–Supporting Information for–

Bare-Minimum Fluorous Mixture Synthesis of a Stereoisomer Library of 4,8,12-Trimethylnonadecanols and Predictions of NMR Spectra of Saturated Oligoisoprenoid Stereoisomers

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General information

All reactions were performed under argon atmosphere unless otherwise noted. All reaction solvents were freshly dried by passing through a column of activated alumina.43 All reagents were purchased commercially and used without further purification unless otherwise mentioned. Reaction progresses were monitored by TLC with 0.25 mm E. Merck precoated silica gel plates. All crude mixtures were purified by flash chromatography with silica gel 60 (0.040−0.063 mm) supplied by Sorbent Technology unless otherwise stated. Products and reactions were analyzed by ^{1}H, ^{13}C, and ^{19}F NMR NMR spectrometry, FT-IR, optical rotation, and HRMS.

The NMR spectra were recorded on a Bruker Advance III 400 MHz, a Bruker Advance III 600 MHz, or a Bruker Advance III 700 MHz spectrometer using deuterated chloroform spiked with 1 mole% trimethylsilane (TMS), unless otherwise indicated. The signals are given as in part per million (d, ppm) and were determined relative to the proton and carbon resonance of TMS at 0 ppm as the internal standard. In the case of ^{19}F NMR NMR spectrometry, no internal standard was used. The spectral data of single molecules were reported in the following order: chemical shift (d), multiplicity, coupling constant (Hz), number of nuclei. The spectral data of mixtures (with the designation M- before number) were not reported, but copies of the spectra are provided.

Infrared (IR) spectra were taken on a Mattson Genesis FT-IR spectrometer as thin film on NaCl plate and the peaks are reported in wave numbers (cm^{-1}). Optical rotations were measured on a Perkin-Elmer 241 polarimeter at a Na D-line (λ = 589 nm) using a 1 dm cell. HPLC analyses and separations were performed on a Waters 600E system with a Waters 2487 dual λ absorption detector. Compound names were obtained from ChemDraw Ultra 12.0 (Cambridge Soft Corp.).

General Procedures

General Procedure 1: the synthesis of fluorinated phenyl chlorothionoformates (6a–g): The corresponding fluorinated phenol in 1N aq. NaOH was added dropwise to a solution of thiophosgene in $CHCl_3$. The resulting mixture was stirred at 0 °C for 1.5 h. The reaction progress was monitored by TLC. After complete consumption of the starting phenol, the reaction was quenched by 1N HCl. The organic layer was dried over $MgSO_4$ and then concentrated. The crude product was used in the next step without further purification.

General Procedure 2: the Roush crotylboration reaction of aldehydes: To a solution of Roush reagent (SS-**8** or RR-**8**, 3 equiv) in toluene was added powdered 4 Å molecular sieves (20 mg/mL), and then cooled to −78 °C. After 10 min, the corresponding aldehyde was added neat to the mixture and the resulting solution was stirred at −78 °C for further 3 h. 2 N NaOH was added to quench the reaction over 20 min at 0 °C then filtered through a pad of celite. The aqueous layer was extracted with ether (10 mL, 3 times). The combined organic layer was dried with K_2CO_3 and concentrated. The crude product was purified by column chromatography (9:1 hexane-diethyl ether).

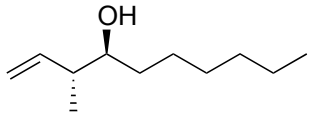
General Procedure 3: thionocarbonate formation (fluorous tagging): To the allylic alcohol in CH_2Cl_2 was added pyridine (anhydrous) at 25 °C. After 10 min, the reaction mixture was cooled to 0 °C. *O*-Phenyl chlorothionoformate (2 equiv) was added dropwise into the reaction mixture, which was slowly warmed to room temperature overnight (16 h). Aqueous NH_4Cl was added to quench the reaction at 0 °C followed by aqueous layer extraction with CH_2Cl_2 (10 mL, 3 times). The combined organic layer was dried over $MgSO_4$ and then concentrated. The crude product was purified by column chromatography (99:1 hexanes-diethyl ether).

General procedure 4, Rh-catalyzed hydroformylation: The pyridone ligand **12** (30 mol%)

and $Rh(CO)_2acac$ (7 mol%) were added to THF under Ar, and the resulting mixture was stirred at room temp. After 10 min, the corresponding alkene was added neat to the premixed catalysts in THF. The resulting mixture was transported to the pressure vessel and stirred at 60 °C under 150 psi of CO/H_2 for 15 h. After complete consumption of the starting alkene, the solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography (3:1 hexanes-diethyl ether).

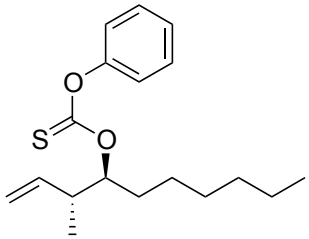
General Procedure 5: radical deoxygenation: To a solution of triphenylthionocarbonate tagged trimethylnonadecanol and 5 equiv of dimethyl-imidazolium carbene-borane (diMe-Imd-BH_3) in benzene-d_6 were added AIBN. The reaction mixture was heated at 80 °C. After 2 h, the solvent was evaporated and the residue was first extracted with hexanes (3 x 5 mL) then concentrated. The crude product was isolated by column chromatography (9:1) hexane-diethyl ether.

Experimental Information and Data on Individual and Mixture Samples

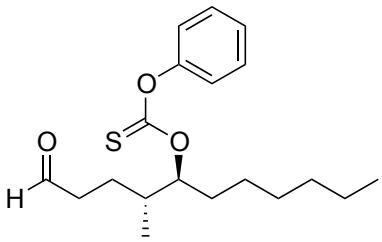


(3*R*,4*S*)-3-Methyldec-1-en-4-ol (10): This crotylation reaction was performed according to General Procedure 2 using heptanal (12 g, 105.1 mmol) and Roush reagent SS-**8** (315 ml, 315 mmol). Allylic alcohol (3*R*,4*S*)-**10** was isolated in 16 g, 89% yield as a colorless oil: $[\alpha]_D^{25} = -0.66$ (c = 1.54, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ = 5.736 (ddd, J = 8.4, 11.3, 16.7 Hz, 1H), 5.096 (d, J = 11.0 Hz, 1H), 5.087 (d, J = 16.8 Hz, 1H), 3.375 (s br, 1H), 2.192 (ddq, J = 6.7, 6.8, 6.9 Hz, 1H), 1.200−1.600 (m, 11H), 1.030 (d, J = 6.9 Hz, 3H), 0.882 (t, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ = 140.40, 116.27, 74.70, 44.14, 34.26, 31.87, 29.42, 25.71, 22.66, 16.32, 14.11; FTIR (thin film) ν_{max} 3372, 3075, 2956, 2928, 2857, 1639, 1459, 999, 961, 912

cm^{-1}; HRMS calcd for $C_{11}H_{22}O$: 170.1668, found 170.1670.

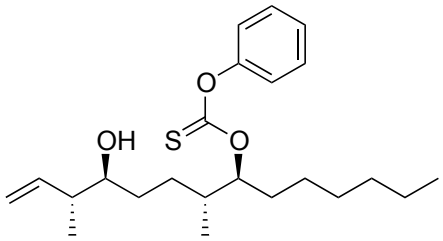


***O*-((3*R*,4*S*)-3-Methyldec-1-en-4-yl) *O*-phenyl carbonothioate (RS-11):** This acylation reaction was performed according to General Procedure 3 using (3*R*,4*S*)-3-methyldec-1-en-4-ol **10** (24 g, 141 mmol) and *O*-phenyl chlorothionoformate (24.3 g, 141 mmol). Alkene (3*R*,4*S*)-**11** was isolated in 34 g, 78% yield as a colorless oil: $[\alpha]_D^{25} = -12.189$ (*c* = 2.33, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ = 7.415 (t, *J* = 7.5 Hz, 2H), 7.283 (t, *J* = 7.5 Hz, 1H), 7.095 (d, *J* = 7.8 Hz, 2H), 5.776 (ddd, *J* = 8.4, 11.3, 16.7 Hz, 1H), 5.372 (dt, *J* = 4.5, 8.4 Hz,1H), 5.130 (d, *J* = 6.3 Hz, 1H), 5.113 (d, *J* = 16.8 Hz, 1H), 2.648 (ddq, *J* = 6.7, 6.8, 6.9 Hz, 1H), 1.500-1.850 (m, 2H), 1.200- 1.500 (m, 8H), 1.099 (d, *J* = 6.9 Hz, 3H), 0.891 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ = 195.17, 153.38, 138.86, 129.45, 126.42, 122.03, 116.06, 88.59, 41.10, 31.69, 30.65, 29.17, 25.25, 22.59, 15.70, 14.08; FTIR (thin film) ν_{max} 3076, 2956, 2928, 2857, 1592, 1490, 1276, 1197, 1002, 918, 768 cm^{-1}; HRMS calcd for $C_{18}H_{26}O_2S$: 306.1658, found 306.1653.

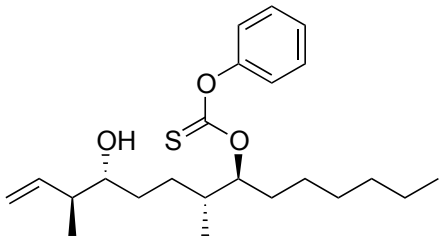


***O*-((4*R*,5*S*)-4-Methyl-1-oxoundecan-5-yl) *O*-phenyl carbonothioate (RS-13):** This Rh-catalyzed hydroformylation reaction was performed according to General Procedure 4 using *O*-((3*R*,4*S*)-3-methyldec-1-en-4-yl) *O*-phenyl carbonothioate RS-**11** (10 g, 330 mmol), pyridone ligand **12** (3.2 g, 100 mmol), and Rh catalyst (0.64 g, 20 mmol). Aldehyde RS-**13** was isolated in 9.3 g, 85% yield as a colorless oil: $[\alpha]_D^{25} = -2.30$ (*c* = 1.87, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 300

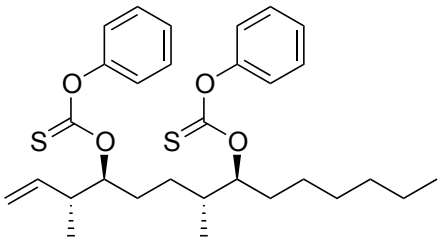
MHz, ppm) δ = 9.799 (t, *J* = 1.2 Hz, 1H), 7.421 (t, *J* = 7.5 Hz, 2H), 7.315 (t, *J* = 7.5 Hz, 1H), 7.099 (d, *J* = 7.8 Hz, 2H), 5.320 (quint, *J* = 4.5 Hz,1H), 2.476-2.593 (m, 2H), 2.008 (ddq, *J* = 6.7, 6.8, 6.9 Hz, 1H), 1.200-1.833 (m, 12H), 0.983 (d, *J* = 6.9 Hz, 3H), 0.898 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ = 201.94, 195.08, 153.34, 129.67, 129.49, 126.49, 122.00, 121.83, 88.98, 41.56, 35.32, 34.68, 31.70, 29.69, 29.22, 25.33, 24.19, 22.67, 22.60, 14.92, 14.15, 14.10; FTIR ν_{max} 2956. 2928, 2857, 2720, 1725, 1592, 1490, 1458, 1358, 1282, 1197, 1003, 770 cm^{-1}; HRMS calcd for $C_{19}H_{28}O_3SNa$: 359.1657, found 359.1672.



***O*-((7*S*,8*R*,11*S*,12*R*)-11-Hydroxy-8,12-dimethyltetradec-13-en-7-yl) *O*-phenyl carbonothioate (RSRS-14):** This crotylation reaction was performed according to General Procedure 2 using aldehyde (4*R*,5*S*)-**13** (1.5 g, 4.46 mmol) and Roush reagent SS-**8** (8.9 ml, 8.9 mmol). Allylic alcohol RSRS-14 was isolated in 1.46 g, 83% yield as a colorless oil: $[\alpha]_D^{25} = -2.64$ (*c* = 1.67, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ = 7.413 (t, *J* = 7.5 Hz, 2H), 7.281 (t, *J* = 7.5 Hz, 1H), 7.102 (d, *J* = 7.8 Hz, 2H), 5.753 (ddd, *J* = 8.4, 11.3, 16.7 Hz, 1H), 5.347 (s br, 1H), 5.133 (d, *J* = 6.9 Hz, 1H), 5.120 (d, *J* = 17.1 Hz, 1H), 3.394 (s br, 1H), 2.217 (ddq, *J* = 6.7, 6.8, 6.9 Hz, 1H), 2.010 (s br, 1H), 1.200-1.800 (m, 14H), 1.043 (d, *J* = 6.9 Hz, 3H), 0.976 (d, *J* = 6.9 Hz, 3H) 0.896 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ = 195.07, 153.38, 140.25, 140.16, 129.43, 126.39, 122.04, 116.51, 116.47, 88.78, 88.53, 74.83, 74.57, 44.23, 44.16, 35.77, 31.71, 31.65, 29.59, 29.38, 29.23, 25.44, 25.38, 22.60, 16.36, 16.31, 15.06, 14.84, 14.08; FTIR ν_{max} 3443, 3072, 2957, 2928, 2859 1592, 1490, 1458, 1369, 1283, 1197, 1002, 914, 769 cm^{-1}; HRMS calcd for $C_{23}H_{36}O_3SNa$: 415.2283, found 415.2260.

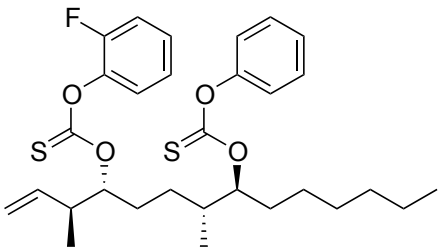


***O*-((7*S*,8*R*,11*R*,12*S*)-11-Hydroxy-8,12-dimethyltetradec-13-en-7-yl) *O*-phenyl carbonothioate (SRRS-14):** This crotylation reaction was performed according to General Procedure 2 using aldehyde RS-**13** (1.2 g, 3.5 mmol) and Roush reagent RR-**8** (10.1 ml, 5.3 mmol). Allylic alcohol SRRS-**14** was isolated in 1.2 g, 83% yield as a colorless oil: $[\alpha]_D^{25} = -0.70$ (*c* = 1.62, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ = 7.410 (t, *J* = 7.5 Hz, 2H), 7.279 (t, *J* = 7.5 Hz, 1H), 7.101 (d, *J* = 7.8 Hz, 2H), 5.752 (ddd, *J* = 8.4, 11.3, 16.7 Hz, 1H), 5.340 (s br, 1H), 5.129 (d, *J* = 6.9 Hz, 1H), 5.118 (d, *J* = 17.1 Hz, 1H), 3.389 (s br, 1H), 2.212 (ddq, *J* = 6.7, 6.8, 6.9 Hz, 1H), 1.994 (s br, 1H), 1.200-1.800 (m, 14H), 1.039 (d, *J* = 6.9 Hz, 3H), 0.971 (d, *J* = 6.9 Hz, 3H) 0.896 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ = 195.10, 153.35, 140.24, 140.14, 129.44, 126.40, 122.03, 116.53, 116.49, 88.77, 88.52, 77.45, 77.23, 77.03, 76.61, 74.80, 74.55, 44.23, 44.16, 35.77, 31.93, 31.70, 31.62, 29.70, 29.53, 29.35, 29.23, 28.50, 28.21, 25.43, 25.38, 22.60, 16.36, 16.31, 15.04, 14.82, 14.08; FTIR ν_{max} 3439, 3072, 2956, 2928, 2858, 1592, 1490, 1458, 1368, 1283, 1197, 1002, 914, 768 cm^{-1}; HRMS calcd for $C_{23}H_{36}O_3SNa$: 415.2283, found 415.2267.



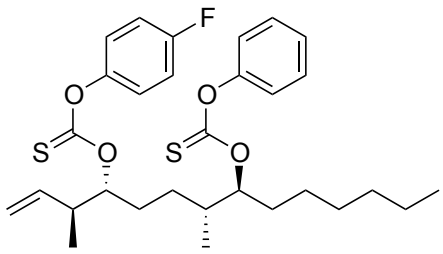
***O*,*O*'-((3*R*,4*S*,7*R*,8*S*)-3,7-Dimethyltetradec-1-ene-4,8-diyl) *O*,*O*'-diphenyl dicarbonothioate:** This acylation reaction was performed according to General Procedure 3 using allylic alcohol RSRS-**14** (2.2 g, 5.6 mmol) and *O*-phenyl chlorothionoformate (1.06 g, 6.2 mmol). The target thionocarbonate (RSRS) was isolated in 2.5 g, 84% yield as a colorless oil: $[\alpha]_D^{25} = -1.68$ (*c* =

1.79, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ = 7.409 (t, *J* = 7.5 Hz, 4H), 7.269 (t, *J* = 7.5 Hz, 2H), 7.089 (d, *J* = 7.8 Hz, 4H), 5.761 (ddd, *J* = 8.4, 11.3, 16.7 Hz, 1H), 5.282-5.386 (m, 2H), 5.141 (d, *J* = 6.9 Hz, 1H), 5.123 (d, *J* = 17.1 Hz, 1H), 2.651 (ddq, *J* = 6.7, 6.8, 6.9 Hz, 2H), 1.995 (s br, 1H), 1.200-1.800 (m, 14H), 1.099 (d, *J* = 6.9 Hz, 3H), 0.981 (d, *J* = 6.9 Hz, 3H) 0.894 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ = 195.13, 195.10, 153.33, 138.72, 138.60, 129.45, 126.45, 126.42, 122.04, 122.01, 116.29, 89.35, 89.21, 88.42, 88.07, 77.46, 77.24, 77.04, 76.61, 41.09, 35.81, 35.76, 31.70, 29.90, 29.77, 29.25, 28.26, 28.11, 27.92, 27.51, 25.26, 22.60, 15.78, 15.60, 15.07, 14.99, 14.09; FTIR ν_{max} 3072, 2058, 2929, 2858, 1592, 1489, 1457, 1358, 1280, 1196, 1121, 1002, 919, 829, 769 cm^{-1}; HRMS calcd for $C_{30}H_{40}O_4S_2Na$: 551.2266, found 551.2318.

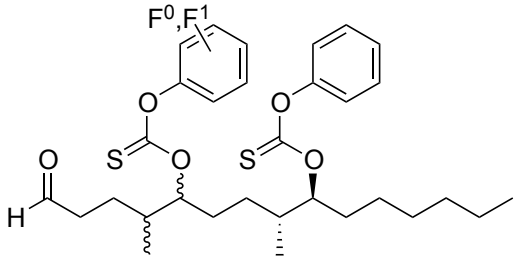


***O*,*O*'-((3*S*,4*R*,7*R*,8*S*)-3,7-Dimethyltetradec-1-ene-4,8-diyl) *O*'-(2-fluorophenyl) *O*-phenyl dicarbonothioate:** This acylation reaction was performed according to General Procedure 3 using allylic alcohol SRRS-**14** (1.1 g, 2.8 mmol) and the crude mixture of *O*-2- fluorophenyl chlorothionoformate **7b** (0.85 g, 4.5 mmol). The target thionocarbonate (2-fluorophenyl-SRRS) was isolated in 1.3 g, 84% yield as a colorless oil: $[\alpha]_D^{25} = -1.22$ (*c* = 1.05, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.090−7.425 (m, 9H), 5.777 (ddd, *J* = 8.1, 10.4, 17.1 Hz, 1H), 5.308-5.390 (m, 2H), 5.128 (d, *J* = 18.1 Hz, 1H), 5.118 (d, *J* = 9.1 Hz, 1H), 2.665 (ddq, *J* = 6.7, 6.8, 6.9 Hz, 2H), 1.931-2.002 (m, 1H), 1.800-1.931 (m, 1H), 1.211-1.800 (m, 12H), 1.110 (d, *J* = 6.9 Hz, 3H), 0.983 (d, *J* = 6.8 Hz, 3H) 0.894 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 195.13, 194.03, 192.43, 155.63, 155.38, 153.39, 152.32, 152.05, 140.99, 140.83, 140.74, 140.58, 138.51, 138.41, 129.47, 128.28, 128.18, 127.78, 127.69, 126.43, 124.75, 124.69, 124.55, 124.50, 124.00, 123. 68, 122.07, 117.31, 117.07, 117.01, 116.77, 116.40, 89.41, 89.25,

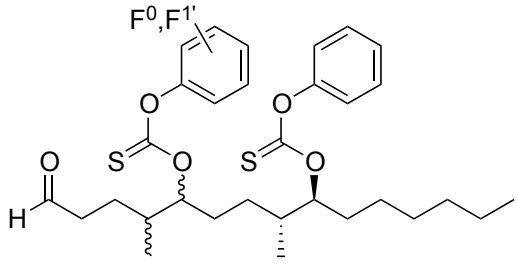
88.96, 41.14, 35.79, 35.67, 31.72, 29.77, 29.68, 29.25, 28.35, 28.26, 27.81, 27.49, 25.35, 22.63, 15.76, 15.61, 15.06, 14.94, 14.11; FTIR ν_{max} 3072, 2958, 2930, 2859, 1600, 1501, 1459, 1363, 1261, 1196, 1101, 1001, 922, 845, 829, 762 cm^{-1}; HRMS calcd for $C_{30}H_{39}O_4S2_FNa$: 569.2172, found 569.2180.



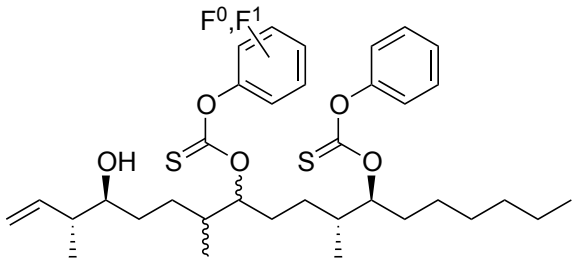
***O*,*O*'-((3*S*,4*R*,7*R*,8*S*)-3,7-Dimethyltetradec-1-ene-4,8-diyl) *O*'-(4-fluorophenyl) *O*-phenyl dicarbonothioate:** This acylation reaction was performed according to General Procedure 3 using allylic alcohol SRRS-**14** (2.2 g, 6.0 mmol) and *O*-4-fluorophenyl chlorothionoformate **7d** (1.3 g, 6.7 mmol). The target thionocarbonate (4-fluorophenyl-SRRS) was isolated in 2.6 g, 85% yield as a colorless oil: $[\alpha]_D^{25} = -1.35$ (*c* = 1.11, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.389 (t, *J* = 7.5 Hz, 2H), 7.269 (t, *J* = 7.5 Hz, 1H), 7.099 (d, *J* = 7.8 Hz, 2H), 7.049 (d, *J* = 6.3 Hz, 4H), 5.785 (ddd, *J* = 8.1, 10.4, 17.1 Hz, 1H), 5.308-5.390 (m, 2H), 5.128 (d, *J* = 18.1 Hz, 1H), 5.118 (d, *J* = 9.1 Hz, 1H), 2.665 (ddq, *J* = 6.7, 6.8, 6.9 Hz, 2H), 1.965-2.033 (m, 1H), 1.833-1.936 (m, 1H), 1.220-1.806 (m, 12H), 1.107 (d, *J* = 6.9 Hz, 3H), 0.983 (d, *J* = 6.8 Hz, 3H) 0.896 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 195.23, 195.16, 161.83, 159.42, 159.39, 153.42, 149.39, 149.36, 149.24, 149.22, 138.70, 138.59, 129.50, 126.47, 126.47, 123.63, 123. 59, 123.55, 123.41, 123.32, 122.09, 116.59, 116.36, 116.31, 116.18, 116.14, 116.07, 115.95, 89.34, 89.21, 88.70, 88.32, 41.16, 36.11, 35.86, 34.71, 34.56, 31.75, 31.63, 30.02, 29.89, 29.30, 29.10, 28.32, 28.13, 27.99, 27.56, 25.32, 25.29, 22.70, 22.65,20.75, 18.81, 15.82, 15.64, 15.13, 15.03, 14.18, 14.14; FTIR ν_{max} 3076, 2958, 2929, 2858, 1502, 1280, 1191, 1003, 922, 839, 738 cm^{-1}; HRMS calcd for $C_{30}H_{39}O_4S_2FNa$: 569.2172, found 569.2173. 86



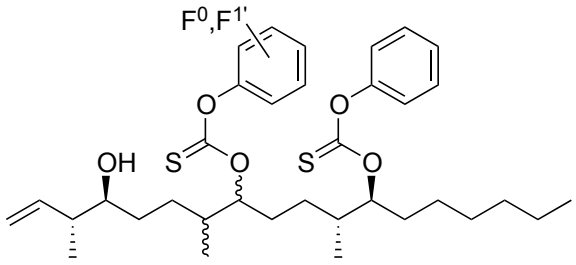
Mixture of *O*,*O*'-((4*R*,5*S*,8*R*,9*S*)-4,8-dimethyl-1-oxopentadecane-5,9-diyl) *O*,*O*'-diphenyl dicarbonothioate and *O*,*O*'-((4*S*,5*R*,8*R*,9*S*)-4,8-dimethyl-1-oxopentadecane-5,9-diyl) *O*'-(2-fluorophenyl) *O*-phenyl dicarbonothioate (M-**15-1):** This Rh-catalyzed hydroformylation reaction was performed according to General Procedure 4 using 1:1 mixture of thionocarbonates (RSRS) + (2-fluorophenyl-SRRS) (2.0 g, 3.8 mmol), pyridone ligand **11** (0.18 g, 12.2 mmol), and Rh catalyst (0.04 g, 2.5 mmol). Aldehyde M-**15** was isolated in 4.4 g, 82% yield as a colorless oil: HRMS calcd for $C_{31}H_{42}O_5S_2Na$: 581.2371, found 581.2336; calcd for $C_{31}H_{41}O_5S_2FNa$: 599.2277, found 599.2228.



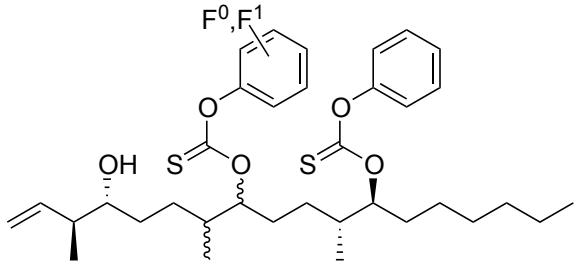
Mixture of *O*,*O*'-((4*R*,5*S*,8*R*,9*S*)-4,8-dimethyl-1-oxopentadecane-5,9-diyl) *O*,*O*'-diphenyl dicarbonothioate and *O*,*O*'-((4*S*,5*R*,8*R*,9*S*)-4,8-dimethyl-1-oxopentadecane-5,9-diyl) *O*'-(4-fluorophenyl) *O*-phenyl dicarbonothioate (M-**15-2):** This Rh-catalyzed hydroformylation reaction was performed according to General Procedure 4 using 1:1 mixture of thioonocarbonates (RSRS) + (4-fluorophenyl-SRRS) (5.08 g, 9.4 mmol), pyridone ligand **11** (0.46 g, 1.7 mmol), and Rh catalyst (0.09 g, 0.33 mmol). Aldehyde M-**15-2** was isolated in 4.4 g, 82% yield as a colorless oil: HRMS calcd for $C_{31}H_{42}O_5S_2Na$: 581.2371, found 581.2393; calcd for $C_{31}H_{41}O_5S_2FNa$: 599.2277, found 599.2264.



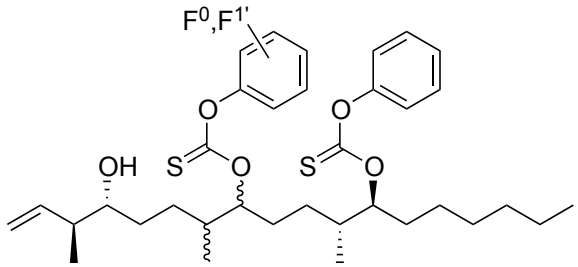
Mixture of *O*,*O*'-((7*S*,8*R*,11*S*,12*R*,15*S*,16*R*)-15-hydroxy-8,12,16-trimethyloctadec-17-ene-7,11-diyl) *O*,*O*'-diphenyl dicarbonothioate and *O*'-(2-fluorophenyl) *O*,*O*'-((7*S*,8*R*,11*R*,12*S*,15*S*,16*R*)-15-hydroxy-8,12,16-trimethyloctadec-17-ene-7,11-diyl) *O*-phenyl dicarbonothioate: This Roush crotylation reaction was performed according to General Procedure 2 using mixture aldehyde M-**15-1** (0.6 g, 0.52 mmol) and Roush reagent SS-**8** (1.0 ml, 1.0 mmol). The resulting allylic alcohol mixture was isolated in 0.52 g, 80% yield as a colorless oil: HRMS calcd for $C_{31}H_{50}O_5S_2Na$: 637.2997, found 637.3007; HRMS calcd for $C_{23}H_{36}O_3S_1F_1Na$: 655.2903, found 655.2900.



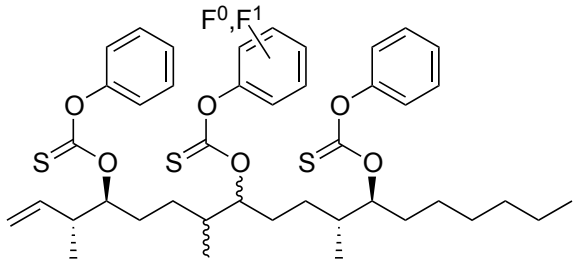
Mixture of *O*,*O*'-((7*S*,8*R*,11*S*,12*R*,15*S*,16*R*)-15-hydroxy-8,12,16-trimethyloctadec-17-ene-7,11-diyl) *O*,*O*'-diphenyl dicarbonothioate and *O*'-(4-fluorophenyl) *O*,*O*'-((7*S*,8*R*,11*R*,12*S*,15*S*,16*R*)-15-hydroxy-8,12,16-trimethyloctadec-17-ene-7,11-diyl) *O*-phenyl dicarbonothioate: This Roush crotylation reaction was performed according to General Procedure 2 using mixture aldehyde M-**15-2** (2.16 g, 3.8 mmol) and Roush reagent **SS-8** (8.0 ml, 8.0 mmol). The resulting allylic alcohol mixturewas isolated in 2.0 g, 84% yield as a colorless oil: HRMS calcd for $C_{31}H_{50}O_5S2Na$: 637.2997, found 637.3015; HRMS calcd for $C_{23}H_{36}O_3SFNa$: 655.2903, found 655.2964.



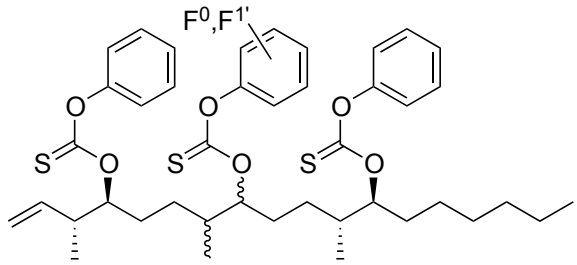
Mixture of *O*,*O*'-((7*S*,8*R*,11*S*,12*R*,15*R*,16*S*)-15-hydroxy-8,12,16-trimethyloctadec-17-ene-7,11-diyl) *O*,*O*'-diphenyl dicarbonothioate and *O*'-(2-fluorophenyl) *O*,*O*'-((7*S*,8*R*,11*R*,12*S*,15*R*,16*S*)-15-hydroxy-8,12,16-trimethyloctadec-17-ene-7,11-diyl) *O*-phenyl dicarbonothioate: This Roush crotylation reaction was performed according to General Procedure 2 using mixture aldehyde M-**15-1** (0.6 g, 0.52 mmol) and Roush reagent RR-**8** (1.0 ml, 1 mmol). The resulting allylic alcohol mixture was isolated in 0.52 g, 79% yield as a colorless oil: HRMS calcd for $C_{31}H_{50}O_5S_2Na$: 637.2997, found 637.3005; HRMS calcd for $C_{23}H_{36}O_3SFNa$: 655.2903, found 655.2878.



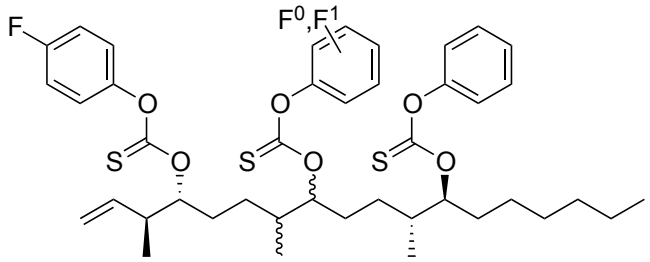
Mixture of *O*,*O*'-((7*S*,8*R*,11*S*,12*R*,15*R*,16*S*)-15-hydroxy-8,12,16-trimethyloctadec-17-ene-7,11-diyl) *O*,*O*'-diphenyl dicarbonothioate and *O*'-(4-fluorophenyl) *O*,*O*'-((7*S*,8*R*,11*R*,12*S*,15*R*,16*S*)-15-hydroxy-8,12,16-trimethyloctadec-17-ene-7,11-diyl) *O*-phenyl dicarbonothioate: This Roush crotylation reaction was performed according to General Procedure 2 using mixture aldehyde M-**15-2** (2.36 g, 4.16 mmol) and Roush reagent RR-**8** (15 ml, 8.3 mmol). The resulting allylic alcohol mixture was isolated in 2.18 g, 83% yield as a colorless oil: HRMS calcd for $C_{31}H_{50}O_5S_2Na$: 637.2997, found 637.3016; HRMS calcd for $C_{23}H_{36}O_3SFNa$: 655.2903, found 655.2924.



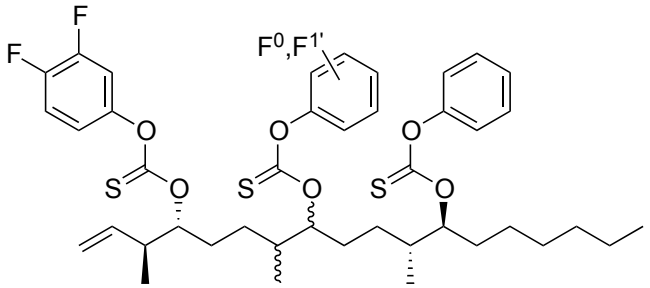
Mixture of *O*,*O*',*O*''-triphenyl *O*,*O*',*O*''((3*R*,4*S*,7*R*,8*S*, 11*R*,12*S*)-3,7,11-trimethyloctadec-1-ene-4,8, 12-triyl) tri-carbonothioate and *O*'-(2-fluorophenyl) *O*,*O*''-diphenyl *O*,*O*',*O*''-((3*R*,4*S*,7*S*,8*R*,11*R*,12*S*)-3,7,11-tri-methyloctadec-1-ene-4,8,12-triyl) tricarbonothioate : This acylation reaction was performed according to General Procedure 3 using mixture allylic alcohol with RSMMRS stereocenters in pilot one study (0.3 g, 0.24 mmol) and *O*-phenyl chlorothionoformate (0.09 g, 0.54 mmol). The target mixture thionocarbonate was isolated in 0.32 g, 88% yield as a colorless oil: HRMS calcd for $C_{42}H_{54}O_6S_3Na$: 773.2980, found 773.2962; HRMS calcd for $C_{42}H_{53}O_6S_3FNa$: 791.2886, found 791.2934.



Mixture of *O*,*O*',*O*''-triphenyl *O*,*O*',*O*''((3*R*,4*S*,7*R*,8*S*, 11*R*,12*S*)-3,7,11-trimethyloctadec-1-ene-4,8, 12-triyl) tricarbonothioate and *O*'-(4-fluorophenyl) *O*,*O*''-diphenyl *O*,*O*',*O*''-((3*R*,4*S*,7*S*,8*R*,11*R*,12*S*)-3,7,11-tri-methyloctadec-1-ene-4,8,12-triyl) tricarbonothioate: This acylation reaction was performed according to General Procedure 3 using mixture allylic alcohol with RSMMRS stereocenters in pilot two study (2.0 g, 3.1 mmol) and *O*-phenyl chlorothionoformate (0.61 g, 3.6 mmol). The target mixture thionocarbonate was isolated in 2.6 g, 86% yield as a colorless oil: HRMS calcd for $C_{42}H_{54}O_6S_3Na$: 773.2980, found 773.2962; HRMS calcd for $C_{42}H_{53}O_6S_3FNa$: 791.2886, found 791.2870.

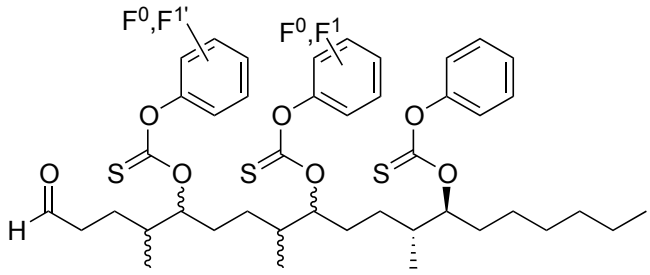


Mixture of *O*''-(4-fluorophenyl) *O*,*O*'-diphenyl *O*,*O*',*O*''-((3*S*,4*R*,7*R*,8*S*,11*R*,12*S*)-3,7,11-trimethyloctadec-1-ene-4,8, 12-triyl) tricarbonothioate and *O*''-(4-fluoro-phenyl) *O*'-(2-fluorophenyl) *O*-phenyl *O*,*O*',*O*''-((3*S*,4*R*,7*S*,8*R*,11*R*,12*S*)-3,7,11-trimethyloctadec-1-ene-4,8, 12-triyl) tricarbonothioate: This acylation reaction was performed according to General Procedure 3 using allylic alcohol with SRMMRS stereocenters in pilot one study (0.3 g, 0.24 mmol) and *O*-4-fluorophenyl chlorothiono-formate (0.1 g, 0.54 mmol). The target mixture thionocarbonate was isolated in 0.32 g, 88% yield as colorless oil: HRMS calcd for $C_{42}H_{52}O_6S_3F_2Na$: 809.2792, found 809.2755; HRMS calcd for $C_{42}H_{53}O_6S_3FNa$: 791.2886, found 791.2934.

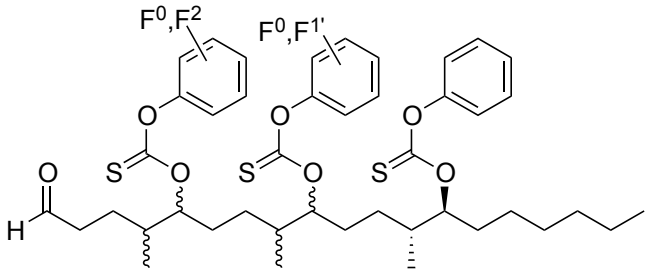


Mixture of *O*''-(3,4-difluorophenyl) *O*,*O*'-diphenyl *O*,*O*',*O*''-((3*S*,4*R*,7*R*,8*S*,11*R*,12*S*)-3,7,11-trimethyloctadec-1-ene-4,8, 12-triyl) tricarbonothioate and *O*''-(3,4-difluoro-phenyl) *O*'-(4-fluorophenyl) *O*-phenyl *O*,*O*',*O*''-((3*S*,4*R*,7*S*,8*R*,11*R*,12*S*)-3,7,11-trimethyloctadec-1-ene-4,8,12-triyl) tricarbonothioate: This acylation reaction was performed according to General Procedure 3 using allylic alcohol with stereocenters SRMMRS in pilot 2 study (2.0 g, 3.16 mmol) and the crude product of *O*-3,4- difluorophenyl chlorothiono-formate **57** (~0.70 g, 3.30 mmol). The target mixture thionocarbonate was isolated in 2.2 g, 88% yield as a colorless oil: HRMS calcd for $C_{42}H_{52}O_6S_3F_2Na$: 809.2792, found 809.2757; HRMS calcd for

$C_{42}H_{51}O_6S_3F_3Na$: 827.2698, found 827.2710.

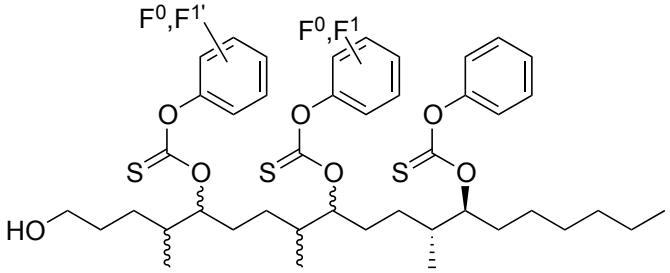


Mixture of *O*,*O*',*O*''-triphenyl *O*,*O*',*O*''-((4*R*, 5*S*, 8*R*, 9*S*, 12*R*,13*S*)-4,8,12-trimethyl-1-oxononadecane-5,9, 13-triyl) tricarbonothioate, *O*'-(2-fluorophenyl) *O*, *O*''-diphenyl *O*,*O*', *O*''-((4*R*,5*S*,8*S*,9*R*,12*R*,13*S*)-4,8,12-trimethyl-1-oxononadecane-5,9,13-triyl) tricarbonothioate, *O*''-(4-fluorophenyl) *O*,*O*'-diphenyl *O*,*O*',*O*''-((4*S*,5*R*,8*R*,9*S*,12*R*,13*S*)-4,8,12-trimethyl-1-oxononadecane-5,9,13-triyl) tricarbonothioate, and *O*''-(4-fluorophenyl) *O*'-(2-fluorophenyl) *O*-phenyl *O*,*O*',*O*''-((4*S*,5*R*,8*S*,9*R*,12*R*,13*S*)-4,8,12-trimethyl-1-oxononadecane-5,9,13-triyl) tricarbonothioate: This Rh-catalyzed hydroformylation reaction was performed according to General Procedure 4 using 1:1 mixture of thionocarbonates (RSMMRS) and (SRMMRS) (0.3 g, 0.39 mmol), pyridone ligand **11** (0.07 g, 0.14 mmol), and Rh catalyst (0.007 g, 0.027 mmol). The resulting aldehyde was isolated in 0.26 g, 83% yield as a colorless oil: HRMS calcd for $C_{43}H_{56}O_7S_3Na$: 803.3086, found 803.3066; HRMS calcd for $C_{43}H_{55}O_7S_3FNa$: 821.2992, found 821.3021; HRMS calcd for $C_{43}H_{54}O_7S_3F_2Na$: 839.2897, found 839.2896.



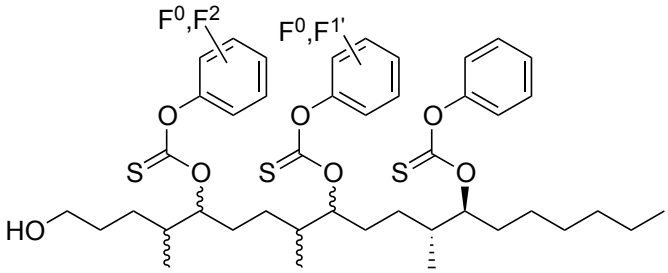
Mixture of *O*,*O*',*O*''-triphenyl *O*,*O*',*O*''-((4*R*, 5*S*, 8*R*, 9*S*, 12*R*,13*S*)-4,8,12-trimethyl-1-oxononadecane-5,9, 13-triyl) tricarbonothioate, *O*'-(4-fluorophenyl) *O*, *O*''-diphenyl *O*,*O*', *O*''-((4*R*,5*S*,8*S*,9*R*,12*R*,13*S*)-4,8,12-trimethyl-1-oxononadecane-5,9,13-triyl) tricarbonothio-

ate, *O*''-(3,4-difluorophenyl) *O*,*O*'-diphenyl *O*,*O*', *O*''-((4*S*,5*R*,8*R*,9*S*,12*R*,13*S*)-4,8,12-trimethyl-1-oxononadecane-5,9,13-triyl) tricarbonothioate, and *O*''-(3,4-difluorophenyl) *O*'-(4-fluorophenyl) *O*-phenyl *O*,*O*',*O*''-((4*S*,5*R*,8*S*,9*R*,12*R*,13*S*)-4,8,12-trimethyl-1-oxo-nonadecane-5,9,13-triyl) tricarbonothioate: This Rh-catalyzed hydroformylation reaction was performed according to General Procedure 4 using 1:1 mixture of thionocarbonates (RSMMRS) and (SRMMRS) (3.6 g, 4.6 mmol), pyridone ligand **11** (0.81 g, 1.6 mmol), and Rh catalyst (0.09 g, 0.32 mmol). The resulting aldehyde was isolated in 3.0 g, 80% yield as a colorless oil: HRMS calcd for $C_{43}H_{56}O_7S_3Na$: 803.3086, found 803.3066; HRMS calcd for $C_{43}H_{55}O_7S_3FNa$: 821.2992, found 821.2988; HRMS calcd for $C_{43}H_{54}O_7S_3F_2Na$: 839.2897, found 839.2916; HRMS calcd for $C_{43}H_{53}O_7S_3F_3Na$: 857.2803, found 857.2819.



