# SUPPORTING INFORMATION

## Transannular *O*-Heterocyclization: A Useful Tool for the Total Synthesis of Murisolin and 16,19-*cis*-Murisolin

Peter Persich, Julia Kerschbaumer, Sandra Helling, Barbara Hildmann, Birgit Wibbeling, and Günter Haufe*

*Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Corrensstraße 40, D-48149 Münster, Germany*

*e-mail: haufe@uni-muenster.de*

# General Information

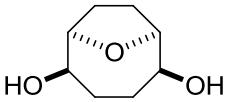
Starting material and reagents for the synthesis were purchased from ABCR, Acros, Sigma-Aldrich, Fluka and Merck and were used, if not stated otherwise, without further purification. (*Z*,*Z*)-1,5-Cyclooctadien was a donation from Degussa AG, Marl. The 40 % peracetic acid (Wofasteril®) was purchased from Kesla Chemie Pharma GmbH, Wolfen. Solvents were purified by distillation and dried by standard procedures if necessary.[1] All reactions were carried out under Ar in flame-dried glassware. Preparative column chromatography was carried out using silica gel 60 (Kieselgel 60, 40 – 63 µm or 63 – 200 µm) of Merck as stationary phase. NMR spectra were recorded in the solvents indicated using the following instruments: Bruker AV300, Bruker AV400, Varian 500 Inova, Varian 600 unity plus. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) are given in Hz. 2D NMR spectroscopy was used for the assignment of $^{1}$H and $^{13}$C NMR signals. Mass spectra with GC or direct inlet and electron impact ionization were recorded either on the double focusing sector field MS MAT8230 (Thermo-Finnigan-MAT, Bremen), or on the instrument GCT (Waters-Micromass, Manchester, UK), or on the instrument Quattromicro GC (Waters-Micromass, Manchester, UK). Exact mass determinations with electron spray ionization were recorded on the MicroTof (Bruker Daltronics, Bremen) equipped with loop inlet. Melting points were measured using the instruments Stuart SMP10 (Bibby Sterilin LTD) and are uncorrected. FT-IR spectra were recorded on Bruker IFS 28 either as film on sodium chloride plates or as KBr pallet. Optical rotations were determined with Polarimeter 341 (Perkin Elmer) at a wavelength of 589 nm at rt. Elemental analyses were carried out on Vario EL III (Elementar-Analysensysteme, Hanau).

X-Ray data set was collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[2] absorption correction Denzo,[3] structure solution SHELXS-97,[4] structure refinement SHELXL-97,[5] graphics XP (BrukerAXS, 2000).

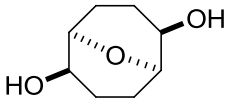
1 Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, Oxford, **1996**.
2 Otwinowski, Z.; Minor, W. *Methods in Enzymology* **1997**, *276*, 307-326.
3 Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Cryst.* **2003**, *A59*, 228-234.
4 Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467-473.
5 Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

# Procedures, Analytical and Spectroscopic Data

**Compounds 8a,b**:[6] 40 % Peracetic acid in AcOH (Wofasteril®, 40.0 g, 210 mmol, 2.3 eq.) was weighed into a 2-necked flask equipped with dropping funnel and thermometer and was cooled with an ice/sodium chloride bath to ca. 0 °C. Under vigorous stirring a solution of (*Z*,*Z*)-1,5-cyclooctadiene (10.0 g, 92 mmol, 1.0 eq.) in AcOH (20 mL) was added dropwise so that the temperature ranged between -5 and +10 °C. After complete addition stirring was continued under cooling. In the course of the reaction the emulsion turned into a clear solution. The reaction mixture was allowed to warm to rt overnight. 10 % aqueous NaOH was added dropwise until the solution had reached pH 10. The hot solution was cooled to rt and exposed to continuous extraction for 3 days with ethyl acetate. The organic layer was stirred with $FeSO_4$ (50 g) until complete destruction of excess peroxides and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by crystallization from acetone affording a mixture of products **8a,b** as colorless crystalline solid (13.5 g, 85 mmol, 92%).



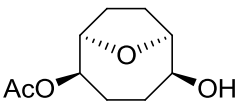

**8a**



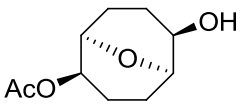

**8b**

Mp: 108 °C; $^1$H NMR (300 MHz, $D_2O$): $\delta$ = 4.47-4.37 (m, 2H, [**8b**]), 4.06-3.89 (m, 2H, [**8a**]; 2H, [**8b**]), 3.81-3.78 (m, 2H, [**8a**]), 2.18-1.54 (m, 8H, [**8a**]; 8H, [**8b**]); $^{13}$C NMR (75 MHz, $D_2O$): 80.4 (d, [**8a**]), 71.1 (d, [**8a**]), 69.4 (d, [**8b**]), 68.0 (d, [**8b**]), 27.2 (t, [**8b**]), 27.1 (t, [**8a**]), 23.7 (t, [**8a**]), 21.5 (t, [**8b**]); IR (KBr): 3403, 2960, 2850, 2931, 1564, 1443, 1259, 1219, 1081, 1018 cm$^{-1}$; MS (EI): *m/z* (%): 158 (6), 140 (9), 130 (2), 122 (2), 112 (10), 101 (36), 97 (32), 96 (19), 84 (53), 79 (66), 71 (23), 70 (45), 69 (81), 68 (77), 67 (96), 58 (28), 57 (100), 55 (66), 44 (28), 43 (38), 41 (49); HRMS (ESI): *m/z* calcd. for $C_8H_{14}O_3Na$ $[M+Na]^+$: 181.0835; found 181.0855.

**Compounds 9a,b**:[6] A solution of diols **8a,b** (3.36 g, 21.3 mmol, 1.0 eq) in vinyl acetate (100 mL) together with immobilized lipase of *candida rugosa* (1302 U/mg, 2.98 g) was frequently shacked at 30 °C. After 16 h the reaction was stopped by filtration when conversion reached 60% by GC-analysis. The solvent was removed under reduced pressure and the residue was purified by column chromatography (cyclohexane/EtOAc, 3:1→0:1) affording a 68:32 mixture[7] of products **9a,b** as a colorless oil (1.70 g, 8.50 mmol, 58%, *ee* = 96% [**9a**], *ee* = 76% [**9b**]).[8]




**9a**




**9b**

$[\alpha]_D^{20}$ = +23.4° (*c* = 1.16, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 5.17-4.98 (m, 1H, [**9a**], 1H, [**9b**]), 4.63-4.50 (m, 1H, [**9a**]), 4.50-4.39 (m, 1H, [**9a**]), 4.17-3.93 (m, 1H, [**9a**], 1H, [**9b**]),

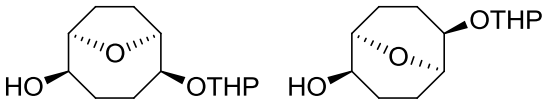
6 Behr, S.; Hegemann, K.; Schimanski, H.; Fröhlich, R.; Haufe, G. *Eur. J. Org. Chem.* **2004**, 3884.

7 The ratio was determined by GC.

8 The enantiomeric excess was determined by $^1$H NMR using 40 mol% $Eu(hfc)_3$ as chiral shift reagent in $CDCl_3$; see spectral data.

3.89-3.86 (m, 1H, [**9b**]), 3.82-3.78 (m, 1H, [**9b**]), 2.23-1.57 (m, 8H, [**9a**], 8H, [**9b**], *overlap*), 2.06 (s, 3H, [**9a**], *overlap*), 2.05 (s, 3H, [**9b**], *overlap*); $^{13}$C NMR (75 MHz, $CDCl_3$): 170.4, 170.3 (2s, [**9a,b**]), 81.5 (d, [**9a**]), 77.7 (d, [**9a**]), 73.7 (d, [**9a**]), 72.0 (d, [**9a**]), 70.7 (d, [**9b**]), 69.7 (d, [**9b**]), 68.4 (d, [**9b**]), 66.5 (d, [**9b**]), 28.5 (t, [**9b**]), 28.3 (t, [**9a**]), 25.5 (t, [**9a**]), ), 25.3 (t, [**9a**]), 25.3 (t, [**9a**]), 23.8 (t, [**9b**]), 22.9 (t, [**9b**]), 21.7 (t, [**9a**]), 21.2 (q, [**9a**]), 21.2 (q, [**9b**]); IR (film): 3625, 3469, 3452, 2975, 2873, 2928, 2852, 1741, 1556, 1446, 1382, 1371, 1250, 1122, 1078, 1038, 983 cm$^{-1}$; MS (EI): *m/z* (%): 200 (<1), 140 (13), 122 (6), 112 (6), 97 (19), 96 (23), 95 (15), 94 (17), 84 (57), 81 (21), 71 (26), 70 (17), 69 (34), 68 (57), 67 (56), 58 (13), 57 (28), 55 (23), 43 (100), 41 (17); HRMS (ESI): *m/z* calcd. for $C_{10}H_{16}O_4Na$ $[M+Na]^+$: 232.0941; found 232.0939.

**Compounds 25a,b**: Dihydropyran (0.77 mL, 8.5 mmol, 1.7 eq) and *p*-TsOH (95 mg, 0.5 mmol, 0.1 eq) were added to a solution of acetates **9a,b** (1.0 g, 5.0 mmol, 1.0 eq) in $CH_2Cl_2$ (8 mL). The mixture was stirred overnight. Then a solution of KOH (1.40 g, 25 mmol, 5.0 eq) in MeOH (13 mL) was added dropwise and the mixture was for additional 20 h. After complete conversion the mixture was neutralized with 4 N aqueous HCl and diluted with water. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (cyclohexane/EtOAc, 3:1→0:1) affording a mixture of products **25a,b** as a yellowish oil (887 mg, 3.61 mmol, 72%).



**25a** **25b**

$[\alpha]_D^{20}$ = +16.9° (*c* = 1.05, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 4.73-4.66 (m, 1H, [**25b**]), 4.66-4.57 (m, 2H, [**25b**]; 1H, [**25a**]), 4.57-4.37 (m, 2H, [**25a**]), 4.08-3.81 (m, 3H, [**25a**]; 4H, [**25b**]), 3.81-3.72 (m, 1H, [**25a**]), 3.56-3.42 (m, 1H, [**25a**]; 1H, [**25b**]), 2.38-1.61 (m, 9H, [**25a**]; 9H, [**25b**]), 1.61-1.44 (m, 5H, [**25a**]; 5H, [**25b**]); $^{13}$C NMR (101 MHz, $CDCl_3$): 98.7 (d, [**25a**]), 98.1, 97.8 (2d, [**25b**]), 97.6 (d, [**25a**]), 81.3, 81.3 (2d, [**25a**]), 79.9, 78.9 (2d, [**25a**]), 76.8, 76.2 (2d, [**25a**]), 73.5, 73.5 (2d, [**25b**]), 72.2, 72.1 (2d, [**25a**]), 69.9, 69.8 (2d, [**25b**]), 68.9 (d, [**25b**]), 68.8 (d, [**25b**]), 67.4 (d, [**25b**]), 62.9, 62.9 (2t, [**25b**]), 62.7 (t, [**25a**]), 31.2, 31.1 (2t, [**25a,b**]), 28.9, 28.8 (2t, [**25b**]), 28.8, 28.4 (2t, [**25a**]), 27.5, 26.0 (2t, [**25b**]), 25.5, 25.4, 25.4, 25.4 (4t, [**25a**]), 25.2, 25.0 (2t, [**25a**]), 24.0, 24.0, (2t, [**25a**]), 22.9, 22.6 (2t, [**25b**]), 22.1, 22.0, (2t, [**25b**]), 19.9, 19.9 (2t, [**25b**]), 19.8 (t, [**25a**]); MS (EI): *m/z* (%): 242 (1), 224 (1), 206 (1), 157 (1), 155 (4), 141 (7) , 139 (7) , 101 (4) , 85 (92) , 84 (61), 83 (23), 81 (15), 79 (21), 71 (32), 70 (23), 69 (33), 68 (28), 67 (61) , 58 (14), 57 (71) , 56 (24), 55 (100), 54 (16), 53 (21), 44 (22), 43 (42), 42 (16), 41 (79), 40 (45); HRMS (ESI): *m/z* calcd. for $C_{13}H_{22}O_4Na$ $[M+Na]^+$: 265.1410; found 265.1407.

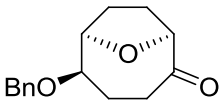
**Compounds 10a,b**: Sodium hydride (60 % in paraffin, 7.0 g, 174 mmol, 1.5 eq) was added in one portion to a solution of THP-ethers **25a,b** (28.1 g, 116 mmol, 1.0 eq) in abs. THF (300 mL) at 0 °C. The reaction mixture was

**10a** **10b**

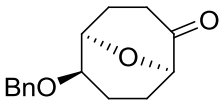
stirred for 20 min at this temperature, then warmed to rt for 1 h. TBAI (4.3 g, 12 mmol, 0.1 eq) and BnBr (23.5 mL, 198 mmol, 1.7 eq) were added successively and the reaction mixture was stirred for 10 min prior to refluxing for 2 h. After cooling to ambient temperature it was quenched with silica gel and transferred with ethyl acetate in a round bottom flask. The solvent was removed under reduced pressure and the crude product absorbed on silica. Column chromatography (cyclohexane/EtOAc, 60:1→10:1) yielded a mixture of products **10a,b** (34.3 g, 103 mmol, 89 %) as a yellowish oil.

$[\alpha]_D^{20}$ = +13.4° (*c* = 0.99, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.36-7.22 (m, 5H, [**10a**]; 5H, [**10b**]), 4.72-4.40 (m, 4H, [**10a**]; 3H, [**10b**]), 4.05-3.69 (m, 9H), 3.53-3.40 (m, 2H) (2m, 5H, [**10a**]; 6H, [**10b**]), 2.34-1.39 (m, 14H, [**10a**]; 14H, [**10b**]); $^{13}$C NMR (101 MHz, $CDCl_3$): 138.9 (s), 138.7 (s), 138.6 (s), 128.4 (d), 128.3 (d), 127.5 (d), 127.5 (d), 127.4 (d), 127.3 (d), 98.5 (d), 98.0 (d), 97.8 (d), 97.6 (d), 80.5 (d), 79.4 (d), 79.3 (d), 79.3 (d), 79.1 (d), 79.0 (d), 77.2 (d), 76.8 (d), 75.4 (d), 75.4 (d), 73.5 (d), 73.5 (d), 71.0 (t), 71.0 (t), 70.5 (t), 70.5 (t), 69.2 (d), 67.7 (d), 67.7 (d), 67.6 (d), 62.9 (t), 62.8 (t), 62.8 (t), 62.6 (t), 31.2 (t), 31.2 (t), 31.3 (t), 27.4 (t), 26.7 (t), 26.4 (t), 26.3 (t), 26.0 (t), 25.4 (t), 25.4 (t), 25.2 (t), 25.2 (t), 25.0 (t), 24.7 (t), 24.7 (t), 22.8 (t), 22.7 (t), 22.6 (t), 22.5 (t), 19.9 (t), 19.8 (t), 19.8 (t), 19.8 (t); IR (film): 2939, 2870, 2363, 1453, 1349, 1201, 1115, 1065, 1029, 990, 896, 870, 736, 698 $cm^{-1}$; MS (EI): *m/z* (%): 332 (1), 314 (1), 247 (1), 225 (1), 155 (3), 142 (10), 141 (21), 139 (21), 124 (10), 97 (10), 95 (23), 92 (14), 91 (100), 85 (55), 84 (27), 83 (21), 71 (42), 67 (23), 65 (15), 57 (16), 55 (25); HRMS (ESI): *m/z* calcd. for $C_{20}H_{28}O_4Na$ $[M+Na]^+$: 355.1880; found 355.1885.

**Compounds 11a,b**: Jones reagent[9] (14.5 mL) and 4.5 M aqueous $H_2SO_4$ (8.6 mL) were added dropwise at 0 °C to a solution of protected diols **10a,b** (3.70 g, 11.1 mmol, 1.0 eq) in acetone (110 mL). A dark green precipitate was formed immediately. The reaction mixture was stirred at rt. After 3.5 h the reaction was quenched with *i*-PrOH (10 mL) and diluted with water (250 mL). The reaction mixture was extracted with $CH_2Cl_2$ (3×50 mL). The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (cyclohexane/EtOAc, 10:1) affording a mixture of products **11a,b** as a yellowish oil (2.42 g, 9.7 mmol, 88%).




**11a**



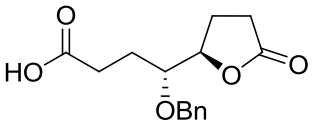

**11b**

$[\alpha]_D^{20}$ = +14.1° (*c* = 0.95, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 7.39-7.25 (m, 5H, [**11a**]; 5H, [**11b**]), 4.71-4.65 (m, 1H, [**11a**]), 4.61(d, *J* = 12.0 Hz, 1H, [**11a**]), 4.57 (d, *J* = 12.0 Hz, 1H, [**11a**]), 4.55 (d, *J* = 12.0 Hz, 1H, [**11b**]), 4.51 (d, *J* = 12.0 Hz, 1H, [**11b**]), 4.42-4.32 (m, 1H, [**11b**], *overlap*), 4.36 (dd, *J* = 9.9, 1.9 Hz, 1H, [**11a**], *overlap*), 4.01 (br d, 1H, *J* = 5.6 Hz, [**11b**]), 3.79 (dt, *J* = 4.6, 11.3 Hz, 1H, [**11a**]), 3.69 (dt, *J* = 5.0, 11.7 Hz, 1H, [**67**]), 2.81-2.66 (m, 1H, [**11a**]; 1H, [**11b**]), 2.39-2.19 (m, 2H, [**11a**]; 2H, [**11b**]), 2.14-1.83 (m, 4H, [**11a**]; 3H, [**11b**]), 1.82-1.69 (m, 1H, [**11b**]), 1.57-1.33 (m, 1H,[ **11a**]; 1H, [**11b**]); $^{13}$C NMR (101 MHz, $CDCl_3$): 217.0 (s, [**11a**]), 215.7 (s, [**11b**]), 138.3 (s, [**11a,b**]), 128.4 (d, [**11a**]), 128.4 (d,

9 preparation: $CrO_3$ (26 g) in conc. $H_2SO_4$ (23 mL), filled up with water to 100 mL.

[**11b**]), 127.7 (d, [**11b**]), 127.7 (d, [**11a**]), 127.5 (d, [**11a,b**]), 83.7 (d, [**11a**]), 80.3 (d, [**11a**]), 78.7 (d, [**11a**]), 76.9 (d, [**11b**]), 74.7 (d, [**11b**]), 71.3 (t, [**11a**]), 70.5 (t, [**11b**]), 67.4 (d, [**11b**]), 36.9 (t, [**11a**]), 34.5 (t, [**11b**]), 31.1 (t, [**11a**]), 26.9 (t, [**11b**]), 24.2 (t, [**11a**]), 23.0 (t, [**11a**]), 22.7 (t, [**11b**]), 18.9 (t, [**11b**]); IR (film): 3064, 3031, 2937, 2872, 2360, 2339 ,1713, 1454, 1086, 1073, 1039, 955, 876, 737, 698 $cm^{-1}$; MS (EI): *m/z* (%): 246 (9), 190 (38), 161 (15), 156 (30), 155 (100), 140 (26), 137 (69), 127 (30), 112 (27), 111 (55), 109 (32), 92 (64), 91 (99), 87 (30), 85 (75), 83 (31), 81 (67), 79 (47), 77 (20), 69 (35), 65 (67), 57 (19), 55 (32), 41 (38), 39 (31); HRMS (ESI): *m/z* calcd. for $C_{15}H_{18}O_3Na$ $[M+Na]^+$: 269.1148; found 269.1161.

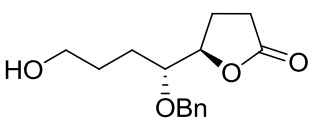
**Compound 12**: Oxone (4.57 g, 7.43 mmol, 1.5 eq) was added in several portions at 0 °C over a 8 h period to a stirred solution of ketones **11a,b** (1.22 g, 4.96 mmol, 1.0 eq) in formic acid (15 mL). The reaction mixture was stirred at 0 °C for 2 days. Then the mixture was diluted with water before $Na_2S_2O_5$ (1.41 g, 7.43 mmol, 1.5 eq) was added at 0 °C. The reaction mixture was extracted with $CH_2Cl_2$. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was dissolved in a small amount of toluene and evaporated, this operation was repeated three times. Acid **12** (1.40 g) was obtained as a viscous yellow oil, which was used without further purification in the next step.



**12**

$[\alpha]_D^{20}$ = +3.7° (*c* = 1.21, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 7.95 (br s, 1H), 7.38-7.12 (m, 5H), 4.71 (d, *J* = 11.4 Hz, 1H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.58-4.49 (m, 1H), 3.54 (dt, *J* = 8.1, 5.0 Hz, 1H), 2.62-2.42 (m, 4H), 2.17-2.05 (m, 1H), 2.05-1.76 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 178.7 (s), 177.2 (s), 137.8 (s), 128.5 (d), 128.0 (d), 127.9 (d), 82.3 (d), 79.1 (d), 73.2 (t), 29.5 (t), 28.4 (t), 25.0 (t), 24.4 (t); IR (film): 2939, 2362, 1772, 1709, 1496, 1454, 1361, 1173, 1098, 1066, 1027, 984 , 919, 812, 734, 697 $cm^{-1}$; MS (EI): *m/z* (%): 278 (2), 193 (10), 176 (6), 147 (10), 126 (31), 92 (15), 91 (100), 85, 65 (19); HRMS (ESI): *m/z* calcd. for $C_{15}H_{18}O_5Na$ $[M+Na]^+$: 301.1064; found 301.1044.

**Compound 26**: A soltion of $BH_3{\cdot}SMe_2$ (0.43 mL, 4.04 mmol, 0.8 eq) in abs. THF (5 mL) was added slowly over a period of 15 min to a stirred solution of crude acid **12** (1.40 g, max. 5.05 mmol, max. 1.0 eq) in abs. THF (5 mL) at -15 °C. The reaction mixture was allowed to warm slowly to rt over night and was quenched at 0 °C with MeOH. The solvent was removed under reduced pressure. The residue was dissolved in a small amount of MeOH and evaporated, this operation was repeated three times. The residue was purified by column chromatography (cyclohexane/EtOAc, 1:1→0:1) affording product **26** as a yellowish oil (845 mg, 3.2 mmol, 65 % over 2 steps).

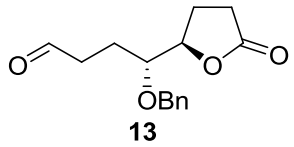


**26**

$[\alpha]_D^{20}$ = -11.7° (*c* = 1.25, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 7.38-7.24 (m, 5H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.57 (td, *J* = 7.3, 5.2 Hz, 1H), 3.67-3.58 (m, 1H), 3.52-3.45 (m, 1H), 2.63-2.40 (m, 2H), 2.29-2.16 (m, 1H), 2.09-1.90 (m, 1H), 1.76-1.56 (m,

4H); $^{13}$C NMR (101 MHz, $CDCl_3$): 177.6 (s), 138.0 (s), 128.5 (d), 127.9 (d), 127.8 (d), 82.1 (d), 80.3 (d), 72.9 (t), 62.5 (t), 28.5 (t), 28.3 (t), 26.3 (t), 24.4 (t); IR (film): 3429, 2929, 2870, 1766, 1454, 1361, 1182, 1061, 1027, 985, 915, 739, 699 cm$^{-1}$; MS (EI): *m/z* (%): 336 (1), 321 (3), 251 (8), 181 (28), 159 (33), 140 (64), 92 (56), 91 (100), 85 (87), 75 (73), 73 (62), 71 (59), 65 (42), 59 (15); HRMS (ESI): *m/z* calcd. for $C_{15}H_{20}O_4Na$ $[M+Na]^+$: 287.1254; found 287.1255.

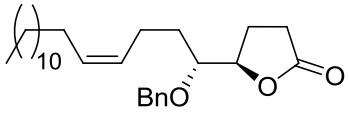
**Compound 13**: A solution of DMSO (0.96 mL, 13.4 mmol, 2.1 eq) in abs. $CH_2Cl_2$ (3 mL) was added to a stirred solution of oxalylchloride (0.61 mL, 7.0 mmol, 1.1 eq) in abs. $CH_2Cl_2$ (13 mL) at -78 °C. It was stirred for 2 min at -78 °C prior to the addition of a solution of alcohol **26** (1.82 g, 6.4 mmol, 1.0 eq) in abs. $CH_2Cl_2$ (9 mL). The mixture was stirred for 15 min at -78 °C before $NEt_3$ (4.43 mL, 32.0 mmol, 5.0 eq) was added at that temperature. It was kept for another 2 min at -78 °C and then warmed quickly to rt. Water (25 mL) was added and the biphasic system was stirred for 1.5 h. Then the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layers were washed successively with brine, 20 % aqueous $H_2SO_4$, water and diluted aqueous $NaHCO_3$, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The pure product **13** was obtained without further purification as a yellowish oil (1.61 g, 6.13 mmol, 96 %).



**13**

$[\alpha]_D^{20}$ = +7.2° (*c* = 0.96, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 9.72 (t, *J* = 1.1 Hz, 1H), 7.40-7.25 (m, 5H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.52 (dt, *J* = 7.3, 5.4 Hz, 1H), 3.50 (dt, *J* = 8.0, 4.9 Hz, 1H), 2.67-2.41 (m, 4H), 2.31-2.19 (m, 1H), 2.07-1.74 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 201.5 (d), 177.0 (s), 137.8 (s), 128.5 (d), 128.1 (d), 128.0 (d), 82.3 (d), 79.2 (d), 73.0 (t), 39.5 (t), 28.3 (t), 24.5 (t), 22.5 (t); IR (film): 2936, 2872, 2731, 2362, 2337, 1768, 1720, 1454, 1361, 1180, 1116, 1068, 1027, 986, 915, 740, 699 cm$^{-1}$; MS (EI): *m/z* (%): 262 (<1), 177 (17), 154 (3), 92 (16), 91 (100), 85 (63), 69 (11), 65 (19); HRMS (ESI): *m/z* calcd. for $C_{15}H_{18}O_4Na$ $[M+Na]^+$: 285.1097; found 285.1087.

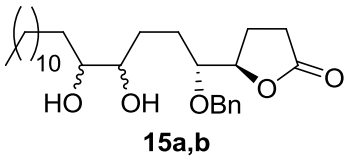
**Compound 14**: A solution of NaHMDS in THF (2M, 32 mL, 32.0 mmol, 1.0 eq) was added dropwise to a stirred solution of (tridecyl)triphenyl-phosphonium bromide (18.5 g, 35.2 mmol, 1.1 eq) while the reaction mixture was kept at rt with a water bath. It was stirred for another 30 min at rt before it was cooled to -78 °C and a solution of aldehyde **13** (8.37 g, 31.9 mmol, 1.0 eq) in abs. THF (48 + 5 mL) was added dropwise via transfer syringe. The color of the reaction mixture changed from bright red-orange to dark yellow. The reaction mixture was allowed to warm slowly to rt overnight. The resulting suspension was quenched at 0 °C with silica (60 g) and was transferred with $Et_2O$ to a 1L round bottom flask and the solvent was removed under reduced pressure. The residue was purified by column chromatography (cyclohexane/EtOAc, 10:1) affording product **14** as a yellowish oil (11.2 g, 26.1 mmol, 82 %, *Z*:*E* = 94:6).



