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Synthesis of secondary thiols from terminal alkenes and P_2S_5

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1. General Procedures

The solvents ($CHCl_3$, $ClCH_2CH_2Cl$ and CH_2Cl_2) were distilled from P_2O_5 immediately prior to use. The solvents (toluene, benzene, hexane, ethyl acetate, THF, and Et_2O) were distilled from CaH_2. Commercially available P_2S_5 (99%, Merck KGaA), 2,2,6,6-tetramethylpiperidin-1-yl-oxyl (TEMPO) (98%, Acros), Et_3N (99%, Merck), Bu^tOOH (70% wt in H_2O, Sigma-Aldrich), 2,2'-azobis(2-methylpropionitrile) (AIBN) (Macklin) were used.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (400.13 MHz (^1H), 100.62 MHz (^{13}C)) (Bruker). $CDCl_3$ was employed as the solvent and the internal standard. 1D spectra were recorded using standard Bruker pulse sequences.

The products were analyzed using a gas chromatograph-mass spectrometer GCMS-QP2010 Ultra equipped with the GC-2010 Plus chromatograph, TD-20 thermal desorber, and an ultrafast quadrupole mass-selective detector (Shimadzu).

Synthesis of alkane-2-thiols 2a-d

A flask with a magnetic stirrer was filled with 264 mg (1.2 mmol) of P_2S_5, 0.25-0.4 ml (2 mmol) of 1-alkene (**1a-d**), 9.4 mg (0.06 mmol) of TEMPO, and 2 mL of solvents. Depending on the boiling point of the substrate and solvent, the reaction was carried out with stirring at a temperature of 30–100 °C. After 3 h, the reaction mixture was decomposed with 10% HCl at 0 °C. Products were extracted with CH_2Cl_2, and the organic layer was dried over Na_2SO_4. The products were analyzed by GC/MS. The crude product was air dried and purified by flash chromatography over silica gel (0.060–0.200 mm 60 A, eluent: petroleum ether) to give **2a-d**.

Hexane-2-thiol (2a). Isolated yield 0.203 g (86%).

^1H NMR (400 MHz, $CDCl_3$) δ_H 0.93 (3H, t, ^3J=6.9 Hz, CH_3); 1.23–1.46 (10H, m, CH_2, SH, CH_3); 1.46-1.83 (2H, m, CH_2CHSH), 3.04 (1H, sext, ^3J=6.7 Hz, CH). ^{13}C NMR (100.13 MHz, $CDCl_3$) δ_C 14.0 (CH_3); 20.6 (CH$_3$CH); 22.6, 29.3 (CH_2); 35.9 (CH$_2$CHSH); 47.3 (CHSH). *m/z* (I, %) [M] = 118 (38), 119 (3), 86 (2), 85 (28), 84 (25), 75 (5), 74 (1), 70 (2), 69 (28), 63 (3), 62 (3), 61 (51), 60 (14), 59 (7), 58 (3), 57 (18), 56 (36), 55 (35), 54 (2), 53 (3), 47 (9), 45 (5), 44 (3), 43 (100), 42 (32), 41 (52), 40 (3).

Octane-2-thiol (2b). Isolated yield 0.239 g (82%).

^1H NMR (400 MHz, $CDCl_3$) δ_H 0.91 (3H, t, ^3J=7.0 Hz, CH_3); 1.19-1.49 (12H, m, CH_2, SH, CH_3); 1.44-1.84 (2H, m, CH_2CHSH); 3.04 (1H, sext, ^3J=6.8 Hz, CH). ^{13}C NMR (100.13 MHz, $CDCl_3$) δ_C 14.1 (CH_3); 20.7 (CH$_3$CH); 22.6, 26.9, 29.1, 31.7 (CH_2); 35.9 (CH$_2$CHSH); 47.2 (CHSH). *m/z* (I, %) [M] = 146 (28), 147 (1), 113 (4), 112 (40), 103 (1), 97 (7), 85 (3), 84 (29), 83 (44), 82 (11), 75 (6), 74 (2), 73 (1), 72 (3), 71 (61), 70 (80), 69 (32), 68 (6), 67 (6), 65 (1), 63 (4), 62 (4), 61 (69), 60 (21), 59 (10), 58 (5), 57 (82), 56 (54), 55 (76), 54 (5), 53 (7), 51 (2), 47 (11), 45 (7), 43 (78), 42 (41), 41 (100), 40 (5).

Nonane-2-thiol (2c). Isolated yield 0.266 g (83%).

^1H NMR (400 MHz, $CDCl_3$) δ_H 0.91 (3H, t, ^3J=7.0 Hz, CH_3); 1.18-1.49 (14H, m, CH_2, SH, CH_3); 1.46-1.86 (2H, m, CH_2CHSH); 3.04 (1H, sext, ^3J=6.8 Hz, CH). ^{13}C NMR (100.13 MHz, $CDCl_3$) δ_C 14.1 (CH_3); 20.7 (CH$_3$CH); 22.7, 27.0, 29.2, 29.4, 31.8 (CH_2); 35.9 (CH$_2$CHSH); 47.2 (CHSH). *m/z* (I, %) [M] = 160 (25), 161 (3), 127 (4), 126 (36), 111 (3), 103 (2), 99 (2), 98 (19), 97 (41), 96 (5), 86 (2), 85 (30), 84 (37), 83 (29), 82 (13), 81 (2), 72 (3), 71 (52), 70 (50), 69 (49), 68 (5), 67 (8), 63 (3), 62 (3), 61 (64), 60 (21), 59 (10), 58 (4), 57 (59), 56 (75), 55 (79), 54 (6), 53 (8), 45 (6), 44 (3), 43 (97), 42 (37), 41 (100).

Decane-2-thiol (2d). Isolated yield 0.299 g (86%).

