ELSEVIER

www.elsevier.com/locate/carres

Carbohydrate Research 335 (2001) 71–90

CARBOHYDRATE RESEARCH

Synthesis and transformations of new annulated pyranosides using the Pauson–Khand reaction

José Marco-Contelles,* Juliana Ruiz-Caro

Laboratorio de Radicales Libres (CSIC), Instituto de Química Organica General, C/Juan de la Cierva 3, ES-28006 Madrid, Spain

Received 21 May 2001; accepted 17 June 2001

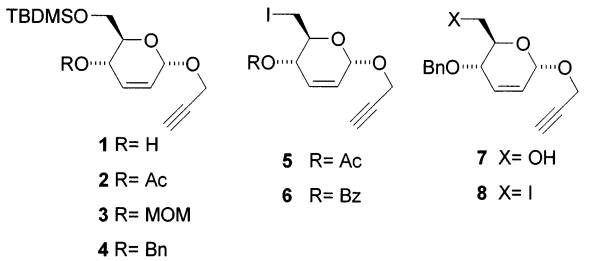
Abstract

The synthesis and transformations of new annulated pyranosides are described. These adducts were prepared by Pauson–Khand reaction on differently functionalized prop-2-ynyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides (**1**–**8**). Compound **1** with a free hydroxyl group at C-4 afforded significant amounts of the hydrogenolysis product **12** in addition to the normal adduct **13**. The C-4 *O*-protected similar precursors (**2**–**8**) gave PK products in yields ranging from 39 to 63%. Pauson–Khand adduct **19** provided intermediate **23** after selective manipulation. The oxidation plus decarbonylation synthetic sequence applied to intermediate **23** gave a poor yield of compound **24** using Wilkinson's catalyst. The *t*-butyl hydroperoxide promoted decarbonylation of product **23** afforded formate **25** in a typical Baeyer–Villiger rearrangement. The Ferrier-II reaction on intermediate **45**, readily available from compound **9**, afforded the hydrindane-type derivative **46** in 34% yield using a Ferrier-II type reaction.

Keywords: Annulated pyranosides; Pauson–Khand reaction; Carbocycles by Ferrier-II reaction; Hanessian–Hullar transformation

1. Introduction

Previous studies in our laboratory have been concerned with the development of new synthetic routes to polycyclic hydrocarbons from carbohydrates via free radical cyclization strategies.[1,2] Simultaneously we have examined the preparation of annulated pyranosides via Pauson–Khand (PK) reaction[3–5] on prop-2-ynyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides. This protocol has resulted in the synthesis of a series of molecules with the perhydro 1,7-dioxacyclopent[*cd*]indene skeleton (**A**) (Scheme 1), whose careful and controlled transformation has afforded adducts of type (**B**).[6–9] These compounds are promising candidates for the synthesis of molecules with the cyclopenta[*c*]pyran skeleton (**C**) found in

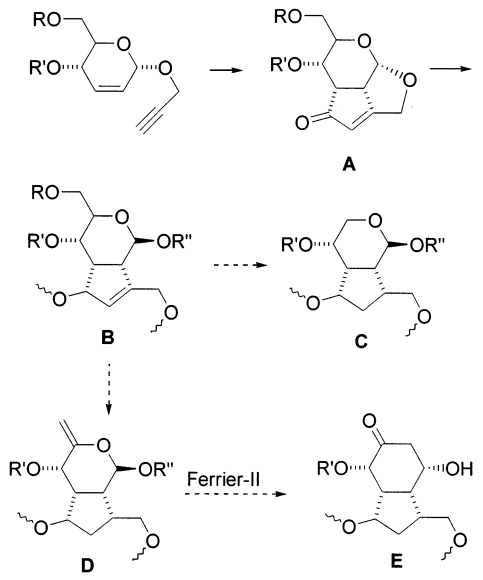


Scheme 1. Possible synthetic strategies for the transformation of adducts of type **B**.

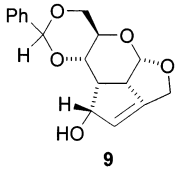
* Corresponding author. Tel.: +34-91-5622900; fax: +34-91-5644853.

E-mail address: iqoc21@iqog.csic.es (J. Marco-Contelles).

0008-6215/01/$ - see front matter
PII: S0008-6215(01)00211-7



Scheme 2. Precursors for the Pauson–Khand reaction.



