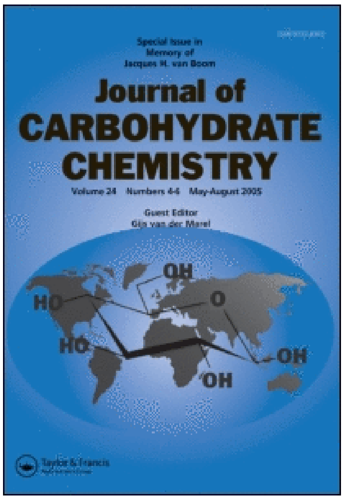

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Palladium(0)-Mediated Synthesis of Acetylated Unsaturated 1,4-Disaccharides

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To cite this Article Frappa, Isabelle , Kryczka, Boguslaw , Lhoste, Paul , Porwanski, Stanislaw , Sinou, Denis and Zawisza, Anna(1998) 'Palladium(0)-Mediated Synthesis of Acetylated Unsaturated 1,4-Disaccharides', Journal of Carbohydrate Chemistry, 17: 7, 1117 — 1130

To link to this Article: DOI: 10.1080/07328309808001888

URL: http://dx.doi.org/10.1080/07328309808001888

J. CARBOHYDRATE CHEMISTRY, 17(7), 1117–1130 (1998)

PALLADIUM(0)-MEDIATED SYNTHESIS OF ACETYLATED UNSATURATED 1,4-DISACCHARIDES

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Received February 11, 1998 - Final Form April 21, 1998

ABSTRACT

Alkylation of ethyl 6-*O*-*tert*-butyldiphenylsilyl-4-*O*-methoxycarbonyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1**) with various peracetylated 1-hydroxy sugars in the presence of a catalytic amount of palladium(0) gave the corresponding unsaturated 1,4-disaccharides and trisaccharides. In all cases the reaction is regio- and stereospecific according to the unsaturated moiety, alkylation occuring only at C-4 of the unsaturated carbohydrate, with overall retention of configuration.

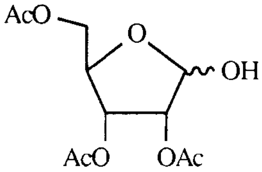
INTRODUCTION

Glycosides and oligosaccharides are constituents of biologically important compounds. Since the pioneering work of Kœnigs-Knorr related to the glycosylation reaction, there has been a considerable interest in the design of new methodologies directed towards the efficiency of this reaction (high chemical yield, regio- and stereoselectivity).[1] Although unsaturated disaccharides have been known since 1934,[2] there are only a few methods for the synthesis of these compounds. Unsaturated disaccharides have been synthesized via a Ferrier reaction between 3,4,6-tri-*O*-acetyl-D-glycal and 1-hydroxy sugars[3] or between disaccharide glycals and various alcohols,[4] by sulfonamidoglycosylation of a glycal,[5] via 3-pentenoyl glycals,[6] or by glycosylation of unsaturated thioglycosides in the presence of $PdCl_2(CH_3CN)_2$.[7] These unsaturated disaccharides are valuable intermediates since the further functionalization of the double bond could lead to a variety of derivatives.

Following our continuing interest in the formation of a carbon-oxygen bond catalysed by palladium(0) complexes and particularly the use of this very mild methodology in carbohydrate chemistry,[8] we presented recently our results concerning the synthesis of unsaturated disaccharides catalysed by palladium(0).[9] This reaction was based on the direct anomeric *O*-alkylation of pyranoses and furanoses, and there are few examples on the use of this methodology in complex saccharide synthesis.[10] However this methodology suffers from the use of isopropylidene or benzylidene as protecting groups, which are sometimes difficult to cleave. We report in this paper the use of peracetylated 1-hydroxy carbohydrates in this reaction.

RESULTS AND DISCUSSION

According to our previous studies, we chose the unsaturated carbohydrate **1** as the π-allyl palladium precursor, and various acetylated 1-hydroxy sugars **2**-**7** as the



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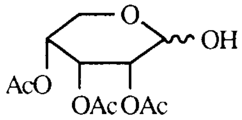

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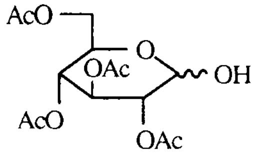

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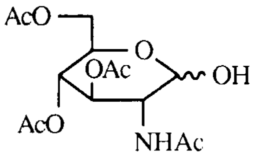

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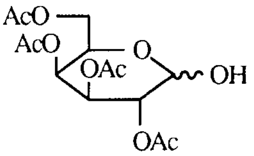

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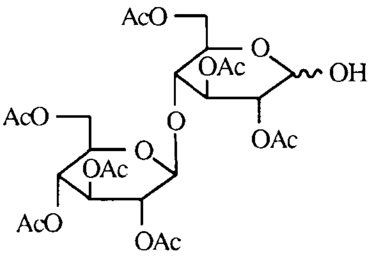

