Rh-Catalyzed Base-Free Decarbonylative Borylation of Twisted Amides

Fusheng Bie,[†,‡,§] Xuejing Liu,[,†,‡,§] Yijun Shi,[†,‡] Han Cao,[†,‡] Ying Han,[†,‡] Michal Szostak[*,#] and Chengwei Liu[*,†,‡,#]*

[†]Zaozhuang University, 1 Bei'an Road, Zaozhuang, Shandong 277160, China

[‡]Shandong Lunan Coal Chemical Research Institute of Engineering and Technology, 1 Bei'an Road, Zaozhuang, Shandong 277160, China

[#]Department of Chemistry, Rutgers University, 73 Warren Street, Newark, New Jersey 07102, United States

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Corresponding author

lxj3786749@126.com; michal.szostak@rutgers.edu; chengwei.liu@rutgers.edu

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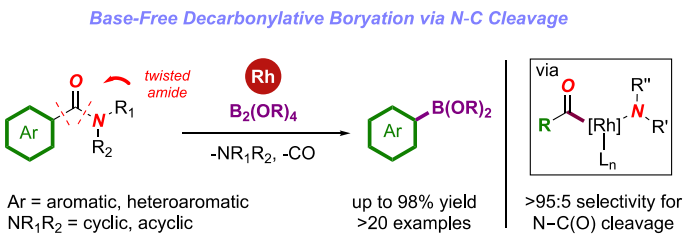


We report the rhodium-catalyzed base-free decarbonylative borylation of twisted amides. The synthesis of versatile arylboronate esters from aryl twisted amides is achieved via decarbonylative rhodium(I) catalysis and highly selective N–C(O) insertion. The method is notable for a very practical, additive-free Rh(I) catalyst system. The method shows broad functional group tolerance and excellent substrate scope, including site-selective decarbonylative borylation/Heck cross-coupling via divergent N–C/C–Br cleavage and late-stage pharmaceutical borylation.

Arylboronate esters are fundamental building blocks in organic synthesis, including the Suzuki-Miyaura cross-coupling for the assembly of significant molecular architectures across various facets of chemical science.[1-3] The versatile utility of arylboronates is captured by their widespread application in drug discovery, functional materials, and molecular sensors.[1-3] The traditional formation of C–B bonds by the reaction between organometallic reagents, such as organomagnesium or organolithium with borates has now been largely replaced by the more functional group tolerant Miyaura borylation of aryl halides.[2] Most commonly, Miyaura borylation involves a Pd(0)/(II) manifold using B_2pin_2 as the diboron reagent, while the cross-coupling of the formed arylboronate esters with organohalides is a common complication of this method. On the other hand, recent advances have been achieved by the cross-coupling of a range of carboxylic acid derivatives as electrophiles by a decarbonylative pathway.[4] Simultaneously, rhodium catalysis has received increased attention in the past years as a tool enabling facile construction of carbon–carbon and carbon–heteroatom bonds.[5-8] Remarkably, rhodium catalysis enables novel and complementary selectivity to other catalytic systems.[8] Furthermore, rhodium-based catalytic systems are frequently able to perform under user-friendly, external-base free conditions in the presence of water or even in water as a sole green solvent.[5] From both the academic and industrial standpoints, benign catalytic methods involving reduced waste generation are highly preferred over stoichiometric use of external bases and additives. In this context, the amide bond resonance ($n_N \rightarrow \pi^*_{C=O}$ conjugation) represents a classic effect in organic chemistry.[9] Typical amides are planar and approximately 40% double bond in character. Amidic resonance means that high activation energy is typically required for N–C bond cleavage. One route to reduce the N–C bond resonance effect is by functionalizing the amide nitrogen atom to enable amide bond twisting. Since 2015, amides as electrophiles have been applied in transition-metal-catalyzed cross-coupling upon amide bond twisting by acyl and decarbonylative coupling.[9-11] We discovered diverse twisted amides characterized by a range of twist angles, which can be applied to generic cross-coupling reactions.[9] In 2015, we reported the palladium-catalyzed decarbonylative Heck cross-coupling, which exploits amides as electrophiles for the synthesis alkenes.[9] We also developed the nickel-catalyzed decarbonylative Suzuki-Miyaura

cross-coupling of amides,[9] among other methods.[12] Besides amide cross-coupling, the field of decarbonylative cross-coupling of carboxylic acids has also enjoyed rapid progress.[13]

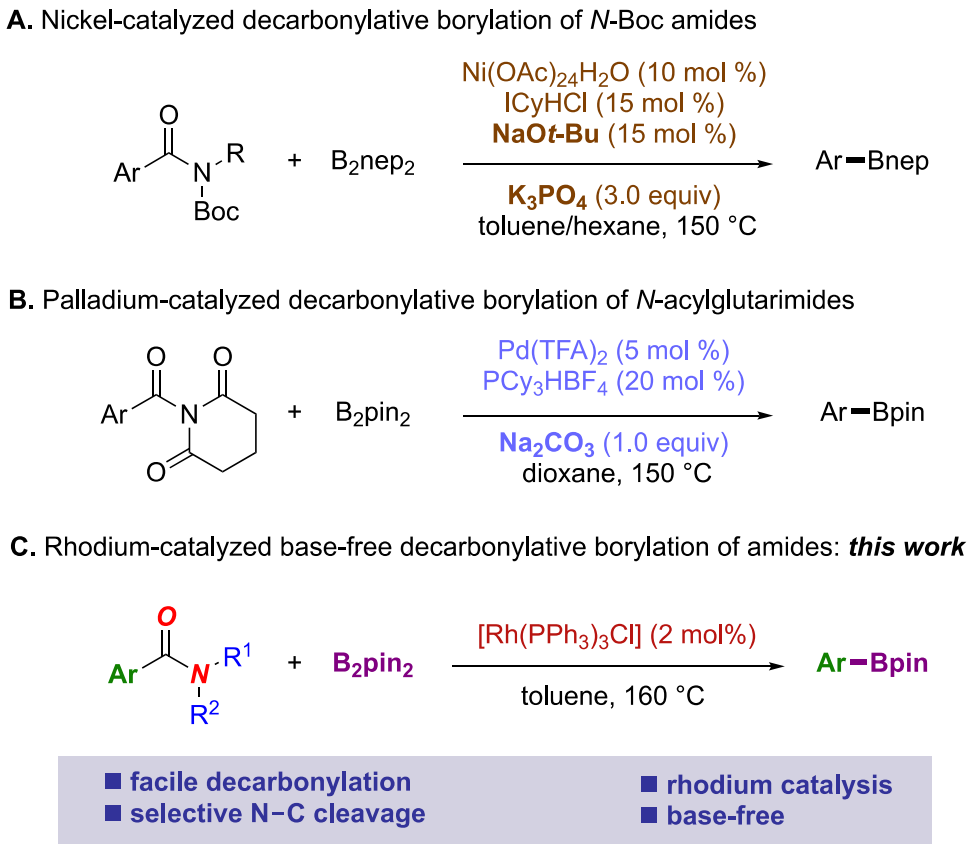


Figure 1. (A) Nickel-catalyzed decarbonylative borylation of *N*-Boc amides. (B) Palladium-catalyzed decarbonylative borylation of *N*-acylglutarimides. (C) Rhodium-catalyzed base-free decarbonylative borylation of amides (this work).

