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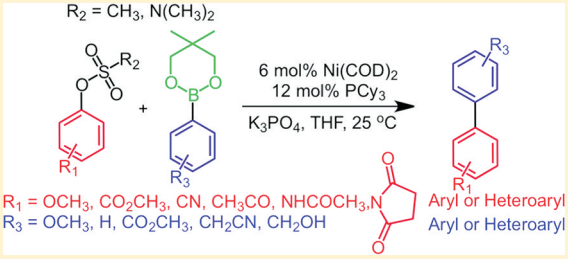
$Ni(COD)_2/PCy_3$ Catalyzed Cross-Coupling of Aryl and Heteroaryl Neopentylglycolboronates with Aryl and Heteroaryl Mesylates and Sulfamates in THF at Room Temperature

Pawaret Leowanawat, Na Zhang, Ana-Maria Resmerita, Brad M. Rosen, and Virgil Percec*

Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States

Supporting Information

ABSTRACT: Reaction conditions for the $Ni(COD)_2/PCy_3$ catalyzed cross-coupling of aryl neopentylglycolboronates with aryl mesylates were developed. By using optimized reaction conditions, $Ni(COD)_2/PCy_3$ was shown to be a versatile catalyst for the cross-coupling of a diversity of aryl neopentylglycolboronates with aryl and heteroaryl mesylates and sulfamates containing both electron-donating and electron-withdrawing substituents in their *para*, *ortho*, and *meta* positions in THF at room temperature. This Ni-catalyzed cross-coupling of aryl neopentylglycolboronates is also effective for the synthesis of heterobiaryls and biaryls containing electrophilic functionalities sensitive to organolithium and organomagnesium derivatives. In combination with the recently developed Ni-catalyzed neopentylglycolborylation, all Ni-catalyzed routes to functional biaryls and heterobiaryls are now easily accessible.



INTRODUCTION

Aryl-aryl and aryl-heteroaryl coupling remains the most efficient and robust strategy for the synthesis of functional substituted biaryls, heterobiaryls, and other complex aromatic derivatives. The Pd-catalyzed Suzuki−Miyaura reaction is extraordinarily effective for the cross-coupling of aryl bromides, iodides, triflates, and nonaflates with aryl boronic acids and esters.[1] While recent advances in Pd catalysts have expanded the scope of Suzuki−Miyaura coupling to include aryl mesylate and tosylate electrophiles,[2] Ni catalysts are generally more effective for cross-coupling of less reactive C−O derived electrophiles.[3] It was in our laboratory that Ni(II) complexes were first discovered to be capable catalysts for the cross-coupling of aryl halides, mesylates, and tosylates with aryl boronic acids.[4] Recently, Garg and others have provided the first examples of Ni(II) catalyzed cross-coupling of aryl sulfamates with aryl boronic acids at 110 °C.[5] Though less convenient or economical than Ni(II) catalysts, Ni(0) catalysts derived from $Ni(COD)_2$ have also been proven efficient for the cross-coupling of aryl sulfonates[6] and other C−O[7] derived electrophiles with aryl boronic acids and potassium aryl trifluoroborates.[8a] However, there are only few reports on the Ni-catalyzed cross-coupling of aryl neopentylglycolboronates and of other boronic esters with aryl C−O derived electrophiles and with aryl halides.[3] They involve a study of the cross-coupling of aryl neopentylglycolboronates with aryl methyl ethers,[3,7c] some preliminary data on several cross-couplings of aryl neopentylglycolboronates with aryl iodides and bromides, two experiments with aryl mesylates, two with aryl tosylates, and one with an aryl chloride.[3]

Often, hard-metalation conditions are unsuitable for the preparation of the critical aryl boronic acid coupling partners containing electrophilic functional groups that are required in Pd- and Ni-catalyzed cross-coupling. Likewise, boronic acids themselves are undesirable reagents in certain reactions where concerns of reaction stoichiometry derived from inconsistent concentrations of boronic acid anhydrides are important. A classic example is provided by step polymerization reactions where perfect stoichiometry is required for the synthesis of high molar mass polymers and of polymers with well-defined chain ends.[8b] Pd-catalyzed Miyaura borylation provides a strategy for the synthesis of functional aryl boronic esters from aryl iodides, bromides, triflates, and nonaflates with tetraalkoxydiboron and dialkoxyborane reagents.[9] Utilization of Ni-derived catalysts for borylation should be more economical than the corresponding Pd-based techniques and could potentially harness the improved reactivity of Ni(0) toward unreactive C−O derived electrophiles. Following a lone report on $Ni(II)(dppp)Cl_2$ catalyzed pinacolborylation of two aryl bromides,[10] we recently developed efficient single-[11] and mixed-ligand[12] based Ni catalysts for the borylation of a diversity of substituted aryl iodides, bromides, chlorides,[12a] and sulfonates[12b] with a novel, efficient, and cost-effective boron source, neopentylglycolborane.

In a preliminary communication on this Ni-catalyzed borylation, we reported that indeed several aryl neopentylglycolboronates could be effectively cross-coupled with aryl bromides and iodides using $Ni(dppe)Cl_2$ as catalyst.[11a] To

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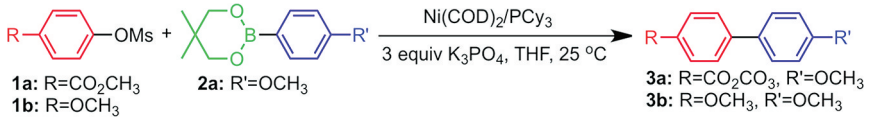
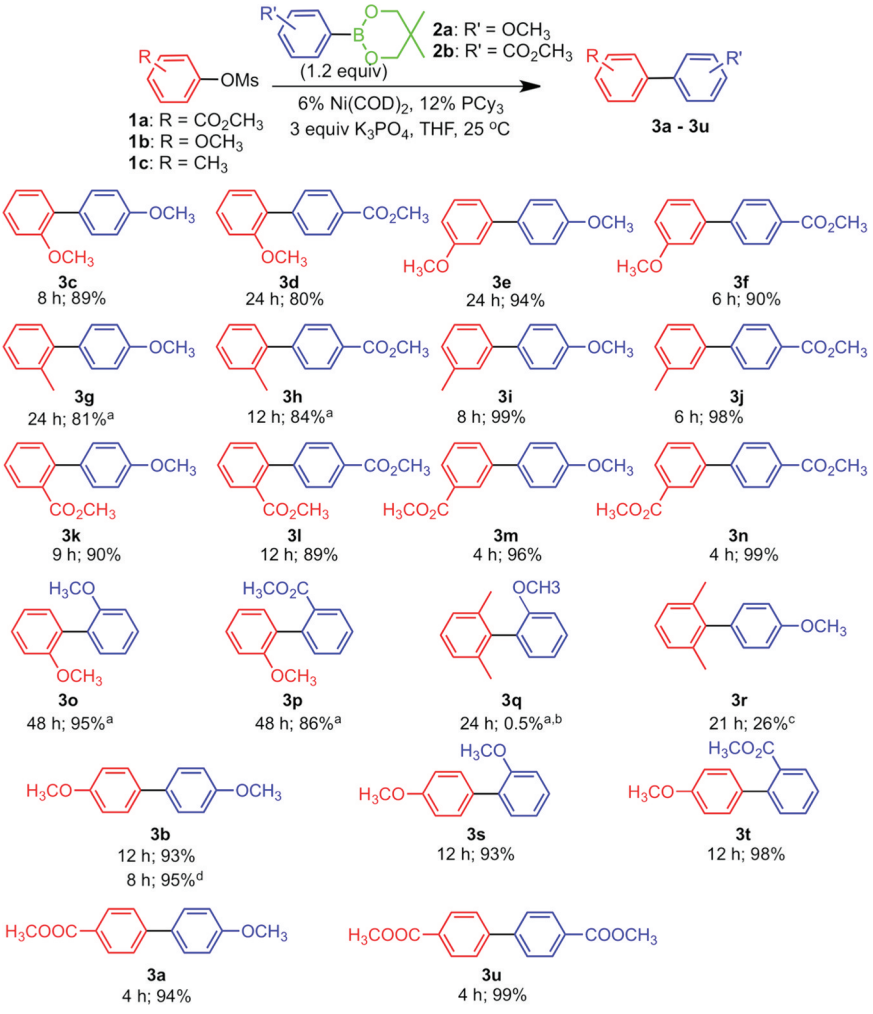
Table 1. Cross-Coupling of *para*-Substituted Aryl Mesylates with *para*-Substituted Aryl Neopentylglycolboronates Catalyzed by $Ni(COD)_2/PCy_3$ in THF at 25 °C



