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Chan–Lam-Type S-Arylation of Thiols with Boronic Acids at Room Temperature

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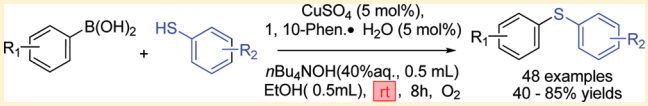
Supporting Information

ABSTRACT: In this work, an efficient $CuSO_4$-catalyzed S-arylation of thiols with aryl and heteroaryl boronic acids at room temperature is established. This catalytic system can tolerate a wide variety of thiols and arylboronic acids in the presence of only 5 mol % of $CuSO_4$ as the catalyst and inexpensive 1,10-phen·H_2O as the ligand. Moreover, this catalytic system used environment-friendly solvent (EtOH) and oxidant (oxygen).



INTRODUCTION

Transition-metal-catalyzed carbon–heteroatom cross-coupling reactions have made a great contribution to the recent growth of organic synthesis.[1] Although the aryl sulfides have broad application in the pharmaceutical industry and material science[2] and as intermediates in organic synthesis,[3] the formation of carbon–sulfur bonds has received less attention. Difficulties in C–S bond formation can be attributed to the sulfur species rapidly and irreversibly deactivating the catalyst.[4] So the efficient formation of the C–S bond is a most important aspect of organic chemistry. Many research groups have made great effort to overcome this problem in recent years, and several excellent catalytic systems that used Pd,[5] Cu,[6] Ni,[7] Fe,[4b,8] and other metals as catalysts have been found for C–S bond formation by couplings of aryl halides with thiols or disulfides.[9] However, the high cost and air sensitivity of Pd catalyst systems limit their applications in large-scale processes, and the scope of Cu and other transition-metal catalyst systems are suitable only for aryl bromides/iodides or triflates. So the development of a milder (room temperature), environment-friendly, cheap, and efficient catalyst system is still desirable.

With the wide variety of commercially available boronic acids and derivatives, the Chan–Lam reaction is emerging as an efficient and valuable alternative to traditional cross-couplings in the construction of carbon–heteroatom bonds.[10] Copper-promoted (mediated or catalyzed) coupling of amines[11] and phenols[12] with organoboronic acids and derivatives has made significant progress in the past few years since the initial report of Chan and Lam, which has found wide applications because of the mildness of the reaction conditions. However, few protocols for the direct coupling of arylboronic acid with thiols have been published.[13] In 2000, Guy et al.[14] reported the first C–S cross-coupling reaction of boronic acids with electron-rich alkyl thiols, albeit promoted by stoichiometric $Cu(OAc)_2$, which made progress in this field (Scheme 1a). Later, a protocol for the copper-catalyzed (20–30 mol %) synthesis of thioethers employing thioimide as a sulfide surrogate was described,[15] which used expensive CuMeSal as the catalyst and THF as the solvent at 50 °C (Scheme 1b). Recently, Tamiguchi[16a,b] and Li[16c] also reported copper-catalyzed C–S cross-coupling reaction of boronic acids with diaryldisulfane using DMSO/H_2O as solvent at 100 °C (Scheme 1c,d). The development of a general room-temperature S-arylation of thiols with arylboronic acids (particularly in environment-friendly solvents) remains a challenge for this field. Herein, we wish to develop a general protocol to achieve the oxidative cross-coupling reactions of diverse boronic acids with thiols using a simple copper catalyst in environment-friendly solvent at room temperature.

RESULTS AND DISCUSSION

Optimization of Reaction Conditions for Cu-Catalyzed Coupling of Phenylboronic Acid and Thiophenol. Our initial attempt to explore an effective catalytic system for the reaction of phenylboronic acid with thiophenol in the presence of $CuSO_4$ and 1,10-phenanthroline monohydrate under O_2 atmosphere at room temperature is shown in Table 1. It was observed that traditional inorganic bases only gave yields from 26% to 35% (Table 1, entries 1–3). Fortunately, when we switched to tetra-*n*-butylammonium hydroxide (nBu$_4$NOH (40% aq)), the yield increased to 48% (entry 4). To our surprise, the yield could be significantly increased when changing the ratio of nBu$_4$NOH (40% aq) and MeOH. We were pleased to find that the use of a 1:1 mixture of nBu$_4$NOH (40% aq) and MeOH gave the highest yield, and any other ratios resulted in lower yields (Table 1, entries 5–8). No significant improvement of the yield of the desired product **1a** was observed when other copper and iron salts, such as CuI, $CuCl_2$, and $FeCl_3$, were used as the catalysts (Table 1, entries 9–11). To improve the yield, different solvents were examined, and EtOH gave the best yield compared with other solvents (Table 1, entries 13–16). Interestingly, when the reaction time was shortened to 8 h, the yield increased slightly to 88% (Table

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Scheme 1. C−S Cross-Coupling Reaction of Boronic Acids

