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Synthesis of Di-, Tri-, and Tetrasulfides through Multifold Carbon−Sulfur Cross-Coupling Reactions with Indium Tri(organothiolates) in a One-Pot Procedure

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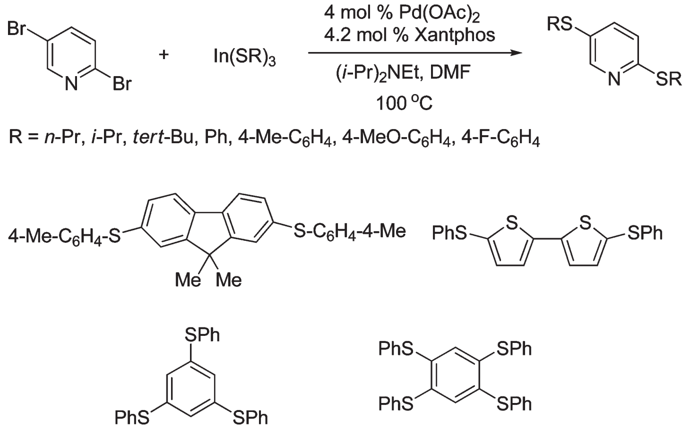

Pd-catalyzed multifold (2-, 3-, and 4-fold) carbon−sulfur cross-coupling reaction of indium tri(organothiolates) with polybromonated aromatic and heteroaromatic compounds was developed in a one-pot procedure. Both 2,5-dibromopyridine and 2,6-dibromopyridine reacted with indium tri(organothiolates) (0.68 equiv) in the presence of 4 mol % of $Pd(OAc)_2$, 4.2 mol % of Xantphos, and 1 equiv of diisopropylethylamine (DIPEA), producing disulfides in good to excellent yields. These results indicate that indium tri(organothiolates) transfer all three alkyl- or arylthio groups attached to indium metal to electrophilic coupling partners. Indium tri(organothiolates) derived from alkyl thiol having a low boiling point, such as *n*-propyl, isopropyl, and *tert*-butyl thiol, acted as good nucleophilic coupling partners. In addition, indium tri(arylthiolates) derived from aryl thiols possessing an electron-withdrawing or -donating group on the aromatic ring participated well in the Pd-catalyzed multifold carbon−sulfur cross-coupling reaction. 4,4′-Dibromo-1,1′-biphenyl, 9,10-dibromoanthracene, 2,4-dibromoanisole, 2,7-dibromo-9,9-dimethylfluorene, 3,4-dibromothiophene, 2,3-dibromothiophene, 2,2′-bithiophene, 1,3,5-tribromobenzene, and 1,2,4,5-tetrabromobenzene were converted smoothly to the corresponding di-, tri-, and tetrasulfides.

Introduction

The transition-metal-catalyzed carbon−sulfur cross-coupling reaction is one of the fundamental processes in organic synthesis because the sulfide functional group is widely used in pharmaceuticals, functional materials, and synthesis of natural products.[1] Over the last decades, transition metals, such as Pd,[2] Ni,[3] Cu,[4] and Fe,[5] have been applied in carbon−sulfur cross-coupling reactions, leading to the effective formation of sulfides with a wide range of functional group tolerance. However, disulfides are frequently formed as byproduct by oxidative processes, and sometimes

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SCHEME 1. Multifold Carbon−Sulfur Cross-Coupling Reaction with Indium Tri(organothiolates)

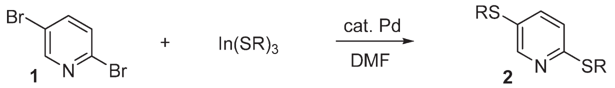
$$\text{Ar—(Br)}_n + \text{In(SR)}_3 \xrightarrow{\text{cat. Pd}} \text{Ar—(SR)}_n$$

