affording 44 mg (45% yield) of a syrup, which crystallized on storage. Recrystallization from ether gave pure compound **10**: mp 96–97 °C; $[\alpha]^{25}_D$ +98.4°; IR (neat) 1750 (carbonyl of CH_3COO); MS m/z (relative intensity) 406 (M^+), 347 (2), 346 (5), 286 (4), 245 (4), 244 (10), 226 (81), 186 (50), 185 (59), 184 (47), 159 (10), 144 (32), 143 (72), 142 (100). Anal. Calcd for $C_{16}H_{22}O_{10}S$ C, 47.29; H, 5.46; S, 7.89. Found: C, 47.55; H, 5.66; S, 7.93.

Evaporation of the fractions having R_f 0.49 gave 42 mg of a syrup. The ^1H NMR spectrum of this material showed it to contain two main components. The mixture was separated by HPLC (Altech R-Sil C-18 column (10 μm), 50 × 1 cm, at a flow rate of 1.2 mL/min) with 1:1 acetone–water. The fractions having t_R 16.1 min were evaporated, affording 24 mg (25% yield) of compound **11**. The other fraction (t_R 18.0 min) gave, upon evaporation, 12 mg (12% yield) of compound **12**.

For **11**: $[\alpha]^{25}_D$ −123° (*c* 0.7); IR (neat) 1750 cm^{-1} (carbonyl of CH_3COO); MS m/z (relative intensity) 406 (M^+), 347 (6), 346 (8), 304 (2), 286 (5), 261 (3), 245 (6), 244 (52), 226 (74), 186 (76), 185 (49), 184 (52), 159 (53), 145 (49), 144 (69), 143 (65), 142 (100). Anal. Calcd for $C_{16}H_{22}O_{10}S$: C, 47.29; H, 5.46; S, 7.89. Found: C, 47.43; H, 5.61; S, 7.72.

For **12**: $[\alpha]^{25}_D$ +39° (c 0.7); IR (neat) 1700 (carbonyl of CH_3COS), 1750 cm^{-1} (carbonyl of CH_3COO); MS m/z (relative intensity) 406 (M^+), 345 (4), 304 (4), 258 (4), 245 (10), 244 (44), 243 (66), 226 (7), 185 (46), 184 (68), 43 (100). Anal. Calcd for $C_{16}H_{22}O_{10}S$: C, 47.29; H, 5.46; S, 7.89. Found: C, 47.39; H, 5.75; S, 7.67.

The acetolysis reaction performed on the crude product (0.3–0.5 g) of alkaline methanolysis of **3** gave compounds **10**, **11**, and **12** in 50–55% overall yield.

4-Thio-D-galactose (15). Compound **10** (81 mg, 0.2 mmol) was added to a solution prepared by dissolving sodium (20 mg) in methanol (10 mL), and the mixture was stirred, under nitrogen, for 1 h at 0 °C. The solution was neutralized with Dowex 50 W (H^+), filtered, and evaporated. The residue was dissolved in water and extracted with ether. The aqueous solution was freeze-dried, affording 37 mg (95% yield) of 4-thio-D-galactose (**15**): $[\alpha]^{25}_D$ +13.5° (*c* 1, water, 10 min) → +12.8° (12 h); ^{13}C NMR (1:1 D_2O–H_2O) δ 84.1 (C-1β), 79.8 (C-1α, C-2β), 76.2 (×2), 76.0, 73.1, 71.6, 65.9 (×2), 51.5 (C-4β), 50.0 (C-4α). Anal. Calcd for $C_6H_{12}O_5S$: C, 36.73; H, 6.16. Found: C, 36.77; H, 6.26.

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Palladium(0)-Based Approach to Functionalized C-Glycopyranosides

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Phenyl 4,6-di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranoside 4α or 5β reacts with ethyl malonate, acetylacetone, methyl acetylacetate, ethyl nitroacetate, and ethyl nitromalonate under neutral conditions in the presence of Pd(0) to give regiospecifically and stereoselectively the α or β C-glycopyranoside in excellent yields. ^1H and ^{13}C NMR parameters have been used for assigning the α or β configuration for a given pair of these anomers.

Introduction

Carbon–carbon bond-forming reactions at the anomeric position of carbohydrates have attracted considerable attention during the last few years in connection with the synthesis of chiral building blocks and naturally occurring products.[1] Current examples include applications of the enolate ester Claisen rearrangement,[2] Lewis acid generation of the oxocarbenium ion followed by nucleophilic addition,[3] glycosyllithium additions,[4] nucleophilic displacement on glycal methanesulfonates,[5] allylstannane coupling with

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Table I. Alkylation of Glycals 4 and 5 with Various Nucleophiles

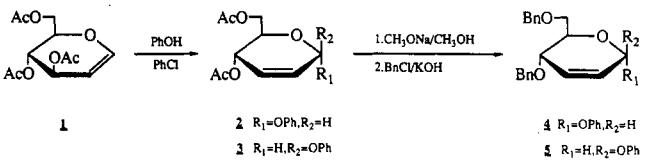
entry	glycal	NuH	solvent/T, °C	phosphine[b]	time, h	product[c] (yield, %)	α/β[d]
1	4	$CH_2(CO_2Et)_2$	CH_3CN/70	dppb	6	6 (60)	75/25
2	4	$CH_2(CO_2Et)_2$	CH_3CN/70	dppb + 3PPh_3	4	6 (65)	45/55
3	4	$CH_2(CO_2Et)_2$	CH_3CN/70	dppb + 8PPh_3	12	no reaction	
4	5	$CH_2(CO_2Et)_2$	CH_3CN/70	dppb	6	6 (82)	0/100
5	4	$CH_2(COCH_3)_2$	CH_3CN/70	dppb	6	7 (67)	75/25
6	4	$CH_2(COCH_3)_2$	CH_3CN/70	PPh_3[e]	6	7 (40)	24/76
7	4	$CH_2(COCH_3)_2$	CH_3CN/70	dppb + 8PPh_3	5	7 (40)	0/100
8	5	$CH_2(COCH_3)_2$	CH_3CN/70	dppb	6	7 (84)	0/100
9	4	$CH_3CO_2CH_2COCH_3$	CH_3CN/70	dppb	5	8 (50)	90/10
10	5	$CH_3CO_2CH_2COCH_3$	CH_3CN/70	dppb	5	8 (54)	0/100
11	4	$NO_2CH_2CO_2Et$	THF/60	PPh_3[f]	18	9 (75)	100/0
12	4	$NO_2CH_2CO_2Et$	THF/60	dppe	5	9 (80)	100/0
13	4	$NO_2CH_2CO_2Et$	THF/60	dppp	2	9 (75)	100/0
14	4	$NO_2CH_2CO_2Et$	THF/60	dppb	4	9 (80)	100/0
15	5	$NO_2CH_2CO_2Et$	THF/60	PPh_3[f]	19	9 (72)	0/100
16	4	$NO_2CH_2CO_2CH_3$	THF/60	dppp	2	10 (75)	100/0
17	4	$NO_2CH(CO_2Et)_2$	THF/60	dppb	4	11 (90)	100/0
18	4	$NO_2CH(CO_2Et)_2$	CH_3CN/70	dppb	3	11 (93)	100/0
19	5	$NO_2CH(CO_2Et)_2$	THF/60	dppb	6	11 (93)	0/100
20	5	$NO_2CH(CO_2Et)_2$	CH_3CN/70	dppb	3	11 (92)	0/100

[a] [Glycal]:[NuH]:[Pd]:[phosphine] = 20:30:1:1.1. [b] dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dppb, 1,4-bis(diphenylphosphino)butane. [c] Isolated yield after column chromatography and not optimized. [d] Determined by ^1H and ^{13}C NMR spectroscopy. [e] $Pd(PPh_3)_4$ was used. [f] [Pd]/[phosphine] = 1:2.2.