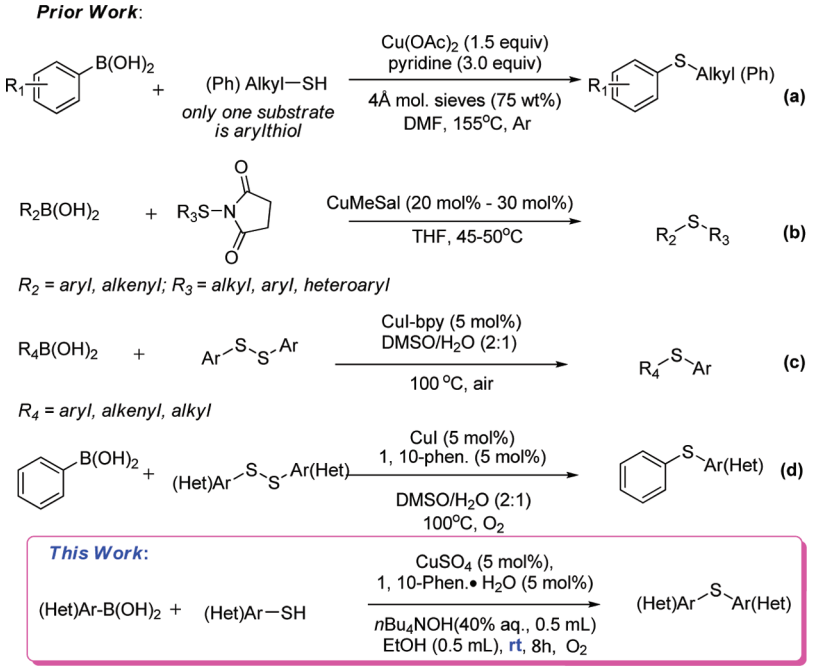
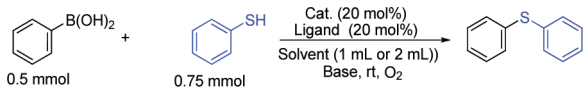


Table 1. Optimization of the Reaction Conditions[a]



entry	cat.	base	solvent	t (h)	yield (%)[b]
1	$CuSO_4$	Na_2CO_3 (5 equiv)	MeOH (2.0 mL)	24	26
2	$CuSO_4$	Cs_2CO_3 (5 equiv)	MeOH (2.0 mL)	24	35
3	$CuSO_4$	KO^{t}Bu (5 equiv)	MeOH (2.0 mL)	24	28
4	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	MeOH (1.5 mL)	24	48
5	$CuSO_4$	nBu$_4$NOH (40% aq, 0.4 mL)	MeOH (0.6 mL)	24	63
6	$CuSO_4$	nBu$_4$NOH (40% aq, 0.6 mL)	MeOH (0.4 mL)	24	51
7	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	MeOH (0.5 mL)	24	80
8	$CuSO_4$	nBu$_4$NOH (40% aq, 1.0 mL)		24	15
9	CuI	nBu$_4$NOH (40% aq, 0.5 mL)	MeOH (0.5 mL)	24	75
10	$CuCl_2$	nBu$_4$NOH (40% aq, 0.5 mL)	MeOH (0.5 mL)	24	58
11	$FeCl_3$	nBu$_4$NOH (40% aq, 0.5 mL)	MeOH (0.5 mL)	24	10
12	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	MeOH (0.5 mL)	24	34[c]
13	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	EtOH (0.5 mL)	24	85
14	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	DMSO (0.5 mL)	24	42
15	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	THF (0.5 mL)	24	73
16	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	DMF (0.5 mL)	24	60
17	**$CuSO_4$**	**nBu$_4$NOH (40% aq, 0.5 mL)**	**EtOH (0.5 mL)**	8	**88**
18	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	EtOH (0.5 mL)	6	80
19	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	EtOH (0.5 mL)	8	87[d]
20	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	EtOH (0.5 mL)	8	81[e]
21	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	EtOH (0.5 mL)	8	87[f]
22	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	EtOH (0.5 mL)	8	80[g]
23	$CuSO_4$	nBu$_4$NOH (40% aq, 0.5 mL)	EtOH (0.5 mL)	8	57[h]

[a]Unless otherwise noted, the reactions were carried out with phenylboronic acid (0.5 mmol), thiophenol (0.75 mmol), catalyst (20 mol %), ligand (1,10-phen·H_2O) (20 mol %), under O_2 atmosphere. [b]Determined by GC. [c]Ligand (2,2′-bipyridyl) (20 mol %), [d]5 mol % of $CuSO_4$, 5 mol % of 1,10-phen·H_2O were used. [e]2 mol % of $CuSO_4$, 2 mol % of 1,10-phen·H_2O were used. [f]1.4 equiv of thiophenol was used. [g]1.3 equiv of thiophenol was used. [h]Under air atmosphere.

1, entry 17). Further experiments indicated that the amount of $CuSO_4$ and 1,10-phenanthroline monohydrate could be decreased respectively to 5 mol % (Table 1, entries 19 and 20). Optimization of the amount of thiophenol showed that 1.4 equiv (with comparison of 1.0 equiv of phenylboronic acid) were necessary to achieve high yield (Table 1, entries 21 and 22). Note that only 57% desired product was obtained when using air as oxidant (Table 1, entry 23).

