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Multifunctionalized α,β-cyclopentenones from *C*-2 and *C*-4-ulopyranosyl compounds: a stereospecific rearrangement initiated by base

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Abstract

Base treatment of *O*-benzyl protected *C*-2- or *C*-4-ulopyranosyl compounds (**4α**, **4β**, and **11**) by either 10% Et_3N or 1% K_2CO_3 in MeOH initiated a β elimination to afford α,β-unsaturated *C*-ulopyranosyl compounds (**5α**, **5β**, and **12**), which further rearranged in a stereocontrolled manner to multifuctionalized α,β-cyclopentenones (**6** and **14**) in 70–80% yield. Both *C*-α- and *C*-β-2-ulosides (**5α** and **5β**) produced the same cyclopentenone **6**, indicating that a 1,2-enolate is formed prior to the cleavage of the C-5–O bond. Because **6** is racemic, it was probably formed by the intramolecular cycloaldolization of two equally populated enantiomeric intermediates. When treated with 90% Et_3N in MeOH, **5α** yielded almost exclusively **15** (isomer of **6**), which was formed by a migration of the double bond in **5α** during the previously described rearrangement. Thus either **6** or **15** was the major product, depending on the base used. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: *C*-Ulosyl compound; Cyclopentenone; Synthesis; Rearrangement

1. Introduction

Cyclopentenones are important structural elements found in prostaglandins[1] and many other natural products, and these compounds serve as intermediates for the synthesis of carbocyclic nucleosides.[2] The synthetic methodology for producing cyclopentenones has been well developed and includes cyclization of 1,4-dicarbonyl functions,[3] Khand–Pauson and modified reactions,[4] other [2 + 3] annulations,[5] photo and radical reactions,[6] as well as approaches from carbohydrate compounds.[7] We report herein a convenient synthesis of multifuctionalized α,β-cyclopentenones from a base-initiated rearrangement of *C*-2- or *C*-4-ulopyranosyl compounds. The reaction has led to the formation of a new carbon–carbon bond between C-1 and C-5 of the ulopyranosyl moiety in a stereocontrolled manner.

2. Results and discussion

In order to convert *C*-α-glycosylic compounds ('α-*C*-glycosides') to *C*-β-glycosylic compounds ('β-*C*-glycosides') we had thought that epimerization at C-1 of an α-*C*-2-ulosyl compound might be achievable via 1,2-enolate

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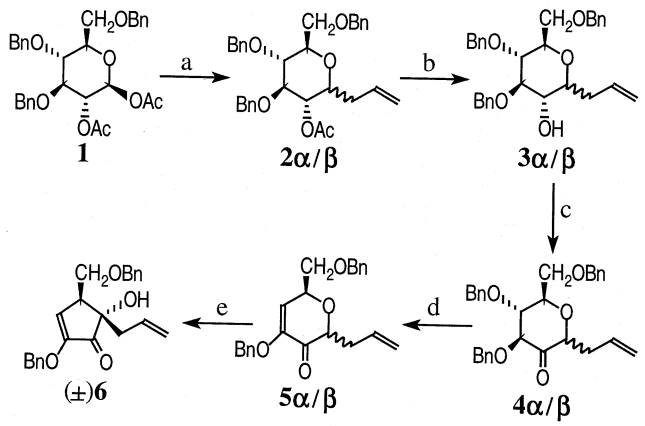
formation, and that this reaction could be a route to a facile synthesis of *C*-β-mannosyl compounds. Therefore, we prepared allyl *C*-α-glucoside (**2α**) from glucose derivative **1**[8] by a procedure described previously,[9] which gave a mixture of both anomers (**2α**/**2β** 8:1, 85%) in which **2α** was the major product. *O*-Deacetylation of **2α**/**2β** with 0.1% NaOMe in MeOH gave **3α**/**3β** (> 90%), which when followed by Moffatt oxidation,[10] afforded the respective allyl *C*-2-ulosides, **4α** and **4β**, in 80–90% yield (Scheme 1). No hydrated form of the ketone was observed by NMR spectroscopic analysis.

Compound **4α** on treatment with base (10% Et_3N or 1% K_2CO_3 in MeOH) was rapidly converted to a slower moving compound as shown by TLC. However, when the compound was isolated (~ 90%) and characterized, it was found to be an α,β-unsaturated *C*-2-uloside (**5α**) instead of epimerized product (**4β**). Under prolonged reaction times, using either of the above bases, **5α** slowly underwent a further transformation to afford ring-contracted compound **6** (70–80% from **4α**, see Scheme 1). It is noteworthy that the skeleton of **6** is also found in mongolicains,[11] a type of tannin isolated from plants.

Compound **6**, an α,β-unsaturated cyclopentenone, must have been derived from **5α** in a rearrangement involving the breakdown of the C-5–O bond and the formation of a C-1–C-5 bond. The stereochemistry of the newly formed C-1–C-5 bond in **6** has the cis configuration, which is consistent with the observation of a strong NOE between CH_2–CH=CH_2 and 6-CH_2, but not H-5. However, we could not detect a significant optical rotation for **6**, and the ^{13}C NMR experiments also excluded the existence of dimeric **6**, which would have created a symmetric center. Therefore, **6** must be a mixture of enantiomers, (1*S*,5*S*) and (1*R*,5*R*).



Scheme 1. Reagents and conditions: (a) Allyl-TMS–TMSOTf in MeCN, −40 °C to rt 8 h; (b) 0.1% NaOMe in MeOH, 2 h at rt; (c) 2:1 Me_2SO–Ac_2O, overnight at rt; (d) 10% Et_3N or 1% K_2CO_3 in MeOH, 1 h; (e) 10% Et_3N or 1% K_2CO_3 in MeOH, 1–3 days.

When we treated β-isomer **5β** with 1:9 Et_3N–MeOH, compound **6** was isolated in 70–80% yield. Therefore, a plausible reaction mechanism for the formation of **6** is proposed in Fig. 1. The β elimination product (**5α** or **5β**) on further treatment with base forms the same 1,2-enolate. This in turn facilitates the breakdown of the C-5–O bond with the formation of a species having a carbon anion at C-5, which then rearranges to a more stable enolate. The presence of two cis-ene enantiomeric conformers of the enolate is critical to the outcome of stereochemistry. Both right- (pro-*R*,*R*) and left-turn (pro-*S*,*S*) conformers are equally populated which on intramolecular cycloaldolization, would then form of both **6** (1*S*,5*S*) and **6** (1*R*,5*R*) in equal amounts.

