FeF_3/I_2-Catalyzed Synthesis of 4-Chalcogen-Substituted Arylamines by Direct Thiolation of an Arene C–H Bond

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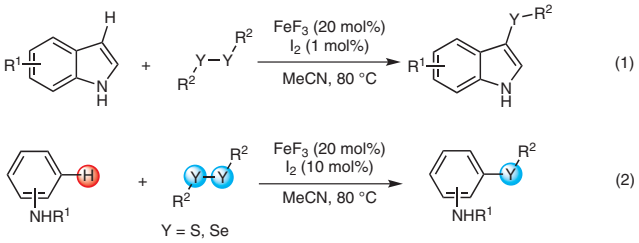
Abstract: An efficient regioselective synthesis of 4-chalcogen-substituted arylamines by FeF_3-catalyzed sulfenylation and selenation of arylamines has been developed. In the presence of FeF_3 and I_2, a variety of arylamines underwent the reaction with disulfides or diselenides to afford the corresponding 4-sulfenyl- or 4-selenenyl-arylamines in moderate to good yields.

Key words: iron, iodine, sulfenylation, selenation, arylamine, 4-chalcogen-substituted arylamine



Scheme 1 Chalcogenation with disulfides or diselenides

Aryl sulfides are a valuable class of compounds that have been widely used as pharmaceuticals and synthetic intermediates.[1] Traditionally, aryl sulfides are prepared by reduction of the corresponding sulfones or sulfoxides under harsh reaction conditions.[2] Transition-metal-catalyzed cross-coupling reactions of thiols with aryl halides[3–5] or aryl triflates[6]provide another alternative access. However, these procedures suffer from the oxidative S–S coupling of thiols and/or catalyst poisoning.[7] To overcome these drawbacks, disulfides are commonly employed to replace thiols.[8]

Recently, the direct functionalization of arene C–H bond has received attention because of its potential low cost and environmentally benign features.[8i,j,9–12] Thus, C–S bond forming reactions through C–H functionalization of arene or heteroarene with various sulfur-containing reagents have been investigated.[10] For example, Yadav and co-workers reported an iron(III) chloride catalyzed direct thiolation of indoles with thiols.[11] We have also developed an iodine-promoted iron-catalyzed chalcogenation of indoles with disulfides or diselenides (Scheme 1, Equation 1.[12] As a continuing interest in the synthetic utility of disulfides,[12,13] we sought to extend these catalytic systems to the thiolation of arylamines. Here, we report an efficient synthesis of sulfenylarylamines and selenenylarylamines by direct thiolation of an arene C–H bond of arylamines with disulfides or diselenides using FeF_3 and I_2 as co-catalysts (Scheme 1, Equation 2).[8i,j]

The reaction between aniline (**1a**) and 1,2-diphenyl disulfide (**2a**) was chosen to investigate the optimal reaction conditions (Table 1). Initially, a series of catalytic systems were investigated. We found that treatment of aniline (**1a**) with disulfide **2a** afforded rather low conversions and yields using either FeF_3 or IPy_2BF_4 as the catalyst alone (Table 1, entries 1 and 2). However, the desired product **3** could be obtained in 63% yield with an 11:1 ratio of *para*- and *ortho*-thiolation isomers using 20 mol% FeF_3 combined with 10 mol% IPy_2BF_4 (entry 3). Other iron salts, such as $FeCl_3$, $FeBr_3$, $Fe_2(SO_4)_3$, and $FeCl_2$, were also examined, but they were less effective than FeF_3 (entries 4–7). We found that I_2 was a more effective catalyst than IPy_2BF_4, enhancing the yield from 63 to 79% (entries 3 and 8). The amount of I_2 affected the reaction: a lower yield was observed when the amount of I_2 was increased to 20 mol% or decreased to 5 mol% (entries 9 and 10). Among the effects of solvent and reaction temperature examination, the reaction in MeCN at 80 °C gave the best results (entries 11–15). Finally, the loading of FeF_3 was evaluated. The results showed that the yield was lowered to some extent in the presence of 10 mol% FeF_3 (entry 16). It is noteworthy that the desired product **3** was formed in 43% yield in the absence of Fe catalysts (entry 17).