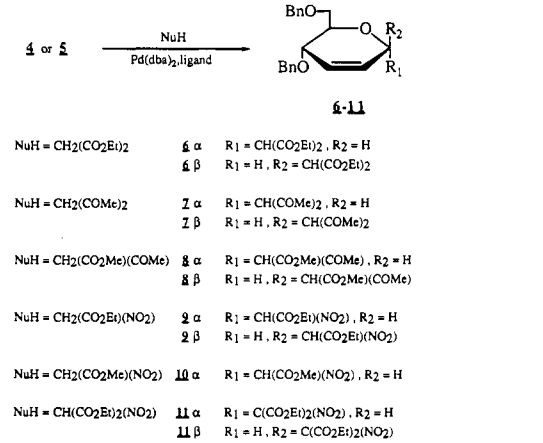
glycosyl halides,[6] carbenoid displacement reaction,[7] addition of an organometallic reagent to a lactone followed by reduction with silane,[8] and glycosyl radical trapping with alkenes.[9] The high stereochemical control accompanying transition-metal-mediated transformations has prompted several groups to employ such methods for C-glycosidations. There have been reports of work on condensation of glucopyranosyl bromide with sodium pentacarbonylmanganate followed by insertion of carbon monoxide and methyl acrylate and then photodemetalation,[10] coupling of organomercury compounds with carbohydrate-derived enol ethers in the presence of stoichiometric amounts of $Pd(OAc)_2$,[11] arylation of acetylated glycals catalyzed by $Pd(OAc)_2$,[12] addition of β-dicarbonyl compounds to acylated glycals in the presence of $PdCl_2(CH_3CN)_2$ or $BF_3{\cdot}Et_2O$,[13] and Pd(0)-catalyzed reaction of acetoxydihydropyran with tertiary carbanions like diethyl sodioformamidomalonate or more recently arylzinc chlorides.[14]

In a general program directed toward the applications of organometallic reagents in carbohydrate chemistry, we have turned our attention to the Pd(0)-catalyzed addition of stabilized carbon nucleophiles to glycals. Effectively, due to the work of Trost and Tsuji,[15] a nucleophilic palladium(0) reagent-controlled C-glycosylation method would be highly stereoselective as stabilized carbanions react with inversion on carboxylic π-allyl complexes.

Scheme I



Scheme II



Results

Our preliminary studies on C-glycosidation of 2,3-unsaturated glycals using ethyl nitroacetate as the nucleophile,[16] together with the Rajan Babu's results on the alkylation of trifluoroacetylglucal using β-diketo nucleophiles,[17] showed that alkylation occurred and was both regio- and stereoselective, taking place exclusively at the

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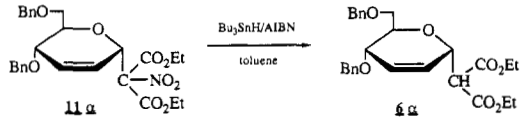
Scheme III



Scheme IV

ring oxygen-bearing carbon atom. Herein we give a more detailed description of the alkylation of 1-phenoxy hex-2-enopyranosides with carbon nucleophiles. Initial experiments to effect palladium(0)-catalyzed C-glycosilation on acetylated carbohydrate glycal, such as the readily available 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-L-*arabino*-hex-1-enitol (or triacetyl-D-glucal), **1**, were unsuccessful, even under drastic conditions. This apparent lack of reactivity of electron-rich allylic acetates having oxygen conjugation in allylic alkylation using Pd(0), according to the methodology developed by Trost,[15] has been observed previously.[18] We hoped that the appropriate choice of a better leaving group than OAc would allow the alkylation to occur. 2,3-Unsaturated phenyl glycosides like **2** are readily obtained from commercial peracetylated glycals using known procedures.[19] In contrast to Ferrier's results, we found that the product was a mixture of α and β anomers **2** and **3** in the ratio of 85/15, separable by column chromatography. Here again, under neutral conditions, using ethyl nitroacetate as the nucleophile in the presence of $Pd(dba)_2$ and diphos, no alkylation of the unsaturated sugar **2** occurred. Therefore phenyl 4,6-di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosides **4** and **5** were prepared by deacetylation and dibenzylation of **2** and **3**, respectively (Scheme I). We found that compounds **4** and **5** reacted with nucleophiles Nu-H, under neutral conditions without formation of the anion, in the presence of 5 mol % bis(dibenzylidene acetone)Pd(0) and various ligands,[20] to give C-glycosides in excellent to moderate yields (Scheme II, Table I). In all cases, the reaction is regiospecific and capture of the nucleophile at C-3 was not observed. The reaction was carried out in THF at 60 °C but gave better results with acetonitrile at 70 °C, whereas dioxane gave lower yields. Catalysts obtained from $Pd(dba)_2$ and 1,2-bis(diphenylphosphino)-ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), or 1,4-bis(diphenylphosphino)butane (dppb) are more reactive than the catalyst prepared with triphenylphosphine (entries 11–14 in Table I).

Alkylation of the β anomer **5** occurred, as expected, with complete retention of configuration at the anomeric center, no matter which nucleophile was used (Table I). In contrast, in the case of the α anomer **4**, the reaction is stereospecific only by using ethyl or methyl nitroacetate (entries 11 and 15, Table I) and ethyl nitromalonate (entries 17 and 18, Table I) as nucleophiles. With the other nucleophiles, the alkylation was nonstereospecific; with methyl acetylacetate as nucleophile, a mixture of C-glycoside 8α and 8β in a ratio of 90:10 was obtained (entry 9); with ethyl malonate or acetylacetone as nucleophiles, the selectivity was lower, and a mixture of C-glycosides $6\alpha/6\beta$ and $7\alpha/7\beta$ in a ratio of 75/25 was obtained (entries 1 and 5, Table I). However, the pure anomer 6α could be obtained very easily by denitration of compound 11α with tributyltin hydride[21] (Scheme III). The reason for the loss of stereospecificity in the alkylation procedure of anomer 4α using ethyl malonate, acetylacetone, or methyl acetylacetate is not clear. Isomerization in palladium(0)-catalyzed reactions is sometimes caused by cis migration of the acetate in the π-allylpalladium intermediate,[22,23] leading to isomerization of the starting material. We therefore treated separately the two anomers 4α and 5β under the conditions of alkylation; ^1H NMR analysis of the recovered material showed that no isomerization had occurred. This indicates that the loss of stereospecificity is probably not caused by the isomerization $\alpha \rightleftarrows \beta$ of the starting material. Furthermore, addition of excess triphenylphosphine is known to inhibit isomerization in the case of acetate. We therefore ran experiments with anomer 4α and ethyl malonate and acetylacetone as nucleophiles in the presence of the catalyst prepared in situ from $Pd(dba)_2$, 1 equiv of dppb, and 8 equiv of triphenylphosphine. The reaction was very sluggish, and in the case of ethyl malonate no reaction occurred after 12 h (entry 3). For acetylacetone, we observed complete inversion of configuration and we obtained only anomer 7β (entry 7). In the case of ethyl malonate, alkylation occurred in the presence of $Pd(dba)_2$, 1 equiv of dppb, and 3 equiv of triphenylphosphine, giving here again a mixture of $6\alpha/6\beta$ in a ratio of 45:55 (entry 2). Moreover, using $Pd(PPh_3)_4$ as catalyst (hence with a ratio of $[Pd]/[PPh_3] = 4$) and acetylacetone as nucleophile, we also obtained a mixture of $7\alpha/7\beta$ in a ratio of 24/76 (entry 6). Therefore we do not observe any decrease of cis addition when increasing the concentration of triphenylphosphine, but on the contrary an increase of the cis addition product is observed. These preliminary results are in agreement with an S_N2' attack (syn) by the nucleophile on a σ-allylpalladium complex like **13** in the presence of an excess of phosphine; this complex would be in equilibrium with the π-allylpalladium complex **12** (Scheme IV). Such a mechanism was proposed to explain the cis addition in the attack of dialkyl amines on π-allylpalladium complexes.[24] However, more work is needed to acquire more knowledge on the mechanism of this reaction.