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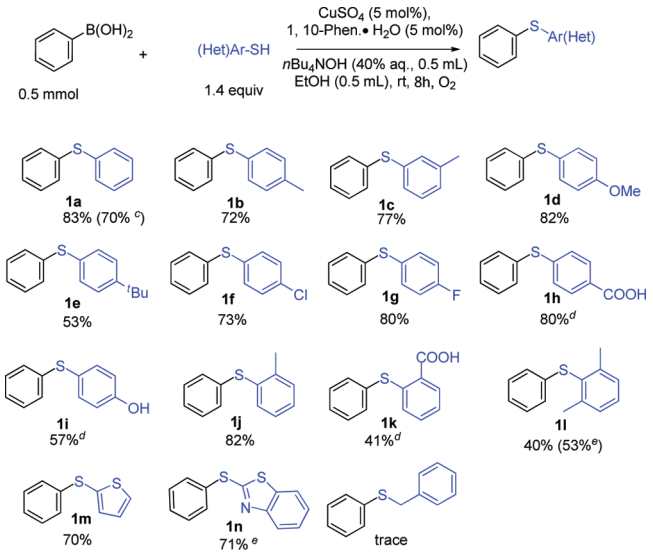
Scope of Cu-Catalyzed Chan–Lam-Type S-Arylation of Thiols with Boronic Acids at Room Temperature. To examine the scope and limitation of this protocol, the reactions of different aryl thiols (1.4 equiv of phenylboronic acid) with phenylboronic acid (0.5 mmol) were carried out under the optimized conditions (5 mol % $CuSO_4$, 5 mol % 1,10-phen·H_2O, nBu$_4$NOH (40% aq 0.5 mL), EtOH (0.5 mL), rt), and the results are summarized in Table 2. Both electron-rich and electron-poor substrates could give good to excellent yields of the corresponding desired products (**1a–h**). More importantly, the coupling of phenylboronic acid with thiophenol on a 20 mmol (gram) scale also gave 70% isolated yield, which made this protocol suitable for industrial application. To our delight, 4-hydroxythiophenol containing an OH group was also successfully coupled in good yield, avoiding oxidative C–O coupling (**1i**). Although 2-methylbenzenethiol gave excellent yield of cross-coupled product (**1j**), the more sterically hindered 2,6-dimethylbenzenethiol and 2-metrcaptobenzoic acid generated only moderate amounts of the S-arylation products (**1k,l**). Furthermore, reactions to generate aryl heteroaryl sulfides also occurred in high yields (**1m,n**), although a higher temperature and a longer reaction time were required for the 2-benzothiazolethiol. Unfortunately, aliphatic thiols (**1o**) were not suitable for this catalytic system.

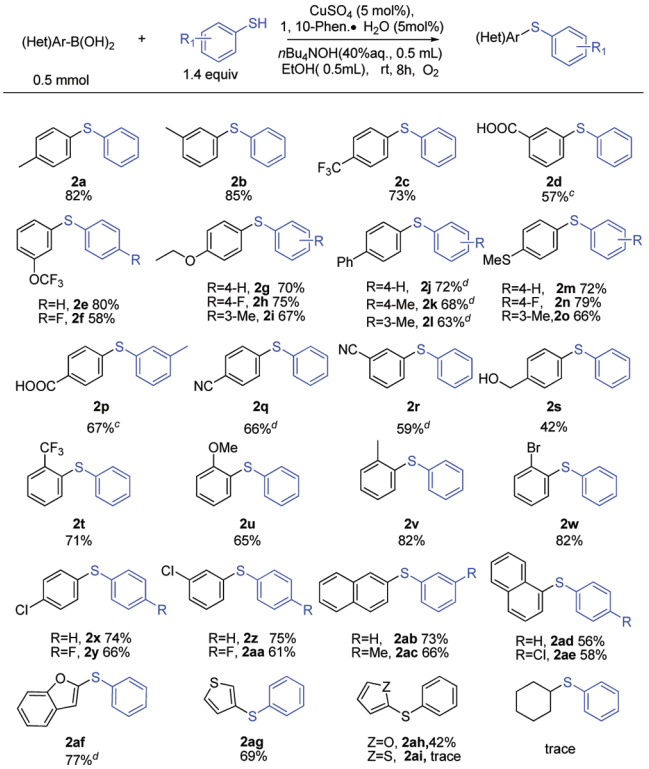
Table 2. Reaction of Phenylboronic Acid with Thiophenols[a,b]



[a]Reactions were carried out using phenylboronic acid (0.5 mmol) and thiols (0.7 mmol) at room temperature under O_2 atmosphere for 8 h. [b]Yields are given for isolated products. [c]Phenylboronic acid (20 mmol), thiophenol (28 mmol), nBu$_4$NOH (40% aq, 20.0 mL), EtOH (20.0 mL). [d]nBu$_4$NOH (40% aq, 1.0 mL), EtOH (1.0 mL), 24 h. [e]$CuSO_4$ (20 mol %), 1,10-phen·H_2O (20 mol %), 60 °C, 24 h.