In order to study whether the rearrangement can be carried out using different substituents, another *C*-4-uloside (**11**) was prepared in multiple steps from **2α** (Scheme 2). The catalytic hydrogenation of **2α** furnished **7** (90%) by removal of *O*-benzyl groups and converting 1-*C*-allyl into 1-*C*-propyl. *O*-Deacetylation (0.1% NaOMe in MeOH) of **7**, followed by benzylidenation [$PhCH(OMe)^2$–H^+], afforded **8**, which was further converted to **9** (99%) by *O*-benzylation (BnBr–NaH). Reductive ring opening of the benzylidene function ($NaCNBH_3$–HCl)[12] gave **10** in 49% yield, together with 1-(2,3-di-*O*-benzyl-α-D-glucopyranosyl)propane (40%). Moffatt oxidation[10] of **10** afforded **11** in 90% yield. When **11** was treated with 10% Et_3N–MeOH, the same β elimination as described above produced **12**, which further rearranged to racemic α,β-cyclopentenone **14** in 68% yield, based on the consumed starting material. Again, the cis configuration at C-4 and C-5 (cyclopent-2-enone numbering) was established by a NOESY experiment. Besides the recovery of **12** (13%), we also isolated, from

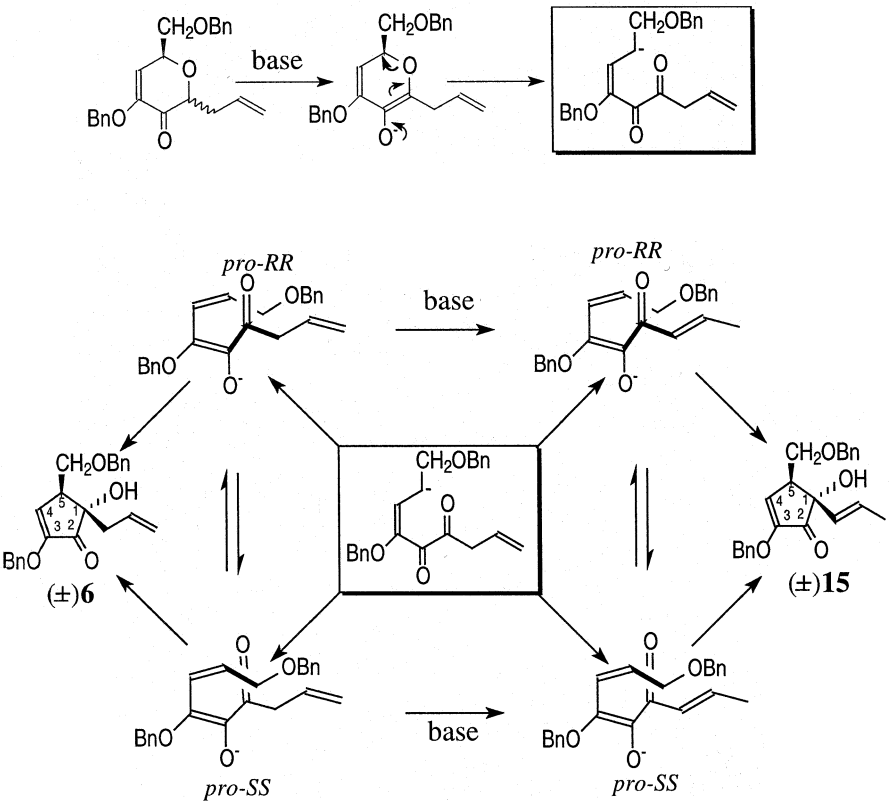
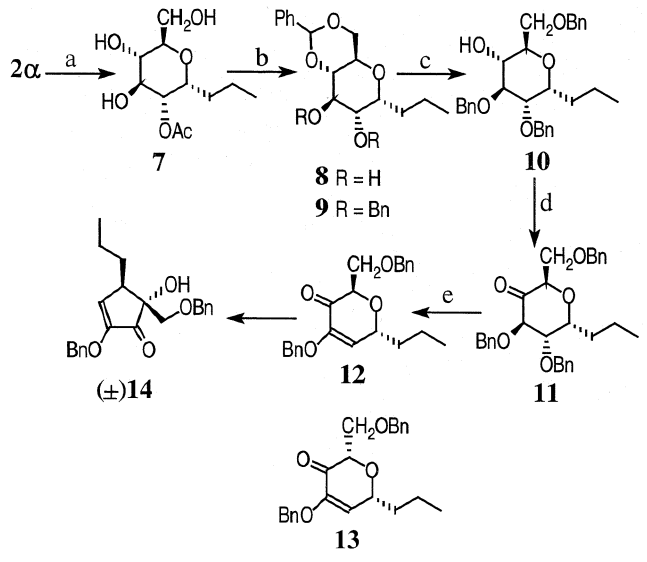


Fig. 1. A proposed mechanism of the rearrangement initiated by base.

the base treatment of **11**, a C-5 (ulopyranosyl numbering) epimerized derivative **13** (27%). A strong NOE between H-1 and H-5, which was not observed in **12**, confirmed the epimerization. This result further supports the mechanism as illustrated in Fig. 1.

We also investigated the effect of different bases on the rearrangement of **5α**. Both 1% K_2CO_3 and 10% Et_3N in MeOH produced good yields of **6** (see Table 1). Using 0.1% NaOMe and LiOMe, **5α** decomposed, and **6** was isolated in poor yield. The addition of LiOBz to 10% Et_3N in MeOH had no effect on the stereoselectivity of the reaction. However, when 10% DBU–CH_2Cl_2 and 30% Et_3N–MeOH were used as bases, we isolated a chromatographically inseparable mixture of **6** and its isomer **15** (see Scheme 3). The chemical shift (δ_H) of the propenyl methyl group showed a doublet at 1.680 ppm (J 6.5 Hz), and another set of protons appeared at 5.408 (d, 1 H, C*H*=CH–CH_3, J_{trans} 15.5) and 5.778 (m, 1 H, CH=CH–CH_3) ppm. Therefore, the propenyl double bond in **15** is in the *E*-form as indicated by a large coupling constant. The migration of the double bond must take place after the cleavage of the C-5–O bond occurs in both intermediates (pro-*S*,*S* and pro-*R*,*R*) in



Scheme 2. Reagents and conditions: (a) H_2/Pd–C in MeOH, 4 h; (b) (i) 0.1% NaOMe in MeOH, 2 h at rt; (ii) Ph-$CH(OMe)_2$–H^+ in CH_3CN, 2 h at rt; (iii) BnBr–NaH in DMF, overnight at rt; (c) $NaCNBH_3$–H^+ in THF, 2 h at 0 °C; (d) 2:1 Me_2SO–Ac_2O, overnight at rt; (e) 10% Et_3N in MeOH, 1–3 days.

Table 1
The effect of base to the rearrangement products

Entry	Base	Solvent	Time (h)	Ratio (**6**:**15**) [a]	Total yield (%) [b]
1	10% Et_3N	CH_3OH	72	40:1	70–80
2	30% Et_3N	CH_3OH	72	2:1	81
3	10% Et_3N–1% LiOBz	CH_3OH	72	35:1	76
4	1% LiOMe	CH_3OH	4	4.2:1	<10
5	0.1% LiOMe	CH_3OH	16	**6** only	20
6	1% K_2CO_3	CH_3OH	16	**6** only	81
7	1% NaOMe	CH_3OH	7	**6** only	19
8	10% DBU	CH_2Cl_2	16	1:1.6	22
9	90% Et_3N	CH_3OH	72	1:25	73

[a] Isomers **6** and **15** were inseparable by silica gel chromatography. The ratio of products was determined by ^1H NMR spectroscopy.
[b] Isolated yield.

