Novel and Direct Nucleophilic Sulfenylation and Thiocyanation of Phenol Ethers Using a Hypervalent Iodine(III) Reagent

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Novel and direct nucleophilic sulfenylation and thiocyanation of phenol ethers and related compounds (**1**) with the hypervalent iodine reagent, phenyliodine(III) bis(trifluoroacetate) (PIFA) have been developed. The reaction proceeded smoothly in 1,1,1,3,3,3-hexafluoro-2-propanol ($(CF_3)_2$-CHOH), a poorly nucleophilic and polar solvent. Various unsymmetrical diaryl sulfides and aryl thiocyanates, which could be applicable to the synthesis of various types of sulfur-containing aromatic compounds, were prepared in good yields. These reactions could be performed under mild conditions without heating or the use of strong Lewis acid catalysts.

Introduction

The direct sulfenylation of aryl compounds is an important subject in synthetic organic chemistry.[1] Due to the useful transformations of the thiocyanato group into various sulfur functional groups[2] and sulfur-containing heterocycles,[3] the direct thiocyanation of aryl compounds is also of prime importance. Several types of sulfenylation methods for aryl compounds have been reported involving (i) nucleophilic substitution of an aryl halide with aromatic thiols catalyzed by nickel(0) and nickel(II) complexes,[4] (ii) Friedel–Crafts reaction using sulfuryl dihalides, arylsulfenyl halides, or diaryl disulfide catalyzed by iron or Lewis acids[5] or under heating,[6,7] and (iii) a modified Ziegler reaction using diazonium salts and aryl thiols.[8] Most of these reactions, however, require high temperature, metals, or strong Lewis acid catalysts and long reaction times. Thiocyanation methods for aromatic compounds have also been reported, involving the reaction between aromatic compounds and thiocyanogen [$(SCN)_2$].[3a] Thiocyanogen is, however, not active enough for direct thiocyanation of phenol ethers and usually needs to be activated by a Lewis acid.

In our continuing efforts to develop new methods for the direct substitution of para-substituted phenol ethers,[9] we have reported a novel and direct aromatic azidation of para-substituted phenol ethers using phenyliodine(III) bis(trifluoroacetate) (PIFA) in 1,1,1,3,3,3-hexafluoro-2-propanol [$(CF_3)_2CHOH$] followed by treatment with trimethylsilyl azide ($TMSN_3$)[9a] and applied it to the direct aromatic substitution of phenol ethers by oxygen and carbon nucleophiles.[9b] We have now examined the possibility of direct substitution of phenol ethers and related compounds by sulfur nucleophiles such as aryl thiols (ArSH) and trimethylsilyl isothiocyanate (TMSNCS).

Results and Discussion

At first, we examined the possibility of direct substitution of phenol ethers by various thiophenols using PIFA in $(CF_3)_2CHOH$.[10] To a solution of *p*-isopropylanisole (**1a**) containing 2 equiv of *S*-(trimethylsilyl)thiophenol (TMSSPh) in $(CF_3)_2CHOH$ was added PIFA to give the direct sulfenylation compound **2a** in 62% yield. The use of thiophenol instead of TMSSPh gave **2a** in nearly the same yield (61%). (Scheme 1).

The reaction proceeded successfully in $(CF_3)_2CHOH$, which is a polar and low-nucleophilic protic solvent, while in other solvents (CH_3CN, CH_2Cl_2, etc.) only a trace of the sulfenylation compound was detected. Furthermore, various types of thiophenols could be employed as sulfur nucleophiles. When **1b** was treated with thiophenols having electron-withdrawing groups such as *p*-nitro and 2,3,5,6-tetrafluoro groups in the presence of PIFA under similar conditions, the corresponding arylthio compounds **3** and **4** were obtained in good yield. Thiophenols having electron-donating groups such as *p*-methoxy and *p*-methyl groups gave the corresponding sulfenylation products **5** and **6** in lower yield due to the generation of byproducts (such as diaryl disulfides). These results are summarized in Table 1.

Other aromatic compounds, alkoxybenzenes (**1c–f**) and methoxynaphthalenes (**1g,h**), similarly reacted with PIFA and PhSH in $(CF_3)_2CHOH$ to give the corresponding unsymmetrical diaryl sulfides **2**. Dialkoxybenzenes **1i–k**, which are very reactive compounds,[11] yielded the diarylthio products **2i–k** without formation of the monoarylthio products (Table 2).

The mechanism of sulfenylation of phenol ethers with PIFA plausibly involves the formation of a CT complex

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(1) Alkyl aryl sulfides are generally prepared by the condensation of aromatic thiols with alkyl halides (Oae, S. *Organic Chemistry of Sulfur*; Plenum Press: New York, 1977; p 231), but the type of aromatic thiols available are limited.

(2) A recent report: Toste, F. D.; Laronde, F.; Still, W. J. *Tetrahedron Lett.* **1995**, *36*, 2946.

(3) Reviews: (a) Wood, J. L. *Organic Reactions*; Adams, R., Ed.; John Wiley & Sons: New York, 1946; Vol. 3, Chapter 6. (b) Guy, R. G. *In the Chemistry of Cyanates and Their Thio Derivatives*; Patai, S., Ed.; John Wiley & Sons: New York, 1977; Part 2, Chapter 18. (c) Harusawa, S.; Shioiri, T. *Yuki Gosei Kagaku Kyokaishi* **1981**, *39*, 741.

