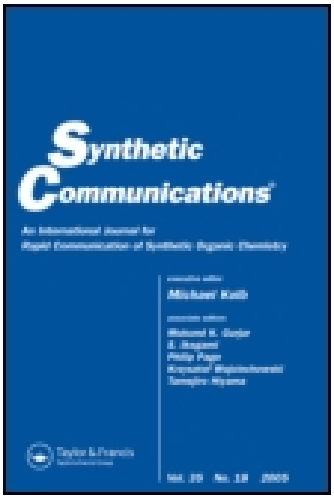

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Iron-Catalyzed Direct C-H Thiolation of Trimethoxybenzene with Disulfides

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IRON-CATALYZED DIRECT C-H THIOLATION OF TRIMETHOXYBENZENE WITH DISULFIDES

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GRAPHICAL ABSTRACT

Abstract *An iron-catalyzed thiolation access to sulfides from disulfides via arene C-H bond cleavage of trimethoxybenzene is described. The procedure tolerates methoxyl, fluoro, chloro, bromo, nitro, and heterocyclic groups, using air as the clean and terminal oxidant.*

Keywords C-H activation; disulfides; Fe-catalyzed; thiolation; trimethoxybenzene

INTRODUCTION

The scope and application of organosulfur compounds have increased tremendously because sulfur-containing groups serve important auxiliary functions in synthetic sequences.[1] Aryl sulfides have been widely used as intermediates in synthetic chemistry and products in the pharmaceutical industry.[2] The transition-metal-catalyzed cross-coupling reactions of ArX [X = Cl, Br, I, OTf, and $B(OH)_2$] with thiol are powerful tools for the formation of C-S bonds (Scheme 1, Eq. (1)).[3] However, the thiols are easily formed with S-S coupling disulfides as the by-product.[4] Furthermore, the combination of sulfur compounds with metal could deactivate the catalyst in the reaction system.[5] Employing ArSSAr may solve these drawbacks (Scheme 1, Eq. (2)).[6] However, in most cases, one or more equivalents of reductants such as Zn or Mg was required in the reaction.

The transition-metal-catalyzed direct C-H bond functionalization has become a versatile synthetic method for organic synthesis,[7] which affords valuable transformations of C-H bonds to C-C,[8] C-X,[9] C-O,[10] and C-N[11] bonds. However, direct

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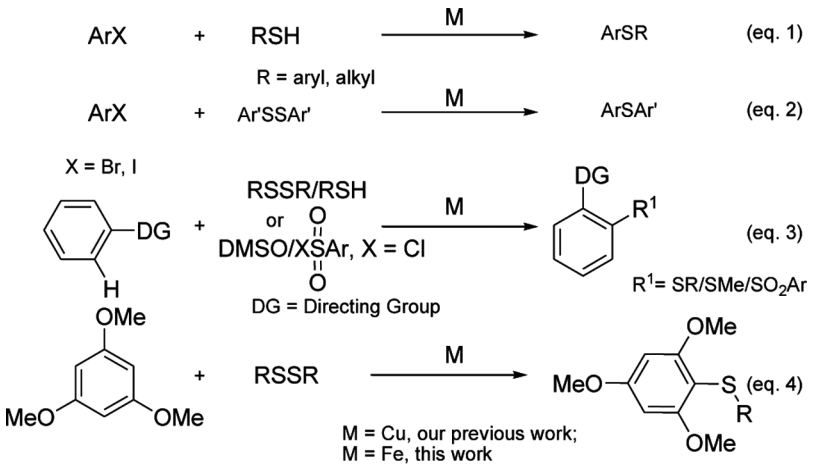


Scheme 1. Formation of C-S bond.

