Iron(III) Chloride: A Versatile Catalyst for the Practical Synthesis of 3-Sulfenylindoles

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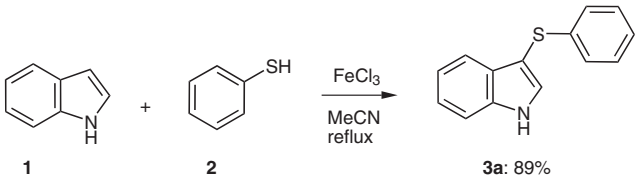
Abstract: The direct sulfenylation of indoles with aromatic thiols has been accomplished in the presence of 20 mol% of $FeCl_3$ in refluxing acetonitrile to produce 3-arylthioindoles in relatively good to excellent yields and with high selectivity. This method works even with 2-unsubstituted indoles.

Key words: thiolation, indoles, thiols, 3-arylthioindoles

The selective introduction of C–S bond into organic molecules, in particular in heterocycles, has played significant role in medicinal chemistry.[1] Specifically, 3-thiolated indoles are popular for their activity towards the treatment of HIV, obesity, cancer, heart diseases, and allergies.[2] Generally, 3-arylthioindoles are prepared via electrophilic substitution of indoles with thiols. A catalytic method has been reported for substitution of indole at the 3-position with disulfide using $AlCl_3$ as a catalyst, but harsh reaction conditions are required and the reported yields of 3-sulfenylindoles are relatively low.[3a] Also heterogeneous vanadium-catalyzed synthesis of 3-sulfenylindoles from indoles and thiols has been reported, but yields are quite low.[3b] However, these methods are limited to 2-substituted indoles only. The direct 3-arylthiolation of indoles has been reported using various sulfenylating agents such as disulfides, sulfenyl halides, quinone mono-*O*,*S*-acetals, *N*-thioarylphthalimides, and by intramolecular capture of sulfides in Pummerer Reaction.[4–6] Various reagents such as *N*-chlorosuccinamide, phenyliodine(III) bistrifluoroacetate, and transition metal catalysts have been utilized for the activation of thiols under mild conditions.[7,8] However, most of these methods require additional steps to prepare activated thiols. Therefore, the development of a simple, convenient, and general methodology for the sulfenylation of indoles utilizing stable and eco-friendly catalysts are desirable to introduce C–S functionality that would extend the scope of this reaction for the discovery of new selective COX-2 inhibitors.[8]

Iron is one of the most abundant transition metals and its salts, in particular anhydrous $FeCl_3$, is used as a powerful Lewis acid catalyst in organic synthesis. It is quite efficient in generating carbon–carbon and carbon–heteroatom bonds by additions, substitutions, and rearrangements, etc.[9] Moreover, iron salts are inexpensive, easy to handle, and are environmentally friendly.

In this article, we report a direct $FeCl_3$-catalyzed selective sulfenylation of indoles at the 3-position with aromatic thiols. We first attempted the coupling of indole (**1**) with thiophenol (**2**) using 20 mol% anhydrous $FeCl_3$ in acetonitrile. The reaction was sluggish at room temperature but went to completion in six hours at reflux temperature giving product **3a** in 89% yield (Scheme 1).



1 **2** **3a**: 89%

Scheme 1

This result provided incentive for further study of reactions with various indoles and thiols. Interestingly, substituted indoles such as 5-bromo-, 5-methoxy-, 7-ethyl-, and 2-methylindole, reacted rapidly with a range of thiols to afford the corresponding 3-arylthioindole derivatives (Table 1, entries **b**–**e**). Furthermore, this method worked equally well with sterically hindered thionaphthol and mercaptobenzothiazole (Table 1, entries **n** and **o**). In addition, *N*-benzylindole also participated well at room temperature (Table 1, entries **f** and **i**). In all cases, the products were 3-sulfenylindoles as confirmed by ^1H NMR spectra. The products were characterized by ^1H NMR, IR, and mass spectroscopy and also by comparison with authentic samples.[1,6,7] The advantages of this procedure include milder conditions than when using corrosive chlorine or sulfuryl chloride, as well as high conversions, and easy workup. This method is effective even with unprotected indoles. There was no considerable difference in yields when comparing protected and unprotected indoles. Unlike reported methods, no bis-sulfenylation was observed in this reaction. This method also avoids the formation of one equivalent of thiol waste that occurs when using a disulfide as the electrophilic sulfur source. No chlorination of indole was observed under the reaction conditions. In most cases, the products were obtained in good to excellent yields with high degree of regioselectively. As solvent, acetonitrile appeared to give the best results. The effects of various Lewis acids such as $InCl_3$, $InBr_3$, $BiCl_3$, $YbCl_3$, YCl_3, and $CeCl_3 \cdot 7H_2O$ were studied for this con-