(4) (a) Takagi, K. *Chem Lett.* **1987**, 2221. (b) Cristau, H.; Charaud, A.; Chene, A.; Chriatol, H. *Synthesis* **1982**, 892.

(5) (a) Fujisawa, T.; Kobori, T.; Ohtsuka, N.; Tsuchihashi, G. *Tetrahedron Lett.* **1968**, *10*, 5073. (b) Mukaiyama, T.; Suzuki, K. *Chem Lett.* **1993**, 1.

(6) Ranken, D. F.; Mckinnie, B. G. *J. Org. Chem.* **1989**, *54*, 2985.

(7) Wang, Z. Y.; Hey, A. S. *Tetrahedron Lett.* **1990**, *31*, 5685.

(8) Petrillo, G.; Novi, M.; Garbarino, G.; Dell'Erba, C. *Tetrahedron Lett.* **1985**, *26*, 6365.

(9) (a) Kita, Y.; Tohma, H.; Inagaki, M.; Hatanaka, K.; Yakura, T. *Tetrahedron Lett.* **1991**, *32*, 4321. (b) Kita, Y.; Tohma, H.; Hatanaka, K.; Takada, T.; Fujita, S.; Mitoh, S.; Sakurai, H.; Oka, S. *J. Am. Chem. Soc.* **1994**, *116*, 3684. (c) Kita, Y.; Tohma, H.; Takada, T.; Mitoh, S.; Fujita, S.; Gyoten, M. *Synlett* **1994**, 427.

(10) For a preliminary communication of a portion of the studies described herein, see: Kita, Y.; Takada, T.; Mihara, S.; Tohma, H. *Synlett* **1995**, 211.

(11) The oxidative potentials (E°) of dialkoxybenzenes are lower than those of alkylbenzenes. (Sankaraman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7824.)

0022-3263/95/1960-7144$09.00/0

Scheme 1

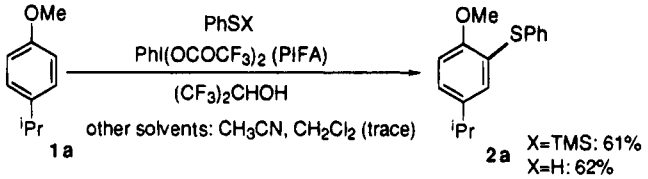
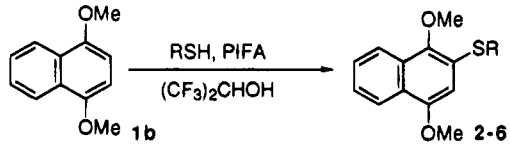
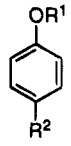
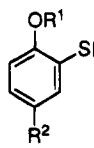
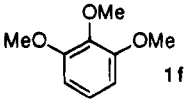
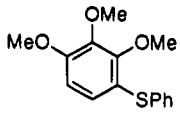
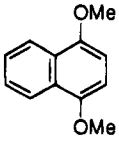
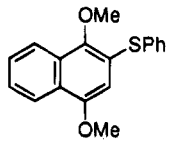
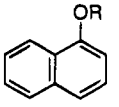
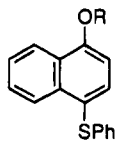
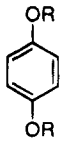
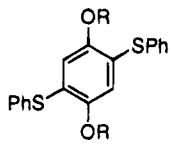
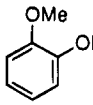
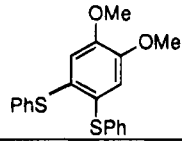


Table 1. Sulfenylation of 1b by Various Thiophenols



substrates	R	products	yields (%)
1b	4-nitrophenyl	3	87
	2,3,5,6-terafluorophenyl	4	72
	phenyl	2b	62
	4-methoxyphenyl	5	37
	4-methylphenyl	6	40

Table 2. Sulfenylation of Phenol Ethers and Alkoxynaphthalenes

Substrates		Products		Yields (%)
	1a: R^1=Me, R^2=^{i}Pr		2a	62
	c: R^1=Et, R^2=^{i}Pr		c	67
	d: R^1=^{i}Pr, R^2=^{i}Pr		d	70
	e: R^1=Me, R^2=^{t}Bu		e	67
	1f		2f	88
	1b		2b	62
	1g: R=Me		2g	81
	h: R=Et		h	86
	1i: R=Me		2i	68
	j: R=Et		j	75
	1k		2k	88

of PIFA with **1** followed by a nucleophilic attack by the thiophenol on the cation radical generated by single electron transfer (SET) from the CT complex (mechanism A[9b]). Product formation, on the other hand, can also be explained by the formation of a diaryl disulfide arising from the reaction of thiophenols with PIFA, followed by a PIFA-promoted Friedel–Crafts reaction of the diaryl disulfide with **1** (mechanism B[12]). The sulfenylation product, however, was not obtained when diaryl disulfides activated with PIFA were treated with **1**. Therefore, we believe that the present sulfenylation proceeds via cation radicals as reactive intermediates formed by SET from the CT complex of **1** and PIFA (mechanism A) (Scheme 2).

The characteristic points of the present reactions are (i) thiophenols, which are easily available can be used as nucleophiles, (ii) the reaction can be performed under mild conditions, (iii) the hypervalent iodine reagent is simpler and safer than metal catalysts, and (iv) unsymmetric diaryl sulfides were directly and selectively obtained.

