CuBr2 Mediated Synthesis of 2-Aminothiazoles from Dithiocarbamic Acid Salts and Ketones

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**Supplemental Materials**

All reagents and solvents were purchased from Sigma-Aldrich and used as obtained. Flash chromatography was performed with a glass column packed with Baker silica gel (30–60 μm). NMR spectra were measured on a Bruker Avance II Plus spectrometer (400 MHz for 1H NMR, 100 MHz for 13C NMR). NMR spectra are referenced according to the residual peak of the solvent based on literature data. Mass data were obtained with a WATERS MS system, Q-tof premier and data analyzed using Mass Lynx4.1. Elemental analysis was performed with a Perkin-Elmer 2400 elemental analyzer.

**Phenyl-N-phenylthiazol-2-amine** (**4a**) [12]



White solid; m.p. 135-136℃.1H NMR (400 MHz, CDCl3): δ = 7.94 (s, 1H), 7.64-7.53 (m, 3H), 7.30-7.26 (m, 4H), 6.98-6.86 (m, 3H); 13C NMR (100 MHz, CDCl3): δ = 165.7, 152.2, 143.1, 133.0, 129.7, 129.6, 129.5, 129.3, 129.0, 127.6, 127.5, 119.0, 116.6, 116.6, 101.1. Elemental analyses: calcd for C15H12N2S: C, 71.40; H, 4.79; N, 11.10; S, 12.71. found: C, 71.39; H, 4.77; N, 11.08; S, 12.69. Elemental analyses: calcd for C16H14N2OS: C, 71.40; H, 4.79; N, 11.10; S, 12.71. found；C, 71.41; H, 4.81; N, 11.13; S, 12.69.

1. **(4-Methoxyphenyl)-N-phenylthiazol-2-amine** (**4b**) [12]



White solid; m.p. 137-140℃; 1H NMR (400 MHz, CDCl3): δ = 7.93 (s, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.64-7.53 (m, 2H), 7.30-7.26 (m, 2H), 6.91 (d, J = 8.4 Hz, 2H), 6.89 (m, 1H), 6.83 (s, 1H), 3.82 (s, 3H); 13C NMR (100 MHz, CDCl3): δ = 160.7, 160.1, 148.1, 143.0, 129.6, 129.5, 128.5, 128.5, 125.5, 125.4, 118.1, 116.5, 116.3, 115.0, 114.7, 101.1, 55.9. Elemental analyses: calcd for C16H14N2OS:C, 68.06; H, 5.00; N, 9.92; O, 5.67; S, 11.36. found: C, 68.03; H, 5.02; N, 9.90; O, 5.68; S, 11.33.

1. **(4-Bromophenyl)-N-phenylthiazol-2-amine** (**4c**)[12]



White solid; m.p. 137-140℃; White Solid; mp156–158℃. 1H NMR (400 MHz, CDCl3): δ = 7.71 (d, J = 8.4 Hz, 2H), 7.51 (d, 2H, J = 8.4 Hz), 7.36 (m, 4H), 7.08 (m, 1H), 6.72 (s, 1H). 13C NMR (100 MHz, CDCl3): δ = 165.1, 150.5, 140.5, 133.6, 132.0, 129.7, 128.0, 123.5, 122.0, 118.6, 102.3. EI-MS m/z [M+H]+ calcd forC15H11BrN2S: 330.99: found: 330.97. Elemental analyses: calcd for C15H11BrN2S: C, 54.39; H, 3.35; Br, 24.12; N, 8.46; S, 9.68. found: C, 54.42; H, 3.34; Br, 24.10; N, 8.45; S, 9.66.

1. **β-Naphthyl-N-phenylthiazol-2-amine (4d)** [6]



White solid; m.p. 148-150℃; 1H NMR (400 MHz, CDCl3): δ = 8.33 (s, 1H), 7.90-7.78 (m, 1H), 7.45-7.29 (m, 7H), 6.82 (s, 1H), 5.73 (s,1H). 13C NMR (100 MHz, CDCl3): δ = 169.1, 151.3, 143.1, 133.6, 132.9, 132.1, 128.7, 128.3, 127.6, 127.5, 126.1, 125.8, 124.9, 124.0, 101.6. EI-MS m/z [M+H]+ calcd forC19H14N2S: 303.09: found: 303.11. Elemental analyses: calcd for C19H14N2S: C, 75.47; H, 4.67; N, 9.26; S, 10.60. found: C, 75.45; H, 4.66; N, 9.28; S, 10.62.

**4-Phenyl-N-(4-methoxyphenyl)thiazol-2-amine** (**4e**) [12]



White solid; m.p. 157-160℃;1H NMR (400 MHz, CDCl3): δ = 7.94 (s, 1H), 7.64-7.53 (m, 3H), 7.30 (dd, J = 7.3, 2.1 Hz, 2H), 7.14 (dd, J = 6.5, 1.9 Hz, 2H), 6.93 (dd, J = 6.5, 2.1 Hz, 2H), 3.74 (s, 3H); 13C NMR (100 MHz, CDCl3): δ = 160.5, 150.7, 148.2, 135.4, 133.2, 129.5, 129.4, 128.9, 127.6, 127.5, 117.5, 117.3, 115.5, 115.1, 100.1, 55.9. Elemental analyses: calcd for C16H14N2OS: C, 68.06; H, 5.00; N, 9.92; S, 11.36. found: C, 68.09; H, 5.01; N, 9.94; S, 11.37.

