Supporting Information

Synthesis of Bishomoinositols and an Entry for Construction of Substituted 3-oxabicyclo[3.3.1]nonane Skeleton

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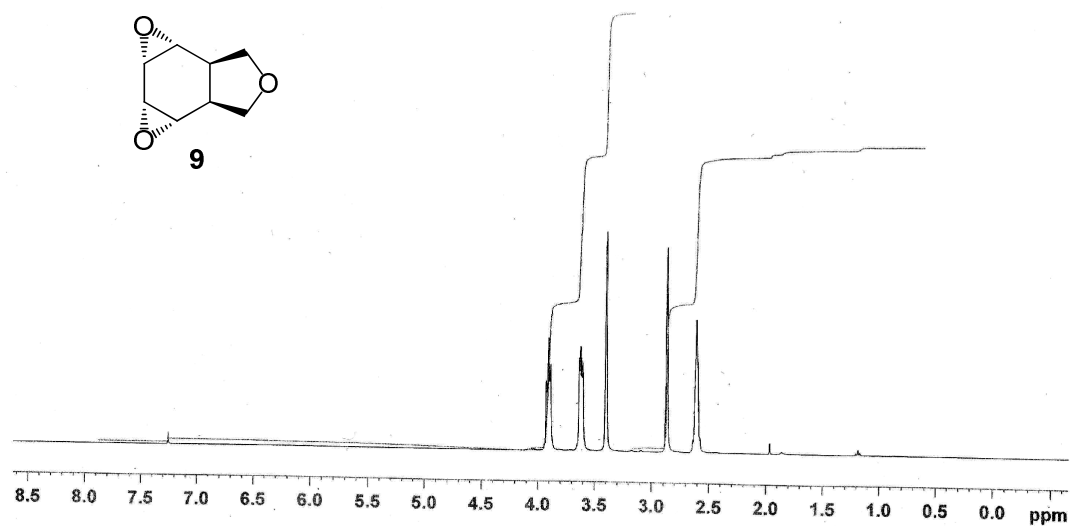*Department of Chemistry, Sakarya University, 54100 Sakarya, Turkey*

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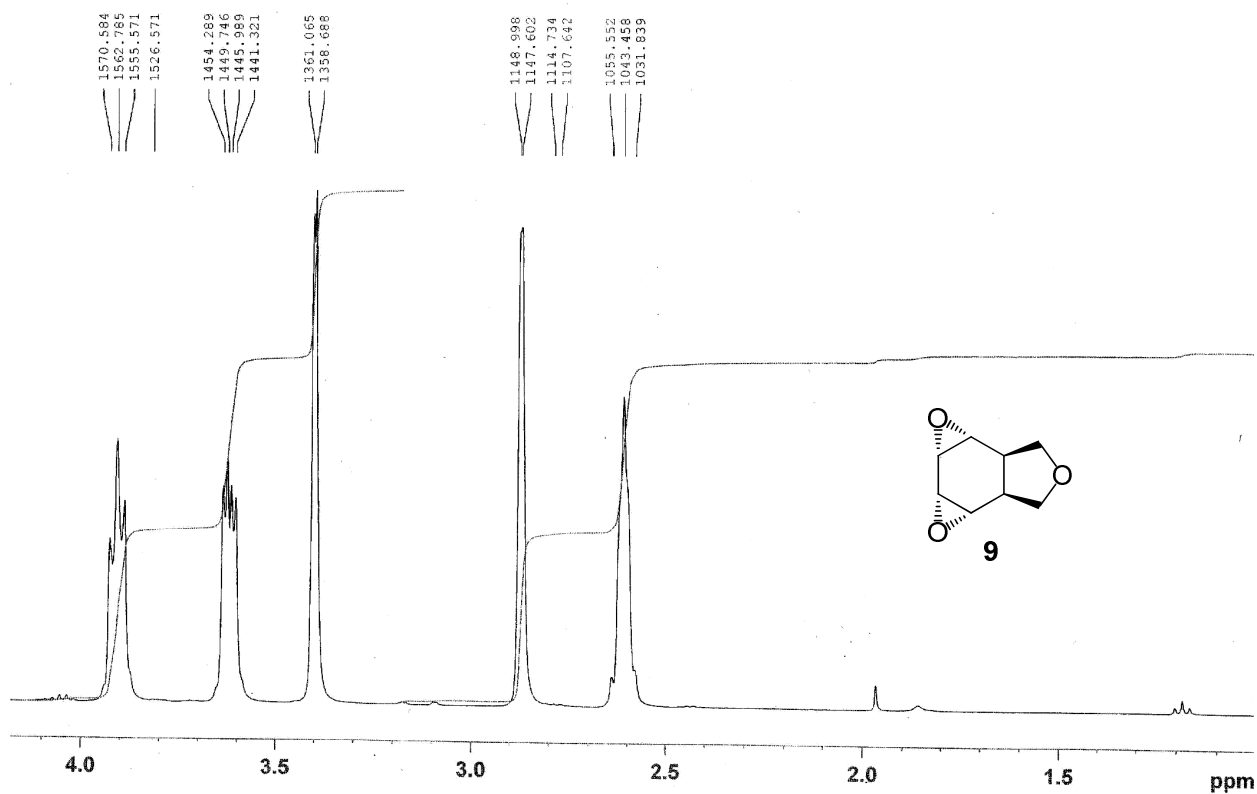
Table of Contents