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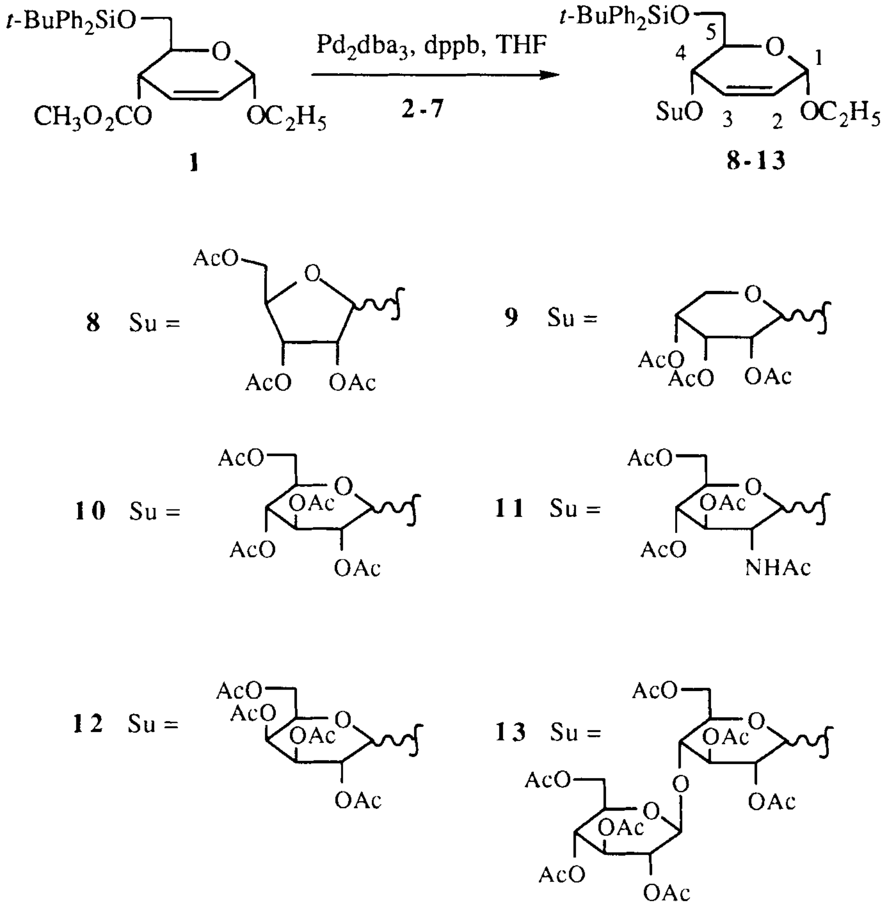
Table 1. Selected ^1H and ^{13}C NMR data for compounds **8-13**.

Compound	Yield (%)[a]	α/β	δ H-1'[b]		$J_{1',2'}$[c]		δ C-1'[b]		δ H-4[b]		$J_{4,5}$[c]	
			α	β	α	β	α	β	α	β	α	β
8	58	28/72	5.38	5.17	4.4	bs	98.25	106.48	4.26	4.31	9.5	8.2
9	82	7/93	5.09	5.01	3.9	4.7	92.47	99.64	4.42	4.47	9.4	10.6
10	55	63/37	5.26	4.65	3.8	8.2	94.03	101.17	4.21	4.41	9.3	9.3
11	51	100/0	5.01	-	3.5	-	94.62	-	4.19	-	9.3	-
12	67	70/30	5.16	4.61	3.8	8.2	94.43	101.89	3.99	4.41	9.3	9.3
13	59	63/37	5.17	4.57	3.8	8.2	94.18	101.32	4.24	4.35	9.6	8.5

a. Yield of pure product.
b. Recorded in $CDCl_3$ with TMS as an external standard.
c. Coupling constant J in Hertz.

nucleophiles. The reaction was performed in tetrahydrofuran at 60 °C in the presence of a catalytic amount of tris(dibenzylideneacetone)dipalladium or $Pd_2(dba)_3$ and 1,4-bis (diphenylphosphino)butane or dppb (Scheme 1).



Scheme 1

As a first example, reaction of 2,3,5-tri-*O*-acetyl-D-ribofuranose (**2**) with unsaturated carbohydrate **1** gave the disaccharides **8** as an α/β mixture (28/72) in 58 % yield; the anomers were separated by chromatography on silica gel. The α and β configuration of the furanose moiety was readily derived from the ^1H NMR data. We observed for H-1' a doublet at δ 5.38 ppm with a coupling constant $J_{1',2'}$ = 4.4 Hz and a broad singlet at δ 5.17 ppm characteristic for an α and β configuration, respectively, in the ribofuranose series.[11] This assignment was confirmed from ^{13}C NMR data, the signal of C-1' corresponding to the α anomer (δ 98.25 ppm) being at higher field than the signal of the β anomer (δ 106.48 ppm), in agreement with the literature data.[12] The overall retention of configuration at C-4 was also observed from the ^{1}H NMR data; the coupling constants $J_{4,5}$ = 9.5 Hz and 8.2 Hz for the α and β anomer, respectively, are characteristic for a *trans* diaxial relationship between H-4 and H-5.

When 2,3,4-tri-*O*-acetyl-D-ribopyranose (**3**) was used as the nucleophile instead of **2**, the disaccharide **9** was obtained as an α/β mixture (7/93) in 82 % yield; the anomers were separated by chromatography on silica gel and characterized by NMR. The H-4' signal appeared at δ 4.97 ppm for the α anomer with $J_{4',5'}$ = 10.0 Hz and 4.6 Hz and $J_{4',3'}$ = 3.4 Hz, and at δ 5.11 ppm for the β anomer with $J_{4',5'}$ = 6.2 Hz and 3.1 Hz and $J_{4',3'}$ = 3.2 Hz. According to literature data concerning alkyl D-ribopyranosides,[13] the α anomer is in the *C1* conformation and the β anomer in the *1C* conformation; so the H-4' signal of the α anomer exhibited a high coupling constant characteristic of an *axial-axial* arrangement (J = 10.0 Hz). This assignment was again confirmed from ^{13}C NMR data, with the signal of C-1' corresponding to the α anomer (δ 92.47 ppm) being at higher field than the signal of the β anomer (δ 99.64 ppm).[14] The *erythro*-configuration, and consequently the overall retention of configuration at C-4, was confirmed by the coupling constant $J_{4,5}$ = 9.4 Hz and 10.6 Hz for the α and β anomers, respectively, characteristic of a *trans* diaxial relationship between H-4 and H-5.

The reaction of unsaturated carbohydrate **1** with 2,3,4,6-tetra-*O*-acetyl-D-gluco pyranose (**4**) gave the disaccharide **10** as an α/β mixture (63/37) in 55 % yield. The α and β configuration of the glucopyranose moiety was derived from the ^{1}H NMR data. We observed for H-1' a doublet at δ 5.26 ppm with a coupling constant $J_{1',2'}$ = 3.8 Hz, and a doublet at δ 4.65 ppm with a coupling constant $J_{1',2'}$ = 8.2 Hz characteristic for the α and β configurations, respectively.[11b, 15] The overall retention of configuration at C-4 was also observed from the ^{1}H NMR data; the coupling constant $J_{4,5}$ = 9.3 Hz for the two anomers is characteristic of the *trans* diaxial relation between H-4 and H-5.

