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Stereochemistry in palladium- and nickel-catalyzed addition of phenylmagnesium bromide to unsaturated carbohydrates

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Abstract

Palladium complex $PdCl_2$(dppf) and nickel complex $NiCl_2$(dppe) catalyze cross-coupling of unsaturated aryloxy carbohydrates with phenylmagnesium bromide. The nickel catalyst leads to inversion of configuration at the anomeric center while only retention occurs in the case of the palladium catalyst. This quite unusal retention is probably due to the influence of the ring oxygen atom

Keywords: Palladium; Nickel; Grignard reagents; Arylation; Stereochemistry; 2,3-Unsaturated glycosides

1. Introduction

Transition-metal catalyzed substitution of allylic substrates with organometallic reagents has emerged as an important and well documented carbon–carbon bond-forming reaction in organic synthesis [1–3]. These organometallics reagents mainly based on magnesium, zinc, tin, aluminium, zirconium and boron, are known to couple under very mild conditions in the presence of palladium or nickel catalysts. The stereochemistry aspect of these reactions has been studied by different groups. So, it has been demonstrated that the coupling of magnesium [4–7], zinc [8–11], tin [12–14], aluminium [15] or zirconium [16] reagents catalyzed by palladium complexes as well as of magnesium [17–19] or boron [20–23] derivatives in the presence of nickel complexes proceeded with overall inversion of configuration. Only quite recently Lautens et al. [24] observed both inversion and retention of configuration in the reaction of Grignard reagents with some unsaturated bicyclic compounds under nickel catalysis.

We recently described a stereospecific palladium or nickel-catalyzed new route to unsaturated α- and β-C-aryl glycopyranosides [25]. If inversion of configuration was observed in the presence of the nickel catalyst $NiCl_2$(dppe) [dppp: 1,2-bis(diphenylphosphino)ethane], unexpected retention was obtained in the presence of the palladium catalyst $PdCl_2$(dppf) [dppf: 1,1′-bis(-diphenylphosphino)ferrocene]. To the best of our knowledge, this result constitutes the first example of a coupling reaction between an allylic substrate and Grignard reagents that proceeds with exclusive net retention in the presence of a palladium catalyst. We describe in this paper some experiments in order to try to have a deeper insight on the scope of this reaction and to propose some explanation for the observed stereospecificity.

2. Results and discussion

The reaction of 2,3-unsaturated carbohydrates 1α and 3α with phenylmagnesium bromide in the presence of $PdCl_2$(dppf) catalyst gave the 2,3-unsaturated C-phenylglycoside **2α** and **4α**, respectively (Scheme 1),

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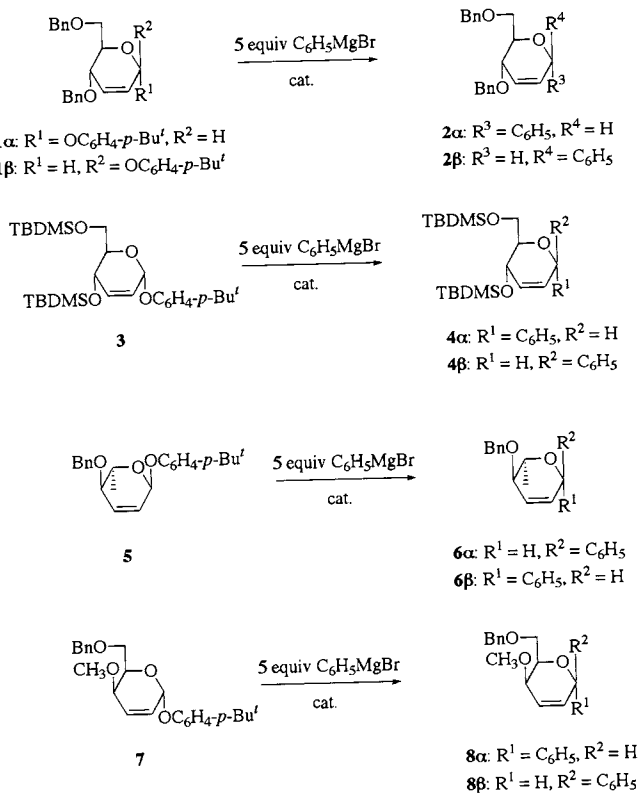


Scheme 1.

having the α configuration only (Table 1, entries 1 and 5) [25]. When the same reaction was performed in the presence of $NiCl_2$(dppe), the 2,3-unsaturated C-phenyl glycoside **2α** and **4β**, having the β configuration, were obtained in quite good yields (Table 1, entries 2 and 6).

