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Cross-Coupling of Mesylated Phenol Derivatives with Potassium Cyclopropyltrifluoroborate

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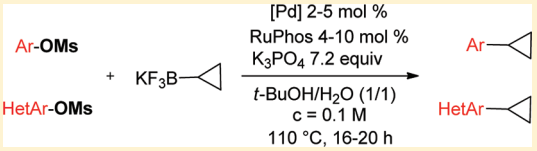
Supporting Information

ABSTRACT: C−O activation of mesylates by a palladium catalyst and subsequent cross-coupling with potassium cyclopropyltrifluoroborate have been achieved with high yield. Both electron-enriched and electron-deficient aryl mesylates are suitable electrophilic partners for the Suzuki−Miyaura reaction. The scope was successfully extended to heteroaryl mesylates with yields up to 94%.



Cyclopropanes are among the more useful subunits that can be incorporated within a target molecule to engender or improve biological activity. The number of newly discovered, biologically active natural products and pharmaceutical or crop protection compounds containing the cyclopropyl ring increases daily.[1−3] Thus, it has become of interest to develop appropriate methods to install the cyclopropyl subunit within existing skeletons.

The cyclopropyl group, a small strained ring with unique hybridization, also exhibits a particular reactivity pattern in transition-metal-catalyzed coupling reactions.[4,5] Among these cross-coupling protocols, the Suzuki−Miyaura reaction is a method of choice because of its mild reaction conditions, excellent tolerance of a broad range of functional groups, and its use of environmentally sound, nontoxic boron species.[6−9] Cyclopropylboronic acid[10−26] has been extensively used, but because of its tendency to protodeboronate easily,[27] recent work is currently more focused on various boronic acid derivatives. For example, Burke et al. have reported the use of cyclopropyl MIDA boronates in cross-coupling reactions with various aryl chlorides.[27] The corresponding commercially available potassium cyclopropyltrifluoroborate, known to be air and moisture stable and resistant to protodeboronation, has also been employed in various contexts.[28−32] Stereodefined potassium cyclopropyltrifluoroborates were first engaged with aryl bromides to afford the cross-coupled products with retention of configuration.[33,34] Our laboratory next developed an efficient method to cross-couple aryl and heteroaryl chloride electrophiles with potassium cyclopropyltrifluoroborate in high yields.[35] In 2009, Hocek reported the synthesis of two purine derivatives from the corresponding bromide or chloride with potassium cyclopropyltrifluoroborate in moderate yields.[36]

Although halides are usually employed as electrophilic partners, phenol derivatives bearing more environmentally sound, less expensive, and easier to handle nucleofuges offer an alternative of choice in terms of the electrophilic partner. Sulfonated phenol derivatives, especially, have emerged as very competitive cross-coupling substrates. Until now, aryl triflates have been successfully engaged in the Suzuki−Miyaura cross-coupling with cyclopropylboronic acid.[13−23] However, triflating reagents such as Tf_2O and $PhNTf_2$ are relatively expensive, and some triflates are known to be unstable.[37] When it comes to nonfluorinated sulfonated alcohols, only one example of the use of an aryl tosylate in the cross-coupling has been disclosed.[24] This method requires the presence of a large excess of cyclopropylboronic acid (3 equiv) to afford the desired compound with a moderate yield. Moreover, to our knowledge, no example of mesylated counterparts has been reported to date. Even though these species are known to be among the least reactive sulfonated species, they display substantial advantages in that they are reasonably atom-economical, are very stable, and have already been proven to be partners of choice for the Suzuki−Miyaura reaction.[24,38−42] We disclose herein the first cross-coupling of both aryl and heteroaryl mesylates through C−O activation with potassium cyclopropyltrifluoroborate.

The catalytic system was first optimized on a model reaction between naphthalen-1-yl methanesulfonate and potassium cyclopropyltrifluoroborate (**1**). Our laboratory already reported that the use of a *t*-BuOH/H_2O (1/1) mixture and potassium phosphate as base was very efficient for the cross-coupling of mesylated counterparts.[39,41,42] On the basis of these observations, we began our study by screening different ligands in combination with the air-stable $Pd(OAc)_2$ catalyst (Table 1). Alkylphosphines and biarylphosphines, as well as monodentate or bidentate phosphines, were tested (Figure 1), and 2-dicyclohexylphosphino-2′,6′-diisopropoxy-1,1′-biphenyl (RuPhos)[43] appeared to be the most relevant ligand to obtain the desired cyclopropylnaphthalene **2a** with total conversion and 87% isolated yield (Table 1, entry 4).