entry	substrate	$Ni(COD)_2$ (%)	PCy_3 (%)	THF (mL)	time (h)	3	yield[a] (%)
1	**1a**	4	8	2	12	**3a**	80[b]
2	**1a**	6	12	2	12	**3a**	100[b]
3	**1a**	6	18	2	8	**3a**	100[b]
4	**1a**	6	12	1	4	**3a**	94
5	**1a**	6	18	1	4	**3a**	96
6	**1a**	5	10	1	4	**3a**	99
7	**1a**	5	15	1	4	**3a**	84
8	**1b**	6	18	1	8	**3b**	95
9	**1b**	6	12	1	12	**3b**	93

[a]Isolated yield in all cases unless noted. [b]Yield determined by GC.

Table 2. Cross-Coupling of Aryl Mesylates with Aryl Neopentylglycolboronates Catalyzed by $Ni(COD)_2/PCy_3$ in THF at 25 °C; Isolated Yield in All Cases unless Noted



[a]10% $Ni(COD)_2$ and 20% PCy_3. [b]GC yield. [c]10% $Ni(COD)_2$, 20% PCy_3 in 0.5 mL of THF. [d]6% $Ni(COD)_2$ and 18% PCy_3.

our knowledge these experiments represented the first examples of Ni-catalyzed cross-coupling of aryl halides with aryl boronates. Shortly thereafter, Chatani found that Ni-$(COD)_2/PCy_3$ provides efficient cross-coupling of highly activated aryl methyl ethers with aryl boronates in the presence of CsF as base.[7c] Later, we demonstrated with two preliminary examples of aryl mesylates, two of aryl sulfonates, and one aryl chloride that $Ni(COD)_2/PCy_3$ in the presence of K_3PO_4 as

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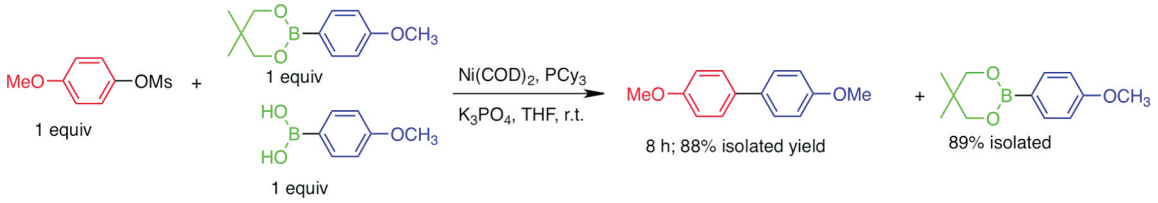
Scheme 1. Competitive Cross-Coupling of an Aryl Mesylate with Both an Aryl Boronic Acid and an Aryl Neopentylglycolboronate



base could expand the Ni-catalyzed cross-coupling of aryl neopentylglycolboronates to aryl chlorides, mesylates, and sulfonates.[11b] To date, no comprehensive investigation of the cross-coupling of aryl boronates with any class of electrophiles has been undertaken for any Ni-catalytic system. Herein, we demonstrate robust catalytic conditions for $Ni(COD)_2/PCy_3$ catalyzed cross-coupling of aryl neopentylglycolboronates with both aryl and heteroaryl mesylates and sulfamates in THF at room temperature.

RESULTS AND DISCUSSION

Optimization of Cross-Coupling Reaction Conditions of Aryl Neopentylglycolboronates with Aryl Mesylates. In a preliminary communication[11b] it was reported that 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane **2a** could be efficiently cross-coupled with aryl chlorides (one example), mesylates (two examples), and tosylates (two examples) using 6 mol % $Ni(COD)_2$ as a zerovalent Ni source in the presence of 18 mol % PCy_3 in THF at 25 °C. In order to develop the most efficient room-temperature Ni-catalyzed cross-coupling conditions for aryl neopentylglycolboronates, the reaction parameters were investigated in detail (Table 1). Methyl 4-(methylsulfonyloxy)benzoate was chosen as a representative electron-deficient aryl mesylate electrophile. It was determined that 4 mol % $Ni(COD)_2$ in conjunction with 8 mol % PCy_3 did not provide complete conversion (80%, Table 1, entry 1). Maintaining the same Ni/ligand ratio but increasing $Ni(COD)_2$ loading to 6 mol % was more effective, providing quantitative conversion within 12 h (Table 1 entry 2). Interestingly, maintaining the same Ni loading but increasing the PCy_3 level to 18 mol %, as described in an earlier report, led to complete conversion in only 8 h (Table 1, entry 3). Higher concentration of PCy_3 appears to either retard decomposition of the catalyst or provide a more reactive tricoordinate complex. The same trend was observed when using 4-methoxyphenyl methanesulfonate as a representative electron-rich aryl mesylate electrophile. It is typically desirable to minimize the loading levels of catalyst and ligand. Increasing the reagent concentration provides an easy way to accelerate reactions that do not need effective heat removal or dilution-based suppression of side reactions.

Here, doubling the reagents concentration (Table 1, entries 4–7) allow for complete conversion and excellent recovered yield for as low as 5 mol % $Ni(COD)_2$ and 10 mol % PCy_3.

Cross-Coupling of Aryl Neopentylglycolboronates with Aryl Mesylates. Generally 6 mol % $Ni(COD)_2$ and 12 mol % PCy_3 in 1 mL of THF provided quantitative or nearly quantitative GC coupling yield (unreported) and excellent recovered yield for a diversity of electron-rich and electron-deficient aryl mesylate electrophiles (Table 2). The cross-coupling of mono-*ortho*-substituted aryl mesylates and/or mono-*ortho*-substituted aryl neopentylglycolboronates typically required a higher catalyst loading of 10 mol % $Ni(COD)_2$ and 20 mol % PCy_3 to achieve excellent GC conversion and isolated yield. Only the cross-coupling of di-*ortho*-substituted 2,6-dimethylphenyl methanesulfonate to form **3q** or **3r** proved to be largely intractable.

Competitive Cross-Coupling of Aryl Neopentylglycolboronates and Aryl Boronic Acids with Aryl Mesylates. It is often improperly assumed that the reactivity of aryl boronate esters in cross-coupling reactions is identical to that of boronic acids. This is both mechanistically and empirically incorrect. Aryl boronate esters tend to react more slowly and in some cases can require more active catalytic systems to efficiently mediate their cross-coupling. A simple experiment was devised to determine the relative rate of aryl boronic acid and aryl boronic ester cross-coupling catalyzed by the $Ni(COD)_2/PCy_3$ system, wherein 4-methoxyphenyl methanesulfonate was subjected to the standard catalytic system in the presence of *p*-methoxyphenylboronic acid and its aryl neopentylglycolboronate analogue (Scheme 1). At the point that 100% GC conversion of 4-methoxyphenyl methanesulfonate was achieved, 89% percent of the boronate ester remained unreacted. This result demonstrates that the rate of cross-coupling with aryl neopentylglycolboronates is at least 8 times slower than for the boronic acids. As there is no evidence of *in situ* hydrolysis under the catalytic conditions, this suggests that transmetalation of the ArOMs-Ni(II)/L complex with arylboronic esters is less rapid than for aryl boronic acid.

