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Polyannulated Glycopyranosides via Radical-Mediated Tandem Reactions. Stereoselective Synthesis of 6·5·6 Dioxatricycles via 5-exo-trig, 6-endo-dig Mode – III.

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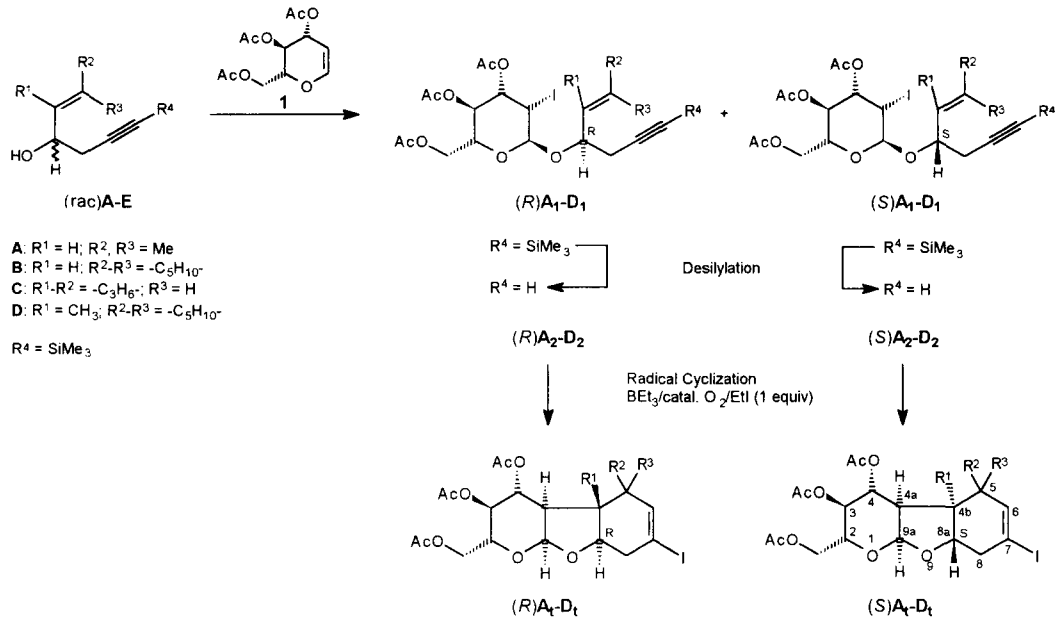
Abstract: A series of C-silylated enynols, e.g. 6-methyl-1-trimethylsilyl-hept-5-en-1-yn-4-ol (*rac*-**A**) was prepared and submitted to *N*-iodosuccinimide mediated iodoalkoxylation of tri-*O*-acetylglycal. Thanks to the presence of the silyl group the resulting diastereomeric glycosides (*S*)$\mathbf{A_1}$ and (*R*)$\mathbf{A_1}$ were readily separated. Triethylborane/oxygen/ethyl iodide promoted iodine transfer afforded doubly annulated glycosides in a 5-exo-trigonal, 6-endo-digonal cascade. The required re-protection of the three acetoxy groups was carried out orthogonally. The newly installed iodocyclohexene moiety served as site for further functionalization, which was accomplished by metal-halogen exchange followed by electrophilic capture or by reduction/epoxidation. © 1997 Elsevier Science Ltd.

In studies directed towards the synthesis of polycyclic glycoconjugates we have developed a radical tandem cyclization[1] of 2β-iodo glucopyranosides.[2] Model studies had shown that a stereoselective consecutive 5-exo-trigonal, 6-endo-digonal cyclization is, in principle, feasible under iodine atom transfer conditions.[3,4] The cyclization precursors were synthesized by *N*-iodosuccinimide (NIS) promoted iodoalkoxylation of cyclic enol ethers.[5]

Using tri-*O*-acetylglycal **1** as an enol ether and various secondary enyne alcohols **A** - **E** as glycosyl acceptors, the yields of iodoglycosylation products were unsatisfactory. In the course of more detailed work we studied *C-trimethylsilylated* enynols. The use of these silylated enynols was advantageous for two reasons. First of all, the iodoglycosylation proceeded in higher yield than with the simple desilylated enynols. More importantly, the resulting diastereomers were now easily separable by conventional flash column chromatography (see Scheme 1). Our diastereomers are defined as either (*S*) or (*R*) by the asymmetric centre of the silylated enynol component. The configuration of the anomeric centre and the remaining four centres of the pyranoside are always unchanged for both (*S*)- and (*R*)-series.

Chemoselective desilylation (KF, 18-crown-6, DMF)[6] furnished the two series of *enantiomerically pure* cyclization precursors (*S*)-$\mathbf{A_2}$ to (*S*)-$\mathbf{E_2}$ and the corresponding (*R*) series (*R*)-$\mathbf{A_2}$ to (*R*)-$\mathbf{E_2}$. These stereodefined precursors allowed us to probe possible transition state models and to optimize yields of polycyclization.

Scheme 1.



The standard Bu_3SnH method of cyclization was unsatisfactory. The cyclization method of choice appears to be the air induced triethylborane protocol.[3,7] Chain-breaking by hydrogen atom transfer, which had been observed as a minor side reaction in our earlier work,[3] was suppressed almost completely. In contrast to the traditional Bu_3SnH method, the cyclization is conducted not only under non-reducing conditions, but also under iodine atom transfer. Careful optimization of the reaction with *additional ethyl iodide*[8] (1 equiv) slowed hydrogen atom transfer to reactive vinylic radicals and improved the termination towards the formation of the desired vinyl iodide. Therefore, our cyclization sequence (Scheme 1) amounts to an atom economical cycloisomerization.[9]

Stereochemical Assignment of Products. The ^1H NMR spectrum of the rigid tricyclization product (*S*)-$\mathbf{A_t}$ (t = tricyclic) showed a well-resolved doublet of doublets ($^3J_{4a,4b}$ = 4.5 Hz, $^3J_{4b,8a}$ = 11.5 Hz) for proton 4b-H.

The bicyclic acetal moiety of the cyclization products is *cis*-fused, in accord with general experience for 5-exo-trigonal annulations. Typically, a small coupling constant $^3J_{4a,9a} \sim 4.5$ Hz was observed. For the (*S*)-series $^3J_{4a,9a}$ is slightly smaller (by ca. 2 Hz) than for the (*R*)-series. In the (*S*)-series proton 8a-H appears 0.6 ppm downfield from the corresponding signal of the (*R*)-series.

In the (*S*)-series the pyranoside ring is a well-developed chair ($^3J_{3,4}$ = 10 Hz), whereas in the (*R*)-series a nonchair conformation is indicated by the corresponding $^3J_{3,4}$ = 1.5 Hz. Repeated crystallization of (*S*)$\mathbf{E_t}$ furnished colorless crystals suitable for X-ray diffraction analysis. The structure confirms the *trans* arrangement of

the fused cyclohexene-furan rings. The pyranosoid chair is also clearly visible.[10] The energetically more costly nonchair conformation of the (*R*)-series is demonstrated by the X-ray crystal structure of a 6·6·5·6 tetraoxatetracycle.[11]

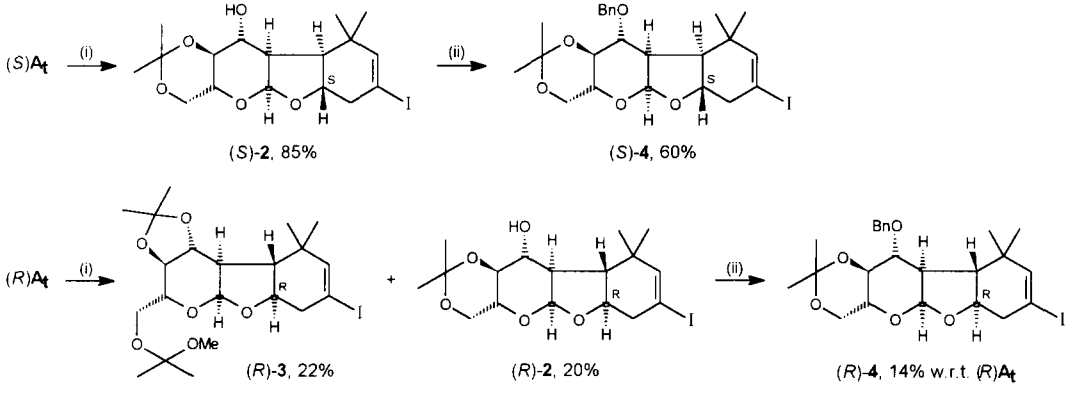
Table 1 shows the variety of 6·5·6 dioxatricycles that have been obtained.

A quaternary centre is readily established (entry 1 - 3). Even *two* contiguous quaternary carbon atoms can be installed in the more favourable (*S*)-series [(*S*)-$\mathbf{D_t}$], containing a pyranosoid chair, but not in the (*R*)-series, where the reaction stops after the first cyclization, giving (*R*)-$\mathbf{D_t}$ (entry 4). A 6-endo-dig cyclization was not observed in this case. The tandem cyclization has also been combined with a spiroannulation (entry 2) and angular annulation (entry 3).

The resulting ring systems are open to the standard reactions of carbohydrate chemistry. For example, the three hydroxy groups of the pyranoside have been chemodifferentiated. Alkaline methanolysis of dioxatricyclic pyranoside (*S*)-$\mathbf{A_t}$ afforded a triol which was converted directly into the primary, secondary 6-membered acetonide (*S*)-**2**. The remaining secondary hydroxy group has been protected orthogonally as benzyl ether (*S*)-**4**.

In the (*R*)-series the pyranoside chair is deformed. Consistently, not only 6-membered, but also 5-membered acetonide, were now formed [(*R*)-**2**/(*R*)-**3**, 1 : 1] (Scheme 2).

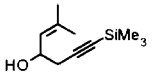
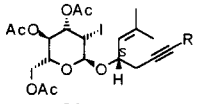
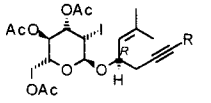
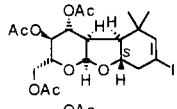
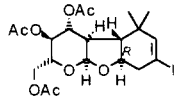
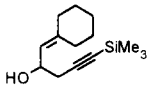
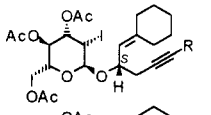
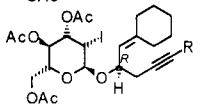
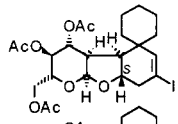
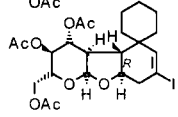
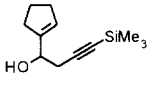
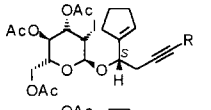
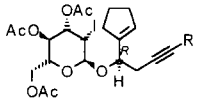
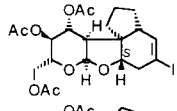
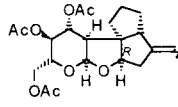
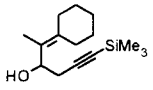
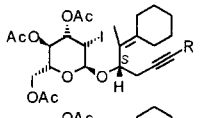
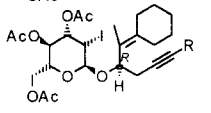
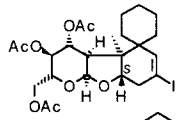
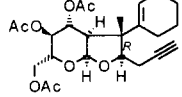
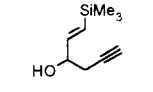
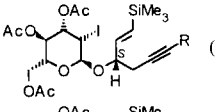
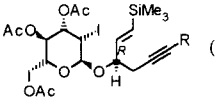
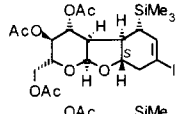
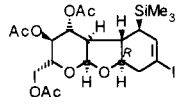
Scheme 2.



(i) 1. NaOMe, MeOH; 2. $(MeO)_2C(CH_3)_2$, H^+, DMF. (ii) BnBr, NaH, nBu$_4$N$^+$I$^-$, THF.

The tandem cycloisomerization generates a vinyl iodide within a rigid glycoconjugate, suitable for further chemoselective manoeuvres. Lithium-iodine exchange in (*S*)-**4** at -78 °C followed by quenching with acetaldehyde[12] was surprisingly efficient, giving allylic alcohol **5** (86%, 1 : 1 diastereomeric mixture), which was oxidized to enone **6** (64%, nonoptimized). Alternatively, (*S*)-**4** was reduced to annulated cyclohexene **7**, which was oxidized to linearly annulated pentacycle **8**, which was diastereomerically pure. Oxidation of cyclohexene **10** with dimethyldioxirane (DDO) at room temperature increased the yield at the expense of stereoselectivity.

Table 1.

