SYNTHESIS AND REACTIVITY OF DIMETHOXY ACTIVATED BENZOTHIAZOLEs

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1. EXPERIMENTAL FOR SYNTHESIS OF DIMETHOXYPHENZOTHIAZOLEs

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\text{max} (KBr): 3264, 2937, 1652, 1600, 1521, 1480, 1459, 1422, 1343, 1291, 1206, 1155, 1067, 830 cm\(^{-1}\). λ\text{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 H\(_4\)), 6.87 (d, J 9.0 Hz, 2H, aryl H\(_2,6\)), 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 H\(_4\)), 7.11 (d, J 2.2 Hz, 2H, aryl H\(_2,6\)), 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), 140.5, 141.0, 149.6, 161.0 (C=O). Mass Spectrum (+EI): m/z (%): 303 (M+1, 100). Anal. Calcd for C\(_{15}\)H\(_{14}\)N\(_2\)O\(_5\): 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\text{max} (KBr): 3264, 3105, 2967, 1662, 1623, 1600, 1566, 1533, 1456, 1422, 1348, 1196, 1152 1061, 841, 731 cm\(^{-1}\). λ\text{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 H\(_4\)), 6.99 (s, 2H, aryl H\(_2,6\)), 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), 140.5, 141.0, 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\(_2\)O\(_5\)·0.2CH\(_3\)OH: 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\(_2\)Cl\(_2\) (100 mL) containing anhydrous K\(_2\)CO\(_3\) (5 g) and 4-chlorobenzoym 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. \( \nu_{\text{max}} \) (KBr): 3436, 2989, 1661, 1613, 1542, 1501, 1483, 1461, 1415, 1285, 1258, 1209, 1155, 1039, 918, 838, 744 cm\(^{-1}\). \( \lambda_{\text{max}} \) (MeOH): 211 nm (\( \varepsilon \) 25,500 cm\(^{-1}\)M\(^{-1}\)), 224 (14,000), 286 (5,900). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 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\(_3\)): \( \delta \) 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, 29.40), 292 (M+1, 19.37), 286 (5.900).

