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Stereoselective synthesis of optically active cyclitol precursors via a chemoenzymatic method

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Abstract—Racemic α′-acetoxy α,β-unsaturated cyclohexanone has been converted to the corresponding enantiomerically enriched α′-hydroxylated and acetoxylated compounds with 97% ee via enzymatic resolution with PLE. OsO_4-Catalyzed dihydroxylation of enantiomerically enriched α′-acetoxylated compound afforded a single diastereomer in 85% chemical yield. The absolute configuration of 2,3,6-triacetoxycylohexanone was determined by X-ray diffraction analysis. Subsequent Luche reduction allowed us to obtain corresponding *syn*-type cyclitol precursors in a highly stereoselective manner as expected.

1. Introduction

Polyhydroxylated cyclohexanes and their derivatives are widespread constituents of biologically important compounds, the most obvious instances being cyclitols,[1] especially inositols.[2] Carbasugars,[3] carbacyclic analogues of sugars first synthesized by McCasland et al.,[4] with their ability to function as glycosidase inhibitors, have potential in many therapeutic areas. Polyhydroxylated cyclohexane rings are also found in the amaryllidaceae family of natural products, most notably pancratistatin, lycoridine and narciclasine and their relatives.[5] Cyclitols have attracted a great deal of attention from synthetic chemists due to their diverse biological activity and their versatility as synthetic intermediates.[6] Various methodologies have been developed for the synthesis of enantiopure cyclitols and their derivatives. Recently, the synthesis of enantiopure cyclitols was achieved via the transformation of other cyclitols.[7] The microbial oxidation of halobenzenes was employed by Hudlickly et al. in the preparation of inositols.[8] The Ferrier-II rearrangement and the free radical cyclization[9] of sugar derivatives are also useful methods developed by Ikegami and Yadav et al., respectively. Furthermore, the reduction of allylsilanes in combination with asymmetric dihydroxylation reported by Landais et al. provides an easy access to cyclitols.[10] Additionally, enzymatic resolution of a hydroxyl group in the presence of an endoperoxide functionality reported by Balcı and Tanyeli et al. provides enantiomerically enriched cyclopentol derivatives.[11]

In connection with our work on the development of novel procedures for the direct oxidation of α,β-unsaturated cyclic ketones with $Mn(OAc)_3$[12] in the synthesis of (±)-6-acetoxy-2-cyclohexen-1-one *rac*-**1** and subsequent PLE catalyzed enzymatic resolution into enantiomerically enriched forms,[13] we herein report the results of OsO_4 catalyzed dihydroxylation and then Luche reduction of the corresponding ketones to obtain structurally very diverse cyclitol precursors.

2. Results and discussion

2.1. Enzymatic hydrolysis of racemic substrate 1

The bioconversion of *rac*-**1** was performed using PLE according to the following procedure, which has already been developed in our group (Scheme 1). To a stirred solution of *rac*-**1** (9.1 mmol) in a phosphate buffer (pH 7.00, 50 mL), PLE (100 μL) was added in one portion and the reaction mixture stirred at room temperature in a pH stat unit. The conversion was monitored by TLC. After 8 h, (*S*)-(−)-6-acetoxy-2-cyclohexen-1-one (*S*)-**1** was obtained with 97% ee in 49% chemical yield.

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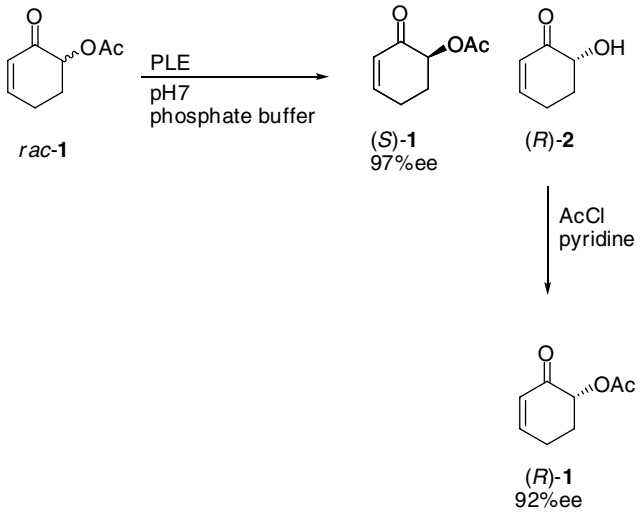


Scheme 1.

