Model Molecules to Classify CH···O Hydrogen-bonds

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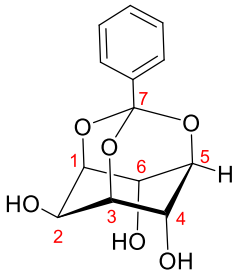
1) Materials and General Procedures

Chromatograms were visualized under UV light and by dipping plates into the solution of chromic acid in 20% aqueous sulphuric acid, followed by heating. The ^{1}H NMR, COSY, NOESY and HMQC spectra were recorded on a Bruker (500 MHz) NMR spectrometer at room temperature unless otherwise stated. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.0 ppm) or with the solvent reference relative to TMS employed as the internal standard ($CDCl_3$, δ 7.26 ppm; DMSO-d_6, δ 2.54 ppm; D_2O, δ 4.79 ppm etc). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m)], coupling constants [Hz], integration and peak identification). All NMR signals were assigned on the basis of ^{1}H NMR, ^{13}C NMR, COSY and HMQC experiments. ^{13}C spectra were recorded with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard. All NMR data were collected at 25 °C. Melting points were determined using Stuart SMP30 melting point apparatus and are uncorrected. Flash column chromatography was performed using Silica Gel (200-400 mesh). All reactions were carried out under argon or nitrogen atmosphere employing oven dried glasswares. All yields are calculated based on the recovered starting material.

X-ray intensity data measurements of freshly grown crystals of 4 were carried out at 293–298 K on a Bruker-KAPPA APEX II CCD diffractometer with graphite-monochromatized (MoKα = 0.71073 Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. Data were collected with a scan width of 0.3° at different settings of φ (0°, 90° and 180°) keeping the sample to detector distance fixed at 40 mm and the detector position (2θ) fixed at 24°. The X-ray data collection was monitored by SMART program. All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs. SHELXL-97 (for compounds 5 and 7) and SHELXL-2014[1] (for 8, 9, 12, 13 and 14) were used for structure solution and full matrix least-squares refinement on F2. Molecular and packing diagrams were generated using Mercury-3.1. Geometrical calculations were performed using SHELXTL and PLATON.[2]

2) Synthetic Procedures and Characterization

a) *Myo*-inositol 1,3,5-orthobenzoate (1)[3]

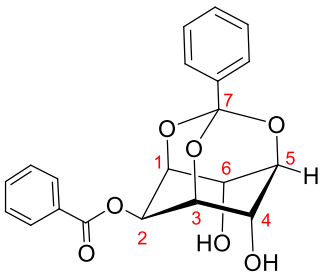


1

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.10 (d, *J* = 12.0 Hz, 1H, C-2-OH), 3.30 (d, *J* = 7.6 Hz, 2H, C-4-OH & C-6-OH), 4.15 (d, *J* = 12.0 Hz, 1H, H-2), 4.36-4.37 (m, 3H, H-1, H-3 & H-5), 4.68-4.69 (m, 2H, H-4 & H-6), 7.30-7.31 (m, 3H, Ar-*H*), 7.55-7.57 (m, 2H, Ar-*H*).

^{1}H NMR (DMSO-d_6, 500 MHz) δ: 4.10 (d, *J* = 6.3 Hz, 1H, H-2), 4.17 (br s, 2H, H-1 & H-3), 4.22 (br s, 1H, H-5), 4.41-4.42 (m, 2H, H-4 & H-6), 5.33 (d, *J* = 6.3 Hz, 1H, C-2-OH), 5.51 (d, *J* = 6.0 Hz, 2H, C-4-OH & C-6-OH), 7.33-7.38 (m, 3H, Ar-*H*), 7.56-7.58 (m, 2H, Ar-*H*).

b) <u>2-*O*-benzoyl-*myo*-inositol 1,3,5-orthobenzoate (2)[4]</u>



2

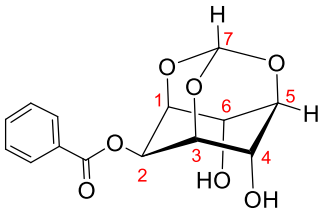
^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.44 (br s, 1H, H-5), 4.59 (br s, 2H, H-1 & H-3), 4.69-4.71 (m, 2H, H-4 & H-6), 5.57 (br s, 1H, H-2), 7.30-7.32 (m, 3H, Ar-*H*), 7.38-7.41 (m, 2H, Ar-*H*), 7.51-7.54 (m, 1H, Ar-*H*), 7.59-7.61 (m, 2H, Ar-*H*), 8.08-8.09 (m, 2H, Ar-*H*).

^{1}H NMR (DMSO-d_6, 500 MHz) δ: 4.33 (s, 1H, H-5), 4.47 (s, 2H, H-1 & H-3), 4.50-4.51 (m, 2H, H-4 & H-6), 5.58 (s, 1H, H-2), 7.36-7.38 (m, 3H, Ar-*H*), 7.54-7.57 (m, 4H, Ar-*H*), 7.66-7.69 (m, 1H, Ar-*H*), 8.02-8.04 (m, 2H, Ar-*H*).

^{1}H NMR (CD_3OD, 500 MHz) δ: 4.30 (br s, 1H, H-5), 4.43-4.44 (m, 2H, H-1 & H-3), 4.52-4.54 (m, 2H, H-4 & H-6), 5.56-5.57 (m, 1H, H-2), 7.24-7.27 (m, 3H, Ar-*H*), 7.39-7.42 (m, 2H, Ar-*H*), 7.51-7.54 (m, 3H, Ar-*H*), 8.01-8.03 (m, 2H, Ar-*H*).

^{1}H NMR (CD_3CN, 500 MHz) δ: 4.41-4.43 (m, 3H, C-4-OH, C-6-OH & H-5), 4.55 (s, 2H, H-1 & H-3), 4.62 (br s, 2H, H-4 & H-6), 5.59 (s, 1H, H-2), 7.38-7.40 (m, 3H, Ar-*H*), 7.51-7.54 (m, 2H, Ar-*H*), 7.61-7.65 (m, 3H, Ar-*H*), 8.09-8.11 (m, 2H, Ar-*H*).

c) <u>2-*O*-benzoyl-*myo*-inositol 1,3,5-orthoformate (3)[5]</u>



3

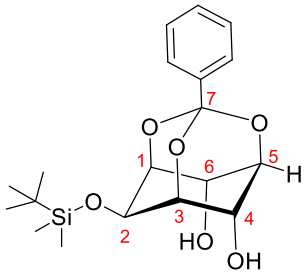
^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.88 (br s, 2H, C-4-OH & C-6-OH), 4.31 (br s, 1H, H-5), 4.41 (br s, 2H, H-1 & H-3), 4.60 (br s, 2H, H-4 & H-6), 5.49 (s, 2H, H-2 & H-7), 7.39-7.42 (m, 2H, Ar-*H*), 7.52-7.55 (m, 1H, Ar-*H*), 8.08-8.09 (m, 2H, Ar-*H*).

^{1}H NMR (DMSO-d_6, 500 MHz) δ: 4.18 (br s, 1H, H-5), 4.27 (s, 2H, H-1 & H-3), 4.38-4.39 (m, 2H, H-4 & H-6), 5.50 (s, 1H, H-2), 5.63 (s, 1H, H-7), 5.71 (d, *J* = 6.0 Hz, 2H, C-4-OH & C-6-OH), 7.56 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.67-7.70 (m, 1H, Ar-*H*), 8.02-8.03 (m, 2H, Ar-*H*).

^{1}H NMR (Acetone-d_6, 500 MHz) δ: 4.15-4.17 (m, 1H, H-5), 4.26-4.27 (m, 2H, H-1 & H-3), 4.42 (br s, 2H, H-4 & H-6), 5.09 (br s, 2H, C-4-OH & C-6-OH), 5.41 (br s, 1H, H-7), 5.48 (d, *J* = 1.0 Hz, 1H, H-2), 7.41-7.44 (m, 2H, Ar-*H*), 7.53-7.56 (m, 1H, Ar-*H*), 7.97-7.99 (m, 2H, Ar-*H*).

^{1}H NMR (CD_3CN, 500 MHz) δ: 4.26-4.27 (m, 1H, H-5), 4.36-4.37 (m, 2H, H-1 & H-3), 4.40 (br s, 2H, C-4-OH & C-6-OH), 4.50 (br s, 2H, H-4 & H-6), 5.51 (d, *J* = 1.5 Hz, 1H, H-2), 5.52 (s, 1H, H-7), 7.52-7.55 (m, 2H, Ar-*H*), 7.64-7.68 (m, 1H, Ar-*H*), 8.08-8.09 (m, 2H, Ar-*H*).

d) <u>2-*O*-*tert*-butyldimethylsilyl-*myo*-inositol 1,3,5-orthobenzoate (4)[6]</u>



4

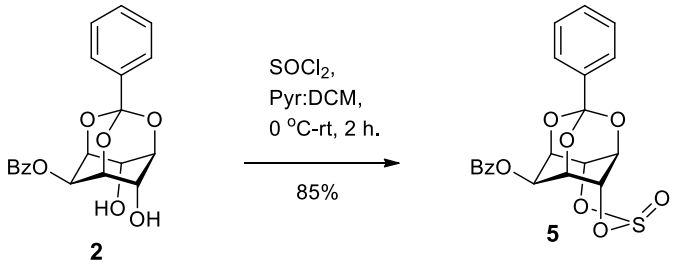
^{1}H NMR (DMSO-d_6, 500 MHz) δ: 0.16 (s, 6H, 2 x Si-*CH*$_3$), 0.96 (s, 9H, 3 x ^{t}Bu-*CH*$_3$), 4.17 (br s, 2H, H-1 & H-3), 4.26 (br s, 1H, H-5), 4.36 (br s, 1H, H-2), 4.45-4.46 (br s, 2H, H-4 & H-6), 5.58 (d, *J* = 6.0 Hz, 2H, 4 & 6-OH), 7.38-7.39 (m, 3H, Ar-*H*), 7.54-7.56 (m, 2H, Ar-*H*).

^{1}H NMR (CD_3OD, 500 MHz) δ: 0.20 (s, 6H, 2 x Si-*CH*$_3$), 1.00 (s, 9H, 3 x ^{t}Bu-*CH*$_3$), 4.23-4.25 (m, 2H, H-1 & H-3), 4.29-4.31 (m, 1H, H-5), 4.43 (t, *J* = 1.9 Hz, 1H, H-2), 4.55 (t, *J* = 4.0 Hz, 2H, H-4 & H-6), 7.33-7.37 (m, 3H, Ar-*H*), 7.61-7.63 (m, 2H, Ar-*H*).

^{1}H NMR (CD_3CN, 500 MHz) δ: 0.19 (s, 6H, 2 x Si-*CH*$_3$), 0.99 (s, 9H, 3 x ^{t}Bu-*CH*$_3$), 4.25 (br s, 1H, 4/6-OH), 4.26 (br s, 1H, 4/6-OH), 4.27-4.28 (m, 2H, H-1 & H-3), 4.30-4.32 (m, 1H, H-5), 4.37 (t, *J* = 1.8 Hz, 1H, H-2), 4.53-4.56 (m, 2H, H-4 & H-6), 7.38-7.42 (m, 3H, Ar-*H*), 7.59-7.60 (m, 2H, Ar-*H*).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.15 (s, 6H, 2 x Si-*CH*$_3$), 0.96 (s, 9H, 3 x ^{t}Bu-*CH*$_3$), 3.84 (br s, 2H, C-4-OH & C-6-OH), 4.11-4.12 (m, 1H, H-5), 4.19-4.20 (m, 2H, H-1 & H-3), 4.23 (t, *J* = 1.6 Hz, 1H, H-2), 4.45-4.47 (m, 2H, H-4 & H-6), 7.36-7.39 (m, 3H, Ar-*H*), 7.62-7.64 (m, 2H, Ar-*H*), data adopted from ref 4.

e) <u>2-*O*-benzoyl-1,3,5-orthobenzoyl-*myo*-inositol 4,6-*O*-sulfite (5)</u>



To a solution of diol **2** (0.10 g, 0.27 mmol) in a mixture of pyridine and dichloromethane (1:4, v/v, 10 mL), thionylchloride (0.04 mL, 0.59 mmol) was added drop wise at 0 ^{o}C for 15 min. The reaction was allowed to stir at room temperature for 2 h. The reaction mixture was then concentrated under reduced pressure and at low temperature (below 40 ^{o}C). The residue was co-evaporated with toluene to dryness. The resulting residue was adsorbed on silica gel by dissolving it into dichloromethane. The crude product thus obtained was purified by column chromatography using ethyl acetate and petroleum ether (2:8, v/v) as eluent to yield **5** (0.055 g, 85%) as a white solid. The sulfite **5** was recrystallized from a mixture of dichloromethane and hexane (1:2, v/v).

mp: 156-158 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.78 (t, *J* = 1.2 Hz, 2H, H-1 & H-3), 5.33 (t, *J* = 4.5 Hz, 2H, H-4 & H-6), 5.59 (br s, 1H, H-2), 6.03 (t, *J* = 4.0 Hz, 1H, H-5), 7.39-7.41 (m, 3H, Ar-*H*), 7.48 (t, *J* = 4.2 Hz, 2H, Ar-*H*), 7.61 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 7.66-7.68 (m, 2H, Ar-*H*), 8.16 (d, *J* = 7.5 Hz, 2H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 60.8, 62.6, 68.5, 70.2, 107.3, 125.3, 128.2, 128.6, 129.2, 130.0, 130.1, 133.6, 135.7, 165.7. Anal. Calcd for $C_{20}H_{16}O_8S$: C, 57.69; H, 3.87; S, 7.70 %. Found: C, 57.78; H, 3.79; S, 7.58 %.

^{1}H NMR (DMSO-d_6, 500 MHz) δ: 4.95 (br s, 2H, H-1 & H-3), 5.57 (br s, 1H, H-2), 5.60-5.61 (m, 2H, H-4 & H-6), 5.91 (br s, 1H, H-5), 7.49-7.51 (m, 3H, Ar-*H*), 7.64-7.67 (m, 4H, Ar-*H*), 7.76-7.79 (m, 1H, Ar-*H*), 8.11 (d, *J* = 7.5 Hz, 2H, Ar-*H*).

^{1}H NMR (CD_3OD, 500 MHz) δ: 4.70 (2H, obscured by H_2O peak, H-1 & H-3), 5.33 (t, *J* = 4.6 Hz, 2H, H-4 & H-6), 5.50 (t, *J* = 2.1 Hz, 1H, H-2), 5.88-5.90 (m, 1H, H-5), 7.27-7.30 (m, 3H, Ar-*H*), 7.40-7.43 (m, 2H, Ar-*H*), 7.53-7.56 (m, 3H, Ar-*H*), 8.01-8.09 (m, 2H, Ar-*H*).

^{1}H NMR (CD_3OD, 500 MHz, 50 °C) δ: 4.83-4.84 (m, 2H, H-1 & H-3), 5.43-5.44 (m, 2H, H-4 & H-6), 5.62 (s, 1H, H-2), 5.99-6.01 (m, 1H, H-5), 7.37-7.41 (m, 3H, Ar-*H*), 7.51-7.54 (m, 2H, Ar-*H*), 7.64-7.67 (m, 3H, Ar-*H*), 8.24-8.15 (m, 2H, Ar-*H*).