In 2016, Shi group reported the nickel-catalyzed decarbonylative borylation of *N*-Boc amides using nickel/NHC catalytic conditions (Figure 1A).[14] In 2019, we reported the palladium-catalyzed decarbonylative borylation of *N*-acylglutarimides, which employed phosphines as ancillary ligands (Figure 1B).[15] It should be noted that both nickel- and palladium-catalytic systems for decarbonylative borylation of amides required strong bases as activators for transmetallation, which limits the applicability of these methods.[16] Considering the facile transmetallation between Rh(I) and diboron reagents,[5–8] we therefore hypothesized that we can utilize Rh(I) catalysts for decarbonylative borylation

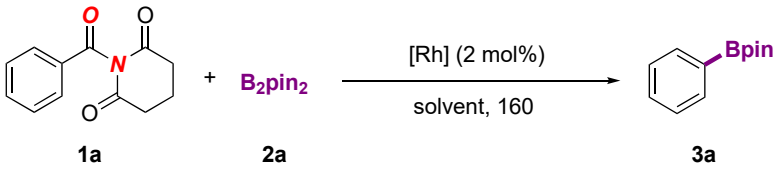
of amides under external-base-free conditions to produce important organoboronates with broad functional group tolerance (Figure 1C).

Herein, we report the first Rh-catalyzed decarbonylative borylation of amides. The following features of our study are noteworthy: (1) significantly expanded substrate scope including halides (Cl, Br) and enolizable carbonyl substrates; (2) very practical, external base-free conditions; (3) the first general application of versatile Rh(I) catalysis in a tandem N–C(O) activation/decarbonylation /cross-coupling, which given the importance of both Rh catalysis and amides in synthetic chemistry, may open up new vistas in this catalysis platform engaging amide bonds in a myriad of transformations. Specifically, the use of external-base free conditions is vastly preferred from both experimental and environmental standpoints. The present method is superior to previous transformations in terms of scope, operational-simplicity and functional group tolerance. The method should be used as the first-choice method for performing decarbonylative borylation of amides.[14,15]

The use of mild Rh(I) conditions allows for expansion of substrate scope. The use of Rh(I) in decarbonylative borylation in the presence of mild bases (KOAc) using thioester substrates has been reported.[16] The present study engages oxidative addition of N–C(O) bond to Rh(I), which is likely to expand the scope of N–C(O) decarbonylative protocols given the importance of amides in organic synthesis, the facility of the transformation and advantageous conditions as well as functional group tolerance.

The proposed Rh(I)-catalyzed external base-free decarbonylative borylation of amides was examined using *N*-benzoyl glutarimide and bis(pinacolato)diboron as model substrates (Table 1).

Table 1. Summary of Optimization Studies[a]



1a **2a** **3a**

entry	catalyst	ligand	base	yield (%)
1[b]	$[Rh(cod)Cl]_2$	dppb	Na_2CO_3	13
2[b]	$[Rh(cod)Cl]_2$	dppb	K_2CO_3	4
3[b]	$[Rh(cod)Cl]_2$	dppb	K_3PO_4	3
4[b]	$[Rh(cod)Cl]_2$	-	Na_2CO_3	7
5[b]	$[Rh(cod)Cl]_2$	dppb	-	14
6[b]	$[Rh(cod)Cl]_2$	-	-	32
7	$[Rh(cod)Cl]_2$	-	-	38
8	$[Rh(cod)_2]BF_4$	-	-	13
9	$[RhCp^*Cl_2]_2$	-	-	17
10	$[Rh(PPh_3)_3Cl]$	-	-	80
11[c]	$[Rh(PPh_3)_3Cl]$	-	-	56
12[d]	$[Rh(PPh_3)_3Cl]$	-	-	28
13[e]	$[Rh(PPh_3)_3Cl]$	-	-	60
14[f]	$[Rh(PPh_3)_3Cl]$	-	-	45
15[g]	$[Rh(PPh_3)_3Cl]$	-	-	18
16[h]	$[Rh(PPh_3)_3Cl]$	-	-	91
17[i]	$[Rh(PPh_3)_3Cl]$	-	-	93

[a]Conditions: **1a** (1.0 equiv), **2a** (1.5 equiv), catalyst (2 mol%), ligand (8 mol%), base (2.0 equiv), toluene, 160 °C, 15 h. [b]dioxane. [c]catalyst (1 mol%). [d]catalyst (0.5 mol%). [e]140 °C. [f]120 °C. [g]100 °C. [h]**2a** (2.0 equiv). [i]**2a** (3.0 equiv).

First, we selected $[Rh(cod)Cl]_2$ as a catalyst, which delivered the desired product in a promising 13% yield (Table 1, entry 1). After a range of control experiments, we identified external ligand- and base-free conditions as optimal for this transformation (Table 1, entries 2-6). We tested different solvents and

identified toluene as the preferred solvent (Table 1, entry 7). Notably, we found Wilkinson's catalyst, [$Rh(PPh_3)_3Cl$], as the best catalyst for this transformation. We further investigated the effect of catalyst loading and the reaction temperature (Table 1, entries 11-15). It is interesting to note that a high valent catalyst [$RhCp^*Cl_2]_2$ also gave the desired product (entry 9). We believe that under certain conditions amide N–C(O) functionalization using Rh(III) is feasible.[17] Finally, the yield was further improved to 91% and 93% by using an excess of the bis(pinacolato)diboron reagent to facilitate transmetallation (Table 1, entries 16-17). The optimized conditions involve *N*-benzoyl glutarimide (1.0 equiv), bis(pinacolato)diboron (2.0 equiv) and [$Rh(PPh_3)_3Cl$] (2 mol%) in toluene (0.2 M) at 160 °C (Table 1, entry 16), which supersedes the previous methods using nickel and palladium catalysis in terms of atom economy, operational-simplicity and reaction efficiency.[14,15]

