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Nickel-Mediated Cross-Coupling of Boronic Acids and Phthalimides for the Synthesis of *Ortho*-Substituted Benzamides

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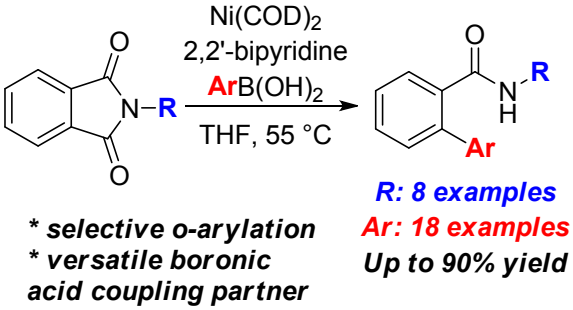


Abstract:

The decarbonylative coupling of phthalimides with aryl boronic acids provides ready access to a broad range of *ortho*-substituted benzamides. This nickel-mediated methodology extends reactivity from previously described air-sensitive diorganozinc reagents of limited availability to easily-handled and widely commercially available boronic acids. The decarbonylative coupling is tolerant of a broad range of functional groups and demonstrates little sensitivity to steric factors on either of the coupling partners.

Introduction:

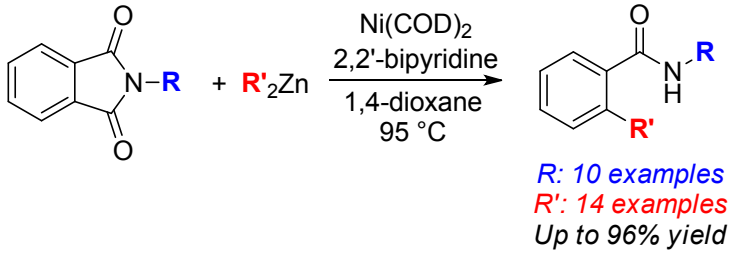
The advent of cross-coupling methodology has revolutionized organic synthesis.[1] In addition to traditional halide and pseudohalides, ever increasing numbers of nucleophilic and electrophilic coupling partners are being utilized in such processes, with innumerable previously unknown retrosynthetic disconnects now available. Ketones[2] and aldehydes[3,4,5,6,7,8] have been

demonstrated to undergo decarbonylative cross-coupling to generate new carbon-carbon single bonds,[9] as have carboxylic acids,[10] esters,[11] anhydrides,[12,13] imides and isatins,[14] and amides.[15] These processes lead to a broad range of products. Along these same lines, our group has investigated the use of phthalimides as decarbonylative cross-coupling reagents.[16]

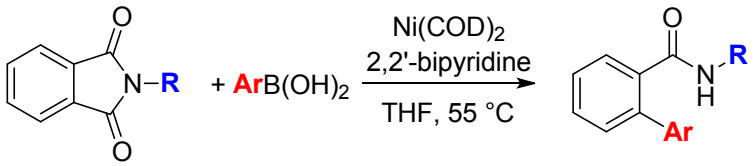
In our previous work, phthalimides were shown to successfully couple with diorganozinc reagents in a nickel-mediated decarbonylative process to selectively generate *ortho*-substituted benzamides (Scheme 1), of interest due to their potential biological activity.[17,18] Although the previously developed decarbonylative methodology is efficient and modular, it is significantly limited by access to the diorganozinc species. Only diphenyl-, diethyl-, and dimethyl-zinc are commercially available; all other diorganozinc reagents require preparation via air-sensitive and tedious lithium-halogen exchange and reaction with zinc chloride. This process necessarily limits the functional groups amenable within the reaction. Representing a further drawback, only one of the two organic substituents of the diorganozinc is ultimately incorporated into the product. With an eye toward increasing the scope of amenable substrates and eliminating the need for pyrophoric and/or highly air sensitive organometallics, we explored the use of boronic acids as mild, bench-stable cross-coupling partners for the arylative decarbonylation of phthalimides.[19,20]

Scheme 1. Methods for the nickel-mediated decarbonylative cross coupling of phthalimides.

Previous method:



This work:

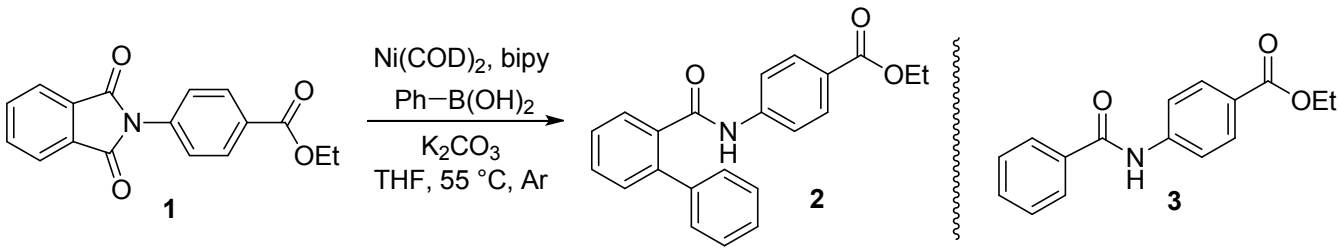


Results and Discussion:

The desired decarbonylative coupling product can be obtained with the use of aryl boronic acids as the nucleophilic coupling partner. The optimized conditions, which include the use of air-

sensitive $Ni(COD)_2$ (COD = 1,5-cyclooctadiene), 2,2'-bipyridine (bipy), potassium carbonate and phenyl boronic acid in THF, produce *ortho*-aryl benzamide **2** in 90% yield as determined by GC/MS (Table 1, entry 1). Initial reaction conditions, very similar to those utilized with diorganozinc reagents, produced **2** in 55% yield (entry 2), a modest conversion that was complicated by the presence of decarbonylated reduction product **3**, a nearly inseparable byproduct. Utilizing ester-substituted *N*-aryl phthalimide **1** as a test substrate, a variety of solvents, metal sources, ligands, and additives were examined. These experiments, briefly summarized in Table 1, led to the identification of conditions that maximized the amount of the desired product formed while also minimizing the amount of the reduction product.[21] As will be shown, this reaction is amenable with a broad range of both aryl boronic acid and phthalimide substrates.

Table 1. Optimization of the decarbonylative coupling of phthalimides with aryl boronic acids.



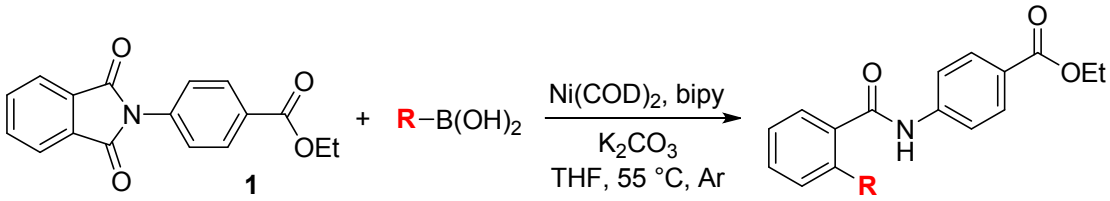
Entry	Change from Standard Conditions[a]	Crude Yield of 2[b]
1	None	90
2	No K_2CO_3	55
3	with NaI instead of K_2CO_3	<5
4	In DME at 75 °C	45
5	In dioxane at 100 °C	20
6	Phenyl boronic acid pinacol ester	<5
7	PPh_3 (2 equiv) instead of bipy	<5

8	No $Ni(COD)_2$	<5
9	$Ni(acac)_2$ with Mn^0 instead of $Ni(COD)_2$	<5
10	$Ni(COD)_2$ (20 mol%), bipy (22 mol%)	19

a) Standard Conditions: Phthalimide **1** (0.5 mmol, 1.0 equiv), $Ni(COD)_2$ (1.0 equiv), bipyridine (1.1 equiv), phenyl boronic acid (2.0 equiv), and K_2CO_3 (2.2 equiv) in THF (2.0 mL) at 55 °C under an inert atmosphere. b) Determined by GC/MS or ^1H NMR.