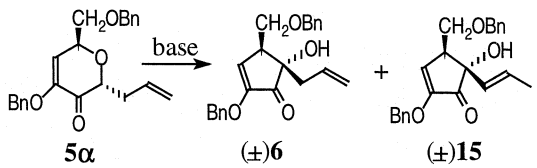
order to form stable α,β-unsaturated conjugates (see Fig. 1). Thus migration and the intramolecular cycloaldolation compete with each other to produce a mixture of **6** and **15**. However, using 90% Et_3N–MeOH, **5α** was converted to **15** in 73% yield, and only very minor quantities of **6** were obtained.

In summary, a base-initiated rearrangement from *C*-2 or -4-ulopyranosyl compounds is described, a reaction that could be very useful for the synthesis of densely functionalized cyclopentenones with various substituents. The starting material is readily prepared, and the reaction conditions are very mild and convenient. Unfortunately, the reaction only affords the racemic products.

3. Experimental

General methods.—^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 500 and 125 MHz, respectively, with an INOVA-500 instrument at 293 K unless otherwise noted. Chemical shifts are given in ppm relative to the signal of internal Me_4Si in $CDCl_3$ for both ^1H and ^{13}C NMR spectra. The ^1H and ^{13}C resonances were assigned on the basis of 2D ^1H-COSY and ^1H–^{13}C chemical-shift correlated experiments. Mass analysis was performed with a JEOL JMS-AX505H spectrometer. Optical rotations were recorded at rt. All chemicals were Aldrich products and were used without further purification. Chromatography was performed on a silica gel column using following solvents: solvent A: 5:1 petroleum ether (35–60 °C)–EtOAc; solvent B: 4:1 petroleum ether (35–60 °C)–EtOAc; solvent C: 3:1 hexane–EtOAc; and solvent D: 2:1 hexane–EtOAc.

*3-C-(2-O-Acetyl-3,4,6-tri-O-benzyl-α,β-D-glucopyranosyl)propene (**2α** and **2β**).*—To a solution of compound **1** (3.4 g, 6.37 mmol) and allyltrimethylsilane (5.0 mL) in dry MeCN (35 mL) was added TMSOTf (0.7 mL) at −40 °C. The mixture was stirred for 8 h while the temperature was slowly raised to rt. The mixture was diluted by the addition of EtOAc (100 mL) and aq $NaHCO_3$ (50 mL). The organic phase was subsequently washed with aq $NaHCO_3$ and water, dried, and concentrated to a residue. Purification of the crude product by chromatography (solvent A) gave crystalline **2α** (2.5 g, 76%). Recrystallization from MeOH gave mp 109–110 °C; $[\alpha]_D$ +63.0° (*c* 1.05, EtOAc). ^1H NMR ($CDCl_3$): δ_H ($CDCl_3$) 1.987 (s, 3 H, 2-OAc), 2.258 and 2.477 (m and m, 1 H each, $CH_2CH{=}CH_2$), 3.631–3.815 (m, 4 H, H-4,5,6,6′), 3.831 (dd, 1 H, H-3, $J_{2,3} = J_{3,4}$ 8.0 Hz), 4.202 (ddd, 1 H, H-1, $J_{1,2}$ 5.0, *J* 5.0, *J* 10.0 Hz), 4.487–4.780 (m, 6 H, 3 × CH_2Ph), 5.046 (dd, 1 H, H-2, $J_{2,3}$ 8.5 Hz), 5.044 and 5.096 (d and d, 1 H each,



5α (±)**6** (±)**15**

Scheme 3.

$CH_2CH{=}CH_2$, J_{cis} 10.0, J_{trans} 16.5 Hz), 5.755 (m, 1 H, $CH_2CH{=}CH_2$), 7.178–7.365 (m, 15 H, 3 × Ph) ppm. FABMS: Anal. Calcd for $C_{32}H_{36}O_6$ [M]: 517.6. Found: 517.4.

Minor product **2β**, which was eluted faster, was also obtained (0.3 g, 9%) as a semicrystalline solid: $[\alpha]_D$ +15.5° (*c* 0.42, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 1.923 (s, 3 H, 2-OAc), 2.275 (dd, 2 H, $CH_2CH{=}CH_2$, *J* 6.5, *J* 6.0 Hz), 3.357 (ddd, 1 H, H-1, *J* 4.5, *J* 6.0, $J_{1,2}$ 9.5 Hz), 3.445 (m, 1 H, H-5), 3.615–3.684 (m, 3 H, H-4,6,6′), 3.721 (dd, 1 H, H-3, $J_{2,3} = J_{3,4}$ 9.5 Hz), 4.548–4.826 (m, 6 H, 3 × CH_2Ph), 4.914 (dd, 1 H, H-2), 5.045 and 5.069 (d and d, 1 H each, $CH_2CH{=}CH_2$, J_{cis} 9.0, J_{trans} 15.5), 5.846 (m, 1 H, $CH_2CH{=}CH_2$), 7.172–7.345 (m, 15 H, 3 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 20.95 (CH_3CO), 36.18 ($CH_2CH{=}CH_2$), 68.83 (C-6), 73.70 (C-2), 73.41, 74.97, 75.12 (3 × CH_2Ph), 77.37 (C-1), 78.35 (C-4), 79.19 (C-5), 84.55 (C-3), 117.01 ($CH_2CH{=}CH_2$), 127.52–128.38 (3 × Ph), 133.93 ($CH_2CH{=}CH_2$), 137.96, 138.21, 138.34 (3 × Ph), 169.78 (C=O) ppm. FABMS: Anal. Calcd for $C_{32}H_{36}O_6$ [M]: 517.6. Found: 517.4.

3-C-*(3,4,6-Tri*-O-*benzyl-α,β*-D-*glucopyranosyl)propene (**3α** and **3β**).*—To a suspension of **2α** (2.3 g, 4.46 mmol) in MeOH (20 mL) was added 1% NaOMe (2.0 mL). The mixture was stirred at rt for 2 h. The clear solution was neutralized by the addition of AcOH (three drops) and then concentrated. Purification by chromatography (solvent B) gave crystalline **3α** (1.9 g, 90%). Recrystallization from petroleum ether (35–60 °C) gave mp 76–77 °C; $[\alpha]_D$ +44.2° (*c* 0.33, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 2.402 (m, 2 H, $CH_2CH{=}CH_2$), 2.899 (d, 1 H, 2-OH, *J* 8.0 Hz), 3.630–3.667 (m, 2 H, H-2,4), 3.696 and 3.817 (dd and dd, 1 H each, H-6,6′, $J_{6,6'}$ 10.0, $J_{5,6}$ 5.5, $J_{5,6'}$ 6.0 Hz), 3.754 (dd, 1 H, H-3, $J_{2,3} = J_{3,4}$ 5.5 Hz), 3.935 (m, 1 H, H-1), 4.056 (m, 1 H, H-5), 4.490–4.659 (m, 6 H, 3 × CH_2Ph), 5.063 and 5.132 (d and d, 1 H each, $CH_2CH{=}CH_2$, J_{cis} 10.0, J_{trans} 17.0 Hz), 5.834 (m, 1 H, $CH_2CH{=}CH_2$), 7.233–7.342 (m, 15 H, 3 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 33.27 ($CH_2CH{=}CH_2$), 68.03 (C-6), 69.06 (C-2), 71.00 (C-1) 72.77, 73.27(2) (3 × CH_2Ph), 73.50 (C-5), 74.75 (C-4), 77.60 (C-3), 116.98 ($CH_2CH{=}CH_2$), 127.58–128.55 (3 × Ph), 134.71 ($CH_2CH{=}CH_2$), 137.41, 137.92, 138.18 (3 × Ph) ppm. HRFABMS: Anal. Calcd for $C_{30}H_{33}O_5$ [M − H]: 473.2328. Found: 473.2332; Anal. Calcd for $C_{30}H_{35}O_5$ [M + H]: 475.2484. Found: 475.2518.