Mixture of *O*,*O*',*O*''-((4*R*,5*S*,8*R*,9*S*,12*R*,13*S*)-1-hydroxy-4,8,12-trimethylnonadecane-5,9,13-triyl) *O*,*O*',*O*''-triphenyl tricarbonothioate, O'-(2-fluorophenyl) *O*,*O*',*O*''-((4*R*,5*S*,8*S*,9*R*,12*R*,13*S*)-1-hydroxy-4,8,12-tri-methylnonadecane-5,9,13-triyl) *O*,*O*''-diphenyl tri-carbono-thioate, *O*''-(4-fluorophenyl) *O*,*O*',*O*''-((4*S*,5*R*,8*R*,9*S*,12*R*,13*S*)-1-hydroxy-4,8,12-trimethyl-nonadecane-5,9,13-triyl) *O*,*O*'-diphenyl tricarbonothioate, and *O*''-(4-fluorophenyl) *O*'-(2-fluorophenyl) *O*,*O*',*O*''-((4*S*,5*R*,8*S*,9*R*,12*R*,13*S*)-1-hydroxy-4,8,12-trimethylnonadecane-5,9, 13-triyl) *O*-phenyl tricarbonothioate M-**16:** To a solution of mixture aldehyde (pilot one) in THF (4 mL) at 0 °C was added DIBAL-*H* (0.30 mL, 0.29 mmol). The reaction was stirred for 3 h at 0 °C. The reaction was quenched by addition of saturated aq NH4Cl (1 mL) followed by extraction of the aqueous layer with Et2O (5 mL, 3 times). The combined organic layers was dried over MgSO4 and concentrated. The crude product was

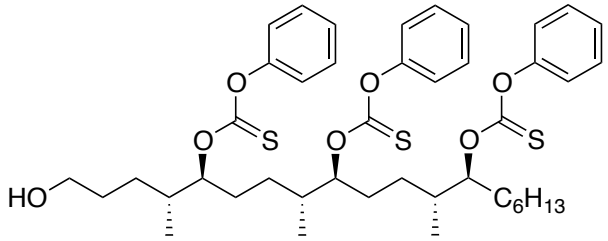
purified by column chromatography (9:1 hexanes-diethylether). Mixture alcohol M-**16 in pilot study one** was isolated in 0.14 g, 71.5% yield as a colorless viscous oil: HRMS calcd for $C_{43}H_{58}O_7S_3Na$: 805.3242, found 805.3220; HRMS calcd for $C_{43}H_{57}O_7S_3F_1Na$: 823.3148, found 823.3088; HRMS calcd for $C_{43}H_{56}O_7S_3F_2Na$: 841.3054, found 841.3113.



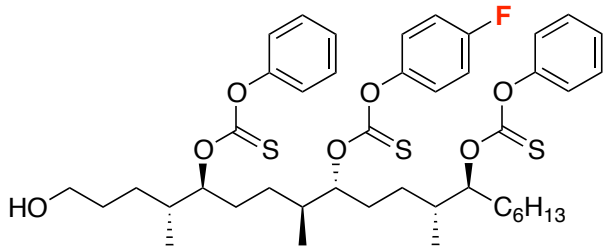
Mixture of *O*,*O*',*O*''-((4*R*,5*S*,8*R*,9*S*,12*R*,13*S*)-1-hydroxy-4,8,12-trimethylnonadecane-5,9,13-triyl) *O*,*O*',*O*''-triphenyl tricarbonothioate, O'-(4-fluorophenyl) *O*,*O*',*O*''-((4*R*,5*S*,8*S*,9*R*, 12*R*,13*S*)-1-hydroxy-4,8,12-trimethylnonadecane-5,9,13-triyl) *O*,*O*''-diphenyl tri-carbono-thioate, *O*''-(3,4-difluorophenyl) *O*,*O*',*O*''-((4*S*,5*R*,8*R*,9*S*,12*R*,13*S*)-1-hydroxy-4,8, 12-tri-methylnonadecane-5,9,13-triyl) *O*,*O*'-diphenyl tricarbonothioate, and *O*''-(3,4-difluoro-phenyl) *O*'-(4-fluorophenyl) *O*,*O*',*O*''-((4*S*,5*R*,8*S*,9*R*,12*R*,13*S*)-1-hydroxy-4,8,12-trimethylnonadecane-5,9,13-triyl) *O*-phenyl tricarbonothioate M-**16:** To a solution of **mixture aldehyde (pilot two)** in THF (10 mL) at 0 °C was added DIBAL-*H* (1.95 mL, 1.95 mmol.). The reaction was stirred for 3 h at 0 °C. The reaction was quenched with addition of saturated aq NH4Cl (3 mL) followed by extraction of the aqueous layer with Et2O (5 mL, 3 times). The combined organic layers was dried over MgSO4 and concentrated. The crude product was purified by column chromatography (9:1 hexanes-diethylether). Mixture alcohol M-**16** was isolated in 0.88 g, 88% yield as a colorless viscous oil: HRMS calcd for $C_{43}H_{58}O_7S_3Na$: 805.3242, found 805.3287; HRMS calcd for $C_{43}H_{57}O_7S_3FNa$: 823.3148, found 823.3119; HRMS calcd for $C_{43}H_{56}O_7S_3F_2Na$: 841.3054, found 841.3100; HRMS calcd for $C_{43}H_{55}O_7S_3F_3Na$: 859.2960, found 859.3012.

Purified Products after Fluorous HPLC demixing

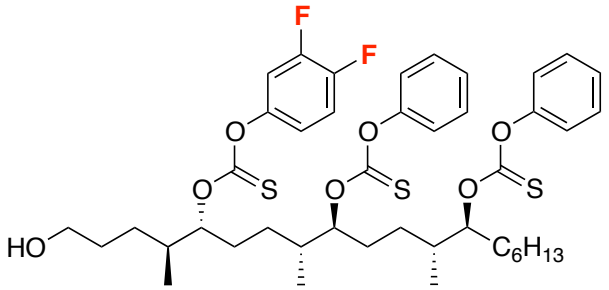
Preparative Demixing: The semi-prep scale F-HPLC demixing of alcohol M-**16 (pilot study two)** was achieved on the PF-C8 column (Fluoro*Flash*® 100 Å, 5 μm) by eluting with a gradient of 60:40 CH3CN/H2O to 100% CH3CN over 1 h (Figure 3.3). Because of the close elution of the four peaks (40 min, 42 min, 44 min, 46 min), the demixing was accomplished by several 1 mL injections of 10 mg/mL of M-**78** in CH3CN. The four different peaks were collected and the products were identified by ^{19}F NMR NMR spectroscopy prior to combination of fractions. Overall, 107 mg of M-**78** was subjected to semi-prep HPLC, and the total of the four indivudual samples was 75 mg (~70%).



***O*,*O*',*O*''-((4*R*,5*S*,8*R*,9*S*,12*R*,13*S*)-1-Hydroxy-4,8,12-trimethylnonadecane-5,9,13-triyl) *O*,*O*',*O*''-triphenyl tricarbonothioate [(4*R*,5*S*,8*R*,9*S*,12*R*,13*S*)-16a]:** (4*R*,5*S*,8*R*,9*S*,12*R*,13*S*)-**16a** was obtained in 32 mg, 74% recovery: $[\alpha]_D^{25}$ = +9.32 (*c* = 0.21, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.380 (t, *J* = 7.8 Hz, 4H), 7.361 (t, *J* = 7.8 Hz, 2H), 7.266 (t, *J* = 7.8Hz 3H), 7.098 (d, *J* = 7.7 Hz, 6H), 5.323-5.344 (m, 3H), 3.638 (t, *J* =6.1, 2H), 1.969-2.036 (m, 3H), 1.251-1.952 (m, 22H), 1.007 (d, *J* = 6.8 Hz, 3H), 1.001 (d, *J* = 6.3 Hz, 3H), 0.985 (d, *J* = 6.7 Hz, 3H), 0.891 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 195.11, 195.08, 153.36, 153.33, 153.30, 129.46, 126.44, 122.04, 122.02, 89.46, 89.14, 89.11, 89.06, 62.96, 35.99, 35.91, 35.88, 35.62, 31.70, 30.23, 30.20, 30.04, 29.77, 29.26, 29.25, 28.47, 28.33, 28.27, 28.06, 28.00, 27.86, 27.66, 27.58, 27.53, 27.41, 27.03, 25.28, 22.60, 15.15, 15.10, 15.04, 14.97, 14.93, 14.87, 14.09; FTIR ν_{max} 3354, 3044, 2959, 2927, 2857, 1592, 1489, 1457, 1359, 1281, 1197, 1003, 769 cm^{-1}; HRMS calcd for $C_{43}H_{58}O_7S_3Na$: 805.3242, found 805.3222.

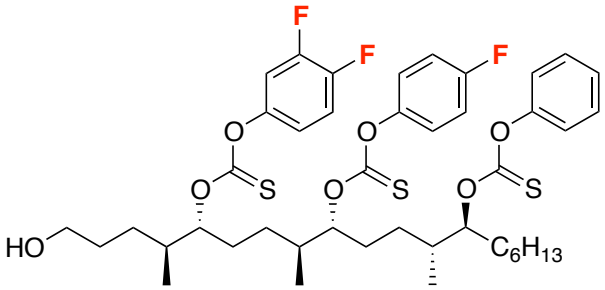


***O*'-(4-Fluorophenyl) *O*,*O*',*O*''-((4*R*,5*S*,8*S*,9*R*,12*R*,13*S*)-1-hydroxy-4,8,12-trimethylnona-decane-5,9,13-triyl) *O*,*O*''-diphenyl tricarbonothioate [(4*R*,5*S*,8*S*,9*R*,12*R*,13*S*)-16b]:** (4*R*,5*S*, 8*S*,9*R*,12*R*,13*S*)-**16b** was obtained in 28 mg, 72% recovery: $[\alpha]_D^{25}$ = +2.33 (*c* = 0.32, $CHCl_3$) ; ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.390 (t, *J* = 7.8 Hz, 4H), 7.383 (t, *J* = 7.8 Hz, 2H), 7.274 (t, *J* = 7.8Hz 3H), 7.098 (d, *J* = 8.2 Hz, 2H), 7.091 (d, *J* = 8.3 Hz, 2H), 7.001-7.068 (m, 4H), 5.313- 5.356 (m, 3H), 3.654 (t, *J* =6.0, 2H), 1.968-2.075 (m, 3H), 1.252-1.939 (m, 22H), 1.002 (d, *J* = 6.5 Hz, 3H), 0.994 (d, *J* = 6.7 Hz, 6H), 0.891 (t, *J* = 6.6 Hz, 3H).) ; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 195.27, 195.23, 195.14, 161.79, 159.35, 153.36, 153.32, 153.29, 149.20, 149.17, 129.48, 126.47, 126.45, 123.66, 123.57, 122.05, 122.03, 116.28, 116.04, 89.41, 89.12, 89.04, 62.93, 36.00, 35.87, 35.65, 31.70, 30.23, 30.20, 30.09, 29.84, 29.27, 28.49, 28.36, 28.30, 28.09, 28.02, 27.86, 27.71, 27.55, 27.41, 27.03, 25.25, 22.60, 15.16, 15.11, 15.08, 15.02, 14.93, 14.90, 14.88, 14.09; FTIR ν_{max} 3352, 2959, 2928, 2859, 1592, 1502, 1457, 1359, 1281, 1198, 1004, 738 cm^{-1}; HRMS calcd for $C_{43}H_{57}O_7S_3FNa$: 823.3148, found 823.3115.



***O*''-(3,4-Difluorophenyl) *O*,*O*',*O*''-((4*S*,5*R*,8*R*,9*S*,12*R*,13*S*)-1-hydroxy-4,8,12-trimethylnona decane-5,9,13-triyl) *O*,*O*'-diphenyl tricarbonothioate [(4*S*,5*R*,8*R*,9*S*,12*R*,13*S*)-16c]:** (4*S*,5*R*, 8*R*,9*S*,12*R*,13*S*)-**16c** was obtained in 30 mg, 71% recovery: $[\alpha]_D^{25}$ = −1.34 (*c* = 0.25, $CHCl_3$) ; ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.347–7.411 (m, 4H), 7.287–7.289 (m, 2H), 7.086–7.176 (m,

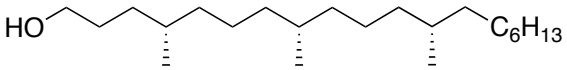
5H), 6.952–7.001 (m, 1H), 6.823-6.865 (m, 1H), 5.323-5.344 (m, 3H), 3.638 (t, J =6.1, 2H), 1.969-2.036 (m, 3H), 1.251-1.952 (m, 22H), 1.007 (d, J = 6.8 Hz, 3H), 1.001 (d, J = 6.3 Hz, 3H), 0.985 (d, J = 6.7 Hz, 3H), 0.891 (t, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 195.22, 195.16, 194.64, 153.39, 153.35, 151.44, 149.91, 148.94, 148.80, 148.74, 148.70, 148.65, 148.62, 148.57, 148.45, 129.50, 129.49, 126.52, 122.06, 118.45, 118.39, 118.35, 117.44, 117.25, 112.51, 112.31, 90.10, 89.64, 89.42, 89.33, 89.11, 62.91, 53.46, 35.98, 35.88, 35.84, 35.61, 31.72, 30.20, 30.02, 29.77, 29.28, 28.51, 28.39, 28.29, 28.12, 28.03, 27.89, 27.67, 27.47, 26.97, 25.30, 22.62, 15.18, 15.11, 15.03, 14.97, 14.94, 14.87, 14.10; FTIR ν_{max} 3385, 2959, 2928, 2858, 1513, 1490, 1458, 1284, 1195, 1004, 771 cm^{-1}; HRMS calcd for $C_{43}H_{56}O_7S_3F_2Na$: 841.3054, found 841.3025.



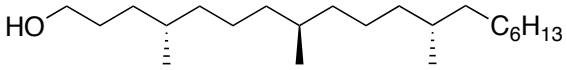
***O*''-(3,4-Difluorophenyl) *O*'-(4-fluorophenyl) *O*,*O*',*O*''-((4*S*,5*R*,8*S*,9*R*,12*R*,13*S*)-1-hydroxy-4,8,12-trimethyl-nonadecane-5,9,13-triyl) *O*-phenyl tricarbonothioate [(4*S*,5*R*,8*S*,9*R*,12*R*, 13*S*)-16d]:** (4*S*,5*R*,8*S*,9*R*,12*R*,13*S*)-**16d** was obtained in 29 mg, 71% recovery: $[\alpha]_D^{25} = -5.811$ (c = 0.22, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ = 7.347–7.412 (m, 2H), 7.287–7.297 (m, 1H), 7.086–7.185 (m, 7H), 6.945–7.001 (m, 1H), 6.818-6.861 (m, 1H), 5.289-5.352 (m, 3H), 3.654 (t, J =6.1, 2H), 1.955-2.080 (m, 3H), 1.195-1.942 (m, 22H), 1.007 (d, J = 6.7 Hz, 3H), 0.994 (d, J = 6.5 Hz, 3H), 0.986 (d, J = 6.7 Hz, 3H), 0.891 (t, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 195.24, 195.15, 194.65, 161.82, 159.38, 153.36, 153.32, 151.43, 151.29, 150.03, 149.91, 149.14, 149.12, 148.80, 148.68, 148.65, 148.60, 148.57, 147.57, 147.45, 129.47, 126.46, 123.61, 123.52, 122.05, 118.38, 118.34, 118.29, 117.43, 117.24, 116.30, 116.06, 112.49, 112.30, 90.06, 89.60, 89.36, 89.11, 89.07, 88.86, 62.90, 35.95, 35.89, 35.66, 31.71, 30.20, 30.10,

29.85, 29.28, 28.50, 28.37, 28.28, 28.11, 28.02, 27.86, 27.62, 27.58, 27.43, 27.01, 26.95, 25.24, 22.61, 15.11, 14.96, 14.89, 14.86, 14.09; FTIR ν_{max} 3377, 2959, 2929, 2859, 1504, 1290, 1198, 1005, 839, 796, 772, 738 cm^{-1}; HRMS calcd for $C_{43}H_{55}O_7S_3F_3Na$: 859.2960, found 859.2902.

Final 4,8,12-Trimethylnonadecan-1-ol Samples

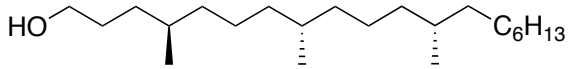


(4*S*,8*S*,12*S*)-4,8,12-Trimethylnonadecan-1-ol [(4*S*,8*S*,12*S*)-1]: This deoxygenation reaction was performed according to General Procedure 5 using triphenylthionocarbonate (4*R*,5*S*,8*R*,9*S*,12*R*,13*S*)-**16a** (0.020 g, 0.024 mmol), diMe-Imd-BH_3 (0.037 g, 0.12 mmol), and AIBN (0.020 g, 0.12 mmol). Alcohol (4*S*,8*S*,12*S*)-**1** was obtained in 0.006 g, 69% yield: $[\alpha]_D^{25}$ = −7.2 (*c* = 0.28, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 700 MHz, ppm) δ = 3.635 (t, *J* = 6.6 Hz, 2H), 1.664−1.504 (m, 2H), 1.443−1.003 (m, 30H), 0.882 (t, *J* = 7.0 Hz, 3H), 0.873 (d, *J* = 6.6 Hz, 3H), 0.840 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 63.51, 37.43, 37.37, 37.33, 37.16, 37.06, 33.00, 32.90, 32.80, 32.77, 32.65, 31.94, 30.36, 30.00, 29.42, 27.10, 25.33, 25.18, 24.47, 24.44, 22.71, 19.79, 19.77, 19.67, 14.15; FTIR ν_{max} 3333, 2959, 2924, 2854 cm^{-1}; HRMS calcd for $C_{22}H_{45}O$: 325.3470, found 325.3443.

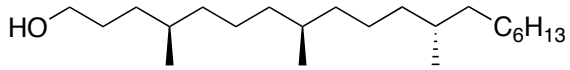


(4*S*,8*R*,12*S*)-4,8,12-Trimethylnonadecan-1-ol [(4*S*,8*R*,12*S*)-1]: This deoxygenation reaction was performed according to General Procedure 5 using triphenylthionocarbonate (4*R*,5*S*,8*S*,9*R*,12*R*,13*S*)-**16b** (0.020 g, 0.025 mmol), diMe-Imd-BH_3 (0.014 g, 0.125 mmol), and AIBN (0.020 g, 0.125 mmol). Alcohol (4*S*,8*R*,12*S*)-**1** was obtained in 0.0052 g, 64% yield: $[\alpha]_D^{25}$ = 1.5 (*c* = 0.38, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 700 MHz, ppm) δ = 3.635 (t, *J* = 6.6 Hz, 2H), 1.664−1.504 (m, 2H), 1.443−1.003 (m, 30H), 0.883 (t, *J* = 7.0 Hz, 3H), 0.874 (d, *J* = 6.6 Hz, 3H), 0.843 (d, *J* = 6.6 Hz, 3H), 0.841 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ =

63.50, 37.42, 37.37, 37.28, 37.15, 32.99, 32.91, 32.76, 32.63, 32.44, 31.94, 30.36, 30.00, 29.71, 29.41, 27.11, 25.32, 25.17, 24.47, 24.43, 22.71, 19.70, 19.66, 19.60, 14.14; FTIR ν_{max} 3349, 2959, 2925, 2855 cm^{-1}; HRMS calcd for $C_{22}H_{45}O$: 325.3470, found 325.3442.



(4*R*,8*S*,12*S*)-4,8,12-Trimethylnonadecan-1-ol [(4*R*,8*S*,12*S*)-1]: This deoxygenation reaction was performed according to General Procedure 5 using triphenylthionocarbonate (4*S*,5*R*,8*R*,9*S*,12*R*,13*S*)-**16c** (0.018 g, 0.022 mmol), diMe-Imd-BH_3 (0.012 g, 0.110 mmol), and AIBN (0.018 g, 0.110 mmol). Alcohol (4*R*,8*S*,12*S*)-**1** was obtained in 0.0047 g, 65.5% yield: $[\alpha]_D^{25}$ = 2.0 (c = 0.29, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 700 MHz, ppm) δ = 3.635 (t, J = 6.6 Hz, 2H), 1.664−1.504 (m, 2H), 1.443−1.003 (m, 30H), 0.883 (t, J = 7.0 Hz, 3H), 0.873 (d, J = 6.6 Hz, 3H), 0.842 (d, J = 6.6 Hz, 3H), 0.841 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 63.51, 37.49, 37.43, 37.38, 37.33, 37.16, 37.06, 32.99, 32.90, 32.78, 32.63, 31.94, 30.37, 30.36, 30.00, 29.71, 29.42, 27.10, 25.18, 24.48, 24.43, 22.71, 19.77, 19.73, 19.61, 14.15; FTIR ν_{max} 3333, 2958, 2925, 2854 cm^{-1}; HRMS calcd for $C_{22}H_{45}O$: 325.3470, found 325.3444.



(4*R*,8*R*,12*S*)-4,8,12-Trimethylnonadecan-1-ol [(4*R*,8*R*, 12*S*)-1]: This deoxygenation reaction was performed according to General Procedure 5 using triphenylthionocarbonate (4*S*,5*R*,8*S*,9*R*,12*R*,13*S*)-**16d** (0.017 g, 0.020 mmol), dime-Imd-BH_3 (0.011 g, 0.100 mmol), and AIBN (0.017 g, 0.100 mmol). Alcohol (4*R*,8*R*,12*S*)-**1** was obtained in 0.0042 g, 63.3% yield: $[\alpha]_D^{25}$ = −2.4 (c = 0.2, $CHCl_3$) ; ^{1}H NMR ($CDCl_3$, 700 MHz, ppm) δ = 3.635 (t, J = 6.6 Hz, 2H), 1.664−1.504 (m, 2H), 1.443−1.003 (m, 30H), 0.882 (t, J = 7.0 Hz, 3H), 0.874 (d, J = 6.6 Hz, 3H), 0.841 (d, J = 6.6 Hz, 3H), 0.840 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ = 63.50, 37.47, 37.43, 37.38, 37.33, 37.16, 33.00, 32.91, 32.78, 32.76, 32.66, 31.93, 30.37, 30.00, 29.41, 27.11, 25.18, 24.46, 24.45, 23.46, 22.70, 19.73, 19.70, 19.67, 14.13; FTIR ν_{max} 3334,

2958, 2925, 2855 cm^{-1}; HRMS calcd for $C_{22}H_{45}O$: 325.3470, found 325.3449.

Figure S1. Predicted appearance of the branched-methyl region of the ^{13}C NMR spectra of all 2,6,10,14-tetramethylhenicosan-1-ol **17** stereoisomers.

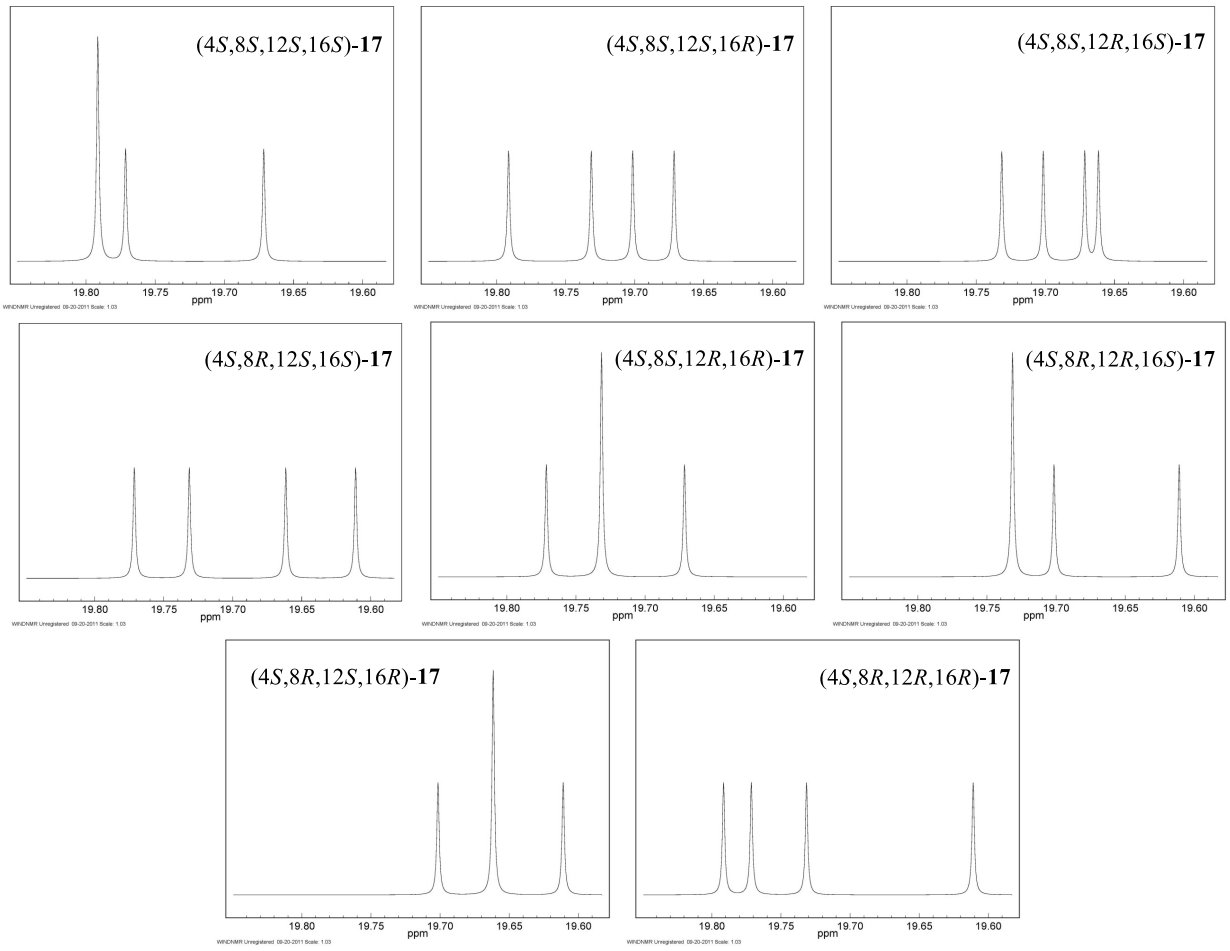


Figure S2. Predicted appearance of the methyl region of the ^{1}H NMR spectra of all 2,6,10,14-tetramethylhenicosan-1-ol **17** stereoisomers.

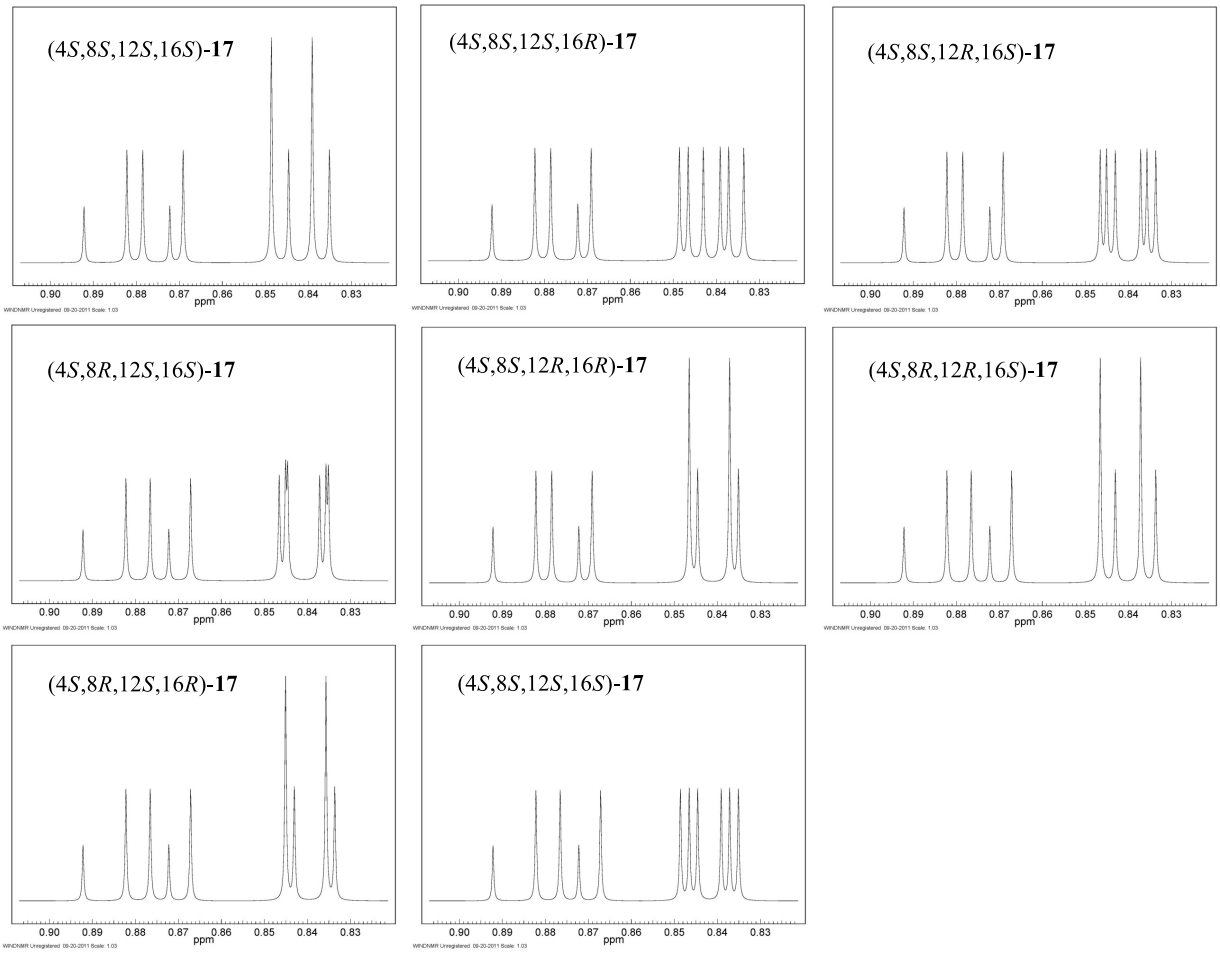
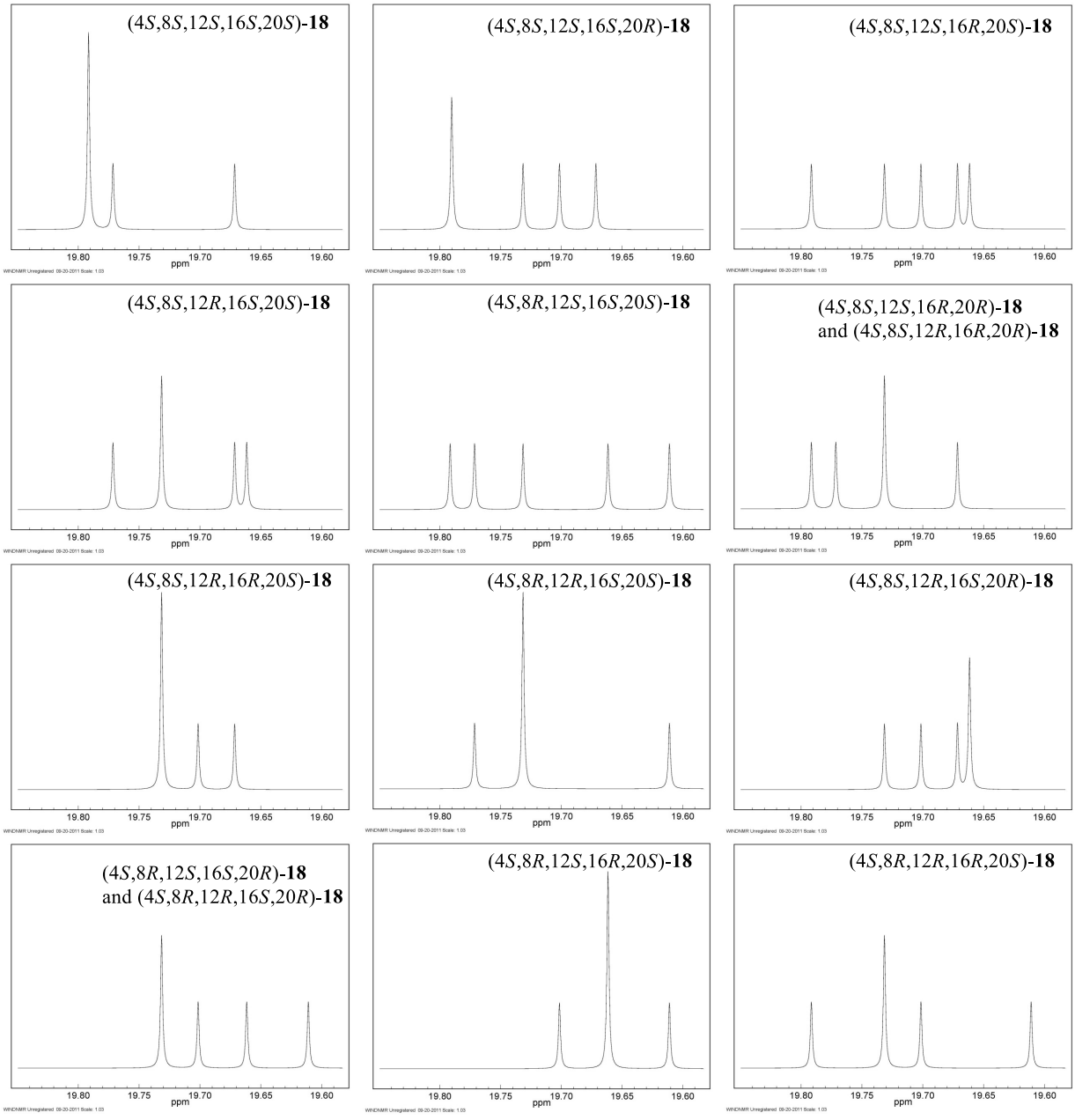
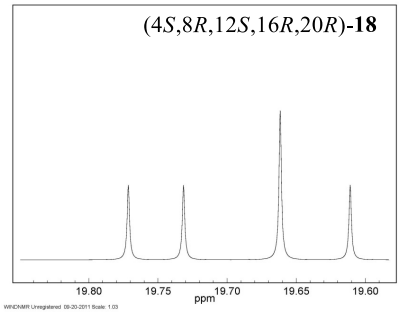


Figure S3. Predicted appearance of the branched-methyl region of the ^{13}C NMR spectra of all 4,8,12,16,20-pentamethylheptacosan-1-ol **18** stereoisomers.




(4S,8R,12S,16R,20R)-18
19.80
19.75
19.70
19.65
19.60
ppm
WINDNMR Unregistered 09-20-2011 Scale: 1.03

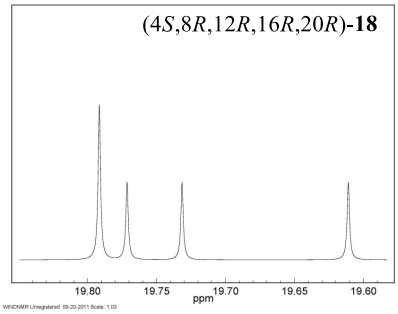
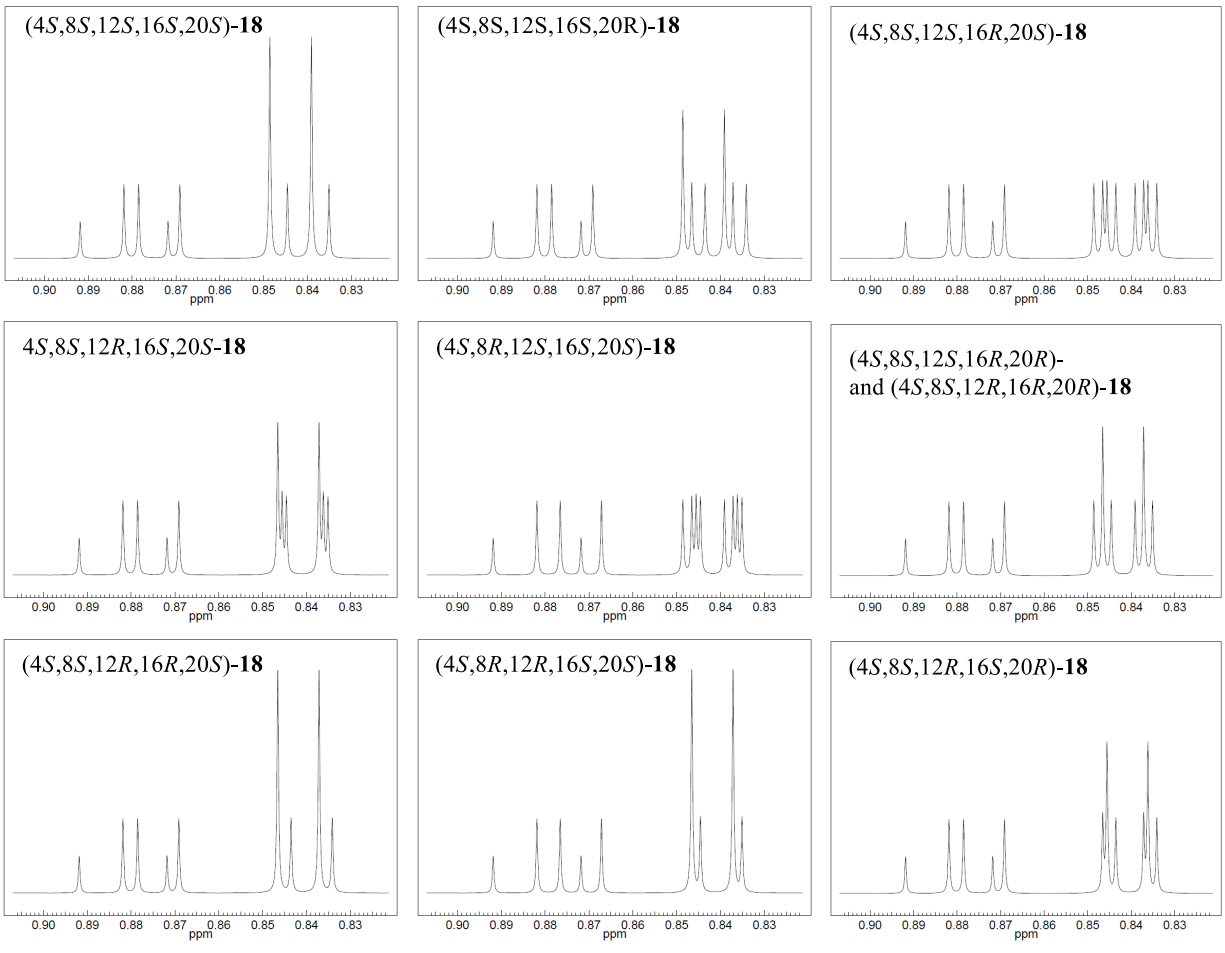
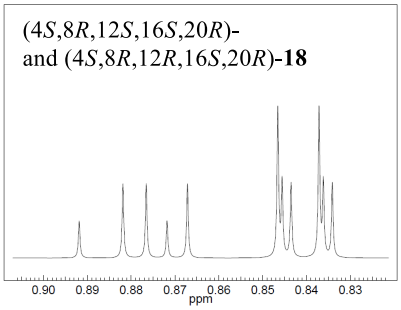
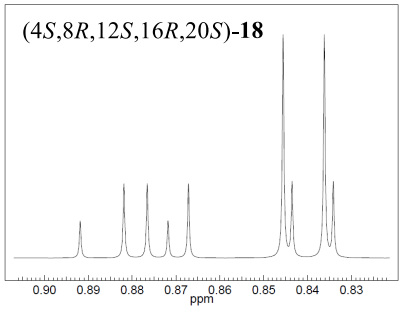
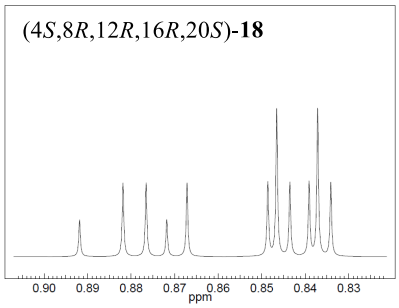

(4S,8R,12R,16R,20R)-18
19.80
19.75
19.70
19.65
19.60
ppm
WINDNMR Unregistered 09-20-2011 Scale: 1.03

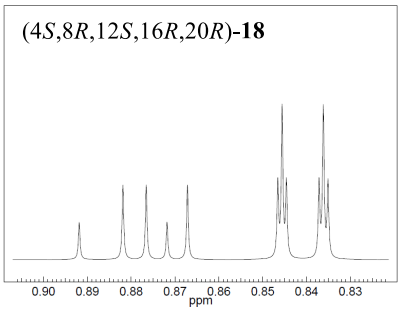
Figure S4. Predicted appearance of the methyl region of the ^{1}H NMR spectra of all 4,8,12,16,20-pentamethylheptacosan-1-ol **18** stereoisomers.