When 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranose (**5**) was used as the nucleophile in this reaction, the corresponding disaccharide **5** was obtained in 51 % yield as a single anomer. The α configuration was attributed from the ^{1}H NMR; the signal of H-1' appeared at δ 5.01 ppm as a doublet with a coupling constant $J_{1',2'}$ = 3.5 Hz characteristic of the α configuration.[16] The signal of C-1' at δ 94.62 ppm is also in agreement with this assignment. Finally the coupling constant $J_{4,5}$ = 9.3 Hz confirmed the *erythro*-configuration of the unsaturated moiety.

The reaction of 2,3,4,6-tetra-*O*-acetyl-D-galactopyranose (**6**) with unsaturated carbohydrate **1** gave the disaccharide **12** in 67 % yield as an α/β mixture (70/30). Confirmation of α and β configuration was based on ^{1}H and ^{13}C NMR data, and particularly noteworthy is the strong deshielding effect observed for H-1' and H-3' going from the β to the α anomer. The signal of H-3' appeared at δ 5.11 ppm and 4.91 ppm for the α and β anomer, respectively, and the signal of H-1' at δ 5.16 and 4.61 ppm, with $J_{1',2'}$ = 3.8 Hz and 8.2 Hz for **12**α and **12**β, respectively.[15, 17] The signal of C-1' appeared also at δ 94.43 and 101.89 ppm for the α and β anomer, respectively, in agreement with the literature data.[17] The coupling constant of the unsaturated moiety $J_{4,5}$ = 9.3 Hz confirmed the *erythro*-configuration and so the overall retention of configuration of the overall process.

Finally reaction of 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-D-glucopyranose (**7**) with unsaturated carbohydrate **1** gave the trisaccharide **13** in 59 % yield as an α/β mixture (63/37), anomers which were separated by column chromatography. As for disaccharide **10**, the α/β configuration at C-1' was based on the ^{1}H NMR data. We effectively observed a doublet at δ 5.17 ppm ($J_{1',2'}$ = 3.8 Hz) and a doublet at 4.57 ppm ($J_{1',2'}$ = 8.2 Hz) characteristic of an α and β configuration, respectively. The chemical shift of C-1' at δ 94.18 ppm and 101.32 ppm for the α and β anomer, respectively, are in agreement with this assignment. We noticed also the overall retention of configuration of the process with $J_{4,5}$ = 9.6 Hz and 8.5 Hz for the α and β anomer, respectively, characteristic of an *erythro*-configuration of the unsaturated moiety.

It can be noted that the ratio of anomers obtained in the palladium-catalyzed reaction is quite close to the ratio of anomers in solution under exactly the same conditions (THF, 50 °C) for compounds **2**-**7**; effectively ^{1}H and ^{13}C NMR data under these conditions showed for carbohydrates **2**-**7** an α/β ratio of 24/76, 13/87, 73/27, 90/10, 68/32, and 77/23 %, respectively. This implies that the palladium-catalyzed alkylation could be fast compared to the α $\rightleftharpoons$ β equilibriation, or that the two anomers reacted practically at the same rate.

CONCLUSION

In this paper, we have shown that unsaturated disaccharides and trisaccharides could be obtained in quite good yields starting from α-*erythro* enoside **1** and various peracetylated 1-hydroxy carbohydrates under neutral conditions using palladium(0) as the catalyst. The reaction is regio- and stereospecific according to the unsaturated carbohydrate, and the α/β ratio of anomers at the saturated carbohydrate corresponds to the α/β ratio of anomers of the 1-hydroxy carbohydrate in solution. The extension of this very mild methodology of glycosylation to the synthesis of various carbohydrates via the functionalisation of the double bond is currently under investigation.

EXPERIMENTAL

General methods. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (60F-254, Merck). Column chromatography was performed on silica gel 60 (230-480 mesh ASTM, Macherey-Nagel). NMR spectra were obtained in $CDCl_3$ and chemical shifts are given in ppm on the δ scale from internal tetramethylsilane; they were recorded on Bruker AC 200 MHz, AM 300 MHz and Varian Unity 500 Mz (H' refers to the saturated moiety of the disaccharide). Optical rotations were measured on a Perkin-Elmer 241 polarimeter. THF was distilled from sodium/ benzophenone and kept under a nitrogen atmosphere. Reactions involving palladium complexes were carried out in a Schlenk tube under a nitrogen atmosphere. $Pd_2(dba)_3$ and 1,4-bis(diphenylphosphino)butane are from a commercial source. The preparation of ethyl 6-*O*-*tert*-butyldiphenylsilyl-4-*O*-methoxycarbonyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**1**) was already described.[9b] 2,3,5-Tri-*O*-acetyl-D-ribofuranose (**2**), 2,3,4-tri-*O*-acetyl-D-ribopyranose (**3**), 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**4**), 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranose (**5**), 2,3,4,6-tetra-*O*-acetyl-D-galactopyranose (**5**) and 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-D-glucopyranose (**6**) were prepared from the corresponding acetates according to literature procedures.[18]

General Procedure for Palladium-Catalysed Alkylation Reaction. The catalytic system was prepared by stirring for 1 h in a Schlenk tube under argon $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol) and dppb (42.6 mg, 0.1 mmol) in tetrahydrofuran (5 mL). This solution was added under argon to a Schlenk tube containing the unsaturated carbohydrate (1 mmol) and the acetylated 1-hydroxy sugar (2 mmol) in tetrahydrofuran (5 mL). The solution was stirred at 60 °C and the reaction followed by TLC. After dissapearence of the starting unsaturated carbohydrate, the solvent was evaporated and the residue was chromatographed on silica gel to give the disaccharide.