^{1}H-NMR in CDCl$_3$

expanded ^{1}H-NMR spectrum

^{13}C-NMR in CDCl$_3$

Peaks: 77.492, 77.174, 76.855, 70.989, 50.410, 47.546, 36.801

^{1}H-NMR in CDCl$_3$

4

^{1}H NMR in benzene-d$_6$

^{1}H-NMR in benzene-d$_6$ (expanded)

^{13}C-NMR in benzene-d$_6$

169.55 169.15 168.75

74.0 73.0 72.0 71.0 70.0 69.0 68.0 67.0 66.0

20.25 20.00 19.75

169.41
169.28
169.09

73.25
70.94
70.81
70.68
70.45
67.12

42.13
40.63

20.12
20.07
20.03
19.97

10

170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20

f1 (ppm)

DEPT spectrum

CH^3 and CH up
CH$_2$ down

3

CH only

10

2

all protonated carbons

1

74   72   70   68   66   64   62   60   58   56   54   52   50   48   46   44   42   40   38   36   34   32   30   28   26   24   22   20   18

COSY spectrum

HETCOR

10

NOESY spectrum

^{1}H NMR in CDCl$_3$

^{13}C NMR spectrum

169.97
169.91

170.0 169.6

OAc

AcO

AcO

OAc

O

11

70.21
69.57
68.08

42.94

21.17
21.02

21.5 21.0 20.5

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

f1 (ppm)

DEPT

OAc

AcO

AcO

OAc

O

11

CH$_3$ and CH up
CH$_2$ down

CH only

all protonated carbons

75 70 65 60 55 50 45 40 35 30 25 20 15

10

COSY spectrum

HETCOR spectrum

11

^{1}H NMR in CDCl$_3$

12

1.00   1.03   0.50   3.06

7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0
f1 (ppm)

^{13}C NMR spectrum

170.8   170.1

69.6   69.0

21.5   21.0

12

170.32
169.96

69.48
69.20
68.69

40.09

21.17
21.04

170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20   1
f1 (ppm)

