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Palladium-Catalyzed Desulfitative Arylation by C−O Bond Cleavage of Aryl Triflates with Sodium Arylsulfinates

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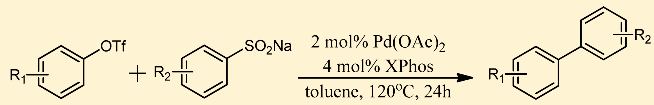
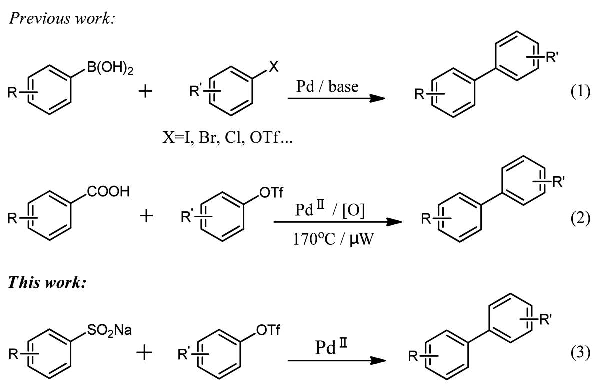
Supporting Information

ABSTRACT: An efficient Pd-catalyzed desulfitative coupling reaction of sodium arylsulfinates as arylation reagents by C−O bond cleavage of aryl triflates was developed. With only 2 mol % of $Pd(OAc)_2$ as catalyst and XPhos as ligand, the reaction proceeded well for a range of substrates.



Unsymmetrical biaryls are common building blocks for the synthesis of pharmaceuticals, natural products, and functional materials.[1] The palladium-catalyzed Suzuki-type cross-coupling reactions using organoboron as aryl donors provide a general and efficient route of C−C bond formation and have been widely applied to various industrial and academic research (Scheme 1, eq 1).[2] On the other hand, decarboxylative cross-coupling of aryl carboxylic acids has emerged in the past few years as an alternative to traditional transition-metal-catalyzed cross-coupling of preformed organometallic reagents (Scheme 1, eq 2).[3] Nevertheless, high reaction temperature (>170 °C) or microwave heating is required for the decarboxylation step.

Scheme 1. Methods for the Preparation of Unsymmetrical Biaryls



Recently, increasing attention has been attracted to the desulfitative coupling for the construction of C−C bonds via releasing SO_2 under relatively mild conditions.[4] Pioneering studies of desulfitative biaryl coupling were reported in 1970 by Garbes,[5] who first applied aryl sulfinic acids and their salts as aryl donors for the C−C bond-forming reactions. In 1992, Sato and Okoshi reported an efficient palladium-catalyzed desulfitative synthesis of biaryls with sodium arylsulfinates and aromatic bromides at 150 °C using *N*-methyl-2-pyrrolidone as solvent.[6] Recently, sodium arylsulfinates were not only investigated to couple with olefins,[7] azoles,[8] indoles[9] and heteroarenes[10] through C−H activation but also reacted with nitriles[11] and *α*,*β*-unsaturated carbonyl compounds[12] via addition reaction, which were used to compose sulphones.[13] Moreover, the Li group developed the rhodium-catalyzed coupling of aldehdyes with sodium arylsulfinates at high temperature (165 °C).[14] To the best of our knowledge, few successful example has been reported to date on the Pd-catalyzed desulfitative coupling reaction of sodium arylsulfinates as arylation reagents by C−O bond cleavage of aryl triflates, which can be readily synthesized from the corresponding phenols in high yields, utilizing sodium arylsulfinates as arylation reagents.

We have reported a palladium-catalyzed desulfitative conjugate addition of arylsulfinic acids with *α*,*β*-unsaturated carbonyl compounds and provided the mechanistic studies by ESI-MS.[12b] In this work, we investigate the utilization of sodium arylsulfinates in the regioselective C−C bond formation and disclose an efficient route for the rapid synthesis of unsymmetrical biaryls via palladium-catalyzed desulfitative arylation of sodium arylsulfinates with C−O bond cleavage of aryl triflates (Scheme 1, eq 3).