Upon identification of optimal reaction conditions, the boronic acid scope was explored using ester-substituted *N*-aryl phthalimide **1** (Table 2). Reactions using electronically diverse boronic acids proceeded well. In many cases, however, isolated yields were significantly lower than starting material conversion due to the challenge of separating the reduction byproduct from the desired product. Notably, the decarbonylative coupling reactivity can be expanded to coupling partners with nucleophile-sensitive functionality (entries 3 and 7). These and similar compounds are not accessible via the previously described diorganozinc coupling, as ketones, nitriles, and esters are incompatible with the harsh conditions required to form the diorganozinc nucleophiles. The reaction demonstrates little sensitivity to steric factors, as reactions utilizing *ortho*-, *meta*-, and *para*- substituted aryl boronic acids proceed with similar efficiencies. While a broad range of aryl boronic acids are competent in the reaction, alkyl boronic acids lead to only traces of the desired benzamide product. While a mixture of compounds are produced, the reduction product is the major compound in these reactions.

Table 2. Scope of boronic acids with *N*-(ester)aryl phthalimide **1**



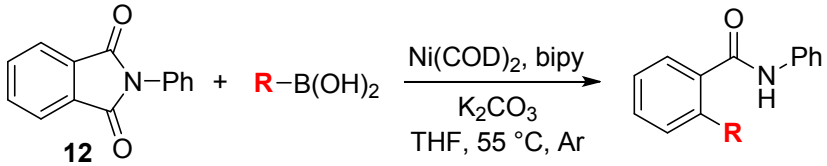
Entry[a]	R (boronic acid)	Product	Yield (GC) (%)[b]	Yield (%)
1	Ph	**2**	90	67

2	4-OMe-C_6H_4	**4**	85	25
3	4-CN-C_6H_4	**5**	91	14
4	3-CF_3-C_6H_4	**6**	83	50
5	3,5-$(CF_3)_2$-C_6H_3	**7**	94	54
6	2-Me-C_6H_4	**8**	88	20
7	2-C(O)Me-C_6H_4	**9**	83	58
8	Me	**10**	<5	-
9	*i*Pr	**11**	<5	-

a) Standard Conditions: Phthalimide **1** (0.5 mmol, 1.0 equiv), $Ni(COD)_2$ (1.0 equiv), bipyridine (1.1 equiv), boronic acid (2.0 equiv), and K_2CO_3 (2.2 equiv) in THF (2.0 mL) at 55 °C under an inert atmosphere. b) Determined by GC/MS or ^1H NMR.

Additional aryl boronic acids were also examined using the parent *N*-phenylphthalimide **12** as the starting material (Table 3). As observed with the ester-substituted phthalimide, the reaction proceeds smoothly with a large range of electronically diverse aryl boronic acids, from simple ethers and alkyl groups to amines, sulfides and fluorinated species. The direct comparison of *ortho*-, *meta*-, and *para*- methoxy-substituted aryl boronic acids (entries 3, 8, and 11) makes it clear that substrate substitution pattern has little impact on the efficiency of the reaction. The generality of the methodology is of significant value owing to the large range of commercially available aryl boronic acids.

Table 3. Scope of boronic acids with *N*-phenylphthalimide **12**



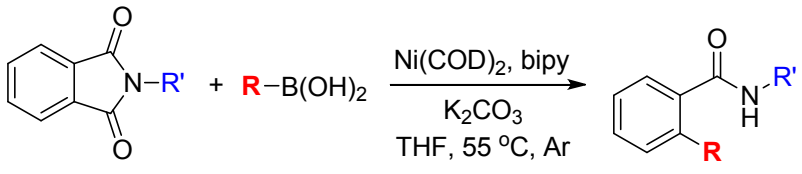
Entry[a]	R (Boronic Acid)	Product	Yield (GC) (%)[b]	Yield (%)
1	4-NMe_2-C_6H_4	**13**	87	68
2	4-SMe-C_6H_4	**14**	82	70
3	4-OMe-C_6H_4	**15**	78	51
4	4-Me-C_6H_4	**16**	76	59
5	4-F-C_6H_4	**17**	88	71
6	4-CF_3-C_6H_4	**18**	99	90
7	4-C(O)Me-C_6H_4	**19**	85	61
8	3-OMe-C_6H_4	**20**	83	58
9	3,5-$(CF_3)_2$-C_6H_3	**21**	79	43
10	2-F-C_6H_4	**22**	68	20
11	2-OMe-C_6H_4	**23**	84	62

a) Standard Conditions: *N*-phenyl phthalimide **12** (0.5 mmol, 1.0 equiv), $Ni(COD)_2$ (1.0 equiv), bipyridine (1.1 equiv), boronic acid (2.0 equiv), and K_2CO_3 (2.2 equiv) in THF (2.0 mL) at 55 °C under an inert atmosphere. b) Determined by GC/MS or ^1H NMR.

The reaction is also quite tolerant of a variety of readily accessible aryl-substituted phthalimides.[22] Reactions with *N*-phenyl imides substituted with electron deficient groups proceed efficiently (Table 4, entries 1-4), generating the desired arylative decarbonylation products in high yields. Electronically neutral (entries 5-8) or rich (entries 9-13) substrates also work well. Consistent with previous observations, reaction yields were largely independent of substitution patterns on the arene: *ortho*-, *meta*-, and *para*-methoxy substituted *N*-phenyl imides all underwent reaction with similar efficiencies (entries 9-11).

Unfortunately, attempts to utilize *N*-alkyl phthalimides result in no appreciable yield of the desired decarbonylative coupling product and primarily return unreacted starting material.[23]

Table 4. Variation of phthalimides with electron deficient boronic acids.

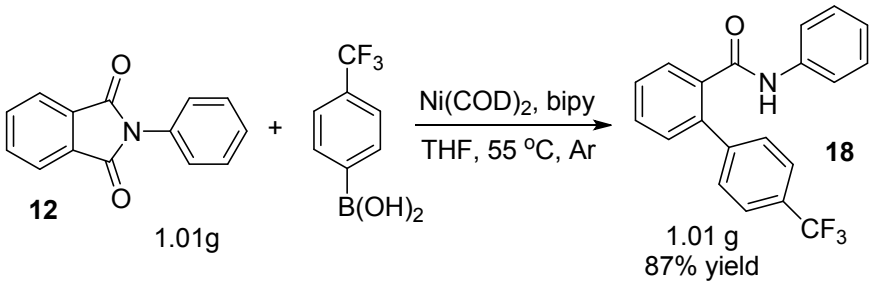


Entry[a]	R' (Imide)	R (Boronic Acid)	Product	Yield (GC) (%)[b]	Yield (%)
1	3,5-$(CF_3)_2$-C_6H_3	2-C(O)Me-C_6H_4	**24**	87	70
2	3,5-$(CF_3)_2$-C_6H_3	3-C(O)Me-C_6H_4	**25**	91	76
3	3,5-$(CF_3)_2$-C_6H_3	4-CF_3-C_6H_4	**26**	76	61
4	3,5-$(CF_3)_2$-C_6H_3	3-CF_3-C_6H_4	**27**	85	65
5	2-F-C_6H_4	3-C(O)Me-C_6H_4	**28**	82	68
6	2-F-C_6H_4	4-CF_3-C_6H_4	**29**	93	64
7	2-F-C_6H_4	2-F-C_6H_4	**30**	81	38
8	4-Cl-C_6H_4	3-CF_3-C_6H_4	**31**	75	39
9	4-OMe-C_6H_4	2-C(O)Me-C_6H_4	**32**	86	69
10	3-OMe-C_6H_4	2-C(O)Me-C_6H_4	**33**	67	52
11	2-OMe-C_6H_4	2-C(O)Me-C_6H_4	**34**	85	58
12	2-OMe-C_6H_4	3-C(O)Me-C_6H_4	**35**	79	62
13	4-OMe-C_6H_4	4-CF_3-C_6H_4	**36**	91	72

a) Standard Conditions: Phthalimide (0.5 mmol, 1.0 equiv), $Ni(COD)_2$ (1.0 equiv), bipyridine (1.1 equiv), boronic acid (2.0 equiv), and K_2CO_3 (2.2 equiv) in THF (2.0 mL) at 55 °C under an inert atmosphere. *b*) Determined by GC/MS.