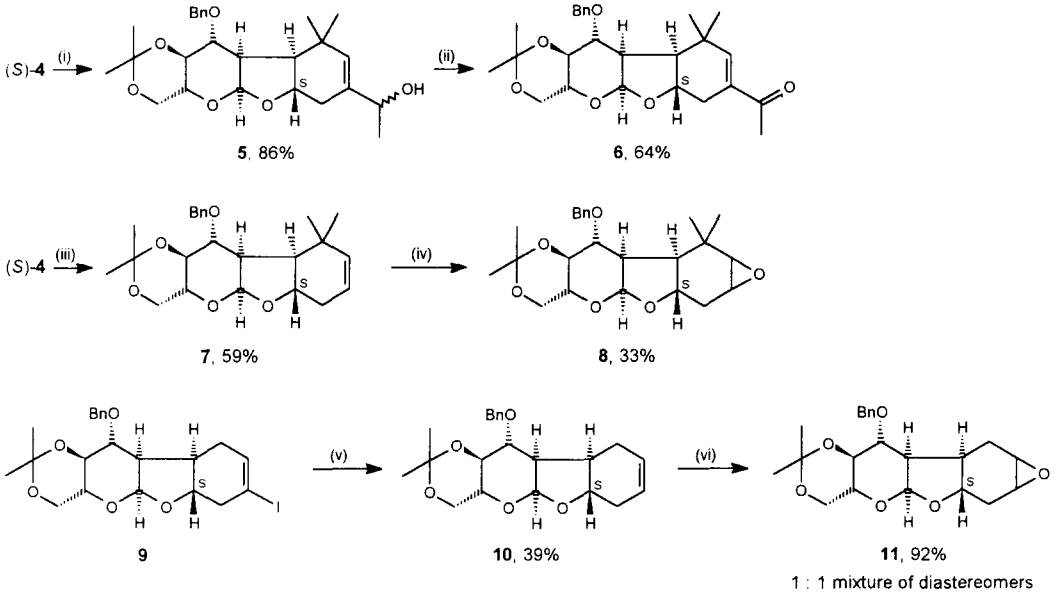
Entry	Aglycon Alcohol	2-β-Iodoglycopyranoside	Yield [%][a]	Cyclization Product	Yield [%]
1	 *rac* **A**	 (*S*)**A**$_1$: R=SiMe$_3$ (*S*)**A**$_2$: R=H  (*R*)**A**$_1$: R=SiMe$_3$ (*R*)**A**$_2$: R=H	69	 (*S*)**A**$_t$  (*R*)**A**$_t$	50 64[b] 51
2	 *rac* **B**	 (*S*)**B**$_1$: R=SiMe$_3$ (*S*)**B**$_2$: R=H  (*R*)**B**$_1$: R=SiMe$_3$ (*R*)**B**$_2$: R=H	38	 (*S*)**B**$_t$  (*R*)**B**$_t$	47 44
3	 *rac* **C**	 (*S*)**C**$_1$: R=SiMe$_3$ (*S*)**C**$_2$: R=H  (*R*)**C**$_1$: R=SiMe$_3$ (*R*)**C**$_2$: R=H	43	 (*S*)**C**$_t$  (*R*)**C**$_t$	78[b] 60[b,c]
4	 *rac* **D**	 (*S*)**D**$_1$: R=SiMe$_3$ (*S*)**D**$_2$: R=H  (*R*)**D**$_1$: R=SiMe$_3$ (*R*)**D**$_2$: R=H	38	 (*S*)**D**$_t$  (*R*)**D**$_t$	35 10
5	 *rac* **E**	 (*S*)**E**$_1$  (*R*)**E**$_1$	53	 (*S*)**E**$_t$  (*R*)**E**$_t$	39 41

[a]The yield refers to the combined trimethylsilylated iodoglycosidation diastereomers. [b]1 eq Et-I. [c]The oxatriquinane (*R*)**C**$_t$ is formed by a *kinetic mistake* during the first 5-exo-trig cyclization which allows a second, 5-exo-dig cyclization accompanied by a *cis* fusion of the tetrahydrofuran/methylenecyclopentane rings. Detailed mechanistic studies are reported in the following paper.

In conclusion, we have elaborated a glycal to 6·5·6 dioxatricycles, which are enantiomerically pure and contain up to 8 stereocentres, in three simple steps (Table 1). Thus, the radical cascade lends itself to asymmetric synthesis. Simple chemical transformations provide enone **6**. The enone group in **6** and the oxirane

group in **8** and **11** open the possibility to prepare a variety of glycoconjugates[2,13,14] containing a novel and rigid spacer. The 6·5·6 fusion of heterocycles improves metabolic stability with respect to glycosidic cleavage. Combination with a lipid and a protein is feasible, e.g. using allylic alcohol **5** and acetylated tetracycle **6**.

Scheme 3.



(i) a) *t*-BuLi, THF, −78 °C; b) CH_3CHO. (ii) Dess-Martin, CH_3CO_2H (trace). (iii) a) *t*-BuLi, THF, −78 °C; b) H_2O. (iv) *m*-CPBA. (v) a) *t*-BuLi, THF, −78 °C; b) H_2O. (vi) dimethyldioxirane.

EXPERIMENTAL

General. Melting points: uncorrected, Büchi apparatus. – Infrared spectra: Perkin-Elmer 1710 spectrometer. – ^1H NMR spectra: At 80, 90 and 200 MHz, Bruker WP 80, WH 90 or WP 200 SY spectrometer, solvent $CDCl_3$ unless stated otherwise. – ^{13}C NMR spectra: Bruker WP 200 SY at 50 MHz. APT (*a*ttached *p*roton *t*est): spin echo base selection of multiplicities of ^{13}C signals. Quaternary C and CH_2 carbon atoms give positive signals (+), while CH and CH_3 give negative signals (−). – MS: Low and high resolution electron impact mass spectra, Finnigan MAT 312 spectrometer, 70 eV, room temperature, unless otherwise stated. Relative intensities in parentheses. – Preparative column chromatography: J. T. Baker silica gel (particle size 30 - 60 μm). – Analytical TLC: Aluminium-backed 0.2 mm silica gel 60 F_{254} plates (E. Merck). – Diethyl ether (E) and THF were distilled from sodium benzophenone ketyl prior to use, CH_2Cl_2 from CaH_2, DMF from BaO. PE refers to light petroleum, bp 30 - 60 °C, redistilled prior to use.

General Procedure for the Preparation of Glycoconjugates via NIS-Addition (Scheme 1). A flame-dried flask was charged with *N*-iodosuccinimide (2 eq) and alcohol (2 eq) at 0 °C under an argon atmosphere. A solution of tri-*O*-acetylglycal in abs. MeCN(1 eq, 1.8 M) was added dropwise at 0 °C. After addition of half of the glycal solution the ice bath was removed und the residual solution was added at r.t. The mixture was stirred for 48 h, then E was added, the organic phase washed with bisulfite solution (8%) and dried ($MgSO_4$). The solvent was evaporated and the crude product purified by chromatography. In this fashion, separation of the diastereomeric adducts was accomplished, e.g. (*S*)**A**$_1$ from (*R*)**A**$_2$, etc. (Table 1).

α-[4′(S),6′-Methyl-1′-trimethylsilyl-hept-5′-en-1′-yn-4′-yl]-3,4,6-tri-O-acetyl-2-deoxy-2-iodo-D-mannopyranoside [(*S*)**A**$_1$] *and α-[4′(R),6′-Methyl-1′-trimethylsilyl-hept-5′-en-1′-yn-4′-yl]-3,4,6-tri-O-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*R*)**A**$_1$]. Glycal (0.95 g, 3.5 mmol), NIS (1.57 g, 7.0 mmol) and alcohol *rac* **A** (1.37 g, 7.0 mmol) were allowed to react according to the general procedure to afford after chromatography (E/PE, 1 : 8) (*S*)**A**$_1$ (660 mg) and (*R*)**A**$_1$ (540 mg) (together 57%), colourless, foaming oils. Data for (*S*)**A**$_1$: IR ($CHCl_3$): ν = 2956 cm^{-1}, 1744, 1608, 1368, 1240, 1116, 1088, 1064; ^{1}H NMR (200 MHz, without TMS): δ = 5.41 (t, *J* = 9.5 Hz, 1H; H-4), 5.14 (s, 1H; H-1), 4.94 (dm, *J* = 9.5 Hz, 1H; H-5′), 4.67 (dd, *J* = 5, 10 Hz, 1H; H-3), 4.56 - 4.40 (m, 2H; H-4′, H-2), 4.38 - 4.06 (m, 3H; H-5, H-6), 2.54 (dd, *J* = 8.5, 17 Hz, 1H; H-3′), 2.34 (dd, *J* = 5, 17 Hz, 1H; H-3′), 2.12, 2.08, 2.04 (3 s, 3×3H; $COCH_3$), 1.76 (d, *J*= 0.5 Hz, 3H; CH_3), 1.73 (d, *J*= 0.5 Hz, 3H; CH_3), 0.16 (s, 9H; $SiMe_3$); ^{13}C NMR (50 MHz, without TMS, APT): δ = 170.56, 169.66, 169.38 (+, $COCH_3$), 140.25 (+, C-6′), 122.32 (–, C-5′), 103.71 (+, C-2′), 97.40 (–, C-1), 85.86 (+, C-1′), 71.08 (–, C-4′), 69.29, 69.04 (–, C-3, C-5), 67.63 (–, C-4), 62.31 (+, C-6), 30.52 (–, C-2), 26.96 (+, C-3′), 25.93 (–, C-7′), 20.97, 20.74, 20.64 (–, $COCH_3$), 18.39 (–, CH_3), 0.00 (–, $SiMe_3$); MS (190 °C, 70 eV): *m/z* (%): 579 (2) [M$^+$ – Me], 483 (3) [M$^+$ – $SiMe_3$], 399 (100), 338 (15), 279 (28), 237 (45), 169 (22). Data for (*R*)**A**$_1$: ^{1}H NMR (200 MHz, without TMS): δ = 5.50 (s, 1H; H-1), 5.38 (t, *J* = 9.5 Hz, 1H; H-4), 5.17 (dm, *J* = 9.5 Hz, 1H; H-5′), 4.74 (dd, *J* = 4.5, 9.5 Hz, 1H; H-3), 4.56 (dd, *J* = 1, 4 Hz, 1H; H-2), 4.53 - 4.42 (m, 1H; H-4′), 4.22 (dd, *J* = 4, 12 Hz, 1H; H-6), 4.10 - 3.95 (m, 2H; H-11, H-6), 2.52 (dd, *J* = 7.5, 19 Hz, 1H; H-3′), 2.32 (dd, *J* = 5, 19 Hz, 1H; H-3′), 2.10, 2.06, 2.04 (3 s, 3×3H; OAc), 1.74 (d, *J*= 0.5 Hz, 3H; CH_3), 1.70 (d, *J*= 0.5 Hz, 3H; CH_3), 0.16 (s, 9H; $SiMe_3$).

α-[4′(S),6′-Cyclohexylidene-1′-trimethylsilyl-hex-5′-en-1′-yn-4′-yl]-3,4,6-tri-O-acetyl-2-deoxy-2-iodo-D-mannopyranoside [(*S*)**B**$_1$] *and α-[4′(R),6′-Cyclohexylidene-1′-trimethylsilyl-hex-5′-en-1′-yn-4′-yl]-3,4,6-tri-O-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*R*)**B**$_1$]. Glycal (1.23 g, 4.5 mmol), NIS (3.45 g, 15.4 mmol) and alcohol *rac* **B** (2.28 g, 6.8 mmol) were allowed to react according to the general procedure to afford after chromatography (E/PE, 1 : 8) (*S*)**B**$_1$ (600 mg) and (*R*)**B**$_1$ (480 mg) (together 38%), colourless, foaming oils. Data for (*S*)**B**$_1$: IR ($CHCl_3$): ν = 2936 cm^{-1}, 2856, 2176, 1744, 1268, 1236, 1040, 844; ^{1}H NMR (200 MHz, without TMS): δ = 5.40 (t, *J* = 10 Hz, 1H; H-4), 5.14 (s, 1H; H-1), 4.86 (d, *J* = 9.5 Hz, 1H; H-5′), 4.67 (dd, *J* = 4, 9.5 Hz, 1H; H-3), 4.58 - 4.44 (m, 2H; H-4′, H-2), 4.38 - 4.28 (m, 1H; H-5), 4.27 - 4.07 (m, 2H; H-6), 2.56 (dd, *J* = 8, 17 Hz, 1H; H-3′), 2.34 (dd, *J* = 5, 17 Hz, 1H; H-3′), 2.24 - 2.00 (m, 4H; H-7′, H-8′), 2.12, 2.09, 2.04 (3 s, 3×3H; $COCH_3$), 1.70 - 1.40 (br. s, 6H; H-9′, H-10′, H-11′), 0.16 (s, 9H; $SiMe_3$); ^{13}C NMR (50 MHz, without TMS, APT): δ = 170.66, 169.77, 169.47 (+, $COCH_3$), 148.39 (+, C-6′), 118.77 (–, C-5′), 103.71 (+, C-2′), 97.36 (–, C-1), 85.85 (+, C-1′), 70.27 (–, C-3), 69.32 (–, C-4), 68.94 (–, C-5), 67.66 (–, C-4′), 62.34 (+, C-6), 37.17 (+, C-11′), 30.54 (–, C-2), 29.37, 28.66, 28.23, 27.24, 26.52 (+, C-3′, C-7′, C-8′, C-9′, C-10′), 20.98, 20.74, 20.63 (–, $COCH_3$), –0.02 (–, $SiMe_3$); MS (70eV): *m/z* (%): 524 (M$^+$–$C_3H_2SiMe_3$,

2), 400 (100), 339 (19), 279 (27), 237 (41). Data for (*R*)**B**$_1$: ^{1}H NMR (200 MHz, without TMS): δ = 5.49 (s, 1H; H-1), 5.43 (t, *J* = 10 Hz, 1H; H-4), 5.10 (d, *J* = 9.5 Hz, 1H; H-5′), 4.67 (dd, *J* = 2.5, 9.5 Hz, 1H; H-3), 4.58 - 4.48 (m, 1H; H-4′), 4.55 (dd, *J* =1, 4.5 Hz, 1H; H-2), 4.30 - 4.18 (m, 1H; H-6), 4.10 - 3.96 (m, 2H; H-5, H-6), 2.54 (dd, *J* = 7.5, 17 Hz, 1H; H-3′), 2.34 (dd, *J* = 5, 17 Hz, 1H; H-3′), 2.17 - 1.98 (m, 4H; H-7′, H-8′), 2.13, 2.09, 2.05 (3 s, 3 × 3H; $COCH_3$), 1.55 (br. s, 6H; H-9′, H-10′, H-11′), 0.17 (s, 9H; $SiMe_3$).

