An Appraisal of Oxoketene Cycloaddition Methodology for the Synthesis of 2,6-Dideoxysugars and Fluorinated 2,6-Dideoxysugars

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NMR spectra were recorded on a Bruker ARX 250 (^{1}H, 250.13 MHz; ^{13}C, 62.90 MHz; ^{19}F, 235.36 MHz) spectrometer, a Bruker DPX 300 (^{1}H, 300.13 MHz; ^{13}C, 75.47 MHz; ^{19}F, 282.40 MHz, COSY, HMQC, HMBC) spectrometer or a Bruker DRX 400 (^{1}H, 400.13 MHz; ^{13}C, 100.62 MHz; ^{19}F, 376.45 MHz, COSY, HMQC, HMBC, NOESY) spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR spectra were recorded using deuterated solvent as the lock and residual solvent as the internal standard. ^{19}F NMR spectra were referenced to CCl_3F as the external standard. Electron Impact (EI) mass spectra were recorded on Kratos Concept 1H mass spectrometer. Chemical Ionization (CI) mass spectra were recorded on a Kratos Concept 1H mass spectrometer using ammonia as the reagent gas. Fast Atom Bombardment (FAB) mass spectra were recorded on a Kratos Concept 1H mass spectrometer using xenon and *m*-nitrobenzyl alcohol as the matrix. Electrospray (ES) mass spectra were recorded on a Micromass Quattro LC mass spectrometer. High Resolution Mass Spectrometry (HRMS) was measured on a Kratos Concept 1H mass spectrometer using peak matching to stable reference peaks, depending on the technique used (Leicester). Other mass spectra were obtained from the EPSRC's National Mass Spectrometry Service Centre, University of Wales Swansea.

Flash column chromatography was performed using silica gel (Fluorochem, Silica gel 60, 40-63μ) and HPFC Biotage Horizon system with Biotage silica prepacked Flash+ purification cartridges and Samplet sample-loading cartridges. Column fractions were collected and monitored by Thin Layer Chromatography (TLC) carried out on precoated aluminium backed silica gel plates supplied by E. Merck, A.G. Darmstadt, Germany (Silica gel 60 F_{254}, thickness 0.2 mm) or on precoated glass plates supplied by Merck (Silica gel 60 F_{254}). The compounds were visualized using UV light (λ = 254 nm), potassium permanganate, *p*-anisaldehyde, 2,4-dinitrophenylhydrazine or phosphomolybdic acid (PMA) stains. Gas Chromatograms were recorded on a Perkin Elmer Autosystem Gas Chromatograph linked to a Perkin Elmer Turbomass mass spectrometer. The chromatograph was fitted with a PE5 MS (5 % phenyl, 95 % dimethylpolysiloxane phase column (30 m)); experiments were carried out between 45 to 250 ºC with a 10 ºC min^{-1} ramp. Microwave experiments were carried in a CEM Discover instrument (variable power, max. 300W). Infra-red (IR) spectra were obtained on a Perkin Elmer 1600 series FT-IR spectrometer from solution samples in dry CH_2Cl_2 (DCM) in a NaCl cell, or as neat samples in a Perkin Elmer SpectrumOne FT-IR spectrometer. X-Ray reflections were collected on a Bruker SMART APEX 4K CCD diffractometer (R_{int} = 0.0202) using Mo-Kα radiation (λ = 0.71073 Å). Refinement was carried out using SHELXL-97. Light petroleum refers to the fraction boiling between 40-60 ºC. Tetrahydrofuran (THF) was dried by refluxing with benzophenone over sodium wire under an atmosphere of nitrogen, and was distilled and collected by syringe as required. Dichloromethane, diethyl ether, toluene and acetonitrile were dried by refluxing with calcium hydride, they were then distilled and collected by dry syringe as required, or from Pure-Solv Solvent Purification Systems from Innovative Technology, Inc.. Dry DMF was used supplied by Aldrich. Acetone was used as reagent grade. *n*-Butyllithium was titrated immediately before use according to the method described by Duhamel *et al*. using 4-phenylbenzylidene benzylamine as the indicator.

(L. Duhamel and J. C. Plaquevent, *J. Organometal. Chem.*, 1993, **448**, 1-3.)

Additional experimental procedures

***n*-butyl-3,4-(*O*-dibenzyl)-2,6-dideoxy-β-DL-arabino-hexapyranoside 18**

NaH (62 mg, 60% suspension in oil, 1.53 mmol) was added slowly at 0°C to a solution of **17** (104 mg, 0.51 mmol) in THF (20 mL). The reaction mixture was stirred for one hour at this temperature. BnBr (262 mg, 1.53 mmol) and TBAI (40 mg, 0.1 mmol) were added to the mixture at 0 °C and the reaction was allowed to warm to room temperature and stirred for 2 days. Water (10 mL) was added slowly to quench the reaction. The mixture was then extracted with ethyl acetate (3 x 25 mL), and the combined organic extracts were washed with brine (50 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford a yellow oil which was purified by flash chromatography on silica gel to deliver 3,4-(*O*-dibenzyl pyranoside **18** as a colorless oil (184 mg, 94%); R_f (20% ethyl acetate in light petroleum) 0.71; ν_{max} (film)/cm^{-1}: 2930w, 1454w, 1365w, 1094s, 1072s, 988m, 733m, 696m; δ_H ($CDCl_3$, 300MHz); 7.23-7.12 (10 H, m), 4.86 (1 H, part of an AB system, ^2J 10.9), 4.58 (1 H, part of an AB system, ^2J 11.7), 4.56 (1 H, part of an AB system, ^2J 10.9), 4.50 (1 H, part of an AB system, ^2J 11.7), 4.31 (1 H, dd, *J* 8.1, 1.8), 3.78 (1 H, dt, ^2J 9.3, *J* 6.6), 3.53 (1 H, ddd, *J* 13.8, 8.7, 5.1), 3.33 (1 H, dt, ^2J 9.3, 6.9), 3.24 (1 H, dq, *J* 9.2, 6.0), 3.05 (1 H, m incl. app. t, *J* 9.1), 2.25 (1 H, ddd, ^2J 12.6, 5.1, 1.8), 1.59-1.44 (3 H, m), 1.32-1.23 (2 H, m), 1.24 (3 H, d, *J* 6.0), 0.83 (3 H, t, *J* 7.2); δ_C ($CDCl_3$, 75MHz) 138.6, 138.5, 128.5, 128.4, 128.1, 127.75, 127.70, 99.6, 83.8, 79.4, 75.3, 71.4, 69.2, 37.1, 31.8, 19.3, 18.2, 13.9; HRMS (EI^+, M^+) Found: 384.23005, Calc. for $C_{24}H_{32}O_4$ 384.23006; *m*/*z* (EI): 384 (M^+, 2%), 310 (28), 193 (5), 84 (100).

3,4-(*O*-dibenzyl)-2,6-dideoxy-β-DL-arabino-hexapyranoside 19

From pyranoside **18** (77 mg, 0.2 mmol) in THF (2 mL) and HCl (2 mL of a 1N solution) in the microwave (80 °C, 300W, 2 hours). The work-up and isolation were performed as for **17** and the crude product **19** was purified on silica gel to afford 3,4-(*O*-dibenzyl)-pyranoside **19** (36 mg, 55%) as a colourless oil, and as a 59:41 mixture of α- and β-anomers; R_f (20% ethyl acetate in light petroleum) 0.11; Mp 68°C; ν_{max} (film)/cm^{-1}: 3355m, 2842w, 1496w, 1452m, 1114s, 1093s, 1071s, 1003s, 981m, 728s, 691s; δ_H ($CDCl_3$, 300MHz) α-anomer: 7.28-7.16 (10 H), 5.22 (1 H, br. d, *J* 2.7), 4.87 (1 H, d, ^2J 11.0), 4.63-4.50 (3 H, m), 3.98-3.83 (2 H, m), 3.05 (1 H, m incl. app. t, *J* 8.9), 2.98 (1 H, br s), 2.22 (1 H, ddd, ^2J 13.2, *J* 5.1, 1.2), 1.66-1.52 (1 H, m), 1.19 (3 H, d, *J* 6.3), δ_H ($CDCl_3$, 300MHz) β-anomer: 7.28-7.16 (10 H, m), 4.86 (1 H, d, ^2J 10.9), 4.64 (1 H, br. d, *J* 9.6), 4.63-4.50 (3 H, m), 3.63-3.43 (1 H, m), 3.31 (1 H, dq, *J* 9.1, 6.0), 3.05 (1 H, m incl. app. t, *J* 9.1), 2.30 (1 H, ddd, ^2J 12.3, *J* 4.8, 1.8), 1.53-1.38 (1 H, m), 1.23 (3 H, d, *J* 6.0); δ_C ($CDCl_3$, 75MHz) α-anomer: 138.6, 138.5, 128.45, 128.35, 128.05, 127.95, 127.75, 127.70, 91.9, 84.3, 76.9, 75.2, 71.5, 67.4, 35.8, 18.2, δ_C ($CDCl_3$, 75MHz) β-anomer: 138.4, 138.1, 128.55, 128.45, 128.15, 128.05, 127.6, 93.9, 83.4, 79.0, 75.3, 71.8, 71.6, 38.4, 18.2; HRMS (EI^+, M^+) Found: 328.16740, Calc. for $C_{20}H_{24}O_4$ 328.16746; *m*/*z* (EI): 328 (M^+, 4%), 237 (47), 131 (31), 91 (100); t_R (GC) 26.36 min.

_n_-butyl-3-(_O_-methyl)-2,6-dideoxy-β-DL-arabino-hexapyranoside 21

NaH (2.8 g, 60% suspension in oil, 70.0 mmol) was added slowly at 0°C to a solution of crude alcohol **14** (2.53 g, 13.6 mmol, see procedure for **15**) in THF (100 mL). The reaction mixture was stirred for 30 minutes at 0°C. MeI (10.0 g, 70 mmol) was added dropwise to the mixture at 0°C and the reaction was stirred at room temperature for one hour. Water (50 mL) was added slowly at 0 °C to quench the reaction. The mixture was then extracted with ethyl acetate (3 x 100 mL), and the combined organic extracts were washed with brine (100 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford methyl ether **20** as an unstable dark yellow oil which was taken on without purification.

Crude **20** (13.6 mmol) in THF (100 mL) underwent hydroboration/oxidation/hydrolysis as for **14** with $BH_3.SMe_2$ (15.0 mL of a 2.0M solution in THF, 30.0 mmol), and solid $NaBO_3.H_2O$ (10.0 g, 65.0 mmol). The reaction, work-up and product isolation were carried out as for **15**. The residue was purified by flash chromatography to deliver 3-*O*-methylpyranoside **21** as a yellow oil (170 mg, 6% over 3 steps); R_f (50% ethyl acetate in light petroleum) 0.38; ν_{max} (film)/cm^{-1}: 3446m, 2959m, 2934m, 2872m, 1374m, 1167m, 1102m, 1067s, 988m, 903m; δ_H ($CDCl_3$, 300MHz); 4.38 (1 H, dd, *J* 9.9, 2.1), 3.80 (1 H, dt, ^2J 9.6, *J* 6.6), 3.37 (1 H, dt, ^2J 9.6, *J* 6.9), 3.32 (3 H, s), 3.25-3.03 (3 H, m), 2.25 (1H, ddd, ^2J 12.3, 4.5, 2.1), 1.56-1.46 (2 H, m), 1.42-1.18 (3 H, m), 1.26 (3 H, d, *J* 6.0), 0.85 (3 H, t, *J* 7.5); δ_C ($CDCl_3$, 75MHz) 99.6, 80.4, 75.1, 71.6, 69.1, 56.1, 35.2, 31.6, 19.1, 17.8, 13.8; HRMS (EI^+, M^+) Found: 218.15186, Calc. for $C_{11}H_{22}O_4$ 218.15181; *m*/*z* (EI): 217 ($M\text{-}H^+$, 5%), 174 (15), 145 (27), 118 (71), 101 (89), 87 (30), 74 (100); t_R (GC) 13.92 min.

3-(_O_-methyl)-2,6-dideoxy-β-DL-arabino-hexapyranoside 22 (Oleandrose)

From pyranoside **21** (277 mg, 1.27 mmol) in THF (3 mL) and HCl (3 mL of a 1N solution) in the microwave (80°C, 300W 1 hour). The work-up and isolation were performed as for **17** and the crude product **22** (DL-oleandrose) (30 mg, 15%) was obtained as a colorless oil, as a 64:36 mixture of α- and β-anomers; R_f (50% ethyl acetate in light petroleum) 0.08; ν_{max} (film)/cm^{-1}: 3396m, 2934w, 1075s, 1046s, 984s, 734m; δ_H ($CDCl_3$, 300MHz) α-anomer: 5.30 (1 H, br. d, *J* 3.0), 3.87 (1 H, dq, *J* 9.3, 6.3), 3.52 (1 H, ddd, *J* 11.4, 9.0, 4.8), 3.34 (3 H, s), 3.15-3.05 (1 H, m), 2.24 (1 H, ddd, ^2J 12.6, *J* 4.8, 1.2), 1.43 (1 H, ddd, ^2J 12.6, *J* 11.4, 3.6), 1.22 (3 H, d, *J* 6.3), δ_H ($CDCl_3$, 300MHz) β-anomer: 4.76 (1 H, dd, *J* 9.6, 2.0), 3.36-3.29 (1 H, m), 3.34 (3 H, s), 3.19-3.02 (2 H, m), 2.35 (1 H, ddd, ^2J 12.0, *J* 4.2, 2.0), 1.38-1.26 (1 H, m), 1.28 (3 H, d, *J* 6.3); δ_C ($CDCl_3$, 75MHz) α-anomer: 92.2, 77.9, 76.2, 67.7, 56.5, 33.9, 17.9, δ_C ($CDCl_3$, 75MHz) β-anomer: 94.1, 80.5, 75.3, 71.8, 56.3, 36.6, 17.9; HRMS (EI^+, M^+) Found: 162.08916, Calc. for $C_7H_{14}O_4$ 162.08921; *m*/*z* (CI): 162 (M^+, 62%), 145 (100), 130 (23), 113 (22); (GC) t_R (GC) 11.18 min. The NMR data were in agreement with those reported by Toshima. (K. Toshima, T. Yoshida, S. Mukaiyama and K. Tatsuta, *Carbohydr. Res.*, 1991, **222**, 173-188).

_n_-butyl-3-(_O_-benzyl)-2,6-dideoxy-β-DL-arabino-hexapyranoside 24

NaH (540 mg, 60% suspension in oil, 14.0 mmol) was added slowly at –78 °C to a solution of crude **14** (521 mg, 2.8 mmol, see procedure for **15**) in a mixture of THF (50 mL) and DMF (10 mL). The reaction mixture was stirred for 30 minutes, allowing warming from –78°C to 0°C. BnBr (2.39 g, 14.0 mmol) was added to the mixture at 0 °C and the reaction was stirred at room temperature for 2 hours. Water (30 mL) was added slowly at 0°C to quench the reaction. The mixture was extracted with ethyl acetate (3 x 50 mL), and the combined organic extracts were washed with brine (30 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford benzyl ether **23** as a yellow oil which was used to the next step without any further purification.

Crude **23** (2.8 mmol) in THF (70 mL) underwent hydroboration/oxidation/hydrolysis as for **14** with $BH_3.SMe_2$ (3.0 mL of a 2.0M solution in THF, 6.0 mmol), and solid $NaBO_3.H_2O$ (2.31 g, 15.0 mmol). The reaction, work-up and product isolation were carried out as for **15**. The residue was purified by flash chromatography to deliver 3-(*O*-benzyl pyranoside **24** as a yellow oil (267 mg, 32% over 2 steps); R_f (20% ethyl acetate in light petroleum) 0.28; ν_{max} (film)/cm^{-1}: 3454w, 2871w, 1369m, 1096m, 1068s, 988m, 697m; δ_H ($CDCl_3$, 300MHz); 7.24-7.18 (5 H, m), 4.60 (1 H, part of an AB system, ^2J 11.7), 4.39 (1 H, part of an AB system, ^2J 11.7), 4.35 (1 H, dd, *J* 9.9, 1.8), 3.80 (1 H, dt, ^2J 9.6, *J* 6.6), 3.40-3.29 (2 H, m), 3.26-3.11 (2 H, m), 2.42 (1 H, br s), 2.26 (1 H, ddd, ^2J 12.3, 4.8, 1.8), 1.55-1.44 (3 H, m), 1.36-1.18 (2 H, m), 1.26 (3 H, d, *J* 5.7), 0.85 (3 H, t, *J* 7.2); δ_C ($CDCl_3$, 75MHz) 138.1, 128.6, 127.9, 127.8, 99.7, 79.0, 75.7, 71.1, 70.4, 68.9, 36.1, 31.7, 19.2, 17.9, 13.9; HRMS (EI^+, M^+) Found: 294.18305, Calc. for $C_{17}H_{26}O_4$ 294.18311; *m*/*z* (EI): 294 (M^+, 2%), 222 (8), 91 (100); t_R (GC) 21.19 min.

_n_-butyl-3-(_O_-benzyl)-4-(_O_-methyl)-2,6-dideoxy-β-DL-arabino-hexapyranoside 25

A solution of **24** (55 mg, 0.194 mmol) in THF (20 mL) was treated with NaH (16 mg, 60% suspension in oil, 0.40 mmol) followed by MeI (85 mg, 0.6 mmol) at room temperature as for **16**. The work-up and isolation were performed as for **16** and the crude product **25** (59 mg, 99%) was characterised and used without purification: R_f (20% ethyl acetate in light petroleum) 0.66; ν_{max} (film)/cm^{-1}: 2931w, 1454w, 1368w, 1094s, 1073m, 997m, 734m, 696m; δ_H ($CDCl_3$, 300MHz); 7.22-7.17 (5 H, m), 4.58 (1 H, part of an AB system, ^2J 12.0), 4.53 (1 H, part of an AB system, ^2J 12.0), 4.30 (1 H, dd, *J* 9.9, 2.0), 3.87 (1 H, dt, ^2J 9.5, *J* 6.6), 3.52 (3 H, s), 3.42 (1 H, ddd, *J* 11.8, 8.7, 5.2), 3.34 (1 H, dt, ^2J 9.5, *J* 6.9), 3.15 (1 H, dq, *J* 9.0, 6.0), 2.76 (1 H, m incl. app. t, *J* 9.0), 2.21 (1 H, ddd, ^2J 12.6, *J* 5.2, 2.0), 1.54-1.45 (3 H, m), 1.33-1.20 (2 H, m), 1.25 (3 H, d, *J* 6.0), 0.84 (3 H, t, *J* 7.5); δ_C ($CDCl_3$, 75MHz) 138.5, 128.4, 127.6, 99.5, 85.9, 79.3, 71.45, 71.40, 69.1, 61.0, 37.0, 31.7, 19.2, 18.0, 13.9; HRMS (EI^+, M^+) Found: 308.19872, Calc. for $C_{18}H_{28}O_4$ 308.19876; *m*/*z* (EI): 308 (M^+, 2%), 234 (5), 91 (100); t_R (GC) 20.70 min.

(2R*,4R*)-2-_n_-butoxy-4-methoxy-6-(fluoromethyl)-2,3-dihydro-4_H_-pyran 33

Was prepared from pyranol **30a** (100 mg, 0.49 mmol) in THF (20 mL), sodium hydride (40 mg, 60%

suspension in oil, 1.0 mmol) and iodomethane (213 mg, 1.5 mmol) as for **20** (see procedure for **21**)**.** Work-up and isolation described for **20** afforded methyl ether **33** as an oil (104 mg, estimated yield 99%) which was characterised and used without purification; R_f (20% ethyl acetate in light petroleum) 0.50; ν_{max} (film)/cm^{-1}: 2936w, 1670m, 1118m, 1050s, 1019s, 660; δ_H ($CDCl_3$, 300MHz); 5.09 (1 H, t, *J* 3.1), 5.00 (1 H, dd, *J* 6.6, 2.5), 4.63 (1 H, part of an ABX system, $^2J_{H\text{-}F}$ 47.6, ^2J 11.2), 4.60 (1 H, part of an ABX system, $^2J_{H\text{-}F}$ 47.3, ^2J 11.2), 3.94-3.91 (1 H, m), 3.78 (1 H, dt, ^2J 9.9, *J* 6.6), 3.45 (1 H, dt, ^2J 9.9, *J* 6.6), 3.28 (3 H, s), 2.24 (1 H, dddd, ^2J 13.6, 6.6, 2.5, 0.6), 2.24 (1 H, dt, ^2J 13.6, 6.6), 1.55-1.47 (2 H, m), 1.33-1.24 (2 H, m), 0.84 (3 H, t, *J* 7.2); δ_C ($CDCl_3$, 75MHz) 148.5 (d, $^2J_{C\text{-}F}$ 15.7), 101.7 (d, $^3J_{C\text{-}F}$ 7.5), 98.4, 81.3 (d, $^1J_{C\text{-}F}$ 168.0), 69.5, 68.9, 55.6, 33.0, 31.5, 19.9, 13.7; δ_F ($CDCl_3$, 282MHz) (–219.5)-(-220.0) (m incl. app. t, $^2J_{F\text{-}H}$ 47.4) HRMS (EI^+, M^+) Found: 218.13177, Calc. for $C_{11}H_{19}FO_3$ 218.13182.

_n_-butyl-3-(_O_-methyl)-2,6-dideoxy-6-fluoro-β-DL-arabino-hexapyranoside 34

Was prepared as for **15** from crude **33** (0.49 mmol) in THF (10 mL), $BH_3.SMe_2$ (0.5 mL of a 2.0M solution in THF, 1.0 mmol) and $NaBO_3.H_2O$ (308 mg, 2.0 mmol). The work-up and isolation described for **15** followed by flash chromatography afforded 3-(*O*-methyl pyranoside **34** as a colorless oil (38 mg, 33% over 2 steps); R_f (50% ethyl acetate in light petroleum) 0.44; ν_{max} (film)/cm^{-1}: 3438w, 2959w, 2873w, 1737w, 1374w, 1106m, 1072s, 985m, 963m; δ_H ($CDCl_3$, 300MHz); 4.62 (1 H, part of an ABMX system, $^2J_{H\text{-}F}$ 47.4, ^2J 9.9, *J* 1.7), 4.56 (1 H, part of an ABMX system, $^2J_{H\text{-}F}$ 47.4, ^2J 9.9, *J* 4.5), 4.43 (1 H, dd, *J* 9.9, 2.1), 3.85 (1 H, dt, ^2J 9.6, *J* 5.4), 3.45-3.28 (6 H, m, (including 3.33 (3 H, s)), 3.19 (1 H, ddd, *J* 12.0, 7.5, 4.8), 2.28 (1 H, ddd, ^2J 12.6, 4.8, 2.1), 1.58-1.22 (5 H, m), 0.85 (3 H, t, *J* 7.2); δ_C ($CDCl_3$, 75MHz) 99.9, 82.5 (d, $^1J_{C\text{-}F}$ 171.1), 80.8, 74.5 (d, $^2J_{C\text{-}F}$ 18.0), 69.4, 69.3, 56.3, 34.9, 31.7, 19.2, 13.8; δ_F ($CDCl_3$, 282MHz) –233.3 (td, $^2J_{F\text{-}H}$ 47.4, $^3J_{F\text{-}H}$ 22.8); HRMS (EI^+, M^+) Found: 235.13450, Calc. for $C_{11}H_{20}FO_4$ 235.13456; *m*/*z* (EI): 235 ($M\text{-}H^+$, 2%), 178 (4), 163 (12), 74 (100); t_R (GC)14.97 min.

3-(_O_-Methyl)-2,6-dideoxy-6-fluoro-β-DL-arabino-hexapyranoside 35

Was prepared from **34** (19 mg, 0.08 mmol) in THF (5 mL) and HCl (5 mL of a 1N aqueous solution) in an Ace tube at 70°C over 90 minutes as described for **27**. Work-up and isolation described for **27** followed by chromatography on silica gel afforded 3-(*O*-methyl)-pyranose **35** (14 mg, 93%) as a yellow oil, as a 69:31 mixture of α- and β-anomers; R_f (20% ethyl acetate in light petroleum) 0.46; ν_{max} (film)/cm^{-1}: 3354m, 2942w, 1268w, 1078m, 1021s, 988s, 735m; δ_H (Acetone d_6, 300MHz) α-anomer: 5.19 (1 H, br. d, *J* 2.4), 4.58-4.31 (2 H, m), 3.77 (1 H, dddd, $^3J_{H\text{-}F}$ 27.2, *J* 10.2, 4.3, 2.0), 3.43 (1 H, ddd, *J* 11.5, 8.7, 4.9), 3.24 (3 H, s), 3.24-3.12 (1 H, m), 2.74 (1 H, br s), 2.05 (1 H, ddd, ^2J 12.6, *J* 4.9, 1.2), 1.24 (1 H, ddd, ^2J 12.6, *J* 11.5, 3.6), δ_H (Acetone d_6, 300MHz) β-anomer: 4.68 (1 H, dd, *J* 9.6, 1.6), 4.58-4.31 (2 H, m), 3.35-3.06 (6 H, m (including 3.25 (3 H, s,))), 2.18 (1 H, ddd, ^2J 12.3, *J* 4.2, 1.6), 1.21-1.09 (1 H, m); δ_C ($CDCl_3$, 75MHz) α-anomer: 92.4, 82.6 (d, $^1J_{C\text{-}F}$ 171.4), 77.9, 70.9 (d, $^2J_{C\text{-}F}$ 17.2), 69.8 (d, $^3J_{C\text{-}F}$ 7.3), 56.5, 33.6, δ_C ($CDCl_3$, 75MHz) β-anomer: 94.4, 82.3 (d, $^1J_{C\text{-}F}$ 170.3), 80.6, 74.5 (d, $^2J_{C\text{-}F}$ 18.4), 69.0, 56.4, 36.1; δ_F

(Acetone d_6, 282MHz) α-anomer: –234.5 (td, $^2J_{F-H}$ 47.9, $^3J_{F-H}$ 27.2), δ_F (Acetone d_6, 282MHz) β-anomer: –233.5 (td, $^2J_{F-H}$ 47.9, $^3J_{F-H}$ 24.5); HRMS (EI^+, M^+) Found: 180.07962, Calc. for $C_7H_{13}FO_4$ 180.07979; *m/z* (EI): 180 (M^+, 2%), 162 (2), 130 (9), 87 (100); t_R (GC)12.54 min.

Prep of *n*-butyl-3-(*O*-benzyl)-2,6-dideoxy-6-fluoro-β-DL-arabino-hexapyranoside 37 *via* (2R*, 4R*)-2-*n*-butoxy-4-benzyloxy-6-(fluoromethyl)-2,3-dihydro-4*H*-pyran 36 Was prepared as for **23** (see procedure for **24**) from **30a** (100 mg, 0.49 mmol), NaH (40 mg, 60% suspension in oil, 1.0 mmol) and BnBr (256 mg, 1.5 mmol) in THF (25 mL). The work-up an isolation described for **23** afforded benzyl ether **36** as a yellow oil which was used without purification.

A solution of crude **36** (0.49 mmol) in THF (30 mL) was treated with $BH_3.SMe_2$ (0.5 mL of a 2.0M solution in THF, 1.0 mmol), water (2 mL) and $NaBO_3.H_2O$ (308 g, 2.0 mmol) as described for **14**. The work-up and isolation described for **15** followed by flash chromatography (20% ethyl acetate in hexane) afforded 3-(*O*-benzyl) pyranoside **37** as a white solid (76 mg, 50% over 2 steps); R_f (20% ethyl acetate in hexane) 0.22; mp 58-60 ^oC; ν_{max} (film)/cm^{-1}: 3346w, 2962w, 2931w, 1366m, 1102m, 1064s, 981s, 954m, 869m, 745m, 696s; δ_H ($CDCl_3$, 300MHz); 7.33-7.17 (5 H, m), 4.60 (1 H, part of an AB, ^2J 11.6), 4.58 (1 H, part of an ABMX system, $^2J_{H-F}$ 47.6, ^2J 9.8, *J* 1.8), 4.52 (1 H, part of an ABMX system, $^2J_{H-F}$ 47.6, ^2J 9.8, *J* 4.7), 4.41-4.36 (2 H, m (incl. 4.39 (1 H, part of an AB, ^2J 11.6)), 3.83 (1 H, dt, ^2J 9.6, *J* 6.6), 3.45-3.27 (4 H, m), 2.56 (1 H, br s), 2.26 (1 H, ddd, ^2J 12.6, 4.2, 1.8), 1.56-1.44 (3 H, m), 1.35-1.23 (2 H, m), 0.84 (3 H, t, *J* 7.2); δ_C ($CDCl_3$, 75MHz) 137.9, 128.6, 128.0, 127.8, 99.9, 82.5 (d, $^1J_{C-F}$ 171.3), 78.9, 74.5 (d, $^2J_{C-F}$ 18.1), 70.8, 69.5 (d, $^3J_{C-F}$ 7.2), 69.3, 35.7, 31.7, 19.2, 13.9; δ_F ($CDCl_3$, 282MHz) –233.2 (td, $^2J_{F-H}$ 47.6, $^3J_{F-H}$ 22.6); HRMS (EI^+, M^+) Found: 312.17364, Calc. for $C_{17}H_{25}FO_4$ 312.17369; *m/z* (EI): 311 ($M-H^+$, 2%), 238 (8), 220 (5), 132 (40), 91 (100); t_R (GC) 21.86 min. Satisfactory microsanalysis could not be obtained for this compound.

***n*-Butyl-3-(*O*-benzyl)-4-(*O*-methyl)-2,6-dideoxy-6-fluoro-β-DL-arabino-hexapyranoside 38**

Was prepared from **37** (75 mg, 0.24 mmol), sodium hydride (20 mg, 60% suspension in oil, 0.48 mmol) and MeI (102 mg, 0.72 mmol) in THF (20 mL) as described for **20** (see preparation of **21**). The work-up and isolation described for **20** followed by flash chromatography (20% ethyl acetate in hexane) afforded **38** (73 mg, 94%); R_f (20% ethyl acetate in light petroleum) 0.47; ν_{max} (film)/cm^{-1}: 2930w, 1454w, 1369m, 1116s, 1096s, 1074s, 991m, 735m, 697m; δ_H ($CDCl_3$, 300MHz); 7.31-7.10 (5 H, m), 4.59-4.37 (2 H, m incl. app. d, $^2J_{H-F}$ 47.4), 4.53 (1 H, part of an AB system, ^2J 11.7), 4.47 (1 H, part of an AB system, ^2J 11.7), 4.28 (1 H, dd, *J* 9.6, 1.6), 3.74 (1 H, dt, ^2J 9.5, *J* 6.6), 3.48-3.37 (4 H, m (incl. 3.44 (3 H, s))), 3.28 (1 H, dt, ^2J 9.5, *J* 6.6), 3.26-2.99 (2 H, m), 2.15 (1 H, ddd, ^2J 12.6, *J* 4.8, 1.6), 1.52-1.38 (3 H, m), 1.28-1.16 (2 H, m), 0.77 (3 H, t, *J* 7.2); δ_C ($CDCl_3$, 75MHz) 138.4, 128.40, 127.7, 127.6, 99.9, 82.3 (d, $^1J_{C-F}$ 171.7), 79.0, 78.9 (d, $^3J_{C-F}$ 6.1), 74.3 (d, $^2J_{C-F}$ 18.5), 71.4, 69.2, 60.7, 36.6, 31.7, 19.2, 13.9; δ_F ($CDCl_3$, 282MHz) –232.4 (td, $^2J_{F-H}$ 47.4, $^3J_{F-H}$ 25.7); HRMS (EI^+, M^+) Found: 326.18934, Calc. for $C_{18}H_{27}FO_4$ 326.18934; *m/z*

(EI): 325 (M-H^+, 2%), 252 (4), 220 (4), 163 (19), 130 (21), 90 (100); t_R (GC) 21.39 min.

_n_-butyl-3-(_O_-benzyl)-4-(_O_-methyl)-6-fluoro-2,6-dideoxy-β-DL-arabino-hexapyranoside 39

Was prepared from **38** (73 mg, 0.22 mmol) in absolute ethanol (10 mL) containing 10% palladium-on-carbon (25 mg, 0.022 mmol) under an atmosphere of hydrogen as described for **26**. The work-up and isolation described for **26** followed by chromatography on silica gel (20% ethyl acetate in hexane) afforded 4-(*O*-methyl) pyranoside **39** (45 mg, 86%) as a white solid; R_f (50% ethyl acetate in light petroleum) 0.5; Mp 50-52 ^oC; ν_{max} (film)/cm^{-1}: 3342m, 2937m, 2869m, 1462m, 1372m, 1113s, 1098s, 1067s, 1012s, 973s, 952s, 895m, 867m; δ_H ($CDCl_3$, 300MHz); 4.60 (1 H, part of an ABMX system, $^2J_{H\text{-}F}$ 47.8, ^2J 10.0, J 2.1), 4.55 (1 H, part of an ABMX system, $^2J_{H\text{-}F}$ 47.8, ^2J 10.0, J 3.0), 4.45 (1 H, dd, J 9.3, 2.1), 3.82 (1 H, dt, ^2J 9.5, J 6.6), 3.66 (1 H, ddd, J 11.6, 8.7, 5.2), 3.50 (3 H, s), 3.37 (1 H, dt, ^2J 9.5, J 6.6), 3.24 (1 H, dddd, $^2J_{H\text{-}F}$ 27.3, J 9.6, 3.0, 2.1), 3.02 (1 H, m incl. app. t, J 9.0), 2.41 (1 H, s), 2.13 (1 H, ddd, ^2J 12.6, 5.2, 2.1), 1.59 (1 H, ddd, ^2J 12.6, J 11.6, 9.3), 1.54-1.46 (2 H, m,), 1.33-1.26 (2 H, m), 0.85 (3 H, t, J 7.5); δ_C ($CDCl_3$, 75MHz) 99.8, 82.2 (d, $^1J_{C\text{-}F}$ 172.5), 80.7 (d, $^3J_{C\text{-}F}$ 5.2), 74.5 (d, $^2J_{C\text{-}F}$ 18.7), 71.4, 69.2, 60.7, 38.5, 31.6, 19.2, 13.8; δ_F ($CDCl_3$, 282MHz) –231.7 (td, $^2J_{F\text{-}H}$ 47.8, $^3J_{F\text{-}H}$ 27.3); HRMS (EI^+, M^+) Found: 236.14230, Calc. for $C_{11}H_{21}FO_4$ 236.14239; *m*/*z* (EI): 235 (M-H^+, 1%), 179 (3), 162 (10), 145 (31), 90 (100); t_R (GC) 15.08 min. Satisfactory microsanalysis could not be obtained for this compound.

4-(_O_-methyl)-2,6-dideoxy-6-fluoro-β-DL-arabino-hexapyranoside 40

Was prepared from **39** (39 mg, 0.165 mmol) in THF (3 mL) and HCl (3 mL of a 1N solution) in an Ace tube at 80 ^oC over 2 hours as described for **27**. Work-up and isolation described for **27** followed by chromatography on silica gel afforded 4-(*O*-methyl) pyranoside **40** (12 mg, 42%) as a pale yellow oil, as a 76:24 mixture of α- and β-anomers; R_f (50% ethyl acetate in light petroleum) 0.08; ν_{max} (film)/cm^{-1}: 3345m, 2849w, 1716s, 1262s, 1095s, 1019s, 725s; δ_H ($CDCl_3$, 300MHz) α-anomer: 5.33 (1 H, br. d, J 3.2), 4.69-4.40 (2 H, m), 4.03 (1 H, ddd, J 12.0, 9.0, 5.1), 3.81 (1 H, m incl. dd, $^2J_{H\text{-}F}$ 29.5, J 9.6), 3.52 (3 H, s), 3.05 (1 H, m incl. app. t, J 9.4), 2.89 (1 H, br s), 2.46 (1 H, br s), 2.10 (1 H, m, incl. dd, ^2J 13.0, J 5.1), 1.65 (1 H, ddd, ^2J 13.0, J 12.0, 3.6), δ_H ($CDCl_3$, 300MHz) β-anomer: 4.80 (1 H, dd, J 8.1, 1.8), 4.69-4.42 (2 H, m), 3.71-3.59 (1 H, m), 3.52 (3 H, s), 3.38-3.19 (1 H, m), 3.04 (1 H, t, J 9.0), 2.24 (1 H, ddd, ^2J 12.3, J 4.8, 1.8), 1.65-1.47 (1 H, m); δ_C ($CDCl_3$, 75MHz) α-anomer: 92.2, 82.4 (d, $^1J_{C\text{-}F}$ 170.8), 81.1 (d, $^3J_{C\text{-}F}$ 5.1), 70.3 (d, $^2J_{C\text{-}F}$ 18.2), 68.5, 61.0, 37.3, δ_C ($CDCl_3$, 75MHz) β-anomer: 94.3, 82.0 (d, $^1J_{C\text{-}F}$ 171.9), 80.4 (d, $^3J_{C\text{-}F}$ 5.0), 74.3 (d, $^2J_{C\text{-}F}$ 17.5), 71.2, 61.0, 40.0; δ_F ($CDCl_3$, 282MHz) α-anomer: –233.4 (td, $^2J_{F\text{-}H}$ 47.9, $^3J_{F\text{-}H}$ 29.5), δ_F ($CDCl_3$, 282MHz) β-anomer: –232.4 (td, $^2J_{F\text{-}H}$ 47.4, $^3J_{F\text{-}H}$ 27.6); HRMS (EI^+, M^+) Found: 180.07976, Calc. for $C_7H_{13}FO_4$ 180.07979; *m*/*z* (EI): 180 (M+, 2%), 162 (1), 144 (4), 74 (100); t_R (GC) 12.75 min.

Transition and product structures for acetylketene dimerisation reactions

Electronic structure calculations were carried out on a Dell Optiplex 755 (Core 2 Quad Processor, 4GB RAM) running Spartan'06 V1.1.0.

Conformational searching was carried out using a Monte Carlo method implemented in Spartan'06 with the MMFF94 force field. Low energy conformers were selected based on the energies of geometries optimised with the B3LYP/6-31G* method. The lowest energy dioxinone and pyranone conformers were used as starting points for transition structure searches which were carried out in PM3 implemented in Spartan'06 by stepping along the reaction coordinate. These structures were then used as the starting points from B3LYP/6-31G*, MP2/6-31G* or MP2/6-311+G** optimisations with full frequency calculation at 298K or 373K.

A number of subtle conformational differences between fluorinated and non-fluorinated systems were detected. The orientation of the methyl group was different in the non-fluorinated and fluorinated systems; the fluoromethyl group was rotated so that the fluorine atom approached within 2.23 Å of the vinylic (H-3) proton. This allows a C-F bond to locate antiparallel to the almost completely formed ketonic carbonyl group, an arrangement which minimises the dipolar repulsion between C-F and C=O bonds. The DFT method aligns a C-H bond with the C=O bond and minimises 1,3–allylic strain. The correlated method rotates the methyl group, positioning a C-H bond orthogonal to C=O presumably allowing a σ/π^* interaction to develop. None of the other bond lengths or angles appear to be perturbed by fluorination.

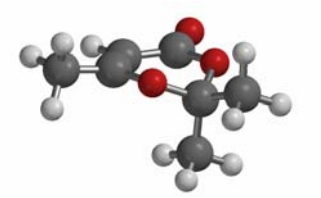
Optimisation at the MP2 level of theory and the 6-311+G** basis had very little effect on bond angles and lengths.

Electronic structure calculations

Energies, Cartesian coordinates, imaginary frequencies (where appropriate) and thermal corrections for:

3, **42a**, **4**, **acetone**, **43a**, **44a**, **methyl vinyl ether**, **5_{eq}**, **5_{ax}**, **46a**, **45a**, **47a**, **48a**, **8**, **42b**, **28**, **43b**, **44b**, **29_{eq} (methyl pyranoside)**, **29_{ax}(methyl pyranoside)**, **46b**, **45b**, **47b**, **48b**.

