# SUPPORTING INFORMATION

## Highly α-Selective Hydrolysis of α,β-Epoxyalcohols using TBAF

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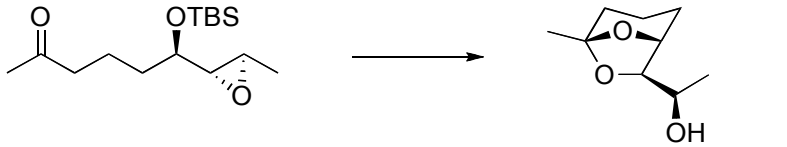
**1. General information**: Starting materials were synthesized as described in cited references or purchased from Sigma-Aldrich or Acros Organics and used without further purification. Sharpless epoxidation and kinetic resolution was performed as described.[1-3] Anhydrous solvents were prepared with 4 Å molecular sieves. Silica gel flash column chromatography was performed on Combiflash RF (Teledyne ISCO®) chromatography systems using ethyl acetate/hexanes or methanol/dichloromethane mixtures as solvents. $^{1}$H and $^{13}$C NMR spectra were obtained on 400, 500, and 600 MHz Varian NMR spectrometers using $CDCl_3$ and acetone-$d_6$ (Cambridge Isotope Laboratories) as solvents. For compounds **4** and **12**, protons and carbons were assigned based on ($^{1}$H,$^{1}$H)-dqfCOSY, ($^{1}$H,$^{1}$H)-NOESY, ($^{1}$H,$^{13}$C)-HSQC, and ($^{1}$H,$^{13}$C)-HMBC spectra.

**2. Procedure for hydrolysis of silylated epoxyalcohols.**

Example: (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)ethanol, (1*R*,1'*R*,5'*R*,7'*R*)-**4**, from silylated epoxyalcohol (6*R*,7*S*,8*R*)-**8**.




(6*R*,7*S*,8*R*)-**8** (1*R*,1'*R*,5'*R*,7'*R*)-**4**

To a mixture of TBDMS-protected epoxyalcohol (6*R*,7*S*,8*R*)-**8**[3] (97% (6*R*,7*S*,8*R*)-diastereomer as determined by $^{1}$H-NMR) 100 mg, 0.35 mmol) and 2 mL acetonitrile in a 20 mL screw cap vial, TBAF (trihydrate, 331 mg, 1.05 mmol) was added, and the resulting mixture was stirred at

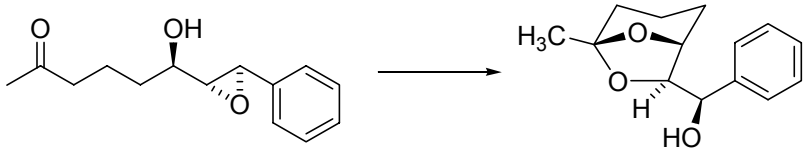
room temperature for 12 h. Solvent was evaporated *in vacuo*, followed by the addition of a small amount of water (20 µL) and acetonitrile (80 µL). The mixture was then stirred at 35-40 $^{o}$C for 24 h. Progress of the reaction was monitored by TLC (methanol:dichloromethane 1:9). For NMR-spectroscopic analysis of the reaction products, solvents were removed *in vacuo* and the residue was diluted with a few drops of $CH_2Cl_2$and filtered over a pad of silica to remove most of the TBAF, using 5% methanol in $CH_2Cl_2$. The filtrate was concentrated and subjected to NMR-spectroscopic analysis, including $^{1}$H-NMR and ($^{1}$H,$^{1}$H)-dqfCOSY spectra. For purification, the crude product was subjected to silica gel flash chromatography (0 to 10 % methanol in $CH_2Cl_2$). (1*R*,1'*R*,5'*R*,7'*R*)-**4** (97% (1*R*,1'*R*,5'*R*,7'*R*)-diastereomer as determined by $^{1}$H-NMR) was obtained in 73% yield (44 mg, 0.26 mmol) as a colorless oil, in addition to 7 mg (4 mmol, 12 %) of epoxyalcohol (6*R*,7*R*,8*R*)-**9**.

(1*R*,1'*R*,5'*R*,7'*R*)-**4**: $^{1}$H NMR (600 MHz, acetone-$d_6$), δ (ppm) 4.41-4.43 (m, 1H, 1'-H), 3.66 (d, *J* = 5.4 Hz, 1H, OH), 3.61 (d, *J* = 7.9 Hz, 1H, 7'-H), 3.39-3.45 (m, 1H, 1-H), 1.80-1.90 (m, 1H, 3'-$H_{ax}$), 1.70-1.76 (m, 1H, 2'-$H_{ax}$), 1.53-1.60 (m, 3H, 3'-$H_{eq}$, 4-H), 1.43-1.47 (m, 1H, 2'-$H_{eq}$), 1.29 (s, 3H, 5'-$CH_3$), 1.14 (d, *J* = 6.4 Hz, 3H, 2-H). $^{13}$C NMR (151 MHz, acetone-$d_6$), δ (ppm) 107.9 (C-5'), 84.7 (C-7'), 76.8 (C-1'), 68.7 (C-1), 35.5 (C-4'), 28.4 (C-2'), 25.2 (5'-$CH_3$), 20.1 (C-2), 17.9 (C-3'). ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_9H_{16}O_3Na$, 195.10; found 195.1.

Minor diastereomer, (1*S*,1'*R*,5'*R*,7'*S*)-**4**: $^{1}$H NMR (600 MHz, acetone-$d_6$), δ (ppm) 4.29 (dq, *J* = 9.4, 6.3 Hz), 1H, 1'-H), 3.79 (d, *J* = 5.2 Hz, 1H, OH), 3.64 (dd, *J* = 9.4, 3.7 Hz, 1H, 7'-H), 3.93-3.99 (m, 1H, 1-H), 1.68-1.75 (m, 1H, 2'-$H_{ax}$), 1.78-1.83 (m, 1H, 2'-$H_{eq}$), 1.52-1.63 (m, 2H, 4'-H, 3'-$H_{eq}$), 1.80-1.90 (m, 2H, 4'-H, 3'-$H_{ax}$), 1.30 (s, 3H, 5'-$CH_3$), 1.27 (d, *J* = 6.3 Hz, 3H, 2-H).

**3. Procedure for hydrolysis of unsilylated epoxyalcohols.**

Example: (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)-1-phenyl-methanol, **12**.



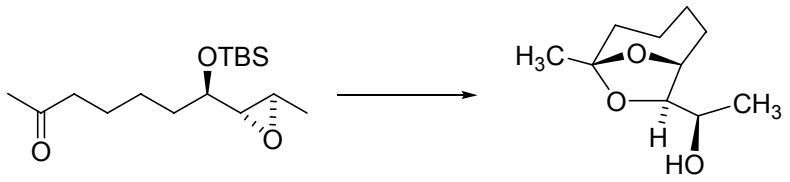

(6*R*,7*R*,8*R*)-**11** (1*R*,1'*R*,5'*R*,7'*R*)-**12**

Alcohol (6*R*,7*R*,8*R*)-**11** (≥99.5% (6*R*,7*R*,8*R*)-diastereomer as determined by $^1$H-NMR, 110 mg, 0.47 mmol)**,** which was synthesized analogous to the procedures described for the preparation of (6*R*,7*S*,8*R*)-**8,**[3] was stirred with TBAF (trihydrate, 480 mg, 1.5 mmol), water (30 µL) and acetonitrile (100 µL) 35-40 $^o$C for 20 h. The reaction was monitored by TLC and NMR spectroscopy as described above. Silica gel flash chromatography (0 to 10 % methanol in $CH_2Cl_2$) yielded (1*R*,1'*R*,5'*R*,7'*R*)-**12** (≥99.5% (1*R*,1'*R*,5'*R*,7'*R*)-diastereomer as determined by $^1$H-NMR) was obtained in 87% yield (96 mg, 0.41 mmol) as a colorless oil. $^1$H NMR (600 MHz, acetone-$d_6$), δ (ppm) 7.39-7.42 (m, 2 H), 7.29-7.3 (m, 2H), 7.22-7.25 (m, 1H), 4.58-4,60 (m, 1H, 1'-H), 4.41 (d, *J* = 4.0 Hz, 1 H, OH), 4.35 (dd, *J* = 7.9, 4.0 Hz, 1H, 1-H), 3.95 (d, *J* = 8.0 Hz, 1H, 7'-H), 1.73-1.84 (m, 2H, 2'-H and 3'-H)), 1.46-1.59 (m, 4H, 2'-H, 3'-H and 4'-H), 1.32 (s, 3H, 5'-$CH_3$). $^{13}$C NMR (151 MHz, acetone-$d_6$), δ (ppm) 143.9, 128.4, 128.0, 127.7, 108.5 (C-5'), 84.1 (C-7'), 77.4 (C-1'), 74.9 (C-1), 34.4 (C-4'), 28.3 (C-2'), 25.1 (5'-$CH_3$), 17.8 (C-3'). ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_{14}H_{18}O_3Na$, 257.12; found 257.1.

**4. Spectroscopic data of additional hydrolysis products listed in Scheme 2.**

Racemic allylic alcohols required as starting materials for Sharpless epoxidation were prepared from appropriate α,β-unsaturated aldehydes and Grignard reagents using described procedures.[3] Sharpless epoxidation and kinetic resolution was performed as usual,[1,3] and isolated epoxyalcohols were silylated. In case of **14**, **16**, and **18**, silylated epoxyalcohols featuring terminal double bonds were converted into the corresponding methyl ketones via Wacker oxidation as described previously (Scheme 1).[3]

(1*R*,1'*R*,6'*R*,8'*R*)-1-(6'-Methyl-7',9'-dioxabicyclo[4.2.1]nonan-8'-yl)ethanol, **15**.




(7*R*,8*S*,9*R*)-**14** (1*R*,1'*R*,6'*R*,8'*R*)-**15**

Reaction of (7*R*,8*S*,9*R*)-**14** (>98.5% (7*R*,8*S*,9*R*)-diastereomer) yielded (1*R*,1'*R*,6'*R*,8'*R*)-**15** (>98.5% (1*R*,1'*R*,6'*R*,8'*R*)-diastereomer) in 82% yield as a colorless liquid. $^{1}$H NMR (400 MHz, $CDCl_3$), δ (ppm) 4.45-4.49 (m, 1H), 3.69-3.77 (m, 1H), 3.67 (dd, *J* = 3.3, 5.8 Hz, 1H), 1.90-2.03 (m, 2H), 1.80-1.90 (m, 1H), 1.70-1.80 (m, 1H), 1.69-1.70 (m, 2H), 1.50-1.60 (m, 3H), 1.41 (s, 3H), 1.18 (d, *J* = 6.3 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$), δ (ppm) 112.4, 85.7, 77.4, 68.8, 41.5, 35.0, 28.3, 24.0, 23.6, 19.2. ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_{10}H_{18}O_3Na$, 209.12; found 209.1.

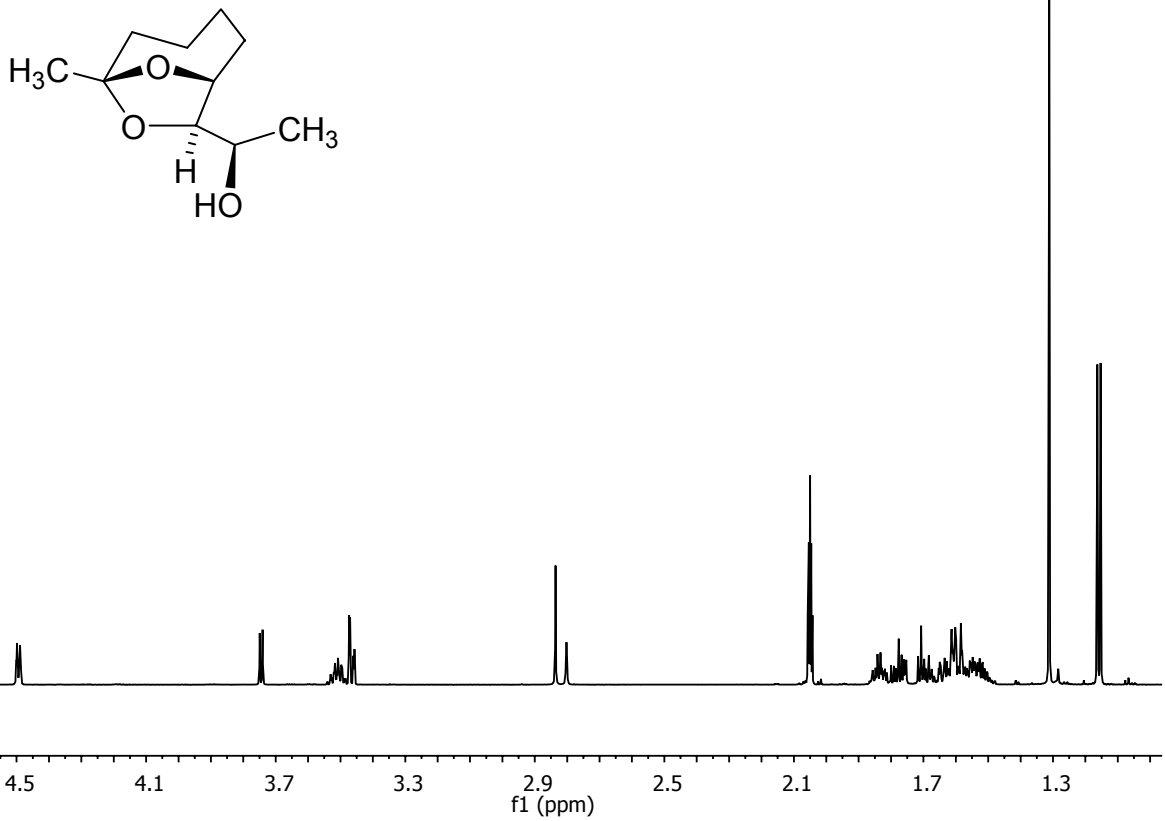



**Figure S1.** $^{1}$H-NMR spectrum (600 MHz, acetone-$d_6$) of (1*R*,1'*R*,6'*R*,8'*R*)-**15** (>98.5% (1*R*,1'*R*,6'*R*,8'*R*)-diastereomer) derived from a sample of (7*R*,8*S*,9*R*)-**14** (>98.5% (7*R*,8*S*,9*R*)-diastereomer)). **For additional spectra of this compound see Figures S2, S10-S15.**

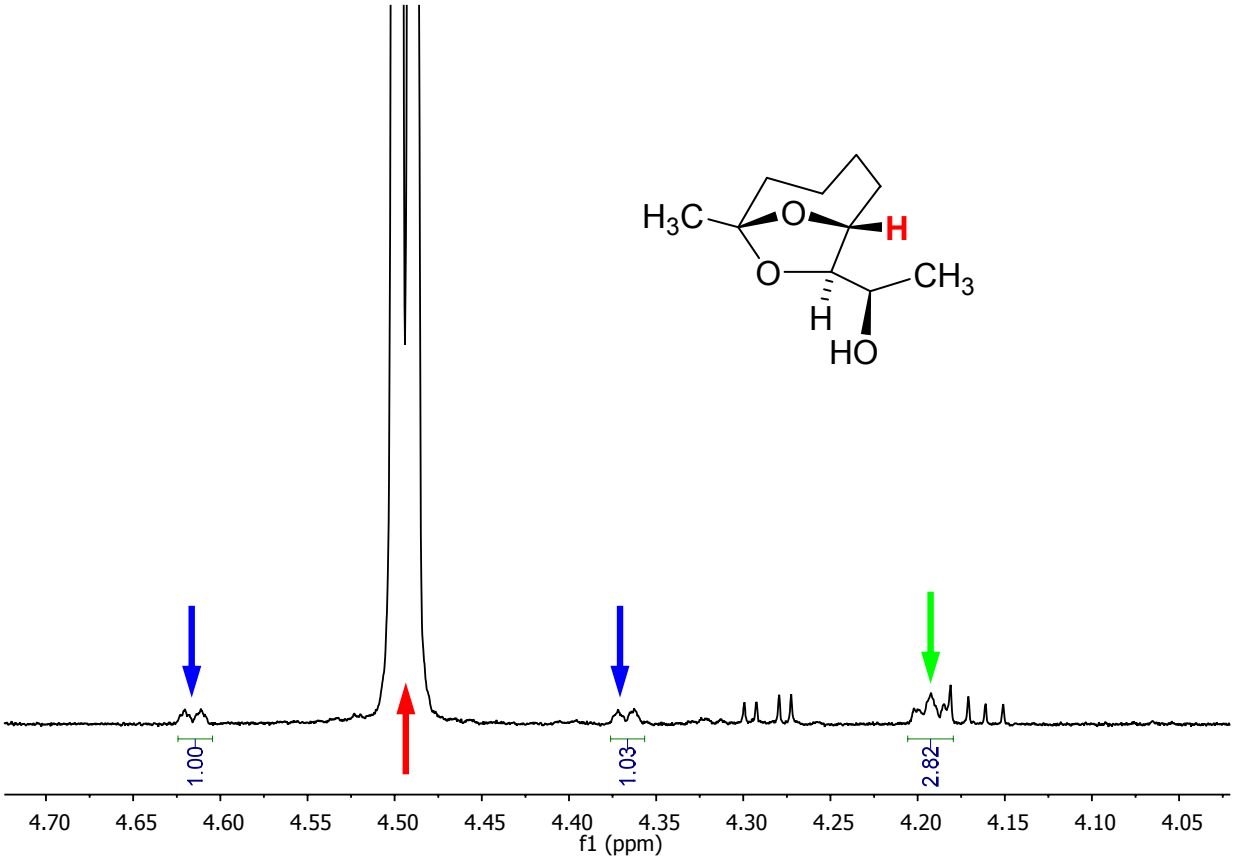
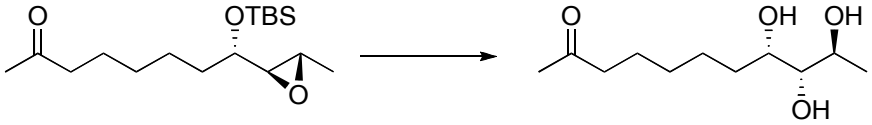



**Figure S2.** 4.0-4.7 ppm region of the $^{1}$H-NMR spectrum (600 MHz, acetone-$d_6$) of (1*R*,1'*R*,6'*R*,8'*R*)-**15** (>98.5% (1*R*,1'*R*,6'*R*,8'*R*)-diastereomer), showing $^{13}$C-satellites (blue arrows, 0.5% intensity of the parent signal) of the proton in position 1 (red) in (1*R*,1'*R*,6'*R*,8'*R*)-**15**, as well as the corresponding signal of the main diastereomer, (1*S*,1'*R*,6'*R*,8'*S*)-**15**, in this sample (green arrow). The integral of the green signal is less than three times the integral of a $^{13}$C-satellite, indicating a diastereomeric ratio of better than 98.5:1.5 for (1*R*,1'*R*,6'*R*,8'*R*)-**15** and (1*S*,1'*R*,6'*R*,8'*S*)-**15**, respectively. Note: The small signals (two dd's) at 4.16 and 4.27 ppm represent trace amounts of a triglyceride contamination. **For additional spectra of this compound see Figures S10-S15.**

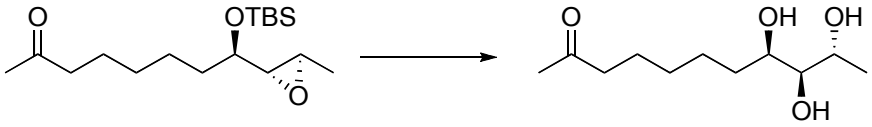
(8*S*,9*S*,10*S*)-8,9,10-Trihydroxyundecan-2-one, (8*S*,9*S*,10*S*)-**17**.




(8*S*,9*R*,10*S*)-**16** (8*S*,9*S*,10*S*)-**17**

(8*S*,9*S*,10*S*)-**17**: 68% yield, white solid, mp 45.6-47 °C. $^1$H NMR (400 MHz, $CDCl_3$), δ (ppm) 3.86-3.95 (m, 1H), 3.74-3.82 (m, 1H), 3.63 (s, 1H), 3.50-3.59 (m, 2H), 3.22-3.29 (m, 1H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.11 (s, 3H), 1.49-1.59 (m, 3H), 1.48-1.38 (m, 2H), 1.24-1.35 (m, 3H), 1.20 (d, *J* = 6.5 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$), δ (ppm) 209.8, 76.0, 70.7, 70.1, 43.8, 33.5, 30.2, 29.2, 25.6, 23.9, 19.1. ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_{11}H_{22}O_4Na$, 241.14; found 241.1.