**4-(4-Fluorophenyl)-N-methylthiazol-2-amine (4f)** [6]



White solid; m.p. 136-138℃；1H NMR (400 MHz, CDCl3) δ (ppm): 7.77-7.70 (m, 2H), 7.09-7.01 (m, 2H), 6.61 (s, 1H), 2.47 (s, 3H). 13C NMR (100 MHz, CDCl3): δ (ppm): 167.2, 163.3, 150.1, 130.9, 130.0, 128.5, 116.1, 116.0, 102.1, 29.5; Elemental analyses: calcd forC10H9FN2S: C, 57.67; H, 4.36; F, 9.12; N, 13.45; S, 15.40. found:

C, 57.69; H, 4.35; F, 9.11; N, 13.42; S, 15.37.

**4-Methylphenyl-N-phenylthiazol-2-amine** **(4g)** [13]



Gummy；1H NMR (400 MHz, CDCl3): δ = 7.30-7.26 (m, 2H), 7.24 (d, J=7.6Hz, 2H), 7.12 (d, J=7.0Hz, 2H), 6.91 (m, 2H), 6.89 (m, 1H), 6.63 (s, 1H), 2.28 (s, 3H); 13C NMR (100 MHz, CDCl3): δ = 160.8, 148.9, 143.1, 138.5, 130.2, 129.6, 129.6, 129.5, 129.5, 127.5, 127.4, 118.8, 116.3, 116.1, 100.7, 24.3; Elemental analyses: calcd forC16H14N2S: C, 72.15; H, 5.30; N, 10.52; S, 12.04. found: C, 72.12; H, 5.29; N, 10.50; S, 12.01.

**4-Phenyl-N-(4-methylphenyl)thiazol-2-amine (4h)** [12]



White solid; m.p. 135-137℃; 1H NMR (400 MHz, CDCl3): δ = 7.94 (s, 1H), 7.64-7.53 (m, 3H), 7.31 (dd, J=7.3, 2.0Hz, 2H), 7.15 (dd, J=6.4, 1.9Hz, 2H), 7.02 (dd, J=6.4, 2.3Hz, 2H), 2.29 (s, 3H); 13C NMR (100 MHz, CDCl3): δ = 160.5, 148.3, 142.1, 136.3, 130.2, 129.9, 129.3, 129.1, 128.8, 128.5, 127.4, 127.3, 116.3, 116.1, 100.1, 24.3; IR (KBr) ν = 3 411, 3 069, 2 975, 1611, l485, 1385, 1290, 1025 cm-1;Elemental analyses: calcd forC16H14N2S: C, 72.15; H, 5.30; N, 10.52; S, 12.04. found: C, 72.12; H, 5.29; N, 10.50; S, 12.01.

**4-Phenyl-N-(2-methylphenyl)thiazol-2-amine(4i)**



White solid; m.p. 106-108℃; 1H NMR (400 MHz, CDCl3): δ =7.91 (s, 1H), 7.64-7.53 (m, 3H), 7.30 (dd, J=7.5, 2.2 Hz, 2H), 7.14-7.01 (m, 3H), 6.62 (t, J=7.3, 1H), 2.15 (s, 3H);13C NMR (100 MHz, CDCl3): δ = 160.5, 148.2, 142.1, 133.3, 130.2, 129.3, 129.2, 129.1, 128.8, 127.5, 127.4, 126.7, 118.7, 116.1, 100.1, 15.5; IR (KBr) ν = 3427，3071，2956，161l，1488，l385，1285，1026 cm-1;Elemental analyses: calcd forC16H14N2S: C, 72.15; H, 5.30; N, 10.52; S, 12.04. found: C, 72.13; H, 5.28; N, 10.49; S, 12.00.

**4-Phenyl-N-(2-chlorophenyl)thiazol-2-amine (4j)**



White solid; m.p. 76-78℃; 1H NMR (400 MHz, CDCl3): δ =7.90 (s, 1H), 7.64-7.53 (m, 4H), 7.36-7.30 (m, 3H), 7.18 (t, J=6.4, 1H), 6.67 (t, J=7.3, 1H); 13C NMR (100 MHz, CDCl3): δ = 160.6, 148.3, 136.6, 133.2, 129.4, 129.3, 128.9, 127.9, 127.6, 127.5, 125.4, 120.7, 117.7, 100.1; IR (KBr) ν = 3435，3052，1610，1491，1276，1022 cm-1; Elemental analyses: calcd forC15H11ClN2S: C, 62.82; H, 3.87; Cl, 12.36; N, 9.77; S, 11.18. found: C, 62.79; H, 3.86; Cl, 12.33; N, 9.79; S, 11.20.