^1H NMR (400 MHz, $CDCl_3$) δ_H 0.90 (3H, t, ^3J=7.0 Hz, CH_3); 1.20-1.50 (16H, m, CH_2, SH, CH_3); 1.47-1.82 (1H, m, CH_2CHSH); 3.04 (1H, sext, ^3J=6.8 Hz, CH). ^{13}C NMR (100.13 MHz, $CDCl_3$) δ_C 14.1 (CH$_3$); 20.7 (CH$_3$CH); 22.7, 27.0, 29.3, 29.45, 29.5, 31.9 (CH_2); 35.9 (CH$_2$CHSH); 47.1 (CHSH). *m/z* (I, %) [M] = 174 (23), 175 (3), 141 (4), 140 (32), 125 (2), 113 (2), 112 (15), 111 (25), 110 (3), 103 (3), 99 (6), 98 (20), 97 (44), 96 (9), 87 (2), 86 (2), 85 (35), 84 (30), 83 (32), 82 (11), 81 (4), 81 (4), 79 (2), 77 (2), 75 (7), 74 (3), 73 (2), 72 (3), 71 (39), 70 (65), 69 (59), 68 (7), 67 (9), 65 (2), 63 (3), 62 (4), 61 (62), 60 (20), 59 (9), 58 (5), 57 (83), 56 (79), 55 (82), 54 (7), 53 (7), 51 (2), 47 (9), 45 (6), 44 (3), 43 (95), 42 (31), 41 (100), 40 (4).

Figure S1. GC-MS of hexane-2-thiol (**2a**)

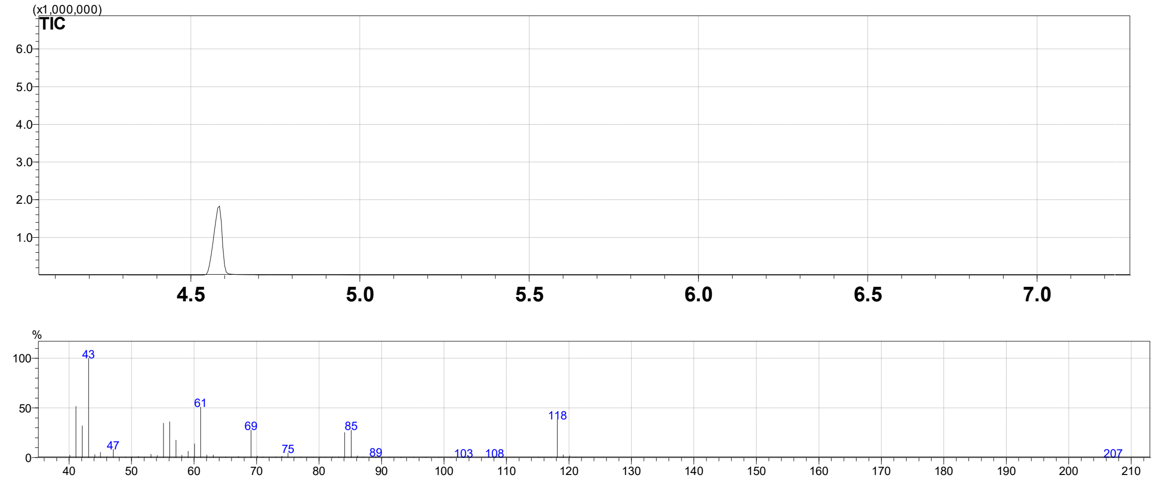

Figure S2. GC-MS of octane-2-thiol (**2b**)

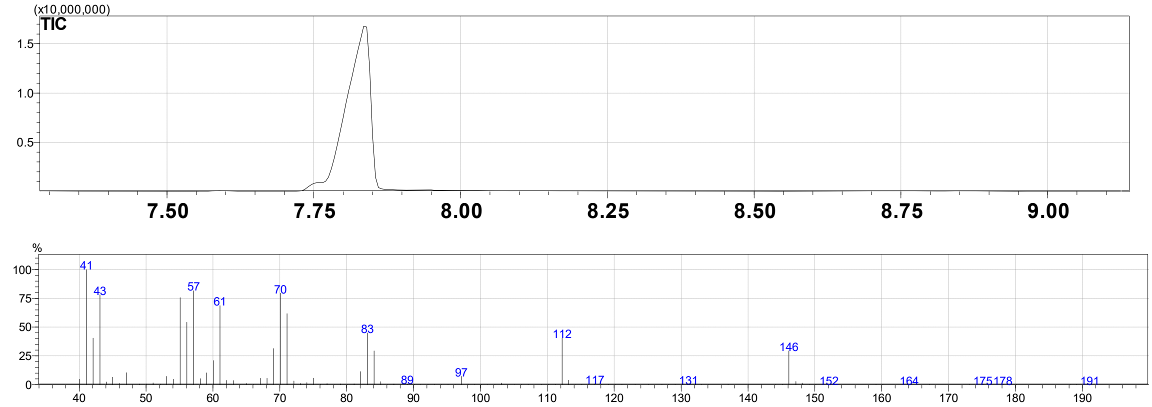

Figure S3. GC-MS of nonane-2-thiol (**2c**)