**14**

$[\alpha]_D^{20}$ = -11.8° (*c* = 0.96, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 7.38-7.26 (m, 5H), 5.40 (dtt, *J* = 10.7, 7.0, 1.3 Hz, 1H), 5.32 (dtt, *J* = 10.7, 7.0, 1.3 Hz, 1H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.57 (td, *J* = 7.2, 5.1 Hz, 1H), 3.50-3.42 (m, 1H), 2.64-2.39 (m, 2H), 2.28-2.10 (m, 3H), 2.07-1.89 (m, 3H), 1.71-1.53 (m, 2H), 1.41-1.12 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 177.3 (s), 138.2 (s), 131.2 (d), 128.4 (d), 128.4 (d), 127.8 (d), 127.8 (d), 81.9 (d), 80.1 (d), 72.8 (t), 31.9 (t), 29.8 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.6 (t), 29.4 (t), 28.5 (t), 27.4 (t), 24.4 (t), 23.0 (t), 22.7 (t), 14.1 (q); IR (film): 3000, 2918, 2850, 1773, 1454, 1188, 1094, 1068, 1068, 1025, 987, 912, 737, 669 $cm^{-1}$; MS (EI): *m/z* (%): 428 (<1), 410 (1), 343 (13), 337 (9), 325 (12), 319 (28), 207 (8), 115 (12), 95 (14), 92 (21), 91 (100), 85 (79), 83 (19), 81 (20), 69 (25), 67 (32), 65 (21), 57 (22), 55 (30); HRMS (ESI): *m/z* calcd. for $C_{28}H_{44}O_3Na$ $[M+Na]^+$: 451.3183; found 451.3179; EA: calcd. for $C_{28}H_{44}O_3$, C: 78.46%, H: 10.35%; found, C: 78.38%, H: 10.53%.

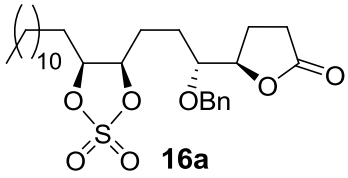
**Compounds 15a,b**: NMO (1.03 g, 8.8 mmol, 1.2 eq) was added to a vigorously stirred suspension of alkene **14** (3.14 g, 7.3 mmol, 1.0 eq) in acetone/water 1:2 (4.5 mL). A solution of $OsO_4$ in *tert*-butanol (2.5 wt%, 55 µL, 44 µmol, 0.6 mol%) was added and stirring was continued at rt with exclusion of light for 25 h. Saturated aqueous $Na_2SO_3$ (75 mL) was added and the mixture was diluted with water. Then the layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (cyclohexane/EtOAc, 1:1→1:2) affording *syn*-diols **15a,b** as a colorless waxy solid (3.07 g, 6.6 mmol, 90 %).



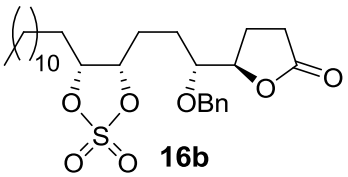
**15a,b**

$[\alpha]_D^{20}$ = -25.6° (*c* = 1.05, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 7.40-7.27 (m, 5H), 4.75-4.61 (m, 2H), 4.62-4.51 (m, 1H), 3.63-3.44 (m, 3H), 2.68-2.39 (m, 2H), 2.33-2.08 (m, 1H), 2.08-1.90 (m, 1H), 1.90-1.75 (m, 1H), 1.73-1.12 (m, 25H), 0.88 (t, *J* = 6.7 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 177.4 (s), 177.3 (s), 138.0 (s), 138.0 (s), 128.5 (d), 128.1 (d), 128.0 (d), 127.9 (d), 127.9 (d), 82.4 (d), 82.0 (d), 80.8 (d), 80.2 (d), 74.7 (d), 74.6 (d), 74.6 (d), 74.3 (d), 73.1 (t), 72.8 (t), 31.9 (t), 31.6 (t), 31.7 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.6 (t), 29.4 (t), 28.5 (t), 26.8 (t), 26.8 (t), 26.2 (t), 26.1 (t), 26.1 (t), 26.0 (t), 24.5 (t), 24.4 (t), 22.7 (t), 14.1 (q); IR (film): 3367, 3087, 3066, 3033, 2915, 2850, 1758, 1467, 1313, 1202, 1098, 1060, 925, 737, 697 $cm^{-1}$; HRMS (ESI): *m/z* calcd. for $C_{28}H_{46}O_5Na$ $[M+Na]^+$: 485.3237; found 485.3238; EA: calcd. for $C_{28}H_{46}O_5$, C: 72.69%, H: 10.02%; found, C: 72.40%, H: 10.16%.

**Compounds 16a,b**: $SOCl_2$ (0.48 mL, 6.56 mmol, 2.2 eq) was added dropwise to a stirred suspension of diols **15a,b** (1.38 g, 2.97 mmol, 1.0 eq) in abs. $CCl_4$ (22 mL) at rt. The mixture was stirred until a clear solution was formed and subsequently refluxed for 20 min. As TLC indicated full conversion, the reaction mixture was cooled to 0 °C and diluted with MeCN (22 mL). $NaIO_4$ (1.91 g, 8.94 mmol, 2.0 eq) and rutheniumtrichloride trihydrate (41% Ru, 31 mg, 60 µmol, 2 mol%) were added followed by water (35 mL). The resulting biphasic mixture was stirred vigorously at 0 °C for 5 min, than at rt for 2 days. The mixture was diluted



**16a**



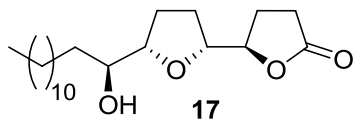
**16b**

with $Et_2O$, the layers were separated and the organic layer was washed successively two times with water and with saturated aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (cyclohexane/EtOAc, 3:1) affording sulfate **16a** (727 mg, 1.39 mmol, 47%) and **16b** (653 mg, 1.25 mmol, 42%) as colorless oils.

Diastereomer **16a**: $[\alpha]_D^{20}$ = +7.2° (*c* = 1.12, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 7.40-7.28 (m, 5H), 4.88-4.80 (m, 1H), 4.77-4.69 (m, 1H), 4.69 (d, *J* = 11.8 Hz, 1H), 4.63 (d, *J* = 11.8 Hz, 1H), 4.56 (td, *J* = 7.3, 5.3 Hz, 1H), 3.52 (dt, *J* = 5.3, 5.3 Hz, 1H), 2.65-2.44 (m, 2H, H-2), 2.31-2.20 (m, 1H), 2.02-1.88 (m, 2H), 1.88-1.62 (m, 3H), 1.57-1.16 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 176.9 (s), 137.8 (s), 128.6 (d), 128.3 (d), 128.1 (d), 86.1 (d), 85.7 (d), 81.8 (d), 78.5 (d), 72.6 (t), 31.9 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.5 (t), 29.3 (t), 29.3 (t), 29.0 (t), 28.4 (t), 28.3 (t), 25.3 (t), 25.3 (t), 24.5 (t), 23.7 (t), 22.7 (t), 14.1 (q); IR (film): 3064, 3032, 2926, 2854, 1776, 1729, 1456, 1380, 1262, 1208, 1065, 1026, 966, 870, 837, 700, 648 cm$^{-1}$; HRMS (ESI): *m/z* calcd. for $C_{28}H_{44}O_7SNa$ $[M+Na]^+$: 547.2700; found 547.2699.

Diastereomer **16b**: $[\alpha]_D^{20}$ = -0.90° (*c* = 1.05, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 7.39-7.28 (m, 5H), 4.90-4.81 (m, 2H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.52 (td, *J* = 7.4, 5.6 Hz, 1H), 3.55-3.47 (m, 1H), 2.65-2.45 (m, 2H), 2.31-2.19 (m, 1H), 2.03-1.92 (m, 1H), 1.89-1.72 (m, 4H), 1.63-1.15 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 176.8 (s), 137.8 (s), 128.6 (d), 128.3 (d), 128.1 (d), 86.4 (d), 86.1 (d), 82.8 (d), 79.8 (d), 73.6 (t), 31.9 (t), 29.7 (t), 29.6 (t), 29.6 (t), 29.5 (t), 29.3 (t), 29.3 (t), 29.1 (t), 28.4 (t), 28.3 (t), 26.5 (t), 25.3 (t), 24.6 (t), 24.6 (t), 22.7 (t), 14.1 (q); IR (film): 3089, 3064, 3032, 2926, 2855, 1776, 1456, 1379, 1208, 1067, 968, 871, 700, 648 cm$^{-1}$; HRMS (ESI): *m/z* calcd. for $C_{28}H_{44}O_7SNa$ $[M+Na]^+$: 547.2700; found 547.2704.

**Compound 17**: A solution of $BCl_3$ in $CH_2Cl_2$ (1M, 2.54 mL, 2.54 mmol, 2.0 eq) was added to stirred solution of cyclic sulfate **16a** (666 mg, 1.27 mmol, 1.0 eq) in abs. $CH_2Cl_2$ (6.5 mL) at -78 °C. The mixture was stirred for 3 min at -78 °C and for 2 h at 0 °C before being cooled again to -78 °C. MeOH (2.5 mL) was added and stirring was continued for 40 min at -78 °C and for further 20 min at 0 °C. The solvent was removed under reduced pressure and residue suspended on EtOH (25 mL). The resulting slurry was added to precooled NaH (60%, 65 mg, 1.66 mmol, 1.3 eq) at 0 °C and allowed to warm slowly to rt overnight. The solvent was removed under reduced pressure and the residue was taken up in $Et_2O$ (25 mL). 20 % aqueous $H_2SO_4$ (100 mL) was added and the biphasic reaction mixture was stirred vigorously for 24 h. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (cyclohexane/EtOAc,

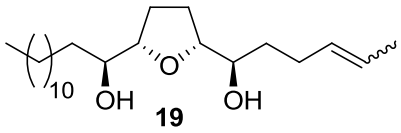


**17**

5:1→3:1) affording THP lactone **17** (300 mg, 0.85 mmol, 67%, *ee* = 92%) as a colorless solid.[10]

Mp: 65 °C; $[\alpha]_D^{20}$ = -25.7° (*c* = 1.32, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 4.52-4.48 (m, 1H), 4.05-4.00 (m, 1H), 3.81 (dt, *J* = 7.3, 6.3 Hz, 1H), 3.41 (dd, *J* = 11.9, 6.1 Hz, 1H), 2.64 (ddd, *J* = 17.6, 10.0, 6.8 Hz, 1H), 2.48 (ddd, *J* = 17.7, 10.0, 6.7 Hz, 1H), 2.36-2.25 (m, 1H), 2.24-2.14 (m, 1H), 2.05-1.85 (m, 4H), 1.81-1.70 (m, 1H), 1.54-1.43 (m, 1H), 1.43-1.34 (m, 2H), 1.34-1.10 (m, 19H), 0.88 (t, *J* = 6.9 H, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 177.6 (s), 83.7 (d), 81.0 (d), 80.8 (d), 74.4 (d), 33.7 (t), 31.9 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.4 (t), 28.3 (t), 27.9 (t), 27.7 (t), 25.6 (t), 24.5 (t), 22.7 (t), 14.1 (q); IR (film): 3400, 2918, 2849, 2362, 2337, 1750, 1467, 1432, 1192, 1076, 1008, 979, 946, 903, 810 $cm^{-1}$; MS (EI): *m/z* (%): 354 (< 1), 269 (6), 251 (1), 233 (2), 185 (5), 181 (5), 157 (27), 156 (26), 155 (15), 138 (100), 112 (16), 111 (21), 110 (22), 96 (19), 85 (15), 83 (28), 81 (22), 71 (33), 69 (38), 67 (28), 60 (50), 57 (52), 55 (61), 43 (52), 44 (45); HRMS (ESI): *m/z* calcd. for $C_{21}H_{38}O_4Na$ $[M+Na]^+$: 377.2662; found 377.2655; EA: calcd. for $C_{21}H_{38}O_4$, C: 71.14%, H: 10.80%; found, C: 71.13%, H: 10.70%.

**Compound 19**: A solution of DIBAL in hexane (1M, 0.78 mL, 0.78 mmol, 2.5 eq) was added dropwise to a stirred solution of THP-lactone **17** (110 mg, 0.31 mmol, 1.0 eq) in abs. THF (1.6 mL) at -78 °C. After 3h MeOH was added and stirring was continued for 1h at -78 °C and then allowed to warm to rt overnight. The solvent was removed under reduced pressure at rt and the residue suspended in THF. In a separate flask ethyl triphenylphosphonium bromide (459 mg, 1.24 mmol, 4.0 eq) was suspended in abs. THF (2.0 mL) and a solution of NaHMDS (2M, 0.64 mL, 1.24 mmol, 4.0 eq) was added dropwise at rt. The resulting ylide solution was added via syringe and the reaction mixture was refluxed for 48h. The reaction was quenched by addition of a 1N aqueous solution of HCl at 0 °C and diluted with ethyl acetate. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (cyclohexane/EtOAc, 8:1) affording alkene **19** (112 mg, 3.04 mmol, 98%, *E/Z* = 16/84) as a colorless solid.



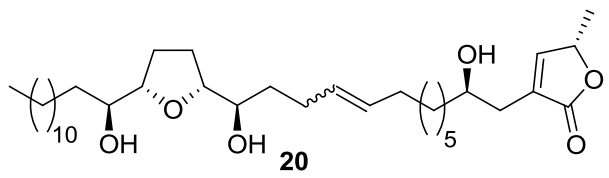
**19**

Mp: 35 °C; $[\alpha]_D^{20}$ = -1.1° (*c* = 0.94, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 5. 53-5.43 (m, 1H), 5.43-5.33 (m, 1H), 3.87-3.73 (m, 2H), 3.48-3.35 (m, 2H), 2.72 (br s, 2H), 2.30-2.11 (m, 2H), 2.00-1.87 (m, 2H), 1.81-1.71 (m, 2H), 1.63 (d, *J* = 6.6 Hz, 3H), 1.59-1.43 (m, 5H), 1.43-1.10 (m, 19H), 0.88 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 130.9 (d), 130.0 (d), 125.4 (d), 124.5 (d), 82.8 (d), 82.8 (d), 74.3 (d), 73.8 (d), 34.1 (t), 33.8 (t), 31.9 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.4 (t), 28.1 (2t), 25.7 (t), 23.1 (t), 22.7 (t), 14.1 (q), 12.8 (q); IR (film): 3326, 2917, 2850, 1468, 1311, 1070, 1018, 969, 721, 663, 565 $cm^{-1}$; MS (EI): *m/z* (%): 368 (4), 350 (1), 269 (9), 199 (6), 170 (21), 169 (4), 125 (21), 109 (13), 99 (55), 97

10 The enantiomeric excess was determined by chiral HPLC: OJ-RH, 150 × 4.6 mm, $H_2O$/acetonitrile 40:60, 0.60 mL/min

(32), 95 (19), 84 (45), 83 (32), 81 (45), 71 (100), 69 (53), 57 (55), 55 (79), 43 (57), 41 (47); HRMS (ESI): *m/z* calcd. for $C_{23}H_{44}O_3Na$ $[M+Na]^+$: 391.3183; found 391.3179; EA: calcd. for $C_{23}H_{44}O_3$, C: 74.95%, H: 12.03%; found, C: 74.53%, H: 11.96%.

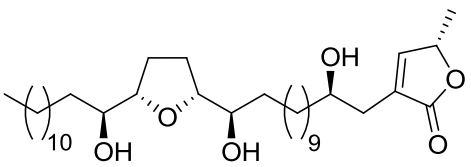
**Compound 20**: 1,4-Benzoquinone (1.7 mg, 0.016 mmol, 0.56 eq) and 2nd generation Hoveyda-Grubbs catalyst (1.8 mg, 0.0028 mmol, 10 mol%) were added to a stirred solution of alkene **19** (10.0 mg, 0.028 mmol, 1.0 eq) and lactone **23**[11] (15.0 mg, 0.06 mmol, 2.15 eq) in $CH_2Cl_2$ (2 mL). The reaction mixture was stirred for 17 h at rt. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography (cyclohexane/EtOAc, 1:1→0:1) affording alkene **20** (11.5 mg, 0.20 mmol, 71%) as a yellowish waxy solid.



**20**

Mp: 38 °C; $[\alpha]_D^{20}$ = +9.9° (*c* = 1.12, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 7.19 (d, *J* = 1.3 Hz, 1H), 5.60-5.30 (m, 2H), 5.06 (qd, *J* = 6.8, 1.3 Hz, 1H), 3.91-3.75 (m, 3H), 3.51-3.37 (m, 2H), 2.57-2.46 (m, 1H), 2.45-2.30 (m, 1H), 2.30-1.86 (m, 6H), 1.86-1.68 (m, 2H), 1.43 (d, *J* = 6.8 Hz, 3H, *overlap*), 1.61-1.39 (m, 7H, *overlap*), 1.39-1.13 (m, 27H), 0.88 (t, *J* = 6.9 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 174.7 (s), 151.9 (d), 131.2 (s), 131.1 (d), 129.7 (d), 82.7 (d), 82.6 (d), 78.0 (d), 74.4 (d), 73.7 (d), 69.9 (d), 37.4 (t), 34.2 (t), 33.9 (t), 33.3 (t), 32.5 (t), 31.9 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.4 (t), 29.3 (t), 29.3 (t), 29.3 (t), 29.2 (t), 28.9 (t), 28.1 (t), 28.1 (t), 28.1 (t), 25.7 (t), 25.5 (t), 22.7 (t), 19.1 (q), 14.1 (q); HRMS (ESI): *m/z* calcd. for $C_{35}H_{62}O_6Na$ $[M+Na]^+$: 601.4439; found 601.4439.

**16,19-*cis*-Murisolin (2)**: A solution of NaOAc (103 mg, 1.26 mmol, 90 eq) in water (4.8 mL) was added via syringe pump over 4 h to a stirred solution of alkene **20** (4.9 mg, 0.014 mmol, 1.0 eq) and *p*-toluenesulfonyl hydrazide (182 mg, 0.98 mmol, 70 eq) in DME (4.1 mL) at 100 °C. Then the reaction mixture was cooled to rt, diluted with water and extracted with ethyl acetate. The combined organic layers were successively washed three times with 0.1 M aqueous HCl and then with brine. The combined aqueous layers extracted again with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (cyclohexane/EtOAc, 2:1) affording 16,19-*cis*-Murisolin **(2)** (4.7 mg, 0.008 mmol, 60%) as a colorless waxy solid.

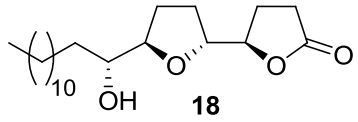


**2**

11 Avedissian, H.; Sinha, S. C.; Yazbak, A.; Sinha, A.; Neogi, P.; Sinha, S. C.; Keinan, E. *J. Org. Chem.* **2000**, *65*, 6035.

Mp: 66 °C [Lit.:[12,13] 75.5-77.5 °C]; $[\alpha]_D^{20}$ = +6.5° (*c* = 0.21, $CHCl_3$); $^1$H NMR (600 MHz, $CDCl_3$): 7.16 (q, *J* = 1.3 Hz, 1H), 5.06 (qq, *J* = 6.8, 1.6 Hz, 1H), 3.85-3.76 (m, 3H), 3.43-3.37 (m, 2H), 2.51 (ddt, *J* = 15.1, 3.2, 1.5 Hz, 1H), 2.38 (ddt, *J* = 15.2, 8.4, 1.2 Hz, 1H), 2.35 (br s, 2H), 2.26 (br s, 1H), 1.95-1.88 (m, 2H), 1.77-1.70 (m, 2H), 1.50-1.20 (m, 42H, *overlap*), 1.41 (d, *J* = 6.8 Hz, 3H, *overlap*), 0.86 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): 174.8 (s), 151.9 (d), 131.4 (s), 82.8 (d), 78.1 (d), 74.5 (d), 70.1 (d), 37.6 (t), 34.3 (t), 34.3 (t), 33.5 (t), 32.1 (t), 29.9 (t), 29.8 (t), 29.8 (t), 29.8 (t), 29.8 (t), 29.8 (t), 29.8 (t), 29.7 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.5 (t), 28.3 (t), 25.9 (t), 25.8 (t), 25.7 (t), 22.9 (t), 19.3 (q), 14.3 (q); IR (film): 3390, 2918, 2850, 1732, 1678, 1598, 1525, 1385, 1339, 1293, 1158, 1090, 968, 859, 814 cm$^{-1}$; HRMS (ESI): *m/z* calcd. for $C_{35}H_{64}O_6Na$ $[M+Na]^+$: 603.4595; found 603.4603.

**Compound 18**: A solution of $BCl_3$ in $CH_2Cl_2$ (1M, 0.53 mL, 0.53 mmol, 2.0 eq) was added to stirred solution of cyclic sulfate **16b** (153 mg, 0.29 mmol, 1.0 eq) in abs. $CH_2Cl_2$ (1.5 mL) at -78 °C. The mixture was stirred for 3 min at -78 °C and for 2 h at 0 °C before being cooled again to -78 °C. MeOH (0.6 mL) was added and stirring was continued for 40 min at -78 °C and for further 20 min at 0 °C. The solvent was removed under reduced pressure and residue suspended on EtOH (5.8 mL). The resulting slurry was added to precooled NaH (60%, 15 mg, 0.38 mmol, 1.3 eq) at 0 °C and allowed to warm slowly to rt overnight. The solvent was removed under reduced pressure and the residue was taken up in $Et_2O$ (5.8 mL). 20 % aqueous $H_2SO_4$ (2.9 mL) was added and the biphasic reaction mixture was stirred vigorously for 24 h. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (cyclohexane/EtOAc, 5:1→3:1) affording THP-lactone **18** (85 mg, 0.24 mmol, 83%, *ee* = 92%) as a colorless solid.[10]



**18**

Mp: 96 °C; $[\alpha]_D^{20}$ = -7.5° (*c* = 0.99, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 4.48 (ddd, *J* = 8.0, 5.4, 2.9 Hz , 1H), 4.09-4.03 (m, 1H), 3.83 (dt, *J* = 8.4, 5.8 Hz, 1H), 3.44-3.34 (m, 1H), 2.72-2.60 (m, 1H), 2.52-2.41 (m, 1H), 2.37-2.10 (m, 3H), 2.10-1.87 (m, 3H), 1.80-1.59 (m, 1H), 1.55-1.35 (m, 3H), 1.35-1.16 (m, 19H), 0.88 (t, *J* = 6.7 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 177.4 (s) , 83.5 (d), 81.2 (d), 80.8 (d), 73.7 (d), 33.8 (t), 31.9 (t), 29.7 (t), 29.7 (t), 29.6 (t), 29.6 (t), 29.4 (t), 28.3 (t), 28.2 (t), 28.1 (t), 25.6 (t), 24.7 (t), 22.7 (t), 14.1 (q); IR (film): 3437, 2918, 2852, 1762, 1472, 1299, 1235, 1198, 1132, 1072, 1022, 945, 719, 685 cm$^{-1}$; MS (EI): *m/z* (%): 354 (<1), 269 (22), 251 (1), 233 (2), 185 (3), 181 (7), 168 (5), 157 (27), 156 (28), 155 (78), 138 (100), 137 (27), 111 (53), 85 (28), 83 (41), 81 (39), 71 (51), 69 (48), 67 (33), 60 (32), 57 (79), 55 (85), 43 (79), 41 (70); HRMS (ESI): *m/z* calcd. for $C_{21}H_{38}O_4Na$ $[M+Na]^+$: 377.2662; found 377.2657; EA: calcd. for $C_{21}H_{38}O_4$, C: 71.14%, H: 10.80%; found, C: 70.91%, H: 10.86%.

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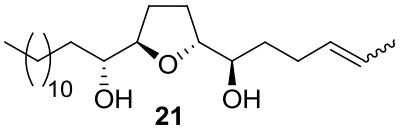
12 Maezaki, N.; Kojima, N.; Sakamoto, A.; Tominaga, H.; Iwata, C.; Tanaka, T.; Monden, M.; Damdinsuren, B.; Nakamori, S. *Chem. Eur. J.* **2003**, 389.

13 Hattori, Y.; Kimura, Y.; Moroda, A.; Konno, H.; Abe, M.; Miyoshi, H.; Goto, T.; Makabe, H. *Chem. Asian J.* **2006**, *1*, 894-904.

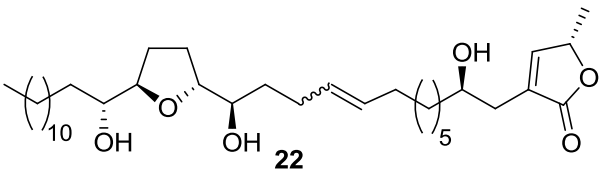
**Compound 21**: A solution of DIBAL in hexane (1M, 0.71 mL, 0.71 mmol, 2.5 eq) was added dropwise to a stirred solution of THP-lactone **18** (100 mg, 0.28 mmol, 1.0 eq) in abs. THF (1.5 mL) at -78 °C. After 3h MeOH was added and stirring was continued for 1h at -78 °C and then allowed to warm to rt overnight. The solvent was removed under reduced pressure at rt and the residue suspended in THF. In a separate flask ethyl triphenylphosphonium bromide (417 mg, 1.13 mmol, 4.0 eq) was suspended in abs. THF (1.9 mL) and a solution of NaHMDS (2M, 0.57 mL, 1.13 mmol, 4.0 eq) was added dropwise at rt. The resulting ylide-solution was added via syringe and the reaction mixture was refluxed for 48h. The reaction was quenched by addition of a 1N aqueous solution of HCl at 0 °C and diluted with ethyl acetate. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (cyclohexane/EtOAc, 8:1) affording alkene **21** (44 mg, 0.12 mmol, 43%, *E/Z* = 15/85) as a colorless solid.



**21**

Mp: 40 °C; $[\alpha]_D^{20}$ = +14.9° (*c* = 0.94, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): 5.53-5.43 (m, 1H), 5.43-5.33 (m, 1H), 3.87-3.72 (m, 2H), 3.49-3.32 (m, 2H), 2.32 (br s, 2H), 2.27-2.14 (m, 2H), 2.05-1.90 (m, 2H), 1.81-1.64 (m, 2H), 1.63 (d, *J* = 6.7 Hz, 3H), 1.55-1.35 (m, 5H), 1.35-1.11 (m, 19H), 0.88 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 130.8 (d), 130.0 (d), 125.4 (d), 124.6 (d), 82.7 (d), 82.6 (d), 74.1 (d), 73.5 (d), 33.5 (t), 33.2 (t), 31.9 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.6 (t), 29.6 (t), 29.4 (t), 28.8 (t), 25.6 (t), 23.0 (t), 22.7 (t), 14.1 (q), 12.8 (q); MS (EI): *m/z* (%): 368 (9), 350 (1), 299 (1), 269 (17), 251 (2), 199 (1), 169 (21), 151 (9), 133 (17), 125 (40), 109 (23), 99 (64), 97 (36), 95 (32), 84 (26), 83 (61), 81 (62), 71 (100), 70 (32), 69 (74), 67 (36), 57 (77), 55 (100), 43 (79), 41 (67); HRMS (ESI): *m/z* calcd. for $C_{23}H_{44}O_3Na$ $[M+Na]^+$: 391.3183; found 391.3182.

**Compound 22**: 1,4-Benzoquinone (0.8 mg, 0.007 mmol, 0.26 eq) and 2$^{nd}$ generation Hoveyda-Grubbs catalyst (1.0 mg, 0.0017 mmol, 6 mol%) were added to a stirred solution of alkene **19** (9.9 mg, 0.028 mmol, 1.0 eq) and lactone **23**[7] (16.1 mg, 0.064 mmol, 2.3 eq) in $CH_2Cl_2$ (2 mL) at 0 °C. The reaction mixture was stirred for 6 h at 0 °C. Then a second portion of 1,4-benzoquinone (0.5 mg, 0.005 mmol, 0.18 eq) and 2$^{nd}$ generation Hoveyda-Grubbs catalyst (0.7 mg, 0.0011 mmol, 4 mol%) were added and the reaction was allowed to warm to rt for 17 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (cyclohexane/EtOAc, 4:1→0:1) affording alkene **22** (5.9 mg, 0.010 mmol, 37%) as a colorless waxy solid.

