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SYNTHESIS AND REACTIVITY OF DIMETHOXY ACTIVATED BENZOTHIAZOLES

Mahiuddin Alamgir, Hao Jiang, Naresh Kumar, and David StC. Black*

School of Chemistry, The University of New South Wales, UNSW Sydney, NSW 2052, Australia. Email: d.black@unsw.edu.au

SUPPLEMENTARY MATERIAL

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1. EXPERIMENTAL FOR SYNTHESIS OF DIMETHOXYBENZOTHIAZOLES

3,5-Dimethoxyamides

Compounds **3a-e** are fully covered in reference 8. Compounds **3f-g** are new.

N-(3,5-Dimethoxyphenyl)-4'-nitrobenzamide (3f). To a solution of 3,5-dimethoxyaniline (5.0 g, 32.7 mmol) in pyridine (50 mL) at 0 ˚C 4-nitrobenzoyl chloride (7.27 g, 39.2 mmol) was added slowly portionwise and the mixture was stirred at room temperature overnight. Water was added and the resulting precipitate was filtered, washed with water and recrystallized from EtOH to give the benzamide **3f** as yellow crystals (9.87 g, 86%), mp 209-210 ˚C. ν_{max} (KBr): 3264, 2937, 1652, 1600, 1521, 1480, 1459, 1422, 1343, 1291, 1206, 1155, 1067, 830 cm^{-1}. λ_{max} (MeOH): 217 nm (ε 33,900 $cm^{-1}M^{-1}$), 249 (14,300). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 6H, OMe), 6.31-6.32 (m, 1H, aryl H4), 6.87 (d, *J* 2.2 Hz, 2H, aryl H2,6), 7.75 (br s, 1H, NH), 8.02 (d, *J* 9.0 Hz, 2H, aryl H), 8.34 (d, *J* 9.0 Hz, 2H, aryl H). ^{1}H NMR (300 MHz, acetone-d_6): δ 3.77 (s, 6H, OMe), 6.30 (s, 1H, aryl H4), 7.11 (d, *J* 2.2 Hz, 2H, aryl H2,6), 8.02 (d, *J* 9.0 Hz, 2H, aryl H), 8.34 (d, *J* 9.0 Hz, 2H, aryl H), 9.73 (br s, 1H, NH), ^{13}C NMR (75 MHz, acetone-d_6): δ 54.6 (OMe), 96.1, 98.5, 123.4, 128.8 (aryl CH), 140.5, 140.9, 149.6, 163.7 (aryl C), 161.0 (C=O). Mass Spectrum (+EI): *m/z* (%) 303 (M+1, 100). Anal. Calcd for $C_{15}H_{14}N_2O_5$: C, 59.60; H, 4.67; N, 9.27. Found: C, 59.62; H, 4.76; N, 9.20.

N-(3,5-Dimethoxyphenyl)-2'-nitrobenzamide (3g). This compound was prepared as described for the amide **3g** from a solution of 3,5-dimethoxyaniline (5.0 g, 32.7 mmol) in pyridine (50 mL) and 2-nitrobenzoyl chloride (7.27 g, 39.2 mmol) under reflux for 2 h to afford the benzamide **3g** as an off white powder (9.87 g, 86%), mp 180-181 ˚C. ν_{max} (KBr): 3266, 3105, 2967, 1662, 1623, 1600, 1566, 1533, 1456, 1422, 1348, 1196, 1152 1061, 841, 731 cm^{-1}. λ_{max} (MeOH): 215 nm (ε 19,800 $cm^{-1}M^{-1}$), 252 (8,400). ^{1}H NMR (300 MHz, acetone-d_6): δ 3.74 (s, 6H, OMe), 6.27 (s, 1H, aryl H4), 6.99 (s, 2H, aryl H2,6), 7.71-7.83 (m, 3H, aryl H), 8.06-8.08 (m, 1H, aryl H), 9.70 (br s, 1H, NH). ^{13}C NMR (75 MHz, acetone-d_6): δ 54.62 (OMe), 96.0, 98.0, 124.1, 128.9, 130.7, 133.6 (aryl CH), 133.1, 140.6, 146.9, 164.1 (aryl C), 161.1 (C=O). Mass Spectrum (+EI): *m/z* (%) 303 (M+1, 100), 241 (90). Anal. Calcd for $C_{15}H_{14}N_2O_5$ 0.2CH_3OH: C, 59.14; H, 4.83; N, 9.07. Found: C, 59.10; H, 4.78; N, 8.98.

5,7-Dimethoxyamides

All compounds except **4e** are known. Compound **4a**: ref 31; compound **4b**: ref. 32; compound **4c**: ref. 33; compound **4f**: ref. 18; compound **4g**: ref. 34.

4'-Chloro-*N*-(2,4-dimethoxyphenyl)benzamide (4e). This compound was prepared from an ice cooled solution of 2,4-dimethoxy aniline (10.0 g, 65.36 mmol) in dry CH_2Cl_2 (100 mL) containing anhydrous K_2CO_3 (5 g) and 4-chlorobenzoyl chloride (13.7 g, 78.43 mmol) under stirring for 4 h to give the

benzamide **4e** as an off white solid (14.91 g, 78%), mp 112-113 ˚C. ν_{max} (KBr): 3436, 2989, 1661, 1613, 1542, 1501, 1483, 1461, 1415, 1285, 1258, 1209, 1155, 1039, 918, 838, 744 cm^{-1}. λ_{max} (MeOH): 211 nm (ε 25,500 $cm^{-1}M^{-1}$), 224 (14,000), 286 (5,900). ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H, OMe), 3.89 (s, 3H, OMe), 6.51-6.54 (m, 2H, aryl H3,5), 7.45 (d, *J* 8.3 Hz, 2H, aryl H), 7.81 (d, *J* 8.3 Hz, 2H, aryl H), 8.26 (br s, 1H, NH), 8.36 (d, *J* 9.4 Hz, 1H, aryl H6). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, 55.7 (OMe), 98.5, 103.8, 120.8, 128.3, 128.8 (aryl CH), 121.0, 133.6, 137.6, 149.5, 156.6 (aryl C), 163.8 (C=O). Mass Spectrum (+EI): *m/z* (%) 294 (M+1, ^{37}Cl, 35), 292 (M+1, ^{35}Cl, 100). Anal. Calcd for $C_{15}H_{14}ClNO_3$: C, 61.76; H, 4.84; N, 4.80. Found: C, 62.04; H, 4.96; N, 4.79.