C-S bond-forming reaction via C-H bond cleavage is rarely reported. Recently, palladium- or copper-catalyzed formations of C-S bonds via 2-phenylpyridine C-H bonds with different sulfur sources have been reported (Scheme 1, Eq. (3)).[12] From the synthetic point of view, the use of cheap catalysts instead of expensive catalysts is highly desirable for the aforementioned transformation. Very recently, Zhang et al. developed a copper-catalyzed thiolation of trimethoxybenzene C-H bond with disulfides using oxygen as the oxidant (Scheme 1, Eq. (4)).[13]

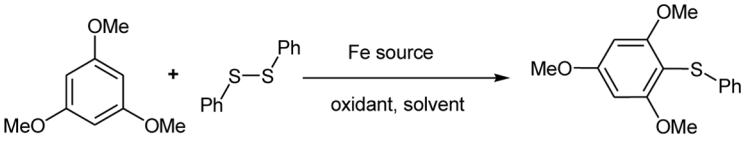
Iron represents a cheap and promising catalyst[14] in the C-H functionalization to form the C-C and C-heteroatom bonds.[15] In 2009, Fang and coworkers reported an iron-catalyzed sulfenylation of indoles C-H bond with diaryl disulfides, where a catalytic amount of iodine was necessary to promote the reaction.[16] On the basis of the previous work, herein we report a non-chelation-assisted iron(III)-catalyzed direct C-H thiolation of trimethoxybenzene with ArSSAr (Scheme 1, Eq. (4)).

Initially, we began to examine the phenylthiolation of 1,3,5-trimethoxybenzene with PhSSPh using iron catalysts, as shown in Table 1. To our delight, the thiolation reaction catalyzed by FeF_3 (20 mol%) took place in DMF in 25% yield (Table 1, entry 1). After the screening of iron salts, the thioether **3a** could be gained in 82% yield using $FeBr_3$ as the catalyst under air in dimethylformanlide (DMF) at 145 °C for 48 h (Table 1, entry 8). Decreasing the amount of iron led to poor yields. The use of other iron salts such as $FeCl_2$, $FeCl_3$, $FeBr_2$, FeI_2, $Fe(OAc)_2$, and $Fe(acac)_3$ as catalysts resulted in lower yields (Table 1, entries 2–7). Other oxidants, such as oxone, $K_2S_2O_8$, $PhI(OAc)_2$, BQ, $Cu(OAc)_2$, $CuBr_2$, and *tert*-butyl hydroperoxide (TBHP), were inferior to air for this transformation (Table 1, entries 9–15). Notably, the use of two RS in $(RS)_2$ in the reaction represents an atom-economical procedure. Under an O_2 atmosphere, the yield decreased to 64%. Only 25% of the product was isolated when the reaction was performed under N_2 atmosphere (Table 1, entry 8). The choice of solvent had dramatic effect on the reaction, and (DMF) turned out to be the best (Table 1, entries 17–20). No product was observed in the absence of metal catalyst (Table 1, entry 16). The reaction conducted on a 10- mmol scale and formed the thiolation product in an acceptable 65% yield.

With the optimal parameters established, the thiolation reactions of trimethoxybenzene with various disulfides are summarized in Fig. 1. A wide range of functional groups, such as methoxy, 2-naphthyl, fluoro, chloro, bromo, nitro, and heterocyclic, were tolerated well, and good product yields were obtained (Fig. 1, **3c, 3d, 3e, 3f, 3 h, 3i, 3j,** and **3n**). Generally, the electron-withdrawing groups on the phenyl ring of ArS-SAr produced thiolation products in better yields (Fig. 1, **3i** and **3j**). The reaction is applicable to the synthesis of a wide variety of substituted disulfides and does not seem to be extremely sensitive to hindrance effects. For example, the *ortho*-substituted substrate **2 g** provided a useful 68% yield of product **3 g**, while **3f** was obtained in 70% yield. Importantly, the halo groups on the phenyl ring of disulfides survived in the procedure (Fig. 1, **3d, 3e, 3f,** and **3g**), which is attractive because halo products could be further synthetic elaboration.

