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Electronic Supplementary Information

Bio-inspired Synthesis of Rare and Unnatural Carbohydrates and Cyclitols through Strain Driven Epimerization

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Table of Contents

1) Materials and methods

All chemicals and solvents were purchased from commercial suppliers and used directly. Reactions were monitored by thin layer chromatography using Merck pre-coated silica plates (60 F254). Plates were visualized under ultraviolet light at 254 nm and also by charring using cerium molybdate solution (235 mL of distilled water, 12 g of ammonium molybdate, 0.5 g of ceric ammonium molybdate and 15 mL of concentrated sulphuric acid). Column chromatography was performed on silica gel (200-400 mesh). ^{1}H, ^{19}F, ^{13}C NMR spectra were recorded using 500, 470 and 125 MHz NMR spectrometers, respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, δ = 0.0) as internal standard and expressed in parts per million. Spin multiplicities were given as s (singlet), d (doublet), t (triplet), (q) quartet, dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet) and m (multiplet). Coupling constants (*J*) are given in Hertz. The assignment of protons and carbons were done using two dimensional spectra COSY, HMQC and HMBC. IR spectra were recorded using IR Prestige-21 (Shimadzu) spectrometer. Melting points were determined by using Stuart, SMP-30 melting point apparatus and were uncorrected. Specific rotations were recorded on a Rudolph Autopol III automatic polarimeter. Elemental analyses were done on Elementar, vario MICRO cube elemental analyzer. X-ray intensity data measurements of freshly grown crystals were carried out at 298K on a Bruker-KAPPA APEX II CCD diffractometer with graphite-monochromatized (MoK = 0.71073Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. Data were collected with scan width of 0.3° at different settings of φ (0°, 90° and 180°) keeping the sample to detector distance fixed at 40 mm. The X-ray data collection was monitored by SMART program (Bruker, 2003).[1] All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2003). SHELX-97 was used for structure solution and full matrix least-squares refinement on *F*2.[2] All the hydrogen atoms were placed in geometrically idealized position and refined in the riding model approximation with C-H = 0.95 Å, and with U_{iso} (H) set to 1.2U_{eq} (C). Molecular diagrams were generated using ORTEP-3.[3] Geometrical calculations were performed using SHELXTL (Bruker, 2003) and PLATON.[4]

2) Comparison of energies of ketal derivatives of *cis* & *trans* diols by quantum mechanical calculations

Quantum mechanical calculations (DFT) has been carried out to compare the relative energies of model compounds I-IV (Fig. S1) by using B3LYP/6-31G(d,p)[5] level of theory (Guassian09).[6] Among alcohols I & II, the *cis* ketal I is more stable by 2.7 Kcal/mol than the alcohol II with *trans* ketal. Interestingly, the difference in energy is more pronounced in the case of ketones III & IV. The ketone III having *cis* ketal is stable by 4.56 Kcal/mol than the ketone IV having *trans* ketal.

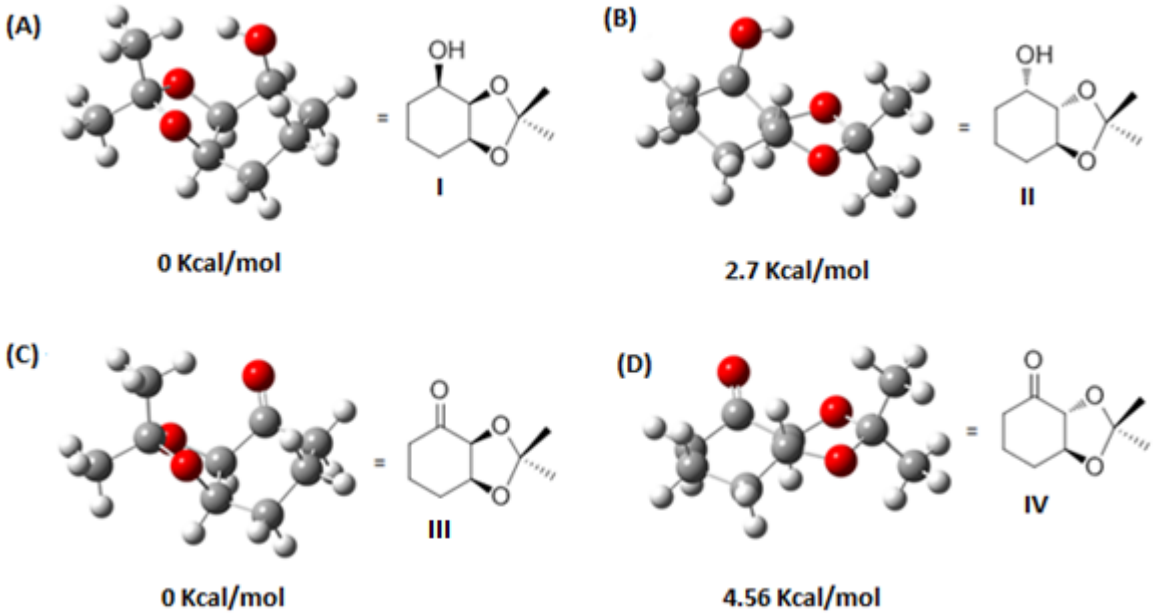


Fig. **S1**: Optimised structures and relative energies of ketals I-IV.

Table S1. Atomic co-ordinates of alcohol I [B3LYP/6-31G(d,p)]

O	-0.93613100	-1.90287200	0.44928200
O	1.02618200	-0.74720100	-0.88200300
O	0.81513100	0.91527300	0.67607400
C	-2.63909500	-0.37213200	-0.19969400
C	-1.37226800	-1.10721700	-0.64095700
C	-0.25019500	-0.12982200	-1.10468000
C	-0.13274900	1.21441800	-0.34919800
C	-1.41698200	1.77282600	0.26068600
C	-2.32228000	0.69127500	0.85746800
C	1.75232700	0.00669200	0.12412700
C	2.22020000	-0.92752400	1.23132800
C	2.90976700	0.73603300	-0.56272500
H	-3.10979900	0.09568900	-1.07589600
H	-1.61130300	-1.75886200	-1.49822100
H	-0.37091500	0.05298800	-2.17962000
H	0.29593400	1.96496900	-1.03188600

H	-1.13763400	2.52431700	1.00699600
H	-1.82503900	0.21278300	1.70664500
H	2.85628300	-1.71610900	0.82023700
H	1.35198000	-1.37006300	1.72351100
H	2.79434600	-0.36990700	1.97600100
H	2.53894000	1.41092700	-1.33837600
H	3.58188100	0.01442700	-1.03506600
H	3.47608100	1.32017200	0.16803500
H	-0.02330200	-2.14506900	0.22960900
H	-1.96028200	2.30416300	-0.53247600
H	-3.24582700	1.14647600	1.23154900
H	-3.34515000	-1.11578900	0.18400400

Table S2. Atomic co-ordinates of alcohol II [B3LYP/6-31G(d,p)]

O	0.99770100	-0.98729200	0.44952800
O	-1.50703300	-1.84359100	-0.73713800
O	1.18297000	1.20072200	-0.30516400
C	-0.23480900	-0.29999500	0.64757200
C	-1.48069700	-1.16286000	0.51215900
C	-2.68901600	-0.20919300	0.59779500
C	-2.60400600	1.01696900	-0.34132200
C	-1.26667800	1.79445200	-0.23711800
C	-0.17089800	0.76440200	-0.42931800
C	1.94811300	0.02187400	0.01086600
C	2.65662200	-0.51325900	-1.22862300
C	2.90040400	0.36889100	1.14822800
H	-0.24712100	0.18225500	1.63900200
H	-1.53237400	-1.88880600	1.33905000
H	-2.77125600	0.12986800	1.63856900

H	-3.44239700	1.68908500	-0.12945100
H	-1.22035800	2.58123900	-0.99720000
H	-0.31517700	0.27933300	-1.40596800
H	3.15417500	-1.46063400	-1.00202500
H	3.40599800	0.20332700	-1.57552200
H	1.93568600	-0.68245000	-2.03244500
H	3.50984200	-0.49905400	1.41426400
H	2.33290600	0.68603200	2.02638600
H	3.56176300	1.18693900	0.84929900
H	-0.62397100	-2.22620400	-0.84983200
H	-3.59674700	-0.78093900	0.37894000
H	-2.73004500	0.67625500	-1.37530600
H	-1.16424800	2.27736400	0.74299200

Table S3. Atomic co-ordinates of ketone III [B3LYP/6-31G(d,p)]

O	0.93796600	2.26872800	-0.01619700
O	-1.10084000	0.66217900	-0.96700600
O	-0.72786800	-0.95608700	0.62163900
C	2.56735100	0.49846300	-0.00512000
C	1.22925500	1.13562100	-0.33694100
C	0.23541900	0.21608100	-1.07763100
C	0.17181700	-1.19462400	-0.46221800
C	1.48318300	-1.78362700	0.04799800
C	2.33067200	-0.77615600	0.83223200
C	-1.70456500	-0.01082600	0.16122200
C	-1.98711100	0.97666900	1.28528200
C	-2.95784100	-0.72661700	-0.33761700
H	3.08302100	0.22644700	-0.93784100

H	0.51504100	0.19542300	-2.13984800
H	-0.28589500	-1.88416500	-1.18855400
H	1.25304200	-2.66318800	0.65874500
H	1.81883800	-0.50955700	1.76326300
H	-2.73808700	1.70244800	0.96252300
H	-1.07549100	1.51436600	1.54800200
H	-2.36512500	0.44732700	2.16466500
H	-2.69708300	-1.47096900	-1.09435700
H	-3.64620500	-0.00645300	-0.78795700
H	-3.46453700	-1.22811900	0.49152100
H	2.04974400	-2.14305000	-0.82135800
H	3.29032000	-1.22449800	1.10993800
H	3.17927100	1.23552700	0.52051700

Table S4. Atomic co-ordinates of ketone IV [B3LYP/6-31G(d,p)]

O	1.17814100	-1.21958700	0.13801100
O	-1.60242100	2.29515600	0.31323300
O	0.97125700	1.06330100	-0.23132600
C	-0.16585900	-0.83149200	0.37528400
C	-1.24615900	-1.83012400	0.00486400
C	-2.60555300	-1.14592700	0.28098000
C	-2.74931600	0.25905400	-0.36578400
C	-1.53500100	1.16820800	-0.12500600
C	-0.25984900	0.43127900	-0.48166000
C	1.93469700	0.00456400	0.00016400
C	2.85079800	-0.14780900	-1.20673500
C	2.67817200	0.32676200	1.29060800
H	-0.29263400	-0.54632200	1.43458800

H	-1.15862900	-2.74814000	0.59448100
H	-2.73110200	-1.04246500	1.36576100
H	-3.63775300	0.77447200	0.00695200
H	-0.34317300	0.12413000	-1.54028400
H	3.52548600	-0.99664300	-1.06444900
H	3.44660800	0.75802700	-1.34576400
H	2.25791500	-0.32307100	-2.10776500
H	3.43022900	-0.43982600	1.49617700
H	1.97825900	0.37123600	2.12840000
H	3.17482500	1.29711800	1.20589200
H	-2.86482400	0.14614700	-1.45294800
H	-3.42380100	-1.78516000	-0.06487400
H	-1.14879200	-2.10754400	-1.05178900

3) Experimental procedures and analytical data

General procedure I: (for Dess-Martin periodinane oxidation)

To a solution of alcohol (1.0 mmol) in dry DCM (15 mL), Dess-Martin periodinane (1.2 mmol) was added at room temperature under nitrogen atmosphere. After completion of the reaction, the reaction mass was quenched with saturated sodium thiosulphate solution and was extracted using dichloromethane. The organic layer was washed with sat. $NaHCO_3$ solution followed by water and brine. The organic layer was separated, dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mass thus obtained was purified by column chromatography.

General Procedure II: (for Swern oxidation)

To a solution of oxalyl chloride (1.2 mmol) in dry CH_2Cl_2 (5 mL), DMSO (2 mmol) was added dropwise at -78 ^oC under nitrogen atmosphere. After stirring for 10 minutes, a solution of alcohol (1 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise over 5 minutes. The reaction mixture was stirred for 15 min, then Et_3N (10 mmol) was added dropwise. After 10 more minutes, the reaction mass was warmed to room temperature and continued the stirring for 1-4 h. Then the reaction mass was quenched with water and extracted with CH_2Cl_2. The organic layer was washed successively with saturated $NaHCO_3$ solution, water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product thus obtained was purified by column chromatography.

General procedure III: (for isomerisation using triethyl amine)

To a solution of ketone (1.0 mmol) in CH_2Cl_2 (10 mL), Et_3N (2.0 mmol) was added at room temperature and the mixture was stirred for 5-6 h. After completion of the reaction, the reaction mixture was diluted with CH_2Cl_2 and washed successively with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product thus obtained was purified by column chromatography.

General procedure IV: (for reduction using sodium borohydride)

Sodium borohydride (1.5 mmol) was added to a solution of ketone (1.0 mmol) in methanol (5 mL) at 0 ^oC. After 30 min, the reaction was quenched by the addition of acetone and the solvent was evaporated. The crude reaction mass was dissolved in ethyl acetate, washed successively with water and brine solution, the organic layer was dried over anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure and purified by column chromatography.

General procedure V: (for reduction using K-selectride)

To a solution of ketone (1.0 mmol) in THF (5 mL) at -78 °C was added slowly a 1 M solution of K-selectride (1.5 mmol), and the mixture was further stirred at -78 °C for 1 h. THF was evaporated off under reduced pressure and the crude reaction mass was extracted with ethyl acetate, washed successively with water and brine solution, and the organic layer was dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography.

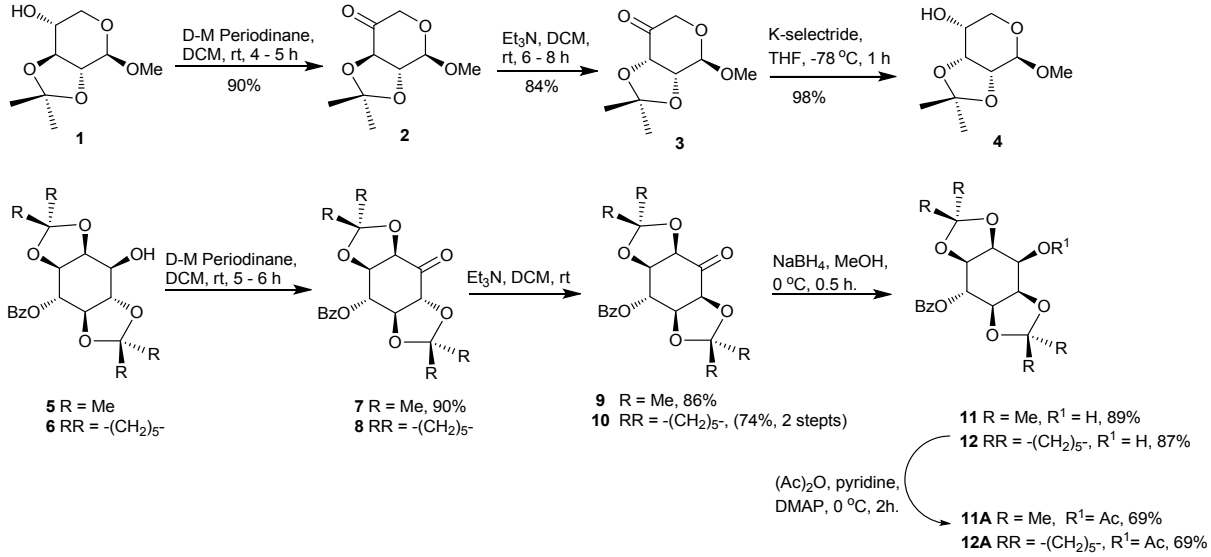
General procedure VI: (for reduction using sodium triacetoxyborohydride)

To a solution of ketone (1 mmol) in dry DCM (5 mL), sodium triacetoxyborohydride (1.5 mmol) was added and the mixture was stirred at rt for 3-4 h. After completion of the reaction, the reaction mass was diluted with ethyl acetate and washed successively with saturated $NaHCO_3$ solution, water and brine. The organic layer was dried over anhydrous Na_2SO_4, and solvent was evaporated under reduced pressure. The crude mass thus obtained was purified by column chromatography.

General procedure VII: (for acetylation)

To a solution of alcohol (1 mmol) in dry pyridine (5 mL), acetic anhydride (5 mmol) and DMAP (0.5 mmol) were added and the mixture was stirred at 0 ^oC for 2 h. After consumption of the starting material, the reaction mass was quenched with sat. NH_4Cl solution. The reaction mass was extracted with ethyl acetate, and the organic layer was washed with sat. $NaHCO_3$ solution, water and brine. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Further purification was done by column chromatography.

Scheme S1:



Methyl 2,3-*O*-isopropylidene-β-D-threo-pentopyranosid-4-ulose (2)

Dess-Martin periodinane oxidation of methyl 2,3-*O*-isopropylidene-β-D-xylopyranoside[7] (**1**) (200 mg, 0.98 mmol) by adopting the general procedure I provided ketone **2** (178 mg, 90%) as a colourless liquid: R_f = 0.71 (ethyl acetate/petroleum ether, 3:2; v/v); $[\alpha]_D^{23}$ = -12.3° (c 0.4, CH_2Cl_2); IR (Neat, cm^{-1}) 1712, 1217, 1097; ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.06 (d, *J* = 6.25 Hz, 1H, H-3), 4.76 (d, *J* = 11.15 Hz, 1H, H-1), 4.18 (d, *J* = 17.6 Hz, 1H, H-5A), 4.12 (d, *J* = 17.6 Hz, 1H, H-5B), 3.91 (dd, *J* = 6.25 Hz, 11.1 Hz, 1H, H-2), 3.4 (s, 3H, OCH_3), 1.43 (s, 3H, CH_3), 1.38 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 202.6, 113.3, 101.2 (C-3), 78.5 (C-1), 77.6 (C-2), 67.7 (C-5), 55.2 (O*C*H$_3$), 26.6, 26.4. Elemental analysis calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.53; H, 7.11.