12

DEPT spectrum

CH₃ and CH up
CH₂ down

CH only

all protonated carbons

COSY spectrum

13

HETCOR spectrum

^{1}H NMR in CDCl$_3$

13

^{13}C NMR spectrum

13

15

DEPT spectrum

13

CH$_3$ and CH up
CH$_2$ down

CH only

all protonated carbons

COSY spectrum

13

HETCOR spectrum

OAc

AcO␣␣OAc

AcO␣␣OAc

OAc

13

^{1}H NMR in DMSO-d$_6$

OH

HO␣␣OH

HO␣␣OH

OH

14

^{1}H NMR spectrum (expanded)

1887.858
1883.945
1850.616
1822.422
1772.305
1735.516
1712.526
1706.391
1631.498
1616.569
1609.235
1589.488
1550.798
1529.419
1520.321
1509.213
1500.511
1479.635
1474.112
1469.137
1442.539
1426.247
1412.886
1406.943
1402.165
1385.615
1378.009
1372.727
1362.200
1350.869
1334.040
1325.195
1311.986
1304.060
1291.576
1288.360
1279.997
1269.505
1241.706

14

4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 ppm

^{13}C NMR in DMSO-d$_6$

75.438
71.907
71.421
70.249
60.907
58.583
43.252
40.081
39.857
39.650
39.441
39.231
39.024
38.815

14

200 180 160 140 120 100 80 60 40 20 0 ppm

18

^{13}C NMR spectrum (expanded)

75.438
71.907
71.421
70.249
60.907
58.583
43.252
40.081
39.857
39.650
39.441
39.231
39.024
38.815

14

75   70   65   60   55   50   45   40   ppm

^{1}H NMR spectrum

18

5.5 5.4 5.3 5.2 5.1 4.6 4.5 4.4 4.3 4.2 4.1 4.0 2.9 2.8 2.7 2.6 2.5 2.4

2.10   2.05

1.00   0.49   0.53   0.47   4.59

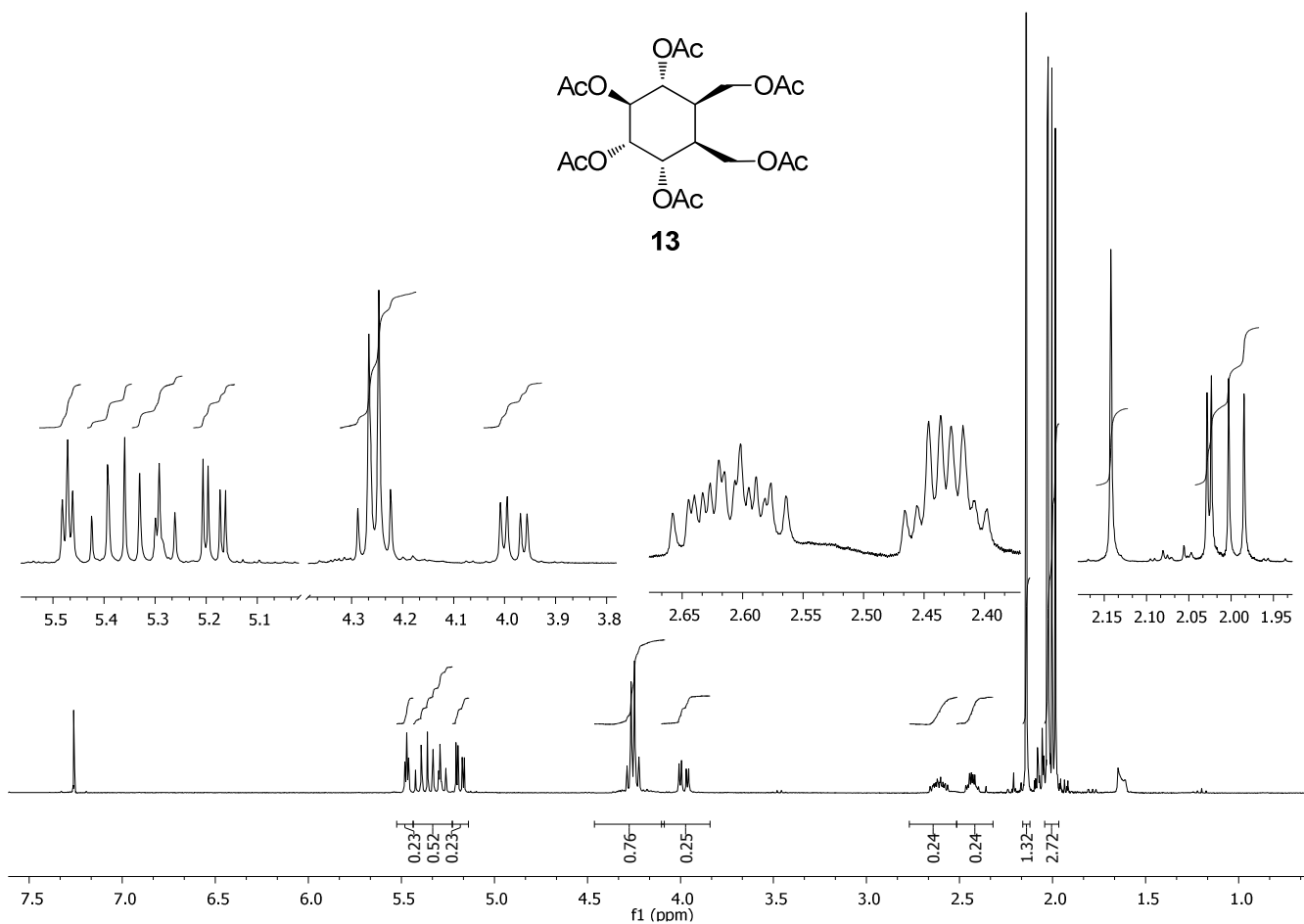7.5   7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0
f1 (ppm)

