SUPPORTING INFORMATION

Effect of β-Alkylthioethyl Substitution in 1,3-Dithianes: Quasi-Anchimeric Assistance in Photoinduced Electron Transfer?

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Synthetic procedures:

1. Preparation of 2-(2-alkylthioethyl)-1,3-dithianes.
1.1. *General procedure.*

(A) Alkanethiol or alkanol was dissolved in 20-30 mL of THF (for thiols) or DMF (for alcohols), then NaH (60% in mineral oil, pre-washed with hexane) was slowly added and the resulting mixture was stirred for 15-20 min at room temperature.

(B) The formed thiolate/alcoholate (from step **A**) was added to a solution of 2-(2-bromoethyl)-1,3-dioxolane in THF or DMF and the resulting mixture was refluxed overnight. The reaction mixture was washed several times with water, brine and extracted with 20 mL of CH_2Cl_2. Organic layer was dried over anhydrous $NaSO_4$ and removed under vacuum.

(C) 2-(2-alkoxyethyl)-1,3-dioxolane or 2-(2-alkylthioethyl)-1,3-dioxolane (from step **B**) and 1,3-propanedithiol were dissolved in 100 mL of CH_2Cl_2, BF_3•Et_2O was added dropwise over 15-20 min and the resulting mixture was stirred overnight at 25ºC. The reaction mixture was washed with 5% aqueous NaOH (2 x 200 mL) and 50 mL of H_2O. The organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated and dried to furnish crude 2-(2-alkylthioethyl)-1,3-dithiane or 2-alkyloxyethyl)-1,3-dithiane, which were subjected to gel filtration using pentane and pentane/ether (15:1) as eluent.

1.2.1. 2-(2-Butylthioethyl)-1,3-dioxolane: From 2 g (22.2 mmol) of 1-butanethiol, 1.17 g (28.9 mmol) of NaH and 4.8 g, (26.7 mmol) of 2-(2-bromoethyl)-1,3-dioxolane in THF; yield 92.5 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.95 (t, 1H, *J* = 4.6 Hz,), 4.01-3.90 (m, 2H), 3.90-3.80 (m, 2H), 2.71-2.55 (m, 2H), 2.55-2.47 (m, 2H), 1.94 (m, 2H), 1.56 (quint, 2H, *J* = 7.4 Hz), 1.38 (sext., 2H, *J* = 7.4 Hz), 0.90 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 103.5, 65.1, 34.3, 32.1, 31.9, 26.6, 22.2, 13.9.

1.2.2. 2-(2-Butylthioethyl)-1,3-dithiane (**1a**): From 4.27 g (22.5 mmol) of 2-(2-butylthioethyl)-1,3-dioxolane, 2.5 mL (24.9 mmol) of 1,3-propanedithiol and 12.0 mL (94.6 mmol) of BF_3•Et_2O in CH_2Cl_2 (150 mL); yield 89 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.19 (t, 1H, *J* = 7.0 Hz), 2.94-2.76 (m, 4H), 2.69 (t, 2H, *J* = 7.4 Hz), 2.51 (t, 2H, *J* = 7.4 Hz), 2.17-2.06 (m, 1H), 2.02 (dt, 2H, *J* = 7.0, 7.4 Hz), 1.94-1.80 (m, 1H), 1.56 (quint, 2H, *J* = 7.4 Hz), 1.40 (sext., 2H, *J* = 7.4 Hz), 0.91 (t, 3H, *J* = 7.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 46.2, 35.4, 31.9, 31.9, 30.4, 29.1, 26.2, 22.2, 13.9. MS *m/z*: 236(M+, 100), 179(25), 146(35).

1.2.3. 2-(2-Butoxyethyl)-1,3-dioxolane: From 1.64 g (22.1 mmol) of 1-butanol, 1.5 g (37.5 mmol) of NaH (60% in mineral oil) and 2.0 g, (11.00 mmol) of 2-(2-bromoethyl)-1,3-dioxolane in DMF. The product was obtained with 43 % yield (0.83 g). ^{1}H NMR (400 M Hz, $CDCl_3$) δ: 4.97 (t, *J* = 4.9 Hz, 1H), 3.96 (m, 2H), 3.87-3.82 (m, 2H), 3.55 (t, *J* = 6.6 Hz, 2H), 3.42 (t, *J* = 6.6 Hz, 2H), 1.94 (dt, *J* = 6.6, 6.6, 4.9 Hz, 2H), 1.62-1.45 (m, 2H), 1.35 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

1.2.4. 2-(2-Butoxyethyl)-1,3-dithiane (**1b**): From 0.83 g (4.76 mmol) of 2-(2-butoxyethyl)-1,3-dioxolane, 0.53 mL (5.24 mmol) of 1,3-propanedithiol and 2.4 mL (19.04 mmol) of BF_3•Et_2O in CH_2Cl_2 (150 mL). The pure product was obtained with 51 % yield (0.54 g). ^{1}H NMR (400 M Hz, $CDCl_3$) δ: 4.20 (t, *J* = 7.11 Hz, 1H), 3.57 (t, *J* = 6.50 Hz, 2H), 3.42 (t, *J* = 6.61 Hz, 2H), 2.99-2.73 (m, 4H), 2.19-2.06 (m, 1H), 2.01 (q, *J* = 6.97, 6.67 Hz, 2H), 1.96-1.78 (m, 1H), 1.63-

1.46 (m, 2H), 1.37 (qd, *J* = 14.53, 7.21 Hz, 2H), 0.92 (t, *J* = 7.33 Hz, 3H). ^{13}C NMR (400 M Hz, $CDCl_3$) δ:70.8, 66.8, 44.1, 35.5, 31.7, 30.2, 26.0, 19.3, 13.9. GCMS *m/z*: 220 (M+, 60), 146 (100), 119 (25).

1.2.5. 2-(2-Ethoxyethyl)-1,3-dioxolane: From 2.0 g (43.5 mmol) of ethanol, 1.0 g (25 mmol) of NaH (60% in mineral oil) and 4.0 g, (22.1 mmol) of 2-(2-bromoethyl)-1,3-dioxolane in DMF. The resulting mixture was refluxed overnight. When the reaction was complete, the mixture was washed with water, brine, HCl (5%) x 2 and extracted with CH_2Cl_2. Organic layer was dried over anhydrous Na_2SO_4 and removed under vacuum. The product was obtained with 15 % yield. ^{1}H NMR (400 M Hz, $CDCl_3$) δ: 4.98 (t, 1H, *J* = 5.0 Hz), 3.96 (m, 2H), 3.85 (m, 2H), 3.56 (t, 2H, *J* = 6.7 Hz), 3.48 (q, 2H, *J* = 7.0 Hz), 1.95 (dt, 2H, *J* = 5.0 Hz, *J* = 6.7 Hz), 1.19 (t, 3H, *J* = 7.0 Hz).

1.2.6. 2-(2-Ethoxyethyl)-1,3-dithiane (**1c**): From 0.24 g (1.6 mmol) of 2-(2-ethoxyethyl)-1,3-dioxolane, 0.18 mL (1.8 mmol) of 1,3-propanedithiol and 0.83 mL (6.5 mmol) of BF_3•Et_2O in CH_2Cl_2 (150 mL), 98 % yield. ^{1}H NMR (400 M Hz, $CDCl_3$) δ: 4.20 (t, 1H, *J* = 7.1 Hz), 3.58 (t, 2H, *J* = 6.3 Hz), 3.49 (q, 2H, *J* = 7.0 Hz), 2.85 (m, 4H), 2.11 (m, 1H), 2.01 (dd, 2H, *J* = 6.4 Hz, *J* = 13.4 Hz), 1.88 (m, 1H), 1.20 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR (400 M Hz, $CDCl_3$) δ: 66.6, 66.3, 44.1, 35.5, 30.2, 26.0, 15.2. GCMS *m/z*: 192 (M+, 100), 146 (90), 119 (30).

1.2.7. 2-(2-Ethylthioethyl)-1,3-dioxolane: From 1.4 g (22.5 mmol) of ethylthiol, 1.1 g (45.83 mmol) of NaH (60% in mineral oil) and 2.0 g, (11.05 mmol) of 2-(2-bromoethyl)-1,3-dioxolane in DMF. The resulting mixture was refluxed overnight. When the reaction was complete, the mixture was washed with water, brine, HCl (5%) x 2 and extracted with CH_2Cl_2. Organic layer was dried over anhydrous NaSO4 and removed under vacuum. The product was obtained with 84 % yield (1.5 g).

1.2.8. 2-(2-Ethylthiolethyl)-1,3-dithiane (**1d**): From 1.5 g (9.2 mmol) of 2-(2-ethylsulfanylethyl)-1,3-dioxolane, 1.02 mL (10.0 mmol) of 1,3-propanedithiol and 4.23 mL (37.0 mmol) of BF_3• Et_2O in CH_2Cl_2 (100 mL). The pure product was obtained with 68 % yield (1.31g). ^{1}H NMR (400 M Hz, $CDCl_3$) δ: 4.27-4.12 (m, 1H), 2.93-2.79 (m, 4H), 2.71 (t, *J* = 7.8 Hz, 2H), 2.54 (q, *J* = 7.39 Hz, 2H), 2.11 (m, 1H), 2.03 (dd, *J* = 14.31, 7.35 Hz, 2H), 1.95-1.77 (m, 1H), 1.26 (t, *J* = 7.39 Hz, 3H). ^{13}C NMR (400 M Hz, $CDCl_3$) δ: 45.9, 35.1, 30.1, 28.4, 25.9, 25.8, 14.7. GCMS *m/z*: 208 (M+, 100), 179 (30), 146 (27).

1.2.9. 1,5,9-Trithiaspiro[5.5]undecane (**1e**): From 0.32 g (2.75 mmol) of tetrahydro-4H-thiopyran-4-one, 0.33 mL (3.00 mmol) of 1,3-propanedithiol and 1.40 mL (11.0 mmol) of BF_3• Et_2O in CH_2Cl_2 (50 mL). The product was obtained with 82 % yield (0.46 g). ^{1}H NMR (400 M Hz, $CDCl_3$) δ: 2.89-2.66 (m, 4H), 2.44-2.19 (m, 2H), 1.98 (m, 1H). ^{13}C NMR (400 M Hz, $CDCl_3$) δ: 49.14, 38.47, 25.71, 25.25, 23.86. GCMS *m/z*: 206 (M+, 100), 99 (50), 45 (24).

1.2.10. 1,5-Dithiaspiro[5.5]undecane (**1f**): From 1.0 g (10.2 mmol) of cyclohexanone, 1.12 mL (11.2 mmol) of 1,3-propanedithiol and 5.17 mL (40.7 mmol) of BF_3• Et_2O in CH_2Cl_2 (70 mL). The product was obtained with 90 % yield (1.73 g). ^{1}H NMR (400 M Hz, $CDCl_3$) δ: 3.05-2.66 (m, 2H), 2.07-1.86 (m, 3H), 1.63 (td, *J* = 11.78, 6.07 Hz, 2H), 1.46 (m, 1H). ^{13}C NMR (400 M Hz, $CDCl_3$) δ: 50.4, 37.9, 26.2, 25.9, 25.9, 22.0.

1.2.11. 2,2-Dimethyl-1,3-dithiane (**1g**): [described in (a) Hoppman, A.; Weyerstahl, P.; Zummack, W. Justus Liebigs Ann. Chem. 9 (1977) 1547-1456. (b) Carey, F.A.; Dailey, O.D.; Hutton, W. C. J. Org. Chem. 43 (1978) 96-101] From 1.0 g (17.2 mmol) of acetone, 1.90 mL (19.0 mmol) of 1,3-propanedithiol and 8.73 mL (68.9 mmol) of BF_3• Et_2O in CH_2Cl_2 (70 mL). The product was obtained with 100 % yield (2.55 g). ^{1}H NMR (400 M Hz, $CDCl_3$) δ: 3.07-2.78 (m, 2H), 2.03-1.89 (m, 1H), 1.70 (s, 3H). ^{13}C NMR (400 M Hz, $CDCl_3$) δ: 45.2, 30.8, 27.0, 25.2.

1.3. Preparation of adducts.

1.3.1. [2-(2-Butylthioethyl)-1,3-dithian-2-yl]phenyl-methanol (**2a**): From 1.0 g (4.24 mmol) of 2-(2-butylthioethyl)-1,3-dithiane (**1a**), 4.2 mL (6.72 mmol) of *n*-BuLi (1.6 M solution in hexane) and 0.71 g (6.70 mmol) of benzaldehyde after purification by column chromatography (silica gel, hexane/AcOEt = 20:1, then 10:1) the adduct **2a** was obtained with 90% yield. ^{1}H NMR (500 M Hz, $CDCl_3$) δ: 7.50 (dd, 2H, *J* = 1.7 Hz, *J* = 7.5 Hz), 7.32 (m, 3H), 5.14 (d, 1H, *J* = 1.19 Hz), 3.29 (d, 1H, *J* = 1.7 Hz), 3.16 (ddd, 1H, *J* = 3.0 Hz, *J* = 11.4 Hz, *J* = 14.3 Hz), 3.02 (ddd, 1H, *J* = 2.9 Hz, *J* = 11.7 Hz, *J* = 14.4 Hz), 2.72 (m, 4H), 2.45 (m, 2H), 2.11 (m, 2H), 1.88 (m, 1H), 1.68 (ddd, 1H, *J* = 4.8 Hz, *J* = 12.0 Hz, *J* = 14.7 Hz), 1.52 (m, 2H), 1.37 (qd, 2H, *J* = 7.3 Hz, *J* = 14.4 Hz), 0.89 (t, 3H, *J* = 7.3 Hz). ^{13}C NMR (400 M Hz, $CDCl_3$) δ: 137.3, 128.6, 128.0, 127.4, 74.1, 58.9, 34.9, 31.8, 31.7, 27.2, 26.5, 25.5, 24.0, 21.9, 13.7.

1.3.2. [2-(2-Butoxyethyl)-1,3-dithian-2-yl]phenyl-methanol (**2b**): From 0.47 g (2.14 mmol) of 2-(2-butoxyethyl)-1,3-dithiane (**1b**), 2 mL (3.20 mmol) of *n*-BuLi (1.6 M solution in hexane) and 0.27 g (2.55 mmol) of benzaldehyde after purification by column chromatography (silica gel, hexane/AcOEt = 20:1, then 10:1) the adduct **2b** was obtained with 80% yield. ^{1}H NMR (400 M Hz, $CDCl_3$) δ: 7.54 (dd, 2H, *J* = 1.7 Hz, *J* = 7.8 Hz), 7.31 (m, 3H), 5.04 (d, 1H, *J* = 4.3 Hz), 4.30 (d, 1H, *J* = 4.3 Hz), 3.76 (ddd, 1H, *J* = 6.1 Hz, *J* = 7.6 Hz, *J* = 9.7 Hz), 3.63 (ddd, 1H, *J* = 5.4 Hz, *J* = 6.5 Hz, *J* = 9.7 Hz), 3.46 (m, 2H), 2.92 (ddd, *J* = 14.3 Hz, *J* = 9.2 Hz, *J* = 3.5 Hz, 2H), 2.85 (ddd, *J* = 14.3 Hz, *J* = 9.2 Hz, *J* = 3.5 Hz, 2H), 2.68 (m, 2H), 2.28 (ddd, 1H, *J* = 6.6 Hz, *J* = 7.6 Hz, *J* = 15.1 Hz), 1.95 (m, 3H), 1.57 (m, 2H), 1.36 (m, 2H), 0.91 (t,

3H, J = 7.4 Hz). ^{13}C NMR (400 M Hz, $CDCl_3$) δ: 138.2, 128.8, 127.8, 127.3, 75.9, 71.1, 67.2, 57.7, 34.9, 31.6, 29.7, 26.4, 25.6, 24.4, 19.3, 13.9.

1.3.3. [2-(2-ethoxyethyl)-1,3-dithian-2-yl]phenyl-methanol (**2c**): From 0.25 g (1.13 mmol) of 2-(2-ethoxyethyl)-1,3-dithiane (**1c**), 1.06 mL (1.70 mmol) of *n*-BuLi (1.6 M solution in hexane) and 0.16 g (1.51 mmol) of benzaldehyde after purification by column chromatography (silica gel, hexane/AcOEt = 20:1, then 10:1) the adduct **2c** was obtained with 85% yield. ^{1}H NMR (400 M Hz, $CDCl_3$) δ: 7.53 (dd, 2H, J = 1.7 Hz, J = 7.8 Hz), 7.31 (m, 3H), 5.05 (d, 1H, J = 4.0 Hz), 4.24 (d, 1H, J = 4.0 Hz), 3.76 (ddd, 1H, J = 6.5 Hz, J = 7.4 Hz, J = 9.6 Hz), 3.64 (ddd, 1H, J = 5.4 Hz, J = 6.8 Hz, J = 9.6 Hz), 3.52 (m, 2H), 2.95 (m, 1H, J = 3.3 Hz, J = 9.4 Hz, J = 14.4 Hz), 2.87 (m, 1H, J = 3.3 Hz, J = 9.4 Hz, J = 14.4 Hz), 2.69 (ddd, 1H, J = 3.4 Hz, J = 6.9 Hz, J = 13.9 Hz), 2.67 (ddd, 1H, J = 3.4 Hz, J = 6.9 Hz, J = 13.9 Hz), 2.27 (td, 1H, J = 7.2 Hz, J = 14.5 Hz), 2.00 (m, 1H), 1.89 (m, 2H), 1.22 (t, 3H, J = 7.0 Hz). ^{13}C NMR (400 M Hz, $CDCl_3$) δ:138.1, 128.8, 127.9, 127.3, 75.7, 67.0, 66.6, 57.7, 34.7, 26.4, 25.6, 24.3, 15.1.