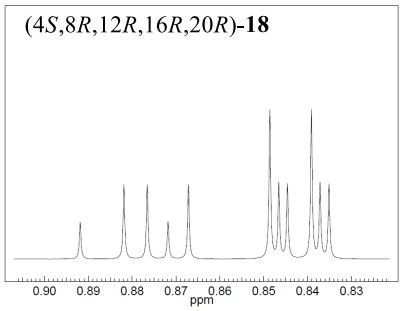



(4S,8R,12S,16S,20R)-
and (4S,8R,12R,16S,20R)-18
0.90 0.89 0.88 0.87 0.86 0.85 0.84 0.83
ppm


(4S,8R,12S,16R,20S)-18
0.90 0.89 0.88 0.87 0.86 0.85 0.84 0.83
ppm


(4S,8R,12R,16R,20S)-18
0.90 0.89 0.88 0.87 0.86 0.85 0.84 0.83
ppm


(4S,8R,12S,16R,20R)-18
0.90 0.89 0.88 0.87 0.86 0.85 0.84 0.83
ppm


(4S,8R,12R,16R,20R)-18
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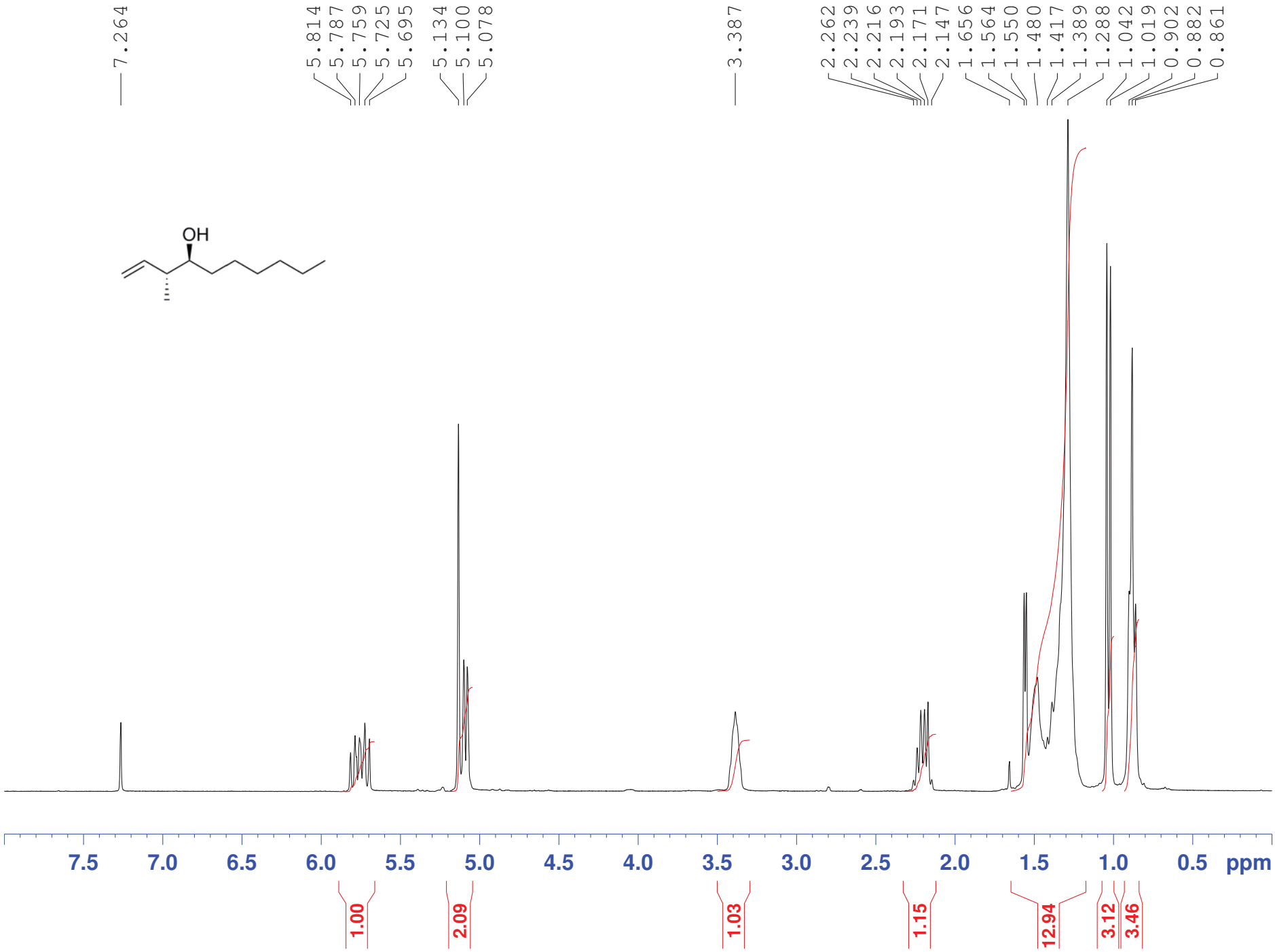
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2.216
2.193
2.171
2.147
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1.564
1.550
1.480
1.417
1.389
1.288
1.042
1.019
0.902
0.882
0.861
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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0.5
ppm
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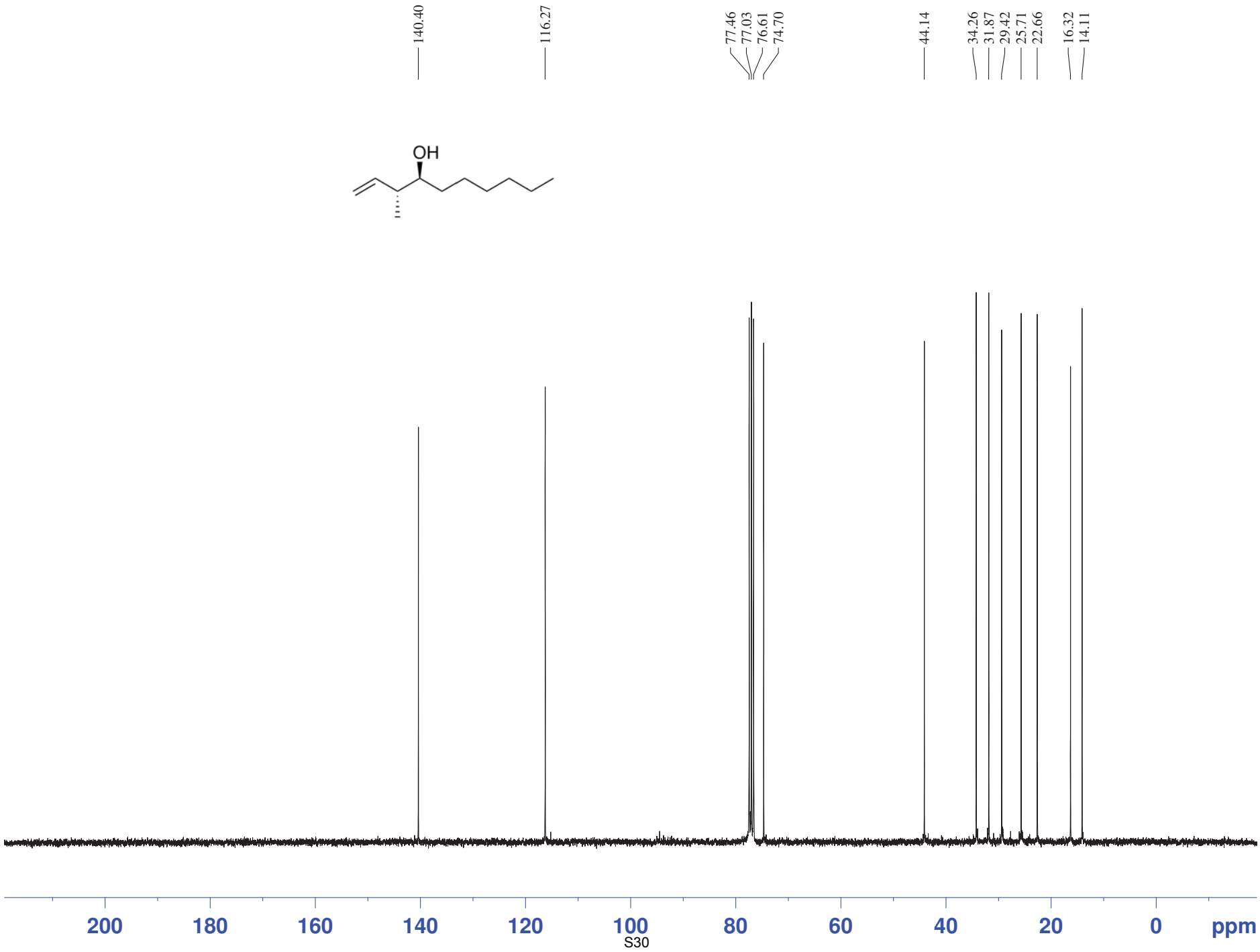
3.46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34.26
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29.42
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16.32
14.11
OH
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180
160
140
120
100
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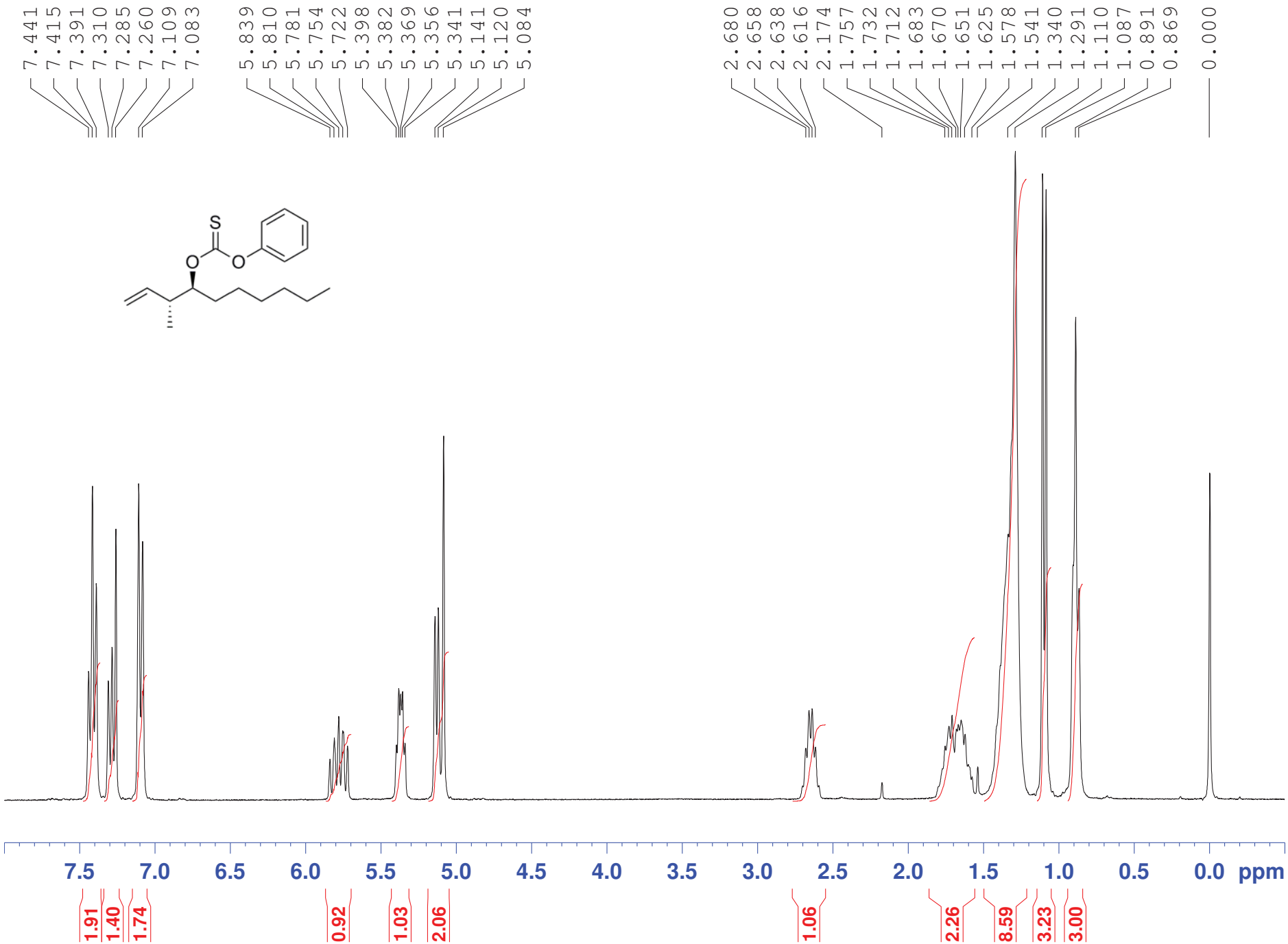
60
40
20
0
ppm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5.398
5.382
5.369
5.356
5.341
5.141
5.120
5.084
2.680
2.658
2.638
2.616
2.174
1.757
1.732
1.712
1.683
1.670
1.651
1.625
1.578
1.541
1.340
1.291
1.110
1.087
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0.869
0.000
S
O
O
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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1.74
0.92
1.03
2.06
1.06
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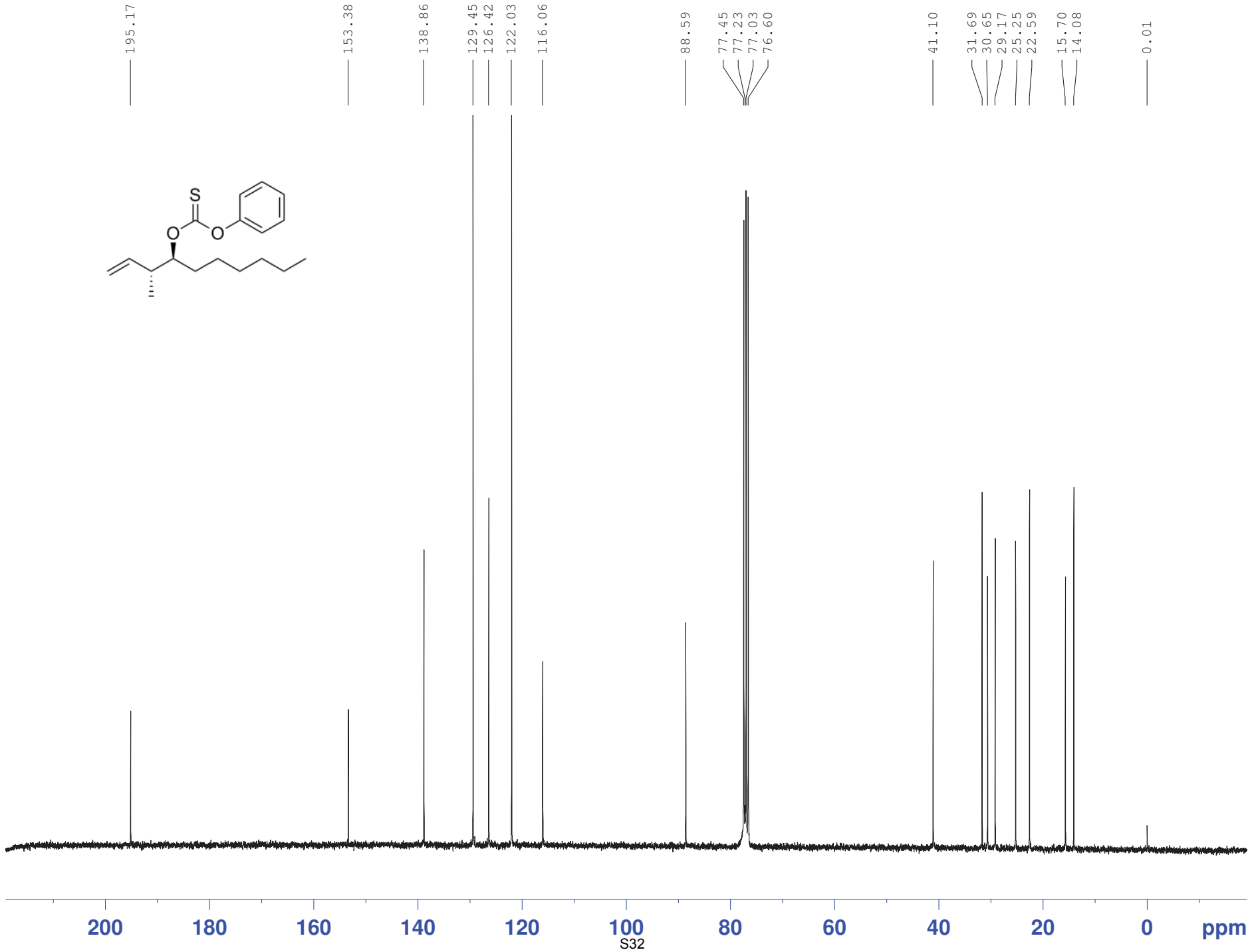
3.00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41.10
31.69
30.65
29.17
25.25
22.59
15.70
14.08
0.01
S
O
O
200
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120
100
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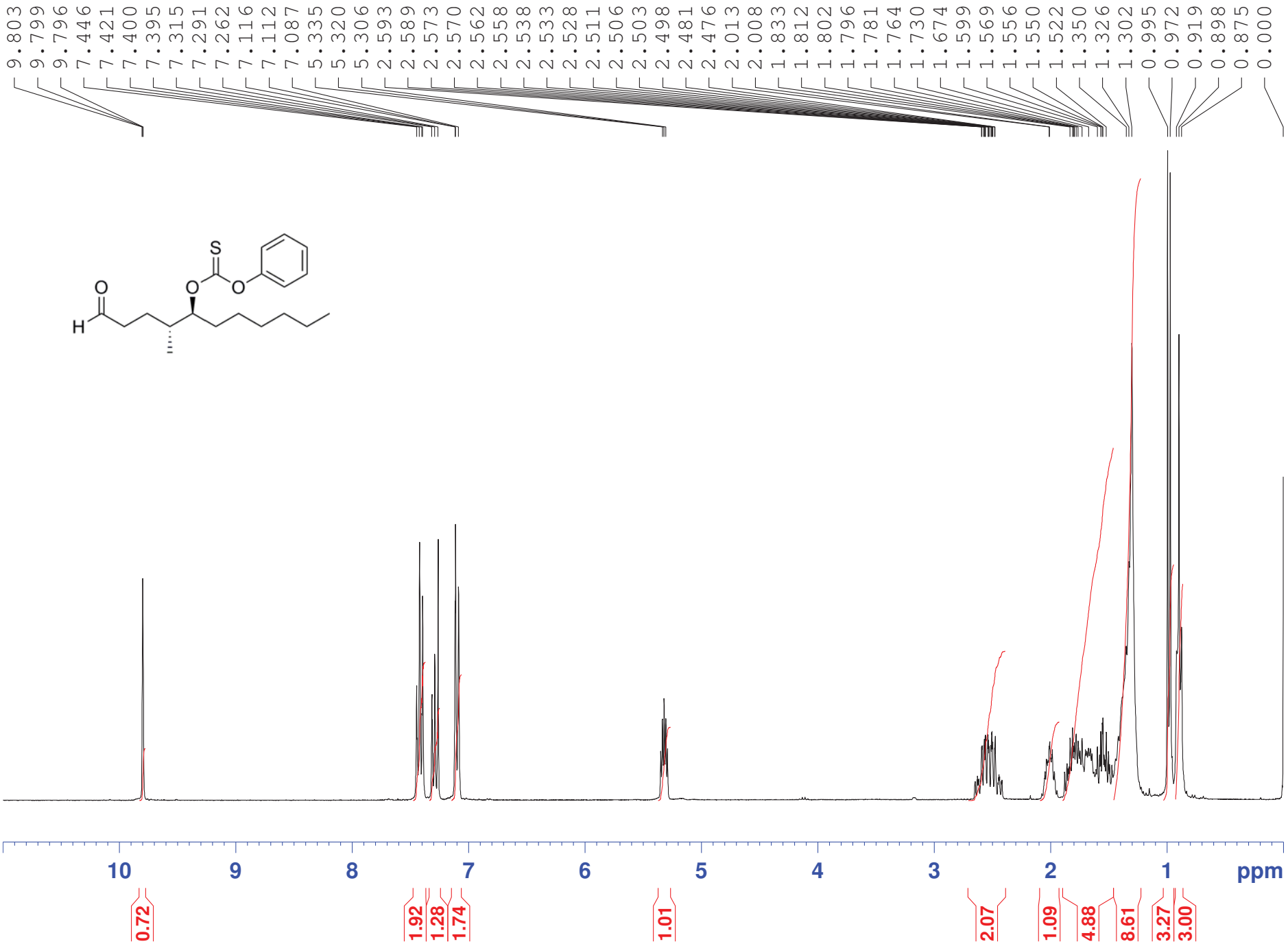
40
20
0
ppm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7.262
7.116
7.112
7.087
5.335
5.320
5.306
2.593
2.589
2.573
2.570
2.562
2.558
2.538
2.533
2.528
2.511
2.506
2.503
2.498
2.481
2.476
2.013
2.008
1.833
1.812
1.802
1.796
1.781
1.764
1.730
1.674
1.599
1.569
1.556
1.550
1.522
1.350
1.326
1.302
0.995
0.972
0.919
0.898
0.875
0.000
S
O
O
O
H
10
9
8
7
6
5
4
3
2
1
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1.28
1.74
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2.07
1.09
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8.61
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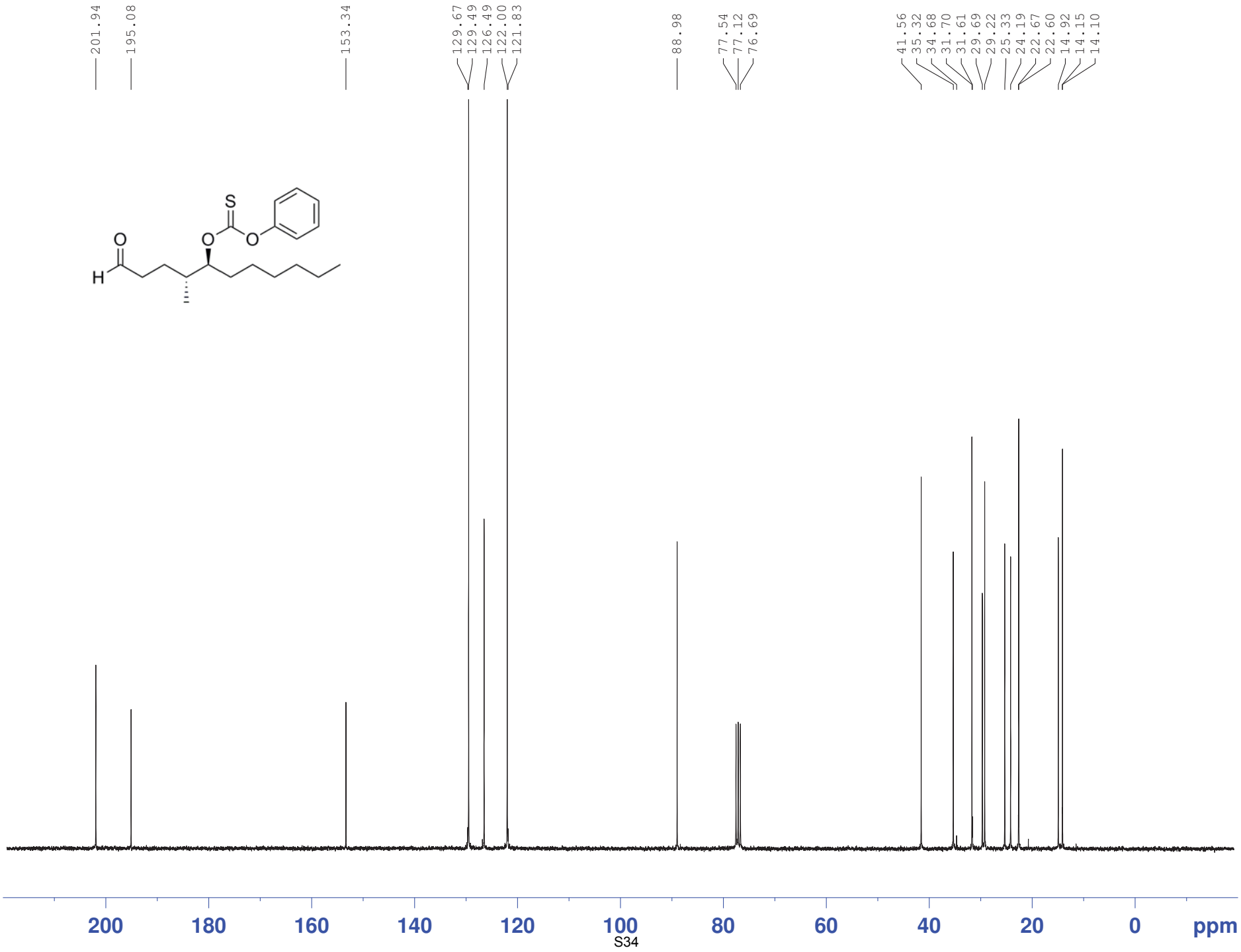
3.00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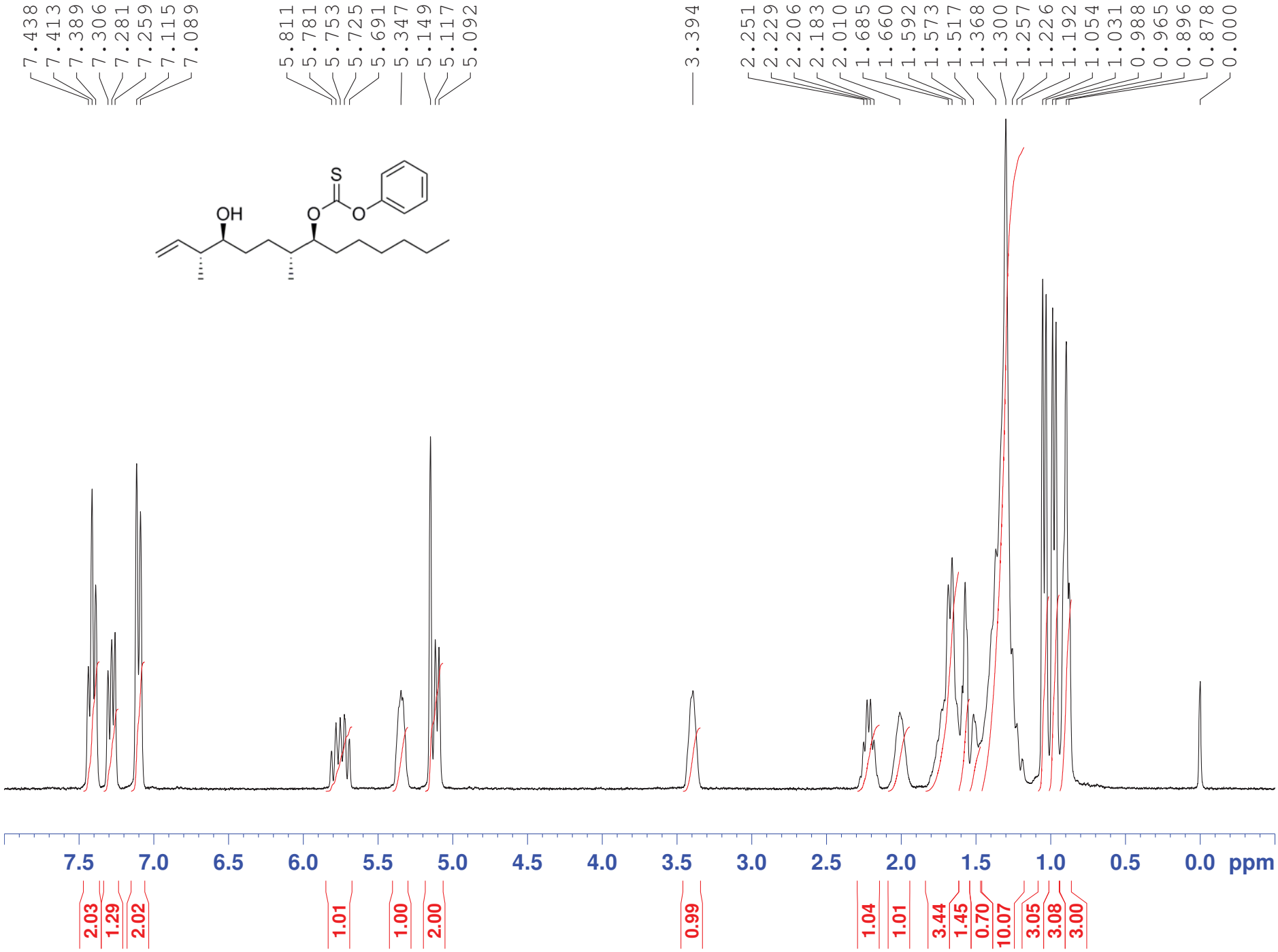
121.83
88.98
77.54
77.12
76.69
41.56
35.32
34.68
31.70
31.61
29.69
29.22
25.33
24.19
22.67
22.60
14.92
14.15
14.10
S
O
O
O
H
200
180
160
140
120
100
80
60
40
20
0
ppm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5.781
5.753
5.725
5.691
5.347
5.149
5.117
5.092
3.394
2.251
2.229
2.206
2.183
2.010
1.685
1.660
1.592
1.573
1.517
1.368
1.300
1.257
1.226
1.192
1.054
1.031
0.988
0.965
0.896
0.878
0.000
OH
O
S
O
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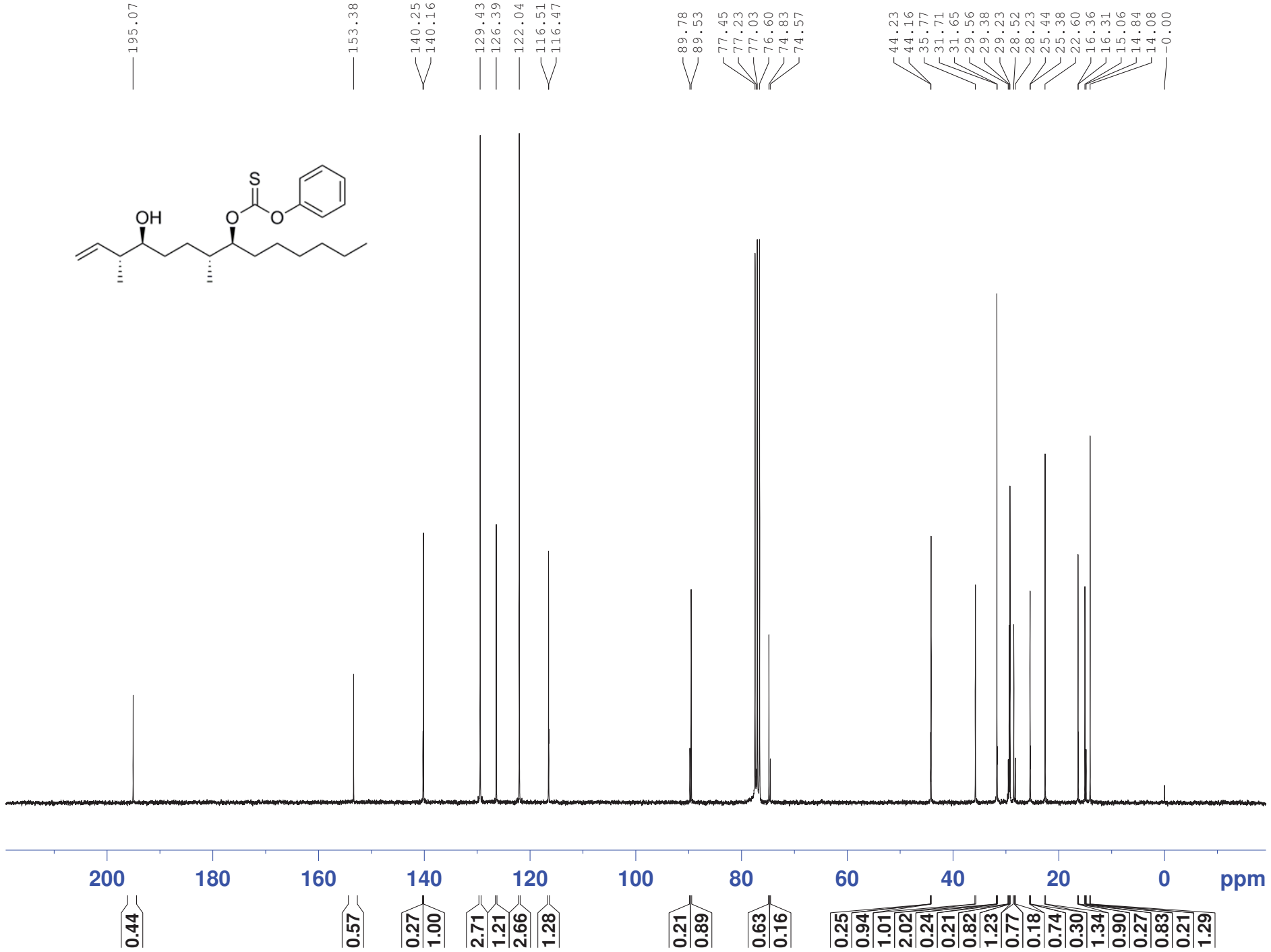
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.03
1.29
2.02
1.01
1.00
2.00
0.99
1.04
1.01
3.44
1.45
0.70
10.07
3.05
3.08
3.00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77.23
77.03
76.60
74.83
74.57
44.23
44.16
35.77
31.71
31.65
29.56
29.38
29.23
28.52
28.23
25.44
25.38
22.60
16.36
16.31
15.06
14.84
14.08
-0.00
OH
O
S
O
200
180
160
140
120
100
80
60
40
20
0
ppm
0.44
0.57
0.27
1.00
2.71
1.21
2.66
1.28
0.21
0.89
0.63
0.16
0.25
0.94
1.01
2.02
0.24
0.21
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0.77
0.18
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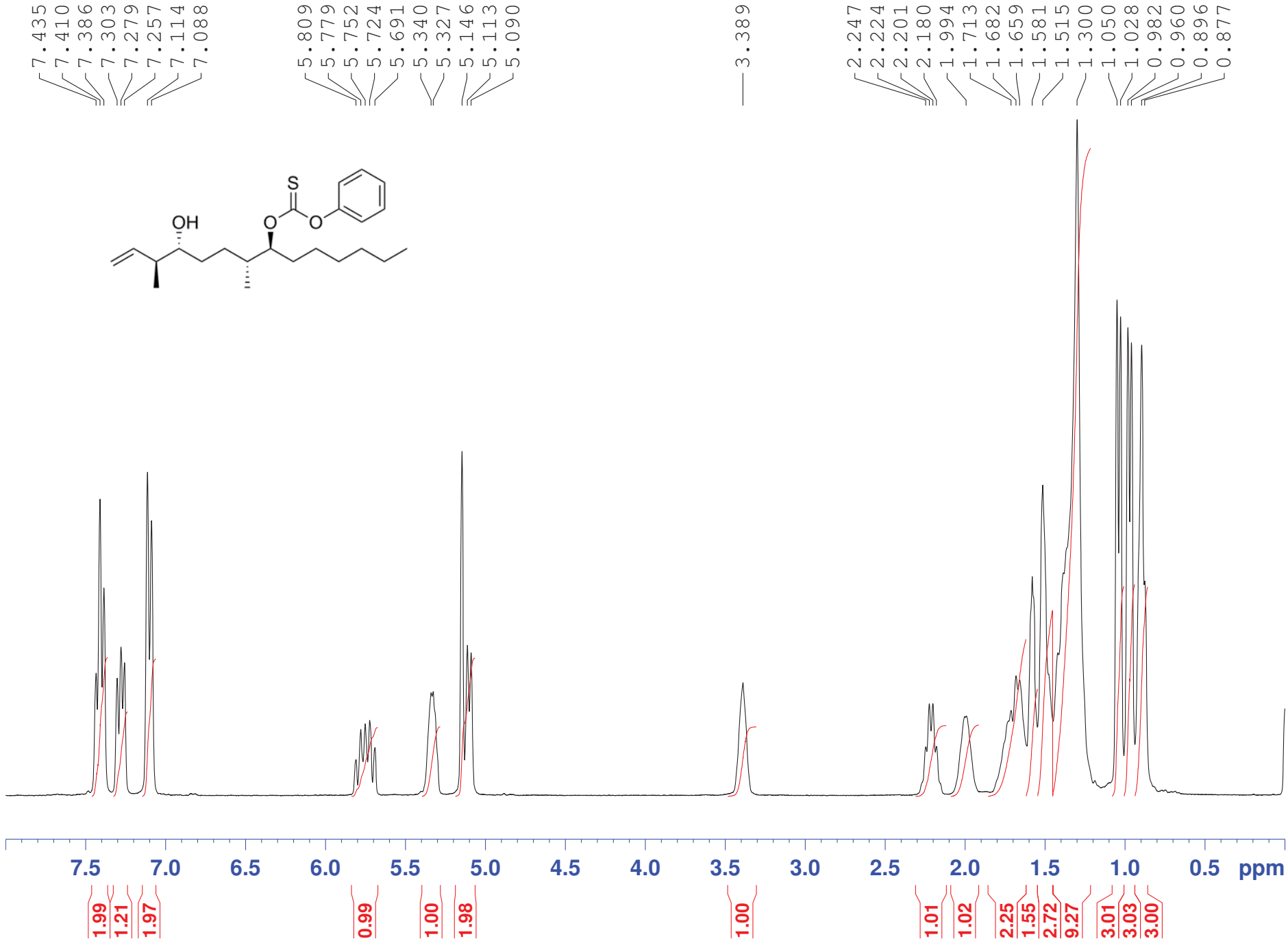
0.90
0.27
0.83
0.21
1.29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5.752
5.724
5.691
5.340
5.327
5.146
5.113
5.090
3.389
2.247
2.224
2.201
2.180
1.994
1.713
1.682
1.659
1.581
1.515
1.300
1.050
1.028
0.982
0.960
0.896
0.877
OH
O
S
O
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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0.99
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2.72
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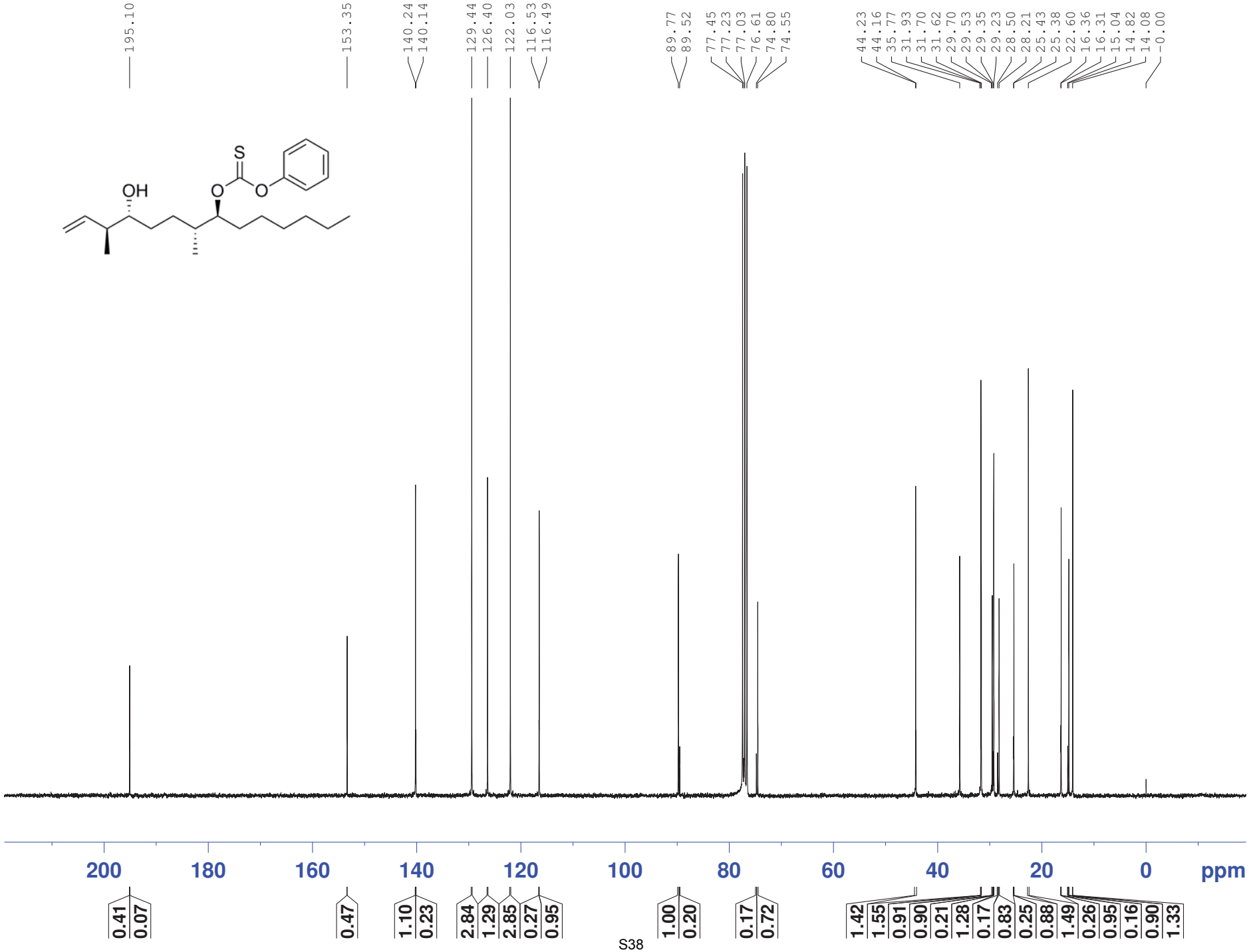
3.00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89.52
77.45
77.23
77.03
76.61
74.80
74.55
44.23
44.16
35.77
31.93
31.70
31.62
29.70
29.53
29.35
29.23
28.50
28.21
25.43
25.38
22.60
16.36
16.31
15.04
14.82
14.08
-0.00
OH
O
S
O
200
180
160
140
120
100
80
60
40
20
0
ppm
0.41
0.07
0.47
1.10
0.23
2.84
1.29
2.85
0.27
0.95
1.00
0.20
0.17
0.72
1.42
1.55
0.91
0.90
0.21
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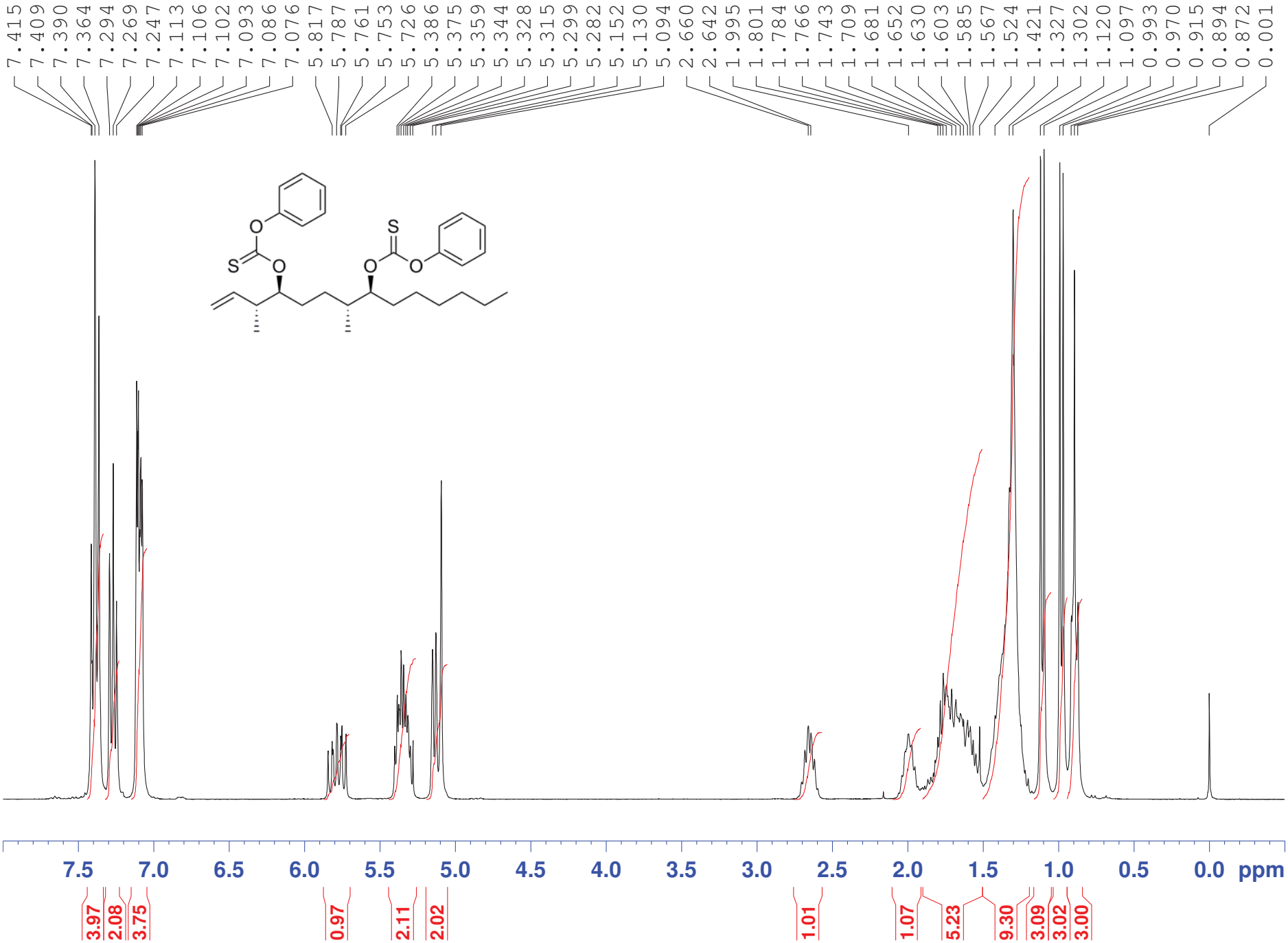
0.17
0.83
0.25
0.88
1.49
0.26
0.95
0.16
0.90
1.33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5.761
5.753
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5.375
5.359
5.344
5.328
5.315
5.299
5.282
5.152
5.130
5.094
2.660
2.642
1.995
1.801
1.784
1.766
1.743
1.709
1.681
1.652
1.630
1.603
1.585
1.567
1.524
1.421
1.327
1.302
1.120
1.097
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0.970
0.915
0.894
0.872
0.001
O
S
O
O
S
O
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6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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1.01
1.07
5.23
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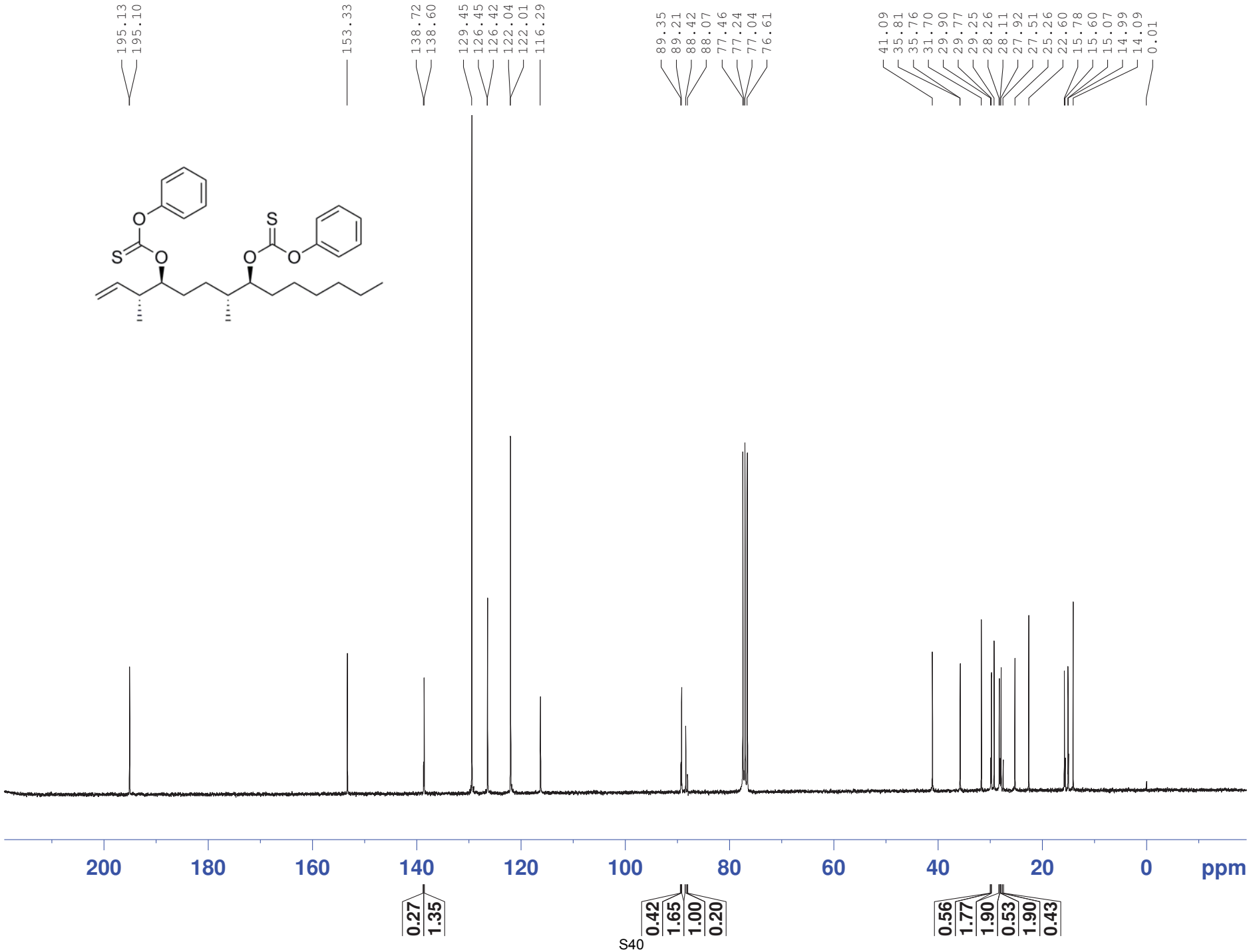
3.02
3.00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122.01
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89.35
89.21
88.42
88.07
77.46
77.24
77.04
76.61
41.09
35.81
35.76
31.70
29.90
29.77
29.25
28.26
28.11
27.92
27.51
25.26
22.60
15.78
15.60
15.07
14.99
14.09
0.01
O
S
O
O
S
O
200
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160
140
120
100
80
60
40
20
0
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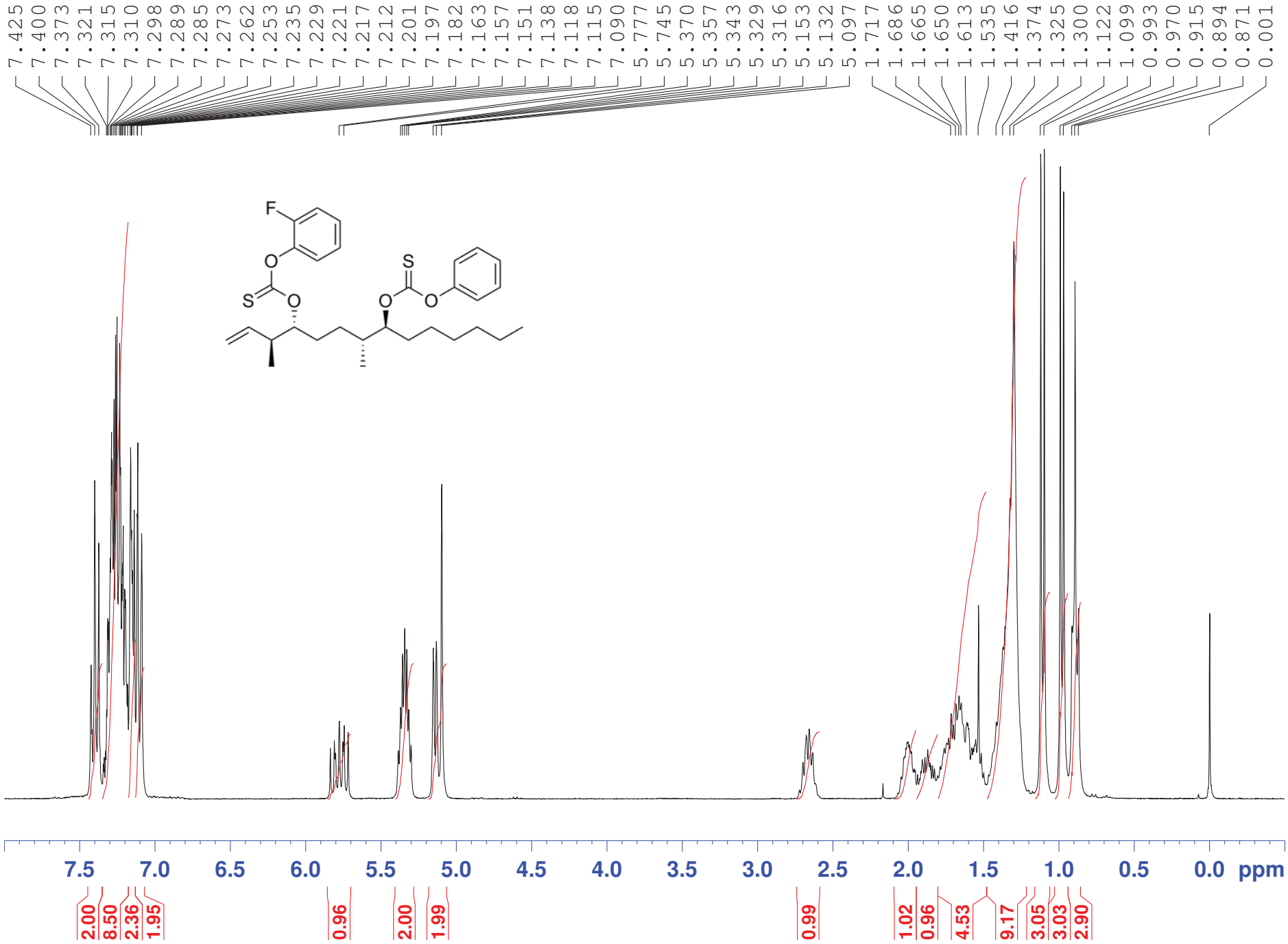
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7.229
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7.217
7.212
7.201
7.197
7.182
7.163
7.157
7.151
7.138
7.118
7.115
7.090
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5.745
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5.357
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5.329
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1.374
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1.300
1.122
1.099
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0.970
0.915
0.894
0.871
0.001
F
O
S
O
S
O
O
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6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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1.02
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4.53
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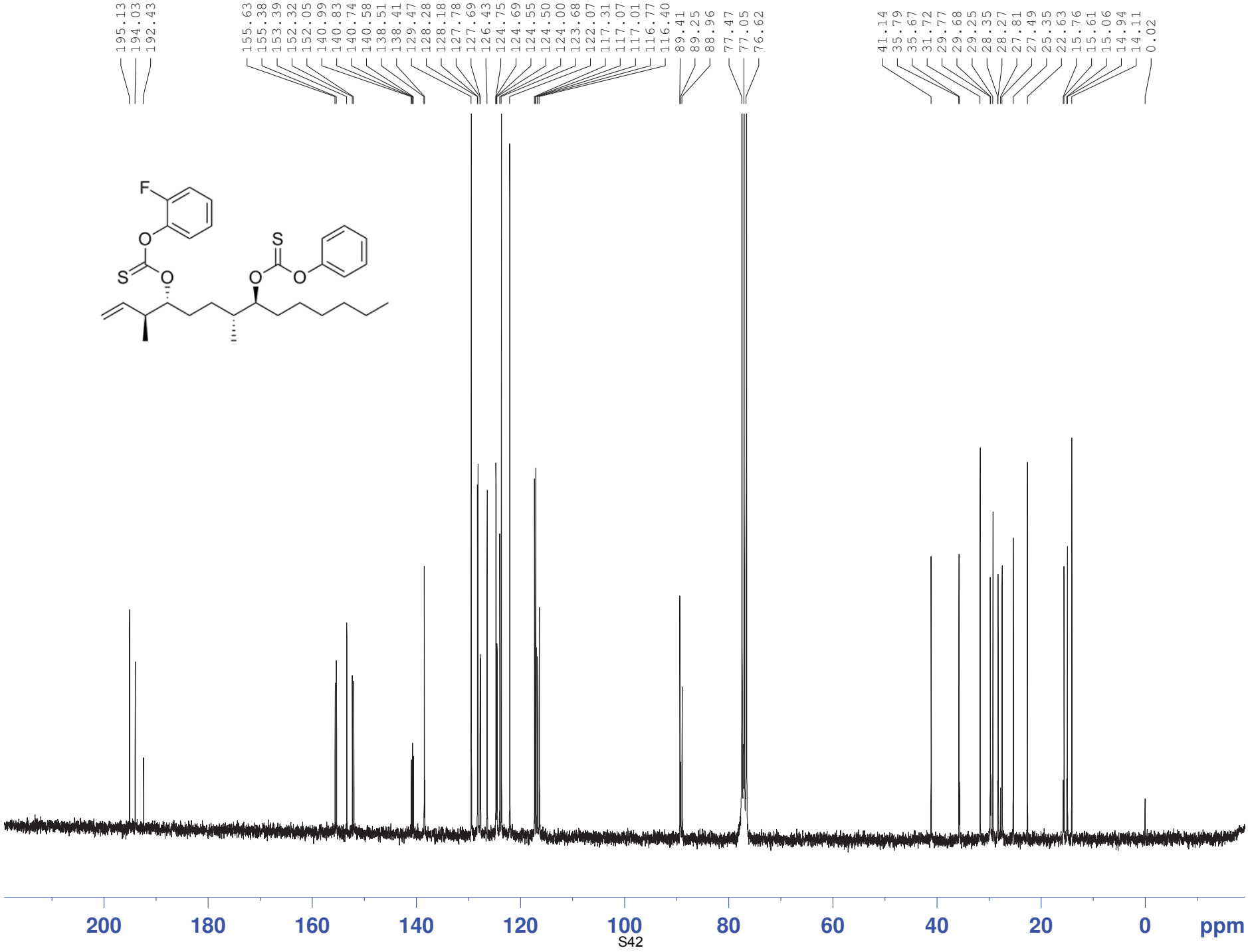
3.03
2.90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128.18
127.78
127.69
126.43
124.75
124.69
124.55
124.50
124.00
123.68
122.07
117.31
117.07
117.01
116.77
116.40
89.41
89.25
88.96
77.47
77.05
76.62
41.14
35.79
35.67
31.72
29.77
29.68
29.25
28.35
28.27
27.81
27.49
25.35
22.63
15.76
15.61
15.06
14.94
14.11
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O
S
O
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120
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40
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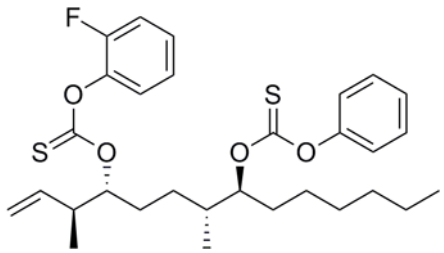
0
ppm