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version. Of these catalysts, anhydrous $FeCl_3$ was found to be effective in terms of conversion. In the absence of catalyst, the reaction failed to give the desired product. The scope and generality of this process is illustrated with respect to various indoles and thiols and the results are presented in the Table 1.

Table 1 Synthesis of 3-Sulfenylindoles Using Anhydrous $FeCl_3$

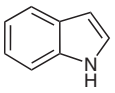
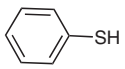
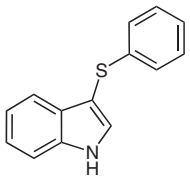
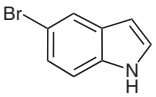
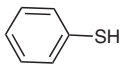
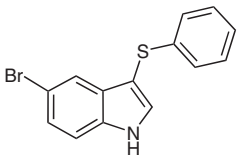
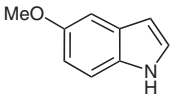
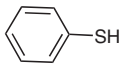
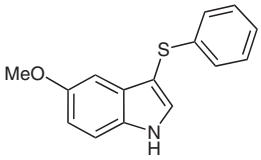
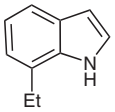
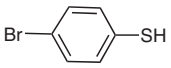
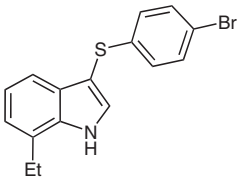
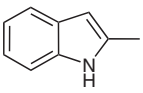
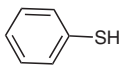
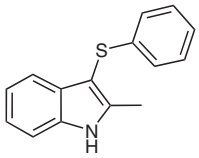
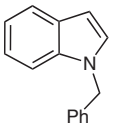
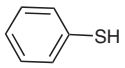
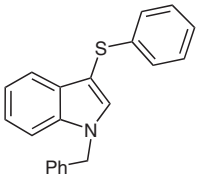
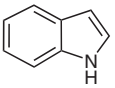
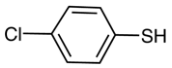
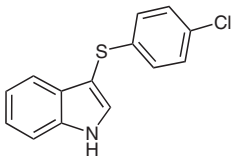
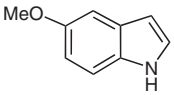
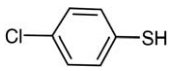
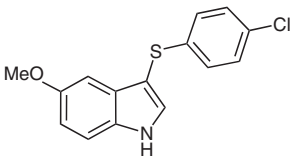
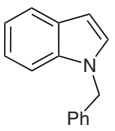
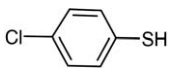
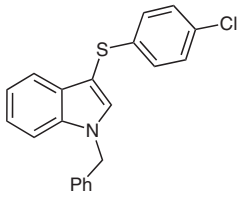
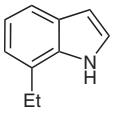
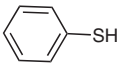
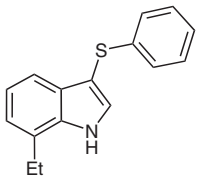
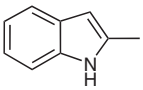
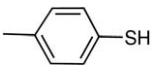
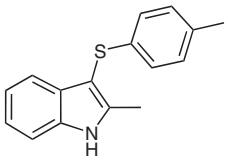
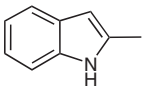
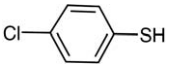
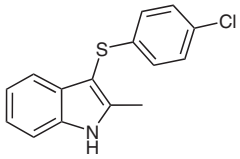
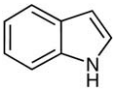
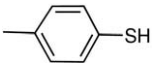
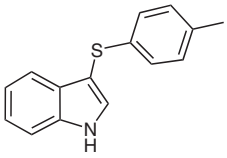
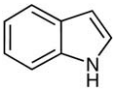
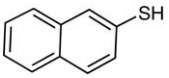
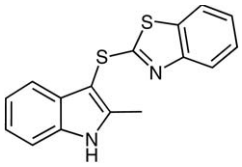
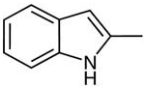
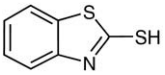
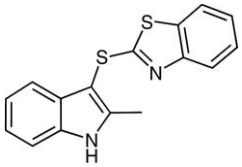
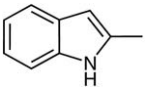
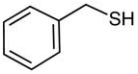
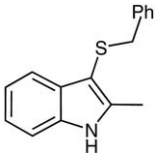
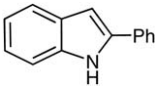
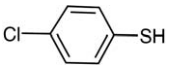
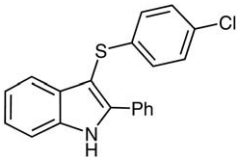
Entry	Indole **1**	Thiol **2**	Product **3**[a]	Time (h)	Yield (%)[b]
a				6.0	89
b				6.0	85
c				6.0	92
d				6.0	89
e				6.0	90
f				6.0	86
g				6.0	89
h				6.0	92
i				6.0	85