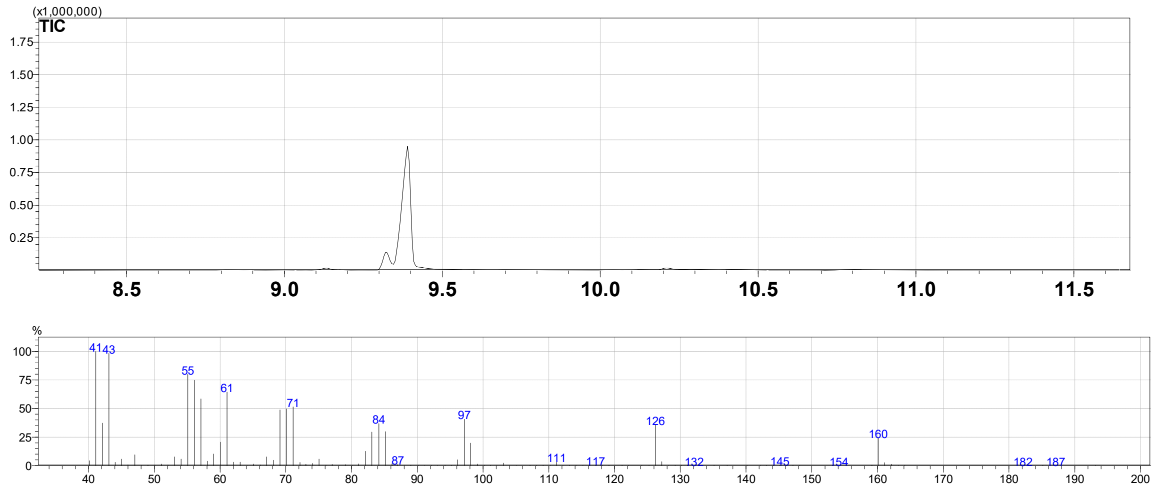

Figure S4. GC-MS of decane-2-thiol (**2d**)

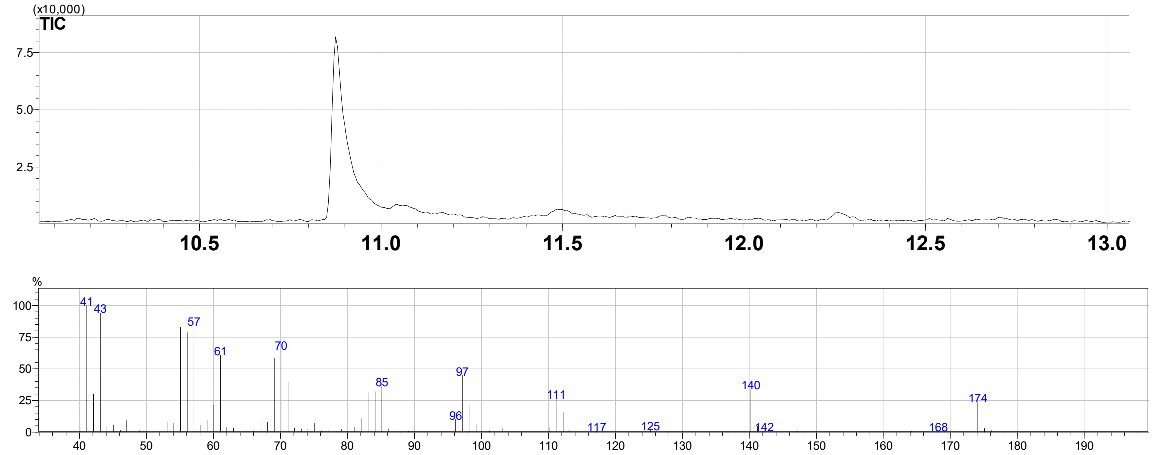

Figure S5. GC-MS of the reaction mass containing decane-2-thiol (**2d**) and 2-octylthiirane (**3d**)

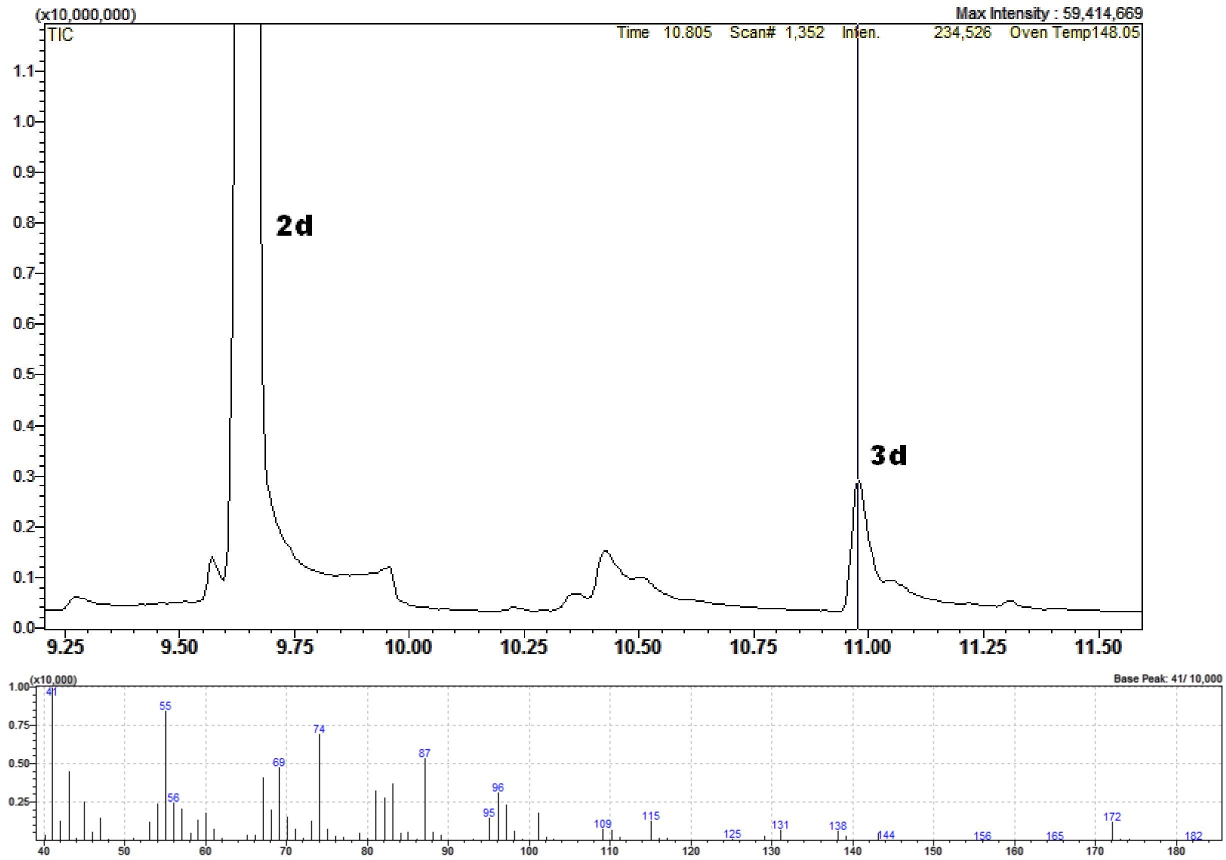

Figure S6. ¹H NMR of hexane-2-thiol (**2a**)