Methyl 2,3-*O*-isopropylidene-β-D-erythro-pentopyranosid-4-ulose (3)

Isomerisation of compound **2** (100 mg, 0.5 mmol) by adopting the general procedure III provided **3**[8] (84 mg, 84%) as a colourless liquid: R_f = 0.8 (ethyl acetate/ petroleum ether, 1:1; v/v); ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.71 (d, *J* = 2.25 Hz, 1H, H-3), 4.46 (d, *J* = 7.15 Hz, 1H, H-1), 4.35 (dd, *J* = 2.2 Hz, 7.15 Hz, 1H, H-2), 4.07 (d, *J* = 16.9 Hz, 1H, H-5A), 4.03 (d, *J* = 16.9 Hz, 1H, H-5B), 3.31 (s, 3H, OCH_3), 1.31 (s, 3H, CH_3), 1.24 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 204.5, 111.4, 99.3 (C-3), 77.7 (C-2), 75.5 (C-1), 66.3 (C-5), 56.2 (O*C*H$_3$), 27.2, 25.8. Elemental analysis calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.26; H, 7.09.

Methyl 2,3-*O*-isopropylidene-β-D-ribopyranoside (4)

Reduction of **3** (20 mg, 0.1 mmol) using sodium borohydride (general procedure IV) and K-selectride (general procedure V) afforded the known compound **4**[8] in 88% (18 mg) and 98% (20 mg) respectively: R_f = 0.5 (ethyl acetate/ petroleum ether, 1:1; v/v); IR (Neat, cm^{-1}) 3597, 1230, 1097; ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.97 (d, *J* = 6.5 Hz, 1H, HO-4), 4.25 (dd, *J* = 3.5 Hz, 5.5 Hz, 1H, H-3), 4.23 (d, *J* = 5 Hz, 1H, H-1), 3.84-3.81 (m, 1H, H-4), 3.77 (t, *J* = 5.25 Hz, 1H, H-2), 3.52 (dd, *J* = 5.5 Hz, 10.5 Hz, 1H, H-5A), 3.34 (t, *J* = 10.25 Hz, 1H, H-5B), 3.25 (s, 3H, OCH_3), 1.37 (s, 3H, CH_3), 1.21 (s, 3H, CH_3); ^{13}C NMR (125 MHz,

DMSO-d_6) δ 109.0, 101.5 (C-1), 75.6 (C-2), 74.7 (C-3), 63.6 (C-4), 62.7 (*C*H$_2$), 55.7 (O*C*H$_3$), 27.4, 25.7. $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 53.10; H, 7.76.

(±)-4-*O*-Benzoyl-2,3:5,6-di-*O*-isopropylidene-*myo*-inosose (7)

Dess-Martin periodinane oxidation of (±)-6-*O*-benzoyl-1,2:4,5-di-*O*-isopropylidene-*myo*-inositol[9] (**5**) (1.0 g, 2.75 mmol) by adopting the general procedure I provided **7** (0.9 g, 90%) as a white solid: m.p. = 214-216 °C; R_f = 0.38 (ethyl acetate/ petroleum ether, 2:3; v/v); IR (KBr, cm^{-1}) 1755, 1722, 1276; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.04 (d, *J* = 7.15 Hz, 2H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 5.69 (dd, *J* = 5.1 Hz, 10.4 Hz, 1H, H-4), 4.88 (d, *J* = 11.1 Hz, 1H, H-6), 4.67 (t, *J* = 5.5 Hz, 1H, H-5), 4.45 (d, *J* = 5.9 Hz, 1H, H-2), 4.32 (t, *J* = 10.7 Hz, 1H, H-3), 1.54 (s, 3H, C*H*$_3$), 1.45 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.1, 165.1, 134.3, 129.9, 129.5, 129.4, 113.5, 111.8, 80.3 (C-5), 79.1 (C-2), 78.5 (C-6), 75.9 (C-4), 75.3 (C-3), 27.5, 27.3, 26.9, 25.7. Elemental analysis calcd for $C_{19}H_{22}O_7$: C, 62.97; H, 6.12. Found: C, 62.74; H, 6.26.

4-*O*-Benzoyl-2,3:5,6-di-*O*-isopropylidene-*epi*-inosose (9)

Isomerisation of compound **7** (50 mg, 0.14 mmol) by adopting the general procedure III provided **9** (43 mg, 86%) as a white solid: m.p. = 172-174 °C; R_f = 0.45 (ethyl acetate/ petroleum ether, 2:3; v/v); IR (KBr, cm^{-1}) 1751, 1722; ^{1}H NMR (500 MHz, C_6D_6) δ 8.14 (d, *J* = 7.05 Hz, 2H), 7.06 (d, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.42 Hz, 2H), 5.59 (t, *J* = 9.1 Hz, 1H, H-4), 4.21 (t, *J* = 8.7 Hz, 2H, H-3 & H-5), 4.03 (d, *J* = 8.3 Hz, 2H, H-2 & H-6), 1.47 (s, 6H, 2x C*H*$_3$), 1.14 (s, 6H, 2x C*H*$_3$); ^{13}C NMR (125 MHz, C_6D_6) δ 198.3, 164.3, 132.2, 129.6, 129.3, 127.6, 111.8, 76.4 (C-2 & C-6), 75.4 (C-3 & C-5), 74.8 (C-6), 26.2, 24.8. Elemental analysis calcd for $C_{19}H_{22}O_7$: C, 62.97; H, 6.12. Found: C, 63.04; H, 6.18.

6-*O*-Benzoyl-1,2:4,5-di-*O*-isopropylidene-*epi*-inositol (11)

Reduction of **9** (50 mg, 0.14 mmol) using sodium borohydride (general procedure IV) and K-selectride (general procedure V) afforded compound **11** in 89% (45 mg) and 83% (42 mg) respectively: m.p. = 251-252 °C; R_f = 0.65 (ethyl acetate/ petroleum ether, 2:3; v/v); IR (KBr, cm^{-1}) 3500, 1720, 1278; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.01 (dd, J = 0.95 Hz, 8.15 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 5.96 (t, *J* = 8.3 Hz, 1H, H-6), 4.94 (d, *J* = 3.3 Hz, 1H, HO-3), 4.31 (t, *J* = 8.3 Hz, 2H, H-1 & H-5), 4.22 (dd, *J* = 2.7 Hz, 8.4 Hz, 2H, H-2 & H-4), 4.06 (m, 1H, H-3), 1.43 (s, 6H, 2x C*H*$_3$), 1.27 (s, 6H, 2x C*H*$_3$); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.6, 133.3, 130.0, 129.2, 128.7, 109.6, 76.0 (C-6), 75.4 (C-1 & C-5), 74.5 (C-2 & C-4), 66.4 (C-3), 26.2, 24.8. Elemental analysis calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.42; H, 6.63.

3-*O*-Acetyl-6-*O*-benzoyl-1,2:4,5-di-*O*-isopropylidene-*epi*-inositol (11A)

Stereochemistry of the newly formed stereocentre (C-3) in **11** was confirmed by acetylation. In the ^{1}H NMR of compound **11A**, H-3 showed a coupling constant 3.6 Hz (triplet) which indicates that H-3 proton is *syn* to H-2 & H-4 protons.

Acetylation of alcohol **11** (30 mg, 0.08 mmol) by adopting the general procedure VII provided **11A** (23 mg, 69%) as a white solid: m.p. = 208-210 °C; R_f = 0.35 (ethyl acetate/ petroleum ether, 3:7; v/v); IR (KBr, cm^{-1}) 1753, 1720, 1273; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.16 (d, *J* = 7.05 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 2H), 6.30 (t, *J* = 8.65 Hz, 1H, H-6), 5.73 (t, *J* = 3.6 Hz, 1H, H-3), 3.99 (t, *J* = 8.4 Hz, 2H, H-1 & H-5), 3.63 (dd, *J* =

3.6 Hz, 8.2 Hz, 2H, H-2 & H-4), 1.9 (s, 3H, OAc), 1.43 (s, 6H, 2x CH_3), 1.15 (s, 6H, 2x CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.8, 164.9, 132.4, 130.6, 129.7, 128.0, 110.6, 75.8 (C-1 & C-5), 75.5 (C-6), 72.8 (C-2 & C-4), 67.1 (C-3), 26.4, 24.5, 20.4. Elemental analysis calcd for $C_{21}H_{26}O_8$: C, 62.06; H, 6.45. Found: C, 62.33; H, 6.67.

4-*O*-Benzoyl-2,3:5,6-di-*O*-cyclohexylidene-*epi*- inosose (10)

Dess-Martin periodinane oxidation of (±)-6-*O*-benzoyl-1,2:4,5-di-*O*-cyclohexylidene-*myo*-inositol (**6**)[10] (100 mg, 0.23 mmol) by adopting the general procedure I provided (±)-4-*O*-benzoyl-2,3;5,6-di-*O*-cyclohexylidene-*myo*-inosose (**8**) (94 mg, crude) as a white solid**.** Its purification by column chromatography was difficult due to the cleavage of *trans* ketal. Thus the crude mixture was subjected to isomerisation by adopting the general procedure III to provide **10** (74 mg, 74%, 2 steps) as a white solid.

^{1}H NMR data of crude **8**: ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.02 (d, J = 7.1 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 5.66 (dd, J = 4.9 Hz, 10.2 Hz, 1H), 4.86 (d, J = 11.1 Hz, 1H), 4.64 (t, J = 5.5 Hz, 1H), 4.4 (d, J = 5.85 Hz, 1H), 4.28 (t, J = 10.7 Hz, 1H), 1.76-1.23 (m, 20H). Data of compound **10**: m.p. = 162-164 ^{o}C; R_f = 0.52 (ethyl acetate/ petroleum ether, 3:7; v/v); IR (KBr, cm^{-1}) 1761, 1716, 1267; ^{1}H NMR (500 MHz, C_6D_6) δ 8.16 (d, J = 7.0 Hz, 2H), 7.04 (d, J = 7.4 Hz, 1H), 7.0 (t, J = 7.4 Hz, 2H), 5.61 (t, J = 9.1 Hz, 1H, H-4), 4.25 (t, J = 8.7 Hz, 2H, H-3 & H-5), 4.06 (d, J = 8.4 Hz, 2H, H-2 & H-6), 1.88-1.45 (m, 16H), 1.16 (m, 2H), 1.05 (m, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 199.5, 164.8, 132.7, 130.1, 129.8, 128.2, 113.2, 76.7 (C-3 & C-5), 75.8 (C-4), 75.6 (C-2 & C-6), 36.6, 35.4, 24.8, 23.7. Elemental analysis calcd for $C_{25}H_{30}O_7$: C, 67.86; H, 6.83. Found: C, 67.59; H, 7.10.

6-*O*-Benzoyl-1,2:4,5-di-*O*-cyclohexylidene-*epi*-inositol (12)

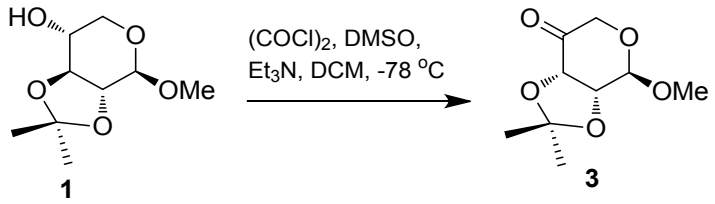
Reduction of **10** (60 mg, 0.135 mmol) by using sodium borohydride as in the general procedure IV provided *epi*-inositol derivative **12** (53 mg, 87%) as a white solid: m.p. = 220-222 ^{o}C; R_f = 0.41 (ethyl acetate/petroleum ether, 2:3; v/v); IR (KBr, cm^{-1}) 3325, 1722. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.02 (d, J = 7.55 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.67 Hz, 2H), 5.94 (t, J = 8.35 Hz, 1H, H-6), 4.90 (d, J = 3.35 Hz, 1H, HO-3), 4.31 (t, J = 8.3 Hz, 2H, H-1 & H-5), 4.21 (dd, J = 2.6 Hz, 8.3 Hz, 2H, H-2 & H-4), 4.09 (m, 1H, H-3), 1.74-1.38 (m, 20H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.6, 133.4, 129.9, 129.3, 128.8, 110.1, 76.1 (C-6), 75.0 (C-1 & C-5), 74.1 (C-2 & C-4), 66.3 (C-3), 35.4, 33.9, 24.6, 23.6, 23.3. Elemental analysis calcd for $C_{25}H_{32}O_7$: C, 67.55; H, 7.26. Found: C, 67.44; H, 7.18.

3-*O*-Acetyl-6-*O*-benzoyl-1,2:4,5-di-*O*-cyclohexylidene-*epi*-inositol (12A)

Stereochemistry of the newly formed stereocentre (C-3) in compound **12** was confirmed by acetylation. In the ^{1}H NMR of compound **12A,** H-3 showed a coupling constant 3.1 Hz (triplet) which indicates that H-3 proton is *syn* to H-2 & H-4 protons.

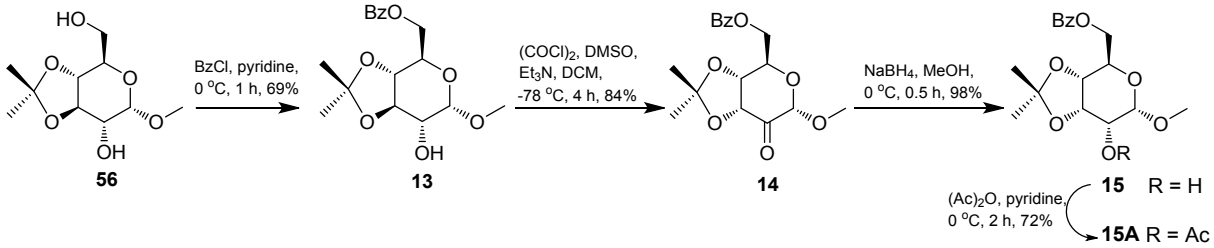
Acetylation of alcohol **12** (40 mg, 0.09 mmol) by adopting the general procedure VII provided **12A** (30 mg, 69%) as a white solid: m.p: 180-182 ^{o}C; R_f = 0.74 (ethyl acetate/ petroleum ether, 3:7; v/v); IR (KBr, cm^{-1}) 1760, 1721; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.03 (d, J = 7.1 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.85 Hz, 2H), 5.79 (t, J = 7.75 Hz, 1H, H-6), 5.5 (t, J = 3.1 Hz, 1H, H-3), 4.4-4.45 (m, 4H, H-1, H-2, H-4 & H-5), 2.1 (s, 3H, OAc), 1.58-1.25 (m, 20H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.0, 164.5, 133.5, 129.6, 129.3, 128.8, 110.4, 75.9 (C-6), 74.7 (C-1 & C-5), 71.8 (C-2 & C-4), 67.6 (C-3), 35.9, 33.8, 24.5, 23.5, 23.2, 20.9. Elemental analysis calcd for $C_{27}H_{34}O_8$: C, 66.65; H, 7.04. Found: C, 66.42; H, 7.24.

Swern oxidation of 1



Swern oxidation of **1** (100 mg, 0.49 mmol) by adopting the general procedure II provided **3** (81.2 mg, 82%) as a colourless liquid.

Scheme S2:



Methyl 6-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-glucopyranoside (13)

Methyl 3,4-*O*-isopropylidene-α-D-glucopyranoside[11] (**56**) (1.44 g, 6.14 mmol) was dissolved in dry pyridine (10 mL) at 0 °C. Benzoyl chloride (0.71 mL, 6.14 mmol) was added dropwise to the reaction mass at this temperature. After 1 h, the reaction mass was quenched with ice cold water. The reaction mass was diluted with ethyl acetate and washed thoroughly with sat. $NaHCO_3$ solution, water and brine. The organic layer was dried over anhydrous Na_2SO_4, evaporated under reduced pressure and the residue was purified by column chromatography using a mixture of dichloromethane and acetone (9:1; v/v) as eluent, to get the benzoate **13** (1.435 g, 69%) as a white solid: m.p. = 114-115 °C; R_f = 0.61 (ethyl acetate/ petroleum ether, 3:7; v/v); $[\alpha]_D^{25.0}$ = 100·8 (c 1.2, CH_2Cl_2); IR (KBr, cm^{-1}) 3512, 1707, 1280; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 5.3 (d, *J* = 6.6 Hz, 1H, HO-2), 4.73 (d, *J* = 2.3 Hz, 1H, H-1), 4.54 (dd, *J* = 2.25 Hz, 12 Hz, 1H, H-6A), 4.34 (dd, *J* = 6.9 Hz, 12.1 Hz, 1H, H-6B), 4.02 (ddd, *J* = 2.2 Hz, 6.95 Hz, 9.5 Hz, 1H, H-5), 3.71 (m, 2H, H-3 & H-2), 3.36 (m, 1H, H-4), 3.32 (s, 3H, OCH_3), 1.39 (s, 3H, CH_3), 1.38 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.4, 133.4, 129.5, 129.1, 128.8, 109.8, 100.3 (C-1), 77.9 (C-2 or C-3), 74.1 (C-4), 70.9 (C-3 or C-2), 69.0 (C-5), 64.0 (C-6), 54.9 (OCH_3), 26.8, 26.4. Elemental analysis calcd for $C_{17}H_{22}O_7$: C, 60.35; H, 6.55. Found: C, 60.29; H, 6.85.

