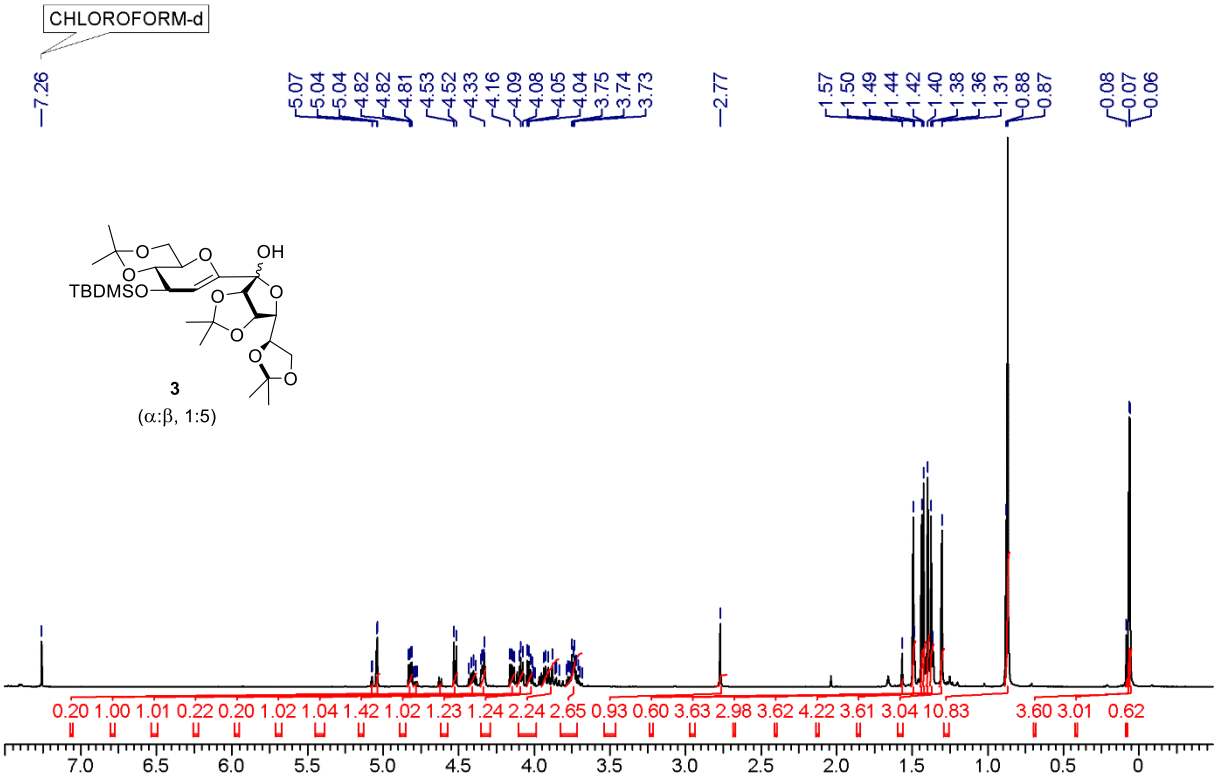
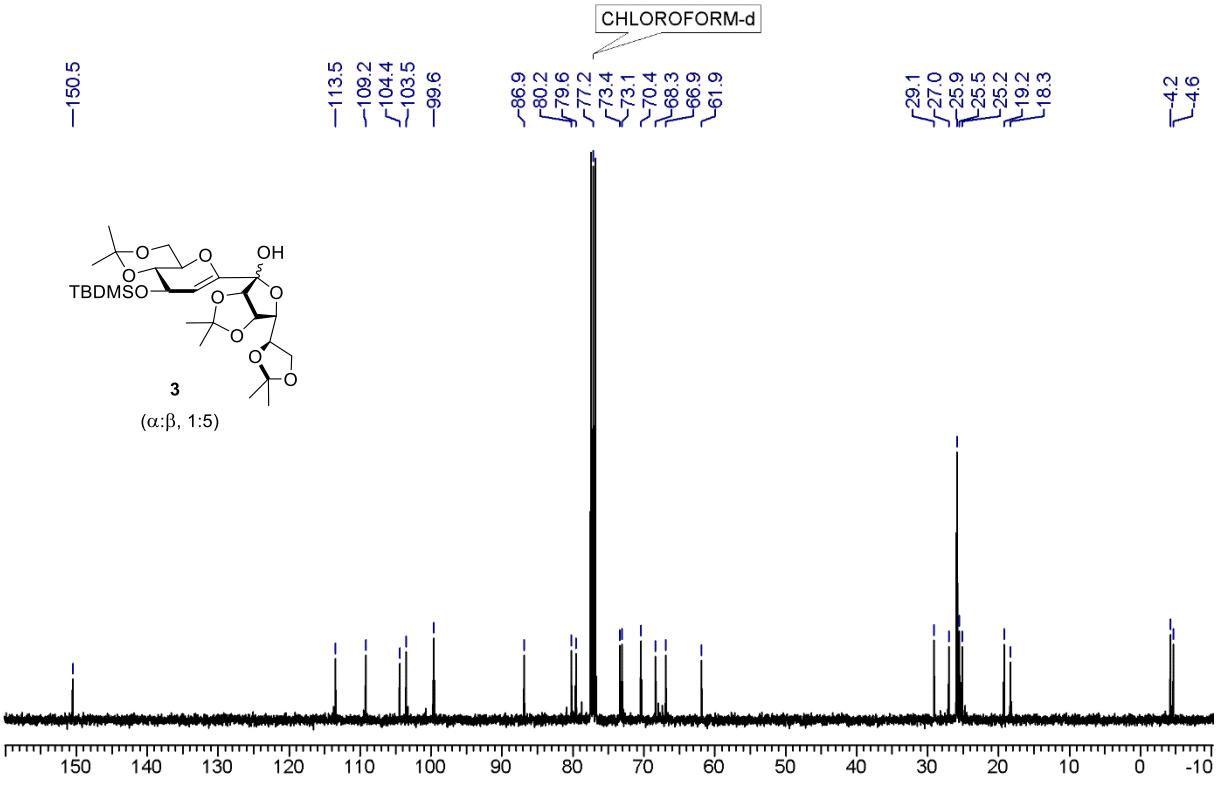
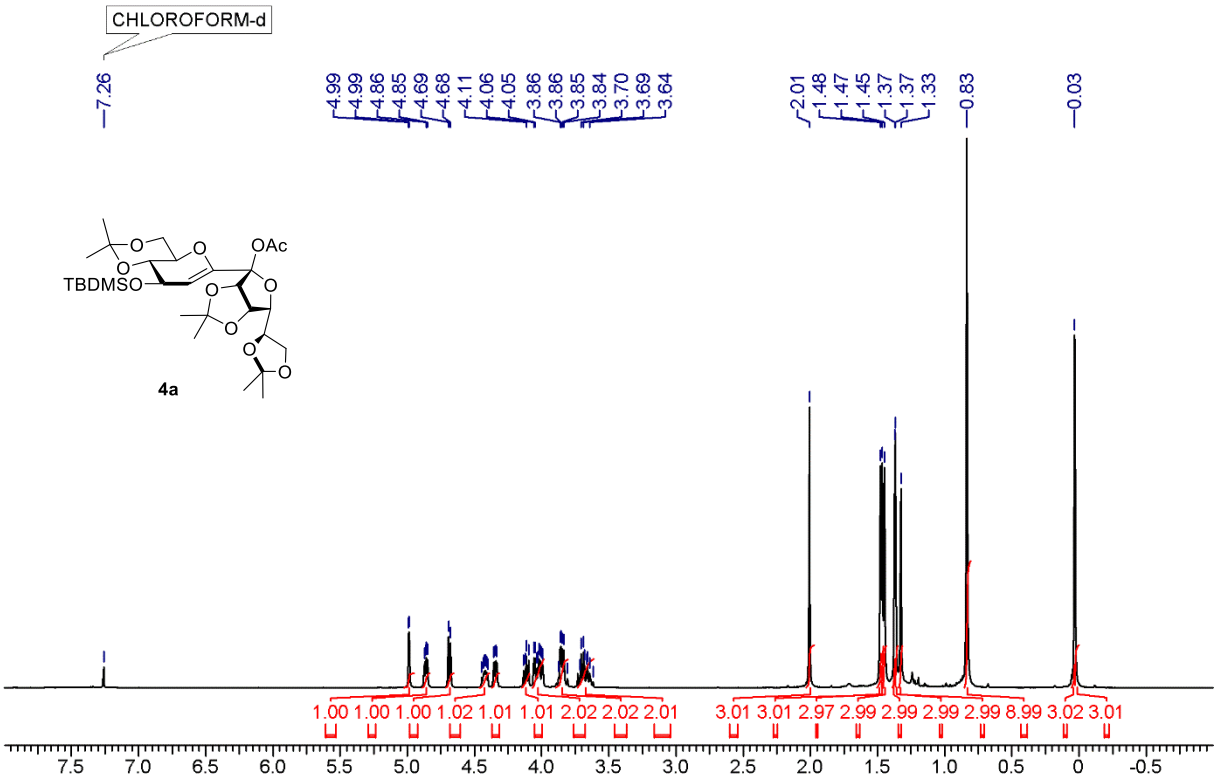
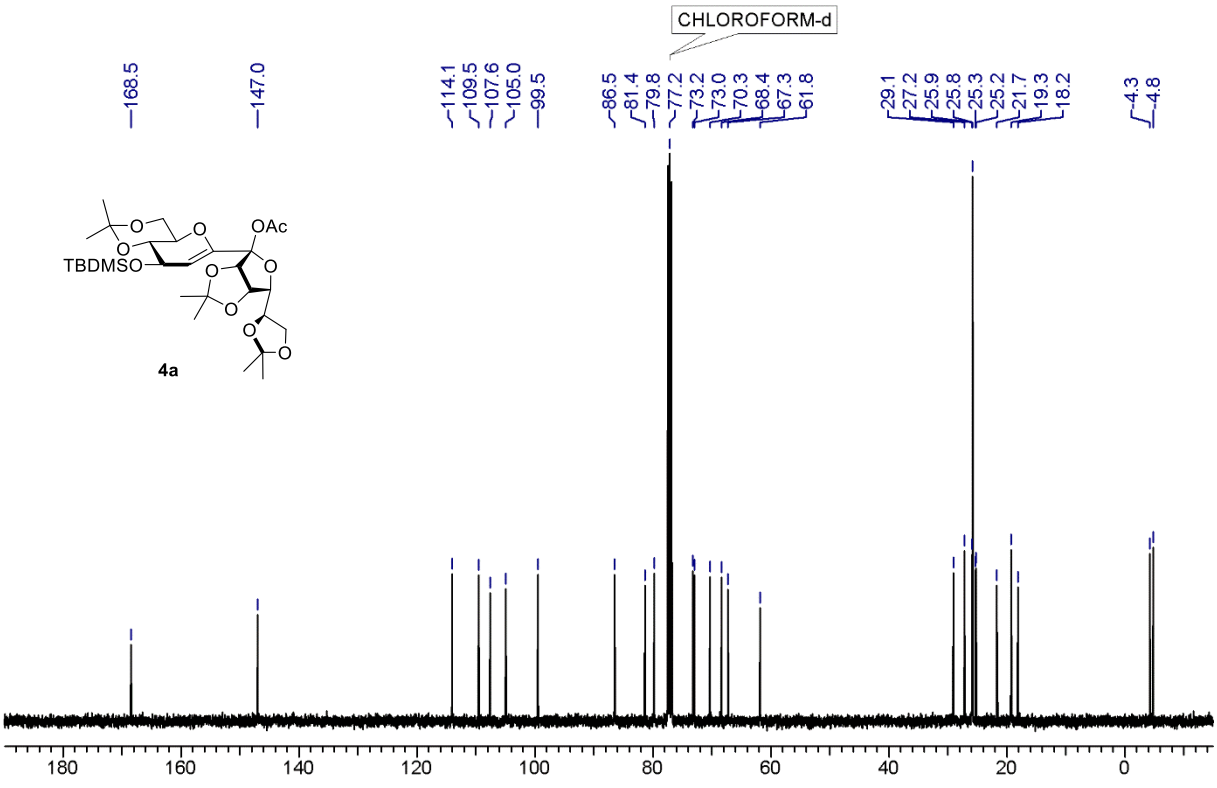
Supporting Information

