# -*trans, cis*-4-Hydroxy-5,6-di-*O*-isopropylidenecyclohex-2-ene-1-one: Synthesis and Facile Dimerization to Decahydrodibenzofurans

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## SUPPORTING INFORMATION

General directions for experimental work (with references) S2

NMR spectra S3-S22

Structure of **9** with MMFF94 energy minimization – pdb coordinates S23-S25

## General Directions

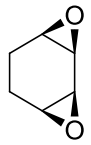
**Solvents and reagents:** Solvents were dried as follows: MeCN and $CH_2Cl_2$ were distilled over $CaH_2$. Alternatively MeCN and $CH_2Cl_2$ were dried and deoxygenated with Grubbs-type solvent purification system. The moisture content of the solvents was monitored by Karl Fischer coulometric titration. $CCl_4$ was stirred over $MgSO_4$ for 1 h. Reagents were used as commercially supplied unless otherwise stated and handled in accordance with COSHH regulations.[1] **Photooxygenation:** These reactions were performed in standard pyrex® round-bottom flasks and direct irradiation from a 300 W sunlamp. **Chromatography:** Flash chromatography was performed on silica gel (60 $F_{254}$, 230-400 mesh) according to the method of W.C. Still.[2] Thin layer chromatography (TLC) was performed on aluminium plates pre-coated with silica (60 $F_{254}$, 0.2 mm) which were developed using standard visualising agents: ultra violet fluorescence (254 nm), $KMnO_4/\Delta$ or vanillin/$\Delta$. **$^1$H NMR spectra:** These were recorded at 500, 400 or 300 MHz. Chemical shifts ($\delta_H$) are quoted in parts per million (ppm) referenced to the appropriate residual solvent peak, with the abbreviations s, d, t, and m denoting singlet, doublet, triplet and multiplet respectively. **$^{13}$C NMR spectra:** These were recorded at 125, 100 or 75 MHz. Chemical shifts ($\delta_C$) are quoted in parts per million (ppm) referenced to the appropriate residual solvent peak, with the abbreviations s, d, t, and q denoting C, CH, $CH_2$ and $CH_3$ respectively. **Infra red spectra:** These were recorded as thin films or as solids. Only selected absorbencies ($\nu_{max}$) are reported. **Mass spectra:** Molecular ions and major peaks only are reported for low resolution spectra. Intensities are given as percentages of the base peak. HRMS values are valid to 5 ppm. **Melting points:** Analyses were carried out using a hot stage and are uncorrected.

## References


(1) http://www.hse.gov.uk/coshh/index.htm.

(2) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

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



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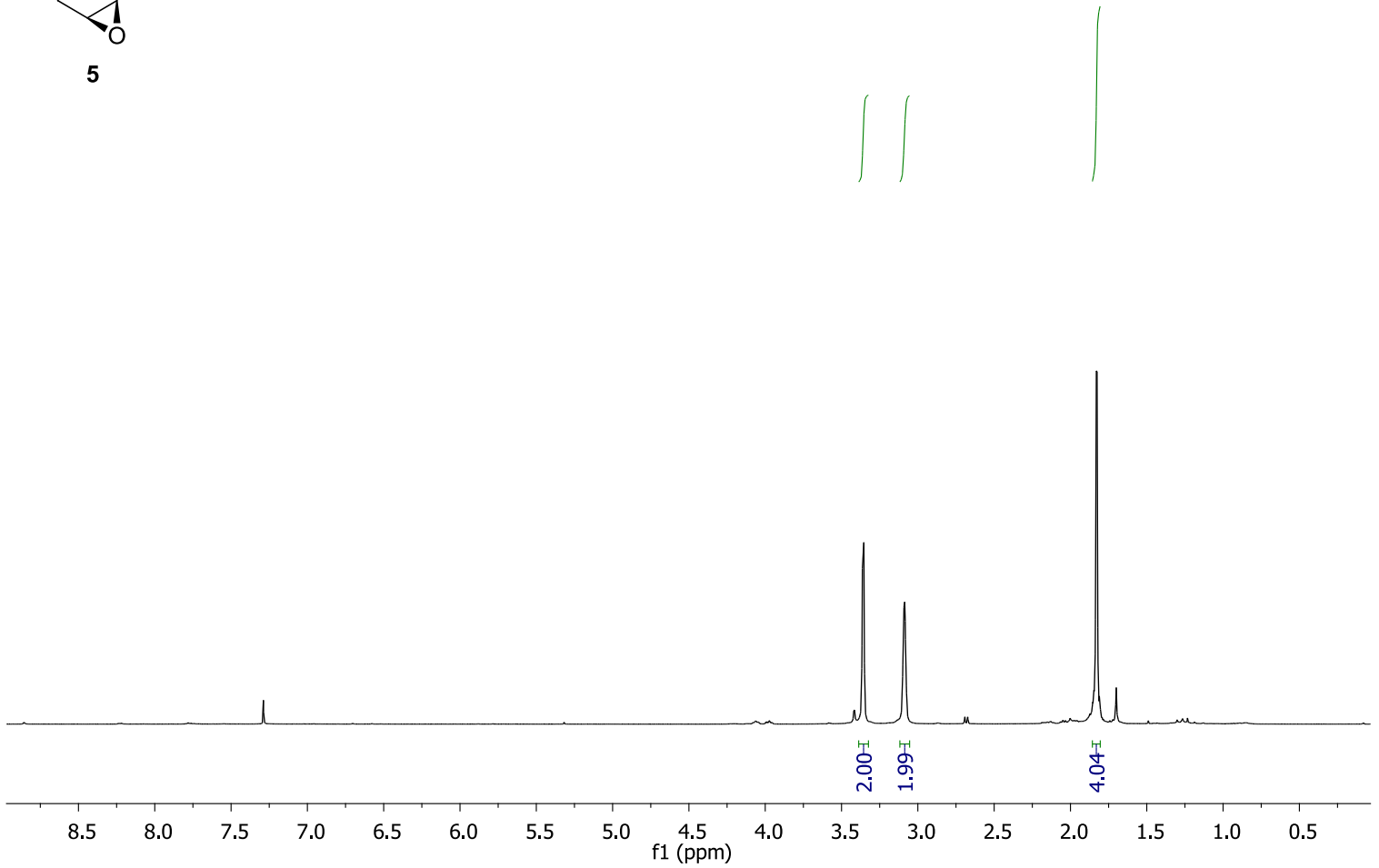
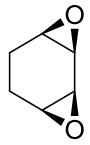


$^{13}C$ NMR, 100 MHz, $CDCl_3$



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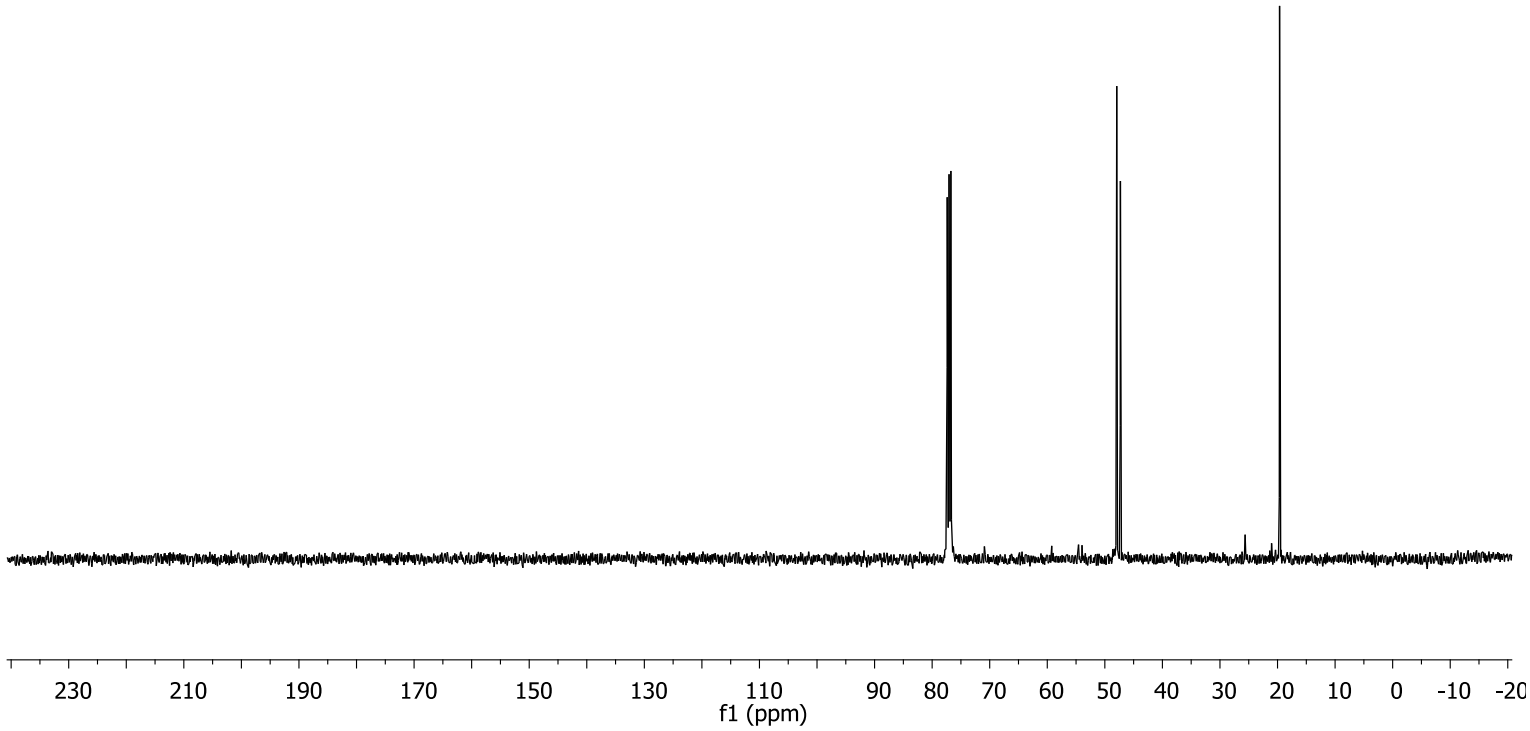
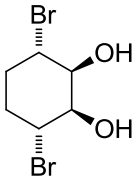