*α-[4′(S)-Cyclopent-5′-enyl-1′-trimethylsilyl-but-1′-ynyl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-manno-pyranoside* [(*S*)**C**$_1$] *and α-[4′(R)-Cyclopent-5′-enyl-1′-trimethylsilyl-but-1′-ynyl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*R*)**C**$_1$]. Glycal and *rac* **C** (1 mmol) were allowed to react according to the general procedure to afford (*S*)**C**$_1$ (146 mg, 24%) and (*R*)**C**$_1$ (115 mg, 19%), yellowish, viscous oils. Data for (*S*)**C**$_1$. IR ($CHCl_3$): ν = 3000 cm^{-1}, 2956, 2928, 2852, 2176, 1744, 1444, 1428, 1368, 1236, 1116, 1036, 968; ^{1}H NMR (200 MHz): δ = 5.67 (m, 1H; H-6′), 5.05 (s, 1H; H-1), 5.37 (br. dt, *J* = 9 Hz, 1H; H-4), 4.63 (dd, *J* = 5, 10 Hz, 1H; H-3), 4.42 (br. dd, *J* = 5, 9 Hz, 1H; H-2), 4.24 - 3.98 (m, 4H; H-4′, H-5, H-6), 2.60 (dd, *J* = 9, 17 Hz, 1H; H-3′), 2.44 (dd, *J* = 5, 17 Hz, 1H; H-3′), 2.31 (m, 4H; CH_2), 2.11, 2.09, 2.05 (3 s, 3×3H; $COCH_3$), 1.95 - 1.71 (m, 2H; CH_2), 0.15 (m, 9H; $SiMe_3$); ^{13}C NMR (50 MHz, APT): δ = 170.61, 169.72, 169.43 (+, $COCH_3$), 142.55 (+, C-5′), 128.46 (–, C-6′), 102.98 (+, C-2′), 101.33 (–, C-1), 86.81 (+, C-1′), 76.20 (–, C-4′), 69.47 (–, C-3), 68.95 (–, C-4), 67.49 (–, C-5), 62.08 (+, C-6), 32.10 (+, CH_2), 31.17 (+, CH_2), 29.80 (–, C-2), 25.78 (+, CH_2), 23.24 (+, CH_2), 20.90, 20.66, 20.61 (–, $COCH_3$), –0.05 (–, $SiMe_3$); MS (70 eV): *m/z* (%): 606 (0) [M$^+$], 401 (3), 399 (100), 338 (10), 279 (32), 237 (60), 210 (9), 183 (10), 169 (19), 152 (25), 139 (16), 117 (28), 97 (28), 73 (83). Data for (*R*)**C**$_1$: ^{1}H NMR (200 MHz): δ = 5.73 (m, 1H; H-6′), 5.43 (t, *J* = 9 Hz, 1H; H-4), 5.11 (br. s, 1H; H-1), 4.68 (dd, *J* = 5, 10 Hz, 1H; H-3), 4.51 (dd, *J* = 1, 5 Hz, 1H; H-2), 4.48 - 4.34 (m, 2H; H-4′, H-5), 4.29 (dd, *J* = 5, 12 Hz, 1H; H-6), 4.13 (dd, *J* = 3, 12 Hz, 1H; H-6), 2.62 (dd, *J* = 9, 17 Hz, 1H; H-3′), 2.41 (dd, *J* = 5, 17 Hz, 1H; H-3′), 2.40 - 1.80 (m, 6H; CH_2), 2.14, 2.09, 2.03 (3 s, 3 × 3H; $COCH_3$), 0.15 (m, 9H; $SiMe_3$).

*α-[4′(S),5′-Methyl-6′-cyclohexylidene-1′-trimethylsilyl-hex-5′-en-1′-yn-4′-yl]-3,4,6-tri-*O*-acetyl-2-des-oxy-2-iodo-D-man-nopyranoside* [(*S*)**D**$_1$] *and α-[4′(R), 5′-Methyl-6′-cyclohexylidene-1′-trimethylsilyl-hex-5′-en-1′-yn-4′-yl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*R*)**D**$_1$]. Glycal (1.09 g, 4.0 mmol), NIS (1.80 g, 8.0 mmol) and alcohol *rac* **D** (2.00 g, 8.0 mmol) were allowed to react according to the general procedure to give after chromatography (E/PE, 1 : 8) (*S*)**D**$_1$ (500 mg) and (*R*)**D**$_1$ (485 mg) (together 38%), light yellow, foaming oils. Data for (*S*)**D**$_1$: IR ($CHCl_3$): ν = 2960 cm^{-1}, 2932, 2856, 2176, 1744, 1368, 1236, 1040; ^{1}H NMR (200 MHz, without TMS). δ = 5.49 (t, *J* = 10 Hz, 1H; H-4), 4.96 (br. s, 1H; H-1), 4.80 (dd, *J* = 5, 9 Hz, 1H; H-4′), 4.69 (dd, *J* = 4, 10 Hz, 1H; H-3), 4.49 (dd, *J* = 1, 4 Hz, 1H; H-2), 4.36 (dt, *J* = 2, 4 Hz, 1H; H-5), 4.31 - 4.20 (m, 1H; H-6), 4.12 (dd, *J* = 2, 12 Hz, 1H; H-6), 2.65 (dd, *J* = 9, 17 Hz, 1H; H-3′), 2.40 - 2.18 (m, 4H; H-7′, H-8′), 2.32 (dd, *J* = 4, 17 Hz, 1H; H-3′), 2.12, 2.08, 2.04 (3 s, 3×3H; $COCH_3$), 1.75 - 1.17 (m, 9H; H-9′, H-10′, H-11′, CH_3), 0.15 (s, 9H; $SiMe_3$); MS (120 °C, 70 eV): *m/z*(%): 538 (3) [M$^+$ – $C_3H_2SiMe_3$], 400 (100), 339 (15), 237 (42), 169 (29). HRMS calcd. for $C_{21}H_{31}O_8I$: 538.1064, found 538.1029. Data for (*R*)**D**$_1$: ^{1}H NMR (200 MHz, without TMS): δ = 5.47 (s, 1H; H-1), 5.42 (t, *J* = 9.5 Hz, 1H; H-4), 4.79 (dd, *J* = 6, 8.5 Hz, 1H; H-4′), 4.66 - 4.56 (m, 2H; H-2, H-3), 4.22 (dd, *J* = 3.5, 12 Hz, 1H; H-6), 3.98 (dd, *J* = 2.5, 12 Hz, 1H; H-6), 3.95 - 3.84 (m, 1H; H-5), 2.63 (dd, *J* = 8.5, 17 Hz, 1H; H-3′), 2.30 (dd, *J* = 6, 17 Hz, 1H; H-3′), 2.13, 2.08, 2.05 (3 s, 3 × 3H; $COCH_3$), 1.73 - 1.30 (m, 10H; H-7′, H-8′, H-9′, H-10′, H-11′), 1.65 (s, 3H; CH_3), 0.17 (s, 9H; $SiMe_3$); ^{13}C NMR (50 MHz, without TMS, APT): δ = 170.79, 169.83, 169.44 (+,

*C*OCH$_3$), 137.82 (+, C-6′), 122.66 (–, C-5′), 103.20 (+, C-2′), 101.51 (–, C-1), 86.32 (+, C-1′), 75.82 (–, C-4′), 69.50 (–, C-3), 69.06 (–, C-5), 67.37 (–, C-4), 61.89 (+, C-6), 31.01, 30.32 (+, C-7′, C-8′), 29.74 (–, C-2), 28.44, 27.94, 26.71, 25.48 (+, C-3′, C-9′, C-10′, C-11′), 20.97, 20.75, 20.66 (–, CO*C*H$_3$), –0.07 (–, SiMe$_3$).

*α-[4′(S),6′-Trimethylsilyl-hex-5′-en-1′-yn-4′-yl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*S*)**E**$_1$] *and α-[4′(R),6′-Trimethylsilyl-hex-5′-en-1′-yn-4′-yl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*R*)**E**$_1$]. Glycal (1.82 g, 6.7 mmol), NIS (2.24 g, 10.0 mmol) and alcohol *rac* **E** (1.37 g, 7.0 mmol) were allowed to react according to the general procedure to give after chromatography (E/PE, 1 : 8) (*S*)**E**$_1$ (1.10 g) and (*R*)**E**$_1$ (1.06 g) (53% altogehter), colourless, foaming oils. Data of (*S*)**E**$_1$: IR ($CHCl_3$): ν = 3294 cm^{-1}, 2954, 2121, 1747, 1369, 1174, 1045, 841; ^{1}H NMR (200 MHz, without TMS): δ = 6.00 (d, *J* = 18 Hz, 1H; H-6′), 5.78 (dd, *J* = 7, 18 Hz, H-5′), 5.43 (br. s, 1H; H-1), 5.38 (t, *J* = 10 Hz, H-4), 4.65 (dd, *J* = 4, 10 Hz, 1H; H-3), 4.57 (dd, *J* = 1, 4 Hz, 1H; H-2), 4.26 - 4.10 (m, 2H; H-4′, H-5), 4.08 - 4.04 (m, 1H; H-6), 4.00 (dt, *J* = 2.5, 5 Hz, 1H; H-6), 2.48 (ddd, *J* = 2.5, 7, 17 Hz, 1H; H-3′), 2.37 (ddd, *J* = 2.5, 7, 17 Hz, 1H; H-3′), 2.09, 2.06, 2.02 (3 s, 3×3H; $COCH_3$), 2.00 (t, *J* = 2.5 Hz, 1H; H-1′), 0.04 (s, 9H; $SiMe_3$); ^{13}C NMR (50 MHz, without TMS, APT): δ = 170.57, 169.78, 169.38 (+, *C*OCH$_3$), 143.18 (–, C-6′), 133.46 (–, C-5′), 101.11 (–, C-1), 79.93 (+, C-2′), 79.43 (–, C-4′), 70.41 (+, C-1′), 69.43 (–, C-3), 68.90 (–, C-4), 67.37 (–, C-5), 61.76 (+, C-6), 29.61 (–, C-2), 25.10 (+, C-3′), 20.90, 20.67, 20.59 (–, CO*C*H$_3$), –1.55 (–, SiMe$_3$); MS (70 eV): *m z* (%): 567 (1) [M$^+$ + 1], 551 (5) [M$^+$ – CH_3], 401 (52), 399 (100), 237 (46), 169 (22), 97 (24). Data of (*R*)**E**$_1$: ^{1}H NMR (200 MHz, without TMS): δ = 5.98 (d, *J* = 18 Hz, 1H; H-6′), 5.77 (dd, *J* = 6.5, 18 Hz, H-5′), 5.40 (t, *J* = 10 Hz, H-4), 5.20 (d, *J* = 1.5 Hz, 1H; H-1), 4.67 (ddd, *J* = 0.5, 4, 10 Hz, 1H; H-3), 4.55 (dd, *J* = 1.5, 4 Hz, 1H; H-2), 4.25 - 4.10 (m, 2H; H-6), 4.36 (ddd, *J* = 2, 4, 10 Hz, 1H; H-5), 2.53 (ddd, *J* = 2.5, 8, 17 Hz, 1H; H-3′), 2.40 (ddd, *J* = 2.5, 5.5, 17 Hz, 1H; H-3′), 2.14, 2.10, 2.07 (3 s, 3 × 3H; $COCH_3$), 2.00 (t, *J* = 2.5 Hz, 1H; H-1′), 0.10 (s, 9H; $SiMe_3$).

General Procedure for the Desilylation. To a solution of silylated pyranoside (cf. Table 1) (1 eq) in DMF was added KF (1.1 eq), 18-crown-6 (0.05 eq) and H_2O (1 drop) at 0 °C. The reaction mixture was stirred for 25 min and then diluted with E. The organic layer was washed with water and the aqueous phase reextracted with E (3 ×). The combined organic phase was washed with brine, dried ($MgSO_4$) and evaporated. The crude product was purified by chromatography.