Next, we examined the possibility of direct thiocyanation of phenol ethers and alkoxynaphthalenes by using TMSNCS as a nucleophile. To a solution of *p*-isopropylanisole **1a** containing 2 equiv of TMSNCS in $(CF_3)_2$CHOH was added PIFA to give 4-isopropyl-2-thiocyanatoanisole **7a** in 66% yield. Other aromatic compounds, alkoxybenzenes **1c–m** and alkoxynaphthalenes **1b,g,h**, similarly reacted with PIFA and TMSNCS in $(CF_3)_2$CHOH to give the corresponding aryl thiocyanato compounds **7b–m**.[13] The thiocyanato group was selectively introduced at the ortho position of para-substituted phenol ethers and at the para position of ortho-substituted phenol ethers. These results are summarized in Table 3.

The reaction mechanism of thiocyanation of phenol ethers with PIFA is the same as that of sulfenylation of phenol ethers described above, that is, nucleophilic attack of TMSNCS on the cation radical generated by SET from the CT complex of PIFA and phenol ethers to give the corresponding aryl thiocyanato compounds. The present reaction is useful for the preparation of aryl thiocyanato compounds and proceeds smoothly without heating or the addition of Lewis acid catalysts.

In conclusion, novel and direct sulfenylation and thiocyanation of phenol ethers and related compounds have been developed using a hypervalent iodine reagent. The present methods could be applicable to the synthesis of various types of sulfur containing aromatic compounds.

Experimental Section

All melting points are uncorrected. Infrared (IR) absorption spectra were recorded with $CHCl_3$ as solvent. E. Merck silica gel 60 for column chromatography and E. Merck precoated TLC plates, silica gel F_{254} for preparative thin layer chromatography (preparative TLC) were used. Organic layers were dried with anhydrous $MgSO_4$. PIFA is commercially available. Starting materials (**1b,f,g,i–m**) were purchased, and compounds (**1a,c–e,h**) were prepared by the reported methods.[14] Thiophenols and TMSNCS were purchased and were used without further purification.

General Experimental Procedure. Nucleophilic Sulfenylation Reaction of Phenol Ethers and Related Compounds with PIFA. To a stirred solution of **1** (0.10 mmol) and aryl thiols (0.20 mmol) in 1,1,1,3,3,3-hexafluoro-2-propanol ($(CF_3)_2$CHOH) (1.0 mL) was added PIFA (0.12–0.15 mmol) at rt under nitrogen. The reaction mixture was stirred for 30 min and then was evaporated in vacuo. The residue was

(12) Kitamura, T.; Matsuyuki, J.; Taniguchi, H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1607.

(13) No aryl isothiocyanato compounds (ArNCS) were generated in these reactions.

(14) Methyl ethers (**1a,e**): Vyas, G. N.; Shah, N. M. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 836. Ethyl ethers (**1c,h**): *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, p 58. Isopropyl ether (**1d**): Sala, T.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2593.

Scheme 2

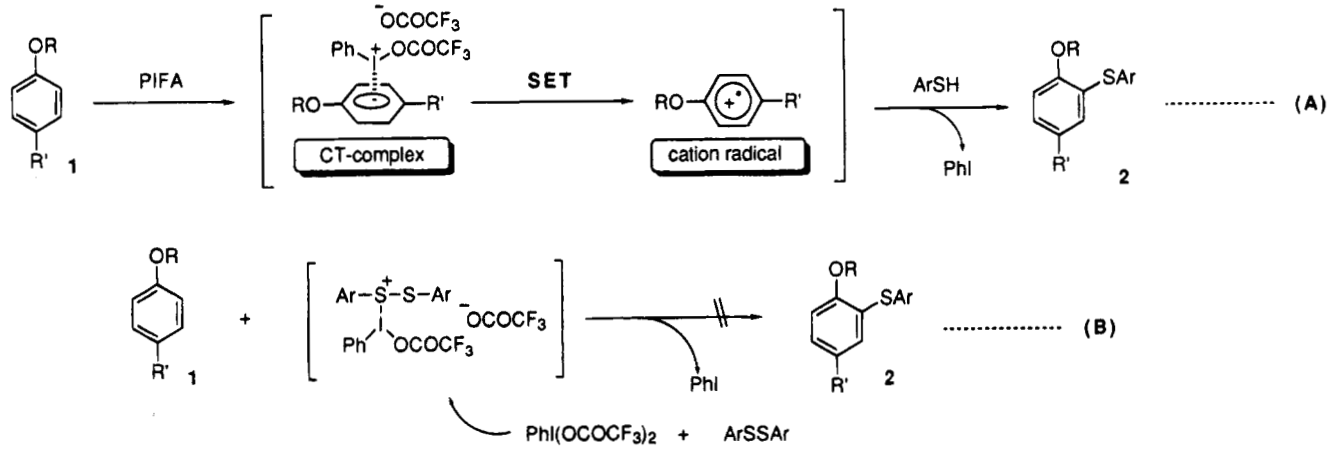
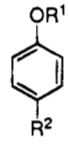
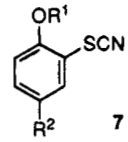
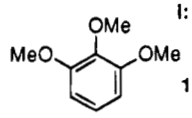
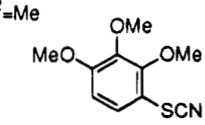
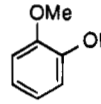
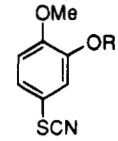
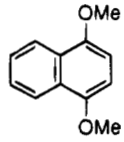
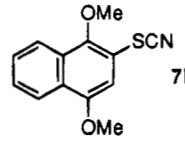
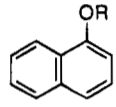
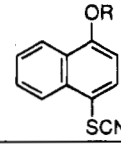