^{1}H- and ^{13}C-NMR-Spectra:

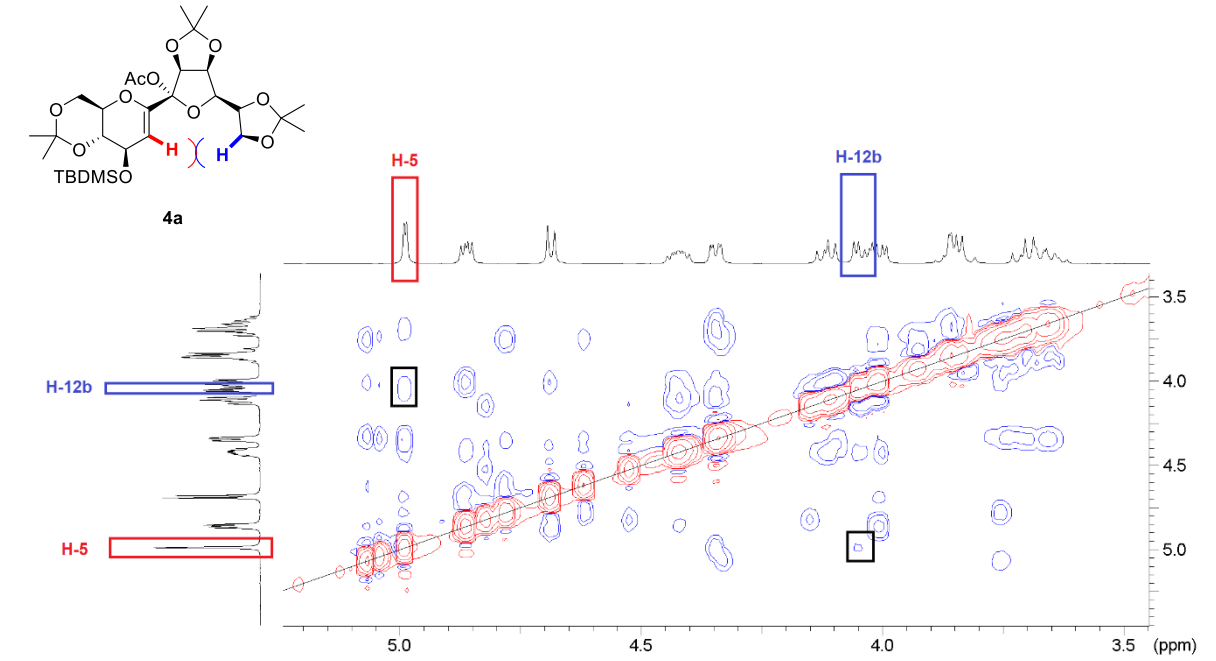


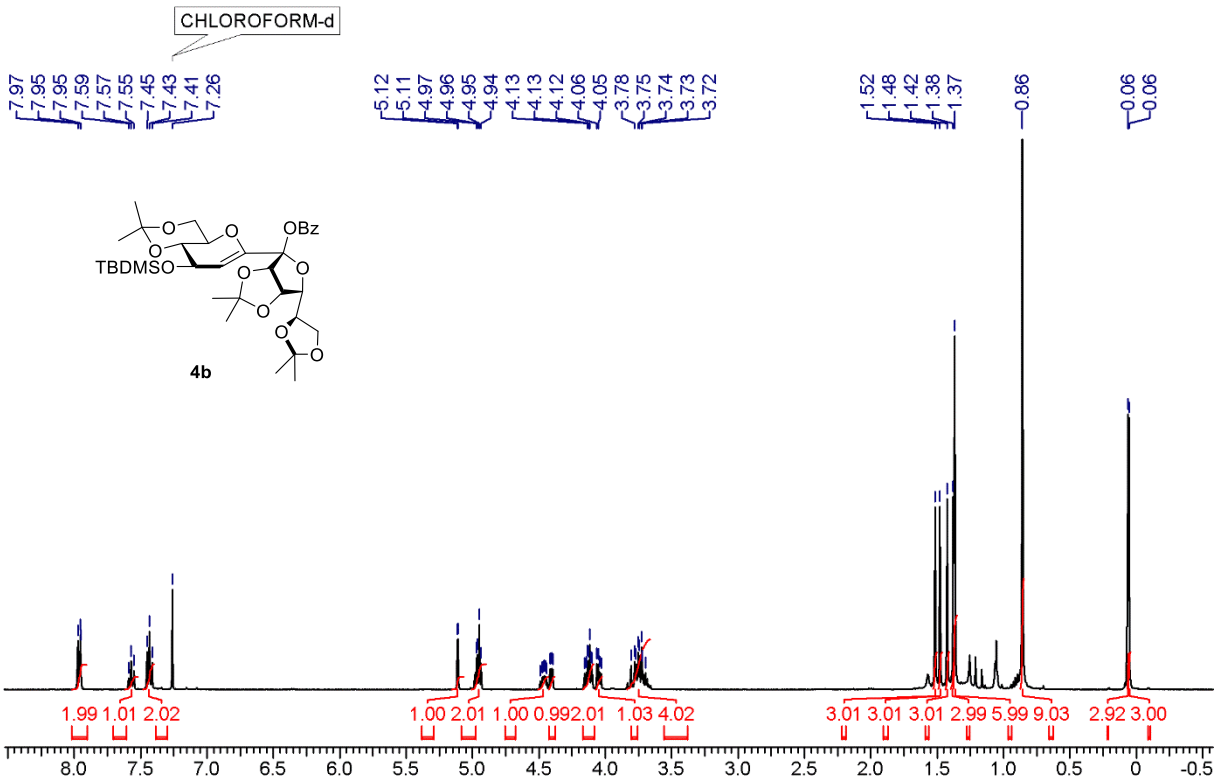


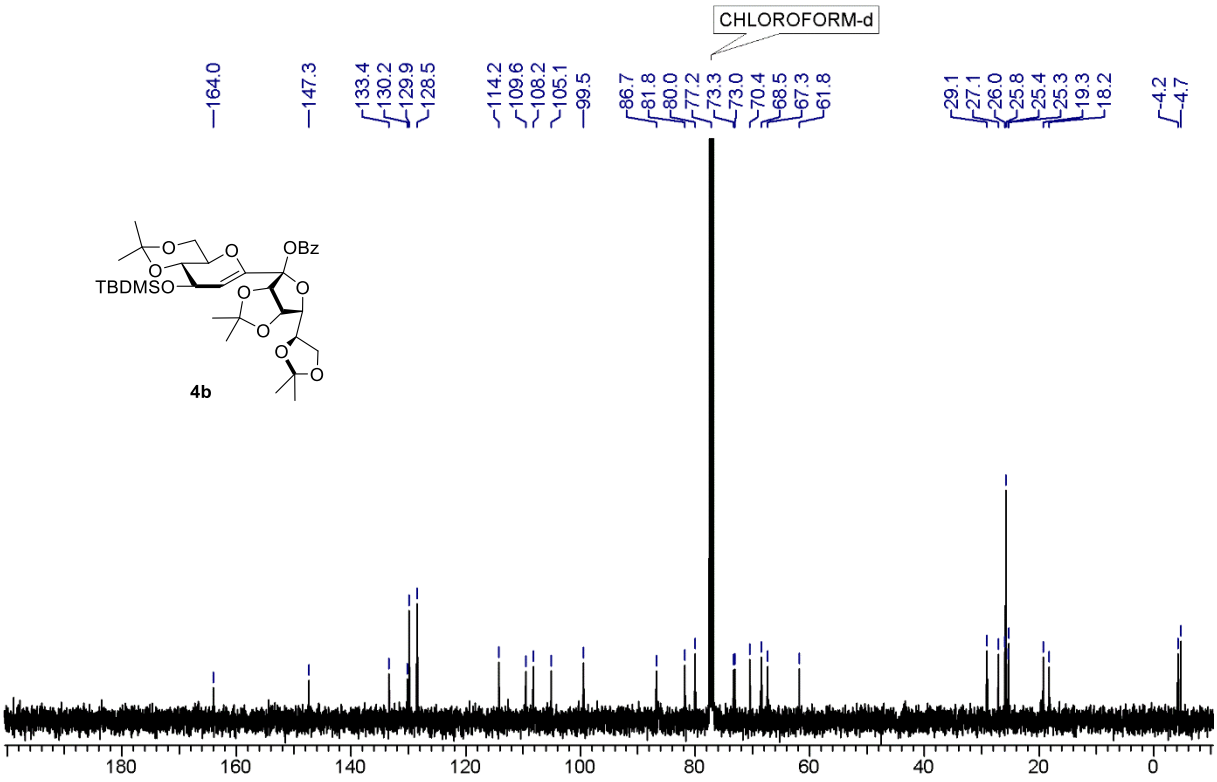

CHLOROFORM-d
7.26
4.99
4.99
4.86
4.85
4.69
4.68
4.11
4.06
4.05
3.86
3.86
3.85
3.84
3.70
3.69
3.64
2.01
1.48
1.47
1.45
1.37
1.37
1.33
0.83
0.03
OAc
TBDMSO
4a
1.00 1.00 1.00 1.02 1.01 1.01 2.02 2.02 2.01
3.01 3.01 2.97 2.99 2.99 2.99 2.99 8.99 3.02 3.01
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5


CHLOROFORM-d
168.5
147.0
114.1
109.5
107.6
105.0
99.5
86.5
81.4
79.8
77.2
73.2
73.0
70.3
68.4
67.3
61.8
29.1
27.2
25.9
25.8
25.3
25.2
21.7
19.3
18.2
4.3
4.8
OAc
TBDMSO
4a
180 160 140 120 100 80 60 40 20 0

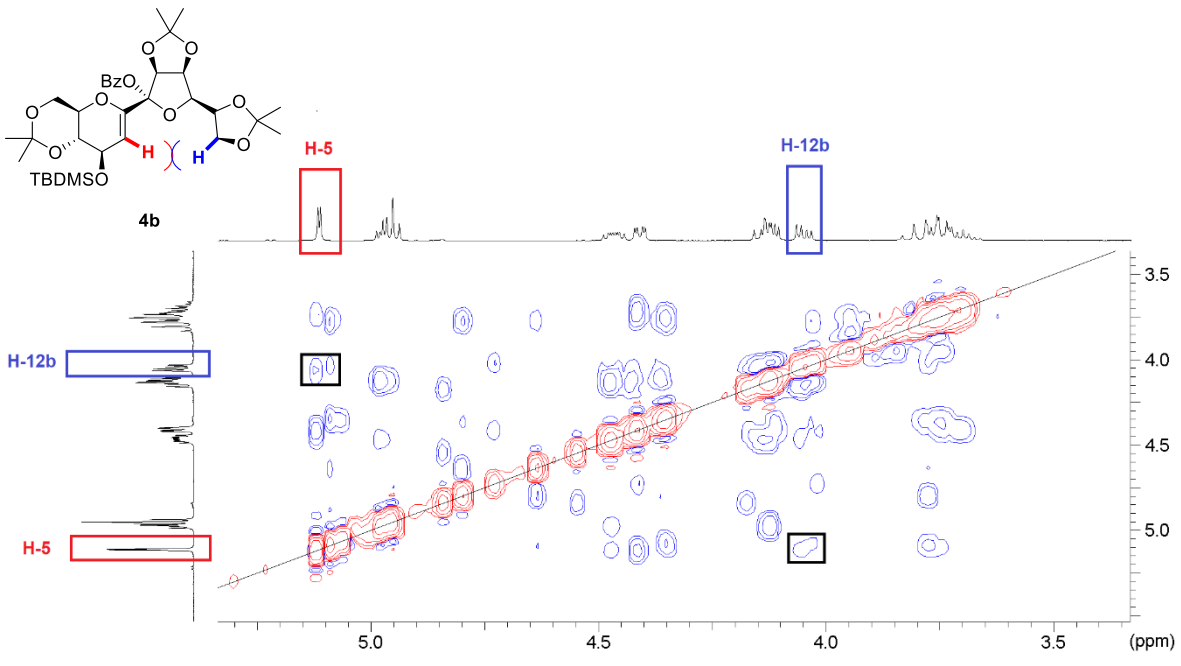
H,H-NOESY NMR ($CDCl_3$):