The optimized conditions were next applied to a wide range of aryl mesylates bearing either electron-donating or electron-withdrawing groups (Table 2). For most of the functionalized mesylates, it was necessary to utilize a catalyst loading of 5 mol %

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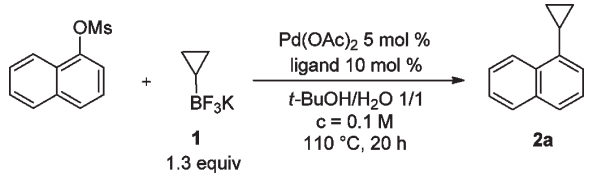
Table 1. Optimization



entry	ligand	conversn (%)	yield (%)[a]
1	$Cy_3P \cdot HBF_4$	32	10
2	XPhos (**I**)	100	68
3	RuPhos (**II**)	100	93
4[b]	RuPhos (**II**)	100	93 (87)[c]
5	SPhos (**III**)	100	79
6	XantPhos (**IV**)	12	traces
7	DPEPhos (**V**)	29	7
8	dippf (**VI**)	63	36

[a] Relative GC yield determined using dodecane as the internal standard. [b] Conditions: 2 mol % of $Pd(OAc)_2$ and 4 mol % of RuPhos. [c] Isolated yield.

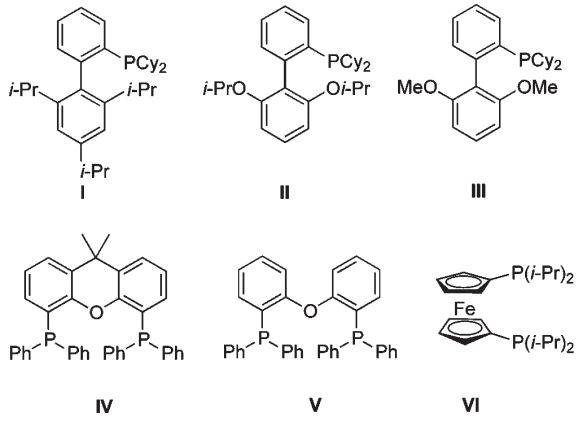
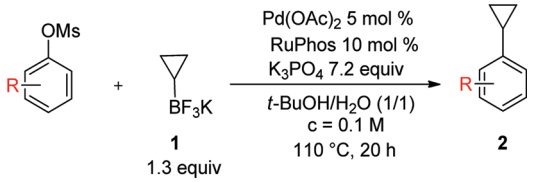
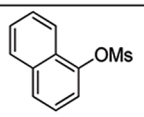
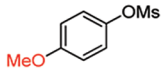
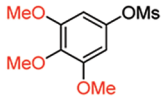
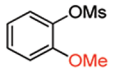
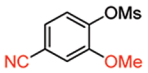
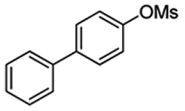
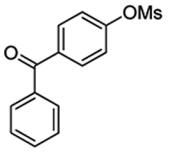
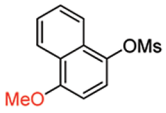
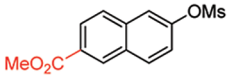
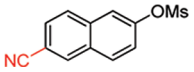


Figure 1. Structures of ligands **I**–**VI**.

for the reaction to go to completion. The reaction proceeded very well with almost all the deactivated electrophilic partners, and the desired compounds **2b**–**d**,**f**,**h** were obtained with yields as high as 96%. It was more difficult to cross-couple electron-deficient mesylates, owing to the competitive sulfonate hydrolysis reaction, which generally occurred more quickly and resulted in the corresponding alcohol as a major product. With a goal to circumvent this problem, another source of palladium ($PdCl_2(COD)$ instead of $Pd(OAc)_2$) was tested in the reaction with two substrates: [1,1′-biphenyl]-4-yl methanesulfonate and 4-benzoylphenyl methanesulfonate. Unfortunately, this effort was unsuccessful, as similar cross-coupled yields were obtained (72% versus 78% for **2f** and 59% versus 56% for **2g**). However, we were pleased to observe that the reaction is compatible with diverse electron-withdrawing substituents such as nitrile, benzoyl, and ester groups to afford the cyclopropyl arene derivatives **2e**,**g**,**i**,**j** with moderate yields. Importantly, by scaling up the reaction to 4.5 mmol of naphth-1-yl mesylate, we were able to reduce the amount of catalyst from 2 mol % to 0.5 mol %, obtaining the desired compound **2a** with a yield of 91% (versus 87% at 0.25 mmol scale). Moreover, to avoid solvent waste on this larger scale, the reaction proved to be as efficient in a more concentrated media (91% yield when the reaction was performed at 0.25 M). Of particular note, most of these unsubstituted cyclopropyl arenes are volatile because of their relatively low molecular weight. Thus, careful handling is required to isolate the product.