Ethyl 4-*O*-(2,3,5-Tri-*O*-acetyl-α-D-ribofuranosyl)-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (8α). Yield 16 %; oil; R_f 0.36 (petroleum ether/ethyl acetate 3:2 v/v); $[\alpha]^{20}_D$ +117.1 (*c* 1.4, chloroform); ^{1}H NMR (500 MHz) δ 1.04 (s, 9H, CMe_3), 1.23 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.93 (s, 3H, $COCH_3$), 2.00 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 3.56 (dq, J = 9.5 and 7.1 Hz, 1H, CH_2CH_3), 3.80-3.94 (m, H-4', H-5, H-6, 5H, CH_2CH_3), 3.97 (dd, J = 12.0 and 3.3 Hz, 1H, H-5'), 4.05 (dd, J = 12.0 and 3.0 Hz, 1H, H-5'), 4.26 (bd, J = 9.5 Hz, 1H, H-4), 4.78 (dd, J = 7.0 and 4.4 Hz, 1H, H-2'), 5.03 (bs, 1H, H-1), 5.11 (dd, J = 7.0 and 3.0 Hz, 1H, H-3'), 5.38 (d, 1H, J = 4.4 Hz, H-1'), 5.76 (ddd, J = 10.2, 2.2 and 1.9 Hz, 1H, H-2), 5.88 (d, J = 10.2 Hz, 1H, H-3), 7.32-7.42 (m, 6 H, C_6H_5), 7.68-7.73 (m, 4H, C_6H_5); ^{13}C NMR (50.3 MHz) δ 15.32 (CH_2CH_3), 19.28 (*C*Me$_3$), 20.55 (2xCO*C*H_3), 20.73 (CO*C*H_3), 26.71 (C*Me*$_3$), 63.30, 63.35 and 63.77 (*C*H_2CH_3, C-5', C-6), 67.80, 69.84, 70.37 and 71.07 (C-4, C-5, C-3', C-4'), 79.38 (C-2'), 94.02 (C-1), 98.25 (C-1'), 126.92 (C-2), 129.60 (C-3), 127.56, 127.64, 129.66, 130.09, 133.54, 133.75, 135.59 and 135.82 (C_6H_5), 170.02 (*C*OCH_3), 170.25 (*C*OCH_3), 170.45 (*C*OCH_3).

Anal. Calcd for $C_{35}H_{46}O_{11}Si$: C, 62.68; H, 6.87. Found: C, 62.76; H, 7.05.

Ethyl 4-*O*-(2,3,5-Tri-*O*-acetyl-β-D-ribofuranosyl)-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (8β). Yield 42 %; oil; R_f 0.49 (petroleum ether/ethyl acetate 3:2 v/v); $[\alpha]^{20}_D$ +9.5 (*c* 1, chloroform); ^{1}H NMR (500 MHz) δ 1.03 (s, 9H, CMe$_3$), 1.18 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 2.01 (s, 3H, COCH$_3$), 2.03 (s, 3H, COCH$_3$), 2.07 (s, 3H, COCH$_3$), 3.50 (dq, J = 9.6 and 7.1 Hz, 1H, C*H*$_2$CH$_3$), 3.76-3.83 (m, 3H, H-5, H-6, C*H*$_2$CH$_3$), 3.87 (dd, J = 11.4 and 4.6 Hz, 1H, H-6), 4.11 (d, J = 11.7 and 4.6 Hz, 1H, H-5'), 4.25 (m, 1H, H-4'), 4.31 (dd, J = 11.7 and 3.5 Hz, 1H, H-5'), 4.31 (bd, J = 8.2 Hz, 1H, H-4), 4.98 (bs, 1H, H-1), 5.11 (dd, J = 4.8 and 1.1 Hz, 1H, H-2'), 5.17 (bs, 1H, H-1'), 5.28 (dd, J = 6.5 and 4.8 Hz, 1H, H-3'), 5.73 (ddd, J = 10.2, 2.5 and 2.2 Hz, 1H, H-2), 6.09 (bd, J = 10.2 Hz, 1H, H-3), 7.30-7.42 (m, 6H, C_6H_5), 7.68-7.74 (m, 4H, C_6H_5); ^{13}C NMR (50.3 MHz) δ 15.26 (CH$_2$*C*H$_3$), 19.32 (*C*Me$_3$), 20.48 (CO*C*H$_3$), 20.42 (CO*C*H$_3$), 20.85 (CO*C*H$_3$), 26.74 (C*Me*$_3$), 63.11, 63.74 and 63.92 (*C*H$_2$CH$_3$, C-5', C-6), 70.33, 71.09 and 71.83 (C-4, C-5, C-4'), 74.94 and 78.53 (C-2', C-3'), 93.97 (C-1), 106.48 (C-1'), 126.82 (C-2), 132.03 (C-3), 127.56, 127.68, 129.60, 133.23, 133.70, 135.57 and 137.78 (C_6H_5), 169.37 (*C*OCH$_3$), 169.59 (*C*OCH$_3$) and 170.64 (*C*OCH$_3$).

Anal. Calcd for $C_{35}H_{46}O_{11}Si$: C, 62.68; H, 6.87. Found: C, 62.58; H, 6.99.

