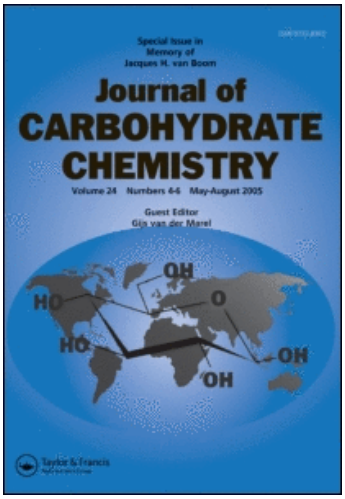

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HIGHLY DEOXYGENATED SUGARS. I. C2-BRANCHED GLUCOSE DERIVATIVES AND CARBON LINKED DEOXYGENATED DISACCHARIDES*

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ABSTRACT

Triacetylglucal (**1**) is converted with high α-selectivity (>9:1) to the corresponding 2,3-unsaturated allyl and benzyl glycosides **2** and **3** using ferric chloride as the catalyst. The 6-*O*-silyl-protected allylic alcohol **5** is transformed to the 3,4-unsaturated C2-branched ester **6** or the amide **7** by Claisen rearrangement. The highly deoxygenated iodo lactone **8**, resulting from the amide **6** by iodolactonization, is a versatile starting material for chiral building blocks **9**–**12**. The 3,4-unsaturated C2-branched ester **6** is reduced to the aldehyde **14** and converted to a carbon linked disaccharide analogue **16** via cycloaddition with Danishefky's diene.

Key Words: Ferrier rearrangement; Claisen rearrangement; Branched sugars; Hetero Diels–Alder reaction; *C*-linked disaccharide

*Dedicated to Professor Dr. Dr. h.c. Frieder Lichtenthaler on the occasion of his 70th birthday.

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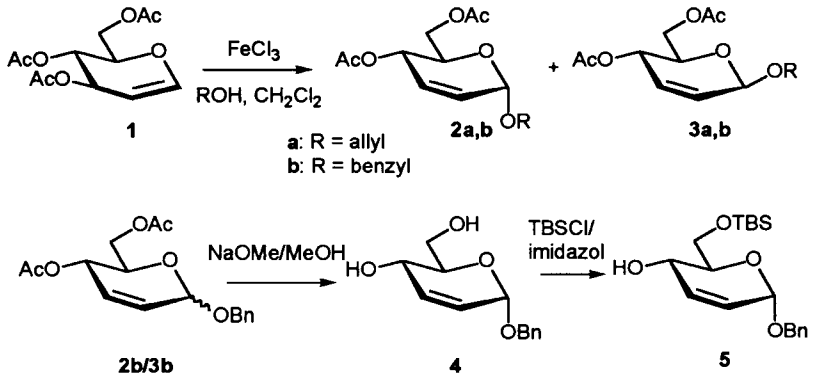
Table 1. Comparison of $FeCl_3$[3] and $Sc(OTf)_3$[4] as the Catalysts in the Ferrier Rearrangement with Glucal Acetate **1**

Entry	Alcohol	Cat. [mol equiv.]	Yield	α/β Selectivity	Time
1	Allyl alcohol	$FeCl_3$ [0.01]	87%	10:1	30 min.
2	Allyl alcohol	$Sc(OTf)_3$ [0.05]	85%	5:1	2.5 h
3	Benzyl alcohol	$FeCl_3$ [0.01]	93%	9:1	15 min.
4	Benzyl alcohol	$Sc(OTf)_3$ [0.05]	87%	7:1	1.5 h

In connection with a new project on the utilization of sugars as starting materials for highly deoxygenated chiral building blocks, we investigated the synthesis of C-2 alkylated sugars[1] obtained by Claisen rearrangement[2] of allyl alcohol **5**. Fortunately, two highly effective new catalysts, $FeCl_3$[3] and $Sc(OTf)_3$[4] were recently proposed for the Ferrier type II rearrangement to prepare the allyl acetates **2** and **3** starting from glucal acetate **1**. With these Lewis acids, much milder reaction conditions and better yields were obtained than described with the previously used boron trifluoride etherate[5] or other catalysts (review[6]). Thus, the first task was to find the best conditions with respect to the anomeric ratio of the glycosides α-**2** and β-**3**, determined by GC analysis. Both catalysts $FeCl_3$ and $Sc(OTf)_3$ were compared, with allyl and benzyl alcohol and glucal acetate **1** as the substrates. The results are summarized in Table 1. The data clearly show the superiority of $FeCl_3$ over $Sc(OTf)_3$ with respect to yield, anomeric ratio and shorter reaction times under the conditions used. In particular, the high predominance of the α-anomers **2** was important for the purity of all subsequent products. It was possible to obtain the starting material **2a** and **2b** as pure α-anomers in crystalline form and record the spectroscopic data and optical rotation. The reaction was also amenable to scale-up and the pure anomers **2a** and **2b** were isolated in multigram quantities (Scheme 1).

The free hydroxyl group was required for the anticipated Claisen rearrangements. This was easily achieved by Zemplén saponification of the esters of the anomeric

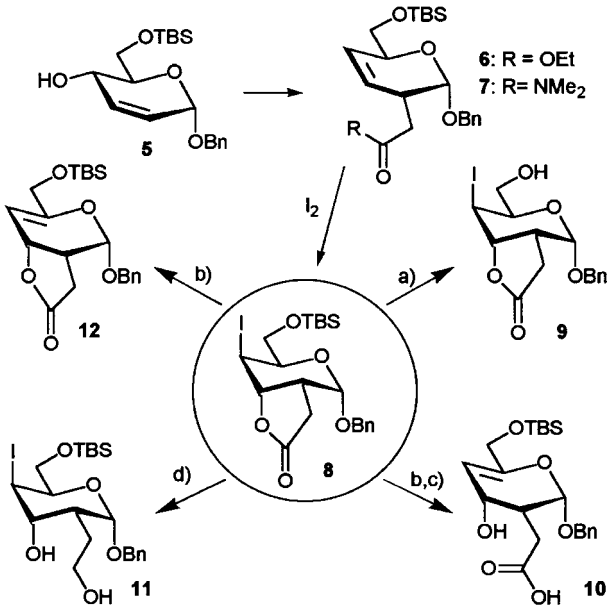


Scheme 1. Fe(Cl)3-catalysed Ferrier reaction of glucal acetale (1) and selective protection as TBS ether 5.

mixture **2b/3b**. The pure deacetylated α-anomer **4** was obtained by chromatography and crystallization. Protection of the primary hydroxyl group at C-6 of **4** was then easily achieved by selective silylation as *tert*-butyldimethylsilyl ether **5**.

