Electronic Supplementary Information

Base-mediated synthesis of cyclic dithiocarbamates from 1-amino-3-chloropropan-2-ol derivatives and carbon disulfide

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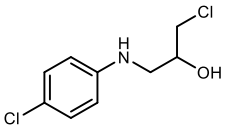
General Information

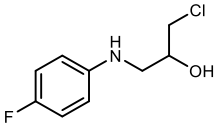
All reagents and solvents were commercial grade and purified prior to use when necessary. Thin layer chromatography (TLC) was performed using TLC aluminum sheets from Merck (silica gel 60 F_{254}, 200 μm), and flash chromatography utilized silica gel from Fuji Silysia Chemical (PSQ60B, 60 μm). Products were visualized by ultraviolet (UV) light and/or TLC stains. Melting points were measured on a Yanaco micro melting point apparatus and were not corrected. Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker Fourier 300 (300 MHz). Chemical shifts are measured relative to residual solvent peaks as an internal standard set to 0.00 (^{1}H) for TMS and 77.0 (^{13}C{^{1}H}) for $CDCl_3$. ^{13}C{^{1}H} NMR peak assignments were confirmed by DEPT135. Data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sep = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. Infrared (IR) spectra were recorded on a Jasco FT/IR-4200 spectrophotometer and are reported in wavenumbers (cm^{-1}). All compounds were analyzed as neat films on a potassium bromide (KBr) plate. Mass spectra were recorded on a Bruker micrOTOF II mass spectrometer by the ionization method noted. A post-acquisition gain correction was applied using sodium formate (HCO_2Na) as the lock mass.

Preparation of Starting Materials

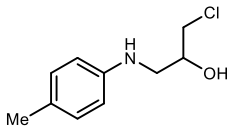
1a-1i and **1n-1p** were prepared according to the literature.[1]



1-Chloro-3-[(4-chlorophenyl)amino]propan-2-ol (2k). To a mixture of *p*-chloroaniline (637.9 mg, 5.0 mmol) and epichlorohydrin (395 μL, 5.0 mmol) was added LiBr (22.0 mg, 0.25 mmol) at room temperature. After stirring at room temperature for 4 h, the resulting mixture was directly purified by flash column chromatography (SiO_2: 25 g, Hexane:EtOAc = 5:1) to give a white solid (596.5 mg, 54%). R_f = 0.30 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 75-76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.11 (m, 2H), 6.60-6.55 (m, 2H), 4.07 (ddt, *J* = 7.2, 6.0, 4.5 Hz, 1H), 3.69 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.62 (dd, *J* = 11.1, 6.0 Hz, 1H), 3.35 (dd, *J* = 13.2, 4.5 Hz, 1H), 3.20 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.66 (br s, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 146.3 (C), 129.2 (CH), 122.8 (C), 114.4 (CH), 69.8 (CH), 47.6 (CH_2), 47.1 (CH_2); IR (KBr) 3337, 3215, 2867, 2831, 1497, 1239, 1086, 820, 745, 666 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_9H_{12}Cl_2NO$ 220.0290, found 220.0299.



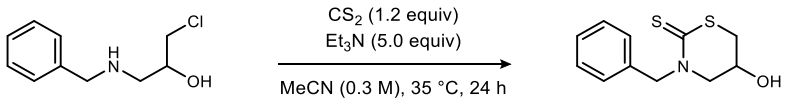
1-Chloro-3-[(4-fluorophenyl)amino]propan-2-ol (2l). To a mixture of *p*-fluoroaniline (556.0 mg, 5.0 mmol) and epichlorohydrin (395 μL, 5.0 mmol) was added LiBr (22.0 mg, 0.25 mmol) at room temperature. After stirring at room temperature for 4 h, the resulting mixture was directly purified by flash column chromatography (SiO_2: 25 g, Hexane:CH_2Cl_2 = 2:1–CH_2Cl_2) to give a white solid (563.0 mg, 55%). R_f = 0.40 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 58-59 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94-6.86 (m, 2H), 6.63-6.56 (m, 2H), 4.07 (ddt, *J* = 7.2, 6.0, 4.5 Hz, 1H), 3.70 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.64 (dd, *J* = 11.4, 6.0 Hz, 1H), 3.34 (dd, *J* = 12.9, 4.5 Hz, 1H), 3.19 (dd, *J* = 12.9, 7.2 Hz, 1H), 2.51 (br s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.3 (d, *J* = 236.0 Hz, C), 144.1 (d, *J* = 1.8 Hz, C), 115.8 (d, *J* = 22.0 Hz, CH), 114.3 (d, *J* = 7.2 Hz, CH), 69.8 (CH), 47.8 (CH_2), 47.7 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ -126.9; IR (KBr) 3282, 3137, 2966, 2929, 2850, 1512, 1430, 1223, 1128, 1103, 1027, 916, 824, 770, 708, 687 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_9H_{12}ClFNO$ 204.0586, found 204.0584.



1-Chloro-3-[(4-methylphenyl)amino]propan-2-ol (2m). To a mixture of *p*-toluidine (536.0 mg, 5.0 mmol) and epichlorohydrin (395 μL, 5.0 mmol) was added LiBr (22.0 mg, 0.25 mmol) at room temperature. After stirring at room temperature for 4 h, the resulting mixture was directly purified by flash column chromatography (SiO_2: 20 g, Hexane:EtOAc = 5:1) to give a white solid (667.9 mg, 67%). R_f = 0.35 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 76-77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02-6.99 (m, 2H), 6.60-6.56 (m, 2H), 4.05 (ddt, *J* = 7.2, 6.0, 4.5 Hz, 1H), 3.67 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.61 (dd, *J* = 11.1, 6.0 Hz, 1H), 3.34 (dd, *J* = 13.2, 4.5 Hz, 1H), 3.19 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.99 (br s, 2H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.4 (C), 129.8 (CH), 127.6 (C), 113.5 (CH), 69.8 (CH), 47.7 (CH_2), 47.5 (CH_2), 20.3 (CH_3); IR (KBr) 3337, 3196, 2923, 2851, 1238, 1088, 1057, 820, 742 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{15}ClNO$ 200.0837, found 200.0840.

General Procedure for the Reaction of 1 with Carbon Disulfide

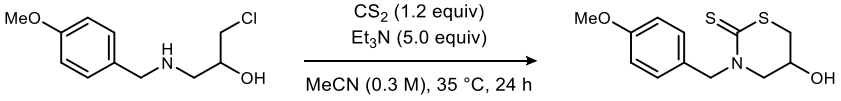
To an oven-dried 10 mL test tube equipped with a stir bar was added **1** (0.3 mmol, 1.0 equiv), MeCN (1.0 mL, 0.3 M), Et_3N (0.21 mL, 1.5 mmol, 5.0 equiv), and CS_2 (22 μL, 0.36 mmol, 1.2 equiv). After stirring at 35 °C for 24 h, the mixture was directly purified by flash column chromatography (SiO_2) to obtain **2**.



3-Benzyl-5-hydroxy-1,3-thiazinane-2-thione (2a). Prepared according to the general procedure using **1a** (59.9 mg, 0.30 mmol). Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 2:1) to obtain a white solid (66.5 mg, 93%). R_f = 0.25 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 112-113 °C; ^{1}H NMR (300 MHz, CD_3OD) δ 7.41-7.27 (m, 5H), 5.55 (d, *J* = 14.7 Hz, 1H), 5.15 (d, *J* = 14.7 Hz, 1H), 4.31-4.24 (m, 1H), 3.51 (ddd, *J* = 13.8, 3.3, 1.2 Hz, 1H), 3.41 (ddd, *J* = 13.8, 6.6, 1.2 Hz, 1H), 3.17. (ddd, *J* = 12.0, 3.6, 1.2 Hz, 1H), 2.93 (ddd, *J* = 12.0, 6.9, 1.2 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, CD_3OD) δ 193.9 (C), 136.8 (C), 129.7 (CH), 129.1 (CH), 128.9 (CH), 63.0 (CH), 59.1 (CH_2), 56.0 (CH_2), 39.0 (CH_2); IR (KBr) 3276, 3026, 2882, 1503, 1350, 939, 738, 696 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaOS_2$ 262.0331, found 262.0341.

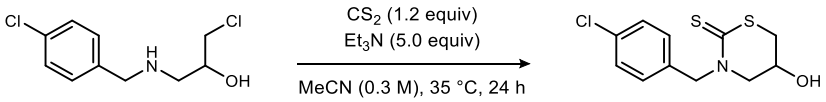
Procedure for gram scale synthesis: To an oven-dried 50 mL round-bottom flask equipped with a stir bar was added **1a** (1198.3 mg, 6.0 mmol), MeCN (20 mL, 0.3 M), Et_3N (4.2 mL, 30 mmol), and CS_2 (0.44 mL, 7.2 mmol). After stirring at 35 °C for 24 h, the mixture was treated with satd NH_4Cl aq (40 mL), and the aqueous layer was extracted with EtOAc (40 mL×3). The organic layers were combined, washed with brine (120 mL), dried over Na_2SO_4 and concentrated. The crude material was triturated with a EtOAc/Hexane (2 mL/8 mL) mixture, and the solid was collected by vacuum filtration and washed with Hexane (20 mL) to obtain **2a** as a white solid (1357.7 mg, 94%).

Procedure for one-pot synthesis: To an oven-dried 20 mL test tube equipped with a stir bar was added epichlorohydrin (138.9 mg, 1.5 mmol), ^{i}PrOH (5 mL, 0.3 M), and benzylamine (330 μL, 3.0 mmol). After stirring at 35 °C for 24 h, CS_2 (110 μL, 1.8 mmol) was added to the mixture. After stirring at 35 °C for 24 h, the mixture was directly purified by flash column chromatography (SiO_2: 25 g, Hexane:EtOAc = 2:1) to obtain **2a** as a white solid (300.6 mg, 84%).

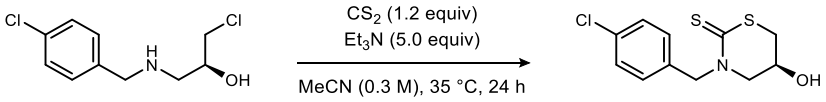


5-Hydroxy-3-(4-methoxybenzyl)-1,3-thiazinane-2-thione (2b). Prepared according to the general procedure using **1b** (68.9 mg, 0.30 mmol). Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 2:1) to obtain a white solid (72.9 mg, 90%). R_f = 0.20 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 133-134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 6.91-6.86 (m, 2H), 5.32 (d, *J* = 14.4 Hz, 1H), 5.25

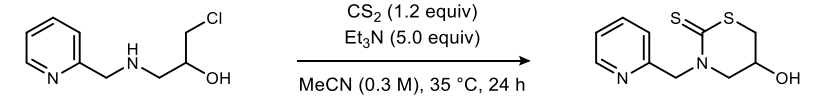
(d, *J* = 14.4 Hz, 1H), 4.41-4.33 (m, 1H), 3.81 (s, 3H), 3.46 (d, *J* = 4.2 Hz, 2H), 3.23 (dd, *J* = 12.3, 3.3 Hz, 1H), 2.95 (dd, *J* = 12.3, 6.3 Hz, 1H), 2.29 (d, *J* = 6.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 191.5 (C), 159.6 (C), 129.8 (CH), 126.9 (C), 114.3 (CH), 62.2 (CH), 57.6 (CH_2), 55.3 (CH_3), 54.5 (CH_2), 38.5 (CH_2); IR (KBr) 3269, 2925, 2881, 2839, 1513, 1502, 1352, 1232, 1187, 1061, 941, 837, 776 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaO_2S_2$ 292.0436, found 292.0427.



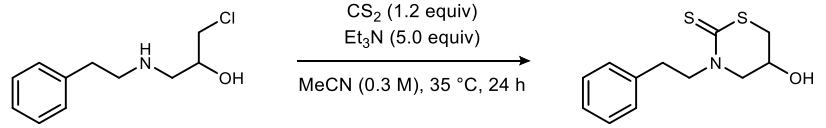
3-(4-Chlorobenzyl)-5-hydroxy-1,3-thiazinane-2-thione (2c). Prepared according to the general procedure using **1c** (70.3 mg, 0.30 mmol). Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 2:1) to obtain a white solid (77.5 mg, 94%). R_f = 0.25 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 157-158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.30 (m, 4H), 5.32 (s, 2H), 4.44-4.36 (m, 1H), 3.47 (d, *J* = 4.2 Hz, 2H), 3.26 (dd, *J* = 12.3, 3.3 Hz, 1H), 2.98 (ddt, *J* = 12.3, 6.3, 0.9 Hz, 1H), 2.25-2.23 (m, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 192.1 (C), 134.2 (C), 133.4 (C), 129.6 (CH), 129.1 (CH), 62.1 (CH), 57.5 (CH_2), 54.8 (CH_2), 38.5 (CH_2); IR (KBr) 3292, 3083, 2904, 1519, 1489, 1353, 1265, 1169, 1077, 1057, 930, 803 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{12}ClNNaOS_2$ 295.9941, found 295.9937.



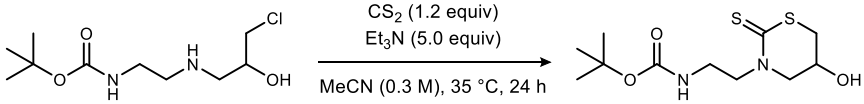
(*S*)-**2c**: Prepared according to the general procedure using (*S*)-**1c** (70.2 mg, 0.30 mmol). White solid (75.5 mg, 92%). The product was determined to be 99% ee by chiral HPLC analysis (Chiralpak AD-3, Hexane:EtOH = 85:15, 1.0 mL/min, t_r(*major*) = 22.7 min, t_r(*minor*) = 24.2 min, 220 nm, 35 °C); $[\alpha]_D^{23}$ -25.7 (*c* 0.1, $CHCl_3$, 99% ee).



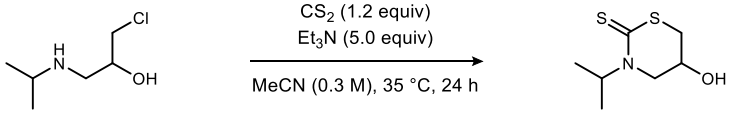
5-Hydroxy-3-(pyridin-2-ylmethyl)-1,3-thiazinane-2-thione (2d). Prepared according to the general procedure using **1d** (60.2 mg, 0.30 mmol). Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 1:1) to obtain a white solid (64.0 mg, 89%). R_f = 0.15 (EtOAc) visualized with $KMnO_4$; mp 140-141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (ddd, *J* = 5.1, 1.5, 0.9 Hz, 1H), 7.74 (td, *J* = 7.8, 1.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.29-7.24 (m, 1H), 6.91 (br s, 1H), 6.45 (d, *J* = 16.2 Hz, 1H), 4.62-4.58 (m, 1H), 4.44 (d, *J* = 16.2 Hz, 1H), 3.99 (ddd, *J* = 13.8, 4.2, 2.4 Hz, 1H), 3.84 (d, *J* = 13.8 Hz, 1H), 3.31 (dd, *J* = 12.3, 3.3 Hz, 1H), 3.10 (dddd, *J* = 12.3, 3.3, 2.4, 0.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 194.5 (C), 154.9 (C), 148.6 (CH), 137.6 (CH), 122.98 (CH), 122.95 (CH), 62.3 (CH), 57.7 (CH_2), 56.9 (CH_2), 40.4 (CH_2); IR (KBr) 3086, 2913, 2728, 1599, 1506, 1480, 1351, 1183, 1172, 1082, 1055, 982, 946, 759 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{12}N_2NaOS_2$ 263.0283, found 263.0301.



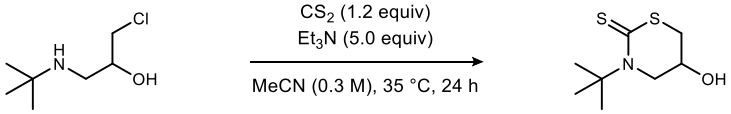
5-Hydroxy-3-(2-phenylethyl)-1,3-thiazinane-2-thione (2e). Prepared according to the general procedure using **1e** (64.3 mg, 0.30 mmol). Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 2:1) to obtain a white solid (67.2 mg, 88%). R_f = 0.15 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 153-154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.22 (m, 5H), 4.37-4.28 (m, 1H), 4.26-4.14 (m, 2H), 3.46-3.34 (m, 2H), 3.22-3.00 (m, 3H), 2.94-2.88 (m, 1H), 2.18 (d, *J* = 7.5 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 190.5 (C), 138.0 (C), 128.9 (CH), 128.7 (CH), 126.8 (C), 62.1 (CH), 58.1 (CH_2), 57.0 (CH_2), 38.3 (CH_2), 32.4 (CH_2); IR (KBr) 3341, 2942, 2871, 1518, 1358, 1147, 1071, 951, 754, 704 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NNaOS_2$ 276.0487, found 276.0481.



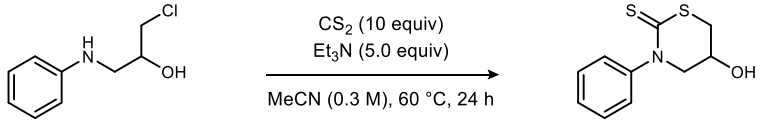
***tert*-Butyl [2-(5-hydroxy-2-thioxo-1,3-thiazinan-3-yl)ethyl]carbamate (2f).** Prepared according to the general procedure using **1f** (75.8 mg, 0.30 mmol). Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 2:1) to obtain a colorless oil (59.9 mg, 68%). R_f = 0.15 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.06-5.02 (m, 1H), 4.79-4.71 (m, 1H), 4.53-4.46 (m, 1H), 3.77-3.54 (m, 5H), 3.45-3.35 (m, 1H), 3.27 (dd, *J* = 12.6, 3.3 Hz, 1H), 2.94 (ddd, *J* = 12.6, 5.1, 0.9 Hz, 1H), 1.45 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.8 (C), 156.8 (C), 80.1 (C), 61.6 (CH), 56.0 (CH_2), 54.8 (CH_2), 38.4 (CH_2), 37.8 (CH_2), 28.3 (CH_3); IR (KBr) 3354, 2976, 2930, 1687, 1506, 1366, 1252, 1167 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{20}N_2NaO_3S_2$ 315.0808, found 315.0819.



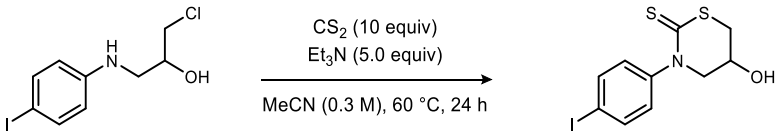
5-Hydroxy-3-(propan-2-yl)-1,3-thiazinane-2-thione (2g). Prepared according to the general procedure using **1g** (45.7 mg, 0.30 mmol). Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 2:1) to obtain a white solid (48.7 mg, 85%). R_f = 0.15 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 115-116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.99 (sept, *J* = 6.9 Hz, 1H), 4.48-4.44 (m, 1H), 3.45 (ddd, *J* = 13.8, 5.7, 1.2 Hz, 1H), 3.41-3.36 (m, 1H), 3.21 (ddd, *J* = 12.0, 3.9, 0.9 Hz, 1H,), 2.96-2.90 (m, 1H), 2.56 (br s, 1H), 1.23 (d, *J* = 6.9 Hz, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 190.3 (C), 62.4 (CH), 52.7 (CH), 48.3 (CH_2), 38.1 (CH_2), 18.7 (CH_3), 18.6 (CH_3); IR (KBr) 3325, 2976, 2891, 1488, 1262, 1182, 1071, 933, 900, 818, 646 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_7H_{13}NNaOS_2$ 214.0331, found 214.0346.



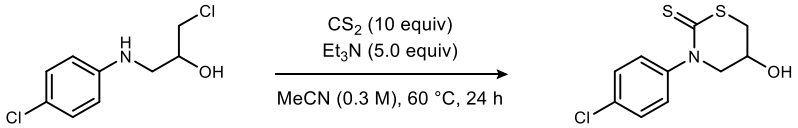
3-*tert*-Butyl-5-hydroxy-1,3-thiazinane-2-thione (2h). Prepared according to the general procedure using **1h** (44.9 mg, 0.30 mmol). Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 2:1) to obtain a white solid (50.6 mg, 82%). R_f = 0.25 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 102-103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.54-4.45 (m, 1H), 3.69 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.62 (dd, *J* = 13.8, 3.9 Hz 1H), 3.14 (dd, *J* = 12.6, 6.0 Hz, 1H), 2.80 (dd, *J* = 12.6, 5.4 Hz, 1H), 2.39 (d, *J* = 6.3 Hz, 1H), 1.74 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.8 (C), 66.4 (CH), 64.8 (C), 54.3 (CH_2), 39.3 (CH_2), 28.8 (CH_3); IR (KBr) 3314, 2987, 2954, 2936, 1324, 1190, 1164, 1112, 1067, 1029, 888, 846, 799 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_8H_{15}NNaOS_2$ 228.0487, found 228.0508.



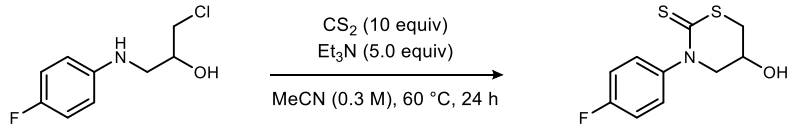
5-Hydroxy-3-phenyl-1,3-thiazinane-2-thione (2i). Prepared according to the general procedure using **1i** (55.9 mg, 0.30 mmol) and CS_2 (181 μL, 3.0 mmol, 10 equiv) at 60 °C for 24 h. Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 5:1–2:1) to obtain a white solid (58.7 mg, 87%). R_f = 0.20 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 115-116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.43 (m, 2H), 7.40-7.34 (m, 1H), 7.29-7.25 (m, 2H), 4.64-4.57 (m, 1H), 3.88 (d, *J* = 3.6 Hz, 2H), 3.44 (dd, *J* = 12.6, 3.3 Hz, 1H), 2.95 (ddt, *J* = 12.6, 5.4, 1.2 Hz, 1H), 2.66 (br s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.9 (C), 146.5 (C), 129.8 (CH), 128.4 (CH), 126.7 (CH), 61.8 (CH), 59.8 (CH_2), 38.8 (CH_2); IR (KBr) 3277, 2925, 1479, 1327, 1071, 1035, 949, 741, 694 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{11}NNaOS_2$ 248.0174, found 248.0189.



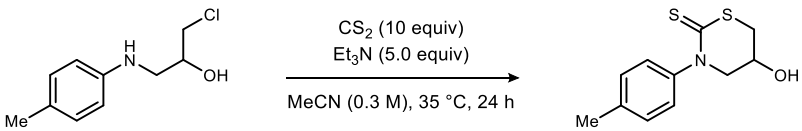
5-Hydroxy-3-(4-iodophenyl)-1,3-thiazinane-2-thione (2j). Prepared according to the general procedure using **1j** (93.7 mg, 0.30 mmol) and CS_2 (181 μL, 3.0 mmol, 10 equiv) at 60 °C for 24 h. Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 5:1–2:1) to obtain a white solid (31.6 mg, 30%). R_f = 0.20 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 139-140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.76 (m, 2H), 7.06-7.01 (m, 2H), 4.62-4.58 (m, 1H), 3.88-3.78 (m, 2H), 3.44 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.09 (dddd, *J* = 12.6, 5.4, 1.2, 0.9 Hz, 1H), 2.54 (d, *J* = 6.0 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.2 (C), 146.1 (C), 139.1 (CH), 128.8 (CH), 93.8 (C), 61.8 (CH), 59.6 (CH_2), 38.9 (CH_2); IR (KBr) 3304, 2920, 1480, 1439, 1317, 1225, 1065, 1038, 948, 849, 814, 751 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{10}INNaOS_2$ 373.9141, found 373.9132.



3-(4-Chlorophenyl)-5-Hydroxy-1,3-thiazinane-2-thione (2k). Prepared according to the general procedure using **1k** (66.1 mg, 0.30 mmol) and CS_2 (181 μL, 3.0 mmol, 10 equiv) at 60 °C for 24 h. Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 5:1–2:1) to obtain a white solid (40.1 mg, 51%). R_f = 0.15 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 157-158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.41 (m, 2H), 7.25-7.20 (m, 2H), 4.65-4.57 (m, 1H), 3.86-3.84 (m, 2H), 3.45 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.10 (ddt, *J* = 12.6, 5.7, 1.2 Hz, 1H), 2.59 (d, *J* = 6.9 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.3 (C), 144.8 (C), 134.2 (C), 130.1 (CH), 128.3 (CH), 61.8 (CH), 59.7 (CH_2), 38.9 (CH_2); IR (KBr) 3303, 2883, 2807, 1488, 1437, 1316, 1064, 1038, 949, 850, 818, 712 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{10}ClNNaOS_2$ 281.9785, found 281.9811.

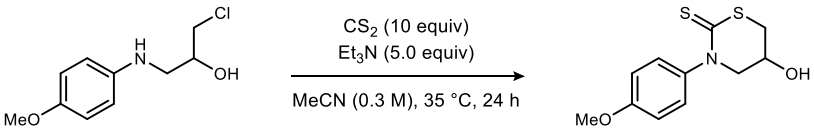


3-(4-Fluorophenyl)-5-Hydroxy-1,3-thiazinane-2-thione (2l). Prepared according to the general procedure using **1l** (61.2 mg, 0.30 mmol) and CS_2 (181 μL, 3.0 mmol, 10 equiv) at 60 °C for 24 h. Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 2:1) to obtain a white solid (69.0 mg, 95%). R_f = 0.15 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 156-157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.22 (m, 2H), 7.18-7.10 (m, 2H), 4.64-4.56 (m, 1H), 3.90-3.80 (m, 2H), 3.45 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.10 (ddt, *J* = 12.6, 5.4, 1.2 Hz, 1H), 2.56 (d, *J* = 6.9 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.4 (C), 161.9 (d, *J* = 248.7 Hz, C), 142.4 (d, *J* = 3.3 Hz, C), 128.6 (d, *J* = 8.8 Hz, CH), 116.8 (d, *J* = 23.1 Hz, CH), 61.8 (CH), 59.9 (CH_2), 39.0 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.3; IR (KBr) 3303, 2983, 2914, 1508, 1472, 1321, 1239, 1215, 1066, 1037, 949, 856, 828, 726 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{10}FNNaOS_2$ 266.0080, found 266.0082.



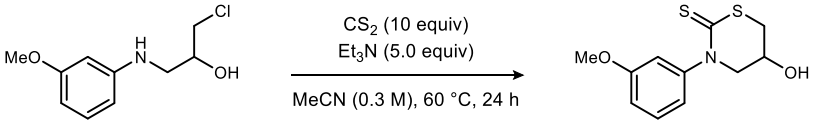
5-Hydroxy-3-(4-methylphenyl)-1,3-thiazinane-2-thione (2m). Prepared according to the general procedure using **1m** (60.0 mg, 0.30 mmol) and CS_2 (181 μL, 3.0 mmol, 10 equiv). Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 5:1–2:1) to obtain a white solid (61.9 mg, 86%). R_f = 0.25 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 157-158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.24 (m, 2H), 7.17-7.13 (m, 2H), 4.62-4.55 (m, 1H), 3.89-3.80 (m, 2H), 3.44 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.09 (ddt, *J* = 12.6, 5.7, 1.2 Hz, 1H), 2.78 (d, *J* = 6.3 Hz, 1H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.9 (C), 144.0 (C), 138.3 (C), 130.5 (CH), 126.3 (CH), 61.8 (CH), 59.9 (CH_2), 38.8 (CH_2), 21.2 (CH_3); IR (KBr) 3428, 2923, 2895,

1508, 1476, 1328, 1227, 1166, 1073, 1038, 943, 809 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaOS_2$ 262.0331, found 262.0333.