$^{1}$H NMR, 400 MHz, $CDCl_3$

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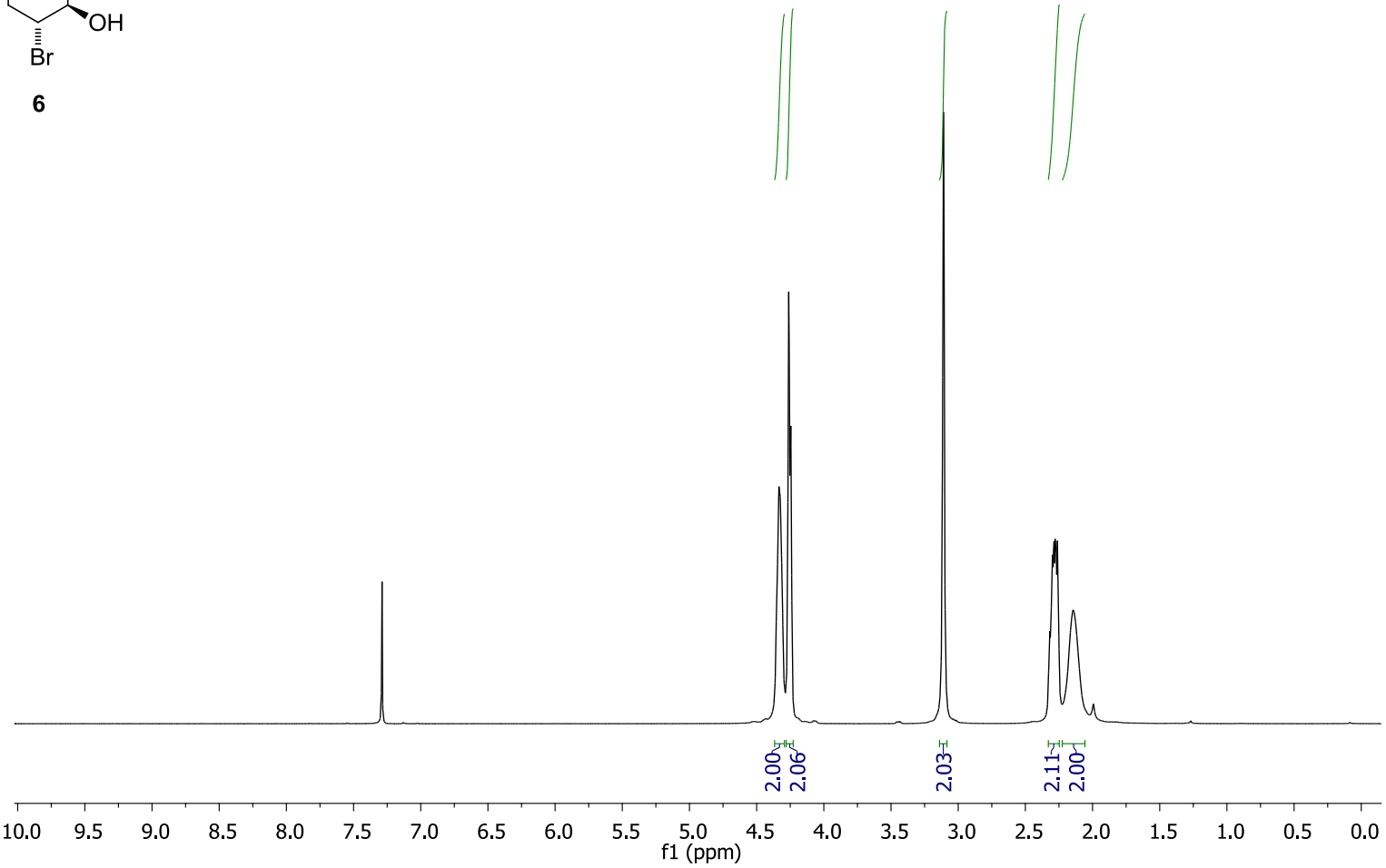
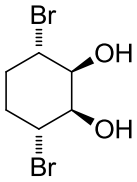
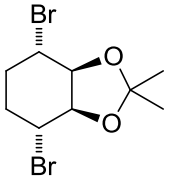


$^{13}C$ NMR, 100 MHz, $CDCl_3$



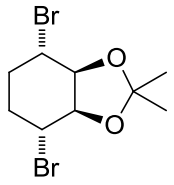

**6**

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



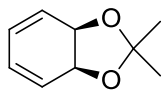

**7**

$^{13}C$ NMR, 100 MHz, $CDCl_3$




**7**

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



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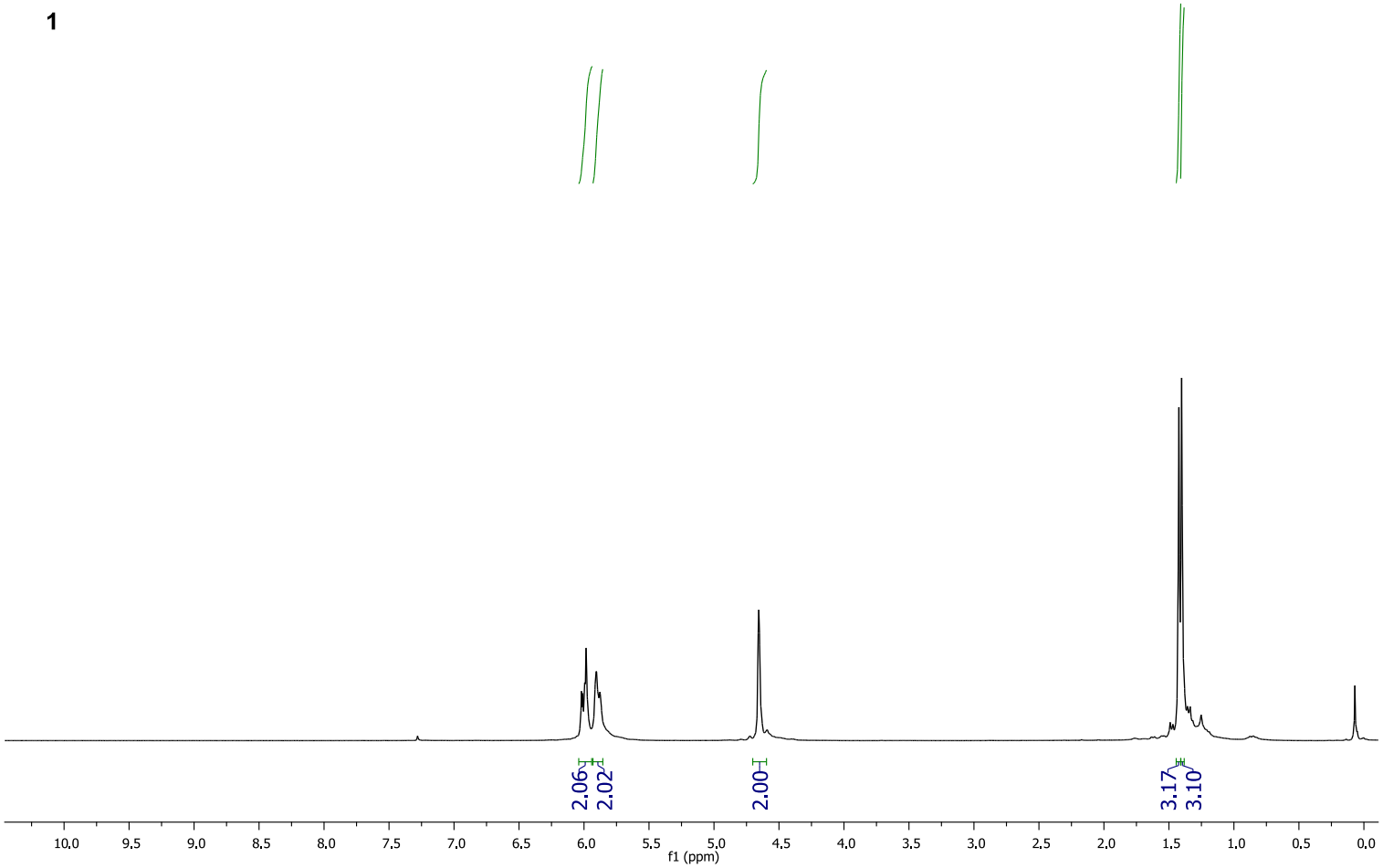
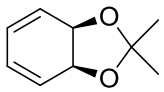


