

Metal-free thioesterification of α,β -unsaturated aldehydes with thiols

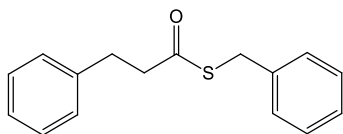
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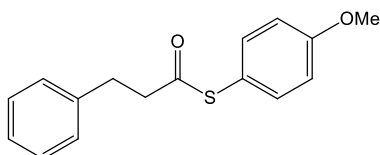
1. Analytical data of isolated products

3a-a: S-Benzyl 3-phenylpropanethioate¹



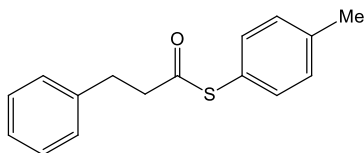
Yellow liquid, isolated yield: 93%; ¹H NMR (400 MHz, CDCl₃, ppm): 2.87 – 2.91 (m, 2H, CH₂), 2.98 – 3.03 (m, 2H, CH₂), 4.14 (m, 2H, SCH₂), 7.15 – 7.26 (m, 4H, Ph), 7.27 – 7.34 (m, 6H, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 31.38 (CH₂), 33.15 (SCH₂), 45.20 (CH₂), 126.32, 127.21, 128.28, 128.50, 128.58, 128.77, 137.52, 139.91, 197.82 (CO); MS m/z (rel. intensity): 51.10 (8), 64.80 (10), 76.80 (8), 91.00 (42), 91.90 (10), 104.00 (30), 105.00 (100), 105.90 (8), 132.80 (22), 255.70 (17, M⁺).

3a-b: S-(4-methoxyphenyl) 3-phenylpropanethioate¹



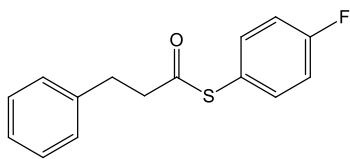
White solid, isolated yield: 90%; ¹H NMR (400 MHz, CDCl₃, ppm): 2.92 – 2.97 (m, 2H, CH₂), 2.99 – 3.05 (m, 2H, CH₂), 3.83 (s, 3H, OCH₃), 6.92 – 6.96 (m, 2H, Ph), 7.20 – 7.25 (m, 3H, Ph), 7.28 – 7.33 (m, 4H, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 31.39 (CH₂), 44.85 (CH₂), 55.34 (OCH₃), 114.86, 118.37, 126.36, 128.37, 128.53, 136.07, 140.00, 160.64, 197.69 (CO); MS m/z (rel. intensity): 91.00 (8), 103.00 (8), 105.00 (33), 105.90 (8), 139.20 (10), 140.10 (100), 14.00 (8), 271.80 (6), 727.70 (3, M⁺).

3a-c: S-(4-methylphenyl) 3-phenylpropanethioate³



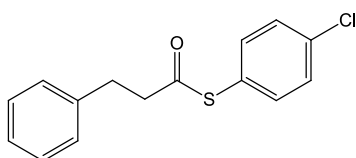
Colourless oil, isolated yield: 85%; ¹H NMR (400 MHz, CDCl₃, ppm): 2.39 (s, 3H, CH₃), 2.94 – 2.99 (m, 2H, CH₂), 3.01 – 3.06 (m, 2H, CH₂), 7.20 – 7.26 (m, 5H, Ph), 7.27 – 7.34 (m, 4H, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 21.30 (CH₃), 31.36 (CH₂), 44.99 (CH₂), 124.07, 126.33, 128.35, 128.50, 129.99, 134.40, 139.64, 139.94, 197.13 (CO); MS m/z (rel. intensity): 103.00 (8), 105.20 (100), 105.90 (13), 124.00 (21), 131.20 (8), 132.90 (40), 237.30 (8), 255.50 (10), 256.80 (12, M⁺).

3a-d: S-(4-fluorophenyl) 3-phenylpropanethioate



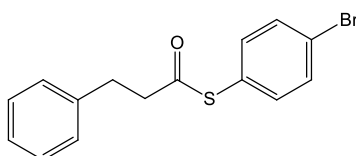
White solid, isolated yield: 87%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.95 – 3.01 (m, 4H, $(\text{CH}_2)_2$), 7.07 – 7.15 (m, 2H, Ph), 7.17 – 7.26 (m, 3H, Ph), 7.29 – 7.38 (m, 4H, Ph); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 31.32 (CH_2), 45.00 (CH_2), 116.42 (d, $J = 22.2$ Hz), 122.92 (d, $J = 3.8$ Hz), 126.43, 128.45 (d, $J = 22.0$ Hz), 136.51 (d, $J = 8.7$ Hz), 139.78, 163.44 (d, $J = 250.1$ Hz), 196.56 (CO); ^{19}F NMR (282.6 MHz, CDCl_3 , ppm): -111.63; MS m/z (rel. intensity): 91.00 (9), 105.00 (100), 105.90 (8), 126.80 (8), 132.80 (44), 260.70 (2, M^+).

3a-e: S-(4-chlorophenyl) 3-phenylpropanethioate²



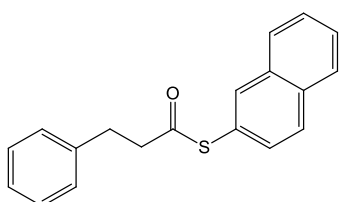
Yellow solid, isolated yield: 95%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.95 – 3.05 (m, 4H, $(\text{CH}_2)_2$), 7.20 – 7.26 (m, 3H, Ph), 7.29 – 7.34 (m, 4H, Ph), 7.36 – 7.41 (m, 2H, Ph); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 31.29 (CH_2), 45.11 (CH_2), 126.05, 126.43, 128.32, 128.55, 129.39, 135.03, 135.77, 139.70, 196.03 (CO); MS m/z (rel. intensity): 102.40 (8), 103.30 (13), 105.20 (100), 106.10 (19), 108.00 (15), 132.90 (93), 237.00 (21), 276.70 (2, M^+).

3a-f: S-(4-bromophenyl) 3-phenylpropanethioate⁴



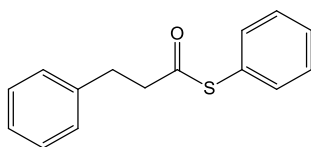
White solid, isolated yield: 87%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.94 – 2.99 (m, 2H, CH_2), 3.00 – 3.05 (m, 2H, CH_2), 7.16 – 7.25 (m, 5H, Ph), 7.28 – 7.33 (m, 2H, Ph), 7.50 – 7.56 (m, 2H, Ph); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 31.32 (CH_2), 45.17 (CH_2), 124.06, 126.47, 126.67, 128.35, 128.58, 132.38, 135.89, 139.71, 195.95 (CO); MS m/z (rel. intensity): 91.00 (19), 105.10 (100), 108.00 (19), 132.80 (37), 321.40 (2, M^+).

3a-g: S-naphth 3-phenylpropanethioate



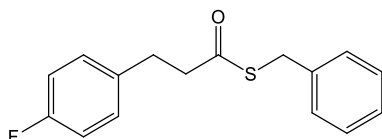
White solid, isolated yield: 89%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.99 – 3.08 (m, 4H, $(\text{CH}_2)_2$), 7.21 – 7.26 (m, 3H, Ph), 7.30 – 7.34 (m, 2H, Ph), 7.41 – 7.44 (m, 1H, Ph), 7.49 – 7.56 (m, 2H, Ph), 7.81 – 7.89 (m, 3H, Ph), 7.90 – 7.94 (m, 1H, Ph); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 31.39 (CH_2), 45.19 (CH_2), 124.94, 126.42, 126.54, 127.13, 127.77, 127.96, 128.39, 128.57, 128.78, 130.89, 133.31, 133.52, 134.33, 139.91, 196.90 (CO); MS m/z (rel. intensity): 91.20 (13), 103.00 (14), 105.20 (100), 106.10 (22), 115.00 (29), 131.20 (10), 133.10 (26), 159.20 (17), 160.10 (87), 161.00 (22), 291.80 (16, M^+).

3a-h: S-phenyl 3-phenylpropanethioate



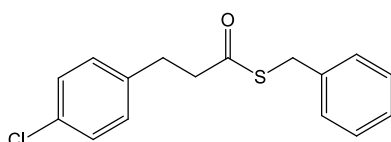
Yellow solid, isolated yield: 97%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.95 – 3.05 (m, 4H, $(\text{CH}_2)_2$), 7.18 – 7.25 (m, 3H, Ph), 7.28 – 7.34 (m, 2H, Ph), 7.35 – 7.46 (m, 5H, Ph); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 31.36 (CH_2), 45.11 (CH_2), 126.39, 127.61, 128.35, 128.54, 129.17, 129.38, 134.46, 139.89, 196.66 (CO); MS m/z (rel. intensity): 91.00 (9), 103.20 (12), 104.20 (100), 106.10 (16), 109.10 (14), 132.90 (70), 242.70 (24, M^+).

3b-a: S-Benzyl 3-(4-fluorophenyl)propanethioate



Yellow oil, isolated yield: 91%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.82 – 2.89 (m, 2H, CH_2), 2.93 – 3.00 (m, 2H, CH_2), 4.12 (s, 2H, SCH_2), 6.92 – 6.98 (m, 2H, Ph), 7.09 – 7.14 (m, 2H, Ph), 7.21 – 7.26 (m, 2H, Ph), 7.26 – 7.34 (m, 3H, Ph); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 30.58 (CH_2), 33.17 (SCH_2), 45.22 (CH_2), 115.27 (d, $J = 21.3$ Hz), 127.25, 128.59, 128.76, 129.74 (d, $J = 7.9$ Hz), 135.50 (d, $J = 3.4$ Hz), 137.47, 161.48 (d, $J = 244.1$ Hz), 197.67 (CO); ^{19}F NMR (282.6 MHz, CDCl_3 , ppm): -117.31; MS m/z (rel. intensity): 45.00 (11), 91.00 (23), 102.80 (13), 108.90 (51), 109.80 (10), 122.10 (56), 122.90 (100), 123.80 (11), 274.80 (16, M^+).

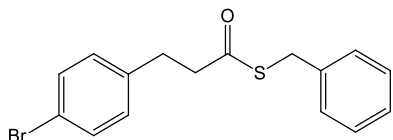
3c-a: S-Benzyl 3-(4-chlorophenyl)propanethioate



Yellow liquid, isolated yield: 90%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.81 – 2.90 (m, 2H, CH_2), 2.93 – 2.98 (m, 2H, CH_2), 4.12 (s, 2H, SCH_2), 7.07 – 7.11 (m, 2H, Ph), 7.21 – 7.25 (m, 4H, Ph), 7.27 – 7.32 (m, 2H, Ph); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 30.71 (CH_2), 33.20 (SCH_2), 44.92

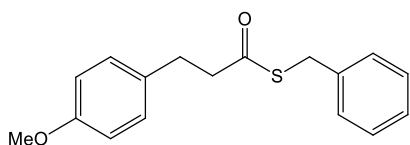
(SCH₂), 127.27, 128.60, 128.62, 128.76, 129.70, 132.13, 137.44, 138.32, 197.52 (CO); MS m/z (rel. intensity): 45.00 (10), 89.00 (12), 91.00 (25), 101.90 (14), 102.80 (31), 103.80 (10), 123.10 (14), 125.00 (37), 125.90 (10), 126.80 (13), 137.20 (12), 138.20 (46), 139.20 (100), 140.10 (34), 141.00 (38), 167.10 (21), 289.80 (45), 290.80 (19, M⁺).

3d-a: S-Benzyl 3-(4-bromophenyl)propanethioate



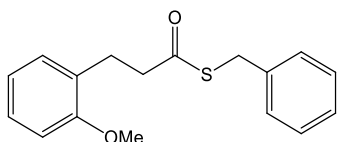
White solid, isolated yield: 90%; ¹H NMR (400 MHz, CDCl₃, ppm): 2.83 – 2.88 (m, 2H, CH₂), 2.92 – 2.98 (m, 2H, CH₂), 4.12 (s, 2H, SCH₂), 7.00 – 7.07 (m, 2H, Ph), 7.21 – 7.28 (m, 3H, Ph), 7.28 – 7.34 (m, 2H, Ph), 7.35 – 7.43 (m, 2H, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 30.73 (CH₂), 33.17 (SCH₂), 44.80 (CH₂), 120.13, 127.25, 128.58, 128.74, 130.08, 131.54, 137.40, 138.80, 197.47 (CO); MS m/z (rel. intensity): 45.00 (22), 91.20 (44), 103.00 (20), 104.00 (24), 169.00 (37), 170.90 (38), 182.20 (49), 183.00 (72), 184.10 (66), 185.00 (74), 255.00 (100), 335.80 (8, M⁺).

3e-a: S-Benzyl 3-(4-methoxyphenyl)propanethioate



Yellow oil, isolated yield: 85%; ¹H NMR (400 MHz, CDCl₃, ppm): 2.83 – 2.88 (m, 2H, CH₂), 2.92 – 2.97 (m, 2H, CH₂), 3.79 (s, 3H, OCH₃), 4.13 (s, 2H, SCH₂), 6.80 – 6.84 (m, 2H, Ph), 7.07 – 7.11 (m, 2H, Ph), 7.21 – 7.26 (m, 1H, Ph), 7.27 – 7.33 (m, 4H, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 30.57 (CH₂), 33.12 (SCH₂), 45.50 (CH₂), 55.21 (OCH₃), 113.88, 127.19, 128.56, 128.76, 129.24, 131.93, 137.55, 158.06, 197.91 (CO); MS m/z (rel. intensity): 119.30 (9), 120.20 (23), 121.20 (100), 122.20 (22), 133.20 (10), 134.20 (54), 135.00 (18), 163.20 (9), 284.80 (12), 285.70 (44), 286.70 (8, M⁺).

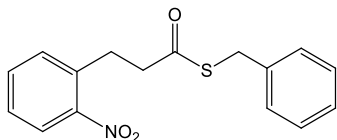
3f-a: S-Benzyl 3-(2-methoxyphenyl)propanethioate



Colourless liquid, isolated yield: 95%; ¹H NMR (400 MHz, CDCl₃, ppm): 2.86 – 2.92 (m, 2H, CH₂), 2.98 – 3.03 (m, 2H, CH₂), 3.82 (s, 3H, OCH₃), 4.14 (s, 2H, SCH₂), 6.84 – 6.90 (m, 2H, Ph), 7.11 – 7.15 (m, 1H, Ph), 7.19 – 7.25, 7.26 – 7.34 (m, 6H, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 26.62 (CH₂), 33.07 (CH₂), 45.31 (SCH₂), 55.12 (OCH₃), 110.17, 120.38, 127.13, 127.65, 128.54,

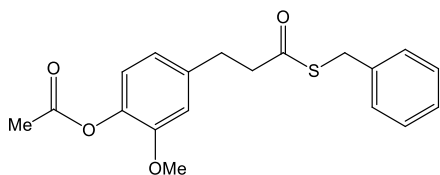
128.77, 129.95, 137.69, 157.39, 198.27 (CO); MS m/z (rel. intensity): 91.00 (31), 91.90 (10), 119.30 (11), 121.00 (100), 122.00 (13), 134.00 (23), 135.00 (32), 161.80 (75), 286.70 (7, M⁺).

3g-a: S-Benzyl 3-(2-nitrophenyl)propanethioate



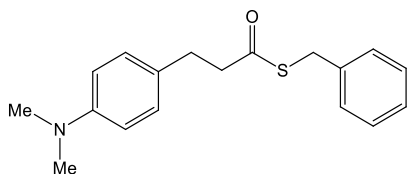
Colourless liquid, isolated yield: 88%; ¹H NMR (400 MHz, CDCl₃, ppm): 2.96 – 3.01 (m, 2H, CH₂), 3.24 – 3.29 (m, 2H, CH₂), 4.12 (m, 2H, SCH₂), 7.18 – 7.26 (m, 2H, Ph), 7.27 – 7.40 (m, 5H, Ph), 7.49 (td, 1H, J_{HH} = 7.5, 1.4 Hz, Ph), 7.96 (dd, 1H, J_{HH} = 8.2, 1.4 Hz, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 28.91 (CH₂), 33.23 (CH₂), 43.89 (SCH₂), 124.99, 127.27, 127.68, 128.59, 128.80, 132.31, 133.24, 135.13, 137.38, 197.32 (CO); MS m/z (rel. intensity): 45.00 (10), 65.00 (10), 77.00 (12), 91.00 (22), 119.90 (34), 128.80 (10), 132.90 (11), 134.00 (24), 147.10 (100), 177.70 (42), 178.70 (13), 301.20 (2, M⁺).

3h-a: S-Benzyl 3-(3-methoxy-4-acetoxyphenyl)propanethioate



Colourless oil, isolated yield: 93%; ¹H NMR (400 MHz, CDCl₃, ppm): 2.31 (s, 3H, CH₃), 2.86 – 2.91 (m, 2H, CH₂), 2.94 – 3.00 (m, 2H, CH₂), 3.79 (s, 3H, OCH₃), 4.14 (s, 2H, SCH₂), 6.73 – 6.79 (m, 2H, Ph), 6.93 (d, 1H, J_{H-H} = 8.0 MHz, Ph), 7.22 – 7.26 (m, 1H, Ph), 7.27 – 7.32 (m, 4H, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 20.65 (CH₃), 31.32 (CH₂), 33.20 (SCH₂), 45.10 (CH₂), 55.80 (OCH₃), 112.53, 120.36, 122.68, 127.26, 128.61, 128.77, 137.48, 138.14, 138.92, 150.91, 169.12, 197.70 (CO); MS m/z (rel. intensity): 137.10 (23), 150.20 (33), 151.20 (10), 221.20 (8), 302.00 (100), 302.80 (16), 344.00 (2, M⁺).

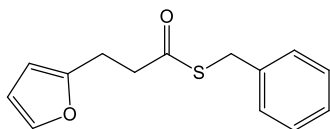
3i-a: S-Benzyl 3-(4-dimethylaminophenyl)propanethioate



Orange liquid, isolated yield: 89%; ¹H NMR (400 MHz, CDCl₃, ppm): 2.82 – 2.89 (m, 2H, CH₂), 2.92 (s, 6H, N(CH₃)₂), 2.94 – 2.99 (m, 2H, CH₂), 4.14 (s, 2H, SCH₂), 6.69 (d, 2H, J_{H-H} = 8.8 Hz, -C₆H₄-), 7.07 (d, 2H, J_{H-H} = 8.8 Hz, -C₆H₄-), 7.20 – 7.25 (m, 1H, Ph), 7.27 – 7.33 (m, 4H, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 30.51 (CH₂), 33.09 (SCH₂), 40.75 (NCH₃), 45.72 (CH₂), 112.89,

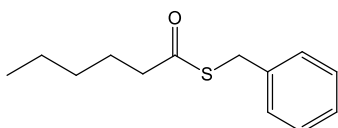
127.14, 127.86, 128.54, 128.76, 128.87, 137.61, 149.25, 198.12 (CO); MS m/z (rel. intensity): 133.20 (10), 134.20 (20), 298.20 (11), 299.10 (100, M⁺).

3j-a: S-Benzyl 3-(2-furanyl)propanethioate



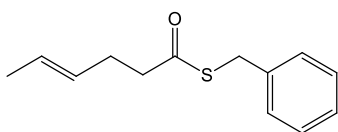
Colourless liquid, isolated yield: 87%; ¹H NMR (400 MHz, CDCl₃, ppm): 2.90 – 2.94 (m, 2H, CH₂), 3.00 – 3.05 (m, 2H, CH₂), 4.15 (s, 2H, SCH₂), 6.02 (dd, 1H, J_{H-H} = 3.2, 0.8 Hz, CH from furan), 6.27 (dd, 1H, J_{H-H} = 3.2, 1.9 Hz, CH from furan), 7.22 – 7.26, 7.27 – 7.34 (m, 6H, Ph and CH from furan); ¹³C NMR (100 MHz, CDCl₃, ppm): 23.71 (CH₂), 33.15 (SCH₂), 41.84 (CH₂), 105.57, 110.16, 127.23, 128.57, 128.77, 137.44, 141.28, 153.45, 197.37 (CO); MS m/z (rel. intensity): 53.00 (23), 65.00 (23), 80.90 (95), 81.80 (20), 91.20 (96), 94.00 (100), 94.90 (57), 112.90 (15), 170.90 (21), 184.90 (19), 243.30 (22), 245.70 (51), 246.70 (45, M⁺).

3k-a: S-Benzyl hexanethioate⁵



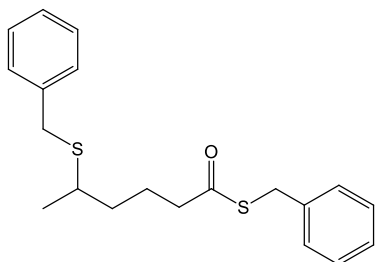
Yellow liquid, isolated yield: 92%; ¹H NMR (400 MHz, CDCl₃, ppm): 0.87 – 0.92 (m, 3H, CH₃), 1.28 – 1.36 (m, 4H, CH₂), 1.63 – 1.72 (m, 2H, CH₂), 2.54 – 2.59 (m, 2H, CH₂), 4.13 (s, 2H, SCH₂), 7.22 – 7.25, 7.26 – 7.34 (m, 5H, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 13.83 (CH₃), 22.26 (CH₂), 25.26 (CH₂), 31.05 (CH₂), 33.08 (SCH₂), 43.76 (CH₂), 127.14, 128.55, 128.75, 137.71, 198.87 (CO); MS m/z (rel. intensity): 45.00 (26), 65.00 (21), 70.90 (27), 91.00 (100), 91.90 (30), 97.20 (23), 98.20 (38), 99.10 (84), 123.80 (43), 130.80 (42), 221.90 (29), 222.70 (39, M⁺).

3l-a: S-Benzyl 4-hexenethioate



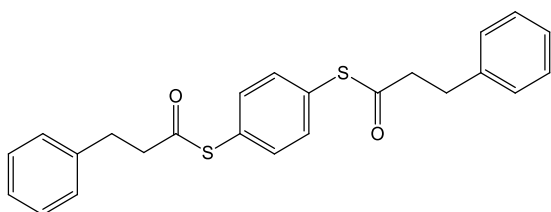
Colourless liquid, isolated yield: 87%; ¹H NMR (400 MHz, CDCl₃, ppm): 1.59 – 1.65 (m, 3H, CH₃), 2.32 – 2.43 (m, 2H, CH₂), 2.59 – 2.65 (m, 2H, CH₂), 4.12 (s, 2H, SCH₂), 5.31 – 5.54 (m, 2H, =CH), 7.20 – 7.25, 7.27 – 7.32 (m, 5H, Ph); ¹³C NMR (100 MHz, CDCl₃, ppm): 17.84 (CH₃), 28.44 (CH₂), 33.11 (SCH₂), 43.63 (CH₂), 125.73, 126.60, 127.18, 128.55, 128.77, 137.69, 198.23 (CO); MS m/z (rel. intensity): 45.00 (11), 55.00 (11), 65.00 (12), 67.20 (11), 69.00 (39), 91.00 (37), 128.80 (100), 220.80 (11, M⁺).

3l-a'': S-benzyl 5-(benzylthio)hexanethioate



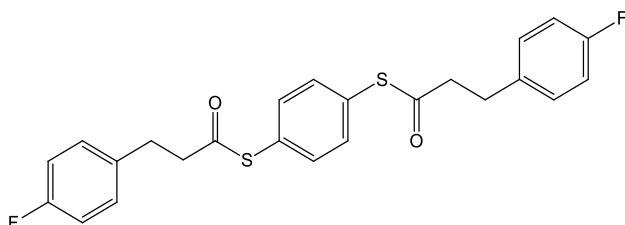
Colourless liquid, isolated yield: 85%; ^1H NMR (400 MHz, CDCl_3 , ppm): 1.25 (d, 3H, $J_{\text{HH}} = 6.8$ Hz, CH_3), 1.44 – 1.60 (m, 2H, CH_2), 1.71 – 1.79 (m, 2H, CH_2), 2.49 (t, 2H, $J_{\text{H-H}} = 7.4$ Hz, $\text{CH}_2\text{C}(\text{O})\text{S}$), 2.61 (h, 1H, $J_{\text{HH}} = 6.7$ Hz, CH), 3.71 (s, 2H, SCH_2), 4.11 (s, 2H, SCH_2), 7.20 – 7.26 (m, 2H, Ph), 7.28 – 7.32 (m, 8H, Ph); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 21.06 (CH_3), 22.81, 33.15, 34.88, 35.66, 38.82, 43.35 (CH_2), 126.86, 127.21, 128.44, 128.59, 128.77, 137.64, 138.55, 198.44 (CO); MS m/z (rel. intensity): 45.00 (12), 65.00 (12), 91.10 (100), 92.20 (20), 101.00 (23), 129.00 (74), 221.00 (52), 253.20 (18, M^+ - PhCH_2^-).

5a: S,S'-1,4-phenylene bis(3-phenylpropanethioate)



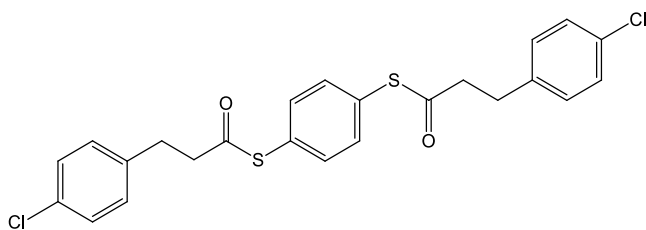
Pale yellow solid, isolated yield: 93%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.94 – 3.06 (m, 8H, CH_2), 7.20 – 7.23 (m, 5H, $-\text{C}_6\text{H}_5$), 7.28 – 7.33 (m, 5H, $-\text{C}_6\text{H}_5$), 7.42 (s, 4H, $-\text{C}_6\text{H}_4-$); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 31.33 (CH_2), 45.62 (CH_2), 126.45, 128.35, 128.58, 129.29, 129.58, 134.75, 139.73, 195.78 (CO).

5b: S,S'-1,4-phenylene bis(3-(4-fluorophenyl)propanethioate)



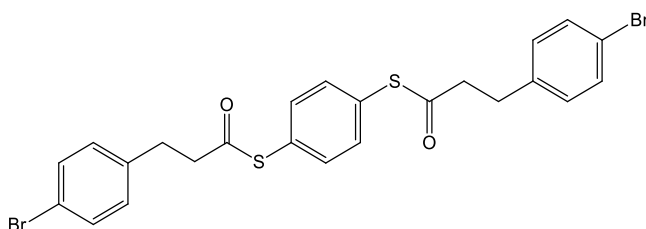
White solid, isolated yield: 87%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.91 – 3.02 (m, 8H, CH_2), 6.96 – 7.01 (m, 4H, $-\text{C}_6\text{H}_4-\text{F}$), 7.14 – 7.18 (m, 4H, $-\text{C}_6\text{H}_4-\text{F}$), 7.40 (s, 4H, $-\text{C}_6\text{H}_4-$); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 30.50 (CH_2), 45.27 (CH_2), 115.36 (d, $J = 21.2$ Hz), 127.30, 129.24, 129.82 (d, $J = 7.9$ Hz), 134.76, 134.92, 135.34 (d, $J = 3.2$ Hz), 161.56 (d, $J = 244.4$ Hz), 195.62 (CO); ^{19}F NMR (282.6 MHz, CDCl_3 , ppm): -117.12.