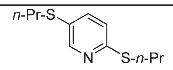
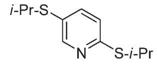
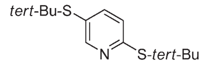
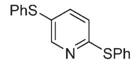
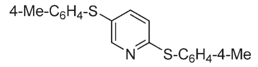
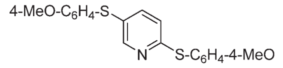
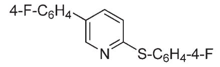
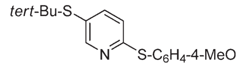
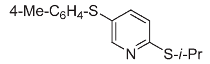
$$\text{Heteroaryl—(Br)}_n + \text{In(SR)}_3 \xrightarrow{\text{cat. Pd}} \text{Heteroaryl—(SR)}_n$$

thiols retard the coupling reaction. In many cases, excessive thiols have been used as nucleophiles in cross-coupling reactions under harsh conditions.[2−5] Development of synthetic method of more than one carbon−sulfur bond through multifold cross-coupling reactions in a one-pot procedure has recently been focused. Therefore, multifold cross-coupling reaction for carbon−sulfur bond formation to produce di-, tri-, and tetrasulfide is of synthetic importance and still a very challenging problem (Scheme 1).

Sarandeses et al. developed an atom-efficient Pd-catalyzed cross-coupling reaction with triorganoindiums (R_3In).[6] Recently, we reported Pd-catalyzed cross-coupling reactions of allylindiums,[7] allenylindiums,[8] 1,3-butadien-2-ylindiums,[9] tetra(organo)indates,[10] and vinylindiums[11] with a variety of electrophiles.[12] Also, we found that indium tri(organothiolates) $(RS)_3In$ were atom-efficient nucleophilic coupling partners in Pd-catalyzed carbon−sulfur cross-coupling reactions.[13] In these reactions, indium organometallics such as triorganoindium[6c,12b] and indium tri(organothiolate)[13] transfer all three organic groups to electrophiles. These results have stimulated our interest in its application to multifold carbon−sulfur cross-coupling reactions in a one-pot procedure. Herein, efficient multifold and sequential Pd-catalyzed carbon−sulfur cross-coupling reactions are described with indium tri(organothiolates) in a one-pot procedure, producing di-, tri-, and tetrasulfides.

TABLE 1. Pd-Catalyzed 2-Fold Carbon−Sulfur Cross-Coupling Reactions of 2,5-Dibromopyridine with Indium Tri(organothiolates)[a]



entry	bis(sulfide)		yield (%)
1		**2a**	80
2		**2b**	91
3		**2c**	85
4		**2d**	83
5		**2e**	78
6		**2f**	85
7		**2g**	93
8		**2h**	80
9		**2i**	81

[a] Reactions were carried out with $In(SR)_3$ (0.68 equiv), 4 mol % of $Pd(OAc)_2$, and 4.2 mol % of Xantphos in the presence of diisopropylethylamine (1 equiv) in DMF at 100 °C for 4 h.

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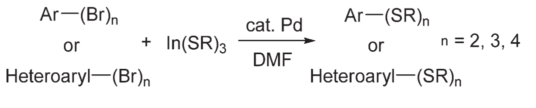
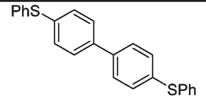
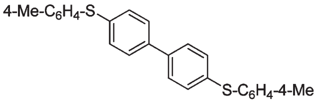
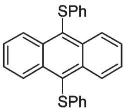
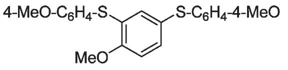
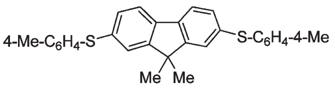
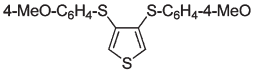
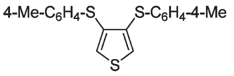
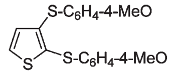
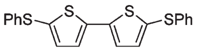
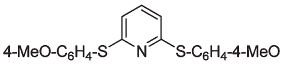
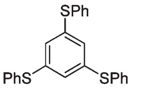
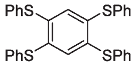
Results and Discussion

