Supplementary Material for
An efficient iron-catalyzed synthesis of 2-mercaptobenzothiazole through
S-arylation/heterocyclization of 2-haloaniline with potassium xanthate

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1. General information:

All experiments were carried out under an atmosphere of argon. Unless otherwise indicated, all materials were obtained from commercial sources and used as received. Flash column chromatography was performed over silica gel 200-300 mesh size. Reaction was monitored by TLC on silica gel. ^1H NMR and ^{13}C NMR spectra were recorded on Agilent 500 MHz DD2 instrument internally referenced to SiMe_4 or chloroform signals. MS analyses were performed on Ploaris QMS instrument (EI) and Shimadzu LCMS-2020 instrument (ESI). All the structure of the compounds were characterized by ^1H NMR, ^{13}C NMR and MS and compared with those of literature.

2. General experimental procedure

A 25 mL reaction tube was charged with 2-haloaniline **1** (0.6 mmol), potassium o-ethyl dithiocarbonate **2** (1.8 mmol), FeF_3 (0.06 mmol), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (0.03 mmol) and DMF (4 mL). The reaction vessel was flushed with argon for three times and sealed. Then the mixture was stirred electromagnetically in an oil bath at 110°C for 3 - 21 hours. The reaction process was monitored by TLC on silica gel. After the reaction was completed, the reaction mixture was cooled to room temperature, then 4 mL HCl (3mol/L) was added and stirred for 30 minutes. Then the reaction mixture solution was extracted by ethyl acetate (3*20 mL). Subsequently, the combined organic solution were dried by anhydrous sodium sulfate and the target product was purified by silica gel column chromatography (eluent: petroleum ether / ethyl acetate) to give the corresponding pure product **3**.

3. Characterization data of **3**

2-mercaptobenzothiazole (**3a**)¹

3a was obtained as a white solid. M.p.: $176\text{--}179^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3 , TMS): δ 11.58 (brs, 1H), 7.48 (d, 1H, $J = 8.0$ Hz), 7.39-7.27 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 190.9, 140.2, 130.0, 127.2, 124.7, 121.4, 112.2; MS (EI^+): m/z calcd for $\text{C}_7\text{H}_6\text{NS}_2$ [$\text{M}+\text{H}$] $^+$: 167.99, found 168.2; Anal. Calcd. for $\text{C}_7\text{H}_5\text{NS}_2$: C, 50.27; H, 3.01; N, 8.37; Found: C, 49.98; H, 3.34; N, 8.46.

6-fluoro-2-mercaptobenzothiazole (**3b**)¹

3b was obtained as a white solid. M.p. 205-209 °C; ¹H NMR (500 MHz, DMSO, TMS): δ 13.81 (brs, 1H), 7.68-7.66 (m, 1H), 7.31-7.25 (m, 2H); ¹³C NMR (125 MHz, DMSO, TMS): δ 189.9, 159.1 (d, *J* = 286.5 Hz), 138.0, 130.7 (d, *J* = 13.5 Hz), 114.7 (d, *J* = 28.5 Hz), 113.4 (d, *J* = 10.5 Hz), 108.9 (d, *J* = 33.0 Hz); MS (EI⁺): *m/z* calcd for C₇H₅FNS₂ [M+H]⁺: 185.98, found 186.7; Anal. Calcd. for C₇H₄FNS₂: C, 45.39; H, 2.18; N, 7.56; Found: C, 45.54; H, 1.99; N, 7.46.

6-chloro-2-mercaptobenzothiazole (3c) ¹

3c was obtained as a white solid. M.p. >280 °C; ¹H NMR (500 MHz, DMSO, TMS): δ 12.41 (brs, 1H), 7.75 (dd, 1H, *J*₁ = 2.0 Hz, *J*₂ = 0.5 Hz), 7.43 (dd, 1H, *J*₁ = 9.0 Hz, *J*₂ = 2.0 Hz), 7.40 (dd, 1H, *J*₁ = 8.5 Hz, *J*₂ = 0.5 Hz); ¹³C NMR (125 MHz, DMSO, TMS): δ 190.1, 140.2, 131.0, 128.5, 127.2, 121.4, 113.4; MS (EI⁺): *m/z* calcd for C₇H₅ClNS₂ [M+H]⁺: 201.95, found 201.1; Anal. Calcd. for C₇H₄ClNS₂: C, 41.68; H, 2.00; N, 6.94; Found: C, 41.42; H, 1.81; N, 7.16.

6-bromo-2-mercaptobenzothiazole (3d) ¹

3d was obtained as a yellow solid. M.p. 264-267 °C; ¹H NMR (500 MHz, DMSO, TMS): δ 13.86 (brs, 1H), 7.98 (d, 1H, *J* = 2.0 Hz), 7.56 (dd, 1H, *J*₁ = 8.5 Hz, *J*₂ = 2.0 Hz), 7.22 (d, 1H, *J* = 8.5 Hz); ¹³C NMR (125 MHz, DMSO, TMS): δ 190.1, 140.5, 131.4, 129.9, 124.1, 116.3, 113.8; MS (EI⁺): *m/z* calcd for C₇H₅BrNS₂ [M+H]⁺: 247.90, found 247.0; Anal. Calcd. for C₇H₄BrNS₂: C, 34.16; H, 1.64; N, 5.69; Found: C, 34.45; H, 1.38; N, 5.51.