3,5-Dimethoxythioamides

Compounds **5c** and **5g** are known: ref. 14. The other thioamides are new.

***N*-(3,5-Dimethoxyphenyl)methanethioamide (5a)**. To a solution of formamide **3a** (5.0 g, 27.59 mmol) in pyridine (50 mL) P_4S_{10} (6.70 g, 30.35 mmol) was added portionwise and the mixture was heated under reflux for 3 h. The solution was allowed to come to room temperature and the resulting precipitate was filtered, washed with water and column chromatographed (CH_2Cl_2/light petroleum; 2:1) to yield the thioamide **5a** as a light yellow powder (0.51 g, 9%), mp 184-185 ˚C. ν_{max} (KBr): 3290, 1620, 1604, 1562, 1468, 1295, 1211, 1155, 982, 816 cm^{-1}. λ_{max} (MeOH): 207 nm (ε 15,000 $cm^{-1}M^{-1}$), 233 (4,800), 313 (10,400). ^1H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 6H, OMe), 6.26 (d, *J* 2.2 Hz, 2H, aryl H2,6), 6.31 -6.32 (m, 1H, aryl H4), 9.22 (br s, 1H, NH), 9.75 (d, *J* 14.7 Hz, 1H, CSH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5 (OMe), 96.1, 97.7 (aryl CH), 140.0, 161.8 (aryl C), 187.4 (C=S). Mass Spectrum (+EI): *m/z* (%) 198 (M+1, 100), 182 (23). HRMS (+ESI): $C_9H_{11}NO_2S$ $[M+Na]^+$ requires 220.0402, found 220.0401. Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62; N, 7.10. Found: C, 54.89; H, 5.82; N, 7.12.

***N*-(3,5-Dimethoxyphenyl)ethanethioamide (5b)**. A mixture of acetamide **3b** (5.0 g, 25.61 mmol) and Lawesson's reagent (6.18 g, 15.3 mmol, 0.6 eq.) in toluene (20 mL) was heated under reflux for 3 h. The solvent was removed and the product was extracted with CH_2Cl_2. The organic extract was washed with water, brine, and dried over $MgSO_4$. The product was purified by short column chromatography using CH_2Cl_2/light petroleum (70:30) as eluent and recrystallized from MeOH/H_2O to give the thioamide **5b** as a brown solid (4.12 g, 76%), mp 88-89 ˚C. ν_{max} (KBr): 3213, 3151, 3059, 1618, 1596, 1549, 1477, 1460, 1426, 1345, 1300, 1213, 1199, 1163, 1060, 839, 727 cm^{-1}. λ_{max} (MeOH): 206 nm (ε 22,600 $cm^{-1}M^{-1}$), 300 (10,200). ^1H NMR (300 MHz, $CDCl_3$): (rotational isomer 1) δ 2.50 (s, 3H, Me), 3.76 (s, 6H, OMe), 6.27 (d, *J* 2.3, 2H, aryl H2,6), 6.38 (t, *J* 2.3 Hz, 1H, aryl H4), 9.79 (br s, 1H, NH). ^1H NMR (300 MHz, $CDCl_3$): (rotational isomer 2) δ 2.66 (s, 3H, Me), 3.72 (s, 6H, OMe), 6.31 (t, *J* 2.3 Hz, 1H, aryl H4), 6.93 (d, *J* 2.3, 2H, aryl H2,6), 9.03 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.12, 56.62 (OMe), 91.84, 127.55, 128.93, 131.33 (aryl CH), 112.02, 116.70, 133.12, 156.65, 158.73, 162.62, 171.43 (aryl C),

188.80 (C=S). Mass Spectrum (+EI): *m/z* (%) 212 (M+1, 26), 211(M, 5), 210 (40), 196 (21), 178 (100), 171 (34), 154 (32). HRMS (+ESI): $C_{10}H_{13}NO_2S$ $[M+Na]^+$ requires 234.0559, found 234.0558. Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63. Found: C, 57.44; H, 6.35; N, 6.69.

***N*-(3,5-Dimethoxyphenyl)-4'-methoxybenzothioamide (5d)**. This compound was prepared from a mixture of benzamide **3d** (5.0 g, 17.42 mmol) and Lawesson's reagent (4.22 g, 10.45 mmol) in toluene (50 mL) under reflux for 3 h to afford the benzothioamide **5d** as a yellow solid (4.07 g, 77%), mp 130-131 ˚C. ν_{max} (KBr): 3162, 3002, 2965, 1599, 1507, 1455, 1344, 1291, 1255, 1208, 1158, 1059, 1015, 835 cm^{-1}. λ_{max} (MeOH): 207 nm (ε 31,600 $cm^{-1}M^{-1}$), 293 (16,700). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.77 (s, 6H, OMe), 3.85 (s, 3H, OMe), 6.36 (s, 1H, aryl H4), 6.88-6.97 (m, 4H, aryl H), 7.80 (d, *J* 7.5, 2H, aryl H), 8.92 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, 55.7 (OMe), 98.9, 101.7, 113.6, 128.7 (aryl CH), 137.2, 140.8, 160.9, 162.2 (aryl C), 197.4 (C=S). Mass Spectrum (+EI): *m/z* (%) 304 (M+1, 45), 303 (M, 18), 320 (100), 288 (23), 270 (21). Anal. Calcd for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.65; N, 4.62. Found: C, 63.50; H, 5.72; N, 4.59.

