SUPPORTING INFORMATION FOR

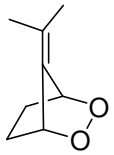
Triphenylphosphine Reduction of Saturated Endoperoxides

Ihsan Erden,* Christian Gärtner, M. Saeed Azimi

San Francisco State University, Department of Chemistry and Biochemistry, 1600 Holloway Avenue, San Francisco, CA 94132, USA, ierden@sfsu.edu

General. Melting points were determined in open class capillary tubes and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz and a 500 MHz NMR spectrometer, using $CDCl_3$ as solvent and TMS as internal standard, unless specified otherwise. IR spectra were obtained on a DTGS FT-IR spectrometer. Column chromatographic separations were carried out with Davison 6-200 Mesh silica gel. For preparative TLC, Merck silica gel (grade 60 PF_{254}) was used. All reactions, except for the photooxygenations, were conducted under an atmosphere of dry nitrogen or argon. Non-deuterated solvents were dried and distilled prior to use. Exact masses of all new products by high resolution mass spectra (HRMS) were determined at the University of Notre Dame Mass Spectrometry Facility (http://www.nd.edu/~massspec/).

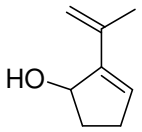
PPh_3 Reduction of 6. The synthesis of the saturated endoperoxide **6** was accomplished as described by Adam and Erden (ref. 13). The data for the 300 MHz ^{1}H NMR spectrum of **6** are listed below:



6

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.85 (t, J= 1.2 Hz, 2H), 2.0 (m, 2H), 1.80 (s, 6H), 1.68 (m, 2H) ppm.

To a solution of 0.7 g (5 mmol) of endoperoxide **6** in 100 mL CH_2Cl_2 was added at 0 ^oC 1.56 g (6 mmol) of triphenylphosphine, and the mixture was stirred first at 0 ^oC for two hours and then overnight at room temperature. The solvent was rotovapped and the product mixture separated by flash chromatography on silica gel, eluting with pet.ether/ether 3:1. The top fraction (100 mg, 16% yield) was isolated as a colorless liquid and proved to be the allenic aldehyde **8** whose ^{1}H NMR spectrum was identical to the one reported by Crandall and Mualla. Since it proved to be sensitive to silica gel and heat, it was immediately converted to its oxime (vide infra). The second fraction was isolated as a colorless liquid (397 mg, 64%).

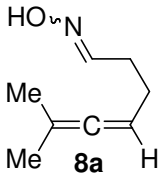


7

2-Isopropenylcyclopent-2-enol (**7**): Though compound **7** was reported previously the spectral data reported for this compound do not match ours, presumably due to the fact that they were obtained on a lower resolution spectrometer. ^{1}H NMR (500 MHz, $CDCl_3$) δ

5.93 (t, J= 2.65 Hz, 1H), 5.2 (s, 1H), 5.04 (m, 1H), 5.02 (s, 1H), 2.62 (m, 1H), 2.35 (m, 1H), 2.26 (m, 1H), 1.90 (m, 1H), 1.94 (s, 3H), 1.7 (br. 1H, OH); ^{13}C NMR (128.5 Hz, $CDCl_3$) δ 146.7, 138.7, 131.9, 113.6, 76.9, 34.4, 31.2, 21.7 ppm; FT-IR (thin film) ν 3341, 3043, 3096, 2967, 2921, 2840, 1631, 1456, 1439, 1374, 1299, 1147, 1042, 978, 931, 884, 832 cm^{-1}; HRMS was unsuccesful, the base peak was at 107 (M-17). MS (ei) 124 (M^+), 107 (100%), 95, 81, 67, 53.

Derivatization of aldehyde 8 as its oxime 8a. To a stirred solution of 100 mg (0.8 mmol) of aldehyde **8**, 4 mL of ethanol under nitrogen were added anhydrous sodium acetate (189 mg, 2.30 mmol) followed by hydroxylamine hydrochloride (556 mg, 0.8 mmol). The mixture was stirred at room temperature for 30 min, then 20 mL of water was added, the mixture extracted with 25 mL of diethyl ether, the organic extract washed with 5 mL of sat. aqueous $NaHCO_3$, dried over $MgSO_4$ and the solvent rotovapped to give a mixture of a 1.1:1 mixture of the *syn* and *anti* oximes, respectively (106 mg, 96% yield). For an analytical sample, the mixture was pruified by preparative TLC, eluting with 40% PE/ 60% EtOAc.

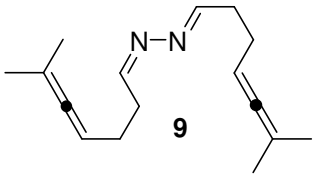


8a

Syn-and anti-6-Methylhepta-4,5-dienal oximes (**8a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.6-8 (br., 1H, NOH), 7.4 (t, J= 5.9 Hz, 1H, HC=CNOH, *syn* isomer), 6.7 (t, J= 5.2 Hz, 1H, HC=CNOH, *anti* isomer), 5.0 (m, 1H, =CH, both isomers), 2.48 (m, 1H); 2.3 (m, 1H), 2.15 (m, 2H), 1.67 (d, J= 3.0 Hz, 6H, Me); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 202.6, 153.4, 152.6, 97.2, 97.1, 88.2, 88.0, 31.2, 29.5, 26.8, 26.2, 24.8, 21.37, 21.36 ppm; FT-IR (thin film): ν 3265, 3105, 2958, 2909, 8852, 1965, 1945, 1442, 1409, 1254, 1086, 1013, 862, 796, 698, 662 cm-1; HMRS calcd for $C_8H_{13}NO$ 139.0997; found 139.0997.

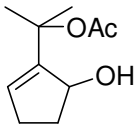
PPh_3 Reduction of 6 in the presence of AcOH. 6,6-Dimethylfulvene (0.796 g ,7.5 mmol) was dissolved in 100 mL of dry CH_2Cl_2, 4 mg of *meso*-tetraphenylporpyhrin was added and the solution was irradiated under a positive pressure of dry oxygen with a 400 W high-pressure sodium vapor lamp at -78 ^{o}C with strirring for 3 h. The progress of the reaction was monitored by TLC. After all starting material had reacted, 8.74g (45 mmol) potassium diazocarboxylate ($K^+O_2CN{=}NCO_2^-K^+$) was added to the cold photolysate, and to this slurry, of with and in situ reduction of the unsaturated endoperoxide with excess diazene, and 6.0 g (0.1 mol) of glacial acetic acid dissolved in 25 mL of dry CH_2Cl_2 was added dropwiswe within 10 min. After complete addition, the mixture was gradually allowed to warm to -40 ^{o}C and held at that temperature for 30 min before the temperature was gradually raised to 0 ^{o}C and the mixture stirred at this temperature for another 30 min. The white precipitate (KOAc) was filtered by suction at 0 ^{o}C and the filter cake washed with cold CH_2Cl_2. The solution was transferred to a 250 mL round-bottomed flask equipped with a pressure-equalizing addition funnel. To this, solution of 1.967 g (7.5 mmol) of PPh_3 in 10 mL was added to the solution and the mixture was stirred at 0 ^{o}C for 30 min and then at room temperature overnight. The solution was then washed with 15 mL of saturated $NaHCO_3$ solution, then 20

mL of H_2O, and dried over anyhdrous Na_2SO_4. After filtration, the solution was rotovapped, and the residue dissolved in 5 mL of 1:1 ether/PE-40-60^o. The solution was stored in the freezer at -30 ^{o}C overnight, and the precipitated $Ph_3P=O$ was filtered off, the solvent rotovapped, and the residue subjected to column chromatography on silica gel (50% PE-40-60^o/50% EtOAc). The products are listed below in order of elution from the column.



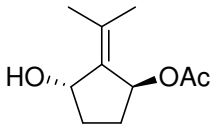
9

6-Methyl-4,5-dienal azine (**9**). 0.09g, 9.6%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (t, J= 6.0 Hz, 2H, C<u>H</u>=N), 5.01 (m, 2H, C<u>H</u>=C=C), 2.46 (m, 4H, C<u>H$_2$</u>-CH=N), 2.18 (m, 4H, C<u>H$_2$</u>-C=C), 1.67 (d, J= 2.7 Hz, 12H, (<u>CH$_3$</u>)$_2$C=); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.7 (C=<u>C</u>=C), 165.0 (<u>C</u>H=N), 96.1 (Me2<u>C</u>=C), 87.4 <u>C</u>H=C=C), 32.0 (<u>C</u>H$_2$-CH=N), 26.2 (<u>C</u>H$_2$-CH=C), 20.5 (<u>C</u>H$_3$) ppm; FT-IR (thin film) n 2974, 2925, 2909, 2852, 1965, 1740, 1695, 1650, 1442, 1364, 1332, 1228, 1185, 1115, 1033, 796, 723 cm^{-1}; HRMS calcd for $C_{16}H_{24}N_2$ 244.1939; found 244.2939.



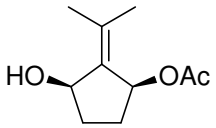
11a

2-(5-Hydroxcyclopent-1-enyl)propan-2-yl acetate (**11a**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (t, J= 2.1 Hz, 1H), 4.79 (m, 1H), 2.64 (br.s, 1H, OH), 2.5 (m, 1H), 2.1-2.3 (m, 2H), 2.00 (s, 3H), 1.85 (m, 1H), 1.622 (s, 3H), 1.621 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 149.6, 131.9, 130.7, 80.8, 77.4, 35.1, 30.3, 28.6, 27.6 ppm; FT-IR (thin film) ν 3432, 3048, 2974, 2938, 2856, 1732.1, 1454, 1430, 1254, 1197, 1131, 1042, 1009, 960, 935, 841, 809 cm^{-1}; HRMS calcd for $C_{10}H_{17}O_3$ 184.1099; found 185.1184.



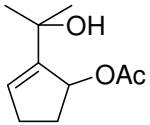
10b

***trans*-3-Hydroxy-2-(propan-2-ylidene)cyclopentyl acetate** (**10b**). ^{1}H NMR (300 MHz, $CDCl_3$) d 5.8 (m, 1H), 4.8 (m, 1H), 1.8-2.1 (m, 4H), 2.02 (s, 3H), 1.96 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 139.2, 138.8, 72.2, 75.4, 34.5, 32.1, 22.2, 22.1, 21.7 ppm.



10a

***cis*-3-Hydroxy-2-(propan-2-ylidene)cyclopentyl acetate** (**10a**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.6 (t, J= 5.6 Hz, 1H), 4.7 (t, J= 4.5 Hz, 1H), 2.05 (s, 3H), 1.83-2.10 (m, 4H), 1.9 (s, 3H), 1.7 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 171.5, 137.8, 137.3, 75.7, 72.6, 34.1, 31.3, 22.0, 21.9, 21.7 ppm; FT-IR (thin film) ν 3422, 2964, 2935, 2854, 1732, 1441, 1374, 1243, 1170, 1151, 1108, 1070, 1040, 1016, 979, 954, 920, 894, 743 cm^{-1}; HMRS calcd for $C_{10}H_{16}O_3$ 184.1099. Found 185.1184.

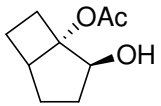


11b

2-(2-Hydroxypropan-2-yl)cyclopent-2-enyl acetate (**11b**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.9 (narrow m, 1H), 5.46 (m, 1H), 2.0 (s, 3H), 1.8-2.7 (m, 4H), 1.61 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 140.2, 129.6, 83.7, 77.2, 31.6, 30.8, 28.4, 28.1, 21.7 ppm.

Synthesis of Endoperoxide 21 (see also ref. 19). In a 500 mL round-bottomed flask, equipped with a magnetic spin-bar and a rubber septum, spiro[2.4]hepta-4,6-diene (.691 g, 7.5 mmol) was dissolved in 250 mL of dry CH_2Cl_2, and 4 mg of *meso*-tetraphenylporphyrin was added. The solution was purged with dry oxygen, and a balloon filled with dry oxygen was inserted through the rubber septum by means of a syringe needle. The flask was immersed in a flat Dewar flask containing dry-ice/acetone and irradiated with a 400 W Na high-pressure vapor lamp while stirring. The progress of the oxygen uptake was monitored by means of TLC. When all the starting

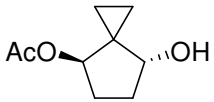
material was consumed, 8.7g of potassium azodicarboxylate ($K^{+-}O_2CN{=}NCO_2^{-+}K$) was added to the photolysate at -78 ^oC, and the oxygen ballon replaced by a pressure-equalizing addition funnel containing 5.1g of glacial acetic acid in 10 mL of dry CH_2Cl_2 and equipped with a drying tube. The acetic acid solution was added to the mixture dropwise within 5 min, and the bath temperature gradually raised to -40 ^oC while stirring. Vigorous gas evolution was observed during gradual warm-up to 0 ^oC. Then the mixture was stirred at 0 ^oC for another 30 min, the salt (KOAc) was filtered by suction, keeping the filter flask in an ice bath. The mixture was then placed in a 500 mL round-bottomed flask immersed in an ice-bath, and 0.45g (7.5 mmol) of glacial acetic acid followed by 1.96g (7.5 mmol) of PPh_3 was added. After stirring overnight at room temperature, the solution was extracted with saturated $NaHCO_3$ (1x50 mL), dried over anhydrous Na_2SO_4 and filtered by gravity. The solvent was rotovapped, the residue subjected to chromatography on silica gel, eluting with 1:1 pet.ether(40-60^o)/EtOAc. The products isolated are listed below in order of their R_f values.



22

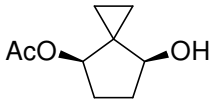
***trans*-2-Hydroxybicyclo[3.2.0]heptan-1-yl acetate** (**22**). 122 mg (13% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 4.0 (m, 1H), 3.83 (br. s, 1H, OH), 2.71 (m, 1H), 2.63 (m, 1H), 2.1 (m, 2H), 2.0 (s, 3H), 1.8-2.0 (m, 2H), 1.7 (m, 1H), 1.2-1.5 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5 (s), 90.9 (s), 79.3 (d), 43.4 (d), 32.4 (t), 27.6 (t), 24.9 (t), 21.9 (q), 19.0 (t) ppm; FT-IR (thin film) ν 3510, 2954, 2860,

1731, 1716 (sh), 1387, 1368, 1344, 1266, 1246, 1181, 1107, 1066, 1042, 1017 cm^{-1}; Anal. calcd for $C_9H_{14}O_3$ C 63.51; H 9.29; found C 63.48, H 9.24; MS (ei): 171 (M+1), 153, 128, 111, 94, 81, 65.



23a

***trans*-7-Hydroxyspiro[2.4]heptan-4-yl acetate** (**23a**). 357 mg (28% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.9 (dd, J= 6.0, 2.1 Hz, 1H), 3.93 (dd, J= 5.7, 4.0 Hz, 1H), 2.3 (m, 1H), 2.1 (m, 1H), 2.0 (s, 3H), 1.7 (m, 2H), 0.86 (m, 1H), 0.81 (m, 1H), 0.6 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 80.5, 76.8, 43.5, 33.8, 30.9, 21.9, 8.9, 8.4 ppm; FT-IR (thin film) ν 3424, 3080.6, 2966, 2942, 1732, 1715 (sh), 1434, 1377, 1307, 1246, 1160, 1086, 1025, 976 cm^{-1}; HMRS calcd for $C_9H_{14}O_3$ 170.0943; found 171.1022; MS (ei) 153 (M+1), 127, 110, 95, 81, 65, 53.