Swern oxidation of 13

Swern oxidation of **13** (100 mg, 0.3 mmol) by adopting the general procedure II provided methyl 6-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-allo-hexopyranosid-2-ulose (**14**, 83.5 mg, 84%) as a colourless liquid**:** R_f = 0.35 (ethyl acetate/petroleum ether, 2:3; v/v); $[\alpha]_D^{27.0}$ = 6.2 (c 0.5, CH_2Cl_2); IR (Neat, cm^{-1}) 1726, 1247; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.99 (d, *J* = 1.35 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.73, 2H), 7.38 (s, 1H, H-1), 4.92 (dd, *J* = 5.8 Hz, 11 Hz, 1H, H-4), 4.66 (d, *J* = 5.85 Hz, 1H, H-3), 4.49 (t, *J* = 6.77 Hz, 1H, H-5), 4.38 (dd, *J* = 6.75 Hz, 11.2 Hz, 1H, H-6A), 4.33 (dd, *J* = 6.65 Hz, 11.2 Hz, 1H, H-6B), 3.6 (s, 3H, OCH_3), 1.34 (s, 3H, CH_3), 1.25 (s, 3H,

C*H*$_3$); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.9, 165.5, 133.5, 129.4, 129.3, 128.8, 112.4, 105.2, 86.7 (C-3), 83.2 (C-5), 81.6 (C-4), 65.3 (C-6), 51.9 (O*C*H$_3$), 25.9, 24.9. Elemental analysis calcd for $C_{17}H_{20}O_7$: C, 60.71; H, 5.99. Found: C, 60.39; H, 6.24.

Methyl 6-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-allopyranoside (15)

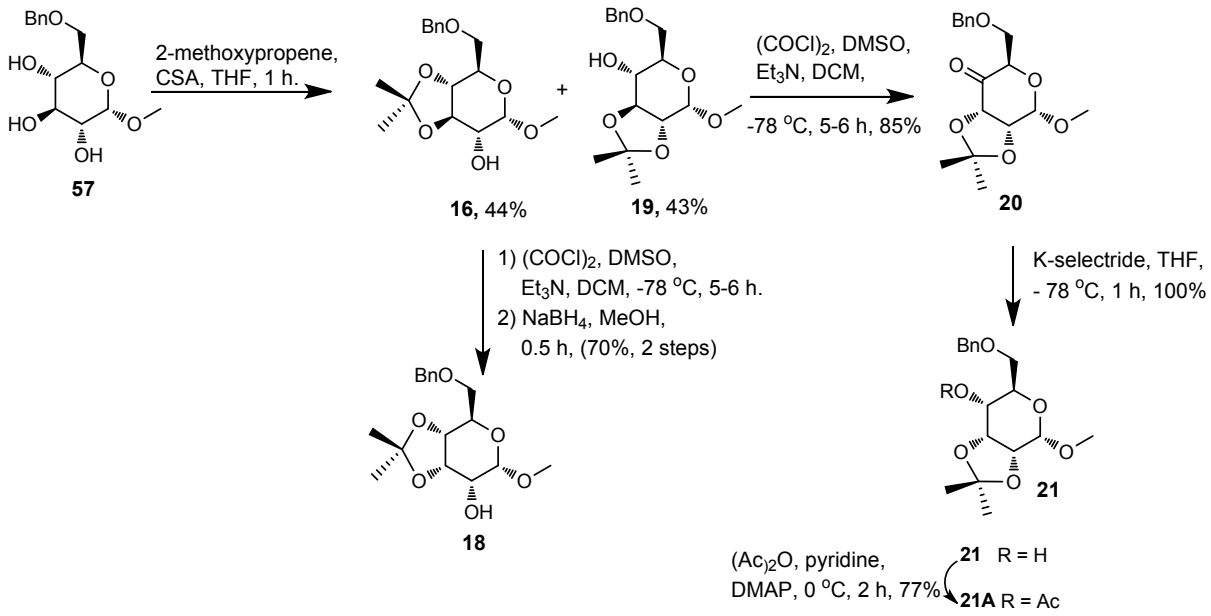
Reduction of **14** (32 mg, 0.1 mmol) using sodium borohydride as in the general procedure IV provided *allo*-pyranoside derivative **15** (31.5 mg, 98%) as a white solid: m.p. = 132-134 ^{o}C; R_f = 0.8 (ethyl acetate/ petroleum ether, 1:1; v/v); $[\alpha]_D^{27.0}$ = 55.0 (c 0.24, CH_2Cl_2); IR (Neat, cm^{-1}) 3510, 1720, 1270; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.04 (dd, *J* = 1.17 Hz, 8.2 Hz, 2H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.6 (t, *J* = 7.75 Hz, 2H), 4.92 (d, *J* = 8.65 Hz, 1H, HO-2), 4.66 (d, *J* = 4.35 Hz, 1H, H-1), 4.53 (dd, *J* = 2.45 Hz, 11.85 Hz, 1H, H-6A), 4.41 (t, *J* = 4.65 Hz, 1H, H-3), 4.37 (dd, *J* = 7.2 Hz, 11.85 Hz, 1H, H-6B), 4.09 (dd, *J* = 4.95 Hz, 9.7 Hz, 1H, H-4), 3.98 (ddd, *J* = 2.3 Hz, 7.1 Hz, 9.5 Hz, 1H, H-5), 3.82 (m, 1H, H-2), 3.34 (s, 3H, OC*H*$_3$), 1.49 (s, 3H, C*H*$_3$), 1.35 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.5, 133.4, 129.5, 129.1, 128.8, 109.4, 98.2 (C-1), 74.4 (C-3), 71.6 (C-4), 66.1 (C-2), 65.2 (C-5), 64.1 (C-6), 54.9 (O*C*H3), 28.4, 26.0. Elemental analysis calcd for $C_{17}H_{22}O_7$: C, 60.35; H, 6.55. Found: C, 60.13; H, 6.53.

Methyl 2-*O*-acetyl-6-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-allopyranoside (15A)

Stereochemistry of the newly formed chiral centre (C-2) in compound **15** was confirmed by acetylation. In the ^{1}H NMR of compound **15A**, H-2 showed a coupling constant 4.4 Hz (triplet), which indicates that H-2 proton is *syn* to H-1 & H-3 protons.

Acetylation of alcohol **15** (12 mg, 0.036 mmol) by adopting the general procedure VII provided **15A** (10 mg, 72%) as a white solid: m.p. = 86-88 ^{o}C; R_f = 0.62 (ethyl acetate/ petroleum ether, 3:7; v/v); $[\alpha]_D^{26.0}$ = 7.7 (c 0.6, CH_2Cl_2); IR (Neat, cm^{-1}) 1735, 1720; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.00 (d, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.75 Hz, 2H), 5.07 (t, *J* = 4.4 Hz, 1H, H-2), 4.83 (d, *J* = 4.35 Hz, 1H, H-1), 4.51 (dd, *J* = 2.3 Hz, 11.95 Hz, 1H, H-6A), 4.46 (t, *J* = 4.9 Hz, 1H, H-3), 4.36 (dd, *J* = 7.1 Hz, 12 Hz, 1H, H-6B), 4.22 (dd, *J* = 5.45 Hz, 9.55 Hz, 1H, H-4), 4.01 (ddd, *J* = 2.2 Hz, 7.1 Hz, 9.3 Hz, 1H, H-5), 3.34 (s, 3H, OC*H*$_3$), 2.1 (s, 3H, OAc), 1.44 (s, 3H, C*H*$_3$), 1.3 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.7, 165.5, 133.5, 129.4, 129.2, 128.8, 110.1, 95.3 (C-1), 71.7 (C-3), 71.6 (C-4), 67.2 (C-2), 66.3 (C-5), 64.0 (C-6), 54.9 (O*C*H$_3$), 27.9, 25.8, 20.7. Elemental analysis calcd for $C_{19}H_{24}O_8$: C, 59.99; H, 6.36. Found: C, 60.11; H, 6.69.

Scheme S3



Methyl 6-*O*-benzyl-3,4-*O*-isopropylidene-α-D-glucopyranoside (16) & methyl 6-*O*-benzyl-2,3-*O*-isopropylidene-α-D-glucopyranoside (19)

To a solution of methyl 6-*O*-benzyl-α-D-glucopyranoside[12] (**57**) (1.0 g, 3.52 mmol) in dry THF (20 mL), 2-methoxypropene (635 mg, 8.8 mmol) and camphorsulfonic acid (164 mg, 0.704 mmol) were added. The resulting mixture was stirred at room temperature for 1 h. After completion of the reaction, the reaction mixture was neutralised by addition of solid $NaHCO_3$. The reaction mass was filtered and the solvents were evaporated under reduced pressure on a rotary evaporator, and the residue was diluted with ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude material thus obtained was purified by column chromatography using a mixture of ethyl acetate and petroleum ether (2:8; v/v) as eluent to obtain the compounds **16** (510 mg, 44%) and **19** (490 mg, 43%) as colourless liquids.

Compound **16**: R_f = 0.54 (ethyl acetate/petroleum ether, 1:1; v/v); $[\alpha]_D^{25.0}$ = 61.4 (c 0.28, CH_2Cl_2); IR (Neat, cm^{-1}) 3562, 1071, 1035; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34-7.27 (m, 5H, Ar*H*), 5.20 (dd, *J* = 2.0 Hz, 4.9 Hz, HO-2), 4.65 (d, *J* = 2.6 Hz, 1H, H-1), 4.52 (s, 2H, ArCH_2), 3.78 (ddd, *J* = 1.9 Hz, 6.2 Hz, 8.35 Hz, 1H, H-5), 3.64-3.61 (m, 3H, H-2, H-3 & H-6A), 3.51 (dd, *J* = 6.3 Hz, 11.2 Hz, H-6B), 3.29 (s, 3H, OCH_3), 3.17-3.14 (m, 1H, H-4), 1.34 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.3, 128.2, 127.4, 127.3, 109.5, 100.2, 77.9 (C-3 or C-2),74.0 (C-4), 72.3 (Ar*C*H_2), 70.9 (C-5), 70.5 (C-2 or C-3), 69.5 (C-6), 55.0, 26.8, 26.4. Elemental analysis calcd for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46. Found: C, 62.69; H, 7.20.

Compound **19:** R_f = 0.71 (ethyl acetate/petroleum ether, 1:1; v/v); $[\alpha]_D^{25.0}$ = 101.3 (c 0.3, CH_2Cl_2); IR (Neat, cm^{-1}) 3596, 1073; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.37-7.29 (m, 5H, Ar*H*), 5.50 (d, *J* = 6.35 Hz, 1H, HO-4), 5.0 (d, *J* = 3.0 Hz, 1H, H-1), 4.53 (s, 2H, ArCH_2), 3.77 (t, *J* = 9.5 Hz, 1H, H-5), 3.73 (dd, *J* = 1.6 Hz, 10.9 Hz, 1H, H-6A), 3.62 (dd, *J* = 5.8 Hz, 10.9 Hz, 1H, H-6B), 3.55 (ddd, *J* = 6.4 Hz, 9.3 Hz, 15.7 Hz, 1H, H-4), 3.42 (m, 1H, H-3), 1.35 (s, 3H, CH_3), 1.34 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.5, 128.2, 127.4, 127.3, 109.4, 96.9, 76.7 (C-5), 75.3 (C-2), 73.1 (C-3), 72.3 (Ar*C*H_2), 69.2 (C-4), 68.9 (C-6),

54.7, 26.8, 26.5. Elemental analysis calcd for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46. Found: C, 62.78; H, 7.63.

Methyl 6-*O*-benzyl-3,4-*O*-isopropylidene-α-D-allopyranoside (18)

Swern oxidation of **16** (100 mg, 0.31 mmol) by adopting the general procedure II provided ketone **17.** However its purification was difficult and hence the crude was used for reduction. Reduction of the crude **17** with sodium borohydride by adopting the general procedure IV provided known pyranoside **18** [13] (70 mg, 70%, 2 steps) as a colourless liquid.

^{1}H NMR (500 MHz, ($CDCl_3$) δ 7.28-7.21 (m, 5H, Ar*H*), 4.7 (d, *J* = 4.65 Hz, 1H), 4.55 (d, *J* = 12.15 Hz, 1H, ArH_A), 4.52 (d, *J* = 12.15 Hz, 1H, ArH_B), 4.38 (t, *J* = 4.9 Hz, 1H), 4.04 (dd, *J* = 5.1 Hz, 9.55 Hz, 1H), 3.82 (t, *J* = 4.7 Hz, 1H), 3.78 (ddd, *J* = 2.1 Hz, 5.4 Hz, 7.5 Hz, 1H), 3.66 (dd, *J* = 2.15 Hz, 10.8 Hz, 1H), 3.54 (dd, *J* = 5.4 Hz, 10.8 Hz, 1H), 3.39 (s, 3H, OCH_3), 1.43 (s, 3H, CH_3), 1.29 (s, 3H, CH_3).

Swern oxidation of 19

Swern oxidation of **19** (100 mg, 0.31 mmol) by adopting the general procedure II provided methyl 6-*O*-benzyl-2,3-*O*-isopropylidene-α-D-allo-hexopyranosid-4-ulose (**20**, 84.5 mg, 85%) as a colourless liquid: R_f = 0.68 (ethyl acetate/petroleum ether, 2:3; v/v); $[\alpha]_D^{25.0}$ = 92.7 (c 0.18, CH_2Cl_2); IR (Neat, cm^{-1}) 1741, 1085, 1023; ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.37-7.29 (m, 5H, Ar*H*), 5.02 (d, *J* = 4.0 Hz, 1H, H-1), 4.7 (dd, *J* = 3.75 Hz, 9.5 Hz, 1H, H-2), 4.63 (dd, *J* = 1.0 Hz, 9.0 Hz, H-3), 4.61 (d, *J* = 12.0 Hz, 2H, ArCH_A), 4.56 (d, *J* = 12.0 Hz, 2H, ArCH_B), 4.07 (t, *J* = 2.0 Hz, 1H, H-5), 3.77 (dd, *J* = 1.5 Hz, 2.5 Hz, 2H, H-6A and 6B), 3.42 (s, 3H, OCH_3), 1.39 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 204.1, 139.1, 129.2, 128.4, 128.3, 111.3, 98.0 (C-1), 77.6 (C-3), 76.8 (C-5), 75.5 (C-2), 74.1 (ArCH_2), 70.9 (C-6), 56.1, 26.5, 25.5. Elemental analysis calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.22; H, 7.08.

Methyl 6-*O*-benzyl-2,3-*O*-isopropylidene-α-D-allopyranoside (21)

Reduction of **20** (30 mg, 0.09 mmol) by using sodium borohydride (general procedure IV) and K-selectride (general procedure V) afforded the compound **21** in 89% (27 mg) and 100% (30 mg) yield respectively: R_f = 0.35 (ethyl acetate/petroleum ether, 3:7; v/v); $[\alpha]_D^{25.0}$ = 28.5 (c 0.4, CH_2Cl_2); IR (Neat, cm^{-1}) 3566, 1061; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.35-7.24 (m, 5H, Ar*H*), 5.08 (d, *J* = 7.5 Hz, 1H, HO-4), 4.53 (d, *J* = 4.5 Hz, 1H, H-1), 4.51 (s, 2H, ArCH_2), 4.32 (t, *J* = 4.75 Hz, 1H, H-3), 4.13 (t, *J* = 5.25 Hz, 1H, H-2), 3.78 (dd, *J* = 5.5 Hz, 10 Hz, 1H, H-5), 3.69-3.63 (m, 2H, H-6A, H-4), 3.54 (dd, *J* = 5.75 Hz, 10.75 Hz, 1H, H-6B), 3.25 (s, 3H, OCH_3), 1.42 (s, 3H, CH_3), 1.24 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.6, 128.2, 127.3, 127.2, 109.5, 96.3, 74.8 (C-3), 73.1 (C-2), 72.3 (ArCH_2), 69.9 (C-6), 67.0 (C-5), 64.1 (C-4), 54.7, 26.0, 25.8. Elemental analysis calcd for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46. Found: C, 63.04; H, 7.12.

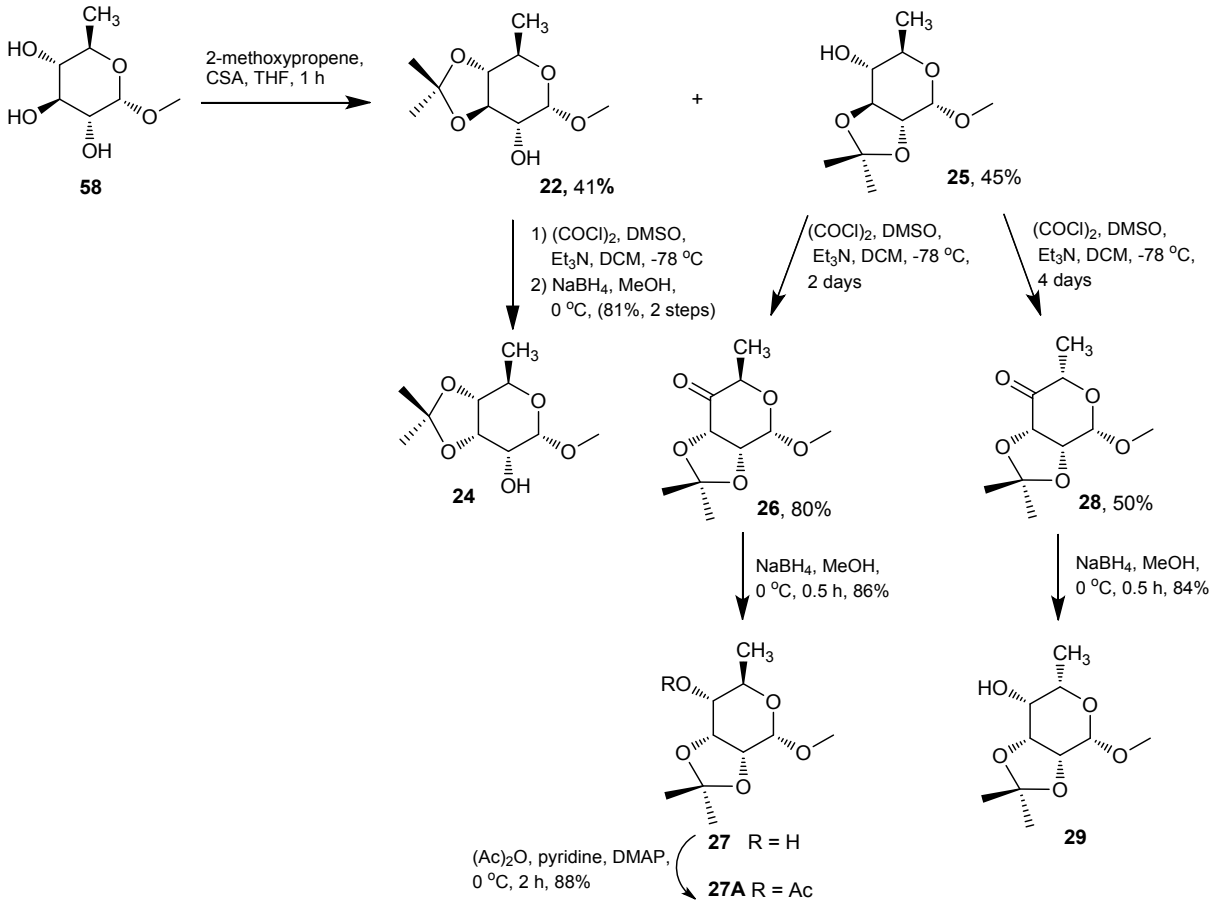
Methyl 4-*O*-acetyl-6-*O*-benzyl-2,3-*O*-isopropylidene-α-D-allopyranoside (21A)

Stereochemistry of the newly formed chiral centre (C-4) in **21** was confirmed by acetylation. ^{1}H NMR of compound **21A** shows a $^3J_{H3H4}$ coupling constant of 4.1 Hz and $^3J_{H4H5}$ of 10.5 Hz, which indicates that H-4 proton is *syn* to H-3 proton and *anti* to H-5 proton.