4'-Chloro-*N*-(3,5-dimethoxyphenyl)benzothioamide (5e). This compound was prepared from a mixture of benzamide **3e** (10.0 g, 34.3 mmol) and Lawesson's reagent (8.30 g, 20.6 mmol) in toluene (100 mL) under reflux for 3 h to afford the thioamide **5e** as a yellow powder (6.95 g, 66%), mp 115-116 ˚C. ν_{max} (KBr): 1618, 1517, 1479, 1461, 1399, 1342, 1208, 1150, 1089, 1058, 1010, 925, 836, 748, 735 cm^{-1}. λ_{max} (MeOH): 214 nm (ε 35,300 $cm^{-1}M^{-1}$), 241 (15,900), 271 (12,900), 318 (8,400). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71 (s, 6H, OMe), 6.31 (s, 1H, aryl H4), 6.91 (s, 2H, aryl H2,6), 7.26 (d, *J* 8.3 Hz, 2H, aryl H), 7.62 (d, *J* 8.3 Hz, 2H, aryl H), 9.20 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4 (OMe), 99.1, 101.9, 128.1, 128.5 (aryl CH), 137.2, 140.3, 141.0, 160.8 (aryl C), 196.5 (C=S). Mass Spectrum (+EI): *m/z* (%) 310 (M+1, ^{37}Cl, 11), 309 (M, ^{37}Cl, 30), 308 (M+1, ^{35}Cl, 100), 307 (M, ^{35}Cl, 9) 294 (^{37}Cl, 20) 292 (^{35}Cl, 54). Anal. Calcd for $C_{15}H_{14}ClNO_2S$: C, 58.53; H, 4.58; N, 4.55. Found: C, 58.81; H, 4.63; N, 4.52.

***N*-(3,5-Dimethoxyphenyl)-4'-nitrobenzothioamide (5f)**. This compound was prepared from a mixture of benzamide **3f** (9.0 g, 29.8 mmol) and Lawesson's reagent (7.18 g, 17.88 mmol) in toluene (100 mL) under reflux for 12 h to afford the thioamide **5f** as an orange red powder (6.55 g, 69%), mp 151-152 ˚C. ν_{max} (KBr): 1611, 1547, 1512, 1473, 1434, 1407, 1380, 1351, 1217, 1164, 1070, 1001, 946, 852, 732, 695 cm^{-1}. λ_{max} (MeOH): 205 nm (ε 37,000 $cm^{-1}M^{-1}$), 280 (15,400). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 6H, OMe), 6.41 (s, 1H, aryl H4), 7.04 (s, 2H, aryl H2,6), 7.92 (d, *J* 8.7 Hz, 2H, aryl H), 8.26 (d, *J* 8.7 Hz, 2H, aryl H), 8.99 (br s, 1H, NH). ^{13}C NMR (75 MHz, acetone-d_6): δ 55.5 (OMe), 99.4, 101.4, 123.8, 127.6 (aryl CH), 127.3, 139.1, 140.0, 148.8 (aryl C), 195.1 (C=S). Mass Spectrum (+EI): *m/z* (%) 319 (M+1, 35), 318 (M, 18), 317 (100). Anal. Calcd for $C_{15}H_{14}N_2O_4S$ $0.2CH_2Cl_2$: C, 54.44; H, 4.33; N, 8.35. Found: C, 54.80; H, 4.35; N, 8.43.

2,4-Dimethoxythioamides

Compound **6d** is known: ref. 14. The other thioamides are new.

***N*-(2,4-Dimethoxyphenyl)methanethioamide (6a)**. This compound was prepared from a solution of amide **4a** (10.0 g, 55.25 mmol) and Lawesson's reagent (13.3 g, 33.15 mmol) in toluene (70 mL) under reflux for 3 h. The crude product was chromatographed using CH_2Cl_2/light petroleum (70:30) as eluent to give the thioamide **6a** as a light brown solid (0.68 g, 6%), mp 78-80 ˚C. ν_{max} (KBr): 3225, 1605, 1542, 1467, 1285, 1211, 1159, 1030, 974, 823, 782 cm^{-1}. λ_{max} (MeOH): 203 nm (ε 27,700 $cm^{-1}M^{-1}$), 292 (10,500), 320 (13,800). ^1H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H, OMe), 3.86 (s, 3H, OMe), 6.44-6.50 (m, 2H, aryl H3,5), 7.15 (d, *J* 8.6 Hz, 1H, aryl H6), 9.44 (br s, 1H, NH), 9.65 (d, *J* 15.1 Hz, 1H, CSH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.6, 55.8 (OMe), 99.3, 104.7, 117.0 (aryl CH), 121.8, 149.1, 158.7 (aryl C), 185.3 (C=S). Mass Spectrum (+EI): *m/z* (%) 198 (M+1, 100). Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62; N, 7.10. Found: C, 55.84; H, 5.69; N, 6.91.

***N*-(2,4-Dimethoxyphenyl)ethanethioamide (6b)**. This compound was prepared from a solution of amide **4b** (1.70 g, 8.70 mmol) and P_4S_{10} (1.95 g, 8.80 mmol) in pyridine (15 mL) under reflux for 2 h to yield the thioamide **6** as a dark brown solid (0.97 g, 53%), mp 78-80 ˚C. ν_{max} (KBr): 3361, 1617, 1539, 1497, 1451, 1389, 1328, 1285, 1267, 1206, 1158, 1125, 1043, 1027, 830, 676 cm^{-1}. λ_{max} (MeOH): 205 nm (ε 26,600 $cm^{-1}M^{-1}$), 280 (11,500). ^1H NMR (300 MHz, $CDCl_3$): (rotational isomer 1) δ 2.71 (s, 3H, Me), 3.79 (s, 3H, OMe), 3.84 (s, 3H, OMe), 6.44-6.50 (m, 2H, aryl H3,5), 8.68 (d, *J* 9.4 Hz, 1H, aryl H6), 8.93 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.5 (Me), 55.4, 55.7 (OMe), 98.6, 103.2, 123.6 (aryl CH), 121.6, 151.3, 158.3 (aryl C), 197.7 (C=S). ^1H NMR (300 MHz, $CDCl_3$): (rotational isomer 2) δ 2.42 (s, 3H, Me), 3.80 (s, 3H, OMe), 3.81 (s, 3H, OMe), 6.44-6.50 (m, 2H, aryl H3,5), 7.03 (d, *J* = 8.3 Hz, 1H, aryl H6), 9.12 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.5 (Me), 55.5, 55.6 (OMe), 99.2, 104.2, 127.0 (aryl CH), 120.2, 154.2, 160.3 (aryl C), 204.9 (C=S). Mass Spectrum (-EI): *m/z* (%) 210 (M-1, 100). HRMS (+ESI): $C_{10}H_{13}NO_2S$ $[M+H]^+$ requires 212.0739, found 212.0730. Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63. Found: C, 56.59; H, 6.14; N, 6.55.