Pd-Catalyzed 2-Fold Carbon−Sulfur Cross-Coupling Reaction of 2,5-Dibromopyridine with Indium Tri(organothiolates). In order to examine the application feasibility of indium tri(organothiolates) to multifold carbon−sulfur cross-coupling reaction in a one-pot procedure, we began our study with 2,5-dibromopyridine **1**. The results are summarized in Table 1. We were mainly interested in introduction of aliphatic and aromatic sulfur moiety with indium tri(organothiolates) $(RS)_3In$ onto pyridine. First, the cross-coupling reaction of **1** with $(n\text{-PrS})_3In$ (0.68 equiv) in the presence of 4 mol % of $Pd(OAc)_2$, 4.2 mol % of Xantphos, and 1 equiv of diisopropylethylamine (DIPEA) in DMF for 4 h produced 2,5-di(*n*-propylthio)pyridine (**2a**) in 80% yield (entry 1). This result indicates that indium tri(*n*-propylthiolate) transfers all three *n*-propylthio groups to **1**. The use of $(n\text{-PrS})_3In$ (0.34 equiv) afforded selectively 5-bromo-2-*n*-propylthiopyridine in 82% yield, suggesting that bromide on the 2-position is more reactive than the one on the 5-position. With these results in hand, treatment of **1** with indium tri(isopropylthiolate) and indium tri(*tert*-butylthiolate) provided the 2-fold carbon−sulfur cross-coupling products **2b** and **2c** in 91% and 85% yields, respectively (entries 2 and 3). It is noteworthy that carbon−sulfur cross-coupling reactions with volatile thiols, such as *n*-propyl, isopropyl, and *tert*-butyl thiol, proceeded smoothly to afford the desired bis(sulfides) in a one-pot procedure. In addition, reaction of **1** with indium tri(phenylthiolate) provided 2,5-di(phenylthio)pyridine (**2d**) in 83% yield (entry 4). Although thiophenol and phenyl disulfide were employed as nucleophilic coupling partners, the desired sulfide was not obtained. 2,5-Dibromopyridine did not react with lithium benzenethiolate under the optimum reaction conditions, indicating that ligand dissociation of $(PhS)_3In$ does not occur during the cross-coupling reactions. Next, we chose indium tri(4-methylphenylthiolate) and tri(4-methoxyphenylthiolate) possessing an electron-rich aryl ligand, producing the corresponding bis(sulfides) **2e** and **2f** in 78% and 85% yields, respectively (entries 5 and 6). Indium tri(4-fluorophenylthiolate) having an electron-deficient ligand provided 2,5-di(4-fluorophenylthio)pyridine (**2g**) in 93% yield (entry 7). The present method was applied to 2-fold carbon−sulfur cross-coupling reactions with different thiolate groups in a one-pot procedure. Reaction of **1** with $(4\text{-MeO-}C_6H_4S)_3In$ (0.33 equiv) in DMF (70 °C, 2 h) in the presence of 4 mol % of $Pd(OAc)_2$, 4.2 mol % of Xantphos, and 1 equiv of DIPEA followed by reaction with $(t\text{-BuS})_3In$ (0.33 equiv) (100 °C, 4 h) produced selectively bis(sulfide) **2h** in 80% yield (entry 8). Sequential treatment of **1** with $(i\text{-PrS})_3In$ (0.33 equiv) and $(4\text{-Me-}C_6H_4S)_3In$ (0.33 equiv) provided the desired bis(sulfide) **2i** in 81% yield (entry 9), indicating that the multifold carbon−sulfur cross-coupling reaction is independent of the type of aliphatic or aromatic ligand attached to the indium. However, bis(sulfide) was not obtained from corresponding chloride under the optimum reaction conditions.

Pd-Catalyzed Multifold Carbon−Sulfur Cross-Coupling Reaction of Aryl Bromide with Indium Tri(organothiolate). Wth these results in hand, Pd-catalyzed multifold carbon−sulfur cross-coupling reactions of indium tri(organothiolates) with a wide range of aryl and heteroaryl bromides were investigated. The results are summarized in Table 2. 4,4′-Dibromo-1,1′-biphenyl was reacted with $(PhS)_3In$ (0.68 equiv) in the presence of 4 mol % of $Pd(OAc)_2$, 4.2 mol % of Xantphos, and 1 equiv of DIPEA to give bis(sulfide) **3a** in 83% yield in DMF for 4 h (entry 1). Under the optimum reaction conditions, **3b** was produced in 84% yield with $(4\text{-Me-}C_6H_4S)_3In$ (0.68 equiv) (entry 2). In the case of 9,10-dibromoanthracene, use of 1 equiv of $(PhS)_3In$ provided the corresponding bis(sulfide) **3c** in 80% yield (entry 3). Also, we were pleased to obtain the desired compounds **3d** (95%) and **3e** (81%) from the respective reaction of 2,4-dibromoanisole