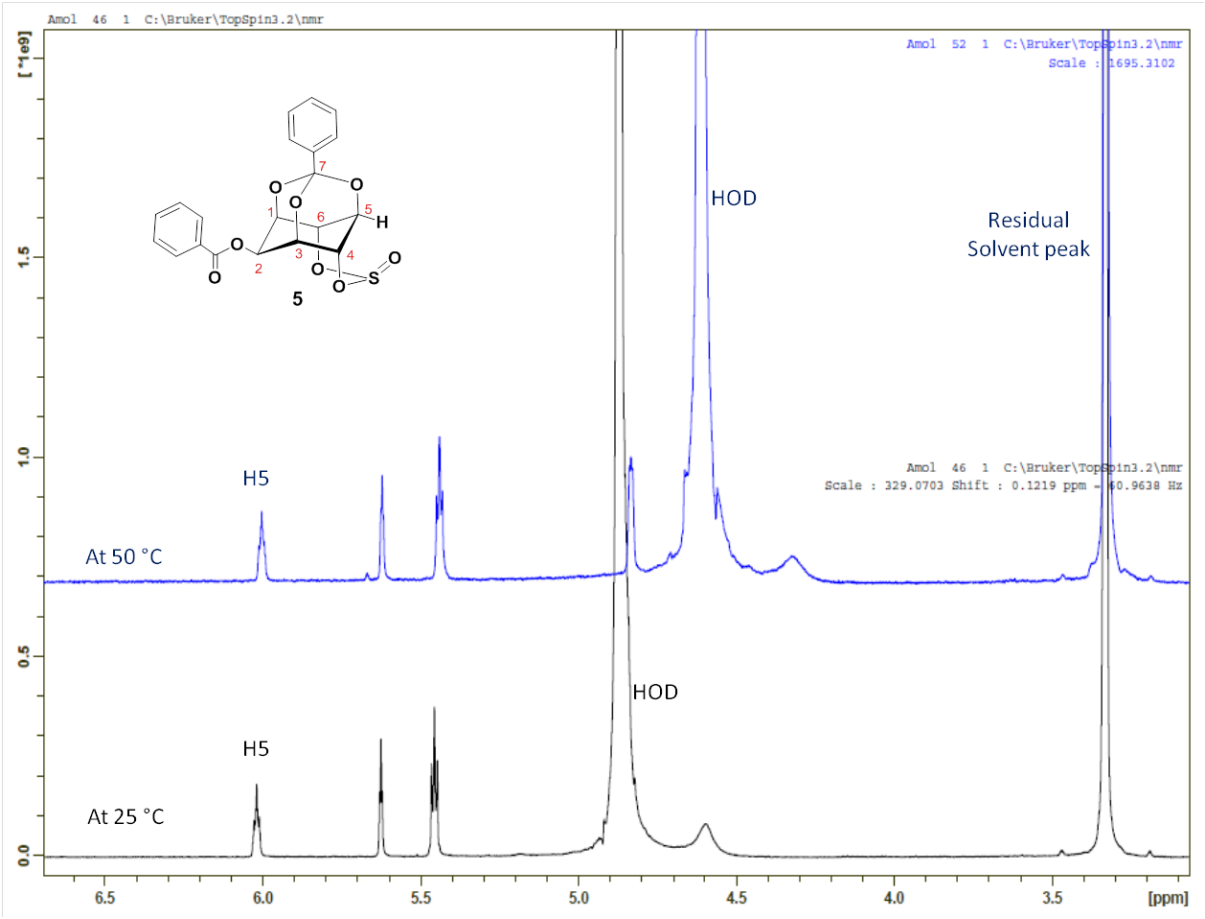
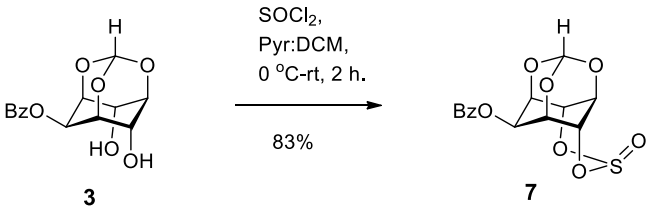


Figure S1. Overlay of partial ^{1}H NMR spectra of sulfite **5** in CD_3OD at 25 (black) and 50 ^{o}C (blue)

f) 2-*O*-benzoyl-1,3,5-orthoformyl-*myo*-inositol 4,6-*O*-sulfite (7)



The sulfite **7** was synthesized as before like the case of sulfite **5** using diol **3** (0.20 g, 0.68 mmol) in a mixture of pyridine and dichloromethane (1:4, v/v, 10 mL) and thionylchloride (0.069 mL, 0.95 mmol) to yield sulfite **7** (0.069 g, 83%) as a white solid. The sulfite **7** was recrystallized from a mixture of dichloromethane and hexane (1:2, v/v).

mp: 181-183 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.52-4.53 (m, 2H, H-1 & H-3), 5.16-5.17 (m, 2H, H-4 & H-6), 5.46 (br s, 1H, H-2), 5.52 (br s, 1H, H-7), 5.79-5.80 (m, 1H, H-5), 7.41 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.54 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 8.09 (d, *J* = 8.0 Hz, 2H, Ar-*H*).

^{1}H NMR (DMSO-d_6, 500 MHz) δ: 4.68-4.69 (m, 2H, H-1 & H-3), 5.44-5.46 (m, 3H, H-2, H-4 & H-6), 5.67-5.68 (m, 1H, H-5), 5.86 (br s, 1H, H-7), 7.59 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.72 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 8.05 (d, *J* = 8.0 Hz, 2H, Ar-*H*).

^{1}H NMR (DMSO-d_6, 500 MHz, 50 ^{o}C) δ: 4.68-4.69 (m, 2H, H-1 & H-3), 5.43-5.45 (m, 3H, H-2, H-4 & H-6), 5.68-5.70 (m, 1H, H-5), 5.83 (br s, 1H, H-7), 7.57 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.71 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 8.06 (d, *J* = 8.0 Hz, 2H, Ar-*H*).

^{1}H NMR (DMSO-d_6, 500 MHz, 100 ^{o}C) δ: 4.67-4.68 (m, 2H, H-1 & H-3), 5.41-5.42 (m, 2H, H-4 & H-6), 5.47 (s, 1H, H-2), 5.70-5.72 (m, 1H, H-5), 5.77 (s, 1H, H-7), 7.57 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.70 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 8.07 (d, *J* = 8.0 Hz, 2H, Ar-*H*).

^{1}H NMR (Acetone-d_6, 500 MHz) δ: 4.56-4.58 (m, 2H, H-1 & H-3), 5.26 (t, *J* = 4.5 Hz, 2H, H-4 & H-6), 5.40 (br s, 1H, H-2), 5.57 (br s, 1H, H-7), 5.63-5.65 (m, 1H, H-5), 7.43 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.54-7.57 (m, 1H, Ar-*H*), 7.97-8.03 (m, 2H, Ar-*H*); ^{13}C NMR (Acetone-d_6, 125 MHz) δ: 60.6, 64.3, 69.3, 69.8, 103.1, 129.5, 130.5, 130.6, 134.4, 166.1. Anal. Calcd for $C_{14}H_{12}O_8S$: C, 49.41; H, 3.55; S, 9.42 %, found: C, 49.23; H, 3.51; S, 9.32 %.

^{1}H NMR (CD_3CN, 500 MHz) δ: 4.61-4.62 (m, 2H, H-1 & H-3), 5.30-5.32 (m, 2H, H-4 & H-6), 5.47 (br s, 1H, H-2), 5.63 (br s, 1H, H-7), 5.77-5.79 (m, 1H, H-5), 7.53-7.56 (m, 2H, Ar-*H*), 7.66-7.69 (m, 1H, Ar-*H*), 8.09-8.10 (m, 2H, Ar-*H*).

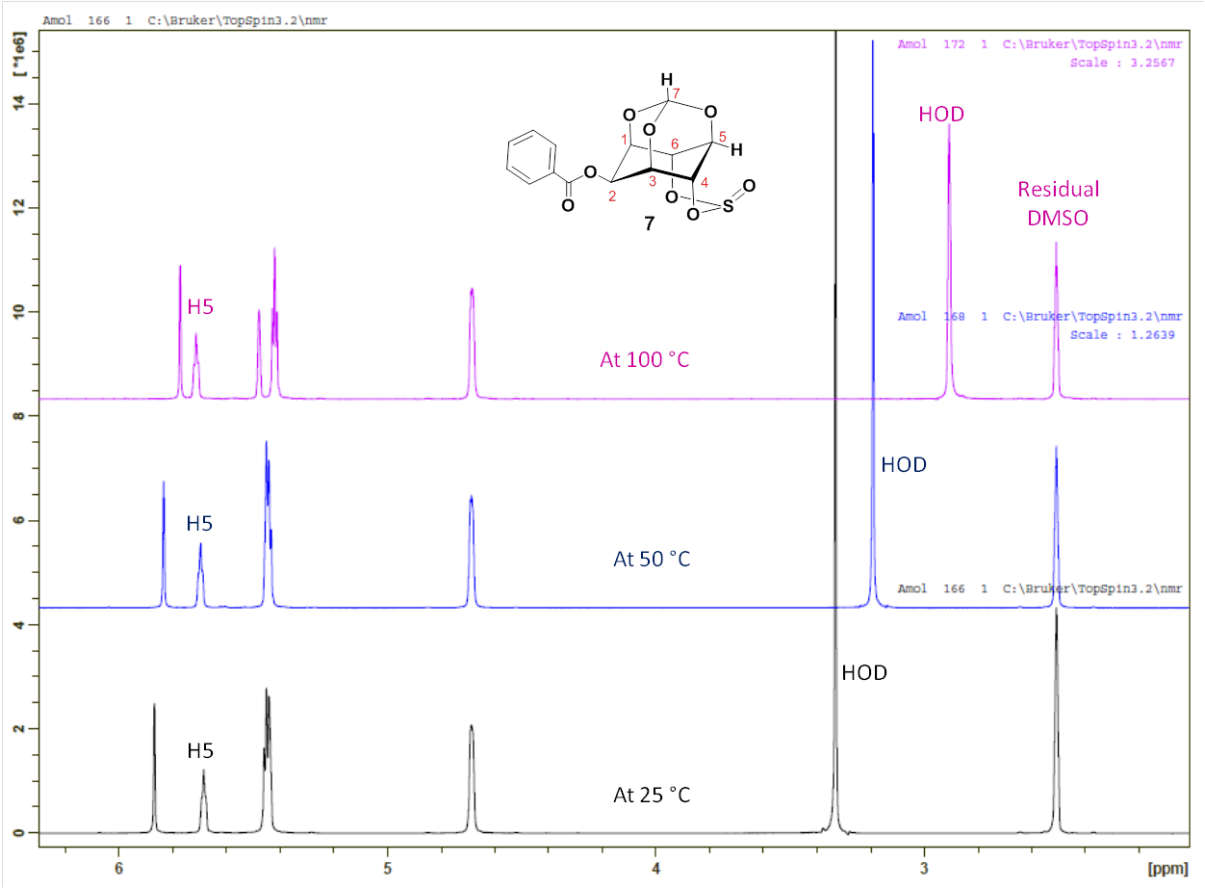
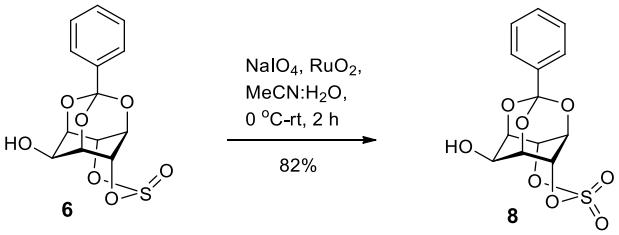


Figure S2. Overlay of partial ^{1}H NMR spectra of sulfite **7** in DMSO-d_6 at 25 (black), 50 (blue) and 100 °C (magenta)

g) 1,3,5-orthbenzoyl-*myo*-inositol 4,6-*O*-sulfate (8)

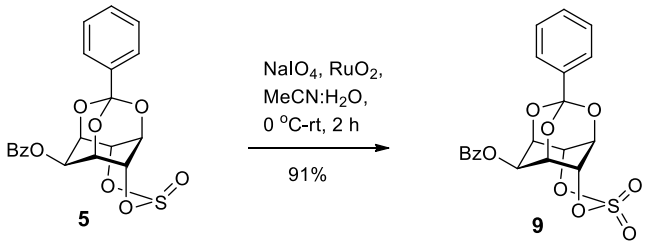


To a cooled solution of sulfite **6**[7] (0.25 g, 0.79 mmol) in a mixture of acetonitrile and water (5:3, v/v, 8 mL), $NaIO_4$ (0.26 g, 1.19 mmol) and catalytic amount of RuO_2 (10 mg) was added. The reaction was allowed to stir at room temperature for 2 h. The reaction mixture was filtered through celite bed and washed with ethyl acetate. The combined filtrate was then

evaporated to get thick residue. The residue was then dissolved in ethyl acetate and washed with water followed by brine. The organic layer was dried over anhyd. Sodium sulfate, filtered and concentrated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using ethyl acetate and petroleum ether (3:7, v/v) as eluent to yield **8** (0.12 g, 82%) as a white solid. The sulfate **8** was recrystallized from a mixture of dichloromethane and hexane (2:3, v/v).

mp: 119-121 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.37 (br s, 1H, H-2), 4.62 (br s, 2H, H-1 & H-3), 5.38 (t, *J* = 4.5 Hz, 2H, H-4 & H-6), 5.57-5.58 (m, 1H, H-5), 7.32-7.39 (m, 3H, Ar-*H*), 7.54 (d, *J* = 7.2 Hz, 2H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 59.6, 60.1, 72.3, 74.0, 107.0, 125.2, 128.3, 130.5, 134.4. Anal. Calcd for $C_{13}H_{12}O_7S$: C, 47.56; H, 3.68; S, 9.77 %. Found: C, 47.38; H, 3.79; S, 9.89 %.

h) <u>2-*O*-benzoyl-1,3,5-orthbenzoyl-*myo*-inositol 4,6-*O*-sulfate (9)</u>



The sulfate **9** was synthesized as before like the case of sulfate **8** using sulfite **5** (0.20 g, 0.48 mmol), $NaIO_4$ (0.15 g, 0.72 mmol) and catalytic amount of RuO_2 (10 mg) in a mixture of acetonitrile and water solvent (5:3, v/v, 8 mL) to yield **9** (0.18 g, 91%) as a white solid. The sulfate **9** was recrystallized from a mixture of dichloromethane and hexane (2:3, v/v).

mp: 134-136 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.94-4.95 (m, 2H, H-1 & H-3), 5.45 (t, *J* = 4.5 Hz, 2H, H-4 & H-6), 5.73-5.76 (m, 2H, H-2 & H-5), 7.39-7.40 (m, 3H, Ar-*H*), 7.42-7.49 (m, 2H, Ar-*H*), 7.59-7.62 (m, 3H, Ar-*H*), 8.10-8.20 (m, 2H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 60.3, 61.8, 70.0, 73.8, 107.0, 125.3, 128.3, 128.6, 129.0, 130.0, 130.3, 133.7, 134.8, 165.4. Anal. Calcd for $C_{20}H_{16}O_9S$: C, 55.55; H, 3.73; S, 7.42 %. Found: C, 55.68; H, 3.99; S, 7.53 %.

^{1}H NMR (DMSO-d_6, 500 MHz) δ: 5.03-5.04 (m, 2H, H-1 & H-3), 5.57-5.58 (m, 1H, H-2), 5.68-5.70 (m, 1H, H-5), 5.80-5.82 (m, 2H, H-4 & H-6), 7.41-7.45 (m, 3H, Ar-*H*), 7.54-7.58 (m, 4H, Ar-*H*), 7.67-7.70 (m, 1H, Ar-*H*), 8.01-8.03 (m, 2H, Ar-*H*).

^{1}H NMR (DMSO-d$_6$, 500 MHz, 100 ^{o}C) δ: 5.02-5.03 (m, 2H, H-1 & H-3), 5.61 (s, 1H, H-2), 5.67-5.68 (m, 1H, H-5), 5.76-5.78 (m, 2H, H-4 & H-6), 7.39-7.43 (m, 3H, Ar-*H*), 7.52-7.55 (m, 2H, Ar-*H*), 7.58-7.59 (m, 2H, Ar-*H*), 7.56-7.68 (m, 1H, Ar-*H*), 8.02-8.03 (m, 2H, Ar-*H*).

^{1}H NMR (CD$_3$OD, 500 MHz) δ: 4.90-4.91 (m, 2H, H-1 & H-3), 5.58-5.60 (m, 2H, H-4 & H-6), 5.62-5.63 (m, 1H, H-2), 5.67-5.69 (m, 1H, H-5), 7.27-7.28 (m, 3H, Ar-*H*), 7.30-7.33 (m, 2H, Ar-*H*), 7.40-7.43 (m, 3H, Ar-*H*), 8.02-8.04 (m, 2H, Ar-*H*).

^{1}H NMR (CD$_3$OD, 500 MHz, 50 ^{o}C) δ: 5.01-5.02 (m, 2H, H-1 & H-3), 5.68-5.70 (m, 2H, H-4 & H-6), 5.75-5.76 (m, 1H, H-2), 5.77-5.80 (m, 1H, H-5), 7.38-7.43 (m, 3H, Ar-*H*), 7.51-7.54 (m, 2H, Ar-*H*), 7.64-7.67 (m, 3H, Ar-*H*), 8.14-8.16 (m, 2H, Ar-*H*).

^{1}H NMR (CD$_3$CN, 500 MHz) δ: 4.91 (br s, 2H, H-1 & H-3), 5.57-5.59 (m, 3H, H-2, H-4 & H-6), 5.64 (br s, 1H, H-5), 7.35-7.41 (m, 3H, Ar-*H*), 7.45-7.48 (m, 2H, Ar-*H*), 7.55-7.61 (m, 3H, Ar-*H*), 8.02-8.04 (m, 2H, Ar-*H*).