Scheme 3. Precursor for the Hanessian–Hullar reaction.

the natural products known as iridoids,[10] and for the synthesis of the biologically interesting hydrindanes (**E**).[11]

In this paper we describe our results on the oxidation and decarbonylation strategy for the synthesis of compounds of type **C** from conveniently functionalized intermediates (**B**), and the synthesis of compounds of type **E** from annulated pyranosides of type **D** via Ferrier-II reaction.[12]

Critical to this approach is the success of the cobalt-promoted cycloannulation of precursors **1**–**8** (Scheme 2) and the selective manipulation of PK adduct **9** (Scheme 3).[9]

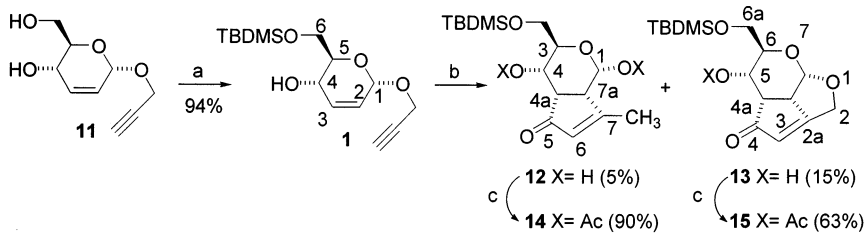
2. Results and discussion

In order to implement the oxidation and decarbonylation strategy for the synthesis of compounds of type **C** from products with structure **B** (Scheme 1), we designed precursors (**1**–**4**) (Scheme 2) with protecting groups at the primary hydroxyl group after which the PK reaction could be easily removed in order to attack the oxidation and the decarbonylation protocol.

The synthesis of precursor **1**[13] was accomplished in high yield by using standard silylation conditions from known diol **11**[8] (Scheme 4) prepared from 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-*arabino*-hex-1-enitol tri-*O*-acetyl-D-glucal (**10**).

All new compounds showed excellent analytical and spectroscopic values (see Tables 1 and 2 for the ^{1}H and ^{13}C NMR data of compounds **2**–**8**, **26**, **27** and **29**).

The PK reaction of substrate **1** afforded a mixture of compounds **12** and **13**[13] in low combined chemical yield (Scheme 4). Compound **12** was isolated as a diastereomerically pure α anomer and the absolute configuration at C-1 was established in its derivative **14** by analysis of the ^{1}H NMR spectrum which showed an nOe effect between proton H-1 (a broad singlet at 6.18 ppm) and H-7a (3.46 ppm, br d, $J_{7a,4a}$ 6.0 Hz). Consequently, product **12** is the product of the partial hydrogenolysis of the O–C(2) bond in product **13**, with retention of the configuration at C-7a. This is a rather unusual reactivity on PK reactions, already reported by Russian researchers,[14] that we have also occasionally observed in other prop-2-ynyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides with a free hydroxyl group at C-4.[8]



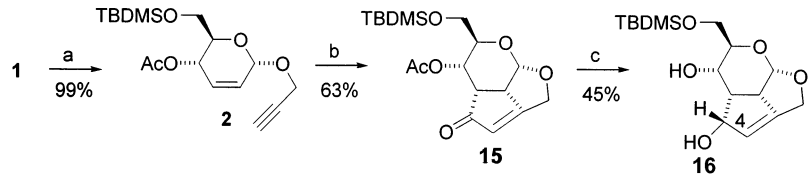
Scheme 4. Synthesis and Pauson–Khand reaction of precursor **1**. Reagents: (a) ClTBDMS, imidazole, DMAP, CH_2Cl_2; (b) (i) $Co_2(CO)_8$; (ii) $NMO{\cdot}H_2O$; (c) Ac_2O, py, rt.

Table 1
^{1}H NMR (300 MHz, $CDCl_3$) data (δ) for 2,3-dideoxy-α-D-*erythro*-2-hex-2-enopyranosides (**2**–**8**, **26**–**29**)