7-chloro-2-mercaptobenzothiazole (3e) ²

3e was obtained as a white solid. M.p. 228-232 °C; ¹H NMR (500 MHz, DMSO, TMS): δ 14.04 (brs, 1H), 7.46-7.42 (m, 1H), 7.41 (dd, 1H, *J*₁ = 8.0 Hz, *J*₂ = 1.0 Hz), 7.27 (dd, 1H, *J*₁ = 7.5 Hz, *J*₂ = 1.0 Hz); ¹³C NMR (125 MHz, DMSO, TMS): δ 189.0, 142.2, 129.0, 128.2, 124.7, 123.7, 111.3; MS (EI⁺): *m/z* calcd for C₇H₄ClNS₂ [M]⁺: 200.95, found 200.2; Anal. Calcd. for C₇H₄ClNS₂: C, 41.68; H, 2.00; N, 6.94; Found: C, 41.76; H, 1.89; N, 7.18.

6-trifluoromethyl-2-mercaptobenzothiazole (3f)¹

3f was obtained as a white solid. M.p. 248-250 °C; ¹H NMR (500 MHz, DMSO, TMS): δ 14.05 (brs, 1H), 8.19 (s, 1H), 7.74 (dd, 1H, *J*₁ = 8.5 Hz, *J*₂ = 1.5 Hz), 7.45 (d, 1H, *J* = 8.5 Hz); ¹³C NMR (125 MHz, DMSO, TMS): δ 191.6, 144.0, 130.1, 124.4 (q, *J* = 32.1 Hz), 124.2 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 270.5 Hz), 119.4 (q, *J* = 4.1 Hz), 112.7; MS (EI⁺): *m/z* calcd for C₈H₅F₃NS₂ [M+H]⁺: 235.98, found 235.5; Anal. Calcd. for C₈H₄F₃NS₂: C, 40.84; H, 1.71; N, 5.95; Found: C, 40.96; H, 1.47; N, 5.74.

6-carbonitrile-2-mercaptobenzothiazole (3g)¹

3g was obtained as a light yellow solid. M.p. 273-275 °C; ¹H NMR (500 MHz, DMSO, TMS): δ 14.12 (brs, 1H), 8.23 (d, 1H, *J* = 1.5 Hz), 7.82 (dd, 1H, *J*₁ = 8.5 Hz, *J*₂ = 2.0 Hz), 7.40 (d, 1H, *J* = 8.5 Hz); ¹³C NMR (125 MHz, DMSO, TMS): δ 191.4, 144.2, 130.9, 129.9, 125.7, 118.3, 112.7, 106.0; MS (EI⁺): *m/z* calcd for C₈H₅N₂S₂ [M+H]⁺: 192.99, found 192.2; Anal. Calcd. for C₈H₄N₂S₂: C, 49.98; H, 2.10; N, 14.57; Found: C, 50.21; H, 1.89; N, 14.51.

6-methyl-2-mercaptobenzothiazole (3h)¹

3h was obtained as a white solid. M.p. 179-181 °C; ¹H NMR (500 MHz, CDCl₃, TMS): δ 11.83 (brs, 1H), 7.27 (s, 1H), 7.23 (d, 1H, *J* = 8.5 Hz), 7.18-7.16 (m, 1H), 2.40 (s, 3H); ¹³C NMR (125 MHz, CDCl₃, TMS): δ 190.1, 138.2, 134.9, 130.2, 128.3, 121.4, 112.0, 21.2; MS (EI⁺): *m/z* calcd for C₈H₈NS₂ [M+H]⁺: 182.01, found 181.7; Anal. Calcd. for C₈H₇NS₂: C, 53.00; H, 3.89; N, 7.73; Found: C, 52.84; H, 3.72; N, 7.91.

5-methyl-2-mercaptobenzothiazole (3i)³

3i was obtained as a white solid. M.p. 181-183 °C; ¹H NMR (500 MHz, CDCl₃, TMS): δ 11.89 (brs, 1H), 7.34 (d, 1H, *J* = 8.0 Hz), 7.16 (s, 1H), 7.10 (d, 1H, *J* = 8.0 Hz), 2.42 (s, 3H); ¹³C NMR (125 MHz, CDCl₃, TMS): δ 190.8, 140.5, 137.8, 126.9, 126.0, 120.9, 112.7, 21.4; MS (EI⁺): *m/z* calcd for C₈H₇NS₂ [M]⁺: 181.0, found 181.0; Anal. Calcd. for C₈H₇NS₂: C, 53.00; H, 3.89; N, 7.73;

Found: C, 53.14; H, 3.76; N, 7.61.

5-(trifluoromethyl)-2-mercaptobenzothiazole (3j)³

3j was obtained as a white solid. M.p. 218-221 °C; ¹H NMR (500 MHz, DMSO, TMS): δ 14.03 (brs, 1H), 7.95 (d, 1H, *J* = 8.5 Hz), 7.64 (d, 1H, *J* = 8.0 Hz), 7.49 (s, 1H); ¹³C NMR (125 MHz, DMSO, TMS): δ 191.0, 141.4, 134.0, 127.5 (q, *J* = 32.3 Hz), 123.8 (q, *J* = 270.6 Hz), 122.9, 120.4, 108.5; MS (EI⁺): *m/z* calcd for C₈H₅F₃NS₂ [M+H]⁺: 235.98, found 235.4; Anal. Calcd. for C₈H₄F₃NS₂: C, 40.84; H, 1.71; N, 5.95; Found: C, 40.59; H, 1.56; N, 6.04;

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4. Copies of ^1H and ^{13}C NMR spectra of 3