Table 2. Scope of Functionalized Aryl Mesylates



entry	Ar-OMs		yield (%)
1		**2a**	87[a] (91)[b] (91)[c]
2		**2b**	96
3		**2c**	91[a]
4		**2d**	91
5		**2e**	49
6		**2f**	78 (72)[d]
7		**2g**	56[a] (59)[a,d]
8		**2h**	90[e]
9		**2i**	44
10		**2j**	58[a]

[a] Conditions: 2 mol % of $Pd(OAc)_2$ 4 mol % of RuPhos. [b] Conditions: 0.5 mol % of $Pd(OAc)_2$ and 1 mol % of RuPhos on a 4.5 mmol scale at a concentration of 0.1 M. [c] Conditions: 0.5 mol % of $Pd(OAc)_2$ and 1 mol % of RuPhos on a 4.5 mmol scale at a concentration of 0.25 M. [d] $PdCl_2$-(COD) was used instead of $Pd(OAc)_2$. [e] Contaminated with 10% of impurities that cannot be separated.

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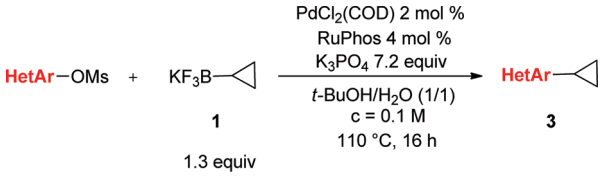
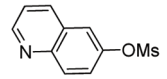
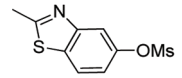
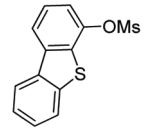
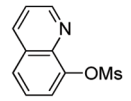
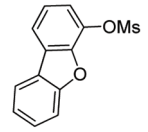
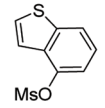
Table 3. Scope of Heteroaryl Mesylates



entry	HetAr-OMs		yield (%)
1		**3a**	94
2		**3b**	85
3		**3c**	89
4		**3d**	46
5		**3e**	72[a]
6		**3f**	93

[a] Conditions: 5 mol % of $PdCl_2(COD)$ 10 mol % of RuPhos.

The compatibility of heterocyclic substrates in the cross-coupling reaction with **1** was also examined. In this regard, the previously optimized conditions were initially applied to quinolin-6-yl methanesulfonate as a representative substrate: it transpired that the desired product **3a** was obtained in only 50% yield, and the reaction did not proceed to complete conversion. Different palladium sources were thus screened, and in this way total conversion was achieved by using 2 mol % of $PdCl_2(COD)$ instead of palladium acetate. The desired product of this reaction was isolated in 94% yield. Using these new reaction conditions, the transformations proceeded very well with a variety of structurally diverse heterocycles. Mesylated quinoline, benzothiazole, dibenzofuran, benzothiophene, and dibenzothiophene proved to be suitable partners, affording the corresponding cyclopropyl heteroarenes **3a**—**c**,**e**,**f** with yields ranging between 72% and 94% (Table 3). Only quinolin-8-yl methanesulfonate afforded the cross-coupled compound **3d** with a moderate yield, perhaps because of the coordination of the nitrogen to the palladium, which may partially inhibit the catalytic cycle.[44−46]

In conclusion, a convenient method to cross-couple a large array of aryl mesylates with potassium cyclopropyltrifluoroborate in high yields has been developed. The method is also efficient, with diverse heterocyclic mesylates as electrophiles, and provides cyclopropyl heteroarenes with very good yields. This new, environmentally sound strategy based on C—O activation of mesylates affords a complementary way to obtain cyclopropyl-functionalized molecules, known to be of interest for their biological properties.