$^{13}C$ NMR, 75 MHz, $CDCl_3$



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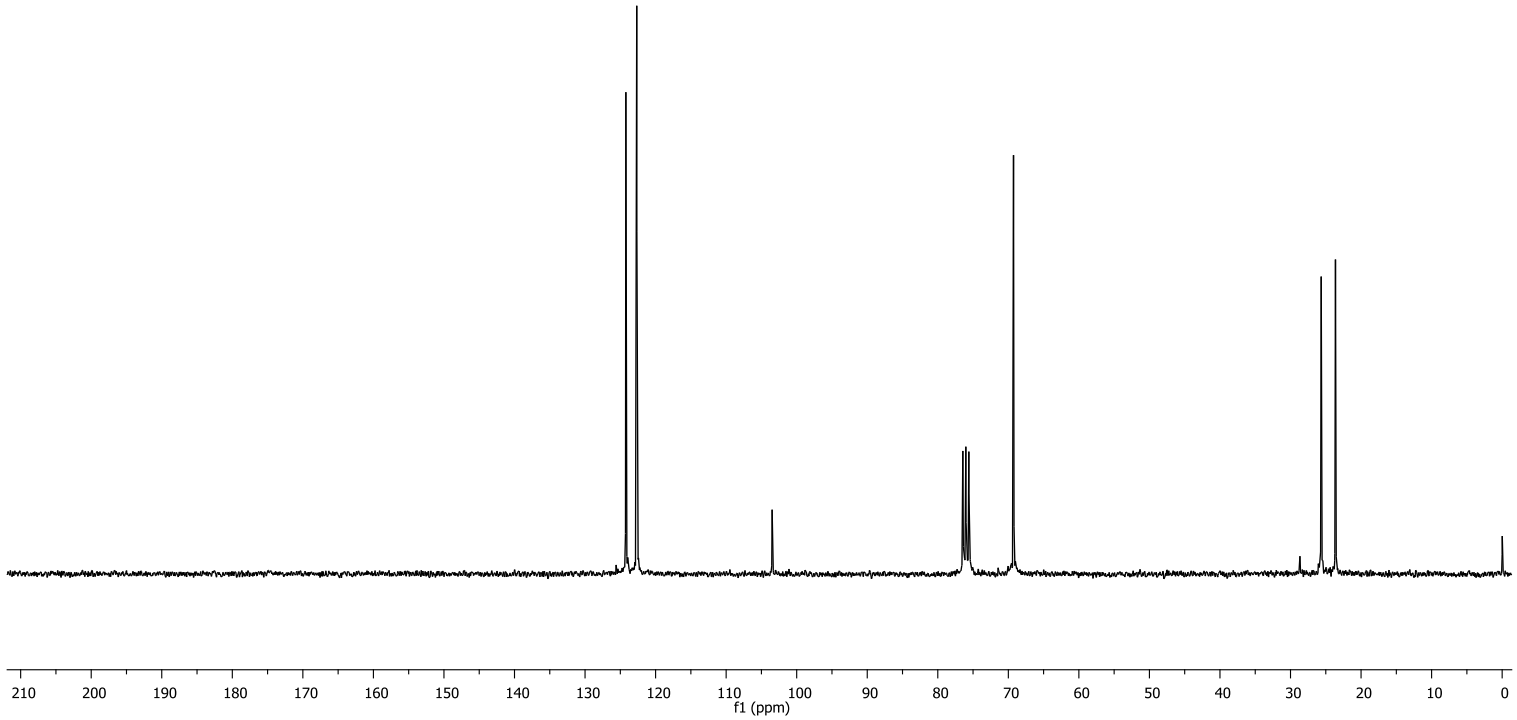
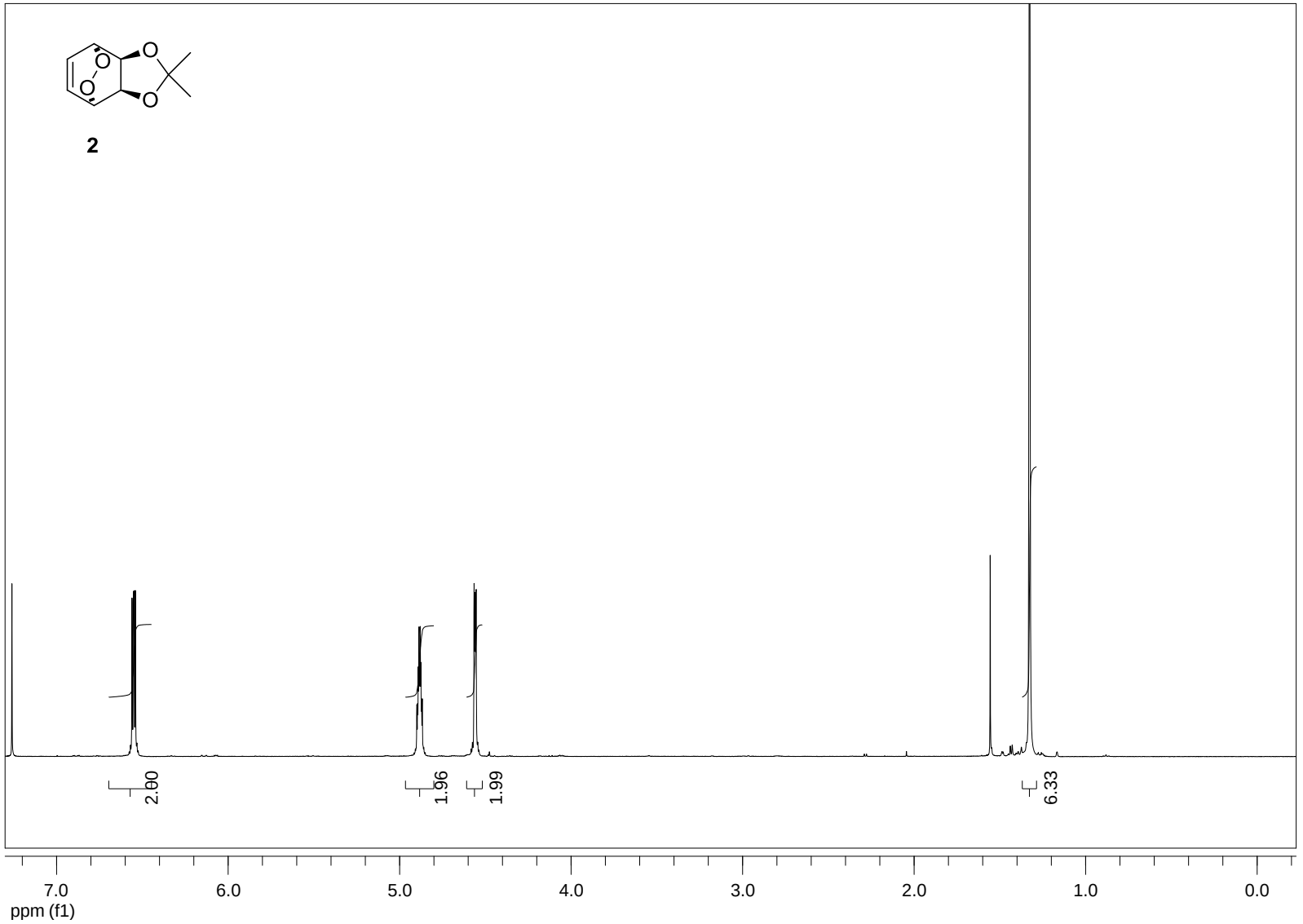
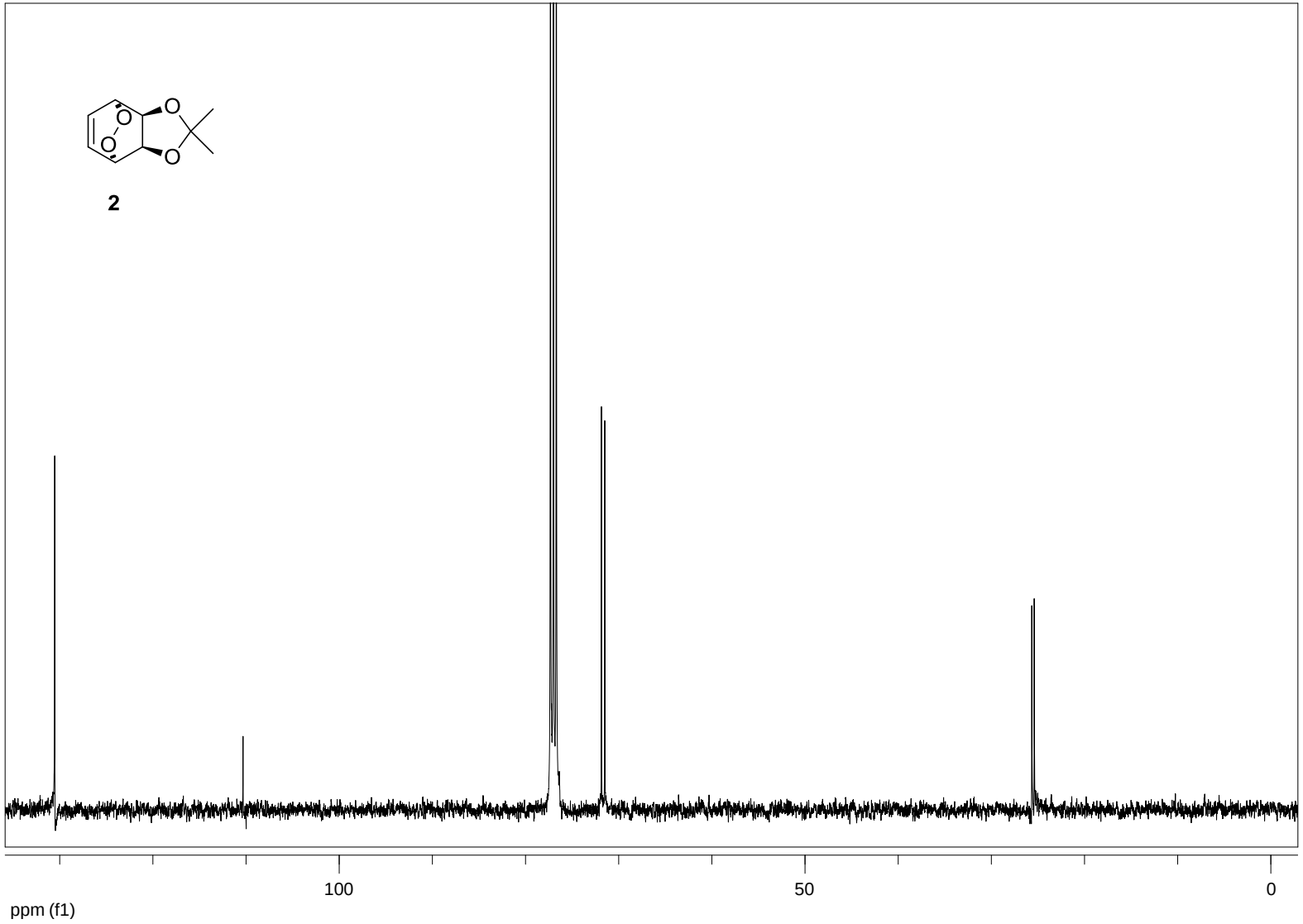