Dioxinone 3



MP2/6-31G*

MP2 total energy: **-496.9266803 hartrees**

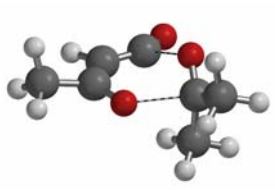
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	-0.0676685	1.3730103	1.2057255
2	H	H2	0.1051718	2.3068510	1.7256346
3	C	C2	-0.2146158	1.3339802	-0.1367342
4	O	O1	-0.4352606	0.1644814	-0.7973612
5	C	C3	-0.1042322	-1.0256331	-0.0477965
6	C	C4	-0.3447969	0.1896048	2.0124165
7	O	O2	-0.6153885	-0.9589642	1.2845379
8	C	C5	1.4037902	-1.2071244	-0.0317434
9	H	H1	1.8927076	-0.3496315	0.4348848
10	H	H5	1.7716846	-1.3161211	-1.0547994
11	H	H7	1.6496673	-2.1051797	0.5396075
12	C	C6	-0.8421648	-2.1543216	-0.7231743
13	H	H6	-0.5189141	-2.2384951	-1.7630969
14	H	H8	-1.9134914	-1.9494464	-0.6897906
15	H	H9	-0.6372624	-3.0903066	-0.1995223
16	O	O3	-0.4408513	0.1617418	3.2245236
17	C	C7	-0.1756725	2.5004343	-1.0634965
18	H	H3	0.6472953	2.3893290	-1.7755941
19	H	H4	-0.0533606	3.4316861	-0.5076039
20	H	H10	-1.1066371	2.5441048	-1.6366172

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 465.6177
Entropy Correction (Hv-TSv) 347.9140

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 479.0335
Entropy Correction (Hv-TSv) 316.8568

Fragmentation transition state 42a



MP2/6-31G*

MP2 total energy: **-496.8727623 hartrees**

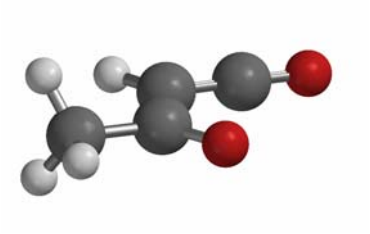
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C4	2.8121750	0.8231621	0.1909584
2	C	C1	1.4217560	0.2235780	0.1142951
3	C	C2	1.3916590	-1.2105330	0.0602764
4	H	H2	2.3403068	-1.7178532	-0.0890785
5	C	C3	0.3559941	-2.1023021	0.1666754
6	O	O1	-0.0310018	-3.2187858	0.1085704
7	O	O3	-1.0539540	-1.0254591	0.8723704
8	C	C5	-1.4492475	-0.0575620	0.1829097
9	O	O2	0.4495668	1.0158884	0.1052878
10	C	C6	-1.5343254	-0.1238904	-1.3175905
11	H	H3	-0.7328932	-0.7363438	-1.7301578
12	H	H5	-1.4958275	0.8748459	-1.7527618
13	H	H7	-2.4958237	-0.5848134	-1.5762692
14	C	C7	-2.2124416	1.0352428	0.8740667
15	H	H8	-1.9378735	1.0589482	1.9286023
16	H	H9	-3.2852684	0.8263573	0.7854848
17	H	H10	-2.0051048	1.9995285	0.4077923
18	H	H1	3.1742673	0.7681178	1.2234166
19	H	H4	2.7680681	1.8704604	-0.1119482
20	H	H6	3.5199683	0.2814132	-0.4429005

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
ν_i = -241.782 cm^{-1}
Temp. Correction Hv 455.6219
Entropy Correction (Hv-TSv) 327.4236

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
ν_i = -241.771 cm^{-1}
Temp. Correction Hv 469.6680
Entropy Correction (Hv-TSv) 293.6525

Oxoketene 4



MP2/6-31G*

MP2 total energy: **-304.3550052 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C2	2.2345470	-0.4291366	0.0000000
2	C	C1	0.8428684	0.1613058	0.0000000
3	O	O1	0.6423646	1.3781117	0.0000000
4	C	C3	-0.2586656	-0.8132449	0.0000000
5	C	C4	-1.5005375	-0.3234213	0.0000000
6	O	O2	-2.5821354	0.1276188	0.0000000
7	H	H5	-0.1171228	-1.8868660	0.0000000
8	H	H1	2.9625417	0.3825782	0.0000000
9	H	H2	2.3817366	-1.0572867	-0.8841844
10	H	H4	2.3817366	-1.0572867	0.8841844

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 208.4237
Entropy Correction (Hv-TSv) 108.8417

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 216.1090
Entropy Correction (Hv-TSv) 82.9707

Acetone

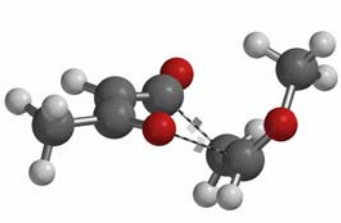
MP2/6-31G*

MP2 total energy: **-192.5239050 hartrees**

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 242.0619
Entropy Correction (Hv-TSv) 153.4834

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 248.3179
Entropy Correction (Hv-TSv) 130.5391

Cycloaddition transition state 43a



MP2/6-31G*

MP2 total energy: -496.8064090 hartrees

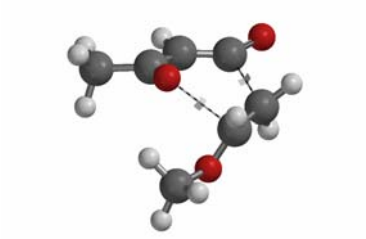
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.5987494	-0.3718375	0.0020858
2	H	H4	2.0714488	1.4892177	-1.0019842
3	C	C2	1.2766522	0.9059670	-0.5452363
4	O	O1	0.7722763	-1.2311997	0.3871395
5	C	C3	0.0610487	1.5476048	-0.5866501
6	O	O2	-0.4877248	2.4714488	-1.1276250
7	C	C4	-1.2680526	-0.4079524	1.1156520
8	H	H8	-0.7999812	-0.8810415	1.9698425
9	C	C5	-1.1944720	0.9535002	0.8689367
10	H	H5	-0.7735550	1.5502164	1.6712640
11	H	H10	-2.0194436	1.4123632	0.3399090
12	C	C6	3.0743745	-0.7053067	0.1207417
13	H	H7	3.2286131	-1.7498376	-0.1599184
14	H	H9	3.3829564	-0.5909776	1.1654499
15	O	O3	-2.0006894	-1.2759891	0.4394701
16	C	C7	-2.5540438	-0.8312137	-0.8107176
17	H	H3	-3.3261357	-0.0742479	-0.6497418
18	H	H11	-2.9896908	-1.7204005	-1.2609996
19	H	H12	-1.7538398	-0.4306061	-1.4382517
20	H	H1	3.7015095	-0.0597079	-0.4993663

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
ν_i = -355.509 cm^{-1}
Temp. Correction Hv 457.7998
Entropy Correction (Hv-TSv) 325.6194

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
ν_i = -355.509 cm^{-1}
Temp. Correction Hv 471.5236
Entropy Correction (Hv-TSv) 290.8877

Cycloaddition transition state 44a



MP2/6-31G*

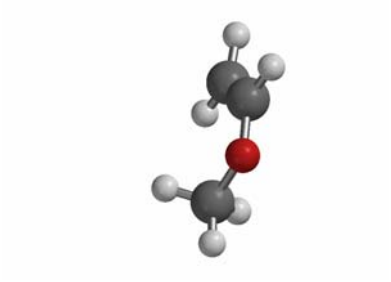
MP2 total energy: **-496.8087338 hartrees**

		Atom	Cartesian Coordinates (Angstroms) X	Y	Z
1	C	C1	1.0791364	-0.4514449	-0.7330427
2	H	H4	2.1364763	1.3192079	-1.3884297
3	C	C2	1.1578256	0.8847262	-1.2053364
4	O	O1	0.0284397	-1.1403668	-0.6599202
5	C	C3	0.1238147	1.7414537	-1.5229895
6	O	O2	-0.0902662	2.7419764	-2.1527240
7	C	C4	-1.6372600	0.2631755	0.2061738
8	C	C5	-1.5295547	1.4551767	-0.4802841
9	H	H5	-1.3448687	2.3412698	0.1187444
10	H	H10	-2.2022662	1.5755283	-1.3216303
11	C	C6	2.3772172	-1.0908307	-0.2773367
12	H	H7	2.3851579	-2.1411279	-0.5778210
13	H	H9	2.4293104	-1.0515626	0.8167157
14	O	O4	-1.1911030	0.1860352	1.4508018
15	C	C8	-1.2046056	-1.1343602	2.0389142
16	H	H2	-0.9140049	-0.9922169	3.0780550
17	H	H1	-0.4947343	-1.7626835	1.5017879
18	H	H6	-2.2117557	-1.5561142	1.9850021
19	H	H11	-2.1551584	-0.6025293	-0.1956892
20	H	H3	3.2581993	-0.5853126	-0.6809911

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
ν_i = -345.919 cm^{-1}
Temp. Correction Hv 457.4228
Entropy Correction (Hv-TSv) 327.5427

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
ν_i = -345.919 cm^{-1}
Temp. Correction Hv 471.1980
Entropy Correction (Hv-TSv) 293.3821

Methyl vinyl ether



MP2/6-31G*

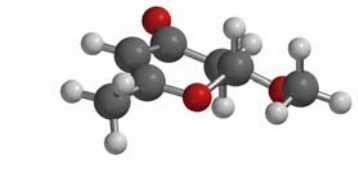
MP2 total energy: **-192.4759785 hartrees**

			Cartesian Coordinates (Angstroms)		
	Atom		X	Y	Z
1	C	C1	1.3685085	-0.4848700	0.0000000
2	H	H2	2.4478285	-0.5632907	0.0000000
3	H	H3	0.8013557	-1.4058992	0.0000000
4	C	C2	0.8155628	0.7363362	0.0000000
5	H	H4	1.4143430	1.6420571	0.0000000
6	O	O1	-0.5080783	1.0613998	0.0000000
7	C	C3	-1.4058701	-0.0450304	0.0000000
8	H	H1	-1.2636324	-0.6626767	-0.8932484
9	H	H5	-2.4063854	0.3846504	0.0000000
10	H	H6	-1.2636324	-0.6626767	0.8932484

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 243.8504
Entropy Correction (Hv-TSv) 159.0624

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 249.8891
Entropy Correction (Hv-TSv) 137.0967

Pyranone 5_{eq}



MP2/6-31G*

MP2 total energy: **-496.8902720 hartrees**

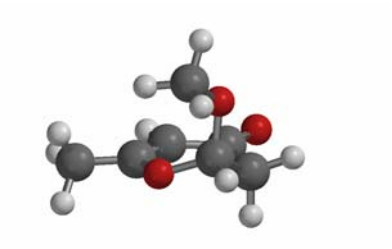
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C5	-0.7970816	-2.7700853	-0.0649793
2	C	C1	-0.7116182	-1.2805777	-0.0295683
3	C	C2	-1.7496149	-0.4356230	0.1924473
4	H	H2	-2.7389699	-0.8303298	0.3969084
5	C	C4	-1.5966365	1.0095966	0.0420699
6	O	O2	-2.5205846	1.8104324	0.1988395
7	C	C6	-0.2079494	1.4522511	-0.3916240
8	H	H7	-0.1378038	1.4206962	-1.4860348
9	C	C3	0.8245597	0.5118456	0.1745533
10	O	O1	0.5614187	-0.8504174	-0.2575932
11	H	H10	-0.0223069	2.4773539	-0.0615976
12	H	H1	-0.1736868	-3.2025248	0.7232496
13	H	H4	-0.4177581	-3.1357972	-1.0239864
14	H	H9	0.7826390	0.4895203	1.2792725
15	O	O3	2.0800132	0.8683488	-0.2778953
16	C	C7	3.1302657	0.0971762	0.3145397
17	H	H3	3.0573178	0.1221579	1.4087790
18	H	H5	4.0610894	0.5672868	-0.0007929
19	H	H6	3.0993175	-0.9388425	-0.0302769
20	H	H8	-1.8281643	-3.1039320	0.0630397

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 467.8255
Entropy Correction (Hv-TSv) 346.9774

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 480.8994
Entropy Correction (Hv-TSv) 315.1693

Pyranone 5_{ax}



MP2/6-31G*

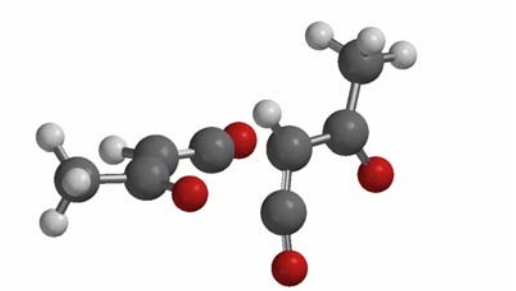
MP2 total energy: **-496.8923195 hartrees**

		Atom	Cartesian Coordinates (Angstroms) X	Y	Z
1	C	C5	0.6199135	-2.7402501	0.1034841
2	C	C1	0.0301314	-1.3807608	-0.0705336
3	C	C2	-1.1582648	-0.9686093	0.4285866
4	H	H2	-1.7502440	-1.6342341	1.0476709
5	C	C4	-1.6850664	0.3588739	0.1276445
6	O	O2	-2.7311987	0.8010907	0.6049414
7	C	C6	-0.8795343	1.1306410	-0.9040284
8	H	H7	-1.2046156	0.8151438	-1.9036295
9	C	C3	0.5929831	0.8350673	-0.7445752
10	O	O1	0.8545476	-0.5839352	-0.8220735
11	O	O3	0.9843524	1.3486224	0.4918135
12	C	C7	2.3817735	1.1957544	0.7465133
13	H	H3	2.9740410	1.6011153	-0.0835677
14	H	H5	2.6461219	0.1458515	0.8974751
15	H	H9	2.5857388	1.7637055	1.6536438
16	H	H6	1.2107215	1.2435881	-1.5562620
17	H	H10	-1.0693751	2.2008651	-0.7954067
18	H	H1	-0.0631468	-3.3915111	0.6516745
19	H	H4	1.5688050	-2.6739676	0.6444439
20	H	H8	0.8287270	-3.1810788	-0.8760407

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 468.2011
Entropy Correction (Hv-TSv) 347.7187

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 481.2176
Entropy Correction (Hv-TSv) 316.0095

Synchronous dimerisation transition state 46a



MP2/6-31G*

MP2 total energy: **-608.7067036 hartrees**

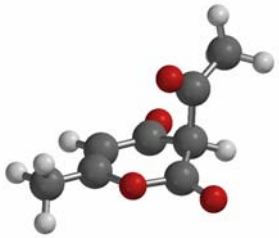
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.0758332	-1.6918855	-0.1980747
2	H	H4	2.6809196	-0.2431977	-0.3912810
3	C	C2	1.6333705	-0.3701206	-0.1272949
4	O	O5	-0.0702413	-2.0364107	0.1739351
5	C	C3	1.0599293	0.7965430	0.2903869
6	O	O2	1.1491306	1.9484755	0.5668146
7	C	C5	-1.1273525	0.3588412	0.3588716
8	H	H10	-1.2095335	-0.0870354	-0.6230891
9	C	C6	2.0009940	-2.7551023	-0.7485389
10	H	H7	1.4132216	-3.6373060	-1.0056470
11	H	H9	2.7342734	-3.0313868	0.0171729
12	H	H3	2.5472554	-2.3973165	-1.6255168
13	C	C7	-1.6558085	1.7101696	0.6585107
14	O	O3	-1.7170543	2.1365180	1.8111610
15	C	C9	-2.0344228	2.5371134	-0.5454892
16	H	H5	-1.1586371	2.6725628	-1.1883533
17	H	H8	-2.3953804	3.5095545	-0.2092708
18	H	H12	-2.8092799	2.0329280	-1.1314593
19	C	C4	-1.0560639	-0.4903020	1.4256699
20	O	O4	-1.0611551	-0.9626425	2.4914926

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
ν_i = -240.684 cm^{-1}
Temp. Correction Hv 420.3632
Entropy Correction (Hv-TSv) 276.8169

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
ν_i = -240.685 cm^{-1}
Temp. Correction Hv 435.9824
Entropy Correction (Hv-TSv) 239.0110

Dehydroacetic acid 45a (enantiomer of TS)



MP2/6-31G*

MP2 total energy: **-608.7736805 hartrees**

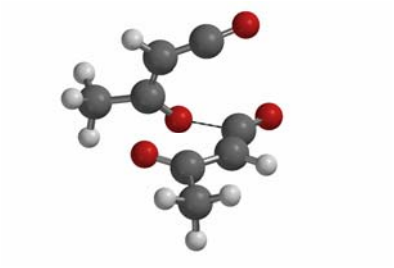
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	0.1913377	1.5495335	0.3321651
2	H	H2	-0.0879847	2.4604243	0.8497768
3	C	C2	0.0747281	1.4726555	-1.0122301
4	C	C3	-0.4632142	2.5369509	-1.9029444
5	H	H4	0.2948897	2.8302493	-2.6348697
6	H	H5	-0.7671053	3.4097605	-1.3230173
7	H	H6	-1.3247245	2.1486369	-2.4542843
8	O	O1	0.4814927	0.3925596	-1.7627453
9	C	C4	1.0119215	-0.7358750	-1.1530908
10	O	O2	1.5731371	-1.5551042	-1.8416248
11	C	C5	0.6956579	0.4312003	1.1069635
12	O	O3	0.9467073	0.4644030	2.3130184
13	C	C6	0.7809428	-0.8799977	0.3265207
14	H	H1	1.5744732	-1.5050390	0.7460373
15	C	C7	-0.5936262	-1.5558420	0.5442145
16	O	O4	-1.4991036	-1.3909196	-0.2623428
17	C	C8	-0.7113502	-2.3656630	1.8046652
18	H	H3	-0.1191644	-3.2811161	1.6977977
19	H	H7	-1.7565193	-2.6246488	1.9776059
20	H	H8	-0.3024954	-1.8021682	2.6483845

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 431.4713
Entropy Correction (Hv-TSv) 299.2593

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 446.2317
Entropy Correction (Hv-TSv) 264.1137

Asynchronous dimerisation transition state 47a



MP2/6-31G*

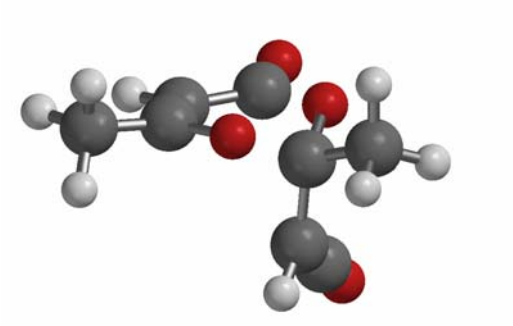
MP2 total energy: -608.7004819 hartrees

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.0700874	1.5709346	0.3210897
2	H	H2	0.7136068	2.4595604	0.8291026
3	C	C2	0.4618023	1.1305461	-0.9117680
4	C	C3	-0.4051826	2.1231863	-1.6244912
5	H	H5	-1.0094368	1.5973082	-2.3622655
6	H	H6	0.2322641	2.8575546	-2.1287397
7	O	O1	0.8029785	0.0890276	-1.5451182
8	C	C4	1.3516412	-1.3457714	-0.6268637
9	O	O2	2.4111875	-1.7072543	-1.0341386
10	C	C5	2.0830153	0.9104935	0.8986386
11	O	O3	3.0027838	0.4006626	1.4124047
12	C	C6	0.3368070	-1.6324089	0.2601906
13	H	H1	0.5311878	-2.5513746	0.8049256
14	C	C7	-0.9218792	-0.9845768	0.4997358
15	O	O4	-1.2993594	0.1342742	0.0793291
16	C	C8	-1.8895812	-1.7755401	1.3602020
17	H	H3	-2.5906883	-1.0862091	1.8340065
18	H	H8	-2.4558966	-2.4663225	0.7262104
19	H	H4	-1.0535580	2.6401899	-0.9153293
20	H	H7	-1.3717797	-2.3642806	2.1228787

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
ν_i = -202.383 cm^{-1}
Temp. Correction Hv 436.7100
Entropy Correction (Hv-TSv) 245.3973
Free Energy (H-TS) (STP): 67.419 kcal/mol (T=298.15)

Dioxolane 48a



MP2/6-31G*

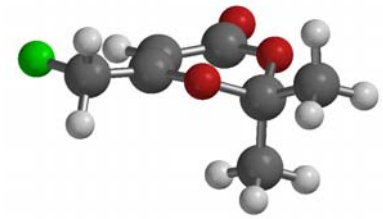
MP2 total energy: **-608.7451639 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	0.8334771	1.3575796	0.6908200
2	H	H2	0.3007942	1.9189942	1.4499802
3	C	C2	0.1120624	0.8664938	-0.5358360
4	C	C3	-0.4030392	1.9726955	-1.4252264
5	H	H4	0.4411645	2.5612678	-1.7881207
6	O	O1	0.9856637	0.0716425	-1.3325328
7	C	C4	1.3265847	-1.1846921	-0.8250527
8	O	O2	2.2999136	-1.7520514	-1.2788521
9	C	C5	2.1493425	1.2290669	0.7986835
10	O	O3	3.3162799	1.1075207	0.9041823
11	C	C6	0.3933477	-1.7227345	0.1551104
12	H	H1	0.6097024	-2.7007237	0.5661707
13	C	C7	-0.7824755	-1.1041968	0.3953858
14	O	O4	-1.0557683	0.1253084	-0.1260336
15	C	C8	-1.9086732	-1.6306518	1.2158626
16	H	H3	-2.0775524	-0.9820986	2.0807413
17	H	H8	-2.8268412	-1.6372299	0.6209249
18	H	H6	-0.9392906	1.5335597	-2.2690765
19	H	H5	-1.0783054	2.6152374	-0.8555976
20	H	H7	-1.6963869	-2.6449878	1.5584667

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 444.6177
Entropy Correction (Hv-TSv) 264.3062
Free Energy (H-TS) (STP): 71.421 kcal/mol (T=298.15)

Dioxinone 8



MP2/6-31G*

MP2 total energy: **-595.9339501 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	-0.0864587	1.3639145	1.2111028
2	H	H2	0.0816819	2.3043422	1.7177013
3	C	C2	-0.2296046	1.3103983	-0.1270089
4	O	O1	-0.4454343	0.1564746	-0.8088311
5	C	C3	-0.1043363	-1.0392931	-0.0624709
6	C	C4	-0.3519006	0.1699438	2.0076969
7	O	O2	-0.6166610	-0.9753762	1.2673842
8	C	C5	1.4046593	-1.2073339	-0.0497006
9	H	H1	1.8884219	-0.3485447	0.4200607
10	H	H5	1.7726921	-1.3109937	-1.0732432
11	H	H7	1.6576591	-2.1053476	0.5185069
12	C	C6	-0.8360652	-2.1684843	-0.7426320
13	H	H6	-0.5123401	-2.2474030	-1.7828201
14	H	H8	-1.9086107	-1.9706292	-0.7076195
15	H	H9	-0.6250505	-3.1049251	-0.2223575
16	O	O3	-0.4453800	0.1271080	3.2183994
17	C	C7	-0.1768243	2.4811138	-1.0585430
18	H	H4	-1.0931844	2.5180776	-1.6571283
19	H	H10	0.6803911	2.3869626	-1.7336858
20	F	F1	-0.0536548	3.6599955	-0.3348112

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 448.0638
Entropy Correction (Hv-TSv) 324.5239

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 462.0454
Entropy Correction (Hv-TSv) 291.9367

Fragmentation transition state 42b

MP2/6-31G*

MP2 total energy: **-595.8849027 hartrees**

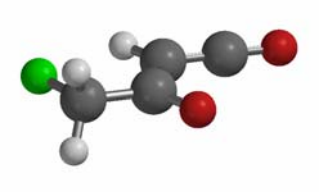
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C4	0.4778956	0.3159423	-2.8535797
2	C	C1	0.4566295	0.1677552	-1.3385363
3	C	C2	1.6977350	-0.1426996	-0.7233696
4	H	H2	2.5309256	-0.3627586	-1.3807325
5	C	C3	2.0259523	-0.2268981	0.6093203
6	O	O1	2.8277561	-0.5188287	1.4278342
7	O	O3	0.6020214	0.6663208	1.4517826
8	C	C5	-0.5472440	0.1768784	1.3438356
9	O	O2	-0.6856724	0.3179832	-0.8348771
10	C	C6	-0.7864316	-1.3067045	1.3092687
11	H	H3	0.0238049	-1.8260838	0.7979610
12	H	H5	-1.7349496	-1.5349470	0.8232341
13	H	H7	-0.8275718	-1.6597840	2.3472510
14	C	C7	-1.7181638	1.0658416	1.6424213
15	H	H8	-1.4331439	2.1066888	1.4908002
16	H	H9	-2.0133216	0.9206457	2.6883815
17	H	H10	-2.5636302	0.8078315	1.0029986
18	H	H1	0.1317159	1.3227739	-3.1052680
19	H	H4	-0.2075967	-0.4160756	-3.2903581
20	F	F1	1.7432892	0.1261185	-3.4083677

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
ν_i = -239.342 cm^{-1}
Temp. Correction Hv 438.7990
Entropy Correction (Hv-TSv) 306.4754

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
ν_i = -239.349 cm^{-1}
Temp. Correction Hv 453.3458
Entropy Correction (Hv-TSv) 271.6118

Oxoketene 28



MP2/6-31G*

MP2 total energy: **-403.3663373 hartrees**

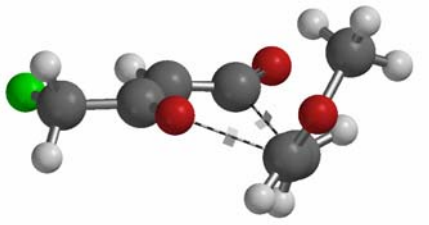
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C2	1.8680341	0.3028898	0.0000000
2	C	C1	0.3658057	0.5335644	0.0000000
3	O	O1	-0.0561476	1.6925912	0.0000000
4	C	C3	-0.4703950	-0.6583008	0.0000000
5	C	C4	-1.7922412	-0.4641227	0.0000000
6	O	O2	-2.9471102	-0.2743338	0.0000000
7	H	H5	-0.0730970	-1.6638938	0.0000000
8	F	F1	2.1861967	-1.0558613	0.0000000
9	H	H2	2.2980833	0.7682004	0.8915048
10	H	H4	2.2980833	0.7682004	-0.8915048

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 191.5845
Entropy Correction (Hv-TSv) 87.4511

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 199.7667
Entropy Correction (Hv-TSv) 60.3811

Cycloaddition transition state 43b



MP2/6-31G*

MP2 total energy: **-595.8191523 hartrees**

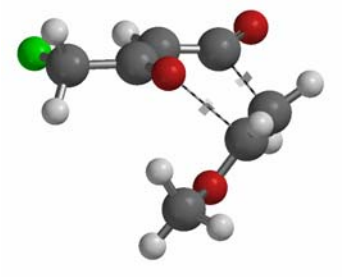
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.5756568	-0.3496425	0.0219029
2	H	H4	2.0843951	1.4799672	-0.9879464
3	C	C2	1.2738748	0.9109370	-0.5453158
4	O	O1	0.7770716	-1.2216945	0.4409963
5	C	C3	0.0519212	1.5434434	-0.6029842
6	O	O2	-0.4920536	2.4540175	-1.1686239
7	C	C4	-1.2737930	-0.3783679	1.1404648
8	H	H8	-0.8082205	-0.8173361	2.0142991
9	C	C5	-1.2051387	0.9751228	0.8437092
10	H	H5	-0.8017700	1.6014892	1.6331084
11	H	H10	-2.0353694	1.4059525	0.2983276
12	C	C6	3.0456634	-0.7354427	0.1139097
13	H	H7	3.2175281	-1.6378369	-0.4807435
14	H	H9	3.2840018	-0.9507890	1.1602195
15	O	O3	-1.9935159	-1.2735865	0.4903105
16	C	C7	-2.5490082	-0.8765871	-0.7761464
17	H	H3	-3.3322930	-0.1263241	-0.6401342
18	H	H11	-2.9699437	-1.7860604	-1.1988290
19	H	H12	-1.7523714	-0.4847448	-1.4133642
20	F	F1	3.9033648	0.2674829	-0.3431600

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
ν_i = -357.156 cm^{-1}
Temp. Correction Hv 440.8429
Entropy Correction (Hv-TSv) 304.7570

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
ν_i = -357.156 cm^{-1}
Temp. Correction Hv 455.0794
Entropy Correction (Hv-TSv) 268.9864

Cycloaddition transition state 44b



MP2/6-31G*

MP2 total energy: **-595.8211729 hartrees**

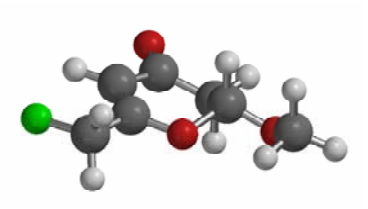
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.0507716	-0.4368576	-0.7320022
2	H	H4	2.1315115	1.3373170	-1.2915840
3	C	C2	1.1482185	0.8936700	-1.1793707
4	O	O1	0.0212240	-1.1648250	-0.6980765
5	C	C3	0.1003164	1.7209175	-1.5400148
6	O	O2	-0.1169050	2.6982145	-2.2023837
7	C	C4	-1.6326588	0.2447964	0.1934766
8	C	C5	-1.5467224	1.4243633	-0.5207177
9	H	H5	-1.3867822	2.3259405	0.0627321
10	H	H10	-2.2251161	1.5135060	-1.3617688
11	C	C6	2.3282926	-1.1131243	-0.2586402
12	H	H7	2.5210761	-1.9947859	-0.8774936
13	H	H9	2.1888163	-1.4343354	0.7795284
14	F	F1	3.4437947	-0.2755011	-0.3170567
15	O	O4	-1.1533242	0.1990102	1.4260063
16	C	C8	-1.1805269	-1.1041473	2.0547623
17	H	H2	-0.6775753	-0.9742491	3.0109859
18	H	H1	-0.6499255	-1.8112186	1.4169473
19	H	H6	-2.2163621	-1.4137912	2.2147317
20	H	H11	-2.1481233	-0.6348999	-0.1800616

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
ν_i = -356.288 cm^{-1}
Temp. Correction Hv 440.2591
Entropy Correction (Hv-TSv) 306.4711

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
ν_i = -356.288 cm^{-1}
Temp. Correction Hv 454.5567
Entropy Correction (Hv-TSv) 271.2699

Pyranone 29$_{eq}$



MP2/6-31G*

MP2 total energy: -**595.8981313 hartrees**

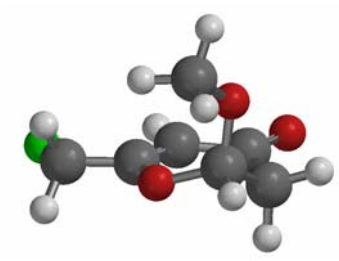
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C5	1.8328894	-1.7390361	0.0824783
2	C	C1	0.9551006	-0.5246691	0.0521011
3	C	C2	1.3819390	0.7391960	-0.1667574
4	H	H2	2.4307109	0.9305364	-0.3580072
5	C	C4	0.4533644	1.8622729	-0.0392957
6	O	O2	0.7824361	3.0375599	-0.2057562
7	C	C6	-0.9560004	1.4710800	0.3809901
8	H	H7	-1.0089200	1.4149405	1.4754207
9	C	C3	-1.3067178	0.1150060	-0.1770508
10	O	O1	-0.3394450	-0.8796109	0.2730322
11	H	H10	-1.6692602	2.2249176	0.0385872
12	H	H1	1.5725602	-2.4115201	-0.7418726
13	H	H4	1.6892412	-2.2722651	1.0283453
14	F	F1	3.1681967	-1.3760360	-0.0379676
15	H	H9	-1.2497482	0.1054974	-1.2808169
16	O	O3	-2.5527250	-0.2682453	0.2722610
17	C	C7	-3.0179970	-1.4852189	-0.3219471
18	H	H3	-2.9666497	-1.4245899	-1.4157915
19	H	H5	-4.0559103	-1.5926465	-0.0094132
20	H	H6	-2.4333929	-2.3399607	0.0258505

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 450.3375
Entropy Correction (Hv-TSv) 323.5050

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 463.9787
Entropy Correction (Hv-TSv) 290.1294

Pyranone 29$_{ax}$



MP2/6-31G*

MP2 total energy: **-595.9002314 hartrees**

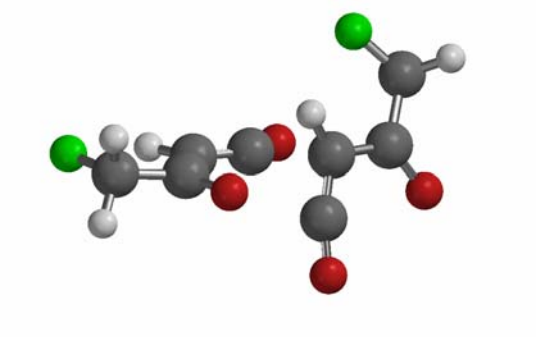
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C5	2.2900948	-0.9136949	0.2039227
2	C	C1	0.9974147	-0.1574262	0.2522416
3	C	C2	0.7920904	1.0651598	-0.2790157
4	H	H2	1.5896233	1.5635542	-0.8164824
5	C	C4	-0.4985990	1.7293705	-0.1107401
6	O	O2	-0.7799567	2.8117766	-0.6253851
7	C	C6	-1.4536467	1.0137343	0.8319986
8	H	H7	-1.2060806	1.3043888	1.8609247
9	C	C3	-1.3128009	-0.4841180	0.6923220
10	O	O1	0.0587726	-0.8982848	0.9156973
11	O	O3	-1.7309174	-0.8222920	-0.5916951
12	C	C7	-1.7339040	-2.2312385	-0.8325651
13	H	H3	-2.3060245	-2.7555971	-0.0571117
14	H	H5	-0.7170811	-2.6313911	-0.8630378
15	H	H9	-2.2150492	-2.3693000	-1.8000541
16	H	H6	-1.8655866	-1.0496894	1.4546993
17	H	H10	-2.4799273	1.3212915	0.6189568
18	H	H1	2.1688367	-1.8287829	-0.3858831
19	H	H4	2.5955437	-1.1899172	1.2189225
20	F	F1	3.2854068	-0.1360976	-0.3743171

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 450.7285
Entropy Correction (Hv-TSv) 324.2669

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 464.3112
Entropy Correction (Hv-TSv) 290.9919

Synchronous dimerisation transition state 46b



MP2/6-31G*

MP2 total energy: **-806.7288936 hartrees**

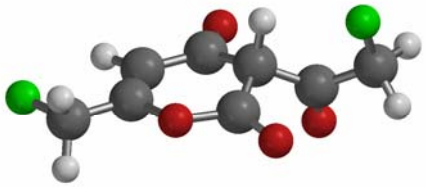
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.0378749	-1.6667336	-0.1786402
2	H	H4	2.6109120	-0.2282480	-0.4871875
3	C	C2	1.5786130	-0.3530749	-0.1755786
4	O	O5	-0.0921429	-2.0571659	0.2069704
5	C	C3	0.9781010	0.8194105	0.1921031
6	O	O2	1.0551712	1.9845539	0.4031161
7	C	C5	-1.1637929	0.3210429	0.3860314
8	H	H10	-1.2234515	-0.0761823	-0.6165760
9	C	C6	1.9353983	-2.7707742	-0.7134326
10	H	H7	2.0946503	-3.5083205	0.0783641
11	H	H3	1.4289690	-3.2536113	-1.5542257
12	C	C7	-1.7010242	1.6498499	0.7185656
13	O	O3	-1.9560450	2.0326997	1.8587609
14	C	C9	-1.8667606	2.6051585	-0.4497508
15	H	H5	-2.9244845	2.8622129	-0.5633184
16	H	H12	-1.2887002	3.5094414	-0.2434443
17	C	C4	-1.1170604	-0.5609369	1.4301117
18	O	O4	-1.1497540	-1.0447711	2.4897002
19	F	F1	3.1736351	-2.2983454	-1.1436662
20	F	F2	-1.4101086	2.0337941	-1.6379033

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
ν_i = -271.836 cm^{-1}
Temp. Correction Hv 386.6720
Entropy Correction (Hv-TSv) 235.3380

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
ν_i = -271.836 cm^{-1}
Temp. Correction Hv 403.2982
Entropy Correction (Hv-TSv) 195.4626

Dehydroacetic acid 45b



MP2/6-31G*

MP2 total energy: **-806.7834790 hartrees**

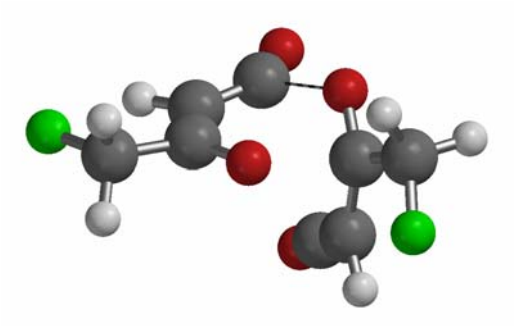
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	0.2478131	1.5342003	0.3109221
2	H	H2	0.0204794	2.4581582	0.8282538
3	C	C2	0.0844919	1.4580336	-1.0241076
4	C	C3	-0.4342414	2.5622528	-1.8920637
5	H	H4	0.3194161	2.8386682	-2.6363991
6	H	H6	-1.3383872	2.2270801	-2.4107885
7	O	O1	0.3949772	0.3810317	-1.8139821
8	C	C4	0.9070084	-0.7814906	-1.2397709
9	O	O2	1.3855299	-1.6167160	-1.9667040
10	C	C5	0.7205515	0.3817074	1.0574196
11	O	O3	0.9758920	0.3769961	2.2608254
12	C	C6	0.7572152	-0.9244124	0.2516501
13	H	H1	1.5548953	-1.5667559	0.6309172
14	C	C7	-0.6017237	-1.5715409	0.5406832
15	O	O4	-1.5716128	-1.4093036	-0.1874219
16	C	C8	-0.7133242	-2.3413340	1.8445956
17	H	H7	-1.4204186	-3.1632388	1.7063626
18	H	H8	-1.0746856	-1.6666168	2.6275967
19	F	F1	-0.7367630	3.6712900	-1.1145002
20	F	F2	0.5228867	-2.8480094	2.2265117

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 396.5395
Entropy Correction (Hv-TSv) 250.7658

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 411.9838
Entropy Correction (Hv-TSv) 211.6514

Asynchronous transition state 47b



MP2/6-31G*

MP2 total energy: **-806.7223105 hartrees**

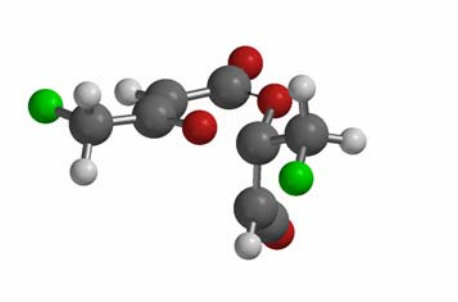
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	0.9930518	1.5916812	0.3649542
2	H	H2	0.5595250	2.4601529	0.8456519
3	C	C2	0.4486938	1.1005761	-0.8686401
4	C	C3	-0.4238586	2.0522779	-1.6494976
5	H	H5	-1.2352846	1.4898735	-2.1100003
6	H	H6	0.1908360	2.5341541	-2.4179466
7	O	O1	0.8778545	0.1027824	-1.5282233
8	C	C4	1.4239289	-1.3266361	-0.6226151
9	O	O2	2.4999702	-1.6628104	-0.9989296
10	C	C5	2.0242429	0.9823791	0.9652216
11	O	O3	2.9568266	0.5099863	1.4899034
12	C	C6	0.3863289	-1.6569418	0.2292958
13	H	H1	0.5538732	-2.5817045	0.7683906
14	C	C7	-0.8603043	-1.0128959	0.4228778
15	O	O4	-1.2641332	0.1051842	0.0055611
16	C	C8	-1.8737634	-1.7397554	1.2945370
17	H	H3	-2.1194126	-1.1053101	2.1514413
18	H	H8	-2.7807090	-1.9094989	0.7066010
19	F	F1	-1.4103576	-2.9671557	1.7671621
20	F	F2	-0.9473083	3.0336611	-0.8157451

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
ν_i = -266.263 cm^{-1}
Temp. Correction Hv 387.1214
Entropy Correction (Hv-TSv) 238.3678

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
ν_i = -266.260 cm^{-1}
Temp. Correction Hv 403.6477
Entropy Correction (Hv-TSv) 199.1529

Dioxolane 48b
SPARTAN 'O6 Quantum Mechanics Program:



MP2/6-31G*

MP2 total energy: **-806.7615399 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	0.8033024	1.4225714	0.6629868
2	H	H2	0.2784362	2.1124626	1.3125748
3	C	C2	0.1169202	0.8770582	-0.5502291
4	C	C3	-0.4072565	1.9708020	-1.4609669
5	H	H4	0.4376908	2.5167144	-1.8862871
6	O	O1	0.9875287	0.1029879	-1.3561558
7	C	C4	1.3356327	-1.1731687	-0.8782779
8	O	O2	2.2981322	-1.7258463	-1.3646027
9	C	C5	2.0783134	1.1446521	0.9001018
10	O	O3	3.2094805	0.8964581	1.1106316
11	C	C6	0.4214180	-1.7199686	0.1146928
12	H	H1	0.6325185	-2.6946280	0.5329065
13	C	C7	-0.7459318	-1.0945585	0.3608161
14	O	O4	-1.0521299	0.1253208	-0.1517924
15	C	C8	-1.8541068	-1.6171304	1.2191505
16	H	H3	-1.9659452	-0.9860797	2.1073116
17	H	H8	-2.7945992	-1.6067714	0.6582580
18	F	F1	-1.5707236	-2.9162098	1.6189699
19	H	H6	-1.0216868	1.5286705	-2.2491038
20	F	F2	-1.1869936	2.8366634	-0.7009848

Standard Thermodynamic quantities at 373.00 K and 1.00 atm
Temp. Correction Hv 410.8506
Entropy Correction (Hv-TSv) 214.2522
Free Energy (H-TS) (STP): 60.209 kcal/mol (T=298.15)

Dioxinone 3

MP2/ 6-311+G**

MP2 total energy: **-497.2224130 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	-0.0621446	1.3692611	1.2010052
2	H	H2	0.1294520	2.3017636	1.7156456
3	C	C2	-0.2161975	1.3293754	-0.1439575
4	O	O1	-0.4490104	0.1656566	-0.7960013
5	C	C3	-0.1175724	-1.0197051	-0.0452948
6	C	C4	-0.3372707	0.1827110	2.0094424
7	O	O2	-0.6420899	-0.9493993	1.2765953
8	C	C5	1.3941572	-1.1976474	-0.0172521
9	H	H1	1.8864642	-0.3402274	0.4471874
10	H	H5	1.7652840	-1.3146914	-1.0384757
11	H	H7	1.6337248	-2.0945300	0.5592702
12	C	C6	-0.8398696	-2.1569862	-0.7280130
13	H	H6	-0.5063533	-2.2342630	-1.7655053
14	H	H8	-1.9147890	-1.9685804	-0.7029714
15	H	H9	-0.6241319	-3.0909201	-0.2044758
16	O	O3	-0.4059206	0.1471356	3.2155377
17	C	C7	-0.1771183	2.5022310	-1.0654522
18	H	H3	0.6424670	2.3885154	-1.7815833
19	H	H4	-0.0467273	3.4288715	-0.5041410
20	H	H10	-1.1123537	2.5514291	-1.6315606

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 459.2348
Entropy Correction (Hv-TSv) 341.1715

Fragmentation transition state 42a

MP2/6-311+G**

MP2 total energy: **-497.1729745 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C4	2.8118539	1.2110076	0.0374335
2	C	C1	1.4195750	0.6103594	-0.0242537
3	C	C2	1.3807569	-0.8239833	-0.0983218
4	H	H2	2.3206029	-1.3400490	-0.2674335
5	C	C3	0.3298503	-1.7072994	0.0127484
6	O	O1	-0.0556398	-2.8135035	-0.0635766
7	O	O3	-1.0322257	-0.6495778	0.7357535
8	C	C5	-1.4349007	0.3187618	0.0595722
9	O	O2	0.4490359	1.3960800	-0.0061921
10	C	C6	-1.5154204	0.2726303	-1.4436913
11	H	H3	-0.7173021	-0.3348189	-1.8710916
12	H	H5	-1.4768212	1.2795817	-1.8598795
13	H	H7	-2.4807339	-0.1807697	-1.7036070
14	C	C7	-2.2131772	1.3996321	0.7539328
15	H	H8	-1.9988507	1.3844255	1.8225429
16	H	H9	-3.2818698	1.2138439	0.5916995
17	H	H10	-1.9608728	2.3725217	0.3287208
18	H	H1	3.0792653	1.3557581	1.0896294
19	H	H4	2.8079876	2.1857657	-0.4532728
20	H	H6	3.5605348	0.5610762	-0.4209431

Standard Thermodynamic quantities at 298.15 K and 1.00 atm

ν_i = -247.564 cm^{-1}

Temp. Correction Hv 449.3776

Entropy Correction (Hv-TSv) 321.5328

Oxoketene 4

MP2/6-311+G**

MP2 total energy: **-304.5253886 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C2	2.2288188	-0.4472373	-0.0001612
2	C	C1	0.8460005	0.1705062	-0.0000532
3	O	O1	0.6648335	1.3821172	0.0001511
4	C	C3	-0.2649264	-0.7996120	0.0001189
5	C	C4	-1.5116902	-0.3177855	-0.0000239
6	O	O2	-2.5836013	0.1243661	-0.0001243
7	H	H5	-0.1272760	-1.8730703	0.0008342
8	H	H1	2.3556681	-1.0770455	0.8859622
9	H	H2	2.9786435	0.3441246	-0.0026609
10	H	H4	2.3538895	-1.0811037	-0.8836335

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 205.6503
Entropy Correction (Hv-TSv) 104.9709

Acetone

MP2/6-311+G**

MP2 total energy: **-192.6552796 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	0.0000000	0.0000000	0.1855266
2	O	O1	0.0000000	0.0000000	1.4052049
3	C	C2	-1.2862571	0.0000000	-0.6168492
4	H	H2	-1.3199073	-0.8815650	-1.2652397
5	H	H1	-1.3199073	0.8815650	-1.2652397
6	H	H4	-2.1454104	0.0000000	0.0541748
7	C	C3	1.2862571	0.0000000	-0.6168492
8	H	H3	1.3199073	-0.8815650	-1.2652397
9	H	H5	2.1454104	0.0000000	0.0541748
10	H	H6	1.3199073	0.8815650	-1.2652397

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 235.8111
Entropy Correction (Hv-TSv) 152.4852

Cycloaddition transition state 43a

MP2/6-311+G**

MP2 total energy: **-497.1121046 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.0555105	-0.4518301	-0.7541453
2	H	H4	2.1323792	1.3585376	-1.2746110
3	C	C2	1.1518203	0.9027215	-1.1715974
4	O	O1	0.0030860	-1.1335247	-0.7614509
5	C	C3	0.1140750	1.7610104	-1.5050331
6	O	O2	-0.0861850	2.7557014	-2.1319224
7	C	C4	-1.6140877	0.2476598	0.1952597
8	C	C5	-1.5321956	1.4301555	-0.5222614
9	H	H5	-1.3825673	2.3312040	0.0649177
10	H	H10	-2.2012761	1.5029922	-1.3725387
11	C	C6	2.3337511	-1.1146959	-0.2710174
12	H	H7	2.4095308	-2.1138760	-0.7080708
13	H	H9	2.2793237	-1.2266590	0.8183909
14	O	O4	-1.1366942	0.2021304	1.4206606
15	C	C8	-1.1540064	-1.0962340	2.0464585
16	H	H2	-0.7894695	-0.9393653	3.0599113
17	H	H1	-0.5004127	-1.7679778	1.4876880
18	H	H6	-2.1765123	-1.4820947	2.0707079
19	H	H11	-2.1320958	-0.6322604	-0.1738670
20	H	H3	3.2260257	-0.5335948	-0.5174792