5c: *S,S'*-1,4-phenylene bis(3-(4-chlorophenyl)propanethioate)



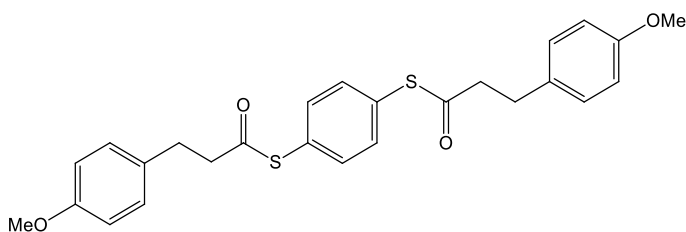
White solid, isolated yield: 90%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.93 – 3.01 (m, 8H, CH_2), 7.11 – 7.15 (m, 4H, $-\text{C}_6\text{H}_4-\text{Cl}$), 7.25 – 7.26, 7.28 – 7.29 (m, 4H, $-\text{C}_6\text{H}_4-\text{Cl}$), 7.41 (s, 4H, $-\text{C}_6\text{H}_4-$); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 30.60 (CH_2), 44.97 (CH_2), 128.68, 129.21, 129.75, 132.26, 134.76, 138.15, 195.50 (CO).

5d: *S,S'*-1,4-phenylene bis(3-(4-bromophenyl)propanethioate)



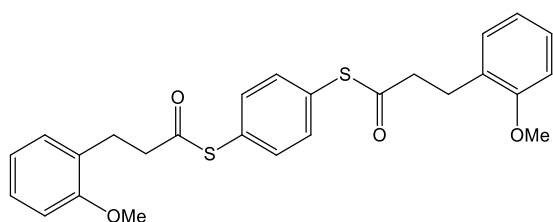
White solid, isolated yield: 89%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.95 – 3.00 (m, 8H, CH_2), 7.08 (d, 4H, $J_{\text{H-H}} = 8.6$ Hz, $-\text{C}_6\text{H}_4-\text{Br}$), 7.40 (s, 4H, $-\text{C}_6\text{H}_4-$), 7.42 (d, 4H, $J_{\text{H-H}} = 8.6$ Hz, $-\text{C}_6\text{H}_4-\text{Br}$); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 30.66 (CH_2), 44.89 (CH_2), 120.31, 129.23, 130.14, 131.66, 134.76, 138.69, 195.44 (CO).

5e: *S,S'*-1,4-phenylene bis(3-(4-methoxyphenyl)propanethioate)



White solid, isolated yield: 92%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.95 (s, 8H, CH_2), 3.79 (s, 6H, OCH_3), 6.84 (d, 4H, $J_{\text{H-H}} = 8.4$ Hz, $-\text{C}_6\text{H}_4-\text{OMe}$), 7.12 (d, 4H, $J_{\text{H-H}} = 8.3$ Hz, $-\text{C}_6\text{H}_4-\text{OMe}$), 7.41 (s, 4H, $-\text{C}_6\text{H}_4-$); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 30.53 (CH_2), 45.57 (CH_2), 55.26 (OCH_3), 113.96, 129.33, 131.78, 134.74, 128.18, 195.86 (CO).

5f: *S,S'*-1,4-phenylene bis(3-(2-methoxyphenyl)propanethioate)



Pale yellow solid, isolated yield: 88%; ^1H NMR (400 MHz, CDCl_3 , ppm): 2.94 – 3.02 (m, 8H, CH_2), 3.85 (s, 6H, OCH_3), 6.85 – 6.91 (m, 4H, $-\text{C}_6\text{H}_4\text{-OMe}$), 7.13 – 7.16 (m, 2H, $-\text{C}_6\text{H}_4\text{-OMe}$), 7.20 – 7.24 (m, 2H, $-\text{C}_6\text{H}_4\text{-OMe}$), 7.41 (s, 4H, $-\text{C}_6\text{H}_4-$); ^{13}C NMR (100 MHz, CDCl_3 , ppm): 26.69 (CH_2), 43.56 (CH_2), 55.21 (OCH_3), 110.25, 120.46, 127.81, 128.06, 129.45, 130.12, 134.70, 157.46, 196.20 (CO).

2. Deuterium-labeling experiment

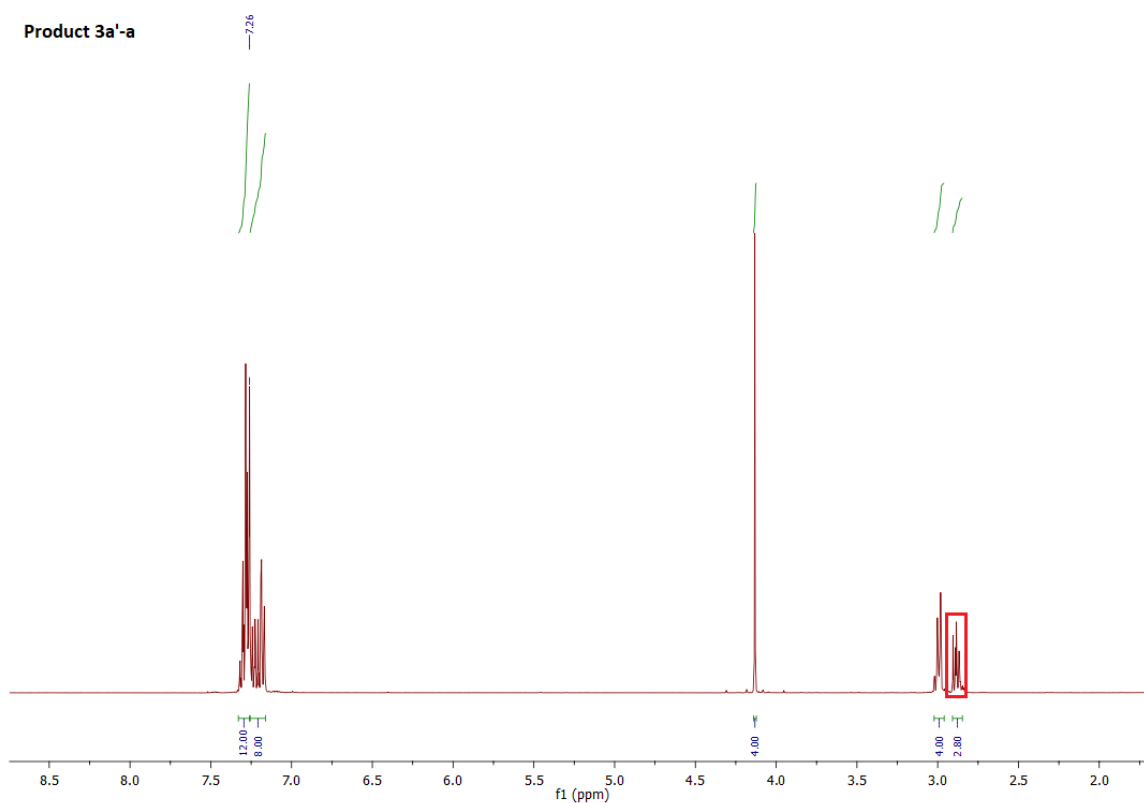
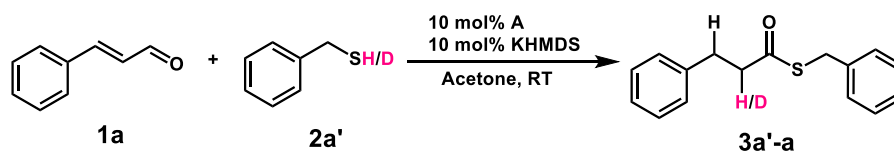


Figure S1. ^1H NMR (400 MHz, CDCl_3) recorded after reaction between 1a and 2a'

^1H , ^{13}C HMBC spectra of 3a-a product – H NMR signals assignment

To differentiate signals coming from two CH_2 groups (indicated in blue and green) we recorded a HMBC spectrum. The multiplet between 2.98 – 3.03 ppm correlates with aryl carbons (indicated with red) giving the signal {3.01, 128.30}. There is no correlation between 2.87 – 2.91 ppm multiplet and aryl carbons. Therefore, we can assign the signals at 2.98 – 3.03 ppm to the methylene group connected directly to the phenyl ring and the signals 2.87 – 2.91 ppm to the methylene group connected to the carbonyl group.

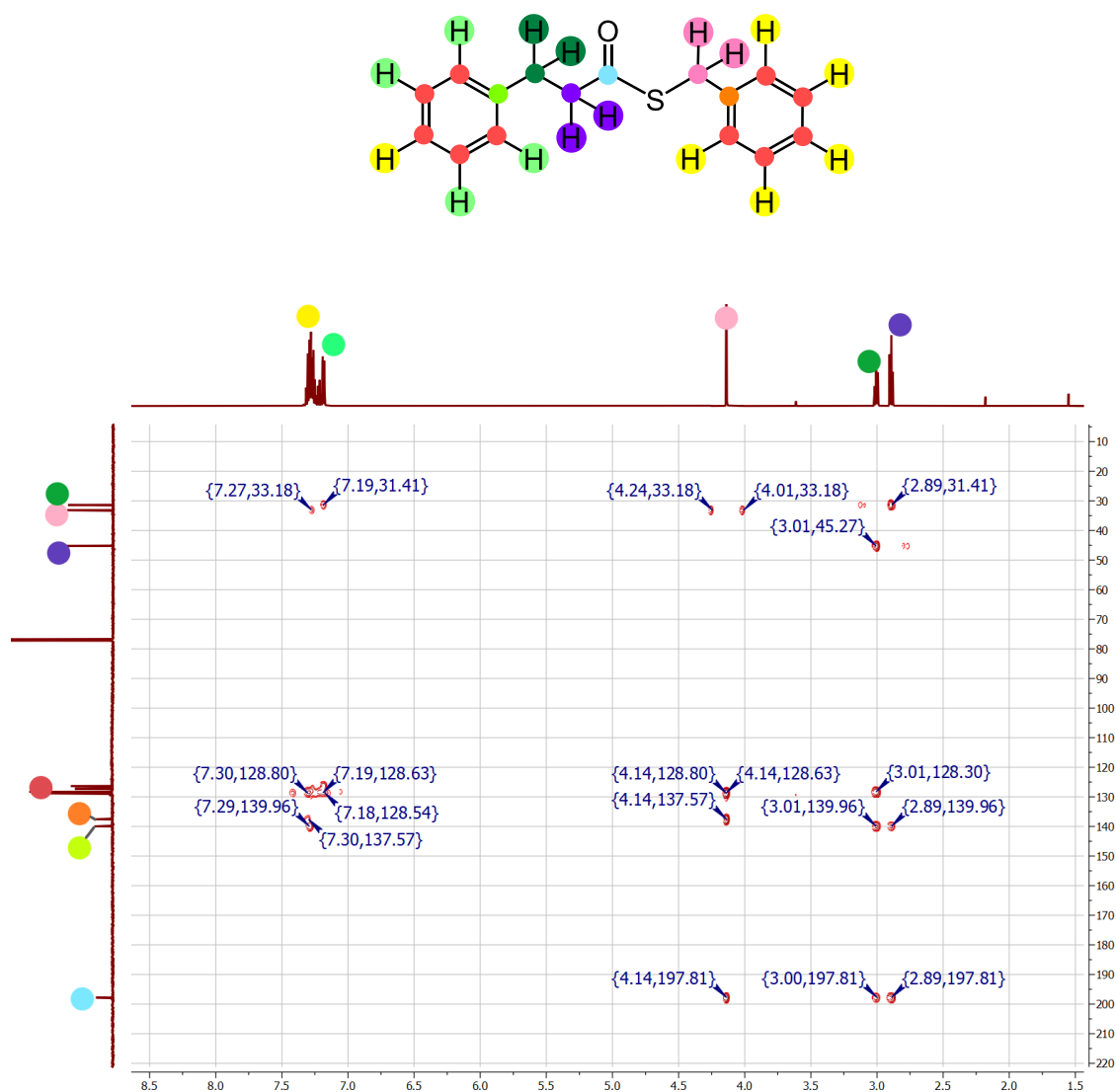


Figure S2. ^1H ^{13}C HMBC (600 MHz, CDCl_3) of S-Benzyl 3-phenylpropanethioate (3a-a)

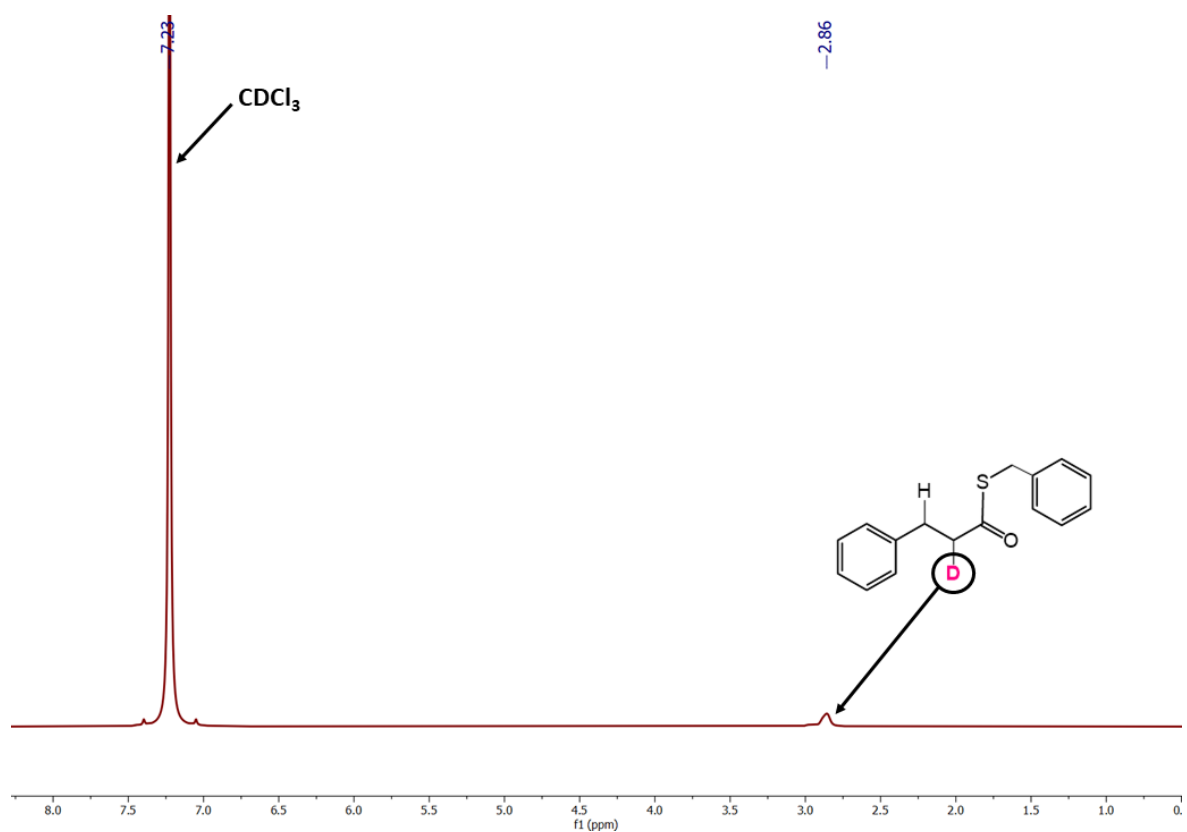


Figure S3. ^2H NMR (600 MHz, CDCl_3) recorded after reaction between 1a and 2a'

3. NMR spectra of isolated products

Product 3a-a

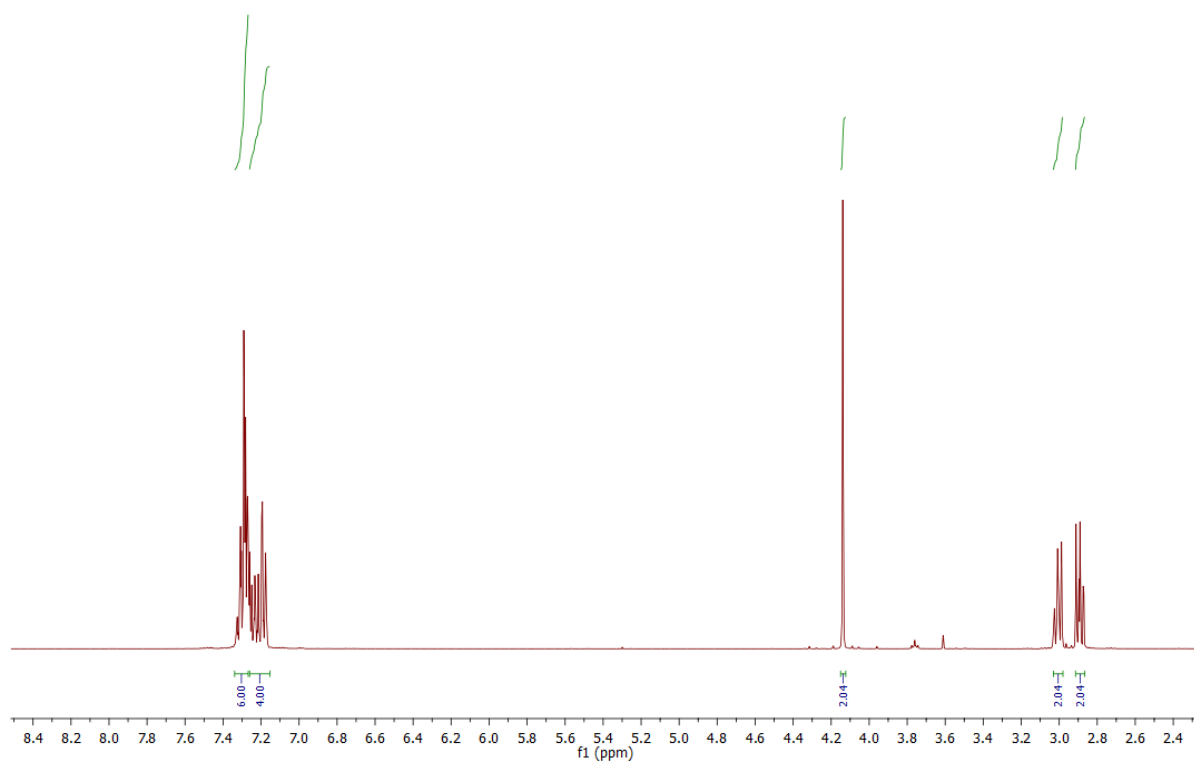


Figure S4. ^1H NMR (400 MHz, CDCl_3) of *S*-Benzyl 3-phenylpropanethioate (3a-a)

Product 3a-a

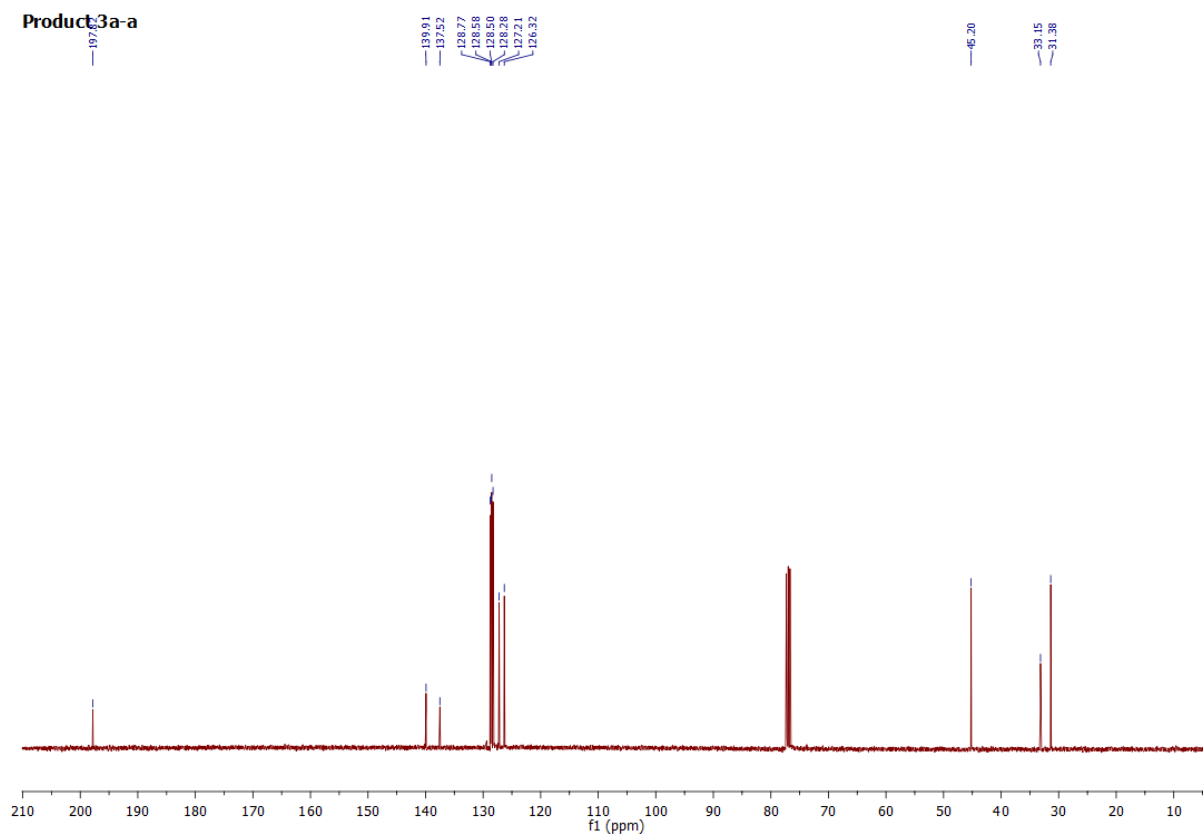


Figure S5. ¹³C NMR (100 MHz, CDCl₃) of *S*-Benzyl 3-phenylpropanethioate (3a-a)

Product 3a-b

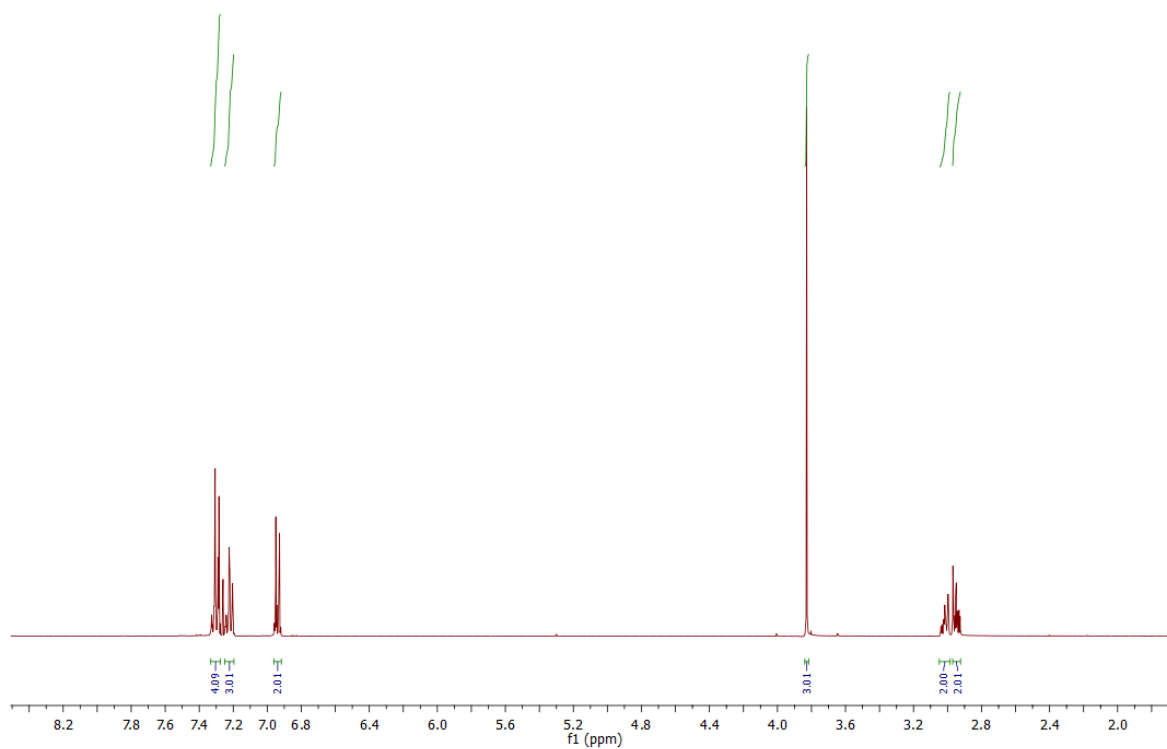


Figure S6. ¹H NMR (400 MHz, CDCl₃) of *S*-(4-methoxyphenyl) 3-phenylpropanethioate (3a-b)

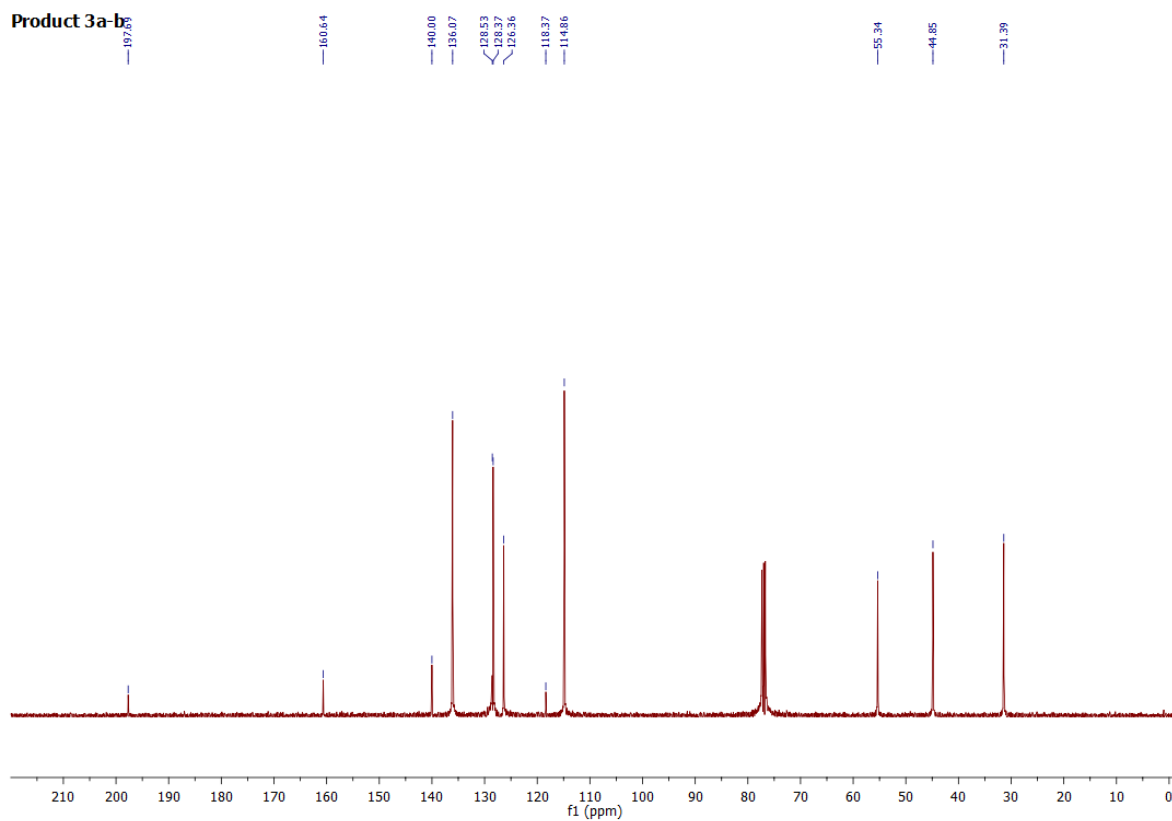


Figure S7. ^{13}C NMR (100 MHz, CDCl_3) of *S*-(4-methoxyphenyl) 3-phenylpropanethioate (3a-b)