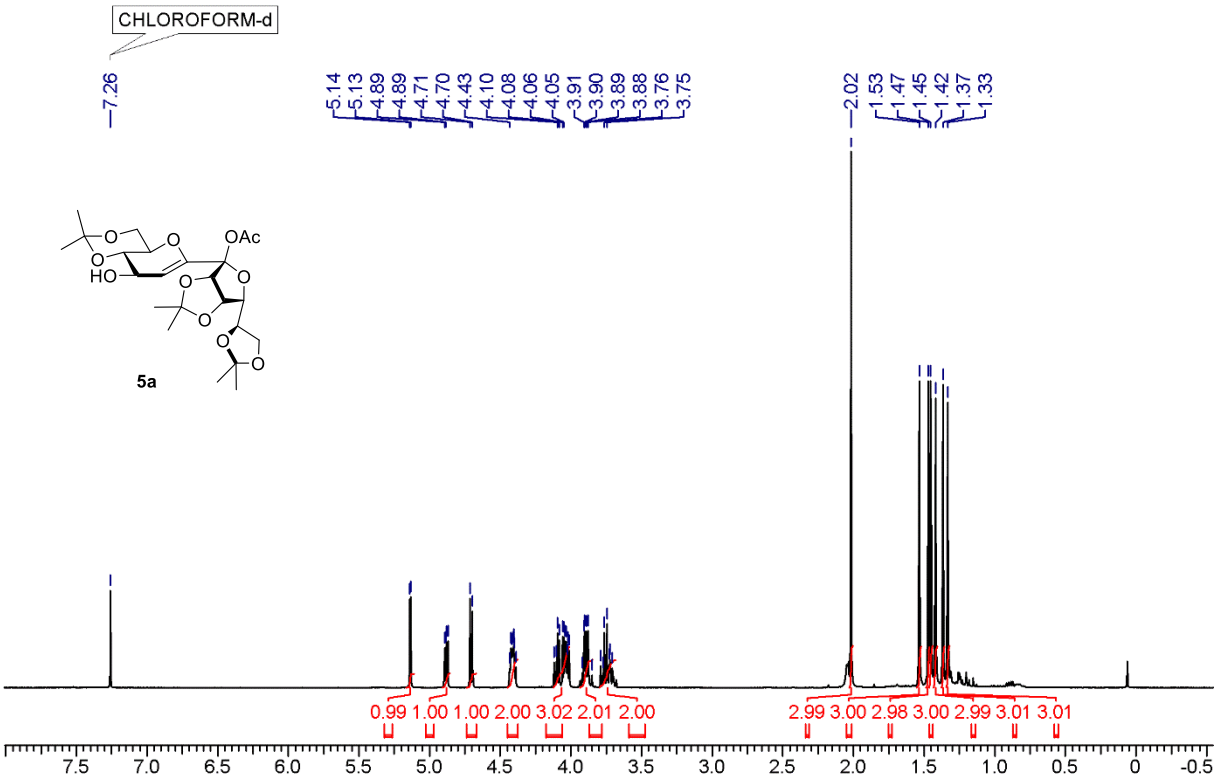


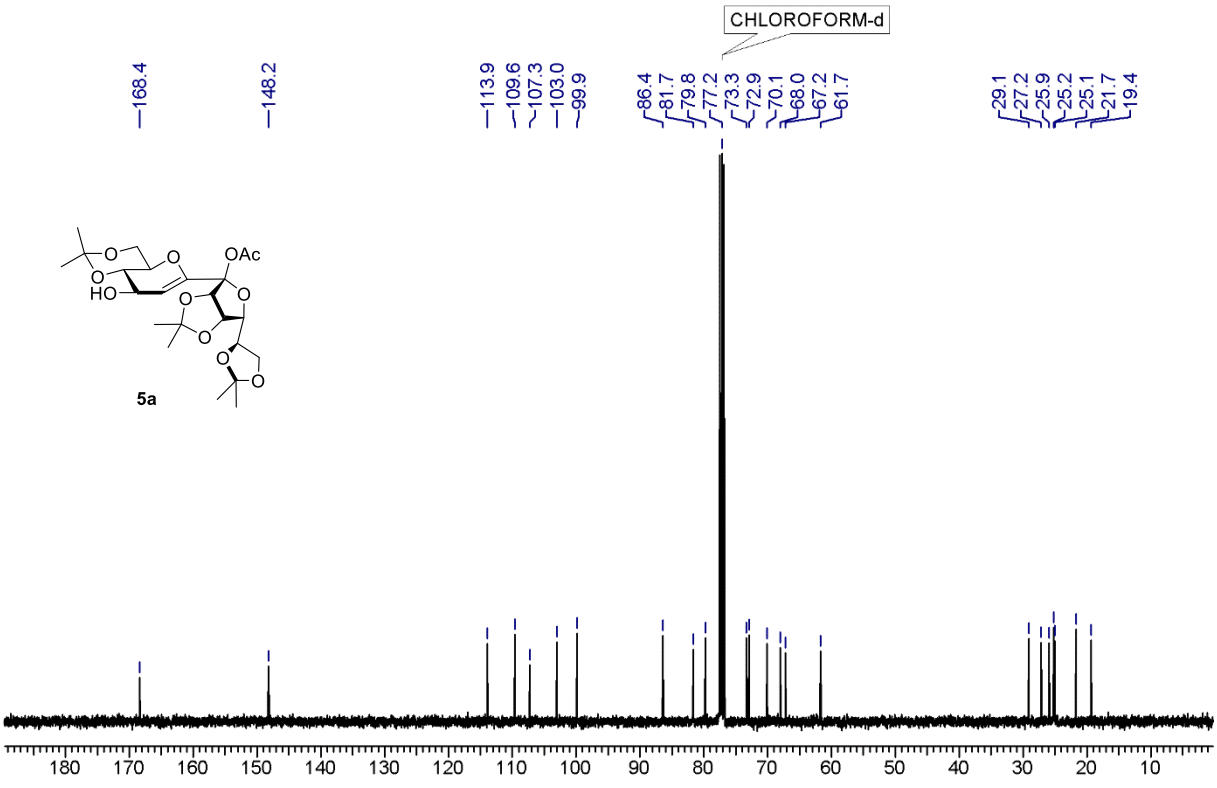


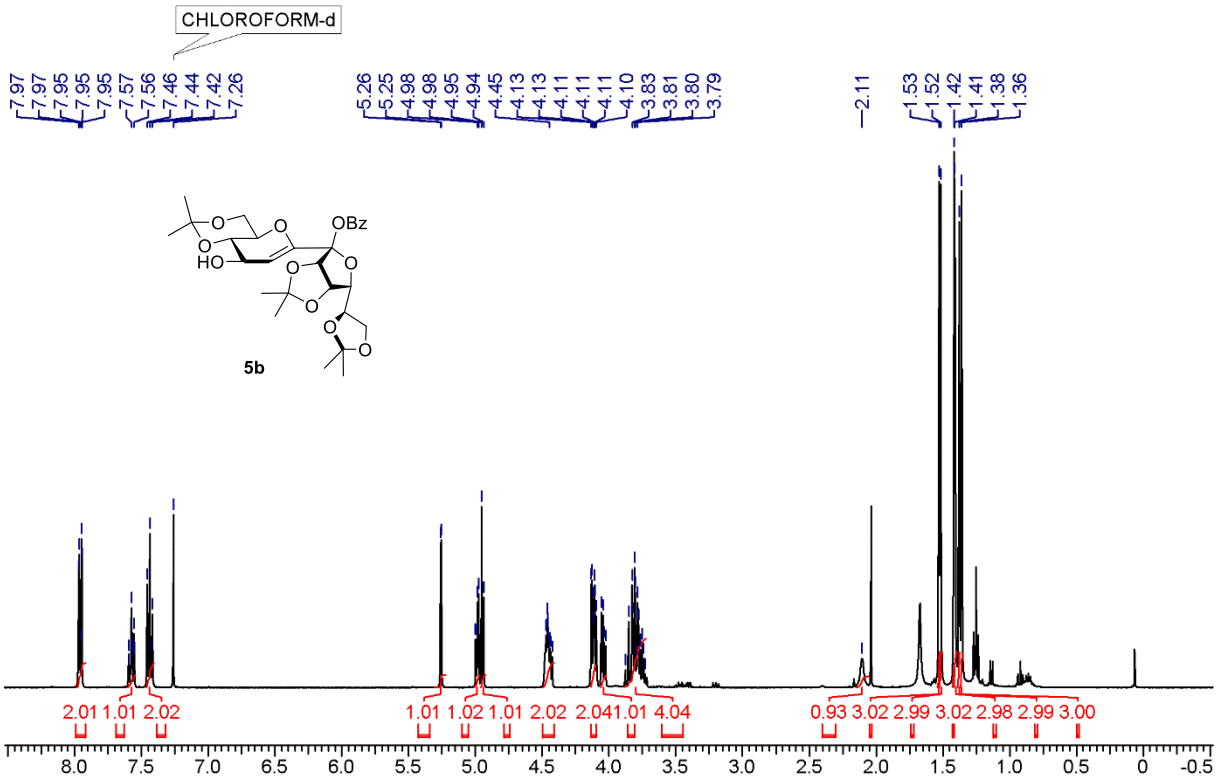


H,H-NOESY NMR ($CDCl_3$):




CHLOROFORM-d
7.26
5.14
5.13
4.89
4.89
4.71
4.70
4.43
4.10
4.08
4.06
4.05
3.91
3.90
3.89
3.88
3.76
3.75
2.02
1.53
1.47
1.45
1.42
1.37
1.33
OAc
HO
5a
0.99 1.00 1.00 2.00 3.02 2.01 2.00
2.99 3.00 2.98 3.00 2.99 3.01 3.01
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5


CHLOROFORM-d
168.4
148.2
113.9
109.6
107.3
103.0
99.9
86.4
81.7
79.8
77.2
73.3
72.9
70.1
68.0
67.2
61.7
29.1
27.2
25.9
25.2
25.1
21.7
19.4
OAc
HO
5a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


CHLOROFORM-d
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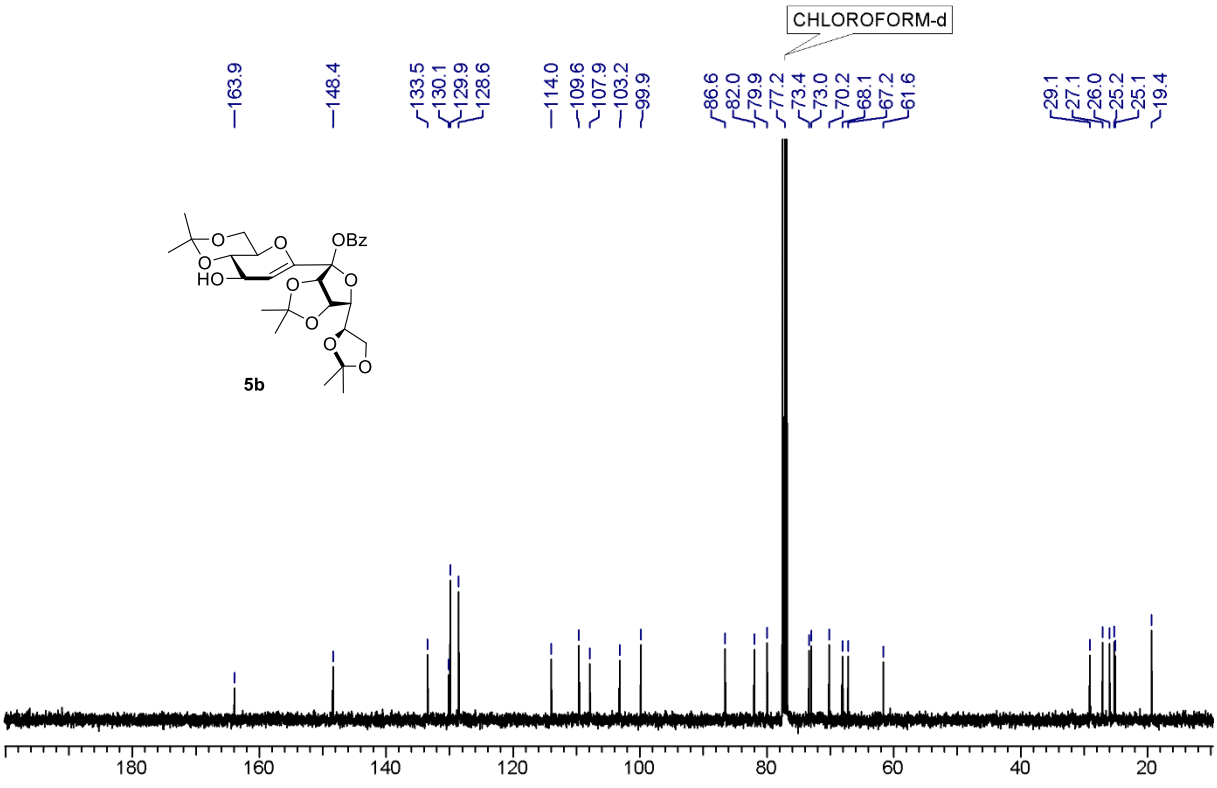
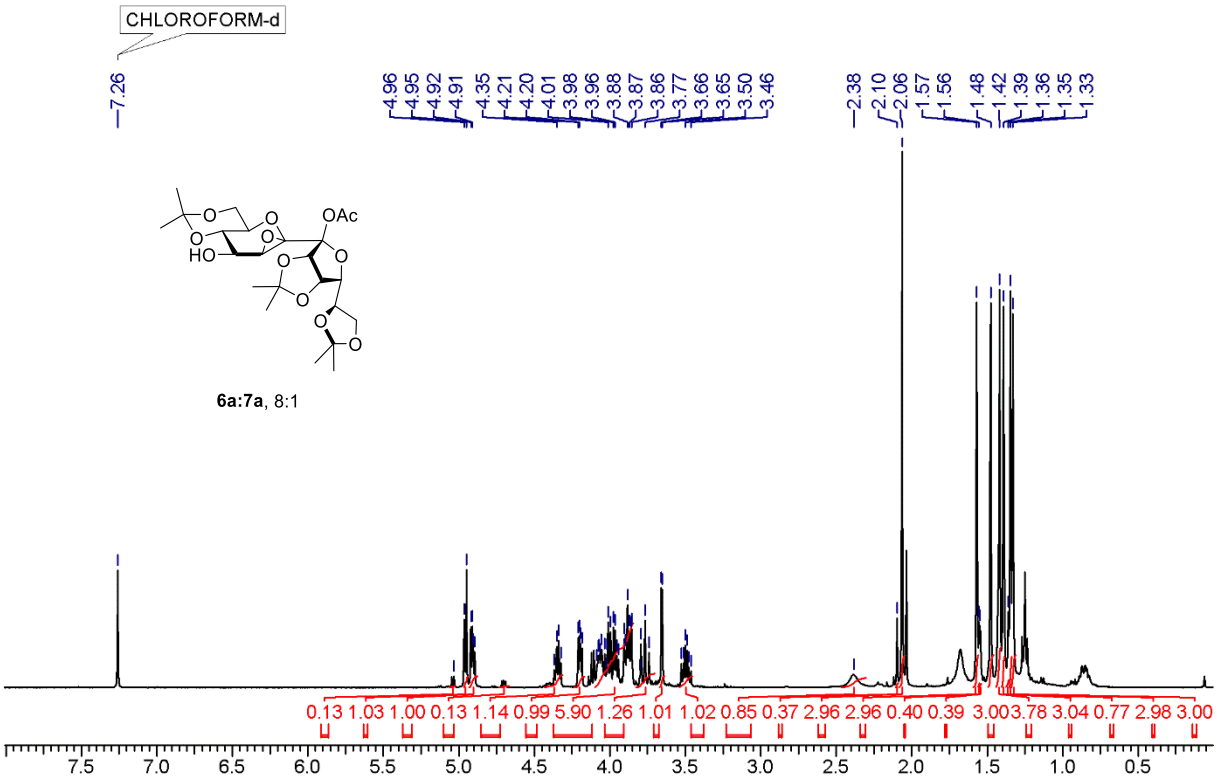
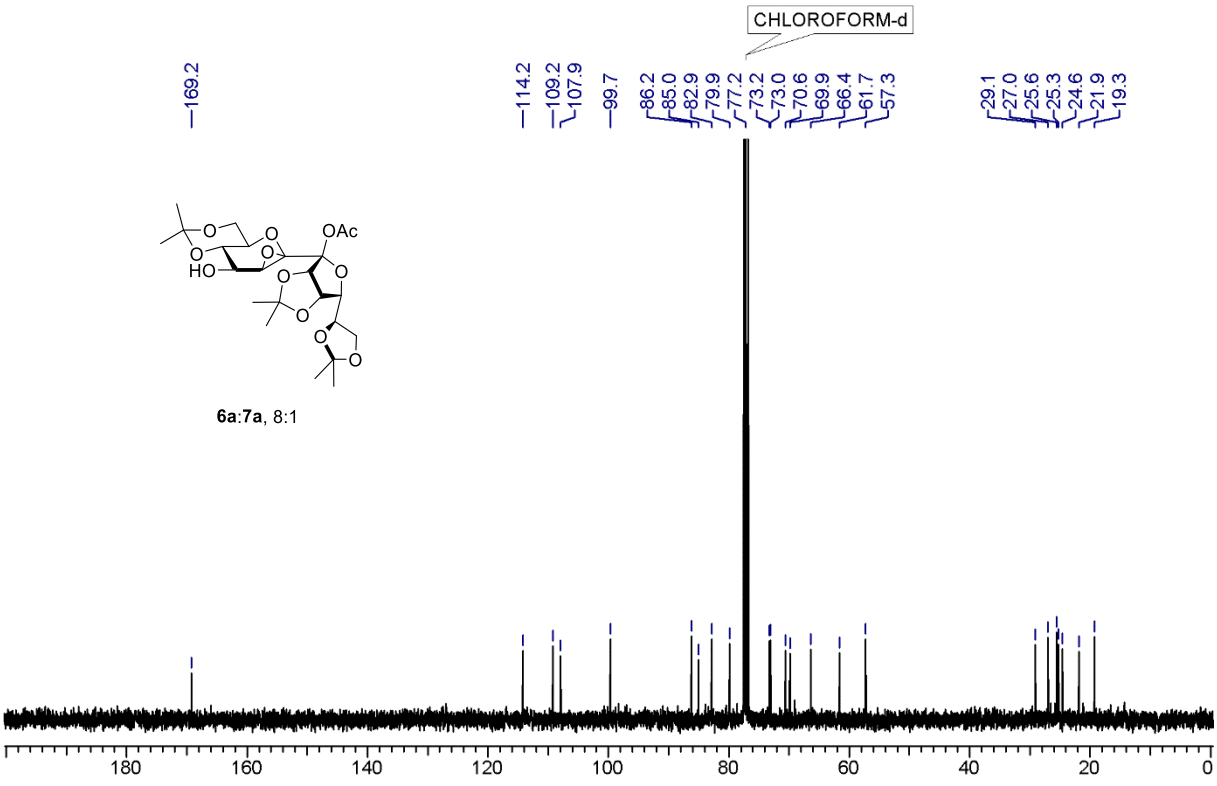
7.97
7.95
7.95
7.95
7.57
7.56
7.46
7.44
7.42
7.26
5.26
5.25
4.98
4.98
4.95
4.94
4.45
4.13
4.13
4.11
4.11
4.11
4.10
3.83
3.81
3.80
3.79
2.11
1.53
1.52
1.42
1.41
1.38
1.36
OBz
HO
5b
2.01 1.01 2.02
1.01 1.02 1.01 2.02 2.04 1.01 4.04
0.93 3.02 2.99 3.02 2.98 2.99 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5

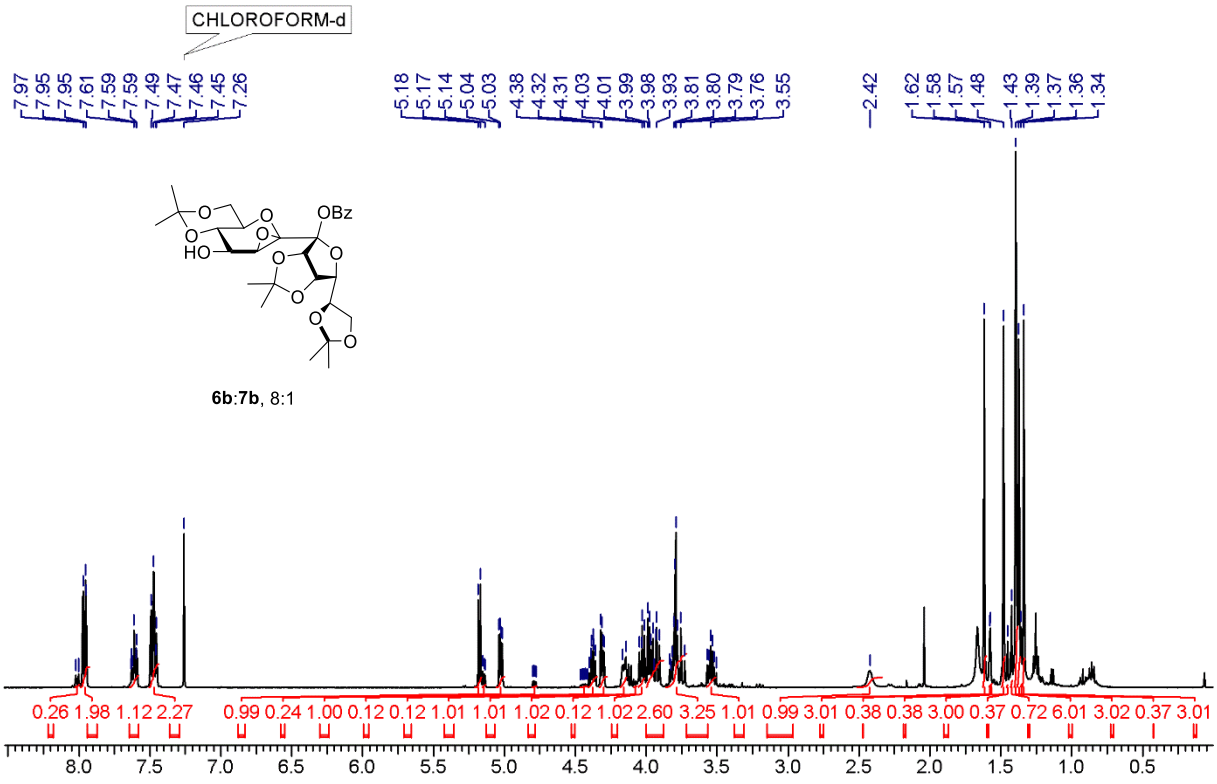

CHLOROFORM-d
163.9
148.4
133.5
130.1
129.9
128.6
114.0
109.6
107.9
103.2
99.9
86.6
82.0
79.9
77.2
73.4
73.0
70.2
68.1
67.2
61.6
29.1
27.1
26.0
25.2
25.1
19.4
OBz
HO
5b
180 160 140 120 100 80 60 40 20

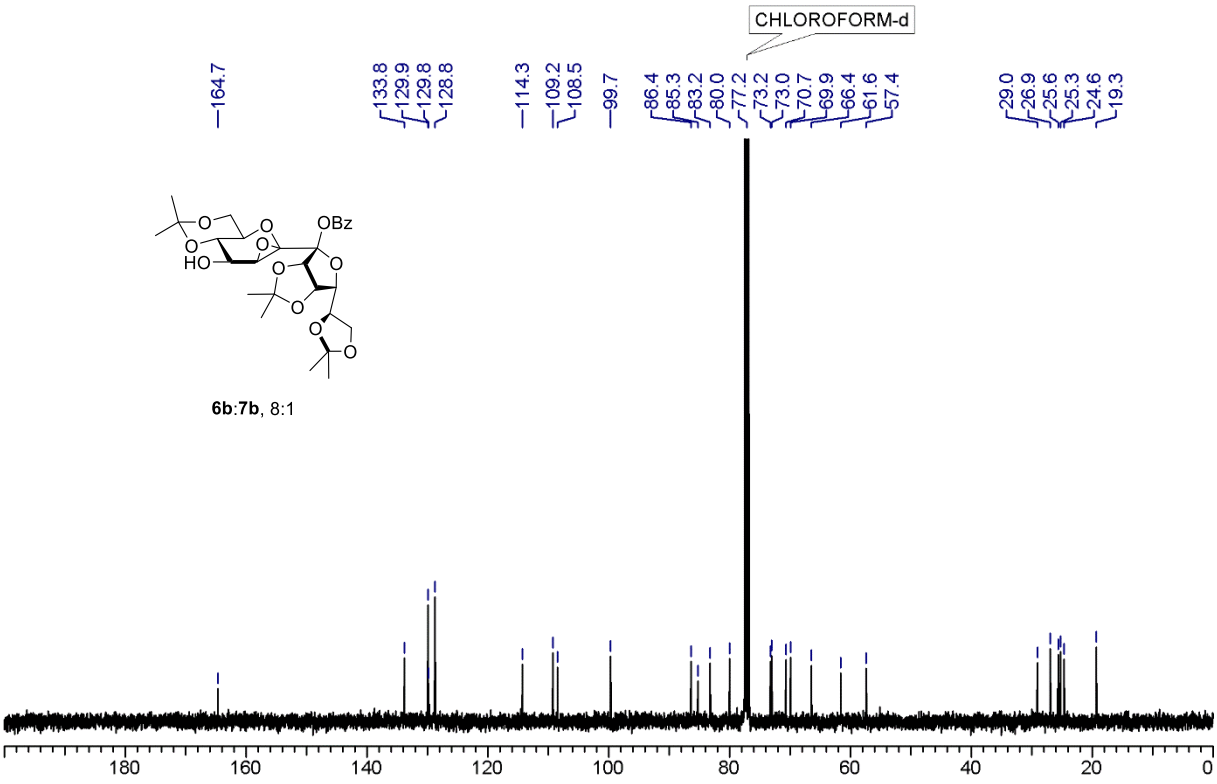


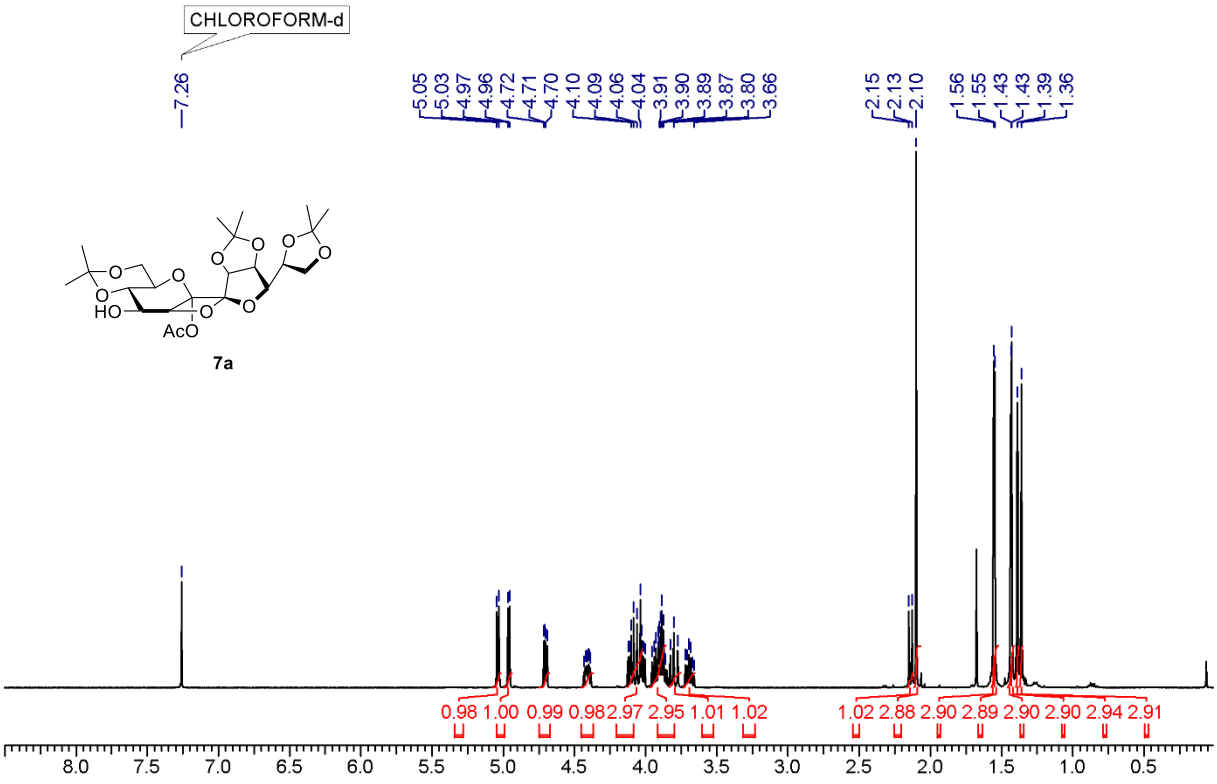
6a:**7a**, 8:1



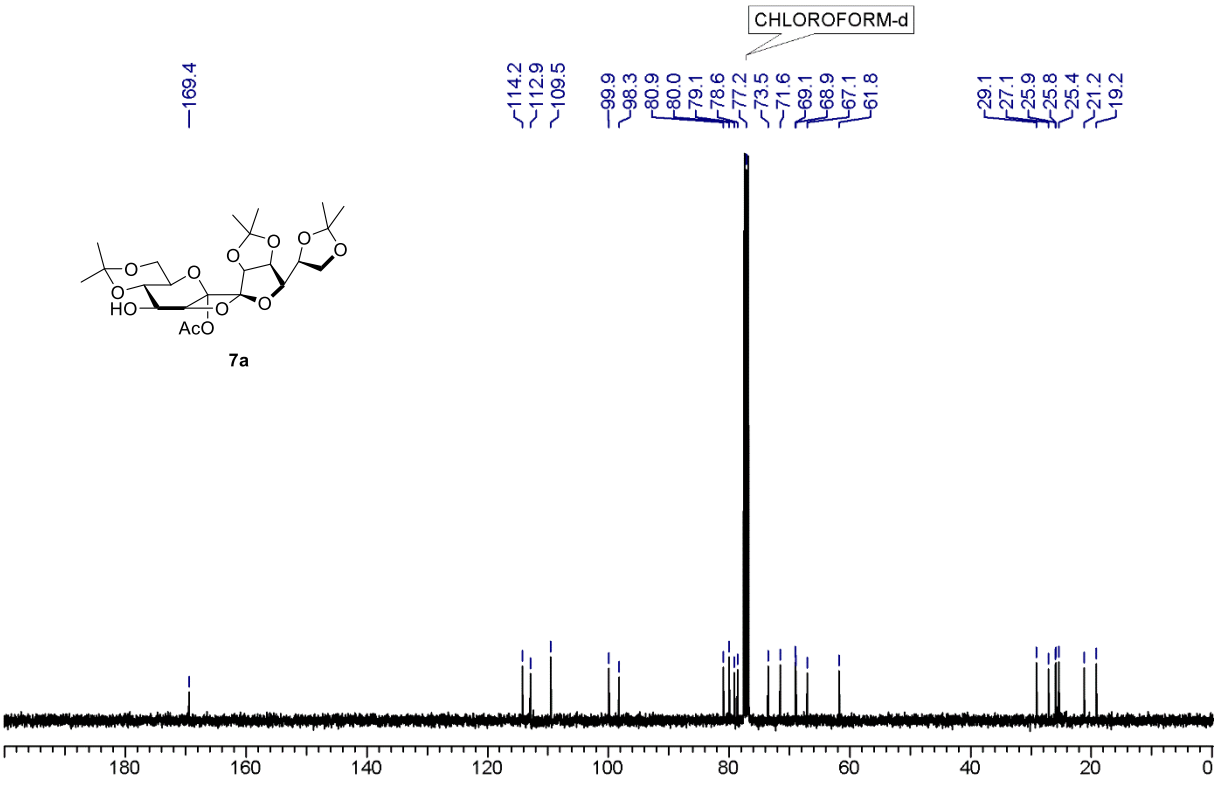
6a:**7a**, 8:1


CHLOROFORM-d
7.97 7.95 7.95 7.61 7.59 7.59 7.49 7.47 7.46 7.45 7.26
5.18 5.17 5.14 5.04 5.03 4.38 4.32 4.31 4.03 4.01 3.99 3.98 3.93 3.81 3.80 3.79 3.76 3.55
2.42
1.62 1.58 1.57 1.48 1.43 1.39 1.37 1.36 1.34
OBz
HO
6b:7b, 8:1
0.26 1.98 1.12 2.27 0.99 0.24 1.00 0.12 0.12 1.01 1.01 1.02 0.12 1.02 2.60 3.25 1.01 0.99 3.01 0.38 0.38 3.00 0.37 0.72 6.01 3.02 0.37 3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