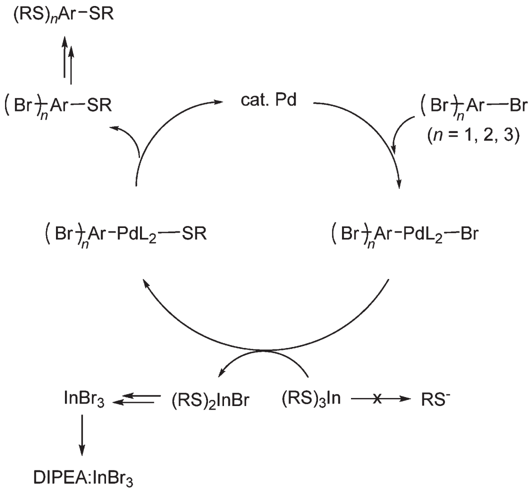
TABLE 2. **Pd-Catalyzed Multifold Carbon−Sulfur Cross-Coupling Reactions with Indium Tri(organothiolate)**[a]



entry	sulfide		yield (%)
1		**3a**	83
2		**3b**	84
3		**3c**	80[b]
4		**3d**	95
5		**3e**	81
6		**3f**	60 (29)[c] 79[d] (16)[c]
7		**3g**	80[d]
8		**3h**	93[d]
9		**3i**	90
10		**3j**	98
11		**3k**	96[b]
12		**3l**	91[e]

[a] Reactions were carried out with $In(SR)_3$ (0.68 equiv), 4 mol % of $Pd(OAc)_2$ and 4.2 mol % Xantphos in the presence of diisopropylethylamine (1 equiv) in DMF at 100 °C for 4 h. [b] $In(SR)_3$ (1 equiv) was used. [c] 3-Bromo-4-(4-methoxyphenyl)thiophene. [d] $In(SR)_3$ (1.36 equiv) was used. [e] $In(SR)_3$ (4.08 equiv) was used. NMP was used as a solvent.

SCHEME 2. Palusible Mechanism of Pd-Catalyzed Multifold Carbon−Sulfur Cross-Coupling Reactions by Using Indium Tri(organothiolates)



and 2,7-dibromo-9,9-dimethylfluorene with the corresponding indium tri(organothiolates) (0.68 equiv) (entries 4 and 5). Although treatment of 3,4-dibromothiophene with (4-MeO-$C_6H_4S)_3In$ (0.68 equiv) gave **3f** and 3-bromo-4-(4-methoxyphenyl)thiophene in 60% and 29% yields, respectively, use of 1.36 equiv of the indium reagent increased the product yield (79% yield, entry 6). Treatment of 3,4-dibromothiophene with (4-Me-$C_6H_4S)_3In$ (1.36 equiv) gave **3g** in 80% yield (entry 7). Exposure of 2,3-dibromothiophene to (4-MeO-$C_6H_4S)_3In$ (1.36 equiv) afforded 2,3-di(4-methoxyphenylthio)thiophene **3h** in 93% yield (entry 8). The present method worked equally well with 2,2′-bithiophene and 2,6-dibromopyridine using 0.68 equiv of indium tri(organothiolates), leading to formation of bis(sulfides) **3i** and **3j** in good to excellent yield (entries 9 and 10). Reaction of 1,3,5-tribromobenzene with $(PhS)_3In$ (1 equiv) furnished 3-fold carbon−sulfur cross-coupling product **3k** in 96% yield in one-pot procedure, indicating that all three phenylthio groups attached to indium were transferred to electrophiles (entry 11). When 1,2,4,5-tetrabromobenzene was subjected to $(PhS)_3In$ (4.08 equiv) in the presence of 4 mol % of $Pd(OAc)_2$, 4.2 mol % of Xantphos, and 1 equiv of DIPEA in NMP, the desired 4-fold carbon−sulfur coupling product **3l** was obtained in 91% yield (entry 12).