Standard Thermodynamic quantities at 298.15 K and 1.00 atm

ν_i = -355.611 cm^{-1}

Temp. Correction Hv 451.7144

Entropy Correction (Hv-TSv) 323.2223

Cycloaddition transition state 44a

MP2/6-311+G**

MP2 total energy: **-497.1099087 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.5828933	-0.3730795	0.0093409
2	H	H4	2.0380451	1.4197010	-1.1235915
3	C	C2	1.2458980	0.8632024	-0.6289277
4	O	O1	0.7667807	-1.2007627	0.4585304
5	C	C3	0.0364127	1.5250478	-0.6743337
6	O	O2	-0.5030013	2.4264914	-1.2417627
7	C	C4	-1.2627917	-0.3460796	1.1595062
8	H	H8	-0.7900380	-0.7416321	2.0503475
9	C	C5	-1.1969675	0.9970413	0.8035817
10	H	H5	-0.7816195	1.6524290	1.5620983
11	H	H10	-2.0346956	1.3948505	0.2459025
12	C	C6	3.0671344	-0.6709405	0.1341647
13	H	H6	3.4413091	-0.2328367	1.0665321
14	H	H7	3.6361010	-0.2429347	-0.6953766
15	H	H9	3.2177583	-1.7515147	0.1734335
16	O	O3	-1.9897633	-1.2595712	0.5581166
17	C	C7	-2.5208243	-0.9147492	-0.7274986
18	H	H3	-3.2821054	-0.1348908	-0.6409112
19	H	H11	-2.9649681	-1.8296103	-1.1135270
20	H	H12	-1.7055580	-0.5801616	-1.3756253

Standard Thermodynamic quantities at 298.15 K and 1.00 atm

ν_i = -345.015 cm^{-1}

Temp. Correction Hv 451.9646

Entropy Correction (Hv-TSv) 321.4491

Methyl vinyl ether

MP2/6-311+G**

MP2 total energy: **-192.6089817 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.3608999	-0.4879982	0.0000077
2	H	H2	2.4410192	-0.5588686	0.0000275
3	H	H3	0.7891257	-1.4061548	-0.0000039
4	C	C2	0.8098898	0.7384488	-0.0000079
5	H	H4	1.4154429	1.6394580	-0.0000015
6	O	O1	-0.5066640	1.0606663	-0.0000205
7	C	C3	-1.3994074	-0.0434944	-0.0000038
8	H	H1	-1.2535562	-0.6602534	-0.8937787
9	H	H5	-2.4032443	0.3784657	0.0000294
10	H	H6	-1.2535056	-0.6602694	0.8937516

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 240.6107
Entropy Correction (Hv-TSv) 155.6146

Pyranone 5_{eq}

MP2/6-311+G**

MP2 total energy: **-497.1886467 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C5	-0.8042624	-2.7691679	-0.0649960
2	C	C1	-0.7061433	-1.2783583	-0.0297191
3	C	C2	-1.7460715	-0.4312346	0.1983621
4	H	H2	-2.7307684	-0.8316994	0.4124430
5	C	C4	-1.5945957	1.0163923	0.0454300
6	O	O2	-2.5084521	1.8162213	0.2117669
7	C	C6	-0.2074276	1.4490234	-0.4080151
8	H	H7	-0.1598335	1.4014959	-1.5029760
9	C	C3	0.8258361	0.5080616	0.1597308
10	O	O1	0.5591321	-0.8524026	-0.2642936
11	H	H10	-0.0106482	2.4739985	-0.0864591
12	H	H1	-0.1819018	-3.2040135	0.7231564
13	H	H4	-0.4301584	-3.1350892	-1.0261997
14	H	H9	0.7805636	0.4877700	1.2635493
15	O	O3	2.0806123	0.8556816	-0.2861065
16	C	C7	3.1215744	0.1010752	0.3331818
17	H	H3	3.0560614	0.1834138	1.4254526
18	H	H5	4.0591569	0.5369596	-0.0102569
19	H	H6	3.0716018	-0.9505939	0.0402894
20	H	H8	-1.8378710	-3.0929954	0.0662195

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 462.6005
Entropy Correction (Hv-TSv) 342.0134

Pyranone 5_{ax}

MP2/6-311+G**

MP2 total energy: **-497.1895365 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C5	0.4851359	-2.7717899	0.1032423
2	C	C1	-0.0324249	-1.3809015	-0.0699047
3	C	C2	-1.2036352	-0.9151055	0.4324584
4	H	H2	-1.8230556	-1.5603019	1.0457467
5	C	C4	-1.6749542	0.4351208	0.1283002
6	O	O2	-2.7009701	0.9180688	0.5917545
7	C	C6	-0.8243998	1.1687692	-0.8979684
8	H	H7	-1.1600256	0.8574953	-1.8948630
9	C	C3	0.6337012	0.8022696	-0.7336472
10	O	O1	0.8256133	-0.6242565	-0.8118297
11	O	O3	1.0533611	1.2959124	0.4968953
12	C	C7	2.4460658	1.1101078	0.7301853
13	H	H3	3.0350462	1.5356460	-0.0925684
14	H	H5	2.6917229	0.0497174	0.8399575
15	H	H9	2.6747560	1.6388539	1.6551307
16	H	H6	1.2668589	1.1804204	-1.5461983
17	H	H10	-0.9600190	2.2472478	-0.7956113
18	H	H1	-0.2338454	-3.3864672	0.6472943
19	H	H4	1.4339241	-2.7531436	0.6487341
20	H	H8	0.6736704	-3.2180890	-0.8781782

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 462.6987
Entropy Correction (Hv-TSv) 342.2853

Calculations for the pyranones were not yet optimised with this basis set
090808_100
090808_90

Dioxinone 8

MP2/6-311+G**

MP2 total energy: **-596.2903687 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	-0.0722326	1.3589651	1.2136406
2	H	H2	0.1172221	2.2946923	1.7213181
3	C	C2	-0.2292991	1.3103044	-0.1262000
4	O	O1	-0.4623280	0.1630215	-0.7999910
5	C	C3	-0.1199216	-1.0304550	-0.0585022
6	C	C4	-0.3382245	0.1594617	2.0090407
7	O	O2	-0.6431135	-0.9661454	1.2622656
8	C	C5	1.3926149	-1.1981914	-0.0366870
9	H	H1	1.8835151	-0.3424631	0.4323226
10	H	H5	1.7619296	-1.3085597	-1.0592939
11	H	H7	1.6378000	-2.0972110	0.5340075
12	C	C6	-0.8384416	-2.1650324	-0.7487907
13	H	H6	-0.5083825	-2.2312276	-1.7881546
14	H	H8	-1.9144324	-1.9842038	-0.7169702
15	H	H9	-0.6139349	-3.1019828	-0.2345733
16	O	O3	-0.3993122	0.1076267	3.2136113
17	C	C7	-0.1767724	2.4789799	-1.0638702
18	H	H4	-1.0769064	2.4850817	-1.6859872
19	H	H10	0.7058022	2.4008895	-1.7065180
20	F	F1	-0.1055820	3.6664495	-0.3606682

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 442.4806
Entropy Correction (Hv-TSv) 318.3891

Fragmentation transition state 42b

MP2/6-311+G**

MP2 total energy: **-596.2449402 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C4	0.4700202	0.2930837	-2.8585370
2	C	C1	0.4534200	0.1777308	-1.3380299
3	C	C2	1.6873822	-0.1440005	-0.7106270
4	H	H2	2.5260816	-0.3885595	-1.3523956
5	C	C3	1.9998663	-0.2010954	0.6345676
6	O	O1	2.7985265	-0.4918043	1.4445966
7	O	O3	0.6111546	0.6821773	1.4373527
8	C	C5	-0.5333492	0.1907479	1.3358260
9	O	O2	-0.6768734	0.3551013	-0.8294245
10	C	C6	-0.7704850	-1.2938589	1.2794101
11	H	H3	0.0344785	-1.8135409	0.7592843
12	H	H5	-1.7234704	-1.5095826	0.7962009
13	H	H7	-0.8098474	-1.6542951	2.3155213
14	C	C7	-1.7094878	1.0643500	1.6589986
15	H	H8	-1.4220097	2.1141800	1.6013278
16	H	H9	-2.0451794	0.8295601	2.6765078
17	H	H10	-2.5268853	0.8537560	0.9668599
18	H	H1	0.1286340	1.2962523	-3.1265717
19	H	H4	-0.2161786	-0.4500025	-3.2727223
20	F	F1	1.7242015	0.0898001	-3.4181453

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 433.2235
Entropy Correction (Hv-TSv) 301.3985

Oxoketene 28

MP2/6-311+G**

MP2 total energy: **-403.5970663 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C2	1.8704839	0.2937357	0.0000000
2	C	C1	0.3657702	0.5357792	0.0000000
3	O	O1	-0.0394777	1.6922725	0.0000000
4	C	C3	-0.4821446	-0.6523079	0.0000000
5	C	C4	-1.8063729	-0.4598518	0.0000000
6	O	O2	-2.9488961	-0.2718587	0.0000000
7	H	H5	-0.0953041	-1.6619569	0.0000000
8	F	F1	2.1911892	-1.0573277	0.0000000
9	H	H2	2.2975860	0.7552322	0.8935986
10	H	H4	2.2975860	0.7552322	-0.8935986

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 189.5611
Entropy Correction (Hv-TSv) 84.6790

Cycloaddition transition state 43b

MP2/6-311+G**

MP2 total energy: **-596.1827108 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.5552874	-0.3418463	-0.0216285
2	H	H4	2.1104464	1.5394424	-0.9179039
3	C	C2	1.2839350	0.9526255	-0.5298155
4	O	O1	0.7292496	-1.2102428	0.3295087
5	C	C3	0.0702763	1.6143021	-0.5684491
6	O	O2	-0.4412587	2.5598231	-1.0837572
7	C	C4	-1.2626895	-0.3649478	1.1396845
8	H	H8	-0.7818688	-0.7644105	2.0251071
9	C	C5	-1.2133715	0.9862046	0.8034254
10	H	H5	-0.8442676	1.6355743	1.5911025
11	H	H10	-2.0477857	1.3736819	0.2319018
12	C	C6	3.0170770	-0.7625871	0.0930593
13	H	H7	3.1784389	-1.6496985	-0.5251155
14	H	H9	3.2245425	-1.0053904	1.1390279
15	O	O3	-1.9837780	-1.2772153	0.5339301
16	C	C7	-2.5268639	-0.9271863	-0.7461711
17	H	H3	-3.3050558	-0.1659673	-0.6452702
18	H	H11	-2.9518535	-1.8469195	-1.1421106
19	H	H12	-1.7207102	-0.5675919	-1.3919187
20	F	F1	3.9102501	0.2223499	-0.3146072

Standard Thermodynamic quantities at 298.15 K and 1.00 atm

ν_i = -351.240 cm^{-1}

Temp. Correction Hv 435.6449

Entropy Correction (Hv-TSv) 300.2351

Cycloaddition transition state 44b

MP2/6-311+G**

MP2 total energy: **-596.1848591 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.0455226	-0.4331275	-0.7504738
2	H	H4	2.1246891	1.3675964	-1.2513305
3	C	C2	1.1452329	0.9077342	-1.1715924
4	O	O1	0.0157669	-1.1524524	-0.7475672
5	C	C3	0.0876310	1.7356624	-1.5303874
6	O	O2	-0.1233167	2.7049404	-2.1906484
7	C	C4	-1.6124381	0.2344866	0.1972893
8	C	C5	-1.5350704	1.4101371	-0.5360405
9	H	H5	-1.3907494	2.3167314	0.0449129
10	H	H10	-2.2171399	1.4726492	-1.3773396
11	C	C6	2.3137669	-1.1266507	-0.2695045
12	H	H7	2.5202421	-1.9813593	-0.9191587
13	H	H9	2.1472846	-1.4809583	0.7527859
14	F	F1	3.4303142	-0.2979778	-0.2679120
15	O	O4	-1.1280841	0.2026848	1.4179759
16	C	C8	-1.1690451	-1.0854010	2.0664495
17	H	H2	-0.6962190	-0.9423890	3.0362069
18	H	H1	-0.6190392	-1.8060570	1.4593331
19	H	H6	-2.2082231	-1.3963096	2.1977587
20	H	H11	-2.1311255	-0.6499399	-0.1607570

Standard Thermodynamic quantities at 298.15 K and 1.00 atm

ν_i = -361.683 cm^{-1}

Temp. Correction Hv 435.4628

Entropy Correction (Hv-TSv) 301.7969

Pyranone 29$_{eq}$

MP2/6-311+G**

MP2 total energy: **-596.2571027 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C5	1.8438912	-1.7256324	0.0651685
2	C	C1	0.9564950	-0.5148288	0.0421758
3	C	C2	1.3696354	0.7557755	-0.1855188
4	H	H2	2.4145364	0.9533884	-0.3920629
5	C	C4	0.4319606	1.8739653	-0.0435557
6	O	O2	0.7445107	3.0451510	-0.2169740
7	C	C6	-0.9653667	1.4625296	0.4015847
8	H	H7	-0.9861107	1.4023979	1.4968093
9	C	C3	-1.3053815	0.1037686	-0.1603903
10	O	O1	-0.3254828	-0.8781572	0.2774448
11	H	H10	-1.6957267	2.2047368	0.0722671
12	H	H1	1.6093449	-2.3747262	-0.7842648
13	H	H4	1.6777885	-2.2765133	0.9960096
14	F	F1	3.1762623	-1.3653584	-0.0116771
15	H	H9	-1.2492248	0.1012074	-1.2635011
16	O	O3	-2.5408393	-0.2992649	0.2847404
17	C	C7	-2.9972521	-1.5002376	-0.3380167
18	H	H3	-2.9885314	-1.3920709	-1.4297314
19	H	H5	-4.0196546	-1.6515694	0.0061238
20	H	H6	-2.3781816	-2.3524991	-0.0469301

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 445.8725
Entropy Correction (Hv-TSv) 319.1865

Pyranone 29_{ax}

MP2/6-311+G**

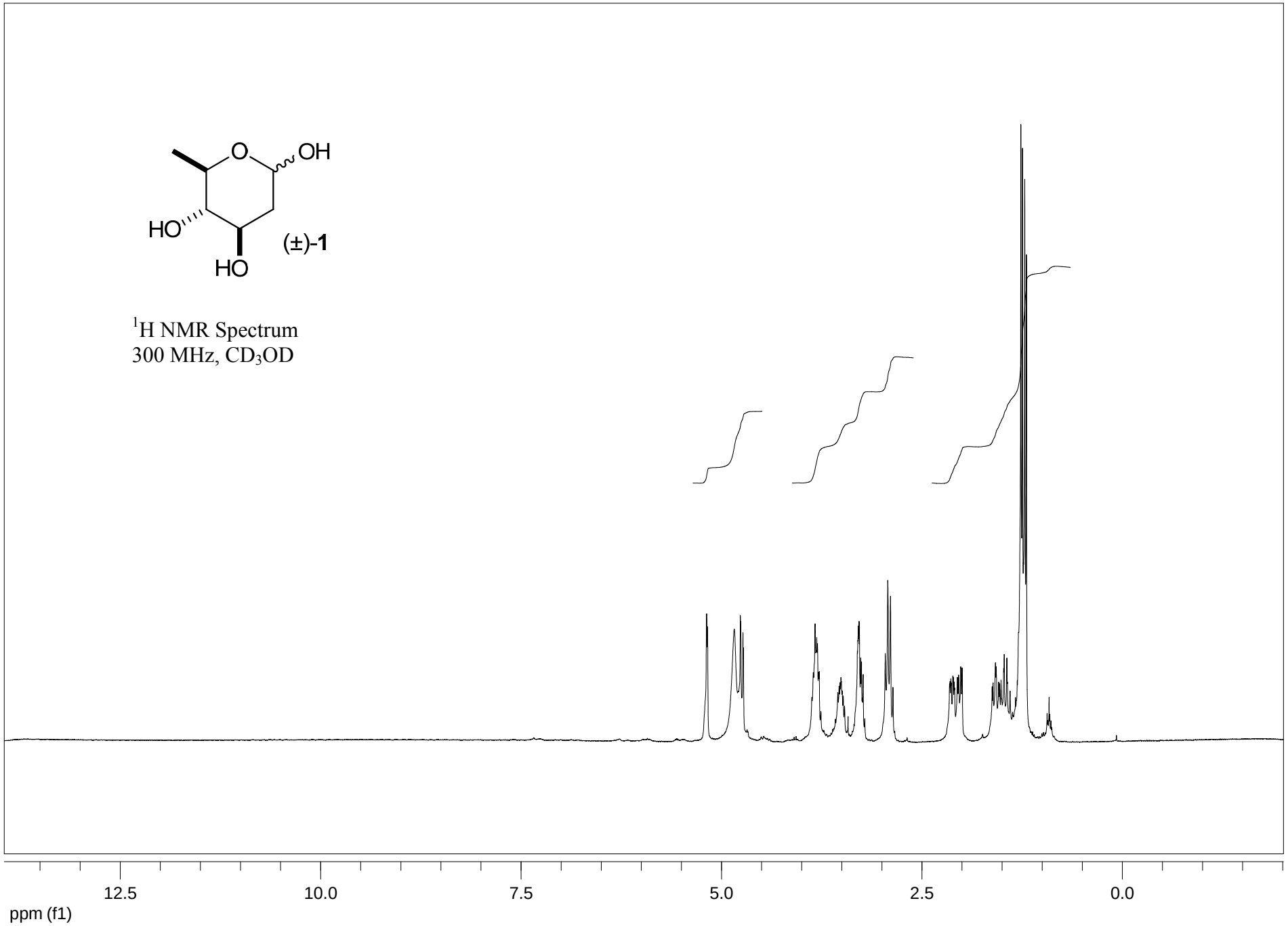
MP2 total energy: **-596.2580563 hartrees**

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C5	2.2814999	-0.9437949	0.1827683
2	C	C1	0.9976278	-0.1679644	0.2361041
3	C	C2	0.8016472	1.0589390	-0.2971906
4	H	H2	1.6043116	1.5475820	-0.8362564
5	C	C4	-0.4792500	1.7446640	-0.1125379
6	O	O2	-0.7450317	2.8306314	-0.6104301
7	C	C6	-1.4353756	1.0295426	0.8322998
8	H	H7	-1.1654917	1.3114657	1.8575214
9	C	C3	-1.3082471	-0.4709832	0.6859076
10	O	O1	0.0578968	-0.8946113	0.8987841
11	O	O3	-1.7409357	-0.8093028	-0.5885491
12	C	C7	-1.7997046	-2.2160289	-0.8088467
13	H	H3	-2.4182837	-2.7001607	-0.0425135
14	H	H5	-0.8000848	-2.6604429	-0.8020978
15	H	H9	-2.2563544	-2.3534010	-1.7884186
16	H	H6	-1.8589234	-1.0282289	1.4538490
17	H	H10	-2.4618281	1.3442791	0.6340496
18	H	H1	2.1527623	-1.8326202	-0.4430451
19	H	H4	2.5611716	-1.2541141	1.1942650
20	F	F1	3.3020111	-0.1771492	-0.3485357

Standard Thermodynamic quantities at 298.15 K and 1.00 atm
Temp. Correction Hv 446.0419
Entropy Correction (Hv-TSv) 319.5682

Characterisation spectra for **1, 6**, **8**, **11**, **17**, **19**, **22**, **27**, **29**, **30a** and **30b**, **31**, **33**, **35**, **40**, **41** and **43**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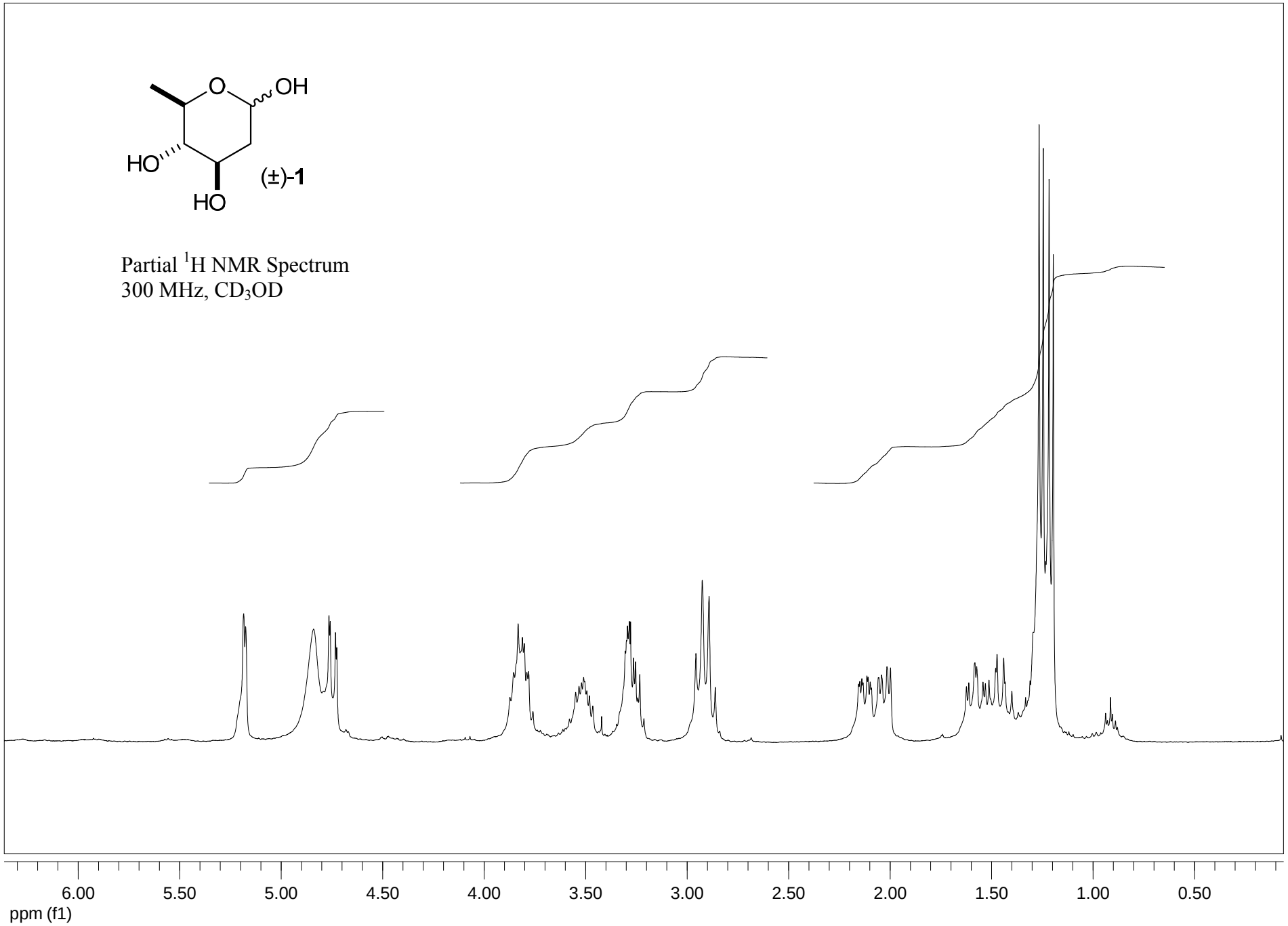
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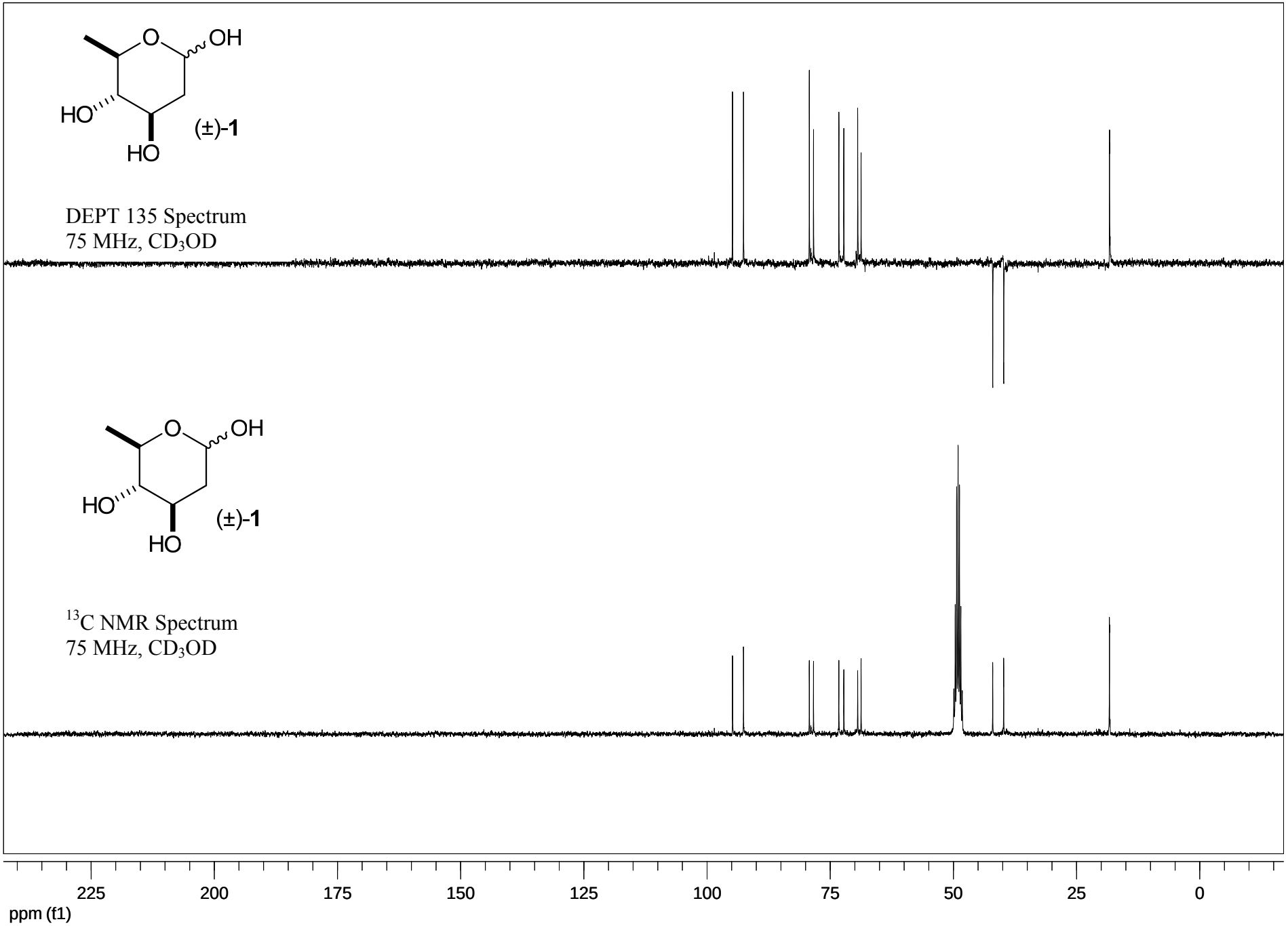
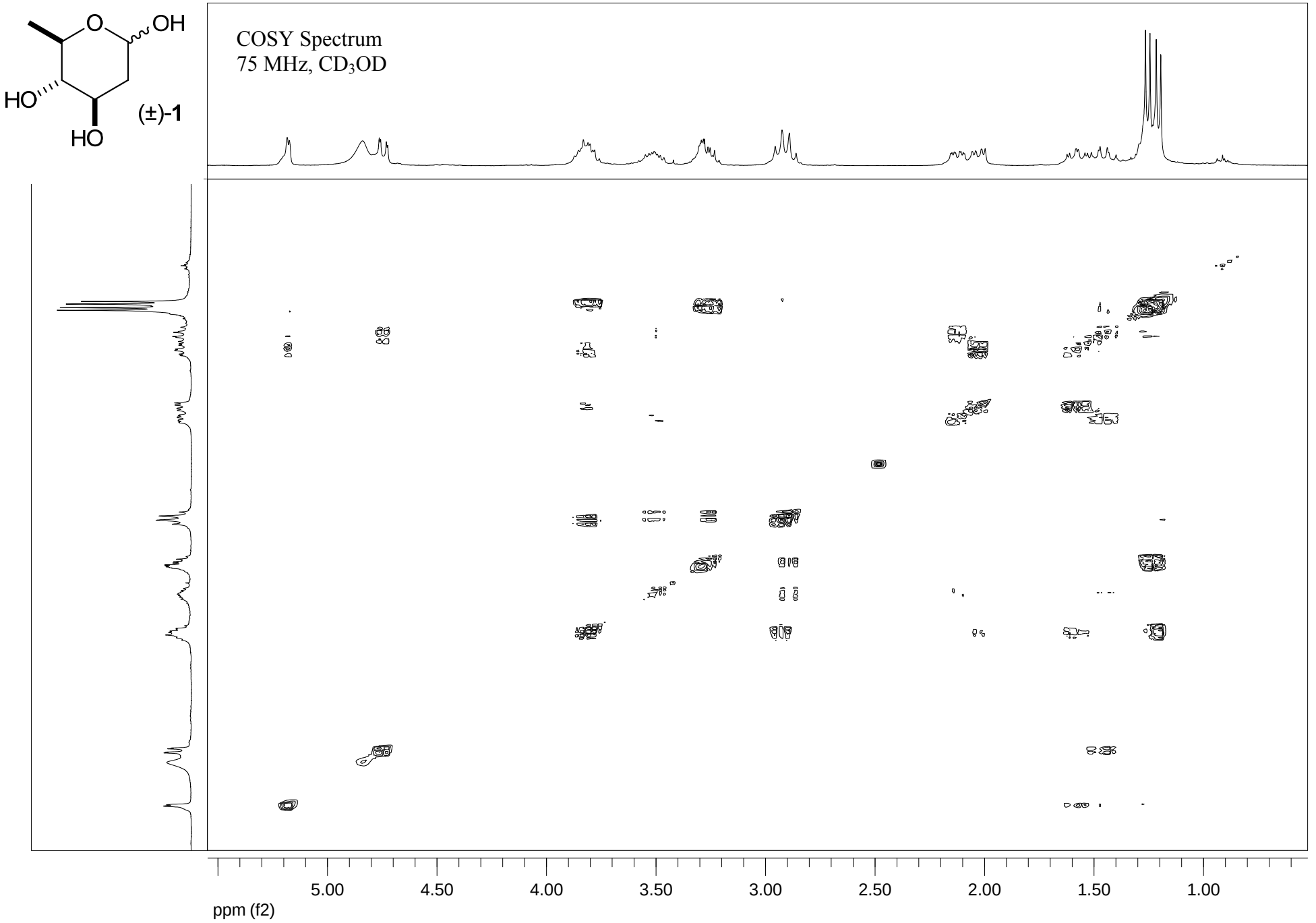
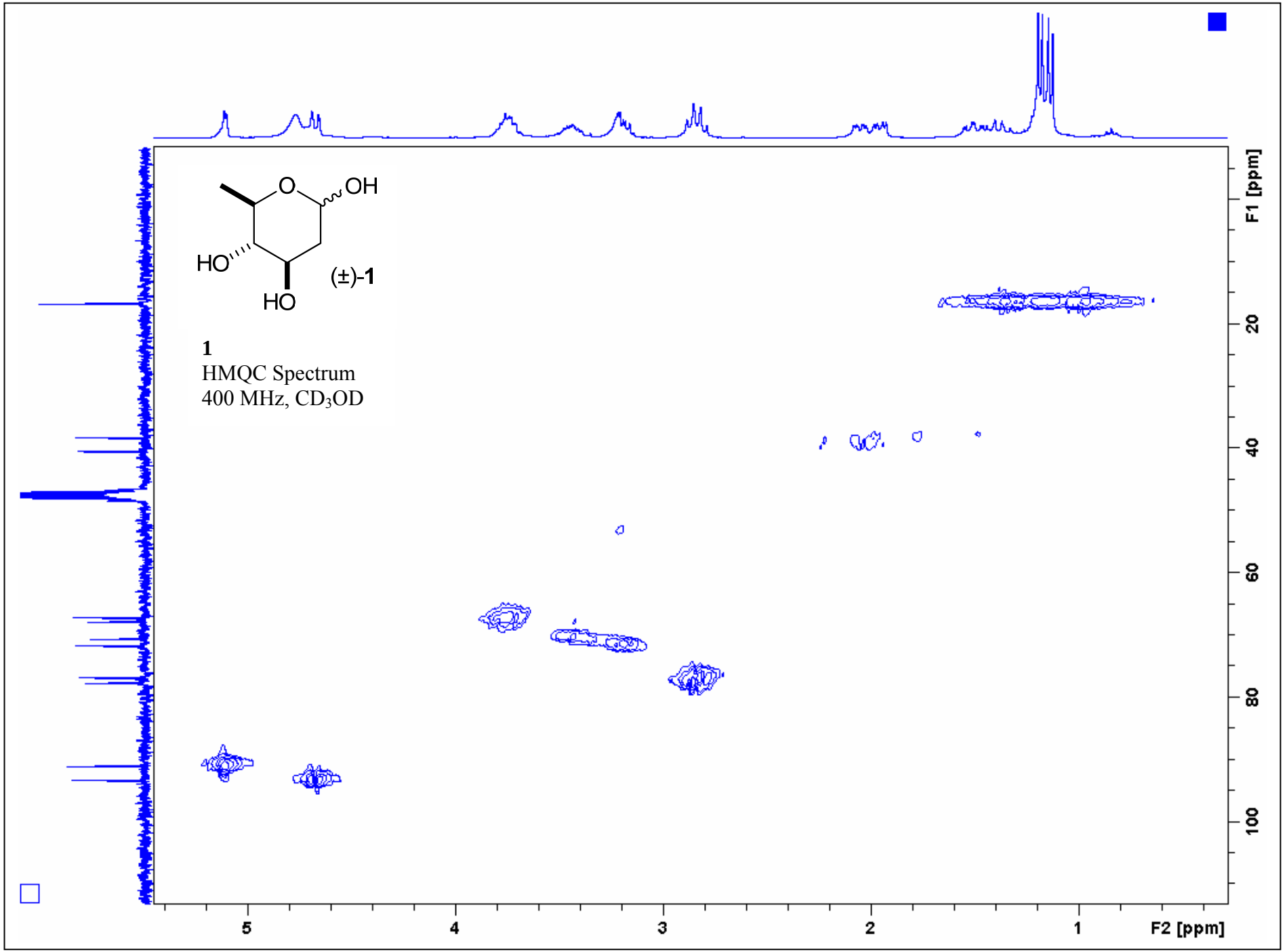
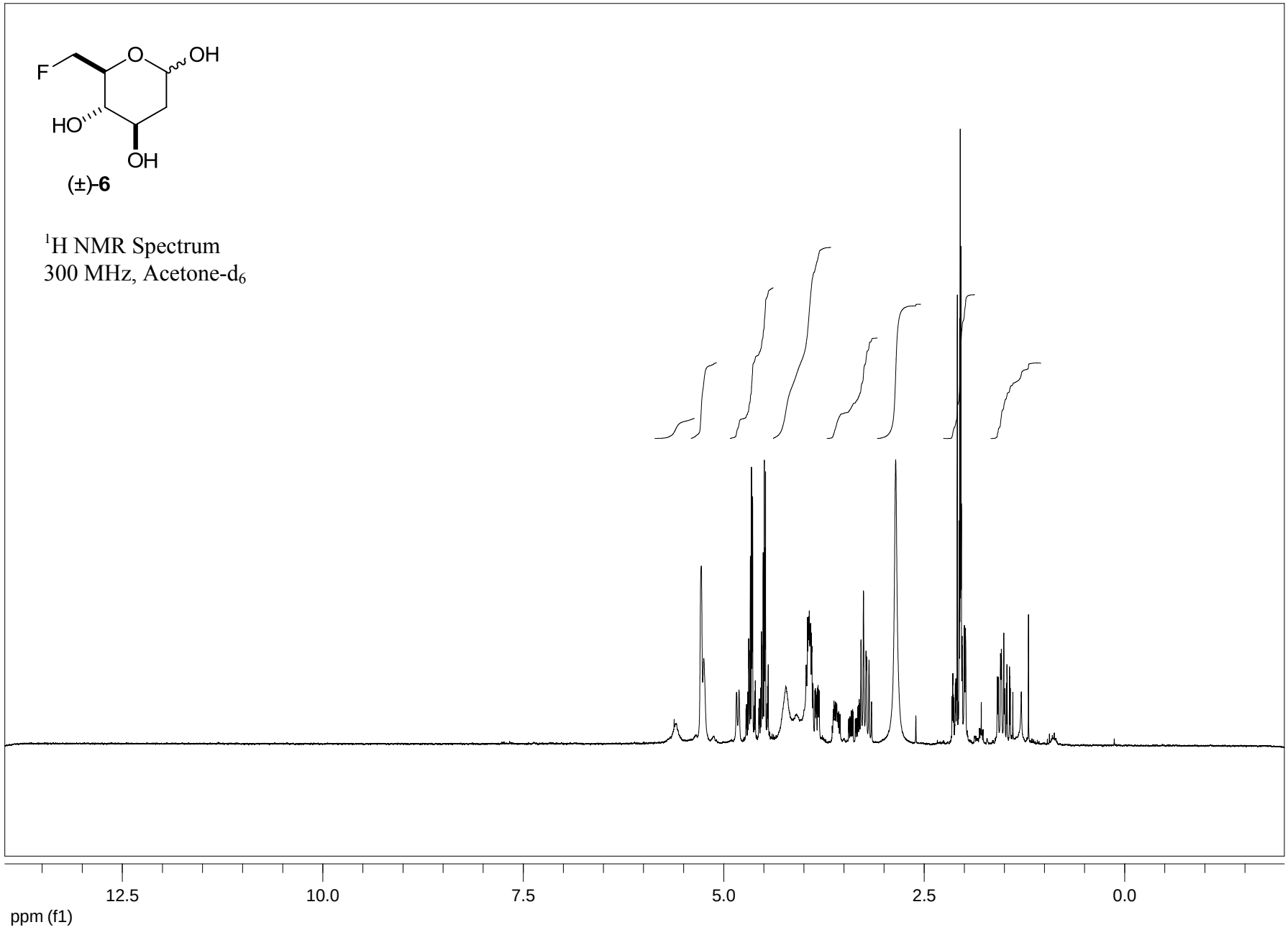
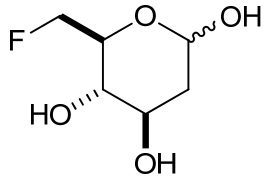
0.50
ppm (f1)


O
OH
HO
HO
(±)-1
DEPT 135 Spectrum
75 MHz, CD3OD
O
OH
HO
HO
(±)-1
13C NMR Spectrum
75 MHz, CD3OD
225
200
175
150
125
100
75
50
25
0
ppm (f1)


O
OH
HO
HO
(±)-1
COSY Spectrum
75 MHz, CD3OD
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (f2)

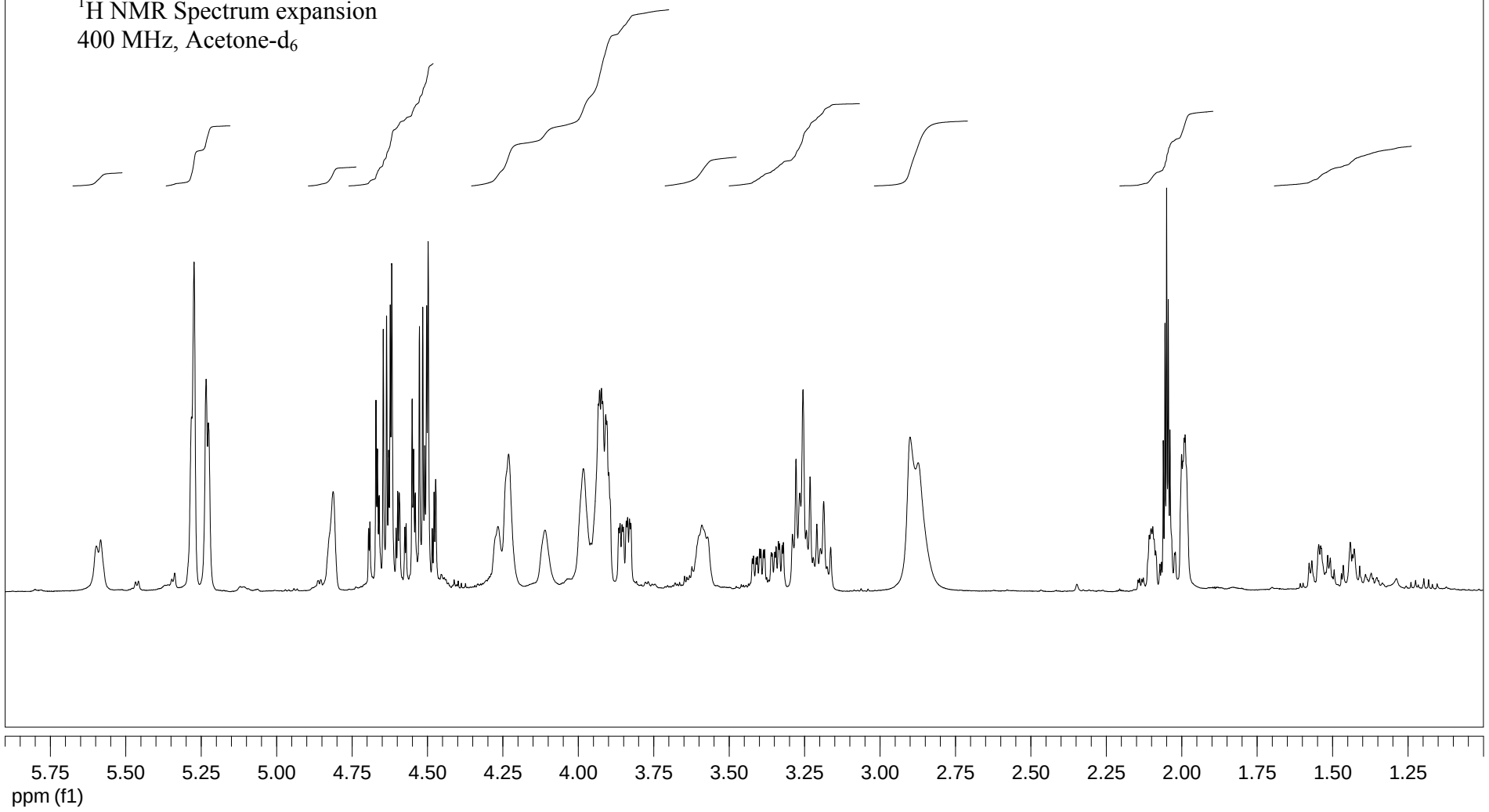

O
OH
HO
HO
(±)-1
1
HMQC Spectrum
400 MHz, CD3OD
F1 [ppm]
20
40
60
80
100
5
4
3
2
1
F2 [ppm]