Compound **3β** was obtained in the same way from **2β** (91%): mp 70–71 °C; $[\alpha]_D$ +11.1° (*c* 0.46, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 2.040 (d, 1 H, 2-OH, *J* 2.5 Hz), 2.312 and 2.560 (m and m, 1 H each, $CH_2CH{=}CH_2$), 3.253 (ddd, 1 H, H-1, *J* 3.5 Hz, 7.5, $J_{1,2}$ 9.5 Hz), 3.369 (ddd, 1 H, H-2, $J_{2,3}$ 8.5 Hz), 3.427 (m, 1 H, H-5), 3.477 (dd, 1 H, H-3, $J_{3,4}$ 9.0 Hz), 3.602 (dd, 1 H, H-4, $J_{4,5}$ 9.5 Hz), 3.698 and 3.717 (dd and dd, 1 H each, H-6,6′, $J_{6,6'}$ 11.0, $J_{5,6}$ 4.5, $J_{5,6'}$ 2.0 Hz), 4.561–4.971 (m, 6 H, 3 × CH_2Ph), 5.070 and 5.126 (d and d, 1 H each, $CH_2CH{=}CH_2$, J_{cis} 10.0, J_{trans} 17.0 Hz), 5.929 (m, 1 H, $CH_2CH{=}CH_2$), 7.203–7.357 (m, 15 H, 3 × Ph) ppm. HRFABMS: Anal. Calcd for $C_{30}H_{33}O_5$ [M − H]: 473.2328. Found: 473.2324; Anal. Calcd for $C_{30}H_{35}O_5$ [M + H]: 475.2484. Found: 475.2549.

3-C-*(3,4,6-Tri*-O-*benzyl-α,β*-D-arabino-*hex-2-ulopyranosyl)propene (**4α** and **4β**).*—A solution of compound **3α** (1.8 g, 3.80 mmol) in 2:1 Me_2SO–Ac_2O (12 mL) was stirred at rt for 24 h. The mixture was diluted with EtOAc (150 mL) and washed with aq $NaHCO_3$ and water, dried and concentrated. Purification by chromatography (solvent A) gave **4α** (1.6 g, 89%) as a syrup: $[\alpha]_D$ +31.4° (*c* 0.21, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 2.477 (dd, 2 H, $CH_2CH{=}CH_2$, $J_1 = J_2$ 7.0 Hz), 3.590 and 3.630 (dd and dd, 1 H each, H-6,6′, $J_{6,6'}$ 10.0, $J_{5,6}$ 4.0, $J_{5,6'}$ 2.0 Hz), 3.909 (dd, 1 H, H-4, $J_{3,4} = J_{4,5}$ 8.5 Hz), 4.038 (m, 1 H, H-5), 4.268 (t, 1 H, H-1, *J* 7.0 Hz), 4.395 (d, 1 H, H-3), 4.424–4.972 (m, 6 H, 3 × CH_2Ph), 5.096 and 5.116 (d and d, 1 H each, $CH_2CH{=}CH_2$, J_{cis} 10.0, J_{trans} 19.5 Hz), 5.767 (m, 1 H, $CH_2CH{=}CH_2$), 7.197–7.409 (m, 15 H, 3 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 34.74 ($CH_2CH{=}CH_2$), 69.50 (C-6), 73.38, 73.80, 74.31 (3 × CH_2Ph), 75.29 (C-5), 78.18 (C-4), 79.82 (C-1), 84.37 (C-3), 118.35 ($CH_2CH{=}CH_2$), 127.69–128.35 (3 × Ph), 132.26 ($CH_2CH{=}CH_2$), 137.46, 137.66, 137.78 (3 × Ph), 207.74 (C-2) ppm. HRFABMS: Anal. Calcd for $C_{30}H_{31}O_5$ [M − H]: 471.2171. Found: 471.2194; Anal. Calcd for $C_{30}H_{33}O_5$ [M + H]: 473.6. Found: 473.3.

Compound **4β** was obtained in the same way from **3β** as crystals (87%): mp 72–73 °C (MeOH); $[\alpha]_D$ −51.7° (*c* 0.29, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 2.410 and 2.624 (m and m, 1 H each, C*H*$_2$CH=CH$_2$), 3.703 (dd, 1 H, H-6, $J_{6,6'}$ 10.0, $J_{5,6}$ 4.0 Hz), 3.753–3.822 (m, 3 H, H-1,5,6′), 3.870 (dd, 1 H, H-4, $J_{3,4}$ 9.0, $J_{4,5}$ 10.0 Hz), 4.179 (d, 1 H, H-3), 4.535–5.007 (m, 6 H, 3 × C*H*$_2$Ph), 5.089 and 5.161 (d and d, 1 H each, CH$_2$CH=C*H*$_2$, J_{cis} 10.0, J_{trans} 19.5 Hz), 5.875 (m, 1 H, CH$_2$C*H*=CH$_2$), 7.171–7.412 (m, 15 H, 3 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 32.91 (*C*H$_2$CH=CH$_2$), 68.85 (C-6), 73.50, 73.73, 74.98 (3 × CH$_2$Ph), 79.32 (C-5), 80.25 (C-4), 80.52 (C-1), 86.65 (C-3), 117.56 (CH$_2$CH=*C*H$_2$), 127.63–128.45 (3 × Ph), 133.73 (CH$_2$*C*H=CH$_2$), 137.54, 137.79, 138.07 (3 × Ph), 201.92 (C-2) ppm. HRFABMS: Anal. Calcd for $C_{30}H_{31}O_5$ [M − H]: 471.2171. Found: 471.2194; Anal. Calcd for $C_{30}H_{33}O_5$ [M + H]: 473.2328. Found: 473.2404.