In our previous work,[13] we showed that 6-hydroxy-2-cyclohexen-1-one (*R*)-**2** could not be isolated due to the racemization and/or rearrangement of α′-hydroxylated cyclic enones. With this in mind, substrate (*R*)-**2** was immediately subjected to acetylation to afford the corresponding (*R*)-(+)-6-acetoxy-2-cyclohexen-1-one (*R*)-**1** with 92% ee in 44% chemical yield.

2.2. Upjohn dihydroxylation of substrates (*S*)-1 and (*R*)-1

Osmium-catalyzed oxidation reaction is one of the most useful methods for the dihydroxylation of olefins so as to give the corresponding diols. The oxidation proceeds in the presence of a catalytic amount of OsO_4 with a cooxidant, such as *N*-methylmorpholine *N*-oxide (Upjohn procedure).[14] The first dihydroxylation was performed with substrate (*S*)-**1** using OsO_4 and NMO prepared in situ according to the following general procedure. 4-Methylmorpholine-*N*-oxide monohydrate 97% (4.94 mmol) was dissolved in H_2O (0.23 mol) under inert atmosphere. The temperature was adjusted to −5 °C, then, 14.07 mL OsO_4 (100 mg/40 mL) stock solution was added to the medium including (*S*)-**1** (4.46 mmol) in acetone and dissolved NMO solution was slowly added. The mixture was allowed to stir for 26 h at −5 °C until all the starting material had been used. $NaHSO_3$ (6.64 mmol), florosil (0.076 mol) and H_2O (0.465 mol) were also added and the resulting solution allowed to stir for 12 h. The conversion was monitored by TLC. The pH of the reaction mixture was adjusted to 2 by using 1 M HCl and compound **3** was obtained as a single diastereomer. This unusual diastereoselectivity is presumably comes from a possible coordination of the α′-acetoxy group to the OsO_4 to afford a *syn*-dihydroxylation reaction. Due to isolation problem, compound **3** was acetylated in situ and (−)-**4** was obtained in 85% chemical yield. By adjusting the same process to (*R*)-(+)-6-acetoxy-2-cyclohexen-1-one (*R*)-**1**, the corresponding diol *ent*-**3** was also obtained. Subsequent acetylation afforded (+)-**4** in 81% chemical yield (Scheme 2).

The absolute configuration of (−)-**4** was determined by X-ray analysis as (1*R*,2*R*,4*S*)-3-oxocyclohexane-1,2,4-triyl triacetate. The absolute configurations of new stereogenic centres formed, C_1 and C_2, were determined relatively by taking the C_4 centre as the reference point (Figs. 1 and 2).