*α-[4′(S),6′-Methyl-hept-5′-en-1′-yn-4′-yl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*S*)**A**$_2$]. (*S*)**A**$_1$ (660 mg, 1.10 mmol) and TBAF (316 mg, 1.0 mmol) were allowed to react according to the general procedure for 2 h. Chromatography (E/PE, 1 : 2) gave (*S*)**A**$_2$, 320 mg (60%), colourless, foaming oil. ^{1}H NMR (200 MHz): δ = 5.44 (s, 1H; H-1), 5.40 (t, *J* = 9.5 Hz, 1H; H-4), 5.20 (dm, *J* = 9.5 Hz, 1H; H-5′), 4.66 (ddd, *J* = 0.5, 5, 10 Hz, 1H; H-3), 4.56 (dd, *J* = 1.5, 4.5 Hz, 1H; H-2), 4.48 (ddd, *J* = 5.5, 7, 9.5 Hz, 1H; H-4′), 4.24 (dd, *J* = 4, 12.5 Hz, 1H; H-6), 4.12 - 3.96 (m, 2H; H-5, H-6), 2.48 (ddd, *J* = 2.5, 7.5, 17 Hz, 1H; H-3′), 2.34 (ddd, *J* = 2.5, 5.5, 17 Hz, 1H; H-3′), 2.12, 2.08, 2.04 (3 s, 3×3H; $COCH_3$), 2.00 (t, *J* = 2.5 Hz, 1H; H-1′), 1.76 (d, *J* = 2.5 Hz, 3H; CH_3), 1.72 (d, *J* = 1.5 Hz, 3H; CH_3).

*α-[4′(R),6′-Methyl-hept-5′-en-1′-yn-4′-yl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside*[(*R*)-**A**$_2$]. (*R*)**A**$_1$ (540 mg, 0.91 mmol), KF (69.5 mg, 1.22 mmol) and 18-crown-6 (14.6 mg, 0.055 mmol) were allowed to react according to the general procedure to afford after chromatography (*R*)**A**$_2$, 505 mg (88%), colourless, foaming oil. ^{1}H NMR (200 MHz): δ = 5.38 (t, *J* = 9.5 Hz, 1H; H-4), 5.13 (s, 1H; H-1), 4.98 (dm, *J*

= 9.5 Hz, 1H; H-5′), 4.76 (ddd, *J* = 1, 4.5, 9.5 Hz, 1H; H-3), 4.64 - 4.42 (m, 2H; H-4′, H-2), 4.34 - 4.20 (m, 1H; H-5), 4.24 (dd, *J* = 4.5, 15.5 Hz, 1H; H-6), 4.14 (dd, *J* = 2, 15.5 Hz, 1H; H-6), 2.52 (ddd, *J* = 2.5, 7.5, 17 Hz, 1H; H-3′), 2.34 (ddd, *J* = 2.5, 5, 19 Hz, 1H; H-3′), 2.12, 2.08, 2.06 (3 s, 3×3H; $COCH_3$), 2.00 (t, *J* = 2.5 Hz, 1H; H-1′), 1.78 (d, *J* = 2.5 Hz, 3H; CH_3), 1.70 (d, *J* = 1.5 Hz, 3H; CH_3).

*α-[4′(S),6′-Cyclohexylidene-hex-5′-en-1′-yn-4′-yl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*S*)**B**$_2$]. (*S*)**B**$_1$ (315 mg, 0.56 mmol), KF (35.4 mg, 0.61 mmol) and 18-crown-6 (7.4 mg, 0.028 mmol) were allowed to react according to the general procedure for 30 min. Chromatography gave (*S*)**B**$_2$, 275 mg (88%), colourless, foaming oil. ^{1}H NMR (200 MHz): δ = 5.44 (s, 1H; H-1), 5.42 (t, *J* = 10 Hz, 1H; H-4), 5.14 (br. d, *J* = 9.5 Hz, 1H; H-5′), 4.67 (ddd, *J* = 0.5, 5, 9.5 Hz, 1H; H-3), 4.62 - 4.48 (m, 2H; H-4′, H-2), 4.25 (dd, *J* = 4, 12.5 Hz, 1H; H-6), 4.12 - 3.96 (m, 2H; H-5, H-6), 2.50 (ddd, *J* = 2.5, 7, 17 Hz, 1H; H-3′), 2.34 (ddd, *J* = 2.5, 5, 17 Hz, 1H; H-3′), 2.26 - 2.03 (m, 4H; H-7′, H-8′), 2.13, 2.08, 2.05 (3 s, 3 × 3H; $COCH_3$), 2.00 (t, *J* = 2.5 Hz, 1H; H-1′), 1.70 - 1.40 (br. s, 6H; H-9′, H-10′, H-11′).

*α-[4′(R),6′-Cyclohexylidene-hex-5′-en-1′-yn-4′-yl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*R*)**B**$_2$]. (*R*)**B**$_1$ (440 mg, 0.79 mmol), KF (35.4 mg, 0.61 mmol) and TBAHS (7.4 mg, 0.028 mmol) were allowed to react according to the general procedure for 5 d to afford after chromatography (*R*)**B**$_2$, 340 mg (77%), colourless, foaming oil. ^{1}H NMR (200 MHz): δ = 5.37 (t, *J* = 10 Hz, 1H; H-4), 5.14 (s, 1H; H-1), 4.93 (d, *J* = 10 Hz, 1H; H-5′), 4.66 (dd, *J* = 4.5, 10 Hz, 1H; H-3), 4.57 - 4.48 (m, 2H; H-4′, H-2), 4.33 - 4.25 (m, 1H; H-5), 4.23 (dd, *J* = 5, 12 Hz, 1H; H-6), 4.14 (dd, *J* = 2.5, 12 Hz, 1H; H-6), 2.52 (dddd, *J* = 0.5, 2.5, 5.5, 17 Hz, 1H; H-3′), 2.36 (dddd, *J* = 0.5, 2.5, 5.5, 17 Hz, 1H; H-3′), 2.24 - 2.16 (m, 2H; H-7′, H-8′), 2.15 - 2.03 (m, 2H; H-7′, H-8′), 2.12, 2.08, 2.06 (3 s, 3×3H; $COCH_3$), 1.99 (t, *J* = 2.5 Hz, 1H; H-1′), 1.65 - 1.48 (br. s, 6H; H-9′, H-10′, H-11′).

*α-[4′(S)-Cyclopent-5′-enyl-but-1′-ynyl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*S*)-**C**$_2$]. (*S*)**C**$_1$ (1 mmol) was allowed to react according to the general procedure to give (*S*)**C**$_2$, 460 mg (86%), colourless, viscous oil. ^{1}H NMR (200 MHz): δ = 5.71 (m, 1H; H-6′), 5.43 (s, 1H; H-1), 5.38 (t, *J* = 9 Hz, 1H; H-4), 4.65 - 4.42 (m, 2H; H-2, H-3), 4.41 (br. t, *J* = 7 Hz, 1H; H-4′), 4.23 - 3.99 (m, 3H; H-5, H-6), 2.58 (ddd, *J* = 2, 9, 17 Hz, 1H; H-3′), 2.50 - 2.24 (m, 5H; H-3′, CH_2), 2.12, 2.09, 2.06 (3 s, 3×3H; $COCH_3$), 2.02 (t, *J* = 3 Hz, 1H; H-1′), 1.99 - 1.79 (m, 2H; CH_2).

*α-[4′(R)-Cyclopent-5′-enyl-but-1′-ynyl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*R*)-**C**$_2$]. (*R*)**C**$_1$ (1 mmol) was allowed to react according to the general procedure to give (*R*)**C**$_2$, 449 mg (84%), colourless, viscous oil. ^{1}H NMR (200 MHz): δ = 5.73 (t, *J* = 2 Hz, 1H; H-6′), 5.38 (t, *J* = 9 Hz, 1H; H-4), 5.11 (br. s, 1H; H-1), 4.68 (dd, *J* = 5, 10 Hz, 1H; H-3), 4.50 (dd, *J* = 1, 5 Hz, 1H; H-2), 4.48 - 4.32 (m, 2H; H-4′, H-5), 4.27 (dd, *J* = 5, 12 Hz, 1H; H-6), 4.13 (dd, *J* = 3, 12 Hz, 1H; H-6), 2.59 (ddd, *J* = 3 ,9 ,17 Hz, 1H; H-3′), 2.45 - 2.18 (m, 5H; H-3′, CH_2), 2.14, 2.09, 2.03 (3 s, 3×3H; $COCH_3$), 1.99 (t, *J* = 3 Hz, 1H; H-1′), 1.98 - 1.82 (m, 2H; CH_2).

*α-[4′(S),5′-Methyl-6′-cyclohexylidene-hex-5′-en-1′-yn-4′-yl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*S*)**D**$_2$]. (*S*)**D**$_1$ (470 mg, 0.72 mmol), KF (50 mg, 0.8 mmol) and 18-crown-6 (10 mg, 0.04 mmol) were allowed to react according to the general procedure for 30 min. Chromatography gave (*S*)**D**$_2$, 320 mg (76%), light yellow, foaming oil. ^{1}H NMR (200 MHz) δ 5.36 (t, *J* = 10 Hz, 1H; H-4), 4.97 (s, 1H; H-1), 4.83 (dd, *J* = 6, 8 Hz, 1H; H-4′), 4.69 (dd, *J* = 4, 10 Hz, 1H; H-3), 4.48 (dd, *J* = 1, 4 Hz, 1H; H-2), 4.32 (ddd, *J* = 2.5, 5, 10 Hz, 1H; H-5), 4.22 (dd, *J* = 5, 12 Hz, 1H; H-6), 4.14 (dd, *J* = 2.5, 12 Hz, 1H; H-6), 2.59 (ddd, *J* =

2.5, 8, 17 Hz, 1H; H-3′), 2.36 - 2.19 (m, 4H; H-7′, H-8′), 2.32 (ddd, *J* = 2.5, 6, 17 Hz, 1H; H-3′), 2.12, 2.10, 2.07 (3 s, 3×3H; $COCH_3$), 1.97 (t, *J* = 2.5 Hz, 1H; H-1′), 1.70 - 1.40 (m, 9H; H-9′, H-10′, H-11′, CH_3).

*α-[4′(S),5′-Methyl-6′-cyclohexylidene-hex-5′-en-1′-yn-4′-yl]-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-D-mannopyranoside* [(*R*)**D**$_2$]. (*R*)**D**$_1$ (430 mg, 0.67 mmol), KF (40 mg, 0.74 mmol) and 18-crown-6 (10 mg, 0.03 mmol) were allowed to react according to the general procedure for 30 min. Chromatography gave (*R*)**D**$_2$, 350 mg (90%), light yellow, foaming oil. ^{1}H NMR (200 MHz): δ = 5.47 - 5.33 (m, 2H; H-1, H-4), 4.80 (dd, *J* = 6, 8 Hz, 1H; H-4′), 4.68 - 4.57 (m, 2H; H-2, H-3), 4.22 (dd, *J* = 4, 12.5 Hz, 1H; H-6), 3.99 (dd, *J* = 2.5, 12.5 Hz, 1H; H-6), 3.93 (ddd, *J* = 2.5, 4, 10 Hz, 1H; H-5), 2.59 (ddd, *J* = 2.5, 8, 17 Hz, 1H; H-3′), 2.39 - 2.03 (m, 4H; H-7′, H-8′), 2.30 (ddd, *J* = 2.5, 6, 17 Hz, 1H; H-3′), 2.12, 2.09, 2.05 (3 s, 3×3H; $COCH_3$), 1.99 (t, *J* = 2.5 Hz, 1H; H-1′), 1.66 (s, 3H; CH_3), 1.64 - 1.40 (m, 6H; H-9′, H-10′, H-11′).

General Procedure for the Cyclization with BEt$_3$/catal. O$_2$/EtI. A flame-dried two-necked flask equipped with reflux condenser, $CaCl_2$ drying tube and septum was charged with cyclization precursor in abs. solvent (0.5 M) under dry air atmosphere. EtI (1 eq) was added and the mixture was heated to reflux. BEt_3 (2 eq, 1 M in hexane) from a freh opened bottle was added dropwise within 10 min. The reaction was monitored by TLC (for cyclizations on a >1 mmol scale dry air from a balloon is blown through the reaction flask every 10 min for a few sec.). After complete reaction the mixture was cooled to r.t., the solvent removed and the crude product purified by chromatography.