EXPERIMENTAL SECTION

All of the mesylates were synthesized following a representative procedure.[42]

Procedure A: 1-Cyclopropylnaphthalene (2a). A Biotage microwave vial was charged with $Pd(OAc)_2$ (1.1 mg, 5.0 μmol), RuPhos (4.7 mg, 10 μmol), naphthalen-1-yl methanesulfonate (55.5 mg, 0.25 mmol), cyclopropyl trifluoroborate (47.2 mg, 0.33 mmol), and K_3PO_4 (382 mg, 1.80 mmol). The test tube was sealed with a cap lined with a disposable Teflon septum , evacuated under vacuum, and purged with argon three times. A *t*-BuOH/H_2O mixture (1.25 mL/1.25 mL) was added under argon. The reaction mixture was heated to 110 °C for 4 h before cooling to room temperature. The reaction mixture was extracted with EtOAc (3 × 2 mL) and then dried ($MgSO_4$). The solvent was removed in vacuo, and the crude product was purified by preparative silica gel chromatography (elution with hexanes/CH_2Cl_2 80/20) to give **2a** in 87% yield (36.6 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.57—7.54 (m, 1H), 7.51—7.48 (m, 1H), 7.40—7.37 (m, 1H), 7.28—7.26 (m, 1H), 2.38—2.33 (m, 1H), 1.09—1.05 (m, 2H), 0.79—0.76 (m, 2H). ^{13}C NMR (125 MHz, acetone-d_6): δ 139.0, 133.6, 133.4, 128.3, 126.3, 125.6, 125.5, 125.4, 124.1, 123.2, 12.7, 6.0. FT-IR (neat): 1596, 1509 cm^{-1}; HRMS (ESI): m/z calcd for $C_{13}H_{13}$ $(M + H)^+$ 169.1017, found 169.1015.

1-Cyclopropyl-4-methoxybenzene (2b). Following procedure A, the reaction was carried out with 4-methoxyphenyl methanesulfonate (101 mg, 0.50 mmol), $Pd(OAc)_2$ (5.6 mg, 25 μmol), and RuPhos (23.3 mg, 50.0 μmol) to give **2b** (71.2 mg, 96%) as a yellow oil after silica gel chromatography (elution with hexanes/EtOAc 98/2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 1.88—1.82 (m, 1H), 0.90—0.87 (m, 2H), 0.62—0.60 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 135.8, 126.8, 113.7, 55.3, 14.6, 8.5. FT-IR (neat): 1613, 1246, 1032 cm^{-1}. HRMS (ESI): m/z calcd for $C_{10}H_{13}O$ $(M + H)^+$ 149.0966, found 149.0963.

5-Cyclopropyl-1,2,3-trimethoxybenzene (2c). Following procedure A, the reaction was carried out with 3,4,5-trimethoxyphenyl methanesulfonate (131 mg, 0.50 mmol) to give **2c** (94.4 mg, 91%) as a yellow oil after silica gel chromatography (elution with hexanes/EtOAc 90/10). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.31 (s, 2H), 3.84 (s, 6H), 3.81 (s, 3H), 1.87—1.84 (m, 1H), 0.95—0.91 (m, 2H), 0.68—0.65 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 140.0, 136.4, 103.2, 61.2, 56.4, 16.2, 9.2. FT-IR (neat): 1585, 1246, 1236, 1127 cm^{-1}. HRMS (ESI): m/z calcd for $C_{12}H_{17}O_3$ $(M + H)^+$ 209.1178, found 209.1171.

1-Cyclopropyl-2-methoxybenzene (2d). Following procedure A, the reaction was carried out with 2-methoxyphenyl methanesulfonate (115 mg, 0.57 mmol), $Pd(OAc)_2$ (6.3 mg, 28 μmol), and RuPhos (26.6 mg, 57.0 μmol) to give **2d** (77.3 mg, 91%) as a yellow oil after silica gel chromatography (elution with hexanes/EtOAc 98/2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15—7.12 (m, 1H), 6.89—6.83 (m, 3H), 3.87 (s, 3H), 2.20—2.15 (m, 1H), 0.94—0.90 (m, 2H), 0.67—0.63 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.1, 131.9, 126.1, 124.7, 120.4, 110.1, 55.5, 9.2, 7.6. FT-IR (neat): 1244, 1029 cm^{-1}. HRMS (ESI): m/z calcd for $C_{10}H_{13}O$ $(M + H)^+$ 149.0966, found 149.0966.