Plausible Mechanism. Although thiophenol and phenyl disulfide were employed as nucleophilic coupling partners, less pleasant results were obtained. In addition, the possibility of carbon−sulfur bond formation through ligand dissociation of $(PhS)_3In$ was examined under the reaction conditions. 2,5-Dibromopyridine did not react with lithium benzenethiolate under the optimum reaction conditions. These results indicate that ligand dissociation of $(PhS)_3In$ does not occur during the cross-coupling reactions and **2d** is produced through 2-fold cross-coupling reaction in a one-pot procedure.

Although the mechanism of Pd-catalyzed cross-coupling reactions with indium tri(organothiolate) has not been firmly established, the details of the present reactions can be described in connection with the generally accepted mechanism in these kind of reactions (Scheme 2).[14] In this mechanism, we accept that all three indium species such as $(RS)_3In$, $(RS)_2InBr$, and $RSInBr_2$ can enter the catalytic cycle and transfer a thiol ligand to palladium. This plausible mechanism was supported by the fact that n-Bu_3In, n-Bu_2InCl, and n-$BuInCl_2$ were effectively used in the Pd-catalyzed cross-coupling reaction and carbonylative cross-coupling reaction.[6,15] The reason as to why cross-coupling reaction proceeded smoothly in the presence of DIPEA may be due to reaction acceleration through acid−base reaction of DIPEA with indium halide. Efficient transfer of three organic groups attached to indium to electrophile can be explained in connection with the weak bond strength between sulfur and indium. In addition, the large difference of heats of formation between In−S and In−X supports the present mechanism.[16]

Conclusion

In conclusion, we have developed an efficient Pd-catalyzed multifold (2-, 3-, and 4-fold) carbon−sulfur cross-coupling reaction of indium tri(organothiolates) with polybromonated aromatic and heteroaromatic compounds in a one-pot procedure, producing di, tri-, and tetrasulfides in good to excellent yields. These results indicate that indium tri(organothiolates) transfer all of three alkyl- or arylthio groups attached to indium metal to electrophilic coupling partners. Indium tri(organothiolates) derived from alkyl thiol having low boiling point, such as *n*-propyl, isopropyl, and *tert*-butyl thiol, acted as good nucleophilic coupling partners. In addition, indium tri(arylthiolates) derived from aryl thiols possessing electron withdrawing or donating group on aromatic ring participated well in Pd-catalyzed multifold carbon−sulfur cross-coupling reaction. These novel features, which is carried out with only a small excess of organometallic reagent and a low catalyst loading, make indium tri(organothiolates) highly useful alternatives to other organometallic reagents used in transition-metal-catalyzed multifold carbon−sulfur cross-coupling reactions and also mark them out as promising reagents for organic synthesis.

Experimental Section

General Methods. Reactions were carried out in oven-dried glassware under nitrogen atmosphere. $In(SAr)_3$, $In(S$-t-$Bu)_3$, $In(S$-i-$Pr)_3$, and $In(S$-n-$Pr)_3$ were prepared by reported procedures.[17] Other commercial available reagents were used

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without purification. DMF and DIPEA were dried with CaH_2. Indium, $InCl_3$, and Xantphos were purchased. All reactions were monitored by TLC using silica gel 60 F_{254} precoated glass plates and purifications were performed by column chromatography using silica gel 60 (0.04−0.063 mm, 230−400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz spectrometer using deuterated chloroform as solvent and chemical shift values (δ) are reported in part per million relative to TMS as internal standard. High-resolution mass spectra and infrared spectra were recorded on each spectrometer.