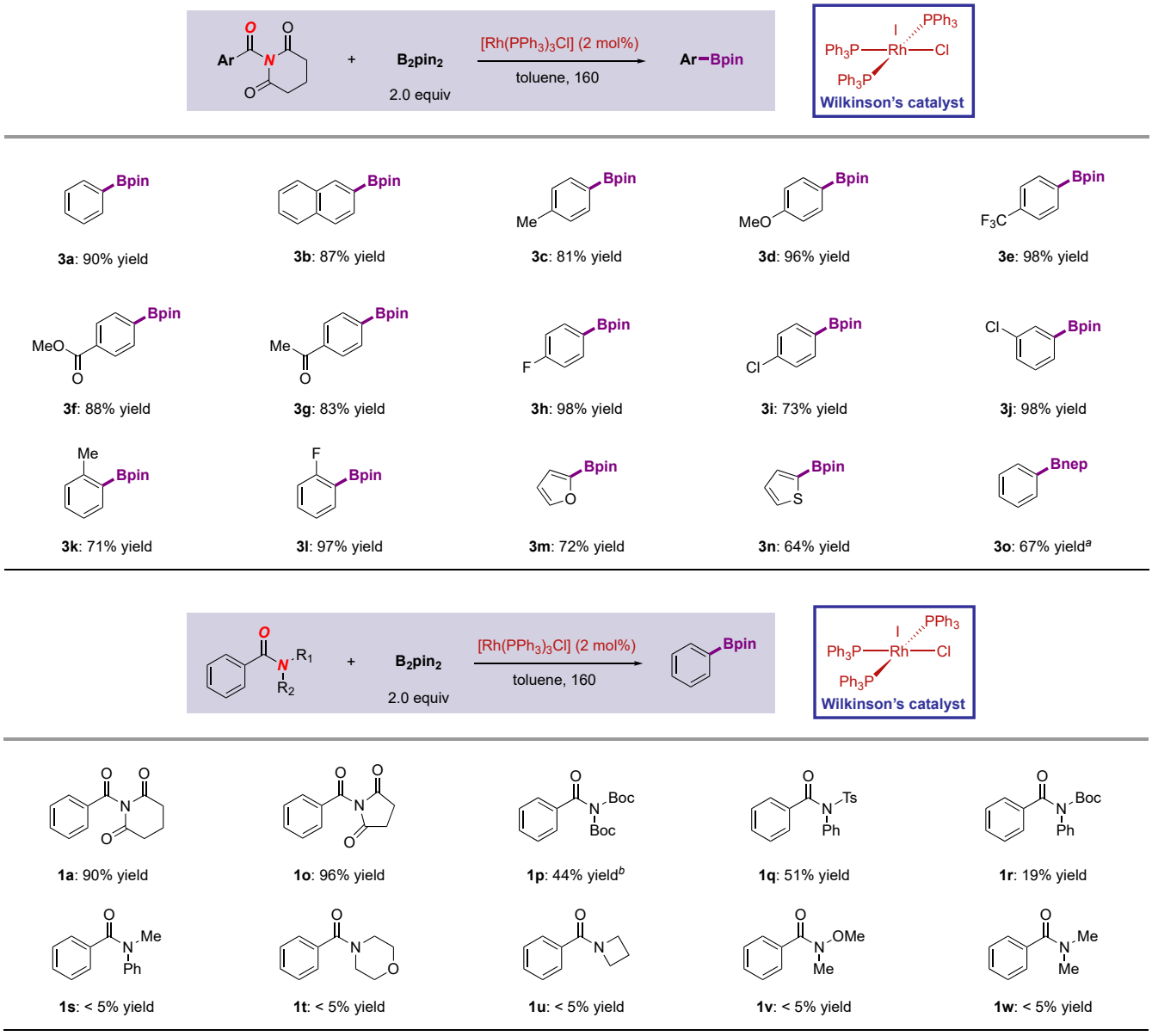


Figure 2. Rhodium-catalyzed base-free decarbonylative borylation of amides. Conditions: amide (1.0 equiv), B_2pin_2 (2.0 equiv), $[Rh(PPh_3)_3Cl]$ (2 mol %), toluene, 160 °C, 15 h. Isolated yields. [a] B_2nep_2 (3.0 equiv). [b] B_2pin_2 (3.0 equiv). Note that the yields of **3a-3o**, Figure 2 (top), correspond to product yields; the yields shown in Figure 2 (bottom) correspond to the product yields (**3a**). Structures of starting materials are shown in Figure 2 (bottom).

With the optimal conditions in hand, we next investigated the substrate scope for this Rh(I)-catalyzed decarbonylative borylation of amides (Figure 2, top). As shown, we first selected *N*-acyl-glutarimides as standard electrophiles. A wide range of amides bearing electron-neutral (**3a**, **3c**), electron-rich (**3d**) and electron-withdrawing (**3e**) substituents is compatible with this decarbonylative Miyaura borylation. Polycyclic aromatic substrates, such as (**3b**) can also be well tolerated, delivering the coupling product in excellent 87% yield. It is worthwhile to note that electrophilic functional groups that would not be compatible in the classic organometallic addition, including esters (**3f**) and ketones (**3g**), can be readily

employed. Furthermore, fluoro- (**3h**), chloro- (**3i**) and bromo- (**3p** see Figure 3B) groups are well compatible with this coupling; note that chloro- and bromo- substituents are not compatible with Pd- or Ni-catalysis.[14,15] As expected, substitution at the meta-position is also compatible, as demonstrated by using the chloro-functionalized substrate (**3j**), which results in 98% yield. Furthermore, sterically-hindered (**3k**) and fluoro-ortho-substituted (**3l**) substrates can be cross-coupled in good to excellent yields. Finally, this method can also be used to borylate electron-rich heterocyclic substrates to give the desired products in good yields (**3m**-**n**). Next, we also employed bis(neopentylglycolato)diboron as the nucleophile (**3o**), which indicates that more sterically hindered diborons are also compatible.

Inspired by the success of *N*-acyl-glutarimides in this Rh(I)-catalyzed decarbonylative borylation of amides, we were curious to test other twisted amides in this versatile coupling (Figure 2, bottom). Importantly, *N*-acyl-succinimides (**1o**), di-Boc-amides (**1p**) and *N*-Ph/Ts-amides (**1q**) are compatible with this coupling. On the other hand, *N*-Ph/Boc-amides (**1r**) afford only low yield of the coupling product due to the ease of *N*–Boc scission. Furthermore, planar amides are not able to undergo oxidative addition, including *N*-Ph/Me-amides (**1s**), *N*-morpholinyl-amides (**1t**), *N*-azetidinyl-amides (**1u**), *N*-OMe/Me-amides (**1v**) and *N*-Me_2-amides (**1w**), resulting in their recovery in most cases.

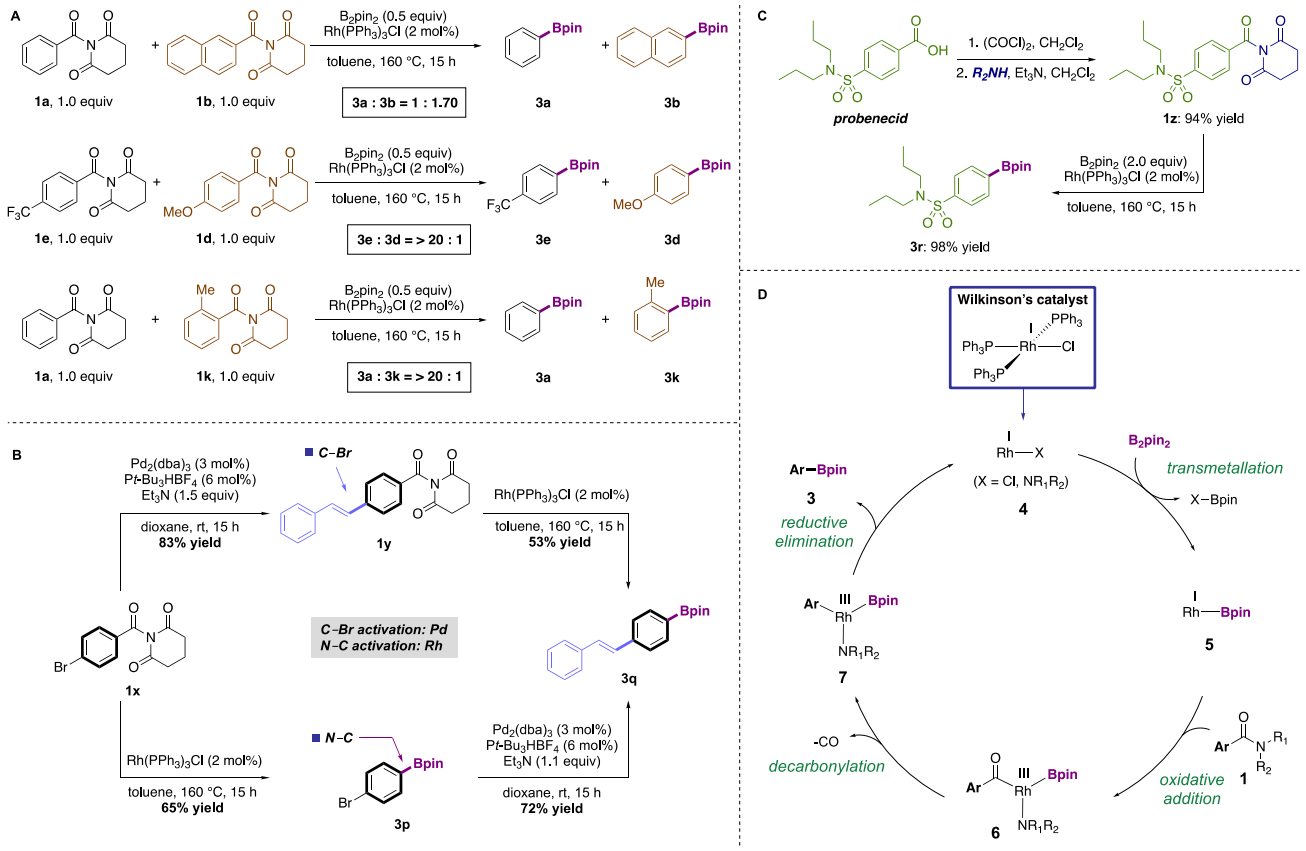


Figure 3. A. Selectivity studies. B. Selective C–Br and C–N bond activation. C. Expedient synthesis of probenecid pinacol ester. D. Proposed mechanism.