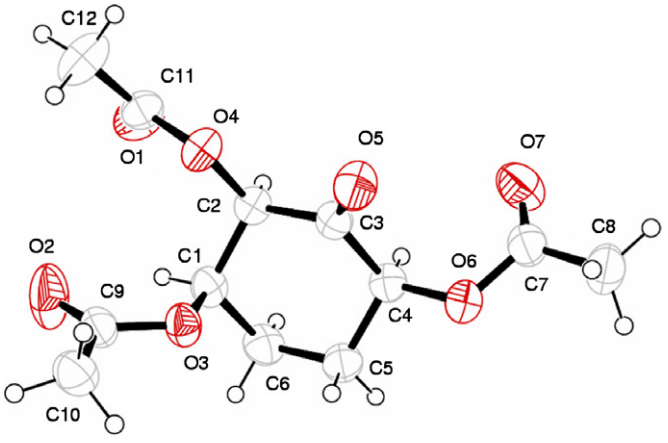
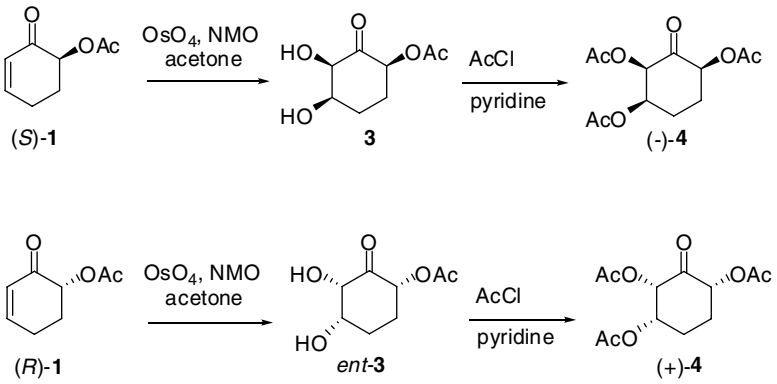


Figure 1. The molecular structure of (1*R*,2*R*,4*S*)-3-oxocyclohexane-1,2,4-triyl triacetate (−)-**4**. Displacement ellipsoids are plotted at the 50% probability level. Selected bond lengths (Å) and angles (°): C3–O5 1.203(4), C2–C3 1.512(3), C1–C2 1.528(3), C4–O6 1.430(3), C2–O4 1.429(3), O1–C11 1.194(3), O4–C2–C3 108.09(9), C2–C3–O5 124.38(10), C3–C4–C5 111.35(12), C2–C1–O3 107.45(10).



Scheme 2.