Claisen type rearrangements are often used in the synthesis of branched sugars (reviews[1,2]). For instance, Corey has introduced C-4 substitution using the Eschenmoser variation in his famous enantioselective prostaglandin synthesis.[7] In our case, we tested the Johnson[8] and Eschenmoser[9] variations on the C-4 allyl alcohol **5** to arrive at substitution at C-2. Previously, C-2 branching was investigated by Ferrier,[10] employing the corresponding vinyl ethers of related C-4 allyl alcohols. However, the yield in this mercury-catalyzed preparation of the corresponding vinyl alcohol was low (30%). Reaction of allyl alcohol **5** with an eightfold excess of orthoacetic ester with catalytic amounts of propionic acid in boiling xylene afforded the ester **6** in 86% yield as one single isomer. The related reaction under Eschenmoser conditions using only 1.5 equiv. of *N*,*N*-dimethylacetamide dimethyl diacetal gave an 89% yield of the corresponding amide **7**. Both the ester **6** and the amide **7** are ideally suited for the investigation of further transformations to afford useful chiral building blocks.

First, the iodolactonization was tried with both the ester **6** and the amide **7**. Much better yields (76%) of the lactone **8** were obtained with the amide **7**. It has to be stressed that the iodolactone **8** possesses a highly condensed array of six functional groups, all of them of different reactivity or orthogonal protection. In Scheme 2, a number of simple transformations of **8** are shown. First, the fluoride mediated cleavage of the silyl ether liberated the primary hydroxyl group to afford the alcohol **9**. All of the transformations en route from **4** to **9** were stereospecific and, not surprisingly, only



Scheme 2. a) TBAF, THF, 30 min, 86%; b) DBU, CH_2Cl_2, 10 h at 20°C, 78%; c) MeOH, KOH, H_2O, 1 h, 93%; d) LAH, THF, 1 h, 86%.

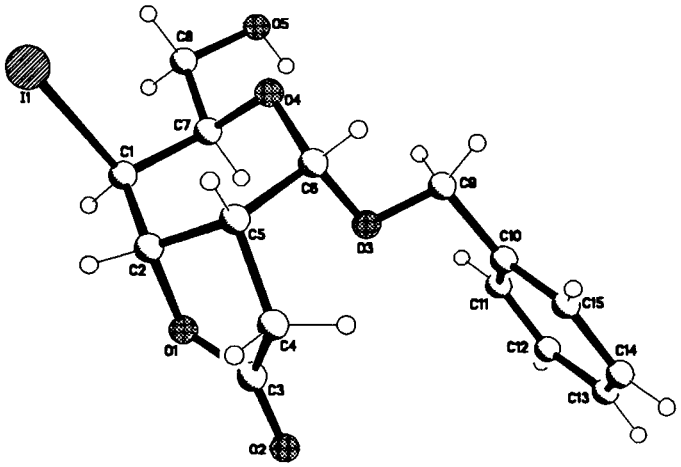
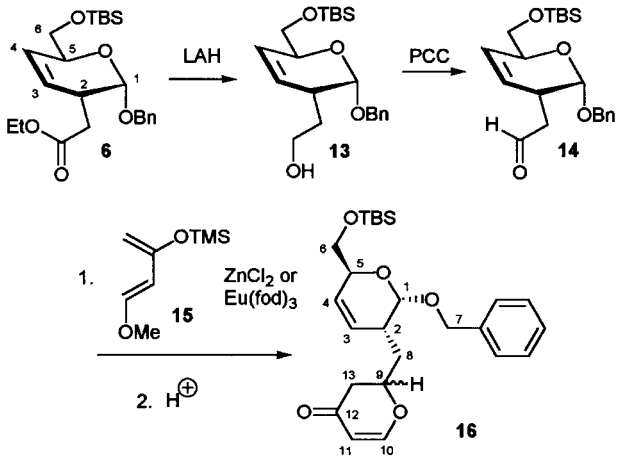


Figure 1. Molecular structure of **9**.

one stereoisomer was obtained, as confirmed by X-ray structure analysis of **9** as shown in Figure 1.

Elimination of hydrogen iodide and opening of the lactone **8** to yield the hydroxy acid **10** was achieved by treatment with DBU followed by aqueous methanolic potassium hydroxide. This saponification also proved the location of the 5,6-C═C double bond chemically. Reductive opening without elimination to yield the diol **11** could be achieved using DIBAH or LAH. Substitution of the iodide with both hetero and carbon based nucleophiles was not successful. Instead, elimination to the lactone olefin **12** took place. This elimination was best achieved using DBU as the base.



Scheme 3. Conversion of ester 6 to the aldehyde 14 and cycloaddition with Danishefky's diene to yield 16.

Finally, we wanted to demonstrate the utility of the C-2-branched glucose derivative **6** in the synthesis of carbon linked disaccharide analogues such as **16**. The synthetic scheme envisioned the reduction of the ester **6** to an aldehyde **14**, suitable for a hetero Diels–Alder reaction[11] using Danishefsky's diene **15**.[12] Thus, the ester **6** was reduced with LAH to the alcohol **13** (93%) and then oxidized with PCC[13] in 92% yield to the aldehyde **14** (Scheme 3). Different catalysts were tried for the hetero Diels–Alder reaction of **14** with **15**. Using $ZnCl_2$,[14] a 77% yield (at 63% conversion) of a major product **16** was obtained after 8 h of reaction time and acidic work up. The intermediate Diels–Alder adduct was not isolated but eliminated to the enone **16** upon acidic workup. Analysis of the NMR spectra of **16** revealed the presence of a ca. 1:1 mixture of diastereoisomers. The stereoselectivity could not be improved employing the chiral shift reagent $Eu(fod)_3$,[15] yielding 47% (at 66% conversion) of **16** in a slow reaction.

