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SUPPLEMENTARY MATERIAL TO

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

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CHARACTERIZATION OF SYNTHESIZED COMPOUNDS

*Diethylcarbamodithioic acid (**K**).* Yield 56 % (99.0 % HPLC); m.p.: 136––138 °C (Lit.: 143–144 °C[1]); Anal. Calcd. for $C_5H_{11}NS_2$: C, 40.23; H, 7.43; N, 9.38; S, 42.96 %. Found: C, 40.28; H, 7.49; N, 9.42; S, 42.81 %; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.22 (6H, *s*, CH_3); 3.74 (4H, *s*, CH_2); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 12.9; 49.8; 192.6; MS (*m*/*z*): 149.03.

Dimethylcarbamodithioic acid. Yield: 56 % (99.0 % HPLC); m.p.: 136–138 °C (Lit.: 143–144 °C[1]); Anal. Calcd. for $C_3H_7NS_2$: 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 %; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 3.61 (6H, *d*, *J* = Hz, CH_3); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 46.5; 193.6; MS (*m*/*z*): 120.01.

*Tetraethylthiuram disulfide (TETD, **L**).* Yield: 58 % (99.0 % HPLC); m.p.: 71 °C (lit.: 72 °C[2]); Anal. Calcd. for $C_{10}H_{20}N_2S_4$: 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. %; IR (KBr, cm^{-1}): 2964, 2912, 2843, 1498, 1456, 1408, 1335, 1256, 1188, 1121 (C=S), 1056, 1042, 986, 910; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.35 (12H, *t*, *J* = 7.9 Hz, CH_3); 4.04 (8H, *q*, *J* = 7.9 Hz, CH_2); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 10.8, 11.7, 46.8, 51.2, 192.9; MS (*m*/*z*): 296.05.

N,N,N′-*Triethylthiourea – $Et_2NC(S)NHEt$ (**1a**).* Yield: 88 % (99.0 % HPLC); m.p.: 86–88 °C (lit.: 87–88 °C[3]); Anal. Calcd. for $C_7H_{16}N_2S$: C, 52.46; H, 10.06; N, 17.48; S, 20.01 %. Found: C, 52.38; H, 9.94; N, 17.43; S, 20.25 %;

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IR (KBr, cm^{-1}): 3282, 3180 (NH), 2942, 2860, 1634 (NH_2), 1530, 1488, 1460, 1251, 1056 (C=S), 1042; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.08–1.32 (9H, *m*, $CH_2C\mathbf{H}_3$), 3.23–3.42 (6H, *m*, $C\mathbf{H}_2CH_3$), 7.11 (1H, *s*, NH); ^{13}C-NMR ($CDCl_3$, δ / ppm): 12.94 ($CH_2\mathbf{C}H_3$), 15.0 ($NHCH_2\mathbf{C}H_3$), 41.37 ($NH\mathbf{C}H_2CH_3$), 44.6 (CH_2CH_3), 181.2 (CS); MS (*m*/*z*): 160.10.

N,N,N′,N′-*Tetraethylthiourea – $Et_2NC(S)NEt_2$ (**1b**)*. Yield: 82 % (99.0 % HPLC), m.p.: 76–78 °C (lit.: 78 °C[3]); Anal. Calcd. for $C_9H_{20}N_2S$: 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 %; IR (KBr, cm^{-1}): 2944, 2875, 1633 (NH), 1538, 1496, 1466, 1250, 1060 (C=S), 1042; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.16 (12H, *t*, J = 7.9 Hz, $CH_2C\mathbf{H}_3$), 3.28 (8H, *q*, J = 7.9 Hz, $C\mathbf{H}_2CH_3$); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 12.92 ($CH_2\mathbf{C}H_3$), 42.68 ($\mathbf{C}H_2CH_3$), 182.3 (CS); MS (*m*/*z*): 188.13.

N′-*(4-Chlorophenyl)*-N,N-*dimethylthiourea (**2a**)*. Yield: 75 % (99.2 % HPLC); m.p.: 150–152 °C (lit.: 150–152 °C[4]); Anal. Calcd. for $C_9H_{11}ClN_2S$: 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 %; IR (KBr, cm^{-1}): 3118, 3045, 2956, 2888, 1594, 1483, 1442, 1238, 1092 (C=S), 1030, 764, 692; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 2.20 (6H, *s*, $N(CH_3)_2$); 7.18 and 7.66 (4H, *dd*, J = 7.5 Hz, C_6H_4); 9.44 (1H, *s*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 44.2, 128.2, 131.8, 133.2, 136.8, 181.4; MS (*m*/*z*): 214.03.