With the optimal reaction conditions in hand, we subsequently explored the scope of both amines and disulfides (Tables 2 and 3). As shown in Table 2, a variety of disulfides **2b–g** were investigated by treating with aniline (**1a**) in the presence of FeF_3 and I_2. The results showed that numerous diaryl disulfides **2b–f** were suitable substrates for this reaction, giving the corresponding products in moderate to good yields with high regioselectivity (Table 2, entries 1–5). For example, 1,2-di(*p*-tolyl)disulfide (**2b**) reacted with amine **1a**, FeF_3, and I_2 to afford the desired product **4** in 75% yield with a 97:3 ratio of *para/ortho*-thiolation isomers (entry 1). Disulfide **2e**, having an electron-withdrawing group on the aromatic ring, was also suitable under the standard conditions (entry 4). Product

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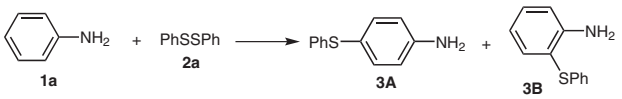
Table 1 Sulfenylation of Aniline (**1a**) with Diphenyl Disulfide (**2a**)[a]



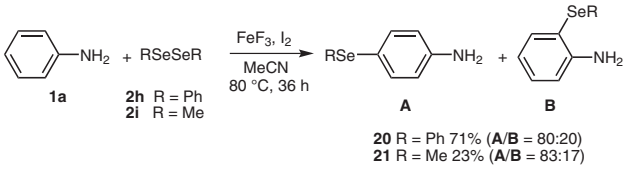
Entry	[Fe] (mol%)	Additive (mol%)	Solvent	Conversion (%)[b]	Yield (%)[c]
1	FeF_3 (20)	–	MeCN	9	8
2	–	IPy_2BF_4 (10)	MeCN	36	16 (4:1)
3	FeF_3 (20)	IPy_2BF_4 (10)	MeCN	88	63 (11:1)
4	$FeCl_3$ (20)	IPy_2BF_4 (10)	MeCN	50	34 (6:1)
5	$FeBr_3$ (20)	IPy_2BF_4 (10)	MeCN	78	trace
6	$Fe_2(SO_4)_3$ (20)	IPy_2BF_4 (10)	MeCN	80	trace
7	$FeCl_2$ (20)	IPy_2BF_4 (10)	MeCN	70	56 (7:1)
8	FeF_3 (20)	I_2 (10)	MeCN	90	79 (13:1)
9	FeF_3 (20)	I_2 (20)	MeCN	82	48 (6:1)
10	FeF_3 (20)	I_2 (5)	MeCN	71	61 (10:1)
11	FeF_3 (20)	I_2 (10)	DMF	93	72 (8:1)
12	FeF_3 (20)	I_2 (10)	DCE	35	23 (3:1)
13	FeF_3 (20)	I_2 (10)	THF	30	18 (7:1)
14[d]	FeF_3 (20)	I_2 (10)	MeCN	trace	trace
15[e]	FeF_3 (20)	I_2 (10)	MeCN	95	73 (8:1)
16	FeF_3 (10)	I_2 (10)	MeCN	86	72 (10:1)
17	–	I_2 (10)	MeCN	58	43 (4:1)

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.4 mmol), [Fe], additive and solvent (3 mL) at 80 °C under N_2 atmosphere for 36 h.
[b] Conversion was determined by GC-MS analysis.
[c] Isolated yield. Ratio of **3A/3B** was determined by GC-MS analysis.
[d] At r.t.
[e] At 110 °C.

8, an important medical intermediate,[14] was isolated in 45% yield from the reaction between heteroaryl disulfide **2f** and aniline (**1a**) (entry 5). However, the reaction of aliphatic dimethyl disulfide (**2g**) gave the corresponding product **9** in a low yield (25%, entry 6).