*2(R),3(S),4(R),4a(R),4b(S),8a(S),9a(S)-2-Acetoxymethyl-5-dimethyl-7-iodo-3,4,4a,4b,5,8,8a,9a-octahydro-2*H*-pyrano[2,3-b]benzofuran-3,4-diol Diacetate* [(*S*)**A**$_t$]. (*S*)**A**$_2$ (320 mg, 0.632 mmol) was allowed to react according to the general procedure for 30 min to afford after chromatography (E/PE, 1 : 3) (*S*)**A**$_t$, 160 mg (50%), white foam, $[\alpha]_D^{20}$ −57.6° (*c* =1.025 in CH_2Cl_2). IR ($CHCl_3$): ν = 3000 cm^{-1}, 2960, 2932, 1748, 1368, 1248, 1064; ^{1}H NMR (200 MHz): δ = 6.06 (dd, *J* = 1, 2.5 Hz, 1H; H-6), 5.55 (d, *J* = 4.5 Hz, 1H; H-9a), 5.12 - 4.98 (m, 2H; H-4, H-3), 4.44 (dd, *J* = 4, 12 Hz, 1H; H-10), 4.34 (ddd, *J* = 6, 9, 11.5 Hz, 1H; H-8a), 4.12 - 4.08 (m, 1H; H-2), 4.06 (dd, *J* = 2, 12 Hz, 1H; H-10), 3.08 (ddd, *J* = 1, 6, 17 Hz, 1H; H-8), 2.68 - 2.52 (m, 2H; H-8, H-4a), 2.08, 2.03, 2.02 (3 s, 3 × 3H; $COCH_3$), 2.08 (dd, *J* = 4.5, 11.5 Hz, 1H; H-4b), 1.11 (s, 3H; CH_3), 0.92 (s, 3H; CH_3); ^{13}C NMR (75 MHz, APT): δ = 170.49, 170.25 (+, *C*OCH_3), 149.09 (−, C-6), 102.02 (−, C-9a), 89.36 (+, C-7), 73.77 (−, C-8a), 70.64 (+, C-4), 69.40 (−, C-3), 67.67 (−, C-2), 61.78 (+, C-10), 51.68 (−, C-4b), 47.42 (+, C-8), 42.39 (−, C-4a), 39.78 (+, C-5), 28.31, 22.90 (−, CH_3), 21.21, 20.73, 20.61 (−, $COCH_3$); MS (150 °C, 70 eV): *m/z* (%): 524 (4) [M^+ + 1], 523 (7) [M^+], 461 (13), 402 (19), 360 (18), 234 (25), 213 (60), 69 (100). $C_{20}H_{27}O_8I$ (522.3): calcd C 45.99, H 5.21; found C 44.97, H 5.42.

*2(R),3(S),4(R),4a(R),4b(R),8a(R),9a(S)-2-Acetoxymethyl-5-dimethyl-7-iodo-3,4,4a,4b,5,8,8a,9a-octahydro-2*H*-pyrano[2,3-b]benzofuran-3,4-diol Diacetate* [(*R*)**A**$_t$]. (*R*)**A**$_2$ (550 mg, 1.05 mmol) was allowed to react according to the general procedure for 30 min to afford after chromatography (E/PE, 1 : 3) (*R*)**A**$_t$, 280 mg (51%), white foam, $[\alpha]_D^{20}$ +142.0° (*c* =1.025 in CH_2Cl_2). IR ($CHCl_3$): ν = 3040 cm^{-1}, 2964, 2872, 1740, 1368, 1232, 1028; ^{1}H NMR (200 MHz): δ = 6.08 (d, *J* = 2.5 Hz, 1H; H-6), 5.52 (d, *J* = 7 Hz, 1H; H-9a), 5.08 (dd, *J* = 1.5, 3 Hz, 1H; H-4), 4.96 (dt, *J* = 1.5, 8.5 Hz, 1H; H-3), 4.23 (d, *J* = 4.5 Hz, 2H; H-10), 4.02 (ddd, *J* = 4.5, 8.5 Hz, 1H; H-2), 3.68 (ddd, *J* = 5.5, 9.5, 11 Hz, 1H; H-8a), 3.00 (ddd, *J* = 1, 5.5, 16.5 Hz, 1H; H-8), 2.72 (ddd, *J* = 3, 9.5, 16.5 Hz, 1H; H-8), 2.56 - 2.32 (m, 1H; H-4a), 2.13, 2.12, 2.10 (3 s, 3×3H; $COCH_3$), 1.84 (dd, *J* = 12, 12.5 Hz, 1H; H-4b), 1.17 (s, 3H; CH_3), 1.02 (s, 3H; CH_3); ^{13}C NMR (75 MHz): δ = 170.43, 169.47, 169.00 (4°, *C*OCH_3), 148.32 (3°, C-6), 98.62 (3°, C-9a), 89.23 (4°, C-7), 74.86 (3°, C-8a), 70.44 (3°, C-4),

68.71 (3°, C-3), 66.65 (3°, C-2), 63.48 (2°, C-10), 49.00 (3°, C-4b), 45.40 (2°, C-8), 40.38 (3°, C-4a), 40.31 (3°, C-5), 29.57, 22.11 (1°, CH_3), 20.83, 20.70, 20.58 (–, $COCH_3$); MS (120 °C, 70 eV): *m/z* (%): 523 (3) [M^+ + 1], 522 (4) [M^+], 461 (28), 402 (48), 360 (84), 347 (70), 189 (56), 107 (57), 81 (100).

2(R),3(S),4(R),4a(R),4b(S),8a(S),9a(S)-2-Acetoxymethyl-5,5-cyclohexylen-7-iodo-3,4,4a,4b,5,8,8a,9a-octahydro-2H-pyrano[2,3-b]benzofuran-3,4-diol Diacetate [(*S*)**B**$_t$]. (*S*)**B**$_2$ (160 mg, 0.28 mmol) was allowed to react according to the general procedure for 20 min to yield after chromatography (E/PE, 1 : 2) (*S*)**B**$_t$, 74.4 mg (47%), white foam, m.p. 67 °C, $[\alpha]_D^{20}$ +118.6° (*c* =1.045 in CH_2Cl_2). IR (KBr): ν = 2928 cm^{-1}, 1752, 1454, 1367, 1245, 1132, 1062; ^{1}H NMR (200 MHz): δ = 6.74 (dd, *J* = 1 Hz, 1H; H-6), 5.53 (d, *J* = 4.5 Hz, 1H; H-9a), 5.14 (t, *J* = 9.5 Hz, 1H; H-4), 5.05 (t, *J* = 9.5 Hz, 1H; H-3), 4.45 (dd, *J* = 4, 12 Hz, 1H; H-10), 4.53 - 4.38 (m, 1H; H-8a), 4.12 (ddd, *J* = 2, 4, 9 Hz, 1H; H-2), 4.04 (dd, *J* = 2, 12 Hz, 1H; H-10), 3.13 (ddd, *J* = 1, 6.5, 17 Hz, 1H; H-8), 2.71 - 2.55 (m, 2H; H-8, H-4a), 2.08, 2.06, 2.02 (m, 1H; H-4b, 3 s, 3×3H; $COCH_3$), 1.85 - 1.22 (m, 10H; H-11, H-12, H-13, H-14, H-15); ^{13}C NMR (50 MHz, APT): δ = 170.68, 170.42, 170.34 (+, *C*OCH_3), 144.60 (–, C-6), 102.09 (–, C-9a), 91.66 (+, C-7), 72.83 (–, C-8a), 71.31 (–, C-4), 69.39 (–, C-3), 67.57 (–, C-2), 61.85 (+, C-10), 53.16 (–, C-4b), 48.33 (+, C-8), 43.08 (+, C-5), 42.30 (–, C-4a), 35.16, 32.53 (+, C-11, C-12), 26.44 (+, C-15), 21.45, 21.24 (+, C-13, C-14), 21.53, 20.84, 20.74 (–, $COCH_3$); MS (70 eV): *m/z* (%): 562 (2) [M^+], 502 (3), 442 (29), 400 (31), 255 (32), 213 (100), 91 (80).

2(R),3(S),4(R),4a(R),4b(R),8a(R),9a(S)-2-Acetoxymethyl-5,5-cyclohexylen-7-iodo-3,4,4a,4b,5,8,8a,9a-octahydro-2H-pyrano[2,3-b]benzofuran-3,4-diol Diacetate [(*R*)**B**$_t$]. (*R*)**B**$_2$ (240 mg, 0.43 mmol) was allowed to react according to the general procedure for 20 min to yield after chromatography (CH_2Cl_2/E, 30 : 1) (*R*)**B**$_t$, 105 mg (44%), white foam, m.p. 62 - 65 °C, $[\alpha]_D^{20}$ –42.7° (*c* =0.955 in CH_2Cl_2). IR (KBr): ν = 2932 cm^{-1}, 2865, 1742, 1454, 1370, 1234, 1036; ^{1}H NMR (200 MHz): δ = 6.76 (dd, *J* = 1.5 Hz, 1H; H-6), 5.48 (d, *J* = 7 Hz, 1H; H-9a), 5.14 (dd, *J* = 1.5, 3 Hz, 1H; H-4), 4.94 (dt, *J* = 1.5, 8.5 Hz, 1H; H-3), 4.23 (d, *J* = 4.5 Hz, 2H; H-10), 4.06 - 3.96 (m, 1H; H-2), 3.79 (ddd, *J* = 5.5, 9.5, 11 Hz, 1H; H-8a), 3.04 (ddd, *J* = 1, 5.5, 17 Hz, 1H; H-8), 2.73 (ddd, *J* = 2.5, 9.5, 17 Hz, 1H; H-8), 2.66 - 2.52 (m, 1H; H-4a), 2.13, 2.11, 2.09 (3 s, 3×3H; $COCH_3$), 1.86 - 1.22 (m, 11H; H-11, H-12, H-13, H-14, H-15), 1.80 (t, *J* = 11 Hz, 1H; H-4b); ^{13}C NMR (50 MHz, APT): δ = 170.71, 169.78, 169.27 (+, *C*OCH_3), 143.57 (–, C-6), 99.20 (–, C-9a), 91.06 (+, C-7), 74.16 (–, C-8a), 70.98 (–, C-4), 68.78 (–, C-3), 66.95 (–, C-3), 63.65 (+, C-10), 50.13 (–, C-4b), 46.40 (+, C-8), 43.50 (+, C-5), 39.77 (–, C-4a), 37.24, 32.22 (+, C-11, C-12), 26.04 (+, C-15), 21.60, 21.47 (+, C-13, C-14), 21.02, 20.92, 20.78 (–, $COCH_3$); MS (70 eV): *m/z* (%): 562 (3) [M^+], 502 (6), 442 (11), 400 (14), 235 (19), 145 (75), 84 (100); HRMS calcd for $C_{21}H_{27}O_6I$: 502.0878, found 502.0852.

Tetracycle [(*S*)**C**$_t$]. (*S*)**C**$_2$ (0.5 mmol) was allowed to react according to the general procedure to yield (*S*)**C**$_t$, 208 mg (78%), colourless crystals, m.p. 63 -66 °C. IR ($CHCl_3$): ν = 3028 cm^{-1}, 2956, 2872, 1748, 1640, 1452, 1368, 1248, 1160, 1072, 1044, 980; ^{1}H NMR (200 MHz): δ = 5.98 (m, 1H; IC=CH), 5.64 (d, *J* = 5 Hz, 1H; OCHO), 5.15 (t, *J* = 9 Hz, 1H; CCHC*H*OAc), 4.97 (t, *J* = 10 Hz, 1H; CCHCH(OAc)C*H*OAc), 4.48 - 4.32 (m, 2H; OC*H*CH_2, C*H*HOAc), 4.06 (dd, *J* = 2, 12 Hz, 1H; CH*H*OAc), 3.99 - 3.87 (m, 1H; C*H*CH_2OAc), 3.07 - 2.89 (m, 1H; C*H*HCI), 2.70 - 2.56 (m, 1H; CH*H*CI), 2.50 (m, 1H; ICCHC*H*), 2.30 (dd, *J* = 5, 9 Hz, 1H; CC*H*OAc), 2.08, 2.03, 2.02 (3 s, 3×3H; $COCH_3$), 1.91 - 1.12 (m, 6H; CH_2); ^{13}C NMR (50 MHz, APT): δ = 170.31, 170.07, 169.84 (+, *C*OCH_3), 142.21 (–, IC=*C*H), 101.69 (–, OCHO), 88.74 (+, CI), 77.76 (–, O*C*HCH_2), 70.91 (–, CCH*C*HOAc), 69.03 (–, CCHCH(OAc)*C*HOAc), 68.12 (–, AcOCH_2*C*H), 61.66 (+, AcO*C*H_2), 53.47 (+, *C*$(CH_2)_3$), 48.93 (–, *C*CHCHOAc), 45.24 (–, ICCH*C*H), 40.84 (+, IC*C*H_2), 29.54, 28.57,

21.81 (+, CH_2), 20.64, 20.50, 20.39 (–, $COCH_3$); MS (120 °C, 70 eV): *m/z* (%): 534 (0) [M^+], 475 (1), 312 (3), 288 (5), 262 (100), 244 (10), 213 (37), 163 (9), 136 (62), 118 (29), 91 (17).