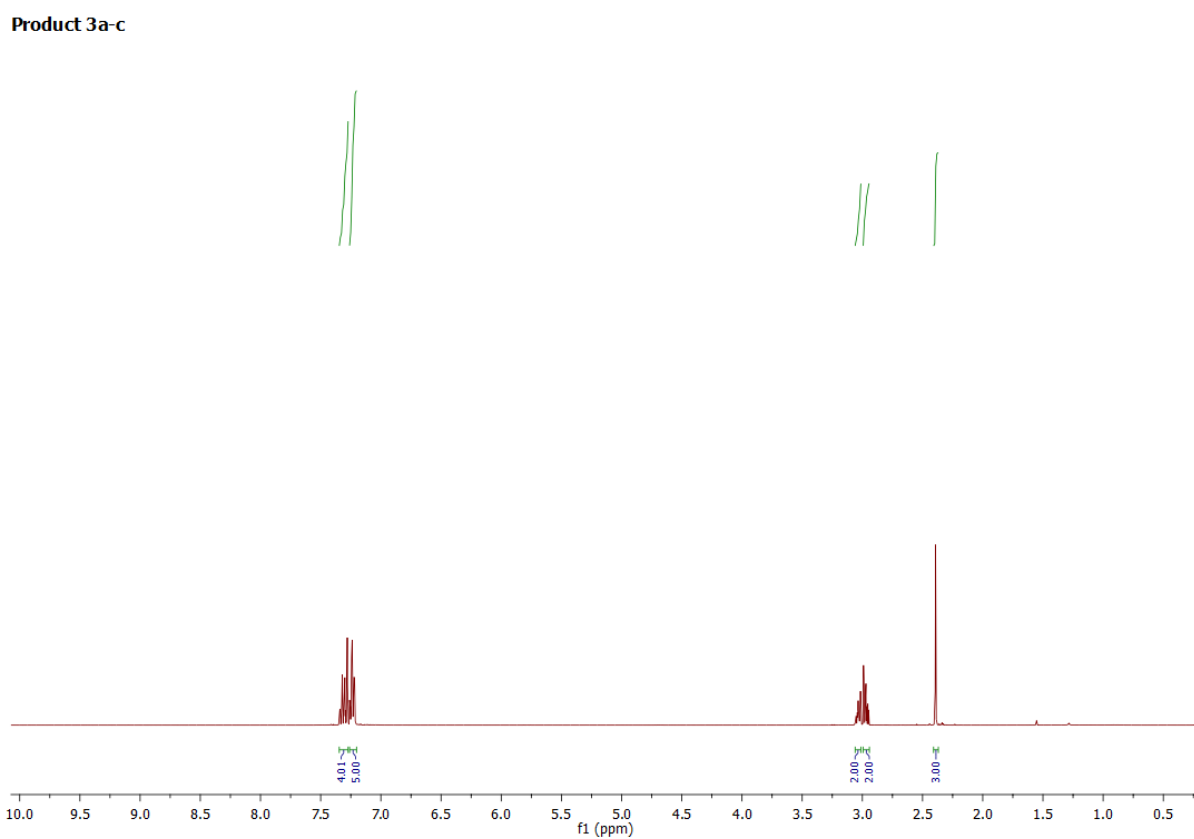


Figure S8. ^1H NMR (400 MHz, CDCl_3) of *S*-(4-methylphenyl) 3-phenylpropanethioate (3a-c)

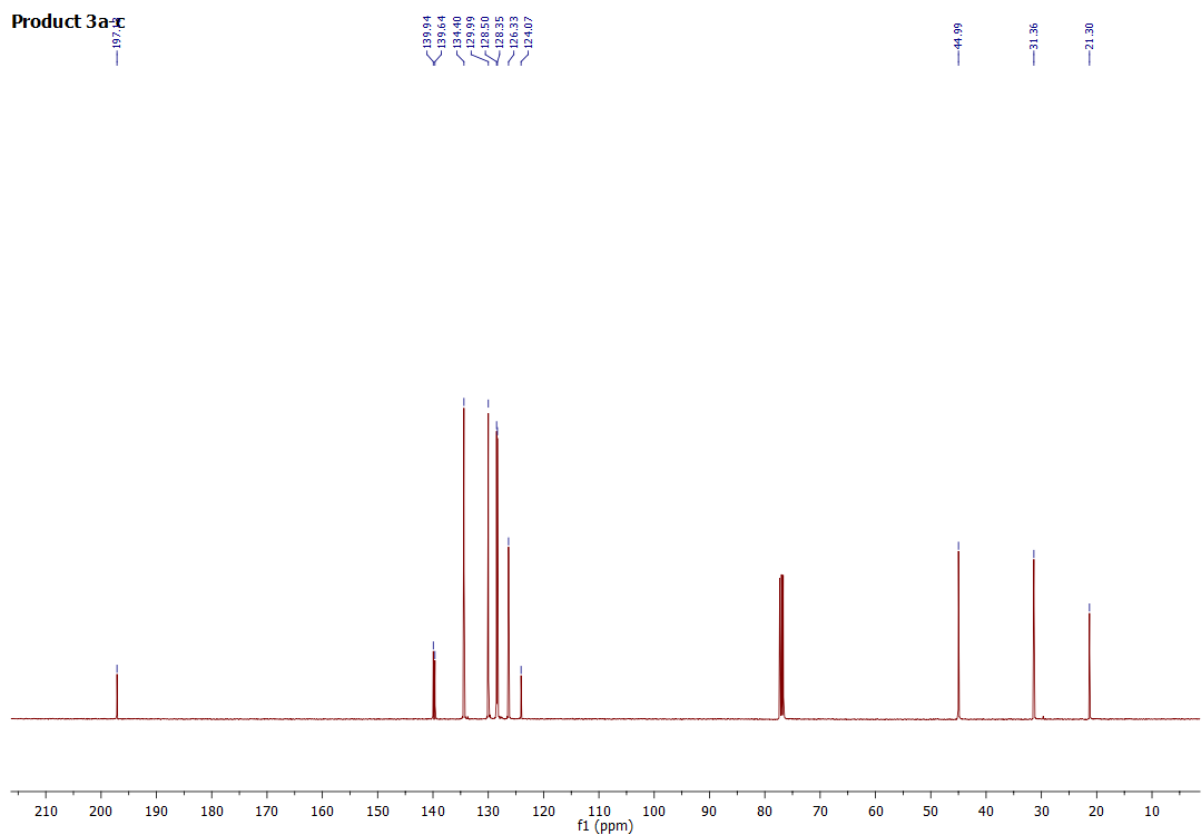


Figure S9. ^{13}C NMR (100 MHz, CDCl_3) of *S*-(4-methylphenyl) 3-phenylpropanethioate (3a-c)

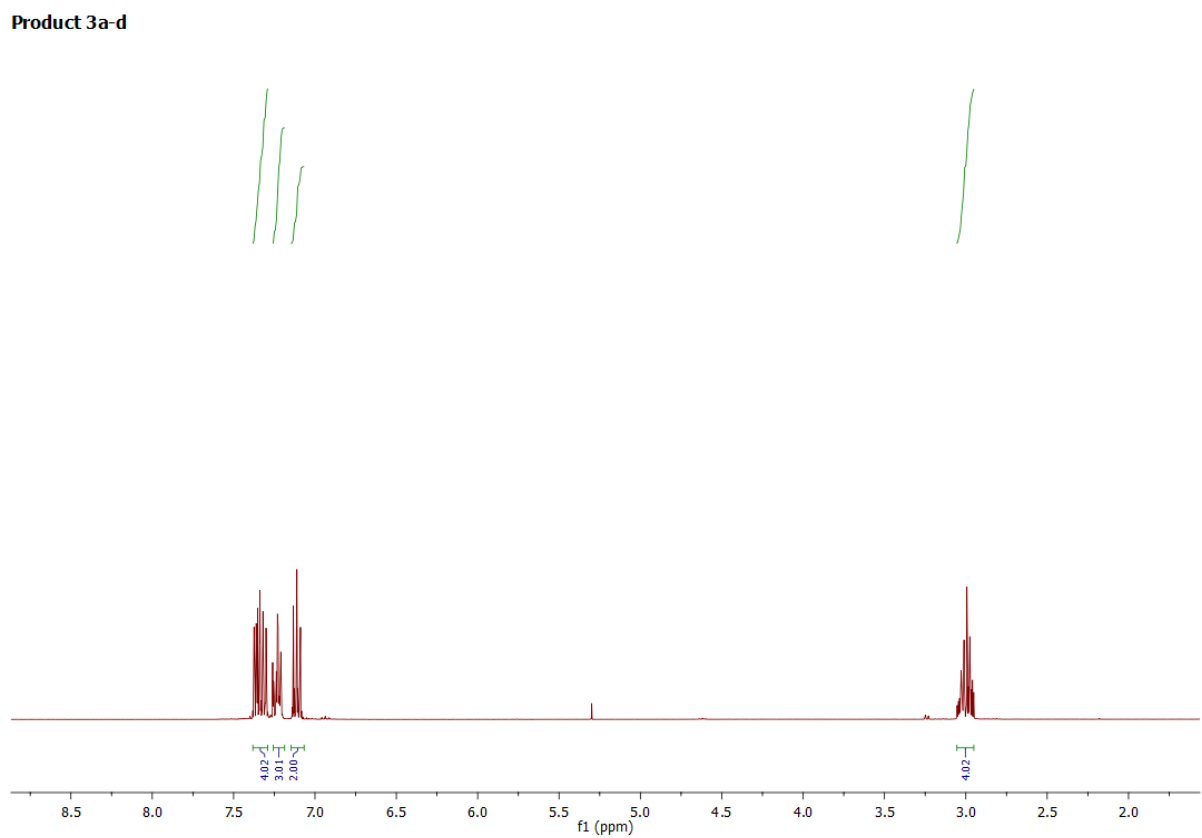


Figure S10. ^1H NMR (400 MHz, CDCl_3) of *S*-(4-fluorophenyl) 3-phenylpropanethioate (3a-d)

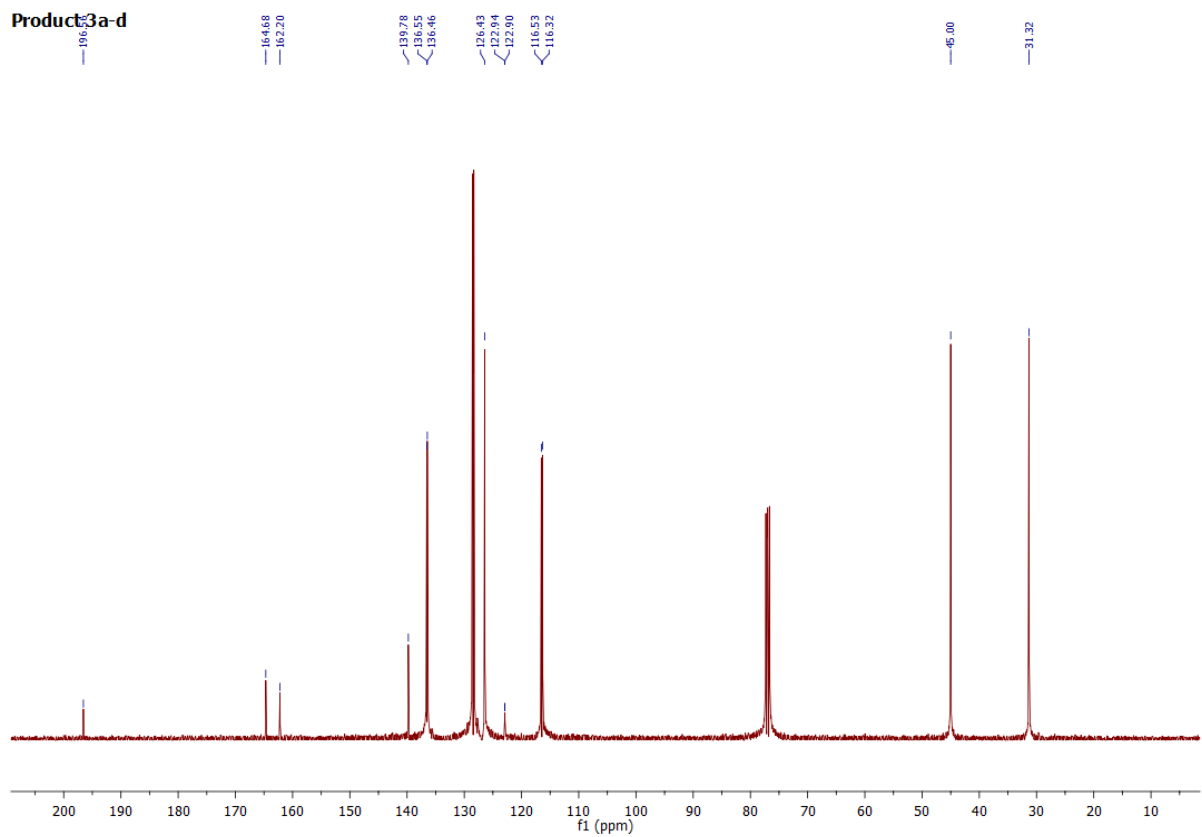


Figure S11. ^{13}C NMR (100 MHz, CDCl_3) of *S*-(4-fluorophenyl) 3-phenylpropanethioate (3a-d)
Product 3a-d

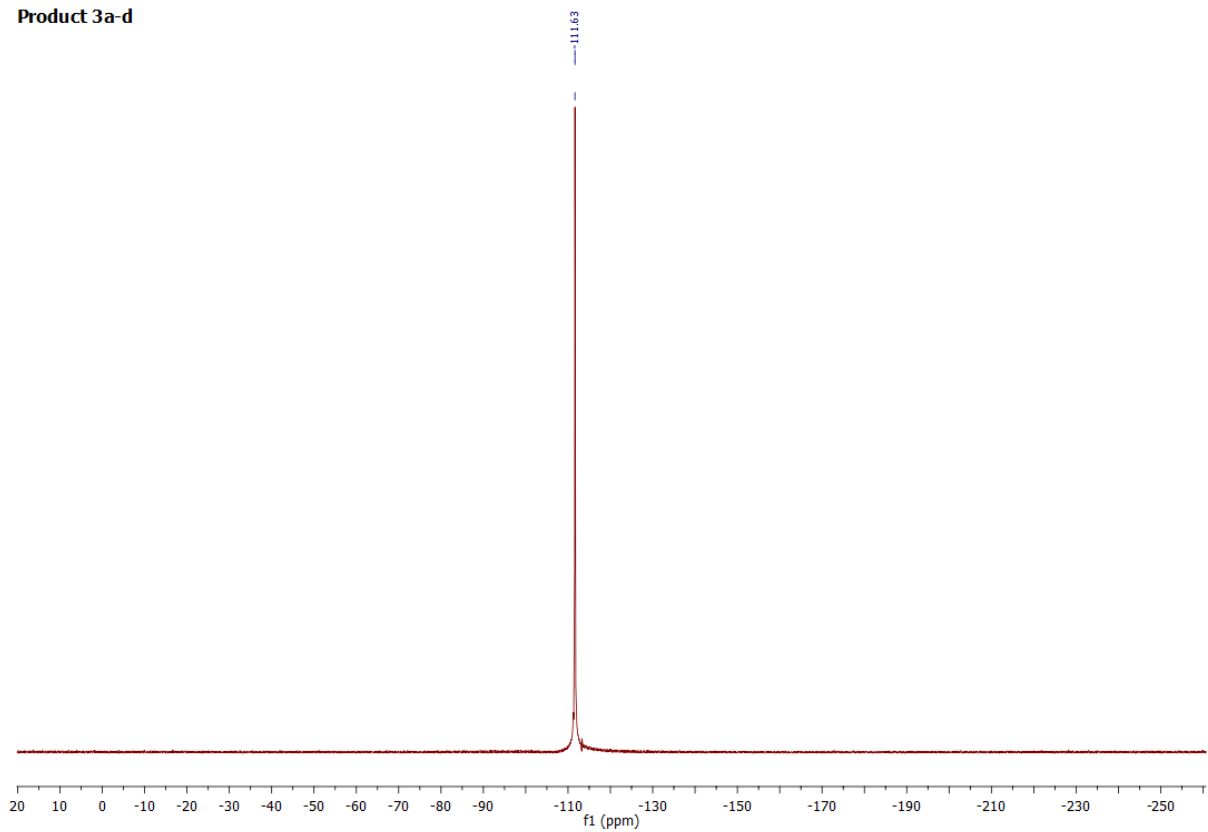


Figure S12. ^{19}F NMR (282.6 MHz, CDCl_3) of *S*-(4-fluorophenyl) 3-phenylpropanethioate (3a-d)

Product 3a-e

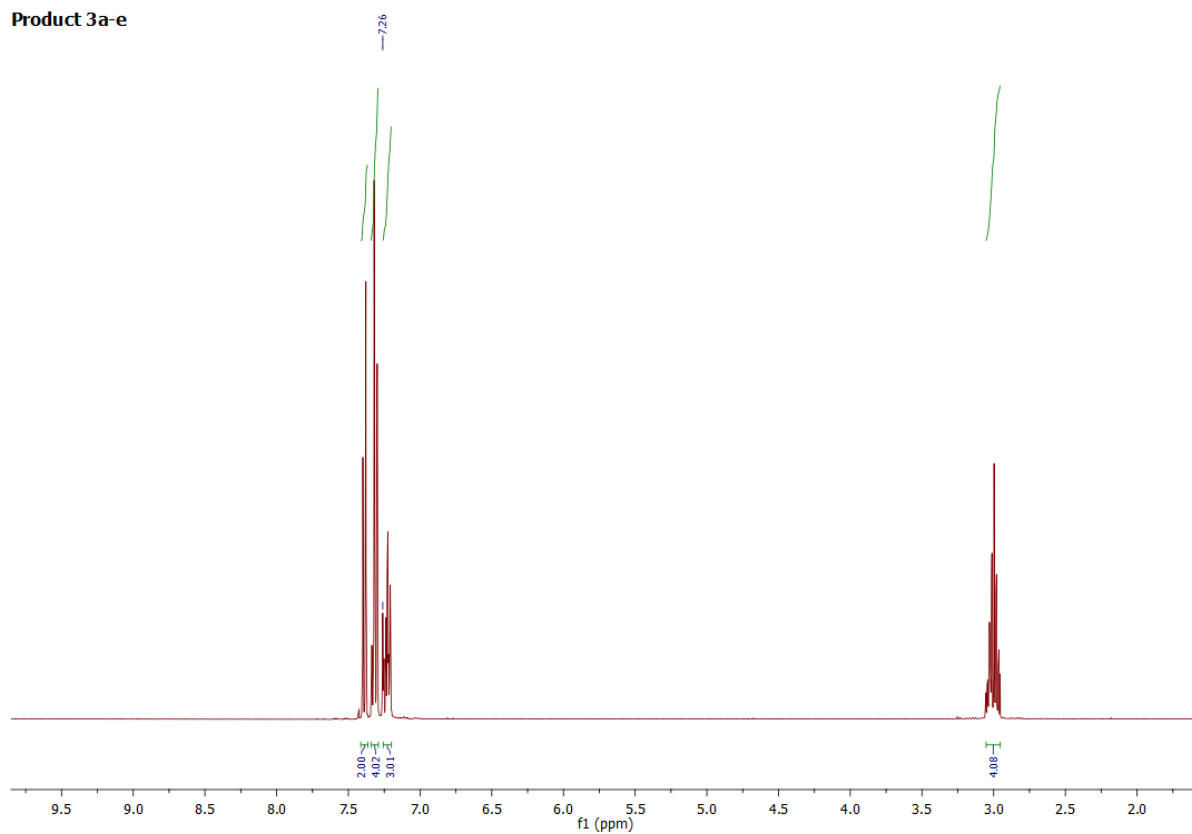


Figure S13. ¹H NMR (400 MHz, CDCl₃) of *S*-(4-chlorophenyl) 3-phenylpropanethioate (3a-e)

Product 3a-e

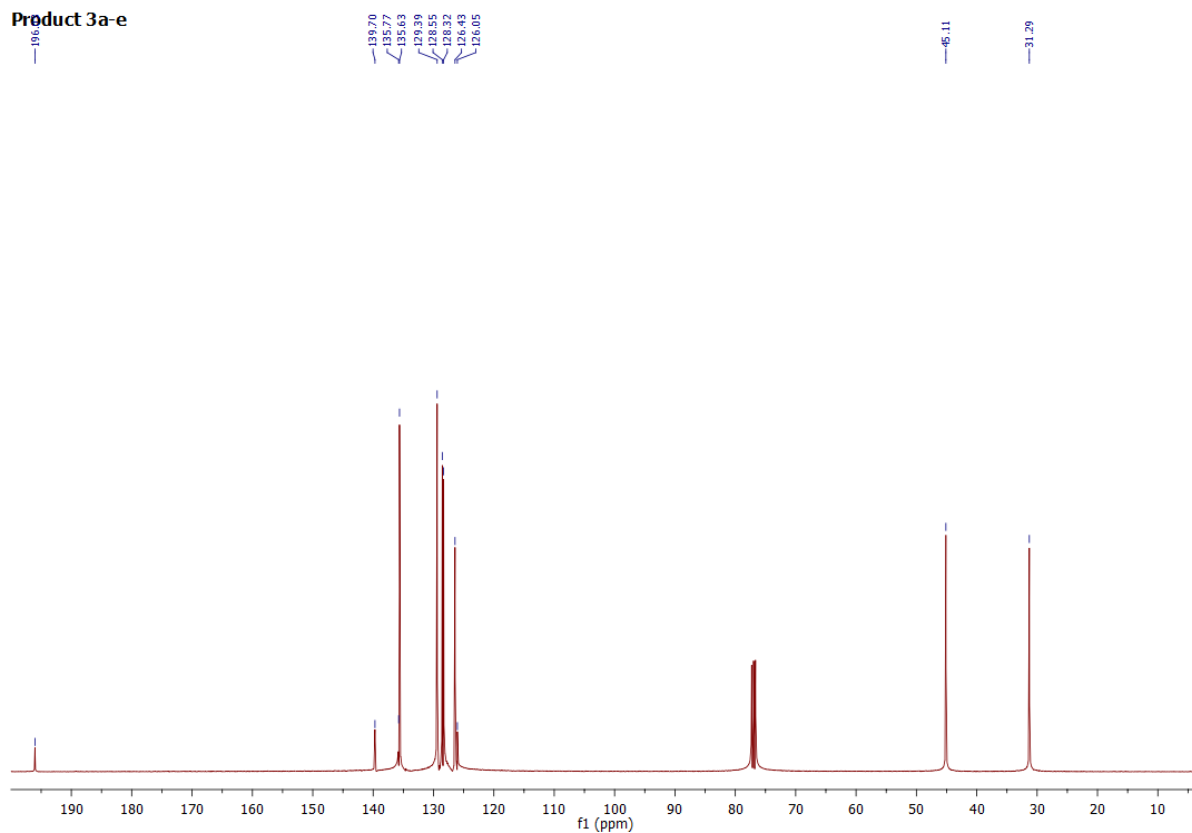


Figure S14. ¹³C NMR (100 MHz, CDCl₃) of *S*-(4-chlorophenyl) 3-phenylpropanethioate (3a-e)

Product 3a-f

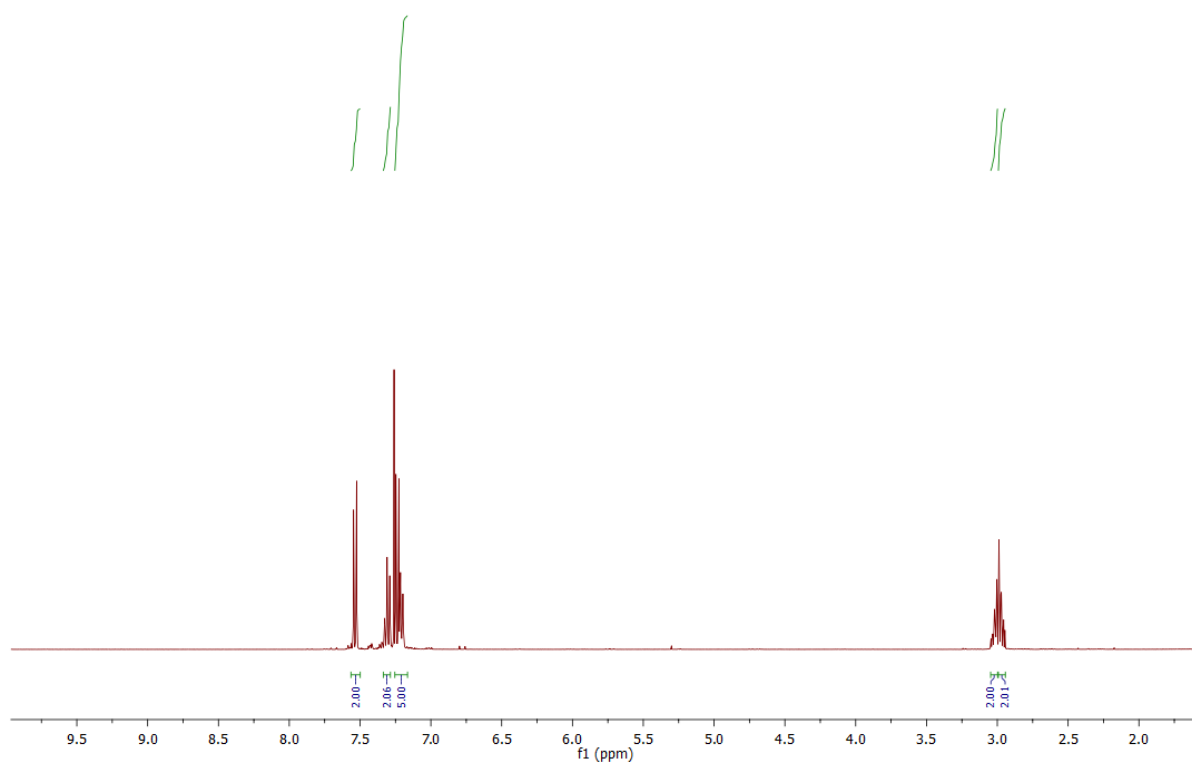


Figure S15. ¹H NMR (400 MHz, CDCl₃) of S-(4-bromophenyl) 3-phenylpropanethioate (3a-f)