Synthetic Procedure of 4,4′-Bis(*p*-tolylthio)biphenyl (3b). To a solution of $Pd(OAc)_2$ (4.5 mg, 4 mol %) and Xantphos (12.1 mg, 4.2 mol %) in DMF (1.0 mL) was added 4,4′-dibromo-1,1′-biphenyl (156 mg, 0.5 mmol) in DMF (0.5 mL) at 25 °C under nitrogen atmosphere. After being stirred for 5 min, $(4\text{-Me-}C_6H_4S)_3In$ (164.7 mg, 0.34 mmol) and DIPEA (87.0 μL, 0.5 mmol) in DMF (1.0 mL) was transferred via double-ended needle, and the mixture was stirred at 100 °C for 4 h. The reaction mixture was quenched with $NaHCO_3$ (satd aq). The aqueous layer was extracted with ether (3 × 20 mL), and the combined organic layers were washed with water and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give **3b** (167.4 mg, 84%) as white solid: mp 159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.36 Hz, 2H), 7.34 (d, J = 8.00 Hz, 2H), 7.30 (d, J = 8.36 Hz, 2H), 7.16 (d, J = 8.00 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.2, 136.9, 132.9, 131.4, 130.6, 130.3, 127.8, 21.6; IR (film) 3431, 809 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{22}S_2$ m/z 398.1163 [M$^+$], found m/z 398.1164.

2,5-Di(propylthio)pyridine (2a): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.48 (d, J = 8.45 Hz, 1H), 7.09 (d, J = 8.45 Hz, 1H), 3.13 (t, J = 7.35 Hz, 2H), 2.82 (t, J = 7.35 Hz, 2H), 1.73 (sextet, J = 7.35 Hz, 2H), 1.67 (sextet, J = 7.35 Hz, 2H), 1.04 (t, J = 7.35 Hz, 3H), 1.00 (t, J = 7.35 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 151.0, 138.5, 128.2, 122.1, 37.0, 32.3, 22.7, 22.6, 13.5, 13.2; IR (film) 3435, 2962, 2870, 1566 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{17}NS_2$ m/z 227.0802 [M$^+$], found m/z 227.0804.

2,5-Di(isopropylthio)pyridine[18] **(2b):** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.53 (d, J = 8.14 Hz, 1H), 7.10 (d, J = 8.14 Hz, 1H), 3.97 (sep, J = 6.75 Hz, 1H), 3.24 (sep, J = 6.75 Hz, 1H), 1.40 (d, J = 6.75 Hz, 6H), 1.27 (d, J = 6.75 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 153.4, 140.8, 126.6, 122.5, 39.3, 35.2, 23.14, 23.12; IR (film) 3435, 2961, 1564, 1449 cm^{-1}.

2,5-Di(*tert*-butylthio)pyridine (2c): white solid; mp 63 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57(s, 1H), 7.62 (d, J = 8.04 Hz, 1H), 7.23 (d, J = 8.04 Hz, 1H), 1.55 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 156.2, 144.2, 125.9, 125.6, 48.0, 46.3, 30.9, 30.8; IR (film) 1433, 1363 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{21}NS_2$ m/z 255.1115 [M$^+$], found m/z 255.1118.

2,5-Di(phenylyhio)pyridine[19] **(2d):** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.61−7.58 (m, 2H), 7.44−7.40 (m, 5H), 7.30 (d, J = 4.34 Hz, 4H), 6.82 (d, J = 8.26 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 151.7, 139.7, 135.1, 134.9, 130.7, 130.6, 129.7, 129.4, 129.3, 128.5, 127.4, 121.5; IR (film) 3434, 3058, 1560, 1475 cm^{-1}.

2,5-Di(*p*-tolylthio)pyridine (2e): white solid; mp 52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.47 (d, J = 8.06 Hz, 2H), 7.33 (d, J = 8.54 Hz, 2H), 7.24−7.21 (m, 4H), 7.11 (d, J = 8.08 Hz, 2H), 6.75 (d, J = 8.54 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 150.8, 139.6, 138.8, 137.9, 135.2, 131.7, 130.7, 130.5, 130.2, 129.3, 126.3, 121.1, 21.3, 21.1; IR (film) 3435, 1560, 1492, 1443, 1349 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{17}NS_2$ m/z 323.0802 [M$^+$], found m/z 323.0799.