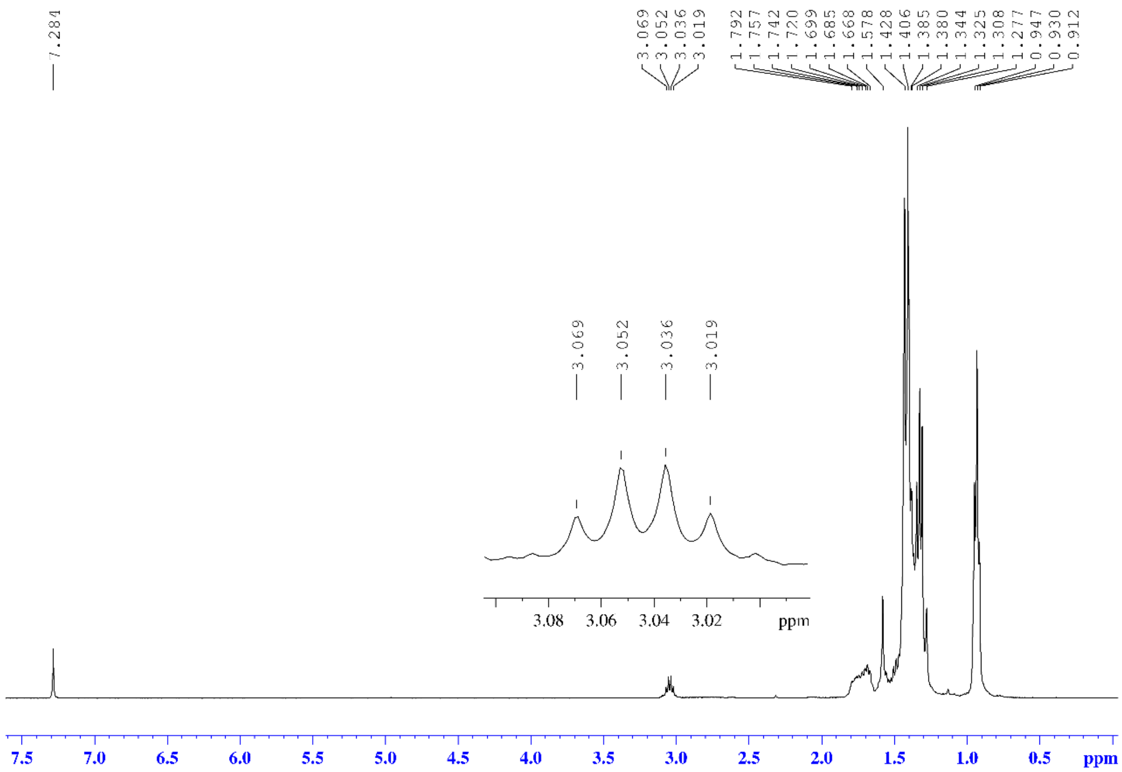

Figure S7. ¹³C NMR of hexane-2-thiol (**2a**)

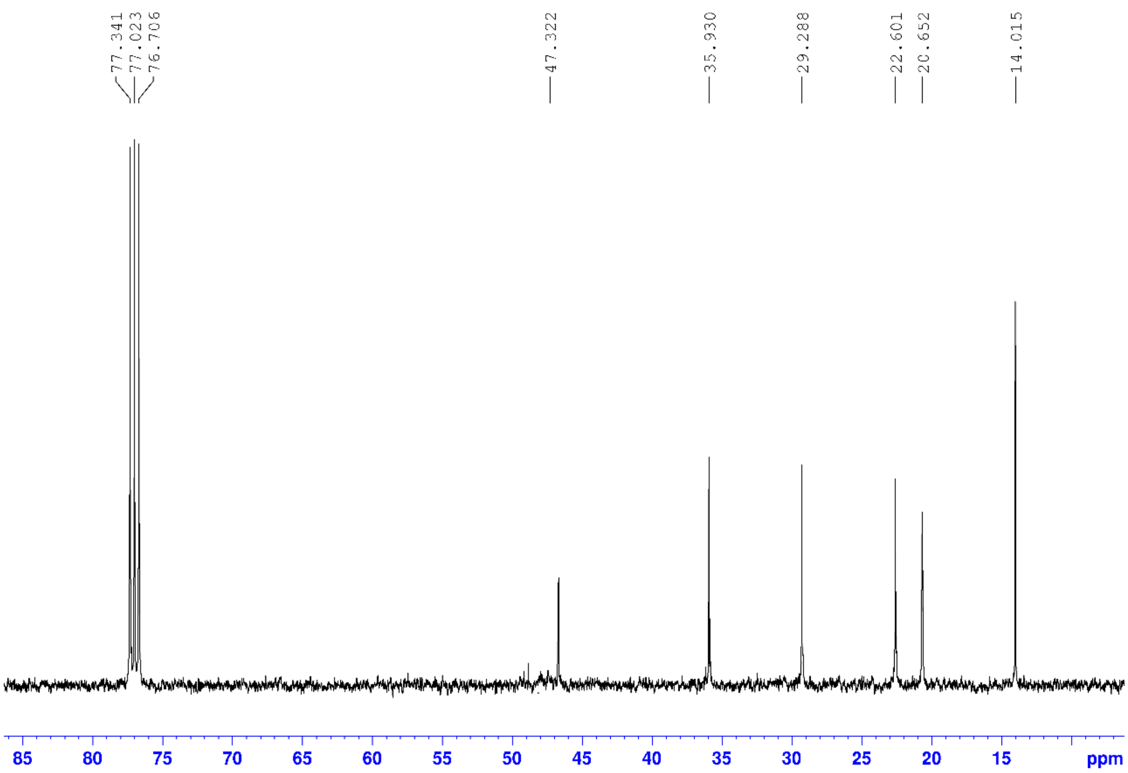

Figure S8. ^{1}H NMR of octane-2-thiol (**2b**)