Cross-Coupling of Aryl Neopentylglycolboronates with Aryl Sulfamates. Aryl mesylates are easily prepared from functional phenols with the extremely inexpensive methanesulfonyl chloride. Even so, there are occasions when arylsulfamates such as *N*,*N*-dimethyl sulfamate provide more appropriate choices. Particularly, the sulfamates can be used for directed *ortho*-metalation to further functionalize the aryl group before cross-coupling.[13] Fortuitously, the $Ni(COD)_2/PCy_3$ conditions developed for the cross-coupling of aryl-mesylates with aryl neopentylglycolboronates extend directly to aryl sulfamate electrophiles without any modification (Table 3). Recovered yields from the cross-coupling of a diversity of substituted aryl sulfamates and aryl neopentylglycolboronates were generally excellent, except when electron-rich *ortho*-substituted aryl sulfamates were cross-coupled with anything other than electron-deficient aryl neopentylglycolboronates. The recovered yield from the cross-coupling of 2,6-dimethylphen-1-ol derived sulfamate to form **3r** was only 13%.

Cross-Coupling of Aryl and Heteroaryl Neopentylglycolboronates with Aryl and Heteroaryl Mesylates and Sulfamates. The cross-coupling of functional aromatics with heteroaromatic compounds is integral to the synthesis of medicinal natural products and for the development of materials for molecular and supramolecular electronics. To date, Ni-catalyzed cross-coupling to form heterobiaryl com-

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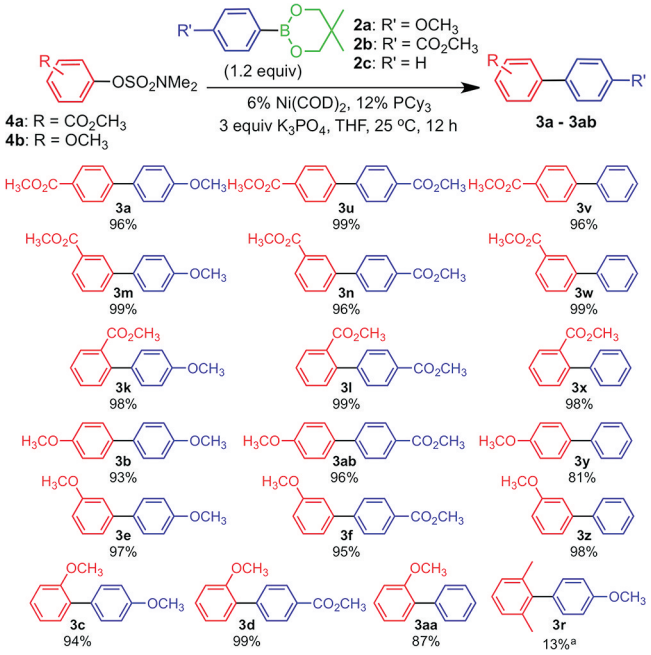
Table 3. Cross-Coupling of Aryl Sulfamates with Aryl Neopentylglycolboronates Catalyzed by $Ni(COD)_2/PCy_3/K_3PO_4$ in THF at 25 °C; Isolated Yield in All Cases



[a]10% $Ni(COD)_2$ and 20% PCy_3, 60 °C, 48 h.

pounds has not been well explored. Using $Ni(COD)_2/PCy_3$ as a catalyst in THF at 25 °C with K_3PO_4, we performed the cross-coupling of aryl mesylates and aryl sulfamates, thienyl boronic esters (Table 4, entries 1–5), aryl boronic esters with *N*-heterocyclic mesylates and sulfamates (Table 4, entries 6–9, 15, 16), and *N*-heterocyclic mesylates and sulfamates with thienyl boronic esters (Table 4, 10–14). Nearly all examples achieved quantitative conversion and excellent recovered yield. Only 1-(4-(thiophen-2-yl)phenyl)ethanone proved difficult to recover (Table 4, entry 3), and the cross-coupling of 8-quinolynyl methanesulfonate with thienyl boronates proved inefficient (Table 4, entries 13 and 14).

Cross-Coupling in the Presence of Sensitive Functional Groups. While the cross-coupling of heteroaryls provides access to a structurally diverse class of heterobiaryl compounds, the cross-coupling of arenes bearing sensitive functionality can prove more challenging. Cyano, keto, hydroxyl, and amido functionality are not trivial coupling partners. In the cross-coupling of aryl mesylates and sulfamates with aryl boronic esters, it is apparent that some functional groups are less readily cross-coupled than others and there is often a preference for delivering the sensitive functionality through the electrophile or the boronic ester (Table 5). Benzonitrile neopentylglycolboronates (Table 5, entry 1) do not undergo cross-coupling, though benzyl nitrile boronic esters do so readily (Table 5, entry 5). Cross-coupling of cyano mesylates is more tractable. 4-Cyanophenyl methanesulfonate is cross-coupled with an electron-rich aryl boronic ester in good yield (Table 5, entry 2) and sluggishly in fair yield with an electron-deficient aryl boronic ester (Table 5, entry 4). Cross-coupling of cyano aryl sulfamates appear slower and less effective than for mesylates (Table 5, entry 3). *p*-Keto functionality is highly compatible if found on the mesylate electrophile (Table 5, entry 6), but not tolerated at all on the aryl boronic ester (Table 5, entry 7). Likewise, free hydroxyl functionality (Table 5, entry 8) results in very low yield, while amides (Table 5, entry 9) and imides (Table 5, entry 10) can be cross-coupled in excellent yield.

■ CONCLUSIONS

$Ni(COD)_2/PCy_3$ in the presence of K_3PO_4 as base provides extremely effective cross-coupling of aryl mesylates and sulfamates with aryl neopentylglycolboronates containing both electron-rich and electron-deficient substituents in their *para*, *ortho*, and *meta* positions, in THF at room temperature. This Ni-catalyzed cross-coupling of aryl neopentylglycolboronates is effective for the synthesis of diverse heterobiaryls and biaryls containing electrophillic functionalities that are sensitive to organolithium and organomagnesium derivatives used in conventional borylation reactions. In conjunction with recently developed techniques for Ni-catalyzed neopentylglycolborylation, particularly the combination of mixed-ligand catalyst with zerovalent metal accelerators,[12b,c] rapid and efficient all-Ni-catalyzed routes to functional biaryls, polyaryls, heterobiaryls, and heteropolyaryls are readily accessible.

■ EXPERIMENTAL SECTION

General Experimental Methods. 4-Methoxyphenol, 3-methoxyphenol, 2-methoxyphenol, *o*-cresol, *m*-cresol, *p*-cresol, 2,6-dimethylphenol, methyl 4-hydroxybenzoate, methyl 2-hydroxybenzoate, methyl 3-hydroxybenzoate, 3-hydroxypyridine, 8-hydroxyquinoline, 4-aminophenol, 4-hydroxybenzonitrile, $Ni(COD)_2$ (98+%), PCy_3, methanesulfonyl chloride, and dimethylsulfamoyl chloride were used as received from commercial sources. THF from a commercial source was distilled over sodium and benzophenone and stored under nitrogen prior to use. K_3PO_4 from a commercial source was dried at 40 °C under vacuum overnight prior to use. Methyl 4-((methylsulfonyl)-oxy)benzoate, 4-methoxyphenyl methanesulfonate, *p*-tolyl methanesulfonate, methyl 3-((methylsulfonyl)oxy)benzoate, *m*-tolyl methanesulfonate, methyl 2-((methylsulfonyl)oxy)benzoate, 2-methoxyphenyl methanesulfonate, *o*-tolyl methanesulfonate, 4-acetylphenyl methanesulfonate (**1e**), quinolin-6-yl methanesulfonate (**1h**), isoquinolin-5-yl methanesulfonate (**1i**), 4-cyanophenyl methanesulfonate (**1j**), and 4-acetamidophenyl methanesulfonate (**1k**) were synthesized according to literature procedures.[4b,8a,12b] 4-Methoxyphenyl dimethylsulfamate and 2,6-dimethylphenyl dimethylsulfamate were prepared according to literature methods.[5a] Methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (**2aa**), methyl 2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-benzoate (**2ab**), 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**2ba**), 2-(2-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**2bb**), 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**2c**), 1-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)ethanone, (4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)methanol, 5,5-dimethyl-2-(thiophen-2-yl)-1,3,2-dioxaborinane, 5,5-dimethyl-2-(thiophen-3-yl)-1,3,2-dioxaborinane, 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile, and 2-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)acetonitrile were synthesized according to the literature procedures.[12a–d] ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded using TMS as internal standard. High-resolution mass spectra of new compounds were obtained on a high-resolution double focusing chemical ionization mass spectrometer. A GC coupled with an FID detector and column HP 19091J-413 (5%-phenyl)-methylpolysiloxane 30 m length, 0.32 mm internal diameter was used to follow the reaction conversions and to assess purity of final compounds complementary to the NMR technique. The crude reaction mixtures were diluted with THF and analyzed by GC as reported in previous related publications from our laboratory.[12a–d]