Acetylation of **21** (20 mg, 0.06 mmol) by adopting the general procedure VII provided the acetate **21A** (17 mg, 77%) as a colourless liquid: R_f = 0.54 (ethyl acetate/ petroleum ether, 1:4; v/v); $[\alpha]_D^{25.0}$ = 42.4 (c 0.16, CH_2Cl_2); IR (Neat, cm^{-1}) 1741, 1234,1039; ^{1}H NMR (500

MHz, $(CD_3)_2CO$) δ 7.19-7.14 (m, 5H, Ar*H*), 4.93 (dd, *J* = 4.1 Hz, 10.5 Hz, 1H, H-4), 4.53 (d, *J* = 4.8 Hz, 1H, H-1), 4.46 (t, *J* = 5.65 Hz, 1H, H-3), 4.45 (d, *J* = 11.9 Hz, 1H, ArCH_A), 4.37 (d, *J* = 11.9 Hz, 1H, ArCH_B), 4.15 (t, *J* = 5.25 Hz, 1H, H-2), 3.98 (ddd, *J* = 2.4 Hz, 4.7 Hz, 7.15 Hz, 1H, H-5), 3.5 (dd, *J* = 2.47 Hz, 10.7 Hz, 1H, H-6A), 3.45 (dd, *J* = 4.75 Hz, 10.7 Hz, H-6B), 3.23 (s, 3H, OCH_3), 1.86 (s, 3H, OAc), 1.36 (s, 3H, CH_3), 1.14 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 170.2, 139.6, 129.1, 128.4, 128.2, 111.4, 98.2 (C-1), 74.5 (C-2), 73.8 (Ar*C*H_2), 73.1 (C-3), 70.2 (C-6), 67.4 (C-4), 65.1 (C-5), 55.5, 26.4, 26.0, 20.8. Elemental analysis calcd for $C_{19}H_{26}O_7$: C, 62.28; H, 7.15. Found: C, 62.01; H, 7.39.

Scheme S4:



Methyl 6-deoxy-3,4-*O*-isopropylidene-α-D-glucopyranoside (22) & methyl 6-deoxy-2,3-*O*-isopropylidene-α-D-glucopyranoside (25)

To a solution of methyl 6-deoxy-α-D-glucopyranoside [14] (**58**) (2.0 g, 11.2 mmol) in dry THF (20 mL), 2-methoxypropene (2.02 g, 28.07 mmol) and camphorsulfonic acid (522 mg, 2.25 mmol) were added. The resulting mixture was stirred at room temperature for 1 h. After completion of the reaction, the reaction mixture was neutralised by the addition of solid $NaHCO_3$. The reaction mass was filtered and the solvents were evaporated under reduced pressure on a rotary evaporator, and the residue was extracted with ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude material thus obtained was purified by column chromatography using a mixture of acetone and dichloromethane (1:9; v/v) as eluent to obtain the compounds **22** (1.0 g, 41%) and **25** (1.1 g, 45%) as colourless liquids.

Compound **22**: R_f = 0.31 (dichloromethane); $[\alpha]_D^{25.0}$ = 134.3 (c 0.3, CH_2Cl_2); IR (Neat, cm^{-1}) 3560, 1035; ^{1}H NMR (500MHz, DMSO-d_6) δ 5.18 (d, *J* = 6.75 Hz, 1H, HO-2), 4.61 (d, *J* = 3.4 Hz, 1H, H-1), 3.72 (ddd, *J* = 6.2 Hz, 9.2 Hz, 12.2 Hz, 1H, H-5), 3.66-3.62 (m, 1H, H-2), 3.58 (q, *J* = 11.35 Hz, 1H, H-3), 3.31(s, 3H, OCH_3), 2.95 (t, *J* = 8.92 Hz, 1H, H-4), 1.37 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.19 (d, *J* = 6.2 Hz, 3H, CH_3-6); ^{13}C NMR (125MHz, DMSO) δ 109.2, 100.3 (C-1), 79.1 (C-4), 77.6 (C-3), 71.2 (C-2), 66.7 (C-5), 55.0 (O*C*H_3), 26.8 (*C*H_3), 26.4 (*C*H_3), 17.9 (C-6). Elemental analysis calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.82; H, 8.46.

Compound **25**: R_f = 0.30 (dichloromethane); $[\alpha]_D^{25.0}$ = 137.8 (c 0.26, CH_2Cl_2); IR (Neat, cm^{-1}) 3604, 1225, 1040; ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.41 (d, *J* = 6.15 Hz, HO-4), 4.92 (d, *J* = 3.0 Hz, H-1), 3.72 (t, *J* = 9.5 Hz, H-3), 3.39 (dd, *J* = 3.05 Hz, 9.55 Hz, H-2), 3.33 (m, 4H, H-5 & OCH_3), 3.25 (ddd, *J* = 6.15 Hz, 9.2 Hz, 15.3 Hz, 1H, H-4), 1.35 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.2 (d, *J* = 6.2 Hz, 3H, CH_3-6); ^{13}C NMR (125 MHz, DMSO-d_6) δ 109.4, 97.0 (C-1), 76.5 (C-3), 75.6 (C-2), 74.2 (C-4), 69.3 (C-5), 54.6, 26.9, 26.5, 17.0 (C-6). Elemental analysis calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.77; H, 8.51.

Methyl 6-deoxy-3,4-*O*-isopropylidene-α-D-allopyranoside (24)

Swern oxidation of **22** (100 mg, 0.46 mmol) by adopting the general procedure II provided ketone **23** (89 mg, crude, 89%). As the purification was difficult, the crude mass was subjected to reduction using sodium borohydride by adopting the general procedure IV. 3-*epi*-quinovose derivative **24** (81 mg, 81%, overall yield) was obtained as a colourless liquid. ^{1}H-NMR of the compound **24** matches with the reported data.[15]

Swern oxidation of 25

Swern oxidation of **25** (200 mg, 0.92 mmol) by adopting the general procedure II for 48 h provided ketone **26** (158.5 mg, 80%) as a colourless liquid.

Swern oxidation of 25 for longer duration

Swern oxidation of **25** (200 mg, 0.92 mmol) by adopting the general procedure II for 4 days provided a mixture of ketones **26** (79.2 mg, 40%) and **28** (99 mg, 50%).

Compound **26:** R_f = 0.3 (acetone/petroleum ether, 1:9; v/v); $[\alpha]_D^{25.0}$ = 65.4 (c 0.46, CH_2Cl_2); IR (Neat, cm^{-1}) 1742, 1200, 1025; ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.93 (d, *J* = 4 Hz, 1H, H-1), 4.84 (dd, *J* = 1 Hz, 9.5 Hz, 1H, H-2), 4.64 (dd, *J* = 4 Hz, 9.5 Hz, 1H, H-3), 3.93 (dq, *J* = 1 Hz, 7 Hz, 1H, H-5), 3.3 (s, 3H, OCH_3), 1.32 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.24 (d, *J* = 7 Hz, 3H, CH_3-6); ^{13}C NMR (125 MHz, DMSO-d_6) δ 206.4 (C-4), 110.0, 95.8 (C-1), 74.3 (C-3), 73.8 (C-2), 71.0 (C-5), 55.4, 25.9, 25.0, 17.5 (C-6). Elemental analysis calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.37; H, 7.70.

Compound **28:** R_f = 0.29 (acetone/petroleum ether, 1:9; v/v); $[\alpha]_D^{25.0}$ = -16.9 (c 0.32, CH_2Cl_2); IR (Neat, cm^{-1}) 1742, 1378, 1098; ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.92 (d, *J* = 2.15 Hz, 1H, H-1), 4.62 (d, *J* = 7.25 Hz, 1H, H-3), 4.53 (dd, *J* = 2.2 Hz, 7.25 Hz, 1H, H-2), 4.18 (q, *J* = 6.6 Hz, 1H, H-5), 3.38 (s, 3H, OCH_3), 1.28 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.18 (d, *J* = 6.6 Hz, 3H, CH_3-6); ^{13}C NMR (125 MHz, DMSO-d_6) δ 204.2 (C-4), 110.1, 98.0 (C-1), 76.5 (C-2), 76.0 (C-3), 72.6 (C-5), 56.3, 26.5, 25.6, 15.5 (C-6). Elemental analysis calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.48; H, 7.64.

Methyl 6-deoxy-2,3-*O*-isopropylidene-α-D-allopyranoside (27)

Reduction of **26** (35 mg, 0.16 mmol) by using sodium borohydride as in the general procedure IV provided **27** (30.4 mg, 86%) as a colourless liquid: R_f = 0.46 (acetone/petroleum ether, 1:9; v/v); $[\alpha]_D^{25.0}$ = 148.0 (c 0.4, CH_2Cl_2); IR (Neat, cm^{-1}) 3570, 1062; ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.99 (d, J = 7.3 Hz, 1H, HO-4), 4.46 (d, J = 4.95 Hz, 1H, H-1), 4.28 (dd, J = 4.47 Hz, 5.47 Hz, 1H, H-3), 4.11 (t, J = 5.25 Hz, 1H, H-2), 3.72-3.66 (m, 1H, H-5), 3.31 (m, 1H, H-4), 3.22 (s, 3H, OCH_3), 1.43 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.11 (d, J = 6.3 Hz, 3H, CH_3-6); ^{13}C NMR (125 MHz, DMSO-d_6) δ 109.5, 96.2 (C-1), 74.6 (C-3), 73.2 (C-2), 69.8 (C-4), 62.1 (C-5), 54.6, 26.1, 25.7, 17.6 (C-6). Elemental analysis calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.11; H, 8.20.

Methyl 6-deoxy-4-*O*-acetyl-2,3-*O*-isopropylidene-α-D-allopyranoside (27A)

Stereochemistry of the newly formed chiral centre (C-4) in **27** was confirmed by acetylation. ^{1}H NMR of compound **27A** shows a $^3J_{H3H4}$ coupling constant of 4.1 Hz and $^3J_{H4H5}$ of 10.1 Hz, which indicates that H-4 proton is *syn* to H-3 proton and *anti* to H-5 proton.

Acetylation of **27** (20 mg, 0.092 mmol) by adopting the general procedure VII provided **27A** (21 mg, 88%) as a colourless liquid: R_f = 0.8 (acetone/petroleum ether, 1:9; v/v); $[\alpha]_D^{25.0}$ = 180.0 (c 0.2, CH_2Cl_2); IR (Neat, cm^{-1}) 1738, 1234, 1065; ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.65 (dd, J = 4.1 Hz, 10.15 Hz, 1H, H-4), 4.56 (d, J = 4.9 Hz, 1H, H-1), 4.42 (dd, J = 4.2 Hz, 5.55 Hz, 1H, H-3), 4.25 (t, J = 5.37 Hz, 1H, H-2), 3.90-3.94 (m, 1H, H-5), 3.25 (s, 3H, OCH_3), 2.06 (s, 3H, OAc), 1.43 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.07 (d, J = 6.35 Hz, 3H, CH_3-6); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.7, 110.2, 96.2 (C-1), 73.0 (C-2), 71.7 (C-3), 70.9 (C-4), 59.7 (C-5), 54.8, 26.1, 25.5, 20.7, 17.1 (C-6). Elemental analysis calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.22; H, 7.78.

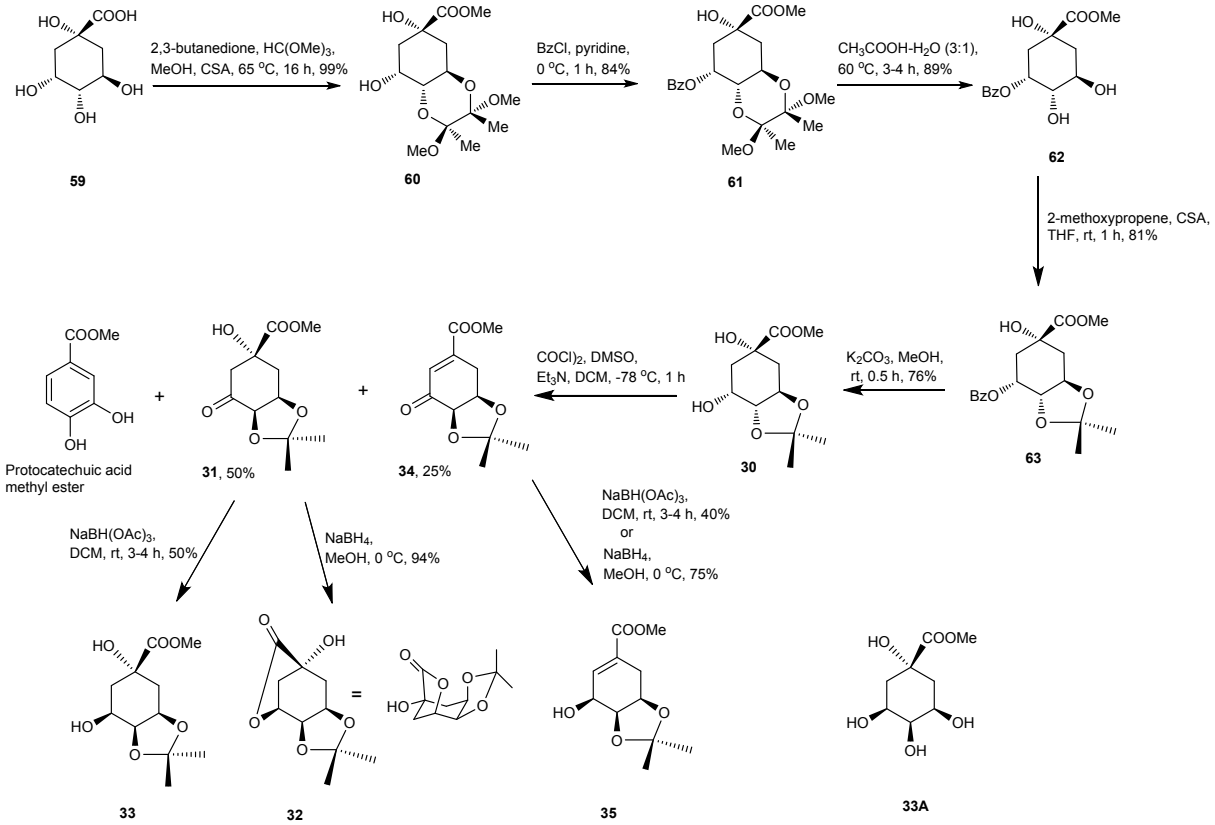
Methyl 6-deoxy-2,3-*O*-isopropylidene-5-*epi*-α-D-allopyranoside (29)

Reduction of **28** (20 mg, 0.09 mmol) by using sodium borohydride as in the general procedure IV provided **29** (16.5 mg, 84%) as a colourless liquid:

^{1}H NMR of compound **29** shows a $^3J_{H3H4}$ coupling constant of 5.4 Hz and $^3J_{H4H5}$ of 1.2 Hz, which indicates that H-4 proton is *syn* to H-3 & H-5 proton.

R_f = 0.6 (acetone/petroleum ether, 1:9; v/v); $[\alpha]_D^{25.0}$ = 136.4 (c 0.14, CH_2Cl_2); IR (Neat, cm^{-1}) 3683, 1024;^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 4.54 (d, J = 2.0 Hz, 1H, H-1), 4.15 (t, J = 5.9 Hz, H-3), 4.05 (dd, J = 3.0 Hz, 6.35 Hz, 1H, H-3), 3.49 (qd, J = 1.2 Hz, 6.4 Hz, 1H, H-5), 3.38 (ddd, J = 1.2 Hz, 5.45 Hz, 6.7 Hz, 1H, H-4), 3.33 (s, 3H, OCH_3), 1.35 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.11 (d, J = 6.4 Hz, CH_3-6); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 110.5, 100.1 (C-1), 75.4 (C-3), 73.2 (C-2), 71.1 (C-5), 67.9 (C-4), 56.5, 26.1, 25.8, 17.4. Elemental analysis calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.19; H, 8.16.