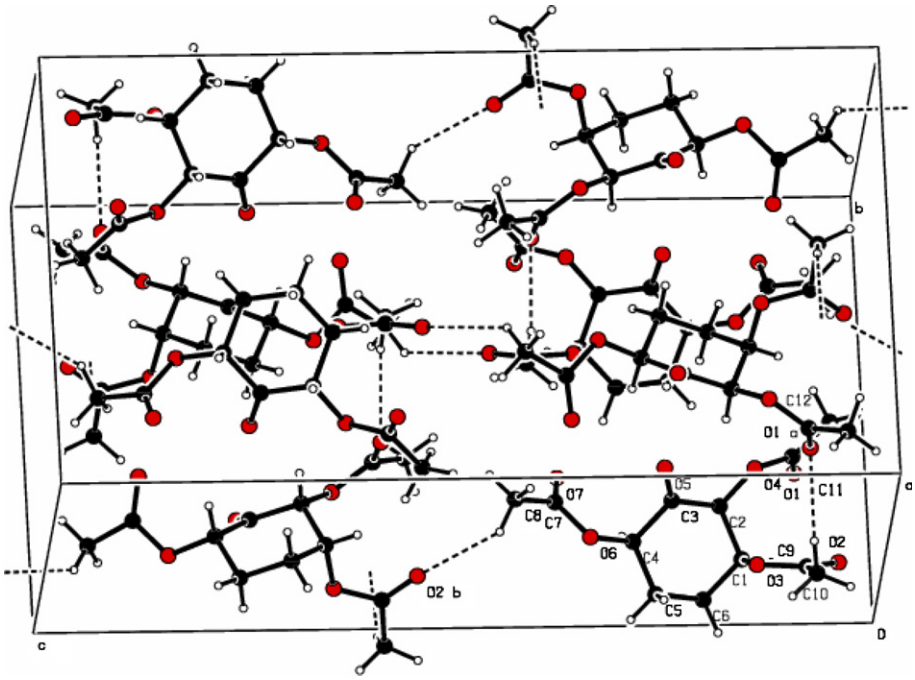


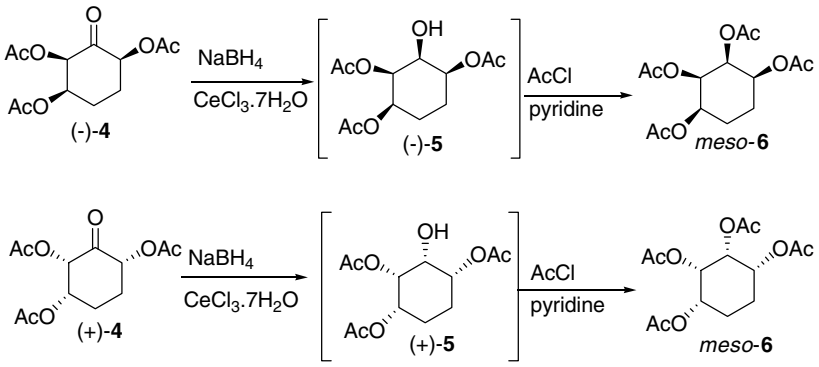
Figure 2. View of intermolecular C–H···O bonds and molecular packing through *a*-axis in compound (1*R*,2*R*,4*S*)-3-oxocyclohexane-1,2,4-triyl triacetate (−)-**4**. [C10–H···O1[a], (a) $\frac{1}{2}+x,\ \frac{1}{2}-y,\ z$; $D\cdots A = 3.314(5)$ Å, D–H···$A = 146°$; C8–H···O2[b], (b) $\frac{1}{2}+-x,\ y,\ \frac{1}{2}+z$; $D\cdots A = 3.346(5)$ Å, D–H···$A = 136°$].

2.3. Luche reduction of substrates (−)-4 and (+)-4

Luche reduction of compound (−)-**4** gave compound (−)-**5** as a single diastereomer in 82% chemical yield. The reduction was performed according to the following general procedure. To a cooled solution, −78 °C, of (1*R*,2*R*,4*S*)-3-oxocyclohexane-1,2,4-triyl triacetate (−)-**4** (0.4 mmol) in methanol (0.1 mol), $NaBH_4$ (0.4 mmol). and $CeCl_3{\cdot}7H_2O$ (0.4 mmol) were added and allowed to stir. After 3 h, the reaction was quenched with H_2O (0.17 mol). The corresponding product (−)-**5** was obtained in 82% chemical yield (Scheme 3). Due to identification problems, protection via direct acetylation was performed to assign clearly the configuration of compound (−)-**5** and the formation of the resulting *meso*-**6** in 84% chemical yield estimated that such reduction provided us only a single diastereomer in the absolute configuration of (1*R*,2*S*,3*S*,4*S*)-3-hydroxycyclohexane-1,2,4-triyl triacetate (−)-**5**. By applying the same process for (1*S*,2*S*,4*R*)-3-oxocyclohexane-1,2,4-triyl triacetate (+)-**4**, single diastereomer in the absolute configuration of (1*S*,2*R*,3*R*,4*R*)-3-hydroxycyclohexane-1,2,4-triyl triacetate (+)-**5** was obtained in 80% chemical yield.

3. Conclusion

Herein, we have improved the direct stereoselective dihydroxylation of enantiomerically enriched α′-acetoxy α,β-unsaturated cyclohexanones (*S*)-**1** and (*R*)-**1** using OsO_4 and NMO in good yields, and have shown that six-membered enone afforded only *syn*-diastereomer **3** from (*S*)-**1** and *ent*-**3** from (*R*)-**1**. The absolute configuration of (1*R*,2*R*,4*S*)-(−)-**4** was determined by X-ray analysis. The enantiomer (1*S*,2*S*,4*R*)-(+)-**4** was also obtained by OsO_4 catalyzed dihydroxylation reaction and subsequent protection and findings confirmed the results obtained in the first set of experiments. Subsequent Luche reduction of compounds (−)-**4** and (+)-**4** allowed structurally very diverse



Scheme 3.

syn-type cyclitol precursors (1*R*,2*S*,3*S*,4*S*)-3-hydroxycyclohexane-1,2,4-triyl triacetate (−)-**5** and (1*S*,2*R*,3*R*,4*R*)-3-hydroxycyclohexane-1,2,4-triyl triacetate (+)-**5** to be obtained respectively.