General Procedure for the Synthesis of Aryl Mesylates. The aryl mesylates were prepared according to literature procedures.[12b] To an oven-dried round-bottom flask equipped with a stirring bar under nitrogen atmosphere were added phenol (38 mmol) and freshly distilled dichloromethane (31 mL) followed by anhydrous pyridine

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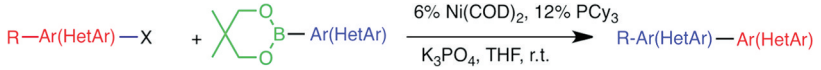
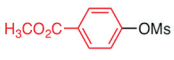
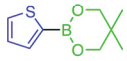
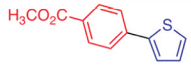
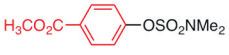
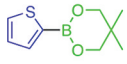
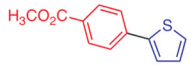
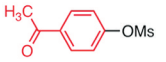
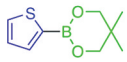
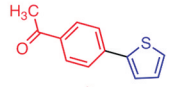
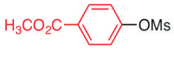
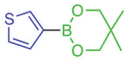
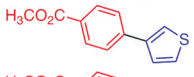
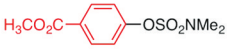
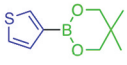
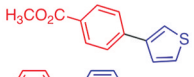
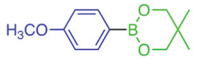
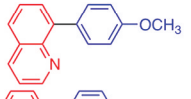
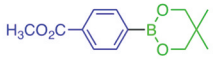
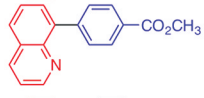
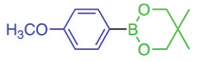
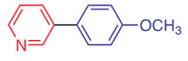
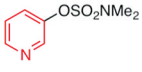
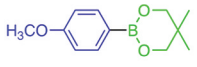
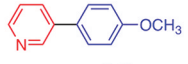
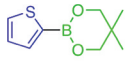
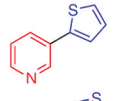
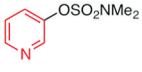
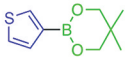
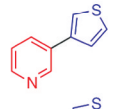
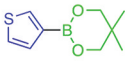
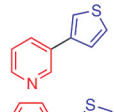
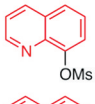
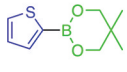
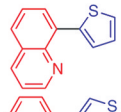
Table 4. Cross-Coupling of Aryl and Heteroaryl Mesylates with Aryl and Heteroaryl Neopentylglycolboronates Catalyzed by $Ni(COD)_2/PCy_3/K_3PO_4$ in THF at 25 °C



entry	electrophile		time (h)	product	3	yield[a] (%)
1			12		**3ac**	99
2			12		**3ac**	95
3			16		**3ad**	64
4			12		**3ae**	97
5			12		**3ae**	99
6			12		**3af**	99
7			12		**3ag**	85
8			12		**3ah**	96
9			12		**3ah**	99
10			12		**3ai**	99
11			14		**3aj**	88
12			14		**3aj**	91
13			47		**3ak**	8[b]
14			21		**3al**	44
15			17		**3am**	96
16			18		**3an**	99

[a]Isolated yield in all cases unless noted. [b]Yield determined by GC.

(15 g, 0.19 mol). The reaction mixture was cooled to 0 °C before methanesulfonyl chloride (45.6 mmol) was added dropwise. The reaction was allowed to stir at 0 °C for 4 h and at room temperature until TLC observed the completion of the starting material. The reaction was quenched by addition of water. The aqueous phase was extracted with dichloromethane three times, and all combined organic layers were washed with 15% HCl and brine and dried over $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography or crystallization.

3-Methoxyphenyl Methanesulfonate[12b] (1bb). Following the general procedure for the synthesis of aryl mesylates, 84%; colorless liquid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, J = 8.2, 1H), 6.94–6.85 (m, 2H), 6.85 (t, J = 2.3, 1H), 3.82 (s, 3H), 3.14 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 150.3, 130.5, 114.0, 113.3, 108.2, 37.5.

2,6-Dimethylphenyl Methanesulfonate[14] (1d). Following the general procedure for the synthesis of aryl mesylates, 78%; colorless

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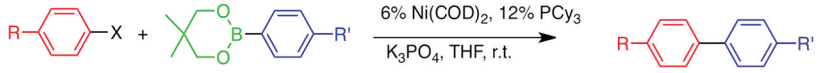
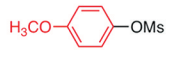
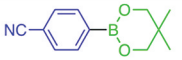
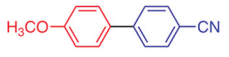
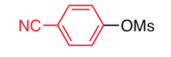
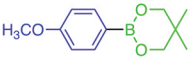
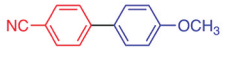
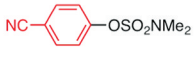
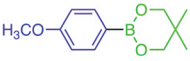
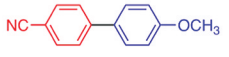
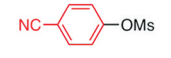
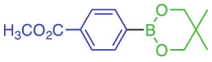
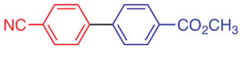
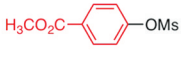
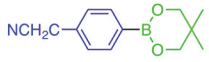
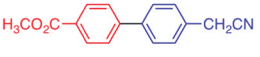
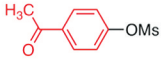
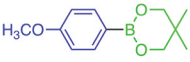
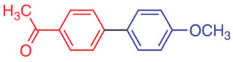
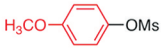
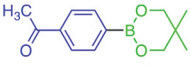
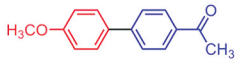
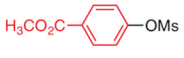
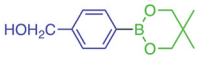
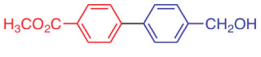
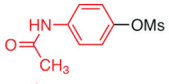
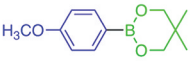
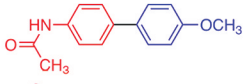
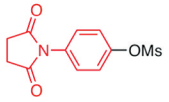
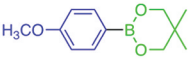
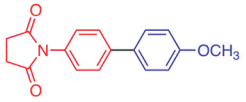
Table 5. Cross-Coupling in the Presence of Sensitive Functional Groups



entry	electrophile	Ar(HetAr)	time (h)	product	3	Yield[a] (%)
1			12		**3ao**	0[b]
2			12		**3ao**	64
3			40		**3ao**	27
4			60		**3ap**	53
5			16		**3aq**	77
6			12		**3ar**	99
7			36		**3ar**	0[b]
8			40		**3as**	10[b]
9			12		**3at**	85
10			12		**3au**	97

[a]Isolated yield in all cases unless noted. [b]Yield determined by GC.

liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (s, 1H), 3.30 (s, 1H), 2.39 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.1, 129.5, 129.5, 127.0, 39.4, 17.7.

