Pergamon

Tetrahedron Vol. 51, No. 27, pp. 7389-7402, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4020/95 $9.50+0.00

0040-4020(95)00389-4

Radical Cascades in Synthesis. Dioxatriquinanes and Doubly-Annulated Glycosides by Triethylborane-Induced Atom Transfer Cyclization of 1,5-Enynes and 1,5-Diynes¶

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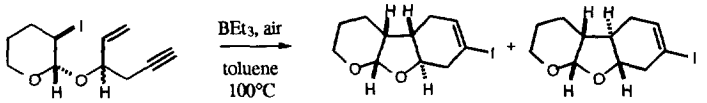
¶*Dedicated to Professor Sir Derek Barton with respect and admiration.*

Abstract: Tandem radical reactions listed in the title afford a convergent and flexible pathway to functionalized, heteroannular tricyclic acetals which are of relevance in natural product chemistry. The cycloisomerization of the 1,5-enyne was carried out under exceptionally mild conditions at -50 to -65°C. For the first time, consecutive 5-exo-digonal / 5-exo-digonal cyclizations using 1,5-diyne systems have been accomplished, again under full stereocontrol.

Academic insight into radical reactions has facilitated advances in organic synthesis and *vice versa*. Radical cascade reactions, in particular, are useful for constructing natural products and their precursors.[1] We here describe convergent routes to functionalized, heteroannular tricyclic acetals *via* the title methodology.

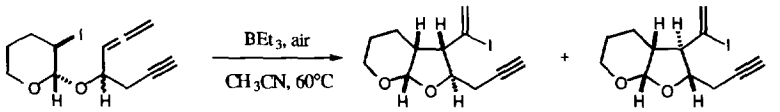
Acetylenes and allenes, unlike alkenes, have been used much less as acceptors in radical cyclizations. Alkynes offer the opportunity of generating reactive vinyl radicals by a radical *addition* under very mild conditions,[2] as an alternative to the homolytic *fission* of a vinyl-halogen bond, which is energetically more costly and accordingly, requires more demanding experimental conditions.



50%

Scheme 1. 5-exo-Trigonal, 6-endo-Digonal Tandem Cycloisomerization of 1,5-Enynes

From our earlier work on cascade reactions,[3] outlined in Scheme 1,[4] a corresponding radical cascade could have been expected, after replacing the alkene by an allene functionality (Scheme 2).[5] However, the attempted cycloisomerization was terminated prematurely, after formation of the 2,3,4,5-tetrasubstituted tetrahydrofuran moiety **2a, b**. Neither a subsequent 5-exo-digonal nor a 6-endo-digonal[6] closure (cf. Scheme 1) occurred.



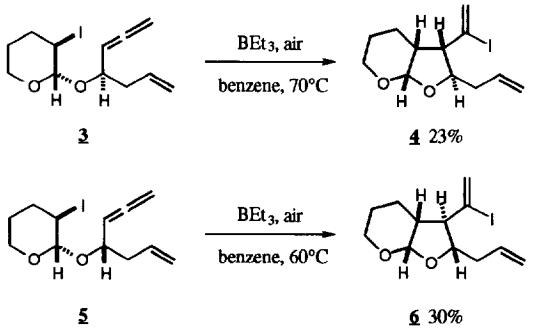
1 mixture of diastereomers

2a **2b**

45% (**2a** : **2b** = 1:1)

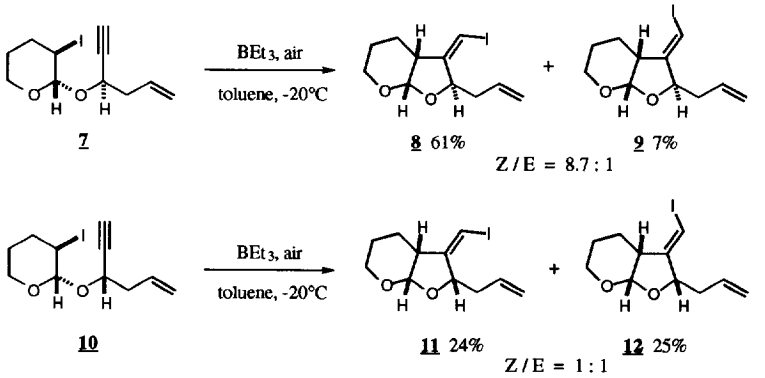
Scheme 2. Radical Cyclization of a 1,2-Heptadiene-6-yne System

A change of triple bond to double bond as radicophile made little difference with respect to the crucial second, carbon-carbon bond-forming step (Scheme 3).



Scheme 3. Triethylborane-Induced Cyclization of the 1,2,6-Heptatriene System

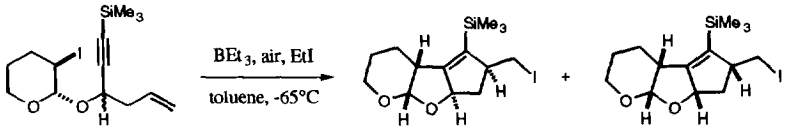
On the assumption that an alkyne is more suitable than an allene for the intended tandem cycloisomerization, we investigated diastereomeric iodo acetals **7** and **10**, which are easily separable and contain a simple 1,5-enyne system. However, cyclization was again arrested after the first ring closure (Scheme 4). A consecutive cyclization (5-exo-digonal or 6-endo-digonal) was not observed.



Scheme 4. Cyclization of Unsubstituted 1,5-Enyne System.

While the transition state for the second ring closure might have benefitted from steric constraint and increased propinquity of the carbon termini, the high reactivity of the vinyl radical is again manifest by irreversible iodine atom abstraction after monocyclization.

Trimethylsilylation of the acetylene terminus made an immediate difference (Scheme 5). Although the starting *secondary* alkyl iodide in **13** and the resulting *primary* alkyl iodide in **14a** and **14b** are separated by only a narrow energy gap,[7] the double cyclization was now shown to be feasible. Apparently, the highly reactive silylated vinyl radical intermediate and the double bond as vinyl radical acceptor provide an excellent kinetic match for the second ring closure. Overall, the tandem cyclization was carried out at the remarkably low temperature of - 65°C!

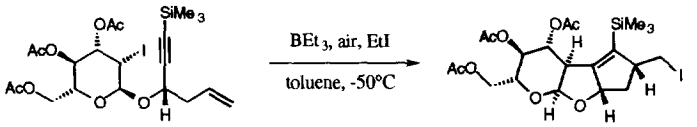


13 (mixture of diastereomers) 14a 14b 44% (mixture of diastereomers)

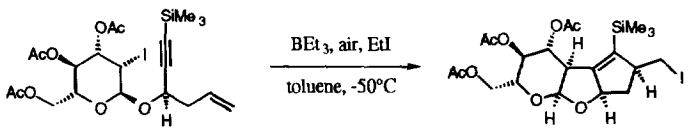
Scheme 5. The Tandem Cycloisomerization of Trimethylsilyl Substituted 1,5-Enyne System

The successful cycloisomerization underlines the mildness of the BEt_3/air method, which serves as the low temperature radical initiator system of choice. By addition of 1 eq of EtI, termination by iodine atom transfer was enhanced further and little or no hydrogen atom transfer occurred. In contrast, the standard tributyltin hydride methodology was unsatisfactory, producing only mixtures of iodine-containing and iodine-free compounds in lower yields.

The ^{13}C NMR spectra of the diastereomeric mixture of tricycles **14a** and **14b** indicated a diastereoselective, second cyclization. Applying the iodoalkoxylation to glucal[8] we were pleased to obtain diastereomerically pure 1,5-enynes **15** and **17**, which, of course, are also enantiopure. The resulting tricyclic acetal **16** possesses a tetrahydropyran chair conformation, was formed enantiopure and in respectable 51% yield. Iodoglycoside **17** reacted poorly and provided diastereomer **18**, the six-membered heterocycle of which exists in a nonchair conformation, in low yield (10%) (Scheme 6).



15 **16** 51%

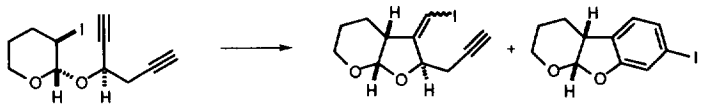


17 **18** ca. 10%

Scheme 6. Diastereoselective Radical Tandem Cycloisomerization to Enantiopure Glycoconjugates

With regard to the stereochemistry of the substituted cyclopentene ring, NOE measurements on tricycle **16** were not informative. However, radical-mediated reaction with Bu_3SnH (**16** -> **19**)[9] provided the deiodinated tricycle **19**, which showed well resolved NOE effects, displaying the syn relationship[10] of the two tertiary cyclopentenoid protons.

In studies directed towards the synthesis of dioxatriquinanes we have explored the potential of functionalized 1,5-diynes in free radical reactions. Unlike the results summarized in Schemes 2-4, experiments on the simple 1,5-diyne system were not totally discouraging (Scheme 7).



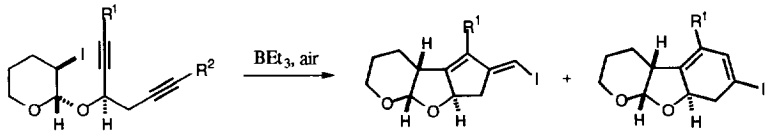
20 BEt_3, air, toluene, 30°C **21** 49% (E/Z = 1:9) --

20 BEt_3, air, benzene, 80°C, 120h -- **22** 8%

Scheme 7. Cyclization of the Parent 1,5-Diyne System

The isolation of crystals of the aromatic tricycle **22** in low yield (8%) suggested that in principle, a twofold annulation was feasible.

Silyl capping of the "first acetylene" was once again immediately successful, affording semicyclic diene **28** from diastereomer **23** in 47% yield and an additional 10% of hydrogen atom transfer product (Scheme 8). Instead of aromatic iodobenzene **22**, its nonbenzenoid precursor **29** was isolated as 6-endo-digonal byproduct.

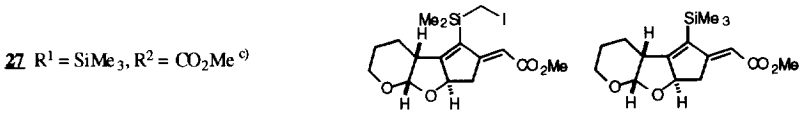


23 $R^1 = SiMe_3$, $R^2 = H$ **28** 47% [a] + **29** 5%

24 $R^1 = SiMe_2Bu^t$, $R^2 = H$ **30** 14% (20%)[b]

25 $R^1 = SiPr^i_3$ (TIPS), $R^2 = H$ 0%

26 $R^1 = Bu^t$, $R^2 = H$ [c] **31** 17%



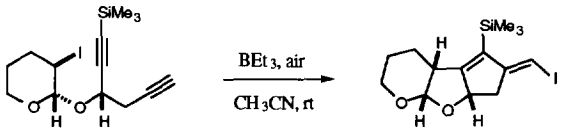
27 $R^1 = SiMe_3$, $R^2 = CO_2Me$ [c]

32 12% + **33** 11%

Scheme 8. Tandem Cyclization Promoted by Substituents on the 1,5-Diyne System
a) Additional 10% of hydrogen atom transfer product was isolated.
b) 1.2 eq $(Bu_3Sn)_2$, 3 eq EtI, h·v, benzene, 70-75°C[11].
c) Precursor could only be obtained as a 1:1 mixture of diastereomers.