3-C-*(3,6-Di*-O-*benzyl-4-deoxy-α,β*-D-glycero-*2-ulopyranosyl)propene (***5α** *and* **5β**).—A solution of compound **4α** (0.25 g, 0.53 mmol) in 10% Et_3N–MeOH (5 mL) was stirred at rt for 1 h. The solvent was evaporated to a residue. Purification by chromatography (solvent A) gave **5α** (0.18 g, 93%) as a syrup: $[\alpha]_D$ −26.2° (*c* 0.65, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 2.551 (m, 2 H, C*H*$_2$CH=CH$_2$), 3.541 and 3.655 (dd and dd, 1 H each, H-6,6′, $J_{6,6'}$ 10.0, $J_{5,6}$ 6.0, $J_{5,6'}$ 5.0 Hz), 4.413 (dd, 1 H, H-1, *J* 5.0, *J* 9.0 Hz), 4.554 (s, 2 H, 6-C*H*$_2$Ph), 4.742 (m, 1 H, H-5), 4.834 (s, 2 H, 3-C*H*$_2$Ph), 5.127 and 5.173 (d and d, 1 H each, CH$_2$CH=C*H*$_2$, J_{cis} 11.0, J_{trans} 16.5 Hz), 5.847 (m, 1 H, CH$_2$C*H*=CH$_2$), 5.877 (d, 1 H, H-4, $J_{4,5}$ 2.0 Hz), 7.280–7.381 (m, 10 H, 2 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 34.01 (*C*H$_2$CH=CH$_2$), 69.47 (C-5), 69.77 (6-*C*H$_2$Ph), 71.28 (C-6), 73.47 (3-*C*H$_2$Ph), 78.48 (C-1), 116.24 (C-4), 117.98 (CH$_2$CH=*C*H$_2$), 127.35–128.59 (Ph), 133.35 (CH$_2$*C*H=CH$_2$), 135.63, 137.67 (2 × Ph), 147.44 (C-3), 191.35 (C-2) ppm. HRFABMS: Anal. Calcd for $C_{23}H_{23}O_4$ [M − H]: 363.1596. Found: 363.1668.

Compound **5β** was obtained as a syrup from **4β** (78%): $[\alpha]_D$ −16.8° (*c* 0.24, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 2.489 and 2.792 (m and m, 1 H each, C*H*$_2$CH=CH$_2$), 3.517 and 3.665 (dd and dd, 1 H each, H-6,6′, $J_{6,6'}$ 10.0, $J_{5,6}$ 6.0, $J_{5,6'}$ 5.0 Hz), 4.066 (m, 1 H, H-1), 4.592 (s, 2 H, C*H*$_2$Ph), 4.612 (m, 1 H, H-5), 4.825 and 4.885 (d and d, 1 H each, C*H*$_2$Ph, *J* 11.5 Hz), 5.086 and 5.163 (d and d, 1 H each, CH$_2$CH=C*H*$_2$, J_{cis} 10.5, J_{trans} 17.0 Hz), 5.902 (m, 1 H, CH$_2$C*H*=CH$_2$), 5.944 (d, 1 H, H-4, $J_{4,5}$ 1.5 Hz), 7.298–7.376 (m, 10 H, 2 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 34.33 (*C*H$_2$CH=CH$_2$), 69.83 (6-*C*H$_2$Ph), 71.91 (C-6), 73.27 (C-5), 73.55 (3-*C*H$_2$Ph), 80.80 (C-1), 116.69 (C-4), 117.58 (CH$_2$CH=*C*H$_2$), 127.38–128.60 (2 × Ph), 133.77 (CH$_2$*C*H=CH$_2$), 135.63, 137.81 (2 × Ph), 148.84 (C-3), 191.29 (C-2) ppm. HRFABMS: Anal. Calcd for $C_{23}H_{23}O_4$ [M − H]: 363.1596. Found: 363.1595.

(±)-c-*5-Allyl-2-benzyloxy*-r-*4-benzyloxymethyl-5-hydroxycyclopent-2-enone* (**6**).—A solution of compound **4α** or **4β** (0.25 g, 0.687 mmol) in 10% Et_3N–MeOH (5 mL) was stirred at rt for 3 days. The solvent was evaporated to a residue. Purification by chromatography (solvent A) gave **6** (0.19 g, 78%) as a syrup: $[\alpha]_D$ 0° (*c* 0.76, EtOAc or $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ_H 2.380 (d, 2 H, C*H*$_2$CH=CH$_2$, *J* 7.0 Hz), 2.702 (s, 1 H, 1-OH), 3.090 (ddd, 1 H, H-5, $J_{4,5}$ 2.0, $J_{5,6}$ 6.5, $J_{5,6'}$ 7.0 Hz), 3.532 and 3.693 (dd and dd, 1 H each, H-6,6′, $J_{6,6'}$ 9.0 Hz), 4.544 (s, 2 H, 6-C*H*$_2$Ph), 4.976 and 4.978 (d and d, 1 H each, 3-C*H*$_2$Ph, *J* 12.0 Hz), 5.136 and 5.194 (d and d, 1 H each, CH$_2$CH=C*H*$_2$, J_{cis} 10.0, J_{trans} 17.5 Hz), 5.831 (m, 1 H, CH$_2$C*H*=CH$_2$), 6.302 (d, 1 H, H-4) ppm; ^{13}C NMR ($CDCl_3$): δ_C 38.96 (*C*H$_2$CH=CH$_2$), 47.19 (C-5), 68.59 (C-6), 71.79 (3-*C*H$_2$Ph), 73.59 (6-*C*H$_2$Ph), 77.66 (C-1), 120.82 (CH$_2$CH=*C*H$_2$), 127.17 (C-4), 127.85–128.87 (2 × Ph), 131.56 (CH$_2$*C*H=CH$_2$), 135.66, 138.04 (2 × Ph), 153.68 (C-3), 202.69 (C-2) ppm. HRFABMS: Anal. Calcd for $C_{23}H_{25}O_4$ [M + H]: 365.1753. Found: 365.1759.

(±)-2-Benzyloxy-r-*4-benzyloxymethyl*-t-*5-hydroxy-5-propenylcyclopent-2-eneone* (**15**).—A solution of compound **5β** (30 mg, 0.082 mmol) in 90% Et_3N–MeOH (1 mL) was stirred at rt for 72 h. Workup following the same procedures as described above for **6** gave **15** (22 mg, 73%) as a syrup: $[\alpha]_D$ 0° (*c* 2.1, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 1.680 (d, 3 H, CH=CH–C*H*$_3$, *J* 6.5 Hz), 2.669 (s, 1 H, 1-

OH), 3.073 (bdd, 1 H, H-5, $J_{5,6}$ 7.0, $J_{5,6'}$ 8.0 Hz), 3.394 and 3.590 (dd and dd, 1 H each, H-6,6′, $J_{6,6'}$ 8.0 Hz), 4.512 (s, 2 H, 6-CH_2Ph), 4.971 and 4.975 (d and d, 1 H each, 3-CH_2Ph, J 11.5 Hz), 5.408 (d, 1 H, CH=CH–CH_3, J_{trans} 15.5 Hz), 5.778 (m, 1 H, CH=CH–CH_3), 6.381 (d, 1 H, H-4), 7.303–7.366 (m, 10 H, 2 × Ph) ppm; δ_C 17.82 (CH=CH–CH_3), 47.87 (C-5), 69.27 (C-6), 71.57 (3-CH_2Ph), 73.31 (6-CH_2Ph), 79.31 (C-1), 120.82 (CH=CH–CH_3), 127.67 (C-4), 127.61–128.58 (2 × Ph), 127.97 (CH=CH–CH_3), 135.34, 137.92 (2 × Ph), 153.86 (C-3), 201.75 (C-2) ppm. FABMS: Anal. Calcd for $C_{23}H_{25}O_4$ [M + H]: 365.5. Found: 365.2.