Quinolin-8-yl Methanesulfonate (1f). To a solution of 8-hydroxyquinoline (1.45 g, 10.0 mmol) and Et_3N (2.1 mL) in CH_2Cl_2 (10 mL) at 0 °C was slowly added methanesulfonyl chloride (1.51 g, 13.2 mmol). The reaction mixture was allowed to warm to rt and was stirrred for 12 h. The reaction mixture was washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (SiO_2, 1:1, EtOAc/hexane) to give a pale yellow solid (2.21 g, 99%,), mp 73−74 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (dd, J = 4.2, 1.6, 1H), 8.23 (dd, J = 8.3, 1.6, 1H), 7.81 (dd, J = 8.2, 1.0, 1H), 7.73 (dd, J = 7.6, 1.2, 1H), 7.58 (t, J = 7.9, 1H), 7.50 (dd, J = 8.3, 4.2, 1H), 3.47 (d, J = 4.7, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.1, 145.7, 141.6, 136.3, 130.0, 127.4, 126.6, 123.9, 122.3, 39.3. The ^{1}H NMR and ^{13}C NMR are comparable to the literature.[8a]

Pyridin-3-yl Methanesulfonate (1g). To a solution of 3-hydroxypyridine (1.43 g, 15.0 mmol) and 2,6-lutidine (2.3 mL) in $CHCl_3$ (20 mL) at 0 °C was slowly added methanesulfonyl chloride (1.16 mL, 15.0 mmol). The reaction mixture was allowed to warm to rt and was stirred for 6 h. The reaction mixture was washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by recrystallization from EtOAc/hexane to give pale yellow solid (2.42 g, 93%), mp 58−59 °C (lit.[15] 57−58 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 2H), 7.72−7.63 (m, 1H), 7.39 (dd, J = 8.3, 4.6, 1H), 3.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 146.1, 143.7, 129.9, 124.6, 37.9.

1-(4-Hydroxyphenyl)pyrrolidine-2,5-dione (1la). A round-bottom flask was charged with a stirring bar, 4-aminophenol (1.64 g, 15.0 mmol), succinic anhydride (1.50 g, 15.0 mmol), and acetic acid (20 mL). The reaction was refluxed for 24 h. The reaction mixture was precipitated in water, and the solid was collected and recrystallized from ethanol; 45%, light gray solid, mp > 225 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.12−7.04 (m, 1H), 6.92−6.83 (m, 1H), 2.81 (s, 2H); ^{13}C NMR (126 MHz, acetone-d_6) δ 177.92, 158.40, 129.56, 126.24, 116.57, 29.57. HRMS (CI+) calcd for $C_{10}H_9NO_3$ (M^+ + H) 192.0661, found 192.0665.

4-(2,5-Dioxopyrrolidin-1-yl)phenyl Methanesulfonate (1l). Following the general procedure for the synthesis of aryl mesylates. Recrystallized from ethanol, 91%, white solid, mp 196−197 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 4H), 3.16 (s, 3H), 2.91 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 148.8, 131.0, 128.2, 122.9, 37.6, 28.5; HRMS (CI+) calcd for $C_{11}H_{12}NO_5S$ (M^+ + Na) 270.0436, found 270.0442.

General Procedure for the Synthesis of Aryl Sulfamates. The aryl sulfamates were prepared according to literature procedures.[5a] To an oven-dried round-bottom flask equipped with a stirring bar under nitrogen atmosphere was added NaH (15.6 mmol, 0.37 g) and the flask was cooled to 0 °C. A solution of the corresponding phenol (13 mmol) in dried DME (16 mL) was added dropwise at 0 °C into the flask. The reaction mixture was allowed to stir at room temperature for 10 min then cooled to 0 °C. The dimethyl sulfamoyl chloride (15.6 mmol, 2.24 g) in DME (4 mL) was added dropwise and the reaction was allowed to stir at room temperature for 12 h. The reaction was quenched by addition of water followed by the evaporation of the solvent. The solid was dissolved in Et_2O and the ether solution was washed with 1 M KOH and water. The combined aqueous layers were extracted with Et_2O, washed with brine, and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography.

Methyl 2-((*N*,*N*-Dimethylsulfamoyl)oxy)benzoate (4aa). Following the general procedure for the synthesis of aryl sulfamates; 80%, white solid, mp 68−69 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, J = 7.8, 1.7, 1H), 7.58−7.52 (m, 1H), 7.49 (dd, J = 8.2, 1.1, 1H), 7.36−7.30 (m, 1H), 3.91 (s, 3H), 3.04 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 148.9, 133.5, 131.9, 126.5, 124.7, 123.3, 52.4, 38.9; HRMS (CI+) calcd for $C_{10}H_{13}NNaO_5S$ (M^+ + Na) 282.0412, found 282.0404.

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Methyl 3-((*N*,*N*-Dimethylsulfamoyl)oxy)benzoate (4ab). Following the general procedure for the synthesis of aryl sulfamates; 75%, white solid, mp 71−74 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 7.4, 1H), 7.95−7.82 (m, 1H), 7.60−7.42 (m, 2H), 3.93 (s, 3H), 3.01 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 149.4, 131.2, 129.0, 127.0, 125.5, 122.0, 51.6, 37.9; HRMS (CI+) calcd for $C_{10}H_{13}NNaO_5S$ (M^+ + Na) 282.0412, found 282.0411.

Methyl 4-((*N*,*N*-Dimethylsulfamoyl)oxy)benzoate (4ac). Following the general procedure for the synthesis of aryl sulfamates; 84%, white solid, mp 67−68 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, J = 8.2, 2H), 7.36 (d, J = 8.2, 2H), 3.93 (s, 3H), 3.01 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 152.9, 130.6, 127.6, 120.6, 51.4, 37.9. HRMS (CI+) calcd for $C_{10}H_{14}NO_5S$ (M^+ + H) 260.0593, found 260.0600.

2-Methoxyphenyl Dimethylsulfamate (4ba). Following the general procedure for the synthesis of aryl sulfamates; 80%, white solid, mp 40−42 °C (lit.[16] 38−42 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, J = 8.0, 1.0, 1H), 7.22 (td, J = 8.3, 1.6, 1H), 7.00−6.92 (m, 2H), 3.89 (s, 3H), 2.967 (s, 3H), 2.966 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 139.5, 127.7, 123.9, 121.0, 113.0, 56.1, 38.8.

3-Methoxyphenyl Dimethylsulfamate (4bb). Following the general procedure for the synthesis of aryl sulfamates;. 80%, colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, J = 8.5, 1H), 6.90−6.86 (m, 1H), 6.83 (dd, J = 7.9, 5.4, 2H), 3.81 (s, 3H), 2.97 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 150.2, 129.2, 112.8, 111.7, 106.8, 54.7, 37.9; HRMS (CI+) calcd for $C_9H_{14}NO_4S$ (M^+ + H) 232.0644, found 232.0650.

Pyridin-3-yl Dimethylsulfamate (4c). In a round-bottom flask were added a stirring bar, 3-hydroxypyridine(0.23 g, 2.4 mmol), dimethylsulfamoyl chloride (0.4 mL, 3.6 mmol), Et_3N (0.4 mL, 3.6 mmol), and toluene (5 mL). The reaction was refluxed for 12 h. The reaction mixture was quenched by adding saturated NH_4Cl solution (25 mL) and extracted using EtOAc. The organic phase was washed with saturated $NaHCO_3$ solution (25 mL) twice. The aqueous phase was collected and extracted with EtOAc (25 mL) three times. The organic phase was combined and dried over $MgSO_4$. The mixture was filtered and dried under vacuum. The product was further purified by column chromatography (SiO_2, 1:1; CH_2Cl_2/EtOAc); 67%, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, J = 2.6, 1H), 8.54 (d, J = 4.7, 1H), 7.67 (ddd, J = 8.4, 2.7, 1.4, 1H), 7.35 (dd, J = 8.4, 4.7, 1H), 3.02 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.0, 146.3, 142.8, 128.5, 123.4, 37.9. HRMS (CI+) calcd for $C_7H_{11}N_2O_3S$ (M^+ + H) 203.0490, found 203.0490.

4-Cyanophenyl Dimethylsulfamate (4d). Following the general procedure for the synthesis of aryl sulfamates; 89%, white solid, mp 69−70 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.8, 2H), 7.40 (d, J = 8.8, 2H), 3.02 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 133.2, 121.6, 117.1, 109.7, 37.9. HRMS (CI+) calcd for $C_9H_{10}N_2O_3S$ (M^+ + H) 227.0490, found 227.0482.