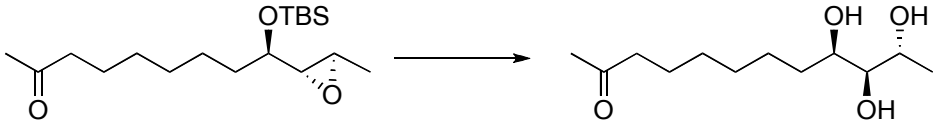
(8*R*,9*R*,10*R*)-8,9,10-Trihydroxyundecan-2-one, (8*R*,9*R*,10*R*)-**17.**




(8*R*,9*S*,10*R*)-**16** (8*R*,9*R*,10*R*)-**17**

(8*R*,9*R*,10*R*)-**17**: 82% yield, white solid, mp 45-47 °C. Spectroscopic data were identical to those of (8*S*,9*S*,10*S*)-**17**.

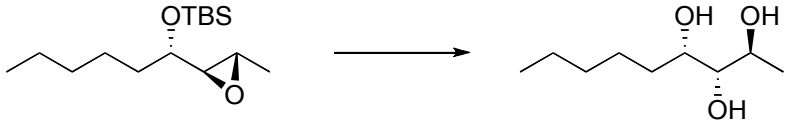
(9*R*,10*R*,11*R*)-9,10,11-Trihydroxydodecan-2-one, **19**.




**18** **19**

**19**: 76% yield, white solid, mp 54-56 °C. $^1$H NMR (400 MHz, $CDCl_3$), δ (ppm) 3.88-3.97 (m, 1H), 3.76-3.83 (m, 1H), 3.49 (d, *J* = 5.8 Hz, 1H), 3.44 (d, *J* = 7.3 Hz, 1H), 3.39 (d, *J* = 4.4 Hz, 1H), 3.23-3.30 (m, 1H), 2.40 (t, *J* = 7.4 Hz, 2H), 2.11 (s, 3H), 1.49-1.60 (m, 2H), 1.38-1.49 (m, 2H), 1.23-1.36 (m, 6H), 1.21 (d, *J* = 6.6 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$), δ (ppm) 209.8, 75.9, 70.8, 70.2, 43.8, 33.6, 30.2, 29.6, 29.3, 25.7, 23.9, 19.2. ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_{12}H_{24}O_4Na$, 255.16; found 255.2.

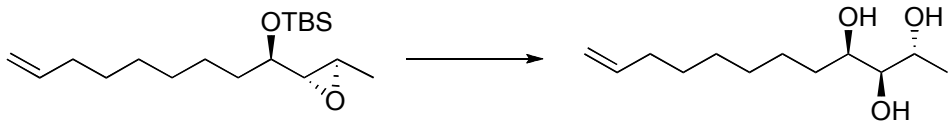
(2*S*,3*S*,4*S*)-Nonane-2,3,4-triol, **21**.




**20** **21**

65% yield, colorless liquid, $^{1}$H NMR (400 MHz, $CDCl_3$), δ (ppm) 3.95-4.03 (m, 1H), 3.84-3.89 (m, 1H), 3.29-3.34 (m, 1H), 2.45-2.80 (broad m, 3H, OH), 1.27-1.67 (m, 8H), 1.25 (d, *J* = 6.6 Hz, 3H), 0.89 (t, *J* = 6.6 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$), δ (ppm) 75.6, 70.9, 70.6, 33.9, 32.1, 25.6, 22.9, 19.2, 14.4. ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_9H_{20}O_3Na$, 199.13; found 199.1.

(2*R*,3*R*,4*R*)-Dodec-11-ene-2,3,4-triol, **23**.

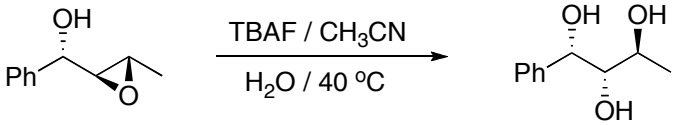



**22** **23**

83% yield, white solid, mp 47-48.5 °C. $^{1}$H NMR (400 MHz, $CDCl_3$), δ (ppm) 5.80 (ddt, *J* = 17.0, 10.0, 6.7 Hz, 1H), 4.89-5.02 (m, 2H), 3.89-4.01 (m, 1H), 3.77-3.86 (m, 1H), 3.22-3.52 (m, 4H), 1.98-2.07 (m, 2H), 1.25-1.61 (m, 10H), 1.22 (d, *J* = 6.6 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$), δ (ppm) 139.2, 114.4, 75.8, 70.9, 70.4, 34.0, 33.8, 29.7, 29.4, 29.1, 25.9, 19.1. ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_{12}H_{24}O_3Na$ 239.16; found 239.2.

## 5. Synthesis of 5-deoxy-L-arabinose

(1*S*,2*S*,3*S*)-1-Phenylbutane-1,2,3-triol, **25**.

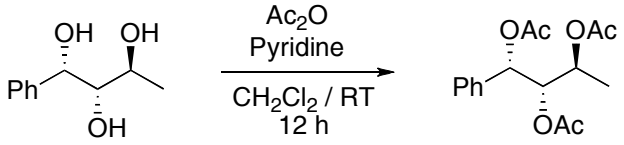



**24** **25**

Epoxyalcohol **24**[1] (1.05 g, 6.40 mmol, >98% *de*) was subjected to the general method for hydrolysis of epoxyalcohols as described above to afford triol **25** (918 mg, 78%, >98% *de*) as a

colorless liquid. $^1$H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.29-7.40 (m, 5H), 4.49 (dd, *J* = 4.3, 3.2 Hz, 1H), 3.87 (qdd, *J* = 6.5, 5.4, 4.2 Hz, 1H), 3.65 (dt, *J* = 5.0, 4.2 Hz, 1H), 3.08 (d, *J* = 3.3 Hz, 1H, OH), 2.56 (d, *J* = 5.0 Hz, 1 H OH), 2.27 (d, *J* = 5.4 Hz, 1H), 1.30 (d, *J* = 6.5 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$), δ (ppm) 141.3, 128.6, 127.9, 126.7, 78.5, 73.2, 68.8, 18.6. ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_{10}H_{14}O_3Na$, 205.09; found 205.2.

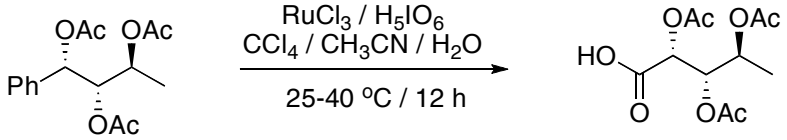
(1*S*,2*S*,3*S*)-1-Phenylbutane-1,2,3-triyl triacetate, **27**.




**25** **27**

Triol **25** (800 mg, 4.39 mmol) was placed into a round-bottom flask under $N_2$ and dissolved in 20 mL dichloromethane. To this solution was added pyridine (7.1 mL, 87.9 mmol) at 0 °C. The reaction mixture was stirred for 10 min and acetic anhydride (4.15 mL, 43.9 mmol) was added dropwise. Subsequently, the reaction mixture was slowly warmed to RT and stirred for 12 h. After the reaction was complete, as determined by TLC, the reaction mixture was cooled to 0 °C and 10 mL methanol was added dropwise. Solvents were evaporated *in vacuo* and the residue was subjected to flash chromatography on silica (15% ethyl acetate/hexane) to afford **27** (1.06 g, 80%) as a white solid, mp 88-90 °C. $^1$H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.39-7.28 (m, 5H), 5.94 (d, *J* = 6.1 Hz, 1H), 5.45 (t, *J* = 5.0 Hz, 1H), 4.88 (dq, *J* = 6.5, 5.0 Hz, 1H), 2.07 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.18 (d, *J* = 6.5 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$), δ (ppm) 170.2, 170.04, 170.02, 136.2, 129.0, 128.9, 127.4, 75.1, 73.6, 68.1, 21.3, 21.2, 20.9, 15.6. ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_{16}H_{20}O_6Na$, 331.12; found 331.2.

(2*R*,3*S*,4*S*)-2,3,4-Triacetoxypentanoic acid**, 28**.[4]

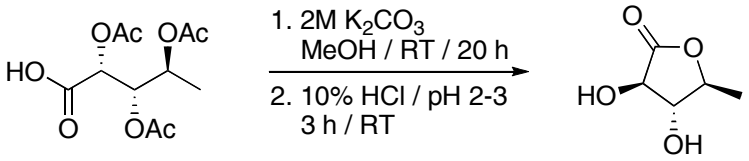



**27** **28**

A 100 mL round-bottom flask equipped with an open air condenser and a stir bar was charged with **27** (1.0 g, 3.24 mmol), carbon tetrachloride (6.4 mL), acetonitrile (6.4 mL) and water (9.6

mL). Periodic acid (10.5 g, 14.1 mmol) was added and the mixture was stirred until both the aqueous and organic phase became clear. The mixture was cooled to 10 $^{o}$C and ruthenium trichloride hydrate was added (13 mg, 0.06 mmol). The reaction mixture was stirred at 25-30 $^{o}$C until all the starting material had disappeared, as monitored by TLC (10% methanol/dichloromethane). The resulting mixture was cooled to 0 $^{o}$C, ether (10 mL) was added and the mixture stirred vigorously for 10 min. The flask contents were transferred to a separating funnel and extracted with ether (3x100 mL). The combined organic layers were washed with brine, dried, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica (5-8% methanol/dichloromethane) affording **28** (715 mg, 80%) as a colorless liquid. $^{1}$H NMR (400 MHz, $CDCl_3$), δ (ppm) 5.50 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.39 (d, *J* = 2.5 Hz, 1H), 5.09 (dq, *J* = 8.3, 6.3 Hz, 1H), 2.17 (s, 3H), 2.11 (s, 3H), 2.03 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$), δ (ppm) 171.8, 170.4, 170.24, 170.20, 72.7, 69.7, 67.4, 22.2, 20.8, 20.6, 16.8. ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_{11}H_{16}O_8Na$, 299.07; found 299.2.

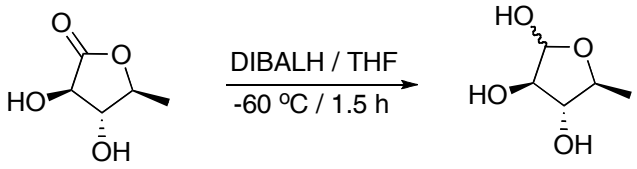
(3*R*,4*S*,5*S*)-3,4-Dihydroxy-5-methyldihydrofuran-2(3*H*)-one, **29**.[5]




**28** **29**

To a solution of **28** (700 mg, 2.53 mmol) in methanol (20 mL) was added 2M aqueous $K_2CO_3$ (6.33 mL, 12.68 mmol) at 4 $^{o}$C, and the resulting mixture was stirred at RT for 20 h. Subsequently, the mixture was cooled to 0 $^{o}$C and acidified to pH 2-3 with 10% HCl and stirred at RT for an additional 3 h. Solvents were evaporated *in vacuo* and the residual white solid was washed with methanol/ethyl acetate (1:1). Washings were combined and dried over anhydrous sodium sulfate and concentrated. The crude product was purified by flash chromatography on silica (12% methanol/dichloromethane) to afford **29** (260 mg, 78%) as a white solid. mp 123.5-125 $^{o}$C, $^{1}$H NMR (400 MHz, $CD_3OD$), δ (ppm) 4.29 (d, *J* = 8.9 Hz, 1H), 4.16 (dq, *J* = 8,0, 6.2 Hz, 1H), 3.77 (dd, *J* = 8.9, 8.0 Hz, 1H), 1.42 (d, *J* = 6.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CD_3OD$), δ (ppm) 176.6, 80.8, 78.7, 75.7, 18.3. ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_5H_8O_4Na$, 155.03; found 155.0.

5-Deoxy-L-arabinose, **26**.[6]




**29** **26**

To a solution of lactone **29** (57 mg, 0.43 mmol) in THF (25 mL) at -60 °C under $N_2$ was added a 1.0 M solution of DIBALH in toluene (1.07 mL, 1.07 mmol) over a period of 1 h. After the addition was complete, the reaction mixture was stirred for an additional 30 min at -60 °C. The mixture was hydrolyzed with water (700 μL), and a saturated solution of $NaHCO_3$ was added -60 °C until pH = 9-10 was reached. Subsequently, the reaction mixture was warmed to 32-35 °C and filtered through Celite 545, using methanol to wash the filter cake. The filtrate was concentrated *in vacuo* and purified by flash chromatography on silica (5-20% methanol in dichloromethane) to provide **26** (25 mg, 43%) as a viscous oil, in addition to 23 mg of a mixture of starting material (**29**) and **26**, which was re-chromatographed yielding a second batch of **26** (14 mg, 24%). $^1$H NMR (major anomer, 400 MHz, $CD_3OD$), δ (ppm) 5.07 (dd, *J* = 2.5, 0.5 Hz, 1H), 4.02 (dq, *J* = 7.2, 6.2 Hz, 1H), 3.88 (dd, *J* = 5.0, 2.5 Hz, 1H), 3.52 (ddd, *J* = 7.2, 5.0, 0.5 Hz, 1H), 1.27 (d, *J* = 6.2 Hz, 3H). $^{13}$C NMR (125 MHz, $CD_3OD$), δ (ppm) 103.2, 84.8, 83.8, 79.4, 18.9. ESIMS (*m/z*): $[M+Na]^+$ calcd. for $C_5H_{10}O_4Na$, 157.05; found 157.0.

**6. References.**

(1) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237-6240.

(2) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922-1925.

(3) Francke, W.; Schroder, F.; Philipp, P.; Meyer, H.; Sinnwell, V.; Gries, G. *Bioorg. Med. Chem.* **1996**, *4*, 363-74.

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(5) Torii, S.; Inokuchi, T.; Masatsugu, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3629-3630.

(6) Fernandez, A. M.; Duhamel, L. *J. Org. Chem.* **1996**, *61*, 8698-8700.

**Figure S3.** (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)ethanol, (1*R*,1'*R*,5'*R*,7'*R*)-**4**, $^{1}$H NMR spectrum, acetone-$d_6$, 600 MHz.

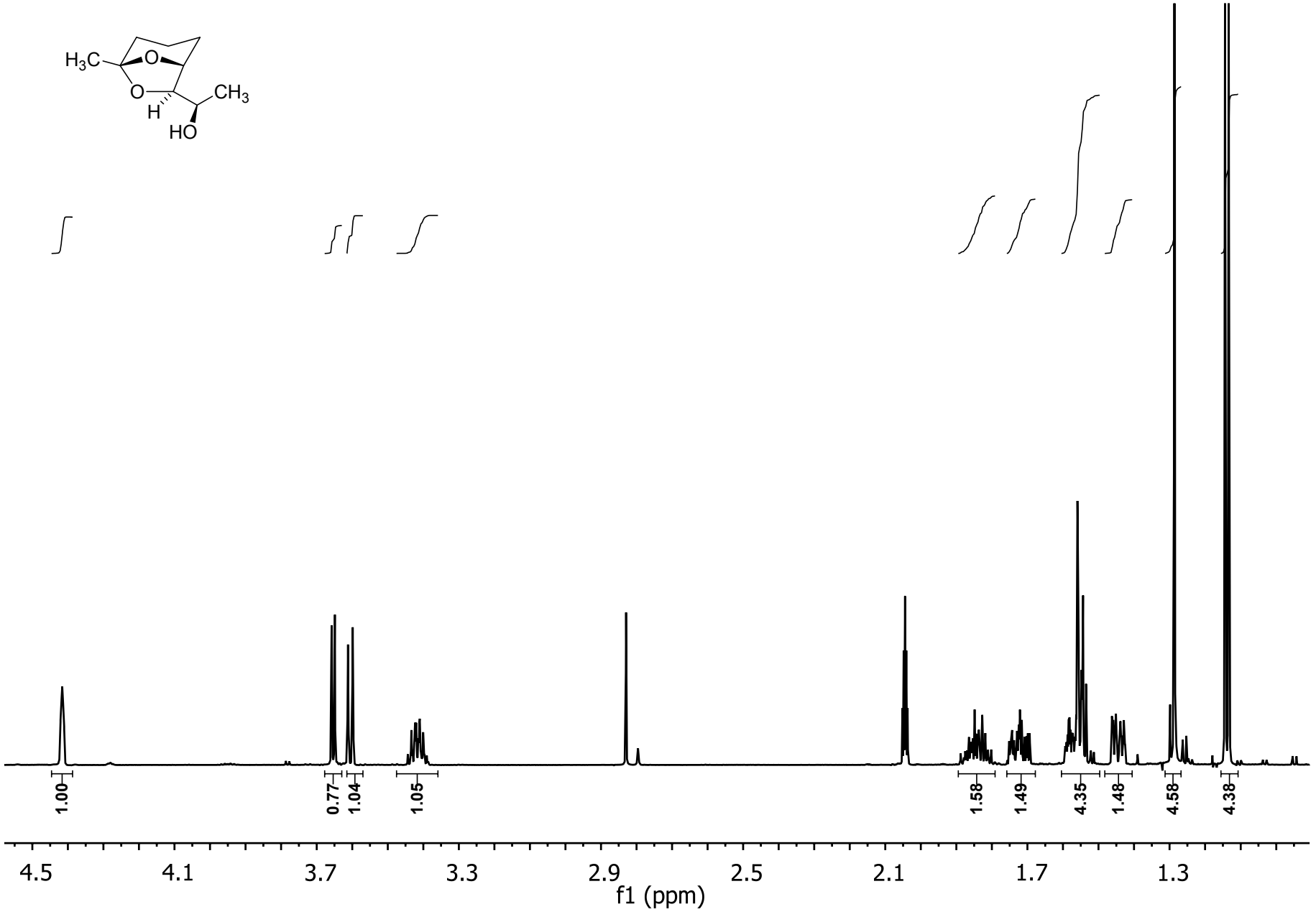


**Figure S4.** (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)ethanol, (1*R*,1'*R*,5'*R*,7'*R*)-**4**, dqfCOSY spectrum, acetone-$d_6$, 600 MHz.

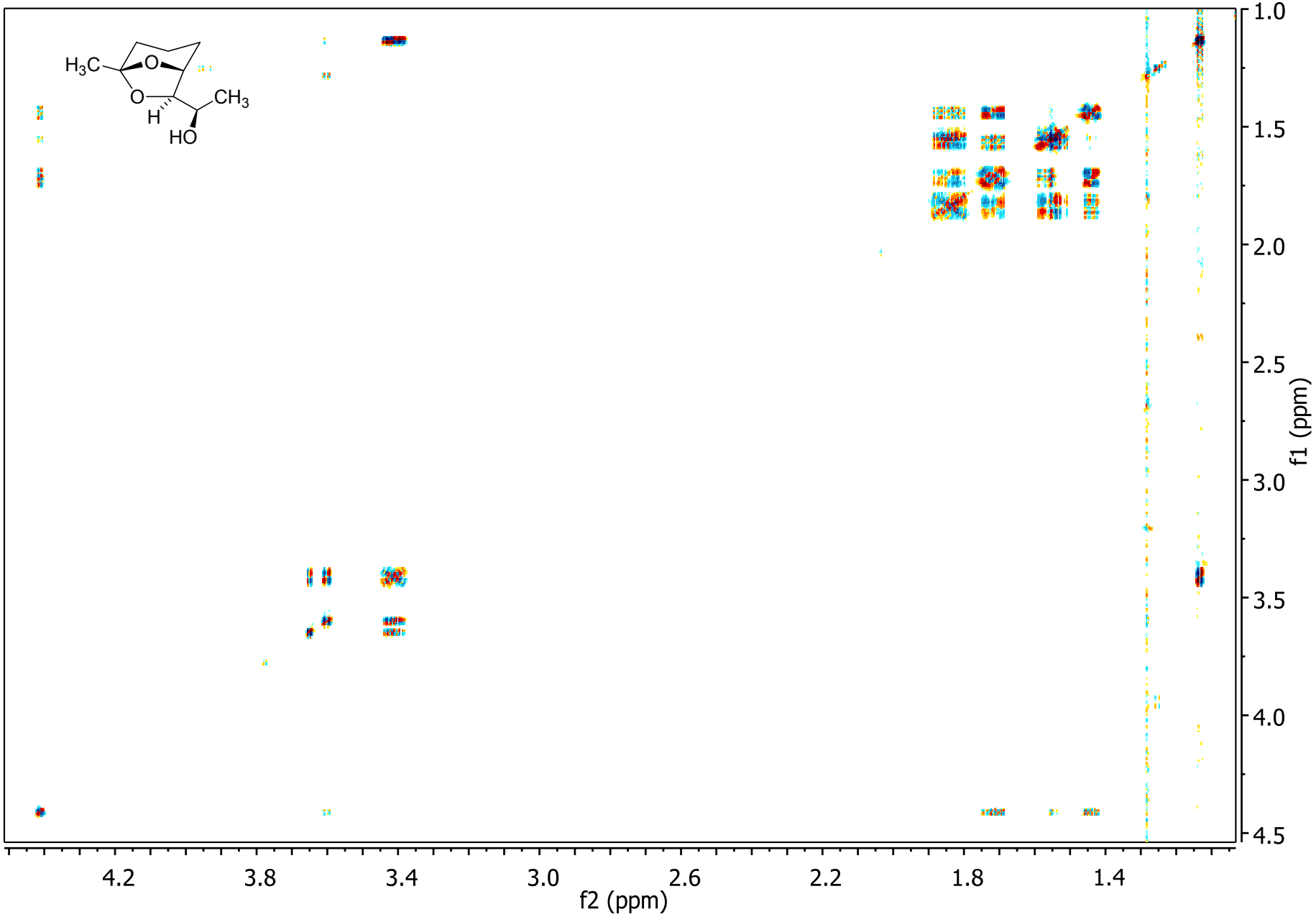


**Figure S5.** (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)ethanol, (1*R*,1'*R*,5'*R*,7'*R*)-**4**, coupled HSQC spectrum, acetone-$d_6$, 600 MHz.