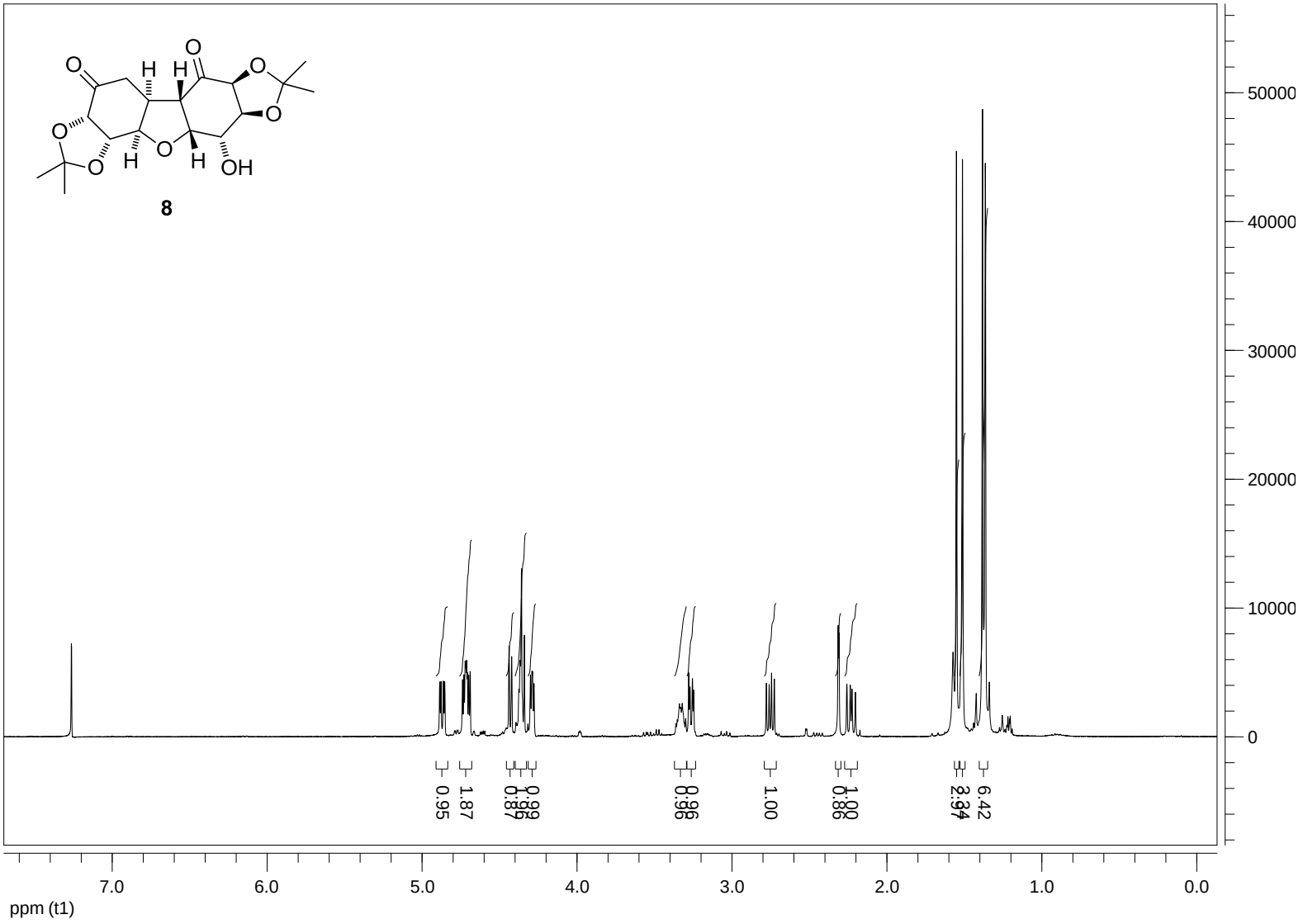
$^{1}$H NMR, 400 MHz, $CDCl_3$



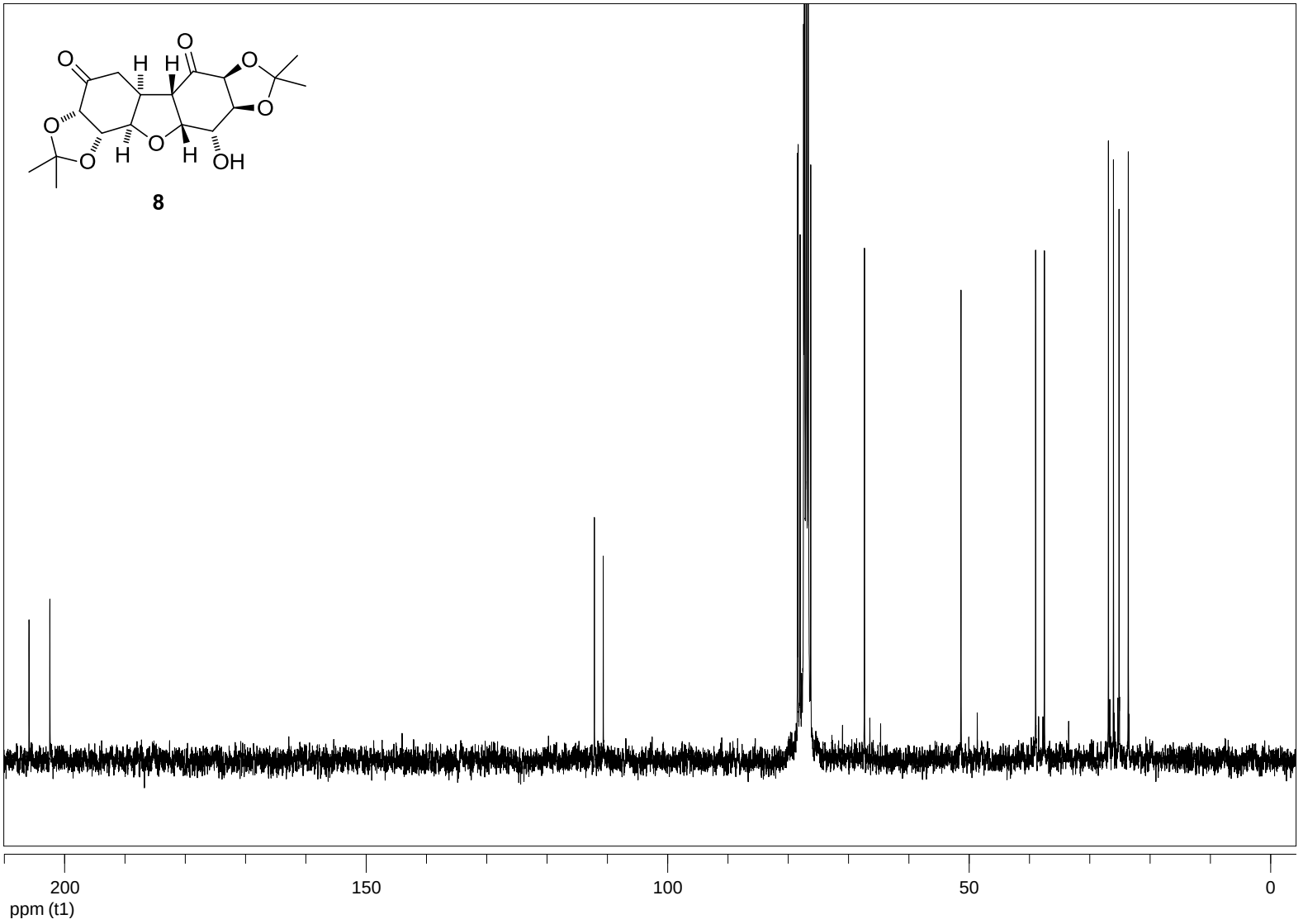
$^{13}C$ NMR, 100 MHz, $CDCl_3$



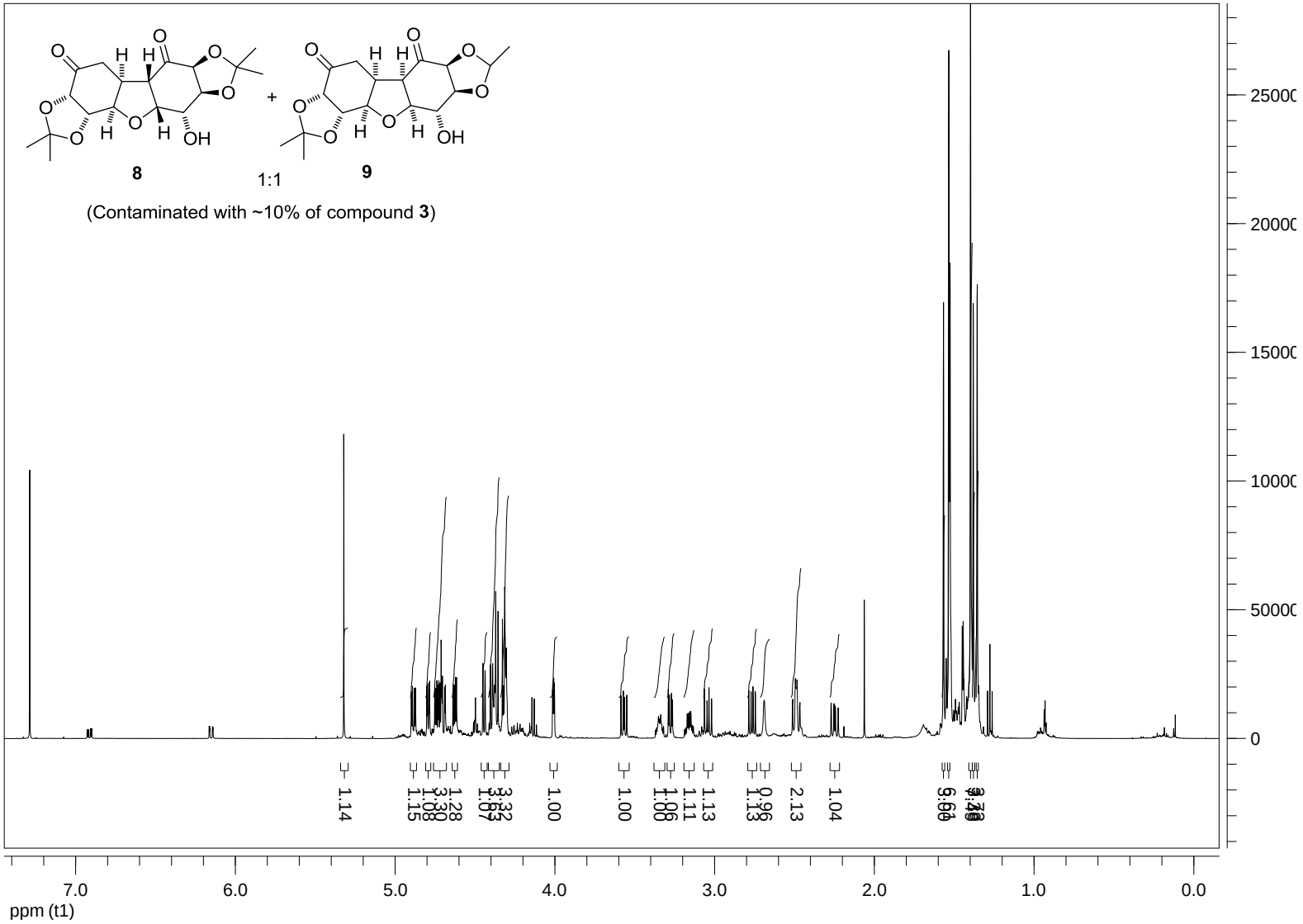
$^{1}$H NMR, 400 MHz, $CDCl_3$



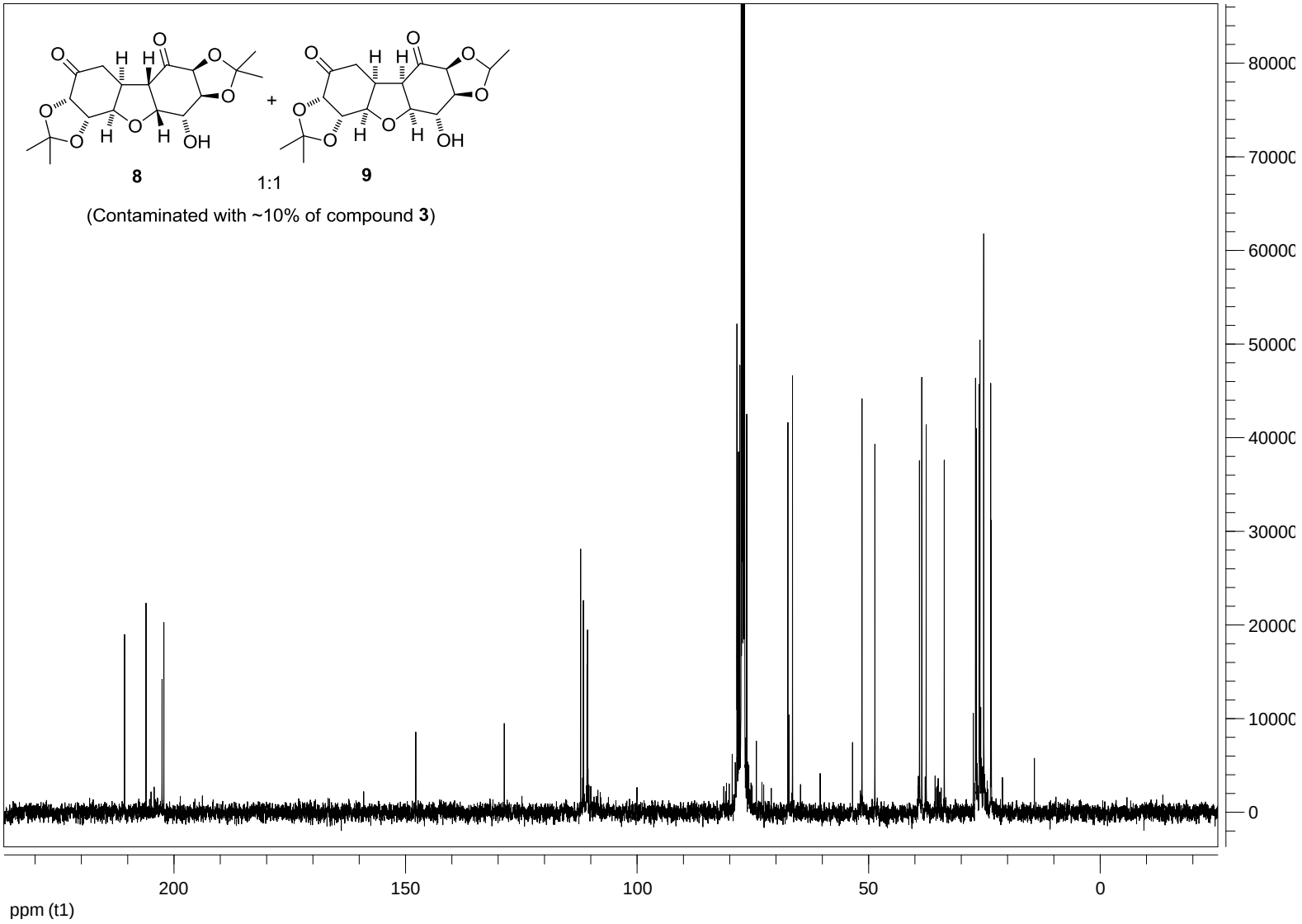
$^{13}$C NMR, 100 MHz, $CDCl_3$



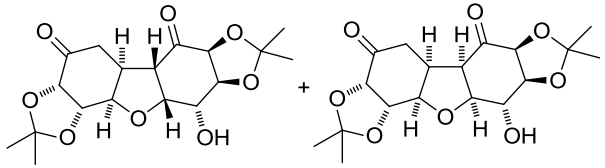
$^{1}$H NMR, 500 MHz, $CDCl_3$



$^{13}C$ NMR, 125 MHz, $CDCl_3$



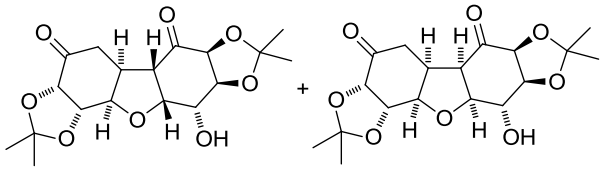
$^{13}$C DEPT, 125 MHz, $CDCl_3$



**8** 1:1 **9**

(Contaminated with ~10% of compound **3**)