F
O
S
O
O
S
O

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-128.11
-128.12
-128.13
-128.15
-128.16
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-110
-115
-120
-125
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-135
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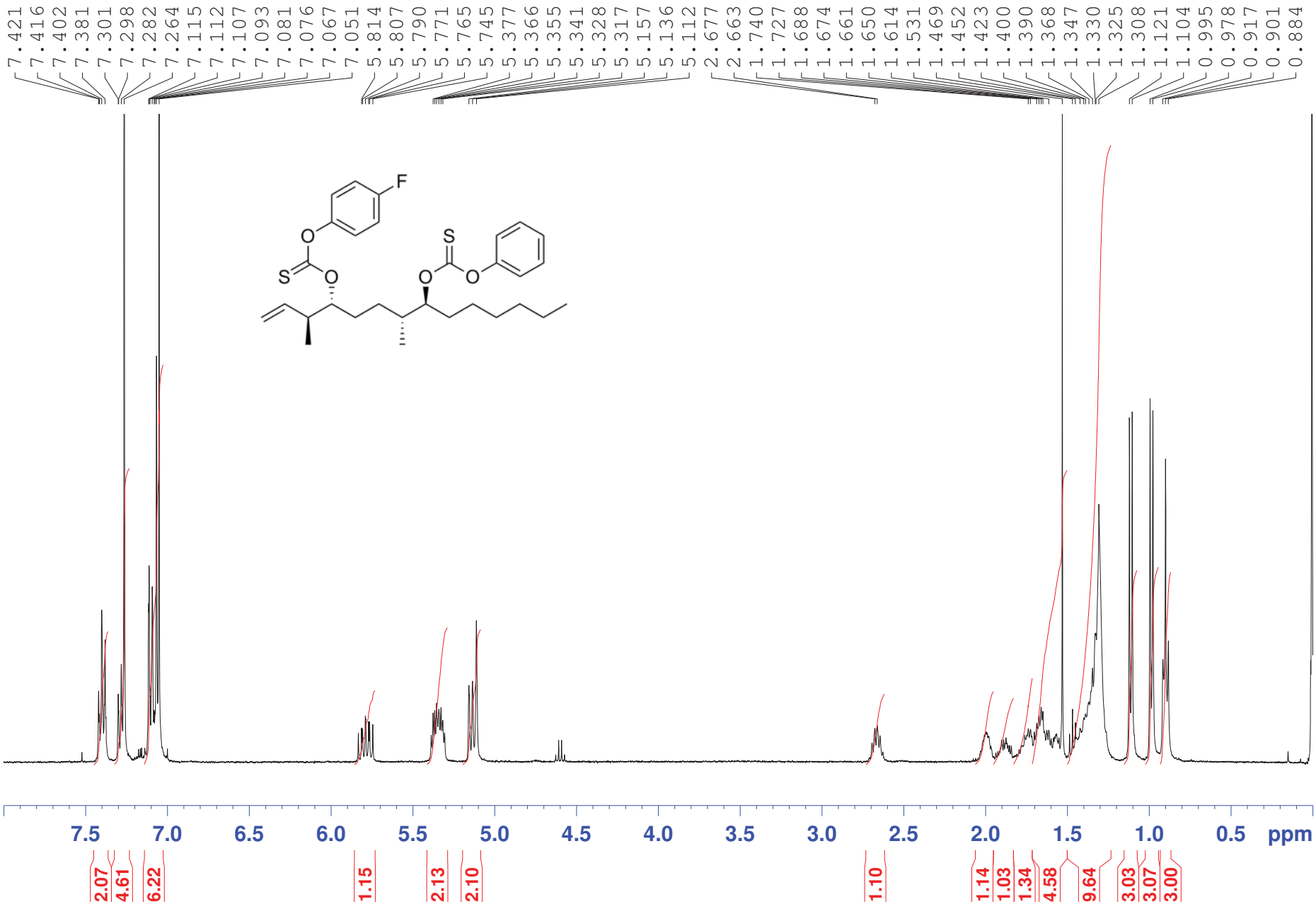
-150
-155
ppm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5.377
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1.661
1.650
1.614
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0.884
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O
S
O
S
O
O
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4.5
4.0
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2.0
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1.0
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6.22
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4.58
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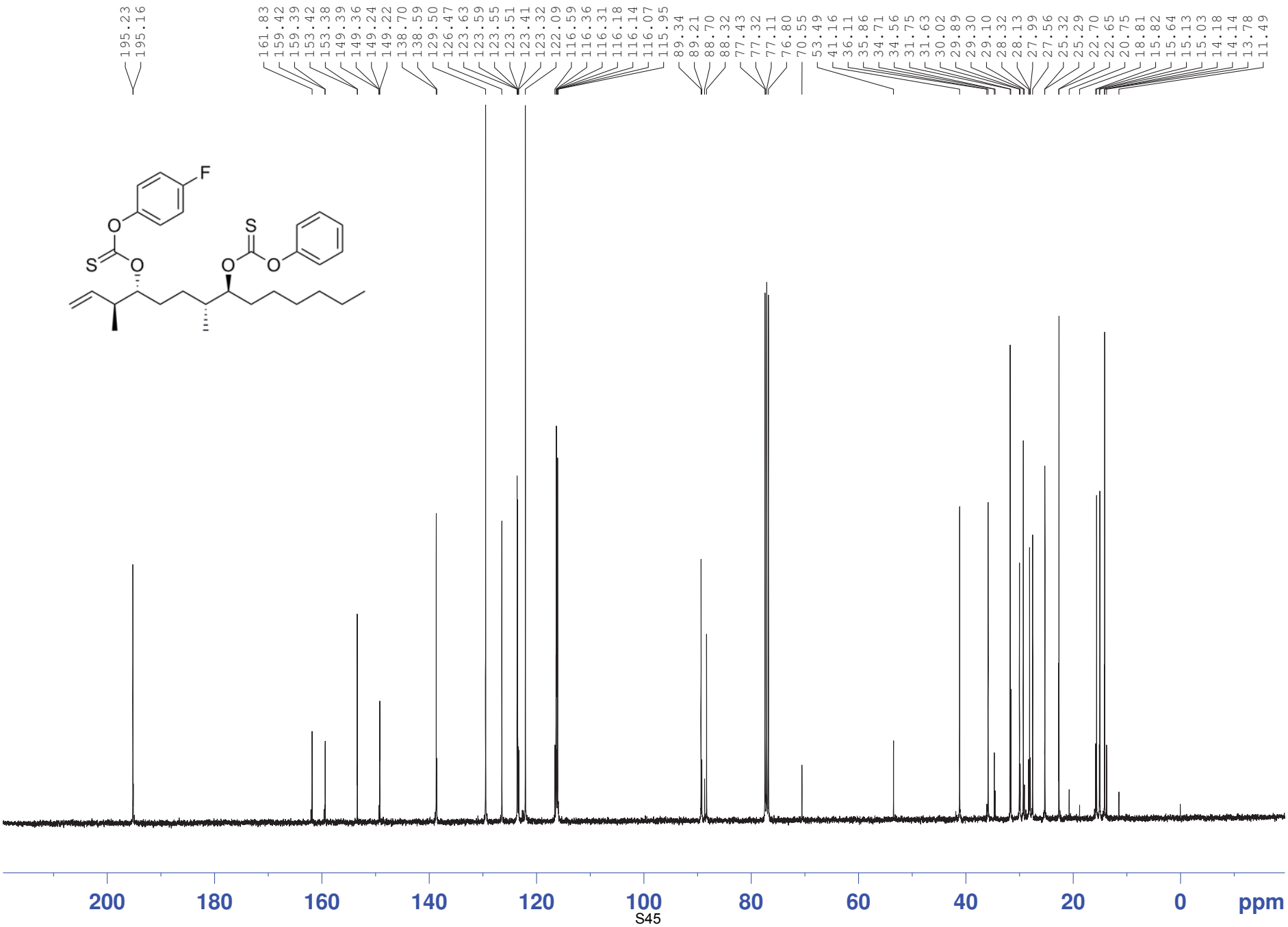
3.00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126.47
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123.59
123.55
123.51
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123.32
122.09
116.59
116.36
116.31
116.18
116.14
116.07
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88.32
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77.32
77.11
76.80
70.55
53.49
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25.29
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22.65
20.75
18.81
15.82
15.64
15.13
15.03
14.18
14.14
13.78
11.49
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O
S
O
O
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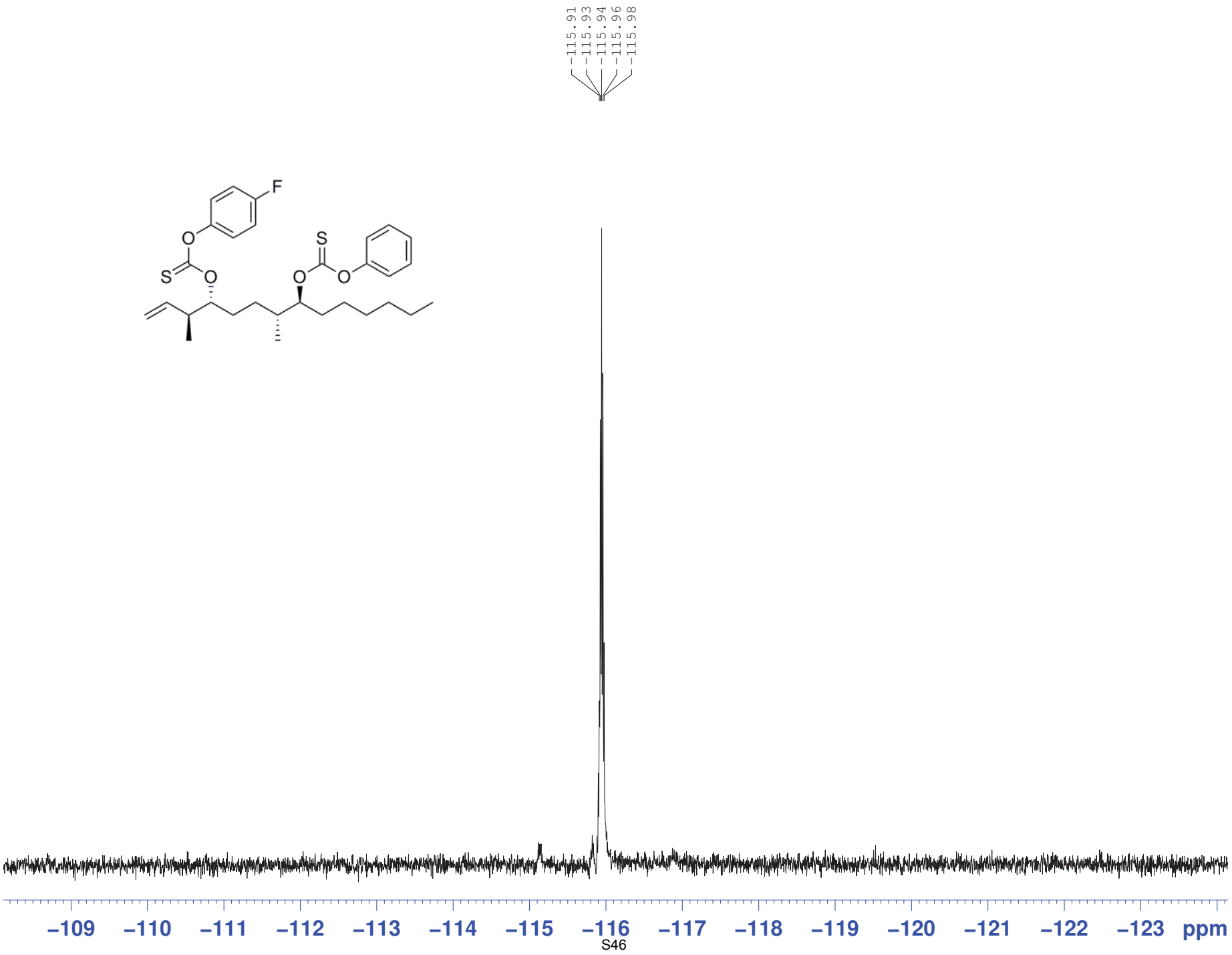
120
100
80
60
40
20
0
ppm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-115.94
-115.96
-115.98
F
O
S
O
O
S
O
–109
–110
–111
–112
–113
–114
–115
–116
–117
–118
–119
–120
–121
–122
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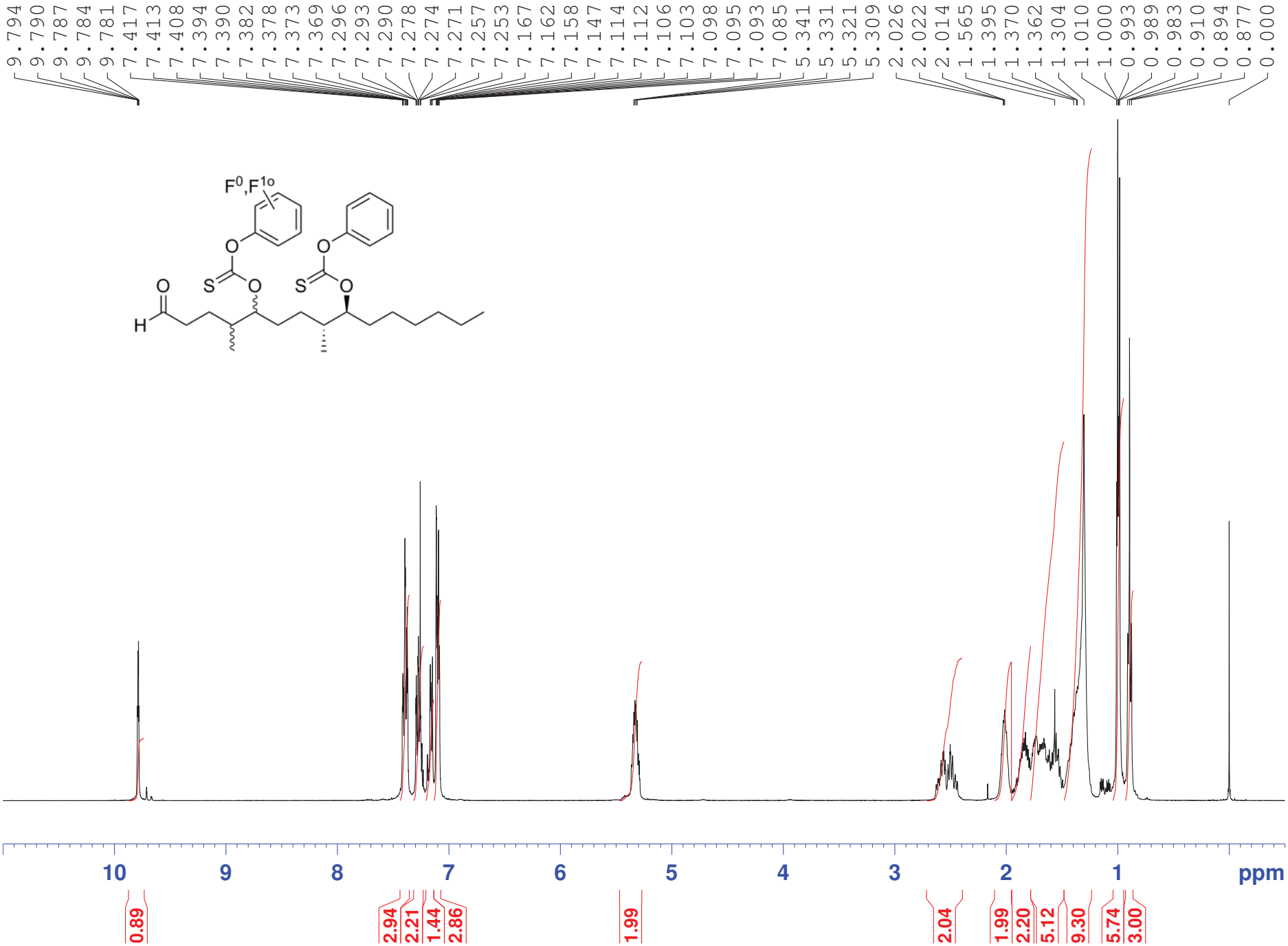
ppm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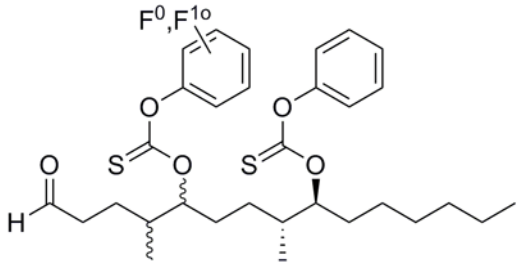