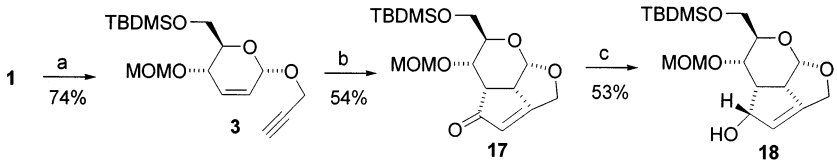
	H-1	H-2	H-3	H-4	H-5	H-6	H-6′	H-7	H-7′	H-9	$OSiMe_2CMe_3$
2	5.23, br s	5.92, br d, $J_{2,3}$ 10.3	5.87, dt, $J_{1,3} = J_{3,4}$ 2.2	5.29, dm, $J_{4,5}$ 9.5	3.93, ddd, $J_{5,6}$ 5.3, $J_{5,6'}$ 2.7	3.77, dd, $J_{6,6}$ 11.4	3.72, dd	4.32, d, $J_{7,9}$ 2.3		2.44, t	0.07, 0.91
3	5.17, br s	6.06, br d, $J_{2,3}$ 10.2	5.75, dt, $J_{1,3} = J_{3,4}$ 2.2	4.15, dd, $J_{4,5}$ 9.5	3.88–3.73, m			4.30, d, $J_{7,9}$ 2.3		2.42, t	0.08, 0.90
4	5.23, m	6.13, br d, $J_{2,3}$ 10.3	5.81, ddd, $J_{1,3}$ 2.6, $J_{3,4}$ 1.7	4.11, dd, $J_{4,5}$ 8.6	3.97–3.72, m			4.34, d, $J_{7,9}$ 2.4		2.46, t	0.14, 0.97
5	5.27, br s	5.90–5.79		5.17, dm, $J_{4,5}$ 9.0	3.90, dt, $J_{5,6}$ 9.0, $J_{5,6'}$ 2.4	3.40, dd, $J_{6,6'}$ 10.9	3.17, dd	4.50, dd, $J_{7,7'}$ 15.8, $J_{7,9}$ 2.4	4.41, dd, $J_{7',9}$ 2.4	2.48, t	
6	5.32, s	5.97, dt, $J_{2,3}$ 10.2, J 1.1	5.86, ddd, $J_{1,3}$ 2.0, $J_{3,4}$ 2.7	5.44, dq, $J_{4,5}$ 9.0, J 1.6	4.08, dt, $J_{5,6}$ 9.0, $J_{5,6'}$ 2.5	3.45, dd, $J_{6,6'}$ 10.8	3.23, dd	4.52, dd, $J_{7,7'}$ 15.6, $J_{7,9}$ 2.4	4.45, dd, $J_{7',9}$ 2.4	2.48, t	
7	5.20, m	6.14, br d, $J_{2,3}$ 10.3	5.78, dt, $J_{1,3} = J_{3,4}$ 2.0	4.12, dm, $J_{4,5}$ 8.9	3.87, ddd, $J_{5,6}$ 5.1, $J_{5,6'}$ 2.6	3.88, dd, $J_{6,6'}$ 12.6	3.77, dd	4.30, d, $J_{7,9}$ 2.4		2.46, t	
8	5.22, br s	6.06, br d, $J_{2,3}$ 10.3	5.77, dt, $J_{1,3} = J_{3,4}$ 2.0	3.90, dq, $J_{4,5}$ 9.0, J 2.0	3.70, ddd, $J_{5,6}$ 7.3, $J_{5,6'}$ 2.4	3.55, dd, $J_{6,6'}$ 10.6	3.27, dd	4.44, dd, $J_{7,7'}$ 15.7, $J_{7,9}$ 2.4	4.37, dd, $J_{7',9}$ 2.4	2.44, t	
26	5.09, br s	5.94, br d, $J_{2,3}$ 10.2	5.70, dt, $J_{1,3} = J_{3,4}$ 2.5	4.17–4.10, m	3.78, ddd, $J_{5,6}$ 4.7, $J_{5,6'}$ 2.4, $J_{4,5}$ 9.5	4.31, dd, $J_{6,6'}$ 11.1	4.25, dd	4.18, d, $J_{7,9}$ 2.4		2.41, t	
27	5.14, m	5.85, br d, $J_{2,3}$ 10.3	5.77, dt, $J_{1,3}$ 1.8, $J_{3,4}$ 2.6	5.18, dq, $J_{4,5}$ 9.4, J 1.5	4.18–4.02, m		4.20, d, $J_{7,9}$ 2.4		2.43, t		
29	5.21, m	5.98, br d, $J_{2,3}$ 10.2	5.84, dt, $J_{1,3} = J_{3,4}$ 2.1	5.43, dq, $J_{4,5}$ 11.1, J 1.7	4.25–4.10, m		4.27, d, $J_{7,9}$ 2.4		2.46, t		