The coupling of various arylboronic acids with an electron-rich thiophenol (*m*-toluenethiol), electron-neutral thiophenol (thiophenol), and electron-poor thiophenol (4-fluorobenzenethiol) were next investigated under the aforementioned optimized conditions (Table 3). The coupling appears to be insensitive to the electronic properties of the substrates. All reactions of both electron-rich and electron-poor arylboronic acids with thiophenols such as *m*-toluenethiol and 4-fluorobenzenethiol proceeded efficiently (**2a–r**). It was noted that for aryl boronic acids with *ortho* substitutents tthat are sterically hindered the yields also could reach to 65–82% (**2t–v**). Furthermore, the bromo or chloro group does not interfere with the transformation, which made additional cross-couplings at the halogenated positions (**2w–aa**). In addition, naphthaleneboronic acids with different substituted positions exhibited slightly different reactivities (**2ab–ae**). We were pleased to find that heteroaryl boronic acids such as 2-benzofuranboronic acid and 3-thiopheneboronic acid also provided the corresponding products in good yields (**2af–ag**), and 2-furanboronic acid gave a moderate yield (**2ah**). However, the reaction of 3-thiopheneboronic acid with thiophenol only gave a trace amount of product. It should be noted that this catalyst system is not suitable for alkyl boronic acids as substrates.

Table 3. Reaction of Arylboronic Acid with Thiols[a,b]



[a]Reactions were carried out using aryl or heteroaryl boronic acids (0.5 mmol) and thiols (0.7 mmol) at room temperature under O_2 atmosphere for 8 h. [b]Yields are given for isolated products. [c]nBu$_4$NOH (40% aq, 1.0 mL), EtOH (1.0, 24 mL), 24 h. [d]24 h.

Proposed Reaction Mechanism of the Copper-Catalyzed Coupling of Thiols with Boronic Acids. On the basis of the experimental observations, we propose the mechanism as follows (Scheme 2). Initially, $CuSO_4$ is quickly coordinated to 1,10-phen·H_2O to form Cu(II) intermediate **A**, followed by a transmetalation of the aryl group from boron to copper. Then there would be two paths to achieve the catalytic cycle. Because thiols are easily oxidized to disulfides by Cu (II) under O_2 atmosphere,[15] Cu(II) intermediate **C** and products are produced by the reaction of 1,2-diaryldisulfane with Cu(II) intermediate **B**.[16a] Then the Cu(II) intermediate **C** is proposed to undergo transmetalation with the aryl boronic acid to form intermediate **D**. Compared with the path **A**, another path is possible, because the reaction of 1,2-diphenyldisulfane with phenylboronic acid gave only diphenyl sulfide in 67% isolated yield under the aforementioned conditions (Scheme 3). This Cu(II) species **B** may undergo another transmetalation to

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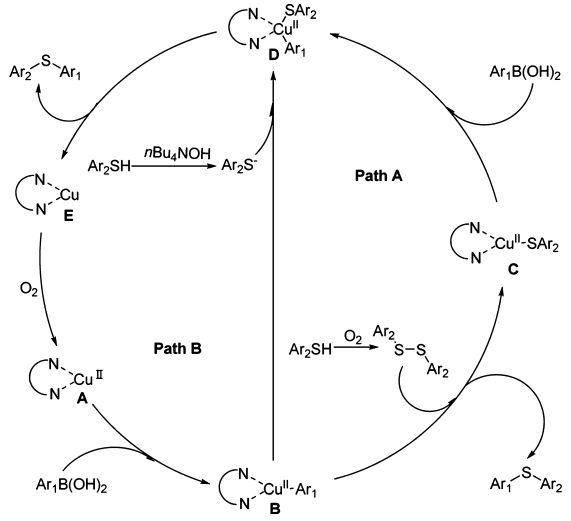
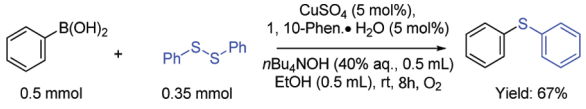
Scheme 2. Proposed Mechanism



Scheme 3. Reaction of 1,2-Diphenyldisulfane with Phenylboronic Acid



directly generate the intermediate **D** (Path B). Reductive elimination ensues to form the products and Cu(0) species, which is then oxidized by O_2 to regenerate the copper(II) to complete the catalytic cycle.

CONCLUSIONS

In summary, we developed a novel and highly efficient Cu-catalyzed protocol for S-arylation reaction of thiols by oxidative coupling with aryl and heteroaryl boronic acids at room temperature. A wide variety of thiols and arylboronic acids had been screened, and most of the substrates afforded the desired S-arylation products in good to excellent yields under mild conditions. This catalytic system used only 5 mol % of simple copper salt ($CuSO_4$) as catalyst and inexpensive 1,10-phen·H_2O as ligand. Moreover, the use of environment-friendly solvent (EtOH) and oxidant (oxygen) will make this methodology a powerful complement to the traditional S-arylation coupling reactions. More detailed mechanistic studies are presently being performed in our laboratory and will be reported in due time.

EXPERIMENTAL SECTION

General Procedures for Optimization of Reaction Conditions. A 25 mL oven-dried Schlenk tube was charged with Cu or Fe sources (2−20 mol %), ligand (2−20 mol %), and phenylboronic acid (0.5 mmol). The tube was evacuated and filled with oxygen (this procedure was repeated three times). Then solvent (0.5−2.0 mL) was added with a syringe under a counter flow of oxygen. After 2 min, nBu$_4$NOH (40% aq) (0.5−1.0 mL) was added with a syringe under a counter flow of oxygen. Next, thiophenol (0.65−0.75 mmol) was added with a syringe under a counter flow of oxygen. The resulting reaction mixture was stirred at 25 °C for 8−24 h. The reaction mixture was then diluted with Et_2O and filtered through silica gel with copious washings (Et_2O), and biphenyl (77 mg, 0.5 mmol) was added as internal standard. The yield was determined by GC.