Ethyl 4-*O*-(2,3,4-Tri-*O*-acetyl-α-D-ribopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (9α). Yield 6 %; oil; R_f 0.46 (petroleum ether/ethyl acetate 1:2 v/v); $[\alpha]^{20}_D$ +89.6 (*c* 1.1, chloroform); ^{1}H NMR (300 MHz) δ 1.07 (s, 9H, *t*-Bu), 1.24 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.95 (s, 3H, COCH$_3$), 2.03 (s, 3H, COCH$_3$), 2.05 (s, 3H, COCH$_3$), 3.41 (dd, J = 10.9 and 4.6 Hz, 1H, H-5'), 3.58 (dt, J = 9.6 and 7.1 Hz, 1H, C*H*$_2$CH$_3$), 3.81-4.02 (m, H-5, H-5', H-6, 5H, C*H*$_2$CH$_3$), 4.42 (bd, J = 9.4 Hz, 1H, H-4), 4.88 (dd, J = 3.9 and 3.5 Hz, 1H, H-2'), 4.97 (ddd, J = 10.0, 4.6 and 3.4 Hz, 1H, H-4'), 5.06 (bs, 1H, H-1), 5.09 (d, J = 3.9 Hz, 1H, H-1'), 5.52 (dd, J = 3.5 and 3.4 Hz, 1H, H-3'), 5.80 (ddd, J = 10.2, 2.5 and 1.9 Hz, 1H, H-3), 5.96 (d, J =10.2 Hz, 1H, H-2), 7.36-7.40 (m, 6 H, C_6H_5), 7.73-7.79 (m, 4 H, C_6H_5); ^{13}C NMR (50.3 MHz) δ 15.30 (CH$_2$*C*H$_3$), 19.32 (*C*Me$_3$), 20.74 (3xCO*C*H$_3$), 26.72 (C*Me*$_3$), 63.16, 63.87 and 63.87 (*C*H$_2$CH$_3$, C-6, C-5'), 65.96, 67.24, 67.24, 67.67 and 70.48 (C-4, C-5, C-2', C-3', C-4'), 92.47 (C-1'), 94.17 (C-1), 127.19 (C-2), 129.43 (C-3), 127.53, 127.59, 129.55, 133.44, 133.88, 135.63 and 135.89 (C_6H_5), 169.49 ($COCH_3$), 170.07 ($COCH_3$), 170.42 ($COCH_3$).

Anal. Calcd for $C_{35}H_{46}O_{11}Si$: C, 62.68; H, 6.87. Found: C, 62.90; H, 7.12.

Ethyl 4-*O*-(2,3,4-Tri-*O*-acetyl-β-D-ribopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (9β). Yield 76 %; oil; R_f 0.54 (petroleum ether/ethyl acetate 1:2 v/v); $[\alpha]^{20}_D$ -3.1 (*c* 1.0, chloroform); ^1H NMR (300 MHz) δ 1.06 (s, 9H, *t*-Bu), 1.20 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.98 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 3.52 (dt, J = 9.6 and 7.1 Hz, 1H, CH_2CH_3), 3.72-3.92 (m, H-5, H-6, 3H, CH_2CH_3), 3.76 (dd, J = 12.2 and 6.2 Hz, 1H, H-5'), 4.01 (dd, J = 12.2 and 3.2 Hz, 1H, H-5'), 4.47 (bd, J = 10.6 Hz, 1H, H-4), 4.92 (dd, J = 4.7 and 3.2 Hz, 1H, H-2'), 5.01 (d, J = 4.7 Hz, 1H, H-1'), 5.02 (bs, 1H, H-1), 5.11 (ddd, J = 6.2, 3.2 and 3.1 Hz, 1H, H-4'), 5.42 (dd, J = 3.2 and 3.2 Hz, 1H, H-3'), 5.77 (ddd, J = 10.2, 2.3 and 2.3 Hz, 1H, H-3), 6.05 (d, J =10.2 Hz, 1H, H-2), 7.34-7.42 (m, 6H, C_6H_5), 7.71-7.79 (m, 4H, C_6H_5); ^{13}C NMR (50.3 MHz) δ 15.26 (CH_2CH_3), 19.35 (CMe_3), 20.66 ($COCH_3$), 20.66 ($COCH_3$), 20.82 ($COCH_3$), 26.75 (CMe_3), 61.39, 62.84 and 63.79 (CH_2CH_3, C-6, C-5'), 66.67, 66.71, 68.80, 70.24 and 71.82 (C-4, C-5, C-2', C-3', C-4'), 94.08 (C-1), 99.64 (C-1'), 127.16 (C-2), 132.01 (C-3), 127.87, 127.68, 129.65, 133.14, 133.81, 135.55 and 135.84 (C_6H_5), 169.35 ($COCH_3$), 169.75 ($COCH_3$), 169.85 ($COCH_3$).

Anal. Calcd for $C_{35}H_{46}O_{11}Si$: C, 62.68; H, 6.87. Found: C, 62.43; H, 6.93.