In summary, we have demonstrated that selectively protected products of the Ferrier rearrangement **5** can be transformed in only one step to C-2 branched unsaturated sugars **6** or **7**, which are both starting materials for a great variety of highly functionalized chiral building blocks **8**–**16**.

EXPERIMENTAL

General remarks and instrumentation. Silica gel 60 F_{254} coated plates from Merck AG Darmstadt were used for TLC. Spots were detected by UV light ($\lambda = 254$ and 366 nm), spraying and heating with 8% ethanolic sulfuric acid or the cerium(IV)molybdato phosphoric acid reagent (Merck AG). Preparative LC were performed using silica gel plates (1 mm) from Macherey und Nagel. Melting points were recorded with a Gallenkamp Melting Point apparatus (uncorrected); IR spectra: NICOLET 510 P; optical rotations: Perkin–Elmer polarimeter 241 (589 nm); elemental analyses: Perkin–Elmer Elementar Analysator 240; mass spectra: FINNIGAN MAT 8200 and FISON MD 800, relative intensities in brackets; NMR spectra: Bruker ARX 200 (200/50 MHz) and Bruker AMX 300 (300/75 MHz) spectrometer. GC: Hewlett Packard 5890 Series II, column: FS-SE-52.

General procedure for the ferrier rearrangements. To a solution of 3,4,6-tri-*O*-acetyl-D-glucal (ca. 5 mmol) and the corresponding alcohol (1.1 equiv.) in CH_2Cl_2 was added a 0.1 M solution of $FeCl_3$[3] (0.01 equiv. in CH_2Cl_2) or $Sc(OTf)_3$[4] (0.25 mmol or 0.05 equiv.). The reaction was monitored by TLC [ca. 30 min for $FeCl_3$, ca. 2 h for $Sc(OTf)_3$] and then quenched by addition of aqueous $NaHCO_3$ solution (100 mL). The phases were separated, the aqueous phase was extracted twice with CH_2Cl_2, and the combined organic phases were washed with brine (50 mL), dried ($MgSO_4$), and the solvent removed under reduced pressure. The crude mixture was analyzed by GC. The mixture was chromatographed on silica gel or crystallized to obtain the pure α-anomers. For yields and conditions see Table 1 and individual compounds.

Allyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2a). 3,4,6-Tri-*O*-acetyl-D-glucal (5.0 g, 18.4 mmol), allyl alcohol (1.4 mL, 20 mmol) in CH_2Cl_2 (100 mL), 0.1 M of $FeCl_3$ (1.9 mL). Mp 42–43°C (MeOH/hexane) (ref. mp 44–46°C),[16] $[\alpha]_D + 115.5°$, (*c* 1.00, $CHCl_3$) (ref. $[\alpha]_D = +111.5°$, (*c* 1.20, $CHCl_3$)).[16]

Benzyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2b). 3,4,6-Tri-*O*-acetyl-D-glucal (5.0 g, 18.4 mmol), benzylic alcohol (2.4 mL, 20 mmol) in CH_2Cl_2 (100 mL), 0.1 of M $FeCl_3$ (1.9 mL). $[\alpha]_D + 75.3°$, (*c* 1.04, MeOH); mp 34.5°C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.10$, (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 4.09–4.36 (m, 3H, 5-H, 6-H), 4.63 (d, $J_{7a,7b} = 12.1$ Hz, 1H, 7_a-H), 4.85, (d, $J_{7a,7b} = 12.1$ Hz, 1H, 7_b-H), 5.16 (br s, 1H, 1-H), 5.36 (m, 1H, 4-H), 5.88–5.94 (m, 2H, 2-H, 3-H), 7.31–7.45 (m, 5H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 21.2$ (q, $COCH_3$), 21.4 (q, $COCH_3$), 63.4 (t, C-6), 65.7 (d, C-5), 67.5 (d, C-4), 70.7 (t, C-7), 94.1 (d, C-1), 127.9 (d, C-arom.), 128.2 (d, C-arom.), 128.3 (d, C-arom.), 128.5 (d, C-arom.), 128.9 (d, C-arom.), 129.4, (d, C-2), 129.7 (d, C-3), 138.0 (s, C-arom.), 170.7, (s, CO), 171.2 (s, CO). MS (CI, *i*-Bu), *m/z* (%): 320 (1) [M^+], 261 (9), 213 (100), 153 (34), 111 (5), 91 (14), 57 (8), 43 (12).

Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.89; H, 6.46.

Benzyl-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside (4). A small piece of sodium (0.02 g, 0.9 mmol) was added to a solution of **2b/3b** (ca. 9:1, 1.00 g, 3.13 mmol) in methanol (50 mL). The reaction was monitored by TLC and adjusted to pH 7 after 2 h by addition of Amberlite IR-120. The solvent was removed under reduced pressure not exceeding an external temperature of 35°C. The residue was dried at 0.1 mm Hg to afford crude **4** (0.71 g, 95%). The anomeric mixture was separated by column chromatography on silica gel (CH_2Cl_2/2% MeOH) and crystallized from MeOH/hexane. Mp 85–87°C (ref. mp 88–90°C);[17] $[\alpha]_D + 48.4°$, (*c* 1.03, $CHCl_3$); (ref. $[\alpha]_D + 49°$, (*c* 1.01, $CHCl_3$)).[17]

Benzyl-6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside (5). A solution of the diol **4** (800 mg, 3.38 mmol) in dry CH_2Cl_2 (50 mL) was treated with imidazole (2 equiv., 460 mg, 5.07 mmol). To this mixture was added at 0°C a solution of *tert*-butyldimethylsilyl chloride (TBSCl) (609 mg, 4.06 mmol, 1.2 equiv.) in dry CH_2Cl_2 (10 mL) and the solution was stirred for 3 h (TLC monitoring). The solution was quenched by addition of aqueous $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (2×20 mL). The combined organic phases were washed with brine (10 mL), dried ($MgSO_4$), filtered, and the solvent removed under reduced pressure to afford **5** (92%, 896 mg) as a colorless oil. $[\alpha]_D = 35.7°$, (*c* 1.05, EtOH); (ref. $[\alpha]_D + 30.4°$, (*c* 1.03, EtOH)).[17]

Anal. Calcd for $C_{19}H_{30}O_4Si$: C, 65.10; H, 8.83. Found: C, 65.04; H, 8.95.