Competition studies were conducted and indicated that π-extended electrophiles, such as 2-naphthyl have a comparable reactivity to unconjugated electrophiles (Figure 3A, **3a**:**3b** = 1:1.7). Furthermore, electron-deficient amides are significantly more reactive than electron-rich amides (**3e**:**3d** >20:1), which is consistent with oxidative addition and decarbonylation. Moreover, steric-hindrance exerts a substantial effect on the coupling (**3a**:**3k** >20:1). In order to further show the synthetic value of this new cross-coupling, we developed sequential borylation/Heck reaction via divergent N–C/C–Br bond cleavage (Figure 3B). Under palladium catalysis, 1-(4-bromobenzoyl)-piperidine-2,6-dione (**1x**) can be chemoselectively converted to the alkene-containing amide (**1y**) by the Heck reaction via C–Br bond cleavage.[18] Then, our standard Rh(I) conditions can achieve decarbonylative borylation to give the desired product (**3q**) by N–C bond cleavage. In another way, decarbonylative borylation of (**1x**) by selective N–C bond cleavage can be performed in the presence of a sensitive bromo-substituent to give

the borylation product (**3p**) via Rh(I)-catalysis, which then can be converted to the final product (**3q**) by the Pd-catalyzed Heck cross-coupling.

Next, we also performed late-stage derivatization of pharmaceuticals (Figure 3C). We were delighted to find that this base-free decarbonylative borylation of an antihyperuricemic, probenecid (**3r**), gave the desired arylboronate product in 98% yield without cleavage of the sulfonamide bond under standard conditions. The proposed mechanism for this Rh(I)-catalyzed base-free decarbonylative borylation of amides is shown in Figure 3D. Transmetallation between Rh(I) species and the diboron reagent gives boryl–Rh(I). Then, oxidative addition of the amide N–C(O) bond and decarbonylation gives aryl–Rh(III). Finally, reductive elimination gives the arylboronate product and regenerates the Rh(I) catalyst. The glutarimide leaving group is likely involved as an internal-base in this process. It is also possible that Rh(I) could first undergo oxidative addition of the amide, followed by decarbonylation, transmetallation and reductive elimination.[12,16] The dissociated amino group may act as an intramolecular base to form NR_2–Bpin species. It is important to point out that the first cycle likely involves the transmetallation of Rh(I) chloride and B_2pin_2 to afford boryl-Rh(I), which typically requires the presence of base. We hypothesize that *N*-glutarimide is released by hydrolysis of a twisted amide in this process.[9] Further studies to elucidate the mechanism of amide cross-coupling and expand the scope are ongoing.

Conclusions

In summary, we have developed the rhodium(I)-catalyzed base-free decarbonylative borylation of twisted amides. The method is notable for operationally-simple, base-free borylation, which is beyond the scope of palladium or nickel catalysis. This versatile decarbonylative Miyaura borylation approach allows rapid access to organoboron compounds from readily available twisted amides, shows broad scope and tolerates a range of functional groups that are incompatible with other catalytic systems. The utility has been demonstrated in sequential divergent couplings and late-stage borylation. With all the

advantages of rhodium catalysis, we believe that the use of Rh(I) will greatly expand the pursuit of decarbonylative cross-coupling reactions of amides in organic chemistry.

Experimental Section

General Methods. All starting materials reported in the manuscript have been prepared according to the method reported previously.[12] All compounds reported in this manuscript have been previously reported or are commercially available. Spectroscopic data matched literature values. General methods have been published.[12]

General Procedure for Amide Synthesis. A previously published procedure was followed. An oven-dried flask (25 mL) equipped with a stir bar was charged with amine (typically, 5.0 mmol, 1.0 equiv), dimethylaminopyridine (typically, 0.025 mmol, 0.005 equiv), triethylamine (typically, 6.0 mmol, 1.2 equiv), and dichloromethane (typically, 10 mL), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Acyl chloride (typically, 5.0 mmol, 1.0 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred 12 h at room temperature. After the indicated time, the reaction mixture was diluted with ethyl acetate (30 mL), washed with 1 M HCl (20 mL), H_2O (20 mL), brine (20 mL). Then the organic layer was dried by Na_2SO_4, filtrated and concentrated. Unless stated otherwise, the crude product was purified by recrystallization (toluene) to give analytically pure product. Characterization data are included in the section below.

General Procedure for *N*-Ph/Ts Amide Synthesis. An oven-dried flask (25 mL) equipped with a stir bar was charged with aniline (typically, 5.0 mmol, 1.0 equiv), pyridine (typically, 12.5 mmol, 2.5 equiv), and dichloromethane (typically, 10 ml), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. *p*-Methylbenzenesulfonyl chloride (typically, 5.0 mmol, 1.0 equiv) was added portions to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred for 2 h at room temperature. After the indicated time, the reaction mixture

was diluted with ethyl acetate (30 mL). The reaction mixture was washed with HCl (10 mL), H_2O (10 mL), brine (10 mL), dried, and concentrated to get crude first-step product. Then an oven-dried flask (25 mL) equipped with a stir bar was charged with crude first-step product (typically, 5.0 mmol, 1.0 equiv), 4-(dimethylamino)pyridine (typically, 0.025 mmol, 0.005 equiv), triethylamine (typically, 6 mmol, 1.2 equiv), and dichloromethane (typically, 10 ml, 0.5 M), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Acyl chloride (typically, 5.0 mmol, 1.0 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred for 12 h at room temperature. After the indicated time, the reaction mixture was diluted with ethyl acetate (30 mL). The reaction mixture was washed with HCl (10 mL), brine (10 mL), H_2O (10 mL), dried, and concentrated. The crude product was purified by recrystallization (toluene) to give analytically pure product. Characterization data are included in the section below.

General Procedure for *N*-Boc$_2$ Amide Synthesis. A previously published procedure was followed. An oven-dried flask (25 mL) equipped with a stir bar was charged with benzamide (typically, 5.0 mmol, 1.0 equiv), dimethylaminopyridine (typically, 0.5 mmol, 0.1 equiv), and dichloromethane (typically, 10 mL, 0.5 M), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Di-*tert*-butyl dicarbonate (typically, 10.0 mmol, 2.0 equiv) was added portions to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred 12 h at room temperature. After the indicated time, the reaction mixture was diluted with ethyl acetate (30 mL), washed with 1 M HCl (20 mL), H_2O (20 mL), brine (20 mL). Then the organic layer was dried, filtrated and concentrated. The crude product was purified by column chromatography (ethyl acetate/hexane) to give pure product. Characterization data are included in the section below.

General Procedure for Rh-Catalyzed Decarbonylative Borylation of Amides. An oven-dried vial equipped with a stir bar was charged with amides (neat, typically, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (typically, 0.2 mmol, 2.0 equiv) and $Rh(PPh_3)_3Cl$ (typically, 0.002 mmol, 0.02 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles

under high vacuum. Toluene (typically, 0.5 ml, 0.2 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with dichloromethane (10 mL), filtered, and concentrated. Purification by chromatography on silica gel (hexane/dichloromethane) afforded the title products. Characterization data are included in the section below.

Representative Procedure for Rh-Catalyzed Decarbonylative Borylation of Amides. An oven-dried vial equipped with a stir bar was charged with 1-benzoylpiperidine-2,6-dione (neat, 0.218 g, 1.0 mmol), bis(pinacolato)diboron (0.508 g, 2.0 mmol, 2.0 equiv) and $Rh(PPh_3)_3Cl$ (18.5 mg, 0.02 mmol, 0.02 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (5 ml, 0.2 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for 15 h at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature. Purification by chromatography on silica gel (hexane/dichloromethane) afforded the title product. Yield 90% (0.184 g). White solid. Characterization data are included in the section below.