Ethyl 4-*O*-(2,3,4,6-Tetra-*O*-acetyl-D-glucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10). Yield 55 % (α/β 63/37); oil; R_f0.55 (petroleum ether/ethyl acetate 3:2 v/v); ^1H NMR ($CDCl_3$, 500 MHz) α anomer (in the α/β mixture) δ 1.04 (s, 9H, *t*-Bu) 1.23 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.90 (s, 3H, $COCH_3$), 1.99 (s, 6H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 3.47-3.96 (m, 7H, H-5, H-6, H-5', H-6', CH_2CH_3), 4.21 (d, J = 9.3 Hz, H-4), 4.78 (dd, J = 10.3 and 3.8 Hz, 1H, H-2'), 4.97 (dd, J = 10.1 and 9.8 Hz, H-4'), 5.01 (bs, 1H, H-1), 5.26 (d, J = 3.8 Hz, 1H, H-1'), 5.35 (dd, J = 10.1 and 9.8 Hz, 1H, H-3'), 5.80 (bd, J = 10.4 Hz, 1H, H-3), 5.83 (bd, J = 10.4 Hz, 1H, H-2), 7.35-7.43 (m, 6H, C_6H_5), 7.69-7.75 (m, 4H, C_6H_5); β anomer (in the α/β mixture) δ 1.05 (s, 9H, *t*-Bu), 1.17 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.73 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 2.00 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 3.47-3.96 (m, 5H, H-5, H-6, H-5', CH_2CH_3), 4.11 (dd, J = 12.3 and 1.9 Hz, 1H, H-6'), 4.19 (dd, J = 12.3 and 4.9 Hz, 1H, H-6'), 4.41 (bd, J = 9.3 Hz, 1H, H-4), 4.65 (d, J = 8.2 Hz, 1H, H-1'), 4.94 (dd, J = 9.3 and 8.2 Hz, 1H, H-2'), 5.01 (bs, 1H, H-1), 5.04 (dd, J = 9.8 and 9.5 Hz, 1H, H-4'), 5.11 (dd, J = 9.5 and 9.3 Hz, 1H, H-3'), 5.72 (bd, J = 10.4 Hz, 1H, H-3), 6.03 (d, J = 10.4 Hz, 1H, H-2), 7.35-7.43 (m, 6H, C_6H_5), 7.69-7.75 (m, 4H, C_6H_5);^{13}C ($CDCl_3$, 50.3 MHz) α anomer (in the α/β mixture) δ 15.17 ($CH_2\mathit{C}H_3$), 19.14 ($\mathit{C}Me_3$), 20.20 (2x$CO\mathit{C}H_3$), 20.59 (2x$CO\mathit{C}H_3$), 26.68 ($C\mathit{Me}_3$), 61.34, 63.49 and 63.76 ($\mathit{C}H_2CH_3$, C-6, C-6'), 67.79, 67.96, 69.14, 69.83, 70.61 and 71.69 (C-4, C-5, C-2', C-3', C-4', C-5'), 93.61 (C-1), 94.03 (C-1'), 126.76-135.74 (C-2, C-3, C_6H_5), 169.32 ($\mathit{C}OCH_3$), 169.84 ($\mathit{C}OCH_3$), 170.19 ($\mathit{C}OCH_3$) and 170.32 ($\mathit{C}OCH_3$); β anomer (in the α/β mixture) δ 15.17 ($CH_2\mathit{C}H_3$), 19.25 ($\mathit{C}Me_3$), 20.20 ($CO\mathit{C}H_3$), 20.43 ($CO\mathit{C}H_3$), 20.50 ($CO\mathit{C}H_3$), 20.59 ($CO\mathit{C}H_3$), 26.75 ($C\mathit{Me}_3$), 61.77, 63.69 and 63.76 ($\mathit{C}H_2CH_3$, C-6, C-6'), 68.26, 69.83, 2 x 69.97, 71.30 and 72.87 (C-4, C-5, C-2', C-3', C-4', C-5'), 93.66 (C-1), 101.17 (C-1'), 126.76-135.74 (C-2, C-3, C_6H_5), 168.86 ($\mathit{C}OCH_3$), 169.26 ($\mathit{C}OCH_3$), 170.12 ($\mathit{C}OCH_3$), 170.48 ($\mathit{C}OCH_3$).

Anal. Calcd for $C_{38}H_{50}O_{13}Si$: C, 61.46; H, 6.74. Found: C, 61.67; H, 6.88.

Ethyl 4-*O*-(2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (11α). Yield 51 %; oil; R_f0.41 (petroleum ether/ethyl acetate 4:1 v/v); $[\alpha]^{20}_D$ +109.4 (*c* 1.0, chloroform); ^1H NMR (500 MHz) δ 1.05 (s, 9H, *t*-Bu), 1.25 (t, J = 7.1 Hz, 3H, $CH_2C\mathit{H}_3$), 1.90 (s, 3H, $COCH_3$), 1.92 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 2.00 (s, 3H, $COCH_3$), 3.56 (dq, J = 9.2 and 7.1 Hz, 1H, $C\mathit{H}_2CH_3$), 3.62-3.68 (m, 2H, H-5', H-6'), 3.81-3.93 (m, 5H, H-4', H-6, H-6', $C\mathit{H}_2CH_3$), 3.96 (ddd, J = 9.3, 5.5 and 2.6 Hz, 1H, H-5), 4.19 (bd, J = 9.3 Hz, 1H, H-4), 4.29 (ddd, *J* = 10.6, 9.6 and 3.5 Hz, 1H, H-2'), 5.01 (d, J = 3.5 Hz, 1H, H-1'), 5.03 (bs, 1H, H-1), 5.00-5.07 (m, 1H, H-4'), 5.05 (dd, J = 10.6 and 10.1 Hz, 1H, H-3'), 5.63 (d, J = 9.6 Hz, 1H, NH), 5.85 (bd, J = 10.6 Hz, 1H, H-3), 5.87 (bd, J = 10.6 Hz, 1H, H-2), 7.35-7.42 (m, 6H, C_6H_5), 7.67-7.71 (m, 4H, C_6H_5); ^{13}C NMR (50.3 MHz) δ 15.31 ($CH_2\mathit{C}H_3$), 19.23 ($\mathit{C}Me_3$), 20.54 ($CO\mathit{C}H_3$), 20.60 ($CO\mathit{C}H_3$), 20.72 ($CO\mathit{C}H_3$), 23.19 ($NHCO\mathit{C}H_3$), 26.76 ($C\mathit{Me}_3$), 51.82 (C-2'), 61.34, 63.79 and 63.98 ($\mathit{C}H_2CH_3$, C-6, C-6'), 67.50, 68.23, 68.49, 70.11 and 70.94 (C-4, C-5, C-3' C-4', C-5'), 93.67 (C-1), 94.62 (C-1'), 127.76 (C-2), 129.81 (C-3), 127.70, 128.04, 128.41, 129.78, 133.01, 133.42, 135.52 and 135.74 (C_6H_5), 169.04 ($\mathit{C}OCH_3$), 170.06 ($\mathit{C}OCH_3$), 170.47 ($\mathit{C}OCH_3$), 171.31 ($\mathit{C}OCH_3$).

Anal. Calcd for $C_{38}H_{51}NO_{12}Si$: C, 61.53; H, 6.88; N, 1.89. Found: C, 61.58; H, 6.57; N, 1.98.

