Supplementary material

Simple one-pot synthesis of thioureas from amine, carbon disulfide and oxidants in water

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SUPPLEMENTARY MATERIAL

CHARACTERIZATION OF SYNTHESIZED COMPOUNDS

Tetraethylthiuram disulfide (TETD). Yield 58 % (99.0% HPLC); m.p. 71 °C (72 °C);[37] IR (KBr) ν_{max} (cm^{-1}): 2964, 2912, 2843, 1498, 1456, 1408, 1335, 1256, 1188, 1121 (νC=S), 1056, 1042, 986, 910 ;^{1}H NMR (500 MHz, $CDCl_3$): 1.35 (12H, t, $C\underline{H}_3$); 4.04 (8H, q, $C\underline{H}_2$);^{13}C NMR (500 MHz, $CDCl_3$): 10.8; 11.7; 46.8; 51.2; 192.9;MS (m/z) 296.05;Elemental analysis: calculated: %C 40.50; %H 6.80; %N 9.45; %S 43.25; found: %C 40.60; %H 6.72; %N 9.55; %S 43.13.

N,N,N'-triethylthiourea - $Et_2NC(S)NHEt$ (**1a**). Yield 88% (99.0% HPLC); 86-88 °C (87-88 °C);[42] IR (KBr) ν_{max} (cm^{-1}): 3282, 3180 (NH), 2942, 2860, 1634 (NH_2), 1530, 1488, 1460, 1251, 1056 (C=S), 1042; ^{1}H NMR ($CDCl_3$) (δ/ppm): 1.08-1.32 (m, 9H, $CH_2C\underline{H}_3$), 3.23-3.42 (m, 6H, $C\underline{H}_2CH_3$), 7.11 (NH); ^{13}C NMR (δ/ppm): 12.94 ($CH_2\underline{C}H_3$), 15.0 ($NHCH_2\underline{C}H_3$), 41.37 ($NH\underline{C}H_2CH_3$), 44.6 ($CH_2\underline{C}H_3$), 181.2 (CS); MS (m/z) 160.10; Elemental analysis: calculated: C 52.45; H 10.06; N 17.48; S 20.01; found: C 52.38; H 9.94; N 17.43; S 20.25.

N,N,N',N'-tetraethylthiourea - $Et_2NC(S)NEt_2$ (**1b**). Yield 82% (99.0% HPLC), m.p. 76-78 °C (78 °C);[42] IR (KBr) ν_{max} (cm^{-1}): 2944, 2875, 1633 (NH), 1538, 1496, 1466, 1250, 1060 (C=S), 1042; ^{1}H NMR ($CDCl_3$) (δ/ppm): 1.16 (t, 12H, $CH_2C\underline{H}_3$), 3.28 (q, 8H, $C\underline{H}_2CH_3$); ^{13}C NMR (δ/ppm): 12.92 ($CH_2\underline{C}H_3$), 42.68 ($\underline{C}H_2CH_3$), 182.3 (CS); MS (m/z) 188.13; Elemental analysis: calculated: C 57.40; H 10.70; N 14.87; S 17.03; found: C 57.26; H 10.62; N 14.78; S 17.34.

Dimethylcarbamodithioic acid. Yield 56 % (99.0% HPLC); m.p. 136-138 °C (143-144 °C);[43] ^{1}H NMR (500 MHz, $CDCl_3$): 3.61 (12H, d, CH_3); ^{13}C NMR (500 MHz, $CDCl_3$): 41.2; 46.5; 193.6; MS: M

(m/z) 120.01;Elemental analysis: calculated: %C 29.72; %H 5.82; %N 11.55; %S 52.90; found: %C 29.80; %H 5.72; %N 11.52; %S 52.96.

N'-(4-chlorophenyl)-N,N-dimethyl thiourea (**2a**). Yield 75% (99.2% HPLC); m.p. 150-152 °C (150–152 °C);[44] IR (KBr) ν_{max} (cm^{-1}): 3118, 3045, 2956, 2888, 1594, 1483, 1442, 1238, 1092 (C=S), 1030, 764, 692; ^{1}H NMR (δ/ppm): 2.20 (6H, *s*, $N(CH_3)_2$); 7.18 and 7.66 (4H, *dd*, C_6H_4); 9.44 (1H, *s*, NH); ^{13}C NMR ($CDCl_3$) (δ/ppm): 44.2, 128.2, 131.8, 133.2, 136.8, 181.4; MS (m/z) 214.03; Elemental analysis: calculated: C 50.34; H 5.16; N 13.05; S 14.93; Cl 16.51; found: C 50.30; H 5.12; N 13.11; S 14.89; Cl 16.58.