$^{1}$H NOESY, 500 MHz, $CDCl_3$



**8** 1:1 **9**

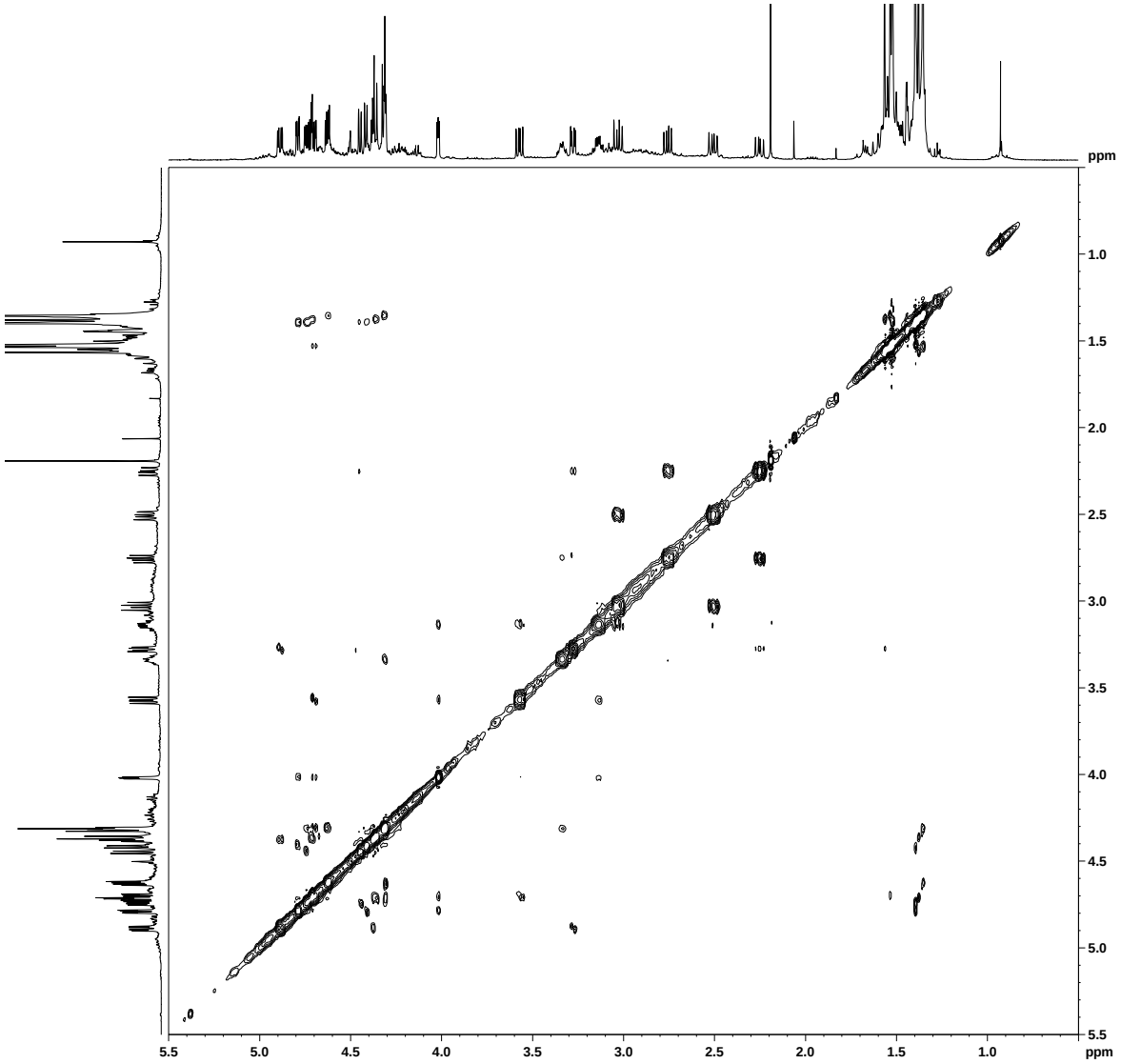
(Contaminated with ~10% of compound **3**)

| | 4a | 5a | 6 | 9β | 9a | 9b |
|---|---|---|---|---|---|---|
| 4a | | | | | | X |
| 5a | | | | | X | |
| 6 | | | | | | |
| 9β | | | | | | X |
| 9a | | X | | | | |
| 9b | X | | | X | | |

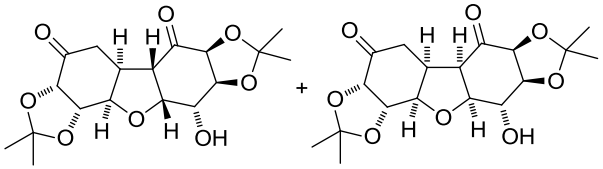
dimer **8** (NOESY)

| | 4a | 5a | 6 | 9β | 9a | 9b |
|---|---|---|---|---|---|---|
| 4a | | X | | | | X |
| 5a | X | | X | | X | X |
| 6 | | X | | | | |
| 9β | | | | | | |
| 9a | | X | | | | X |
| 9b | X | X | | | X | |

dimer **9** (NOESY)



$^1$H COSY, 500 MHz, $CDCl_3$

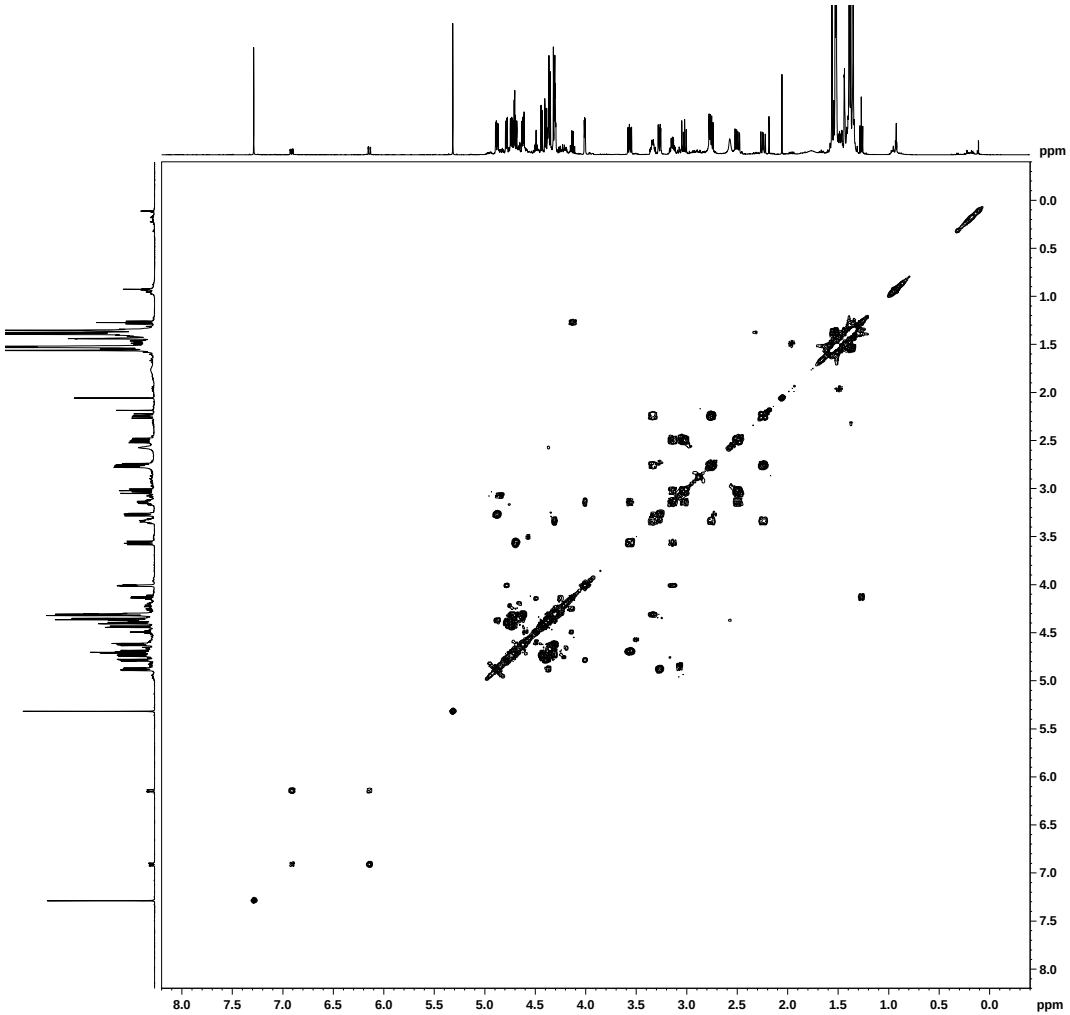


**8** 1:1 **9**

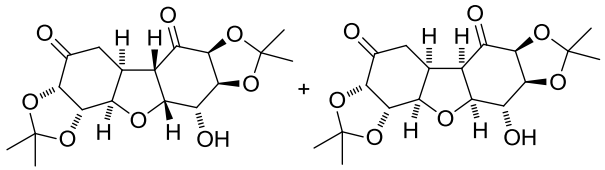
(Contaminated with ~10% of compound **3**)

***cis, trans, cis*-Decahydrodibenzofuran 8**. $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 1.36 (3H, s, $CH_3$), 1.38 (3H, s, $CH_3$), 1.51 (3H, s, $CH_3$), 1.57 (3H, s, $CH_3$), 2.23 (1H, dd, *J* = 13.3, 8.8, $H_{9\beta}$), 2.31 (1H, d, *J* = 2.2, OH), 2.75 (1H, dd, *J* = 13.3, 7.2, $H_{9\alpha}$), 3.26 (1H, dd, *J* = 9.5, 3.3, $H_{9b}$), 3.33 (1H, m, $H_{9a}$), 4.29 (1H, dd, *J* = 5.4, 3.7, $H_{5a}$), 4.34 (1H, d, *J* = 7.5, $H_2$), 4.37 (1H, m, $H_4$), 4.43 (1H, d, *J* = 6.7, $H_7$), 4.70 (1H, dd, *J* = 7.5, 3.9, $H_3$), 4.73 (1H, dd, *J* = 6.7, 3.7, $H_6$), 4.87 (1H, dd, *J* = 9.5, 3.4, $H_{4a}$); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta_C$ 23.6 (q), 25.1 (q), 26.1 (q), 26.9 (q), 37.5 (d), 39.0 (t), 51.3 (d), 67.4 (d), 76.3 (s), 77.3 (s), 77.4 (s) 78.0 (s), 78.4 (s), 78.4 (s), 110.7 (s), 112.1 (q), 202.4 (s), 205.9 (s).

***cis, cis, cis*-Decahydrodibenzofuran 9** $^1$H NMR (500 MHz, $CDCl_3$): $\delta_H$ 1.39 (6H, s, 2 × $_{CH3}$), 1.53 (6H, s, 2 × $CH_3$), 2.49 (1H, dd, *J* = 14.0, 8.8, $H_{9\beta}$), 2.70 (1H, bs, OH), 3.04 (1H, dd, *J* = 14.0, 8.2, $H_{9\alpha}$), 3.16 (1H, m, $H_{9a}$), 3.57 (1H, dd, *J* = 10.9, 7.2, $H_{9b}$), 4.01 (1H, dd, *J* = 3.6, 2.2, $H_{5a}$), 4.30 (1H, d, *J* = 7.5, $_{H2}$), 4.32 (1H, d, *J* = 7.5, $H_4$), 4.40 (1H, d, *J* = 6.6, $H_7$), 4.63 (1H, dd, J = 7.5, 3.7, $H_3$), 4.70 (1H, dd, *J* = 6.6, 2.2, $H_6$), 4.79 (1H, dd, *J* = 10.9, 2.1, $H_{4a}$); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta_C$ 23.5 (q), 25.1 (q), 26.0 (q), 26.7 (q), 33.7 (t), 38.5 (d), 48.6 (d), 66.4 (d), 76.9 (s), 77.0 (s), 77.2 (s), 77.3 (s), 77.5 (s), 77.8 (s), 110.8 (s), 111.6 (s), 202.6 (s), 210.7 (s).