Table 3. Thiocyanation of Phenol Ethers and Alkoxynaphthalenes

Substrates		Products		Yields (%)
	**1a**: R^1=Me, R^2=^{i}Pr			71
	c: R^1=Et, R^2=^{i}Pr			94
	d: R^1=^{i}Pr, R^2=^{i}Pr			91
	e: R^1=Me, R^2=^{t}Bu		**7**	59
	i: R^1=Me, R^2=OMe			66
	j: R^1=Et, R^2=OEt			90
	l: R^1=Me, R^2=Me			55
	**1f**		**7f**	73
	**1k**: R=OMe		**7k**	95
	1m: R=Me		**m**	62
	**1b**		**7b**	96
	**1g**: R=Me		**7g**	78
	h: R=Et		**h**	57

purified by column chromatography or preparative TLC on silica gel to give the corresponding diaryl sulfides **2**.

Nucleophilic Thiocyanation Reaction of Phenol Ethers and Related Compounds with PIFA. To a stirred solution of **1** (0.10 mmol) and TMSNCS (0.20–0.50 mmol) in $(CF_3)_2$CHOH (1.0 mL) was added PIFA (0.15–0.20 mmol) at rt under nitrogen. The reaction mixture was stirred for 30 min and then was evaporated in vacuo. The residue was purified by column chromatography or preparative TLC on silica gel to give the corresponding thiocyanato compounds **7**.

4-Isopropyl-2-(phenylthio)anisole (2a). 1a (13.3 mg, 0.089 mmol), PhSH (0.018 mL, 0.177 mmol), PIFA (57.1 mg, 0.133 mmol), and $(CF_3)_2$CHOH (1.0 mL) gave **2a** (14.5 mg, 62%) as an oil: IR ($CHCl_3$) ν 1580, 1490 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 1.16 (d, J = 7.0 Hz, 6H), 2.78 (m, 1H), 3.83 (s, 3H), 6.85 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 7.12 (dd, J = 8.4, 2.4 Hz 1H), 7.20–7.30 (m, 5H); HRMS calcd for $C_{16}H_{18}OS$ 258.1082, found 258.1077.

1,4-Dimethoxy-2-(phenylthio)naphthalene (2b). 1b (10.7 mg, 0.057 mmol), PhSH (0.012 mL, 0.114 mmol), PIFA (29.4 mg, 0.068 mmol), and $(CF_3)_2$CHOH (1.0 mL) gave **2b** (10.4 mg, 62%) as an oil: IR ($CHCl_3$) ν 1590, 1460 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 3.80 (s, 3H), 3.97 (s, 3H), 6.55 (s, 1H), 7.22–7.37 (m, 5H), 7.48 (m, 2H), 8.07 (d, J = 7.5 Hz, 1H), 8.20 (d, J = 7.5 Hz, 1H); HRMS calcd for $C_{18}H_{16}O_2S$ 296.0883, found 296.0871. Anal. Calcd for $C_{18}H_{16}O_2S$: C, 73.25; H, 5.62. Found: C, 72.95; H, 5.44.

1,4-Dimethoxy-2-[(4-nitrophenyl)thio]naphthalene (3). 1b (11.4 mg, 0.061 mmol), 4-nitrothiophenol (18.8 mg, 0.121 mmol), PIFA (39.1 mg, 0.091 mmol), and $(CF_3)_2$CHOH (1.0 mL) gave **3** (18.1 mg, 87%) as crystals: mp 138–139 °C (from n-hexane); IR ($CHCl_3$) ν 1580, 1520 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 3.94 (s, 6H), 6.75 (s, 1H), 7.23 (d, J = 9.0 Hz, 2H), 7.59–7.64 (m, 2H), 8.07 (d, J = 9.0 Hz, 2H), 8.11–8.15 (m, 1H), 8.27–8.31 (m, 1H); HRMS calcd for $C_{18}H_{15}NO_4S$ 341.0722, found 341,0722. Anal. Calcd for $C_{18}H_{15}NO_4S$: C, 63.09; H, 4.48; N, 4.07; S, 9.42. Found: C, 63.33; H, 4.43; N, 4.10; S, 9.39.

1,4-Dimethoxy-2-[(2,3,5,6-tetrafluorophenyl)thio]naphthalene (4). 1b (36.3 mg, 0.193 mmol), 2,3,5,6-tetrafluorothiophenol (0.047 mL, 0.386 mmol), PIFA (124.5 mg, 0.290 mmol), and $(CF_3)_2$CHOH (1.0 mL) gave **4** (48.8 mg, 72%) as crystals: mp 102–103 °C (from CH_2Cl_2–n-hexane); IR ($CHCl_3$) ν 1590, 1490 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 3.87 (s, 3H), 4.01 (s, 3H), 6.55 (s, 1H), 7.08 (m, 1H), 7.43–7.49 (m, 2H), 8.00 (dd, J = 7.6, 1.4 Hz, 1H), 8.19 (dd, J = 7.6, 1.4 Hz, 1H); HRMS calcd for $C_{18}H_{12}O_2F_4S$ 368.0493, found 368.0493. Anal. Calcd for $C_{18}H_{12}O_2F_4S$: C, 58.69; H, 3.28. Found: C, 58.75; H, 3.52.