N'-(4-bromophenyl)-N,N-dimethyl thiourea (**2b**). Yield 72% (99.3% HPLC); m.p. 165-166 °C (165–167 °C);[45] IR (KBr) ν_{max} (cm^{-1}): 3122, 3052, 2958, 2876, 1591, 1480, 1452, 1242, 1088 (C=S), 1026, 774, 689; ^{1}H NMR (δ/ppm): 2.11 (6H, *s*, $N(CH_3)_2$); 7.36 and 7.52 (4H, *dd*, C_6H_4); 9.51 (1H, *s*, NH); ^{13}C NMR ($CDCl_3$) δ/ppm): 43.2, 122.2, 131.6, 132.2, 137.8, 182.4; MS (m/z) 257.98 (M+2 259.98); Elemental analysis: calculated: C 41.71; H 4.28; N 10.81; S 12.37; Br 30.83; found: C 41.69; H 4.22; N 10.84; S 12.44; Br 30.81.

N,N-dimethyl-N'-(4-nitrophenyl)thiourea (**2c**). Yield 66% (99.0% HPLC); m.p. 123-125 °C (124–126 °C);[46] IR (KBr) ν_{max} (cm^{-1}): 3176, 3048, 29550, 2836, 1611, 1494, 1432, 1250, 1095 (C=S), 1018, 782, 714; ^{1}H NMR (δ/ppm): 2.33 (6H, *s*, $N(CH_3)_2$); 6.85 and 7.98 (4H, *dd*, C_6H_4); 9.66 (1H, *s*, NH);^{13}C NMR ($CDCl_3$) (δ/ppm): 43.6, 124.2, 124.9, 143.6, 144.8, 182.9;
MS (m/z) 225.06; Elemental analysis: calculated: C 47.99; H 4.92; N 18.65; S 14.23; O 14.20; found: C 47.89; H 4.96; N 18.70; S 14.20; O 14.25.

N,N'-Dibenzylthiourea (**3a**).Yield 81 % - ether/$CHCl_3$ (99.2% HPLC); m.p. 137–138 °C (138–139 °C);[47] IR (KBr) ν_{max} (cm^{-1}): 3186, 3044, 1589, 1532, 765, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$): 4.94 (br s, 4 H), 5.86 (br s, 2 H), 7.20–7.44 (m, 10 H); ^{13}C NMR ($CDCl_3$): 54.2, 126.2, 127.6, 130.2, 134.8, 182.9; MS (m/z) 256.10; Elemental analysis: calculated: C 70.27; H 6.29; N 10.93; S 12.51; found: C 70.22; H 6.35; N 10.84; S 12.59.

N,N'-Diphenylthiourea (**3b**). Yield 68 % (99.3% HPLC); m.p. 151-153 °C (152 °C);[48] IR (KBr) ν_{max} (cm^{-1}): 3207, 3035, 1554, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 7.22–7.52 (m, 10H, ArH), 8.10 (s, 2H, NH) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): 125.6, 127.4, 129.9, 137.5, 180.1 ppm. MS (m/z) 228.07;Elemental analysis: calculated: C 68.39; H 5.30; N 12.27; S 14.04; found: C 68.32; H 5.26; N 12.22; S 14.20.

Bis(4-methylphenyl)thiourea (**3c**). Yield 74 % (99.2% HPLC) mp 180-182 °C (182 °C);[48] IR (KBr) ν_{max} (cm^{-1}): 3155, 3139, 2951, 1581, 822 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 2.32 (s, 6H), 7.10 (d, 4H), 7.32 (d, 4H), 9.31 (br.s., 2H); ^{13}C NMR (500 MHz, $CDCl_3$ + DMSO): 20.9, 124.5, 129.2, 134.1, 136.4, 180.4, ppm. MS (m/z) 256.10; Elemental analysis: calculated: C 70.27; H 6.29; N 10.93; S 12.51; found: C 70.22; H 6.34; N 10.88; S 12.56.

Bis(4-ethylphenyl)thiourea (**3d**). Yield 72 % (99.0% HPLC); m.p. 140-142 °C (142 °C);[48] IR (KBr) ν_{max} (cm^{-1}): 3218, 3029, 2962, 1554, 842 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$): 1.28 (t, 6H), 2.72 (q, 4H), 7.20 (d, 4H, Ar), 7.26 (d, 4H, Ar), 7.99 (br.s., 2H), ppm;^{13}C NMR (500 MHz, $CDCl_3$):

15.7, 28.9, 125.9, 129.4, 135.1, 143.4, 180.5 ppm; MS (m/z) 284.13; Elemental analysis: calculated: C 71.79; H 7.09; N 9.85; S 11.27; found: C 71.76; H 7.14; N 9.86; S 11.24.

Bis(2-methoxyphenyl)thiourea (**3e**). Yield 62 % (99.1% HPLC); m.p. 130 - 132 °C (132 °C);[48] FTIR (KBr) ν_{max} (cm^{-1}): 3330, 3126, 2950, 1563, 1512, 1027, 758 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 3.88 (s, 6H), 6.92–8.10 (m, 8H, Ar), 8.11 (s, 2H),; ^{13}C NMR (500 MHz, $CDCl_3$ + DMSO): 56.0, 111.4, 116.1, 120.8, 124.2, 126.8, 151.5, 178.6; MS (m/z) 288.09;Elemental analysis: calculated: C 62.48; H 5.59; N 9.71; S 11.12, O 11.10; found: C 62.38; H 5.62; N 9.82; S 11.20; O 10.98.