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) \( P_2S_{10} \) (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\(_2\)Cl\(_2\)/light petroleum; 2:1) to yield the thioamide 5a as a light yellow powder (0.51 g, 9%), mp 184-185 °C. \( \nu_{\text{max}} \) (KBr): 3290, 1620, 1604, 1562, 1468, 1295, 1211, 1155, 982, 816 cm\(^{-1}\). \( \lambda_{\text{max}} \) (MeOH): 207 nm (\( \varepsilon \) 15,000 cm\(^{-1}\)M\(^{-1}\)), 233 (4,800), 313 (10,400). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 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\(_3\)): \( \delta \) 55.4 (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): \( C_{9}H_{11}NO_{2}S \) [M+Na]\(^+\) requires 220.0402, found 220.0401. Anal. Calcd for \( C_{9}H_{11}ClNO_{2}S \): 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, 15.33 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\(_2\)Cl\(_2\). The organic extract was washed with water, brine, and dried over MgSO\(_4\). The product was purified by short column chromatography using CH\(_2\)Cl\(_2\)/light petroleum (70:30) as eluent and recrystallized from MeOH/H\(_2\)O to give the thioamide 5b as a brown solid (4.12 g, 76%), mp 88-89 °C. \( \nu_{\text{max}} \) (KBr): 3213, 3151, 3059, 1618, 1596, 1549, 1477, 1460, 1426, 1345, 1300, 1213, 1199, 1163, 1060, 839, 727 cm\(^{-1}\). \( \lambda_{\text{max}} \) (MeOH): 206 nm (\( \varepsilon \) 22,600 cm\(^{-1}\)M\(^{-1}\)), 300 (10,200). \(^1\)H NMR (300 MHz, CDCl\(_3\)): (rotational isomer 1) \( \delta \) 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). \(^1\)H NMR (300 MHz, CDCl\(_3\)): (rotational isomer 2) \( \delta \) 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\(_3\)): \( \delta \) 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_{2}S [M+Na]^+ requires 234.0559, found 234.0558. Anal. Calcd for C_{10}H_{13}NO_{2}S: C, 56.85; H, 6.20; N, 6.69. 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⁻¹M⁻¹), 293 (16,700). ^1H NMR (300 MHz, CDCl₃): δ 3.77 (s, 6H, OMe), 3.85 (s, 3H, OMe), 6.36 (s, 1H, aryl H), 6.88-6.97 (m, 4H, aryl H), 7.30 (d, J 7.5 Hz, 2H, aryl H), 7.62 (d, J 8.3 Hz, 2H, aryl H), 8.92 (br s, 1H, NH). ^13C NMR (75 MHz, CDCl₃): 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), 288 (23), 270 (21). Anal. Calcd for C_{16}H_{17}NO_{3}S: 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 115-121 °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⁻¹M⁻¹), 241 (15,900), 271 (12,900), 318 (8,400). ^1H NMR (300 MHz, CDCl₃): δ 3.71 (s, 6H, OMe), 6.31 (s, 1H, aryl H), 6.91 (s, 2H, aryl H), 7.26 (d, J 8.5 Hz, 2H, aryl H), 7.62 (d, J 8.3 Hz, 2H, aryl H), 9.20 (br s, 1H, NH). ^13C NMR (75 MHz, CDCl₃): 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, ^35Cl, 11), 309 (M, ^35Cl, 30), 308 (M+1, ^35Cl, 100), 307 (M, ^35Cl, 9) 294 (^37Cl, 20) 292 (^35Cl, 54). Anal. Calcd for C_{16}H_{15}ClNO_{2}S: 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⁻¹M⁻¹), 280 (15,400). ^1H NMR (300 MHz, CDCl₃): δ 3.81 (s, 6H, OMe), 6.41 (s, 1H, aryl H), 7.04 (s, 2H, aryl H), 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). ^13C NMR (75 MHz, acetone-d₆): 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_{16}H_{14}N_{2}O_{4}S 0.2CH₂Cl₂: 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 CH₂Cl₂/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<sub>max</sub> (KBr): 3225, 1605, 1542, 1467, 1285, 1211, 1159, 1030, 974, 823, 782 cm<sup>-1</sup>. λ<sub>max</sub> (MeOH): 203 nm (ε 27,700 cm<sup>-1</sup>M<sup>-1</sup>), 292 (10,500), 320 (13,800). <sup>1</sup>H NMR (300 MHz, CDCl₃): 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). <sup>13</sup>C NMR (75 MHz, CDCl₃): 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<sub>9</sub>H<sub>11</sub>NO₂S: C, 54.80; H, 5.62; N, 5.70. 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 P₄S₁₀ (1.95 g, 8.80 mmol) in pyridine (15 mL) under reflux for 2 h to yield the thioamide 6b as a dark brown solid (0.97 g, 53%), mp 78-80 °C. ν<sub>max</sub> (KBr): 3361, 1617, 1539, 1497, 1451, 1389, 1328, 1285, 1267, 1206, 1158, 1125, 1043, 1027, 830, 676 cm<sup>-1</sup>. λ<sub>max</sub> (MeOH): 205 nm (ε 26,600 cm<sup>-1</sup>M<sup>-1</sup>), 280 (11,500). <sup>1</sup>H NMR (300 MHz, CDCl₃): (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). <sup>13</sup>C NMR (75 MHz, CDCl₃): 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). <sup>1</sup>H NMR (300 MHz, CDCl₃): (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). <sup>13</sup>C NMR (75 MHz, CDCl₃): 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): C₁₀H₁₃NO₂S [M+H]<sup>+</sup> requires 212.0739, found 212.0730. Anal. Calcd for C₁₀H₁₃NO₂S: 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 P₄S₁₀ (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<sub>max</sub> (KBr): 3347, 2998, 1614, 1594, 1521, 1468, 1436, 1419, 1379, 1329, 1283, 1236, 1208, 1161, 1126, 1033, 990, 915, 836, 794, 744 cm<sup>-1</sup>. λ<sub>max</sub> (MeOH): 204 nm (ε 36,100 cm<sup>-1</sup>M<sup>-1</sup>), 236 (19,400), 281 (11,000). <sup>1</sup>H NMR (300 MHz, CDCl₃): 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). <sup>13</sup>C NMR (75 MHz, CDCl₃): 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),