To further demonstrate utility, the reaction was performed on a gram scale with *N*-phenylphthalimide **12** and 4-trifluoromethylphenyl boronic acid (Scheme 2). The reaction proceeded smoothly, producing the desired decarbonylative coupling product **18** in 87% isolated yield.

Scheme 2. Gram-scale decarbonylative coupling of **12** and 4-trifluoromethylphenyl boronic acid

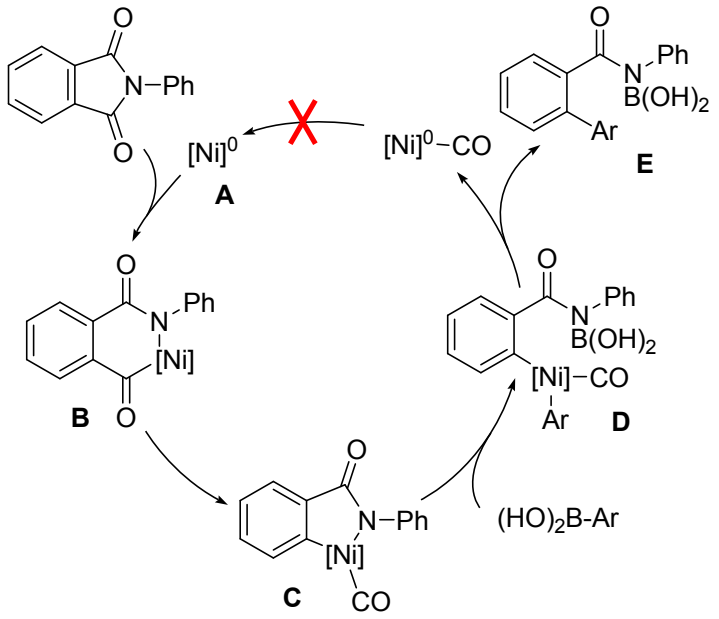


Proposed Mechanism

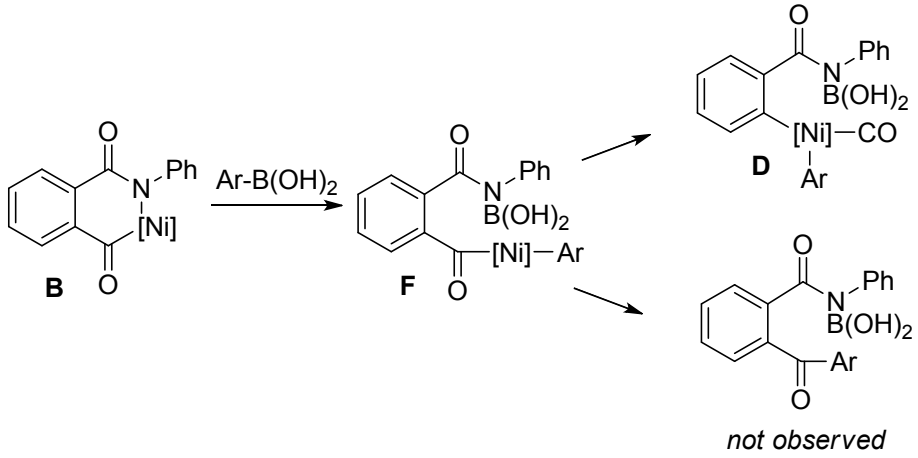
The proposed mechanism, based largely upon the analysis of similar reactions by our group, is provided in Scheme 3.[24] It is hypothesized that the nickel(0) and bipy combine to form catalytically active species **A**, which inserts into the imide to create 6-membered metalacycle **B**. Metalacycle **B** undergoes decarbonylation, leading to 5-membered metalacycle **C** which transmetalates with the boronic acid to generate intermediate **D**.[25] Reductive elimination from **D** to generate **E** yields the desired product upon acidic workup. The reductive elimination step simultaneously regenerates a new nickel(0) species that was initially envisioned to lose carbon monoxide and regenerate nickel complex **A**, closing the catalytic cycle. Unfortunately, the strength of the nickel-carbonyl bond prevents ready dissociation and a failure to achieve catalysis.[26,27] Efforts to identify conditions to accelerate carbonyl dissociation and induce catalysis are described below.

In contrast to the pathway described above, decarbonylation and transmetalation could also occur in the reverse order. Transmetalation of metalacycle **B** with the boronic acid yields intermediate **F**, which can undergo subsequent decarbonylation to generate the common intermediate **D** (Scheme 4). Although the mechanistic pathway has yet to be investigated, the sequence shown in Scheme 3 is considered the more likely, as the latter pathway has the potential to undergo reductive elimination from **F** to generate the keto-amide, but no such species have been observed.

Scheme 3. Proposed mechanism



Scheme 4. Alternative mechanistic proposal

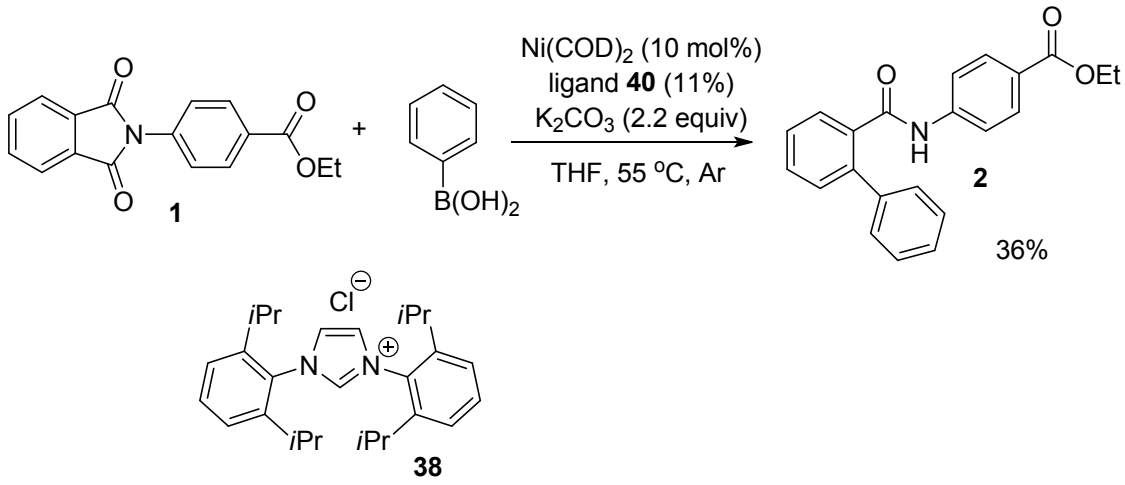


Efforts toward Catalysis

In order to further improve the utility of the current methodology, efforts were made to render the reaction catalytic in nickel (Scheme 5). As previously mentioned, the lack of catalyst turnover is largely attributed to the strength of the nickel-carbonyl bond that stems from backbonding from the metal into a pi* orbital of the carbon monoxide. Literature examples demonstrating catalytic nickel decarbonylation typically rely on two facets: high temperatures and electron deficient substrates.[28] In addition, we rationalized that π-accepting ligands such as phosphines or *N*-heterocyclic carbenes (NHC) could weaken the nickel-carbonyl bond and thus

promote the dissociation of carbon monoxide. Using 10 mol% of the nickel precatalyst with 11 mol% of the ligand, a number of solvents, ligands, and additives were tested and examined for turnover.[29] Despite significant screens, results were modest at best, peaking with the observation of 3 catalyst turnovers when performed with the isopropyl-substituted NHC ligand **38** (Scheme 5). It is anticipated that the achievement of reasonably efficient catalysis will necessitate the use of a different transition metal with a lesser affinity for carbon monoxide, but to date, no such system has been discovered.