Tetracycle [(*R*)**C**$_t$]. (*R*)**C**$_2$ (0.5 mmol) was allowed to react according to the general procedure to give (*R*)**C**$_t$. The two diastereomers were separated to yield 75 mg (28%) of unpolar diastereomer and 43 mg (16%) of polar diastereomer. *E*- and *Z*-isomer could not be separated completely by chromatography. Data of unpolar diastereomer, colourless crystals, m.p. 58 - 61 °C. IR ($CHCl_3$): ν = 3308 cm^{-1}, 3028, 2956, 2908, 1748, 1452, 1368, 1268, 1172, 1132, 1068, 1044, 976; ^{1}H NMR (200 MHz): δ = 6.03 (q, *J* = 2, 5 Hz, 1H; ICH), 5.37 (d, *J* = 5 Hz, 1H; OCHO), 5.11 (t, *J* = 9 Hz, 1H; CCHC*H*OAc), 5.01 (t, *J* = 9 Hz, 1H; CCHCH(OAc)C*H*OAc), 4.37 (dd, *J* = 4, 12 Hz, 1H; OC*H*CH$_2$), 4.18 - 3.99 (m, 3H; AcOCH_2C*H*), 2.96 - 2.83 (br. dd, *J* = 2, 9 Hz, 1H; OCHC*H*H), 2.72 - 2.61 (m, 2H; OCHCH*H*, ICH=CC*H*), 2.30 (dd, *J* = 5, 8 Hz, 1H; CC*H*CHOAc), 2.09, 2.07, 2.02 (3 s, 3×3H; $COCH_3$), 1.98 - 1.41 (m, 6H; CH_2); ^{13}C NMR (50 MHz, APT): δ = 170.48, 170.21, 169.86 (+, COCH_3), 157.93 (+, ICH=*C*), 100.61 (–, OCHO), 86.54 (–, O*C*HCH$_2$), 71.84 (–, ICH), 71.56 (–, CCH*C*HOAc), 69.24 (–, AcOCH$_2$*C*H), 69.19 (–, CCHCH(OAc)*C*HOAc), 63.57 (+, AcO*C*H$_2$), 62.03 (+, *C*(CH$_2$)$_3$), 52.12 (–, ICH=*C*CH), 51.10 (–, *C*CHCHOAc), 43.31 (+, OCH*C*H$_2$), 40.60, 34.69, 25.62 (+, CH_2), 20.81, 20.61, 20.57 (–, $COCH_3$); MS (120 °C, 70 eV): *m/z* (%): 533 (1) [M^+ – 1], 473 (6), 348 (13), 308 (26), 245 (30), 207 (40), 160 (16), 136 (56), 19 (100), 97 (19), 79 (19). Data of polar diastereomer, colourless oil (semi-solid). IR ($CHCl_3$): ν = 2956 cm^{-1}, 1748, 1624, 1452, 1368, 1236, 1172, 1044, 976; ^{1}H NMR (200 MHz): δ = 6.03 (m, 1H; ICH), 5.37 (d, *J* = 5 Hz, 1H; OCHO), 5.12 (m, 2H; CCHC*H*(OAc)C*H*OAc), 4.30 (dd, *J* = 4, 12 Hz, 1H; OC*H*CH$_2$), 4.23 - 3.93 (m, 3H; AcOCH_2C*H*), 3.07 (m, 1H; OCHC*H*H), 2.65 (m, 1H; OCHCH*H*), 2.64 - 2.20 (m, 2H; ICH=CC*H*, CC*H*CHOAc), 2.08, 2.05, 2.02 (3 s, 3×3H; $COCH_3$), 2.00 - 1.41 (m, 6H; CH_2); ^{13}C NMR (50 MHz, APT): δ = 170.59, 169.84, 169.72 (+, COCH_3), 157.39 (+, ICH=*C*), 100.09 (–, OCHO), 86.63 (–, O*C*HCH$_2$), 71.71 (–, CCHCH(OAc)*C*HOAc), 71.85 (–, ICH), 69.01 (–, CCH*C*HOAc, AcOCH$_2$*C*H), 62.56 (+, AcO*C*H$_2$), 62.32 (+, *C*(CH$_2$)$_3$), 52.94 (–, ICH=*C*CH), 52.51 (–, *C*CHCHOAc), 41.19 (+, OCH*C*H$_2$), 36.69, 34.27, 25.68 (+, CH_2), 20.98, 20.80, 20.69 (–, $COCH_3$); MS (120 °C, 70 eV): *m/z* (%): 534 (5) [M^+], 474 (30), 359 (22), 304 (20), 262 (50), 245 (100), 227 (21), 161 (15), 117 (32), 91 (28), 79 (20).

*5′-Cyclohexenyl-5′-methyl-6(*R*)-prop-2′-ynyl-hexahydro-4(*R*),5(*S*)-diacetoxy-6(*S*)-acetoxymethylpyrano[2,3-b]furan* [(*R*)**D**$_t$]. (*R*)**D**$_2$ (350 mg, 0.61 mmol) was allowed to react according to the general procedure for 3 h to afford after chromatography (CH_2Cl_2/E, 30 : 1) (*R*)**D**$_t$, 27 mg (10%), white foam, m.p. 52 - 54 °C, $[\alpha]_D^{20}$ +87.2° (*c* = 0.96 in CH_2Cl_2). IR ($CHCl_3$): ν = 3308 cm^{-1}, 2936, 2120, 1748, 1364, 1248; ^{1}H NMR (200 MHz): δ = 5.68 (d, *J* = 4.5 Hz, 1H; H-9a), 5.51 (br. s, 1H; H-5′), 5.10 (t, *J* = 8 Hz, 1H; H-6), 4.99 (t, *J* = 9.5 Hz, 1H; H-3), 4.65 (dd, *J* = 2.5, 9 Hz, 1H; H-6), 4.49 (dd, *J* = 4, 13 Hz, 1H; H-8), 4.11 - 3.99 (m, 2H; H-2, H-8), 2.53 (dt, *J* = 2.5, 17 Hz, 1H; H-3′), 2.38 - 2.25 (m, 2H; H-3′, H-4a), 2.08 (t, *J* = 2.5 Hz, 1H; H-1′), 2.07, 1.99, 1.98 (3 s, 3×3H; $COCH_3$), 1.88 - 1.50 (m, 4H; H-6′, H-8′), 1.44 - 1.77 (m, 4H; H-7′, H-9′), 1.08 (s, 3H; CH_3); MS (70 eV): *m/z* (%): 409 (1) [$M^+ - C_3H_3$], 381 (3), 260 (33), 200 52), 176 (100).

*2(*R*),3(*S*),4(*R*),4a(*R*),4b(*S*),8a(*S*),9a(*S*)-2-Acetoxymethyl-4b-methyl-5,5-cyclohexylen-7-iodo-3,4,4a,4b,5,8,8a,9a-octahydro-2*H*-pyrano[2.3-b]benzofuran-3,4-diol Diacetate* [(*S*)**D**$_t$]. (*S*)**D**$_2$ (300 mg, 0.52 mmol) was allowed to react according to the general procedure for 2 h to yield after chromatography (two columns, first E/PE, 1 : 3, twice CH_2Cl_2/E, 30 : 1) (*S*)**D**$_t$, 104 mg (35%), white foam, m.p. 60 - 62 °C, $[\alpha]_D^{20}$ +0.9° (*c* =0.985 in CH_2Cl_2). IR ($CHCl_3$): ν = 3040 cm^{-1}, 2984, 2936, 1748, 1368, 1232, 1068, 1048; ^{1}H NMR (200 MHz): δ =

6.56 (dd, *J* = 1, 2.5 Hz, 1H; H-2), 5.46 (d, *J* = 6 Hz, 1H; H-7), 5.22 (t, *J* = 9.5 Hz, 1H; H-9), 5.22 (dd, *J* = 9.5, 10 Hz, 1H; H-10), 4.27 (dd, *J* = 6, 12 Hz, 1H; H-12a), 4.14 - 3.98 (m, 2H; H-5, H-11), 3.90 (dd, *J* = 6, 11 Hz, 1H; H-12b), 2.88 (ddd, *J* = 1, 6, 17 Hz, 1H; H-6a), 2.75 - 2.57 (m, 2H; H-6b, H-8), 2.10, 2.08, 2.05 (3 s, 3×3H; $COCH_3$), 1.87 - 1.15 (m, 10H; H-1′, H-2′, H-3′, H-4′, H-5′), 1.03 (s, 3H; CH_3); ^{13}C NMR (75 MHz, APT): δ = 170.58, 169.97, 169.69 (+, *C*OCH_3), 142.41 (–, C-2), 98.24 (–, C-7), 89.82 (+, C-1), 78.02 (–, C-5), 72.16 (+, C-9), 69.62 (–, C-10), 68.96 (–, C-11), 62.80 (+, C-12), 48.22 (–, C-8), 46.22, 46.04 (+, C-4, C-6), 42.05 (+, C-3), 34.20, 31.52 (+, C-1′, C-2′), 26.42 (+, C-5′), 22.07, 21.57 (+, C-3′, C-4′), 20.93, 20.81, 20.65 (–, CO*C*H_3), 11.81 (–, CH_3); MS (70 eV): *m/z* (%): 576 (0) [M^+], 518 (19), 415 (92), 376 (51), 287 (54), 244 (80), 91 (100); FAB-MS: 575 [M^+ – 1].

2(R),3(S),4(R),4a(R),4b(R),5(R),8a(S),9a(S)-2-Acetoxymethyl-5-trimethylsilyl-7-iodo-3,4,4a,4b,5,8,8a,9a-octahydro-2H-pyrano[2,3-b]benzofuran-3,4-diol Diacetate [(*S*)**E**$_t$]. (*S*)**E**$_1$ (500 mg, 0.88 mmol) was allowed to react according to the general procedure for 2 h to yield after chromatography (E/PE, 1 : 3) (*S*)**E**$_t$, 193 mg (39%), white crystals, m.p. 133 °C, $[\alpha]_D^{20}$ +123.8° (*c* =0.96 in CH_2Cl_2). IR ($CHCl_3$): ν = 3040 cm^{-1}, 2956, 2928, 1748, 1252, 1172, 1084, 836; ^1H NMR (200 MHz, without TMS): δ = 6.13 (br. t, *J* = 2 Hz, 1H; H-6), 5.62 (d, *J* = 4.5 Hz, 1H; H-9a), 5.22 (t, *J* = 9.5 Hz, 1H; H-4), 4.99 (t, *J* = 9.5 Hz, 1H; H-3), 4.40 (dd, *J* = 4, 12 Hz, 1H; H-10), 4.20 (dt, *J* = 5, 10 Hz, 1H; H-8a), 4.04 (dd, *J* = 2, 12 Hz, 1H; H-10), 4.00 (ddd, *J* = 2,4,9.5 Hz, 1H; H-2), 2.95 (ddd, *J* = 2, 5, 18 Hz, 1H; H-8), 2.65 - 2.45 (m, 2H; H-8, incl. 2.52, dt, *J* = 4.5, 9.5 Hz, H-4a), 2.07, 2.01, 1.99 (3s, 3×3H; $COCH_3$), 1.90 (dt, *J* = 4.5, 9.5 Hz, 1H; H-4b), 1.65 (dm, *J* = 9.5 Hz, 1H; H-5), 0.05 (s, 9H; $SiMe_3$); ^{13}C NMR (50 MHz, without TMS, APT): δ = 170.50, 169.89, 169.71 (+, *C*OCH_3), 138.33 (–, C-6), 102.07 (–, C-9a), 85.94 (+, C-7), 78.50 (–, C-8a), 69.71 (+, C-4), 68.94 (–, C-3), 68.05 (–, C-2), 61.71 (+, C-10), 45.13 (+, C-8), 43.48 (+, C-4b), 42.68 (–, C-4a), 30.57 (–, C-5), 26.77 (+, C-4b), 21.00, 20.62, 20.55 (–, CO*C*H_3), –2.67 (–, $SiMe_3$); MS (140 °C, 70 eV): *m/z* (%): 566 (1) [M^+], 551 (1), 439 (3) [M^+ – I], 379 (9), 319 (22), 277 (21), 73 (100). HRMS calcd for $C_{21}H_{31}O_8Si$: 439.1788, found 439.1784. X-ray crystal structure see ref. 10.

2(R),3(S),4(R),4a(R),4b(S),5(S),8a(R),9a(S)-2-Acetoxymethyl-5-trimethylsilyl-7-iodo-3,4,4a,4b,5,8,8a,9a-octahydro-2H-pyrano[2,3-b]benzofuran-3,4-diol Diacetate [(*R*)**E**$_t$]. (*R*)**E**$_1$ (340 mg, 0.60 mmol) was allowed to react according to the general procedure for 45 min. Chromatography (E/PE, 1 : 5) gave (*R*)**E**$_t$, 138 mg (41%), light yellow oil, which decomposed rapidly at r.t., but was sufficiently stable at –78 °C, $[\alpha]_D^{20}$ –61.4° (*c* =0.945 in CH_2Cl_2). IR ($CHCl_3$): ν = 3040 cm^{-1}, 2956, 2928, 1748, 1252, 1172, 1120, 1032; ^1H NMR (200 MHz, without TMS): δ = 6.20 (br. s, 1H; H-6), 5.55 (d, *J* = 7.5 Hz, 1H; H-9a), 5.10 (br. s, 1H; H-4), 4.95 (dt, *J* = 0.5, 9 Hz, 1H; H-3), 4.20 (dd, *J* = 3.5, 12 Hz, 1H; H-10), 4.10 (dd, *J* = 5, 12 Hz, 1H; H-10), 3.88 (ddd, *J* = 3.5, 5, 9 Hz, 1H; H-2), 3.57 (dt, *J* = 5, 10 Hz, 1H; H-8a), 2.97 (dm, *J* = 17 Hz, 1H; H-8), 2.74 (dddd, *J* = 2.5, 5, 10, 17 Hz, 1H; H-8), 2.30 (ddd, *J* = 1, 7.5, 10 Hz, 1H; H-4a), 2.07, 2.05 (2s, 9H; $COCH_3$), 1.80 (q, *J* = 10 Hz, 1H; H-4b), 1.6 (ddd, *J* = 2, 5, 10 Hz, 1H; H-5), 0.10 (s, 9H; $SiMe_3$); ^{13}C NMR (50 MHz, without TMS, APT): δ = 170.57, 169.27, 169.81 (+, *C*OCH_3), 138.37 (–, C-6), 99.63 (–, C-9a), 89.74 (+, C-7), 79.70 (–, C-8a), 70.24 (+, C-4), 68.53 (–, C-3), 66.60 (–, C-2), 63.76 (+, C-10), 45.11 (+, C-4a), 44.06 (+, C-8), 42.08 (–, C-4b), 37.69 (–, C-5), 20.86, 20.81, 20.70 (–, CO*C*H_3), –2.06 (–, $SiMe_3$); MS (140 °C, 70 eV): *m/z* (%): 567 (1) [M^+ + 1], 434 (7) [M^+ – $SiMe_3$, OAc], 379 (9), 301 (20), 229 (15), 118 (26), 73 (100). HRMS calcd for $C_{16}H_{19}O_6I$: 434.0226, found 434.0221.