Initially, we investigated the desulfitative cross-coupling reaction by using 2-cyanophenyl triflate (**1a**) with sodium phenylsulfinate (**2a**) as a model reaction and screened several experimental parameters (ligand, solvent, etc.) shown in Table 1. We were pleased to find that with 2 mol % $Pd(OAc)_2$/dppp as the catalyst and dioxane as solvent, the reaction gave 2-cyanobiphenyl (**3a**) in 52% GC yield (Table 1, entry 1). Phosphine-type ligands such as dppf and PPh_3 were much more active than the nitrogen-type ligand phenanthroline (Table 1, entries 2−4). The biaryl phosphine-type ligand XPhos, which was relatively cheaper and more effective in the decarboxylative coupling reaction and C−O bond cleavage,[15] gave **3a** in 66% GC yield (Table 1, entry 5), and after prolonging the reaction time, 95% of 2-cyanobiphenyl (**3a**) was obtained (Table 1, entriy 7). Screening of solvents revealed that the toluene was the best solvent, and 99% GC yield is achieved even at 120 °C

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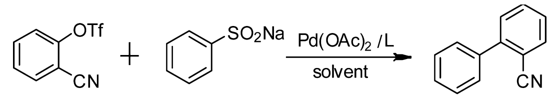
Table 1. Optimization of Reaction Conditions[a]



1a 2a 3a

entry	ligand/mol %	solvent	time (h)	yield[b] (%)
1	dppp/2	dioxane	16	52
2	dppf/2	dioxane	16	35
3	PPh_3/4	dioxane	16	37
4	phenanthroline/4	dioxane	16	nd
5	XPhos[c]/4	dioxane	16	66
6	dppp/2	dioxane	40	71
7	XPhos/4	dioxane	24	99 (95[d])
8	XPhos/4	NMP	24	15
9	XPhos/4	digylme	24	88
10	XPhos/4	dioxane/DMSO (9:1)	24	37
11	XPhos/4	toluene	24	97
12[e]	**XPhos/4**	**toluene**	**24**	**99 (97[d])**
13[f]	XPhos/4	toluene	24	77
14[e,g]	XPhos/4	toluene	24	trace

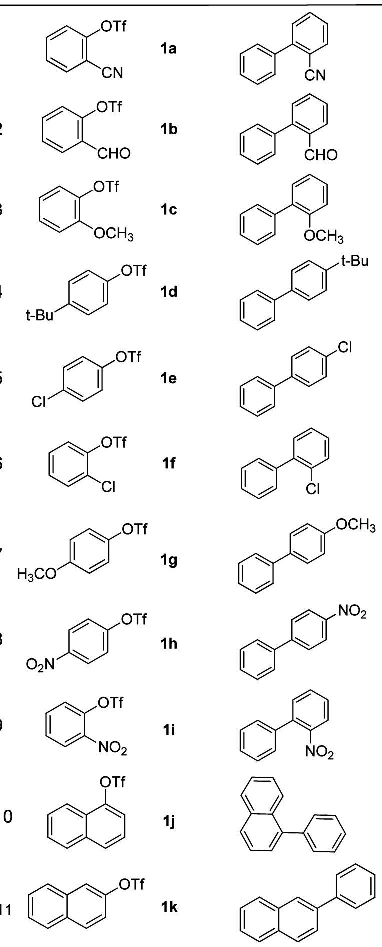
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $Pd(OAc)_2$ (2 mol %), and ligand in a solvent (1 mL) under nitrogen at 150 °C unless otherwise noted. [b]GC yield based on **1a**. [c]2-(Dicyclohexylphosphino)-2′,4′,6′-triisopropylbiphenyl. [d]Yield after column chromatography. [e]120 °C. [f]100 °C. [g]$Cu(OAc)_2$ (1 equiv).