1-C-*(2*-O-*Acetyl*-α-D-*glucopyranosyl)propane* (**7**).—To a solution of **2α** (1.60 g, 3.10 mmol) in MeOH (10 mL) was added 10% Pd–C (0.5 g, 50% water). The mixture was subjected to hydrogenation (50 psi H_2) overnight. Removal of solvent gave **7** (0.704 g, 90%) as a solid. Recrystalization from EtOAc gave mp 109–110 °C; $[\alpha]_D$ +119° (*c* 0.38, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 0.945 (t, 3 H, $CH_2CH_2CH_3$, J 7.5 Hz), 1.287 and 1.402 (m and m, 1 H each, $CH_2CH_2CH_3$), 1.486 and 1.708 (m and m, 1 H each, $CH_2CH_2CH_3$), 2.129 (s, 3 H, CH_3CO), 3.498 (m, 1 H, H-5), 3.581 (dd, 1 H, H-4, $J_{3,4}$ 9.5, $J_{4,5}$ 9.0 Hz), 3.781 (m, 1 H, H-6), 3.822–3.855 (m, 2 H, H-3,6′), 4.129 (dd, 1 H, H-1, $J_{1,2}$ 5.5, J 7.0 Hz), 4.849 (dd, 1 H, H-2, $J_{2,3}$ 9.3 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ_C 13.78 ($CH_2CH_2CH_3$), 18.43 ($CH_2CH_2CH_3$), 20.94 (CH_3CO), 27.06 ($CH_2CH_2CH_3$), 61.60 (C-6), 70.41 (C-4), 71.73 (C-5), 72.11 (C-3), 72.79 (C-1), 73.28 (C-2), 170.93 (CH_3CO) ppm. HRFABMS: Anal. Calcd for $C_{11}H_{21}O_6$ [M + H]: 249.1338. Found: 249.1325.

1-C-*(4,6*-O-*benzylidene*-α-D-*glucopyranosyl)propane* (**8**).—A solution of **7** (0.614 g, 2.47 mmol) in 0.1% NaOMe–MeOH (15 mL) was kept at rt for 2 h. The solution was neutralized by Dowex-50W × 8 (100 mesh, H^+) resin, and the filtrate was concentrated to a residue. To a solution of above residue in CH_3CN (30 mL) was added $PhCH(OMe)_2$ (0.85 mL) and TsOH (20 mg). The mixture was stirred for 3 h at the end of which time the reaction was judged completed, and it was then neutralized by the addition of Et_3N (0.5 mL). After evaporating the solvent, the residue was purified by column chromatography (solvent C) to afford **8** (0.706 g, 97%) as crystals: mp 187 °C (EtOAc–hexane); $[\alpha]_D$ +28° (*c* 0.44, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 0.967 (t, 3 H, $CH_2CH_2CH_3$, J 7.5 Hz), 1.340 and 1.492 (m and m, 1 H each, $CH_2CH_2CH_3$), 1.649–1.708 (m, 2 H, $CH_2CH_2CH_3$), 2.565 (s, 1 H, OH), 2.832 (s, 1 H, OH), 3.435 (dd, 1 H, H-4, $J_{4,5}$ 9.5, $J_{3,4}$ 8.5 Hz), 3.583 (ddd, 1 H, H-5, $J_{5,6}$ 10.0, $J_{5,6'}$ 5.0 Hz), 3.685 (dd, 1 H, H-6, $J_{6,6'}$ 10.5 Hz), 3.820–3.853 (m, 2 H, H-2, H-3), 4.043 (m, 1 H, H-1), 4.256 (dd, 1 H, H-6′), 5.519 (s, 1 H, PhCH), 7.370–7.501 (m, 15 H, 3 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 13.85 ($CH_2CH_2CH_3$), 18.58 ($CH_2CH_2CH_3$), 26.568 ($CH_2CH_2CH_3$), 63.28 (C-5), 69.45 (C-6), 71.64 (C-2), 72.32 (C-3), 76.37 (C-1), 82.14 (C-4), 101.95 (PhCH), 126.24, 128.38, 129.31, 137.08 (Ph) ppm. HRFABMS: Anal. Calcd for $C_{16}H_{23}O_5$ [M]: 295.1546. Found: 295.1573.

1-C-*(2,3-Di*-O-*benzyl*-*4,6*-O-*benzylidene*-α-D-*glucopyranosyl)propane* (**9**).—To a solution of **8** (0.705 g, 2.39 mmol) in DMF (6 mL) was added 60% NaH (0.23 g). After 0.5 h BnBr (1.14 mL) was added to the mixture, and the mixture was stirred overnight and diluted by the addition of EtOAc (150 mL), and subsequently washed with 1 N HCl, aq $NaHCO_3$, water, dried, and concentrated. Purification by chromatography (solvent A) afforded **9** (1.130 g, 99%) as a solid. $[\alpha]_D$ −0.9° (*c* 0.44, EtOAc); ^{1}H NMR ($CDCl_3$): δ_H 0.941 (t, 3 H, $CH_2CH_2CH_3$, J 7.5 Hz), 1.291 and 1.454 (m and m, 1 H each, $CH_2CH_2CH_3$), 1.677 and 1.762 (m and m, 1 H each, $CH_2CH_2CH_3$), 3.601 (ddd, 1 H, H-5, $J_{4,5}$ 8.5, $J_{5,6}$ 9.5, $J_{5,6'}$ 4.5 Hz), 3.637 (dd, 1 H, H-4, $J_{3,4}$ 8.5 Hz), 3.675 (dd, 1 H, H-6, $J_{6,6'}$ 10.5 Hz), 3.729 (dd, 1 H, H-2, $J_{2,3}$ 9.0, $J_{1,2}$ 5.5 Hz), 3.866 (dd, 1 H, H-3), 3.975–4.027 (m, 1 H, H-1), 4.255 (dd, 1 H, H-6′), 4.635 and 4.764 (d and d, 1 H each, CH_2Ph, J 12.0 Hz), 4.809 and 4.913 (d and d, 1 H each, CH_2Ph, J 11.0 Hz), 5.563 (s, 1 H, PhCH), 7.264–7.493 (m, 15 H, 3 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 13.85 ($CH_2CH_2CH_3$), 18.47 ($CH_2CH_2CH_3$), 27.50 ($CH_2CH_2CH_3$), 63.36 (C-5), 69.56 (C-6), 73.51 (CH_2Ph), 74.87 (CH_2Ph), 75.12 (C-1), 78.87 (C-3), 79.70 (C-2), 82.89 (C-4), 101.15 (PhCH), 125.97–128.85, 137.47, 138.28, 138.73 (3 × Ph) ppm.

HRFABMS: Anal. Calcd for $C_{30}H_{33}O_5$ [M − H]: 473.2328. Found: 473.2345; Anal. Calcd for $C_{30}H_{35}O_5$ [M + H]: 475.2485. Found: 475.2458.