The same stereoselectivity was observed when the coupling reaction was realized on the β anomer **1β**. The palladium complex led exclusively to the unsaturated C-glycoside **2β** with retention of configuration at the anomeric center, in 87% yield (Table 1, entry 3), while the nickel complex gave the anomer **2α**, with inversion of configuration, in 50% yield, the reaction being however incomplete in this case (Table 1, entry 4).

We performed the same reactions on the α-unsaturated carbohydrate **5**, lacking the ether function at position 6 [25]. The coupling reaction with C_6H_5MgBr catalyzed by palladium and nickel complex gave respectively the C-phenyl glycoside **6α** with retention of configuration and **6β** with inversion of configuration (Scheme 1) (Table 1, entries 7 and 8).

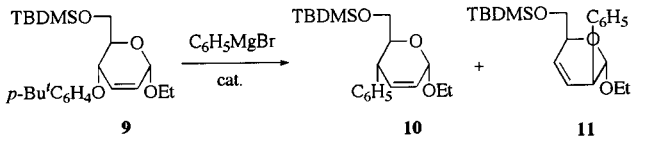
To have a deeper insight on the possible role of the oxygen atom at C-4 in the unsaturated carbohydrate structure on the stereoselectivity of the reaction, we performed the reactions on the erythro derivative **7**. In the coupling reaction of this compound with C_6H_5MgBr in the presence of $NiCl_2$(dppe), only degradation products were observed, or no reaction at all. However, in the presence of $PdCl_2$(dppf) as the catalyst, coupling reaction occured with retention of configuration to give compound **8α** in 44% yield (Table 1, entries 9 and 10).

These last results clearly showed that the oxygen function at C-4 or at C-6 have no influence in the unexpected retention of configuration observed with $PdCl_2$(dppf) as the catalyst.

Table 1
Stereoselectivity in the reaction of 2,3-unsaturated carbohydrates with phenylmagnesium bromide in the presence of palladium and nickel complexes

Entry	Substrate	Catalyst	T (°C) (t/h)	Product (yield%)	Retention/inversion[a] (%)
1	**1α**	$PdCl_2$(dppf)	25 (2)	**2α** (95)	100/0
2		$NiCl_2$(dppe)	−40 (24)	**2β** (70)	0/100
3	**1β**	$PdCl_2$(dppf)	25 (2)	**2** (87)	95/5
4		$NiCl_2$(dppe)	−40 (24)	**2α** (50)	0/100
5	**3**	$PdCl_2$(dppf)	25 (2)	**4α** (80)	100/0
6		$NiCl_2$(dppe)	−40 (2)	**4β** (83)	0/100
7	**5**	$PdCl_2$(dppf)	25 (24)	**6α** (51)	100/0
8		$NiCl_2$(dppe)	−40 (24)	**6β** (68)	0/100
9	**7**	$PdCl_2$(dppf)	25 (20)	**8α** (44)	100/0
10		$NiCl_2$(dppe)	−40 to 0	degradation or no reaction	

[a] Isomeric purity determined by ^{1}H-NMR and ^{13}C-NMR.

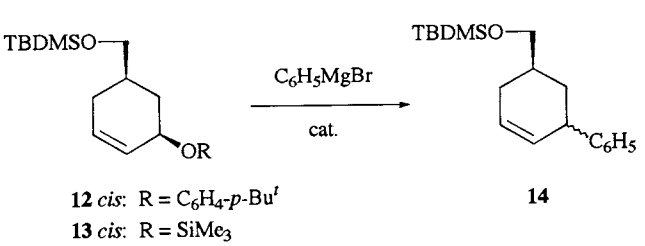


Scheme 2.

Other substrates were also used in this coupling reaction, and particularly the unsaturated carbohydrate **9** and the cyclohexenyl derivatives **12**. The unsaturated ethyl glycoside **9** was obtained by reaction of *p-tert*-butylphenol on ethyl 6-*O*-(*tert*-butyldimethylsilyl)-4-*O*-methoxycarbonyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside [26] in the presence of $Pd_2(dba)_3$ and dppb [1,4-bis(diphenylphosphino)butane] in THF. The cyclohexenyl derivatives **12** and **13** were prepared from *cis* 5-(hydroxymethyl)cyclohex-2-en-1-ol [27]. Monosilylation of this diol with *tert*-butyldimethylsilyl chloride gave the monosilylated derivative, which was treated with trimethylsilyl chloride to afford compound **13**. On the other hand, transformation of the monosilylated compound into the carbonate, followed by reaction with *p-tert*-butylphenol in the presence of $Pd_2(dba)_3$ and dppb as the catalyst gave compound **12**.