Product 3a-f

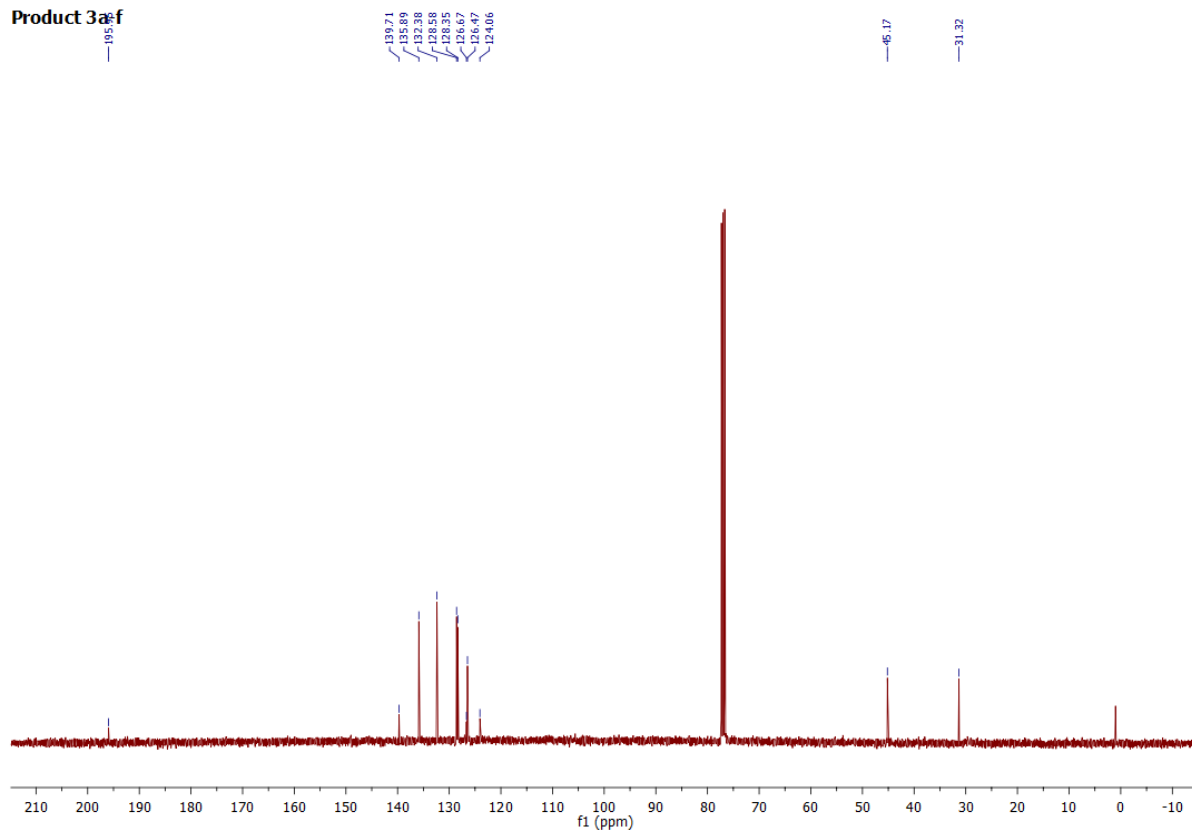


Figure S16. ¹³C NMR (100 MHz, CDCl₃) of S-(4-bromophenyl) 3-phenylpropanethioate (3a-f)

Product 3a-g

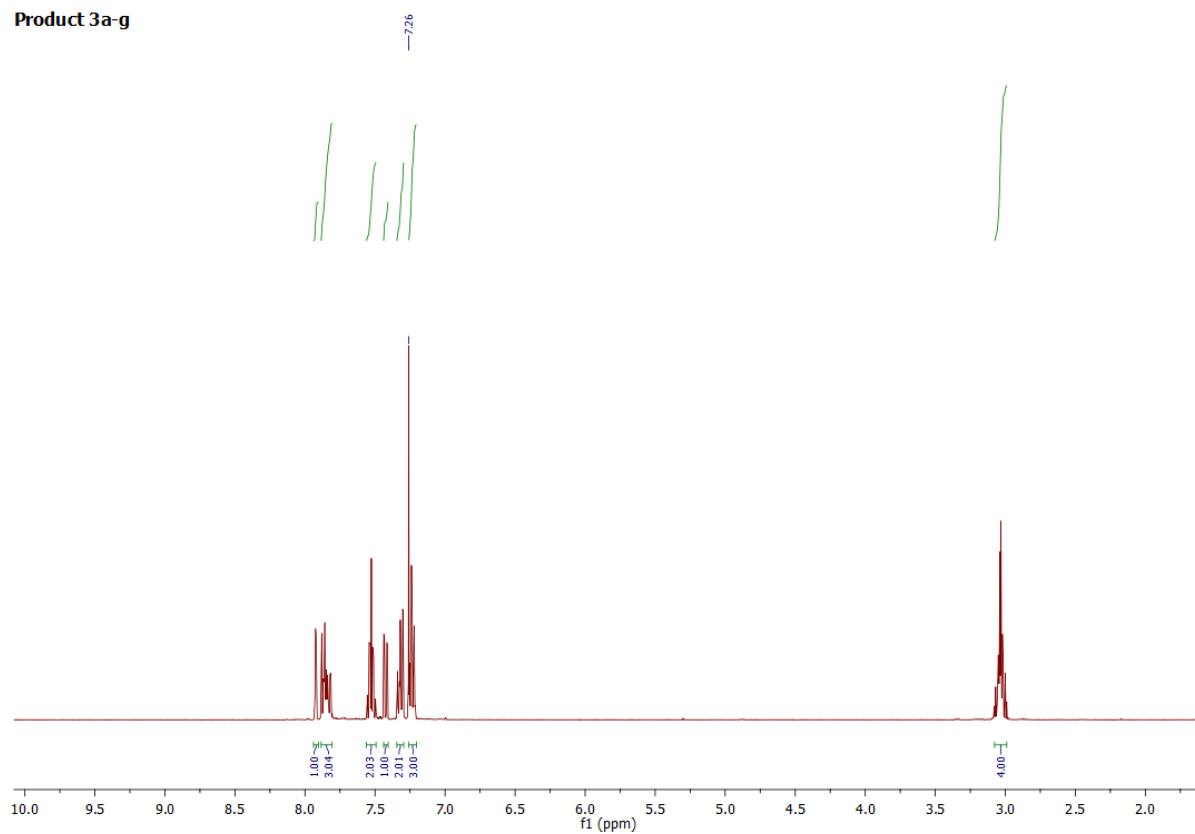


Figure S17. ¹H NMR (400 MHz, CDCl₃) of *S*-naphth 3-phenylpropanethioate (3a-g)

Product 3a-g

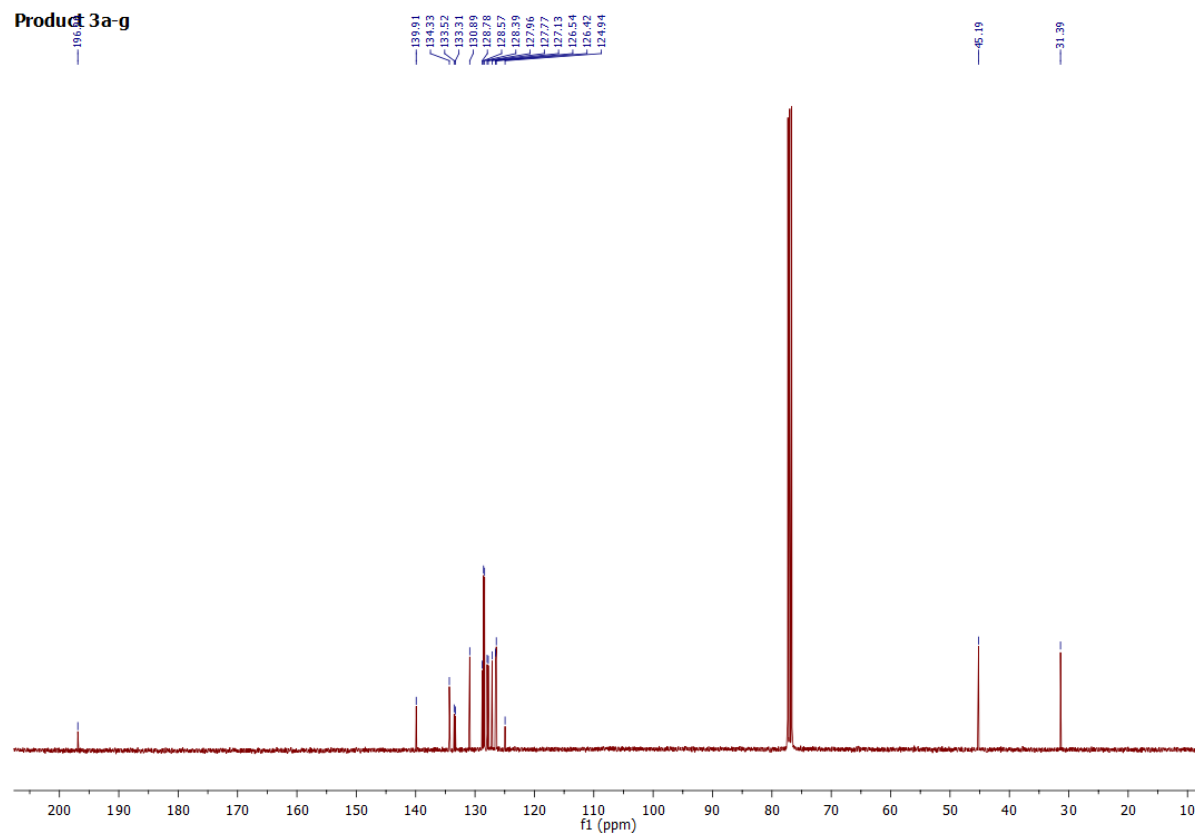


Figure S18. ¹³C NMR (100 MHz, CDCl₃) of *S*-naphth 3-phenylpropanethioate (3a-g)

Product 3a-h

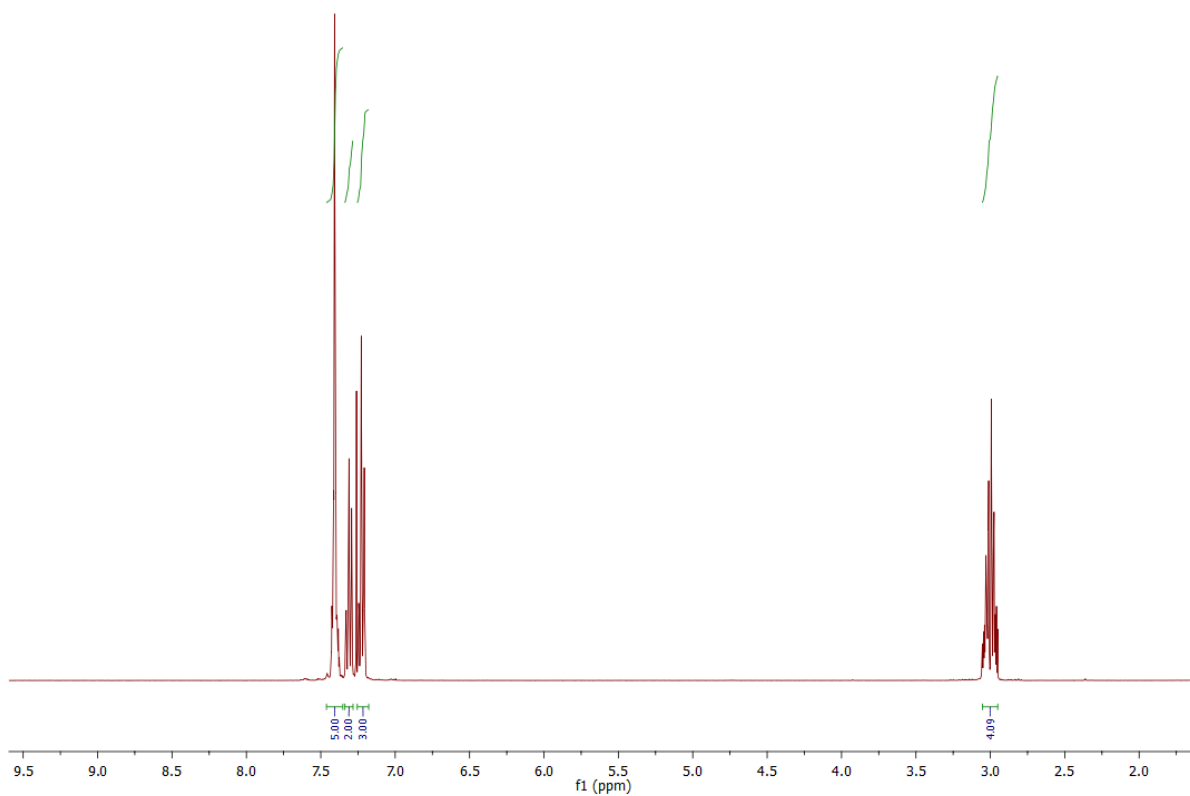


Figure S19. ¹H NMR (400 MHz, CDCl₃) of S-phenyl 3-phenylpropanethioate (3a-h)

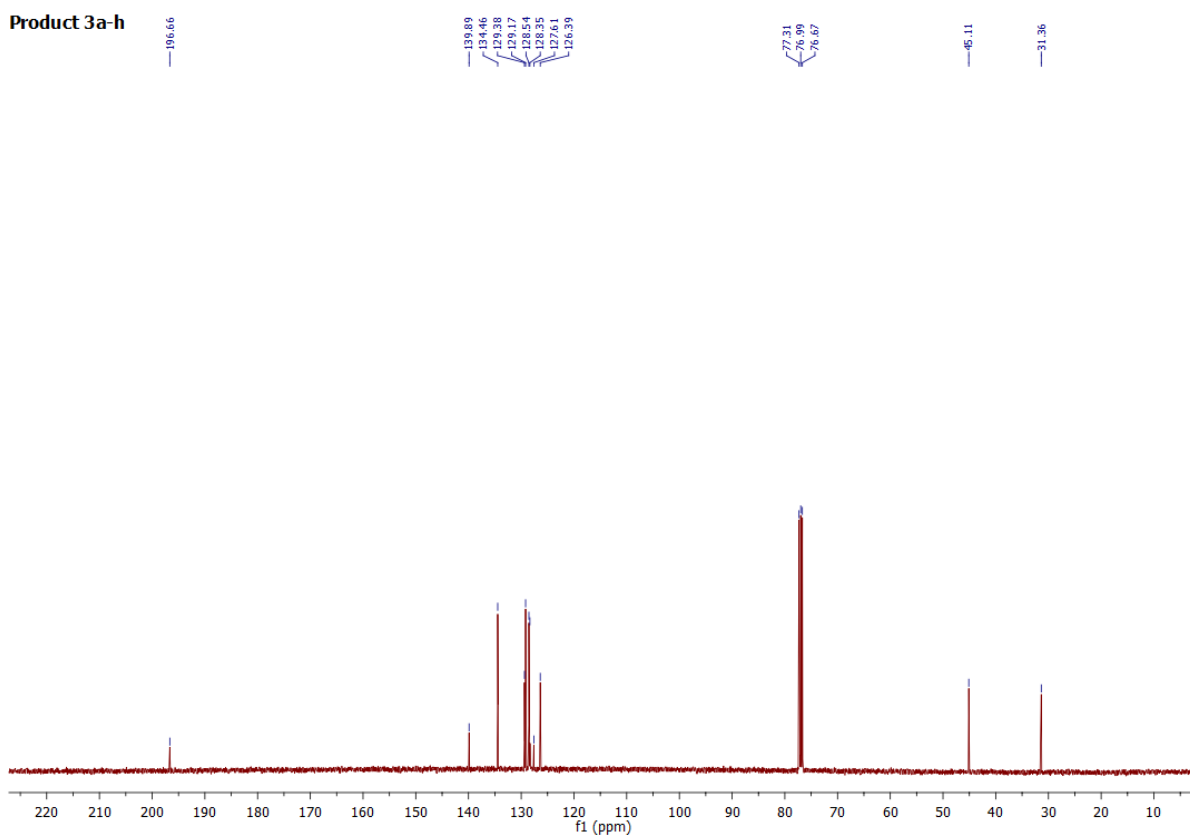


Figure S20. ¹³C NMR (100 MHz, CDCl₃) of S-phenyl 3-phenylpropanethioate (3a-h)

Product 3b-a

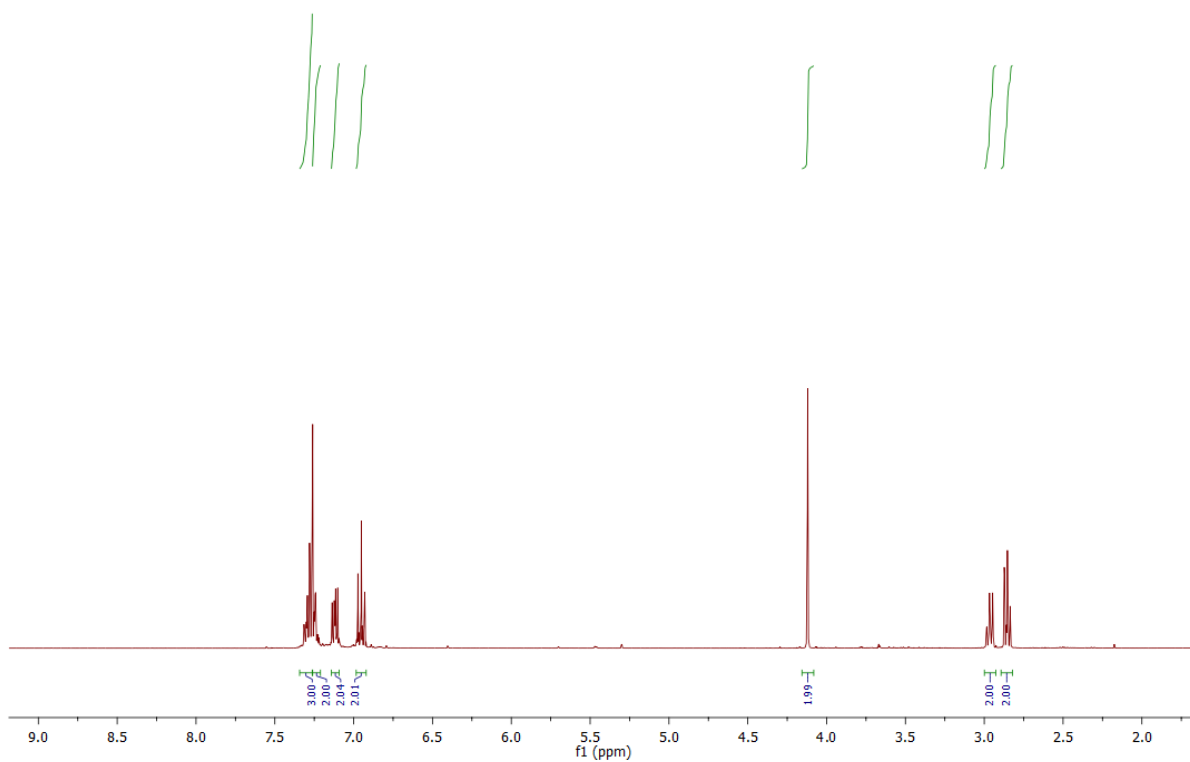


Figure S21. ¹H NMR (400 MHz, CDCl₃) of S-Benzyl 3-(4-fluorophenyl)propanethioate (3b-a)

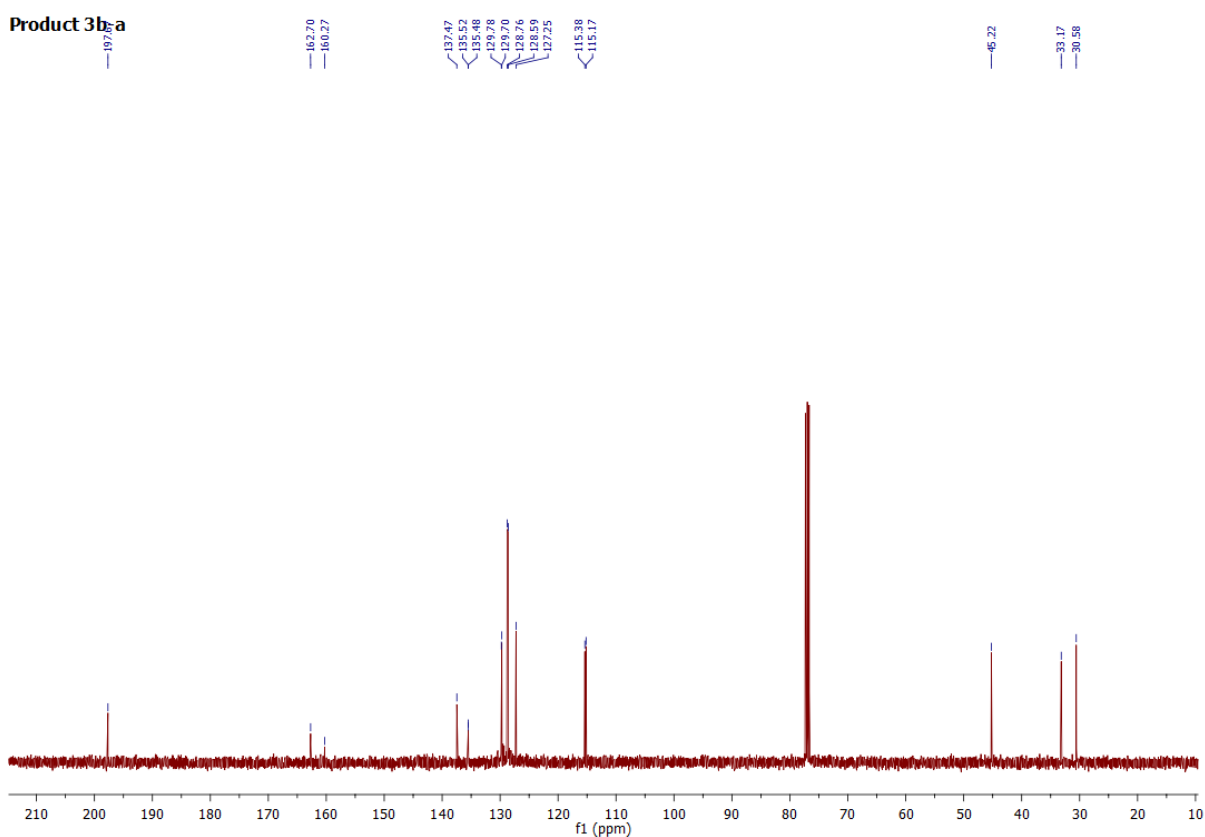


Figure S22. ¹³C NMR (100 MHz, CDCl₃) of S-Benzyl 3-(4-fluorophenyl)propanethioate (3b-a)

Product 3b-a

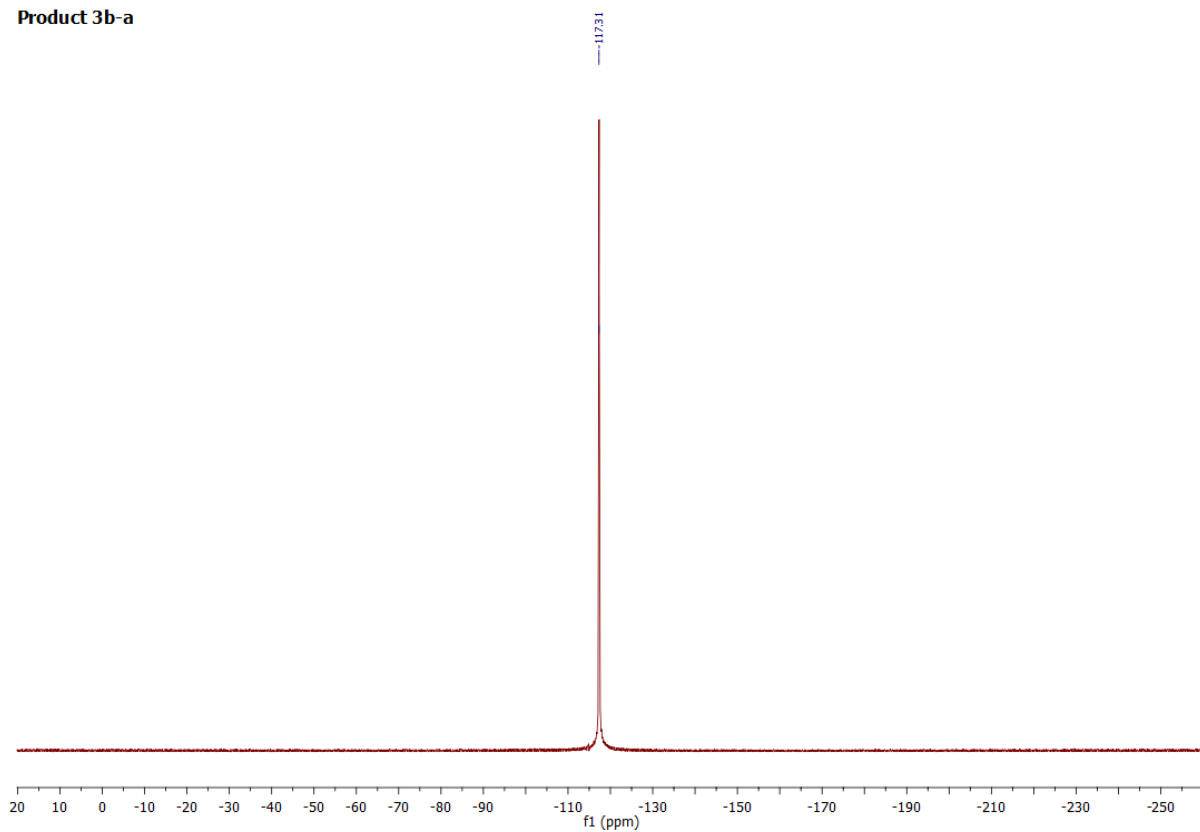


Figure S23. ^{19}F NMR (282.6 MHz, CDCl_3) of *S*-(4-fluorophenyl) 3-phenylpropanethioate (3b-a)