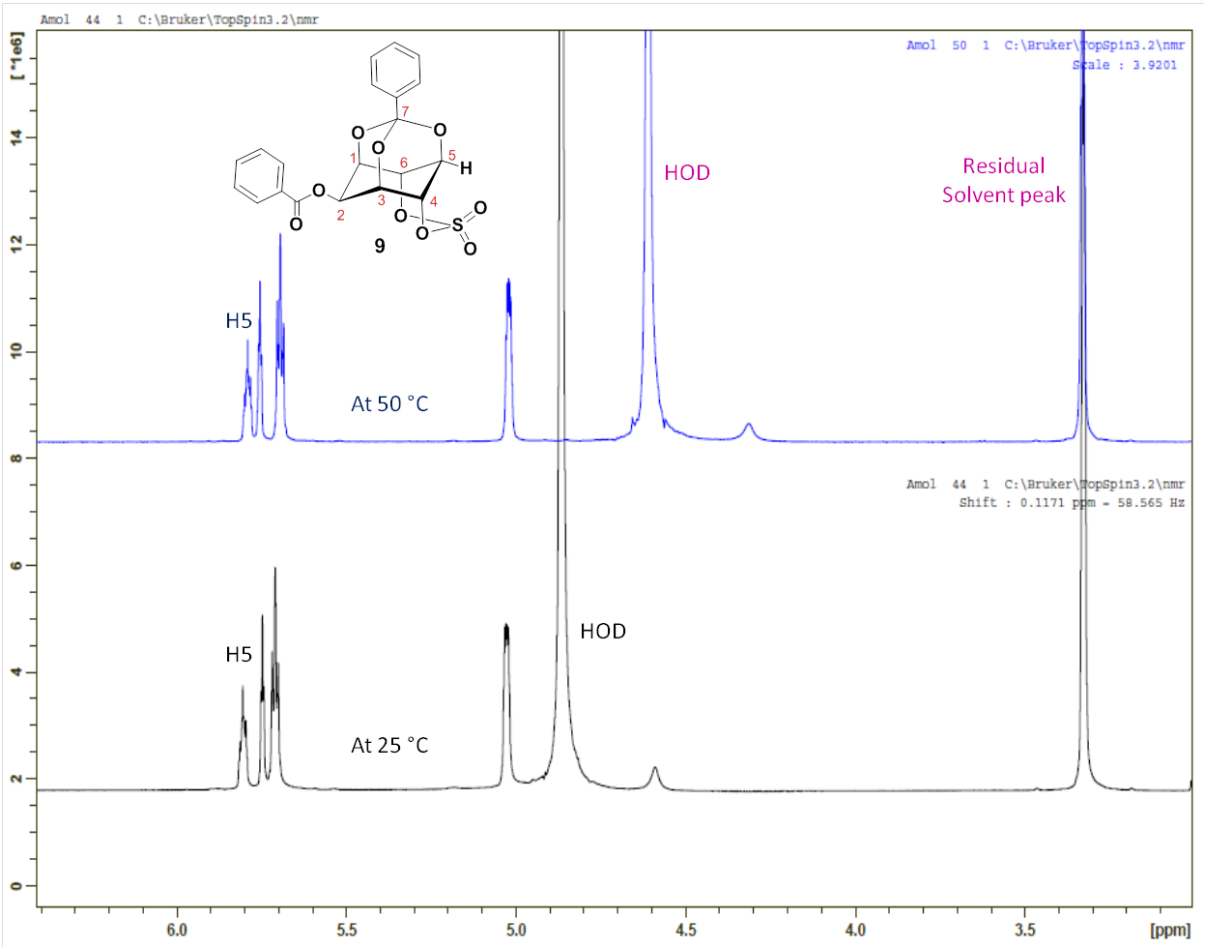


Figure S3. Overlay of partial ^{1}H NMR spectra of sulfite **9** in CD$_3$OD at 25 (black) and 50 ^{o}C (blue)

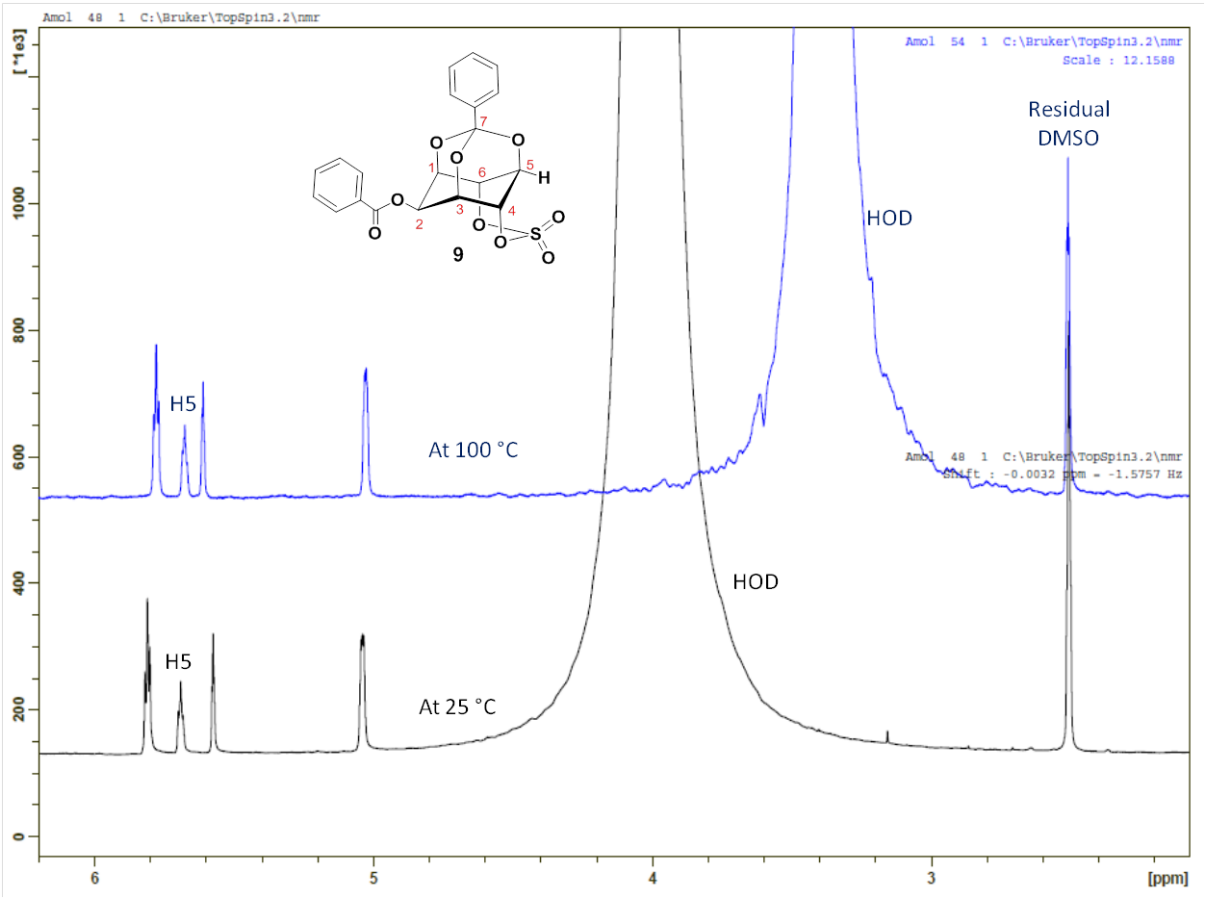
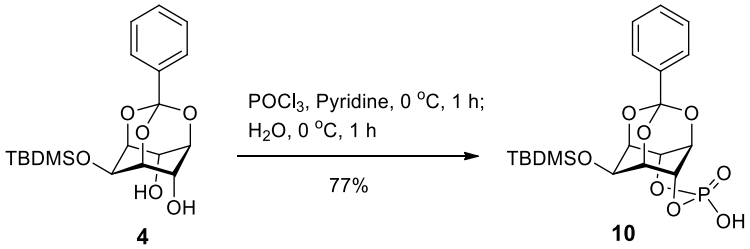


Figure S4. Overlay of partial ^{1}H NMR spectra of sulfite **9** in DMSO-d_6 at 25 (black) and 100 °C (blue)

i) 2-*O*-tert-Butyldimethylsilyl-1,3,5-orthobenzoyl-*myo*-inositol 4,6-cyclic-phosphate (10)



To a cooled solution of diol **4** (0.10 g, 0.26 mmol) in dry pyridine (5 mL) $POCl_3$ (0.027 mL, 0.29 mmol) was added. The reaction was stirred at 0 °C for 1 h. When TLC showed complete consumption of the starting material, reaction was quenched by addition of water (1 mL). The reaction was stirred for another 1 h at 0 °C. The reaction mixture was then concentrated under reduced pressure. The residue was co-evaporated with toluene to dryness. The resulting residue was then dissolved in ethyl acetate and washed with water (20 mL, 2 times) followed by brine. The organic layer thus obtained was dried over anhyd. sodium

sulfate and concentrated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using ethyl acetate and methanol (9:1, v/v) as eluent to yield **10** (0.082 g, 77%) as a white hygroscopic solid. The attempts to crystallize phosphate **10** from different solvents were failed.

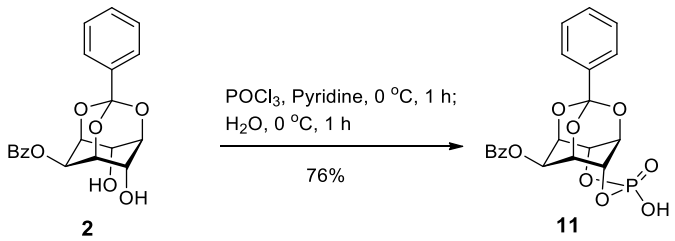
mp: phosphate **10** turned off white above 250 ^{o}C and decomposed at 280 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.10 (s, 6H, 2 x Si-*CH*$_3$), 0.89 (s, 9H, 3 x ^{t}Bu-*CH*$_3$), 4.37 (br s, 2H, H-1 & H-3), 4.42 (br s, 1H, H-2), 5.02 (br s, 2H, H-4 & H-6), 5.36 (br s, 1H, H-5), 7.22-7.28 (m, 3H, Ar-*H*), 7.55-7.56 (m, 2H, Ar-*H*).

^{1}H NMR (DMSO-d_6, 500 MHz) δ: 0.16 (s, 6H, 2 x Si-*CH*$_3$), 0.95 (s, 9H, 3 x ^{t}Bu-*CH*$_3$), 4.28 (br s, 2H, H-1 & H-3), 4.52 (br s, 1H, H-2), 4.66 (br s, 2H, H-4 & H-6), 5.36 (br s, 1H, H-5), 7.40 (br s, 3H, Ar-*H*), 7.55-7.56 (m, 2H, Ar-*H*); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: -4.1, 18.3, 26.2. 61.0, 64.1, 64.3, 67.3, 67.4, 75.0, 106.4, 125.6, 128.2, 129.7, 137.8; ^{31}P NMR (DMSO-d_6, 202 MHz) δ: -11.7; HRMS (ESI) mass calcd for $C_{19}H_{27}O_8PSi$ $[M]^+$ 442.1213; found 442.1251.

^{1}H NMR (CD_3OD, 500 MHz) δ: 0.23 (s, 6H, 2 x Si-*CH*$_3$), 1.00 (s, 9H, 3 x ^{t}Bu-*CH*$_3$), 4.40 (br s, 2H, H-1 & H-3), 4.62 (br s, 1H, H-2), 4.90-4.93 (m, 2H, H-4 & H-6), 5.30 (br s, 1H, H-5), 7.33-7.38 (m, 3H, Ar-*H*), 7.62-7.64 (m, 2H, Ar-*H*).

^{1}H NMR (CD_3CN, 500 MHz) δ: 0.18 (s, 6H, 2 x Si-*CH*$_3$), 0.95 (s, 9H, 3 x ^{t}Bu-*CH*$_3$), 4.39 (br s, 2H, H-1 & H-3), 4.56 (br s, 1H, H-2), 4.97 (br s, 2H, H-4 & H-6), 5.51 (br s, 1H, H-5), 7.31-7.39 (m, 3H, Ar-*H*), 7.57-7.58 (m, 2H, Ar-*H*).

j) <u>2-*O*-benzoyl-1,3,5-orthobenzoyl-*myo*-inositol 4,6-cyclic-phosphate (11)</u>

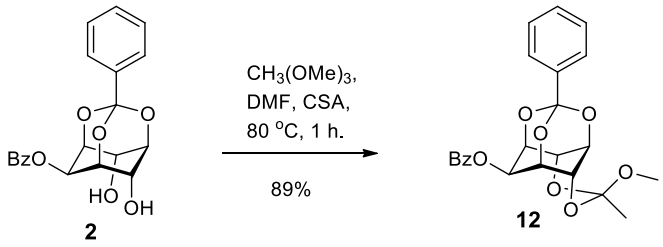


2 **11**

The phosphate **11** was synthesized as before like in the case of phosphate **10** using diol **2** (0.10 g, 0.27 mmol), $POCl_3$ (0.027 mL, 0.29 mmol) and dry pyridine (5 mL) to yield **11** (0.086 g, 76%) as a white hygroscopic solid. The attempts to crystallize phosphate **11** from different solvents were failed.

mp: 285-287 ^{o}C (melted and decomposed). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.71 (br s, 2H, H-1 & H-3), 4.87 (br s, 2H, H-4 & H-6), 5.58 (br s, 1H, H-5), 5.70 (br s, 1H, H-2), 7.40-7.42 (m, 3H, Ar-*H*), 7.58-7.61 (m, 4H, Ar-*H*), 7.71 (t, *J* = 7.1 Hz, 1H, Ar-*H*), 8.06-8.08 (m, 2H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 63.5, 67.0, 71.6, 106.1, 125.1, 127.9, 128.8, 129.3, 129.4, 129.5, 133.6, 136.7, 165.0; ^{31}P NMR (202 MHz, $CDCl_3$) δ: -13.64. HRMS (ESI) mass calcd for $C_{20}H_{17}O_9P$ $[M]^+$ 432.0610; found 432.0629.

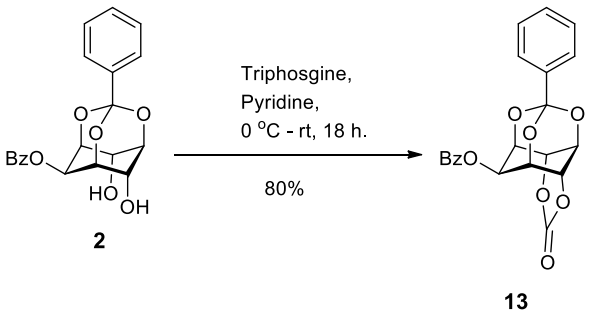
k) <u>2-*O*-benzoyl-1,3,5-orthobenzoyl-*myo*-inositol 4,6-*O*-orthoacetate (12)</u>



To a solution of diol **2** (0.10 g, 0.27 mmol) in dry DMF (5 mL) trimethyl orthoformate (0.037 mL, 0.29 mmol) followed by camphor sulfonic acid (0.006 g, 0.027 mmol) was added. The reaction was stirred at 80 ^{o}C for 1 h. When optimum product formation takes place (checked by TLC), the reaction mixture was concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate and washed with water (20 mL, 2 times) followed by brine. The organic layer was dried over anhyd. sodium sulfate, filtered and concentrated under reduced pressure. The crude product thus obtained was purified by flash column chromatography using ethyl acetate and petroleum ether (2:8, v/v) as eluent to yield **12** (0.045 g, 89%) as a white solid. The orthoacetate **12** was recrystallized from a mixture of ethyl acetate and hexane (2:8, v/v).

mp: 176-178 ^{o}C. ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 1.42 (s, 3H, *CH*$_3$), 3.23 (s, 3H, O*CH*$_3$), 4.61-4.62 (m, 2H, H-1 & H-3), 4.77 (t, 2H, H-4 & H-6), 5.26 (t, *J* = 4.5 Hz, 1H, H-5), 5.47 (t, *J* = 2.1 Hz, 1H, H-2), 7.32-7.34 (m, 3H, Ar-*H*), 7.50-7.54 (m, 4H, Ar-*H*), 7.64 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 8.00-8.03 (m, 2H, Ar-*H*); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 22.3, 50.4, 62.3, 63.7, 63.8, 70.7, 106.0, 111.6, 125.1, 128.0, 128.9, 129.3, 129.38, 129.5, 133.7, 136.8, 165.1. Anal. Calcd for $C_{23}H_{22}O_8$: C, 64.78; H, 5.20 %. Found: C, 64.59; H, 5.08 %.