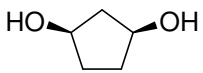


23b

***cis*-7-Hydroxyspiro[2.4]heptan-4-yl acetate** (**23b**). 344 mg (27% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73 (dd, J= 6.0 Hz, 2.4 Hz, 1H), 3.58 (t, J= 2.4 Hz, 1H), 1.7-2.2 (m, 4H), 2.0 (s, 3H), 0.6-0.9 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5 (s), 82.9 (d), 80.1 (d),

34.4 (t), 34.7 (s), 22.0 (q), 15.3 (t), 5.82 (t) ppm; FT-IR (thin film) ν 3432, 3076.5, 2962, 2938, 2868, 1728, 1712 (sh), 1434, 1373, 1242, 1176, 1078, 1025, 972 cm^{-1}; HRMS calcd for $C_9H_{14}O_3$ 170. 0943; found 173.1166.

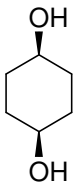
Triphenylphophine reduction of 2,3-dioxabicyclo[2.2.1]heptane (**3**). Cyclopentadiene (0.62 mL, 7.55 mmol) was photooxygenated and then reduced with diazene, generated in situ from potassium azodicarboxylate (8.74 g, 45 mmol) and 4.9 mL of acetic acid (85 mmol), as described for spiro[2.4]hepta-4,6-diene. After KOAc was suction filtered and the filtrate washed with 15 mL of a saturated aqueous solution of $NaHCO_3$, the organic layer was dried of anhydrous Na_2SO_4. After filtration, the CH_2Cl_2 solution of the saturated endoperoxide **3** was placed into a 500 mL round-bottomed flask equipped, the flask cooled in an ice-bath, a few drops of H_2O were added followed by PPh_3 (1.967 g, 7.5 mmol) at 0 ^oC while stirring. The mixture was first stirred at 0 ^{o} for an hour, and at room temperature overnight. The solvent was rotovapped, the residue taken up in 5 mL of ethyl acetate/petroleum ether 40-60^o (1:1), and the solution left in the freezer at -30 oC for two hours. Afterwards, the bulk of PPh_3=O that had precipitated was filtered off, and the residue purified on a silica gel column eluting with a 1:1 mixture of EtOAc/pet. ether 40-60^o to give 708 mg (92% yield) of *cis*-cyclopentane-1,3-diol (**28a**). This compound was identical to an authentic sample (*vide infra*) in all respects, with no traces of the *trans* isomer.



28a

***cis*-Cyclopentane-1,3-diol** (**28a**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.340 (s, 2H), 3.8 (br. s, 2H, OH), 1.87 (s, 4H), 1.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.8, 44.46, 34.13 ppm.

Triphenylphosphine reduction of 2,3-dioxabicyclo[2.2.2]octane (**27**). The saturated endoperoxide derived from cyclohexadiene was prepared as described. Endoperoxide **27** (0.2 g, 1.75 mmol) was dissolved in 15 mL of CH_2Cl_2. After adding a few drops of H_2O, 0.46 g (1.75 mmol) of PPh_3 was added, and the mixture was stirred at room temperature overnight. The solvent was totovapped, the residue purified by preparative TLC, eluting with 1:1 EtOAc/pet.ether 40-60^{o} to give 0.16 g (79%) cis-cyclohexane-1,4-diol (**28b**).

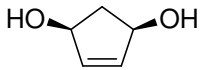


28b

***cis*-Cyclohexane-1,4-diol** (**28b**) ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.79 (s, 2H), 1.66 (m, 2H), 1.62 (m, 2H), 1.52 (br. s, 2H, OH); ^{13}C NMR (128.5 MHz, $CDCl_3$) δ 67.4, 30.3 ppm.

Independent synthesis of *cis*-diol 28a.

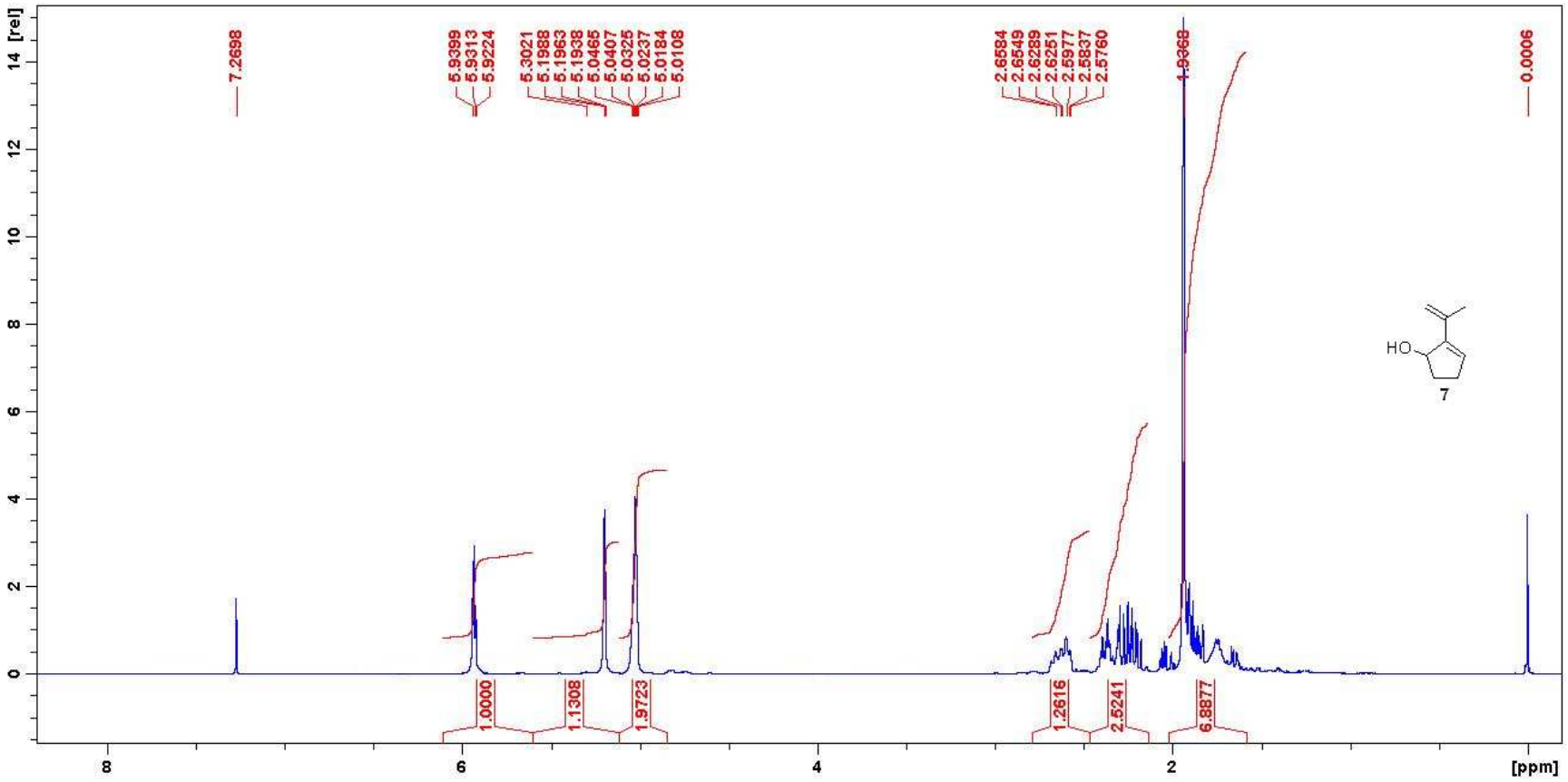
a) Cyclopentadiene (0.62 mmol, 7.5 mmol) was dissolved in 250 mL of methanol, 0.628 g (8.25 mmol) of thiourea and 5 mg of rose bengal were added, and the mixture was photooxygenated at -78 ^{o}C for 3 h. After the solvet was rotovapped, the residue was purified on a silica gel column (1:1 EtOAc/pet. ether 40-60^{o}) to give 0.437 g (69.4%) of **34a**.