4. Experimental

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker Spectrospin Avance DPX 400 spectrometer. Chemical shifts are given in parts per million downfield from tetramethylsilane. Apparent splittings are given in all cases. Infrared spectra were obtained from KBr pellets on a Mattson 1000 FT-IR spectrophotometer. Optical rotations were measured in a 1 dm cell using a Rudolph Research Analytical Autopol III polarimeter at 20 °C. HPLC measurements were performed with Thermo-Finnigan Spectra System instrument. Separations were carried out on Chiralcel OD-H analytical column (250 × 4.60 mm) with hexane/2-propyl alcohol as eluent. Column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2-mm silica gel 60 F_{254} analytical aluminium plates. PLE (Pig Liver Esterase) was purchased from Sigma as a suspension in ammonium sulfate solution (3.2 mol/L).

4.1. General procedure for the enzymatic hydrolysis of *rac*-1

To a stirred solution of (1.4 g, 9.1 mmol) *rac*-**1**, in 50 mL of pH 7.00 phosphate buffer, 100 μL PLE was added in one portion and the reaction mixture stirred at 20 °C in a pH stat unit. The conversion was monitored by TLC. The reaction mixture were extracted with ethyl acetate, dried over $MgSO_4$ and concentrated under reduced pressure. The product was purified by flash column chromatography (EtOAc/hexane, 1:3). Compound (*S*)-(−)-**1** was isolated and is in accordance with the literature data.[13] The isolated product (*R*)-**2** was directly subjected to an acetylation reaction to prevent its complete racemization. To a stirred solution of (*R*)-**2** (0.191 g, 1.71 mmol) in CH_2Cl_2 (25 mL), dry pyridine (0.268 g, 3.39 mmol) was added at 0 °C and stirred for 30 min. Acetylchloride (0.202 g, 2.56 mmol) was then added dropwise. The resultant mixture was stirred for 12 h at room temperature. The organic phase was extracted with 0.1 M HCl (3 × 20 mL), saturated $NaHCO_3$ (3 × 20 mL) and brine (2 × 20 mL), dried over $MgSO_4$ and the solvent was evaporated under reduced pressure to afford quantitatively (*R*)-(+)-**1**. All are in accordance with the literature data.[13]

4.1.1. (*S*)-(−)-6-Acetoxy-2-cyclohexenone (*S*)-(−)-1. (0.690 g, 49%) as a colourless oil; 97% ee $[\alpha]_D^{20} = -88.7$ (*c* 0.5, MeOH).

4.1.2. (*R*)-(+)-6-Acetoxy-2-cyclohexenone (*R*)-(+)-1. (0.116 g, 44%) as a colourless oil; 92% ee, $[\alpha]_D^{20} = +84.2$ (*c* 0.5, MeOH).

4.2. General procedure for the dihydroxylation of (*S*)-(−)-1 and (*R*)-(+)-1

4-Methylmorpholine-*N*-oxide monohydrate 97% (0.668 g, 4.94 mmol) was dissolved in H_2O (4.19 mL, 0.23 mol) under argon atmosphere. The temperature of (*S*)-(−)-6-acetoxy-2-cyclohexen-1-one (*S*)-(−)-**1** (0.690 g, 4.46 mmol) was adjusted to −5 °C and dry acetone (9.9 g, 0.062 mol) was added. NMO was allowed to dissolve completely in water. Then, 14.07 mL OsO_4 (100 mg/40 mL) stock solution was added to the medium including (*S*)-(−)-6-acetoxy-2-cyclohexen-1-one (*S*)-(−)-**1** in acetone and the subsequent dissolved NMO solution was slowly added. The mixture was allowed to stir for 26 h at −5 °C by TLC monitoring. After the required conversion was obtained, $NaHSO_3$ (0.690 g, 6.64 mmol), florosil (4.29 g, 0.076 mol) and H_2O (8.37 g, 0.465 mol) were also added and allowed the resulting solution to stir for additional 12 h. The pH of the reaction mixture was adjusted to 2 by using 1 M HCl. The solution was diluted with an equal amount of ethyl acetate and the organic phase was dried over $MgSO_4$ and evaporated in vacuo. The product was purified by flash column chromatography (EtOAc/hexane, 1:3) and the corresponding diol **3** was obtained (0.630 g, 75% chemical yield).