Ethyl [2-Benzyloxy-6-(*tert*-butyldimethylsilanyloxymethyl)-3,6-dihydro-2*H*-pyran-3-yl]-acetate (6). A solution of allyl alcohol **5** (3.00 g) in xylene (200 mL) was treated with an eightfold excess of triethyl orthoacetate (10 mL) and propionic acid (0.5 mL). The mixture was refluxed for 2 d, the solvent removed under reduced pressure, and the residue purified by column chromatography on silica gel (petroleum ether:ethyl acetate = 15:1) to yield ester 6 (1.7 g, 86%) and 1.36 g of unreacted starting material **5** (55% conversion). $[\alpha]_D + 6.1°$, (*c* 2.20, MeOH). IR (Film): ν [cm^{-1}] = 2955 (C—H), 2929 (C—H), 2884 (C—H), 2856 (C—H), 1729 (C═O, ester), 1652 (C═C), 1628 (C═C), 1488 (C—H), 1388 (C—H), 1258 (C—O), 1090 (C—O). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.11$ (s, 6H, $Si(CH_3)_2$), 0.93 (s, 9H, $C(CH_3)_3$), 1.22 (t, $J_{11,10} = 7.2$ Hz, 3H, 11-H), 2.39 (dd, $J_{8a,2} = 7.2$ Hz, $J_{8a,8b} = 16.2$ Hz, 1H, 8_a-H), 2.57 (dd, $J_{8b,2} = 8.1$ Hz,

$J_{8a,8b}$ = 16.2 Hz, 1H, 8b-H), 2.97 (m, 1H, 2-H), 3.54 (m, 2H, 6-H), 4.08 (q, $J_{10,11}$ = 7.1 Hz, 2H, 10-H), 4.23 (m, 1H, 5-H), 4.57 (d, $J_{7a,7b}$ = 11.7 Hz, 1H, 7_a-H), 4.79 (d, $J_{7a,7b}$ = 11.7 Hz, 1H, 7_b-H), 5.11 (d, $J_{1,2}$ = 4.2 Hz, 1H, 1-H), 5.66 (m, 1H, 3-H), 5.82 (m, 1H, 4-H), 7.33–7.35 (m, 5H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.50 (q, $SiCH_3$), −5.45 (q, $SiCH_3$), 14.0 (q, C-11), 18.2 (s, SiC), 26.2 (q, $C(CH_3)_3$), 35.2 (d, C-2), 35.5 (t, C-8), 60.7 (t, C-10), 66.0 (t, C-6), 69.5 (t, C-7), 69.8 (d, C-5), 96.5 (d, C-1), 126.34 (d, C-3), 126.9 (d, C-4), 128.0 (d, C-arom.), 128.3 (d, C-arom.), 128.7 (d, C-arom.), 138.3 (s, C-arom.), 172.6 (s, C-9). MS (EI, 70 eV, 200°C), *m/z* (%): 422 (2), 363 (7), 313 (6), 255 (47), 227 (10), 195 (12), 167 (7), 105 (63), 91 (100), 75 (27), 73 (23), 65 (6), 57 (7).

Anal. Calcd for $C_{23}H_{36}O_5Si$: C, 65.68; H, 8.63. Found: C, 65.65; H, 8.73.

2-[2-Benzyloxy-6-(*tert*-butyldimethylsilanyloxymethyl)-3,6-dihydro-2*H*-pyran-3-yl]-*N,N*-dimethylacetamide (7). The reaction was performed as described for **6** with 2.00 g of **5**, *N*,*N*-dimethylacetamide dimethyl acetal (1.4 mL of a 90% solution in hexane, 8.6 mmol, 1.5 equiv). The mixture was slowly heated within 2 h to the boiling point and refluxed for 12 h. Column chromatography on silica gel (petroleum ether:ethyl acetate = 15:1 to 5:1) afforded **7** (2.10 g, 89%) as an oil. $[\alpha]_D$ −4.6°, (*c* 1.08, MeOH). IR (Film): ν [cm^{-1}] = 3063 (C—H), 2950 (C—H), 2929 (C—H), 2857 C—H), 1641 (C═O, amide), 1497 (C═C), 1471 (C═C), 1398 (C—H), 1264 (C—O), 1098 (C—O), 1021 (C═C—H). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.11 (s, 6H, $Si(CH_3)_2$), 0.94 (s, 9H, $C(CH_3)_3$), 2.27 (dd, $J_{8a,2}$ = 6.5 Hz, $J_{8a,8b}$ = 16.1 Hz, 1H, 8_a-H), 2.57 (dd, $J_{8b,2}$ = 8.1 Hz, $J_{8a,8b}$ = 16.1 Hz, 1H, 8b-H), 2.92, (s, 3H, 10-H),* 2.95 (s, 3H, 11-H),* 3.10 (m, 1H, 2-H), 3.66 (dd, $J_{6a,5}$ = 6.5 Hz, $J_{6a,6b}$ = 10.5 Hz, 1H, 6a-H), 3.79 (dd, $J_{6b,5}$ = 6.5 Hz, $J_{6a,6b}$ = 10.5 Hz, 1H, 6b-H), 4.26 (m, 1H, 5-H), 4.55 (d, $J_{7a,7b}$ = 12.1 Hz, 1H, 7_a-H), 4.82 (d, $J_{7a,7b}$ = 12.1 Hz, 1H, 7_b-H), 5.16 (d, $J_{1,2}$ = 4.8 Hz, 1H, 1-H), 5.79 (m, 1H, 3-H), 5.84 (m, 1H, 4-H), 7.29–7.37 (m, 5H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = −4.85 (q, $SiCH_3$), −4.78 (q, $SiCH_3$), 18.8 (s, SiC), 26.2 (q, $C(CH_3)_3$), 34.1 (t, C-8), 37.6 (d, C-2), 35.5 (q, C-10)*, 35.8 (q, C-11)*, 66.1 (t, C-6), 69.8 (d, C-5) 69.8 (t, C-7), 97.2 (d, C-1), 126.7 (d, C-3), 127.5 (d, C-4), 128.0 (d, C-arom.), 128.5 (d, C-arom.), 128.7 (d, C-arom.), 138.6 (s, C-arom.), 172.7 (s, C-9). *These signals could not be assigned. MS (EI, 70 eV, 200°C), *m/z* (%): 420 (2) [$M+H^+$], 362 (30), 332 (4), 274 (30), 254 (70), 226 (34), 180 (28), 166 (100), 122 (18), 91 (12).