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. v_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). ^1H 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). ^13C 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_{13}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 167-168 °C. v_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). ^1H 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). ^13C 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, 65); 317 (76), 303 (52), 287 (25). Anal. Calcd for C_{13}H_{14}NO_2S: 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_2S_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. v_max (KBr): 3190, 1605, 1518, 1459, 1438, 1382, 1340, 1294, 1260, 1199, 1110, 1037, 1025, 988, 936, 825, 733, 701 cm^{-1}. λ_max (MeOH): 211 nm (ε 23,900 cm^{-1}M^{-1}). ^1H 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). ^13C 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_{13}H_{14}NO_2S 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$_3$Fe(CN)$_6$ (0.67 g, 2.02 mmol, 4 eq.) in H$_2$O (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. $\nu_{\max}$ (KBr): 3440, 1745, 1650, 1600,1537, 1463, 1415, 1302, 1207, 1161, 1033 cm$^{-1}$. $\lambda_{\max}$ (MeOH): 206 nm (ε 23,900 cm$^{-1}$M$^{-1}$), 252 (10,600). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 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 (+EI): $m/z$ (%) 197 (M+2, 13), 196 (M+1, 12), 195 (M, 10). HRMS (+ESI): C$_9$H$_9$NO$_2$S [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$_3$Fe(CN)$_6$ (62.5 g, 0.19 mol, 4 eq.) in H$_2$O (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. $\nu_{\max}$ (KBr): 2970, 1597, 1575, 1522, 1473, 1453, 1427, 1412, 1343, 1308, 1220, 1202, 1172, 1152, 1119, 1094, 1034, 930, 829, 648 cm$^{-1}$. $\lambda_{\max}$ (MeOH): 205 nm (ε 25,200 cm$^{-1}$M$^{-1}$), 224 (21,400), 307 (2,500). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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$_2$S: 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$_3$Fe(CN)$_6$ (24.11 g, 73.24 mmol, 4 eq.) in H$_2$O (120 mL) at 80-90 °C for 1 h to give the benzothiazole 1c as an off white solid (3.7 g, 74%), mp 81-82 °C. $\nu_{\max}$ (KBr): 2992, 1602, 1578, 1470, 1445, 1421, 1306, 1214, 1199, 1149, 1124, 1040, 936, 803, 755, 681, 635 cm$^{-1}$. $\lambda_{\max}$ (MeOH): 207 (29,200 nm (ε 75 cm$^{-1}$M$^{-1}$), 238 (16,000), 294 (12,700). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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).
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 K₃Fe(CN)₆ (20.86 g, 63.36 mmol, 4 eq.) in H₂O (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. νₑₓₘₐₓ (KBr): 3000, 1605, 1598, 1462, 1430, 1413, 1351, 1307, 1252, 1224, 1203, 1158, 1121, 1111, 1036, 1023, 935, 831, 732 cm⁻¹. λₑₓₘₐₓ (MeOH): 211 nm (ε 24,200 cm⁻¹M⁻¹), 306 (15,600). ¹H NMR (300 MHz, CDCl₃): δ 3.87 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.95 (s, 3H, OMe), 6.47 (d, 1H, ary1 H6), 7.76 (d, 1H, ary1 H6), 7.16 (d, 1H, ary1 H6), 7.17 (d, 1H, ary1 H6), 7.44 (d, 1H, ary1 H6). ¹³C NMR (75 MHz, CDCl₃): 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, 161.2, 170.2 (aryl C). Mass Spectrum (+EI): m/z (%) 303 (M+2, 20), 302 (M+1, 100). Anal. Calcd for C₃H₆N₂O₂S: 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 K₃Fe(CN)₆ (24.8 g, 75.44 mmol, 4 eq.) in H₂O (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. νₑₓₘₐₓ (KBr): 1580, 1470, 1446, 1312, 1218, 1204, 1152, 1126, 1085, 1039, 934, 813 cm⁻¹. λₑₓₘₐₓ (MeOH): 209 nm (ε 27,900 cm⁻¹M⁻¹), 239 (14,200), 260 (11,800), 302 (14,400). ¹H NMR (300 MHz, CDCl₃): δ 3.89 (s, 3H, OMe), 3.96 (s, 3H, OMe), 6.05 (d, 1H, ary1 H6), 7.17 (d, 1H, ary1 H6), 7.17 (d, 1H, ary1 H6), 7.76 (d, 1H, ary1 H6), 7.44 (d, 1H, ary1 H6), 8.03 (d, 1H, ary1 H6). ¹³C NMR (75 MHz, CDCl₃): δ 55.7, 55.9 (OMe), 97.5, 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, 37Cl, 10), 308 (M+1, 37Cl, 18), 307 (M+2, 35Cl, 18), 306 (M+1, 35Cl, 100), 272 (12). Anal. Calcd for C₁₅H₁₂ClNO₄S: 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 K₃Fe(CN)₆ (20.70 g, 62.88 mmol, 4 eq.) in H₂O (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. νₑₓₘₐₓ (KBr): 1604, 1578, 1527, 1428, 1351, 1311, 1154, 1126, 853 cm⁻¹. λₑₓₘₐₓ (MeOH): 203 nm (ε 40,400 cm⁻¹M⁻¹), 229 (23,800), 333 (17,600). ¹H NMR (300 MHz, CDCl₃): δ 3.91 (s, 3H, OMe), 3.98 (s, 3H, OMe), 6.55 (d, 1H, ary1 H6), 7.21 (d, 1H, ary1 H6), 8.23 (d, 1H, ary1 H6), 8.33 (d, 1H, ary1 H6). ¹³C NMR (75 MHz, CDCl₃): δ 55.7, 56.0 (OMe), 97.5, 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 C₁₅H₁₂N₂O₄S 0.3H₂O: 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 K3Fe(CN)6 (4.0 g, 12.56 mmol, 4 eq.) in H2O (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. v_max (KBr): 1600, 1580, 1531, 1463, 1413, 1360, 1303, 1224, 1155, 1125, 1040 cm⁻¹. λ_max (MeOH): 206 nm (ε 27,500 cm⁻¹M⁻¹), 227 (20,500), 296 (8,500). ¹H NMR (300 MHz, CDCl₃): 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, 2H, aryl H), 7.86 (d, J = 1.1 Hz, 1H, aryl H), 7.89 (d, J = 1.1 Hz, 1H, aryl H). ¹³C NMR (75 MHz, CDCl₃): 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 C₁₂H₁₂N₂O₄S: 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 K₃Fe(CN)₆ (3.34 g, 10.15 mmol, 4 eq.) in H₂O (10 mL) at 80 °C for 30 min to give the benzothiazole 2a as a brown solid (25 mg, 25%), mp 106-108 °C. v_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⁻¹M⁻¹), 308 (4,800). ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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 K₃Fe(CN)₆ (3.1 g, 9.44 mmol, 4 eq.) in H₂O (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. v_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⁻¹M⁻¹), 270 (7,300). ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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): C₁₀H₁₁NO₂S [M+Na⁺] requires 232.0402, found 232.0401. Anal. Calcd for C₁₀H₁₁NO₂S: 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 K₃Fe(CN)₆ (31.3 g, 95.2 mol, 4 eq.) in H₂O (100 mL) at 80-90 °C for 1 h to give the benzothiazole 2e as a yellow solid (5.05 g, 78%), mp 122-123 °C. νₘₐₓ (KBr): 1592, 1573, 1510, 1479, 1447, 1289, 1211, 1150, 1051, 1034, 974, 812, 682 cm⁻¹. λₘₐₓ (MeOH): 214 nm (ε 29,000 cm⁻¹M⁻¹), 265 (8,800), 316 (16,000).¹H NMR (300 MHz, CDCl₃): 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).¹³C NMR (75 MHz, CDCl₃): 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 C₁₅H₁₃NO₅S: C, 63.77; H, 4.02; N, 4.65. Found: C, 63.81; H, 4.75; N, 4.79.