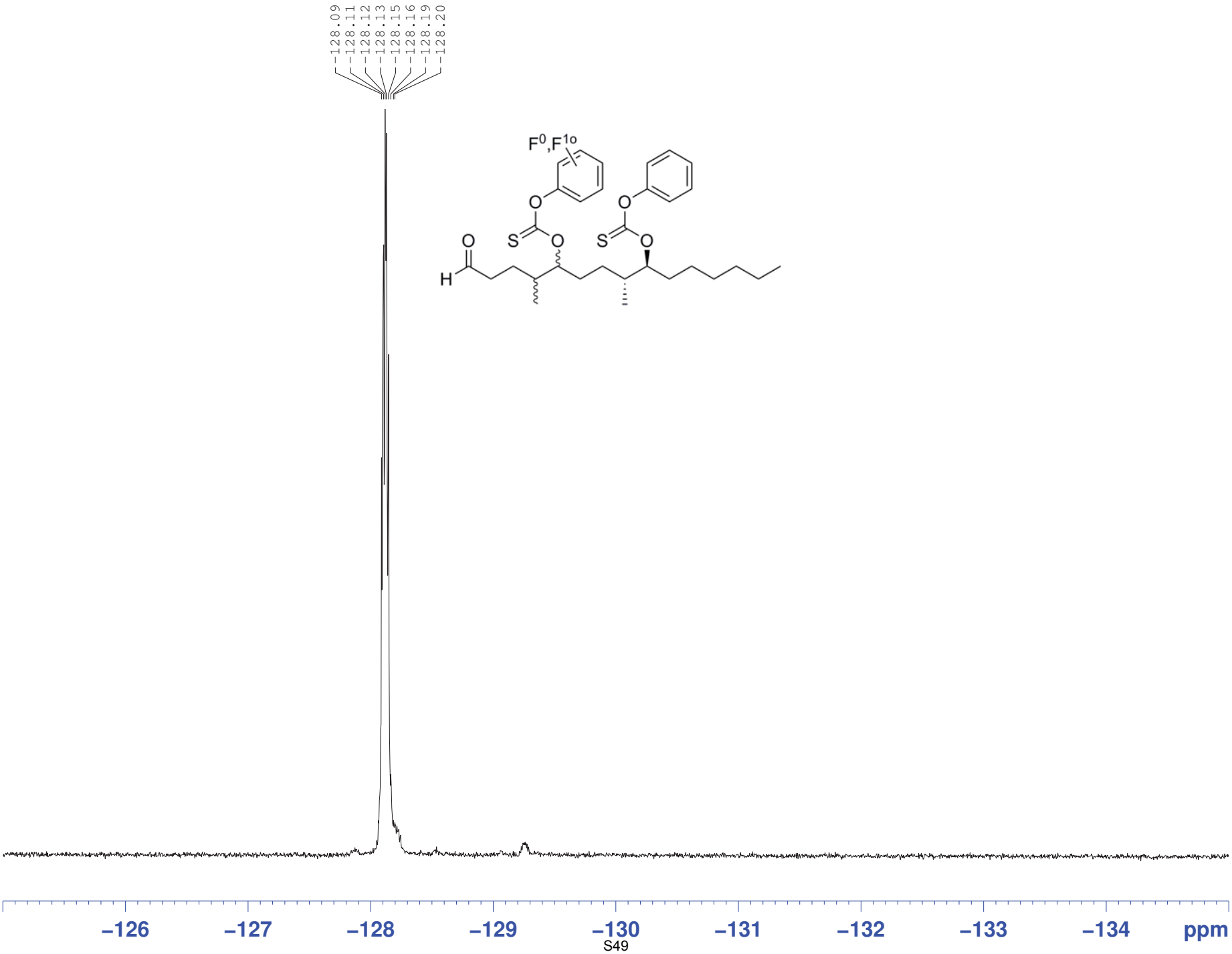
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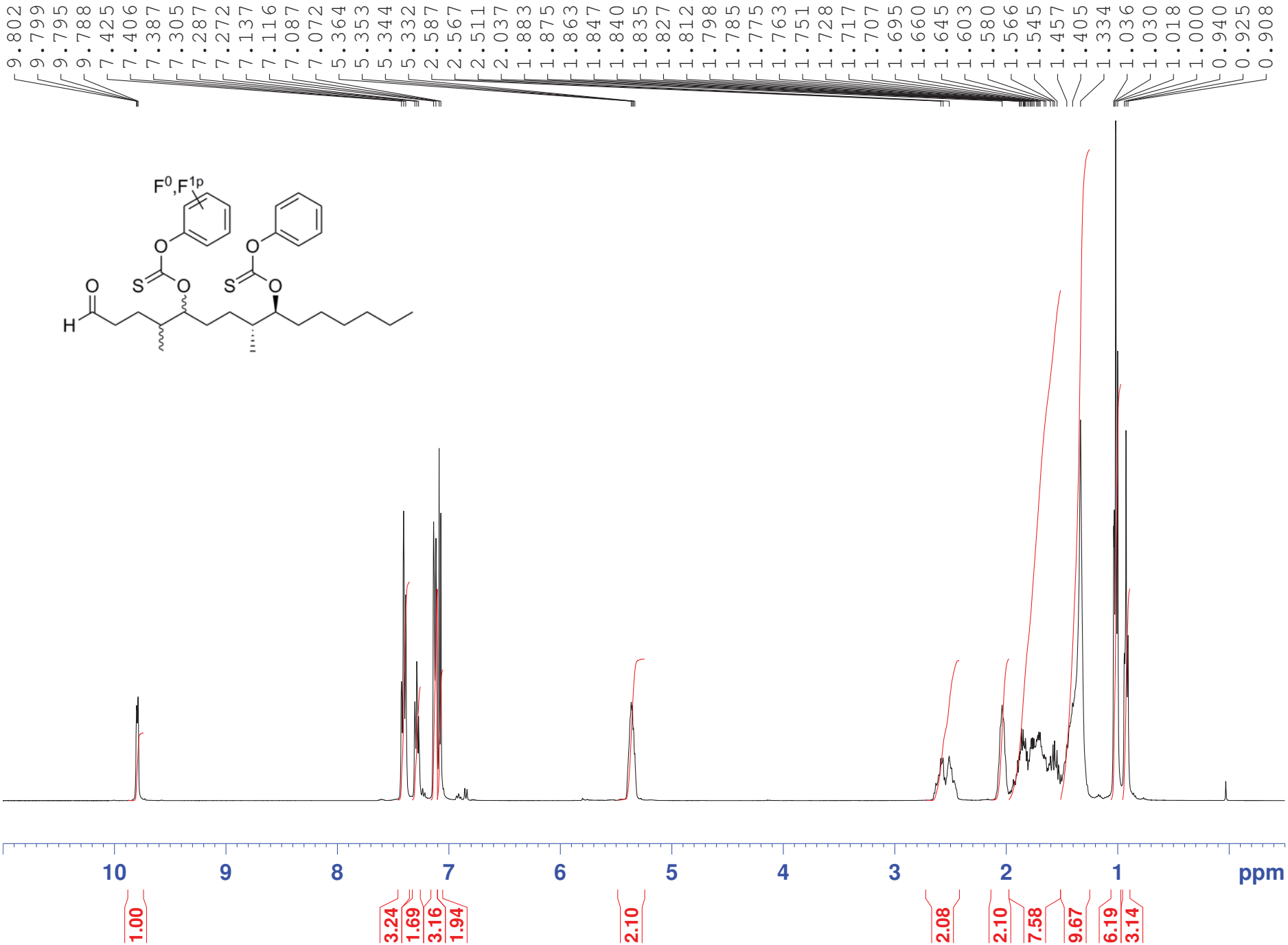
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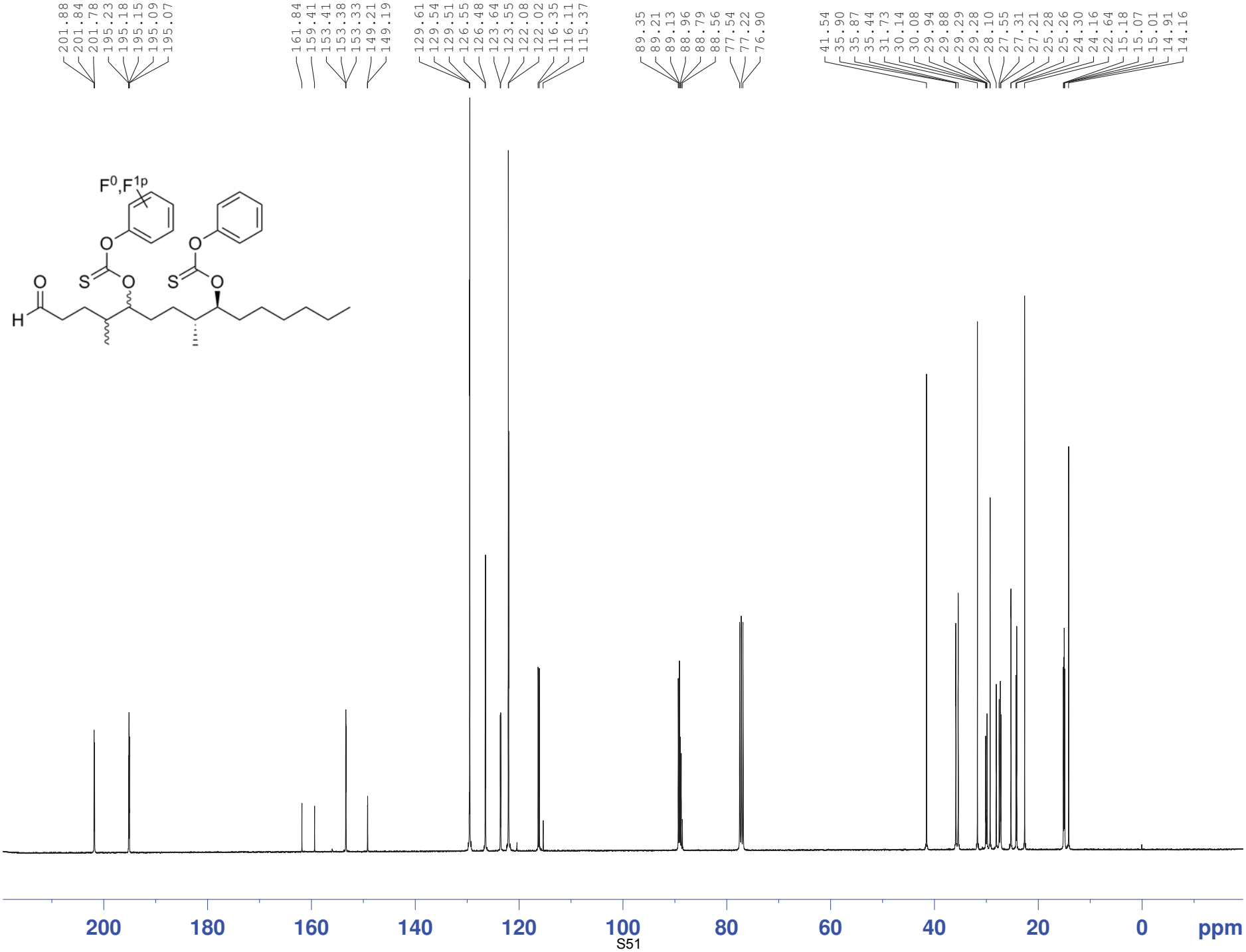
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24.16
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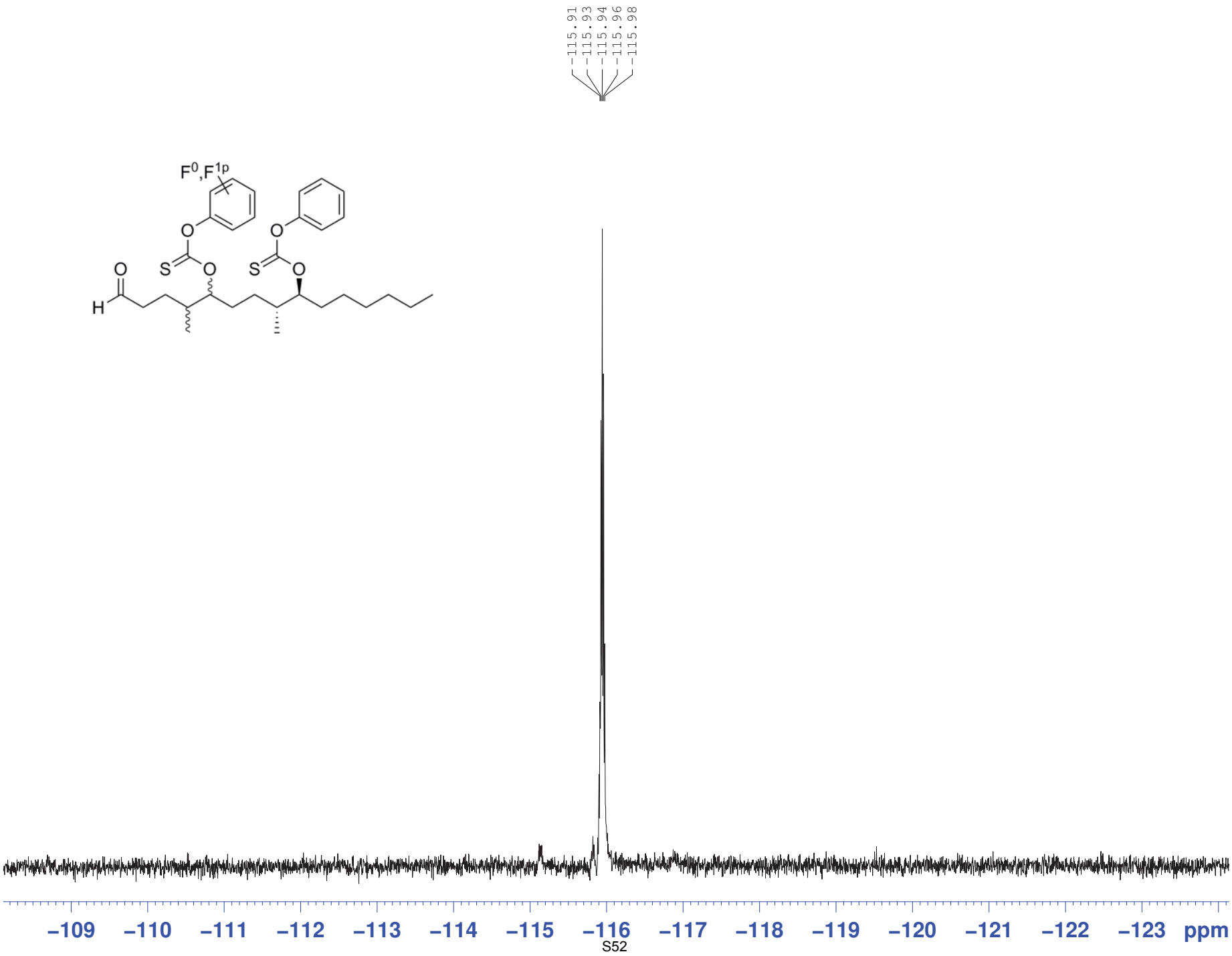
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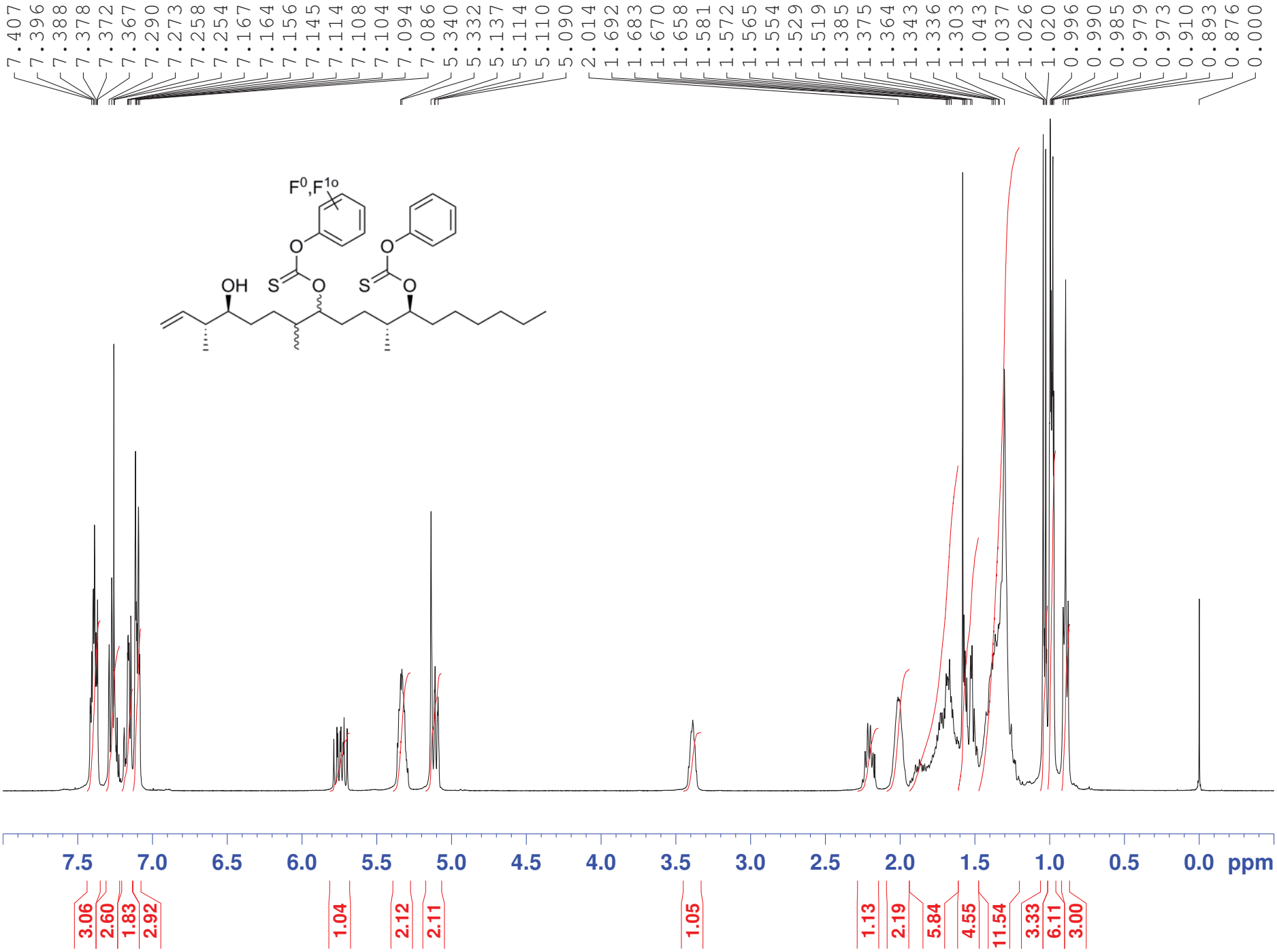
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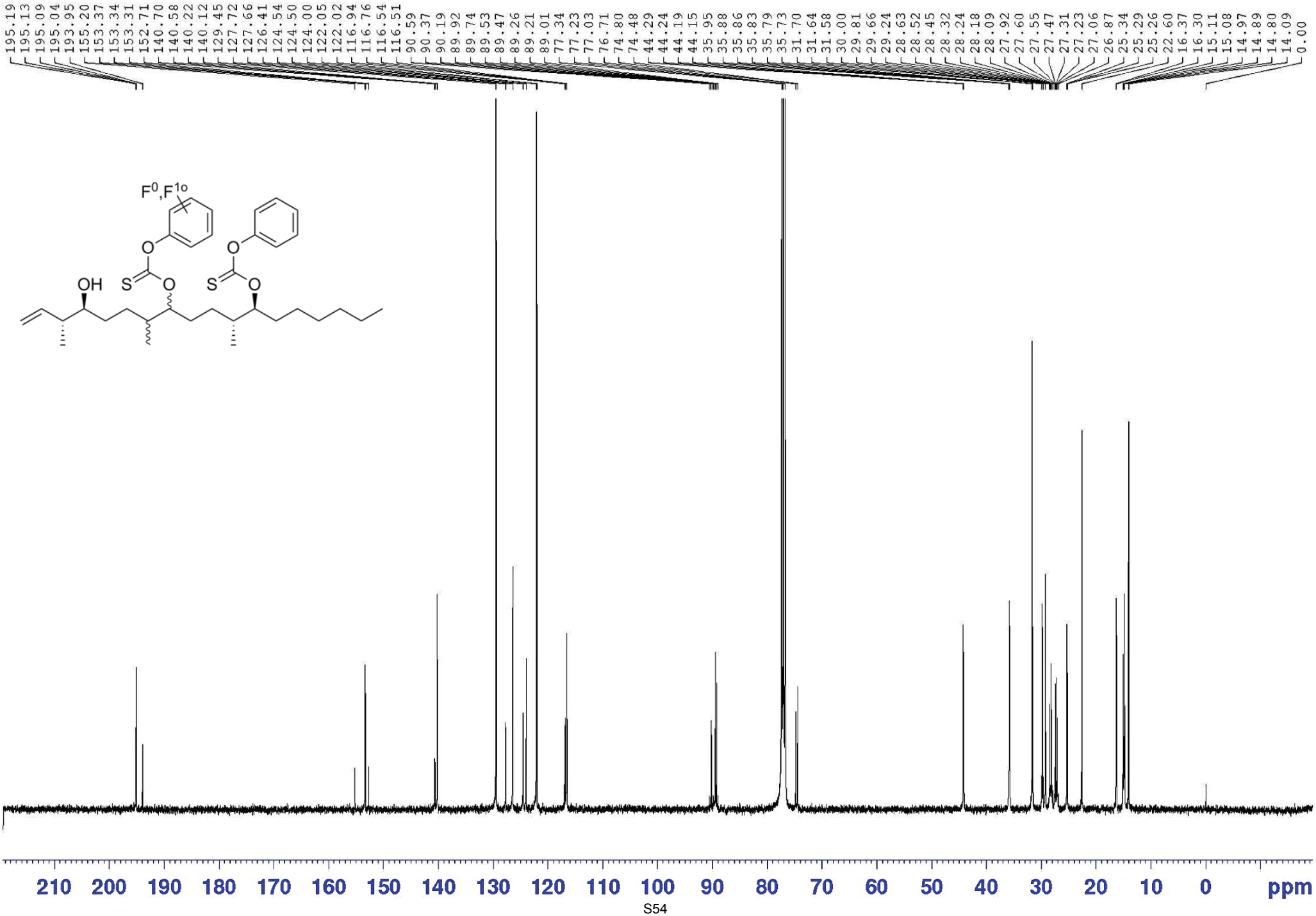
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22.60
16.37
16.30
15.11
15.08
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S
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OH
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S
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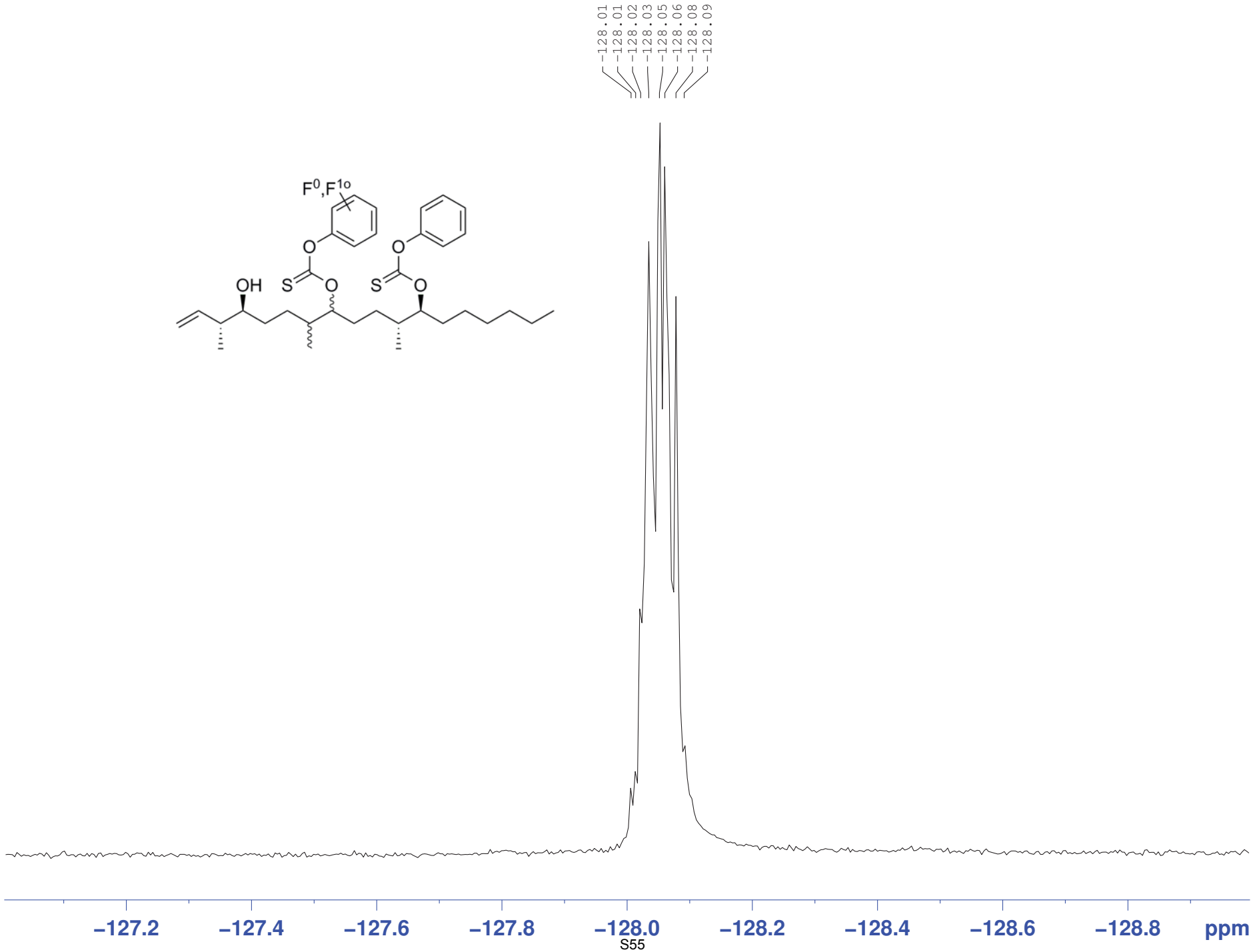
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O
S
O
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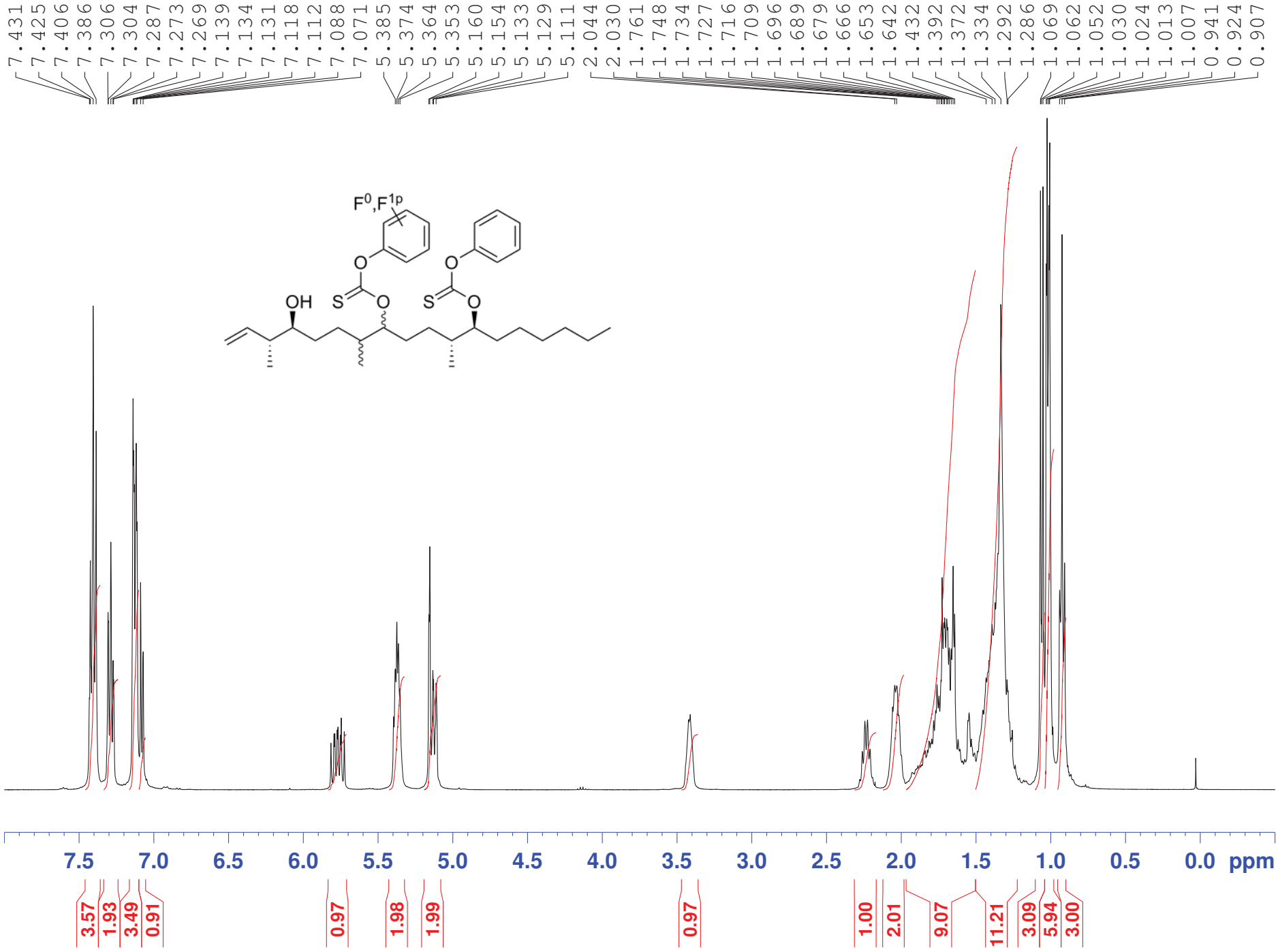
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0.907
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0.5
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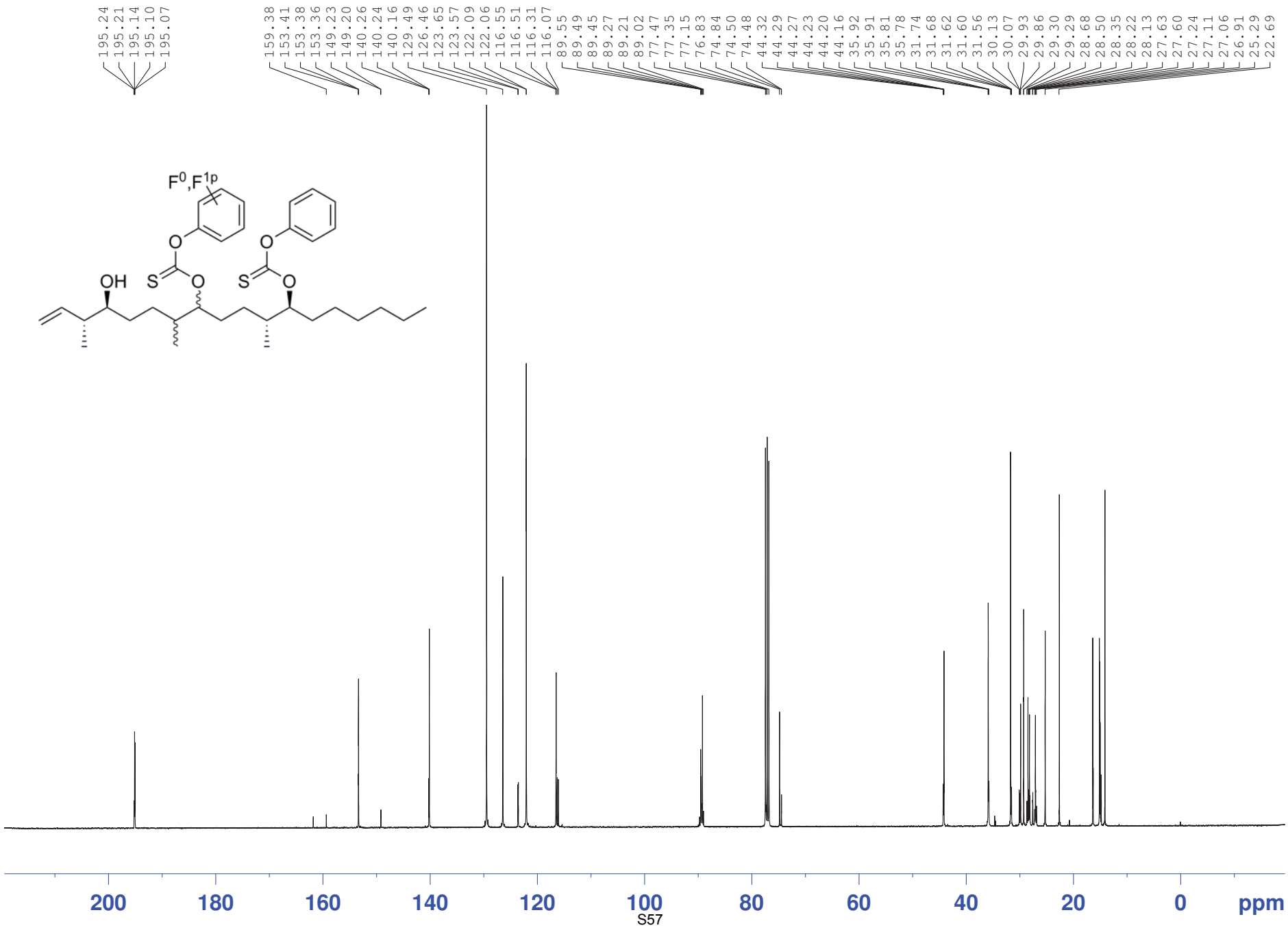
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74.48
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44.20
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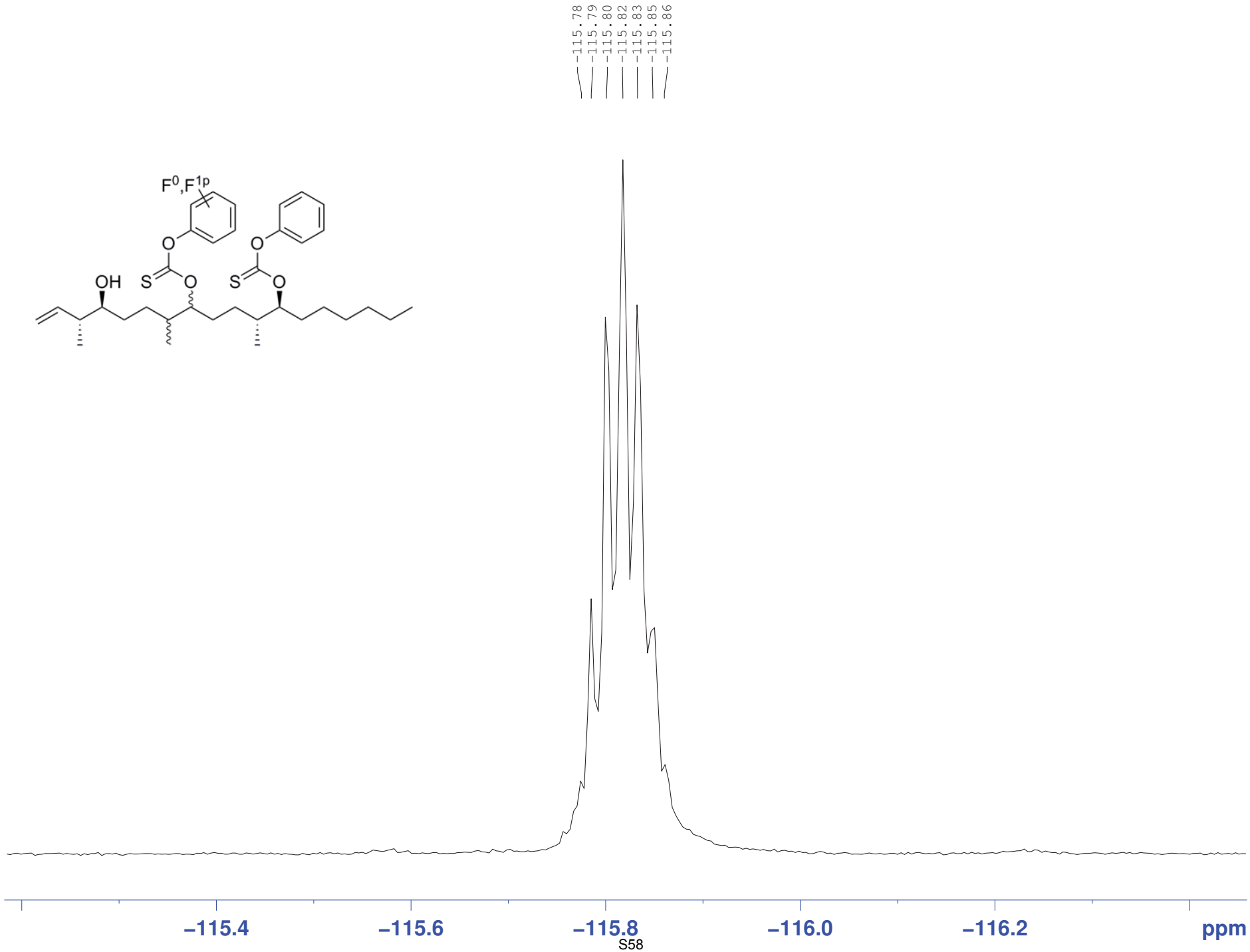
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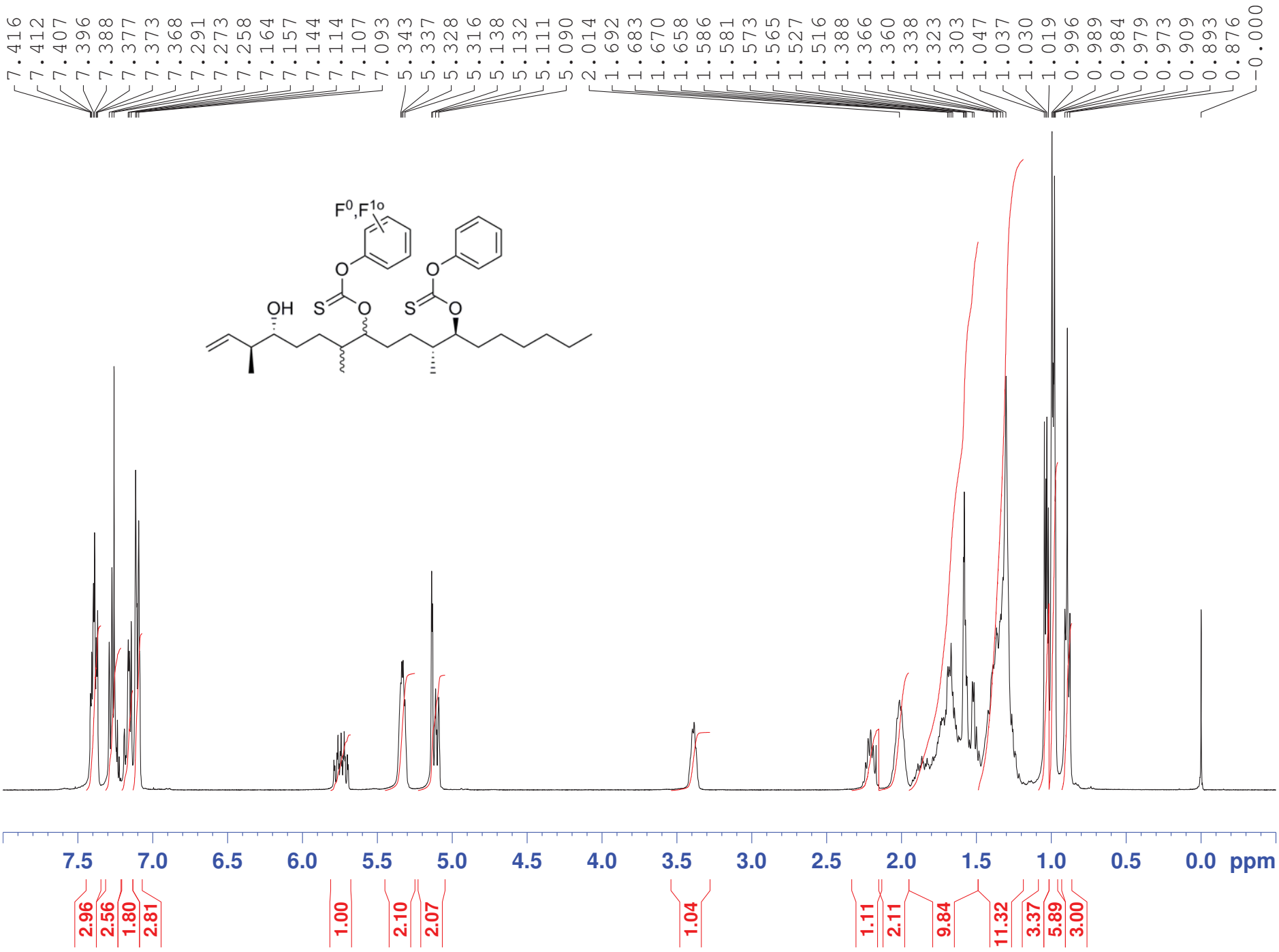
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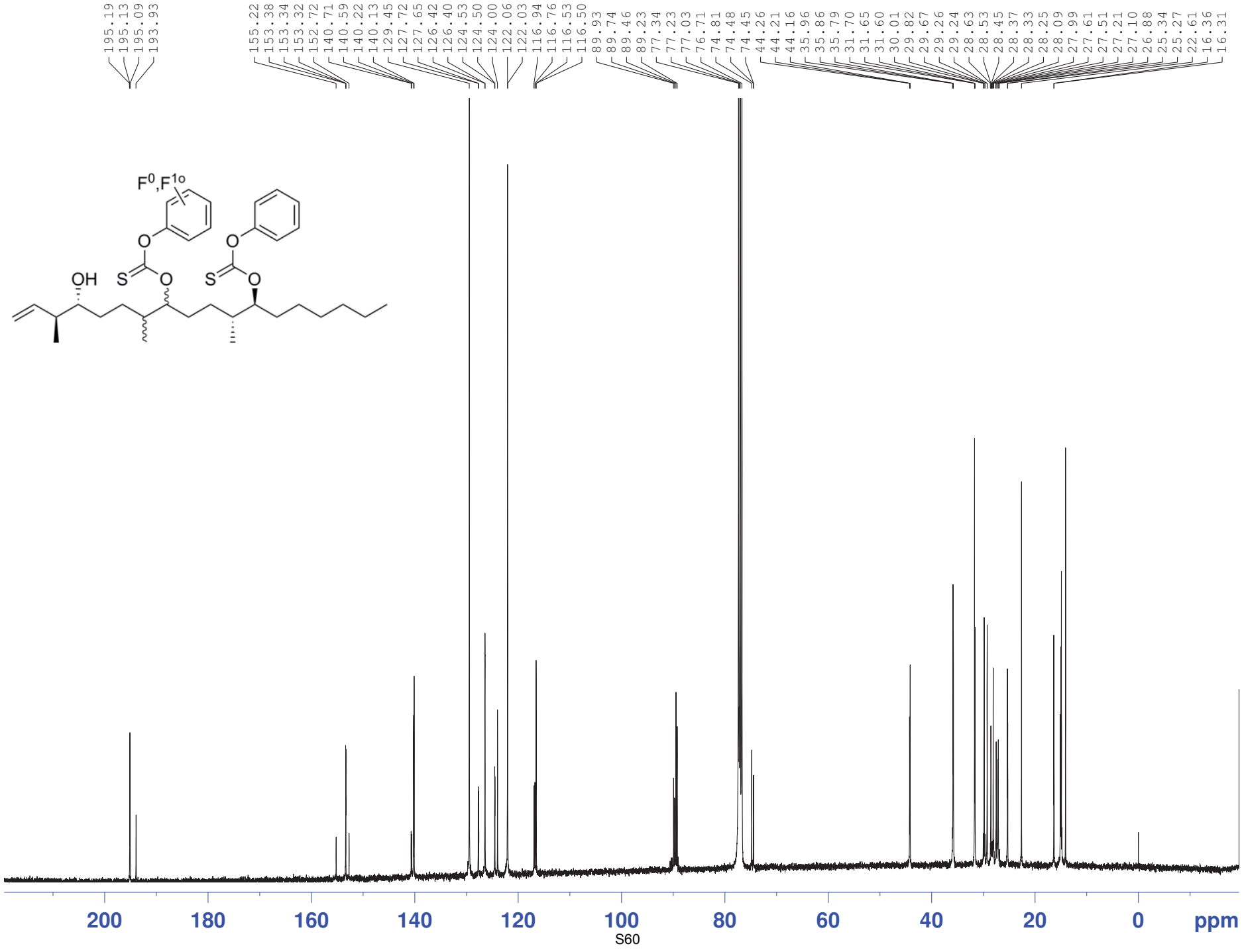
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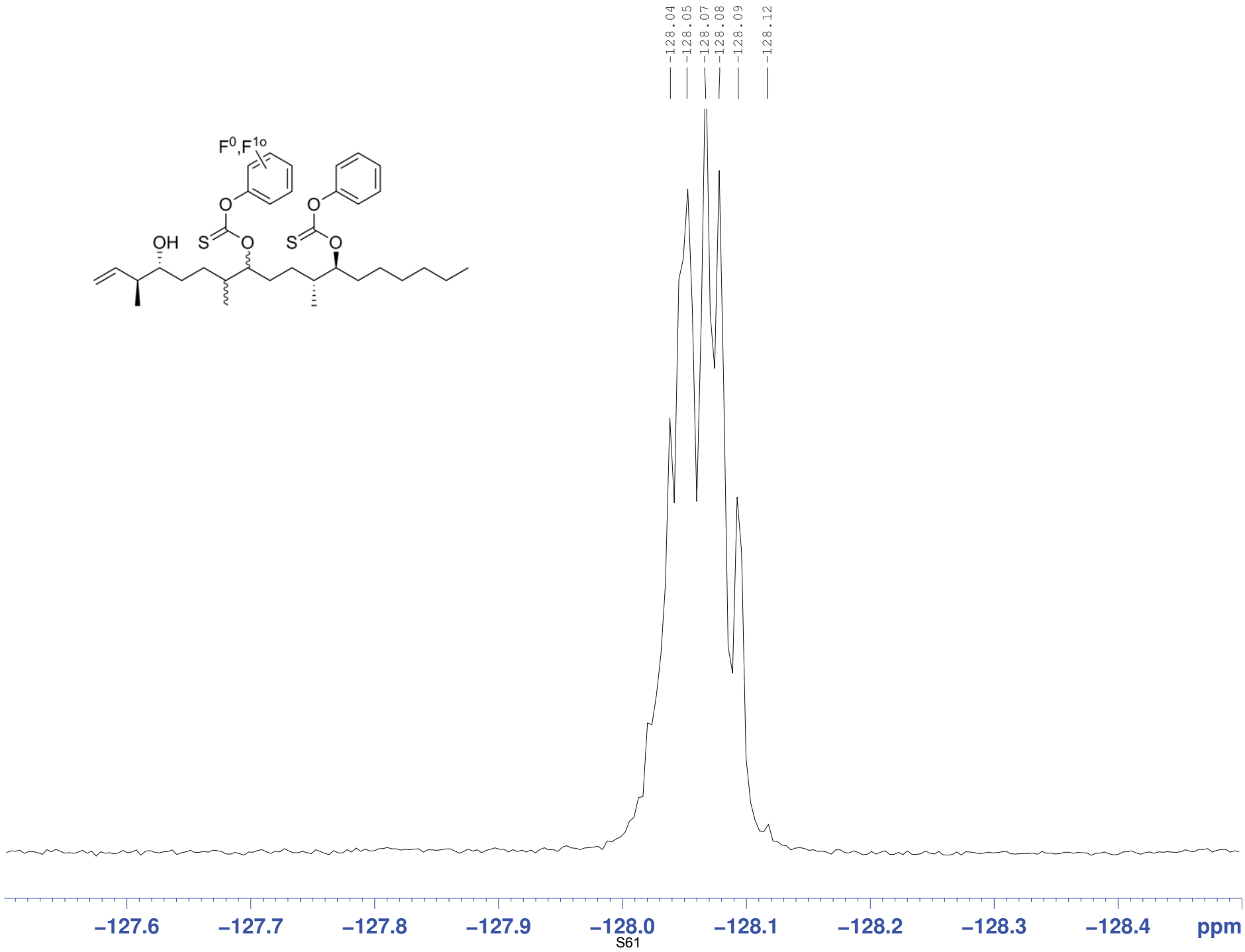
ppm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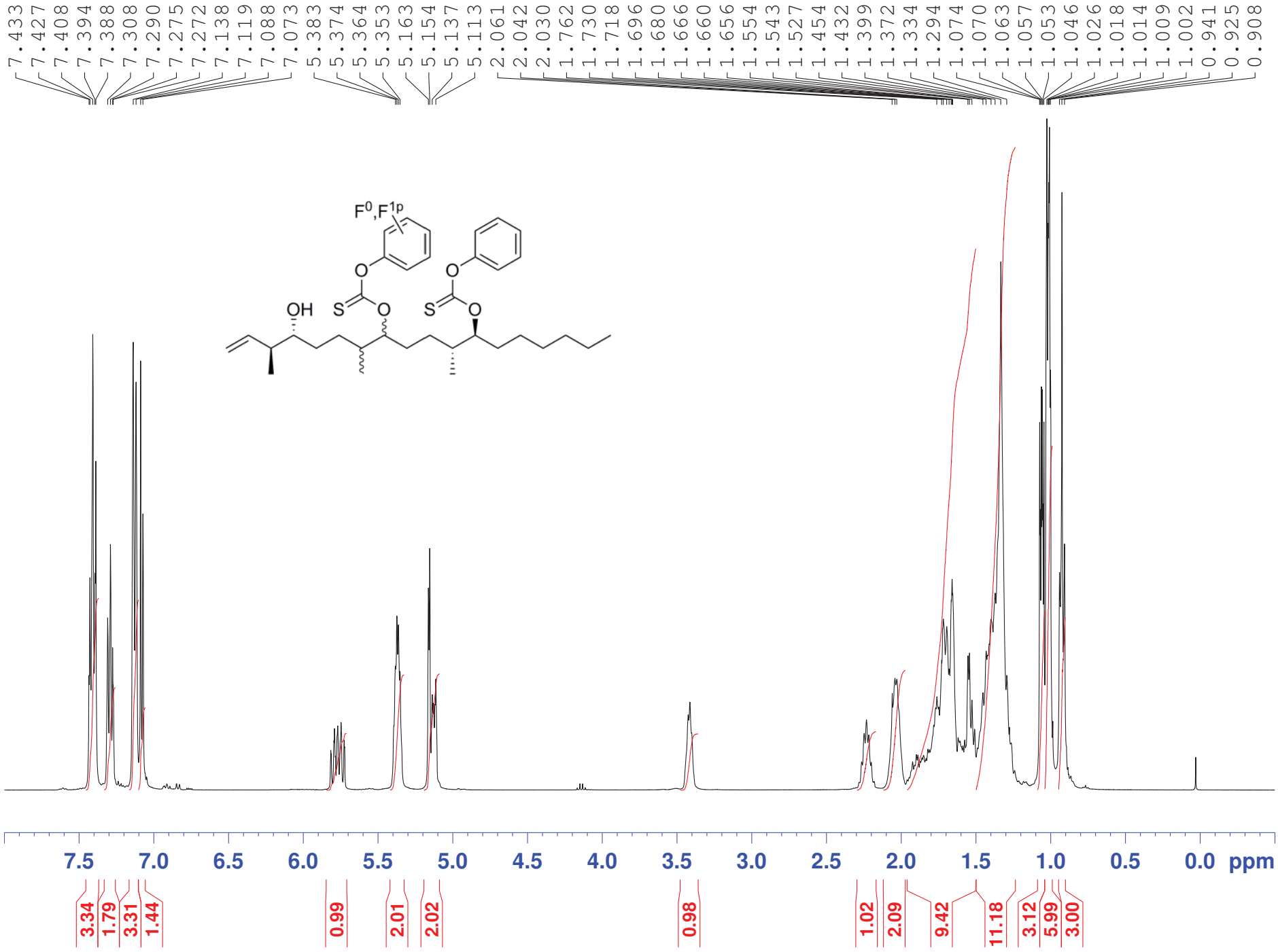
ppm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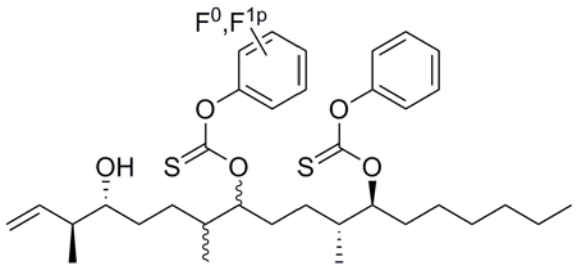

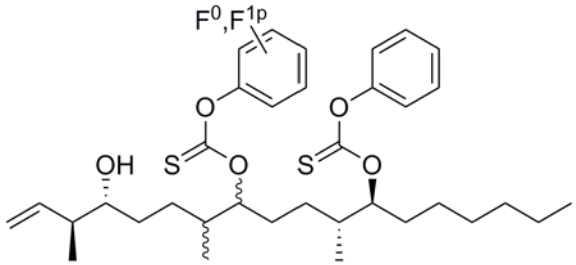
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O