1,4-Dimethoxy-2-[(4-methoxyphenyl)thio]naphthalene (5). 1b (12.1 mg, 0.064 mmol), 4-methoxythiophenol (0.016 mL, 0.129 mmol), PIFA (55.3 mg, 0.129 mmol), and $(CF_3)_2$CHOH (1.0 mL) gave **5** (7.8 mg, 37%) as an oil: IR ($CHCl_3$) ν 1590, 1500, 1460 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 3.74 (s, 3H), 3.83 (s, 3H), 3.99 (s, 3H), 6.35 (s, 1H), 6.91 (d, J = 8.8 Hz, 2H), 7.43 (td, J = 7.0, 1.6 Hz, 1H), 7.44 (d, J = 9.0 Hz, 2H), 7.53 (td, J = 7.0, 1.6 Hz, 1H), 8.03 (dd, J = 8.2, 1.6 Hz, 1H), 8.15 (dd, J = 8.2, 1.6 Hz, 1H); HRMS calcd for $C_{19}H_{18}O_3S$ 326.0977, found 326.0977.

1,4-Dimethoxy-2-[(4-methylphenyl)thio]naphthalene (6). 1b (11.6 mg, 0.062 mmol), 4-methylthiophenol (15.3 mg, 0.123 mmol), PIFA (53.0 mg, 0.123 mmol), and $(CF_3)_2$CHOH (1.0 mL) gave **6** (11.8 mg, 40%) as an oil: IR ($CHCl_3$) ν 1590, 1490, 1460 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 2.34 (s, 3H), 3.78 (s, 3H), 3.97 (s, 3H), 6.49 (s, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.42–7.58 (m, 2H), 8.05 (dd, J = 8.0, 1.6 Hz, 1H), 8.16 (dd, J = 8.0, 1.6 Hz, 1H); HRMS calcd for $C_{19}H_{18}O_2S$ 310.1014, found 310.1025. Anal. Calcd for $C_{19}H_{18}O_2S$: C, 73.43; H, 5.89; S, 10.33. Found: C, 73.52; H, 5.84; S, 10.33.

1-Ethoxy-4-isopropyl-2-(phenylthio)benzene (2c). 1c (16.3 mg, 0.099 mmol), PhSH (0.020 mL, 0.198 mmol), PIFA (64.0 mg, 0.149 mmol), and $(CF_3)_2$CHOH (1.0 mL) gave **2c** (18.2 mg, 67%) as an oil: IR ($CHCl_3$) ν 1580, 1480 cm^{-1}; ^1H NMR

(200 MHz) ($CDCl_3$) δ 1.15 (d, J = 7.0 Hz, 6H), 1.29 (t, J = 6.8 Hz, 3H), 2.76 (m, 1H), 4.02 (q, J = 6.8 Hz, 2H), 6.81 (d, J = 8.4 Hz, 1H), 7.05 (s, 1H), 7.20–7.32 (m, 6H); HRMS calcd for $C_{17}H_{20}OS$ 272.1253, found 272.1235.

1-Isopropoxy-4-isopropyl-2-(phenylthio)benzene (2d). **1d** (10.7 mg, 0.060 mmol), PhSH (0.012 mL, 0.120 mmol), PIFA (38.7 mg, 0.090 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **2d** (12.1 mg, 70%) as an oil: IR ($CHCl_3$) ν 1580, 1480 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 1.15 (d, J = 7.0 Hz, 6H), 1.24 (d, J = 7.0 Hz, 6H), 2.77 (m, 1H), 4.49 (m, 1H), 6.82 (d, J = 8.2 Hz, 1H), 7.04 (s, 1H), 7.21–7.35 (m, 6H); HRMS calcd for $C_{18}H_{22}OS$ 286.1386, found 286.1389. Anal. Calcd for $C_{18}H_{22}OS$: C, 75.34; H, 7.71; S, 11.16. Found: C, 75.48; H, 7.74; S, 11.19.

4-*tert*-Butyl-2-(phenylthio)anisole (2e). **1e** (15.6 mg, 0.095 mmol), PhSH (0.020 mL, 0.190 mmol), PIFA (61.3 mg, 0.143 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **2e** (17.3 mg, 67%) as an oil: IR ($CHCl_3$) ν 1580, 1490 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 1.22 (s, 9H), 3.83 (s, 3H), 6.85 (d, J = 8.4 Hz, 1H), 7.23–7.29 (m, 7H); HRMS calcd for $C_{17}H_{20}OS$ 272.1230, found 272.1232.