Reaction of phenylmagnesium bromide with compound **9**, having the leaving group at C-4 instead at the anomeric center, in the presence of $PdCl_2$(dppf), gave the arylated product **10** in 46% yield, at 25°C (Scheme 2). In this case, we observed again a net retention of configuration at the new created carbon center. When the same reaction was performed in the presence of a $NiCl_2$(dppe) at −20°C, the formation of compound **11** was observed in 54% yield. In this case, due to some steric effects, the alkylation occurs only at C-2, but with complete inversion of configuration. So it seems that the position of the leaving group at the anomeric center is not crucial for the observed retention of configuration with palladium complex.

However, when the cyclohexenyl derivatives **12** *cis* and **13** *cis* were reacted with C_6H_5MgBr in the presence of $PdCl_2$(dppf) or $NiCl_2$(dppe) (Scheme 3), we mainly observed inversion of the configuration (Table 2). The $NiCl_2$(dppe) mediated reaction was completely stereoselective, giving only the *trans* isomer **14** *trans*, although the palladium catalyzed reaction gave a mixture of *cis* and *trans* isomers, the former being however preponderant. These results are in agreement with those already described by Hayashi et al. ([7]b).



Scheme 3.

3. Conclusion

The reaction of 2,3-unsaturated carbohydrates with phenylmagnesium bromide gave the corresponding 2,3-unsaturated C-phenylglycoside, with inversion of configuration in the presence of $NiCl_2$(dppe), but with retention of configuration in the presence of $PdCl_2$(dppf). From these experiments concerning the addition mechanism of phenylmagnesium bromide to these unsaturated carbohydrates, it seems that the ring-oxygen atom plays a crucial role on the retention of configuration observed in the case of the palladium catalyzed reaction.

4. Experimental

4.1. General methods and materials

NMR spectra were obtained in $CDCl_3$, and chemical shifts are given in ppm on the δ scale from internal tetramethylsilane. THF was distilled from sodium/benzophenone, purged, and kept under a nitrogen atmosphere. Reactions involving palladium or nickel complexes were carried out in a Schlenk tube under a nitrogen atmosphere.

$PdCl_2$(dppf) [28], $NiCl_2$(dppe) [29], compounds **1** [30], **3** [30], **5** [30], **7** [30], ethyl 6-*O*-(*tert*-butyldimethylsilyl)-4-*O*-methoxycarbonyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside [26] and *cis* 5-(hydroxymethyl)cyclohex-2-en-1-ol [27] were prepared according to known procedures.

4.2. Synthesis of ethyl 6-O-(tert-butyldimethylsilyl)-4-O-(p-tert-butylphenyl)-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (9)

To a solution of ethyl 6-*O*-(*tert*-butyldimethylsilyl)-4-*O*-methoxycarbonyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside [26] (1.0 g, 2.9 mmol) and *p-tert*-butylphenol (2.17 g, 14.4 mmol) in 10 ml of dry THF was added the catalytic system obtained by reacting $Pd_2(dba)_3$ (130 mg, 0.15 mmol) and dppb (250 mg, 0.58 mmol) in 2 ml of THF. The mixture was stirred at 25°C for 24 h. Evaporation of the solvent under reduced pressure, followed by column chromatography on silica gel using petroleum ether/ethyl acetate (1/5) as the eluent gave 1.1 g of compound **9** (90%). $[\alpha]_D^{20} + 125.5$ (c 1.5, CH_2Cl_2). ^{1}H-NMR (200 MHz) δ 0.04 (s, 3H), 0.05 (s, 3H), 0.89 (s, 9H), 1.27 (t, 3H, $J = 7.1$ Hz), 1.31 (s, 9H), 3.58 (dq, 1H, $J = 9.6$, 7.1 Hz), 3.78–3.96 (m, 3H),

Table 2
Diastereoselectivity in the reaction of cyclohexenyl derivatives **12** and **13** with phenylmagnesium bromide in the presence of palladium and nickel complexes

Entry	Substrate	Catalyst	Yield (%)	Isomeric ratio[a] *cis*/*trans* (%)	Retention/inversion(%)
1	**12** *cis*	$PdCl_2$(dppf)	72	30/70	30/70
2		$NiCl_2$(dppe)	70	0/100	0/100
3	**13** *cis*	$PdCl_2$(dppf)	60	37/63	37/63

[a] Isomeric purity determined by ^{1}H-NMR and ^{13}C-NMR.