Experimental Procedures for Reaction of Boronic Acids with Thiophenols (Tables 2 and 3). *General Procedure* ***A***. A 25 mL oven-dried Schlenk tube was charged with $CuSO_4$ (5 mol %, 4.0 mg), 1,10-phen·H_2O (5 mol %, 4.9 mg), aryl or heteroaryl boronic acids (0.5 mmol), and thiols (0.70 mmol) (if solid). The tube was evacuated and filled with oxygen (this procedure was repeated three times). Then EtOH (0.5 mL) was added with a syringe under a counter flow of oxygen. After 2 min, nBu$_4$NOH (40% aq) (0.5 mL) was added with a syringe under a counter flow of oxygen. Next, thiol (0.70 mmol) (if liquid) was added with a syringe under a counter flow of oxygen. The resulting reaction mixture was stirred at 25 °C for 8 h. The reaction mixture was then diluted with Et_2O, filtered through silica gel with copious washings (Et_2O or EtOAc), concentrated, and purified by column chromatography.

General Procedure ***B***. A 25 mL oven-dried Schlenk tube was charged with $CuSO_4$ (5 mol %, 4.0 mg), 1,10-phen·H_2O (5 mol %, 4.9 mg), aryl or heteroaryl boronic acids (0.5 mmol), and thiols (0.70 mmol) (if solid). The tube was evacuated and filled with oxygen (this procedure was repeated three times). Then EtOH (1.0 mL) was added with a syringe under a counter flow of oxygen. After 2 min, nBu$_4$NOH (40% aq) (1.0 mL) was added with a syringe under a counter flow of oxygen. Next, thiol (0.70 mmol) (if liquid) was added with a syringe under a counter flow of oxygen. The resulting reaction mixture was stirred at 25 °C for 24 h. The reaction mixture was then diluted with Et_2O, filtered through silica gel with copious washings (Et_2O or EtOAc), concentrated, and purified by column chromatography.

General Procedure ***C***. A 25 mL oven-dried Schlenk tube was charged with $CuSO_4$ (20 mol %, 16.0 mg), 1,10-phen·H_2O (20 mol %, 20.0 mg), aryl or heteroaryl boronic acids (0.5 mmol), and thiols (0.70 mmol) (if solid). The tube was evacuated and filled with oxygen (this procedure was repeated three times). Then EtOH (0.5 mL) was added with a syringe under a counter flow of oxygen. After 2 min, nBu$_4$NOH (40% aq) (0.5 mL) was added with a syringe under a counter flow of oxygen. Next, thiol (0.70 mmol) (if liquid) was added with a syringe under a counter flow of oxygen. The resulting reaction mixture was stirred at 60 °C for 24 h. The reaction mixture was then diluted with Et_2O, filtered through silica gel with copious washings (Et_2O or EtOAc), concentrated, and purified by column chromatography.

General Procedure ***D***. A 25 mL oven-dried Schlenk tube was charged with $CuSO_4$ (5 mol %, 4.0 mg), 1,10-phen·H_2O (5 mol %, 4.9 mg), aryl or heteroaryl boronic acids (0.5 mmol), and thiols (0.70 mmol) (if solid). The tube was evacuated and filled with oxygen (this procedure was repeated three times). Then EtOH (0.5 mL) was added with a syringe under a counter flow of oxygen. After 2 min, nBu$_4$NOH (40% aq) (0.5 mL) was added with a syringe under a counter flow of oxygen. Next, thiol (0.70 mmol) (if liquid) was added with a syringe under a counter flow of oxygen. The resulting reaction mixture was stirred at 25 °C for 24 h. The reaction mixture was then diluted with Et_2O, filtered through silica gel with copious washings (Et_2O or EtOAc), concentrated, and purified by column chromatography.

Diphenyl Sulfide (1a).[6p] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.30 (m, 5H), 7.28−7.19 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8, 131.0, 129.2, 127.0.

4-Methylphenyl Phenyl Sulfide (1b and 2a).[6p] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−6.20 (m, 9H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 137.2, 132.4, 131.4, 130.1, 129.8, 129.1, 126.5, 21.2.

3-Methylphenyl Phenyl Sulfide (1c and 2b).[6p] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.15 (m, 8H), 7.05 (d, J = 6.9 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 136.2, 135.3, 131.9, 130.8, 129.2, 129.1, 128.4, 128.1, 126.9, 21.3.

4-Methoxyphenyl Phenyl Sulfide (1d).[6p] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 8.7 Hz, 2H), 7.16−7.05 (m, 5H), 6.81 (d, J = 8.7 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 138.6, 135.3, 128.9, 128.3, 125.8, 124.4, 115.0, 55.3.

4-*tert*-Butylphenyl Phenyl Sulfide (1e).[17] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.17 (m, 9H), 1.31 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 136.7, 131.5, 131.7, 130.3, 129.1, 126.6, 126.3, 34.6, 31.3.