Ethyl 4-*O*-(2,3,4,6-Tetra-*O*-acetyl-D-galactopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (12). Yield 67 % (α/β 70/30); R_f0.59 (petroleum ether/ethyl acetate 2:3 v/v); ^1H NMR ($CDCl_3$, 500 MHz) α anomer (in the α/β mixture) δ 1.02 (s, 9H, *t*-Bu), 1.27 (t, J = 7.1 Hz, 3H, $CH_2C\mathit{H}_3$), 1.56 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 2.13 (s, 3H, $COCH_3$), 3.99 (d, J = 9.3 Hz, H-4), 3.46-3.86 (m, 4H,

$C\mathit{H}_2CH_3$, H-6'), 3.93-4.03 (m, 2H, H-5, H-5'), 3.99 (d, J = 9.3 Hz, 1H, H-4), 4.97 (dd, J = 10.9 and 3.8 Hz, 1H, H-2'), 5.03 (bs, 1H, H-1), 5.11 (dd, J = 10.9 and 3.8 Hz, 1H, H-3'), 5.16 (d, J = 3.8 Hz, 1H, H-1'), 5.22 (d, J = 3.8 Hz, 1H, H-4'), 5.72 (bd, J = 10.4 Hz, 1H, H-3), 5.82 (bd, J = 10.4 Hz, 1H, H-2), 7.34-7.47 (m, 6H, C_6H_5), 7.70-7.73 (m, 4H, C_6H_5); β anomer (in the α/β mixture) δ 1.05 (s, 9H, *t*-Bu), 1.18 (t, J = 7.1 Hz, 3H, $CH_2C\mathit{H}_3$), 1.72 (s, 3H, $COCH_3$), 1.96 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 2.13 (s, 3H, $COCH_3$), 3.46-3.86 (m, 4H, $C\mathit{H}_2CH_3$, H-6'), 3.93-4.03 (m, 2H, H-5, H-5'), 4.09 (dd, J = 11.2 and 6.6 Hz, 1H, H-6), 4.14 (dd, J = 11.2 and 6.8 Hz, 1H, H-6), 4.41 (bd, J = 9.3 Hz, 1H, H-4), 4.61 (d, J = 8.2 Hz, 1H, H-1'), 4.91 (dd, J = 10.4 and 3.5 Hz, 1H, H-3'), 5.00 (bs, 1H, H-1), 5.15 (dd, J = 10.4 and 3.5 Hz, 1H, H-2'), 5.33 (d, J = 3.0 Hz, 1H, H-4'), 5.71 (bd, J = 10.4 Hz, 1H, H-3), 6.05 (d, J = 10.4 Hz, 1H, H-2), 7.34-7.47 (m, 6H, C_6H_5), 7.70-7.73 (m, 4H, C_6H_5); ^{13}C ($CDCl_3$, 50.3 MHz) α anomer (in the α/β mixture) δ 15.35 ($CH_2\mathit{C}H_3$), 19.23 ($\mathit{C}Me_3$), 20.18 ($CO\mathit{C}H_3$), 20.68 ($CO\mathit{C}H_3$), 20.87 ($2xCO\mathit{C}H_3$), 26.65 ($C\mathit{Me}_3$), 62.19, 63.99 and 64.19 ($\mathit{C}H_2CH_3$, C-6, C-6'), 66.88, 67.20, 68.07, 68.14, 69.63 and 70.53 (C-4, C-5, C-2', C-3', C-4', C-5'), 93.69 (C-1), 94.43 (C-1'), 126.99-135.88 (C-2, C-3, C_6H_5), 169.85 ($\mathit{C}OCH_3$), 170.28 ($\mathit{C}OCH_3$), 170.39 ($\mathit{C}OCH_3$), 170.65 ($\mathit{C}OCH_3$); β anomer (in the α/β mixture) δ 15.35 ($CH_2\mathit{C}H_3$), 19.44 ($\mathit{C}Me_3$), 20.47 ($CO\mathit{C}H_3$), 20.74 ($CO\mathit{C}H_3$), 20.87 ($2xCO\mathit{C}H_3$), 26.88 ($C\mathit{Me}_3$), 61.37, 62.60 and 63.96 ($\mathit{C}H_2CH_3$, C-6, C-6'), 66.89, 69.01, 70.16, 70.80, 71.05 and 71.92 (C-4, C-5, C-2', C-3', C-4', C-5'), 94.19 (C-1), 101.89 (C-1'), 126.99-135.88 (C-2, C-3, C_6H_5), 169.13 ($\mathit{C}OCH_3$), 170.22 ($\mathit{C}OCH_3$), 170.28 ($\mathit{C}OCH_3$), 170.65 ($\mathit{C}OCH_3$).

Anal. Calcd for $C_{38}H_{50}O_{13}Si$: C, 61.46; H, 6.74. Found: C, 61.56; H, 6.90.