1-C-*(2,3,6-Tri*-O-*benzyl*-α-D-*glucopyranosyl)propane* (**10**).—To a solution of **9** (0.56 g, 1.18 mmol), $NaCNBH_3$ (1.1 g) and 3 Å molecular sieves (5 g) in THF (20 mL) was added satd HCl–Et_2O solution at 0 °C until pH 3 was attained. The mixture was stirred for 2 h, at the end of which time the reaction was complete. The filtrate was diluted with EtOAc (150 mL), subsequently washed with aq $NaHCO_3$, water, dried, and concentrated. Purification on column chromatography (solvent D) afforded the debenzylidenated product (0.193 g, 42%) and **10** (0.274 g, 49%) as a syrup: $[\alpha]_D$ + 33° (*c* 0.45, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 0.934 (t, 3 H, $CH_2CH_2CH_3$, *J* 7.0 Hz), 1.280 and 1.477 (m and m, 1 H each, $CH_2CH_2CH_3$), 1.574 and 1.712 (m and m, 1 H each, $CH_2CH_2CH_3$), 2.698 (d, 1 H, 4-OH, *J* 2.0 Hz), 3.633–3.714 (m, 6 H, H-2,3,4,5,6,6′), 3.990 (m, 1 H, H-1), 4.562–4.878 (m, 6 H, 3 × CH_2Ph), 7.368–7.267 (m, 15 H, 3 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 13.94 ($CH_2CH_2CH_3$), 18.63 ($CH_2CH_2CH_3$), 27.73 ($CH_2CH_2CH_3$), 70.03 (C-6), 71.09 (C-4), 71.55 (C-5), 72.83 (CH_2Ph), 72.93 (C-1), 73.50 (CH_2Ph), 74.67 (CH_2Ph), 79.18 (C-2), 80.42 (C-3), 127.58–128.51, 138.05, 138.66 (3 × Ph) ppm. HRFABMS: Anal. Calcd for $C_{30}H_{36}O_5$ [M]: 476.2563. Found: 476.2526.

1-C-*(2,3,6-Tri*-O-*benzyl*-α-D-xylo-*hex-4-ulopyranosyl)propane* (**11**).—A solution of **10** (0.255 g, 0.536 mmol) in 2:1 Me_2SO–Ac_2O (4.5 mL) was kept at rt for 8 h. The solution was diluted with EtOAc (150 mL) and subsequently washed with aq $NaHCO_3$, water, dried, and concentrated. The residue was purified by chromatography (solvent D) to obtain **11** (0.23 g 90%) as a solid. Recrystallization from MeOH gave mp 91–92 °C, $[\alpha]_D$ + 67° (*c* 0.15, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 0.923 (t, 3 H, $CH_2CH_2CH_3$, *J* 7.0 Hz), 1.322 and 1.487 (m and m, 1 H each, $CH_2CH_2CH_3$), 1.616 and 1.745 (m and m, 1 H each, $CH_2CH_2CH_3$), 3.775 (dd, 1 H, H-6, $J_{6,6'}$ 10.0, $J_{5,6}$ 6.5 Hz), 3.803–3.850 (m, 2 H, H-2, 6′), 4.074 (m, 1 H, H-1), 4.190 (d, 1 H, H-3, $J_{2,3}$ 6.0 Hz), 4.281 (m, 1 H, H-5), 4.524–4.842 (m, 6 H, 3 × CH_2Ph), 7.266–7.373 (m, 15 H, 3 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 13.93 ($CH_2CH_2CH_3$), 18.85 ($CH_2CH_2CH_3$), 29.69 ($CH_2CH_2CH_3$), 68.42 (C-6), 73.11 (CH_2Ph), 73.26 (CH_2Ph), 73.50 (CH_2Ph), 74.15 (C-1), 77.72 (C-5), 81.05 (C-2), 82.30 (C-3), 127.61–128.43, 137.34, 137.82, 137.91 (3 × Ph), 205.01 (C-4) ppm. HRFABMS: Anal. Calcd for $C_{30}H_{34}O_5$ [M]: 474.2406. Found: 474.2442.

1-C-*(3,6-Di*-O-*benzyl-2-deoxy*-α-D-glycero-*hex-2-eno-4-ulopyranosyl)propane* (**12**) *and 1*-C-*(3,6-di*-O-*benzyl-2-deoxy*-β-L-glycero-*hex-2-eno-4-ulopyranosyl)propane* (**13**).—A solution of **11** (18 mg) in 10% Et_3N–MeOH (2 mL) was kept at rt for 4 h. The solvent was removed, and the residue was purified by preparative TLC (solvent D). Compounds **12** (3 mg, 17%) and **13** (8 mg, 44%) were obtained as major products. Small amounts of starting material **11** and ring-contraction product **14** were also obtained.

Data for **12**: R_f 0.62 (solvent D); $[\alpha]_D$ + 7.4° (*c* 0.24, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 0.935 (t, 3 H, $CH_2CH_2CH_3$, *J* 7.0 Hz), 1.344 and 1.438 (m and m, 1 H each, $CH_2CH_2CH_3$), 1.528 and 1.697 (m and m, 1 H each, $CH_2CH_2CH_3$), 3.794 and 3.908 (dd and dd, 1 H each, H-6,6′, $J_{6,6'}$ 11.0, $J_{5,6}$ 6.0, $J_{5,6'}$ 2.5 Hz), 4.474 (dd, 1 H, H-5), 4.560 (s, 2 H, CH_2Ph), 4.699 (m, 1 H, H-1), 5.846 (d, 1 H, H-2, $J_{1,2}$ 2.5 Hz), 4.877 (s, 2 H, CH_2Ph), 7.353–7.274 (m, 10 H, 2 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 13.90 ($CH_2CH_2CH_3$), 18.68 ($CH_2CH_2CH_3$), 36.59 ($CH_2CH_2CH_3$), 69.50 (C-6), 69.77 (CH_2Ph), 71.02 (C-1), 73.50 (CH_2Ph), 77.96 (C-5), 120.83 (C-2) 127.33–129.90, 135.83, 138.54 (2 × Ph), 147.39 (C-3), 190.35 (C-4) ppm. HRFABMS: Anal. Calcd for $C_{23}H_{25}O_4$ [M − H]: 365.1753. Found: 365.1835.

Data for **13**: R_f 0.59 (solvent D); $[\alpha]_D$ + 9.7° (*c* 0.29, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 0.945 (t, 3 H, $CH_2CH_2CH_3$, *J* 7.0 Hz), 1.397–1.484 (m, 2 H, $CH_2CH_2CH_3$), 1.610 and 1.686 (m and m, 1 H each, $CH_2CH_2CH_3$), 3.800 and 4.046 (dd and dd, 1 H each, H-6,6′, $J_{6,6'}$ 11.2, $J_{5,6}$ 7.0, $J_{5,6'}$ 2.0 Hz), 4.213 (d, 1 H, H-5), 4.449 (dd, 1 H, H-1), 4.600–4.906 (m, 4 H, 2 × CH_2Ph), 5.828 (s, 1 H, H-2), 7.273–7.361 (m,

10 H, 2 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 13.96 ($CH_2CH_2CH_3$), 18.15 ($CH_2CH_2CH_3$), 37.91 ($CH_2CH_2CH_3$), 68.99 (C-6), 69.82 (CH_2Ph), 73.46 (C-1), 73.63 (CH_2Ph), 81.19 (C-5), 120.34 (C-2), 127.33–128.62, 135.82, 138.16 (2 × Ph), 148.34 (C-3), 190.21 (C-4) ppm. HRFABMS: Anal. Calcd for $C_{23}H_{25}O_4$ [M − H]: 365.1753. Found: 365.1778.