Anal. Calcd for $C_{23}H_{37}NO_4Si$: C, 65.83; H, 8.89; N 3.34. Found: C, 65.30; H, 9.21; N 3.26.

4-Benzyloxy-6-(*tert*-butyldimethylsilanyloxymethyl)-7-iodotetrahydrofuro[3,2-c] pyran-2-one (8). A solution of amide **7** (1.00 g, 2.4 mmol) in a 3:1 mixture of THF/water (50 mL) was treated with I_2 (900 mg, 3.5 mmol, 1.5 equiv.) at 0 °C and the mixture was then stirred for 12 h at 20°C. The solution was washed with a 10% aqueous solution of sodium thiosulfate (100 mL), the phases were separated, and the aqueous phase was extracted with dichloromethane (2 × 35 mL). The combined organic phases were washed with brine (35 mL), dried ($MgSO_4$), and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica (petroleum ether:ethyl acetate = 9:1) to afford the lactone **8** (920 g, 76%) as an oil. $[\alpha]_D$ +90.1°, (*c* 0.95, MeOH). IR (Film): ν [cm^{-1}] = 2955 (m, C—H), 2924 (m, C—H), 2857 (m, C—H), 1791 (s, C═O, lactone), 1471 (w, C═C), 1264 (w, C—C), 1155 (s, C—O), 1107 (s, C—O), 835, 772. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.11 (s, 6H,

$Si(CH_3)_2$), 0.93 (s, 9H, $C(CH_3)_3$), 2.56 (m, 2H, 8-H), 3.05 (m, 1H, 2-H), 3.35 (m, 1H, 5-H), 3.50 (dd, $J_{6a,5}=6.2$ Hz, $J_{6a,6b}=10.4$ Hz, 1H, 6a-H), 3.68 (dd, $J_{6b,5}=6.1$ Hz, $J_{6a,6b}=10.4$ Hz, 1H, 6b-H), 4.55 (d, $J_{7a,7b}=12.3$ Hz, 1H, 7_a-H), 4.69 (br s, 1H, 4-H), 4.78 (d, $J_{7a,7b}=12.3$ Hz, 1H, 7_b-H), 4.92 (m, 1H, 3-H), 4.97 (d, $J_{1,2}=5.4$ Hz, 1H, 1-H), 7.28-7.42 (m, 5H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=-5.0$ (q, $SiCH_3$), -4.9 (q, $SiCH_3$), 18.6 (s, SiC), 26.4 (q, $C(CH_3)_3$), 29.7 (d, C-4), 33.6 (t, C-8), 34.7 (d, C-2), 63.8 (d, C-5), 67.8 (t, C-6) 69.7 (t, C-7), 81.7 (d, C-3), 96.0 (d, C-1), 128.1 (d, C-arom.), 128.5 (d, C-arom.), 128.9 (d, C-arom.), 137.2 (s, C-arom.), 176.3 (s, C-9). MS (EI, 70 eV, 200°C), *m/z* (%): 288 (43), 270 (58), 231 (37), 158 (36), 130 (39), 91 (52), 65 (37), 60 (100), 42 (51), 30 (51).

Anal. Calcd for $C_{21}H_{31}IO_5Si$: C, 48.65; H, 6.03. Found: C, 49.06; H, 6.10.

4-Benzyloxy-6-hydroxymethyl-7-iodotetrahydrofuro[3,2-c]pyran-2-one (9). A solution of the iodolactone **8** (400 mg, 0.77 mmol) in dry THF (50 mL) was treated in small portions with TBAF (290 mg, 0.92 mmol, 1.2 equiv.) and the mixture was stirred for 30 min (TLC monitoring). The reaction was quenched by addition of water (40 mL) and the mixture was extracted with diethyl ether (3×20 mL). The combined organic phases were washed with brine (5 mL), dried ($MgSO_4$), and the solvent removed under reduced pressure to yield a solid that was recrystallized from EtOAc/pentane to yield the alcohol **9** (266 mg, 86%) as colorless needles. Mp 163°C; $[\alpha]_D+121.1°$, (*c* 0.97, MeOH). IR (KBr): ν [cm^{-1}] = 3457 (OH), 2909 (C—H), 2862 (C—H), 1776 (C═O, lactone), 1426 (C═C), 1424 (C═C), 1258 (C—H), 1145 (C—O), 1097 (C—O). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=1.93$ (br, 1H, OH), 2.59 (m, 2H, 8-H), 3.05 (m, 1H, 2-H), 3.44 (m, 1H, 5-H), 3.57 (m, 1H, 6_a-H), 3.77 (m, 1H, 6_b-H), 4.54 (d, $J_{7a,7b}=12.3$ Hz, 1H, 7_a-H), 4.61 (br s, 1H, 4-H), 4.80 (d, $J_{7a,7b}=12.3$ Hz, 1H, 7_b-H), 4.86 (m, 1H, 3-H), 4.99 (d, $J_{1,2}=5.7$ Hz, 1H, 1-H), 7.28–7.45 (m, 5H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=27.8$ (d, C-4), 33.6 (t, C-8), 34.6 (d, C-2), 63.9 (d, C-5), 68.2 (t, C-6), 69.9 (t, C-7), 81.7 (d, C-3), 96.1 (d, C-1), 128.1 (d, C-arom.), 128.4 (d, C-arom.), 129.0 (d, C-arom.), 137.0 (s, C-arom.), 176.3 (s, C-9). MS (EI, 70 eV, 200°C), *m/z* (%): 404 (2) [M^+], 373 (3), 279 (5), 201 (5), 171 (50), 141 (10), 108 (71), 91 (100), 65 (28), 57 (12).

Anal. Calcd for $C_{15}H_{17}IO_5$: C, 44.57; H, 4.24. Found: C, 44.72; H, 4.42.