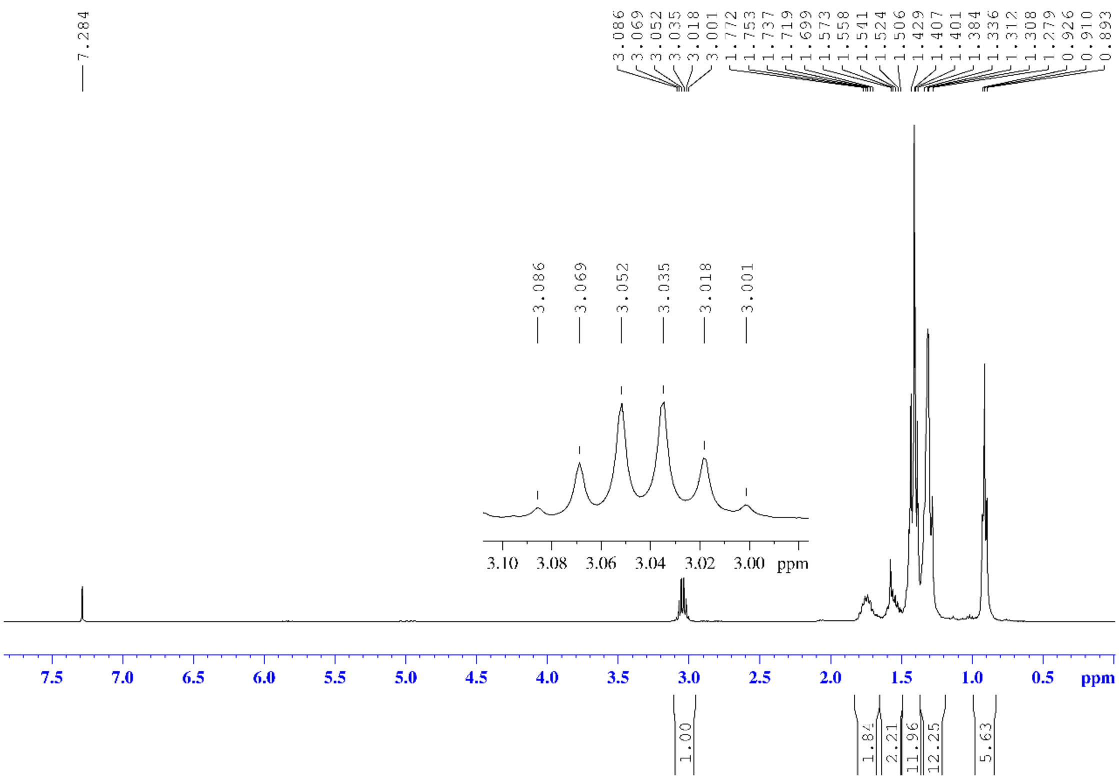

Figure S9. ^{13}C NMR of octane-2-thiol (**2b**)

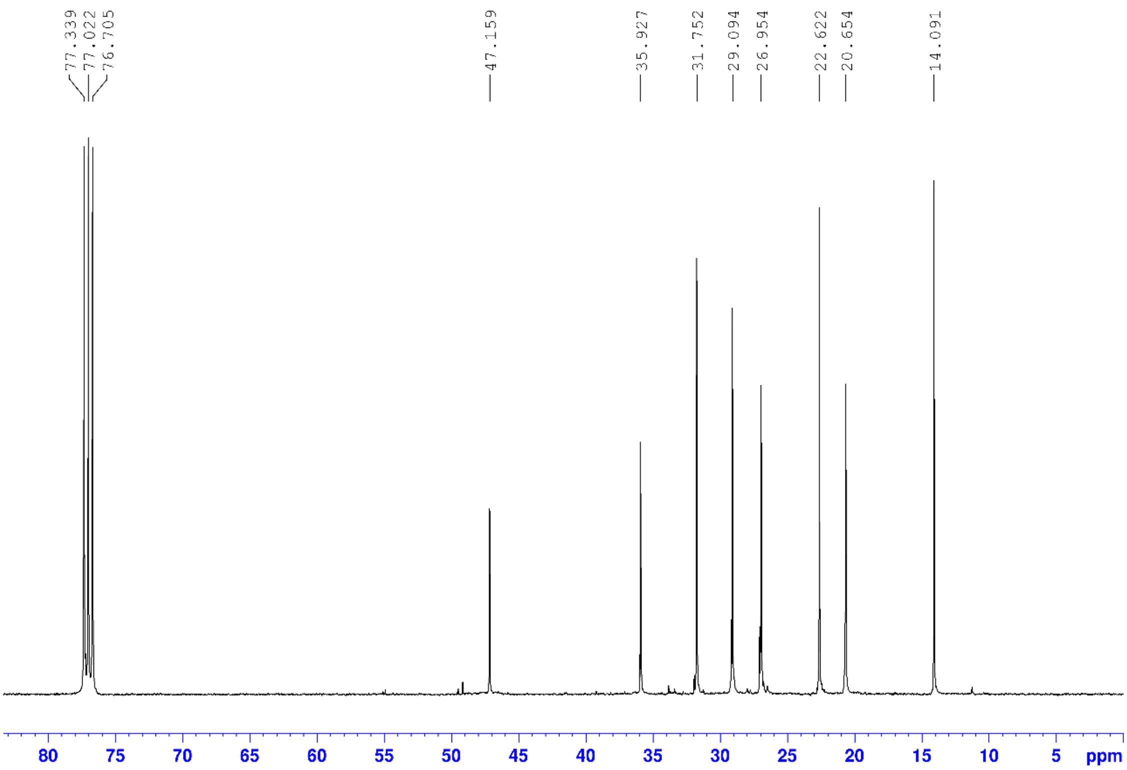

Figure S10. ^{13}C NMR (DEPT) of octane-2-thiol (**2b**)