Notably, PhSeSePh was subjected to the procedure, and the mono-selenation product **3o** was obtained in 30% yield, along with 20% of the diselenation product **3p**. Fortunately, the compatibility of benzyl and allyl groups is synthetically useful

Table 1. Screening for the optimum conditions[a]



1a **2a** **3a**

Entry	Fe source	Solvent	Oxidant	Yield (%)
1	FeF_3	DMF	Air	25
2	$FeCl_2$	DMF	Air	45
3	$FeCl_3$	DMF	Air	40
4	$FeBr_2$	DMF	Air	30
5	FeI_2	DMF	Air	63
6	$Fe(OAc)_2$	DMF	Air	30
7	$Fe(acac)_3$	DMF	Air	35
8	$FeBr_3$	DMF	Air	82 (64)[b] (25)[c]
9	$FeBr_3$	DMF	Oxone (0.2 mmol)	40
10	$FeBr_3$	DMF	$K_2S_2O_8$ (0.2 mmol)	55
11	$FeBr_3$	DMF	$PhI(OAc)_2$ (0.2 mmol)	45
12	$FeBr_3$	DMF	BQ (0.2 mmol)	78
13	$FeBr_3$	DMF	$Cu(OAc)_2$ (0.2 mmol)	77
14	$FeBr_3$	DMF	$CuBr_2$ (0.2 mmol)	70
15	$FeBr_3$	DMF	TBHP (0.2 mmol)	60
16		DMF	Air	0
17	$FeBr_3$	Xylene	Air	15
18	$FeBr_3$	DMSO	Air	63
19	$FeBr_3$	NMP	Air	60
20	$FeBr_3$	THF	Air	10

[a]All reactions were run with **1a** (0.2 mmol), PhSSPh **2a** (21.8 mg, 0.1 mmol), Fe sources (20 mol %), dry solvent (2 mL), under air, 145 °C in a sealed tube, 48 h.

[b]Under O_2.

[c]Under N_2.

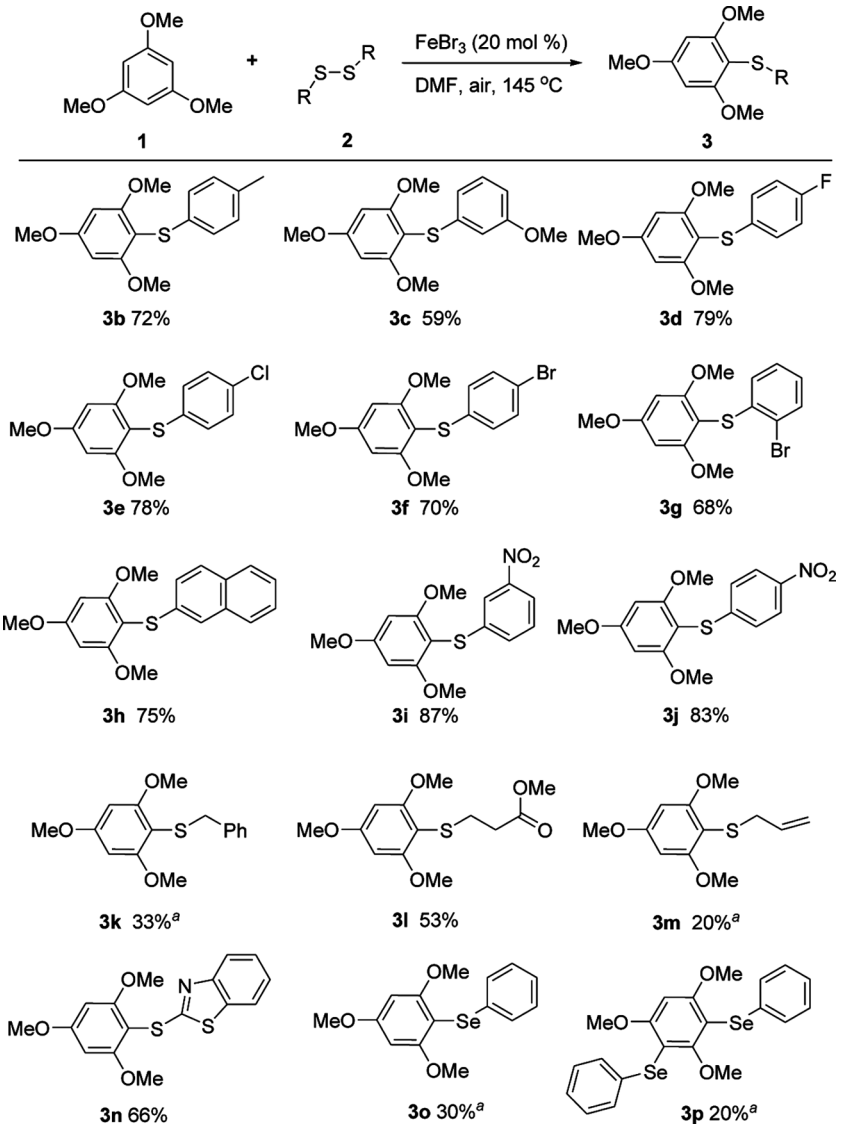


Figure 1. Reaction conditions: **1a** (0.2 mmlo), RSSR 2 (0.1 mmol), $FeBr_3$ (20 mol %), dry DMF (2 mL), air, 145 °C in a sealed tube, 48 h. [a]60 h.