Preparation of Neopentylglycolborane. A procedure elaborated in our laboratory was used.[11] To a cooled solution (0 °C) of neopentylglycol (6.0 mmol, 2.0 equiv) in toluene (3 mL) was slowly added $(CH_3)_2S{\cdot}BH_3$ (6 mmol, 2.0 equiv) under nitrogen. The reaction was allow to stir at 0 °C for 30 min and then at room temperature for 90 min. The neopentylglycolborane was used directly without further purification.

General Procedure for Neopentylglycolborylation. The aryl boronic esters were prepared according to previously reported procedures.[11,12a−d] To an oven-dried 25 mL Schlenk tube were added Zn powder (6.0 mmol), $NiCl_2$(dppp) (1.5 mmol), and PPh_3 (3.0 mmol) along with the appropriate aryl halide (if it is solid) (3.0 mmol). The aryl halide, catalyst, and PPh_3 were degassed by pumping and backfilling with nitrogen three times. Dry toluene (3 mL) was added to the reaction mixture along with the appropriate aryl halide (if it is liquid) and Et_3N (9.0 mmol). The neopentylglycolborane was added dropwise to the reaction mixture. The reaction was placed into an oil bath at 100 °C with stirring under nitrogen. After the starting material was consumed, the reaction was quenched by addition of saturated NH_4Cl solution and extracted with EtOAc 3 times. The organic fractions were combined and dried over $MgSO_4$, followed by filtration and evaporation of the solvent. The crude product was purified by column chromatography.

General Procedure for Cross-Coupling. To an oven-dried test tube (15 mm × 85 mm) were added aryl mesylate or aryl sulfamate (0.3 mmol), aryl neopentylglycolboronate (0.36 mmol), and K_3PO_4 (0.9 mmol). The tube was taken into a glovebox and PCy_3 (0.036 mmol) and $Ni(COD)_2$ (0.018 mmol) were added. Dried THF (1.0 mL) was then added, and the tube was capped with rubber septum. The reaction was stirred at room temperature under nitrogen for 4−60 h inside the glovebox (see Tables 2−5). The crude mixture was filtered through a short column of silica gel. The solvent was evaporated, and the product was purified by column chromatography with dichloromethane/hexane or EtOAc/hexane as eluent.

Methyl 4′-Methoxy-[1,1′-biphenyl]-4-carboxylate (3a). White solid, mp 172−173 °C (lit.[11a] 173−174 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15−8.00 (m, 2H), 7.69−7.51 (m, 4H), 7.05−6.88 (m, 2H), 3.93 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 159.8, 145.1, 132.3, 130.0, 128.3, 128.15, 126.4, 114.3, 55.3, 52.0.

4,4′-Dimethoxy-1,1′-biphenyl (3b). White solid, mp 171−172 °C (lit.[17] 172−174 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.8, 4H), 6.95 (d, J = 8.8, 4H), 3.84 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 133.6, 127.9, 114.3, 55.5.

2,4′-Dimethoxy-1,1′-biphenyl (3c). White solid, mp 64−66 °C (lit.[18] 69.7−70.4 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 8.8, 2H), 7.34−7.26 (m, 2H), 7.00 (td, J = 7.4, 1.0, 1H), 6.99−6.88 (m, 3H), 3.83 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 156.6, 131.0, 130.8, 130.7, 130.5, 128.3, 121.0, 113.6, 111.3, 55.7, 55.4.

Methyl 2′-Methoxy-[1,1′-biphenyl]-4-carboxylate (3d). White solid, mp 80 °C (lit.[19] 79 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2, 2H), 7.60 (d, J = 8.3, 2H), 7.38−7.27 (m, 2H), 7.02 (tt, J = 3.9, 1.9, 1H), 6.98 (d, J = 8.2, 1H), 3.91 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 156.6, 143.5, 130.8, 129.7, 129.6, 129.5, 129.4, 128.6, 121.0, 111.4, 55.6, 52.1.

3,4′-Dimethoxy-1,1′-biphenyl (3e). White solid, mp 56−58 °C (lit.[20] 60−61 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.7, 2H), 7.32 (t, J = 7.9, 1H), 7.14 (d, J = 7.7, 1H), 7.12−7.06 (m, 1H), 6.96 (d, J = 8.7, 2H), 6.85 (dd, J = 8.2, 2.4, 1H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 159.4, 142.5, 133.8, 129.8, 128.3, 119.4, 114.3, 112.7, 112.2, 55.5, 55.4.

Methyl 3′-Methoxy-[1,1′-biphenyl]-4-carboxylate (3f). White solid, mp 52−54 °C (lit.[21] 55 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.6, 2H), 7.65 (d, J = 8.6, 2H), 7.38 (t, J = 7.9, 1H), 7.21 (ddd, J = 7.7, 1.6, 0.9, 1H), 7.17−7.13 (m, 1H), 6.94 (dd, J = 8.2, 1.7, 1H), 3.94 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 159.2, 144.7, 140.7, 130.2, 129.2, 129.1, 128.2, 126.3, 118.9, 112.7, 112.2, 54.5, 51.3.

4′-Methoxy-2-methyl-1,1′-biphenyl[22] (3g). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.7, 2H), 7.32 (t, J = 7.9, 1H), 7.14 (d, J = 7.7, 1H), 7.12−7.06 (m, 1H), 6.96 (d, J = 8.7, 2H), 6.85 (dd, J = 8.2, 2.4, 1H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 141.7, 135.6, 134.5, 130.4, 130.4, 130.0, 127.1, 125.9, 113.6, 55.4, 20.7.

Methyl 2′-Methyl-[1,1′-biphenyl]-4-carboxylate[23] (3h). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 8.5, 2H), 7.40 (d, J = 8.5, 2H), 7.32−7.19 (m, 4H), 3.94 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 146.9, 141.0, 135.3, 130.6, 129.7, 129.6, 129.4, 128.8, 128.0, 126.0, 52.3, 20.5.

4′-Methoxy-3-methyl-1,1′-biphenyl (3i). White solid, mp 50 °C (lit.[24] 51−52 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.7, 2H), 7.34 (d, J = 12.0, 2H), 7.28 (t, J = 7.5, 1H), 7.10 (d, J = 7.4, 1H), 6.94 (d, J = 8.7, 2H), 3.81 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 140.9, 138.4, 134.0, 128.8, 128.3, 127.7, 127.5, 124.0, 114.3, 55.4, 21.7.

Methyl 3′-Methyl-[1,1′-biphenyl]-4-carboxylate (3j). White solid, mp 58−59 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.1, 2H), 7.66 (d, J = 8.1, 2H), 7.43 (d, J = 8.9, 2H), 7.36 (t, J = 7.6, 1H), 7.21 (d, J = 7.4, 1H), 3.94 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 145.0, 139.2, 137.7, 129.2, 128.0, 127.98,

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127.96, 127.2, 126.2, 123.5, 51.3, 20.7; HRMS (CI+) calcd for $C_{15}H_{15}O_2$ (M^+ + H) 227.1072, found 227.1073.

Methyl 4′-Methoxy-[1,1′-biphenyl]-2-carboxylate[25] (3k). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.7, 1H), 7.50 (td, J = 7.6, 1.4, 1H), 7.37 (t, J = 7.9, 2H), 7.24 (d, J = 8.7, 2H), 6.93 (d, J = 8.8, 2H), 3.84 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 159.1, 142.1, 133.8, 131.3, 131.0, 130.9, 129.9, 129.6, 126.9, 113.7, 55.4, 52.1.

Dimethyl [1,1′-Biphenyl]-2,4′-dicarboxylate[26] (3l). White solid, mp 56−58 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16−8.04 (m, 2H), 7.88 (dd, J = 7.8, 1.1, 1H), 7.55 (td, J = 7.6, 1.4, 1H), 7.45 (td, J = 7.6, 1.3, 1H), 7.37 (td, J = 8.1, 1.4, 3H), 3.94 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.1, 146.4, 141.8, 131.6, 130.70, 130.68, 130.3, 129.5, 129.0, 128.6, 128.0, 52.3, 52.1.