1,2,3-Trimethoxy-4-(phenylthio)benzene (2f). **1f** (12.4 mg, 0.074 mmol), PhSH (0.015 mL, 0.147 mmol), PIFA (47.5 mg, 0.111 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **2f** (18.0 mg, 88%) as an oil: IR ($CHCl_3$) ν 1580, 1480 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 3.82 (s, 3H), 3.87 (s, 3H), 3.88 (s, 3H), 6.65 (d, J = 8.6 Hz, 1H), 7.02 (d, J = 8.6 Hz, 1H), 7.18–7.27 (m, 5H); HRMS calcd for $C_{15}H_{16}O_3S$ 276.0826, found 276.0820. Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.42; H, 5.87; S, 11.60. Found: C, 65.19; H, 5.84; S, 11.60.

1-Methoxy-4-(phenylthio)naphthalene (2g). **1g** (15.8 mg, 0.100 mmol), PhSH (0.021 mL, 0.200 mmol), PIFA (64.4 mg, 0.150 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **2g** (21.4 mg, 81%) as crystals: mp 88–89 °C (from CH_2Cl_2–n-hexane); IR ($CHCl_3$) ν 1590 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 4.03 (s, 3H), 6.82 (d, J = 8.0 Hz, 1H), 7.01–7.24 (m, 5H), 7.49–7.53 (m, 2H), 7.79 (d, J = 8.0 Hz, 1H), 8.30–8.34 (m, 2H); HRMS calcd for $C_{17}H_{14}OS$ 266.0755, found 266.0762. Anal. Calcd for $C_{17}H_{14}OS$: C, 76.49; H, 5.37; S, 11.88. Found: C, 76.66; H, 5.30; S, 12.04.

1-Ethoxy-4-(phenylthio)naphthalene (2h). **1h** (17.7 mg, 0.103 mmol), PhSH (0.021 mL, 0.206 mmol), PIFA (66.4 mg, 0.155 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **2h** (24.8 mg, 86%) as crystals; mp 106–107 °C (from CH_2Cl_2–n-hexane); IR ($CHCl_3$) ν 1580 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 1.58 (t, J = 7.0 Hz, 3H), 4.25 (q, J = 7.0 Hz, 2H), 6.81 (d, J = 8.2 Hz, 1H), 6.99–7.15 (m, 5H), 7.48–7.53 (m, 2H), 7.78 (d, J = 8.2 Hz, 1H), 8.28–8.38 (m, 2H); HRMS calcd for $C_{18}H_{16}OS$ 280.0905, found 280.0920. Anal. Calcd for $C_{18}H_{16}OS$: C, 77.22; H, 5.75; S, 11.41. Found: C, 77.11; H, 5.75; S, 11.43.

1,4-Dimethoxy-2,5-bis(phenylthio)benzene (2i). **1i** (10.8 mg, 0.078 mmol), PhSH (0.020 mL, 0.195 mmol), PIFA (83.9 mg, 0.195 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **2i** (18.9 mg, 68%) as crystals: mp 145–146 °C (from CH_2Cl_2–n-hexane); IR ($CHCl_3$) ν 1580, 1480 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 3.65 (s, 6H), 6.65 (s, 2H), 7.29–7.35 (m, 10H); HRMS calcd for $C_{20}H_{18}O_2S_2$ 354.0748, found 354.0748.

1,4-Diethoxy-2,5-bis(phenylthio)benzene (2j). **1j** (12.3 mg, 0.074 mmol), PhSH (0.019 mL, 0.185 mmol), PIFA (79.6 mg, 0.185 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **2j** (21.2 mg, 75%) as crystals: mp 93–94 °C (from CH_2Cl_2–n-hexane); IR ($CHCl_3$) ν 1590, 1470 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 1.23 (t, J = 6.8 Hz, 6H), 3.83 (q, J = 6.8 Hz, 4H), 6.63 (s, 2H), 7.25–7.39 (m, 10H); HRMS calcd for $C_{22}H_{22}O_2S_2$ 382.1072, found 382.1061. Anal. Calcd for $C_{22}H_{22}O_2S_2$: C, 69.04; H, 5.84. Found: C, 69.08; H, 5.80.

1,2-Dimethoxy-4,5-bis(phenylthio)benzene (2k). **1k** (12.0 mg, 0.087 mmol), PhSH (0.018 mL, 0.174 mmol), PIFA (56.0 mg, 0.130 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **2k** (27.2 mg, 88%) as crystals: mp 79–80 °C (from CH_2Cl_2–n-hexane); IR ($CHCl_3$) ν 1580, 1480, 1460 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 3.73 (s, 6H), 6.83 (s, 2H), 7.19–7.29 (m, 10H); HRMS calcd for $C_{20}H_{18}O_2S_2$ 354.0746, found 354.0744. Anal. Calcd for $C_{20}H_{18}O_2S_2$: C, 67.77; H, 5.12; S, 18.09. Found: C, 67.77; H, 5.20; S, 17.99.

4-Isopropyl-2-thiocyanatoanisole (7a). **1a** (11.1 mg, 0.074 mmol), TMSNCS (0.021 mL, 0.148 mmol), PIFA (47.7 mg, 0.111 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7a** (10.9 mg, 71%) as an oil: IR ($CHCl_3$) ν 2160, 1600, 1500, 1460, 1440 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 1.24 (d, J = 7.5 Hz, 6H), 2.90 (m, J = 7.5 Hz, 1H), 3.89 (s, 3H), 6.86 (d, J = 7.8 Hz, 1H), 7.21 (dd, J = 8.0, 1.8 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H); HRMS calcd for $C_{11}H_{13}NOS$ 207.0721, found 207.0718.