(Table 1, entry 12). It is noteworthy that different from the decarboxylative coupling, the addition of $Cu(OAc)_2$ did not have a beneficial effect on the desulfitative cross-coupling reaction (Table 1, entry 14).

Under optimized conditions (2 mol % $Pd(OAc)_2$, 4 mol % XPhos, toluene, N_2, 120 °C, 24 h), the scope of the new protocol with regard to the aryl triflates coupling with sodium phenylsulfinate (**2a**) was investigated (Table 2). Notably, both electron-withdrawing groups as well as electron-donating groups at aryl triflates gave target products in good to excellent yields (Table 2, entries 1−6). Substituents, such as cyano, formyl, methoxy, and chloro, at the *ortho*-position did not show steric effects on the C−O bond cleavage and were all coupled in good yields (Table 2, entries 1−3 and 6). The yield of the 4-methoxyphenyl triflate was moderate (Table 2, entry 7). When there is a nitro group at the aryl triflate, the reaction almost did not take place, presumably due to the catalyst inactivation since the precipitation of Pd black was observed (Table 2, entries 8 and 9). Moreover, the 1-naphthyl and 2-naphthyl triflates substrates also reacted with **2a** smoothly (Table 2, entries 10 and 11).

Since 2-cyanobiphenyl compounds are key intermediates in the synthesis of angiotensin II receptor antagonists, for example, Losartan, Irbesartan, Valsartan, and Candesartan,[16] we further explored the scope of the desulfitative process with respect to various sodium arylsulfinate structures coupled with 2-cyanophenyltriflates (**1a**), which is summarized in Table 3. Sodium arylsulfinates bearing 4-methyl, methoxy, trifluoromethyl, and chloro groups coupled with 2-cyanophenyl triflate (**1a**) provided the target products in excellent yields (Table 3, entries 1 and 3−5). The yields of sodium arylsulfinates bearing 2-methyl and fluoro groups were moderate (Table 3, entries 2 and 7). Similar to the nitro aryl triflates (Table 2, entries 7 and 8), the reaction of sodium arylsulfinate bearing the nitro group almost did not take place (Table 3, entry 8). This may be

Table 2. Desulfitative Arylation of 2a with Various Aryl Triflates[a]



Entry	R_1	Product	Yield (%)
1	1a	3a	97
2	1b	3b	97
3	1c	3c	89
4	1d	3d	77
5	1e	3e	81
6	1f	3f	68
7	1g	3g	40[b]
8	1h	3h	25[b]
9	1i	3i	trace
10	1j	3j	79
11	1k	3k	60[c]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $Pd(OAc)_2$ (2 mol %), XPhos (4 mol %), and toluene (1 mL) in a sealed tube stirred at 120 °C for 24 h under nitrogen. [b]GC yield. [c]40 h.

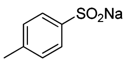
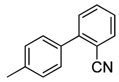
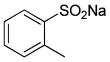
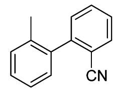
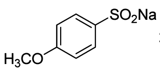
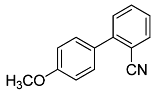
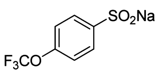
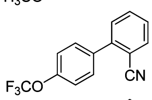
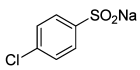
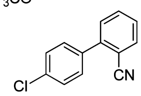
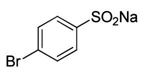
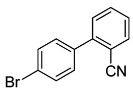
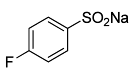
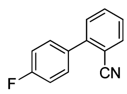
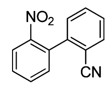
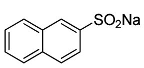
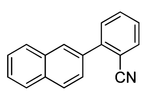
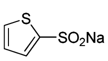
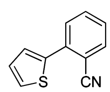
related to the poor solubility of the substrates and the catalyst inactivation, since the precipitation of Pd black in the reaction was also observed. Gratifyingly, the method was suitable for 2-naphthyl sodium sulfinate and heteroaromatic sodium sulfinate, which gave the desired product (**3u**) in excellent yield (92%) (Table 3, entries 9 and 10).