Methyl 4′-Methoxy-[1,1′-biphenyl]-3-carboxylate (3m). White solid, mp 68−70 °C (lit.[27] 71−73 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 1.7, 1H), 7.97 (d, J = 7.7, 1H), 7.75 (d, J = 7.7, 1H), 7.57 (d, J = 8.7, 2H), 7.49 (t, J = 7.7, 1H), 7.00 (d, J = 8.7, 2H), 3.95 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 158.7, 140.2, 131.8, 130.2, 129.8, 128.0, 127.4, 127.0, 126.9, 113.5, 54.5, 51.3.

Dimethyl [1,1′-Biphenyl]-3,4′-dicarboxylate (3n). White solid, mp 95 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (t, J = 1.7, 1H), 8.16−8.10 (m, 2H), 8.09−8.03 (m, 1H), 7.86−7.77 (m, 1H), 7.71−7.65 (m, 2H), 7.54 (t, J = 7.8, 1H), 3.96 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.01, 166.98, 144.6, 140.4, 131.8, 131.0, 130.4, 129.5, 129.3, 129.2, 128.5, 127.3, 52.4, 52.3; HRMS (CI +) calcd for $C_{16}H_{15}O_4$ (M^+ + H) 271.0970, found 271.0974.

2,2′-Dimethoxy-1,1′-biphenyl (3o). White solid, mp 152−154 °C (lit.[28] 154−155 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (td, J = 8.2, 1.7, 2H), 7.31 (dd, J = 7.4, 1.6, 2H), 7.06 (t, J = 7.4, 2H), 7.03 (d, J = 8.3, 2H), 3.82 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 131.6, 128.7, 128.0, 120.5, 111.2, 55.8.

Methyl 2′-Methoxy-[1,1′-biphenyl]-2-carboxylate[29] (3p). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, J = 7.8, 1.3, 1H), 7.54 (td, J = 7.6, 1.4, 1H), 7.39 (td, J = 7.6, 1.3, 1H), 7.33 (tdd, J = 6.0, 4.3, 1.7, 2H), 7.27−7.22 (m, 1H), 7.03 (td, J = 7.4, 1.0, 1H), 6.90 (d, J = 8.2, 1H), 3.71 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 156.2, 138.9, 131.74, 131.68, 131.5, 130.7, 130.1, 129.5, 129.0, 127.2, 120.9, 110.3, 55.4, 51.8.

2′-Methoxy-2,6-dimethyl-1,1′-biphenyl (3q). Not isolated.

4′-Methoxy-2,6-dimethyl-1,1′-biphenyl (3r). White solid, mp 46−48 °C (lit.[30] 50.3−50.9 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19−7.02 (m, 5H), 6.96 (d, J = 8.7, 2H), 3.85 (s, 3H), 2.04 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 141.7, 136.7, 133.5, 130.2, 127.4, 127.0, 114.0, 55.4, 21.0.

Dimethyl [1,1′-Biphenyl]-4,4′-dicarboxylate (3u). White solid, mp 212−214 °C (lit.[28] 215.5−216.5 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.2, 4H), 7.69 (d, J = 8.2, 4H), 3.95 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 144.5, 130.3, 129.9, 127.4, 52.3.

Methyl [1,1′-Biphenyl]-4-carboxylate (3v). White solid, mp 110 °C (lit.[31] 110−112 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.1, 2H), 7.67 (d, J = 8.2, 2H), 7.63 (d, J = 7.4, 2H), 7.47 (t, J = 7.7, 2H), 7.40 (t, J = 7.1, 1H), 3.95 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 144.8, 139.2, 129.2, 128.1, 127.3, 126.4 126.2, 51.3.

Methyl [1,1′-Biphenyl]-3-carboxylate[32] (3w). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (t, J = 1.5, 1H), 8.01 (d, J = 7.8, 1H), 7.77 (d, J = 7.8, 1H), 7.65−7.58 (m, 2H), 7.49 (t, J = 7.7, 1H), 7.45 (t, J = 7.6, 2H), 7.36 (t, J = 7.4, 1H), 3.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 141.6, 140.2, 131.6, 130.8, 129.01, 128.97, 128.5, 128.4, 127.9, 127.3, 52.3.

Methyl [1,1′-Biphenyl]-2-carboxylate[33] (3x). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.8, 1H), 7.52 (td, J = 7.6, 1.4, 1H), 7.43−7.33 (m, 5H), 7.33−7.28 (m, 2H), 3.63 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 142.6 141.5, 131.4, 131.0, 130.8, 129.9, 128.5, 128.2 127.4, 127.3, 52.1.

4-Methoxy-1,1′-biphenyl (3y). White solid, mp 85 °C (lit.[4b] 85−87 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.50 (m, 4H), 7.41 (t, J = 7.7, 2H), 7.30 (t, J = 7.4, 1H), 7.01−6.95 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 141.0, 133.9, 128.9, 128.3, 126.9, 126.8, 114.4, 55.5.

3-Methoxy-1,1′-biphenyl[34] (3z). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 5.2, 3.3, 2H), 7.41 (dd, J = 10.4, 4.9, 2H), 7.33 (td, J = 7.6, 3.5, 2H), 7.15 (dt, J = 4.1, 2.9, 2H), 6.88 (dd, J = 8.2, 2.5, 1H), 3.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 142.9, 141.2, 129.9, 128.9, 127.5, 127.3, 119.8, 113.0, 112.8, 100.0, 55.4.

2-Methoxy-1,1′-biphenyl[34] (3aa). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8, 2H), 7.39 (t, J = 7.6, 2H), 7.33−7.28 (m, J = 7.2, 3H), 7.02 (t, J = 7.4, 1H), 6.97 (d, J = 8.6, 1H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 138.7, 131.0, 130.9, 129.7, 128.7, 128.1, 127.0, 121.0, 111.4, 55.7.

Methyl 4-(Thiophen-2-yl)benzoate (3ac). Pale yellow solid, mp 138−139 °C (lit.[35] 139−140 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5, 2H), 7.66 (d, J = 8.5, 2H), 7.57 (dd, J = 2.7, 1.5, 1H), 7.45−7.39 (m, 2H), 3.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 140.4, 139.2, 129.4, 127.8, 125.8, 125.4, 125.3, 121.0, 51.2.

1-(4-(Thiophen-2-yl)phenyl)ethanone (3ad). Pale yellow solid, mp 121 °C (lit.[36] 124−126 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4, 2H), 7.70 (d, J = 8.4, 2H), 7.44 (dd, J = 3.6, 1.0, 1H), 7.37 (dd, J = 5.1, 1.0, 1H), 7.12 (dd, J = 5.0, 3.7, 1H), 2.62 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 134.9, 128.3, 127.5, 125.6, 124.8, 123.8, 25.7.

Methyl 4-(Thiophen-3-yl)benzoate (3ae). Pale yellow solid, mp 160−161 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3, 2H), 7.67 (d, J = 8.2, 2H), 7.57 (dd, J = 2.7, 1.5, 1H), 7.46−7.40 (m, 2H), 3.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 140.4, 139.2, 129.4, 127.8, 125.8, 125.4, 125.3, 121.0, 51.3; HRMS (CI+) calcd for $C_{12}H_{11}O_2S$ (M^+ + H) 219.0480, found 219.0480.

8-(4-Methoxyphenyl)quinoline (3af). White solid, mp 113−114 °C (lit.[37] 117−118 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.1, 1.7, 1H), 8.18 (dd, J = 8.2, 1.5, 1H), 7.78 (d, J = 8.1, 1H), 7.71 (dd, J = 7.1, 1.2, 1H), 7.66 (d, J = 8.7, 2H), 7.58 (t, J = 7.6, 1H), 7.39 (dd, J = 8.2, 4.1, 1H), 7.04 (d, J = 8.7, 2H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 150.3, 146.3, 140.7, 136.4, 132.1, 131.9, 130.1, 128.9, 127.2, 126.4, 121.0, 113.7, 55.5.