Scheme 5. Efforts toward catalysis



Conclusion

In summary, this method for the nickel-mediated decarbonylative coupling of phthalimides and boronic acids provides ready and selective access to *ortho*-substituted benzamides, a common motif within compounds with demonstrated bioactivity. The use of aryl boronic acids as coupling partners allows the incorporation of ketones, nitriles and other nucleophile-sensitive functionality not amenable in previous methodology. The wide range of functional group tolerance on both coupling partners, tied with the efficient preparation of phthalimides and the commercial availability of boronic acids, provides a route to innumerable *ortho*-substituted benzamides via a simple and robust chemical transformation.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of nitrogen or argon in oven dried glassware with magnetic stirring. Solvents, including toluene, tetrahydrofuran, and diethyl ether, were purged with argon and passed through two columns of neutral alumina or molecular sieves. All starting materials are commercially available and used without purification or prepared according to procedures provided. All phthalimides were obtained commercially or prepared via the condensation of phthalic acid with the appropriate amine in either refluxing toluene (Dean-Stark conditions) or in refluxing acetic acid.[22]

^{1}H and ^{13}C NMR spectra were obtained using standard acquisition parameters and are referenced to TMS unless otherwise noted. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Crude yields were determined by ^{1}H NMR or through GC/MS using xylene, triphenylphosphine, or mesitylene as standards.

General Method for Decarbonylative Coupling of Phthalimides with Boronic Acids will be illustrated with a specific example. 2,2'-bipyridyl (85.8 mg, 0.55 mmol), potassium carbonate (151.8 mg, 1.10 mmol), *N*-phenyl phthalimide **12** (111.6 mg, 0.50 mmol), and 4-(trifluoromethyl)phenyl boronic acid (152.0 mg, 1.0 mmol) were combined in an oven-dried 10 mL round-bottomed flask equipped with a stir bar. The flask was transferred to a nitrogen atmosphere glove box where $Ni(COD)_2$ (190.0 mg, 0.5 mmol) was added and the flask was sealed with a septum. The flask was removed from the glove box, and THF (2 mL) was added via syringe. The solution was then heated and stirred in a 55 °C oil bath for 18 h. The resulting mixture was cooled to room temperature, and diethyl ether (5 mL) was added. The reaction was quenched with 2 M aqueous HCl (5 mL). The product was extracted with diethyl ether (3 × 15 mL), and the combined organic layers were washed with brine (2 × 15 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting product was purified by column chromatography (hexane:EtOAc, 9:1) to provide **18** in 90% yield.

Gram-Scale Method for the Decarbonylative Coupling of Phthalimide 1 with Phenyl Boronic Acid. 2,2'-bipyridyl (542 mg, 3.47 mmol), potassium carbonate (1.048 g, 7.51 mmol), *N*-phenyl phthalimide **12** (1.009 g, 3.42 mmol), and 4-trifluorophenyl boronic acid (819 mg, 4.31 mmol, 1.25 equiv) were combined in an oven-dried 100 mL round-bottomed flask equipped with

a stir bar. The flask was transferred to a nitrogen atmosphere glove box where $Ni(COD)_2$ (950 mg, 3.45 mmol) was added and the flask was sealed with a septum. The flask was removed from the glove box and THF (35 mL) was added via cannula. The solution was then heated and stirred in a 55 °C oil bath for 18 h. The resulting mixture was cooled to room temperature and quenched with 2 M aqueous HCl (25 mL). The product was extracted with diethyl ether (3 × 50 mL) and the combined organic layers were washed with brine (2 × 25 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting product was purified by column chromatography (hexane:EtOAc, 9:1) to provide **18** in 87% yield.

General Method for the Catalytic Decarbonylative Coupling of Phthalimides with Boronic Acids will be illustrated with a specific example. 1,3-Bis(2,6-di-i-propylphenyl)imidazolium chloride (**38**) (22.8 mg, 0.054 mmol), potassium carbonate (152.7 mg, 1.10 mmol), *N*-para ester phthalimide **1** (135.5 mg, 0.46 mmol), and phenyl boronic acid (110.2 mg, 0.90 mmol) were combined in an oven-dried 100 mL round-bottomed flask equipped with a stir bar. The flask was transferred to a nitrogen atmosphere glove box where $Ni(COD)_2$ (13.0 mg, 0.47 mmol) was added and the flask sealed with a septum. The flask was removed from the glove box and THF (2 mL) was added via syringe. The solution was then heated and stirred in a 55 °C oil bath for 18 h. The resulting mixture was cooled to room temperature and diethyl ether (5 mL) was added. The reaction was quenched with 2 M aqueous HCl (5 mL). The product was extracted with diethyl ether (3 × 15 mL) and the combined organic layers were washed with brine (2 × 15 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting product was purified by column chromatography (hexane:EtOAc, 9:1) to provide **2** in 36% yield.

Ethyl 4-([1,1'-biphenyl]-2-carboxamido)benzoate (2): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **2** (116 mg, 0.34 mmol, 67% yield) as a white flaky solid. R_f = 0.32 (2:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (t, J = 8.6 Hz, 3H), 7.51-7.40 (mult, 8H), 7.17 (d, J = 7.8 Hz, 2H), 7.00 (s, 1H), 4.33 (q, J = 7.3 Hz, 2H), 1.37 (t, J = 7.3 Hz, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 167.1, 166.1, 141.6, 139.8, 139.7, 134.7, 131.1, 130.6, 130.4, 129.8, 129.1, 128.9, 128.3, 128.1, 126.1, 118.7, 60.8, 14.3. IR (diamond ATR) 3052, 2997, 2972, 2930, 1708 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO_3$ 346.1438; Found 346.1420.

Ethyl 4-(4'-methoxy-[1,1'-biphenyl]-2-ylcarboxamido)benzoate (4): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **4** (47 mg, 0.13 mmol, 25% yield) as a white powder. R_f = 0.29 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.14 (s, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H) ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.4, 166.1, 159.7, 141.7, 139.3, 134.6, 131.9, 131.0, 130.6, 130.5, 130.1, 129.7, 127.6, 126.0, 118.8, 114.5, 60.8, 55.4, 14.3. IR (diamond ATR), 3287, 3253, 3187, 3115, 3067, 2977, 2930, 2893, 2832, 1716, 1705 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}NO_4$, 376.1543; Found 376.1552.

Ethyl 4-(4'-cyano-[1,1'-biphenyl]-2-carboxamido)benzoate (5): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **5** (26 mg, 0.07 mmol, 14% yield) as a white flaky solid. R_f = 0.21 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.96 (br s, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.62-7.49 (mult, 5H), 6.91 (d, *J* = 8.2 Hz, 1H), 4.38 (qrt, *J* = 7.3 Hz, 2H), 1.41 (t, *J* = 7.3 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.2, 165.9, 159.8, 142.0, 134.5, 134.2, 132.3, 132.0, 130.9, 130.8, 129.0, 127.1, 126.3, 119.3, 119.2, 116.3, 103.8, 61.0, 14.4. IR (diamond ATR) 3305, 3059, 2963, 2227, 1701, 1685, 1664, 1594 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}N_2O_3$, 371.1390; Found 371.1382.

Ethyl 4-(3'-(trifluoromethyl)-[1,1'-biphenyl]-2-ylcarboxamido)benzoate (6): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **6** (103 mg, 0.25 mmol, 50% yield) as a yellow oil. R_f = 0.30 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.75 (s, 1H), 7.63 (t, *J* = 6.1 Hz, 1H), 7.59 (td, *J* = 7.4, 1.3 Hz, 2H), 7.52 (td, *J* = 7.4, 1.3 Hz, 2H), 7.47 (t, *J* = 7.1 Hz, 1H) 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.2, 166.0, 141.4, 140.5, 138.2, 135.4, 132.1, 131.4 (q, *J* = 33 Hz), 131.2, 130.7, 130.4, 129.3, 129.1, 128.6, 126.4,

125.3 (q, J = 4 Hz), 124.8 (q, J = 4 Hz), 123.9 (q, J = 273 Hz), 118.8, 60.9, 14.3. IR (diamond ATR) 1713, 1690, 1607, 1593, 1516 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}F_3NO_3$, 414.1312; Found 414.1310.