because they can be further functionalized, although the thiolation products were isolated in poor yields (Fig. 1, **3k** and **3 m**). Furthermore, the alkyl ester gave the product **3 l** in 53% yield. Disappointingly, under the current condition, MeSSMe would not be compatible.

Next, we investigated the substrate scope with regard to other electron-rich arenes, as shown in Fig. 2. 1,3-Dimethoxysubstituted and the 1,2,4-trimethoxysubstituted benzenes underwent the reaction to generate the products **3s** and **3t**, albeit in poor yields, where no other isomer were observed by analysis of gas chromatography–mass

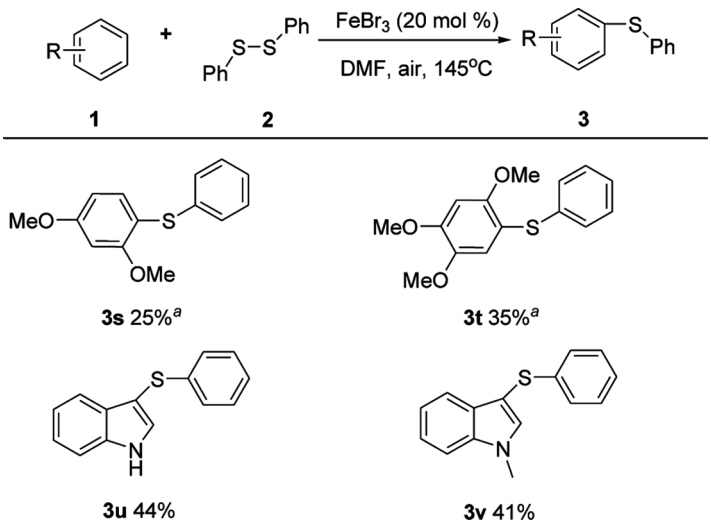


Figure 2. Reaction conditions: **1** (0.2 mmol), PhSSPh **2a** (0.1 mmol), $FeBr_3$ (20 mol %), dry DMF (2 mL), air, 145 °C in a sealed tube, 48 h. *a*60 h.

spectrometry (GC-MS). Particularly, the indole could also deliver the corresponding thiolation products in moderate yields (Fig. 2, **3u** and **3v**).

In conclusion, we have demonstrated an efficient and straightforward method for the iron-catalyzed thiolation of trimethoxybenzene C-H bond with disulfide. The employment of cheap iron as the catalyst and air as the clean oxidant significantly improved the practicality of this C-H functionalization reaction.

EXPERIMENTAL

Chemicals were either purchased or purified by standard techniques without special instructions. The $FeBr_3$ (99%), which contained less than 25 ppm transition metals such as palladium or copper through analysis of inductively coupled plasma (ICP), was purchased from J&K. ^1H NMR and ^{13}C NMR spectra were measured on a 500 MHz (^1H 500-MHz, ^{13}C 125 MHz) spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in parts per million (ppm) relative to TMS, and the coupling constants *J* are given in hertz (Hz).

General Procedure

Under an air atmosphere, a sealed reaction tube was charged with 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol), RSSR (0.1 mmol), $FeBr_3$ (11.6 mg, 20 mol %), and dry DMF (2 mL). The mixture was stirred at 145 °C for 48 h. After the completion of the reaction, as monitored by thin-layer chromatography (TLC), the solvent was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel (300–400 mesh) with petroleum ether–EtOAc as eluent to give the product.