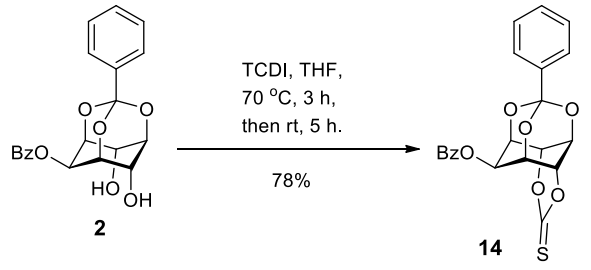
l) <u>2-*O*-benzoyl-1,3,5-orthobenzoyl-*myo*-inositol 4,6-*O*-carbonate (13)</u>



To a cooled solution of diol **2** (0.20 g, 0.54 mmol) in dry pyridine (5 mL) triphosgine (0.17 g, 0.59 mmol) was added. The reaction was initially stirred at 0 °C for 10 min and then allowed to stir at room temperature for 18 h. The vigorous stirring at room temperature made the reaction mixture dark brown coloured. When optimum product formation takes place (checked by TLC), the reaction mixture was concentrated under reduced pressure and at low temperature (below 42 °C). The residue thus obtained was co-evaporated with toluene to dryness. The resulting residue was dissolved in ethyl acetate and washed with water (20 mL, 2 times) followed by brine. The organic layer was dried over anhyd. sodium sulfate and concentrated under reduced pressure. The crude product thus obtained was purified by column chromatography using ethyl acetate and petroleum ether (2:8, v/v) as eluent to yield **13** (0.12 g, 80%) as a white solid. The carbonate **13** was recrystallized from a mixture of ethyl acetate and hexane (2:8, v/v).

mp: 194-196 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.77 (t, *J* = 3.1 Hz, 1H, H-5), 4.89-4.87 (m, 2H, H-1 & H-3), 5.16 (t, *J* = 5.0 Hz, 2H, H-4 & H-6), 5.29 (t, *J* = 2.1 Hz, 1H, H-2), 7.37-7.32 (m, 3H, Ar-*H*), 7.41 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 7.55-7.53 (m, 1H, Ar-*H*), 87.60-7.58 (m, 2H, Ar-*H*),.07-8.06 (m, 2H, Ar-*H*), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.4, 144.5, 135.2, 133.8, 130.3, 130.0, 128.9, 128.6, 128.2, 125.3, 107.1, 70.8, 69.6, 61.8, 61.4. Anal. Calcd for $C_{21}H_{16}O_8$: C, 63.64; H, 4.07 %. Found: C, 63.78; H, 4.09 %.

m) <u>2-*O*-benzoyl-1,3,5-orthobenzoyl-*myo*-inositol 4,6-*O*-thiocarbonate (14)</u>



To a solution of diol **2** (0.20 g, 0.54 mmol) in dry THF (5 mL), thiocarbonyl diimidazole (TCDI) (0.23 g, 1.31 mmol) was added in portions (four times with interval of 15 min). The reaction was first heated up to reflux for 3 h followed by stirring at room temperature for 5 h. The reaction mixture was then concentrated under reduced pressure and co-evaporated with toluene to dryness. The resulting residue was adsorbed on silica gel by dissolving it into dichloromethane and purified by flash column chromatography using ethyl acetate and petroleum ether (1:6, v/v) as eluent to yield **14** (0.098 g, 78%) as a white solid. The thiocarbonate **14** was recrystallized from a mixture of dichloromethane and hexane (1:2, v/v).

mp: 221-223 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.80 (t, *J* = 4.3 Hz, 1H, H-5), 4.88-4.89 (m, 2H, H-1 & H-3), 5.25-5.27 (m, 3H, H-2, H-4 & H-6), 7.32-7.37 (m, 3H, Ar-*H*), 7.40 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 7.53-7.56 (m, 1H, Ar-*H*), 7.57-7.60 (m, 2H, Ar-*H*), 8.04-8.06 (m, 2H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 60.1, 60.8, 69.7, 69.9, 106.2, 124.2, 127.2, 127.3, 127.6, 127.8, 129.50, 129.2, 132.8, 133.9, 164.2, 182.7. Anal. Calcd for $C_{21}H_{16}O_7S$: C, 61.16; H, 3.91; S, 7.77 %. Found: C, 61.39; H, 3.72; S, 7.82 %.

3) Crystallographic data

a) Crystal data for 5

CCDC No: 1576754, Refined formula: $C_{20}H_{16}O_8S$, Formula weight: M = 416.40, colorless block, 0.42 x 0.20 x 0.18 mm^3, Triclinic, space group: P-1, Unit cell dimensions and volume: a = 6.1387(10), b = 12.306(2), c = 12.412(2) Å, V = 904.6(3) Å^3, No of formula units in the unit cell Z = 2, T = 298(2) K, $2\theta_{max}$ = 52.30°, Calculated density $\rho_{calcd:}$ (g cm^{-3}) = 1.529, F(000) = 465, Linear absorption coefficient μ: 0.225 mm^{-1}, 9556 reflections collected, 3591 unique reflections (R_{int} = 0.0615), multi-scan absorption correction, T_{min} = 0.6895, T_{max} = 0.8467, number of parameters = 262, number of restraints = 0, GoF = 1.043, R_1 = 0.0491, wR_2 = 0.1171, R indices based on 2949 reflections with I >2sigma(I) (refinement on F2). $\Delta\rho_{max}$ = 0.001, $\Delta\rho_{min}$ = 0.000 (eÅ^{-3}).

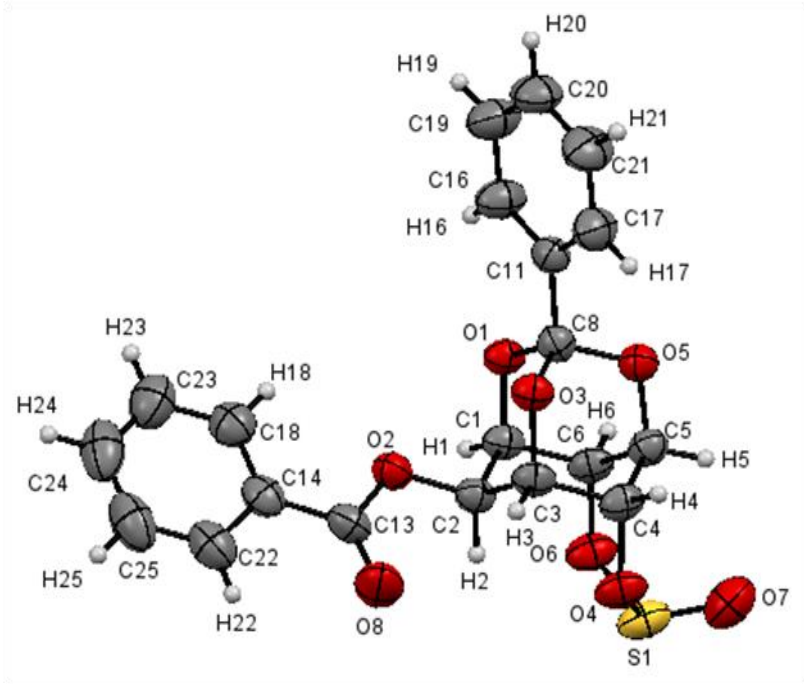


Figure S5. ORTEP diagram of **5** showing boat conformation for heterocyclic ring comprising sulfite moiety. (Ellipsoid probability: 50%)

Table S1. Prominent non-covalent interactions in **5**

Interaction	D-H···A	H···A (Å)	D-H···A (°)	d-vdW (Å)	Symmetry code
CH···O	C3-H3···O1	2.70	131	-0.02	1+x,y,z
	C24-H24···O3	2.52	141	-0.20	-x,1-y,-z
	C21-H21···O7	2.55	135	-0.17	1-x,2-y,1-z
	C6-H6···O4	2.62	131	-0.10	-1+x,y,z

b) Crystal data for 7

CCDC No: 1576755, Refined formula: $C_{14}H_{12}O_8S$, Formula weight: M = 340.30, colorless block, 0.42 x 0.34 x 0.32 mm^3, Triclinic, space group: P -1, Unit cell dimensions and volume: a = 6.2082(8), b = 7.2693(12), c = 16.148(2) Å, V = 677.20(16) $Å^3$, No of formula units in the unit cell Z = 2, T = 293(2) K, $2\theta_{max}$ = 57.888°, Calculated density $\rho_{calcd:}$ (g cm^{-3}) = 1.669, F(000) = 352, Linear absorption coefficient μ: 0.284 mm^{-1}, 4561 reflections collected, 2755 unique reflections (R_{int} = 0.0514), multi-scan absorption correction, T_{min} = 0.8901, T_{max} = 0.9147, number of parameters = 208, number of restraints = 0, GoF = 1.068, R_1 = 0.0408,

wR_2 = 0.1072, R indices based on 2203 reflections with I >2sigma(I) (refinement on F2). $\Delta\rho_{max}$ = 0.000, $\Delta\rho_{min}$ = 0.000 ($eÅ^{-3}$).

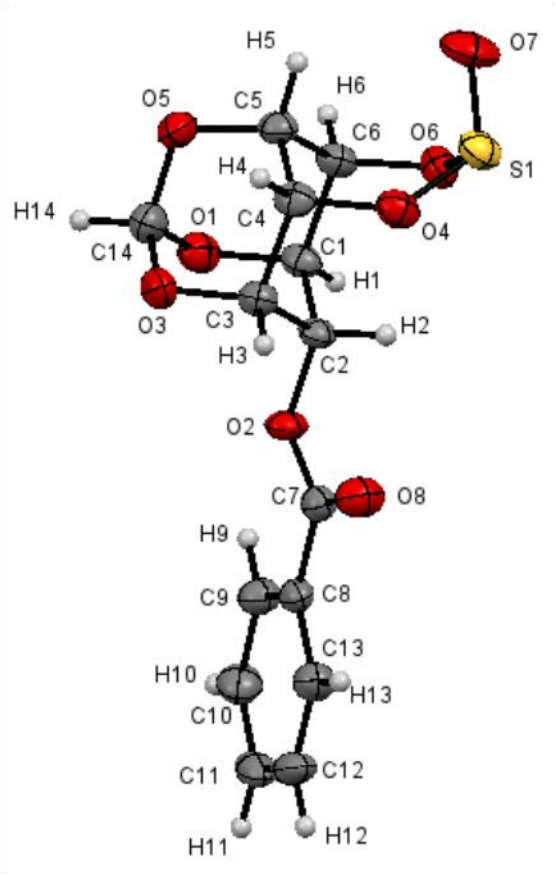


Figure S6. ORTEP diagram of **7** showing boat conformation for heterocyclic ring comprising sulfite moiety. (Ellipsoid probability: 50%)

Table S2. Prominent non-covalent interactions in **7**

Interaction	D-H···A	H···A (Å)	D-H···A (°)	d-vdW (Å)	Symmetry code
CH···O	C1-H1···O8	2.52	156	-0.20	1+x,y,z
	C11-H11···O3	2.65	131	-0.07	1-x,2-y,-z
	C5-H5···O7	2.61	123	-0.11	2-x,1-y,1-z
	C6-H6···O7	2.66	118	-0.06	2-x,1-y,1-z
CH···π	C2-H2···C11	2.82	147	-0.08	1-x,1-y,-z

c) <u>Crystal data for 8</u>

CCDC No: 1576758, Refined formula: $C_{13}H_{12}O_8S$, Formula weight: M = 328.29, block, 0.20 x 0.15 x 0.15 mm^3, Triclinic, space group: P-1, Unit cell dimensions and volume: a = 7.8234(7), b = 9.9598(9), c = 9.9951(9) Å, V = 655.56(10) $Å^3$, No of formula units in the unit cell Z = 2, T = 296(2) K, $2\theta_{max}$ = 56.28°, Calculated density $\rho_{calcd:}$ (g cm^{-3}) = 1.663, F(000) = 340, Linear absorption coefficient μ: 0.290 mm^{-1}, 10874 reflections collected, 3195 unique reflections (R_{int} = 0.0742), multi-scan absorption correction, T_{min} = 0.9444, T_{max} = 0.9579, number of parameters = 199, number of restraints = 1, GoF = 1.072, R_1 = 0.0558, wR_2 = 0.1232, R indices based on 2560 reflections with I >2\s(I) (refinement on F2). $\Delta\rho_{max}$ = 0.000, $\Delta\rho_{min}$ = 0.000 ($eÅ^{-3}$).

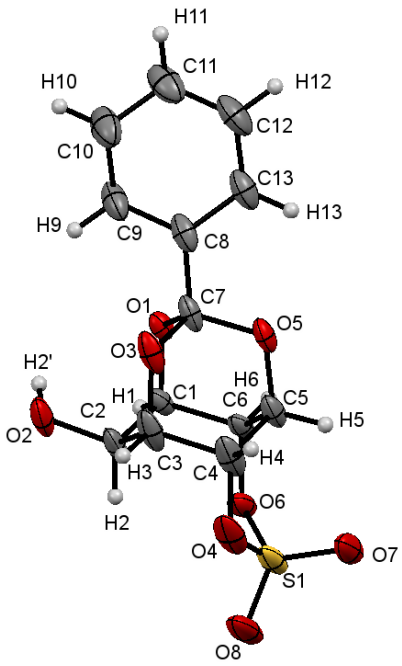


Figure S7. ORTEP diagram of **8** showing boat conformation for heterocyclic ring comprising sulfate moiety (Ellipsoid probability: 50%)

Table S3. Prominent non-covalent interactions in **8**

Interaction	D-H···A	H···A (Å)	D-H···A (°)	d-vdW (Å)	Symmetry code
CH···O	C12-H12···O6	2.55	163	-0.17	x,y,1+z
	C10-H10···O3	2.62	143	-0.10	1-x,1-y,1-z

	C3-H3···O8	2.43	142	-0.29	2-x,1-y,-z
	C6-H6···O1	2.35	141	-0.37	2-x,2-y,1-z
	C6-H6···O7	2.52	134	-0.20	3-x,2-y,1-z
CH···π	C4-H4···C8	2.86	146	-0.04	2-x,1-y,1-z

d) Crystal data for 9

CCDC No: 1576760, Refined formula: $C_{20}H_{16}O_9S$, Formula weight: M = 432.39, colorless block, 0.25 x 0.15 x 0.10 mm^3, Triclinic, space group: P-1, Unit cell dimensions and volume: a = 12.1168(10), b = 12.9658(10), c = 25.4643(19) Å, V = 3900.0(5) $Å^3$, No of formula units in the unit cell Z = 8, T = 296(2) K, $2\theta_{max}$ = 48.72°, Calculated density $\rho_{calcd:}$ (g cm^{-3}) = 1.473, F(000) = 1792, Linear absorption coefficient μ: 0.218 mm^{-1}, 36375 reflections collected, 10892 unique reflections (R_{int} = 0.1510), multi-scan absorption correction, T_{min} = 0.9489, T_{max} = 0.9791, number of parameters = 1082, number of restraints = 0, GoF = 1.059, R_1 = 0.0958, wR_2 = 0.2523, R indices based on 6314 reflections with I > 2\s(I) (refinement on F2). $\Delta\rho_{max}$ = 0.000, $\Delta\rho_{min}$ = 0.000 ($eÅ^{-3}$).