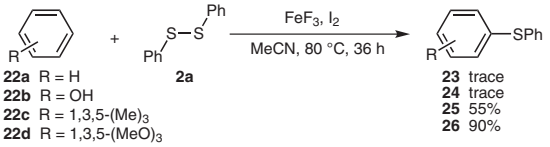
Encouraged by these results, we next evaluated the scope of arylamines for the reaction with diphenyl disulfide (**2a**) (Table 3). The results showed that electronic effects of substituents affected the reaction (Table 3, entries 1–10). When treated with substrate **2a**, anilines bearing an electron-donating substituent on the aryl moiety, such as methyl or methoxy, gave the thiolation products in moderate yields and higher regioselectivity (entries 1–6). A good yield was obtained from the reaction of **1h**, which has both a chloro and a methoxy groups on the aromatic ring (entry 7). However, a low yield was observed when 2-chloroaniline (**1i**), bearing an electron-withdrawing group, was used as a coupling partner (entry 8). N-Substituted anilines were also investigated. The reaction between *N*-methylaniline and diphenyl disulfide (**2a**) proceeded smoothly under the standard conditions to afford the corresponding product in 90% yield (entry 9). However, no product was observed in the reaction of *N*-phenylacetamide with diphenyl disulfide (**2a**) (entry 10), presumably because of the strong electron-withdrawing effect of the acyl group.

Selenylation of aniline (**1a**) with diselenides **2** was also tested under the standard reaction conditions (Scheme 2). In the presence of 20 mol% FeF_3 and 10 mol% I_2, 1,2-diphenyl diselenide (**2h**) underwent the selenylation reaction with aniline (**1a**) to give the corresponding product in 71% yield. However, dimethyl diselenide (**2i**) displayed less reactivity, giving the target product **21** in 23% yield.

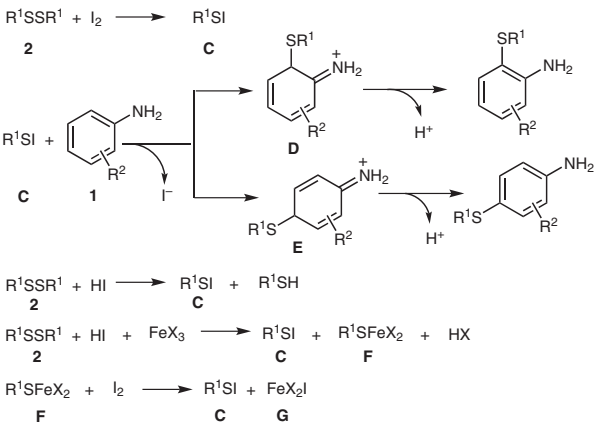


Scheme 2 Selenation of aniline (**1a**) with diselenides (**2**)

In light of these above results, a number of arenes were tested under the standard conditions (Scheme 3). However, the reactions of benzene (**22a**) or phenol (**22b**) with 1,2-diphenyl disulfide (**2a**) were unsuccessful in the presence of FeF_3 and I_2. To our delight, the electron-rich aromatic compounds **22c** and **22d** were suitable for this reaction. For example, 1,3,5-trimethoxybenzene (**22d**) was reacted with 1,2-diphenyl disulfide (**2a**) to give the corresponding product **26** in 90% yield.

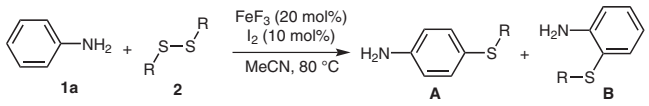


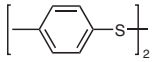
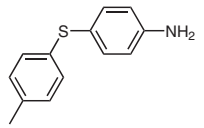
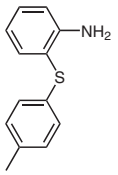
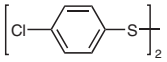
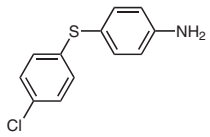
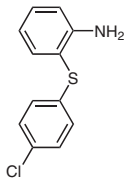
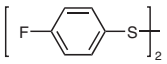
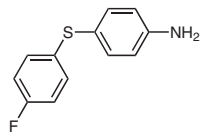
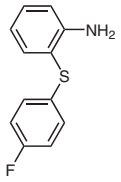
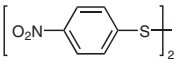
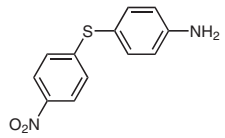
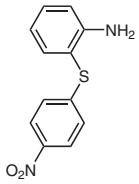
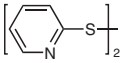
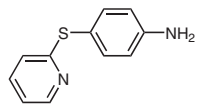
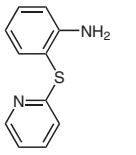
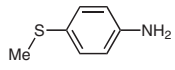
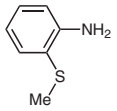
Scheme 3 Sulfenylation of arenes **22** with 1,2-diphenyl disulfide (**2a**)