In conclusion, we have developed an efficient protocol for the Pd(II)-catalyzed desulfitative coupling reaction of sodium arylsulfinates with aryl triflates for the construction of C−C bonds. With only 2 mol % of $Pd(OAc)_2$ as catalyst and XPhos as ligand, aryl triflates and sodium arylsulfinates reacted smoothly at 120 °C, giving corresponding biaryls with moderate to excellent yields. This protocol, which is particularly suitable for arenesulfinates substrates, represents an important route in the evolution of desulfitative couplings into true synthetic alternatives to traditional couplings of preformed organometallic reagents.

■ EXPERIMENTAL SECTION

Preparation of Aryl Triflates.[17] Aryl triflates can be prepared by slowly adding a solution of Tf_2O (6 mmol) at a rate to maintain the reaction temperature <10 °C to a cooled (0 °C) biphasic mixture of toluene (10 mL), 30% (w/v) aqueous K_3PO_4 (10 mL), and the phenol (5 mmol). The reaction was allowed to a warm to ambient

Table 3. Desulfitative Arylation of 1a with Various Sodium Arylsulfinates[a]

Entry	R_2		Product		Yield (%)
1		2b		3l	90
2		2c		3m	80
3		2d		3n	89
4		2e		3o	95
5		2f		3p	91
6		2g		3q	22[b]
7		2h		3r	71[c]
8		2i		3s	trace
9		2j		3t	83
10		2k		3u	92

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $Pd(OAc)_2$ (2 mol %), XPhos (4 mol %), and toluene (1 mL) in a sealed tube stirred at 120 °C for 24 h under nitrogen. [b]GC yield. [c]$Pd(OAc)_2$ (3 mol %), XPhos (6 mol %) at 140 °C for 24 h.

temperature and stirred for 30 min. Then, the layers were separated and exteacted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with water (10 mL), dried over Na_2SO_4, filtered, concentrated in vacuo, and then purified by column chromatography to give the corresonding triflate.

General Procedure for the Cross-Coupling of Aryl Triflate with Sodium Arylsulfinate. A flame-dried test tube with a magnetic stirring bar was charged with $Pd(OAc)_2$ (0.9 mg, 0.004 mmol), XPhos (3.8 mg, 0.008 mmol), aryl triflate (0.2 mmol), sodium arylsulfinate (0.24 mmol), and toluene (1 mL) and purged with nitrogen three times. The mixture reacted at the 120 °C for 24 h and cooled to room temperature. The resulting solution was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent of petroleum ether and ethyl acetate. All physical data of the known compounds were in agreement with those reported in the literature.

[1,1′-Biphenyl]-2-carbonitrile (3a, CAS: 24973-49-7).[18] Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) to give a slightly yellow oil, 34.6 mg, 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.59 − 7.54 (m, 2H), 7.52 − 7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 138.3, 133.9, 133.0, 130.2, 128.9, 127.7, 118.9, 111.4; GC−MS (EI): *m*/*z* = 179 $[M]^+$.

[1,1′-biphenyl]-2-carbaldehyde (3b, CAS: 1203-68-5).[19] Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/40) to give a colorless oil; 35.1 mg, 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (d, *J* = 0.8 Hz, 1H), 8.03 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.64 (td, *J* = 7.2, 1.2 Hz, 1H), 7.53 − 7.43 (m, 5H), 7.38 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 146.2, 137.9, 133.9, 133.7, 130.9, 130.3, 128.6, 128.3, 128.0, 127.7; GC−MS (EI): *m*/*z* = 181 $[M − H]^+$.