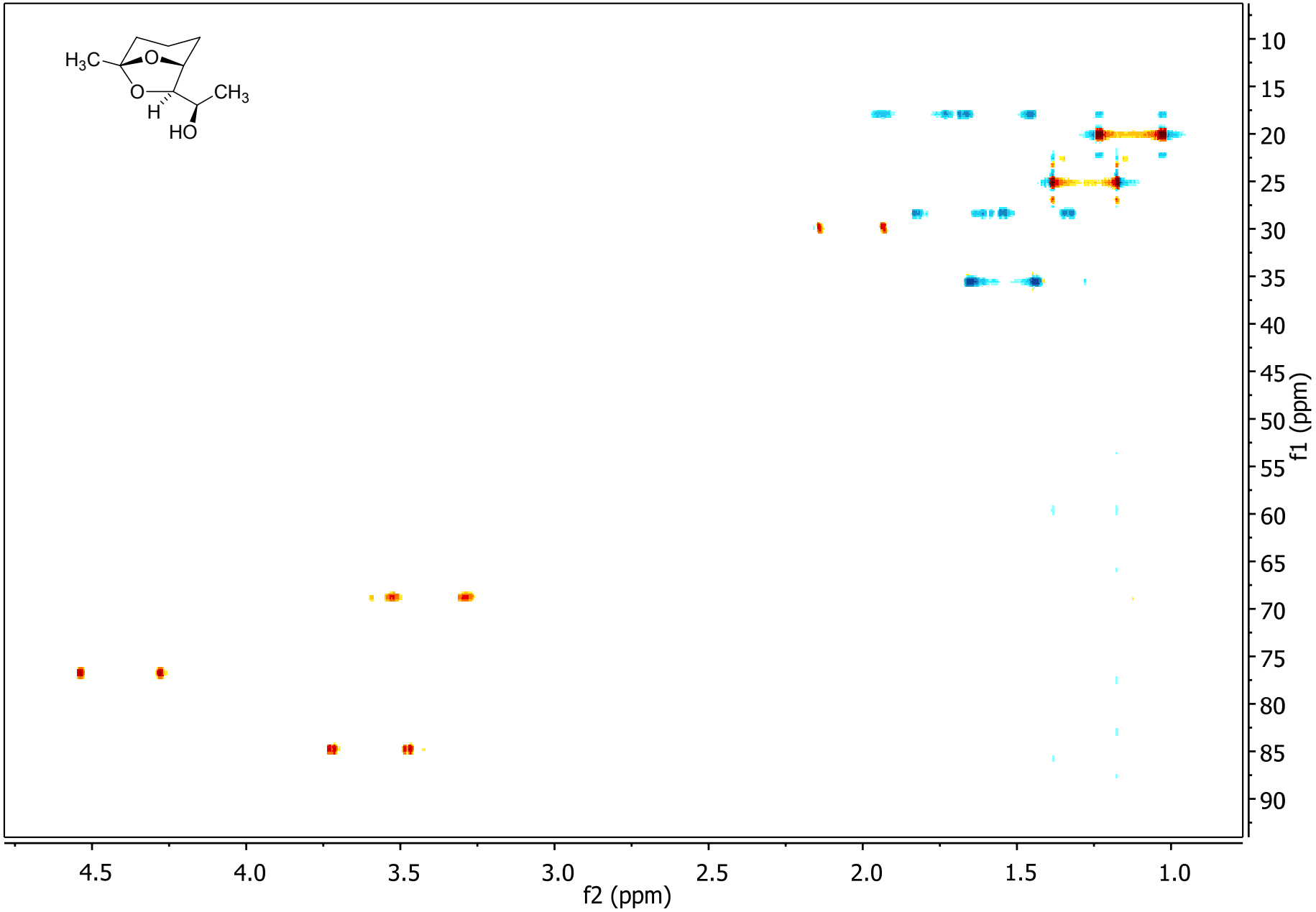


**Figure S6.** (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)ethanol, (1*R*,1'*R*,5'*R*,7'*R*)-**4**, HMBC spectrum, acetone-$d_6$, 600 MHz.

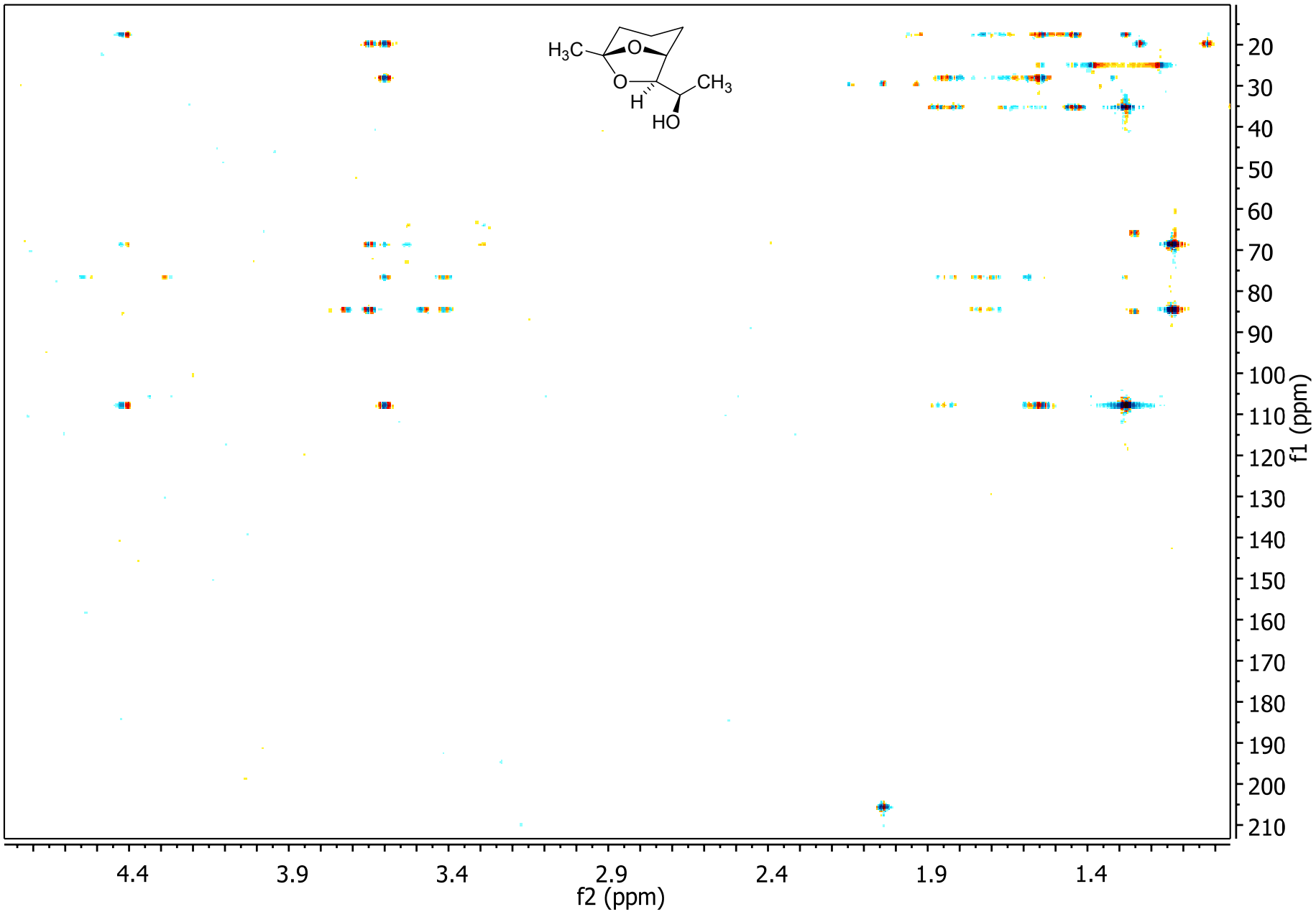


**Figure S7.** (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)-1-phenyl-methanol, **12**, $^{1}$H NMR spectrum, $CDCl_3$, 400 MHz.

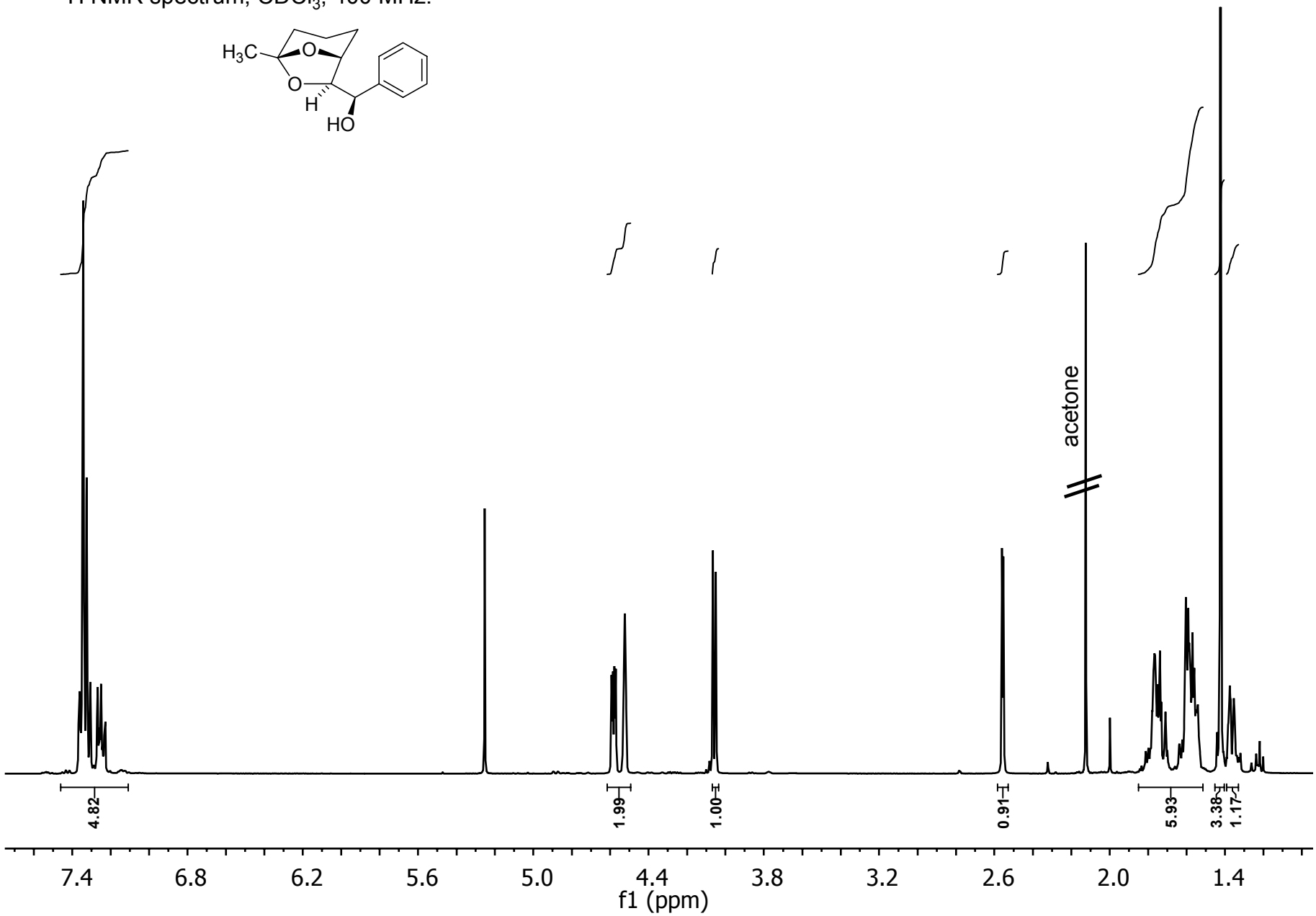
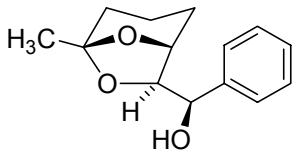


**Figure S8.** (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)-1-phenyl-methanol, **12**, $^{13}C$ NMR spectrum, $CDCl_3$, 125 MHz.



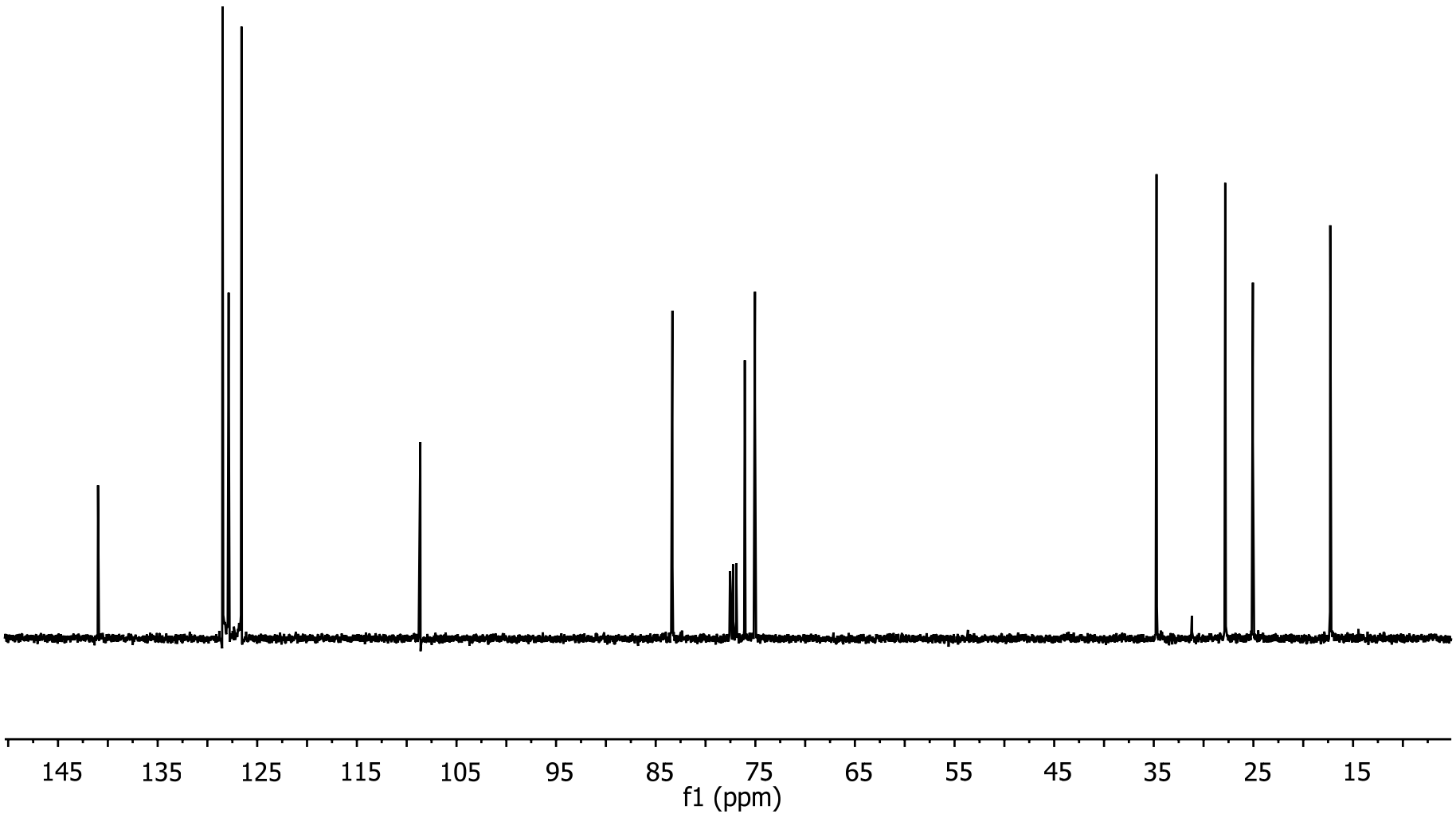



**Figure S9.** (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)-1-phenyl-methanol, **12**, $^{1}$H NMR spectrum, acetone-$d_6$, 600 MHz.

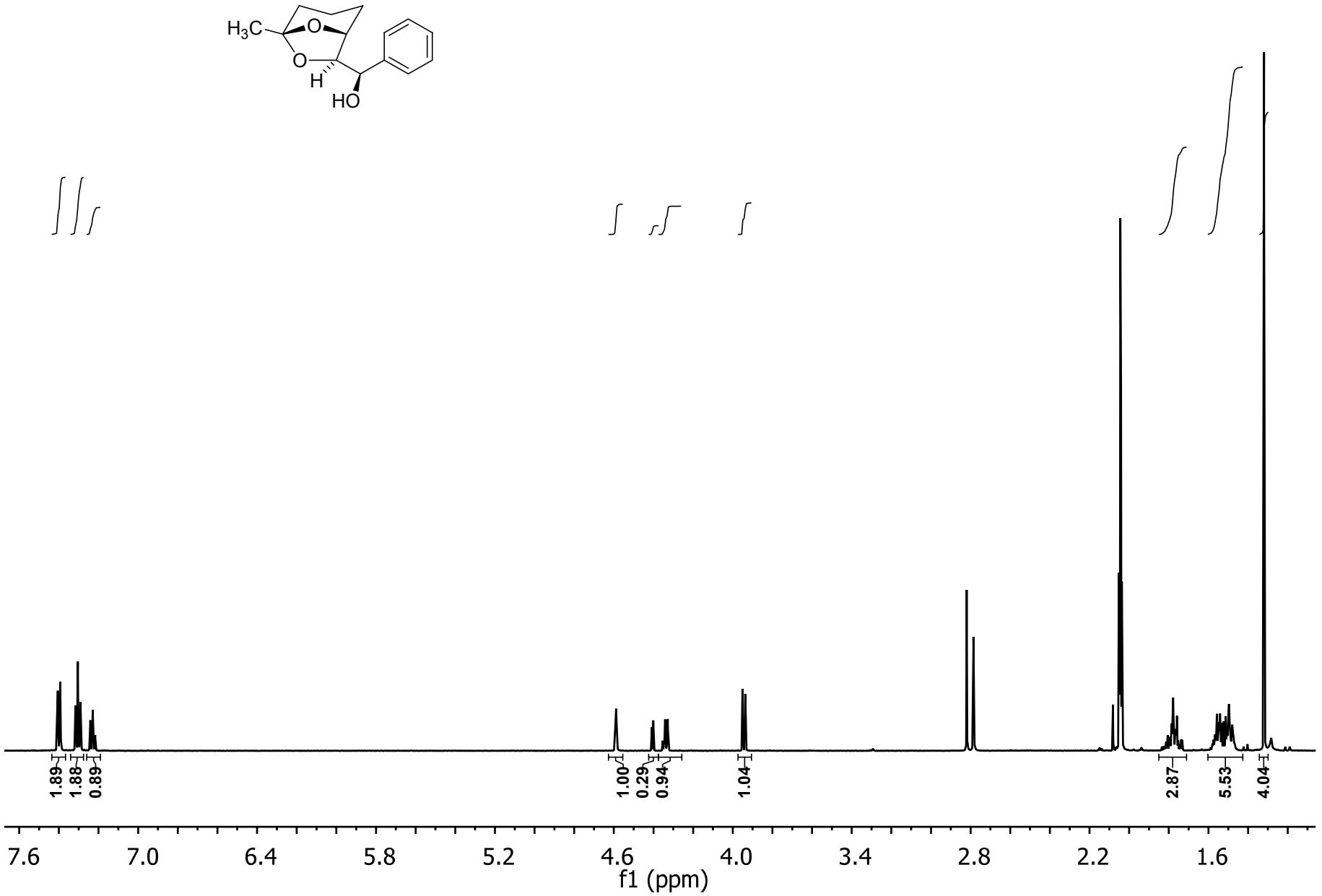


**Figure S10.** (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)-1-phenyl-methanol, **12**, decoupled HSQC spectrum, acetone-$d_6$, 600 MHz.