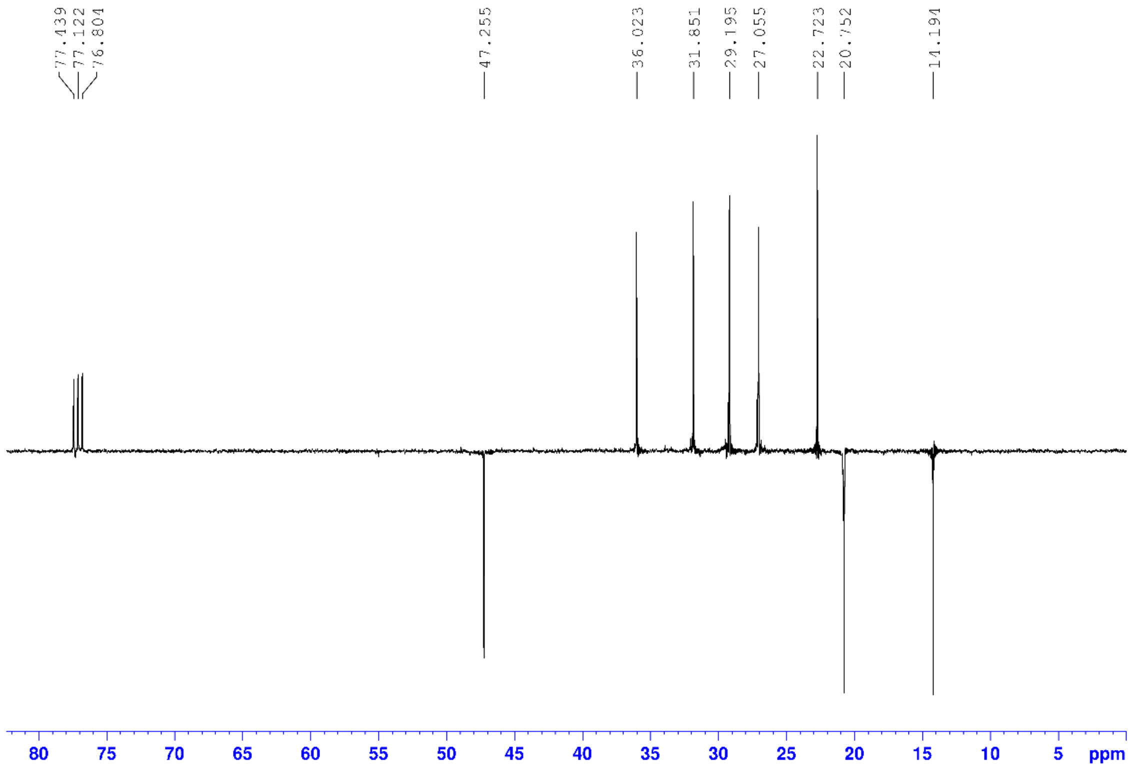

Figure S11. ^{1}H NMR of nonane-2-thiol (**2c**)

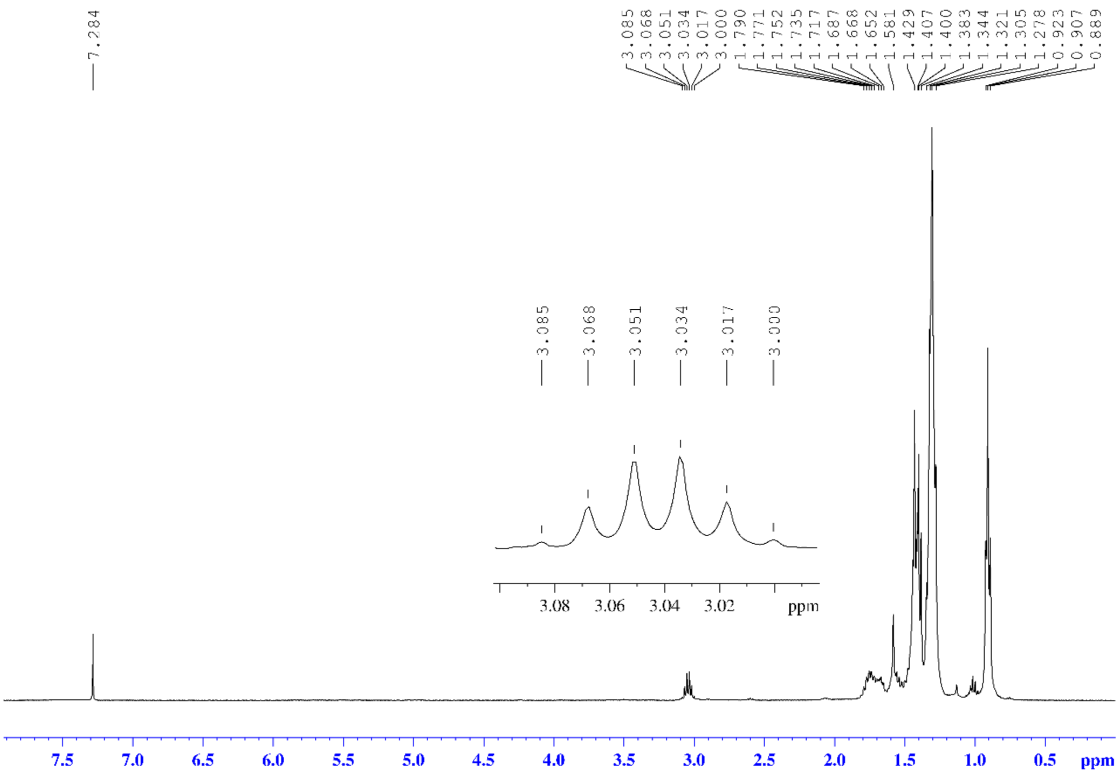

Figure S12. ^{13}C NMR of nonane-2-thiol (**2c**)