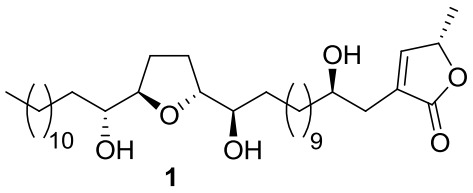


**22**

Mp: 51 °C; $^1$H NMR (400 MHz, $CDCl_3$): 7.20 (d, *J* = 1.3 Hz, 1H), 5.51-5.28 (m, 2H), 5.06 (qd, *J* = 6.8, 1.4 Hz, 1H), 3.90-3.74 (m, 3H), 3.49-3.35 (m, 2H), 2.59-2.30 (m, 6H), 2.28-1.90 (m, 2H), 1.78-1.58 (m, 2H), 1.43 (d, *J* = 6.8 Hz, 3H, *overlap*), 1.58-1.14 (m, 34H, *overlap*), 0.88 (t, *J* = 6.7 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): 174.7 (s), 151.9 (d), 131.1 (s), 131.1

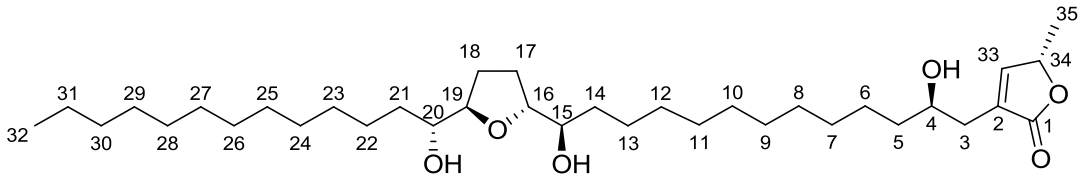
(d), 129.7 (d), 82.7 (d), 82.6 (d), 78.0 (d), 74.1 (d), 73.4 (d), 69.9 (d), 37.3 (t), 33.7 (t), 33.3 (t), 33.3 (t), 32.5 (t), 31.9 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.3 (t), 29.3 (t), 29.0 (t), 28.8 (t), 28.6 (t), 28.1 (t), 27.0 (t), 26.9 (t), 25.6 (t), 25.5 (t), 22.7 (t), 19.1 (q), 14.1 (q); HRMS (ESI): *m/z* calcd. for $C_{35}H_{62}O_6Na$ $[M+Na]^+$: 601.4439; found 601.4452.

**Murisolin (1)**: A solution of NaOAc (428 mg, 5.22 mmol, 90 eq) in water (20 mL) was added via syringe pump over 4 h to a stirred solution of alkene **22** (34 mg, 0.058 mmol, 1.0 eq) and *p*-toluenesulfonyl hydrazide (767mg, 4.12 mmol, 70 eq) in DME (17 mL) at 100 °C. Then the reaction mixture was cooled to rt, diluted with water and extracted with ethyl acetate. The combined organic layers were successively washed three times with 0.1 M aqueous HCl and then with brine. The combined aqueous layers extracted again with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (cyclohexane/EtOAc, 2:1) affording Murisolin **(1)** (10 mg, 0.016 mmol, 30%) as a colorless waxy solid.



**1**

Mp: 63 °C [Lit.:[12,13] 72.0-73.5 °C]; $[\alpha]_D^{20}$ = +10.4° (*c* = 0.15, $CHCl_3$) [Lit: $[\alpha]_D^{20}$ = +21.5° (*c* = 0.36, $CHCl_3$);[12] $[\alpha]_D^{20}$ = +20.6° (*c* = 0.42, $CHCl_3$);[13] $^1$H NMR (600 MHz, $CDCl_3$): 7.18 (q, *J* = 1.4 Hz, 1H), 5.06 (qq, *J* = 6.8, 1.6 Hz, 1H), 3.87-3.77 (m, 3H), 3.45-3.38 (m, 2H), 2.53 (ddt, *J* = 15.2, 3.1, 1.5 Hz, 1H), 2.40 (ddt, *J* = 15.2, 8.3, 1.3 Hz, 1H), 2.34 (br s, 3H), 2.02-1.95 (m, 2H), 1.73-1.64 (m, 2H), 1.54-1.21 (m, 42H, *overlap*), 1.43 (d, *J* = 6.8 Hz, 3H, *overlap*), 0.88 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): 174.5 (s), 151.7 (d), 131.2 (s), 82.6 (d), 78.0 (d), 74.0 (d), 70.0 (d), 37.4 (t), 33.5 (t), 33.4 (t), 31.9 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.7 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.5 (t), 29.5 (t), 29.5 (t), 29.5 (t), 29.3 (t), 28.7 (t), 25.6 (t), 25.6 (t), 25.5 (t), 22.7 (t), 19.1 (q), 14.1 (q); IR (film): 3472, 3291, 2916, 2850, 1750, 1469, 1341, 1165, 1073, 1030, 961, 932, 849, 814, 671 $cm^{-1}$; HRMS (ESI): *m/z* calcd. for $C_{35}H_{64}O_6Na$ $[M+Na]^+$: 603.4595; found 603.4588.




**1**

**Table S-1**. Comparison of the recorded $^{13}C$ NMR data ($CDCl_3$) of murisolin (**1**) with literature data.[14]

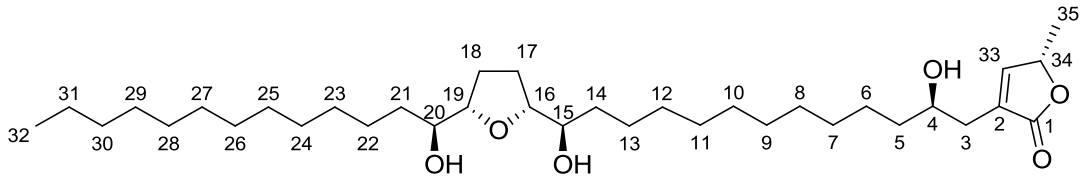
| **Experimental (150 MHz) δ [ppm]** | **Literature[14] (151 MHz) δ [ppm]** | **Δδ** | **Position** |
|---|---|---|---|
| 174.5 | 174.2 | +0.3 | 1 |
| 151.7 | 151.9 | -0.2 | 33 |
| 131.2 | 131.3 | -0.1 | 2 |
| 82.6 (2C)[15] | 82.7 | -0.1 | 16, 19 |
| | 82.7 | -0.1 | |
| 78.0 | 78.1 | -0.1 | 34 |
| 74.0 | 74.1 | -0.1 | 15, 20 |
| 70.0 | 70.0 | 0 | 4 |
| 37.4 | 37.5 | -0.1 | 5 |
| 33.5 (2C) | 33.6 (2C) | -0.1 | 3, 14, 21 |
| 33.4 | 33.4 | 0 | |
| 31.9 | 32.0 | -0.1 | 30 |
| 29.7 | 29.8 | -0.1 | 6-13<br>22-29 |
| 29.7 | 29.8 | -0.1 | |
| 29.7 | 29.8[15] | -0.1 | |
| 29.7 | | -0.1 | |
| 29.6 | 29.7 | -0.1 | |
| 29.6 | 29.7 | -0.1 | |
| 29.6 | 29.7 | -0.1 | |
| 29.5 | 29.7 | -0.2 | |
| 29.5 | 29.6 | -0.1 | |
| 29.5 | 29.6 | -0.1 | |
| 29.5 | 29.5 | 0 | |
| 29.3 | 29.4 | -0.1 | |
| 28.7 (2C) | 28.8 (2C) | -0.1 | 17, 18 |
| 25.6 | 25.7 | -0.1 | 6-13<br>22-29 |
| 25.6 | 25.6 (2C)[15] | 0 | |
| 25.5 | | -0.1 | |
| 22.7 | 22.8 | -0.1 | 31 |
| 19.1 | 19.2 | -0.1 | 35 |
| 14.1 | 14.2 | -0.1 | 32 |

14. Curran, D. P.; Zhang, Q.; Richard, C.; Lu, H.; Gudipati, V.; Wilcox, C. S. *J. Am. Chem. Soc.* **2006**, *128*, 9561.
15. NMR spectra were recorded using the same frequencies as in literature. Nevertheless, some signals, especially of the aliphatic chain-carbons, that are reported as single peaks turned out to be in fact two very closely adjacent signals. For an excellent article on NMR studies of murisolins see also: Curran, D. P.; Zhang, Q.; Lu, H.; Gudipati, V. *J. Am. Chem. Soc.* **2006**, *128*, 9943.

**Table S-2**. Comparison of the recorded $^{1}$H NMR data ($CDCl_3$) of murisolin (**1**) with literature data.[14]

| **Experimental (600 MHz) δ [ppm] mult. (*J* in Hz)** | **Literature[14] (600 MHz) δ [ppm] mult. (*J* in Hz)** | **Δδ** | **Position** |
|---|---|---|---|
| 7.18 q (1.6) | 7.19 s | -0.01 | 33 |
| 5.06 qq (6.8, 1.6) | 5.07 q (6.6) | -0.01 | 34 |
| 3.87-3.77 m | 3.86-3.79 m | 0 | 4, 16, 19 |
| 3.45-3.38 m | 3.43-3.40 m | 0 | 15, 20 |
| 2.53 ddt (15.2, 3.1, 1.5) | 2.53 d (15.3) | 0 | 3a |
| 2.40 ddt (15.2, 8.3, 1.3) | 2.41 dd (15.1, 8.9) | -0.01 | 3b |
| 2.34 br s[16] | -- | -- | OH |
| 2.02-1.95 m | 2.02-1.96 m | 0 | 17a, 18a |
| 1.73-1.64 m | 1.72-1.64 m | 0 | 17b, 18b |
| 1.54-1.21 m | 1.54-1.45 m<br>1.43-1.39 m | -0.01 | 5-14<br>21-31 |
| 1.43 d (6.8) | 1.44 d (6.8) | -0.01 | 35 |
| 0.88 t (7.1) | 0.89 t (6.8) | -0.01 | 32 |

16 The appearance and shift of the OH-protons is concentration dependant.



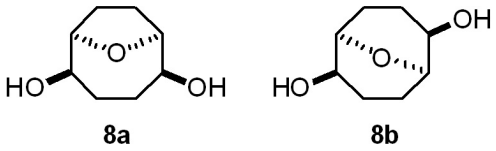

**2**

**Table S-3**. Comparison of the recorded $^{13}C$ NMR data ($CDCl_3$) of 16,19-*cis*-murisolin (**2**) with literature data.[14]

| **Experimental (150 MHz)** | **Literature[14] (151 MHz)** | **Δδ** | **Position** |
|---|---|---|---|
| 174.8 | 174.7 | +0.1 | 1 |
| 151.9 | 151.9 | 0 | 33 |
| 131.4 | 131.3 | +0.1 | 2 |
| 82.8 (2C) | 82.8 (2C) | 0 | 16, 19 |
| 78.1 | 78.1 | 0 | 34 |
| 74.5 (2C) | 74.5 (2C) | 0 | 15,20 |
| 70.1 | 70.1 | 0 | 4 |
| 37.6 | 37.5 | +0.1 | 5 |
| 34.3 | 34.2 | +0.1 | 3, 14, 21 |
| 34.3 | 34.2 | +0.1 | |
| 33.5 | 33.4 | +0.1 | |
| 32.1 | 32.0 | +0.1 | 30 |
| 29.9 | 29.8[15] | +0.1 | 6-14<br>22-29 |
| 29.8 | | 0 | |
| 29.8 | 29.8 | 0 | |
| 29.8 | 29.7 | +0.1 | |
| 29.8 | 29.7[15] | +0.1 | |
| 29.8 | | +0.1 | |
| 29.8 | 29.7[15] | +0.1 | |
| 29.7 | | 0 | |
| 29.6 | 29.7 | -0.1 | |
| 29.6 | 29.6[15] | 0 | |
| 29.6 | | 0 | |
| 29.6 | 29.6 | 0 | |
| 29.6 | 29.5 | +0.1 | |
| 29.5 | 29.4 | +0.1 | |
| 28.3 (2C) | 28.2 (2C) | +0.1 | 17, 18 |
| 25.9 | 25.8 | +0.1 | 6-14<br>22-29 |
| 25.8 | 25.7 | +0.1 | |
| 25.7 | 25.6 | +0.1 | |
| 22.9 | 22.8 | +0.1 | 31 |
| 19.3 | 19.2 | +0.1 | 35 |
| 14.3 | 14.2 | +0.1 | 32 |

**Table S-4**. Comparison of the recorded $^{1}$H NMR data ($CDCl_3$) of 16,19-*cis*-murisolin (**2**) with literature data.[14]

| **Experimental (600 MHz) δ [ppm] mult. (*J* in Hz)** | **Literature[14] (600 MHz) δ [ppm] mult. (*J* in Hz)** | **Δδ** | **Position** |
|---|---|---|---|
| 7.16 q (1.3) | 7.19 q (1.4) | -0.03 | 33 |
| 5.06 qq (6.8, 1.6) | 5.07 qq (6.6, 1.5) | -0.01 | 34 |
| 3.85-3.76 m | 3.87-3.80 m | -0.03 | 4, 16,1 9 |
| 3.43-3.37 m | 3.44-3.41 m | -0.02 | 15, 20 |
| 2.51 ddt (15.1, 3.2, 1.5) | 2.54 ddt (15.1, 3.4, 1.5) | -0.03 | 3a |
| 2.38 ddt (15.2, 8.4, 1.2) | 2.41 ddt (15.1, 8.9, 1.2) | -0.03 | 3b |
| 2.35 br s[16] | -- | -- | OH |
| 2.26 br s[16] | 1.66-1.69 m | +0.58 | OH |
| 1.95-1.88 m | 1.99-1.91 m | -0.03 | 17a, 18a |
| 1.77-1.70 m | 1.79-1.72 m | -0.02 | 17b, 18b |
| 1.50-1.20 m | 1.53-1.45 m<br>1.42-1.32 m<br>1.32-1.24 m | -0.03 | 5-14<br>21-31 |
| 1.41 d (6.8) | 1.44 d (6.8) | -0.03 | 35 |
| 0.86 t (7.1) | 0.89 t (6.9) | -0.03 | 32 |

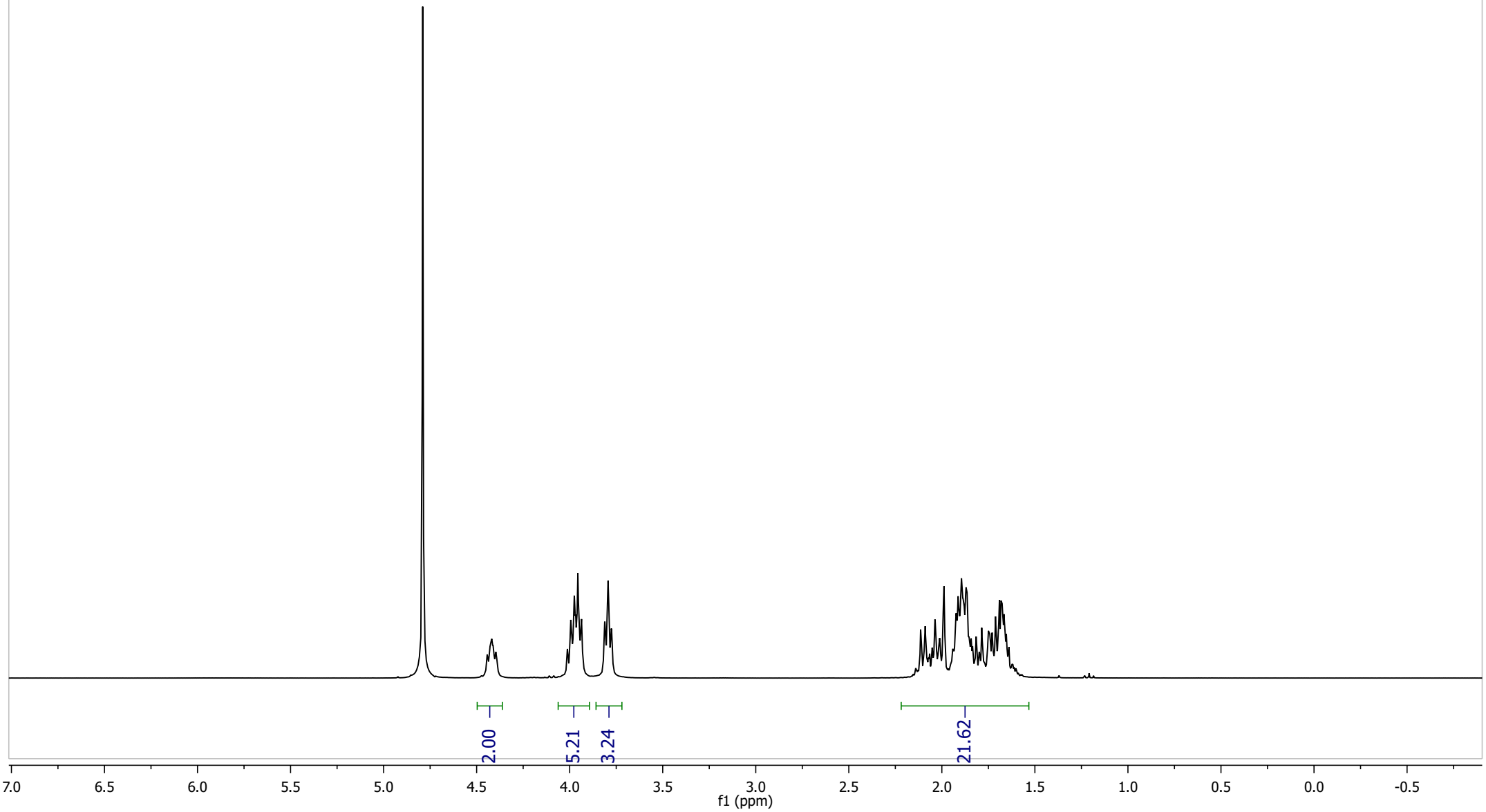


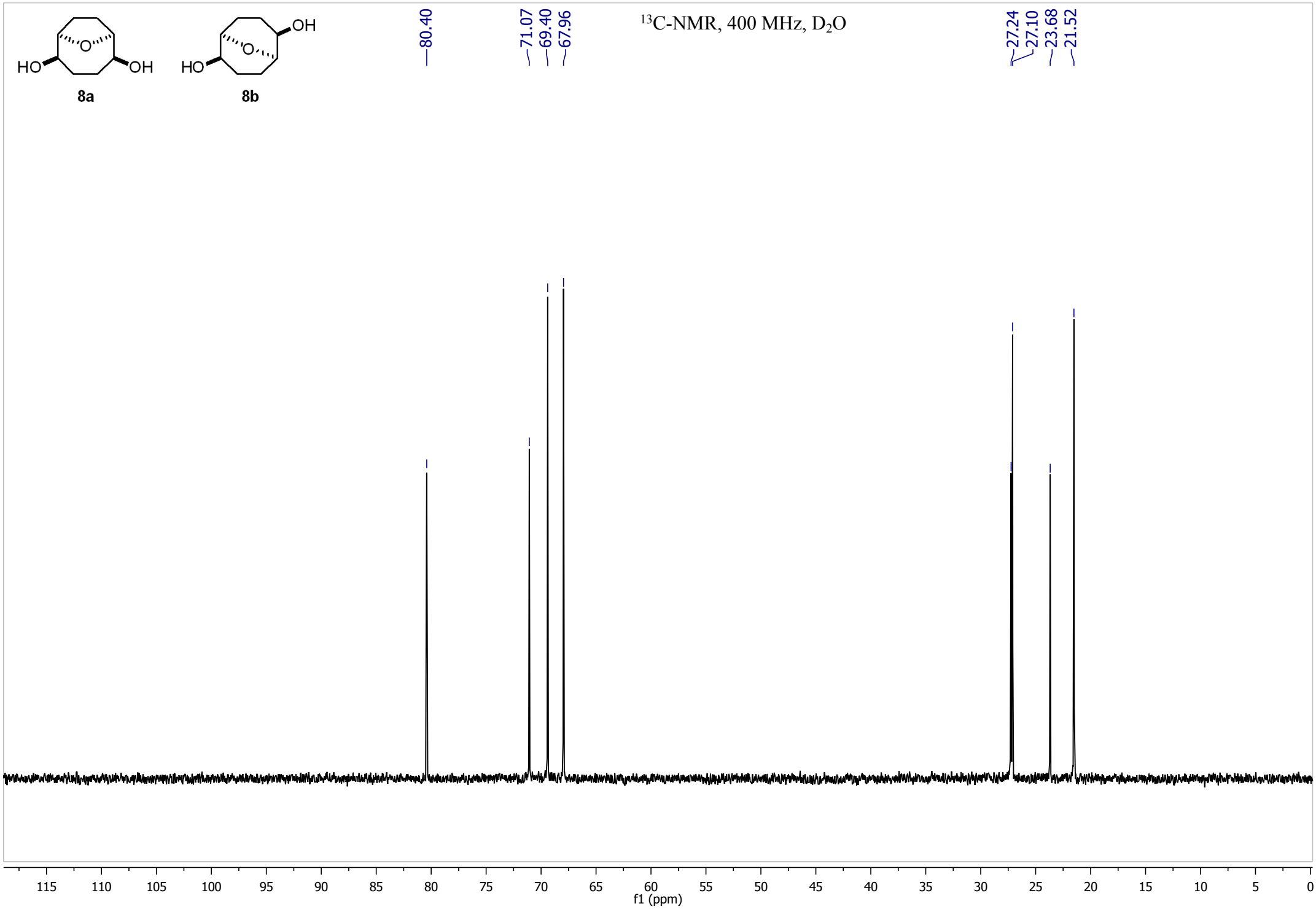

**8a**

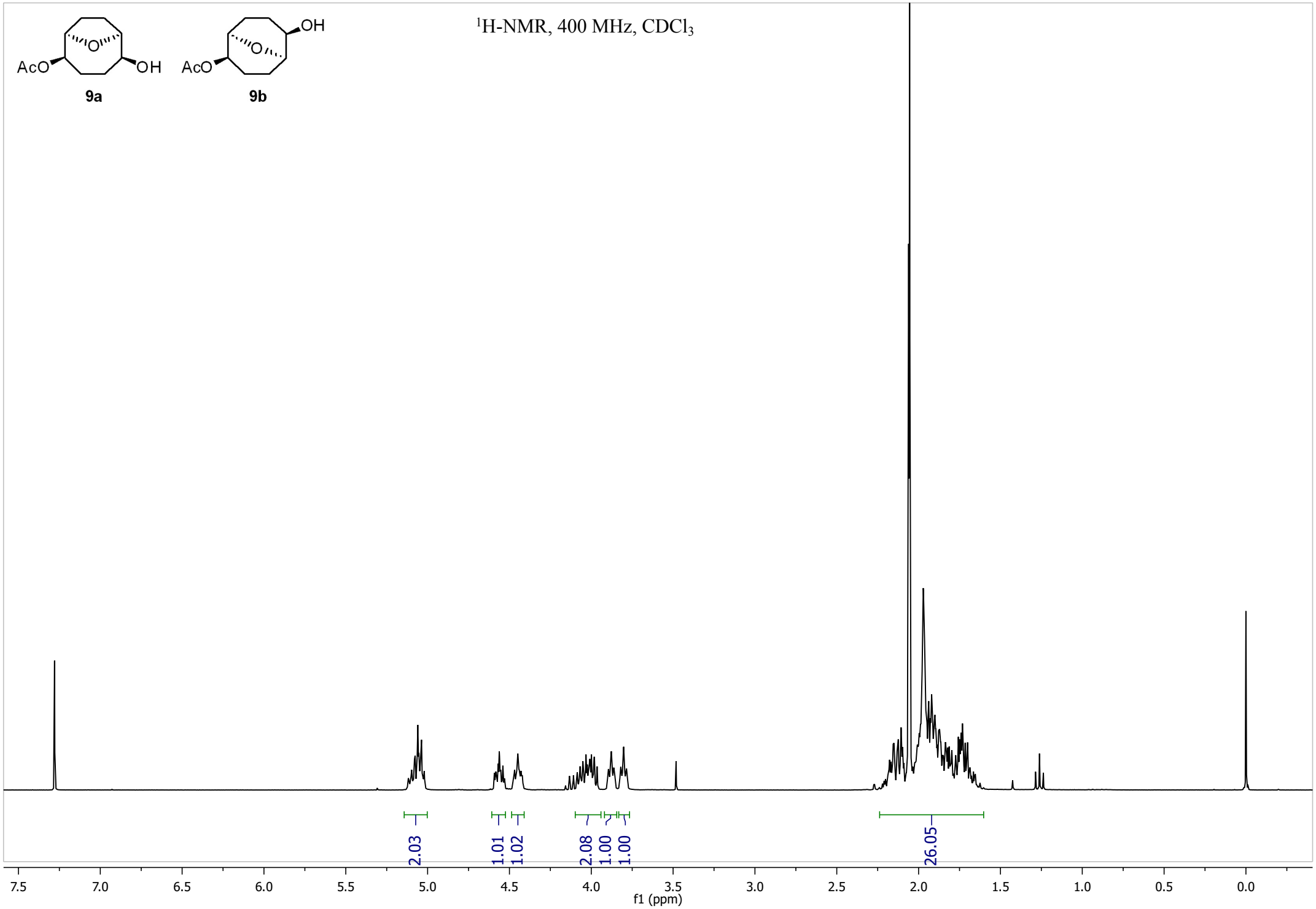


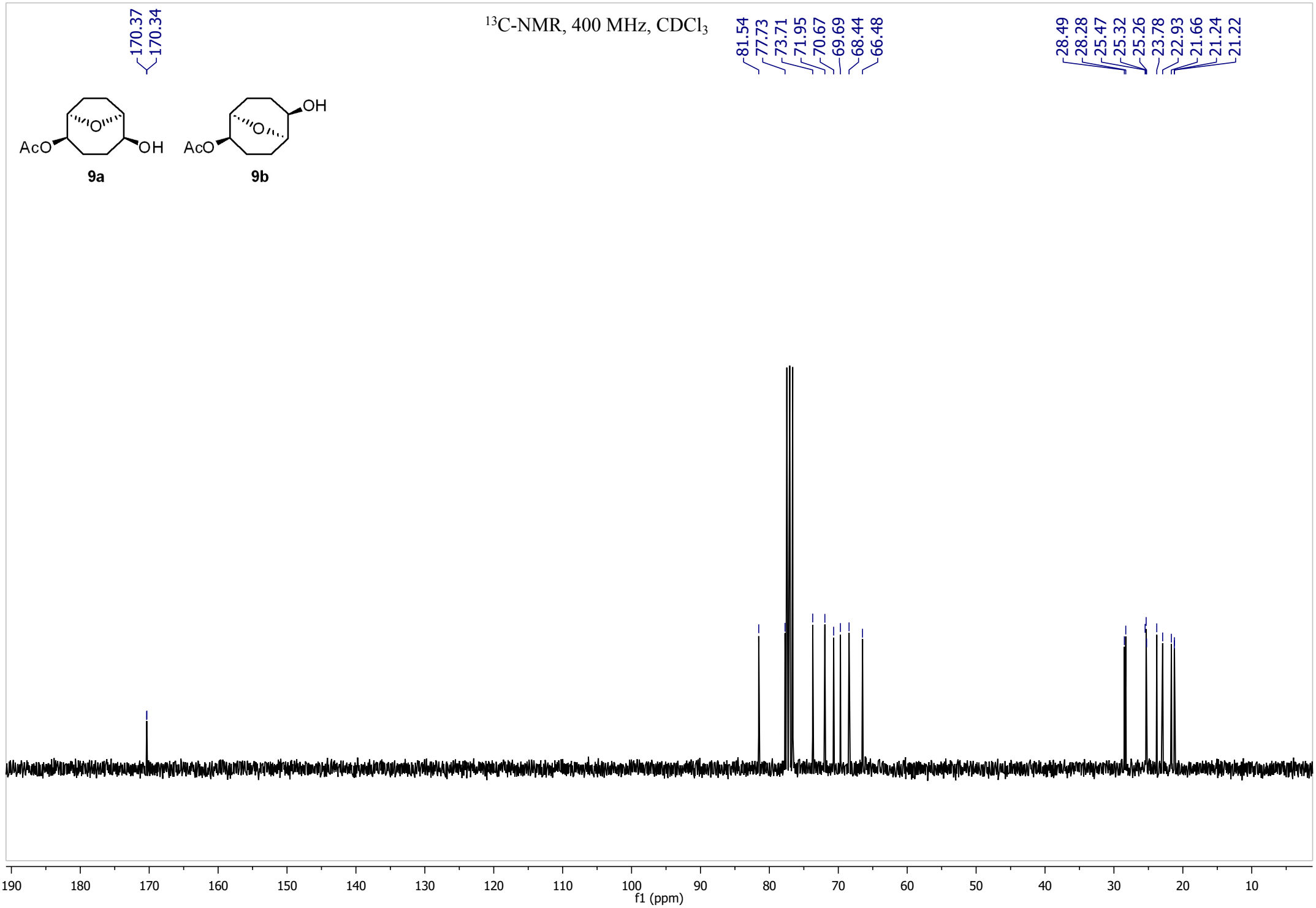

**8b**

$^{1}$H-NMR, 400 MHz, $D_2O$




HO
OH
8a
HO
OH
8b
80.40
71.07
69.40
67.96
27.24
27.10
23.68
21.52
13C-NMR, 400 MHz, D2O
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