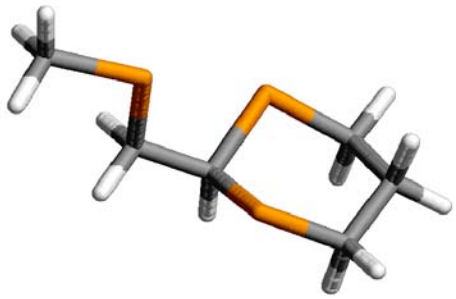
COMPUTATIONAL DETAILS

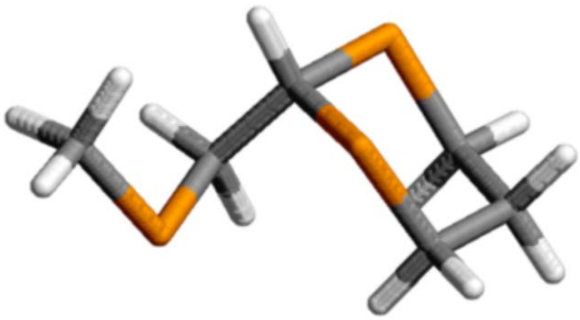
Gaussian Full Citation:

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

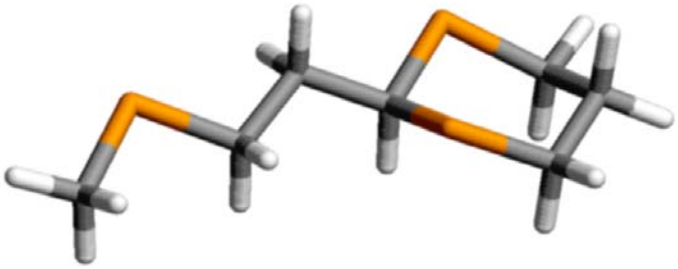
α-SULFIDE

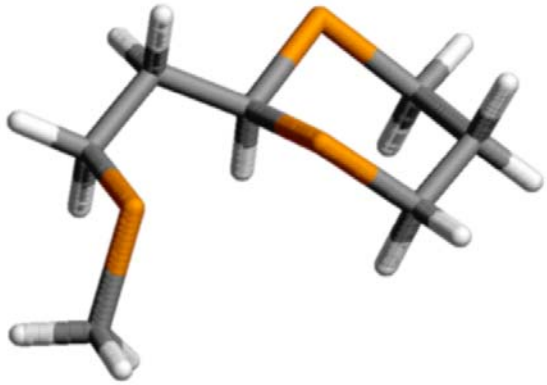
Methylthiomethyl-1,3-Dithiane	endocyclic S-S distance: 3.072 Å exocyclic S-S distances: 3.357 Å, 4.414 Å
C 3.1254 -0.3847 -0.0985 C 2.7142 0.9738 0.4616 S 1.1446 1.6323 -0.2212 C 0.0047 0.2637 0.2471 S 0.4899 -1.3632 -0.4498 C 2.1678 -1.5131 0.2736 C -1.3885 0.6474 -0.2338 S -2.6636 -0.5316 0.3713 C -4.1489 0.4024 -0.1269 H 3.2224 -0.3237 -1.1849 H 4.1148 -0.6316 0.3064 H 3.4547 1.7353 0.2134 H 2.6335 0.9382 1.5516 H 0.0133 0.1824 1.3354 H 2.5350 -2.4695 -0.1012 H 2.0748 -1.6030 1.3596 H -1.6326 1.6380 0.1555 H -1.4162 0.6830 -1.3246 H -4.1819 0.5376 -1.2084 H -4.1923 1.3705 0.3734 H -5.0073 -0.1945 0.1798	 File: eq.log SCF Done: E(RB+HF-LYP) = -1430.58976356 A.U. after 1 cycles Zero-point vibrational energy 450123.8 (Joules/Mol) 107.58217 (Kcal/Mol) Zero-point correction= 0.171443 (Hartree/Particle) Thermal correction to Energy= 0.182614 Thermal correction to Gibbs Free Energy= 0.133295 Sum of electronic and zero-point Energies= -1430.418320

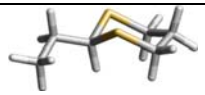
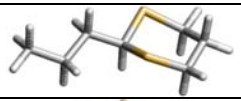
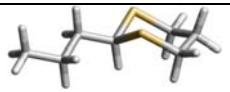
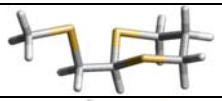
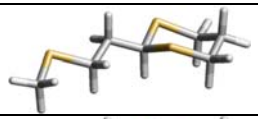
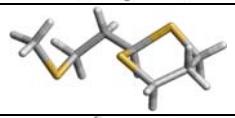
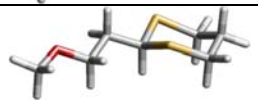
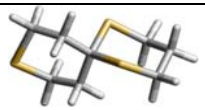
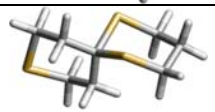
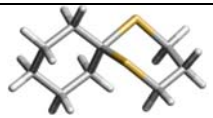
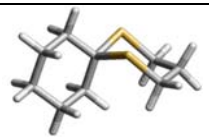
Methylthiomethyl-1,3-Dithiane Radical Cation	endocyclic S-S distance: 2.928 Å exocyclic S-S distances: 3.194 Å, 3.194 Å
C 2.9297 0.0000 -0.6234 C 2.4093 1.2755 0.0349 S 0.5889 1.4666 -0.0434 C 0.0685 -0.0000 0.9236 S 0.5889 -1.4667 -0.0434 C 2.4094 -1.2755 0.0349 C -1.4461 -0.0000 1.0550 S -2.1931 -0.0000 -0.6140 C -3.9575 0.0001 -0.1816 H 2.6881 0.0000 -1.6880 H 4.0213 0.0001 -0.5396 H 2.7883 2.1621 -0.4739 H 2.6991 1.3371 1.0872 H 0.5450 -0.0000 1.9038 H 2.7884 -2.1620 -0.4739 H 2.6992 -1.3371 1.0872 H -1.7750 -0.8892 1.5994 H -1.7750 0.8891 1.5994 H -4.5029 0.0000 -1.1236 H -4.2061 0.8961 0.3871 H -4.2062 -0.8959 0.3871	 File: eq_cr.log SCF Done: E(UB+HF-LYP) = -1430.31375343 A.U. after 1 cycles Zero-point vibrational energy 449634.8 (Joules/Mol) 107.46529 (Kcal/Mol) Zero-point correction= 0.171257 (Hartree/Particle) Thermal correction to Energy= 0.182441 Thermal correction to Gibbs Free Energy= 0.132638 Sum of electronic and zero-point Energies= -1430.142497

Methylthiomethyl-1,3-Dithiane Radical Cation	endocyclic S-S distance: 2.967 Å exocyclic S-S distances: 2.925 Å, 4.424 Å
C 2.4629 1.1041 0.3258 C 1.0677 1.7233 0.2156 S 0.0278 0.9105 -1.0589 C -0.0563 -0.8185 -0.4306 S 1.6193 -1.5015 -0.3738 C 2.4537 -0.3512 0.7878 C -0.9164 -0.8835 0.8345 S -2.2395 0.3816 0.7279 C -3.4179 -0.3550 -0.4477 H 2.9884 1.1902 -0.6270 H 3.0231 1.6958 1.0572 H 1.1211 2.7594 -0.1193 H 0.5374 1.7064 1.1687 H -0.5375 -1.3635 -1.2433 H 3.4697 -0.7438 0.8403 H 2.0129 -0.4625 1.7806 H -1.3473 -1.8740 0.9791 H -0.3560 -0.6261 1.7318 H -3.7931 -1.2929 -0.0393 H -4.2352 0.3586 -0.5374 H -2.9675 -0.5129 -1.4261	 File ax2_cr.log SCF Done: E(UB+HF-LYP) = -1430.31581908 A.U. after 1 cycles Zero-point vibrational energy 451278.2 (Joules/Mol) 107.85807 (Kcal/Mol) Zero-point correction= 0.171883 (Hartree/Particle) Thermal correction to Energy= 0.182986 Thermal correction to Gibbs Free Energy= 0.133836 Sum of electronic and zero-point Energies= -1430.143936

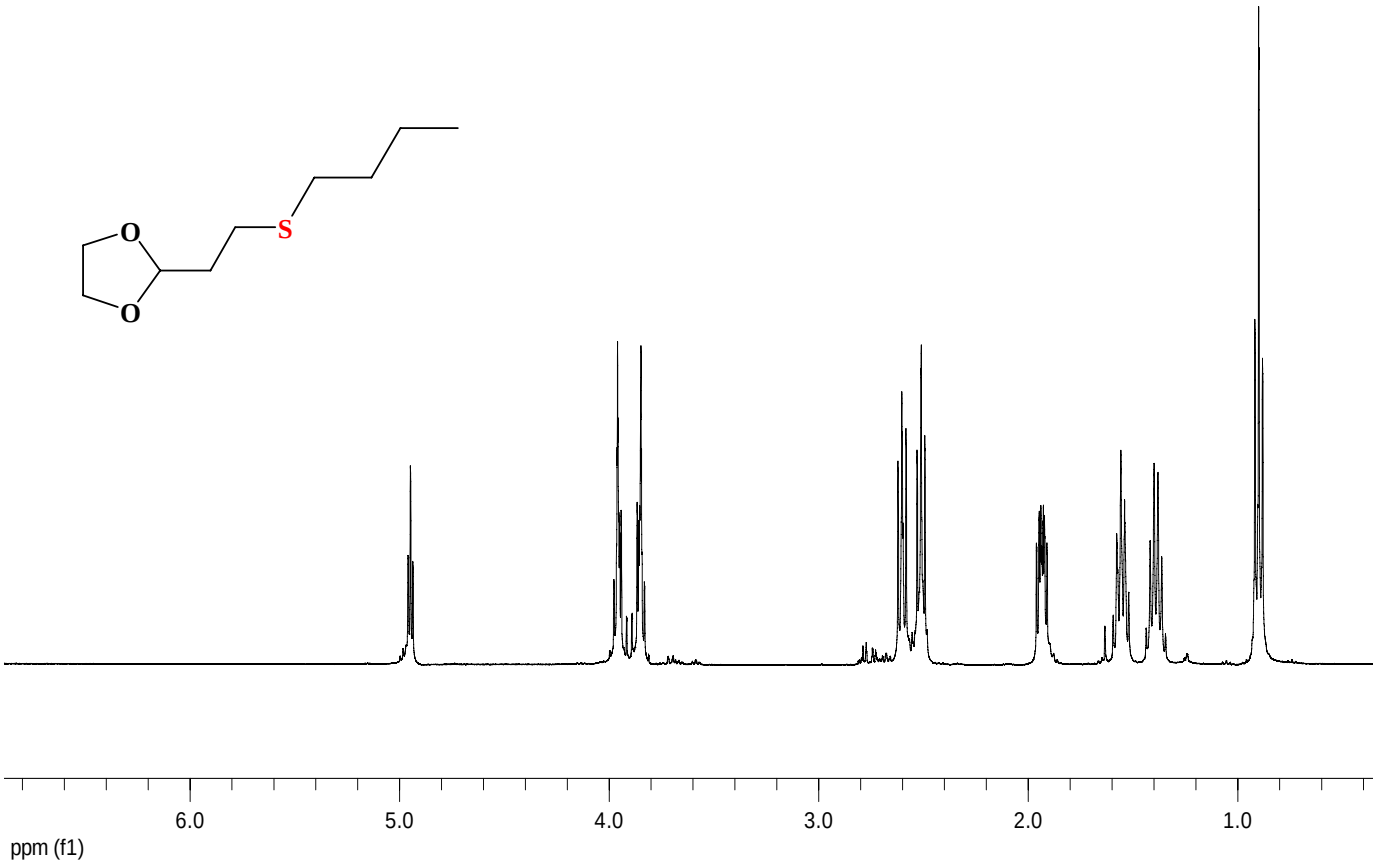
β-SULFIDE

Methylthioethyl-1,3-Dithiane	endocyclic S-S distance: 3.061 Å exocyclic S-S distances: 4.929 Å, 5.442 Å
C 3.6103 0.5237 -0.0737 C 2.5953 1.6126 0.2628 S 0.9349 1.3553 -0.4711 C 0.5191 -0.2771 0.2621 S 1.7306 -1.5907 -0.1650 C 3.2598 -0.8408 0.5134 C -0.8651 -0.7297 -0.2108 S -3.6120 -0.5429 -0.2159 C -1.9976 0.1733 0.2792 C -4.7238 0.7739 0.3774 H 3.7206 0.4433 -1.1575 H 4.5824 0.8287 0.3338 H 2.9179 2.5766 -0.1326 H 2.4870 1.7233 1.3455 H 0.5247 -0.1650 1.3488 H 4.0398 -1.5694 0.2882 H 3.1697 -0.7848 1.6020 H -0.8763 -0.7837 -1.3025 H -1.0275 -1.7461 0.1606 H -1.9159 1.1729 -0.1487 H -1.9711 0.2625 1.3681 H -5.7382 0.4624 0.1303 H -4.6450 0.8972 1.4580 H -4.5113 1.7189 -0.1233	 File: eq.log SCF Done: E(RB+HF-LYP) = -1469.91676363 A.U. after 1 cycles Zero-point vibrational energy 524878.4 (Joules/Mol) 125.44895 (Kcal/Mol) Zero-point correction= 0.199916 (Hartree/Particle) Thermal correction to Energy= 0.212489 Thermal correction to Gibbs Free Energy= 0.159385 Sum of electronic and zero-point Energies= -1469.716848

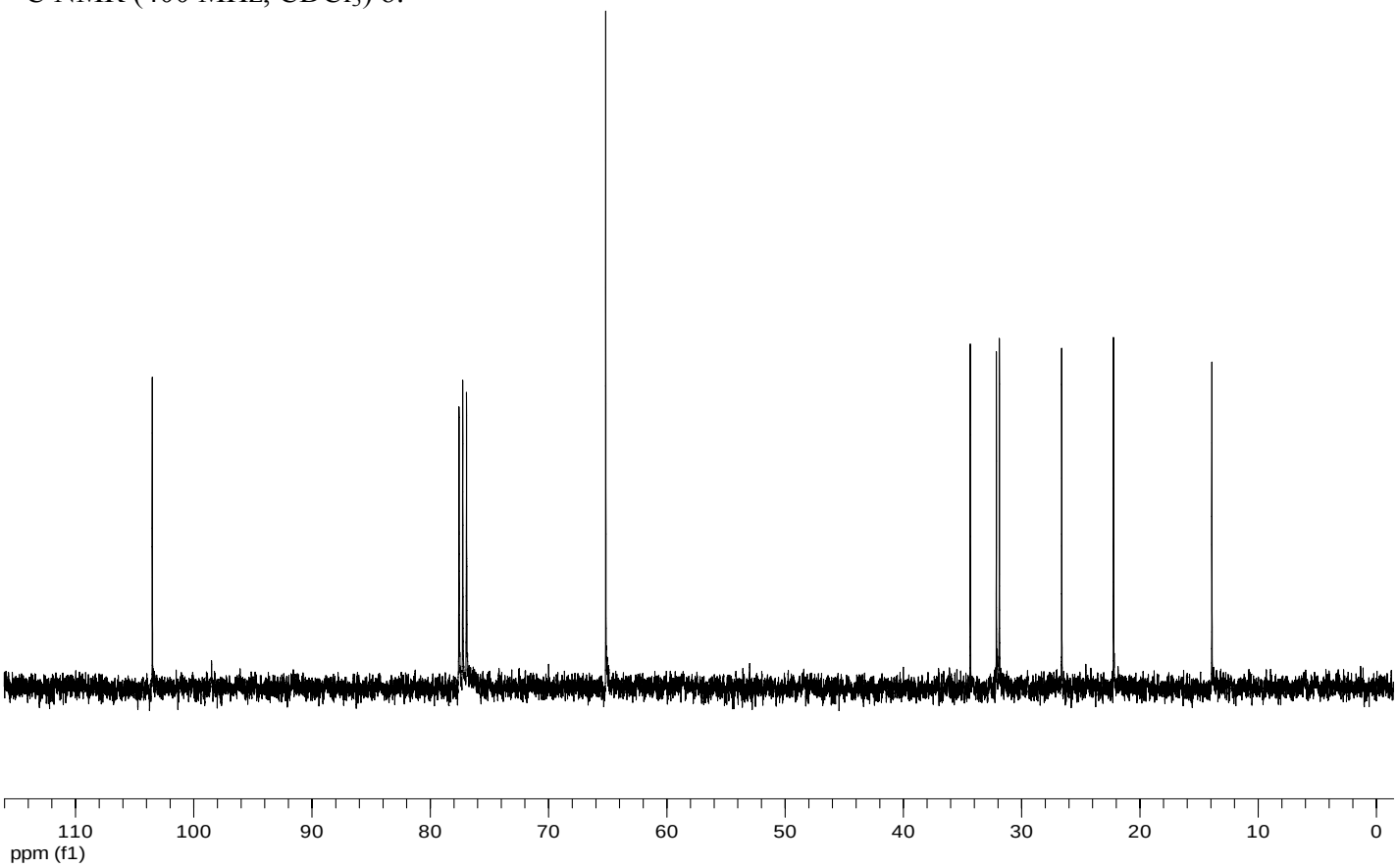
Methylthioethyl-1,3-Dithiane Radical Cation	endocyclic S-S distance: 2.902 Å exocyclic S-S distances: 2.993 Å, 5.026 Å
C -2.8336 -1.3572 0.0792 C -1.3899 -1.8726 0.1526 S -0.2383 -0.7862 -0.7747 C -0.3864 0.7330 0.2344 S -2.0701 1.3642 -0.1023 C -3.0332 0.0220 0.7023 C 0.6970 1.7350 -0.1516 S 2.6892 -0.2221 -0.4696 C 2.0893 1.3203 0.3357 C 3.6169 -1.0163 0.8793 H -3.1701 -1.3502 -0.9590 H -3.4613 -2.0764 0.6168 H -1.2981 -2.8507 -0.3191 H -1.0334 -1.9492 1.1818 H -0.3080 0.4592 1.2879 H -4.0706 0.3408 0.5958 H -2.7926 0.0251 1.7678 H 0.6946 1.9053 -1.2315 H 0.4570 2.6949 0.3140 H 2.0957 1.1581 1.4141 H 2.8123 2.1034 0.1027 H 4.4473 -0.3739 1.1723 H 4.0048 -1.9514 0.4794 H 2.9683 -1.2140 1.7312	 File: eq_cr3.log SCF Done: E(UB+HF-LYP) = -1469.65137571 A.U. after 1 cycles Zero-point vibrational energy 526106.3 (Joules/Mol) 125.74242 (Kcal/Mol) Zero-point correction= 0.200383 (Hartree/Particle) Thermal correction to Energy= 0.212657 Thermal correction to Gibbs Free Energy= 0.160793 Sum of electronic and zero-point Energies= -1469.450992

Entry	Dithiane	Geometry	B3LYP: basis set and zpe energy correction	Energy, Hartrees	Radical Cation	Energy, Hartrees	IP, eV
1	R = R' = H		6-31G(d) 6-311+G(2d,p) 6-311+G(2d,p) + ZPE	- -953.72778 -953.61303		- -953.44000 -953.32500	 7.83 7.84
2	R = Me R' = H		6-31G(d) 6-311+G(2d,p) 6-311+G(2d,p) + ZPE	- -993.05533 -992.91269		- -992.77388 -992.63114	- 7.66 7.66
3	R = Et R' = H		6-31G(d) 6-311+G(2d,p) 6-311+G(2d,p) + ZPE	-1032.25013 -1032.37909 -1032.20827		-1031.97273 -1032.10071 -1031.92961	7.55 7.57 7.58
4	R = Pr R' = H		6-31G(d) 6-311+G(2d,p) 6-311+G(2d,p) + ZPE	-1071.56386 -1071.70432 -1071.50516		-1071.28755 -1071.42703 -1071.22758	7.52 7.55 7.55
5	R = SMe R' = H		6-31G(d) 6-311+G(2d,p) 6-311+G(2d,p) + ZPE	-1391.11763 -1391.26523 -1391.12218		-1390.83747 -1390.98359 -1390.84083	7.62 7.66 7.66
6	R = CH_2SMe R' = H		6-31G(d) 6-311+G(2d,p) 6-311+G(2d,p) + ZPE	-1430.43091 -1430.58976 -1430.41832		-1430.15712 -1430.31375 -1430.14250	7.45 7.51 7.51
7	R = CH_2CH_2SMe R' = H		6-31G(d) 6-311+G(2d,p) 6-311+G(2d,p) + ZPE	- -1469.91676 -1469.71685		- -1469.65138 -1469.45099	- 7.22 7.23
8	R = CH_2CH_2OMe R' = H		6-31G(d) 6-311+G(2d,p) 6-311+G(2d,p) + ZPE	-1146.76274 -1146.93083 -1146.72715		-1146.48887 -1146.65326 -1146.44920	7.45 7.55 7.56
9	R,R' = $(CH_2CH_2)_2S$		6-31G(d) 6-311+G(2d,p) 6-311+G(2d,p) + ZPE 6-31G(d) 6-311+G(2d,p) 6-311+G(2d,p) + ZPE	-1507.85577 -1508.03217 -1507.82314	 chair-chair boat-chair	-1507.58113 -1507.75574 -1507.54683 -1507.58346 -1507.75820 -1507.54892	7.47 7.52 7.52 7.41 7.46 7.46
10	R,R' = $-(CH_2)_3-$		6-311+G(2d,p) 6-311+G(2d,p) + ZPE	-1149.14307 -1148.90678		-1148.87263 -1148.63568	7.36 7.38