Table 1 Synthesis of 3-Sulfenylindoles Using Anhydrous $FeCl_3$ (continued)

Entry	Indole **1**	Thiol **2**	Product **3**[a]	Time (h)	Yield (%)[b]
j				6.0	89
k				6.0	91
l				6.0	90
m				6.0	87
n				7.0	84
o				7.0	82
p				6.0	80
q				7.0	82

[a] All products were characterized by ^1H NMR, IR, and mass spectroscopy.
[b] Yield refers to pure products after chromatography.

In summary, anhydrous $FeCl_3$ has proved to be a useful and highly efficient catalyst for the sulfenylation of indoles at the 3-position under mild conditions. In addition to its simplicity and efficiency, this method produces 3-sufenylindoles in excellent yields in reasonable reaction times. This method provides an easy access to a wide range of potentially valuable 3-sulfenylindoles. The use of readily available $FeCl_3$ makes this method simple, convenient, cost-effective, and practical.

Melting points were recorded on Büchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. ^1H NMR spectra were recorded on Varian Unity 300 spectrometer in $CDCl_3$ using TMS as inter-

nal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV.

3-Sulfenylindoles; 3-(Phenylthio)-1*H*-indole (3a); Typical Procedure

A mixture of indole (**1**; 117 mg, 1 mmol), thiophenol (**2**; 110 mg, 1 mmol) and anhyd $FeCl_3$ (32 mg, 20 mol%) in MeCN (5 mL) was stirred at 80 °C for the appropriate time (Table 1). After complete conversion as indicated by TLC, the reaction mixture was quenched with H_2O (15 mL) and extracted with CH_2Cl_2 (2 × 15 mL). The combined extracts were dried (Na_2SO_4) and concentrated in vacuo. The resulting crude product was purified by column chromatography on silica gel (Merck, 100–200 mesh, EtOAc–hexane, 1:9) to afford pure **3a**; yield: 200 mg (89%); liquid.

IR (neat): 3405, 3051, 2923, 2853, 1738, 1754, 1574, 1455, 1335, 1234, 1087, 741 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.30 (br s, 1 H), 6.85–7.72 (m, 10 H).

LC-MS: *m*/*z* = 248 (M + Na).

5-Bromo-3-(phenylthio)-1*H*-indole (3b)

Brown solid; mp 109–111 °C.

IR (KBr): 3413, 2923, 2853, 1713, 1454, 739 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.43 (br s, 1 H), 7.71 (s, 1 H), 7.44 (d, *J* = 8.1 Hz, 1 H), 7.21–7.34 (m, 2 H), 7.11–7.18 (m, 2 H), 6.99–7.06 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2, 136.5, 132.8, 129.0, 128.3, 128.6, 126.5, 123.9, 120.7, 117.2, 106.3, 101.4.

LC-MS: *m*/*z* = 305 (M + H).

5-Methoxy-3-(phenylthio)-1*H*-indole (3c)

Liquid.