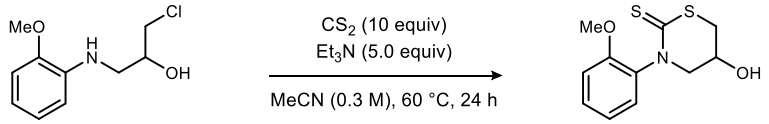


5-Hydroxy-3-(4-methoxyphenyl)-1,3-thiazinane-2-thione (2n). Prepared according to the general procedure using **1n** (64.9 mg, 0.30 mmol) and CS_2 (181 μL, 3.0 mmol, 10 equiv). Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 2:1) to obtain a white solid (70.6 mg, 92%). R_f = 0.10 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 172-173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21-7.16 (m, 2H), 6.98-6.93 (m, 2H), 4.62-4.55 (m, 1H), 3.86 (d, *J* = 3.6 Hz, 1H), 3.82. (s, 3H), 3.43 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.08 (ddd, *J* = 12.6, 5.7, 0.9 Hz, 1H), 2.58 (d, *J* = 7.2 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.1 (C), 159.1 (C), 139.4 (C), 127.7 (CH), 114.9 (CH), 62.0 (CH), 60.1 (CH_2), 55.4 (CH_3), 38.9 (CH_2); IR (KBr) 3350, 2955, 1507, 1476, 1442, 1291, 1243, 1216, 1066, 918, 828, 725, 630 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaO_2S_2$ 278.0280, found 278.0284.

Procedure for one-pot synthesis: To an oven-dried 20 mL test tube equipped with a stir bar was added epichlorohydrin (138.9 mg, 1.5 mmol), *p*-anisidine (369.5 mg, 3.0 mmol), and LiBr (6.5 mg, 75 μmol). After stirring at 35 °C for 24 h, MeCN (5 mL, 0.3 M), Et_3N (1.05 mL, 7.5 mmol), and CS_2 (0.91 mL, 15 mmol) were added to the mixture. After stirring at 35 °C for 24 h, the mixture was directly purified by flash column chromatography (SiO_2: 25 g, Hexane:EtOAc = 2:1) to obtain **2n** as a white solid (352.6 mg, 92%).



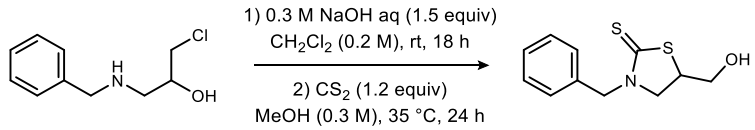
5-Hydroxy-3-(3-methoxyphenyl)-1,3-thiazinane-2-thione (2o). Prepared according to the general procedure using **1o** (64.9 mg, 0.30 mmol) and CS_2 (181 μL, 3.0 mmol, 10 equiv) at 60 °C for 24 h. Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 5:1–2:1) to obtain a white solid (47.6 mg, 62%). R_f = 0.20 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 165-166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (t, *J* = 8.1 Hz, 1H), 6.91 (ddd, *J* = 8.1, 2.1, 0.9 Hz, 1H), 6.86 (ddd, *J* = 8.1, 2.1, 0.9 Hz, 1H), 6.81 (t, *J* = 2.1 Hz, 1H), 4.62-4.56 (m, 1H), 3.87 (d, *J* = 3.6 Hz, 2H), 3.82 (s, 3H), 3.44 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.09 (ddt, *J* = 12.6, 5.7, 1.2 Hz, 1H), 2.55-2.53 (m, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.7 (C), 160.6 (C), 147.5 (C), 130.5 (CH), 118.7 (CH), 114.1 (CH), 112.5 (CH), 61.9 (CH), 59.8 (CH_2), 55.5 (CH_3), 38.8 (CH_2); IR (KBr) 3303, 2980, 1600, 1483, 1440, 1329, 1289, 1212, 1187, 1071, 1031, 953, 802, 790, 692 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaO_2S_2$ 278.0280, found 278.0290.



5-Hydroxy-3-(2-methoxyphenyl)-1,3-thiazinane-2-thione (2p). Prepared according to the general procedure using **1p** (64.9 mg, 0.30 mmol) and CS_2 (181 μL, 3.0 mmol, 10 equiv) at 60 °C for 24 h. Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 5:1–2:1) to obtain a white solid (17.6 mg, 23%). R_f = 0.25 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; mp 132-133 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.32 (m, 1H), 7.26-7.21 (m, 1H), 7.08-6.99 (m, 2H), 4.59-4.52 (m, 1H), 3.93-3.65 (m, 2H+1H×77/100), 3.91 (s, 3H×77/100), 3.86 (s, 3H×23/100), 3.41-3.35 (m, 1H), 3.16-3.05 (m, 1H), 2.80 (br s, 1H×23/100); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.7 (C, *major*), 193.0 (C, *minor*), 154.0 (C, *minor*), 152.7 (C, *major*), 134.6 (C, *minor*), 134.5 (C, *major*), 130.0 (CH, *major*), 129.8 (CH, *minor*), 128.7 (CH, *major*), 128.5 (CH, *minor*), 121.7 (CH, *major*), 121.3 (CH, *minor*), 112.7 (CH, *major*), 112.5 (CH, *minor*), 62.1 (CH, *minor*), 61.6 (CH, *major*), 58.6 (CH_2, *major*), 58.5 (CH_2, *minor*), 56.3 (CH_3, *major*), 55.9 (CH_3, *minor*), 39.6 (CH_2, *major*), 38.7 (CH_2, *minor*); IR (KBr) 3332, 2988, 2834, 1500, 1472, 1298, 1272, 1227, 1063, 917, 763, 739, 637 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaO_2S_2$ 278.0280, found 278.0286.

Appendix

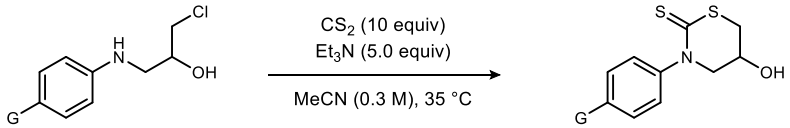
We performed the reaction of an epoxy amine with CS_2. The epoxy amine was freshly prepared by treatment of **1a** with aqueous NaOH in CH_2Cl_2 followed by extraction, and used directly for the reaction without further purification due to its instability. As a result, five-membered cyclic carbamate **2a'** was obtained in high yield with high selectivity (88% combined yield, **2a'**:**2a** = >20:1).

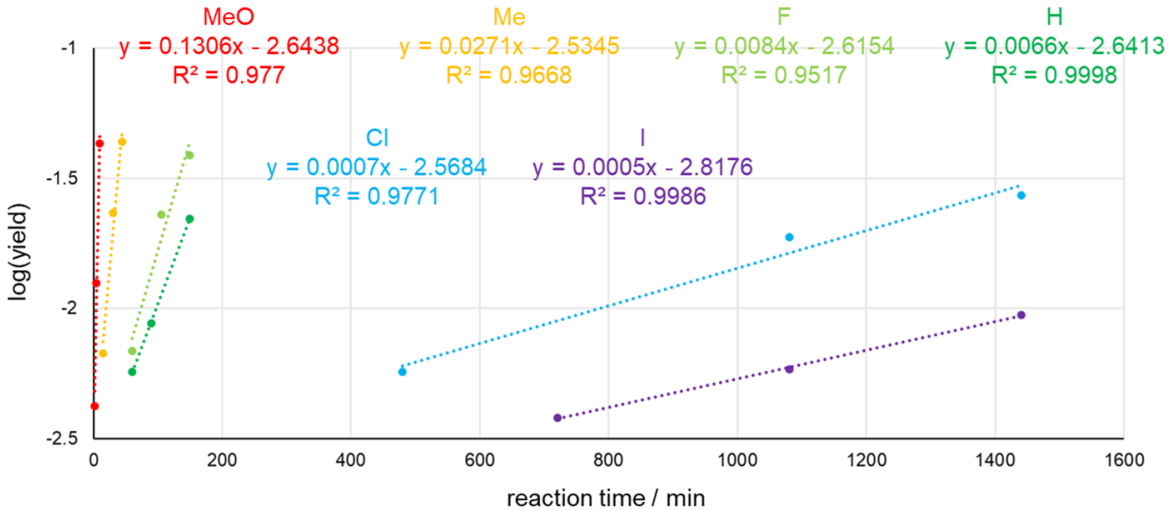


3-Benzyl-5-(hydroxymethyl)-1,3-thiazolidine-2-thione (2a'). To an oven-dried test tube equipped with a stir bar was added **1a** (59.9 mg, 0.30 mmol), CH_2Cl_2 (1.5 mL, 0.2 M), and 0.3 M NaOH aq (1.5 mL, 1.5 equiv). After stirring at rt for 18 h, the organic layer was separated, washed with H_2O (×2), dried over Na_2SO_4, and concentrated. The unpurified material was diluted with MeOH (1.0 mL, 0.3 M) and then CS_2 (22 μL, 0.36 mmol, 1.2 equiv) was added to the solution. After stirring at 35 °C for 24 h, the mixture was concentrated and purified by flash column chromatography (SiO_2: 8 g, Hexane:EtOAc = 3:1) to obtain a colorless oil (63.5 mg, 88% combined yield, 98:2 mixture of **2a'** and **2a**). R_f = 0.25 (Hexane:EtOAc = 1:1) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.24 (m, 5H), 4.96 (s, 2H), 4.00 (dd, *J* = 12.0, 7.5 Hz, 1H), 3.87 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.73-3.58 (m, 3H), 2.72 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6 (C), 134.8 (C), 129.0 (CH), 128.3 (CH), 128.2 (CH), 63.9 (CH_2), 57.7 (CH_2), 52.7 (CH_2), 44.0 (CH); HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaOS_2$ 262.0331, found 262.0333.

We monitored the reaction of **1** (0.3 mmol) with CS_2 (10 equiv) using Et_3N (5.0 equiv) in MeCN (0.3 M) at 35 °C by ^{1}H NMR. Samplings from the reaction were taken to perform ^{1}H NMR experiments.

Table S1. Monitoring Reaction Progress[a]



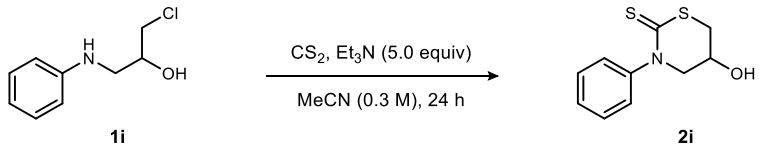


	MeO	Me	H	F	Cl	I
1	9.3 (2.5)	11.4 (15)	10.6 (60)	11.5 (60)	10.6 (480)	8.9 (720)
2	14.9 (5.0)	19.5 (30)	12.8 (90)	19.4 (105)	17.8 (1080)	10.7 (1080)
3	25.5 (10)	25.7 (45)	19.1 (150)	24.4 (150)	20.9 (1440)	13.2 (1440)

[a]NMR yield of **2** is shown. Reaction time is shown in parentheses.

In the case of **1i** bearing a phenyl group, a decreased yield was obtained under the optimal conditions for *N*-alkyl groups. After several trials, we found that the reaction using 10 equiv of CS_2 at 60 °C for 24 h furnished product **2i** in high yield. These conditions were used for subsequent reactions.

Table S2. Optimization of Reaction Conditions[a]

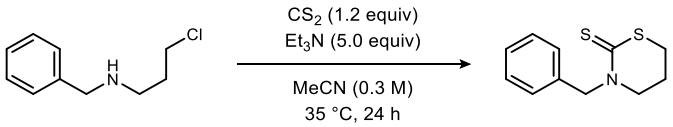


1i **2i**

Entry	CS_2 (equiv)	Temp. (°C)	Yield (%)[b]
1	1.2	35	17
2	5.0	35	51
3	10	35	63
4	1.2	60	53
5	5.0	60	85
6	10	60	87

[a]All reactions were carried out with **1a** (0.30 mmol)
[b]Isolated yield of **2i** is shown.

The reaction of the substrate without a hydroxy group, namely *N*-benzyl-3-chloropropan-1-amine, was performed for comparison. The corresponding cyclic dithiocarbamate was obtained in 97% yield under the same conditions, suggesting that the hydroxy group is not required for the reaction.



3-Benzyl-1,3-thiazinane-2-thione (S1). Prepared according to the general procedure using *N*-benzyl-3-chloropropan-1-amine (55.3 mg, 0.30 mmol).[2] Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 2:1) to obtain a white solid (65.0 mg, 97%). R_f = 0.30 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; mp 123-124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 5.38 (s, 2H), 3.47-3.43 (m, 2H), 3.01-2.97 (m, 2H), 2.24-2.16 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.6 (C), 135.2 (C), 128.8 (CH), 127.97 (CH), 127.95 (CH), 57.8 (CH_2), 49.4 (CH_2), 32.2 (CH_2), 23.2 (CH_2); IR (KBr) 1500, 1448, 1427, 1345, 1225, 1187, 1145, 941, 703 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NNaS_2$ 246.0382, found 246.0394.

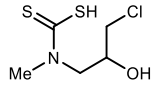
DFT Studies

Quantum mechanical calculations were performed using Gaussian 16 (Revision C.01).[3]

The pK_a values of a Brønsted acid (HA) in DMSO were predicted according to the reported method.[4] The free energy of acid dissociation in DMSO (ΔG^*_{soln}) can be obtained through eq 1. The solvation free energy of a proton ($\Delta G^*_{solv}(H^+)$) was set to -1126.572121 kJ mol^{-1} (ca. -269 kcal mol^{-1}), where the pK_a value of phenol in DMSO can be adjusted to 18.0 (cf. Bordwell pK_a Table). The geometries were optimized at the B3LYP/6-31+G(d) level of theory in gas-phase. The thermal corrections to Gibbs free energy (G_{gas}_correct) were obtained by frequency calculations at the same level of theory. The energies in solution phase were obtained by SMD calculation (M06-2X/6-311++G(2df,2p)) with the gas-phase geometries.

$$\Delta G^*_{soln} = \Delta G^*_{gas} + \Delta G^*_{solv}(A^-) + \Delta G^*_{solv}(H^+) - \Delta G^*_{solv}(HA) \qquad (1)$$

Table S3. p*K*a Calculation for a Dithiocarbamic Acid[a]

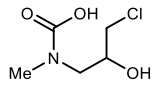


ΔG^*_{soln} = 28.0 kJ/mol, p*K*a 4.9 (DMSO)

	AH	A^-	H^+	ΔG_{gas} (au)	ΔG^*_{gas} (kJ/mol)
E_{gas} (au)	-1583.105934	-1582.585535	0		
G_{gas} (au)	-1582.992782	-1582.482360	-0.01	0.500422	1321.784552
$G_{gas\_correct}$ (au)	0.113152	0.103175	-0.01		
E_{SMD} (au)	-1583.095016	-1582.638288			
G_{SMD} (au)	-1582.981864	-1582.535113			
ΔG^*_{solv} (au)	0.010918	-0.052753			
ΔG^*_{solv} (kJ/mol)	28.666283	-138.502621	-1126.572121		

[a]At the M06-2X/6-311++G(2df,2p)-SMD(DMSO)//B3LYP/6-31+G(d) level of theory.

Table S4. p*K*a Calculation for a Carbamic Acid[a]



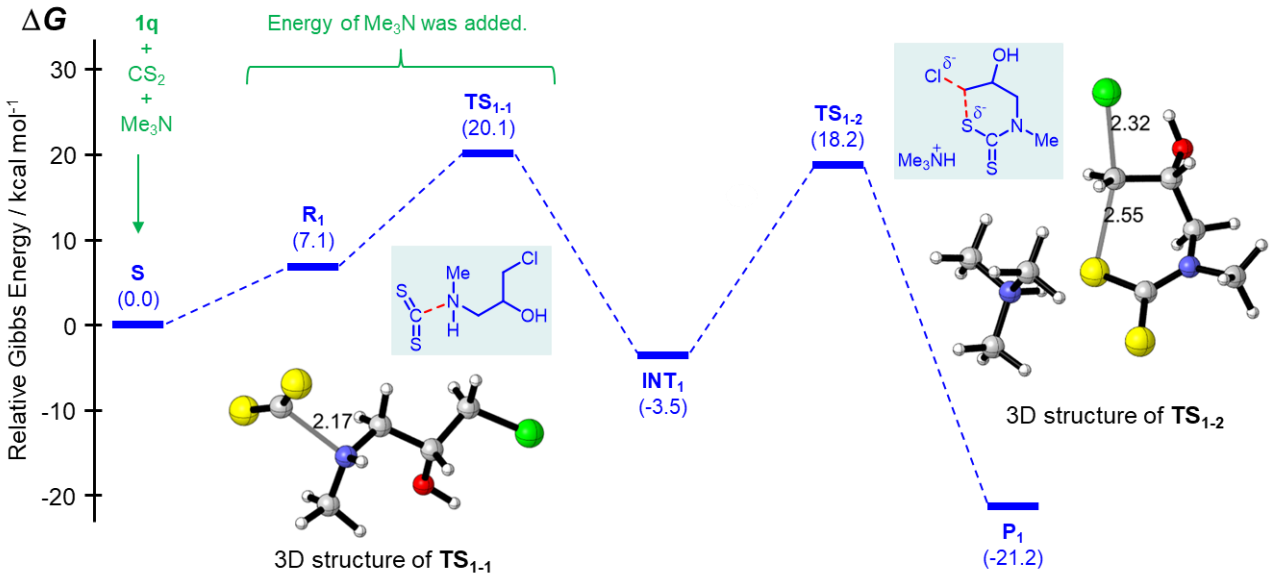
ΔG^*_{soln} = 84.7 kJ/mol, p*K*a 14.8 (DMSO)

	AH	A^-	H^+	ΔG_{gas} (au)	ΔG^*_{gas} (kJ/mol)
E_{gas} (au)	-937.210843	-936.669005	0		
G_{gas} (au)	-937.088843	-936.560875	-0.01	0.517968	1367.85157
$G_{gas\_correct}$ (au)	0.122000	0.108130	-0.01		
E_{SMD} (au)	-937.200276	-936.718093			
G_{SMD} (au)	-937.078276	-936.609963			
ΔG^*_{solv} (au)	0.010567	-0.049088			
ΔG^*_{solv} (kJ/mol)	27.743370	-128.881317	-1126.572121		

[a]At the M06-2X/6-311++G(2df,2p)-SMD(DMSO)//B3LYP/6-31+G(d) level of theory.

All geometries were optimized using the ωB97X-D density functional,[5] the 6-31+G(d) basis set, and an ultrafine integration grid within the IEFPCM model in acetonitrile.[6] Single-point energies were calculated using ωB97X-D, the polarized, triple-ζ valence quality def2-TZVPP basis set of Weigend and Ahlrichs[7] and an ultrafine integration grid within the IEFPCM model in acetonitrile. The resulting energies were used to correct the energies obtained from the ωB97X-D optimizations. The free energy corrections were calculated at 1 atm and 298.15 K. All depicted 3D structures were generated using the CYLview program.[8]

Table S5. Energy Profile[a]



		E (a.u.)	*G*_corr (a.u.)	*G* (a.u.)
R1	optimization		0.109890	-1582.838250
	single-point	-1583.16360313	N/A	-1583.053713
TS1-1	optimization		0.114040	-1582.821210
	single-point	-1583.14703918	N/A	-1583.032999
INT1	optimization		0.234535	-1757.194636
	single-point	-1757.69945262	N/A	-1757.464918
TS1-2	optimization		0.235829	-1757.161543
	single-point	-1757.66613376	N/A	-1757.430305
P1	optimization		0.233249	-1757.224858
	single-point	-1757.72633531	N/A	-1757.493086

[a]At the ωB97X-D/def2-TZVPP-IEFPCM(MeCN)//ωB97X-D/6-31+G(d)-IEFPCM(MeCN) level of theory.

R_1

The lowest frequency = 16.1167 cm^{-1}

Number of imaginary frequencies = 0

C	1.4521294883	0.1084095121	1.0286690125
H	1.4263753289	-0.3900225323	2.0089341559
C	1.7743712866	1.5845489863	1.2313653985
H	1.0523064819	2.0582182639	1.8972718259
C	0.0721455922	-0.0208043214	0.3605100315
H	0.207526667	0.1482853466	-0.7157925012
H	-0.5762896553	0.7796073718	0.7343558243
O	2.4090662718	-0.5202361526	0.1898786719
N	-0.6425390769	-1.2721363948	0.5489985929
C	0.0305921928	-2.4694308165	0.0571615915
H	-0.6442180377	-3.3242039652	0.1661958628
H	0.9760880647	-2.6990723697	0.5693288271
H	0.2497029275	-2.3422280573	-1.0084746619
C	-2.4177770787	0.1800792357	-2.2810671584
H	3.2583565624	-0.5468022877	0.652122312
H	1.8091266618	2.1151275939	0.2780157121
Cl	3.3990638468	1.8068817174	2.0015897527
H	-0.8740038439	-1.3870267853	1.5316483117
S	-3.0523505321	1.3148630249	-1.4261848607
S	-1.7846360578	-0.9498532499	-3.1427153613

$TS_{1\text{-}1}$

The lowest frequency = -288.8037 cm^{-1}

Number of imaginary frequencies = 1

C	-3.0155034051	-1.0751815919	-0.0733427672
H	-3.4268584064	-1.4066238683	0.8908416745
C	-2.45977081	0.3371655655	0.0857245416
H	-3.2262462993	1.024133272	0.4457172126
C	-4.1342871472	-1.0517444709	-1.1214581661
H	-3.6805512369	-1.0356567066	-2.1192927429
H	-4.7200628738	-0.133798235	-1.0023414676
O	-2.0211808591	-1.9813309349	-0.517606197
N	-5.0789557559	-2.1618284462	-1.0734108581
C	-4.5452988496	-3.4921445202	-1.3338418151
H	-5.3701884783	-4.2088394501	-1.3125902081
H	-3.780668788	-3.787756786	-0.6091570498
H	-4.0979940439	-3.4979632271	-2.3329554246
C	-6.654795221	-1.6655726206	-2.4845151085
H	-1.3726647005	-2.1057331064	0.1892099431
H	-2.0388071987	0.7025363192	-0.8525383465
Cl	-1.1233852957	0.3765632106	1.3026669014
H	-5.6146864498	-2.1428326669	-0.2088811804
S	-7.7706289998	-1.0107639958	-1.5462564386
S	-6.094628631	-2.1206554505	-3.9038867427

INT_1

The lowest frequency = 13.1290 cm^{-1}

Number of imaginary frequencies = 0

C	-2.5971399433	-0.5410004087	-1.0384126399
H	-2.8573049064	0.148107191	-1.8540863089

H	-1.3820023079	0.9117871841	0.0281631213
C	-1.4180081483	-1.4235399218	-1.4702732695
H	-1.7432241943	-2.0262692762	-2.323639261
H	-1.1465081047	-2.0974923905	-0.6591019177
O	-3.6680544727	-1.4368369417	-0.8017128355
N	-0.2516709126	-0.6431693539	-1.8677484306
C	-0.3739169129	0.0471123301	-3.1512733816
H	-0.4412752783	1.1303599026	-3.0111515478
H	-1.2777563332	-0.3060884909	-3.6499889252
H	0.4905211516	-0.1662533293	-3.7833724783
C	0.8483742008	-0.4920014278	-1.0946558571
N	2.6455395049	0.8811130118	1.9377108505
C	4.0797559362	0.9899829547	1.5696758083
H	4.1430011851	1.3265185641	0.535243273
H	4.5404056926	0.0063734369	1.6666747208
H	4.566064038	1.7015023255	2.2393822694
C	1.9227643192	2.1636408634	1.7400291972
H	2.0482941352	2.4710287134	0.7019663167
H	2.334619576	2.9130385226	2.4184261336
H	0.8649250452	2.0034824635	1.9522017438
C	2.4649736438	0.3544297173	3.3148127726
H	2.8959219793	1.0592084356	4.0278402062
H	2.9662743967	-0.611039946	3.3891864699
H	1.398167876	0.2309215725	3.5043394154
H	2.1983075931	0.1712394825	1.2986184556
H	-4.4744125644	-0.9263555599	-0.6455486102
H	-2.0748842848	-0.3700431198	1.0612078262
Cl	-3.6192453247	1.3776243429	0.63984639
S	2.1152791392	0.5404179709	-1.6251081094
S	0.9642485946	-1.336834136	0.4224160362
C	-2.2498555393	0.2742100271	0.1996637957

TS$_{1\text{-}2}$

The lowest frequency = -508.8298 cm^{-1}

Number of imaginary frequencies = 1

C	-4.1892635411	0.4591065078	-0.0244467415
H	-4.4991043589	1.4213686222	-0.4521380251
H	-2.9922941975	1.6509980792	1.4802347131
C	-3.2687486375	-0.2331032387	-1.0427611048
H	-3.8550385017	-0.3923014521	-1.9489088943
H	-2.9691837777	-1.2078052916	-0.6524854419
O	-5.2948315292	-0.4084168993	0.1072871032
N	-2.0939789809	0.5501076601	-1.3943185169
C	-2.1065948931	1.2557018468	-2.6739391517
H	-1.6952688196	2.2588172315	-2.5519019006
H	-3.1370658643	1.3297881347	-3.0221224613
H	-1.5086115265	0.7201538807	-3.4186252488
C	-1.0212721635	0.5822520336	-0.5834513804
N	0.6019029126	2.0469462551	2.4998322874
C	2.0632715113	1.7930623311	2.3973464554
H	2.3685928234	1.9629545005	1.3650804435
H	2.2584370883	0.7571773653	2.6757733839
H	2.5873035852	2.4721535186	3.071864239

C	0.2502340559	3.4224683269	2.0579562371
H	0.6082562263	3.5586269862	1.0379511483
H	0.7222154357	4.1383029729	2.7328439659
H	-0.8335849602	3.5353354101	2.0889372913
C	0.0802776651	1.7577323572	3.8620336993
H	0.5461336655	2.4418517226	4.5725778251
H	0.3202881346	0.7256310557	4.1180367661
H	-1.0011995157	1.8965044388	3.8581628067
H	0.1231507098	1.3746410845	1.8601654636
H	-5.9087983899	0.0162755898	0.7292484381
H	-3.6049346646	0.0114023265	2.1092638065
Cl	-5.4054929027	1.7970722585	2.2506236592
S	0.4346425694	1.3421793789	-1.0417175357
S	-1.2080455895	-0.173807321	0.9753350474
C	-3.5582439988	0.747997257	1.3223915531

P_1

The lowest frequency = 17.7865 cm^{-1}

Number of imaginary frequencies = 0

C	-2.5180973551	-0.4331302249	-0.7722259771
H	-2.9492116314	0.4424940285	-1.2750506697
H	-1.3782503406	1.1166182572	0.2529892817
C	-1.6499926808	-1.223002644	-1.7553929332
H	-2.1260778439	-1.2680277055	-2.7337452085
H	-1.5628240504	-2.2455906452	-1.3705022114
O	-3.5388854135	-1.3190725051	-0.3795398492
N	-0.2986177778	-0.6759559144	-1.9295154946
C	0.1460076035	-0.3846078604	-3.2907799069
H	0.903831001	0.3987207367	-3.269125311
H	-0.7134871169	-0.0459341104	-3.8694454807
H	0.5713690043	-1.2806551554	-3.754564222
C	0.5566100073	-0.6755010546	-0.9091504399
N	2.8548868271	1.0368127302	1.7349178117
C	4.1898716476	1.6150936788	1.4215654867
H	4.0971478422	2.2549066423	0.5439201262
H	4.8845125324	0.8004791712	1.2165209395
H	4.5322620639	2.1963884163	2.2789437407
C	1.831502227	2.0967851682	1.9417687361
H	1.7649991034	2.6995869651	1.0358356066
H	2.1323049192	2.7169011229	2.7873364806
H	0.8721961749	1.6209541704	2.1440449055
C	2.9198701548	0.0940494628	2.883584382
H	3.2499051724	0.6398719024	3.7686280514
H	3.6271175351	-0.7002341072	2.6441897923
H	1.9281698677	-0.3274461311	3.0465193827
H	2.5721013464	0.4853416602	0.893138408
H	-4.2507522003	-0.7829270213	0.0386137236
H	-2.2613086582	0.0260648613	1.3348022446
Cl	-5.6125514621	0.6274855	0.8948631243
S	2.231877168	-0.5070707454	-1.0583965583
S	-0.1541433047	-0.8857339267	0.6950693576
C	-1.6822878826	0.0787199967	0.410330541