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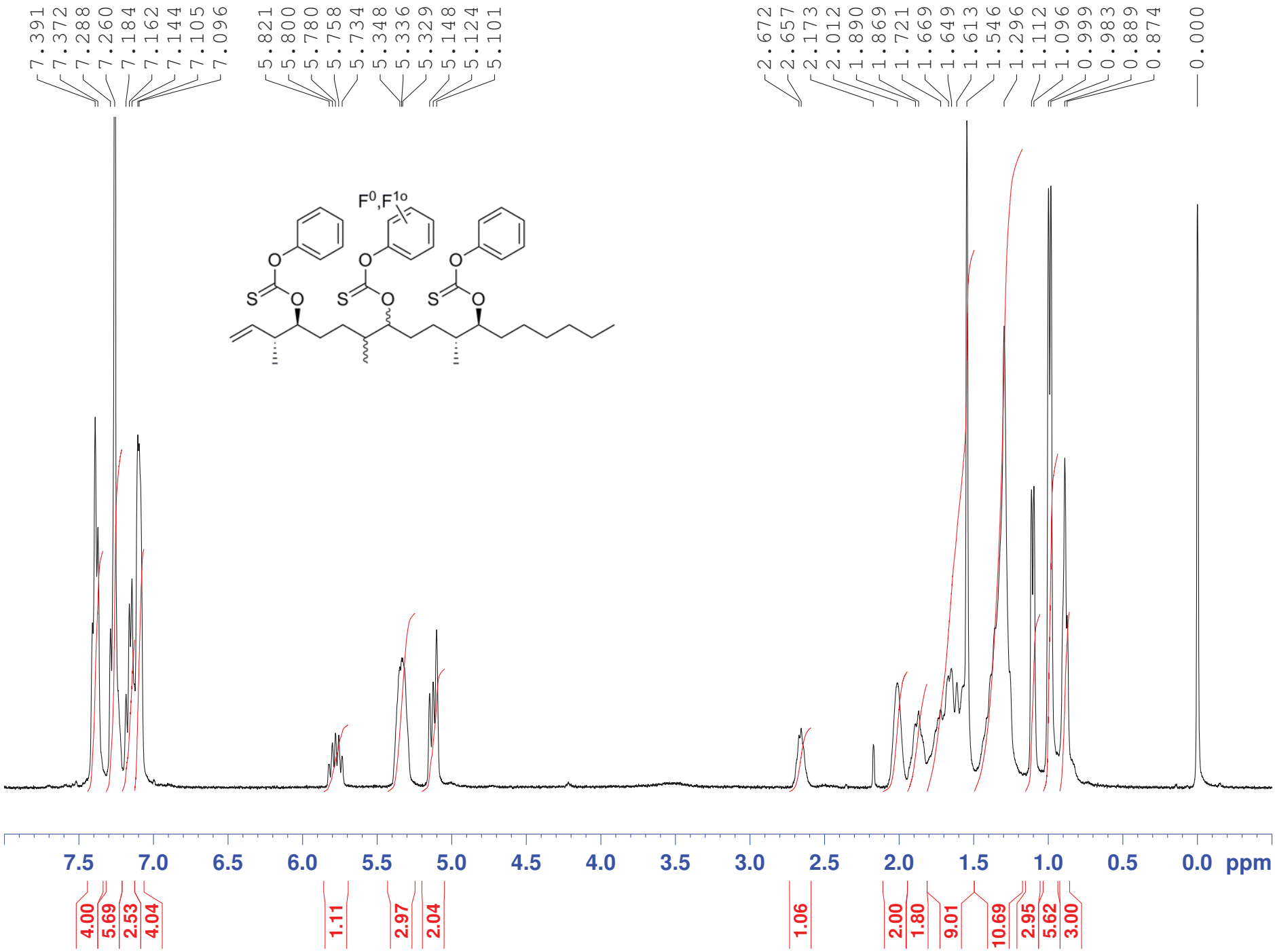
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5.734
5.348
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5.124
5.101
2.672
2.657
2.173
2.012
1.890
1.869
1.721
1.669
1.649
1.613
1.546
1.296
1.112
1.096
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0.983
0.889
0.874
0.000
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O
S
O
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6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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9.01
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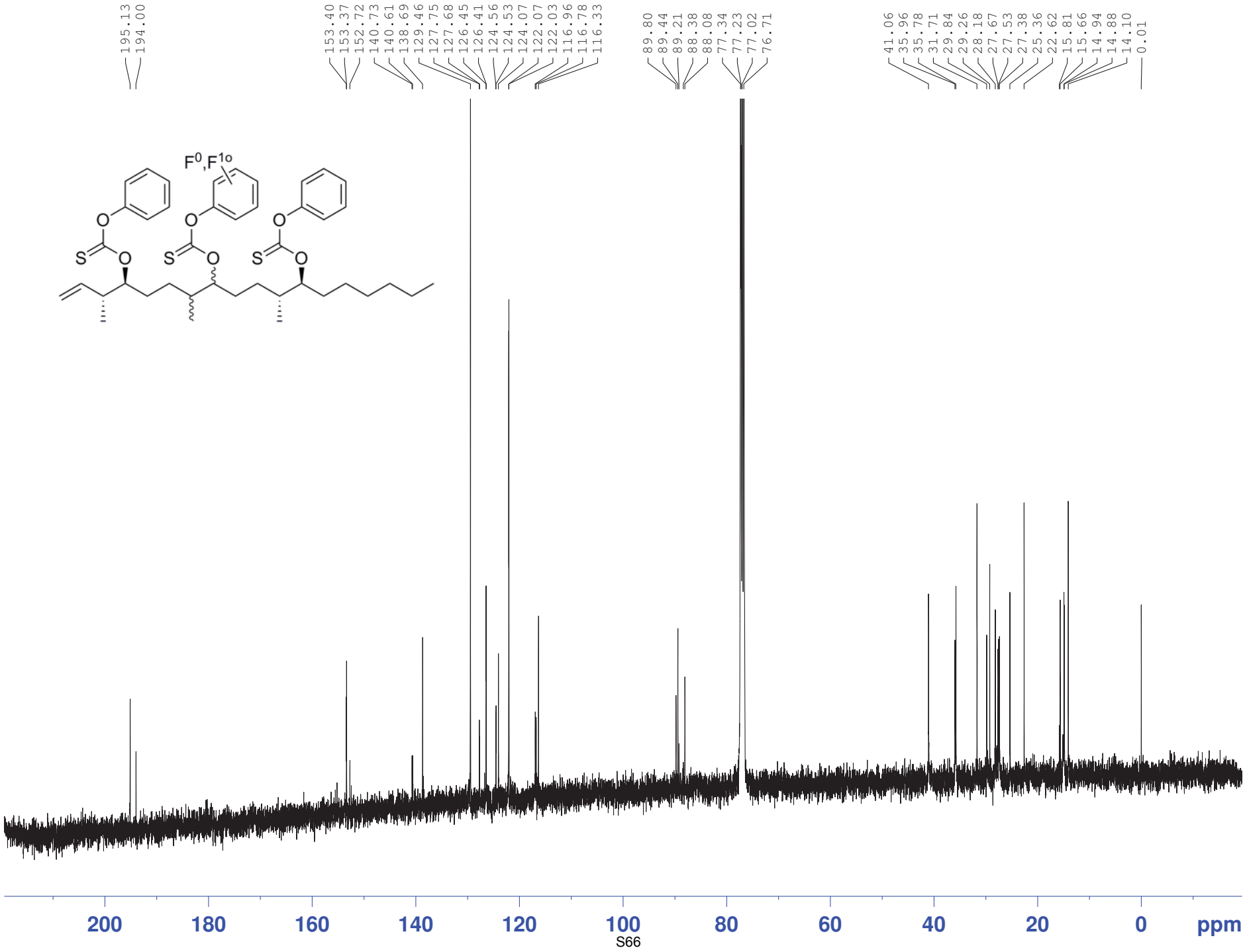
3.00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25.36
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15.81
15.66
14.94
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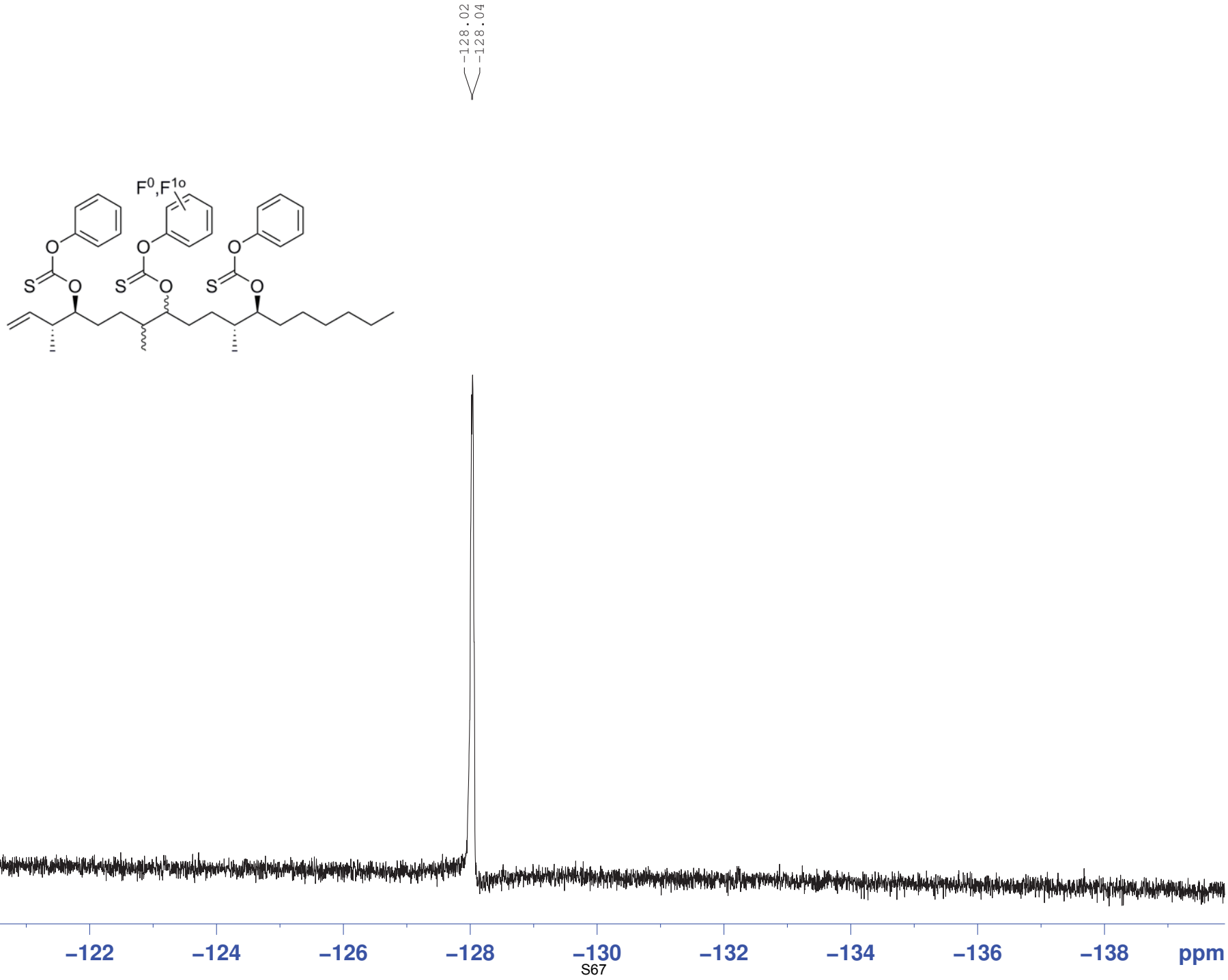
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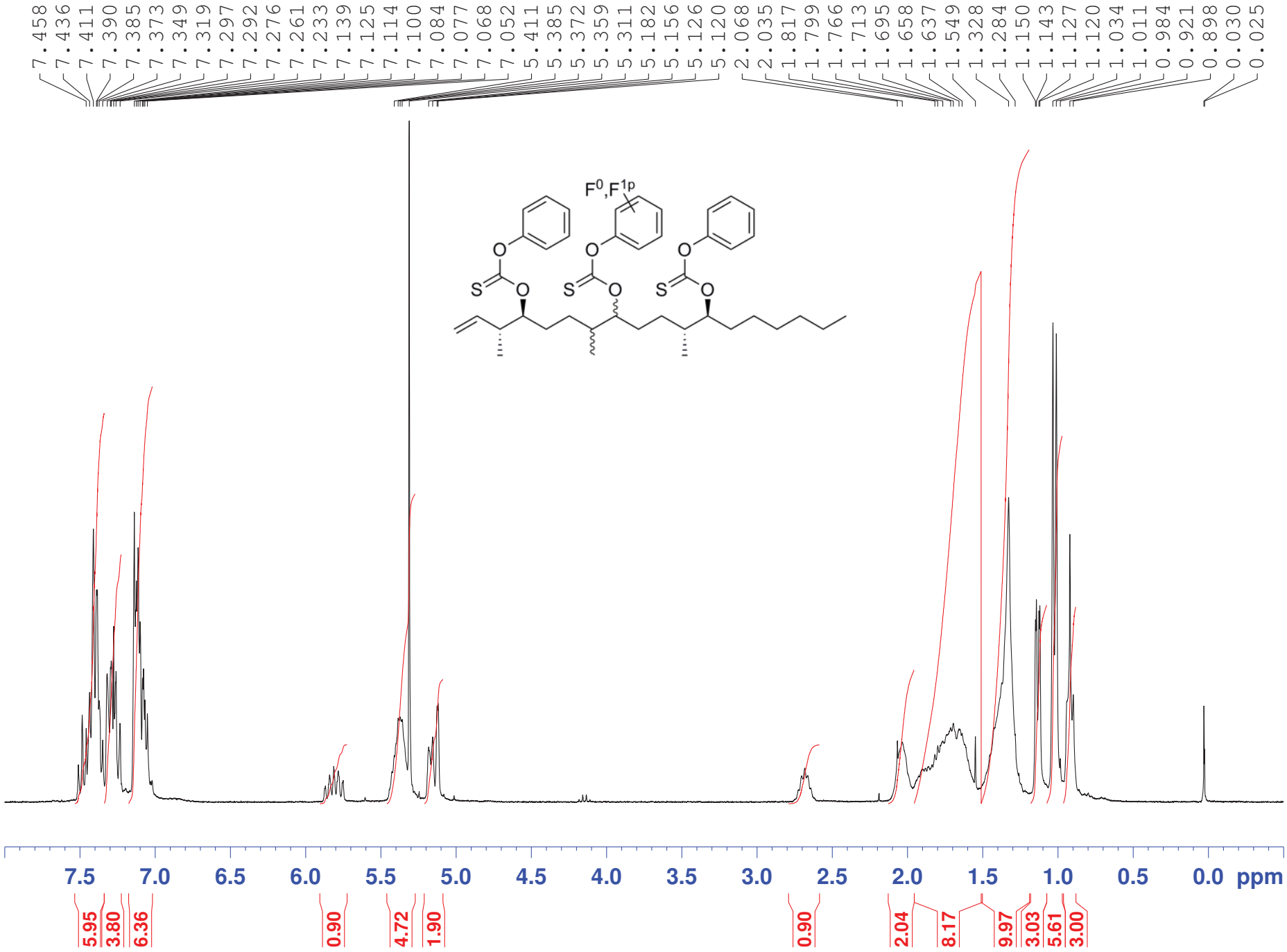
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7.077
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5.156
5.126
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1.766
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0.921
0.898
0.030
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S
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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0.0
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3.03
5.61
3.00

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195.20
194.88

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116.06

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89.18
89.09
88.41
88.06
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77.12
76.70

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41.18
35.90
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30.15
29.84
29.33
28.31
28.17
28.06
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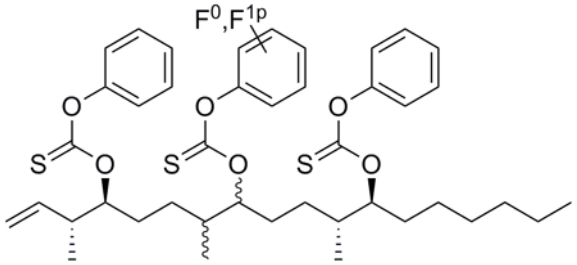
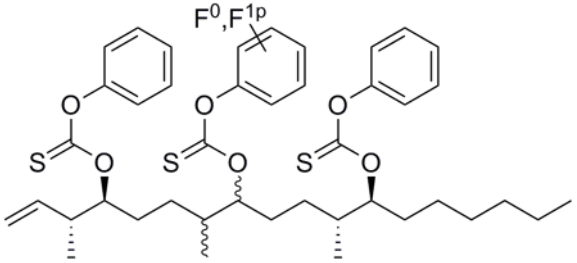
15.17
15.01
14.18

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O
S
O
O
S
O
O
S
O

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−116.5
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−117.5
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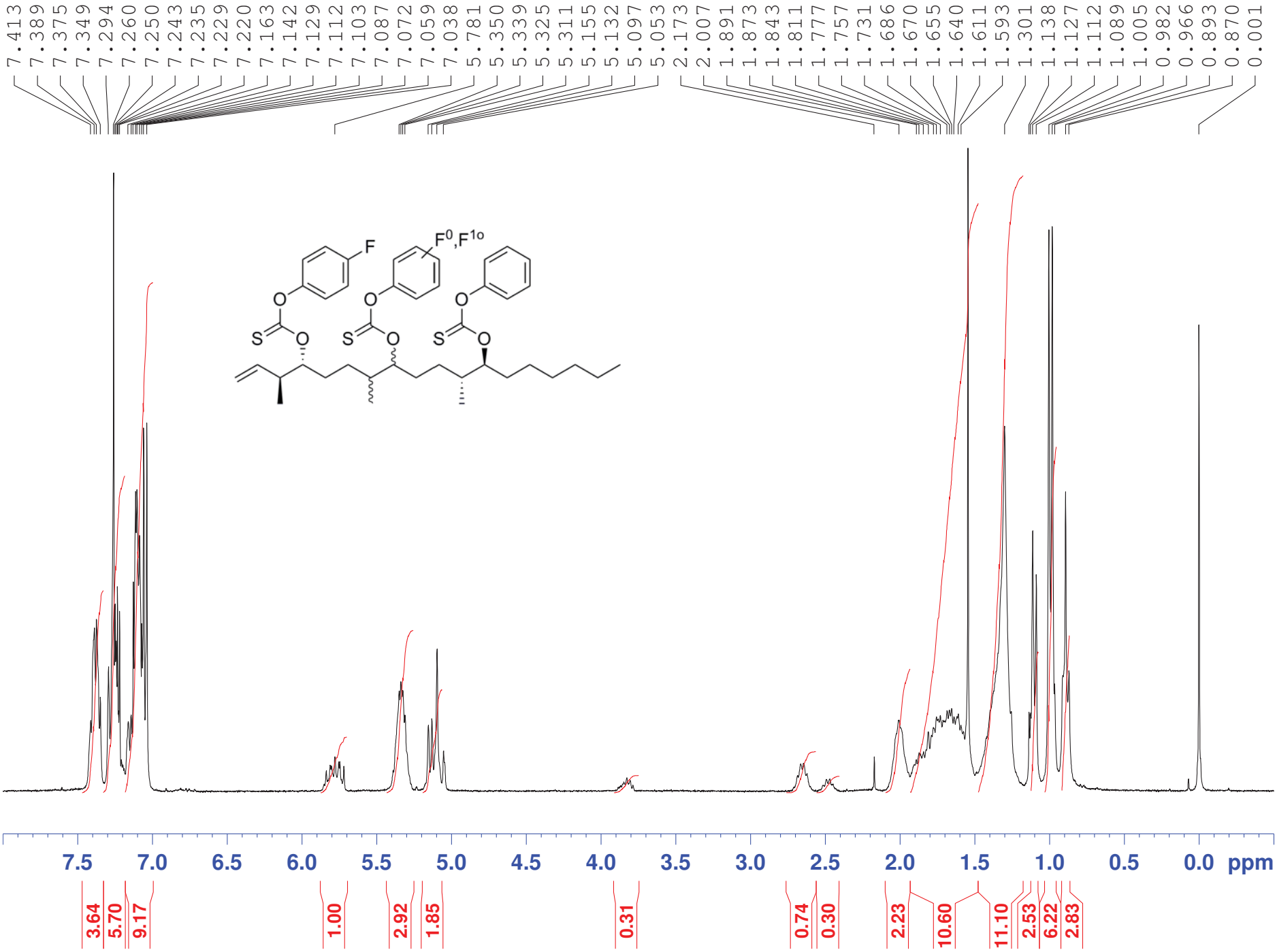
ppm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7.129
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7.103
7.087
7.072
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5.311
5.155
5.132
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1.777
1.757
1.731
1.686
1.670
1.655
1.640
1.611
1.593
1.301
1.138
1.127
1.112
1.089
1.005
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0.966
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0.870
0.001
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F0,F1o
O
S
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1.5
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0.0
ppm
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0.74
0.30
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10.60
11.10
2.53
6.22
2.83

195.22
195.17
195.13
159.37
159.33
159.27
153.39
153.35
149.20
149.17
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146.75
138.64
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126.43
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123.56
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122.43
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122.34
122.05
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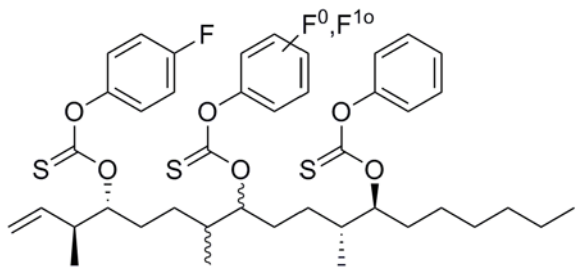
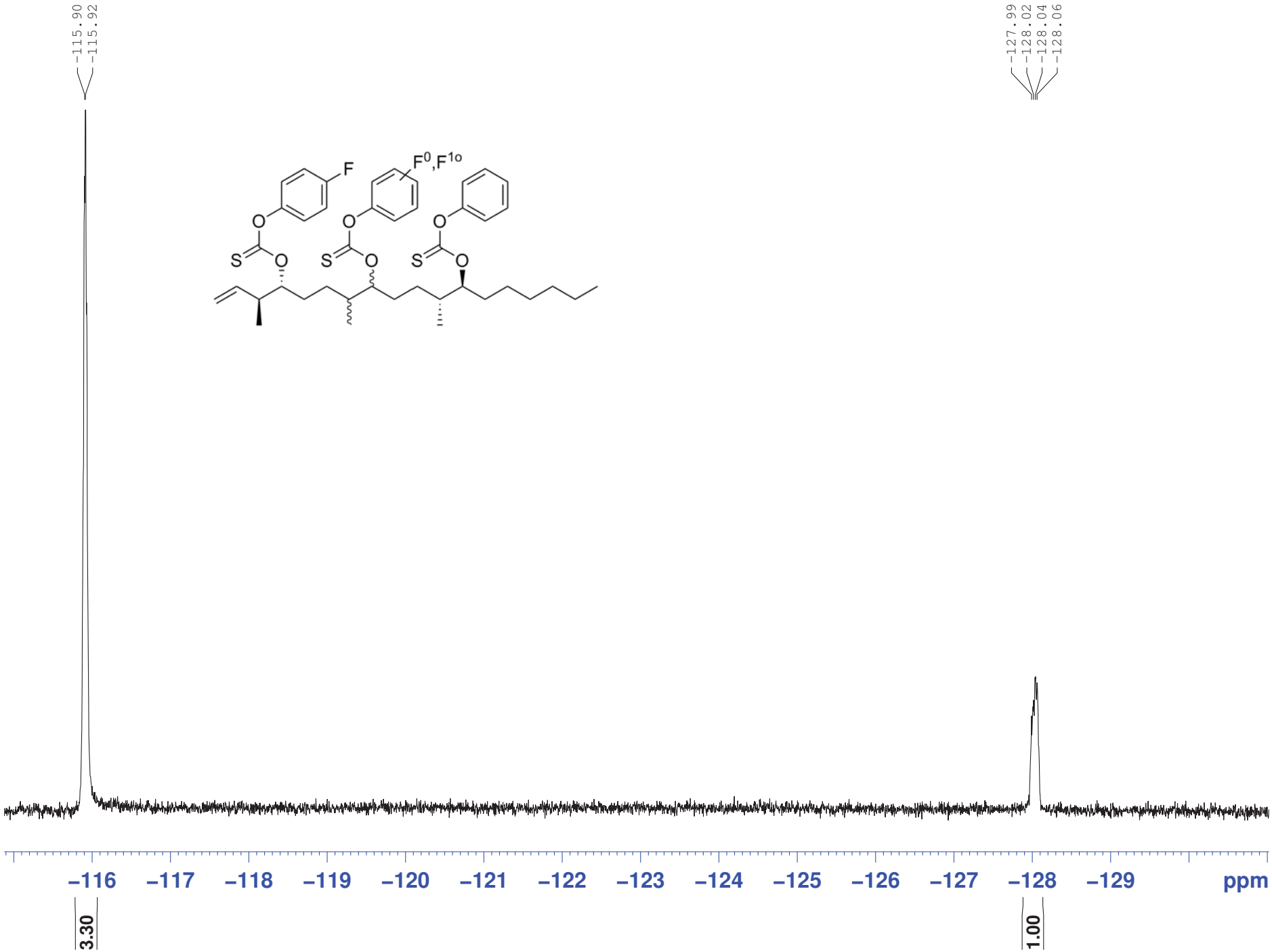
14.09
13.99



200 180 160 140 120 100 80 60 40 20 0 ppm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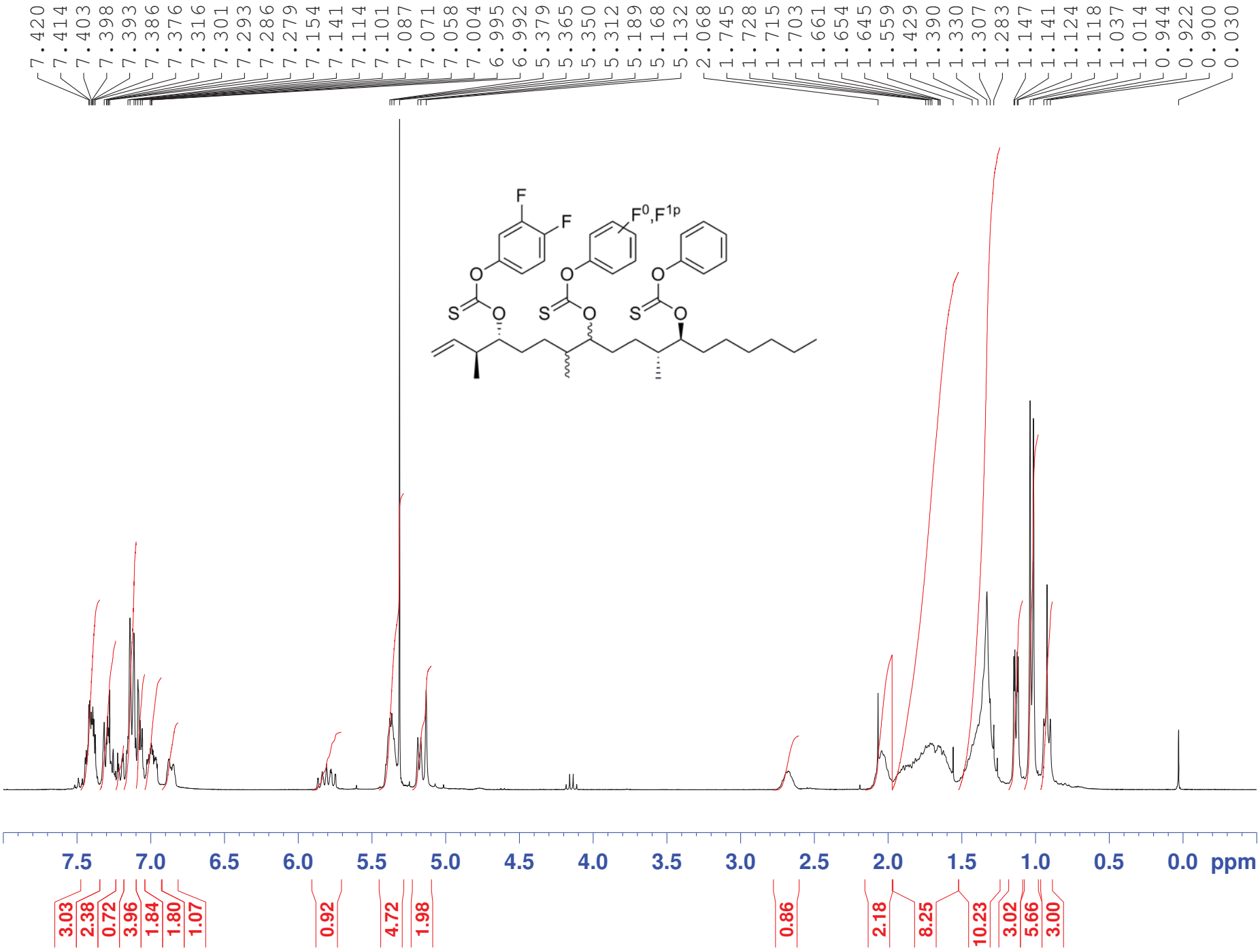
-128.02
-128.04
-128.06
F
F0,F10
O
S
O
O
S
O
O
S
O
−116
−117
−118
−119
−120
−121
−122
−123
−124
−125
−126
−127
−128
−129
ppm
3.30
1.00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7.101
7.087
7.071
7.058
7.004
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6.992
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5.365
5.350
5.312
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5.132
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1.715
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1.124
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0.922
0.900
0.030
F
F
F0,F1p
O
S
O
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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3.96
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1.80
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1.98
0.86
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10.23
3.02
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3.00

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195.20
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123.58
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118.10
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117.46
117.27
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116.48
116.32
116.09
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112.31
112.28
112.08
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89.13
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88.94
88.62
77.44
77.12
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41.20
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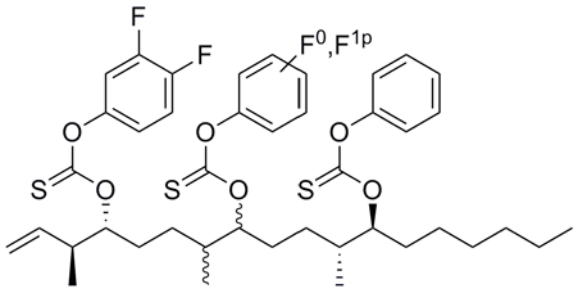

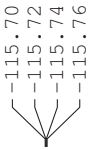
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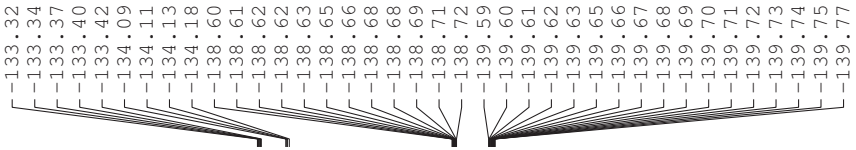
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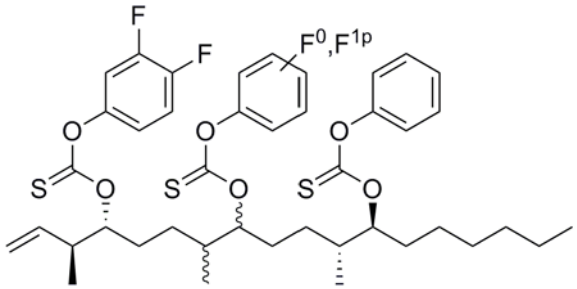
139.77


F
F
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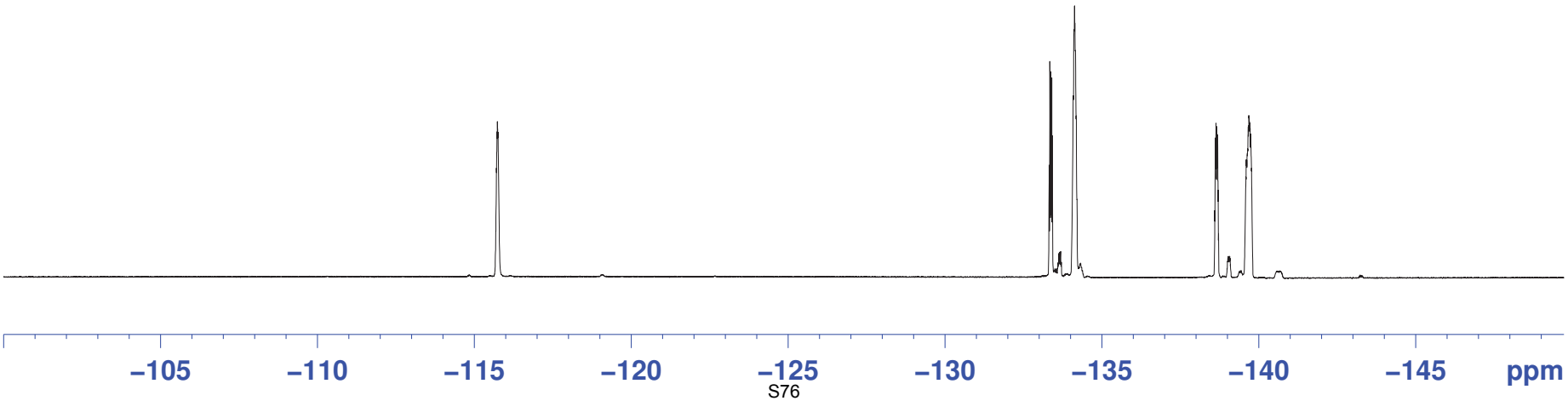
S
O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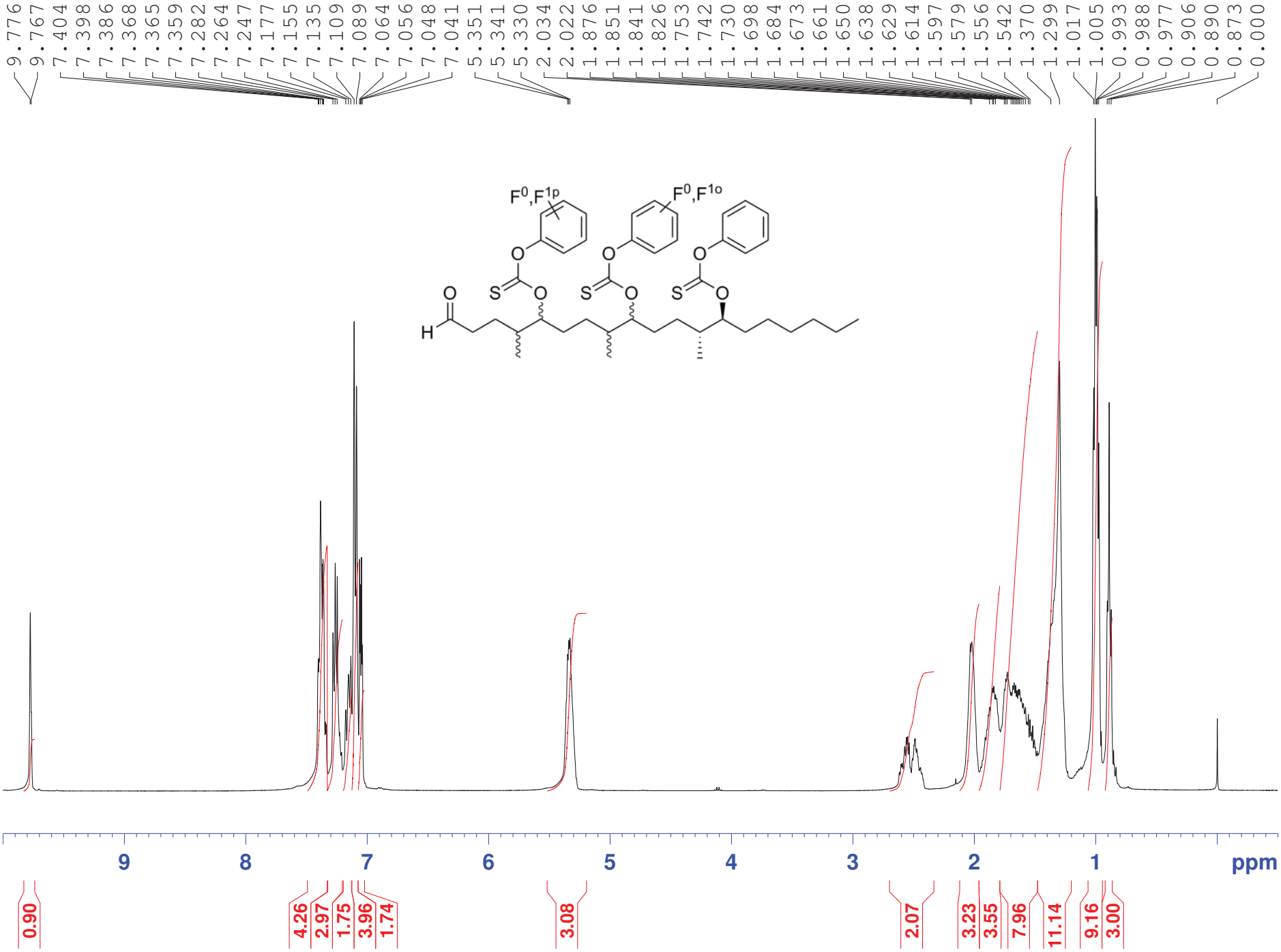
ppm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7.089
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7.048
7.041
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2.022
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1.614
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1.370
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1.005
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0.977
0.906
0.890
0.873
0.000
F0,F1p
F0,F1o
O
S
H
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8
7
6
5
4
3
2
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ppm
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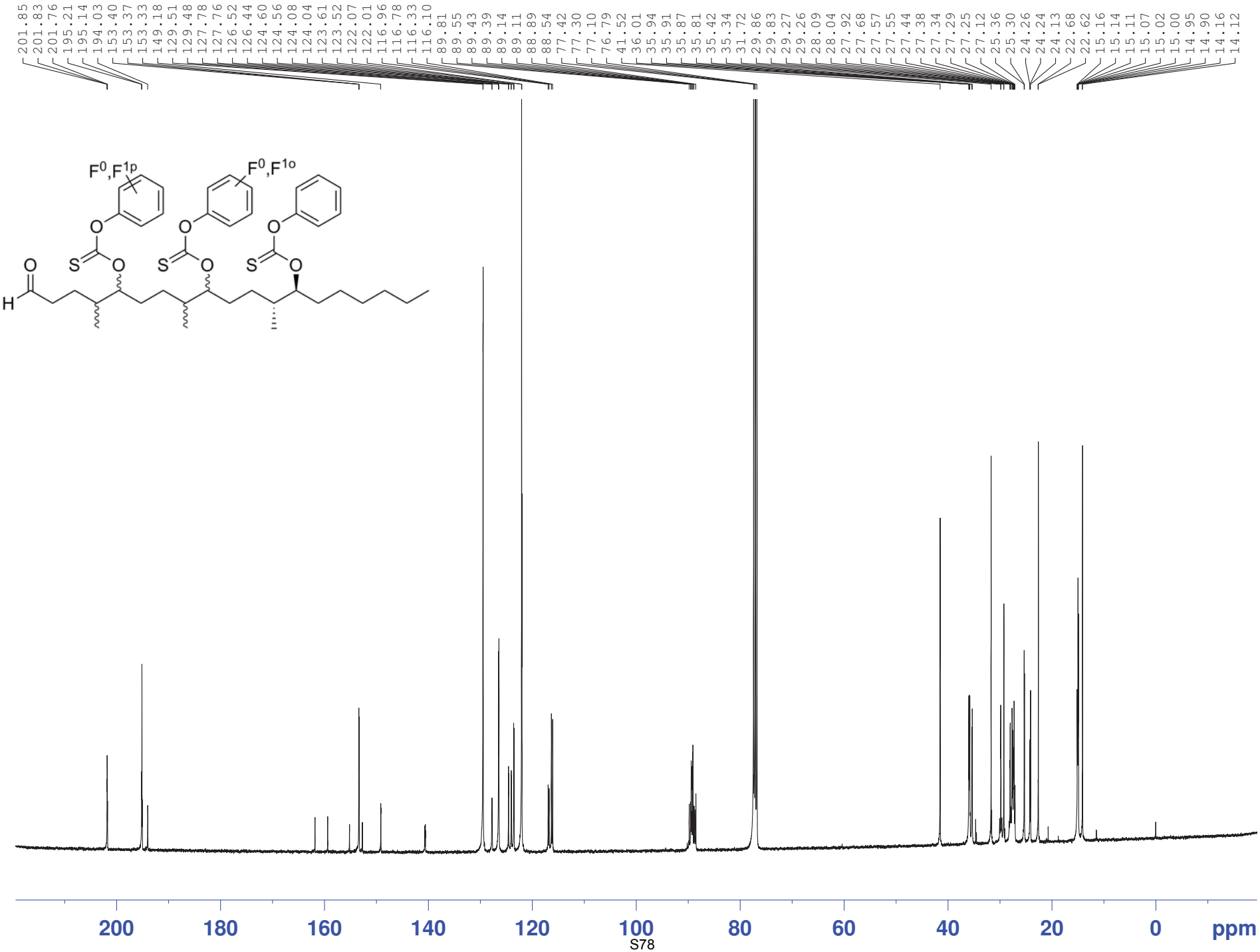
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24.24
24.13
22.68
22.62
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15.14
15.11
15.07
15.02
15.00
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14.90
14.16
14.12
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F0,F1o
O
S
H
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100
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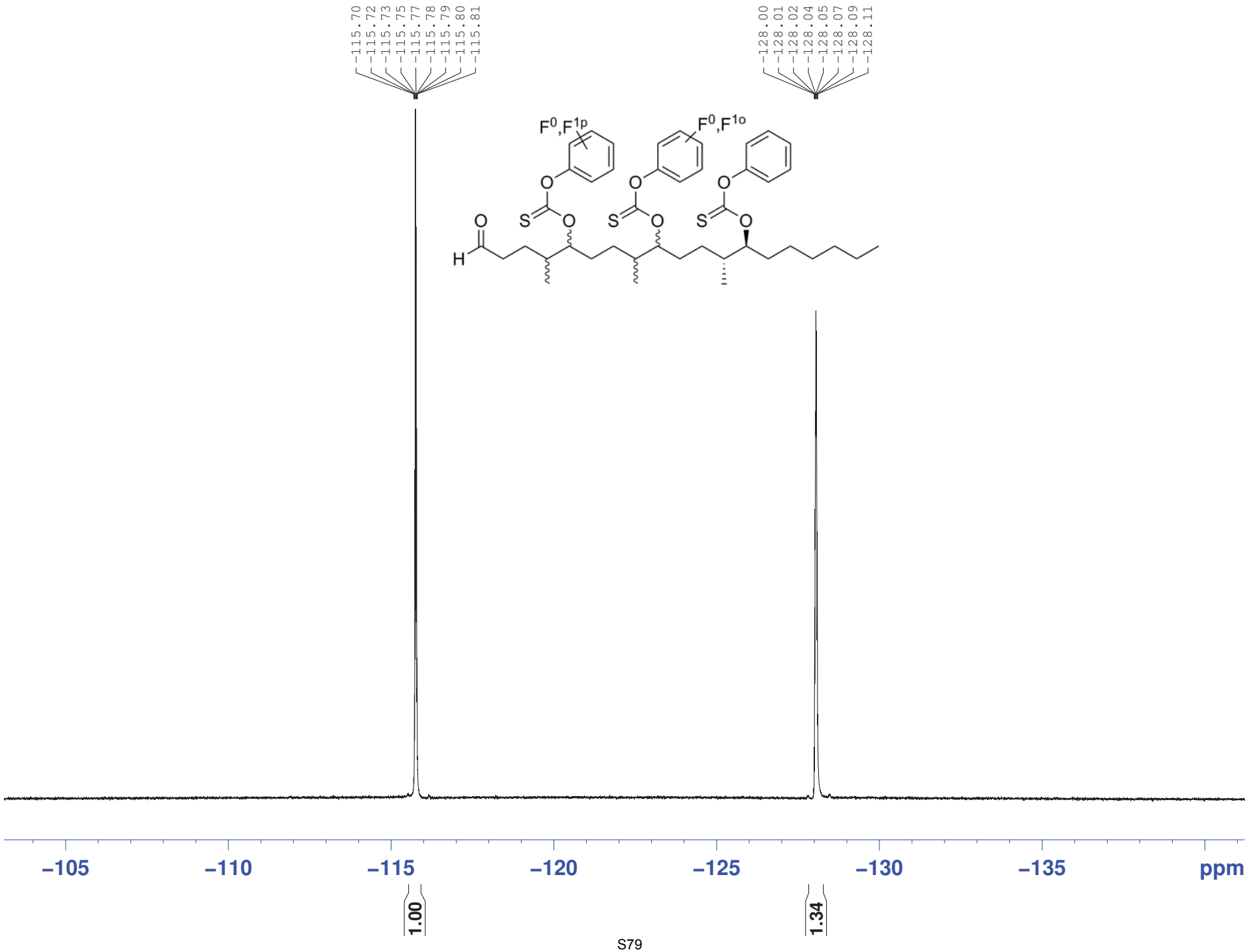
60
40
20
0
ppm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-128.05
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-128.09
-128.11
F0,F1p
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S
H
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ppm
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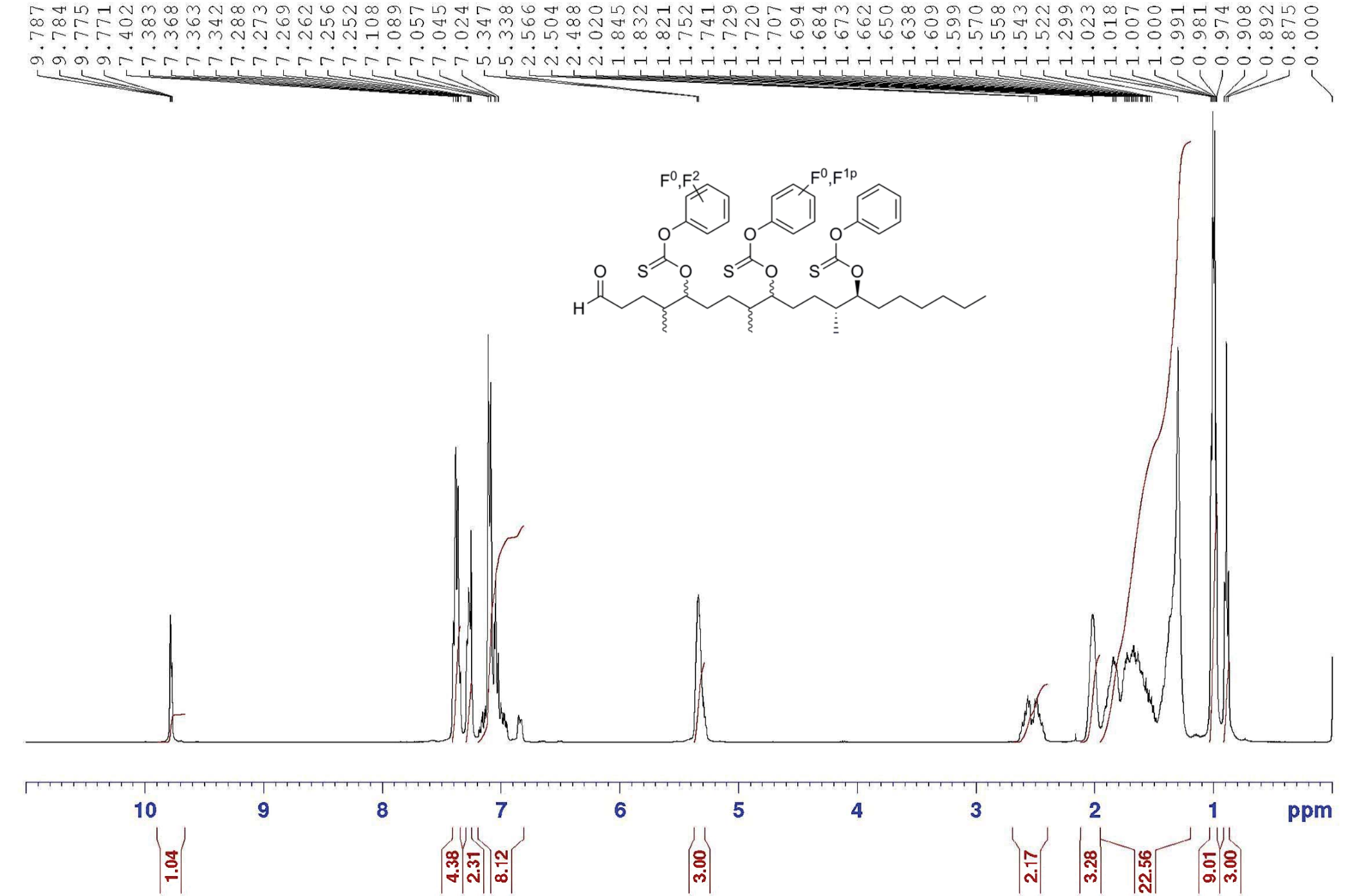
1.34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1.000
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0.892
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0.000
F0,F2
F0,F1p
O
S
H
10
9
8
7
6
5
4
3
2
1
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4.38
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8.12
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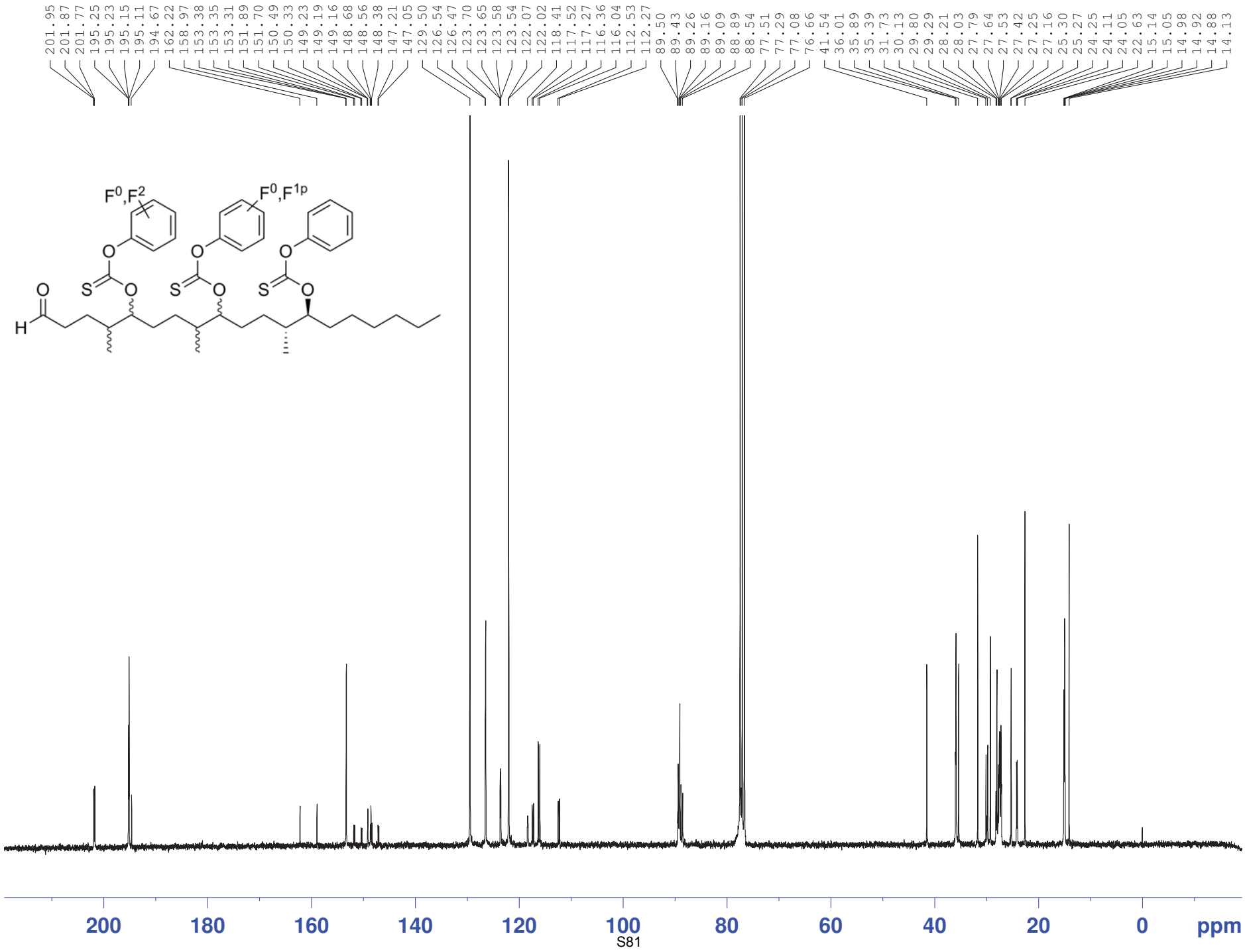
3.00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14.88
14.13
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S
H
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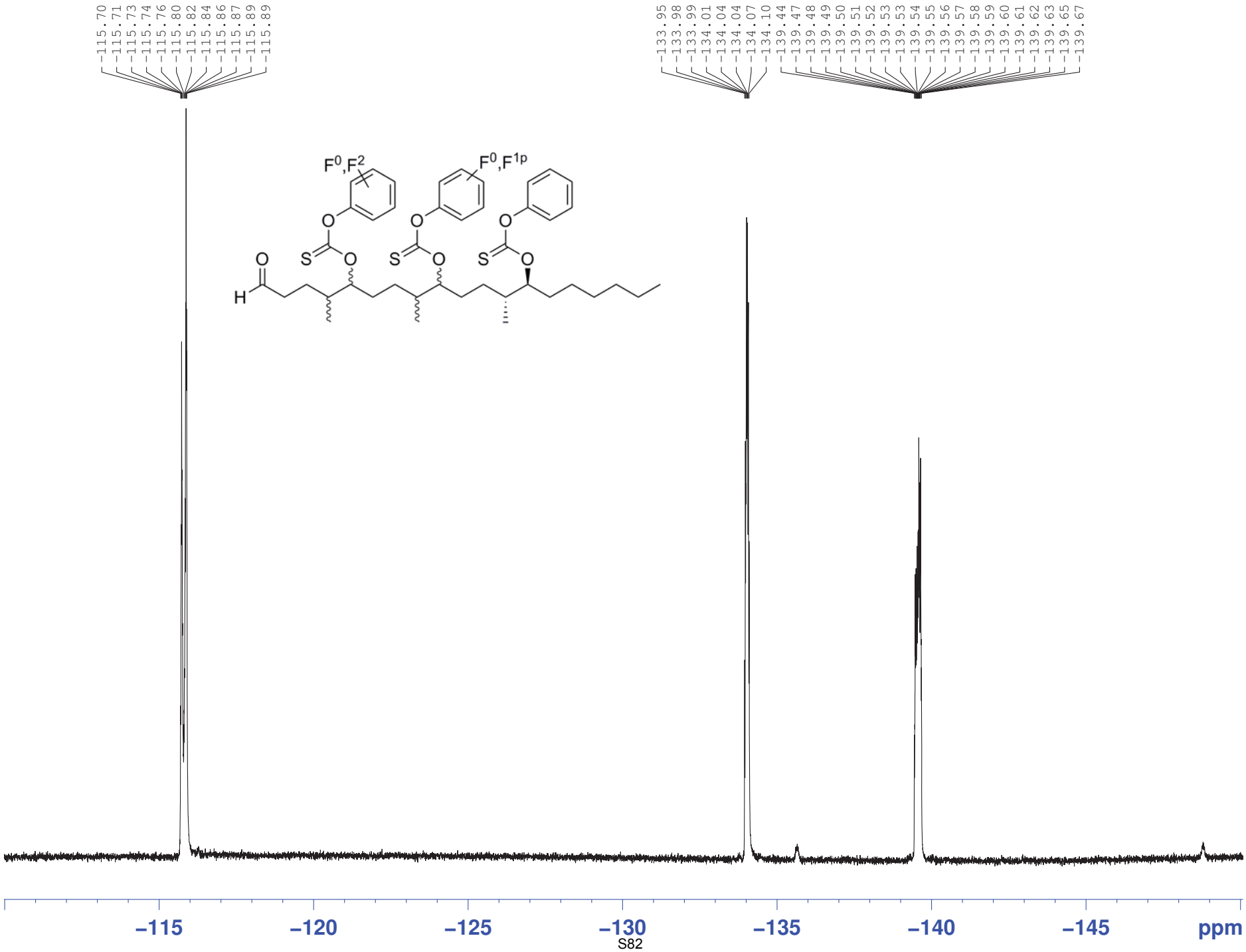
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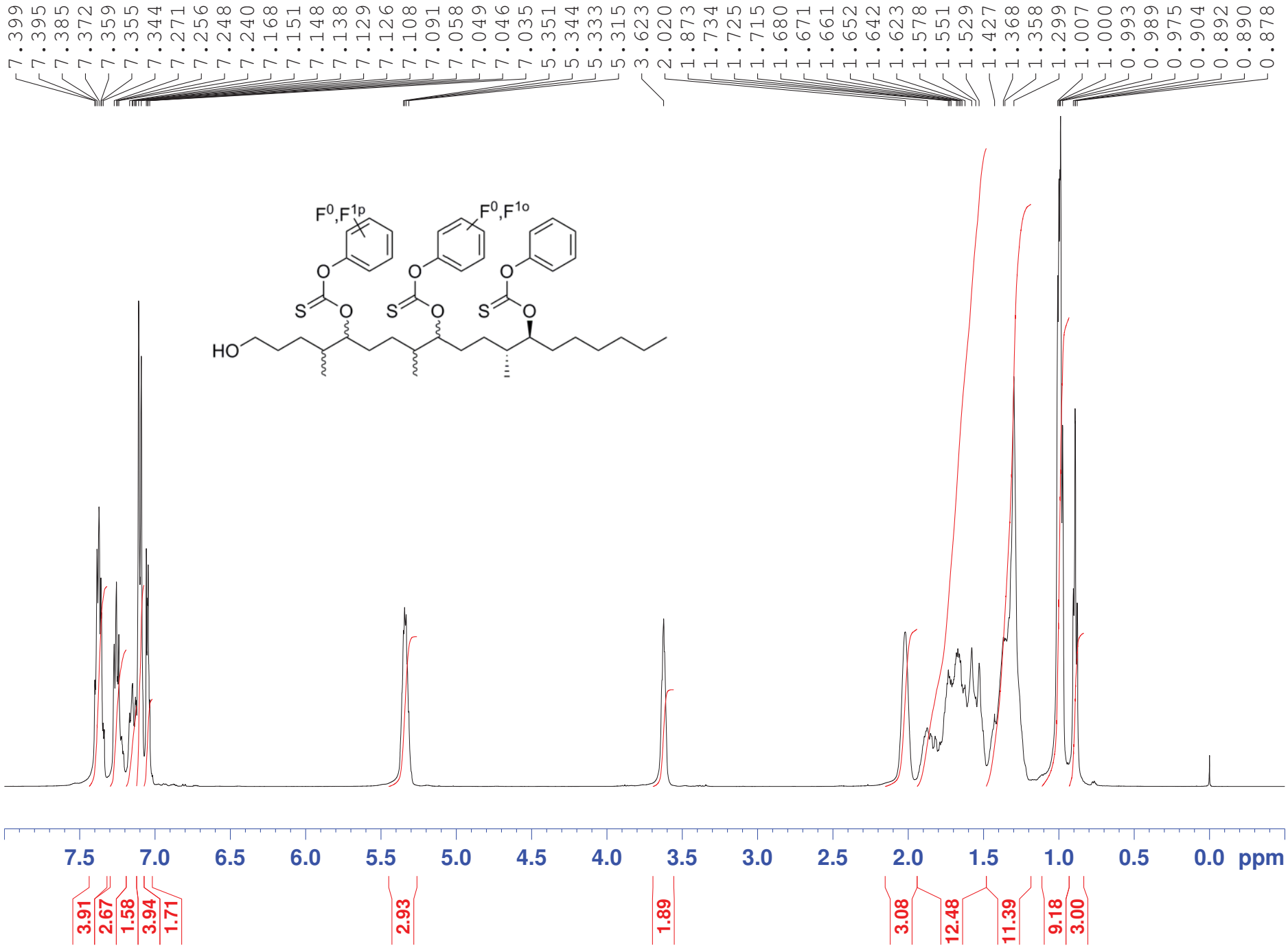
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7.058
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5.344
5.333
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2.020
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1.734
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1.680
1.671
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1.642
1.623
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1.551
1.529
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1.358
1.299
1.007
1.000
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0.989
0.975
0.904
0.892
0.890
0.878
F0,F1p
F0,F1o
HO
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3.0
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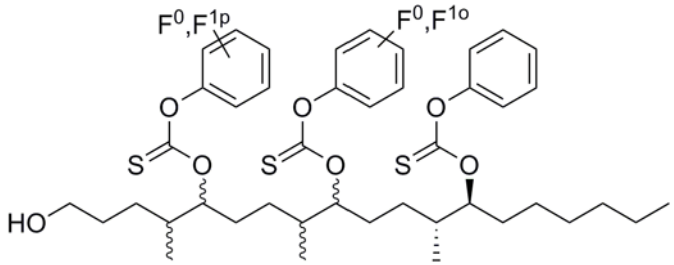
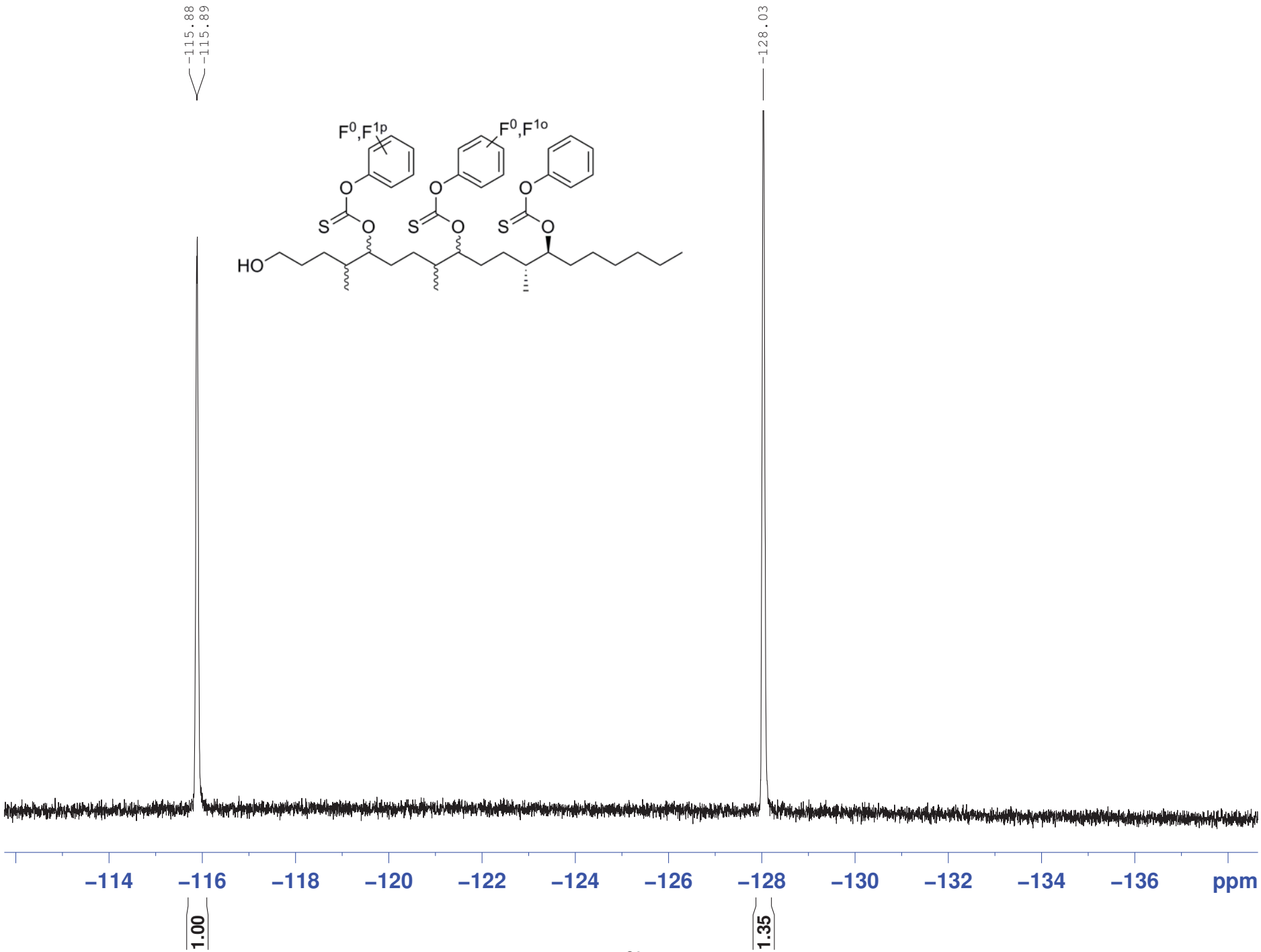
14.17