AcO
OH
9a
AcO
OH
9b
$^1$H-NMR, 400 MHz, $CDCl_3$
2.03
1.01
1.02
2.08
1.00
1.00
26.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

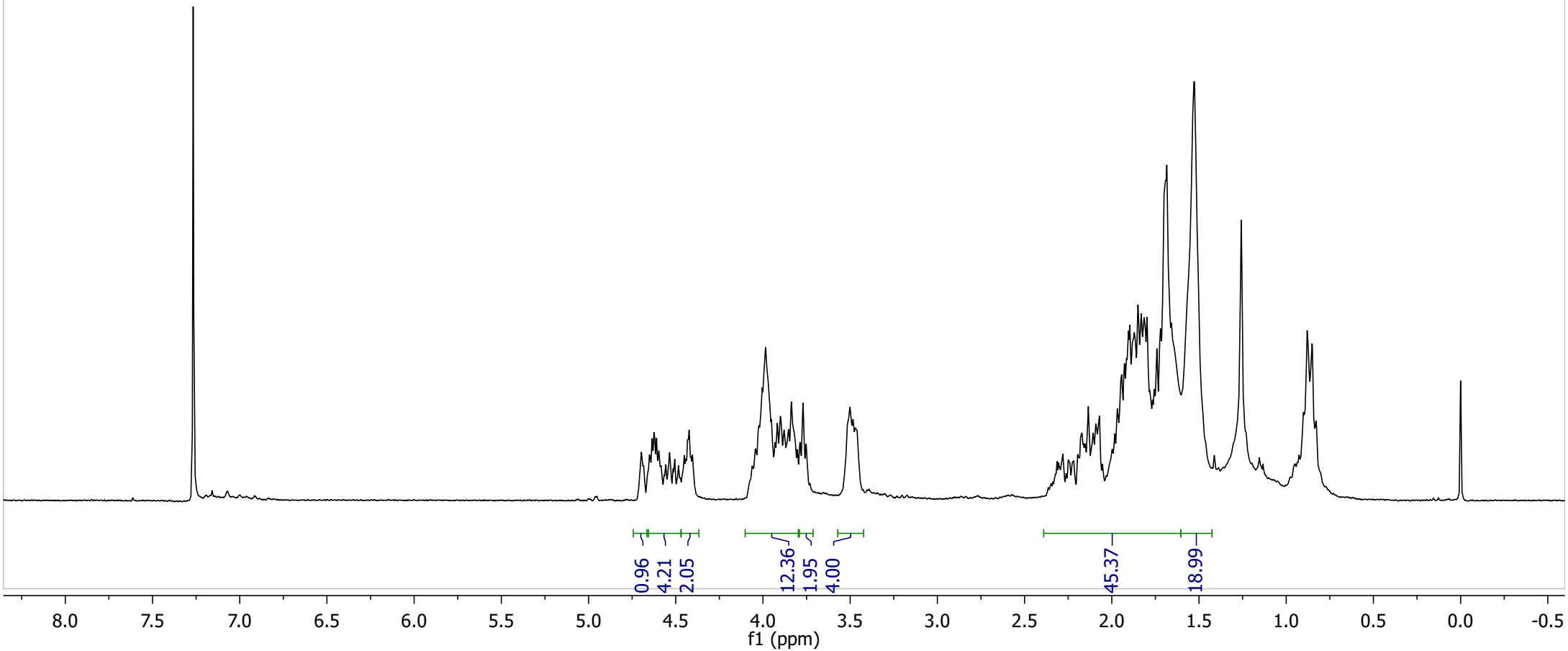

$^{13}$C-NMR, 400 MHz, $CDCl_3$
170.37
170.34
81.54
77.73
73.71
71.95
70.67
69.69
68.44
66.48
28.49
28.28
25.47
25.32
25.26
23.78
22.93
21.66
21.24
21.22
AcO
OH
9a
AcO
OH
9b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

$^{1}$H-NMR, 400 MHz, $CDCl_3$


**25a**

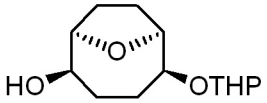



**25b**

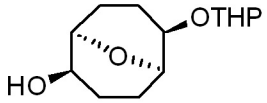


98.75 98.22 97.93 97.72 81.39 81.33 79.96 78.97 76.87 76.32 73.60 73.54 72.35 72.26 69.99 69.90 69.01 68.91 67.51 63.02 62.98 62.79 31.26 31.23 28.99 28.93 28.89 28.50 27.57 27.01 26.10 25.54 25.52 25.50 25.30 25.03 24.11 24.08 22.95 22.68 22.16 22.05 20.00 19.97 19.90

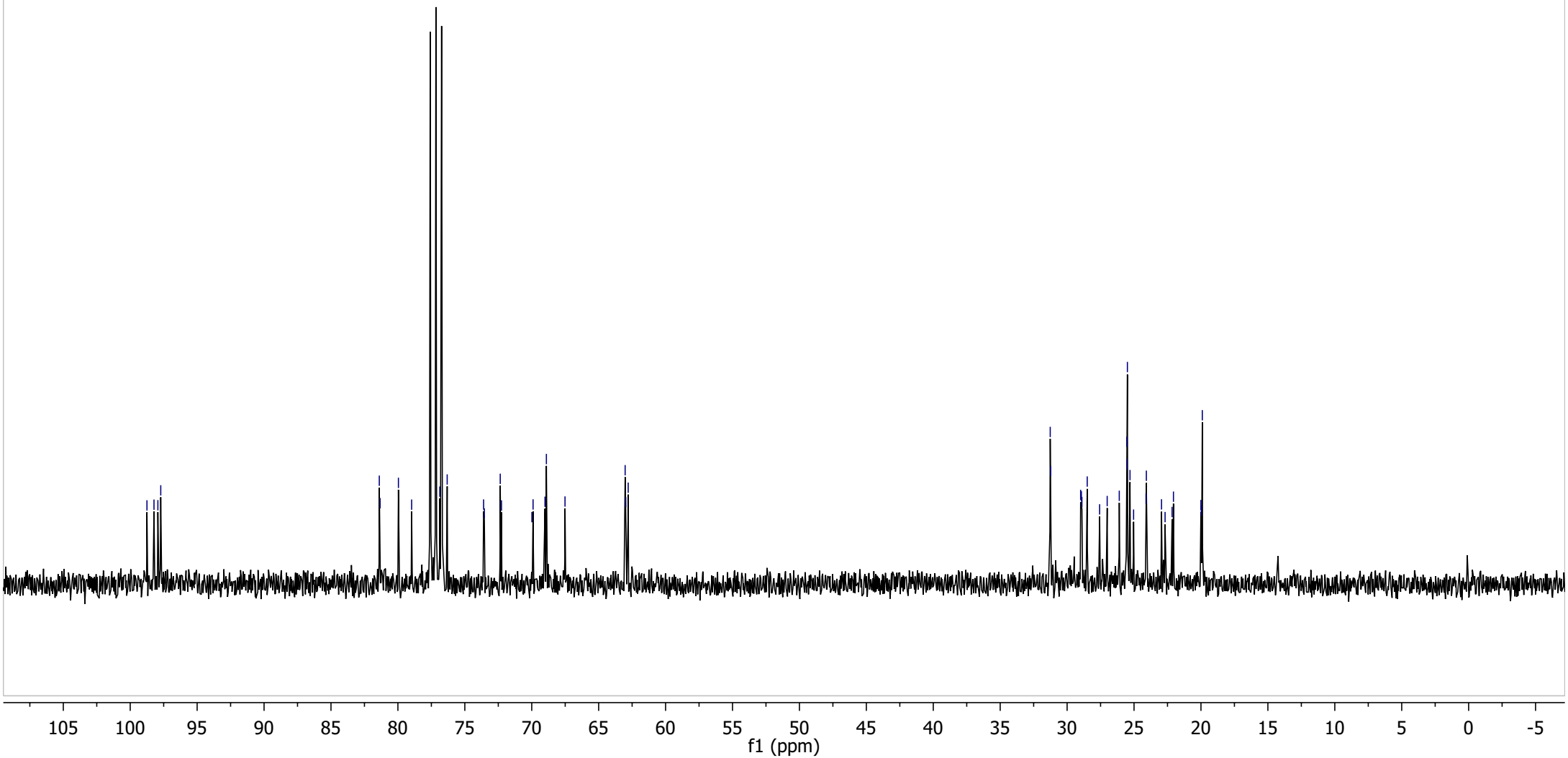
$^{13}$C-NMR, 400 MHz, $CDCl_3$



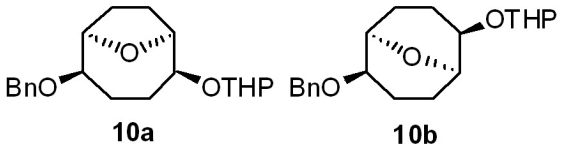

**25a**



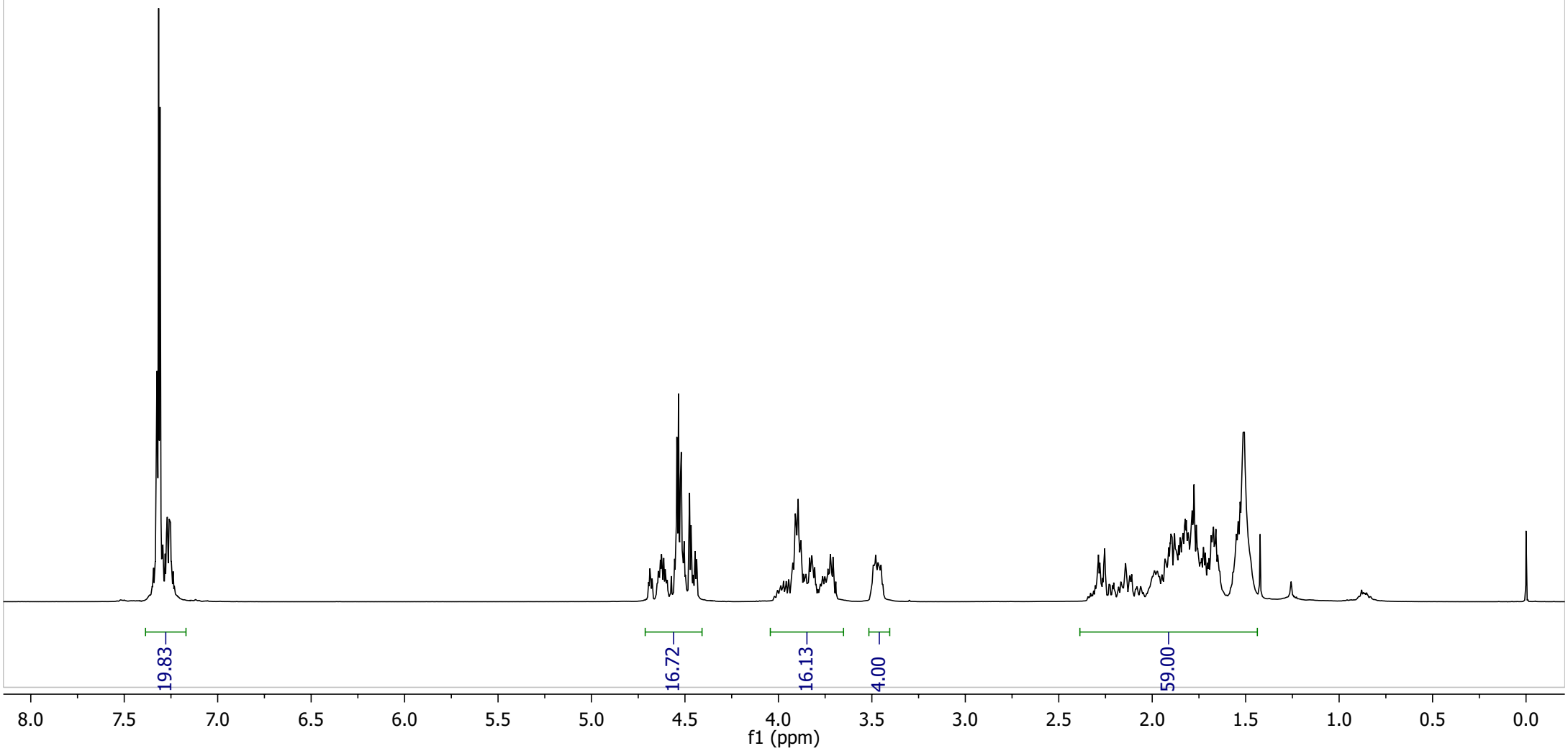

**25b**

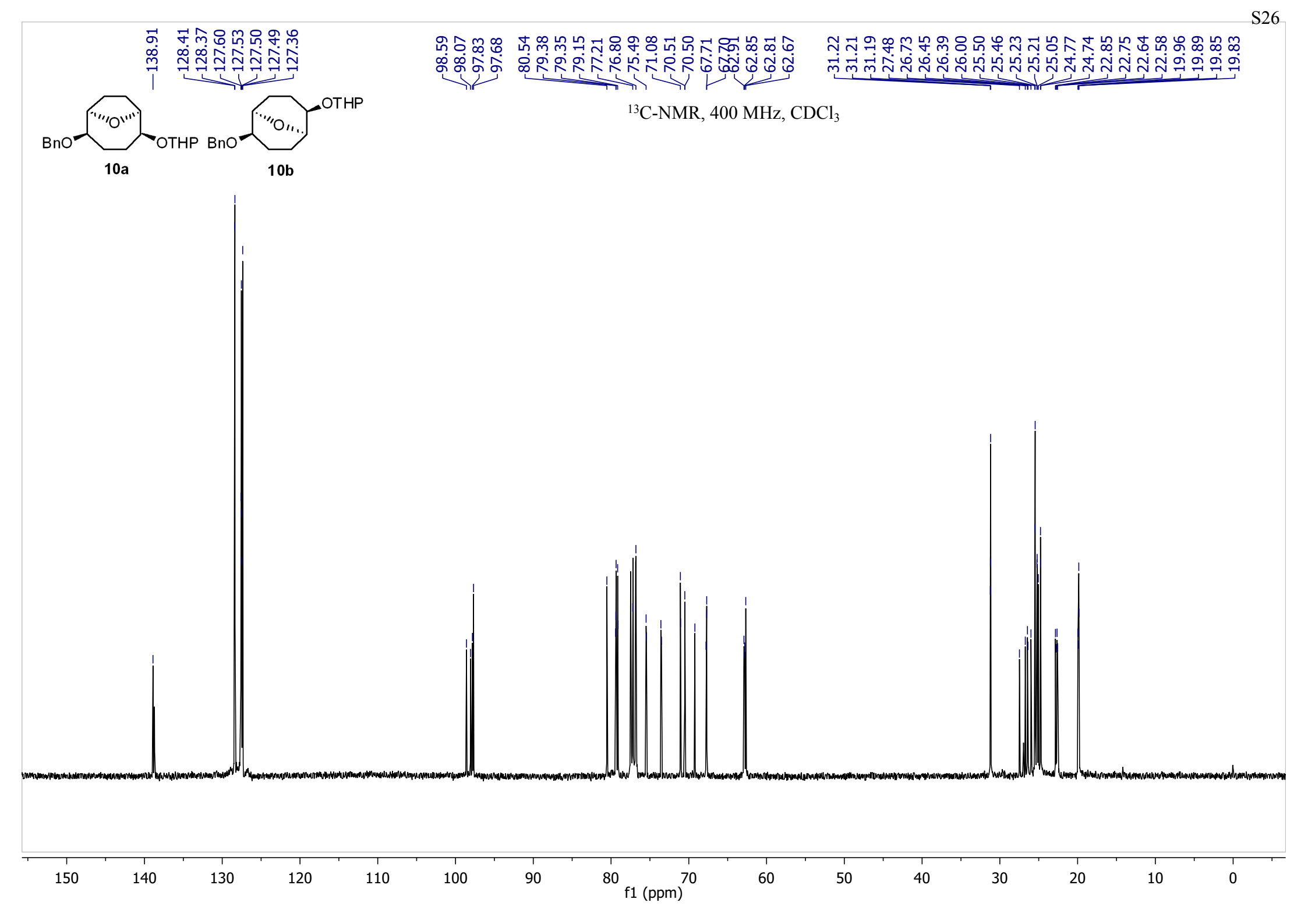


$^{1}$H-NMR, 400 MHz, $CDCl_3$

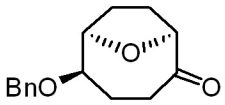



**10a** **10b**

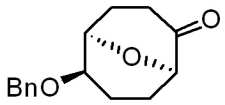





$^{13}$C-NMR, 400 MHz, $CDCl_3$

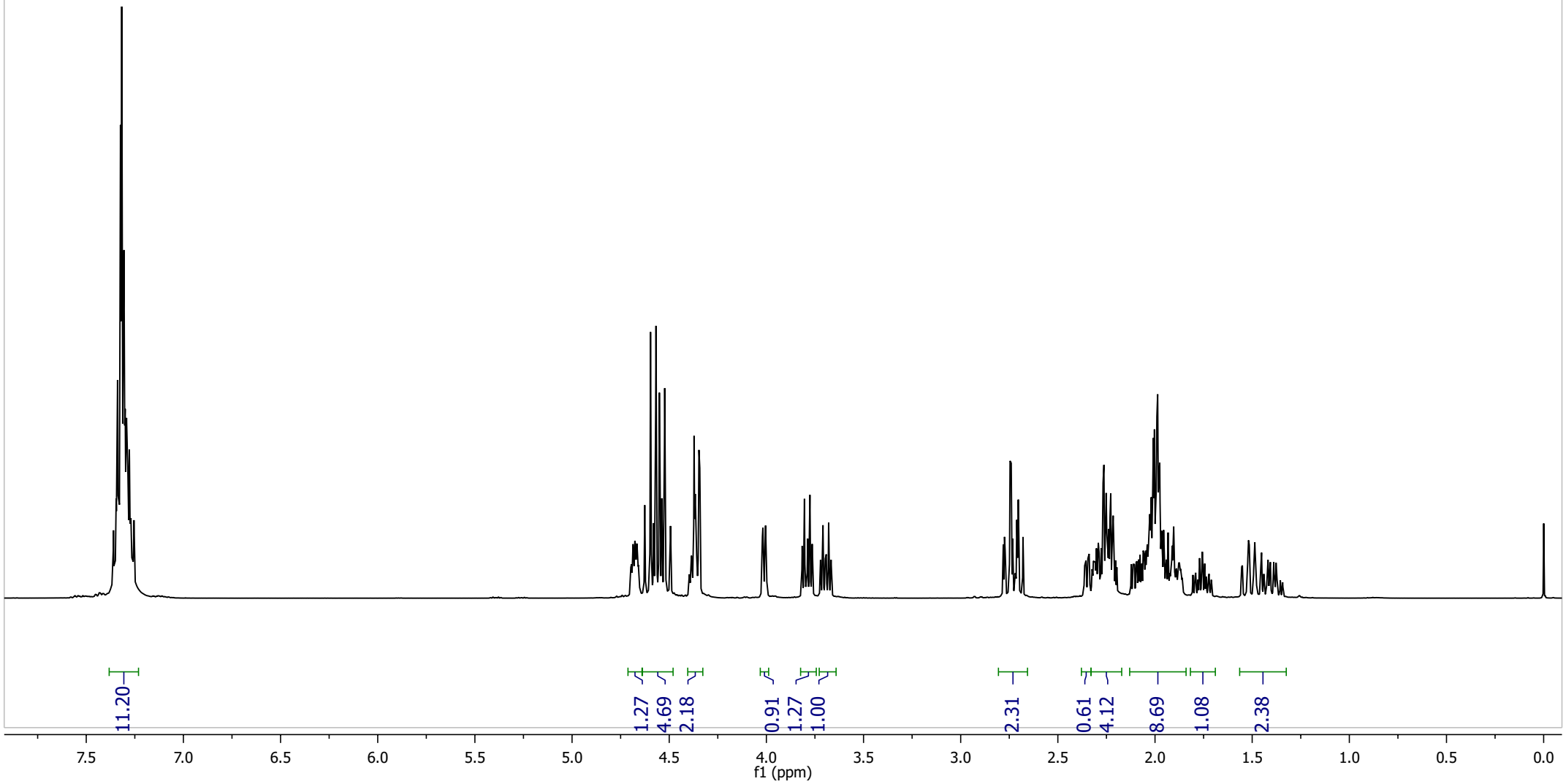


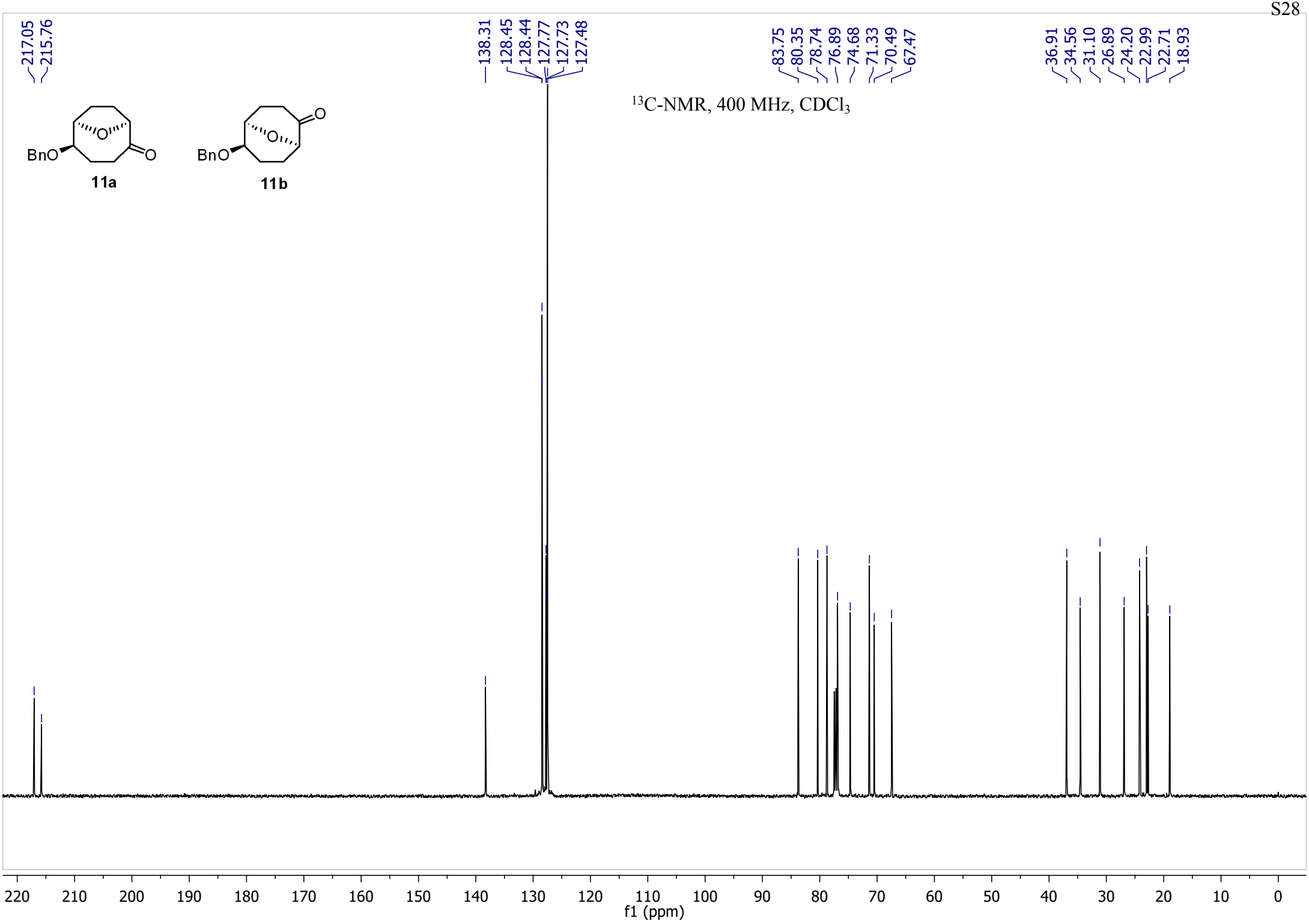

**11a**



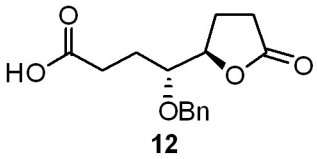

**11b**

$^{1}$H-NMR, 400 MHz, $CDCl_3$

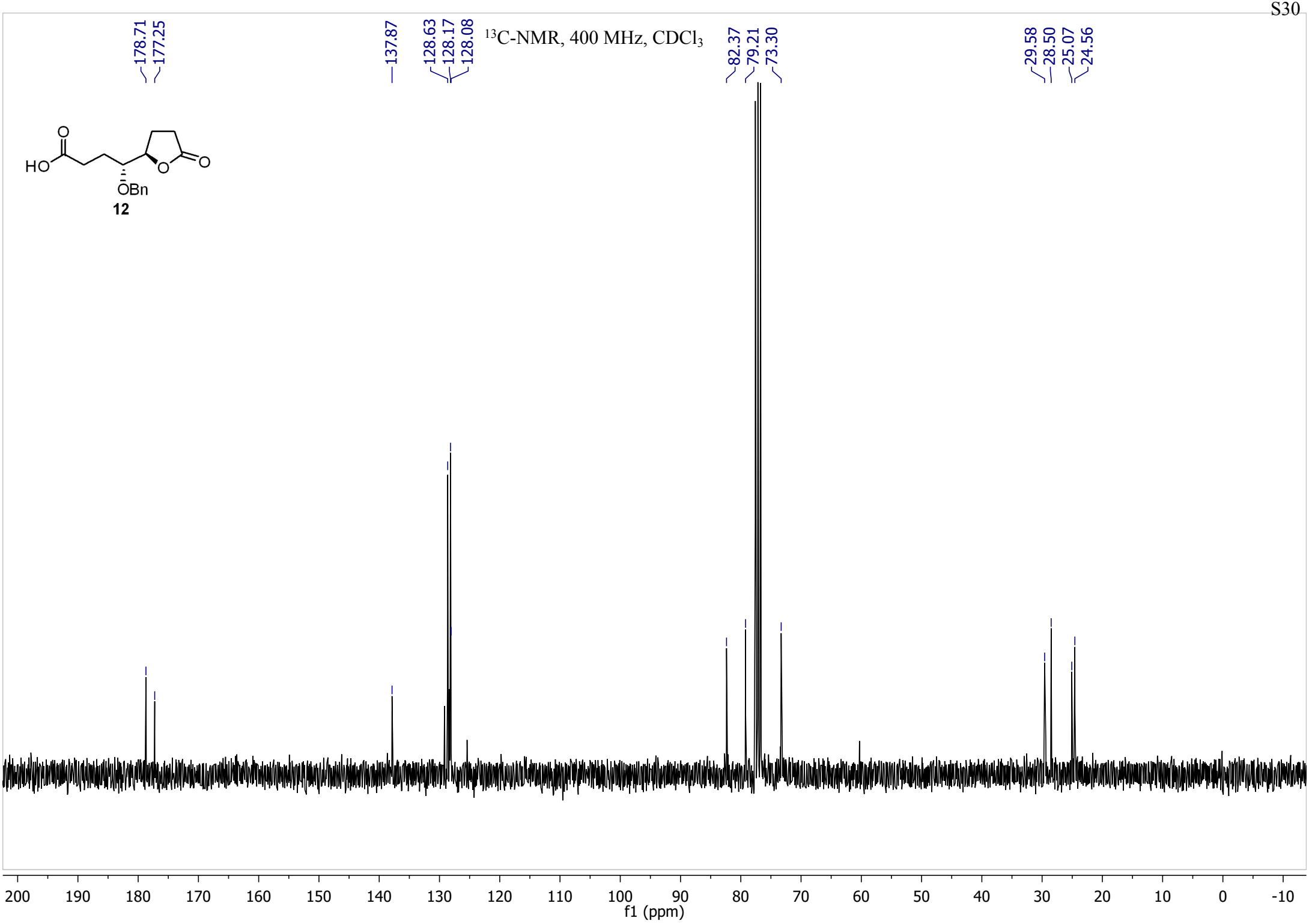



217.05
215.76
138.31
128.45
128.44
127.77
127.73
127.48
83.75
80.35
78.74
76.89
74.68
71.33
70.49
67.47
36.91
34.56
31.10
26.89
24.20
22.99
22.71
18.93
$^{13}$C-NMR, 400 MHz, $CDCl_3$
BnO
O
O
11a
BnO
O
O
11b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