Product 3c-a

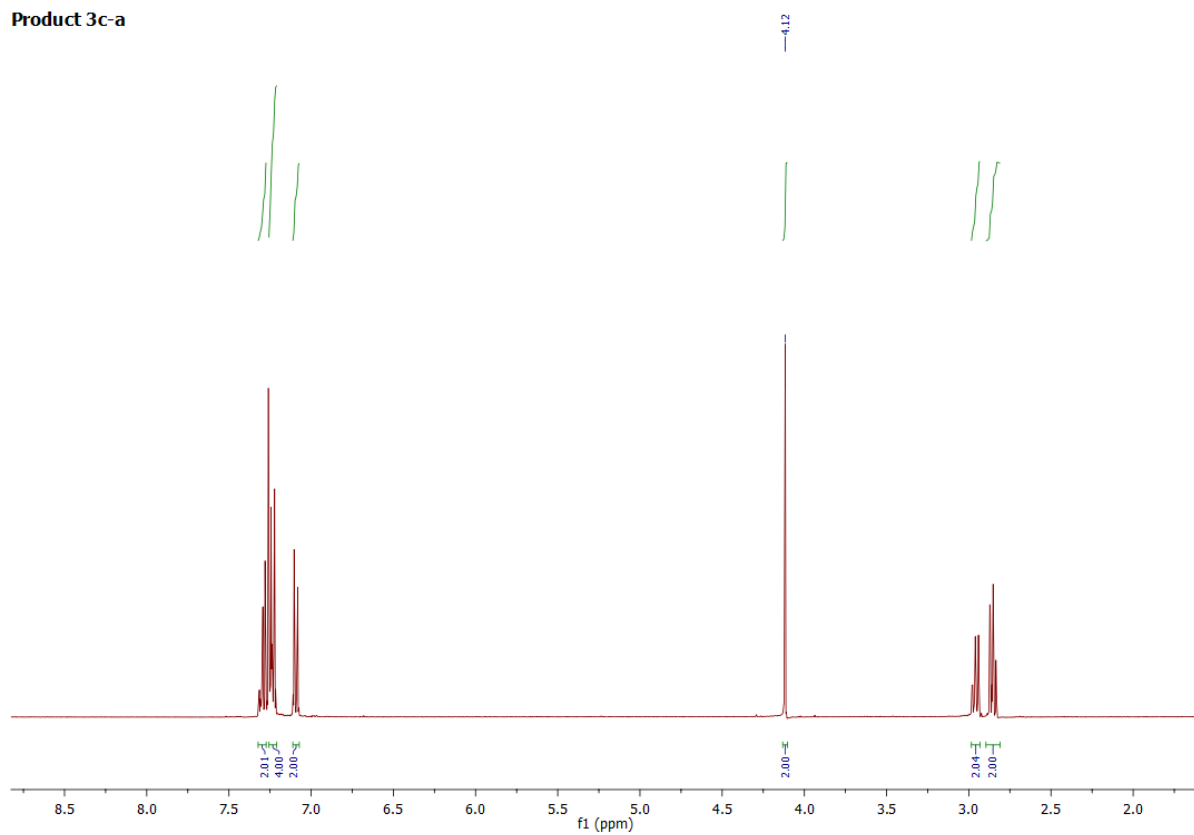


Figure S24. ^1H NMR (400 MHz, CDCl_3) of *S*-Benzyl 3-(4-chlorophenyl)propanethioate (3c-a)

Product 3c-a

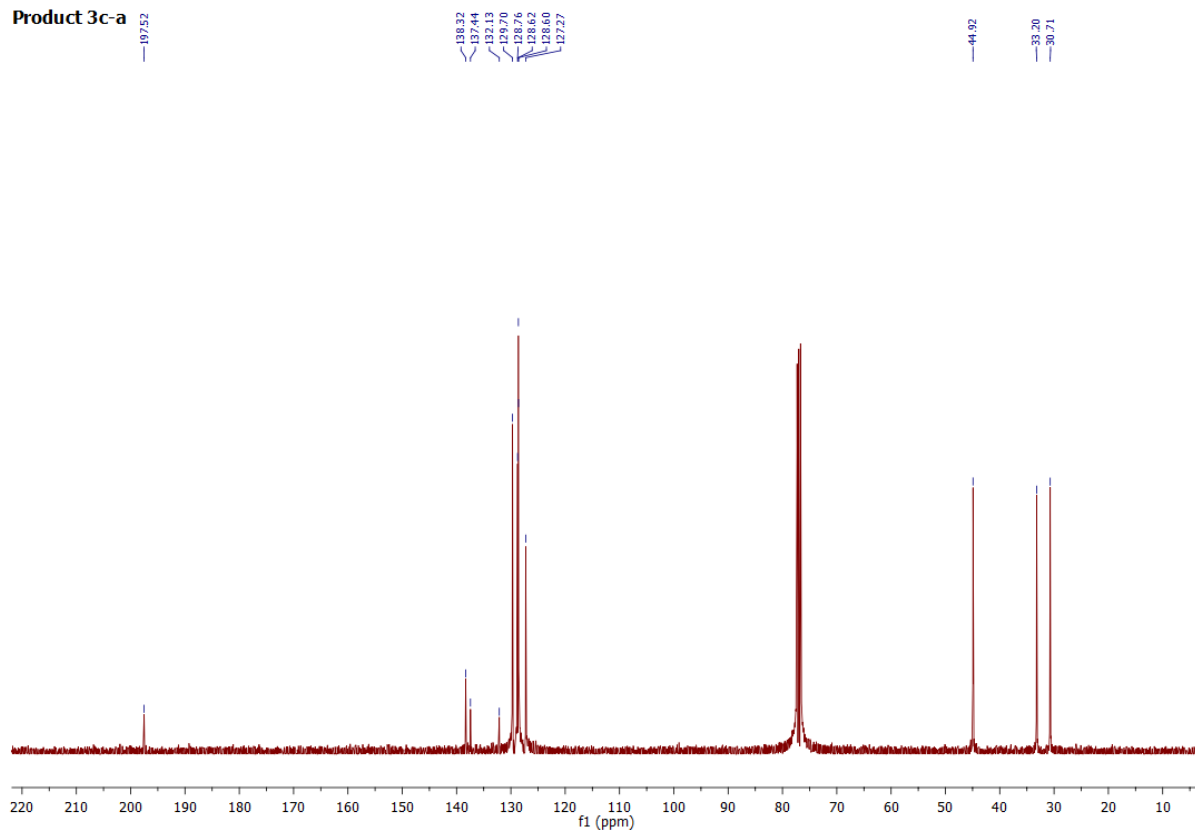


Figure S25. ¹³C NMR (100 MHz, CDCl₃) of S-Benzyl 3-(4-chlorophenyl)propanethioate (3c-a)

Product 3d-a

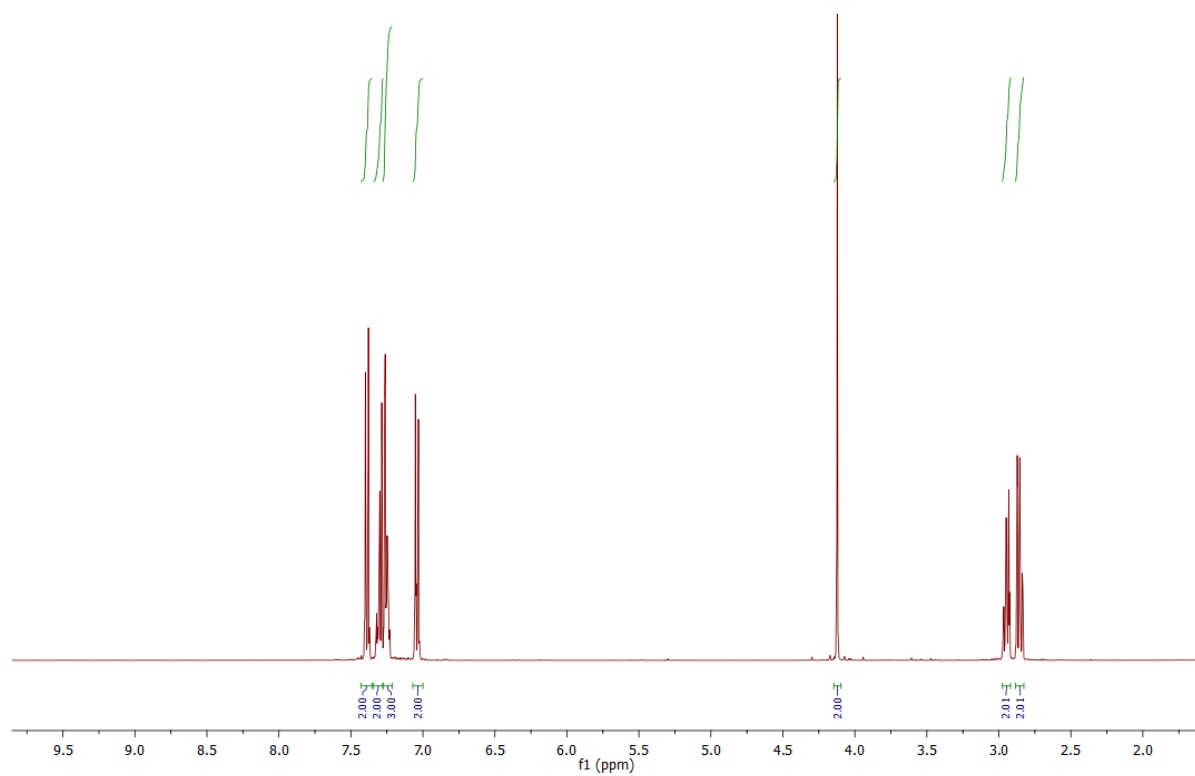


Figure S26. ¹H NMR (400 MHz, CDCl₃) of S-Benzyl 3-(4-bromophenyl)propanethioate (3d-a)

Product 3d-a

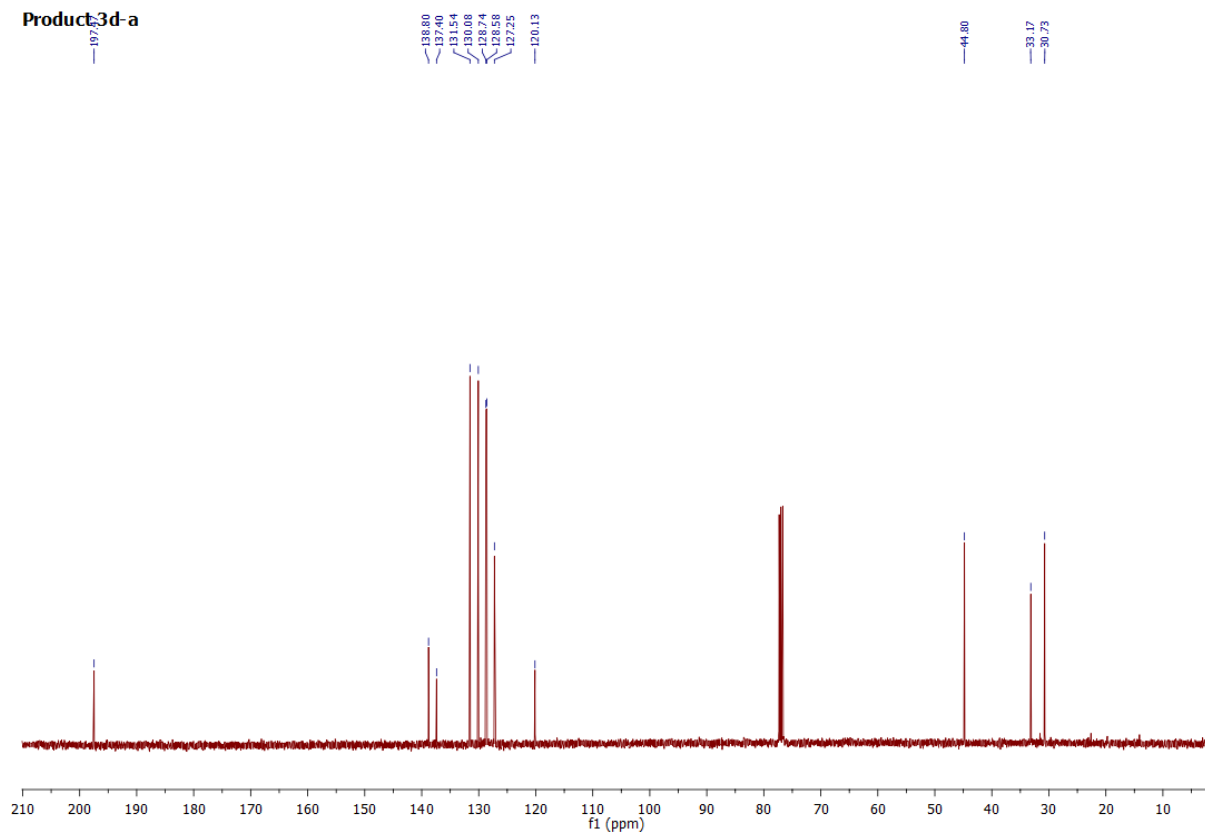


Figure S27. ^{13}C NMR (100 MHz, CDCl_3) of *S*-Benzyl 3-(4-bromophenyl)propanethioate (3d-a)

Product 3e-a

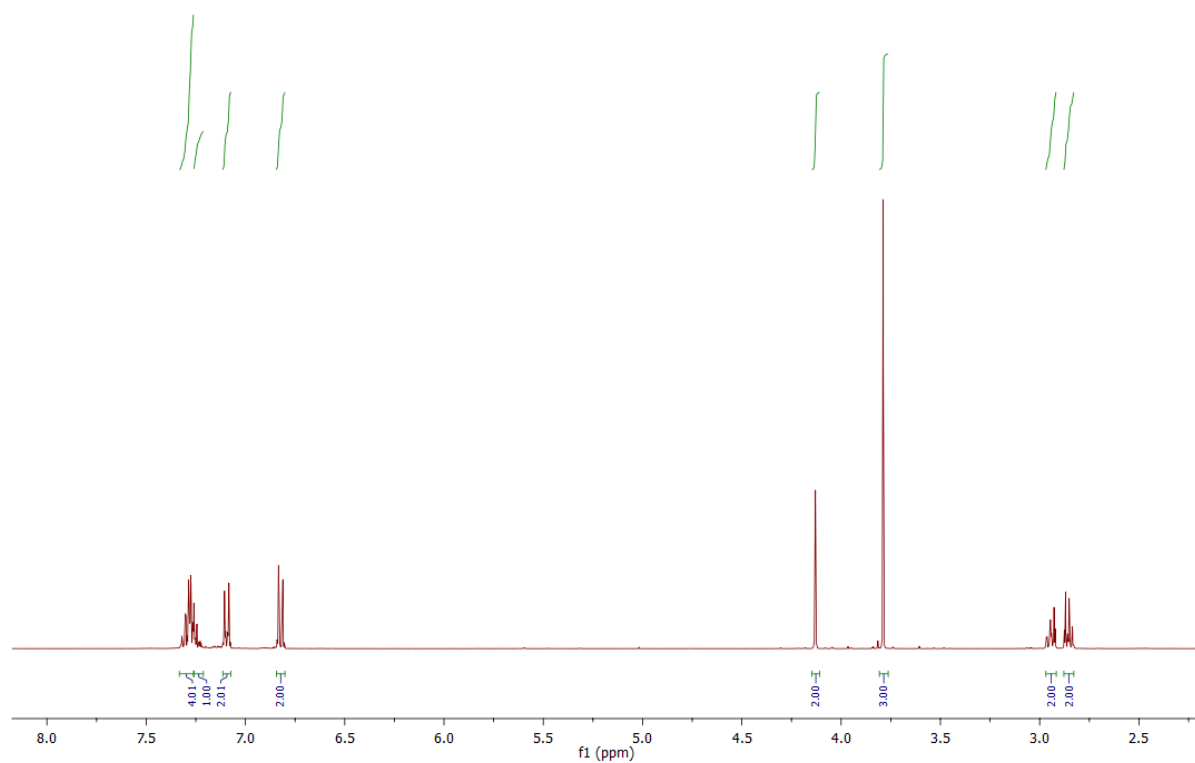


Figure S28. ^1H NMR (400 MHz, CDCl_3) of *S*-Benzyl 3-(4-methoxyphenyl)propanethioate (3e-a)

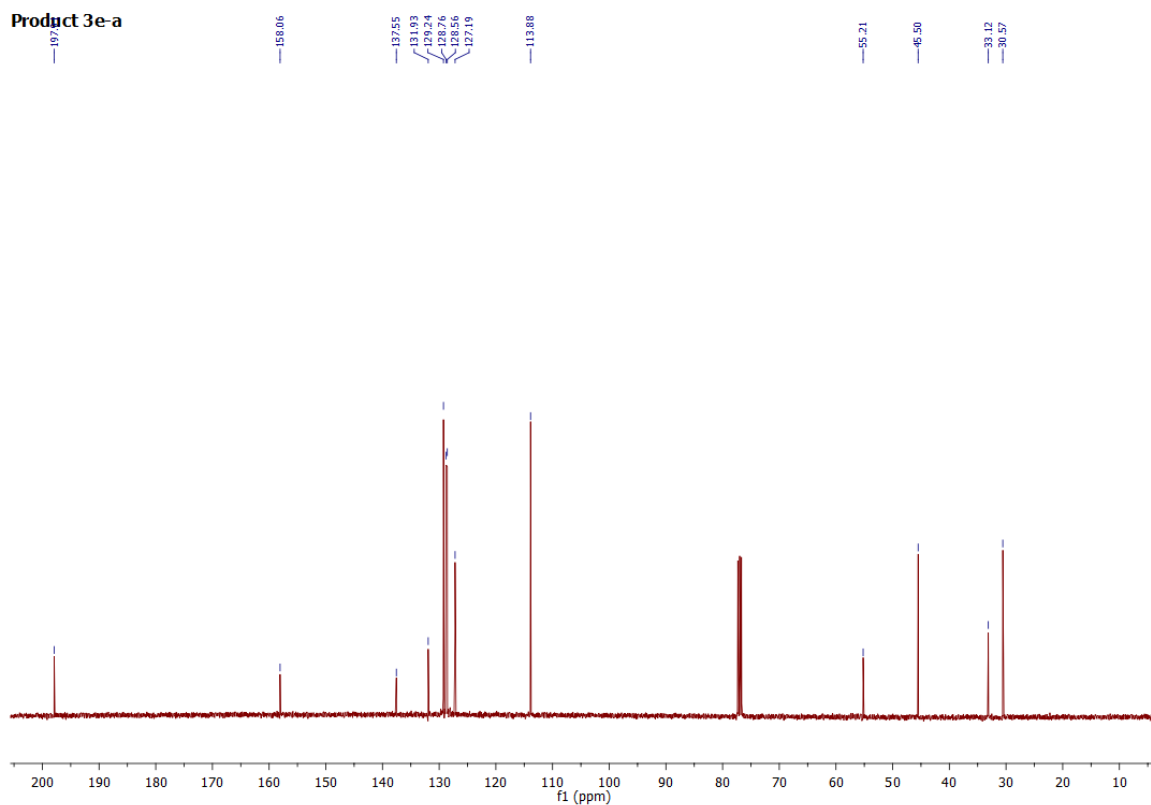


Figure S29. ^{13}C NMR (100 MHz, CDCl_3) of *S*-Benzyl 3-(4-methoxyphenyl)propanethioate (3e-a)

Product 3f-a

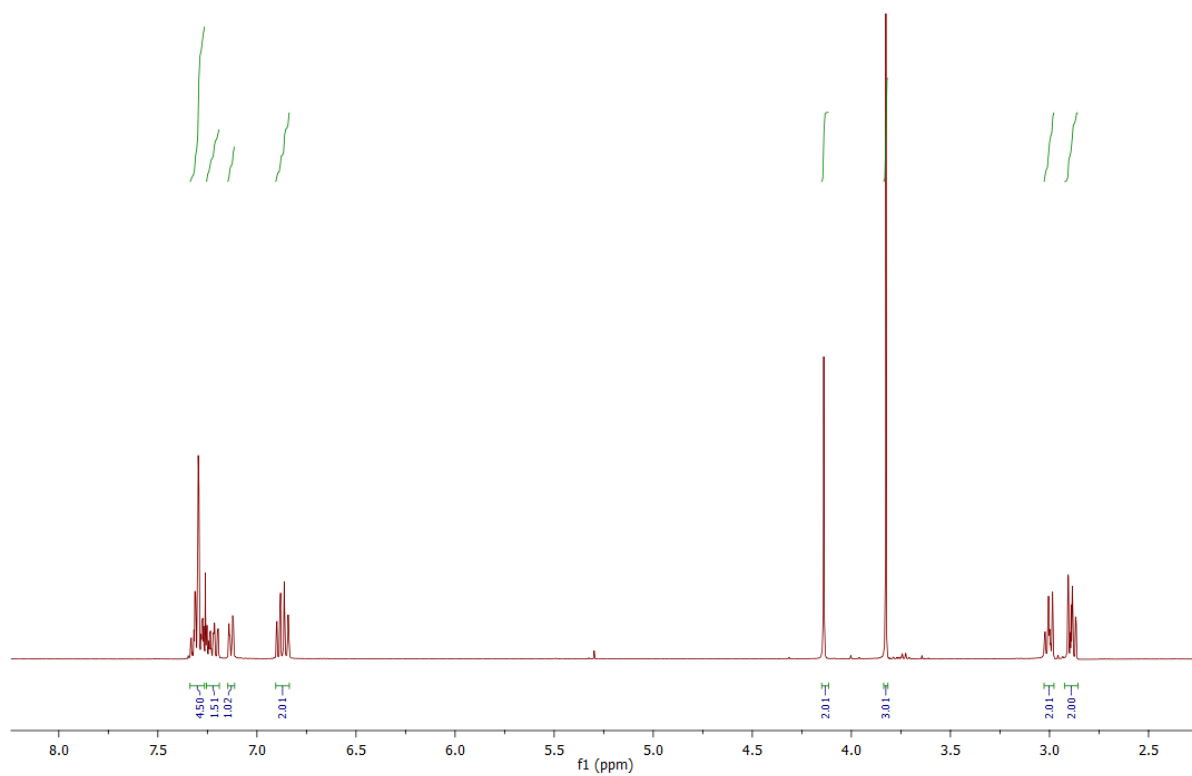


Figure S30. ^1H NMR (400 MHz, CDCl_3) of *S*-Benzyl 3-(2-methoxyphenyl)propanethioate (3f-a)

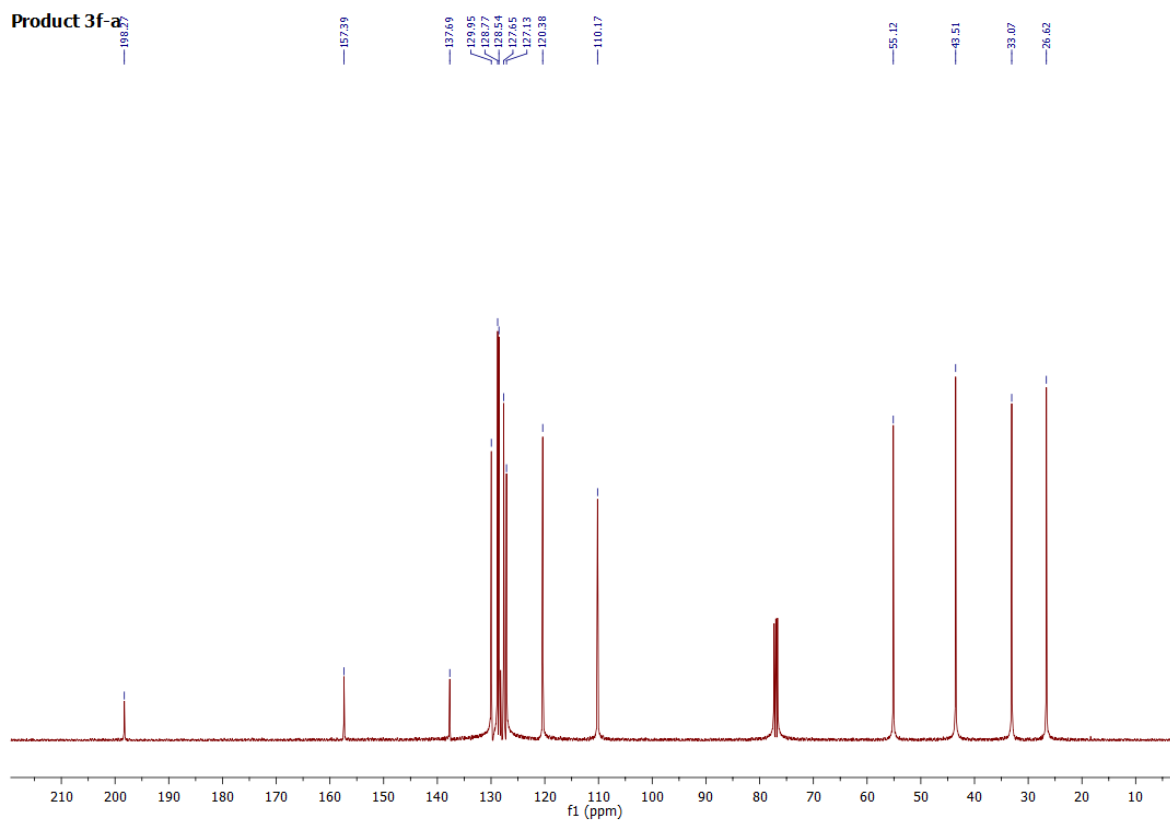


Figure S31. ^{13}C NMR (100 MHz, CDCl_3) of *S*-Benzyl 3-(2-methoxyphenyl)propanethioate (3f-a)

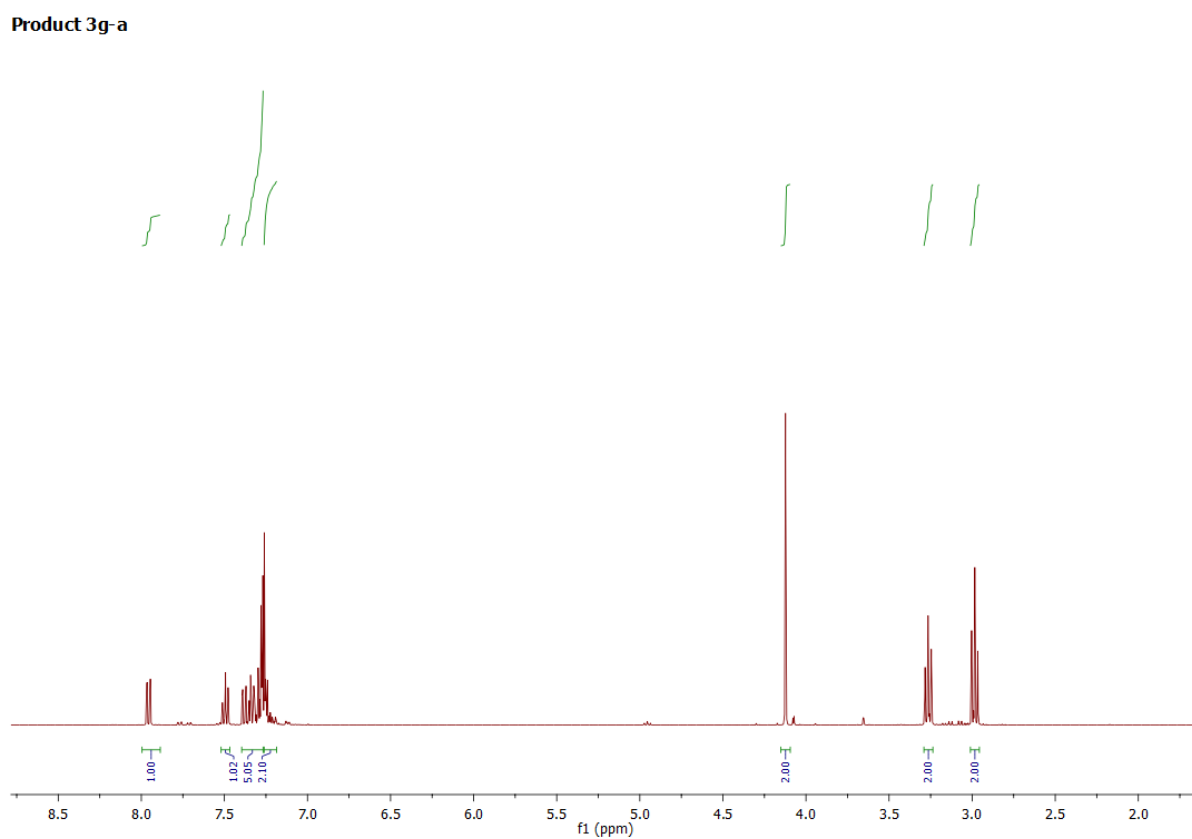


Figure S32. ^1H NMR (400 MHz, CDCl_3) of *S*-Benzyl 3-(2-nitrophenyl)propanethioate (3g-a)