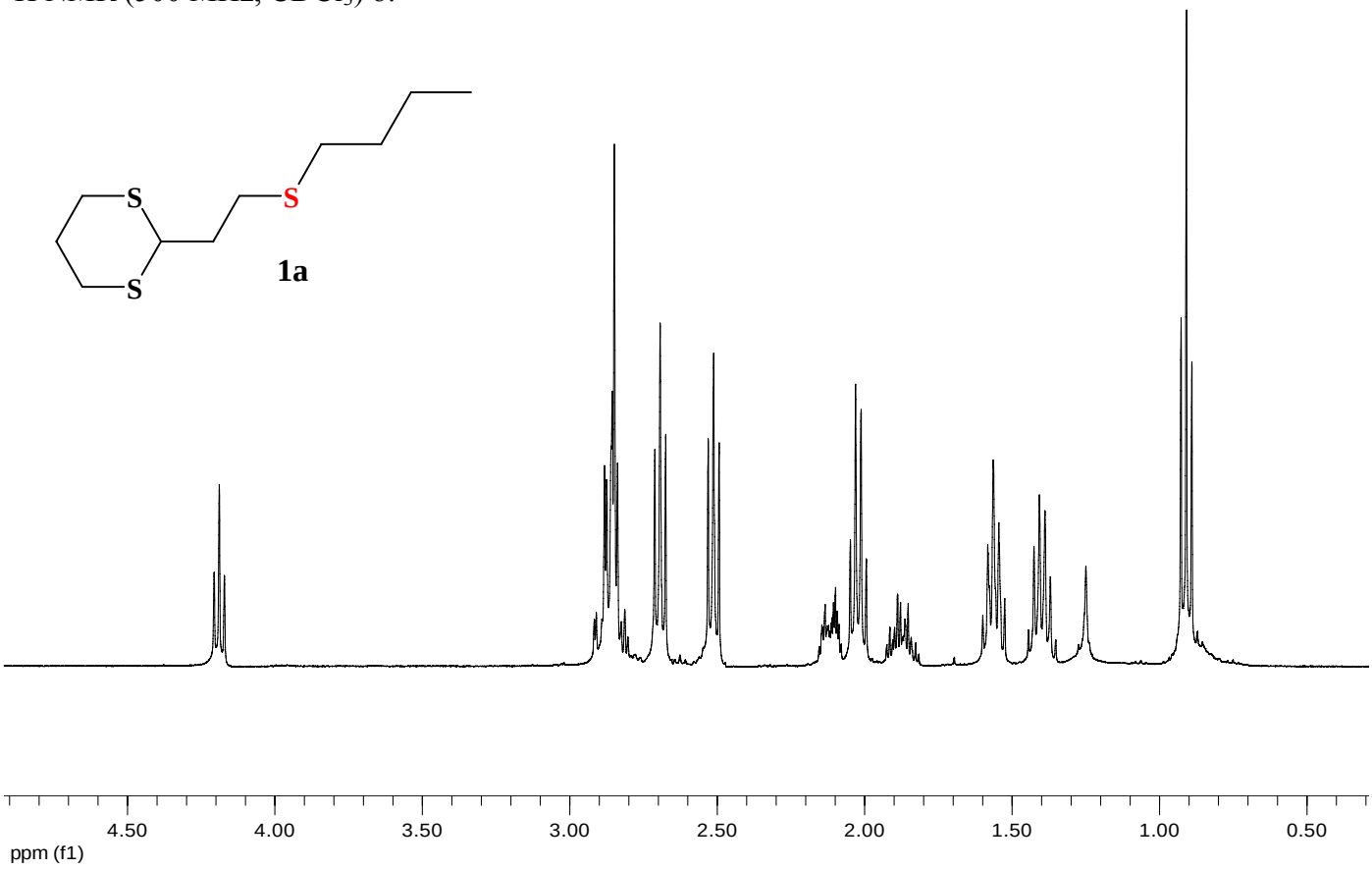
^{1}H NMR (500 MHz, $CDCl_3$) δ:



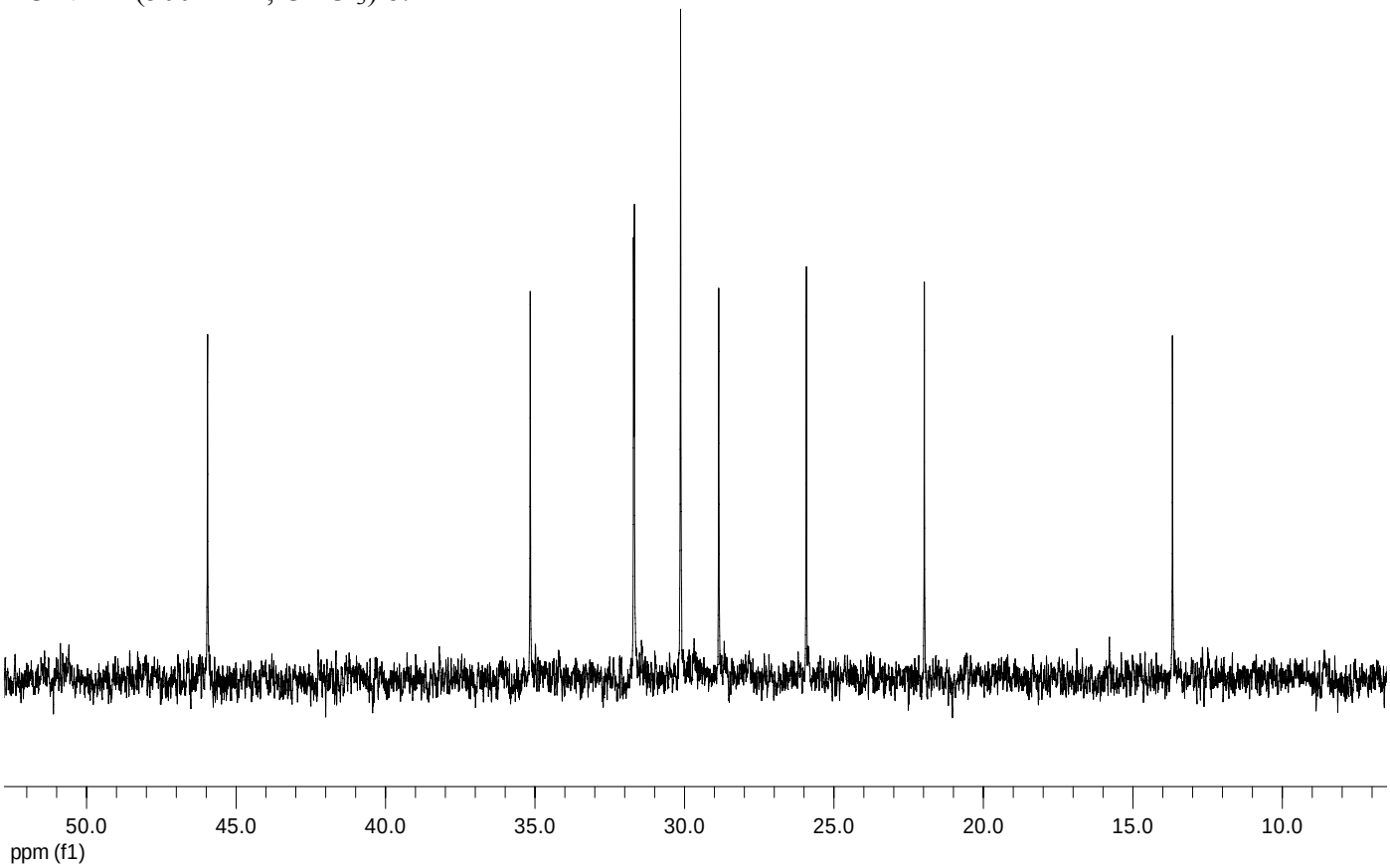
^{13}C NMR (400 MHz, $CDCl_3$) δ:



^{1}H NMR (500 MHz, $CDCl_3$) δ:



^{13}C NMR (500 MHz, $CDCl_3$) δ:



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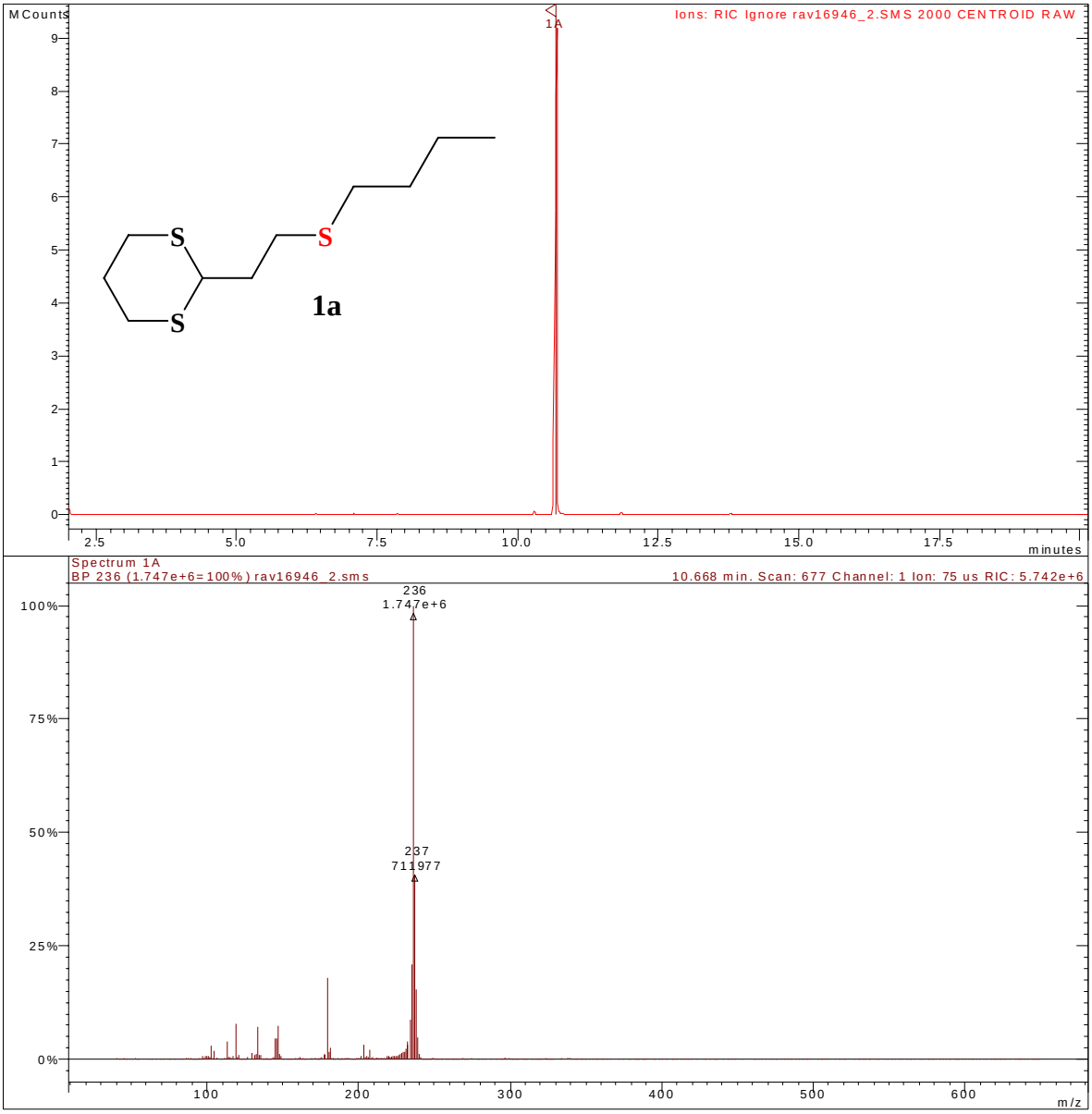
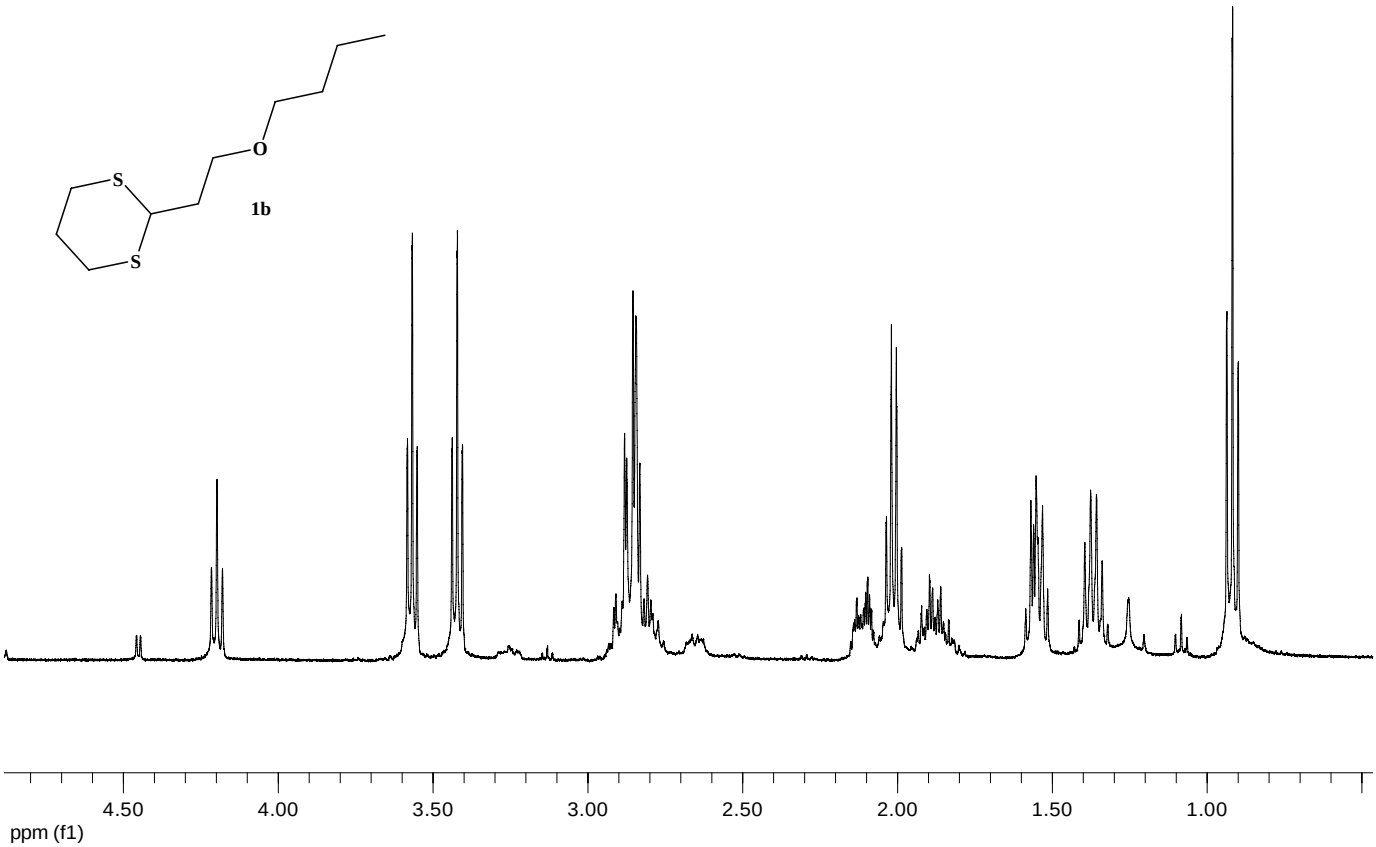
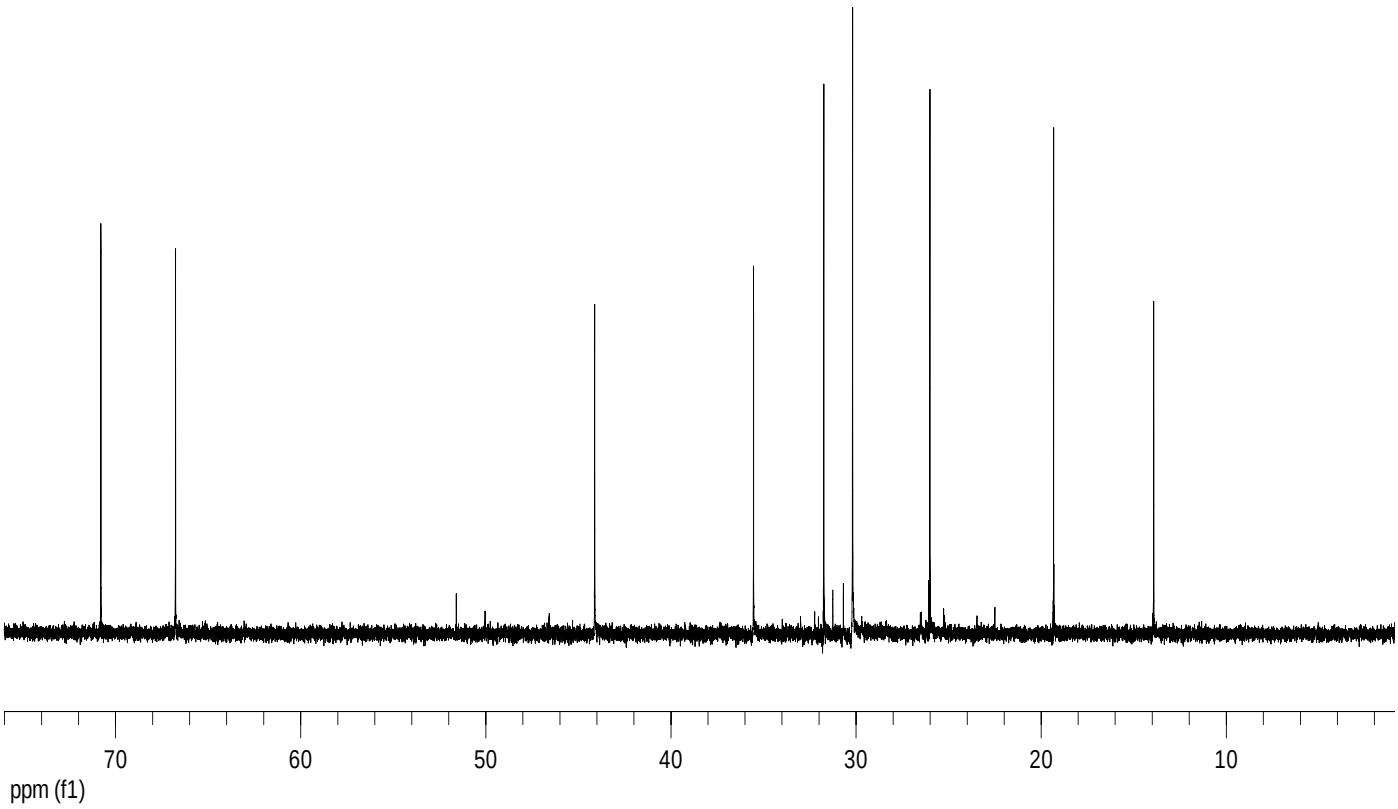