***N*-(2,4-Dimethoxyphenyl)benzothioamide (6c)**. This compound was prepared from a solution of amide **4c** (8.50 g, 33.07 mmol) and P_4S_{10} (8.08 g, 36.38 mmol) in pyridine (30 mL) under reflux for 2 h to yield the benzothioamide **6c** as yellow crystals (6.92 g, 77%), mp 85-86 ˚C. ν_{max} (KBr): 3347, 2998, 1614, 1594, 1521, 1468, 1436, 1419, 1379, 1329, 1283, 1236, 1208, 1161, 1126, 1033, 990, 915, 836, 794, 744 cm^{-1}. λ_{max} (MeOH): 204 nm (ε 36,100 $cm^{-1}M^{-1}$), 236 (19,400), 281 (11,000). ^1H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H, OMe), 3.88 (s, 3H, OMe), 6.53 (m, 2H, aryl H3,5), 7.39-7.50 (m, 3H, aryl H), 7.83-7.86 (m, 2H, aryl H), 8.95 (d, *J* 9.4 Hz, 1H, aryl H6), 9.43 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 55.9 (OMe), 98.6, 103.2, 123.0, 126.6, 128.5, 130.8 (aryl CH), 122.2, 143.8, 151.4, 158.3 (aryl C), 195.1 (C=S). Mass Spectrum (+EI): *m/z* (%) 274 (M+1, 53), 272 (M-1, 24), 242 (20), 240 (69),

121 (100). Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 65.99; H, 5.63; N, 5.10.

4'-Chloro-*N*-(2,4-dimethoxyphenyl)benzothioamide (6e). This compound was prepared from a solution of amide **4e** (14.0 g, 48 mmol) and Lawesson's reagent (11.58 g, 28.8 mmol) in toluene (120 mL) under reflux for 3 h to give the benzothioamide **6e** as yellow crystals (8.85 g, 60%), mp 137-138 ˚C. ν_{max} (KBr): 1613, 1526, 1496, 1460, 1401, 1370, 1330, 1284, 1260, 1201, 1154, 1125, 1087, 1033, 988, 828 cm^{-1}. λ_{max} (MeOH): 208 nm (ε 23,900 $cm^{-1}M^{-1}$), 244 (12,300). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H, OMe), 3.85 (s, 3H, OMe), 6.50-6.52 (m, 2H, aryl H3,5), 7.35 (d, *J* 8.7 Hz, 2H, aryl H), 7.76 (d, *J* 8.7 Hz, 2H, aryl H), 8.83 (d, *J* 9.4 Hz, aryl H6), 9.38 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 55.9 (OMe), 98.6, 103.2, 123.0, 128.0, 128.6 (aryl CH), 121.9, 137.0, 141.9, 151.5, 158.5 (aryl C), 193.4 (C=S). Mass Spectrum (+EI): *m/z* (%) 311 (M+1, ^{37}Cl, 6), 310 (M, ^{37}Cl, 33), 309 (M+1, ^{35}Cl, 18), 308 (M, ^{35}Cl, 100). Anal. Calcd for $C_{15}H_{14}ClNO_2S$: C, 58.53; H, 4.58; N, 4.55. Found: C, 58.76; H, 4.73; N, 4.50.

***N*-(2,4-Dimethoxyphenyl)-4'-nitrobenzothioamide (6f)**. This compound was prepared from a solution of amide **4f** (9.0 g, 29.8 mmol) and Lawesson's reagent (7.20 g, 17.88 mmol) in toluene (100 mL) under reflux for 12 h. The crude product was chromatographed using CH_2Cl_2/light petroleum (70:30) as eluent to give the benzothioamide **6f** as a red solid (7.51 g, 79%), mp 188-190 ˚C. ν_{max} (KBr): 3356, 1615, 1535, 1519, 1348, 1200, 1157, 1118, 1035, 857, 825, 674 cm^{-1}. λ_{max} (MeOH): 203 nm (ε 42,600 $cm^{-1}M^{-1}$), 264 (18,600). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H, OMe), 3.90 (s, 3H, OMe), 6.55 (d, *J* 2.6 Hz, 2H, aryl H3,5), 7.95 (d, *J* 8.7 Hz, 2H, aryl H), 8.27 (d, *J* 8.7 Hz, 2H, aryl H), 8.95 (d, *J* 9.8 Hz, 1H, aryl H6), 9.45 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 56.0 (OMe), 98.7, 103.2, 122.6, 123.8, 127.6 (aryl CH), 121.8, 148.7, 148.7, 151.2, 158.7 (aryl C), 191.8 (C=S). Mass Spectrum (+EI): *m/z* (%) 320 (M+2, 19), 319 (M+1, 100), 318 (M. 15), 317 (76), 303 (52), 287 (25). Anal. Calcd for $C_{15}H_{14}N_2O_4S$: C, 56.59; H, 4.43; N, 8.80. Found: C, 56.56; H, 4.46; N, 8.78.

***N*-(2,4-Dimethoxyphenyl)-2'-nitrobenzothioamide (6g)**. This compound was prepared from a solution of amide **4g** (2.50 g, 8.27 mmol) and P_4S_{10} (2.02 g, 9.1 mmol) in pyridine (15 mL) under reflux for 3 h to yield the benzothioamide **6g** as a light orange powder (1.2 g, 46%), mp 167-168 ˚C. ν_{max} (KBr): 3190, 1605, 1518, 1459, 1438, 1382, 1340, 1294, 1260, 1209, 1110, 1037, 1025, 988, 936, 825, 733, 701 cm^{-1}. λ_{max} (MeOH): 211 nm (ε 23,600 $cm^{-1}M^{-1}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H, OMe), 3.85 (s, 3H, OMe), 6.50-6.57 (m, 2H, aryl H3,5), 7.51-7.58 (m, 3H, aryl H), 8.01 (d, *J* 7.9 Hz, 1H, aryl H), 8.89 (d, *J* 8.7 Hz, 1H, aryl H6), 9.13 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 55.9 (OMe), 98.8, 103.3, 123.0, 124.6, 128.8, 129.5, 133.4 (aryl CH), 121.5, 133.2, 139.8, 151.3, 158.7 (aryl C), 191.7 (C=S). Mass Spectrum (+EI): *m/z* (%) 320 (M+2, 10), 319 (M+1, 40), 287 (21), 273 (100), 255 (20). Anal. Calcd for $C_{15}H_{14}N_2O_4S$ $0.3H_2O$: C, 55.65; H, 4.55; N, 8.65. Found: C, 55.52; H, 4.43; N, 8.60.