General Procedure for Pd-Catalyzed Heck Reaction. An oven-dried vial equipped with a stir bar was charged with bromo-para-substituted amides (neat, typically, 0.1 mmol, 1.0 equiv), styrene (typically, 0.15 mmol, 1.5 equiv), $Pd_2(dba)_3$ (typically, 0.003 mmol, 0.03 equiv), ligand (typically, 0.006 mmol, 0.06 equiv) and triethylamine (typically, 0.15 mmol, 1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (typically, 0.5 ml, 0.2 M) was added with vigorous stirring at room temperature, the reaction mixture was stirred for 15 h at room temperature. After the indicated time, the reaction mixture was diluted with dichloromethane (10 mL), filtered, and concentrated. Purification by chromatography on silica gel (hexane/dichloromethane) afforded the title products. Characterization data are included in the section below.

General Procedure for Selectivity Studies. An oven-dried vial equipped with a stir bar was charged with two amide substrates (neat, typically, 0.1 mmol, 1.0 equiv each), bis(pinacolato)diboron (typically, 0.05 mmol, 0.5 equiv) and $Rh(PPh_3)_3Cl$ (typically, 0.002 mmol, 0.02 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (typically, 0.5 ml, 0.2 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with dichloromethane (10 mL), filtered, and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 400 MHz) and GC-MS to obtain conversion and yield using internal standard and comparison with authentic samples.

1-Benzoylpiperidine-2,6-dione (1a).[12] Yield: 80% (0.867 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88-7.86 (d, *J* = 8.0 Hz, 2 H), 7.66-7.62 (t, *J* = 8.0 Hz, 1 H), 7.51-7.47 (t, *J* = 8.0 Hz, 2 H), 2.80-2.76 (t, *J* = 8.0 Hz, 4 H), 2.19-2.12 (m, 2 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.0, 170.9, 135.1, 131.9, 130.3, 129.3, 32.5, 17.7.

1-(2-Naphthoyl)piperidine-2,6-dione (1b).[19] Yield: 92% (1.240 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.34 (s, 1 H), 7.95-7.87 (m, 3 H), 7.89-7.87 (d, *J* = 8.3 Hz, 2 H), 7.66-7.62 (m, 1 H), 7.58-7.54 (m, 1 H), 2.84-2.81 (t, *J* = 6.5 Hz, 4 H), 2.23-2.16 (m, 2 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.2, 171.0, 136.6, 132.8, 132.6, 130.0, 129.6, 129.3, 129.3, 128.0, 127.3, 124.9, 32.6, 17.7.

1-(4-Methylbenzoyl)piperidine-2,6-dione (1c).[12] Yield: 70% (0.813 g). Light brown solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76-7.74 (d, *J* = 8.0 Hz, 2 H), 7.29-7.27 (d, *J* = 8.0 Hz, 2 H), 2.78-2.75 (t, *J* = 8.0 Hz, 4 H), 2.42 (s, 3 H), 2.17-2.10 (m, 2 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.0, 170.5, 146.5, 130.4, 130.0, 129.3, 32.5, 22.0, 17.6.

1-(4-Methoxybenzoyl)piperidine-2,6-dione (1d).[12] Yield: 92% (1.131 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83-7.81 (d, *J* = 9.0 Hz, 2 H), 6.95-6.93 (d, *J* = 9.0 Hz, 2 H), 3.86 (s, 3 H), 2.76-2.73

(t, J = 6.5 Hz, 4 H), 2.14-2.08 (m, 2 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 172.1, 169.7, 165.2, 132.9, 124.5, 114.6, 55.8, 32.5, 17.6.

1-(4-(Trifluoromethyl)benzoyl)piperidine-2,6-dione (1e).[12] Yield: 72% (1.026 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98-7.96 (d, J = 8.0 Hz, 2 H), 7.76-7.74 (d, J = 8.0 Hz, 2 H), 2.81-2.78 (t, J = 8.0 Hz, 4 H), 2.20-2.13 (m, 2 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 172.1, 170.2, 136.6 (C-F, $^{2}J^{C-F}$ = 33 Hz), 134.9, 130.5, 126.4 (C-F, $^{3}J^{C-F}$ = 3.0 Hz), 124.7 (C-F, $^{1}J^{C-F}$ = 271.0 Hz), 32.5, 17.6. **^{19}F (376 MHz, $CDCl_3$)** δ -63.38.

Methyl 4-(2,6-dioxopiperidine-1-carbonyl)benzoate (1f).[12] Yield: 83% (1.140 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15-8.12 (m, 2 H), 7.92-7.90 (m, 2 H), 3.95 (s, 3 H), 2.81-2.76 (t, J = 8.0 Hz, 4 H), 2.20-2.13 (m, 2 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz $CDCl_3$)** δ 172.1, 170.5, 165.9, 135.5, 135.3, 130.4, 130.1, 52.8, 32.5, 17.6.

1-(4-Acetylbenzoyl)piperidine-2,6-dione (1g).[12] Yield: 53% (0.693 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05-8.02 (m, 2 H), 7.95-7.93 (m, 2 H), 2.80-2.77 (t, J = 4.0 Hz, 4 H), 2.64 (s, 3 H), 2.19-2.13 (m, 2 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 197.2, 172.1, 170.5, 141.5, 135.2, 130.4, 129.0, 32.5, 27.1, 17.6.

1-(4-Fluorobenzoyl)piperidine-2,6-dione (1h).[12] Yield: 85% (1.076 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90-7.87 (m, 2 H), 7.18-7.13 (m, 2 H), 2.78-2.75 (t, J = 6.5 Hz, 4 H), 2.17-2.10 (m, 2 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 172.0, 169.7, 167.0 (C-F, $^{1}J^{C-F}$ = 256.9 Hz), 133.1 (C-F, $^{3}J^{C-F}$ = 9.8 Hz), 128.4 (C-F, $^{4}J^{C-F}$ = 2.8 Hz), 116.6 (C-F, $^{2}J^{C-F}$ = 22.3 Hz), 32.5, 17.6. **^{19}F (376 MHz, $CDCl_3$)** δ -101.25.

1-(4-Chlorobenzoyl)piperidine-2,6-dione (1i).[12] Yield: 72% (0.906 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80-7.78 (d, J = 8.6 Hz, 2 H), 7.47-7.45 (d, J = 8.6 Hz, 2 H), 2.79-2.77 (t, J = 6.5 Hz, 4 H), 2.18-2.11 (m, 2 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 172.0, 170.0, 141.8, 131.6, 130.4, 129.7, 32.5, 17.6.

1-(3-Chlorobenzoyl)piperidine-2,6-dione (1j).[12] Yield: 77% (0.966 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (s, 1 H), 7.75-7.72 (m, 1 H), 7.62-7.59 (m, 1 H), 7.45-7.42 (t, *J* = 8.2 Hz, 1 H), 2.80-2.76 (t, *J* = 6.5 Hz, 4 H), 2.18-2.12 (m, 2 H). **^{13}C{^{1}H} NMR (100 MHz $CDCl_3$)** δ 172.0, 170.0, 135.5, 135.0, 133.6, 130.6, 130.1, 128.3, 32.5, 17.6.

1-(2-Methylbenzoyl)piperidine-2,6-dione (1k).[12] Yield: 68% (0.788 g). Light brown solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50-7.48 (d, *J* = 7.6 Hz, 1 H), 7.47-7.45 (t, *J* = 7.6 Hz, 1 H), 7.33-7.31 (d, *J* = 7.6 Hz, 1 H), 7.27-7.23 (t, *J* = 7.6 Hz, 1 H), 2.77-2.74 (t, *J* = 6.6 Hz, 4 H), 2.68 (s, 3 H), 2.16-2.09 (m, 2 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.2, 170.8, 142.6, 133.9, 132.5, 131.2, 130.8, 126.3, 32.5, 22.0, 17.5.