Table 2
^{13}C NMR (75 MHz, $CDCl_3$) data (δ) for 2,3-dideoxy-α-D-*erythro*-2-hex-2-enopyranosides (**2**–**8**, **26**–**29**)

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	$OSi(Me)_2C(Me)_3$
2	92.3	129.9	127.3	65.5	69.8	62.6	54.7	79.2	74.1	25.9, 18.4, −5.4, −5.5
3	92.4	132.3	125.9	69.5	70.9	62.4	54.5	79.4	74.3	25.8, 18.3, −5.3, −5.4
4	92.4	131.2	126.1	70.2	70.8	62.6	54.4	79.4	74.3	25.9, 18.3, −5.4, −5.3
5	92.7	129.4	127.5	69.6	69.1	5.1	55.4	79.1	74.9	
6	92.6	129.4	127.5	69.7	69.1	5.3	55.3	79.0	75.0	
7	92.9	131.1	125.9	70.1	70.0	62.1	54.9	79.4	74.6	
8	92.8	130.2	126.3	74.5	69.4	7.3	55.1	79.3	74.7	
26	92.6	133.4	125.8	63.1	70.0	69.0	54.9	79.1	74.7	
27	92.4	129.3	127.2	64.9	66.9	68.2	55.0	68.2	74.8	
29	92.6	129.3	127.4	65.3	67.2	58.3	55.2	79.0	74.9	



Scheme 5. Synthesis and Pauson–Khand reaction of precursor **2**. Reagents: (a) Ac_2O, py, rt; (b) (i) $Co_2(CO)_8$; (ii) $NMO{\cdot}H_2O$; (c) DIBALH, −78 °C, toluene.



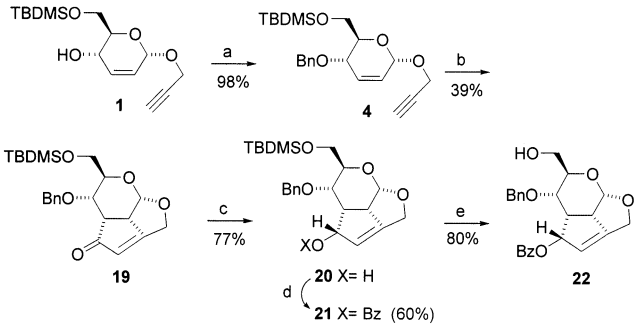
Scheme 6. Synthesis and Pauson–Khand reaction of precursor **3**. Reagents: (a) MOMCl, NaH, DMF, rt; (b) (i) $Co_2(CO)_8$; (ii) $NMO{\cdot}H_2O$; (c) DIBALH, −78 °C, toluene.

Prompted by this unsatisfactory result, we prepared a series of 4-*O*-protected enyne precursors. Acetylation of alcohol **1** gave **2** {^1H NMR: (δ) [($OCOCH_3$ (2.07, s); ^{13}C NMR: (δ) [OCO (170.3) CH_3 (21.0)]} (Scheme 5). The PK reaction on this molecule provided enone **15** in good yield. This product was identical to the compound previously isolated after acetylation of compound **13** (Scheme 4). The DIBALH-mediated reduction of ketone **15** gave diol **16** in moderate yield, but with high stereoselectivity, as only one isomer at C-4 was detected.[8]

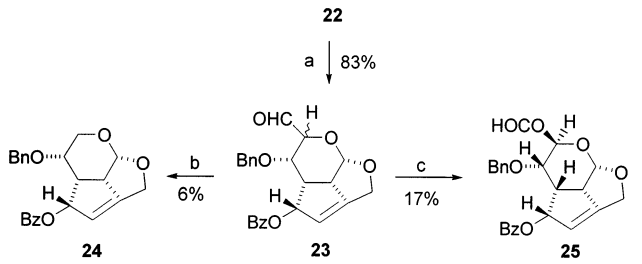
The synthesis of compound **3** {^1H NMR: (δ) [CH_3 (3.39) OCH_2 (4.73/4.69, d, d, *J* 7.0 Hz]; ^{13}C NMR: (δ) [CH_3 (55.6) OCH_2 (96.3)O)]} from precursor **1**, and the subsequent PK reaction have been carried out as shown in Scheme 6. The DIBALH reduction of ketone **17** in toluene afforded alcohol **18** in moderate yield.[8]

Compound **1** was transformed into precursor **4** {^1H NMR: (δ) [OCH_2 (4.70/4.58, d, d, *J* 11.6 Hz) C_6H_5 (7.43–7.29, m)]; ^{13}C NMR: (δ) [OCH_2 (70.7) C_6H_5 (138.1–127.6)]} by standard O-benzylation conditions. Subsequent PK reaction to give ketone **19** followed by DIBALH reduction and benzoylation of alcohol **20** afforded benzoate **21**, whose final desilylation gave free primary alcohol **22** in satisfactory yield (Scheme 7).