2-Methoxy-1,1′-biphenyl (3c, CAS: 86-26-0).[19] Following the general procedure, the crude product was purified over a silica gel column using petroleum ether to give a slightly yellow oil; 32.7 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 6.6 Hz, 3H), 7.05 − 6.94 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 138.7, 131.0, 130.9, 129.7, 128.8, 128.1, 127.1, 121.0, 111.4, 55.7, 55.7; GC−MS (EI): *m*/*z* = 184 $[M]^+$.

4-(*tert*-Butyl)-1,1′-biphenyl (3d, CAS: 1625-92-9).[20] Following the general procedure, the crude product was purified over a silica gel column using petroleum ether to give a white solid, 43.0 mg, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.55 − 7.50 (m, 2H), 7.47 − 7.38 (m, 4H), 7.31 (t, *J* = 7.2 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 141.2, 138.5, 128.9, 127.2, 127.2, 127.0, 126.8, 125.9, 125.8, 34.7, 31.6; GC−MS (EI): *m*/*z* = 210 $[M]^+$

4-Chloro-1,1′-biphenyl (3e, CAS: 2051-62-9).[21] Following the general procedure, the crude product was purified over a silica gel column using petroleum ether to give a white solid, 31.7 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 − 7.46 (m, 4H), 7.45 − 7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 139.8, 133.5, 129.2, 129.1, 128.9, 128.6, 128.4, 127.8, 127.1; GC−MS (EI): *m*/*z* = 188 $[M]^+$.

2-Chloro-1,1′-biphenyl (3f, CAS:2051-60-7).[21] Following the general procedure, the crude product was purified over a silica gel column using petroleum ether to give a slightly yellow oil, 27.1 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 − 7.36 (m, 5H), 7.36 − 7.28 (m, 2H), 7.27 − 7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.5, 132.6, 131.5, 130.1, 129.6, 128.6, 128.2, 127.7, 127.0; GC−MS (EI): *m*/*z* = 188 $[M]^+$.

1-Phenylnaphthalene (3j, CAS: 605-02-7.).[22] Following the general procedure, the crude product was purified over a silica gel column using petroleum ether to give a colorless liquid, 34.5 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.55 − 7.38 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.4, 134.0, 131.8, 130.3, 128.4, 127.8, 127.4, 127.1, 126.19, 125.9, 125.6; GC−MS (EI): *m*/*z* = 204 $[M]^+$.

2-Phenylnaphthalene (3k, CAS: 612-94-2).[22] Following the general procedure, the crude product was purified over a silica gel column using petroleum ether to give a white solid, 24.2 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.95 − 7.83 (m, 3H), 7.76 − 7.71 (m, 3H), 7.54 − 7.43 (m, 4H), 7.38 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 138.7, 133.9, 132.8, 129.0, 128.6, 128.4, 127.8, 127.6, 127.5, 126.5, 126.1, 126.0, 125.8; GC−MS (EI): *m*/*z* = 204 $[M]^+$; HRMS (EI -TOF) calcd for $C_{16}H_{12}$ $[M]^+$ 204.0939, found 204.0935.

4′-Methyl-[1,1′-biphenyl]-2-carbonitrile (3l, CAS: 114772-53-1).[18] Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) to give a white solid, 35.1 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.51 − 7.38 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 138.8, 135.4, 133.9, 132.9, 130.1, 129.6, 128.8, 127.4, 21.4; GC−MS (EI): *m*/*z* = 193 $[M]^+$.

2′-Methyl-[1,1′-biphenyl]-2-carbonitrile (3m, CAS: 157366-46-6).[18] Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) to give a yellow oil, 31.0 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.62 (td, *J* = 7.7, 1.2 Hz, 1H), 7.44 (td, *J* = 7.7, 1.2 Hz, 1H), 7.38 − 7.24 (m, 4H), 7.20 (d, *J* = 7.7 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 138.2, 135.8, 133.0, 132.6, 130.6, 129.6, 128.9, 127.7, 126.0, 118.3, 113.0,

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20.0; GC−MS (EI): m/z = 193 $[M]^+$; HRMS (ESI-TOF) calcd for $C_{14}H_{11}NNa$ $[M + Na]^+$ 216.0789, found 216.0782.