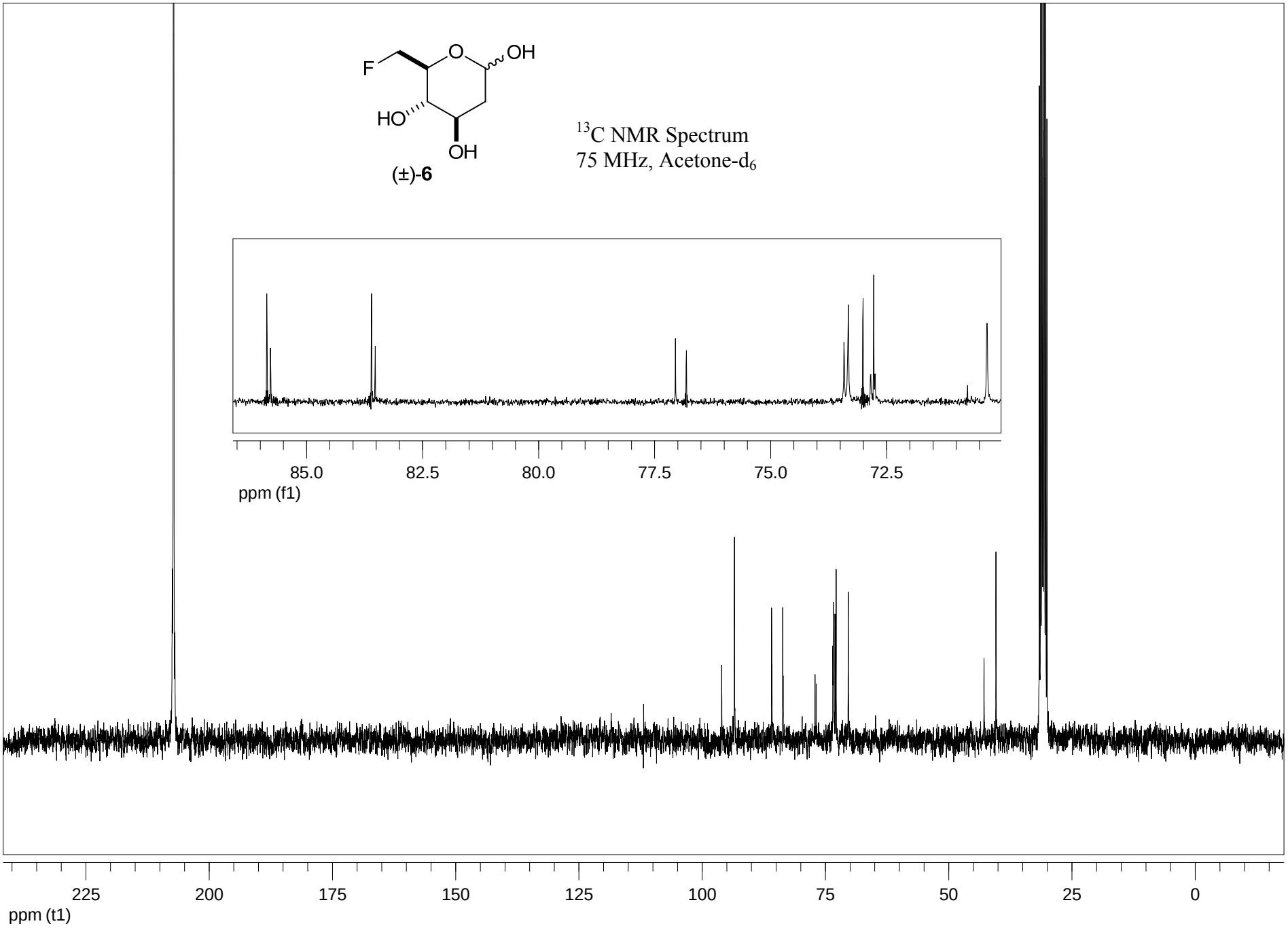

F
O
OH
HO
OH
(±)-6
1H NMR Spectrum
300 MHz, Acetone-d6
12.5
10.0
7.5
5.0
2.5
0.0
ppm (f1)

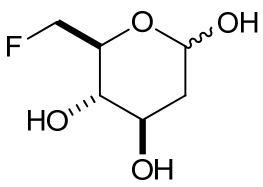


(±)-**6**

^{1}H NMR Spectrum expansion
400 MHz, Acetone-d_6

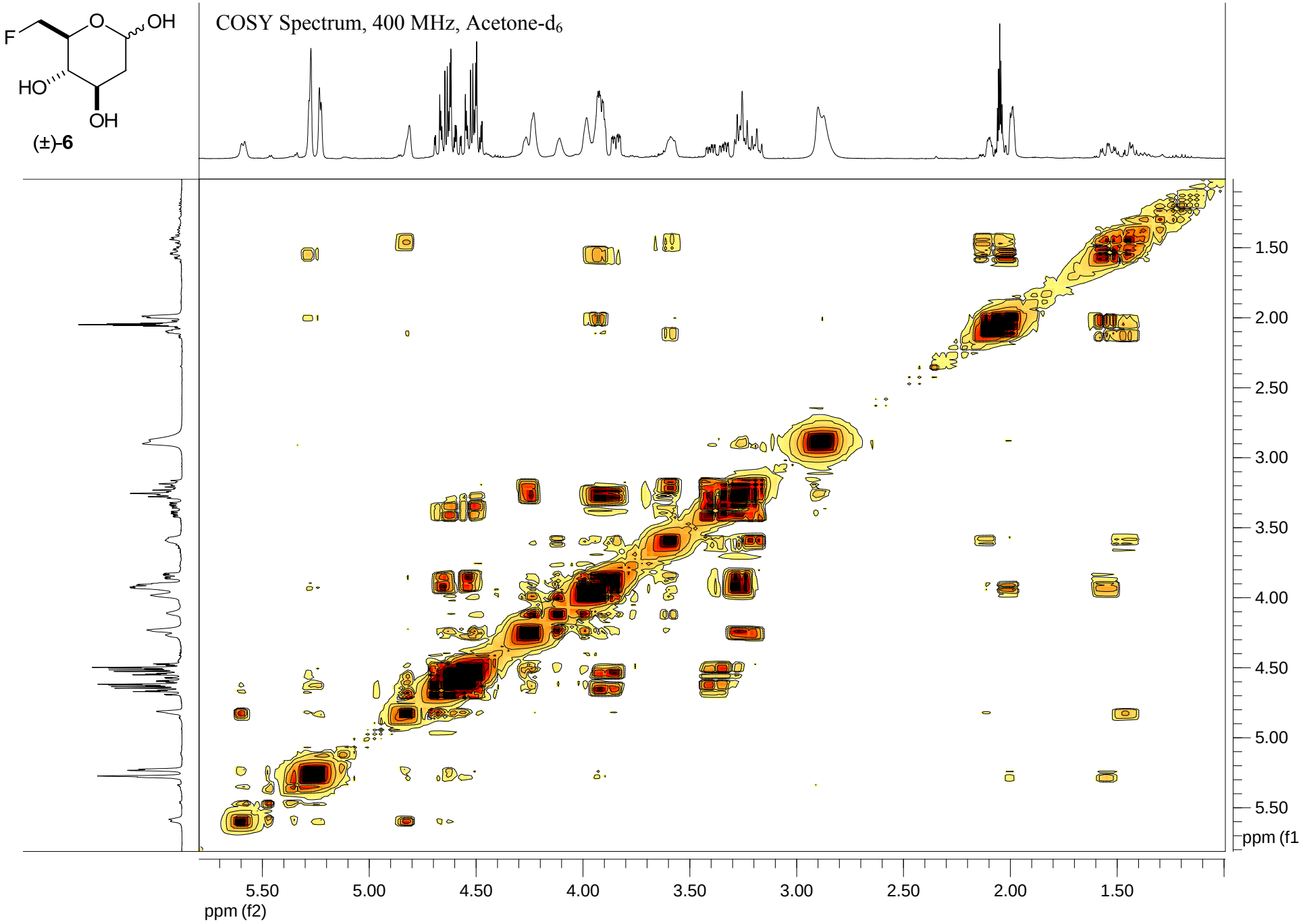


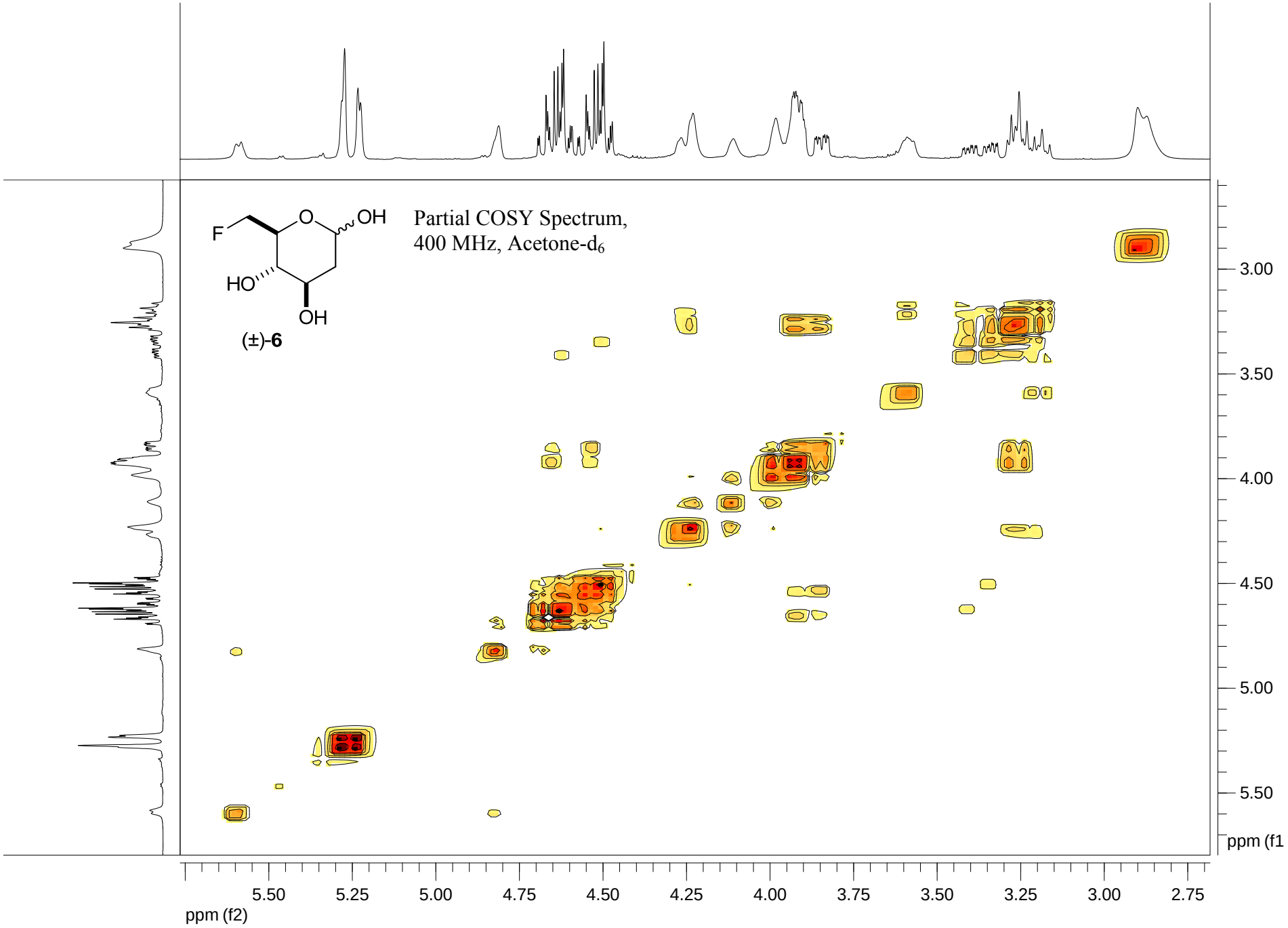

F
O
OH
HO
OH
(±)-6
^{13}C NMR Spectrum
75 MHz, Acetone-d$_6$
85.0
82.5
80.0
77.5
75.0
72.5
ppm (f1)
225
200
175
150
125
100
75
50
25
0
ppm (t1)

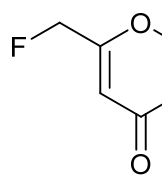


(±)-**6**

^{19}F NMR Spectrum
282 MHz, Acetone-d_6

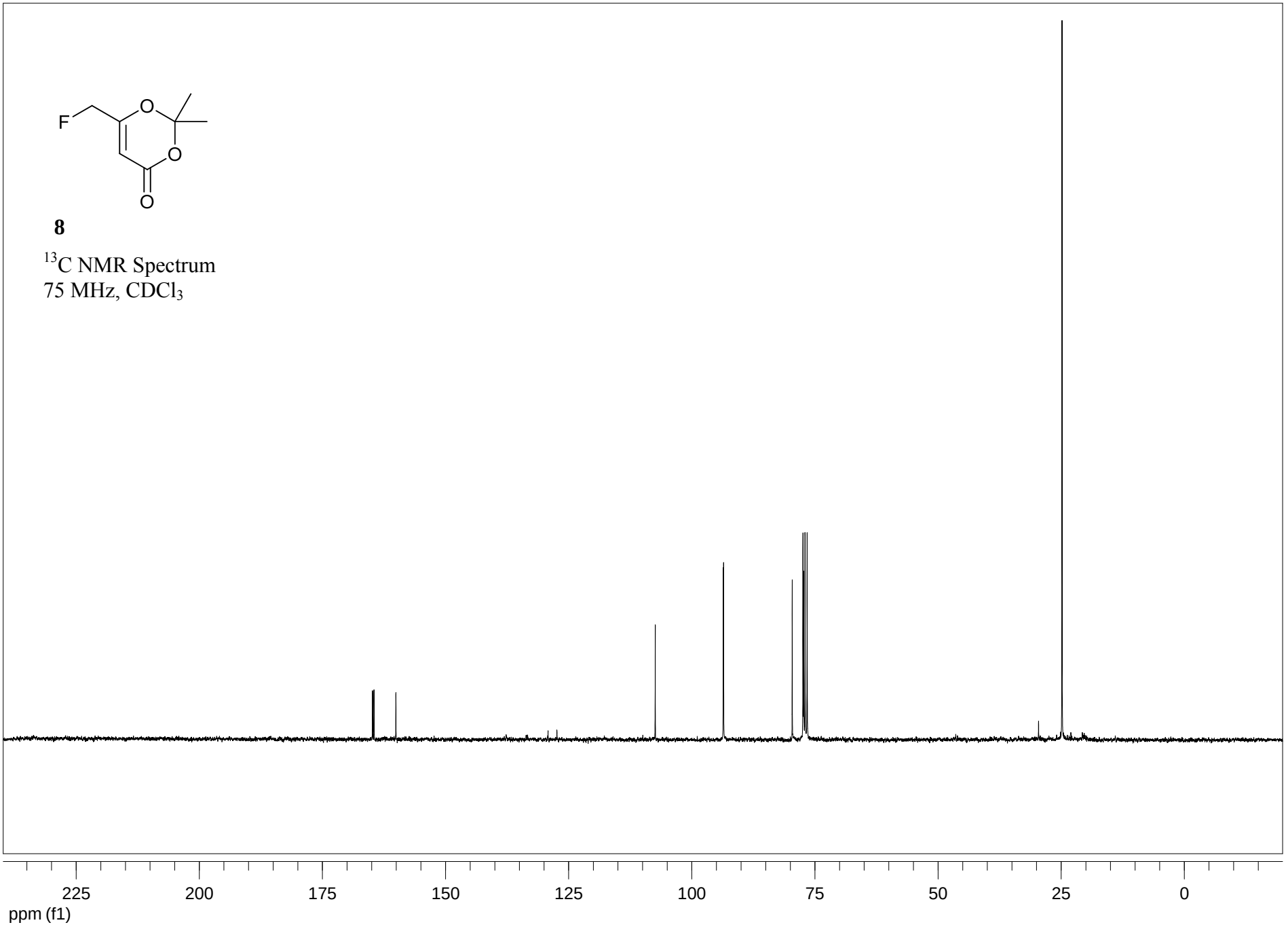

F
O
OH
HO
OH
(±)-6
COSY Spectrum, 400 MHz, Acetone-d6
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
ppm (f1
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
ppm (f2)

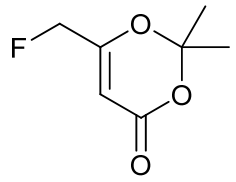

F
O
OH
HO
OH
(±)-6
Partial COSY Spectrum,
400 MHz, Acetone-d6
3.00
3.50
4.00
4.50
5.00
5.50
ppm (f1
5.50
5.25
5.00
4.75
4.50
4.25
4.00
3.75
3.50
3.25
3.00
2.75
ppm (f2)



8

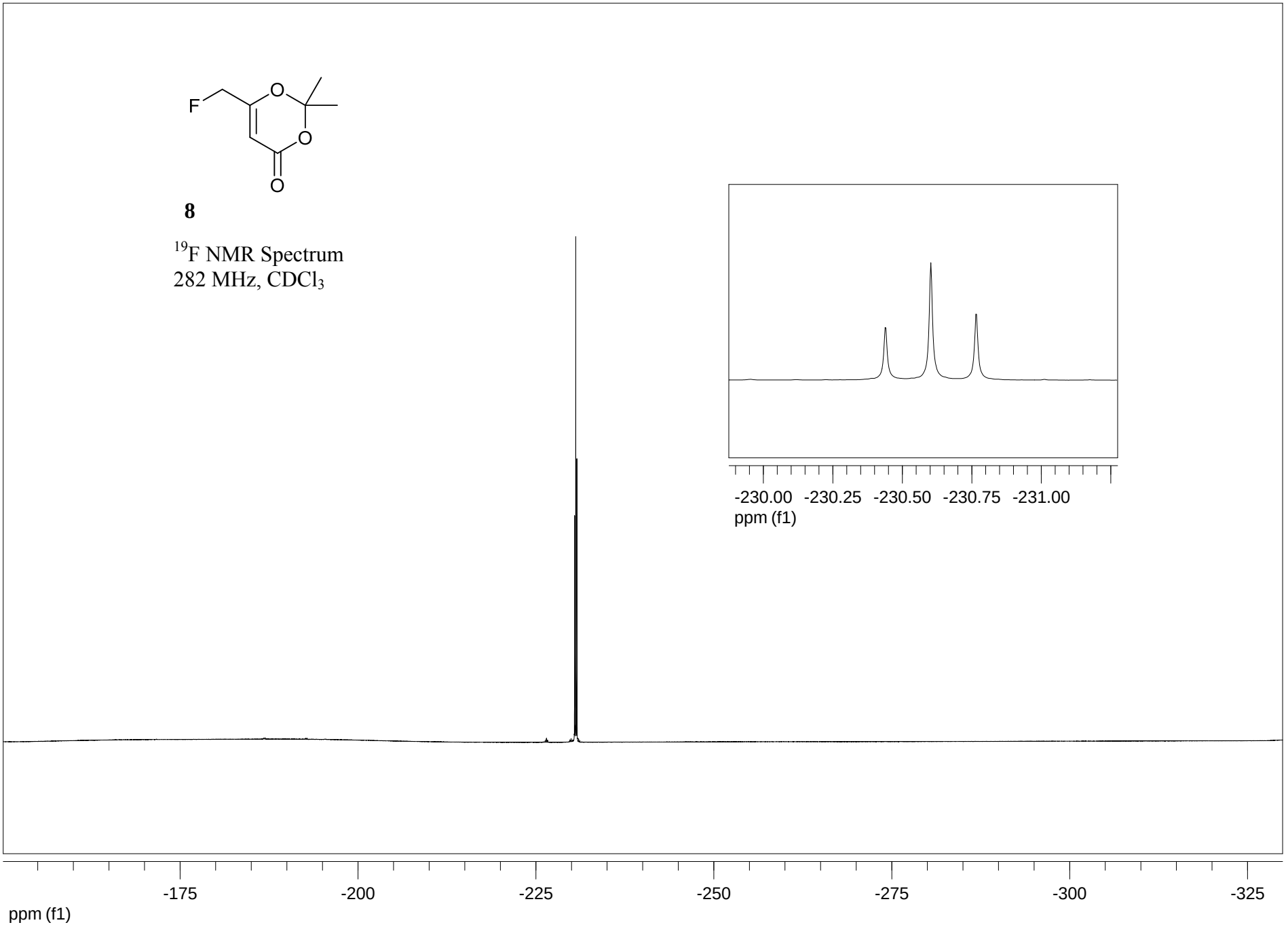
^{1}H NMR Spectrum
300 MHz, $CDCl_3$

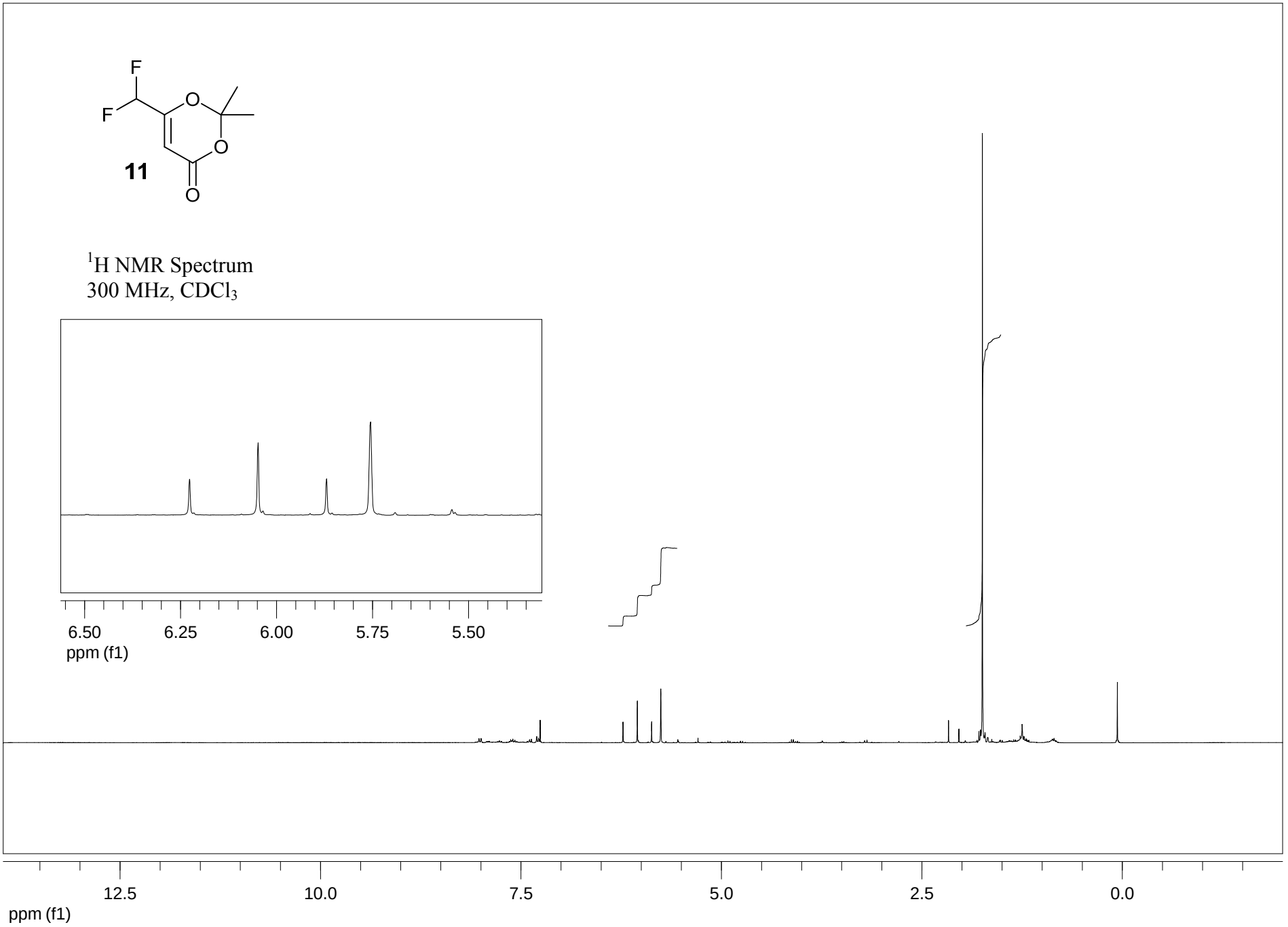

F
O
O
O
8
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)

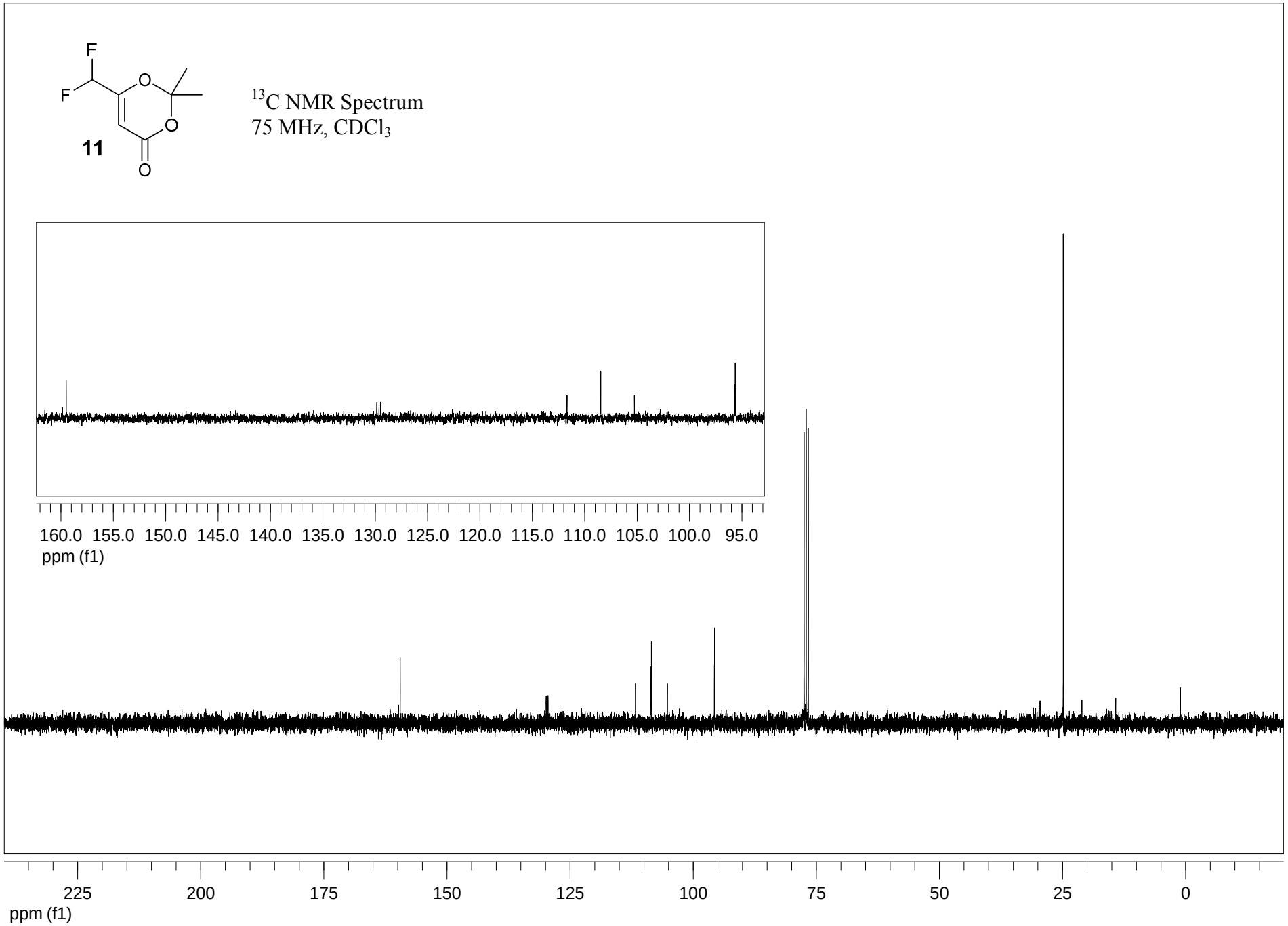


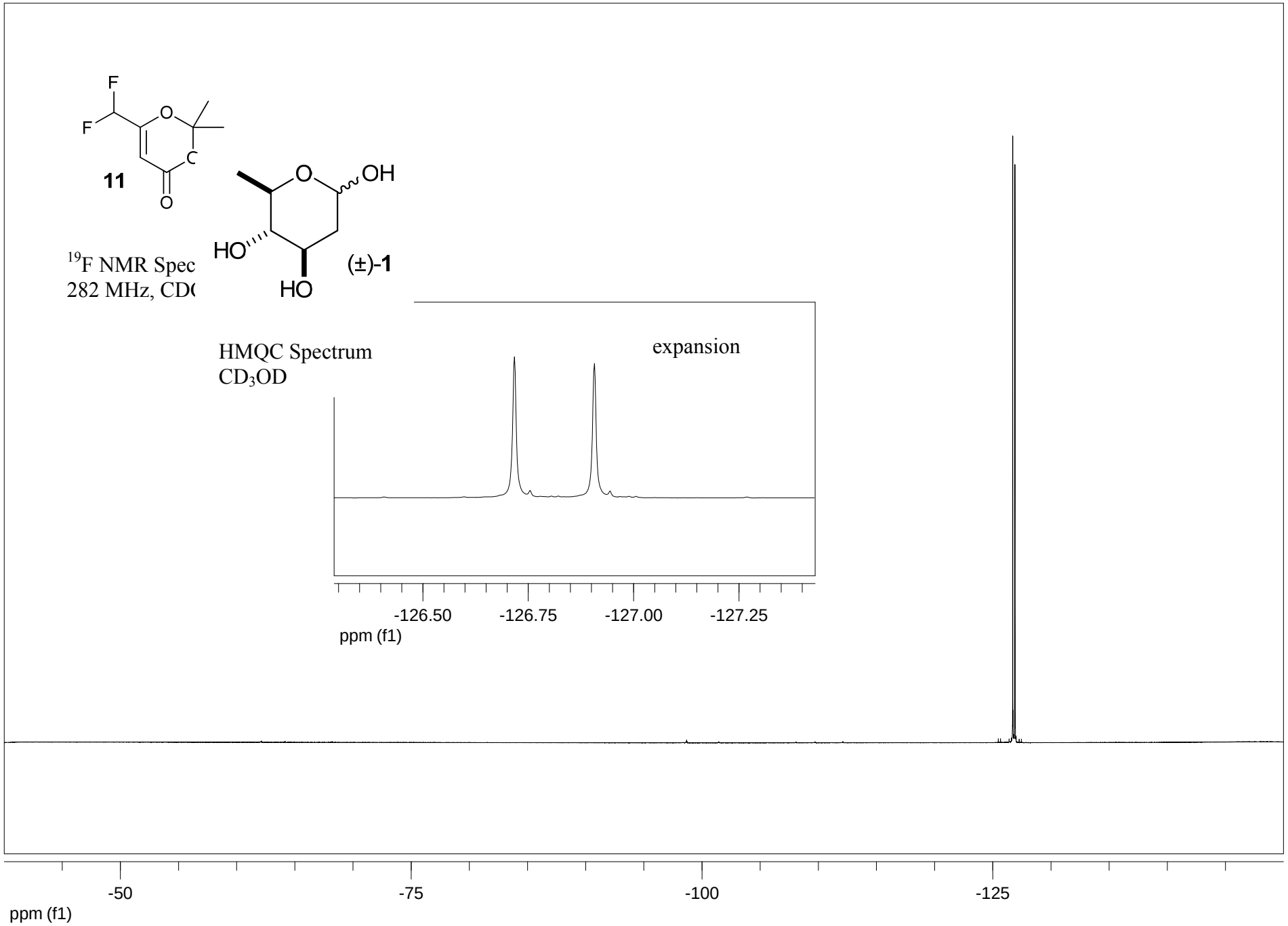
8

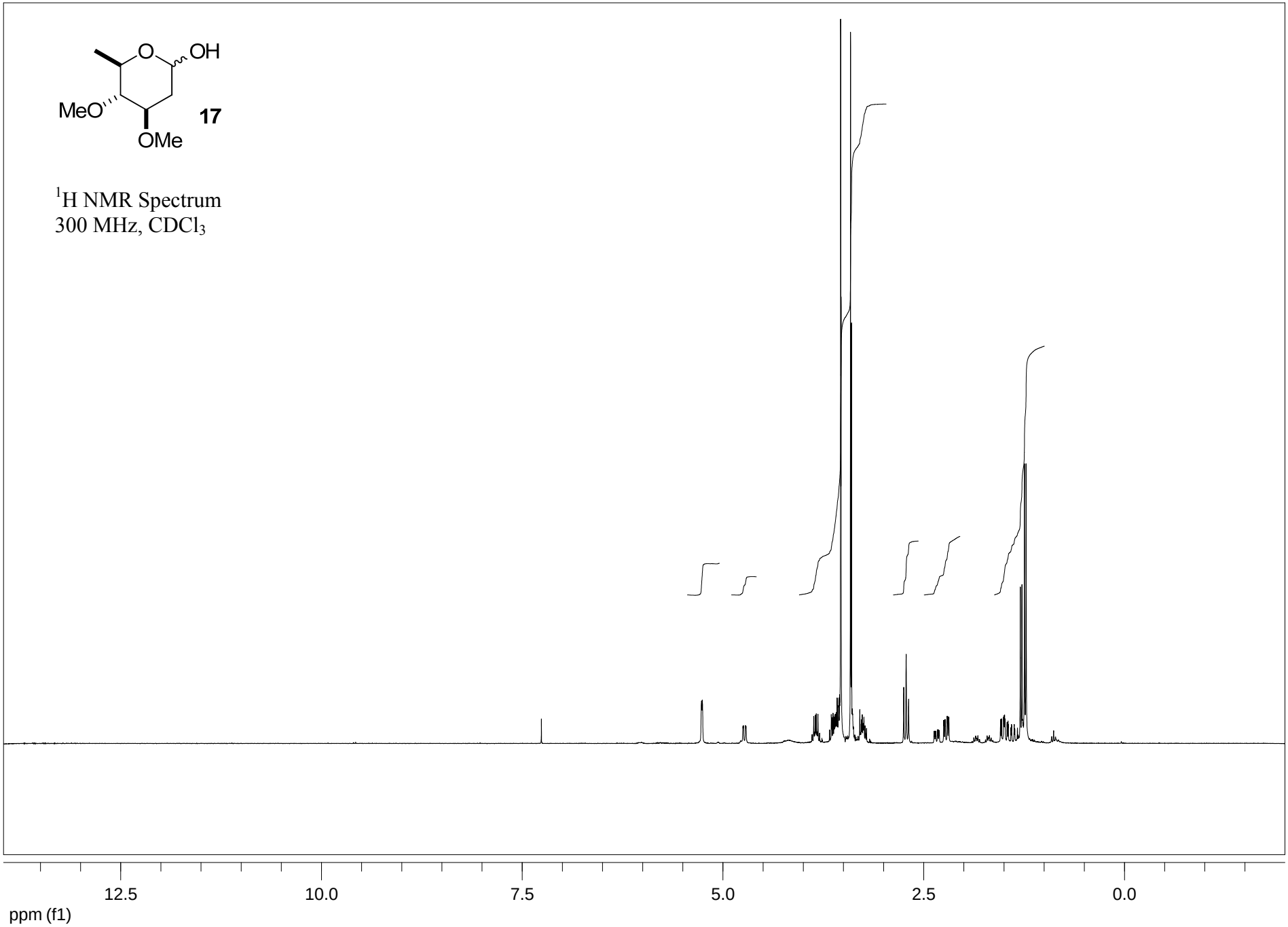
^{13}C NMR Spectrum (expansion)
75 MHz, $CDCl_3$

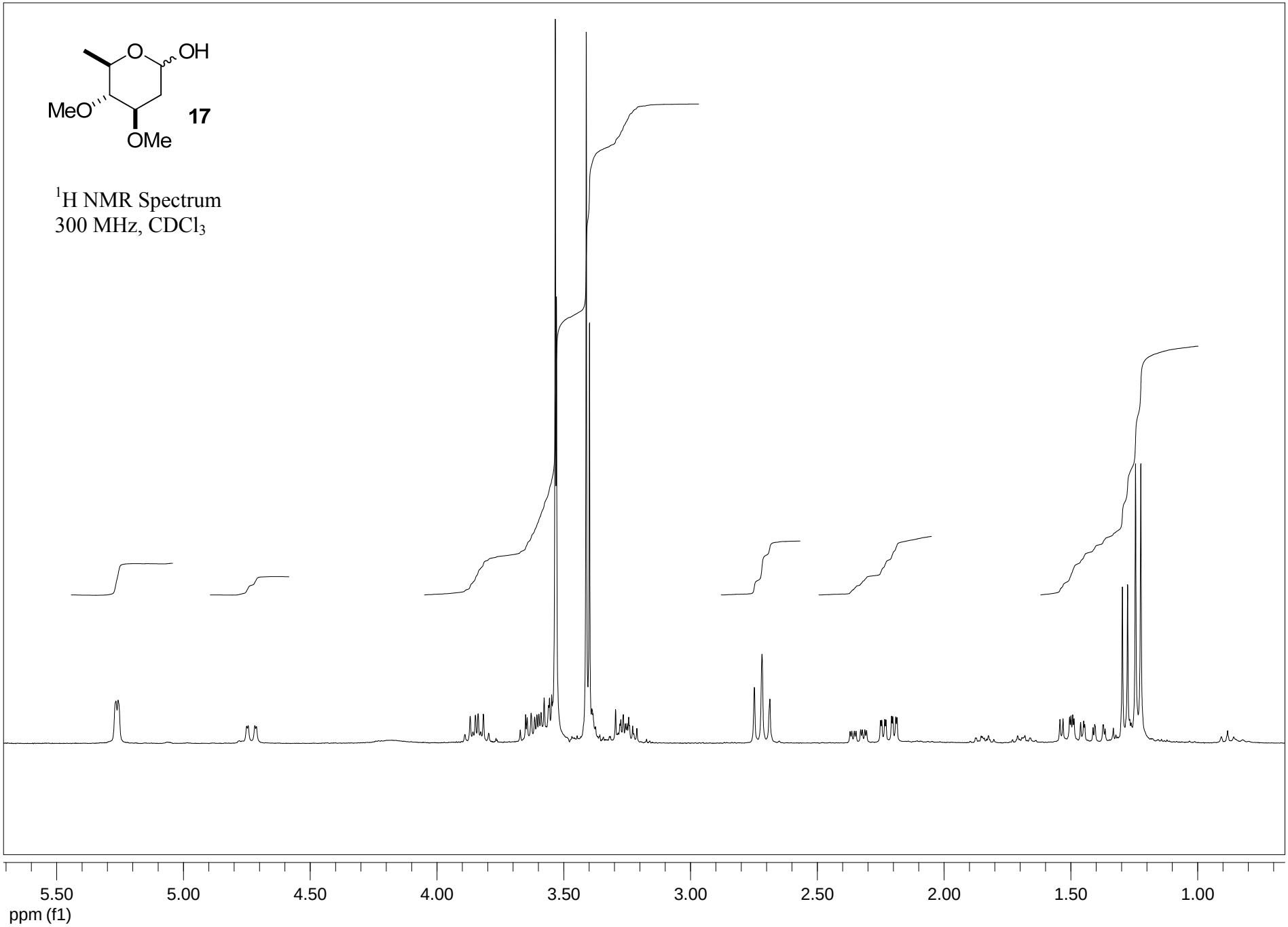

F
O
O
O
8
19F NMR Spectrum
282 MHz, CDCl3
-230.00
-230.25
-230.50
-230.75
-231.00
ppm (f1)
-175
-200
-225
-250
-275
-300
-325
ppm (f1)

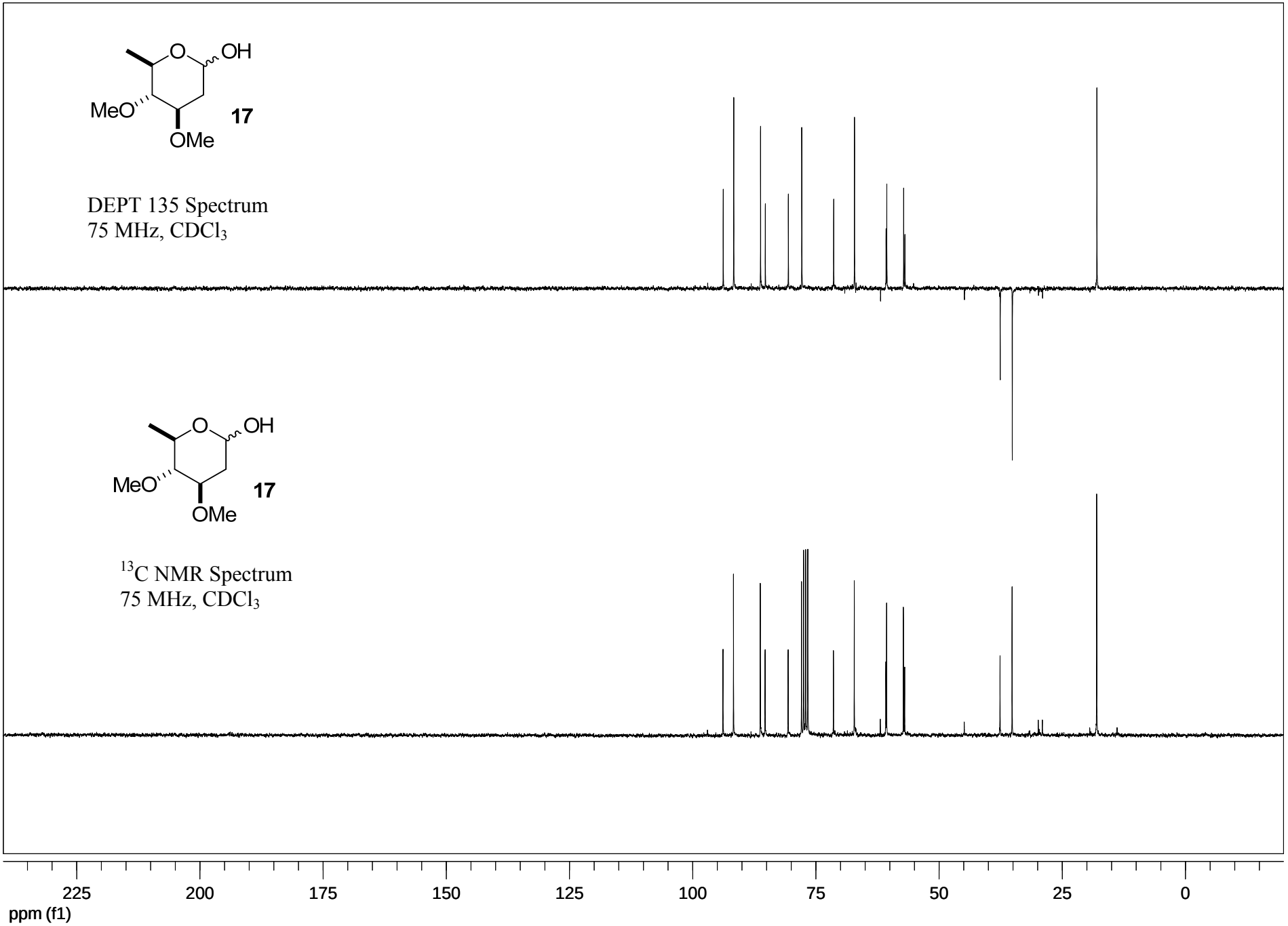

F
F
O
O
O
11
^{1}H NMR Spectrum
300 MHz, $CDCl_3$
6.50
6.25
6.00
5.75
5.50
ppm (f1)
12.5
10.0
7.5
5.0
2.5
0.0
ppm (f1)