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4-Chlorophenyl Phenyl Sulfide (1f and 2x).[6p] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33−7.28 (m, 5H), 7.27−7.25 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 134.7, 133.0, 132.0, 131.4, 129.4, 129.3, 127.5.

4-Fluorophenyl Phenyl Sulfide (1g).[17] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−35 (m, 2H), 7.28−7.21 (m, 5H), 7.02 (t, J = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 160.8, 136.7, 134.2, 134.1, 130.2, 130.0, 129.2, 126.8, 116.6, 116.3.

4-(Phenylthio)benzoic Acid (1h).[8b] Following general procedure B, white soild, mp 173.4−174.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.09 (brs, 1H), 7.95 (d, J = 8.7 Hz, 2H), 7.53−7.50 (m, 2H), 7.44−7.40 (m, 3H), 7.20 (d, J = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 146.0, 134.1, 131.9, 130.7, 129.7, 128.9, 127.2, 126.4.

4-Phenylsulfanyl-phenol (1i).[6p] Following general procedure B, a light yellow soid, mp 50.2−50.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 8.7 Hz, 2H), 7.28−7.12 (m, 5H), 6.83 (d, J = 8.7 Hz, 2H), 5.11 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 138.3, 135.4, 128.8, 128.1, 125.7, 124.3, 116.4.

2-Methylphenyl Phenyl Sulfide (1j and 2v).[6p] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31−7.13 (m, 9H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 136.3, 133.8, 133.1, 130.7, 129.7, 129.2, 128.0, 126.8, 126.4, 20.6.

2-(Phenylthio)benzoic Acid (1k).[4b] Following general procedure B, white soild, mp 166.5−167.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (brs, 1H), 8.14 (dd, J = 7.8, 1.6 Hz, 1H), 7.61−7.57 (m, 2H), 7.46−7.44 (m, 3H), 7.31−7.25 (m, 1H), 7.15 (td, J = 7.6, 1.1 Hz, 1H), 6.81 (dd, J = 8.2, 1.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 144.6, 135.8, 133.1, 132.2, 132.1, 129.8, 129.3, 127.2, 125.4, 124.3.

2,6-Dimethylphenyl Phenyl Sulfide (1l).[5j] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.27 (m, 1H), 7.25−7.19 (m, 4H), 7.12−7.07 (m, 1H), 6.98−6.98 (m, 2H), 2.47 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 138.1, 130.5, 129.3, 128.9, 128.5, 125.7, 124.6, 21.8.

2-(Phenylthio)thiophene (1m).[5j] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (dd, J = 5.4, 1.3 Hz, 1H), 7.29−7.13 (m, 6H), 7.05 (dd, J = 5.4, 3.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 136.1, 131.3, 131.2, 129.0, 128.0, 127.2, 126.1.

2-Phenylsulfanyl-benzothiazole (1n).[4b] Following general procedure C, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 1H), 7.66−7.63 (m, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.42−7.26 (m, 4H), 7.16 (td, J = 7.5, 1.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5, 153.8, 135.5, 135.3, 130.3, 129.8, 126.1, 124.3, 121.9, 120.7.

4-Trifluoromethylphenyl Phenyl Sulfide (2c).[5j] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.47 (m, 4H), 7.41−7.38 (m, 3H), 7.27 (d, J = 10.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 133.5, 132.6, 129.7, 128.6, 128.3, 127.9, 125.82 (q, J = 3.8 Hz), 122.3.

3-(Phenylthio)benzoic acid (2d).[5k] Following general procedure B, yellow solid, mp 107.7−108.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.04 (brs, 1H), 8.05 (t, J = 1.6 Hz, 1H), 7.95 (dt, J = 7.7, 1.3 Hz, 1H), 7.56−7.46 (m, 1H), 7.43−7.32 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 137.7, 135.3, 134.2, 132.1, 131.6, 130.3, 129.5, 129.3, 128.4, 127.9.

3-Ttrifluoromethoxyphenyl Phenyl Sulfide (2e). Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44−7.27 (m, 5H), 7.23 (s, 1H), 7.14 (d, J = 7.9 Hz, 1H), 7.07 (s, 1H), 7.02 (d, J = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 139.5, 133.5, 132.7, 130.1, 129.5, 128.2, 127.6, 122.1, 121.7, 118.7. HRMS calcd for $C_{13}H_9F_3OS$ (M+) 270.0326; found 270.0321.

3-Ttrifluoromethoxyphenyl 4-Fluorophenyl Sulfide (2f). Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, J = 8.9, 5.2 Hz, 2H), 7.22 (t, J = 4.0 Hz, 1H), 7.07−6.97 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9 (d, J = 249.2 Hz), 139.5, 135.3 (d, J = 8.3 Hz), 135.0, 130.1, 128.6, 127.0, 126.5, 116.74 (d, J = 22.0 Hz). HRMS calcd for $C_{13}H_8F_4OS$ (M+) 288.0232; found 288.0234.