19

¹³C NMR spectrum

COSY spectrum

HETCOR spectrum

18

^{1}H NMR in CD$_3$OD

19

^{13}C NMR in CD$_3$OD

73.26
71.68
61.22
43.22

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

^{1}H NMR spectrum in CDCl$_3$

1.92   1.00   2.90

2.15   2.10   2.05   2.00

1.00   3.19   4.26   2.07   19.44

7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0
f1 (ppm)

22

^{13}C NMR spectrum

COSY spectrum

23

HETCOR spectrum

20

f1 (ppm)

^{1}H NMR spectrum in D$_2$O

22

^{13}C NMR spectrum at 60 ^{o}C

115.149
109.626
70.575
68.684
60.913
56.980
40.746

22

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

^{1}H NMR in CDCl$_3$

21

0.96   0.83   0.97

2.15 2.11 2.07 2.03 1.99 1.95

1.00 0.91   1.86   0.91   9.06

7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5

f1 (ppm)

^{13}C NMR spectrum

170.75

169.84
169.71

170.75
169.84
169.71

170.2   168.9
f1 (ppm)

21.13
21.08
20.97

21.13
21.08
20.97

21.20   21.00 20.80
f1 (ppm)

69.50
67.64

61.38

37.32

21

180   170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20
f1 (ppm)

COSY spectrum

21

f1 (ppm)

5.0   4.5   4.0   3.5   3.0   2.5   2.0

2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5

HETCOR spectrum

^{1}H NMR in CD$_3$OD

^{13}C NMR in CD$_3$OD at 80 °C

^{1}H NMR spectrum in CDCl$_3$

Expanded ^{1}H NMR spectrum in CDCl$_3$

Expanded ^{1}H NMR spectra in CDCl$_3$

24

^{13}C NMR spectrum in CDCl$_3$

170.46
170.43
170.19
170.14

73.88
71.74
70.22
69.68
68.60
66.72

39.71
38.84

21.46
21.29
21.17
20.93

24

DEPT spectrum

CH$_3$ and CH up
CH$_2$ down

CH only

all protonated carbons

24

COSY spectrum

Expanded COSY spectra

HETCOR spectrum

HETCOR (expanded)