Phenyl(2,4,6-trimethoxyphenyl)sulfane (3a)[17]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.17–7.14 (m, 2H), 7.03–7.01 (m, 3H), 6.22 (s, 2H), 3.87 (s, 3H), 3.80 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.9, 162.5, 138.7, 128.5, 125.7, 124.3, 98.9, 91.2, 56.3, 55.4.

4-Tolyl(2,4,6-trimethoxyphenyl)sulfane (3b)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.99–6.95 (m, 4H), 6.21 (s, 2H), 3.86 (s, 3 H), 3.81 (s, 6H), 2.25 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.8, 162.5, 135.0, 134.1, 129.2, 126.0, 99.4, 91.1, 56.4, 55.6, 20.9.

(3-Methoxyphenyl)(2,4,6-trimethoxyphenyl)sulfane (3c)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.08–7.05 (m, 1H), 6.62–6.57 (m, 3H), 6.21 (s, 2H), 3.86 (s, 3H), 3.81 (s, 6H), 3.71 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.0, 162.6, 159.7, 140.2, 129.3, 118.0, 111.2, 110.0, 98.4, 91.2, 56.3, 55.4, 55.1.

(4-Fluorophenyl)(2,4,6-trimethoxyphenyl)sulfane (3d)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.04–7.01 (m, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 6.20 (s, 2H), 3.86 (s, 3H), 3.81 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.9, 162.4, 160.8 (d, $J_{C\text{-}F} = 241.8$ Hz), 133.6, 127.9 (d, $J_{C\text{-}F} = 7.6$ Hz), 115.5 (d, $J_{C\text{-}F}$ - $= 21.9$ Hz), 99.6, 91.3, 56.3, 55.4.

(4-Chlorophenyl)(2,4,6-trimethoxyphenyl)sulfane (3e)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.11 (d, $J = 8.5$ Hz, 2H), 6.94 (d, $J = 8.5$ Hz, 2H), 6.21 (s, 2H), 3.87 (s, 3H), 3.80 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.1, 162.4, 137.4, 130.0, 128.5, 126.9, 98.3, 91.2, 56.3, 55.4.

(4-Bromophenyl)(2,4,6-trimethoxyphenyl)sulfane (3f)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.18 (d, $J = 8.1$ Hz, 2H), 6.80 (d, $J = 7.8$ Hz, 2H), 6.14 (s, 2H), 3.80 (s, 3H), 3.73 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.1, 162.4, 138.1, 131.4, 127.2, 117.8, 98.1, 91.2, 56.3, 55.4.

(2-Bromophenyl)(2,4,6-trimethoxyphenyl)sulfane (3g)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, $J = 7.9$ Hz, 1H), 7.04–7.01 (m, 1H), 6.90–6.87 (m, 1H), 6.50 (d, $J = 8.0$ Hz, 1H), 6.23 (s, 2H), 3.88 (s, 3H), 3.79 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.3, 162.6, 139.8, 132.4, 127.2, 125.4, 125.1, 120.1, 97.8, 91.2, 56.3, 55.4.

Naphthalen-2-yl(2,4,6-trimethoxyphenyl)sulfane (3h)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, $J = 8.0$ Hz, 1H), 7.65–7.60 (m, 2H), 7.38–7.32 (m, 3H), 7.21 (dd, $J = 9.0$, 7.0 Hz, 1H), 6.26 (s, 2H), 3.90 (s, 3H), 3.81 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.0, 162.6, 136.3, 133.8, 131.2, 127.9, 127.6, 126.8, 126.1, 124.8, 124.7, 123.0, 98.7, 91.3, 56.3, 55.4.

(3-Nitrophenyl)(2,4,6-trimethoxyphenyl)sulfane (3i)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.87 (d, $J = 8.0$ Hz, 1H), 7.77 (s, 1H), 7.36–7.26 (m, 2H), 6.24 (s, 2H), 3.89 (s, 3H), 3.82 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.6, 162.4, 148.6, 142.0, 131.3, 129.0, 120.0, 119.3, 96.6, 91.4, 56.3, 55.5.

(4-Nitrophenyl)(2,4,6-trimethoxyphenyl)sulfane (3j)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.00 (d, $J = 9.0$ Hz, 2H), 7.04 (d, $J = 9.0$ Hz, 2H), 6.23 (s, 2H), 3.89 (s, 6H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): 163.8, 162.4, 149.4, 144.6, 124.8, 123.7, 96.0, 91.3, 56.3, 55.5.