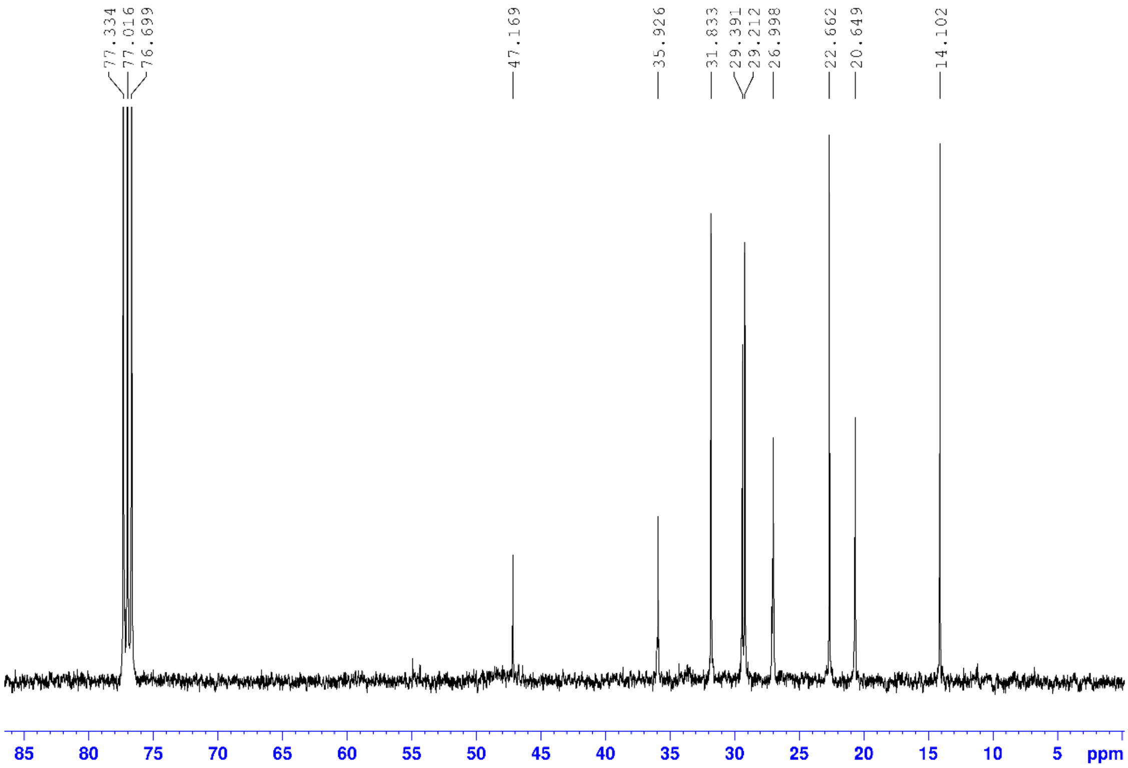

Figure S13. ^{13}C NMR (DEPT) of nonane-2-thiol (**2c**)

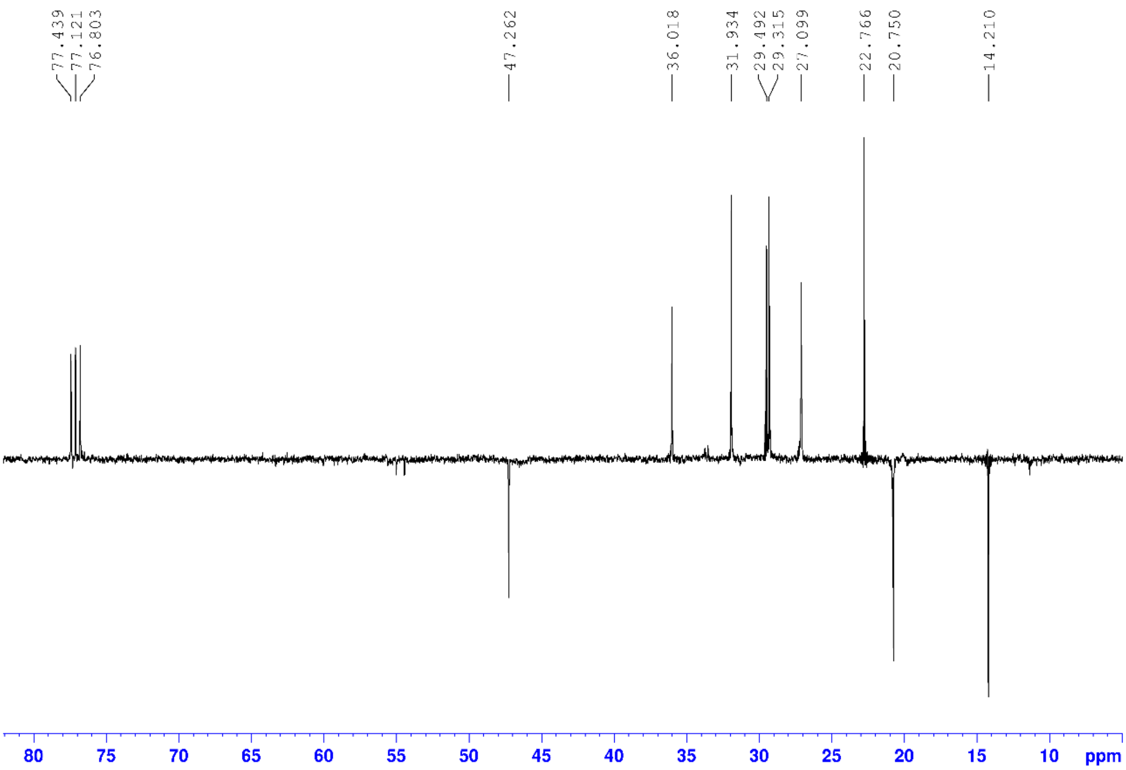

Figure S14. ^{1}H NMR of decane-2-thiol (**2d**)