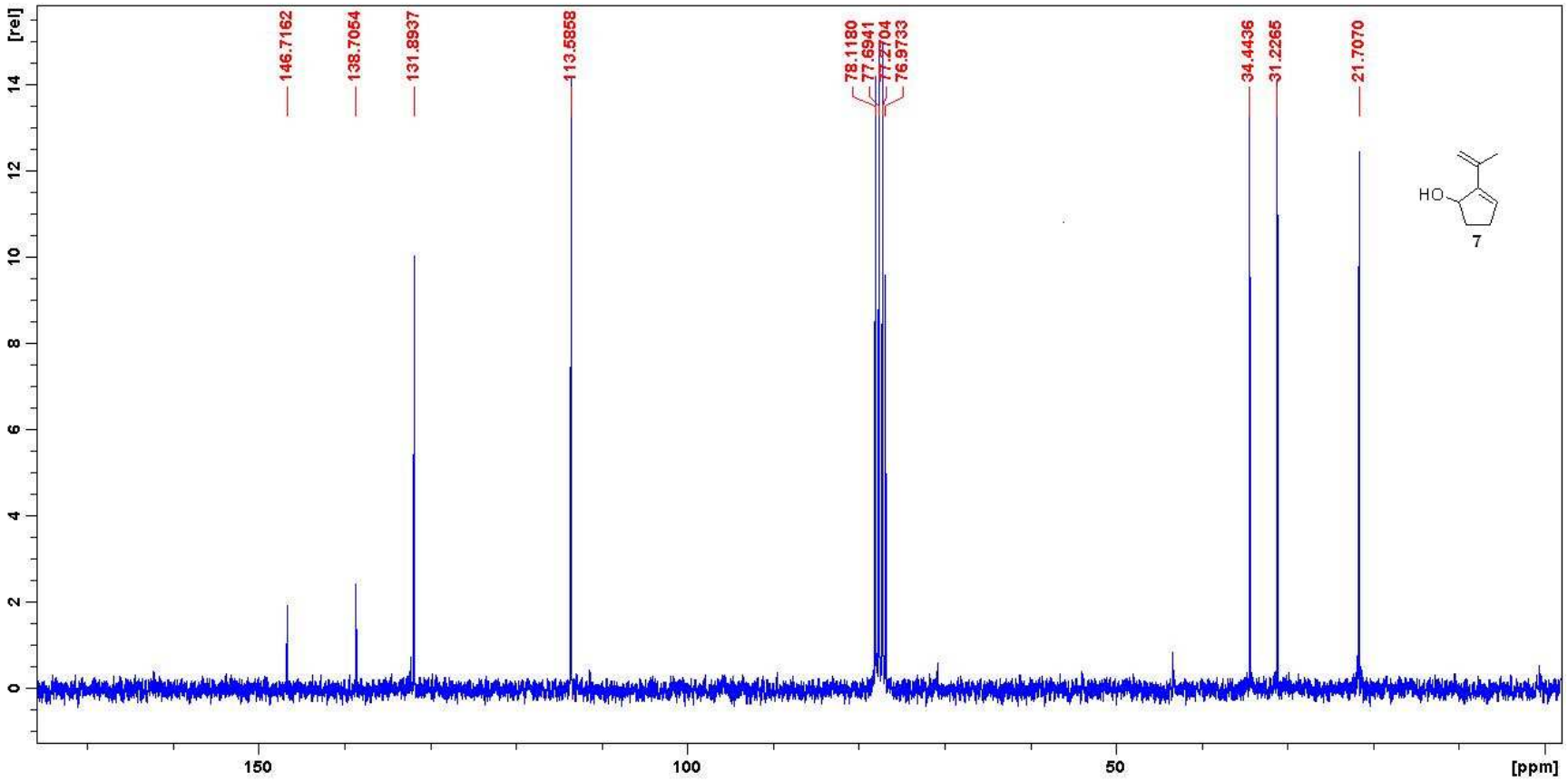


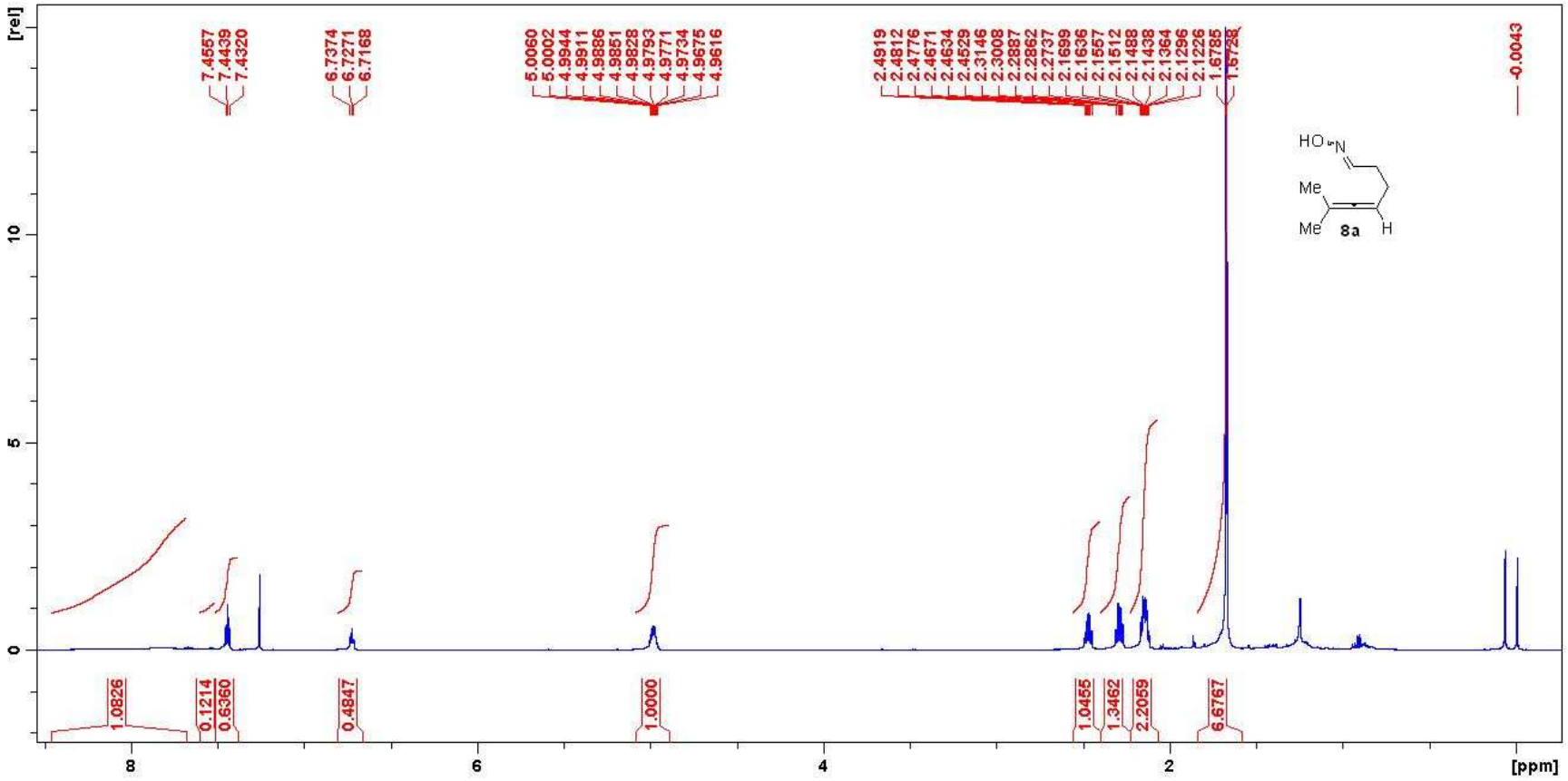
34a

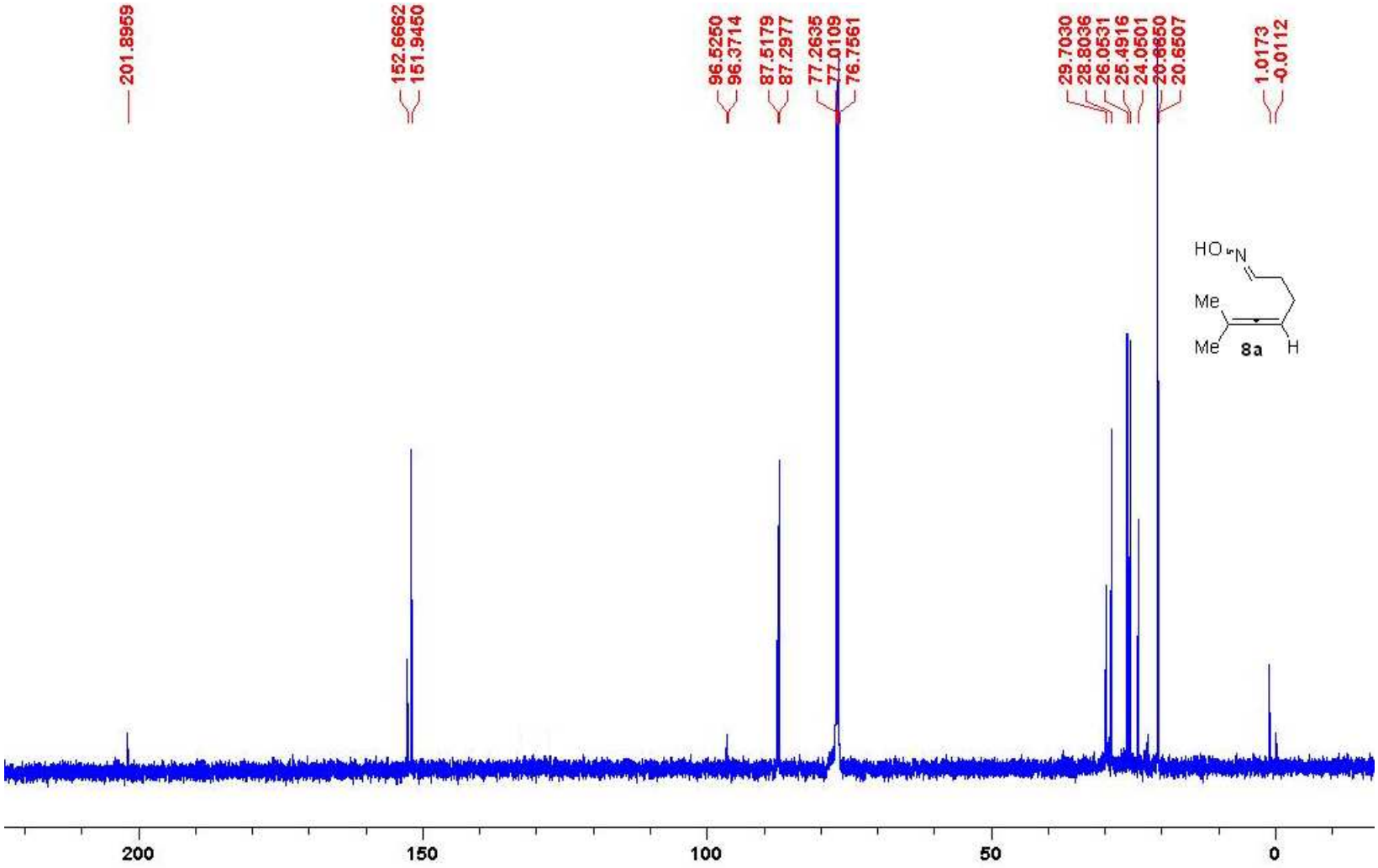
***cis*-Cyclopentene-1,3-diol** (**34a**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.0 (t, J= 2.4 Hz, 2H), 4.64 (m, quint., J= 3.6 Hz, 2H), 3.4 (br. s, 2H, OH), 2.7 (m, 1H), 1.55 (d, ^{2}J= 14.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 75.6, 44.1 ppm.

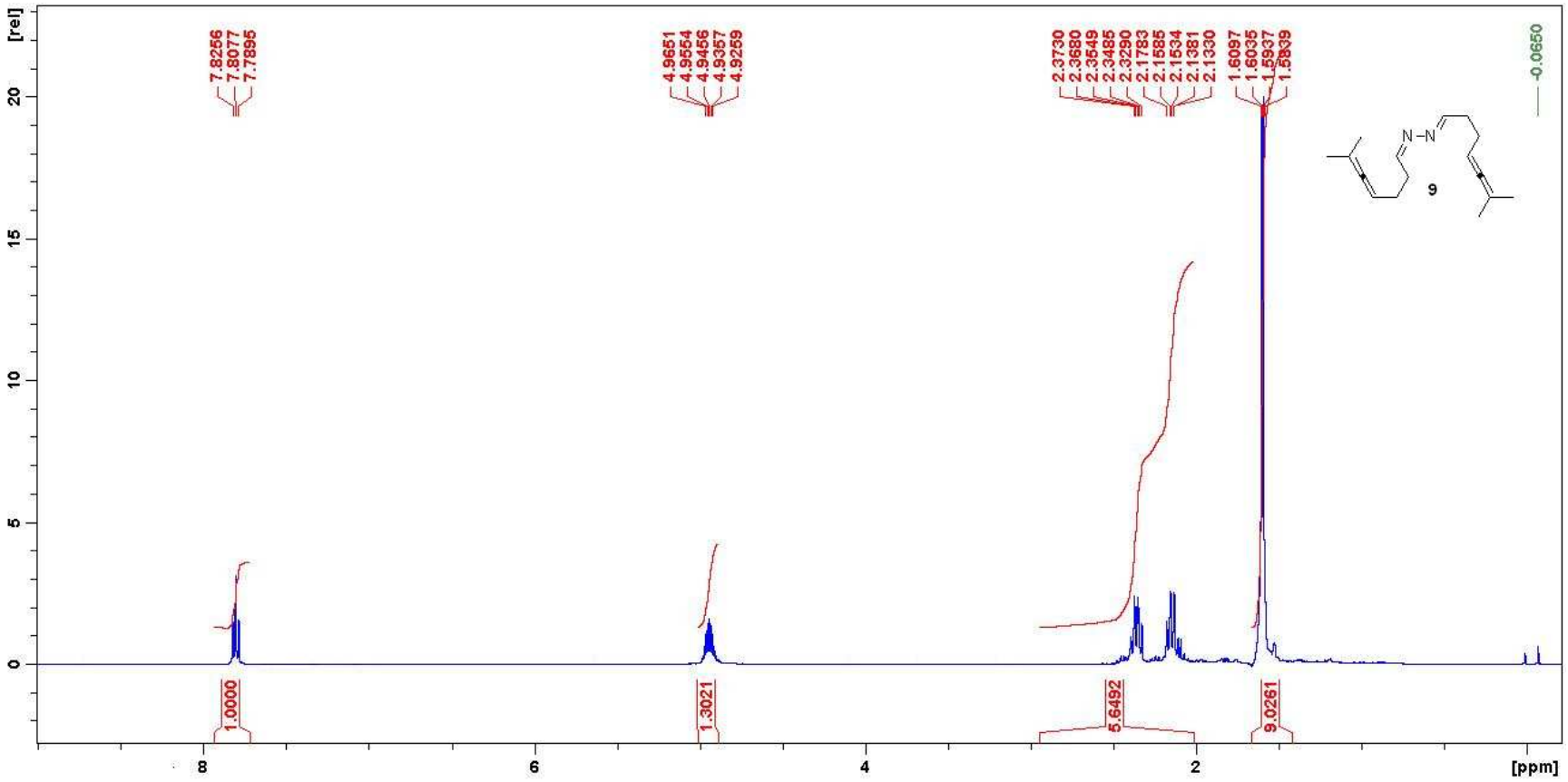
b) **Diazene reduction of *cis*-cyclopentene-1,3-diol** (**34a**). Diol **34a** (0.436g, 4.36 mmol) was dissolved in 50 mL of dry methanol. After cooling to 0 ^{o}C in an ice bath, potassium azodicarboxylate (5g, 26.16 mmol) was added, and while stirring, glacial acetic acid 3 mL (52.32 mmol) was added dropwise. The mixture was then stirred for 2 hours, filtered and the solvent rotovapped. The resulting product (0.420 mg, 94%) was identical to the *cis*-cyclopentane-1,3-diol (**28a**) obtained by PPh_3 reduction of **3** (*vide supra*).

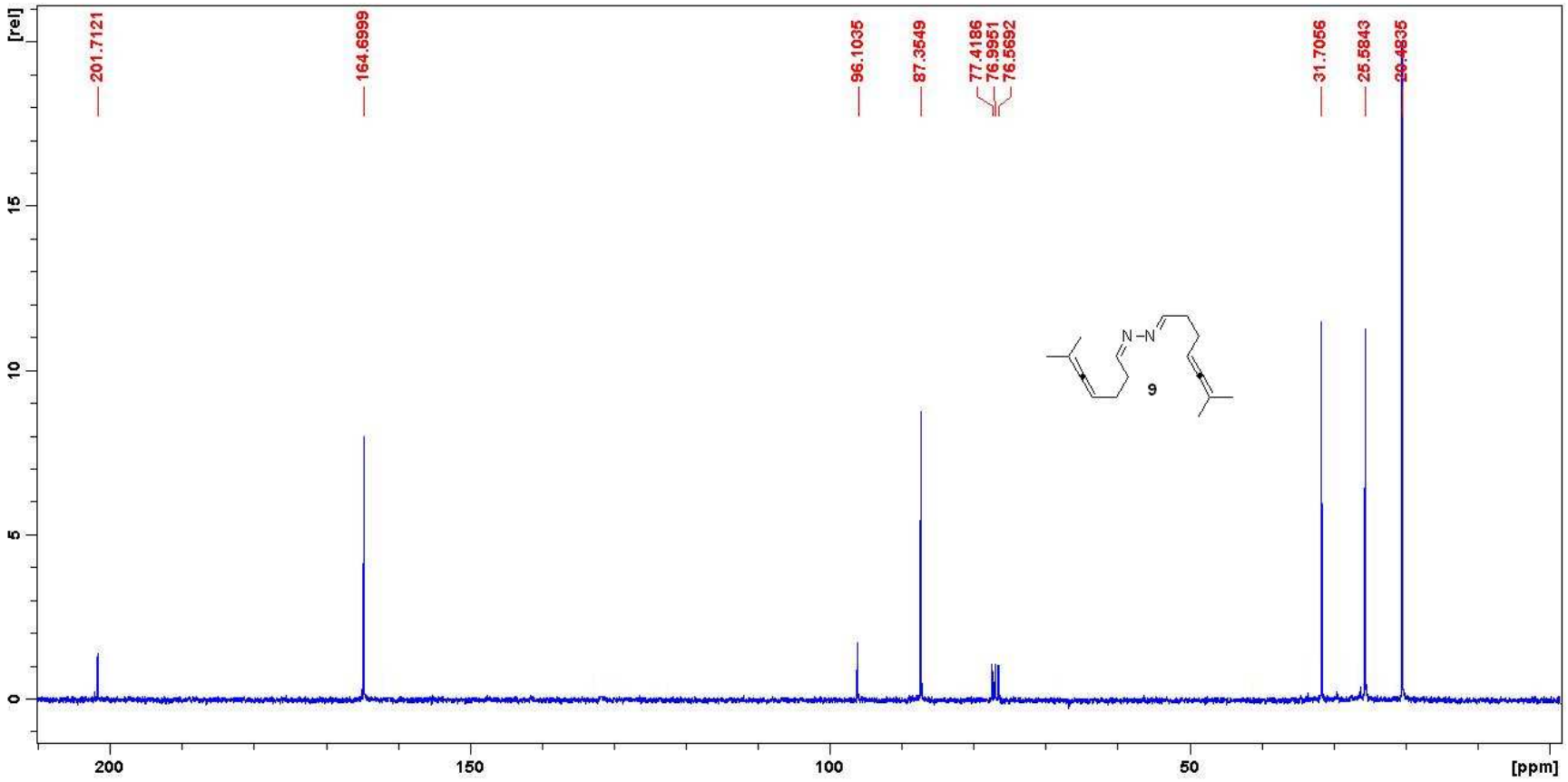

14 [rel]
12
10
8
6
4
2
0
7.2698
5.9399
5.9313
5.9224
5.3021
5.1988
5.1963
5.1938
5.0485
5.0407
5.0325
5.0237
5.0184
5.0108
2.6584
2.6549
2.6289
2.6251
2.5977
2.5837
2.5760
1.9368
0.0006
1.0000
1.1308
1.9723
1.2616
2.5241
6.8877
8
6
4
2
[ppm]
HO
7