The oxidation of alcohol **22** using the Dess–Martin method[15] gave the aldehyde **23** in good yield (83%) (Scheme 8). This compound was isolated as a mixture of isomers in a 2:1 ratio which, without separation, were submitted to decarbonylation[16] using the Wilkinson's catalyst,[17–19] to give compound **24**



Scheme 7. Synthesis and Pauson–Khand reaction of precursor **4**. Reagents: (a) NaH, BnBr, Bu_4NF, THF; (b) (i) $Co_2(CO)_8$; (ii) $NMO{\cdot}H_2O$; (c) DIBALH, −78 °C, toluene; (d) ClBz, py, rt; (e) Bu_4NF, THF.



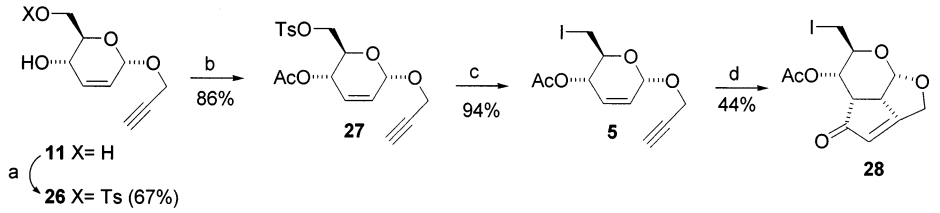
Scheme 8. Oxidation of compound **22** and decarbonylation of intermediate **23**. Reagents: (a) Dess–Martin; (b) $RhCl(PPh_3)_3$, toluene, rt; (c) t-Bu_2O_2, toluene, 110 °C.

in poor yield (6%). Reaction of **23** with t-butyl hydroperoxide[20] afforded the formate **25** in 17% yield. In the NMR spectra, we could detect a singlet at 8.05 ppm for *H*C(O)O and a signal at 160.1 ppm for H*C*(O)O. The absolute configuration at C-6 was tentatively assigned as *R* by inspection of the ^{1}H NMR spectrum which showed proton H-6 at 6.35 ppm as a doublet with a vicinal coupling constant (6.7 Hz) for an axial–equatorial arrangement of protons H-6 and H-5. A clear nOe effect between these protons confirmed this assignment. The formation of the diastereomerically pure formate **25** from the mixture of epimeric aldehydes **23** is the result of a Baeyer–Villiger reaction mediated by t-butyl hydroperoxide with retention of the configuration at C-6.[21]

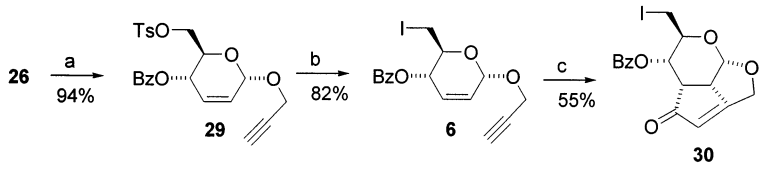
In order to implement the strategy for the synthesis of compounds **E** via intermediates **D** from compounds of type **B** (Scheme 1), three possibilities were faced for the synthesis of suitable iodide or bromide precursors: (i) Sodium iodide reaction with C-6–*O*-tosyl, prop-2-ynyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides, followed by PK reaction; (ii) the direct iodination of free C-6 hydroxy, prop-2-ynyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides, followed by PK reaction; and (iii) the Hanessian–Hullar (HH) transformation [22] on benzylidene derivatives.