1-(2-Fluorobenzoyl)piperidine-2,6-dione (1l).[12] Yield: 83% (0.979 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10-8.06 (m, 1 H), 7.64-7.58 (m, 1 H), 7.32-7.28 (m, 1 H), 7.13-7.08 (m, 1 H), 2.75-2.72 (t, *J* = 6.5 Hz, 4 H), 2.14-2.07 (m, 2 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 171.8, 167.0 (C-F, $^6J^{C-F}$ = 1.5 Hz), 162.0 (C-F, $^1J^{C-F}$ = 256.1 Hz), 137.0 (C-F, $^3J^{C-F}$ = 10.0 Hz), 133.1, 125.2 (C-F, $^5J^{C-F}$ = 3.5 Hz), 120.5 (C-F, $^4J^{C-F}$ = 8.0 Hz), 117.2 (C-F, $^2J^{C-F}$ = 23.6 Hz), 32.5, 17.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.52.

1-(Furan-2-carbonyl)piperidine-2,6-dione (1m).[20] Yield: 75% (0.783 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (s, 1H), 7.40-7.39 (d, *J* = 3.7 Hz, 1H), 6.61-6.60 (dd, *J* = 3.7, 1.7 Hz, 1H), 2.77-2.74 (t, *J* = 6.5 Hz, 4H), 2.15-2.08 (m, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 171.7, 159.4, 148.3, 147.6, 122.1, 113.7, 32.5, 17.5.

1-(Thiophene-2-carbonyl)piperidine-2,6-dione (1n).[12] Yield: 74% (0.827 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77-7.76 (dd, *J* = 5.0, 1.2, 1H), 7.69-7.68 (dd, *J* = 3.9, 1.2, 1H), 7.16-7.14 (dd, *J* =5.0, 3.9, 1H), 2.78-2.74 (t, *J* = 6.5, 4H), 2.15-2.08 (m, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 171.7, 163.7, 137.7, 136.9, 136.1, 128.9, 32.5, 17.5.

1-Benzoylpyrrolidine-2,5-dione (1o).[20] Yield: 89% (0.908 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86-7.84 (d, *J* = 8.2 Hz, 2H), 7.69-7.65 (t, *J* = 7.5 Hz, 1H), 7.52-7.48 (t, *J* = 7.8 Hz, 2H), 2.93 (s, 4H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 174.7, 167.8, 135.3, 131.5, 130.7, 129.1, 29.2.

***N*,*N*-Bis(*tert*-butoxycarbonyl)benzamide (1p)**.[21] Yield 78% (1.269 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84-7.82 (d, *J* = 7.6 Hz, 2 H), 7.61-7.58 (d, *J* = 7.4 Hz, 1 H), 7.49-7.45 (d, *J* = 7.8 Hz, 2 H), 1.37 (s, 18 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 169.5, 149.9, 134.4, 133.6, 129.2, 128.8, 84.4, 27.7.

***N*-Phenyl-*N*-tosylbenzamide (1q)**.[12] Yield: 76% (1.344 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84-7.82 (d, *J* = 8.4 Hz, 2H), 7.45-7.43 (d, *J* = 7.0 Hz, 2H), 7.32-7.30 (d, *J* = 8.2 Hz, 2H), 7.28-7.26 (m, 4H), 7.18-7.14 (m, 4H), 2.45 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.0, 145.0, 137.5, 135.3, 133.6, 131.9, 130.5, 129.6, 129.4, 129.2, 129.2, 128.1, 21.8.

***tert*-Butyl benzoyl(phenyl)carbamate (1r)**.[22] Yield 73% (1.090 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74-7.72 (m, 2H), 7.54-7.50 (m, 1H), 7.46-7.41 (m, 4H), 7.36-7.32 (m, 1H), 7.28-7.25 (m, 2H), 1.22 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.9, 153.4, 139.2, 137.1, 131.8, 129.3, 128.4, 128.2, 128.1, 127.9, 83.6, 27.6.

***N*-Methyl-*N*-phenylbenzamide (1s)**.[20] Yield 89% (0.944 g). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30-7.28 (d, *J* = 7.0 Hz, 2 H), 7.23-7.19 (m, 3 H), 7.16-7.10 (m, 3 H), 7.03-7.02 (d, *J* = 7.8 Hz, 2 H), 3.49 (s, 3 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.7, 145.0, 136.0, 129.7, 129.2, 128.8, 127.8, 127.0, 126.6, 38.5.

Morpholino(phenyl)methanone (1t).[23] Yield 91% (0.872 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 (s, 5 H), 3.76 (brs, 4 H), 3.63 (brs, 2 H), 3.44 (brs, 2 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.6, 135.4, 130.0, 128.7, 127.2, 67.0, 48.3, 42.6.

Azetidin-1-yl(phenyl)methanone (1u).[19] Yield 76% (0.612 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45-7.44 (d, *J* = 5.6 Hz, 2 H), 7.26-7.18 (m, 3 H), 4.07-4.04 (t, *J* = 6.0 Hz, 2 H), 4.00-3.97 (t, *J* = 6.0 Hz, 2 H), 2.11-2.05 (m, 2 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 170.3, 133.3, 130.9, 128.4, 127.8, 53.4, 49.0, 16.1.

***N*-Methoxy-*N*-methylbenzamide (1v)**.[19] Yield 85% (0.706 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65-7.63 (d, *J* = 6.6 Hz, 2 H), 7.44-7.35 (m, 3 H), 3.52 (s, 3 H), 3.33 (s, 3 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 169.9, 134.1, 130.6, 128.1, 128.0, 61.0, 33.8.

***N,N*-Dimethylbenzamide (1w)**.[10a] Yield 78% (0.582 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42-7.37 (m, 5 H), 3.11 (s, 3 H), 2.97 (s, 3 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 171.5, 136.3, 129.4, 128.3, 127.0, 39.5, 35.2.

1-(4-Bromobenzoyl)piperidine-2,6-dione (1x).[20] Yield 74% (1.112 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72-7.70 (d, *J* = 8.6 Hz, 2 H), 7.64-7.62 (d, *J* = 8.6 Hz, 2 H), 2.79-2.75 (t, *J* = 6.6 Hz, 4 H), 2.17-2.11 (m, 2 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.0, 170.3, 132.7, 131.6, 130.8, 130.7, 32.5, 17.6.

(*E*)-1-(4-Styrylbenzoyl)piperidine-2,6-dione (1y). Yield 83% (0.133 g). *New compound*. White solid. **Mp** = 178-180 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85-7.83 (d, *J* = 8.3 Hz, 2 H), 7.61-7.59 (d, *J* = 8.3 Hz, 2 H), 7.55-7.53 (d, *J* = 7.4 Hz, 2 H), 7.41-7.37 (t, *J* = 7.2 Hz, 2 H), 7.33-7.30 (t, *J* = 7.2 Hz, 1 H), 7.27-7.23 (d, *J* = 16.1 Hz, 1 H), 7.14-7.10 (d, *J* = 16.1 Hz, 1 H), 2.81-2.78 (d, *J* = 6.4 Hz, 4 H), 2.19-2.13 (m, 2 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.1, 170.3, 144.2, 136.5, 132.9, 130.9, 130.5, 129.0, 128.8, 127.2, 127.1, 32.6, 17.7. **IR:** 2927, 2879, 2851, 1742, 1705, 1678, 1599, 1414, 1344, 1321, 1246, 1173, 1145, 1049, 1004, 965, 920, 873, 826, 800, 758 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{20}H_{17}NO_3Na$ (M^+ + Na) 342.1100, found 342.1104.

