equiv), Na_2CO_3 (1.0 equiv), $Pd(TFA)_2$ (5 mol %), and PCy_3HBF_4 (20 mol %), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (0.25 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 150 °C, and stirred for the indicated time at 150 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. A sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and gas chromatography–mass spectrometry (GC–MS) to obtain conversion, yield, and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexanes/ethyl acetate) afforded the title products. **Caution**: Reactions involving high pressure must be carried out in a well-ventilated hood with appropriate pressure vessels, pressure relief equipment, and/or blast shields.

4.4. Representative Procedure for Decarbonylative Borylation of Amides. *4.4.1. 1.0 mmol Scale.* An oven-dried vial equipped with a stir bar was charged with 1-(4-methylbenzoyl)piperidine-2,6-dione (neat, 1.0 mmol, 231.3

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mg, 1.0 equiv), bis(pinacolato)diboron (1.2 mmol, 304.8 mg, 1.2 equiv), sodium carbonate (1.0 mmol, 106.0 mg, 1.0 equiv), $Pd(TFA)_2$ (5 mol %, 16.6 mg), and PCy_3HBF_4 (20 mol %, 73.6 mg), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (4.0 mL) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 150 °C, and stirred for 15 h at 150 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. A sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) and GC−MS to obtain conversion, yield, and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on the silica gel (hexanes/ethyl acetate) afforded the title product in yield 61% (133.5 mg) as a white solid. Characterization data are included in the section below.

4.5. General Procedure for Selectivity Studies. An oven-dried vial equipped with a stir bar was charged with two amide substrates (1.0 equiv each), B_2pin_2 (0.5 equiv), Na_2CO_3 (1.0 equiv), $Pd(TFA)_2$ (5 mol %), and PCy_3HBF_4 (20 mol %), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (0.25 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 150 °C, and stirred for the indicated time at 150 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 500 MHz) and GC−MS to obtain conversion and yield using internal standard and compared with authentic samples.

4.6. Characterization Data of Cross-Coupling Products. *4.6.1. 4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane(Table 2, **2a**).*[18e] According to the general procedure, the reaction of amide **1a** (0.20 mmol), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), and Na_2CO_3 (1.0 equiv) in dioxane (0.25 M) for 15 h at 150 °C afforded after work-up and chromatography the title product in 68% yield (27.7 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 7.5 Hz, 2H), 7.46 (t, J = 7.0 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 1.35 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.74, 131.26, 127.71, 83.78, 24.89.

*4.6.2. 4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (Table 2, **2b**).*[18e] According to the general procedure, the reaction of amide **1b** (1.0 mmol), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), and Na_2CO_3 (1.0 equiv) in dioxane (0.25 M) for 15 h at 150 °C afforded after work-up and chromatography the title product in 61% yield (133.5 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, J = 7.0 Hz, 2H), 7.19 (d, J = 7.0 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.54, 134.94, 128.66, 83.76, 25.00, 21.87.

*4.6.3. 4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (Table 2, **2c**).*[18e] According to the general procedure, the reaction of amide **1c** (0.20 mmol), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), Na_2CO_3 (1.0 equiv) in dioxane (0.25 M) for 15 h at 150 °C afforded after work-up and chromatography the title product in 66% yield (35.9 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 7.5 Hz, 2H), 1.36 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.14, 132.96 (q, J^F = 32.5 Hz), 124.46 (q, J^F = 3.8 Hz), 124.28 (q, J^F = 271.2 Hz), 84.42, 25.00. ^{19}F NMR (471 MHz, $CDCl_3$): δ −63.04.

*4.6.4. 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, **2d**).*[18e] According to the general procedure, the reaction of amide **1c** (0.20 mmol), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), and Na_2CO_3 (1.0 equiv) in dioxane (0.25 M) for 15 h at 150 °C afforded after work-up and chromatography the title product in 71% yield (33.2 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.28, 136.64, 113.44, 83.68, 55.23, 25.00.

*4.6.5. 2-(Benzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, **2e**).*[9f] According to the general procedure, the reaction of amide **1e** (0.20 mmol), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), and Na_2CO_3 (1.0 equiv) in dioxane (0.25 M) for 15 h at 150 °C afforded after work-up and chromatography the title product in 76% yield (37.7 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 7.7 Hz, 1H), 7.24 (s, 1H), 6.83 (d, J = 7.6 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.29, 147.32, 129.85, 114.07, 108.42, 100.86, 83.84, 24.97.

*4.6.6. 1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (Table 2, **2f**).*[18c] According to the general procedure, the reaction of amide **1f** (0.20 mmol), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), and Na_2CO_3 (1.0 equiv) in dioxane (0.25 M) for 15 h at 150 °C afforded after work-up and chromatography the title product in 68% yield (44.9 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 4H), 1.35 (s, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.02, 83.99, 25.02.

*4.6.7. 4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (Table 2, **2g**).*[18c] According to the general procedure, the reaction of amide **1g** (0.20 mmol), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), Na_2CO_3 (1.0 equiv) in dioxane (0.25 M) for 15 h at 150 °C afforded after work-up and chromatography the title product in 60% yield (30.5 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.82−7.79 (m, 3H), 7.52−7.46 (m, 2H), 1.39 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.37, 135.14, 132.93, 130.52, 128.75, 127.81, 127.09, 127.08, 125.90, 84.02, 25.03.

*4.6.8. 2-(6-Methoxynaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, **2h**).*[18a] According to the general procedure, the reaction of amide **1h** (0.20 mmol), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), and Na_2CO_3 (1.0 equiv) in dioxane (0.25 M) for 15 h at 150 °C afforded after work-up and chromatography the title product in 67% yield (38.0 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.13 (d, J = 9.0 Hz, 2H), 3.93 (s, 3H), 1.39 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.66, 136.56, 136.12, 131.25, 130.38, 128.51, 126.04, 118.81, 105.75, 83.93, 55.43, 25.07, 25.01.

*4.6.9. 2-([1,1′-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, **2i**).*[18a] According to the general procedure, the reaction of amide **1i** (0.20 mmol), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), and Na_2CO_3 (1.0 equiv) in dioxane (0.25 M) for 15 h at 150 °C afforded after work-up and chromatography the title product in 63% yield (35.3 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.89 (d, J = 8.0 Hz, 2H), 7.65−7.59 (m, 4H), 7.44 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 1H), 1.37 (s, 12H). ^{13}C

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NMR (125 MHz, $CDCl_3$): δ 144.03, 141.16, 135.39, 128.90, 127.69, 127.37, 126.60, 83.97, 67.24, 25.03.

4.6.10. 2-(4′-Methoxy-[1,1′-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, 2j).[18c] According to the general procedure, the reaction of amide **1j** (0.20 mmol), B_2pin_2 (1.2 equiv), $Pd(TFA)_2$ (5 mol %), PCy_3HBF_4 (20 mol %), and Na_2CO_3 (1.0 equiv) in dioxane (0.25 M) for 15 h at 150 °C afforded after work-up and chromatography the title product in 72% yield (44.6 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 3.0 Hz, 2H), 7.56 (d, J = 4.0 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H), 1.36 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.54, 143.61, 135.39, 133.65, 128.40, 126.13, 114.36, 83.92, 55.51, 25.03.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00081.

^{1}H and ^{13}C NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: michal.szostak@rutgers.edu.

ORCID

Shicheng Shi: 0000-0001-8124-9235

Michal Szostak: 0000-0002-9650-9690

Notes

The authors declare no competing financial interest.

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