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 K₃Fe(CN)₆ (10.86 g, 33 mmol, 4 eq.) in H₂O (20 mL) at 80-90 °C for 1 h to give the benzothiazole 2d as a yellow powder (1.77 g, 71%), mp 146-147 °C. νₘₐₓ (KBr): 1604, 1571, 1519, 1487, 1452, 1412, 1332, 1287, 1248, 1214, 1154, 1043, 969, 840, 824, 790 cm⁻¹. λₘₐₓ (MeOH): 214 nm (ε 51,750 cm⁻¹M⁻¹), 321 (40,200).¹H NMR (300 MHz, CDCl₃): 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).¹³C NMR (75 MHz, CDCl₃): 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 C₁₆H₁₅NO₅S: 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 K₃Fe(CN)₆ (34.0 g, 104.04 mol, 4 eq.) in H₂O (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. νₘₐₓ (KBr): 1600, 1567, 1510, 1453, 1289, 1269, 1211, 1089, 1045, 823 cm⁻¹. λₘₐₓ (MeOH): 215 nm (ε 37,000 cm⁻¹M⁻¹), 236 (19,300), 268 (12,000), 322 (19,800).¹H NMR (300 MHz, CDCl₃): 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).¹³C NMR (75 MHz, CDCl₃): 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, 37Cl, 6), 308 (M, 35Cl, 18), 306 (M, 37Cl, 100). HRMS (+ESI): C₁₅H₁₂ClNO₂S [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 K₃Fe(CN)₆ (29 g, 88.05 mmol, 4 eq.) in H₂O (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. \( \nu_{\text{max}} \) (KBr): 1589, 1523, 1340, 1292, 1213, 1156, 1047, 852 cm\(^{-1}\). \( \lambda_{\text{max}} \) (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\(_2\)O\(_4\)S: C, 56.95; H, 3.82; N, 8.86. Found: C, 56.79; H, 3.85; N, 8.88.