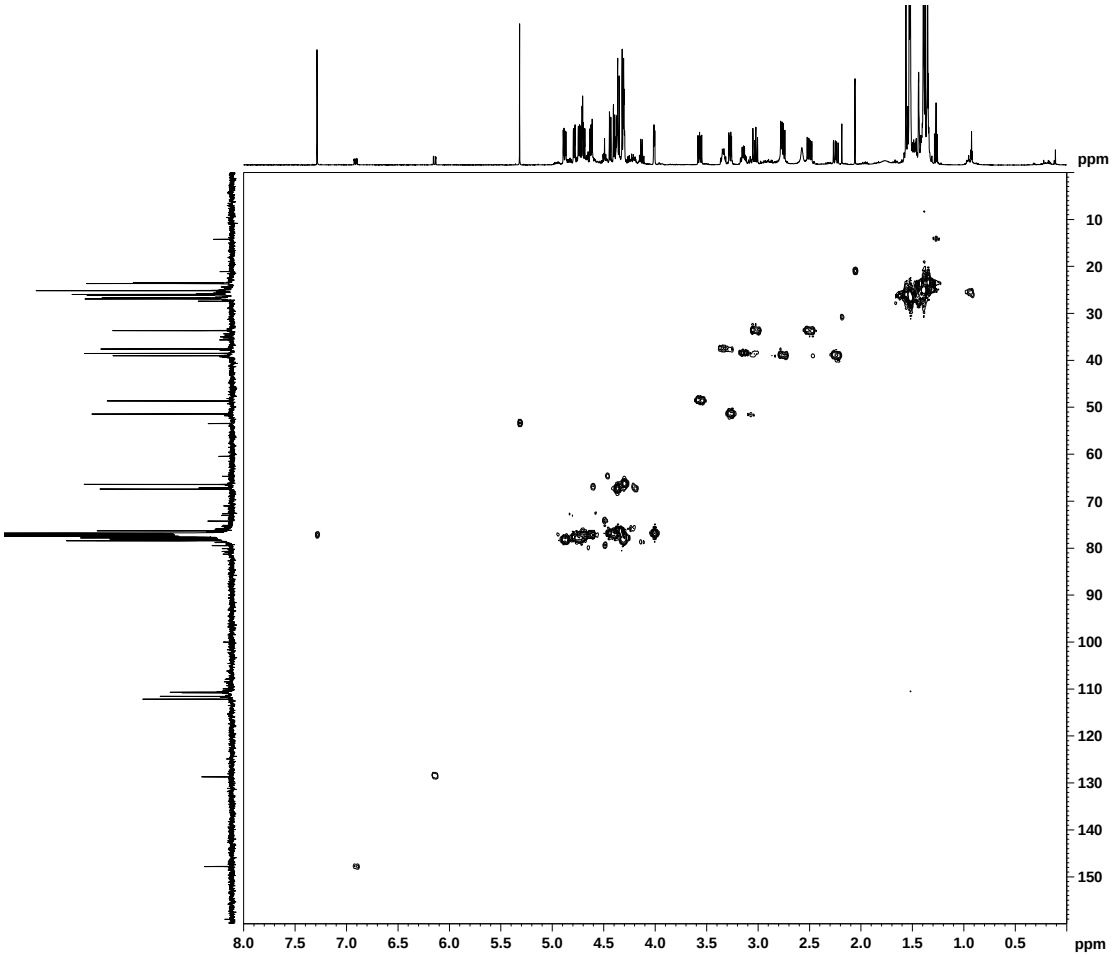


$^{1}H$-$^{13}C$ HMQC 500/125MHz, $CDCl_3$

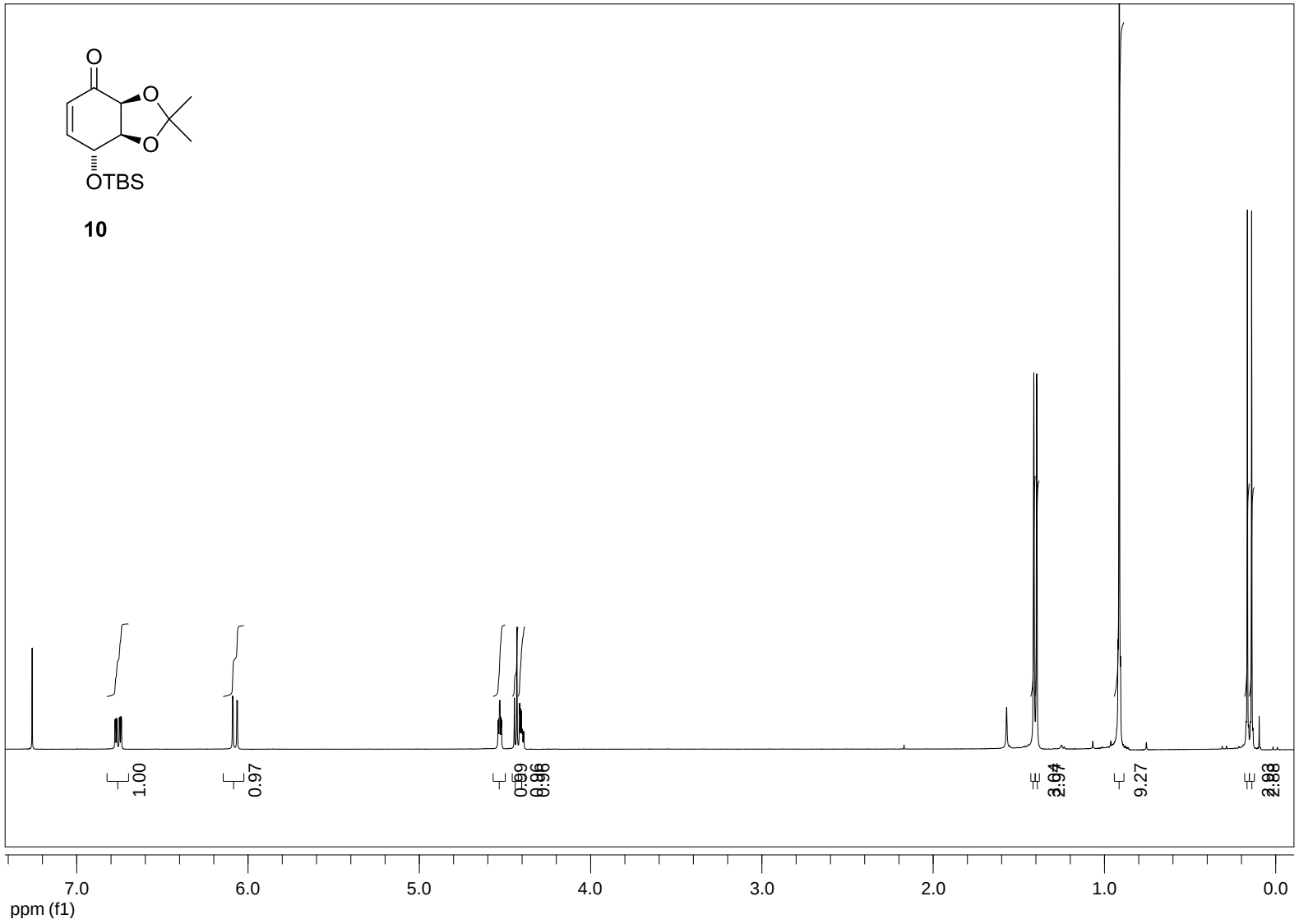


**8** 1:1 **9**

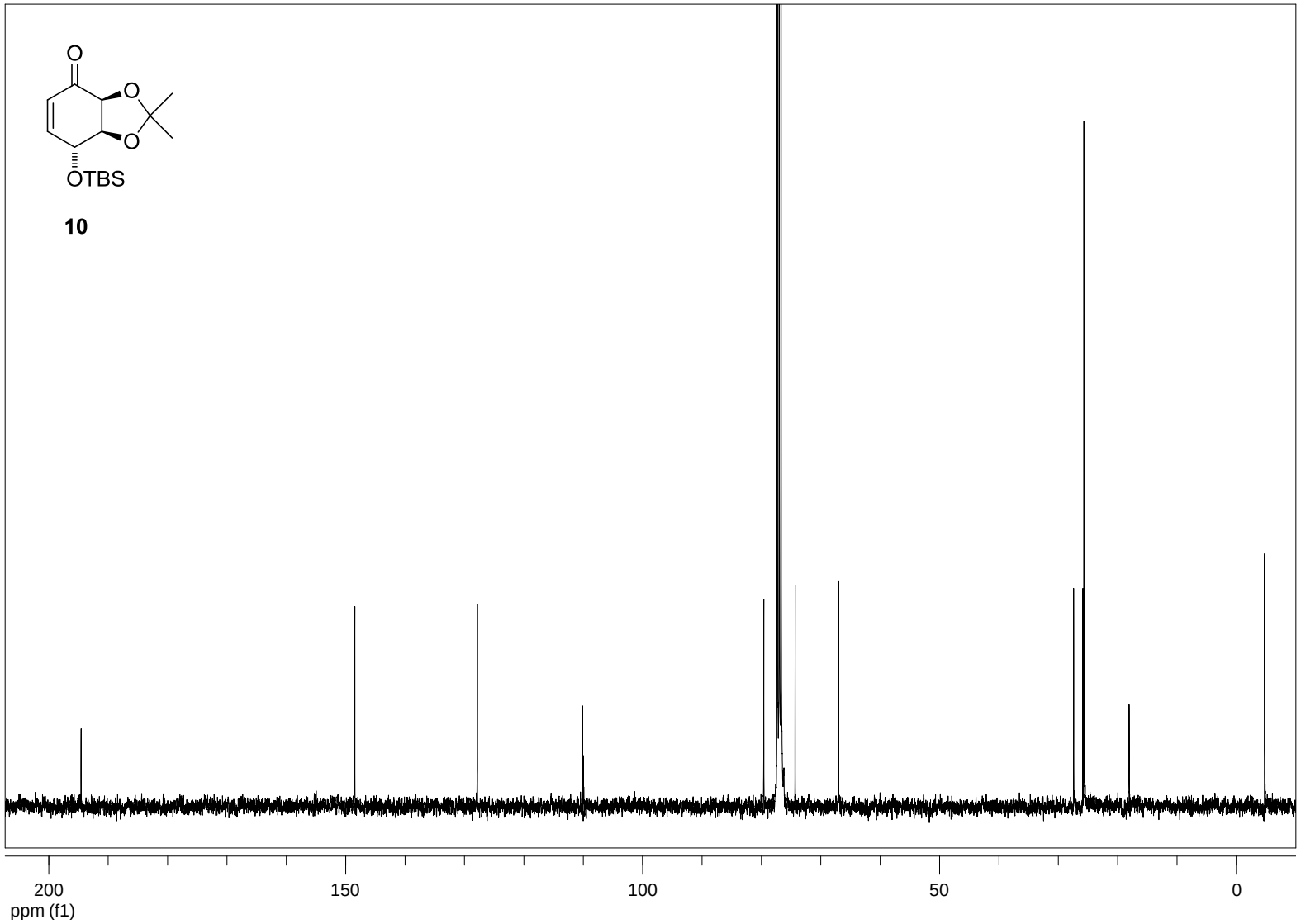
(Contaminated with ~10% of compound **3**)



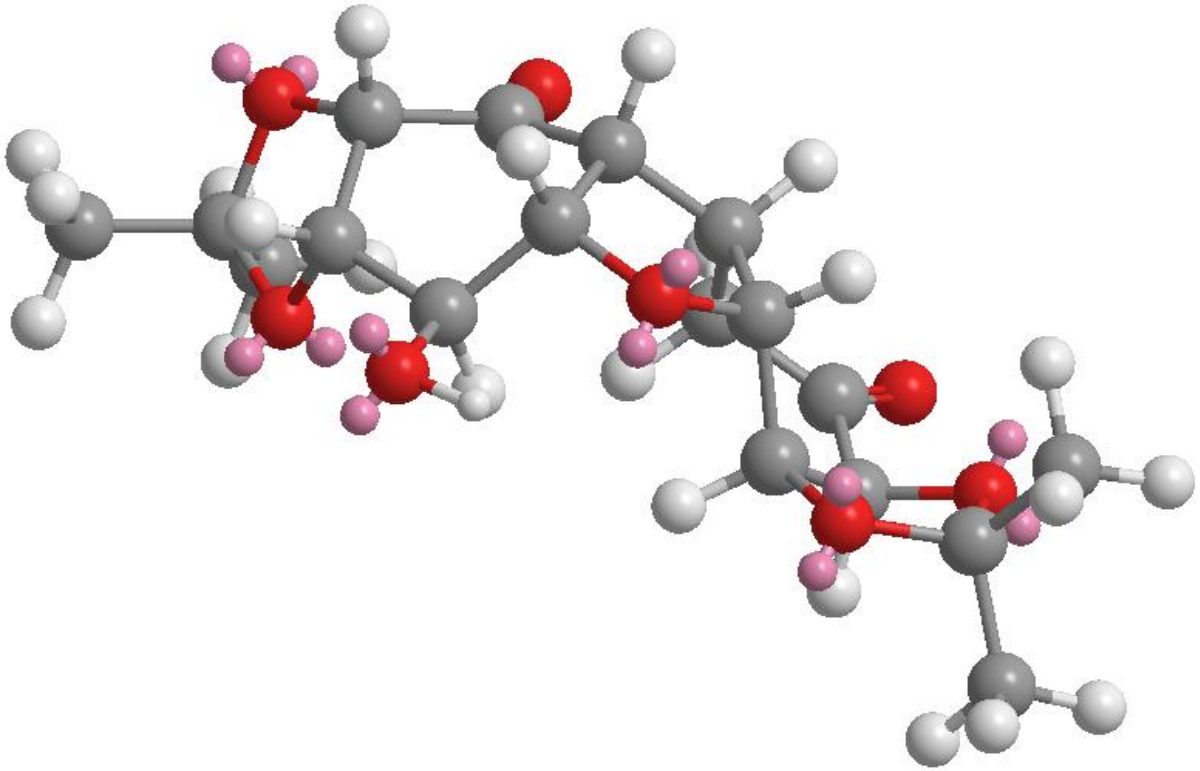
$^{1}$H NMR, 400 MHz, $CDCl_3$

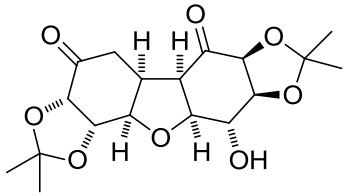


$^{13}C$ NMR, 100 MHz, $CDCl_3$



Structure of **9** with MMFF94 energy minimization (Chem 3D):






**9**

PDB coordinates for structure of **9** (MMFF94):

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HETATM    3  C           1      -0.495  -0.790  -1.467
HETATM    4  O           1       0.785  -1.451  -1.434
HETATM    5  C           1       1.821  -0.506  -1.141
HETATM    6  C           1       2.234  -0.677   0.325
HETATM    7  C           1       3.289   0.345   0.747
HETATM    8  C           1       3.334   1.610  -0.079
HETATM    9  C           1       1.946   1.950  -0.632
HETATM   10  C           1      -0.930   1.326  -0.117
HETATM   11  C           1      -2.382   0.897  -0.122
HETATM   12  C           1      -2.636  -0.602  -0.072
HETATM   13  C           1      -1.387  -1.400  -0.365
HETATM   14  O           1       1.432   3.059  -0.500
HETATM   15  O           1       2.993   0.830   2.066
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HETATM   17  O           1       3.872   2.589   0.798
HETATM   18  O           1      -3.566  -1.080  -1.033
HETATM   19  C           1      -3.237  -2.464  -1.203
HETATM   20  O           1      -1.878  -2.680  -0.797
HETATM   21  O           1      -3.293   1.722  -0.142
HETATM   22  H           1      -0.705   1.205  -2.217
HETATM   23  H           1       1.511   1.090  -2.510
HETATM   24  H           1       2.672  -0.755  -1.788
HETATM   25  H           1      -0.913  -1.012  -2.455
HETATM   26  C           1       4.908   2.042   2.894
HETATM   27  C           1       2.623   3.085   2.807
HETATM   28  C           1      -3.397  -2.838  -2.670
HETATM   29  C           1      -4.146  -3.318  -0.322
HETATM   30  O           1       2.751  -2.002   0.502
ETATM   31  H           1       1.358  -0.615   0.981