Crystal structure determination of 9:[18] $C_{15}H_{17}IO_5$, Mr = 404.2, monoclinic, space group P 2_1, a = 9.511(2), b = 5.699(2), c = 15.210(5) Å, $\beta=106.85(1)°$, V = 789.0(4) Å^3, Z = 2, $D_x=1.701$ g/cm^3, F(000) = 400, T = 293(2) K. Bruker-AXS P4 diffractometer, graphite monochromator, λ(MoKα) = 0.71073 Å, $\mu=2.05$ mm^{-1}, colorless crystal, size $0.50\times0.22\times0.07$ mm^3, ω scans, 4184 intensities collected $4<2\theta<55°$, $-12<h<12$, $-7<k<7$, $-19<l<19$, 3 standards every 397 reflections showed only random deviations, Lp correction, face indexed absorption correction, 3663 unique intensities ($R_{int}=0.017$). Structure solved by direct methods, full-matrix least-squares refinement based on F^2 and 191 parameters, all but H atoms refined anisotropically, H atoms refined with riding model on idealized positions with U = 1.5 U_{iso}(O) and 1.2 U_{iso}(C). Refinement converged at R1(F) = 0.062, wR2(F^2, all data) = 0.172, S = 1.07, absolute structure parameter (Flack) $-0.04(6)$, max(δ/σ) < 0.001, min/max height in final ΔF map $-0.90/1.19$ e/Å^3 (near I position). Figure 1 shows the molecular structure. Programs used: SHELXTL.[19]

[2-Benzyloxy-6-(*tert*-butyldimethylsilanyloxymethyl)-4-hydroxy-3,4-dihydro-2*H*-pyran-3-yl]-acetic acid (10). A solution of the unsaturated lactone **12** (200 mg) in dry THF (50 mL) was treated at 20°C with methanolic KOH (1 mol/L), 6 mL) and the mixture was stirred for 1 h (TLC monitoring). The solution was the adjusted to pH 7 by addition of 10% HCl and extracted diethyl ether (3×20 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and the solvent removed under reduced pressure to yield the acid **10** (198 mg, 93%) as a colorless oil. $[\alpha]_D + 76.9°$, (*c* 1.0, MeOH). IR (Film): ν [cm^{-1}] = 2955 (C—H), 2924 (C—H), 2862 (C—H), 1735 (C═O, acid), 1450 (C═C), 1419 (C═C), 1259 (C—O), 1119 (C—O). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.13$ (s, 6H, $Si(CH_3)_2$), 0.96 (s, 9H, $C(CH_3)_3$), 2.49 (m, 1H, 2-H), 2.64 (dd, $J_{8a,2} = 6.7$ Hz, $J_{8a,8b} = 16.7$ Hz, 1H, 8_a-H), 2.92 (dd, $J_{8b,2} = 7.4$.Hz, $J_{8a,8b} = 16.7$ Hz, 1H, 8_b-H), 4.07 (br s, 3H, 3-H, 6-H), 4.56 (d, $J_{7a,7b} = 12.0$ Hz, 1H, 7_a-H), 4.80 (d, $J_{7a,7b} = 12.0$ Hz, 1H, 7_b-H), 5.26 (br s, 1H, 1-H), 5.35 (d, $J_{4,3} = 5.4$ Hz, 1H, 4-H), 7.30–7.44 (m, 5H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.90$ (q, $SiCH_3$), -4.86 (q, $SiCH_3$), 18.8 (s, SiC), 26.3 (q, $C(CH_3)_3$), 31.6 (t, C-8), 38.6 (d, C-2), 62.0 (d, C-3), 62.8 (t, C-6), 70.8 (t, C-7), 98.7 (d, C-1), 101.1 (d, C-4), 128.3 (d, C-arom.), 128.5 (d, C-arom.), 129.0 (d, C-arom.), 137.3 (s, C-arom.), 150.7 (s, C-5), 177.5 (s, C-9). MS (CI, *i*-Bu), *m/z* (%): 391 (100) [M^+-H_2O], 333 (13), 283 (8), 249 (7), 169 (9), 91 (18), 43 (19).

Anal. Calcd for $C_{21}H_{32}O_6Si$: C, 61.73; H, 7.89. Found: C, 61.90; H, 8.24.

Benzyloxy-6-(*tert*-butyldimethylsilanyloxymethyl)-2-(2-hydroxyethyl)-4-iodo-tetrahydropyran-3-ol (11). A solution of the iodolactone **8** (200 mg, 0.4 mmol) in dry THF (50 mL) was treated under argon at 0°C with lithium aluminum hydride (LAH) (18 mg, 0.44 mmol). The mixture was allowed to warm to 20°C and stirring was continued for 1 h (TLC monitoring). The reaction was worked up by addition of $Na_2SO_4 \cdot 10\ H_2O$ (200 mg). The mixture was filtered, washed with brine (10 mL), dried ($MgSO_4$), and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel (PE/EtOAc 4:1) to yield the diol **11** (178 mg, 86%) as an oil. $[\alpha]_D + 85.5°$, (*c* 0.97, MeOH). IR (Film): ν [cm^{-1}] = 3420 (OH), 2930 (C—H), 2859 (C—H), 1455 (C═C), 1256 (C—O), 1052 (C—O).—^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.15$ (s, 6H, $Si(CH_3)_2$), 0.96 (s, 9H, $C(CH_3)_3$), 1.71–1.95 (m, 1H, 2-H, 2H, 8-H, 1H, OH), 2.85 (br, 1H, OH), 3.45–3.64 (m, 6H, 3-H, 5-H, 6-H, 9-H), 4.46 (br s, 1H, 4-H), 4.54 (d, $J_{7a,7b} = 12.0$ Hz, 1H, 7_a-H), 4.81 (d, $J_{7a,7b} = 12.0$ Hz, 1H, 7_b-H), 4.91 (d, $J_{1,2} = 3.8$ Hz, 1H, 1-H), 7.30–7.42 (m, 5H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.9$ (q, $SiCH_3$), -4.8 (q, $SiCH_3$), 18.7 (s, SiC), 26.3 (q, $C(CH_3)_3$), 31.5 (t, C-8), 34.6 (d, C-2), 36.8 (d, C-4), 60.3 (t, C-9), 65.4 (d, C-3), 68.8 (t, C-6), 70.0 (t, C-7), 73.9 (d, C-5), 99.7 (d, C-1), 128.7 (d, C-arom.), 129.0 (d, C-arom.), 138.0 (s, C-arom.). MS (CI, *i*-Bu), *m/z* (%): 523 (4) [$M + H^+$], 415 (19), 397 (100), 339 (18), 269 (509), 253 (38), 213 (8), 137 (2), 91 (4), 57 (15).