Product 3g-a

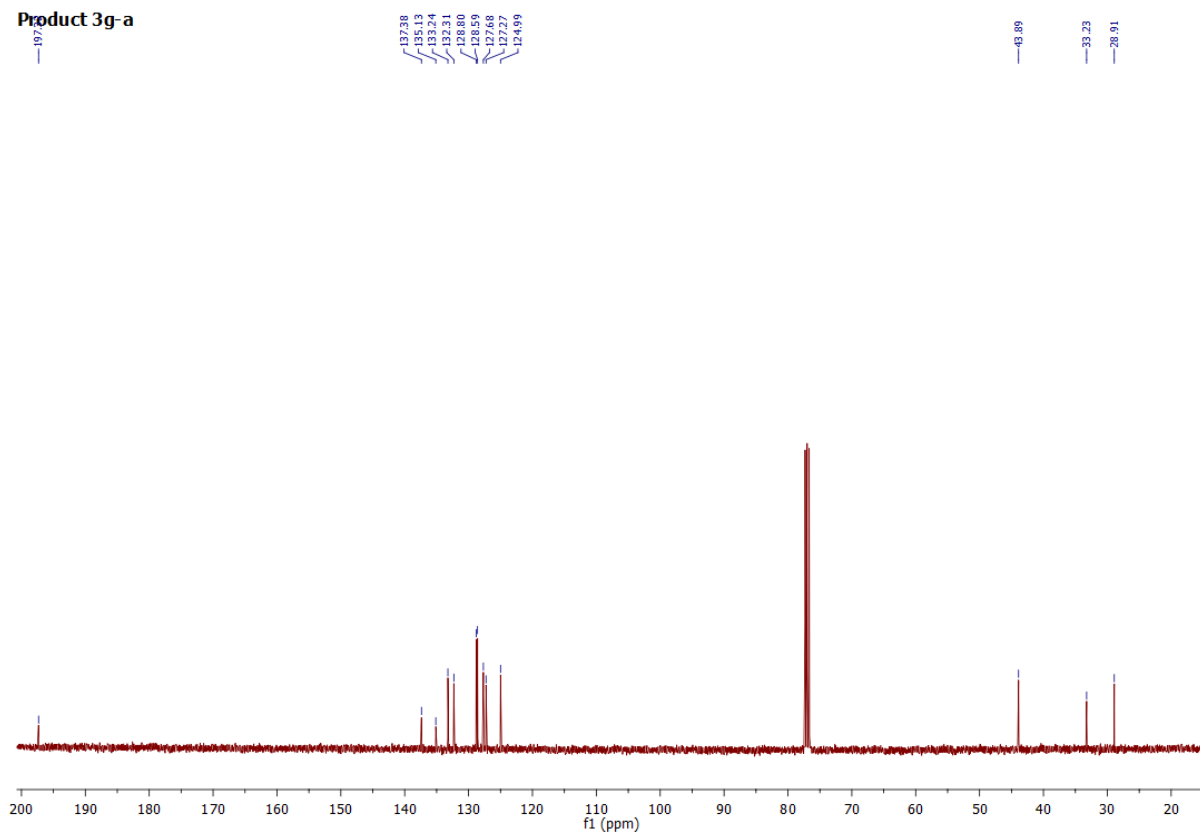


Figure S33. ¹³C NMR (100 MHz, CDCl₃) of S-Benzyl 3-(2-nitrophenyl)propanethioate (3g-a)

Product 3h-a

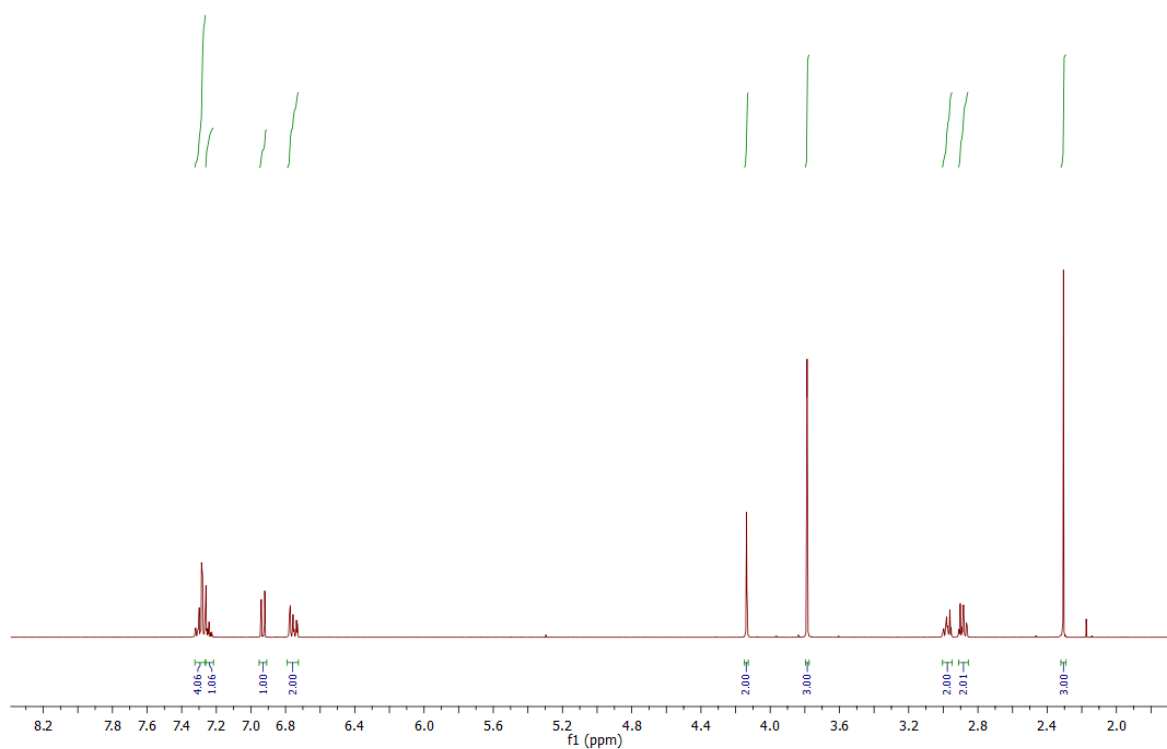


Figure S34. ¹H NMR (400 MHz, CDCl₃) of S-Benzyl 3-(3-methoxy-4-acetoxyphenyl)propanethioate (3h-a)

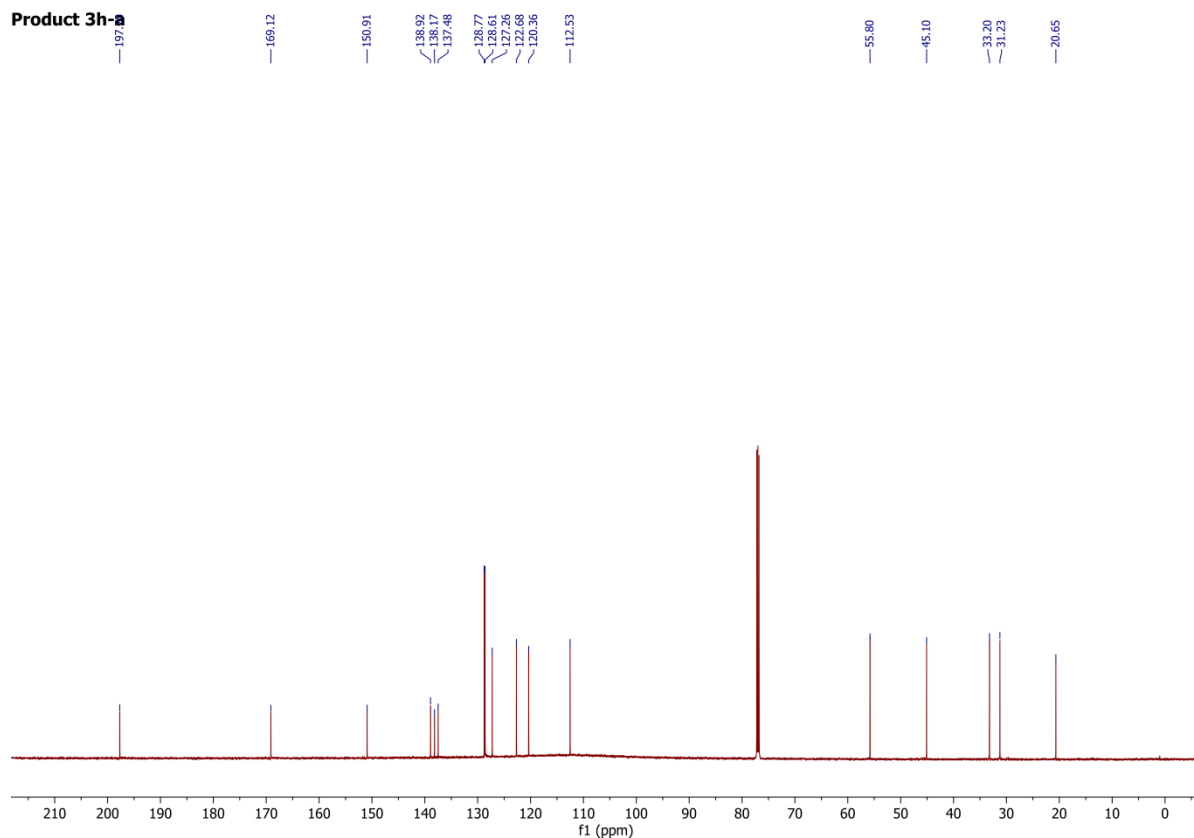


Figure S35. ^{13}C NMR (100 MHz, CDCl_3) of *S*-Benzyl 3-(3-methoxy-4-acetoxyphenyl)propanethioate (3h-a)

Product 3i-a

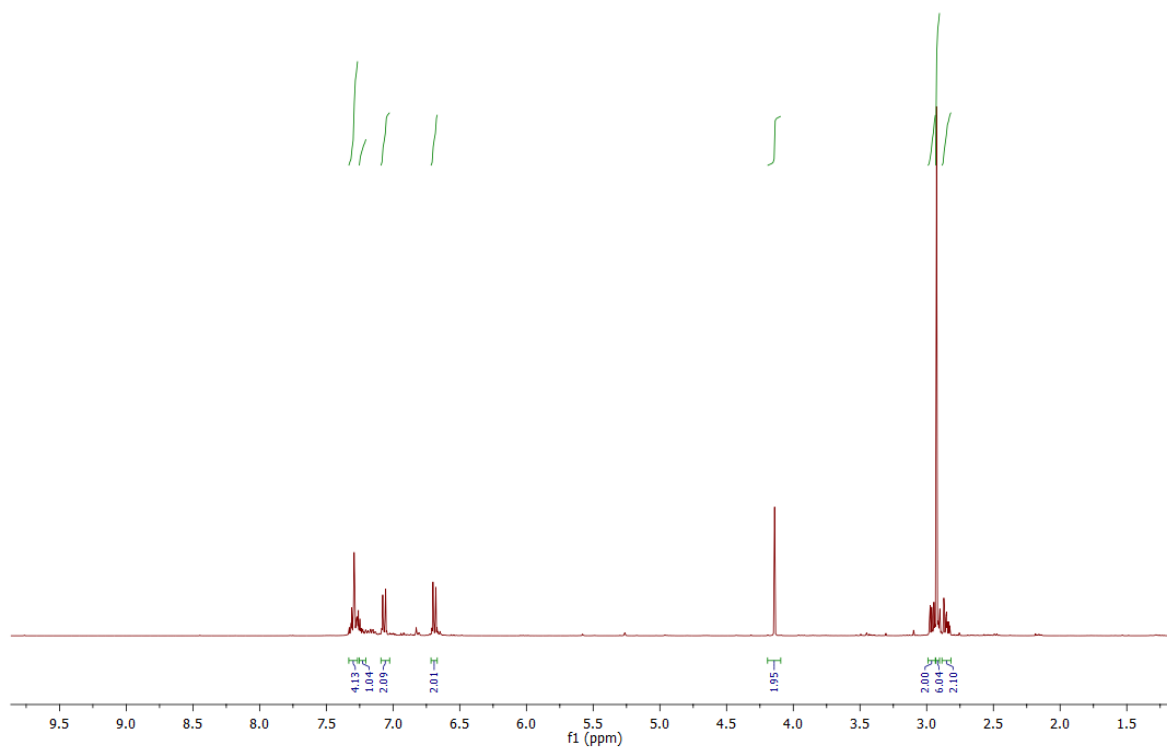


Figure S36. ^1H NMR (400 MHz, CDCl_3) of *S*-Benzyl 3-(4-dimethylaminophenyl)propanethioate (3i-a)

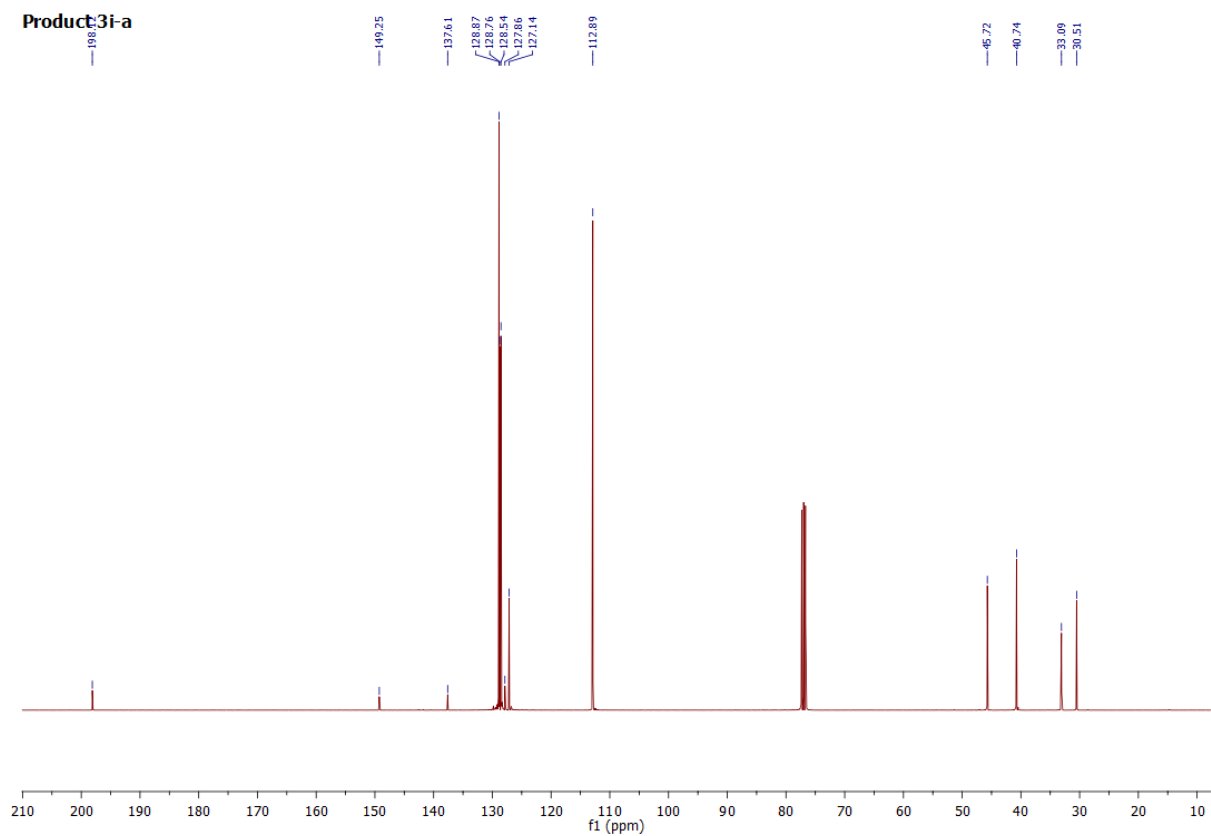


Figure S37. ^{13}C NMR (100 MHz, CDCl_3) of *S*-Benzyl 3-(4-dimethylaminophenyl)propanethioate (3i-a)

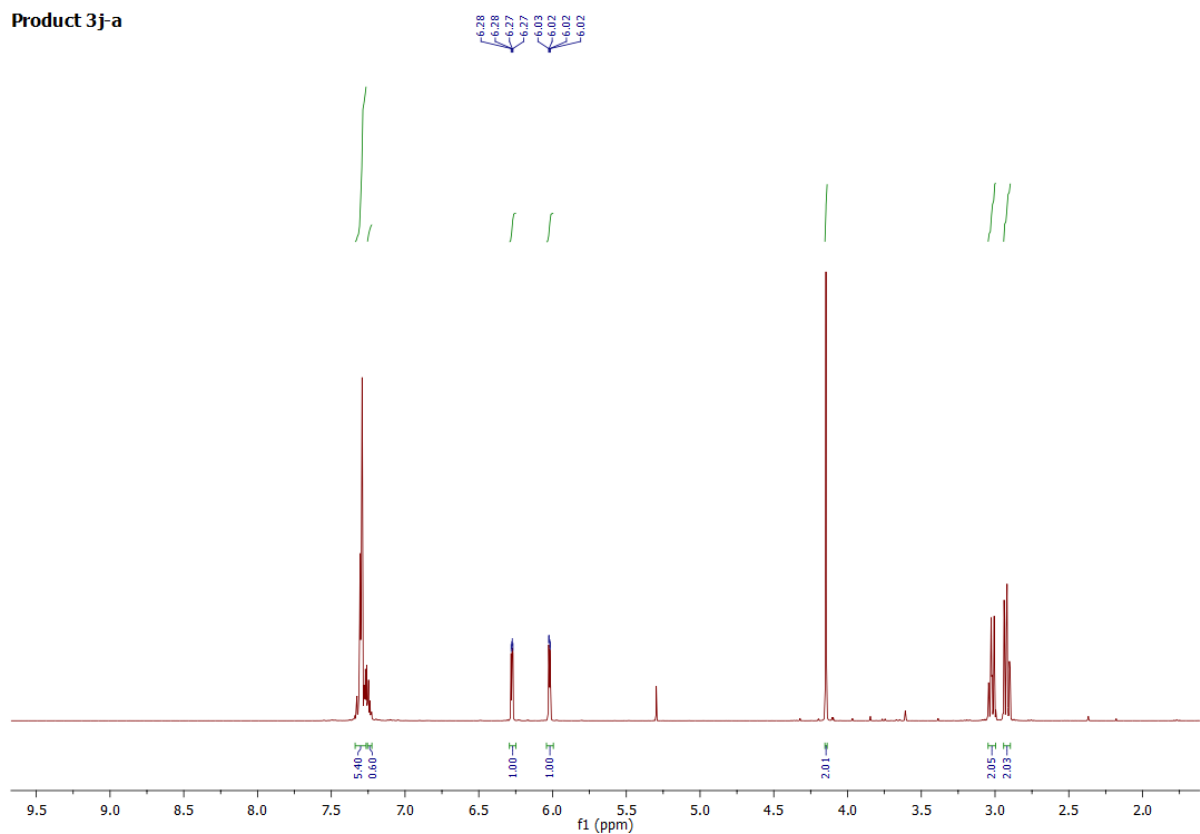


Figure S38. ^1H NMR (400 MHz, CDCl_3) of *S*-Benzyl 3-(2-furanyl)propanethioate (3j-a)

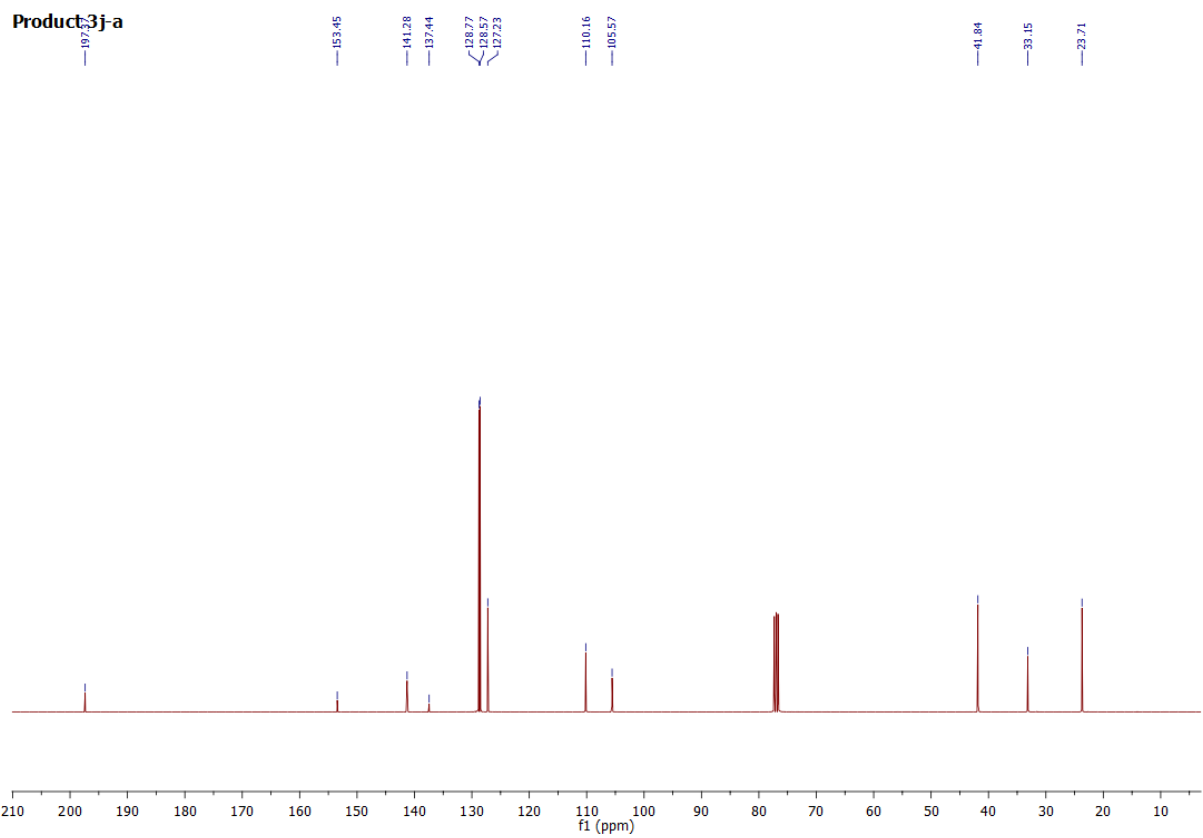


Figure S39. ^{13}C NMR (100 MHz, CDCl_3) of *S*-Benzyl 3-(2-furanyl)propanethioate (3j-a)

Product 3k-a

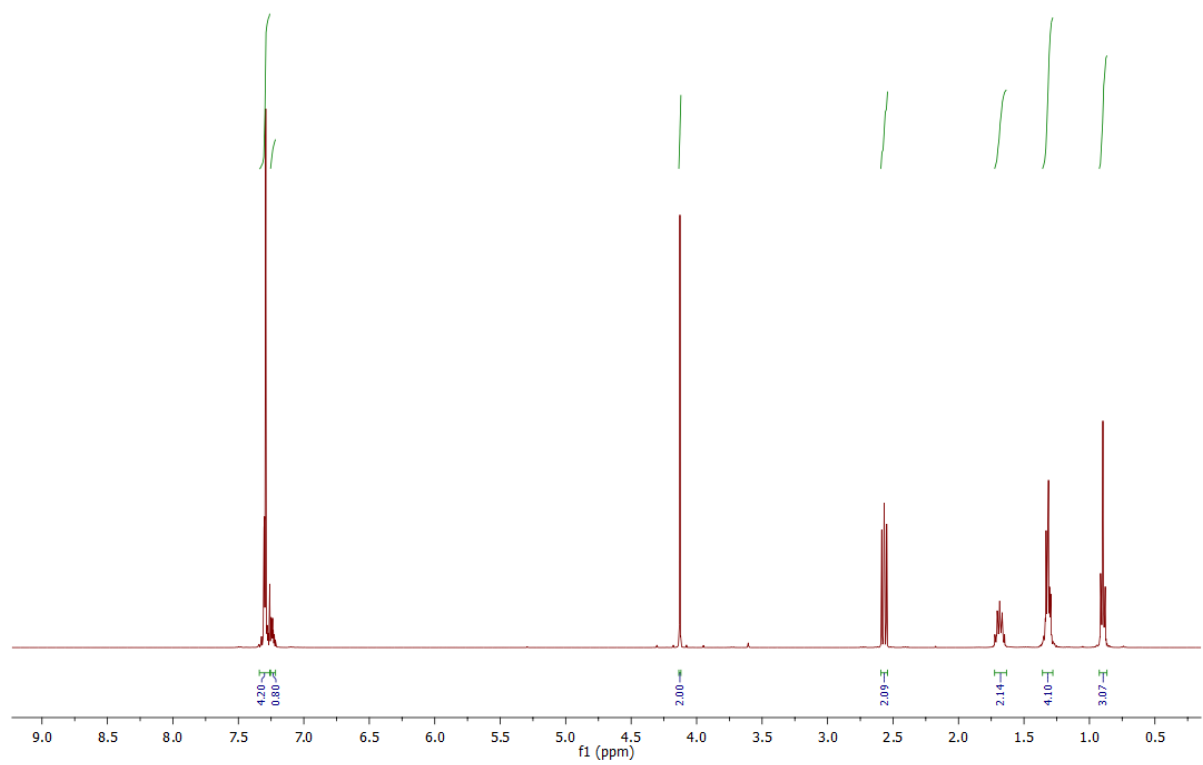


Figure S40. ^1H NMR (400 MHz, CDCl_3) of *S*-Benzyl hexanethioate (3k-a)