4-Ethoxyphenyl Phenyl Sulfide (2g).[18] Following general procedure A, a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 8.9 Hz, 2H), 7.25−7.10 (m, 5H), 6.87 (d, J = 8.8 Hz, 2H), 4.03 (q, J = 7.0 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 138.7, 135.4, 128.91, 128.2, 125.7, 124.1, 115.5, 63.6, 14.8.

4-Ethoxyphenyl 4-Fluorophenyl Sulfide (2h). Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 8.9 Hz, 2H), 7.25−7.15 (m, 2H), 6.95 (t, J = 8.7 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 4.03 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ161.6 (d, J = 245.9 Hz), 159.1, 134.5, 133.2 (d, J = 3.3 Hz), 131.0 (d, J = 8.0 Hz), 125.0, 116.0 (d, J = 22.0 Hz), 115.5, 63.6, 14.8. HRMS calcd for $C_{14}H_{13}FOS$ (M+) 248.0671; found 248.0675.

4-Ethoxyphenyl 3-Methylphenyl Sulfide (2i). Following general procedure A, a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 8.9 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 7.03 (s, 1H), 6.99−6.95 (m, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.05 (q, J = 7.0 Hz, 2H), 2.28 (s, 3H), 1.43 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 138.7, 138.3, 135.2, 128.9, 128.8, 126.7, 125.5, 124.4, 115.5, 63.6, 21.3, 14.8. HRMS calcd for $C_{15}H_{16}OS$ (M+) 244.0922; found 244.0919.

4-Phenylphenyl Phenyl Sulfide (2j).[19] Following general procedure D, white solid, mp 69.9−70.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57−7.50 (m, 4H), 7.44−7.22 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 140.0, 135.8, 135.0, 131.3, 131.2, 129.3, 128.9, 127.9, 127.5, 127.2, 127.0.

4-Phenylphenyl 4-Methylphenyl Sulfide (2k). Following general procedure D, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59− 7.56 (m, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.44−7.41 (m, 2H), 7.38−7.33 (m, 5H), 7.17 (d, J = 7.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 139.5, 137.8, 136.5, 132.5, 131.4, 130.3, 130.2, 129.0, 127.9, 127.5, 127.1, 21.3. HRMS calcd for $C_{19}H_{16}S$ (M+) 276.0973; found 276.0965.

4-Phenylphenyl 3-Methylphenyl Sulfide (2l). Following general procedure D, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57−7.49 (m, 4H), 7.44−7.32 (m, 5H), 7.23−7.19 (m, 3H), 7.07 (s, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 139.8, 139.2, 135.3, 135.2, 132.0 131.0, 129.1, 128.9, 128.5, 128.2, 127.8, 127.5, 127.0, 21.3. HRMS calcd for $C_{19}H_{16}S$ (M+) 276.0973; found 276.0968.

4-Methylthiophenyl Phenyl Sulfide (2m).[20] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31−7.17 (m, 9H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 136.5, 132.3, 131.5, 130.2, 129.2, 127.2 126.8, 15.8.

4-Methylthiophenyl 4-Fluorophenyl Sulfide (2n). Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33−7.29 (m, 2H), 7.26−7.12 (m, 4H), 6.99 (t, J = 8.7 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ162.2 (d, J = 247.4 Hz), 137.9, 133.2 (d, J = 8.1 Hz), 132.4, 131.3, 131.0 (d, J = 3.3 Hz), 127.3, 116.4 (d, J = 22.0 Hz), 15.8. HRMS calcd for $C_{13}H_{11}FS_2$ (M+) 250.0286; found 250.0290.

4-Methylthiophenyl 3-Methylphenyl Sulfide (2o). Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 8.5 Hz, 2H), 7.21−7.03 (m, 6H), 2.48 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 138.0, 136.0, 132.1, 131.9, 131.0, 129.0, 127.8, 127.5, 127.2, 21.3, 15.8. HRMS calcd for $C_{14}H_{14}S_2$ (M+) 246.0537; found 246.0542.

4-(*m*-Tolylthio)benzoic Acid (2p). Following general procedure B, white solid, mp 166.4−167.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (brs, 1H), 7.97 (d, J = 8.5 Hz, 2H), 7.37−7.21 (m, 6H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 146.3, 139.7, 134.7, 131.4, 131.2, 130.6, 129.8, 129.5, 127.1, 126.2, 21.3. HRMS calcd for $C_{14}H_{12}O_2S$ (M+) 244.0558; found 244.0556.

4-(Phenylthio)benzonitrile (2q).[6p] Following general procedure A, a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53−7.41 (m, 7H), 7.17 (d, J = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7, 134.5, 132.4, 130.9, 129.9, 129.4, 127.4, 118.8, 108.8.

3-(Phenylthio)benzonitrile (2r).[5j] Following general procedure D, a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47−7.31 (m,

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9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 133.4, 132.9, 132.2, 131.7, 129.8, 129.6, 129.5, 128.8, 118.3, 113.4.

(4-(Phenylthio)phenyl)methanol (2s).[5j] Following general procedure A, white soild, mp 47.8−48.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.22 (m, 9H), 4.65 (s, 2H), 1.85 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 135.8, 135.0, 131.3, 131.0, 129.2, 127.8, 127.1, 64.8.