Ethyl 4-(3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-2-ylcarboxamido)benzoate (7): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **7** (130 mg, 0.27 mmol, 54% yield) as a greenish powder. R_f = 0.32 (2:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.2 Hz, 2H), 7.92 (s, 2H), 7.85 (s, 1H), 7.75 (dd, J = 7.5, 1.1 Hz, 1H), 7.63 (td, J = 7.5, 1.3 Hz, 1H), 7.57 (td, J = 7.5, 1.3 Hz, 1H), 7.48 (d, J = 7.3 Hz, 1H), 7.41 (d, J = 8.2 Hz, 2H), 7.38 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 166.9, 166.0, 141.8, 141.1, 137.2, 135.8, 132.0 (q, J = 34 Hz), 131.3, 130.8, 130.6, 129.2, 128.8, 128.4, 126.7, 123.1 (q, J = 272 Hz), 121.6 (mult, J = 3 Hz), 118.9, 61.0, 14.3. IR (diamond atr) 3329, 2921, 2241, 1689, 1663, 1594, 1525 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}F_6NO_3$, 482.1185; Found 482.1172.

Ethyl 4-(2'-methyl-[1,1'-biphenyl]-2-ylcarboxamido)benzoate (8): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **8** (36 mg, 0.10 mmol, 20% yield) as a white flaky solid. R_f = 0.42 (2:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 7.6, 1.3 Hz, 1H), 7.88 (d, J = 8.6 Hz, 2H), 7.58 (td, J = 7.6, 1.5 Hz, 1H), 7.53 (td, J = 7.6, 1.5 Hz, 1H), 7.42-7.38 (mult, 2H), 7.36-7.32 (mult, 2H), 7.29 (s, 1H), 7.28 (dd, J = 7.6, 1.3 Hz, 1H), 7.08 (d, J = 8.6 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 2.11 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 166.1, 165.8, 141.7, 139.8, 139.1, 136.7, 133.7, 131.4, 131.0, 130.6, 130.5, 130.3, 129.3, 128.9, 128.2, 126.8, 125.9, 118.6, 60.8, 19.9, 14.3. IR (diamond atr) 3224, 3107, 3058, 3015, 2984, 2925, 2901, 1685, 1607, 1592 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{23}H_{22}NO_3$, 360.1594; Found 360.1600.

Ethyl 4-(2'-acetyl-[1,1'-biphenyl]-2-ylcarboxamido)benzoate (9): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 4:1

hex:EtOAc yielded **9** (112 mg, 0.29 mmol, 58% yield) as white crystals. R_f = 0.26 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): 9.12 (s, 1H), 7.77 (dd, *J* = 8.8 Hz, 1.9 Hz, 2H), 7.70 (dd, *J* = 7.8 Hz, 1.3 Hz, 1H), 7.60 (dd, *J* = 7.4 Hz, 1.6 Hz, 1H), 7.22 (dd, *J* = 8.7 Hz, 1.9 Hz, 2H), 7.28-7.42 (mult, 4H), 6.94 (dd, *J* = 7.5 Hz, 1.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 207.0, 167.8, 166.2, 142.4, 139.5, 138.7, 136.7, 131.6, 131.2, 130.5, 130.0, 128.8, 128.5, 128.1, 127.9, 127.2, 125.5, 118.4, 60.7, 30.9, 29.6, 14.3. IR (diamond ATR): 3121, 3082, 2987, 1712, 1701, 1632, 1518 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{24}H_{22}NO_4$, 388.1543; Found 388.1542.

4'-(Dimethylamino)-*N*-phenylbiphenyl-2-carboxamide (13): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 10:1 hex:EtOAc yielded **13** (107 mg, 0.34 mmol, 68% yield) as a yellow solid. R_f = 0.55 (in 2:1 hex:EtOAc). mp 158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.81 (d, *J* = 7.2 Hz,1H), 7.42, (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.20-7.04 (mult, 4H), 7.02 (br s, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 2H), 2.90 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 167.5, 150.4, 139.8, 137.9, 134.7, 130.6, 130.4, 129.78, 129.75, 128.8, 127.2, 127.0, 124.2, 120.1, 112.8, 40.5. IR (diamond ATR) 3299, 3059, 2889, 1659, 1611, 1529, 1440, 1320 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{21}N_2O$, 317.1648; Found 317.1652.

4'-(Methylthio)-*N*-phenylbiphenyl-2-carboxamide (14): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **14** (112 mg, 0.35 mmol, 70% yield) as a white solid. R_f = 0.28 (in 2:1 hex:EtOAc). mp 155-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.77 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.36-7.29 (mult, 3H), 7.27-7.05 (mult, 6H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.88 (br s, 1H) 2.41 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 167.3, 138.9, 137.6, 136.4, 135.3, 130.7, 130.3, 129.5, 129.2, 128.9, 128.88, 127.9, 126.8, 124.5, 120.0, 15.7. IR (diamond ATR) 3383, 2965, 2846, 1658, 1608, 1539, 1432, 1324, 1242 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{18}NOS$, 320.1104; Found 320.1093.

4'-Methoxy-*N*-phenylbiphenyl-2-carboxamide (15): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **15** (78 mg, 0.26 mmol, 51% yield) as a white solid. R_f = 0.41 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.39-7.33 (mult, 4H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.88 (s, 1H), 3.76 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.3, 160.6, 139.2, 137.6, 135.2, 132.1, 130.0, 129.5, 129.4, 129.0, 128.8, 127.5, 124.3, 119.9, 114.4, 55.4. IR (diamond ATR) 3238, 3183, 3129, 3059, 3002, 2962, 2839, 1653, 1599, 1289 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{18}NO_2$, 304.1332; Found 304.1321.

4'-Methyl-*N*-phenylbiphenyl-2-carboxamide (16): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **16** (86 mg, 0.30 mmol, 59% yield) as a white solid. R_f = 0.39 (in 2:1 hex:EtOAc). mp 148-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.87 (d, *J* = 7.0 Hz, 1H), 7.52, (dt, *J* = 7.5, 1.3 Hz, 1H), 7.45 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.27-7.20 (mult, 4H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.95 (br s, 1H), 2.39 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 167.2, 139.6, 137.9, 137.6, 137.0, 135.2, 130.6, 130.4, 129.7, 129.5, 128.8, 128.7, 127.7, 124.3, 119.9, 21.2. IR (diamond ATR) 3282, 3053, 3020, 2921, 1656, 1599, 1536, 1438, 1322 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{18}NO$, 288.1383; Found 288.1382.

4'-Fluoro-*N*-phenylbiphenyl-2-carboxamide (17): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **17** (105 mg, 0.36 mmol, 71% yield) as a white solid. R_f = 0.37 (in 2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.54 (td, *J* = 7.6, 1.6 Hz, 1H), 7.50-7.44 (mult, 3H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.14-7.06 (mult, 3H), 6.92 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.2, 162.7 (d, *J* = 248 Hz), 138.4, 137.5, 135.9 (d, *J* = 3 Hz), 135.6, 130.6 (d, *J* = 33 Hz), 130.5, 130.4, 129.3, 129.0, 128.0, 124.6, 119.9, 115.9 (d, *J* = 22 Hz). IR (diamond ATR), 3220, 3182, 3127, 3060, 3038, 2919, 2850, 1648, 1620 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{19}H_{15}FNO$, 292.1132; Found 292.1124.

***N*-Phenyl-4'-(trifluoromethyl)biphenyl-2-carboxamide (18):** Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **18** (307 mg, 0.45 mmol, 90% yield) as a white solid. R_f = 0.38 (in 2:1 hex:EtOAc). mp 148 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): 7.74 (d, J = 7.1 Hz, 1H), 7.63-7.43 (mult, 6H), 7.37 (d, J = 7.5 Hz, 1H), 7.21-7.08 (mult, 4H), 7.02 (t, J = 7.3 Hz, 1H), 6.86 (br s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 167.0, 143.6, 138.3, 137.3, 135.9, 130.8, 130.0, 129.1, 129.05, 129.0, 128.6, 125.7 (qrt, $J_{C\text{-}F}$ = 3.7 Hz), 124.8, 124.1 (qrt, $J_{C\text{-}F}$ = 271 Hz), 122.7, 119.9. IR (diamond ATR) 2920, 2849, 1650, 1443, 1324, 1119 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{15}F_3NO$, 342.1100; Found 342.1096.