In the case of nonsymmetrical nucleophiles $\{CH_2(NO_2)CO_2Et$, $CH_2(NO_2)CO_2Me$, and $CH_2(COMe)CO_2Me\}$ the reaction was not selective at C-2. A mixture of epimers was obtained in a ratio of 60:40 for compounds 8α, 8β, and 9β, 75:25 for compound 9α and 70:30 for 10α. The use of various ligands did not improve the C-2 selectivity in the case of the alkylation of **4** with ethyl nitroacetate (entries 11–14 in Table I); even a chiral diphosphine like Diop, which could show some enhancement of the selectivity by double asymmetric induction, disappointingly gave the same selectivity as the other chelating diphosphines.

Structural Assignments

The structures of the C-glycosides, and particularly the α or the β configuration, were determined on the basis of

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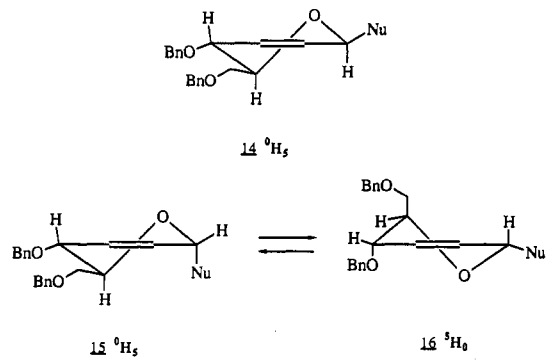
Table II. Spectral Data Pertinent to Stereochemical Assignments of Compounds 6-11[a]

compd		δ(H-1')[b]	δ(H-2)[c]	$J_{4',5'}$	δ(C-1')	δ(C-5')
6α		4.86	3.75	7.0	71.22	71.93
6β		4.78	3.54	8.2	73.25	77.75
7α		4.92	4.09[d]	7.2	71.66	72.15
7β		4.85	3.81[d]	8.4	73.57	77.28
8α	60%	4.88	3.94	7.4	71.29	72.09
	40%	4.84	3.86	7.4	70.82	72.17
8β	60%	4.82	3.60	8.4	73.70	77.31
	40%	4.79	3.81	8.1	73.20	77.49
9α	75%	5.02	5.35	7.0	71.13	72.27
	25%	5.01	5.29	7.0	70.16	72.84
9β	60%	5.00	5.09	9.2	72.96	77.63
	40%	4.95	5.33	9.2	72.89	78.05
10α	70%	5.04	5.37	7.5	71.17	72.32
	30%	4.96	5.30	7.5	70.25	72.96
11α		5.20[e]		6.7	72.64	72.85
11β		5.17[e]		8.6	75.24	78.85

[a] δ in ppm; J in hertz. [b] dddd. [c] d. [d] H-3. [e] ddd.

Scheme V



spectrometric data. Pertinent ^1H and ^{13}C nuclear magnetic resonance data for the assignment of the configuration of the various C-glycosides are summarized in Table II. According to the mechanism of double inversion associated with this type of reaction using Pd(0), the unsaturated α-phenyl glycoside would lead to the unsaturated α C-glycoside and the β to the β C-glycoside.

From the work of Achmatowitz,[25] the β anomer is expected to be conformationally stable in the $^0H_5$ conformation **14**, since all substituents are in the preferred equatorial orientation. The α anomer should be an equilibrating mixture of the $^0H_5$ and $^5H_0$ conformations **15** and **16** (Scheme V). Effectively, higher coupling constants $J_{4',5'}$ were observed for the β anomer ($J_{4',5'}$ values from 8.1 to 9.2 Hz) than for the α anomer ($J_{4',5'}$ values from 6.6 to 7.5 Hz). However, in the case of the α anomer, the relatively high values of $J_{4',5'}$ suggested a higher contribution of the $^0H_5$ conformation.

The assignment of configuration at the anomeric center relied primarily on ^{13}C parameters. As expected from the γ-gauche effect of Stothers observed in cyclohexanes[26] and also in unsaturated C-glycopyranosyl compounds,[14b,27] the α anomer shows a C-5' signal at a higher field (δ from 71.93 to 72.85 ppm) than the β anomer (δ from 77.28 to 78.85 ppm) (Table II). For the same reason, an upfield shift of the C-1' in the α anomer was also found, in comparison to the downfield shift for the β anomer, but this effect was not so important.

NOE experiments were also used to assign the configuration at C-1'. Irradiation at the C-5' methine proton (δ = 3.66 ppm) in compound **11β** at 300 MHz ($CDCl_3$) showed an enhancement of 8% in the C-1' methine proton signal at δ = 5.17 ppm. Likewise, irradiation of the C-1' methine proton signal showed similar enhancement (9%) of the C-5' methine signal and also of the C-2' methine proton at 6.02 ppm (10%). Similar experiments, made on compounds **6β** and **9β** by irradiation of the C-1' methine proton signal at 4.78 and 5.00 ppm, respectively, showed an enhancement of 12% and 15% for the C-5' methine signal at 3.70 for **6β** and 3.64–3.75 ppm for **9β**. An NOE experiment on compound **11α** using the C-1' methine signal (δ = 5.20 ppm) showed an enhancement of 12% of the H-2' at 6.07 ppm; a similar experiment using the C-5' methine signal (δ = 4.17 ppm) showed an enhancement of 10% for H-3' at 6.19 ppm only. In this case, irradiation of the C-6' methine signals at 3.67 and 3.60 ppm showed an enhancement of 7% in the C-1' methine signal (δ = 5.20 ppm), 10% in the C-5' methine signal (δ = 4.17 ppm) and 4.5% in the C-4' methine signal (δ = 4.03 ppm).

These NOE experiments also allowed the unambiguous assignment of the H-2' and H-3' signals. In all compounds, H-3' is deshielded relative to H-2'. This is in agreement with the results of Rajan Babu[17] but contradicts some previous assignments in the case of unsaturated C-glycosides.[3a,c,11,14]

The ^1H NMR parameters also show, for the anomeric pairs of C-glycosides, that both H-1' and the appendent CH group resonate at higher frequencies in the β anomer; this is in agreement with the earlier observation of Fraser-Reid.[28] In each compound, H-4' resonates at a higher field than H-5', except for **11α** where H-5' is more shielded than H-4'.

In the case of nonsymmetrical nucleophiles, the ^1H NMR spectrum indicated the presence of a mixture of epimers and in particular the H-2 signal (or the H-3 signal for compound **7**) appeared as two doublets. That they were mixtures was also evident from the ^{13}C NMR spectrum, which showed a pair of signals particularly for C-1' and C-5'.

According to the Hudson rules of isorotation,[29] for an anomeric pair of glycosides, the more dextrorotatory is the α anomer, and this rule generally applies also to C-glycosides.[30-34] For the unsaturated C-glycosides **6** and

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11, the α anomer is the less dextrorotatory, disobeying Hudson's rule. Compounds **8** and **9**, which are a mixture of epimers, behave similarly. Only compound **7** obeys Hudson's rule. This peculiar behavior of unsaturated C-glycosides had been previously noticed by different groups.[12b,25,35-37]

In summary, alkylation of unsaturated phenyl glycosides with stabilized nucleophiles in the presence of Pd(0) and under neutral conditions occurs regiospecifically at the anomeric center, stereospecifically for the β anomer and stereoselectively for the α anomer. The ratio of ligand to palladium seems crucial for obtaining stereospecificity or high stereoselectivity. The unsaturated C-glycosides obtained in this manner are useful intermediates for further elaborations at the sugar moiety or/and at the introduced functional group and for synthesis of chiral tetrahydropyrans. Additional work is now in progress in these two directions.

