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 oC (72 oC);37 IR (KBr) νmax (cm-1): 2964, 2912, 2843, 1498, 1456, 1408, 1335, 1256, 1188, 1121 (νC=S), 1056, 1042, 986, 910 ;1H NMR (500 MHz, CDCl3): 1.35 (12H, t, CH3); 4.04 (8H, q, CH2);13C NMR (500 MHz, CDCl3): 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 - Et2NC(S)NHEt* (**1a**).Yield 88% (99.0% HPLC); 86-88 oC (87-88 oC);42 IR (KBr) νmax (cm-1): 3282, 3180 (NH), 2942, 2860, 1634 (NH2), 1530, 1488, 1460, 1251, 1056 (C=S), 1042; 1H NMR (CDCl3) (δ/ppm): 1.08-1.32 (m, 9H, CH2CH3), 3.23-3.42 (m, 6H, CH2CH3), 7.11 (NH); 13C NMR (δ/ppm): 12.94 (CH2CH3), 15.0 (NHCH2CH3), 41.37 (NHCH2CH3), 44.6 (CH2CH3), 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 - Et2NC(S)NEt2* (**1b**). Yield82% (99.0% HPLC), m.p. 76-78 oC (78 oC);42 IR (KBr) νmax (cm-1): 2944, 2875, 1633 (NH), 1538, 1496, 1466, 1250, 1060 (C=S), 1042; 1H NMR (CDCl3) (δ/ppm): 1.16 (t, 12H, CH2CH3), 3.28 (q, 8H, CH2CH3); 13C NMR (δ/ppm): 12.92 (CH2CH3), 42.68 (CH2CH3), 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 oC (143-144 oC);43 1H NMR (500 MHz, CDCl3): 3.61 (12H, d, CH3); 13C NMR (500 MHz, CDCl3): 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) νmax (cm-1): 3118, 3045, 2956, 2888, 1594, 1483, 1442, 1238, 1092 (C=S), 1030, 764, 692; 1H NMR (δ/ppm): 2.20 (6H, *s*, N(CH3)2); 7.18 and 7.66 (4H, *dd*, C6H4); 9.44 (1H, *s*, NH); 13C NMR (CDCl3) (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) νmax (cm-1): 3122, 3052, 2958, 2876, 1591, 1480, 1452, 1242, 1088 (C=S), 1026, 774, 689; 1H NMR (δ/ppm): 2.11 (6H, *s*, N(CH3)2); 7.36 and 7.52 (4H, *dd*, C6H4); 9.51 (1H, *s*, NH); 13C NMR (CDCl3) 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) νmax (cm-1): 3176, 3048, 29550, 2836, 1611, 1494, 1432, 1250, 1095 (C=S), 1018, 782, 714; 1H NMR (δ/ppm): 2.33 (6H, *s*, N(CH3)2); 6.85 and 7.98 (4H, *dd*, C6H4); 9.66 (1H, *s*, NH);13C NMR (CDCl3) (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/CHCl3 (99.2% HPLC);m.p. 137–138 °C (138–139 °C);47 IR (KBr) νmax (cm-1): 3186, 3044, 1589, 1532, 765, 702 cm-1; 1H NMR (CDCl3): 4.94 (br s, 4 H), 5.86 (br s, 2 H), 7.20–7.44 (m, 10 H); 13C NMR (CDCl3): 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 oC (152 oC);48 IR (KBr) νmax (cm-1): 3207, 3035, 1554, 698 cm-1; 1H NMR (500 MHz, CDCl3): 7.22–7.52 (m, 10H, ArH), 8.10 (s, 2H, NH) ppm. 13C NMR (500 MHz, CDCl3): 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 oC (182 oC);48 IR (KBr) νmax (cm-1): 3155, 3139, 2951, 1581, 822 cm-1; 1H NMR (500 MHz, CDCl3): 2.32 (s, 6H), 7.10 (d, 4H), 7.32 (d, 4H), 9.31 (br.s., 2H); 13C NMR (500 MHz, CDCl3 + 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 oC (142 oC);48 IR (KBr) νmax (cm-1): 3218, 3029, 2962, 1554, 842 cm-1;1H NMR (500 MHz, CDCl3): 1.28 (t, 6H), 2.72 (q, 4H), 7.20 (d, 4H, Ar), 7.26 (d, 4H, Ar), 7.99 (br.s., 2H), ppm;13C NMR (500 MHz, CDCl3): 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 oC (132 oC);48 FTIR (KBr) νmax (cm-1): 3330, 3126, 2950, 1563, 1512, 1027, 758 cm-1; 1H NMR (500 MHz, CDCl3): 3.88 (s, 6H), 6.92–8.10 (m, 8H, Ar), 8.11 (s, 2H),; 13C NMR (500 MHz, CDCl3 + 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 oC (99-101 oC);49 IR (KBr) νmax (cm-1): 3122, 3090, 1508, 1212, 1072 cm-1; 1H NMR (CDCl3): 1.18 (t, *J* = 7.4 Hz, 3H, CH3), 3.48–3.60 (q, *J =* 7.1 Hz, 2H, CH2), 3.80 (*s*, 3H, CH3), 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);

13C NMR (500 MHz, CDCl3): 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 oC (125-130 oC);49 IR (KBr) νmax (cm-1): 3209, 3005, 1514, 1292, 1257, 1147 cm-1; 1H NMR (CDCl3): 1.20 (t. *J* = 7.4 Hz, 3H, CH3), 3.60 (q, *J* = 7.2 Hz, 2H, CH2), 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); 13C NMR (500 MHz, CDCl3): 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 oC (105-109 oC);49 IR (KBr) νmax (cm-1): 3221, 3005, 1509, 1453, 1378, 1292, 1254, 1156 cm-1; 1H-NMR (CDCl3): 1.19 (t, *J* = 7.2 Hz, 3H, CH3), 1.42 (t, *J =* 7.0 Hz, 3H, CH3), 3.74 (q, *J* = 7.3 Hz, 2H, CH2), 4.12 (q, *J* = 6.9 Hz, 2H, CH2), 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; 13C NMR (500 MHz, CDCl3): 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 oC (85-90 oC);49 IR (KBr) νmax (cm-1): 3202, 3004, 1559, 1503, 1467, 1452, 1378, 1261, 1205 cm-1; 1H NMR (CDCl3): 1.23 (t, *J* = 7.3 Hz, 3H, CH3), 1.29 (t, *J* = 7.8 Hz, 3H, CH3), 2.77 (q, *J* = 7.8 Hz, 2H, CH2), 3.75 (q. *J* = 7.3 Hz, 2H, CH2), 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;13C NMR (500 MHz, CDCl3): 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.