Scheme 4 Possible mechanism for direct sulfenylation of arylamines

Table 2 FeF_3/I_2-Catalyzed Sulfenylation of Aniline (**1a**) with Disulfides **2**[a]



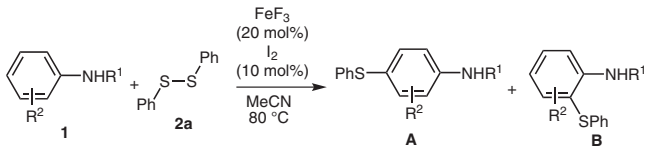
Entry	Disulfide **2**	Products		Yield (%)[b]
1	 **2b**	 **4A**	 **4B**	75 (97:3)
2	 **2c**	 **5A**	 **5B**	82 (96:4)
3	 **2d**	 **6A**	 **6B**	76 (97:3)
4	 **2e**	 **7A**	 **7B**	60 (90:10)
5	 **2f**	 **8A**	 **8B**	45 (89:11)
6	 **2g**	 **9A**	 **9B**	27 (75:25)

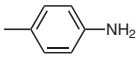
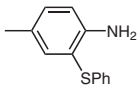
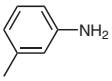
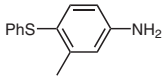
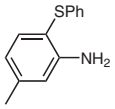
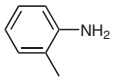
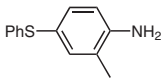
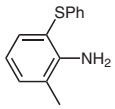
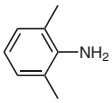
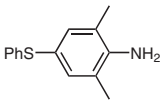
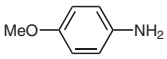
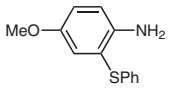
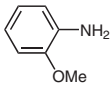
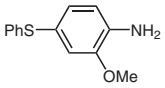
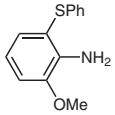
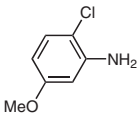
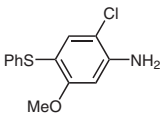
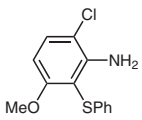
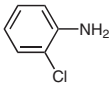
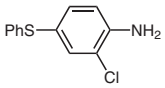
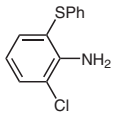
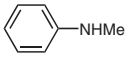
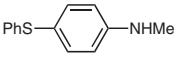
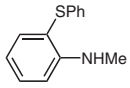
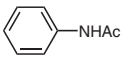
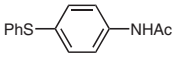
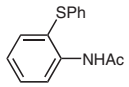
[a] Reaction conditions: **1a** (0.4 mmol), **2** (0.4 mmol), FeF_3 (20 mol%), and I_2 (10 mol%) in MeCN (3 mL) at 80 °C for 36 h.
[b] Isolated yield. Ratio of *para*/*ortho*-products **A** and **B** was determined by GC-MS analysis.

The present results show that the reaction could take place in the presence of FeF_3 or I_2 alone, suggesting an electrophilic addition process (Table 1, entry 17). Therefore, a possible mechanism as outlined in Scheme 4 is proposed.[12,15] Intermediate RSI (**C**), which is generated in situ from the reaction of RSSR (**2**) with I_2, undergoes the electrophilic addition to aniline **1** leading to intermediates **D** and/or **E** with the aid of FeF_3 catalyst. Deprotonation of intermediates **D** and **E** affords the desired product and HI. The reaction of HI with RSSR (**2**) may take place to provide the active intermediate RSI (**C**) and an inactive RSH intermediate.