5,7-Dimethoxybenzothiazoles

Compounds **1c**, **1d**, and **1f** are known. Compound **1c**: ref. 16. Compound **1d**: ref. 17. Compound **1f**: ref. 18. The other compounds are new. As these are key compounds, our details of all compounds **1a-g** are provided.

5,7-Dimethoxybenzothiazole (1a). The thioamide **5a** (0.10 g, 0.51 mmol) was suspended in absolute ethanol (1 mL) and 30% NaOH solution (0.55 mL, 8 eq.) was added dropwise with stirring. The resulting mixture was stirred for 5 min, diluted with water to make 10% NaOH solution and stirred again for 5 min. This solution was slowly added to a previously heated (80 ˚C) solution of $K_3Fe(CN)_6$ (0.67 g, 2.02 mmol, 4 eq.) in H_2O (5 mL) and the mixture stirred for 30 min. The reaction was cooled to room temperature and the resulting precipitate was filtered, washed with water, purified by flash chromatography and recrystallized from EtOH and dried to give the benzothiazole **1a** as a brown solid (94 mg, 19%), mp 110-112 ˚C. ν_{max} (KBr): 3440, 1745, 1650, 1600,1537, 1463, 1415, 1302, 1207, 1161, 1033 cm^{-1}. λ_{max} (MeOH): 206 nm (ε 23,900 $cm^{-1}M^{-1}$), 252 (10,600). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.78 (s, 3H, OMe), 3.85 (s, 3H, OMe), 6.47 (d, *J* 2.3 Hz, 1H, aryl H6), 7.06 (d, *J* 2.3 Hz, 1H, aryl H4), 8.39 (d, *J* 2.3 Hz, 1H, aryl H2). Mass Spectrum (+ESI): *m/z* (%) 197 (M+2, 13), 196 (M+1, 12), 195 (M, 10). HRMS (+ESI): $C_9H_9NO_2S$ $[M+H]^+$ requires 196.0427, found 196.0440.

5,7-Dimethoxy-2-methylbenzothiazole (1b). This compound was prepared from a solution of thioamide **5b** (10.0 g, 47.40 mmol) in absolute EtOH (10 mL), 30% NaOH solution (50 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (62.5 g, 0.19 mol, 4 eq.) in H_2O (120 mL) at 80-90 ˚C for 1 h to give the benzothiazole **1b** as a brown solid (5.4 g, 55%), mp 91-92 ˚C. ν_{max} (KBr): 2970, 1597, 1575, 1522, 1473, 1453, 1427, 1412, 1343, 1308, 1220, 1202, 1172, 1152, 1119, 1094, 1034, 930, 829, 648 cm^{-1}. λ_{max} (MeOH): 205 nm (ε 25,200 $cm^{-1}M^{-1}$), 224 (21,400), 307 (2,500). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.79 (s, 3H, Me), 3.86 (s, 3H, OMe), 3.91 (s, 3H, OMe), 6.45 (d, *J* 2.3 Hz, 1H, aryl H6), 7.06 (d, *J* 2.3 Hz, 1H, aryl H4). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.0 (Me), 55.6, 55.8 (OMe), 96.2, 97.1 (aryl CH), 116.4, 154.1, 155.0, 160.0, 168.0 (aryl C). Mass Spectrum (+EI): *m/z* (%) 211 (M+2, 12), 210 (M+1, 100), 195 (13). Anal. Calcd for $C_{10}H_{11}NO_2S$: C, 57.39; H, 5.30; N, 6.69. Found: C, 57.12; H, 5.39; N, 6.64.

5,7-Dimethoxy-2-phenylbenzothiazole (1c). This compound was prepared from a solution of thioamide **5c** (5.0 g, 18.31 mmol) in absolute EtOH (20 mL), 30% NaOH solution (20 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (24.11 g, 73.24 mmol, 4 eq.) in H_2O (120 mL) at 80-90 ˚C for 1 h to give the benzothiazole **1c** as an off white solid (3.71 g, 74%), mp 81-82 ˚C. ν_{max} (KBr): 2992, 1602, 1578, 1470, 1445, 1421, 1306, 1214, 1199, 1149, 1124, 1040, 936, 803, 755, 681, 635 cm^{-1}. λ_{max} (MeOH): 207 (29,200 nm (ε $cm^{-1}M^{-1}$), 238 (16,000), 294 (12,700). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 6H, OMe), 3.95 (s, 3H, OMe), 6.49 (d, *J* 2.3 Hz, 1H, aryl H6), 7.19 (d, *J* 2.3 Hz, 1H, aryl H4), 7.46-7.49 (m, 3H, aryl H), 8.05-8.08 (m, 2H, aryl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 55.8 (OMe), 96.9, 97.5, 127.2, 128.9, 130.7 (aryl CH), 116.1, 133.6, 154.3, 155.6, 160.3, 169.2 (aryl C). Mass Spectrum (+EI): *m/z* (%) 273 (M+2, 19), 272 (M+1, 100).

Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.49; H, 4.97; N, 5.12.