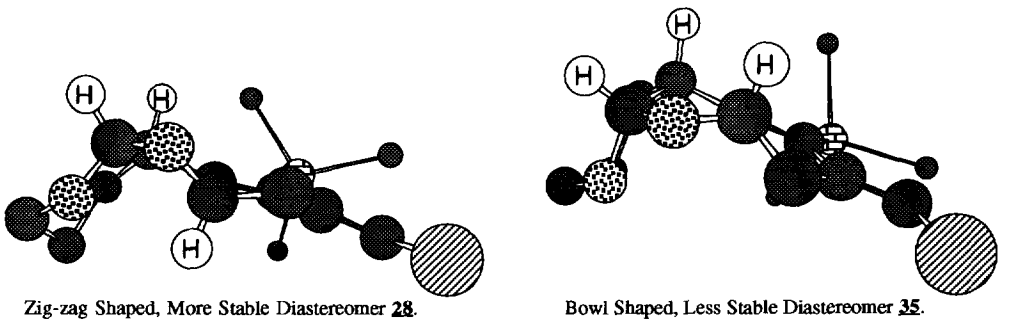
Sterically more demanding silyl groups were less satisfactory (**24**, **25**). Carbon analog **26** of the silylated diyne **23** furnished tricyclic iododiene **31** (17%), which served to prove the *E*-selective formation of the exocyclic vinyl iodide by NOE measurements.[12] Methoxycarbonylation of the "second acetylene" failed to improve the overall yield. In this case, iodomethylated silane **32** was also observed (12%), which underlines the high reactivity of the second, acceptor-substituted vinyl radical. Intramolecular 1,5-hydrogen atom transfer is possible due to favourable geometry, similar to the Hofmann-Löffler-Freytag and the first Barton reaction.[13]

Of the 1,5-diyne cyclizations studied by us, the results with the diastereomerically pure pair of iododiynes **23** and **34** were most informative. Whereas zig-zag shaped dioxatricycle **28** was formed cleanly in 47% yield (together with the deiodinated diene in 10% yield), the bowl shaped epimer **35** could only be isolated in ca. 20% yield (Scheme 9). MM2 calculations suggest that diastereomer **35**, with the more exposed cyclopentenoid double bond and its three syn-axial hydrogen atoms on the outer face, is indeed less stable (by ca. 3kcal/mole) than diastereomer **28** (Scheme 10).



34 35 ca. 20%

Scheme 9. Cycloisomerization of the Diastereomer **34** Leading to the Sensitive Tricycle **35** with the Syn-triaxial Configuration of the Bridgehead Hydrogens.

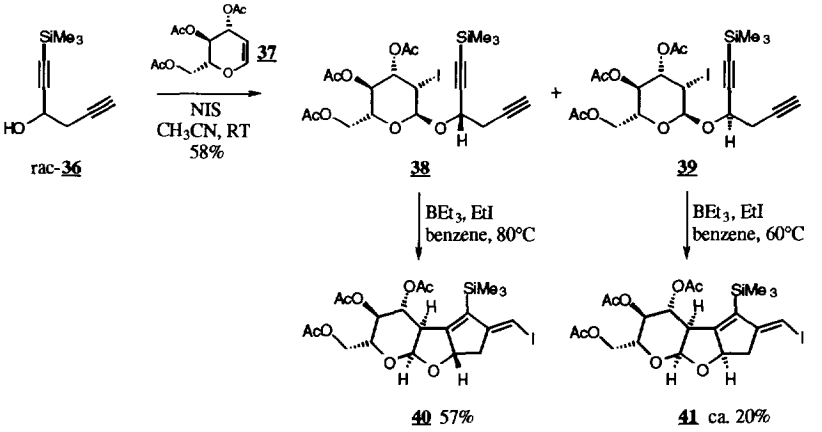


Zig-zag Shaped, More Stable Diastereomer **28**.
MM2-Energy: 33.74 kcal/mole

Bowl Shaped, Less Stable Diastereomer **35**.
MM2-Energy: 36.83 kcal/mole

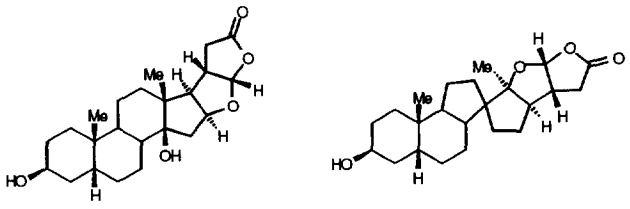
Scheme 10. 3D-Models of the Tricycles **28** and **35**.

Diyne rac-**36**, which is readily prepared from propargylic alcohol in three steps (84% overall), was applied to the synthesis of novel glycoconjugates. Diastereomeric 2β-iodo-α-glycopyranosides **38** and **39** were separable by chromatography and crystallization (Scheme 11). Tricyclic glycoconjugate **40**, which is again enantiopure, contains a chair like tetrahydropyran ring and was formed in 57% yield. In contrast, synthesis of the nonchair tricycle **41** was less satisfactory (ca. 20%).



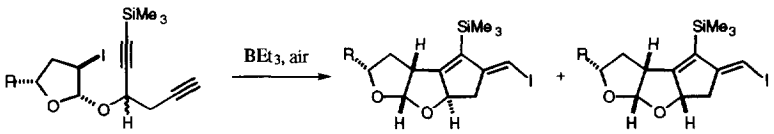
Scheme 11. Rigid, Enantiopure Tricyclic Glycoconjugates *via* Consecutive 5-exo-Digonal, 5-exo-Digonal Cycloisomerization (NIS = N-Iodosuccinimide)

Functionalized 1,5-diynol rac-**36** also serves to bisannulate dihydrofurans, according to Scheme 13. The resulting dioxatriquinane moiety occurs as a substructure in the aglycone of steroidal cardiac glycosides, such as isogenine[14] and C-norcardanolide[15] (Scheme 12).



Isogenine, an Epoxycardanolide **C-Norcardanolide**

Scheme 12. Steroids with Dioxatriquinane Substructure



42 R = H **44a** + **44b** 67% a)
43 R = CH_2OPiv b) **45a** + **45b** 48% c)

Scheme 13. Dioxatriquinanes by Triethylborane Induced Atom Transfer Cyclization of 1,5-Diynes
a) Mixture of diastereomers: **44a** : **44b** = 1.4 : 1, yield includes 8% H-atom transfer product.
b) Absolute configuration is *(S)*, originating from L-glutamic acid.
c) Mixture of diastereomers: **45a** : **45b** = 2.9 : 1.

Conclusions. We have been able to tame vinyl radicals in tandem cycloisomerizations of 1,5-enynes and 1,5-diynes. Capping of the "first" acetylenic terminus by a trimethylsilyl group is a *sine qua non* for promoting tandem cycloisomerizations (Schemes 5, 6, 8, 9, 11, 13). Without trimethylsilyl capping, the radical chain is terminated prematurely (Schemes 2, 3, 4, 7); the only tandem product is annulated iodobenzene, which is obtained in poor yield (8%, Scheme 7).

Consecutive 5-exo-digonal, 5-exo-digonal cyclizations of 1,5-diynes have, to our knowledge, not been accomplished before. Moreover, the second 5-(π-endo)-exo-digonal closure involves an *acyclic* vinyl radical, which is conformationally mobile.[16] These radicals appear to be more difficult to handle experimentally than *cyclic* vinyl radicals, which are conformationally constrained.[17]

The cycloisomerization of 1,5-diynes, which, by definition, is also atom economical,[18] provides access to strained semicyclic, conjugated dienes with a functionalized dioxatriquinane framework (Scheme 11). The new stereogenic centres are established with complete stereocontrol (*cis*-selective first annulation and *E*-selective vinyl iodide; Schemes 8, 9, 13). The chemoselective 5-exo-digonal, 5-exo-trigonal sequence, like other reactions studied in this paper, is triggered by molecular oxygen and proceeds under exceptionally mild conditions at - 65°C, in a perfectly matched radical cascade. Again, two stereocentres are installed with complete stereocontrol (Schemes 5, 6).

In summary, tandem cycloisomerizations of 1,5-enynes and 1,5-diynes provide a convergent, one step route to functionalized dioxatricycles under mild conditions and with twofold stereocontrol.

Acknowledgments. We thank Zoë E. Thorn and Henning Reuter for experimental contributions and Dr. H. Laurent of Schering AG for discussions. Our work was kindly supported by the Fonds der Chemischen Industrie by a PhD fellowship to T. J. W.

EXPERIMENTAL

General. Melting points: uncorrected, Büchi apparatus. — Infrared spectra: Perkin Elmer 1710 spectrometer. — ^{1}H NMR spectra: At 80, 200 and 300 MHz, Bruker WP 80, WP 200 SY and AM 300 spectrometer, solvent $CDCl_3$ unless stated otherwise. — ^{13}C NMR spectra: Bruker WP 200 SY at 50 MHz or Bruker AM 300 at 75 MHz. APT (Attached Proton Test): 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-baked 0.2 mm silica gel 60 F_{254} plates (E. Merck). — THF and diethyl ether (E) were distilled from sodium benzophenone ketyl prior to use, CH_2Cl_2 from CaH_2. PE refers to light petroleum, bp 30-60°C, redistilled prior to use.

General Procedure for the Triethylborane-Induced Radical Cyclization. A flame-dried two-necked flask was flushed with dry air and charged with the cyclization precursor and the given solvent. After heating or cooling to the indicated temperature the triethylborane solution (1 M in hexane) was added until TLC showed total or almost total consumption of the starting material. Aqueous workup was performed with 1 M NaOH sol., H_2O and brine, followed by drying over $MgSO_4$. Removal of the solvent in vacuo yielded the crude product, which was purified by chromatography with E/PE. Separation from non-iodinated byproducts was performed by a second chromatography with CH_2Cl_2.