Benzyl(2,4,6-trimethoxyphenyl)sulfane (3k)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.19–7.13 (m, 5H), 6.09 (s, 2H), 3.88 (s, 2H), 3.81 (s, 3H), 3.74 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.2, 161.9, 138.9, 128.9, 127.9, 126.5, 101.5, 91.0, 56.1, 55.3, 39.2.

Methyl 3-(2,4,6-Trimethoxyphenylthio)propanoate (3l)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.15 (s, 2H), 3.86 (s, 6H), 3.83 (s, 3H), 3.63 (s, 3H), 2.96 (t, $J = 7.5$ Hz, 2H), 2.50 (t, $J = 7.6$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.3, 172.7, 162.0, 126.7, 91.0, 56.1, 55.4, 51.6, 34.6, 22.7.

Allyl(2,4,6-trimethoxyphenyl)sulfane (3m)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.14 (s, 2H), 5.84–5.75 (m, 1H), 4.88–4.84 (m, 2H), 3.86 (s, 6H), 3.82 (s, 3H), 3.35 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.1, 161.7, 134.6, 116.3, 93.3, 91.0, 56.1, 55.3, 37.6.

2-(2,4,6-Trimethoxyphenylthio)benzo[d]thiazole (3n)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.83 (d, $J = 8.0$ Hz, 1H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.37–7.34 (m, 1H), 7.19 (d, $J = 8.0$ Hz, 1H), 6.23 (s, 2H), 3.89 (s, 3H), 3.83 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.4, 162.6, 154.5, 140.3, 135.4, 127.2, 125.6, 121.4, 120.9, 97.2, 91.3, 56.3, 55.5.

Phenyl(2,4,6-trimethoxyphenyl)selane (3o)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.20–7.18 (m, 2H), 7.15–7.07 (m, 3H), 6.21 (s, 2H), 3.87 (s, 3H), 3.79 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.0, 162.0, 133.6, 128.9, 128.7, 125.3, 93.0, 91.3, 56.3, 55.4.

1,3,5-Trimethoxy-2,4-bis(phenylselanyl)benzene (3p)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25–7.24 (m, 4H), 7.17–7.10 (m, 6H), 6.41 (s, 1H), 3.83 (s, 6H), 3.77 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.8, 163.1, 133.3, 129.4, 128.8, 125.7, 104.6, 92.5, 62.1, 56.4.

2,4-Dimethoxyphenyl)(phenyl)sulfane (3s)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54–7.10 (m, 5H), 6.53–6.47 (m, 3H), 3.81 (s, 3H), 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.9, 160.9, 136.7, 129.9, 129.1, 128.8, 127.8, 125.4, 106.2, 100.5, 55.5, 55.3.

Phenyl(2,4,5-trimethoxyphenyl)sulfane (3t)[13]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.24–7.21 (m, 2H), 7.15–7.12 (m, 3H), 7.11 (s, 1H), 6.95 (s, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.4, 150.4, 143.6, 138.1, 128.9, 127.2, 125.7, 119.0, 110.9, 98.2, 57.0, 56.3, 55.9.

3-(Phenylthio)-1*h*-indole (3u)[18]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.48 (s, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 2.5$ Hz, 1H), 7.45 (d, $J = 8.5$ Hz, 1H), 7.25–7.23 (m, 1H), 7.18–7.05 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.2, 136.5, 130.6, 129.1, 128.7, 125.8, 124.7, 123.0, 120.9, 119.7, 111.5, 102.8.

1-Methyl-3-(phenylthio)-1*h*-indole (3v)[19]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (d, $J = 8.0$ Hz, 1H), 7.31 (d, $J = 8.5$ Hz, 1H), 7.24–7.18 (m, 1H), 7.10–7.06 (m, 3H), 7.02–7.00 (m, 2H), 6.98–6.95 (m, 1H), 3.77 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.7, 137.5, 135.0, 129.8, 128.6, 125.7, 124.6, 122.5, 120.5, 119.7, 109.7, 100.5, 33.1.

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