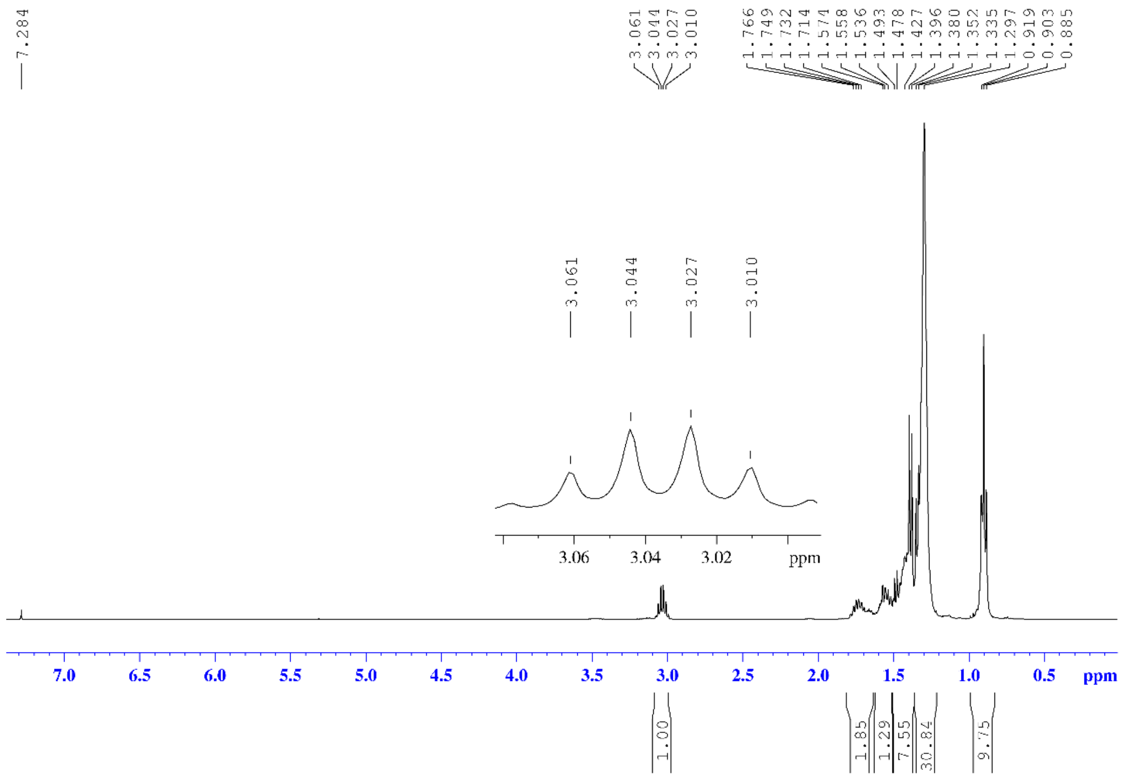

Figure S15. ^{13}C NMR of decane-2-thiol (**2d**)

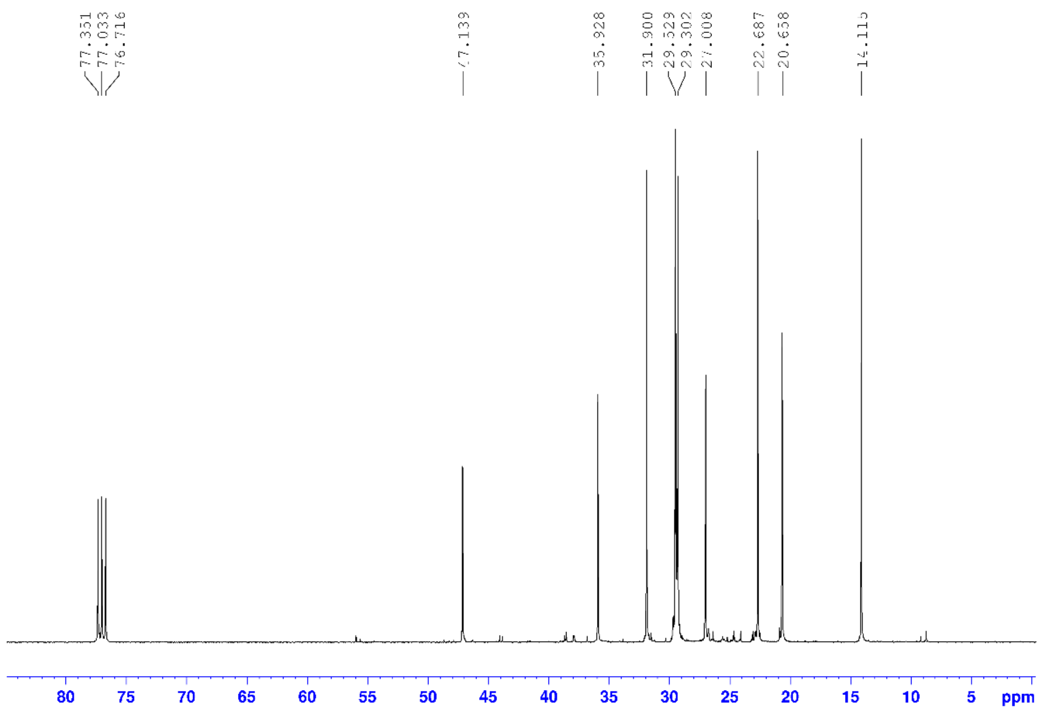

Figure S16. ^{13}C NMR (DEPT) of decane-2-thiol (**2d**)