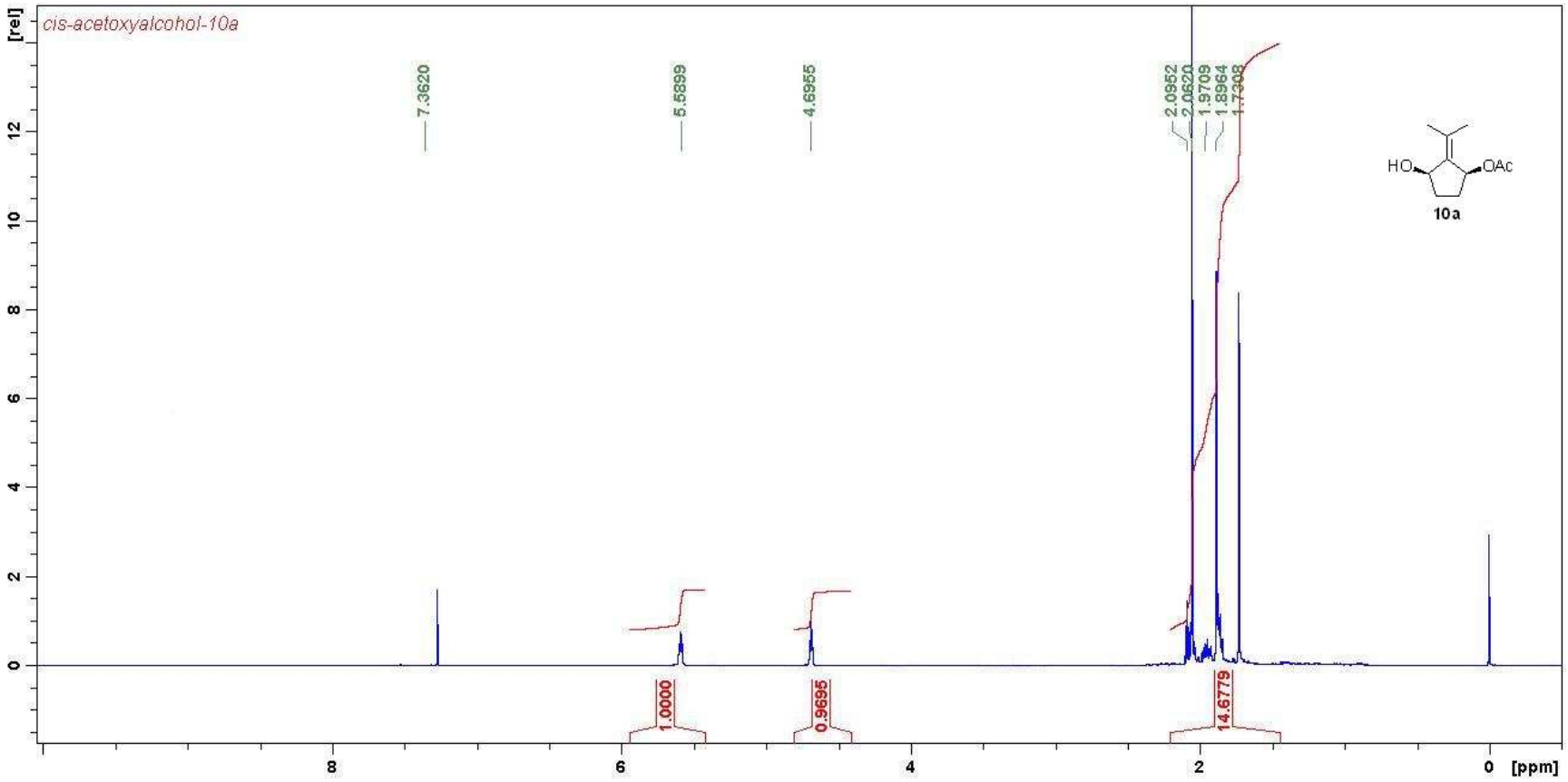

[rel]
146.7162
138.7054
131.8937
113.5858
78.1180
77.6941
77.2704
76.9733
34.4436
31.2265
21.7070
HO
7
150
100
50
[ppm]

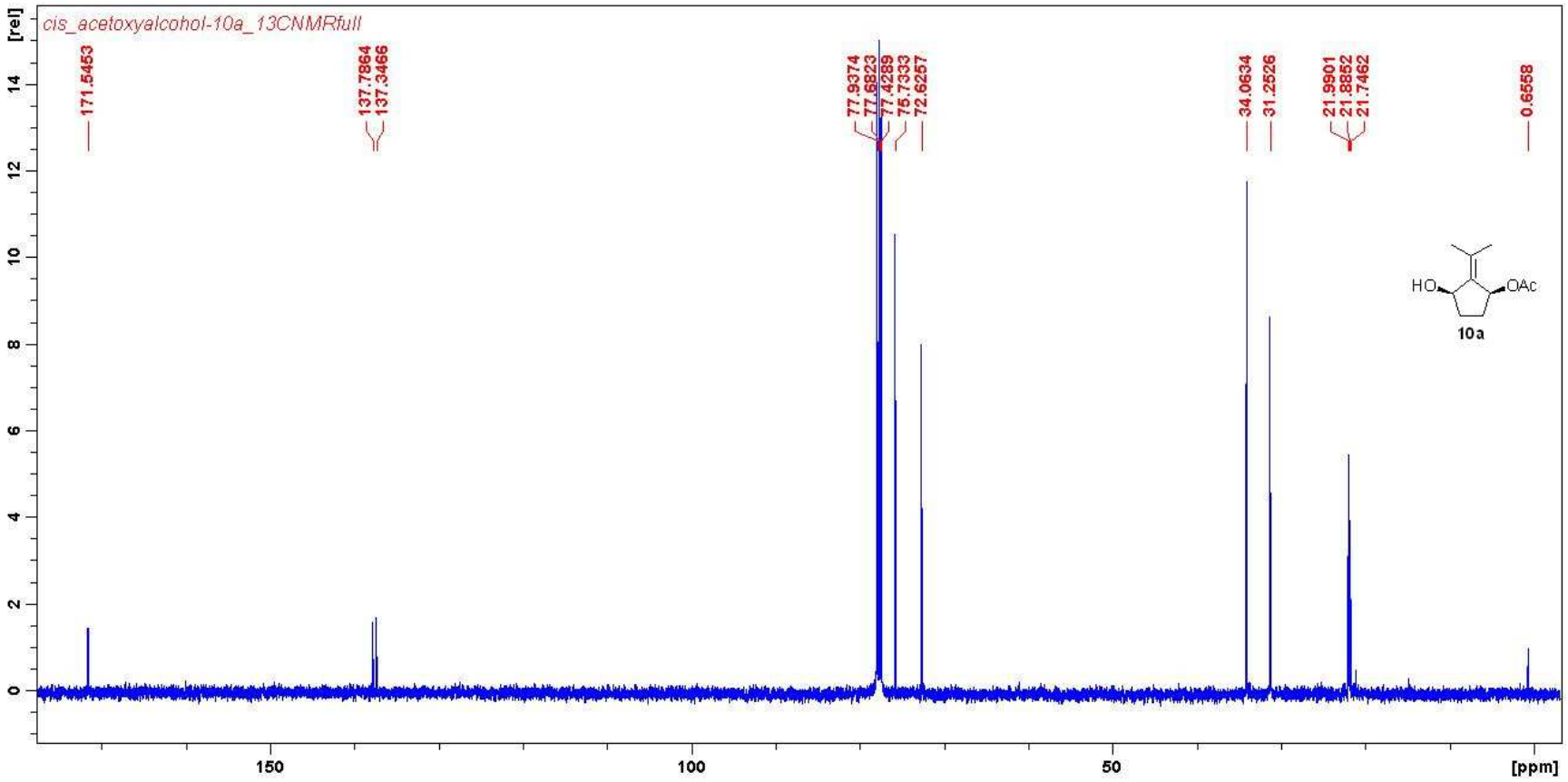

[rel]
7.4557
7.4439
7.4320
6.7374
6.7271
6.7168
5.0060
5.0002
4.9944
4.9911
4.9886
4.9851
4.9828
4.9793
4.9771
4.9734
4.9675
4.9616
2.4919
2.4812
2.4776
2.4671
2.4634
2.4529
2.3146
2.3008
2.2887
2.2862
2.2737
2.1699
2.1636
2.1557
2.1512
2.1488
2.1438
2.1364
2.1296
2.1226
1.6785
1.6728
-0.0043
HO
N
Me
Me
8a
H
1.0826
0.1214
0.6360
0.4847
1.0000
1.0455
1.3462
2.2059
6.6767
[ppm]

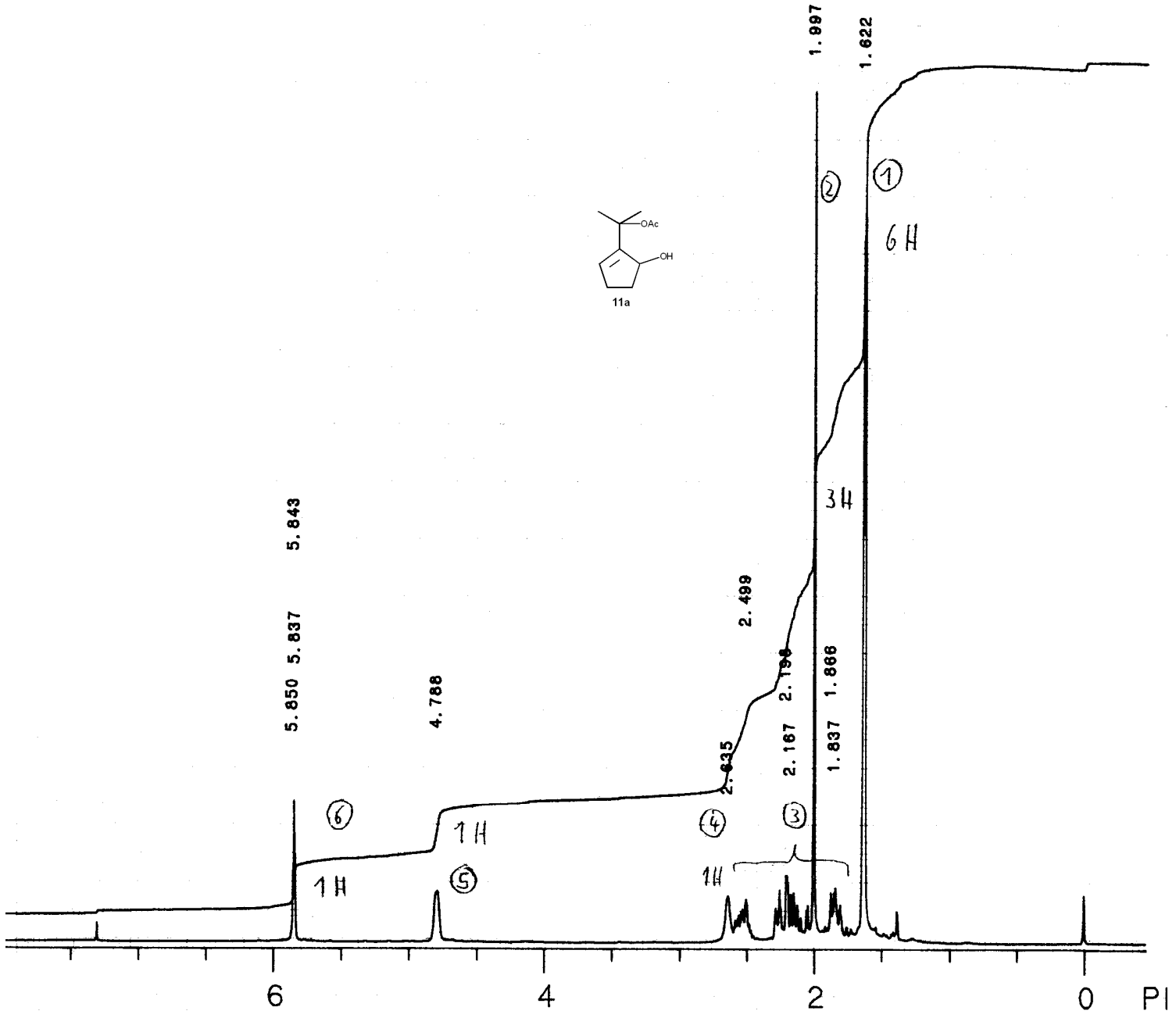

201.8959
152.6662
151.9450
96.5250
96.3714
87.5179
87.2977
77.2635
77.0109
76.7561
29.7030
28.8036
26.0531
25.4916
24.0501
20.6850
20.6507
1.0173
-0.0112
HO
N
Me
Me
8a
H
200
150
100
50
0

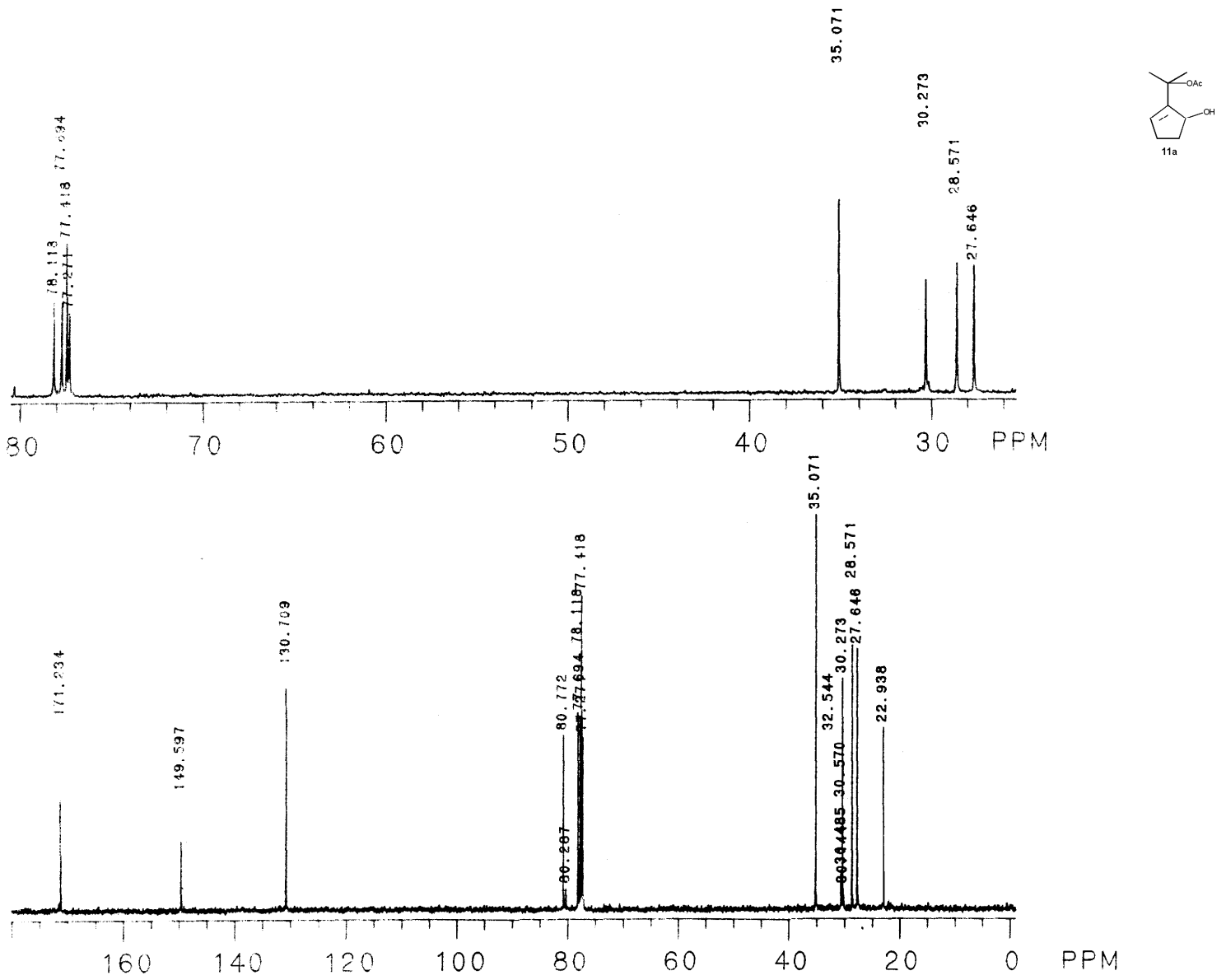

[rel]
20
15
10
5
0
7.8256
7.8077
7.7895
4.9651
4.9554
4.9456
4.9357
4.9259
2.3730
2.3680
2.3549
2.3485
2.3290
2.1783
2.1585
2.1534
2.1381
2.1330
1.6097
1.6035
1.5937
1.5839
-0.0650
N–N
9
1.0000
1.3021
5.6492
9.0261
8
6
4
2
[ppm]