5,7-Dimethoxy-2-(4'-methoxyphenyl)benzothiazole (1d). This compound was prepared from a solution of thioamide **5d** (4.80 g, 15.84 mmol) in absolute EtOH (25 mL), 30% NaOH solution (17 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (20.86 g, 63.36 mmol, 4 eq.) in H_2O (50 mL) at 80-90 ˚C for 1 h to give the benzothiazole **1d** as white crystals (4.77 g, 95%), mp 131-131 ˚C. ν_{max} (KBr): 3000, 1605, 1598, 1462, 1430, 1413, 1351, 1307, 1252, 1224, 1203, 1158, 1121, 1111, 1036, 1023, 935, 831, 732 cm^{-1}. λ_{max} (MeOH): 211 nm (ε 24,200 $cm^{-1}M^{-1}$), 306 (15,600). ^1H NMR (300 MHz, $CDCl_3$): δ 3.87 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.95 (s, 3H, OMe), 6.47 (d, *J* 2.3 Hz, 1H, aryl H6), 6.98 (d, *J* 8.3 Hz, 2H, aryl H), 7.16 (d, *J* 2.3 Hz, 1H, aryl H4), 8.01 (d, *J* 8.3 Hz, 2H, aryl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 58.9, 59.2, 59.3 (OMe), 100.0, 100.8, 117.8, 132.3 (aryl CH), 119.3, 130.0, 157.7, 159.3, 163.7, 165.2, 172.5 (aryl C). Mass Spectrum (+EI): *m/z* (%) 303 (M+2, 20), 302 (M+1, 100). Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 64.07; H, 5.18; N, 4.63.

2-(4'-Chlorophenyl)-5,7-dimethoxybenzothiazole (1e). This compound was prepared from a solution of thioamide **5e** (8 g, 18.86 mmol) in absolute EtOH (10 mL), 30% NaOH solution (20 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (24.8 g, 75.44 mmol, 4 eq.) in H_2O (100 mL) at 80-90 ˚C for 1 h to give the benzothiazole **1e** as a white solid (5.23 g, 91%), mp 201-202 ˚C. ν_{max} (KBr): 1580, 1470, 1446, 1312, 1218, 1204, 1152, 1126, 1085, 1039, 934, 813 cm^{-1}. λ_{max} (MeOH): 209 nm (ε 27,900 $cm^{-1}M^{-1}$), 239 (14,200), 260 (11,800), 302 (14,400). ^1H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H, OMe), 3.96 (s, 3H, OMe), 6.50 (d, *J* 1.5 Hz, 1H, aryl H6), 7.17 (d, *J* 1.5 Hz, 1H, aryl H4), 7.44 (d, *J* 8.7 Hz, 2H, aryl H), 8.03 (d, *J* 8.7 Hz, 2H, aryl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 55.9 (OMe), 97.1, 97.4, 128.4, 129.2 (aryl CH), 116.2, 132.1, 136.8, 154.3, 155.5, 160.5, 167.8 (aryl C). Mass Spectrum (+EI): *m/z* (%) 309 (M+2, ^{37}Cl, 10), 308 (M+1, ^{37}Cl, 38), 307 (M+2, ^{35}Cl, 18), 306 (M+1, ^{35}Cl, 100), 272 (12). Anal. Calcd for $C_{15}H_{12}ClNO_2S$: C, 58.92; H, 3.96; N, 4.58. Found: C, 58.98; H, 4.05; N, 4.52.

5,7-Dimethoxy-2-(4'-nitrophenyl)benzothiazole (1f). This compound was prepared from a solution of thioamide **5f** (5 g, 15.72 mmol) in absolute EtOH (10 mL), 30% NaOH solution (16.7 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (20.70 g, 62.88 mmol, 4 eq.) in H_2O (25 mL) at 80-90 ˚C for 1 h to give the benzothiazole **1f** as a yellow solid (4.77 g, 96%), mp 240-241 ˚C. ν_{max} (KBr): 1604, 1578, 1527, 1428, 1351, 1311, 1154, 1126, 853 cm^{-1}. λ_{max} (MeOH): 203 nm (ε 40,400 $cm^{-1}M^{-1}$), 229 (23,800), 333 (17,600). ^1H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 3H, OMe), 3.98 (s, 3H, OMe), 6.55 (d, *J* 2.3 Hz, 1H, aryl H6), 7.21 (d, *J* 2.3 Hz, 1H, aryl H4), 8.23 (d, *J* 9.0 Hz, 2H, aryl H), 8.33 (d, *J* 9.0 Hz, 2H, aryl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 56.0 (OMe), 97.7, 97.8, 124.3, 127.9 (aryl CH), 103.1, 139.2, 148.8, 154.3, 155.7, 160.8, 165.9 (aryl C). Mass Spectrum (+EI): *m/z* (%) 318 (M+2, 20), 317 (M+1, 100). Anal. Calcd for $C_{15}H_{12}N_2O_4S$ $0.3H_2O$: C, 56.00; H, 3.95; N, 8.71. Found: C, 56.04; H, 3.89; N, 8.66.

5,7-Dimethoxy-2-(2'-nitrophenyl)benzothiazole (1g). This compound was prepared from a solution of

thioamide **5g** (1 g, 3.14 mmol) in absolute EtOH (1 mL), 30% NaOH solution (3.3 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (4.0 g, 12.56 mmol, 4 eq.) in H_2O (10 mL) at 80-90 ˚C for 1 h to give the benzothiazole **1g** as a yellow powder (0.20 g, 20%), mp 202 ˚C. ν_{max} (KBr): 1600, 1580, 1531, 1463, 1413, 1360, 1303, 1224, 1155, 1125, 1040 cm^{-1}. λ_{max} (MeOH): 206 nm (ε 27,500 $cm^{-1}M^{-1}$), 227 (20,500), 296 (8,500). ^1H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H, OMe), 3.96 (s, 3H, OMe), 6.53 (d, *J* = 2.3 Hz, 1H, aryl H6), 7.16 (d, *J* = 2.3 Hz, 1H, aryl H4), 7.58-7.80 (m, 2H, aryl H), 7.86 (d, *J* = 1.1 Hz, 1H, aryl H), 7.89 (d, *J* = 1.1 Hz, 1H, aryl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 55.9 (OMe), 97.5, 97.8, 124.3, 130.7, 131.5, 132.2 (aryl CH), 117.2, 127.8, 148.9, 154.2, 155.2, 160.5, 163.3 (aryl C). Mass Spectrum (+EI): *m/z* (%) 318 (M+2, 18), 317 (M+1, 100). Anal. Calcd for $C_{15}H_{12}N_2O_4S$: C, 56.95; H, 3.82; N, 8.86. Found: C, 57.04; H, 3.93; N, 8.89.