Experimental Section

Thin-layer chromatography and column chromatography were carried out on silica gel GF_{254} (230–400 mesh Merck). Proton and carbon NMR spectra were recorded on a Brucker MSL 300 spectrometer with $CDCl_3$ as solvent and Me_4Si as internal standard. Heteronuclear chemical shift correlation (COSY) experiments were carried out by using furnished software. Mass spectra were obtained on a mass spectrometer VG 30F in chemical ionization (CI, NH_3) mode. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Microanalyses were performed by the Laboratoire Central de Microanalyse du CNRS, Vernaison, France. All solvents were distilled from an appropriate drying agent and stored under nitrogen. All air-sensitive reactions were performed under an atmosphere of nitrogen. 3,4,6-Tri-*O*-acetyl-D-glucal was purchased from Fluka Chemical, and $Pd(dba)_2$ was purchased from Aldrich Chemical or prepared according to the literature.[38]

Phenyl 4,6-Di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosides, 2 and 3. 3,4,6-Tri-*O*-acetyl-D-glucal (12.0 g, 22.7 mmol) and phenol (30 g, 320 mmol) were heated in boiling chlorobenzene (180 mL) for 3 h. The solvent and the phenol were removed under vacuum. After addition of CH_2Cl_2 (300 mL), the residual phenol was extracted with 5% sodium carbonate (3 × 150 mL), and the solution was washed with water (3 × 150 mL) and then dried. Removal of the solvent and column chromatography of the syrup on silica gel GF_{254} (230–400 mesh Merck) with use of a mixture of AcOEt/hexane (25/75) as eluent afforded compounds **2** and **3** in a ratio of 85/15, yield 80%.

α Anomer **2**: mp 47–48 °C; TLC R_f 0.53 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +165.5° (*c* 1.45, C_2H_5OH) {lit.[19] $[\alpha]^{20}_D$ +131.7° (*c* 1.45, C_2H_5OH)}; $[\alpha]^{20}_D$ +157.4° (*c* 0.5, CH_2Cl_2); ^1H NMR δ 1.96 (s, 3 H, OAc), 2.09 (s, 3 H, OAc), 4.13 (dd, 1 H, *J* = 11.6 and 1.8 Hz, H-6), 4.20–4.25 (m, 1 H, *J* = 9.5, 5.6, and 1.8 Hz, H-5), 4.28 (dd, 1 H, *J* = 11.6 and 5.6 Hz, H-6′), 5.39 (ddd, 1 H, *J* = 9.5, 1.0, and 1.0 Hz, H-4), 5.69 (dd, 1 H, *J* = 1.9 and 1.7 Hz, H-1), 5.95–6.05 (b s, 2 H, H-2, H-3), 7.0–7.3 (m, 5 H, Ph); ^{13}C NMR δ 20.41 (Me), 20.73 (Me), 62.48 (C-6), 64.96 (C-4), 67.75 (C-5), 92.67 (C-1), 126.99 (C-3), 129.89 (C-2), 116.89, 122.19, 129.22 and 156.88 (Ph), 169.69 (OC=O), 170.04 (OC=O). Anal. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.90; H, 5.98.

β Anomer **3**: oil; TLC R_f 0.47 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +72.5° (*c* 1.1, CH_2Cl_2); ^1H NMR δ 1.83 (s, 3 H, OAc), 2.09 (s, 3 H, OAc), 4.19 (dd, 1 H, *J* = 9.4 and 6.1 Hz, H-6), 4.25 (ddd, 1 H, *J* = 6.1, 5.1, and 2.7 Hz, H-5), 4.32 (dd, 1 H, 9.4 and 2.7 Hz, H-6′), 5.18 (ddd, 1 H, *J* = 5.1, 1.8, and 1.8 Hz, H-4), 5.79 (b s, 1 H, H-1), 6.11 (ddd, 1 H, *J* = 11.6, 1.8, and 1.8 Hz, H-3), 6.15 (ddd, 1 H, *J* = 11.6, 1.8, and 1.8 Hz, H-2), 7.0–7.3 (m, 5 H, Ph); ^{13}C NMR δ 20.16 (Me), 20.72 (Me), 63.16 (C-6), 63.28 (C-4), 72.68 (C-5), 91.53 (C-1), 125.30 (C-3), 129.32 (C-2), 116.15, 121.98, 129.28, and 156.64 (Ph), 170.05 (OC=O), 170.35 (OC=O). Anal. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.74; H, 5.94.

Phenyl 4,6-Di-*O*-benzyl-2,3-dideoxy-D-*erythro*-hex-2-enopyranosides, 4 and 5. A solution of 2.0 g (6.52 mmol) of glycoside **2** (or **3**) in methanol (100 mL) containing 18 mg (0.33 mmol) of CH_3ONa was stirred at 25 °C for 30 min. The solution was treated with Amberlite IR-120 H^+, and the methanol evaporated under vacuum. The crude diol obtained was dissolved in DMSO (20 mL) in the presence of KOH (1.35 g, 24.2 mmol). The mixture was stirred for 15 min at 0 °C, and benzyl chloride (2.3 g, 18.2 mmol) was added slowly. The reaction mixture was stirred at room temperature for 14 h and then partitioned between water (100 mL) and $CHCl_3$ (30 mL). The aqueous layer was washed with additional $CHCl_3$ (3 × 30 mL), and the combined extracts were dried over anhydrous sodium sulfate and filtered. After evaporation, the crude product was chromatographed on silica gel, eluting with EtOAc/hexane (4/1) to afford the product **4**α (or **5**β).

α Anomer **4**: 80%; mp 43–44 °C; TLC R_f 0.46 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +43.7° (*c* 1.5, CH_2Cl_2); ^1H NMR δ 3.67 (dd, 1 H, *J* = 11.0 and 1.8 Hz, H-6), 3.75 (dd, 1 H, *J* = 11.0 and 3.7 Hz, H-6′), 4.08 (ddd, 1 H, *J* = 9.8, 3.7, and 1.8 Hz, H-5), 4.29 (ddd, 1 H, *J* = 9.8, 2.5, and 0.6 Hz, H-4), 4.46 and 4.49 (2 d, 2 × 1 H, *J* = 11.6 Hz, OCH_2Ph), 4.58 and 4.64 (2 d, 2 × 1 H, *J* = 11.6 Hz, OCH_2Ph), 5.71 (dd, 1 H, *J* = 2.4 and 0.6 Hz, H-1), 5.91 (ddd, 1 H, *J* = 10.4, 2.4, and 2.4 Hz, H-3), 6.21 (ddd, 1 H, *J* = 10.4, 0.6, and 0.6 Hz, H-2), 7.0–7.4 (m, 15 H, Ph); ^{13}C NMR δ 68.78 (C-6), 70.16 (C-4), 70.27 (C-5), 71.19 (CH_2Ph), 73.25 (CH_2Ph), 93.30 (C-1), 125.83 (C-3), 131.66 (C-2), 117.16, 122.12, 126.75, 127.55, 127.78, 128.35, 129.41, 138.12, and 157.46 (Ph). Anal. Calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51. Found: C, 77.80; H, 6.52.

β Anomer **5**: 72%, oil; TLC R_f 0.44 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +32.9° (*c* 1.6, CH_2Cl_2); ^1H NMR δ 3.64 (dd, 1 H, *J* = 10.2 and 5.6 Hz, H-6), 3.73 (dd, 1 H, *J* = 10.2 and 5.9 Hz, H-6′), 4.01 (dddd, 1 H, *J* = 4.6, 3.6, 1.2, and 1.1 Hz, H-4), 4.19 (ddd, 1 H, *J* = 5.9, 5.6, and 4.6 Hz, H-5), 4.47 (b s, 2 H, OCH_2Ph), 4.58 (b s, 2 H, OCH_2Ph), 5.76 (ddd, 1 H, *J* = 1.4, 1.3, and 1.1 Hz, H-1), 5.90 (ddd, 1 H, *J* = 10.2, 2.0, and 1.2 Hz, H-3), 6.14 (ddd, 1 H, *J* = 10.2, 3.6, and 1.4 Hz, H-2), 6.9–7.4 (m, 15 H, Ph); ^{13}C NMR δ 68.68 (C-6), 69.74 (C-4), 70.58 (CH_2Ph), 72.94 (CH_2Ph), 74.99 (C-5), 92.98 (C-1), 127.25 (C-3), 129.11 (C-2), 116.80, 121.76, 127.46, 127.59, 127.96, 128.07, 128.71, 137.70, 137.87, and 156.77 (Ph). Anal. Calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51. Found: C, 77.65; H, 6.75.