N′-*(4-Bromophenyl)*-N,N-*dimethylthiourea (**2b**)*. Yield: 72 % (99.3 % HPLC); m.p.: 165–166 °C (lit.: 165–167 °C[5]); Anal. Calcd. for $C_9H_{11}BrN_2S$: 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 %; IR (KBr, cm^{-1}): 3122, 3052, 2958, 2876, 1591, 1480, 1452, 1242, 1088 (C=S), 1026, 774, 689; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 2.11 (6H, *s*, $N(CH_3)_2$); 7.36 and 7.52 (4H, *dd*, J = 7.55 Hz, C_6H_4); 9.51 (1H, *s*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 43.2, 122.2, 131.6, 132.2, 137.8, 182.4; MS (*m*/*z*): 257.98, 259.98 (M+2).

N,N-*Dimethyl*-N′-*(4-nitrophenyl)thiourea (**2c**)*. Yield: 66 % (99.0 % HPLC); m.p.: 123–125 °C (lit.: 124–126 °C[6]); Anal. Calcd. for $C_9H_{11}N_3O_2S$: 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; IR (KBr, cm^{-1}): 3176, 3048, 2955, 2836, 1611, 1494, 1432, 1250, 1095 (C=S), 1018, 782, 714; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 2.33 (6H, *s*, $N(CH_3)_2$); 6.85 and 7.98 (4H, *dd*, J = 7.6 Hz, C_6H_4); 9.66 (1H, *s*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 43.6, 124.2, 124.9, 143.6, 144.8, 182.9; MS (*m*/*z*): 225.06.

N,N′-*Dibenzylthiourea (**3a**)*. Yield: 81 % (99.2 % HPLC); m.p.: 137–138 °C (lit. 138–139 °C[7]); Anal. Calcd. for $C_{15}H_{16}N_2S$: 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 %; IR (KBr, cm^{-1}): 3186, 3044, 1589, 1532, 765, 702; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 4.94 (4H,

brs, CH_2), 5.86 (2H, *brs*, NH), 7.20–7.44 (10H, *m*, C_6H_5); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 54.2, 126.2, 127.6, 130.2, 134.8, 182.9; MS (*m*/*z*): 256.10.

N,N′-*Diphenylthiourea* (***3b***). Yield: 68 % (99.3 % HPLC); m.p.: 151–153 °C (lit.: 152 °C[8]); Anal. Calcd. for $C_{13}H_{12}N_2S$: 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 %; IR (KBr, cm^{-1}): 3207, 3035, 1554, 698; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 7.22–7.52 (10H, *m*, Ar-H), 8.10 (2H, *s*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 125.6, 127.4, 129.9, 137.5, 180.1; MS (*m*/*z*) 228.07.

N,N′-*Bis(4-Methylphenyl)thiourea* (***3c***). Yield: 74 % (99.2 % HPLC); m.p.: 180–182 °C (lit.: 182 °C[8]); Anal. Calcd. for $C_{15}H_{16}N_2S$: 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 %; IR (KBr, cm^{-1}): 3155, 3139, 2951, 1581, 822; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 2.32 (6H, *s*, CH_3), 7.10 (4H, *d*, C_6H_4), 7.32 (4H, *d*, C_6H_4), 9.31 (2H, *brs*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$ + DMSO 1/1, δ / ppm): 20.9, 124.5, 129.2, 134.1, 136.4, 180.4; MS (*m*/*z*): 256.10.

N,N′-*Bis(4-ethylphenyl)thiourea* (***3d***). Yield: 72 % (99.0 % HPLC); m.p.: 140–142 °C (lit.: 142 °C[8]); Anal. Calcd. for $C_{17}H_{20}N_2S$: 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 %; IR (KBr, cm^{-1}): 3218, 3029, 2962, 1554, 842; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.28 (6H, *t*, CH_3), 2.72 (4H, *q*, CH_2), 7.20 (4H, *d*, Ar-H), 7.26 (4H, *d*, Ar-H), 7.99 (2H, *brs*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 15.7, 28.9, 125.9, 129.4, 135.1, 143.4, 180.5; MS (*m*/*z*): 284.13.

N,N′-*Bis(2-methoxyphenyl)thiourea* (***3e***). Yield: 62 % (99.1 % HPLC); m.p.: 130–132 °C (lit.: 132 °C[8]); Anal. Calcd. for $C_{15}H_{16}N_2O_2S$: C, 62.48; H, 5.59; N, 9.71; S, 11.12. Found: C, 62.38; H, 5.62; N, 9.82; S, 11.20; FTIR (KBr, cm^{-1}): 3330, 3126, 2950, 1563, 1512, 1027, 758; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 3.88 (6H, *s*, OCH_3), 6.92–8.10 (8H, *m*, Ar-H), 8.11 (2H, *s*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$ + DMSO 1/1, δ / ppm): 56.0, 111.4, 116.1, 120.8, 124.2, 126.8, 151.5, 178.6; MS (*m*/*z*): 288.09.