4-(2,6-Dioxopiperidine-1-carbonyl)-*N,N*-dipropylbenzenesulfonamide (1z). Yield 94% (1.782 g). *New compound*. White solid. **Mp** = 129-131 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97-7.95 (d, *J* = 8.6

Hz, 2 H), 7.91-7.89 (d, *J* = 8.6 Hz, 2 H), 3.19-3.05 (t, *J* = 7.6 Hz, 4 H), 2.81-2.77 (t, *J* = 6.5 Hz, 4 H), 2.19-2.13 (m, 2 H), 1.60-1.51 (m, 4 H), 0.89-0.85 (t, *J* = 7.4 Hz, 6 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 172.1, 170.2, 145.9, 134.8, 130.8, 127.8, 50.3, 32.5, 22.2, 17.5, 11.3. **IR:** 2967, 2928, 2875, 1760, 1716, 1676, 1598, 1467, 1396, 1331, 1244, 1176, 1143, 1005, 989, 937, 845, 798, 748, 736 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{18}H_{25}N_2O_5S$ (M^+ + H) 381.1478, found 381.1482.

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (3a, Figure 2).[15] According to the general procedure, the reaction of 1-benzoylpiperidine-2,6-dione (218.0 mg, 1.0 mmol, 1.0 equiv), bis(pinacolato)diboron (508.0 mg, 2.0 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (18.5 mg, 0.02 mmol, 0.02 equiv) in toluene (5.0 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 90% yield (184.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82-7.80 (d, *J* = 6.6 Hz, 2 H), 7.48-7.44 (t, *J* = 7.4 Hz, 1 H), 7.39-7.35 (t, *J* = 7.6 Hz, 2 H), 1.35 (s, 12 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 134.9, 131.4, 127.9, 83.9, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (3b, Figure 2).[13] According to the general procedure, the reaction of 1-(2-naphthoyl)piperidine-2,6-dione (26.7 mg, 0.10 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 87% yield (22.1 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.38 (s, 1 H), 7.90-7.88 (d, *J* = 7.6 Hz, 1 H), 7.84-7.82 (m, 3 H), 7.53-7.45 (m, 2 H), 1.40 (s, 12 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 136.4, 135.2, 132.9, 130.5, 128.8, 127.8, 127.1, 125.9, 84.1, 25.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-Tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (3c, Figure 2).[15] According to the general procedure, the reaction of 1-(4-methylbenzoyl)piperidine-2,6-dione (23.1 mg, 0.10 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in

81% yield (17.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72-7.70 (d, *J* = 7.9 Hz, 2 H), 7.20-7.18 (t, *J* = 7.6 Hz, 2 H), 2.37 (s, 3 H), 1.34 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 141.6, 134.9, 128.7, 83.8, 25.0, 21.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d, Figure 2).[15] According to the general procedure, the reaction of 1-(4-methoxybenzoyl)piperidine-2,6-dione (24.7 mg, 0.10 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 96% yield (22.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77-7.74 (d, *J* = 8.6 Hz, 2 H), 6.91-6.89 (d, *J* = 8.6 Hz, 2 H), 3.83 (s, 3 H), 1.33 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 162.3, 136.6, 113.4, 83.7, 55.2, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (3e, Figure 2).[15] According to the general procedure, the reaction of 1-(4-(trifluoromethyl)benzoyl)piperidine-2,6-dione (28.5 mg, 0.10 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (26.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92-7.90 (d, *J* = 7.7 Hz, 2 H), 7.62-7.60 (d, *J* = 7.7 Hz, 2 H), 1.36 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 135.1, 133.4 (C-F, $^{2}J^{C\text{-}F}$ = 31.9 Hz), 125.6 (C-F, $^{1}J^{C\text{-}F}$ = 270.8 Hz), 124.5 (C-F, $^{3}J^{C\text{-}F}$ = 3.8 Hz), 84.4, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.02.

Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3f, Figure 2).[13] According to the general procedure, the reaction of methyl 4-(2,6-dioxopiperidine-1-carbonyl)benzoate (27.5 mg, 0.10 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002

mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 88% yield (23.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03-8.01 (d, *J* = 8.3 Hz, 2 H), 7.88-7.86 (d, *J* = 8.3 Hz, 2 H), 3.92 (s, 3 H), 1.35 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 166.3, 133.8, 131.4, 127.7, 83.3, 51.3, 24.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanone (3g, Figure 2).[15] According to the general procedure, the reaction of 1-(4-acetylbenzoyl)piperidine-2,6-dione (25.9 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 83% yield (20.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85-7.83 (d, *J* = 8.0 Hz, 2 H), 7.16-7.14 (t, *J* = 8.0 Hz, 2 H), 2.49 (s, 3 H), 1.35 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.4, 135.2, 126.3, 122.7, 84.2, 25.0, 23.4. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h, Figure 2).[24] According to the general procedure, the reaction of 1-(4-fluorobenzoyl)piperidine-2,6-dione (23.5 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (21.7 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81-7.78 (m, 2 H), 7.07-7.02 (m, 2 H), 1.34 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.2 (C-F, $^{1}J^{C\text{-}F}$ = 248.7 Hz), 137.1 (C-F, $^{3}J^{C\text{-}F}$ = 8.1 Hz), 115.0 (C-F, $^{2}J^{C\text{-}F}$ = 20.1 Hz), 84.1, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -108.45.

2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i, Figure 2).[13] According to the general procedure, the reaction of 1-(4-chlorobenzoyl)piperidine-2,6-dione (25.2 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02

equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 73% yield (17.3 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64-7.62 (d, *J* = 8.4 Hz, 2 H), 7.25-7.23 (d, *J* = 8.4 Hz, 2 H), 1.24 (s, 12 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 137.7, 136.3, 128.2, 84.2, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(3-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j, Figure 2).[13] According to the general procedure, the reaction of 1-(3-chlorobenzoyl)piperidine-2,6-dione (25.2 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (23.3 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (s, 1 H), 7.67-7.65 (d, *J* = 7.3 Hz, 1 H), 7.43-7.41 (m, 1 H), 7.32-7.28 (t, *J* = 7.5 Hz, 1 H), 1.34 (s, 12 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 134.7, 134.2, 132.8, 131.4, 129.3, 84.3, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-Tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (3k, Figure 2).[13] According to the general procedure, the reaction of 1-(2-methylbenzoyl)piperidine-2,6-dione (23.1 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 71% yield (15.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77-7.75 (d, *J* = 7.9 Hz, 1 H), 7.34-7.30 (t, *J* = 7.5 Hz, 1 H), 7.17-7.14 (t, *J* = 6.2 Hz, 2 H), 2.54 (s, 3 H), 1.34 (s, 12 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 145.0, 136.0, 130.9, 129.9, 124.8, 83.6, 25.0, 22.4. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

2-(2-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l, Figure 2).[25] According to the general procedure, the reaction of 1-(2-fluorobenzoyl)piperidine-2,6-dione (23.5 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02

equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 97% yield (21.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76-7.72 (m, 1 H), 7.46-7.40 (m, 1 H), 7.15-7.12 (t, J = 7.4 Hz, 1 H), 7.05-7.00 (t, J = 8.6 Hz, 1 H), 1.36 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.3 (C-F, $^{1}J^{C-F}$ = 249.2 Hz), 137.0 (C-F, $^{4}J^{C-F}$ = 8.0 Hz), 133.4 (C-F, $^{3}J^{C-F}$ = 8.7 Hz), 123.7 (C-F, $^{5}J^{C-F}$ = 3.1 Hz), 115.4 (C-F, $^{2}J^{C-F}$ = 23.8 Hz), 84.0, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -102.65.