Scheme S5



Methyl (1R,3R,4S,5R)-1-hydroxy-4,5-[(2S,3S)-2,3-dimethoxybutan-2,3-dioxy)]-3-*O*-benzoyl-cyclohexan-1-carboxylate (61)

To a solution of bis-ketal[16] **60** (0.5 g, 1.56 mmol) in a mixture of pyridine (3 mL) and dichloromethane (10 mL) at 0 °C, benzoyl chloride (0.2 mL, 1.72 mmol) was added dropwise and the reaction mixture were stirred gradually warming to room temperature. After completion of the reaction, the solvent was evaporated in a rotary evaporator and the residue was dissolved in ethyl acetate, washed thoroughly with $NaHCO_3$ solution, water and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude material thus obtained was purified by column chromatography using a mixture of ethyl acetate and petroleum ether (2:8; v/v) as eluent. The monobenzoate **61** was obtained as a white solid (556 mg, 84%): m.p. = 89-91 °C; R_f = 0.8 (ethyl acetate/petroleum ether, 1:1; v/v); $[\alpha]_D^{21.0} = 119.0$ (c 1.0, CH_2Cl_2); IR (Neat, cm^{-1}) 3525, 1732, 1132; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.35 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 5.42 (d, *J* = 2.85 Hz, 1H, H-3), 4.47 (q, *J* = 9.4 Hz, 1H, H-5), 3.68 (s, 3H, COOC*H*$_3$), 3.67 (dd, *J* = 2.85 Hz, 10.15 Hz, 1H, H-4), 3.24 (s, 3H, OC*H*$_3$), 3.2 (s, 3H, OC*H*$_3$), 2.2 (d, *J* = 15.2 Hz, 1H, H-2A), 2.1 (dd, *J* = 2.95 Hz, 15.45 Hz, 1H, H-2B), 1.98 (d, *J* = 8.75 Hz, 2H, H-6A and 6B), 1.2 (s, 3H, C*H*$_3$), 1.16 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 166.3, 132.8, 130.1, 129.9, 128.3, 100.1, 99.6, 74.6, 71.4 (C-4), 70.2 (C-3), 62.8 (C-5), 53.3, 48.0, 47.9, 38.8 (C-6), 36.8 (C-2), 17.8, 17.6. Elemental analysis calcd for $C_{21}H_{28}O_9$: C, 59.43; H, 6.65. Found: C, 59.43; H, 6.42.

Methyl (1R,3R,4S,5R)-1,4,5-trihydroxy-3-*O*-benzoyl-cyclohexan-1-carboxylate (62)

The benzoate **61** (100 mg, 0.71 mmol) was treated with a mixture of acetic acid and water (3:1, 10 mL) and stirred at 60 ^{o}C for 5-6 h. The resulting yellow mixture was concentrated in vacuo to afford the crude triol **62**. The crude product was purified through column chromatography using a mixture of ethyl acetate and petroleum ether (1:1; v/v) as eluent. The triol **62** was obtained as a white solid (65 mg, 89%): m.p. = 116-118 ^{o}C; R_f = 0.1 (ethyl acetate/petroleum ether, 1:1; v/v); $[\alpha]_D^{25.0}$ = -3.5 (c 0.4, CH_2Cl_2); IR (Neat, cm^{-1}) 3450, 1716, 1280; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.0 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 5.52 (d, *J* = 2.75 Hz, 1H, H-3), 4.26 (td, *J* = 4.45 Hz, 10.45 Hz, 1H, H-5), 3.74 (s, 3H, COOC*H*$_3$), 3.64 (d, *J* = 9.05 Hz, 1H, H-4), 3.1 (s, 1H, OH), 2.47 (br, 1H, OH), 2.41 (br, 1H, OH), 2.21-2.12 (m, 3H, H-6A, H-2A and H-2B), 1.88 (t, *J* = 12.17 Hz, 1H, H-6B); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 166.6, 133.2, 130.0, 129.9, 128.5, 75.2 (C-4), 74.5, 71.9 (C-3), 67.3 (C-5), 53.3, 40.9 (C-6), 36.4 (C-2), 29.7. Elemental analysis calcd for $C_{15}H_{18}O_7$: C, 58.06; H, 5.85. Found: C, 58.01; H, 5.87.

Methyl (1R,3R,4S,5R)-1-hydroxy-4,5-*O*-isopropylidene-3-*O*-benzoyl-cyclohexan-1-carboxylate (63)

To a solution of triol **62** (1.04 g, 3.35 mmol) in dry THF (10 mL), 2-methoxypropene (484 mg, 6.7 mmol) and camphorsulfonic acid (156 mg, 0.67 mmol) were added. The resulting mixture was stirred at room temperature for 1 h. After completion of the reaction, the reaction mixture was neutralized by the addition of solid $NaHCO_3$. The reaction mass was filtered and the solvents were evaporated under reduced pressure on a rotary evaporator, and the residue was diluted with ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude material thus obtained was purified by column chromatography using a mixture of ethyl acetate and petroleum ether (3:7; v/v) as eluent to obtain the compound **63** (950 mg, 81%) as a white solid: m.p. = 178-180 ^{o}C; R_f = 0.85 (ethyl acetate/ petroleum ether, 1:1; v/v); $[\alpha]_D^{26.4}$ = -33.0 (c 0.2, CH_2Cl_2); IR (KBr, cm^{-1}) 3498, 1741, 1714, 1282, 1105; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.91 (d, *J* = 7.05 Hz, 2H), 7.58 (m, 1H), 7.46 (t, *J* = 7.67 Hz, 2H), 5.56 (s, 1H, HO-1), 5.5 (dd, *J* = 2.8 Hz, 5.6 Hz, 1H, H-3), 4.27 (m, 1H, H-5), 3.59 (s, 3H, COOC*H*$_3$), 3.55 (dd, *J* = 3.0 Hz, 9.5 Hz, 1H, H-4), 2.21 (m, 1H, H-6A), 2.17-2.06 (m, 2H, H-2A and 2B) 1.81 (t, *J* = 12.0 Hz, 1H, H-6B), 1.29 (s, 3H, C*H*$_3$), 1.19 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, DMSO-d_6) δ 174.7, 165.1, 133.2, 130.2, 129.2, 128.6, 109.0, 79.1 (C-4), 74.5, 70.5 (C-5), 67.9 (C-3), 52.2 (C-4), 37.5 (C-6), 36.2 (C-2), 27.0, 26.4. Elemental analysis calcd for $C_{18}H_{22}O_7$: C, 61.71; H, 6.33. Found: C, 61.95; H, 6.42.

Methyl (1R,3R,4R,5R)-1,3-dihydroxy-4,5-*O*-isopropylidene-cyclohexan-1-carboxylate (30)

A suspension of benzoate **63** (840 mg, 2.4 mmol) and K_2CO_3 (166 mg, 1.2 mmol) in methanol (15 mL) was stirred at room temperature. After 30 minutes, the reaction mass was quenched with water and diluted with ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude material thus obtained was purified by column chromatography using a mixture of ethyl acetate and petroleum ether (3:7; v/v) as eluent. The diol **30** was obtained as a white solid (449 mg, 76 %): m.p. = 102-103 ^{o}C; R_f = 0.1 (ethyl acetate/petroleum ether, 1:4; v/v); $[\alpha]_D^{26.8}$ = -38.5 (c 0.2, CH_2Cl_2); IR (KBr, cm^{-1}) 3442, 1741, 1224; ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.34 (s, 1H, HO-1), 4.58 (d, *J* = 5.5 Hz, HO-3), 4.17-4.15 (m, 1H, H-3), 4.04 (ddd, *J* = 4.05 Hz, 9.45 Hz, 12.1 Hz, 1H, H-5), 3.57 (s, 3H, COOC*H*$_3$), 3.28 (m, 1H, H-4), 2.14 (ddd, *J* = 2.1 Hz, 3.95 Hz, 6.1 Hz, 1H, H-6A), 1.88 (dt, *J* = 2.5 Hz, 5.0 Hz, 1H, H-2A), 1.81 (dd, *J* = 3.2 Hz, 14.9 Hz, 1H, H-2B), 1.7 (t, *J* = 12.0 Hz, H-6B), 1.2 (s, 6H, 2x

CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 174.5, 108.5, 81.6 (C-4), 75.5, 75.4, 69.6 (C-5), 65.5 (C-3), 52.1, 38.8 (C-2), 38.1 (C-6), 27.1, 26.7. Elemental analysis calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.93; H, 7.12.

Swern oxidation of 30

Swern oxidation of **30** (200 mg, 0.82 mmol) for 1 h, by adopting the general procedure II provided ketone **31** (100 mg, 50%) and the known enone[17] **34** (46 mg, 25%). Prolonged reaction (15 hours) leads to the formation of protocatechuic acid methyl ester.[18]

Ketone **31:** m.p. = 74-76 ^{o}C; R_f = 0.25 (ethyl acetate/petroleum ether, 3:7; v/v); $[\alpha]_D^{23}$ = 6.0 (c 0.6, CH_2Cl_2); IR (Neat, cm^{-1}) 3533, 1735, 1240; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65 (q, *J* = 6.9 Hz, 1H, H-5), 4.49 (d, *J* = 6.75 Hz, 1H, H-4), 3.76 (s, 3H, COOCH_3), 3.23 (br, 1H, OH), 2.86 (d, *J* = 16.9 Hz, 1H, H-2A), 2.5 (m, 1H, H-2B), 2.36 (ddd, *J* = 2.3 Hz, 6.8 Hz, 9.15 Hz, 1H, H-6A), 2.07 (dd, *J* = 7.2 Hz, 13.9 Hz, 1H, H-6B), 1.4 (s, 3H, CH_3), 1.3 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.3, 174.4, 110.7, 78.1, 73.8 (C-4), 73.3 (C-5), 53.5, 47.8 (C-2), 37.3 (C-6), 27.3, 25.6. Elemental analysis calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 54.05; H, 6.91.

Enone **34:** ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 6.78 (d, *J* = 2.15 Hz, H-2), 4.63 (td, *J* = 1.57 Hz, 5.2 Hz, H-5), 4.23 (d, *J* = 4.95 Hz, 1H, H-4), 3.79 (s, 3H, COOCH_3), 3.15 (d, *J* = 20.2 Hz, 1H, H-6), 2.81 (ddd, *J* = 2.8 Hz, 5.0 Hz, 7.8 Hz, 1H, H-6), 1.34 (s, 3H, CH_3), 1.26 (s, 3H, CH_3).

(1R,3R,4R,5S)-1-hydroxy-3,4-*O*-isopropylidene-cyclohexane-1,5-lactone (32)

Reduction of **31** (12 mg, 0.05 mmol) using sodium borohydride as in the general procedure IV provided **32** (10 mg, 94%) as a white solid: m.p. = 222-223 ^{o}C; R_f = 0.13 (ethyl acetate/ petroleum ether, 2:3; v/v); $[\alpha]_D^{25.0}$ = 9.4 (c 0.34, CH_2Cl_2); IR (KBr, cm^{-1}) 1792, 1088; ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 4.76 (s, 1H, HO-1), 4.47-4.49 (m, 1H, H-5), 4.4 (ddd, *J* = 1.05 Hz, 2.6 Hz, 3.6 Hz, 1H, H-3), 4.08 (dd, *J* = 2.6 Hz, 6.15 Hz, 1H, H-4), 2.30 (ddd, *J* = 2.45 Hz, 6.8 Hz, 9.2 Hz, 1H, H-6A), 2.06 (m, 2H, H-2A and 2B), 1.91 (m, 1H, H-6B), 1.28 (s, 3H, CH_3), 1.14 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 177.7, 109.9, 76.5, 74.7 (C-5), 72.9 (C-4), 71.7 (C-3), 39.8 (C-6), 36.8 (C-2), 25.8, 25.7. Elemental analysis calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 55.85; H, 6.24.

Methyl (1R,3S,4S,5R)-1,3-dihydroxy-4,5-*O*-isopropylidene-cyclohexan-1-carboxylate (33)

Reduction of ketone **31** (30 mg, 0.12 mmol) using sodium triacetoxyborohydride as in the general procedure VI provided alcohol **33** (18 mg, 60%) as a white solid: m.p. = 73-75 ^{o}C; R_f = 0.17 (ethyl acetate/petroleum ether, 2:3; v/v); $[\alpha]_D^{25.0}$ = 6.0 (c 0.05, CH_2Cl_2); IR (KBr, cm^{-1}) 3376, 1729, 1245, 1036; ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 4.2-4.16 (m, 2H, H-4 & H-5), 4.15 (s, 1H, HO-1), 4.07-4.01 (m, 1H, H-3), 2.67 (s, 3H, COOCH_3), 3.49 (d, *J* = 7.95 Hz, 1H, OH-3), 1.89 (m, 1H, H-2A), 1.79-1.68 (m, 3H, H-6A, H-6B & H-2B), 1.3 (s, 3H, CH_3), 1.2 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 176.0, 109.2, 76.9, 75.0, 74.1, 65.9, 52.6, 37.7 (C-2), 37.4 (C-6), 28.6, 26.5. Elemental analysis calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.45; H, 7.25.

Crystal data for 33A: When tried to crystallise the compound **33** from a mixture of ethyl acetate and hexane, it underwent isopropylidene deprotection to tetrol **33A** which got

crystallised. CCDC No 973079, Molecular formula = $C_8H_{14}O_6$, Formula weight = 206.19, colorless blocks, 0.25 x 0.20 x 0.15 mm**,** Orthorhombic, space group Pna2(1), a = 6.696(5), b = 18.484(5), c = 7.461(5) Å, V = 923.4(10) $Å^3$, Z = 4, T = 296(2) K, $2\theta_{max}$ = 50.00°, D_{calc} (g cm^{-3}) = 1.483, F(000) = 440, μ (mm^{-1}) = 0.128, 1386 reflections measured, 1360 unique reflections (R_{int} = 0.0885), multi-scan absorption correction, T_{min} = 0.9659, T_{max} = 0.9901, number of parameters = 131, number of restraints = 1, GoF = 1.091, R1 = 0.0226, wR_2 = 0.0617, R indices based on 1360 reflections with I >2s(I). $\Delta\rho_{max}$ = 0.000, $\Delta\rho_{min}$ = 0.000 ($eÅ^{-3}$).

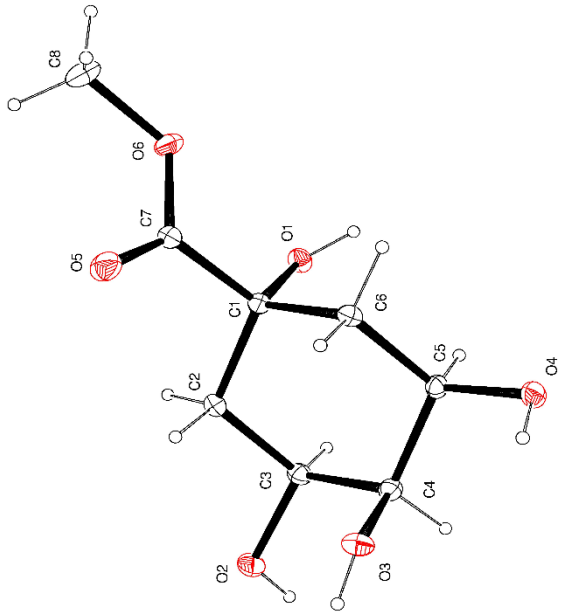
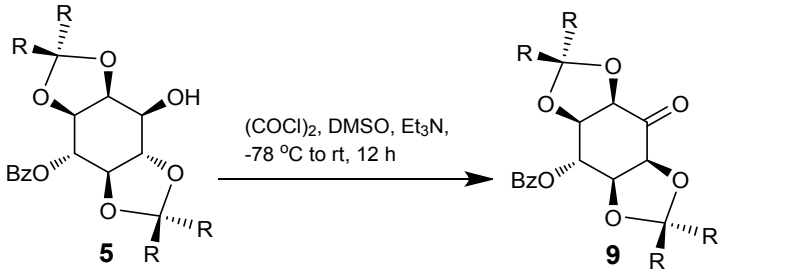


Fig. S2: ORTEP diagram of **33A**

Methyl (3S,4R,5R)-3-hydroxy-4,5-*O*-isopropylidene-cyclohexen-1-carboxylate (35)

Reduction of **34** (20 mg, 0.09 mmol) using sodium borohydride (general procedure IV) and sodium triacetoxyborohydride (general procedure VI) afforded the known ester **35** [19] in 75% (15 mg) and 40% (8.2 mg) respectively.