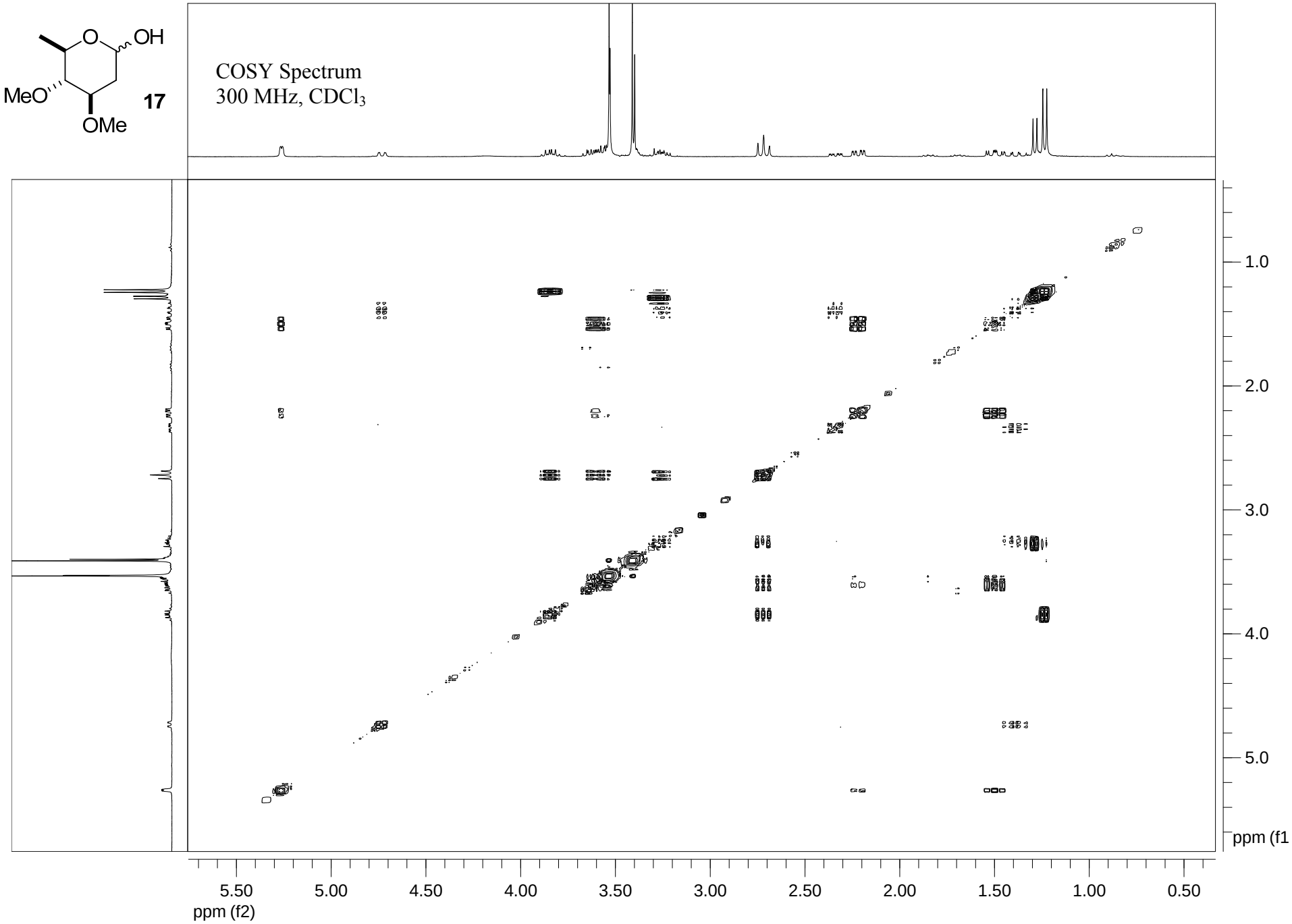

F
F
O
O
O
11
^{13}C NMR Spectrum
75 MHz, $CDCl_3$
160.0 155.0 150.0 145.0 140.0 135.0 130.0 125.0 120.0 115.0 110.0 105.0 100.0 95.0
ppm (f1)
225 200 175 150 125 100 75 50 25 0
ppm (f1)

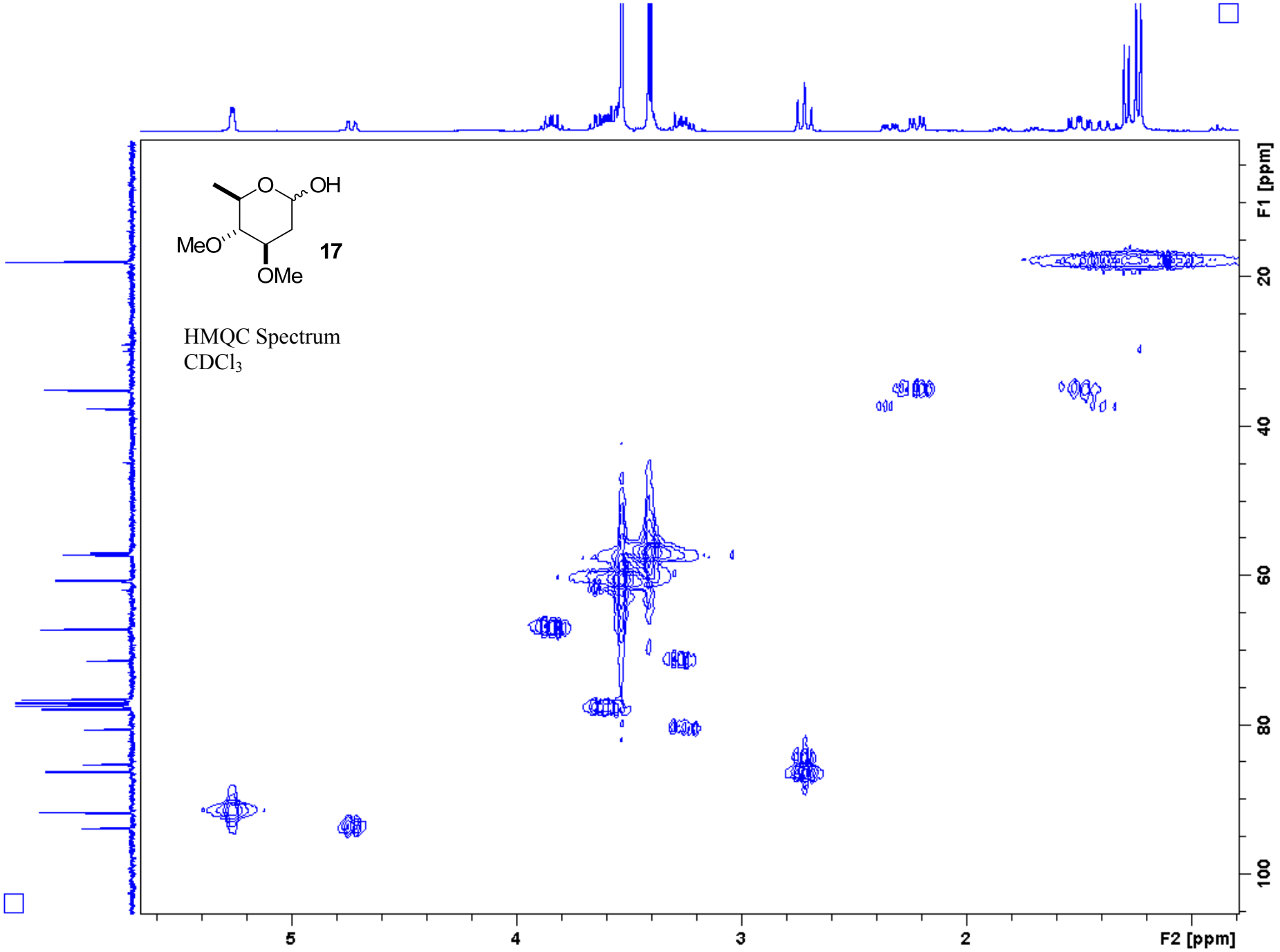

F
F
O
C
O
11
O
OH
HO
HO
(±)-1
19F NMR Spec
282 MHz, CD(
HMQC Spectrum
CD3OD
expansion
-126.50
-126.75
-127.00
-127.25
ppm (f1)
-50
-75
-100
-125
ppm (f1)

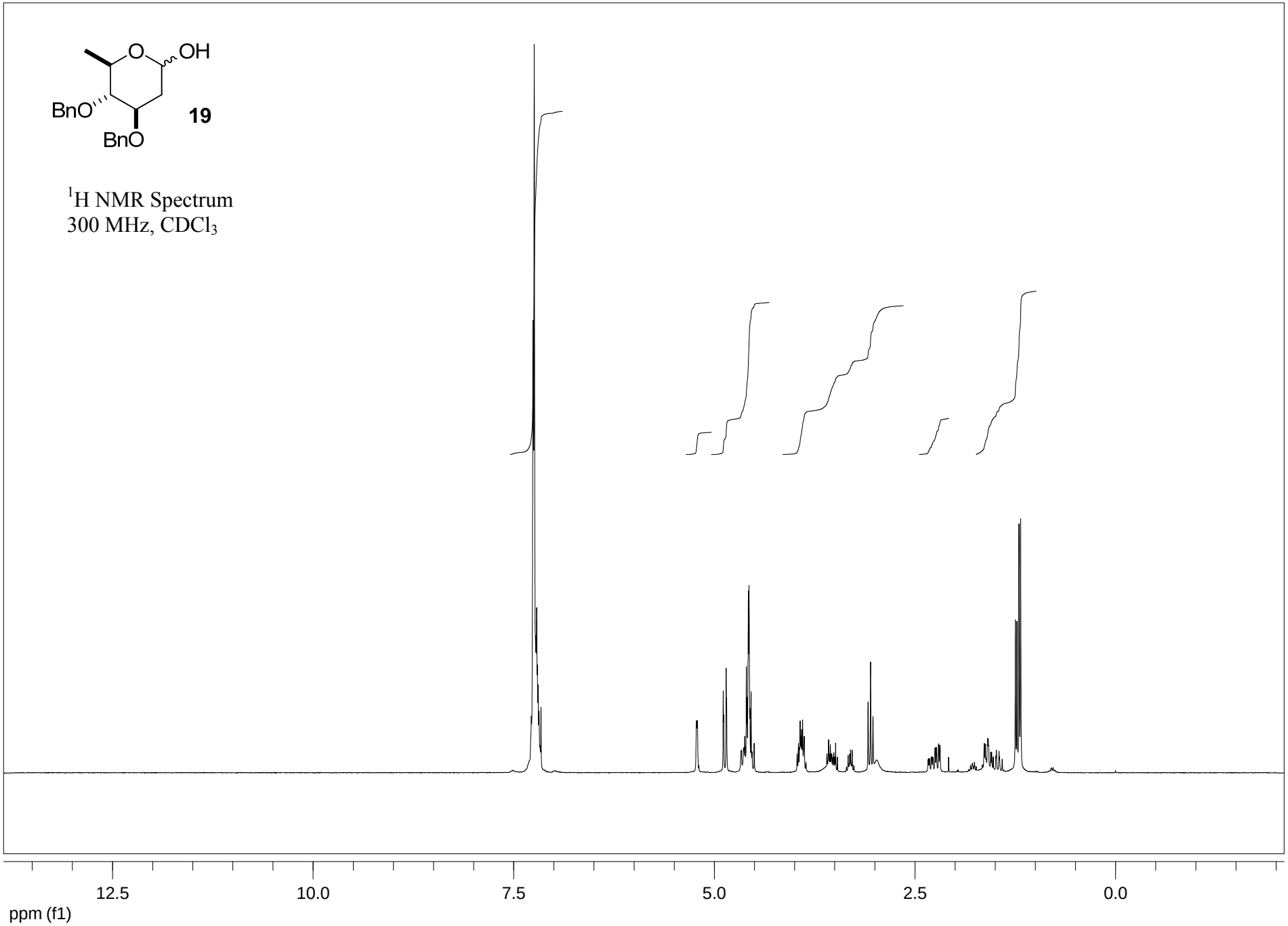

O
OH
MeO
OMe
17
^{1}H NMR Spectrum
300 MHz, $CDCl_3$
12.5
10.0
7.5
5.0
2.5
0.0
ppm (f1)


O
OH
MeO
OMe
17
1H NMR Spectrum
300 MHz, CDCl3
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (f1)

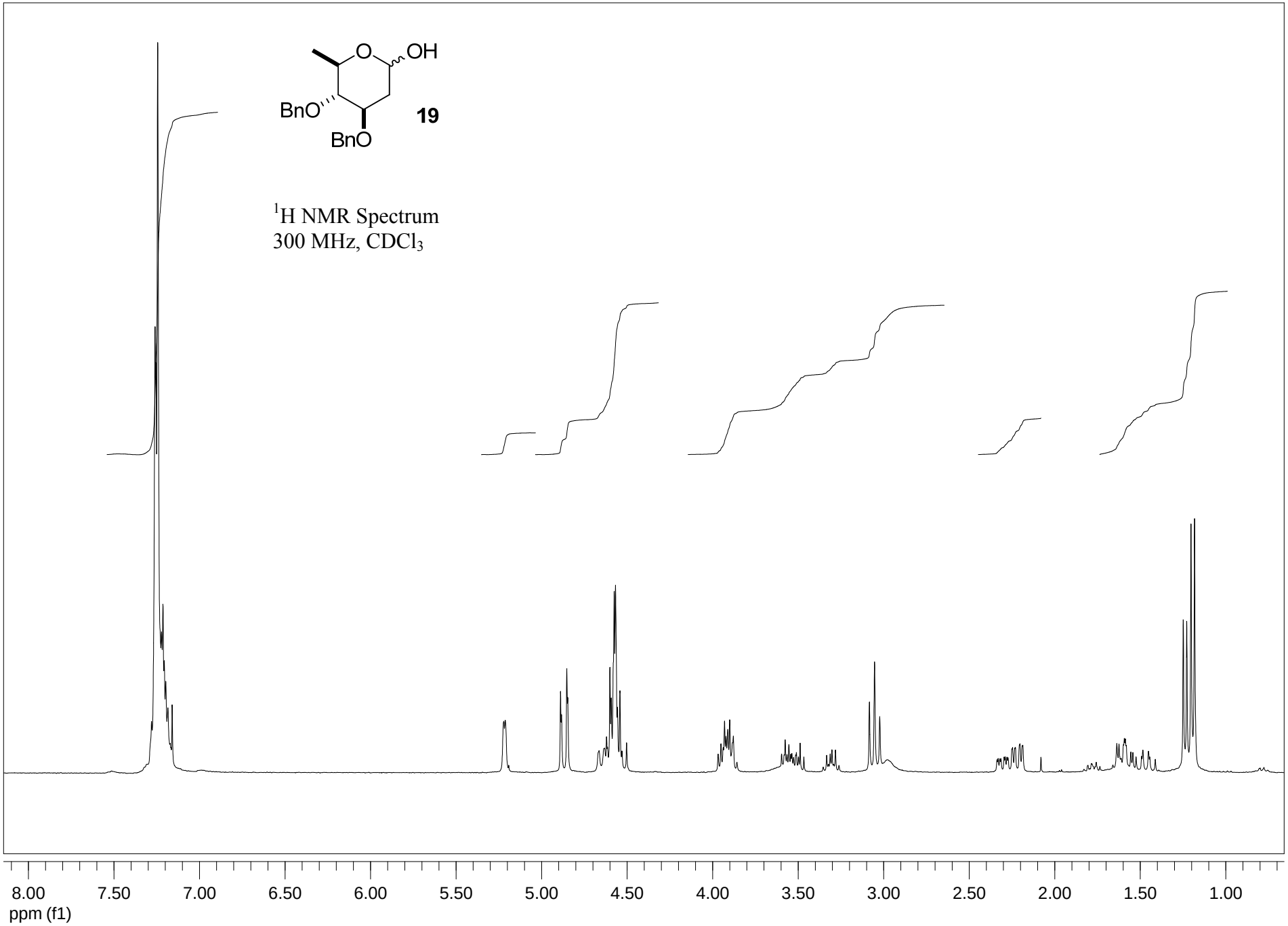

O
OH
MeO
OMe
17
DEPT 135 Spectrum
75 MHz, CDCl3
O
OH
MeO
OMe
17
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)

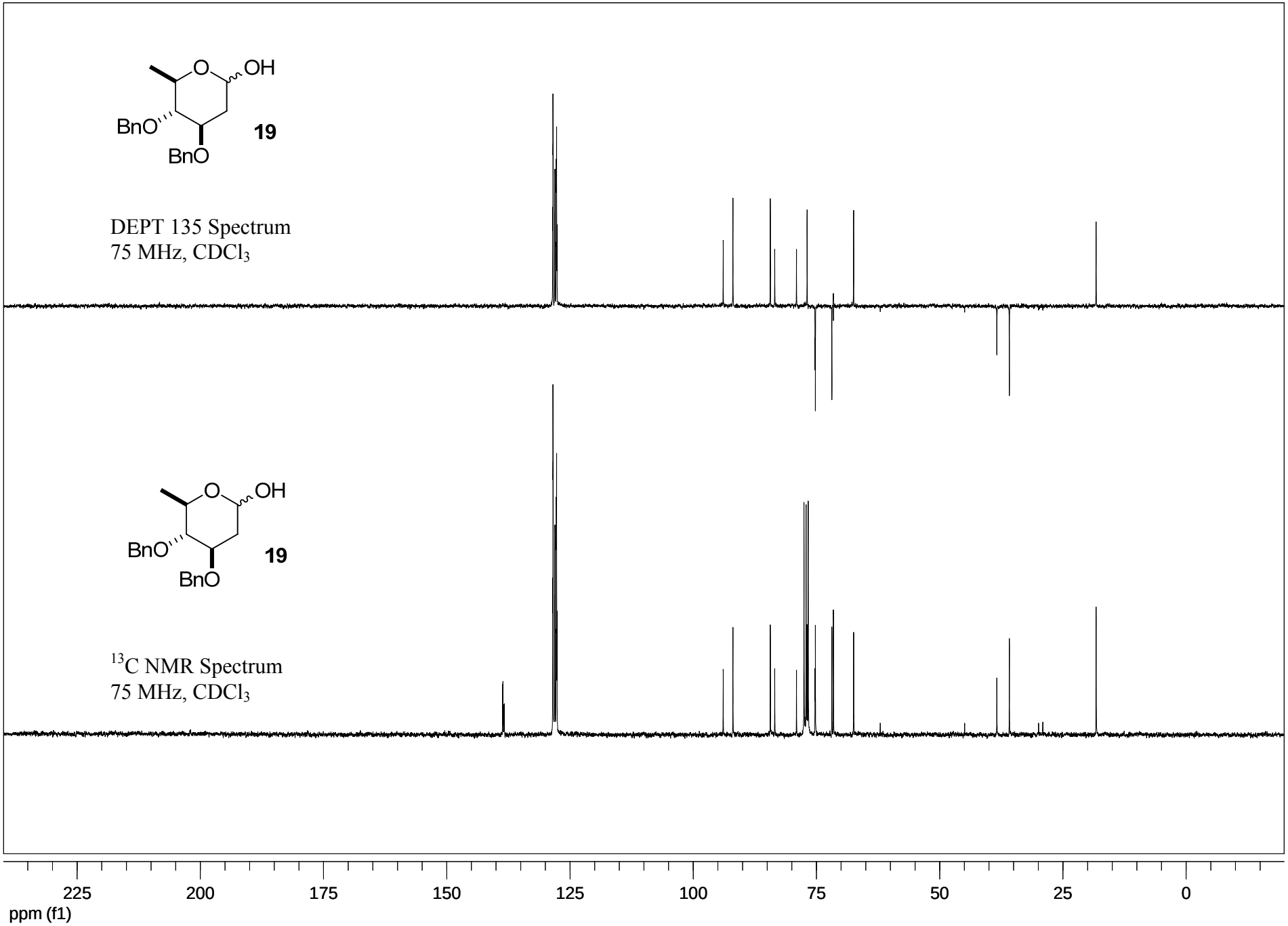

O
OH
MeO
OMe
17
COSY Spectrum
300 MHz, $CDCl_3$
1.0
2.0
3.0
4.0
5.0
ppm (f1
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (f2)

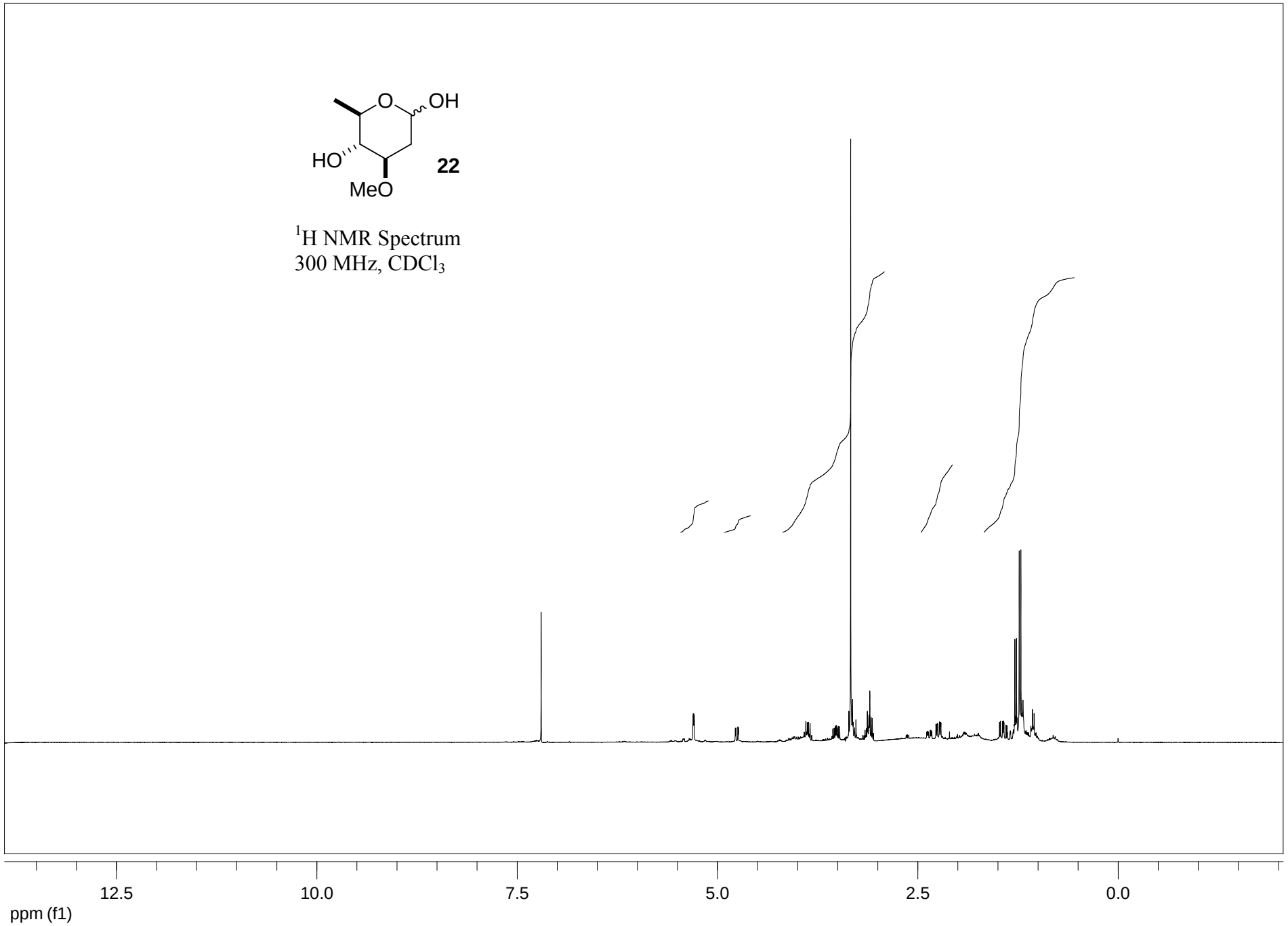

O
OH
MeO
OMe
17
HMQC Spectrum
CDCl3
F1 [ppm]
20
40
60
80
100
5
4
3
2
F2 [ppm]



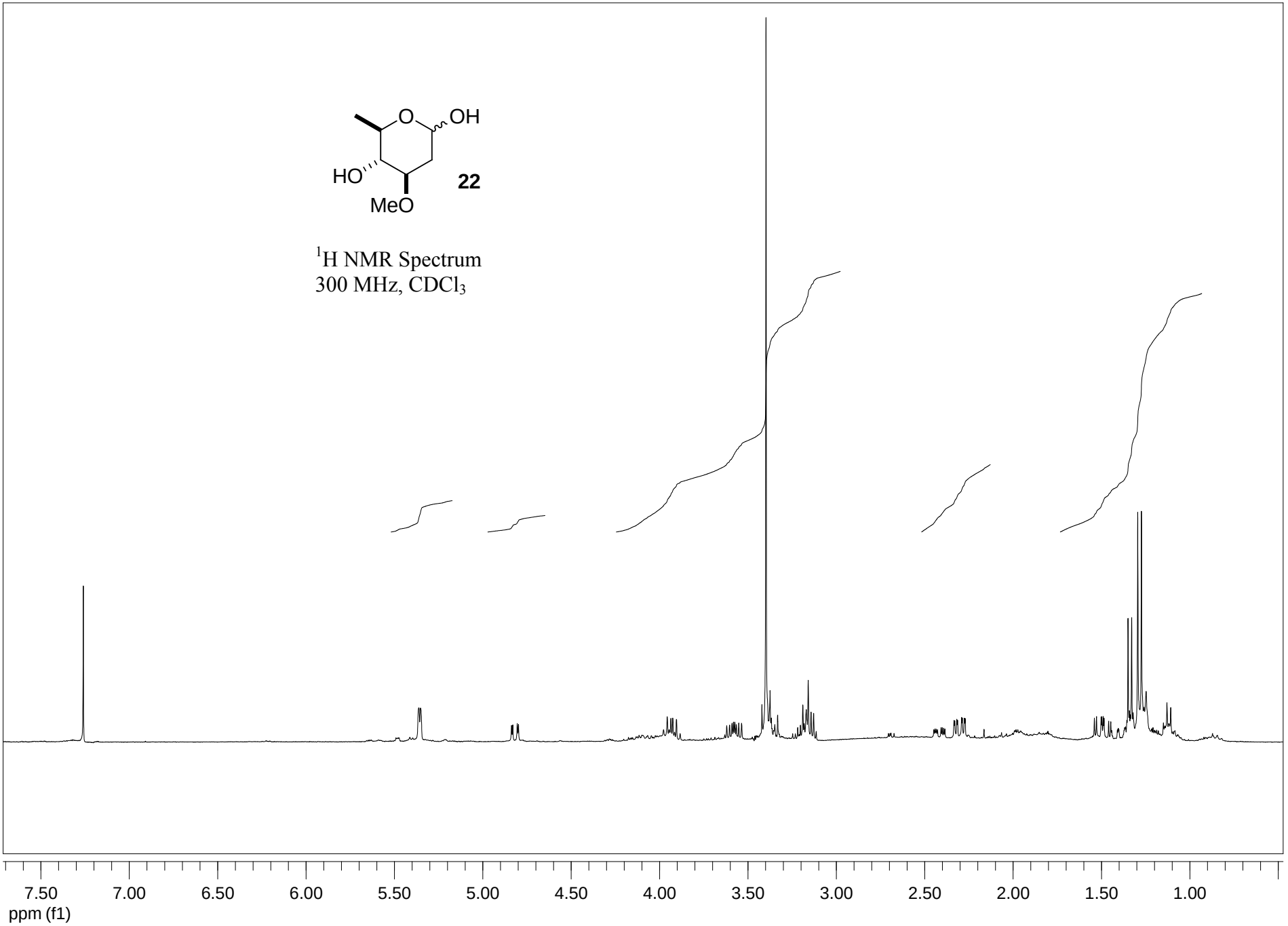
^{1}H NMR Spectrum
300 MHz, $CDCl_3$


O
OH
BnO
BnO
19
1H NMR Spectrum
300 MHz, CDCl3
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (f1)

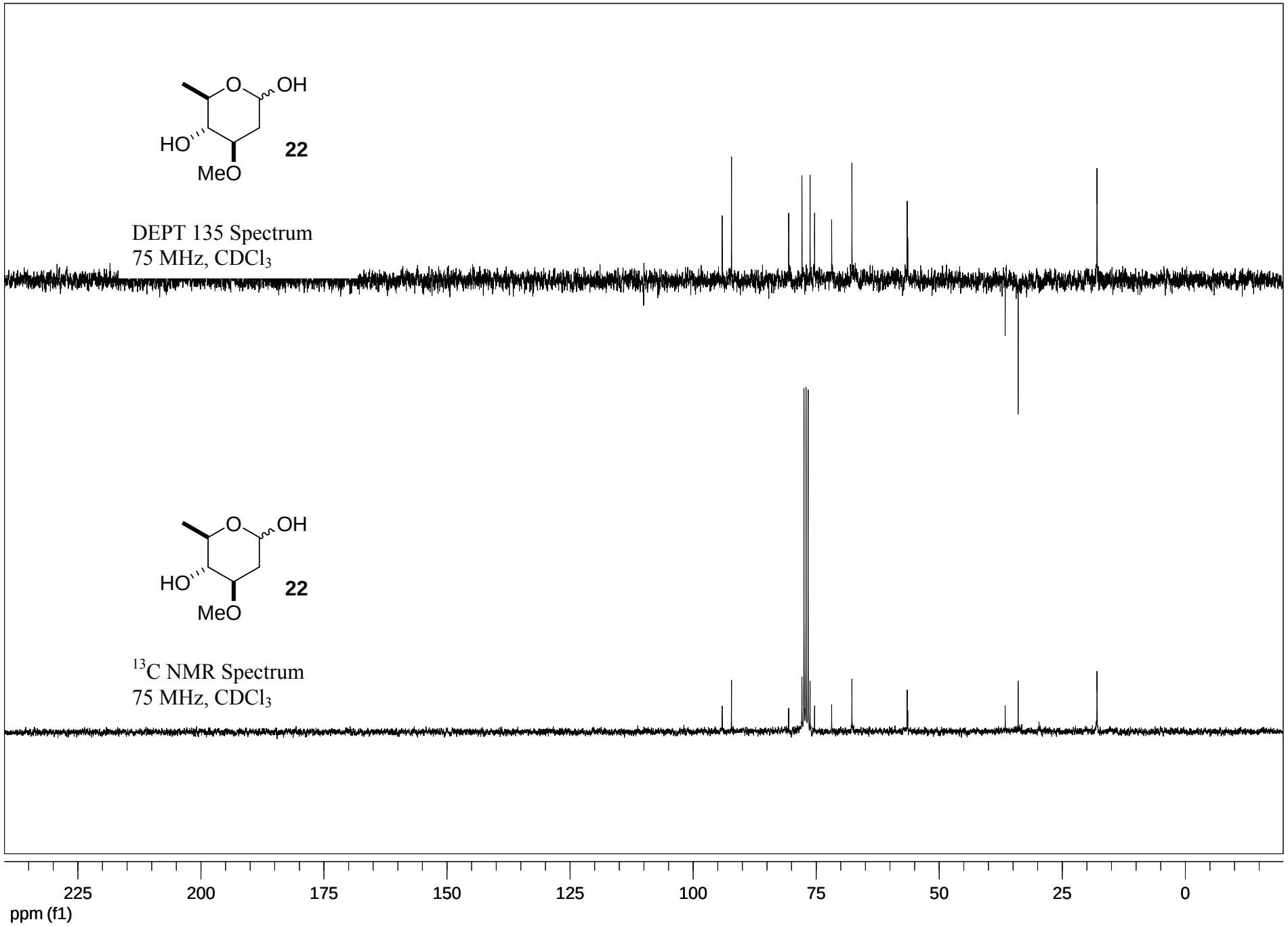

OH
O
BnO
BnO
19
DEPT 135 Spectrum
75 MHz, CDCl3
OH
O
BnO
BnO
19
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)

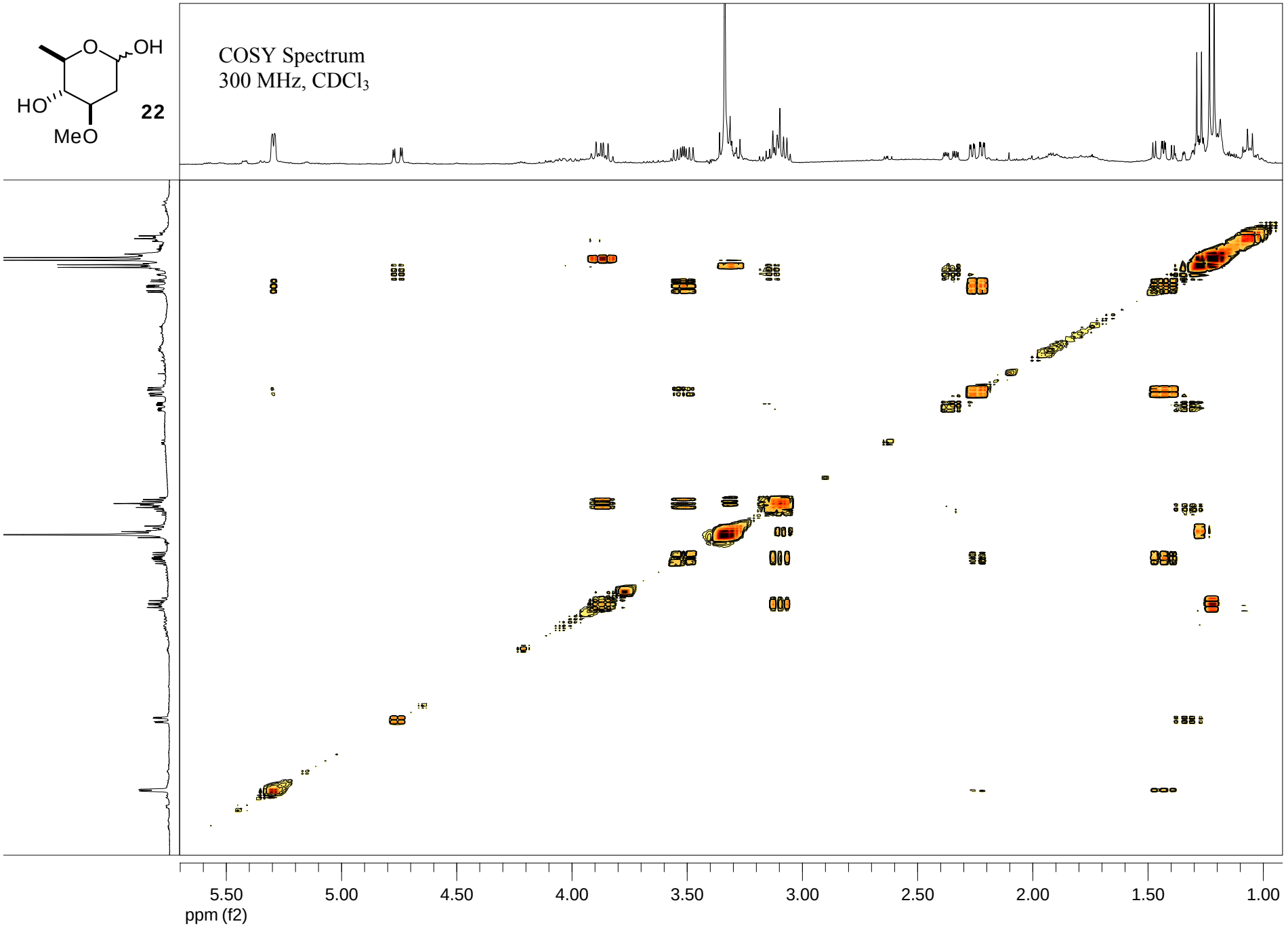


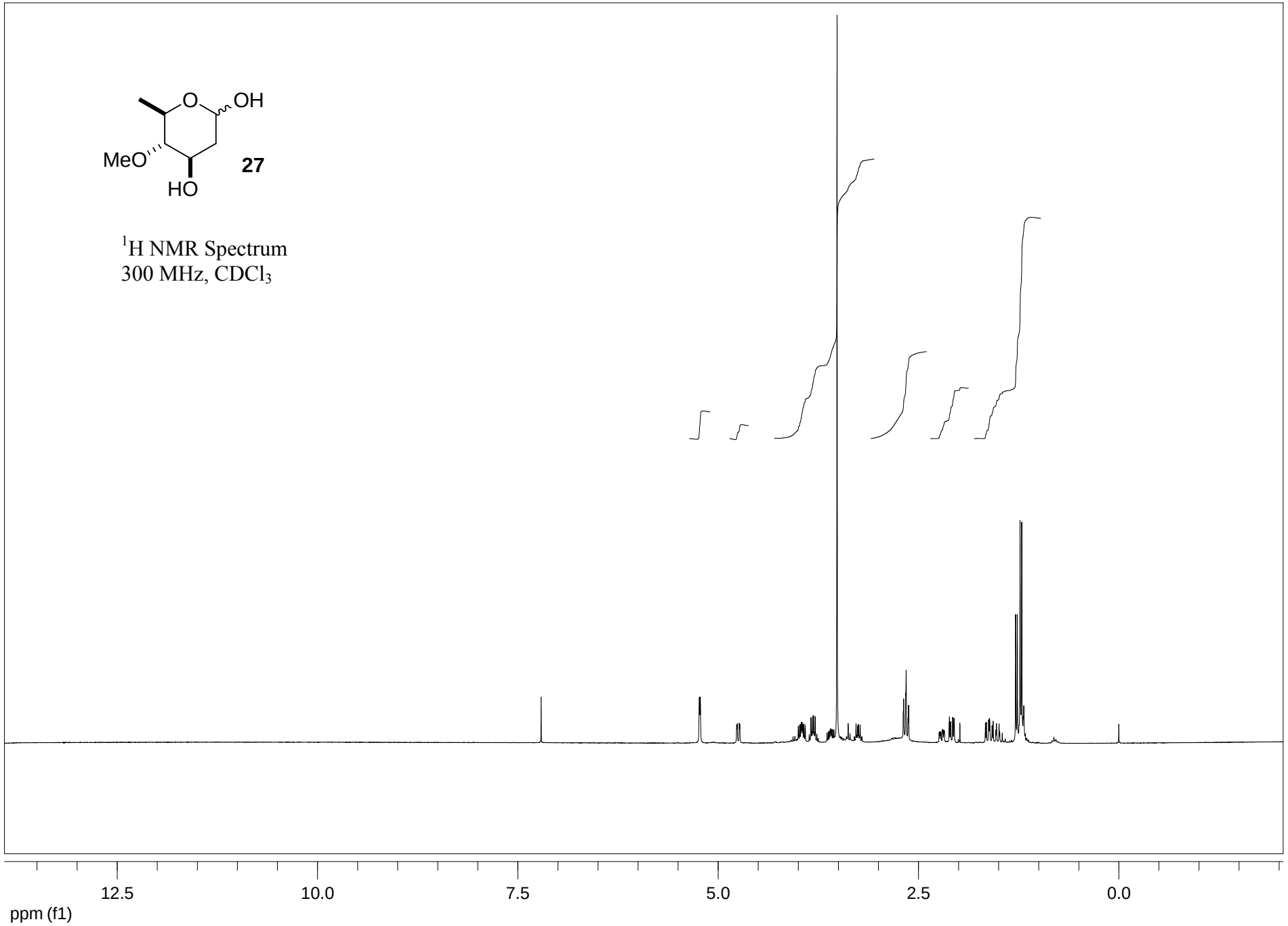
^{1}H NMR Spectrum
300 MHz, $CDCl_3$



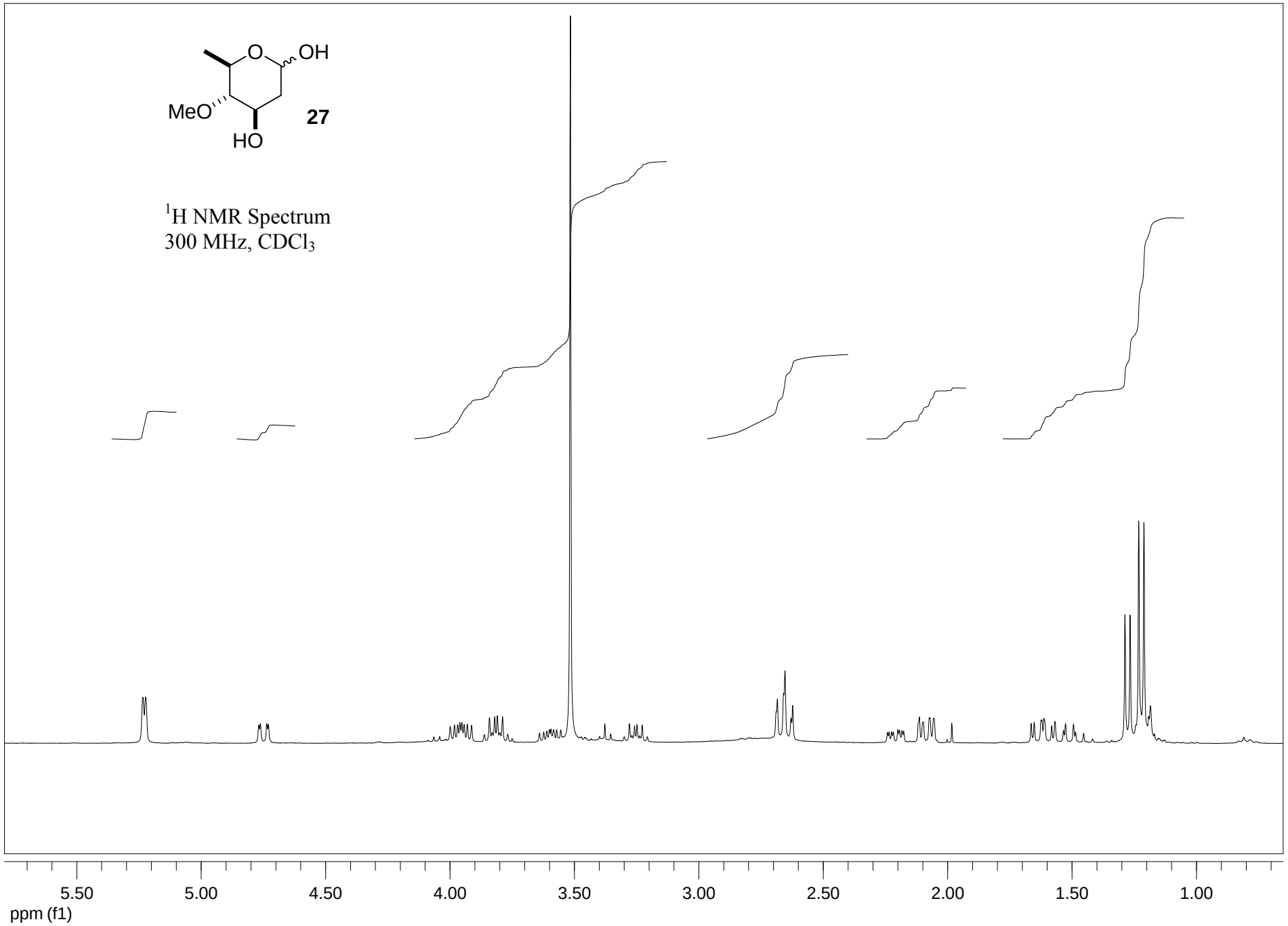
^{1}H NMR Spectrum
300 MHz, $CDCl_3$

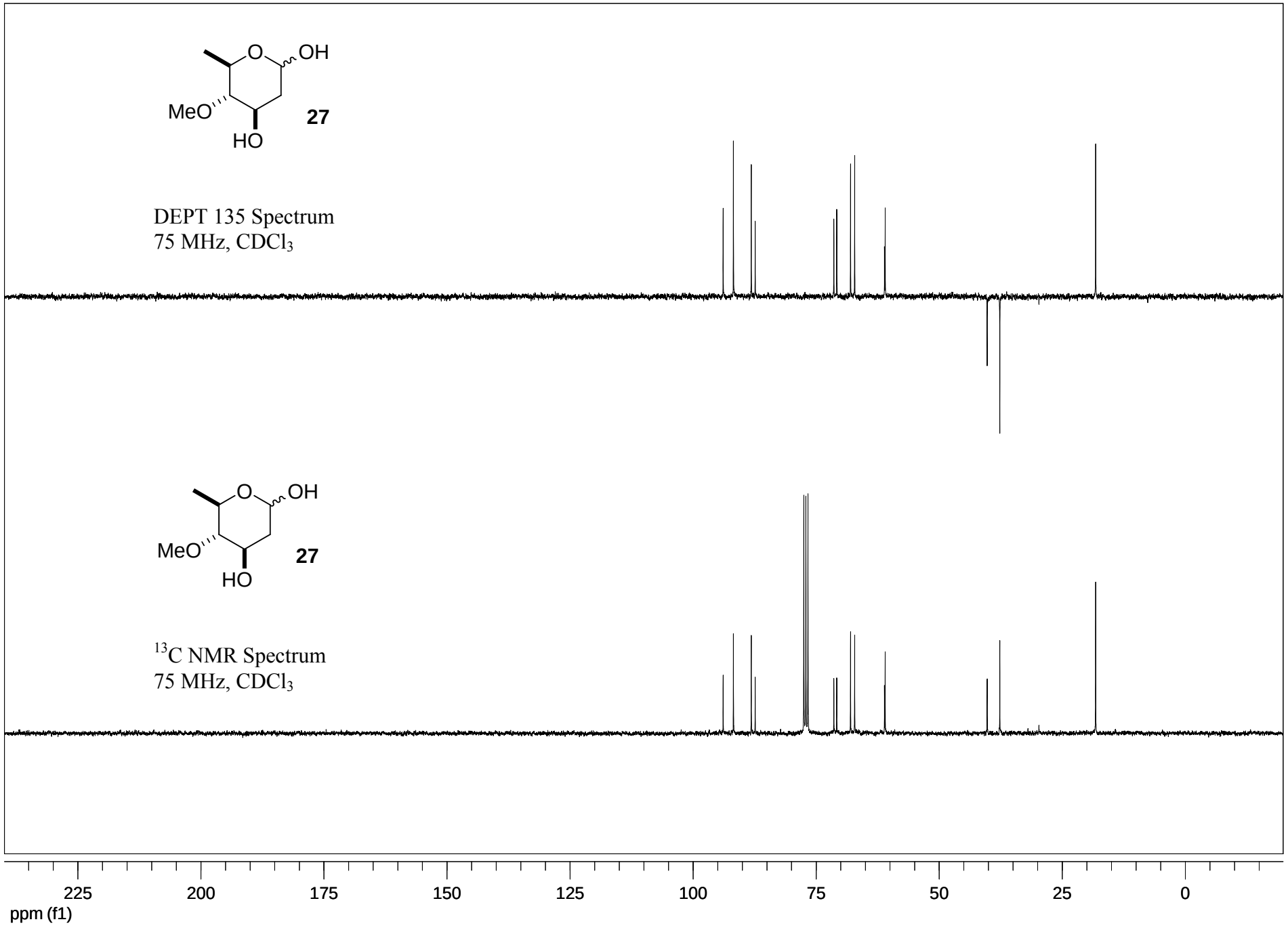

O
OH
HO
MeO
22
DEPT 135 Spectrum
75 MHz, CDCl3
O
OH
HO
MeO
22
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)