33

^{1}H NMR spectrum

^{13}C NMR in CDCl$_3$

COSY spectrum

^{1}H NMR in CDCl$_3$

Expanded ^{1}H NMR spectra in CDCl$_3$

^{13}C NMR spectrum in CDCl$_3$

DEPT spectrum

26

CH₃ and CH up
CH₂ down

CH only

all protonated carbons

f1 (ppm)

COSY spectrum

26

f2 (ppm)

^{1}H NMR spectrum in CDCl$_3$

Expanded ^{1}H NMR spectra in CDCl$_3$

Expanded ^{1}H NMR spectra in CDCl$_3$

27

3.79
3.77
3.75
3.74

3.60
3.58
3.57

3.55
3.54
3.53
3.53
3.53
3.52
3.52
3.51
3.51

3.43
3.42
3.42
3.42
3.41
3.41
3.41
3.40

1.00

0.77

1.12

0.95

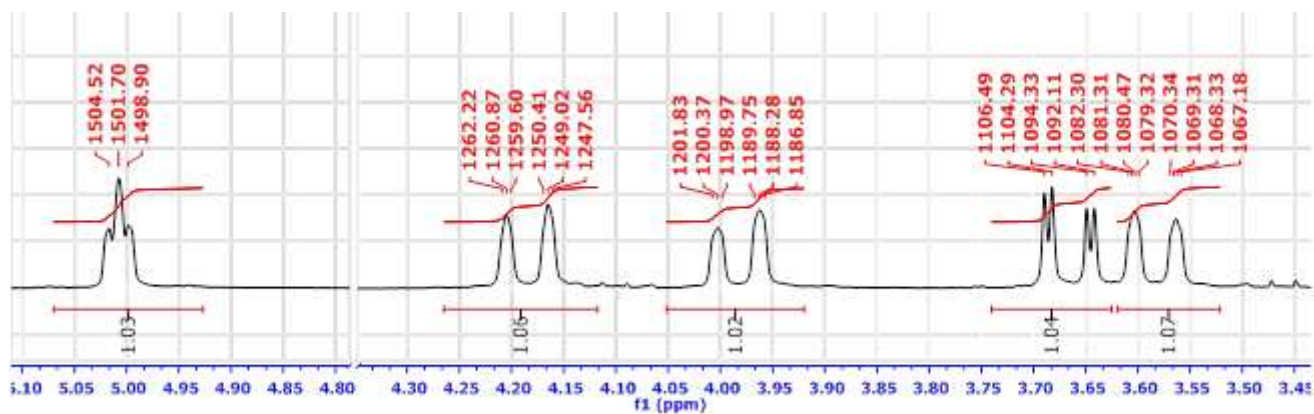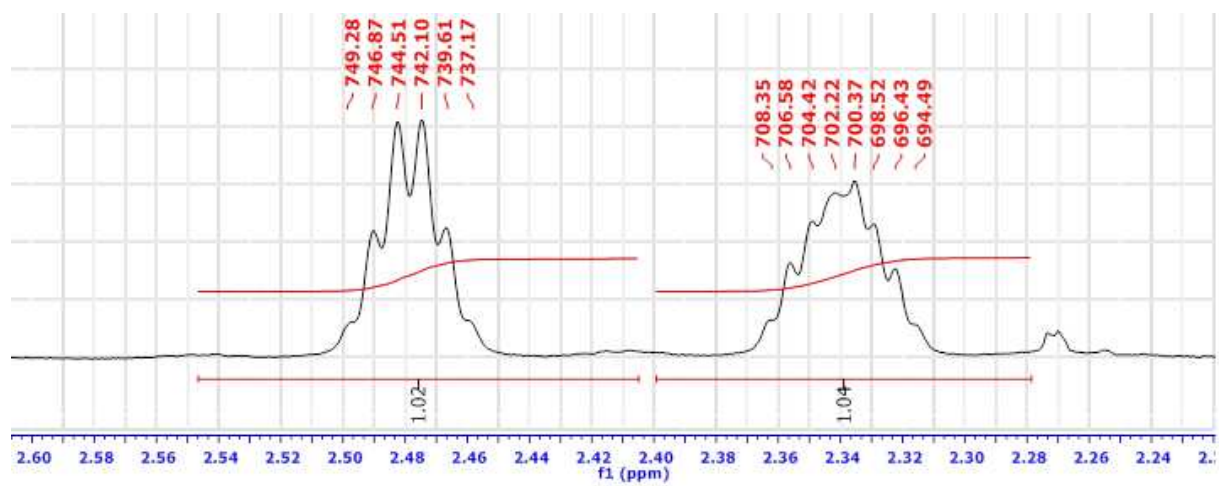3.86 3.84 3.82 3.80 3.78 3.76 3.74 3.72 3.70 3.68 3.66 3.64 3.62 3.60 3.58 3.56 3.54 3.52 3.50 3.48 3.46 3.44 3.42 3.40 3.38 3.36 3.34
f1 (ppm)