Scheme S6:



5 R = CH_3
6 R = -$(CH_2)_5$-

9 R = CH_3, 87%
10 R = -$(CH2)_5$-, 84%

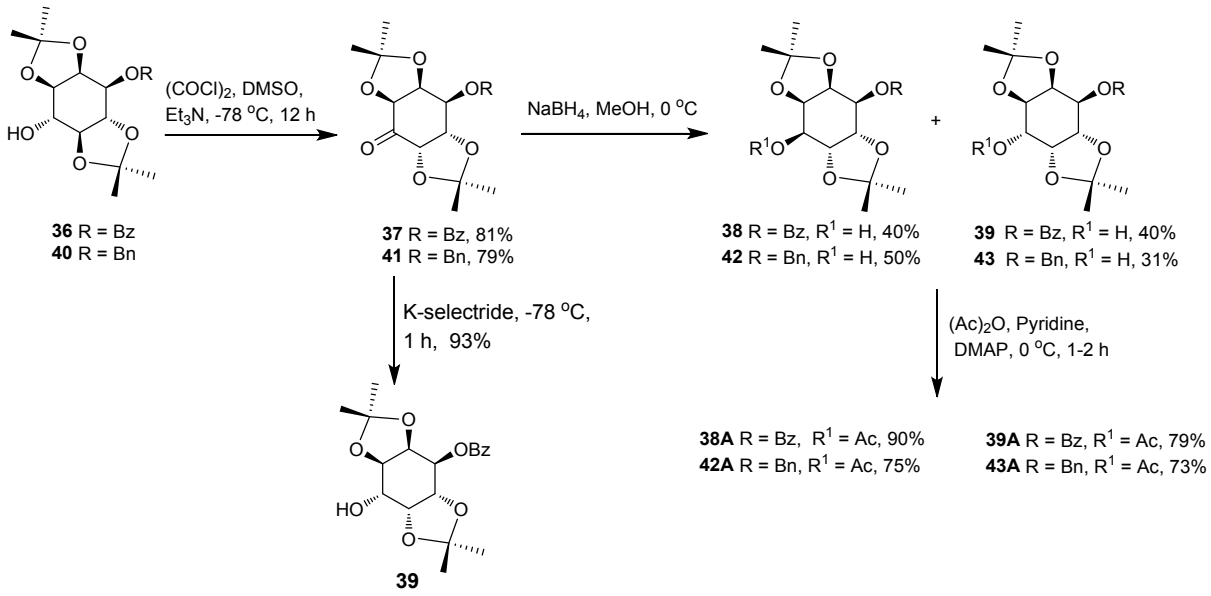
Swern oxidation of 5

Swern oxidation of **5** (100 mg, 0.27 mmol) by adopting the general procedure II provided the symmetrical ketone **9** (86.5 mg, 87%) as a white solid.

Swern oxidation of 6

Swern oxidation of **6** (100 mg, 0.23 mmol) by adopting the general procedure II provided the symmetrical ketone **10** (84 mg, 84%) as a white solid.

Scheme S7:



Swern oxidation of 36

Swern oxidation of (±)-3-*O*-benzoyl-1,2:4,5-di-*O*-isopropylidene-*myo*-inositol[20] (**36**) (500 mg, 1.37 mmol) by adopting the general procedure II provided the (±)-4-*O*-Benzoyl-2,3:5,6-di-*O*-isopropylidene cyclohexanone (**37**, 403 mg, 81%) as a white solid: m.p. = 152 °C: R_f = 0.28 (ethyl acetate/petroleum ether, 2:3; v/v); IR (KBr, cm^{-1}) 1747, 1724; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.83 (d, J = 7.3 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 5.42 (1H, dd, J = 2.0 Hz, 4.5 Hz, H-3), 5.07 (m, 2H, H-1 & H-2), 4.86 (dd, J = 4.3 Hz, 7.4 Hz, 1H, H-4), 4.69 (d, J = 7.4 Hz, 1H, H-5), 1.56 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.2 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 202.2, 164.5, 134.4, 129.9, 129.3, 129.2, 112.4, 110.2, 76.9 (C-5), 76.3 (C-4), 75.8 (C-1 or C-2), 74.8 (C-2 or C-1), 68.9 (C-3), 26.1, 26.0, 24.5, 24.1. Elemental analysis calcd for $C_{19}H_{22}O_7$: C, 62.97; H, 6.12. Found: C, 63.01; H, 6.12.

Crystal data for 37: CCDC N0. 973080, Molecular formula = $C_{19}H_{22}O_7$, Formula weight = 362.37, colorless blocks, 0.20 x 0.15 x 0.10 mm**,** Orthorhombic, space group Pbca, a = 17.615(5), b = 10.145(5), c = 20.328(5) Å, V = 3633(2) Å^3, Z = 8, T = 293(2) K, $2\theta_{max}$ = 50.00°, D_{calc} (g cm^{-3}) = 1.323, F(000) = 1536, μ (mm^{-1}) = 0.101, 13731 reflections measured, 3148 unique reflections (R_{int} = 0.0578), multi-scan absorption correction, T_{min} = 0.9800, T_{max} = 0.9899, number of parameters = 236, number of restraints = 0, GoF = 1.013, R1 = 0.0520, wR_2 = 0.1286, R indices based on 3148 reflections with I >2s(I). $\Delta\rho_{max}$ = 0.195, $\Delta\rho_{min}$ = -0.214 (eÅ^{-3}).

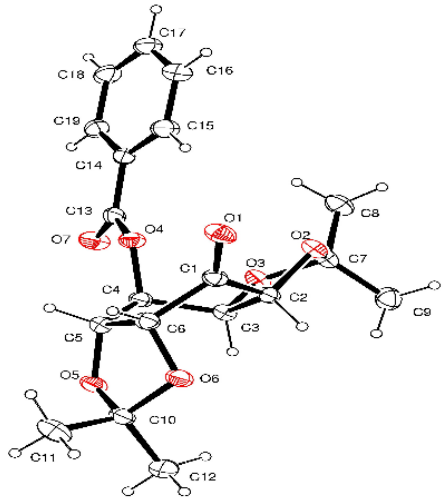


Fig. S3: ORTEP diagram of ketone **37**

(±)-1-*O*-Benzoyl-2,3:5,6-di-*O*-isopropylidene-*allo*-inositol (38) & (±)-3-*O*-benzoyl-1,2:4,5-di-*O*-isopropylidene-*neo*-inositol (39)

Reduction of **37** (326 mg, 0.9 mmol) using sodium borohydride as in the general procedure IV provided compounds **38** (131 mg, 40%) and **39** (131 mg, 40%) as white solids.

Reduction of ketone 37 with lithium borohydride

To a solution of ketone **37** (10 mg, 0.027 mmol) in dry THF (5 mL), lithium borohydride (0.7 mg, 0.033 mmol) was added at 0 ^{o}C. After completion of the reaction, the reaction was quenched with sat. NH_4Cl solution. The organic solvent was evaporated under reduced pressure. The crude reaction mass was extracted with ethyl acetate. The organic layer was washed successively with water and brine, dried over anhydrous Na_2SO_4 and was concentrated under reduced pressure. ^{1}H NMR of the crude product showed the presence of alcohols **38** & **39** in the ratio of 2:3.

Reduction of ketone 37 with lithium aluminium hydride

To a solution of ketone **37** (10 mg, 0.027 mmol) in dry THF (5 mL), lithium aluminiumhydride (1 mg, 0.027mmol) was added at 0 ^{o}C. After completion of the reaction, the reaction was quenched with sat. NH_4Cl solution. THF was evaporated under reduced pressure. The crude reaction mass was extracted with ethyl acetate. The organic layer was washed successively with water and brine, dried over anhydrous Na_2SO_4, concentrated under reduced pressure. ^{1}H NMR of the crude product showed the presence of alcohols **38** & **39** in the ratio of 1:2.

Reduction of ketone 37 with sodium triacetoxyborohydride

Reduction of ketone **37** (10 mg, 0.027 mmol) by using sodium triacetoxyborohydride as in the general procedure VI provided alcohols **38** & **39** in the ratio of 2:1.

Reduction of 37 with K-selectride

Reduction of **37** (50 mg, 0.14 mmol) using K-selectride as in the general procedure IV provided compound **39** (46.8 mg, 93%) exclusively.

Table S5. Summary of reduction of **37** with different reducing agents

Entry	Reagent	Solvent	Temp	dr[(a)] (**38**:**39**)
1	$NaBH_4$	MeOH	0 °C	1:1
2	$LiBH_4$	THF	0 °C – rt	2:3
3	$LiAlH_4$	THF	0 °C – rt	1:2
4	$NaBH(OAc)_3$	DCM	Rt	2:1
5	K-selectride	THF	-78 °C	0:1

dr = diasteromeric ratio (based on ^{1}H NMR)

Compound **38**: m.p. = 132-134 °C; R_f = 0.41 (ethyl acetate/petroleum ether, 2:3; v/v); IR (KBr, cm^{-1}) 3444, 1720, 1211; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.99 (d, J = 7.1 Hz, 2H), 7.70 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.72 Hz, 2H), 5.44 (d, J = 5.8 Hz, 1H, HO-4), 4.99 (dd, J = 3.3 Hz, 9.6 Hz, 1H, H-1), 4.61 (dd, J = 3.3 Hz, 7.8 Hz, 1H, H-6), 4.54 (t, J = 8.2 Hz, 1H, H-2), 4.47 (dd, J = 2.7 Hz, 7.8 Hz, 1H, H-5), 4.32 (t, J = 8.2 Hz, 1H, H-3), 3.80-3.77 (m, 1H, H-4), 1.45 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.25 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.1, 133.6, 129.4, 129.3, 128.8, 108.6, 108.2, 76.9 (C-5), 76.7 (C-3), 73.0 (C-1), 72.9 (C-6), 72.7 (C-2), 69.0 (C-4), 27.0, 25.7, 24.3, 23.3. Elemental analysis calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.66; H, 6.55.

Crystal data for 38: CCDC No. 973081, Molecular formula = $C_{19}H_{24}O_7$, Formula weight = 364.38, colorless blocks, 0.20 x 0.15 x 0.10 mm**,** Monoclinic, space group P2(1)/c, a = 19.5709(6), b = 11.6089(3), c = 17.9337(5)Å, V = 3849.08(19) Å^3, Z = 8, T = 296(2) K, $2\theta_{max}$ = 50.00°, D_{calc} (g cm^{-3}) = 1.258, F(000) = 1552, μ (mm^{-1}) = 0.096, 6775 reflections measured, 4268 unique reflections (R_{int} = 0.0328), multi-scan absorption correction, T_{min} = 0.9811, T_{max} = 0.9905, number of parameters = 514, number of restraints = 2, GoF = 1.046, R1 = 0.0689, wR_2 = 0.1962, R indices based on 4268 reflections with I >2s(I). $\Delta\rho_{max}$ = 0.000, $\Delta\rho_{min}$ = 0.000 (eÅ^{-3}).

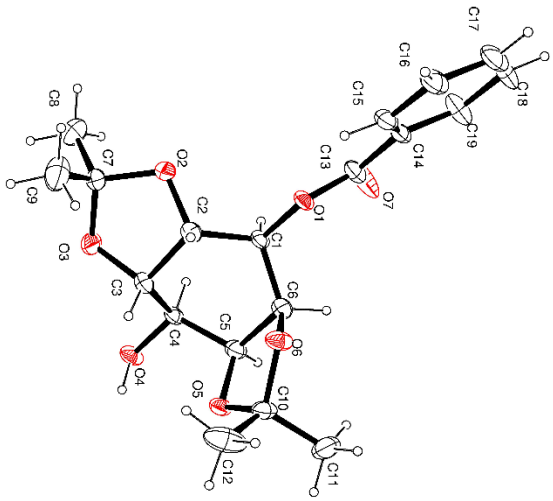


Fig. S4: ORTEP diagram of alcohol **38**

Compound **39**: m.p. = 156-157 °C; R_f = 0.76 (ethyl acetate/petroleum ether, 2:3; v/v); IR (KBr, cm^{-1}) 3446, 1718, 1276; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.98 (d, J = 8 Hz, 2H), 7.70 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.6 Hz, 2H), 5.49 (d, J = 5.15 Hz, 1H, HO-6), 5.41 (m, 1H, H-3), 4.56 (dd, J = 3.1 Hz, 7.6 Hz, 1H, H-4), 4.49 (dd, J = 4.55 Hz, 7.3 Hz, 1H, H-2), 4.45 (dd, J = 2.5 Hz, 7.45 Hz, 1H, H-1) 4.38 (dd, J = 5.5 Hz, 7.5 Hz, 1H, H-5), 4.09 (m, 1H, H-6), 1.43

(s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.26 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.2, 133.6, 129.4, 129.3, 128.8, 108.6, 108.2, 76.5 (C-1),72.0 (C-5), 75.1 (C-1), 73.5 (C-2), 72.0 (C-4), 70.9 (C-3), 68.2 (C-6), 26.1, 25.9, 23.9, 23.8. Elemental analysis calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.92; H, 6.67.

Crystal data for 39: CCDC No. 973083, Molecular formula = $C_{19}H_{24}O_7$, Formula weight = 364.38, colorless blocks, 0.20 x 0.15 x 0.10 mm**,** Monoclinic, space group C2/c, a = 34.7719(12), b = 6.3173(2), c = 16.9757(6) Å, V = 3695.5(2) Å^3, Z = 8, T = 293(2) K, $2\theta_{max}$ = 50.00°, D_{calc} (g cm^{-3}) = 1.310, F(000) = 1552, μ (mm^{-1}) = 0.100, 13229 reflections measured, 3217 unique reflections (R_{int} = 0.0231), multi-scan absorption correction, T_{min} = 0.9803, T_{max} = 0.9901, number of parameters = 240, number of restraints = 1, GoF = 1.071, R1 = 0.0427, wR_2 = 0.1027, R indices based on 3217 reflections with I >2s(I). $\Delta\rho_{max}$ = 0.192, $\Delta\rho_{min}$ = - 0.169 (eÅ^{-3}).

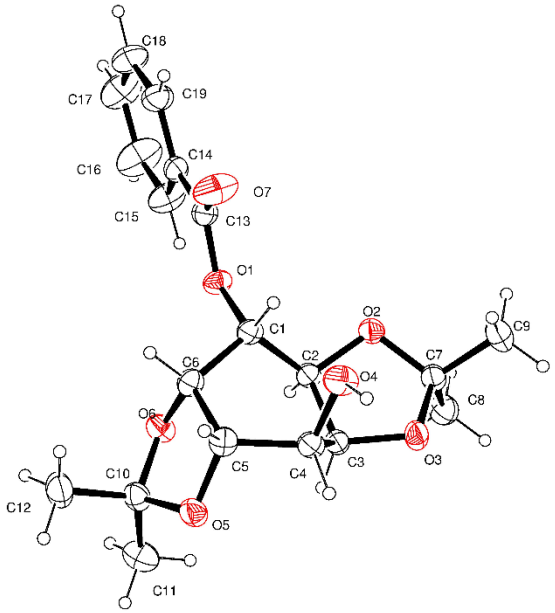


Fig. S5: ORTEP diagram of alcohol **39**

(±)-1-*O*-Acetyl-4-*O*-benzoyl-2,3:5,6-di-*O*-isopropylidene-*allo*-inositol (38A)

Acetylation of **38** (80 mg, 0.22 mmol) by adopting the general procedure VII provided **38A** (80 mg, 90%) as a white solid: m.p. = 200 °C; R_f = 0.65 (ethyl acetate/petroleum ether, 3:7; v/v); IR (Neat, cm^{-1}) 1728, 1274; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.98 (m, 2H), 7.71 (t, *J* = 6.8 Hz, 1H), 7.55 (t, *J* = 6.9 Hz, 2H), 5.16 (dd, *J* = 3.0 Hz, 9.2 Hz, 1H, H-4), 5.0 (dd, *J* = 2.95 Hz, 9.05 Hz, 1H, H-1), 4.7 (dd, *J* = 3.0 Hz, 7.85 Hz, 1H, H-5), 4.66-4.60 (m, 2H, H-3 & H-6), 4.52 (t, *J* = 8.6 Hz, 1H, H-2), 2.1 (s, 3H, OAc), 1.45 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.23 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.7, 165.0, 133.8, 129.3, 129.1, 128.9, 109.5, 109.0, 73.4 (C-6 or C-3), 73.3 (C-3 or C-6), 73.1 (C-5), 73.0 (C-2), 72.7 (C-4), 71.9 (C-1), 26.8, 25.5, 24.3, 23.2, 20.8. Elemental analysis calcd for $C_{21}H_{26}O_8$: C, 62.06; H, 6.45. Found: C, 61.81; H, 6.41.

Crystal data for 38A: CCDC No. 973082, Molecular formula = $C_{21}H_{26}O_8$, Formula weight = 406.43, colorless blocks, 0.25 x 0.20 x 0.15 mm**,** Triclinic, space group P-1, a = 10.2227(4), b = 13.8627(5), c = 15.3841(6) Å, V = 2114.06(14) Å^3, Z = 4, T = 296(2) K, $2\theta_{max}$ = 50.00°, D_{calc} (g cm^{-3}) = 1.277, F(000) = 864, μ (mm^{-1}) = 0.098, 7453 reflections measured, 4829 unique reflections (R_{int} = 0.0232), multi-scan absorption correction, T_{min} = 0.9759, T_{max} =

0.9855, number of parameters = 596, number of restraints = 0, GoF = 1.018, R1 = 0.0678, wR_2 = 0.1946, R indices based on 4829 reflections with I >2s(I). $\Delta\rho_{max}$ = 0.471, $\Delta\rho_{min}$ = -0.390 (eÅ^{-3}).

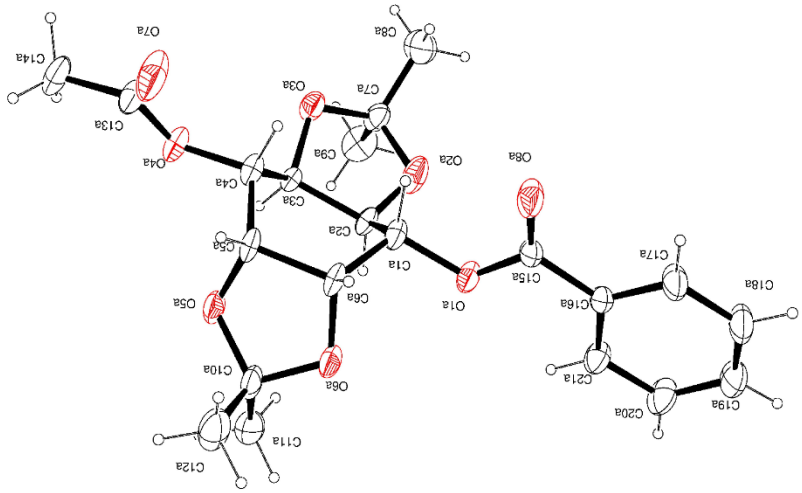


Fig. S6: ORTEP diagram of acetate **38A**

(±)-4-*O*-Acetyl-1-*O*-benzoyl-2,3:5,6-di-*O*-isopropylidene-*neo*-inositol (39A)

Acetylation of **39** (50 mg, 0.14 mmol) by adopting the general procedure VII provided **39A** (45 mg, 79%) as a liquid: R_f = 0.72 (ethyl acetate/petroleum ether, 2:3; v/v); IR (Neat, cm^{-1}) 1732, 1259; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.99 (d, J = 1.3 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H) 7.58 (t, J = 7.7 Hz, 2H), 5.47 (dd, J = 2.3 Hz, 6.3 Hz, 1H, H-4), 5.39 (t, J = 3.2 Hz, 1H, H-1), 4.65 (dd, J = 3.2 Hz, 7.7 Hz, 1H, H-6), 4.63-4.59 (m, 2H, H-2 & H-3), 4.55 (t, J = 7.0 Hz, 1H, H-5), 2.15 (s, 3H, OAc), 1.44 (s, 3H, CH_3), 1.29 (s, 6H, 2x CH_3), 1.23 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.5, 164.5, 133.7, 129.3, 128.8, 109.4, 108.9, 73.5 (C-3 or C-2), 73.3 (C-2 or C-3), 72.6 (C-5), 71.8 (C-6), 70.9 (C-4), 69.9 (C-1), 25.9, 25.8, 23.9, 23.7, 20.8. Elemental analysis calcd for $C_{21}H_{26}O_8$: C, 62.06; H, 6.45. Found: C, 62.39; H, 6.44.