3-(1-Iodovinyl)-2-prop-2-ynyl-hexahydro-furo[2,3-b]pyran (**2a** and **2b**). Prepared according to the general procedure from the diastereomeric mixture **1** (320 mg, 1.0 mmol) by treatment with 2.0 mL of BEt_3 sol. in 2 mL of dry CH_3CN at 60°C for 5 h. Yield: 164 mg (45% incl. 9% of H atom transfer product) of a colourless oil, mixture of **2a** and **2b**. IR (neat) ν 3296, 3088, 2932, 2119, 1616, 1220, 1148, 1084, 1040, 960, 896 cm^{-1}; ^{1}H NMR, diastereomeric mixture δ 6.39 / 5.93 (each d, J = 1 Hz, 1 H, C=C*H*H); 6.05 (dd, J = 2.5, 2 Hz) / 5.97 (dd, J = 2.5, 1.5 Hz) (1 H, C=CH*H*); 5.49 (d, J = 4 Hz) / 5.01 (d, J = 3.5 Hz) (1 H, OC*H*O); 4.41 (dt, J = 9, 4.5 Hz) / 4.11 (dt, J = 7.5, 6 Hz) (1 H, OC*H*); 3.96-3.86 (m) / 3.76-3.62 (m) / 3.40 (dt, J = 11, 2.5 Hz) (2 H, OCH_2); 3.37-3.28 (m, 0.5 H, C=C(I)C*H* only from one diastereomer); 2.67 (ddd, J = 17, 4, 2.5 Hz) / 2.59 (dd, J = 6, 2.5 Hz) / 2.39 (ddd, J = 17, 4, 2.5 Hz) (2 H, CH_2C≡CH); 2.38-2.17 (m, 3 H, C=C(I)C*H* only from one diastereomer and OCH(O)C*H*); 2.07 / 2.03 (each t, J = 2.5 Hz, 1 H, C≡C*H*); 1.84-1.53 (m, 3 H, OCH$_2$CH*H*CH$_2$); 1.44-1.20 (m, 1 H, OCH$_2$C*H*HCH$_2$); ^{13}C NMR, diastereomeric mixture δ 129.67 / 126.15 (+, C=*C*H$_2$); 113.45 / 105.03 (+, H$_2$C=*C*(I)CH); 101.50 / 101.00 (-, O*C*HO); 82.08 / 73.91 (-, O*C*H); 80.16 / 80.13 (+, *C*≡CH); 71.03 / 70.33 (+, C≡*C*H); 64.54 / 60.61 (+, O*C*H$_2$); 58.29 / 55.38 (-, C=C(I)*C*H); 45.36 / 38.96 (-, OCH(O)*C*H); 25.21 / 24.21 / 22.89 / 20.95 / 20.33 / 19.95 (+, *C*H$_2$C≡CH, OCH$_2$*C*H$_2$*C*H$_2$); MS *m/z* no M$^+$, 278 (M-39, 64), 152 (20), 123 (100). HRMS Calcd. for $C_9H_{12}IO_2$ (M-39): 278.988207; Found: 278.988007.

2-Allyl-3-(1-iodovinyl)-hexahydro-furo[2,3-b]pyran (**4**). Prepared according to the general procedure from **3** (240 mg, 0.75 mmol) by treatment with 1.5 mL of BEt_3 sol. in 1 mL of dry benzene at 70°C for 4.5 h. Yield: 55 mg (23%) of **4**, colourless oil. ^{1}H NMR δ 6.02 (dd, J = 2.5, 2 Hz, 1 H, IC=C*H*H); 5.96 (dd, J = 2.5, 1.5 Hz, 1 H, IC=CH*H*); 5.89 (m, 1 H, CH$_2$C*H*=CH$_2$); 5.38 (d, J = 4 Hz, 1 H, OC*H*O); 5.16 (m, 1 H, CH$_2$CH=C*H*H); 5.05 (m, 1 H, CH$_2$CH=CH*H*); 4.35 (ddd, J = 9, 6, 4 Hz, 1 H, OC*H*); 3.81-3.61 (m, 2 H, OCH_2); 3.05 (ddt, J = 9, 6, 1.5 Hz, 1 H, C=C(I)C*H*); 2.48 (dddt, J = 14, 7, 4, 1.5 Hz, 1 H, CH*H*CH=CH$_2$); 2.34-2.16 (m, 2 H, C*H*HCH=CH$_2$ and OCH(O)C*H*); 1.77-1.52 (m, 3 H, OCH$_2$CH*H*C*H*$_2$); 1.40-1.19 (m, 1 H, OCH$_2$C*H*HCH$_2$).

2-Allyl-3-(1-iodovinyl)-hexahydro-furo[2,3-b]pyran (**6**). Prepared according to the general procedure from **5** (240 mg, 0.75 mmol) by treatment with 1.5 mL of BEt_3 sol. in 1 mL of dry benzene at 60°C for 3 h. Yield: 73 mg (30%) of **6**, colourless oil. IR (neat) ν 3078, 2927, 1610, 1222, 1159, 1092, 1056, 1037, 900 cm^{-1}; ^{1}H NMR δ 6.32 (d, J = 1.1 Hz, 1 H, IC=C*H*H); 5.93 (d, J = 1.2 Hz, 1 H, IC=CH*H*); 5.89 (m, 1 H, CH$_2$C*H*=CH$_2$); 5.13 (m, 1 H, CH$_2$CH=C*H*H); 5.07 (m, 1 H, CH$_2$CH=CH*H*); 4.99 (d, J = 2.4 Hz, 1 H, OC*H*O); 4.05-3.88 (m, 2 H, OC*H* and OC*H*H); 3.40 (td, J = 11.7, 2.5 Hz, 1 H, OCH*H*); 2.46-2.39 (m, 2 H, C=C(I)C*H* and C*H*HCH=CH$_2$); 2.27-2.15 (m, 2 H, CH*H*CH=CH$_2$ and OCH(O)C*H*); 1.83-1.51 (m, 3 H, OCH$_2$CH*H*C*H*$_2$); 1.43-1.35 (m, 1 H, OCH$_2$C*H*HCH$_2$); MS *m/z* no M$^+$, 279 (M-41, 63), 151 (18), 124 (100).

2-Allyl-3-iodomethylene-hexahydro-furo[2,3-b]pyran (**8**) and (**9**). Prepared according to the general procedure from **7** (300 mg, 1.0 mmol) by treatment with 2.5 mL of BEt_3 sol. in 2 mL of dry toluene at -20°C for 1.5 h. Yield: 200 mg (61%) of **8**, colourless oil, and 28 mg (7%) of **9**, colourless oil.

Spectroscopic data for **8** (*Z*)-isomer (polar): IR (neat) ν 3073, 2943, 1641, 1210, 1103, 1072, 1053, 1034, 981, 906 cm^{-1}. ^{1}H NMR δ 6.01 (dd, J = 2.77, 2.17 Hz, 1 H, C=C*H*I); 5.82 (m, 1 H, CH$_2$C*H*=CH$_2$); 5.20-

5.04 (m, 2 H, $CH_2CH=CH_2$); 5.19 (d, J = 4 Hz, 1 H, OC*H*O); 4.71 (ddt, J = 6, 4, 2 Hz, 1 H, OC*H*C=CHI); 3.85 (dtt, J = 12, 4, 2.5 Hz, 1 H, OCH*H*); 3.39 (td, J = 12, 2.5 Hz, 1 H, OC*H*H); 2.71-2.38 (m, 3 H, OCH(O)C*H* and C*H*HCH=CH_2); 2.12-2.00 (m, 1 H, OCH_2CH_2CHH); 1.98-1.79 (m, 1 H, OCH_2CH_2CHH); 1.73-1.50 (m, 1 H, OCH_2CHHCH_2); 1.34-1.21 (m, 1 H, OCH_2CHHCH_2); ^{13}C NMR δ 150.76 (+, *C*=CHI); 133.26 (-, $CH_2CH=CH_2$); 117.73 (+, $CH_2CH=CH_2$); 100.80 (-, O*C*HO); 84.00 (-, O*C*HC=CHI); 68.50 (-, C=*C*HI); 64.72 (+, OCH_2); 45.89 (-, OCH(O)*C*H); 36.64 (+, $CH_2CH=CH_2$); 21.56 (+, $OCH_2CH_2CH_2$); 19.77 (+, $OCH_2CH_2CH_2$); MS *m/z* no M^+, 265 (M-41, 100); HRMS Calcd. for $C_8H_{10}IO_2$ (M-41): 264.972557; Found: 264.972809.

Spectroscopic data for **9** (*E*)-isomer (nonpolar): IR (neat) ν 3074, 2942, 1640, 1153, 1077, 1057, 1035, 980, 910 cm^{-1}. ^1H NMR δ 6.02 (t, J = 2 Hz, 1 H, C=C*H*I); 5.85 (m, 1 H, $CH_2CH=CH_2$); 5.33 (d, J = 4 Hz, 1 H, OC*H*O); 5.16 (m, 1 H, $CH_2CH=CHH$); 5.09 (m, 1 H, $CH_2CH=CHH$); 4.73 (ddt, J = 7, 5, 2 Hz, 1 H, OC*H*C=CHI); 3.93-3.81 (m, 1 H, OCH*H*); 3.66 (dtd, J = 11, 4, 1.5 Hz, 1 H, OC*H*H); 2.78-2.67 (m, 1 H, OCH(O)C*H*); 2.53-2.28 (m, 2 H, $CH_2CH=CH_2$); 2.13-1.97 (m, 1 H, OCH_2CH_2CHH); 1.82-1.51 (m, 3 H, OCH_2CH_2CHH); MS *m/z* no M^+, 305 (M-1, 1), 265 (M-41, 100); HRMS Calcd. for $C_8H_{10}IO_2$ (M-41): 264.972557; Found: 264.972625.

2-Allyl-3-iodomethylene-hexahydro-furo[2,3–b]pyran (**11**) and (**12**). Prepared according to the general procedure from **10** (200 mg, 0.65 mmol) by treatment with 1.6 mL of BEt_3 sol. in 1.3 mL of dry toluene at -20°C for 2.5 h. Yield: 48 mg (24%) of **11**, colourless oil, and 50 mg (25%) of **12**, colourless oil.

Spectroscopic data for **11** (*Z*)-isomer (polar): IR (neat) ν 3073, 2943, 1640, 1216, 1156, 1069, 1054, 1035, 986, 901 cm^{-1}. ^1H NMR δ 6.07 (dd, J = 2.43, 1.72 Hz, 1 H, C=C*H*I); 6.00 (m, 1 H, $CH_2CH=CH_2$); 5.27-5.09 (m, 2 H, $CH_2CH=CH_2$); 5.21 (d, J = 4 Hz, 1 H, OC*H*O); 4.41 (dtd, J = 10, 2, 1 Hz, 1 H, OC*H*C=CHI); 3.88 (ddd, J = 11, 7, 4 Hz, 1 H, OCH*H*); 3.55 (m, 1 H, OC*H*H); 3.00 (dddt; J = 15, 7, 2.5, 1 Hz, 1 H, C*H*HCH=CH_2); 2.69 (m, 1 H, OCH(O)C*H*); 2.60-2.45 (m, 1 H, CH*H*CH=CH_2); 1.82 (m, 2 H, $OCH_2CH_2CH_2$); 1.59-1.43 (m, 2 H, $OCH_2CH_2CH_2$); MS *m/z* no M^+, 265 (M-41, 100); HRMS Calcd. for $C_8H_{10}IO_2$ (M-41): 264.972557; Found: 264.972565.

Spectroscopic data for **12** (*E*)-isomer (nonpolar): IR (neat) ν 3075, 2944, 1641, 1216, 1162, 1083, 1043, 913 cm^{-1}. ^1H NMR δ 5.95 (dd, J = 2, 1.5 Hz, 1 H, C=C*H*I); 5.88 (m, 1 H, $CH_2CH=CH_2$); 5.23 (d, J = 4 Hz, 1 H, OC*H*O); 5.17 (m, 1 H, $CH_2CH=CHH$); 5.11 (m, 1 H, $CH_2CH=CHH$); 4.35 (td, J = 6, 2 Hz, 1 H, OC*H*C=CHI); 3.85 (m, 1 H, OCH*H*); 3.72 (m, 1 H, OC*H*H); 2.67 (m, 1 H, OCH(O)C*H*); 2.48 (m, 2 H, $CH_2CH=CH_2$); 2.26-2.13 (m, 1 H, OCH_2CH_2CHH); 1.69-1.38 (m, 3 H, OCH_2CH_2CHH); MS *m/z* no M^+, 265 (M-41, 100); HRMS Calcd. for $C_8H_{10}IO_2$ (M-41): 264.972557; Found: 264.972992.