2-Trifluoromethylphenyl Phenyl Sulfide (2t).[6d] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 6.7 Hz, 1H), 7.45−7.23 (m, 1H), 7.18 (d, J = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 133.9, 133.0, 132.4, 132.1, 129.5, 128.2, 126.7 (q, J = 5.6 Hz), 126.3, 125.6, 122.0.

2-Methoxyphenyl Phenyl Sulfide (2u).[6p] Following general procedure A, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.27 (m, 4H), 7.26−7.20 (m, 2H), 7.09 (dd, J = 7.7, 1.7 Hz, 1H), 6.91−6.83 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 134.6, 131.7, 131.5, 129.1, 128.4, 127.1, 124.1, 121.3, 110.9, 55.9.

2-Bromophenyl Phenyl Sulfide (2w).[6p] Following general procedure A, a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, J = 7.9, 1.4 Hz, 1H), 7.48−7.37 (m, 5H), 7.18−7.12 (m, 1H), 7.06−7.01 (m, 1H), 6.95 (dd, J = 7.8, 1.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 133.5, 133.1, 133.0, 129.9, 129.6, 128.4, 127.8, 127.3, 123.2.

4-Chlorophenyl 4-Fluorophenyl Sulfide (2y).[21] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, J = 8.9, 5.2 Hz, 2H), 7.25−7.21 (m, 2H), 7.18−7.15 (m, 2H), 7.03 (t, J = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (d, J = 248.5 Hz), 135.43 (s), 134.3 (d, J = 8.2 Hz), 132.8, 131.0 129.7 (d, J = 3.4 Hz), 129.3, 116.6 (d, J = 22.0 Hz).

3-Chlorophenyl Phenyl Sulfide (2z).[22] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.29 (m, 5H), 7.24−7.23 (m, 1H), 7.18−7.12 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 134.9, 134.0, 132.3, 130.1, 129.5, 129.1,128.0, 127.9, 126.8.

3-Chlorophenyl 4-Fluorophenyl Sulfide (2aa).[23] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, J = 8.8, 5.2 Hz, 2H), 7.23−7.13 (m, 3H), 7.12−7.03 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 161.2, 139.5, 135.3, 135.2,135.0, 130.1, 128.6, 127.0, 126.5, 116.9, 116.6.

Naphthalen-2-yl(phenyl)sulfane (2ab).[4b] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83−7.70 (m, 4H), 7.46−7.20 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9, 133.8, 133.1, 132.3, 131.0, 129.9, 129.3, 128.9, 128.8, 127.8, 127.5, 127.1, 126.6, 126.2.

Naphthalen-2-yl(*m*-tolyl)sulfane (2ac). Following general procedure A, white soild, mp 60.4−60.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80−7.65 (m, 4H), 7.44−7.36 (m, 3H), 7.21−7.17 (m, 3H), 7.05 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 135.4, 133.9, 133.4, 132.3, 131.8 129.6, 129.1, 128.8, 128.7, 128.3, 128.1, 127.8, 127.5, 126.6, 126.2, 21.3. HRMS calcd for $C_{17}H_{14}S$ (M+) 250.0816; found 250.0820.

Naphthalen-1-yl(phenyl)sulfane (2ad).[6p] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40−8.35 (m, 1H), 7.88−7.83 (m, 2H), 7.66 (dd, J = 7.2, 1.2 Hz, 1H), 7.52−7.41 (m, 2H), 7.41 (dd, J = 8.2, 7.2 Hz, 1H), 7.22−7.12 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 134.3, 133.6, 132.6, 131.3, 129.2, 129.1, 129.0, 128.6, 127.0, 126.5, 126.2, 125.8, 125.7.

(4-Chlorophenyl)(naphthalen-1-yl)sulfane (2ae).[24] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (dd, J = 6.2, 3.3 Hz, 1H), 7.85 (d, J = 7.4 Hz, 2H), 7.67 (d, J = 7.1 Hz, 1H), 7.50 (dd, J = 6.3, 3.3 Hz, 2H), 7.42 (t, J = 7.7 Hz, 1H), 7.15 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 8.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7, 134.2, 133.5, 132.9, 131.8, 130.4, 129.8, 129.5, 129.0, 128.5, 127.0, 126.4, 125.7, 125.4.

2-(Phenylthio)benzofuran (2af). Following general procedure D, white solid, mp 73.7−74.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 9.0 Hz, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.35−7.21 (m, 7H), 7.02 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 148.0, 134.3, 129.3, 129.2, 128.4, 127.2, 125.2, 123.1, 121.0, 114.3, 111.4. HRMS calcd for $C_{14}H_{10}OS$ (M+) 226.0452; found 226.0455.

3-(Phenylthio)thiophene (2ag).[5k] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.35 (m, 2H), 7.28−7.18 (m, 5H), 7.04 (dd, J = 4.3, 2.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 131.2, 129.4, 129.0, 128.5, 128.1, 126.7, 126.2.

2-(Phenylthio)furan (2ah).[25] Following general procedure A, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, J = 1.9, 0.8 Hz, 1H), 7.27−7.22 (m, 2H), 7.18−7.13 (m, 3H), 6.74 (dd, J = 3.2, 0.8 Hz, 1H), 6.46 (dd, J = 3.2, 2.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 143.2, 136.3, 129.1, 127.6, 126.4, 119.5, 111.9.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for the products. 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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