N-*Ethyl*-N′-*(2-methoxyphenyl)thiourea* (***4a***). Yield 62 % (98.9 % HPLC); m.p.: 98–100 °C (lit.: 99–101 °C[9]); Anal. Calcd. for $C_{10}H_{14}N_2OS$: C 57.11; H, 6.71; N, 13.32; S, 15.25. Found: C, 57.18; H, 6.82; N, 13.30; S, 15.30; FTIR (KBr, cm^{-1}): 3122, 3090, 1508, 1212, 1072; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.18 (3H, *t*, J = 7.4 Hz, CH_3), 3.48–3.60 (2H, *q*, J = 7.1 Hz, CH_2), 3.80 (3H, *s*, CH_3), 7.50 (1H, *t*, J = 7.4 Hz, NH), 7.56–7.67 (2H, *q*, J = 5.1 Hz, Ar-H), 7.99 (2H, *t*, J = 9.5 Hz, Ar-H), 8.08 (1H, *s*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 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.

N-*Ethyl*-N′-*(4-methoxyphenyl)thiourea* (***4b***). Yield: 64 % (99.3 % HPLC); m.p.: 126–128 °C (lit. 125–130 °C[9]); Anal. Calcd. for $C_{10}H_{14}N_2OS$: C, 57.11; H, 6.71; N, 13.32; S, 15.25. Found: C, 57.15; H, 6.80; N, 13.36; S, 15.32; FTIR

(KBr, cm^{-1}): 3209, 3005, 1514, 1292, 1257, 1147; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.20 (3H, *t*. *J* = 7.4 Hz, CH_3), 3.60 (2H, *q*, *J* = 7.2 Hz, CH_2), 3.88 (3H, *s*, CH_3), 5.84 (1H, *brs*, NH), 6.90 (2H, *d*, *J* = 3.12 Hz, Ar-H), 7.22 (2H, *d*, *J* = 3.12 Hz, Ar-H), 7.81 (1H, *s*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 15.8, 41.2, 55.6, 114.8, 127.8, 130.9, 159.2, 179.8; MS (*m*/*z*): 210.08.

N-*(4-Ethoxyphenyl)*-N′-*ethylthiourea* ***(4c)***. Yield: 65 % (98.7 % HPLC); m.p.: 106–108 °C (lit.: 105–109 °C[9]); Anal. Calcd. for $C_{11}H_{16}N_2OS$: C, 58.90; H, 7.19; N, 12.49; S, 14.29. Found: C, 58.88; H, 7.15; N, 12.42; S, 14.46; FTIR (KBr, cm^{-1}): 3221, 3005, 1509, 1453, 1378, 1292, 1254, 1156; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.19 (3H, *t*, *J* = 7.2 Hz, CH_3), 1.42 (3H, *t*, *J* = 7.0 Hz, CH_3), 3.74 (2H, *q*, *J* = 7.3 Hz, CH_2), 4.12 (2H, *q*, *J* = 6.9 Hz, CH_2), 5.72 (1H, *brs*, NH), 7.01 (2H, *d*, *J* = 8.7 Hz, Ar-H), 7.19 (2H, *d*, *J* = 8.8 Hz, Ar-H), 7.26 (1H, *s*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 14.9, 15.7, 40.2, 63.2, 114.6, 127.2, 130.5, 158.1, 179.4; MS (*m*/*z*): 224.10.

N-*Ethyl*-N′-*(4-ethylphenyl)thiourea* ***(4d)***. Yield: 68 % (98.9 % HPLC); m.p.: 87–89 °C (lit.: 85–90 °C[9]); Anal. Calcd. for $C_{11}H_{16}N_2S$: 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 %; IR (KBr, cm^{-1}): 3202, 3004, 1559, 1503, 1467, 1452, 1378, 1261, 1205; ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 1.23 (3H, *t*, *J* = 7.3 Hz, CH_3), 1.29 (3H, *t*, *J* = 7.8 Hz, CH_3), 2.77 (2H, *q*, *J* = 7.8 Hz, CH_2), 3.75 (2H, *q*. *J* = 7.3 Hz, CH_2), 5.95 (1H, *brs*, NH), 7.17 (2H, *d*, *J* = 4.9 Hz, Ar-H), 7.24 (2H, *d*, *J* = 2.1 Hz, Ar-H), 7.89 (1H, *brs*, NH); ^{13}C-NMR (50 MHz, $CDCl_3$ δ / ppm): 14.4, 15.4, 28.5, 40.1, 126.4, 128.2, 135.5, 144.7, 179.1; MS (*m*/*z*): 208.10.

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