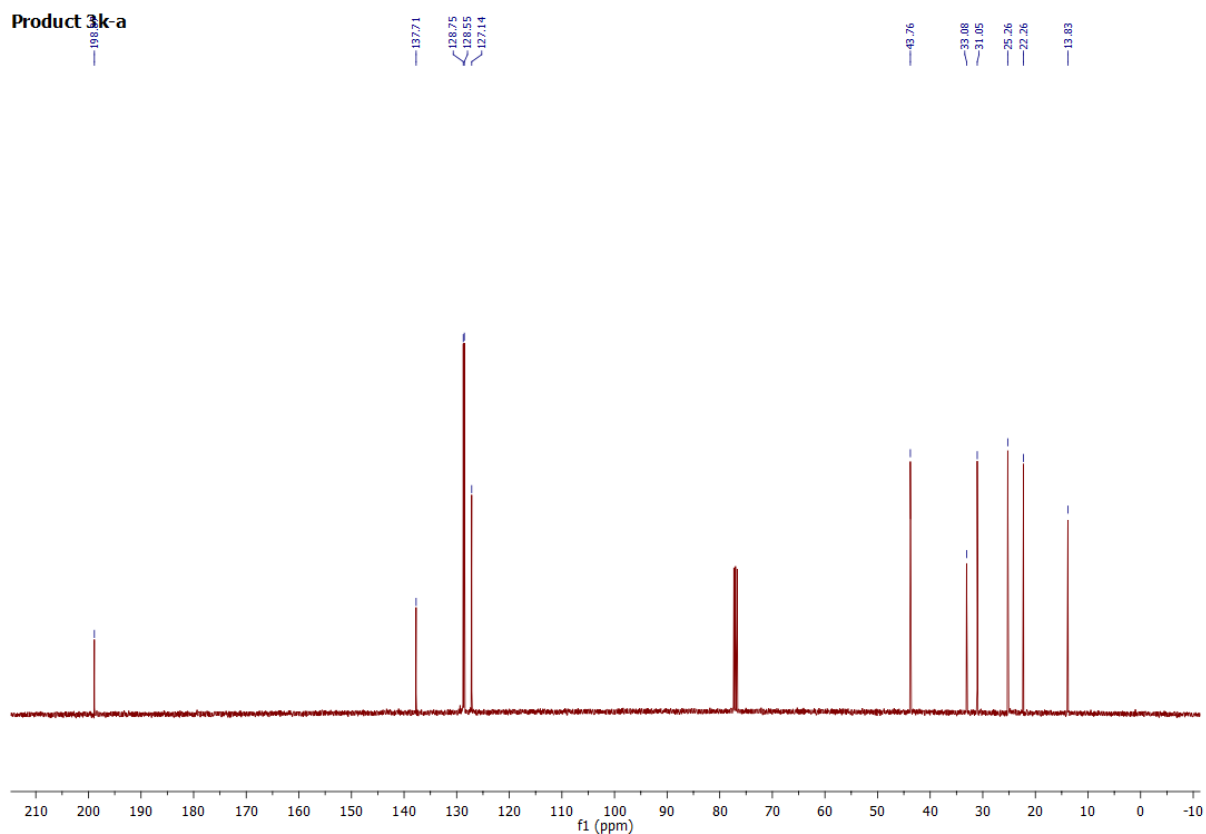


Figure S41. ^{13}C NMR (100 MHz, CDCl_3) of *S*-Benzyl hexanethioate (3k-a)

Product 3l-a

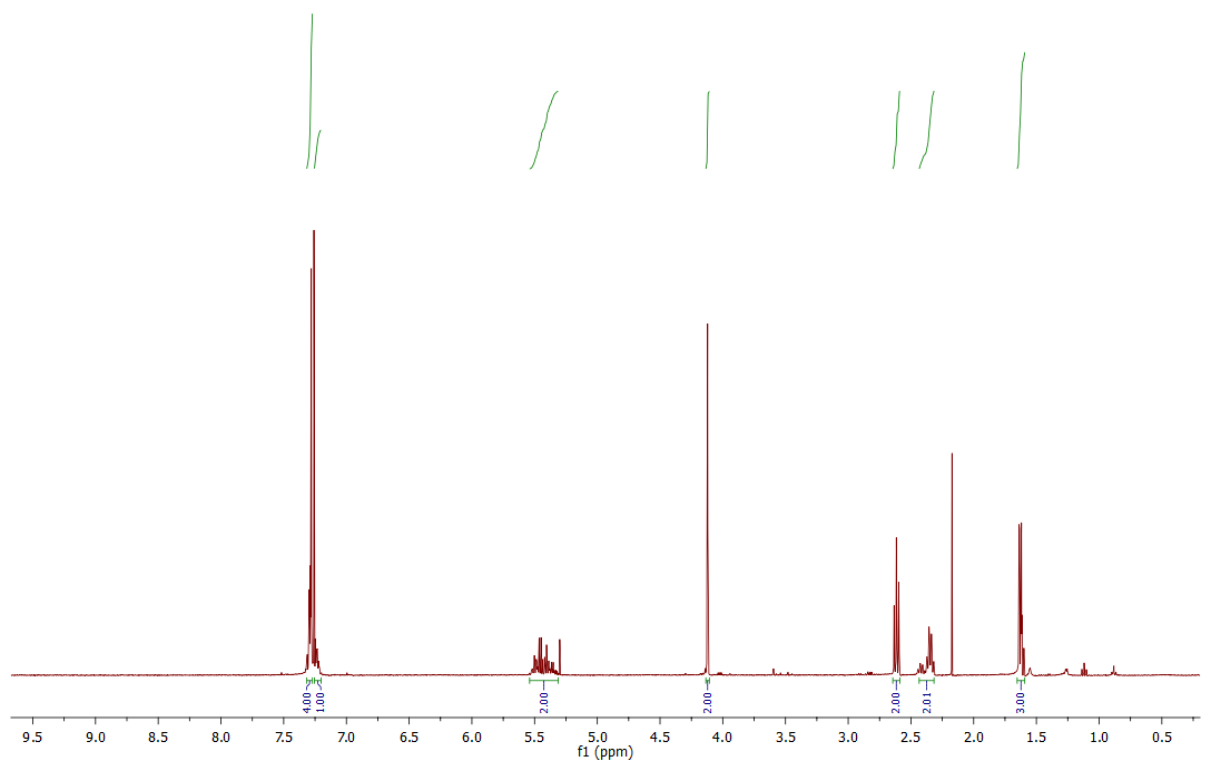


Figure S42. ^1H NMR (400 MHz, CDCl_3) of *S*-Benzyl 4-hexenethioate (3l-a)

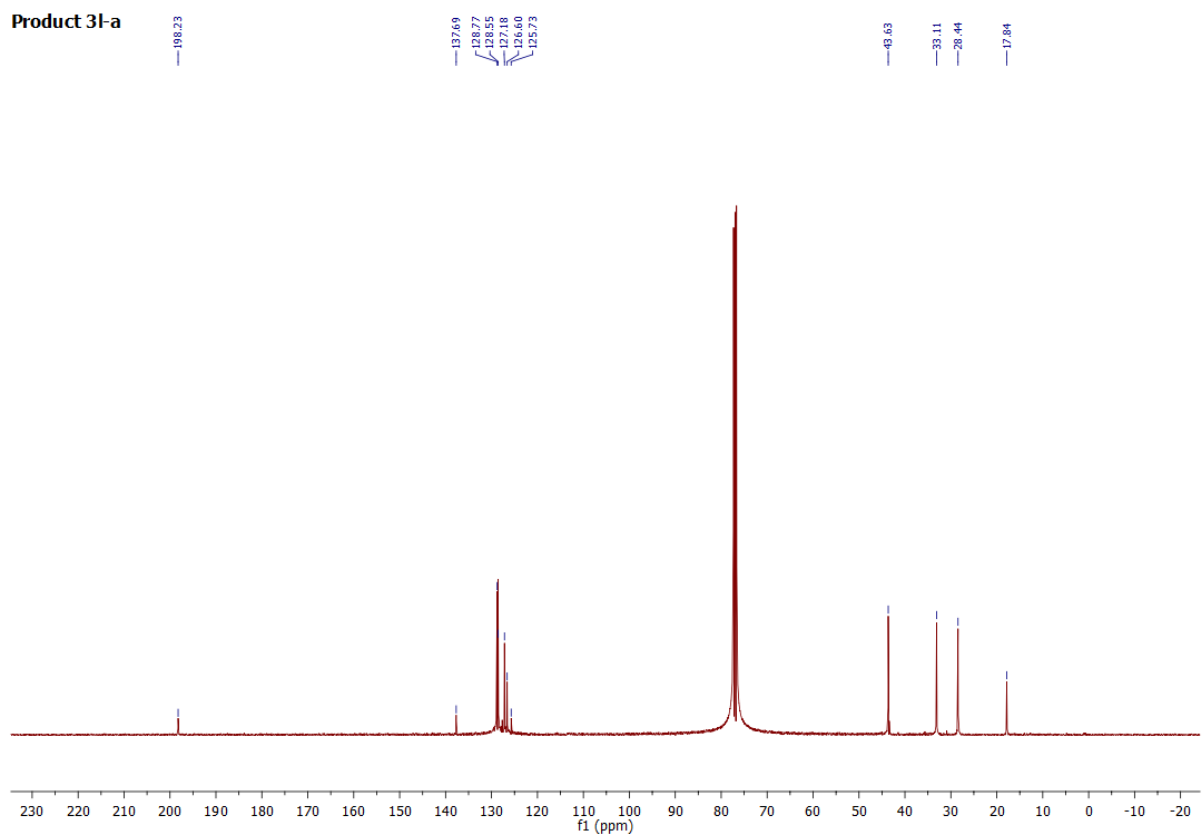


Figure S43. ^{13}C NMR (100 MHz, CDCl_3) of *S*-Benzyl 4-hexenethioate (3I-a)
Product 3I-a'

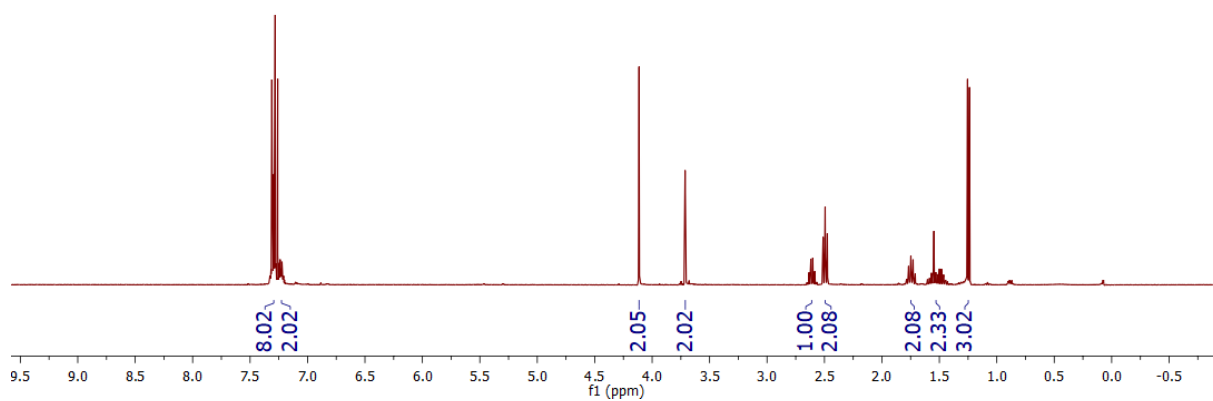


Figure S44. ^1H NMR (400 MHz, CDCl_3) of *S*-benzyl 5-(benzylthio)hexanethioate (3I-a'')

Product 3I-a

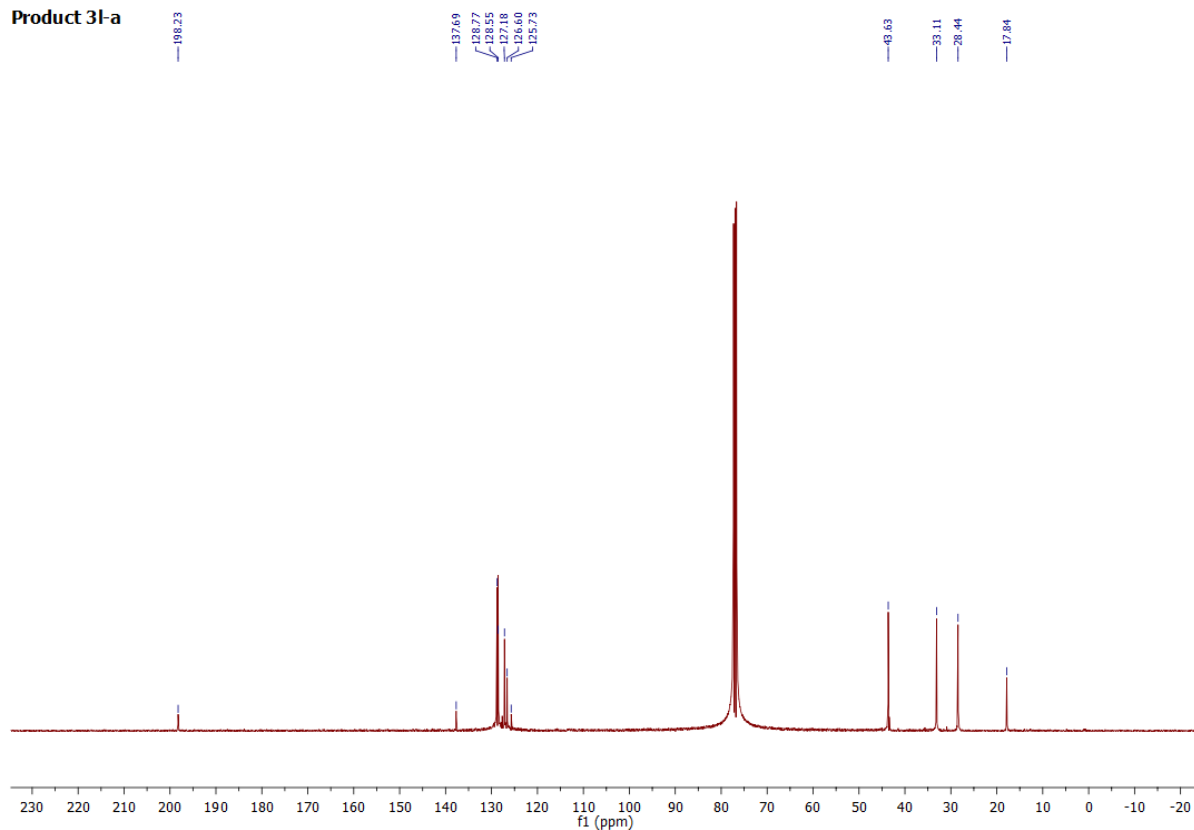


Figure S45. ¹³C NMR (100 MHz, CDCl₃) of *S*-benzyl 5-(benzylthio)hexanethioate (3I-a'')

Product 5a

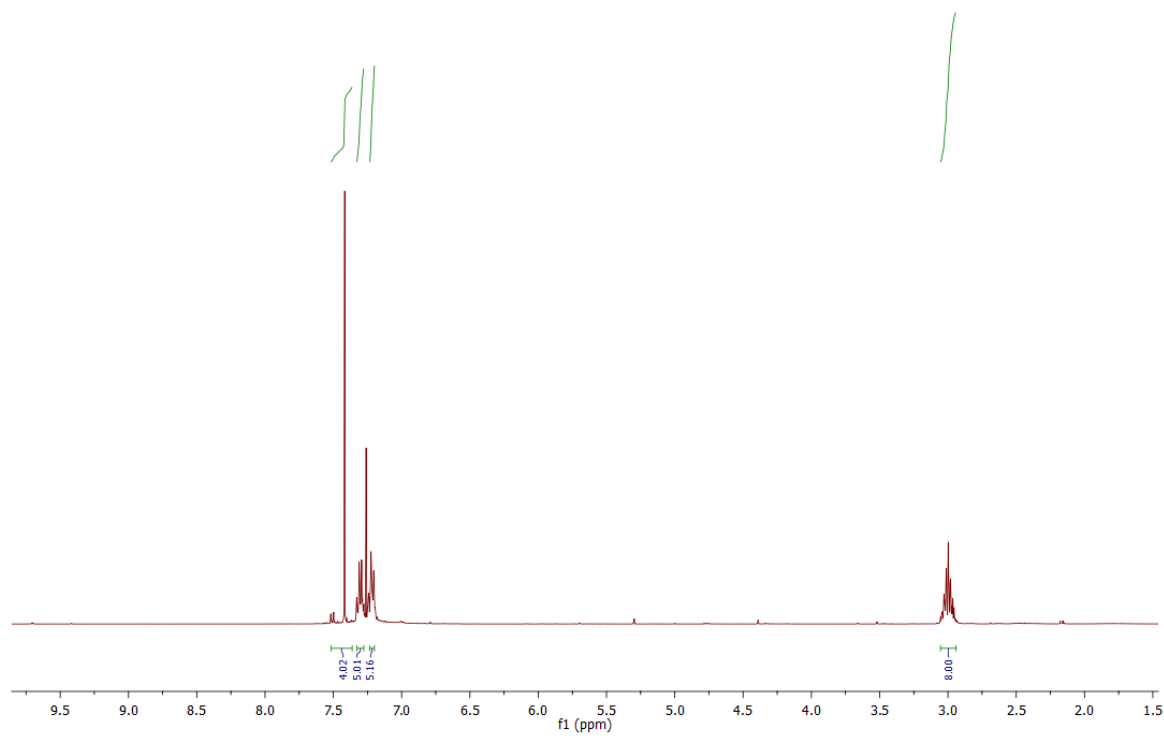


Figure S46. ¹H NMR (400 MHz, CDCl₃) of *S,S'*-1,4-phenylene bis(3-phenylpropanethioate) (5a)

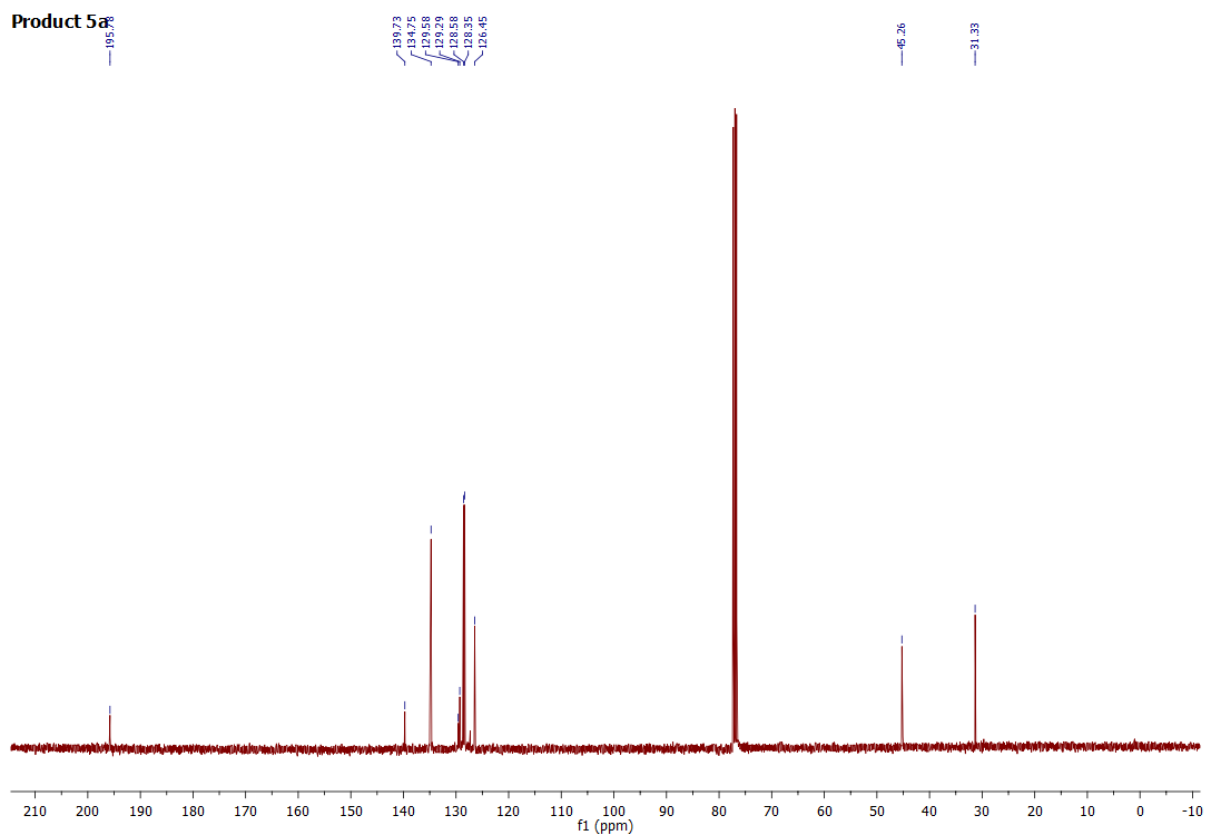


Figure S47. ^{13}C NMR (100 MHz, CDCl_3) of *S,S'*-1,4-phenylene bis(3-phenylpropanethioate) (5a)

Product 5b

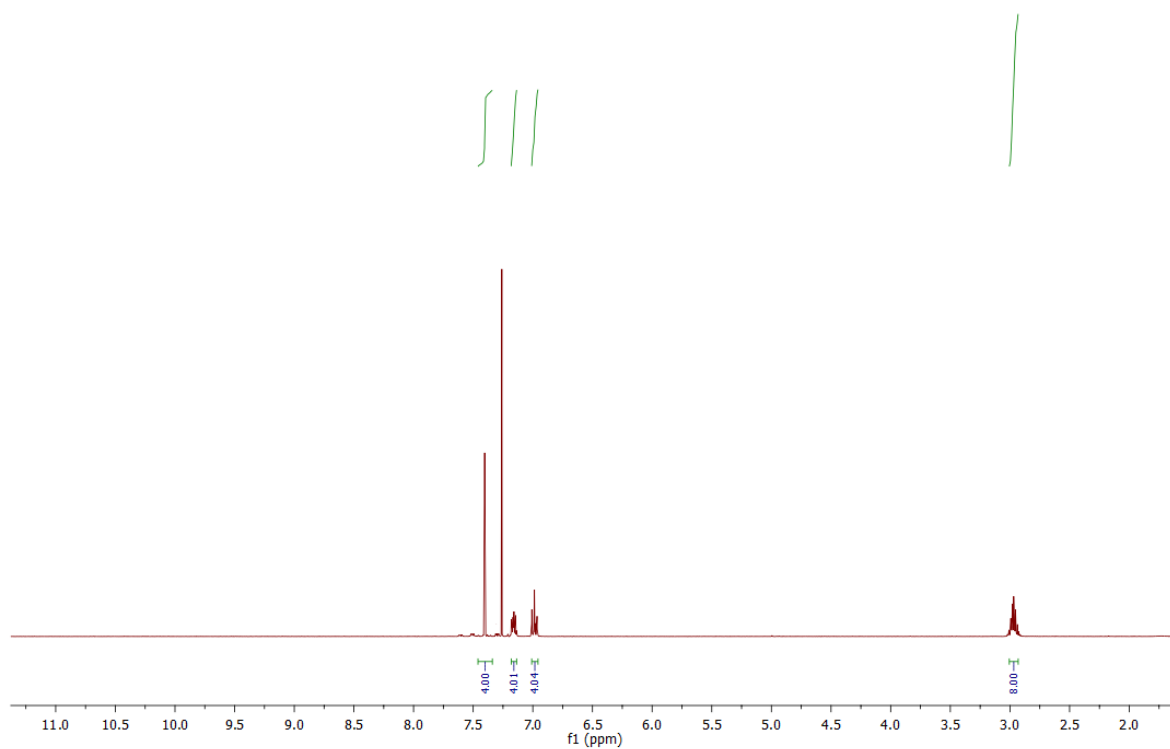


Figure S48. ^1H NMR (400 MHz, CDCl_3) of *S,S'*-1,4-phenylene bis(3-(4-fluorophenyl)propanethioate) (5b)

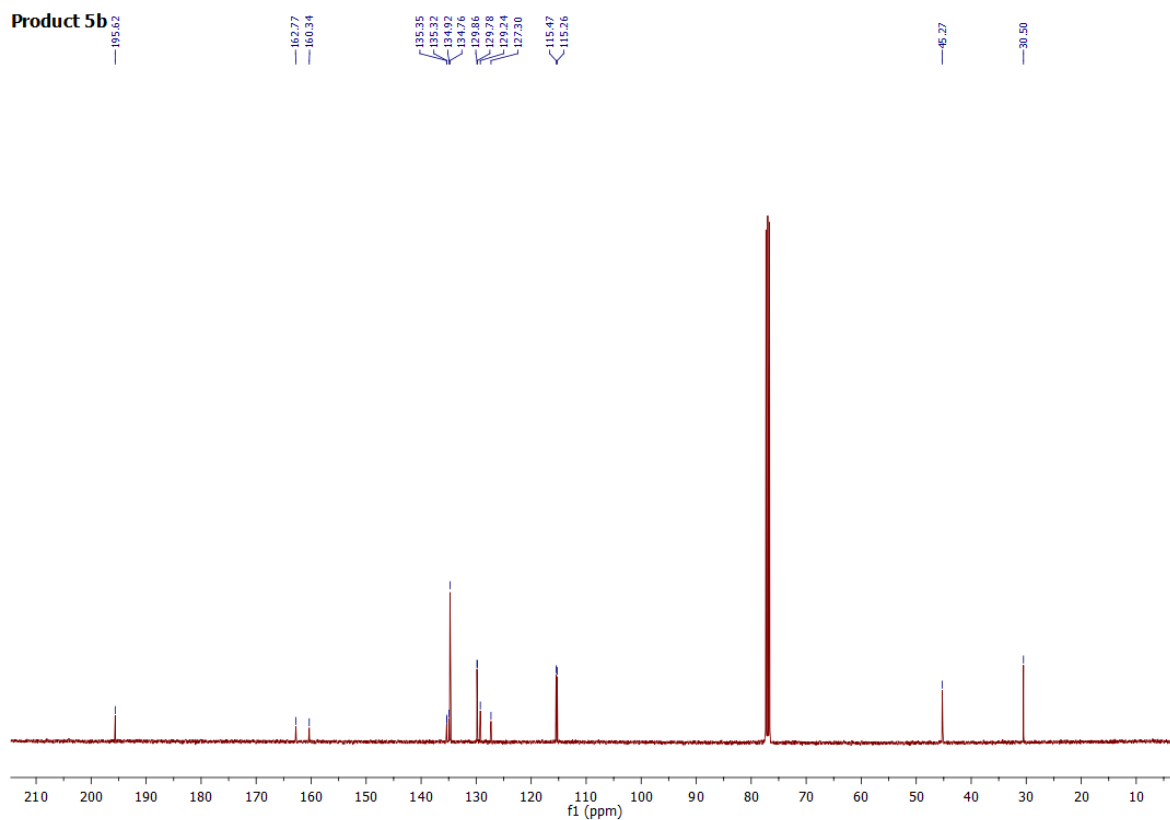


Figure S49. ^{13}C NMR (100 MHz, CDCl_3) of *S,S'*-1,4-phenylene bis(3-(4-fluorophenyl)propanethioate) (5b)