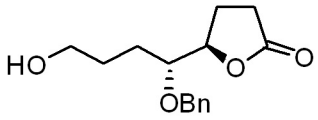
$^{1}$H-NMR, 400 MHz, $CDCl_3$



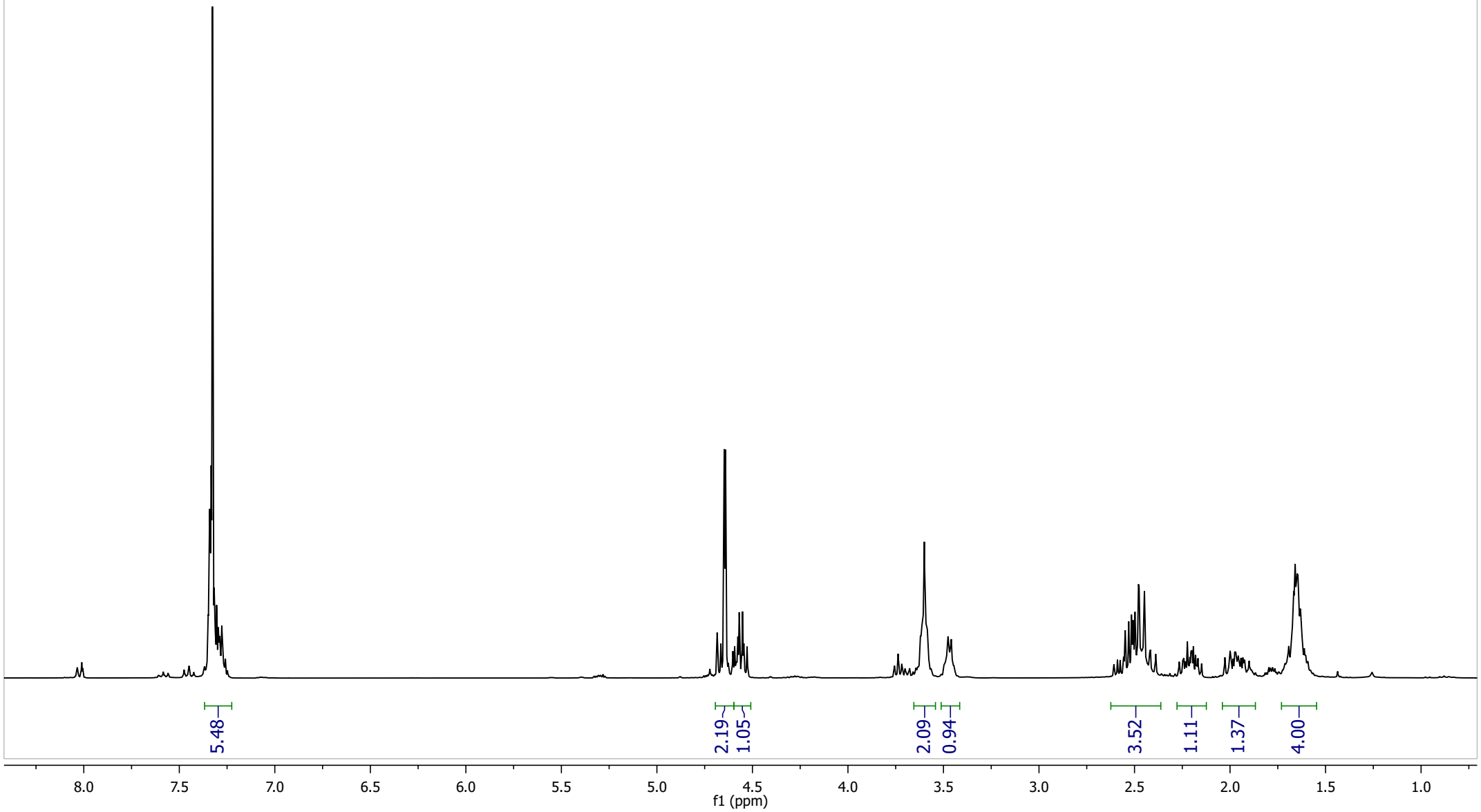

**12**

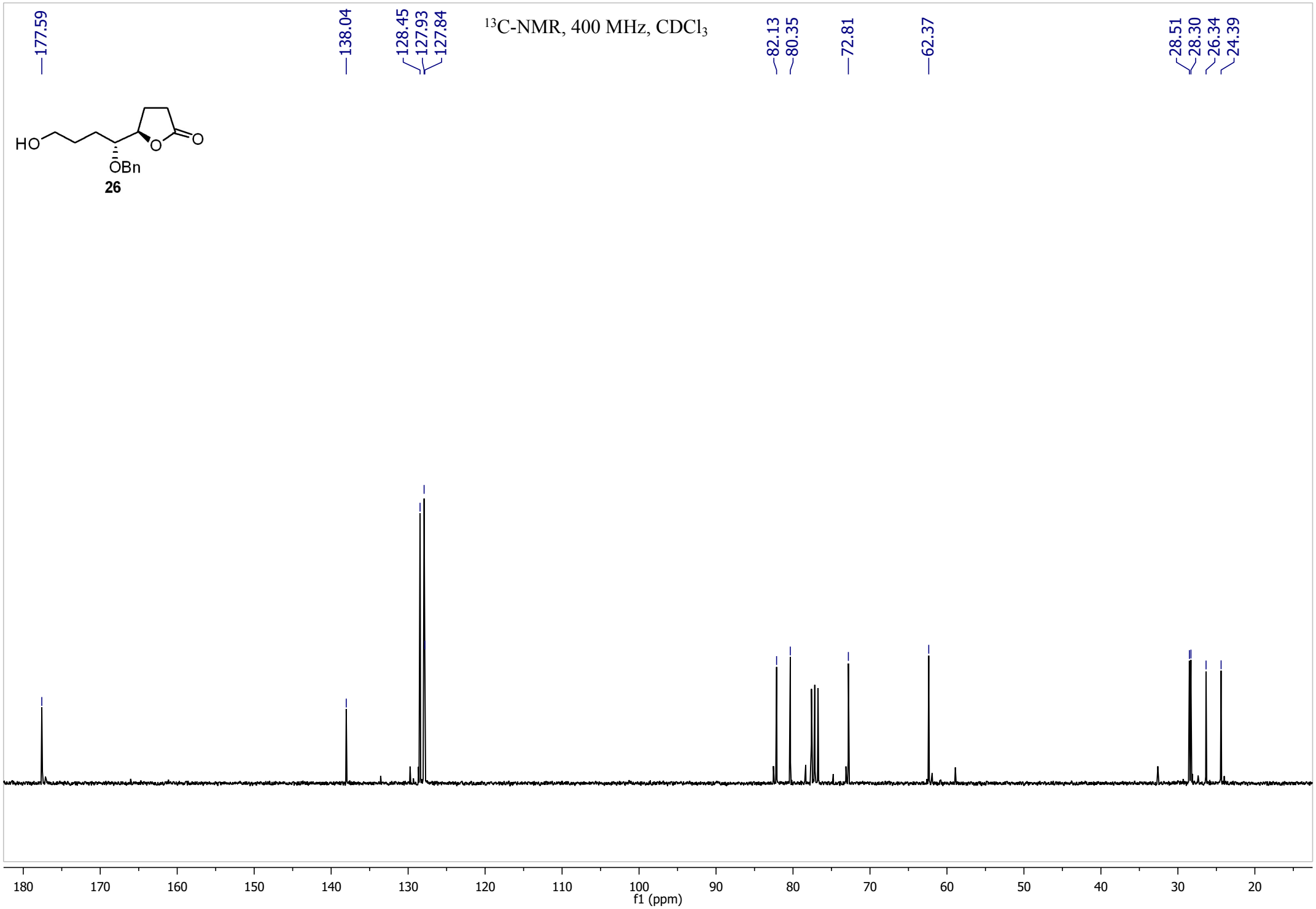

178.71
177.25
137.87
128.63
128.17
128.08
82.37
79.21
73.30
29.58
28.50
25.07
24.56
$^{13}$C-NMR, 400 MHz, $CDCl_3$
HO
O
O
O
OBn
12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

$^1$H-NMR, 400 MHz, $CDCl_3$

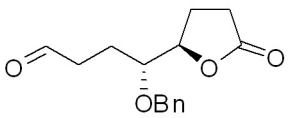



**26**

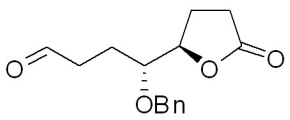



177.59
138.04
128.45
127.93
127.84
$^{13}$C-NMR, 400 MHz, $CDCl_3$
82.13
80.35
72.81
62.37
28.51
28.30
26.34
24.39
HO
O
O
OBn
26
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

$^{1}$H-NMR, 400 MHz, $CDCl_3$



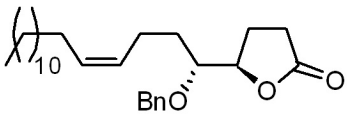

**13**



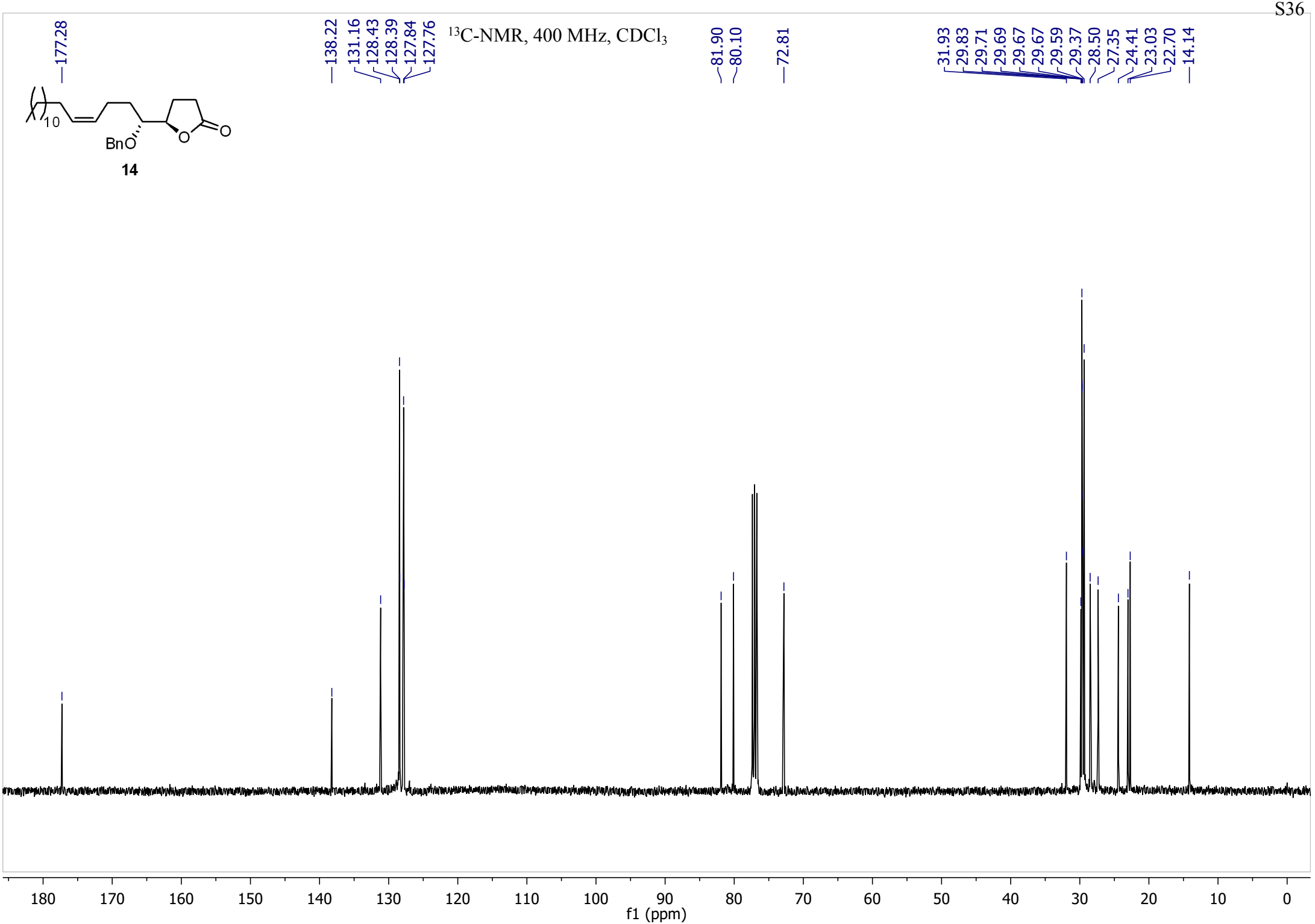

**13**

$^{13}$C-NMR, 400 MHz, $CDCl_3$

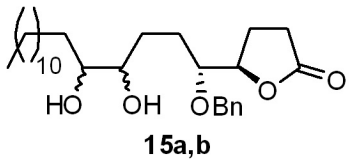
$^1$H-NMR, 400 MHz, $CDCl_3$



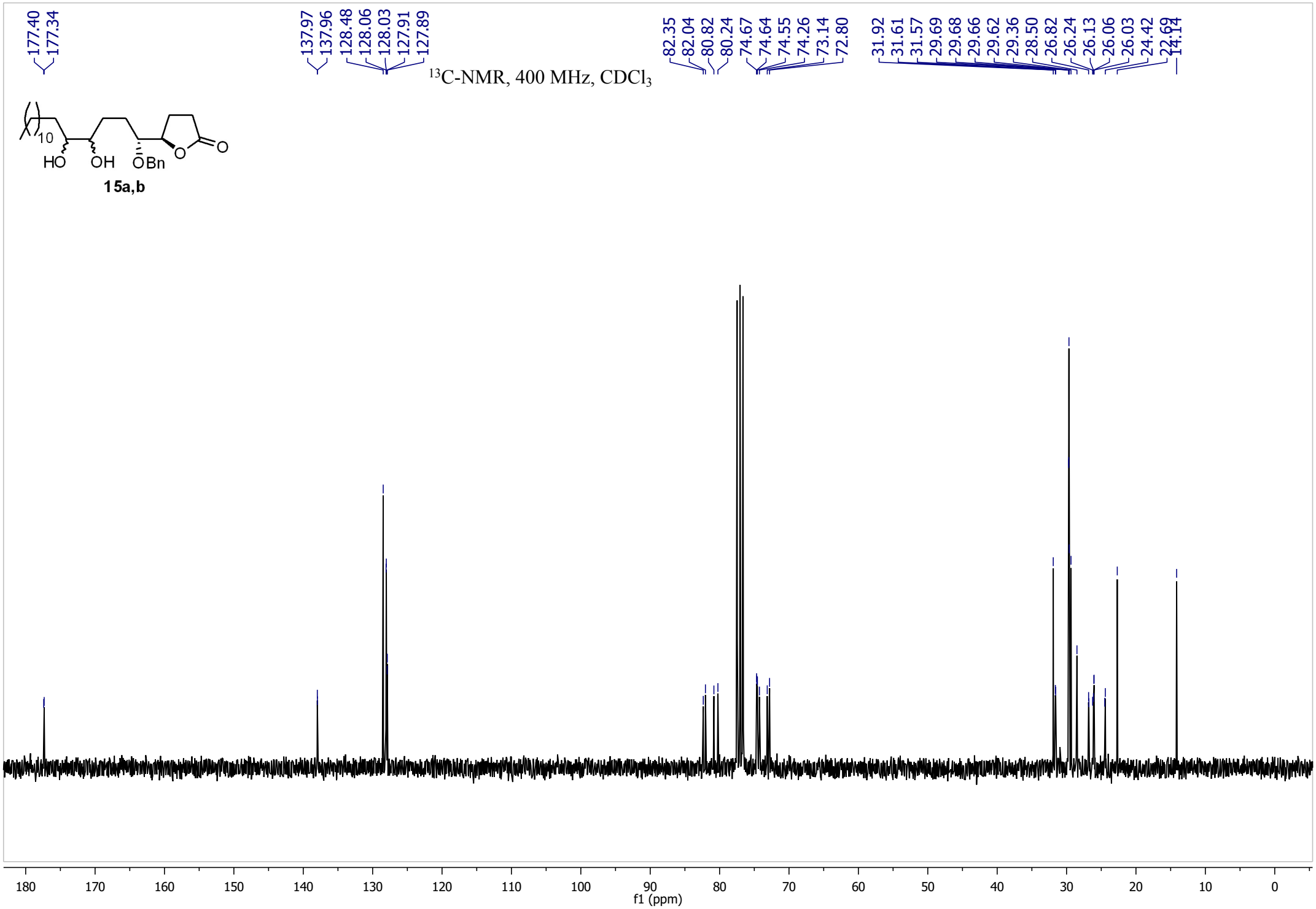

**14**


177.28
138.22
131.16
128.43
128.39
127.84
127.76
$^{13}$C-NMR, 400 MHz, $CDCl_3$
81.90
80.10
72.81
31.93
29.83
29.71
29.69
29.67
29.67
29.59
29.37
28.50
27.35
24.41
23.03
22.70
14.14
10
BnO
O
O
14
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

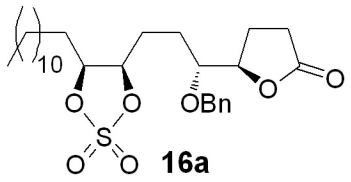
$^1$H-NMR, 400 MHz, $CDCl_3$



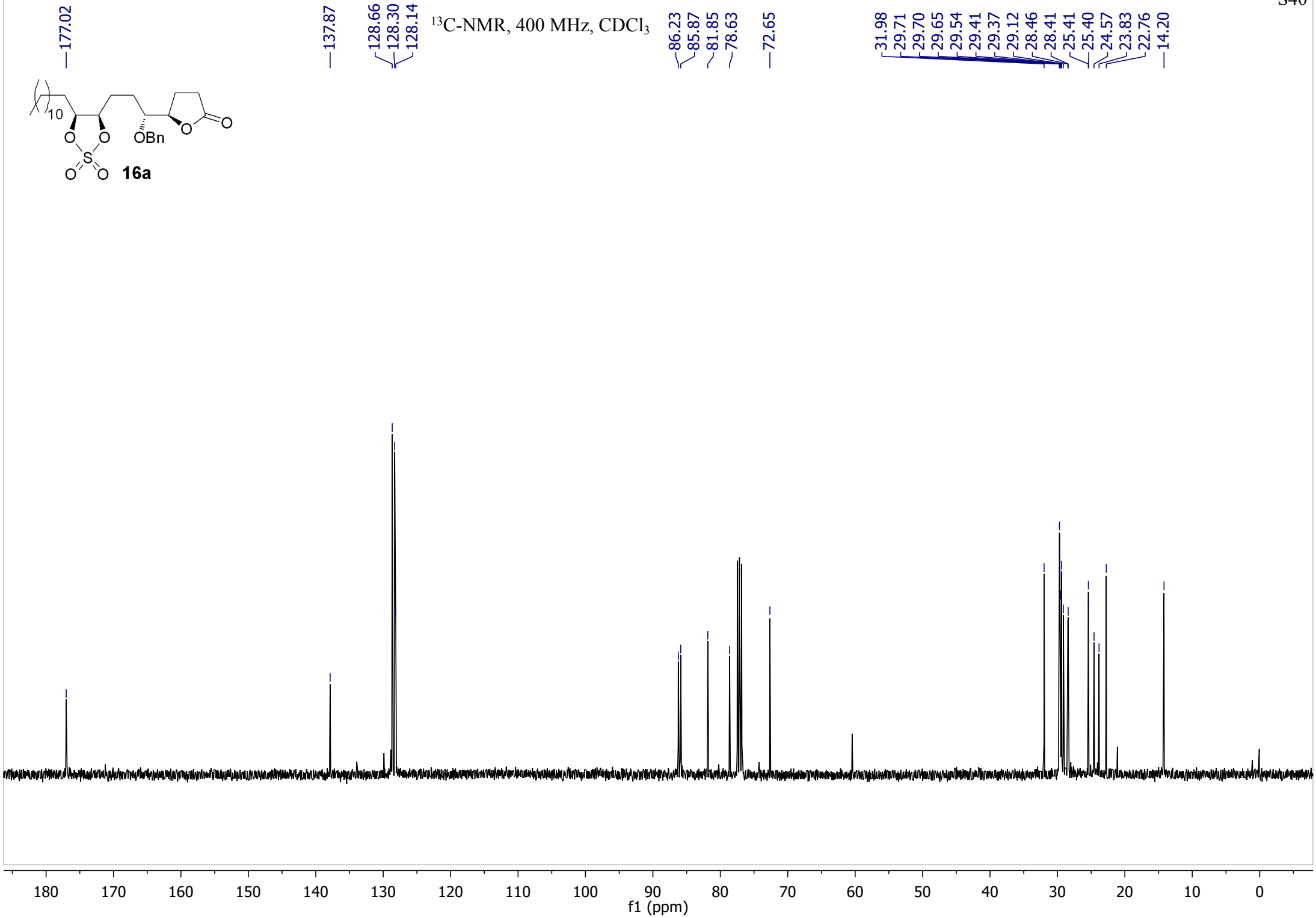

**15a,b**

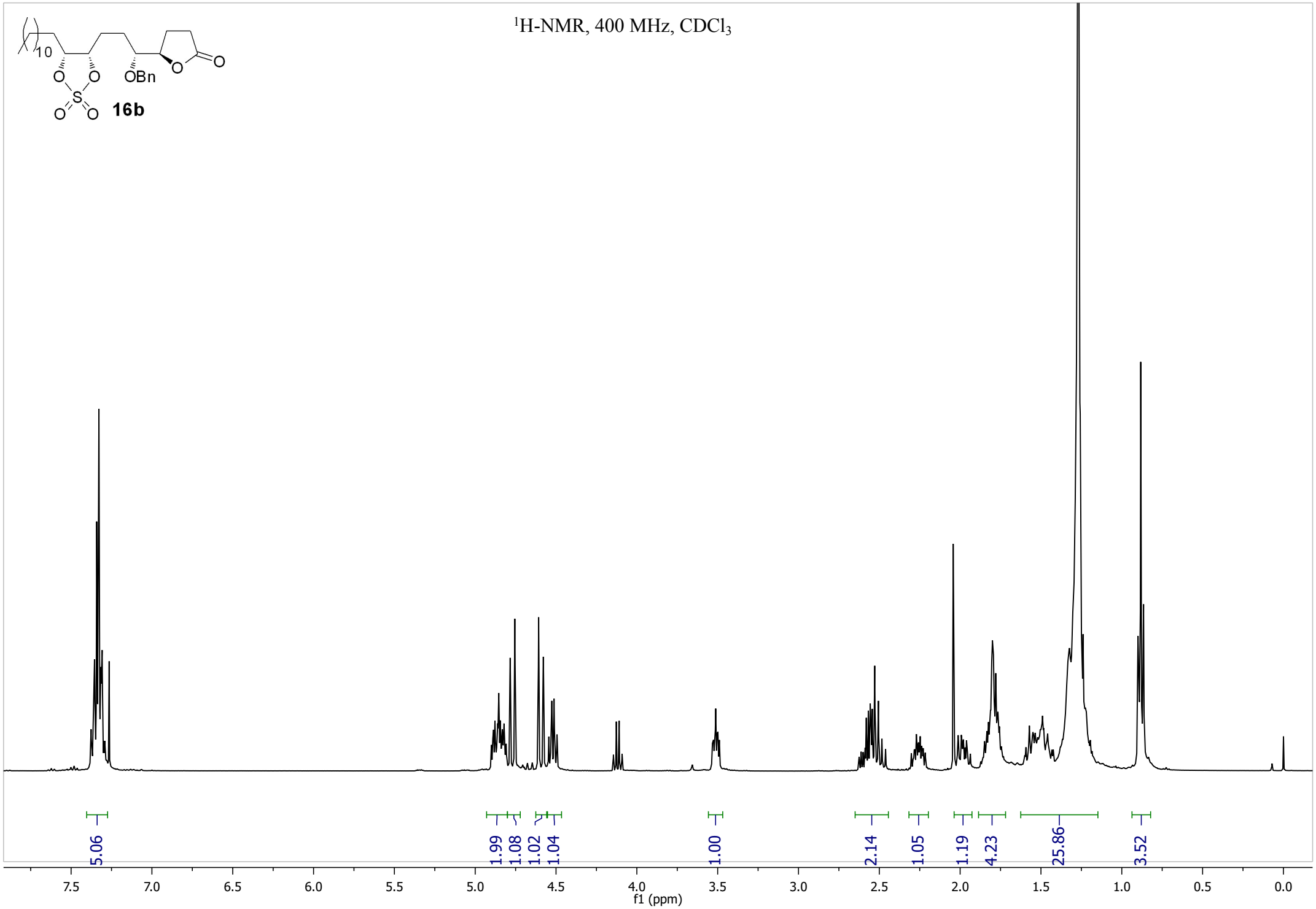

177.40
177.34
137.97
137.96
128.48
128.06
128.03
127.91
127.89
82.35
82.04
80.82
80.24
74.67
74.64
74.55
74.26
73.14
72.80
31.92
31.61
31.57
29.69
29.68
29.66
29.62
29.36
28.50
26.82
26.24
26.13
26.06
26.03
24.42
22.69
14.14
13C-NMR, 400 MHz, CDCl3
10
HO
OH
OBn
O
O
15a,b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