HETATM   32  H           1       4.285  -0.113   0.797
HETATM   33  H           1       4.000   1.509  -0.943
HETATM   34  H           1      -0.906   2.420  -0.154
HETATM   35  H           1      -0.471   1.008   0.825
HETATM   36  H           1      -3.016  -0.841   0.929
HETATM   37  H           1      -0.795  -1.561   0.543
HETATM   38  H           1       4.752   1.655   3.907
HETATM   39  H           1       5.605   1.362   2.392
HETATM   40  H           1       5.400   3.019   2.953
HETATM   41  H           1       1.670   3.119   2.267
HETATM   42  H           1       3.019   4.105   2.831
HETATM   43  H           1       2.399   2.761   3.829
HETATM   44  H           1      -2.762  -2.209  -3.302
HETATM   45  H           1      -3.104  -3.878  -2.849
HETATM   46  H           1      -4.429  -2.691  -3.007
HETATM   47  H           1      -5.201  -3.157  -0.565
HETATM   48  H           1      -4.015  -3.064   0.736
HETATM   49  H           1      -3.910  -4.383  -0.425
HETATM   50  H           1       2.102  -2.609   0.092
CONECT    1    2    5    9   23
CONECT    2    1    3   10   22
CONECT    3    2    4   13   25
CONECT    4    3    5
CONECT    5    1    4    6   24
CONECT    6    5    7   30   31
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CONECT    8    7    9   17   33
CONECT    9    1    8   14
CONECT   10    2   11   34   35
CONECT   11   10   12   21
CONECT   12   11   13   18   36
CONECT   13    3   12   20   37
CONECT   14    9
CONECT   15    7   16
CONECT   16   15   17   26   27
CONECT   17    8   16
CONECT   18   12   19
CONECT   19   18   20   28   29
CONECT   20   13   19
CONECT   21   11
CONECT   22    2
CONECT   23    1
CONECT   24    5
CONECT   25    3
CONECT   26   16   38   39   40
CONECT   27   16   41   42   43
CONECT   28   19   44   45   46
CONECT   29   19   47   48   49
CONECT   30    6   50
CONECT   31    6
CONECT   32    7
CONECT   33    8
CONECT   34   10
CONECT   35   10
CONECT   36   12
CONECT   37   13
CONECT   38   26
CONECT   39   26
CONECT   40   26
CONECT   41   27
CONECT   42   27
CONECT   43   27
CONECT   44   28
CONECT   45   28
CONECT   46   28
CONECT   47   29
CONECT   48   29
CONECT   49   29
CONECT   50   30
```