2-(Furan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m, Figure 2).[26] According to the general procedure, the reaction of 1-(furan-2-carbonyl)piperidine-2,6-dione (20.7 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 72% yield (13.9 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65-7.64 (d, J = 1.4 Hz, 1 H), 7.08-7.07 (d, J = 3.3 Hz, 1 H), 6.44-6.43 (m, 1 H), 1.34 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 147.5, 123.4, 110.5, 84.4, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (3n, Figure 2).[13] According to the general procedure, the reaction of 1-(thiophene-2-carbonyl)piperidine-2,6-dione (22.3 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 64% yield (13.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66-7.63 (m, 2 H), 7.21-7.19 (m, 1 H), 1.35 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 137.3, 132.5, 128.4, 84.2, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane (3o, Figure 2).[13] According to the general procedure, the reaction of 1-benzoylpiperidine-2,6-dione (21.7 mg, 0.1 mmol, 1.0 equiv), bis(neopentyl

glycolato)diboron (67.8 mg, 0.3 mmol, 3.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 67% yield (12.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ7.81-7.79 (d, *J* = 8.0 Hz, 2 H), 7.44-7.41 (t, *J* = 7.4 Hz, 1 H), 7.37-7.33 (t, *J* = 7.5 Hz, 2 H), 3.77 (s, 4 H), 1.03 (s, 6 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 134.0, 130.8, 127.7, 72.5, 32.0, 22.1. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

1-Benzoylpiperidine-2,6-dione (1a, Figure 2).[15] According to the general procedure, the reaction of 1-benzoylpiperidine-2,6-dione (218.0 mg, 1.0 mmol, 1.0 equiv), bis(pinacolato)diboron (508.0 mg, 2.0 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (18.5 mg, 0.02 mmol, 0.02 equiv) in toluene (5.0 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 90% yield (184.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82-7.80 (d, *J* = 6.6 Hz, 2 H), 7.48-7.44 (t, *J* = 7.4 Hz, 1 H), 7.39-7.35 (t, *J* = 7.6 Hz, 2 H), 1.35 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**□δ 134.9, 131.4, 127.9, 83.9, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

1-Benzoylpyrrolidine-2,5-dione (1o, Figure 2).[19] According to the general procedure, the reaction of 1-benzoylpyrrolidine-2,5-dione (20.3mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 96% yield (19.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82-7.80 (d, *J* = 6.6 Hz, 2 H), 7.48-7.44 (t, *J* = 7.4 Hz, 1 H), 7.39-7.35 (t, *J* = 7.6 Hz, 2 H), 1.35 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)**□δ 134.9, 131.4, 127.9, 83.9, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

***N,N*-Bis(*tert*-Butoxycarbonyl)benzamide (1p, Figure 2).**[21] According to the general procedure, the reaction of *N,N*-Bis(tert-Butoxycarbonyl)benzamide (32.1 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (76.2 mg, 0.3 mmol, 3.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 44% yield (9.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82-7.80 (d, *J* = 6.6 Hz, 2 H), 7.48-

7.44 (t, *J* = 7.4 Hz, 1 H), 7.39-7.35 (t, *J* = 7.6 Hz, 2 H), 1.35 (s, 12 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 134.9, 131.4, 127.9, 83.9, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

***N*-Phenyl-*N*-tosylbenzamide (1q, Figure 2).**[12] According to the general procedure, the reaction of *N*-Phenyl-*N*-tosylbenzamide (35.1 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 51% yield (10.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82-7.80 (d, *J* = 6.6 Hz, 2 H), 7.48-7.44 (t, *J* = 7.4 Hz, 1 H), 7.39-7.35 (t, *J* = 7.6 Hz, 2 H), 1.35 (s, 12 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 134.9, 131.4, 127.9, 83.9, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

***tert*-Butyl benzoyl(phenyl)carbamate (1r, Figure 2).**[21] According to the general procedure, the reaction of t-Butyl benzoyl(phenyl)carbamate (29.7 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 19% yield (3.9 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82-7.80 (d, *J* = 6.6 Hz, 2 H), 7.48-7.44 (t, *J* = 7.4 Hz, 1 H), 7.39-7.35 (t, *J* = 7.6 Hz, 2 H), 1.35 (s, 12 H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 134.9, 131.4, 127.9, 83.9, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

***N*-Methyl-*N*-phenylbenzamide (1s, Figure 2).**[20] According to the general procedure, the reaction of *N*-Methyl-*N*-phenylbenzamide (21.1 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in less than 5% yield.

Morpholino(phenyl)methanone (1t, Figure 2).[23] According to the general procedure, the reaction of Morpholino(phenyl)methanone (19.1 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2

mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in less than 5% yield.

***N*-Methoxy-*N*-methylbenzamide (1u, Figure 2).**[19] According to the general procedure, the reaction of *N*-methoxy-*N*-methylbenzamide (16.1 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mg, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in in less than 5% yield.

***N*-Methoxy-*N*-methylbenzamide (1v, Figure 2).**[19] According to the general procedure, the reaction of *N*-methoxy-*N*-methylbenzamide (16.5 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in in less than 5% yield.

***N,N*-Dimethylbenzamide (1w, Figure 2).**[10a] According to the general procedure, the reaction of *N,N*-dimethylbenzamide (14.9 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in in less than 5% yield.

2-(4-Bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p, Figure 3B).[27] According to the general procedure, the reaction of 1-(4-bromobenzoyl)piperidine-2,6-dione (148.1 mg, 0.5 mmol, 1.0 equiv), bis(pinacolato)diboron (253.9 mg, 1.0 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (9.3 mg, 0.01 mmol, 0.02 equiv) in toluene (2.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 65% yield (183.9 mg) after work-up and chromatography. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67-7.65 (d, *J* = 8.3 Hz, 2 H), 7.51-7.49 (d, *J* = 8.3 Hz, 2 H), 1.34 (s, 12 H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 136.4, 131.1, 126.4, 84.2, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

(*E*)-4,4,5,5-Tetramethyl-2-(4-styrylphenyl)-1,3,2-dioxaborolane (3q, Figure 3B).[28] According to the general procedure, the reaction of 1-(4-bromobenzoyl)piperidine-2,6-dione (148.1 mg, 0.5 mmol, 1.0

equiv), styrene (78.1 mg, 0.75 mmol, 1.5 equiv), $Pd_2(dba)_3$ (13.8 mg, 0.015 mmol, 0.03 equiv), P*t*-Bu_3HBF_4 (8.8 mg, 0.03 mmol, 0.06 equiv), triethylamine (55.7 mg, 0.75 mmol, 1.5 equiv) in dioxane (2.0 ml) at room temperature for 15h afforded (*E*)-1-(4-styrylbenzoyl)piperidine-2,6-dione (**1y**) after work-up and column chromatography in 83% yield (132.2 mg). White solid. Then the reaction of **1y** (31.9 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 53% yield (16.2 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81-7.79 (d, *J* = 8.0 Hz, 2 H), 7.53-7.51 (d, *J* = 7.9 Hz, 4 H), 7.38-7.34 (t, *J* = 7.3 Hz, 2 H), 7.28-7.25 (t, *J* = 7.4 Hz, 1 H), 7.16 (s, 1 H), 7.13 (s, 1 H), 1.35 (s, 12 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 140.1,137.3, 135.3, 129.8, 128.8, 128.7, 127.9, 126.7, 125.9, 83.9, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

***N,N*-Dipropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonamide (3r, Figure 3C).**[13] According to the general procedure, the reaction of 4-(2,6-dioxopiperidine-1-carbonyl)-*N,N*-dipropylbenzenesulfonamide (38.0 mg, 0.1 mmol, 1.0 equiv), bis(pinacolato)diboron (50.8 mg, 0.2 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (1.9 mg, 0.002 mmol, 0.02 equiv) in toluene (0.5 ml) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (35.9 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92-7.90 (d, *J* = 8.3 Hz, 2 H), 7.79-7.76 (d, *J* = 8.3 Hz, 2 H), 3.08-3.04 (t, *J* = 7.6 Hz, 4 H), 1.57-1.48 (m, 4 H), 1.35 (s, 12 H), 0.87-0.83 (t, *J* = 7.4 Hz, 6 H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 142.5, 135.3, 126.2, 84.5, 50.1, 25.0, 22.1, 11.3. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

Supporting Information Available. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

Author Information. Corresponding authors: lxj3786749@126.com; michal.szostak@rutgers.edu; chengwei.liu@rutgers.edu

Author Contributions: [§]F.B. and X.L. contributed equally to this work.

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