General Procedure for Pd(0)-Catalyzed C-Glycosylation. To a solution of 36 mg (0.062 mmol) of $Pd(dba)_2$ and 0.07 mmol of diphosphine (or 0.14 mmol of triphenylphosphine) in 3 mL of THF or CH_3CN was added 502 mg (1.25 mmol) of the unsaturated sugar. To the above mixture was added 2.5 mmol of the nucleophile Nu-H, and the mixture was stirred at the desired temperature until no more starting material was visible on TLC. Concentration and column chromatography in the indicated solvents furnished the C-glycosides.

Ethyl 2-(4′,6′-Di-*O*-benzyl-2′,3′-dideoxy-D-*erythro*-hex-2′-enopyranosyl)-2-(ethoxycarbonyl)acetate, 6. α Anomer: oil; TLC R_f 0.55 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +51.0° (*c* 1, CH_2Cl_2); ^1H NMR δ 1.19 (t, 3 H, *J* = 7.1 Hz, Me), 1.22 (t, 3 H, *J* = 7.1 Hz, Me), 3.60 (dd, 1 H, *J* = 10.2 and 2.3 Hz, H-6′), 3.65–3.75 (m, 1 H, H-5′), 3.71 (dd, 1 H, *J* = 10.2 and 4.7 Hz, H-6″), 3.75 (d, 1 H, *J* = 10.3 Hz, H-2), 4.04 (dddd, 1 H, *J* = 7.0, 2.0, 1.6, and 1.0 Hz, H-4′), 4.16 (q, 2 H, *J* = 7.1 Hz, OCH_2CH_3), 4.17 (q, 2 H, *J* = 7.1 Hz, OCH_2CH_3), 4.46 and 4.57 (2 d, 2 × 1 H, *J* = 12.1 Hz, OCH_2Ph), 4.46 and 4.58 (2 d, 2 × 1 H, *J* = 11.5 Hz, OCH_2Ph), 4.86 (dddd, 1 H, *J* = 10.3, 1.6, 1.3, and 1.3 Hz, H-1′), 5.98 (ddd, 1 H, *J* = 10.5, 2.0, and 1.3 Hz, H-2′), 6.02 (ddd, 1 H, *J* = 10.5, 1.3, and 1.0 Hz, H-3′), 7.25–7.30 (m, 10 H, Ph); ^{13}C NMR δ 13.97 (Me), 55.53 (C-2), 61.57 and 61.61 (OCH_2CH_3), 68.80 (C-6′), 69.68 (C-4′), 71.17 and 73.30 (OCH_2Ph), 71.22 (C-1′), 71.93 (C-5′), 127.57, 127.75, 127.83, 127.87, 128.02, 128.17, 128.18, 128.36, 138.0, 138.1 (C-2′, C-3′, and Ph), 166.76 and 166.81 (C=O); CI MS (NH_3) *m/z* 486 (M + NH_4^+). Anal. Calcd for $C_{27}H_{32}O_7$: C, 69.21; H, 6.88. Found: C, 69.19; H, 6.92.

β Anomer: oil; TLC R_f 0.44 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +79.5° (*c* 1, CH_2Cl_2); ^1H NMR δ 1.24 (t, 6 H, *J* = 7.2 Hz, Me), 3.54 (d,

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1 H, J = 8.6 Hz, H-2), 3.58 (dd, 1 H, J = 9.9 and 4.3 Hz, H-6′), 3.63 (dd, 1 H, J = 9.9 and 4.5 Hz, H-6″), 3.64–3.75 (ddd, 1 H, J = 8.2, 4.5, and 4.3 Hz, H-5′), 4.04 (dddd, 1 H, J = 8.2, 2.9, 1.3, and 1.7 Hz, H-4′), 4.19 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 4.20 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 4.48 and 4.62 (2 d, 2 × 1 H, J = 11.5 Hz, OCH_2Ph), 4.53 and 4.58 (2 d, 2 × 1 H, J = 12.3 Hz, OCH_2Ph), 4.78 (dddd, 1 H, J = 8.6, 2.9, 1.7, and 1.3 Hz, H-1′), 5.93 (ddd, 1 H, J = 10.5, 1.3, and 1.3 Hz, H-2′), 6.00 (ddd, 1 H, J = 10.5, 1.7, and 1.7 Hz, H-3′), 7.28–7.38 (m, 10 H, Ph); ^{13}C NMR δ 14.02 (Me), 56.92 (C-2), 61.43 and 61.47 (OCH_2CH_3), 69.45 (C-6′), 70.10 (C-4′), 71.18 and 73.30 (OCH_2Ph), 73.25 (C-1′), 77.75 (C-5′), 127.43, 127.63, 127.73, 127.86, 128.16, 128.25, 128.35, 138.04, 138.51 (C-2′, C-3′, and Ph), 166.60 and 166.90 (C=O); CI MS (NH_3) m/z 486 ($M + NH_4^+$). Anal. Calcd for $C_{27}H_{32}O_7$: C, 69.21; H, 6.88. Found: C, 69.06; H, 6.89.

3-(4′,6′-Di-*O*-benzyl-2′,3′-dideoxy-D-*erythro*-hex-2′-enopyranosyl)-3-acetylpropanone, 7. α Anomer: oil; TLC R_f 0.42 (35% AcOEt/hexane); $[\alpha]^{20}_D$ 131° (c 1.1, CH_2Cl_2); ^1H NMR δ 2.16 (s, 3 H, Me), 2.26 (s, 3 H, Me), 3.56 (dd, 1 H, J = 10.5 and 3.0 Hz, H-6′), 3.63 (dd, 1 H, J = 10.5 and 5.0 Hz, H-6″), 3.75 (ddd, 1 H, J = 7.2, 5.0, and 3.0 Hz, H-5′), 3.98 (dddd, 1 H, J = 7.2, 2.2, 1.7, and 1.6 Hz, H-4′), 4.09 (d, 1 H, J = 10.4 Hz, H-3), 4.44 and 4.56 (2 d, 2 × 1 H, J = 11.4 Hz, OCH_2Ph), 4.45 and 4.56 (2 d, 2 × 1 H, J = 12.1 Hz, OCH_2Ph), 4.92 (dddd, 1 H, J = 10.4, 2.6, 2.2, and 1.7 Hz, H-1′), 5.78 (ddd, 1 H, J = 10.4, 2.1, and 2.1 Hz, H-2′), 5.98 (ddd, 1 H, J = 10.4, 2.6, and 1.5 Hz, H-3′), 7.24–7.30 (m, 10 H, Ph); ^{13}C NMR δ 28.64 (Me), 30.91 (Me), 68.78 (C-6′), 69.45 (C-3), 71.26 and 73.34 (OCH_2Ph), 71.28 (C-4′), 71.66 (C-1′), 72.15 (C-5′), 127.54, 127.70, 127.82, 127.84, 127.88, 128.13, 128.20, 128.35, 128.42, 137.85, 137.94 (C-2′, C-3′, and Ph), 200.53 and 201.57 (C=O); CI MS (NH_3) m/z 426 ($M + NH_4^+$). Anal. Calcd for $C_{25}H_{28}O_5$: C, 73.51; H, 6.91. Found: C, 73.69; H, 7.10.