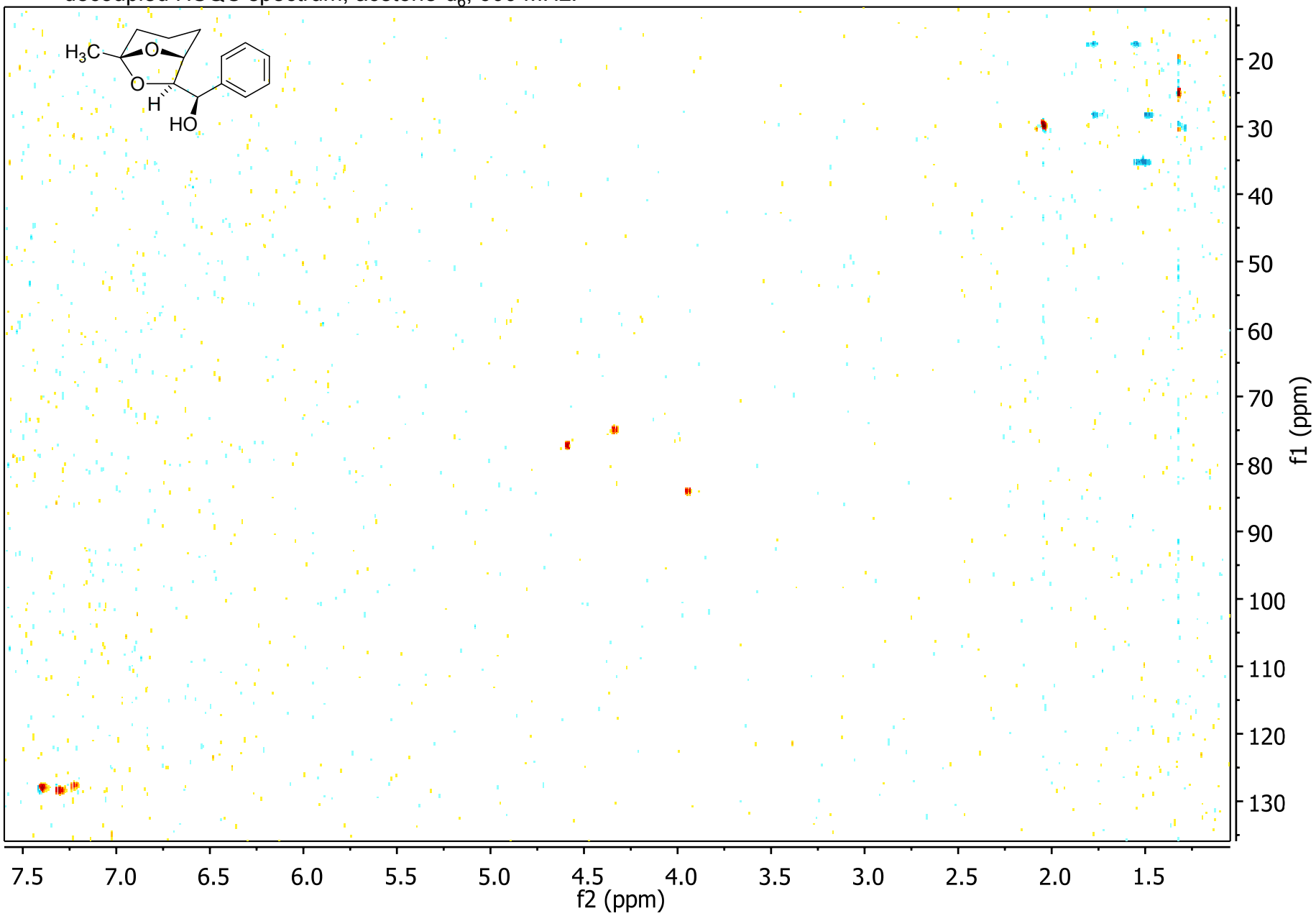


**Figure S11.** (1*R*,1'*R*,5'*R*,7'*R*)-1-(5'-Methyl-6',8'-dioxabicyclo[3.2.1]octan-7'-yl)-1-phenyl-methanol, **12**, HMBC spectrum, acetone-$d_6$, 600 MHz.

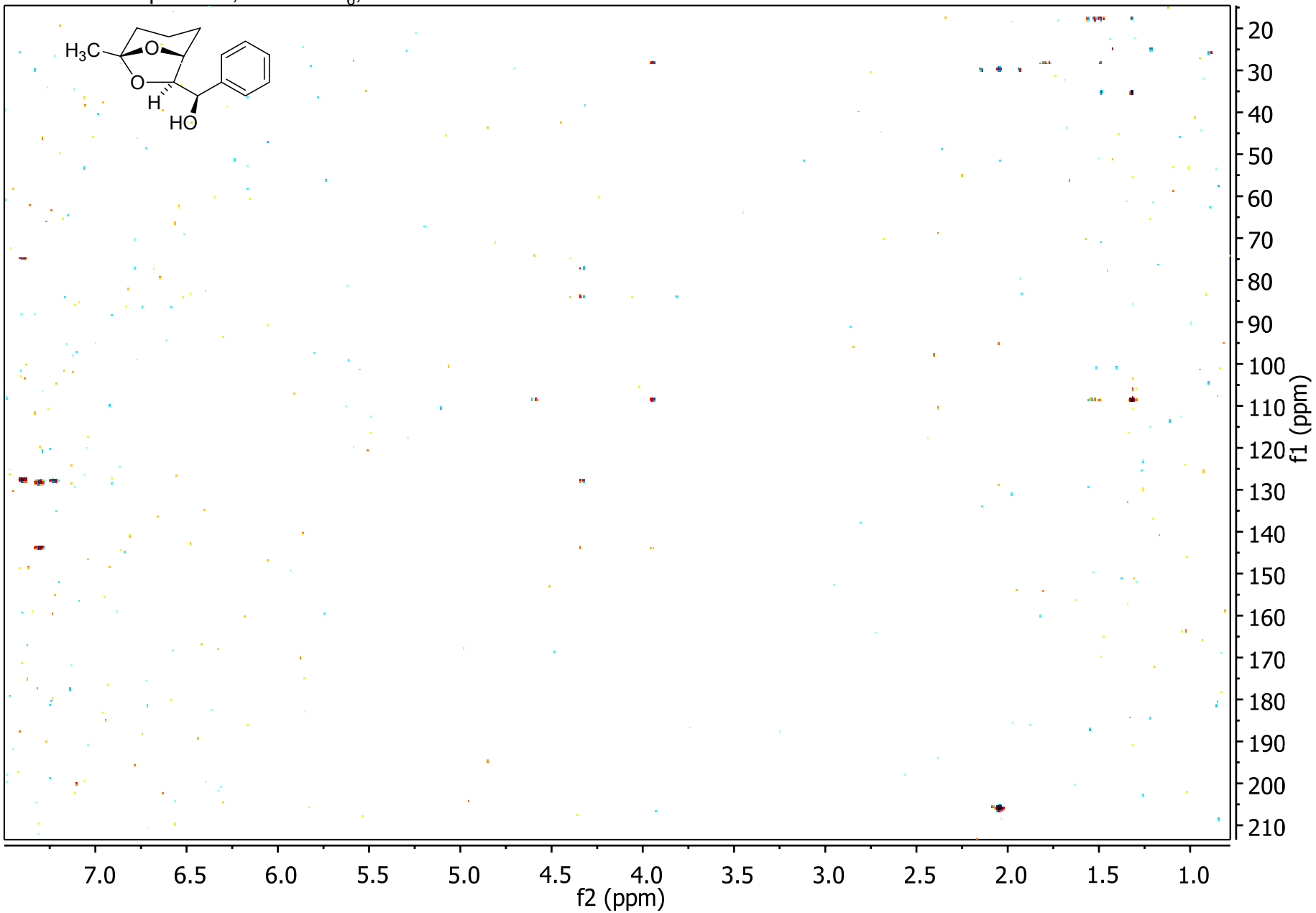


**Figure S12.** (1*R*,1'*R*,6'*R*,8'*R*)-1-(6'-Methyl-7',9'-dioxabicyclo[4.2.1]nonan-8'-yl)ethanol, **15**, $^{1}H$ NMR spectrum, $CDCl_3$, 400 MHz.

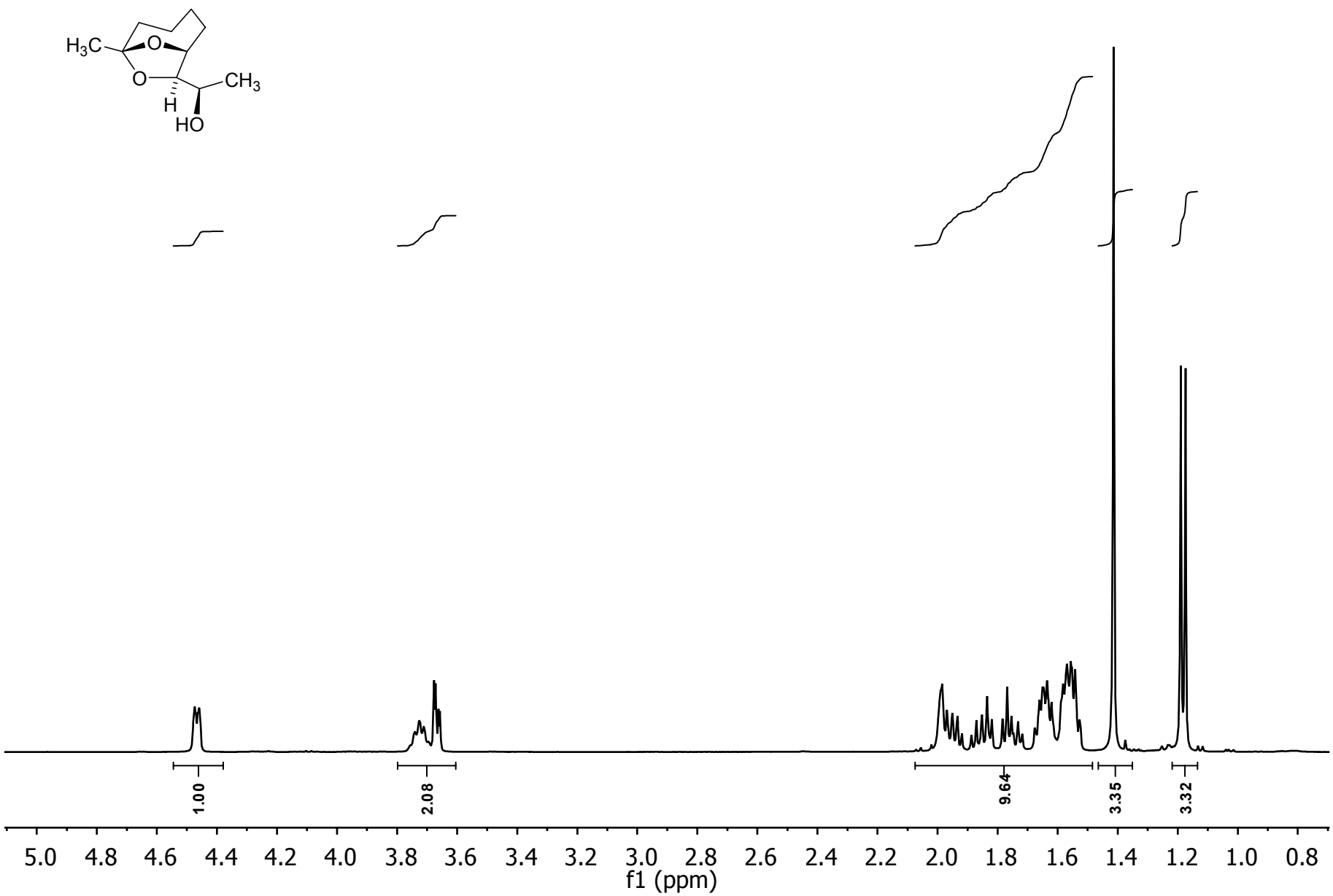
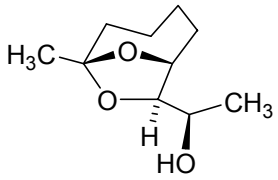


**Figure S13.** (1*R*,1'*R*,6'*R*,8'*R*)-1-(6'-Methyl-7',9'-dioxabicyclo[4.2.1]nonan-8'-yl)ethanol, **15**, $^{13}C$ NMR spectrum, $CDCl_3$, 125 MHz.



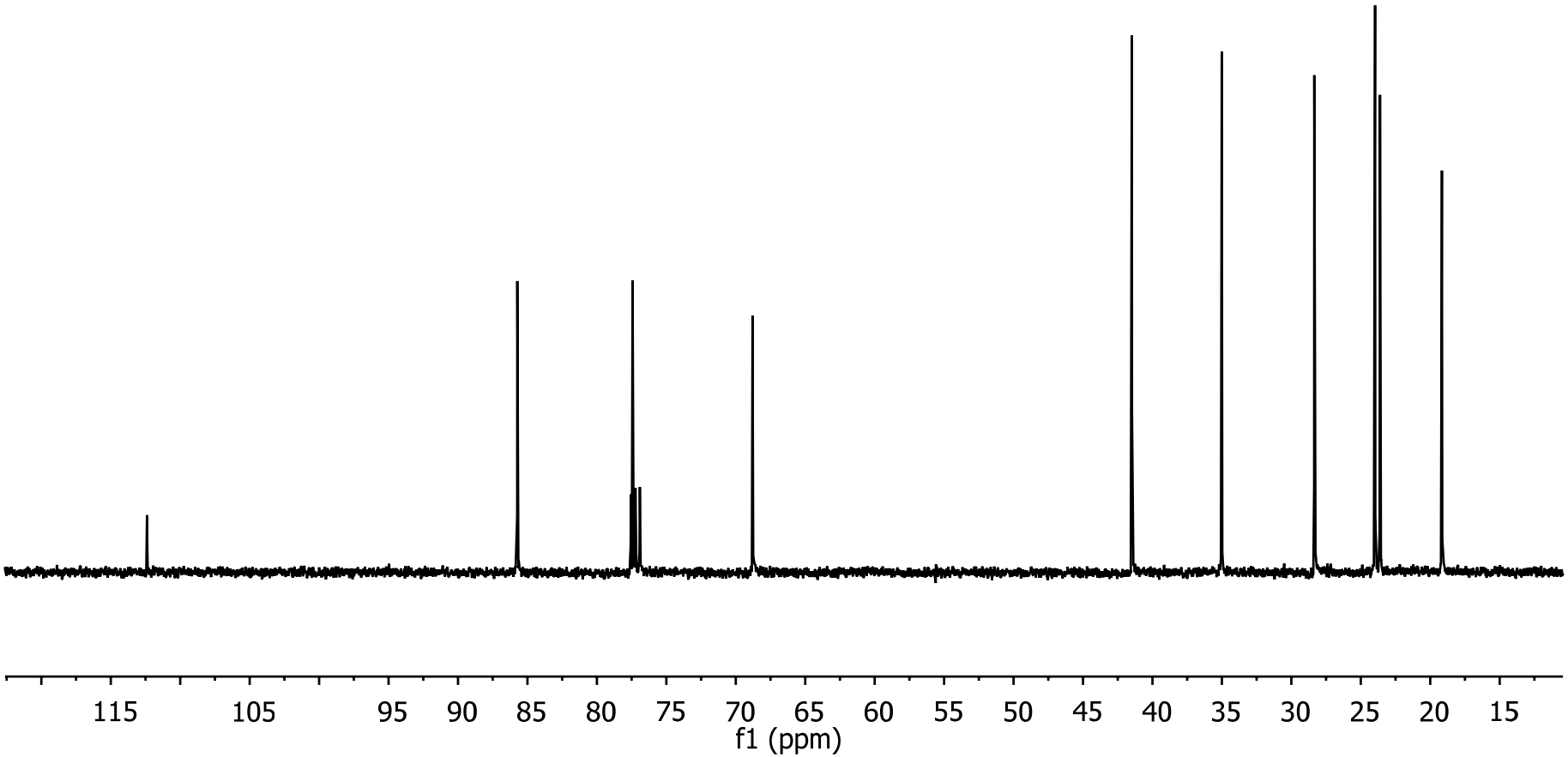



**Figure S14.** (1*R*,1'*R*,6'*R*,8'*R*)-1-(6'-Methyl-7',9'-dioxabicyclo[4.2.1]nonan-8'-yl)ethanol, **15**, $^{1}$H NMR spectrum, acetone-$d_6$, 600 MHz.

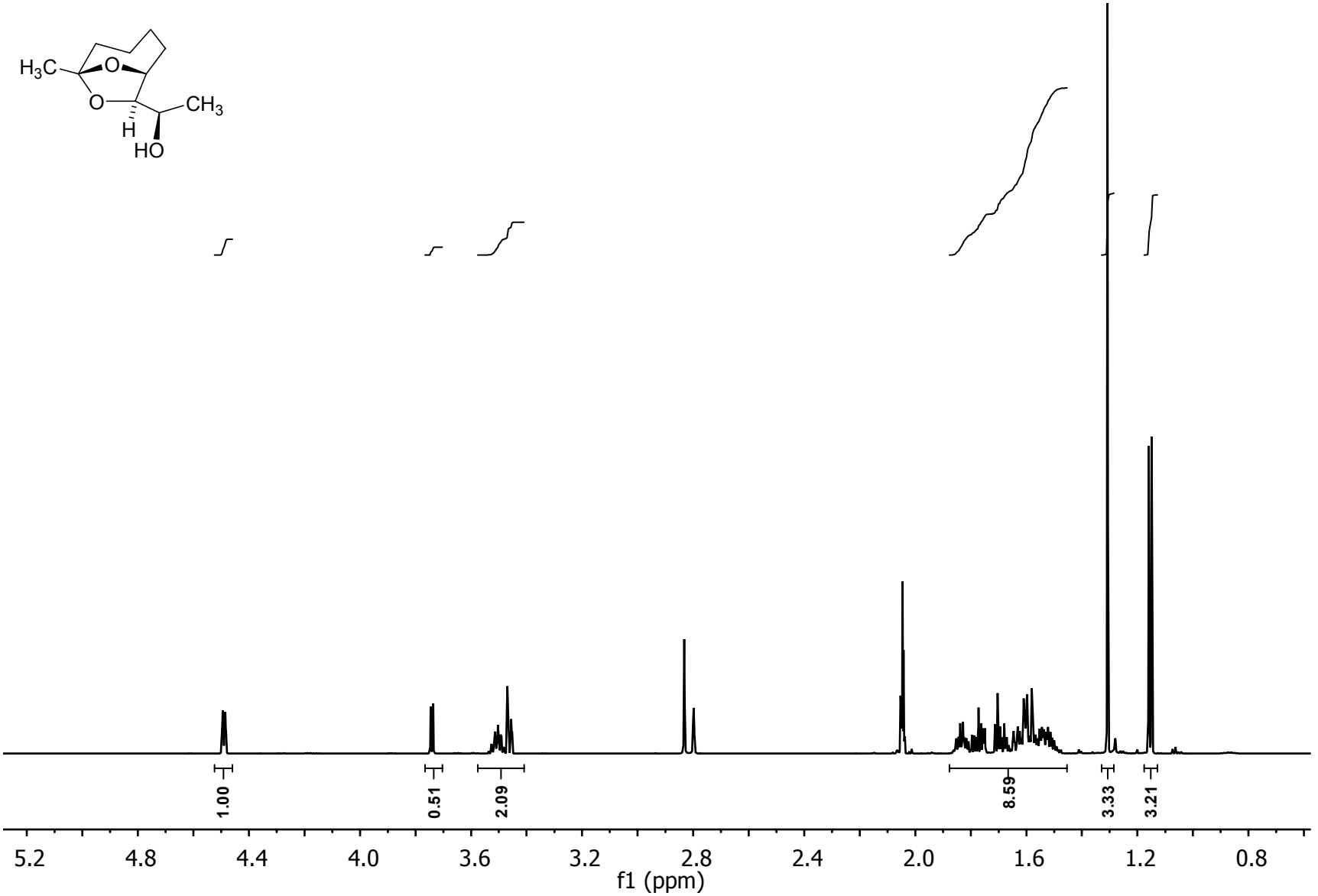


**Figure S15.** (1*R*,1'*R*,6'*R*,8'*R*)-1-(6'-Methyl-7',9'-dioxabicyclo[4.2.1]nonan-8'-yl)ethanol, **15**, dqfCOSY spectrum, acetone-$d_6$, 600 MHz.