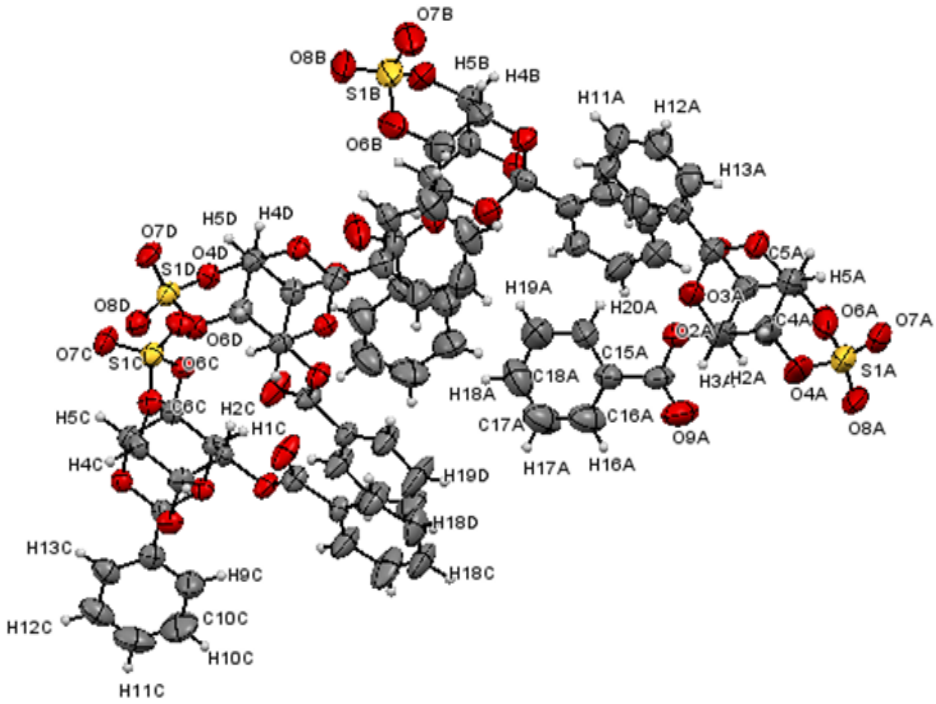


Figure S8. ORTEP diagram of **9** showing boat conformation for heterocyclic ring comprising sulfate moiety (Ellipsoid probability: 50%)

Table S4. Prominent non-covalent interactions in **9**

Interaction	D-H⋯A	H⋯A (Å)	D-H⋯A (°)	d-vdW (Å)	Symmetry code
CH⋯O	C12A-H12A⋯O3B	2.72	143	-0.00	-1+x,y,z
	C12D-H12D⋯O8A	2.56	144	-0.16	x,-1+y,z
	C13D-H13D⋯O9A	2.44	150	-0.28	x,-1+y,z
	C12C-H12C⋯O8B	2.58	144	-0.14	1-x,-y,1-z
	C13C-H13C⋯O9B	2.45	151	-0.27	1-x,-y,1-z
	C19C-H19C⋯O7C	2.53	135	-0.19	x,1+y,z
	C2C-H2C⋯O8C	2.62	118	-0.10	-x,-y,1-z
	C6C-H6C⋯O6D	2.71	128	-0.01	x,y,z
	C6D-H6D⋯O6C	2.69	129	-0.03	x,y,z
	C5D-H5D⋯O9C	2.41	127	-0.31	-x,-y,1-z
	C6D-H6D⋯O9C	2.68	114	-0.04	-x,-y,1-z
	C5C-H5C⋯O9D	2.40	127	-0.32	1-x,-y,1-z
	C6C-H6C⋯O9D	2.68	114	-0.04	1-x,-y,1-z
	C19D-H19D⋯O7D	2.50	138	-0.22	x,1+y,z
	C2D-H2D⋯O8D	2.61	118	-0.11	1-x,-y,1-z
CH⋯π	C5A-H5A⋯C12A	2.88	145	-0.02	-1-x,1-y,-z
	C6A-H6A⋯C_gB	2.70	144	-0.20	-x,1-y,-z
	C4A-H4A⋯C12C	2.68	158	-0.22	-x,1-y,1-z
	C6B-H6B⋯C12D	2.68	157	-0.22	x,y,z
	C4C-H4C⋯C12D	2.85	157	-0.05	-x,-y,1-z
	C4C-H4C⋯C13D	2.74	129	-0.16	-x,-y,1-z
	C4D-H4D⋯C12C	2.87	157	-0.03	1-x,-y,1-z
	C4D-H4D⋯C13C	2.77	129	-0.13	1-x,-y,1-z

e) <u>Crystal data for 12</u>

CCDC No: 1576756, Refined formula: $C_{23}H_{22}O_8$, Formula weight: M = 426.40, colorless block, 0.20 x 0.15 x 0.15 mm^3, Orthorhombic, space group: P2(1)2(1)2(1), Unit cell dimensions and volume: a = 6.5124(3), b = 15.0561(7), c = 20.2887(10) Å, V = 1989.33(16) $Å^3$, No of formula units in the unit cell Z = 4, T = 296(2) K, $2\theta_{max}$ = 59.94°, Calculated density $\rho_{calcd:}$ (g cm^{-3}) = 1.423, F(000) = 896, Linear absorption coefficient μ: 0.108 mm^{-1}, 9670 reflections collected, 3460 unique reflections (R_{int} = 0.0414), multi-scan absorption correction, T_{min} = 0.979, T_{max} = 0.984, number of parameters = 283, number of restraints = 0, GoF = 0.851, R_1 = 0.0312, wR_2 = 0.0748, R indices based on 2998 reflections with I >2s(I) (refinement on F2). $\Delta\rho_{max}$ = 0.011, $\Delta\rho_{min}$ = 0.001 ($eÅ^{-3}$).

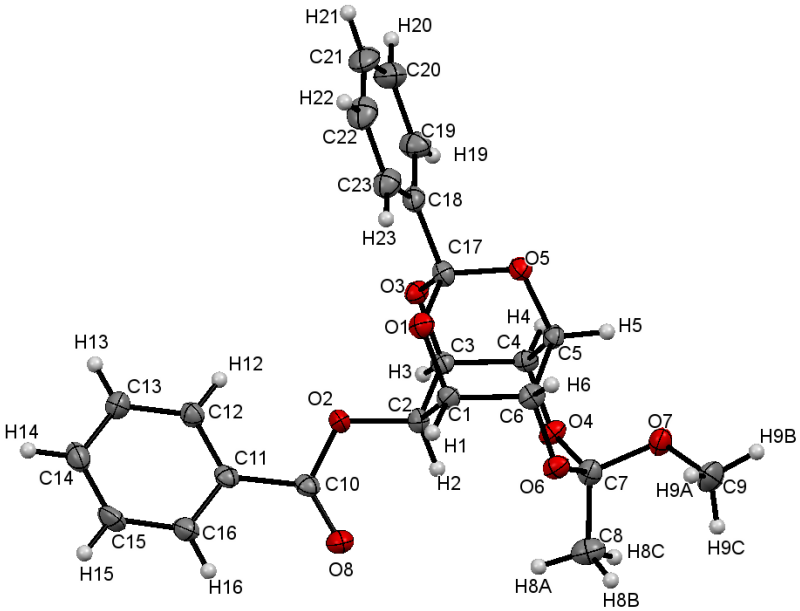


Figure S9. ORTEP diagram of **12** showing boat conformation for heterocyclic ring comprising orthoacetate moiety (Ellipsoid probability: 50%)

Table S5. Prominent non-covalent interactions in **12**

Interaction	D-H···A	H···A (Å)	D-H···A (°)	d-vdW (Å)	Symmetry code
CH···O	C4-H4···O1	2.66	134	-0.06	1+x,y,z
	C8-H8C···O8	2.71	133	-0.01	1+x,y,z
	C1-H1···O4	2.66	134	-0.06	-1+x,y,z
	C1-H1···O7	2.39	151	-0.33	-1+x,y,z

	C13-H13···O1	2.65	152	-0.07	-x,-1/2+y,1/2-z
CH···π	C3-H3···C12	2.90	152	-0.00	1+x,y,z

f) Crystal data for 13

CCDC No: 1576757, Refined formula: $C_{21}H_{16}O_8$, Formula weight: M = 396.34, colorless block, 0.25 x 0.15 x 0.10 mm^3, Triclinic, space group: P-1, Unit cell dimensions and volume: a = 9.1816(4), b = 13.2228(6), c = 14.5348(6) Å, V = 1761.52(13) $Å^3$, No of formula units in the unit cell Z = 4, T = 296(2) K, $2\theta_{max}$ = 66.32°, Calculated density $\rho_{calcd:}$ (g cm^{-3}) = 1.494, F(000) = 824, Linear absorption coefficient μ: 0.116 mm^{-1}, 27972 reflections collected, 6156 unique reflections (R_{int} = 0.0410), multi-scan absorption correction, T_{min} = 0.9715, T_{max} = 0.9885, number of parameters = 523, number of restraints = 0, GoF = 1.024, R_1 = 0.0353, wR_2 = 0.0920, R indices based on 5474 reflections with I >2\s(I) (refinement on F2). $\Delta\rho_{max}$ = 0.005, $\Delta\rho_{min}$ = 0.000 ($eÅ^{-3}$).

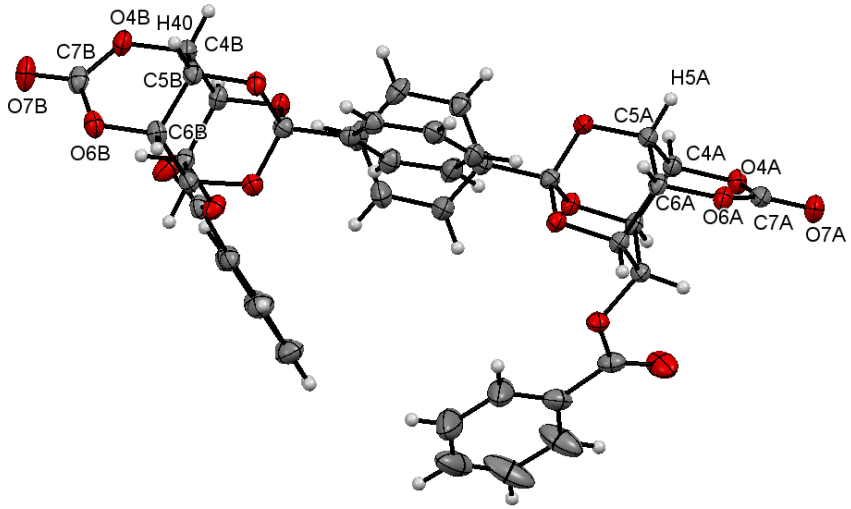


Figure S10. ORTEP diagram of **13** showing envelop conformation for heterocyclic ring comprising carbonate moiety (Ellipsoid probability: 50%)

Table S6. Prominent non-covalent interactions in **13**

Interaction	D-H···A	H···A (Å)	D-H···A (°)	d-vdW (Å)	Symmetry code
CH···O	C3A-H3A···O7B	2.53	141	-0.19	-1+x,-1+y,z
	C5B-H40···O4A	2.70	130	-0.02	-1+x,-1+y,z
	C2A-H2A···O8B	2.31	141	-0.41	x,-1+y,z
	C6A-H6A···O4B	2.72	112	-0.00	x,-1+y,z
	C3B-H28···O6A	2.49	134	-0.24	x,1+y,z
	C3B-H28···O7A	2.61	170	-0.11	x,1+y,z
	C20B-H20B···O1A	2.59	175	-0.13	x,y,z
	C5B-H40···O5B	2.70	144	-0.02	2-x,2-y,-z
CH···π	C13A-H13A···C21A	2.88	152	-0.02	-x,1-y,1-z
	C20A-H20A···C9B	2.84	135	-0.06	x,y,z
	C5A-H5A···C20B	2.85	134	-0.05	1-x,1-y,-z
	C4A-H4A···C18B	2.82	145	-0.08	1-x,1-y,-z
	C1B-H36···C13B	2.90	143	-0.00	1-x,2-y,1-z

g) Crystal data for 14

CCDC No: 1576759, Refined formula: $C_{21}H_{16}O_7S.2H_2O$, Formula weight: M = 444.40, colorless block, 0.20 x 0.15 x 0.15 mm^3, Triclinic, space group: P-1, Unit cell dimensions and volume: a = 5.9531(11), b = 12.597(3), c = 14.559(3) Å, V = 1034.4(4) $Å^3$, No of formula units in the unit cell Z = 2, T = 296(2) K, $2\theta_{max}$ = 49.72°, Calculated density $\rho_{calcd:}$ (g cm^{-3}) = 1.427, F(000) = 460, Linear absorption coefficient μ: 0.208 mm^{-1}, 8578 reflections collected, 3489 unique reflections (R_{int} = 0.0655), multi-scan absorption correction, T_{min} = 0.960, T_{max} = 0.970, number of parameters = 299, number of restraints = 0, GoF = 1.051, R_1 = 0.0486, wR_2 = 0.1342, R indices based on 2678 reflections with I >2\s(I) (refinement on F2). $\Delta\rho_{max}$ = 0.001, $\Delta\rho_{min}$ = 0.000 ($eÅ^{-3}$).

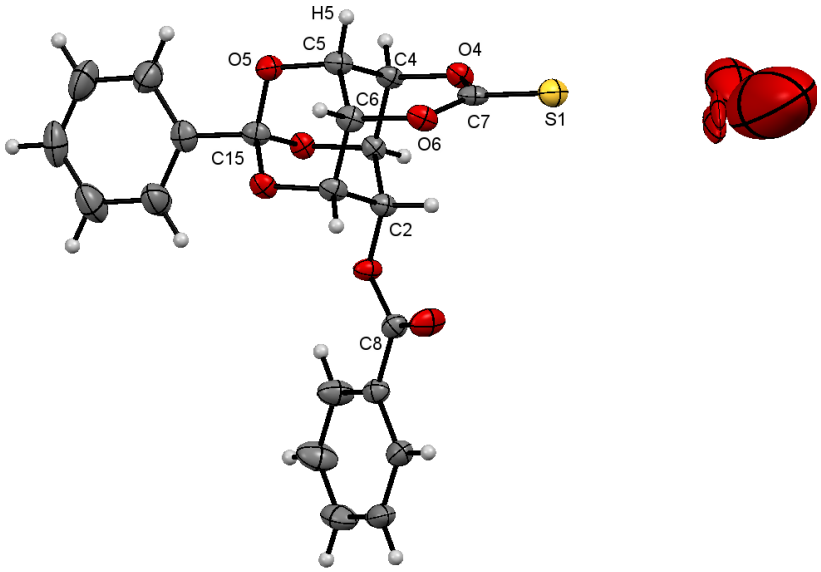


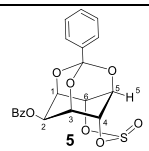
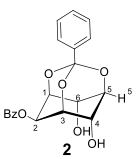
Figure S11. ORTEP diagram of **14** showing envelop conformation for heterocyclic ring comprising thiocarbonate moiety (Ellipsoid probability: 50%)

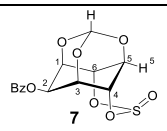
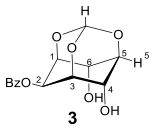
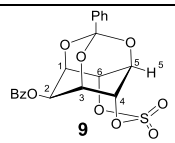
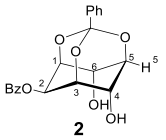
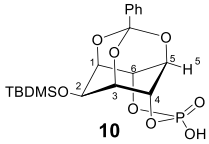
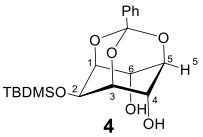
Table S7. Prominent non-covalent interactions in **14**

Interaction	D-H···A	H···A (Å)	D-H···A (°)	d-vdW (Å)	Symmetry code
CH···O	C4-H4···O6	2.45	133	-0.27	1+x,y,z
	C1-H1···O3	2.47	130	-0.25	-1+x,y,z
	C14-H14···O7	2.62	148	-0.10	-x,1-y,1-z

4) NMR in different solvents

Table S8. δ H-5 of compound **5**, **7**, **9** and **10** in solvents of variable polarity and its comparison with δ H-5 of parent diols **2**-**4**

Entry	Compound	δ H-5 in **$CDCl_3$**	δ H-5 in **DMSO-d_6**	δ H-5 in **CD_3OD**	δ H-5 in **CD_3CN**	δ H-5 in **$(CD_3)_2CO$**
1	 **5**	6.03	5.91	5.90		
		Δδ **1.59**	Δδ **1.58**	Δδ **1.60**	--[a]	--[a]
	 **2**	4.44	4.33	4.30		

2	 **7**  **3**	5.80 Δδ **1.49** 4.31	5.68 Δδ **1.50** 4.18	-- [a]	5.78 Δδ **1.51** 4.27	5.64 Δδ **1.44** 4.16
3	 **9**  **2**	5.75 Δδ **1.31** 4.44	5.69 Δδ **1.36** 4.33	5.68 Δδ **1.38** 4.30	5.64 Δδ **1.23** 4.41	--[a]
4	 **10**  **4**	5.26 Δδ **1.15** 4.11	5.36 Δδ **1.10** 4.26	5.30 Δδ **1.00** 4.30	5.51 Δδ **1.20** 4.31	--[a]

[a]Not determined.