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O
S
HO
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−126
−128
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−136
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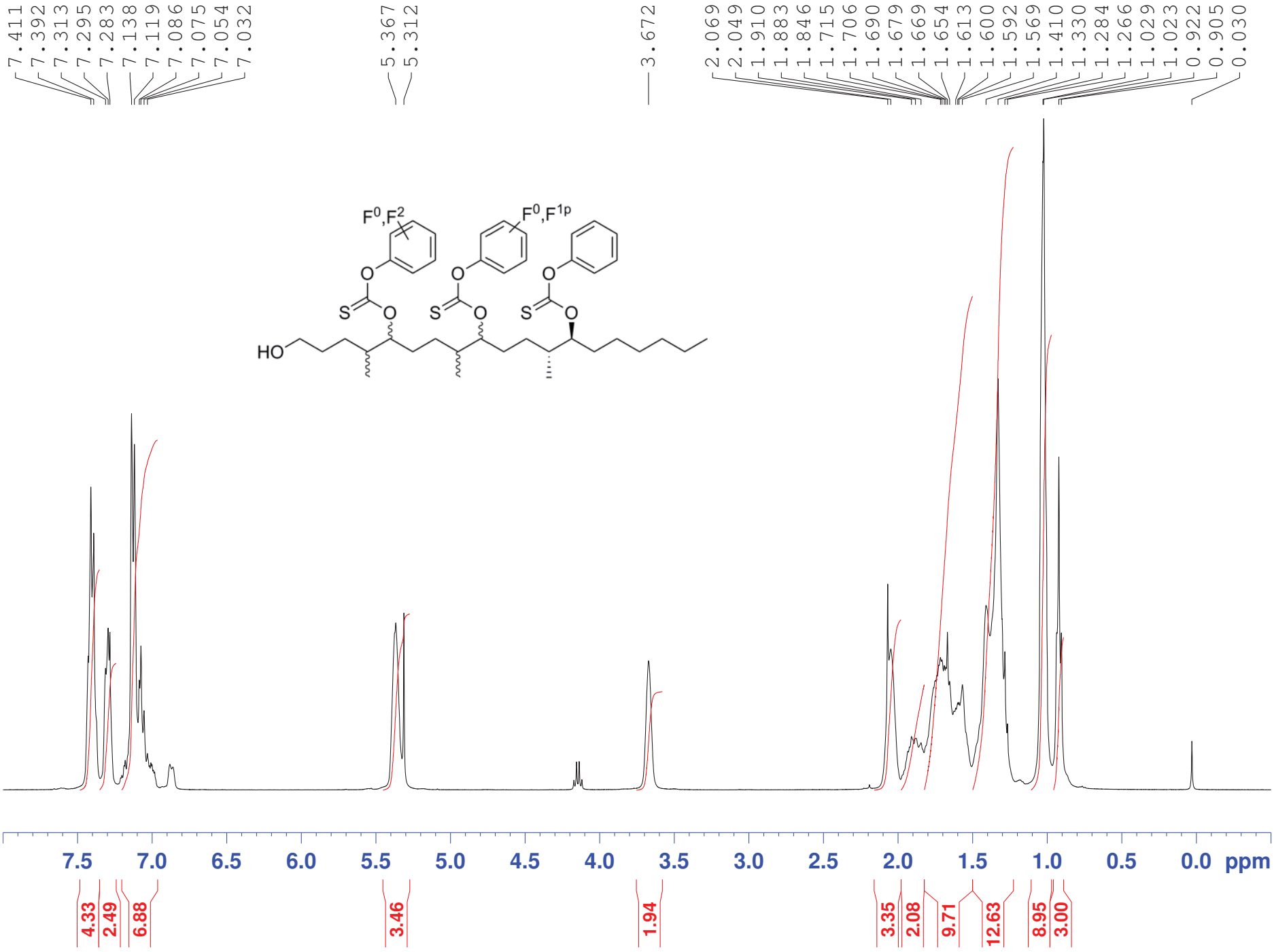
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1.883
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1.715
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1.690
1.679
1.669
1.654
1.613
1.600
1.592
1.569
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1.330
1.284
1.266
1.029
1.023
0.922
0.905
0.030
F0,F2
F0,F1p
HO
S
O
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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3.46
1.94
3.35
2.08
9.71
12.63
8.95
3.00

195.25
195.23
195.15
195.11
153.39
153.36
153.34
153.33
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126.48
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123.64
123.61
123.55
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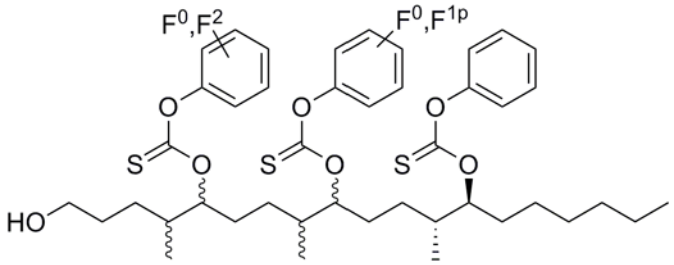

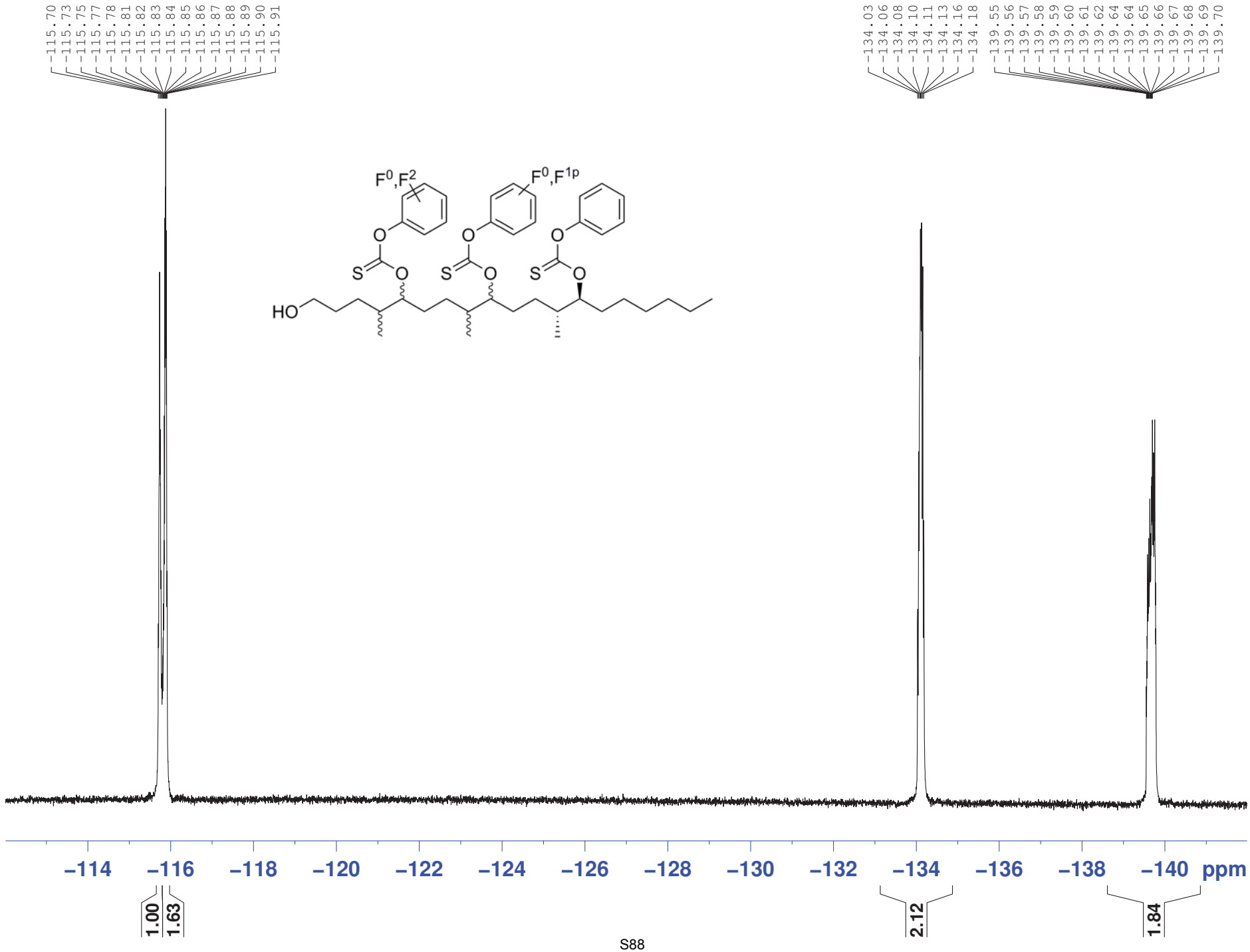
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-115.89
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-139.67
-139.68
-139.69
-139.70
F0,F2
F0,F1p
HO
S
O
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−116
−118
−120
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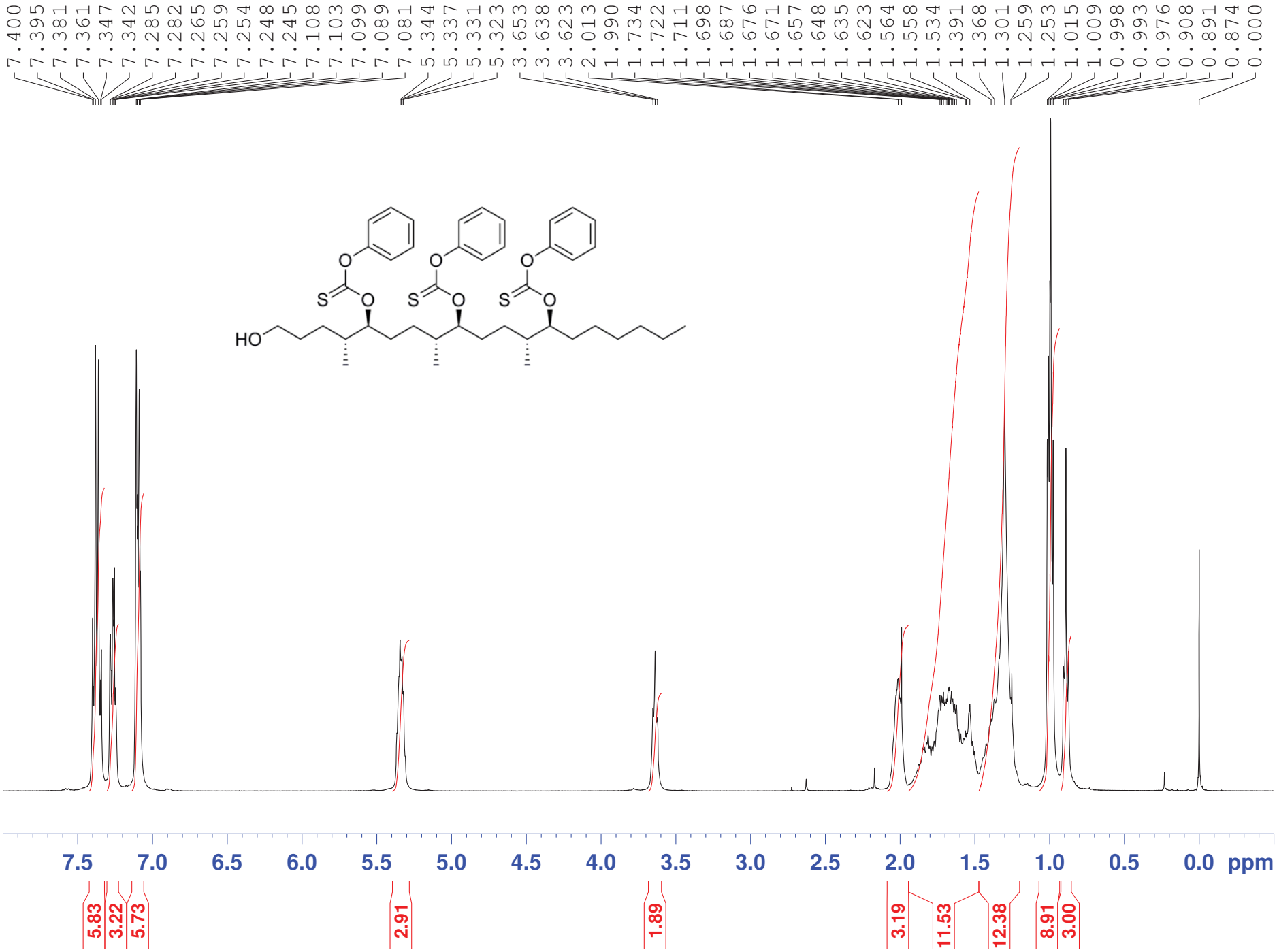
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7.254
7.248
7.245
7.108
7.103
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7.089
7.081
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5.323
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3.638
3.623
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1.671
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0.891
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0.000
HO
S
O
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6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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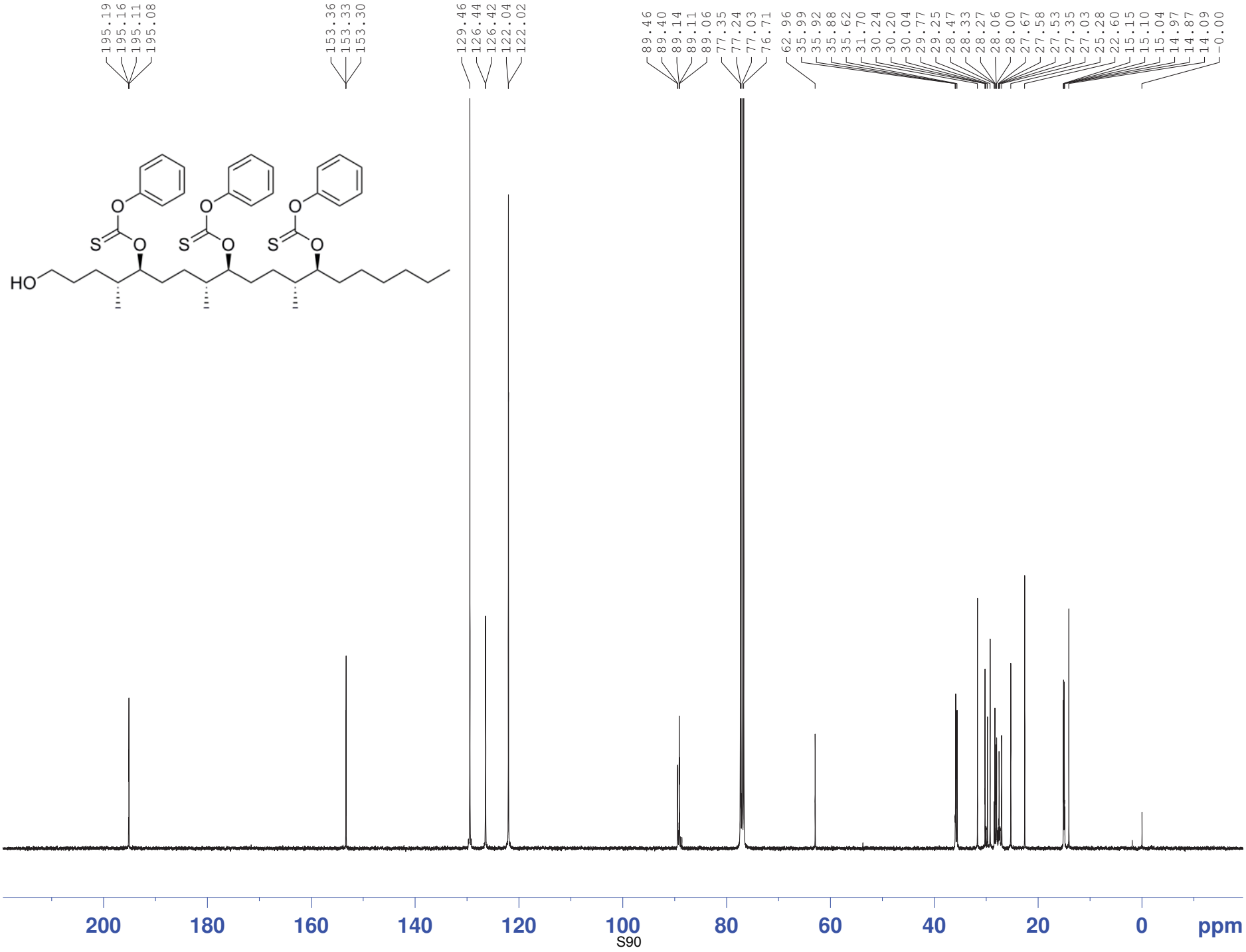
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35.62
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27.03
25.28
22.60
15.15
15.10
15.04
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HO
O
S
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120
100
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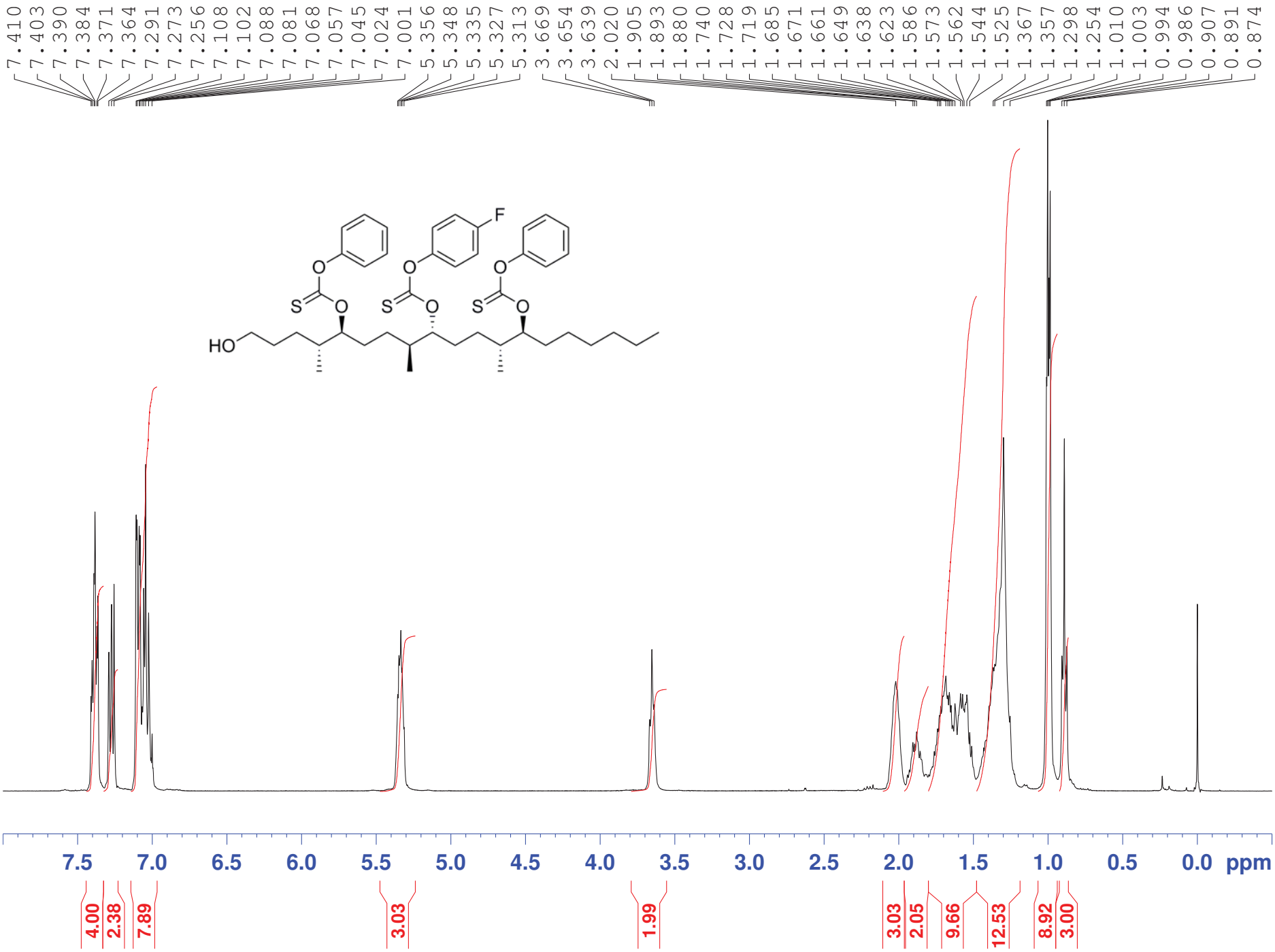
60
40
20
0
ppm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0.891
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F
O
S
HO
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6.0
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4.0
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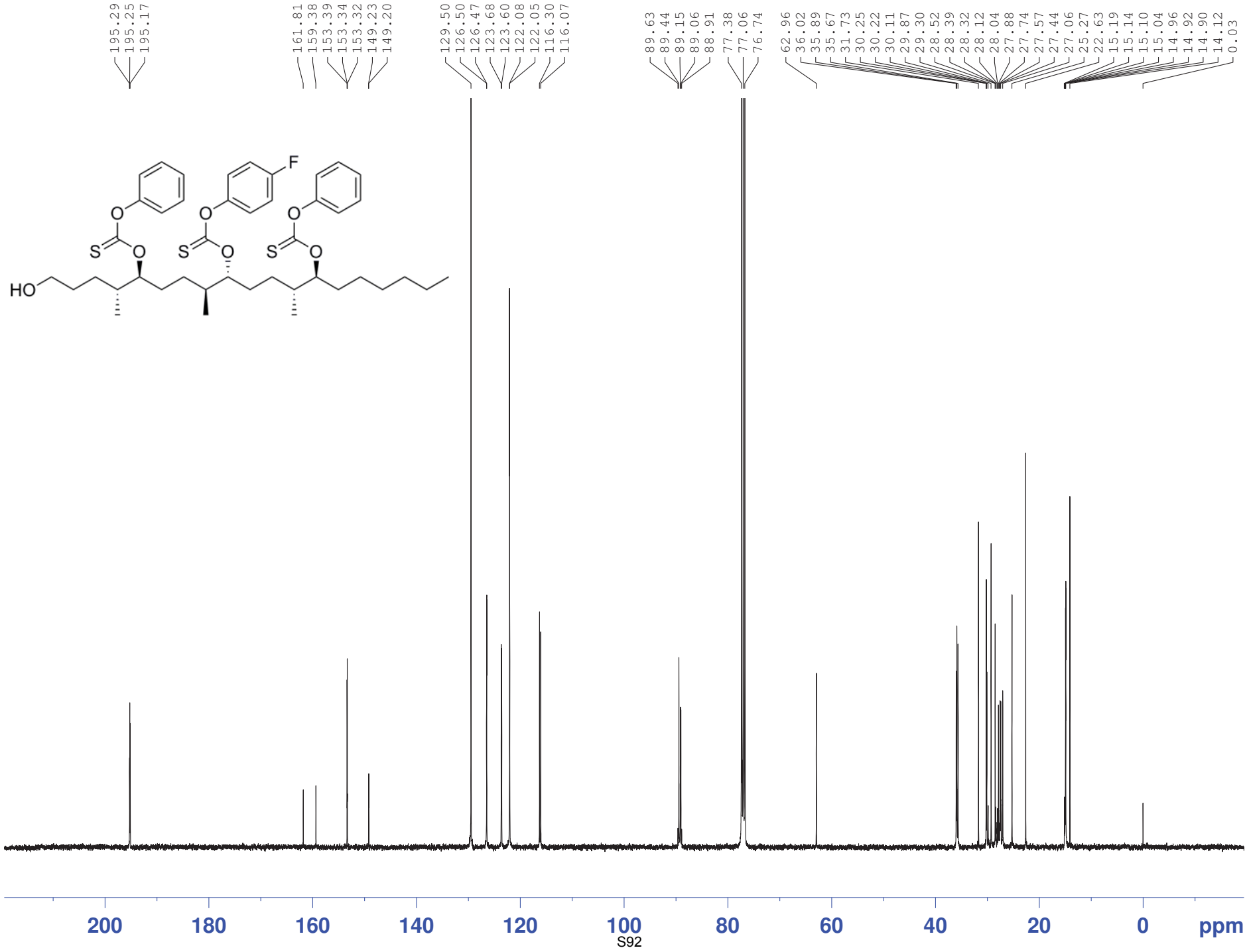
3.00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27.44
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25.27
22.63
15.19
15.14
15.10
15.04
14.96
14.92
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O
S
HO
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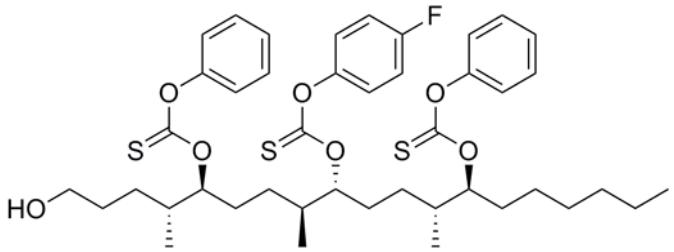
120
100
80
60
40
20
0
ppm