2,5-Di(4-methoxyphenylthio)pyridine (2f): white solid; mp 112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.50 (d, J = 8.65 Hz, 2H), 7.34 (d, J = 8.68 Hz, 2H), 7.24 (d, J = 8.38 Hz, 1H), 6.94 (d, J = 8.65 Hz, 2H), 6.85 (d, J = 8.68 Hz, 2H), 6.68 (d, J = 8.38 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 160.9, 160.4, 150.0, 137.9, 137.6, 135.1, 124.3, 121.4, 121.1, 115.7, 115.5, 55.8; IR (film) 3434, 1592, 1550, 1494, 1412, 1249 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{17}NO_2S_2$ m/z 355.0701 [M$^+$], found m/z 355.0700.

2,5-Di(4-fluorophenylthio)pyridine (2g): white solid; mp 72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33(s, 1H), 7.56 (dd, J = 8.31, 8.4 Hz, 2H), 7.37−7.31 (m, 3H), 7.11 (dd, J = 8.5, 8.58 Hz, 2H), 7.00 (dd, J = 8.31, 8.4 Hz, 2H), 6.80 (d, J = 8.41 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 150.8, 139.6, 138.8, 137.9, 135.2, 131.7, 130.7, 130.5, 130.2, 129.3, 126.3, 121.1, 21.3, 21.1; IR (film) 3441, 1588, 1489, 1224 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{11}F_2NS_2$ m/z 331.0301 [M$^+$], found m/z 331.0301.

5-(*tert*-Butylthio)-2-(4-methoxyphenylthio)pyridine (2h): white solid; mp 95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.56−7.53 (m, 3H), 6.98 (d, J = 8.7 Hz 2H), 6.73 (d, J = 8.4 Hz, 1H), 3.85 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 161.3, 156.8, 145.4, 137.8, 125.2, 120.9, 120.2, 115.8, 55.8, 46.7, 31.2; IR (film) 3434, 1592, 1550, 1494, 1412, 1249 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{19}NOS_2$ m/z 305.0908 [M$^+$], found m/z 305.0910.

2-(Isopropylthio)-5-(*p*-tolylthio)pyridine (2i): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.24 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.5 Hz, 1H), 3.95 (sep, J = 6.7 Hz, 1H), 2.33 (s, 3H), 1.39 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 151.1, 138.5, 137.6, 131.3, 131.2, 130.1, 128.5, 122.9, 35.3, 23.1, 21.1; IR (neat) 3435, 1560, 1492, 1443, 1349 cm^{-1}; HRMS (EI) calcd. for $C_{15}H_{17}NS_2$ m/z 275.0802 [M$^+$], found m/z 275.0804.

4,4′-Di(phenylthio)-1,1′-biphenyl[20] **(3a):** yellow solid; mp 113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.28 Hz, 2H), 7.41−7.37 (m, 4H), 7.35−7.31 (m, 2H), 7.29−7.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 135.4, 135.35, 131.3, 131.1, 129.3, 127.6, 127.3; IR (film) 3435, 1645, 1476 cm^{-1}.

9,10-Di(phenylthio)anthracene[21] **(3c):** yellow solid; mp 215 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 6.82 Hz, 2H), 7.57 (d, J = 6.82 Hz, 2H), 7.12 (dd, J = 7.92, 7.24 Hz, 2H), 7.04 (dd, J = 7.92, 7.24 Hz, 1H), 6.96 (d, J = 7.24 Hz, 2H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 135.6, 130.3, 129.4, 128.1, 127.8, 126.9, 125.6; IR (film) 3434, 1643 cm^{-1}.

2,4-Di(4-methoxyphenylthio)-1-methoxybenzene (3d): white solid; mp 79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.69 Hz, 2H), 7.20 (d, J = 8.88 Hz, 2H), 7.02 (d, J = 8.42 Hz, 1H), 6.85 (d, J = 8.69 Hz, 2H), 6.77 (d, J = 8.88 Hz, 2H), 6.75 (d, J = 8.42 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 159.3, 154.2, 136.5, 133.9, 129.3, 129.1, 128.5, 127.7, 125.8, 121.5, 115.1, 114.7, 110.8, 56.0, 55.3; IR (film) 3435, 1592, 1493, 1288 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{20}O_3S_2$ m/z 384.0854 [M$^+$], found m/z 384.0850.