5) NMR at different temperatures

Table S9. δ H-5 of **5**, **7** and **9** in CD_3OD and DMSO-d_6 at various temperatures

Entry	Solvent	Temperature	δ H-5 of **5**	δ H-5 of **7**	δ H-5 of **9**
1	CD_3OD	25°	5.90	--	5.68
		50°	6.01	--	5.78
2	DMSO-d_6	25°	--	5.68	5.69
		50°	--	5.70	--
		100°	--	5.72	5.68

6) Computational Methods

Model systems given in Figure 5 in the manuscript were optimized at the MP2 level of theory using the 6-31G* and 6-311+G** basis sets. Frequency calculations were also done at the MP2/6-31G*, which showed that the stationary points obtained are minima on their resepective potential energy surfaces. To account for the steric hindrance in the orthoester

model system, two configurations each for two other model systems (entries 10 to 13 in Table S10) were considered and treated at these levels of theory. The energies of the different configurations, wherever possible, were compared to examine the stabilization due to CH…O H-bonding. Actual systems given in Figure 2 (**5** to **14**) were optimized using the MP2/6-31G* level to study the CH…O H-bonding interaction. All optimization and frequency calculations were done using the Gaussian 09 program.[8] Atoms in molecules (AIM)[9] calculations were done using the AIMALL program package[10] using the wave function obtained at the MP2/6-31G* level. Natural bond orbital (NBO)[11] analysis was performed on all these systems to quantify the strength of the CH…O H-bonding. Structural representations of the computed structures were generated using the VMD program.[12] For analysing the correlation between the NBO interaction energies, the experimental Δδ was corrected for the magnetic anisotropy effect of S=O and C-O bonds using McConnell's equations[13] (eq. 1 & 2). The $\Delta\chi$, $\Delta\chi_{parl}$, and $\Delta\chi_{perp}$values for the C-O and S=O bonds were obtained from published studies,[14,15] and the geometric parameters R, φ, θ_1, and $\theta_2$as defined before were calculated based on the optimized geometries obtained using the MP2/6-31G* method (given below). The experimental Δδ, after accounting for the magnetic anisotropy, was used to examine its correlation with the second orbital perturbative orbital interaction energies corresponding to CH…O H-bonding interactions.

$$\delta_{anis} = \Delta\chi(3\cos^2\varphi - 1)/3R^3 \qquad \text{… eq. 1}$$

$$\delta_{anis} = [\Delta\chi_{parl}(3\cos^2\theta_1 - 1) + \Delta\chi_{perp}(3\cos^2\theta_2 - 1)/3R^3 \qquad \text{… eq. 2}$$

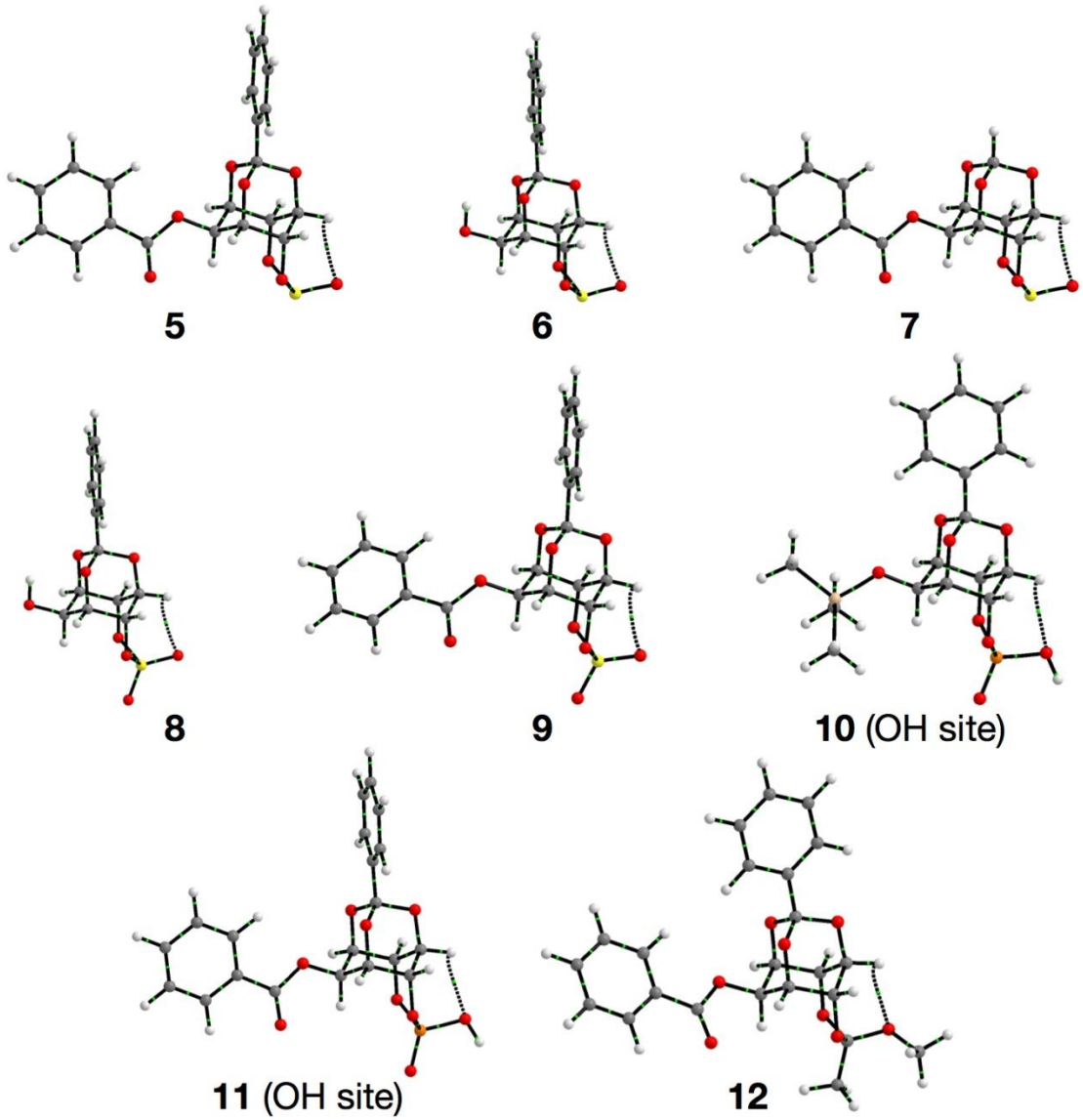


Figure S12. AIM plots obtained at the MP2/6-31G* level showing the bond critical points and the paths between the hydrogen and the acceptor oxygen corresponding to the CH…O H-bonding interactions

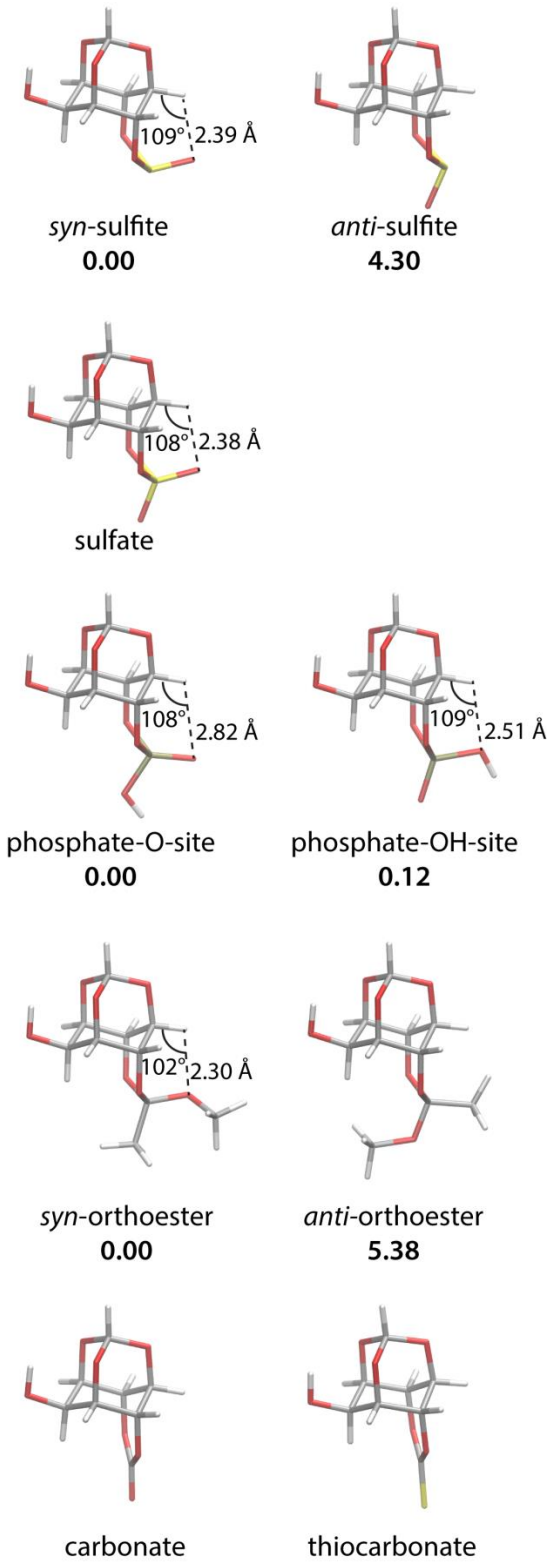
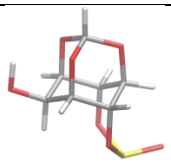
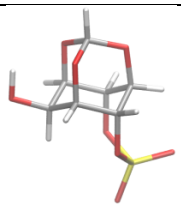
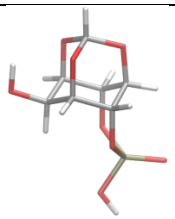
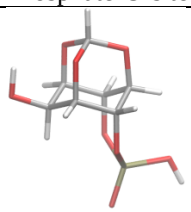
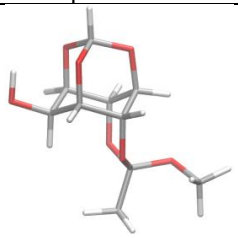
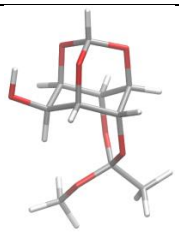
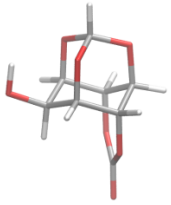
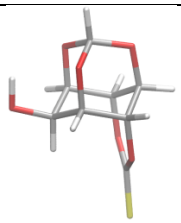
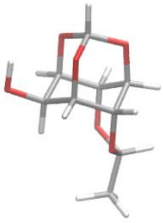
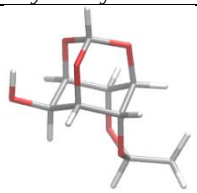
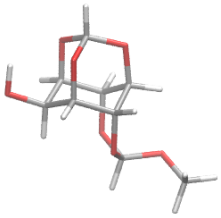
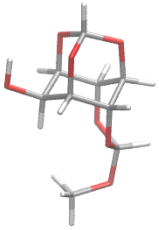


Figure S13. Structural representations of the optimized geometries obtained for the sulfite, sulfate, phosphate, orthoester, carbonate and thiocarbonate model systems given in Figure 5 along with the relative energies wherever applicable (in kcal/mol) obtained at the MP2/6-311+G** level

Table S10: Total and relative energies of the different configurational forms of the conceived models (Figure 5) obtained at the MP2/ level of theory using the 6-311+G** and 6-31G* basis sets

	Model	MP2/6-311+G**		MP2/6-31G*	
Entry		**Total Energy (au)**	**Relative energy (kcal/mol)**	**Total Energy (au)**	**Relative energy (kcal/mol)**
1	 *syn*-sulfite	-1193.94024	0.00	-1193.47448	0.00
2	 *anti*-sulfite	-1193.93339	4.30	-1193.46521	5.82
3	 sulfate	-1269.00029	-	-1268.49795	-
4	 Phosphate-O-site	-1212.96237	0.00	-1212.44257	0.00
5	 Phosphate-OH-site	-1212.96217	0.12	-1212.44218	0.24
6	 *syn*-orthoacetate	-913.90572	0.00	-913.37160	0.00

7	 *anti*-orthoacetate	-913.89716	5.38	-913.36218	5.91
8	 carbonate	-834.34466	-	-833.88700	-
9	 thiocarbonate	-1156.90549	-	-1156.45743	-
10	 *syn*-ethylidene	-799.63209	0.00	-799.16774	0.00
11	 *anti*-ethylidene	-799.62355	5.36	-799.15981	4.98
12	 *syn*-orthoformate	-874.70040	0.00	-874.19566	0.00
13	 *anti*-orthoformate	-874.69604	2.73	-874.19011	3.48

Sulfates can have only one CB conformation, and hence the relative energy of stabilization cannot be calculated by this method. Phosphates have two CH…O bonding possibilities *viz.* P-OH…H and P=O…H, both having the CB conformations. As both forms can form CH…O bonding, the difference in energy cannot be correlated to the strength of the CH…O H-Bond. However, comparison of the energies of these two configurations suggests that the P-OH site is more preferred donor than P=O. This is not surprising as the P-OH is more polarizable than P=O (P-OH can ionize to various extents depending on the solvent). The difference in energy between two configurations in CB conformations of orthoester suggest that the configuration having CH…O H-bond is stabilized by 5.4 kcal/mol. However it is to be noted that the repulsive interaction between the H and methyl group in the anti-conformer would have contributed to this high energy difference. This is clear from the relative energies of the ethylidene derivatives (entries 10-11); the H and methyl repulsive interaction is about 5.0 kcal/mol. Thus, to account for this destabilization, we have used orthoformates (entries 12-13) for calculations. The stabilization energy in the isomer with CH…O H-bond is found to be 2.73 kcal/mol.

Table S11. Comparison of the experimental and computed (MP2/6-31G*) geometric parameters showing good agreement

Comp	$R_{C5...O7}$ **(Å)**		$r_{H5...O7}$ **(Å)**		$\Theta_{C5-H5...O7}$ **(°)**	
	Expt	***MP2***	***Expt***	***MP2***	***Expt***	***MP2***
5	2.98	2.92	2.45	2.37	113	110
7	3.02	2.92	2.49	2.36	114	110
8	2.90	2.89	2.35	2.36	114	108
9	2.73	2.89	2.40	2.35	114	109
12	2.83	2.75	2.33	2.30	110	103
13	3.94	3.96	3.95	4.03	82	79
14	4.35	4.39	4.31	4.46	85	80

Table S12. Donor-acceptor natural bond orbital interactions (kcal/mol) obtained using the second order perturbation analysis in the NBO basis

Model (Figure 5)	E(2)	Compound	E(2)
syn-sulfite	1.38	**5**	1.39
		6	1.36
		7	1.42
sulfate	1.28	**8**	1.26
		9	1.33
phosphate-O-site	0.30	**10-O site**	0.24
		11-O site	0.31
phosphate-OH-site	0.80	**10-OH site**	0.73
		11-OH site	0.88
syn-orthoester	0.96	**12**	0.97
carbonate	0.00	**13**	0.00
thiocarbonate	0.00	**14**	0.00

7) Cartesian coordinates

Cartesian coordinates (atomic number followed by x, y and z coordinates) of the MP2/6-311+G unique optimized structures of the models given in Figure 5 in the manuscript.**

Sulfite

Name: *syn*-sulfite

6	-0.492027	-0.955710	1.225249
1	-1.070963	-1.055897	2.145281
6	1.162445	-2.062473	0.000000
1	1.792885	-2.948239	0.000000
6	-1.407062	-0.988007	0.000000
1	-2.078836	-0.129967	0.000000
6	-0.492027	-0.955710	-1.225249
1	-1.070963	-1.055897	-2.145281
6	0.375813	0.306036	-1.242897
1	0.983235	0.346847	-2.150571
6	0.375813	0.306036	1.242897
1	0.983235	0.346847	2.150571
6	1.270098	0.272945	0.000000
1	2.003466	1.077144	0.000000
8	2.013288	-0.946964	0.000000
8	0.375813	-2.104185	1.164445
8	0.375813	-2.104185	-1.164445
8	-2.221340	-2.139796	0.000000
1	-1.623936	-2.898099	0.000000
8	-0.527886	1.437354	-1.251883
8	-0.527886	1.437354	1.251883
16	-0.464278	2.548851	0.000000
8	0.856199	3.170040	0.000000