2-Iodomethyl-3-trimethylsilyl-1,2,3b,4,5,6,7a,8a-octahydro-7,8-dioxa-cyclopenta[a]indene (**14a** and **14b**). Prepared according to the general procedure from **13** (190 mg, 0.5 mmol) by treatment with 2.0 mL of BEt_3 sol. in 1.3 mL of dry toluene in the presence of EtI (40 µL, 0.5 mmol) at -65°C for 1 h. Yield: 85 mg (44%) of a slightly yellow oil, mixture of **14a** and **14b**. IR ($CHCl_3$) ν 2956, 1636, 1252, 1136, 1072, 836 cm^{-1}. ^1H NMR, diastereomeric mixture δ 5.43 (d, J = 5.5 Hz) / 5.37 (d, J = 4 Hz) (1 H, OC*H*O); 5.05 (bt, J = 7.5 Hz) / 4.57 (ddt, J = 9, 7, 1.5 Hz) (1 H, OC*H*C=C$SiMe_3$); 3.94-3.66 (m, 2 H, OCH_2); 3.61 (d, J = 6 Hz, 1 H, CHC*H*HI); 3.32-3.01 (m, 2 H, CHCH*H*I and C*H*CH*H*I); 2.76-2.43 (m, 2 H, OCH(O)C*H* and OCHC*H*HCHCH_2I); 2.00-1.84 (m, 1 H, OCH_2CH_2CHH); 1.73-1.49 (m, 3 H, OCH_2CH_2CHH); 1.41-1.25 (m, 1 H, OCHCH*H*CHCH_2I); 0.20 / 0.19 (each s, 9 H, $Si(CH_3)_3$); ^{13}C NMR, diastereomeric mixture δ 163.93 / 161.05 (+, *C*=C$SiMe_3$); 136.72 / 133.89 (+, C=*C*$SiMe_3$); 104.71 / 102.39 (-, O*C*HO); 85.18 / 84.07 (-, O*C*HC=C$SiMe_3$); 61.07 / 60.27 (+, OCH_2); 54.72 / 52.82 (-, *C*HCH_2I); 42.65 / 40.05 (+, OCH*C*H_2CHCH_2I); 37.33 / 36.58 (-, OCH(O)*C*H); 25.06 / 23.37 (+, $OCH_2CH_2CH_2$); 22.36 / 20.81 (+, $OCH_2CH_2CH_2$); 15.10 / 14.34 (+, CH*C*H_2I); 0.14 / 0.09 (-, $Si(CH_3)_3$); MS (80°C) *m/z* no M^+, 377 (M-1, 2), 251 (10), 133 (20), 105 (33), 73 (100).

(2R,3S,4R,4aR,6S,7aS,8aS)-2-[(Acetoxy)methyl]-6-(iodomethyl)-5-(trimethylsilyl)-3,4,4a,7,7a,8a-hexahydro-2H,6H-cyclopenta[4,5]furo[2,3-b]pyran-3,4-diol diacetate (**16**). Prepared according to the general procedure from **15** (220 mg, 0.4 mmol) by treatment with 0.8 mL of BEt_3 sol. in 1 mL of dry toluene in the presence of EtI (30 µL, 0.4 mmol) at -50°C for 1 h. Yield: 114 mg (51%) of **16**, white solid, mp 92°C, $[\alpha]_D^{20}$: - 25.8° (c = 0.248, $CHCl_3$). IR (KBr) ν 2957, 1752, 1435, 1367, 1241, 1158, 1065, 1045, 842 cm^{-1}; ^1H NMR δ 5.41 (d, J = 4 Hz, 1 H, OC*H*O); 5.27 (t, J = 10 Hz, 1 H, 3-Glc-C*H*); 5.21 (bt, J = 7 Hz, 1 H, OC*H*C=C$SiMe_3$); 5.06 (t, J = 10 Hz, 4-Glc-C*H*); 4.41 (dd, J = 12, 4 Hz, 1 H, 6-Glc-C*H*H); 4.22 (ddd, J = 10, 4, 2 Hz, 1 H, 5-Glc-C*H*); 4.08 (dd, J = 12, 2 Hz, 1 H, 6-Glc-CH*H*); 3.57 (d, J = 6 Hz, 1 H, CHC*H*HI); 3.17 (m, 2 H, CHCH*H*I and C*H*CH_2I); 2.95 (dd, J = 10, 4 Hz, 1 H, 2-Glc-C*H*); 2.62 (ddd, J = 12, 7, 5 Hz,

1 H, OCHC*H*HCHCH$_2$I); 2.09 (s, 3 H) / 2.03 (s, 6 H) (OCOC*H*$_3$); 1.42 (m, 1 H, OCHCH*H*CHCH$_2$I); 0.20 (s, 9 H, Si(C*H*$_3$)$_3$); ^{13}C NMR δ 170.71 / 170.00 / 169.71 (+, O*C*OCH$_3$); 154.46 (+, *C*=CSiMe$_3$); 141.90 (+, C=*C*SiMe$_3$); 102.09 (-, O*C*HO); 85.06 (-, O*C*HC=CSiMe$_3$); 70.80 (-, 3-Glc-*C*H); 69.35 (-, 5-Glc-*C*H); 67.71 (-, 4-Glc-*C*H); 61.87 (+, 6-Glc-*C*H$_2$); 52.86 (+, *C*HCH$_2$I); 44.81 (-, 2-Glc-*C*H); 42.17 (+, OCH*C*H$_2$CHCH$_2$I); 20.82 / 20.69 / 20.58 (-, OCO*C*H$_3$); 14.52 (+, CH*C*H$_2$I); 0.33 (-, Si(*C*H$_3$)$_3$); MS (120°C) *m/z* no M$^+$, 379 (M-187, 63), 160 (56), 141 (78), 117 (57), 73 (100).

(2R,3S,4R,4aR,6R,7aR,8aS)-2-[(Acetoxy)methyl]-6-(iodomethyl)-5-(trimethylsilyl)-3,4,4a,7,7a,8a-hexahydro-2H,6H-cyclopenta[4,5]furo[2,3-b]pyran-3,4-diol diacetate (**18**). Prepared according to the general procedure from **17** (220 mg, 0.4 mmol) by treatment with 1.2 mL of BEt$_3$ sol. in 1 mL of dry toluene in the presence of EtI (30 µL, 0.4 mmol) at -50°C for 2 h. Yield: 26 mg (12%) of **18**, colourless oil. IR (neat) ν 2957, 1752, 1435, 1367, 1241, 1158, 1065, 1045, 842 cm^{-1}; ^{1}H NMR δ 5.81 (d, *J* = 6 Hz, 1 H, OC*H*O); 5.26 (t, *J* = 4.5 Hz, 1 H, 3-Glc-C*H*); 5.05 (dd, *J* = 9, 4.5 Hz, 1 H, 4-Glc-C*H*); 4.65 (ddt, *J* = 10, 6.5, 2 Hz, OC*H*C=CSiMe$_3$); 4.33 (dd, *J* = 12.5, 5.5 Hz, 1 H, 6-Glc-CH*H*); 4.25-4.11 (m, 1 H, 5-Glc-C*H*); 4.21 (dd, *J* = 12.5, 2 Hz, 1 H, 6-Glc-CH*H*); 3.55 (dd, *J* = 9, 2 Hz, 1 H, CHC*H*HI); 3.30-3.10 (m, 3 H, CHCH*H*I, C*H*CH$_2$I and 2-Glc-C*H*); 2.57 (ddd, *J* = 12, 7, 5 Hz, 1 H, OCHC*H*HCHCH$_2$I); 2.16 / 2.15 / 2.11 (each s, each 3 H) (OCOC*H*$_3$); 1.63-1.39 (m, 1 H, OCHCH*H*CHCH$_2$I); 0.28 (s, 9 H, Si(C*H*$_3$)$_3$); MS (60°C) *m/z* no M$^+$, 506 (M-60, 10), 376 (20), 333 (23), 290 (24), 278 (34), 263 (40), 250 (89), 221 (58), 219 (56), 191 (78), 189 (100).

(2R,3S,4R,4aR,6S,7aS,8aS)-2-[(Acetoxy)methyl]-6-methyl-5-(trimethylsilyl)-3,4,4a,7,7a,8a-hexahydro-2H,6H-cyclopenta[4,5]furo[2,3-b]pyran-3,4-diol diacetate (**19**). To a solution of **16** (45 mg, 0.08 mmol) and AIBN (ca. 5 mg) in 2 mL of dry benzene at 80°C Bu$_3$SnH (0.11 mL, 0.4 mmol) was added over a period of 5 min, followed by another 30 min reflux. The reaction mixture was allowed to reach room temperature and the tin residues were removed by chromatography with pure PE. The top silica gel plug was transferred onto a second column and the pure product was obtained by chromatography with E/PE. Yield: 33 mg (95%) of **19**, slightly yellow oil. IR (neat) ν 2956, 1752, 1245, 1050, 840 cm^{-1}; ^{1}H NMR δ 5.37 (d, *J* = 4 Hz, 1 H, OC*H*O); 5.22 (t, *J* = 10 Hz, 1 H, 3-Glc-C*H*); 5.15 (bt, *J* = 7 Hz, 1 H, OC*H*C=CSiMe$_3$); 5.04 (t, *J* = 10 Hz, 4-Glc-C*H*); 4.39 (dd, *J* = 12, 4 Hz, 1 H, 6-Glc-CH*H*); 4.20 (ddd, *J* = 10, 4, 2 Hz, 1 H, 5-Glc-C*H*); 4.06 (dd, *J* = 12, 2 Hz, 1 H, 6-Glc-CH*H*); 2.93 (m, 1 H, C*H*CH$_3$); 2.90 (dd, *J* = 9, 4 Hz, 1 H, 2-Glc-C*H*); 2.45 (ddd, *J* = 11, 6, 5.5 Hz, 1 H, OCHC*H*HCHCH$_3$); 2.07 (s, 3 H) / 2.01 (s, 6 H) (OCOC*H*$_3$); 1.27-1.14 (m, 1 H, OCHCH*H*CHCH$_3$); 1.13 (d, *J* = 7 Hz, 3 H, CHC*H*$_3$); 0.14 (s, 9 H, Si(C*H*$_3$)$_3$); MS (100°C) *m/z* no M$^+$, 381 (M-59, 1), 380 (M-60, 2), 232 (21), 214 (43), 195 (22), 160 (44), 142 (52), 73 (100); HRMS Calcd. for $C_{19}H_{28}O_6Si$ (M-60): 380.165517; Found: 380.165771.