4-Cyclopropyl-3-methoxybenzonitrile (2e). Following procedure A, the reaction was carried out with 4-cyano-2-methoxyphenyl methanesulfonate (56.8 mg, 0.25 mmol), $Pd(OAc)_2$ (2.8 mg, 12 μmol), and RuPhos (11.7 mg, 25.0 μmol) to give **2e** (28.1 mg, 91%) as a white solid after preparative silica gel chromatography (elution with hexanes/EtOAc

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90/10). Mp: 82−83 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (d, J = 7.9 Hz, 1H), 7.03 (s, 1H), 6.83 (d, J = 7.9 Hz, 1H), 3.88 (s, 3H), 2.25−2.20 (m, 1H), 1.04−1.00 (m, 2H), 0.71−0.68 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 138.9, 125.1, 125.0, 119.4, 112.9, 109.4, 55.9, 9.7, 9.1. FT-IR (neat): 2224, 1508, 1266, 1036 cm^{-1}. HRMS (ESI): m/z calcd for $C_{11}H_{11}NO$ $(M)^+$ 173.0841, found 173.0843.

4-Cyclopropyl-1,1′-biphenyl (2f). Following procedure A, the reaction was carried out with [1,1′-biphenyl]-4-yl methanesulfonate (124 mg, 0.50 mmol), $Pd(OAc)_2$ (5.6 mg, 25 μmol), and RuPhos (23.3 mg, 50.0 μmol) to give **2f** (40.4 mg, 42%) as a white solid after silica gel chromatography (elution with petroleum ether). Mp: 68−71 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 7.3 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.47−7.45 (m, 2H), 7.44−7.34 (m, 1H), 7.18 (d, J = 8.3 Hz, 2H), 2.00−1.94 (m, 1H), 1.05−1.01 (m, 2H), 0.79−0.77 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.4, 141.3, 138.5, 128.9, 127.2, 127.1, 126.2, 15.3, 9.5. FT-IR (neat): 1488 cm^{-1}. HRMS (ESI) m/z calcd. for $C_{15}H_{15}$ $(M + H)^+$ 195.1174, found 195.1176.

4-Cyclopropylphenylmethanone (2g). Following procedure A, the reaction was carried out with 4-benzoylphenyl methanesulfonate (69.0 mg, 0.25 mmol) to give **2g** (31.1 mg, 56%) as an off-white solid after preparative silica gel chromatography (elution with hexanes/EtOAc 95/5). Mp: 60−62 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 7.7 Hz, 2H), 7.71 (d, J = 7.9 Hz, 2H), 7.58−7.55 (m, 1H), 7.48−7.45 (m, 2H), 7.14 (d, J = 7.9 Hz, 2H), 1.99−1.94 (m, 1H), 1.08−1.06 (m, 2H), 0.80−0.79 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.5, 149.9, 138.2, 134.8, 132.3, 130.6, 130.0, 128.3, 125.4, 15.9, 10.5. FT-IR (neat): 1648, 1605 cm^{-1}. HRMS (ESI): m/z calcd for $C_{16}H_{15}O$ $(M + H)^+$ 223.1123, found 223.1129.

1-Cyclopropyl-4-methoxynaphthalene (2h). Following procedure A, the reaction was carried out with 4-methoxynaphthalen-1-yl methanesulfonate (63.0 mg, 0.25 mmol), $Pd(OAc)_2$ (2.8 mg, 12 μmol), and RuPhos (11.7 mg, 25.0 μmol) to give **2h** (44.5 mg, 90%) as a colorless oil after preparative silica gel chromatography (elution with petroleum ether/hexanes/EtOAc 68/30/2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (d, J = 8.3 Hz, 1H), 8.34 (d, J = 8.3 Hz, 1H), 7.63−7.60 (m, 1H), 7.56−7.53 (m, 1H), 7.23 (d, J = 7.9 Hz, 1H), 6.74 (d, J = 7.9 Hz, 1H), 4.00 (s, 3H), 2.30−2.25 (m, 1H), 1.06−1.04 (m, 2H), 0.76−0.74 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.4, 134.5, 131.3, 126.4, 125.8, 125.2, 124.5, 124.3, 122.5, 103.3, 55.6, 13.1, 6.2. FT-IR (neat): 1588, 1271, 1098 cm^{-1}. HRMS (ESI): m/z calcd for $C_{14}H_{14}O$ $(M)^{+\cdot}$ 198.1045, found 198.1047.