4'-Acetyl-*N*-phenyl-[1,1'-biphenyl]-2-carboxamide (19): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 4:1 hex:EtOAc yielded **19** (96 mg, 0.31 mmol, 61% yield) as colorless, spine-like crystals. R_f = 0.19 (3:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 7.8 Hz, 1H), 7.62-7.49 (mult, 4H), 7.45 (d, J = 8.2 Hz, 1H), 7.18-7.29 (mult, 4H), 7.08 (t, J = 7.1 Hz, 1H), 6.98 (s, 1H), 2.60 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 197.7, 167.2, 144.7, 138.6, 137.5, 136.4, 135.8, 130.8, 130.3, 129.02, 129.01, 128.98, 128.8, 128.5, 124.7, 119.9, 26.7. IR (diamond ATR): 3078, 2997, 2956, 1709, 1689, 1654, 1632, 1523 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{18}NO_2$, 316.1332; Found 316.1321.

3'-Methoxy-*N*-phenylbiphenyl-2-carboxamide (20): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **20** (88 mg, 0.29 mmol, 58% yield) as an off white solid. R_f = 0.15 (in 2:1 hex:EtOAc). mp 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.82 (d, J = 7.7 Hz, 1H), 7.46 (dt, J = 7.3, 1.8 Hz, 1H), 7.40 (dt, J = 7.5, 1.8 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.28 (t, J = 8.2 Hz, 1H), 7.15 (*d*, J = 7.8 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 7.01-6.83 (mult, 5H), 3.68 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 167.1, 160.0, 141.4, 139.4, 137.6, 135.2, 130.6, 130.2, 130.0, 129.6, 128.8, 128.0, 124.4, 121.2, 120.0, 114.2, 114.1, 55.4. IR (diamond ATR) 3380, 3065, 2957, 2848, 1659, 1650,

1537, 1440, 1322 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{18}NO_2$, 304.1332; Found 304.1330.

***N*-Phenyl-3',5'-bis(trifluoromethyl)biphenyl-2-carboxamide (21):** Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **21** (90 mg, 0.22 mmol, 43% yield) as a white flaky solid. R_f = 0.42 (2:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 2H), 7.84 (s, 1H), 7.71 (d, *J* = 7.1 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.1 Hz, 1H), 7.46 (d, *J* = 7.1 Hz, 1H), 7.31-7.28 (mult, 5H), 7.13-7.10 (mult, 1H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 166.8, 142.0, 137.1, 136.2, 131.9 (q, *J* = 33 Hz), 130.9, 130.4, 129.1, 129.0, 128.8, 128.7, 128.3, 125.1, 123.1 (q, *J* = 272 Hz), 121.5 (mult, *J* = 4 Hz), 120.1. IR (diamond ATR), 3202, 3132, 3039, 1639, 1620, 1598, 1546 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{14}F_6NO$, 410.0974. Found 410.0966.

2'-Fluoro-*N*-phenyl-[1,1'-biphenyl]-2-carboxamide (22): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **22** (amount, 0.10 mmol, 20% yield) as a white flaky solid. R_f = 0.42 (2:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$): 7.86 (d, *J* = 7.6 Hz, 2H), 7.61-7.31 (mult, 7H), 7.19-6.98 (mult, 5H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) 166.8, 159.5 (d, *J* = 243 Hz), 137.6, 136.3, 133.4, 131.2, 130.6, 130.1 (d, *J* = 8.1 Hz), 129.1, 128.9, 128.8, 128.5, 127.6, (d, *J* = 16 Hz), 127.1, 120.2, 120.0, 115.9 (d, *J* = 22 Hz). IR (diamond ATR): 3078, 3022, 2972, 1652, 1620, 1478 cm^{-1}.. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{19}H_{15}FNO$, 292.1132; Found 292.1110.

2'-Methoxy-*N*-phenylbiphenyl-2-carboxamide (23): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 9:1 hex:EtOAc yielded **23** (94 mg, 0.31 mmol, 62% yield) as a white solid. R_f = 0.18 (in 2:1 hex:EtOAc). mp 128 °C. ^1H NMR (400 MHz, $CDCl_3$): 7.85 (d, *J* = 7.5 Hz, 1H), 7.47 (dt, *J* = 7.5, 1.7 Hz, 1H), 7.40 (dt, *J* = 7.4, 1.5 Hz, 1H), 7.34 – 7.22 (mult, 4H), 7.18 – 7.06 (mult, 4H), 7.02 (t, *J* = 7.4, 1H), 6.95 (tt, *J* = 7.1, 1.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.59 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) 166.8, 156.4, 137.9, 136.0, 135.8, 131.0, 130.7, 130.1, 129.9, 129.0, 127.9, 127.0,

124.0, 121.3, 119.5, 111.1, 55.6. IR (diamond ATR) 2957, 2870, 1774, 1687, 1599, 1536 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{18}NO_2$, 304.1332. Found 304.1334.

2'-Acetyl-*N*-(3,5-bis(trifluoromethyl)phenyl)-[1,1'-biphenyl]-2-carboxamide (24): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 4:1 hex:EtOAc yielded **24** (158 mg, 0.35 mmol, 70% yield) as a dark yellow, viscous oil. R_f = 0.12 (4:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$): 9.49 (s, 1H), 7.76 (dd, *J* = 7.5 Hz, 1.56 Hz, 1H), 7.71-7.66 (mult, 3H), 7.51-7.40 (mult, 5H), 7.26-7.22 (mult, 1H) 7.03 (dd, *J* = 7.5 Hz, 1.4 Hz, 1H), 2.70 (s, 3H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) 206.7, 168.1, 139.6, 139.3, 138.8, 138.6, 136.2, 132.0 (q, *J* = 33 Hz), 131.8, 131.3, 130.4, 128.8, 128.6, 128.2, 128.1, 127.0, 123.1 (q, *J* = 271 Hz), 119.0, 117.1 (q, *J* = 4 Hz), 29.8. IR (diamond ATR): 3067, 2987, 2980, 1709, 1685, 1643, 1452 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{23}H_{16}F_6NO_2$, 452.1080; Found 452.1065.

3'-Acetyl-*N*-(3,5-bis(trifluoromethyl)phenyl)-[1,1'-biphenyl]-2-carboxamide (25): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 2:1 hex:EtOAc yielded **25** (171 mg, 0.38 mmol, 76% yield) as white crystals. R_f = 0.390 (1:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$): 8.09 (s, 1H), 7.97 (dt, *J* = 7.8 Hz, 1.3 Hz, 1H), 7.83 (dd, *J* = 7.6 Hz, 1.1 Hz, 1H), 7.75-7.59 (mult, 5H), 7.59-7.47 (mult, 4H), 7.23 (br s, 1H), 2.58 (s, 3H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) 197.5, 167.5, 140.3, 138.8 (q, *J* = 4 Hz), 137.8, 134.6, 133.4, 132.3 (q, *J* = 33 Hz), 131.5, 130.6, 129.4, 129.2, 128.6, 128.2, 128.15, 122.9 (q, *J* = 272 Hz), 119.6 (mult), 118.0, 117.9 (mult), 26.6. IR (diamond ATR) 3123, 3019, 2973, 1708, 1691, 1632 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{23}H_{16}F_6NO_2$, 452.1080; Found 452.1069.

***N*-(3,5-bis(trifluoromethyl)phenyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (26):** Prepared according to the general procedure. Column chromatography with 9:1 hex:EtOAc yielded **26** (143 mg, 0.30 mmols, 61% yield) as a white flaky solid. R_f = 0.42 (2:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8 Hz, 2H), 7.63-7.53 (mult, 7H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.21 (s, 1H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) 167.1, 143.3,

138.7, 138.4, 134.5, 132.4 (q, J = 33 Hz), 131.5, 130.6 (q, J = 33 Hz), 130.5, 129.3, 129.1, 128.8, 125.9 (mult, J = 4 Hz), 123.8 (q, J = 270 Hz), 122.9 (q, J = 270 Hz), 119.4, 118.0 (mult, J = 4 Hz). IR (diamond ATR): 3247, 3175, 3081, 1656, 1619, 1571 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{22}H_{13}F_9NO$, 478.0848; Found 478.0819.