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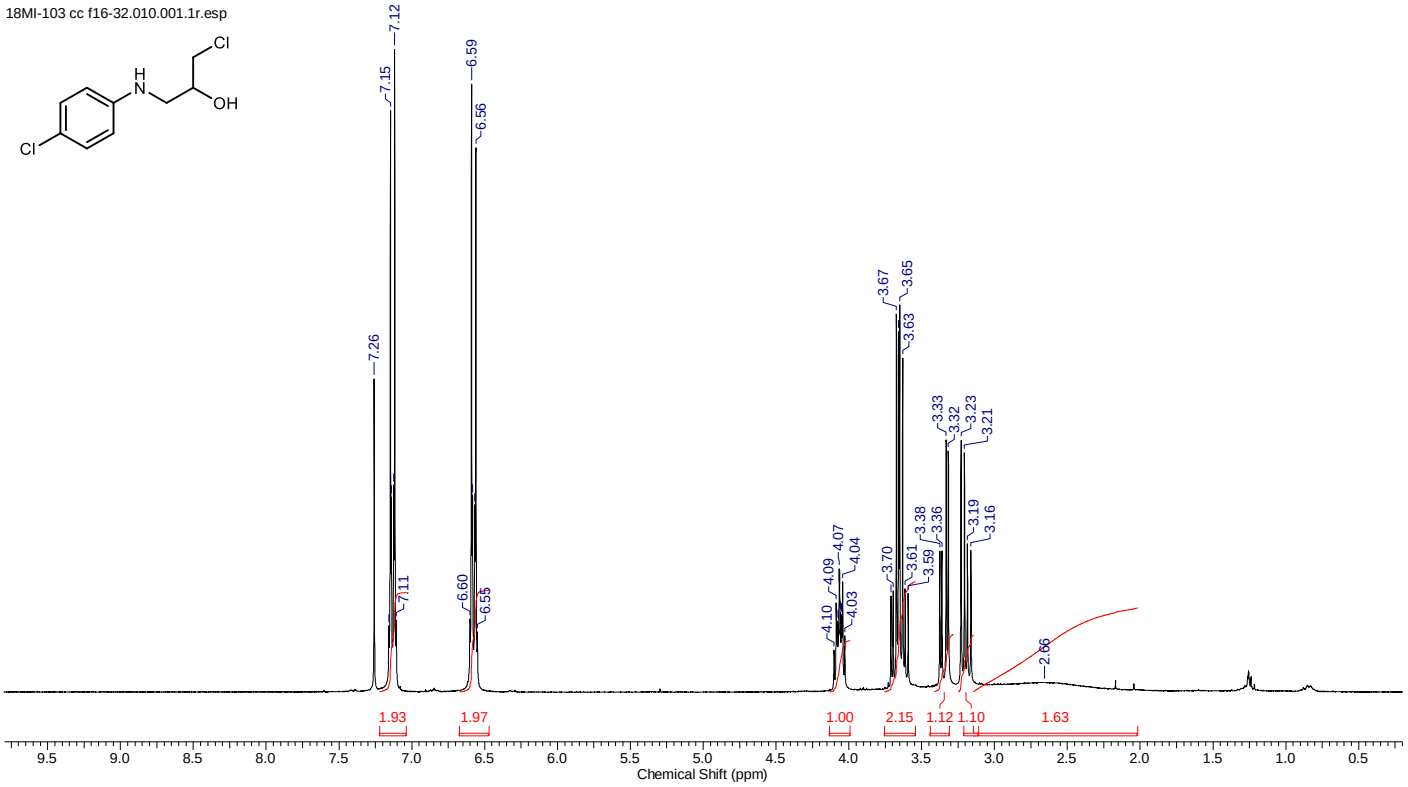
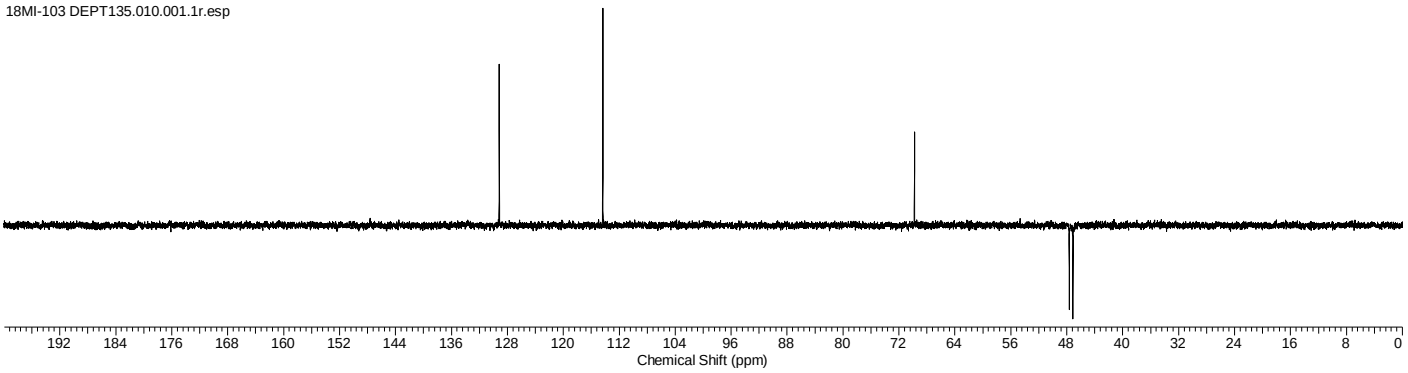
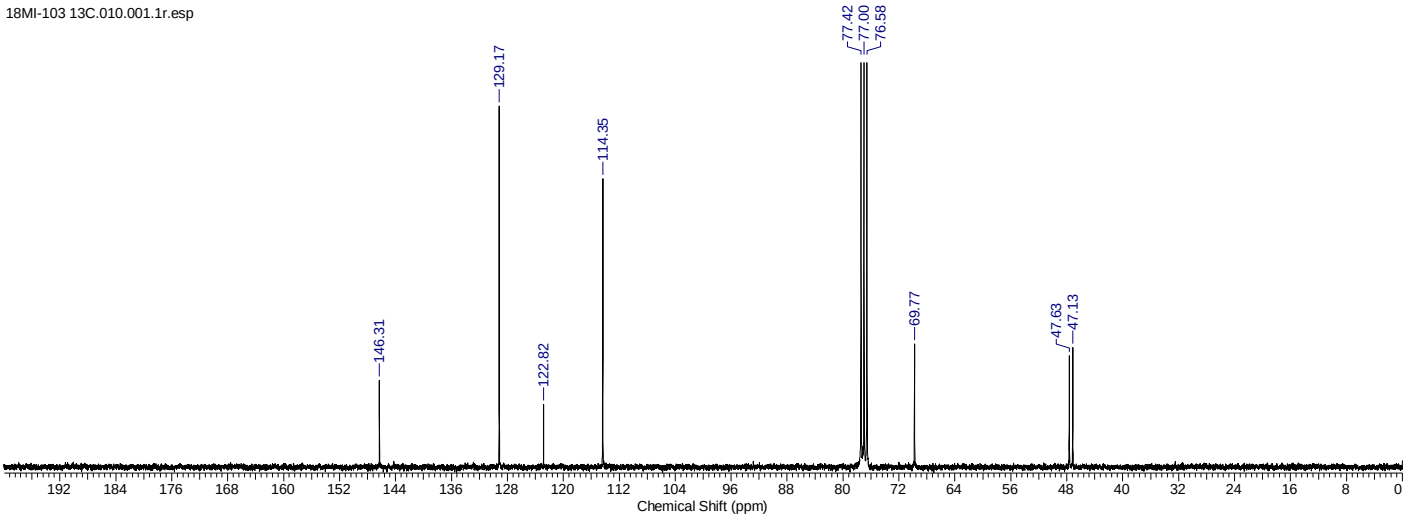
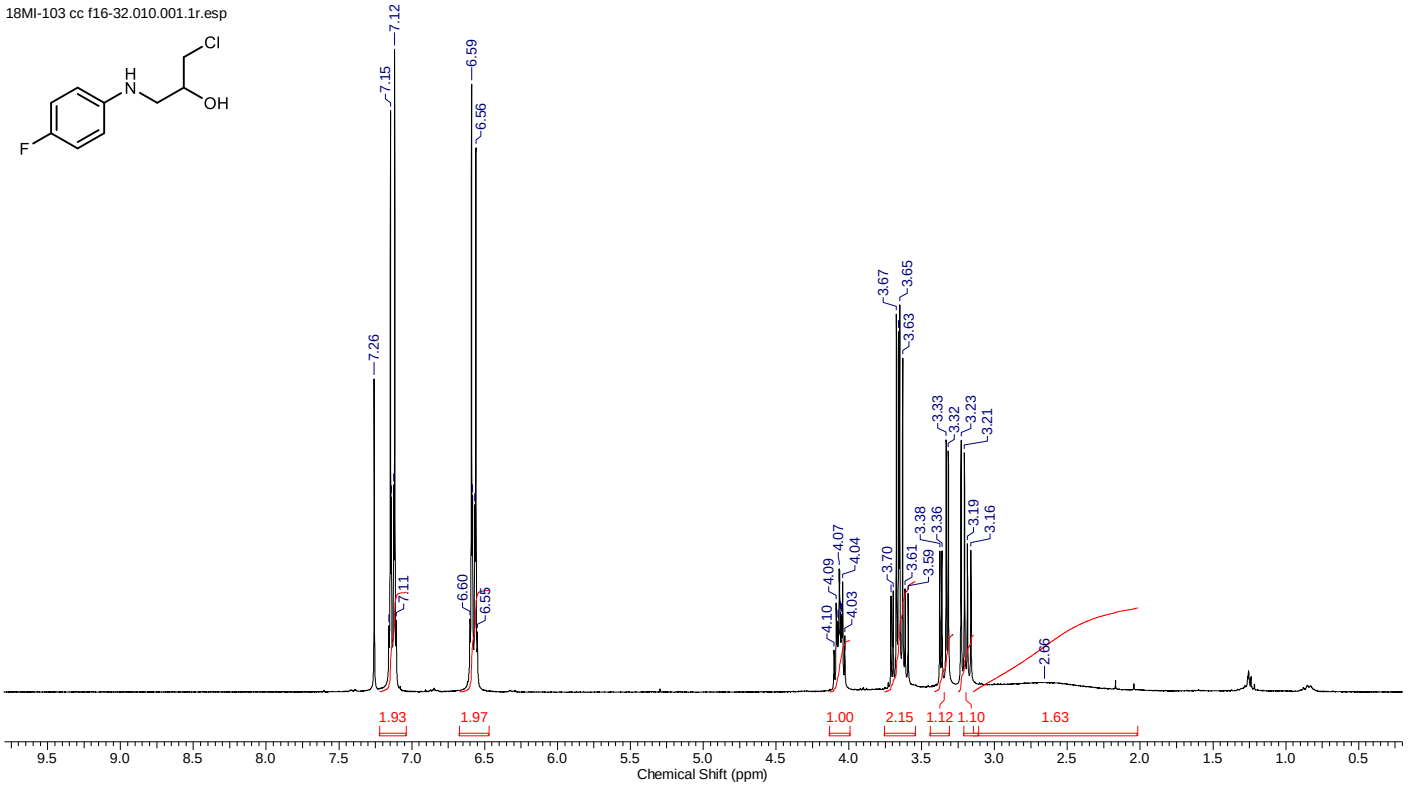
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 1k

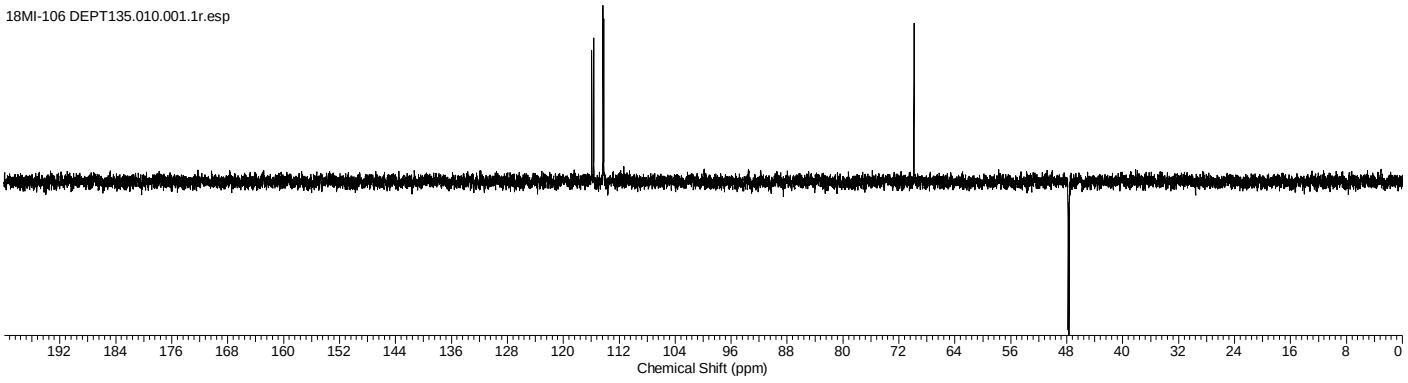


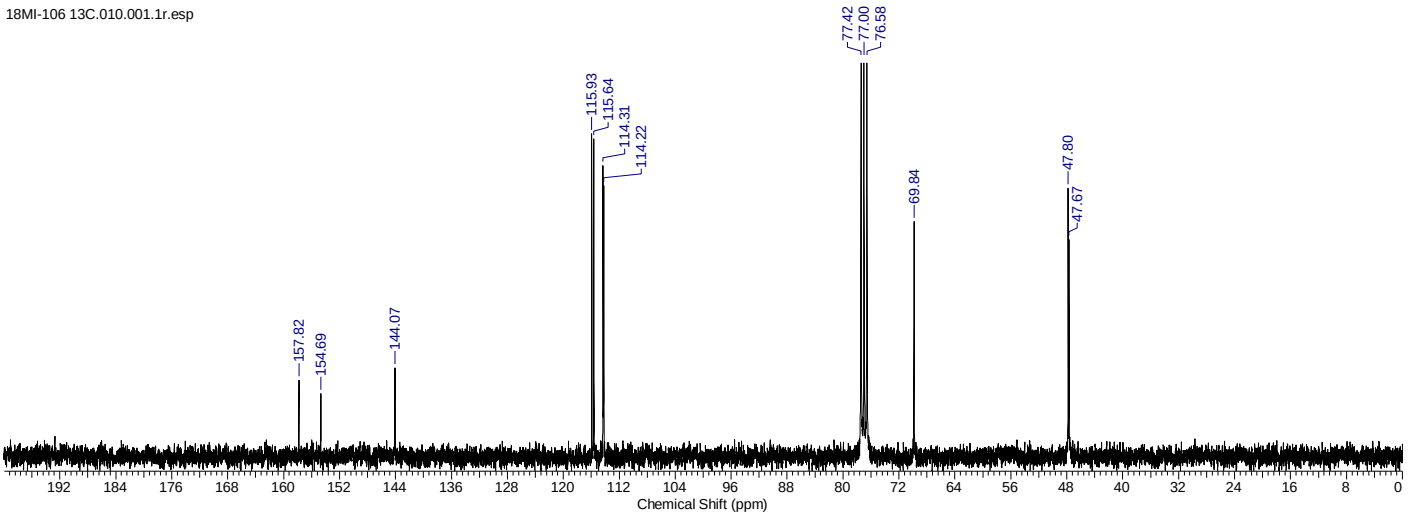




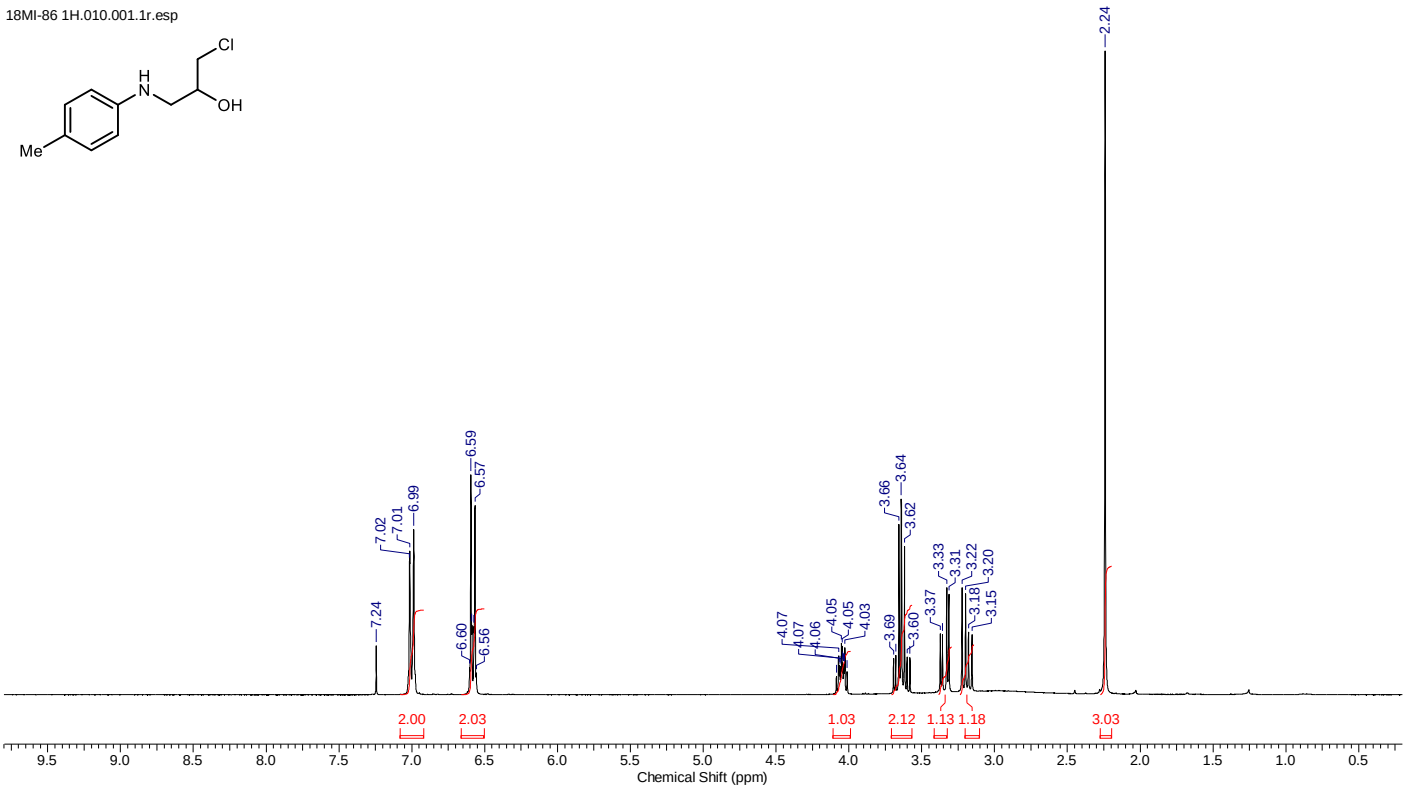
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 1l

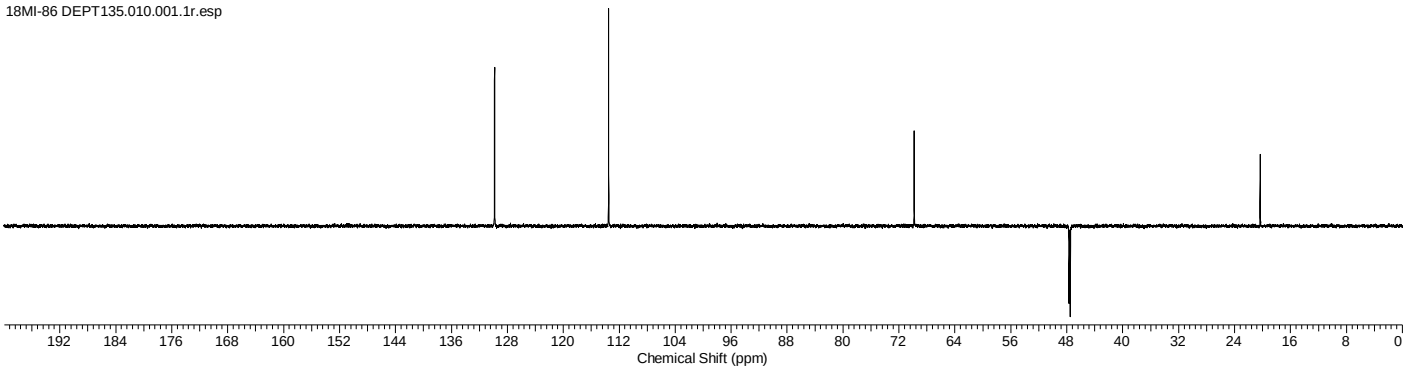


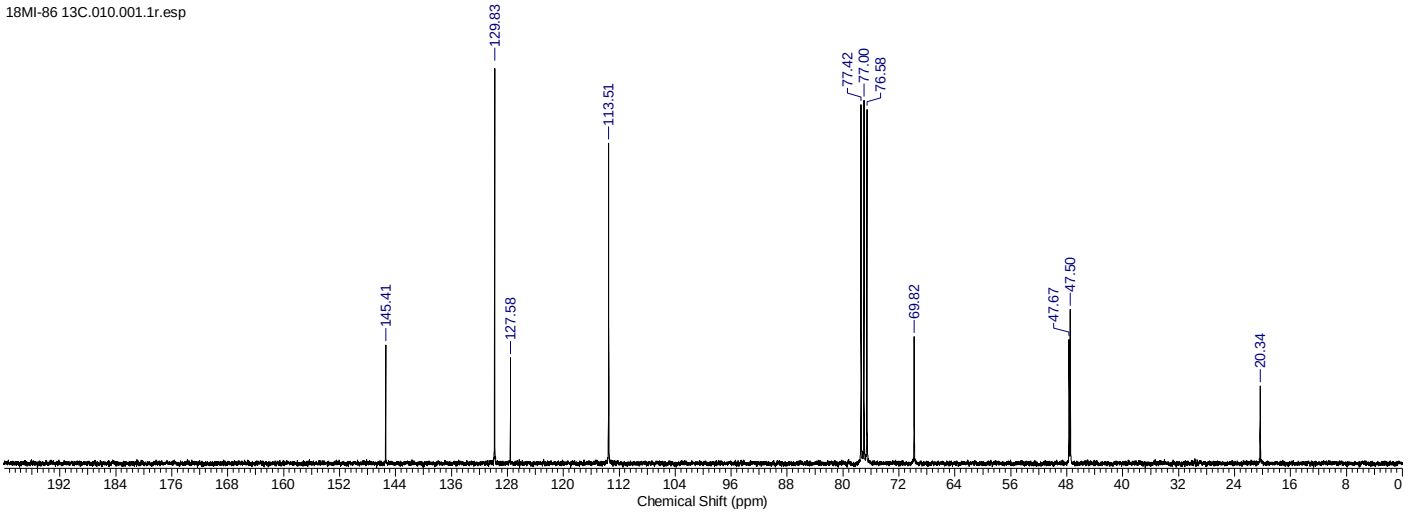




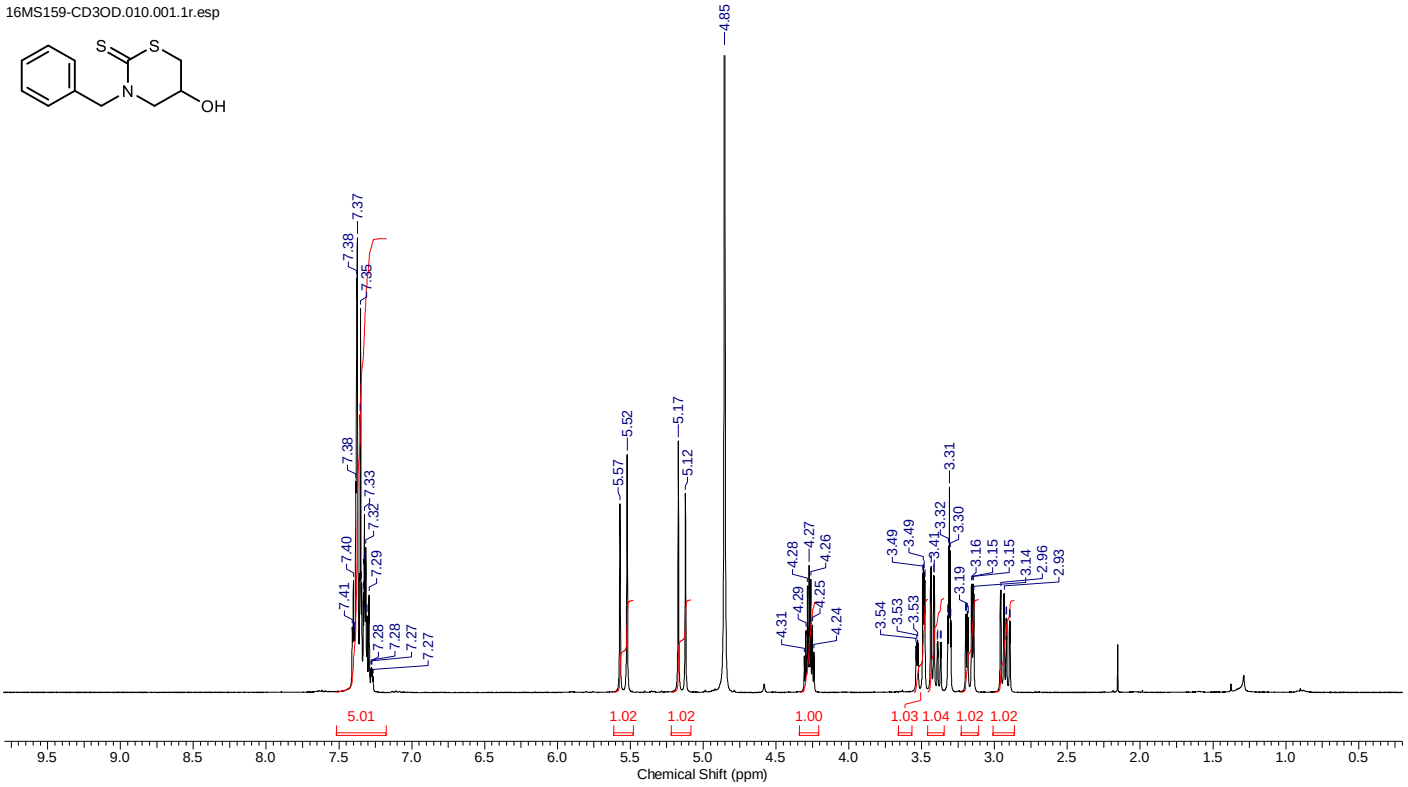
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 1m