F
O
S
O
HO

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-115.95
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−111
−112
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−114
−115
−116
−117
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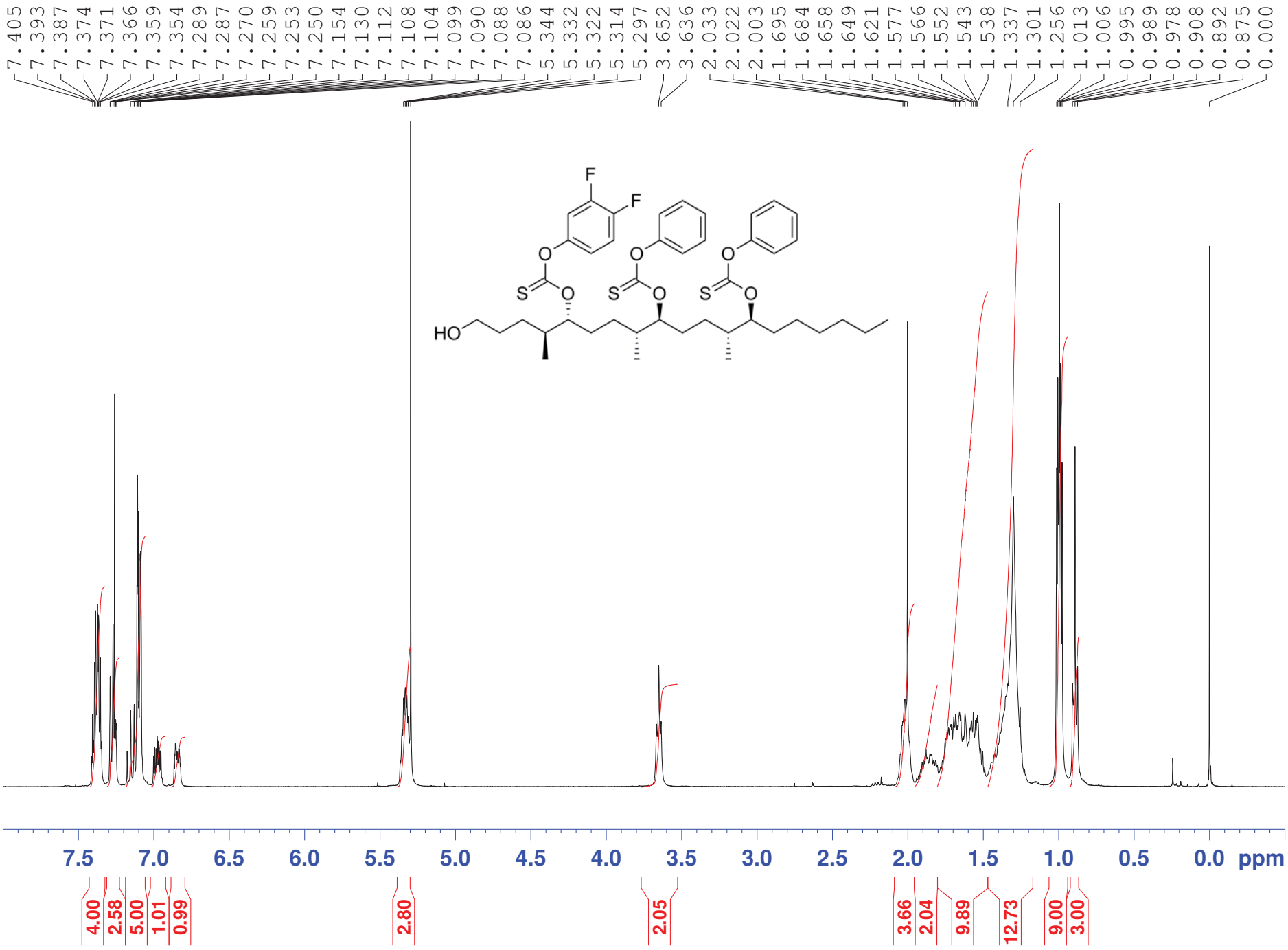
−119
−120
−121
ppm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7.090
7.088
7.086
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5.322
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5.297
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O
S
O
HO
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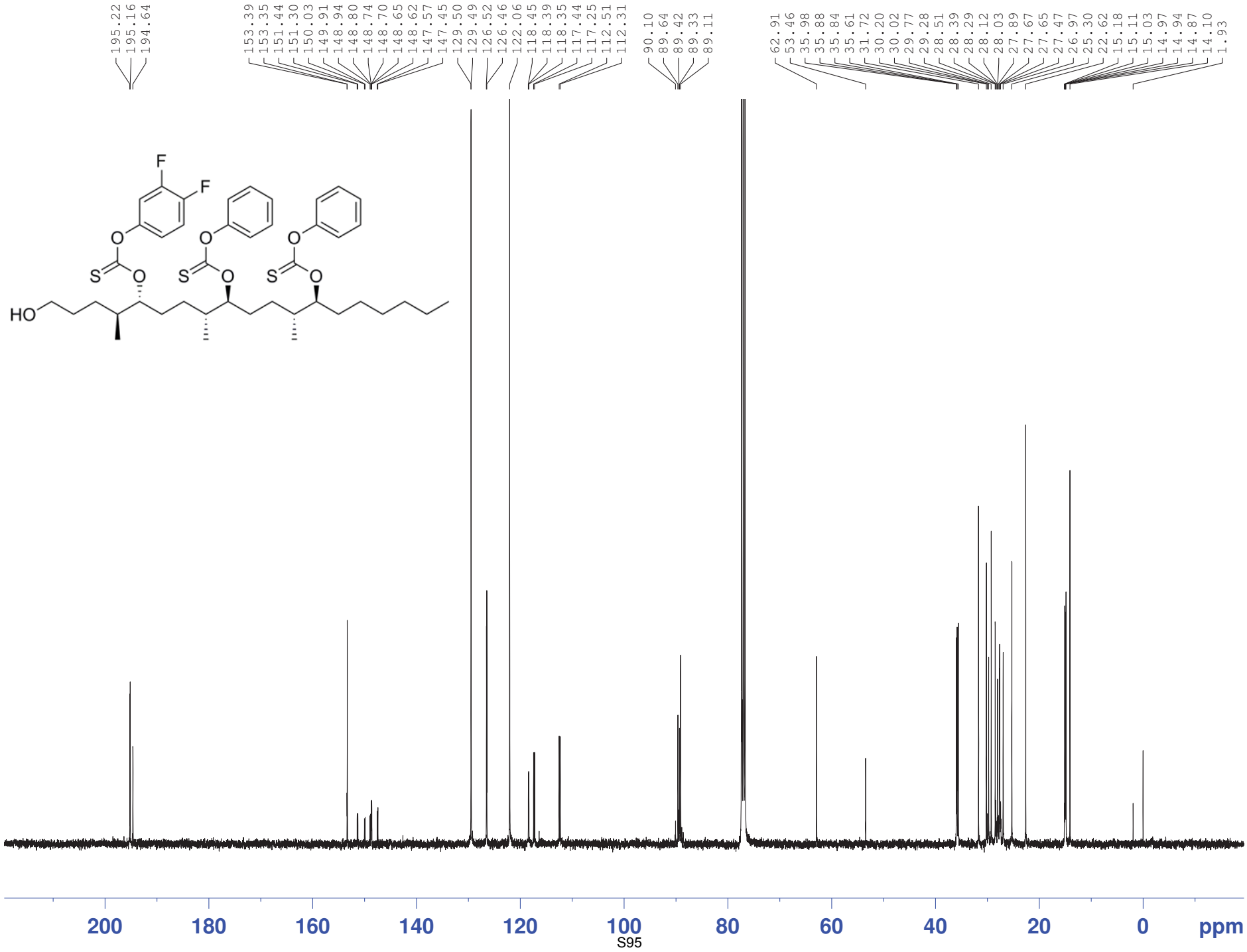
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14.10
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O
S
O
HO
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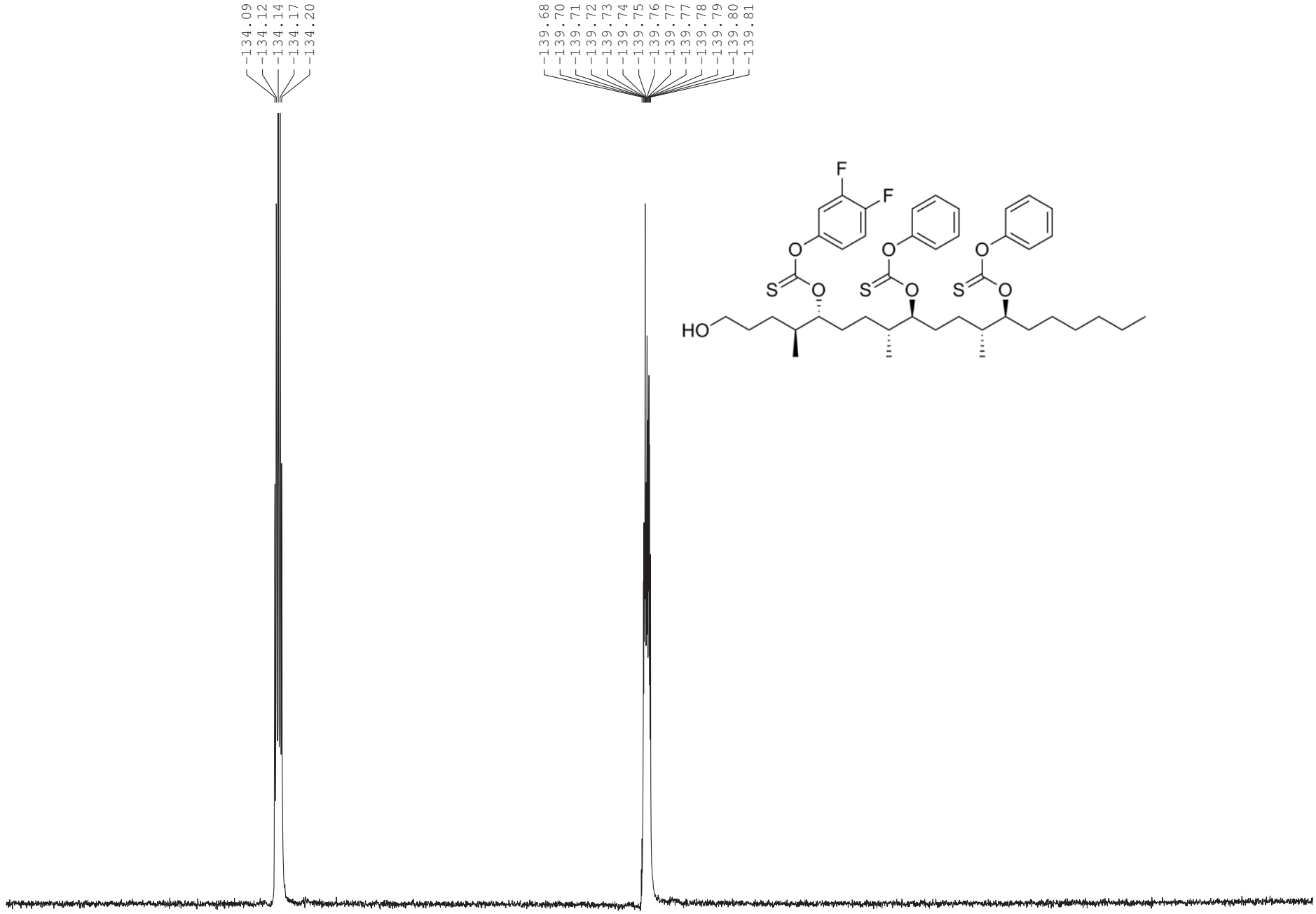
0
ppm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-139.75
-139.76
-139.77
-139.77
-139.78
-139.79
-139.80
-139.81
F
F
O
S
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S
O
HO
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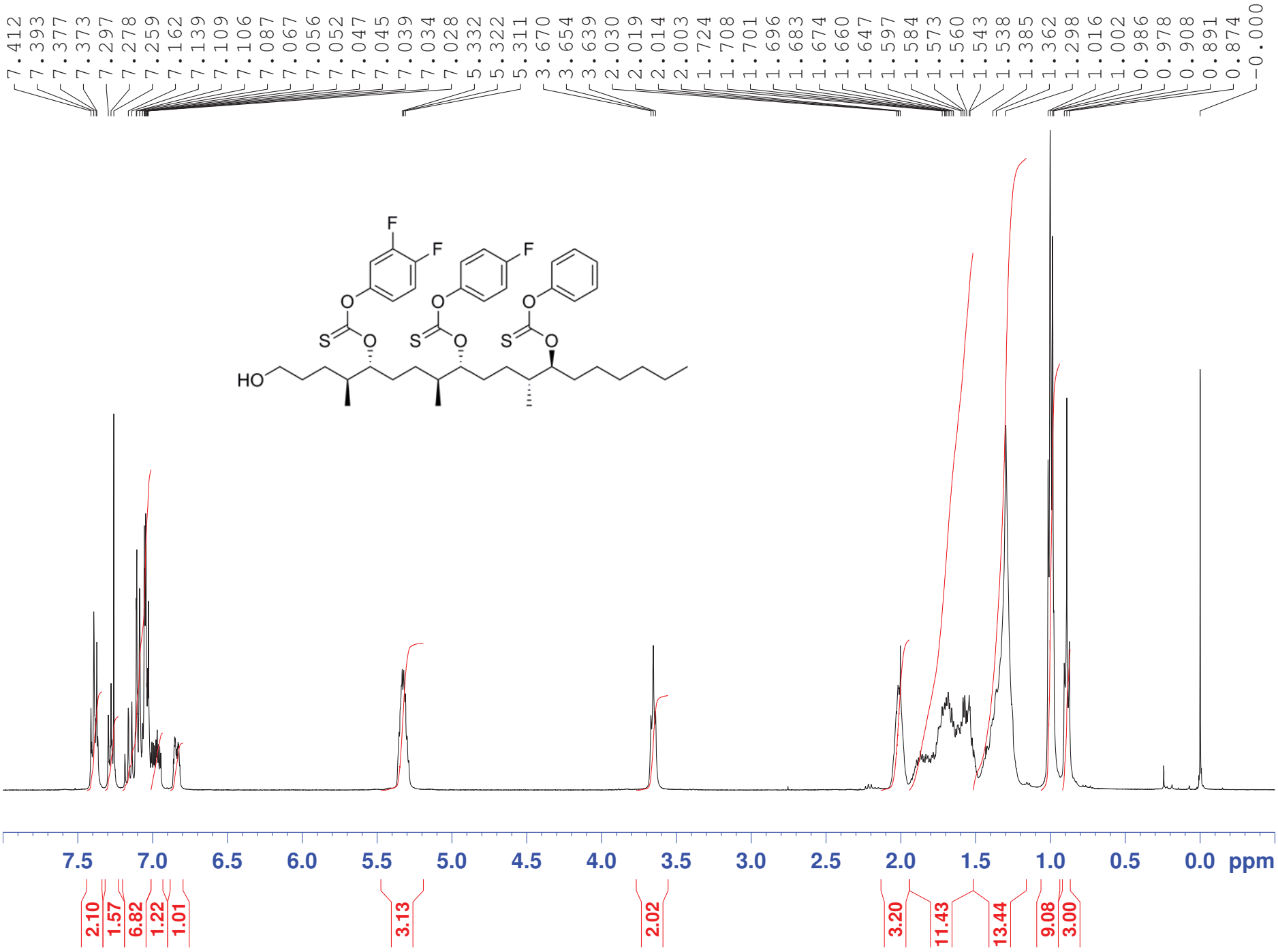
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7.052
7.047
7.045
7.039
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3.639
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2.019
2.014
2.003
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1.696
1.683
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F
F
F
O
O
O
S
O
S
O
S
O
HO
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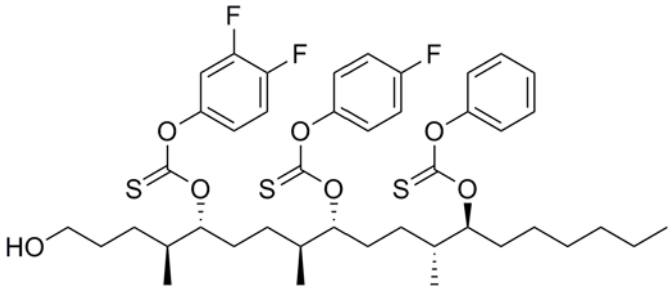

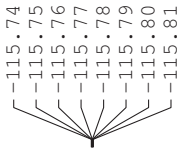
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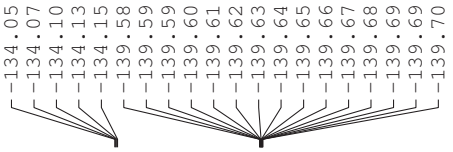
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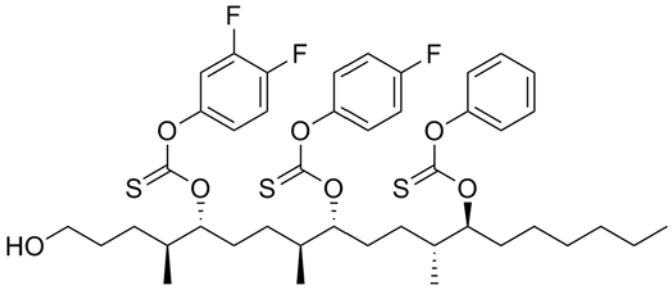
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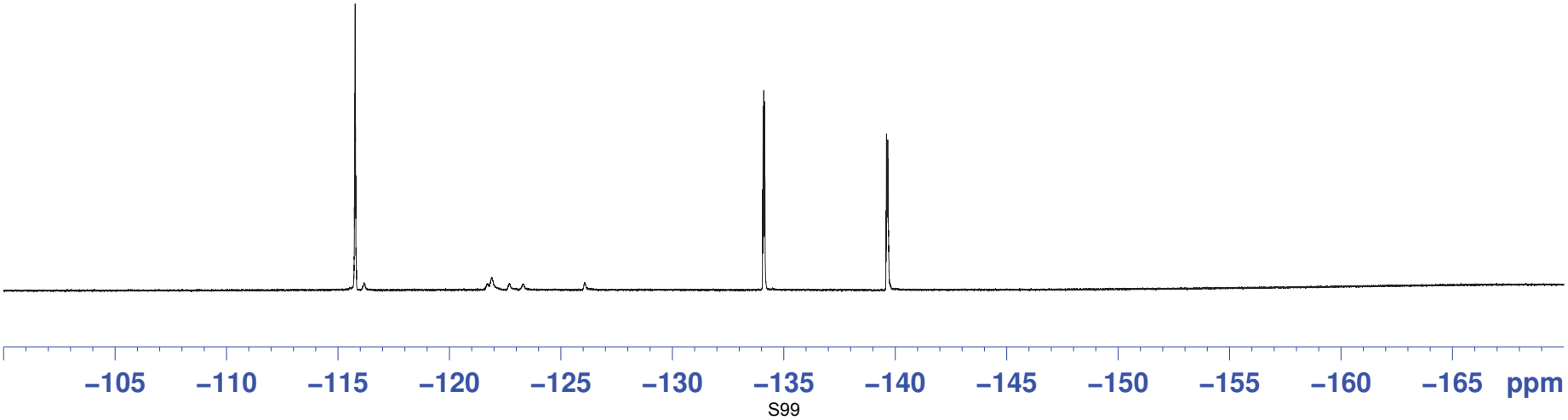
HO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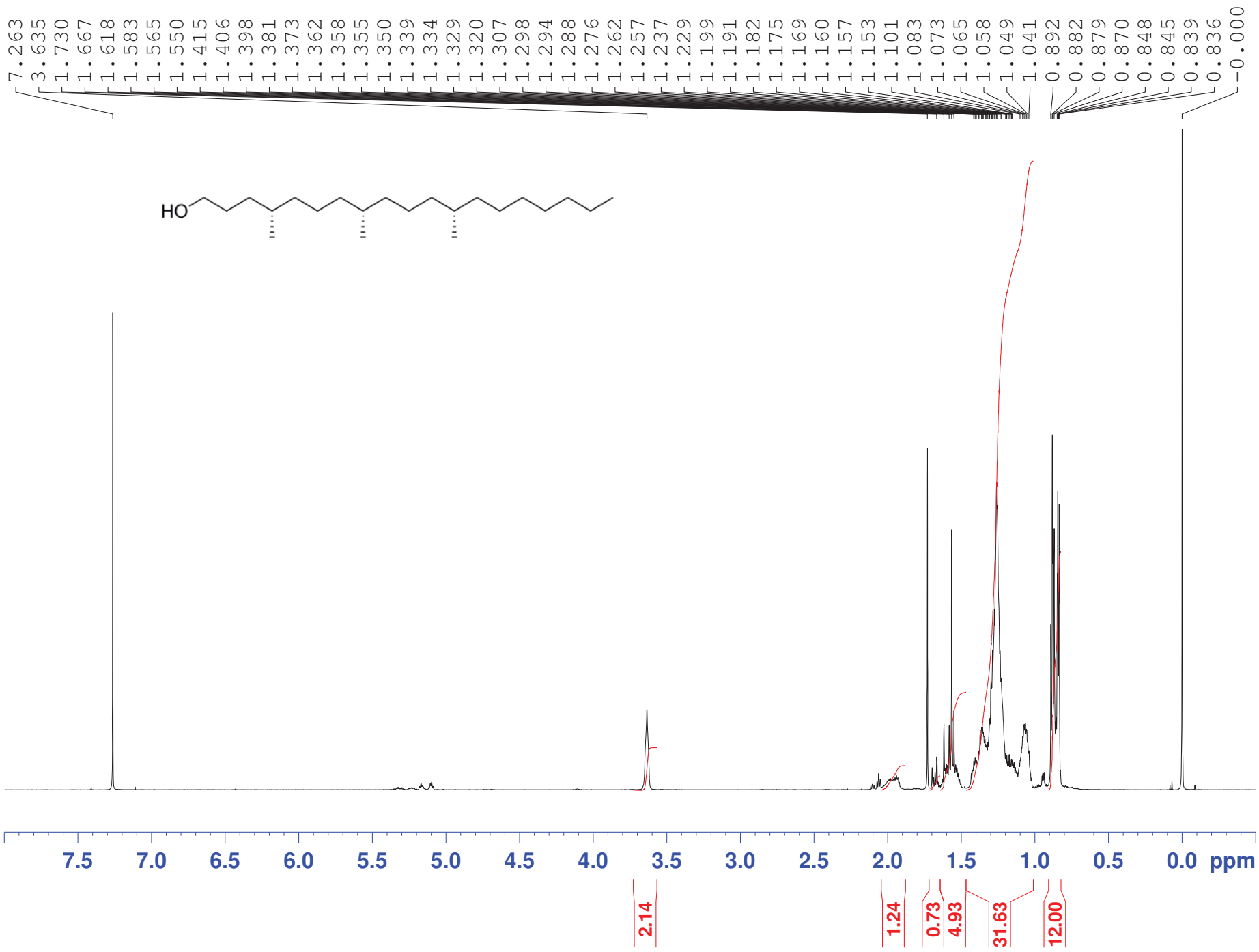
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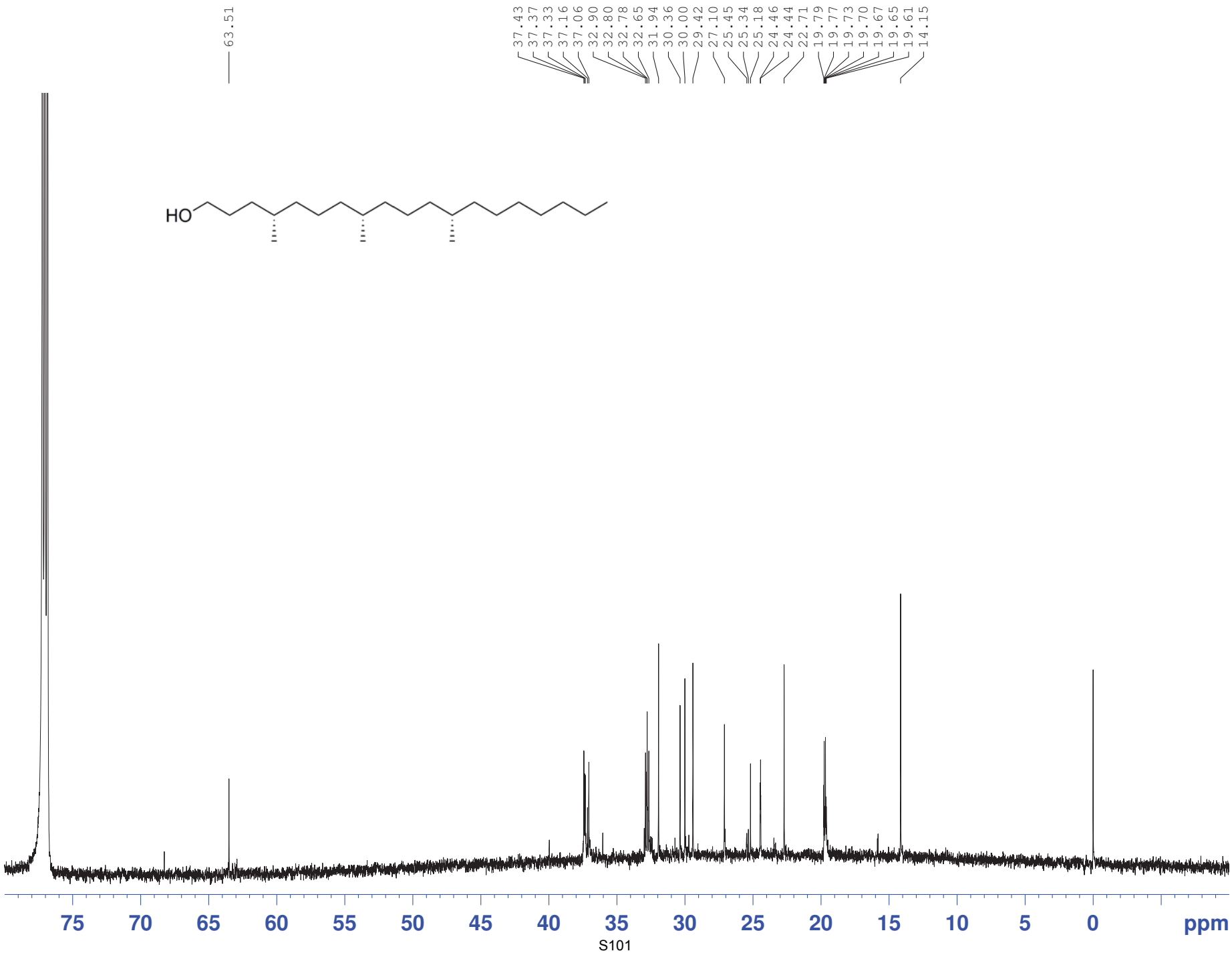
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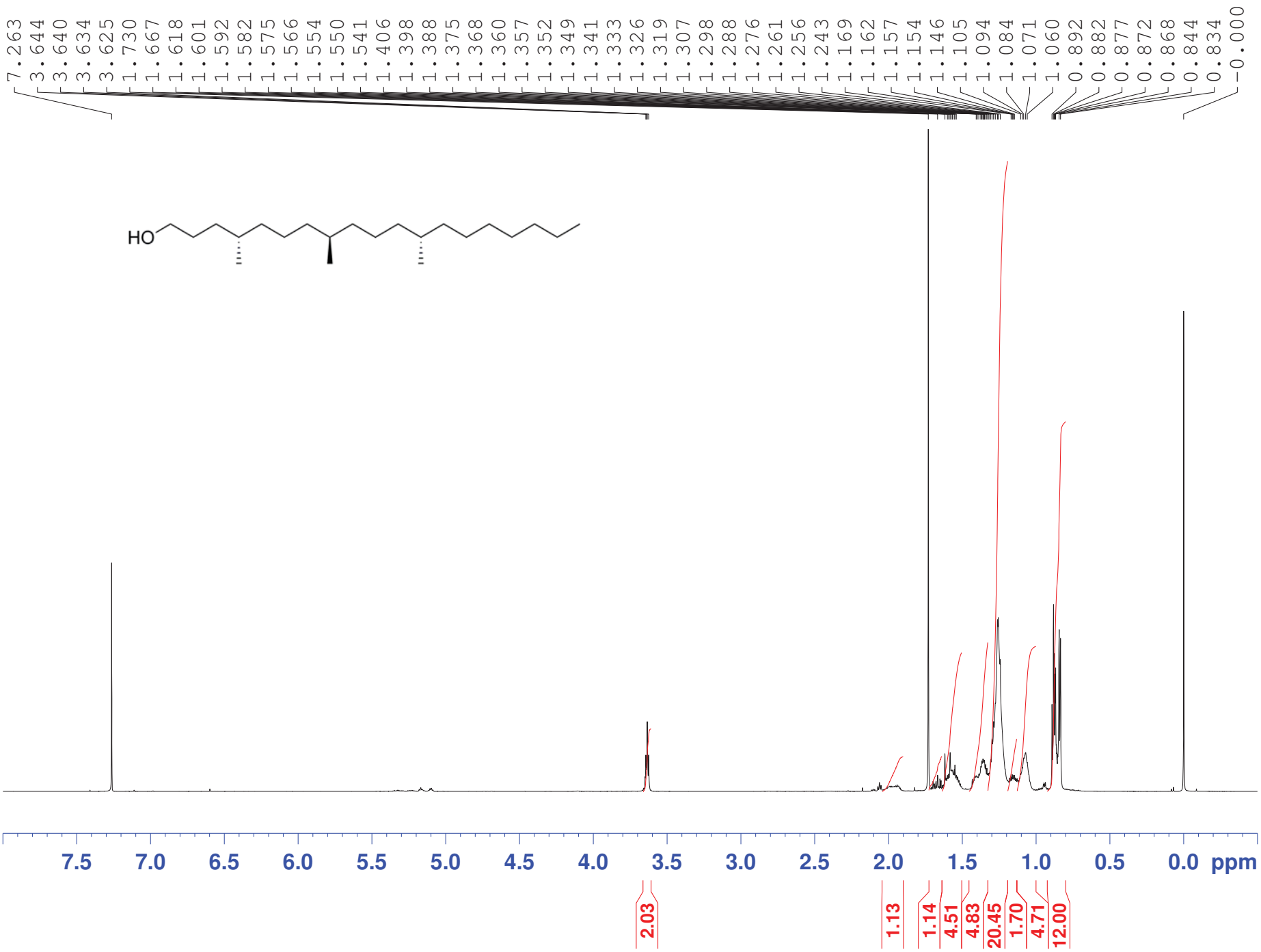
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1.307
1.298
1.288
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1.243
1.169
1.162
1.157
1.154
1.146
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1.071
1.060
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0.882
0.877
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0.844
0.834
-0.000
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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1.14
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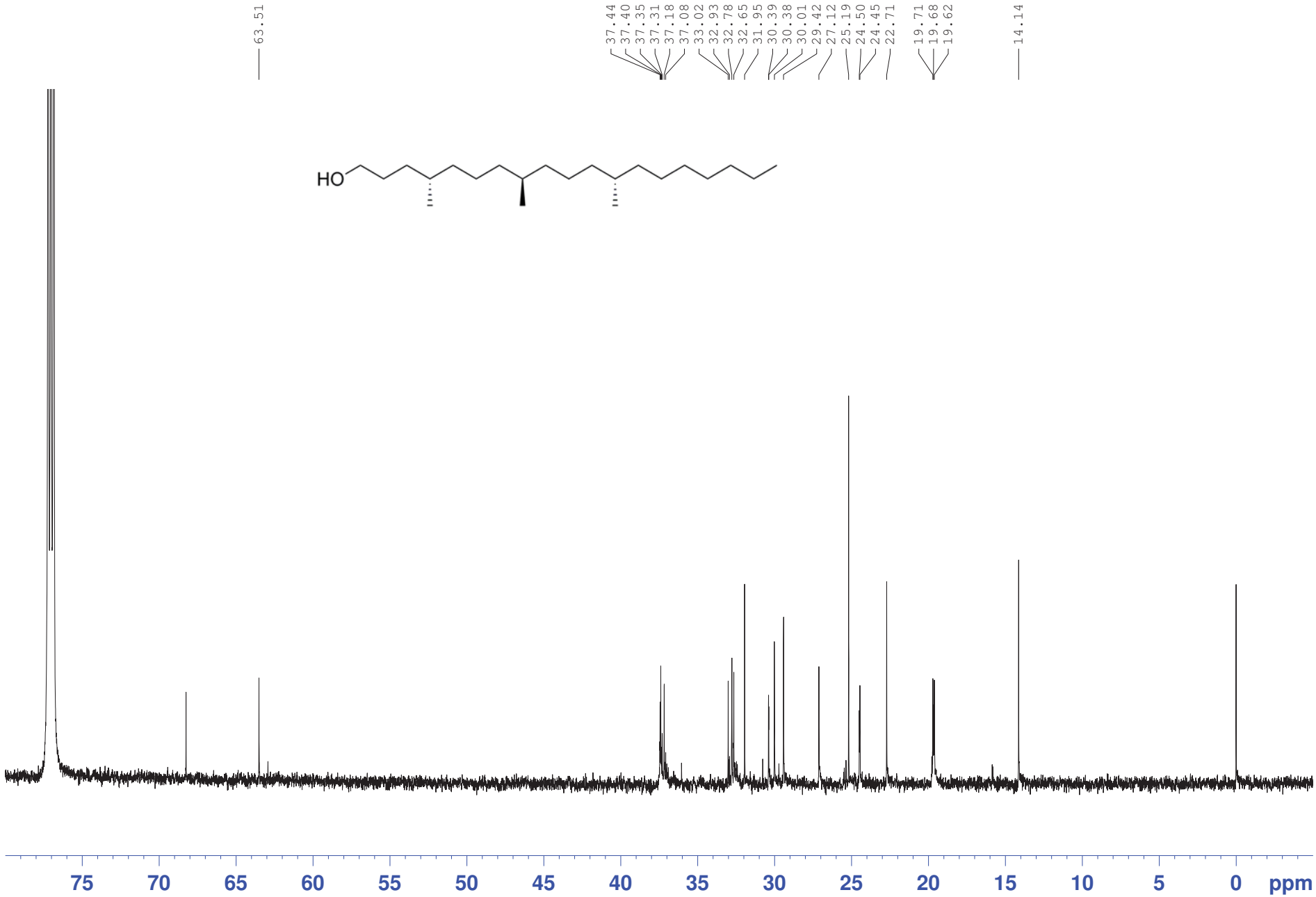
4.71
12.00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27.12
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24.45
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19.71
19.68
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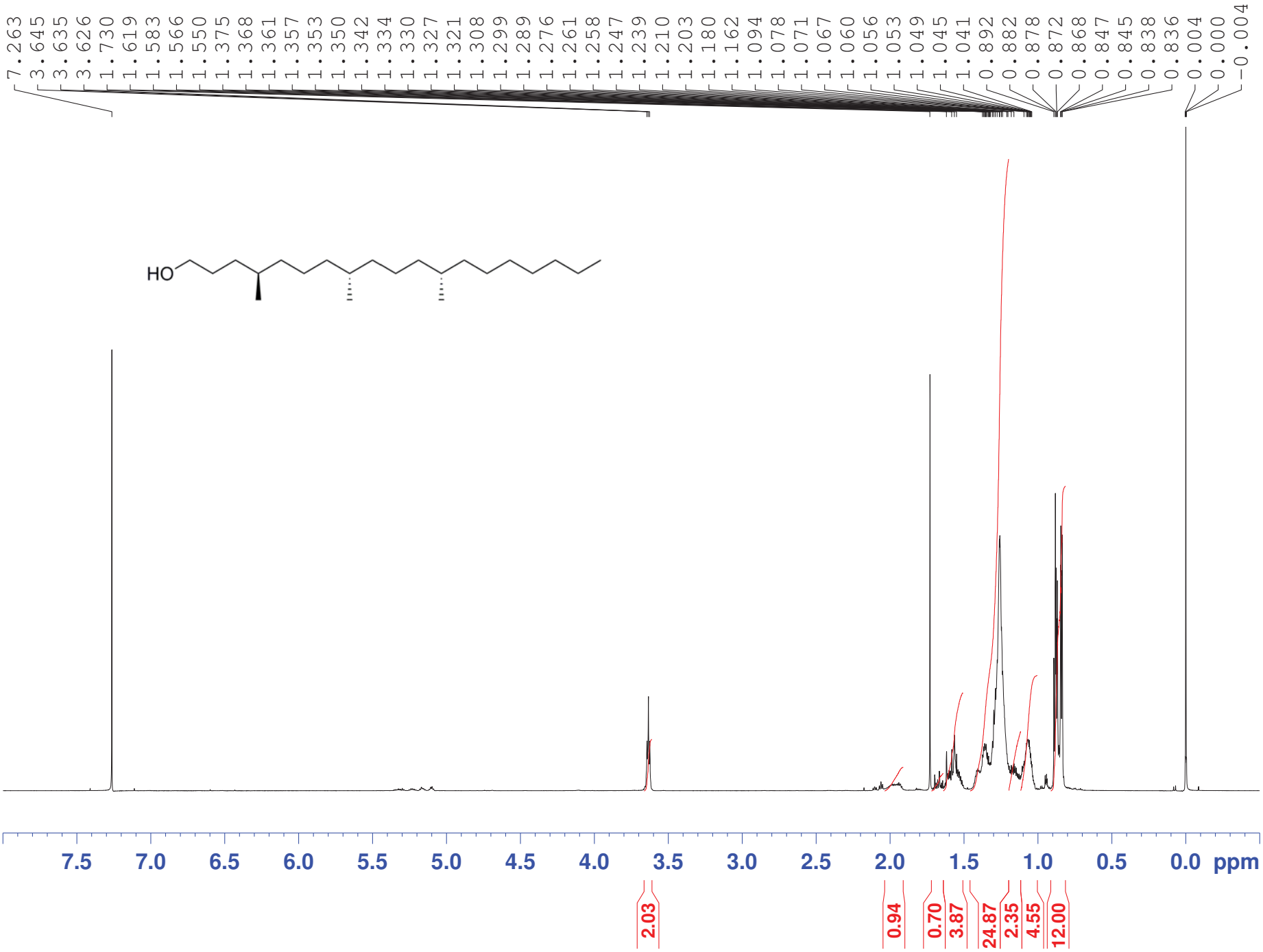
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1.334
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1.321
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1.299
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1.261
1.258
1.247
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1.203
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1.094
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1.071
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1.060
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1.053
1.049
1.045
1.041
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0.882
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0.872
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0.847
0.845
0.838
0.836
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0.000
-0.004
HO
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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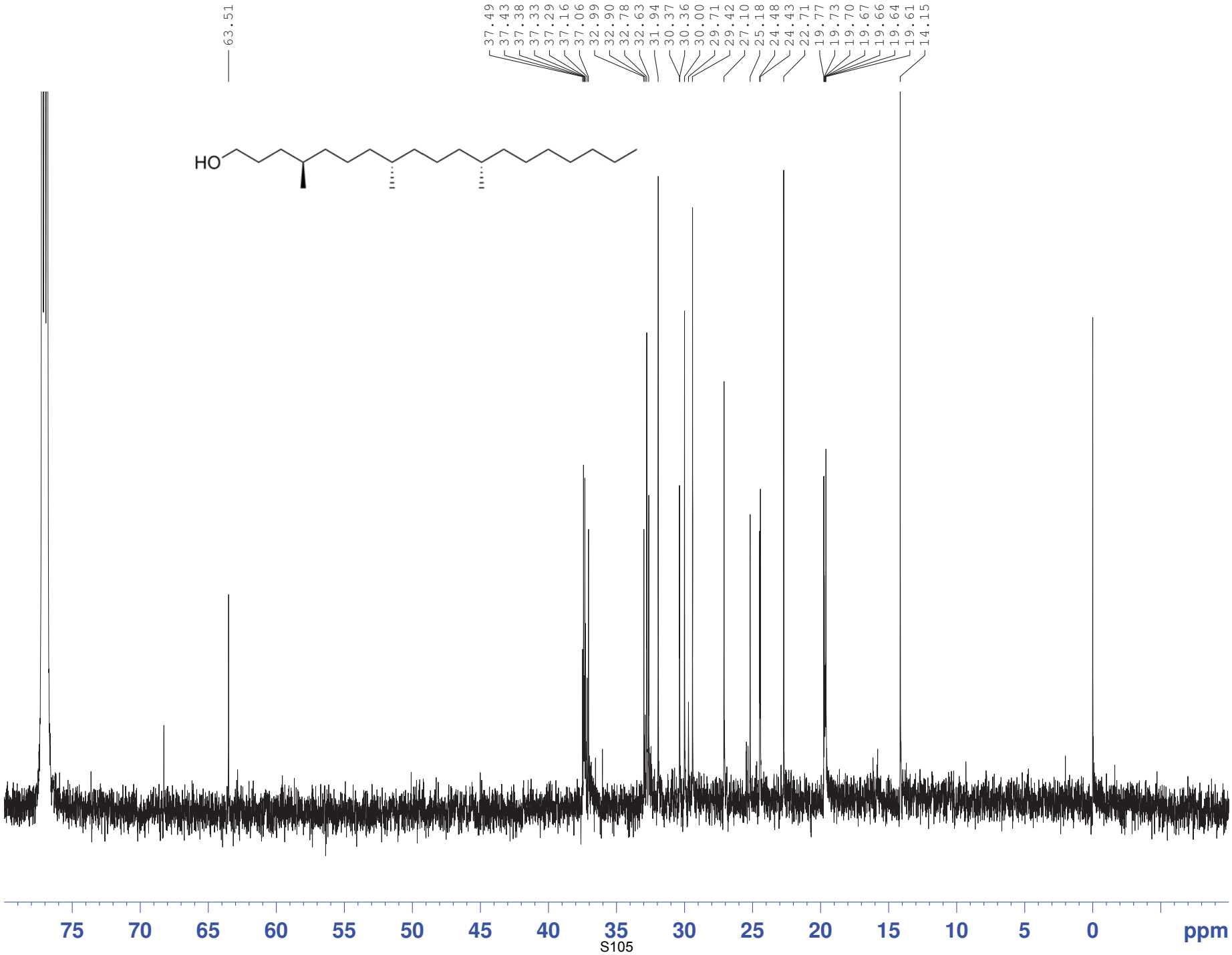
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30.00
29.71
29.42
27.10
25.18
24.48
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22.71
19.77
19.73
19.70
19.67
19.66
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19.61
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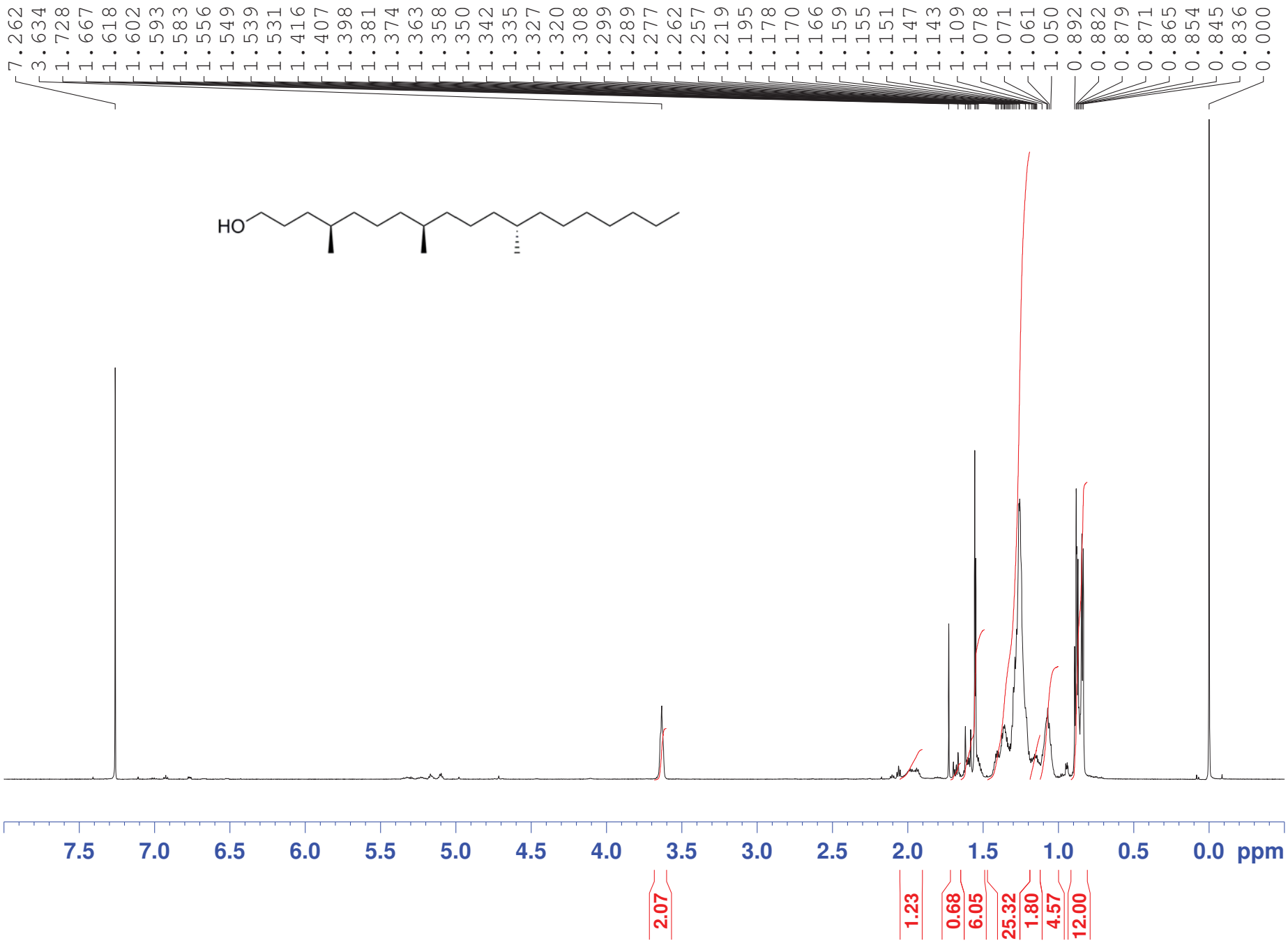
ppm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6.0
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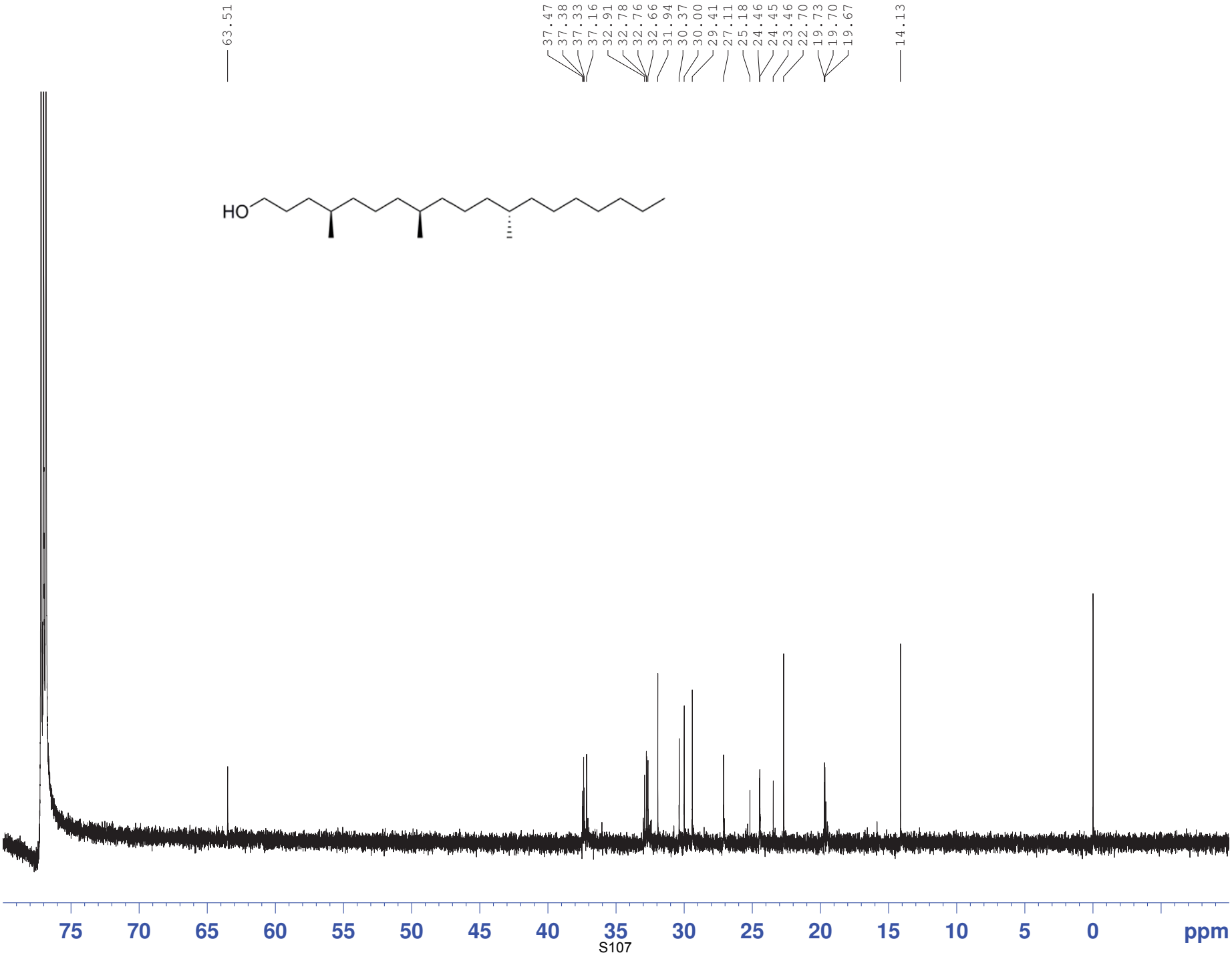
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HO
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15
10
5
0
ppm