Anal. Calcd for $C_{21}H_{35}IO_5Si$: C, 48.27; H, 6.75. Found: C, 48.81; H, 6.84.

4-Benzyloxy-6-(*tert*-butyldimethylsilanyloxymethyl)-3a,7a-dihydro-3*H*,4*H*-furo[3,2-c]pyran-2-one (12). A solution of the iodolactone **9** (200 mg, 0.38 mmol) in dry CH_2Cl_2 (20 mL) was treated at 20°C with DBU (0.12 mL, 0.76 mmol) and the mixture was stirred for 10 h (TLC monitoring). Methanol (5 mL), Na_2CO_3 (63.6 mg, 0.6 mmol), water (5 mL) and HCl (1 mol/L, 0.5 mL) were then added successively

with stirring. The phases were separated and the organic phase extracted with CH_2Cl_2 (2×1 mL). The combined organic phases were washed with aqueous $NaHCO_3$ solution followed by brine (5 mL), dried ($MgSO_4$), and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel (PE/EtOAc 4:1) to yield the olefin **12** (117 mg, 78%) as an oil. $[\alpha]_D + 149.5°$ (*c* 1.0, MeOH). IR (Film): ν [cm^{-1}] = 2940 (C—H), 2862 (C—H), 1766 (C═O, lactone), 1476 (C═C), 1181 (C—C), 1130 (C—O), 1094 (C—O). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.13 (s, 6H, $Si(CH_3)_2$), 0.95 (s, 9H, $C(CH_3)_3$), 2.61 (m, 2H, 8-H), 2.86 (m, 1H, 2-H), 4.05 (s, 2H, 6-H), 4.62 (d, $J_{7a,7b}$ = 12.8 Hz, 1H, 7_a-H), 4.84 (d, $J_{7a,7b}$ = 12.8 Hz, 1H, 7_b-H), 4.95 (m, 1H, 3-H), 5.09 (d, $J_{1,2}$ = 3.7 Hz, 1H, 1-H), 5.35 (d, $J_{4,3}$ = 4.2 Hz, 1H, 4-H), 7.30–7.42 (m, 5H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = −5.0 (q, $SiCH_3$), −4.9 (q, $SiCH_3$), 18.7 (s, SiC), 26.3 (q, $C(CH_3)_3$), 30.8 (t, C-8), 37.5 (d, C-2), 62.4 (t, C-6), 70.7 (t, C-7), 72.3 (d, C-3), 95.4 (d, C-4), 96.2 (d, C-1), 128.2 (d, C-arom.), 128.4 (d, C-arom.), 129.0 (d, C-arom.), 137.2 (s, C-arom.), 155.0 (s, C-5), 176.5 (s, C-9). MS (CI, *i*-Bu), *m/z* (%): 391 (40) [M + H^+], 333 (3), 283 (3), 254 (11), 176 (45), 133 (5), 91 (6), 57 (100), 43 (19).

Anal. Calcd for $C_{21}H_{30}O_5Si$: C, 64.58; H, 7.74. Found: C, 64.56; H, 7.93.

2-[2-Benzyloxy-6-(*tert*-butyldimethylsilanyloxymethyl)-3,6-dihydro-2*H*-pyran-3-yl]-ethanol (13). A solution of ester **6** (1.80 g, 4.3 mmol) in dry THF (200 mL) was reduced with LAH (245 mg, 6.5 mmol) as described for **12**, to afford the alcohol **13** (1.50 g, 93%) as an oil. $[\alpha]_D - 4.2°$, (*c* 2.5, MeOH). IR (Film): ν [cm^{-1}] = 3410 (OH), 3038 (C—H), 2951 (C—H), 2919 (C—H), 2847 (C—H), 1471 (C═C), 1362 (C—C), 1253 (C—O), 1093 (C—O), 1021 (C═C—H). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.13 (s, 6H, $Si(CH_3)_2$), 0.94 (s, 9H, $C(CH_3)_3$), 1.73 (m, 2H, 8-H), 1.96 (br s, 1H, OH), 2.65 (m, 1H, 2-H), 3.60–3.84 (m, 4H, 6-H, 9-H), 4.29 (m, 1H, 5-H), 4.60 (d, $J_{7a,7b}$ = 11.7 Hz, 1H, 7_a-H), 4.87 (d, $J_{7a,7b}$ = 11.7 Hz, 1H, 7_b-H), 5.01 (d, $J_{1,2}$ = 4.0 Hz, 1H, 1-H), 5.67 (m, 1H, 3-H), 5.82 (m, 1H, 4-H), 7.32–7.40 (m, 5H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = −4.8 (q, $SiCH_3$), −4.8 (q, $SiCH_3$), 18.8 (s, SiC), 26.3 (q, $C(CH_3)_3$), 33.5 (t, C-8), 35.9 (d, C-2), 60.7 (t, C-9), 66.1 (t, C-6), 69.5 (t, C-7), 70.2 (d, C-5), 97.2 (d, C-1), 126.4 (d, C-3), 127.2 (d, C-4), 127.3 (d, C-arom.), 128.1 (d, C-arom.), 128.8 (d, C-arom.), 138.3 (s, C-arom.). MS (EI, 70 eV, 200°C), *m/z* (%): 327 (4), 269 (11), 253 (58), 213 (28), 195 (26), 143 (13), 125 (58), 121 (58), 91 (100), 65 (12), 41 (18).

Anal. Calcd for $C_{21}H_{34}O_4Si$: C, 66.62; H, 9.05. Found: C, 66.16; H, 9.38.