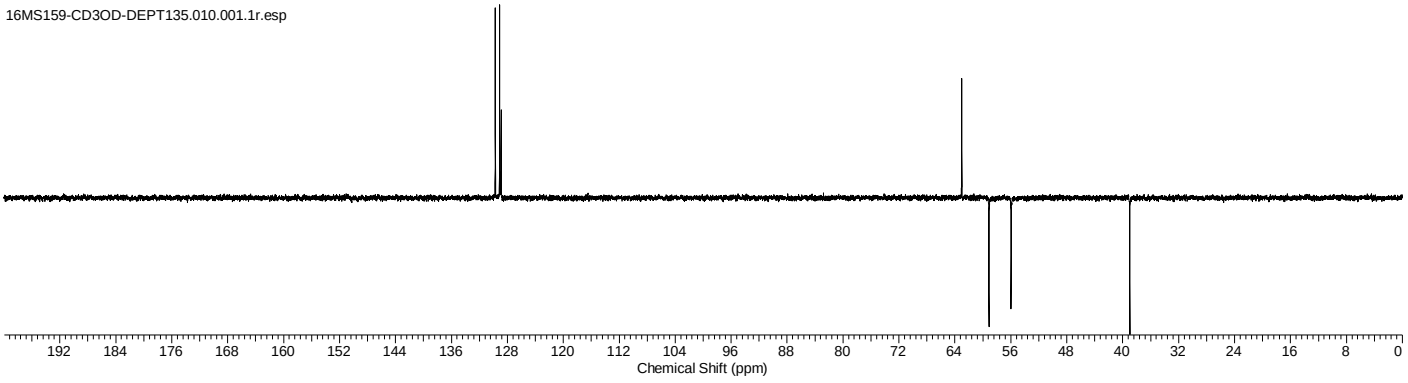


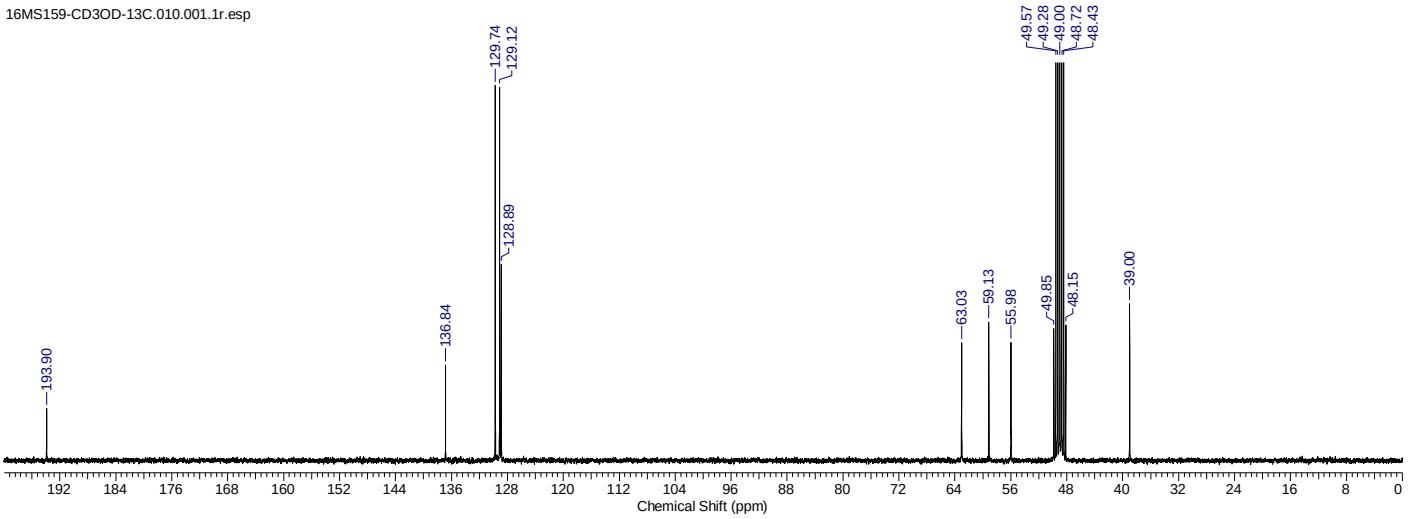




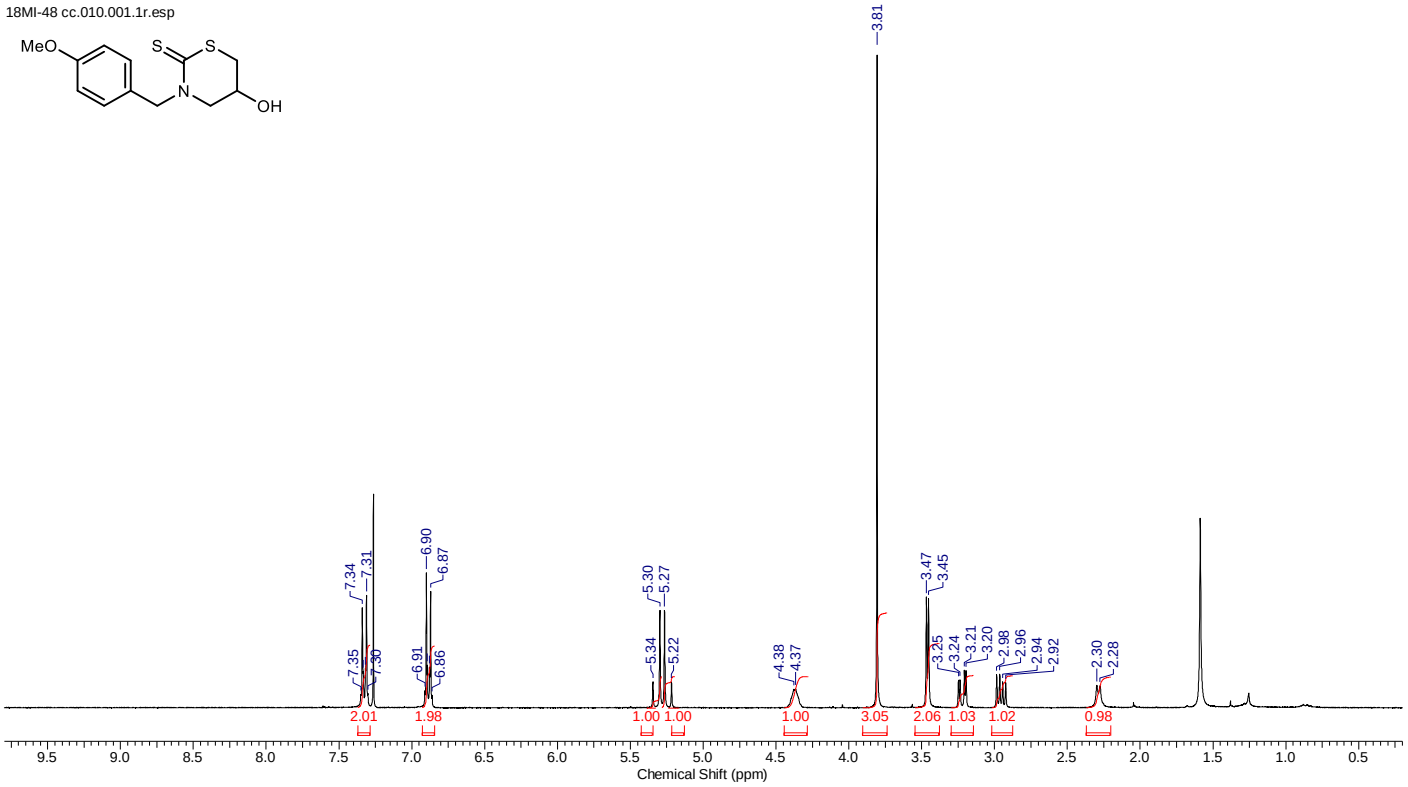
^{1}H (300 MHz, CD_3OD) & $^{13}C\{^{1}H\}$ NMR (300 MHz, CD_3OD) Spectra of 2a

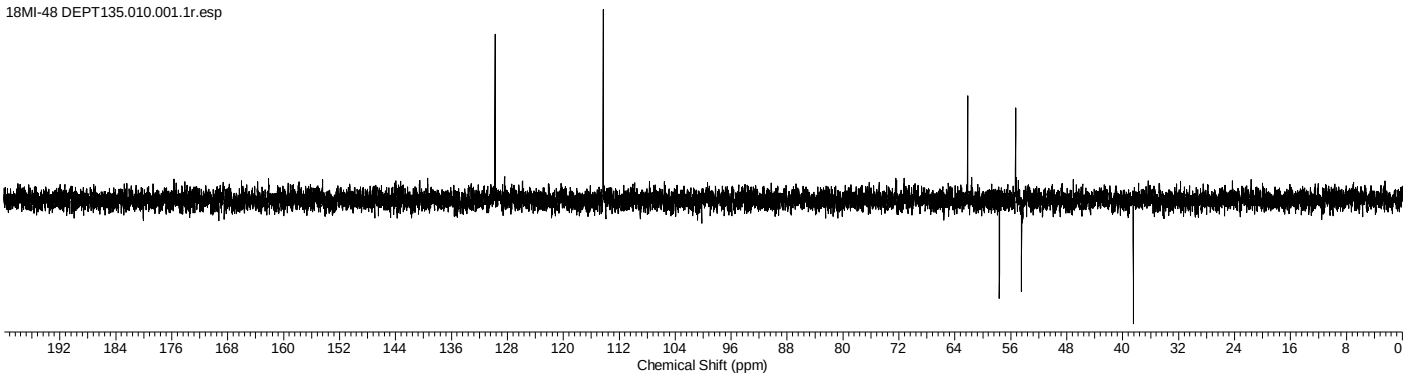


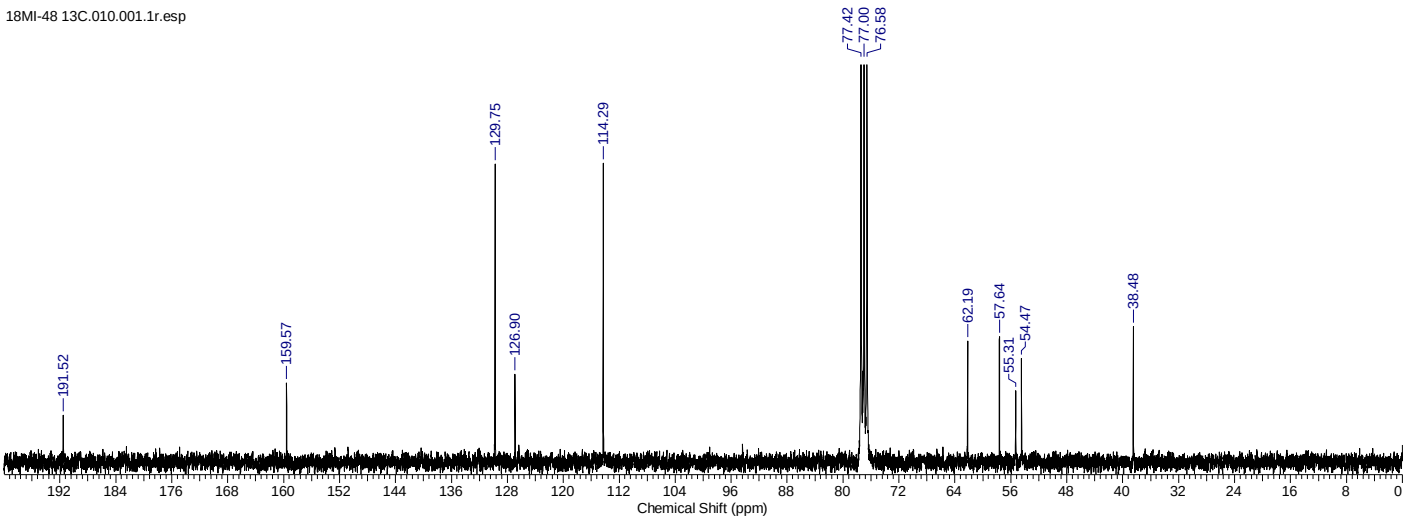




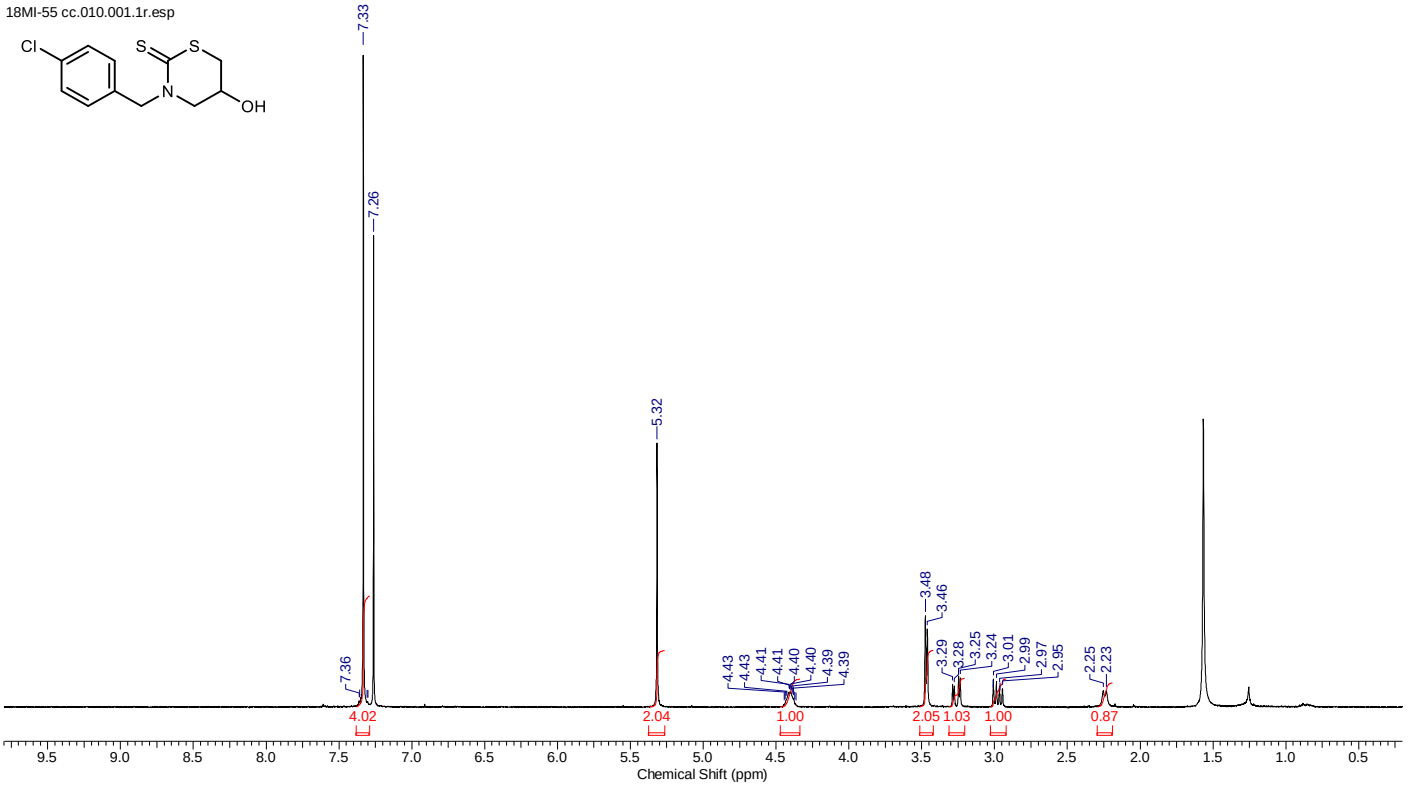
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2b

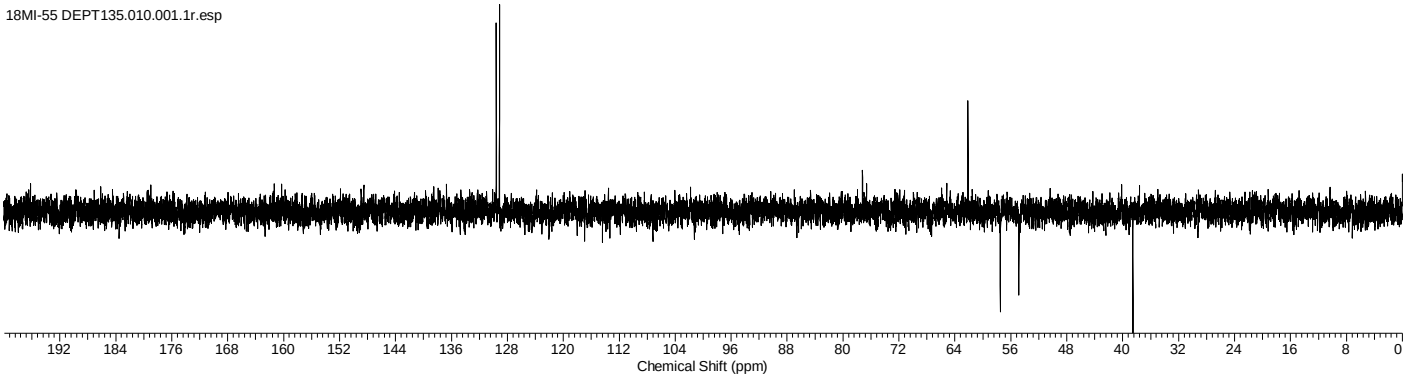


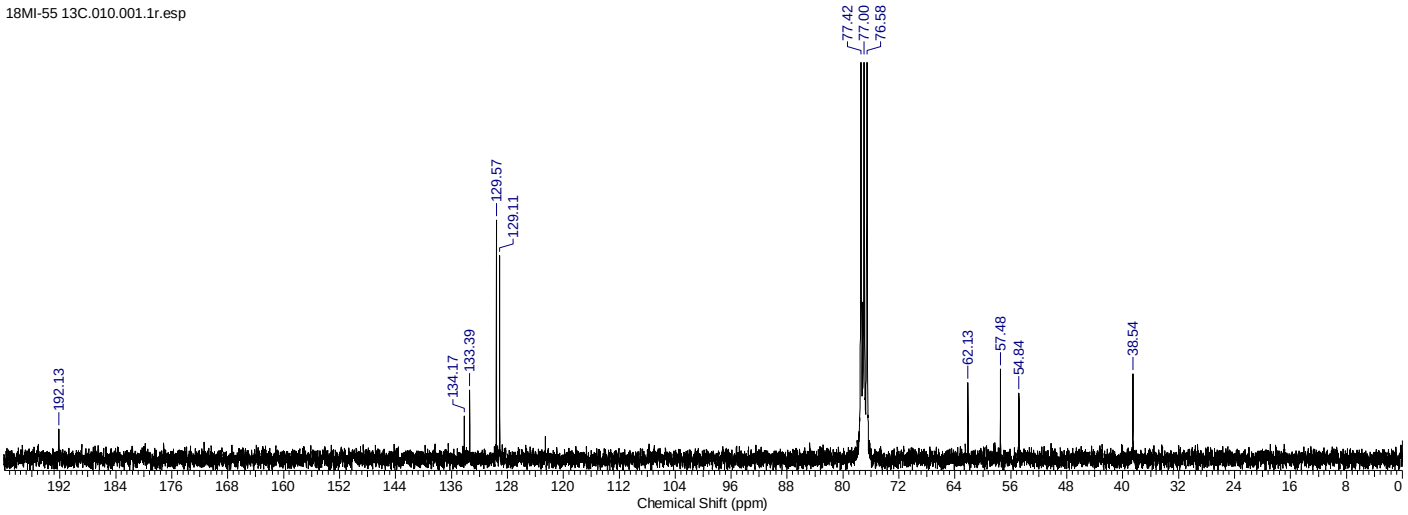




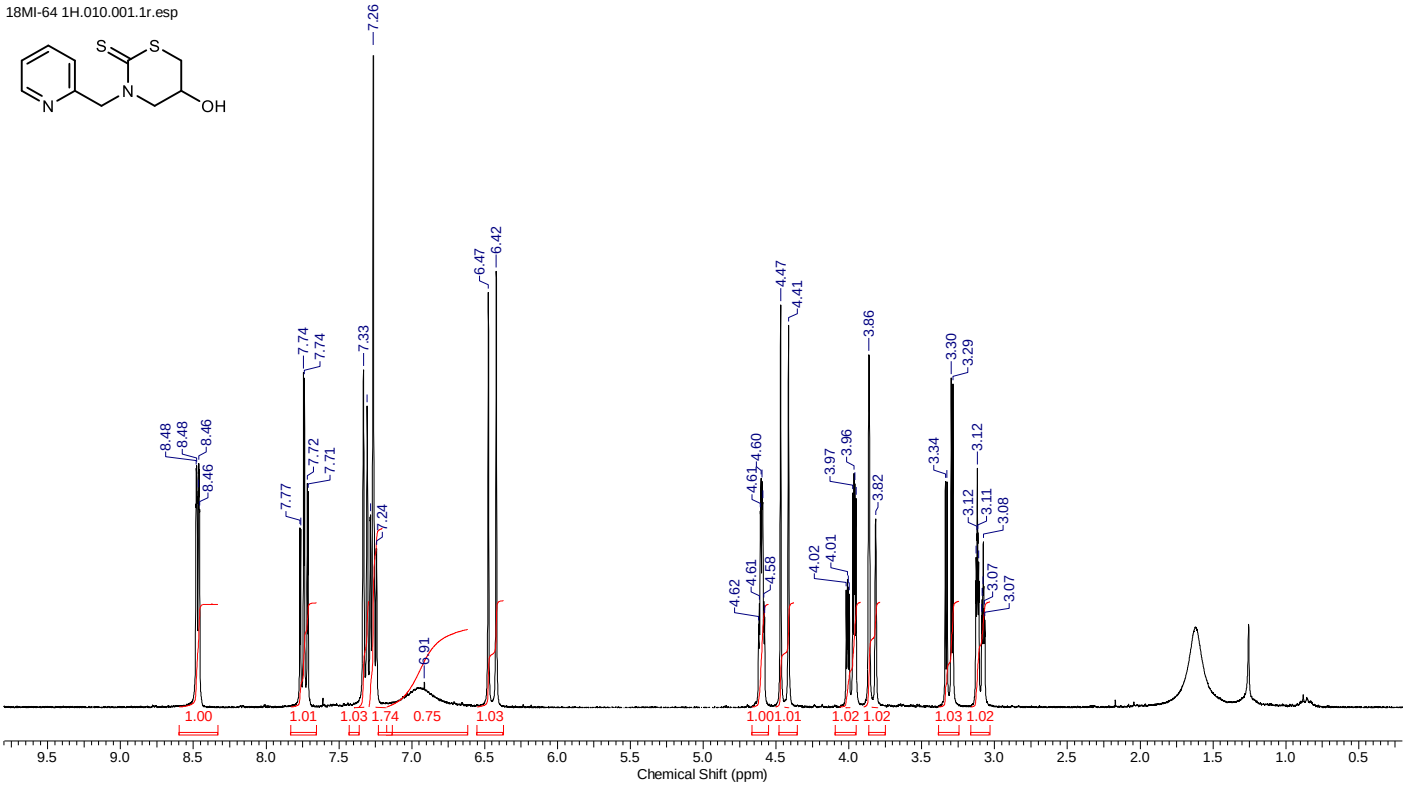
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2c

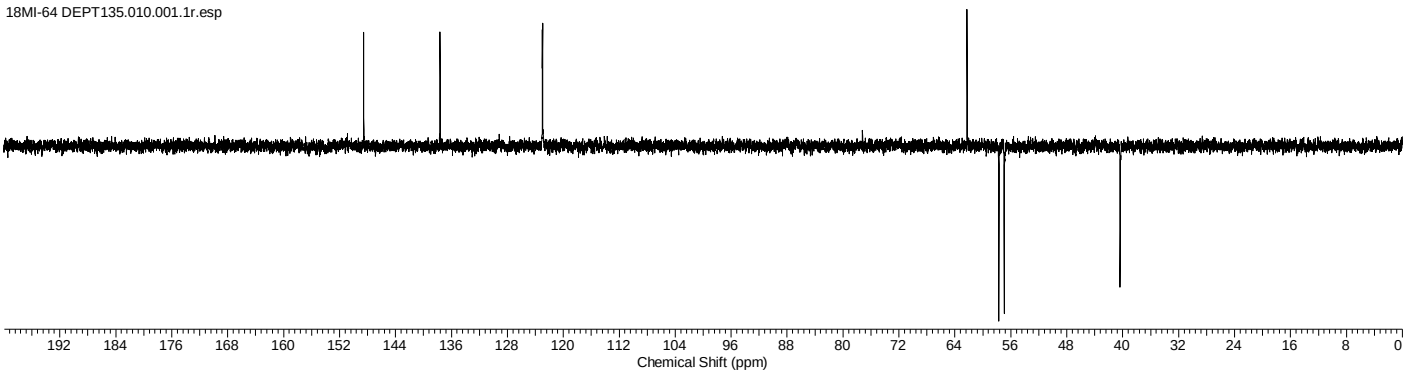


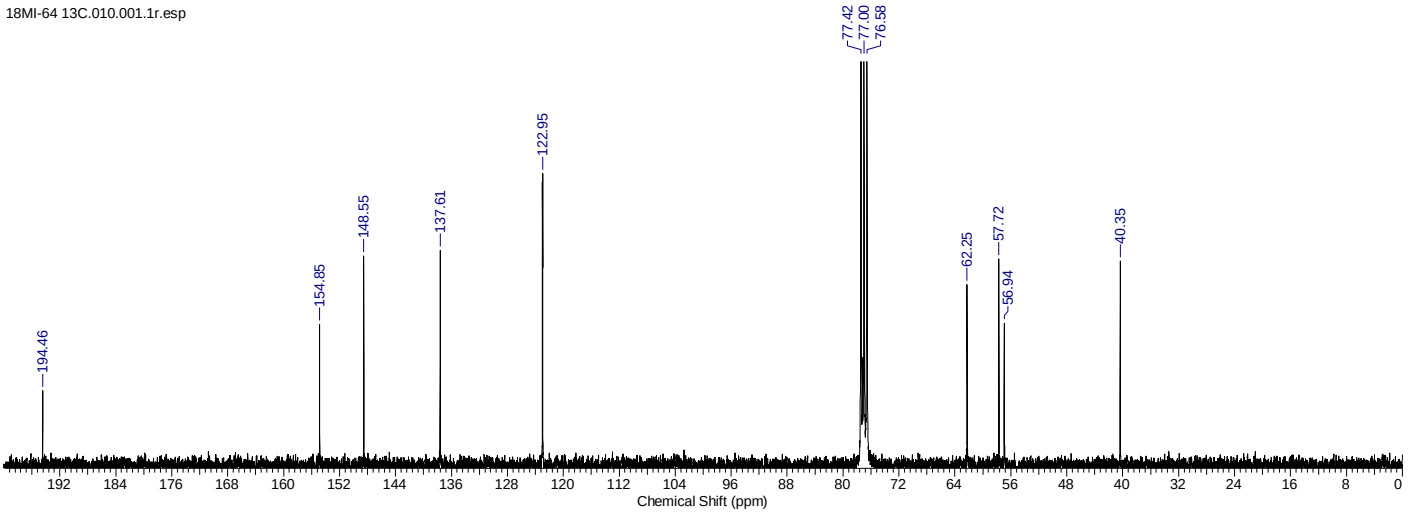




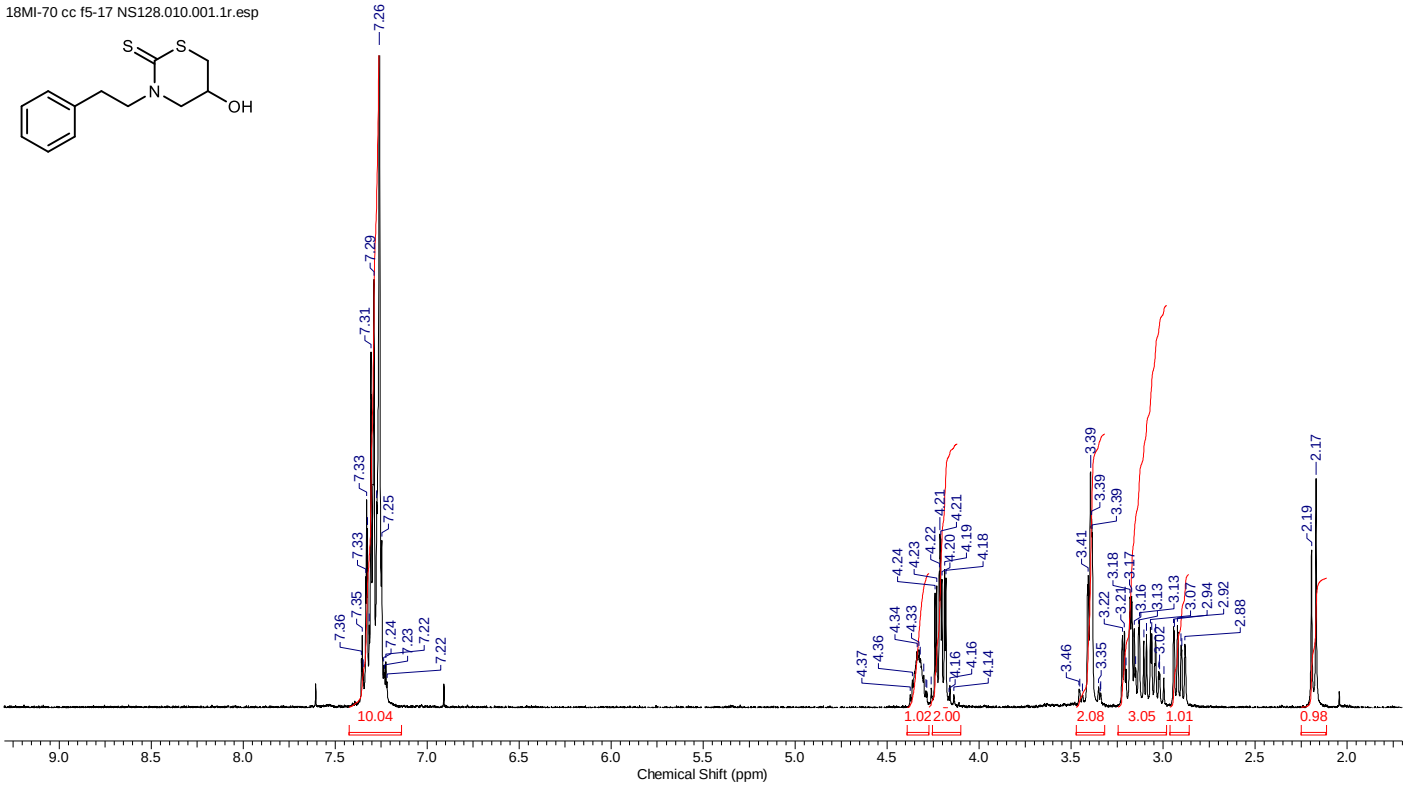
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2d