By adjusting the same process to (*R*)-(+)-6-acetoxy-2-cyclohexen-1-one (*R*)-(+)-**1**, corresponding diol *ent*-**3** (0.175 g, 72% chemical yield) was obtained. The corresponding diols were subjected to acetylation. Compound **3** (0.630 g, 3.35 mmol), was mixed with (1.32 g, 13.4 mol) dry pyridine in CH_2Cl_2 (25 mL) under an inert atmosphere, at 0 °C for 1/2 h. Then, acetylchloride (0.79 g, 10.1 mol) was added and mixed for 16 h at room temperature. The organic phase was extracted with 0.1 M HCl (3 × 20 mL), $NaHCO_3$ (3 × 20 mL), brine (3 × 20 mL), respectively, then dried over $MgSO_4$, filtrated and evaporated. The crude product was separated by flash column chromatography using ethyl acetate/hexane (1:2) as the eluent to afford (1*R*,2*R*,4*S*)-3-oxocyclohexane-1,2,4-triyl triacetate (−)-**4** (0.780 g, 85%). (1*S*,2*S*,4*R*)-3-Oxocyclohexane-1,2,4-triyl triacetate (+)-**4** (0.205 g, 81%) was also obtained by applying the same procedure.

4.2.1. (1*S*,3*R*,4*R*)-3,4-Dihydroxy-2-oxocyclohexyl acetate 3. ^{1}H NMR ($CDCl_3$): δ 5.19 (dd, $J = 6.8$ and $J = 12.2$ Hz, 1H), 4.32 (br s, 1H), 4.23 (br s, 1H), 3.72 (br s, 1H), 2.60 (br s, 1H), 2.14–2.15 (m, 2H), 2.11 (s, 3H), 1.80–1.86 (m, 2H).

4.2.2. (1*R*,2*R*,4*S*)-3-Oxocyclohexane-1,2,4-triyl triacetate (−)-4. (0.780 g, 85% yield) as white crystals, mp: 104–106 °C; $[\alpha]_D^{20} = -7.25$ (*c* 0.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.65 (br s, 1H), 5.41 (d, $J = 3.3$ Hz, 1H), 5.34 (dd, $J = 4.9$ and $J = 6.8$ Hz, 1H), 2.17–2.24 (m, 2H), 2.19 (s, 3H), 2.16 (s, 3H), 2.10 (s, 3H), 1.91–2.16 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 195.8, 169.8, 160.5, 169.4, 75.4, 74.5, 72.3, 26.8, 25.0, 20.8, 20.5, 20.4.

4.2.3. (1*S*,2*S*,4*R*)-3-Oxocyclohexane-1,2,4-triyl triacetate (+)-4. (0.205 g, 81% yield) as white crystals; $[\alpha]_D^{20} = +6.75$ (*c* 0.02, $CHCl_3$).