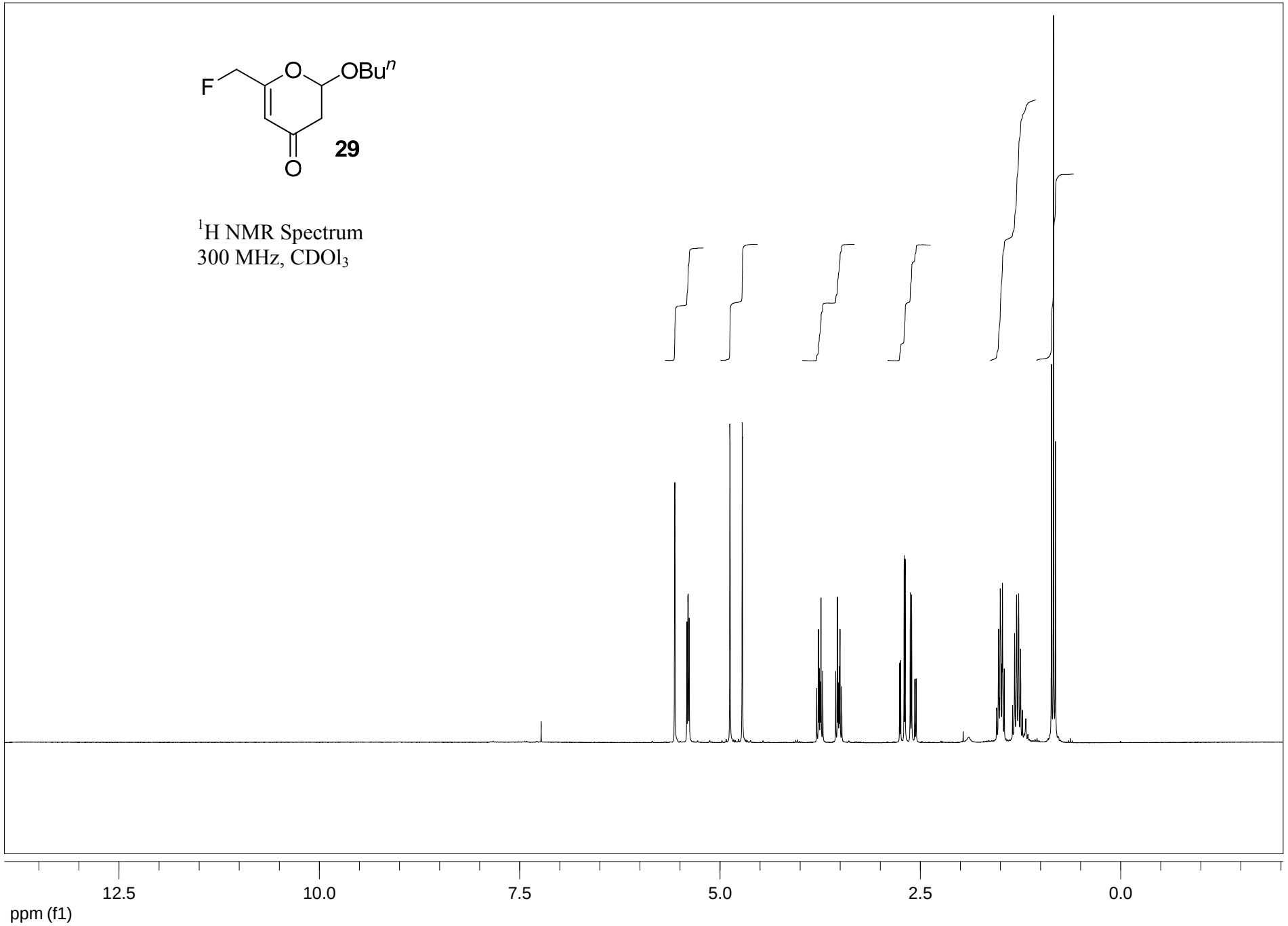

O
OH
HO
MeO
22
COSY Spectrum
300 MHz, CDCl3
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (f2)

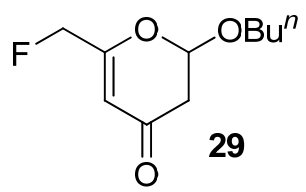


^{1}H NMR Spectrum
300 MHz, $CDCl_3$


O
OH
MeO
HO
27
1H NMR Spectrum
300 MHz, CDCl3
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (f1)

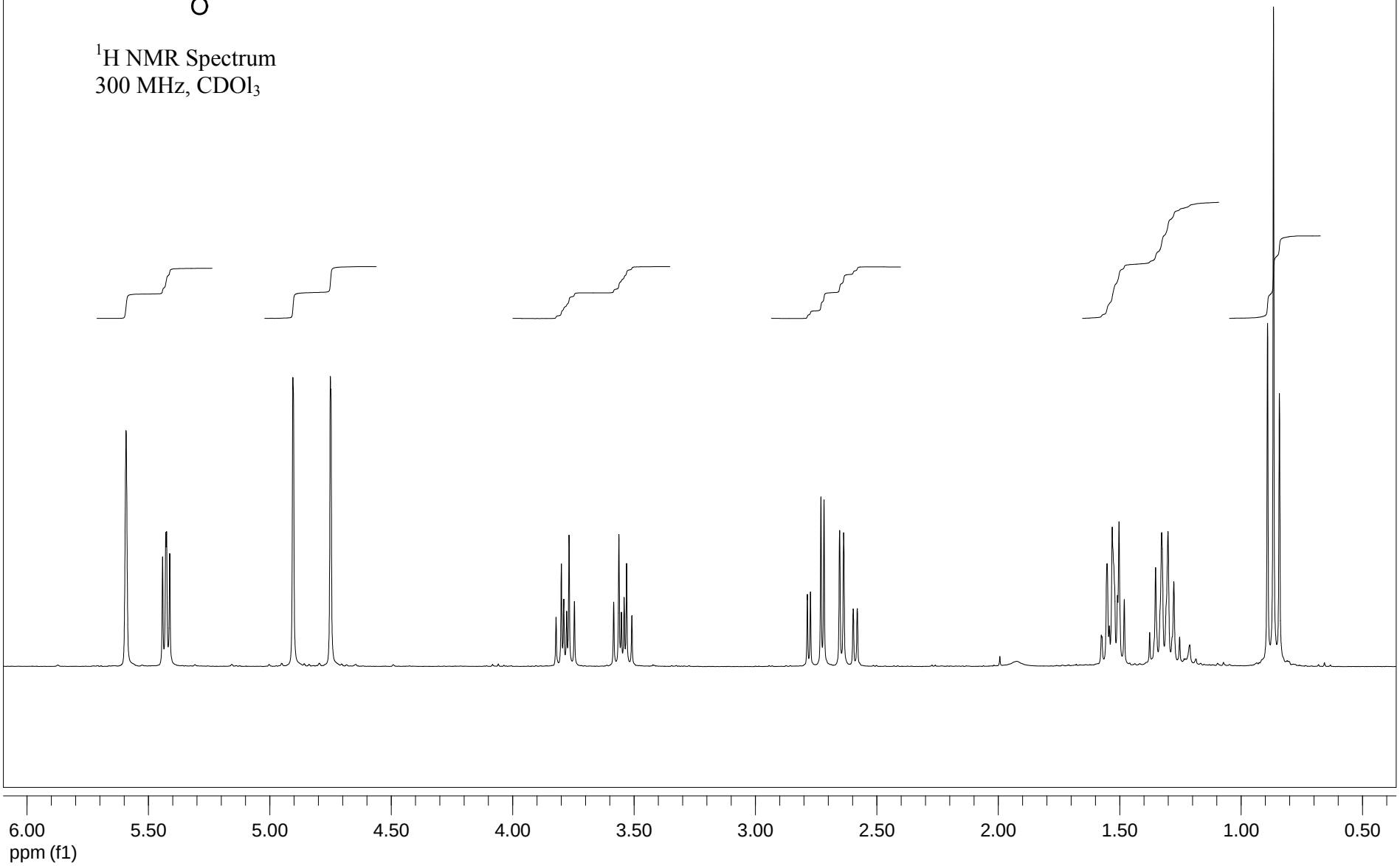

OH
O
MeO
HO
27
DEPT 135 Spectrum
75 MHz, CDCl3
OH
O
MeO
HO
27
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)

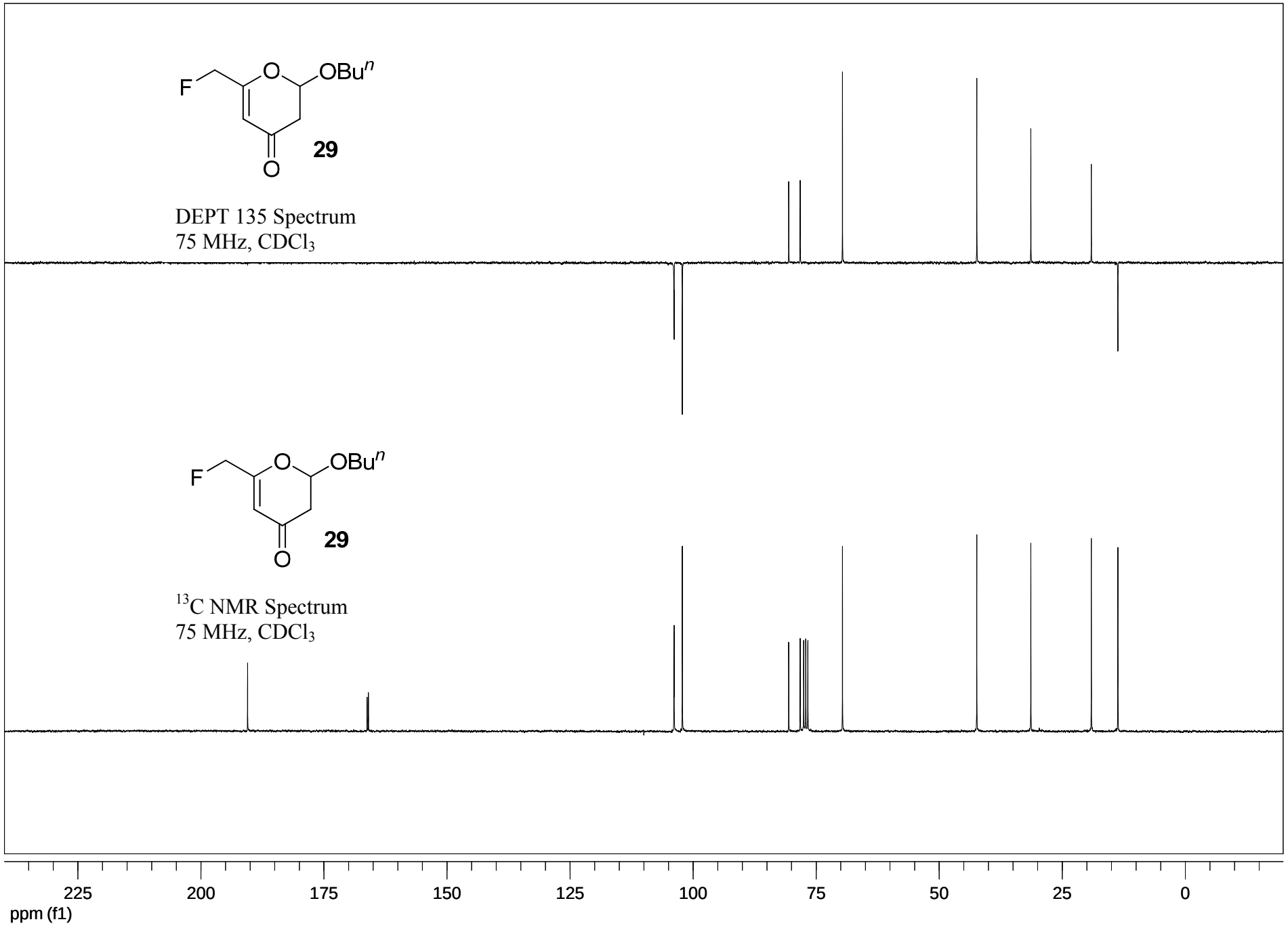

F
O
OBu^n
O
29
^{1}H NMR Spectrum
300 MHz, CDOl$_3$
12.5
10.0
7.5
5.0
2.5
0.0
ppm (f1)

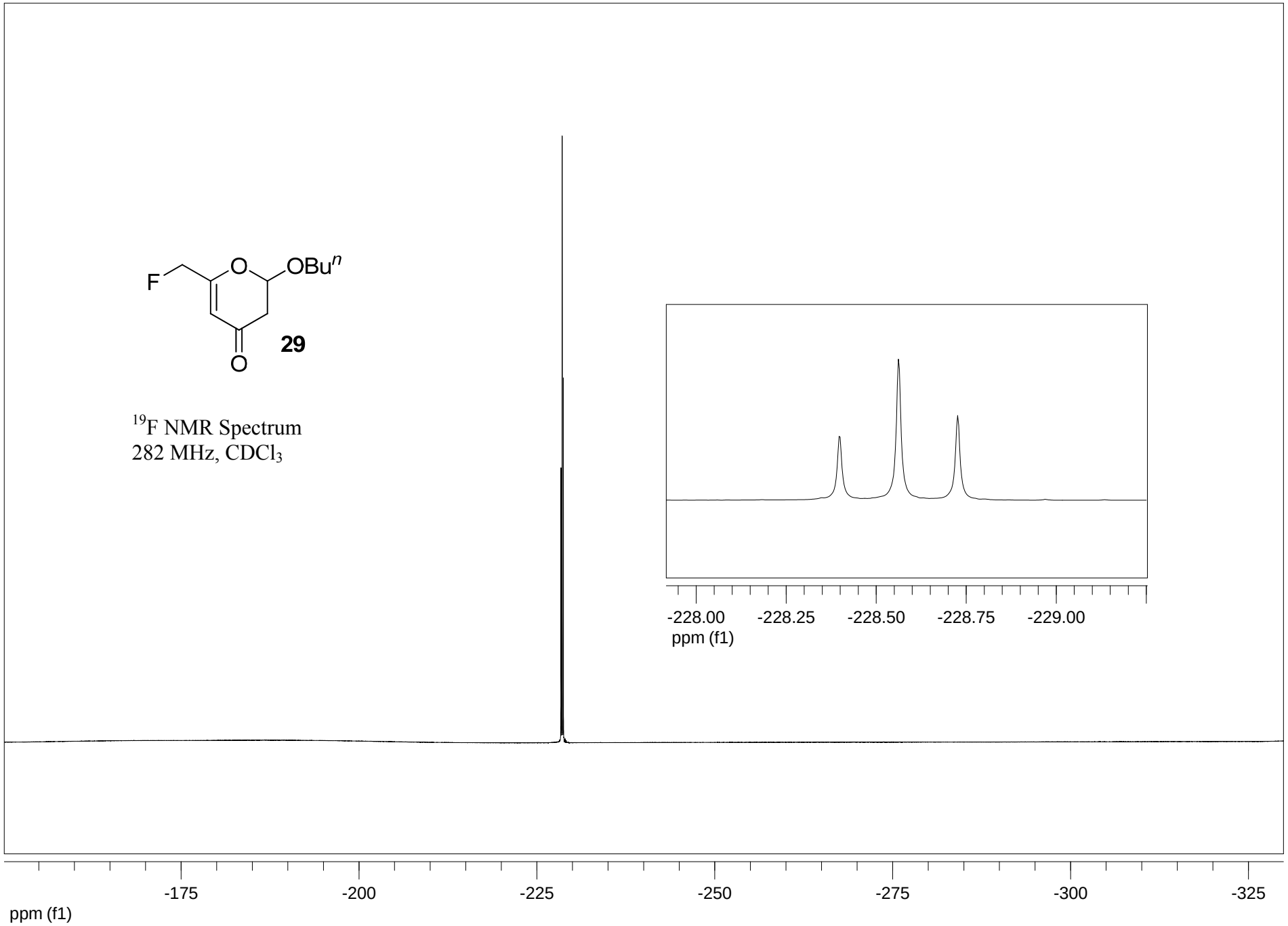


29

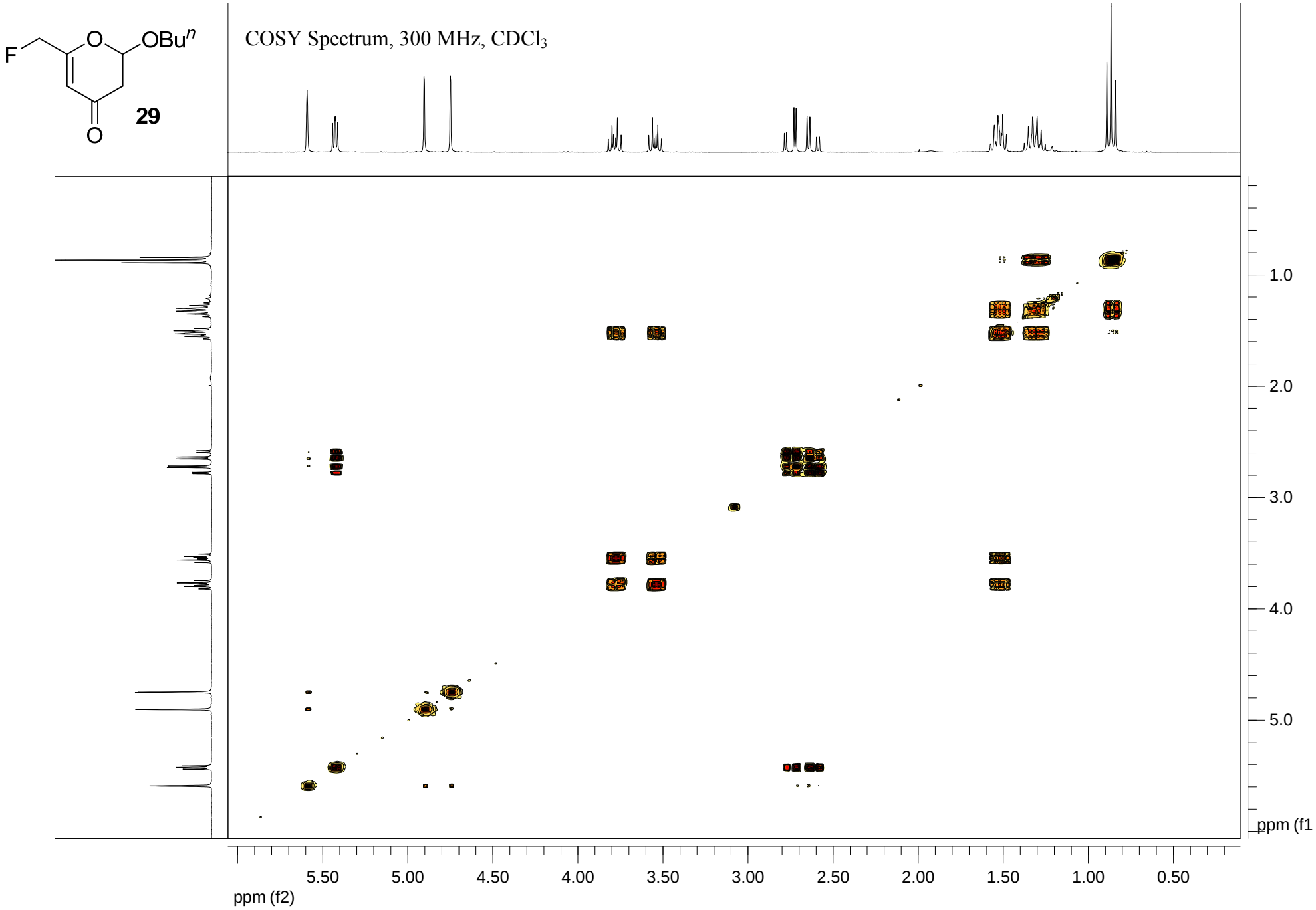
^{1}H NMR Spectrum
300 MHz, $CDOl_3$

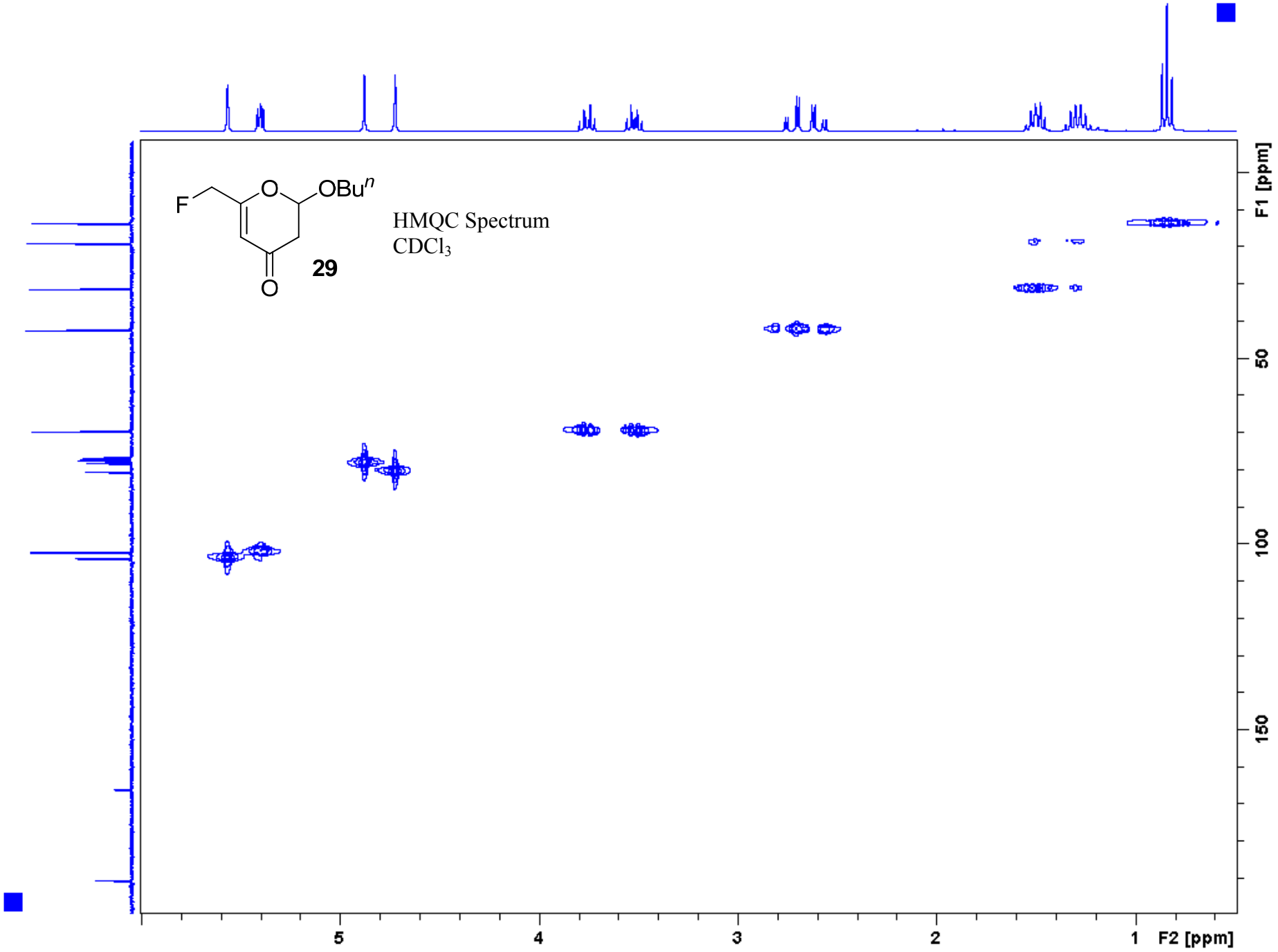


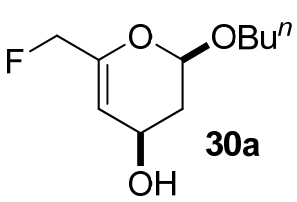

F
O
OBu^n
29
O
DEPT 135 Spectrum
75 MHz, $CDCl_3$
F
O
OBu^n
29
O
^{13}C NMR Spectrum
75 MHz, $CDCl_3$
225
200
175
150
125
100
75
50
25
0
ppm (f1)



^{19}F NMR Spectrum
282 MHz, $CDCl_3$

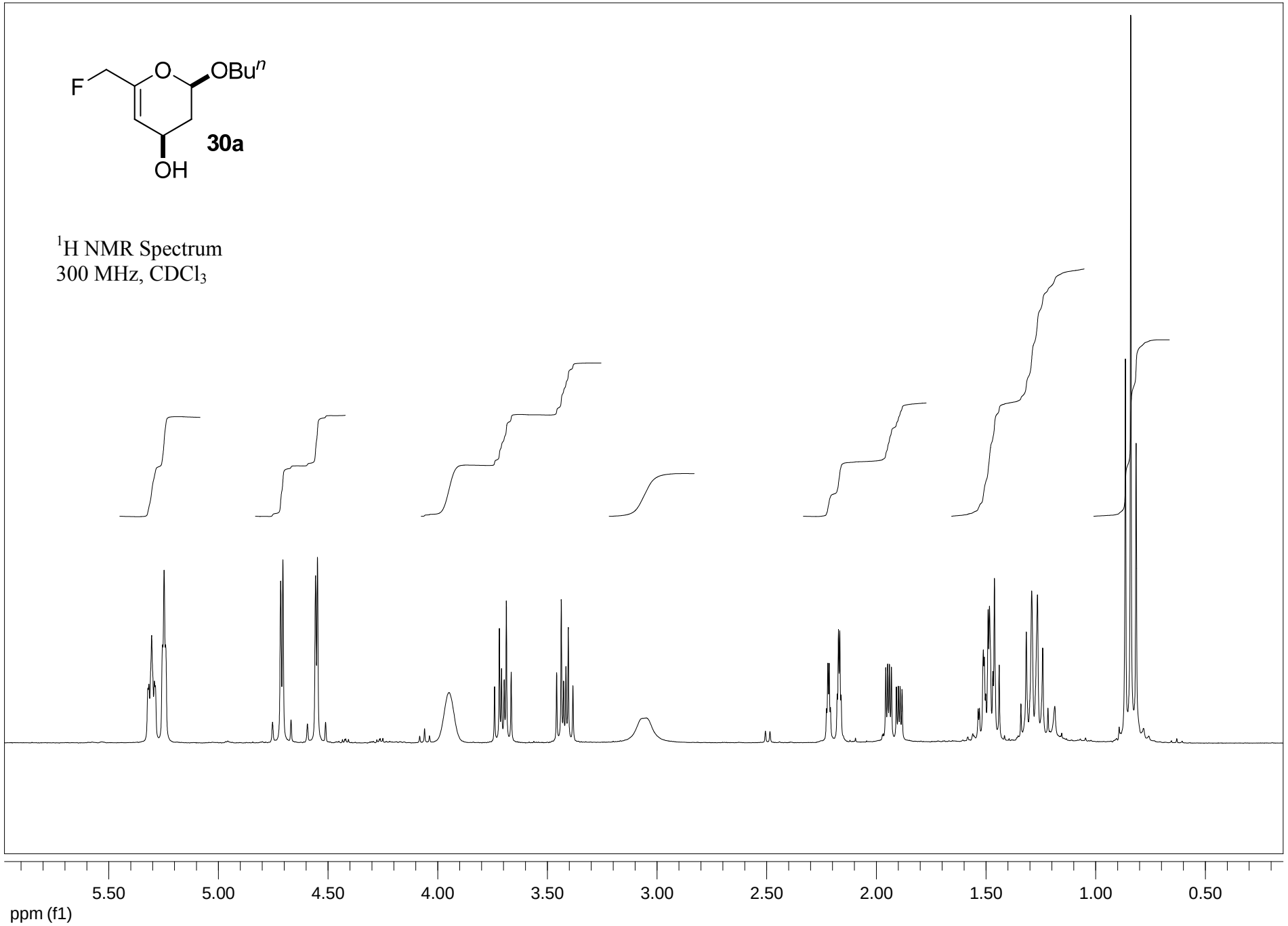

F
O
OBu^n
O
29
COSY Spectrum, 300 MHz, CDCl3
1.0
2.0
3.0
4.0
5.0
ppm (f1
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (f2)

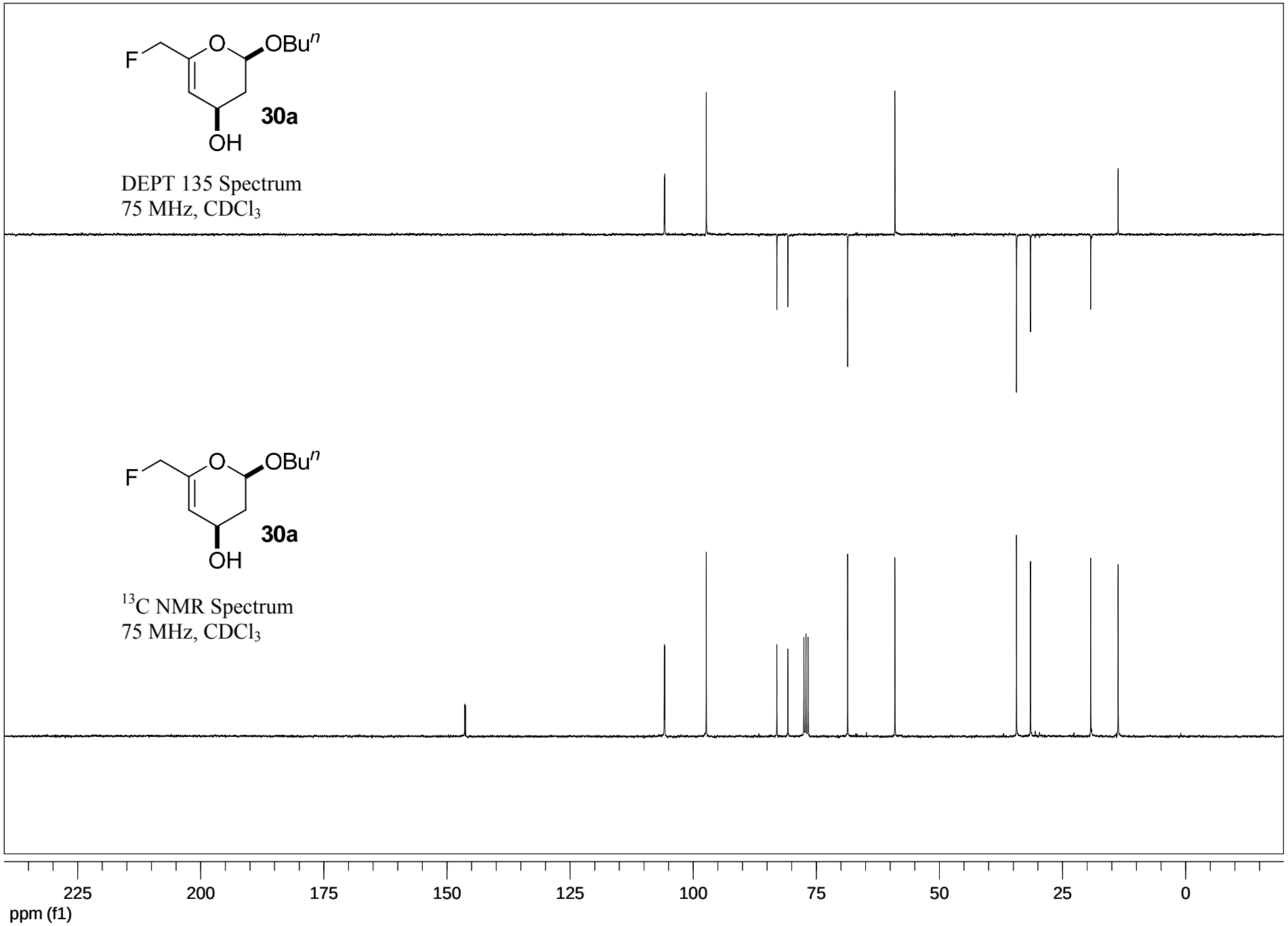

F
O
OBu^n
O
29
HMQC Spectrum
$CDCl_3$
F1 [ppm]
50
100
150
5
4
3
2
1
F2 [ppm]

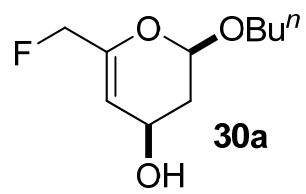


30a

^{1}H NMR Spectrum
300 MHz, $CDCl_3$

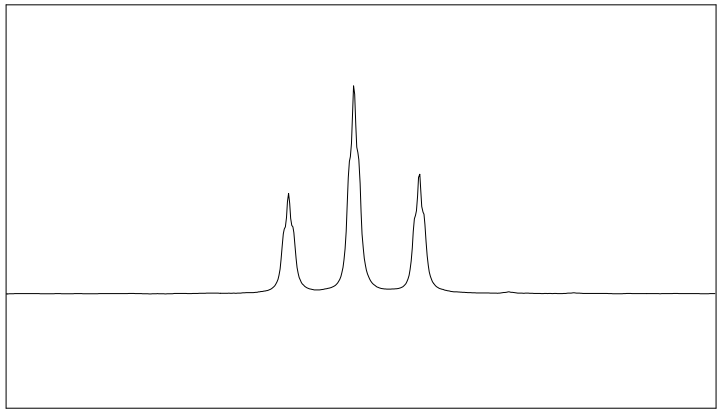

F
O
OBu^n
OH
30a
[1]H NMR Spectrum
300 MHz, CDCl3
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (f1)

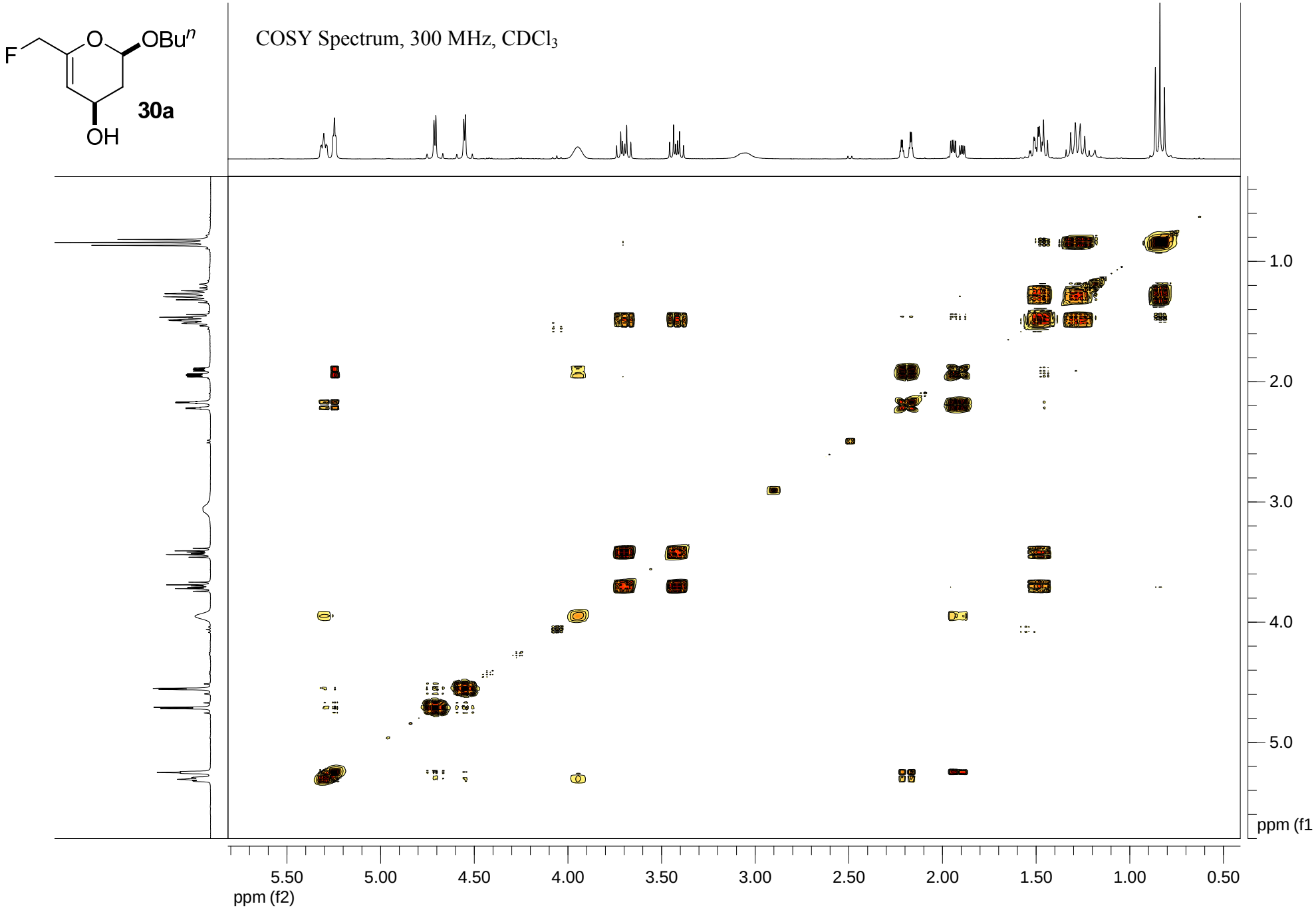

F
O
OBu^n
30a
OH
DEPT 135 Spectrum
75 MHz, CDCl3
F
O
OBu^n
30a
OH
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)

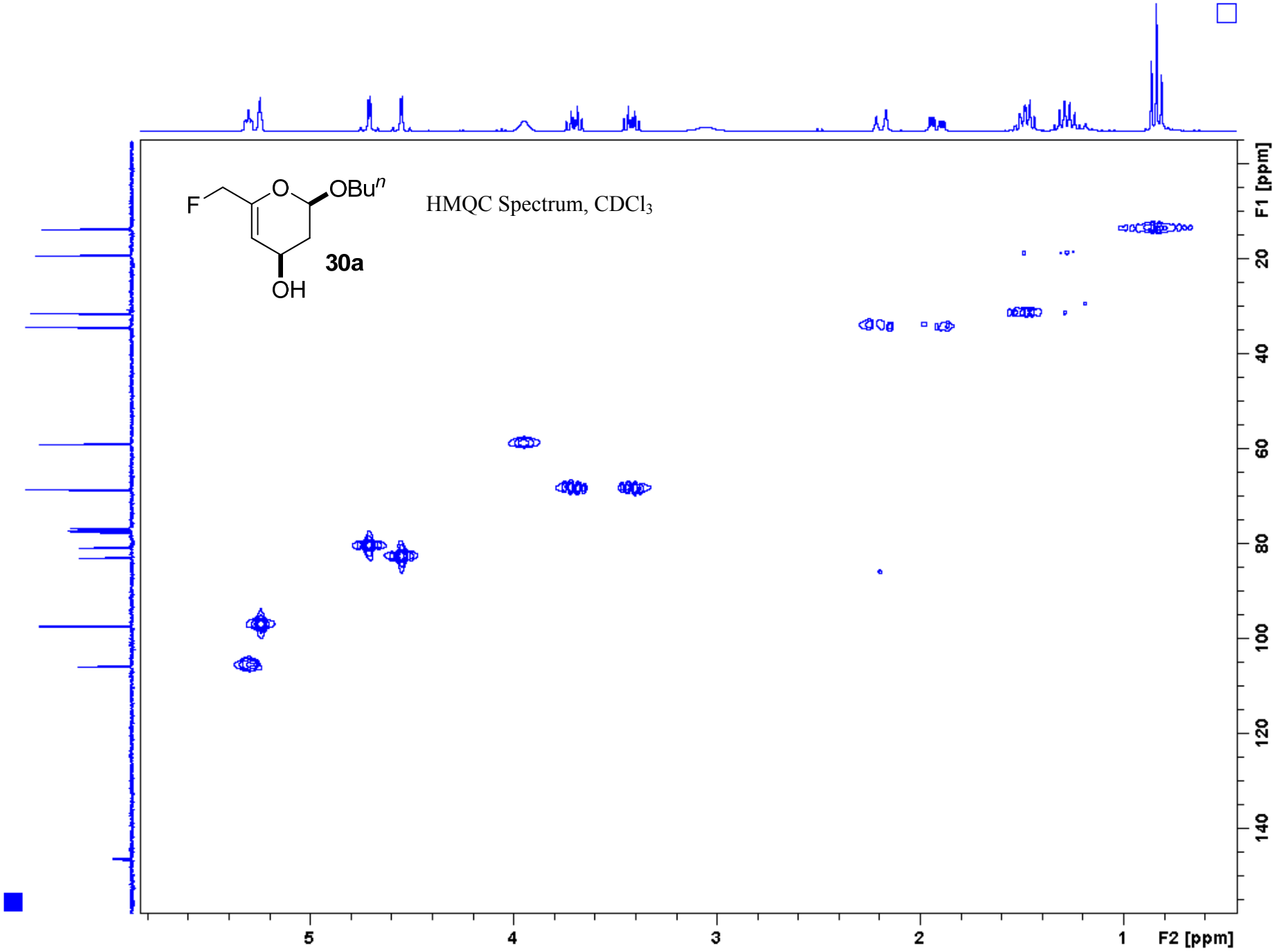


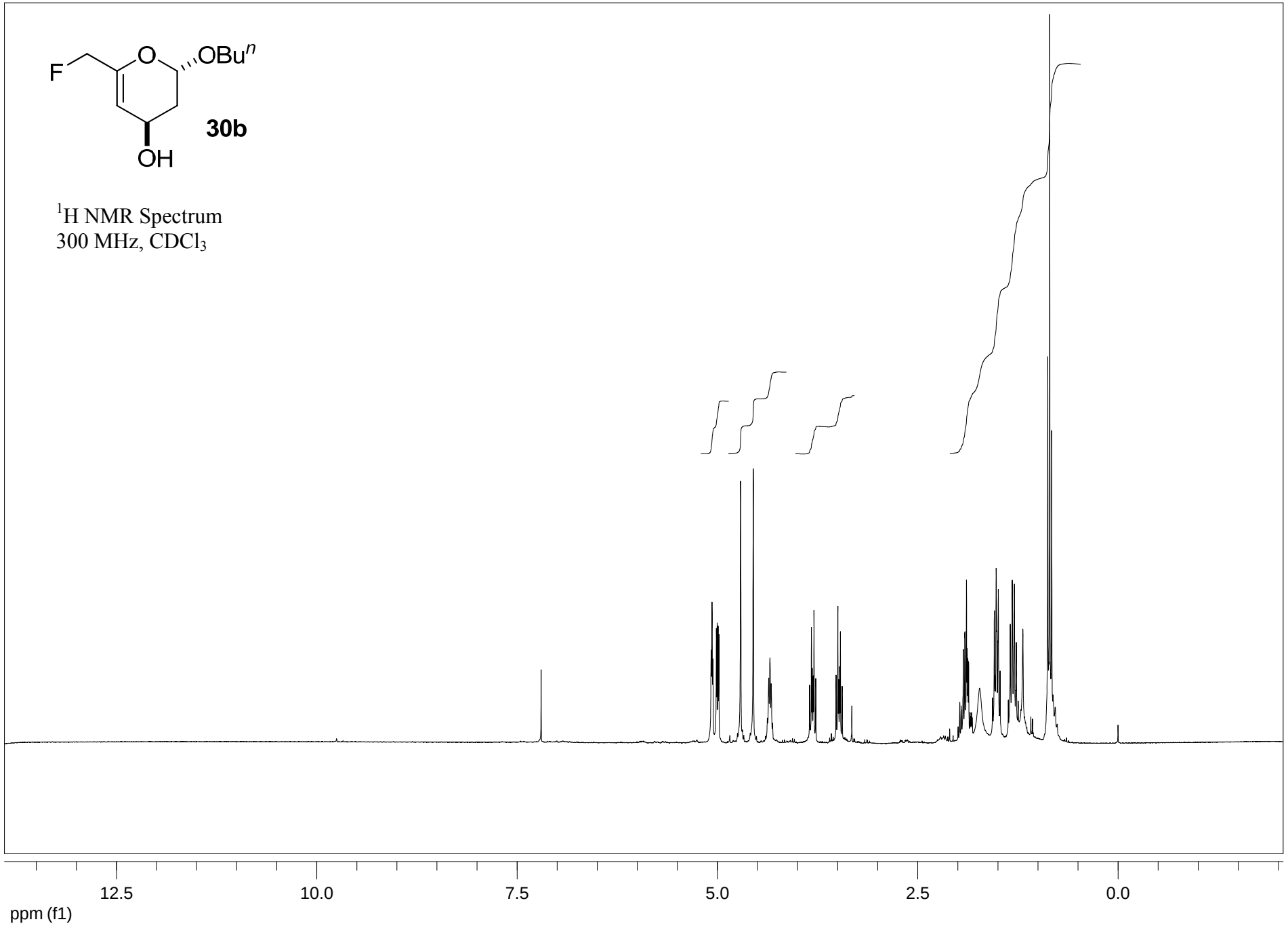
30a

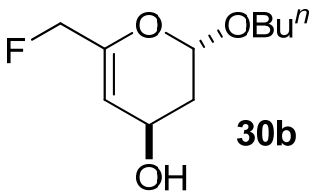
^{19}F NMR Spectrum
282 MHz, $CDCl_3$




F
O
OBu^n
OH
30a
COSY Spectrum, 300 MHz, CDCl3
1.0
2.0
3.0
4.0
5.0
ppm (f1
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (f2)

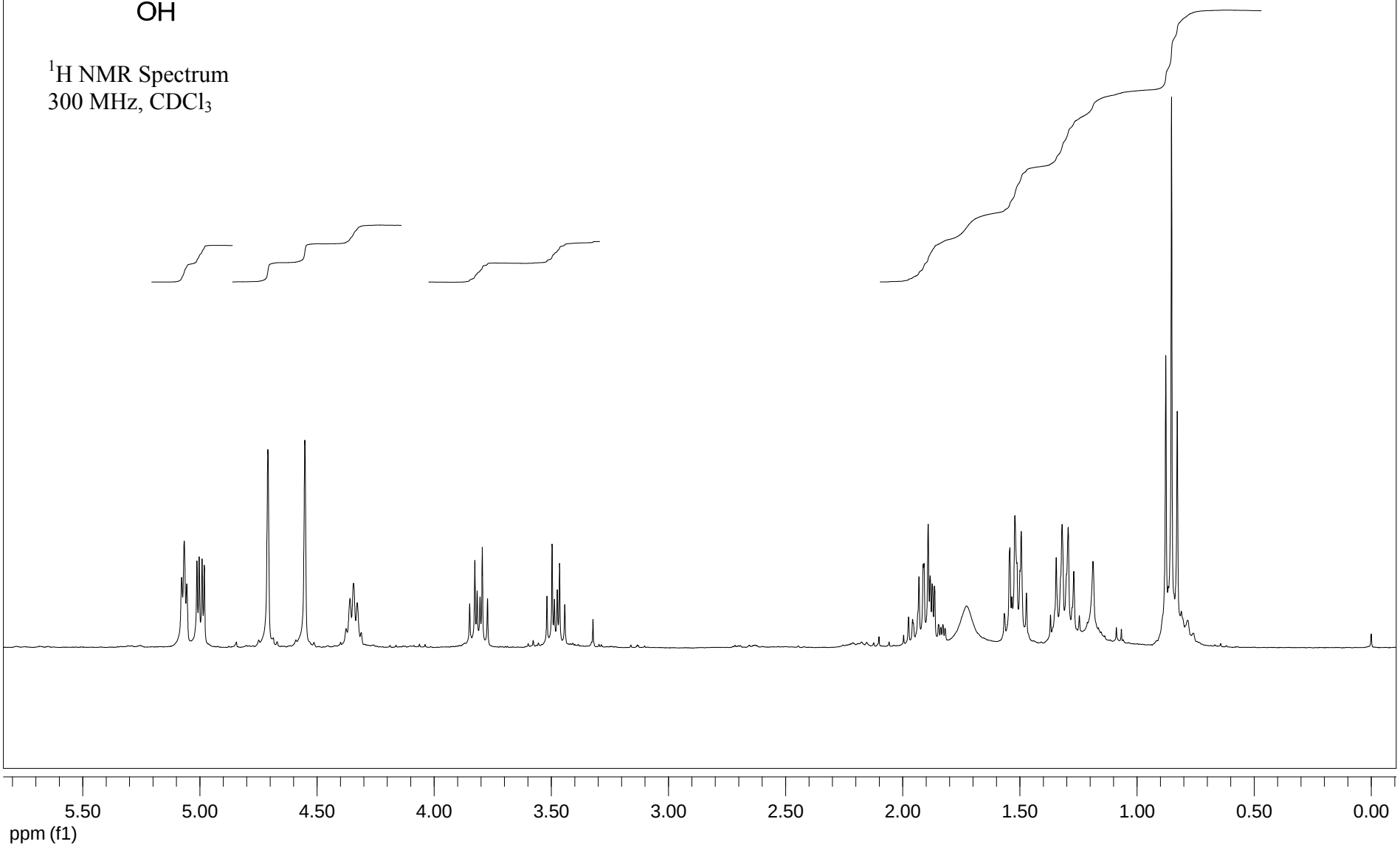

F
O
OBu^n
OH
30a
HMQC Spectrum, $CDCl_3$
F1 [ppm]
20
40
60
80
100
120
140
5
4
3
2
1
F2 [ppm]

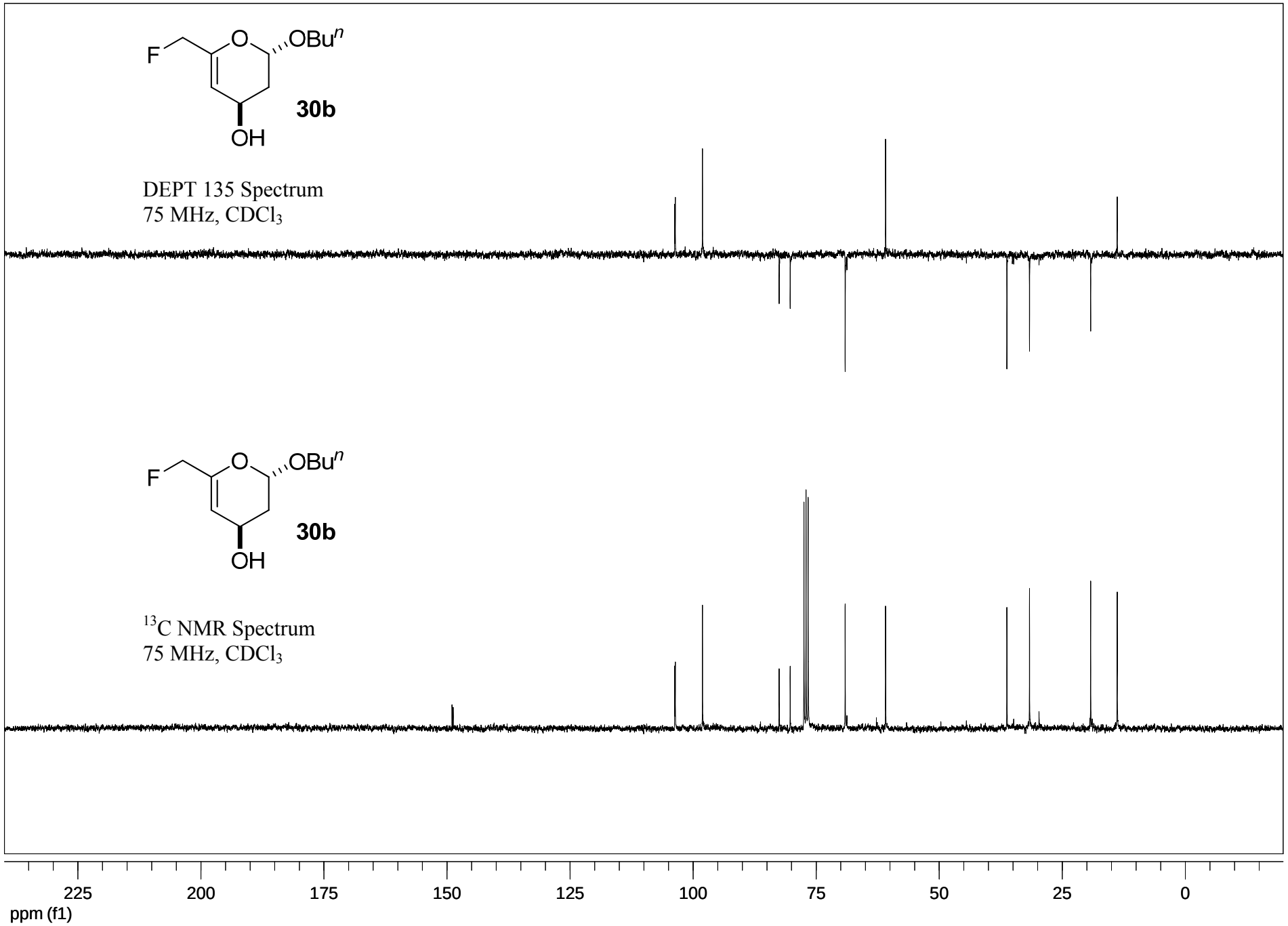

F
O
OBu^n
OH
30b
^{1}H NMR Spectrum
300 MHz, $CDCl_3$
12.5
10.0
7.5
5.0
2.5
0.0
ppm (f1)

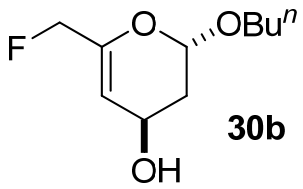


30b

^{1}H NMR Spectrum
300 MHz, $CDCl_3$

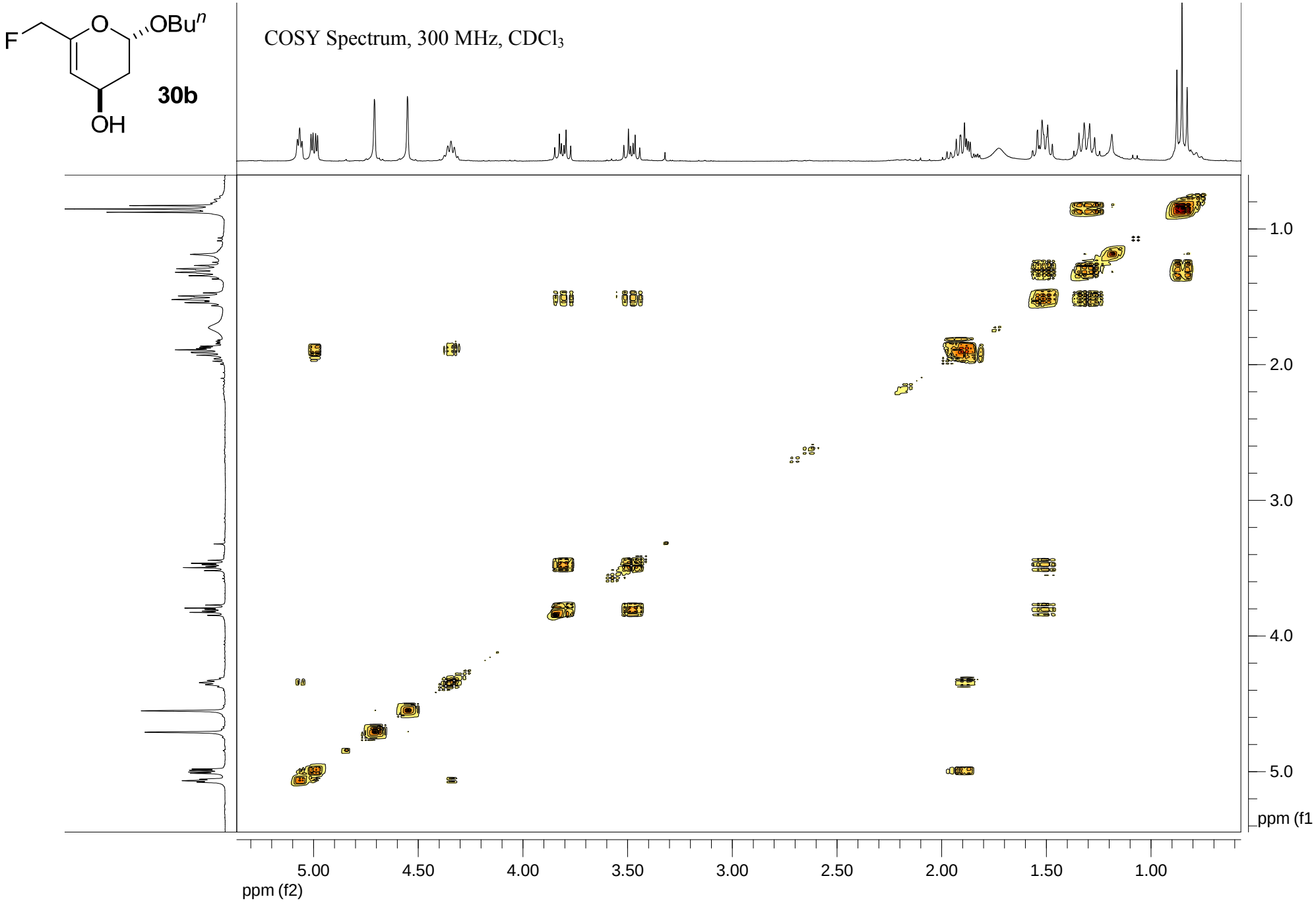


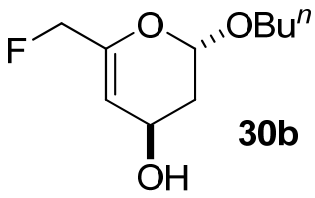

F
O
OBu^n
30b
OH
DEPT 135 Spectrum
75 MHz, CDCl3
F
O
OBu^n
30b
OH
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)



30b

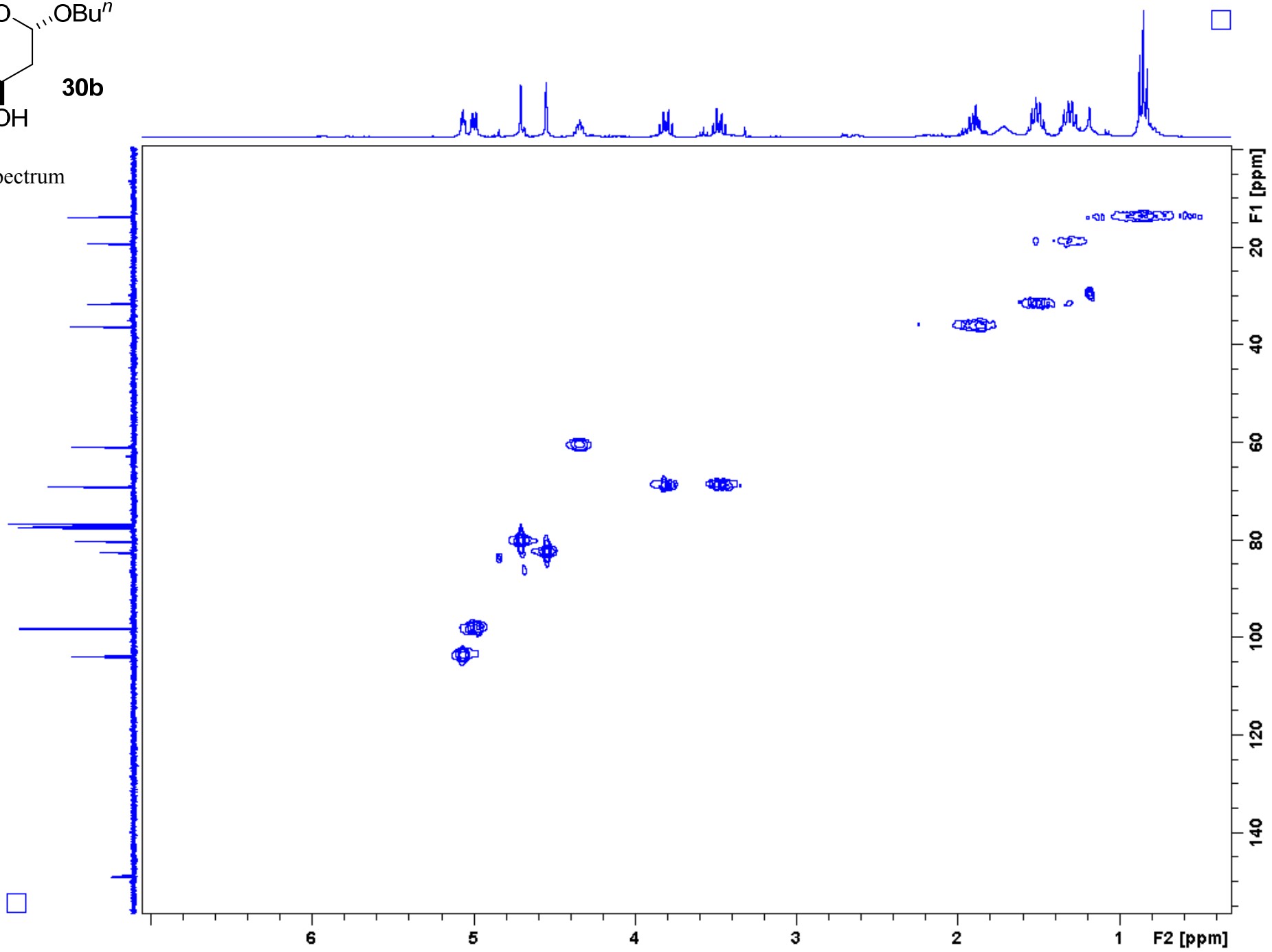
^{19}F NMR Spectrum
282 MHz, $CDCl_3$

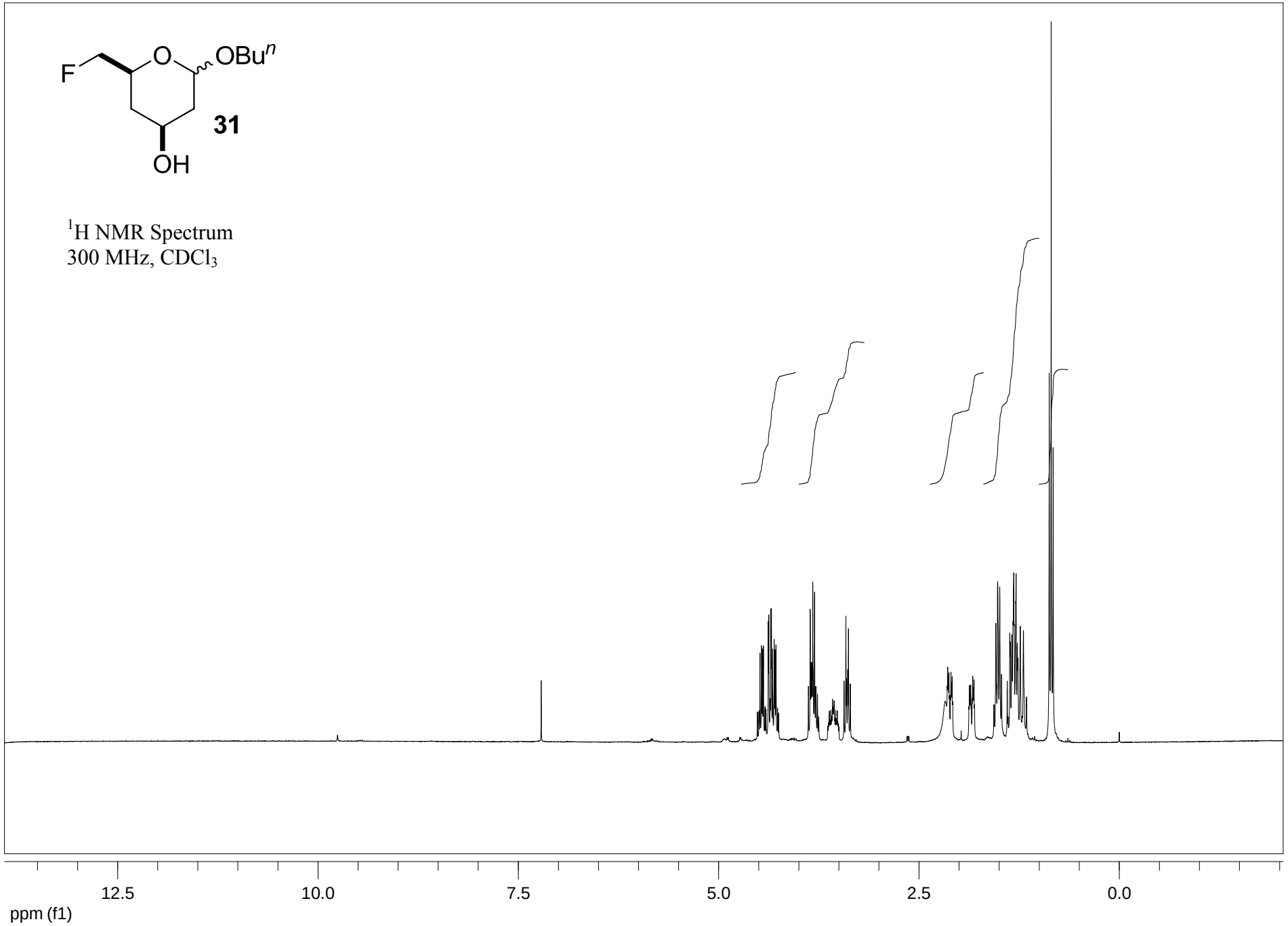

F
O
OBu^n
OH
30b
COSY Spectrum, 300 MHz, CDCl3
1.0
2.0
3.0
4.0
5.0
ppm (f1
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (f2)

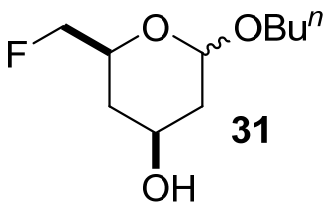


30b

HMQC Spectrum
$CDCl_3$

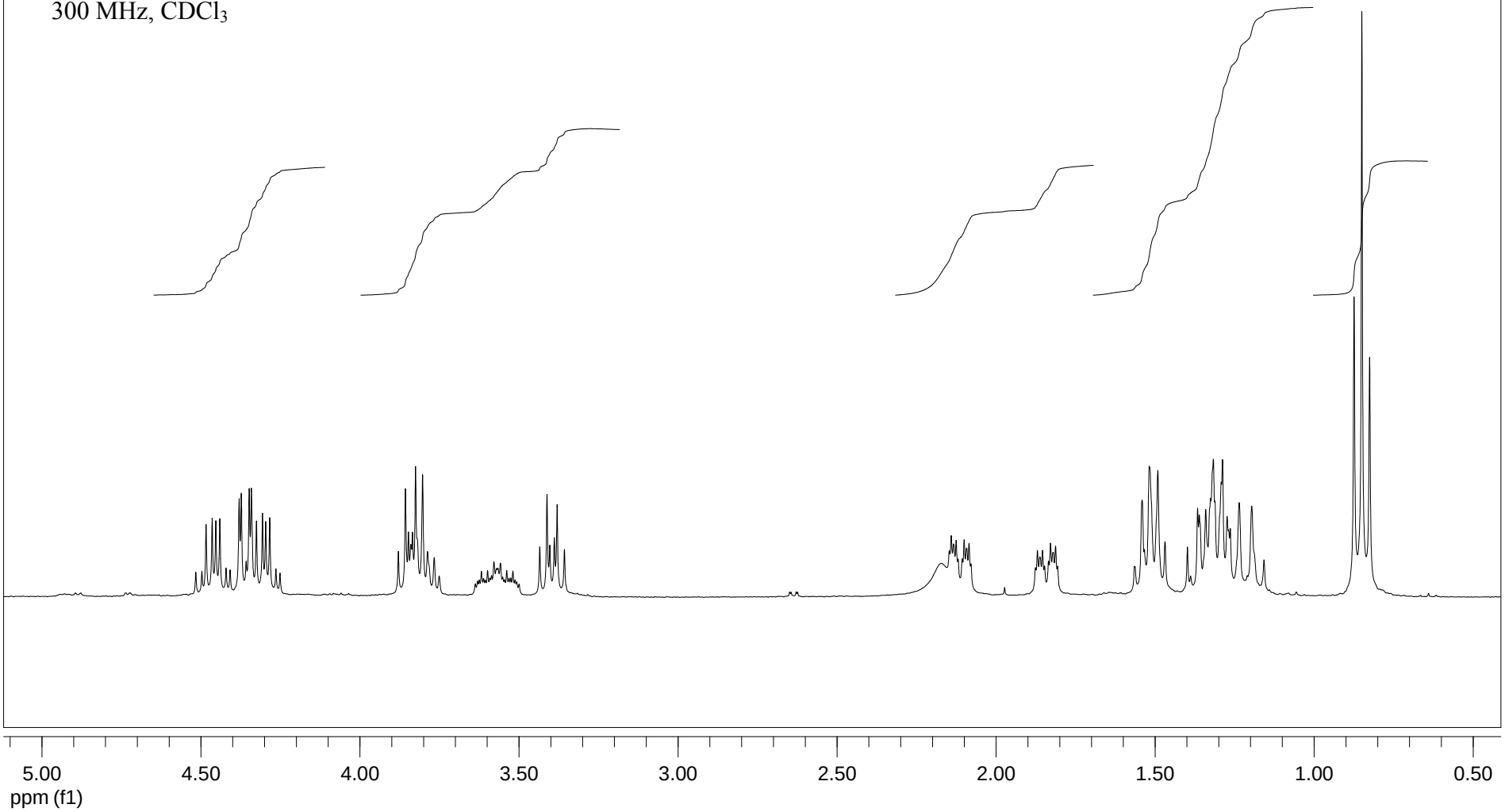


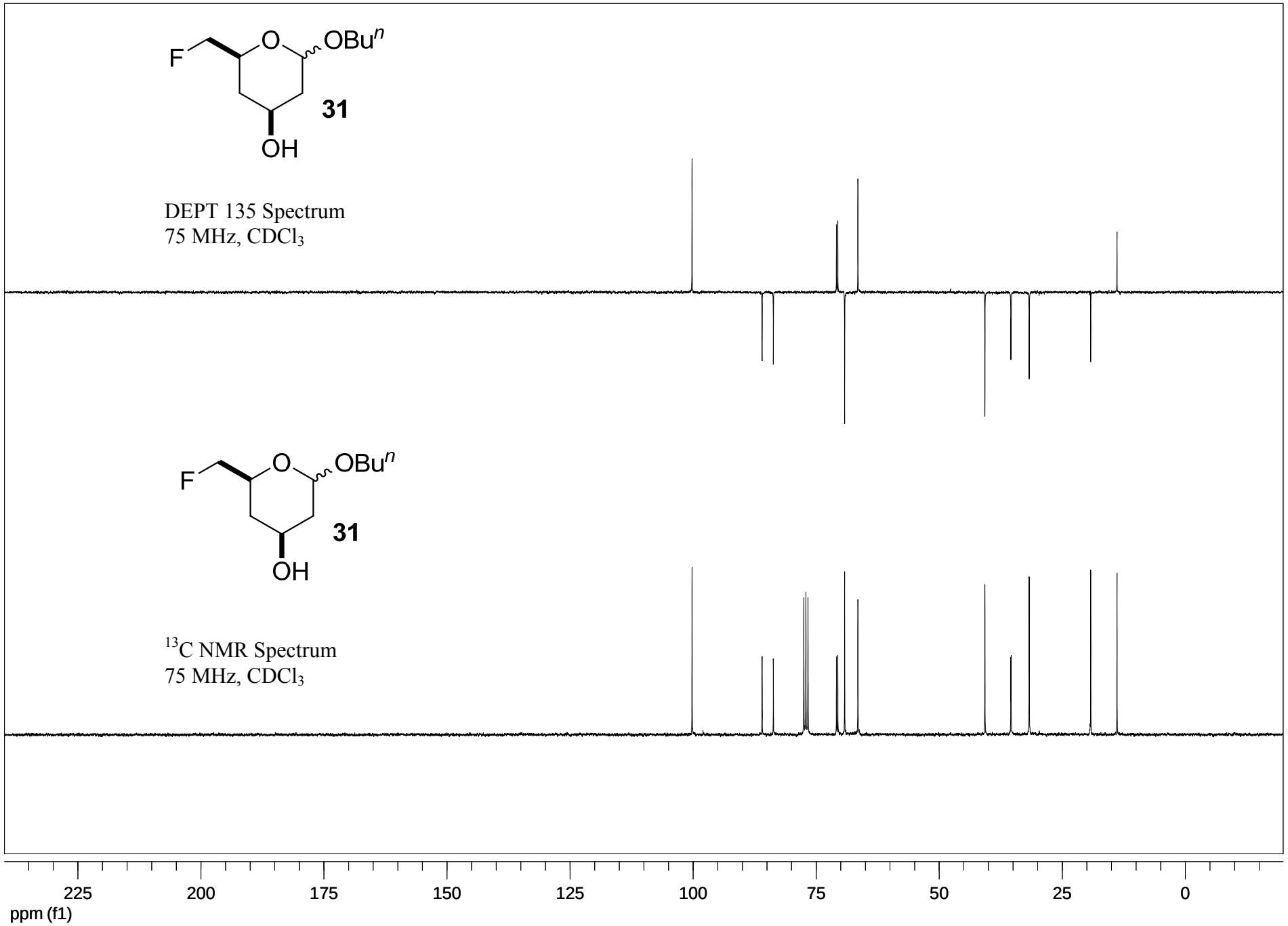

F
O
OBu^n
OH
31
1H NMR Spectrum
300 MHz, CDCl3
12.5
10.0
7.5
5.0
2.5
0.0
ppm (f1)

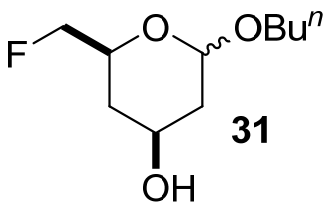


31

Partial ^{1}H NMR Spectrum
300 MHz, $CDCl_3$

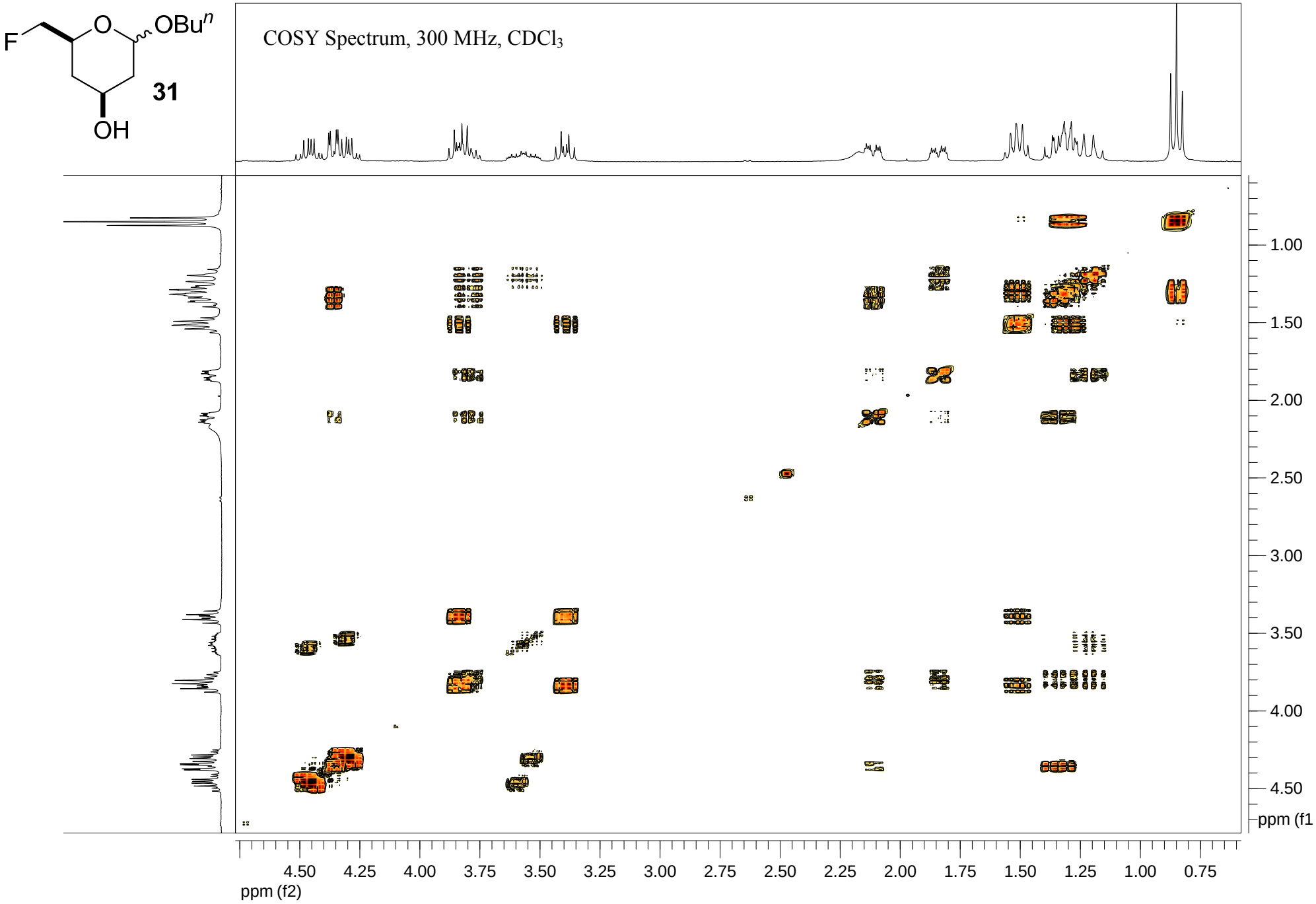


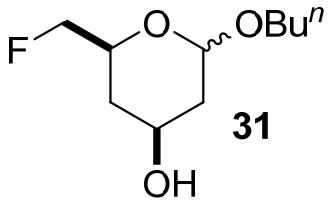

F
O
OBu^n
31
OH
DEPT 135 Spectrum
75 MHz, CDCl3
F
O
OBu^n
31
OH
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)



31

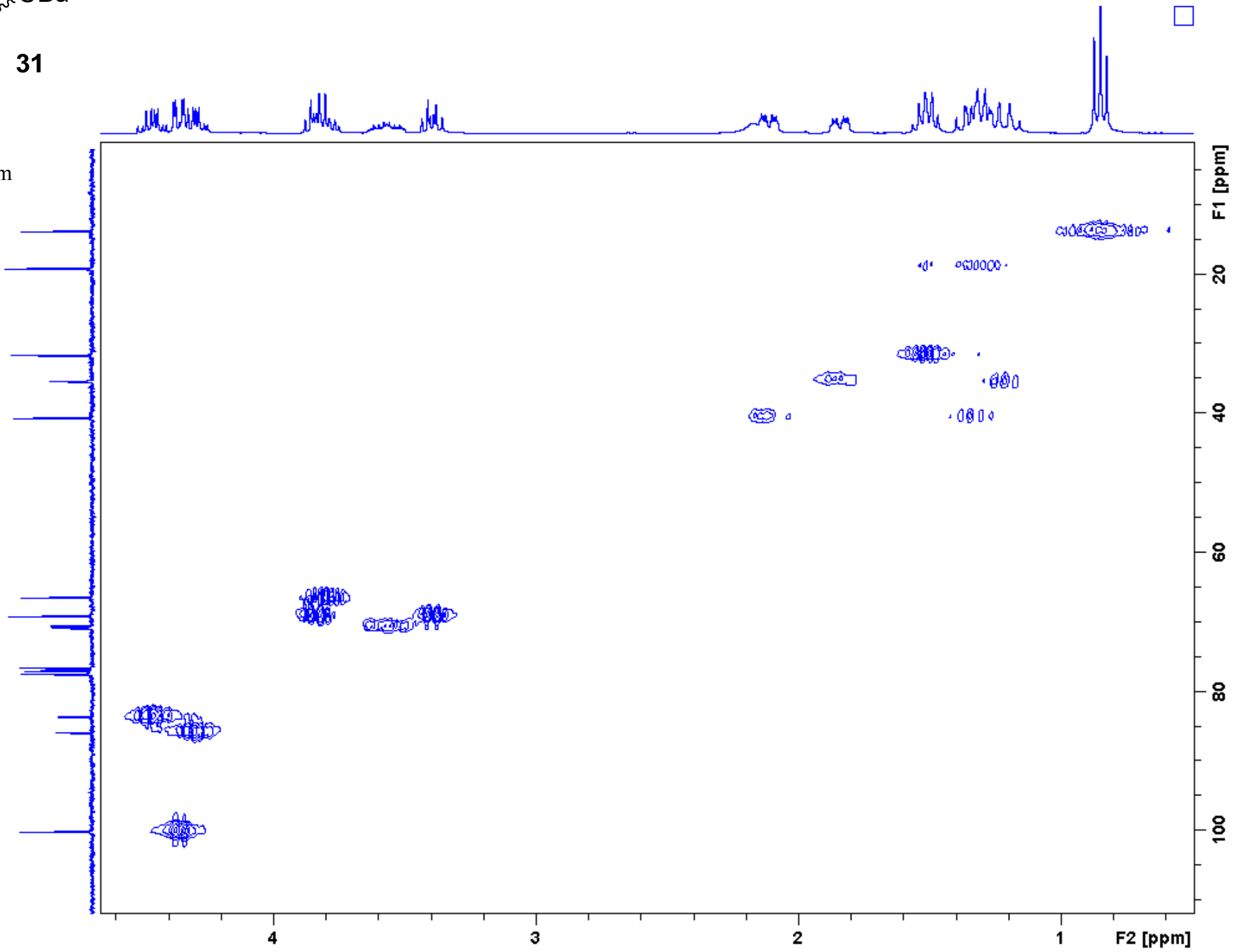
^{19}F NMR Spectrum
282 MHz, $CDCl_3$

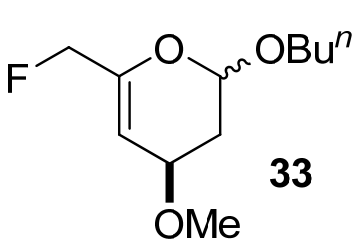

F
O
OBu^n
31
OH
COSY Spectrum, 300 MHz, CDCl3
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
ppm (f1
4.50
4.25
4.00
3.75
3.50
3.25
3.00
2.75
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
ppm (f2)



31

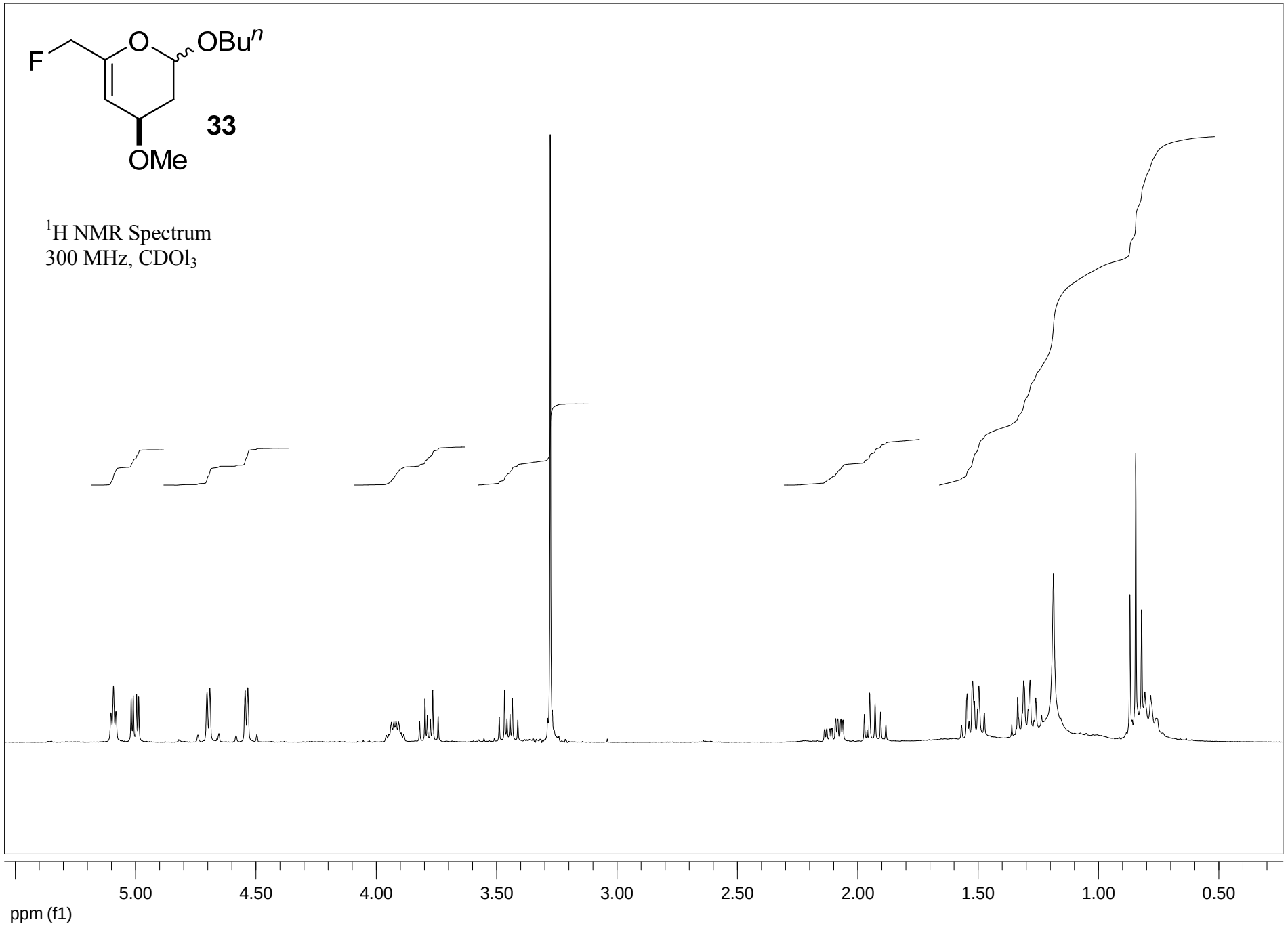
HMQC Spectrum
$CDCl_3$

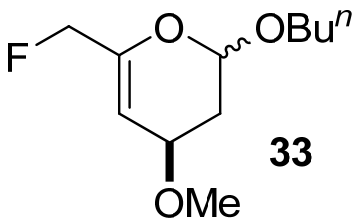




33

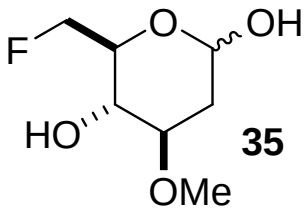
^{1}H NMR Spectrum
300 MHz, $CDOl_3$


F
O
OBu^n
OMe
33
^{1}H NMR Spectrum
300 MHz, CDOl$_3$
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (f1)



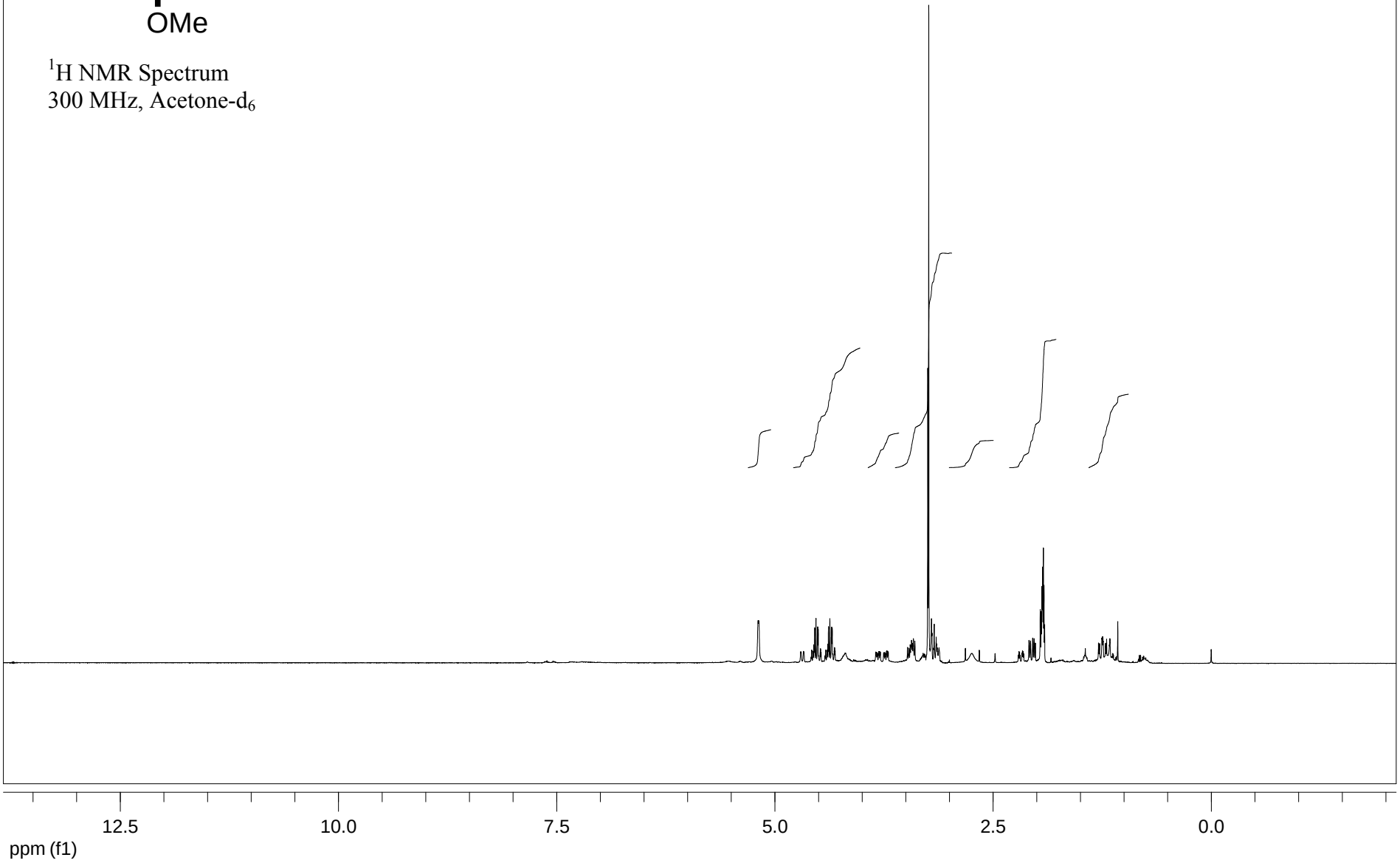
33

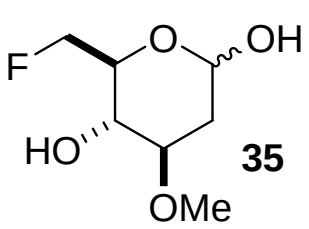
^{19}F NMR Spectrum
282 MHz, $CDCl_3$



35

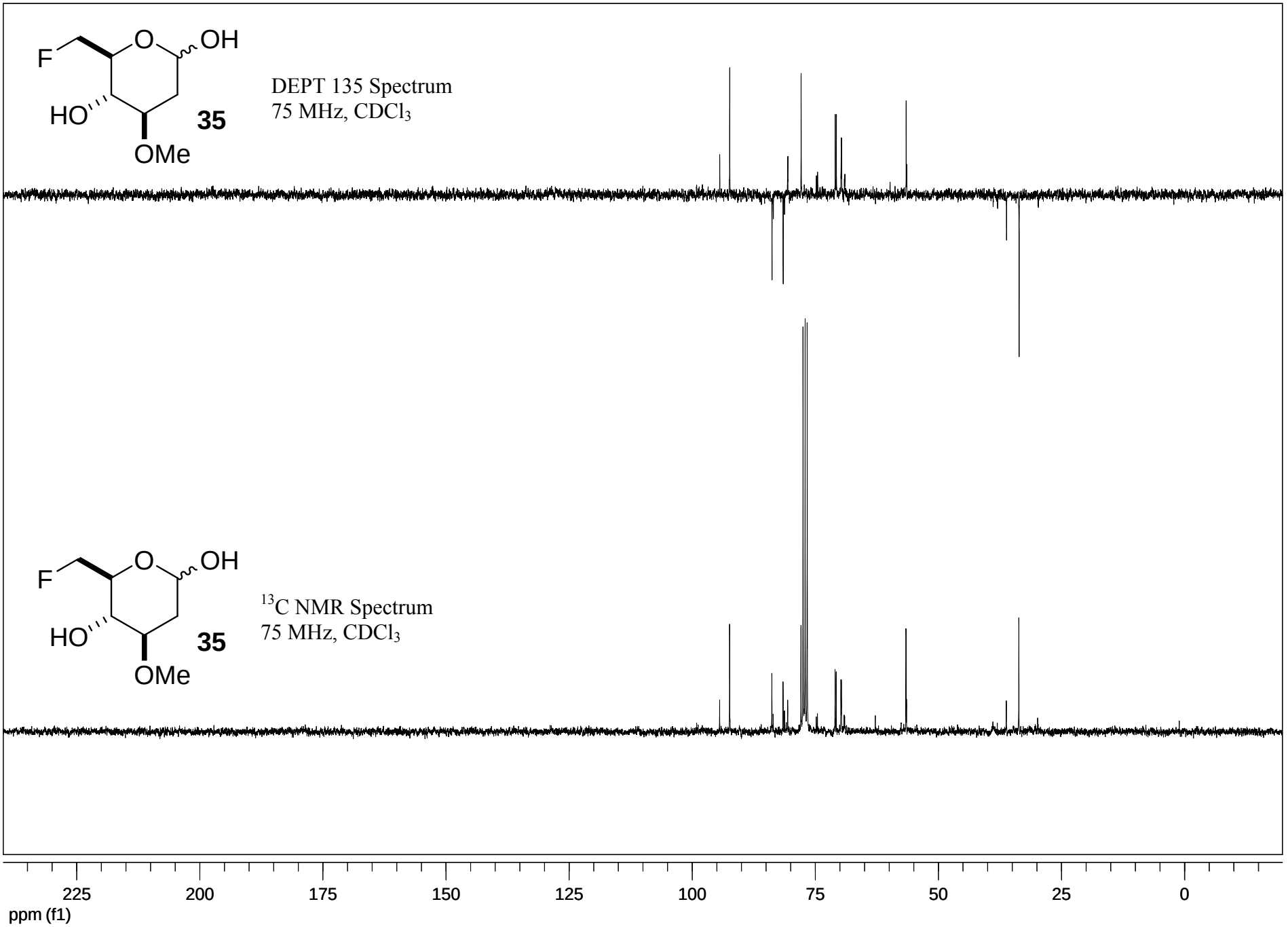
^{1}H NMR Spectrum
300 MHz, Acetone-d_6

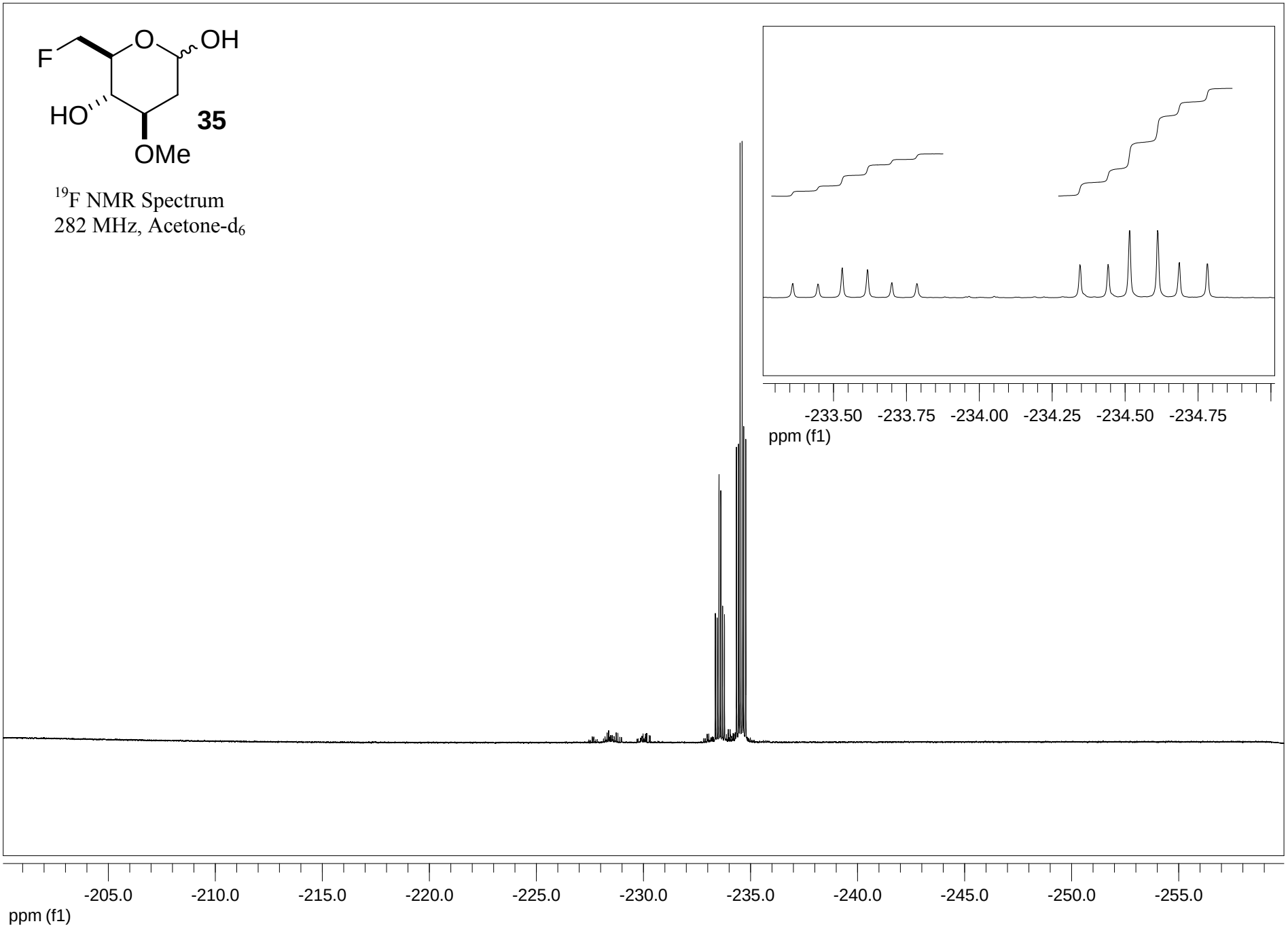


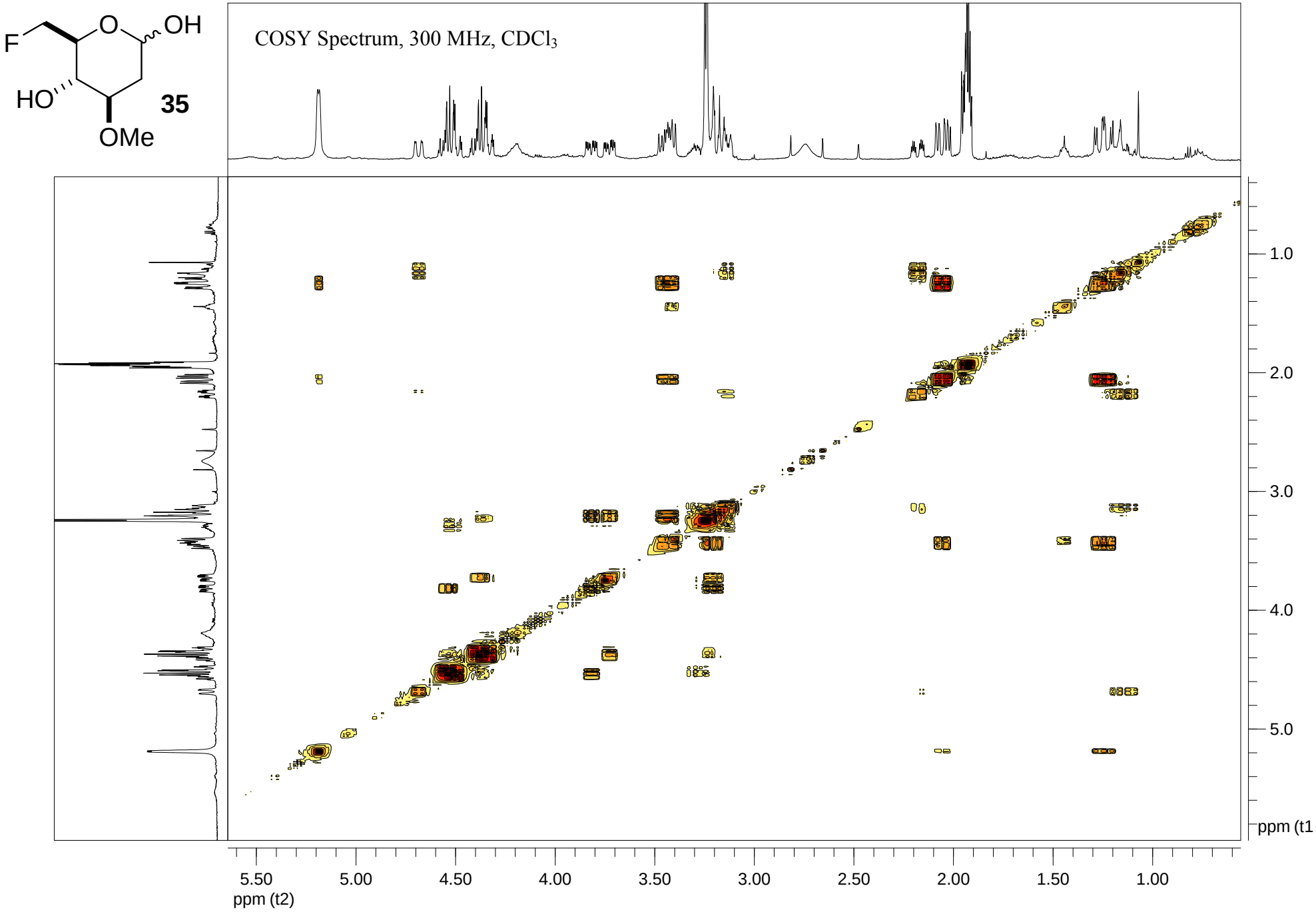


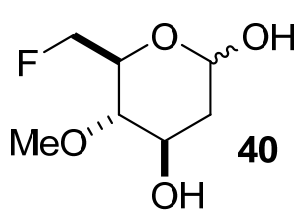
35

^{1}H NMR Spectrum
expansion


F
O
OH
HO
35
OMe
DEPT 135 Spectrum
75 MHz, CDCl3
F
O
OH
HO
35
OMe
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)

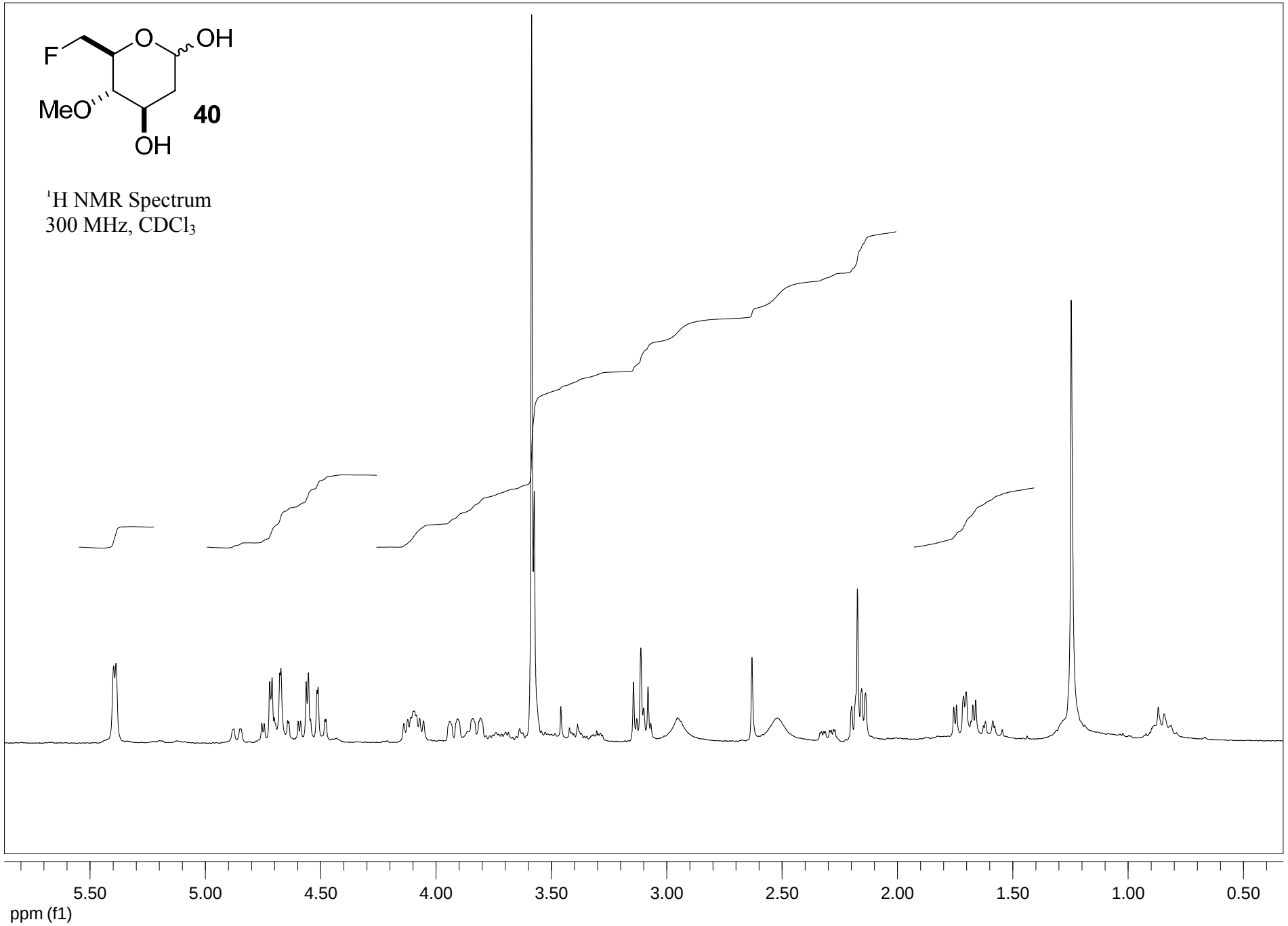

F
O
OH
HO
35
OMe
19F NMR Spectrum
282 MHz, Acetone-d6
-233.50
-233.75
-234.00
-234.25
-234.50
-234.75
ppm (f1)
-205.0
-210.0
-215.0
-220.0
-225.0
-230.0
-235.0
-240.0
-245.0
-250.0
-255.0
ppm (f1)

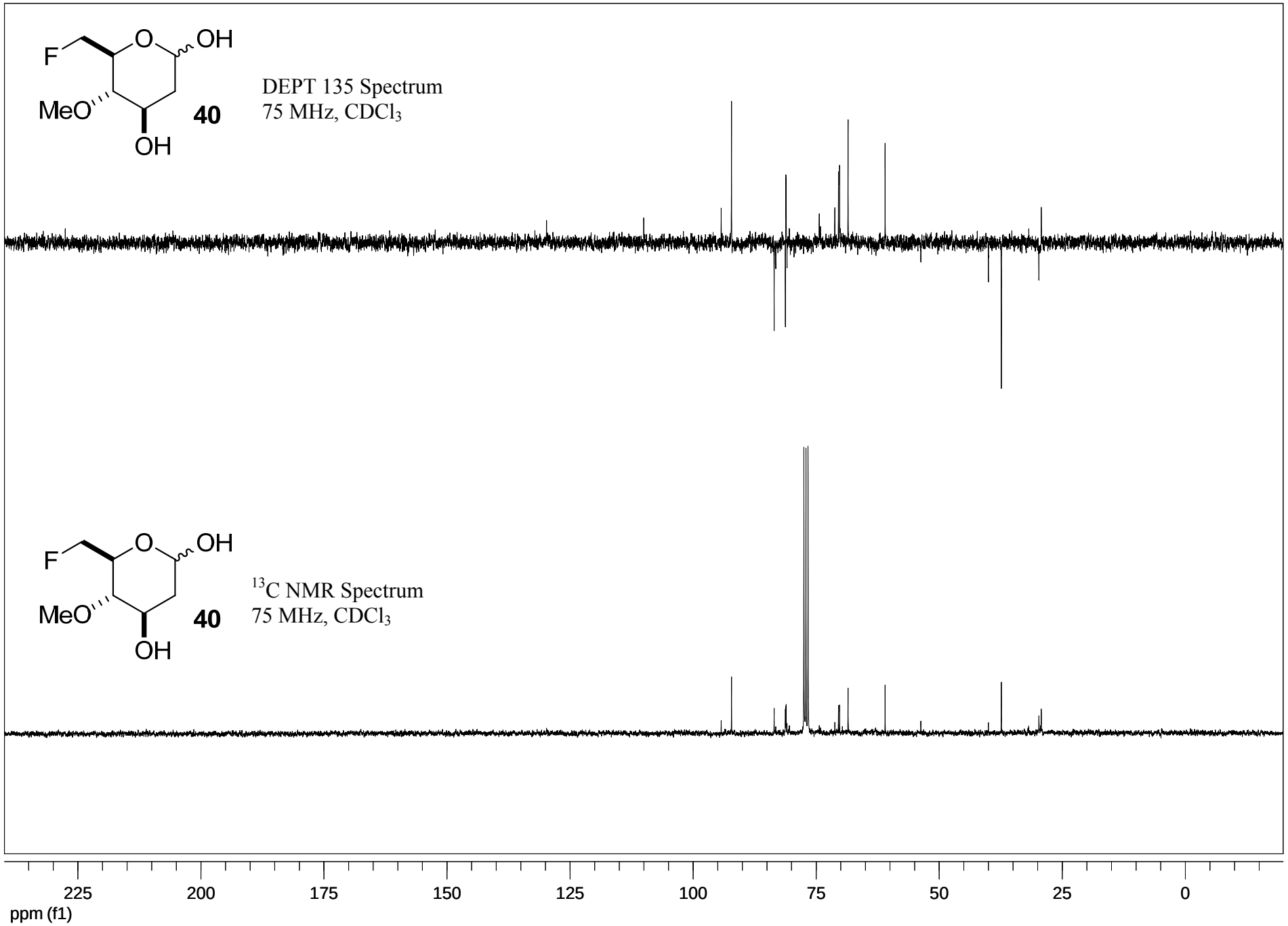

F
O
OH
HO
35
OMe
COSY Spectrum, 300 MHz, CDCl3
1.0
2.0
3.0
4.0
5.0
ppm (t1
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (t2)

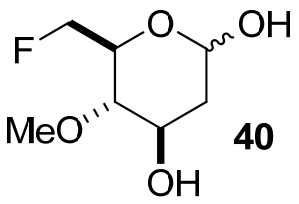


40

^{1}H NMR Spectrum
300 MHz, $CDCl_3$

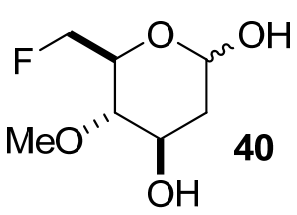

F
O
OH
MeO
OH
40
1H NMR Spectrum
300 MHz, CDCl3
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (f1)


F
O
OH
MeO
OH
40
DEPT 135 Spectrum
75 MHz, CDCl3
F
O
OH
MeO
OH
40
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)



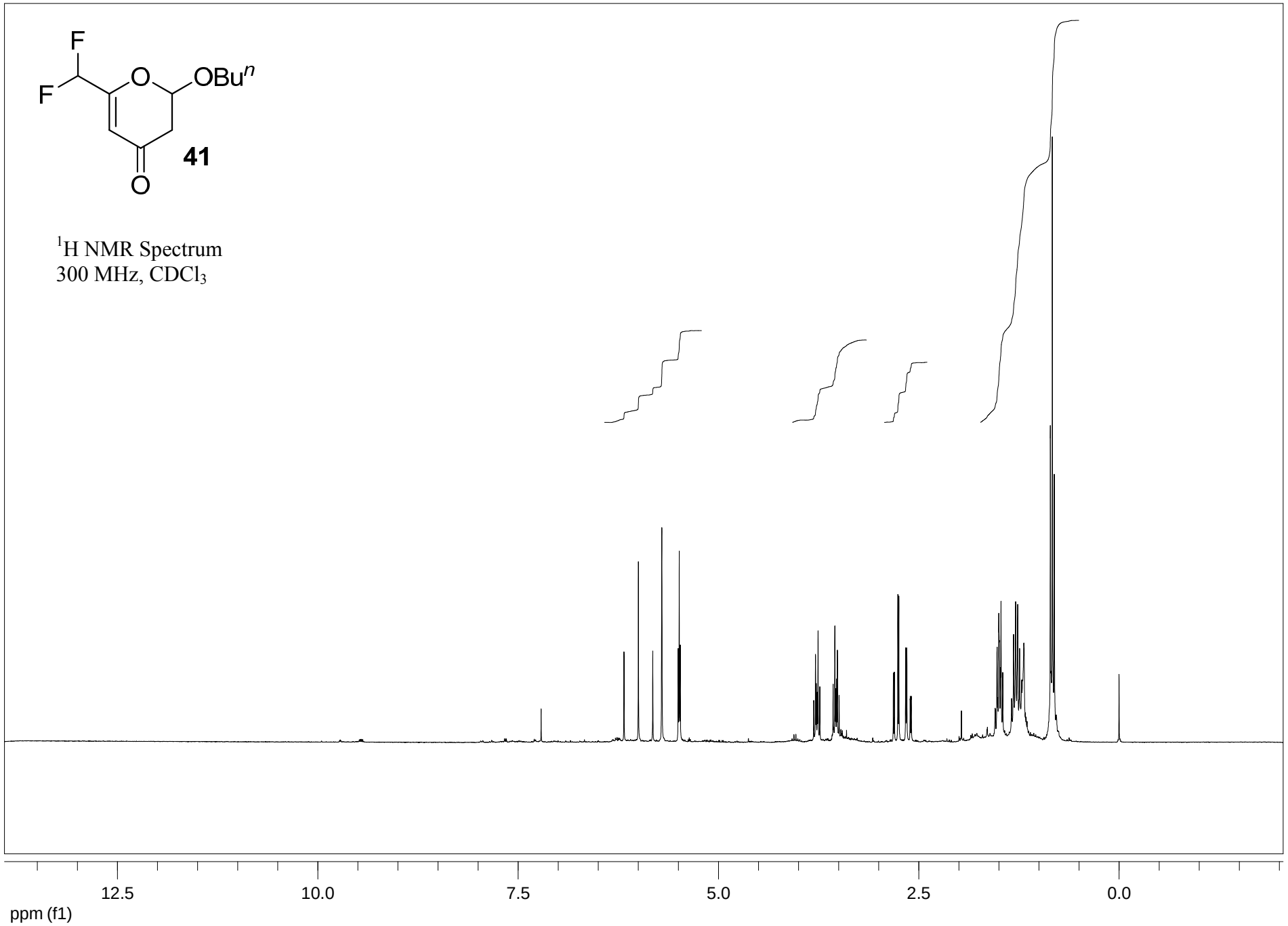
40

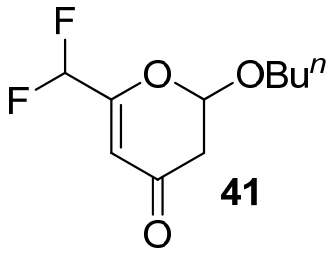
^{19}F NMR Spectrum
282 MHz, $CDCl_3$


F
O
OH
MeO
OH

40

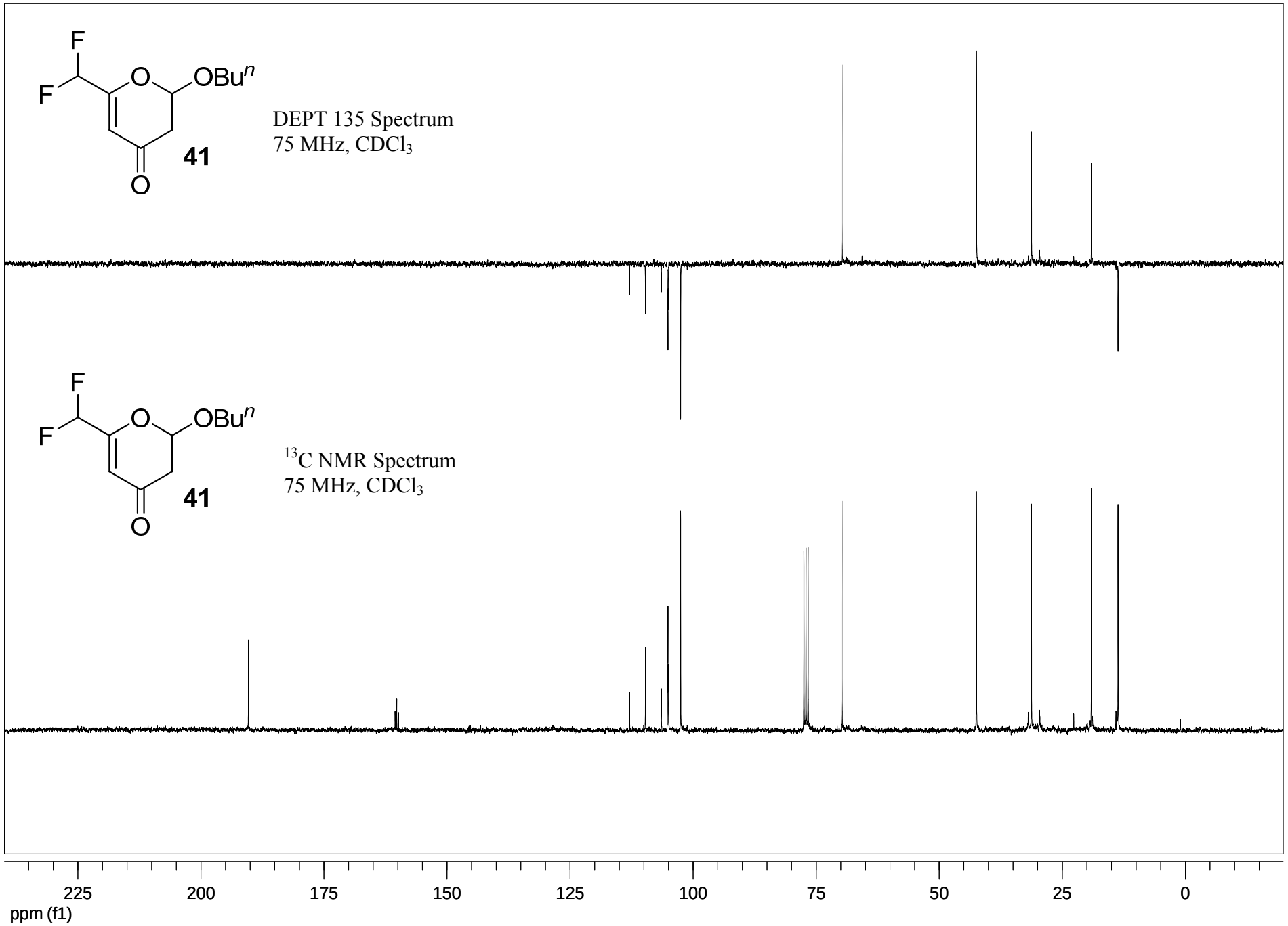
COSY Spectrum, 300 MHz, CDCl3
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (f2)

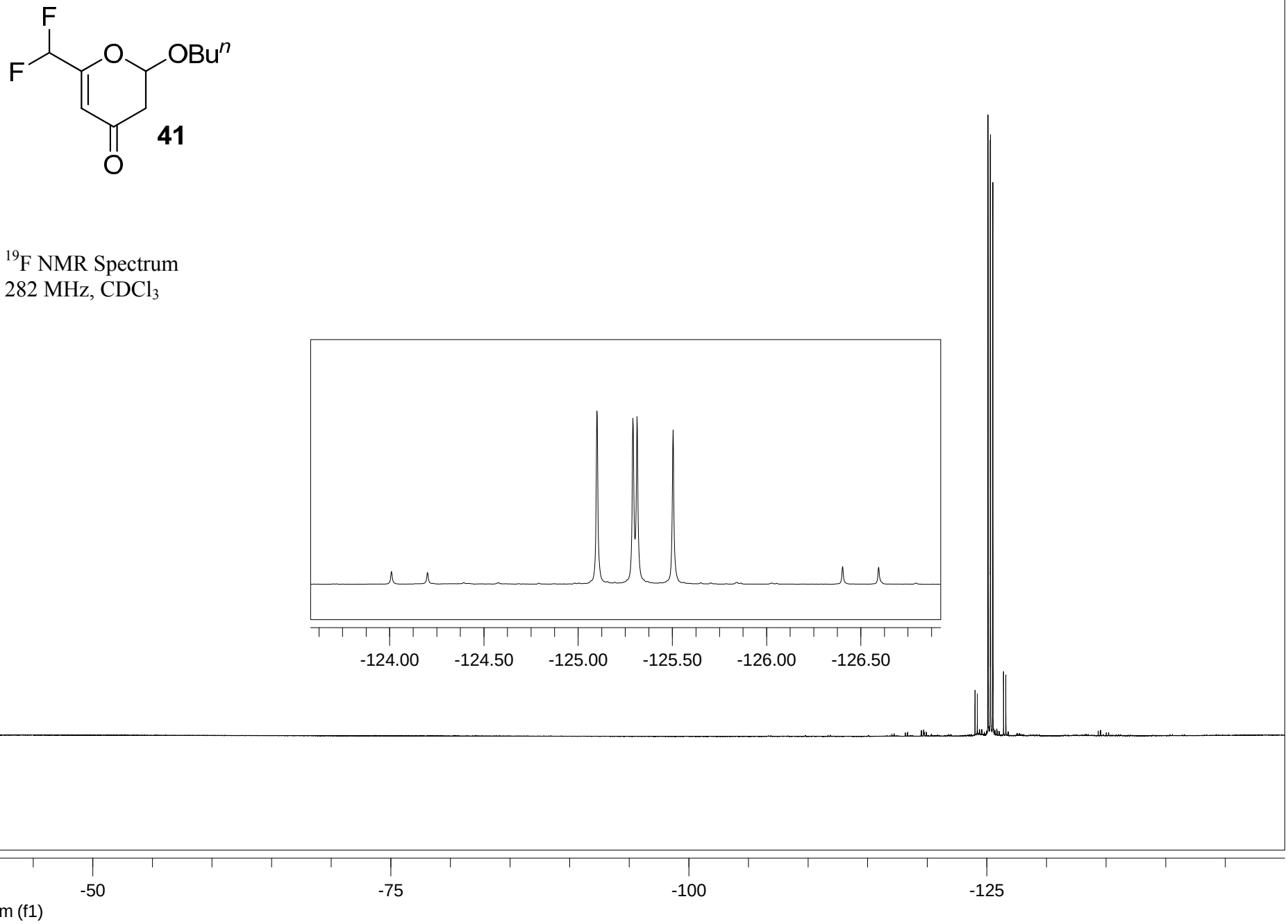

F
F
O
OBu^n
41
O
[1]H NMR Spectrum
300 MHz, CDCl3
12.5
10.0
7.5
5.0
2.5
0.0
ppm (f1)

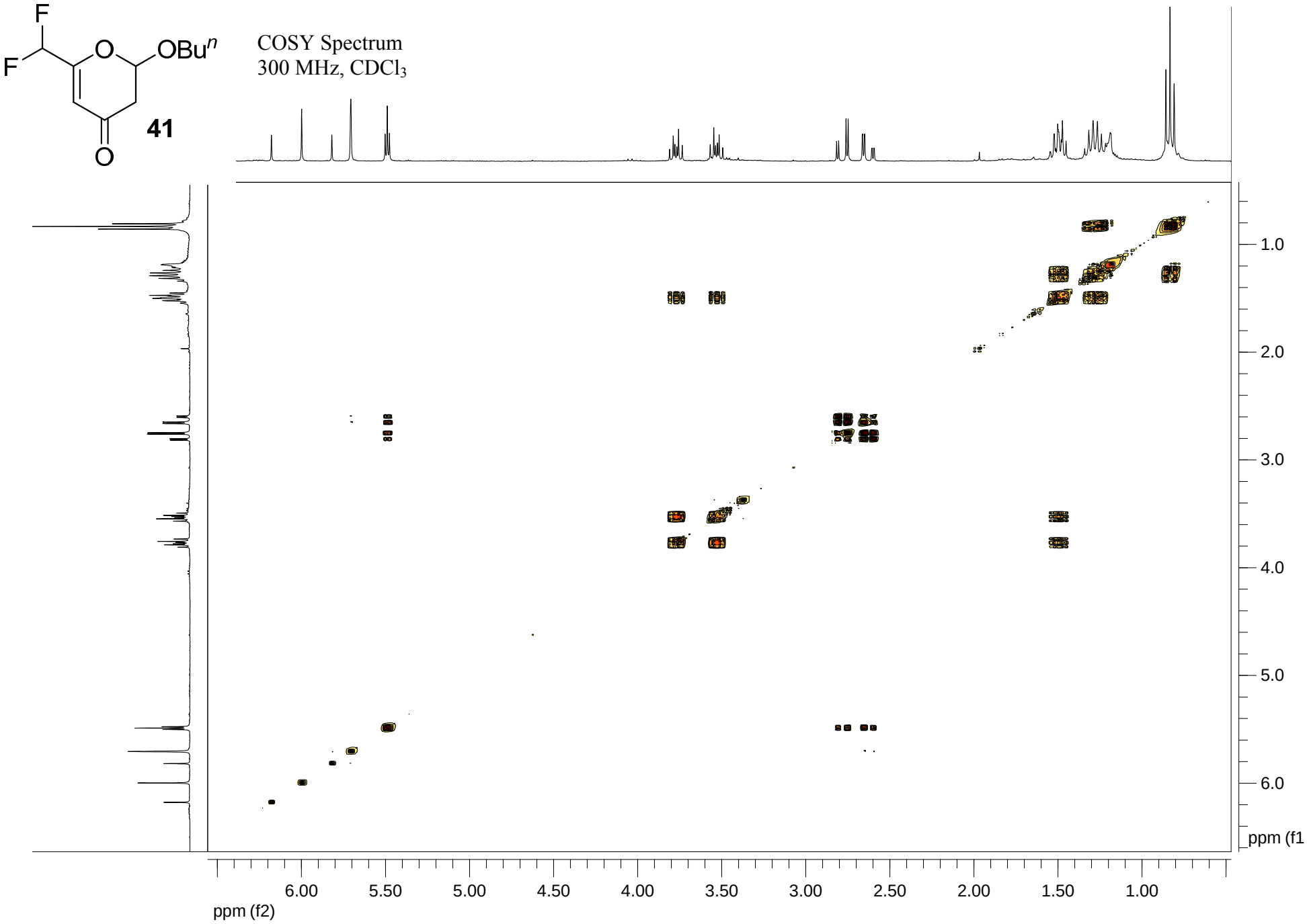


41

^{1}H NMR Spectrum expansion
300 MHz, $CDCl_3$


F
F
O
OBu^n
41
O
DEPT 135 Spectrum
75 MHz, CDCl3
F
F
O
OBu^n
41
O
13C NMR Spectrum
75 MHz, CDCl3
225
200
175
150
125
100
75
50
25
0
ppm (f1)


F
F
O
OBu^n
41
O
19F NMR Spectrum
282 MHz, CDCl3
-124.00
-124.50
-125.00
-125.50
-126.00
-126.50
-50
-75
-100
-125
ppm (f1)


F
F
O
OBu^n
41
O
COSY Spectrum
300 MHz, CDCl$_3$
1.0
2.0
3.0
4.0
5.0
6.0
ppm (f1
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (f2)