In summary, we have developed a new, simple FeF_3/I_2 co-catalyzed thiolation method for the synthesis of 4-chalcogen-substituted arylamines. Compared with other synthetic methods, the FeF_3/I_2 catalytic system has the advantages of simplicity, low cost, and regioselectivity for the thiolation of arylamines. Moreover, we found the

Table 3 FeF_3/I_2-Catalyzed Sulfenylation of Anilines (**1**) with 1,2-Diphenyl Disulfide (**2a**)[a]



Entry	Amine **1**	Products		Yield (%)[b]
1	 **1b**		 **10B**	64
2	 **1c**	 **11A**	 **11B**	62 (91:9)
3	 **1d**	 **12A**	 **12B**	58 (99:1)
4	 **1e**	 **13A**		63
5	 **1f**		 **14B**	40
6	 **1g**	 **15A**	 **15B**	76 (98:2)
7	 **1h**	 **16A**	 **16B**	83 (>99:1)
8	 **1i**	 **17A**	 **17B**	23 (>99:1)
9	 **1j**	 **18A**	 **18B**	90 (95:5)
10	 **1k**	 **19A**	 **19B**	trace

[a] Reaction conditions: **1** (0.4 mmol), **2a** (0.4 mmol), FeF_3 (20 mol%), and I_2 (10 mol%) in MeCN (3 mL) at 80 °C for 36 h.
[b] Isolated yield. Ratio of *para*/*ortho*-products **A** and **B** was determined by GC-MS analysis.

FeF_3/I_2 catalytic system to be a versatile coupling system with wide applicability, producing good yields in both the reaction of aniline with diphenyl selenides and in the reactions of the other electron-rich aromatic compounds (mesitylene and 1,3,5-trimethoxybenzene) with diphenyl disulfide.

NMR spectroscopy was performed on a Bruker 300 or 500 spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR) or 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). TMS was used an internal standard and $CDCl_3$ was used as the solvent. Mass spectrometric analysis was performed on GC-MS analysis (Shimadzu GCMS-QP2010 plus).

FeF_3/I_2-Catalyzed Synthesis of 4-Chalcogen-Substituted Arylamines; Typical Procedure

A mixture of aniline **1** (0.4 mmol), disulfide **2** (0.4 mmol), FeF_3 (20 mol%), and I_2 (10 mol%) in MeCN (3 mL) was stirred at 80 °C under N_2 atmosphere for 36 h until complete consumption of starting material was indicated by TLC. After the reaction was complete, the mixture was poured into EtOAc (5 mL) and the EtOAc layer was washed with brine (5 mL). The aqueous layer was extracted with EtOAc (3 × 5 mL) and the combined organic layers were dried (Na_2SO_4) and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc) to give the desired product.

4-(Phenylthio)aniline (3A)[16]

Pale brown solid; mp 92.2–93.1 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (br s, 2 H), 6.64 (d, *J* = 8.5 Hz, 2 H), 7.10–7.13 (m, 5 H), 7.30 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ =147.0, 139.7, 136.1, 128.8, 127.2, 125.2, 120.3, 115.8.

LRMS (EI, 70 eV): *m*/*z* (%) = 201 (M^+, 100), 169 (27), 124 (6), 80 (25).

4-(*p*-Tolylthio)aniline (4A)[4a]

Brown solid; mp 68.4–70.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 3.62 (br s, 2 H), 6.62 (d, *J* = 8.5 Hz, 2 H), 7.01–7.09 (m, 4 H), 7.23–7.27 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.7, 135.6, 135.5, 135.4, 129.7, 128.2, 121.6, 115.8, 21.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 215 (M^+, 100), 200 (25), 183 (5), 183 (26), 124 (12), 91 (7).

4-(4-Chlorophenylthio)aniline (5A)[17]

Brown solid; mp 54.7–56.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (br s, 2 H), 6.66 (d, *J* = 8.5 Hz, 2 H), 7.02 (m, 2 H), 7.15 (m, 2 H), 7.28 (d, *J* = 9.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.3, 138.5, 136.2, 131.0, 128.9, 128.4, 119.8, 115.9.

LRMS (EI, 70 eV): *m*/*z* (%) = 235 (M^+, 100), 199 (28), 124 (27), 44 (90).

4-(4-Fluorophenylthio)aniline(6A)[18]

Brown solid; mp 58.6–60.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (br s, 2 H), 6.63 (d, *J* = 8.5 Hz, 2 H), 6.88–6.94 (m, 2 H), 7.10–7.15 (m, 2 H), 7.25 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.1 (d, $J_{C,F}$ = 243.4 Hz), 146.9, 135.4, 134.2, 129.8 (d, $J_{C,F}$ = 7.8 Hz), 121.1, 115.8 (d, $J_{C,F}$ = 21.7 Hz), 115.7.