3-Iodomethylene-2-prop-2-ynyl-hexahydro-furo[2,3-b]pyran (**21** (*E*) and (*Z*)).[19] Prepared according to the general procedure from **20** (500 mg, 1.64 mmol) by treatment with 2 mL of BEt$_3$ sol. in 1.6 mL of dry toluene at 30°C for 2 h. Yield: 245 mg (49%) of **21**, colourless oil (E/Z = 1:9).

Spectroscopic data for **21** (*Z*)-isomer (polar): IR ($CHCl_3$) ν 3308, 3000, 2928, 2100, 1644, 1452, 1416, 1260, 1132, 1072, 904 cm^{-1}. ^{1}H NMR δ 6.08 (m, 1 H, C=C*H*I); 5.29 (d, *J* = 4 Hz, 1 H, OC*H*O); 4.71 (m, 1 H, OC*H*C=CHI); 3.87 (dm, *J* = 12 Hz, 1 H, OCH*H*); 3.41 (td, *J* = 12, 2 Hz, 1 H, OC*H*H); 2.92 (m, 2 H, OCH(O)C*H* and C*H*HC≡CH); 2.70 (ddd, *J* = 17, 3.6, 2.5 Hz, 1 H, CH*H*C≡CH); 1.96 (m, 1 H, CH$_2$C≡C*H*); 2.09 / 2.01-1.82 / 1.62 / 1.29 (m, 4 H, OCH$_2$C*H*$_2$C*H*$_2$); ^{13}C NMR δ 150.49 (+, *C*=CHI); 101.17 (-, O*C*HO); 82.59 (-, O*C*HC=CHI); 80.16 (+, *C*≡CH); 69.92 / 69.13 (+, C≡*C*H and C=*C*HI); 64.67 (+, O*C*H$_2$); 46.07 (-, OCH(O)*C*H); 23.03 / 21.84 / 19.78 (+, *C*H$_2$C≡CH, OCH$_2$*C*H$_2$CH$_2$ and OCH$_2$CH$_2$*C*H$_2$); MS *m/z* 304 (M$^+$, 7), 265 (M-39, 100); HRMS Calcd. for $C_{11}H_{13}IO_2$: 303.9960; Found: 303.9959.

Spectroscopic data for **21** (*E*)-isomer (nonpolar): IR (neat) ν 3294, 3059, 2943, 2120, 1637, 1451, 1260, 1153, 1078, 965, 909 cm^{-1}. ^{1}H NMR δ 6.29 (m, 1 H, C=C*H*I); 5.44 (d, *J* = 4 Hz, 1 H, OC*H*O); 4.78 (m, 1 H, OC*H*C=CHI); 3.87 (m, 1 H, OCH*H*); 3.68 (m, 1 H, OC*H*H); 2.77 (m, 1 H, OCH(O)C*H*); 2.55 (dd, *J* = 5.9, 2.5 Hz, 2 H, C*H*$_2$C≡CH); 2.04 (t, *J* = 2.5 Hz, 1 H, CH$_2$C≡C*H*); 1.78-1.52 (m, 4 H, OCH$_2$C*H*$_2$C*H*$_2$); ^{13}C NMR δ 154.37 (+, *C*=CHI); 99.02 (-, O*C*HO); 80.20 (+, *C*≡CH); 77.24 (-, O*C*HC=CHI); 70.80 / 70.15 (+, C≡*C*H and C=*C*HI); 61.54 (+, O*C*H$_2$); 44.95 (-, OCH(O)*C*H); 25.21 / 22.41 / 20.01 (+, *C*H$_2$C≡CH, OCH$_2$*C*H$_2$CH$_2$ and OCH$_2$CH$_2$*C*H$_2$); MS (90°C)*m/z* no M$^+$, 303 (M-1, 3), 265 (M-39, 100); HRMS Calcd. for $C_8H_{10}IO_2$ (M-39): 264.9725; Found: 264.9726.

7-Iodo-3,4,4a,9a-tetrahydro-1,9-dioxa-fluorene (**22**).[19] Isolated from a reaction of **20** (450 mg, 1.48 mmol) with 4.5 mL of BEt$_3$ sol. in 30 mL of dry benzene at 80°C for 120 h. Yield: 28 mg (8%) of **22**, white solid, mp 72°C. IR (KBr) ν 3052, 2975, 1953, 1472, 1269, 1218, 1111, 1081, 985, 901, 873 cm^{-1}; ^{1}H NMR δ 7.24 (m, 2 H, arom. H); 6.88 (dd, *J* = 8, <1 Hz, arom. H); 5.89 (d, *J* = 6 Hz, 1 H, OC*H*O); 3.74 (m, 2 H,

OCH_2); 3.27 (m, J = 6 Hz, 1 H, OCH(O)C*H*); 2.14-1.42 (m, 4 H, $OCH_2CH_2CH_2$); MS *m/z* 302 (M^+, 13), 301 (M-1, 100).

2-(E)-Iodomethylene-3-trimethylsilyl-1,2,3b,4,5,6,7a,8a-octahydro-7,8-dioxa-cyclopenta[a]indene (**28**) and *7-iodo-5-trimethylsilyl-3,4,4a,8,8a,9a-hexahydro-2H-1,9-dioxa-fluorene* (**29**). Prepared according to the general procedure from **23** (580 mg, 1.5 mmol) by treatment with 2.2 mL of BEt_3 sol. in 3.4 mL of dry CH_3CN at 60°C for 1 h. Yield: 270 mg (47%) of **28**, slightly yellow solid, mp 88-90°C, and 28 mg (5%) of **29**, slightly yellow oil.

Spectroscopic data for **28**: IR (KBr) ν 3074, 2952, 1615, 1252, 1134, 1073, 840 cm^{-1}; ^1H NMR δ 5.92 (dd, J = 2.4, 1.3 Hz, 1 H, C=C*H*I); 5.32 (d, J = 4.2 Hz, 1 H, OC*H*O); 5.12 (bt, J = 6 Hz, 1 H, OC*H*C=CSiMe_3); 3.77-3.64 (m, 2 H, OCH_2); 2.97 (ddd, J = 15.8, 6.9, 1.3 Hz, 1 H, OCHCH*H*C=CHI); 2.67-2.58 (m, 1 H, OCH(O)C*H*); 2.32 (ddd, J = 15.8, 5.1, 2.9 Hz, 1 H, OCHC*H*HC=CHI); 1.94-1.84 (m, 1 H, OCH_2CHHCH_2); 1.58-1.53 (m, 3 H, OCH_2CHHCH_2); 0.16 (s, 9 H, Si(CH_3)$_3$); ^{13}C NMR δ 168.31 (+, *C*=CSiMe_3); 160.07 (+, *C*=CHI); 135.61 (+, C=*C*SiMe_3); 102.53 (-, O*C*HO); 82.62 (-, O*C*HC=CSiMe_3); 68.09 (-, C=*C*HI); 60.14 (+, OCH_2); 45.96 (+, $OCHCH_2C$=CHI); 37.08 (-, OCH(O)*C*H); 23.37 (+, $OCH_2CH_2CH_2$); 21.95 (+, $OCH_2CH_2CH_2$); -0.58 (-, Si(CH_3)$_3$); MS (60°C) *m/z* 376 (M^+, 5), 249 (11), 203 (18), 185 (10), 163 (16), 131 (17), 103 (37), 73 (100); HRMS Calcd. for $C_{14}H_{21}IO_2Si$: 376.035561; Found: 376.037214.

Spectroscopic data for **29**: IR (neat) ν 2950, 1626, 1250, 1148, 1089, 890, 875, 834 cm^{-1}; ^1H NMR δ 6.61 (d, J = 3 Hz, 1 H, C*H*=CI); 5.43 (d, J = 4 Hz, 1 H, OC*H*O); 4.87 (ddd, J = 16, 8, 1 Hz, 1 H, OC*H*C=CSiMe_3); 3.91-3.66 (m, 2 H, OCH_2); 2.86 (ddd, J = 16, 8, 1 Hz, 1 H, OCHCH*H*CI=CH); 2.61 (m, 1 H, OCH(O)C*H*); 2.57 (td, J = 16, 3 Hz, 1 H, OCHC*H*HCI=CH); 1.88-1.76 (m, 1 H, OCH_2CHHCH_2); 1.66-1.45 (m, 3 H, OCH_2CHHCH_2); 0.16 (s, 9 H, Si(CH_3)$_3$); ^{13}C NMR δ 150.98 (+, *C*=CSiMe_3); 137.99 (-, *C*H=CI); 128.85 (+, C=*C*SiMe_3); 101.58 (-, O*C*HO); 89.99 (+, CH=*C*I); 75.21 (-, O*C*HC=CSiMe_3); 60.55 (+, OCH_2); 42.87 (+, $OCHCH_2CI$=CH); 39.00 (-, OCH(O)*C*H); 24.75 (+, $OCH_2CH_2CH_2$); 22.57 (+, $OCH_2CH_2CH_2$); -0.51 (-, Si(CH_3)$_3$); MS *m/z* 376 (M^+, 2), 374 (M-2, 4), 331 (4), 293 (7), 103 (20), 73 (100); HRMS Calcd. for $C_{14}H_{21}IO_2Si$: 376.035561; Found: 376.035217.

3-(tert.-Butyldimethylsilyl)-2-(E)-iodomethylene-1,2,3b,4,5,6,7a,8a-octahydro-7,8-dioxa-cyclopenta[a] indene (**30**). Prepared according to the general procedure from **24** (180 mg, 0.4 mmol) by treatment with 1.3 mL of BEt_3 sol. in 0.8 mL of dry CH_3CN at 70°C for 2.5 h. Yield: 25 mg (14%) of **30**, slightly yellow solid, mp 97-98°C (dec.). IR (KBr) ν 3080, 2948, 2932, 2852, 1600, 1400, 1248, 1136, 976, 820 cm^{-1}; ^1H NMR δ 6.01 (bd, J = 2.5 Hz, 1 H, C=C*H*I); 5.36 (d, J = 4 Hz, 1 H, OC*H*O); 5.19 (bt, J = 6 Hz, 1 H, OC*H*C=CSiMe_2Bu^t); 3.89-3.68 (m, 2 H, OCH_2); 3.07 (ddd, J = 18, 6.5, 1 Hz, 1 H, OCHC*H*HC=CHI); 2.69-2.58 (m, 1 H, OCH(O)C*H*); 2.39 (ddd, J = 18, 5.5, 2.5 Hz, 1 H, OCHCH*H*C=CHI); 2.00-1.87 (m, 1 H, OCH_2CHHCH_2); 1.70-1.45 (m, 3 H, OCH_2CHHCH_2); 0.87 (s, 9 H, SiC(CH_3)$_3$); 0.21 / 0.17 (each s, each 3 H, Si(CH_3)$_2$); ^{13}C NMR δ 170.16 (+, *C*=CSiMe_2Bu^t); 160.63 (+, *C*=CHI); 134.02 (+, C=*C*SiMe_2Bu^t); 102.47 (-, O*C*HO); 82.58 (-, O*C*HC=CSiMe_2Bu^t); 69.44 (-, C=*C*HI); 60.34 (+, OCH_2); 46.63 (+, $OCHCH_2C$=CHI); 37.75 (-, OCH(O)*C*H); 26.79 (-, SiC(CH_3)$_3$); 23.50 (+, $OCH_2CH_2CH_2$); 22.17 (+, $OCH_2CH_2CH_2$); 17.39 (+, Si*C*(CH_3)$_3$); -3.97 / -4.09 (-, Si(CH_3)$_2$); MS *m/z* 418 (M^+, 1.2), 417 (M-1, 5), 360 (10), 290 (11), 233 (14), 185 (16), 131 (27), 103 (100).