4.04 (ddd, 1H, $J = 9.2$, 5.1, 2.0 Hz), 4.79 (dd, 1H, $J = 9.2$, 1.2 Hz), 5.08 (brs, 1H), 5.83 (brd, 1H, $J = 9.2$ Hz), 6.09 (brd, 1H, $J = 10.2$ Hz), 6.85 (d, 2H, $J = 8.8$ Hz), 7.30 (d, 2H, $J = 8.8$ Hz). Anal. Calcd for $C_{24}H_{40}O_4Si$: C, 68.53; H, 9.58. Found: C, 68.67; H, 9.49.

4.3. Synthesis of cis 5-[(tert-butyldimethylsilyoxy) methyl]cyclohex-2-en-1-ol

Cis 5-(hydroxymethyl)cyclohex-2-en-1-ol [27] (1.1 g, 8.7 mmol) was treated with 1.25 equiv of TBDMSCl (1.62 g, 10.8 mmol), 1.3 equiv of NEt_3 (1.6 ml, 11.2 mmol), and 0.05 equiv of imidazole (30 mg, 0.43 mmol) in CH_2Cl_2 (30 ml) at r.t. for 24 h. After addition of 25 ml of water and extraction with 3×30 ml of CH_2Cl_2, the organic layer was dried. Evaporation of the solvent under reduced pressure, and column chromatography of the residue on silica gel using petroleum ether/ethyl acetate (5/1) as the eluent gave 840 mg of *cis* 5-[(*tert*-butyldimethylsilyoxy)methyl]cyclohex-2-en-1-ol as an oil (40%). ^{1}H-NMR (200 MHz) δ 0.06 (s, 6H), 0.90 (s, 9H), 1.58–2.19 (m, 6H), 3.55 (brd, 2H, $J = 5.9$ Hz), 4.30 (m, 1H), 5.69 (d, 1H, $J = 10.0$ Hz), 5.79 (d, 1H, $J = 10.0$ Hz). ^{13}C-NMR (50 MHz) δ -5.4 ($SiCH_3$), 18.4 ($SiCMe_3$), 26.0 ($SiCMe_3$), 28.3 (C-6), 35.6 (C-4), 35.8 (C-5), 67.6 (C-1), 67.6 (CH_2O), 128.4 and 131.2 (C-2 and C-3).

4.4. Synthesis of cis 5-[(tert-butyldimethylsilyoxy) methyl]-1-(p-tert-butylphenoxy) cyclohex-2-ene (**12**)

To a solution of 850 mg (3.5 mmol) of *cis* 5-[(*tert*-butyldimethylsilyoxy)methyl]-1-(*p*-*tert*-butylphenoxy) cyclohex-2-en-1-ol in 30 ml of CH_2Cl_2 at r.t. was added 65 mg (0.7 mmol) of DMAP, 1.4 ml (17.5 mmol) of pyridine, and 1.35 ml (17.5 mmol) of methyl chloroformate. The mixture was stirred at r.t. for 24 h. After addition of 30 ml of a water of $CuSO_4 \cdot 5H_2O$, the solution was extracted with 4×25 ml of Et_2O. Removal of the solvent under reduced pressure gave the crude carbonate which was immediatly mixed with *p*-*tert*-butylphenol (530 mg, 3.5 mmol) in 5 ml of dry THF. To this solution was added the catalytic system obtained by reacting $Pd_2(dba)_3$ (31.6 mg, 0.036 mmol) and dppb (61 mg, 0.14 mmol) in 2 ml of THF. The mixture was stirred at 25°C for 24 h. Evaporation of the solvent under reduced pressure, followed by column chromatography on silica gel using petroleum ether/ethyl acetate (30/1) as the eluent gave 510 mg of compound **12** (40%). ^{1}H-NMR (200 MHz) δ 0.00 (s, 6H), 0.85 (s, 9H), 1.26 (s, 9H), 1.57-2.25 (m, 5H), 3.48 (d, 2H, $J = 5.9$ Hz), 4.85 (m, 1H), 5.65 (brd, 1H, $J = 10.0$ Hz), 5.85 (d, 1H, $J = 10.0$ Hz), 6.83 (d, 2H, $J = 8.0$ Hz), 7.25 (d, 2H, $J = 8.0$ Hz). ^{13}C-NMR (50 MHz) δ -5.3 ($SiCH_3$), 18.4 ($SiCMe_3$), 26.0 ($SiCMe_3$), 28.5 (C-6), 31.6 (CMe_3), 32.2 (C-4), 34.1 (CMe_3), 35.9 (C-5), 67.5 (CH_2O), 73.3 (C-1), 115.4, 126.3, 127.9, 129.6, 143.4 and 155.6 (C_6H_4, C-2 and C-3). Anal. Calcd for $C_{23}H_{38}O_2Si$: C, 73.74; H, 10.22. Found: C, 73.60; H, 10.24.