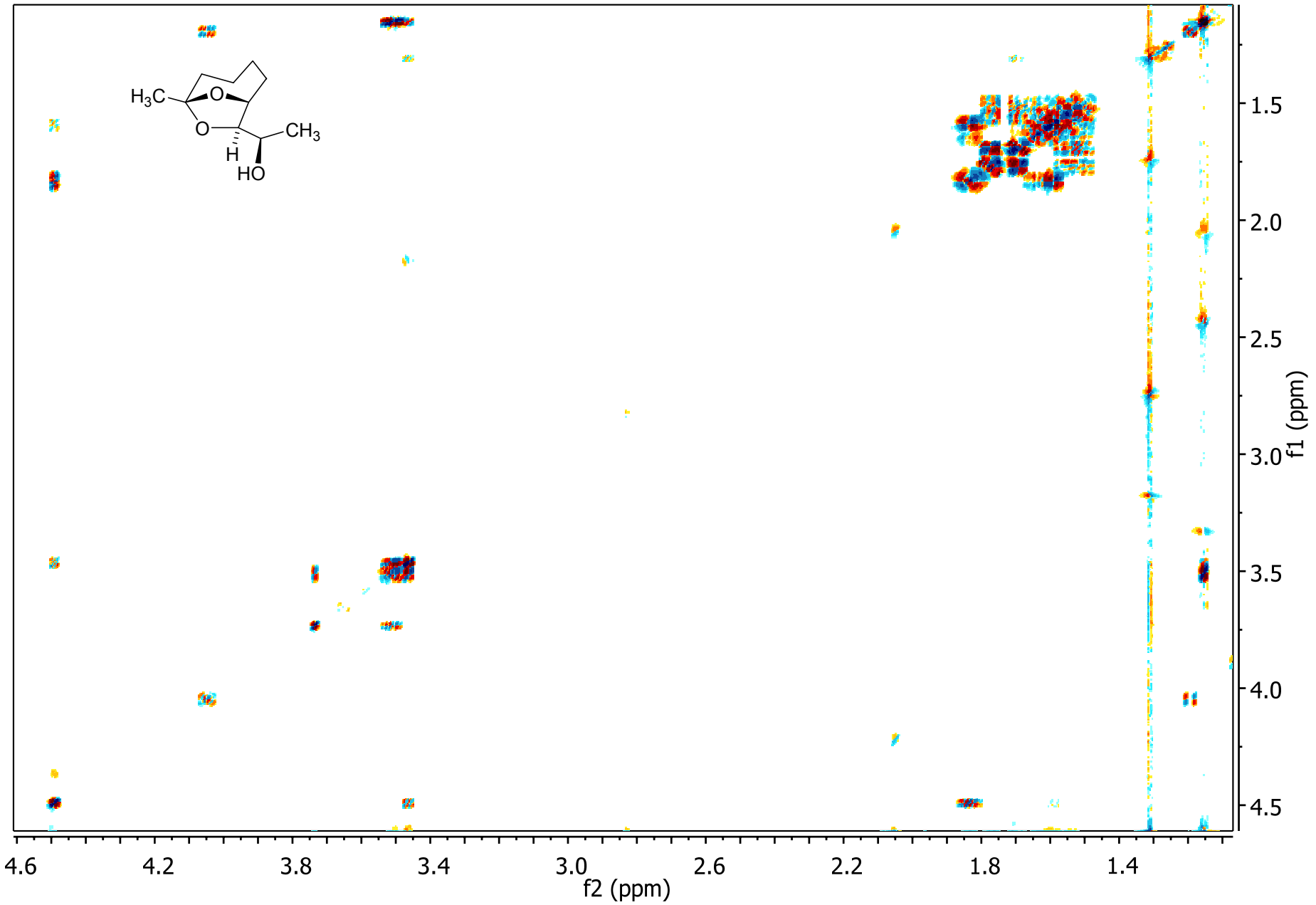


**Figure S16.** (1*R*,1'*R*,6'*R*,8'*R*)-1-(6'-Methyl-7',9'-dioxabicyclo[4.2.1]nonan-8'-yl)ethanol, **15**, coupled HSQC spectrum, acetone-$d_6$, 600 MHz.

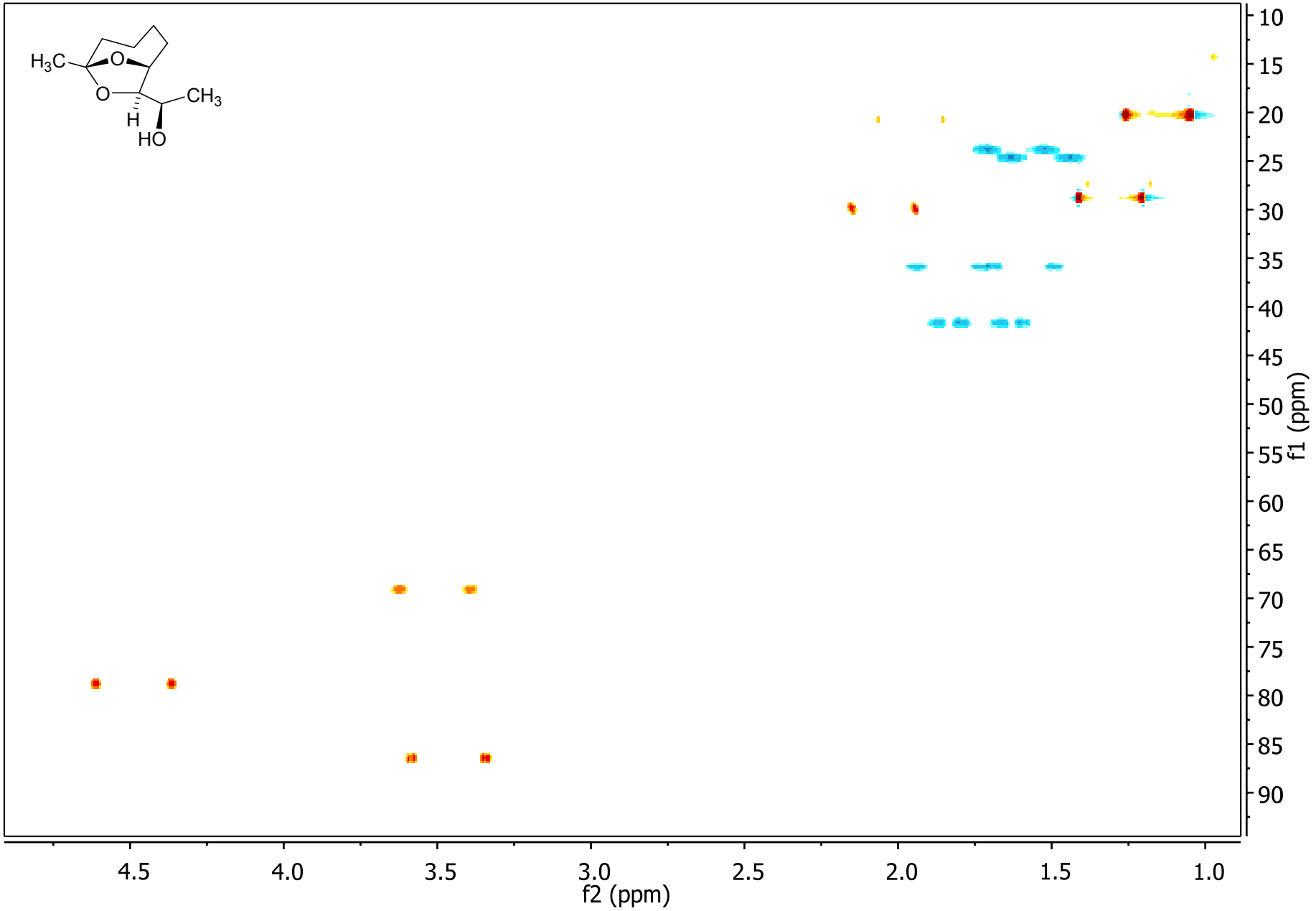


**Figure S17.** (1*R*,1'*R*,6'*R*,8'*R*)-1-(6'-Methyl-7',9'-dioxabicyclo[4.2.1]nonan-8'-yl)ethanol, **15**, HMBC spectrum, acetone-$d_6$, 600 MHz.

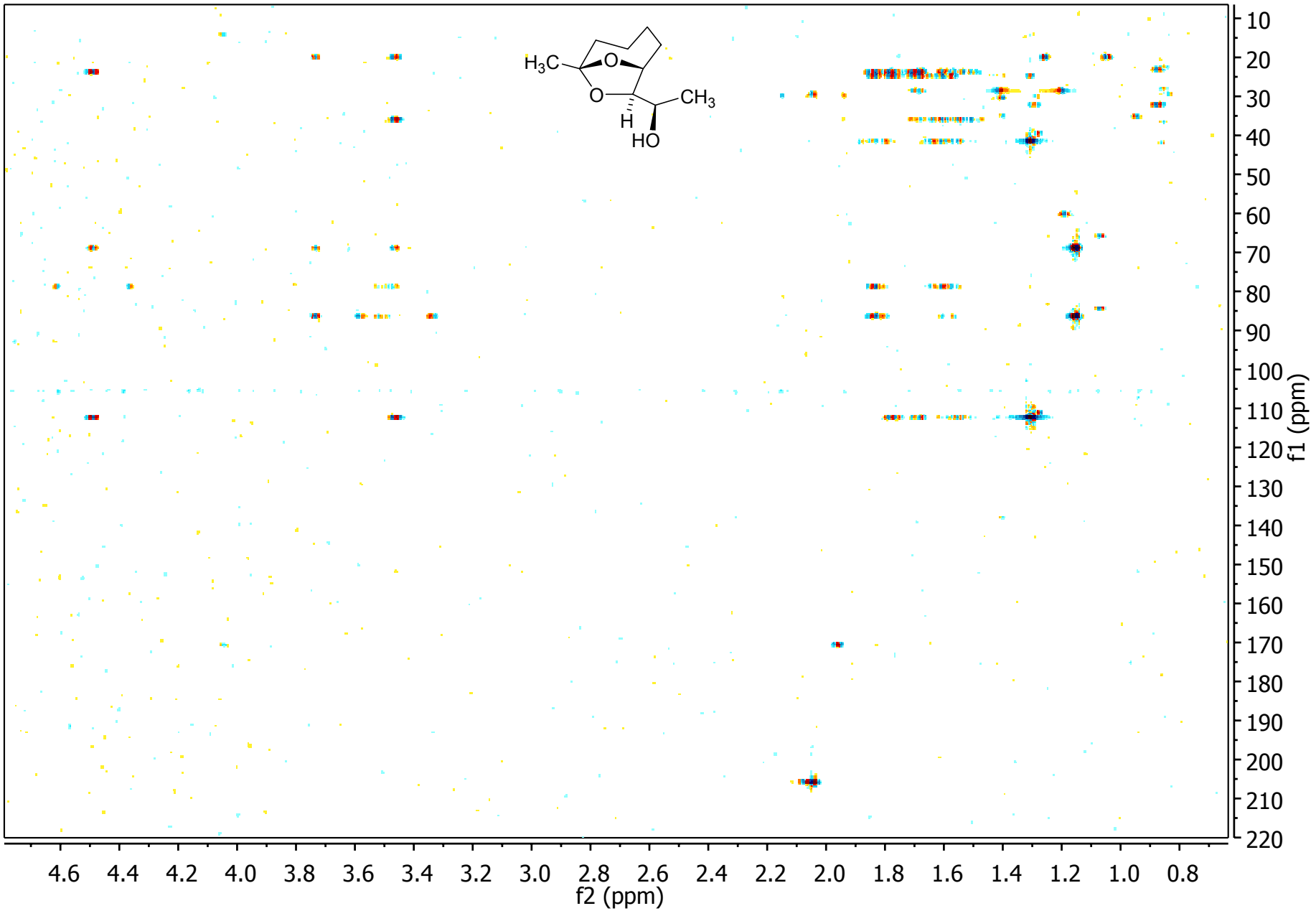


**Figure S18.** (8*S*,9*S*,10*S*)-8,9,10-Trihydroxyundecan-2-one, (8*S*,9*S*,10*S*)-**17**,
$^{1}$H NMR spectrum, $CDCl_3$, 400 MHz.

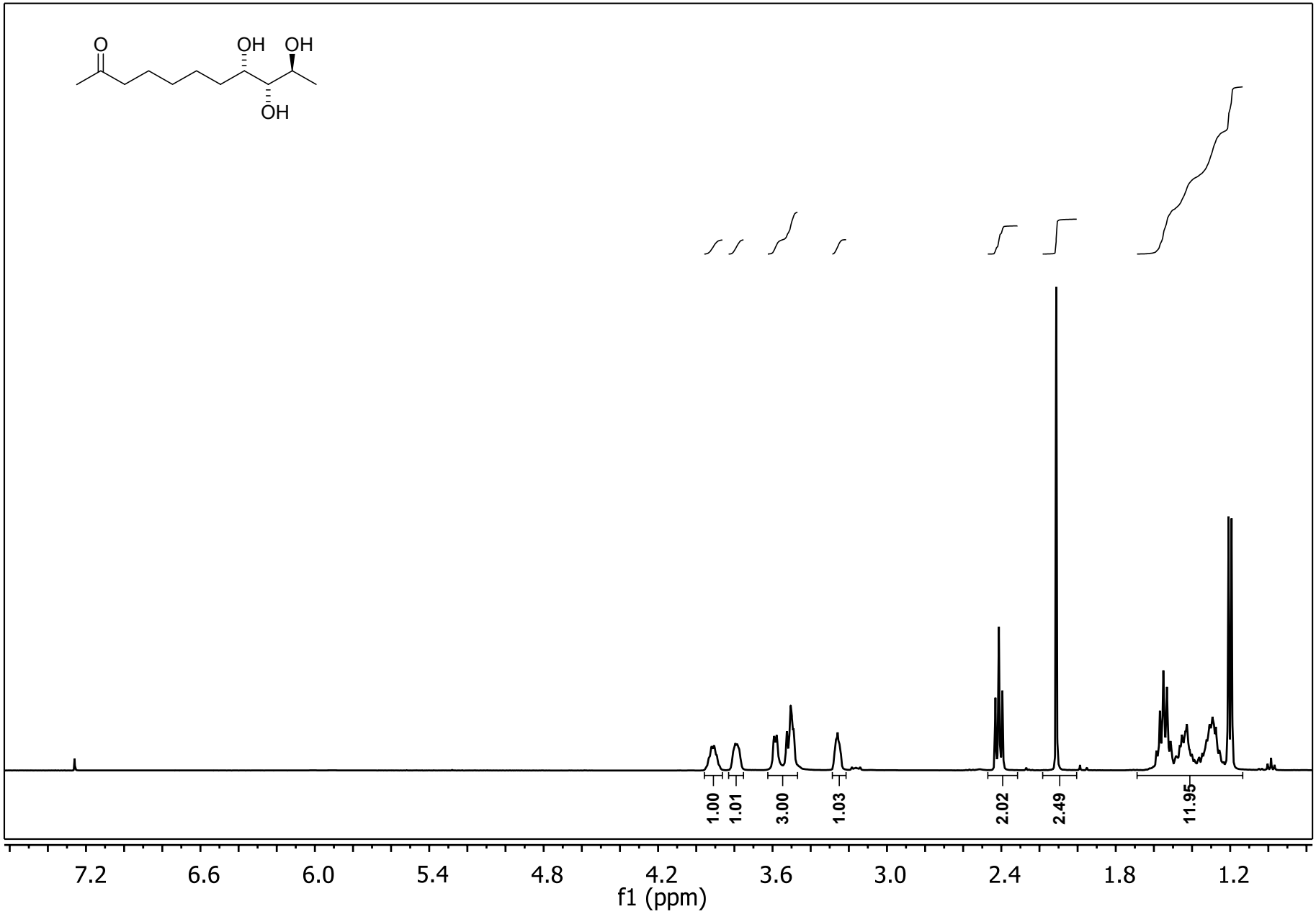


**Figure S19.** (8*S*,9*S*,10*S*)-8,9,10-Trihydroxyundecan-2-one, (8*S*,9*S*,10*S*)-**17**, $^{13}C$ NMR spectrum, $CDCl_3$, 125 MHz.