4,6-Dimethoxybenzothiazoles

Compounds **2b**, **2c**, **2d**, and **2g** are known. Compound **2b**: ref. 20. Compound **2c**: ref. 21. Compound **2d**: refs. 14 and 17. Compound 2g: ref. 19. The other compounds are new. As these are key compounds, our details of all compounds **2a-g** are provided.

4,6-Dimethoxybenzothiazole (2a). This compound was prepared from a solution of thioamide **6a** (0.50 g, 2.53 mmol) in absolute EtOH (1 mL), 30% NaOH solution (2.7 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (3.34 g, 10.15 mmol, 4 eq.) in H_2O (10 mL) at 80 ˚C for 30 min to give the benzothiazole **2a** as a brown solid (25 mg, 25%), mp 106-108 ˚C. ν_{max} (KBr): 3441, 1673, 1602, 1578, 1451, 1406, 1308, 1218, 1151, 1121, 1089, 852, 822 cm^{-1}. λ_{max} (MeOH): 220 nm (ε 29,800 $cm^{-1}M^{-1}$), 308 (4,800). ^1H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 3H, OMe), 3.95 (s, 3H, OMe), 6.53 (d, *J* 2.3 Hz, 1H, aryl H5), 6.76 (d, *J* 2.3 Hz, 1H, aryl H7), 8.99 (d, *J* 2.3 Hz, 1H, aryl H2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 55.9 (OMe), 97.2, 97.6, 98.2 (aryl CH), 132.1, 143.4, 153.6, 160.3 (aryl C). Mass Spectrum (+ESI): *m/z* (%) 196 (M+1, 100), 195 (M, 35).

4,6-Dimethoxy-2-methylbenzothiazole (2b). This compound was prepared from a solution of thioamide **6b** (0.50 g, 2.36 mmol) in absolute EtOH (2 mL), 30% NaOH solution (2.5 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (3.1 g, 9.44 mmol, 4 eq.) in H_2O (10 mL) at 80-90 ˚C for 1 h to give the benzothiazole **2b** as a brown solid (0.13 g, 27%), mp 46-48 ˚C. ν_{max} (KBr): 1599, 1572, 1525, 1457, 1432, 1332, 1287, 1219, 1198, 1159, 1045 818 cm^{-1}. λ_{max} (MeOH): 227 nm (ε 25,400 $cm^{-1}M^{-1}$), 270 (7,300). ^1H NMR (300 MHz, $CDCl_3$): δ 2.76 (s, 3H, Me), 3.82 (s, 3H, OMe), 3.96 (s, 3H, OMe), 6.48 (d, *J* 2.3 Hz, 1H, aryl H5), 6.82 (d, *J* 2.3 Hz, 1H, aryl H7). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.7 (Me), 55.7, 55.8 (OMe), 95.0, 97.3 (aryl CH), 137.6, 138.0, 153.0, 158.4, 162.8 (aryl C). Mass Spectrum (+EI): *m/z* (%) 211 (M+2, 12), 210 (M+1, 100). HRMS (+ESI): $C_{10}H_{11}NO_2S$ $[M+Na]^+$ requires 232.0402, found 232.0401. Anal. Calcd for $C_{10}H_{11}NO_2S$: C, 57.39; H, 5.30; N, 6.69. Found: C, 57.58; H, 4.59; N, 6.67.

4,6-Dimethoxy-2-phenylbenzothiazole (2c). This compound was prepared from a solution of thioamide

6c (6.50 g, 23.8 mmol) in absolute EtOH (10 mL), 30% NaOH solution (25.3 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (31.3 g, 95.2 mol, 4 eq.) in H_2O (100 mL) at 80-90 ˚C for 1 h to give the benzothiazole **2c** as a yellow solid (5.05 g, 78%), mp 122-123 ˚C. ν_{max} (KBr): 1592, 1573, 1510, 1479, 1447, 1289, 1211, 1150, 1051, 1034, 974, 812, 682 cm^{-1}. λ_{max} (MeOH): 214 nm (ε 29,000 $cm^{-1}M^{-1}$), 265 (8,800), 316 (16,000). ^1H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H, OMe), 4.04 (s, 3H, OMe), 6.55 (d, *J* 1.9 Hz, 1H, aryl H5), 6.93 (d, *J* 1.9 Hz, 1H, aryl H7), 7.43-7.45 (m, 3H, aryl H), 8.04-8.08 (m, 2H, aryl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 56.0 (OMe), 95.1, 97.9, 127.2, 128.7, 130.2 (aryl CH), 133.6, 137.4, 139.2, 153.8, 158.9, 164.0 (aryl C). Mass Spectrum (+EI): *m/z* (%) 273 (M+2, 17), 272 (M+1, 100). Anal. Calcd for $C_{15}H_{13}NO_2S$ $0.1CH_2Cl_2$: C, 64.81; H, 4.75; N, 5.01. Found: C, 64.72; H, 4.79; N, 4.96.

4,6-Dimethoxy-2-(4'-methoxyphenyl)benzothiazole (2d). This compound was prepared from a solution of thioamide **6d** (2.50 g, 8.25 mmol) in absolute EtOH (5 mL), 30% NaOH solution (8.8 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (10.86 g, 33 mmol, 4 eq.) in H_2O (20 mL) at 80-90 ˚C for 1 h to give the benzothiazole **2d** as a yellow powder (1.77 g, 71%), mp 122-123 ˚C. ν_{max} (KBr): 1604, 1571, 1519, 1487, 1452, 1412, 1332, 1304, 1287, 1248, 1214, 1154, 1043, 969, 840, 824, 790 cm^{-1}. λ_{max} (MeOH): 214 nm (ε 51,750 $cm^{-1}M^{-1}$), 321 (40,200). ^1H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H, OMe), 3.86 (s, 3H, OMe), 4.02 (s, 3H, OMe), 6.53 (d, *J* 2.3 Hz, 1H, aryl H5), 6.90 (d, *J* 8.6 Hz, 1H, aryl H7), 6.95 (d, *J* 8.6 Hz, 2H, aryl H), 7.99 (d, *J* 8.6 Hz, 2H, aryl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 55.7, 56.0 (OMe), 95.2, 97.7, 114.1, 128.8 (aryl CH), 126.5, 137.1, 139.2, 153.5, 158.6, 161.3, 164.0 (aryl C). Mass Spectrum (+EI): *m/z* (%) 303 (M+2, 20), 302 (M+1, 100). Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.81; H, 5.10; N, 4.67.