LRMS (EI, 70 eV): *m*/*z* (%) = 219 (M^+, 100), 187 (25), 124 (23), 80 (23).

4-(4-Nitrophenylthio)aniline (7A)[19]

Yellow solid; mp 138.2–140.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.99 (br s, 2 H), 6.75 (d, *J* = 9.0 Hz, 2 H), 7.07 (d, *J* = 9.0 Hz, 2 H), 7.32 (d, *J* = 9.0 Hz, 2 H), 8.02 (d, *J* = 9.3 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.0, 148.3, 144.7, 137.2, 125.1, 123.8, 116.2, 116.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 246 (M^+, 100), 200 (25), 167 (14), 124 (42), 57 (26).

4-(Pyridin-2-ylthio)aniline (8A)[14a]

Brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (br s, 2 H), 6.70–6.78 (m, 3 H), 6.93–6.95 (m, 1 H), 7.37–7.41 (m, 3 H), 8.38–8.40 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6, 149.2, 147.9, 137.3, 136.5, 120.0, 119.1, 117.4, 115.9.

LRMS (EI, 70 eV): *m*/*z* (%) = 202 (M^+, 63), 201 (100), 124 (19), 78 (13).

4-(Methylthio)aniline (9A)[20]

Brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 3.34 (br s, 2 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 7.19 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.0, 131.0, 125.8, 115.7, 18.7.

LRMS (EI, 70 eV): *m*/*z* (%) = 139 (M^+, 82), 124 (100), 80 (40), 44 (13).

4-Methyl-2-(phenylthio)aniline (10B)[21]

Yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3 H), 4.11 (br s, 2 H), 6.69 (d, *J* = 8.1 Hz, 1 H), 7.02–7.11 (m, 4 H), 7.17–7.27 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.4, 137.5, 136.9, 131.8, 128.9, 128.0, 126.3, 125.2, 115.4, 114.1, 20.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 215 (M^+, 100), 200 (20), 138 (8), 77 (24).

3-Methyl-4-(phenylthio)aniline (11A)[17]

Brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 3.62 (br s, 2 H), 6.51 (m, 1 H), 6.61 (m, 1 H), 7.00–7.08 (m, 3 H), 7.15–7.20 (m, 2 H), 7.32 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.6, 143.9, 139.3, 137.9, 128.7, 126.1, 124.6, 118.9, 117.1, 113.4, 20.8.

LRMS (EI, 70 eV): *m*/*z* (%) = 215 (M^+, 100), 200 (8), 138 (9), 94 (35), 77 (22).

2-Methyl-4-(phenylthio)aniline (12A)[22]

Brown solid; mp 60.8–61.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3 H), 3.73 (br s, 2 H), 6.64 (d, *J* = 8.0 Hz, 1 H), 7.07–7.12 (m, 3 H), 7.17–7.20 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.3, 139.9, 137.0, 133.8, 128.7, 127.0, 125.0, 123.2, 120.0, 115.5, 17.2.

LRMS (EI, 70 eV): *m*/*z* (%) = 215 (M^+, 100), 200 (13), 183 (21), 138 (19), 77 (20).

2,6-Dimethyl-4-(phenylthio)aniline (13A)[18]

Brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 6 H), 3.59 (br s, 2 H), 7.05–7.20 (m, 7 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.7, 140.2, 135.0, 128.8, 127.0, 125.0, 122.7, 119.1, 17.5.

LRMS (EI, 70 eV): *m*/*z* (%) = 229 (M^+, 100), 214 (11), 197 (24), 152 (17), 120 (6), 91 (16), 77 (10).

4-Methoxy-2-(phenylthio)aniline (14B)[23]
Yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 3 H), 6.73–6.76 (m, 1 H), 6.85 (d, *J* = 7.5 Hz, 1 H), 7.01–7.03 (m, 1 H), 7.09–7.14 (m, 3 H), 7.20–7.25 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.4, 142.7, 136.5, 129.1, 126.7, 125.6, 121.0, 118.2, 116.7, 115.3, 55.9.