***N*-(3,5-bis(trifluoromethyl)phenyl)-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (27):** Prepared according to the general procedure. Column chromatography with 9:1 hex:EtOAc yielded **27** (155 mg, 0.32 mmol, 65% yield) as a white powder. R_f = 0.47 (2:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, J = 7.9, 1.0 Hz, 1H), 7.72 (s, 1H), 7.63 (t, J = 10.7 Hz, 3H), 7.60 (dd, J = 7.7, 1.4 Hz, 2H) 7.55 (mult, 3H), 7.48 (t, J = 7.6 Hz, 1H), 7.30 (s, 1H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.4, 140.5, 138.7, 138.4, 134.7, 132.4 (q, J = 33 Hz), 132.1, 131.6 (q, J = 33 Hz), 131.5, 130.5, 129.6, 129.1, 128.7, 125.3 (mult, J = 3 Hz), 125.0 (mult, J = 3 Hz), 123.8 (q, J = 272 Hz), 123.0 (q, J = 272 Hz), 119.6, 118.0 (mult, J = 4 Hz). IR (diamond ATR) 3229, 3071, 2980, 1656, 1617, 1598, 1542 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{22}H_{13}F_9NO$, 478.0848; Found 478.0817.

3'-Acetyl-*N*-(2-fluorophenyl)-[1,1'-biphenyl]-2-carboxamide (28): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 4:1 hex:EtOAc yielded **28** (113 mg, 0.34 mmol, 68% yield) as a colorless film. R_f = 0.15 (2:1 hex:EtOAc). ^1H NMR (400 MHz, $CDCl_3$): 8.27 (t, J = 8.0 Hz, 1H), 8.06 (s, 1H), 7.95 (td, J = 8.0, 1.4 Hz, 1H), 7.83 (dd, J = 7.7, 1.1 Hz, 1H), 7.67 (d, J = 7.70 Hz, 1H), 7.59 (td, J = 7.5, 1.6 Hz, 1H), 7.52 (dt, J = 7.6, 1.5 Hz, 1H), 7.50-7.40 (mult, 2H), 7.10 (t, J = 8.0 Hz, 1H), 7.04-6.91 (mult, 3H) 2.57 (s, 3H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) 197.8, 167.2, 152.3 (d, J = 240 Hz), 140.2, 138.9, 137.6, 135.4, 133.3, 131.0, 130.6, 129.1 (d, J = 4 Hz), 128.6, 128.3, 127.9, 126.1, 126.0, 124.7, 124.5, 121.6, 114.7 (d, J = 19 Hz), 26.7. IR (diamond ATR) 3017, 2987, 2870, 1707, 1690, 1639, 1548, 1274 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{17}FNO_2$, 334.1238; Found 334.1225.

***N*-(2-Fluorophenyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (29):** Prepared according to the general procedure. Column chromatography with 9:1 hex:EtOAc yielded **29**

(115 mg, 0.32 mmol, 64% yield) as a white flaky solid. R_f = 0.44 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (t, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 3H), 7.53 (triplet of doublets, *J* = 7.6, 1.3 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.26 (s, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.00 (mult, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.0, 152.3 (d, *J* = 243 Hz), 143.4, 138.6, 135.5, 131.0, 130.5, 130.2 (q, *J* = 32 Hz), 129.1, 128.5, 126.0 (d, *J* = 10 Hz), 125.7 (q, *J* = 3 Hz), 124.7 (d, *J* = 8 Hz), 124.6, 124.5, 124.1 (q, *J* = 272 Hz) 121.6, 114.7 (d, *J* = 19 Hz). IR (diamond ATR) 3240, 3189, 3135, 3067, 3023, 1653, 1619, 1601, 1537 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{14}F_4NO$, 360.1006. Found 360.0983.

2'-fluoro-*N*-(2-fluorophenyl)-[1,1'-biphenyl]-2-carboxamide (30): Prepared according to the general procedure. Column chromatography with 9:1 hex:EtOAc yielded **30** (59 mg, 0.19 mmol, 38% yield) as an off white powder. R_f = 0.42 (2:1 hex:EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$): 8.33 (t, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.48-7.32 (mult, 4H), 7.22 (t, 7.2 Hz, 1H), 7.14-6.94 (mult, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 165.7, 158.5 (d, *J* = 250 Hz), 151.3 (d, *J* = 243 Hz), 135.0, 132.7, 130.4, 130.0 (d, *J* = 3 Hz), 129.9, 129.2 (d, *J* = 8 Hz), 127.7, 127.4, 126.3 (d, *J* = 15 Hz), 125.3 (d, *J* = 10 Hz), 123.6 (d, *J* = 4 Hz), 123.5 (d, *J* = 4 Hz), 123.3 (d, *J* = 8 Hz), 120.6, 114.8 (d, *J* = 22 Hz), 113.6 (d, *J* = 19 Hz). IR (diamond ATR) 3079, 3024, 3053, 2969, 1668, 1489, 1457 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{19}H_{14}F_2NO$, 310.1038; Found 310.1057.

***N*-(4-Chlorophenyl)-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (31)** Prepared according to the general procedure. Column chromatography with 9:1 hex:EtOAc yielded **31** (73 mg, 0.19 mmol, 39% yield) as an off white powder. R_f = 0.37 (2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.4 Hz, 1H), 7.75 (s, 1H), 7.62 (d, *J* = 7.9 Hz, 2H) 7.58 (td, *J* = 7.5, 1.4 Hz, 1H) 7.52 (t, *J* = 7.7 Hz, 1H), 7.51 (td, *J* = 7.7, 1.4 Hz, 1H) 7.45 (d, *J* = 7.5 Hz, 1H) 7.21 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H) 6.94 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.1, 140.6, 138.1, 135.9, 135.5, 132.1, 131.4 (q, *J* = 32 Hz), 131.0, 130.4, 129.8, 129.3, 129.1, 129.0, 128.6, 125.3 (q, *J* = 4 Hz), 124.8 (q, *J* = 4 Hz), 123.9 (q, *J* = 272 Hz), 121.1. IR (diamond ATR) 3236, 3179, 3115, 3060, 2924, 2851, 1648, 1595, 1535 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{20}H_{14}ClF_3NO$, 376.0711. Found 376.0710.

2'-Acetyl-*N*-(4-methoxyphenyl)-[1,1'-biphenyl]-2-carboxamide (32): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 4:1 hex:EtOAc yielded **32** (119 mg, .35 mmol, 69% yield) as a yellow film. R_f = 0.15 (4:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): 8.71 (s, 1H), 7.77 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 1.4 Hz, 1H), 7.43 (t, *J* = 1.8 Hz, 1H), 7.41 (d, *J* = 1.4 Hz, 1H), 7.39 (d, *J* = 1.4 Hz, 1H), 7.30-7.26 (mult, 1H), 7.08 (t, *J* = 2.2 Hz, 2H), 7.00 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.71 (t, *J* = 2.3 Hz, 2H), 3.72 (s, 3H), 2.63 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 205.2, 167.3, 156.1, 139.9, 138.8, 138.7, 137.0, 131.5, 131.4, 131.3, 129.7, 128.7, 128.5, 128.0, 127.8, 127.2, 121.3, 113.9, 55.4, 30.9. IR (diamond ATR) 3089, 2987, 2920, 1716, 1686, 1642, 1616, 1452 cm^{-1}. HRMS (ESI+) HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{22}H_{20}NO_3^+$, 346.1438; Found 346.1452.