4.3. General procedure for the reduction of (−)-4 and (+)-4

To a cooled solution, −78 °C of (1*R*,2*R*,4*S*)-3-oxocyclohexane-1,2,4-triyl triacetate (−)-**4** (0.109 g, 0.4 mmol) in

methanol (4.04 mL, 0.1 mol), $NaBH_4$ (0.016 g, 0.4 mmol) and $CeCl_3{\cdot}7H_2O$ (0.156 g, 0.4 mmol) were added and allowed to stir for 3 h. The reaction was quenched with H_2O (3 mL, 0.17 mol), and then diluted with the equal amount of Et_2O, washed with brine and dried over $MgSO_4$, filtrated and evaporated. The crude product was separated by flash column chromatography using ethyl acetate/hexane (1:2) to afford compound (1*R*,2*S*,3*S*,4*S*)-3-hydroxycyclohexane-1,2,4-triyl triacetate (−)-**5** in 82% chemical yield; $[\alpha]_D^{25} = -1.3$ (*c* 0.02, $CHCl_3$). Compound (+)-**5** was obtained in 80% chemical yield; $[\alpha]_D^{25} = +1.1$ (*c* 0.02, $CHCl_3$). Compound (−)-**5** (0.089 g, 0.3 mmol) was mixed with dry pyridine (0.048 g, 0.6 mmol) in 25 mL CH_2Cl_2 under inert atmosphere, at 0 °C for 1/2 h. Then, acetylchloride (0.036 g, 0.5 mol) was added and mixed for 5 h at room temperature. The organic phase was extracted with 0.1 M HCl (3×20 mL), $NaHCO_3$ (3×20 mL), brine (3×20 mL), respectively, dried over $MgSO_4$, filtrated and evaporated. The crude product was separated by flash column chromatography using ethyl acetate/hexane (1:2) as eluent to afford (1*R*,2*R*,3*S*,4*S*)-cyclohexane-1,2,3,4-tetrayl tetraacetate *meso*-**6** (0.088 g, 87%).

4.3.1. (1*R*,2*R*,3*S*,4*S*)-Cyclohexane-1,2,3,4-tetrayl tetraacetate *meso*-6. (0.088 g, 87% yield) as a yellowish liquid; $[\alpha]_D^{25} = 0$ (*c* 0.02, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.97 (br s, 2H), 5.22 (m, 2H), 2.08 (s, 6H), 2.07 (s, 6H), 1.65–1.78 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 169.9, 69.0, 68.4, 22.9, 20.9, 20.7.

4.4. X-ray structure analysis

For the crystal structure determination, a single crystal of compound $C_{12}H_{16}O_7$ (−)-**4** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer equipped with a two-dimensional area IP detector. The graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and oscillation scans technique with $\Delta\omega = 5°$ for one image were used for data collection. Image for (−)-**4** was taken successfully by varying ω with three sets of different χ and ϕ values. For each compounds the 108 images for six different runs covering about 99.8% of the Ewald spheres were performed. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear software.[15] The structures were solved by direct methods (SHELXS-97)[16] and non-H atoms were refined by full-matrix least-squares method with anisotropic temperature factors (SHELXL-97).[16]

4.5. Crystal data for compound (−)-4

$C_{12}H_{16}O_7$, crystal system, space group: orthorhombic, *Pcab*; (no: 61); unit cell dimensions: $a = 9.6841(8)$, $b = 12.3287(9)$, $c = 22.2173(9)$ Å, $\beta = 90°$; volume: 2652.58(2) Å^3; $Z = 8$; calculated density: 1.36 mg/m^3; absorption coefficient: 0.113 mm^{-1}; $F(000)$: 1152; crystal size: $0.025 \times 0.018 \times 0.014$ mm^3; θ range for data collection 2.8–30.6°; completeness to θ: 30.6°, 99.8%; refinement method: full-matrix least-square on F^2; data/restraints/parameters: 4048/0/179; goodness-of-fit on F^2: 1.557; final *R* indices [$I > 2\sigma(I)$]: $R_1 = 0.094$, $wR_2 = 0.120$; *R* indices (all data): R_1=0.113, $wR_2 = 0.135$; extinction coefficient: 0.0003; largest diff. peak and hole: 0.232 and −0.162 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structure of (−)-**4** in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 622254. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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