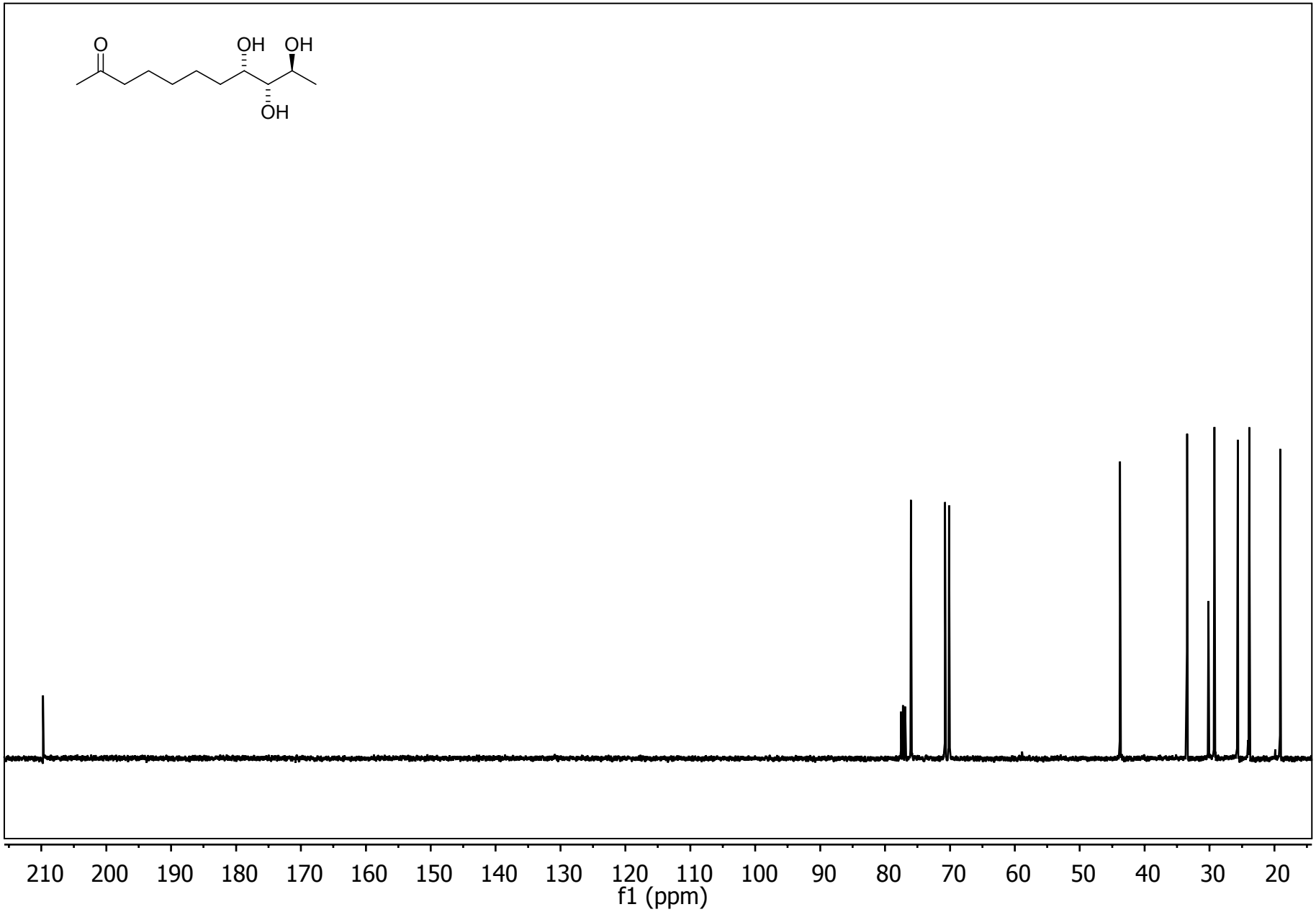


**Figure S20.** (9*R*,10*R*,11*R*)-9,10,11-Trihydroxydodecan-2-one, **19**,
$^{1}$H NMR spectrum, $CDCl_3$, 400 MHz.

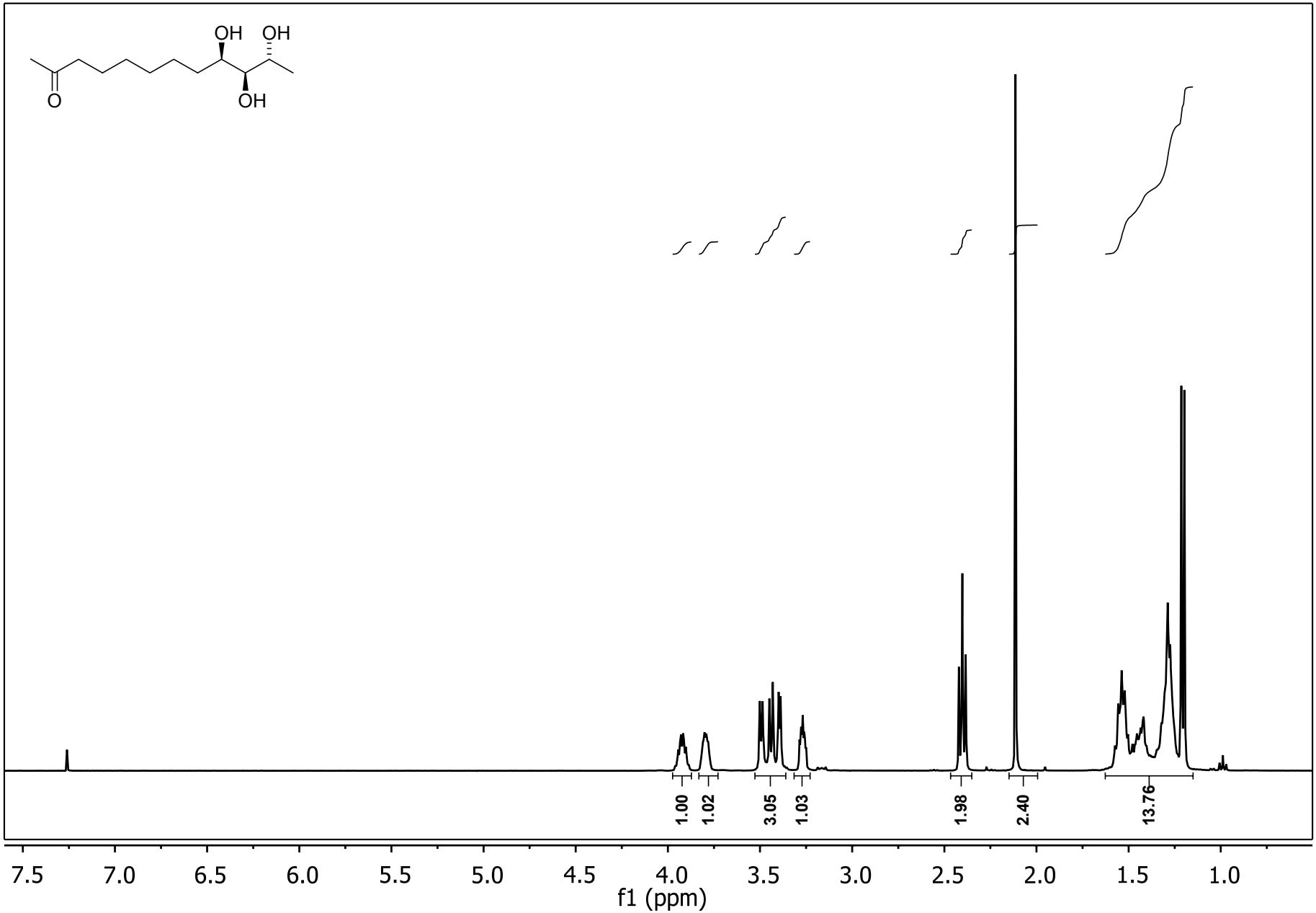


**Figure S21.** (9*R*,10*R*,11*R*)-9,10,11-Trihydroxydodecan-2-one, **19**,
$^{13}C$ NMR spectrum, $CDCl_3$, 125 MHz.

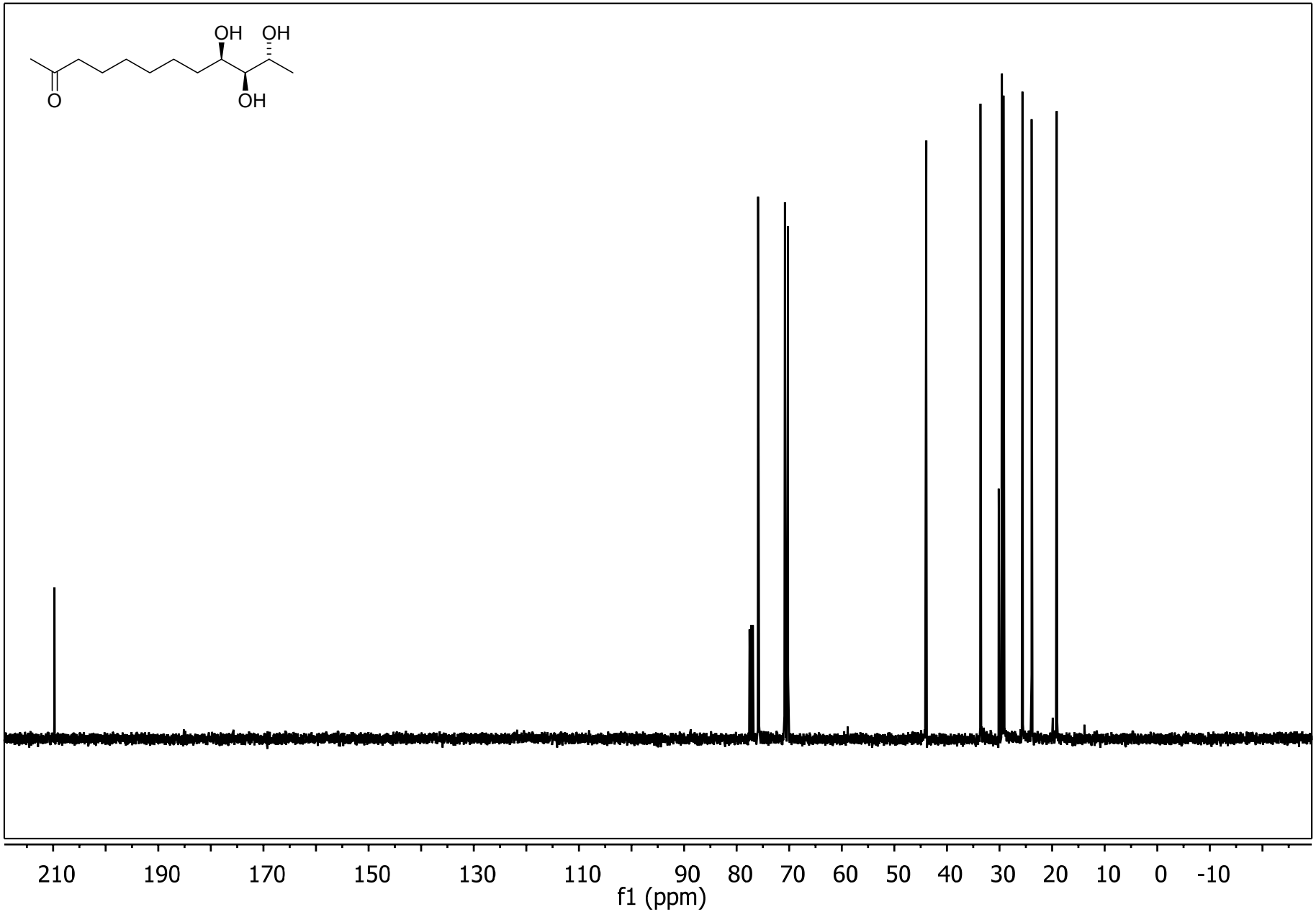


**Figure S22.** (2*S*,3*S*,4*S*)-Nonane-2,3,4-triol, **21** ,
$^{1}$H NMR spectrum, $CDCl_3$, 400 MHz.

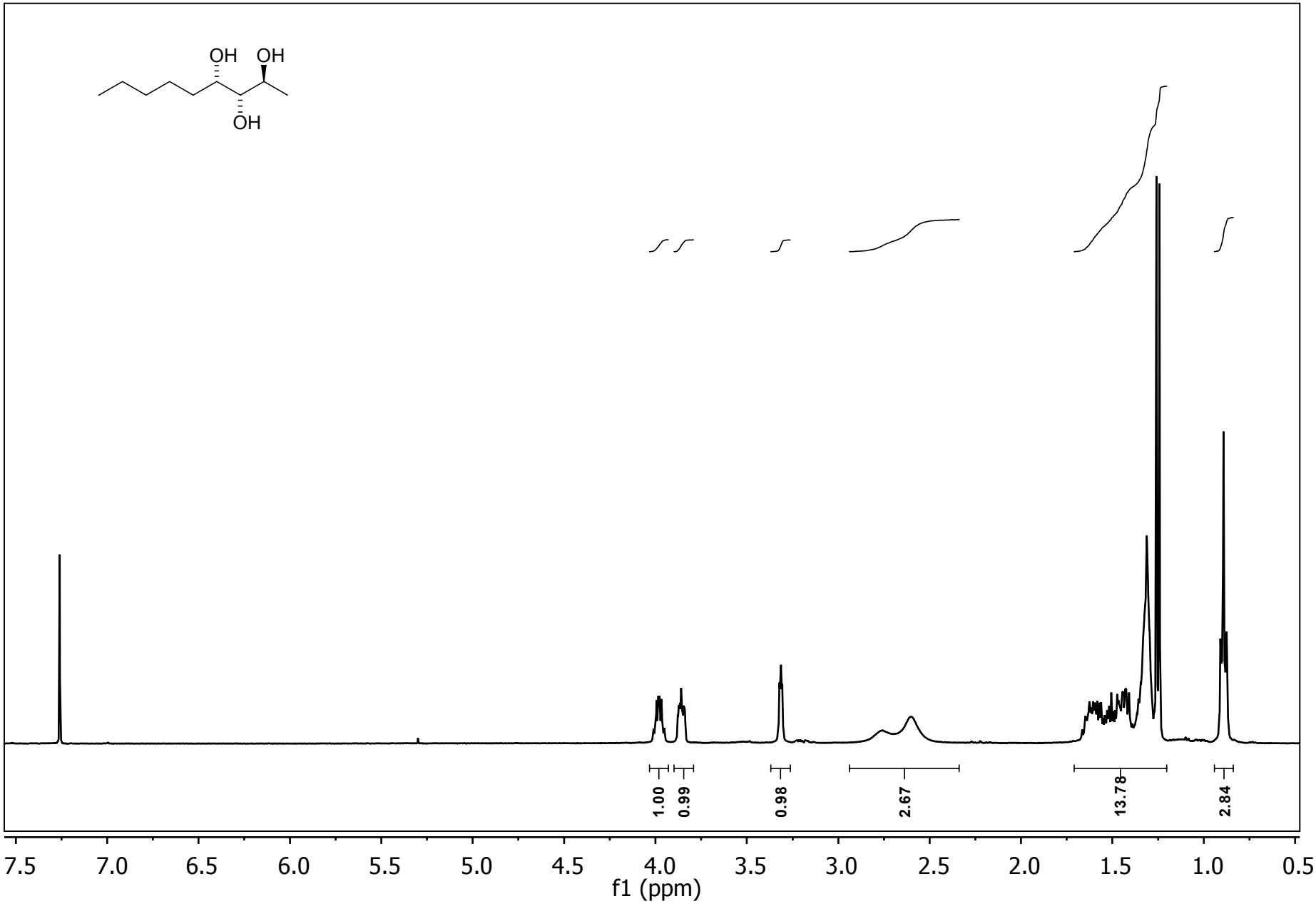


**Figure S23.** (2*S*,3*S*,4*S*)-Nonane-2,3,4-triol, **21** ,
$^{13}C$ NMR spectrum, $CDCl_3$, 125 MHz.

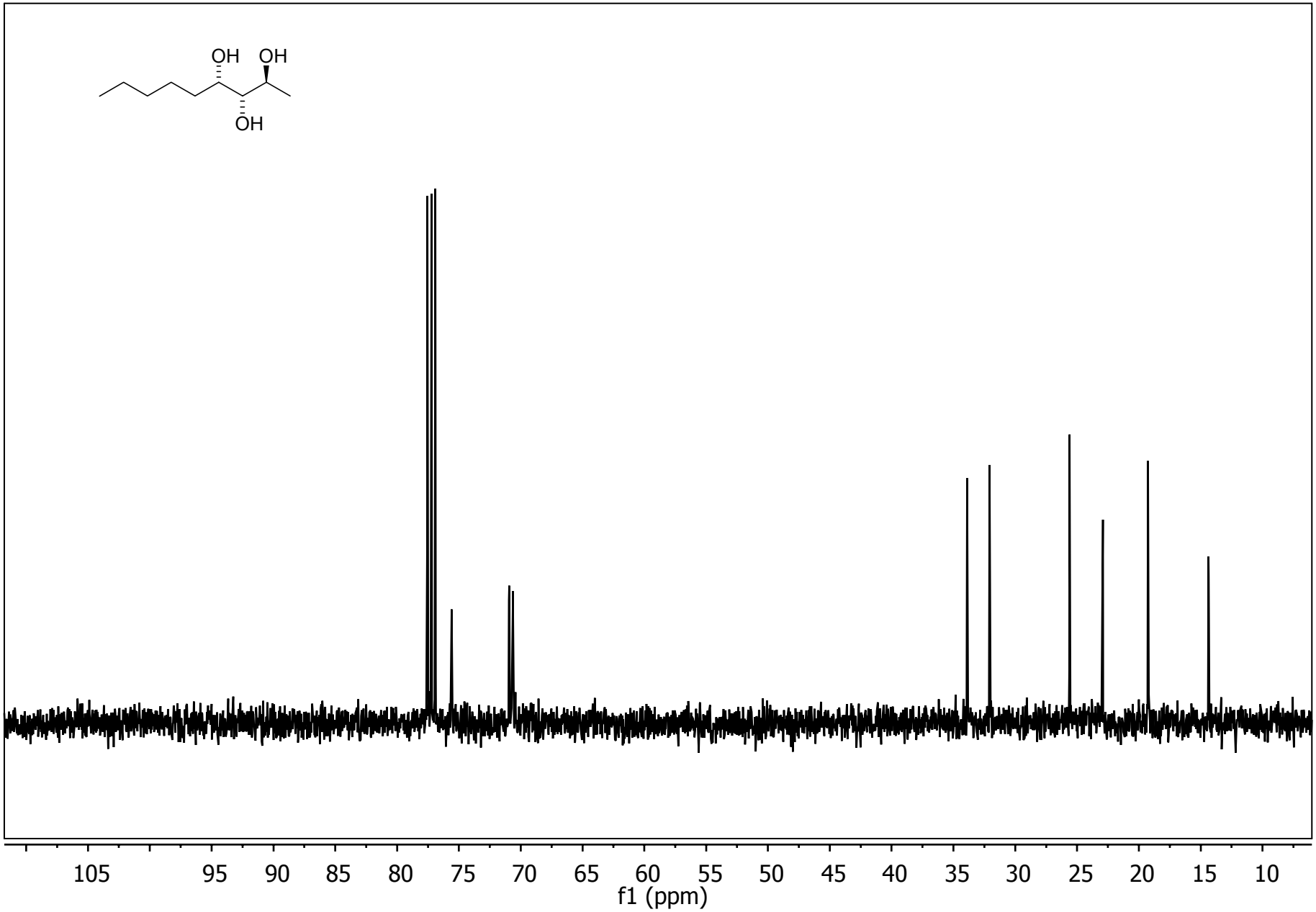


**Figure S24.** (2*R*,3*R*,4*R*)-Dodec-11-ene-2,3,4-triol, **23**,
$^{1}$H NMR spectrum, $CDCl_3$, 400 MHz.