2-(4'-Chlorophenyl)-4,6-dimethoxybenzothiazole (2e). This compound was prepared from a solution of thioamide **6e** (8 g, 26.01 mmol) in absolute EtOH (10 mL), 30% NaOH solution (28 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (34.0 g, 104.04 mol, 4 eq.) in H_2O (100 mL) at 80-90 ˚C for 1 h to give the benzothiazole **2e** as a yellow powder (5.03 g, 87%), mp 146-147 ˚C. ν_{max} (KBr): 1600, 1567, 1510, 1453, 1289, 1269, 1211, 1152, 1089, 1045, 823 cm^{-1}. λ_{max} (MeOH): 215 nm (ε 37,000 $cm^{-1}M^{-1}$), 236 (19,300), 268 (12,000), 322 (19,800). ^1H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H, OMe), 4.03 (s, 3H, OMe), 6.55 (d, *J* 2.3 Hz, 1H, aryl H5), 6.92 (d, *J* 2.3 Hz, 1H, aryl H7), 7.41 (d, *J* 8.3 Hz, 2H, aryl H), 7.99 (d, *J* 8.3 Hz, 2H, aryl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 56.0 (OMe), 95.1, 98.0, 128.4, 128.9 (aryl CH), 132.1, 136.2, 137.4, 139.2, 153.8, 159.1, 162.5 (aryl C). Mass Spectrum (+EI): *m/z* (%) 309 (M+1, ^{37}Cl, 6), 308 (M, ^{37}Cl, 42), 307 (M+1, ^{35}Cl, 18), 306 (M, ^{35}Cl, 100). HRMS (+ESI): $C_{15}H_{12}ClNO_2S$ $[M+H]^+$ requires 306.0350, found 306.0342.

4,6-Dimethoxy-2-(4'-nitrophenyl)benzothiazole (2f). This compound was prepared from a solution of thioamide **6f** (7.0 g, 22.01 mmol) in absolute EtOH (5 mL), 30% NaOH solution (23.5 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (29 g, 88.05 mmol, 4 eq.) in H_2O (40 mL) at 80-90 ˚C for 1 h to give the

benzothiazole **2f** as a yellow solid (5.96 g, 86%), mp 218-220 ˚C. ν_{max} (KBr): 1589, 1523, 1340, 1292, 1213, 1156, 1047, 852 cm^{-1}. λ_{max} (MeOH): 205 nm (ε 43,300 $cm^{-1}M^{-1}$), 228 (25,200), 279 (12,400), 372 (20,800). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 3H, OMe), 4.06 (s, 3H, OMe), 6.58 (d, *J* 2.3 Hz, 1H, aryl H5), 6.96 (d, *J* 2.3 Hz, 1H, aryl H7), 8.22 (d, *J* 8.6 Hz, 2H, aryl H), 8.31(d, *J* 8.6 Hz, 2H, aryl H). The sample was not soluble enough for ^{13}C NMR measurement. Mass Spectrum (+EI): *m/z* (%) 318 (M+2, 19), 317 (M+1, 100). Anal. Calcd for $C_{15}H_{12}N_2O_4S$: C, 56.95; H, 3.82; N, 8.86. Found: C, 56.79; H, 3.85; N, 8.88.

4,6-Dimethoxy-2-(2'-nitrophenyl)benzothiazole (2g). This compound was prepared from a solution of thioamide **6g** (1.0 g, 3.14 mmol) in absolute EtOH (1 mL), 30% NaOH solution (3.3 mL, 8 eq.) and a solution of $K_3Fe(CN)_6$ (4.1 g, 12.56 mmol, 4 eq.) in H_2O (10 mL) at 80-90 ˚C for 1 h to give the benzothiazole **2g** as a light brown powder (0.25 g, 25%), mp 141-143 ˚C. ν_{max} (KBr): 1599, 1566, 1537, 1467, 1360, 1289, 1216, 1158, 1043, 970, 828, 744, 712 cm^{-1}. λ_{max} (MeOH): 209 nm (ε 44,500 $cm^{-1}M^{-1}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H, OMe), 3.98 (s, 3H, OMe), 6.54 (d, *J* 2.3 Hz, 1H, aryl H5), 6.91 (d, *J* 2.3 Hz, 1H, aryl H7), 7.57-7.67 (m, 2H, aryl H), 7.74-7.77 (m, 1H, aryl H), 7.90-7.93 (m, 1H, aryl H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8, 56.1 (OMe), 94.9, 98.4, 124.3, 130.4, 132.0, 132.3 (aryl CH), 128.5, 138.5, 138.7, 148.7, 154.2, 157.9, 159.4 (aryl C). Mass Spectrum (+EI): *m/z* (%) 318 (M+2, 19), 317 (M+1, 100). Anal. Calcd for $C_{15}H_{12}N_2O_4S$: C, 56.95; H, 3.82; N, 8.86. Found: C, 57.12; H, 3.94; N, 8.85.

2. SELECTED HYDROGEN-BOND PARAMETERS FOR COMPOUNDS 28 AND 29

Table 1. Selected hydrogen-bond parameters (Compound 28)

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
N2—H2A···O3^{i}	0.86	2.37	2.995 (2)	129.6
N2—H2B···N1	0.86	2.08	2.741 (2)	132.7
C12—H12···O1^{ii}	0.93	2.38	3.270 (3)	160.7
C18—H18B···O3	0.96	2.45	2.983 (2)	114.6
C19—H19B···O3	0.96	2.48	3.005 (2)	114.1

Symmetry code(s): (i) *x*-1, *y*, *z*; (ii) -*x*+2, -*y*+1, -*z*+1.

Table 2. Selected hydrogen-bond parameters (Compound 29)

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
N2—H2···N1	0.88	2.30	2.8100 (19)	117.0
N3—H3···O3^{i}	0.88	1.91	2.7903 (19)	173.0
C7—H7B···O1^{ii}	0.98	2.75	3.400 (2)	123.9

Symmetry code(s): (i) -*x*+1, -*y*-1, -*z*+1; (ii) -*x*+3/2, *y*-1/2, -*z*+3/2.