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Synthesis of enantiopure cyclitols from (±)-3-bromocyclohexene mediated by intramolecular oxyselenenylation employing (*S,S*)-hydrobenzoin and (*S*)-mandelic acid as chiral sources

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Abstract—Reaction of 3-bromocyclohexene with (*S,S*)-hydrobenzoin and (*S*)-mandelic acid and subsequent intramolecular oxyselenenylation of the resulting allylic ethers followed by oxidation–elimination afforded the valuable *cis*-fused bicyclic olefins, (1*S*,3*S*,4*S*,6*R*)-3,4-diphenylbicyclo[4,4,0]-2,5-dioxa-7-decene and (1*S*,3*S*,4*R*)-3-phenyl-4a,7,8,8a-tetrahydro-benzo[1,4]dioxan-2-one, respectively. Further stereoselective transformation of these *cis*-fused bicyclic olefins afforded the enantiopure cyclohexitols, *muco*-quercitol, D-*chiro*-inocitol and *allo*-inocitol.

1. Introduction

Cyclitols have recently attracted a great deal of attention due to their diverse biological activities and their versatilities as synthetic intermediates.[1] Polyhydroxy cyclohexanes, such as inositols and quercitols, and polyhydroxy cyclohexenes, such as conduritols, belong to a family of cyclitols (Fig. 1). These compounds can exist in a number of different stereoisomers; inositols, quercitols, and conduritols have 9, 16, and 6 possible stereoisomers, respectively. Among them, the inositols have been studied the most because of their important biological properties.[2] For example, D-*myo*-inositol 1,4,5-trisphosphate is a second messenger that controls many cellular processes by generating internal calcium signals.[3] Also, D-*chiro*-inositol is considered to be one of the significant constituents of putative insulin mediators.[4] Aminocyclohexitols and aminocyclopentitols, which are nitrogen analogs of cyclitols, have also been the focus of much attention in recent years mainly because of their glycosidase inhibitory activities.[5]

A great deal of effort has been devoted to the development of various methodologies for the synthesis of enantiopure cyclitols and their derivatives.[1a–d,6] Recently, the synthesis

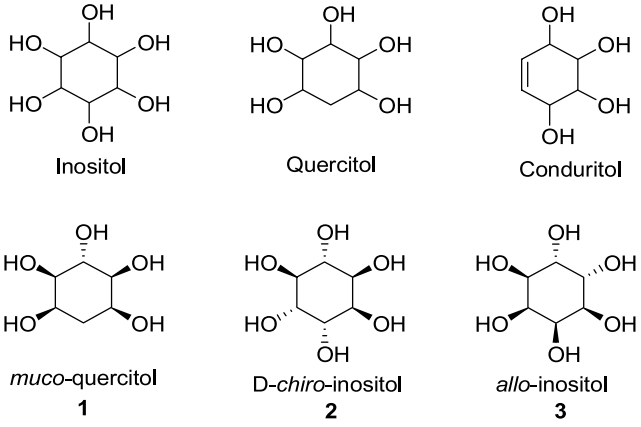

Figure 1.

of enantiopure cyclitols was achieved by transformation of other cyclitols by some groups.[7] The microbial oxidation of halobenzens was employed by Hudlicky et al. in the preparation of inositols.[8] The ring-closing metathesis (RCM) reaction has also been applied in the asymmetric synthesis of cyclitols using sugars,[9] tartrates,[10] and polyhydroxyl allylsilanes[11] as chiral building blocks. The Ferrier-II rearrangement[12] and the free radical cyclization[13] of sugar derivatives are other useful methods developed by Ikegami and Yadav et al., respectively. In addition, the reduction of arylsilanes in combination with the asymmetric dihydroxylation reported by Landais and co-workers

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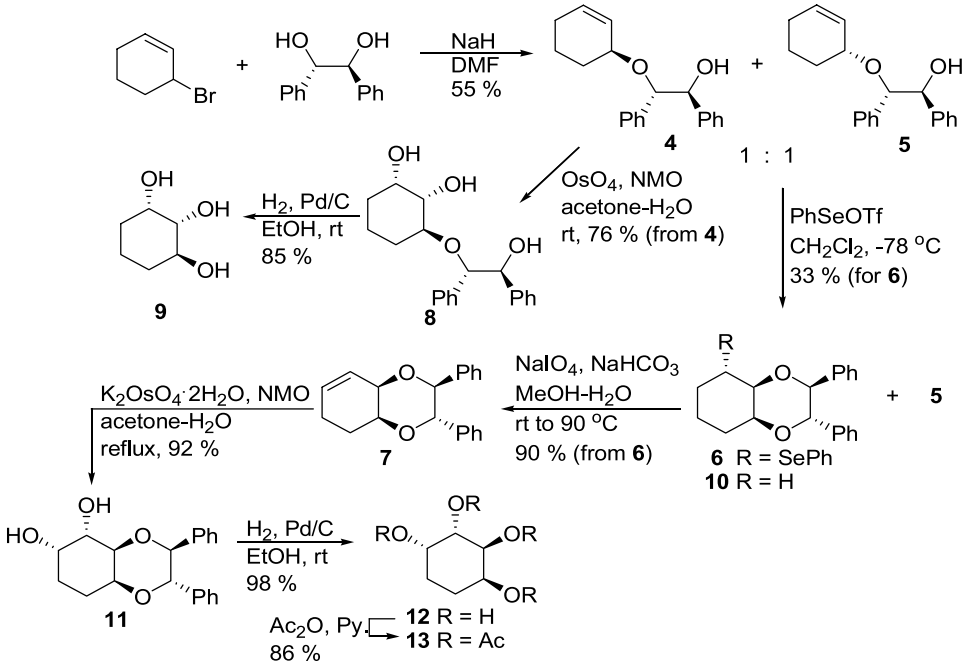
provides an easy access to cyclitols.[14] Even though there are a number of methods available for the asymmetric synthesis of cyclitols, they are generally target-specific and limited in applications. In this regard, there still remains a need for developing new methodologies that employ cheap and simple starting materials to accommodate structurally diverse cyclitol derivatives. Furthermore, it is highly desirable to develop a method that can also be applied to the synthesis of other functionalized cyclic compounds such as five-membered cyclopentitols and amino group-containing aminocyclitols. We have previously reported the preliminary work on the synthesis of enantiopure cyclitols from the cyclohexene mediated by sequential oxyselenenylation.[15] Herein we report the facile synthesis of biologically important cyclitols, *muco*-quercitol (**1**), D-*chiro*-inositol (**2**), and *allo*-inositol (**3**), from (±)-3-bromocyclohexene. The key reaction step features the application of (*S*,*S*)-hydrobenzoin and (*S*)-mandelic acid, as the source of oxygen atom and chirality in the stereoselective *cis*-diol formation of the cyclohexene ring system.

2. Results and discussion

Treating 3-bromocyclohexene with (*S*,*S*)-hydrobenzoin, which was pre-treated with sodium hydride, in DMF afforded an inseparable mixture of diastereomeric allylic ethers **4** and **5** in a ratio of 1 to 1 as shown in Scheme 1. Intramolecular oxyselenenylation of the mixture of **4** and **5** with PhSeOTf, which was generated in situ from PhSeBr and AgOTf in CH_2Cl_2, produced only a *cis*-fused bicyclic phenylselenenyl dioxane **6** in 33% yield, based on the mixture, along with the unreacted **5**. Both regiochemistry and stereochemistry were completely controlled in this intramolecular oxyselenenylation step. It is noteworthy to mention that the intermolecular oxyselenenylation of both cyclic[16] and acyclic[17] allylic alcohols usually provides 1,3-diol derivatives rather than 1,2-diol derivatives. Oxidation of selenide **6** with $NaIO_4$ in the presence of $NaHCO_3$, and subsequent *syn* elimination of the resulting selenoxide provided a valuable intermediate, bicyclic olefin **7**, in 90% yield. To better understand why the compound **5** is unreactive towards the cyclization under the oxyselenenylation condition, we have considered the transition state model for the intramolecular cyclization. The episelenonium ion, which would be the first intermediate that forms during the cyclization step, can possess either the conformation **5A** or **5B** (Fig. 2). The conformation **5B** is expected to be less favorable since there is a non-bonding interaction between one of the phenyl groups and the pseudoaxial hydrogen at the C-6 position. Thus, it is speculated that the conformation **5A** is the pre-dominant species under the given reaction conditions. In order for the conformation **5A** to achieve the *trans*-1,2-diaxial opening of the episelenonium ion, the hydroxyl group should attack the C-3 carbon leading to a seven-membered cyclic ring formation. Since it is unfavorable to form a seven-membered cyclic ring system, perhaps the cyclization of the allylic ester **5** does not occur under our intramolecular oxyselenation reaction conditions.

Absolute and relative stereochemistry at the newly generated stereocenters of the allylic ether **4** and the bicyclic olefin **7** was determined by their transformation to known compounds as shown in Scheme 1. Dihydroxylation of pure olefin **4** with OsO_4 and *N*-methylmorpholine *N*-oxide (NMO),[18] and subsequent hydrogenolysis of the resulting diol **8** afforded the triol **9**. The absolute configuration of **9** was assigned on the basis of its ^1H NMR spectrum and by comparing its specific rotation with the reported value of an authentic material.[19] Therefore, the configuration of allylic carbon of the compound **4** was assigned as *S*. Reduction of the selenide **6** with Bu_3SnH gave compound **10**. Dihydroxylation of the olefin **7** with NMO in the presence of a catalytic



Scheme 1.

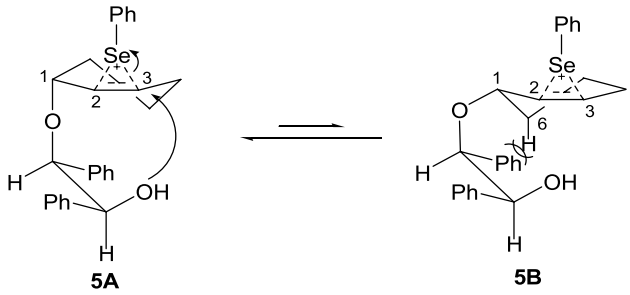


Figure 2.

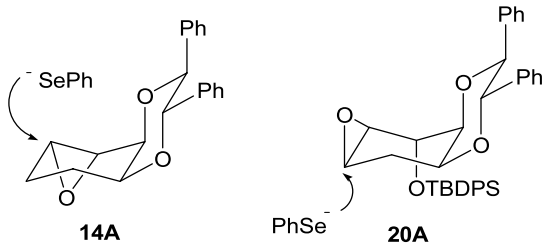
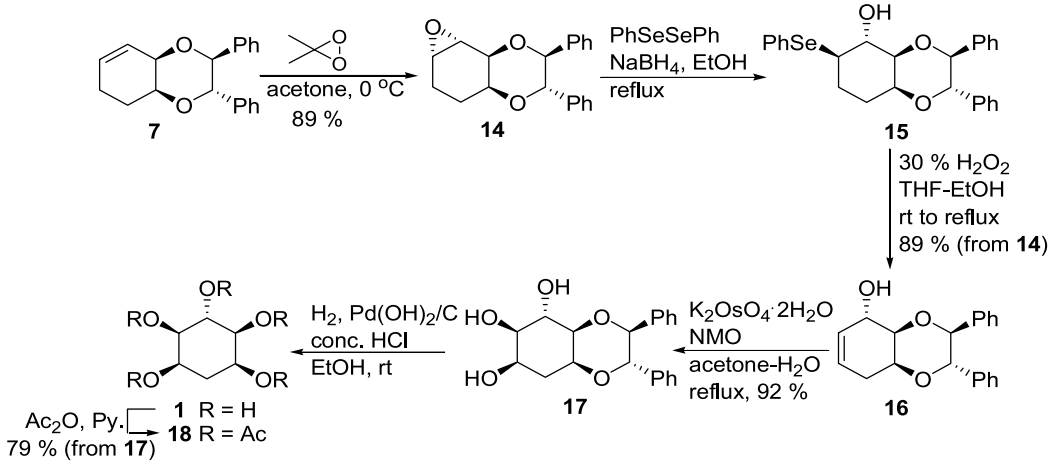


Figure 3.

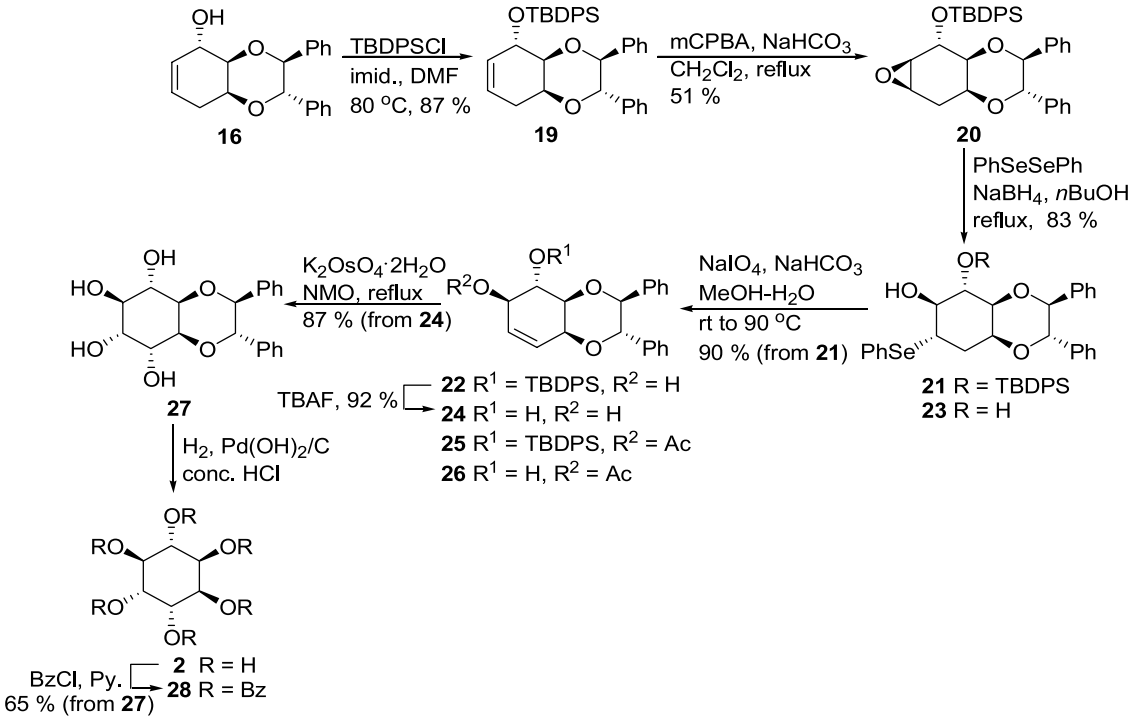
amount of $K_2OsO_4 \cdot 2H_2O$, and subsequent hydrogenolysis of the resulting diol **11** gave the tetrol **12**, which was converted to the tetraacetate **13** by acetylation. The relative stereochemistry of **7** was easily determined as *cis* by examining the ^{1}H NMR spectrum of **10** and by comparing the ^{1}H NMR of **13** with that of its known racemate.[20] Consequently, the configurations of the bicyclic olefin **7** at the C-1 and C-2 carbon centers were unambiguously determined to be *S* and *R*, respectively.

Epoxidation of **7** with dimethyldioxirane (DMDO) in acetone at 0 °C afforded the epoxide **14** in 89% yield, in which the major isomer has an epoxide ring *trans* to the dioxane ring, along with a small amount (ca. 5%) of the *cis* isomer (Scheme 2). On the other hand, treating **7** with MCPBA in methylene chloride gave the epoxide **14** with a lower stereoselectivity where a mixture of *trans* and *cis* isomers was obtained in a ratio of 7:3. Treating **14** with sodium benzeneselenoate, which was generated in situ from diphenyldiselenide (DPDS) and $NaBH_4$, gave the hydroxyselenide **15** in an excellent yield. Exclusive formation of **15** can be explained by the fact that the stable conformation of the bicyclic ring system **14** would be one (**14A**) with two bulky phenyl groups in the diequatorial position. The diaxial opening of the epoxide ring with PhSeNa should be regiospecific as shown in Figure 3. Oxidation of **15** with H_2O_2 followed by the elimination provided the allylic alcohol **16** in a high yield. Attempt to convert the epoxide **14** to the allylic alcohol **16** by employing the trialkysilyl triflate and the organic base[21] was not satisfactory. Dihydroxylation of **16** with NMO in the presence of a catalytic amount of $K_2OsO_4 \cdot 2H_2O$ occurred from the opposite face of the allylic hydroxyl group in **16** to afford exclusively the triol **17** in 92% yield. Hydrogenolysis of **17** with Pearlman's catalyst provided *muco*-quercitol (**1**), whose spectroscopic data and physical properties were identical with those of an authentic one. The structure of **1** was further confirmed by transforming it to the known pentaacetate **18**.[22]

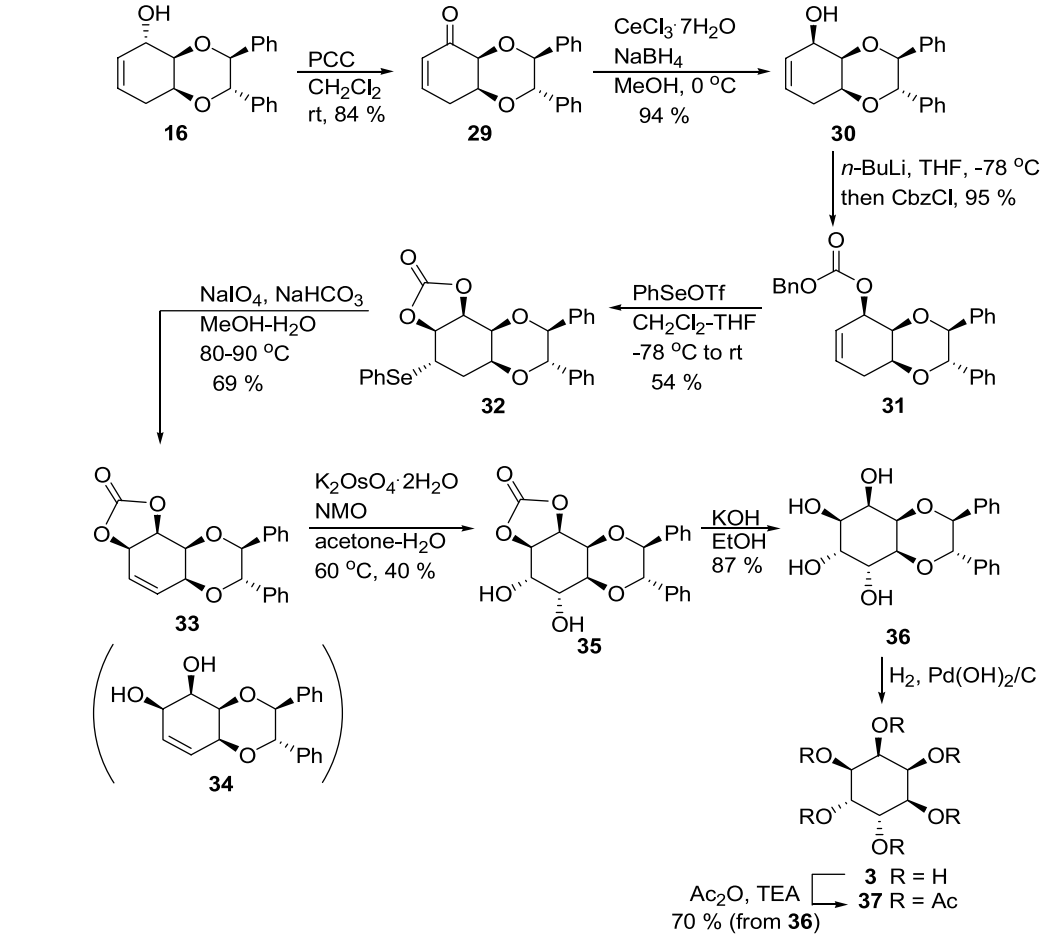
Protection of the hydroxyl group in **16** with sterically demanding *tert*-butyldiphenylsilyl (TBDPS) group and subsequent epoxidation of the resulting silyl ether **19** with MCPBA afforded the desired *trans*-epoxide **20** (*trans* to the OTBDPS group) along with *cis*-epoxide (*trans*/*cis*=3:2) in 85% yield (Scheme 3). However, epoxidation of **16**, its methyl ether, and benzyl ether with MCPBA gave the undesired *cis*-epoxide as the major product. Regiospecific diaxial opening of the epoxide ring **20**, of which stable conformation would be **20A** with two phenyl groups in the diequatorial position as shown in Figure 3, with sodium benzeneselenoate afforded the hydroxyselenide **21** in 83% yield as a mixture of two rotational isomers (3:2) about one of the single bonds in OTBDPS group. The mixture of two rotamers, **21a** and **21b**, was easily separated by flash column chromatography, and no isomerization was detected at room temperature. Oxidation of each rotamer of **21** with $NaIO_4$ followed by elimination of the resulting selenoxide also gave a stable and separable mixture of rotamers of the allylic alcohol **22** (**22a**/**22b**=3:2). One evidence for the rotational isomerism in compounds **21** and **22** can be acquired by removing the TBDPS group. Deprotection of each rotamer **21** (**21a** and **21b**) with tetrabutylammonium fluoride gave the identical diol **23** that did not show rotational isomerism. Similarly, the diol **24**, obtained from each rotamer of **22**, did not show rotational isomerism. It is,



Scheme 2.



Scheme 3.

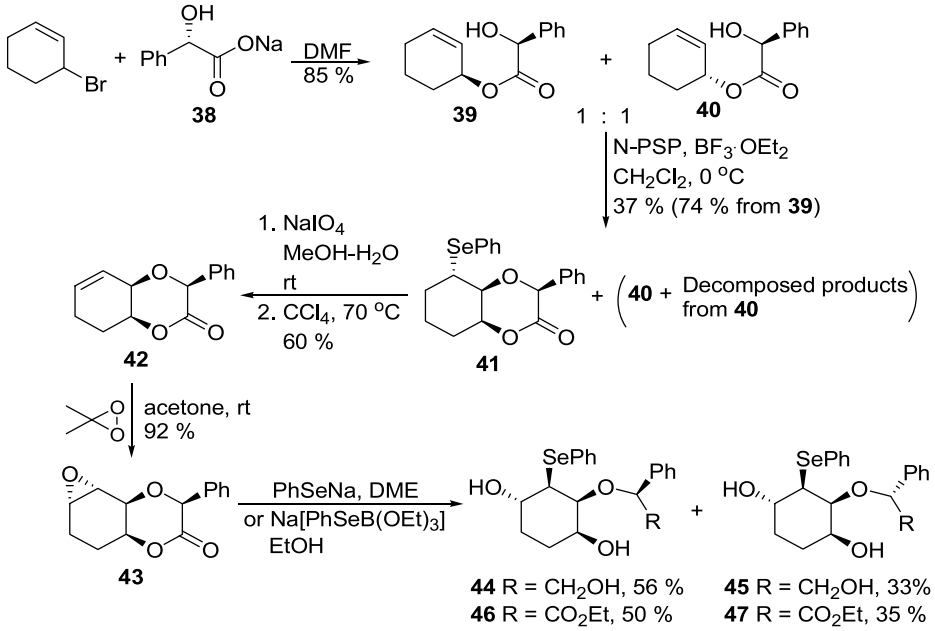


Scheme 4.

however, known that the TBDPS group can migrate among different hydroxyl groups resulting the formation of regioisomers.[23] In order to clarify whether that the isomers **22a** and **22b** are rotamers or regioisomers, the compound was acetylated to give **25** followed by desilyation. This reaction sequence provided **26** as a single compound indicating that the mixtures of compounds **21** and **22** were two rotational isomers. Dihydroxylation of **24** with $K_2OsO_4\cdot 2H_2O$ and NMO followed by hydrogenolysis of the resulting tetrol **27** with palladium hydroxide on carbon (Degussa type) in the presence of a trace amount of concentrated HCl gave D-*chiro*-inositol (**2**), of which physical properties are identical with those of authentic. Perbenzoate **28**[24] was prepared for further characterization of **2**.

Oxidation of the allylic alcohol **16** with pyridinium chlorochromate, and subsequent stereoselective reduction of the resulting ketone **29** with $NaBH_4$ in the presence of $CeCl_3$[25] provided the allylic alcohol **30** that has a hydroxyl group at the pseudoequatorial position (Scheme 4). The benzyl carbonate **31** was obtained in 95% yield by treating alkoxide of **30** with benzyl chloroformate. The Selenium (II) mediated cyclization of **31** was carried out with PhSeOTf in methylene chloride at −78 °C to afford the cyclic carbonate **32** in 54% yield. Upon oxidation with $NaIO_4$ in the presence of $NaHCO_3$ followed by elimination, the olefin **33** was obtained along with a small amount of the diol **34**, which was formed by hydrolysis of the cyclic carbonate group of **33**. Dihydroxylation of the olefin **33** with $K_2OsO_4\cdot 2H_2O$ and NMO followed by hydrolysis of the resulting dihydroxy carbonate **35** with KOH gave the tetrol **36**. Hydrogenolysis of **36** gave *allo*-inositol (**3**) which was converted to the known hexaacetate **37**.

The (*S*)-mandelic acid sodium salt was used to transform 3-bromocyclohexene in DMF to inseperable 1:1 mixture of diastereomeric allylic ethers **39** and **40** in 85% yield as shown in Scheme 5. Intramolecular oxyselenenylation of the mixture of **39** and **40** with *N*-(phenylseleno)phthalimide (*N*-PSP) in the presence of a catalytic amount of $BF_3\cdot OEt_2$ provided the bicyclic oxyselenide **41** (74% from **39**) and the unreacted **40** along with the decomposed by-products. A similar reasoning as that of **5** can be used to explain why the compound **40** is unreactive towards the oxyseleneylation condition (Fig. 2). Oxidation of the selenide **41** with $NaIO_4$ in methanol followed by elimination of the resulting selenoxide in carbon tetrachloride at 70 °C provided the olefin **42**. Epoxidation of the olefin **42** with dimethyldioxirane gave exclusively the epoxide **43**, in which the epoxide ring is *trans* to the dioxanone ring, in 92% yield. Ring opening of the epoxide **43** with PhSeNa afforded the hydroxyselenide **44** and its epimer **45**, both of which are undesired regioisomers. Attempts to synthesize desired hydroxyselenide by ring opening of the epoxide **43** using $Na[PhSeB(OEt)_3]$, PhSeSePh/Na, PhSeH/NaH, or PhSeH/$BF_3\cdot OEt_2$ were not successful. For example, reaction of **43** with $Na[PhSeB(OEt)_3]$ gave the undesired hydroxyselenide



Scheme 5.

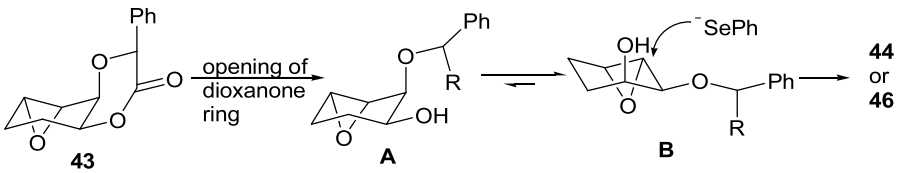
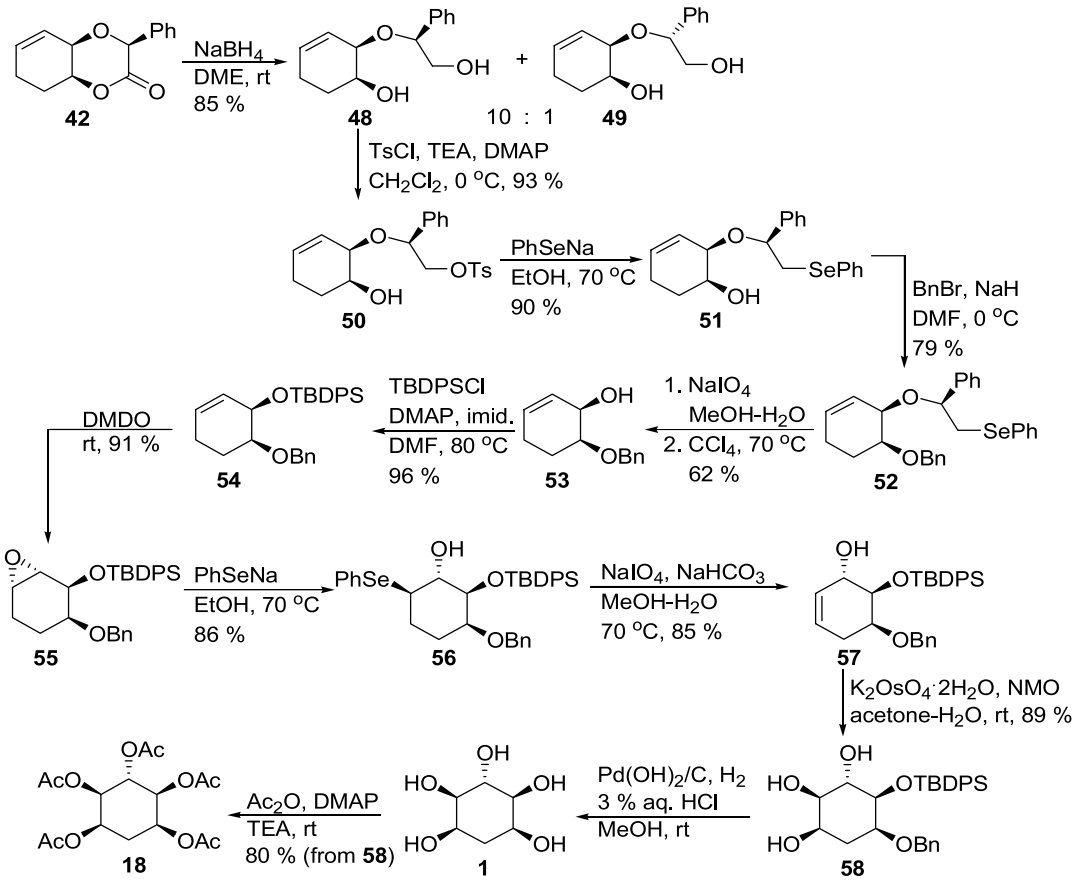


Figure 4.



Scheme 6.

46 and its epimer **47**. Formation of the undesired hydroxyselenides **44** and **46** can be explained by assuming that the dioxanone ring was opened prior to the diaxial opening of the epoxide by the $PhSe^-$ anion attack as shown in Figure 4. Once the lactone ring has been opened, the conformation **B** with the bulky benzylic ether group in the equatorial position is expected to be more stable than conformation **A** with that group in the axial position. Therefore, diaxial opening of the epoxide **B** with $PhSe^-$ would give the undesired hydroxyselenides **44** and **46**.

Before epoxidation of **42**, we decided to remove the dioxanone ring of **42**. It would be more desirable to produce a differentially protected cyclohexene diol than to make cyclohexene diol directly by nonselective cleavage of **42** by using Na/NH_3 or H_2-Pd/C. Treatment of **42** with $NaBH_4$ in DME provided diol **48** and a small amount of its epimer **49** (10:1) in 85% yield (Scheme 6). Tosylation of the primary hydroxyl group of **48** and subsequent displacement of the resulting tosylate **50** with PhSeNa provided the selenide **51** in high yield. Benzylation of the hydroxyl group of **51** and subsequent oxidation of the resulting benzyl-protected selenide **52** followed by elimination of the resulting selenoxide and a concomitant cleavage of enol ether afforded the allylic alcohol **53**. Protection of the hydroxyl group with bulky TBDPS group and subsequent epoxidation of the resulting allylic TBDPS ether **54** with dimethyldioxirane afforded exclusively the epoxide **55**, in which the epoxide ring is *trans* to the OTBDPS group. The ring opening reaction of the epoxide **55** with PhSeNa was completely regio- and stereoselective to provide exclusively the desired oxyselenide **56**. Regio- and stereoselectivity of this ring opening reaction of the epoxide **55** can be explained by assuming that the conformation **55A** with the OTBDPS group at the axial position is more favorable over the conformation **55B** with the OTBDPS group at the equatorial position (Fig. 5).[26] Oxidation of the selenide **56** with $NaIO_4$ in the presence of $NaHCO_3$ followed by elimination of the resulting selenoxide provided the allylic alcohol **57** in 85% yield. Dihydroxylation of the olefin **57** with $K_2OsO_4 \cdot 2H_2O$ and NMO occurred from the opposite face of the allylic hydroxyl group to afford exclusively the triol **58** in 89% yield. Hydrogenolysis of **58** with palladium hydroxide in the presence of aqueous 3% HCl directly gave *muco*-quercitol (**1**) in an excellent yield.[27] Further characterization of **1** was performed by its transformation to the known pentaacetate **18**.[22]

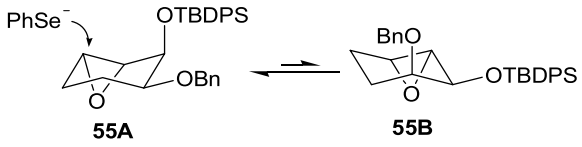


Figure 5.

3. Conclusion

We have synthesized *muco*-quercitol (**1**), D-*chiro*-inositol (**2**), and *allo*-inositol (**3**) from the (±)-3-bromocyclohexene

mediated by sequential oxyselenenylation. We also developed a novel method for the stereoselective construction of the *cis*-diol functionality into the cyclohexane ring from 3-bromocyclohexene, by employing (*S*,*S*)-hydrobenzoin and (*S*)-mandelic acid. Particularly, our methodology has shown that the use of 3-bromocyclohexene as the starting material is more convenient in the preparation of the versatile intermediate **6** than that of cyclohexene. In addition, we have found that the mixtures in **21** and **22** are rotational isomers resulting from introducing a bulky TBDPS group, not the regioisomers resulting from the migration of silyl group to the next hydroxyl group. On the synthetic route to *muco*-quercitol (**1**) from 3-bromohexene and (*S*)-mandelic acid, we have gained an easy access to the useful key intermediates such as differentially protected cyclohexene diol **53** and **57**, and demonstrated their versatility in the synthesis of enantiopure cyclohexitols. The usefulness of these compounds will be further demonstrated in the preparation of other important natural products.

4. Experimental

4.1. General

All reactions were conducted under a positive pressure of dry argon with dry, freshly distilled solvents unless otherwise noted. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Flash column chromatography was performed employing 230–400 mesh silica gel. Thin-layer chromatography was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Melting points are uncorrected. IR spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer. NMR spectra were recorded on a Bruker 250 NMR spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) unless otherwise noted. Optical rotations were measured with a Rudolph Autopol III automatic polarimeter.

4.1.1. (1*S*,2*S*,1′*S*)- and (1*S*,2*S*,1′*R*)-2-(Cyclohex-2′-enyloxy)-1,2-diphenylethanol (4 and 5). To a solution of (*S*,*S*)-hydrobenzoin (2.37 g, 0.01 mol) in DMF (60 mL) was added NaH (0.96 g, 0.2 mol). After stirring 5 min at rt, 3-bromocyclohexene (2.09 g, 0.02 mol) was added. The resulting solution was stirred further 1 h at rt, then quenched with H_2O and diluted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 7:1) to give a mixture (1.63 g, 55%) of **4** and **5**: R_f=0.31 (hexane/EtOAc, 7:1).

4.1.2. (1*S*,2*S*,3*S*)-3[(1*S*,2*S*)-2-Hydroxy-1,2-diphenylethoxy]-1,2-cyclohexanediol (8). To a solution of compound **4** (130 mg, 0.44 mmol) in acetone (8 mL) and H_2O (2 mL) were added NMO (63 mg, 0.54 mmol) and a catalytic amount of OsO_4 at rt. After stirring for 24 h at rt, the reaction mixture was quenched with $NaHSO_4$ (10 mg), and diluted with H_2O and EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 3:2) to give the title compound **8** (109 mg, 76%) as a white solid. R_f=0.23 (hexane/EtOAc, 1:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.13–1.26 (m, 1H), 1.31–1.53 (m, 3H), 1.71–1.77 (m, 1H), 1.95–1.99 (m, 1H), 2.67 (br s, 1H), 3.12 (br s, 1H), 3.45–3.52 (m, 2H), 3.72 (br s, 1H), 3.96–3.99 (m, 1H), 4.37 (d, J=7.8 Hz, 1H), 4.65 (d, J=7.8 Hz, 1H), 7.00–7.06 (m, 4H), 7.13–7.21 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.3, 27.9, 29.6, 69.2, 74.5, 76.1, 78.1, 83.9, 127.1, 127.7, 127.9, 128.2, 128.3, 138.1, 139.3. FAB HRMS calcd for $C_{20}H_{24}O_4Na$ $(M+Na)^+$: m/z 351.1572. Found: 351.1556.

4.1.3. [1*S*-(1α,2α,3β)]-Cyclohexanetriol (9). A solution of compound **8** (65 mg, 0.20 mmol) and Pd/C (78 mg, 5% Pd) in EtOH (3 mL) was vigorously stirred at 50–55 psi under H_2 gas. After stirring for 8 h at rt, the reaction mixture was passed through Celite pad and concentrated. The residue was purified by flash column chromatography (CH_2Cl_2/MeOH, 3:1) to give the title compound **9** (22 mg, 85%) as a white solid. R_f=0.15 (EtOAc only); mp 125–126 °C; $[\alpha]_D$=+70.2 (c 0.65, H_2O); ^{1}H NMR (250 MHz, D_2O) δ 1.22–1.37 (m, 1H), 1.43–1.66 (m, 3H), 1.71–1.79 (m, 1H), 1.82–1.89 (m, 1H), 3.38 (dd, J=3.0, 8.2 Hz, 1H), 3.70–3.79 (m, 1H), 3.97–4.02 (m, 1H); ^{13}C NMR (63 MHz, D_2O) δ 19.3, 31.1, 32.4, 71.0, 71.1, 76.9. Anal. calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.41; H, 9.21.

4.1.4. (1*S*,3*S*,4*S*,6*S*,7*R*)-3,4-Diphenyl-7-phenylselenobicyclo[4,4,0]-2,5-dioxadecane (6). To a solution of the mixture of compounds **4** and **5** (1.63 g, 5.5 mmol) and PhSeBr (1.61 g, 6.8 mmol) in CH_2Cl_2 (50 mL) at −78 °C was added a THF (5 mL) solution of AgOTf (1.88 g, 7.3 mmol). After stirring for 30 min at −78 °C, the reaction mixture was warmed to rt, then diluted with CH_2Cl_2 and neutralized with saturated $NaHCO_3$ solution. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 14:1) to give the title compound **6** (0.81 g, 33%) as a white solid. R_f=0.45 (hexane/EtOAc, 7:1); mp 174–177 °C; $[\alpha]_D$=−34.45 (c 0.43, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.81–1.92 (m, 3H), 2.16–2.27 (m, 1H), 2.43–2.56 (m, 1H), 3.78 (s, 3H), 4.27 (s, 1H), 4.39 (d, J=9.3 Hz, 1H), 4.71 (d, J=9.3 Hz, 1H), 6.98–7.00 (m, 4H), 7.15–7.18 (m, 6H), 7.26–7.28 (m, 3H), 7.56–7.59 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.4, 24.6, 26.6, 45.6, 70.4, 76.5, 76.7, 85.2, 127.6, 127.7, 127.9, 128.05, 128.11, 128.2, 129.4, 133.8, 137.9, 138.0; IR ($CHCl_3$, film) 1216, 1097 cm^{-1}. HRMS calcd for $C_{26}H_{26}O_2Se$ $(M)^+$: m/z 450.1098. Found: 450.1099.

4.1.5. (1*S*,3*S*,4*S*,6*R*)-3,4-Diphenylbicyclo[4,4,0]-2,5-dioxadecane (10). To a solution of compound **6** (90 mg, 0.20 mmol) in the presence of a catalytic amount of AIBN in benzene (3 mL) was slowly added (n-Bu)$_3$SnH (108 μL, 2 equiv). After the resulting solution was degassed by bubbling N_2 gas, it was heated to reflux for 3 h and was allowed to rt. The reaction mixture was concentrated to remove benzene. The residue was dissolved in 10% aqueous KF solution (5 mL) and ether (5 mL), then it was stirred for further 10 min at rt. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 10:1) to give the title compound **10** (56 mg, 95%) as a white

solid. R_f=0.38 (hexane/EtOAc, 9:1); ^{1}H NMR (250 MHz, DMSO-d_6) δ 1.18–2.07 (m, 7H), 2.48 (dq, J_d=12.7 Hz, J_q=3.7 Hz, 1H), 3.87 (m, 1H), 4.18 (d, J=2.0 Hz, 1H), 4.44 (d, J=9.3 Hz, 1H), 4.70 (d, J=9.3 Hz, 1H), 7.01–7.10 (m, 4H), 7.18–7.29 (m, 6H). HRMS calcd for $C_{20}H_{22}O_2$ $(M)^+$: m/z 294.1620. Found: 294.1691.

4.1.6. (1*S*,3*S*,4*S*,6*R*)-3,4-Diphenylbicyclo[4,4,0]-2,5-dioxa-7-decene (7). A solution of compound **6** (0.17 g, 0.38 mmol) and $NaIO_4$ (0.21 g, 0.96 mmol) in methanol (20 mL) and H_2O (3 mL) in the presence of $NaHCO_3$ (40 mg, 0.48 mmol) was stirred for 10 min at rt and for 48 h at 90 °C. After removal of methanol by evaporation, the concentrated solution was diluted with H_2O and EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified by flash column chromatography (hexane/EtOAc, 10:1) to give the title compound **7** (98 mg, 90%) as a white solid. R_f=0.42 (hexane/EtOAc, 7:1); mp 149–152 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.78–1.82 (m, 1H), 2.10–2.29 (m, 1H), 2.34–2.38 (m, 1H), 2.61–2.68 (m, 1H), 4.05 (dt, J_d=13.0 Hz, J_t=3.5 Hz, 1H), 4.38 (t, J=4.4 Hz, 1H), 4.48 (d, J=9.1 Hz, 1H), 4.75 (d, J=9.1 Hz, 1H), 5.84 (m, 1H), 6.00 (m, 1H), 7.02–7.05 (m, 4H), 7.12–7.25 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.5, 26.2, 70.5, 72.6, 77.2, 84.9, 125.1, 127.8, 128.1, 133.4, 138.0, 138.2. HRMS calcd for $C_{20}H_{20}O_2$ $(M)^+$: m/z 292.1463. Found: 292.1466.

4.1.7. (1*S*,3*S*,4*S*,6*S*,7*S*,8*S*)-3,4-Diphenylbicyclo[4,4,0]-2,5-dioxa-7,8-decanediol (11). To a solution of compound **7** (50 mg, 0.11 mmol) in acetone (4 mL) and H_2O (1 mL) were added NMO (32 mg, 0.27 mmol) and a catalytic amount of $K_2OsO_4\cdot 2H_2O$ at rt. After the resulting solution was heated to reflux for 20 h, it was allowed to rt and quenched with $NaHSO_4$ (10 mg). After stirring for further 10 min at rt, the reaction mixture was diluted with H_2O and EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified by flash column chromatography (hexane/EtOAc, 1:2) to give the title compound **11** (54 mg, 92%) as a white solid. R_f=0.20 (hexane/EtOAc, 1:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.73–1.87 (m, 3H), 2.42–2.54 (m, 1H), 2.63 (br s, 1H), 3.03 (br s, 1H), 3.98–4.04 (m, 2H), 4.17–4.22 (m, 2H), 4.38 (d, J=9.3 Hz, 1H), 4.68 (d, J=9.3 Hz, 1H), 6.95–7.01 (m, 4H), 7.14–7.22 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.9, 26.2, 68.6, 69.7, 72.2, 76.8, 77.0, 85.2, 127.6, 127.9, 128.11, 128.13, 128.2, 128.3, 137.7. FAB HRMS calcd for $C_{20}H_{22}O_4Na$ $(M+Na)^+$: m/z 349.1416. Found: 349.1436.

4.1.8. [1*S*-(1α,2α,3β,4β)]-Cyclohexanetetrol (12). Compound **11** (47 mg, 0.14 mmol) was subjected to the same reaction conditions as that for the preparation of **9** from **8**. The reaction mixture was purified by flash column chromatography (CH_2Cl_2/MeOH, 2:1) to give the title compound **12** (20 mg, 98%) as a white solid. R_f=0.45 (CH_2Cl_2/MeOH, 2:1); ^{1}H NMR (250 MHz, D_2O) δ 1.54–1.65 (m, 4H), 3.63 (br s, 2H), 3.87 (br s, 2H); ^{13}C NMR (63 MHz, D_2O) δ 25.7, 70.0, 72.4. Anal. calcd for $C_6H_{12}O_4$: C, 48.64; H, 8.16. Found: C, 48.44; H, 8.28.

4.1.9. (1*S*,3*S*,4*S*,6*R*,7*S*,8*S*)-3,4-Diphenylbicyclo[4,4,0]-2,5-dioxa-7,8-epoxydecane (14). A solution of compound **7** (98 mg, 0.34 mmol) and dimethyldioxirane (2 equiv, ca. 0.05 M) in acetone (20 mL) was stirred for 3 h at 0 °C. The reaction mixture was concentrated by removing acetone. The residue was purified by flash column chromatography (hexane/EtOAc, 10:1) to give the title compound **14** (94 mg, 89%) as a white solid. R_f=0.30 (hexane/EtOAc, 10:1); mp 153–155 °C; $[\alpha]_D$=−126.9 (c 0.11, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.56 (s, 1H), 2.04–2.25 (m, 1H), 2.50–2.52 (m, 1H), 2.54–2.57 (m, 1H), 3.28 (t, J=3.4 Hz, 1H), 3.35 (t, J=2.6 Hz, 1H), 4.00 (m, 1H), 4.46 (d, J=9.3 Hz, 1H), 4.58 (s, 1H), 4.69 (d, J=9.3 Hz, 1H), 7.00–7.06 (m, 4H), 7.16–7.22 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.8, 23.2, 52.4, 55.6, 69.7, 71.9, 76.8, 85.0, 127.7, 127.8, 128.2, 137.7, 137.8. Anal. calcd for $C_{20}H_{20}O_3$: C, 77.89; H, 6.53. Found: C, 77.78; H, 6.50.

4.1.10. (1*S*,3*S*,4*S*,6*R*,7*S*)-3,4-Diphenylbicyclo[4,4,0]-2,5-dioxa-8-decen-7-ol (16). To a solution of compound **14** (109 mg, 0.35 mmol) in EtOH (15 mL) was slowly added a solution of DPDS (66 mg, 0.21 mmol) and $NaBH_4$ (16 mg, 0.42 mmol) in EtOH (5 mL). After the resulting solution was heated to reflux for 4 h, it was allowed to rt. To this solution were added THF (10 mL) and 30% H_2O_2 (1 mL). The resulting solution was stirred at rt until TLC analysis showed no intermediate **15**, at which point it was heated to reflux for 6 h, then it was allowed to rt. The reaction mixture was diluted with EtOAc and neutralized with saturated $NaHCO_3$ solution. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 1:1) to give the title compound **16** (97 mg, 89%) as a white solid. R_f=0.43 (hexane/EtOAc, 1:1); mp 154–156 °C; $[\alpha]_D$=+3.0 (c 0.20, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.31–2.41 (m, 1H), 3.04 (t, J=10.1 Hz, 1H), 4.22–4.33 (m, 3H), 4.48 (d, J=9.4 Hz, 1H), 5.83 (d, J=1.1 Hz, 1H), 5.97 (s, 1H), 6.95–6.99 (m, 2H), 7.02–7.06 (m, 2H), 7.14–7.21 (m, 6H). Anal. calcd for $C_{20}H_{20}O_3$: C, 77.89; H, 6.53. Found: C, 77.55; H, 6.68.

4.1.11. (1*S*,3*S*,4*S*,6*R*,7*S*,8*R*,9*R*)-3,4-Diphenylbicyclo-[4,4,0]-2,5-dioxa-7,8,9-decan-triol (17). Compound **16** (84 mg, 0.27 mmol) was subjected to the same reaction conditions as that for the preparation of **11** from **7**. The reaction mixture was purified by flash column chromatography (hexane/EtOAc, 1:7) to give the title compound **17** (86 mg, 92%) as a white solid. R_f=0.38 (hexane/EtOAc, 1:7); mp 220–222 °C; $[\alpha]_D$=−50.5 (c 0.11, EtOH); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.16–1.24 (m, 1H), 1.64–1.68 (m, 1H), 3.70 (s, 1H), 3.94–4.00 (m, 2H), 4.70 (d, J=9.4 Hz, 1H), 4.78 (d, J=9.3 Hz, 1H), 7.08–7.10 (m, 4H), 7.12–7.22 (m, 6H). Anal. calcd for $C_{20}H_{22}O_5$: C, 70.15; H, 6.47. Found: C, 70.18; H, 6.69.

4.1.12. *muco*-Quercitol pentaacetate (18) from 17. To a solution of compound **17** (12 mg, 0.035 mmol) in EtOH (3 mL) were added a catalytic amount of $Pd(OH)_2$/C and 2 drops of conc. HCl. After stirring for 2 h at rt under H_2 (1 atm), the reaction mixture was passed through Celite pad, which was washed with EtOH several times. The filtrate was concentrated thoroughly under vacuum to give *muco*-Quercitol (**1**) as a white solid. Without any further purification, **1** was dissolved in pyridine (2 mL). To this solution was added Ac_2O (0.5 mL). After stirring for 12 h at rt, the reaction mixture was diluted with EtOAc. The

organic layer was washed with aqueous 1 N HCl solution several times, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 2:3) to give the title compound **18** (11 mg, 79%) as a white solid. R_f=0.43 (hexane/EtOAc, 2:3); mp 162–164 °C; $[\alpha]_D$=0 (*c* 0.8, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.85–1.94 (dt, J_d=15.8 Hz, J_t=3.4 Hz, 1H), 2.03 (s, 6H), 2.05 (s, 3H), 2.10 (s, 1H), 2.29–2.38 (dt, J_d=15.8 Hz, J_t=4.2 Hz, 1H), 4.97–5.02 (dd, *J*=9.4, 3.5 Hz, 2H), 5.34–5.38 (dt, J_d=3.7 Hz, J_t=3.6 Hz, 2H), 5.62–5.70 (t, *J*=9.4 Hz, 1H); IR ($CHCl_3$, film) 1749, 1242 cm^{-1}. Anal. calcd for $C_{16}H_{22}O_{10}$: C, 51.33; H, 5.92. Found: C, 51.36; H, 5.98.

4.1.13. (1*S*,3*S*,4*S*,6*S*,7*S*)-3,4-Diphenylbicyclo[4,4,0]-2,5-dioxa-7-*tert*-butyldiphenylsilyloxy-8-decene (19). A solution of compound **16** (66 mg, 0.21 mmol), TBDPSCl (115 mg, 0.42 mmol) and imidazole (29 mg, 0.42 mmol) in DMF (3 mL) was stirred for 14 h at 80 °C. The reaction mixture was allowed to rt, quenched with water and dilute with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 12:1) to give the title compound **19** (101 mg, 87%) as a white solid. R_f=0.68 (hexane/EtOAc, 4:1); $[\alpha]_D$=+1.78 (*c* 1.1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.10 (s, 9H), 2.31-2.41 (m, 1H), 3.04 (t, *J*=10.1 Hz, 1H), 4.13 (s, 1H), 4.26 (d, *J*=9.7 Hz, 2H), 4.43 (s, 1H), 4.66 (d, *J*=9.4 Hz, 1H), 5.52 (s, 1H), 5.83 (s, 1H), 6.90 (d, *J*=5.7 Hz, 2H), 7.02 (d, *J*=3.9 Hz, 2H), 7.13–7.20 (m, 6H), 7.35–7.43 (m, 5H), 7.67–7.72 (m, 5H). Anal. calcd for $C_{36}H_{38}O_3Si$: C, 79.08; H, 7.00. Found: C, 79.00; H, 7.01.

4.1.14. (1*S*,3*S*,4*S*,6*S*,7*S*,8*R*,9*R*)-3,4-Diphenylbicyclo-[4,4,0]-2,5-dioxa-7-*tert*-butyldiphenylsilyloxy-8,9-epoxy-decane (20). A solution of compound **19** (43 mg, 0.079 mmol), mCPBA (41 mg, 0.24 mmol) and $NaHCO_3$ (16 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) was heated to reflux for 20 h. The reaction mixture was allowed to rt, then diluted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/$CHCl_3$/EtOAc, 20:5:1) to give the title compound **20** (23 mg, 51%) and its diastereomer (14 mg, 32%) as a white solid, respectively. R_f=0.40 (hexane/$CHCl_3$/EtOAc, 20:5:1); $[\alpha]_D$=−22.3 (*c* 0.74, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.14 (s, 9H), 2.30 (m, 1H), 2.73 (t, *J*=12.9 Hz, 1H), 3.01 (t, *J*=1.7 Hz, 1H), 3.31 (t, *J*=4.4 Hz, 1H), 3.99 (s, 1H), 4.12 (d, *J*=9.3 Hz, 1H), 4.30–4.35 (m, 1H), 4.47 (s, 1H), 4.56 (d, *J*=9.3 Hz, 1H), 6.92–7.00 (m, 4H), 7.12–7.20 (m, 6H), 7.37–7.44 (m, 6H), 7.65–7.72 (m, 4H). FAB HRMS calcd for $C_{36}H_{38}O_4SiNa$ $(M+Na)^+$: *m*/*z* 585.2437. Found: 585.2442.

4.1.15. (1*S*,3*S*,4*S*,6*S*,7*S*,8*S*,9*S*)-3,4-Diphenylbicyclo-[4,4,0]-2,5-dioxa-7-*tert*-butyldiphenylsilyloxy-9-phenyl-selenodecan-8-ol (21). To a solution of compound **20** (25 mg, 0.044 mmol) in *n*-BuOH (3 mL) was slowly added a solution of DPDS (10 mg, 0.031 mmol) and $NaBH_4$ (2 mg, 0.062 mmol) in *n*-BuOH (3 mL). After the resulting solution was heated to reflux for 24 h, it was allowed to rt, quenched with water and diluted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 7:1) to give the title compound **21a** (16 mg, 50%) and **21b** (10 mg, 33%) as a white solid, respectively. Compound **21a**: R_f=0.44 (hexane/EtOAc, 7:1); $[\alpha]_D$=−48.2 (*c* 0.12, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.21 (s, 9H), 2.04 (s, 1H), 3.16 (td, J_t=9.4 Hz, J_d=3.7 Hz, 1H), 3.52 (d, *J*=9.5 Hz, 1H), 3.81 (d, *J*=3.0 Hz, 2H), 3.98 (d, *J*=9.5 Hz, 1H), 4.11 (d, *J*=2.1 Hz, 1H), 4.33 (d, *J*=9.5 Hz, 1H), 4.66 (d, *J*=9.5 Hz, 1H), 4.89 (dt, J_d=4.6 Hz, J_t=3.0 Hz, 1H), 6.81 (m, 2H), 6.92 (m, 2H), 7.12–7.18 (m, 6H), 7.25–7.29 (m, 4H), 7.40–7.48 (m, 6H), 7.65 (m, 2H), 7.72 (m, 2H), 7.81 (m, 1H). Anal. calcd for $C_{42}H_{44}O_4SiSe$: C, 70.07; H, 6.16. Found: C, 70.01; H, 6.52. Compound **21b**: R_f=0.28 (hexane/EtOAc, 7:1); $[\alpha]_D$=−21.3 (*c* 0.28, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.90 (d, *J*=12.8 Hz, 1H), 2.35 (d, *J*=6.0 Hz, 1H), 3.44 (td, J_t=8.7 Hz, J_d=3.9 Hz, 1H), 3.59 (s, 1H), 4.17 (d, *J*=1.7 Hz, 2H), 4.29 (s, 1H), 4.45 (d, *J*=9.2 Hz, 1H), 4.63–4.74 (m, 2H), 7.05–7.25 (m, 14H), 7.31–7.40 (m, 7H), 7.62–7.70 (m, 4H).

4.1.16. 23: Desilylation of silyl ether 21a and 21b. To a solution of compound **21a** (or **21b**) (20 mg, 0.028 mmol) in THF (3 mL) was added *n*-Bu_4NF (83 μL, 0.083 mmol, 1.0 M solution in THF). After stirring for 5 h at rt, the reaction mixture was quenched with water and diluted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to give the same compound **23** (12 mg, 90%) from **21a** and **21b** as a white solid. R_f=0.35 (hexane/EtOAc, 2:1); $[\alpha]_D$=+5.5 (*c* 0.3, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.95–1.99 (m, 1H), 2.86 (s, 1H), 3.38–3.42 (m, 2H), 3.66–3.71 (m, 1H), 3.83 (d, *J*=5.1 Hz, 1H), 4.19 (s, 2H), 4.65 (d, *J*=9.7 Hz, 1H), 4.71–4.75 (m, 1H), 4.86 (d, *J*=9.7 Hz, 1H), 6.96–6.99 (m, 4H), 7.17–7.22 (m, 6H), 7.30–7.33 (m, 3H), 7.58–7.62 (m, 2H). HRMS calcd for $C_{26}H_{26}O_4Se$ $(M)^+$: *m*/*z* 482.0996. Found: 482.0997.

4.1.17. (1*S*,3*S*,4*S*,6*S*,7*S*,8*R*)-3,4-Diphenylbicyclo[4,4,0]-2,5-dioxa-7-*tert*-butyldiphenylsilyloxy-decen-8-ol (22). Compound **21** (32 mg, 0.04 mmol) was subjected to the same reaction conditions as that for the preparation of **7** from **6**. The reaction mixture was purified by flash column chromatography (hexane/EtOAc, 5:1) to give the title compound **22a** (13 mg, 54%) and **22b** (9 mg, 36%) as a white solid, respectively. Compound **22a**: R_f=0.50 (hexane/EtOAc, 5:1); $[\alpha]_D$=−5.0 (*c* 0.08, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.08 (d, *J*=5.4 Hz, 9H), 2.96 (d, *J*=10.1 Hz, 1H), 3.88 (s, 1H), 4.11–4.33 (m, 3H), 4.72 (d, *J*=9.1 Hz, 1H), 4.89 (s, 1H), 5.98 (d, *J*=10.5 Hz, 1H), 6.23 (d, *J*=8.1 Hz, 1H), 6.89 (d, *J*=5.7 Hz, 2H), 7.00 (d, *J*=4.1 Hz, 2H), 7.15–7.18 (m, 6H), 7.39–7.45 (m, 5H), 7.63–7.68 (m, 5H). HRMS calcd for $C_{36}H_{38}O_4Si$ $(M)^+$: *m*/*z* 562.2539. Found: 562.2542. Compound **22b**: R_f=0.23 (hexane/EtOAc, 5:1); $[\alpha]_D$=+31.3 (*c* 0.14, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.12 (s, 9H), 4.02 (d, *J*=18.0 Hz, 2H), 4.24 (s, 1H), 4.48 (d, *J*=9.0 Hz, 1H), 4.57 (s, 1H), 4.63 (d, *J*=9.0 Hz, 1H), 5.85 (d, *J*=9.6 Hz, 1H), 5.94 (d, *J*=9.5 Hz, 1H), 7.04–7.10 (m, 6H), 7.18–7.25 (m, 6H), 7.42–7.45 (m, 4H), 7.72–7.76 (m, 4H).

4.1.18. 25a: Acetylation of allylic alcohol 22a. To a solution of compound **22a** (10 mg) in pyridine (2 mL) was

added Ac_2O (0.5 mL). After stirring for 2 h, the reaction mixture was quenched with water and diluted with EtOAc. The organic layer was washed with aqueous 1 N HCl several times, dried over $MgSO_4$ and concentrated to give **25a** (11 mg). R_f=0.51 (hexane/EtOAc, 5:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.10 s, 9H), 1.98 (s, 3H), 4.16–4.17 (m, 1H), 4.21–4.22 (m, 1H), 4.33 (d, J=8.9 Hz, 1H), 4.50 (d, J=8.9 Hz, 1H), 4.83 (d, J=3.4 Hz, 1H), 5.14 (s, 1H), 6.09 (s, 2H), 7.37–7.70 (m, 20H). FAB HRMS calcd for $C_{38}H_{40}O_5SiNa$ $(M+Na)^+$: m/z 627.2543. Found: 627.2522.

4.1.19. 25b: Acetylation of allylic alcohol 22b. R_f=0.41 (hexane/EtOAc, 5:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.91 (s, 3H), 4.01 (s, 1H), 4.29 (s, 1H), 4.48–4.50 (m, 2H), 4.62 (d, J=4.5 Hz, 1H), 5.23 (br s, 1H), 5.86 (d, J=5.3 Hz, 1H), 5.92 (d, J=5.3 Hz, 1H), 7.02–7.78 (m, 20H). FAB HRMS calcd for $C_{38}H_{40}O_5SiNa$ $(M+Na)^+$: m/z 627.2543. Found: 627.2525.

4.1.20. 26: Desilylation of silyl ether 25a and 25b. Compound **25a** (or **25b**) (4 mg) was subjected to the same reaction conditions as that for the preparation of **23** from **21a** and **21b** to give the same compound **26** (2 mg). R_f=0.1 (hexane/EtOAc, 5:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.13 (s, 3H), 3.34 (br s, 1H), 4.17–4.21 (m, 1H), 4.30–4.33 (m, 1H), 4.47 (d, J=8.9 Hz, 1H), 4.55 (d, J=8.9 Hz, 1H), 4.72 (d, J=3.4 Hz, 1H), 5.13 (br s, 1H), 6.06–6.10 (m, 2H), 6.99–7.22 (m, 10H). FAB HRMS calcd for $C_{22}H_{22}O_5Na$ $(M+Na)^+$: m/z 389.1365. Found: 389.1381.

4.1.21. (1*S*,3*S*,4*S*,6*R*,7*S*,8*R*)-3,4-Diphenylbicyclo[4,4,0]-2,5-dioxa-9-decen-7,8-diol (24). To a solution of compound **22** (12 mg, 0.02 mmol) in THF (3 mL) was added *n*-Bu_4NF (64 μL, 0.064 mmol, 1.0 M solution in THF). After stirring for 5 h at rt, the reaction mixture was quenched with water and diluted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 1:1) to give the title compound **24** (6 mg, 92%) as a white solid. R_f=0.40 (hexane/EtOAc, 1:1); $[\alpha]_D$=+23.0 (c 0.1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.90 (s, 1H), 3.12 (d, J=11.6 Hz, 1H), 3.98 (d, J=10.0 Hz, 1H), 4.32 (s, 1H), 4.43 (d, J=9.1 Hz, 1H), 4.74 (d, J=9.2 Hz, 2H), 5.96 (d, J=10.4 Hz, 1H), 6.24–6.27 (m, 1H), 6.94–7.03 (m, 4H), 7.15–7.23 (m, 6H). HRMS calcd for $C_{20}H_{20}O_4$ $(M)^+$: m/z 324.1361. Found: 324.1359.

4.1.22. (1*S*,3*S*,4*S*,6*R*,7*S*,8*S*,9*R*,10*R*)-3,4-Diphenylbicyclo-[4,4,0]-2,5-dioxadecan-7,8,9,10-tetrol (27). Compound **24** (24 mg, 0.074 mmol) was subjected to the same reaction conditions as that for the preparation of **17** from **16**. The reaction mixture was purified by flash column chromatography (EtOAc only) to give the title compound **27** (22 mg, 87%) as a white solid. R_f=0.28 (EtOAc); $[\alpha]_D$=−68.1 (c 0.32, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.31 (s, 1H), 3.54 (s, 1H), 3.98 (d, J=13.9 Hz, 2H), 4.08–4.16 (m, 2H), 4.29–4.47 (m, 4H), 4.78 (d, J=9.4 Hz, 2H), 6.89 (d, J=6.1 Hz, 2H), 7.01 (d, J=6.4 Hz, 2H), 7.16–7.23 (m, 6H). Anal. calcd for $C_{20}H_{22}O_6$: C, 67.02; H, 6.18. Found: C, 67.00; H, 6.27.

4.1.23. D-*chiro*-Inocitol hexabenzoate (28). To a solution of compound **27** (11 mg, 0.031 mmol) in EtOH (3 mL) were added a catalytic amount of $Pd(OH)_2$/C and 2 drops of conc. HCl. After stirring for 2 h at rt under H_2 (1 atm), the reaction mixture was passed through Celite pad, which was washed with EtOH several times. The filtrate was concentrated thoroughly under vacuum to give *chiro*-Inocitol (**2**) as a white solid. Without any further purification, **2** was dissolved in pyridine (2 mL). To this solution was added BzCl (0.5 mL). After stirring for 12 h at rt, the reaction mixture was diluted with EtOAc. The organic layer was washed with aqueous 1 N HCl solution several times, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to give the title compound **28** (16 mg, 65%) as a white solid. R_f=0.30 (hexane/EtOAc, 2:1); $[\alpha]_D$=+69.9 (c 0.30, $ClCH_2$-CH_2Cl); ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.03–6.08 (m, 2H), 6.09–6.14 (m, 2H), 6.29–6.34 (m, 2H), 7.27–7.34 (m, 8H), 7.42–7.49 (m, 4H), 7.56 (t, J=7.5 Hz, 4H), 7.67 (t, J=7.4 Hz, 2H), 7.83–7.92 (m, 8H), 8.16 (d, J=7.2 Hz, 4H). Anal. calcd for $C_{48}H_{36}O_{12}$: C, 71.63; H, 4.50. Found: C, 71.61; H, 4.56.

4.1.24. (1*S*,3*S*,4*S*,6*R*)-3,4-Diphenylbicyclo[4,4,0]-2,5-dioxa-8-decen-7-one (29). To a solution of compound **16** (20 mg, 0.065 mmol) in CH_2Cl_2 (10 mL) was added PCC (43 mg, 0.20 mmol). After stirring for 3 h at rt, the reaction mixture was diluted with H_2O and CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 7:1) to give the title compound **29** (17 mg, 84%) as a white solid. R_f=0.3 (hexane/EtOAc, 3:1); mp 191–192 °C; $[\alpha]_D$=−134.7 (c 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.57–2.66 (m, 1H), 3.35–3.46 (m, 1H), 4.43–4.46 (m, 2H), 4.52 (d, J=9.3 Hz, 1H), 4.81 (d, J=9.3 Hz, 1H), 6.21 (d, J=9.9 Hz, 1H), 6.97–7.05 (m, 4H), 7.16–7.26 (m, 7H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.4, 71.0, 77.4, 78.0, 84.1, 127.7, 127.9, 128.1, 128.2, 128.4, 128.5, 129.2, 137.0, 149.2, 194.0; IR ($CHCl_3$, film) 1679 cm^{-1}. Anal. calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.38; H, 5.85.

4.1.25. (1*S*,3*S*,4*S*,6*R*,7*R*)-3,4-Diphenylbicyclo[4,4,0]-2,5-dioxa-8-decen-7-ol (30). To a solution of compound **29** (16 mg, 0.053 mmol) and $CeCl_3 \cdot 7H_2O$ (24 mg, 0.064 mmol) in MeOH (5 mL) at 0 °C was added $NaBH_4$ (3.0 mg, 0.074 mmol). After stirring for 10 min at 0 °C, the reaction mixture was diluted with H_2O and EtOAc. The organic layer was separated, passed through Celite pad, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 5:1) to give the title compound **30** (15 mg, 94%) as a white solid. R_f=0.27 (hexane/EtOAc, 3:1); mp 105–106 °C; $[\alpha]_D$=−85.5 (c 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.28–2.39 (m, 1H), 2.72 (s, 1H), 2.96–3.08 (m, 1H), 4.22–4.30 (m, 1H), 4.36 (d, J=4.5 Hz, 1H), 4.48 (s, 1H), 4.49 (d, J=9.4 Hz, 1H), 4.76 (d, J=9.4 Hz, 1H), 5.68 (d, J=10.3 Hz, 1H), 5.78–5.85 (m, 1H), 6.96–7.06 (m, 4H), 7.19–7.26 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 23.5, 67.5, 70.0, 74.9, 76.6, 85.4, 124.9, 127.7, 128.0, 128.1, 128.26, 128.31, 128.6, 137.4, 137.6; IR ($CHCl_3$, film) 3551, 3428, 3059, 2920, 2879 cm^{-1}. Anal. calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.87; H, 6.60.

4.1.26. Carbonic acid benzyl ester 2,3-diphenyl-2,3,4a,5,8,8a-hexahydro-benzo[1,4]dioxin-5-yl ester (31). To a solution of compound **30** (15 mg, 0.050 mmol) in THF (4 mL) at −78 °C was added *n*-BuLi (31 μL, 0.050 mmol, 1.6 M in hexanes). After stirring for 10 min at −78 °C, CbzCl (26 mg, 0.15 mmol) was added. The resulting solution was stirred for 10 min at −78 °C, then quenched with water and diluted with CH_2Cl_2. The organic layer was separated, passed through Celite pad, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 10:1) to give the title compound **31** (21 mg, 95%). R_f=0.29 (hexane/EtOAc, 7:1); $[\alpha]_D$=−8.9 (*c* 1.05, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.33–2.40 (m, 1H), 3.06–3.16 (m, 1H), 4.24–4.30 (m, 1H), 4.46 (d, *J*=9.4 Hz, 1H), 4.64 (s, 1H), 4.71 (d, *J*=9.4 Hz, 1H), 5.13 (s, 2H), 5.44 (s, 1H), 5.65 (d, *J*=10.2 Hz, 1H), 5.93–5.99 (m, 1H), 6.93–7.05 (m, 4H), 7.12–7.25 (m, 11H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 23.8, 69.4, 69.7, 72.8, 73.7, 76.8, 84.9, 123.5, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.6, 135.3, 137.5, 137.7, 154.8; IR ($CHCl_3$, film) 3029, 2921, 1735, 1252 cm^{-1}. Anal. calcd for $C_{28}H_{26}O_5$: C, 76.00; H, 5.92. Found: C, 75.92; H, 5.98.

4.1.27. 7,8-Diphenyl-4-phenylselenyl-octahydro-1,3,6,9-tetraoxa-cyclopenta[a]naphthalene-2-one (32). To a solution of PhSeBr (24 mg, 0.10 mmol) in CH_2Cl_2 (5 mL) at −78 °C was added a THF (1.5 mL) solution of AgOTf (31 mg, 0.12 mmol). To this solution was added the compound **31** (24 mg, 0.054 mmol). After stirring for 20 min at −78 °C, the reaction mixture was warmed to rt, diluted with CH_2Cl_2 and neutralized with saturated $NaHCO_3$ solution. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 7:1) to give the title compound **32** (15 mg, 54%). R_f=0.3 (hexane/EtOAc, 3:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.05–2.14 (m, 1H), 3.03–3.21 (m, 1H), 4.18–4.27 (m, 2H), 4.42–4.57 (m, 3H), 4.73–4.77 (m, 1H), 4.96–5.02 (m, 1H), 6.81–6.82 (m, 2H), 6.84–6.97 (m, 2H), 7.11–7.26 (m, 7H), 7.34–7.39 (m, 3H), 7.62–7.63 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 37.7, 68.0, 72.0, 74.0, 77.37, 77.44, 85.0, 126.9, 127.1, 127.9, 128.1, 128.3, 128.7, 129.2, 129.3, 129.9, 134.8, 135.4, 136.4, 136.9, 154.3; IR ($CHCl_3$, film) 1807, 1740, 1591 cm^{-1}.

4.1.28. 7,8-Diphenyl-3a,5a,7,8,9a,9b-hexahydro-1,3,6,9-tetraoxa-cyclopenta[a]naphthalene-2-one (33). Compound **32** (15 mg, 0.030 mmol) was subjected to the same reaction conditions as that for the preparation of **7** from **6**. The reaction mixture was purified by flash column chromatography (hexane/EtOAc, 3:1) to give the title compound **33** (7 mg, 69%) as a white solid. R_f=0.65 (hexane/EtOAc, 1:4); mp 237–238 °C; $[\alpha]_D$=89.9 (*c* 0.15, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.50 (d, *J*=2.1 Hz, 1H), 4.54–4.61 (m, 3H), 4.89 (dd, *J*=3.3, 3.2 Hz, 1H), 5.05–5.08 (m, 1H), 6.25 (d, *J*=10.4 Hz, 1H), 6.34–6.40 (m, 1H), 6.81–6.84 (m, 2H), 6.98–7.01 (m, 2H), 7.06–7.26 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 68.8, 69.4, 70.7, 73.5, 78.9, 83.8, 123.8, 127.3, 127.8, 127.9, 128.1, 128.2, 128.6, 134.9, 136.5, 136.9, 154.6; IR ($CHCl_3$, film) 1802, 1642, 1350, 1144, 1088, 1047 cm^{-1}. HRMS calcd for $C_{21}H_{18}O_5$ $(M)^+$: *m*/*z* 350.1154. Found: 350.1155.

4.1.29. 4,5-Dihydroxy-7,8-diphenyl-octahydro-1,3,6,9-tetraoxa-cyclopenta[a]naphthalene-2-one (35). To a solution of compound **33** (20 mg, 0.057 mmol) in acetone (4 mL) and H_2O (1 mL) were added NMO (66 mg, 0.57 mmol) and $K_2OsO_4\cdot 2H_2O$ (10 mg, 0.02 mmol) at rt. After the resulting solution was stirred for 48 h at 60 °C, it was allowed to rt and quenched with $NaHSO_4$ (10 mg). After stirring for further 10 min at rt, it was diluted with H_2O and EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 1:4) to give the title compound **35** (9 mg, 40%) as a white solid. R_f=0.35 (hexane/EtOAc, 1:4); mp 83–90 °C (decom.); $[\alpha]_D$=−16.5 (*c* 0.35, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.78–2.94 (m, 2H), 4.13 (s, 1H), 4.50–4.62 (m, 4H), 4.85 (s, 2H), 4.99 (s, 1H), 6.78–6.82 (m, 2H), 7.01–7.02 (m, 2H), 7.17–7.26 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 68.2, 70.1, 71.9, 72.5, 73.9, 77.9, 78.9, 84.8, 127.1, 127.9, 128.2, 128.3, 128.9, 136.1, 136.5, 154.1; IR ($CHCl_3$, film) 3425, 2922, 2357, 1802 cm^{-1}.

4.1.30. 2,3-Diphenyl-octahydro-benzo[1,4]dioxine-5,6,7,8-tetrol (36). To a solution of compound **35** (9 mg, 0.023 mmol) in EtOH (2 mL) was added KOH (3 mg, 0.046 mmol) at rt, and the resulting solution was heated to 60 °C. After stirring 4 h at 60 °C, the reaction mixture was allowed to rt, neutralized with 3 drops of aqueous 1 N HCl solution and diluted with H_2O and EtOAc. The organic layer was separated, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 1:4) to give the title compound **36** (7 mg, 87%) as a white solid. R_f=0.65 (CHCl3/MeOH, 2:1); mp 80–85 °C (decom.); $[\alpha]_D$=−9.7 (*c* 0.35, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.48 (s, 2H), 2.77 (d, *J*=4.8 Hz, 1H), 2.94 (d, *J*=3.8 Hz, 1H), 4.10–4.12 (m, 1H), 4.17–4.18 (m, 2H), 4.41–4.43 (m, 2H), 4.50 (s, 1H), 4.82 (d, *J*=4.7 Hz, 1H), 4.90 (d, *J*=4.7 Hz, 1H), 6.92–6.94 (m, 2H), 7.03–7.04 (m, 2H), 7.21–7.26 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 63.4, 66.9, 72.2, 73.1, 73.4, 76.8, 77.9, 85.8, 127.6, 127.9, 128.3, 128.5, 128.7, 128.8, 136.65, 136.70; IR ($CHCl_3$, film) 3368 cm^{-1}. Anal. calcd for $C_{28}H_{26}O_5$: C, 76.00; H, 5.92. Found: C, 75.92; H, 5.98.

4.1.31. *allo*-Inositol hexaacetate (37). To a solution of compound **36** (7 mg, 0.02 mmol) in EtOH (2 mL) were added a catalytic amount of $Pd(OH)_2$/C. After stirring for 1 h at rt under H_2 (1 atm), the reaction mixture was passed through Celite pad, which was washed with EtOH several times. The filtrate was concentrated thoroughly under vacuum to give *allo*-Inositol (**3**) as a white solid. Without any further purification, **3** was dissolved in TEA (1 mL). To this solution were added Ac_2O (0.5 mL) and a catalytic amount of DMAP. After stirring for 3 h at rt, the reaction mixture was diluted with EtOAc. The organic layer was washed with saturated NH_4Cl solution several times, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to give the title compound **37** (6 mg, 70%) as a white solid. R_f= 0.35 (hexane/EtOAc, 1:1); $[\alpha]_D$=0 (*c* 0.35, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.07 (br s, 18H), 5.33 (m, 2H), 5.46 (m, 4H). Anal. calcd for $C_{18}H_{24}O_{12}$: C, 50.00; H, 5.59. Found: C, 50.12; H, 5.51.

4.1.32. (1*S*,1′*S*)- and (1*S*,1′*R*)-Cyclohex-2′-enyl hydroxyphenylacetate (39 and 40). To a solution of (+)-mandelic acid (2.0 g, 13.1 mmol) in DMF (60 mL) was added NaH (60%, 0.58 g, 14.5 mmol). After stirring 1 h at rt, 3-bromocyclohexene (2.32 g, 14.4 mmol) was added. The resulting solution was stirred further 8 h at rt, and diluted with EtOAc. The organic layer was washed with saturated NH_4Cl solution, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 7:1) to give a mixture (2.59 g, 85%) of **39** and **40** as a yellow oil. R_f=0.25 (hexane/EtOAc, 7:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.50–2.01 (m, 6H), 3.59–3.64 (t, J=6.3 Hz, 1H), 5.13–5.16 (d, J=6.1 Hz, 1H), 5.29–5.31 (m, 1H), 5.47–5.75 (m, 1H), 5.83–6.00 (m, 1H), 7.28–7.44 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.4, 18.8, 24.80, 24.83, 27.9, 28.2, 70.0, 70.5, 72.97, 73.00, 124.68, 124.71, 126.48, 126.51, 128.3, 128.5, 133.4, 133.8, 138.6, 138.7, 173.4, 173.5; IR ($CHCl_3$, film) 3460, 1730, 1453, 1183, 1098, 1065, 1006, 907, 736 cm^{-1}. Anal. calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.43; H, 6.84.

4.1.33. (1*S*,3*S*,4*S*,5*S*)-3-Phenyl-5-phenylselenyl-hexahydro-benzo[1,4]dioxin-2-one (41). To a solution of the mixture of **39** and **40** (0.53 g, 2.3 mmol) and NPSP (0.82 g, 2.7 mmol) in CH_2Cl_2 (20 mL) was slowly added $BF_3\cdot OEt_2$ (34 μL, 0.27 mmol) at 0 °C. The resulting solution was stirred for 20 min at 0 °C, diluted with CH_2Cl_2 and neutralized with saturated $NaHCO_3$ solution. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 7:1) to give the title compound **41** (0.33 g, 37%) as a yellow oil. R_f=0.25 (hexane/EtOAc, 7:1); $[\alpha]_D$=+3.0 (*c* 2.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.48–1.77 (m, 4H), 1.84–1.95 (m, 1H), 2.09–2.16 (m, 1H), 3.55–3.58 (m, 1H), 4.26–4.31 (m, 1H), 4.37–4.42 (dd, J=8.2, 2.7 Hz, 1H), 5.46 (s, 1H), 7.23–7.64 (m, 10H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 20.6, 27.9, 30.4, 43.3, 67.0, 75.3, 80.8, 127.0, 127.2, 128.4, 128.6, 128.8, 129.2, 135.8, 136.0, 167.0; IR ($CHCl_3$, film) 1743, 1223, 1065 cm^{-1}. Anal. calcd for $C_{20}H_{20}O_3Se$: C, 62.02; H, 5.20. Found: C, 62.04; H, 5.39.

4.1.34. (1*S*,3*S*,4*R*)-3-Phenyl-4a,7,8,8a-tetrahydro-benzo[1,4]dioxan-2-one (42). To a solution of compound **41** (1.40 g, 3.60 mmol) in MeOH (60 mL) and H_2O (10 mL) at rt was added $NaIO_4$ (1.86 g, 8.70 mmol). The resulting solution was stirred at rt until TLC analysis showed no starting material **41**, at which point it was concentrated thoroughly to remove the solvents (MeOH and H_2O). The residue was dissolved in CCl_4 (60 mL), and the solution was heated to 70 °C. After stirring 5 h at 70 °C, it was allowed to rt and diluted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1) to give the title compound **42** (0.50 g, 60%) as a yellow oil. R_f=0.45 (hexane/EtOAc, 3:1); $[\alpha]_D$=−53.3 (*c* 3.2, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.76–1.89 (m, 1H), 1.95–2.14 (m, 2H), 2.26–2.40 (m, 1H), 4.14–4.20 (m, 1H), 4.88 (m, 1H), 5.46 (s, 1H), 5.72–5.76 (m, 1H), 5.98–6.05 (m, 1H), 7.32–7.50 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.8, 24.6, 65.0, 74.4, 75.1, 123.1, 126.8, 128.7, 128.9, 132.6, 135.6, 167.8; IR ($CHCl_3$, film) 1730, 1387, 1229, 1104, 1045 cm^{-1}. Anal. calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.05; H, 6.24.

4.1.35. (1*S*,4*S*,6*S*,7*S*,8*R*)-6-Phenyl-hexahydro-1,4,7-trioxa-cyclopropa-[a]naphthalene-5-one (43). A solution of compound **42** (25 mg, 0.1 mmol) and dimethyldioxirane (2 equiv, ca. 0.05 M) in acetone (10 mL) was stirred for 2 h at rt. The reaction mixture was concentrated by removing acetone. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1) to give the title compound **43** (23 mg, 92%) as a colorless oil. R_f=0.38 (hexane/EtOAc, 3:1); $[\alpha]_D$=−53.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.44–1.59 (m, 1H), 1.64–1.75 (m, 1H), 1.95–2.04 (m, 1H), 2.10–2.24 (m, 1H), 3.32–3.34 (dd, J=3.5, 1.7 Hz, 1H), 3.40–3.41 (d, J=2.5 Hz, 1H), 3.91–3.95 (m, 1H), 4.58–4.60 (d, J=3.9 Hz, 1H), −5.53 (s, 1H), 7.36–7.47 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.4, 19.5, 52.4, 53.1, 60.9, 75.0, 75.6, 127.1, 128.9, 129.0, 134.7, 166.4; IR ($CHCl_3$, film) 1749, 1229, 1058 cm^{-1}. Anal. calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.28; H, 5.76.

4.1.36. (1*S*,2*S*,3*R*,4*S*,1′*S*)-2-(2-Hydroxy-1-phenyl-ethoxy)-3-phenylselanyl-cyclohexane-1,4-diol (44) and (1*S*,2*S*,3*R*,4*S*,1′*R*)-2-(2-hydroxy-1-phenyl-ethoxy)-3-phenylselanyl-cyclohexane-1,4-diol (45). To a solution of compound **43** (220 mg, 0.9 mmol) and DPDS (420 mg, 1.3 mmol) in DME (4 mL) was added $NaBH_4$ (120 mg, 3.1 mmol). After stirring for 3 h at rt, the reaction mixture was quenched with water, diluted with EtOAc. The organic layer was washed with saturated NH_4Cl solution several times, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 1:10) to give the title compound **44** (204 mg, 56%) and **45** (119 mg, 33%) as a colorless oil, respectively. Compound **44**: R_f=0.40 (hexane/EtOAc, 1:10); $[\alpha]_D$=+22.9 (*c* 2.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.13–1.28 (m, 1H), 1.76–2.03 (m, 3H), 2.50 (s, 1H), 2.91–3.02 (m, 1H), 3.37–3.83 (m, 7H), 4.43–4.47 (dd, J=7.4, 3.7 Hz, 1H), 7.26–7.66 (m, 10H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 26.9, 27.0, 47.6, 67.2, 73.1, 73.6, 76.0, 79.5, 126.1, 126.2, 127.3, 128.7, 128.9, 129.2, 137.0, 137.7; IR ($CHCl_3$, film) 3434, 1578, 1453, 1058 cm^{-1}. Anal. calcd for $C_{20}H_{24}O_4Se$: C, 58.97; H, 5.94. Found: C, 58.98; H, 5.98. Compound **45**: R_f=0.25 (hexane/EtOAc, 1:10); $[\alpha]_D$=−15.7 (*c* 3.5, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.26–1.80 (m, 4H), 2.89–3.00 (m, 1H), 3.51–3.61 (m, 4H), 3.83–3.91 (t, J=9.8 Hz, 1H), 3.95 (m, 1H), 4.20 (br s, 2H), 4.47–4.52 (dd, J=7.7, 4.3 Hz, 1H), 7.12–7.65 (m, 10H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 27.4, 30.1, 48.3, 68.5, 73.5, 76.9, 79.7, 85.2, 126.2, 126.9, 127.8, 128.3, 128.4, 129.2, 136.4, 140.2; IR ($CHCl_3$, film) 3427, 1578, 1453, 1440, 1223, 1052 cm^{-1}. Anal. calcd for $C_{20}H_{24}O_4Se$: C, 58.97; H, 5.94. Found: C, 58.98; H, 5.98.

4.1.37. (1*S*,2*R*,1′*S*)-2-(2-Hydroxy-1-phenyl-ethoxy)-cyclohex-3-enol (48) and (1*S*,2*R*,1′*R*)-2-(2-hydroxy-1-phenyl-ethoxy)-cyclohex-3-enol (49). To a solution of compound **42** (0.31 g, 1.30 mmol) in DME (10 mL) was added $NaBH_4$ (0.10 g, 2.70 mmol). After stirring 1 h at rt, the reaction mixture was diluted with EtOAc and neutralized with saturated NH_4Cl solution. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography

(hexane/EtOAc, 1:3) to give the title compound **48** (0.24 g, 77%) and conpound **49** (24 mg, 8%) as a colorless oil, respectively. Compound **48**: R_f=0.28 (hexane/EtOAc, 1:3); $[\alpha]_D$=+37.5 (*c* 1.7, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.73–1.84 (m, 1H), 1.89–2.05 (m, 2H), 2.17–2.29 (m, 1H), 2.55 (m, 2H), 3.53–3.79 (m, 3H), 4.04 (s, 1H), 4.63–4.68 (dd, *J*=8.5, 3.8 Hz, 1H), 5.65–5.71 (m, 1H), 5.80–5.86 (m, 1H), 7.32–7.39 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 22.1, 23.8, 66.3, 67.4, 74.4, 80.5, 127.0, 127.4, 128.6, 128.9, 130.9, 138.8; IR ($CHCl_3$, film) 3421, 1453, 1229, 1111, 1051 cm^{-1}. Anal. calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.75; H, 7.75. Compound **49**: R_f=0.35 (hexane/EtOAc, 1:3); $[\alpha]_D$=−164.9 (*c* 2.5, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.26–2.15 (m, 4H), 3.23 (br s, 2H), 3.54–3.63 (m, 1H), 3-65-3.76 (m, 2H), 4.36 (m, 1H), 4.67–4.72 (dd, *J*=8.3, 4.3 Hz, 1H), 5.75–5.88 (m, 2H), 7.28–7.37 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 24.3, 24.4, 64.2, 67.8, 76.2, 81.3, 126.7, 126.9, 128.2, 128.6, 131.6, 139.4; IR ($CHCl_3$, film) 3375, 1453, 1433, 1104, 1058 cm^{-1}. Anal. calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.73; H, 7.70.

4.1.38. (1*S*,2*R*,1′*S*)-Toluene-4-sulfonic acid 2-(6-hydroxy-cyclohex-2-enyloxy)-2-phenyl-ethyl ester (50). To a solution of compound **48** (118 mg, 0.50 mmol) and DMAP (19 mg, 0.16 mmol) in CH_2Cl_2 (20 mL) and TEA (10 mL) at 0 °C was added TsCl (96 mg, 0.50 mmol). After stirring 1 h at 0 °C, the reaction mixture was diluted with CH_2Cl_2. The organic layer was washed with saturated NH_4Cl solution several times, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1) to give the title compound **50** (183 mg, 93%) as a colorless oil. R_f=0.33 (hexane/EtOAc, 2:1); $[\alpha]_D$=+63.4 (*c* 2.5, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.63–1.76 (m, 1H), 1.85–2.00 (m, 2H), 2.17–2.26 (m, 1H), 2.28–2.31 (d, *J*=5.5 Hz, 1H), 2.44 (s, 2H), 3.48-3.55 (m, 1H), 3.99–4.00 (m, 1H), 4.04–4.16 (m, 2H), 4.74–4.79 (dd, *J*=7.4, 4.5 Hz, 1H), 5.61–5.67 (m, 1H), 5.78–5.83 (m, 1H), 7.26–7.39 (m, 7H), 7.72–7.75 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 21.8, 22.1, 23.5, 66.0, 72.9, 75.0, 77.2, 127.0, 128.0, 129.0, 129.1, 130.0, 131.0, 133.1, 137.2, 145.0; IR ($CHCl_3$, film) 3421, 1355, 1177, 1098 cm^{-1}. Anal. calcd for $C_{21}H_{24}O_5S$: C, 64.93; H, 6.23; S, 8.25. Found: C, 64.84; H, 6.24; S, 8.71.

4.1.39. (1*S*,2*R*,1′*S*)-2-(1-Phenyl-2-phenylselanyl-ethoxy)-cyclohex-3-enol (51). To a solution of compound **50** (184 mg, 0.5 mmol) in EtOH (10 mL) at rt was added $NaBH_4$ (54 mg, 1.4 mmol) and DPDS (222 mg, 0.7 mmol). After stirring for 3 h at 70 °C, the reaction mixture was quenched with water and concentrated to remove EtOH. The aqueous solution was neutralized with saturated NH_4Cl solution, and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1) to give the title compound **51** (160 mg, 90%) as a colorless oil. R_f=0.55 (hexane/EtOAc, 3:1); $[\alpha]_D$=+29.5 (*c* 3.0, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.64–1.75 (m, 1H), 1.83–1.98 (m, 2H), 2.23–2.35 (m, 1H), 2.38–2.39 (d, *J*=4.0 Hz, 1H), 3.09–3.15 (dd, *J*=12.5, 4.5 Hz, 1H), 3.32–3.41 (dd, *J*=12.5, 8.8 Hz, 1H), 3.43–3.50 (m, 1H), 3.96 (s, 1H), 4.68–4.73 (dd, *J*=8.8, 4.5 Hz, 1H), 5.61–5.67 (m, 1H), 5.77–5.82 (m, 1H), 7.23–7.51 (m, 10H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 22.0, 23.9, 35.8, 66.0, 74.6, 79.4, 126.7, 127.0, 127.2, 128.5, 128.9, 129.2, 130.9, 132.5, 141.5; IR ($CHCl_3$, film) 3421, 1098 cm^{-1}. Anal. calcd for $C_{20}H_{22}O_2Se$: C, 64.34; H, 5.94. Found: C, 64.34; H, 5.95.

4.1.40. (1*S*,2*R*,1′*S*)-Benzoic acid 2-(1-phenyl-2-phenylselanyl-ethoxy)-cyclohex-3-enyl-ester (52). To a solution of compound **51** (87 mg, 0.2 mmol) in DMF (5 mL) at 0 °C was added NaH (60%, 12 mg, 0.3 mmol). After stirring for 30 min at 0 °C, benzyl bromide (47 mg, 0.3 mmol) was added. The resulting solution was stirred for 12 h at 0 °C, diluted with EtOAc and washed with saturated NH_4Cl solution several times. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 10:1) to give the title compound **52** (86 mg, 79%) as a yellow oil. R_f=0.38 (hexane/EtOAc, 10:1); $[\alpha]_D$=−26.8 (*c* 0.5, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.66–1.71 (m, 1H), 1.94–2.10 (m, 2H), 2.37–2.40 (m, 1H), 3.11–3.15 (dd, *J*=12.3, 4.8 Hz, 1H), 3.33-3.39 (dd, *J*=12.2, 8.4 Hz, 1H), 3.54–3.56 (m, 1H), 4.00 (m, 1H), 4.50–4.53 (d, *J*=6.1 Hz, 1H), 4.61–4.64 (d, *J*=6.1 Hz, 1H), 4.65–4.66 (m, 1H), 5.65–5.67 (m, 1H), 5.78–5.80 (m, 1H), 7.22–7.48 (m, 15H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 22.5, 24.2, 36.0, 71.7, 73.4, 74.2, 79.4, 126.0, 126.8, 127.1, 127.4, 127.8, 128.2, 128.3, 128.6, 129.1, 130.8, 131.3, 132.4, 139.4, 142.0; IR ($CHCl_3$, film) 1578, 1480, 1453, 1104 cm^{-1}. HRMS calcd for $C_{27}H_{28}O_2Se$ $(M)^+$: *m*/*z* 464.1255. Found: 464.1252.

4.1.41. (1*S*,6*S*)-6-Benzyloxy-cyclohex-2-enol (53). Compound **52** (110 mg, 0.2 mmol) was subjected to the same reaction conditions as that for the preparation of **42** from **41**. The reaction mixture was purified by flash column chromatography (hexane/EtOAc, 7:1) to give the title compound **53** (30 mg, 62%) as a yellow oil. R_f=0.35 (hexane/EtOAc, 3:1); $[\alpha]_D$=−120.7 (*c* 1.5, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.69–1.71 (m, 1H), 1.88–2.03 (m, 2H), 2.24–2.27 (m, 1H), 2.51–2.52 (d, *J*=5.1 Hz, 1H), 3.95 (m, 2H), 4.63–4.65 (d, *J*=11.7 Hz, 1H), 4.68–4.71 (d, *J*=11.7 Hz, 1H), 5.71–5.73 (m, 1H), 5.88–5.90 (m, 1H), 7.30–7.36 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 23.1, 26.6, 67.0, 71.1, 73.9, 124.8, 127.9, 128.6, 131.9, 138.5; IR ($CHCl_3$, film) 3430, 1216, 1074 cm^{-1}. HRMS calcd for $C_{13}H_{16}O_2$ $(M)^+$: *m*/*z* 204.1150. Found: 204.1168.

4.1.42. (1*R*,6*S*)-(6-Benzyloxy-cyclohex-2-enyloxy)-*tert*-butyl-diphenyl-silane (54). A solution of compound **53** (40 mg, 0.2 mmol) and TBDPSCl (82 mg, 0.3 mmol) in the presence of DMAP (7 mg, 0.06 mmol) and imidazole (40 mg, 0.6 mmol) in DMF (5 mL) was stirred for 12 h at 80 °C. The reaction mixture was allowed to rt, dilute with EtOAc and washed with saturated NH_4Cl solution several times. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 15:1) to give the title compound **54** (83 mg, 96%) as a colorless oil: R_f=0.50 (hexane/EtOAc, 15:1); $[\alpha]_D$=−55.2 (*c* 4.5, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.10 (s, 9H), 1.42–1.49 (m, 1H), 1.70–1.81 (m, 1H), 1.91–2.17 (m, 2H), 3.81 3.84 (t, *J*=3.5 Hz, 1H), 3.94–4.00 (dt, J_d=10.5 Hz, J_t=3.1 Hz, 1H), 4.62–4.67 (d, *J*=12.2 Hz, 1H), 4.77–4.82 (d, *J*=12.2 Hz, 1H), 5.53–5.75 (m, 2H), 7.20–7.43 (m, 11H), 7.70–7.74 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.4, 25.0, 26.3, 27.2,

72.3, 72.6, 74.2, 126.0, 127.3, 127.6, 127.7, 128.3, 129.66, 129.69, 130.7, 134.3, 134.7, 135.0, 136.0, 139.6; IR ($CHCl_3$, film) 1216, 1111 cm^{-1}. HRMS calcd for $C_{29}H_{34}O_2SiNa$ $(M+Na)^+$: *m/z* 465.2226. Found: 465.2253.

4.1.43. (1*R*,2*R*,3*S*,6*R*)-(3-Benzyloxy-7-oxa-bicyclo[4,1,0]-hept-2-yloxy)-*tert*-butyl-diphenyl-silane (55). Compound **54** (96 mg, 0.2 mmol) was subjected to the same reaction conditions as that for the preparation of **43** from **42**. The reaction mixture was purified by flash column chromatography (hexane/EtOAc, 10:1) to give the title compound **55** (91 mg, 91%) as a colorless oil. R_f=0.50 (hexane/EtOAc, 10:1); $[\alpha]_D$=−5.3 (*c* 4.0, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.08 (s, 9H), 1.12–1.17 (m, 1H), 1.51–1.64 (m, 1H), 1.72–1.83 (m, 1H), 2.01–2.14 (m, 1H), 3.17–3.18 (d, *J*=3.8 Hz, 1H), 3.22–3.25 (t, *J*=3.3 Hz, 1H), 3.53–3.54 (d, *J*=2.8 Hz, 1H), 4.00–4.04 (m, 1H), 4.54–4.59 (d, *J*=12.0 Hz, 1H), 4.61–4.66 (d, *J*=12.0 Hz, 1H), 7.17–7.44 (m, 11H), 7.64–7.72 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.5, 20.5, 23.4, 27.2, 52.7, 54.5, 68.0, 72.3, 76.3, 127.5, 127.6, 127.7, 127.8, 128.4, 129.6, 129.7, 134.1, 134.5, 136.0, 136.2, 138.5; IR ($CHCl_3$, film) 1427, 1216, 1111 cm^{-1}. HRMS calcd for $C_{29}H_{35}O_3Si$ $(M+H)^+$: *m/z* 459.2355. Found: 459.2348.

4.1.44. (1*R*,2*R*,3*S*,6*R*)-3-Benzyloxy-2-(*tert*-butyl-diphenyl-silanyloxy)-6-phenylselanyl-cyclohexanol (56). Compound **55** (32 mg, 0.07 mmol) was subjected to the same reaction conditions as that for the preparation of **51** from **50**. The reaction mixture was purified by flash column chromatography (hexane/EtOAc, 10:1) to give the title compound **56** (37 mg, 86%) as a colorless oil. R_f=0.35 (hexane/EtOAc, 10:1); $[\alpha]_D$=−7.9 (*c* 3.0, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 0.98 (s, 9H), 1.25–1.36 (m, 1H), 1.56–1.66 (m, 1H), 1.83–1.90 (m, 1H), 2.00–2.18 (m, 1H), 2.90–3.01 (m, 2H), 3.07–3.12 (dd, *J*=9.2, 2.4 Hz, 1H), 4.04–4.12 (dd, *J*=10.3, 9.4 Hz, 1H), 4.16 (m, 1H), 4.22–4.26 (d, *J*=12.2 Hz, 1H), 4.37–4.42 (d, *J*=12.1 Hz, 1H), 7.13–7.78 (m, 20H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.4, 26.7, 27.1, 31.9, 47.7, 68.3, 71.4, 71.6, 84.2, 127.5, 127.6, 127.7, 127.9, 128.4, 129.1, 129.6, 129.8, 133.6, 134.4, 134.9, 136.1, 136.4, 136.9, 138.3; IR ($CHCl_3$, film) 3414, 1216, 1111 cm^{-1}. HRMS calcd for $C_{35}H_{40}O_3SeSi$ $(M)^+$: *m/z* 616.1912. Found: 616.1918.

4.1.45. (1*S*,5*S*,6*R*)-5-Benzyloxy-6-(*tert*-butyl-diphenyl-silanyloxy)-cyclohex-2-enol (57). A solution of compound **56** (30 mg, 0.05 mmol) and $NaIO_4$ (32 mg, 0.2 mmol) in methanol (6 mL) and H_2O (1 mL) in the presence of $NaHCO_3$ (8 mg, 0.1 mmol) was stirred for 10 min at rt, and then for 10 h at 70 °C. After removal of methanol by evaporation, the aqueous solution was diluted with H_2O and CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1) to give the title compound **57** (19 mg, 85%) as a colorless oil. R_f= 0.40 (hexane/EtOAc, 3:1); $[\alpha]_D$=+65.6 (*c* 0.5, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.06 (s, 9H), 1.94–1.95 (d, *J*= 3.1 Hz, 1H), 2.01–2.04 (m, 1H), 2.18–2.22 (m, 1H), 3.38–3.39 (d, *J*=6.6 Hz, 1H), 4.25 (s, 1H), 4.40–4.42 (d, *J*= 11.9 Hz, 1H), 4.60 (s, 1H), 4.63–4.65 (d, *J*=11.9 Hz, 1H), 5.57–5.59 (m, 1H), 5.70–5.72 (m, 1H), 7.25–7.74 (m, 15H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.5, 27.1, 33.4, 67.6, 69.3, 71.6, 83.1, 126.0, 127.7, 128.5, 129.8, 133.8, 134.7, 136.0, 136.2, 138.7; IR ($CHCl_3$, film) 3421, 1624, 1111 cm^{-1}. HRMS calcd for $C_{29}H_{34}O_3SiNa$ $(M+Na)^+$: *m/z* 481.2175. Found: 481.2163.

4.1.46. (1*R*,2*R*,3*S*,4*R*,5*S*)-5-Benzyloxy-4-(*tert*-butyl-diphenyl-silanyloxy)-cyclohex-1,2,3-triol (58). To a solution of compound **57** (23 mg, 0.05 mmol) in acetone (4 mL) and H_2O (1 mL) were added NMO (47 mg, 0.4 mmol) and $K_2OsO_4 \cdot 2H_2O$ (5 mg, 0.01 mmol) at rt. After stirring for 30 h at rt, $NaHSO_4$ (10 mg) was added. The reaction mixture was stirred for further 10 min at rt, then diluted with H_2O and EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 1:3) to give the title compound **58** (22 mg, 89%) as a colorless oil. R_f=0.30 (hexane/EtOAc, 1:3); $[\alpha]_D$=+1.2 (*c* 0.4, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.09 (s, 9H), 1.44–1.50 (m, 1H), 2.25–2.32 (dt, J_d=11.0 Hz, J_t=4.0 Hz, 1H), 2.48 (m, 1H), 2.87 (m, 1H), 3.05–3.08 (d, *J*=8.5 Hz, 1H), 3.35–3.43 (m, 1H), 3.98–4.31 (m, 6H), 7.00–7.74 (m, 15H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.4, 27.2, 33.1, 70.7, 71.5, 72.1, 75.5, 77.4, 81.8, 127.5, 127.6, 127.7, 128.0, 128.4, 130.1, 130.2, 133.0, 136.3, 136.6, 138.0; IR ($CHCl_3$, film) 3441, 1631, 1117, 1071 cm^{-1}. HRMS calcd for $C_{29}H_{36}O_5Si$ $(M)^+$: *m/z* 492.2332. Found: 492.2318.

4.1.47. *muco*-Quercitol pentaacetate (18) from 58. To a solution of compound **58** (10 mg, 0.02 mmol) in EtOH (3 mL) were added a catalytic amount of $Pd(OH)_2/C$ and 3% aqueous HCl solution. After stirring for 24 h at rt under H_2 gas (1 atm), the reaction mixture was passed through Celite pad, which was washed with EtOH several times. The filtrate was concentrated thoroughly under vacuum to give *muco*-Quercitol (**1**) as a white solid. Without any further purification, **1** was dissolved in TEA (1 mL). To this solution were added Ac_2O (0.5 mL) and a catalytic amount of DMAP. After stirring for 3 h at rt, the reaction mixture was diluted with EtOAc. The organic layer was washed with saturated NH_4Cl solution several times, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc, 1:1) to give the title compound **18** (6 mg, 80%) as a white solid. The spectroscopic data and physical properties of the pentaacetate **18** were completely identical with those of **18** obtained from **17**.

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References and notes

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18. Although compound **4** was obtained as an inseparable mixture with its diastereomer **5** in the present work, pure **4** could be obtained by the procedure of our previous work, see: Ref. 15.
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