2,7-Di(*p*-tolylthio)-9,9-dimethyl-9*H*-fluorene (3e): white solid; mp 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.98 Hz, 2H), 7.38 (s, 2H), 7.29 (d, J = 7.96 Hz, 4H) 7.22 (d, J = 7.98 Hz, 2H), 7.13 (d, J = 7.96 Hz, 4H), 2.34 (s, 6H), 1.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 137.9, 137.7, 135.9, 132.5, 131.8, 130.5, 130.2, 129.8, 128.9, 125.3, 120.9, 47.4, 27.4, 21.6; IR (film) 3435, 2960, 1600, 1491 cm^{-1}; HRMS (EI) calcd. for $C_{29}H_{26}S_2$ m/z 438.1476 [M$^+$], found m/z 438.1479.

3,4-Di(4-methoxyphenylthio)thiophene (3f): white solid; mp 157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.86 Hz, 4H), 7.00 (s, 2H), 6.85 (d, J = 8.86 Hz, 4H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 134.3, 133.4, 125.5, 125.2,

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114.8, 55.3; IR (film) 2938, 2834, 1591, 1493, 1288 cm^{-1}; HRMS (EI) calcd. for $C_{18}H_{16}O_2S_3$ m/z 360.0312 [M$^+$], found m/z 360.0313.

3,4-Di(*p*-tolylthio)thiophene (3g): white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.13 Hz, 4H), 7.18 (s, 2H), 7.08 (d, J = 8.13 Hz, 4H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 134.1, 132.1, 131.0, 130.3, 127.5, 21.5; IR (film) 1590, 1493, 1288 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}S_3$ m/z 328.0414 [M$^+$], found m/z 328.0418.

2,3-Di(4-methoxyphenylthio)thiophene (3h): white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.30 (m, 4H), 7.20 (d, J = 5.51 Hz, 1H), 6.84−6.81 (m, 4H), 6.66 (d, J = 5.51 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 159.6, 138.9, 134.3, 132.4, 131.3, 130.7, 128.8, 127.5, 125.8, 115.3, 115.2, 55.8; IR (film) 3099, 3019, 2919, 1596 cm^{-1}; HRMS (EI) calcd. for $C_{18}H_{16}O_2S_3$ m/z 360.0312 [M$^+$], found m/z 360.0316.

2-(Phenylthio)-5-[5-(phenylthio)thiophen-2-yl]thiophene[22] **(3i):** yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.25 (m, 8H), 7.20−7.17 (m, 4H), 7.09 (d, J = 3.67 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 138.0, 136.6, 131.3, 129.1, 127.6, 126.4, 124.5; IR (film) 3435, 1644, 1491, 1127 cm^{-1}.

2,6-Di(4-methoxyphenylthio)pyridine (3j): white solid; mp 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.81 Hz, 4H), 7.14 (dd, J = 7.85, 7.85 Hz, 1H), 6.93 (d, J = 8.81 Hz, 4H), 6.39 (d, J = 7.85 Hz, 2H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 161.1, 137.7, 137.2, 121.4, 116.2, 115.6, 55.8; IR (film) 3435, 2938, 2834, 1591, 1572 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{17}NO_2S_2$ m/z 355.0701 [M$^+$], found m/z 355.0705.

1,3,5-Tri(phenylthio)benzene[22] **(3k):** white solid; mp 55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.30 (m, 6H), 7.29−7.26 (m, 9H), 6.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 133.8, 132.9, 129.8, 128.4, 127.9; IR (film) 3436, 1550, 1475, 790, 739 cm^{-1}.

1,2,4,5-Tetra(phenylthio)benzene[23] **(3l):** white solid; mp 142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 10H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 133.7, 132.9, 132.4, 129.8, 128.2; IR (film) 3446, 1644, 1475, 1427, 746 cm^{-1}.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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