4′-Methoxy-[1,1′-biphenyl]-2-carbonitrile (3n, CAS: 125610-78-8).[23] Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) to give a white solid, 37.8 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.52 − 7.47 (m, 3H), 7.39 (t, J = 8.0 Hz, 1H), 7.09 − 6.96 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 145.4, 133.9, 132.9, 130.7, 130.2, 130.0, 127.2, 119.2, 114.4, 111.2, 55.5; GC−MS (EI): m/z = 209 $[M]^+$.

4′-Trifluoromethoxy-[1,1′-biphenyl]-2-carbonitrile (3o). Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) to give a white solid, 49.7 mg, 95% yield, mp 46.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.52 − 7.45 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 144.2, 136.8, 134.0, 133.2, 130.5, 130.2, 128.2, 121.3, 118.6, 111.4; GC−MS (EI): m/z = 268 $[M]^+$; HRMS (ESI-TOF) calcd for $C_{14}H_8F_3NONa$ $[M + Na]^+$ 286.0456, found 286.0466.

4′-Chloro-1,1′-biphenyl-2-carbonitrile (3p, CAS: 89346-58-7).[24] Following the general procedure, the crude product was purified over a silica gel column using using ethyl acetate/petroleum ether (1/10) to give a white solid, 38.3 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.7 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.52 − 7.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 136.7, 135.2, 134.0, 133.1, 130.2, 130.1, 129.1, 128.0, 118.6, 111.3; GC−MS (EI): m/z = 236 $[M]^+$.

4′-Fluoro-[1,1′-biphenyl]-2-carbonitrile (3r, CAS: 89346-55-4).[25] Following the general procedure, the crude product was purified over a silica gel column using using ethyl acetate/petroleum ether (1/10) to give a slightly yellow solid, 27.9 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.57 − 7.41 (m, 4H), 7.18 (t, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 144. 6, 134.3, 133.9, 133.0, 130.8, 130.7, 130.1, 127.8, 118.7, 116.0, 115.8, 111.4; GC−MS (EI): m/z = 197 $[M]^+$.

2-(Naphthalen-2-yl)benzonitrile (3t, CAS: 66252-13-9).[23] Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/10) to give a white solid, 38.1 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.95 − 7.87 (m, 2H), 7.81 (d, J = 7.6 Hz, 1H), 7.71 − 7.60 (m, 3H), 7.56 − 7.53 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145. 7, 135.7, 134.1, 133.4, 133.3, 133.1, 130.6, 128.8, 128.5, 128.4, 127.9, 127.0, 126.5, 126.4, 119.0, 111.7; GC−MS (EI): m/z = 229 $[M]^+$.

2-(Thiophen-2-yl)benzonitrile (3u, CAS: 125610-77-7).[26] Following the general procedure, the crude product was purified over a silica gel column using ethyl acetate/petroleum ether (1/25) to give a yellow oil; 34.0 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 1H), 7.65 − 7.58 (m, 3H),7.43 (dd, J = 5.2, 0.8 Hz, 1H), 7.38 (td, J = 8.0, 0.8 Hz, 1H), 7.15 (td, J = 5.2, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 137.7, 134.5, 133.1, 129.9, 128.4, 127.7, 127.5, 119.0, 110.2; GC−MS (EI): m/z = 185 $[M]^+$; HRMS (ESI-TOF) calcd for $C_{11}H_7NNaS$ $[M + Na]^+$ 208.0197, found 208.0189.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR, ^{13}C NMR, and MS(EI) spectra of all compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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