Ethyl 4-*O*-[4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (13α). Yield 37 %; oil; R_f 0.53 (petroleum ether/ethyl acetate 2:3 v/v); $[\alpha]^{20}_D$ +63.2 (*c* 1, chloroform); ^1H NMR (500 MHz) δ 1.03 (s, 9H, *t*-Bu), 1.19 (t, J = 7.1 Hz, 3H, $CH_2C\mathit{H}_3$), 1.88 (s, 3H, $COCH_3$), 1.95 (s, 3H, $COCH_3$), 1.96 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 3.49 (dq, J = 9.3 and 7.1 Hz, 1H, $C\mathit{H}_2CH_3$), 3.60 (dd, J = 9.6, 4.1 and 2.2 Hz, 1H, H-5"), 3.66 (dd, J = 9.8 and 9.6 Hz, 1H, H-4'), 3.78-3.92 (m, 5H, H-6, H-5, H-5', $C\mathit{H}_2CH_3$), 3.95 (dd, J = 12.5 and 4.5 Hz, 1H, H-6"), 4.00 (dd, J = 12.5 and 2.1 Hz, 1H, H-6'), 4.21 (dd, J = 12.5 and 1.6 Hz, 1H, H-6"), 4.24 (dl, J = 9.6 Hz, 1H, H-4), 4.34 (dd, J = 12.5 and 4.4 Hz, 1H, H-6'), 4.47 (d, J = 8.4 Hz, 1H, H-1"), 4.74 (dd, J = 9.8 and 3.8 Hz, 1H, H-2'), 4.87 (dd, J = 9.3 and 8.4 Hz, 1H, H-2"), 4.96 (bs, 1H, H-1), 5.06 (dd, J = 9.5 and 9.3 Hz, 1H, H-4"), 5.10 (dd, J = 9.3 and 9.0 Hz, 1H, H-3"), 5.17 (d, J = 3.8 Hz, 1H, H-1'), 5.33 (dd, J = 9.8 and 9.5 Hz, 1H, H-3'), 5.78 (ddd, J = 10.6, 2.4 and 1.9 Hz, 1H, H-3), 5.87 (d, J =10.6 Hz, 1H, H-2), 7.33-7.42 (m, 6H, C_6H_5), 7.67-7.70 (m, 4H, C_6H_5); ^{13}C NMR (50.3 MHz) δ 15.23 (CH_2CH_3), 19.29 (*C*Me$_3$), 20.49, 20.54 and 20.68 (7 CO*C*H$_3$), 26.79 (C*Me*$_3$), 61.56, 61.87, 63.44 and 63.85 (*C*H$_2$CH$_3$, C-6, C-6', C-6"), 67.75, 68.84, 69.67, 70.07, 70.07, 71.04, 71.80, 71.96, 73.14 and 76.55 (C-4, C-5, C-2', C-3', C-4', C-5', C-2", C-3", C-4", C-5"), 93.66 (C-1), 94.18 (C-1'), 100.87 (C-1"), 128.01 (C-2), 129.88 (C-3), 127.70, 129.12,129.71, 133.18, 133.61, 135.56 and 135.69 (C_6H_5), 168.98 (*C*OCH$_3$), 169.29 (*C*OCH$_3$), 169.43 (*C*OCH$_3$), 170.17 (*C*OCH$_3$), 170.29 (*C*OCH$_3$), 170.43 (*C*OCH$_3$), 170.54 (*C*OCH$_3$).

Anal. Calcd for $C_{50}H_{66}O_{21}Si$: C, 58.25; H, 6.41. Found: C, 58.34; H, 6.54.

Ethyl 4-*O*-[4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (13β). Yield 22 %; oil; R_f 0.64 (petroleum ether/ethyl acetate 2:3 v/v); $[\alpha]^{20}_D$ +9.6 (*c* 1.1, chloroform); ^{1}H NMR (500 MHz) δ 1.03 (s, 9H, *t*-Bu), 1.17 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.69 (s, 3H, COCH$_3$), 1.96 (s, 3H, COCH$_3$), 1.98 (s, 3H, COCH$_3$), 1.99 (s, 3H, COCH$_3$), 2.00 (s, 3H, COCH$_3$), 2.06 (s, 3H, COCH$_3$), 2.08 (s, 3H, COCH$_3$), 3.45-3.53 (m, C*H*$_2$CH$_3$, 2H, H-5'), 3.62 (dd, J = 9.5, 4.1 and 2.2 Hz, 1H, H-5"), 3.72 (dd, J = 9.5 and 9.5 Hz, 1H, H-4'), 3.73-3.82 (m, 4H, H-5, H-6, C*H*$_2$CH$_3$), 4.00 (dd, J = 12.5 and 1.7 Hz, 1H, H-6"), 4.04 (dd, J = 12.0 and 5.2 Hz, 1H, H-6'), 4.34 (dd, J = 12.5 and 3.5 Hz, 1H, H-6"), 4.35 (bd, J = 8.5 Hz, 1H, H-4), 4.48 (d, J = 7.9 Hz, 1H, H-1"), 4.52 (dd, J = 12.0 and 1.6 Hz, 1H, H-6'), 4.57 (d, J = 8.2 Hz, 1H, H-1'), 4.85 (dd, J = 9.6 and 7.9 Hz, 1H, H-2"), 4.90 (dd, J = 9.3 and 8.2 Hz, 1H, H-2'), 4.99 (bs, 1H, H-1), 5.04 (dd, J = 9.5 and 9.3 Hz, 1H, H-3'), 5.07 (dd, J = 9.5 and 9.3 Hz, 1H, H-4"), 5.12 (dd, J = 9.6 and 9.3 Hz, 1H, H-3"), 5.71 (ddd, J = 10.6, 2.2 and 2.2 Hz, 1H, H-3), 6.00 (d, J =10.2 Hz, 1H, H-2), 7.34-7.43 (m, 6H, C_6H_5), 7.69-7.73 (m, 4H, C_6H_5); ^{13}C NMR (50.3 MHz) δ 15.27 (CH$_2$*C*H$_3$), 19.35 (*C*Me$_3$), 20.30, 20.54, 20.65 and 20.79 (7 CO*C*H$_3$), 26.79 (C*Me*$_3$), 61.54, 61.54, 61.47 and 63.79 (*C*H$_2$CH$_3$, C-6, C-6', C-6"), 67.77, 70.00, 71.66, 71.99, 72.64, 72.71, 72.90 and 76.46 (C-4, C-5, C-2', C-3' C-4', C-5', C-2", C-3", C-4", C-5"), 94.09 (C-1), 100.84 (C-1"), 101.32 (C-1'), 126.82 (C-2), 129.88 (C-3), 127.66, 127.85, 129.73, 132.15, 133.07, 133.61, 135.52 and 135.84 (C_6H_5), 169.03, 169.31, 169.76, 170.29 and 170.51 (7 *C*OCH$_3$).

Anal. Calcd for $C_{50}H_{66}O_{21}Si$: C, 58.25; H, 6.41. Found: C, 58.47; H, 6.46.

ACKNOWLEDGMENTS

This work was supported by a grant awarded to S. P. by the Région Rhône-Alpes and a fellowship to I. F. by the M.E.S.R.

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