IR (neat): 3410, 3057, 2924, 2853, 1720, 1623, 1581, 1480, 1285, 1207, 1167, 1028, 741 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (br s, 1 H), 7.43 (d, *J* = 2.2 Hz, 1 H), 7.27–7.33 (m, 1 H), 7.12–7.22 (m, 2 H), 6.96–7.11 (m, 4 H), 6.90 (dd, *J* = 2.2, 8.0 Hz, 1 H), 3.80 (s, 3 H).

LC-MS: *m*/*z* (%) = 256 (87, M + H,), 245 (55), 229 (75), 220 (77), 181 (100), 172 (172).

3-[(4-Bromophenyl)sulfanyl]-7-ethyl-1*H*-indole (3d)

Brown solid; mp 125–127 °C.

IR (KBr): 3412, 2961, 2923, 2852, 1716, 1470, 1006, 809, 749 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (br s, 1 H), 6.86–7.48 (m, 8 H), 2.89 (q, *J* = 7.5 Hz, 2 H), 1.41 (t, *J* = 7.5 Hz, 3 H).

LC-MS: *m*/*z* = 333 (M + H).

2-Methyl-3-(phenylthio)-1*H*-indole (3e)

Semi-solid.

IR (neat): 3399, 3053, 2922, 2853, 1581, 1541, 1477, 1455, 1403, 1290, 1224, 1078, 1022, 783 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (br s, 1 H), 7.50 (d, *J* = 8.1 Hz 1 H), 7.20–7.33 (m, 1 H), 6.89–7.19 (m, 7 H), 2.51 (s, 3 H).

LC-MS: *m*/*z* = 240 (M + H).

1-Benzyl-3-(phenylthio)-1*H*-indole (3f)

Liquid.

IR (neat): 3029, 2923, 2853, 1690, 1606, 1578, 1458, 1303, 1224, 1179, 748 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.80–7.69 (m, 15 H), 5.15–5.52 (m, 2 H).

LC-MS: *m*/*z* = 315 (M$^+$).

3-(4-Chlorophenylthio)-1*H*-indole (3g)

Pale brownish solid; mp 126–130 °C.

IR (KBr): 3403, 2923, 1640, 1505, 1473, 1452, 1090, 1008, 811, 745 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (br s, 1 H), 7.32–7.58 (m, 4 H), 6.89–7.20 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 100.6, 111.5, 119.5, 121.1, 123.4, 127.5, 128.7, 130.6.

LC-MS: *m*/*z* (%) = 260 (M + H, 45), 161 (100), 177 (30), 169 (20), 149 (15), 117 (10), 101 (5).

HRMS: *m*/*z* calcd for $C_{14}H_{10}ClNS$: 259.0144; found: 259.0141.

3-(4-Chlorophenylthio)-5-methoxy-1*H*-indole (3h)

Pale brownish solid; mp 97–105 °C.

IR (KBr): 3406, 2922, 2852, 1632, 1581, 1475, 1285, 1206, 1090, 1030, 813 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.36 (br s, 1 H), 7.41 (s, 1 H), 7.20–7.33 (m, 2 H), 7.02–7.18 (m, 1 H), 6.77–7.03 (m, 4 H), 3.78 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.2, 99.3, 101.5, 106.5, 109.5, 125.7, 125.9, 126.0, 126.8, 128.0, 128.1, 128.2, 155.2.

LC-MS: *m*/*z* (%) = 289 (M$^+$, 30), 279 (20), 257 (10), 197 (20), 169 (15), 147 (100), 117 (10).

HRMS: *m*/*z* calcd for $C_{15}H_{12}ClNOS$: 289.0249; found: 289.0250.

1-Benzyl-3-(4-chlorophenylthio)-1*H*-indole (3i)

Liquid.

IR (neat): 2923, 2853, 1690, 106, 1458, 739, 696 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.14–5.36 (m, 2 H), 6.57–7.64 (m, 14 H).

LC-MS: *m*/*z* = 350 (M + H).

7-Ethyl-3-(phenylthio)-1*H*-indole (3j)

Liquid.

IR (neat): 3414, 2959, 2926, 2856, 1758, 1586, 1469, 1380, 1214, 1112, 755 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (br s, 1 H), 7.41 (m, 2 H), 6.94–7.20 (m, 7 H), 2.89 (q, *J* = 7.5 Hz, 2 H), 1.41 (t, *J* = 7.5 Hz, 3 H).