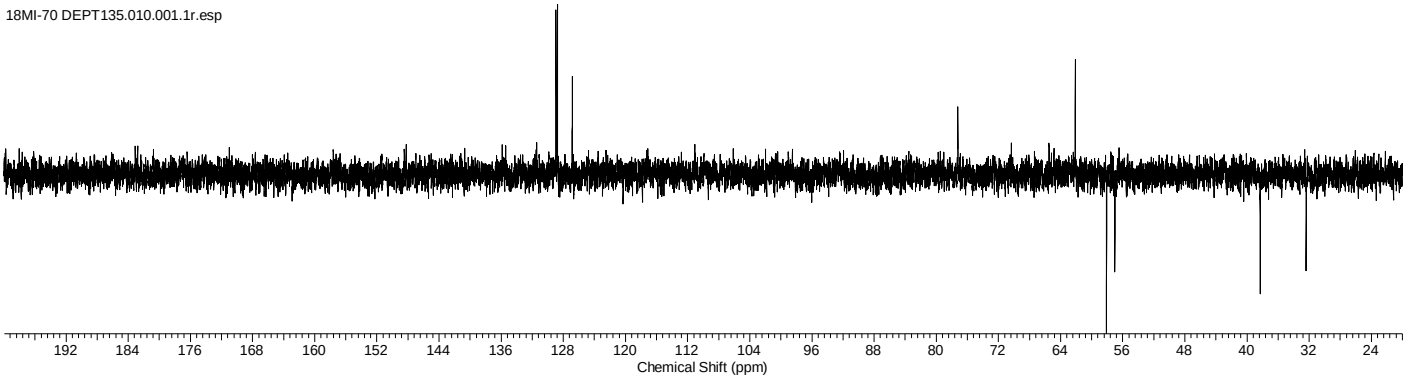


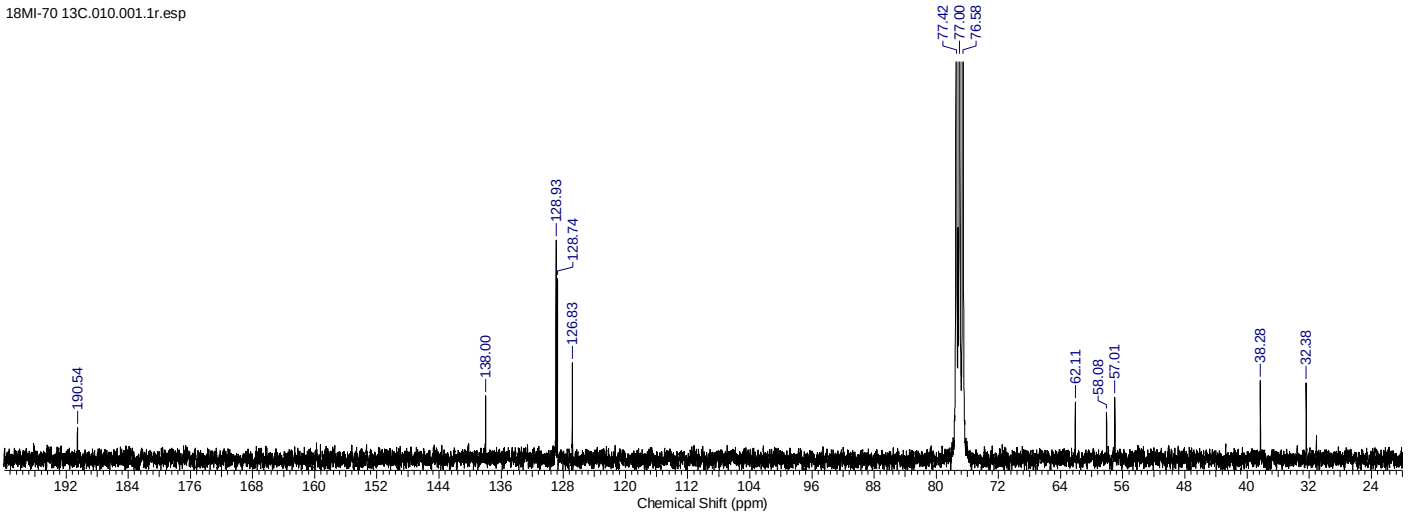




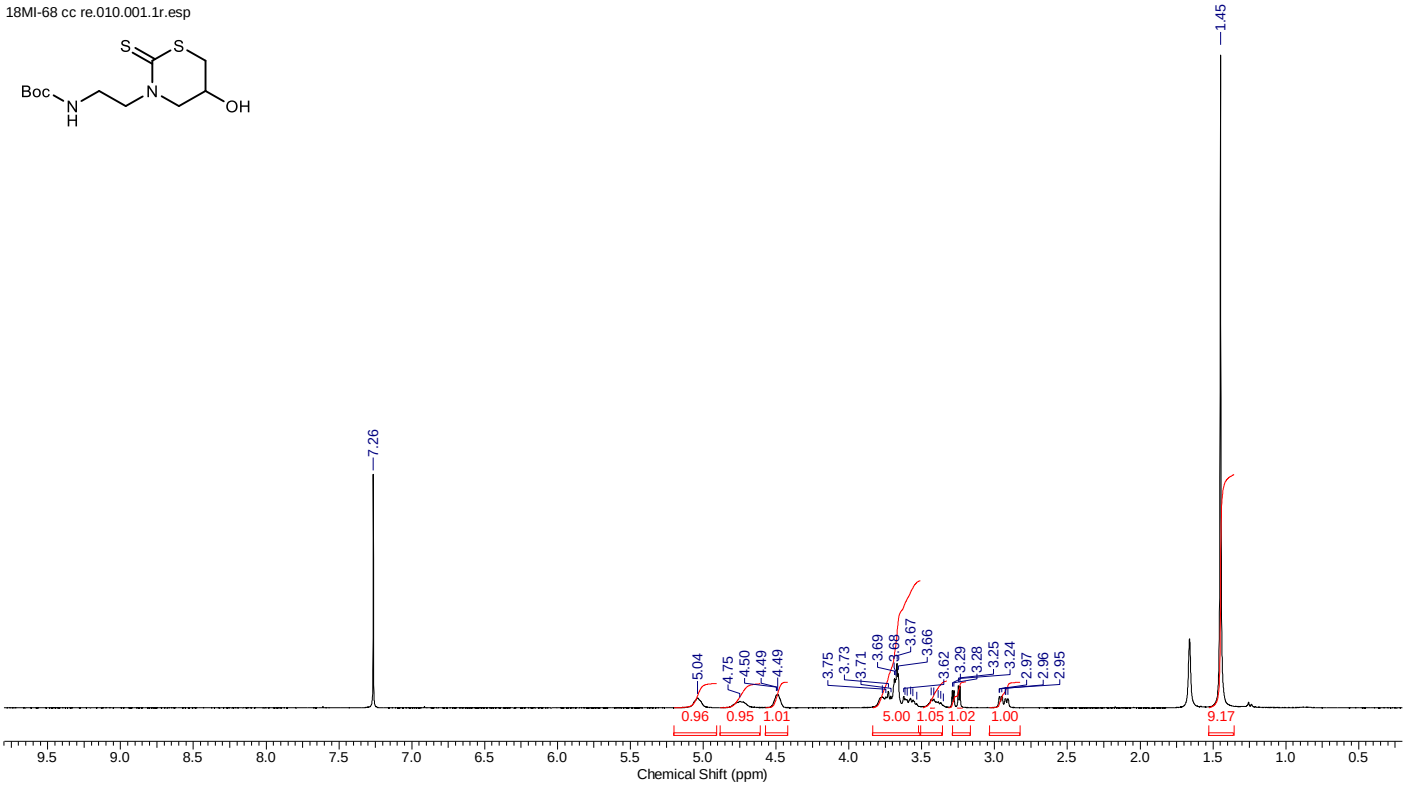
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2e

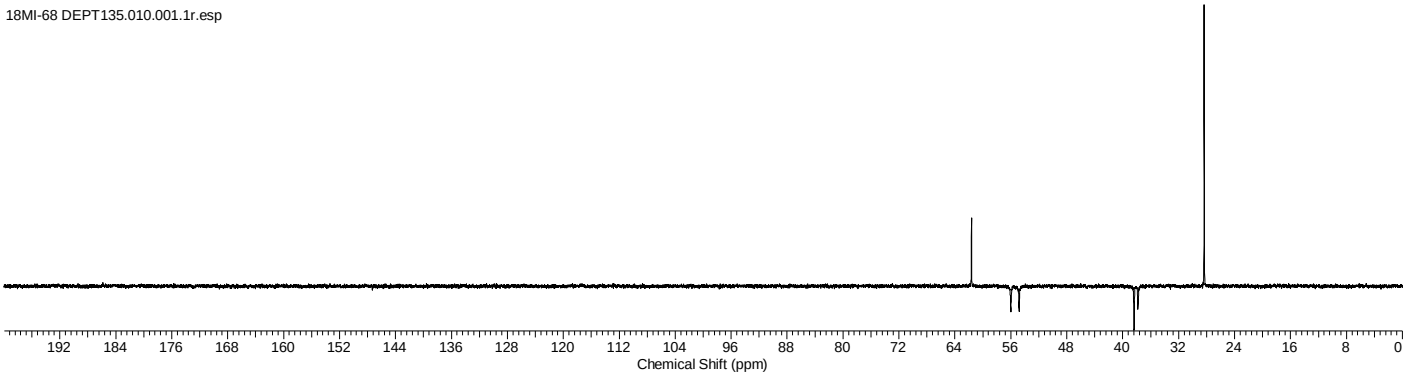


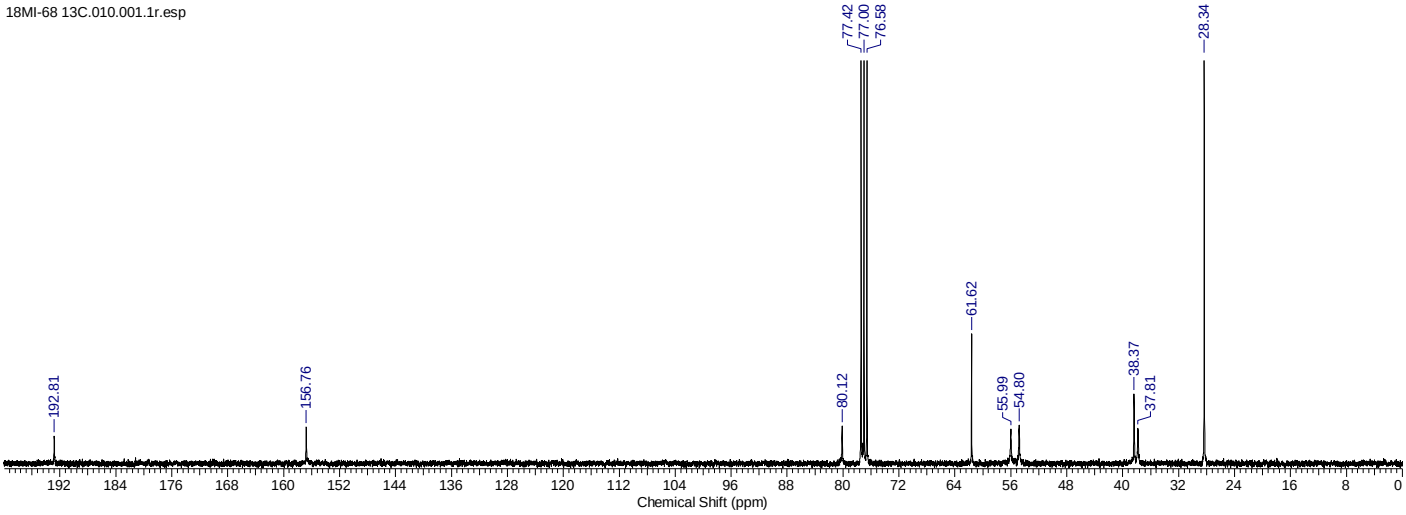




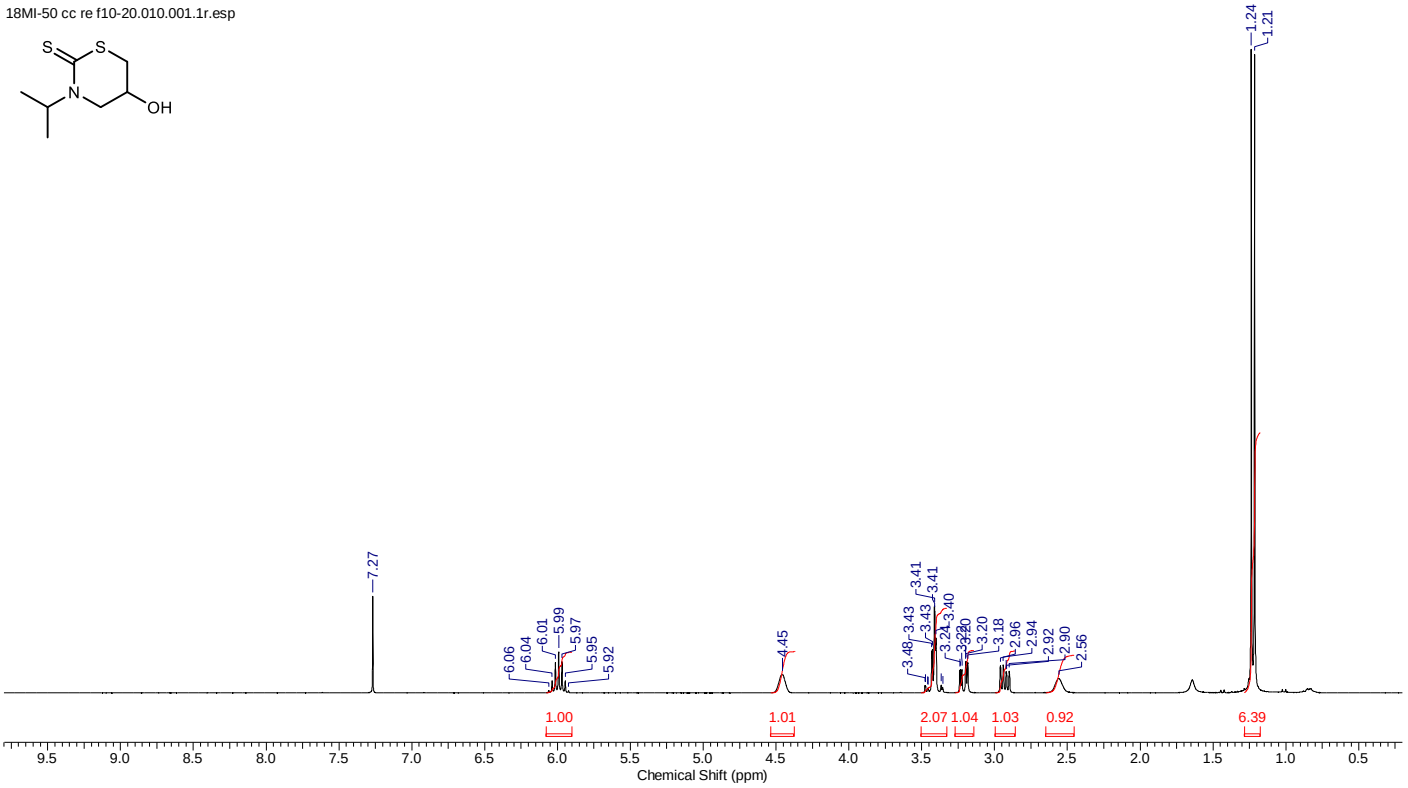
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2f

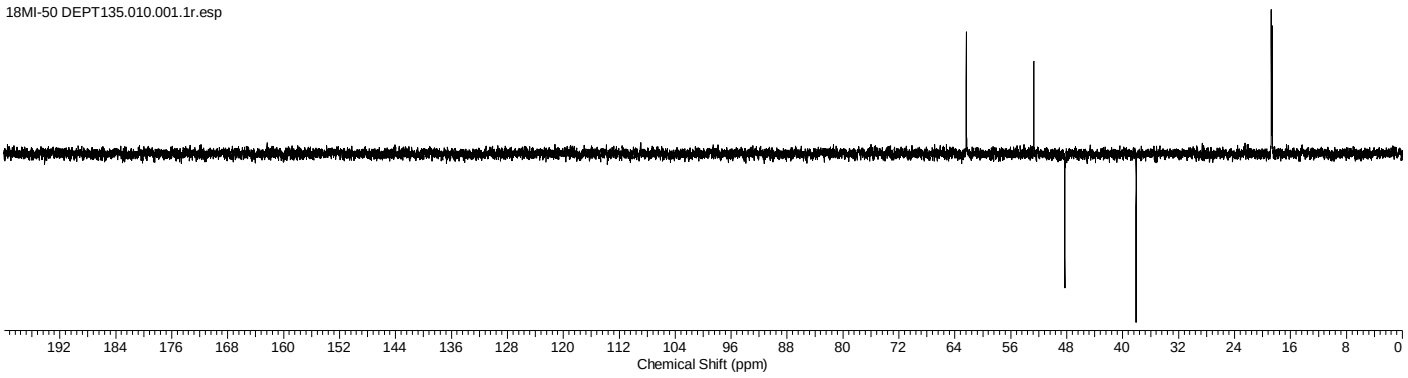


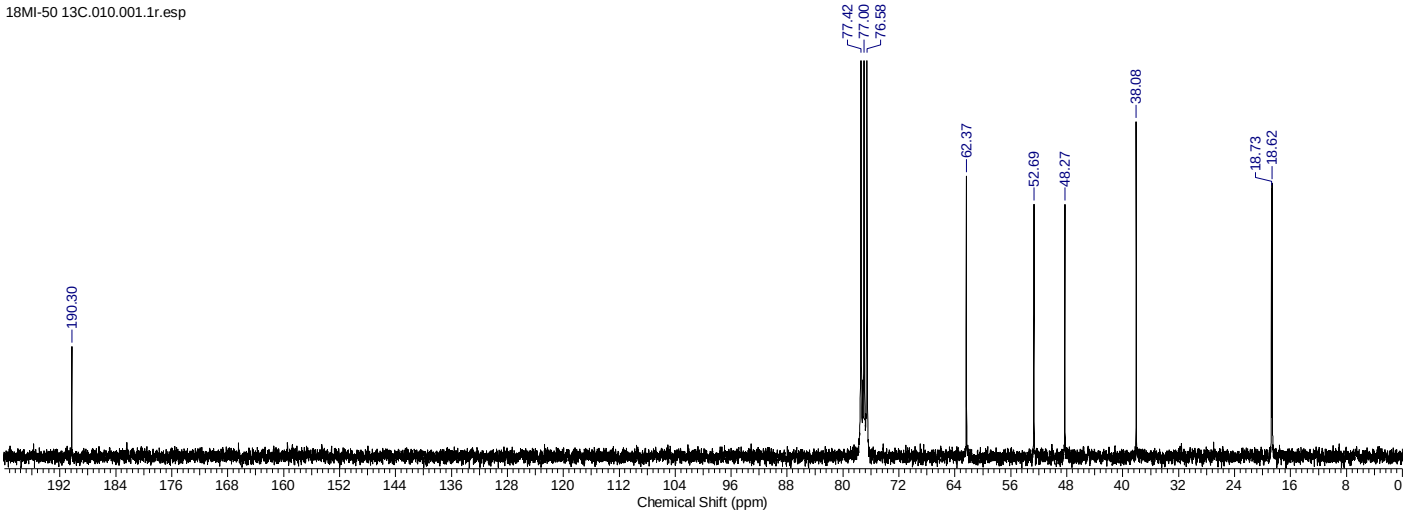




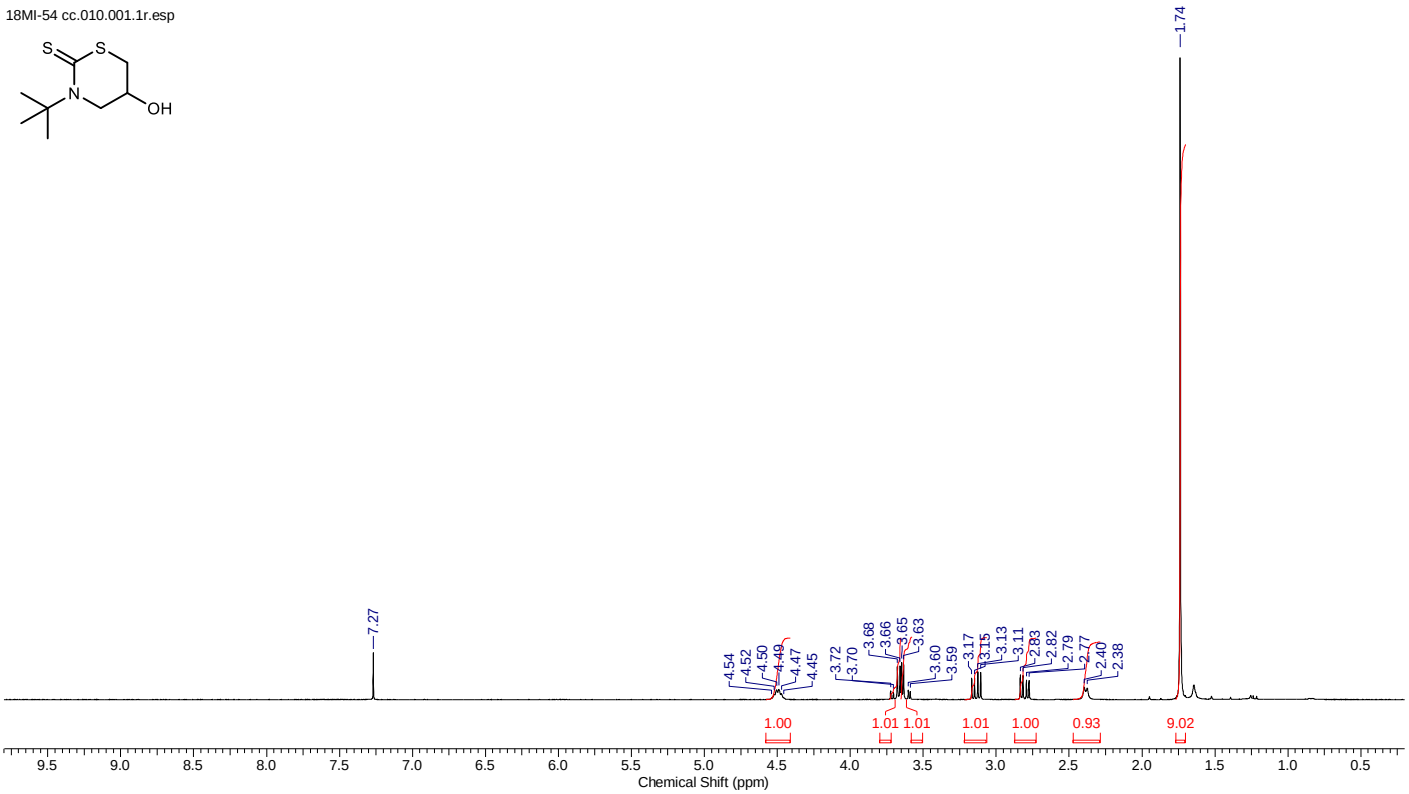
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2g