3-tert.-Butyl-2-(E)-iodomethylene-1,2,3b,4,5,6,7a,8a-octahydro-7,8-dioxa-cyclopenta[a]indene (**31**). Prepared according to the general procedure from **26** (1.00 g, 2.8 mmol) by treatment with 12 mL of BEt_3 sol. in 5.5 mL of dry CH_3CN at 60°C for 3.5 h (incomplete conversion). Yield: 170 mg (17%) of **31**, yellow oil. IR (neat) ν 3101, 2955, 2871, 1632, 1466, 1241, 1138, 1082, 953, 891 cm^{-1}; ^1H NMR δ 6.19 (bd, J = 3 Hz, 1 H, C=C*H*I); 5.41 (d, J = 4 Hz, 1 H, OC*H*O); 5.05 (bt, J = 6 Hz, 1 H, OC*H*C=CCMe$_3$); 3.87-3.67 (m, 2 H, OCH_2); 3.08 (ddd, J = 15.5, 6.5, 1 Hz, 1 H, OCHC*H*HC=CHI); 3.00-2.87 (m, 1 H, OCH(O)C*H*); 2.39 (ddd, J = 15.5, 5, 3 Hz, 1 H, OCHCH*H*C=CHI); 2.09-1.90 (m, 1 H, OCH_2CHHCH_2); 1.69-1.50 (m, 3 H, OCH_2CHHCH_2); 1.25 (s, 9 H, C(CH_3)$_3$); ^{13}C NMR δ 154.35 (+, *C*=CHI); 152.07 (+, C=*C*CMe$_3$); 143.09 (+, *C*=CCMe$_3$); 102.90 (-, O*C*HO); 80.81 (-, O*C*HC=CCMe$_3$); 69.28 (-, C=*C*HI); 60.26 (+, OCH_2); 47.27 (+, $OCHCH_2C$=CHI); 37.79 (-, OCH(O)*C*H); 34.17 (+, *C*(CH_3)$_3$); 30.03 (-, C(*C*H$_3$)$_3$); 23.98 (+, $OCH_2CH_2CH_2$); 22.41 (+, $OCH_2CH_2CH_2$); MS *m/z* 360 (M^+, 6), 345 (2), 262 (10), 234 (15), 165 (22), 145 (92), 131 (58), 117 (59), 105 (69), 91 (100).

Methyl-[3-(iodomethyl-dimethyl-silyl)-3b,4,5,6,7a,8a-hexahydro-1H-7,8-dioxa-cyclopenta[a]inden-2-ylidene] acetate (**32**) and *methyl-(3-trimethylsilyl-3b,4,5,6,7a,8a-hexahydro-1H-7,8-dioxa-cyclopenta[a]inden-2-ylidene] acetate* (**33**). Prepared according to the general procedure from **27** (500 mg, 1.5 mmol) by treatment with 2.3 mL of BEt_3 sol. in 2.3 mL of dry benzene in the presence of EtI (92 µL, 1.5

mmol) at 60°C for 5 h. Yield: 61 mg (12%) of **32**, yellow solid, mp 104-107°C, and 39 mg (11%) of **33**, colourless oil.

Spectroscopic data for **32**: IR ($CHCl_3$) ν 3000, 2952, 1704, 1628, 1252, 1180, 1156, 1136, 1076, 840 cm^{-1}; ^1H NMR δ 5.68 (dd, J = 3, 1 Hz, 1 H, C=C*H*CO_2Me); 5.42 (d, J = 4 Hz, 1 H, OC*H*O); 5.23 (bt, J = 5.5 Hz, 1 H, OC*H*C=C$SiMe_2CH_2I$); 3.80-3.73 (m, 2 H, O*C*H_2); 3.78 (ddd, J = 17, 6.5, 1 Hz, 1 H, OCHC*H*HC=CHCO_2Me); 3.69 (s, 3 H, CO_2CH_3); 2.83-2.72 (m, 1 H, OCH(O)C*H*); 2.57 (ddd, J = 17, 4.5, 3 Hz, 1 H, OCHCH*H*C=CHCO_2Me); 2.17 / 2.11 (each d, J = 12.5 Hz, each 1 H, $(H_3C)_2SiCH_2I$); 2.05-1.95 (m, 1 H, OCH_2CHHCH_2); 1.65-1.59 (m, 3 H, OCH_2CHHCH_2); 0.41 / 0.40 (each s, each 3 H, $(H_3C)_2SiCH_2I$); ^{13}C NMR δ 176.20 (+, *C*=$CHCO_2Me$); 169.03 (+, *C*=$CSiMe_2CH_2I$); 167.33 (+, *C*O_2CH_3); 133.79 (+, C=*C*$SiMe_2CH_2I$); 110.54 (-, C=*C*HCO_2Me); 102.62 (-, O*C*HO); 84.81 (-, O*C*HC=C$SiMe_2CH_2I$); 60.34 (+, O*C*H_2); 51.02 (-, CO_2CH_3); 41.10 (+, OCH*C*H_2C=CHCO_2Me); 37.61 (-, OCH(O)*C*H); 23.84 (+, $OCH_2CH_2CH_2$); 21.91 (+, $OCH_2CH_2CH_2$); -1.44 / -1.87 (-, $(H_3C)_2SiCH_2I$); -14.49 (+, $(H_3C)_2SiCH_2I$); MS (110°C) *m/z* 434 (M^+, 22), 419 (3), 307 (20), 293 (17), 204 (51), 199 (85), 171 (90), 158 (92), 132 (100); HRMS Calcd. for $C_{16}H_{23}IO_4Si$: 434.041040; Found: 434.041504.

Spectroscopic data for **33**: IR (neat) ν 2950, 1714, 1600, 1251, 1194, 1183, 1137, 1077, 841 cm^{-1}; ^1H NMR δ 5.75 (dd, J = 3, 1 Hz, 1 H, C=C*H*CO_2Me); 5.39 (d, J = 4 Hz, 1 H, OC*H*O); 5.21 (bt, J = 5 Hz, 1 H, OC*H*C=C$SiMe_3$); 3.86-3.63 (m, 2 H, O*C*H_2); 3.76 (ddd, J = 17, 6.5, 1 Hz, 1 H, OCHC*H*HC=CHCO_2Me); 3.69 (s, 3 H, CO_2CH_3); 2.83-2.70 (m, 1 H, OCH(O)C*H*); 2.56 (ddd, J = 17, 4.5, 3 Hz, 1 H, OCHCH*H*C=CHCO_2Me); 2.03-1.89 (m, 1 H, OCH_2CHHCH_2); 1.70-1.50 (m, 3 H, OCH_2CHHCH_2); 0.24 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR δ 173.88 (+, *C*=$CHCO_2Me$); 169.05 (+, *C*=$CSiMe_3$); 167.65 (+, *C*O_2CH_3); 136.95 (+, C=*C*$SiMe_3$); 110.55 (-, C=*C*HCO_2Me); 102.73 (-, O*C*HO); 84.90 (-, O*C*HC=C$SiMe_3$); 60.37 (+, O*C*H_2); 50.94 (-, CO_2CH_3); 41.07 (+, OCH*C*H_2C=CHCO_2Me); 37.41 (-, OCH(O)*C*H); 23.80 (+, $OCH_2CH_2CH_2$); 21.98 (+, $OCH_2CH_2CH_2$); -0.47 (-, $Si(CH_3)_3$); MS (110°C) *m/z* 308 (M^+, 6), 307 (M-1, 22), 235 (21), 204 (38), 175 (21), 158 (94), 132 (100).

2-(E)-Iodomethylene-3-trimethylsilyl-1,2,3b,4,5,6,7a,8a-octahydro-7,8-dioxa-cyclopenta[a]indene (**35**). Prepared according to the general procedure from **34** (300 mg, 0.8 mmol) by treatment with 1.6 mL of BEt_3 sol. in 1.6 mL of dry CH_3CN at room temperature for 3.5 h. Yield: 80 mg (ca. 20%) of **35**, yellow-brown, rapidly decomposing oil. IR (neat) ν 3090, 2953, 1697, 1250, 1091, 839 cm^{-1}; ^1H NMR δ 6.00 (dd, J = 3, 1 Hz, 1 H, C=C*H*I); 5.37 (d, J = 5 Hz, 1 H, OC*H*O); 4.54 (tdd, J = 6.5, 2, 1 Hz, 1 H, OC*H*C=C$SiMe_3$); 3.88-3.67 (m, 2 H, O*C*H_2); 3.03 (ddd, J = 15, 7, 1 Hz, 1 H, OCHCH*H*C=CHI); 2.75 (m, 1 H, OCH(O)C*H*); 2.47 (ddd, J = 15, 6, 3 Hz, 1 H, OCHCH*H*HC=CHI); 2.04-1.90 (m, 1 H, OCH_2CHHCH_2); 1.67-1.45 (m, 3 H, OCH_2CHHCH_2); 0.21 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR δ 173.21 (+, *C*=$CSiMe_3$); 161.28 (+, *C*=CHI); 134.04 (+, C=*C*$SiMe_3$); 103.82 (-, O*C*HO); 82.43 (-, O*C*HC=C$SiMe_3$); 67.65 (-, C=*C*HI); 61.59 (+, O*C*H_2); 44.09 (+, OCH*C*H_2C=CHI); 36.99 (-, OCH(O)*C*H); 26.69 (+, $OCH_2CH_2CH_2$); 21.90 (+, $OCH_2CH_2CH_2$); -0.34 (-, $Si(CH_3)_3$); MS *m/z* 376 (M^+, 2), 337 (2), 293 (12), 249 (3), 203 (5), 180 (6), 165 (7), 134 (11), 105 (21), 73 (100); HRMS Calcd. for $C_{14}H_{21}IO_2Si$: 376.035561; Found: 376.032043.