Methyl 6-Cyclopropyl-2-naphthoate (2i). Following procedure A, the reaction was carried out with methyl 6-((methylsulfonyl)-oxy)-2-naphthoate (70.0 mg, 0.25 mmol), $Pd(OAc)_2$ (2.8 mg, 12 μmol), and RuPhos (11.7 mg, 25.0 μmol) to give **2i** (24.7 mg, 44%) as a colorless oil after preparative silica gel chromatography (elution with hexanes/EtOAc 98/2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.55 (s, 1H), 7.23 (d, J = 8.5 Hz, 1H), 3.97 (s, 3H), 2.10−2.05 (m, 1H), 1.10−1.06 (m, 2H), 0.86−0.83 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 144.7, 135.9, 131.0, 131.0, 129.5, 127.5, 126.5, 125.6, 125.4, 123.7, 52.3, 16.0, 9.9. FT-IR (neat): 1706, 1292, 1209 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{14}O_2$ $(M + H)^+$ 227.1072, found 227.1075.

6-Cyclopropyl-2-naphthonitrile (2j). Following procedure A, the reaction was carried out with 6-cyanonaphthalen-2-yl methanesulfonate (61.8 mg, 0.25 mmol), $Pd(OAc)_2$ (2.8 mg, 12 μmol), and RuPhos (11.7 mg, 25.0 μmol) to give **2j** (28.0 mg, 58%) as a white solid after preparative silica gel chromatography (elution with hexanes/EtOAc 90/10). Mp: 103−104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.56−7.54 (m, 2H), 7.28 (dd, J = 8.6, 1.7 Hz, 1H), 2.11−2.05 (m, 1H), 1.12−1.10 (m, 2H), 0.86−0.85 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.6, 134.8, 133.8, 130.5, 128.3, 128.3, 126.5, 126.2, 123.7, 119.4, 108.0, 15.8, 9.9. FT-IR (neat): 2226, 1626 cm^{-1}. HRMS (ESI): m/z calcd for $C_{14}H_{12}N$ $(M + H)^+$ 194.0970, found 194.0973.

Procedure B: 6-Cyclopropylquinoline (3a). A Biotage microwave vial was charged with $PdCl_2(COD)$ (1.4 mg, 5.0 μmol), RuPhos (4.7 mg, 10 μmol), quinolin-6-yl methanesulfonate (55.8 mg, 0.25 mmol), cyclopropyl trifluoroborate (47.2 mg, 0.33 mmol), and K_3PO_4 (382 mg, 1.80 mmol). The test tube was sealed with a cap lined with a disposable Teflon septum, evacuated under vacuum, and purged with argon three times. A t-BuOH/H_2O mixture (1.25 mL/1.25 mL) was added under argon. The reaction mixture was heated to 110 °C for 16 h before cooling to room temperature. The reaction mixture was extracted with EtOAc (3 × 2 mL) and then dried ($MgSO_4$). The solvent was removed in vacuo, and the crude product was purified by preparative silica gel chromatography (elution with hexanes/EtOAc 80/20) to give **3a** in 94% yield (39.6 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.46 (s, 1H), 7.40 (d, J = 8.8 Hz, 1H), 7.33−7.31 (m, 1H), 2.08−2.05 (m, 1H), 1.06−1.04 (m, 2H), 0.81−0.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 147.0, 142.3, 135.2, 129.2, 128.2, 128.1, 123.3, 121.0, 15.4, 9.4. FT-IR (neat): 1592, 1499 cm^{-1}. HRMS (ESI): m/z calcd for $C_{12}H_{12}N$ $(M + H)^+$ 170.0970, found 170.0975.

5-Cyclopropyl-2-methylbenzo[*d*]thiazole (3b). Following procedure B, the reaction was carried out with 2-methylbenzo[d]thiazol-5-yl methanesulfonate (60.8 mg, 0.25 mmol) to give **3b** (40.3 mg, 85%) as a yellow oil after silica gel chromatography (elution with hexanes/EtOAc 95/5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, J = 8.3 Hz, 1H), 7.63 (d, J = 1.5 Hz, 1H), 7.09 (dd, J = 8.3, 1.5 Hz, 1H), 2.80 (s, 3H), 2.04−1.99 (m, 1H), 1.02−0.98 (m, 2H), 0.77−0.73 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 153.8, 142.3, 132.4, 123.3, 120.8, 118.9, 20.0, 15.3, 9.4. FT-IR (neat): 1525 cm^{-1}. HRMS (ESI): m/z calcd for $C_{11}H_{12}NS$ $(M + H)^+$ 190.0690, found 190.0695.