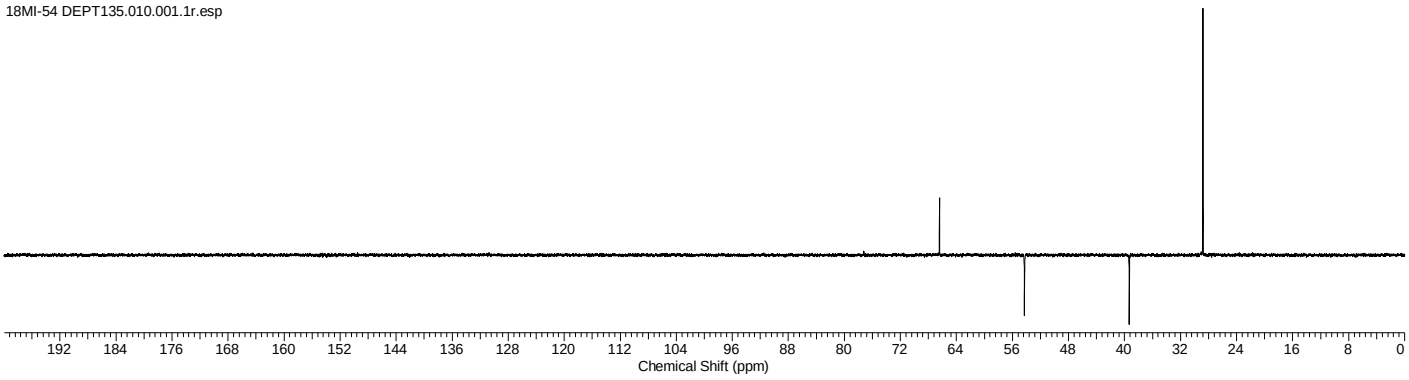


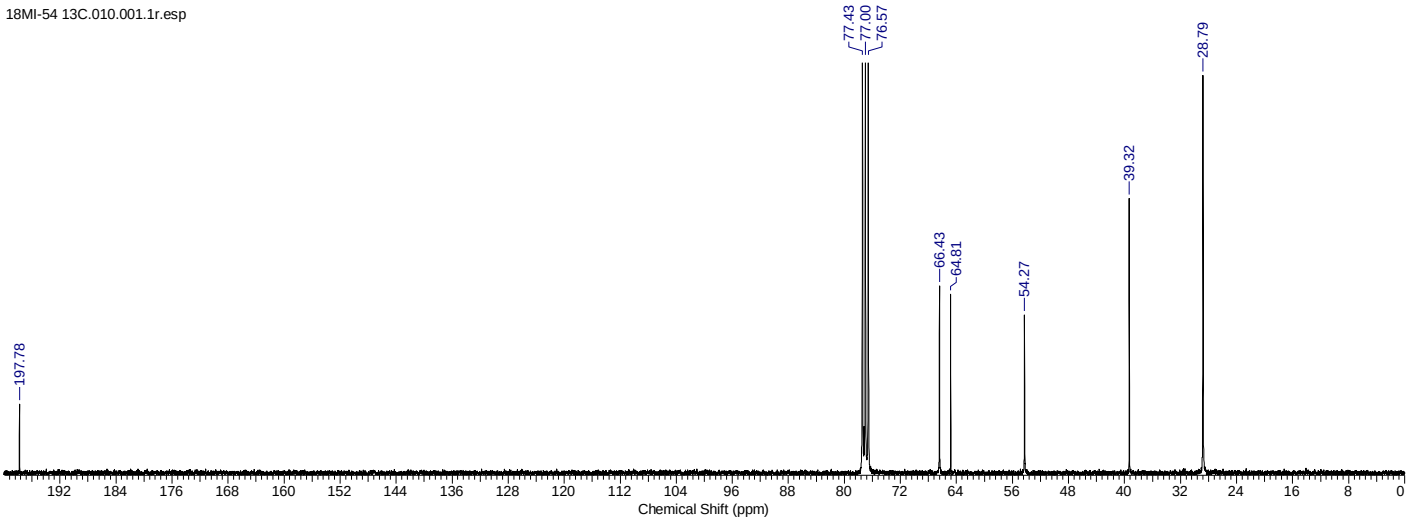




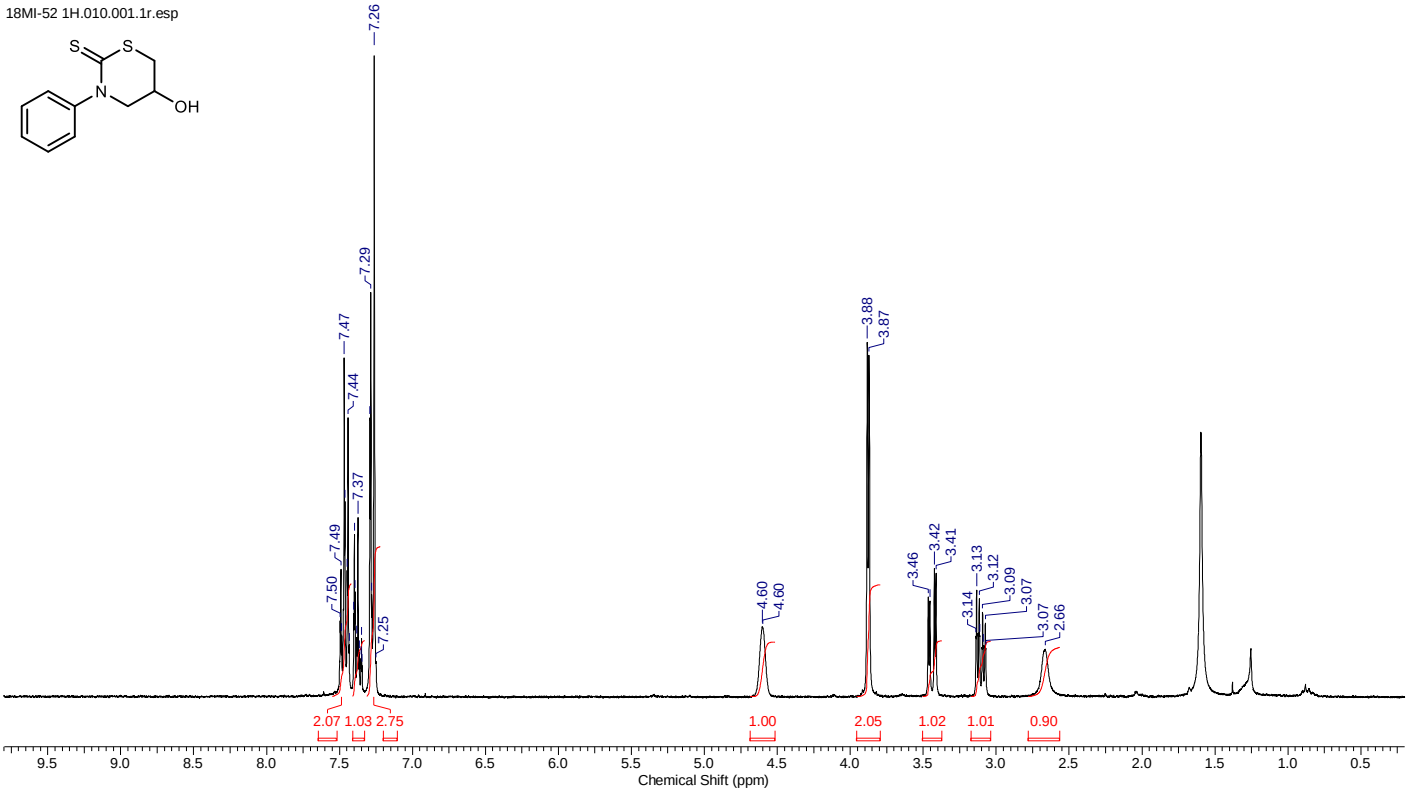
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2h

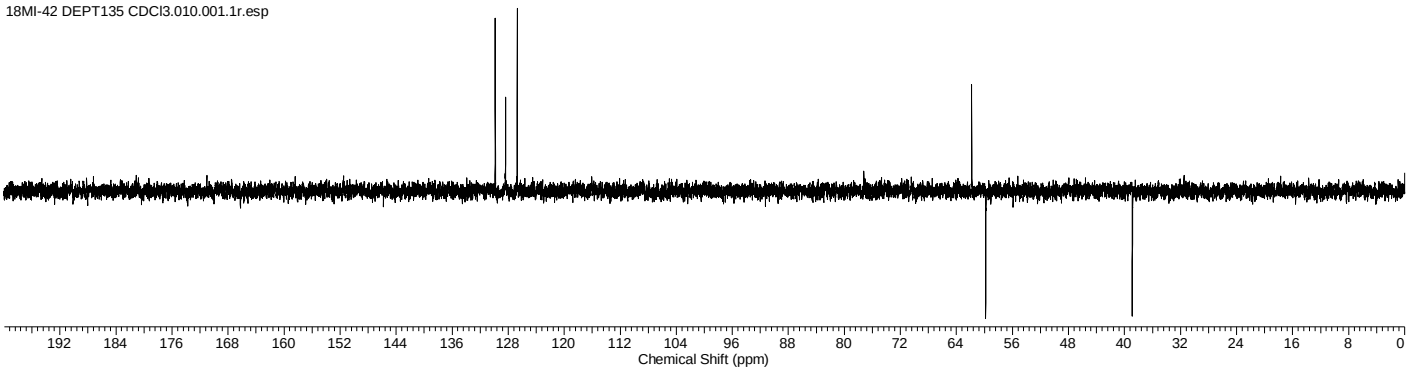


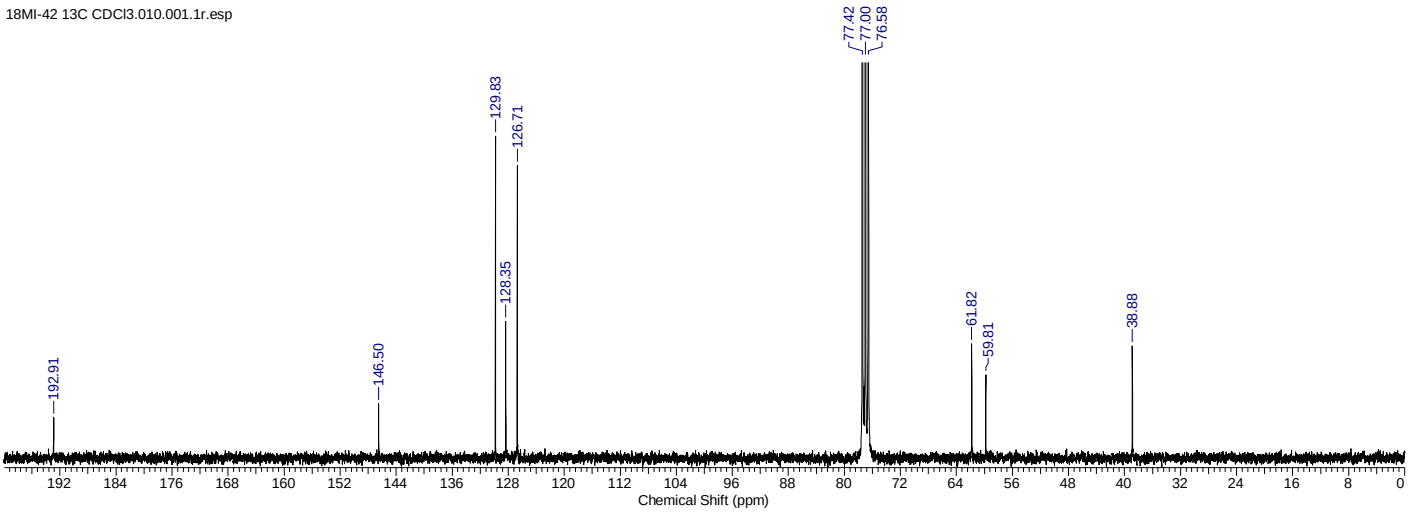




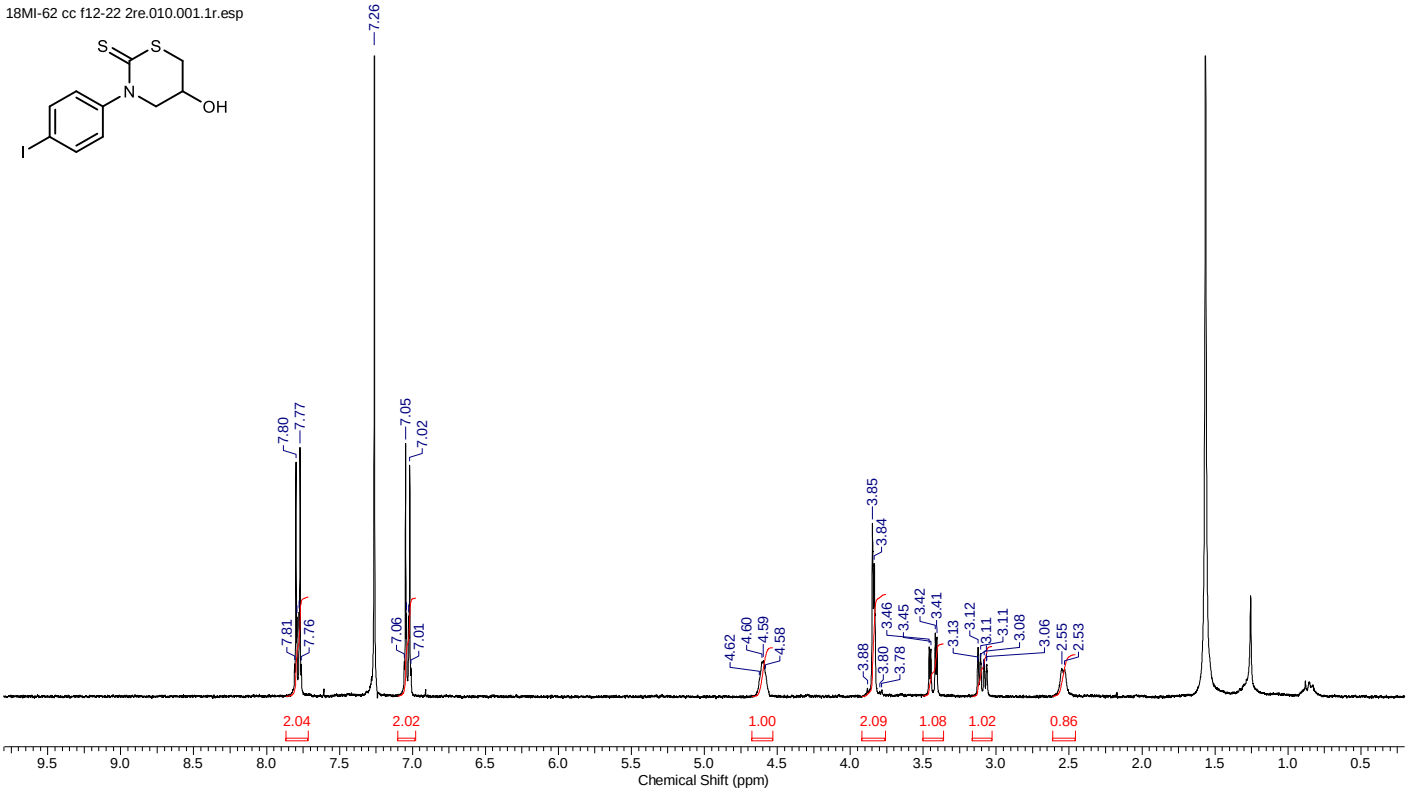
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2i

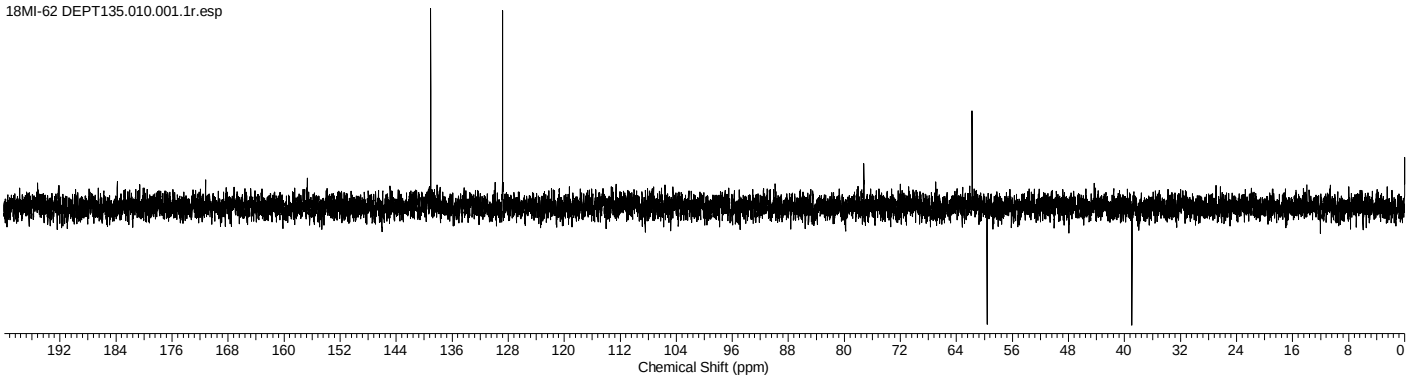


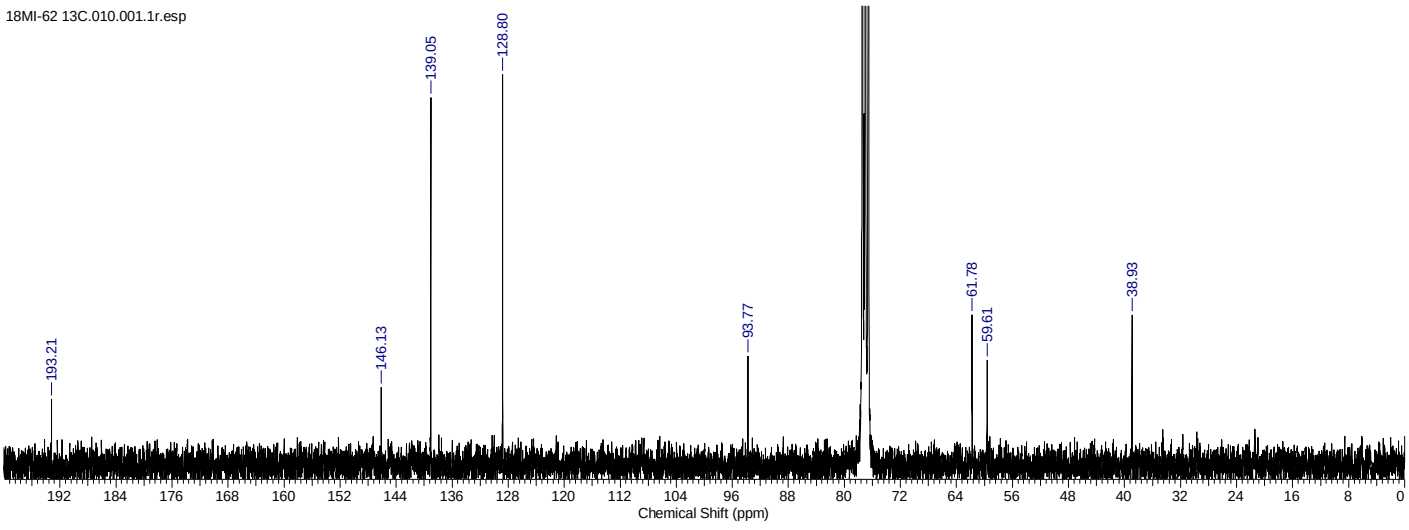




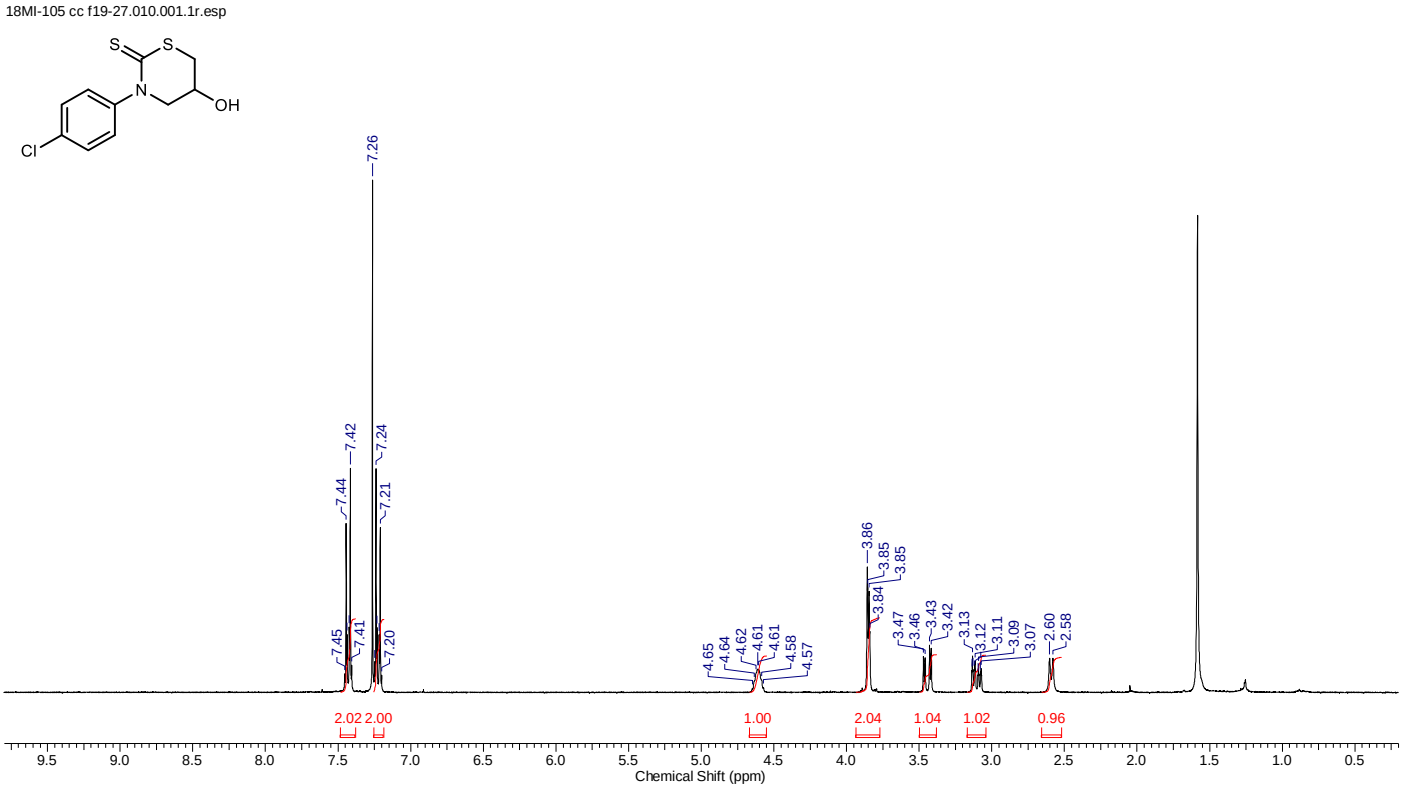
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2j

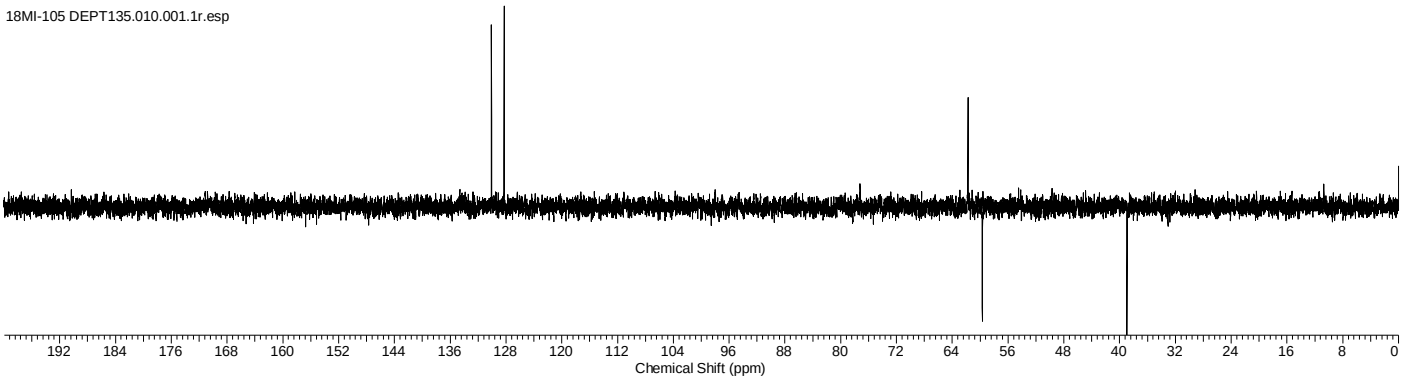


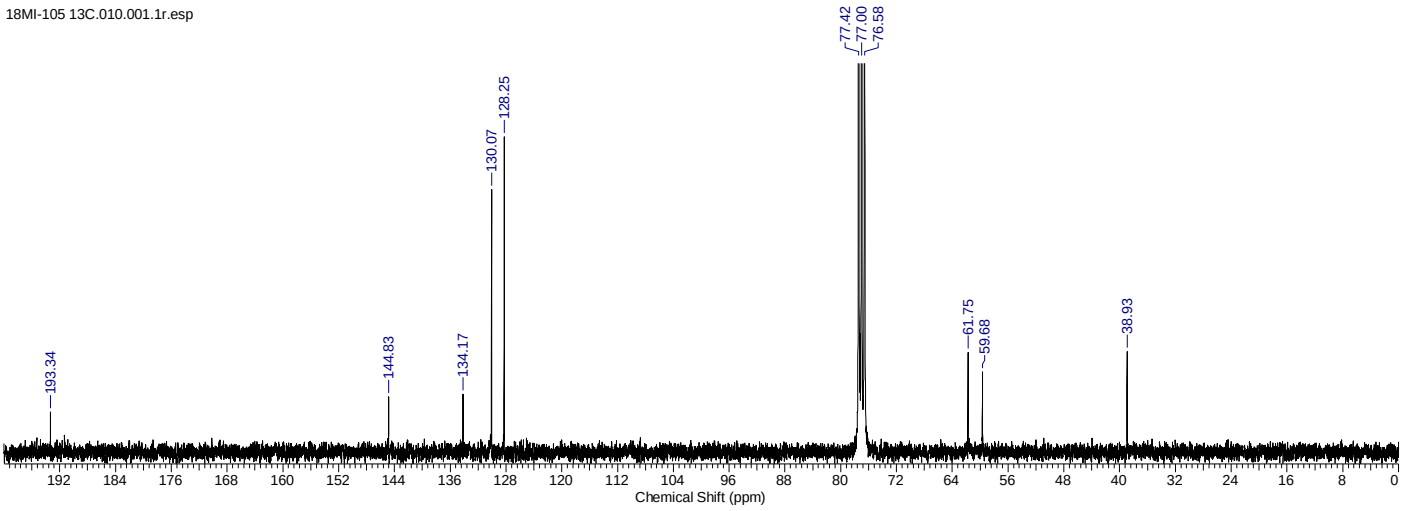




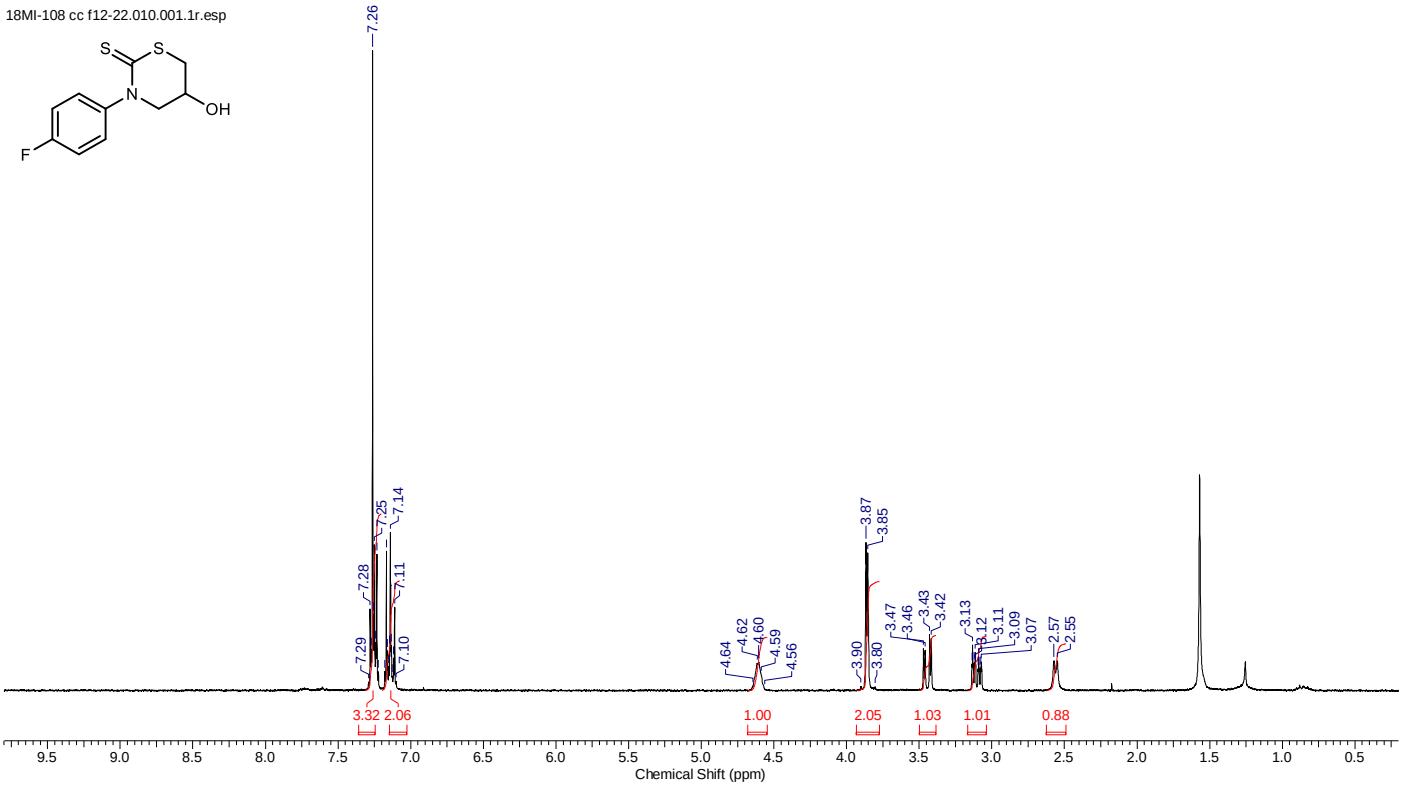
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2k