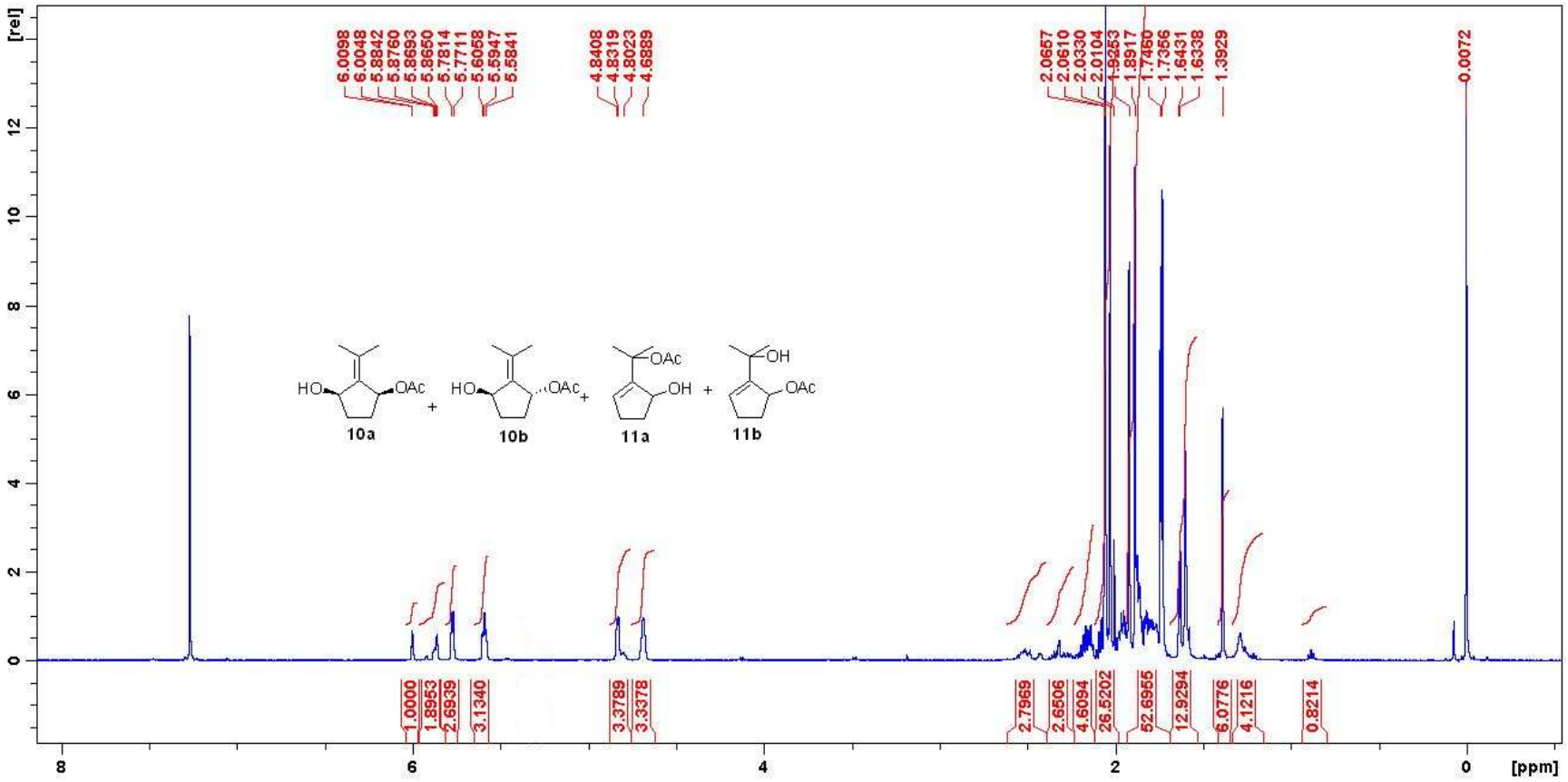

[rel]
201.7121
164.6999
96.1035
87.3549
77.4186
76.9951
76.5692
31.7056
25.5843
20.4835
N–N
9
0
5
10
15
200
150
100
50
[ppm]

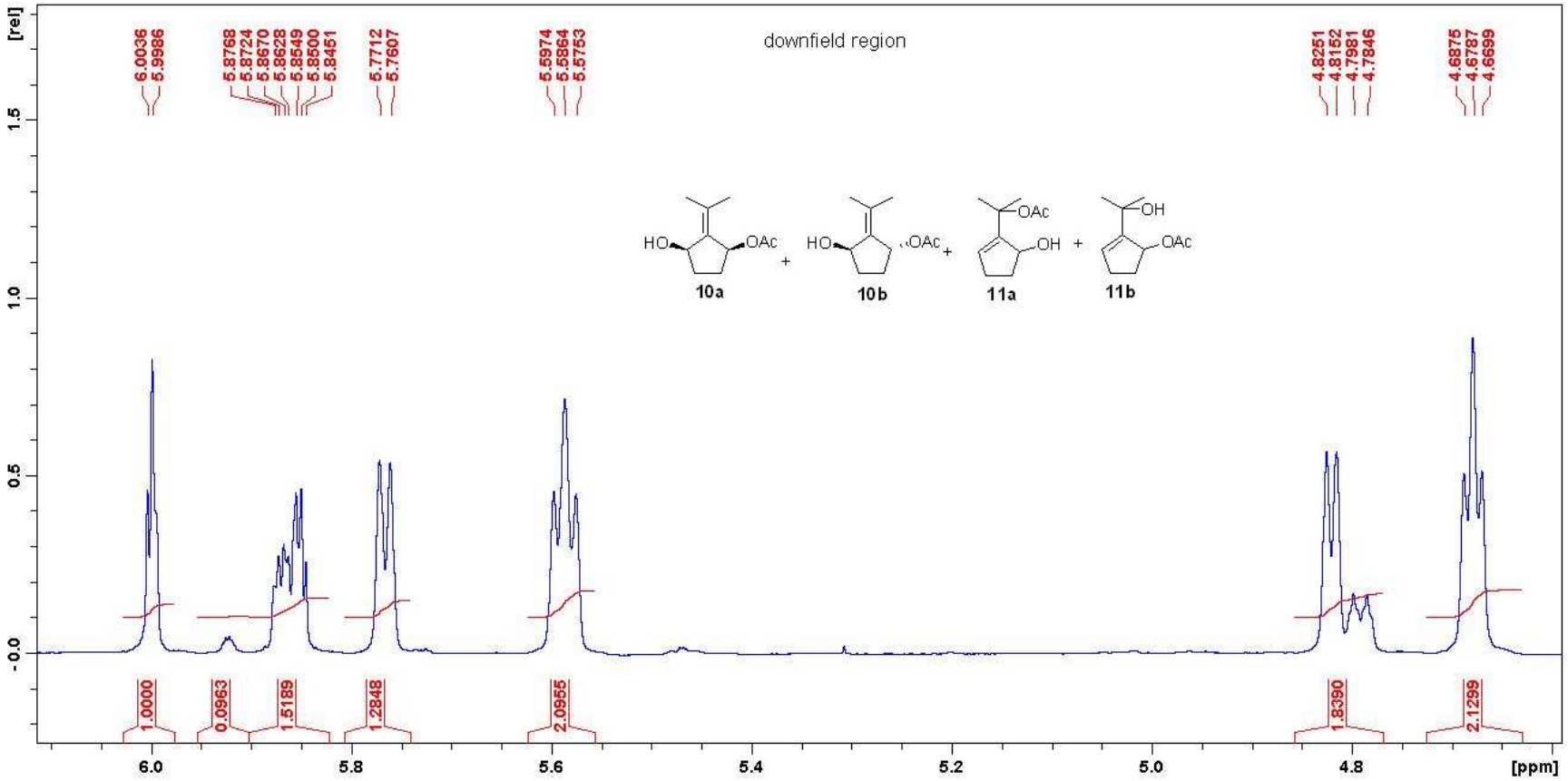

cis-acetoxyalcohol-10a
[rel]
7.3620
5.5899
4.6955
2.0952
2.0620
1.9709
1.8964
1.7308
HO
OAc
10a
1.0000
0.9695
14.6779
8
6
4
2
0
[ppm]

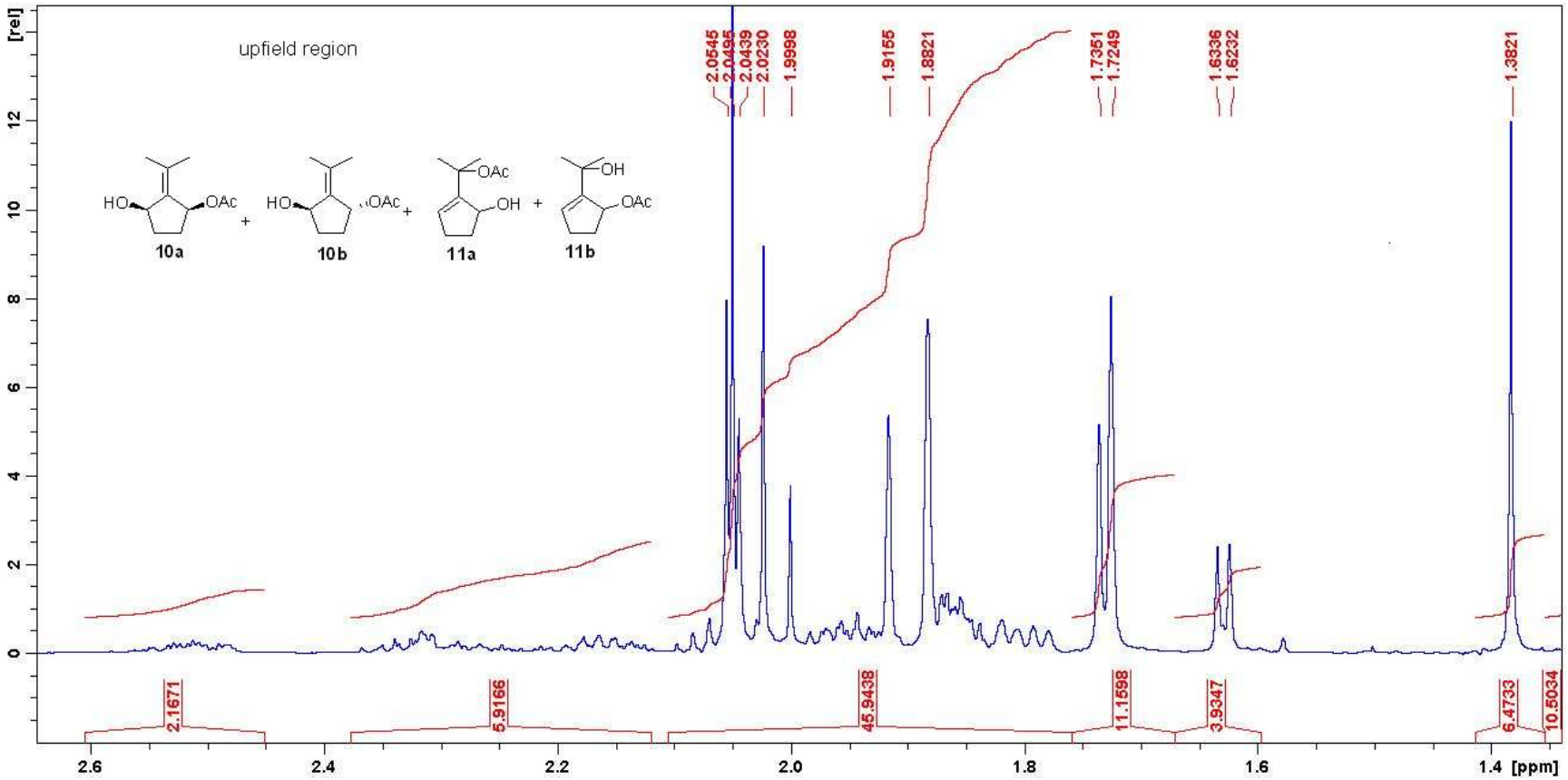

cis_acetoxyalcohol-10a_13CNMRfull
[rel]
171.5453
137.7864
137.3466
77.9374
77.6823
77.4289
75.7333
72.6257
34.0634
31.2526
21.9901
21.8852
21.7462
0.6558
HO
OAc
10a
150
100
50
[ppm]