2'-Acetyl-N-(3-methoxyphenyl)-[1,1'-biphenyl]-2-carboxamide (33): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 4:1 hex:EtOAc yielded **33** (90 mg, 0.26 mmol, 52% yield) as an off white, clumpy solid. R_f = 0.43 (1:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): 8.87 (s, 1H), 7.77 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.68 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.48-7.37 (mult, 5H), 7.07-6.98 (mult, 3H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.54 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.47 (s, 3H), 2.64 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 205.3, 167.6, 159.9, 139.7, 139.4, 138.8, 138.7, 137.0, 131.6, 131.3, 129.8, 129.4, 128.7, 128.5, 128.0, 127.8, 127.3, 111.8, 109.7, 105.2, 55.2, 29.6. IR (diamond ATR): 3057, 3012, 2992, 1712, 1695, 1662, 1421 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{22}H_{20}NO_3$, 346.1438. Found 346.1418.

2'-Acetyl-N-(2-methoxyphenyl)-[1,1'-biphenyl]-2-carboxamide (34): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 4:1 hex:EtOAc yielded **34** (100 mg, 0.29 mmol, 58% yield) as a yellowish/brown film. R_f = 0.39 (1:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): 8.41 (s, 1H), 8.32 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 7.3 Hz, 1H), 7.71 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.49-7.36 (mult, 5H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.08 (dd,

J = 7.3, 1.6 Hz, 1H), 6.96 (td, *J* = 8.0, 1.6 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 3.63 (s, 3H), 2.45 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 204.8, 166.7, 165.1, 141.3, 138.5, 137.9, 137.7, 135.7, 130.6, 130.2, 129.5, 129.0, 128.8, 127.7, 127.5, 127.4, 127.1, 126.9, 126.1, 124.5, 117.35, 117.33, 59.7, 28.6. IR (diamond ATR): 3012, 2967, 1711, 1683, 1673, 1612, 1583, 1475 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{22}H_{20}NO_3$, 346.1438. Found 346.1447.

3'-Acetyl-N-(2-methoxyphenyl)-[1,1'-biphenyl]-2-carboxamide (35): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 4:1 hex:EtOAc yielded **35** (107 mg, 0.31 mmol, 62% yield) as a yellow/white, oily film. R_f = 0.12 (4:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): 8.38 (d, *J* = 8.2 Hz, 1H), 8.07 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.73 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.59-7.44 (mult, 4H), 6.99 (t, *J* = 7.9 Hz, 1H), 6.93 (t, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 7.7, 1H), 3.56 (s, 3H), 2.53 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 197.9, 167.1, 147.8, 140.4, 138.8, 137.4, 136.2, 133.5, 130.7, 130.5, 129.2, 128.9, 128.2, 127.5, 123.9, 121.0, 119.6, 109.7, 55.4, 26.6. IR (diamond ATR): 3097, 3012, 2967, 1709, 1669, 1582, 1464 cm^{-1}. HRMS (ESI-TOF) m/z$[M+H]^+$ Calcd for $C_{22}H_{20}NO_3$, 346.1438. Found 346.1429.

N-(4-methoxyphenyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (36): Prepared according to the general procedure for decarbonylation with boronic acids. Column chromatography with 1:1 hex:EtOAc yielded **36** (134 mg, 0.36 mmol, 72% yield) as an off white, flaky solid. R_f = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$): 7.81 (dd, *J* = 7.5 Hz, 1.1 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.57-7.50 (mult, 2H), 7.45 (dd, *J* = 7.6 Hz, 1.1 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 2H), 6.82 (broad s, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.77 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) 167.0, 156.8, 143.7, 138.2, 136.0, 130.7, 130.4, 130.3, 129.9, 129.1, 129.0, 128.5, 125.8, 125.7, 121.8, 114.2, 55.5. IR (diamond ATR) 3209, 3124, 3053, 3018, 2963, 1638, 1467, 1321 cm^{-1}. HRMS (ESI-TOF) m/z $[M+H]^+$ Calcd for $C_{21}H_{17}F_3NO_2$, 372.1206; Found 372.1183.

Supporting Information Available

Optimization results and NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] For example, see: Tsunoda, T.; Yamazaki, A.; Iwamoto, H.; Sakamoto, S. Practical Synthesis of *N*-{4-[(2-Methyl-4,5-dihydroimidazo[4,5-*d*][1]benzazepin- 6(1*H*)-yl)carbonyl]phenyl}biphenyl-2-carboxamide Monohydrochloride: an Arginine Vasopressin Antagonist. *Org. Process Res. Dev.* **2003**, *7*, 883-887. MaGlacken, G. P.; Bateman, L. M. Recent advances in aryl–aryl bond formation by direct arylation. *Chem. Soc. Rev.* **2009**, *38*, 2447 and references therein.

[18] C-H activation and photoredox arylation pathways may also be used to access these species: a) Kalyani, D. McMurtrey, K. B.; Neufeldt, S. R.; Sanford, M. S. Room-Temperature C–H Arylation: Merger of Pd-Catalyzed C–H Functionalization and Visible-Light Photocatalysis. *J. Am. Chem. Soc.* **2011**, *133*, 18566-18569. Also b) Gao, P.; Liu, L.; Shi, Z.; Yuan, Y. Iridium(III)-catalyzed regioselective direct arylation of sp^2 C–H bonds with diaryliodonium salts. *Org. Biomol Chem*, **2016**, *14*, 7109-7113.

[19] Similar compounds can be made with C-H activation/boronic acids: Chinnagolla, R. K.; Jeganmohan, M. Regioselective *Ortho*-Arylation and Alkenylation of *N*-Alkyl Benzamides with Boronic Acids via Ruthenium-Catalyzed C–H Bond Activation: An Easy Route to Fluorenones Synthesis. *Org. Lett.*, **2012**, *14*, 5246-5249.

[20] A similar coupling utilizing aryl halides to coupling with phthalimides has been recently reported: Samanta, P. K.; Biswas, P. Palladium Catalyzed Regioselective Synthesis of Substituted Biaryl Amides though Decarbonylative Arylation of Phthalimides. *J. Org. Chem.* **2019**, *84*, 3968-3976.

[21] Reactions with low yields of **2** primarily resulted in recovered starting material with moderate (~20%) amounts of reduction product 3. The source of the reduction product remains unknown. Drying the aryl boronic acid prior to use reduces but does not completely eliminate its formation.

[22] Bilyard, K. G.; Garratt, P. J.; Hunter, R.; Lete, E. Comparative study of the reactions of dilithiated vicinal diesters and dilithiated 1,2-dicarboximides with methyl iodide, α,ω-dihalides, α,ω-ditosylates and ω -bromo esters. *J. Org. Chem.* **1982**, *47*, 4731-4736.

[23] No obvious cleavage of the N-alkyl bond was observed. See Rahman, M. M.; Buchspies, J.; Szostak, M. N-Acylphthalimides: Efficient Acyl Coupling Reagents in Suzuki–Miyaura Cross-Coupling by N–C Cleavage Catalyzed by Pd–PEPPSI Precatalysts *Catalysts*, **2019**, *9*, 129.

[24] See reference 16b for the mechanistic investigation of a similar reaction with diorganozinc reagents.

[25] Transmetallation to form the *o*-boronic acid may also be possible, which could subsequently be the source of the reduction product.

[26] Ni_CO bond strengths have been estimated to be anywhere from 28.3 to 47.1 kcal/mol; see: Sunderlin, L. S.; Wang, D.; Squires, R. R. Metal (iron and nickel) carbonyl bond strengths in $Fe(CO)_n^-$ and $Ni(CO)_n^-$. *J. Am. Chem. Soc.* **1992**, *114*, 2788.

[27] Li, J.; Schreckenbach, G.; Ziegler, T. A Reassessment of the First Metal-Carbonyl Dissociation Energy in $M(CO)_4$ (M = Ni, Pd, Pt), $M(CO)_5$ (M = Fe, Ru, Os), and $M(CO)_6$ (M = Cr, Mo, W) by a Quasirelativistic Density Functional Method. *J. Am. Chem. Soc.* **1995**, *117*, 486.

[28] Hu, J.; Zhao, Y.; Liu, J.; Zhang, Y.; Shi, Z. Nickel-Catalyzed Decarbonylative Borylation of Amides: Evidence for Acyl C-N Bond Activation. *Angew. Chem. Int. Ed.* **2016**, *55*, 8718-8722.

[29] See supporting information for full details.