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Synthesis of highly oxygenated carbocyclic derivatives: decalins and cyclohexanes from sugar allyltins

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Abstract—Sugar allyltin derivatives are readily converted into the carbobicyclic compounds with precisely defined stereochemistry. Model functionalization of the carbocyclic skeleton in such precursors with the decalin structure provides either highly oxygenated bi- or monocarbocyclic derivatives.

1. Introduction

Over the past few years, we have described a general methodology for the preparation of highly oxygenated carbobicyclic derivatives from sugar allyltins **2** and **3**, which are readily available from the corresponding allylic alcohols **1** (Fig. 1).[1] These organometallics can be regarded as precursors of either fully oxygenated bicyclic (decalins and perhydroindanes) or monocyclic (cyclohexane and cylopentane) sugar mimetics.

The synthesis and biological properties of such monocarbocyclic derivatives are very well documented.[2] However, the chemistry of the bicyclic analogues is almost unexplored. Mehta and Ramesh described a convenient route to the *racemic*, fully oxygenated bicyclo[4.3.0]nonanes and bicyclo[4.4.0]decanes and found that such derivatives might possess interesting inhibitory glucosidase activity.[3] The highly oxygenated decalin skeleton can also be found in the structure of macrolide antibiotics such as nargenicin A, the synthesis of which in enantiomerically pure form was realized by Roush in 1996.[4]

Our methodology,[1] as shown in Figure 1, allows us to obtain enantiomerically pure bicyclic derivatives with the hydrindane and decalin structures. The sugar allyltin derivatives (either primary **2** or secondary **3**) undergo a controlled fragmentation to *E*-dienoaldehydes **5** upon treatment with a Lewis acid (the best being $ZnCl_2$),[5,6] while

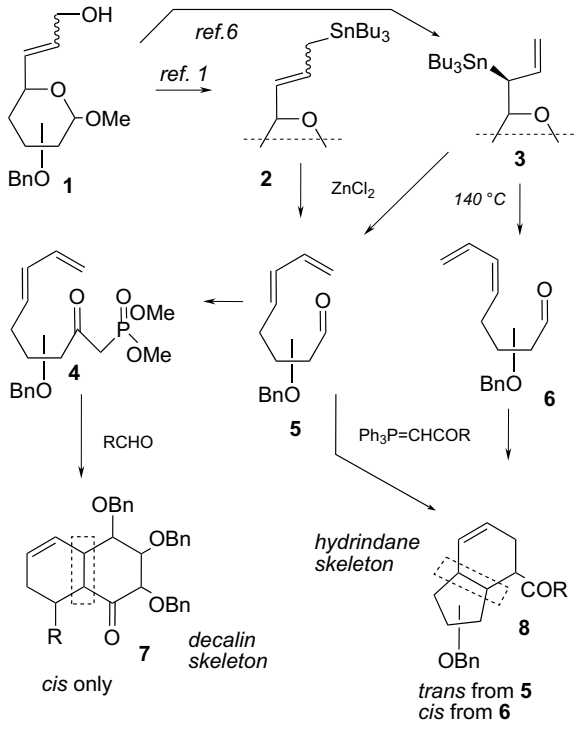

Figure 1. Synthesis of highly oxygenated carbobicyclic derivatives from sugar allyltins.

at high temperature (boiling xylene) the secondary ones **3** are converted into *Z*-dienoaldehyde **6** (the primary analogues **2** remain unchanged under these conditions).[6] These highly reactive dienes are precursors of enantiomerically

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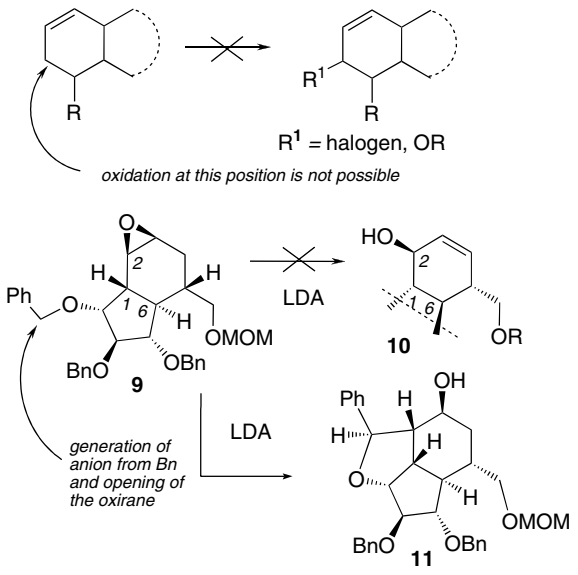


Figure 2. Attempts to oxidize the allylic methylene group.

pure carbobicycles with well-defined structures. We were able to prepare *cis*-decalins **7** and *trans*- or *cis*-hydrindanes **8** in good yields (Fig. 1).[†,1]

Proper functionalization of the allylic system either in **7** or **8** should afford the fully oxygenated derivatives including also the analogues containing heteroatoms other than oxygen. For example, osmylation of the double bond in such carbobicyclic precursors led to the *cis*-diols, while epoxidation, followed by the opening of the epoxide ring provided *trans*-diols in good yields.[8] However, derivatization of the allylic methylene group in such derivatives was found to be troublesome. Direct allylic oxidation (or bromination) did not give any expected product. The well-known base-induced isomerization of the corresponding epoxides[9] was also not applicable to our precursors; for example, treatment of epoxide **9** with LDA led to the rearrangement product **11** instead of the desired allylic alcohol **10** (Fig. 2).[10]

Herein, we report the functionalization of the decalin of type **7** leading either to highly oxygenated bicyclic or monocylic compounds.

2. Results and discussion

Adduct **12** (readily obtained from the corresponding D-*gluco*-configurated allyltin according to Ref. 11) was chosen as a precursor of a highly oxygenated decalin (after functionalization of the C6–C8 allylic system in ring **A**) and a highly functionalized cyclohexane. The monocyclic derivatives can be obtained from **12** either by transformation of ring **A**[‡] or

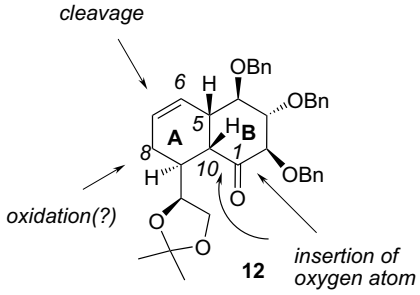


Figure 3. Possible routes of functionalization of the bicyclic precursor **12**.

B (via a Baeyer–Villiger oxidation[12] of the C1-carbonyl group), see Figure 3.

These two approaches which open the routes to carbocyclic sugar mimics will be discussed.

2.1. Model synthesis of highly functionalized cyclohexane derivative from adduct 12

The Baeyer–Villiger oxidation,[13] which directly converts ketones to esters (lactones) upon their treatment with peroxy reagents, was the most obvious choice for the transformation of ring **B**. We decided to apply the simplest oxidant, that is, *m*-chloroperbenzoic acid (MCPBA) to introduce an oxygen atom into the cyclohexane ring **B**. To avoid possible epoxidation of the double bond in **12**, the olefin was converted into *cis*-diol **13** via simple osmylation, which provided diol **13** as the only product in 72% isolated yield. Its structure was proven by NMR experiments performed on diacetate **13a**, in which the NOESY correlation peak between H-4 and H-6 was observed[§] (see Scheme 1).

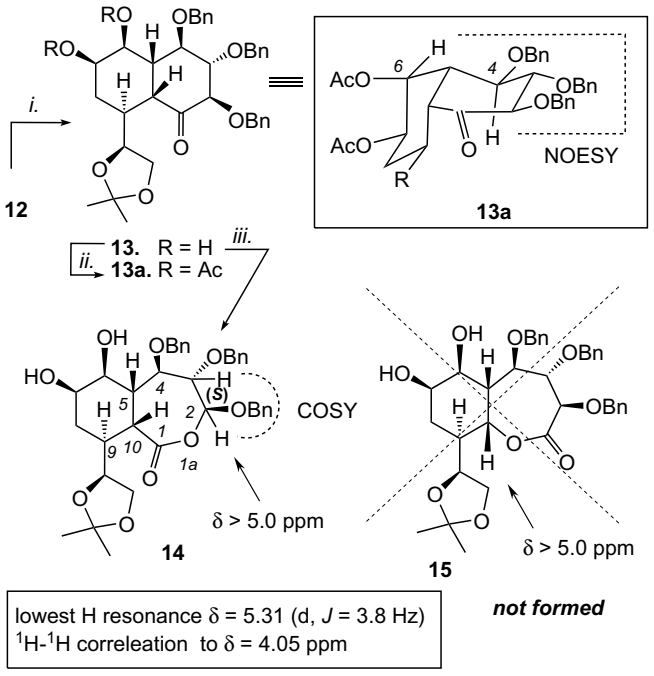
Treatment of keto-diol **13** with MCPBA resulted in formation of the Baeyer–Villiger product [*m*/*z*: 641.2743 = $C_{36}H_{42}O_9Na$ ($M+Na^+$)]. From two possible structures **14** and **15** the latter was excluded on the basis of the NMR data. In the COSY spectrum of the Baeyer–Villiger product, the lowest resonance ($\delta = 5.31$ ppm) corresponded to the low field signal at $\delta = 4.05$ ppm.; moreover it was coupled to only one proton (H-2). These results pointed unequivocally at the structure **14** and excluded **15** in which the lowest resonance should be coupled to two high field resonating protons: H-9 and H-5. Although we were unable to assign the configuration at the new stereogenic centre (C-2),[¶] structure **14** was proposed (and not the epimer at the C-2 position), which is based on the well-known fact that the configuration is retained during the Baeyer–Villiger oxidation.[14]

[†] The synthesis of enantiomerically pure derivatives of this type of sugars was first reported by Herczegh, who used a 'classical' approach, see Ref. 7.

[‡] This obvious alternative: cleavage of the C6–C7 bond will not be discussed in this Letter.

[§] These protons are in *cis*-relationship and are relatively close to each other. In the alternative structure, no such correlation is possible. Moreover, the stereochemical outcome of this reaction (attack of OsO_4 from the 'upper' side) is analogous to one observed earlier by us for a similar bicyclic compound (see Ref. 8).

[¶] For reasons of clarity, we keep the numbering as in precursors **12** and **13** and the extra oxygen atom in ring **B** in compound **14** is assigned the '*1a*' label.



Scheme 1. Reagents and conditions: (i) THF, H_2O, ^tBuOH, NMO, OsO_4 (cat.), 72%; (ii) Ac_2O, py, quant.; (iii) MCPBA, $NaHCO_3$, CH_2Cl_2, 65%.

2.2. Approach to highly oxygenated decalis: functionalization of the allylic C6–C8 fragment in 12

As pointed out in the Introduction (see also Refs. 1 and 10), the most obvious choice for the oxidation of the allylic methylene group, that is, direct oxidation or base-catalyzed rearrangement of the corresponding epoxides, is not applicable to our bicyclic compounds. A solution to this problem is provided by the highly regioselective opening of the oxirane ring in the epoxides derived from the bicyclic olefin **16**. Reaction of the nucleophile (AcO^-, N_3^-) with epoxides **17** and **20** furnished the corresponding *trans*-diols or azidoalcohols **18** and **19** in high yields (Fig. 4).[8]

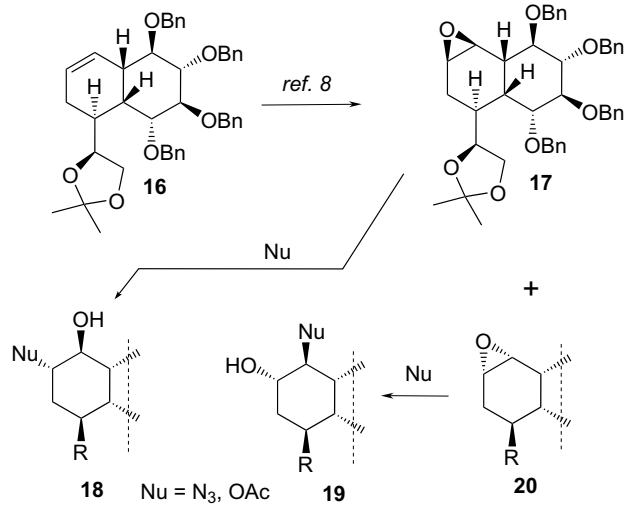


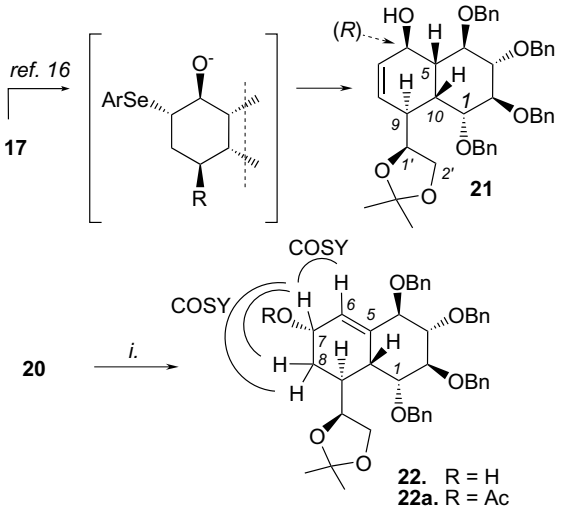
Figure 4. Model study on the oxidation of the precursors of highly oxygenated decalins.

Recently we have applied the well established selenium methodology[15] for the opening of the epoxide ring in **17**, which provided the expected allylic alcohol **21** in good yield (Scheme 2).[16]

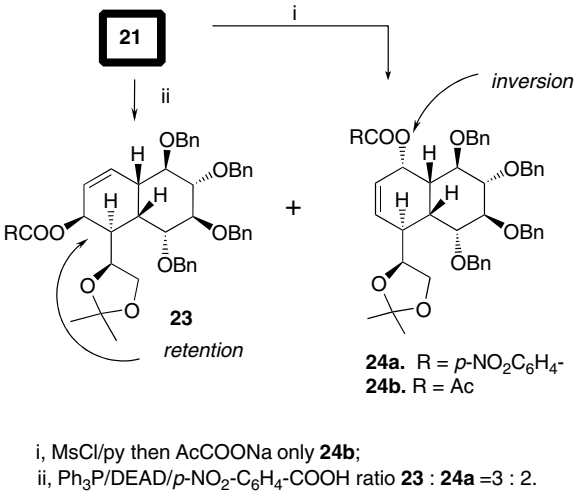
The isomeric (to **17**) epoxide **20** might be a convenient precursor of olefin **22**, a useful building block for the stereoselective synthesis of carbobicyclic derivatives bearing a quaternary carbinol centre. Thus, treatment of oxirane **20** with the phenylselenide anion followed by oxidative work-up provided alcohol **22** in good yield (Scheme 2). Its structure was thoroughly verified by NMR analysis performed on its acetate derivative **22a**. The signal of the H-7 proton occurring at $\delta = 5.30$ ppm correlated to the olefinic H-6 ($\delta = 6.06$ ppm) and two high field resonances ($\delta = 1.85$ and 1.45 ppm) in the COSY spectrum of **22a**. These two high field protons correlated to the secondary carbon at $\delta = 29.2$ ppm proving the presence of the CH_2– group at the C-8 position.

Compound **22** is (or should be) a convenient precursor of highly oxygenated decalins bearing a quaternary carbinol centre (at C-5) or carbasugars (via a cleavage of the double bond followed by reduction of the resulting ketone into the 5-CH_2 group).

Exploring the synthetic potential of the '*allyltin approach*' to highly oxygenated carbobicycles, we turned our attention to allylic alcohol **21** with the (*R*)-configuration at the carbinol (C-6) centre. Besides the obvious functionalization of the double bond (osmylation, aminohydroxylation, epoxidation) this compound can be converted into the C-6 epimer by simple inversion of the configuration at this stereogenic centre, which will open a route to new, configurationally different, highly oxidized decalins. Treatment of alcohol **21** with the Mitsunobu reagent[17] gave quite unexpectedly two products: the desired S_N2 product **24a** and the rearranged S_N2' alcohol **23** (Scheme 3), although it is known that the S_N2' reaction under the Mitsunobu conditions are very rare.[18,19]

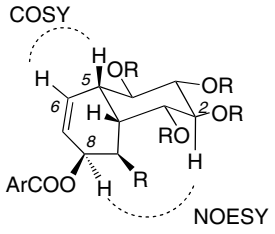


Scheme 2. Reagents and conditions: (i) (1) PhSe–SePh, $NaBH_4$, EtOH; (2) H_2O_2, 71% overall.



Scheme 3.

The structure of the rearranged product **23** was proven by NMR experiments. In the COSY spectrum, the correlation peak between the olefinic (H-6) and high-field H-5 signals was observed. The relative *cis*-relationship between the H-8 and H-2 was assigned by the corresponding correlation peak in the NOESY spectrum (Fig. 5). This showed that



23. Ar = *p*-$NO_2C_6H_4$-

Figure 5. Assignment of the configuration of the rearranged Mitsunobu product.

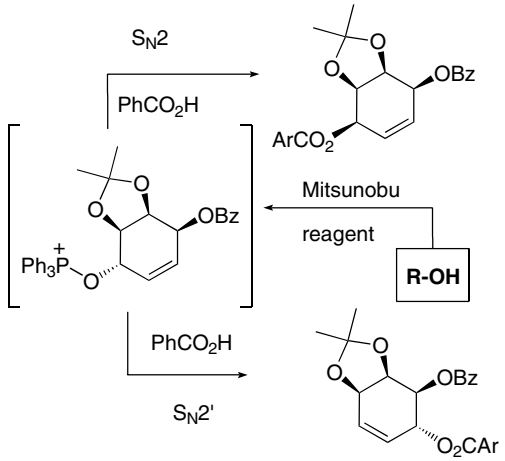


Figure 6. The example of the allylic rearrangement under Mitsunobu conditions.

the attack of the carboxylic acid (ArCOOH = *p*-nitrobenzoic acid) on the allylic system (as activated by the Mitsunobu reagent alcohol **21**) occurred on the opposite site (inversion) in an S_N2 mode and from the same side (retention) in an S_N2' mode (Scheme 3).

The addition of the nucleophile from the same side as the pre-existing OH grouping is in agreement with the recent observation on such allylic Mitsunobu rearrangements, observed during the synthesis of conduritols (Fig. 6).[‖,19]

The expected S_N2 compound, alcohol **24**, was obtained as acetate **24b**, however, as the only product in the reaction of the corresponding mesylate with acetate anion. Compound **24b** was different from acetate **21-Ac**; in the NOESY spectrum of **24b** no correlation between the H-6 and H-4 was seen (which were visible in the spectrum of the starting carbinol **21**).

Work on functionalization of all allylic alcohols **21** and **22** and those obtained after hydrolysis of esters (**23** and **24**) is currently in progress and will be reported in due course.

3. Conclusion

We have explored the route leading to highly functionalized decalins and cyclohexanes from sugar allyltin derivatives. We have observed that the Mitsunobu reaction, proceeding in most cases in an S_N2 mode, afforded a rearranged (S_N2') product when applied to the bicyclic allylic alcohols. Such rearrangements, although reported in the literature, are rare under the Mitsunobu conditions.

4. Experimental

4.1. General

NMR spectra were recorded with a Bruker AM 500 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). Most of the resonances were assigned by COSY (^1H–^1H) and/or HETCOR and DEPT correlations. The ^1H- and ^{13}C-aromatic resonances occurring at the typical δ values were omitted for simplicity. Mass spectra were recorded with an ESI/MS Mariner (PerSeptive Biosystem) mass spectrometer. Optical rotations were measured with a Digital Jasco polarimeter DIP-360 ($\lambda = 589$ nm) for solutions in $CHCl_3$ ($c = 1$) at room temperature. Column chromatography was performed on silica gel (Merck, 70-230 or 230–400 mesh). Methylene chloride was distilled from CaH_2 and THF from potassium prior to use. Organic solutions were dried over anhydrous magnesium or sodium sulfate.

‖ This rearrangement is, however, rather an exception. For similar cyclic allylic alcohols the Mitsunobu inversion proceeded without any rearrangement (see Ref. 20).

4.2. (2*R*,3*S*,4*R*,5*R*,6*S*,7*R*,9*S*,10*R*)-{2,3,4-Tri-*O*-benzyl-6,7-dihydroxy-1-keto-9-[(1′*R*)-5,5-dimethyl-2,4-dioxolane-1′-yl]}bicyclo[4.4.0]decane 13

Osmylation of the double bond was conducted under standard catalytic conditions.[21] To a solution of olefin **12**[11] (350 mg, 0.62 mmol) in THF (10 mL), *tert*-butanol (1 mL) and water (0.1 mL), *N*-methyl morpholine *N*-oxide (100 mg) and osmium tetraoxide (3.1 mL of ca 2% solution in toluene) were added. The mixture was stirred for 24 h at room temperature, and partitioned between brine (15 mL) and ethyl acetate (20 mL). The organic layer was separated and the aqueous one extracted with ethyl acetate (2×20 mL), and the combined organic solutions were dried and concentrated. Purification of the crude product by column chromatography (hexane–ethyl acetate, 2:1) afforded the title diol **13** as an oil (267 mg, 72%). This compound was further characterized as a diacetate: $[\alpha]_D = +17.7$; HRMS [ESI] *m*/*z*: 709.2990 [$C_{36}H_{44}O_8Na$ ($M+Na^+$) requires 709.2983]. Anal. Calcd for $C_{40}H_{46}O_{10}$: C, 69.95; H, 6.75. Found: C, 69.62, H, 6.90%. ^{1}H NMR δ: 5.71 (~t, $J_{5,6} = J_{6,7}$ 2.7, H-6), 4.98 (m, H-7), 4.62 (d, $J_{2,3}$ 10.0, H-2), 4.00 (m, H-2′a, H-4), 3.89 (m, H-1′), 3.66 (dd, $J_{3,4}$ 8.8, H-3), 3.55 (m, H-2′b), 2.70 (dd, $J_{9,10} = J_{5,10}$ 5.0, H-10), 2.28 (m, H-9), 2.10 (m, H-5), 2.08 and 1.99 [$2 \times$ s, $2 \times$ C(O)CH_3], 1.58 (m, H-8); ^{13}C NMR δ: 205.4 (C-1), 169.9 and 169.4 [$2 \times$ O*C*(O)CH$_3$], 109.6 (C-3′), 86.7 (C-3), 84.9 (C-2), 78.6 (C-1′), 77.1 (C-4), 76.1, 75.6 and 72.8 ($3 \times$ OCH$_2$Ph), 68.0 (C-7), 67.6 (C-2′), 66.8 (C-6), 51.3 (C-10), 43.6 (C-5), 40.0 (C-9), 27.0 (C-8), 26.7 and 25.9 [*C*(CH$_3$)$_2$], 20.9 and 20.8 [$2 \times$ C(O)*C*H$_3$].

4.3. (2*S*,3*S*,4*R*,5*R*,6*S*,7*R*,9*S*,10*R*)-{2,3,4-Tri-*O*-benzyl-6,7-dihydroxy-1-keto-9-[(1′*R*)-5,5-dimethyl-2,4-dioxolane-1′-yl]}bicyclo[4.5.0]-2-oxa-undecane 14

Diol **13** (75 mg 0.12 mmol) was dissolved in CH_2Cl_2 (10 mL) to which $NaHCO_3$ (16 mg) and *m*-chloroperbenzoic acid (89 mg, 55% purity) were added and the mixture stirred for 16 days at room temperature. The organic layer was washed with saturated $NaHCO_3$ solution, water, dried, concentrated and the product was isolated by column chromatography (hexane–ethyl acetate, 4:1) to yield lactone **14** (48 mg, 65%) as an oil; $[\alpha]_D = -5.1$; HRMS *m*/*z*: 641.2743 [$C_{36}H_{42}O_9Na$ ($M+Na^+$) requires: 641.2721]. ^{1}H NMR δ: 5.31 (d, $J_{3,4}$ 3.8, H-2), 4.52 (m, H-1′), 4.14 (m, H-2′a), 4.05 (dd, $J_{4,5}$ 3.8, H-3), 3.88 (m, H-4, H-7), 3.64 (m, H-6, H-10, H-2′b), 2.44 (m, H-5), 2.30 (m, H-8a), 2.05 (m, H-9), 1.61 (m, H-8b), 1.30 and 1.26 [C(CH_3)$_2$]; ^{13}C NMR δ: 172.6 (C-1), 109.1 (C-3′), 104.6 (C-2), 84.4 (C-3), 80.2 (C-4), 75.9 (C-1′), 75.2, 74.3, 71.3 ($3 \times$ OCH$_2$Ph), 73.8 (C-6), 68.5 (C-2′), 38.8 (C-10), 37.8 (C-9), 37.0 (C-5), 30.0 (C-8), 27.7 and 27.1 [C(*C*H$_3$)$_2$].

4.4. (1*R*,2*R*,3*S*,4*R*,7*S*,9*S*,10*R*)-{1,2,3,4-Tetra-*O*-benzyl-7-hydroxy-9-[(1′*R*)-5,5-dimethyl-2,4-dioxolane-1′-yl]}bicyclo-[4.4.0]dec-5, 6-ene 22

To a solution of diphenyldiselenide (58 mg, 0.19 mmol) in anhydrous ethanol (5 mL), sodium borohydride was added in portions (31 mg, 0.82 mmol) and the mixture was stirred for 15 min until the yellow colour disappeared. Then a solution of epoxide **20** (177 mg, 0.26 mmol) in THF (2 mL) was added and the mixture was boiled at reflux for 2 h. After cooling to 5 °C (ice bath), hydrogen peroxide (30% in water, 1 mL) was added, and the mixture was stirred for 24 h at room temperature, and quenched with saturated sodium carbonate (5 mL). Water (100 mL) was added, and the product was extracted with diethyl ether (3×15 mL). The organic fraction was washed with brine, dried, concentrated and the product was isolated by column chromatography (hexane–ethyl acetate, 2:1) to give olefin **22**(126 mg; 71%) as an oil. MS *m*/*z*: 699.2 [$C_{43}H_{48}O_7$ ($M+Na^+$)]. Anal. Calcd for $C_{43}H_{48}O_7$: C, 76.31; H, 7.15. Found: C, 76.20; H 7.24. This compound was further characterized as acetate **22a**: $[\alpha]_D = +19.9$; ^{1}H NMR δ: 6.07 (m, H-6), 5.29 (m, H-7), 4.25, 4.11, 3.80 (4H, H-1, H-2, H-3, H-4), 3.94 (m, H-2′), 3.89 (m, H-1′), 3.50 (t, $J_{1'2'} = J_{2'a,2'b}$ 8.1, H-2′), 2.50 (m, H-10), 2.21 (m, H-9), 2.00 [s, 3H, C(O)CH_3], 1.84 (m, H-8a), 1.45 (m, H-8b); ^{13}C NMR δ: 170.8 [O*C*(O)CH$_3$], 140.7 (C-5), 123.2 (C-6), 108.9 [*C*(CH$_3$)$_2$], 81.7, 79.5, 78.6 and 77.1 (C-1, C-2, C-3, C-4), 78.5 (C-1′), 67.7 (C-2′), 66.0 (C-7), 38.8 (C-10), 33.5 (C-9), 29.2 (C-8), 25.8 and 25.7 [C(*C*H$_3$)$_2$], 21.3 [C(O)*C*H$_3$].

4.5. Mitsunobu reaction of alcohol 21

A solution of **21** (64 mg, 0.09 mmol), triphenylphosphine (52.5 mg, 0.2 mmol), diisopropylazadicarboxylate (40.5 mg, 0.2 mmol) and 4-nitrobenzoic acid (33.4 mg, 0.2 mmol) in anhydrous THF (10 mL) was stirred for 3 days at room temperature, and then boiled at reflux for 5 h. The reaction mixture was partitioned between saturated sodium bicarbonate (5 mL) and ethyl acetate (10 mL). The organic phase was separated and the aqueous one extracted with EtOAc (3×10 mL). The combined organic fractions were washed with brine (2×10 mL), dried, concentrated and the products were isolated by column chromatography (hexane–ethyl acetate, 3:1) to afford **23** as an oil (33 mg; 42%) and **24** (23 mg; 29%).

4.6. (1*R*,2*R*,3*S*,4*R*,5*R*,8*S*,9*S*,10*R*)-{1,2,3,4-Tetra-*O*-benzyl-8-(4-*O*-*p*-nitrobenzoyl)-9-[(1′*R*)-5,5-dimethyl-2,4-dioxolane-1′-yl]}bicyclo[4.4.0]dec-6,7-ene 23

$[\alpha]_D = -1.0$; HRMS *m*/*z*: 848.3381 [$C_{50}H_{41}NO_{10}Na$ ($M+Na^+$) requires 848.3405]. ^{1}H NMR δ: 6.24 (dd, $J_{5,6}$ 5.5, $J_{6,7}$ 9.9, H-6), 5.86 (dd, $J_{7,8}$ 3.9, H-7), 5.59 (m, H-8), 4.78 (m, H-1′), 3.98 (t, $J_{1,2} = J_{2,3}$ 9.2, H-2), 3.88 (t, $J_{1'2'} = J_{2'a,2'b}$ 8.8, H-2′a), 3.83 (t, *J* 9.2 , H-4), 3.67 (m, H-2′b, H-3), 3.60 (dd, $J_{1,10}$ 4.4, H-1), 2.78 (m, H-9), 2.36 (m, H-5), 2.12 (m, H-10), 1.18 (m, 6H, [CH_3)$_2$C]; ^{13}C NMR δ: 164.3 [Ar-*C*(O)O-], 134.9 (C-6), 125.7 (C-7), 108.6 [(CH$_3$)$_2$*C*], 86.6 (C-3), 83.4 (C-4), 81.96 (C-2), 81.90 (C-1), 75.48 (C-1′), 70.4 (C-8), 65.7 (C-2′), 39.5 (C-9), 38.8 (C-5), 38.0 (C-10), 26.0 and 24.2 [(*C*H$_3$)$_2$C].

4.7. (1*R*,2*R*,3*S*,4*R*,5*R*,6*S*,9*S*,10*R*)-{1,2,3,4-Tetra-*O*-benzyl-6-(4-*O*-*p*-nitrobenzoyl)-9-[(1′*R*)-5,5-dimethyl-2,4-dioxolane-1′-yl]}bicyclo[4.4.0]dec-7,8-ene 24a

$[\alpha]_D = -4.5$; HRMS *m*/*z*: 848.3442 [$C_{50}H_{41}NO_{10}Na$ ($M+Na^+$) requires 848.3405]. ^{1}H NMR δ: 6.14 (dd, $J_{8,9}$

2.3, $J_{7,8}$ 10.1, H-8), 5.88 (ddd, $J_{7,9}$ 1.0, $J_{6,7}$ 5.5, H-7), 5.65 (dd, $J_{5,6}$ 1.3, H-6), 5.08 (m, H-1′), 3.86 (m, H-2), 3.78 (t, $J_{1',2'a} = J_{2'a,2'b} = 7.2$, H-2′a), 3.59 (m, H-1, H-3), 3.52 (t, H-2′b), 3.42 (m, H-4), 2.80 (m, H-9), 2.00 (m, H-5, H-10), 1.40 and 1.25 (6H, [CH_3)$_2$C]; ^{13}C NMR δ: 163.6 [CH$_3$C(O)], 132.6 (C-8), 124.0 (C-7),108.6 [(CH$_3$)$_2$$C$], 86.3 and 83.3 (C-1, C-3), 82.5 (C-2), 77.8 (C-4), 75.5 (C-1′), 68.1 (C-6), 64.6 (C-2′), 41.4 and 33.1 (C-5, C-10), 37.1 (C-9), 32.6 (C-10), 25.9 and 24.5 [(CH$_3$)$_2$C].

4.8. Synthesis of the 'inverted' alcohol 24 by S_N2 reaction of the corresponding mesylate

To a vigorously stirred solution of alcohol **21** (53.4 mg, 0.079 mmol) in dichloromethane/triethylamine (3:1 v/v, 4 mL) containing catalytic amounts of DMAP (3 mg), mesyl chloride (90 mg, 0.79 mmol) was added and the mixture was stirred for 4 h. It was then concentrated and the crude mesylate was purified by column chromatography (hexane–diethyl acetate, 3:1) to afford the mesylation product (40 mg). This was dissolved in DMF (5 mL) to which sodium acetate (82 mg, 1 mmol) was added and the reaction mixture was kept at 110 °C until disappearance of the starting material (3 days). The mixture was partitioned between water (10 mL) and ether (20 mL), the organic fractions were collected, washed with brine, dried, concentrated and the product was isolated by column chromatography (hexane–ethyl acetate, 3:1) to afford the desired compound **24b** (21 mg; 37%) as an oil.

4.9. (1*R*,2*R*,3*S*,4*R*,5*R*,6*S*,9*S*,10*R*)-{1,2,3,4-Tetra-*O*-benzyl-6-(*O*-acetyl)-9-[(1′*R*)-5,5-dimethyl-2,4-dioxolane-1′-yl]}bicyclo[4.4.0]dec-7,8-ene 24b

$[\alpha]_D = -13.0$; *m*/*z*: 741.3 [$C_{45}H_{50}O_8Na$ (M+Na$^+$)]. ^{1}H NMR δ: 6.07 (dd, $J_{8,9}$ 2.8, $J_{7,8}$ 10.2, H-8), 5.86 (ddd, $J_{7,9}$ 1.7, $J_{6,7}$ 5.4, H-7), 5.39 (dd, $J_{5,6} = 2.2$, H-6), 5.03 (m, H-1′), 3.85-3.78 (m, H-2, H-2′), 3.60-3.52 (m, H-4, H-3, H-2′), 3.37 (dd, *J* 9.1, *J* 11.5, H-1), 2.75 (m, H-9), 2.06 (m, H-10), 2.01 [s, CH_3C(O)O], 1.85 (m, H-5), 1.41 and 1.21 [6H, (CH_3)$_2$C]; ^{13}C NMR δ: 169.9 [CH$_3$$C$(O)], 131.4 (C-8), 124.7 (C-7), 108.6 [(CH$_3$)$_2$$C$], 86.3, 83.7 (C-4, C-3), 82.6 (C-2), 78.1 (C-1), 75.6 (C-1′), 66.3 (C-6), 64.7 (C-2′), 41.4 (C-5), 36.9 (C-9), 32.6 (C-10), 26.0 and 24.5 [(CH$_3$)$_2$C], 21.1 [CH$_3$C(O)].

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