Methyl 4-(Quinolin-8-yl)benzoate (3ag). White solid, mp 92−93 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.1, 1.7, 1H), 8.21 (dd, J = 8.3, 1.6, 1H), 8.17 (d, J = 8.4, 2H), 7.86 (d, J = 8.1, 1H), 7.78 (d, J = 8.4, 2H), 7.74 (dd, J = 7.1, 1.3, 1H), 7.62 (t, J = 7.6, 1H), 7.43 (dd, J = 8.2, 4.1, 1H), 3.95 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 150.6, 146.0, 144.5, 140.0, 136.5, 130.8, 130.5, 129.4, 129.1, 128.9, 128.4, 126.4, 121.4, 52.2; HRMS (CI+) calcd for $C_{17}H_{14}NO_2$ (M^+ + H) 264.1025, found 264.1030.

3-(4-Methoxyphenyl)pyridine (3ah). White solid, mp 60−61 °C (lit.[38] 62−63 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.54 (d, J = 4.7, 1H), 7.83 (ddd, J = 7.9, 2.3, 1.7, 1H), 7.52 (d, J = 8.8, 2H), 7.33 (dd, J = 7.9, 4.8, 1H), 7.01 (d, J = 8.8, 2H), 3.86 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 147.1, 147.0, 135.4, 133.0, 129.4, 127.4, 122.6, 113.7, 54.5.

3-(Thiophen-2-yl)pyridine (3ai). Light brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.52 (s, 1H), 7.87 (d, J = 7.4, 1H), 7.36 (d, J = 4.3, 2H), 7.31 (s, 1H), 7.14−7.10 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 147.1, 140.6, 133.1, 130.6, 128.4, 126.2, 124.4, 123.8. The ^{1}H NMR and ^{13}C NMR are comparable to the literature.[39]

3-(Thiophen-3-yl)pyridine (3aj). White solid, mp 76−77 °C (lit.[40] 75−77 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.54 (d, J = 3.7, 1H), 7.86 (d, J = 7.9, 1H), 7.52 (d, J = 1.8, 1H), 7.45 (dd, J = 4.8, 3.1, 1H), 7.40 (d, J = 5.0, 1H), 7.32 (dd, J = 7.8, 4.8, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 147.9, 139.0, 133.6, 131.7, 127.1, 126.1, 123.8, 121.6.

8-(Thiophen-2-yl)quinoline[41] (3ak). Pale yellow oil. ^{1}H NMR (500 MHz, CDCl3) δ 9.02 (dd, J = 4.1, 1.8, 1H), 8.19 (dd, J = 8.2, 1.7, 1H), 8.08 (dd, J = 7.3, 1.3, 1H), 7.79 (dd, J = 3.7, 1.1, 1H), 7.76 (dd, J = 8.1, 1.1, 1H), 7.57 (t, J = 7.7, 1H), 7.49 (dd, J = 5.1, 1.1, 1H), 7.45 (dd, J = 8.3, 4.1, 1H), 7.18 (dd, J = 5.1, 3.7, 1H). ^{13}C NMR (126 MHz, CDCl3) δ 148.7, 143.9, 138.9, 135.5, 132.3, 128.0, 127.2, 127.1, 126.3, 125.9, 125.8, 125.6, 120.4.

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8-(Thiophen-3-yl)quinoline[41] (3al). Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.19 (d, J = 5.9, 1H), 7.90 (s, 1H), 7.87 (d, J = 7.1, 1H), 7.78 (d, J = 5.7, 1H), 7.67 (d, J = 5.0, 1H), 7.58 (t, J = 6.0, 1H), 7.47−7.39 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0, 145.9, 139.5, 136.3, 135.1, 129.7, 129.4, 128.8, 127.3, 126.3, 124.6, 124.5, 120.9.

6-(4-Methoxyphenyl)quinoline (3am). White solid, mp 108−109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (d, J = 2.7, 1H), 8.17 (d, J = 8.4, 2H), 7.98−7.91 (m, 2H), 7.66 (d, J = 8.8, 2H), 7.41 (dd, J = 8.3, 4.2, 1H), 7.07−7.01 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 149.2, 146.6, 138.1, 135.3, 131.9, 128.9, 128.2, 127.7, 127.7, 123.8, 120.6, 113.6, 54.5. The ^{1}H NMR and ^{13}C NMR are comparable to the literature.[42]

5-(4-Methoxyphenyl)isoquinoline (3an). White solid, mp 63−65 °C (lit.[2b] 68−69 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.48 (d, J = 5.9, 1H), 7.95 (dd, J = 6.0, 3.3, 1H), 7.74 (d, J = 5.9, 1H), 7.64 (dd, J = 8.0, 5.2, 2H), 7.41 (d, J = 8.6, 2H), 7.05 (d, J = 8.6, 2H), 3.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 153.0, 143.4, 139.1, 134.5, 131.5, 131.1, 131.0, 129.2, 127.0, 126.9, 118.8, 114.2, 55.5.

4′-Methoxy-[1,1′-biphenyl]-4-carbonitrile (3ao). White solid, mp 102−103 °C (lit.[43] 102−103 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4, 2H), 7.64 (d, J = 8.1, 2H), 7.54 (d, J = 8.8, 2H), 7.01 (d, J = 8.8, 2H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 144.4, 131.7, 130.5, 127.5, 126.3, 118.2, 113.7, 109.3, 54.6.

Methyl 4′-Cyano-[1,1′-biphenyl]-4-carboxylate (3ap). White solid, mp 141−142 °C (lit.[44] 144−145 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.3, 1H), 7.76 (d, J = 8.2, 1H), 7.72 (d, J = 8.4, 1H), 7.66 (d, J = 8.3, 1H), 3.96 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 144.6, 143.6, 132.9, 130.5, 130.4, 128.1, 127.4, 118.8, 112.0, 52.5.

Methyl 4′-(Cyanomethyl)-[1,1′-biphenyl]-4-carboxylate (3aq). White solid, mp 150−151 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.12 (d, J = 8.5, 2H), 7.69−7.61 (m, 4H), 7.44 (d, J = 8.4, 2H), 3.95 (s, 3H), 3.81 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 143.7, 139.1, 129.3, 129.0, 128.4, 127.7, 127.1, 126.1, 116.8, 51.3, 22.5. HRMS (CI+) calcd for $C_{16}H_{13}NO_2Na$ (M^+ + Na) 274.0844, found 274.0834.

1-(4′-Methoxy-[1,1′-biphenyl]-4-yl)ethanone (3ar). White solid, mp 154−155 °C (lit.[45] 157 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.6, 1H), 7.65 (d, J = 8.6, 1H), 7.58 (d, J = 8.8, 1H), 7.00 (d, J = 8.8, 1H), 3.87 (s, 2H), 2.63 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 159.1, 144.5, 134.5, 131.4, 128.1, 127.5, 125.8, 113.6, 54.5, 25.8.

Methyl 4′-(Hydroxymethyl)-[1,1′-biphenyl]-4-carboxylate (3as). Not isolated.

***N*-(4′-Methoxy-[1,1′-biphenyl]-4-yl)acetamide (3at).** White solid, mp 203−205 °C (lit.[46] 207−208 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64−7.40 (m, 6H), 6.96 (d, J = 8.4, 2H), 3.84 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 159.2, 137.1, 136.7, 133.2, 128.0, 127.3, 120.4, 114.4, 55.5, 24.8.

1-(4′-Methoxy-[1,1′-biphenyl]-4-yl)pyrrolidine-2,5-dione (3au). White solid, mp 212−213 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.5, 2H), 7.52 (d, J = 8.8, 2H), 7.33 (d, J = 8.5, 2H), 6.98 (d, J = 8.8, 2H), 3.85 (s, 3H), 2.92 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.4, 159.6, 141.5, 132.9, 130.5, 128.4, 127.7, 126.8, 114.5, 55.5, 28.6. HRMS (CI+) calcd for $C_{17}H_{15}NO_3$ (M^+ + H) 282.1130, found 282.1122.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR, ^{13}C NMR, and HRMS for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: percec@sas.upenn.edu.

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