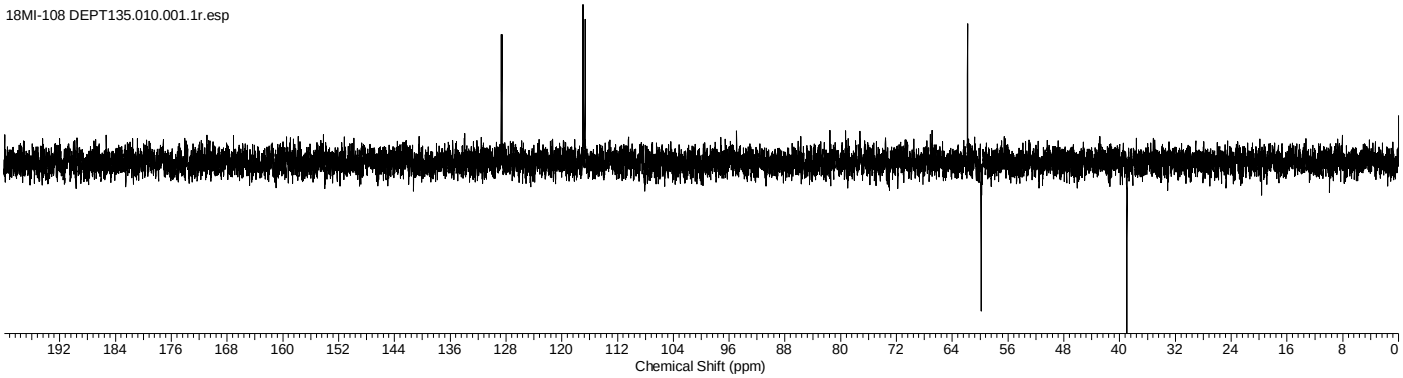


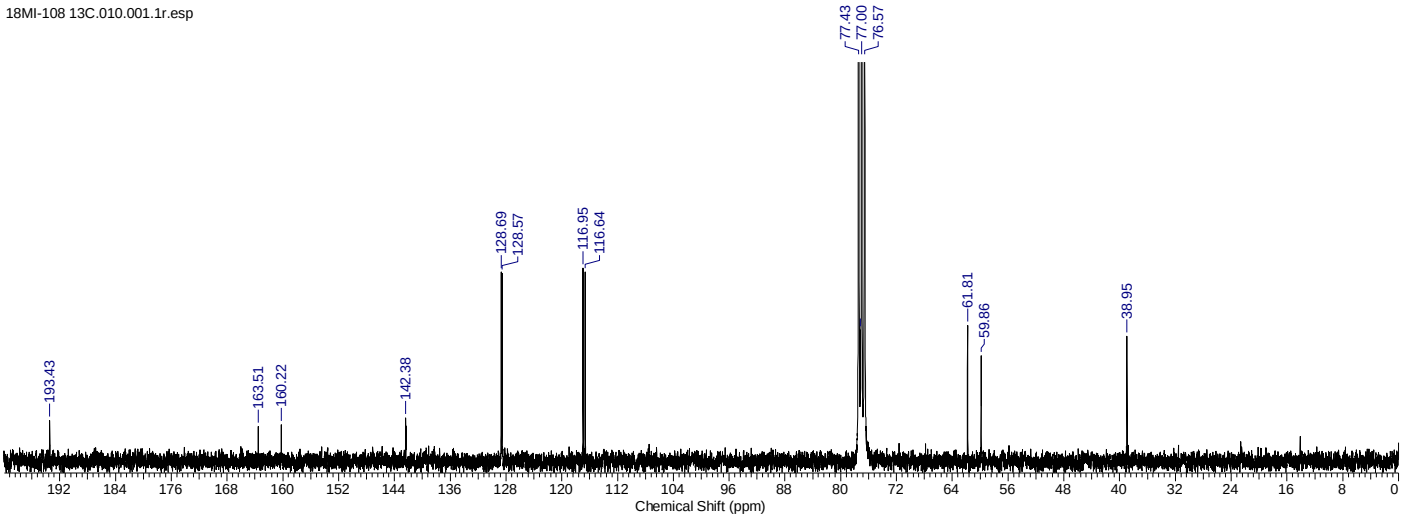




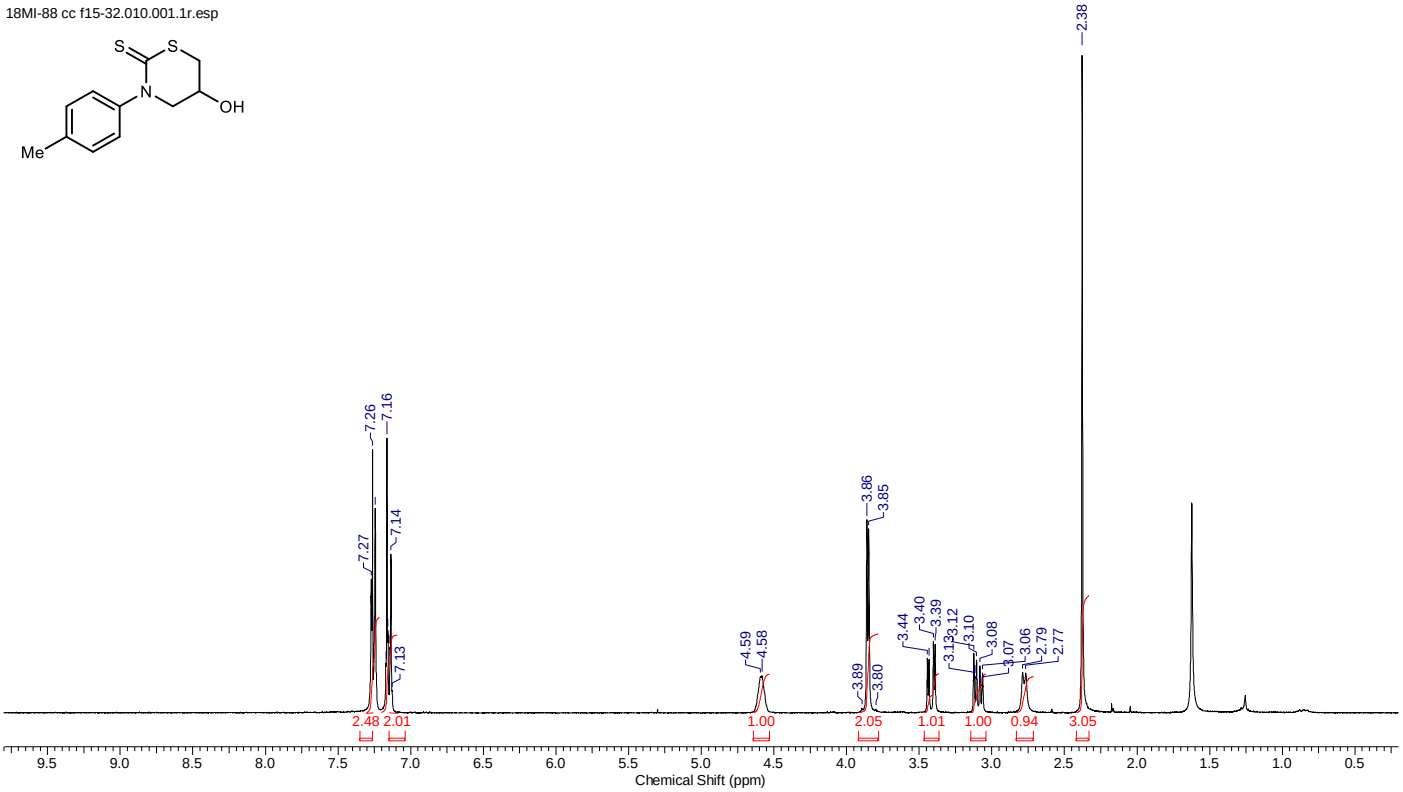
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2l

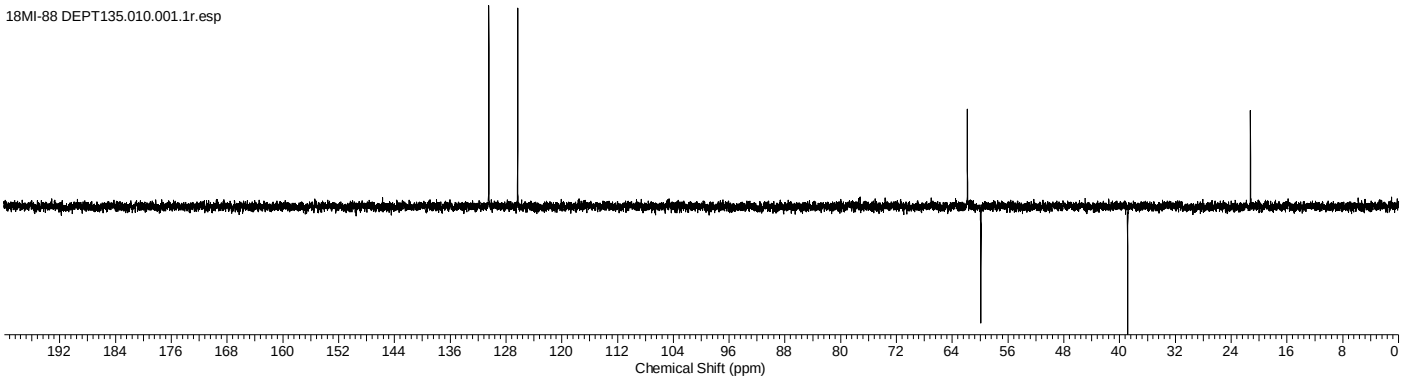


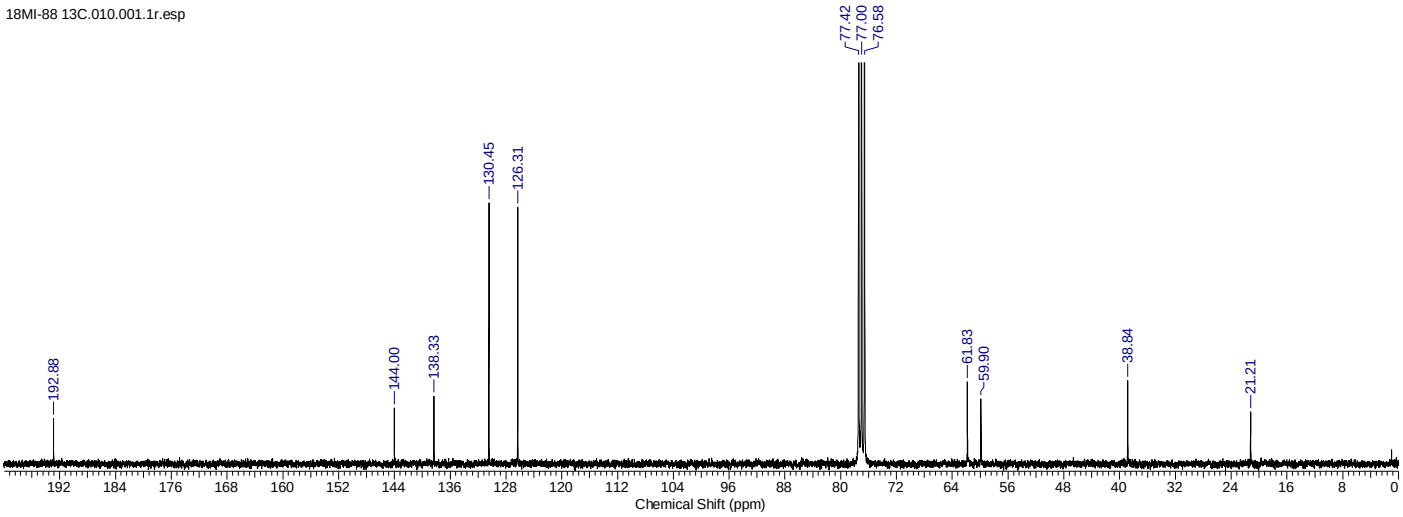




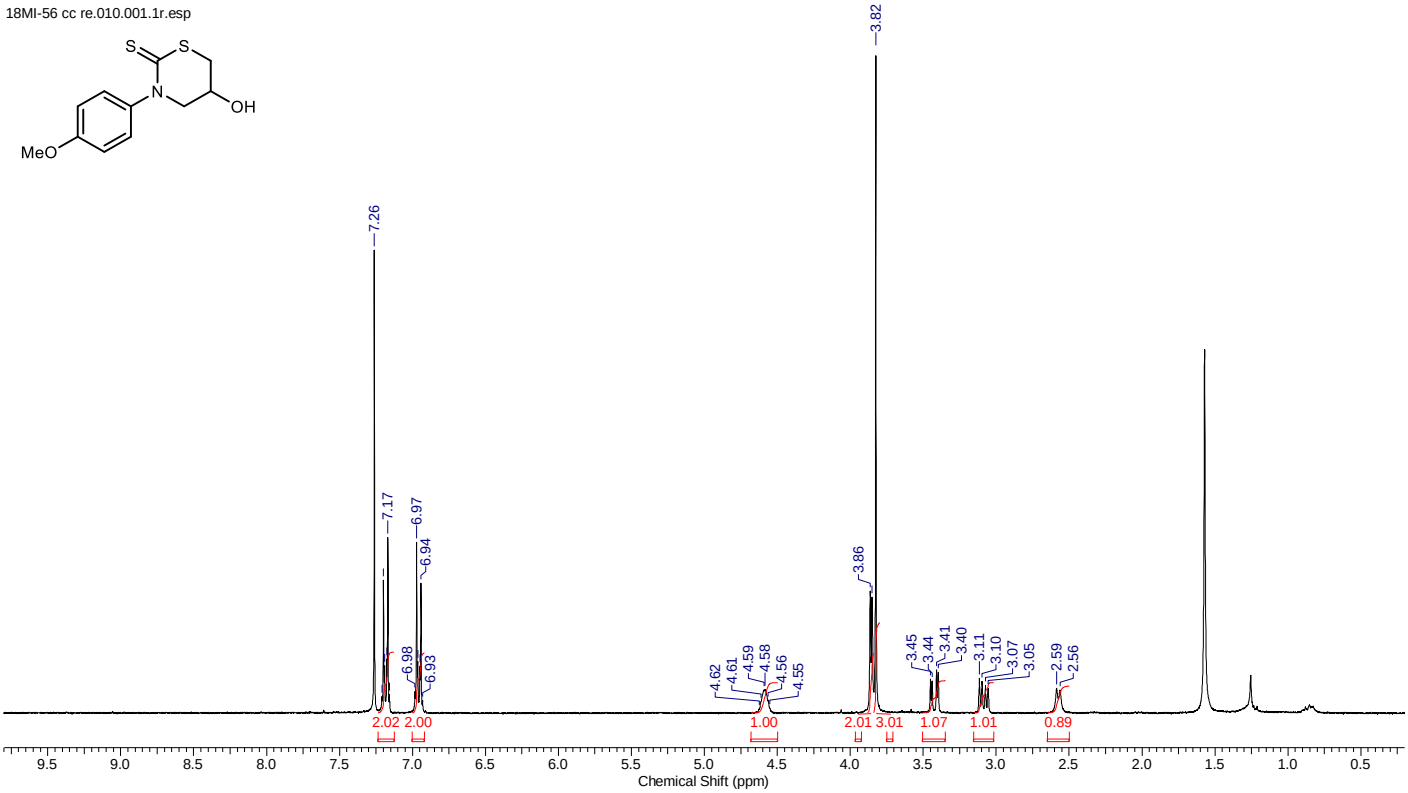
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2m

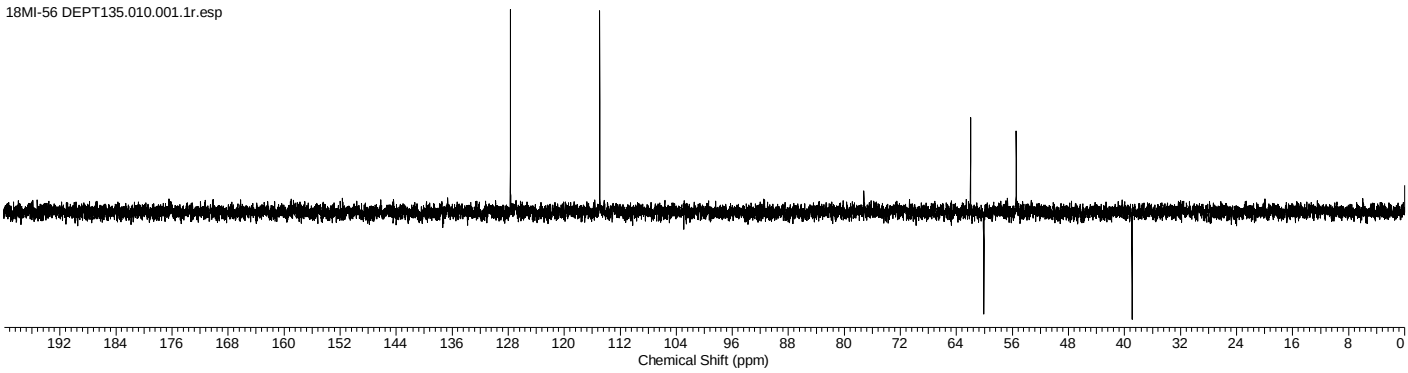


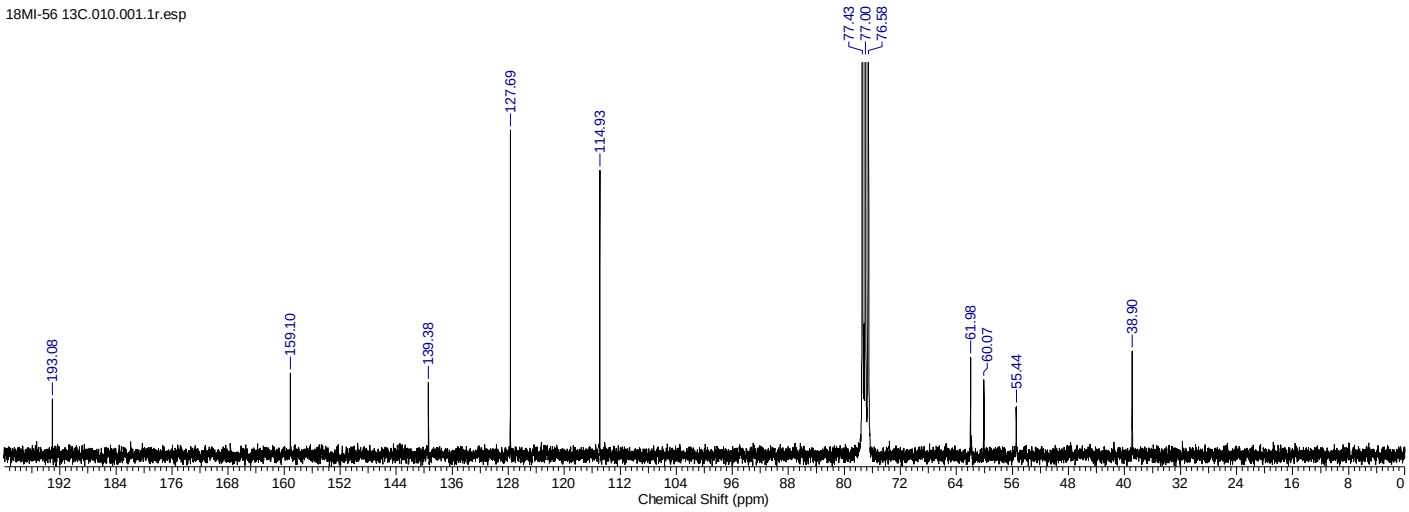




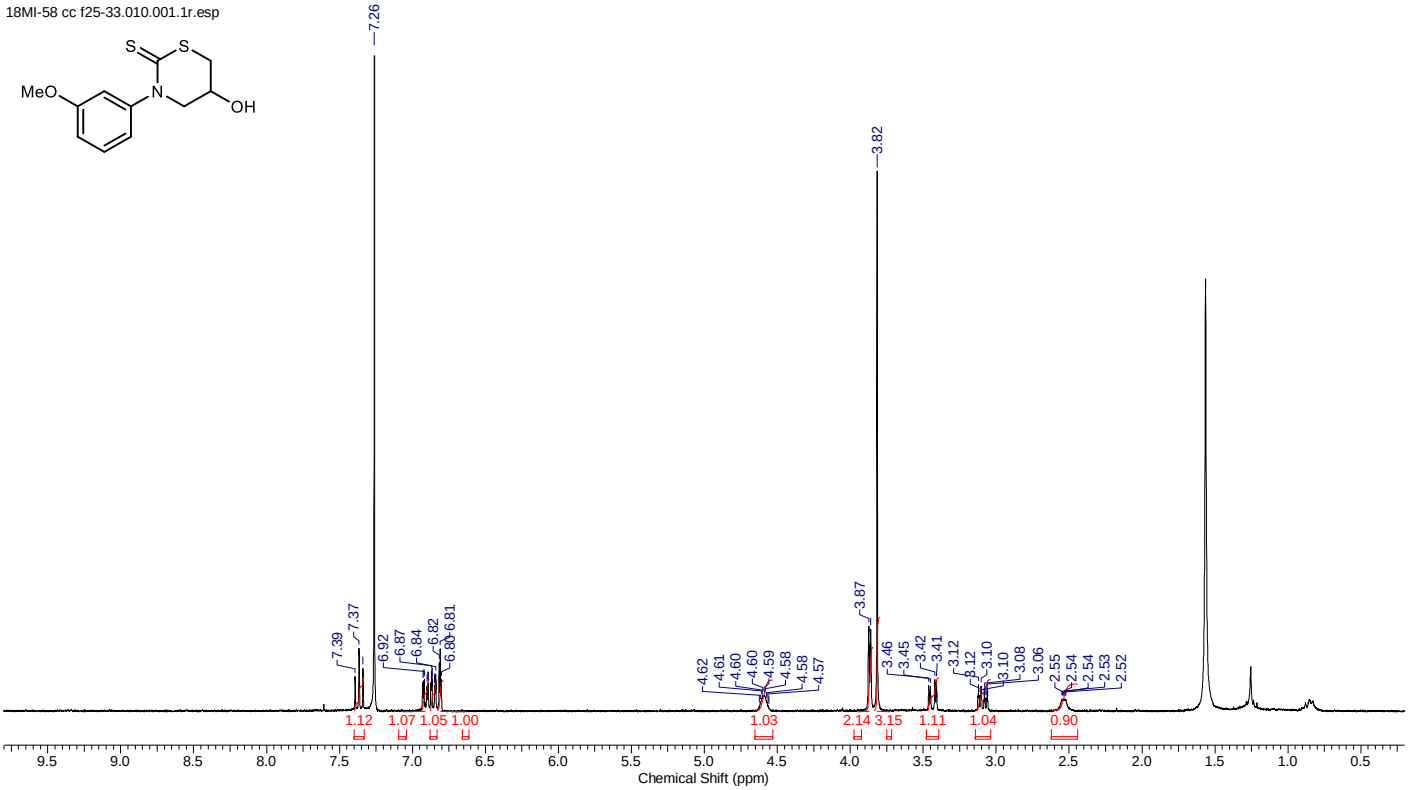
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2n