4.5. Synthesis of cis 5-[(tert-butyldimethylsilyloxy) methyl]-1-(trimethylsilyloxy) cyclohex-2-ene (**13**)

To a solution of 100 mg (0.4 mmol) of *cis* 5-[(*tert*-butyldimethylsilyloxy)methyl]-1-(*p*-*tert*-butylphenoxy) cyclohex-2-ene in 25 ml of THF at r.t. was added 4 equiv of Et_3N (0.06 mmol) and 3 equiv of Me_3SiCl (0.15 ml). After being stirred for 24 h, 50 ml of cold water was added and the solution was extracted with 3×25 ml of CH_2Cl_2. Evaporation of the solvent and column chromatography on silica gel neutralized with 1% Et_3N using petroleum ether/ethyl acetate (5/1) as the eluent gave 120 mg of compound **13** (96%). ^{1}H-NMR (200 MHz) δ 0.05 (s, 6H), 0.15 (s, 9H), 0.90 (s, 9H), 1.14–2.06 (m, 5H), 3.49 (d, 2H, $J = 5.7$ Hz), 4.35 (m, 1H), 5.58 (d, 1H, $J = 10.3$ Hz), 6.02 (d, 1H, $J = 10.3$ Hz). ^{13}C-NMR (50 MHz) δ -5.2 ($SiCH_3$), 0.4 ($SiCH_3$), 18.4 ($SiCMe_3$), 26.0 ($SiCMe_3$), 28.4 (C-6), 36.1 (C-4), 36.3 (C-5), 67.8 (CH_2O), 68.4 (C-1), 127.8 and 132.1 (C-2 and C-3).

4.6. General procedure for palladium- and nickel-catalyzed reaction

To a solution of the unsaturated substrate (0.44 mmol) and $PdCl_2$(dppf) (31.9 mg, 0.044 mmol) or $NiCl_2$(dppe) (23 mg, 0.044 mmol) in 2 ml of THF was added at the desired temperature a solution of the

Grignard reagent prepared from magnesium (64 mg, 2.6 mmol) and phenyl bromide (2.18 mmol) in 5 ml THF. After the time indicated in the Tables, diethylether (50 ml) was added, the ethereal solution was washed with water (2 × 10 ml) and dried. Concentration and column chromatography furnished the phenyl derivative.

4.6.1. (4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)benzene ***(2α)***

$[\alpha]_D^{20} + 18.5$ (c 0.9, CH_2Cl_2). ^{1}H-NMR (300 MHz) δ 3.50-3.70 (m, 3H), 4.19 (brd, 1H, $J = 7.3$ Hz), 4.46 (d, 1H, $J = 11.5$ Hz), 4.61 (d, 1H, $J = 11.5$ Hz), 4.43 (d, 1H, $J = 12.1$ Hz), 4.58 (d, 1H, $J = 12.1$ Hz), 5.30 (brs, 1H), 6.06 (brd, 1H, $J = 10.9$ Hz), 6.13 (brd, 1H, $J =$ 10.9 Hz), 7.20–7.50 (m, 15H). 13C-NMR (50 MHz) δ 69.1, 71.1 and 73.2 (C-6, 2xCH_2), 70.1 and 70.7 (C-4 and C-5), 74.1 (C-1), 127.1, 127.5, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.3, 128.3, 129.5, 138.2, 138.2 and 139.5 (C-2, C-3 and C_6H_5). Anal. Calcd for $C_{26}H_{26}O_3$: C, 80.80, H, 6.78. Found: C, 80.37; H, 6.69.