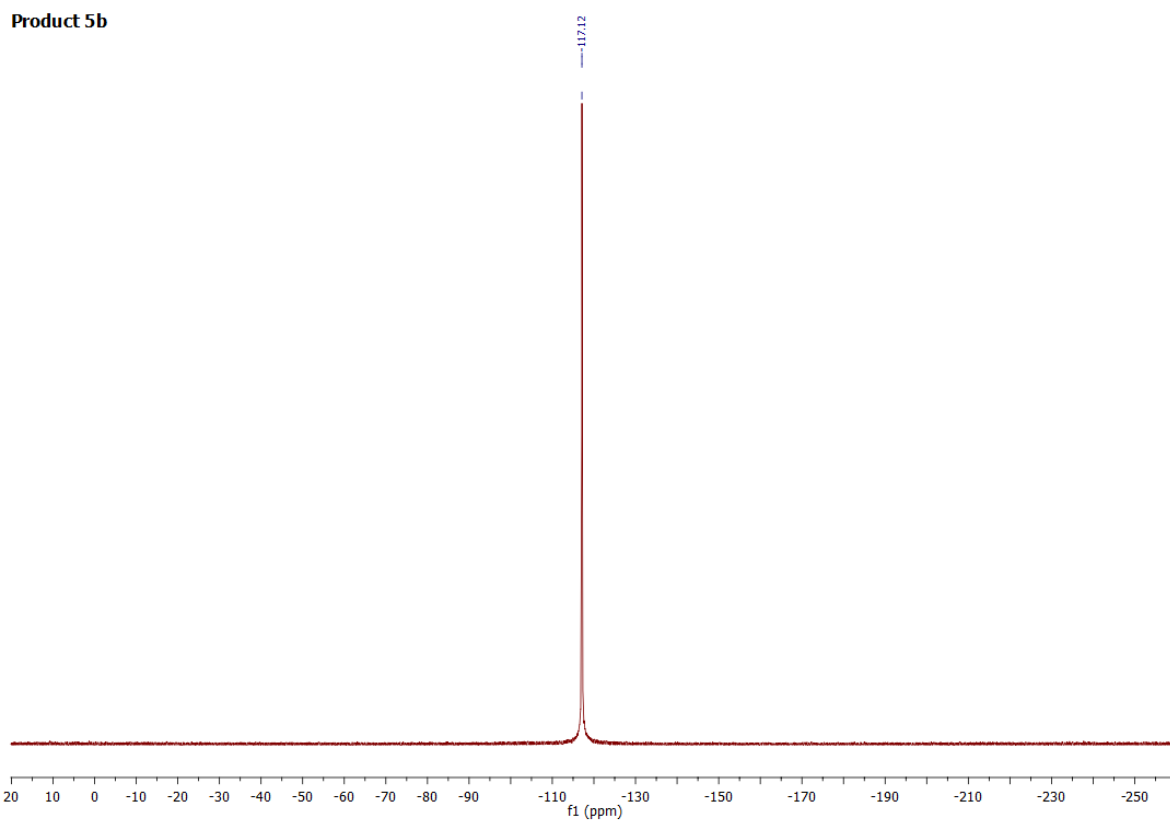


Figure S50. ^{19}F NMR (282.6 MHz, CDCl_3) of *S,S'*-1,4-phenylene bis(3-(4-fluorophenyl)propanethioate) (5b)

Product 5c

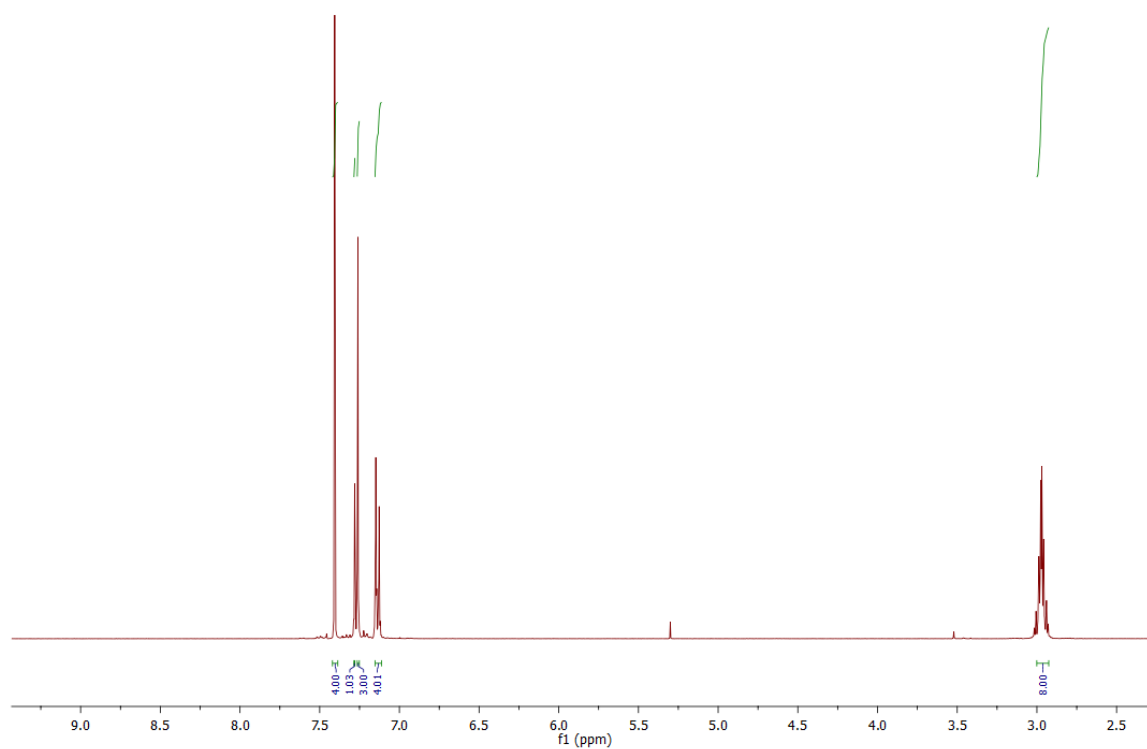


Figure S51. ^1H NMR (400 MHz, CDCl_3) of *S,S'*-1,4-phenylene bis(3-(4-chlorophenyl)propane-thioate) (5c)

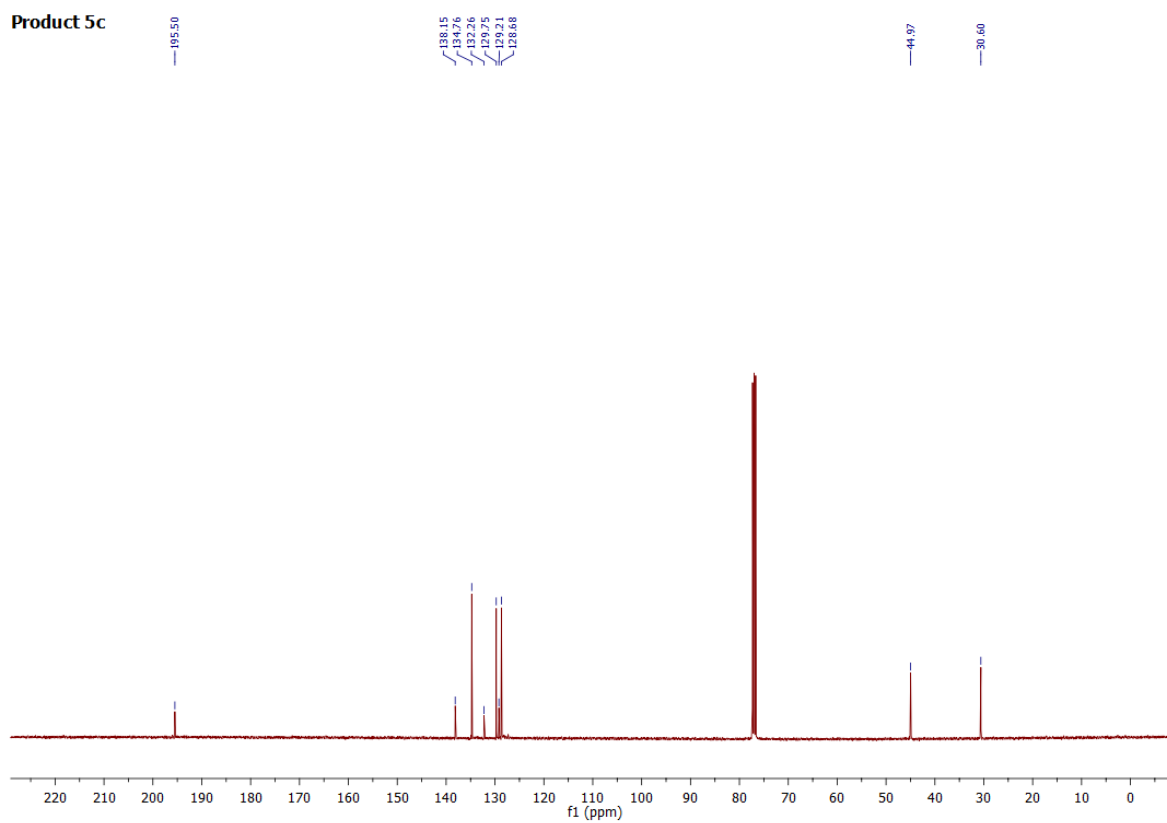


Figure S52. ^{13}C NMR (100 MHz, CDCl_3) of *S,S'*-1,4-phenylene bis(3-(4-chlorophenyl)propane-thioate) (5c)

Product 5d

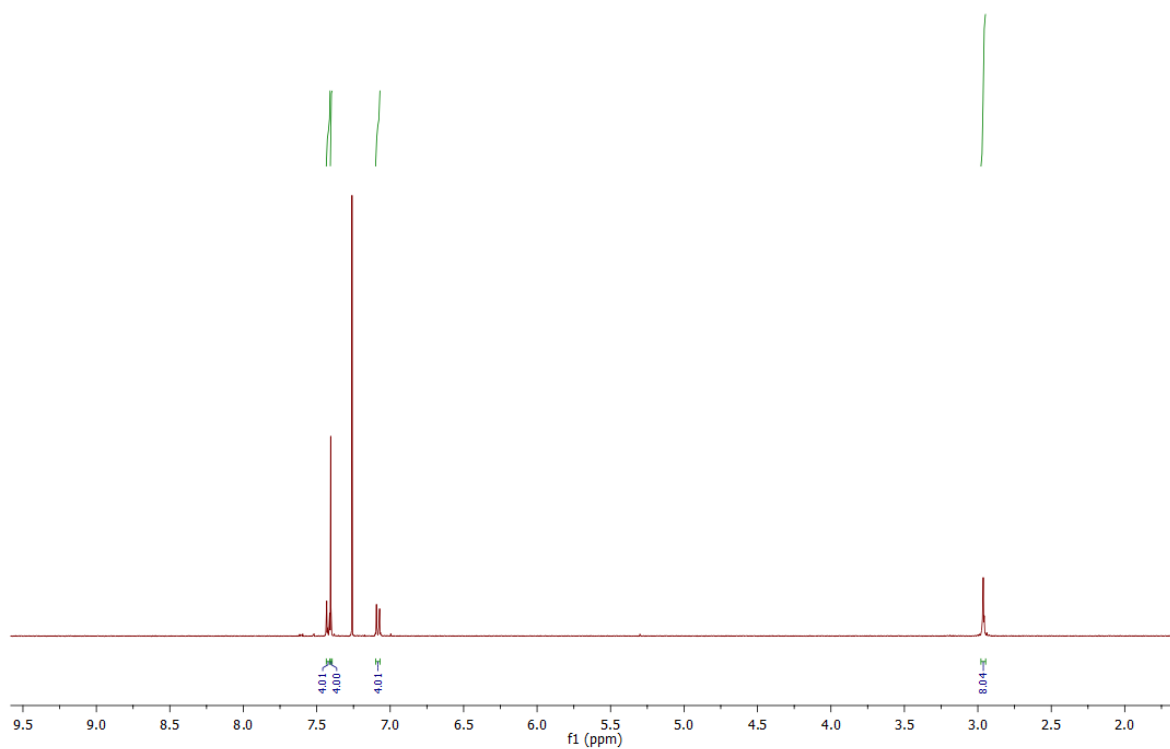


Figure S53. ¹H NMR (400 MHz, CDCl₃) of *S,S'*-1,4-phenylene bis(3-(4-bromophenyl)propanethioate) (5d)

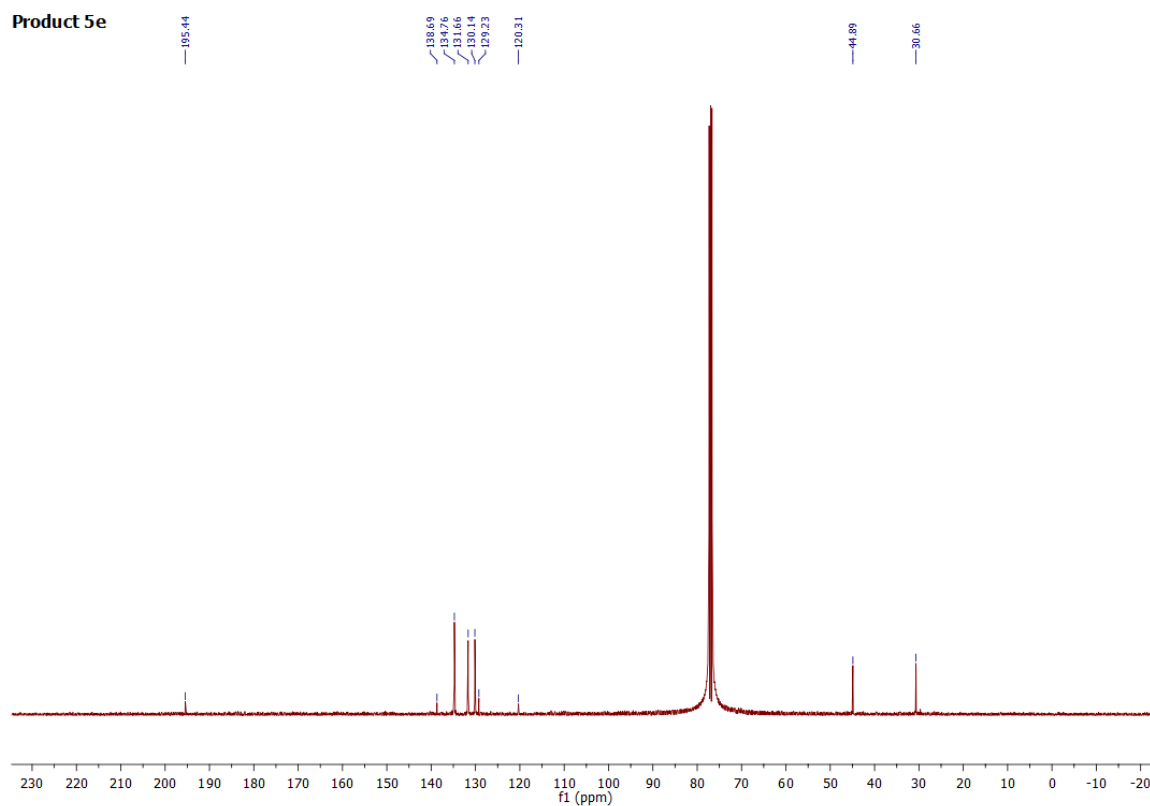


Figure S54. ¹³C NMR (100 MHz, CDCl₃) of *S,S'*-1,4-phenylene bis(3-(4-bromophenyl)propanethioate) (5d)

Product 5e

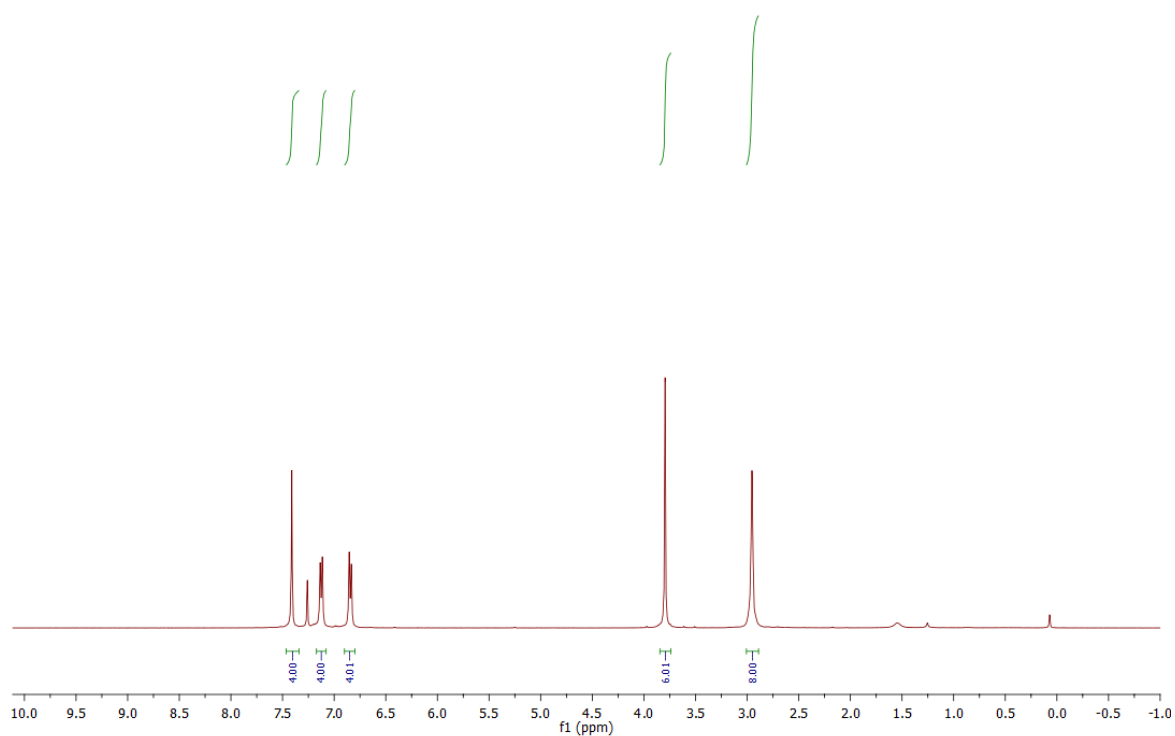


Figure S55. ¹H NMR (400 MHz, CDCl₃) of *S,S'*-1,4-phenylene bis(3-(4-methoxyphenyl)propanethioate) (5e)

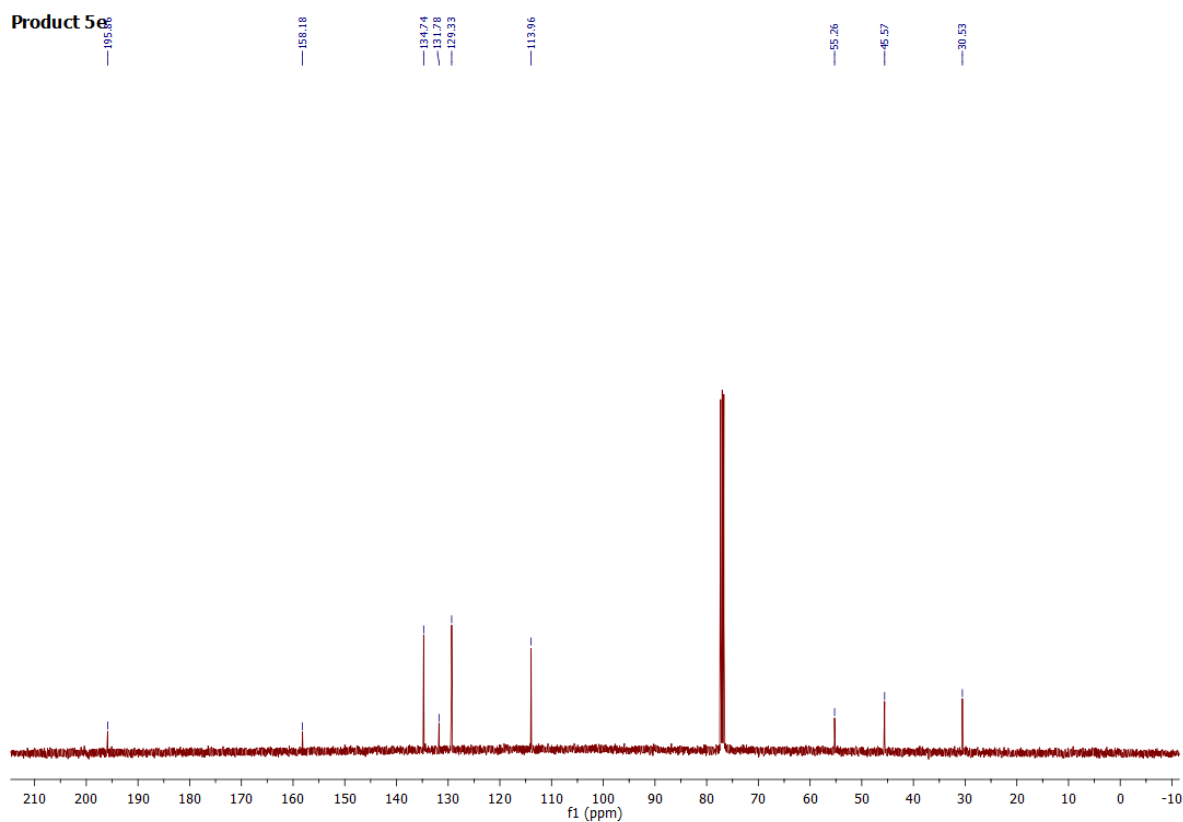


Figure S56. ¹³C NMR (100 MHz, CDCl₃) of *S,S'*-1,4-phenylene bis(3-(4-methoxyphenyl)propanethioate) (5e)

Product 5f

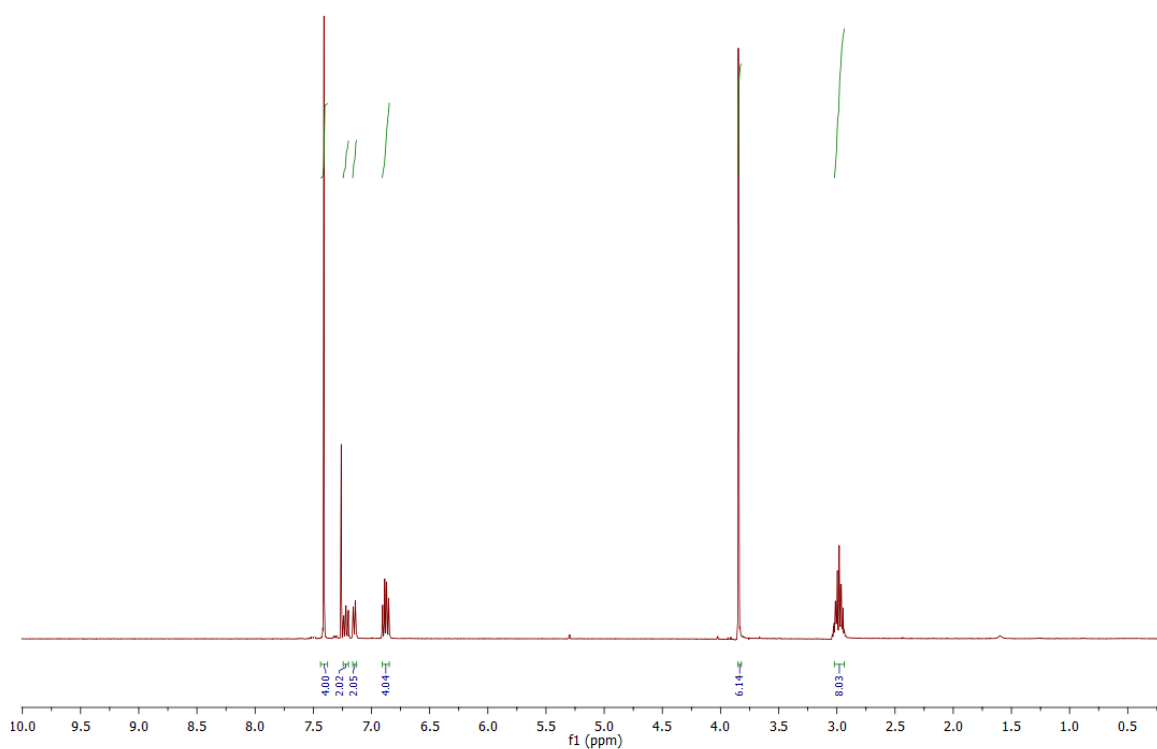


Figure S57. ^1H NMR (400 MHz, CDCl_3) of *S,S'*-1,4-phenylene bis(3-(2-methoxyphenyl)propanethioate) (5f)

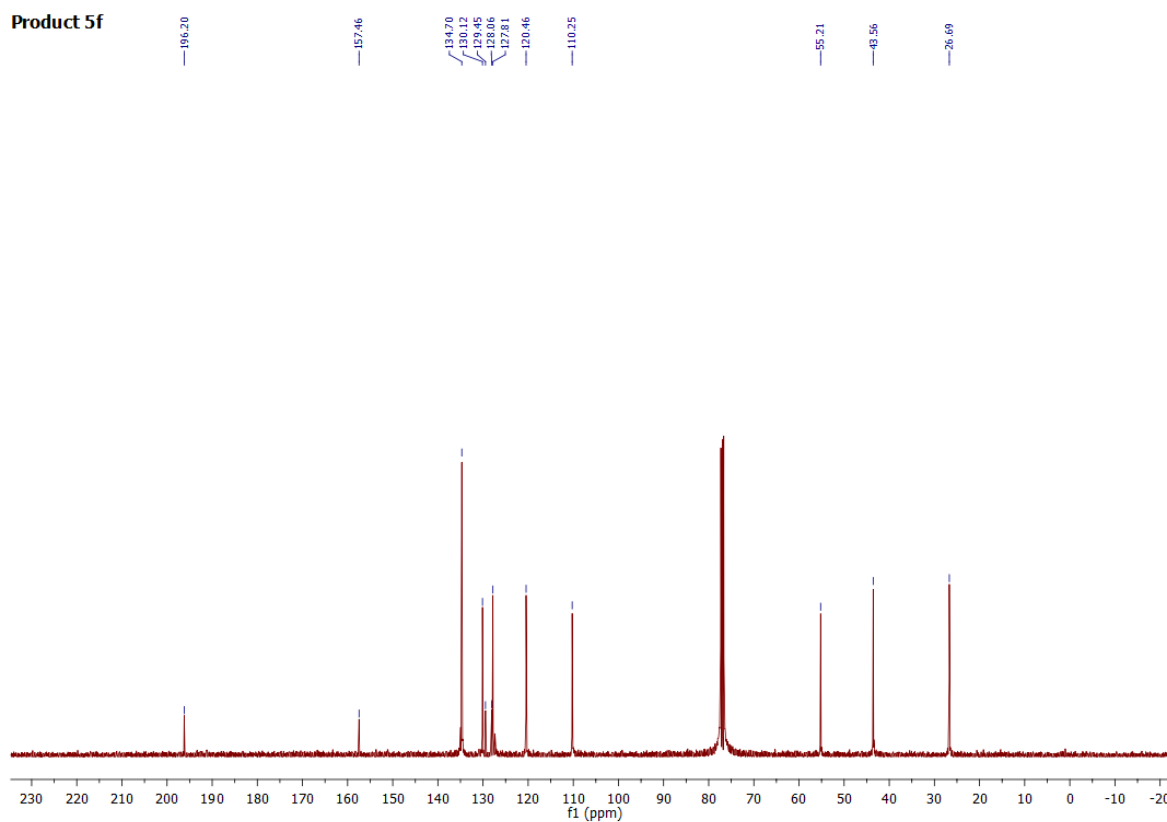


Figure S58. ^{13}C NMR (100 MHz, CDCl_3) of *S,S'*-1,4-phenylene bis(3-(2-methoxyphenyl)propanethioate) (5f)

4. References

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