General Procedure for the Deacetylation. A flame-dried flask was charged with triacetylated educt (Scheme 2) in abs. MeOH (1 eq, 0.1 M). NaOMe (2.5 eq) was added at r.t. After complete reaction (ca. 2 h) the mixture was acidified (pH 6) with Amberlyst and filtered. The residue was washed with MeOH. The combined organic phase was evaporated. The crude product was dissolved in DMF (0.8 M solution of deprotected glycoside) and 2,2-dimethoxypropane (10 eq) was added. The reaction mixture was acidified (pH 3) with *p*-TsOH and stirred for 16 h. EtOAc was added and the organic layer was extracted with sat. aq. $NaHCO_3$ solution. After removal of the solvent the crude product was purified by chromatography.

4a(S),4b(R),5(R),5a(S),9a(R),10a(S),11a(S)-2-Iodo-7,7,4,4-tetramethyl-1,4,4a,4b,5,5a,9,9a,10a,11a-decahydro-6,8,10,11-tetraoxabenzo[b]fluoren-5-ol [(*S*)-**2**]. (*S*)**A**$_t$ (1.9 mmol) was allowed to react according to the general procedure to afford (*S*)-**2** (85%), colourless crystals, m.p. 173 °C. IR (KBr): ν = 3473 cm^{-1}, 2993, 1616, 1269, 1134, 1084, 942; ^{1}H NMR (200 MHz): δ = 6.08 (m, 1H; H-3), 5.45 (d, *J* = 5 Hz, 1H; H-10a), 4.28 (ddd, *J* = 6, 9, 12 Hz, 1H; H-11a), 3.91 (ddd, *J* = 6, 9, 12 Hz, 1H; H-9a), 3.70 (dd, *J* = 9, 11 Hz, 1H; H-5b), 3.69 (dd, *J* = 9, 9 Hz, 1H; H-5), 3.61 (dd, *J* = 5, 9 Hz, 1H; H-9), 3.53 (dm, *J* = 9 Hz, 1H; H-9), 3.05 (dd, *J* = 6, 11 Hz, 1H; H-1), 2.83 (br. s, 1H; OH), 2.55 (ddd, *J* = 3, 9, 11 Hz, 1H; H-1), 2.28 (ddd, *J* = 5, 6, 9 Hz, 1H; H-4b), 2.01 (dd, *J* = 6, 12 Hz, 1H; H-4a), 1.51, 1.43, 1.24, 1.17 (4 s, 4×3H; CH_3); ^{13}C NMR (50 MHz, APT): δ = 150.03 (–, C-3), 102.49 (–, C-10a), 99.78 (+, C-7), 89.26 (+, C-2), 74.17 (–, C-11a), 74.06 (–, C-5a), 67.20 (–, C-9a), 63.04 (–, C-5), 62.34 (+, C-9), 51.78 (–, C-4a), 47.63 (+, C-1), 44.60 (–, C-4b), 40.46 (+, C-4), 29.06, 28.13, 22.33, 19.17 (–, CH_3); MS (80 °C, 70 eV)): *m/z* (%): 437 (1) [M^+ + 1], 436 (7) [M^+], 435, 421, 131, 108, 107, 106, 105, 101 (100), 92, 91, 81.

4a(S),4b(S),5(R),8a(R),9(R),10a(S),11a(R)-9-Dimethylmethoxymethyl-2-iodo-7,7,4,4-tetramethyl-1,4,4a,4b,5,8a,9,10a,11a-nonahydro-6,8,10,11-tetraoxacyclopenta[a]fluorene [(*R*)-**3**]. (*R*)**A**$_t$ (3.8 mmol) was allowed to react according to the general procedure to give (*R*)-**2** (20%) and (*R*)-**3** (22%). Data for (*R*)-**3**, waxy crystals, m.p. 54 - 58 °C. IR (KBr): ν = 2986 cm^{-1}, 2933, 1612, 1077, 944; ^{1}H NMR (200 MHz): δ = 6.07 (m, 1H; H-3), 4.94 (d, *J* = 3 Hz, 1H; H-10a), 4.25 - 3.79 (m, 6H; H-5, H-8a, H-9, H-11a, H-12), 3.94 (ddd, *J* = 1, 6, 16 Hz, 1H; H-1), 3.36 (s, 3H; OMe), 2.56 (ddd, *J* = 2, 10, 16 Hz, 1H; H-1), 2.34 (ddd, *J* = 3, 6, 9 Hz, 1H; H-4b), 1.74 (dd, *J* = 9, 11 Hz, 1H; H-4a), 1.43, 1.41 (2 s, 2 × 3H; CH_3), 1.35 (s, 6H; CH_3), 1.13, 1.01 (2 s, 2×3H; CH_3); ^{13}C NMR (50 MHz, APT): δ = 149.47 (–, C-3), 109.90 (+, C-13), 109.31 (+, C-7), 106.90 (–, C-10a), 89.04 (+, C-2), 81.90 (–, C-11a), 80.45 (–, C-5), 77.46 (–, C-8a), 75.08 (–, C-9), 68.36 (+, C-12), 55.14 (–, C-4a), 52.26 (–, OMe), 50.34 (–, C-4b), 45.60 (+, C-4), 40.42 (+, C-1), 29.58, 27.49, 27.44, 26.47, 25.45, 22.92 (–, CH_3); MS (90 °C, 70 eV): *m/z* (%): 493 (9) [M^+ – CH_3], 449, 143, 107, 105, 101 (100), 91, 79.

General Procedure for the Benzylation (Scheme 3). A flame-dried flask was charged with the alcohol in abs. THF (1 eq, 0.6 M) under an argon atmosphere. NaH (2 eq, suspension in mineral oil, 60%) was added in portions (H_2 !). After complete reaction the mixture was warmed gently. After 30 min benzyl bromide (2 eq) was added carefully, followed by tetra-*n*-butylammonium iodide (0.05 eq). The mixture was stirred for 18 h at r.t. and then quenched carefully with water (H_2 !). The aqueous phase was extracted with E, the combined organic layer was washed with sat. aq. NH_4Cl solution and dried ($MgSO_4$). The crude product was purified by chromatography.

4a(S),4b(R),5(R),5a(S),9a(R),10a(S),11a(S)-2-Iodo-7,7,4,4-tetramethyl-1,4,4a,4b,5,5a,9,9a,10a,11a-decahydro-6,8,10,11-tetraoxabenzo[b]fluoren-5-yl Benzyl Ether [(*S*)-**4**]. (60% w.r.t. (*S*)$\mathbf{A_t}$), colourless crystals, m.p. 100 °C. IR (KBr): ν = 2991 cm^{-1}, 2936, 1621, 1268, 1084, 942; ^{1}H NMR (200 MHz): δ = 7.39 - 7.26 (m, 5H; arom. H), 6.04 (dd, *J* = 1, 3 Hz, 1H; H-3), 5.45 (d, *J* = 5 Hz, 1H; H-10a), 5.00 (d, *J* = 12 Hz, 1H; H-12), 4.56 (d, *J* = 12 Hz, 1H; H-12), 4.32 (ddd, *J* = 6, 9, 12 Hz, 1H; H-11a), 3.92 (ddd, *J* = 2, 5, 10 Hz, 1H; H-9a), 3.80 (dd, *J* = 8, 10 Hz, 1H; H-5a), 3.76 (dd, *J* = 8, 8 Hz, 1H; H-5), 3.70 (dd, *J* = 2, 8 Hz, 1H; H-9), 3.61 (dd, *J* = 5, 8 Hz, 1H; H-9), 3.08 (ddd, *J* = 1, 6, 17 Hz, 1H; H-1), 2.56 (ddd, *J* = 3, 9, 17 Hz, 1H; H-1), 2.42 (ddd, *J* = 5, 6, 8 Hz, 1H; H-4b), 2.01 (dd, *J* = 6, 12 Hz, 1H; H-4a), 1.39, 1.35 (2 s, 2×3H; CH_3), 1.13 (s, 6H; CH_3); ^{13}C NMR (50 MHz, APT): δ = 149.62 (–, C-3), 139.15 (+, arom. C), 128.06, 127.02, 126.68 (–, arom. C), 102.26 (–, C-10a), 98.94 (+, C-7), 89.45 (+, C-2), 74.57 (–, C-11a), 74.42 (–, C-5a), 73.98 (–, C-9a), 71.75 (+, C-12), 61.98 (+, C-9), 62.60 (–, C-5), 51.24 (–, C-4a), 47.52 (+, C-1), 43.73 (–, C-4b), 40.23 (+, C-4), 29.05, 28.02, 22.15, 18.73 (–, CH_3); MS (70 eV): *m/z* (%): 526 (2) [M^+], 318, 150, 107, 105, 101, 95, 92, 91 (100), 81.

4a(R),4b(R),5(R),5a(S),9a(R),10a(S),11a(R)-2-Iodo-7,7,4,4-tetramethyl-1,4,4a,4b,5,5a,9,9a,10a,11a-decahydro-6,8,10,11-tetraoxabenzo[b]fluoren-5-yl Benzyl Ether [(*R*)-**4**]. (14% w.r.t. (*R*)$\mathbf{A_t}$), colourless, glassy oil. IR ($CHCl_3$): ν = 3000 cm^{-1}, 2960, 2936, 1604, 1196, 1088, 992; ^{1}H NMR (200 MHz): = δ 7.42 - 7.31 (m, 2H; arom. H), 7.26 - 7.10 (m, 3H; arom. H), 5.88 (dd, *J* = 1, 2 Hz, 1H; H-3), 5.11 (d, *J* = 8 Hz, 1H; H-10a), 4.89 (d, *J* = 12 Hz, 1H; H-12), 4.48 (d, *J* = 12 Hz, 1H; H-12), 3.98 (dd, *J* = 10, 16 Hz, 1H; H-9), 3.87 - 3.63 (m, 3H; H-5, H-9, H-9a), 3.44 (dd, *J* = 4, 7 Hz, 1H; H-5a), 3.11 (ddd, *J* = 5, 10, 11 Hz, 1H; H-11a), 2.84 (ddd, *J* = 1, 5, 16 Hz, 1H; H-1), 2.51 (ddd, *J* = 2, 11, 16 Hz, 1H; H-1), 2.05 (ddd, *J* = 4, 8, 10 Hz, 1H; H-4b), 1.42 (s, 3H; CH_3), 1.31 (dd, *J* = 10, 10 Hz, 1H; H-4a), 1.17, 0.78, 0.56 (3 s, 3×3H; CH_3); ^{13}C NMR (50 MHz, APT): δ = 148.58 (–, C-3), 138.39 (+, arom. C), 128.23, 127.69, 127.49 (–, arom. C), 100.73 (–, C-10a), 99.06 (+, C-7), 89.33 (+, C-2), 82.28 (–, C-11a), 72.96 (+, C-12), 72.96 (–, C-5a), 72.12 (–, C-9a), 63.47 (–, C-5), 62.27 (+, C-9), 58.46 (–, C-4a), 45.48 (+, C-1), 43.36 (–, C-4b), 40.74 (+, C-4), 29.07, 28.93, 22.68, 19.02 (–, CH_3); FAB-MS: 527 (M^+ + 1].

Metal-Halogen Exchange. Preparation of Alcohol **5**. A flame-dried flask was charged with the cyclohexenyl iodide (*S*)-**4** in abs. THF (1 eq, 0.3 M) under an argon atmosphere. The solution was cooled to –78 °C and *t*-BuLi (2.3 eq) was added dropwise (the temperature of the solution should be maintained at ca. –78 °C). After complete addition the mixture was stirred for 30 min at -78 °C, then was acetaldehyde (4 eq) added. The mixture was allowed to reach r.t., quenched with sat. aq. NH_4Cl solution and extracted with E. The combined organic phase was washed with brine, dried ($MgSO_4$) and evaporated. The crude product was purified by chromatography to afford alcohol **5**.