1-Ethyl-3-(2-methoxyphenyl)thiourea (**4a**). Yield 62% (98.9% HPLC); m.p. 98 - 100 °C (99-101 °C);[49] IR (KBr) ν_{max} (cm^{-1}): 3122, 3090, 1508, 1212, 1072 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.18 (t, *J* = 7.4 Hz, 3H, CH_3), 3.48–3.60 (q, *J* = 7.1 Hz, 2H, CH_2), 3.80 (*s*, 3H, CH_3), 7.50 (t, *J* = 7.4 Hz, 1H, NH), 7.56–7.67 (q, *J* = 5.1 Hz, 2H, HAr), 7.99 (t, *J* = 9.5 Hz, 2H, HAr), 8.08 (s, 1H, NH); ^{13}C NMR (500 MHz, $CDCl_3$): 15.3, 40.4, 55.7, 113.6, 121.6, 125.6, 125.8, 128.9, 154.2, 179.0; MS (m/z) 210.08; Elemental analysis: calculated: C 57.11; H 6.71; N 13.32; S 15.25; O 7.61; found: C 57.18; H 6.82; N 13.30; S 15.30; O 7.40.

1-Ethyl-3-(4-methoxyphenyl)thiourea (**4b**). Yield 64% (99.3% HPLC); m.p. 126 - 128 °C (125-130 °C);[49] IR (KBr) ν_{max} (cm^{-1}): 3209, 3005, 1514, 1292, 1257, 1147 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.20 (t. *J* = 7.4 Hz, 3H, CH_3), 3.60 (q, *J* = 7.2 Hz, 2H, CH_2), 3.88 (s, 3H, CH3), 5.84 (br. s, 1H, NH), 6.90 (d, *J* = 3.12 Hz, 2H, HAr), 7.22 (d, *J* = 3.12 Hz, 2H, HAr), 7.81 (s, 1H, NH); ^{13}C NMR (500 MHz, $CDCl_3$): 15.8, 41.2, 55.6, 114.8, 127.8, 130.9, 159.2, 179.8; MS (m/z) 210.08; Elemental analysis: calculated: C 57.11; H 6.71; N 13.32; S 15.25; O 7.61; found: C 57.15; H 6.80; N 13.36; S 15.32; O 7.37.

1-(4-Ethoxyphenyl)-3-ethylthiourea (**4c**). Yield 65% (98.7% HPLC); m.p. 106 - 108 °C (105-109 °C);[49] IR (KBr) ν_{max} (cm^{-1}): 3221, 3005, 1509, 1453, 1378, 1292, 1254, 1156 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 1.19 (t, *J* = 7.2 Hz, 3H, CH_3), 1.42 (t, *J* = 7.0 Hz, 3H, CH_3), 3.74 (q, *J* = 7.3 Hz, 2H, CH_2), 4.12 (q, *J* = 6.9 Hz, 2H, CH_2), 5.72 (br. s, 1H, NH), 7.01 (d, *J* = 8.7 Hz, 2H, CHAr), 7.19 (d, *J* = 8.8 Hz, 2H, CHAr), 7.26 (s, 1H, NH) ppm; MS (m/z) 224.10; ^{13}C NMR (500 MHz, $CDCl_3$): 14.9, 15.7, 40.2, 63.2, 114.6, 127.2, 130.5, 158.1, 179.4; MS (m/z) 210.08; Elemental analysis: calculated: C 58.90; H 7.19; N 12.49; S 14.29; O 7.13; found: C 58.88; H 7.15;; N 12.42; S 14.46; O 7.09.

1-Ethyl-3-(4-ethylphenyl)thiourea (**4d**). Yield 68% (98.9% HPLC); m.p. 87-89 °C (85-90 °C);[49] IR (KBr) ν_{max} (cm^{-1}): 3202, 3004, 1559, 1503, 1467, 1452, 1378, 1261, 1205 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.23 (t, *J* = 7.3 Hz, 3H, CH_3), 1.29 (t, *J* = 7.8 Hz, 3H, CH_3), 2.77 (q, *J* = 7.8 Hz, 2H, CH_2), 3.75 (q. *J* = 7.3 Hz, 2H, CH_2), 5.95 (br. s, 1H, NH), 7.17 (d, *J* = 4.9 Hz, 2H, CHAr), 7.24 (d. *J* = 2.1 Hz, 2H, HAr), 7.89 (br. s, 1H, NH) ppm;^{13}C NMR (500 MHz, $CDCl_3$): 14.4, 15.4, 28.5, 40.1, 126.4, 128.2, 135.5, 144.7, 179.1; MS (m/z) 208.10; Elemental analysis: calculated: C 63.42; H 7.74; N 13.45; S 15.39; found: C 63.35; H 7.62; N 13.48; S 15.55.