1-Trimethylsilyl-hexa-1,5-diyn-3-ol (**36**). 3-Trimethylsilyl-prop-2-yn-1-ol[20] (8.0 g, 62 mmol) was oxidized using PCC (94 mmol, 50% on silica gel) in 190 mL of dry CH_2Cl_2 to yield the corresponding aldehyde, which, after silica gel filtration and concentration at reduced pressure, was directly used in the next step. The 3-trimethylsilyl-prop-2-yn-1-al was added to a solution of propargylmagnesium bromide in diethyl ether (94 mmol)[21] at -10°C, the mixture was stirred for 15 min and worked up with sat. NH_4Cl sol., 1 M HCl sol., sat. $NaHCO_3$ sol. and brine. After drying with $MgSO_4$ and removal of the solvent in vacuo the crude product was purified by bulb to bulb distillation. Yield: 9.28 g (89%) of **36**, colourless oil. IR (neat) ν 3400, 3306, 2961, 2177, 2120, 1592, 1413, 1252, 1062, 844 cm^{-1}; ^1H NMR δ 4.51 (q, J = 6 Hz, 1 H, C*H*OH); 2.67 (ddd, J = 17, 6, 2.5 Hz, 1 H, C*H*HC≡CH); 2.65 (ddd, J = 17, 6, 2.5 Hz, 1 H, CH*H*C≡CH); 2.37 (d, J = 6 Hz, 1 H, O*H*); 2.11 (t, J = 2.5 Hz, 1 H, $CH_2C{\equiv}CH$); 0.17 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR δ 104.61 (+, *C*≡C$SiMe_3$); 90.12 (+, C≡*C*$SiMe_3$); 79.40 (+, $CH_2C{\equiv}CH$); 71.19 (+, $CH_2C{\equiv}CH$); 60.97 (-, *C*HOH); 28.28 (+, *C*H_2C≡CH); -0.33 (-, $Si(CH_3)_3$); MS *m/z* no M^+, 165 (M-1, 2), 151 (5), 127 (100); HRMS Calcd. for $C_6H_{11}OSi$ (M-39): 127.057918; Found: 127.057060.

[(3S/3R)-1-Trimethylsilyl)hexa-1,5-diyn-3-yl]3,4,6-tri-O-acetyl-2-deoxy-2-iodo-α-D-mannopyranoside (**38** (3*S*) and **39** (3*R*)). To a solution of N-iodosuccinimide (1.93 g, 8.6 mmol) in 0.5 mL of dry CH_3CN was added diynol **36** (1.43 g, 8.6 mmol) and a solution of 3,4,6-tri-*O*-acetyl-D-glucal **37** (1.17 g, 4.3 mmol) in 1.2 mL of dry CH_3CN at 0°C. The reaction was stirred at room temperature until TLC indicated total consumption of the glucal. Workup was performed using diethyl ether, $Na_2S_2O_3$ sol. and brine, followed by drying

($MgSO_4$). After removal of the solvent *in vacuo* the crude product was purified by chromatography and crystallization from E/PE. Yield: 1.41 g (58%) of **38** and **39**, slightly yellow oil, separable by chromatography and crystallization.

Spectroscopic data for **38** (colourless solid, mp 123-124°C, $[\alpha]_D^{20}$: - 11.3° (c = 0.32, $CHCl_3$)): IR (KBr) ν 3272, 2960, 2174, 2130, 1740, 1380, 1232, 1124, 1044, 844 cm^{-1}; ^1H NMR δ 5.46 (bs, 1 H, OC*H*O); 5.41 (t, *J* = 9.5 Hz, 1 H, 4-Glc-C*H*); 4.64 (dd, *J* = 9, 4 Hz, 1 H, 3-Glc-C*H*); 4.53 (dd, *J* = 4, 1 Hz, 1 H, C*H*I); 4.41 (dd, *J* = 8, 5.5 Hz, 1 H, OC*H*C≡CSiMe_3); 4.31 (bdt, *J* = 11, 3 Hz, 1 H, 5-Glc-C*H*); 4.24 (dd, *J* = 12, 3.5 Hz, 1 H, 6-Glc-C*H*H); 4.10 (dd, *J* = 12, 2 Hz, 1 H, 6-Glc-CH*H*); 2.67 (ddd, *J* = 17, 8, 2.5 Hz, 1 H, C*H*HC≡CH); 2.54 (ddd, *J* = 17, 5.5, 2.5 Hz, 1 H, CH*H*C≡CH); 2.10 / 2.06 / 2.02 (each s, each 3 H, OCOCH_3); 2.03 (t, *J* = 2.5 Hz, 1 H, CH_2C≡C*H*); 0.14 (s, 9 H, Si(CH_3)$_3$); ^{13}C NMR δ 170.62 / 169.75 / 169.33 (+, O*C*OCH$_3$); 101.86 (+, *C*≡CSiMe_3); 101.42 (-, O*C*HO); 92.23 (+, C≡*C*SiMe_3); 79.24 (+, CH_2*C*≡CH); 70.77 (+, CH_2C≡*C*H); 69.92 / 68.80 / 67.86 / 67.19 (-, *C*HOC≡CSiMe_3, 3-, 4- and 5-Glc-*C*H); 61.53 (+, 6-Glc-*C*H_2); 29.18 (-, *C*HI); 26.75 (+, *C*H_2C≡CH); 20.86 / 20.68 / 20.56 (-, OCO*C*H_3); -0.41 (-, Si(*C*H_3)$_3$); MS (200°C)*m/z* 564 (M^+, 1), 549 (4), 398 (52), 278 (29), 237 (44), 184 (38), 170 (28), 97 (69), 73 (100); HRMS Calcd. for $C_{20}H_{26}IO_8Si$ (M-15): 549.044174; Found: 549.043462.

Spectroscopic data for **39** (colourless solid, mp 104°C, $[\alpha]_D^{20}$: + 82.5° (c = 0.126, $CHCl_3$)): IR (KBr) ν 3300, 2956, 2170, 2125, 1736, 1252, 1028, 1008, 844 cm^{-1}; ^1H NMR δ 5.48 (d, *J* = 0.5 Hz, 1 H, OC*H*O); 5.35 (m, 1 H, 4-Glc-C*H*); 4.61-4.53 (m, 2 H, 3-Glc-C*H* and C*H*I); 4.42 (dd, *J* = 7.5, 6 Hz, 1 H, OC*H*C≡CSiMe_3); 4.18 (m, 1 H, 5-Glc-C*H*); 4.14 (bs, 2 H, 6-Glc-CH_2); 2.66 (ddd, *J* = 17, 7.5, 2.5 Hz, 1 H, C*H*HC≡CH); 2.57 (ddd, *J* = 17, 6, 2.5 Hz, 1 H, CH*H*C≡CH); 2.09 / 2.05 / 2.02 (each s, each 3 H, OCOCH_3); 2.04 (t, *J* = 2.5 Hz, 1 H, H-1); 0.14 (s, 9 H, Si(CH_3)$_3$); ^{13}C NMR δ 170.56 / 169.66 / 169.39 (+, O*C*OCH$_3$); 100.76 (+, *C*≡CSiMe_3); 98.46 (-, O*C*HO); 92.90 (+, C≡*C*SiMe_3); 79.64 (+, CH_2*C*≡CH); 70.66 (+, CH_2C≡*C*H); 69.63 / 68.93 / 65.21 / 61.97 (-, *C*HOC≡CSiMe_3, 3-, 4- and 5-Glc-*C*H); 61.97 (+, 6-Glc-*C*H_2); 29.26 (-, *C*HI); 25.94 (+, *C*H_2C≡CH); 20.86 / 20.68 / 20.57 (-, OCO*C*H_3); -0.36 (-, Si(*C*H_3)$_3$); MS (140°C)*m/z* no M^+, 549 (M-15, 4), 399 (77), 338 (100), 279 (24), 237 (46), 183 (69), 97 (70), 73 (100); HRMS Calcd. for $C_{20}H_{26}IO_8Si$ (M-15): 549.044174; Found: 549.043240.

(2R,3S,4R,4aR,7aS,8aS)-2-[(Acetoxy)methyl]-6-[(E)-iodomethylene]-5-(trimethylsilyl)-3,4,4a,7,7a,8a-hexahydro-2H,6H-cyclopenta[4,5]furo[2,3-b]pyran-3,4-diol diacetate (**40**). Prepared according to the general procedure from **38** (400 mg, 0.7 mmol) by treatment with 1.4 mL of BEt_3 sol. in 1.4 mL of dry benzene at 80°C for 0.5 h. Yield: 226 mg (57%) of **40**, yellow solid, mp 53-54°C, $[\alpha]_D^{20}$: + 30° (c = 0.27, $CHCl_3$). IR (KBr) ν 2956, 1752, 1428, 1368, 1240, 1160, 1044, 1012, 840 cm^{-1}; ^1H NMR δ 5.99 (dd, *J* = 2 Hz, 1 H, C=C*H*I); 5.40 (d, *J* = 4 Hz, 1 H, OC*H*O); 5.21 (bt, *J* = 6 Hz, 1 H, OC*H*C=CSiMe_3); 5.17 (t, *J* = 9 Hz, 1 H, 3-Glc-C*H*); 5.00 (t, *J* = 10 Hz, 4-Glc-C*H*); 4.35 (dd, *J* = 12, 4 Hz, 1 H, 6-Glc-C*H*H); 4.12 (ddd, *J* = 10, 4, 2 Hz, 1 H, 5-Glc-C*H*); 4.00 (dd, *J* = 12, 2 Hz, 1 H, 6-Glc-CH*H*); 3.02 (ddd, *J* = 16, 6.5, 1.5 Hz, 1 H, OCHC*H*HC=CHI); 2.98 (dd, *J* = 9, 4 Hz, 1 H, 2-Glc-C*H*); 2.35 (ddd, *J* = 16, 5, 3 Hz, 1 H, OCHCH*H*C=CHI); 2.01 / 1.96 / 1.95 (each s, each 3 H, OCOCH_3); 0.14 (s, 9 H, Si(CH_3)$_3$); ^{13}C NMR δ 170.42 (+, *C*=CSiMe_3); 169.48 (+, 2 x O*C*OCH$_3$); 161.36 / 159.06 (+, *C*=CHI and O*C*OCH$_3$); 139.25 (+, C=*C*SiMe_3); 102.44 (-, O*C*HO); 83.47 (-, *C*HOC=CSiMe_3); 70.75 / 70.15 / 69.31 / 67.25 (-, C=*C*HI, 3-, 4- and 5-Glc-*C*H); 61.62 (+, 6-Glc-*C*H_2); 45.95 (+, OCH*C*H_2C=CHI); 44.39 (-, 2-Glc-*C*H); 20.53 / 20.45 / 20.42 (-, OCO*C*H_3); -0.67 (-, Si(*C*H_3)$_3$); MS (150°C) *m/z* 564 (M^+, 7), 520 (3), 398 (18), 356 (27), 275 (10), 229 (14), 147 (26), 117 (29), 73 (100); HRMS Calcd. for $C_{21}H_{29}IO_8Si$: 564.067649; Found: 564.067280.