4-Cyclopropyldibenzo[*b*,*d*]thiophene (3c). Following procedure B, the reaction was carried out with dibenzo[b,d]furan-4-yl methanesulfonate (69.5 mg, 0.25 mmol) to give **3c** (49.7 mg, 89%) as a colorless oil after silica gel chromatography (elution with hexanes/EtOAc 95/5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17−8.14 (m, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.91−7.89 (m, 1H), 7.48−7.45 (m, 2H), 7.42−7.39 (m, 1H), 7.13 (d, J = 7.3 Hz, 1H), 2.18−2.12 (m, 1H), 1.12−1.08 (m, 2H), 0.89−0.86 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.8, 139.6, 137.7, 136.3, 135.5, 126.7, 124.9, 124.4, 123.2, 122.9, 121.9, 119.3, 15.0, 7.3. FT-IR (neat): 1442 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{12}S$ $(M)^+$ 224.0660, found 224.0662.

8-Cyclopropylquinoline (3d). Following procedure B, the reaction was carried out with quinolin-8-yl methanesulfonate (55.8 mg, 0.25 mmol) to give **3d** (19.3 mg, 46%) as a red oil after preparative silica gel chromatography (elution with hexanes/EtOAc 80/20). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.99 (dd, J = 3.9, 1.4 Hz, 1H), 8.15 (dd, J = 8.2, 1.4 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.47−7.40 (m, 2H), 7.20 (d, J = 7.0 Hz, 1H), 3.22−3.16 (m, 1H), 1.20−1.18 (m, 2H), 0.87−0.85 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 147.7, 142.7, 136.6, 128.4, 126.5, 125.2, 123.2, 121.1, 10.7, 9.6. FT-IR (neat): 1498 cm^{-1}. HRMS (ESI): m/z calcd for $C_{12}H_{12}N$ $(M + H)^+$ 170.0970, found 170.0977.

4-Cyclopropyldibenzo[*b*,*d*]furan (3e). Following procedure B, the reaction was carried out with dibenzo[b,d]furan-4-yl methanesulfonate (65.5 mg, 0.25 mmol), $PdCl_2(COD)$ (3.6 mg, 12 μmol), and RuPhos (11.8 mg, 25.0 μmol) to give **3e** (47.0 mg, 72%) as a colorless oil after preparative silica gel chromatography (elution with pentane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, J = 7.7 Hz, 1H), 7.76 (dd, J = 7.7, 0.9 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.49−7.47 (m, 1H), 7.37−7.35 (m, 1H), 7.28−7.25 (m, 1H), 7.04 (d, J = 7.7 Hz, 1H), 2.48−2.42 (m, 1H), 1.15−1.11 (m, 2H), 1.01−0.98 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.2, 155.3, 128.2, 127.1, 124.7, 123.8, 123.1, 123.0, 122.7, 120.9, 117.6, 111.8, 10.3, 8.2. FT-IR (neat): 1450, 1186, 1068 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{12}O$ $(M)^+$ 208.0888, found 208.0886.

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4-Cyclopropylbenzo[*b*]thiophene (3f). Following procedure B, the reaction was carried out with benzo[*b*]thiophen-4-yl methanesulfonate (57.0 mg, 0.25 mmol) to give **3f** (40.3 mg, 93%) as a yellow oil after silica gel chromatography (elution with pentane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 8.1 Hz, 1H), 7.67 (dd, J = 5.6, 0.9 Hz, 1H), 7.47 (d, J = 5.6 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 2.35−2.29 (m, 1H), 1.07−1.04 (m, 2H), 0.83−0.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.0, 139.7, 138.6, 125.9, 124.5, 122.3, 120.5, 120.1, 13.8, 7.5. FT-IR (neat): 1449, 1408 cm^{-1}. HRMS (ESI): m/z calcd for $C_{11}H_{11}S$ $(M + H)^+$ 175.0581, found 175.0579.

■ ASSOCIATED CONTENT

Supporting Information. Figures giving ^{1}H NMR and ^{13}C NMR spectral data for compounds **2a**−**j** and **3a**−**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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