β Anomer: oil; TLC R_f 0.39 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +33.1° (c 1, CH_2Cl_2); ^1H NMR δ 2.21 (s, 3 H, Me), 2.23 (s, 3 H, Me), 3.62 (dd, 1 H, J = 10.0 and 5.7 Hz, H-6′), 3.66 (dd, 1 H, J = 10.0 and 3.8 Hz, H-6″), 3.63–3.78 (m, 1 H, J = 8.4, 5.7, and 3.8 Hz, H-5′), 3.81 (d, 1 H, J = 8.4 Hz, H-3), 4.02 (dddd, 1 H, J = 8.4, 3.0, 1.9, and 1.6 Hz, H-4′), 4.52 and 4.54 (2 d, 2 × 1 H, J = 11.5 Hz, OCH_2Ph), 4.49 and 4.61 (2 d, 2 × 1 H, J = 11.5 Hz, OCH_2Ph), 4.85 (dddd, 1 H, J = 8.4, 3.0, 1.9, and 1.6 Hz, H-1′), 5.73 (ddd, 1 H, J = 10.5, 1.9, and 1.9 Hz, H-2′), 5.97 (ddd, 1 H, J = 10.5, 1.6, and 1.6 Hz, H-3′), 7.19–7.27 (m, 10 H, Ph); ^{13}C NMR δ 29.73 (Me), 30.75 (Me), 69.42 (C-6′), 69.92 (C-3), 71.19 and 73.19 (OCH_2Ph), 72.20 (C-4′), 73.57 (C-1′), 77.28 (C-5′), 127.53, 127.82, 127.88, 128.18, 128.21, 128.32, 128.39, 137.87, 138.25 (C-2′, C-3′, and Ph), 202.31 and 202.51 (C=O); CI MS (NH_3) m/z 426 ($M + NH_4^+$). Anal. Calcd for $C_{25}H_{28}O_5$: C, 73.51; H, 6.91. Found: C, 73.39; H, 7.10.

Methyl 2-(4′,6′-Di-*O*-benzyl-2′,3′-dideoxy-D-*erythro*-hex-2′-enopyranosyl)-2(*R*,*S*)-acetylacetate, 8. α Anomer: oil; TLC R_f 0.32 (25% AcOEt/hexane); $[\alpha]^{20}_D$ 72.0° (c 0.9, CH_2Cl_2); ^1H NMR δ 2.21 and 2.30 (2 s, 0.4 × 3 H and 0.6 × 3 H, Me), 3.67 and 3.69 (2 s, 0.4 × 3 H and 0.6 × 3 H, OMe), 3.6–3.8 (m, 2 H, H-6′, H-6″), 3.7–3.8 (m, 1 H, H-5′), 3.86 (d, 0.6 H, J = 10.5 Hz, H-2), 3.94 (d, 0.4 H, J = 9.8 Hz, H-2), 3.99 (dddd, 0.6 H, J = 7.4, 1.8, 1.6, and 1.5 Hz, H-4′), 4.02 (dddd, 0.4 H, J = 7.4, 1.9, 1.6, and 1.5 Hz, H-4′), 4.45 and 4.47 (2 d, 2 × 1 H, J = 11.4 Hz, OCH_2Ph), 4.46 and 4.56 (2 d, 2 × 1 H, J = 12.1 Hz, OCH_2Ph), 4.84 (dddd, 0.4 H, J = 10.5, 2.5, 1.9, and 1.6 Hz, H-1′), 4.88 (dddd, 0.6 H, J = 9.8, 2.5, 1.8, and 1.6 Hz, H-1′), 5.90 (ddd, 0.4 H, J = 10.4, 1.9, and 1.9 Hz, H-2′), 5.92 (ddd, 0.6 H, J = 10.4, 1.8, and 1.8 Hz, H-2′), 5.99 (2 ddd, 0.6 H and 0.4 H, J = 10.4, 2.5, and 1.5 Hz, H-3′), 7.27–7.31 (m, 10 H, Ph); ^{13}C NMR δ 29.75 and 30.17 (0.6 and 0.4 CH_3), 52.26 and 52.50 (0.4 and 0.6 C-2), 61.86 and 63.00 (0.6 and 0.4 OMe), 68.85 and 68.92 (0.4 and 0.6 C-6′), 69.52 and 69.63 (0.6 and 0.4 C-4′), 70.82 and 71.29 (0.4 and 0.6 C-1′), 71.13 and 71.18 (OCH_2Ph), 72.09 and 72.17 (0.6 and 0.4 C-5′), 73.26 and 73.33 (OCH_2Ph), 127.55, 127.63, 127.70, 127.78, 127.86, 128.24, 128.31, 128.40, 137.84, 137.90, 137.94, and 138.07 (C-2′, C-3′, and Ph), 167.44 (OC=O), 200.53 and 200.91 (0.4 and 0.6 C=O); CI MS (NH_3) m/z 442 ($M + NH_4^+$). Anal. Calcd for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65. Found: C, 70.80; H, 6.75.

β Anomer: oil; TLC R_f 0.39 (25% AcOEt/hexane); $[\alpha]^{20}_D$ 90.3° (c 3, CH_2Cl_2); ^1H NMR δ 2.25 and 2.31 (2 s, 0.4 × 3 H and 0.6 × 3 H, Me), 3.60 (d, 0.6 H, J = 9.3 Hz, H-2), 3.71 (s, 3 H, OMe), 3.6–3.8 (m, 2 H, H-6′, H-6″), 3.6–3.8 (m, 1 H, H-5′), 3.81 (d, 0.4 H, J = 7.0 Hz, H-2), 4.05 (dddd, 0.4 H, J = 8.1, 2.9, 1.5, and 1.5 Hz, H-4′), 4.07 (m, 0.6 H, J = 8.4, 2.9, 1.5, and 1.5 Hz, H-4′), 4.46 and 4.48 (2 d, 2 × 1 H, J = 11.5 Hz, OCH_2Ph), 4.56 and 4.61 (2 d, 2 × 1 H, J = 11.4 Hz, OCH_2Ph), 4.79 (dddd, 0.4 H, J = 7.0, 2.9, 1.5, and 1.5 Hz, H-1′), 4.82 (dddd, 0.6 H, J = 9.3, 2.9, 1.5 and 1.5 Hz, H-1′), 5.83 (ddd, 1 H, J = 10.4, 1.5, and 1.5 Hz, H-2′), 5.91 and 5.99 (2 ddd, 0.4 H and 0.6 H, J = 10.4, 1.5, and 1.5, H-3′), 7.29–7.33 (m, 10 H, Ph); ^{13}C NMR δ 30.55 and 30.92 (0.6 and 0.4 CH_3), 52.43 (C-2), 63.46 and 63.50 (0.6 and 0.4 OMe), 69.28 and 69.47 (0.6 and 0.4 C-6′), 69.91 and 69.94 (0.6 and 0.4 C-4′), 71.17 and 71.28 (OCH_2Ph), 73.20 and 73.70 (0.4 and 0.6 C-1′), 73.23 (OCH_2Ph), 77.31 and 77.49 (0.6 and 0.4 C-5′), 127.52, 127.57, 127.80, 127.88, 127.90, 128.06, 128.17, 128.32, 128.40, 137.91, 137.90, 138.33, and 138.38 (C-2′, C-3′, and Ph), 167.42 and 167.90 (0.6 and 0.4 OC=O), 201.45 and 201.60 (0.4 and 0.6 C=O); CI MS (NH_3) m/z 442 ($M + NH_4^+$). Anal. Calcd for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65. Found: C, 70.53; H, 6.52.