Dess-Martin Periodinane Oxidation. Preparation of Enone **6**. A solution of alcohol **5** in CH_2Cl_2 (1 eq, 0.1 M) was treated with Dess-Martin reagent (1.1 eq). To this mixture was added acetic acid (1 drop). The mixture was stirred for 20 min, then diluted with CH_2Cl_2 and stirred with $Na_2S_2O_3$ solution (1 g/mmol Dess-Martin reagent) until two clear phases appeared. The organic layer was washed with water and brine, dried ($MgSO_4$) and evaporated. The crude product was chromatographed to afford enone **6** (39%), colourless crystals, m.p. 154 °C, $[\alpha]_D^{20}$ +119.0° (*c* =1.05 in CH_2Cl_2). IR (film): ν = 2994 cm^{-1}, 1744, 1670, 1627, 1366, 1202, 1175; ^{1}H NMR (200 MHz): δ = 7.40 - 7.28 (m, 5H; arom. H), 6.47 (d, *J* = 2 Hz, 1H; H-3),5.46 (d, *J* = 5 Hz, 1H; H-10a), 5.02 (d, *J* = 12 Hz, 1H; H-12), 4.58 (d, *J* = 12 Hz, 1H; H-12), 4.23 (ddd, *J* = 6,9,12 Hz, 1H;

H-11a), 3.93 (ddd, *J* = 6, 9, 10 Hz, 1H; H-9a), 3.89 - 3.64 (m, 4H; H-5, H-5a, H-9), 3.02 (dd, *J* = 6, 17 Hz, 1H; H-1), 2.45 (ddd, *J* = 5, 6 , 8 Hz,1H; H-4b),2.29 (s, 3H; CH_3CO), 2.07 (ddd, *J* = 2, 9, 17 Hz, 1H; H-1), 1.93 (dd, *J* = 6, 12 Hz, 1H; H-4a), 1.39, 1.35, 1.23, 1.19 (4 s, 4×3H; CH_3); ^{13}C NMR (50 MHz, APT): δ = 199.00 (+, CO), 151.45 (–, C-3), 139.31 (+, arom. C), 133.31 (+, C-2), 128.22, 127.17, 126.80 (–, arom. C), 102.47 (–, C-10a), 99.17 (+, C-7), 74.70 (–, C-5a), 74.70 (–, C-11a), 73.86 (–, C-9a), 71.86 (+, C-12), 62.75 (–, C-5), 62.19 (+, C-9), 52.55 (–, C-4a), 43.92 (–, C-4b), 36.96 (+, C-4), 32.04 (+, C-1), 29.13 (CH_3CO), 28.65, 25.69, 22.00, 18.85 (–, CH_3); MS (180 °C, 70 eV): *m/z* (%): 442 (0.5) [M^+], 205, 149, 131, 125, 123, 121, 116, 111, 109, 105, 101, 99, 97, 96, 95, 93, 92, 91 (100).

4a(S),4b(R),5(R),5a(S),9a(R),10a(S),11a(S)-4,4,7,7-Tetramethyl-1,4,4a,5,5a,9,9a,10a,11a-octahydro-6,8,10,11-tetraoxabenzo[b]fluoren-5-yl Benzyl Ether (**7**). Cyclohexenyl iodide (*S*)-**4** (0.37 mmol) in abs. THF (1 eq, 0.07 M) was allowed to react as described above. Instead of acetaldehyde water (3 - 5 eq) was used as electrophile. Yield of **7**: 59%, highly viscous, colourless oil. IR (film): ν = 2993 cm^{-1}, 2937, 1762, 1607, 1171, 1084, 1069; ^1H NMR (200 MHz): δ = 7.38 - 7.26 (m, 5H; arom. H), 5.44 (d, *J* = 5 Hz, 1H; H-10a), 5.37 (d, *J* = 2 Hz, 2H; H-2, H-3), 5.01 (d, *J* = 12 Hz, 1H; H-12), 4.58 (d, *J* = 12 Hz, 1H; H-12), 4.25 (ddd, *J* = 2, 4, 9 Hz, 1H; H-11a), 3.93 (ddd, *J* = 2, 4, 9 Hz, 1H; H-9a), 3.84 - 3.64 (m, 4H; H-5, H-5a, H-9), 2.60 (ddd, *J* = 2, 6, 17 Hz, 1H; H-1), 2.45 (ddd, *J* = 5, 6, 7 Hz, 1H; H-4b), 2.05 (dd, *J* = 9, 17 Hz, 1H; H-1), 1.97 (dd, *J* = 6, 12 Hz, 1H; H-4a), 1.38, 1.34, 1.12, 1.10 (4 s, 4×3H; CH_3); ^{13}C NMR (50 MHz, APT): δ = 140.77 (–, C-3), 139.49 (+, arom. C), 128.17, 127.08, 126.84 (–, arom. C), 119.91 (–, C-2), 102.31 (–, C-10a), 99.11 (+, C-7), 74.96 (–, C-11a), 74.80 (–, C-5a), 74.23 (–, C-9a), 71.87 (+, C-12), 62.60 (–, C-5), 62.29 (+, C-9), 53.21 (–, C-4a), 44.10 (–, C-4b), 36.51 (+, C-4), 33.96 (+, C-1), 29.17, 28.57, 22.81, 18.87 (–, CH_3); MS (80 °C, 70 eV): *m/z* (%): 385 (2) [M^+ – 15], 163, 131, 107, 101, 91 (100), 86, 84, 82.

Epoxidation with m-*CPBA*. To a solution of **7** (1 eq, 0.49 mmol) in CH_2Cl_2 (2 mL) was added *m*-CPBA (1.1 eq, 0.54 mmol) portionwise at 0 °C. After complete addition the reaction mixture was stirred for 2 h at r.t. and then cooled to 0 °C. The mixture was treated with $Ca(OH)_2$ (3 eq, 1.5 mmol) to remove peracid and acid. The viscous suspension was suction-filtered and washed with CH_2Cl_2. The organic layer was dried ($MgSO_4$), the solvent removed and the crude product chromatographed to afford epoxide **8** (30%), white foam, m.p. 148 - 154 °C, $[\alpha]_D^{20}$ +43.0° (*c* =2.50 in CH_2Cl_2). IR (KBr): ν = 3020 cm^{-1}, 2986, 1362, 1175, 1065, 855; ^1H NMR (200 MHz): δ = 7.36 - 7.27 (m, 5H; arom. H), 5.37 (d, *J* = 5 Hz, 1H; H-10a), 5.01 (d, *J* = 12 Hz, 1H; H-12), 4.59 (d, *J* = 12 Hz, 1H; H-12), 4.11 (ddd, *J* = 7, 9, 12 Hz, 1H; H-11a), 3.88 (ddd, *J* = 1, 5, 9 Hz, 1H; H-9a), 3.80 - 3.52 (m, 4H; H-5, H-5a, H-9), 3.30 (ddd, *J* = 5, 6, 8 Hz, 1H; H-4b), 3.11 (dd, *J* = 4, 5 Hz, 1H; H-2), 2.70 (d, *J* = 4 Hz, 1H; H-3), 2.47 (ddd, *J* = 5, 7, 17 Hz, 1H; H-1), 2.07 (dd, *J* = 6, 12 Hz, 1H; H-4a), 1.90 (dd, *J* = 9, 17 Hz, 1H; H-1), 1.38, 1.34, 1.20, 1.16 (4 s, 4×3H; CH_3); ^{13}C NMR (50 MHz, APT): δ = 139.21 (+, arom. C), 128.15, 127.14, 126.91 (–, arom. C), 102.43 (–, C-10a), 99.09 (+, C-7), 74.71 (–, C-5a), 74.61 (–, C-9a), 71.90 (+, C-12), 71.86 (–, C-11a), 64.21 (–, C-5), 62.75 (–, C-2), 62.14 (+, C-9), 51.23 (–, C-4a), 45.78 (–, C-4b), 43.25 (–, C-3), 33.40 (+, C-4), 29.09 (–, CH_3), 29.03 (+, C-1), 25.20, 18.77, 18.69 (–, CH_3); MS (140 °C, 70 eV): *m/z* (%): 401 (1) [M^+ – 15], 179, 131, 92, 91 (100).

4a(R),4b(R),5(R),5a(S),9a(S),10a(S),11a(S)-7,7-Dimethyl-1,4,4a,5,5a,9,9a,10a,11a-octahydro-6,8,10,11-tetraoxabenzo[b]fluoren-5-yl Benzyl Ether (**10**). Cyclohexenyl iodide **9** [prepared as described for (*S*)-**4**] (0.47 mmol) was allowed to react as described for compound **7** to afford **10**, highly viscous, glassy oil. IR (KBr): ν = 3034 cm^{-1}, 2993, 2938, 1757, 1635, 1116; ^1H NMR (200 MHz): δ = 7.37 - 7.25 (m, 5H; arom. H),

5.64 (m, 2H; H-2, H-3), 5.51 (d, J = 5 Hz, 1H; H-10a), 4.97 (d, J = 12 Hz, 1H; H-12), 4.93 (dd, J = 6, 11 Hz, 1H; H-9a), 4.85 (dd, J = 10, 11 Hz, 1H; H-5a), 4.73 (dd, J = 10, 12 Hz, 1H; H-5), 4.60 (dd, J = 6, 9 Hz, 1H; H-9), 4.59 (d, J = 12 Hz, 1H; H-12), 4.55 (dd, J = 2, 9 Hz, 1H; H-9), 4.01 (ddd, J = 6, 10, 10 Hz, 1H; H-11a), 2.57 (dm, J = 15 Hz, 1H; H-1), 2.43 - 2.26 (m, 2H; H-4, H-4b), 2.15 - 1.99 (m,3H; H-1, H-4, H-4a), 1.50, 1.42 (2 s, 2×3H; CH_3); ^{13}C NMR (50 MHz, APT): δ = 139.87 (+, arom. C), 128.30 (–, arom. C), 127.63 (–, C-3), 127.50, 127.30 (–, arom. C), 124.21 (–, C-2), 102.55 (–, C-10a), 99.12 (+, C-7), 78.18 (–, C-11a), 75.14 (–, C-5a), 75.14 (–, C-9a), 73.41 (+, C-12), 63.68 (–, C-5), 62.19 (+, C-9), 45.13 (–, C-4a), 43.44 (–, C-4a), 32.63 (+, C-4), 29.21 (–, CH_3), 26.64 (+, C-1), 19.16 (–, CH_3); MS (50 °C) m/z 372 (1) [M^+], 165, 135, 131, 117, 102, 92, 91 (100), 87, 84.

Epoxidation with DDO. To a solution of **10** (1 eq, 0.19 mmol) in CH_2Cl_2 was added dimethyldioxirane (1.4 eq) in acetone. After 15 min the reaction is complete and the solvents were removed. The crude product was purified by chromatography to afford epoxide **11** (mixture of diastereomers, 1 : 1) (92%), white foam. Data for unpolar diastereomer: m.p. 84 - 91 °C, $[\alpha]_D^{20}$ +42.8° (c =1.40 in CH_2Cl_2). IR (KBr): ν = 2991 cm^{-1}, 2942, 1367, 1111, 1084, 941; ^1H NMR (200 MHz): δ = 7.43 - 7.30 (m, 5H; arom. H), 5.46 (d, J = 5 Hz, 1H; H-10a), 4.97 (d, J = 12 Hz, 1H; H-12), 4.62 (d, J = 12 Hz, 1H; H-12), 3.91 (dd, J = 6, 9 Hz, 1H; H-5), 3.77 (dd, J = 8, 10 Hz, 1H; H-9), 3.76 (m, 1H; H-11a), 3.72 (dd, J = 10, 10 Hz, 1H; H-5a), 3.54 - 3.48 (m, 2H; H-9, H-9a), 3.16 (m, 1H; H-3), 3.09 (dd, J = 4, 5 Hz, 1H; H-2), 2.49 (ddd, J = 5, 6, 12 Hz, 1H; H-1), 2.38 (dm, J = 12 Hz, 1H; H-1), 2.24 (m, 1H; H-4b), 2.09 (dddd, J = 4, 6, 10, 12 Hz, 1H; H-4a), 1.87 (dd, J = 10, 14 Hz, 1H; H-4), 1.65 (ddd, J = 2, 12, 14 Hz, 1H; H-4), 1.48, 1.42 (2 s, 2×3H; CH_3); MS (70 °C, 70 eV): m/z (%): 390 (1) [M^+ + 2], 331, 181, 151, 150, 133, 131 (100), 121, 107, 105, 103, 101. Data for polar diastereomer: m.p. 120 - 129 °C, $[\alpha]_D^{20}$ +45.1° (c =0.90 in CH_2Cl_2). IR (KBr). ν = 2993 cm^{-1}, 2925, 1365, 1116, 1083, 942; ^1H NMR (200 MHz): δ = 7.43 - 7.23 (m, 5H; arom. H), 5.43 (d, J = 5 Hz, 1H; H-10a), 4.98 (d, J = 12 Hz, 1H; H-12), 4.69 (d, J = 12 Hz, 1H; H-12), 3.99 (ddd, J = 5, 10, 10 Hz, 1H; H-11a), 3.91 (dd, J = 6, 10 Hz, 1H; H-5), 3.78 (dd, J = 9, 10 Hz, 1H; H-9), 3.70 (dd, J = 6, 10 Hz, 1H; H-5a), 3.61 - 3.42 (m, 2H; H-9, H-9a), 3.27 (m, 1H; H-2), 3.18 (dd, J = 4, 5 Hz, 1H; H-3), 2.76 (ddd, J = 2, 5, 14 Hz, 1H; H-1), 2.23 - 2.19 (m, 2H; H-1, H-4b), 1.96 - 1.79 (m, 2H; H-4), 1.75 - 1.55 (m, 1H; H-4a), 1.47, 1.41 (2 s, 2×3H; CH_3); MS (90 °C, 70 eV): m z (%): 388 (1) [M^+], 131, 101, 91 (100), 84, 82, 79, 77.

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