Swern oxidation of 40

Swern oxidation of (±)-3-*O*-benzyl-1,2:4,5-di-*O*-isopropylidene-*myo*-inositol[21] (**40**) (100 mg, 0.3 mmol) by adopting the general procedure II provided the (±)-4-*O*-benzyl-2,3:5,6-di-*O*-isopropylidene allo-inosose (**41**, 79 mg, 79%) as a colourless liquid: R_f = 0.32 (ethyl acetate/petroleum ether, 3:7; v/v); IR (Neat, cm^{-1}) 1747, 1722, 1274; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.36-7.28 (m, 5H, Ar*H*), 4.91 (dd, J = 2.5 Hz, 8.4 Hz, 1H, H-2 or H-4), 4.80 (dd, J = 5.65 Hz, 8.05 Hz, 1H, H-4 or H-2), 4.74-4.65 (m, 4H, ArC*H2* , H-1 & H-5), 3.83 (dd, J = 2.4 Hz, 5.5 Hz, 1H, H-3), 1.45 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 201.9, 138.1, 128.1, 127.4, 127.2, 110.7, 110.3, 77.1 (C-2 or C-4), 76.3 (C-4 or C-2), 75.7 (C-5 or C-1), 75.4 (C-1 or C-5), 74.7 (C-3), 72.0 (Ar*C*H$_2$), 26.0, 25.7, 24.0, 23.9. Elemental analysis calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.21; H, 7.07.

(±)-1-*O*-Benzyl-2,3:5,6-di-*O*-isopropylidene-*allo*-inositol (42) & (±)-1-*O*-benzyl-2,3:5,6-di-*O*-isopropylidene-*neo*-inositol (43)

Reduction of **41** (100 mg, 0.29 mmol) by using sodium borohydride as in the general procedure IV provided alcohols **42** (50 mg, 50%) and **43** (31 mg, 31%) respectively.

Compound **42**: R_f = 0.38 (ethyl acetate/petroleum ether, 2:3; v/v); IR (Neat, cm^{-1}) 3525, 1373, 1207; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.36-7.28 (m, 5H, Ar*H*), 5.16 (d, *J* = 6.05 Hz, 1H, HO-4), 4.65 (s, 2H, ArCH_2), 4.57 (dd, *J* = 2.95 Hz, 7.95 Hz, 1H, H-6), 4.32 (dd, *J* = 3.05 Hz, 7.9 Hz, 1H, H-5), 4.30 (t, *J* = 8.47 Hz, 1H, H-2), 4.17 (t, *J* = 8.47 Hz, 1H, H-3), 3.52 (dd , *J* = 2.9 Hz, 8.8 Hz, 1H, H-1), 3.51-3.48 (m, 1H, H-4), 1.40 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.25 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.6, 128.1, 127.4, 127.3, 107.9, 107.5s, 76.9 (C-1), 76.3 (C-5), 76.2 (C-2), 75.2 (C-3), 73.0 (C-6), 70.6 (Ar*C*H$_2$), 68.9 (C-4), 27.1, 25.7, 24.2, 23.3. Elemental analysis calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 65.10; H, 7.48.

Compound **43**: m.p. = 58-60 ^{o}C; R_f = 0.77 (ethyl acetate/petroleum ether, 2:3; v/v); IR (Neat, cm^{-1}) 3572, 1265; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.36-7.28 (m, 5H, Ar*H*), 5.12 (d, *J* = 4.95 Hz, 1H, HO-4), 4.67 (d, *J* = 12.05, 1H, ArCH_A), 4.94 (d, *J* = 12.0, 1H, ArCH_B), 4.5 (dd, *J* = 2.8 Hz, 7.6 Hz, 1H, H-2 or H-6), 4.37 (dd, *J* = 5.1 Hz, 7.7 Hz, 1H, H-6 or H-2), 4.31 (dd, *J* = 2.8 Hz, 7.65 Hz, 1H, H-5 or H-3), 4.25 (dd, *J* = 4.75 Hz, 7.6 Hz, 1H, H-3 or H-5), 3.93-3.88 (m, 2H, H-1 & H-4), 1.41 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.27 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.6, 128.1, 127.4, 127.3, 107.9, 107.8, 76s.3 (C-1), 76.2 (C-3 or C-5), 74.9 (C-6 or C-6), 74.8 (C-5 or C-3), 73.1 (C-2 or C-6), 71.6 (Ar*C*H$_2$), 67.8 (C-4), 26.2, 26.1, 24.1, 23.9. Elemental analysis calcd for $C_{19}H_{26}O_6$: C, 65.13; H 7.48. Found: C, 64.97; H 7.39.

(±)-1-*O*-Acetyl-4-*O*-benzyl-2,3:5,6-di-*O*-isopropylidene-*allo*-inositol (42A)

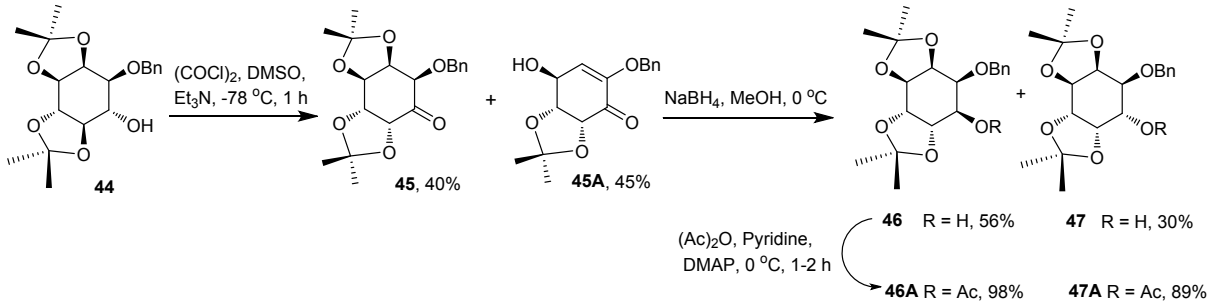
Acetylation of **42** (20 mg, 0.057 mmol) by adopting the general procedure VII provided **42A** (16.8 mg, 75%) as a liquid: R_f = 0.71 (ethyl acetate/petroleum ether, 3:7; v/v); IR (Neat, cm^{-1}) 1718, 1701, 1271; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.37-7.28 (m, 5H, ArH), 5.2 (t, *J* = 2.5 Hz, 1H, H-1), 4.73 (d, *J* = 11.95 Hz, 1H, ArCH_A), 4.68 (d, *J* = 11.95 Hz, 1H, ArCH_B), 4.51 (dd, *J* = 2.8 Hz, 7.7 Hz, 1H, H-5), 4.51-4.46 (m, 2H, H-3 & H-6), 4.37 (dd, *J* = 5.7 Hz, 7.4 Hz, 1H, H-2), 3.88 (t, *J* = 3.37 Hz, 1H, H-4), 2.06 (s, 3H, OAc), 1.39 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.27 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.5, 138.3, 128.2, 127.4, 108.7, 108.6, 75.4 (C-4), 74.7 (C-6 or C-3), 73.2 (C-3 or C-6), 73.1 (C-2), 72.2 (C-5), 72.1 (Ar*C*H$_2$), 70.9 (C-1), 26.0, 24.0, 23.8, 20.9. Elemental analysis calcd for $C_{21}H_{28}O_7$: C, 64.27; H, 7.19. Found: C, 64.28; H, 7.34.

(±)-4-*O*-Acetyl-1-*O*-benzyl-2,3:5,6-di-*O*-isopropylidene-*neo*-inositol (43A)

Stereochemistry of the newly formed stereocentre (C-4) in compound **43** was confirmed by acetylation. ^{1}H NMR of the acetate **43A** shows a $^3J_{H3H4}$ coupling constant of 8.4 Hz and $^3J_{H4H5}$ of 3.5 Hz, which indicates that H-4 proton is *anti* to H-3 and *syn* to H-5.

Acetylation of **43** (20 mg, 0.057 mmol) by adopting the general procedure VII provided **43A** (16.3 mg, 73%) as a liquid: R_f = 0.66 (ethyl acetate/petroleum ether, 2:3; v/v); IR (Neat, cm^{-1}) 1739, 1211; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.36-7.28 (m, 5H, Ar*H*), 4.76 (dd, *J* = 3.5 Hz, 8.4 Hz, 1H, H-4), 4.69-4.67 (m, 3H, ArCH_2 & H-6), 4.48 (dd, *J* = 3.2 Hz, 7.9 Hz, 1H, H-5), 4.43-4.38 (m, 2H, H-2 & H-3), 3.74 (dd, *J* = 2.87 Hz, 7.25 Hz, 1H, H-1), 2.1 (s, 3H, OAc), 1.42 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.25 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.8, 138.4, 128.1, 127.5, 127.4, 108.8, 108.4, 76.7 (C-1), 75.6 (C-3 or C-2), 73.5 (C-6), 72.8 (C-5), 72.7 (C-2 or C-3), 71.9 (C-4), 70.7 (Ar*C*H$_2$), 27.0, 25.6, 24.3, 23.2, 20.8. Elemental analysis calcd for $C_{21}H_{28}O_7$: C, 64.27; H, 7.19. Found: C, 63.99; H, 7.15.

Scheme S8:



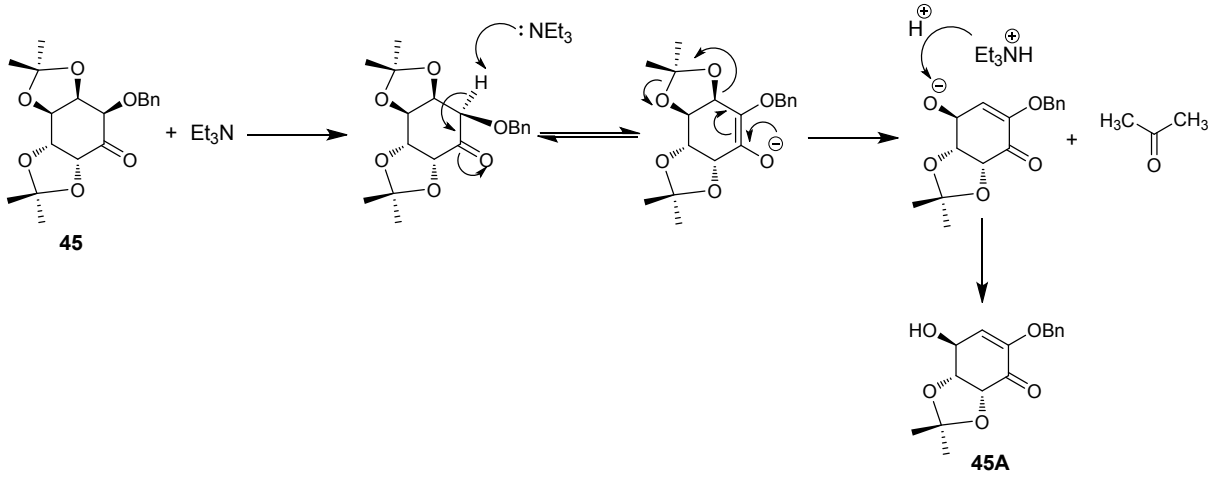
Swern oxidation of **44**

Swern oxidation of (±)-3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol (**44**)[21] (500 mg, 1.43 mmol) by adopting the general procedure II provided the ketone **45** (199 mg, 40%) and enone **45A** (187 mg, 45%) as colourless liquids. The enone **45A** might have formed through $E1_{CB}$ elimination as shown in Chart S1.

Ketone **45:** R_f = 0.76 (ethyl acetate/petroleum ether, 3:7; v/v); IR (Neat, cm^{-1}) 1747, 1384, 1213; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.38-7.32 (5H, m, Ar*H*), 4.85 (dd, *J* = 3.7 Hz, 6.5 Hz, 1H, H-6), 4.73 (dd, *J* = 1.8 Hz, 6.6 Hz, 1H, H-5), 4.7-4.66 (m, 2H, ArCH_A & H-4), 4.63 (dd, *J* = 1.5 Hz, 6.27 Hz, 1H, H-3), 4.49 (d, *J* = 12 Hz, 1H, ArCH_B), 4.25 (d, *J* = 8.6 Hz, 1H, H-2), 1.3 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.24 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 202.2, 137.9, 128.8, 128.4, 128.3, 110.8, 109.3, 77.7 (C-6), 76.8 (C-3), 76.3 (C-2), 75.0 (C-4), 72.6 (C-5), 71.3 (Ar*C*H$_2$), 26.6, 26.5, 24.6, 24.4. Elemental analysis calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94, Found: C, 65.36; H, 6.73.

Enone **45A:** R_f = 0.66 (ethyl acetate/petroleum ether, 2:3; v/v); IR (Neat, cm^{-1}) 3591, 1728, 1708, 1230; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.42-7.34 (m, 5H, Ar*H*), 6.06 (1H, d, *J* = 5.05 Hz, H-3), 5.69 (d, *J* = 6.6 Hz, 1H, OH), 4.88 (d, *J* = 12.0 Hz, 1H, ArCH_A), 4.83 (d, *J* = 12.0 Hz, 1H, ArCH_B), 4.56 (d, *J* = 5.45 Hz, 1H, H-6), 4.52-4.49 (m, 1H, H-4), 4.40 (dd, *J* = 1.5 Hz, 4.0 Hz, 1H, H-5), 1.33 (s, 3H, CH_3), 1.23 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 189.6, 148.8, 136.15, 128.4, 128.0, 127.9, 127.8, 116.5, 108.9, 78.3 (C-5), 75.0 (C-6), 69.1 (Ar*C*H$_2$), 63.1 (C-4), 27.4, 25.6. Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.01; H, 5.99.

Chart S1: Plausible mechanism for the formation of **45A** from **45**



(±)-3-*O*-Benzyl-1,2:5,6-di-*O*-isopropylidene-*allo*-inositol (46) & 3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-*neo*-inositol (47)

Reduction of **45** (75 mg, 0.22 mmol) using sodium borohydride as in the general procedure IV provided alcohols **46** (42.2 mg, 56%) and **47** (22.6 mg, 30%).

Compound **46**: R_f = 0.46 (ethyl acetate/petroleum ether, 3:7; v/v); IR (Neat, cm^{-1}) 3558, 1382, 1211; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.39-7.28 (m, 5H, Ar*H*), 4.93 (d, *J* = 2.7 Hz, 1H, HO-4), 4.6 (s, 2H, ArCH_2), 4.37 (t, *J* = 6.85 Hz, 1H, H-2), 4.32 (t, *J* = 6.8 Hz, 1H, H-1), 4.18 (dd, *J* = 3.8 Hz, 8.3 Hz, 1H, H-5), 4.14 (m, 1H, H-4), 4.02 (dd, *J* = 6.05 Hz, 8.2 Hz, 1H, H-6), 3.41 (d, *J* = 6.1 Hz, 1H, H-3), 1.42 (s, 3H, CH_3), 1.4 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.27 (3H, s, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 139.0, 128.7, 128.0, 127.8, 109.1, 108.6, 79.8 (C-3), 78.6 (C-1), 78.4 (C-6), 78.0 (C-2), 75.3 (C-5), 70.7 (Ar*C*H$_2$), 67.2 (C-4), 27.9, 26.8, 25.3, 25.1. Elemental analysis calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 65.32; H, 7.42.

Compound **47**: R_f = 0.3 (ethyl acetate/petroleum ether, 3:7; v/v); IR (Neat, cm^{-1}) 3414, 1068; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.4-7.26 (m, 5H, Ar*H*), 4.73 (d, *J* = 5.9 Hz, 1H, HO-4), 4.68 (d, *J* = 12.0 Hz, 1H, ArCH_A), 4.65 (d, *J* = 12.0 Hz, 1H, ArCH_B), 4.53 (dd, *J* = 3.8 Hz, 7.55 Hz, 1H, H-2), 4.39 (m, 3H, H-5, H-6 & H-1), 3.87 (m, 1H, H-4), 3.61 (dd, *J* = 3.8 Hz, 10.1 Hz, 1H, H-3), 1.38 (s, 3H, CH_3), 1.3 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.26 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 139.4, 128.5, 128.1, 127.7, 108.0, 107.9, 75.9 (C-6 or C-5), 74.9 (C-5 or C-6), 74.7 (C-1), 73.7 (C-2), 73.3 (C-3), 71.8 (Ar*C*H$_2$), 65.4 (C-4), 26.4, 26.3, 24.2, 24.1. Elemental analysis calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48. Found: C, 65.02; H, 7.61.