LRMS (EI, 70 eV): *m*/*z* (%) = 231 (M^+, 100), 216 (44), 200 (5), 154 (6), 77 (8).

2-Methoxy-4-(phenylthio)aniline (15A)[24]
Brown solid; mp 54.9–56.1 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.72 (s, 3 H), 6.59 (d, *J* = 8.0 Hz, 1 H), 6.85–6.92 (m, 2 H), 7.01–7.14 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.4, 139.8, 137.0, 128.7, 128.3, 126.9, 125.1, 119.7, 116.6, 115.0, 55.5.

LRMS (EI, 70 eV): *m*/*z* (%) = 231 (M^+, 100), 216 (35), 199 (6), 154 (6), 139(4), 78 (8).

2-Chloro-5-methoxy-4-(phenylthio)aniline (16A)
Brown solid; mp 65.7–66.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.72 (s, 3 H), 4.23 (br s, 2 H), 6.32 (s, 1 H), 7.08–7.12 (m, 3 H), 7.18–7.24 (m, 2 H), 7.32 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 145.0, 137.8, 136.4, 128.8, 127.2, 125.4, 110.6, 109.2, 98.9, 55.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 265 (M^+, 93), 230 (100), 215 (15), 186 (25), 115 (17), 77 (10).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{12}ClNOS$ (M^+): 265.0328; found: 265.0331.

2-Chloro-4-(phenylthio)aniline (17A)[25]
Brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.19 (br s, 2 H), 6.74 (d, *J* = 8.3 Hz, 1 H), 7.13–7.25 (m, 6 H), 7.42 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.4, 138.6, 135.1, 134.0, 129.0, 127.9, 125.8, 121.7, 119.4, 116.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 235 (M^+, 100), 199 (35), 124 (30).

***N*-Methyl-4-(phenylthio)aniline (18A)[17]**
Yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.83 (s, 3 H), 3.88 (br s, 1 H), 6.58 (d, *J* = 9.3 Hz, 2 H), 7.08–7.11 (m, 3 H), 7.16–7.19 (m, 2 H), 7.33–7.37 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.8, 140.3, 136.4, 128.8, 126.8, 125.0, 118.2, 113.1, 30.5.

LRMS (EI, 70 eV): *m*/*z* (%) = 215 (M^+, 100), 200 (17), 138 (7), 77 (57).

4-(Phenylselanyl)aniline (20A)[26]
Pale brown solid; mp 86.1–87.9 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (br s, 2 H), 6.63 (d, *J* = 8.5 Hz, 2 H), 7.16–7.25 (m, 3 H), 7.27–7.30 (m, 2 H), 7.40 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8, 137.1, 134.1, 130.0, 129.0, 126.0, 116.3, 116.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 249 (M^+, 35), 169 (100).

4-(Methylselanyl)aniline (21A)[27]
Brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.66 (s, 3 H), 3.72 (br s, 2 H), 6.61 (d, *J* = 9.0 Hz, 2 H), 7.31 (d, *J* = 9.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.5, 133.9, 118.5, 115.8, 9.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 187 (M^+, 100), 172 (62).

Mesityl(phenyl)sulfide (25)[16]
Yellow oil.

^{1}H NMR (500 MHz): δ = 7.19 (s, 2 H), 7.1–7.18 (m, 1 H), 6.99–6.94 (m, 2 H), 7.56 (d, *J* = 7.5 Hz, 2 H), 2.31 (s, 6 H), 2.25 (s, 3 H).

^{13}C NMR (125 MHz): δ = 143.7, 139.3, 138.4, 129.3, 128.8, 125.4, 124.4, 21.7, 21.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 228 (M^+, 100), 91 (28), 119 (14), 150 (28), 229 (160).

Phenyl(2,4,6-trimethoxyphenyl)sulfide (26)[28]
White solid; mp 119.6–121.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.76 (s, 6 H), 3.82 (s, 3 H), 6.18 (s, 2 H), 6.97–7.01 (m, 3 H), 7.09–7.14 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9, 162.5, 138.6, 128.4, 125.5, 124.3, 98.4, 91.1, 56.2, 55.4.

LRMS (EI, 70 eV): *m*/*z* (%) = 276 (M^+, 100).

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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