1,4-Dimethoxy-2-thiocyanatonaphthalene (7b). **1b** (31.1 mg, 0.165 mmol), TMSNCS (0.047 mL, 0.330 mmol), PIFA (106.4 mg, 0.248 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7b** (38.8 mg, 96%) as crystals: mp 95–96 °C (from CH_2Cl_2–n-hexane); IR ($CHCl_3$) ν 2160, 1620, 1580, 1510, 1460, 1440 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 3.95 (s, 3H), 4.04 (s, 3H), 6.89 (s, 1H), 7.53 (td, J = 7.0, 1.6 Hz, 1H), 7.61 (td, J = 7.0, 1.6 Hz, 1H), 7.97 (dd, J = 7.2, 2.2 Hz, 1H), 8.25 (dd, J = 7.6, 2.2 Hz, 1H); HRMS calcd for $C_{13}H_{11}NO_2S$ 245.0509, found 245.0509. Anal. Calcd for $C_{13}H_{11}NO_2S$: C, 63.48; H, 4.54; N, 5.67. Found: C, 63.65; H, 4.52; N, 5.71.

1-Ethoxy-4-isopropyl-2-thiocyanatobenzene (7c). **1c** (11.7 mg, 0.071 mmol), TMSNCS (0.040 mL, 0.285 mmol), PIFA (61.3 mg, 0.143 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7c** (14.9 mg, 94%) as an oil: IR ($CHCl_3$) ν 2160, 1600, 1500, 1480, 1460 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 1.23 (d, J = 7.0 Hz, 6H), 1.44 (t, J = 7.0 Hz, 3H), 2.89 (m, J = 7.0 Hz, 1H), 4.11 (q, J = 7.0 Hz, 2H), 6.84 (d, J = 8.4 Hz, 1H), 7.17 (dd, J = 8.4, 2.0 Hz, 1H), 7.39 (d, J = 2.0 Hz, 1H); HRMS calcd for $C_{12}H_{15}NOS$ 221.0881, found 221.0874. Anal. Calcd for $C_{12}H_{15}NOS$: C, 64.81; H, 6.75; N, 6.22. Found: C, 65.12; H, 6.83; N, 6.33.

1-Isopropoxy-4-isopropyl-2-thiocyanatobenzene (7d). **1d** (10.4 mg, 0.058 mmol), TMSNCS (0.033 mL, 0.233 mmol), PIFA (50.1 mg, 0.117 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7d** (12.6 mg, 91%) as an oil: IR ($CHCl_3$) ν 2160, 1600, 1500, 1480, 1460 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 1.24 (d, J = 6.8 Hz, 6H), 1.37 (d, J = 6.0 Hz, 6H), 2.89 (m, J = 6.8 Hz, 1H), 4.58 (m, J = 6.0 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 7.16 (dd, J = 8.5, 1.8 Hz, 1H), 7.38 (d, J = 1.8 Hz, 1H); HRMS calcd for $C_{13}H_{17}NOS$ 235.1020, found 235.1028.

4-*tert*-Butyl-2-thiocyanatoanisole (7e). **1e** (10.2 mg, 0.062 mmol), TMSNCS (0.018 mL, 0.124 mmol), PIFA (40.1 mg, 0.093 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7e** (7.8 mg, 57%) as an oil: IR ($CHCl_3$) ν 2160, 1600, 1500, 1460, 1440 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 1.32 (s, 9H), 3.90 (s, 3H), 6.87 (d, J = 8.8 Hz, 1H), 7.38 (dd, J = 8.8, 2.4 Hz, 1H), 7.56 (d, J = 2.2 Hz, 1H); HRMS calcd for $C_{12}H_{15}NOS$ 221.0867, found 221.0872.

1,2,3-Trimethoxy-4-thiocyanatobenzene (7f). **1f** (13.4 mg, 0.080 mmol), TMSNCS (0.045 mL, 0.320 mmol), PIFA (68.8 mg, 0.160 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7f** (13.1 mg, 73%) as an oil: IR ($CHCl_3$) ν 2160, 1580, 1480, 1460 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 3.88 (s, 3H), 3.89 (s, 3H), 4.00 (s, 3H), 6.73 (d, J = 8.5 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H); HRMS calcd for $C_{10}H_{11}NO_3S$ 225.0459, found 225.0459. Anal. Calcd for $C_{10}H_{11}NO_3S$: C, 53.50; H, 5.00; N, 6.20. Found: C, 53.32; H, 4.92; N, 6.22.

1-Methoxy-4-thiocyanatonaphthalene (7g). **1g** (22.1 mg, 0.139 mmol), TMSNCS (0.078 mL, 0.556 mmol), PIFA (119.5 mg, 0.278 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7g** (23.4 mg, 78%) as crystals: mp 106–107 °C (from CH_2Cl_2–n-hexane); IR ($CHCl_3$) ν 2150, 1620, 1590, 1570, 1510, 1460, 1440 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 4.03 (s, 3H), 6.80 (d, J = 8.2 Hz, 1H), 7.59 (td, J = 7.5, 1.0 Hz, 1H), 7.72 (td, J = 7.0, 1.0 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 8.28 (d, J = 8.6 Hz, 1H), 8.34 (d, J = 8.3 Hz, 1H); HRMS calcd for $C_{12}H_9NOS$ 215.0406, found 215.0406. Anal. Calcd for $C_{12}H_9NOS$: C, 66.61; H, 4.31; N, 6.47. Found: C, 66.95; H, 4.21; N, 6.51.