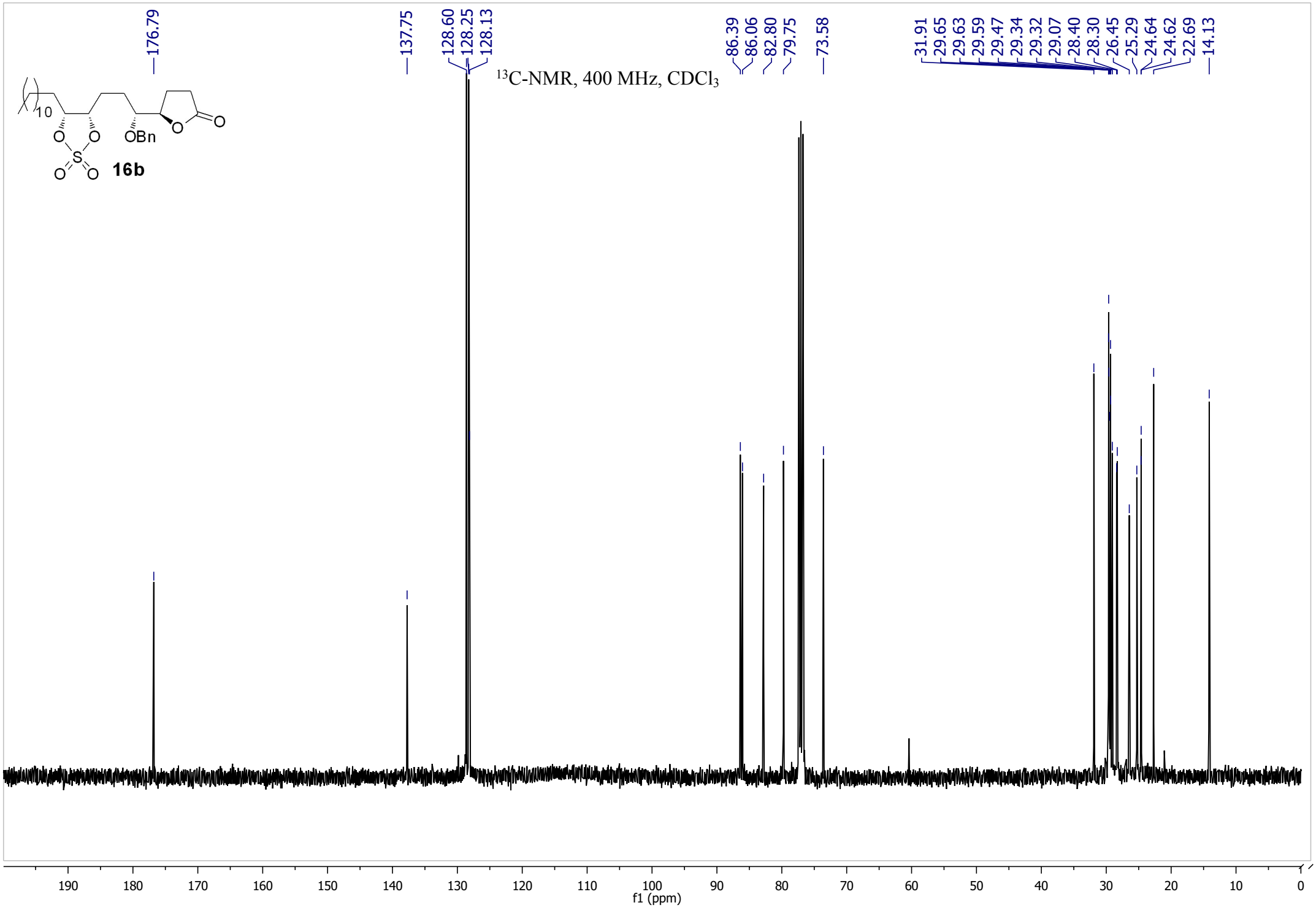
$^{1}$H-NMR, 400 MHz, $CDCl_3$



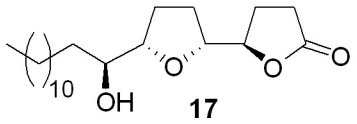

**16a**


177.02
137.87
128.66
128.30
128.14
$^{13}$C-NMR, 400 MHz, $CDCl_3$
86.23
85.87
81.85
78.63
72.65
31.98
29.71
29.70
29.65
29.54
29.41
29.37
29.12
28.46
28.41
25.41
25.40
24.57
23.83
22.76
14.20
10
OBn
16a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

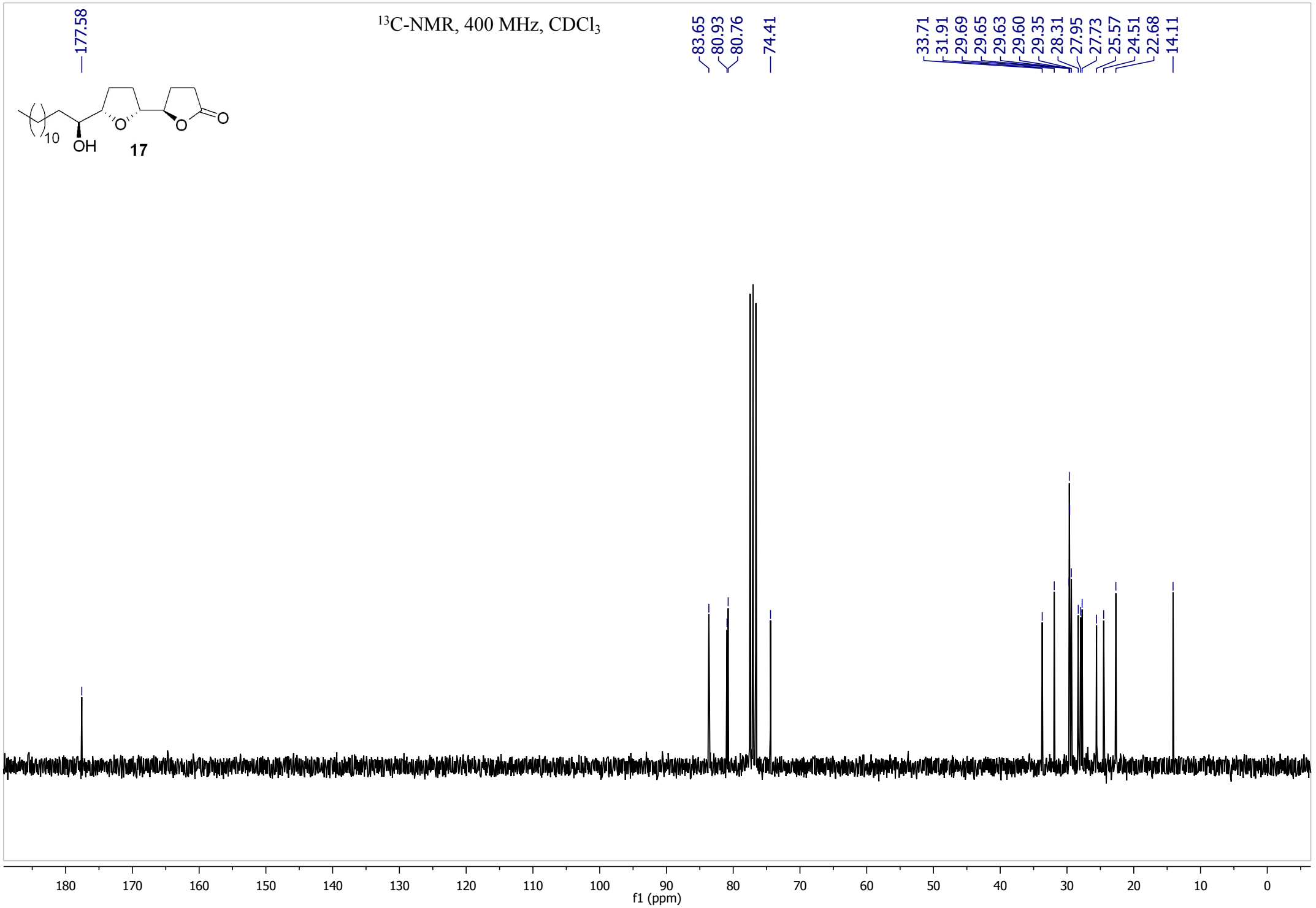

$^1$H-NMR, 400 MHz, $CDCl_3$
10
O
O
OBn
O
O
S
O
O
16b
5.06
1.99
1.08
1.02
1.04
1.00
2.14
1.05
1.19
4.23
25.86
3.52
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

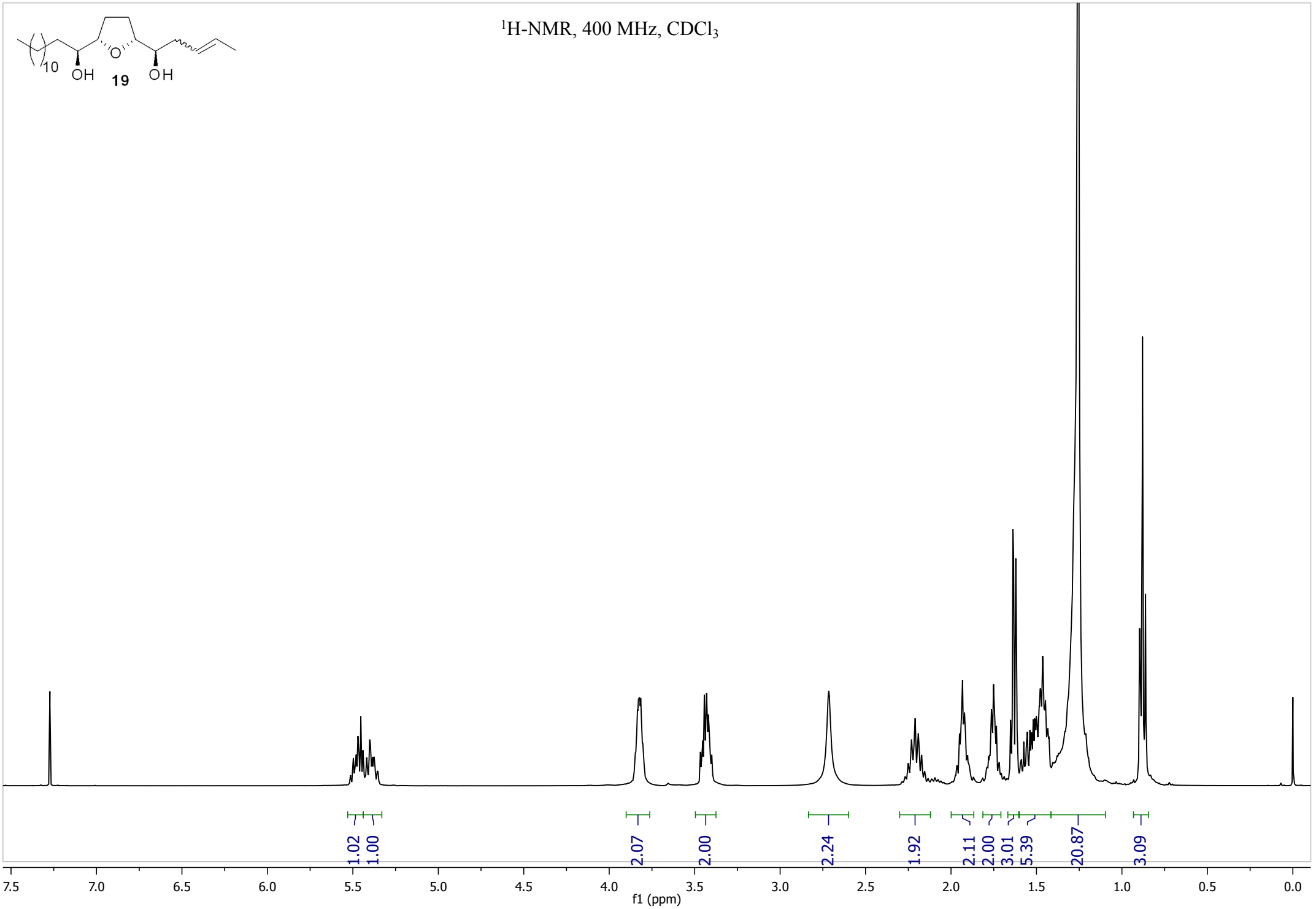

176.79
137.75
128.60
128.25
128.13
86.39
86.06
82.80
79.75
73.58
31.91
29.65
29.63
29.59
29.47
29.34
29.32
29.07
28.40
28.30
26.45
25.29
24.64
24.62
22.69
14.13
13C-NMR, 400 MHz, CDCl3
10
O
O
OBn
O
O
S
O
O
16b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

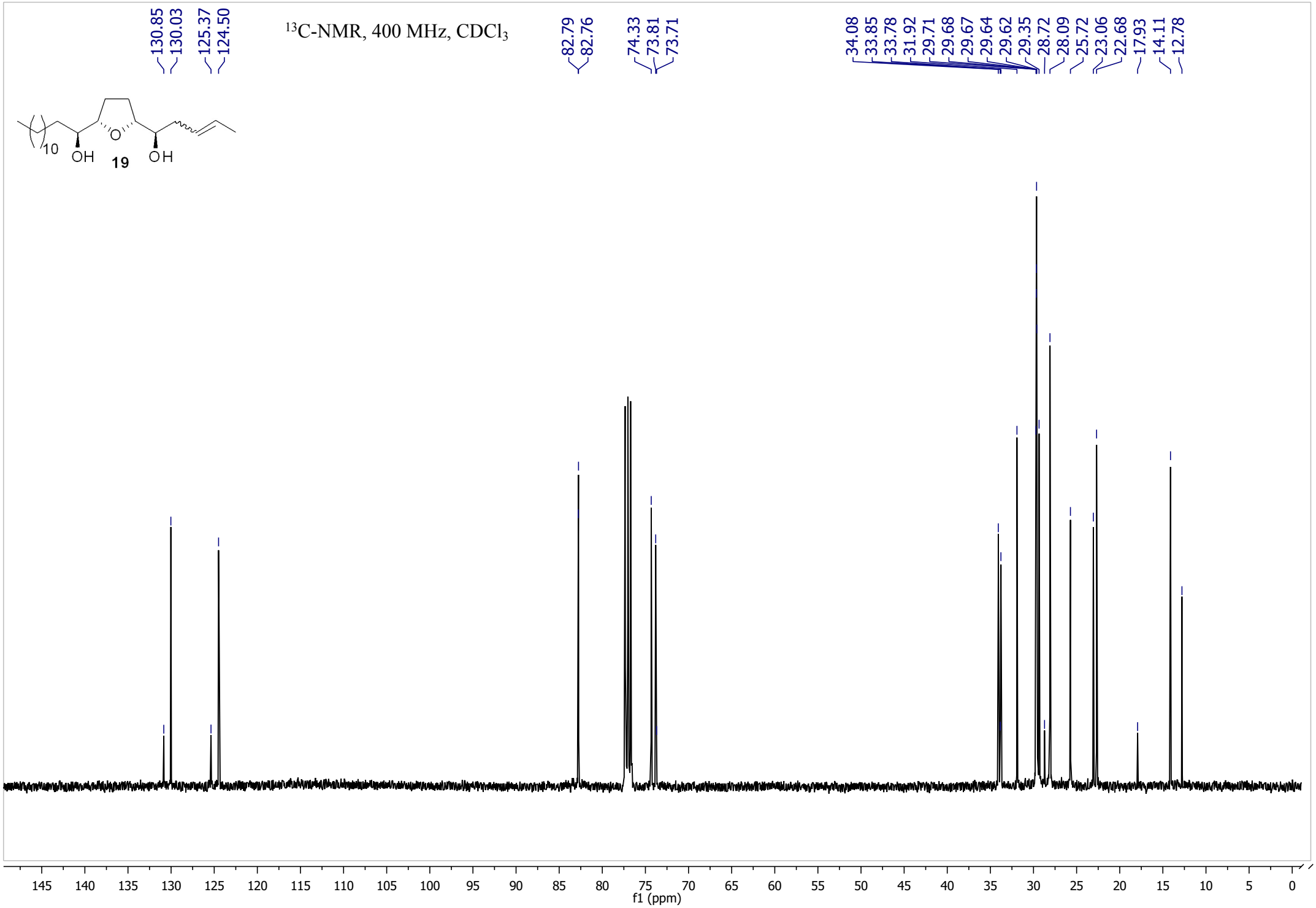
$^1$H-NMR, 400 MHz, $CDCl_3$



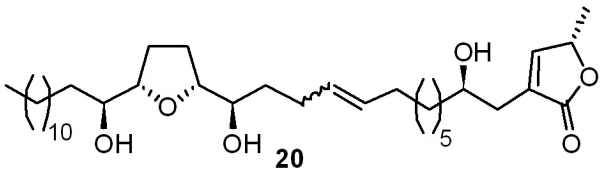

**17**


$^{13}$C-NMR, 400 MHz, $CDCl_3$
177.58
83.65
80.93
80.76
74.41
33.71
31.91
29.69
29.65
29.63
29.60
29.35
28.31
27.95
27.73
25.57
24.51
22.68
14.11
10
OH
O
O
O
17
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

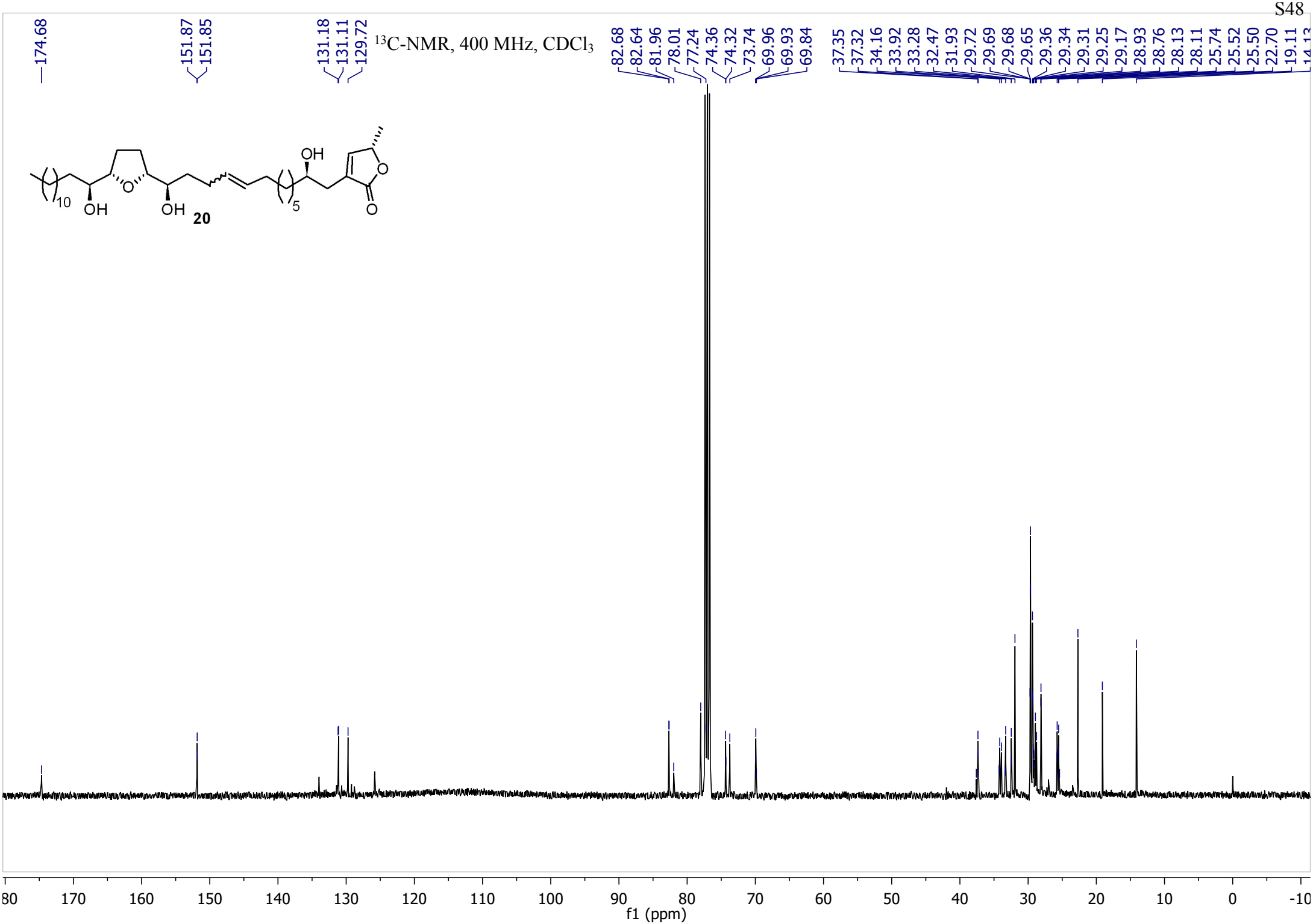

$^1$H-NMR, 400 MHz, $CDCl_3$
10
OH
19
OH
1.02
1.00
2.07
2.00
2.24
1.92
2.11
2.00
3.01
5.39
20.87
3.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


130.85
130.03
125.37
124.50
82.79
82.76
74.33
73.81
73.71
34.08
33.85
33.78
31.92
29.71
29.68
29.67
29.64
29.62
29.35
28.72
28.09
25.72
23.06
22.68
17.93
14.11
12.78
$^{13}$C-NMR, 400 MHz, $CDCl_3$
10
OH
OH
19
f1 (ppm)

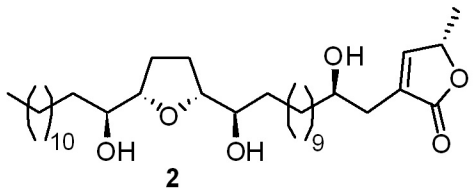
$^1$H-NMR, 400 MHz, $CDCl_3$



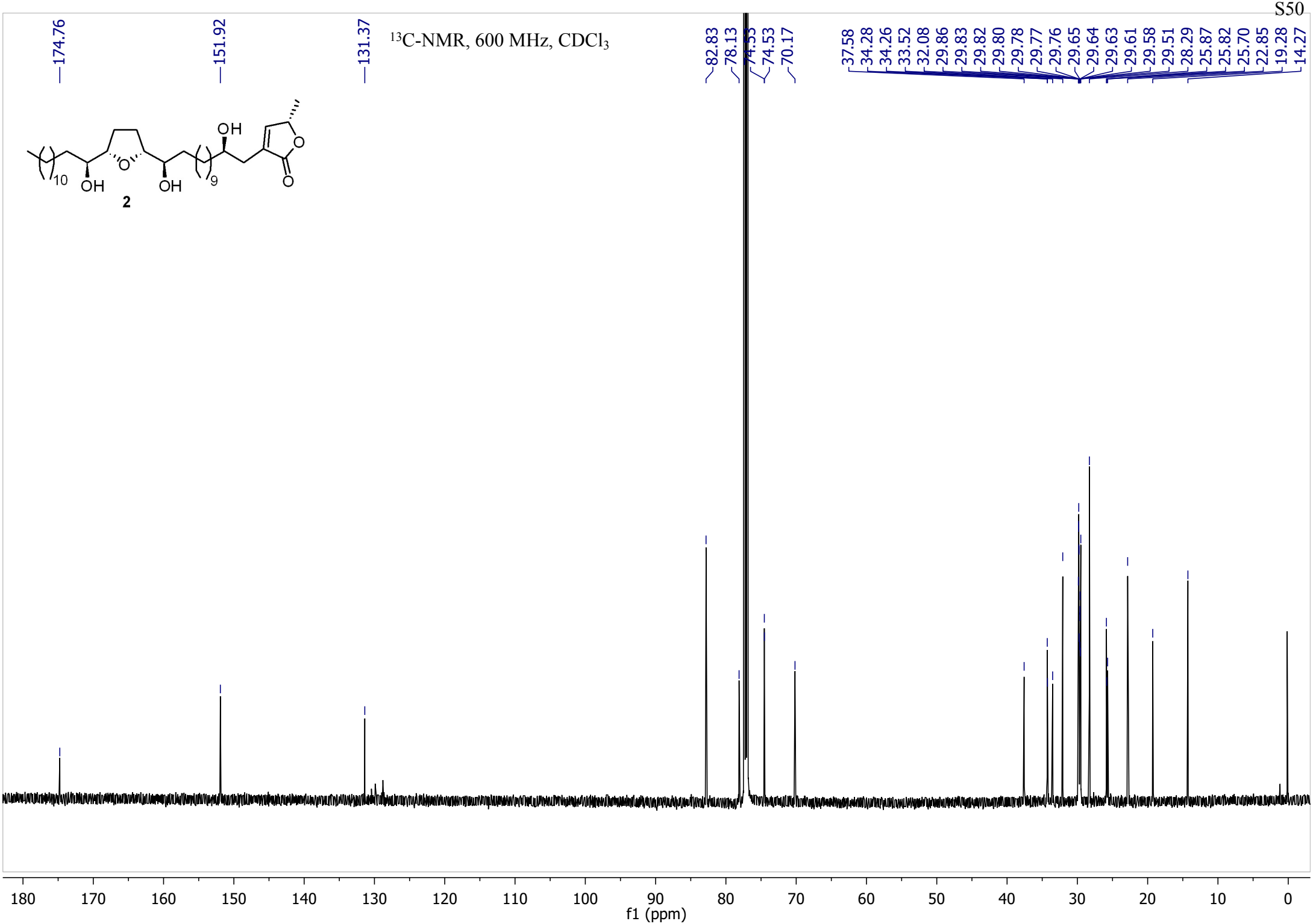

**20**

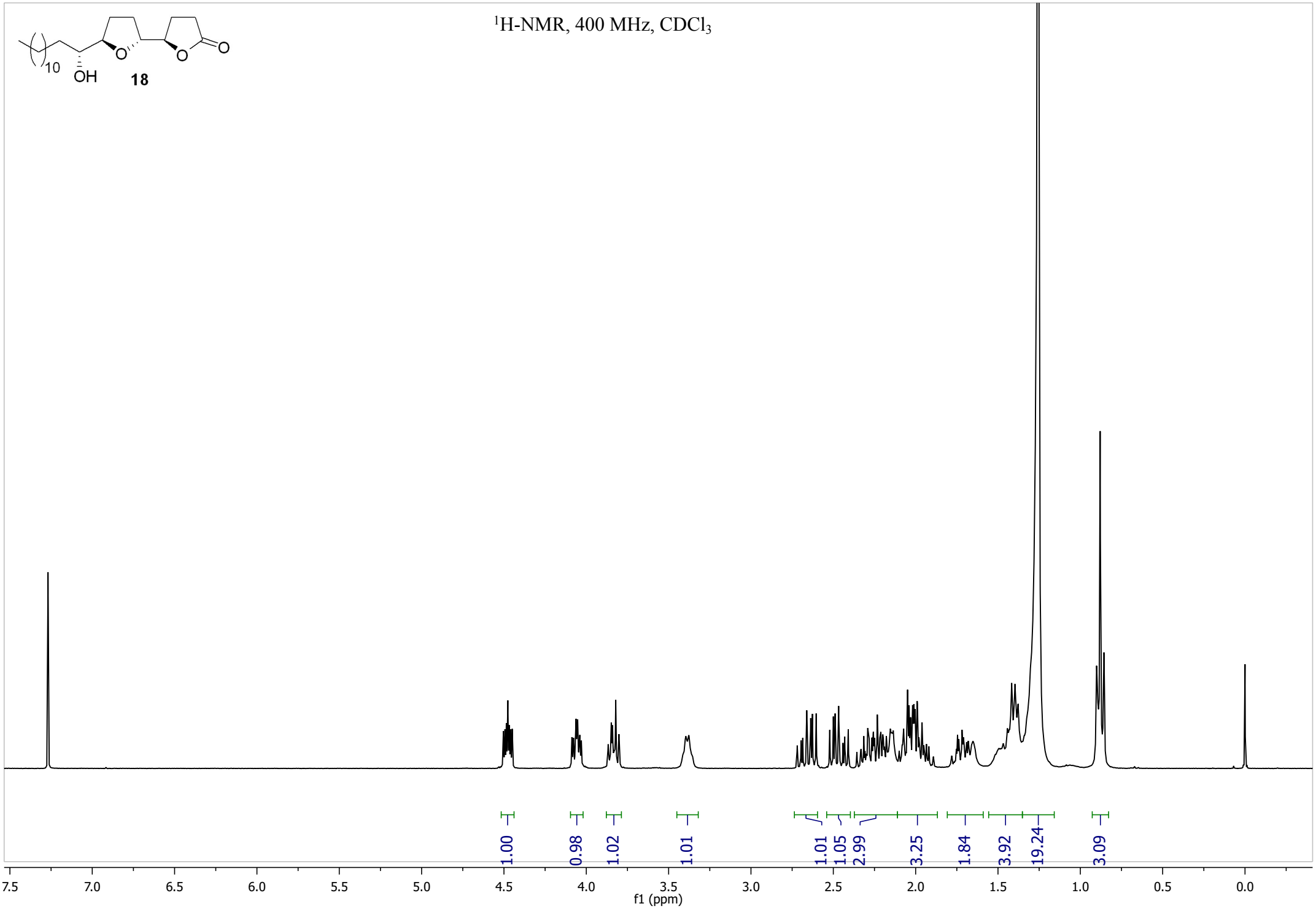

174.68
151.87
151.85
131.18
131.11
129.72
82.68
82.64
81.96
78.01
77.24
74.36
74.32
73.74
69.96
69.93
69.84
37.35
37.32
34.16
33.92
33.28
32.47
31.93
29.72
29.69
29.68
29.65
29.36
29.34
29.31
29.25
29.17
28.93
28.76
28.13
28.11
25.74
25.52
25.50
22.70
19.11
$^{13}$C-NMR, 400 MHz, $CDCl_3$
OH
OH
OH
O
O
O
10
5
20
f1 (ppm)