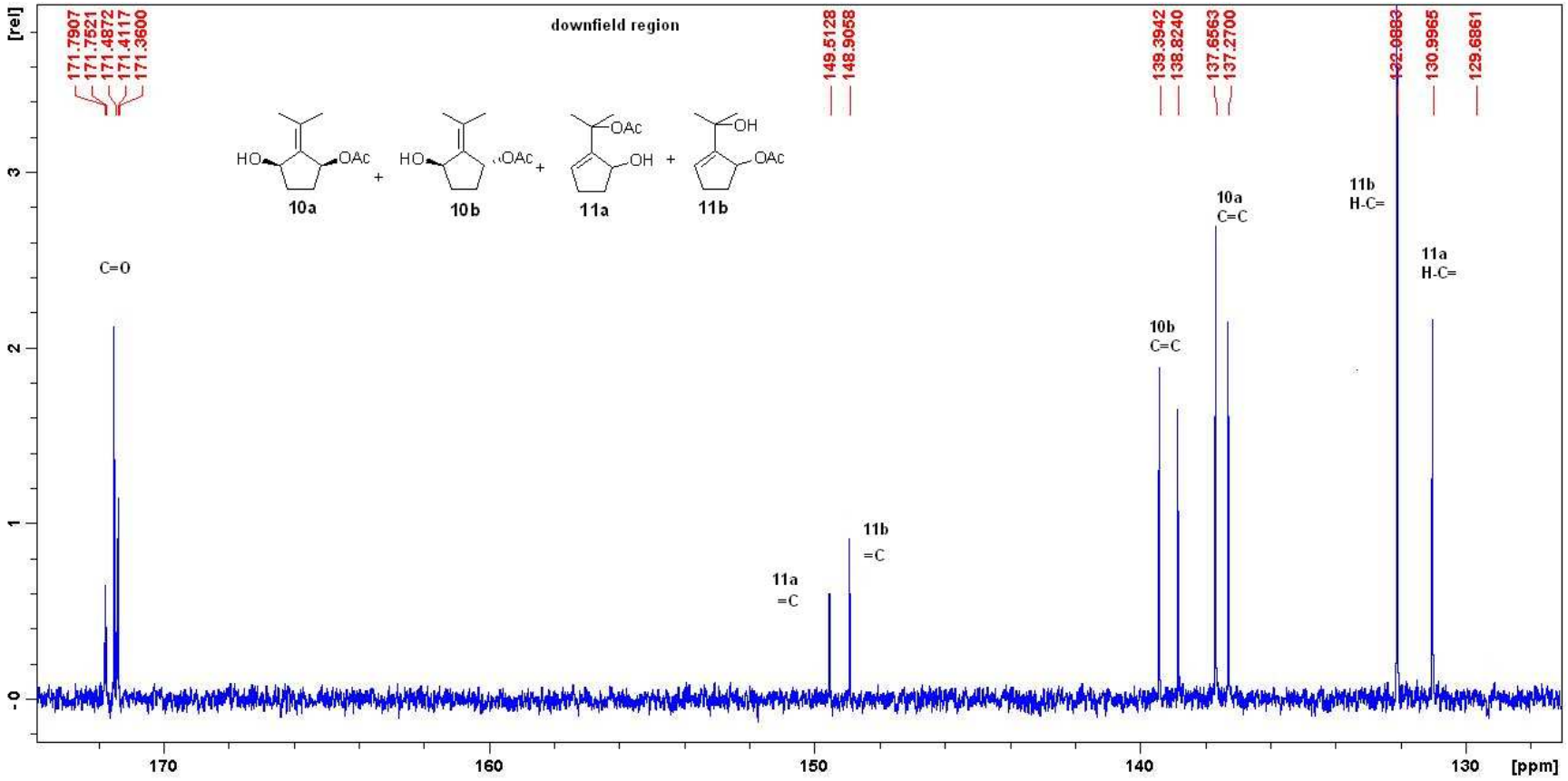

OAc
OH
11a
1.997
1.622
6 H
3H
5.843
5.837
5.850
4.788
2.499
2.196
1.866
2.635
2.167
1.837
1 H
1 H
1H
6
4
2
0
PI

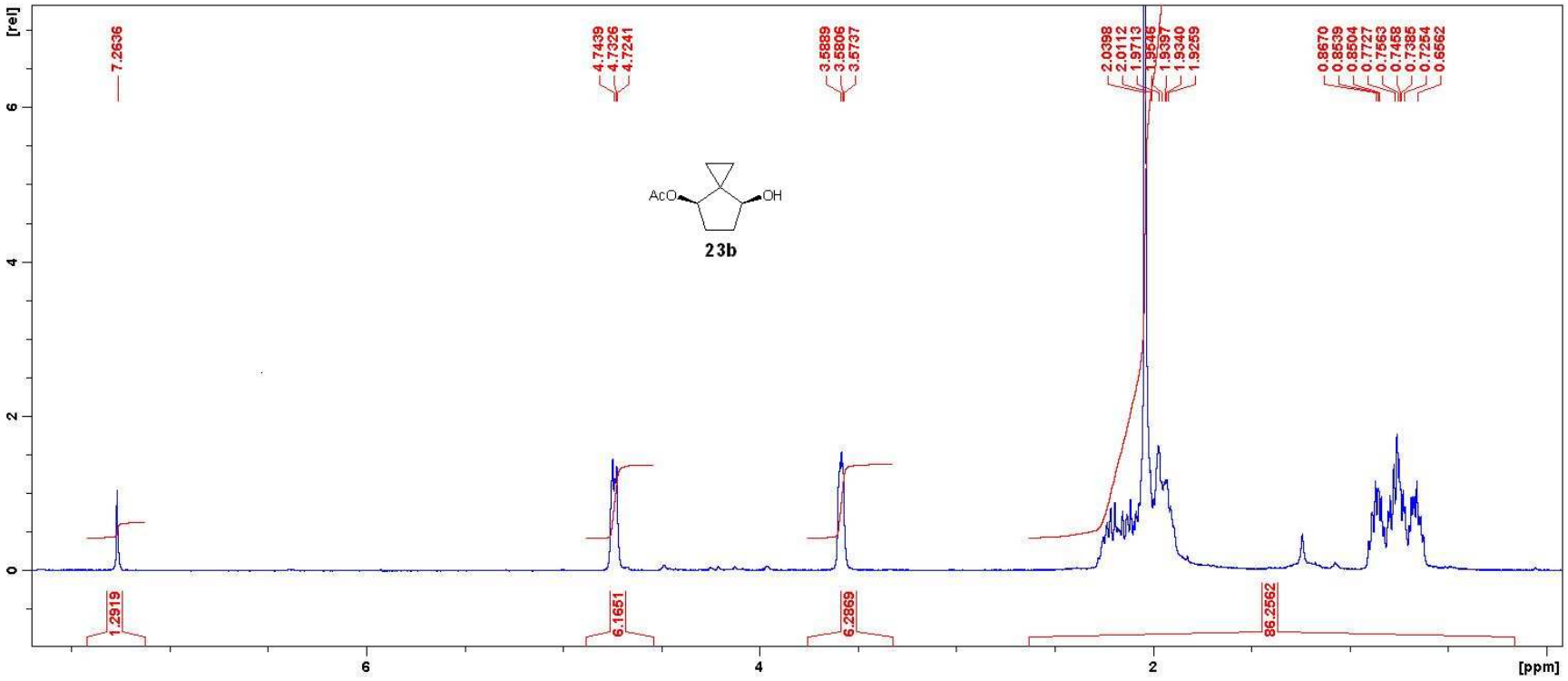

35.071
30.273
28.571
27.646
OAc
OH
11a
80
70
60
50
40
30
PPM
171.234
149.597
130.709
80.772
77.418
35.071
32.544
30.273
28.571
27.646
22.938
160
140
120
100
80
60
40
20
0
PPM

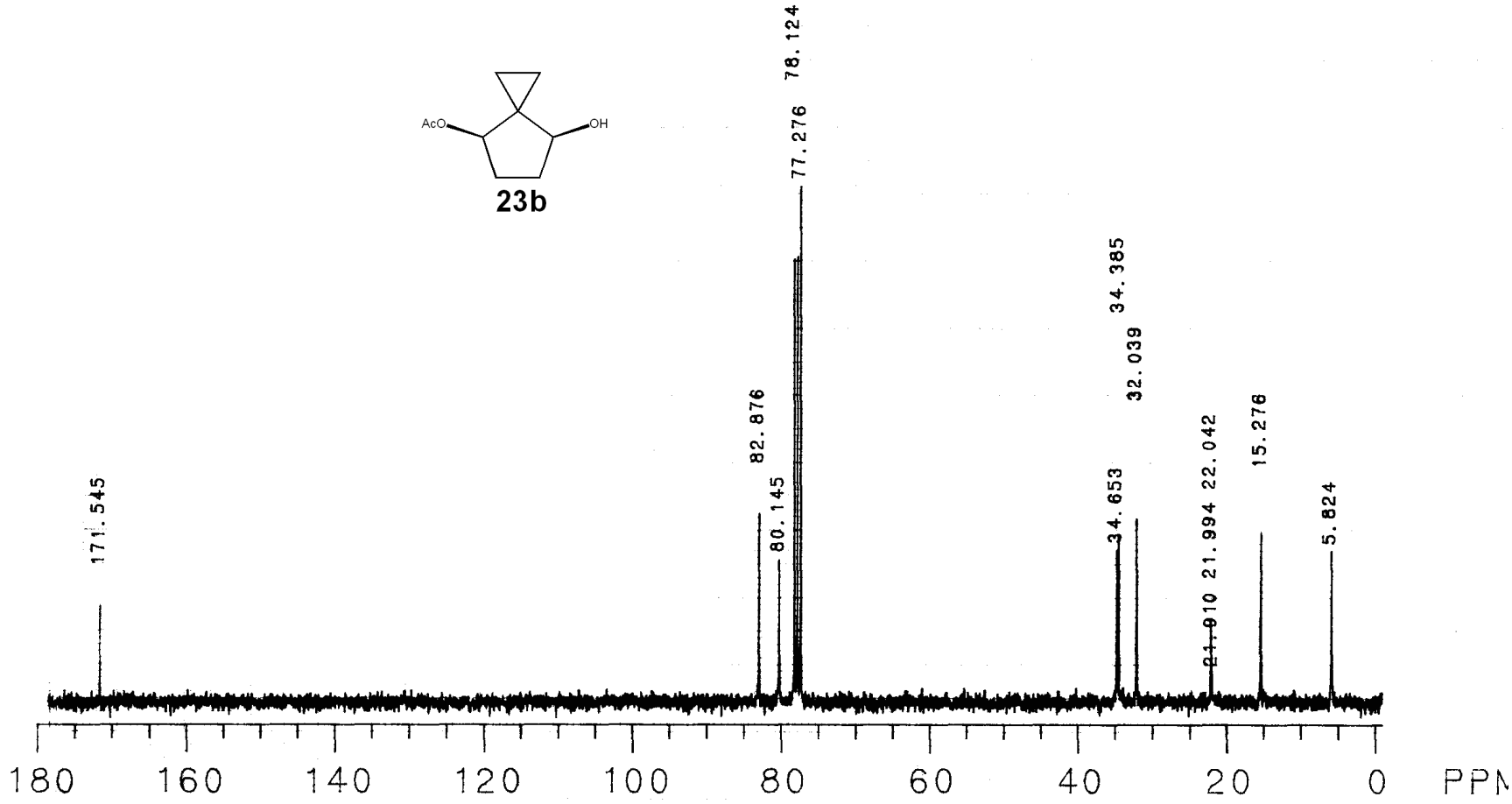

[rel]
6.0098
6.0048
5.8842
5.8760
5.8693
5.8650
5.7814
5.7711
5.6058
5.5947
5.5841
4.8408
4.8319
4.8023
4.6889
2.0657
2.0610
2.0330
2.0104
1.9253
1.8917
1.7460
1.7356
1.6431
1.6338
1.3929
0.0072
HO
OAc
10a
HO
OAc
10b
OAc
OH
11a
OH
OAc
11b
1.0000
1.8953
2.6939
3.1340
3.3789
3.3378
2.7969
2.6506
4.6094
26.5202
52.6955
12.9294
6.0776
4.1216
0.8214
8
6
4
2
0
[ppm]

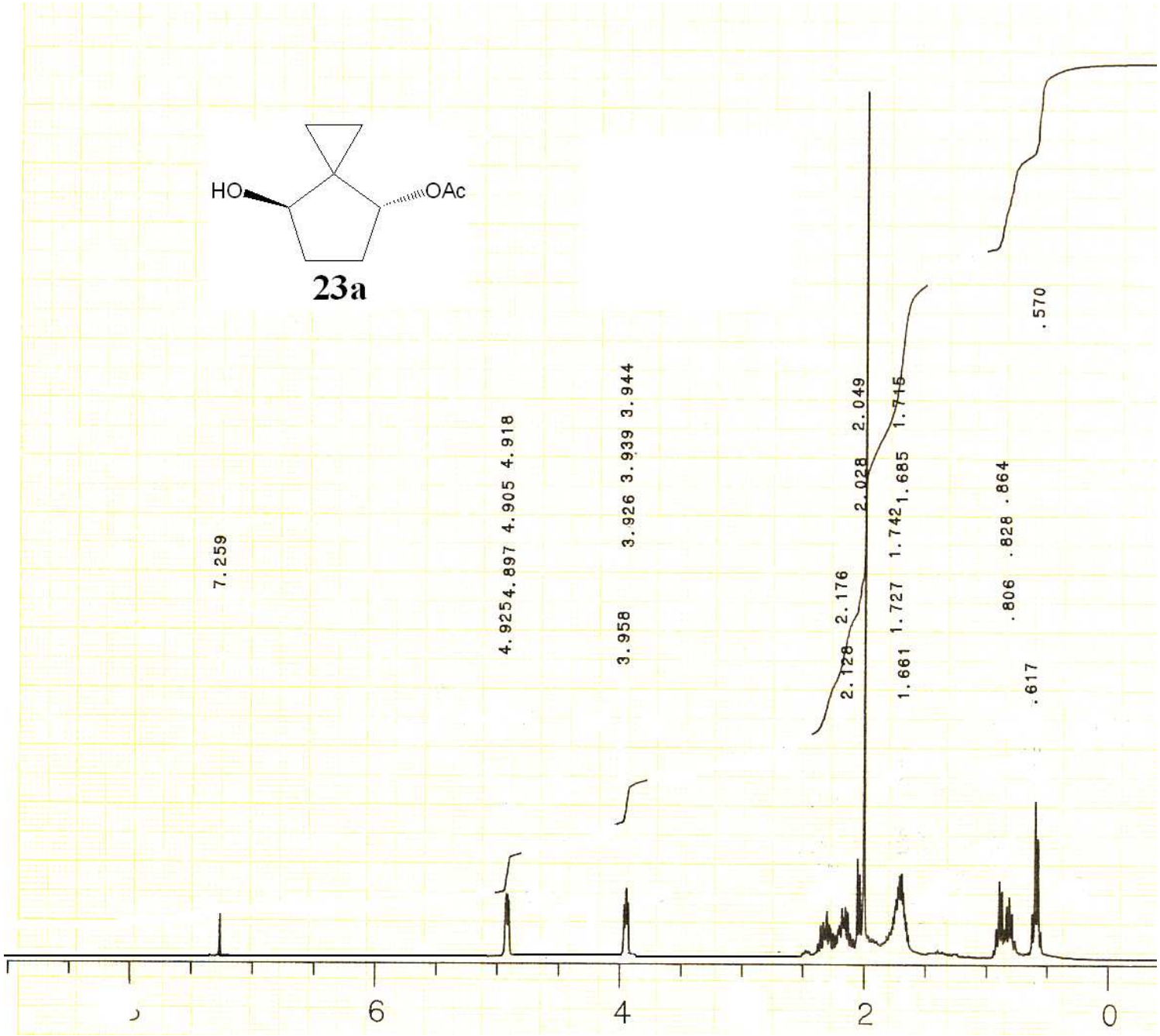

downfield region
6.0036
5.9986
5.8768
5.8724
5.8670
5.8628
5.8549
5.8500
5.8451
5.7712
5.7607
5.5974
5.5864
5.5753
4.8251
4.8152
4.7981
4.7846
4.6875
4.6787
4.6699
HO
OAc
10a
HO
OAc
10b
OAc
OH
11a
OH
OAc
11b
[rel]
1.5
1.0
0.5
-0.0
1.0000
0.0963
1.5189
1.2848
2.0955
1.8390
2.1299
6.0
5.8
5.6
5.4
5.2
5.0
4.8
[ppm]