(±)-4-*O*-Acetyl-3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-*allo*-inositol (46A)

Stereochemistry of the newly formed stereocentre (C-4) in compound **46** was confirmed by acetylation. ^{1}H NMR of the acetate **46A** shows a $^3J_{H3H4}$ coupling constant of 4.0 Hz and $^3J_{H4H5}$ of 8.2 Hz, which indicates that H-4 proton is *syn* to H-3 and *anti* to H-5.

Acetylation of **46** (20 mg, 0.06 mmol) by adopting the general procedure VII provided **46A** (23 mg, 98%) as a liquid: R_f = 0.81 (ethyl acetate/petroleum ether, 3:7; v/v); IR (Neat, cm^{-1}) 3068, 1712, 1220; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.37-7.28 (m, 5H, Ar*H*), 5.57 (t, *J* = 2 Hz, 1H, H-4), 4.64 (d, *J* = 12.0 Hz, 1H, ArCH_A), 4.57 (d, *J* = 12.0 Hz, 1H, ArCH_B) 4.42 (dd, *J* = 4.2 Hz, 8.2 Hz, 1H, H-5), 4.39-4.34 (m, 2H, H-2 & H-1), 4.17 (dd, *J* = 4.5 Hz, 8.0 Hz, 1H, H-6), 3.61 (d, *J* = 5.0 Hz, 1H, H-3), 2.05 (s, 3H, OAc), 1.40 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.26 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.8, 138.4, 128.6, 128.0, 127.9, 109.2, 108.9, 79.6 (C-1), 78.0 (C-6), 77.5 (C-2), 77.3 (C-3), 72.8 (C-5), 70.7 (ArCH_2), 68.6 (C-4), 31.1, 27.8, 26.8, 25.3, 24.9, 21.2. Elemental analysis calcd for $C_{21}H_{28}O_7$: C, 64.27; H, 7.19. Found: C 64.51; H, 7.15.

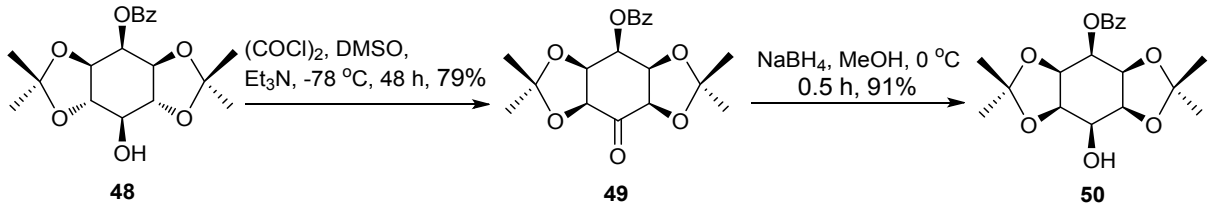
(±)-4-*O*-Acetyl-3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-*neo*-inositol (47A)

Stereochemistry of the newly formed stereocentre (C-4) in compound **47** was confirmed by acetylation. ^{1}H NMR of the acetate **47A** shows a $^3J_{H3H4}$ coupling constant of 10.9 Hz and $^3J_{H4H5}$ of 2.65 Hz, which indicates that H-4 proton is *anti* to H-3 and *syn* to H-5.

Acetylation of **47** (10 mg, 0.03 mmol) by adopting the general procedure VII provided **47A** (10 mg, 89%) as a liquid: R_f = 0.55 (ethyl acetate/petroleum ether, 3:7; v/v); IR (Neat, cm^{-1}) 1732, 1060; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.38-7.28 (m, 5H, Ar*H*), 5.15 (dd, *J* = 2.6 Hz, 10.9 Hz, 1H, H-4), 4.66-4.62 (m, 2H, H-2 & ArCH_A), 4.59 (d, *J* = 12.5 Hz, ArCH_B), 4.52 (m,

3H, H-1, H-5 & H-6), 3.78 (dd, *J* = 3.7 Hz, 10.9 Hz, 1H, H-3), 2.06 (s, 3H, OAc), 1.42 (s, 3H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$), 1.30 (s, 3H, C*H*$_3$), 1.25 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 170.3, 138.9, 128.7, 128.0, 127.9, 108.6, 108.5, 74.1 (C-6 or C-5 or C-1), 73.9 (C-1 or C-6 or C-5), 73.3 (C-5 or C-1 or C-6), 73.2 (C-2), 71.5 (Ar*C*H$_2$), 71.1 (C-3), 68.2 (C-4), 26.3, 26.0, 24.2, 24.0, 21.3. Elemental analysis calcd for $C_{21}H_{28}O_7$: C, 64.27; H, 7.19. Found: C, 64.36; H, 7.12.

Scheme S9:



48 **49** **50**

Swern oxidation of 48

Swern oxidation of (±)-2-*O*-benzoyl-1,6:3,4-di-*O*-isopropylidene-*myo*-inositol[22] (**48**, 70 mg, 0.19 mmol) by adopting the general procedure II provided the symmetrical ketone **49** (55 mg, 79%) as a white solid: m.p. = 132-134 °C; R$_f$ = 0.53 (acetone/ dichloromethane, 1:9; v/v); IR (KBr, Cm^{-1}) 1735, 1720; ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 7.71 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.25 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 5.65 (t, *J* = 2.5 HZ, 1H, H-4), 4.85 (dd, *J* = 2.25 Hz, 9.75 Hz, 2H, H-3 & H-5), 4.80 (d, *J* = 9.5 Hz, 2H, H-2 & H-6), 1.20 (s, 3H, C*H*$_3$), 1.02 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 200.2, 164.4, 133.5, 129.4, 129.1, 128.6, 110.4, 75.3 (C-2 & C-6), 73.9 (C-3 & C-5), 67.6 (C-4), 25.7, 24.4. Elemental analysis calcd for $C_{19}H_{22}O_7$: C, 62.97; H, 6.12. Found: C, 62.66; H, 6.11.

Crystal data for 49:CCDC No. 973084, Molecular formula = $C_{19}H_{22}O_7$, Formula weight = 362.37, colorless rectangular blocks, 0.30 x 0.25 x 0.10 mm, Triclinic, space group P-1, a = 11.573(2), b = 11.787(2), c = 15.259(3) Å, V = 1870.7(6) Å^3, Z = 4, T = 296(2) K, $2\theta_{max}$ = 50.00°, D_{calc} (g cm^{-3}) = 1.287, F(000) = 768, μ (mm^{-1}) = 0.098, 7279 reflections measured, 3096 unique reflections (R_{int} = 0.0909), multi-scan absorption correction, T_{min} = 0.9711, T_{max} = 0.9902, number of parameters = 469, number of restraints = 0, GoF = 0.914, R1 = 0.0743, wR_2 = 0.1734, R indices based on 3096 reflections with I >2s(I). $\Delta\rho_{max}$ = 0.045, $\Delta\rho_{min}$ = 0.006 (eÅ^{-3}).

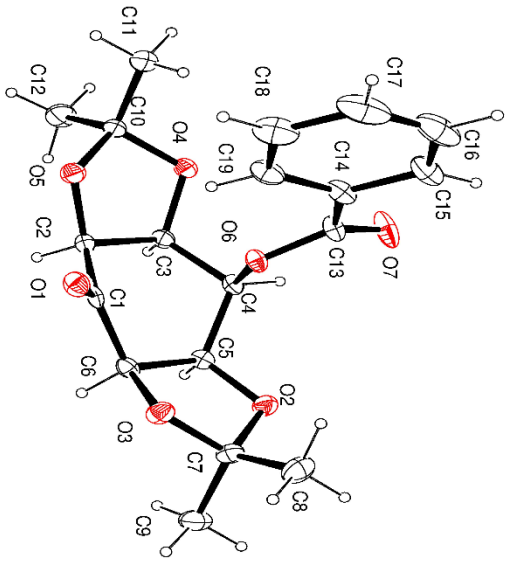


Fig. S7: ORTEP diagram of Ketone **49**

1-*O*-Benzoyl-2,3:5,6-di-*O*-isopropylidene-*cis*-inositol (50)

Reduction of **49** (20 mg, 0.06 mmol) using sodium borohydride as in the general procedure IV provided alcohol **50** (18.3 mg, 91%): m.p.= 150-151 °C; R_f = 0.50 (acetone/ dichloromethane, 1:9; v/v); IR (KBr, cm^{-1}) 3483, 1718, 1274; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H,), 7.49 (t, *J* = 7.7 Hz, 2H), 5.12 (t, *J* = 4.25 Hz, 1H, H-1), 4.47 (dd, *J* = 4.5 Hz, 8.0 Hz, 2H, H-2 & H-6), 4.35 (d, *J* = 7.5 Hz, 1H, 4-OH), 4.3 (dd, *J* = 4.0 Hz, 8.0 Hz, 2H, H-3 & H-5), 3.80-3.77 (m, 1H, H-4), 1.4 (s, 3H, CH_3), 1.2 (s, 3H, CH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.2, 133.5, 129.6, 129.4, 128.8, 109.0, 74.5 (C-3 & C-5), 72.1 (C-2 & C-6), 68.0 (C-1), 64.3 (C-4), 25.7, 23.7. Elemental analysis calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.53; H, 6.85.

Crystal data for 50: CCDC No. 973085, Molecular formula = $C_{19}H_{24}O_7$, Formula weight = 364.38, colorless rectangular blocks, 0.35 x 0.15 x 0.10 mm**,** Monoclinic, space group P2(1)/c, a = 9.0182(9), b = 26.030(3), c = 15.8147(15) Å, V = 3696.5(7) Å^3, Z = 8, T = 293(2) K, $2\theta_{max}$ = 50.00°, D_{calc} (g cm^{-3}) = 1.309, F(000) = 1552, μ (mm^{-1}) = 0.100, 9238 reflections measured, 3069 unique reflections (R_{int} = 0.0885), multi-scan absorption correction, T_{min} = 0.9659, T_{max} = 0.9901, number of parameters = 469, number of restraints = 0, GoF = 0.954, R1 = 0.0816, wR_2 = 0.1807, R indices based on 3069 reflections with I >2s(I). $\Delta\rho_{max}$ = 0.055, $\Delta\rho_{min}$ = 0.008 (e$Å^{-3}$).

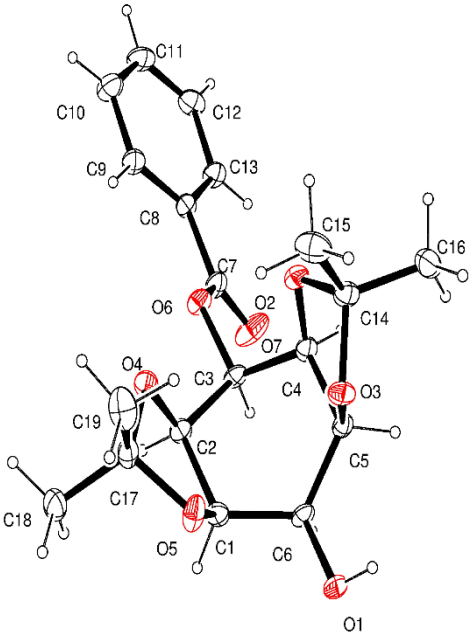
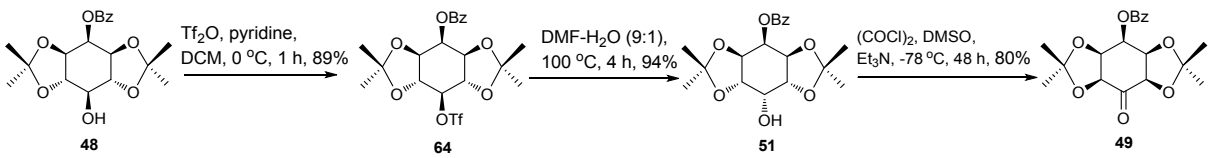


Fig. S8: ORTEP diagram of alcohol **50**

Scheme S10:



2-*O*-Benzoyl-5-*O*-trifluoromethanesulfonyl-1,6:3,4-di-*O*-isopropylidene-*myo*-inositol (64)

Tf_2O (152 mg, 0.54 mmol) was added dropwise to a solution of **48** (100 mg, 0.27 mmol) in a mixture of pyridine (2 mL) and CH_2Cl_2 (10 mL) at 0 °C. After 1 h, the solvent was evaporated, the reaction mass was extracted with ethyl acetate, and was washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using a mixture of ethyl acetate and petroleum ether (1:9, v/v) as eluent, to get compound **64** (120 mg, 89%) as a white solid. m.p. = 120-122 °C; R_f = 0.92 (ethyl acetate/petroleum ether, 3:7; v/v); IR (KBr, cm^{-1}) 1738, 1406, 1208; ^{19}F NMR (470 MHz, DMSO-*d*6) δ ppm –74.41 (s, 3F, CF_3); ^1H NMR (500 MHz, DMSO-d_6) δ 8.16 (dd, *J* = 1.15 Hz, 8.3 Hz, 2H), 7.72-7.69 (m, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 5.97 (t, *J* = 2.17 Hz, 1H, H-5), 5.61 (t, *J* = 9.35 Hz, 1H, H-2), 4.40 (t, *J* = 9.42 Hz, 2H, H-4 & H-6), 4.23 (dd, *J* = 2.2 Hz, 9.47 Hz, 2H, H-1 & H-3), 1.41 (s, 6H, 2x CH_3), 1.31 (s, 6H, 2x CH_3); ^{13}C NMR (125 MHz, DMSO- d_6) δ 164.7, 133.8, 129.7, 128.9, 112.7, 84.5 (C-5), 75.5 (C-1 & C-3), 74.8 (C-4 & C-6), 63.6 (C-2), 26.5, 26.2. Elemental analysis calcd for $C_{20}H_{23}F_3O_9S$: C, 48.39; H, 4.67; S, 6.46. Found: C, 48.07; H, 4.69; S, 6.09.

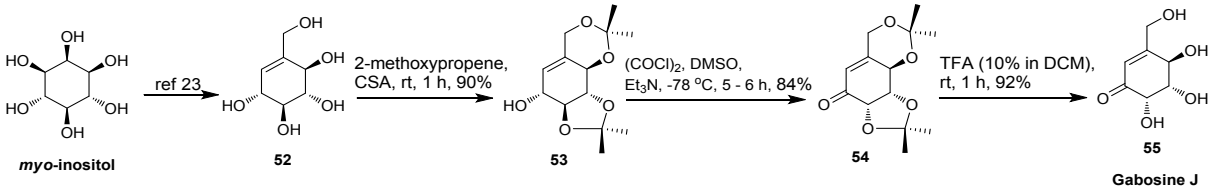
2-*O*-Benzoyl-1,6:3,4-di-*O*-isopropylidene-*neo*-inositol (51)

A solution of compound **64** (80 mg, 0.16 mmol) in a mixture of DMF (9 mL) and water (1 mL) was heated at 100 °C for 4 h. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and was washed successively with water and brine. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. Further purification by column chromatography using ethyl acetate and petroleum ether (3:7, v/v) as eluent, afforded compound **51** as a white solid (55 mg, 94%). m.p. = 197-199 °C; R_f = 0.13 (ethyl acetate/petroleum ether, 3:7; v/v); IR (KBr, cm^{-1}) 3478, 1738, 1102; ^1H NMR (500 MHz, DMSO-d_6) δ 8.06 (d, *J* = 7.1 Hz, 2H), 7.69 (t, *J* = 7.1 Hz, 1H), 7.56 (t, *J* = 7.78 Hz, 2H), 5.94 (t, *J* = 2.0 Hz, 1H, H-2), 5.55 (d, *J* = 4.45 Hz, HO-5), 4.52 (t, *J* = 2.2 Hz, 1H, H-5), 4.13-4.07 (m, 4H, H-1, H-3, H-4 & H-6), 1.35 (s, 6H, 2x CH_3), 1.24 (s, 6H, 2x CH_3); ^{13}C NMR (125 MHz, DMSO) δ 164.9, 133.5, 129.4, 129.3, 128.9, 110.8, 75.8 (C-1 & C-3), 72.9 (C-4 & C-6), 65.1 (C-2), 62.7 (C-5), 26.7, 26.5. Elemental analysis calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.76; H, 6.95.

Swern oxidation of 51

Swern oxidation of **51** (30 mg, 0.08 mmol) by adopting the general procedure II provided the symmetrical ketone **49** (24 mg, 80%) as a white solid.

Scheme S11:



(1R,2S,3S,4R)-5-(methyl ketal)-2,3:4,7-di-*O*-isopropylidene-cyclohex-5-ene-1-ol (53)

To a solution of pentol **52** (0.5 g, 2.84 mmol) in dry DMF (10 mL), 2-methoxypropene (614 mg, 8.51 mmol) and camphorsulfonic acid (66 mg, 0.284 mmol) were added. The resulting mixture was stirred at room temperature for 1 h. After completion of the reaction, the reaction

mixture was neutralised by addition of solid $NaHCO_3$. The reaction mass was filtered and the solvents were evaporated under reduced pressure on a rotary evaporator, and the residue was diluted with ethyl acetate. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude material thus obtained was purified by column chromatography using a mixture of ethyl acetate and petroleum ether (1:9; v/v) as eluent to obtain the compound **53** (655 mg, 90%) exclusively. ^{1}H NMR of the compound **53** matches with the reported data.[24]

Swern oxidation of 53

Swern oxidation of **53** (50 mg, 0.19 mmol) by adopting the general procedure II provided the ketone **54** (41.6 mg, 84%). ^{1}H-NMR of the compound **54** matches with the reported data.[25]

Gabosine J (55)

To a 10% solution of TFA in DCM (10 mL), ketone **54** (40 mg, 0.157 mmol) was added at room temperature, and the reaction mixture was stirred for 1 h at the same temperature. DCM was evaporated off to dryness to get a white solid. The residue was further purified by washing with DCM (10 mL x 3) to get pure gabosine J (25 mg, 92%) as a white solid. ^{1}H-NMR of the compound **55** matches with the reported data.[25]

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