1-Ethoxy-4-thiocyanatonaphthalene (7h). **1h** (10.4 mg, 0.060 mmol), TMSNCS (0.017 mL, 0.121 mmol), PIFA (39.0 mg, 0.091 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7h** (7.9 mg, 57%) as crystals: mp 74–76 °C (from CH_2Cl_2–n-hexane); IR ($CHCl_3$) ν 2150, 1590, 1570, 1510 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 1.58 (t, J = 6.8 Hz, 3H), 4.24 (q, J = 6.8 Hz, 2H), 6.80 (d, J = 8.5 Hz, 1H), 7.59 (td, J = 7.5, 1.0 Hz, 1H), 7.72 (td, J = 7.5, 1.0 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H); HRMS calcd for $C_{13}H_{11}NOS$ 229.0563, found 229.0562.

1,4-Dimethoxy-2-thiocyanatobenzene (7i). **1i** (16.2 mg, 0.117 mmol), TMSNCS (0.099 mL, 0.702 mmol), PIFA (100.6 mg, 0.234 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7i** (15.0 mg, 66%) as crystals: mp 68–69 °C (from CH_2Cl_2–*n*-hexane); IR ($CHCl_3$) ν 2160, 1590, 1490, 1460, 1440 cm^{-1}; ^1H NMR (250 MHz) (CD_3OD) δ 3.79 (s, 3H), 3.87 (s, 3H), 6.94 (dd, J = 9.3, 2.5 Hz, 1H), 7.01 (d, J = 9.3 Hz, 1H), 7.08 (d, J = 2.5 Hz, 1H); HRMS calcd for $C_9H_9NO_2S$ 195.0359, found 195.0354. Anal. Calcd for $C_9H_9NO_2S$: C, 55.06; H, 4.63; N, 7.11. Found: C, 55.37; H, 4.65; N, 7.17.

1,4-Diethoxy-2-thiocyanatobenzene (7j). **1j** (10.4 mg, 0.063 mmol), TMSNCS (0.035 mL, 0.250 mmol), PIFA (53.8 mg, 0.125 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7j** (12.5 mg, 90%) as an oil: IR ($CHCl_3$) ν 2160, 1580, 1500, 1470 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 1.40 (t, J = 7.3 Hz, 3H), 1.42 (t, J = 7.5 Hz, 3H), 4.00 (q, J = 7.0 Hz, 2H), 4.06 (q, J = 7.0 Hz, 2H), 6.84 (s, 2H), 7.09 (s, 1H); HRMS calcd for $C_{11}H_{13}NO_2S$ 223.0662, found 223.0665. Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.20; H, 5.86; N, 6.33; S, 14.22. Found: C, 59.17; H, 5.87; N, 6.27; S, 14.36.

1,2-Dimethoxy-4-thiocyanatobenzene (7k). **1k** (20.8 mg, 0.151 mmol), TMSNCS (0.085 mL, 0.604 mmol), PIFA (129.9 mg, 0.302 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7k** (28.1 mg, 95%) as crystals: mp 49–50 °C (from CH_2Cl_2–*n*-hexane); IR ($CHCl_3$) ν 2150, 1590, 1510, 1460, 1440 cm^{-1}; ^1H NMR (250 MHz) ($CDCl_3$) δ 3.91 (s, 3H), 3.92 (s, 3H), 6.89 (d, J = 8.5 Hz, 1H), 7.05 (d, J = 2.5 Hz, 1H), 7.16 (dd, J = 8.5, 2.5 Hz, 1H); HRMS calcd for $C_9H_9NO_2S$ 195.0330, found 195.0354. Anal. Calcd for $C_9H_9NO_2S$: C, 55.22; H, 4.61; N, 7.14; S, 16.35. Found: C, 55.37; H, 4.65; N, 7.17; S, 16.42.

4-Methyl-2-thiocyanatoanisole (7l). **1l** (12.6 mg, 0.103 mmol), TMSNCS (0.058 mL, 0.412 mmol), PIFA (88.6 mg, 0.206 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7l** (10.2 mg, 55%) as an oil: IR ($CHCl_3$) ν 2160, 1600, 1500 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 2.32 (s, 3H), 3.88 (s, 3H), 6.82 (d, J = 8.2 Hz, 1H), 7.14 (dd, J = 8.2, 2.0 Hz, 1H), 7.36 (d, J = 2.0 Hz, 1H); HRMS calcd for C_9H_9NOS 179.0411, found 179.0405.

2-Methyl-4-thiocyanatoanisole (7m). **1m** (22.9 mg, 0.187 mmol), TMSNCS (0.110 mL, 0.748 mmol), PIFA (160.8 mg, 0.374 mmol), and $(CF_3)_2CHOH$ (1.0 mL) gave **7m** (20.8 mg, 62%) as an oil: IR ($CHCl_3$) ν 2150, 1590, 1570, 1490, 1460, 1440 cm^{-1}; ^1H NMR (200 MHz) ($CDCl_3$) δ 2.22 (s, 3H), 3.85 (s, 3H), 6.84 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 2.5 Hz, 1H), 7.38 (dd, J = 8.5, 2.5 Hz, 1H); HRMS calcd for C_9H_9NOS 179.0385, found 179.0404.

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