^{13}C NMR spectrum in CDCl$_3$

27

170.8 170.4

170.83
170.67

126.51
124.57

89.30

70.65
67.84

53.36
52.62

36.57

21.3 21.0

21.27
21.20

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)

40

COSY spectrum

HMBC spectrum

41

X-Ray Structural Analysis of 24 and 12

The absolute configuration of the compound **24** was confirmed by X-ray crystallography (Figure 1), which also confirmed the *cis* and *trans* stereochemistry of the acetate groups.

Figure 1. Atomic displacement parameters representation of structure **24** with displacement ellipsoids drawn at the 40% probability level and numbering scheme.

Figure 2. View of the cell packing along the *a*-axis.

Crystallograpy: For the crystal structure determination, the single-crystal of the compound **24** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromatized Mo K$_\alpha$ radiation (λ=0.71073 Å) and oscillation scans technique with $\Delta\omega$=5˚ for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with F^2>2σ(F^2). Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear (Rigaku/MSC Inc., 2005) software [1]. The structures were solved by direct methods using SHELXS-97 [2] and refined by a full-matrix least-squares procedure using the program SHELXL-97 [2]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined by using the riding model with SHELXL-default d(C–H) values. Thermal parameters of the H atoms used were set to Uiso(H) = 1.2Ueq(C). The final difference Fourier maps showed no peaks of chemical significance. Crystal data for 4a: $C_{16}H_{22}O_9$, crystal system, space group: monoclinic, $P2_1$/a; (no:14); unit cell dimensions: a= 8.8325(4), b=14.1648(4), c=14.7778(5)Å, α=90 β=99.154(5), γ=90˚ ; volume: 1825.3(2) Å^3; Z=4; calculated density: 1.30 g/cm^3; absorption coefficient: 0.107 mm^{-1}; F(000): 760; θ-range for data collection 2.7 –26.4˚; refinement method: full-matrix least-square on F^2; data/parameters: 3728/227; goodness-of-fit on F^2: 1.045; final R indices [I>2σ(I)]: R_1= 0.075, wR_2=0.202; R indices (all data): R$_1$=0.152, wR_2=0.252; largest diff. peak and hole: 0.250 and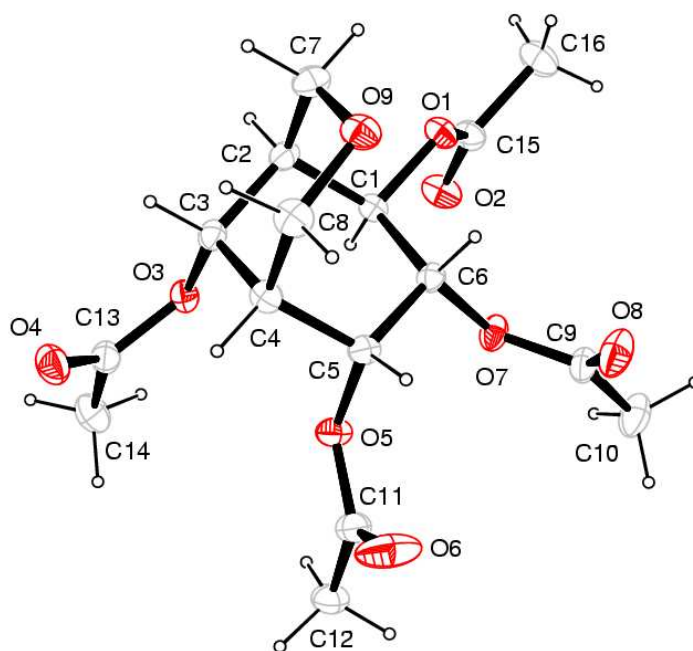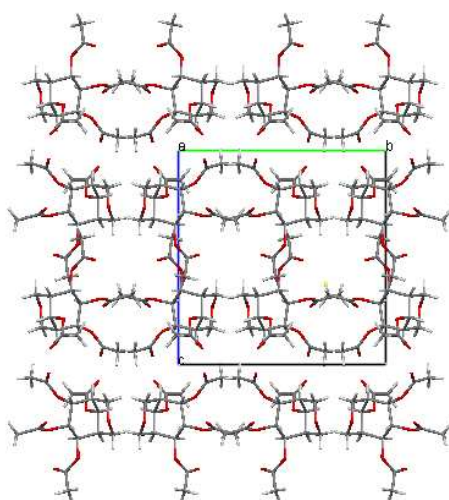 -0.206 e Å^{-3}; **CCDC-855316** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References
1. Rigaku/MSC, Inc., 9009 new Trails Drive, The Woodlands, TX 77381.
2. Sheldrick, G. M., *SHELXS97* and *SHELXL97*, University of Göttingen, Germany, 1997