LC-MS: *m*/*z* = 254 (M + H).

2-Methyl-3-(*p*-tolylthio)-1*H*-indole (3k)

Liquid.

IR (KBr): 3395, 2924, 2854, 1735, 1626, 1456, 1220, 1082, 1019, 803, 764 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (br s, 1 H), 7.44–7.55 (m, 1 H), 7.20–7.29 (m, 1 H), 6.99–7.17 (m, 2 H), 6.83–6.96 (m, 4 H), 2.50 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.1, 20.7, 100.0, 110.5, 119.0, 120.6, 122.1, 125.8, 129.4, 130.3, 135.4, 135.6, 140.8.

LC-MS: *m*/*z* (%) = 254 (M + H, 100), 175 (40), 140 (20).

HRMS: *m*/*z* calcd for $C_{16}H_{16}NS$: 254.1003; found: 254.1011.

3-(4-Chlorophenylthio)-2-methyl-1*H*-indole (3l)

Liquid.

IR (KBr): 3393, 2920, 2851, 1576, 1542, 1473, 1455, 1088, 1009, 814, 745 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.20 (br s, 1 H), 7.44–7.55 (m, 1 H), 7.02–7.32 (m, 5 H), 6.86–6.99 (m, 2 H), 2.50 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.1, 99.1, 110.7, 118.8, 120.8, 122.3, 126.7, 128.7, 130.0, 130.3, 135.4, 137.9, 141.1.

LC-MS: *m*/*z* (%) = 274 (M + H, 100), 260 (50), 206 (35), 132 (20), 120 (10).

HRMS: *m*/*z* calcd for $C_{15}H_{13}ClNS$: 274.0457; found: 274.0459.

3-(*p*-Tolylthio)-1*H*-indole (3m)
White solid; mp 123–125 °C.

IR (KBr): 3401, 2920, 2851, 1717, 1461, 722 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 8.30 (br s, 1 H), 6.87–7.69 (m, 9 H), 2.25 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.9, 138.4, 136.3, 130.7, 129.0, 128.6, 126.4, 125.7, 122.9, 120.8, 119.5, 111.6, 102.6, 21.3.

LC-MS: *m*/*z* = 240 (M + H).

3-(2-Naphthylsulfanyl)-1*H*-indole (3n)
Solid; mp 175–177 °C.

IR (KBr): 3410, 2923, 1780, 1732, 1478, 741 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.35 (br s, 1 H), 7.05–7.96 (m, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.3, 128.3, 127.67, 127.0, 127.5, 126.7, 126.2, 125.7, 125.0, 124.8, 123.6, 123.2, 121.1, 120.0, 111.5, 96.2.

LC-MS: *m*/*z* = 276 (M + H).

2-(2-Methyl-1*H*-indol-3-ylthio)benzo[*d*]thiazole (3o)
White solid; mp 165–168 °C.

IR (KBr): 3638, 3212, 2922, 1663, 1544, 1454, 1426, 1229, 981, 747 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.44 (br s, 1 H), 7.85 (d, *J* = 8.3 Hz, 1 H), 7.65 (d, *J* = 8.0 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 7.32–7.40 (m, 2 H), 7.14–7.37 (m, 3 H), 2.65 (s, 3 H).

LC-MS: *m*/*z* = 297 (M + H).

3-(Benzylsulfanyl)-2-methyl-1*H*-indole (3p)
Liquid.

IR (neat): 3405, 2922, 2853, 1632, 1452, 745 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.86 (br s, 1 H), 7.56–7.84 (m, 1 H), 7.06–7.24 (m, 6 H), 6.86–6.94 (m, 2 H), 3.70 (s, 3 H).

LC-MS: *m*/*z* = 254 (M + H).

3-(4-Chlorophenylthio)-2-phenyl-1*H*-indole (3q)
Liquid.

IR (neat): 3420, 2928, 1719, 1457, 1221, 756 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.48 (br s, 1 H), 7.70 (d, *J* = 7.9 Hz, 2 H), 7.55 (d, *J* = 7.9 Hz, 1 H), 7.31–7.48 (m, 5 H), 7.04–7.20 (m, 3 H), 6.98 (d, *J* = 8.0 Hz, 2 H).

LC-MS: *m*/*z* = 336 (M + H).

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