4,6-Dimethoxy-2-(2'-nitropheryl)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\(_3\)Fe(CN)\(_6\) (4.1 g, 12.56 mmol, 4 eq.) in H\(_2\)O (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. \( \nu_{\text{max}} \) (KBr): 1599, 1566, 1537, 1467, 1360, 1289, 1216, 1158, 1043, 970, 828, 744, 712 cm\(^{-1}\). \( \lambda_{\text{max}} \) (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\(_2\)O\(_4\)S: 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)

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<tr>
<th>D—H···A</th>
<th>D—H (Å)</th>
<th>H···A (Å)</th>
<th>D···A (Å)</th>
<th>D—H···A (°)</th>
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<td>2.995 (2)</td>
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<td>C12—H12···O1</td>
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<td>2.45</td>
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<td>C19—H19B···O3</td>
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Symmetry code(s):  (i) x-1, y, z; (ii) -x+2, -y+1, -z+1.

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

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<th>D—H (Å)</th>
<th>H···A (Å)</th>
<th>D···A (Å)</th>
<th>D—H···A (°)</th>
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<td>N2—H2···N1</td>
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<td>N3—H3···O3</td>
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<td>1.91</td>
<td>2.7903 (19)</td>
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<tr>
<td>C7—H7B···O1</td>
<td>0.98</td>
<td>2.75</td>
<td>3.400 (2)</td>
<td>123.9</td>
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</table>

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