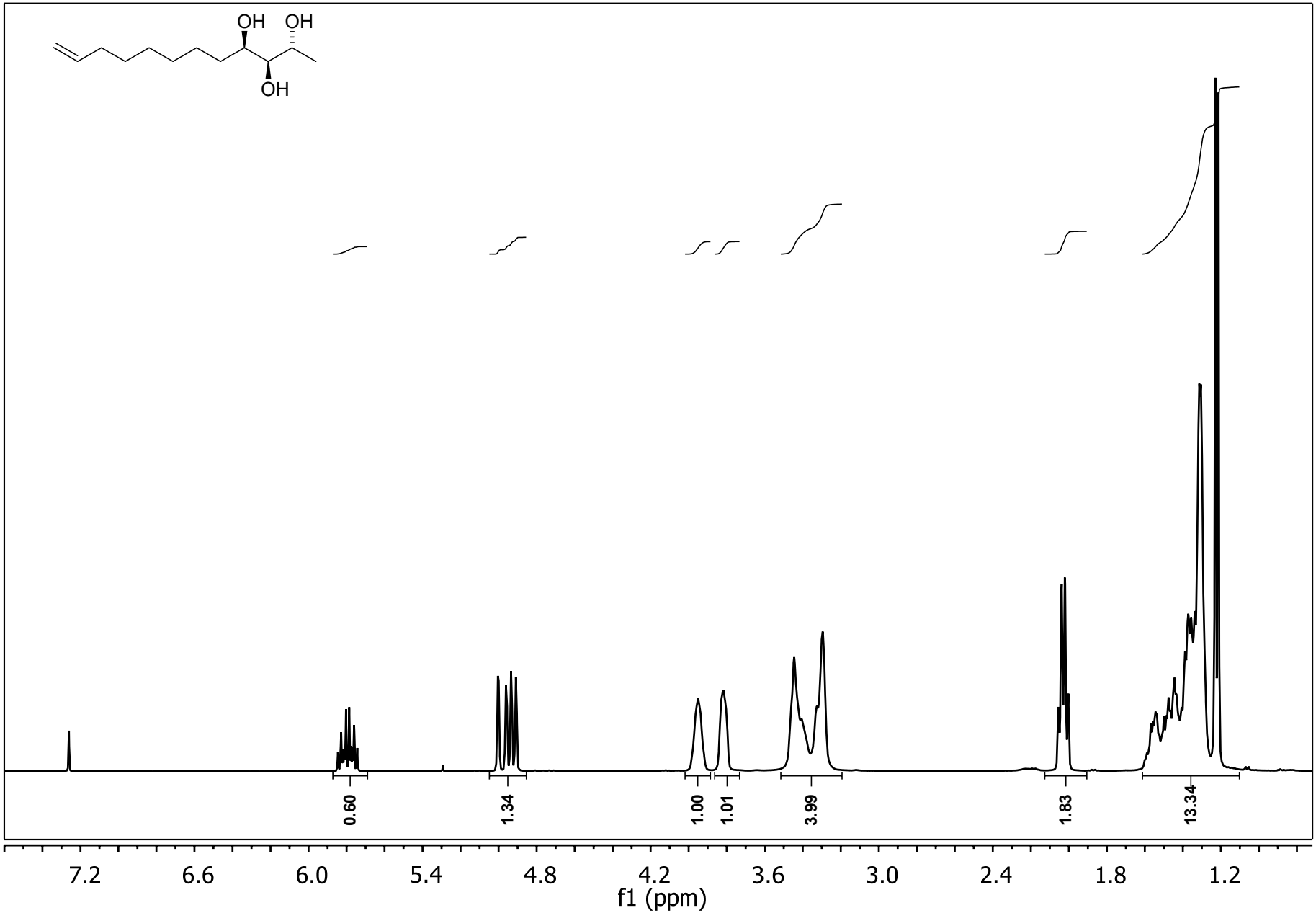


**Figure S25.** (2*R*,3*R*,4*R*)-Dodec-11-ene-2,3,4-triol, **23**,
$^{13}C$ NMR spectrum, $CDCl_3$, 125 MHz.

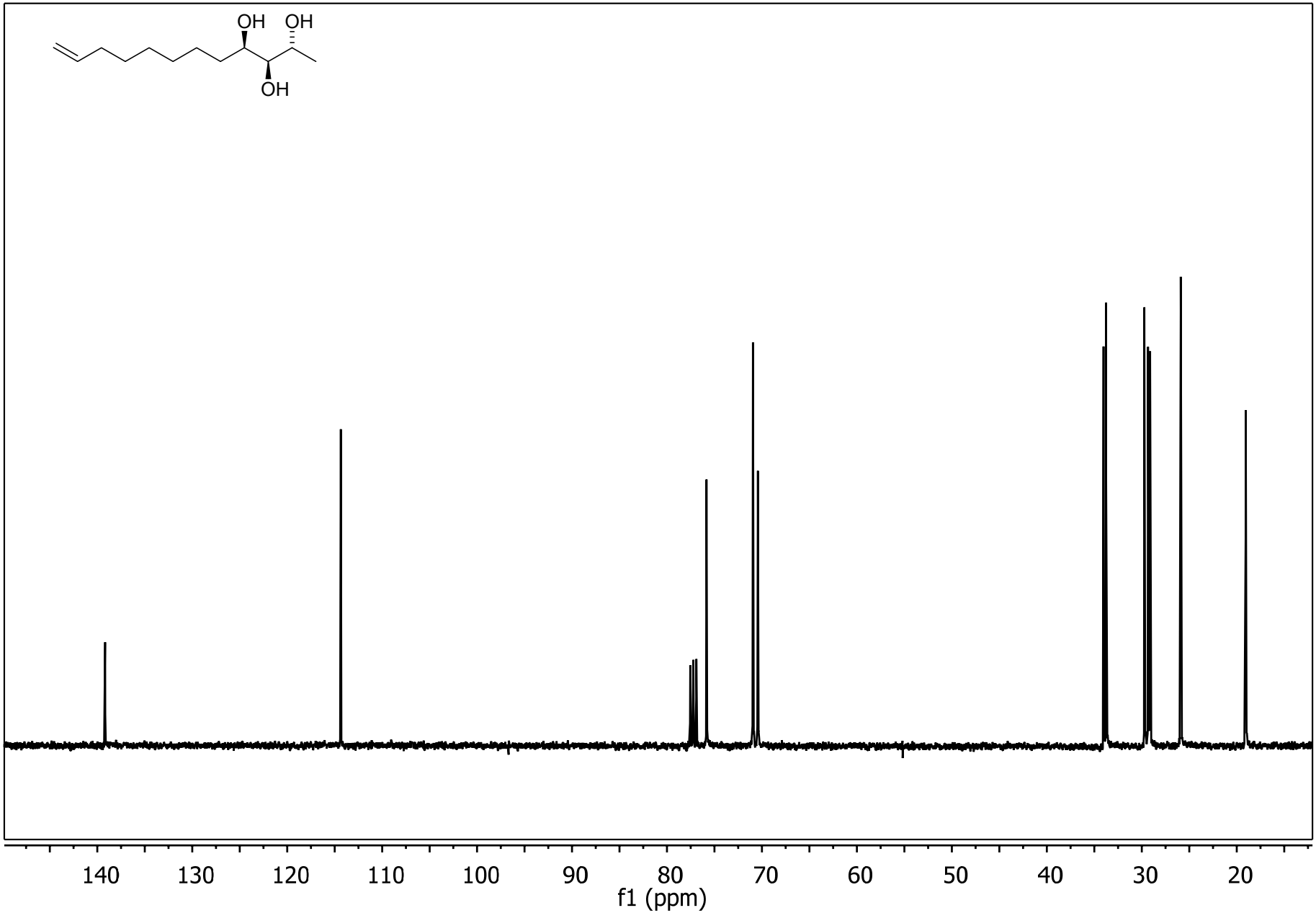


**Figure S26.** (1*S*,2*S*,3*S*)-1-Phenylbutane-1,2,3-triol, **25**,
$^{1}$H NMR spectrum, $CDCl_3$, 400 MHz.

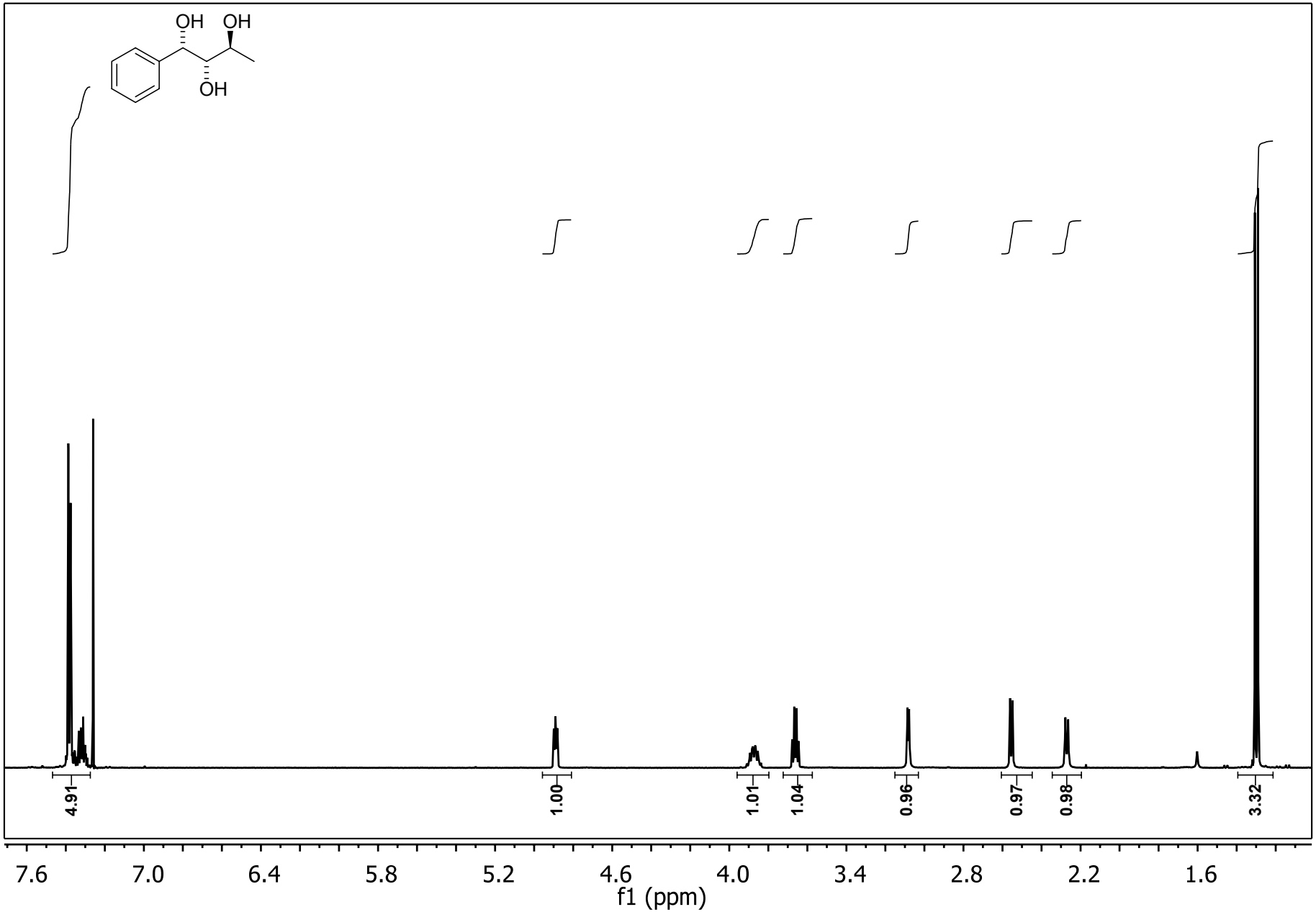


**Figure S27.** (1*S*,2*S*,3*S*)-1-Phenylbutane-1,2,3-triol, **25**,
$^{13}C$ NMR spectrum, $CDCl_3$, 125 MHz.

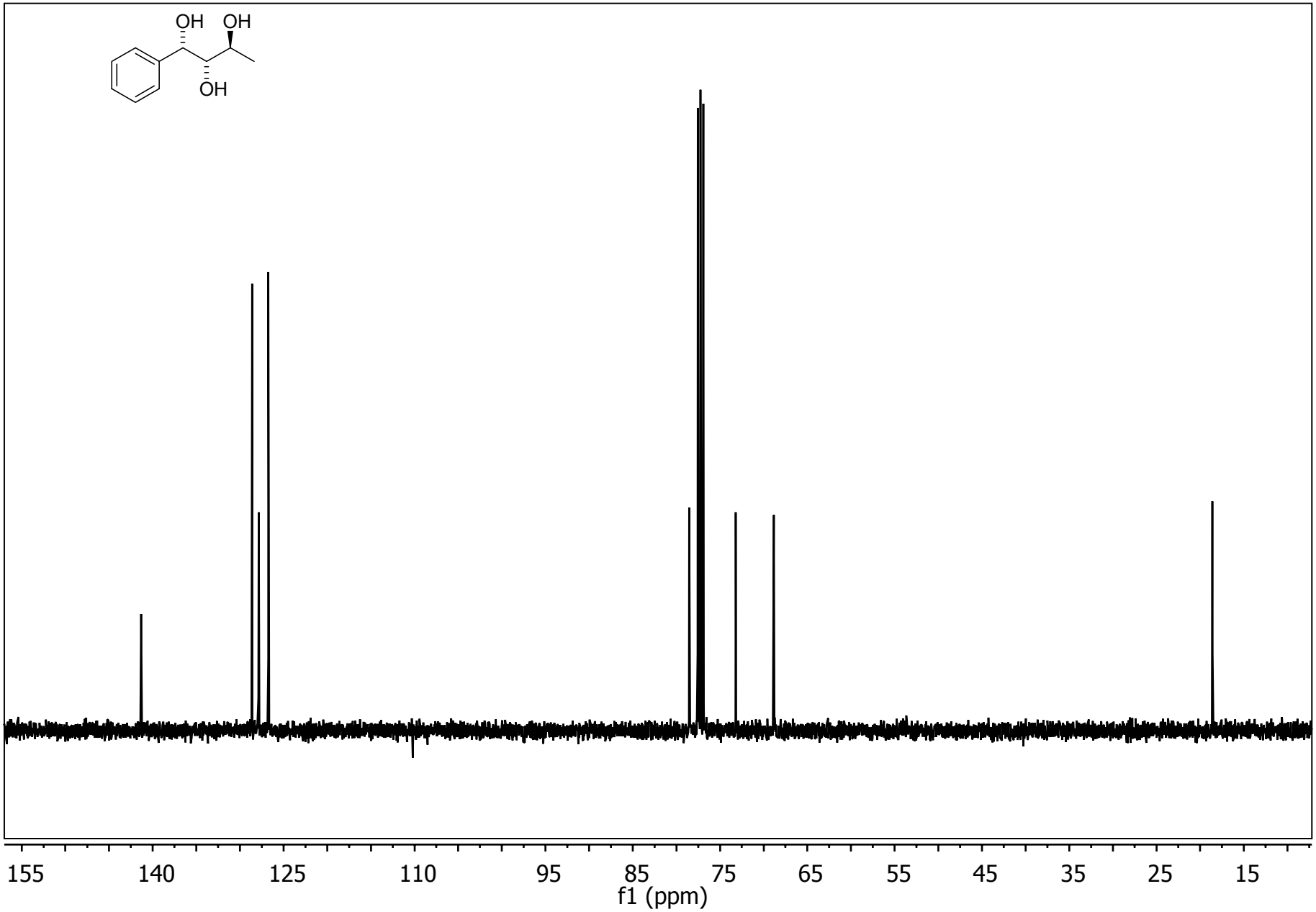


**Figure S28.** (1*S*,2*S*,3*S*)-1-Phenylbutane-1,2,3-triyl triacetate, **27**,
$^{1}$H NMR spectrum, $CDCl_3$, 400 MHz.

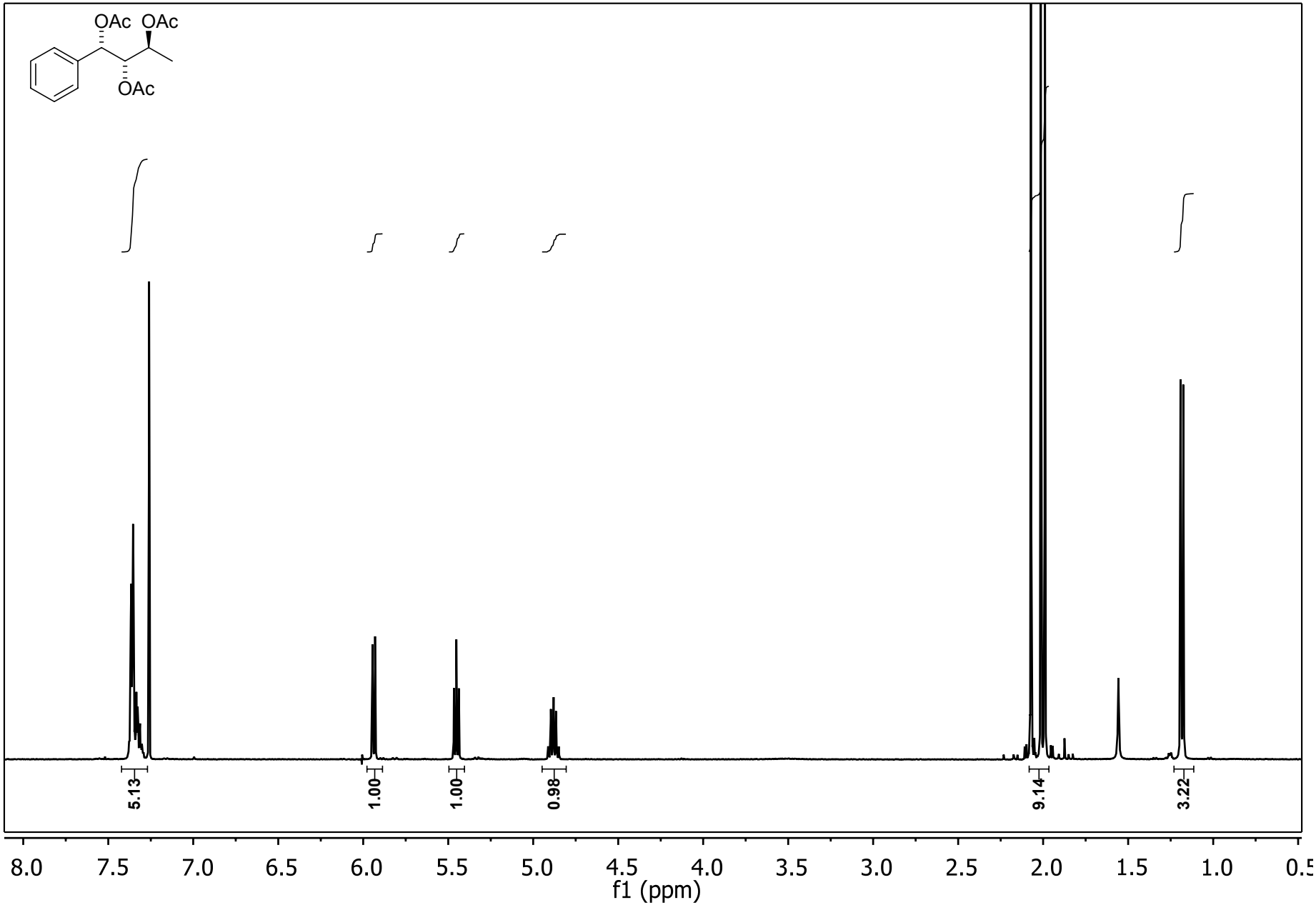


**Figure S29.** (1*S*,2*S*,3*S*)-1-Phenylbutane-1,2,3-triyl triacetate, **27**,
$^{13}C$ NMR spectrum, $CDCl_3$, 125 MHz.