Ethyl 2-(4′,6′-Di-*O*-benzyl-2′,3′-dideoxy-D-*erythro*-hex-2′-enopyranosyl)-2(*R*,*S*)-nitroacetate, 9. α Anomer: oil; TLC R_f 0.47 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +65.4° (c 1.25, CH_2Cl_2); ^1H NMR δ 1.24 and 1.26 (2 t, 0.25 × 3 H and 0.75 × 3 H, J = 7.3 Hz, Me), 3.62 (dd, 1 H, J = 11.6 and 3.7 Hz, H-6′), 3.72 (dd, 1 H, J = 11.6 and 4.3 Hz, H-6″), 3.60–3.73 (ddd, 1 H, J = 7.0, 4.3, and 3.7 Hz, H-5′), 4.17 (dddd, 1 H, J = 7.0, 2.1, 1.8, and 1.8 Hz, H-4′), 4.28 and 4.29 (2 q, 2 H, J = 7.3 Hz, OCH_2CH_3), 4.35 and 4.61 (2 d, 2 × 1 H, J = 12.1 Hz, OCH_2Ph), 4.46 and 4.59 (2 d, 2 × 1 H, J = 11.4 Hz, OCH_2Ph), 5.01 (dddd, 0.25 H, J = 8.5, 2.1, 2.0, and 2.0 Hz, H-1′), 5.02 (dddd, 0.75 H, J = 10.4, 2.1, 2.0, and 2.0 Hz, H-1′), 5.29 (d, 0.25 H, J = 8.5 Hz, H-2), 5.35 (d, 0.75 H, J = 10.4 Hz, H-2), 5.89 and 5.90 (2 ddd, 0.25 H and 0.75 H, J = 10.4, 2.0, and 1.8 Hz, H-2′), 6.15 (ddd, 1 H, J = 10.4, 2.0, and 1.8 Hz, H-3′), 7.2–7.4 (m, 10 H, Ph); ^{13}C NMR δ 13.80 (Me), 63.12 and 63.23 (0.25 and 0.75 CH_2CH_3), 68.45 and 68.78 (0.75 and 0.25 C-6′), 68.99 and 69.21 (0.25 and 0.75 C-4′), 70.16 and 71.13 (0.25 and 0.75 C-1′), 70.99 (OCH_2Ph), 71.39 (OCH_2Ph), 72.27 and 72.84 (0.75 and 0.25 C-5′), 73.21 (OCH_2Ph), 73.25 (OCH_2Ph), 88.26 (C-2), 124.18 and 124.82 (0.75 and 0.25 C-2′), 130.88 and 131.11 (0.75 and 0.25 C-3′), 127.55, 127.69, 127.81, 128.36, 128.45, 137.91, 138.14, and 138.40 (Ph), 162.05 (C=O); CI MS (NH_3) m/z 459 ($M + NH_4^+$). Anal. Calcd for $C_{24}H_{27}NO_7$: C, 65.29; H, 6.16; N, 3.17. Found: C, 65.62; H, 6.05; N, 2.87.

β Anomer: oil; TLC R_f 0.32 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +81.8° (c 1.3, CH_2Cl_2); ^1H NMR δ 1.24 and 1.25 (2 t, 0.4 × 3 H and 0.6 × 3 H, J = 7.3 Hz, Me), 3.63 (dd, 1 H, J = 11.1 and 5.3 Hz, H-6′), 3.72 (dd, 1 H, J = 11.1 and 4.3 Hz, H-6″), 3.60–3.75 (m, 1 H, H-5′), 3.96 and 4.08 (2 dddd, 0.4 H and 0.6 H, J = 8.6, 2.8, 2.1, and 1.8 Hz, H-4′), 4.27 (q, 2 H, J = 7.3 Hz, OCH_2CH_3), 4.43 and 4.61 (2 d, 0.4 × 2 H, J = 11.6 Hz, OCH_2Ph), 4.45 and 4.59 (2 d, 0.6 × 2 H, J = 11.6 Hz, OCH_2Ph), 4.52 and 4.54 (2 d, 2 H, J = 11.2 Hz, OCH_2Ph), 4.95 (dddd, 0.4 H, J = 5.2, 1.8, and 1.8 Hz, H-1′), 5.00 (dddd, 0.6 H, J = 9.0, 1.8, and 1.8 Hz, H-1′), 5.09 (d, 0.6 H, J = 9.0 Hz, H-2), 5.33 (d, 0.4 H, J = 5.2 Hz, H-2), 5.85 and 5.88 (2 ddd, 0.4 H and 0.6 H, J = 10.7, 1.8, and 1.8 Hz, H-2′), 6.10 (ddd, 1 H, J = 10.7, 2.1, and 1.8 Hz, H-3′), 7.2–7.4 (m, 10 H, Ph); ^{13}C NMR δ 13.75 (Me), 63.04 and 63.12 (0.4 and 0.6 CH_2CH_3), 68.91 and 69.39 (0.4 and 0.6 C-6′), 69.67 (C-4′), 71.37 and 71.50 (0.4 and 0.6 OCH_2Ph), 72.89 and 72.96 (0.4 and 0.6 C-1′), 73.33 (OCH_2Ph), 77.63 and 78.05 (0.6 and 0.4 C-5′), 89.28 and 90.13 (0.4 and 0.6 C-2), 124.20 and 124.74 (0.6 and 0.4 C-2′), 129.96 and 131.25 (0.4 and 0.6 C-3′), 127.48, 127.57, 127.80, 128.24, 128.34, 137.77, and 138.33 (Ph), 161.82 and 161.97 (0.4 and 0.6 C=O); CI MS (NH_3) m/z 459 ($M + NH_4^+$). Anal. Calcd for $C_{24}H_{27}NO_7$: C, 65.29; H, 6.16; N, 3.17. Found: C, 65.42; H, 6.13; N, 3.46.

Methyl 2-(4′,6′-di-*O*-benzyl-2′,3′-dideoxy-α-D-*erythro*-hex-2′-enopyranosyl)-2(*R*,*S*)-nitroacetate, 10: oil; TLC R_f 0.45 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +81.0° (c 1.2, CH_2Cl_2); ^1H NMR δ 3.55–3.70 (m, 2 H, H-6′, H-6″), 3.68 and 3.69 (2 ddd, 0.3 H and 0.7 H, J = 7.5, 6.0, and 4.3 Hz, H-5′), 3.79 and 3.80 (2 s, 0.7 × 3 H and 0.3 × 3 H, OMe), 4.05 and 4.17 (2 dddd, 0.3 H and 0.7 H, J = 7.5, 3.0, 2.1, and 2.0 Hz, H-4′), 4.43 and 4.45 (2 d, 2 × 0.7 × 1 H, OCH_2Ph), 4.58 and 4.58 (2 d, 2 × 0.3 × 1 H, OCH_2Ph), 4.57 and 4.59 (2 d, 2 × 1 H, OCH_2Ph), 4.96 (dddd, 0.3 H, J = 8.4, 3.0, 2.2, and 2.1 Hz, H-1′), 5.04 (dddd, 0.7 H, J = 10.1, 3.0, 2.2, 2.1 Hz, H-1′), 5.30 (d, 0.3 H, J = 8.4 Hz, H-2), 5.37 (d, 0.7 H, J = 10.1 Hz, H-2), 5.87 and 5.89 (2 ddd, 0.3 H and 0.7 H, J = 10.4, 2.2, and 2.0 Hz, H-2′), 6.12 (ddd, 1 H, J = 10.4, 2.1, and 2.1 Hz,

H-3′), 7.27–7.32 (m, 10 H, Ph); ^{13}C NMR δ 53.62 and 53.71 (0.3 and 0.7 Me), 63.38 and 63.75 (0.7 and 0.3 C-6′), 69.07 and 69.26 (0.3 and 0.7 C-4′), 70.25 and 71.17 (0.3 and 0.7 C-1′), 71.59 (OCH_2Ph), 72.32 and 72.96 (0.7 and 0.3 C-5′), 73.3 and 73.4 (OCH_2Ph), 88.09 and 89.94 (0.7 and 0.3 C-2), 124.12 and 124.85 (0.7 and 0.3 C-2′), 131.07 and 131.32 (0.7 and 0.3 C-3′), 127.52, 127.57, 127.61, 127.65, 127.83, 127.91, 128.34, 128.43, 137.68, 137.71, and 137.92 (Ph), 162.37 and 162.47 (0.3 and 0.7 C=O); CI MS (NH_3) m/z 445 (M + NH_4^+). Anal. Calcd for $C_{23}H_{25}NO_7$: C, 64.63; H, 5.90; N, 3.28. Found: C, 64.37; H, 5.91; N, 3.51.