Structure 12

Data Collection

A colorless chunk crystal of $C_{16}H_{22}O_9$ having approximate dimensions of 0.70 x 0.30 x 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation.

Indexing was performed from 0° oscillations that were exposed for 0 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

a = 17.04(2) Å
b =   8.094(12) Å
c = 26.81(3) Å
V = 3697.9(83) Å^3

For Z = 8 and F.W. = 358.34, the calculated density is 1.29 g/cm^3. Based on the systematic absences of:

0kl: l ± 2n
h0l: h ± 2n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

Pca2$_1$ (#29)

The data were collected at a temperature of 20 ± 1^{O}C to a maximum 2θ value of 50.1^O. A total of 135 oscillation images were collected. A sweep of data was done using w oscillations from 0.0 to 180.0° in 4.0^O steps. The exposure rate was 30.0 [sec./^{O}]. The detector swing angle was 0.08^O. A second sweep was performed using w oscillations from 0.0 to 180.0^O in 4.0^O steps. The exposure rate was 30.0 [sec./^{O}]. The detector swing angle was 0.08^O. Another sweep was performed using w oscillations from 0.0 to 180.0^O in 4.0^O steps. The exposure rate was 30.0 [sec./^{O}]. The detector swing angle was 0.08^O. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 113812 reflections that were collected, 3726 were unique (R_{int} = 0.047); equivalent reflections were merged.

The linear absorption coefficient, μ, for Mo-Kα radiation is 1.1 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.78 to 1.00. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

Experimental Section

General: Melting points are uncorrected. Infrared spectra were obtained from solution in 0.1 mm cells or KBr pellets on a regular instrument. The ^{1}H and ^{13}C NMR spectra were recorded on 300 (75) and 400 (100) MHz spectrometers. Apparent splitting is given in all cases. Column chromatography was performed on silica gel (60-mesh, Merck), TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates.