Stereoselective Glycosylation Using Oxathiane Glycosyl Donors

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Crystal Structure Determination of compound 8

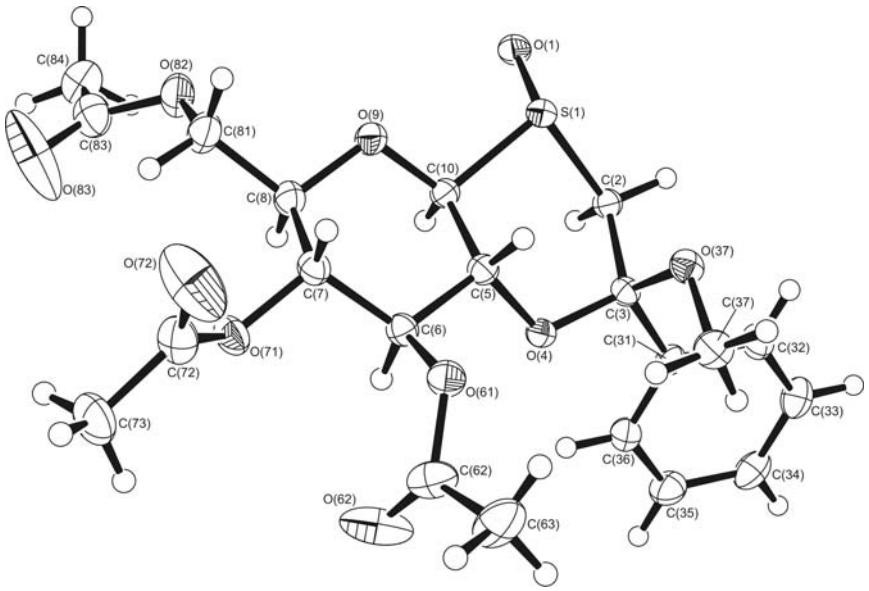
Measurements for the crystal was carried out at 150 K on a Bruker-Nonius Apex X8 diffractometer equipped with an Apex II CCD detector and using graphite monochromated Mo-Kα radiation from a FR591 rotating anode generator.

The structure was solved by direct methods and refined using SHELXL-97. Compound **8** crystallises in the chiral space group *P*212121 and the configuration was established on the basis of the refined Flack parameter and of the known stereochemistry of the penta-*O*-acetyl-D-glucopyranose starting material from which **8** was prepared. Despite the reasonable refinement, the terminal oxygen atoms, O62, O72, O83, of the three acetyl groups displayed elongated displacement ellipsoids. If this was due to rotational disorder about the O-C axes (O61-C62, O71-C72, O82-C83), one would expect there to be a corresponding elongated ellipsoid associated with the methyl C atoms (C63, C73, C84) of the acetyl groups but that does not occur. Despite that, for the O82, C83, O83, C84 group, an attempt was made to model a disorder over two positions using the 'split' positions of O83 as a starting point. This gave an unsatisfactory result with one of the split methyl C atoms becoming non-positive definite, despite the application of restraints, and so the initial model with elongated displacement ellipsoids was retained. All non-hydrogen atoms were refined anisotropically, and they could be located in a difference Fourier map. However, in the final stages of the refinement, they were placed in calculated positions and refined using a riding model.

The structure has been deposited at the Cambridge Crystallographic Data Centre and information on the structure can be obtained by quoting the number given below at:
http://www.ccdc.cam.ac.uk/deposit

Telephone: (44) 01223 762910
Facsimile: (44) 01223 336033
Postal Address: CCDC, 12 Union Road, CAMBRIDGE CB2 1EZ, UK

Figure S1. Crystal data and structure refinement for oxathiane-S-oxide **8**

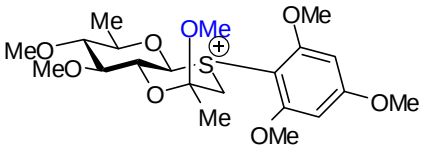


CCDC code	733122
Formula	$C_{21}H_{26}O_{10}S$
Formula weight	470.48
Size	0.30 x 0.07 x 0.04 mm
Crystal morphology	Colourless needle
Temperature	150K
Wavelength	0.71073 Å [Mo-K_α]
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 5.8256(4) Å α = 90°
	b = 14.5183(12) Å β = 90°
	c = 27.760(3) Å γ = 90°
Volume	2347.9(4) Å^3
Z	4
Density (calculated)	1.331 Mg/m^3
Absorption coefficient	0.19 mm^{-1}
F(000)	992
Data collection range	$2.94 \le \theta \le 27.96°$
Index ranges	$-7 \le h \le 7$, $-18 \le k \le 19$, $-36 \le l \le 36$
Reflections collected	48554
Independent reflections	5609 [R(int) = 0.0426]
Observed reflections	5047 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	0.9924 and 0.8278
Refinement method	Full
Data / restraints / parameters	5609 / 0 / 293
Goodness of fit	1.061
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0370, wR_2 = 0.0904
R indices (all data)	R_1 = 0.0452, wR_2 = 0.0964
Largest diff. peak and hole	0.540 and -0.343e.Å^{-3}
Absolute structure parameter	0.04(6)

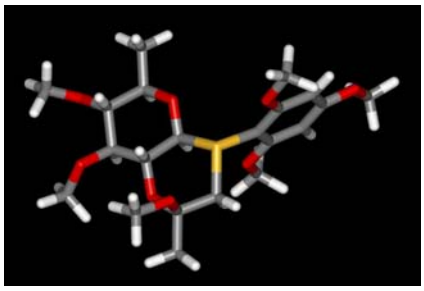
Density functional theory calculations

Density functional theory calculations were performed to determine the barrier to rotation for the trimethoxyphenyl group in sulfonium ion **11**. In order to reduce computational time, a simplified structure was used in which the equatorial substituent on the oxathiane ring, primary carbon on the sugar ring and the protecting groups on O-3 and O-4 were all abbreviated to methyl groups (see below). All calculations were performed in Gaussian03[1] and used Becke's 3-parameter hybrid exchange functional[2] and the Lee-Yang-Parr exchange functional (B3LYP/6-31G*).[3] All stationary points identities were verified by frequency calculations. The energy of the transition state is quoted relative to the sulfonium ion in its lowest energy conformation.

Oxathiane sulfonium ion 11

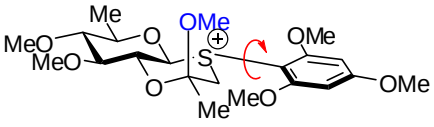


0.0 kcal mol^{-1}

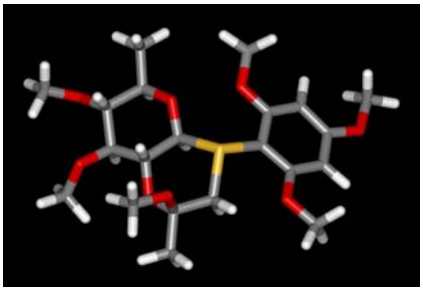


O1	0.2775	-1.9787	0.1716	H23	1.7739	-2.7204	-1.0709	C45	0.2792	3.2159	1.5128
C2	1.6066	-2.5438	0.0030	H24	2.5592	-1.4201	1.5863	H46	1.3133	2.8877	1.3660
C3	1.6262	-3.8606	0.7563	H25	2.7531	-0.2501	-1.2246	H47	0.0003	3.0922	2.5605
C4	2.6674	-1.5383	0.4980	H26	1.4121	-3.7000	1.8182	H48	0.1804	4.2718	1.2394
O5	3.9337	-2.0721	0.1660	H27	2.6135	-4.3184	0.6582	O49	-1.5412	-0.9266	-3.1838
C6	4.9309	-1.9572	1.1797	H28	0.8774	-4.5463	0.3497	O50	-3.8345	-1.6042	0.8681
C7	2.4935	-0.1553	-0.1601	H29	5.8398	-2.3989	0.7653	O51	-5.2923	-3.8123	-3.1811
O8	3.3485	0.7719	0.4805	H30	4.6441	-2.5128	2.0839	C52	-1.3426	-1.1629	-4.5853
C9	4.1137	1.5966	-0.3965	H31	5.1161	-0.9108	1.4431	H53	-2.2111	-0.8299	-5.1626
C10	1.0365	0.3155	-0.0396	H32	4.7336	2.2301	0.2419	H54	-1.1486	-2.2231	-4.7762
C11	0.1192	-0.8009	-0.5495	H33	3.4696	2.2277	-1.0200	H55	-0.4686	-0.5719	-4.8588
S12	-1.6369	-0.2504	-0.2228	H34	4.7648	0.9904	-1.0403	C56	-4.8514	-2.2008	1.6794
C13	-1.5485	1.3655	-1.1173	H35	0.8231	0.4977	1.0194	H57	-4.6862	-1.8078	2.6823
C14	-0.3626	2.2039	-0.5915	H36	0.2204	-0.9402	-1.6326	H58	-4.7535	-3.2916	1.6898
O15	0.8716	1.5111	-0.7972	H37	-2.4967	1.8660	-0.9106	H59	-5.8492	-1.9135	1.3307
C16	-0.2478	3.4960	-1.3994	H38	-1.4435	1.1572	-2.1806	C60	-6.3793	-4.4882	-2.5428
C17	-2.7094	-1.2868	-1.1649	H39	-0.1259	3.2715	-2.4622	H61	-6.0170	-5.1602	-1.7569
C18	-2.5705	-1.5497	-2.5548	H40	0.6292	4.0609	-1.0748	H62	-6.8602	-5.0705	-3.3284
C19	-3.4574	-2.4005	-3.1943	H41	-1.1409	4.1118	-1.2606	H63	-7.0965	-3.7723	-2.1256
C20	-4.4944	-3.0066	-2.4613	H42	-3.3846	-2.6239	-4.2499				
C21	-4.6541	-2.7643	-1.0906	H43	-5.4552	-3.2309	-0.5373				
C22	-3.7622	-1.9064	-0.4433	O44	-0.6389	2.3986	0.7718				

Oxathiane sulfonium ion 11: transition state for aryl group rotation



+13.4 kcal mol^{-1}

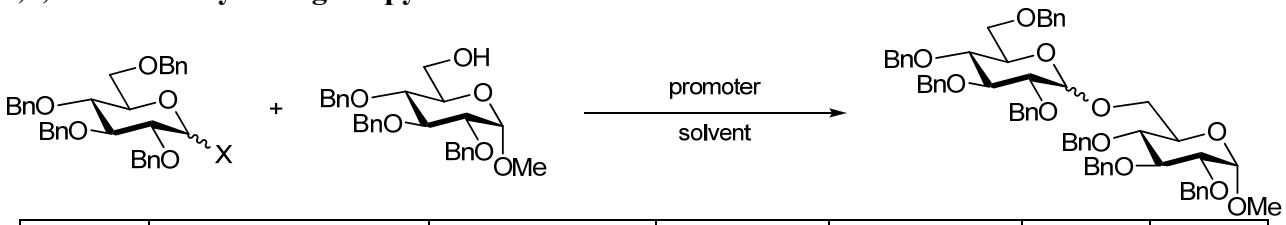


O1	-1.0167	-1.5119	-0.9677	O23	6.0349	-0.9403	0.7183	H45	-1.0138	3.8172	1.6397
C2	-1.9517	-2.4337	-0.3391	C24	6.4456	-2.3065	0.7989	H46	-2.4522	4.2165	0.6979
C3	-2.0132	-3.6798	-1.2031	C25	3.8338	-1.6007	-0.0627	H47	-0.8566	4.7798	0.1460
C4	-3.3279	-1.7590	-0.1872	C26	2.5676	-1.1718	-0.4689	H48	3.4985	4.3973	-0.3993
O5	-4.1266	-2.6193	0.5999	O27	1.6085	-2.0153	-0.8998	H49	4.8129	3.2683	-0.8318
C6	-5.4832	-2.7529	0.1770	C28	1.9351	-3.3856	-1.1411	H50	4.3024	3.4433	0.8798
C7	-3.2047	-0.3819	0.4801	H29	-1.5746	-2.6824	0.6646	H51	5.2803	1.4227	0.4603
O8	-4.4396	0.2958	0.3589	H30	-3.7636	-1.6177	-1.1874	H52	7.4747	-2.2808	1.1567
C9	-4.9055	0.9339	1.5476	H31	-2.9475	-0.5312	1.5389	H53	6.4123	-2.7868	-0.1857
C10	-2.0972	0.4508	-0.1967	H32	-2.2697	-3.4184	-2.2349	H54	5.8245	-2.8637	1.5097
C11	-0.7990	-0.3755	-0.2052	H33	-2.7799	-4.3491	-0.8046	H55	4.0642	-2.6554	-0.0440
S12	0.5704	0.6615	-1.0905	H34	-1.0591	-4.2125	-1.2027	H56	1.0517	-3.8126	-1.6123
C13	0.2449	2.2662	-0.1949	H35	-5.9569	-3.4375	0.8839	H57	2.1462	-3.9119	-0.2034
C14	-1.2326	2.6699	-0.1886	H36	-5.5432	-3.1833	-0.8328	H58	2.7908	-3.4686	-1.8193
O15	-2.0037	1.6838	0.4905	H37	-6.0047	-1.7905	0.1890	O59	-1.5888	2.7967	-1.5408
C16	-1.3938	3.9561	0.6241	H38	-5.8751	1.3710	1.2991	C60	-2.9180	3.2610	-1.8238
C17	2.2119	0.1951	-0.4543	H39	-4.2213	1.7248	1.8741	H61	-3.0549	3.1182	-2.8967
C18	3.2353	1.1480	-0.1828	H40	-5.0379	0.2059	2.3590	H62	-3.0242	4.3251	-1.5883
O19	2.9434	2.4577	-0.3699	H41	-2.3847	0.6136	-1.2404	H63	-3.6675	2.6805	-1.2758
C20	3.9647	3.4408	-0.1618	H42	-0.4066	-0.5809	0.8015				
C21	4.4931	0.7202	0.2245	H43	0.8374	3.0058	-0.7232				
C22	4.7892	-0.6477	0.3027	H44	0.6144	2.1487	0.8238				

Selected literature examples of glycosylation reactions using acceptor alcohols from Table 1

When developing α-selective glycosylation procedures it is common practise to include control experiments in which 2-*O*-benzylated glycosyl donors are employed to illustrate the difference in stereoselectivity achieved when using a glycosyl donor bearing a traditional non-participating group. However, as stated in the main article, it was not possible to apply our activation procedure to 2-*O*-benzylated glycosyl sulfoxides as the trimethoxybenzene was glycosylated in preference over alcohol acceptors. Therefore, we have collated the following tables of examples (Tables S1-S4) in way of comparison with existing methods. The tables are not a comprehensive list of literature syntheses for the target disaccharides, but rather a representative set of common glycosylation methods which are intended to illustrate "typical" stereoselectivities for 2-*O*-benzyl donors. As our method employs dichloroethane (DCE) as a solvent, we have mostly selected methods employing chlorinated solvents; however, as ethereal solvents are often preferred for α-glycosylations, some examples in Et_2O have also been included for comparison (e.g. Table 1, entries 5-6). No attempt has been made to compare molar equivalents or reaction temperatures.

Table S1. Literature syntheses of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside



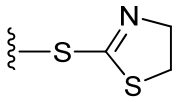
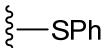
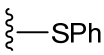
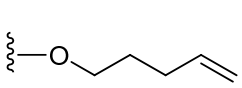
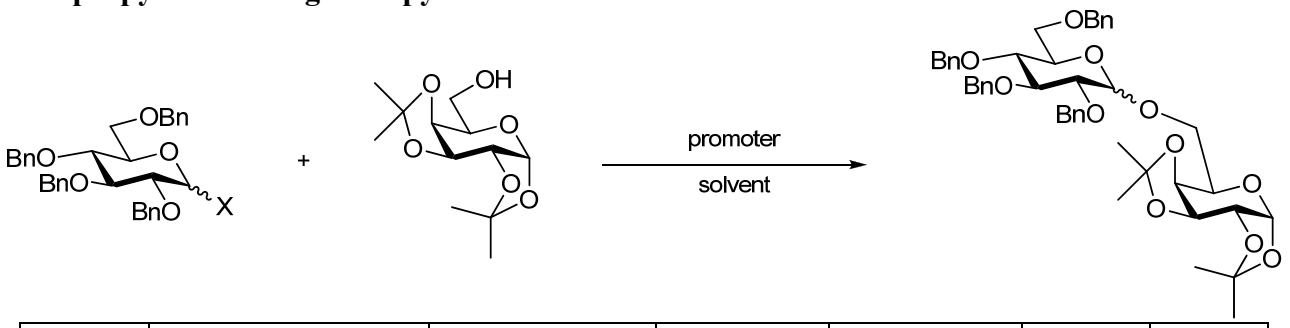
Entry	X	Promoter	Solvent	Yield (%)	α:β	Ref
1		MeI	DCE	89	89:11	[4]
2		NIS/TMSOTf	DCM	97	57:43	[5]
3		$Ph_3P{=}O$	DCM	89	96:4	[6]
4		Ph_2SO/Tf_2O	DCM	88	24:76	[7]
5		$HClO_4$	Et_2O	98	92:8	[8]
6		$LiClO_4$/NBS	Et_2O	70	100:0	[9]
7		PhSeOTf	Toluene	91	88:12	[10]
8		IDCP	Et_2O/ DCM	96	88:12	[11]

Table S2. Literature syntheses of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose



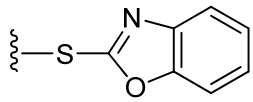
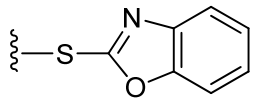
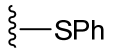
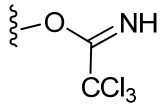
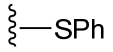
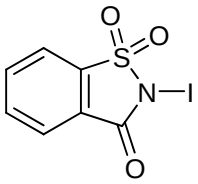
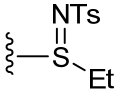
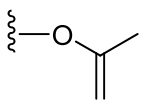
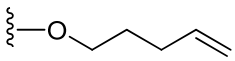
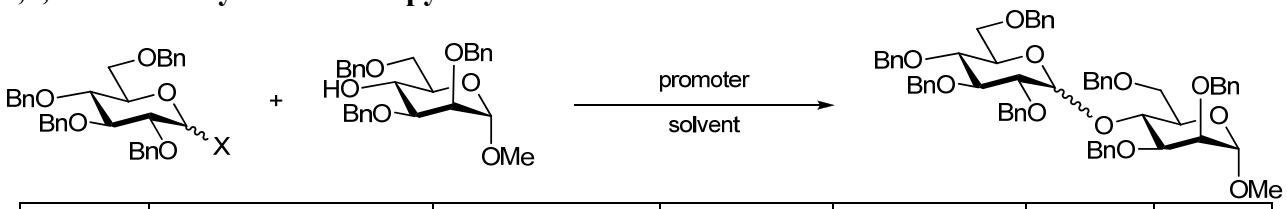
Entry	X	Promoter	Solvent	Yield (%)	α:β	Ref
1		MeOTf	DCE	98	50:50	[12]
2		$Cu(OTf)_2$	Toluene/ dioxane	89	84:16	[13]
3		Ph_2SO/ Tf_2O	DCM	85	40:60	[14]
4		$Ph_3P{=}O$	$CHCl_3$	90	94:6	[14]
5		$LiClO_4$	DCE	80	50:50	[15]
6			DCE	51	57:43	[16]
7		DTBPI/Bu_4NI	DCM	91	94:6	[17]
8		$Cu(OTf)_2$/ CuO	DCM	quant.	60:40	[18]
9		TMSOTf	DCM	64	55:45	[19]
10		IDCP	DCE	80	42:58	[20]

Table S3. Literature synthesis of 2,3,4,6-tetra -*O*-benzyl-α-D-glucopyranosyl-(1→4)-methyl-2,3,6-tri-*O*-benzyl-α-D-mannopyranoside



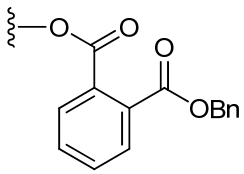
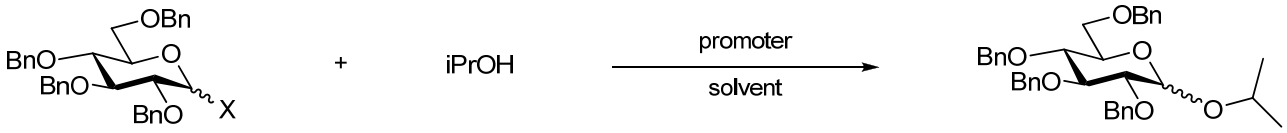
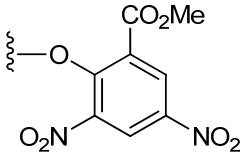
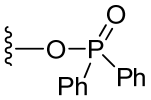
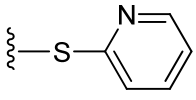
Entry	X	Promoter	Solvent	Yield (%)	α:β	Ref
1		TMSOTf	DCM	66	40:60	21

Table S4. Literature syntheses of iso-propyl 2,3,4,6-tetra -*O*-benzyl-α-D-glucopyranoside



Entry	X	Promoter	Solvent	Yield (%)	α:β	Ref
1		-	DCM	98	93:7	22
2		TMSOTf	DCM	93	23:77	23
3		Ph_2SO/Tf_2O	DCM	86	27:73	7
4		MeI	DCM	85	82:18	24

Synthetic chemistry methods

All solvents were dried prior to use, according to standard methods.[25] Methyl trifluoromethanesulfonate (MeOTf), trifloromethanesulfonic anhydride (Tf_2O), and trimethylsilyl trifluoromethanesulfonate (TMSOTf) were distilled under a N_2(g) atmosphere. Boron trifluoride diethyl etherate (BF_3•OEt_2) was distilled over calcium hydride, and all other commercially available reagents were used as received. Where appropriate anhydrous quality material was purchased. All solvents used for flash chromatography were GPR grade, except hexane and ethyl acetate, when HPLC grade was used. All concentrations were performed *in vacuo,* unless otherwise stated. All reactions were performed in oven dried glassware under a N_2(g) atmosphere, unless otherwise stated.

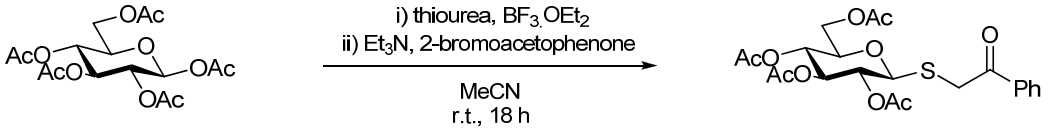
^{1}H NMR spectra were recorded at 500 MHz on a Bruker Avance 500 instrument or at 300 MHz on a Bruker Avance 300 instrument. ^{13}C NMR spectra were recorded at 75 MHz on a Bruker Avance 300 instrument. Chemical shifts are given in parts per million downfield from tetramethylsilane. The following abbreviations are used in ^{1}H NMR analysis: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, dt = double triplet, td = triple doublet, ddd = double double doublet. For disaccharides, the reducing terminal residue is labelled “a” and the non-reducing terminal residue is “b”.

Electrospray (ES+) ionisation mass spectra were obtained on a Micromass LCT-KA111 mass spectrometer, and high resolution ES+ were performed on a Bruker Daltonics MicroTOF mass spectrometer. Infra-red spectra were recorded on a Perkins-Elmer Spectrum One FT-IR spectrometer. Melting points were obtained on a Reichert hot-stage apparatus and are uncorrected. Microanalyses were performed using a Carlo Erba MOD 1106 instrument. Optical rotations were measured at the sodium D-line with an Optical Activity AA-1000 polarimeter. $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}

Analytical TLC was performed on silica gel 60-F^{254} (Merck) with detection by fluorescence and/or charring following immersion in a 5% H_2SO_4/Methanol solution, unless otherwise stated.

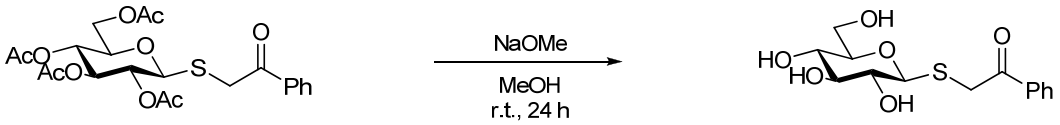
Mr Simon Barrett, Mrs Tanya Marinko-Covell and Mr Martin Huscroft are thanked for assistance with NMR, mass spectrometry and microanalysis.

2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranosyl acetophenone (3)[26]



BF_3•OEt_2 (20.5 mL, 101 mmol) was added in portions (3 x 6.8 mL) every 15 min to a solution of thiourea (6.43 g, 88 mmol), and β-D-glucose-pentaacetate **1** (30g, 76 mmol) in acetonitrile (150 mL) at 90 ºC. The reaction mixture was heated under reflux for 40 min, and then allowed to cool to r.t. Triethylamine (33.2 mL, 238 mmol), followed by 2-bromoacetophenone **2** (30.6 g, 154 mmol) in acetonitrile (50 mL) were then added to the reaction mixture, which was stirred for 18 h, and then concentrated. The residue was dissolved in ethyl acetate (75 mL), and washed with aq. NaCl (2 x 100 mL), dried (Na_2SO_4) and concentrated. The resulting residue was recrystallised from methanol to afford **3** (23.65 g, 64%) as colourless needles, mp. 109.7-111.3 °C (from methanol) (lit.[26] m.p. 120.5 °C (from methanol)); $\mathbf{[\alpha]_D^{25}}$ –69.7 (*c* 0.7, $CHCl_3$) [lit.[26] $\mathbf{[\alpha]_D}$ –88 (*c* 0.2, $CHCl_3$)]; $\mathbf{\delta_H}$ (500 MHz, $CDCl_3$); 7.96 (dd, 2H, ArH), 7.58 (t, 1H, *J* 7.5 Hz, ArH), 7.48 (t, 2H, *J* 7.5 Hz, ArH), 5.22 (dd, 1H, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 9.8 Hz, H-3), 5.08 (dd, 1H, $J_{3,4}$ 9.8 Hz, $J_{4,5}$ 9.8 Hz, H-4), 5.05 (dd, 1H, $J_{1,2}$ 9.8 Hz, $J_{2,3}$ 9.8 Hz, H-2), 4.60 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.21 (dd, 1H, $J_{6,6'}$ 11.4 Hz, $J_{5,6}$ 3.7 Hz, H-6), 4.09 (dd, 1H, $J_{6,6'}$ 11.4 Hz, $J_{5,6'}$ 2.1 Hz, H-6'), 4.06 (m, 2H, SCH_2), 3.71 (ddd, 1H, $J_{4,5}$ 9.8 Hz, $J_{5,6}$ 3.7 Hz, $J_{5,6'}$ 2.1 Hz, H-5), 2.05 (s, 3H, C(O)CH_3), 2.02 (s, 3H, C(O)CH_3), 1.99 (s, 3H, C(O)CH_3), 1.92 (s, 3H, C(O)CH_3); $\mathbf{\delta_C}$ (75 MHz, $CDCl_3$); 194.3, 170.6, 170.1, 169.4, 169.5 (C=O), 135.2, 133.6, 128.7, 128.6, (ArC), 82.3 (C-1), 77.2 (C-3), 76.0 (C-2), 73.8 (C-5), 69.8 (C-2), 68.2 (C-4), 61.9 (C-6), 35.4 (SCH_2), 20.7, 20.6, 20.5 (C(O)$\underline{C}H_3$); **HRMS**: Found $[M+Na]^+$ 505.1155, $C_{22}H_{26}O_{10}SNa$ requires 505.1139.

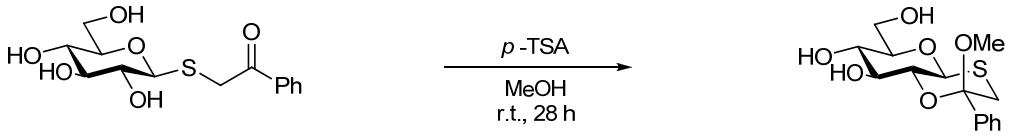
1-Thio-β-D-glucopyanosyl acetophenone (4)



Sodium methoxide in methanol (0.5 M, 14 mL, 74 mmol) was added to a solution of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranosyl acetophenone **3** (17.9 g, 37 mmol) in methanol (60 mL), and the reaction mixture was stirred for 24 h at r.t. The reaction mixture was then neutralised with Amberlite H+ resin, filtered and concentrated to leave a crude solid, which was purified by flash column chromatography (silica gel; 9:1(v/v) DCM-methanol) to afford **4** 11.62 g, 99%) as a colourless glassy solid; $\mathbf{[\alpha]_D^{24}}$ –63.2 (*c* 0.5, H_2O); $\mathbf{\delta_H}$ (500 MHz, CD_3OD); 8.05 (dd, 2H, *J* 8.6 Hz, *J* 0.8 Hz, ArH), 7.63 (t, 1H, *J* 7.5 Hz, ArH), 7.53 (t, 2H, *J* 7.5 Hz, ArH), 4.45 (d, 1H, $J_{1,2}$ 9.7 Hz, H-

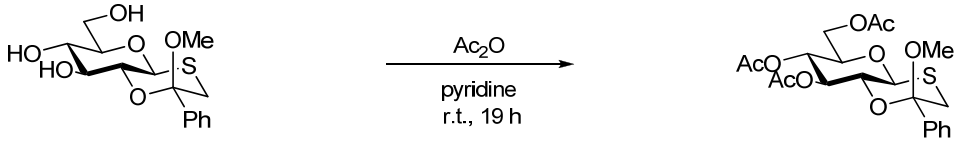
1), 4.28 (d, 1H, $J_{CH2,CH2'}$ 15.0 Hz, SCH_2), 4.18 (d, 1H, $J_{CH2,CH2'}$ 15.0 Hz, SCH_2'), 3.86 (dd, 1H, $J_{6,6'}$ 12.0 Hz, $J_{5,6}$ 1.9 Hz, H-6), 3.65 (dd, 1H, $J_{6,6'}$ 12.0 Hz, $J_{5,6'}$ 5.4 Hz, H-6'), 3.37-3.26 (m, 3H, H-3, H-4, H-5), 3.24 (t, 1H, $J_{1,2}$ 9.7 Hz, $J_{2,3}$ 9.7 Hz, H-2); δ_C (75 MHz, CD_3OD); 198.2 (C=O), 137.4, 135.0, 130.2, 130.1 (ArC), 86.2 (C-1), 82.4, 79.8, 74.7, 71.7 (C-2,3,4,5), 63.2 (C-6), 36.6 (SCH_2); **HRMS**: Found $[M+H]^+$ 315.0887, $C_{14}H_{18}O_6S$ requires 315.0897.

2-Methoxy-2-(*S*)-phenyl-(1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (5)



p-Toluenesulfonic acid (1.45 g, 8.54 mmol) was added to a solution of 1-thio-β-D-glucopyranosyl acetophenone **4** (2.7 g, 8.54 mmol) in methanol (290 mL), and the reaction mixture was stirred at r.t. for 28 h. The reaction mixture was then neutralised with triethylamine and concentrated. The crude residue was purified by flash column chromatography (silica gel; 99:1→9:1 (v/v) DCM-methanol) to afford **5** (1.7 g, 61%) as a yellow glassy foam; $[\alpha]_D^{25}$ +34.2 (*c* 0.7, $CHCl_3$); δ_H (500 MHz, $CDCl_3$); 7.47 (m, 2H, ArH), 7.36 (m, 5H, ArH), 7.48 (t, 2H, ArH), 4.52 (d, 1H, $J_{1,2}$ 9.0 Hz, H-1), 3.95 (dd, 1H, $J_{6,6'}$ 11.1 Hz, $J_{5,6}$ 3.0 Hz, H-6), 3.88 (dd, 1H, $J_{1,2}$ 9.0 Hz, $J_{2,3}$ 9.0 Hz, H-2), 3.86 (m, 1H, H-6'), 3.80 (m, 2H, H-3, H-4), 3.53 (m, 1H, H-5), 3.15 (s, 3H, OCH_3), 3.00 (s, 1H, SCH_2), 2.99 (s, 1H, SCH_2); δ_C (75 MHz, $CDCl_3$); 126.6, 126.5, 124.1 (ArC), 95.1 (C-OMe), 81.0 (C-5), 76.0 (C-1), 75.6 (C-4), 75.0 (C-2), 70.4 (C-3), 62.1 (C-6), 57.0 (OCH_3), 39.2 (SCH_2); **HRMS**: Found $[M+Na]^+$ 351.0868, $C_{15}H_{20}O_6SNa$ requires 351.0873.

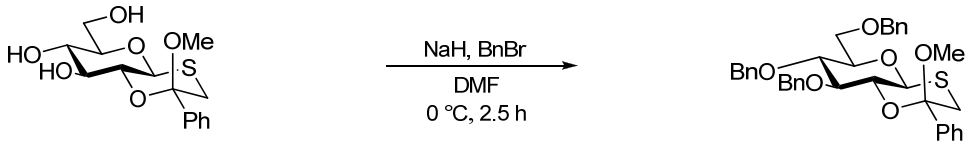
2-Methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (6)



Acetic anhydride (237 μL, 2.5 mmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane **5** (179 mg, 0.5 mmol) in pyridine (2.5 mL) at 0 °C. The reaction mixture was warmed to r.t. and stirred for a further 19 h. The mixture was then quenched with aq. $NaHCO_3$ (5 mL), diluted with DCM (10 mL), separated, washed with aq. NaCl (2 x 10 mL), dried ($MgSO_4$) and concentrated to leave as a yellow syrup. The syrup was purified by flash column chromatography (silica gel; 3:1 (v/v) hexane-ethyl acetate) to afford **6** (189 mg, 76%)

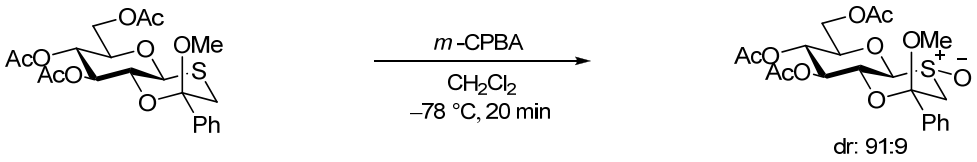
as colourless needles, m.p. 164.2-166.8 ºC (from methanol); $[\alpha]_D^{25}$ + 93.0 (*c* 0.8, $CHCl_3$); δ_H (300 MHz, $CDCl_3$); 7.44-7.31 (m, 5H, ArH), 5.35 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 9.7 Hz, H-3), 5.20 (dd, 1H, $J_{3,4}$ 9.7 Hz, $J_{4,5}$ 9.7 Hz, H-3), 4.56 (d, 1H, $J_{1,2}$ 9.2 Hz, H-1), 4.26 (dd, 1H, $J_{6,6'}$ 12.5 Hz, $J_{5,6}$ 4.6 Hz, H-6), 4.16 (dd, 1H, $J_{6,6'}$ 12.5 Hz, $J_{5,6'}$ 2.7 Hz, H-6'), 4.07 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{1,2}$ 9.2 Hz, H-2) 3.83 (ddd, 1H, $J_{4,5}$ 9.7 Hz, $J_{5,6}$ 4.6 Hz, $J_{5,6'}$ 2.7 Hz, H-5), 3.05 (s, 3H, OCH_3), 3.02 (s, 1H, SCH_2), 2.11 (s, 3H, $C(O)CH_3$), 2.07 (s, 3H, $C(O)CH_3$), 2.01 (s, 3H, $C(O)CH_3$); δ_C (75 MHz, $CDCl_3$); 171.2, 170.6, 170.0 (C=O), 139.7, 129.0, 126.6 (ArC), 97.4 (C-OMe), 77.4 (C-1), 76.2, 73.2, 73.0, 68.9 (C-2, C-3, C-4, C-5), 62.5 (C-6), 50.0 (OCH_3), 39.2 (SCH_2), 21.5, 21.2, 21.1 ($C(O)\underline{C}H_3$); **m/z** (ES+, %); 477.3 ($[M+Na]^+$, 20); **HRMS**: Found $[M+Na]^+$ 477.1189, $C_{21}H_{26}O_9SNa$ requires 477.1190.

2-Methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (7)



NaH (60% dispersion in oil, 38 mg, 0.945 mmol) was added in portions to a stirred solution of 2-methoxy-2-(*S*)-phenyl-(1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane **5** (100 mg, 0.305 mmol) in DMF (1.5 mL) at 0°C, and stirred for 70 min while H_2(g) evolved. Benzyl bromide (112 μL, 0.945 mmol) was then added dropwise at 0°C, and the reaction mixture stirred for a further 2 h 30 min. The reaction mixture was quenched with methanol (3 mL), and diluted with DCM (20 mL). The solution was then washed with aq. NaCl (2 x 20 mL), dried ($MgSO_4$) and concentrated to leave a crude syrup. The syrup was purified by flash column chromatography (silica; 4:1 (v/v) hexane-ethyl acetate) to afford **7** (162 mg, 87%) as a colourless foam; $[\alpha]_D^{25}$ +58.5 (*c* 1.8, $CHCl_3$); δ_H (500 MHz, $CDCl_3$); 7.52-7.15 (m, 20H, ArH), 5.03 (d, 1H, *J* 10.9 Hz, $OC\underline{H}_2Ph$), 4.89 (d, 1H, *J* 11.9 Hz, $OC\underline{H}_2Ph$), 4.88 (d, 1H, *J* 10.9 Hz, $OC\underline{H}_2Ph$), 4.63 (d, 1H, *J* 12.2 Hz, $OC\underline{H}_2Ph$), 4.56 (d, 1H, *J* 11.9 Hz, $OC\underline{H}_2Ph$), 4.55 (d, 1H, *J* 12.2 Hz, $OC\underline{H}_2Ph$), 4.45 (d, 1H, $J_{1,2}$ 9.4 Hz, H-1), 4.08 (dd, 1H, $J_{1,2}$ 9.4 Hz, $J_{2,3}$ 8.2 Hz, H-2), 3.78-3.75 (m, 4H, H-3, H-4, H-6, H-6'), 3.60 (m, 1H, H-5), 3.16 (s, 3H, OCH_3), 3.01-2.99 (m, 2H, $SC\underline{H}_2$); δ_C (75 MHz, $CDCl_3$); 140.1-126.2 (ArC), 97.0 (C-OMe), 83.6 (C-4), 80.4 (C-5), 77.7 (C-3), 76.6 (C-2), 75.9, 75.4, 73.5 ($\underline{C}H_2OPh$), 75.6 (C-1), 68.7 (C-6), 49.9 (OCH_3), 39.0 (SCH_2); **HRMS**: Found $[M+Na]^+$ 621.2282, $C_{36}H_{38}O_6SNa$ requires 621.2281.

2-Methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (*R*)-*S*-oxide (8-*R*)

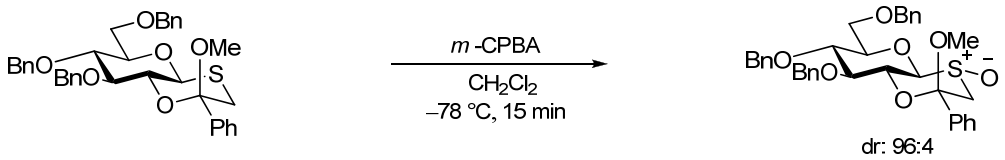


dr: 91:9

A solution of m-CPBA (215 mg, 1.05 mmol) in DCM (4 mL) was slowly added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-gluco-pyranoso)[1,2-*e*]-1,4-oxathiane **6** (400 mg, 0.885 mmol) in DCM (4 mL) at −78 °C. The reaction mixture was stirred for 20 min at −78 °C and then quenched with aq. $NaHCO_3$ (5 mL), diluted with DCM (10 mL), washed with aq. NaCl (2 x 10 mL), dried ($MgSO_4$) and concentrated to leave a crude colourless solid (dr: 91:9). The crude solid was purified by flash column chromatography (silica; 2:1 (v/v) hexane-ethyl acetate→1:1 (v/v) hexane-ethyl acetate) to afford **8-*R*** as the major diastereomer (335 mg, 81%) as colourless needles, m.p. 181.3-185.4 ºC (from 1:1 (v/v) hexane-ethyl acetate) and **8-*S*** as the minor diastereomer (59 mg, 14%) as colourless needles; m.p. 185.7-188.2 ºC (from 1:1 (v/v) hexane-ethyl acetate);

8-*R*: Equatorial = Major Diastereomer: $[\alpha]_D^{25}$ +7.8 (*c* 1.2, $CHCl_3$); **δ_H** (500 MHz, $CDCl_3$); 7.45-7.38 (m, 5H, ArH), 5.51 (dd, 1H, $J_{4,5}$ 9.5 Hz, $J_{3,4}$ 9.5 Hz, H-4), 5.22 (dd, 1H, $J_{3,4}$ 9.5 Hz, $J_{2,3}$ 9.8 Hz, H-3), 4.39 (dd, 1H, $J_{6,6'}$ 12.7 Hz, $J_{5,6}$ 4.4 Hz, H-6), 4.34 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.22 (dd, 1H, $J_{6,6'}$ 12.7 Hz, $J_{5,6'}$ 1.9 Hz, H-6'), 3.85-3.90 (m, 3H, H-2, H-5, SCH_{eq}), 2.94 (s, 3H, OCH_3), 2.86 (d, 1H, $J_{SCHax\text{-}eq}$ 12.8 Hz, SCH_{ax}), 2.11 (s, 3H, $C(O)CH_3$), 2.07 (s, 3H, $C(O)CH_3$), 2.01 (s, 3H, $C(O)CH_3$); **δ_C** (75 MHz, $CDCl_3$); 171.1, 170.3, 169.9 (C=O), 137.1, 129.7, 129.4, 126.3 (ArC), 102.2 (C-OMe), 95.6 (C-1), 77.5 (C-4), 73.1 (C-2), 68.4 (C-5), 67.9 (C-3), 61.9 (C-6), 61.3 (SCH_2), 49.8 (OCH_3), 21.2, 21.1, 21.0 ($C(O)\underline{C}H_3$); **HRMS**: 493.1141, $C_{21}H_{26}O_{10}SNa$ requires 493.1139.**8-*S*: Axial = Minor Diastereomer: $[\alpha]_D^{25}$** −60 (*c* 0.1, $CHCl_3$); **δ_H** (500 MHz, $CDCl_3$); 7.47-7.33 (m, 5H, ArH), 5.57 (dd, 1H, $J_{3,4}$ 9.6 Hz, $J_{4,5}$ 9.6 Hz, H-4), 5.23 (dd, 1H, $J_{3,4}$ 9.6 Hz, $J_{2,3}$ 9.8 Hz, H-3), 4.91 (dd, 1H, $J_{1,2}$ 9.7 Hz, $J_{2,3}$ 9.8 Hz, H-2), 4.31 (dd, 1H, $J_{6,6'}$ 12.6 Hz, $J_{5,6}$ 5.3 Hz, H-6), 4.23 (dd, 1H, $J_{6,6'}$ 12.6 Hz, $J_{5,6'}$ 2.3 Hz, H-6'), 4.22 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1), 3.87 (ddd, 1H, $J_{4,5}$ 9.6 Hz, $J_{5,6}$ 5.3 Hz, $J_{5,6'}$ 2.3 Hz, H-5), 3.61 (d, 1H, $J_{SCHax\text{-}eq}$ 15.2 Hz, SCH_{eq}), 3.05 (s, 3H, OCH_3), 2.53 (d, 1H, $J_{SCHax\text{-}eq}$ 15.2 Hz, SCH_{ax}), 2.10 (s, 3H, $C(O)CH_3$), 2.08 (s, 3H, $C(O)CH_3$), 2.03 (s, 3H, $C(O)CH_3$); **δ_C** (75 MHz, $CDCl_3$); 170.0 (C=O), 129.0, 128.8, 125.8 (ArC), 98.0 (C-OMe), 84.0 (C-1), 77.2 (C-5), 73.0 (C-4), 68.0 (C-3), 62.1 (C-6), 61.8 (C-2), 54.1 (SCH_2), 49.6 (OCH_3), 20.8, 20.6 ($C(O)\underline{C}H_3$); **m/z** (ES+, %); 493.2 ($[M+Na]^+$, 5); **HRMS**: Found $[M+Na]^+$ 493.1141, $C_{21}H_{26}O_{10}SNa$ requires 493.1139.

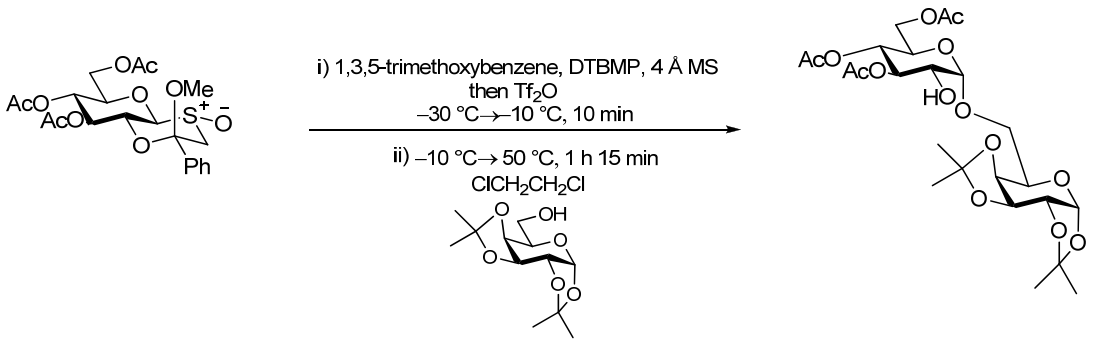
2-Methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (*R*)-*S*-oxide (9-*R*)



A solution of m-CPBA (119 mg, 0.568 mmol) in DCM (2 mL) was slowly added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane **7** (283 mg, 0.472 mmol) in DCM (3 mL) at −78 °C. The reaction mixture was stirred for 15 min at −78 °C and then quenched with aq. $NaHCO_3$ (5 mL), diluted with DCM (10 mL), washed with aq. NaCl (2 x 10 mL), dried ($MgSO_4$) and concentrated to leave a crude colourless solid (dr: 96:4). The crude solid was purified by flash column chromatography (silica; 2:1 (v/v) hexane-ethyl acetate) to afford **9-*R*** (252 mg, 87%) as colourless plates, m.p. 36-41 ºC; $[\alpha]_D^{21}$ +13.0 (*c* 2, $CHCl_3$); δ_H (500 MHz, $CDCl_3$); 7.52-7.17 (m, 20H, ArH), 5.01 (d, 1H, *J* 10.9 Hz, OC$\underline{H}_2$Ph), 4.86 (d, 1H, *J* 10.9 Hz, OC$\underline{H}_2$Ph), 4.85 (d, 1H, *J* 10.6 Hz, OC$\underline{H}_2$Ph), 4.68 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.61 (d, 1H, *J* 10.6 Hz, OC$\underline{H}_2$Ph), 4.54 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.22 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1), 3.94-3.87 (m, 5H, H-2, H-3, H-4, H-6, H-6'), 3.83 (d, 1H, $J_{SCH2,SCH2'}$ 12.8 Hz, SCH'$_2$), 3.61 (m, 1H, H-5), 3.03 (s, 3H, OCH_3), 2.83 (d, 1H, $J_{SCH2,SCH2'}$ 12.8 Hz, SCH_2); δ_C (75 MHz, $CDCl_3$); 138.4, 138.1, 129.5, 129.4, 129.3, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 126.3 (ArC), 102.2 (C-OMe), 96.1 (C-1), 84.1, 80.1, 77.6, 71.3 (C-2, C-3, C-4, C-5), 76.3, 75.8, 74.2 (OCH_2Ph), 68.4 (C-6), 61.5 (SCH_2), 50.0 (OCH_3); **HRMS**: Found $[M+Na]^+$ 637.2211, $C_{36}H_{38}O_7SNa$ requires 637.2230.

Table 1, entry 1.

3,4,6-Tri-*O*-acetyl-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (S1)

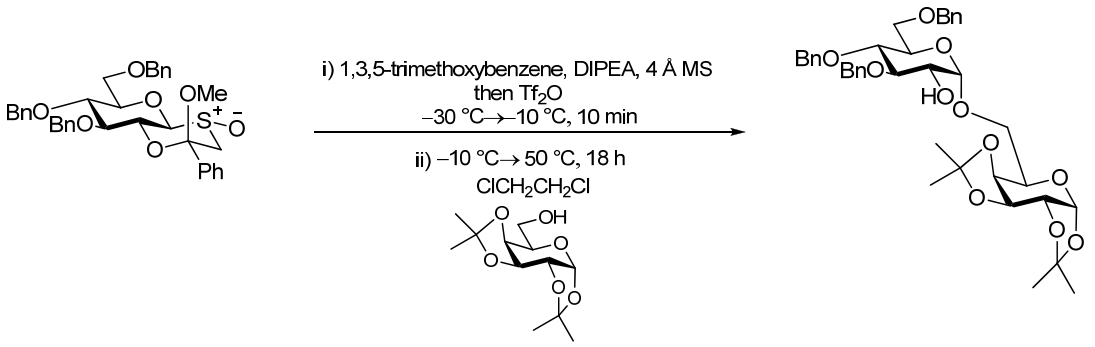


Tf_2O (31 μL, 0.184 mmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane (*R*)-*S*-oxide **8-*R*** (79 mg, 0.168 mmol),

DTBMP (248 mg, 1.21 mmol), 1,3,5-trimethoxybenzene (31 mg, 0.184 mmol) and 4 Å molecular sieves (79 mg) in DCE (650 μL) at −30 ºC. The reaction mixture was warmed to −10 ºC over 10 min, then a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (109 mg, 0.420 mmol) in DCE (150 μL) was added. The reaction mixture was then heated at 50 ºC for 1 h 15 min, allowed to cool and diluted with DCM (10 mL), washed with 1M HCl (3 x 10 mL), aq. $NaHCO_3$ (2 x 10 mL) and aq. NaCl (2 x 10 mL) and concentrated to afford a crude yellow oil. The crude oil was dissolved in DCM (1 mL), cat. BF_3•OEt_2 and MeOH (0.163 mmol) was added, after stirring for 30 min at r.t. the reaction mixture was diluted with DCM (5 mL) washed with aq. NaCl (5 mL), dried ($MgSO_4$) and concentrated to afford a crude yellow oil. The crude oil was purified by flash chromatography (silica; 3:1 (v/v) hexane-ethyl acetate) to afford **S1** as a colourless oil (78 mg, 85%); $\mathbf{[\alpha]_D^{21}}$ +38.2 (*c* 7, $CHCl_3$); $\mathbf{\delta_H}$ (500 MHz, $CDCl_3$); 5.52 (d, 1H, $J_{1a,2a}$ 5.0 Hz, H-1a), 5.24 (dd, 1H, $J_{3b,4b}$ 9.9 Hz, $J_{2b,3b}$ 9.6 Hz, H-3b), 5.01 (dd, $J_{4b,5b}$ 10.0 Hz, $J_{3b,4b}$ 9.9 Hz, H-4b), 4.96 (d, 1H, $J_{1b,2b}$ 3.7 Hz, H-1b), 4.64 (dd, 1H, $J_{3a,4a}$ 7.9 Hz, $J_{2a,3a}$ 2.5 Hz, H-3a), 4.35-4.33 (m, 1H, H-2a), 4.31-4.28 (m, 2H, H-4a, H-6b), 4.10-4.05 (m, 2H, H-5a, H-6'b), 4.00 (m, 1H, H-5b), 3.94 (dd, 1H, $J_{6a,6'a}$ 10.5 Hz, $J_{5a,6a}$ 7.2 Hz, H-6a), 3.74 (dd, 1H, $J_{6a,6'a}$ 10.5 Hz, $J_{5a,6'a}$ 5.6 Hz, H-6'a), 3.67 (dd, 1H, $J_{2b,2\text{-}OH}$ 11.1 Hz, $J_{1b,2b}$ 3.7 Hz, H-2b), 2.88 (d, 1H, $J_{2b,2\text{-}OH}$ 11.1 Hz, 2-OH), 2.09 (s, 3H, C(O)CH_3), 2.07 (s, 3H, C(O)CH_3), 2.04 (s, 3H, C(O)CH_3), 1.55 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.34 (s, 3H, CH_3); $\mathbf{\delta_C}$ (75 MHz, $CDCl_3$); 171.0, 170.7, 169.6 (C=O), 109.6, 108.8 ($\underline{C}(OR)_2(CH_3)_2$), 99.0 (C-1b), 96.2 (C-1a), 73.5 (C-3b), 71.0, 70.9, 70.7, 70.5 (C-2a, C-3a, C-2b, C-4a), 68.1 (C-6a), 68.0 (C-5a), 66.0 (C-5b), 61.9 (C-6b), 26.0, 25.9, 24.9, 24.4 ($\underline{C}H_3$), 20.9, 20.8, 20.7 (C(O)$\underline{C}H_3$); **HRMS**: Found $[M+Na]^+$ 571.1975, $C_{24}H_{36}O_{14}Na$ requires 571.1997.

Table 1, entry 2.

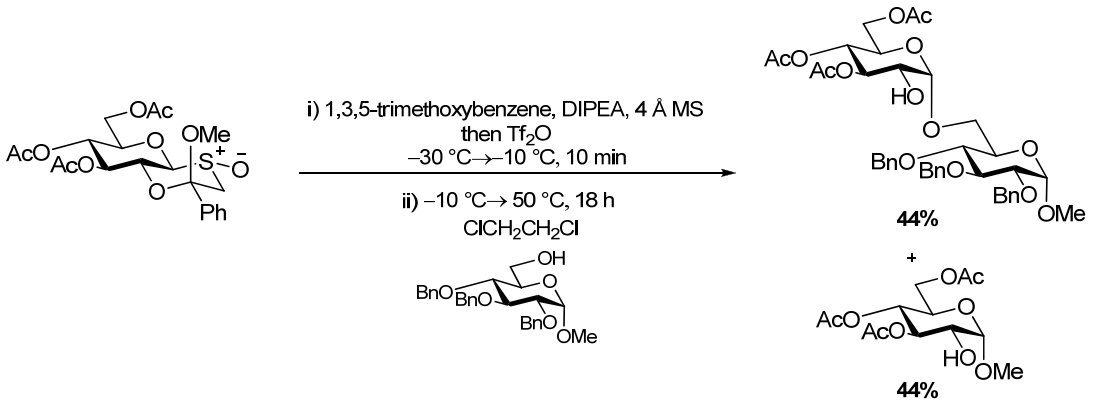
3,4,6-Tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (S2)[27]



Tf_2O (15 μL, 90 μmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane-4-(*R*)-*S*-oxide **9-*R*** (50 mg, 81 μmol), DIPEA (17 μL, 98 μmol), 1,3,5-trimethoxybenzene (30 mg, 0.179 mmol) and 4 Å molecular sieves (50 mg) in DCE (310 μL) at −30 ºC. The reaction mixture was warmed to −10 ºC and stirred for 10 min, then DIPEA (85 μL, 0.489 mmol) followed by a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (53 mg, 0.204 mmol) in DCE (80 μL) was added. The reaction mixture was then heated at 50 ºC for 18 h, allowed to cool and diluted with DCM (10 mL), washed with 1M HCl (3 x 10 mL), aq. $NaHCO_3$ (2 x 10 mL) and aq. NaCl (2 x 10 mL) and concentrated to afford a crude syrup. The syrup was redissolved in DCM (1 mL), cat. BF_3•OEt_2 and MeOH (7 μL, 0.162 mmol) was added, after stirring for 30 min at r.t. the reaction mixture was diluted with DCM (5 mL) washed with aq. NaCl (5 mL), dried ($MgSO_4$) and concentrated to afford a crude syrup. The crude syrup was purified by size exclusion chromatography (Sephadex LH-20 resin; eluted with methanol (50 mL/h))) to afford **S2** (49 mg, 88%) as a colourless syrup; $\mathbf{[\alpha]_D}^{28}$ +38.8 (*c* 0.5, $CHCl_3$) [lit.[27] $\mathbf{[\alpha]_D}^{22}$ +27.7 (*c* 0.35, $CHCl_3$)]; $\mathbf{\delta_H}$ (500 MHz, $CDCl_3$); 7.40-7.13 (m, 15H, ArH), 5.52 (d, 1H, $J_{1a,2a}$ 5.0 Hz, H-1a), 4.98 (d, 1H, *J* 11.1 Hz, OC$\underline{H}_2$Ph), 4.92 (d, 1H, $J_{1b,2b}$ 3.4 Hz, H-1b), 4.83 (d, 1H, *J* 10.9 Hz, OC$\underline{H}_2$Ph), 4.81 (d, 1H, *J* 11.1 Hz, OC$\underline{H}_2$Ph), 4.63 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 4.62 (dd, 1H, H-3a), 4.49 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 4.48 (d, 1H, *J* 10.9 Hz, OC$\underline{H}_2$Ph), 4.32 (dd, 1H, $J_{1a,2a}$ 5.0 Hz, $J_{2a,3a}$ 2.5 Hz, H-2a), 4.24 (dd, 1H, $J_{3a,4a}$ 7.7 Hz, $J_{4a,5a}$ 1.7 Hz, H-4a), 3.99 (td, 1H, $J_{5a,6a}$ 6.7 Hz, $J_{5a,6'a}$ 6.7 Hz, $J_{4a,5a}$ 1.7 Hz, H-5a), 3.90 (dd, 1H, $J_{6a,6'a}$ 10.3 Hz, $J_{5a,6a}$ 6.7 Hz, H-6a), 3.85 (m, 1H, H-5b), 3.77-3.62 (m, 6H, H-2b, H-3b, H-4b, H-6b, H6'b, H6'a), 1.52 (s, 3H, C$\underline{H}_3$), 1.44 (s, 3H, C$\underline{H}_3$), 1.34 (s, 3H, C$\underline{H}_3$), 1.33 (s, 3H, C$\underline{H}_3$); $\mathbf{\delta_C}$ (75 MHz, $CDCl_3$); 128.3, 128.3, 127.9, 127.9, 127.8, 127.6, 127.6, 127.5 (ArC), 109.5, 108.7 ($\underline{C}(OR)_2(CH_3)_2$), 99.2 (C-1b), 96.3 (C-1a), 75.2, 75.0, 73.5 (OCH_2Ph), 71.1, 70.9, 70.7 (C-2a, C-3a, C-4a), 26.1, 26.0, 24.9, 24.6 ($\underline{C}H_3$), 83.4, 73.3, 70.5, 68.5, 67.1, 65.8, 62.4 (C-2b, C-3b, C-4b, C-5b, C-6b, C-5a, C-6a); **m/z** (ES+, %); 710.5 ($[M+NH_4]^+$, 95).

Table 1, entry 3.

Methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (S3)



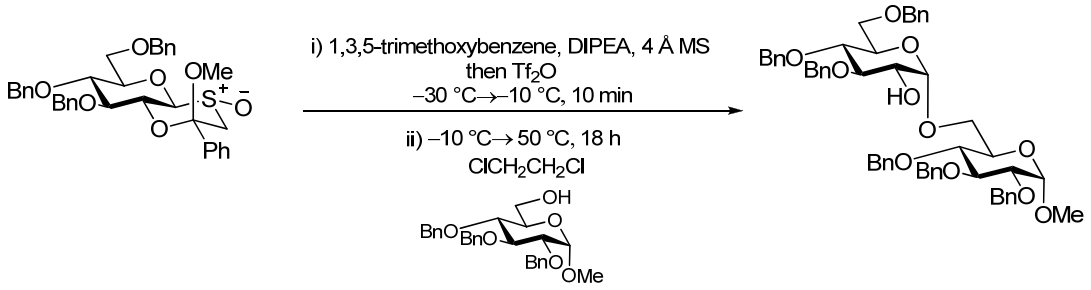
Tf_2O (28 μL, 0.164 mmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane-4-(*R*)-*S*-oxide **8-*R*** (70 mg, 0.149 mmol), DIPEA (31 μL, 0.179 mmol), 1,3,5-trimethoxybenzene (55 mg, 0.328 mmol) and 4 Å molecular sieves (70 mg) in DCE (570 μL) at −30 ºC. The reaction mixture was warmed to −10 ºC and stirred for 10 min, then DIPEA (216 μL, 1.09 mmol) followed by a solution of methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (173 mg, 0.372 mmol) in DCE (140 μL) was added. The reaction mixture was then heated at 50 ºC for 18 h, allowed to cool and diluted with DCM (10 mL), washed with 1M HCl (3 x 10 mL), aq. $NaHCO_3$ (2 x 10 mL) and aq. NaCl (2 x 10 mL) and concentrated to afford a crude syrup. The syrup was redissolved in DCM (1 mL), cat. BF_3•OEt_2 and MeOH (12 μL, 0.298 mmol) was added, after stirring for 30 min at r.t. the reaction mixture was diluted with DCM (5 mL) washed with aq. NaCl (5 mL), dried ($MgSO_4$) and concentrated to afford a crude oil. The crude oil was purified by purified size exclusion chromatography (Sephadex LH-20 resin; eluted with methanol (50 mL/h)) to afford **S3** (49 mg, 44%) as a colourless oil; $[\alpha]_D^{21}$ +16.5 (*c* 3, $CHCl_3$); δ_H (500 MHz, $CDCl_3$); 7.40-7.25 (m, 15H, ArH), 5.17 (dd, 1H, $J_{2b,3b}$ 9.7 Hz, $J_{3b,4b}$ 9.8 Hz, H-3b), 5.00 (d, 1H, *J* 10.8 Hz, OC$\underline{H}_2$Ph), 4.98 (dd, 1H, $J_{3b,4b}$ 9.8 Hz, $J_{4b,5b}$ 9.4 Hz, H-4b), 4.95 (d, 1H, *J* 11.6 Hz, OC$\underline{H}_2$Ph), 4.94 (d, 1H, $J_{1b,2b}$ 3.3 Hz, H-1b), 4.80 (d, 1H, *J* 10.8 Hz, OC$\underline{H}_2$Ph), 4.79 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 4.68 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 4.61 (d, 1H, $J_{1a,2a}$ 3.5 Hz, H-1a), 4.60 (d, 1H, *J* 11.6 Hz, OC$\underline{H}_2$Ph), 4.14 (dd, 1H, $J_{6a,6'a}$ 12.2 Hz, $J_{5a,6a}$ 4.4 Hz, H-6a), 3.99 (dd, 1H, $J_{3a,4a}$ 9.9 Hz, $J_{2a,3a}$ 9.6 Hz, H-3a), 3.99-3.97 (m, 1H, H-6'a), 3.94-3.88 (m, 2H, H-5b, H-6b), 3.82-3.78 (m, 1H, H-5a), 3.71-3.62 (m, 2H, H-2b, H-6'b), 3.55 (dd, 1H, $J_{1a,2a}$ 3.5 Hz, $J_{2a,3a}$ 9.6 Hz, H-2a), 3.46 (dd, 1H, $J_{3a,4a}$ 9.9 Hz, $J_{4a,5a}$ 9.6 Hz, H-4a), 3.39 (s, 3H, OCH_3), 2.28 (d, 1H, $J_{2b,2\text{-OH}}$ 10.5 Hz, 2-OH), 2.07 (s, 3H, C(O)CH_3), 2.01 (s, 3H, C(O)CH_3), 2.01 (s, 3H, C(O)CH_3); δ_C (75 MHz, $CDCl_3$); 171.3, 171.0,

169.9 (C(O)CH_3), 139.0, 138.5, 128.9, 128.8, 128.5, 128.4, 128.3, 128.3, 128.2 (ArC), 99.1 (C-1b), 98.4 (C-1a), 82.4 (C-2a), 80.7, 77.8, 73.8, 71.5, 70.0, 68.4, 68.3 (C-3a, C-4a, C-5a, C-2b, C-3b, C-4b, C-5b), 76.2, 75.3, 73.9 (OCH_2Ph), 67.8 (C-6b), 62.3 (C-6a), 55.8 (OCH_3), 21.3, 21.1, 21.0 (C(O)CH_3); **HRMS**: Found $[M+Na]^+$ 775.2919, $C_{40}H_{48}O_{14}Na$ requires 775.2942.

Methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside[28, 29] (S4) (21 mg, 44%) was isolated as a byproduct as a colourless oil; $[\alpha]_D^{25}$ +186.6 (*c* 0.3, $CHCl_3$) [lit. [28] $[\alpha]_D$ +117.5 (*c* 1.5, $CHCl_3$)]; δ_H (500 MHz, $CDCl_3$); 5.23 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 9.7 Hz, H-3), 5.01 (dd, 1H, $J_{4,5}$ 9.9 Hz, $J_{3,4}$ 9.7 Hz, H-4), 4.83 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.27 (dd, 1H, $J_{6,6'}$ 12.3 Hz, $J_{5,6}$ 4.6 Hz, H-6), , 4.09 (dd, 1H, $J_{6,6'}$ 12.3 Hz, $J_{5,6'}$ 1.3 Hz, H-6'), 3.94 (m, 1H, H-5), 3.71 (ddd, 1H, $J_{2,OH-2}$ 11.2 Hz, $J_{2,3}$ 9.7 Hz, $J_{1,2}$ 3.6 Hz, H-2), 2.16 (d, 1H, $J_{2,OH-2}$ 11.2 Hz, 2-OH), 2.10 (s, 3H, C(O)CH_3), 2.08 (s, 3H, C(O)CH_3), 2.03 (s, 3H, C(O)CH_3); δ_C (75 MHz, $CDCl_3$); 171.5, 171.1, 170.0 (C=O), 99.6 (C-1), 73.8, 71.3, 68.4, 68.0 (C-2, C-3, C-4, C-5), 62.4 (C-6), 56.1 (OCH_3), 21.3, 21.2, 21.1 (C(O)CH_3); **m/z** (ES+, %); 343.1 ($[M+Na]^+$, 10).

Table 1, entry 4.

Methyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (S5)[30]

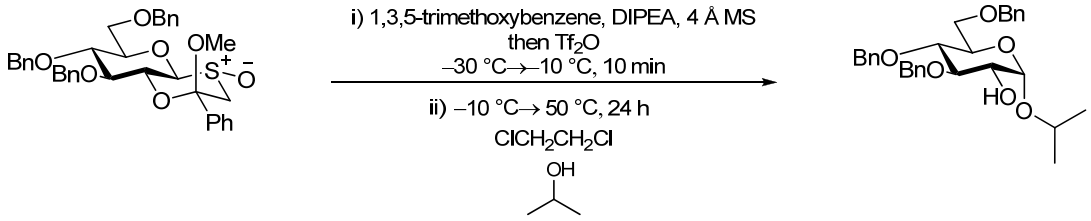


Tf_2O (26 µL, 0.152 mmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane-4-(*R*)-*S*-oxide **9-*R*** (85 mg, 0.138 mmol), DIPEA (29 µL, 0.166 mmol), 1,3,5-trimethoxybenzene (51 mg, 0.304 mmol) and 4 Å molecular sieves (85 mg) in DCE (530 µL) at −30 ºC. The reaction mixture was warmed to −10 ºC and stirred for 10 min, then DIPEA (145 µL, 0.831 mmol) followed by a solution of methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (161 mg, 0.346 mmol) in DCE (130 µL) was added. The reaction mixture was then heated at 50 ºC for 18 h, allowed to cool and diluted with DCM (10 mL), washed with 1M HCl (3 x 10 mL), aq. $NaHCO_3$ (2 x 10 mL) and aq. NaCl (2 x 10 mL) and concentrated to afford a crude syrup. The syrup was redissolved in DCM (1 mL), cat. BF_3•OEt_2 and MeOH (11 µL, 0.277 mmol) was added, after stirring for 30 min at r.t. the reaction mixture was diluted with DCM (5 mL) washed with aq. NaCl (5 mL), dried ($MgSO_4$) and concentrated to afford a crude syrup. The crude

syrup was purified by flash chromatography (silica; 6:1→3:2 (v/v) hexane-ethyl acetate) to afford **S5** (89 mg, 72%) as a colourless syrup; $[\alpha]_D^{21}$ +44.5 (*c* 2.5, $CHCl_3$) [lit.[30] $[\alpha]_D^{22}$ +73.6 (*c* 1, $CHCl_3$)]; δ_H (500 MHz, $CDCl_3$); 7.30-7.05 (m, 30H, ArH), 4.92 (d, 1H, *J* 10.9 Hz, OC$\underline{H}_2$Ph), 4.86-4.83 (m, 3H, 2 x OC$\underline{H}_2$Ph, H-1b), 4.74 (d, 1H, *J* 10.9 Hz, OC$\underline{H}_2$Ph), 4.73 (d, 1H, *J* 10.9 Hz, OC$\underline{H}_2$Ph), 4.71 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.69 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.53 (d, 1H, $J_{1a,2a}$ 3.4 Hz, H-1a), 4.49 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 4.53 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 4.53 (d, 1H, *J* 11.7 Hz, OC$\underline{H}_2$Ph), 4.39 (d, 1H, *J* 10.9 Hz, OC$\underline{H}_2$Ph), 4.35 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 3.92 (dd, 1H, $J_{2a,3a}$ 9.3 $J_{3a,4a}$ 9.3 Hz, H-3a), 3.85 (dd, $J_{6'a,6a}$ 11.5 Hz, $J_{5a,6a}$ 4.5 Hz, H-6a), 3.72-3.52 (m, 7H, H-5a, H-6'a, H-2b, H-3b, H-5b, H-6b, H-6'b), 3.62-3.59 (m, 2H, H-4a, H-5a), 3.47-3.38 (m, 3H, H-2a, H-4a, H-4b), 3.29 (s, 3H, OCH_3), 2.1 (br s, 1H, 2-OH); δ_C (75 MHz, $CDCl_3$); 139.1, 139.1, 138.8, 138.6, 138.5, 138.4, 128.9, 128.9, 128.8, 128.8, 128.8, 128.7, 128.7, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0 (ArC), 99.6 (C-1b), 98.3 (C-1a), 83.6, 82.5, 80.6, 78.2, 77.7, 73.6, 71.2, 70.0 (C-2a, C-3a, C-4a, C-5a, C-2b, C-3b, C-4b, C-5b), 76.1, 75.6, 75.4, 75.3, 73.9, 73.7 (OCH_2Ph), 68.8 (C-6b), 67.4 (C-6a), 55.7 (OCH_3); **HRMS**: Found $[M+Na]^+$ 919.4011, $C_{55}H_{60}O_{11}Na$ requires 919.4028.

Table 1, entry 5.

Isopropyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (S6)

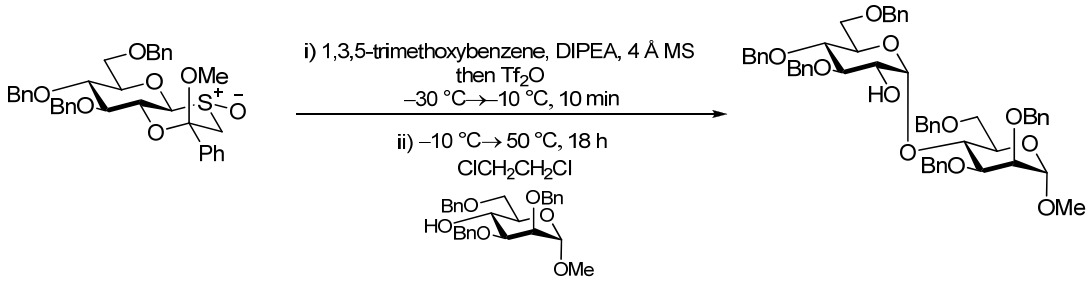


Tf_2O (28 µL, 0.152 mmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane-4-(*R*)-*S* oxide **9-*R*** (91 mg, 0.148 mmol), DIPEA (31 µL, 0.177 mmol), 1,3,5-trimethoxybenzene (55 mg, 0.326 mmol) and 4 Å molecular sieves (91 mg) in DCE (570 µL) at −30 ºC. The reaction mixture was warmed to −10 ºC and stirred for 10 min, then DIPEA (155 µL, 0.889 mmol) followed by a solution of isopropanol (57 µL, 0.741 mmol) in DCE (135 µL) was added. The reaction mixture was then heated at 50 ºC for 24 h, allowed to cool and diluted with DCM (10 mL), washed with 1M HCl (3 x 10 mL), aq. $NaHCO_3$ (2 x 10 mL) and aq. NaCl (2 x 10 mL) and concentrated to afford a crude syrup. The syrup was redissolved in DCM (1 mL), cat. BF_3•OEt_2 and MeOH (12 µL, 0.296 mmol) was added, after stirring for 30 min at r.t. the reaction mixture was diluted with DCM (5 mL) washed with aq. NaCl (5 mL), dried ($MgSO_4$) and concentrated to afford a crude oil. The crude oil was purified by size

exclusion chromatography (Sephadex LH-20 resin; eluted with methanol (50 mL/h)) to afford **S6** (56 mg, 77%) as a colourless oil; $[\alpha]_D^{21}$ −1.9 (*c* 1.5, $CHCl_3$); δ_H (500 MHz, $CDCl_3$); 7.40-7.13 (m, 15H, ArH), 4.99 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.97 (d, 1H, *J* 11.1 Hz, OC$\underline{H}_2$Ph), 4.83 (d, 1H, *J* 11.1 Hz, OC$\underline{H}_2$Ph), 4.82 (d, 1H, *J* 10.6 Hz, OC$\underline{H}_2$Ph), 4.64 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 4.50 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 4.48 (d, 1H, *J* 10.6 Hz, OC$\underline{H}_2$Ph), 3.95 (septet, 1H, *J* 6.2 Hz, C$\underline{H}$(CH$_3$)$_2$), 3.86-3.84 (m, 1H, H-5), 3.78-3.62 (m, 4H, H-2, H-4, H-6, H-6'), 2.03 (d, 1H, $J_{2,2\text{-OH}}$ 9.3 Hz, 2-OH), 1.22 (d, 3H, *J* 6.2 Hz, CH(C$\underline{H}_3$)$_2$), 1.18 (d, 3H, *J* 6.2 Hz, CH(C$\underline{H}_3$)$_2$); δ_C (75 MHz, $CDCl_3$); 138.9, 138.3, 138.1, 128.4, 128.0, 127.9, 127.7, 127.7, 127.6 (ArC), 96.9 (C-1), 83.8 (C-2), 75.3, 75.1, 73.6 (OCH$_2$Ph), 77.5, 73.0, 70.6, 70.3 (C-3, C-4, C-5, C$\underline{H}$(CH$_3$)$_2$), 68.7 (C-6), 23.3, 21.7 (CH(C$\underline{H}_3$)$_2$); **HRMS**: Found $[M+Na]^+$ 515.2385, $C_{30}H_{36}O_6Na$ requires 515.2410.

Table 1, entry 6.

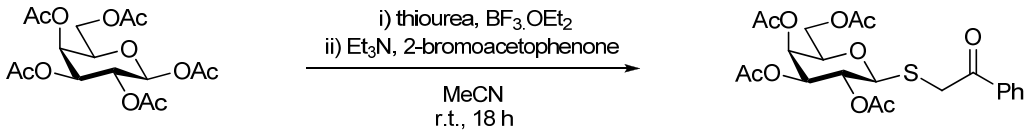
Methyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (S7)



Tf_2O (15 µL, 90 µmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-glucopyranoso)[1,2-*e*]-1,4-oxathiane-4-(*R*)-*S*-oxide **9-*R*** (50 mg, 81 µmol), DIPEA (17 µL, 99 µmol), 1,3,5-trimethoxybenzene (30 mg, 0.179 mmol) and 4 Å molecular sieves (50 mg) in DCE (310 µL) at −30 ºC. The reaction mixture was warmed to −10 ºC and stirred for 10 min, then DIPEA (111 µL, 0.637 mmol) followed by a solution of methyl 2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (94 mg, 0.203 mmol) in DCE (180 µL) was added. The reaction mixture was then heated at 50 ºC for 18 h, allowed to cool and diluted with DCM (10 mL), washed with 1M HCl (3 x 10 mL), aq. $NaHCO_3$ (2 x 10 mL) and aq. NaCl (2 x 10 mL) and concentrated to afford a crude yellow syrup. The syrup was redissolved in DCM (1 mL), cat. BF_3•OEt_2 and MeOH (6.6 µL, 0.163 mmol) was added, after stirring for 30 min at r.t. the reaction mixture was diluted with DCM (5 mL) washed with aq. NaCl (5 mL), dried ($MgSO_4$) and concentrated to afford a crude oil. The crude oil was purified by size exclusion chromatography (Sephadex LH-20 resin; eluted with methanol (50 mL/h)) to afford **S7** (48 mg, 66%) as a colourless syrup; $[\alpha]_D^{28}$ +104.0 (*c* 0.5, $CHCl_3$); δ_H (500 MHz, $CDCl_3$); 7.24-7.06 (m, 30H, ArH), 5.04 (d, 1H, $J_{1b,2b}$ 2.4 Hz, H-1b), 4.74 (d, 1H, $J_{1a,2a}$ 1.7 Hz,

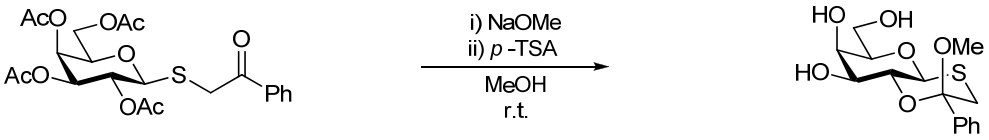
H-1a), 4.73 (d, 1H, *J* 10.1 Hz, OC$\underline{H}_2$Ph), 4.65 (d, 1H, *J* 11.1 Hz, OC$\underline{H}_2$Ph), 4.59 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 4.53 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.53 (d, 1H, *J* 12.2 Hz, OC$\underline{H}_2$Ph), 4.49-4.46 (m, 4H, OC$\underline{H}_2$Ph), 4.37 (d, 1H, *J* 10.1 Hz, OC$\underline{H}_2$Ph), 4.36 (d, 1H, *J* 11.3 Hz, OC$\underline{H}_2$Ph), 4.35 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.15 (dd, 1H, $J_{2a,3a}$ 9.6 $J_{3a,4a}$ 9.6 Hz, H-3a), 3.86-3.84 (m, 2H, H-2a, H-6'b), 3.78-3.66 (m, 2H, H-4b, H-6b), 3.62-3.59 (m, 2H, H-4a, H-5a), 3.55-3.52 (m, 2H, H-2b, H-3b, H-6'a), 3.48-3.40 (m, 2H, H-5b, H-6a), 3.28 (s, 3H, OCH_3), 1.18 (br s, 1H, 2-OH); $\boldsymbol{\delta_C}$ (75 MHz, $CDCl_3$); 138.1, 137.6, 137.5, 137.1, 137.0, 135.9, 127.5, 127.4, 127.3, 127.3, 127.2, 127.1, 126.9, 126.8, 126.8, 126.7, 126.6, 126.4, 126.4, 126.3 (ArC), 100.9 (C-1b), 97.6 (C-1a), 82.8 (C-2b), 78.2 (C-2a), 76.2, 76.0, 75.3, 73.3, 72.4, 71.0 (C-3a, C-4a, C-5a, C-3b, C-5b), 74.1, 73.9, 72.4, 72.2, 71.4, 70.0 (OCH_2Ph), 70.6 (C-4b), 68.3 (C-6b), 67.8 (C-6a), 53.9 (OCH_3); **HRMS**: Found $[M+Na]^+$ 919.4025, $C_{55}H_{60}O_{11}Na$ requires 919.4028.

2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-galactopyranosyl acetophenone (S9) [31]



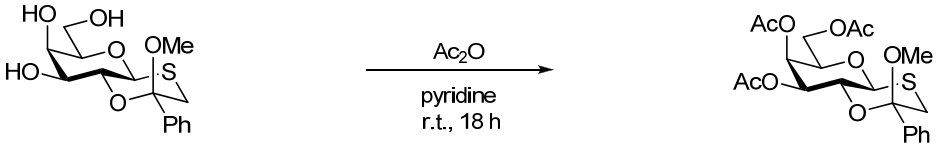
BF_3•OEt_2 (8.31 mL, 64.2 mmol) was added dropwise over 10 minutes to a solution of thiourea (2.56 g, 33.6 mmol), and β-galactose-pentaacetetate **S8** (11.93 g, 30.6 mmol) in acetonitrile (60 mL) at 85ºC. The reaction mixture was heated under reflux for 75 min, and then allowed to cool to r.t. Triethylamine (13.17 mL, 94.7 mmol), followed by 2-bromoacetophenone (12.17 g, 60.1 mmol) in acetonitrile (15 mL) were then added to the reaction mixture, which was stirred for a further 18 h and then concentrated. The residue was redissolved in ethyl acetate (30 mL), washed with 1M HCl (2 x 20 mL), dried ($MgSO_4$) and concentrated. The crude oil was then purified by flash column chromatography (silica gel; 2:1 (v/v) hexane-ethyl acetate) to afford **S9** (7.42 g, 50%) as a colourless solid; $\boldsymbol{[\alpha]_D^{22}}$ –75.1 (*c* 1, $CHCl_3$); [lit.[31] $\boldsymbol{[\alpha]_D}$ –32 (*c* 0.88, $CHCl_3$)]; $\boldsymbol{\delta_H}$ (500 MHz, $CDCl_3$); 7.98 (dd, 2H, *J* 8.2 Hz, *J* 1.0 Hz, ArH), 7.63 (t, 1H, *J* 7.8 Hz, ArH), 7.51 (t, 2H, *J* 8.2 Hz, ArH), 5.45 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{4,5}$ 0.8 Hz, H-4), 5.27 (dd, 1H, $J_{1,2}$ 10.0 Hz, $J_{2,3}$ 10.0 Hz, H-2), 5.07 (dd, 1H, $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 3.4 Hz, H-3), 4.63 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1), 4.13-4.01 (m, 4H, H-6, H-6', SCH_2, SCH_2'), 3.95 (m, 1H, H-5), 2.17 (s, 3H, $C(O)CH_3$), 2.03 (s, 3H, $C(O)CH_3$), 1.99 (s, 3H, $C(O)CH_3$), 1.95 (s, 3H, $C(O)CH_3$); $\boldsymbol{\delta_C}$ (75 MHz, $CDCl_3$); 195.0 (Ph$\underline{C}$=O) 170.7, 170.5, 170.3, 170.1 (C=O), 135.7, 133.9, 129.1, 128.9 (ArC), 83.3 (C-1), 75.0 (C-5), 72.2 (C-3), 67.5 (C-2), 66.9 (C-4), 61.7 (C-6), 35.8 (SCH_2), 21.2, 21.0, 20.9, 20.9 ($C(O)\underline{C}H_3$); **HRMS**; Found $[M+Na]^+$ 505.1133, $C_{22}H_{26}O_{10}SNa$ requires 505.1139.

2-Methoxy-2-(*S*)-phenyl-(1,2-dideoxy-β-D-galactopyranoso)[1,2-*e*]-1,4-oxathiane (S10)



Sodium methoxide in methanol (0.5 M, 6.2 mL, 30.8 mmol) was added to a solution of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranosyl acetophenone **S9** (7.42 g, 15.4 mmol) in methanol (20 mL), and the reaction mixture was stirred at r.t. for 24 h. The reaction mixture was then neutralised with Amberlite H^+ resin, filtered and concentrated to leave a crude solid. The crude solid was redissolved in methanol (768 mL), *p*-toluenesulfonic acid (2.93 g, 15.0 mmol) was then added and the reaction mixture was stirred at r.t. for 28 h. The reaction mixture was neutralised with triethylamine and concentrated. The crude residue was purified by flash column chromatography (silica gel; DCM-methanol 99:1→9:1) to afford **S10** (2.54 g, 50%) as a colourless glassy solid; **$[\alpha]_D^{22}$** +43.6 (*c* 1, $CHCl_3$); **δ_H** (500 MHz, MeOD); 7.56 (m, 2H, ArH), 7.40 (t, 2H, *J* 6.1 Hz, ArH), 7.35 (d, 1H, *J* 5.9 Hz, ArH), 4.53 (d, 1H, $J_{1,2}$ 9.1 Hz, H-1), 4.17 (t, 1H, $J_{1,2}$ 9.1 Hz, $J_{2,3}$ 9.1 Hz, H-2), 4.01 (dd, 1H, $J_{3,4}$ 4.1 Hz, $J_{4,5}$ 1.2 Hz, H-4), 3.79-3.69 (m, 4H, H-3, H-6, H-6', H-5), 3.14 (s, 3H, OCH_3), 3.05 (d, 1H, *J* 9.2 Hz, SCH_2), 3.02 (d, 1H, *J* 9.2 Hz, SCH'_2); **δ_C** (75 MHz, MeOD); 129.7, 129.6, 127.9, 128.9 (ArC), 99.1 (C-OMe), 82.3 (C-1), 78.2 (C-5), 76.5 (C-3), 74.4 (C-2), 71.5 (C-4), 63.1 (C-6), 49.8 (OCH_3), 40.1 (SCH_2); **HRMS**; Found $[M+Na]^+$ 351.0864, $C_{15}H_{20}O_6SNa$ requires 351.0873.

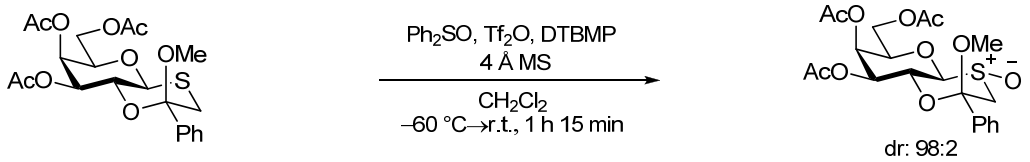
2-Methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-galactopyranoso) [1,2-*e*]-1,4-oxathiane (S11)



Acetic anhydride (1.21 mL, 12.71 mmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(1,2-dideoxy-β-D-galactopyranoso)[1,2-*e*]-1,4-oxathiane **S10** (948 mg, 2.89 mmol) in pyridine (10 mL). After stirring for 15 h the reaction was then quenched with aq. $NaHCO_3$ (15 mL), diluted with DCM (15 mL), separated, washed with aq. NaCl (2 x 15 mL), dried ($MgSO_4$) and concentrated to leave a crude yellow oil. The crude oil was purified by flash column chromatography (silica gel; 3:1 (v/v) hexane: ethyl acetate) to afford **S11** (550 mg, 42%) as a colourless foam; **$[\alpha]_D^{22}$** +112.5 (*c* 1, $CHCl_3$); **δ_H** (500 MHz, $CDCl_3$); 7.43 (m, 2H, ArH), 7.37 (m, 1H, ArH), 7.32 (m, 2H, ArH), 5.55

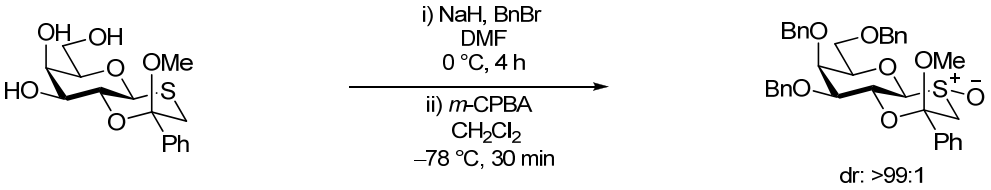
(dd, 1H, $J_{3,4}$ 3.5, Hz, $J_{4,5}$ 1.1 Hz, H-4), 5.28 (dd, 1H, $J_{2,3}$ 10.2 Hz, $J_{3,4}$ 3.5 Hz, H-3), 4.59 (d, 1H, $J_{1,2}$ 9.3 Hz, H-1), 4.33 (dd, 1H, $J_{1,2}$ 9.3 Hz, $J_{2,3}$ 10.2 Hz, H-2) 4.13-4.15 (m, 2H, H-6, H-6'), 4.05 (m, 1H, H-5), 3.07 (s, 3H, OCH_3), 3.04 (s, 2H, SCH_2), 2.18 (s, 3H, $C(O)CH_3$), 2.08 (s, 3H, C(O)CH3), 1.99 (s, 3H, $C(O)CH_3$); δ_C (75 MHz, $CDCl_3$); 171.3, 170.2, 169.6 (C=O), 139.9, 129.0, 128.9, 126.6 (ArC), 97.8 (C-OMe), 77.1 (C-1), 76.1, 70.9, 70.3 (C-2, C-3, C-5), 68.4 (C-4), 62.1 (C-6), 49.8 (OCH_3), 39.5 (SCH_2), 21.1, 20.9, 20.6 ($C(O)\underline{C}H_3$); **HRMS**: Found $[M+Na]^+$ 477.1192, $C_{21}H_{26}O_9SNa$ requires 477.1190.

2-Methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-galactopyranoso) [1,2-*e*]-1,4-oxathiane (*R*)-*S*-oxide (12)



Tf_2O (52 μL, 0.31 mmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-galactopyranoso)[1,2-*e*]-1,4-oxathiane **S11** (100 mg, 0.22 mmol), diphenyl sulfoxide (124 mg, 0.62 mmol), DTBMP (134 mg, 0.60 mmol) and 4Å molecular sieves (50 mg) in DCM (1 mL) at −60ºC. The reaction mixture was gradually raised to r.t. over 1h 15 min and was then quenched with aq. $NaHCO_3$ (2 mL), diluted with DCM (5 mL), washed with aq. NaCl (2 x 5 mL), dried ($MgSO_4$) and concentrated to leave a crude colourless oil. The crude oil was then purifyied by flash column chromatography (silica; 2.1 (v/v) hexane-ethyl acetate→1:1 (v/v) hexane-ethyl acetate) to afford **12** (68 mg, 66%, dr 98:2) as a colourless foam; $[\alpha]_D^{22}$ +86.4 (*c* 1, $CHCl_3$); δ_H (500 MHz, $CDCl_3$); 7.45-7.38 (m, 5H, ArH), 5.53 (d, 1H, $J_{3,4}$ 3.5 Hz, H-4), 5.42 (dd, 1H, $J_{2,3}$ 9.9 Hz, $J_{3,4}$ 3.5 Hz, H-3), 4.37 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1), 4.22 (m, 2H, H-6, H-6'), 4.14-4.05 (m, 2H, H-5, H-2), 3.86 (d, 1H, $J_{SCHax\text{-}eq}$ 12.8 Hz, SCH_{eq}), 2.97 (s, 3H, OCH_3), 2.88 (d, 1H, $J_{SCHax\text{-}eq}$ 12.8 Hz, SCH_{ax}), 2.19 (s, 3H, $C(O)CH_3$), 2.07 (s, 3H, C(O)CH3), 2.00 (s, 3H, $C(O)CH_3$); δ_C (75 MHz, $CDCl_3$); 171.3, 171.1, 170.2 (C=O), 129.3, 128.9, 125.9 (ArC), 101.7 (C-OMe), 95.8 (C-1), 75.7 (C-5), 70.4 (C-3), 67.4 (C-4), 65.1 (C-2), 61.4 (C-6), 61.2 (SCH_2), 49.4 (OCH_3); **HRMS**; Found $[M+Na]^+$ 493.1137, $C_{21}H_{26}O_{10}SNa$ requires 493.1139.

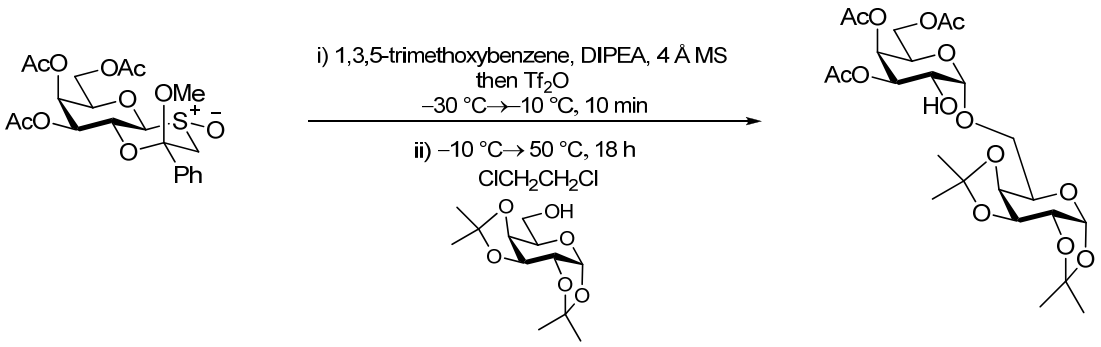
2-Methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-galactopyranoso)[1,2-*e*]-1,4-oxathiane (*R*)-*S*-oxide (13)



NaH (60% dispersion in oil, 201 mg, 0.503 mmol) was added in portions to a stirred solution of 2-methoxy-2-(*S*)-phenyl-(1,2-dideoxy-β-D-galactopyranoso)[1,2-*e*]-1,4-oxathiane **S10** (500 mg, 0.152 μmol) in DMF (8 mL) at 0°C, and stirred for 70 min while H_2(g) evolved. Benzyl bromide (598 μL, 0.503 mmol) was then added dropwise at 0°C, and the reaction mixture stirred for a further 4h. The reaction mixture was quenched with methanol (5 mL), and diluted with DCM (20 mL). The solution was then washed with aq. NaCl (2 x 20 mL), dried ($MgSO_4$) and concentrated to leave a crude solid. The crude solid was redissolved in DCM (8 mL) and cooled to −78 °C, and a solution of *m*-CPBA (327 mg, 0.183 mmol) in DCM (6 mL) was slowly added. The reaction mixture was stirred for 30 min at −78 °C and then quenched with aq. $NaHCO_3$ (10 mL), diluted with DCM (20 mL), washed with aq. NaCl (2 x 20 mL), dried ($MgSO_4$) and concentrated to leave a crude colourless solid (dr: >99:1). The crude solid was purified by flash column chromatography (silica; 1:1 (v/v) hexane-ethyl acetate) to afford **13** (418 mg, 46%) as colourless plates, m.p. 39-46 ºC; $\mathbf{[\alpha]_D^{21}}$ +2 (*c* 0.4, $CHCl_3$); $\mathbf{\delta_H}$ (500 MHz, $CDCl_3$); 7.50-7.22 (m, 20H, ArH), 4.96 (d, 1H, *J* 11.5 Hz, OC$\underline{H}_2$Ph), 4.85 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.77 (d, 1H, *J* 12.1 Hz, OC$\underline{H}_2$Ph), 4.65 (d, 1H, *J* 11.5 Hz, OC$\underline{H}_2$Ph), 4.47 (d, 1H, *J* 11.7 Hz, OC$\underline{H}_2$Ph), 4.44 (d, 1H, *J* 11.7 Hz, OC$\underline{H}_2$Ph), 4.32-4.26 (m, 1H, H-6), 4.25 (d, 1H, $J_{1,2}$ 10.1 Hz, H-1), 4.11 (br d, 1H, H-5), 3.83-3.70 (m, 5H, SCH'$_2$, H-2, H-3, H-4, H-6'), 3.04 (s, 3H, OCH_3), 2.83 (d, 1H, $J_{SCH2,SCH2'}$ 12.7 Hz, SCH_2); $\mathbf{\delta_C}$ (75 MHz, $CDCl_3$); 138.9, 138.6, 138.5, 138.1, 129.4, 129.2, 129.0, 128.89, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 126.3 (ArC), 102.0 (C-OMe), 96.5 (C-1), 80.5, 78.8, 74.5, 68.3 (C-2, C-3, C-4, C-5), 75.5, 74.5, 73.6 (OCH_2Ph), 68.0 (C-6), 61.9 (SCH_2), 49.9 (OCH_3); **HRMS**: Found $[M+Na]^+$ 637.2224, $C_{36}H_{38}O_7SNa$ requires 637.2236.

Table 1, entry 7.

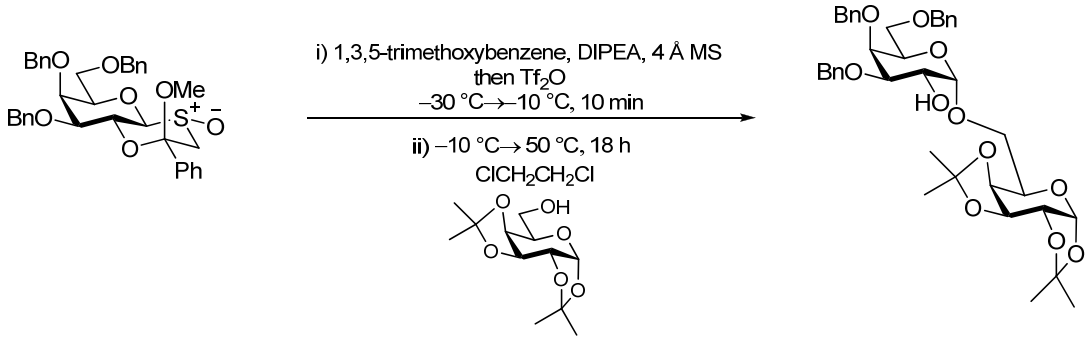
3,4,6-Tri-*O*-acetyl-α-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D galactopyranose (S12) [32]



Tf_2O (26 µL, 0.154 mmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-galactopyranoso)[1,2-*e*]-1,4-oxathiane (*R*)-*S*-oxide **12-*R*** (66 mg, 0.140 mmol), DIPEA (29 µL, 1.69 mmol), 1,3,5-trimethoxybenzene (52 mg, 0.308 mmol) and 4 Å molecular sieves (66 mg) in DCE (540 µL) at −30 ºC. The reaction mixture was warmed to −10 ºC and stirred for 10 min, then DIPEA (167 µL, 0.842 mmol) followed by a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (59 mg, 0.228 mmol) in DCE (120 µL) was added. The reaction mixture was then heated at 50 ºC for 18 h, allowed to cool and diluted with DCM (10 mL), washed with 1M HCl (3 x 10 mL), aq. $NaHCO_3$ (2 x 10 mL) and aq. NaCl (2 x 10 mL) and concentrated to afford a crude syrup. The syrup was redissolved in DCM (1 mL), cat. $BF_3 \bullet OEt_2$ and MeOH (5.7 µL, 0.140 mmol) was then added, after stirring for 30 min at r.t. the reaction mixture was diluted with DCM (5 mL) washed with aq. NaCl (5 mL), dried ($MgSO_4$) and concentrated to afford a crude syrup. The crude syrup was purified using size exclusion chromatography (Sephadex LH-20 resin; eluted with methanol (50 mL/h)) to afford **S12** as a colourless oil (60 mg, 78%); $\mathbf{[\alpha]_D^{22}}$ +43.7 (*c* 1, $CHCl_3$); $\mathbf{\delta_H}$ (500 MHz, $CDCl_3$); 5.52 (d, 1H, $J_{1a,2a}$ 5.1 Hz, H-1a), 5.40 (dd, 1H, $J_{4b,3b}$ 3.3 Hz, $J_{4b,5b}$ 0.8 Hz, H-4b), 5.12 (dd, $J_{2b,3b}$ 10.4 Hz, $J_{3b,4b}$ 3.3 Hz, H-3b), 5.01 (d, 1H, $J_{1b,2b}$ 3.8 Hz, H-1b), 4.64 (dd, 1H, $J_{3a,4a}$ 7.9 Hz, $J_{2a,3a}$ 2.4 Hz, H-3a), 4.33 (dd, 1H, $J_{2a,3a}$ 2.4 Hz, $J_{1a,2a}$ 5.1 Hz, H-2a), 4.31-4.25 (m, 2H, H-5a, H-4a), 4.10-4.08 (d, 2H, $J_{6a,6a'}$ 10 Hz, H-6a, H-6a'), 4.00-3.98 (m, 2H, H-5b, H-2b), 3.95 (m, 1H, H-6b) 3.73 (m, 1H, H-6'b) 2.52 (d, 1H, $J_{2b,2\text{-OH}}$ 11.1 Hz, 2-OH), 2.18 (s, 3H, $C(O)CH_3$), 2.02 (s, 3H, $C(O)CH_3$), 2.14 (s, 3H, $C(O)CH_3$), 1.69 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.28 (s, 6H, CH_3); $\mathbf{\delta_C}$ (75 MHz, $CDCl_3$); 171.0, 170.8, 170.5 (C=O), 109.9, 109.1 ($\underline{C}(OR)_2(CH_3)_2$), 99.7 (C-1b), 96.6 (C-1a), 71.4, 71.1, 71.1, 70.9 (C-2a, C-5a, C-4a, C-3a), 68.7 (C-4b), 68.2 (C-6b), 67.5, 67.5, 66.4 (C-5b, C-2b, C3b), 62.1 (C-6b), 26.4, 26.3, 25.2, 24.8 (CH_3), 21.2, 21.1, 21.0 ($C(O)\underline{C}H_3$); **HRMS**: Found $[M+Na]^+$ 571.1975, $C_{24}H_{36}O_{14}Na$ requires 571.1997.

Table 1, entry 8.

3,4,6-Tri-*O*-benzyl-α-D-galactopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (S13)



Tf_2O (17 μL, 0.1 mmol) was added to a solution of 2-methoxy-2-(*S*)-phenyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-galactopyranoso)[1,2-*e*]-1,4-oxathiane-(*R*)-*S*-oxide **13-*R*** (56 mg, 91 μmol), DIPEA (19 μL, 0.109 mmol), 1,3,5-trimethoxybenzene (34 mg, 0.2 mmol) and 4 Å molecular sieves (50 mg) in DCE (350 μL) at −30 ºC. The reaction mixture was warmed to −10 ºC and stirred for 10 min, then DIPEA (95 μL, 0.547 mmol) followed by a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (59 mg, 0.228 mmol) in DCE (85 μL) was added. The reaction mixture was then heated at 50 ºC for 18 h, allowed to cool and diluted with DCM (10 mL), washed with 1M HCl (3 x 10 mL), aq. $NaHCO_3$ (2 x 10 mL) and aq. NaCl (2 x 10 mL) and concentrated to afford a crude syrup. The syrup was redissolved in DCM (1 mL), cat. BF_3•OEt_2 and MeOH (7.4 μL, 0.184 mmol) was added, after stirring for 30 min at r.t. the reaction mixture was diluted with DCM (5 mL) washed with aq. NaCl (5 mL), dried ($MgSO_4$) and concentrated to afford a crude syrup. The crude syrup was purified size exclusion chromatography (Sephadex LH-20 resin; eluted with methanol (50 mL/h)) to afford **S13** (50 mg, 79%) as a colourless oil; $[\alpha]_D^{21}$ +35.7 (*c* 2.5, $CHCl_3$); δ_H (500 MHz, $CDCl_3$); 7.39-7.23 (m, 15H, ArH), 5.51 (d, 1H, $J_{1a,2a}$ 5.0 Hz, H-1a), 4.95 (d, 1H, $J_{1b,2b}$ 3.9 Hz, H-1b), 4.90 (d, 1H, *J* 11.5 Hz, OCH_2Ph), 4.75 (d, 1H, *J* 12.0 Hz, OCH_2Ph), 4.72 (d, 1H, *J* 12.0 Hz, OCH_2Ph), 4.60 (dd, 1H, $J_{3a,4a}$ 7.9 Hz, $J_{2a,3a}$ 2.3 Hz, H-3a), 4.57 (d, 1H, *J* 11.5 Hz, OCH_2Ph), 4.49 (d, 1H, *J* 11.8 Hz, OCH_2Ph), 4.43 (d, 1H, *J* 11.8 Hz, OCH_2Ph), 4.31 (dd, 1H, $J_{1a,2a}$ 5.0 Hz, $J_{2a,3a}$ 2.3 Hz, H-2a), 4.21 (dd, 1H, $J_{3a,4a}$ 7.8 Hz, $J_{4a,5a}$ 1.7 Hz, H-4a), 4.16 (m, 1H, H-2b), 4.04-3.98 (m, 3H, H-5a, H-4b, H-5b), 3.87 (dd, 1H, $J_{6a,6'a}$ 10.6 Hz, $J_{5a,6a}$ 7.0 Hz, H-6a), 3.72 (dd, 1H, $J_{6a,6'a}$ 10.6 Hz, $J_{5a,6'a}$ 5.8 Hz, H-6'a), 3.68 (dd, 1H, $J_{3b,4b}$ 10.1 Hz, $J_{2b,3b}$ 2.7 Hz, H-3b), 3.60 (dd, 1H, $J_{6b,6'b}$ 9.2 Hz, $J_{5b,6b}$ 7.6 Hz, H-6b), 3.54 (dd, 1H, $J_{6b,6'b}$ 9.2 Hz, $J_{5b,6'b}$ 5.8 Hz, H-6'b), 1.52 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.33 (s, 3H, CH_3); δ_C (75 MHz, $CDCl_3$); 139.1, 139.0, 138.5, 128.8, 128.8, 128.6, 128.6, 128.2, 128.1, 128.0, 127.9 (ArC), 109.9, 109.1 ($\underline{C}(OR)_2(CH_3)_2$), 99.7 (C-1b), 96.7 (C-1a), 80.1 (C-3b), 74.7, 66.5 (C-4b, C-5b), 75.1, 73.8, 72.9 (OCH_2Ph), 71.5, 71.1,

71.0, 70.3, 69.8 (C-2a, C-3a, C-4a, C-5a, C-2b), 69.1 (C-6b), 67.6 (C-6a), 26.5, 26.4, 25.3, 24.9 (CH_3); **HRMS**: Found $[M+Na]^+$ 715.3089, $C_{39}H_{48}O_{11}Na$ requires 715.3094.

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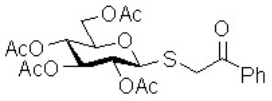

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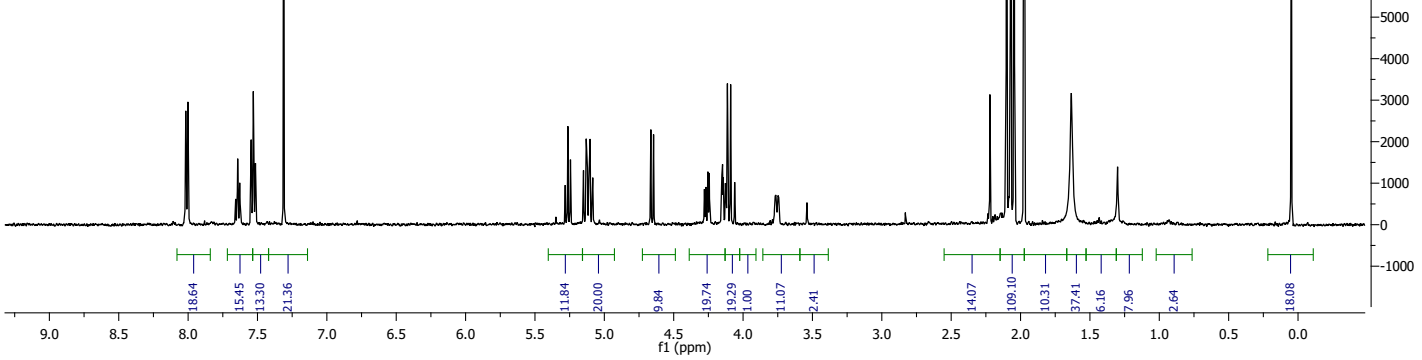

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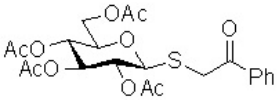

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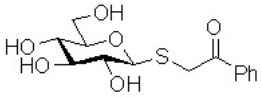

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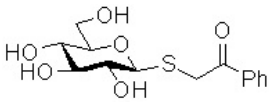

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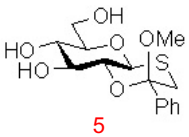

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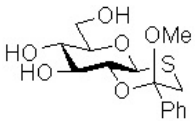

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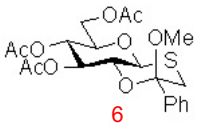

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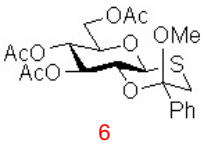

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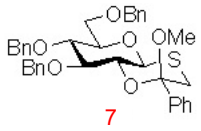

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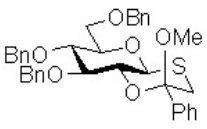

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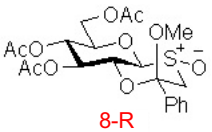

8-R

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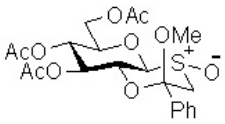

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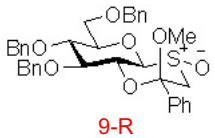
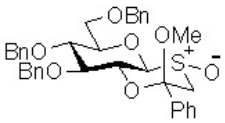
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



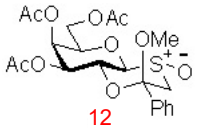
9-R

	Parameter	Value
1	Solvent	CDCl3
2	NAME	samH6141
3	EXPNO	10
4	PROCNO	1
5	INSTRUM	dpx300
6	SF	75.4677190 MHz
7	Temp	
8	PULPROG	zgpg30
9	Nucleus	13C
10	SFO1	75.4756440 MHz
11	SWH	18832.393 Hz
12	NS	2400

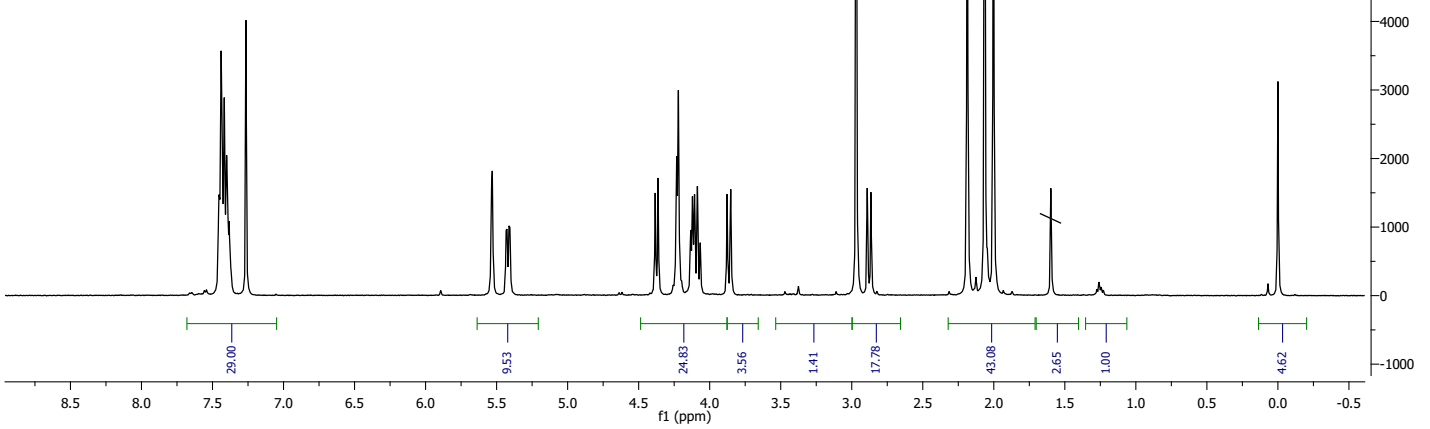


9-R

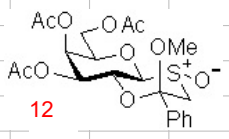
	Parameter	Value
1	NAME	Sam58086
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300241 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



12

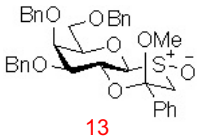


	Parameter	Value
1	Title	samH5617
2	Spectrometer	dpx300
3	Solvent	CDCl3
4	Temperature	300.0
5	Pulse Sequence	zgpg30
6	Number of Scans	2400
7	Spectrometer Frequency	75.48
8	Spectral Width	18832.4
9	Nucleus	13C



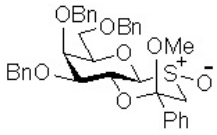
12

	Parameter	Value
1	NAME	Sam59635
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300443 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



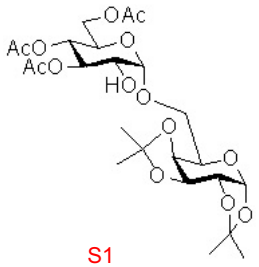
13

	Parameter	Value
1	Solvent	CDCl3
2	NAME	samH7898
3	EXPNO	10
4	PROCNO	1
5	INSTRUM	dpx300
6	SF	75.4677190 MHz
7	Temp	
8	PULPROG	zgpg30
9	Nucleus	13C
10	SFO1	75.4756440 MHz
11	SWH	18832.393 Hz
12	NS	2400



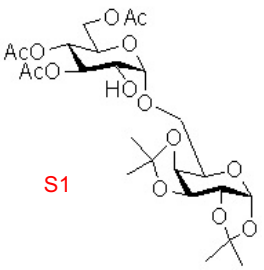
13

	Parameter	Value
1	NAME	Sam54302
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300165 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



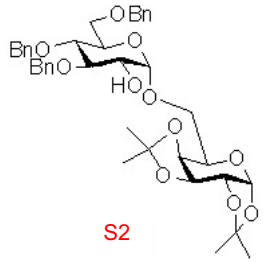
S1

	Parameter	Value
1	Solvent	CDCl3
2	NAME	samH277
3	EXPNO	10
4	PROCNO	1
5	INSTRUM	dpx300
6	SF	75.4677477 MHz
7	Temp	
8	PULPROG	zgpg30
9	Nucleus	13C
10	SFO1	75.4756440 MHz
11	SWH	18832.393 Hz
12	NS	2400



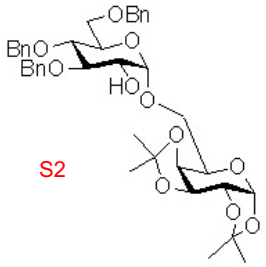
S1

	Parameter	Value
1	NAME	Sam54559
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300272 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



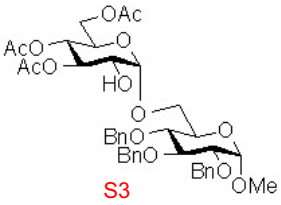
S2

	Parameter	Value
1	Solvent	CDCl3
2	NAME	samG8282
3	EXPNO	10
4	PROCNO	1
5	INSTRUM	dpx300
6	SF	75.4677490 MHz
7	Temp	
8	PULPROG	zgpg30
9	Nucleus	13C
10	SFO1	75.4756440 MHz
11	SWH	18832.393 Hz
12	NS	2400



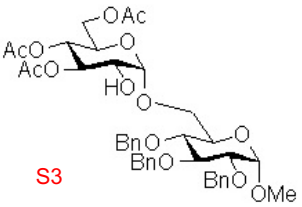
S2

	Parameter	Value
1	NAME	Sam59051
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300254 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



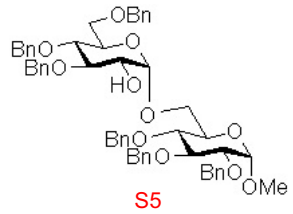
S3

	Parameter	Value
1	Solvent	CDCl3
2	NAME	samH6615
3	EXPNO	10
4	PROCNO	1
5	INSTRUM	dpx300
6	SF	75.4677190 MHz
7	Temp	
8	PULPROG	zgpg30
9	Nucleus	13C
10	SFO1	75.4756440 MHz
11	SWH	18832.393 Hz
12	NS	2400



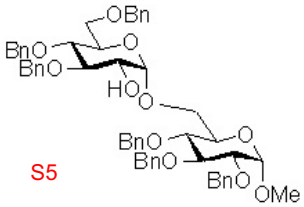
S3

	Parameter	Value
1	NAME	Sam59015
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300281 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



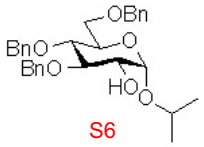
S5

	Parameter	Value
1	Solvent	CDCl3
2	NAME	samH6558
3	EXPNO	10
4	PROCNO	1
5	INSTRUM	dpx300
6	SF	75.4677190 MHz
7	Temp	
8	PULPROG	zgpg30
9	Nucleus	13C
10	SFO1	75.4756440 MHz
11	SWH	18832.393 Hz
12	NS	2400



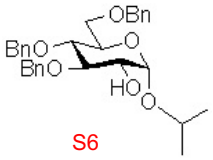
S5

	Parameter	Value
1	NAME	Sam59986
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300257 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



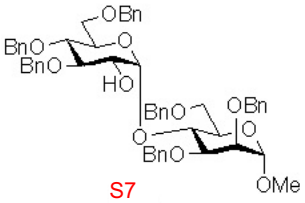
S6

	Parameter	Value
1	Solvent	CDCl3
2	NAME	samH7470
3	EXPNO	11
4	PROCNO	1
5	INSTRUM	dpx300
6	SF	75.4677475 MHz
7	Temp	
8	PULPROG	zgpg30
9	Nucleus	13C
10	SFO1	75.4756440 MHz
11	SWH	18832.393 Hz
12	NS	2400

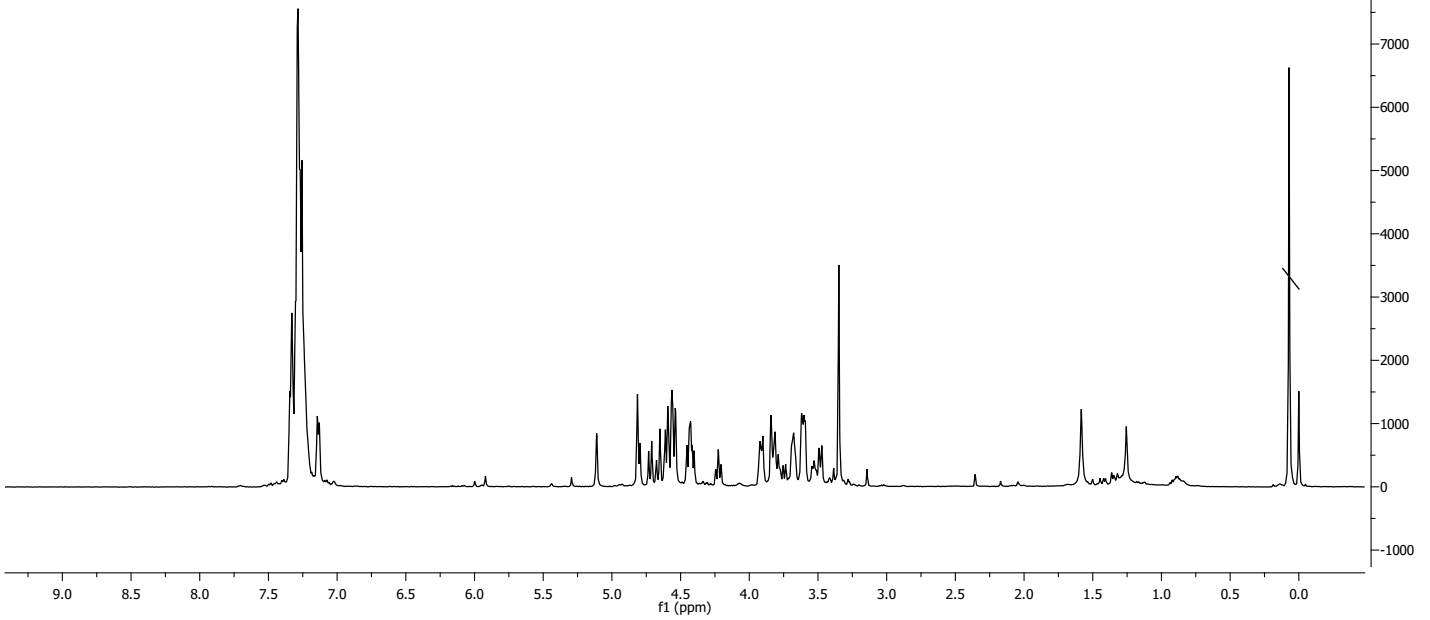


S6

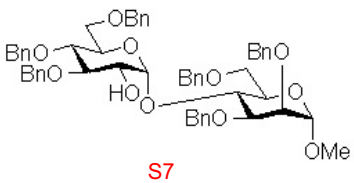
	Parameter	Value
1	NAME	Sam58675
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300640 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



S7

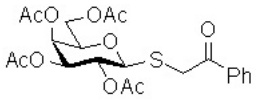


	Parameter	Value
1	Solvent	CDCl3
2	NAME	samH6217
3	EXPNO	10
4	PROCNO	1
5	INSTRUM	dpx300
6	SF	75.4678253 MHz
7	Temp	
8	PULPROG	zgpg30
9	Nucleus	13C
10	SFO1	75.4756440 MHz
11	SWH	18832.393 Hz
12	NS	2400



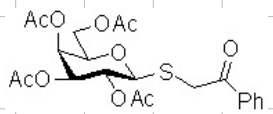
S7

	Parameter	Value
1	NAME	Sam57763
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300118 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



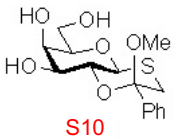
S9

	Parameter	Value
1	Title	samH5012
2	Spectrometer	dpx300
3	Solvent	CDCl3
4	Temperature	300.0
5	Pulse Sequence	zgpg30
6	Number of Scans	2400
7	Spectrometer Frequency	75.48
8	Spectral Width	18832.4
9	Nucleus	13C



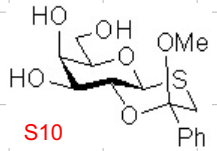
S9

	Parameter	Value
1	NAME	Sam58532
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300642 MHz
6	Solvent	MeOD
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



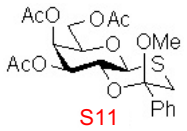
S10

	Parameter	Value
1	Title	samH7012
2	Spectrometer	dpx300
3	Solvent	MeOH
4	Temperature	300.0
5	Pulse Sequence	zgpg30
6	Number of Scans	2400
7	Spectrometer Frequency	75.47
8	Spectral Width	18832.4
9	Nucleus	13C



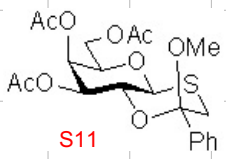
S10

	Parameter	Value
1	NAME	Sam57942
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300239 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



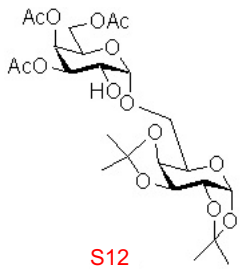
S11

	Parameter	Value
1	Title	samH5408
2	Spectrometer	dpx300
3	Solvent	CDCl3
4	Temperature	300.0
5	Pulse Sequence	zgpg30
6	Number of Scans	160
7	Spectrometer Frequency	75.48
8	Spectral Width	18832.4
9	Nucleus	13C



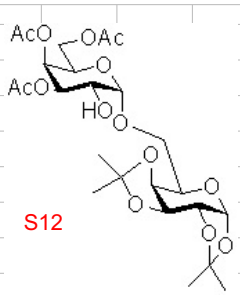
S11

	Parameter	Value
1	NAME	Sam58521
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300190 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



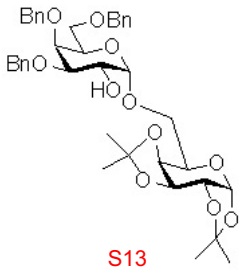
S12

	Parameter	Value
1	Title	samH5990
2	Spectrometer	dpx300
3	Solvent	CDCl3
4	Temperature	300.0
5	Pulse Sequence	zgpg30
6	Number of Scans	2400
7	Spectrometer Frequency	75.48
8	Spectral Width	18832.4
9	Nucleus	13C



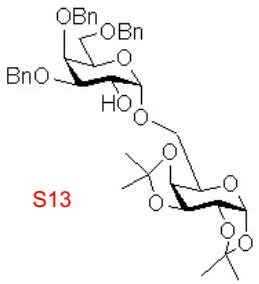
S12

	Parameter	Value
1	NAME	Sam59969
2	EXPNO	10
3	PROCNO	1
4	INSTRUM	avance500
5	SF	500.2300292 MHz
6	Solvent	CDCl3
7	Temp	300.0 K
8	PULPROG	zg30
9	Nucleus	1H
10	SFO1	500.2327513 MHz
11	SWH	7002.801 Hz
12	NS	32



S13

	Parameter	Value
1	Solvent	CDCl3
2	NAME	samH7897
3	EXPNO	10
4	PROCNO	1
5	INSTRUM	dpx300
6	SF	75.4677190 MHz
7	Temp	
8	PULPROG	zgpg30
9	Nucleus	13C
10	SFO1	75.4756440 MHz
11	SWH	18832.393 Hz
12	NS	2400



S13