4.6.2. (4,6-Di-O-benzyl-2,3-dideoxy-β-D-erythro-hex-2-enopyranosyl)benzene ***(2β)***

$[\alpha]_D^{20} + 60.8$ (c 0.7, CH_2Cl_2). ^{1}H-NMR (300 MHz) δ 3.60-3.90 (m, 3H), 4.16 (dm, 1H, $J = 8.6$ Hz), 4.51 (d, 1H, $J = 11.5$ Hz), 4.66 (d, 1H, $J = 11.5$ Hz), 4.56 (d, 1H, $J = 12.1$ Hz), 4.64 (d, 1H, $J = 12.1$ Hz), 5.18 (brs, 1H), 5.86 (ddd, 1H, $J = 10.3$, 1.6, 1.6 Hz), 6.01 (ddd, 1H, $J = 10.3$, 2.0, 2.0 Hz), 7.20–7.40 (m, 15H). 13C-NMR (50 MHz) δ 69.9, 71.2 and 73.4 (C-6 and 2xCH_2), 70.5 (C-4), 77.4 (C-5), 77.8 (C-1), 125.8, 126.0, 127.1, 127.5, 127.9, 128.2, 128.3, 128.4, 128.5, 131.7, 138.1, 138.4 and 140.8 (C-2, C-3 and C_6H_5). Anal. Calcd. for $C_{26}H_{26}O_3$: C, 80.80, H, 6.78. Found: C, 80.38; H, 6.82.

4.7. [4,6-Di-O-(tert-butyldimethylsilyl)-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl] benzene ***(4α)***

$[\alpha]_D^{20} + 3.9$ (*c* 1.0, CH_2Cl_2). ^{1}H-NMR (200 MHz) δ 0.02 (s, 3H), 0.04 (s, 3H), 0.07 (s, 3H), 0.08 (s, 3H), 0.87 (s, 9H), 0.89 (s, 9H), 3.41 (ddd, 1H, $J = 8.1$, 6.2, 2.3 Hz), 3.70 (dd, 1H, $J = 11.1$, 6.2 Hz), 3.85 (dd, 1H, $J = 11.1$, 2.3 Hz), 4.20 (dddd, 1H, $J = 8.1$, 1.9, 1.9, 1.9 Hz), 5.28 (m, 1H), 5.88 (ddd, 1H, $J = 10.3$, 1.9, 1.9 Hz), 6.07 (ddd, 1H, $J = 10.3$, 3.1, 1.7 Hz), 7.25-7.49 (m, 5H). 13C-NMR (50 MHz) δ −5.2 ($SiMe_3$), −5.0 ($SiMe_3$), −4.6 ($SiMe_3$), −4.0 ($SiMe_3$), 18.1 ($SiCMe_3$), 18.5 ($SiCMe_3$), 25.9 ($SiCMe_3$), 26.1 ($SiCMe_3$), 63.4 (C-6), 64.3 (C-4), 73.7 (C-5), 74.6 (C-1), 127.5, 127.6, 128.4, 128.5, 130.9 and 140.4 (C-2, C-3 and C_6H_5). Anal. Calcd for $C_{24}H_{42}O_3Si_2$: C, 66.30, H, 9.74. Found: C, 66.51; H, 9.84.

4.7.1. [4,6-Di-O-(tert-butyldimethylsilyl)-2,3-dideoxy-β-D-erythro-hex-2-enopyranosyl] benzene ***(4β)***

$[\alpha]_D^{20} + 189.1$ (*c* 1.0, CH_2Cl_2). ^{1}H-NMR (200 MHz) δ 0.04 (s, 6H), 0.13 (s, 3H), 0.14 (s, 3H), 0.90 (s, 9H), 0.93 (s, 9H), 3.51 (ddd, 1H, $J = 8.5$, 4.5, 2.1 Hz), 3.84 (dd, 1H, $J = 11.4$, 4.5 Hz), 3.93 (dd, 1H, $J = 11.4$, 2.1 Hz), 4.38 (dd, 1H, $J = 8.5$, 2.9 Hz), 5.16 (d, 1H, $J = 2.9$ Hz), 5.77 (s, 2H), 7.27-7.36 (m, 5H). 13C-NMR (50 MHz) δ −5.0 ($SiMe_3$), −4.9 ($SiMe_3$), −4.6 ($SiMe_3$), −4.1 ($SiMe_3$), 18.2 ($SiCMe_3$), 18.6 ($SiCMe_3$), 26.0 ($SiCMe_3$), 26.1 ($SiCMe_3$), 63.1 (C-6), 63.6 (C-4), 77.3 (C-1), 80.7 (C-5), 127.1, 127.8, 128.4, 129.9, 130.7 and 141.5 (C-2, C-3 and C_6H_5). Anal. Calcd. for $C_{24}H_{42}O_3Si_2$: C, 66.30, H, 9.74. Found: C, 66.00; H, 9.71.

4.7.2. (4-O-Benzyl-2,3,6-trideoxy-α-D-erythro-hex-2-enopyranosyl)benzene ***(6α)***

$[\alpha]_D^{20} - 20.6$ (*c* 1.0, CH_2Cl_2). ^{1}H-NMR (200 MHz) δ 1.25 (d, 3H, $J = 6.0$ Hz), 3.69-3.77 (m, 2H), 4.60 (d, 1H, $J = 11.6$ Hz), 4.70 (d, 1H, $J = 11.6$ Hz), 5.21 (s, 1H), 6.07 (brd, 1H, $J = 11.3$ Hz), 6.14 (brd, 1H, $J = 11.3$ Hz), 7.25–7.45 (m, 10H). 13C-NMR (50 MHz) δ 18.4 (CH_3), 67.9 (C-5), 71.1 (CH_2), 73.7 (C-4), 75.8 (C-1), 126.7, 127.9, 128.0, 128.1, 128.1, 128.5, 128.7, 130.3, 138.5 and 140.1 (C-2, C-3 and C_6H_5). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40, H, 7.19. Found: C, 81.23; H, 7.15.

4.7.3. (4-O-Benzyl-2,3, 6-trideoxy-β-L-erythro-hex-2-enopyranosyl)benzene ***(6β)***

$[\alpha]_D^{20} - 219.2$ (c 1.0, CH_2Cl_2). ^{1}H-NMR (200 MHz) δ 1.38 (d, 3H, $J = 5.9$ Hz), 3.73 (dq, 1H, $J = 8.4$, 5.9 Hz), 3.85 (dm, 1H, $J = 8.4$ Hz), 4.60 (d, 1H, $J = 11.6$ Hz), 4.73 (d, 1H, $J = 11.6$ Hz), 5.14 (brs, 1H), 5.85 (brd, 1H, $J = 10.3$ Hz), 6.02 (brd, 1H, $J = 10.3$ Hz), 7.24-7.39 (m, 10H). 13C-NMR (50 MHz) δ 19.2 (CH_3), 71.6 (CH_2), 74.5 (C-4), 76.7 (C-5), 77.8 (C-1), 126.6, 127.6, 128.1, 128.3, 128.3, 128.8, 128.9, 131.9, 138.6 and 141.2 (C-2, C-3 and C_6H_5). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40, H, 7.19. Found: C, 81.17; H, 7.10.

4.7.4. (6-O-Benzyl-4-O-methyl-2,3-dideoxy-α-D-threo-hex-2-enopyranosyl)benzene ***(8α)***

$[\alpha]_D^{20} - 173.6$ (*c* 1.0, CH_2Cl_2). ^{1}H-NMR (300 MHz) δ 3.45 (s, 3H), 3.68 (dd, 1H, $J = 10.2$, 7.0 Hz), 3.75 (dd, 1H, $J = 10.2$, 5.4 Hz), 3.64-3.71 (m, 1H), 3.96 (ddd, 1H, $J = 7.0$, 5.4, 2.8 Hz), 4.49 (d, 1H, $J = 11.9$ Hz), 4.56 (d, 1H, $J = 11.9$ Hz), 5.35 (brs, 1H), 6.23 (ddd, 1H, $J =$ 10.3, 2.8, 1.5 Hz), 6.32 (dd, 1H, $J = 10.3$, 2.8 Hz), 7.22–7.44 (m, 10H). 13C-NMR (50 MHz) δ 56.8 (CH_3), 69.2 and 73.3 (CH_2 and C-6), 70.2 and 71.2 (C-4 and C-5), 73.8 (C-1), 114.9, 124.6, 126.4, 127.6, 127.7, 127.8, 128.5, 138.5, 139.3 and 132.5 (C-2, C-3 and C_6H_5). Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.39, H, 7.14. Found: C, 78.07; H, 7.16.

4.7.5. Ethyl 6-O-(tert-butyldimethylsilyl)-4-phenyl-2,3,4-trideoxy-α-D-erythro-hex-2-enopyran oside ***(10)***

$[\alpha]_D^{20} + 91.6$ (*c* 1.0, CH_2Cl_2). ^{1}H-NMR (200 MHz) δ −0.04 (s, 6H), 0.85 (s, 9H), 1.25 (t, 3H, $J = 7.1$ Hz), 3.45 (bd, 1H, $J = 11.2$ Hz), 3.49–3.65 (m, 3H), 3.90 (dq, 1H, $J = 9.6$, 7.1 Hz), 3.86 (m, 1H), 5.09 (bs, 1H), 5.86 (dd, 1H, $J = 10.1$, 2.1 Hz), 5.93 (d, 1H, $J = 10.1$ Hz), 7.19–7.30 (m, 5H). ^{13}H-NMR (50 MHz) δ −5.3 ($SiCH_3$), −5.2 ($SiCH_3$), 15.5 (CH_3), 18.5 ($SiCMe_3$), 26.0 ($SiCMe_3$), 42.5 (C-4), 63.4 and 63.6 (C-6 and CH_2), 73.8 (C-5), 94.2 (C-1), 125.6, 127.0, 128.6, 128.8, 133.6 and 140.9 (C-2, C-3 and C_6H_5). Anal. Calcd for $C_{20}H_{32}O_3Si$: C, 68.92; H, 9.25. Found: C, 68.81; H, 9.24.

4.7.6. Ethyl 6-O-(tert-butyldimethylsilyl)-2-phenyl-2,3,4-trideoxy-α-D-threo-hex-3-enopyrano side ***(11)***

$[\alpha]_D^{20} + 147.8$ (c 1.0, CH_2Cl_2). ^{1}H-NMR (300 MHz) δ 0.11 (s, 6H), 0.93 (s, 9H), 1.25 (t, 3H, $J = 7.1$ Hz), 3.34 (m, 1H), 3.55 (dq, 1H, $J = 9.8$, 7.1 Hz), 3.73-3.90 (m, 3H), 4.28 (m, 1H), 4.84 (bs, 1H), 5.86 (ddd, 1H, $J =$ 10.4, 1.4, 1.4 Hz), 5.97 (dm, 1H, $J = 10.4$ Hz), 7.22–7.37 (m, 5H). ^{13}H-NMR (50 MHz) δ −5.1 ($SiCH_3$), 15.3 (CH_3), 18.6 ($SiCMe_3$), 26.1 ($SiCMe_3$), 46.2 (C-2), 63.4 and 65.9 (C-6 and CH_2), 68.7 (C-5), 100.8 (C-1), 126.1, 126.6, 126.9, 128.5, 128.8 and 141.1 (C-3, C-4 and C_6H_5). Anal. Calcd for $C_{20}H_{32}O_3Si$: C, 68.92; H, 9.25. Found: C, 69.47; H, 9.32.

4.7.7. Trans 5-[(tert-butyldimethylsilyoxy)methyl]-1-phenylcyclohex-2-ene ***(14)***

^{1}H-NMR (200 MHz) δ −0.01 (s, 3H), 0.01 (s, 3H), 0.86 (s, 9H), 1.66–2.30 (m, 5H), 3.41–3.55 (m, 3H), 5.75 (dm, 1H, $J = 10.2$ Hz), 6.02 (dm, 1H, $J = 10.2$ Hz), 7.18–7.34 (m, 5H). ^{13}C-NMR (50 MHz) δ −5.2 ($SiCH_3$), 18.5 ($SiCMe_3$), 26.7 ($SiCMe_3$), 28.3 (C-6), 32.0 (C-5), 34.0 (C-4), 39.8 (C-1), 67.3 (CH_2), 126.1, 128.1, 128.3, 132.1 and 146.1 (C-2, C-3 and C_6H_5). Anal. Calcd. for $C_{19}H_{30}OSi$: C, 75.43; H, 10.00. Found: C, 75.58; H, 9.91.

4.7.8. Cis 5-[(tert-butyldimethylsilyoxy)methyl]-1-phenylcyclohex-2-ene ***(14)***

^{13}C-NMR (50 MHz) in the mixture of *cis* and *trans* isomers δ −5.2 ($SiCH_3$), 18.6 ($SiCMe_3$), 26.2 ($SiCMe_3$), 28.7 (C-6), 36.6 (C-4), 37.6 (C-5), 43.3 (C-1), 68.3 (CH_2), 126.2, 127.4, 127.6, 128.6, 131.1 and 146.9 (C-2, C-3 and C_6H_5).

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