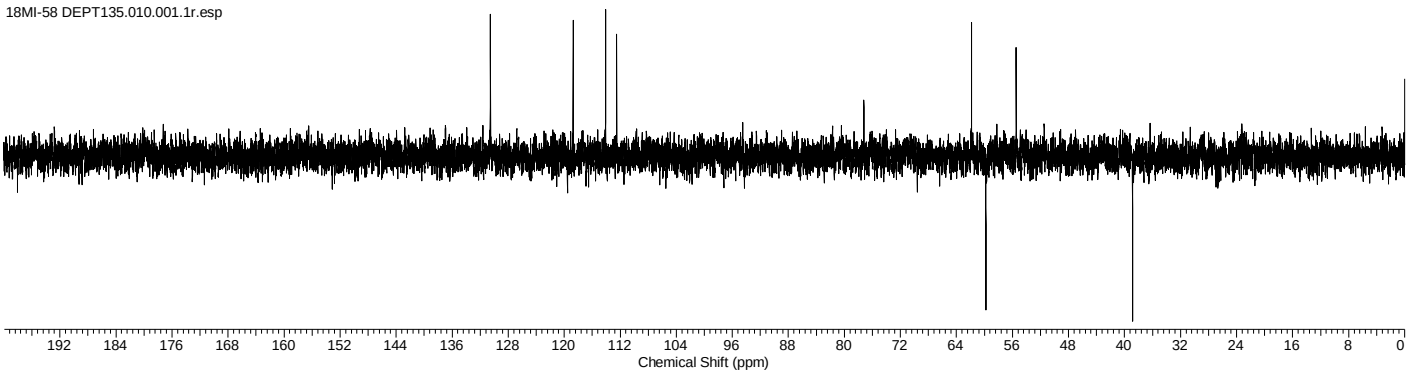


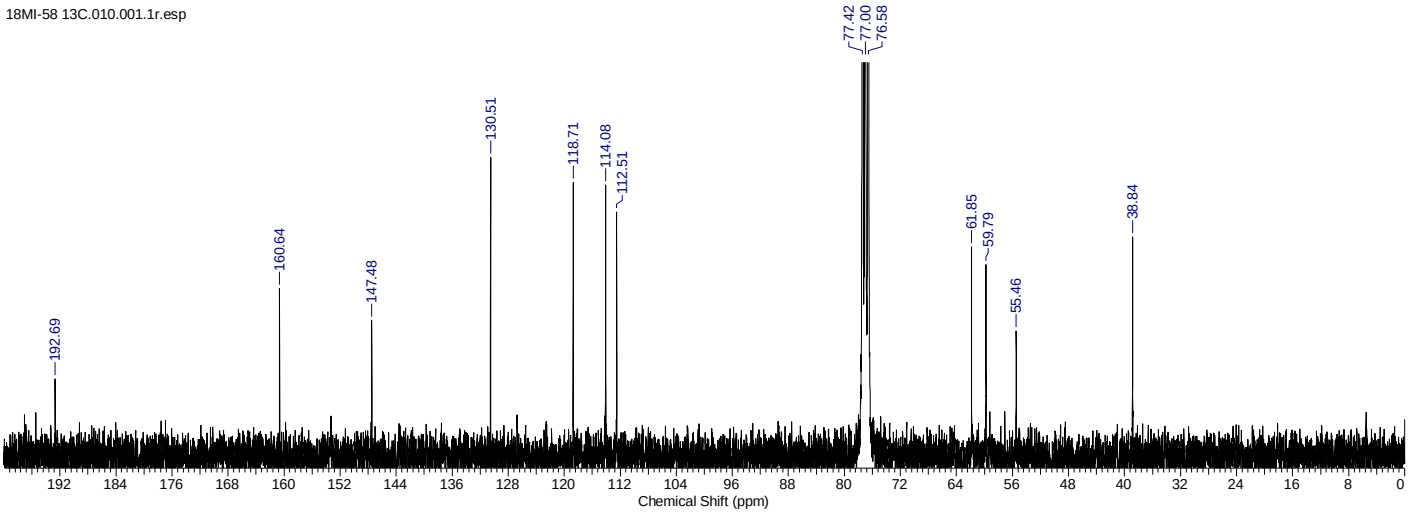




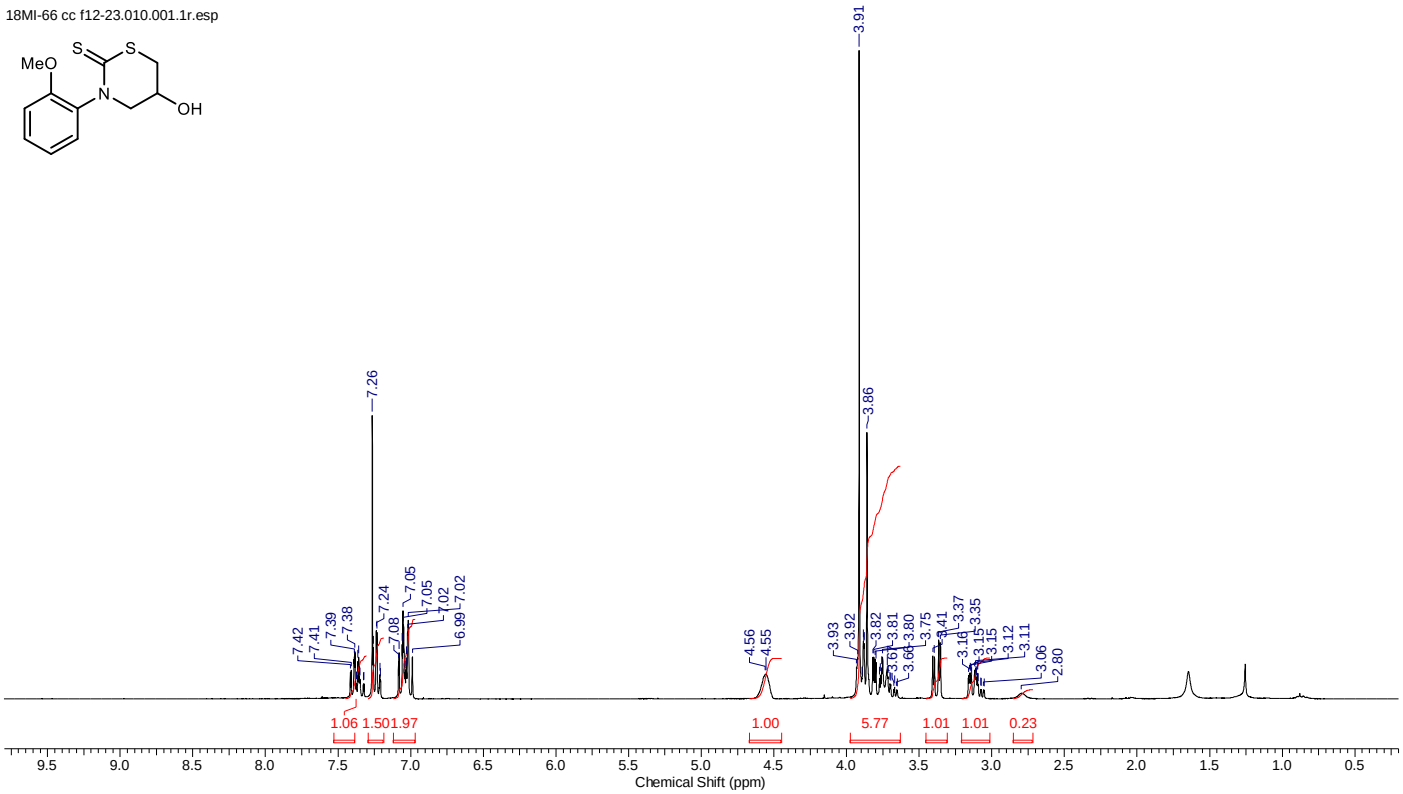
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2o

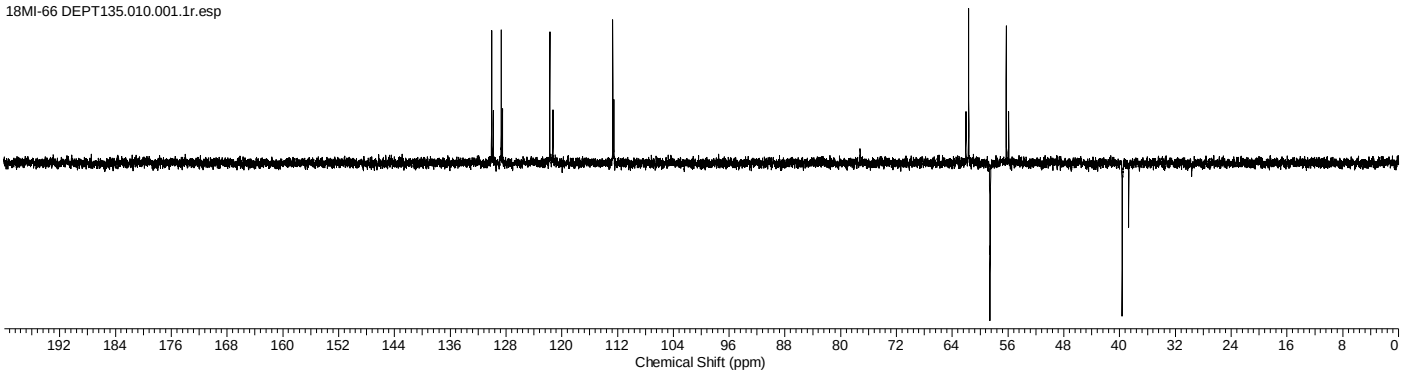


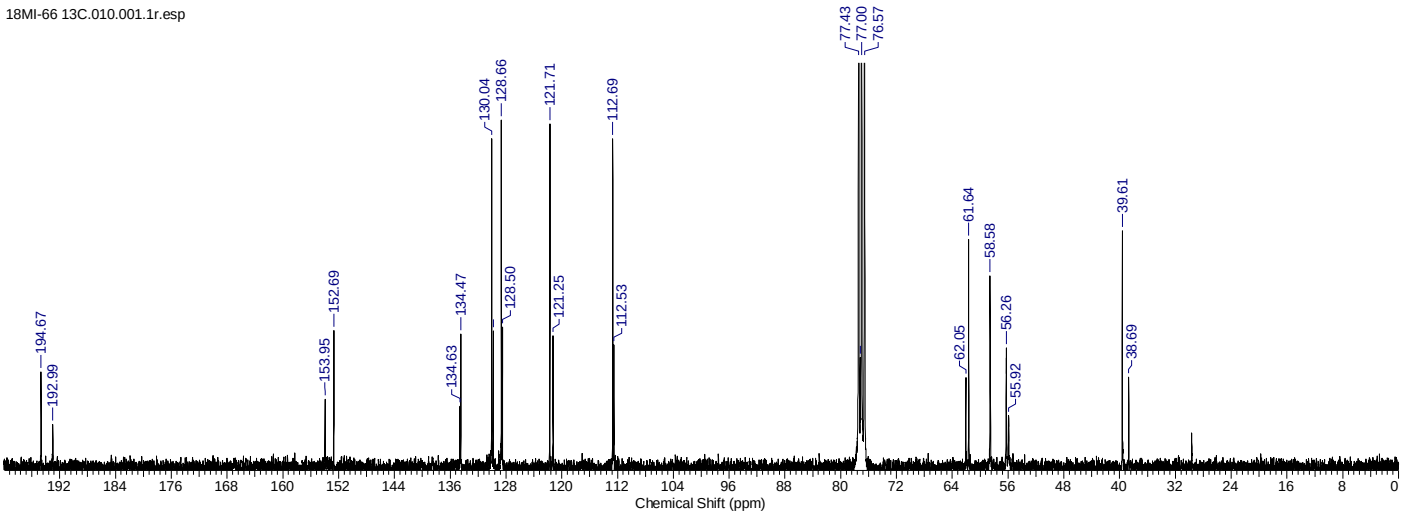




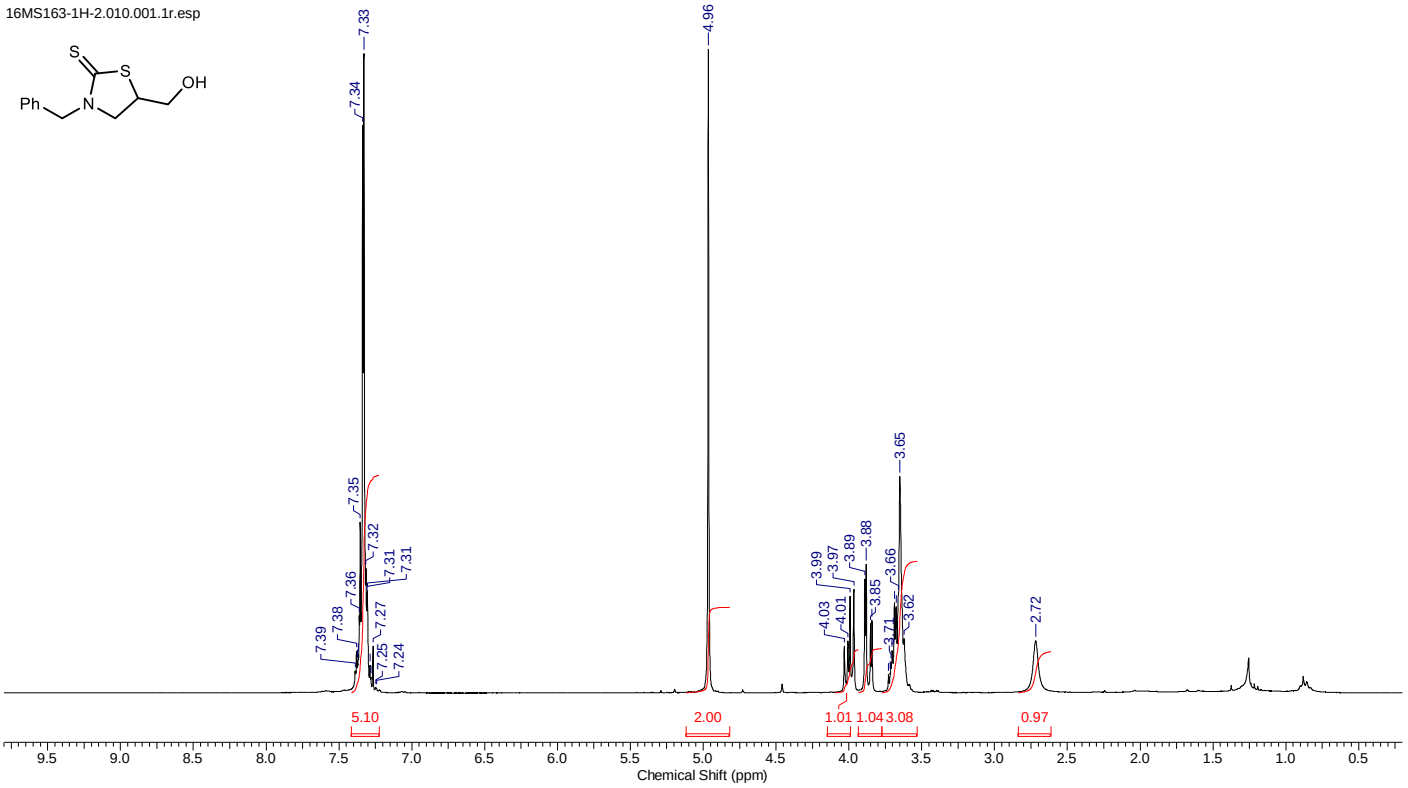
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2p

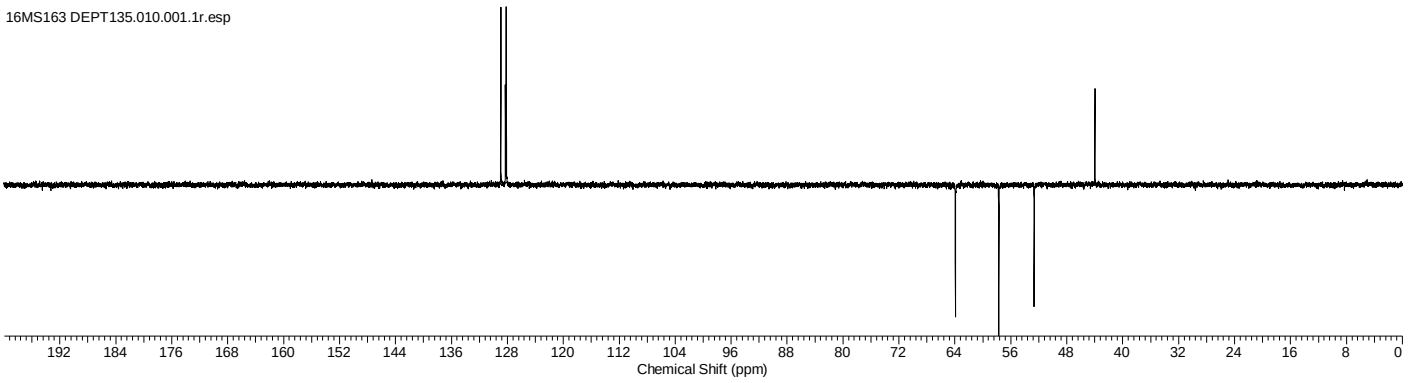


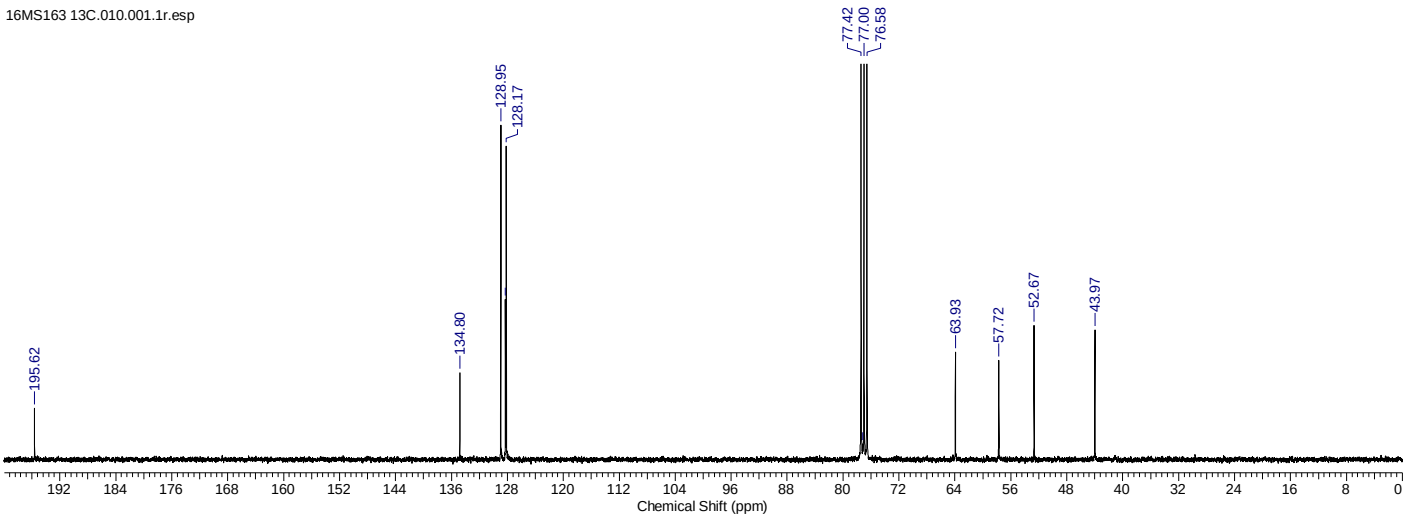




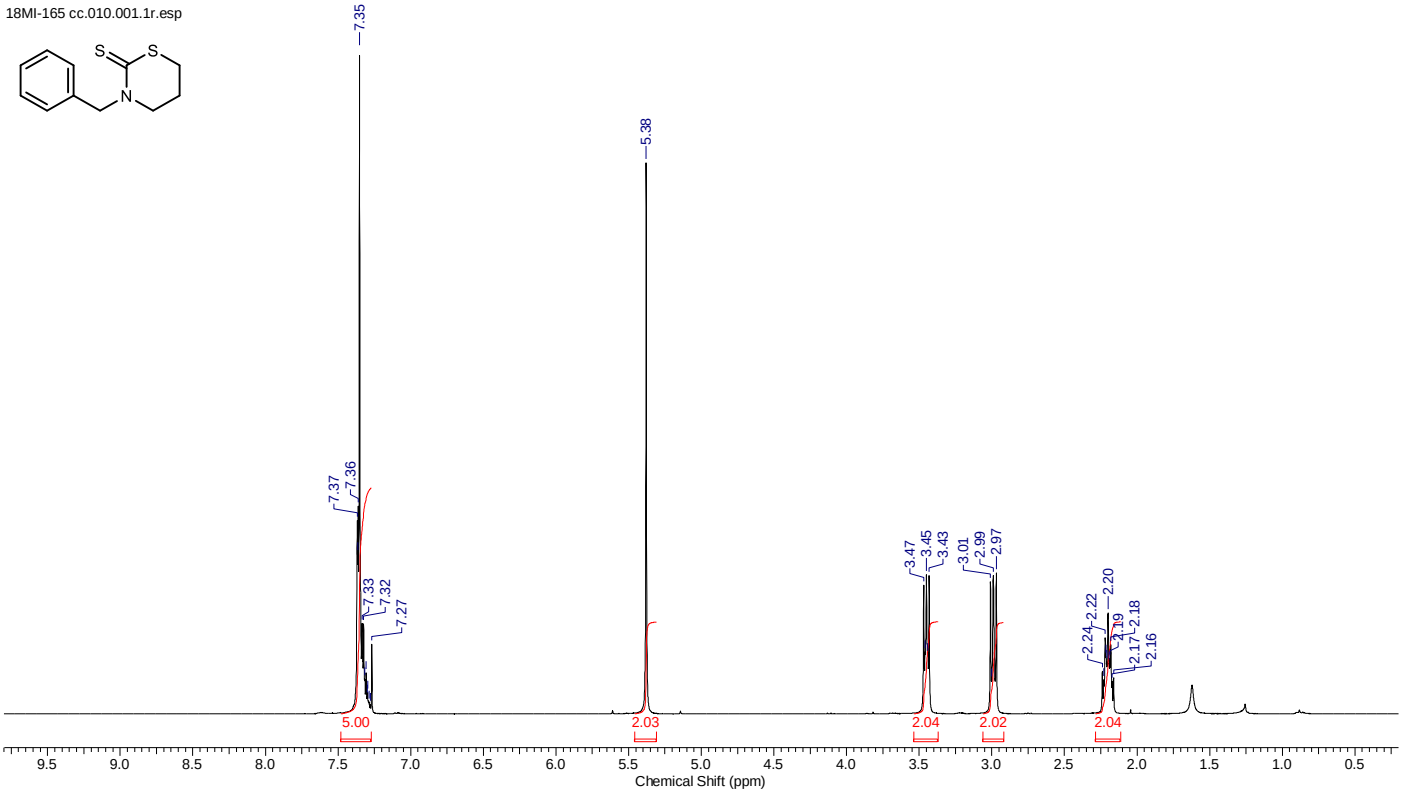
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of 2a'

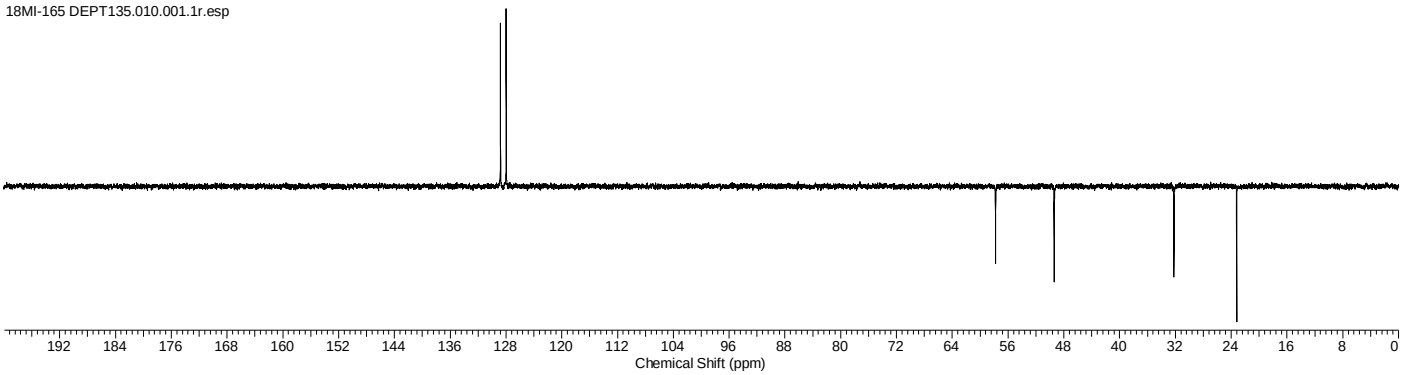


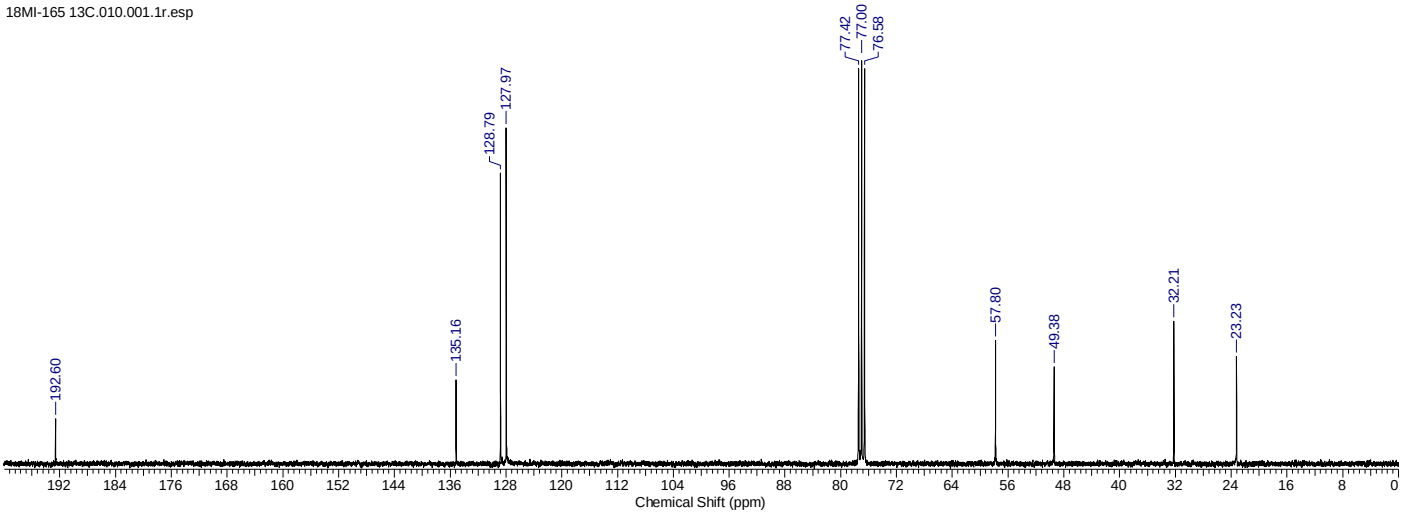




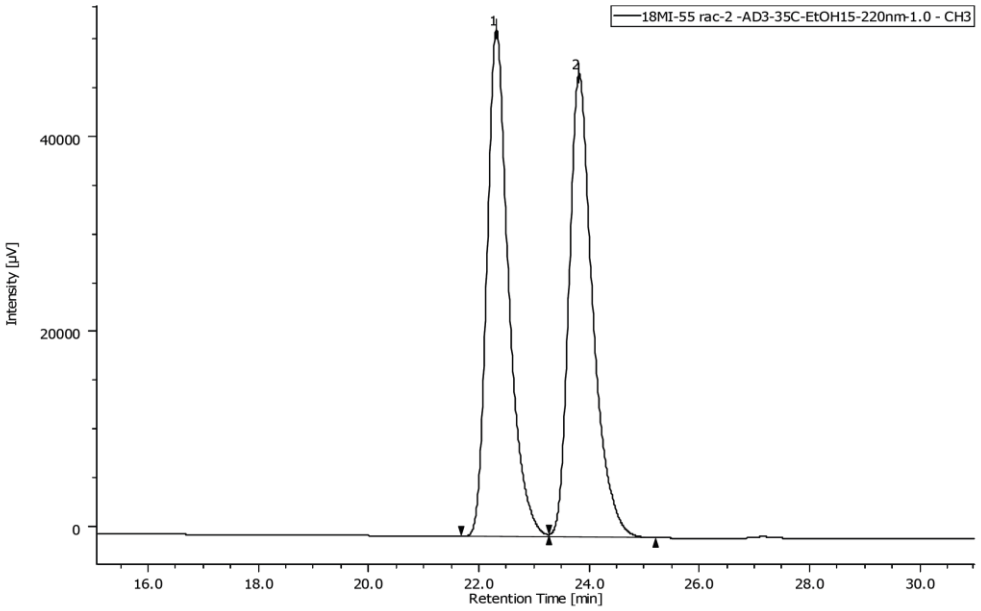
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$) Spectra of S1







HPLC Trace of 2c



# Peak	CH	tR	面積	高さ	面積%
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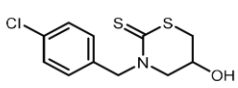
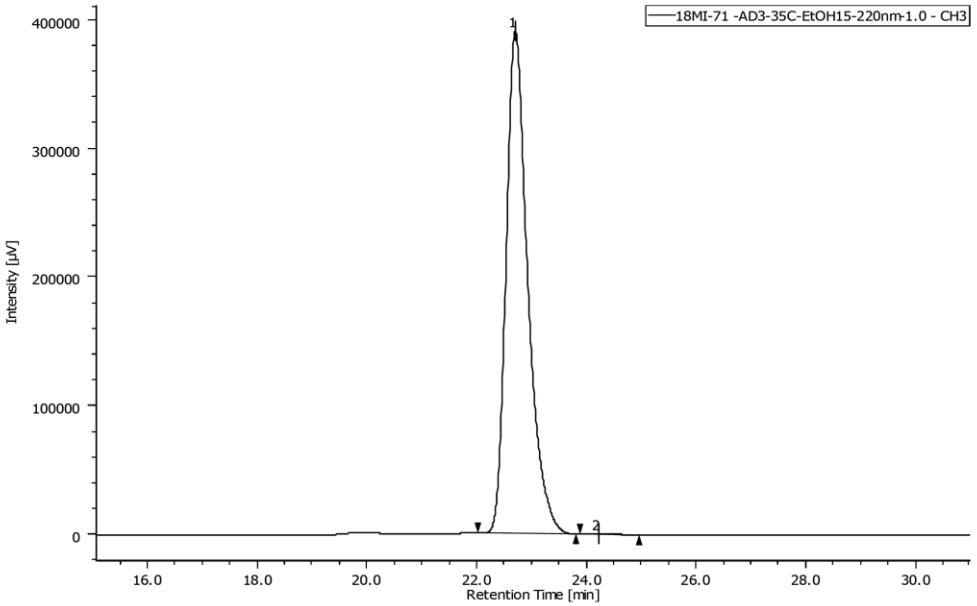
2	3	23.808	1415083	47475	50.014





# Peak	CH	tR (min)	Area	Height	Area%
1	3	22.7	10696565	389894	99.777
2	3	24.208	23869	926	0.223

99% ee