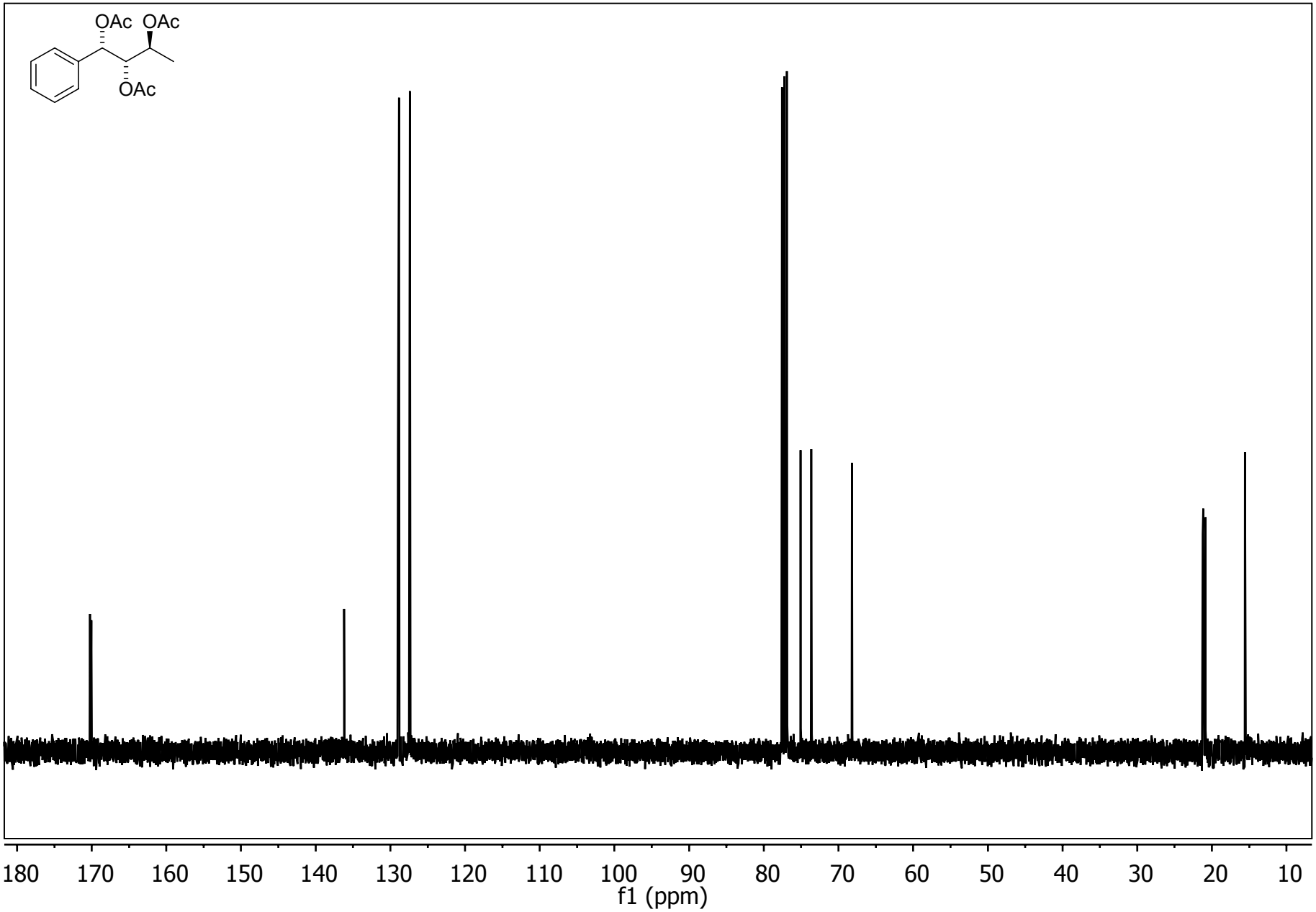


**Figure S30.** (2*R*,3*S*,4*S*)-2,3,4-Triacetoxypentanoic acid, **28**,
$^{1}$H NMR spectrum, $CDCl_3$, 400 MHz.

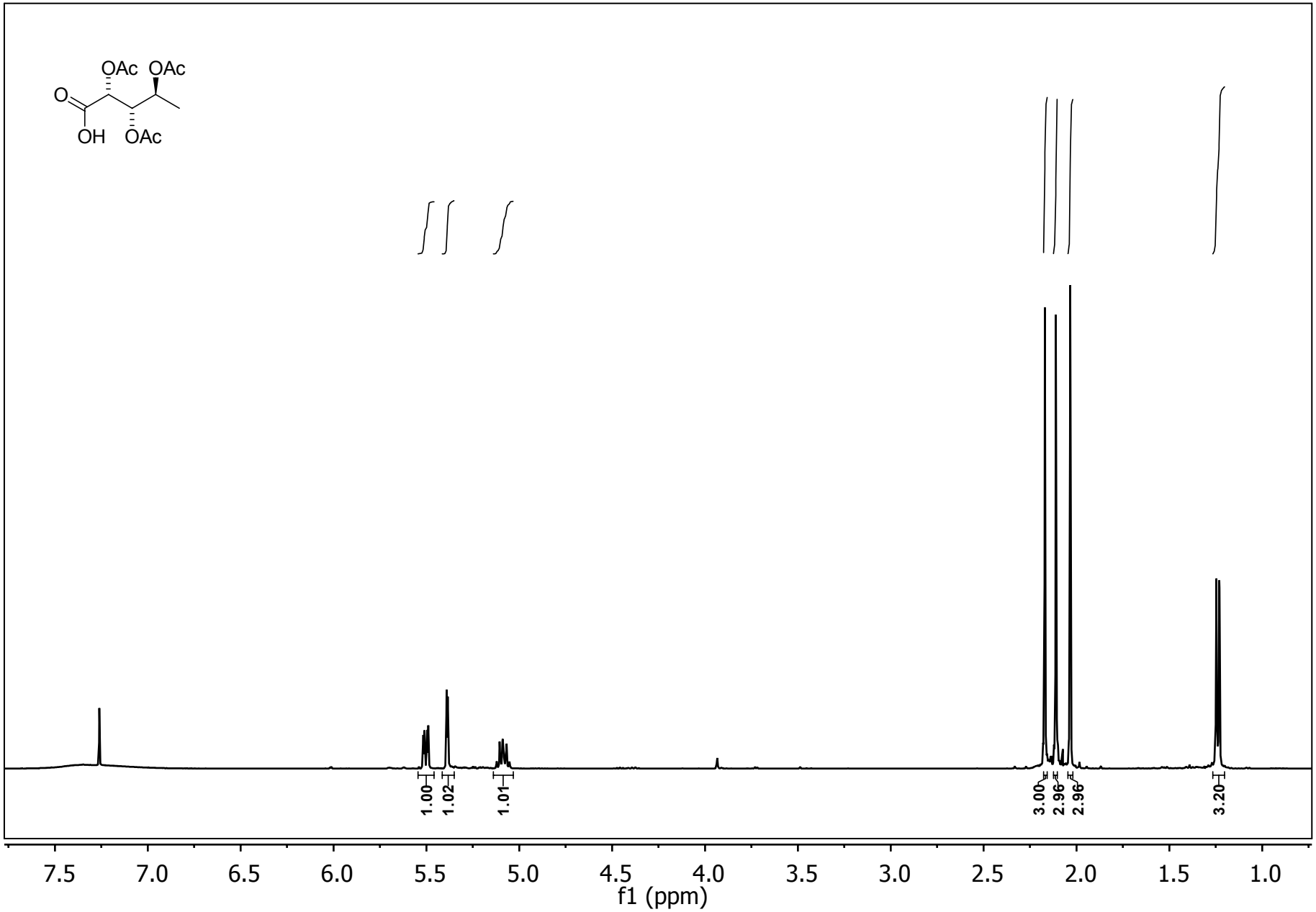


**Figure S31.** (2*R*,3*S*,4*S*)-2,3,4-Triacetoxypentanoic acid, **28**,
$^{13}C$ NMR spectrum, $CDCl_3$, 125 MHz.

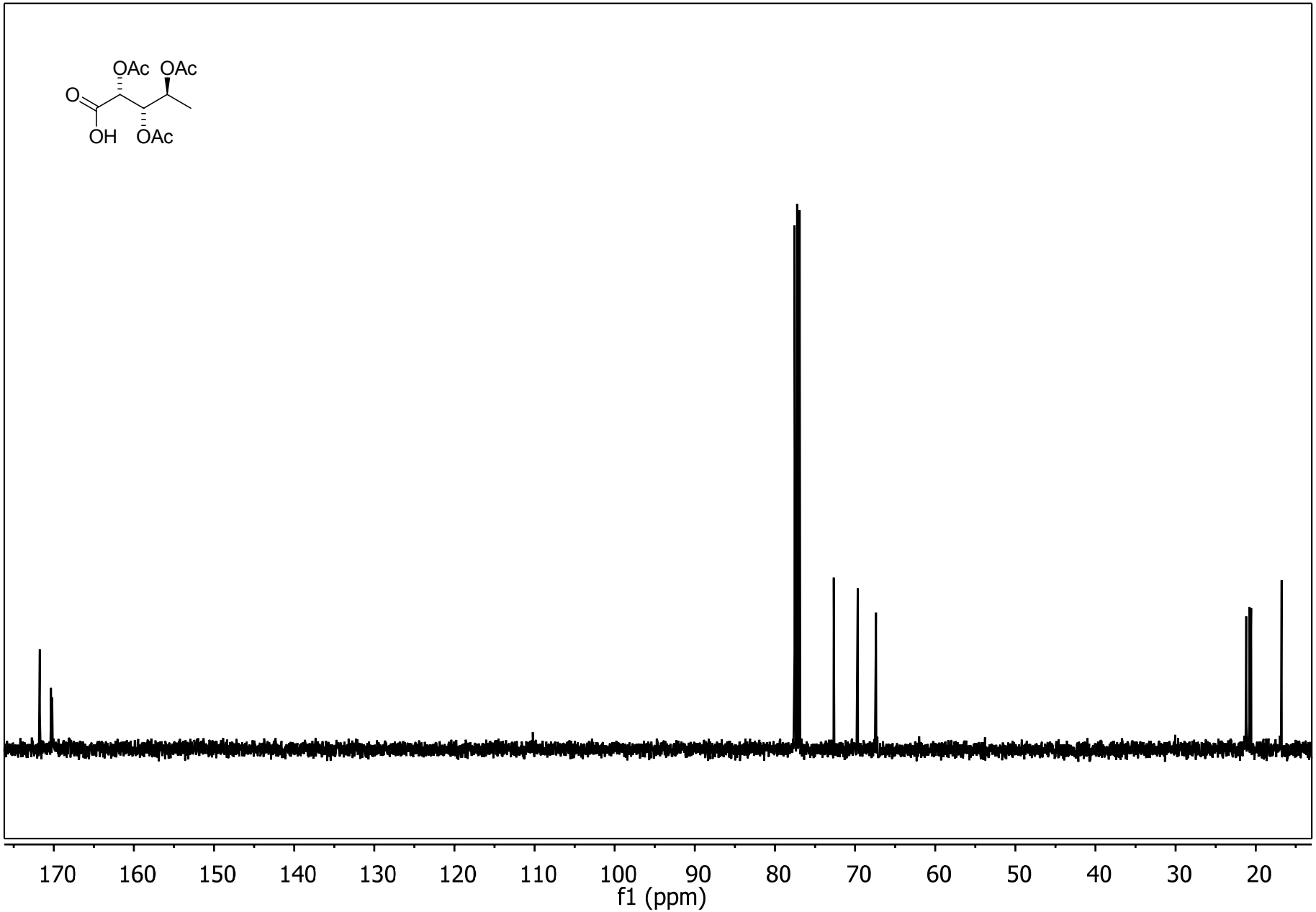


**Figure S32.** (3*R*,4*S*,5*S*)-3,4-Dihydroxy-5-methyldihydrofuran-2(3*H*)-one, **29**,
$^{1}$H NMR spectrum, $CD_3OD$, 400 MHz.

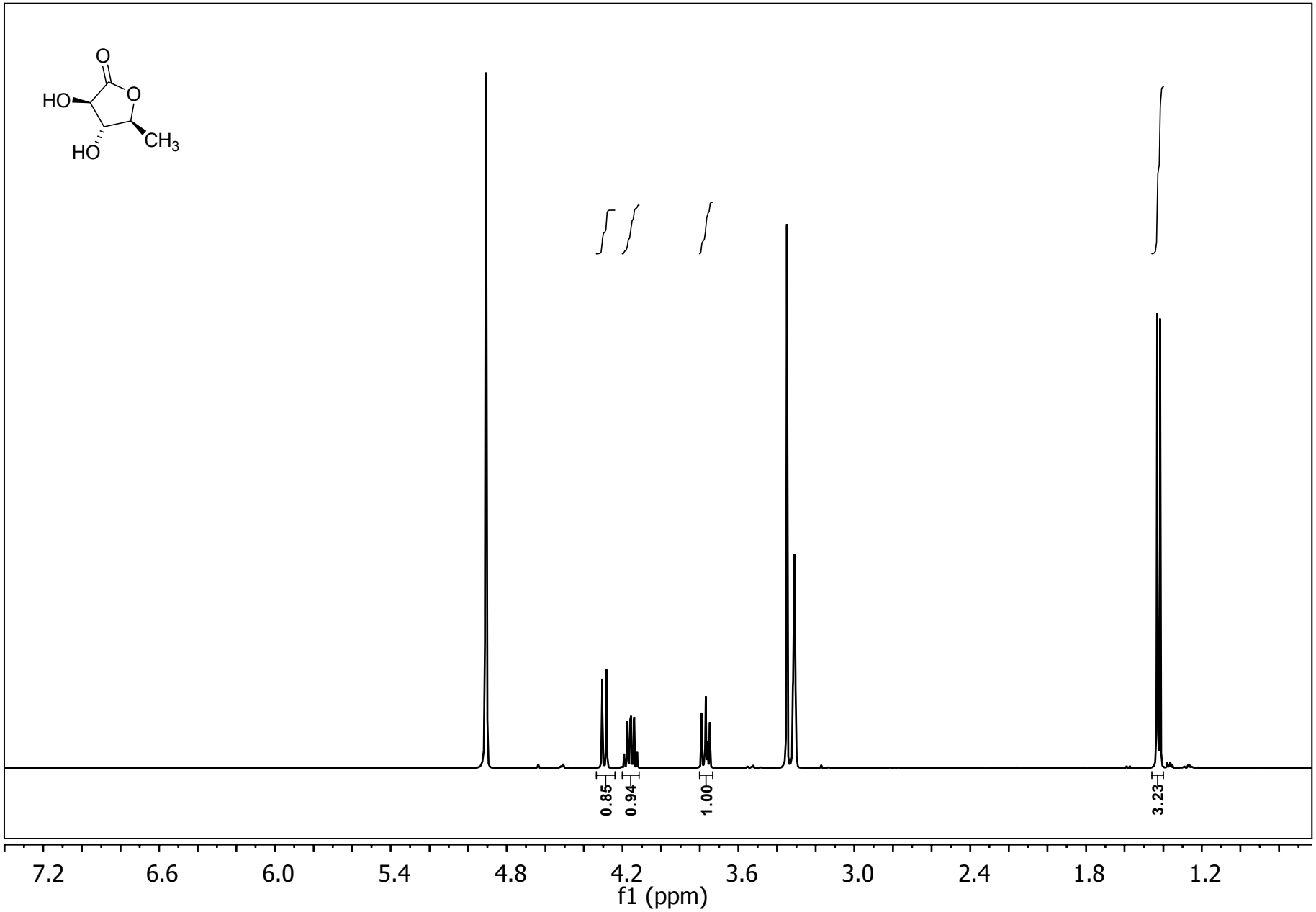


**Figure S33.** (3*R*,4*S*,5*S*)-3,4-Dihydroxy-5-methyldihydrofuran-2(3*H*)-one, **29**,
$^{13}C$ NMR spectrum, $CD_3OD$, 125 MHz.

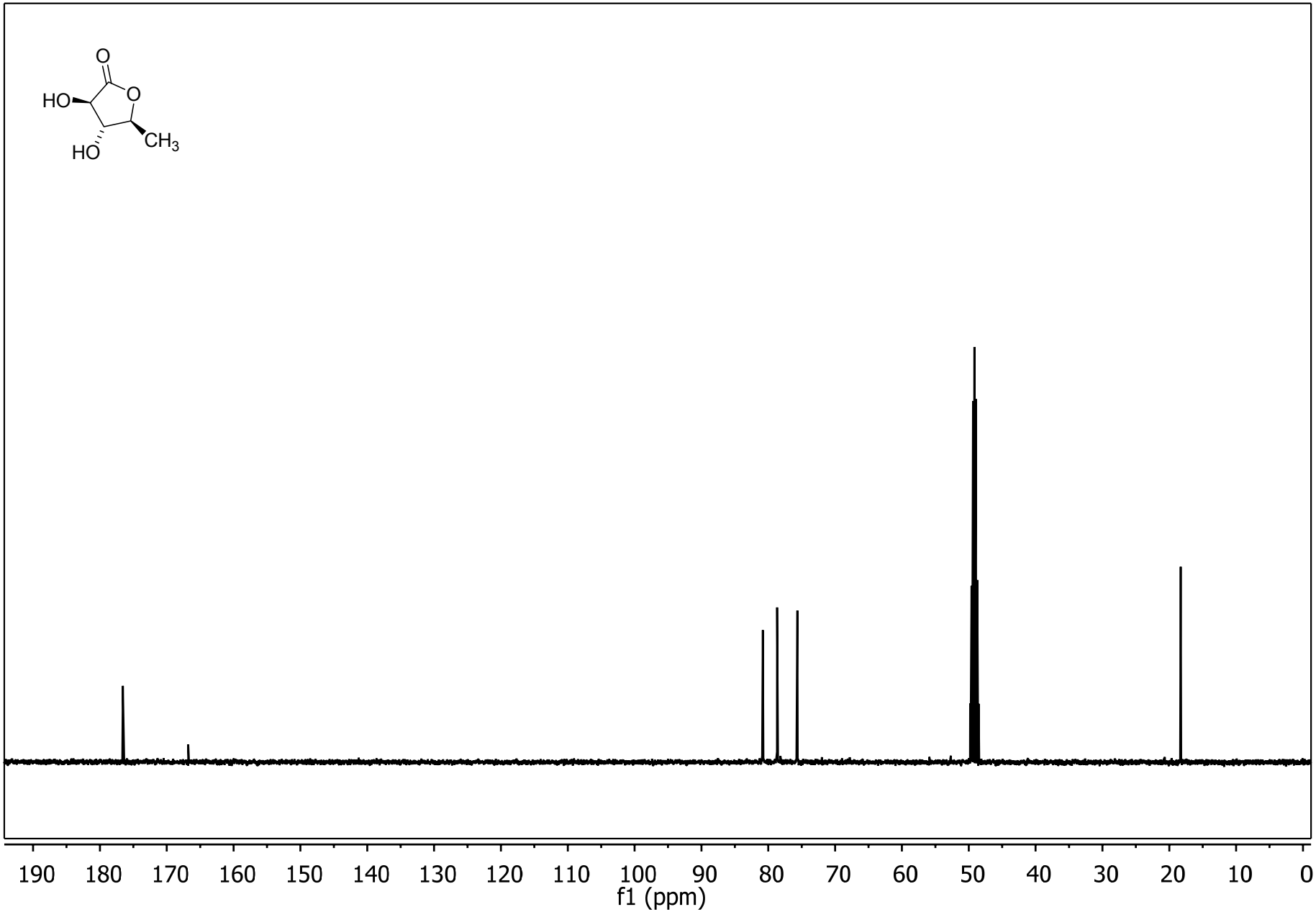


**Figure S34.** 5-Deoxy-L-arabinose, **26**, mixture of anomers,
$^1$H NMR spectrum, $CD_3OD$, 400 MHz.

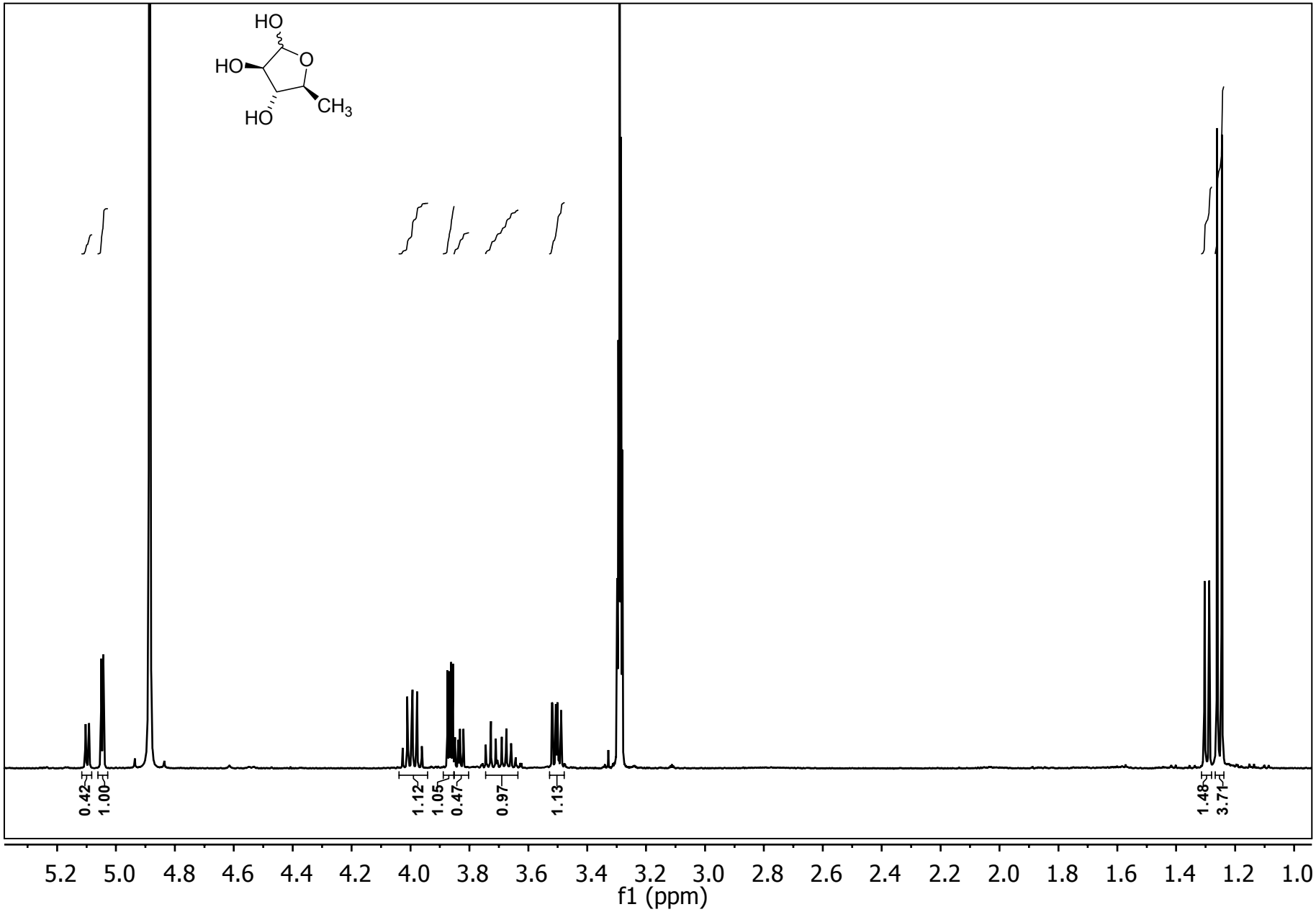


**Figure S35.** 5-Deoxy-L-arabinose, **26**, mixture of anomers,
$^{13}C$ NMR spectrum, $CD_3OD$, 125 MHz.