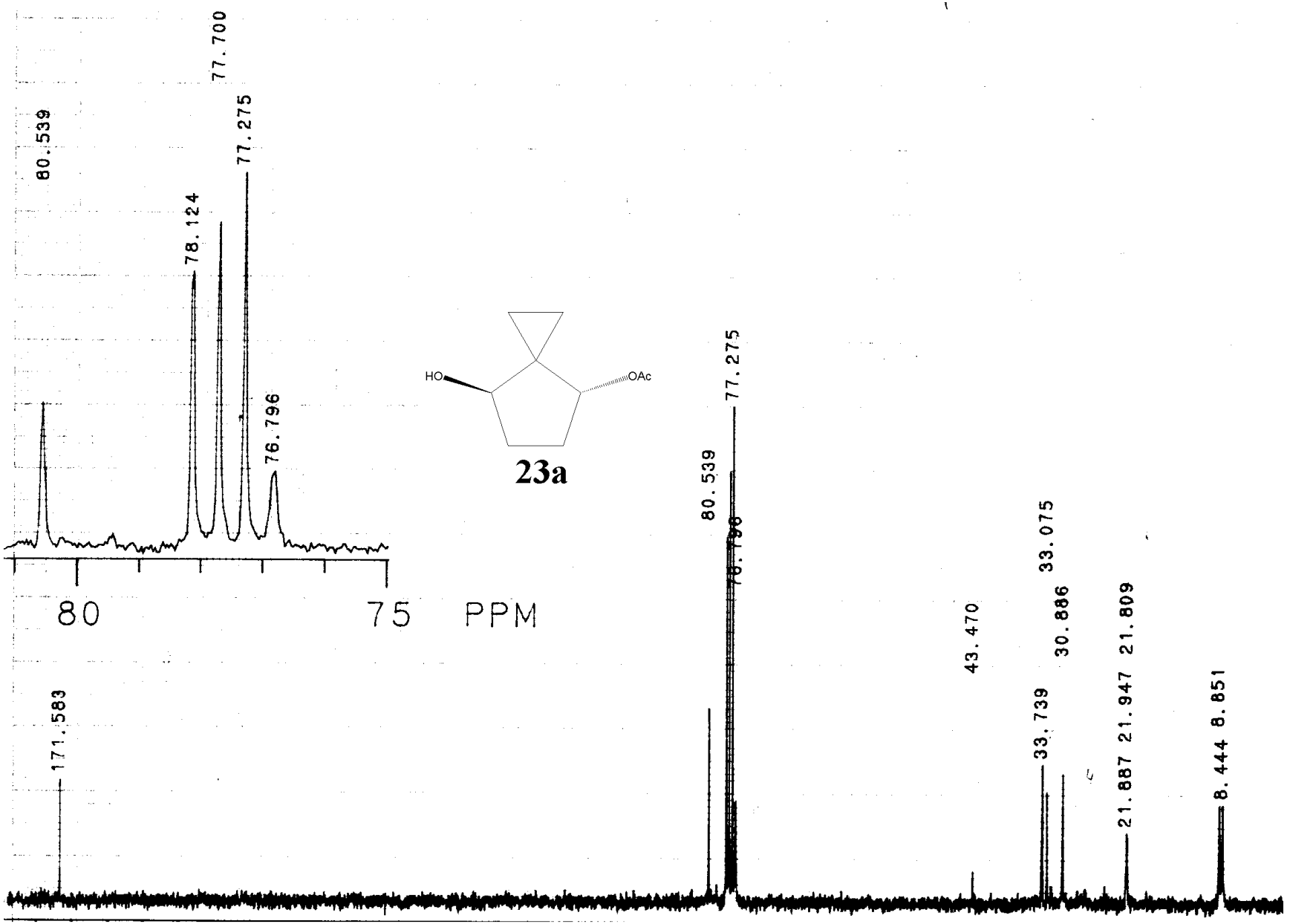

upfield region
HO
OAc
10a
HO
OAc
10b
OAc
OH
11a
OH
OAc
11b
2.0545
2.0495
2.0439
2.0230
1.9998
1.9155
1.8821
1.7351
1.7249
1.6336
1.6232
1.3821
2.1671
5.9166
45.9438
11.1598
3.9347
6.4733
10.5034
[rel]
[ppm]


[rel]
downfield region
171.7907
171.7521
171.4872
171.4117
171.3600
149.5128
148.9058
139.3942
138.8240
137.6563
137.2700
122.0883
130.9965
129.6861
HO
OAc
10a
HO
OAc
10b
OAc
OH
11a
OH
OAc
11b
C=O
11a
=C
11b
=C
10b
C=C
10a
C=C
11b
H-C=
11a
H-C=
170
160
150
140
130
[ppm]

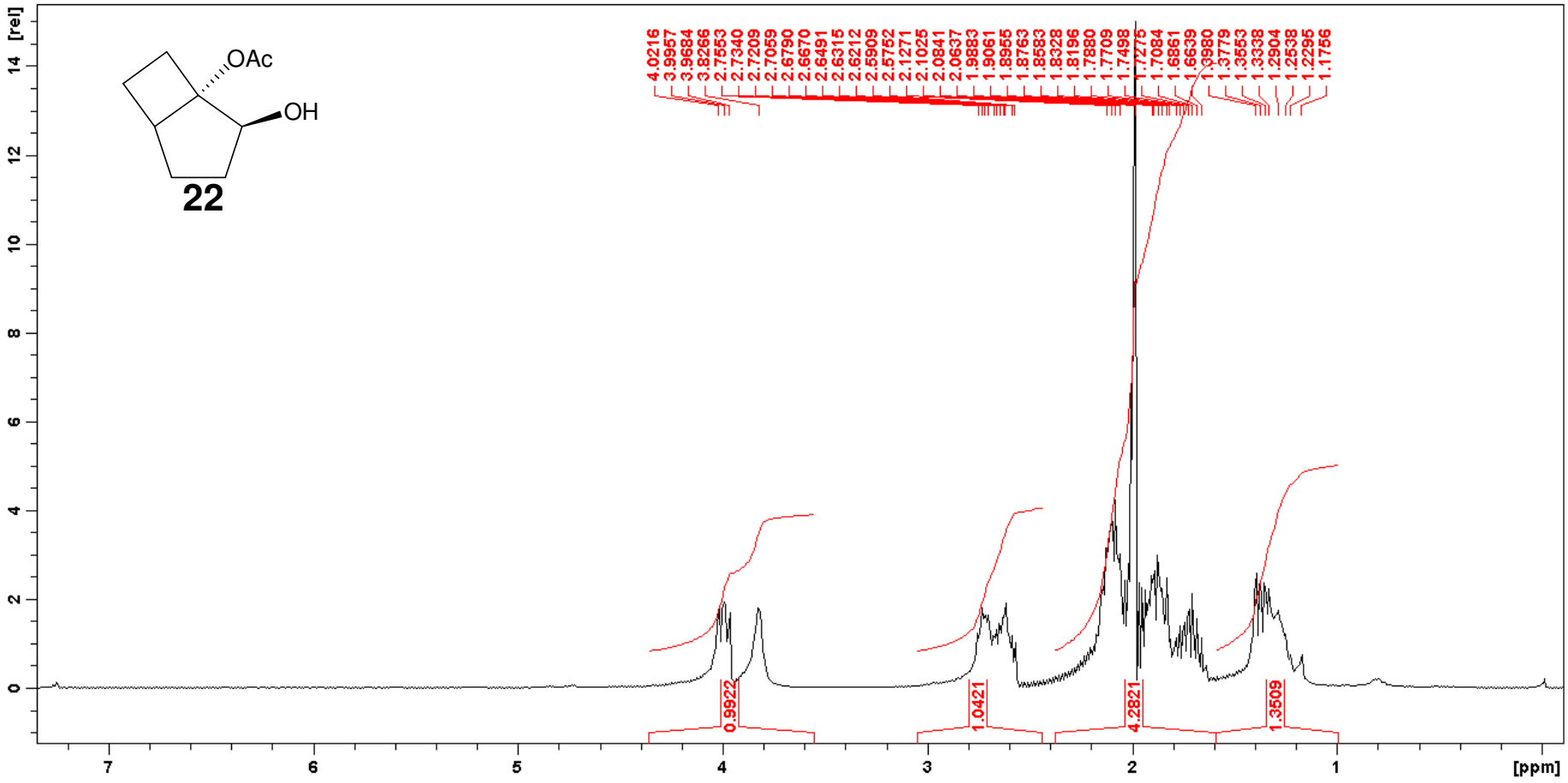

[rel]
7.2636
4.7439
4.7326
4.7241
3.5889
3.5806
3.5737
2.0398
2.0112
1.9713
1.9546
1.9397
1.9340
1.9259
0.8670
0.8539
0.8504
0.7727
0.7563
0.7458
0.7385
0.7254
0.6562
AcO
OH
23b
1.2919
6.1651
6.2869
86.2562
6
4
2
[ppm]

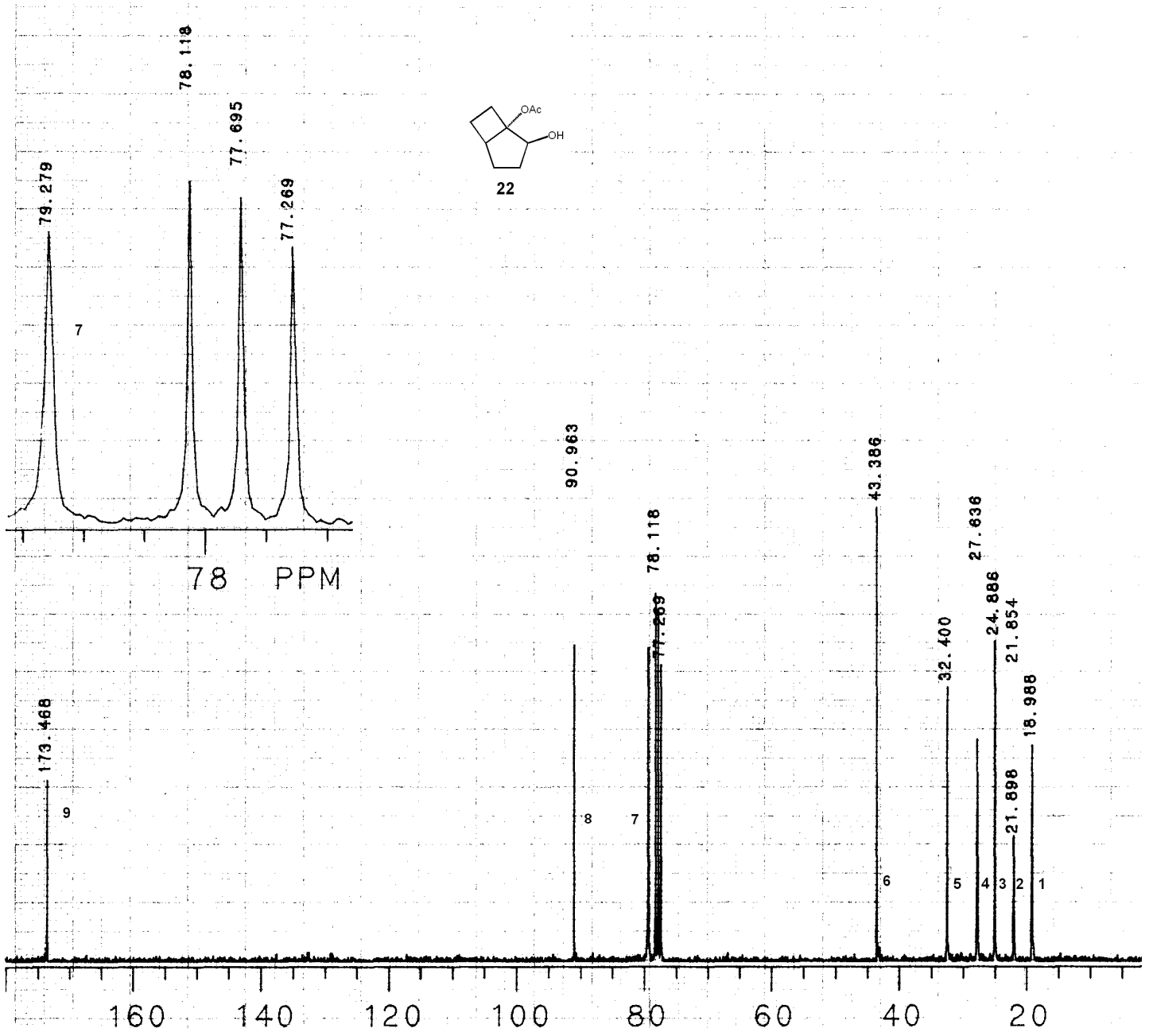

AcO
OH
23b
171.545
82.876
80.145
78.124
77.276
34.385
32.039
34.653
21.994
22.042
15.276
5.824
180
160
140
120
100
80
60
40
20
0
PPM

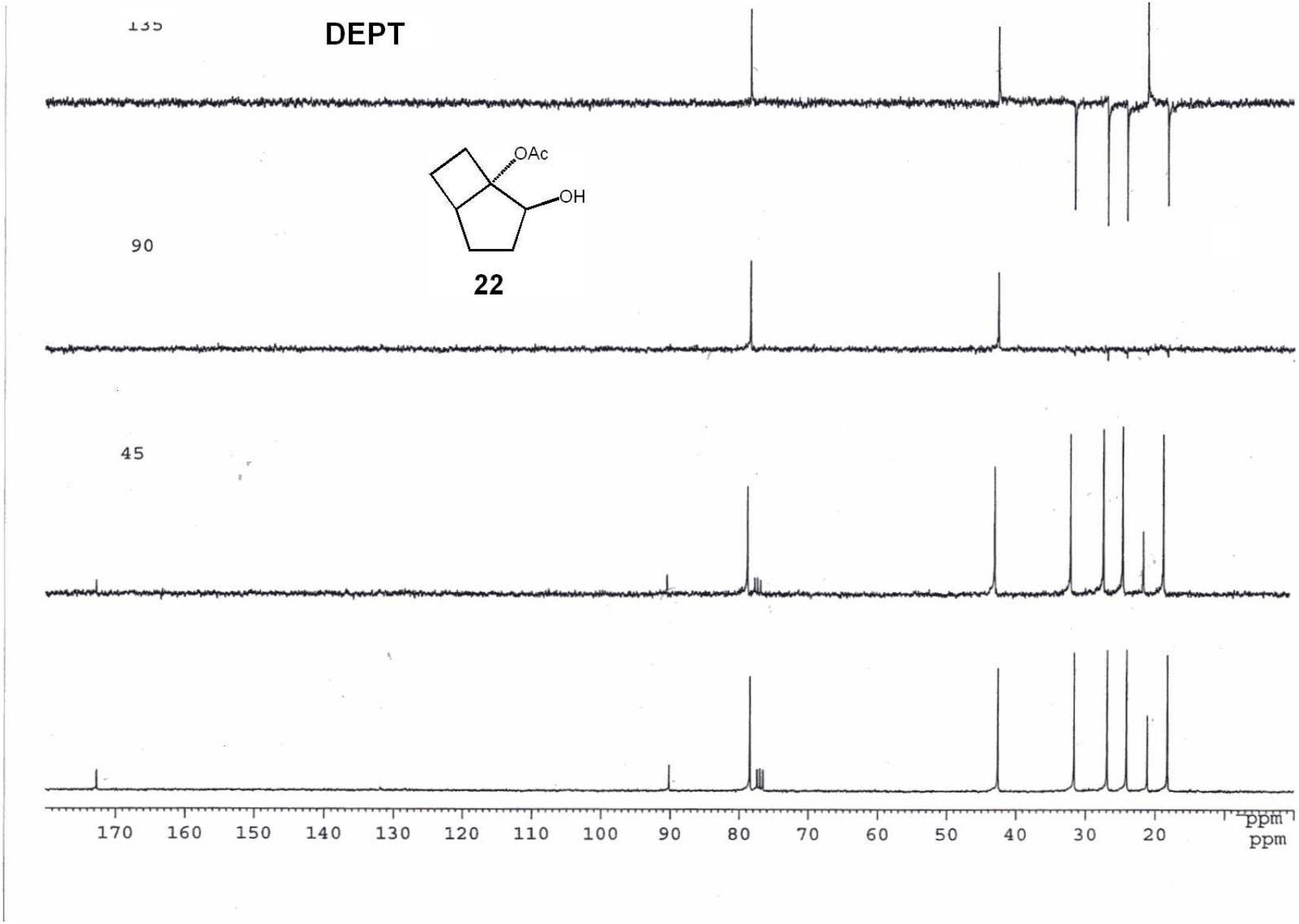

HO
OAc
23a
7.259
4.925
4.897
4.905
4.918
3.958
3.926
3.939
3.944
2.128
2.176
2.028
2.049
1.661
1.727
1.742
1.685
1.715
.806
.828
.864
.617
.570
6
4
2
0