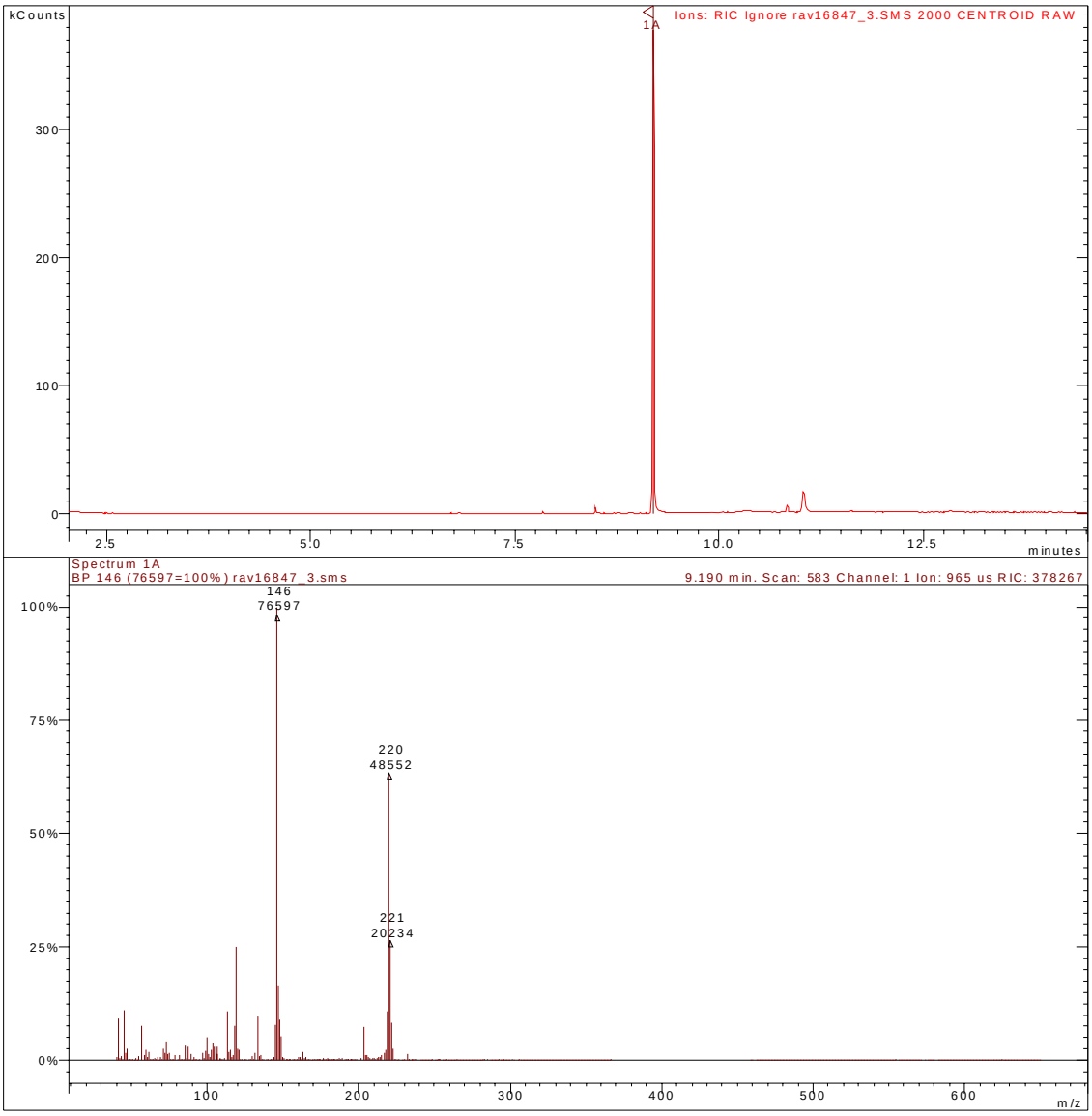
^{1}H NMR (400 MHz, $CDCl_3$) δ:



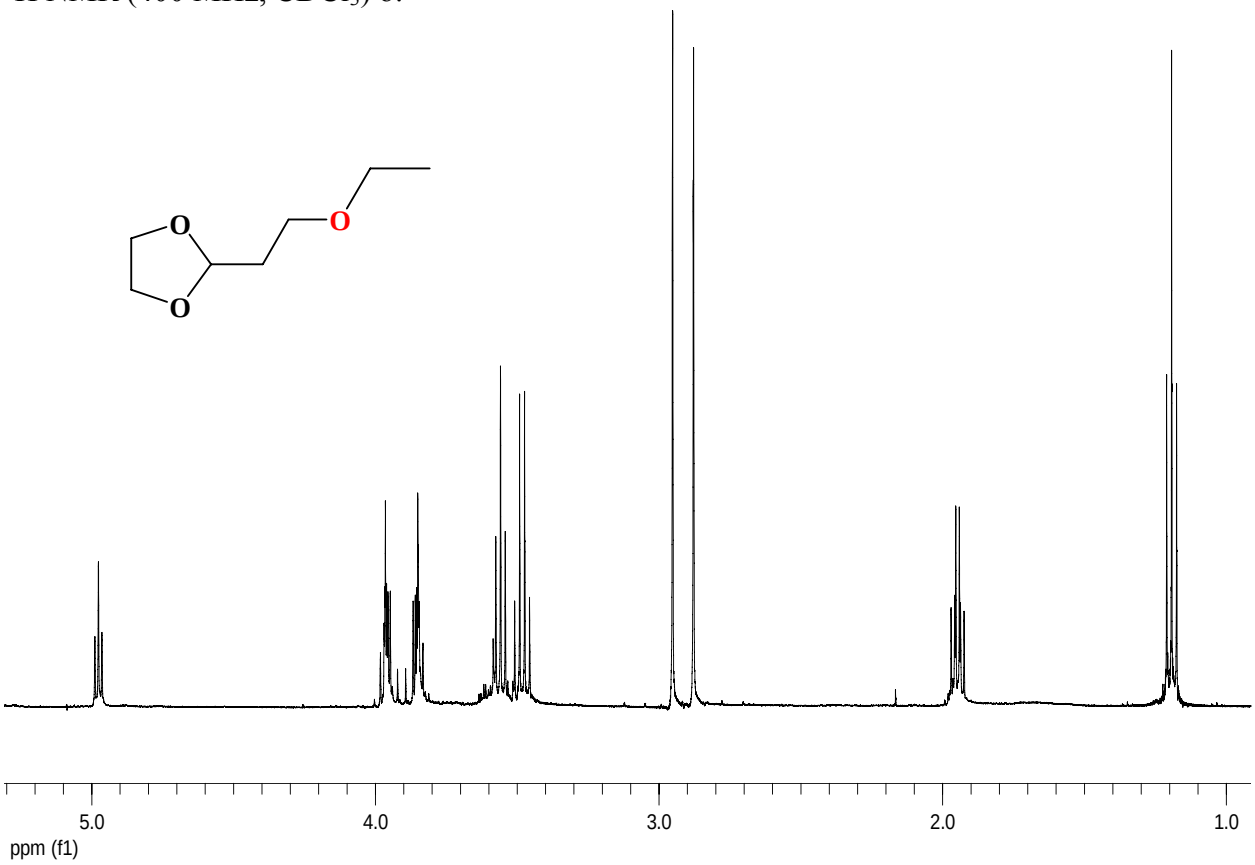
^{13}C NMR (400 MHz, $CDCl_3$) δ:



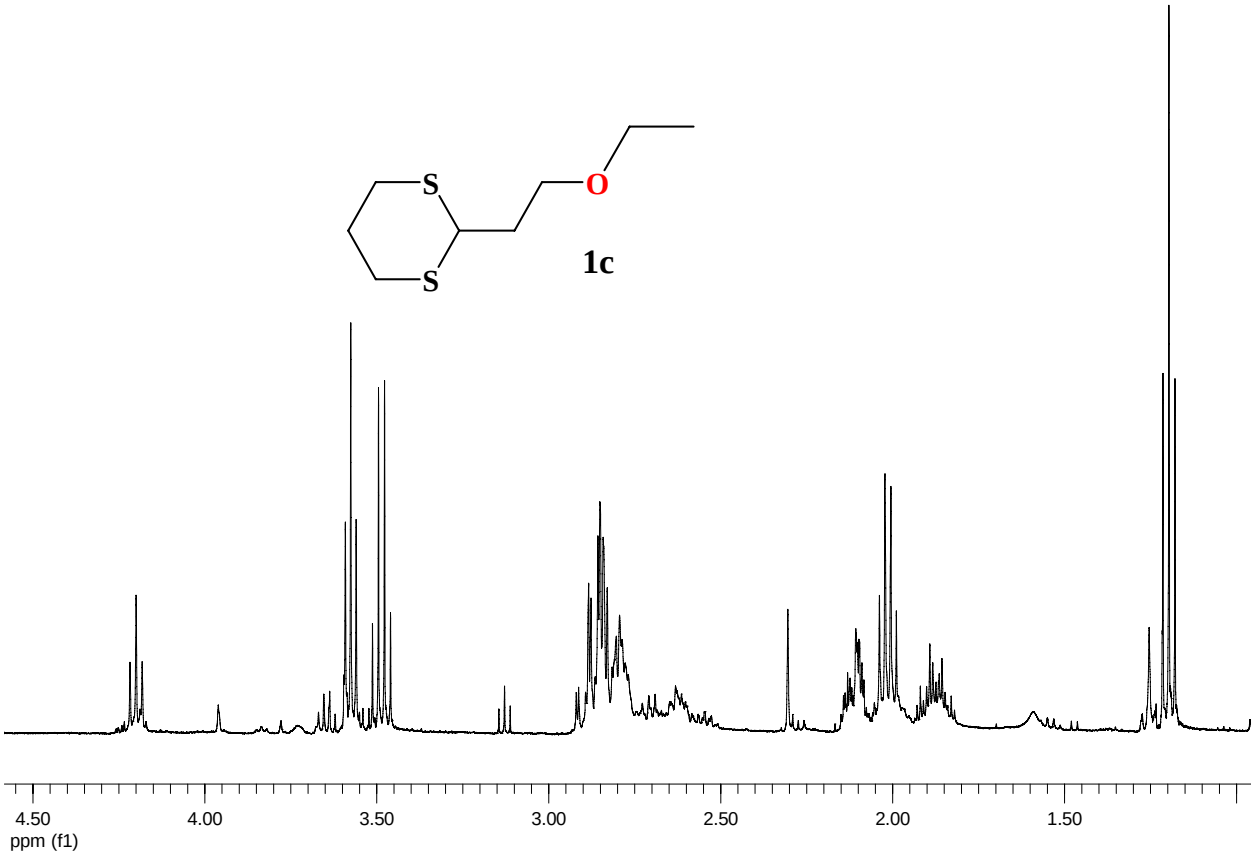
MS Data Review Active Chromatogram and Spectrum Plots - 4/23/2008 5:21 PM



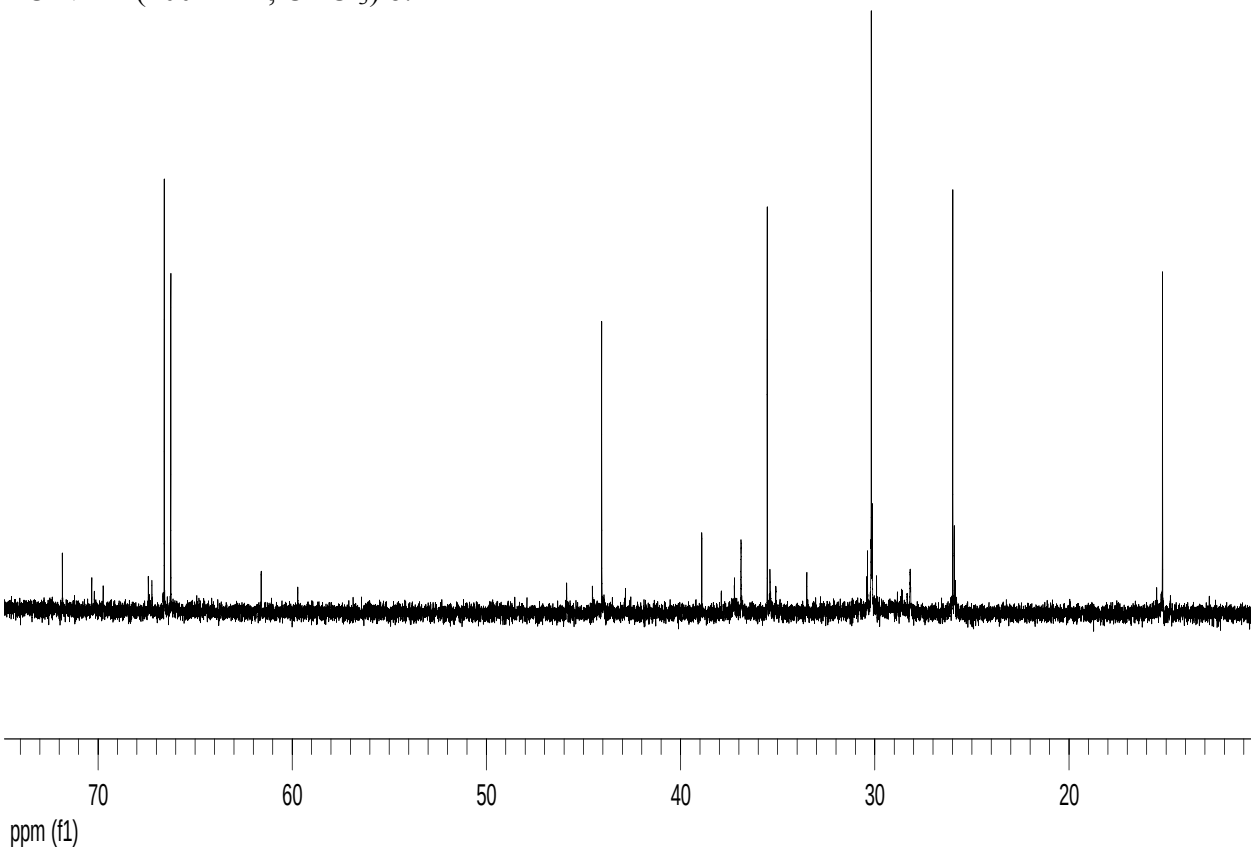
^{1}H NMR (400 MHz, $CDCl_3$) δ:



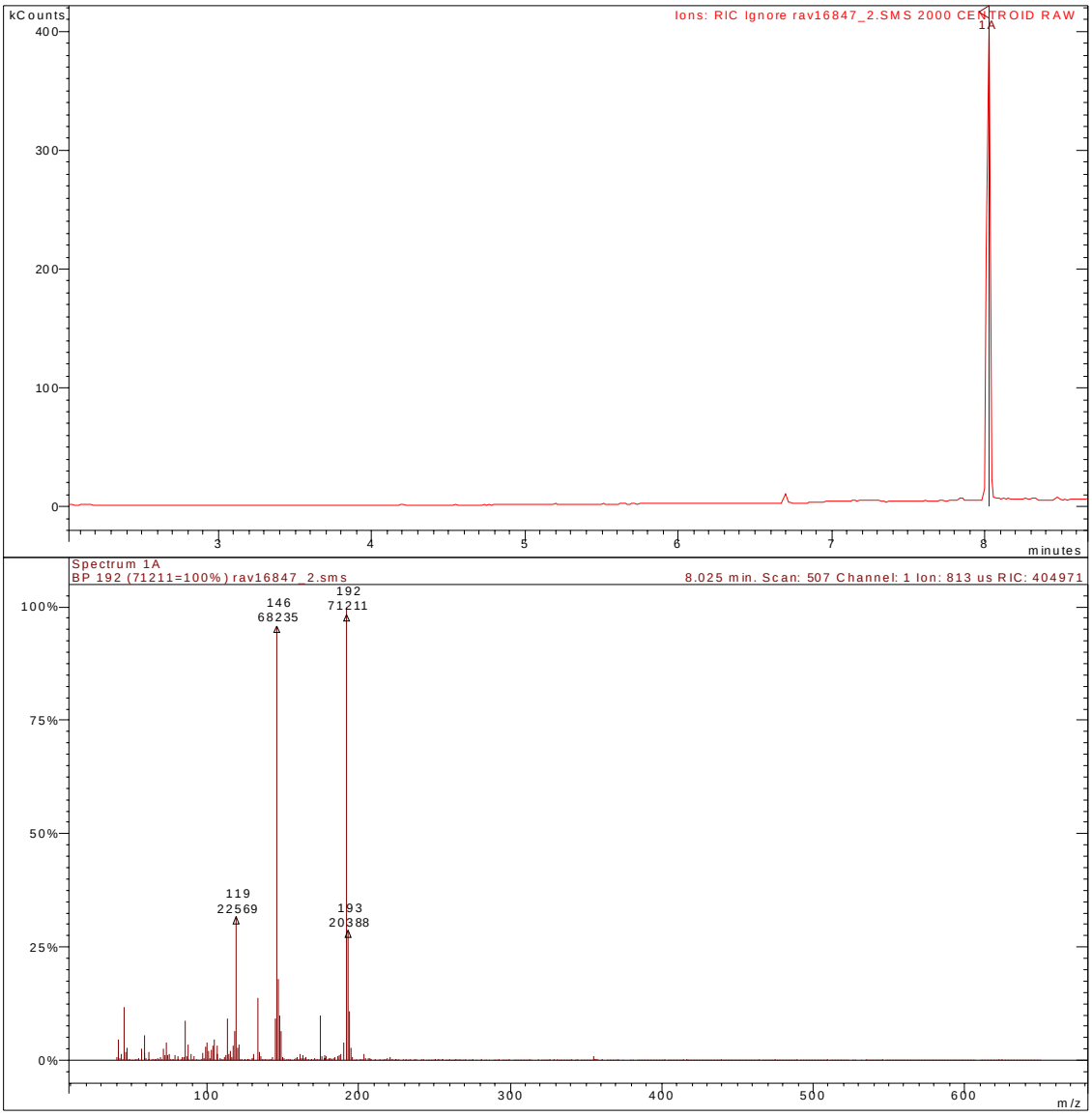
^{1}H NMR (400 MHz, $CDCl_3$) δ:



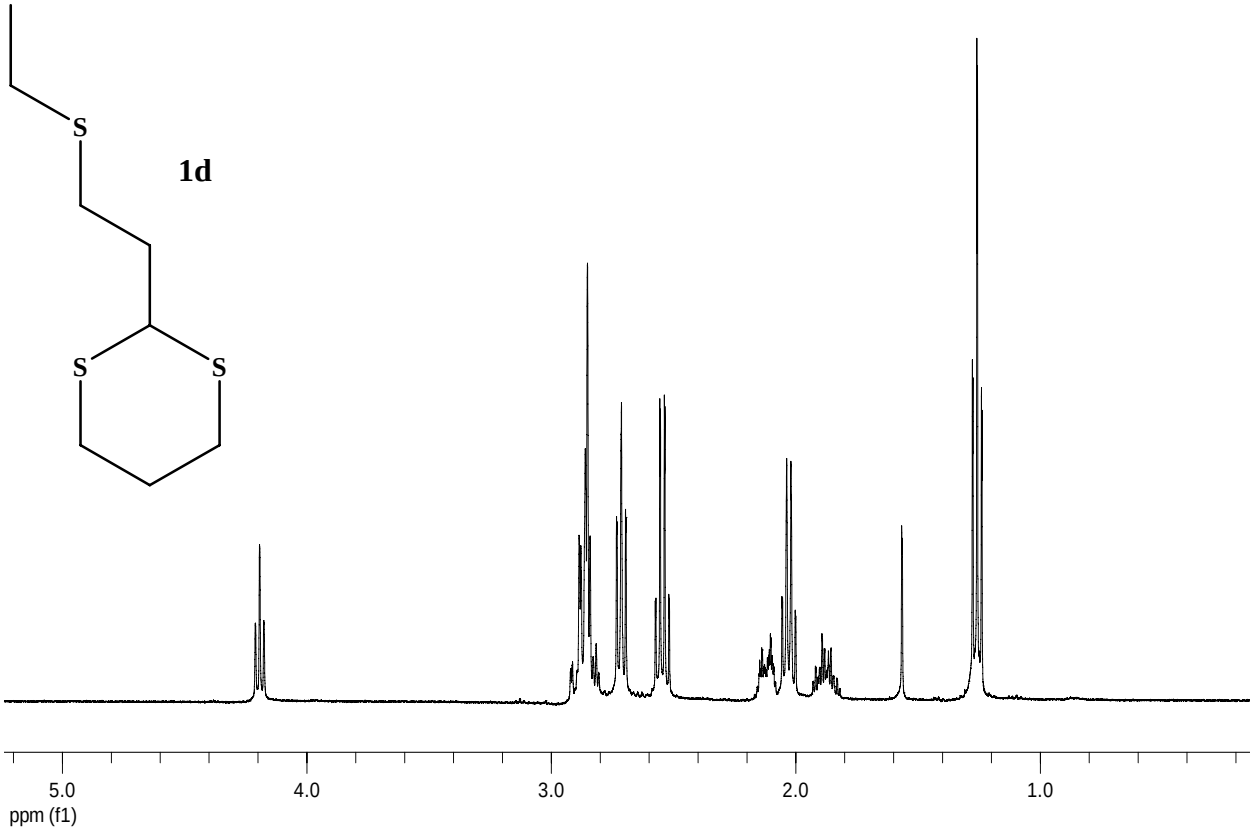
^{13}C NMR (400 MHz, $CDCl_3$) δ:



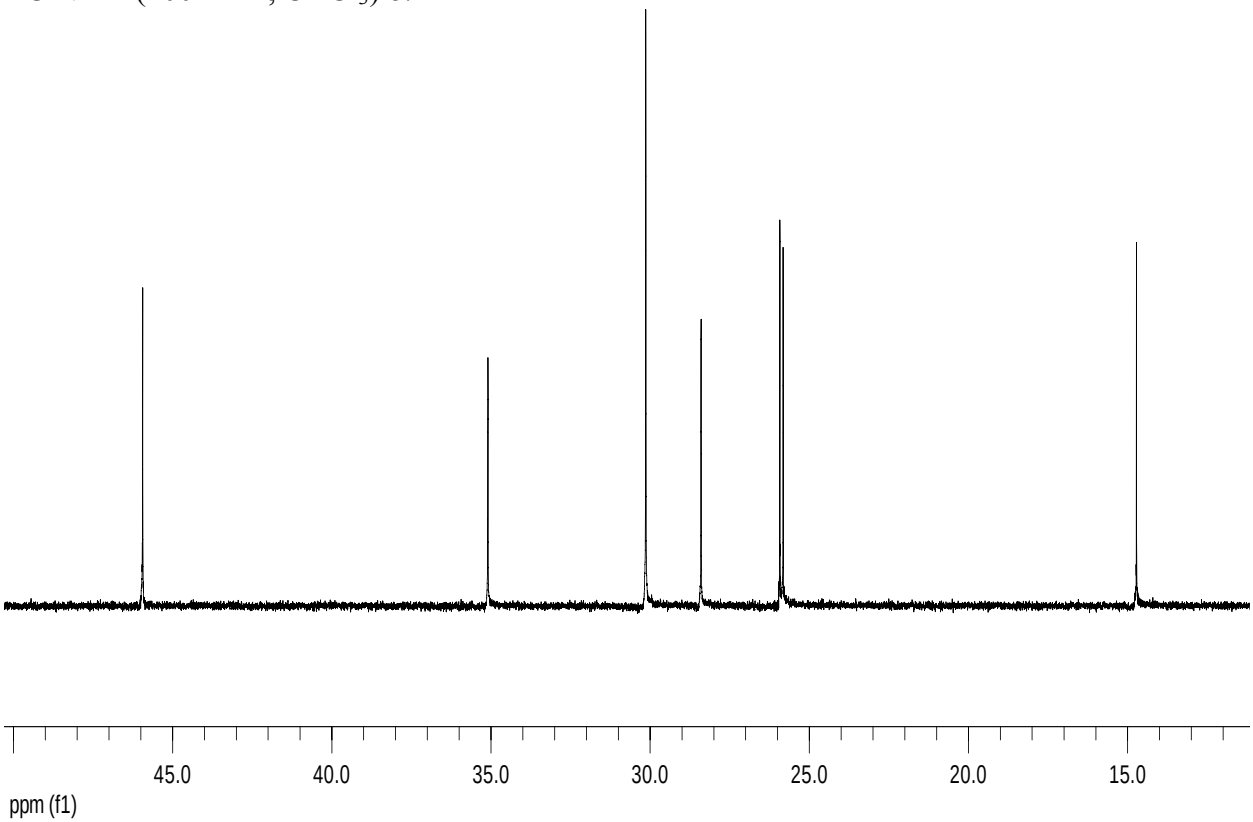
MS Data Review Active Chromatogram and Spectrum Plots - 4/23/2008 5:20 PM



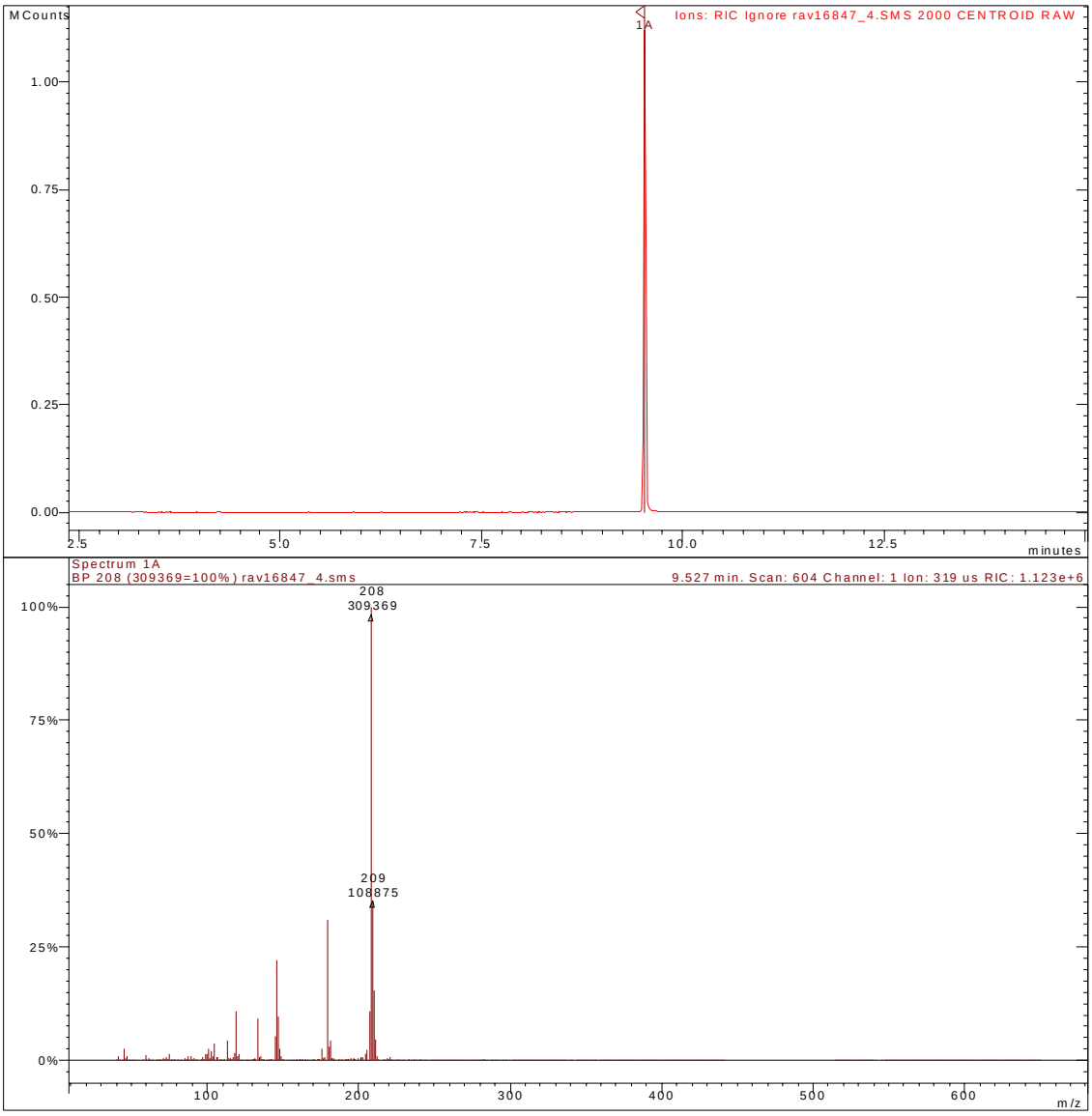
^{1}H NMR (400 MHz, $CDCl_3$) δ:



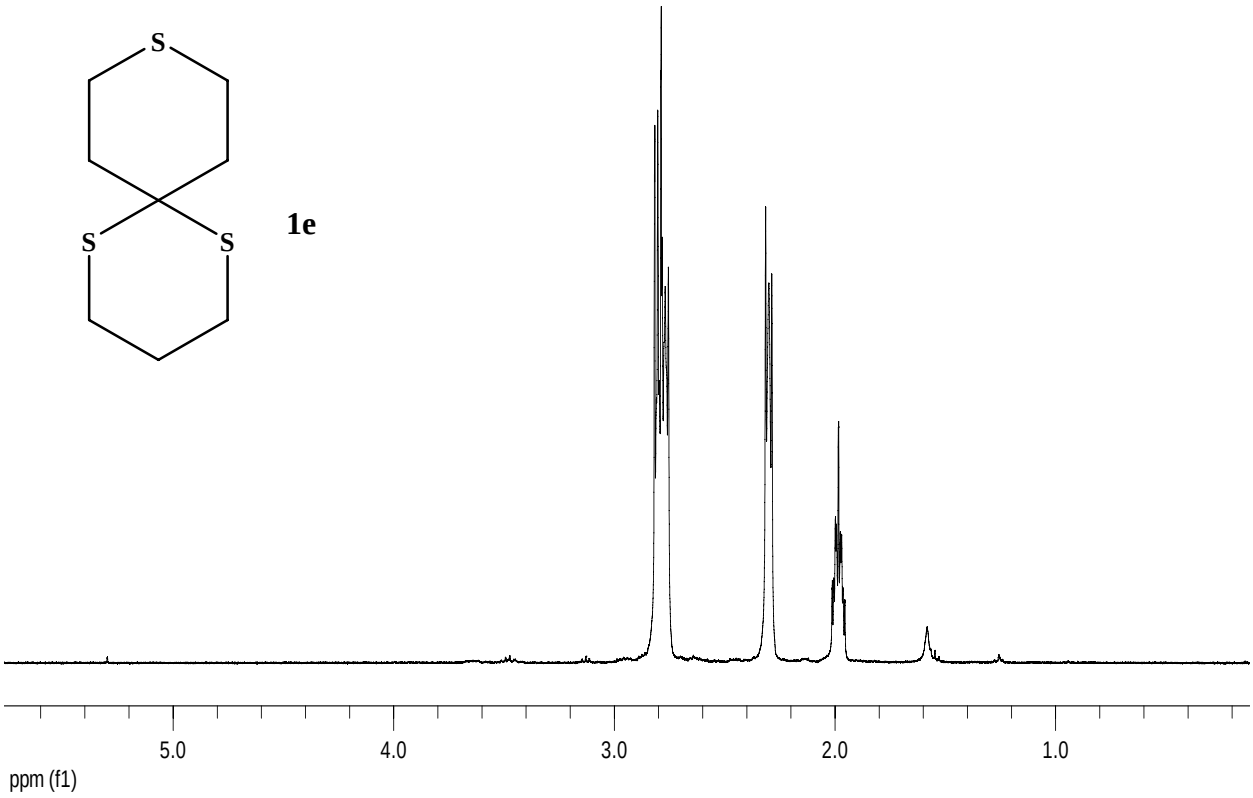
^{13}C NMR (400 MHz, $CDCl_3$) δ:



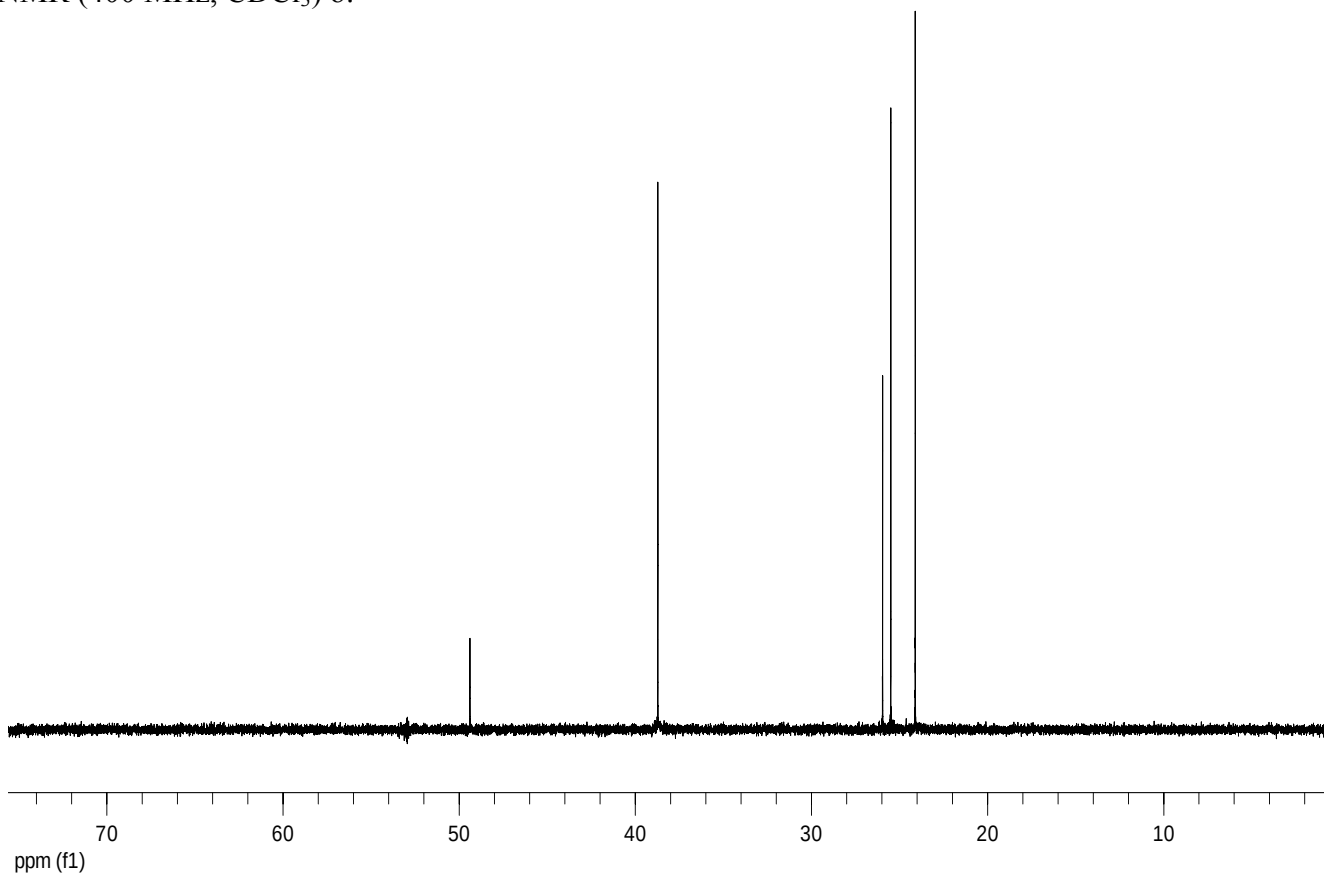
MS Data Review Active Chromatogram and Spectrum Plots - 4/23/2008 5:22 PM



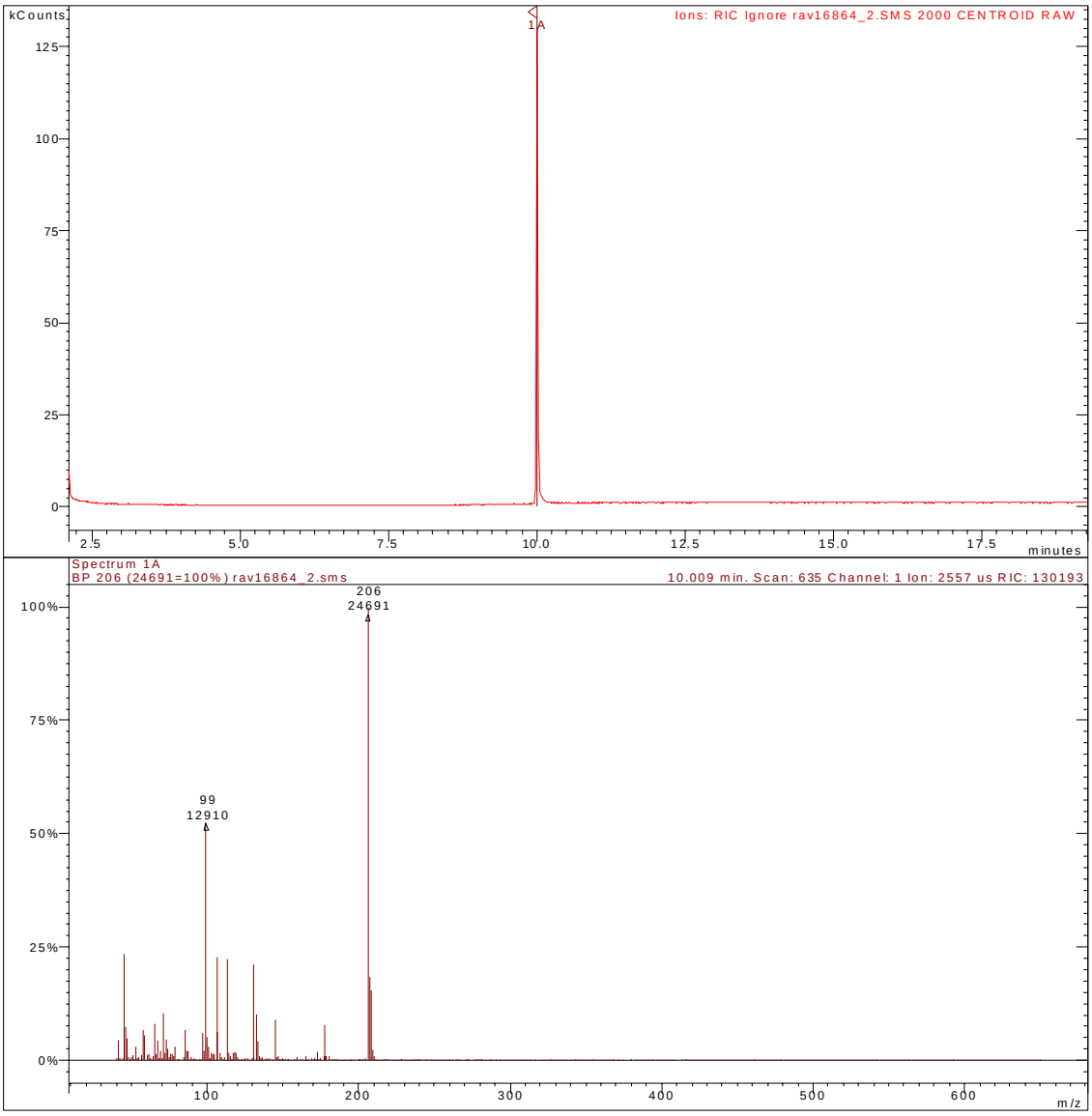
^{1}H NMR (400 MHz, $CDCl_3$) δ:



^{13}C NMR (400 MHz, $CDCl_3$) δ:

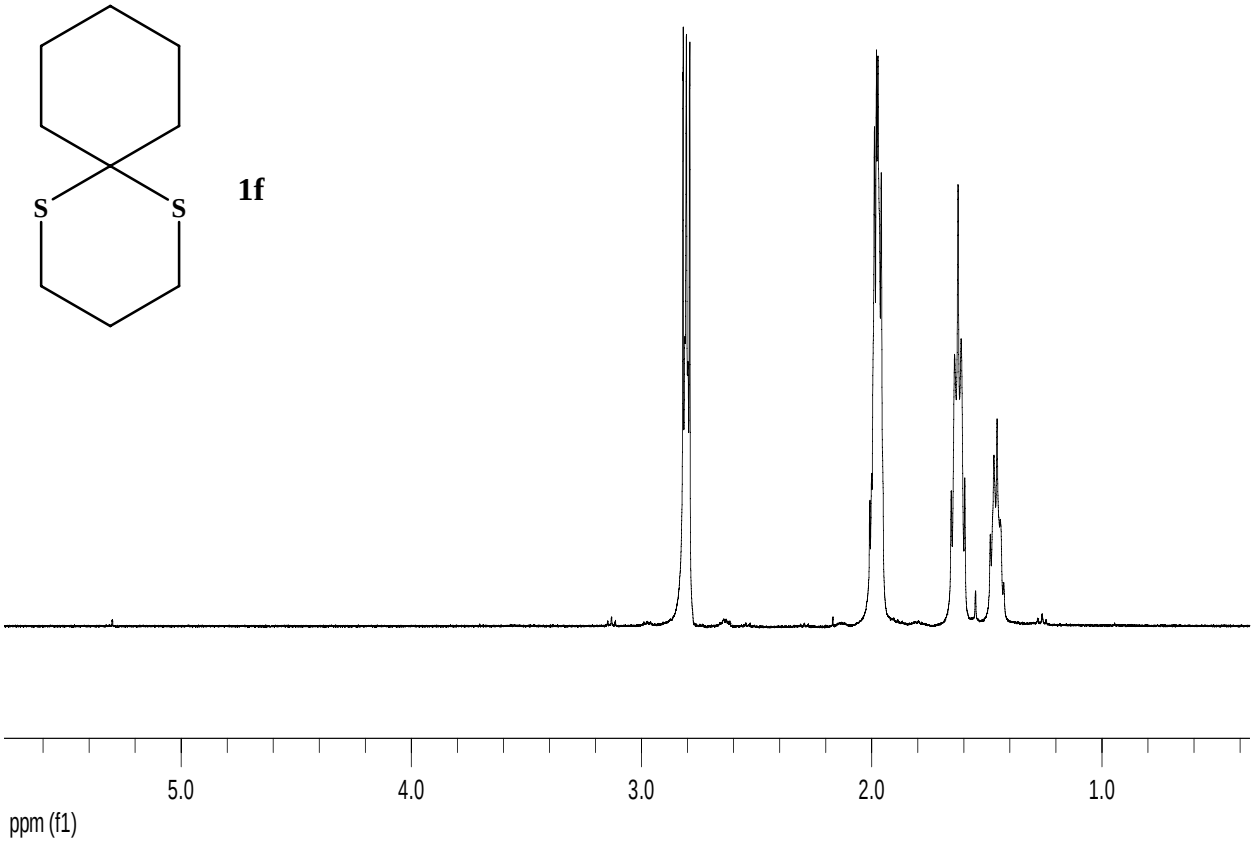


MS Data Review Active Chromatogram and Spectrum Plots - 4/23/2008 7:09 PM

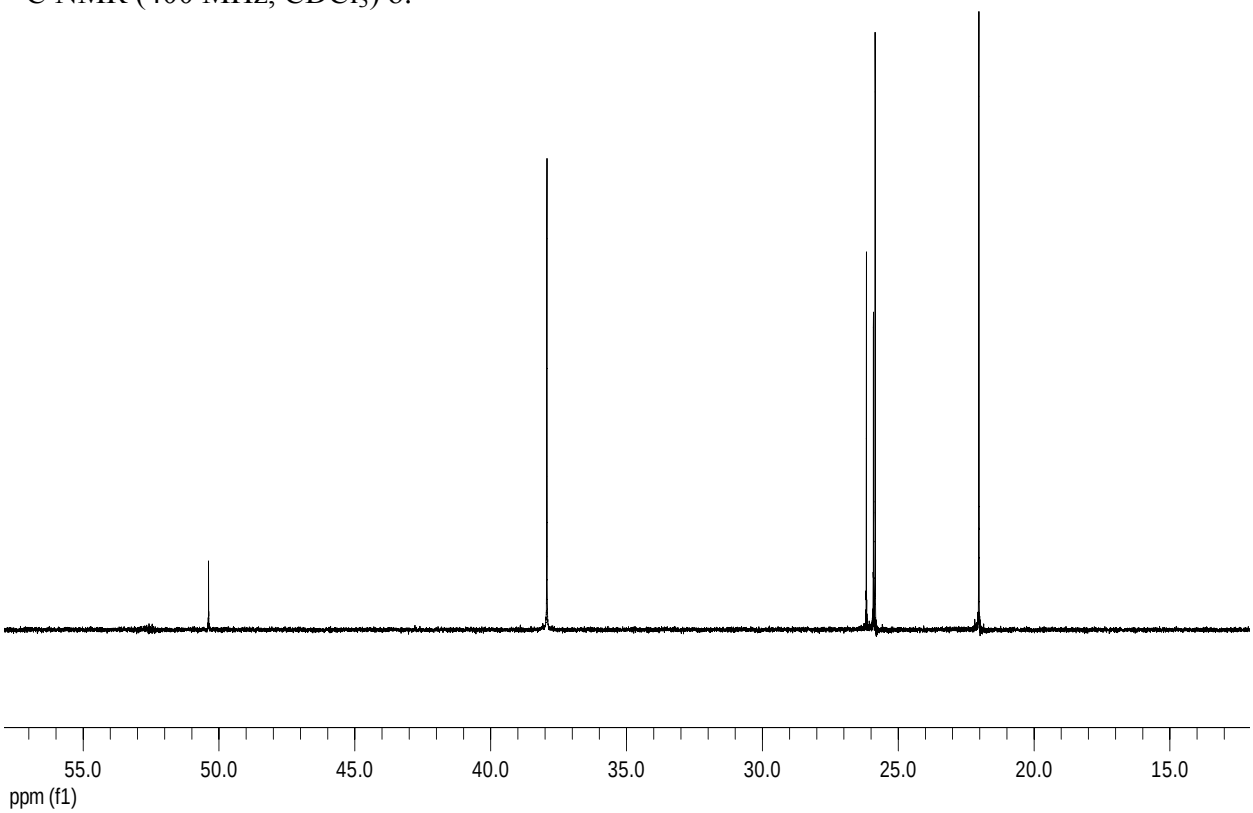


^{1}H NMR (400 MHz, $CDCl_3$) δ:

1f

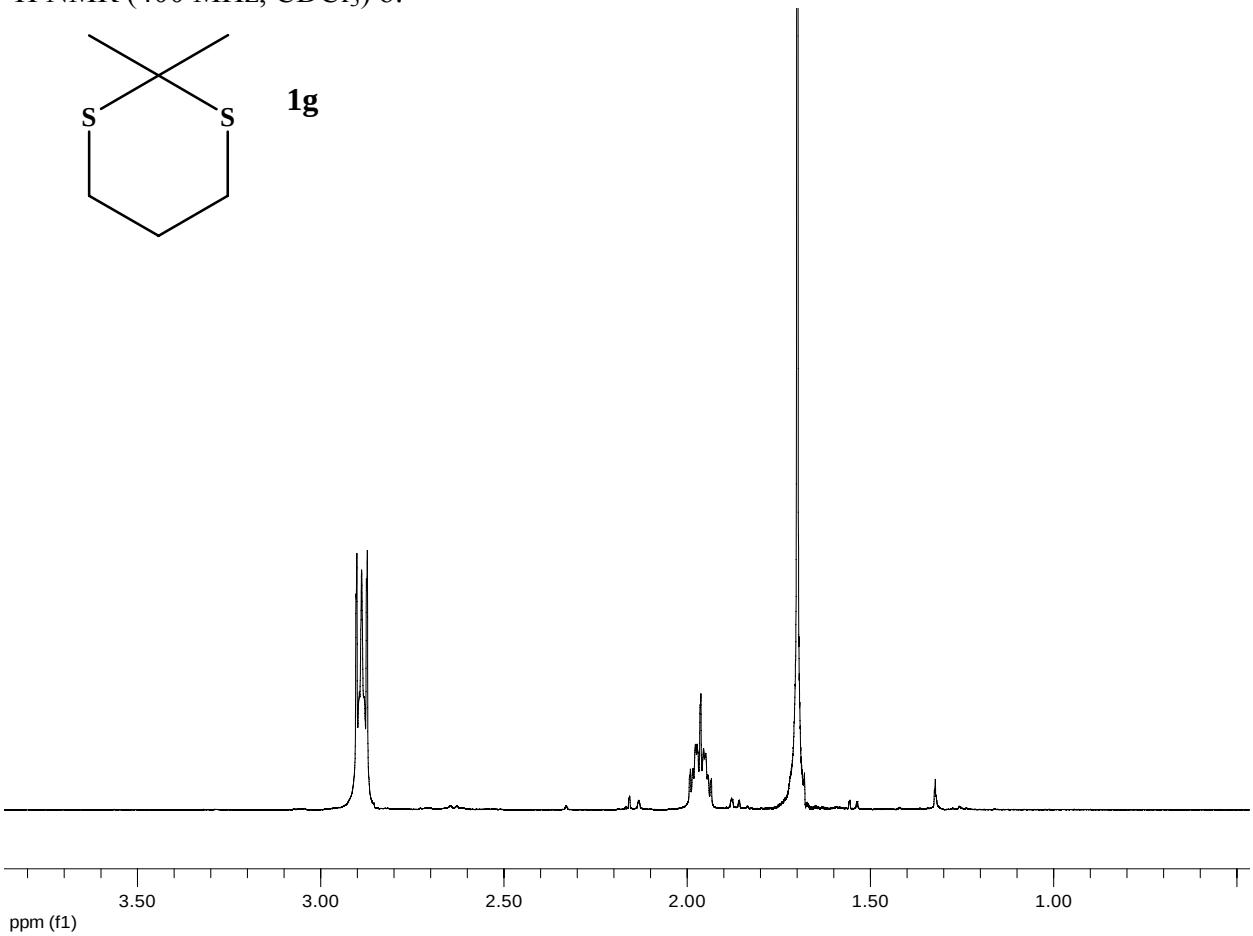


^{13}C NMR (400 MHz, $CDCl_3$) δ:

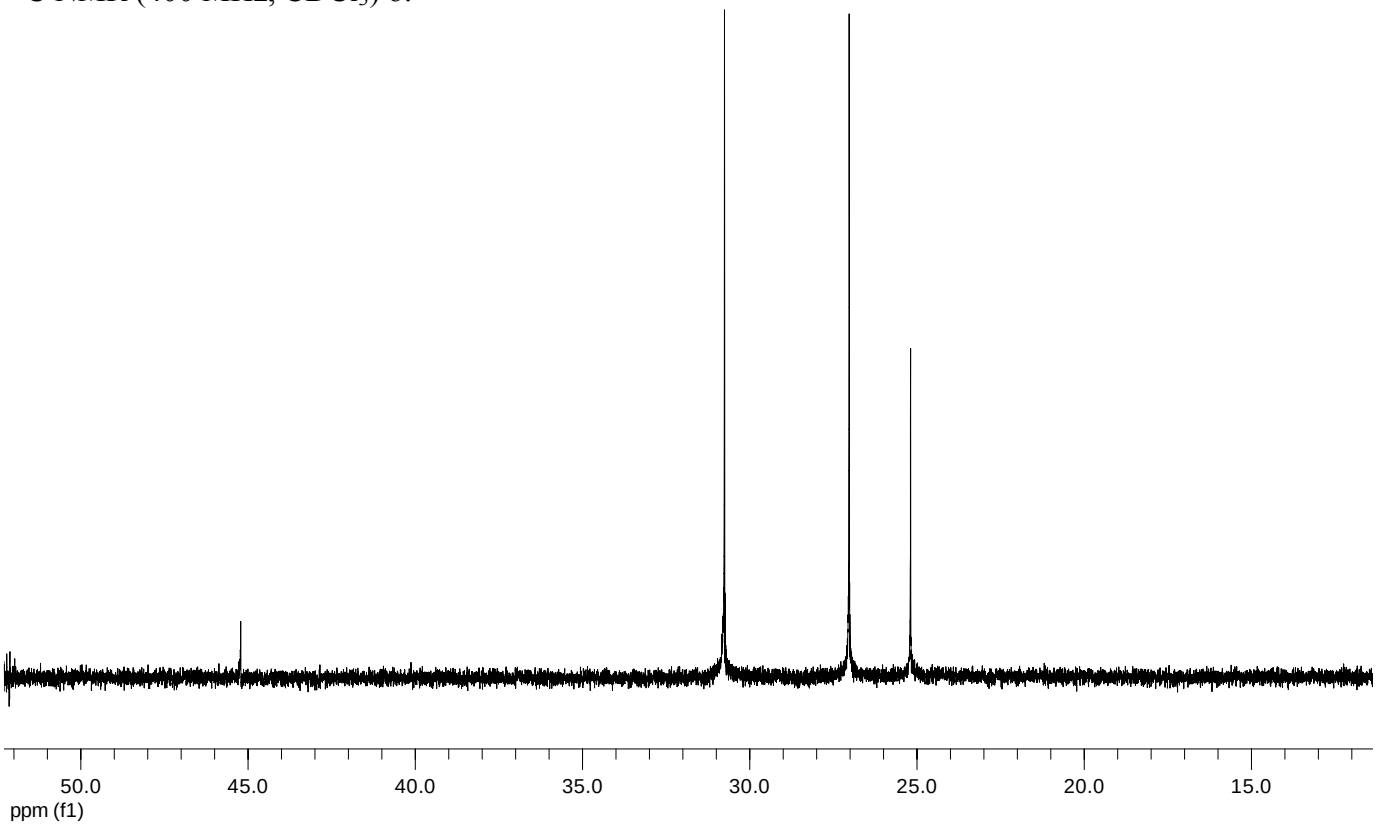


^{1}H NMR (400 MHz, $CDCl_3$) δ:

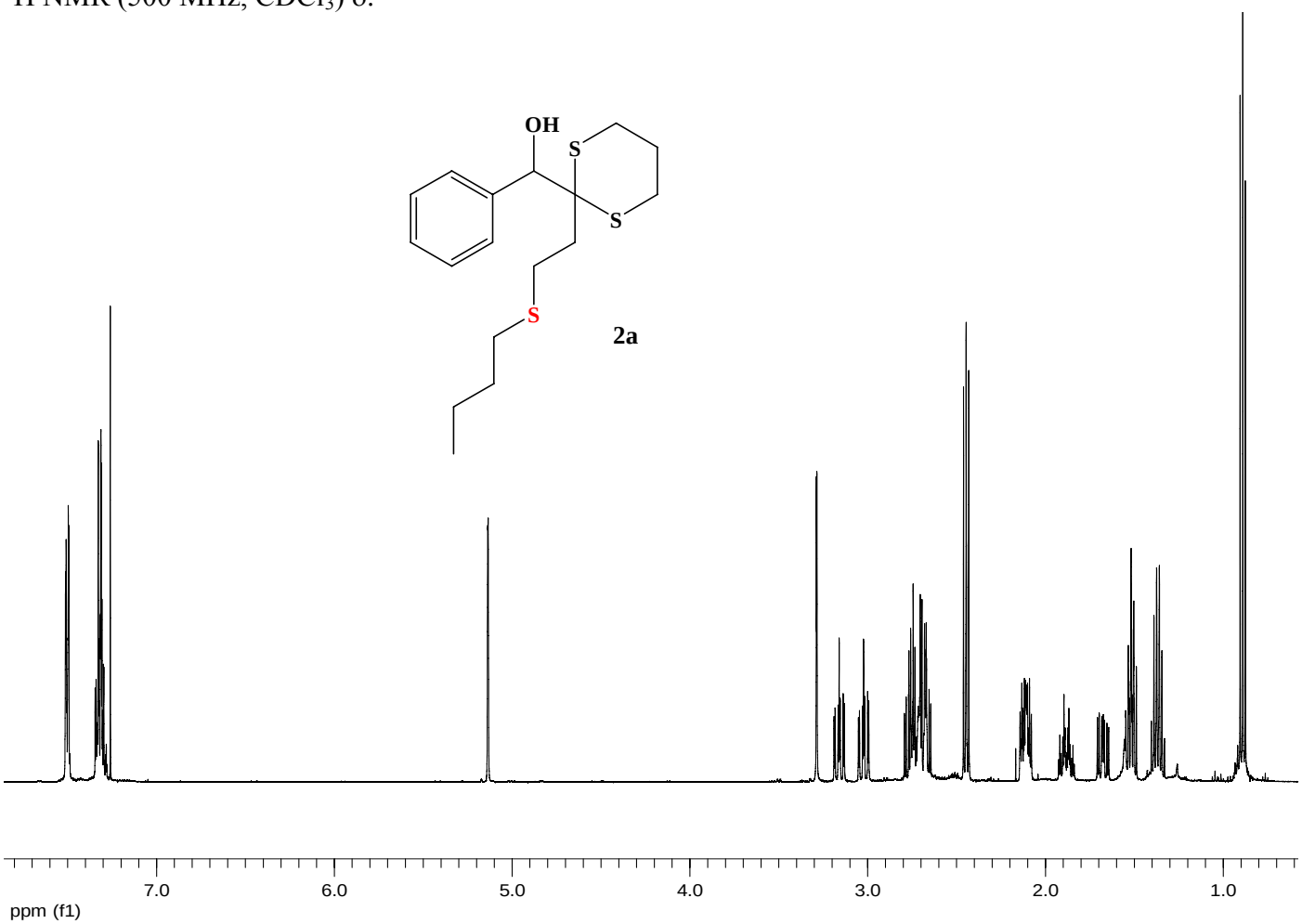
1g



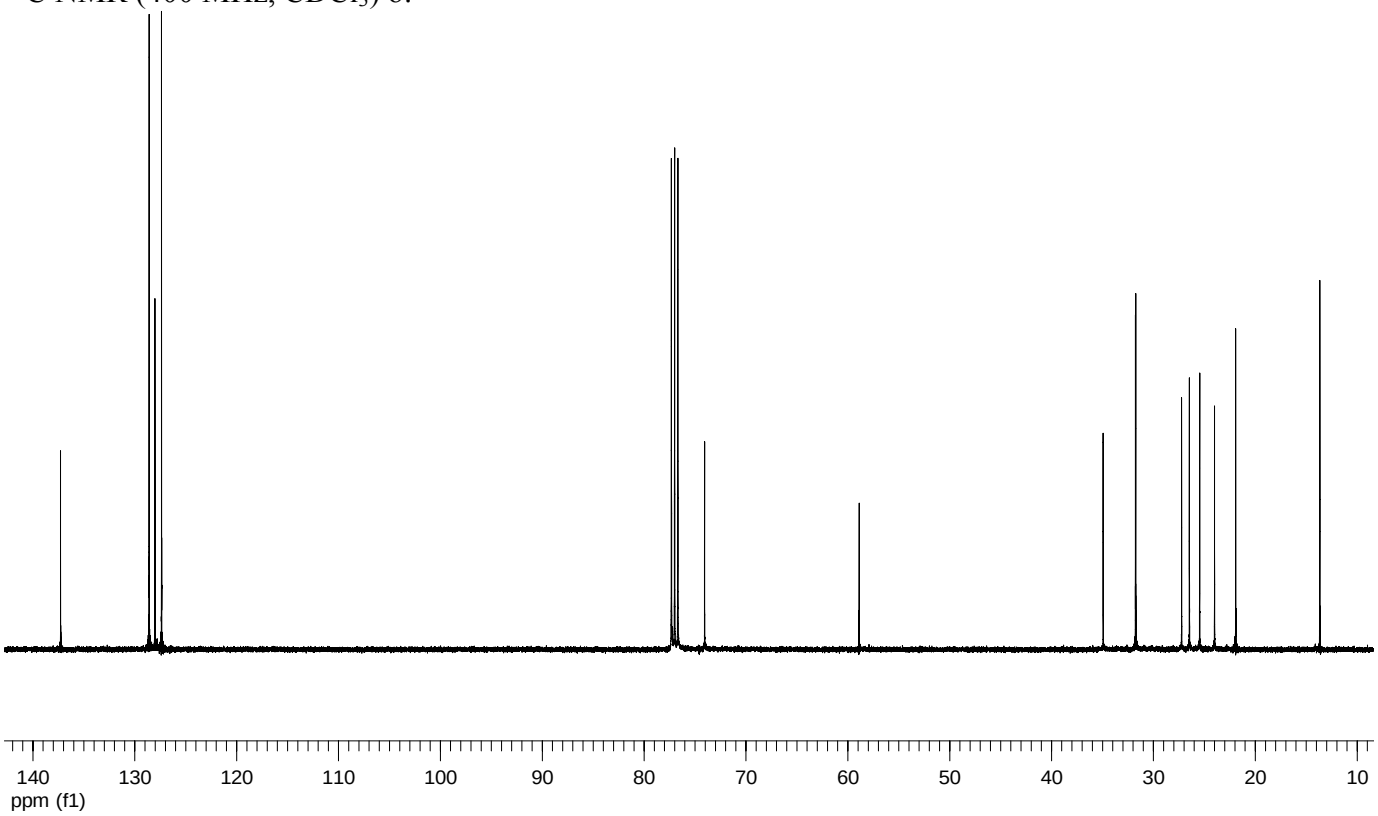
^{13}C NMR (400 MHz, $CDCl_3$) δ:



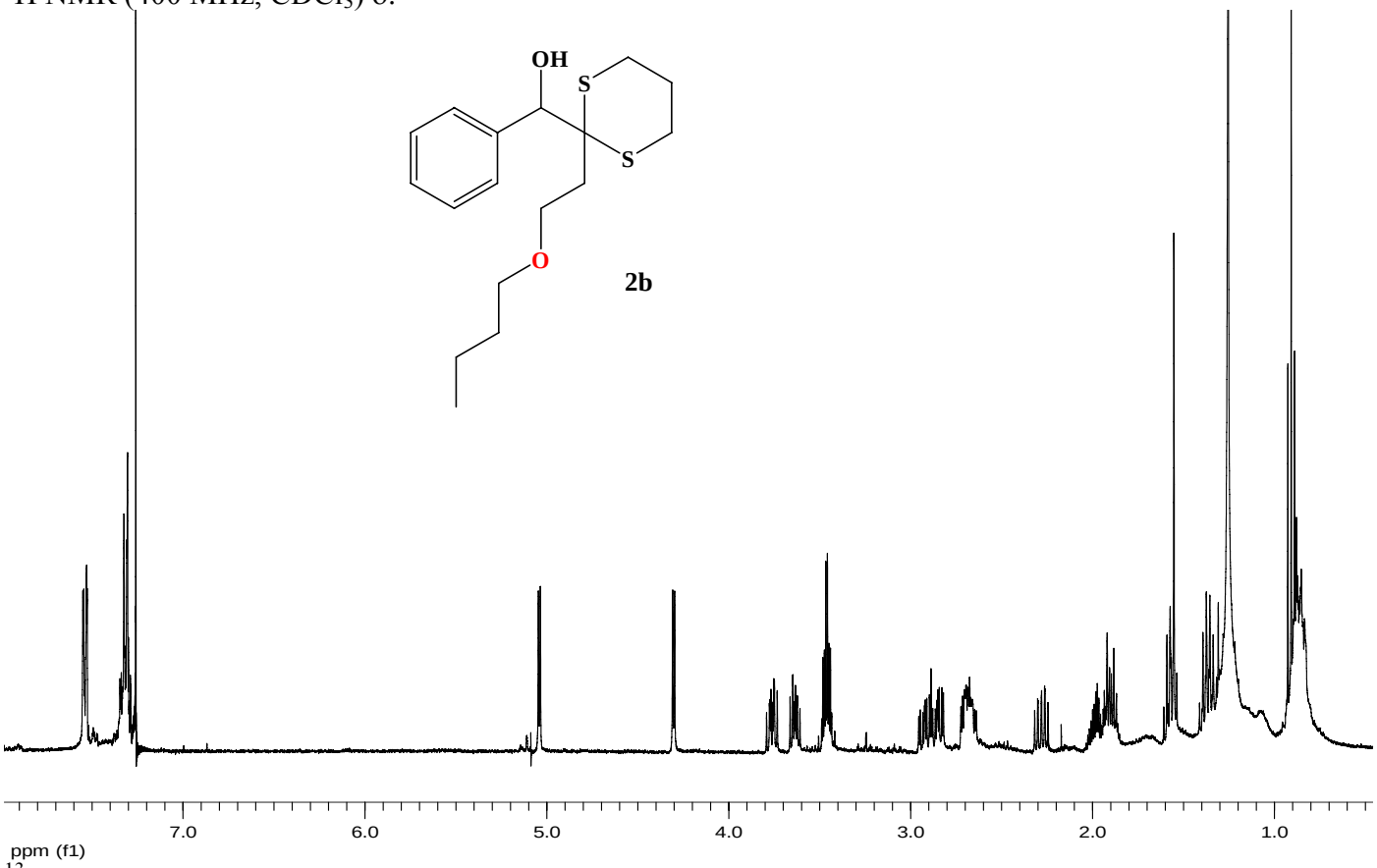
^{1}H NMR (500 MHz, $CDCl_3$) δ:



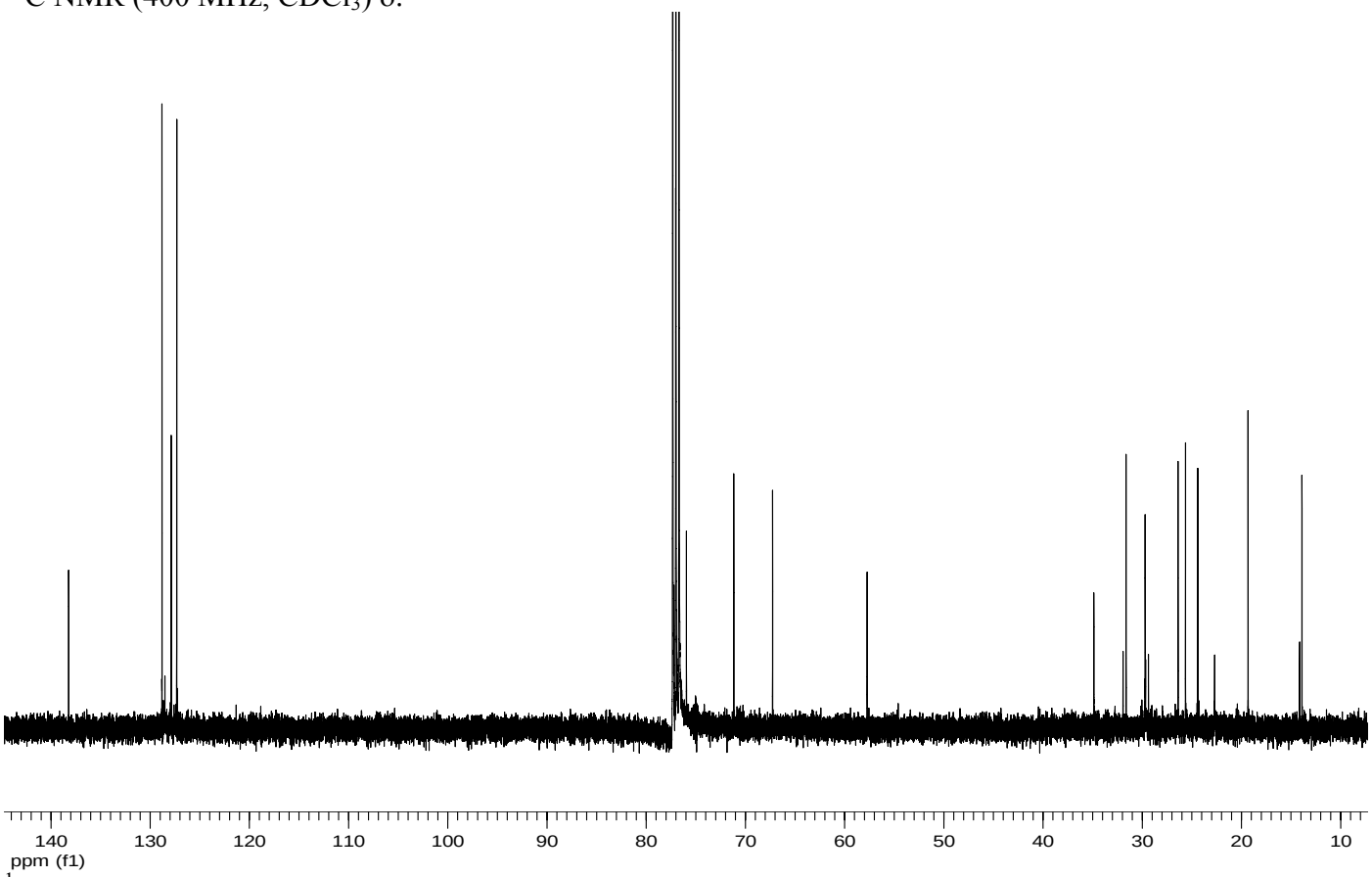
^{13}C NMR (400 MHz, $CDCl_3$) δ:



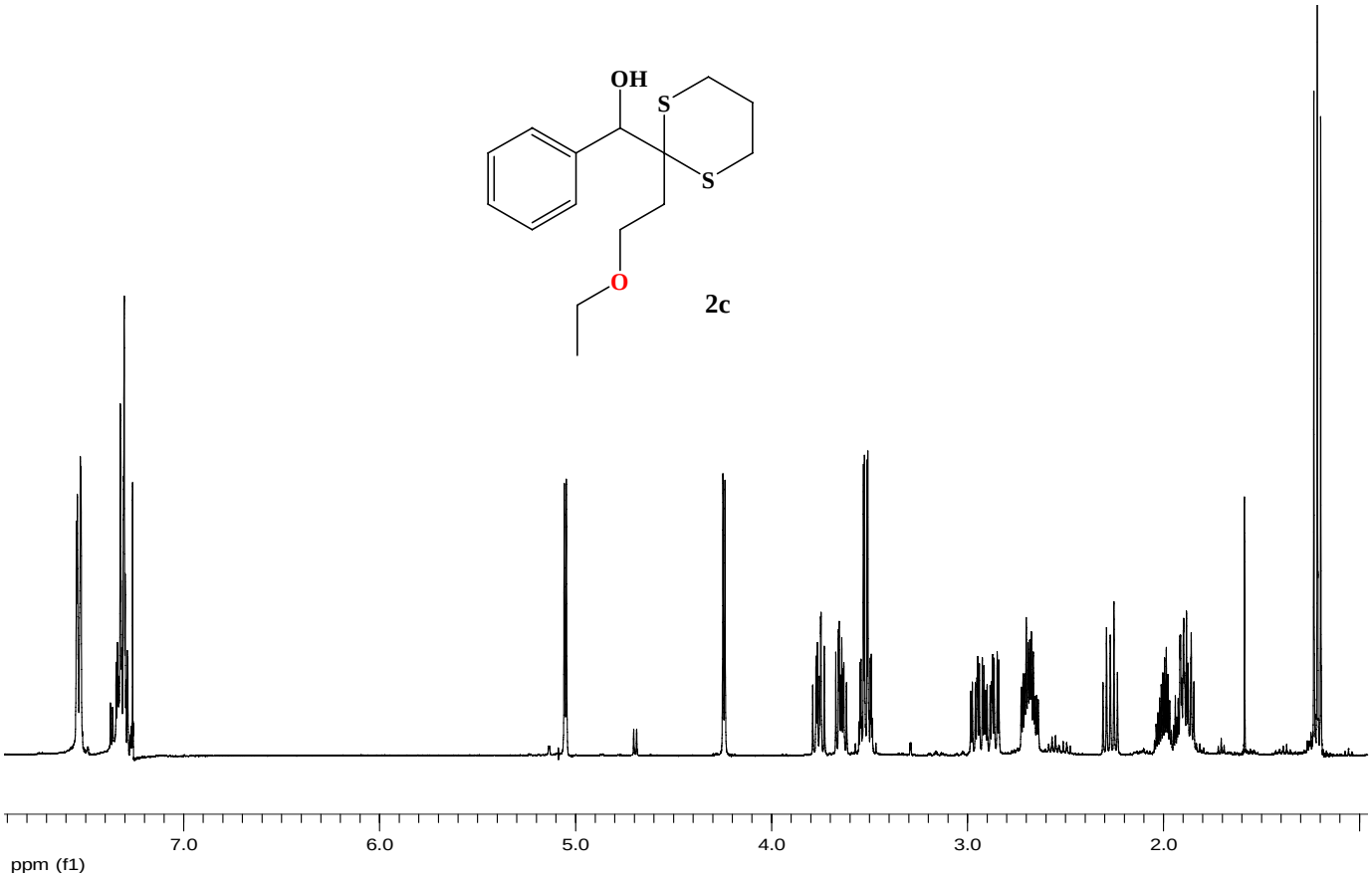
^{1}H NMR (400 MHz, $CDCl_3$) δ:



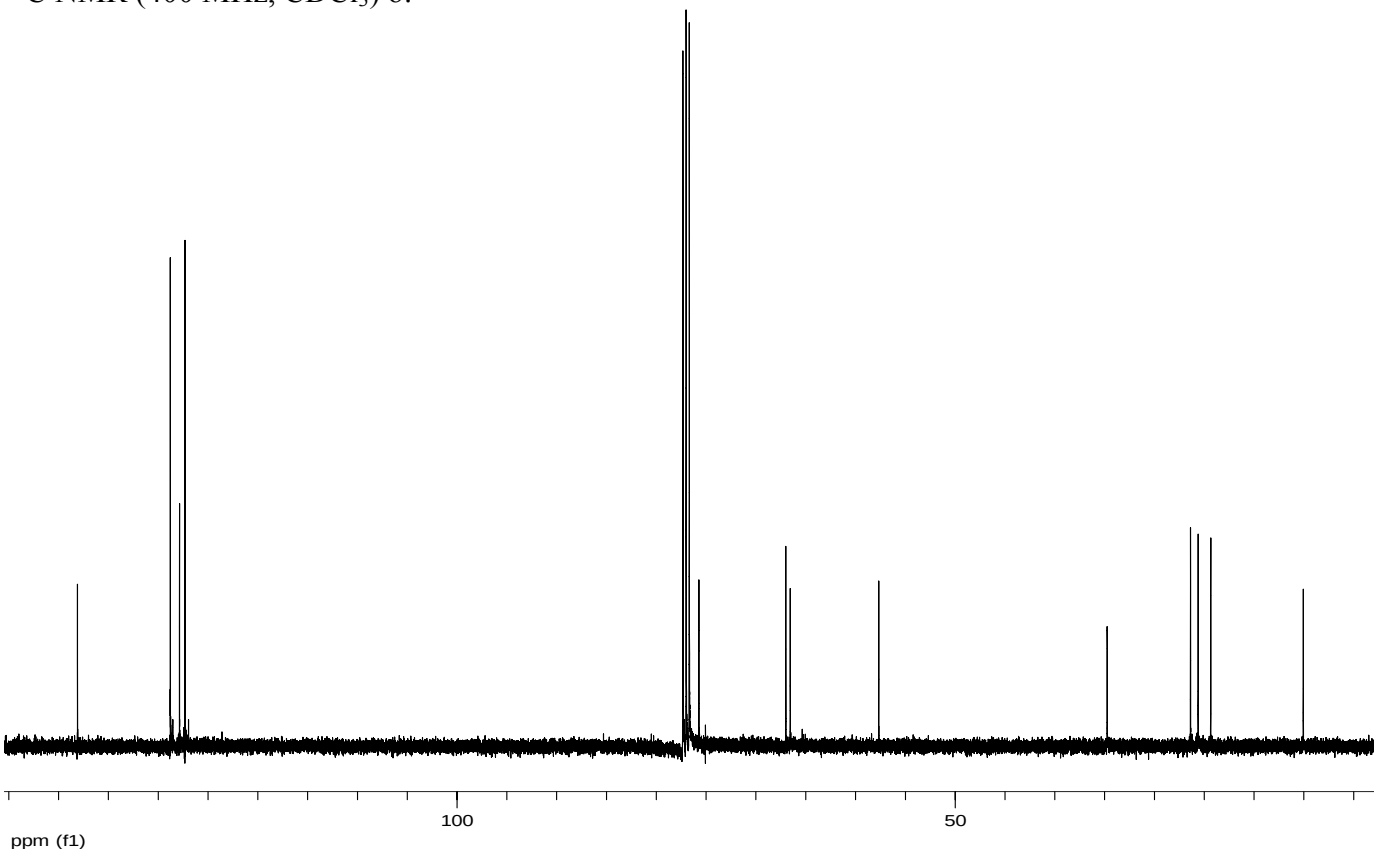
^{13}C NMR (400 MHz, $CDCl_3$) δ:



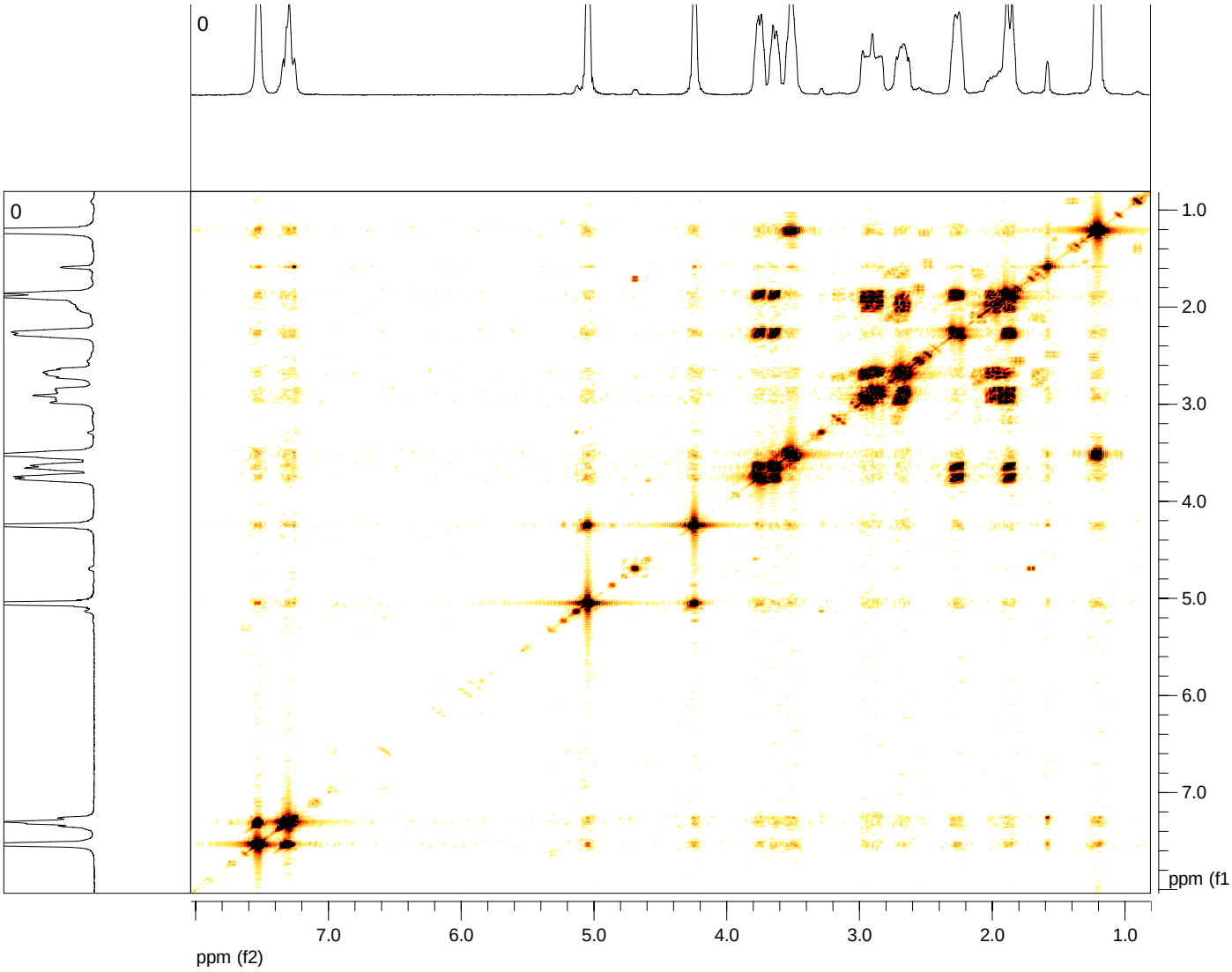
^{1}H NMR (400 MHz, $CDCl_3$) δ:



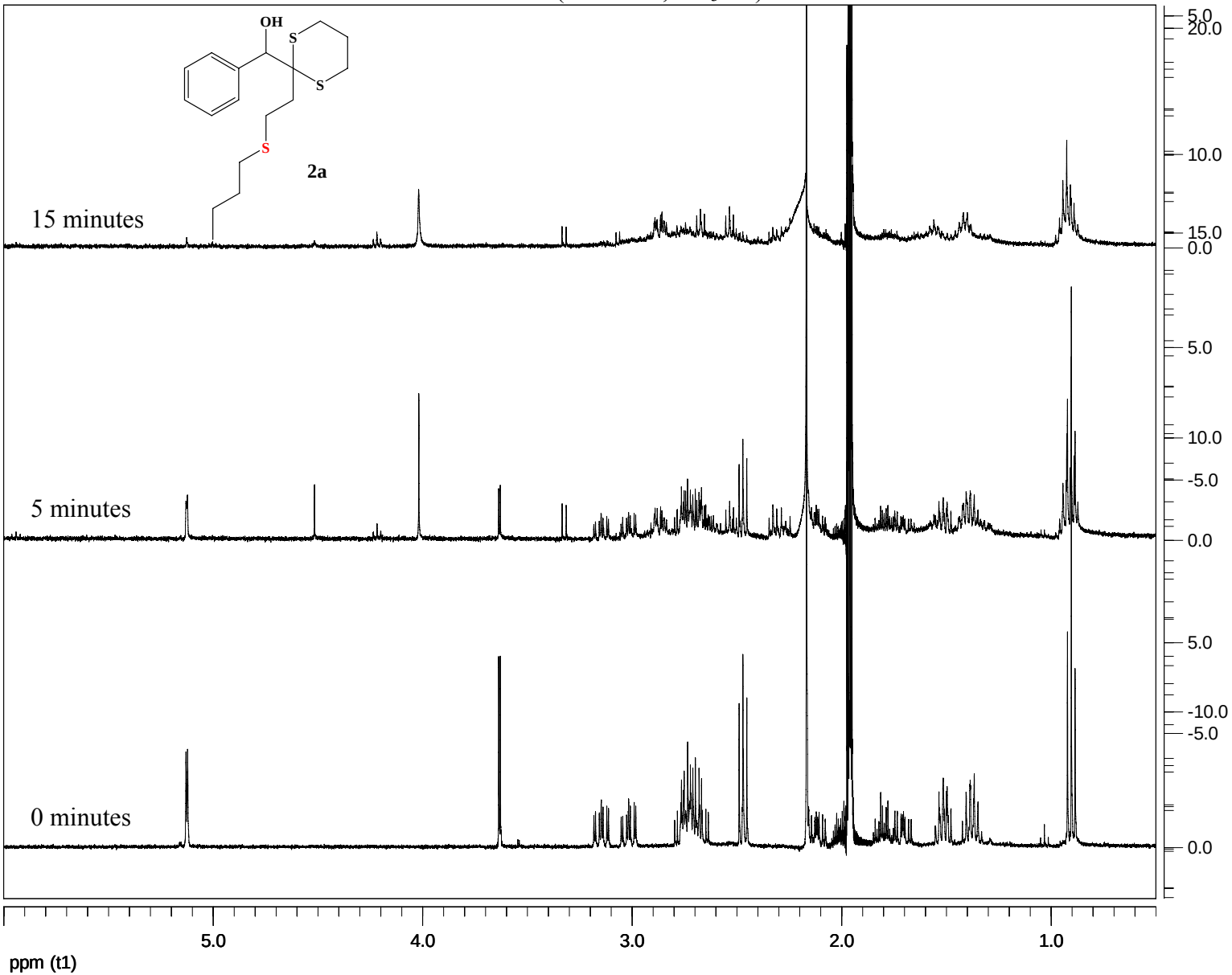
^{13}C NMR (400 MHz, $CDCl_3$) δ:



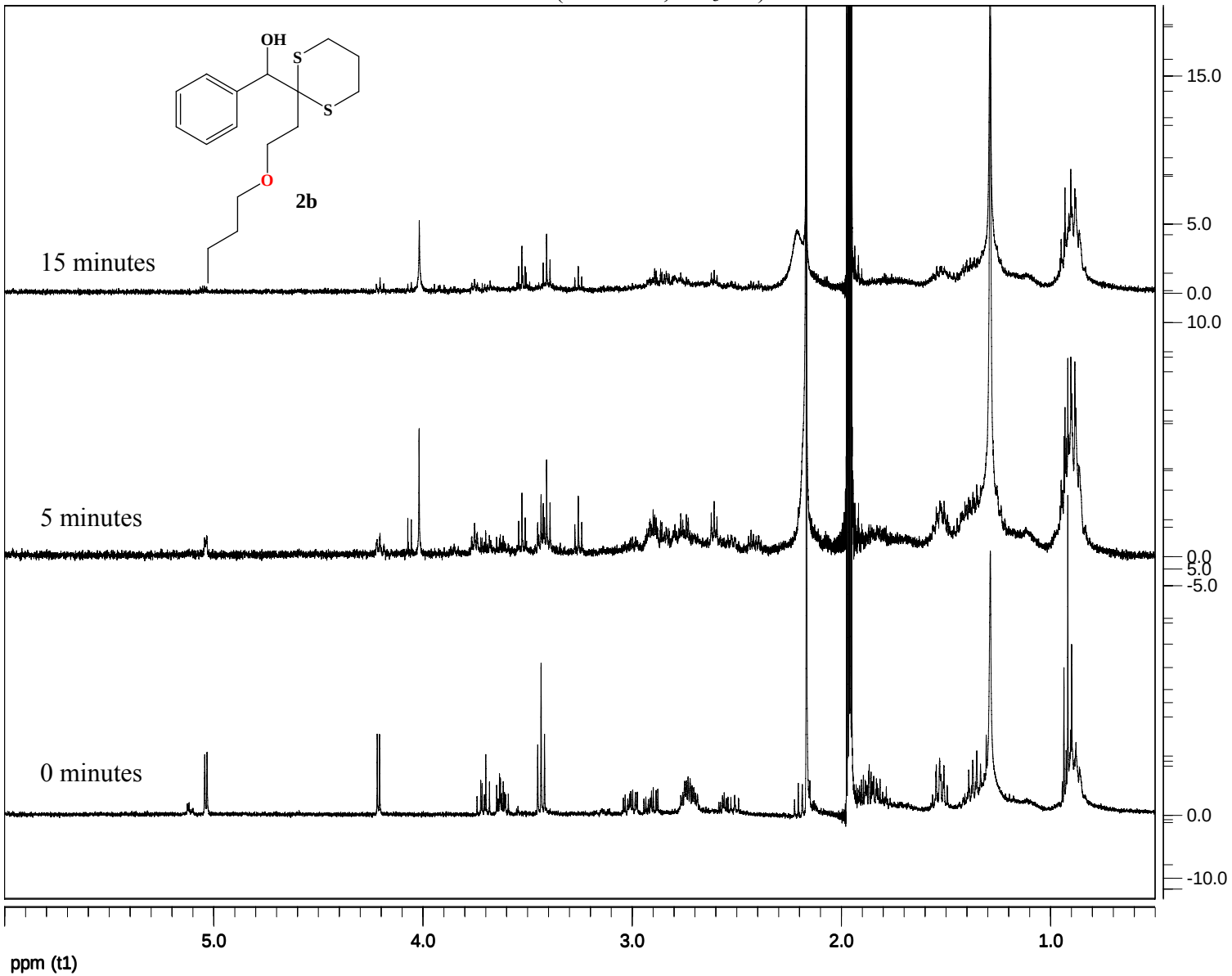
COSY (400 MHz, $CDCl_3$) δ:



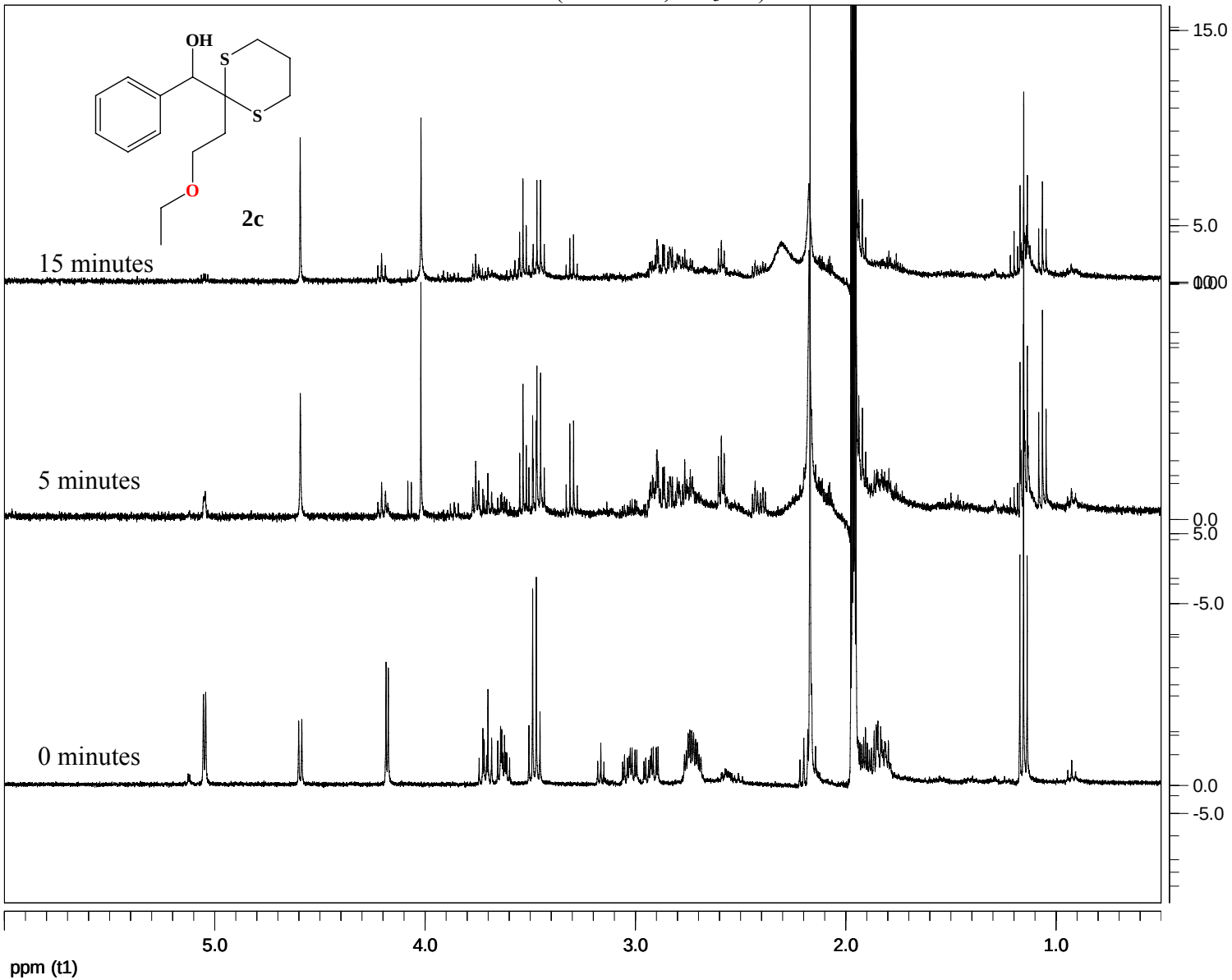
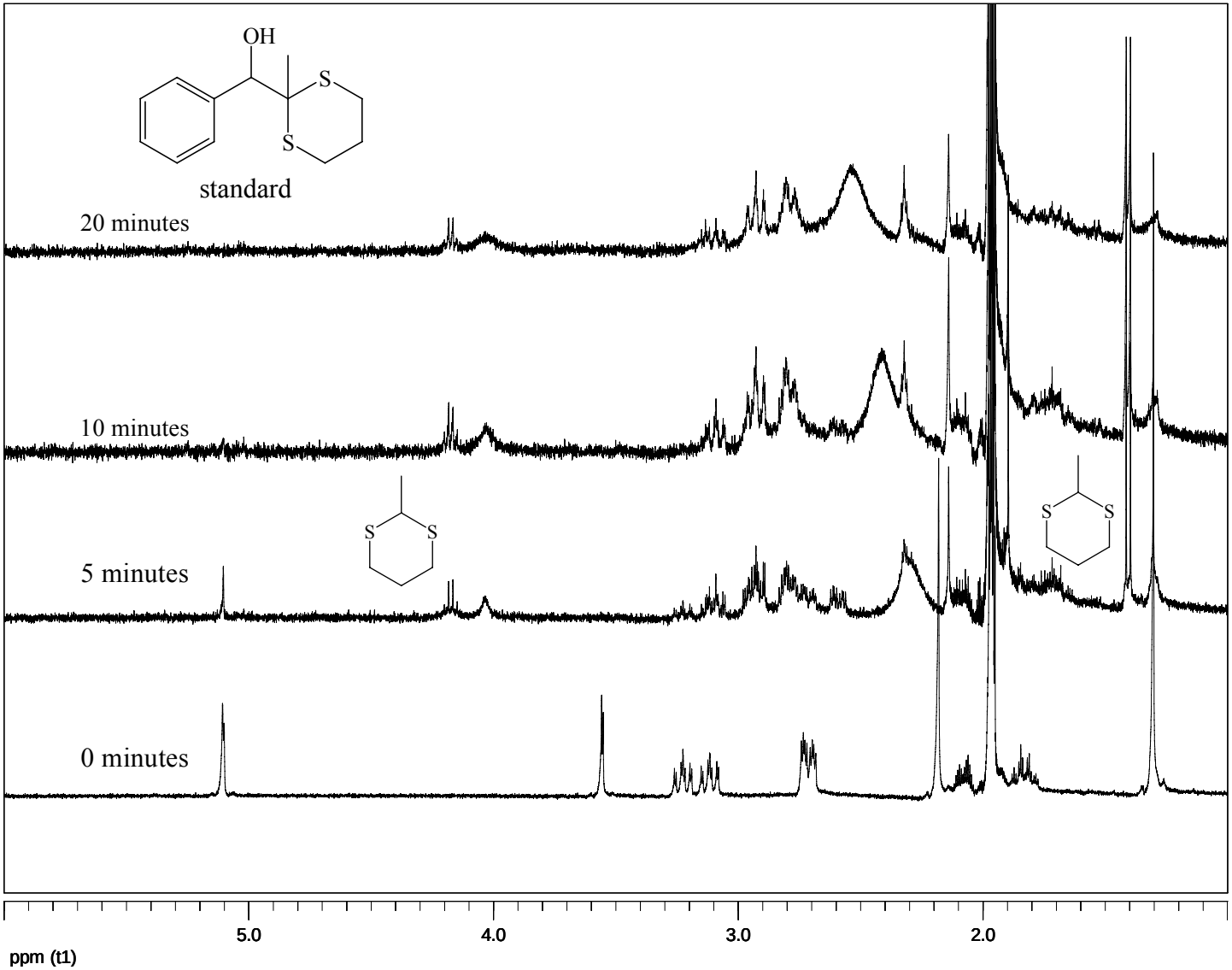
^{1}H NMR (400 MHz, CD_3CN):



^{1}H NMR (400 MHz, CD_3CN):



^{1}H NMR (400 MHz, CD_3CN):



^{1}H NMR (400 MHz, CD_3CN):