**4-Phenyl-N-(4-chlorophenyl)thiazol-2-amine (4k)** [8]



White solid; m.p. 148-151℃; 1H NMR (400 MHz, CDCl3): δ =7.93 (s, 1H), 7.64-7.53 (m, 3H), 7.30-7.24 (m, 6H); 13C NMR (100 MHz, CDCl3): δ = 160.6, 148.3, 141.2, 133.2, 129.7 (2C), 129.5 (2C), 128.9, 127.6 (2C), 124.3, 117.8, 117.7, 100.1; IR (KBr) ν = 3424，3050，1606，1498，1280，1029 cm-1;Elemental analyses: calcd forC15H11ClN2S: C, 62.82; H, 3.87; Cl, 12.36; N, 9.77; S, 11.18. found: C, 62.78; H, 3.85; Cl, 12.34; N, 9.75; S, 11.19.

**4-Phenyl-N-(4-nitrophenyl)thiazol-2-amine (4l)**



Yellow solid; m.p. 201-204℃; 1H NMR (400 MHz, CDCl3): δ = 8.23 (dd, J=6.4, 1.9Hz, 2H), 7.94 (s, 1H), 7.64-7.53 (m, 3H), 7.31-7.28 (m, 4H); 13C NMR (100 MHz, CDCl3): δ = 160.6, 149.2, 148.3, 138.4, 133.1, 129.5 (2C), 128.8, 127.5 (2C), 121.9 (2C), 117.2 (2C), 100.1; IR (KBr) ν = 3453，3040，1611，1509，1267，l035 cm-1; Elemental analyses: calcd forC20H16N2S: C, 60.59; H, 3.73; N, 14.13; S, 10.78. found: C, 60.56; H, 3.74; N, 14.11; S, 10.76.

**4-(naphthalen-2-yl)-N-benzylthiazol-2-amine (4m)** [6]



White solid; mp 131-132℃; 1H NMR (400 MHz, CDCl3): δ = 8.33 (s, 1H), 7.90-7.78 (m, 4H), 7.45-7.29 (m, 7H), 6.83 (s, 1H), 4.56-4.54 (d, J=4.7Hz, 2H); 13C NMR (100 MHz, CDCl3): δ = 169.5, 151.3, 137.5, 133.6, 132.9, 132.2, 128.6, 1289.3, 128.0, 127.6, 127.5, 126.1, 125.8, 124.9, 124.0, 101.7, 49.8. Elemental analyses: calcd forC20H16N2S: C, 75.92; H, 5.10; N, 8.85. Found: C, 75.81; H, 5.23; N, 8.72.

**Ethyl-2-(2-(phenylamino)thiazol-4-yl)acetate (4n)** [12]



Gummy; 1H NMR (400 MHz, CDCl3): δ = 7.79-7.32 (m, 4H), 7.03 (m, 1H), 6.44 (s, 1H), 4.17 (q, *J*=7.2Hz, 2H), 3.64 (s, 2H), 1.26 (t, *J*=7.2Hz, 3H) ; 13C NMR (100 MHz, CDCl3): δ = 170.4, 165.1, 144.6, 140.5, 129.6, 123.1, 118.6, 104.6, 61.2, 37.5, 14.3;

IR (KBr) ν = 3337，3064，2981，1731，1603，l526, 1497, 1370, 1246, 1030 cm-1; Elemental analyses: calcd forC13H14N2O2S: C, 59.52; H, 5.38; N, 10.68; S, 12.22. found: C, 59.50; H, 5.36; N, 10.67; S, 12.20.

**4,5-Dimethyl-n-phenylthiazol-2-amine (4o)** [12]



Yellow solid; mp 111-114℃; 1H NMR (400 MHz, CDCl3): δ = 7.34-7.25 (m, 4H), 7.02 (t, *J*=6.8Hz, 1H), 2.33 (s, 3H), 2.18 (s, 3H) ; 13C NMR (100 MHz, CDCl3): δ = 161.8, 143.0, 141.1, 129.5, 122.6, 118.3, 114.2, 14.8, 11.2; IR (KBr) ν = 3241, 3194，3138, 3068, 2916, 1605, 1569, 1499, 1424, 1376, 1297, 1222, 991, 847 cm-1; Elemental analyses: calcd forC11H12N2S: C, 64.67; H, 5.92; N, 13.71; S, 15.70. found: C, 64.68; H, 5.91; N, 13.74; S, 15.72.

**2-Nnilino-4,5,6,7-tetrahydrobenzothiazol (4p)**



White solid; mp 130-132℃ ; 1H NMR (400 MHz, CDCl3): δ = 7.36-7.28 (m, 4H), 7.04-7.00 (m, 1H), 2.63-2.61 (m, 4H), 1.85-1.82 (m, 4H) ; 13C NMR (100 MHz, CDCl3): δ = 158.4, 149.1, 143.6, 129.8, 129.6, 119.9, 118.8, 116.5 (2C), 25.2, 24.6, 22.5 (2C); IR (KBr) ν = 3254, 3184, 2934, 2855, 1601, 1550, 1529, 1459, 1313, 750; Elemental analyses: calcd forC13H14N2S: C, 67.79; H, 6.13; N, 12.16; S, 13.92. found: C, 67.82; H, 6.12; N, 12.13; S, 13.90.