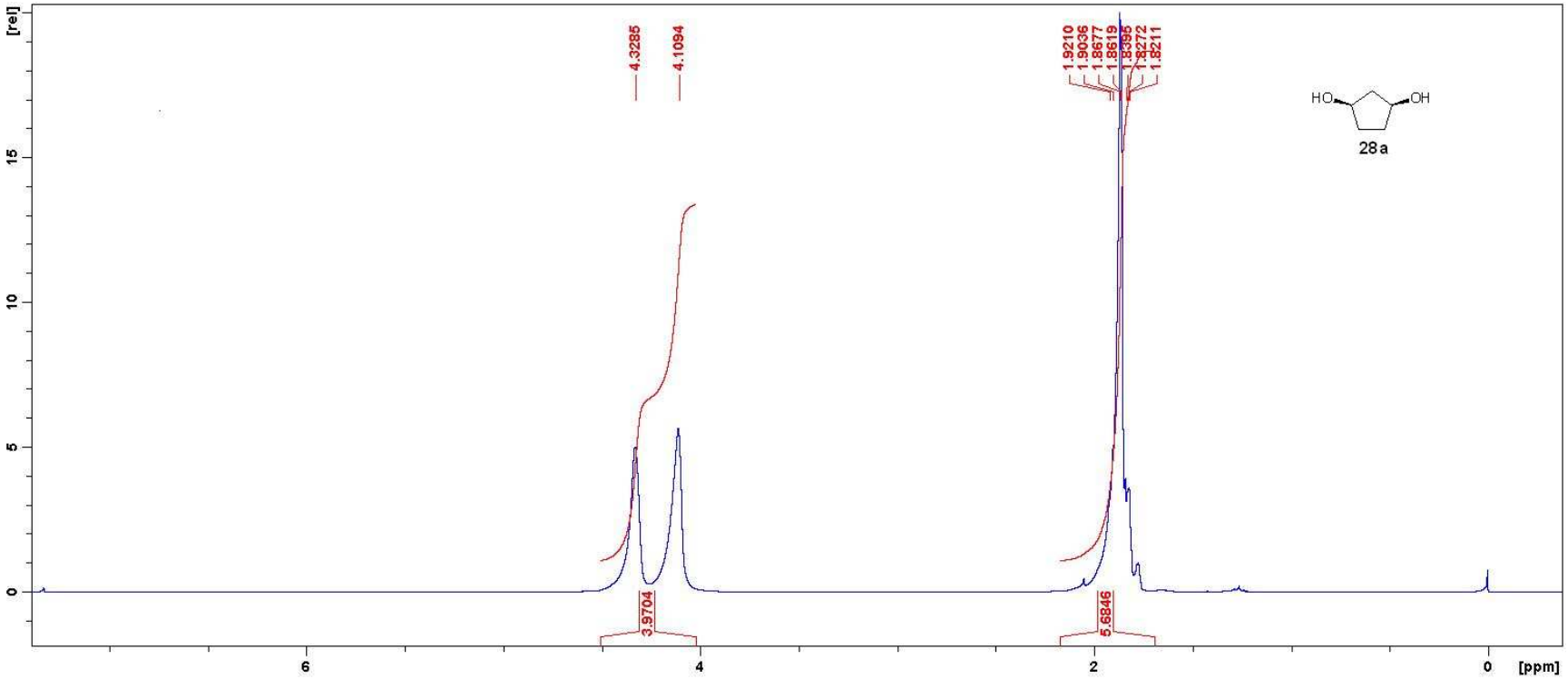

80.539
78.124
77.700
77.275
76.796
80
75
PPM
HO
OAc
171.583
80.539
77.275
43.470
33.739
33.075
30.886
21.887
21.947
21.809
8.444
8.851

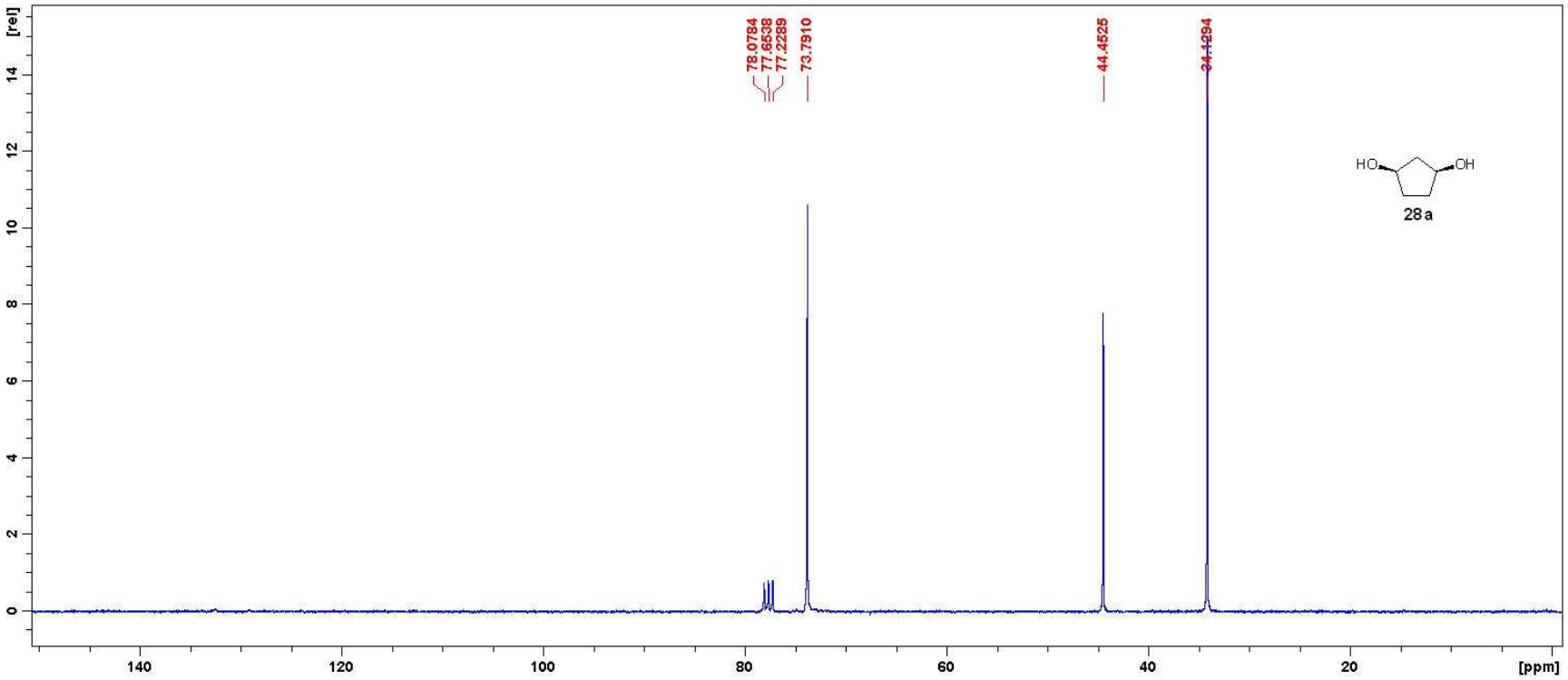
23a

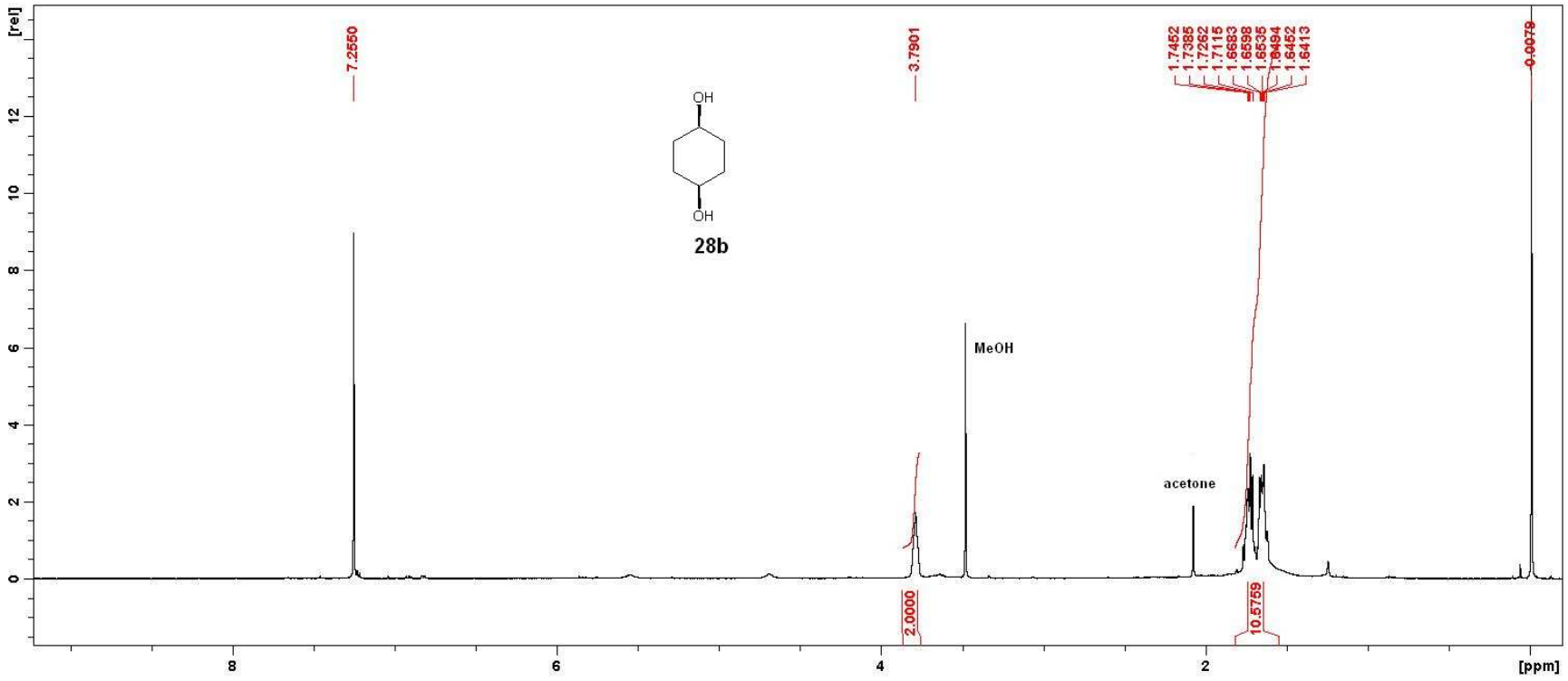

OAc
OH
22
4.0216
3.9957
3.9684
3.8266
2.7553
2.7340
2.7209
2.7059
2.6790
2.6670
2.6491
2.6315
2.6212
2.5909
2.5752
2.1271
2.1025
2.0841
2.0637
1.9883
1.9061
1.8955
1.8763
1.8583
1.8328
1.8196
1.7880
1.7709
1.7498
1.7275
1.7084
1.6861
1.6639
1.3980
1.3779
1.3553
1.3338
1.2904
1.2538
1.2295
1.1756
0.9922
1.0421
4.2821
1.3509
[rel]
[ppm]

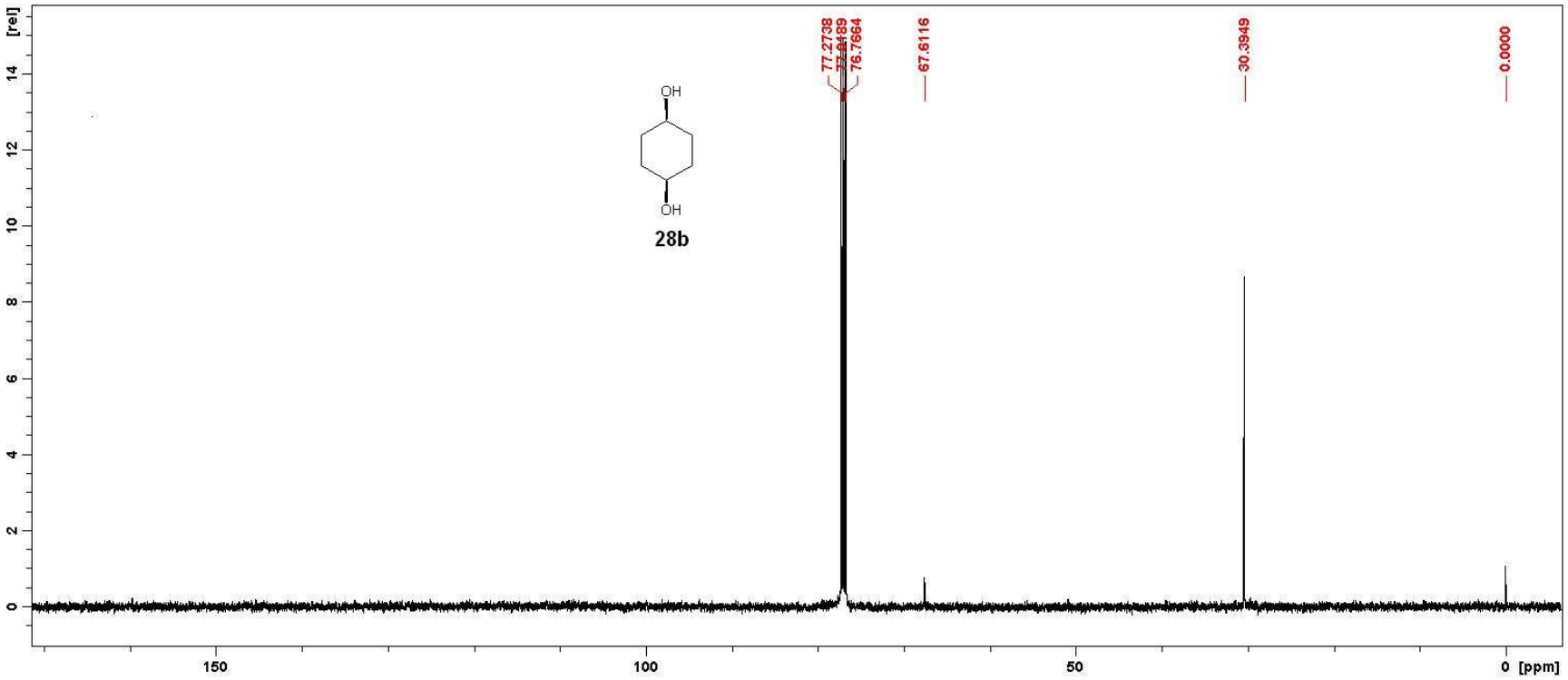

OAc
OH
22
79.279
78.118
77.695
77.269
7
78 PPM
173.468
90.963
78.118
77.269
43.386
32.400
27.636
24.886
21.854
21.898
18.988
9
8
7
6
5
4
3
2
1
160
140
120
100
80
60
40
20


DEPT
135
90
45
OAc
OH
22
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
ppm


[rel]
15
10
5
0
4.3285
4.1094
1.9210
1.9036
1.8677
1.8619
1.8395
1.8272
1.8211
HO
OH
28a
3.9704
5.6846
6
4
2
0
[ppm]


78.0784
77.6538
77.2289
73.7910
44.4525
34.1294
HO
OH
28a
[rel]
0
2
4
6
8
10
12
14
140
120
100
80
60
40
20
[ppm]


[rel]
7.2550
3.7901
1.7452
1.7385
1.7262
1.7115
1.6683
1.6598
1.6535
1.6494
1.6452
1.6413
0.0079
OH
OH
28b
MeOH
acetone
2.0000
10.5759
8
6
4
2
[ppm]


[rel]
14
12
10
8
6
4
2
0
77.2738
76.7664
67.6116
30.3949
0.0000
OH
OH
28b
150
100
50
0 [ppm]