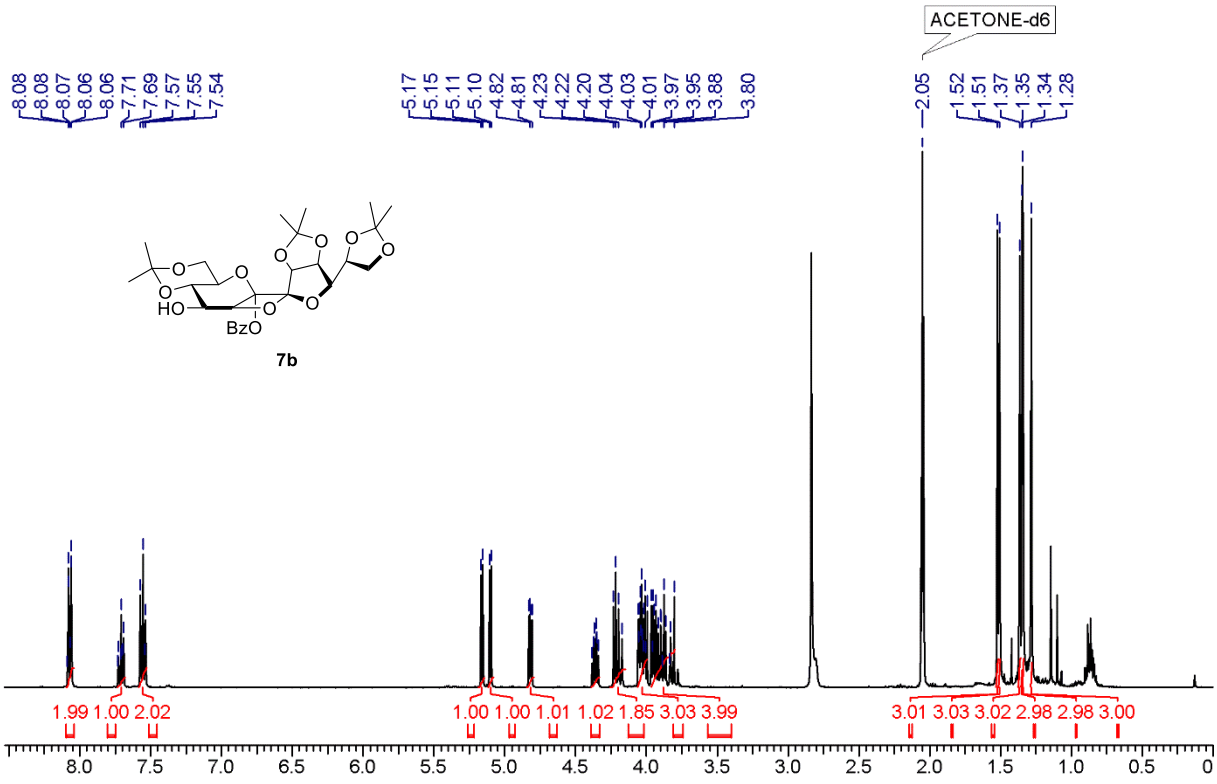

CHLOROFORM-d
164.7
133.8 129.9 129.8 128.8
114.3
109.2 108.5
99.7
86.4 85.3 83.2 80.0 77.2 73.2 73.0 70.7 69.9 66.4 61.6 57.4
29.0 26.9 25.6 25.3 24.6 19.3
OBz
HO
6b:7b, 8:1
180 160 140 120 100 80 60 40 20 0

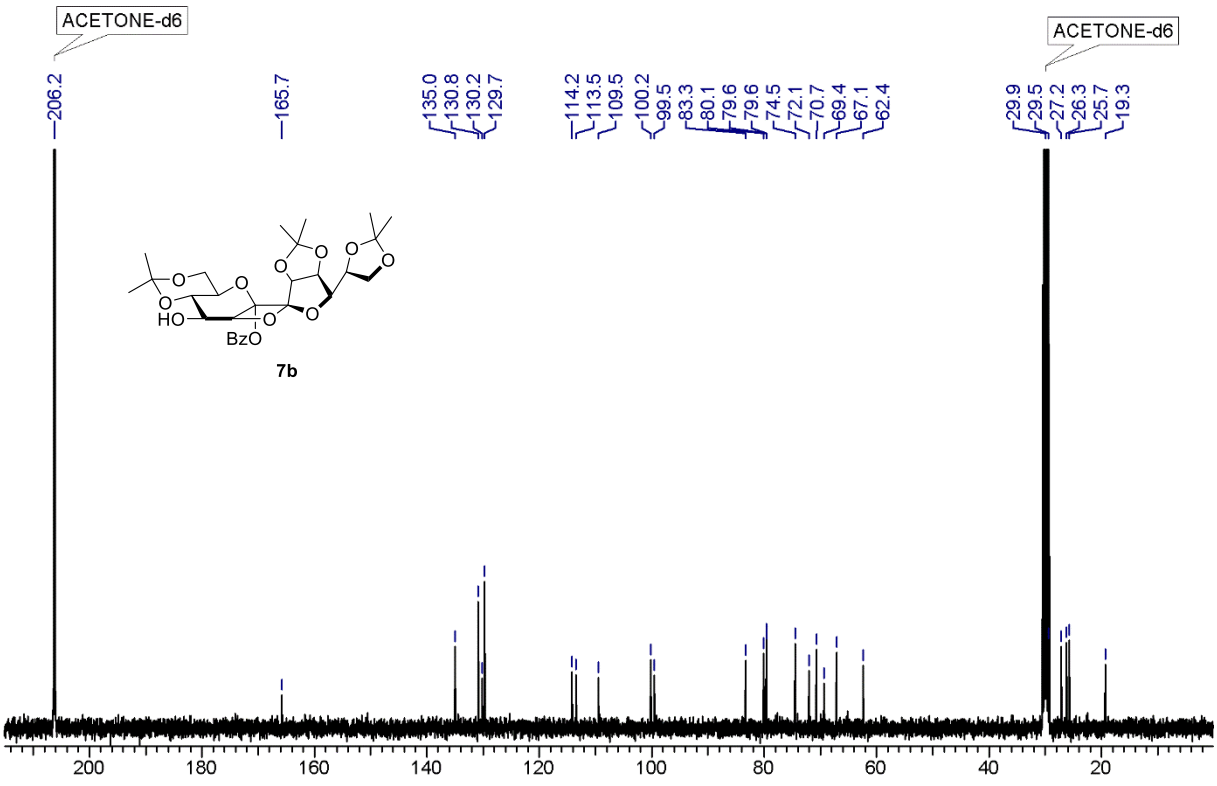

CHLOROFORM-d
7.26
5.05
5.03
4.97
4.96
4.72
4.71
4.70
4.10
4.09
4.06
4.04
3.91
3.90
3.89
3.87
3.80
3.66
2.15
2.13
2.10
1.56
1.55
1.43
1.39
1.36
HO
AcO
0.98 1.00 0.99 0.98 2.97 2.95 1.01 1.02
1.02 2.88 2.90 2.89 2.90 2.90 2.94 2.91
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

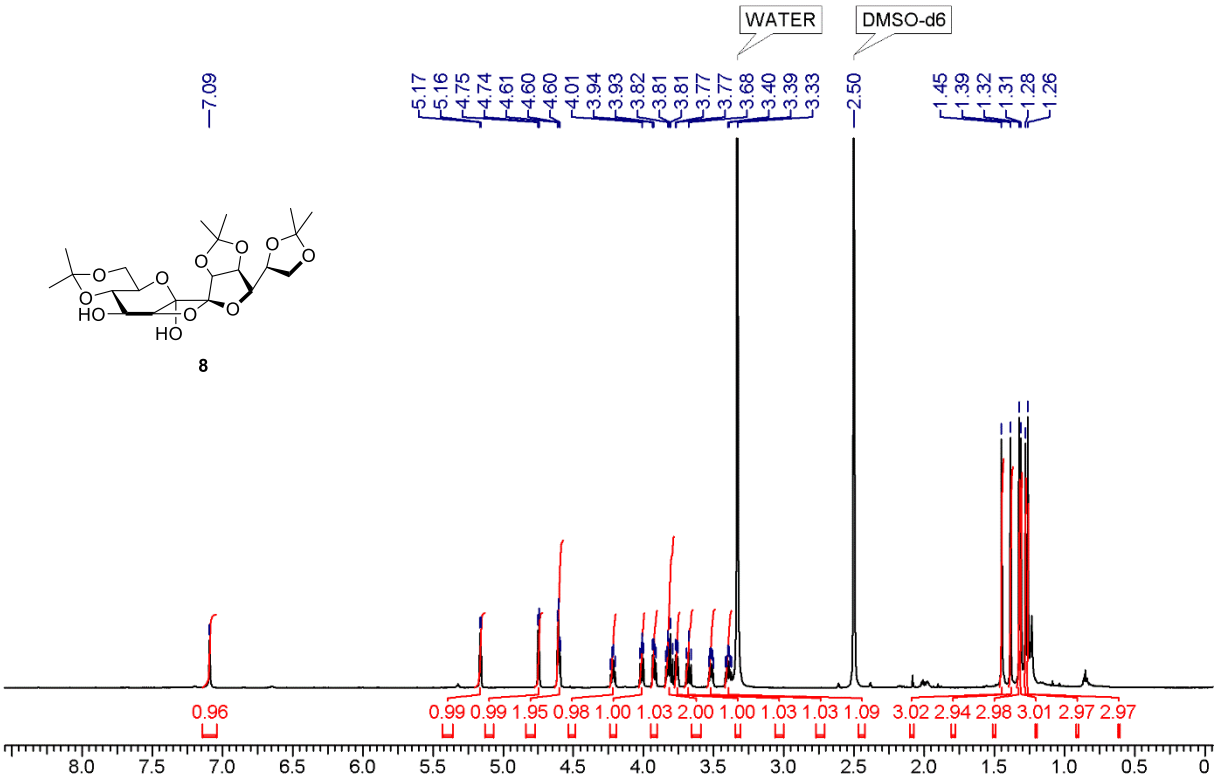
7a


CHLOROFORM-d
169.4
114.2
112.9
109.5
99.9
98.3
80.9
80.0
79.1
78.6
77.2
73.5
71.6
69.1
68.9
67.1
61.8
29.1
27.1
25.9
25.8
25.4
21.2
19.2
HO
AcO
180 160 140 120 100 80 60 40 20 0