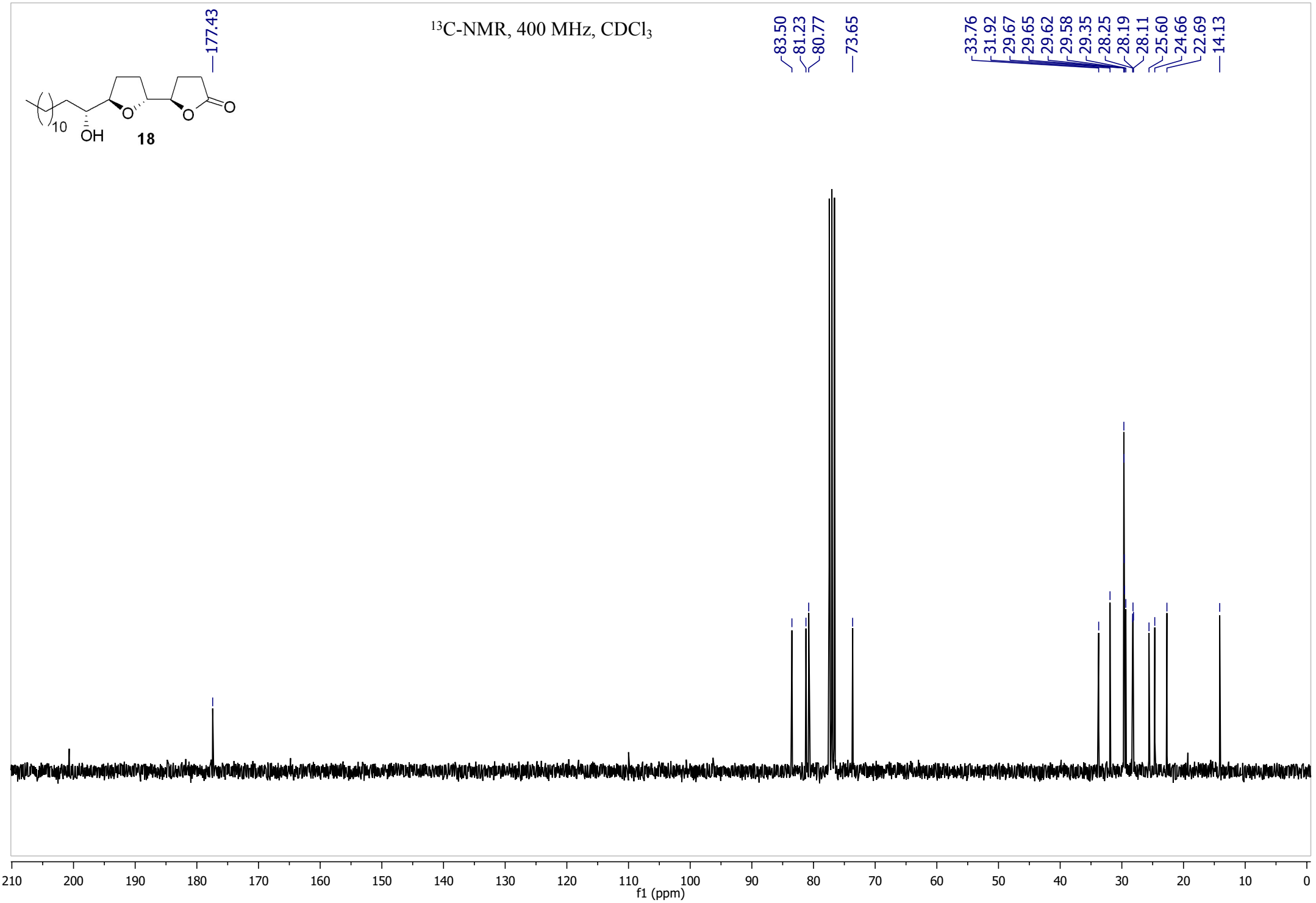
$^{1}$H-NMR, 600 MHz, $CDCl_3$

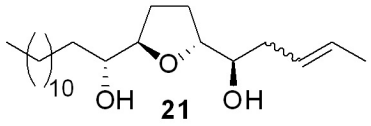



**2**

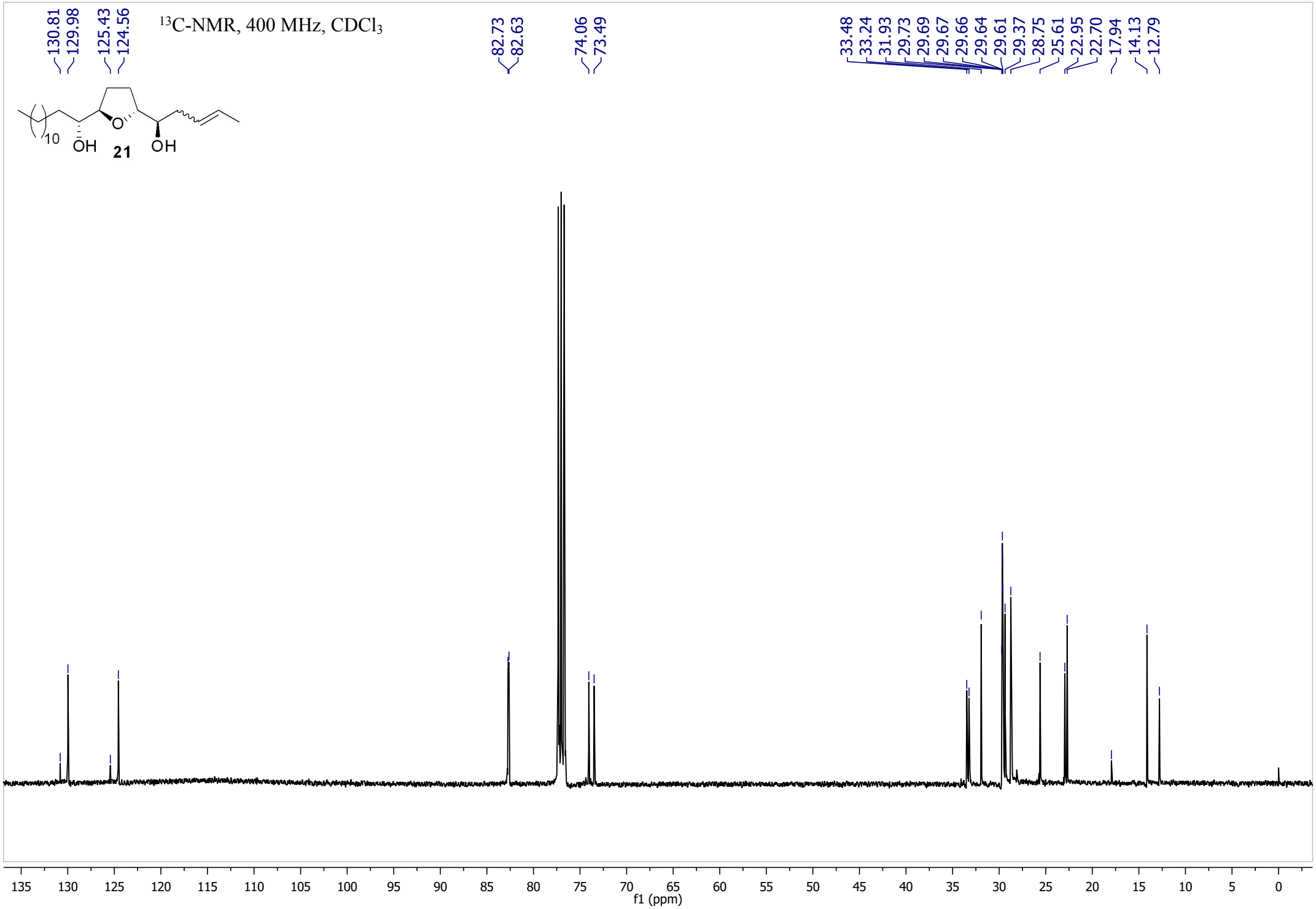

174.76
151.92
131.37
82.83
78.13
74.53
74.53
70.17
37.58
34.28
34.26
33.52
32.08
29.86
29.83
29.82
29.80
29.78
29.77
29.76
29.65
29.64
29.63
29.61
29.58
29.51
28.29
25.87
25.82
25.70
22.85
19.28
14.27
13C-NMR, 600 MHz, CDCl3
OH
OH
OH
O
O
O
10
9
2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


$^1$H-NMR, 400 MHz, $CDCl_3$
10
OH
18
O
O
O
1.00
0.98
1.02
1.01
1.01
1.05
2.99
3.25
1.84
3.92
19.24
3.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

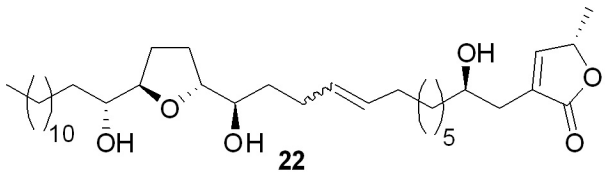

$^{13}$C-NMR, 400 MHz, $CDCl_3$
177.43
83.50
81.23
80.77
73.65
33.76
31.92
29.67
29.65
29.62
29.58
29.35
28.25
28.19
28.11
25.60
24.66
22.69
14.13
10
OH
18
f1 (ppm)




$^{1}$H-NMR, 400 MHz, $CDCl_3$


130.81
129.98
125.43
124.56
$^{13}$C-NMR, 400 MHz, $CDCl_3$
82.73
82.63
74.06
73.49
33.48
33.24
31.93
29.73
29.69
29.67
29.66
29.64
29.61
29.37
28.75
25.61
22.95
22.70
17.94
14.13
12.79
10
OH
21
OH
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

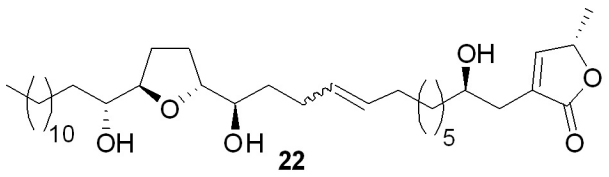
$^{1}$H-NMR, 400 MHz, $CDCl_3$



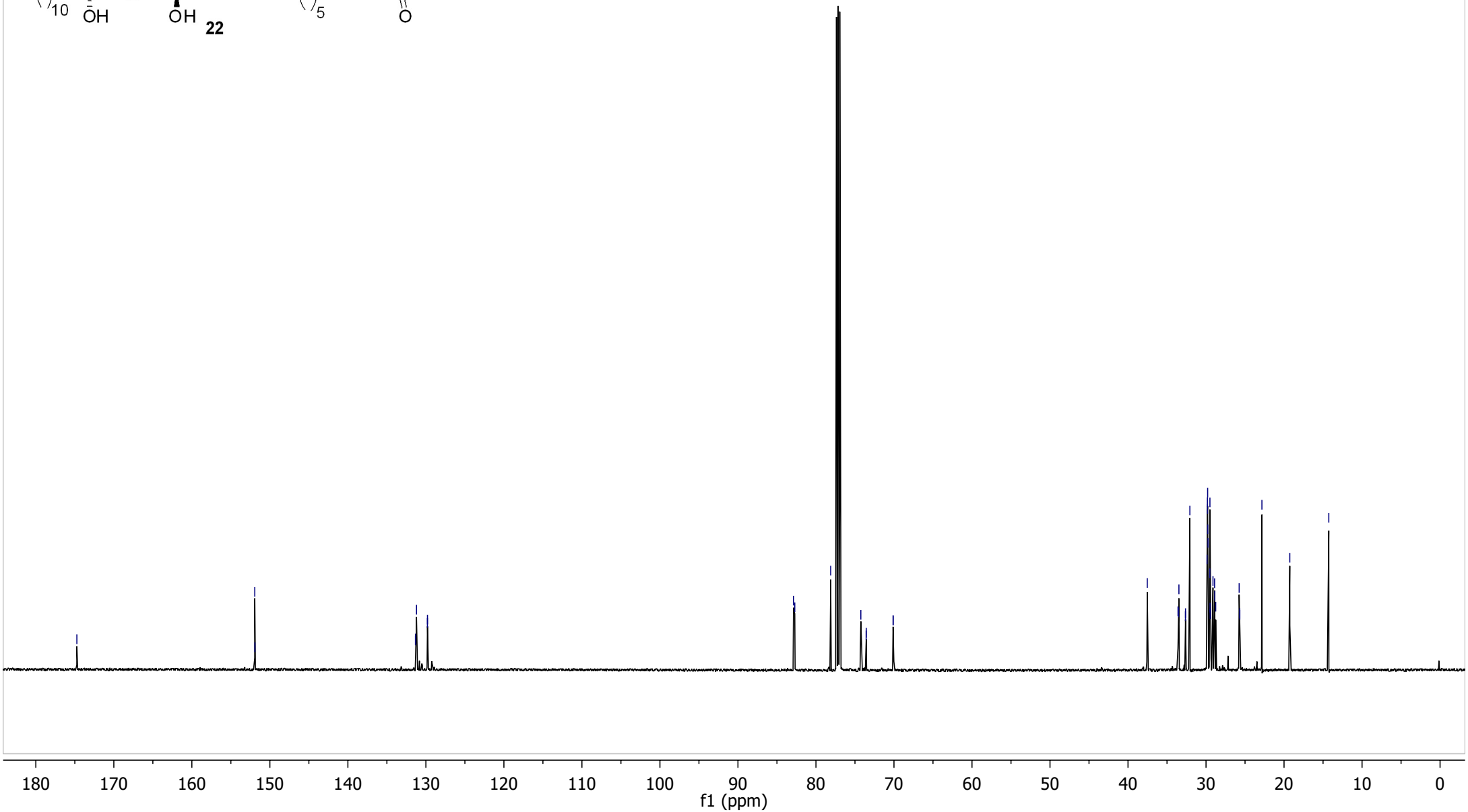

**22**

$^{13}$C-NMR, 400 MHz, $CDCl_3$

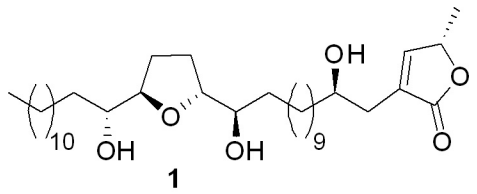
174.74
151.93
151.92
131.34
131.33
131.21
129.80
129.80
82.88
82.72
78.11
74.25
73.57
73.56
70.11
70.10
37.53
33.59
33.52
33.47
32.63
32.07
29.87
29.83
29.81
29.79
29.78
29.75
29.51
29.50
29.48
29.47
29.11
28.90
28.89
28.76
25.75
25.68
22.84
19.26



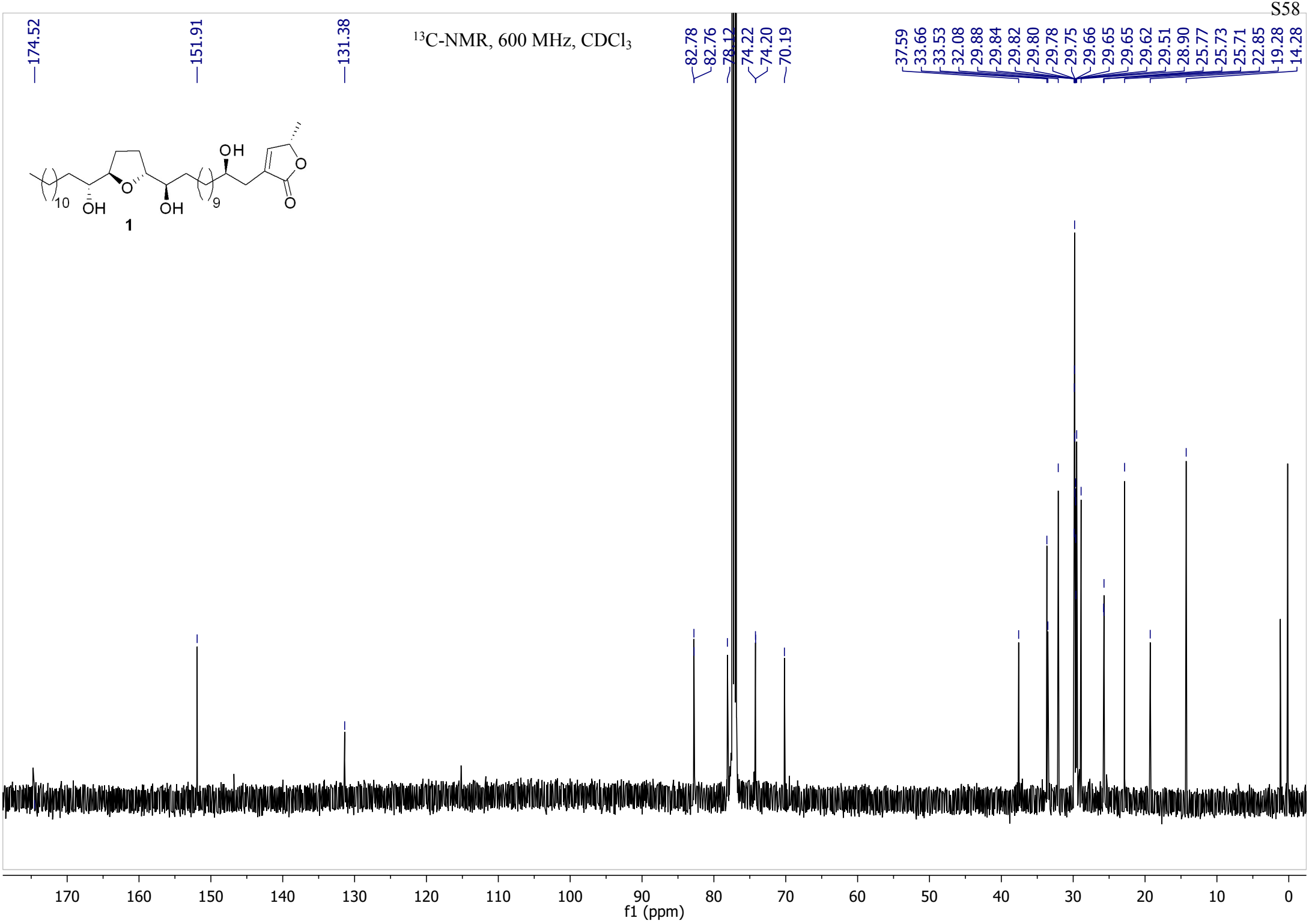

**22**

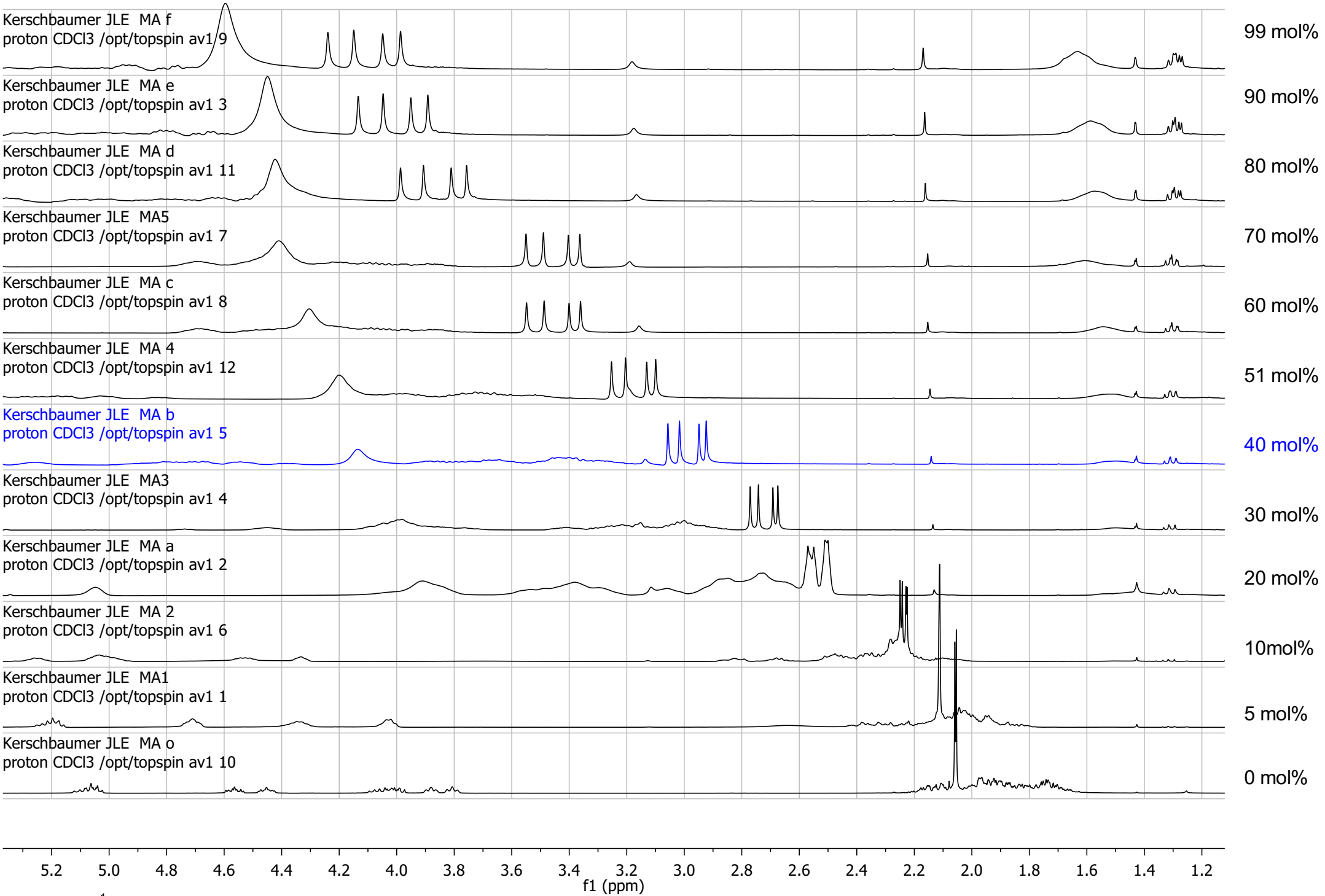


$^{1}$H-NMR, 600 MHz, $CDCl_3$



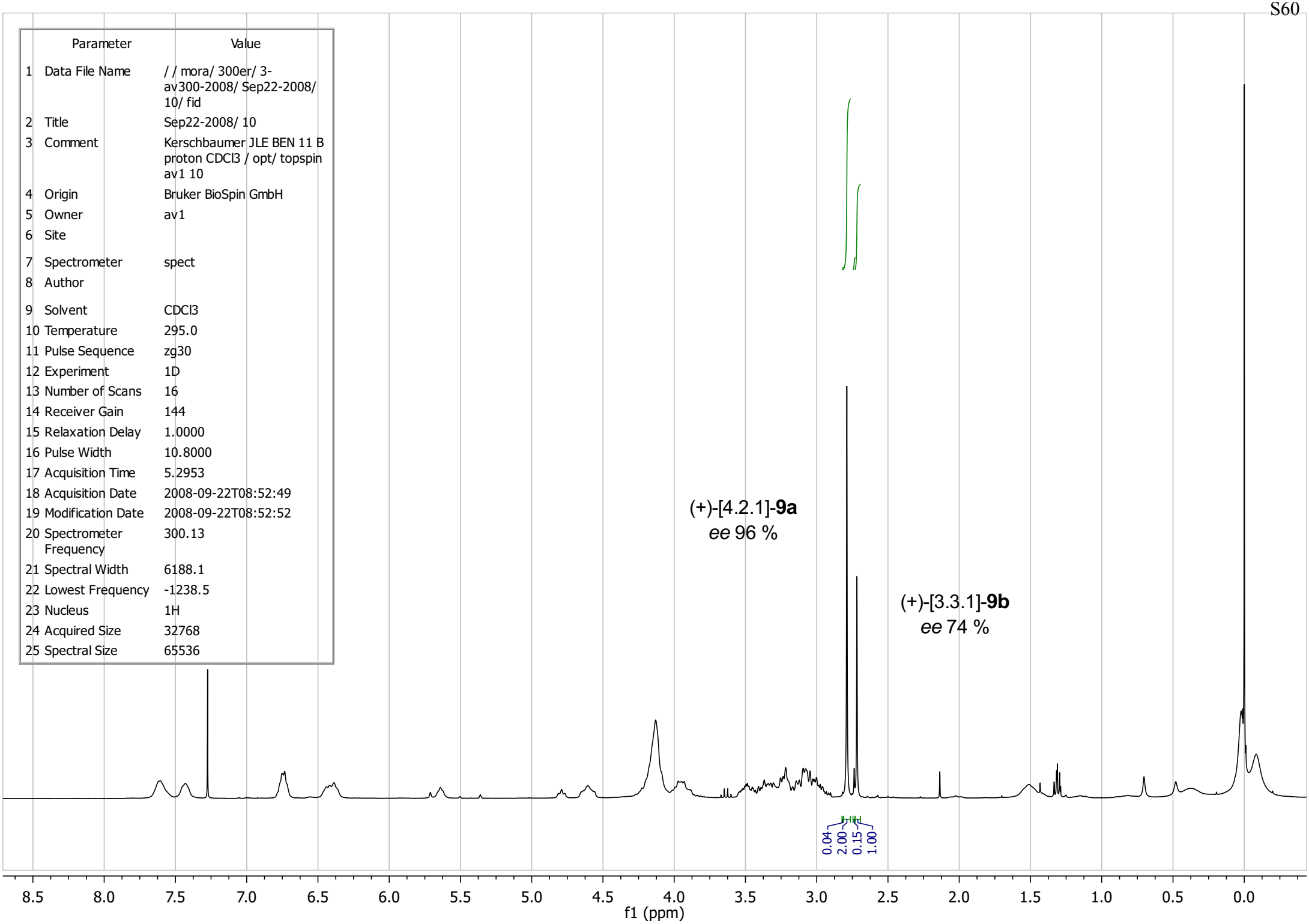

**1**


174.52
151.91
131.38
82.78
82.76
78.12
74.22
74.20
70.19
37.59
33.66
33.53
32.08
29.88
29.84
29.82
29.80
29.78
29.75
29.66
29.65
29.65
29.62
29.51
28.90
25.77
25.73
25.71
22.85
19.28
14.28
13C-NMR, 600 MHz, CDCl3
OH
OH
OH
O
O
O
10
9
1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

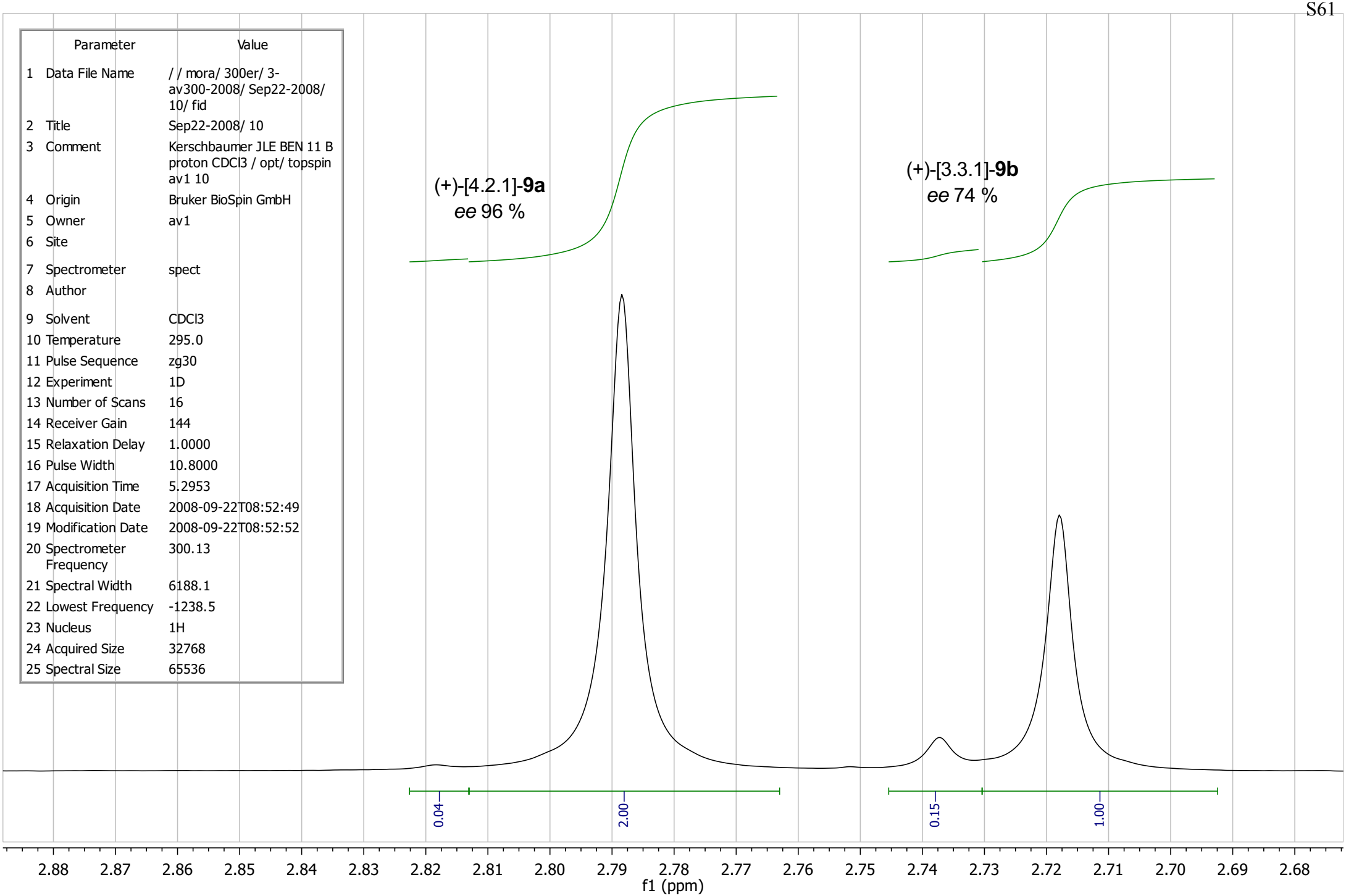



Parts of the $^{1}$H NMR spectra (300 MHz) of the racemic 52:48 mixture (GC) of monoacetates **9a** and **9b** in $CDCl_3$ with $Eu(hfc)_3$ (0 to 99 mol%)

| | Parameter | Value |
|---|---|---|
| 1 | Data File Name | / / mora/ 300er/ 3-av300-2008/ Sep22-2008/ 10/ fid |
| 2 | Title | Sep22-2008/ 10 |
| 3 | Comment | Kerschbaumer JLE BEN 11 B proton CDCl3 / opt/ topspin av1 10 |
| 4 | Origin | Bruker BioSpin GmbH |
| 5 | Owner | av1 |
| 6 | Site | |
| 7 | Spectrometer | spect |
| 8 | Author | |
| 9 | Solvent | CDCl3 |
| 10 | Temperature | 295.0 |
| 11 | Pulse Sequence | zg30 |
| 12 | Experiment | 1D |
| 13 | Number of Scans | 16 |
| 14 | Receiver Gain | 144 |
| 15 | Relaxation Delay | 1.0000 |
| 16 | Pulse Width | 10.8000 |
| 17 | Acquisition Time | 5.2953 |
| 18 | Acquisition Date | 2008-09-22T08:52:49 |
| 19 | Modification Date | 2008-09-22T08:52:52 |
| 20 | Spectrometer Frequency | 300.13 |
| 21 | Spectral Width | 6188.1 |
| 22 | Lowest Frequency | -1238.5 |
| 23 | Nucleus | 1H |
| 24 | Acquired Size | 32768 |
| 25 | Spectral Size | 65536 |



| | Parameter | Value |
|---|---|---|
| 1 | Data File Name | / / mora/ 300er/ 3-av300-2008/ Sep22-2008/ 10/ fid |
| 2 | Title | Sep22-2008/ 10 |
| 3 | Comment | Kerschbaumer JLE BEN 11 B proton CDCl3 / opt/ topspin av1 10 |
| 4 | Origin | Bruker BioSpin GmbH |
| 5 | Owner | av1 |
| 6 | Site | |
| 7 | Spectrometer | spect |
| 8 | Author | |
| 9 | Solvent | CDCl3 |
| 10 | Temperature | 295.0 |
| 11 | Pulse Sequence | zg30 |
| 12 | Experiment | 1D |
| 13 | Number of Scans | 16 |
| 14 | Receiver Gain | 144 |
| 15 | Relaxation Delay | 1.0000 |
| 16 | Pulse Width | 10.8000 |
| 17 | Acquisition Time | 5.2953 |
| 18 | Acquisition Date | 2008-09-22T08:52:49 |
| 19 | Modification Date | 2008-09-22T08:52:52 |
| 20 | Spectrometer Frequency | 300.13 |
| 21 | Spectral Width | 6188.1 |
| 22 | Lowest Frequency | -1238.5 |
| 23 | Nucleus | 1H |
| 24 | Acquired Size | 32768 |
| 25 | Spectral Size | 65536 |



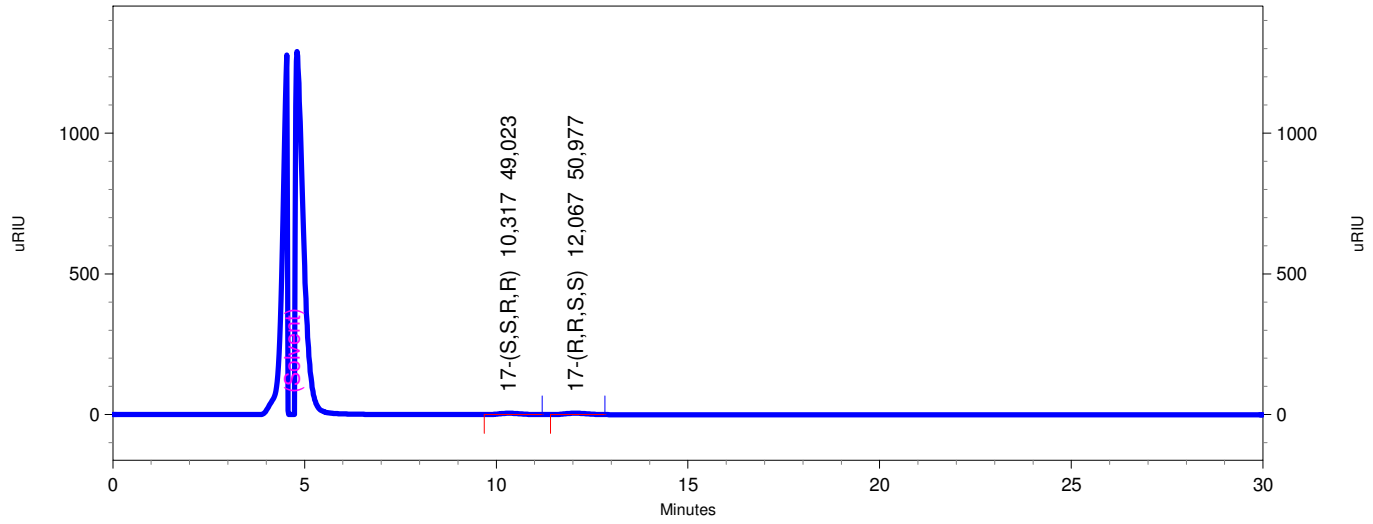

Part of the $^{1}$H NMR Spectrum (300 MHz) of a 62:38 mixture (GC) of the monoacetates **9a** and **9b** after lipase catalyzed monoacetylation of the diols **8a** and **8b** with addition of 40 mol% of $Eu(hfc)_3$.

Sample ID: PEP 12-1 40-60 OJ-RH

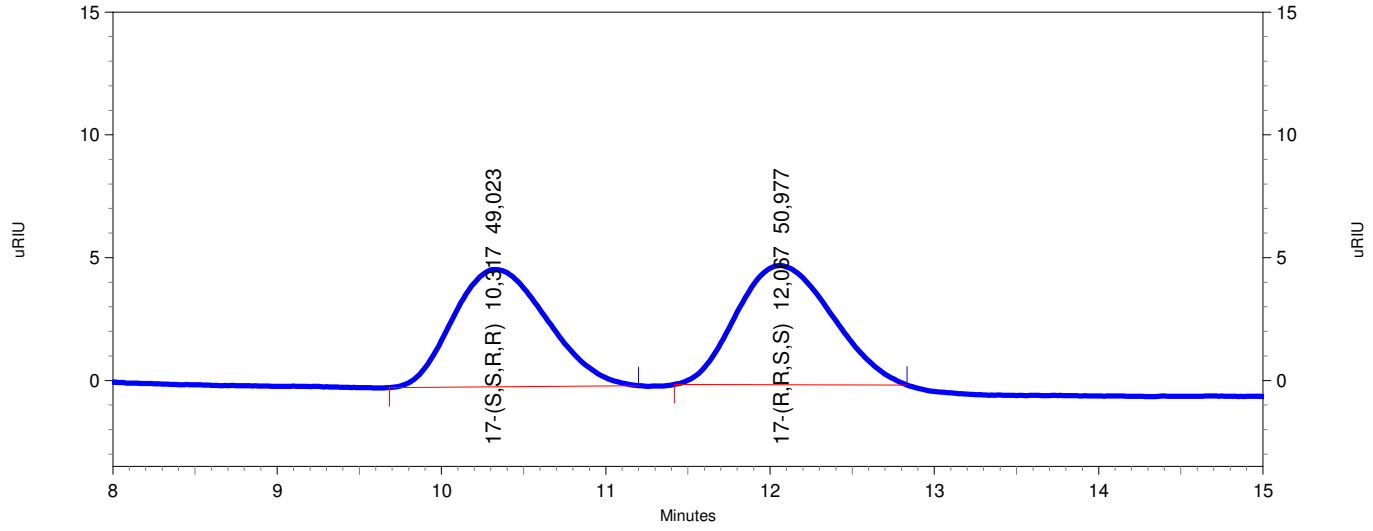
Filename: C:\EZChrom Elite\Enterprise\Projects\Uni Münster\Peter\Data\PEP 12-1 40-60 OJ-RH.dat

Run Time: 28.05.2010 13:03:02
Print Time: 10.10.2012 14:26:18

Overview




*ee*-Determination




Ri-Detektor S 2300 Results

| Name | Retention Time | Area Percent |
|---|---|---|
| Solvent | | |
| 17-(S,S,R,R) | 10,317 | 49,023 |
| 17-(R,R,S,S) | 12,067 | 50,977 |
| Totals | | 100,000 |

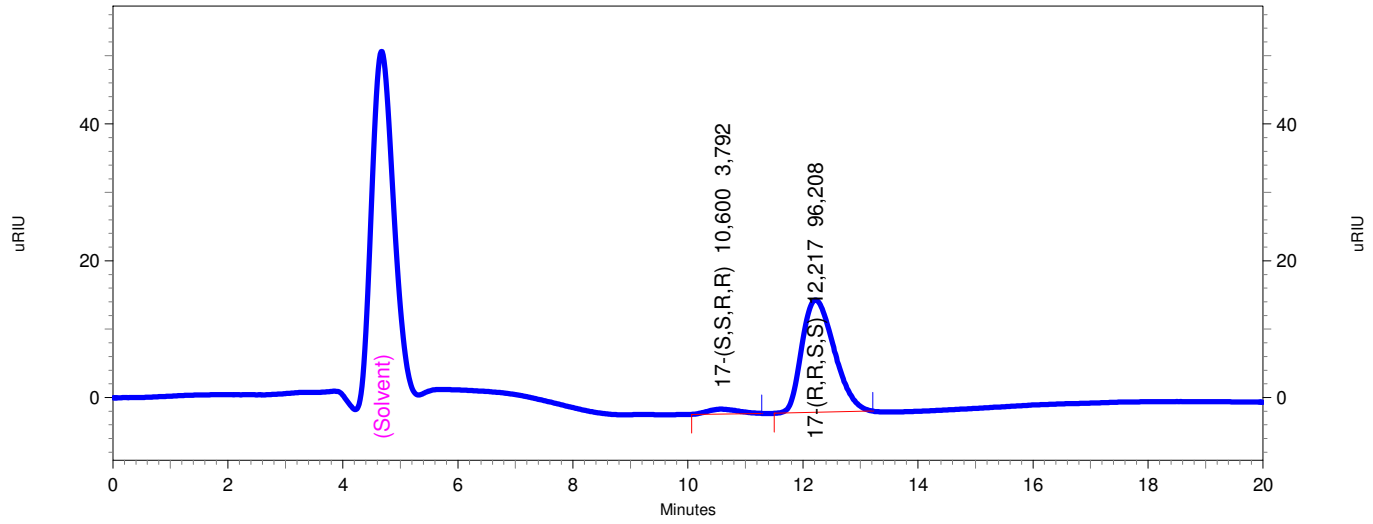
HPLC of the racemic mixture of compound **17**.

Sample ID: PEP 12-2 40-60 OJ-RH

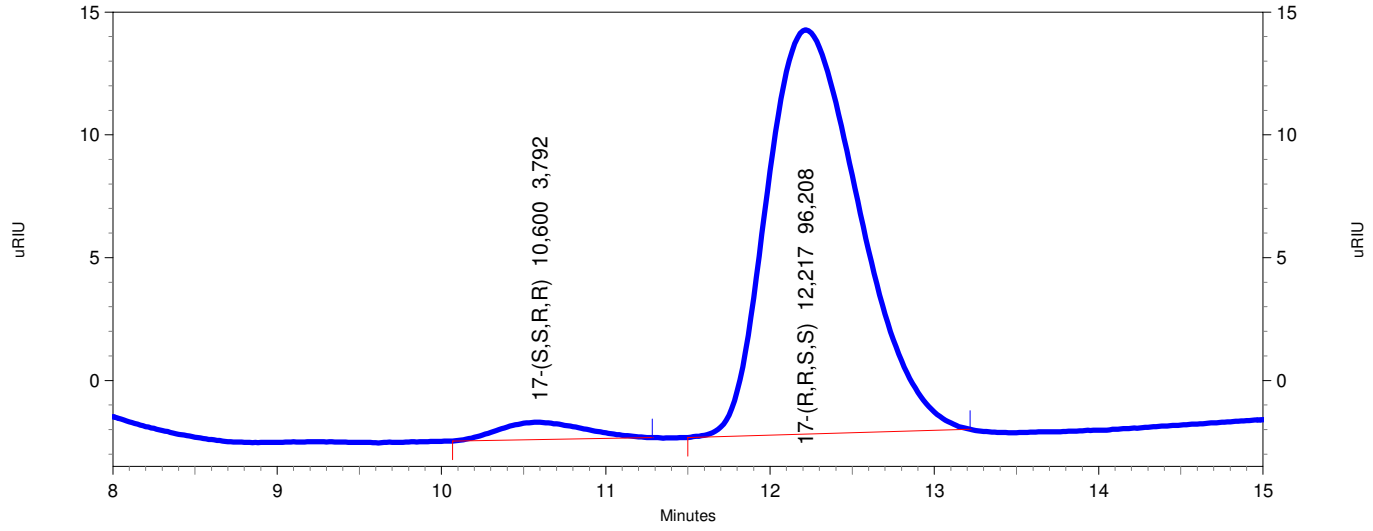
Filename: C:\EZChrom Elite\Enterprise\Projects\Uni Münster\Peter\Data\PEP 12-2 40-60 OJ-RH

Run Time: 28.05.2010 13:48:23
Print Time: 10.10.2012 14:33:35

Overview




*ee*-Determination




Ri-Detektor S 2300 Results

| Name | Retention Time | Area Percent |
|---|---|---|
| Solvent | | |
| 17-(S,S,R,R) | 10,600 | 3,792 |
| 17-(R,R,S,S) | 12,217 | 96,208 |
| Totals | | 100,000 |

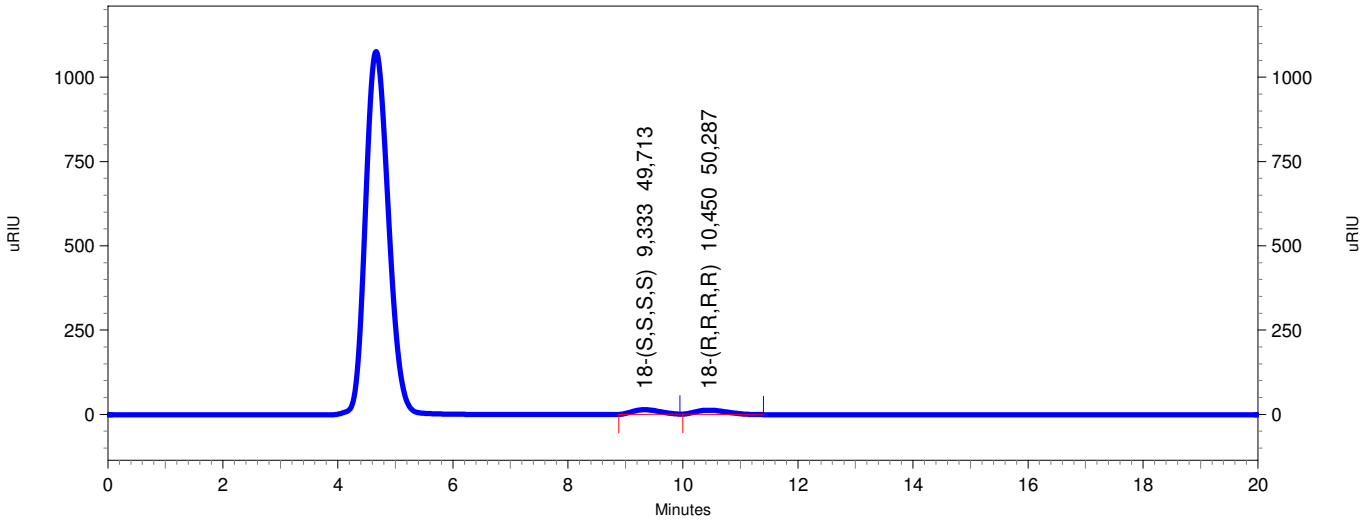
HPLC of (*R*,*R*,*S*,*S*)-**17** (92% *ee*).

Sample ID: PEP 12-4 (40-60) rac OJ-RH

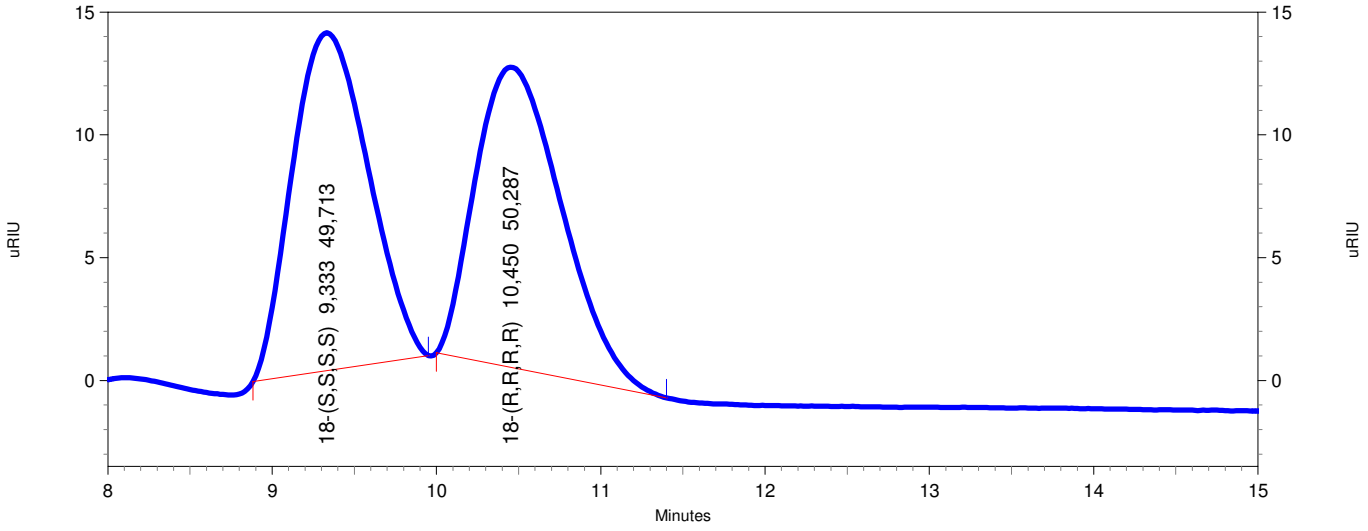
Filename: C:\EZChrom Elite\Enterprise\Projects\Uni Münster\Peter\Data\PEP 12-4 (40-60) rac OJ-RH.dat

Run Time: 02.06.2010 15:39:41
Print Time: 10.10.2012 15:03:52

Overview




*ee*-Determination




Ri-Detektor S 2300 Results

| Name | Retention Time | Area Percent |
|---|---|---|
| 18-(S,S,S,S) | 9,333 | 49,713 |
| 18-(R,R,R,R) | 10,450 | 50,287 |

| | | |
|---|---|---|
| Totals | | 100,000 |

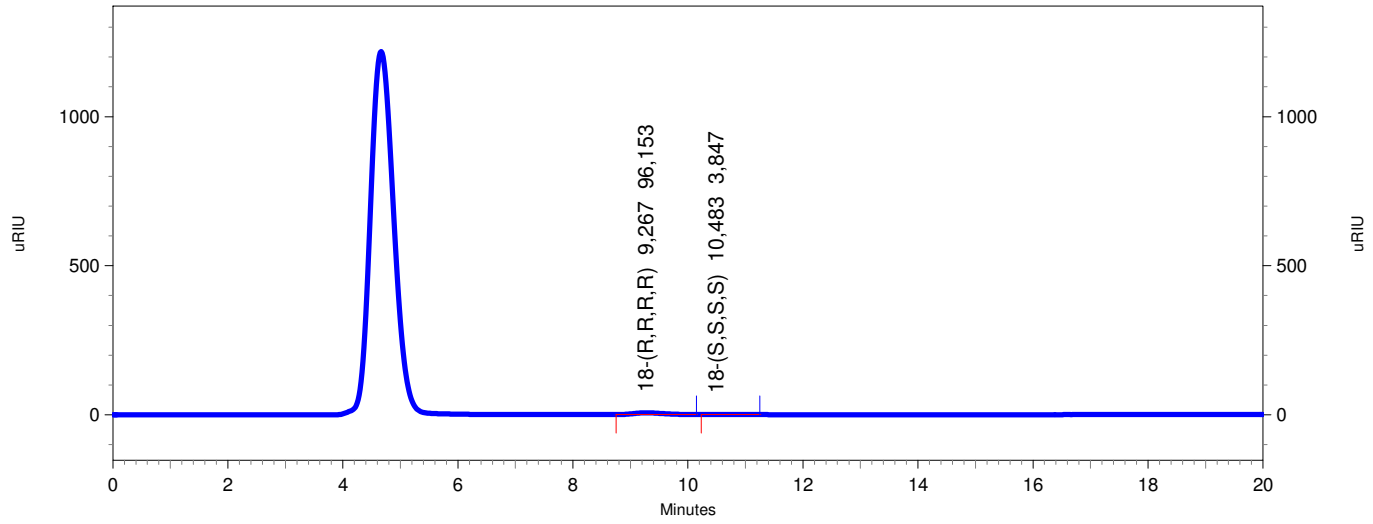
HPLC of the racemic mixture of compound **18**.

Sample ID: PEP 12-3 (40-60) OJ-RH

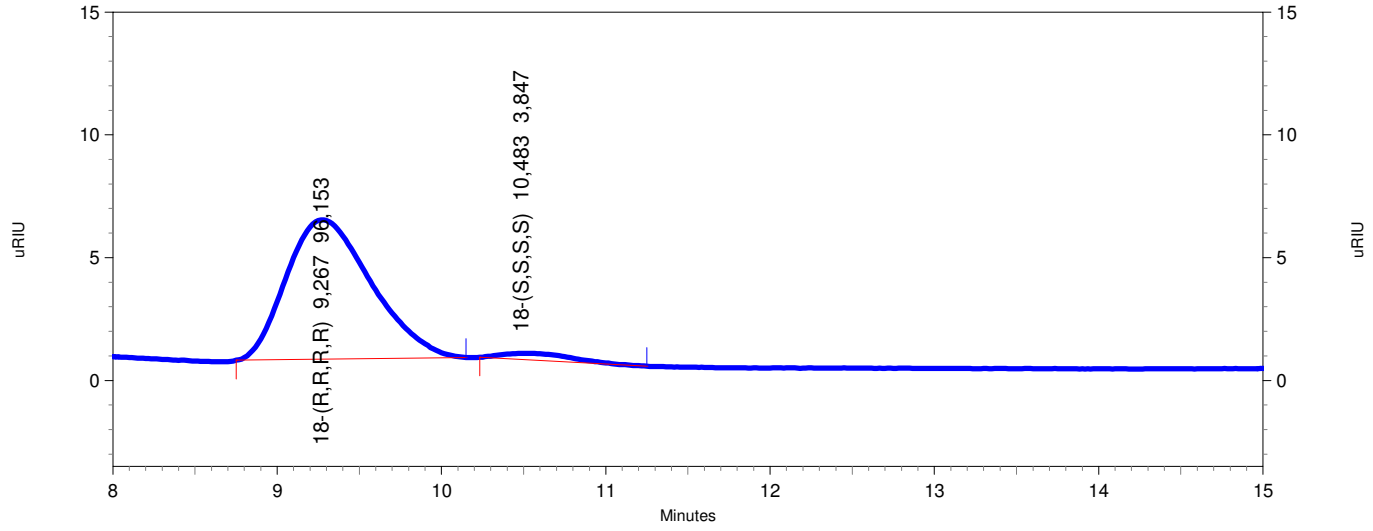
Filename: C:\EZChrom Elite\Enterprise\Projects\Uni Münster\Peter\Data\PEP 12-3 (40-60) OJ-RH.dat

Run Time: 02.06.2010 13:33:54
Print Time: 10.10.2012 14:42:41

Overview




*ee*-Determination




Ri-Detektor S 2300 Results

| Name | Retention Time | Area Percent |
|---|---|---|
| 18-(R,R,R,R) | 9,267 | 96,153 |
| 18-(S,S,S,S) | 10,483 | 3,847 |

| | | |
|---|---|---|
| Totals | | 100,000 |

HPLC of (*R*,*R*,*R*,*R*)-**18** (92% *ee*).