[2-Benzyloxy-6-(*tert*-butyldimethylsilanyloxymethyl)-3,6-dihydro-2H-pyran-3-yl]-acetaldehyde (14). To a suspension of pyridinium chlorochromate (PCC) (522 mg, 2.4 mmol) in dry CH_2Cl_2 (100 mL) was added under argon a solution of the alcohol **13** (900 mg, 2.4 mmol) in CH_2Cl_2 (150 mL). After 2 h (TLC monitoring) the reaction was filtered through a short column of silica gel (CH_2Cl_2) to afford the aldehyde **14** (828 mg, 92%) as an oil. $[\alpha]_D + 4.7°$ (*c* 1.05, MeOH). IR (Film): ν [cm^{-1}] = 2955 (m, C—H), 2924 (m, C—H), 2852 (m, C—H), 1729 (s, C═O), 1471 (HC═CH), 1409 (w, C═C), 1362 (s, C—O), 1254 (s, C—O), 1021 (s, C═C—H), 834, 778, 736. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.13 (s, 6H, $Si(CH_3)_2$), 0.95 (s, 9H, $C(CH_3)_3$), 2.49 (m, 1H, 8_a-H), 2.68 (m, 1H, 8_b-H), 3.03 (m, 1H, 2-H), 3.50 (m, 2H, 6-H), 4.26 (m, 1H, 5-H), 4.56 (d, $J_{7a,7b}$ = 12.3 Hz, 1H, 7_a-H), 4.84 (d, $J_{7a,7b}$ = 12.3 Hz, 1H, 7_b-H), 5.10 (d, $J_{1,2}$ = 4.1 Hz, 1H, 1-H), 5.64 (m, 1H, 3-H), 5.82 (m, 1H, 4-H), 7.30–7.37 (m, 5H, Ar-H), 9.78 (s, 1H, 9-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = −4.9 (q,

$SiCH_3$), −4.3 (q, $SiCH_3$), 18.8 (s, SiC), 26.3 (q, $C(CH_3)_3$), 33.7 (t, C-2), 44.8 (d, C-8), 66.0 (t, C-6), 69.7 (t, C-7), 69.9 (d, C-5), 96.5 (d, C-1), 126.2 (d, C-3), 127.4 (d, C-4), 128.2 (d, C-arom.), 128.3 (d, C-arom.), 128.8 (d, C-arom.), 138.3 (s, C-arom.), 201.6 (d, C-9). MS (EI, 70 eV, 200°C), *m/z* (%): 355 (12), 327 (4), 269 (18), 253 (100), 237 (23), 213 (32), 195 (26), 143 (13), 125 (54), 121 (77), 91 (62), 65 (10), 41 (16).

Anal. Calcd for $C_{21}H_{32}O_4Si$: C, 66.98; H, 8.57. Found: C, 65.97; H, 8.33.

2-[2-Benzyloxy-6-(*tert*-butyldimethylsilanyloxymethyl)-3,6-dihydro-2*H*-pyran-3-ylmethyl]-2,3-dihydropyran-4-one (16). A solution of the aldehyde **14** (100 mg, 0.27 mmol) in dry CH_2Cl_2 (20 mL) was treated with dry $ZnCl_2$ (4 mg, 0.03 mmol) and diene 15 (0.1 mL, 0.6 mmol, 2 equiv.).[12] The mixture was stirred for 8 h (TLC monitoring) and then quenched by addition of 10% HCl solution (10 mL). After stirring for 1 h, the phases were separated, the aqueous phase was extracted with CH_2Cl_2 (2×3 mL), washed with saturated $NaHCO_3$ solution (20 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel (PE/EtOAc 3:1) to afford the oily adduct **16** (49 mg, 77%) and unreacted starting material **14** (37 mg, 63% conversion) as a 1:1 mixture of stereoisomers. Using $MgBr_2$ (25%, at 60% conversion) or $Eu(fod)_3$ (47% at 66% conversion) gave the same mixture of isomers. $[\alpha]_D - 28.3°$, (*c* 1.1, MeOH). IR (film): ν [cm^{-1}] = 2955 (C—H), 2929 (C—H), 2862 (C—H), 1683 (C═O), 1595 (C═C), 1409 (C═C), 1264 (C—C), 1104 (C—O), 1041 (C—O). ^{1}H NMR (200 MHz, $CDCl_3$) (isomeric mixture): $\delta = 0.12$ (s, 6H, $Si(CH_3)_2$), 0.95 (s, 9H, $C(CH_3)_3$), 1.73 (m, 2H, 8-H), 2.05 (m, 1H, 9-H), 2.45 (m, 2H, 13-H), 2.73 (m, 1H, 2-H), 3.66 (dd, $J_{6a,5} = 5.9$ Hz, $J_{6a,6b} = 10.1$ Hz, 1H, 6a-H), 3.79 (dd, $J_{6b,5} = 3.9$ Hz, $J_{6a,6b} = 10.1$ Hz, 1H, 6b-H), 4.28 (m, 1H, 5-H), 4.85 (d, $J_{7a,7b} = 12.1$ Hz, 1H, 7_a-H), 4.84 (d, $J_{7a,7b} = 12.1$ Hz, 1H, 7_b-H), 5.00 (br s, 1H, 1-H), 5.38 (m, 1H, 11-H), 5.65 (m, 1H, 4-H), 5.84 (m, 1H, 3-H), 7.34–7.38 (m, 6H, 10-H, Ar-H). ^{13}C NMR (50 MHz, $CDCl_3$) (major isomer): $\delta = -4.85$ (q, $SiCH_3$), −4.8 (q, $SiCH_3$), 18.8 (s, SiC), 26.3 (q, $C(CH_3)_3$), 34.4 (d, C-2), 35.9 (t, C-8), 42.7 (t, C-13), 66.1 (t, C-6), 69.3 (t, C-7), 69.9 (d, C-9), 70.2 (d, C-5), 65.6 (d, C-1), 107.5 (d, C-11), 126.8 (d, C-4), 127.1 (d, C-3), 127.4 (d, C-arom.), 128.2 (d, C-arom.), 128.5 (d, C-arom.), 128.8 (d, C-arom.), 128.9 (d, C-arom.), 137.9 (s, C-arom.), 163.3 (d, C-10), 192.7 (s, C-12). MS (EI, 70 eV, 200°C), *m/z* (%): 444 (1) [M^+], 387 (2), 369 (1), 279 (7), 209 (8), 157 (6), 129 (6), 105 (12), 91 (100), 74 (30), 65 (10), 57 (8), 28 (18).

Anal. Calcd for $C_{25}H_{36}0_5Si$: C, 67.53; H, 8.16. Found: C, 66.43; H, 7.67.

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18. Full crystallographic data (excluding structure factors) for **9** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-177341. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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