7a


ACETONE-d6
8.08
8.08
8.07
8.06
8.06
7.71
7.69
7.57
7.55
7.54
5.17
5.15
5.11
5.10
4.82
4.81
4.23
4.22
4.20
4.04
4.03
4.01
3.97
3.95
3.88
3.80
2.05
1.52
1.51
1.37
1.35
1.34
1.28
HO
BzO
7b
1.99 1.00 2.02
1.00 1.00 1.01 1.02 1.85 3.03 3.99
3.01 3.03 3.02 2.98 2.98 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0


ACETONE-d6
ACETONE-d6
206.2
165.7
135.0
130.8
130.2
129.7
114.2
113.5
109.5
100.2
99.5
83.3
80.1
79.6
79.6
74.5
72.1
70.7
69.4
67.1
62.4
29.9
29.5
27.2
26.3
25.7
19.3
HO
BzO
7b
200 180 160 140 120 100 80 60 40 20


WATER
DMSO-d6
7.09
5.17
5.16
4.75
4.74
4.61
4.60
4.60
4.01
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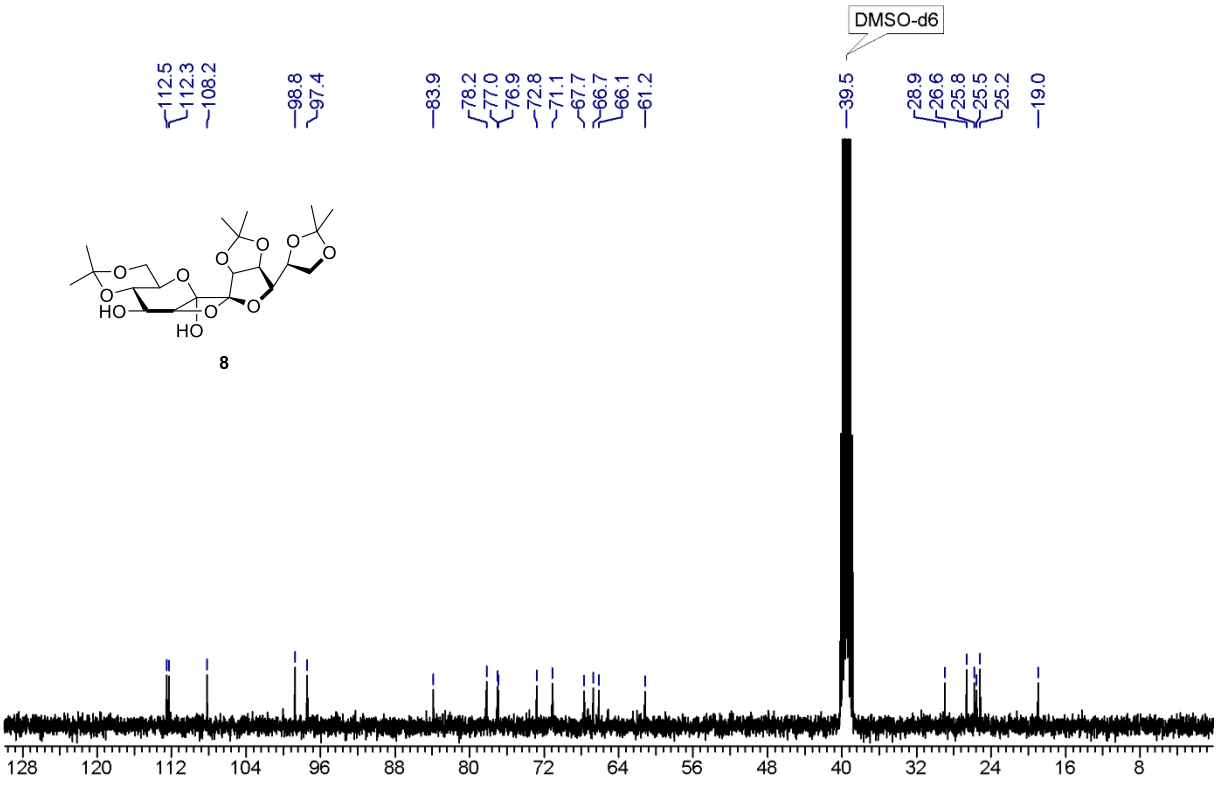
3.93
3.82
3.81
3.81
3.77
3.77
3.68
3.40
3.39
3.33
2.50
1.45
1.39
1.32
1.31
1.28
1.26
HO
HO
8
0.96
0.99 0.99 1.95 0.98 1.00 1.03 2.00 1.00 1.03 1.03 1.09 3.02 2.94 2.98 3.01 2.97 2.97
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0


DMSO-d6
112.5
112.3
108.2
98.8
97.4
83.9
78.2
77.0
76.9
72.8
71.1
67.7
66.7
66.1
61.2
39.5
28.9
26.6
25.8
25.5
25.2
19.0
HO
HO
8
128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8

X-ray crystal structure

Single crystals were selected, coated with Parabar 10312 (previously known as Paratone N, Hampton Research) and fixed on a microloop.

Compound **5a** was recrystallized from *n*-hexane and ethyl acetate to afford crystals suitable for X-Ray crystallography. Crystals from **7a** were grown by overlaying a satured solution of **7a** in methylene chloride with *n*-heptane and slowly evaporating the methylene chloride. Data for product C were collected on a Bruker APEX DUO instrument equipped with an IμS microfocus sealed tube and QUAZAR optics for MoK$_\alpha$ radiation (λ = 0.71073 Å). The Data collection strategy was determined using COSMO [1] employing ω- scans. Raw data were processed using APEX [2] and SAINT [3], corrections for absorption effects were applied using SADABS [4]. The structure was solved by direct methods and refined against all data by full-matrix least-squares methods on F^2 using SHELXTL [5] and Shelxle [6].

The absolute structure can't be verified by X-Ray, but the synthesis was carried out with the defined enantiomere.

The X-ray crystal structures of compounds **5a** and **7a** were uploaded at the cambridge crystallographic data centre with the deposition numbers CCDC 1969672 for **5a** and CCDC 1969673 for **7a**.

Crystal Data and Structure Refinements of

Compound 5a:

Identification code	mo_MB88_0m	
Empirical formula	C23 H34 O11	
Formula weight	486.50	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.9453(18) Å	a= 90°.
	b = 13.283(2) Å	b= 90°.
	c = 16.573(3) Å	g = 90°.
Volume	2409.6(7) $Å^3$	
Z	4	
Density (calculated)	1.341 Mg/m^3	
Absorption coefficient	0.107 mm^{-1}	
F(000)	1040	
Crystal size	0.466 x 0.106 x 0.071 mm^3	
Theta range for data collection	1.965 to 28.681°.	
Index ranges	-14<=h<=14, -17<=k<=17, -22<=l<=22	
Reflections collected	36180	
Independent reflections	6215 [R(int) = 0.0733]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	6215 / 0 / 316
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0899
R indices (all data)	R1 = 0.0423, wR2 = 0.0937
Absolute structure parameter	0.5(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.291 and -0.200 e.Å^{-3}

Compound 7a:

Identification code	mo_MB113_0m	
Empirical formula	C23 H34 O12	
Formula weight	502.50	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.7150(7) Å	a= 90°.
	b = 10.7844(9) Å	b= 90.937(3)°.
	c = 12.8286(11) Å	g = 90°.
Volume	1205.55(17) Å^3	
Z	2	
Density (calculated)	1.384 Mg/m^3	
Absorption coefficient	0.112 mm^{-1}	
F(000)	536	
Crystal size	0.314 x 0.056 x 0.053 mm^3	
Theta range for data collection	1.588 to 28.720°.	
Index ranges	-10<=h<=11, -14<=k<=14, -17<=l<=15	
Reflections collected	22893	
Independent reflections	6246 [R(int) = 0.0916]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6246 / 1 / 328	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0505, wR2 = 0.0998	
R indices (all data)	R1 = 0.0761, wR2 = 0.1134	
Absolute structure parameter	0.4(12)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.315 and -0.243 e.Å^{-3}	

[1] *COSMO v. 1.61*, Bruker AXS Inc., Madison, WI, 2012.
[2] APEX 3 V. 2017.3-0, Bruker AXS Inc., Madison, WI, 2017.
[3] *SAINT v. 8.38A*, Bruker AXS Inc., Madison, WI, 2017.
[4] *SADABS* Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48,** 3-10.
[5] *SHELXT* *Acta Cryst.* (2015), A**71**, 3-8.
[6] SHELXLE, C. B. Hubschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281-1284.