(2R,3S,4R,4aR,7aR,8aS)-2-[(Acetoxy)methyl]-6-[(E)-iodomethylene]-5-(trimethylsilyl)-3,4,4a,7,7a,8a-hexahydro-2H,6H-cyclopenta[4,5]furo[2,3-b]pyran-3,4-diol diacetate (**41**). Prepared according to the general procedure from **39** (250 mg, 0.44 mmol) by treatment with 1.0 mL of BEt_3 sol. in 0.9 mL of dry benzene at 60°C for 0.5 h. Yield: 63 mg (ca. 20%) of **41**, yellow-brown, rapidly decomposing oil. IR ($CHCl_3$) ν 3040, 2956, 1748, 1700, 1368, 1236, 1132, 1072, 1040, 844 cm^{-1}; ^1H NMR δ 6.11 (dd, *J* = 2.5 Hz, 1 H, C=C*H*I); 5.77 (d, *J* = 6 Hz, 1 H, OC*H*O); 5.17 (dd, *J* = 4, 3 Hz, 1 H, 3-Glc-C*H*); 4.83 (tdd, *J* = 6, 4, 1 Hz, 1 H, 4-Glc-C*H*); 4.64 (btd, *J* = 7, 2 Hz, OC*H*C=CSiMe_3); 4.20 (s, 2 H, 6-Glc-CH_2); 4.25-4.12 (m, 1 H, 5-Glc-C*H*); 3.18-3.11 (m, 1 H, 2-Glc-C*H*); 3.01 (ddd, *J* = 15, 7, 1 Hz, 1 H, OCHC*H*HC=CHI); 2.46 (ddd, *J* = 15, 6.5, 3 Hz, 1 H, OCHCH*H*C=CHI); 2.09 / 2.06 / 1.93 (each s, each 3 H, OCOCH_3); 0.22 (s, 9 H, Si(CH_3)$_3$); MS (80°C) *m/z* 564 (M^+, 3), 504 (2), 423 (4), 400 (7), 369 (7), 328 (7), 289 (6), 275 (13), 254 (20), 175 (11), 128 (19), 84 (100).

5-(E)-Iodomethylene-4-trimethylsilyl-3,3a,5,6,6a,7a-hexahydro-2H-1,7-dioxa-cyclopenta[a]pentalene (**44**). Prepared according to the general procedure from **42** (325 mg, 0.9 mmol) by treatment with 3.0 mL of BEt_3 sol. in 2.0 mL of dry benzene in the presence of EtI (80 µL, 1.0 mmol) at 60°C for 0.75 h. Yield: 209 mg (67%) of a yellow oil, mixture of **44a** and **44b** (1.4 : 1, contains 8% of H atom transfer product). IR (neat) ν 2957, 1251, 971, 935, 840 cm^{-1}; MS *m/z* 362 (M^+, 5), 347 (3), 197 (10), 164 (13), 127 (32), 99 (30), 73 (100).

Spectroscopic data for **44a**: ^1H NMR δ 5.99 (dd, *J* = 2.8, 0.9 Hz, 1 H, C=C*H*I); 5.92 (d, *J* = 4.7 Hz, 1 H, OC*H*O); 4.99 (ddd, *J* = 6.1, 4.9, 0.6 Hz, 1 H, OC*H*C=CSiMe$_3$); 4.08-3.89 (m, 2 H, OCH_2CH$_2$); 3.33 (dddd, *J* = 10.2, 5.8, 3.3, 1.2 Hz, 1 H, OCH(O)C*H*); 2.99 (ddd, *J* = 16.0, 6.8, 1.4 Hz, 1 H, OCHC*H*HC=CHI); 2.37 (ddd, *J* = 16.0, 4.8, 2.9 Hz, 1 H, OCHCH*H*C=CHI); 2.25 (m, 1 H, OCH$_2$C*H*H); 1.93 (m, 1 H, OCH$_2$CH*H*); 0.25 (s, 9 H, Si(CH_3)$_3$); ^{13}C NMR δ 168.89 (+, *C*=CSiMe$_3$); 161.42 (+, *C*=CHI); 135.44 (+, C=*C*SiMe$_3$); 112.64 (-, O*C*HO); 85.59 (-, O*C*HC=CSiMe$_3$); 68.92 (+, O*C*H$_2$CH$_2$); 68.12 (-, C=*C*HI); 45.01 (+, OCH*C*H$_2$C=CHI); 42.89 (-, OCH(O)*C*H); 31.48 (+, OCH$_2$*C*H$_2$); -0.58 (-, Si(*C*H$_3$)$_3$).

Spectroscopic data for **44b**: ^1H NMR δ 6.02 (dd, *J* = 2.5, 1 Hz, 1 H, C=C*H*I); 5.97 (d, *J* = 5 Hz, 1 H, OC*H*O); 4.71 (bddd, *J* = 6, 5, 1 Hz, 1 H, OC*H*C=CSiMe$_3$); 4.08-3.92 (m, 1 H, OC*H*HCH$_2$); 3.89-3.75 (m, 1 H, OCH*H*CH$_2$); 3.33 (bdddd, *J* = 10, 6, 3.5, 1 Hz, 1 H, OCH(O)C*H*); 2.94 (ddd, *J* = 16, 7, 1 Hz, 1 H, OCHC*H*HC=CHI); 2.45 (ddd, *J* = 16, 5, 2.5 Hz, 1 H, OCHCH*H*C=CHI); 2.19-2.04 (m, 1 H, OCH$_2$C*H*H); 1.68-1.56 (m, 1 H, OCH$_2$CH*H*); 0.25 (s, 9 H, Si(CH_3)$_3$); ^{13}C NMR δ 171.77 (+, *C*=CSiMe$_3$); 161.20 (+, *C*=CHI); 134.16 (+, C=*C*SiMe$_3$); 112.31 (-, O*C*HO); 84.86 (-, O*C*HC=CSiMe$_3$); 67.96 (-, C=*C*HI); 66.61 (+, O*C*H$_2$CH$_2$); 43.81 (-, OCH(O)*C*H); 43.28 (+, OCH*C*H$_2$C=CHI); 33.88 (+, OCH$_2$*C*H$_2$); -0.55 (-, Si(*C*H$_3$)$_3$).

(S)-2-(tert.-Butylcarbonyloxymethyl)-5-(E)-iodomethylene-4-trimethylsilyl-3,3a,5,6,6a,7a-hexahydro-2H-1,7-dioxa-cyclopenta[a]pentalene (**45**). Prepared according to the general procedure from **43**[22] (480 mg, 1.0 mmol) by treatment with 3.0 mL of BEt_3 sol. in 2.0 mL of dry CH_3CN at 65°C for 2 h. Yield: 230 mg (48%) of a yellow oil, mixture of **45a** and **45b** (2.9 : 1). IR (neat) ν 3078, 2959, 2873, 1731, 1480, 1251, 1158, 1010, 839 cm^{-1}; MS (110°C) *m/z* 476 (M^+, 3), 391 (3), 349 (18), 292 (27), 247 (11), 220 (12), 129 (10), 82 (70), 73 (100).

Spectroscopic data for **45a**: ^1H NMR δ 6.01 (dd, *J* = 3, 1.5 Hz, 1 H, C=C*H*I); 5.86 (d, *J* = 5 Hz, 1 H, OC*H*O); 5.10 (bt, *J* = 6 Hz, 1 H, OC*H*C=CSiMe$_3$); 4.32-4.08 (m, 3 H, OC*H*CH_2OPiv); 3.40-3.27 (m, 1 H, OCH(O)C*H*); 2.98 (ddd, *J* = 16, 6.5, 1.5 Hz, 1 H, OCHC*H*HC=CHI); 2.45 (ddd, *J* = 16, 5, 3 Hz, 1 H, OCHCH*H*C=CHI); 2.29 (m, 1 H, OCHC*H*H); 1.69-1.52 (m, 1 H, OCHCH*H*); 1.22 (s, 9 H, (*H*$_3$C)$_3$CCO$_2$); 0.23 (s, 9 H, Si(CH_3)$_3$); ^{13}C NMR δ 178.08 (+, (H$_3$C)$_3$*C*CO$_2$); 167.72 (+, *C*=CSiMe$_3$); 161.43 (+, *C*=CHI); 135.73 (+, C=*C*SiMe$_3$); 112.45 (-, O*C*HO); 83.14 (-, O*C*HC=CSiMe$_3$); 76.89 (-, O*C*HCH$_2$OPiv); 68.52 (-, C=*C*HI); 65.10 (+, OCH*C*H$_2$OPiv); 43.63 (+, OCH*C*H$_2$C=CHI); 43.03 (-, OCH(O)*C*H); 38.61 (+, (H$_3$C)$_3$*C*CO$_2$); 32.48 (+, OCH*C*H$_2$); 27.02 (-, (H$_3$*C*)$_3$CCO$_2$); -0.70 (-, Si(*C*H$_3$)$_3$).

Spectroscopic data for **45b**: ^1H NMR δ 6.04 (m, 1 H, C=C*H*I); 5.93 (d, *J* = 5.5 Hz, 1 H, OC*H*O); 4.75 (btd, *J* = 6, 1 Hz, 1 H, OC*H*C=CSiMe$_3$); 4.31-3.95 (m, 3 H, OC*H*CH_2OPiv); 3.42-3.28 (m, 1 H, OCH(O)C*H*); 2.98 (ddd, *J* = 16, 7, 1.5 Hz, 1 H, OCHC*H*HC=CHI); 2.50 (ddd, *J* = 16, 5.5, 3 Hz, 1 H, OCHCH*H*C=CHI); 2.36-2.22 (m, 1 H, OCHC*H*H); 1.74-1.53 (m, 1 H, OCHCH*H*); 1.20 (s, 9 H, (*H*$_3$C)$_3$CCO$_2$); 0.24 (s, 9 H, Si(CH_3)$_3$); ^{13}C NMR δ 178.08 (+, (H$_3$C)$_3$*C*CO$_2$); 171.71 (+, *C*=CSiMe$_3$); 161.31 (+, *C*=CHI); 134.49 (+, C=*C*SiMe$_3$); 112.45 (-, O*C*HO); 83.14 (-, O*C*HC=CSiMe$_3$); 76.89 (-, O*C*HCH$_2$OPiv); 68.31 (-, C=*C*HI); 66.08 (+, OCH*C*H$_2$OPiv); 44.36 (-, OCH(O)*C*H); 43.81 (+, OCH*C*H$_2$C=CHI); 38.51 (+, (H$_3$C)$_3$*C*CO$_2$); 35.39 (+, OCH*C*H$_2$); 27.02 (-, (H$_3$*C*)$_3$CCO$_2$); -0.56 (-, Si(*C*H$_3$)$_3$).

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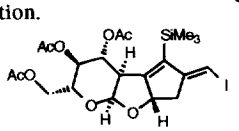
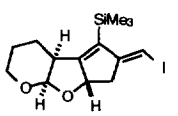
§ Throughout this paper the Maehr convention is used (Maehr, H. *J. Chem. Ed.* **1985**, *62*, 114). Solid and broken *lines* refer to racemic materials and *relative* configuration, whereas solid and broken *wedges* are used to indicate *absolute* configuration.



1 stereoisomer



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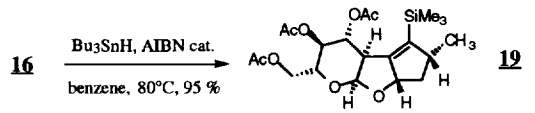

10 We think that the 1,3-syn selective formation of the cyclopentene system might have its origin in a chair-like transition state for the second cyclization. The alternative transition state, with the anti relationship, would follow through a boat-like conformation and is supposed to have an additional 1,3-diaxial repulsive interaction (cf. Houk, K. N.; Spellmeyer, D. C. *J. Org. Chem.* **1987**, *52*, 959).

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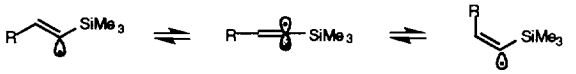

bent linear bent

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(*Received in Germany* 8 *April* 1995; *accepted* 15 *May* 1995)