Ethyl 2-(4′,6′-Di-*O*-benzyl-2′,3′-dideoxy-D-*erythro*-hex-2′-enopyranosyl)-2-nitro-2-(ethoxycarbonyl)acetate, 11. α Anomer: oil; TLC R_f 0.61 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +15.3° (*c*, 1, CH_2Cl_2); ^{1}H NMR δ 1.28 (t, 3 H, *J* = 7.1 Hz, Me), 1.29 (t, 3 H, *J* = 7.1 Hz, Me), 3.60 (dd, 1 H, *J* = 10.8 and 3.2 Hz, H-6′), 3.67 (dd, 1 H, *J* = 10.8 and 4.4 Hz, H-6″), 4.03 (dddd, 1 H, *J* = 6.7, 2.4, 2.3, and 1.8 Hz, H-4′), 4.17 (ddd, 1 H, *J* = 6.7, 4.4, and 3.2 Hz, H-5′), 4.32 (q, 4 H, *J* = 7.1 Hz, OCH_2CH_3), 4.47 and 4.56 (2 d, 2 × 1 H, *J* = 12.2 Hz, OCH_2Ph), 4.49 and 4.60 (2 d, 2 × 1 H, *J* = 11.7 Hz, OCH_2Ph), 5.20 (ddd, 1 H, *J* = 2.4, 2.4, and 2.4 Hz, H-1′), 6.07 (ddd, 1 H, *J* = 10.6, 2.4, and 1.8 Hz, H-2′), 6.19 (ddd, 1 H, *J* = 10.6, 2.4, and 2.3 Hz, H-3′), 7.26–7.30 (m, 10 H, Ph); ^{13}C NMR δ 13.63 (Me), 13.74 (Me), 63.60 (OCH_2), 63.63 (OCH_2), 68.78 (C-6′), 68.84 (C-4′), 70.75 (OCH_2Ph), 72.64 (C-1′), 72.85 (C-5′), 73.19 (OCH_2Ph), 98.58 (C-2), 123.64 (C-2′), 131.03 (C-3′), 127.60, 127.70, 127.74, 127.80, 128.31, 128.33, and 138.07 (Ph), 160.76 (C=O), 161.03 (C=O); CI MS (NH_3) m/z 531 (M + NH_4^+). Anal. Calcd for $C_{27}H_{31}NO_9$: C, 63.15; H, 6.08; N, 2.73. Found: C, 63.01; H, 6.29; N, 2.71.

β Anomer: oil; TLC R_f 0.64 (25% AcOEt/hexane); $[\alpha]^{20}_D$ +98.6° (*c* 1.3, CH_2Cl_2); ^{1}H NMR δ 1.26 (t, 3 H, *J* = 7.2 Hz, Me), 1.27 (t, 3 H, *J* = 7.2 Hz, Me), 3.69 (dd, 1 H, *J* = 10.7 and 4.5 Hz, H-6′), 3.70 (dd, 1 H, *J* = 10.7 and 3.6 Hz, H-6″), 3.67 (ddd, 1 H, *J* = 8.6, 4.5, and 3.6 Hz, H-5′), 4.04 (dddd, 1 H, *J* = 8.6, 2.9, 1.9, and 1.5 Hz, H-4′), 4.31 (q, 4 H, *J* = 7.2 Hz, OCH_2CH_3), 4.52 and 4.64 (2 d, 2 × 1 H, *J* = 11.6 Hz, OCH_2Ph), 4.58 and 4.62 (2 d, 2 × 1 H, *J* = 12.1 Hz, OCH_2Ph), 5.17 (ddd, 1 H, *J* = 2.8, 2.3, and 1.8 Hz, H-1′), 6.02 (ddd, 1 H, *J* = 10.6, 2.3, and 2.0 Hz, H-2′), 6.14 (ddd, 1 H, *J* = 10.6, 2.0, and 1.8 Hz, H-3′), 7.30–7.34 (m, 10 H, Ph); ^{13}C NMR δ 13.64 (Me), 13.74 (Me), 63.60 (2 OCH_2), 69.15 (C-6′), 69.37 (C-4′), 71.50 (OCH_2Ph), 73.26 (OCH_2Ph), 75.24 (C-1′), 78.14 (C-5′), 98.13 (C-2), 123.96 (C-2′), 132.26 (C-3′), 127.41, 127.54, 127.64, 127.70, 128.26, 128.41, 137.75, and 138.53 (Ph), 160.52 (C=O), 160.86 (C=O); CI MS (NH_3) m/z 531 (M + NH_4^+). Anal. Calcd for $C_{27}H_{31}NO_9$: C, 63.15; H, 6.08; N, 2.73. Found: C, 63.27; H, 6.03; N, 2.64.

Pd(0)-Catalyzed Isomerization of Phenyl 4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside, 4. The α-phenyl glycoside **4** (251 mg, 0.62 mmol) was dissolved in CH_3CN (2.5 mL), $Pd(dba)_2$ (18 mg, 0.031 mmol) and 1,4-bis(diphenylphosphino)butane (15 mg, 0.035 mmol) in 2.5 mL of CH_3CN were added, and the mixture was stirred at 70 °C for 6 h. After concentration and column chromatography, the product was shown by ^{1}H NMR analysis to consist of only the starting material **4α**. The same procedure was used for the β anomer **5**, and the starting material was also recovered.

Denitration of Compound 11α. To a stirred solution of Bu_3SnH (400 mg, 1.3 mmol) in 0.3 mL of toluene was added a solution of **11α** (34 mg, 0.066 mmol) and AIBN (8 mg, 0.05 mmol) in 0.7 mL of toluene at 110 °C, and the resulting mixture was stirred at this temperature for 90 min. Column chromatography (silica gel; hexane/ethyl acetate, 3:1) gave **6α**: 30 mg (90%).

Registry No. **1**, 2873-29-2; **2**, 62398-09-8; **3**, 113019-34-4; **4**, 113019-35-5; **5**, 113019-36-6; **α-6**, 119366-97-1; **β-6**, 119366-98-2; **α-7**, 119366-99-3; **β-7**, 119367-00-9; **α-8**, 119367-01-0; **β-8**, 119434-14-9; **α-9**, 113019-37-7; **β-9**, 113084-95-0; **α-10**, 119367-02-1; **α-11**, 119367-03-2; **β-11**, 119367-04-3; $CH_2(CO_2Et)_2$, 105-53-3; $CH_2(COCH_3)_2$, 123-54-6; $CH_3COCH_2CO_2CH_3$, 105-45-3; $O_2NCH_2CO_2Et$, 626-35-7; $O_2NCH_2CO_2CH_3$, 2483-57-0; $O_2NCH(CO_2Et)_2$, 603-67-8.

Supplementary Material Available: NMR spectra for compounds **6β**, **9β**, **11α**, and **11β** (4 pages). Ordering information is given on any current masthead page.

Sclerophytin C–F: Isolation and Structures of Four New Diterpenes from the Soft Coral *Sclerophytum capitalis*

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The marine soft coral *Sclerophytum capitalis* was found to contain four new diterpenes, which were isolated and identified as sclerophytins C–F. The structures of the isolated compounds were determined by spectroscopic and/or by X-ray crystallographic methods. The absolute configuration of sclerophytin C was determined by X-ray crystallography and constitutes the first absolute configuration determined in this family of diterpenes.

In a survey conducted, almost a decade ago, under the auspices of the National Cancer Institute, a number of marine invertebrates were found to have promising cytotoxic activity against a variety of cancerous cell lines. One such invertebrate, *Sclerophytum capitalis*, has been a subject of investigation in our laboratory. We recently reported the isolation and structures of two novel tetracyclic diterpenes, sclerophytins A and B (I and II), from this coral.[1] Sclerophytin A was found to be active against L1210 cell line at a 1×10^{-6} mg/mL level. Both sclerophytin A and B were suggested to have been derived from a deacetylation product of the diterpene cladiellin (III),[2] which in turn has been proposed to have been derived from an isocembrene.[3] In this communication we report the isolation and structures of four new diterpenes (sclero-

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