*(±)-2-Benzyloxy-*c*-5-benzyloxymethyl-5-hydroxy-*r*-4-propylcyclopent-2-enone* (**14**).—A solution of **11** (19 mg) in 10% Et_3N–MeOH (2 mL) was kept at rt for 4 days. The solvent was evaporated, and separation on preparative TLC (solvent D) furnished three compounds, **12** (2.4 mg, 13%), **13** (5.3 mg, 27%), and **14** (10.8 mg, 55%).

Data for **14**: R_f 0.41 (solvent D); $[\alpha]_D$ 0° (*c* 0.4, EtOAc). ^{1}H NMR ($CDCl_3$): δ_H 0.939 (t, 3 H, $CH_2CH_2CH_3$, *J* 7.0 Hz), 1.314 and 1.399 (m, 2 H, $CH_2CH_2CH_3$), 1.654–1.721 (m, 2 H, $CH_2CH_2CH_3$), 2.722 (dt, 1 H, H-1, *J* 7.5, $J_{1,2}$ 2.0 Hz,), 3.063 (s, OH), 3.521 (s, 2 H, H-6), 4.490 (s, 2 H, CH_2Ph), 4.944 and 4.981 (d and d, 1 H each, CH_2Ph, *J* 12.0 Hz), 6.282 (d, 1 H, H-2), 7.352–7.275 (m, 10 H, 2 × Ph) ppm; ^{13}C NMR ($CDCl_3$): δ_C 14.11 ($CH_2CH_2CH_3$), 21.08 ($CH_2CH_2CH_3$), 30.67 ($CH_2CH_2CH_3$), 45.76 (C-1), 71.38 (CH_2Ph), 71.93 (C-6), 73.60 (CH_2Ph), 78.71 (C-5), 127.54–128.57, 129.80 (C-2), 135.54 (Ph), 137.52 (Ph), 153.67 (C-3), 202.26 (C-4) ppm. HRFABMS: Anal. Calcd for $C_{23}H_{27}O_4$ [M + H]: 367.1910. Found: 367.1964.

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References

1. Collins, P.; Djuric, S. W. *Chem. Rev.* **1993**, *93*, 1533–1564.
2. (a) Borthwick, A. D.; Biggadike, K. *Tetrahedron* **1992**, *48*, 571–623;
   (b) Marien, C. L.; Esmans, E. L.; Lemiere, F.; Dommisse, R. A. *Synth. Commun.* **1997**, *27*, 205–224.
3. (a) McCurry, P. M.; Singh, R. K. J. *J. Org. Chem.* **1974**, *39*, 2316–2317;
   (b) Ong, C. W.; Chen, C. M.; Juang, S. H. *J. Org. Chem.* **1994**, *59*, 7915–7916;
   (c) Denmark, S. E.; Jones, T. K. *J. Am. Chem. Soc.* **1982**, *104*, 2642–2645.
4. (a) Schore, N. E. *Org. React.* **1991**, *40*, 1–90;
   (b) Cadierno, V.; Pilar Gamasa, M.; Gimeno, J.; Moreto, J. M.; Ricart, S.; Roig, A.; Molins, E. *Organometallics* **1998**, *17*, 697–706;
   (c) Belanger, D. B.; O'Mahony, D. J. R.; Livinghouse, T. *Tetrahedron Lett.* **1998**, *39*, 7637–7640;
   (d) Hanzawa, Y.; Kakuuchi, A.; Yabe, M.; Narita, K.; Tabuchi, N.; Taguchi, T. *Tetrahedron Lett.* **2001**, *42*, 1737–1740;
   (e) Takahashi, T.; Huo, S.; Hara, R.; Noguchi, Y.; Naka-Jima, K.; Sun, W.-H. *J. Am. Chem. Soc.* **1999**, *121*, 1094–1095;
   (f) Kondo, T.; Nakamura, A.; Okada, T.; Suzuki, N.; Wada, K.; Mitsudo, T. *J. Am. Chem. Soc.* **2000**, *122*, 6319–6320;
   (g) Trost, B. M.; Pinkerton, A. B. *Org. Lett.* **2000**, *2*, 1601–1603;
   (h) Morisaki, Y.; Kondo, T.; Mitsudo, T. *Org. Lett.* **2000**, *2*, 949–952;
   (i) Molins, E. *Organometallics* **1998**, *17*, 697–706;
   (j) Periasamy, M. *Organometallics* **1996**, *15*, 442–445.
5. (a) Takahashi, T.; Li, Y.; Tsai, F.-Y.; NakaJima, K. *Organometallics* **2001**, *20*, 595–597;
   (b) Takeda, K.; Ohtani, Y.; Ando, E.; FuJimoto, K.; Yoshii, E.; Koizumi, T. *Chem. Lett.* **1998**, *11*, 1157–1158;
   (c) Takeda, K.; Nakayama, I.; Yoshii, E. *Synlett* **1994**, *3*, 178.
6. (a) Paquette, L. A.; Gallou, F.; Zhao, Z.; Young, D. G.; Liu, J.; Yang, J.; Friedrich, D. *J. Am. Chem. Soc.* **2000**, *122*, 9610–9620;
   (b) Toru, T. *J. Org. Chem.* **1998**, *63*, 3899–3904.
7. (a) Armstrong, A.; Hayter, B. R. *Tetrahedron: Asymmetry* **1997**, *8*, 1677–1684;
   (b) Kuhn, C.; Florent, J.-C. *Tetrahedron Lett.* **1998**, *39*, 4247–4250.
8. Pozsgay, V.; Jennings, H. J. *Synthesis* **1990**, 724–726.
9. (a) Bombard, S.; Maillet, M.; Capmau, M.-L. *Carbohydr. Res.* **1995**, *275*, 433–440;
   (b) Marron, T. G.; Woltering, T. J.; Weitz-Schmidt, G.; Wong, C.-H. *Tetrahedron Lett.* **1996**, *37*, 9037–9040;
   (c) McDevitt, J. P.; Lansbury, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 3818–3828.
10. Jones, G. H.; Moffatt, J. G. *Methods Carbohydr. Chem.* **1972**, *6*, 315–322.
11. Nonaka, C.-I.; Ishimaru, K.; Mihashi, K.; Iwase, Y.; Ageta, M.; Nishioka, I. *Chem. Pharm. Bull.* **1988**, *36*, 857–869.
12. Garegg, P. J.; Hultberg, H.; Wallin, S. *Carbohydr. Res.* **1982**, *108*, 97–101.