Name: *anti*-sulfite

6	0.528744	0.868176	1.224058
1	1.114634	0.845980	2.144670
6	-0.859890	2.296554	0.000000
1	-1.294743	3.292887	0.000000
6	1.429960	0.704270	0.000000
1	1.901523	-0.278853	0.000000
6	0.528744	0.868176	-1.224058
1	1.114634	0.845980	-2.144670
6	-0.588458	-0.177912	-1.246993
1	-1.196955	-0.062588	-2.148727
6	-0.588458	-0.177912	1.246993
1	-1.196955	-0.062588	2.148727
6	-1.448124	0.039810	0.000000
1	-2.333590	-0.602118	0.000000
8	-1.931373	1.381546	0.000000
8	-0.083734	2.172518	1.163420
8	-0.083734	2.172518	-1.163420
8	2.470547	1.657153	0.000000
1	2.048426	2.525388	0.000000
8	0.027551	-1.478369	-1.270390
8	0.027551	-1.478369	1.270390
16	-0.281108	-2.557534	0.000000
8	0.863898	-3.440812	0.000000

Sulfate

6	0.505093	1.091485	1.225306
1	1.090293	1.127802	2.145985
6	-1.018737	2.372529	0.000000
1	-1.548760	3.321573	0.000000
6	1.419851	1.023206	0.000000
1	1.997212	0.098084	0.000000
6	0.505093	1.091485	-1.225306
1	1.090293	1.127802	-2.145985

6	-0.497696	-0.065871	-1.242290
1	-1.100286	-0.053435	-2.153099
6	-0.497696	-0.065871	1.242290
1	-1.100286	-0.053435	2.153099
6	-1.384885	0.064996	0.000000
1	-2.200914	-0.655330	0.000000
8	-1.989069	1.356129	0.000000
8	-0.234947	2.325278	1.165038
8	-0.234947	2.325278	-1.165038
8	2.351658	2.080311	0.000000
1	1.841969	2.900199	0.000000
8	0.289105	-1.287481	-1.243930
8	0.289105	-1.287481	1.243930
16	0.108577	-2.319520	0.000000
8	-1.238515	-2.831715	0.000000
8	1.268499	-3.151907	0.000000

Phosphate

Name: phosphate-O-site

6	0.510475	1.098695	1.225557
1	1.097760	1.117000	2.145582
6	-0.970181	2.434119	0.000000
1	-1.463525	3.402790	0.000000
6	1.420257	0.995927	0.000000
1	1.960362	0.047909	0.000000
6	0.510475	1.098695	-1.225557
1	1.097760	1.117000	-2.145582
6	-0.537202	-0.015996	-1.245988
1	-1.147920	0.049303	-2.149489
6	-0.537202	-0.015996	1.245988
1	-1.147920	0.049303	2.149489
6	-1.413202	0.147590	0.000000
1	-2.246589	-0.559404	0.000000
8	-1.980715	1.455873	0.000000
8	-0.186525	2.359235	1.163955
8	-0.186525	2.359235	-1.163955
8	2.395598	2.015164	0.000000
1	1.917147	2.853478	0.000000
8	0.151556	-1.281160	-1.258442
8	0.151556	-1.281160	1.258442
15	-0.000690	-2.282662	0.000000
8	-1.176931	-3.170060	0.000000
8	1.422133	-2.999291	0.000000
1	1.321564	-3.958328	0.000000

Name: phosphate-OH-site

6	-1.111134	0.507812	1.225092
1	-1.142920	1.092940	2.145957
6	-2.406205	-1.009325	0.000066
1	-3.361356	-1.528334	0.000104
6	-1.037459	1.421199	-0.000013
1	-0.109551	1.995421	-0.000058
6	-1.111231	0.507810	-1.225104
1	-1.143076	1.092894	-2.145990
6	0.030769	-0.510576	-1.243722
1	-0.018554	-1.121096	-2.148361
6	0.030825	-0.510600	1.243741
1	-0.018503	-1.121112	2.148382
6	-0.108078	-1.390797	0.000018
1	0.621142	-2.203119	-0.000028
8	-1.401099	-1.993510	0.000046
8	-2.351918	-0.224272	1.164205
8	-2.351998	-0.224290	-1.164106
8	-2.087984	2.362110	0.000085
1	-2.910314	1.856640	0.000143
8	1.280128	0.204216	-1.262360
8	1.280231	0.204123	1.262339
8	3.230806	1.348864	-0.000159
15	2.277796	0.235396	-0.000030
8	2.938109	-1.239995	0.000097
1	3.901061	-1.186278	-0.001361

Orthoester

Name: *syn*-orthoester

6	-1.316632	0.602763	1.125266
1	-1.486031	1.290583	1.956306
6	-2.330619	-1.204659	0.043110
1	-3.218376	-1.832667	0.053824
6	-1.267142	1.356827	-0.204270
1	-0.418214	2.039398	-0.225461
6	-1.125826	0.290351	-1.291095
1	-1.150363	0.742094	-2.284988
6	0.147065	-0.543497	-1.084174
1	0.279994	-1.244726	-1.914259
6	-0.042751	-0.229328	1.334520
1	-0.042306	-0.689355	2.326638
6	-0.004121	-1.293936	0.239724
1	0.787977	-2.019506	0.401554
8	-1.224723	-2.039646	0.237998
8	-2.459245	-0.276457	1.091284
8	-2.276674	-0.574795	-1.213673
8	-2.425287	2.141890	-0.397904
1	-3.173108	1.532030	-0.373656
8	1.262299	0.362526	-1.067317
8	1.072923	0.671963	1.247978
8	2.667443	-0.689917	0.457919
6	3.647856	-1.047631	-0.515124
1	4.514792	-0.380380	-0.470041
1	3.965538	-2.059344	-0.260928
1	3.225172	-1.036424	-1.524582
6	2.807658	1.722457	0.069531
1	3.407569	1.808729	0.977649
1	3.459045	1.660193	-0.803698
1	2.165541	2.598572	-0.031368
6	1.942662	0.484371	0.169635

Name: *trans*-orthoester

6	-1.016308	0.518857	1.220825
1	-0.947948	1.095825	2.145435
6	-2.554945	-0.752412	-0.000024
1	-3.586029	-1.098082	-0.000033
6	-0.811567	1.413243	0.000018
1	0.189339	1.833865	0.000030
6	-1.016304	0.518909	-1.220821
1	-0.947949	1.095905	-2.145412
6	-0.031955	-0.662121	-1.221041

1	-0.147489	-1.241627	-2.142501
6	-0.031965	-0.662181	1.221013
1	-0.147514	-1.241719	2.142452
6	-0.354494	-1.518584	-0.000034
1	0.185034	-2.462719	-0.000054
8	-1.734058	-1.887261	-0.000038
8	-2.365129	0.007969	1.166618
8	-2.365118	0.007998	-1.166638
8	-1.707929	2.504494	0.000035
1	-2.596421	2.128323	0.000140
8	1.304844	-0.146051	-1.175958
8	1.304824	-0.146090	1.175972
8	3.108471	0.544293	0.000033
6	2.744025	1.924951	0.000011
1	3.689055	2.467692	0.000005
1	2.177923	2.180706	-0.899055
1	2.177921	2.180731	0.899070
6	2.776877	-1.725007	0.000003
1	3.403739	-1.784736	0.891800
1	2.077506	-2.559057	-0.000087
1	3.403876	-1.784668	-0.891703
6	2.080256	-0.371199	0.000003

Carbonate

6	-0.576987	0.528609	1.219843
1	-0.523118	1.102780	2.146625
6	-2.076681	-0.797979	0.000029
1	-3.099288	-1.166467	0.000024
6	-0.390727	1.431656	0.000020
1	0.602191	1.887584	0.000029
6	-0.576896	0.528456	-1.219707
1	-0.523038	1.102653	-2.146477
6	0.416964	-0.638468	-1.213663
1	0.330247	-1.211156	-2.139216
6	0.416935	-0.638363	1.213641
1	0.330294	-1.211058	2.139198
6	0.133653	-1.506297	0.000015
1	0.749198	-2.408831	0.000070
8	-1.230167	-1.919683	0.000055
8	-1.905719	-0.028445	1.164456
8	-1.905658	-0.028505	-1.164408
8	-1.309738	2.499476	-0.000089
1	-2.190708	2.104844	-0.000117
8	1.768053	-0.158152	-1.172043
8	1.768022	-0.158012	1.171970
6	2.416660	0.091999	-0.000042
8	3.533545	0.518566	-0.000059

Thiocarbonate

6	0.805780	0.543564	-1.219540
1	0.691044	1.108030	-2.146754
6	2.436459	-0.617243	0.000069
1	3.492108	-0.876318	0.000218
6	0.522342	1.421834	-0.000030
1	-0.514450	1.767331	-0.000251
6	0.805318	0.543451	1.219489
1	0.690484	1.108068	2.146616
6	-0.059455	-0.721787	1.212081
1	0.076488	-1.280888	2.139884
6	-0.059260	-0.721574	-1.212196
1	0.076406	-1.280707	-2.140030
6	0.313021	-1.555928	-0.000139
1	-0.204152	-2.518074	-0.000346
8	1.713052	-1.822469	-0.000149
8	2.185895	0.130262	-1.164162
8	2.185519	0.130129	1.164330
8	1.322769	2.581212	0.000369
1	2.240916	2.282730	0.000767
8	-1.454616	-0.377560	1.167622
8	-1.454282	-0.376591	-1.167671
6	-2.109359	-0.165602	-0.000042
16	-3.654038	0.325605	-0.000060

Cartesian coordinates (atomic number followed by x, y and z coordinates) of the MP2/6-31G* unique optimized structures of the structures given in Figure 2 in main text.

Structure 5

6	-0.598182	-0.621473	1.224484
1	-0.074740	-0.895922	2.144808
6	-1.220867	1.296040	0.000021
6	0.119796	-1.166870	-0.000267
1	0.157026	-2.257343	-0.000324
6	-0.598382	-0.621296	-1.224813
1	-0.075095	-0.895612	-2.145265
6	-2.055844	-1.090675	-1.242230
1	-2.562493	-0.749200	-2.149907
6	-2.055645	-1.090845	1.242085
1	-2.562142	-0.749499	2.149895
6	-2.740594	-0.520784	0.000022
1	-3.813984	-0.712954	0.000098
8	-2.590559	0.904467	0.000099
8	-0.585951	0.817236	1.169328
8	-0.586136	0.817407	-1.169460
8	1.451446	-0.634058	-0.000404
8	-2.032820	-2.547388	-1.255598
8	-2.032636	-2.547562	1.255239
16	-2.776636	-3.374475	-0.000175
8	-4.208597	-3.045799	-0.000052
6	-1.179908	2.794326	0.000128
6	-1.200119	3.487304	1.214091
6	-1.200256	3.487492	-1.213725
6	-1.219422	4.882142	1.209325
1	-1.188156	2.935414	2.148613
6	-1.219554	4.882328	-1.208738
1	-1.188395	2.935745	-2.148332
6	-1.231076	5.581742	0.000348
1	-1.228796	5.423977	2.151971
1	-1.229025	5.424313	-2.151297
1	-1.246253	6.669010	0.000432
6	2.472744	-1.543182	0.000439
8	2.309084	-2.753234	0.001299
6	3.790515	-0.858759	0.000090
6	3.895899	0.538869	-0.000675
6	4.938815	-1.660209	0.000575
6	5.160365	1.126485	-0.000960
1	2.997770	1.148897	-0.001027
6	6.196788	-1.061202	0.000281
1	4.826894	-2.740900	0.001173
6	6.309972	0.331822	-0.000487
1	5.249475	2.210022	-0.001554
1	7.090582	-1.680120	0.000657
1	7.292592	0.797688	-0.000717

Structure 6

6	0.704349	1.033146	1.224457
1	0.872842	1.596280	2.146240
6	-1.074307	0.063169	-0.000017
6	1.075874	1.867601	0.000784
1	2.139184	2.112688	0.000897
6	0.704374	1.034191	-1.223609
1	0.872888	1.598112	-2.144908
6	1.425975	-0.312816	-1.242167
1	1.187660	-0.875780	-2.149732
6	1.425950	-0.313876	1.241880
1	1.187616	-0.877614	2.148959
6	0.994241	-1.090829	-0.000480
1	1.376587	-2.111797	-0.000912
8	-0.435860	-1.203449	-0.000544
8	-0.722395	0.787782	1.166844
8	-0.722370	0.788777	-1.166242
8	0.374472	3.096465	0.001303
1	-0.571683	2.855346	0.001214
8	2.854312	-0.019416	-1.254377
8	2.854287	-0.020489	1.254370
16	3.802339	-0.600705	-0.000242
8	3.741763	-2.068752	-0.000871
6	-2.554512	-0.173543	-0.000095
6	-3.231560	-0.321925	1.214108
6	-3.231863	-0.319850	-1.214377
6	-4.598883	-0.598044	1.208964
1	-2.691107	-0.210295	2.148839
6	-4.599189	-0.595969	-1.209354
1	-2.691648	-0.206627	-2.149052
6	-5.284295	-0.736749	-0.000229
1	-5.129812	-0.707714	2.151447
1	-5.130361	-0.704019	-2.151888
1	-6.350184	-0.951681	-0.000280

Structure 7

6	-0.794943	0.519284	1.226425
1	-0.327048	0.157931	2.146164
6	-1.094505	2.491008	0.001737
6	-0.184250	-0.142225	-0.000603
1	-0.342783	-1.221516	-0.001377
6	-0.795394	0.521297	-1.226298
1	-0.327845	0.161468	-2.146807
6	-2.313158	0.308284	-1.242731
1	-2.753045	0.732307	-2.150281
6	-2.312703	0.306256	1.243090
1	-2.752249	0.728794	2.151497
6	-2.892565	0.986503	0.000841
1	-3.982553	0.977548	0.001035
8	-2.501214	2.364794	0.001885
8	-0.543587	1.936288	1.171419
8	-0.544013	1.938213	-1.169063
8	1.222596	0.140081	-0.000816
8	-2.542035	-1.129858	-1.256290
8	-2.541595	-1.131904	1.254377
16	-3.416257	-1.818428	-0.001353
8	-4.770711	-1.249196	-0.000661
6	2.058174	-0.943022	0.000407
8	1.672506	-2.101506	0.001732
6	3.480993	-0.518197	-0.000066
6	3.848893	0.834032	-0.001760
6	4.457613	-1.521885	0.001248
6	5.201436	1.172695	-0.002129

1	3.082020	1.602267	-0.002758
6	5.806012	-1.171180	0.000853
1	4.143820	-2.562022	0.002554
6	6.180319	0.175336	-0.000831
1	5.493742	2.219847	-0.003435
1	6.566818	-1.947756	0.001869
1	7.233213	0.447212	-0.001133
1	-0.865085	3.554363	0.002567

Structure 8

6	0.487310	1.012851	1.224855
1	0.661969	1.573639	2.146818
6	-1.302229	0.060525	-0.000014
6	0.867039	1.844453	0.000697
1	1.932044	2.085184	0.000796
6	0.487330	1.013792	-1.224107
1	0.662006	1.575288	-2.145636
6	1.192065	-0.342286	-1.242270
1	0.961002	-0.902567	-2.152283
6	1.192046	-0.343240	1.241986
1	0.960968	-0.904220	2.151566
6	0.752541	-1.117682	-0.000443
1	1.123738	-2.142893	-0.000834
8	-0.675605	-1.214997	-0.000493
8	-0.940022	0.777617	1.167873
8	-0.940002	0.778514	-1.167335
8	0.173932	3.076383	0.001165
1	-0.774793	2.845364	0.001085
8	2.627207	-0.054605	-1.250533
8	2.627187	-0.055568	1.250494
16	3.513961	-0.616487	-0.000229
8	3.479515	-2.068144	-0.000788
8	4.735683	0.145515	0.000074
6	-2.784028	-0.160432	-0.000078
6	-3.462116	-0.301676	1.214547
6	-3.462370	-0.299833	-1.214770
6	-4.832155	-0.563652	1.209081
1	-2.921362	-0.195668	2.149731
6	-4.832411	-0.561813	-1.209411
1	-2.921817	-0.192414	-2.149908
6	-5.518783	-0.695197	-0.000193
1	-5.364258	-0.667347	2.151494
1	-5.364711	-0.664073	-2.151869
1	-6.586764	-0.899087	-0.000235

Structure 9

6	-0.663834	-0.396016	1.067866
1	-0.264485	-0.978185	1.900744
6	-0.433164	1.724531	0.050417
6	-0.359451	-1.060569	-0.271431
1	-0.803340	-2.057576	-0.333426
6	-0.852918	-0.124439	-1.363704
1	-0.588015	-0.499587	-2.356158
6	-2.355991	0.127386	-1.236972
1	-2.718178	0.751072	-2.058438
6	-2.166314	-0.150515	1.223503
1	-2.395558	0.264978	2.208250
6	-2.604319	0.806349	0.112489
1	-3.641261	1.122975	0.227629
8	-1.818017	1.998875	0.188609
8	-0.007090	0.882922	1.106828
8	-0.187436	1.143257	-1.220481
8	1.059660	-1.137064	-0.472169
8	-3.012280	-1.175476	-1.344282
8	-2.816188	-1.459050	1.129812
16	-3.900646	-1.678169	-0.068432
8	-5.020284	-0.773157	0.122134
8	-4.052635	-3.101462	-0.221795
6	0.360033	2.990790	0.126132
6	1.753825	2.876512	0.179239
6	-0.255164	4.243464	0.107422
6	2.534416	4.030174	0.223099
1	2.209185	1.889675	0.193163
6	0.535981	5.393146	0.153123
1	-1.337089	4.315428	0.063453
6	1.927195	5.289372	0.209806
1	3.617679	3.948339	0.268307
1	0.063537	6.372318	0.143142
1	2.538292	6.188023	0.245515
6	1.701047	-2.101898	0.248816
8	1.118722	-2.884201	0.985056
6	3.166505	-2.061207	0.020449
6	3.762394	-1.072679	-0.775174
6	3.948515	-3.041061	0.643996
6	5.146402	-1.076439	-0.944891
1	3.145295	-0.319127	-1.255264
6	5.330408	-3.035393	0.465749
1	3.460300	-3.792611	1.258294
6	5.931465	-2.053637	-0.326901
1	5.615250	-0.312905	-1.560723
1	5.940730	-3.795783	0.946495
1	7.010184	-2.050715	-0.463960

Structure 10 (O site)

6	0.245658	0.032459	1.140477
1	0.545876	0.598339	2.026989
6	-1.710743	-0.615095	-0.016219
6	0.794059	0.669910	-0.132700
1	1.888711	0.589905	-0.149821
6	0.208540	-0.113758	-1.300848
1	0.481690	0.346115	-2.254884
6	0.614923	-1.586089	-1.241548
1	0.223776	-2.125704	-2.108500
6	0.653306	-1.436827	1.245520
1	0.290601	-1.868966	2.182325
6	0.046103	-2.174458	0.050860
1	0.226326	-3.253171	0.112571
8	-1.373062	-1.995129	0.062717
8	-1.192527	0.071924	1.108420
8	-1.228408	-0.069994	-1.229947
8	0.356950	2.015103	-0.224169
8	2.063142	-1.669588	-1.279943
8	2.102622	-1.513711	1.249601
15	2.851768	-2.249404	0.013113
8	3.010474	-3.719483	0.101012
8	4.215758	-1.403013	-0.058990

1	4.977304	-2.012389	-0.037997
14	1.444612	3.291457	0.023898
6	2.228958	3.133881	1.726657
1	1.470208	3.158139	2.514970
1	2.794607	2.201707	1.830111
1	2.926492	3.957886	1.911205
6	0.395057	4.832853	-0.110882
1	0.997052	5.736255	0.029986
1	-0.081133	4.895129	-1.093361
1	-0.395146	4.832595	0.645078
6	2.780292	3.247152	-1.299143
1	3.370063	2.325538	-1.257889
1	2.343843	3.321609	-2.299757
1	3.476245	4.083707	-1.175340
6	-3.197494	-0.444266	-0.002943
6	-3.689574	0.861998	-0.100616
6	-4.066338	-1.530575	0.107419
6	-5.066235	1.077729	-0.088638
1	-2.987763	1.687592	-0.185430
6	-5.444309	-1.303647	0.118190
1	-3.668190	-2.537255	0.182628
6	-5.945304	-0.004086	0.020766
1	-5.455584	2.090132	-0.164726
1	-6.127820	-2.145032	0.203207
1	-7.019235	0.166567	0.029643

Structure 10 (OH Site)

6	0.261813	0.048014	1.137007
1	0.554986	0.617324	2.023578
6	-1.685839	-0.629280	-0.017277
6	0.796627	0.695847	-0.136907
1	1.892882	0.640914	-0.155618
6	0.224925	-0.100475	-1.303457
1	0.491061	0.361104	-2.258560
6	0.652897	-1.567010	-1.241724
1	0.269507	-2.111442	-2.109067
6	0.690861	-1.415640	1.241223
1	0.335736	-1.850783	2.179482
6	0.094591	-2.163773	0.049608
1	0.287951	-3.238587	0.111932
8	-1.327793	-2.003832	0.062439
8	-1.176887	0.065560	1.106724
8	-1.212530	-0.078790	-1.232016
8	0.331853	2.030665	-0.229095
8	2.100470	-1.636535	-1.288624
8	2.139688	-1.477345	1.252592
8	4.386808	-1.645325	-0.047773
15	2.974508	-2.066342	0.000538
8	2.739444	-3.670655	0.106294
1	3.601545	-4.127802	0.113738
6	-3.174855	-0.479517	-0.003014
6	-4.028345	-1.577647	0.109879
6	-3.685223	0.819602	-0.102175
6	-5.409355	-1.370058	0.121616
1	-3.616021	-2.578521	0.186267
6	-5.064762	1.016053	-0.089208
1	-2.995026	1.654746	-0.188891
6	-5.928534	-0.077768	0.022672
1	-6.081036	-2.220734	0.208591
1	-5.468283	2.022791	-0.166467
1	-7.004730	0.077891	0.032301
14	1.387226	3.334327	0.024998
6	2.724279	3.329845	-1.296362
1	3.342682	2.427211	-1.255698
1	2.287033	3.392542	-2.297436
1	3.394660	4.186750	-1.170683
6	2.170490	3.192206	1.729212
1	1.409319	3.191681	2.515594
1	2.764177	2.277508	1.831299
1	2.843033	4.035721	1.918283
6	0.295146	4.846325	-0.107057
1	0.871814	5.765564	0.037242
1	-0.180962	4.898255	-1.090186
1	-0.495831	4.822129	0.647716

Structure 11 (O Site)

6	0.665775	-0.344123	-1.073411
1	0.278962	-0.933926	-1.907019
6	0.383938	1.770310	-0.051603
6	0.384384	-1.020296	0.263783
1	0.862644	-2.001890	0.322320
6	0.848957	-0.073390	1.358195
1	0.592234	-0.457575	2.349411
6	2.342087	0.224196	1.234947
1	2.664095	0.878779	2.049651
6	2.157930	-0.053672	-1.233494
1	2.352136	0.395724	-2.211369
6	2.569499	0.906421	-0.115968
1	3.608621	1.232405	-0.229835
8	1.761588	2.085814	-0.189855
8	-0.023821	0.919485	-1.107714
8	0.149854	1.178077	1.216449
8	-1.032494	-1.148126	0.465173
8	3.071114	-1.022819	1.344358
8	2.880283	-1.307935	-1.162112
15	3.923288	-1.535015	0.059987
8	5.283767	-0.973600	-0.107932
8	3.833971	-3.123655	0.254774
1	4.727483	-3.511850	0.203848
6	-0.443133	3.015675	-0.123478
6	-1.833379	2.865300	-0.178084
6	0.138076	4.284367	-0.099581
6	-2.644487	3.997891	-0.218396
1	-2.261912	1.866637	-0.196351
6	-0.683126	5.412959	-0.141682
1	1.217718	4.384212	-0.054551
6	-2.071090	5.272779	-0.199790
1	-3.725210	3.887390	-0.264769
1	-0.236694	6.404272	-0.127564
1	-2.705790	6.155088	-0.232687
6	-1.639220	-2.138318	-0.247855
8	-1.032451	-2.909357	-0.976700
6	-3.106416	-2.144068	-0.021599
6	-3.735725	-1.167960	0.763444
6	-3.855210	-3.155040	-0.635991
6	-5.119103	-1.215471	0.931862

1	-3.144022	-0.389564	1.235812
6	-5.236841	-3.193142	-0.459340
1	-3.341565	-3.895693	-1.242743
6	-5.870957	-2.224026	0.323006
1	-5.613560	-0.461419	1.539342
1	-5.821264	-3.977780	-0.933359
1	-6.949430	-2.255019	0.458747

Structure 11 (OH Site)

6	0.627335	-0.295953	-1.224324
1	0.202825	-0.705639	-2.145189
6	0.687253	1.722942	0.000084
6	0.087948	-1.019105	0.000205
1	0.345608	-2.081154	0.000243
6	0.627357	-0.295838	1.224653
1	0.202867	-0.705440	2.145565
6	2.156804	-0.324685	1.243720
1	2.533246	0.161115	2.148338
6	2.156780	-0.324785	-1.243425
1	2.533198	0.160939	-2.148092
6	2.652135	0.411370	0.000111
1	3.740618	0.514772	0.000091
8	2.115937	1.738992	0.000064
8	0.216273	1.083924	-1.169099
8	0.216289	1.084030	1.169315
8	-1.337605	-0.867495	0.000239
8	2.591233	-1.705495	1.272075
8	2.591266	-1.705584	-1.271679
8	3.335468	-3.855440	0.000415
15	3.327883	-2.382510	0.000208
8	4.797805	-1.687977	-0.000053
1	5.484776	-2.381285	0.001365
6	0.223236	3.147992	-0.000038
6	0.046807	3.818269	-1.214109
6	0.045312	3.818129	1.213887
6	-0.330659	5.161196	-1.209314
1	0.191908	3.285837	-2.148723
6	-0.332155	5.161059	1.208768
1	0.189262	3.285601	2.148621
6	-0.518712	5.835166	-0.000349
1	-0.475123	5.683440	-2.151971
1	-0.477784	5.683199	2.151304
1	-0.813377	6.881829	-0.000472
6	-2.076308	-2.020231	-0.000029
8	-1.590832	-3.139677	-0.000356
6	-3.529552	-1.715873	-0.000137
6	-4.008444	-0.398590	0.000115
6	-4.418603	-2.797802	-0.000504
6	-5.384612	-0.174340	-0.000009
1	-3.308544	0.431413	0.000391
6	-5.791577	-2.560697	-0.000618
1	-4.018832	-3.808078	-0.000700
6	-6.276807	-1.250035	-0.000367
1	-5.763086	0.844853	0.000182
1	-6.484963	-3.398036	-0.000899
1	-7.348767	-1.067080	-0.000461

Structure 12

6	-0.768108	-0.110014	1.433864
1	-0.484016	-0.477110	2.424436
6	-0.360670	1.714717	-0.009262
6	-0.310469	-1.062608	0.342537
1	-0.761757	-2.052188	0.431483
6	-0.654713	-0.411969	-0.991725
1	-0.290684	-1.009784	-1.830463
6	-2.165311	-0.166806	-1.092770
1	-2.411569	0.230184	-2.083846
6	-2.279135	0.128818	1.332287
1	-2.624037	0.739735	2.172763
6	-2.545526	0.828375	0.001588
1	-3.576215	1.167324	-0.081672
8	-1.737804	2.010346	-0.110405
8	-0.083104	1.144857	1.260399
8	0.025158	0.854917	-1.067940
8	1.117306	-1.154500	0.494809
8	-2.831484	-1.435777	-0.927870
8	-2.922105	-1.160260	1.405718
8	-4.770326	-0.782359	0.192830
6	-5.623720	-1.041408	-0.927381
1	-6.173026	-1.979749	-0.800783
1	-6.333340	-0.214299	-0.952359
1	-5.052999	-1.071376	-1.859135
6	-3.886482	-3.054880	0.413956
1	-4.536681	-3.195498	1.279259
1	-4.367961	-3.448341	-0.482304
1	-2.945709	-3.584381	0.568983
6	-3.603981	-1.579025	0.253366
6	0.453111	2.967077	-0.121959
6	-0.137817	4.230182	-0.065959
6	1.840536	2.831762	-0.243215
6	0.668642	5.367490	-0.144347
1	-1.215145	4.317032	0.031808
6	2.637758	3.972567	-0.319406
1	2.277091	1.837379	-0.285554
6	2.053635	5.241731	-0.269475
1	0.213599	6.354364	-0.105427
1	3.716182	3.872991	-0.417765
1	2.677300	6.130517	-0.330380
6	1.720335	-2.148515	-0.208598
8	1.111009	-2.964446	-0.886225
6	3.196471	-2.104863	-0.044272
6	3.826843	-1.083445	0.679915
6	3.950916	-3.114244	-0.653950
6	5.216776	-1.084095	0.792295
1	3.230056	-0.306904	1.149031
6	5.339202	-3.105432	-0.533890
1	3.435942	-3.890310	-1.213506
6	5.974379	-2.090974	0.187737
1	5.711773	-0.294467	1.352379
1	5.927992	-3.888770	-1.004827
1	7.057975	-2.085220	0.279333

Structure 13

6	1.124700	0.643550	1.358125
1	0.772279	0.913194	2.357569
6	1.302802	-1.250524	-0.056049

6	0.341133	1.370130	0.278742
1	0.428847	2.459323	0.345099
6	0.848022	0.846773	-1.059639
1	0.290527	1.275294	-1.894853
6	2.354554	1.079656	-1.202956
1	2.680537	0.781035	-2.202503
6	2.628487	0.877304	1.199926
1	3.163394	0.423044	2.037883
6	3.070983	0.285824	-0.126332
1	4.157812	0.335718	-0.245651
8	2.705592	-1.095198	-0.203164
8	0.896831	-0.771735	1.217711
8	0.631437	-0.575989	-1.106681
8	-1.024900	0.982918	0.483463
8	2.679172	2.478691	-1.083851
8	2.941422	2.282547	1.245380
6	2.960242	3.059737	0.119630
8	3.224676	4.231810	0.190549
6	0.927413	-2.697140	-0.130445
6	1.891700	-3.705985	-0.112960
6	-0.435933	-3.009223	-0.179903
6	1.484459	-5.040936	-0.156442
1	2.944855	-3.447548	-0.071636
6	-0.832163	-4.344676	-0.221739
1	-1.167796	-2.205783	-0.193297
6	0.126690	-5.362013	-0.209639
1	2.230431	-5.831881	-0.147398
1	-1.889764	-4.593537	-0.264446
1	-0.184802	-6.403242	-0.243606
6	-1.945673	1.690181	-0.233688
8	-1.649774	2.626260	-0.961341
6	-3.317246	1.170067	-0.011906
6	-3.557792	0.036785	0.777538
6	-4.375691	1.842087	-0.635205
6	-4.866837	-0.414797	0.941167
1	-2.728966	-0.474412	1.258044
6	-5.679618	1.382051	-0.463193
1	-4.159484	2.715262	-1.244609
6	-5.927340	0.253467	0.323163
1	-5.060850	-1.292856	1.552252
1	-6.504337	1.902218	-0.943883
1	-6.945697	-0.104179	0.455340

Structure 14

6	-1.112078	0.029286	-1.340005
1	-0.901198	0.421262	-2.338788
6	-0.523987	-1.791463	0.059547
6	-0.670946	0.999734	-0.257684
1	-1.181536	1.966823	-0.314635
6	-0.922429	0.310015	1.077951
1	-0.574095	0.917511	1.915457
6	-2.398856	-0.067801	1.225733
1	-2.584544	-0.465988	2.226316
6	-2.585629	-0.347217	-1.173497
1	-2.912581	-0.961450	-2.016181
6	-2.754128	-1.073529	0.147781
1	-3.772337	-1.455014	0.271017
8	-1.874725	-2.200073	0.212594
8	-0.346613	-1.183969	-1.211810
8	-0.164917	-0.913868	1.113174
8	0.735865	1.180522	-0.471190
8	-3.241550	1.100972	1.112014
8	-3.420569	0.831125	-1.204916
6	-3.705567	1.544617	-0.083620
16	-4.594474	2.901439	-0.174948
6	1.311512	2.184315	0.253084
8	0.678135	2.919410	0.995643
6	2.774954	2.247627	0.018593
6	3.434386	1.309418	-0.787839
6	3.489689	3.274334	0.647474
6	4.814044	1.410698	-0.962754
1	2.868930	0.519230	-1.272613
6	4.867864	3.365951	0.464006
1	2.953197	3.985122	1.269980
6	5.532090	2.434824	-0.339268
1	5.331996	0.686821	-1.587076
1	5.426072	4.162869	0.948890
1	6.607811	2.507898	-0.480376
6	0.389147	-2.975153	0.121093
6	-0.102239	-4.281354	0.102519
6	1.765972	-2.727292	0.160345
6	0.796496	-5.349550	0.134502
1	-1.172621	-4.456888	0.069252
6	2.654670	-3.800348	0.190774
1	2.124106	-1.701199	0.174728
6	2.171752	-5.112267	0.177398
1	0.420650	-6.369729	0.124407
1	3.725409	-3.614424	0.225393
1	2.867037	-5.947889	0.202534

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