In order to explore the first alternative, we prepared iodide **5** {^{1}H NMR: (δ) [$OCOCH_3$ (2.11, s)]; ^{13}C NMR: (δ) [OCO (170.2) CH_3 (21.0)]} from diol **11**[8] via intermediates **26** {^{1}H NMR: (δ) [CH_3 (2.42, s) C_6H_4 (7.79/7.33, d, d, J 8.5 Hz) OSO_2]; ^{13}C NMR: (δ) [(CH_3 (21.6) C_6H_4 (145.0–127.9) OSO_2)]} and **27** {^{1}H NMR: (δ) [CH_3 (2.43, s) C_6H_4 (7.77/7.33, d, d, J 8.3 Hz) OSO_2; $OCOCH_3$ (1.99)]; ^{13}C NMR: (δ) [(CH_3 (21.6) C_6H_4 (144.9–128.0) OSO_2); OCO (170.0) CH_3 (20.8)]}, as shown in Scheme 9. The PK reaction of precursor **5** afforded compound **28** in 44% yield.

A similar protocol starting from tosylate **26** afforded intermediate **29** {^{1}H NMR: (δ) [CH_3 (2.31, s) C_6H_4 (7.73/7.20, d, d, J 8.3 Hz) OSO_2; $OCOC_6H_5$ (7.91–7.43)]; ^{13}C NMR: (δ) [(CH_3 (21.6) C_6H_4 (144.9–128.0) OSO_2; OCO (165.4) C_6H_5 (144.9–128.4)]}, which was transformed into precursor **6** {^{1}H NMR: (δ) [$OCOC_6H_5$ (8.02–7.45, m)]; ^{13}C NMR: (δ) [OCO (165.6) C_6H_5 (133.5–128.4)]}, whose PK reaction gave adduct **30** in 55% yield (Scheme 10).



Scheme 9. Synthesis and Pauson–Khand reaction of precursor **5**. Reagents: (a) ClTs, py; (b) Ac_2O, py, rt; (c) NaI, DMF; (d) (i) $Co_2(CO)_8$; (ii) $NMO{\cdot}H_2O$.



Scheme 10. Synthesis and Pauson–Khand reaction of precursor **6**. Reagents: (a) ClBz, py; (b) NaI, DMF; (c) (i) $Co_2(CO)_8$; (ii) $NMO{\cdot}H_2O$.

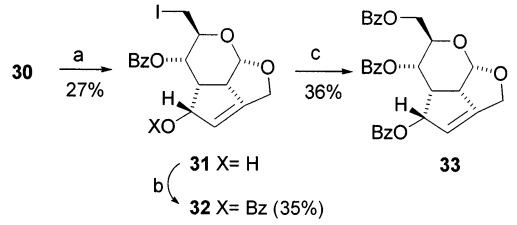
We used this intermediate for the synthesis of a suitable Ferrier-II reaction precursor as follows. The reaction of compound **30** with DIBALH followed by benzoylation of alcohol **31** gave iodide **32**. The reaction of this compound with silver fluoride[23] in pyridine did not afford the desired enol-ether, but the unexpected perbenzoate **33** (Scheme 11).

In view of this result, we prepared the analogous intermediate **37** (Scheme 13) from precursor **8** (Scheme 1) as follows. Desilylation (90%) of compound **4** gave alcohol **7** {^{1}H NMR: (δ) [OCH_2 (4.69/4.56, d, d, J 11.6 Hz) C_6H_5 (7.48–7.27, m), OH (2.11, br s)]; ^{13}C NMR: (δ) [OCH_2 (71.0) C_6H_5 (137.8–127.8)]} (Scheme 12). The PK reaction of precursor **7** afforded adduct **34** in 47% yield.

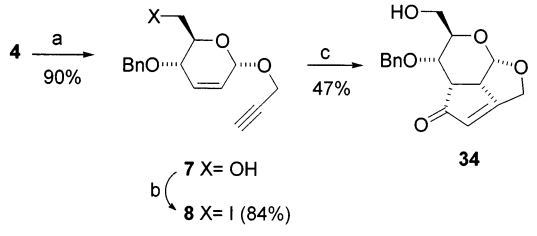
Iodination of **7** under Garegg's conditions[24] provided compound **8** {^{1}H NMR: (δ) [OCH_2 (4.69/4.54, d, d, J 11.6 Hz) C_6H_5 (7.39–7.30, m)]; ^{13}C NMR: (δ) [OCH_2 (70.9) C_6H_5 (137.5–127.9)]} (Scheme 12), whose PK reaction gave adduct **35** in 55% yield (Scheme 13). Unfortunately, the benzoylated derivative **37**, prepared from the alcohol **36**, afforded the useless derivative **38**, under silver fluoride reaction.[23]

Finally, we tested the benzylidene approach. We started with precursor **9** (Scheme 3), a compound recently described by us.[9] Hydrolysis with methanol in mild acid conditions gave the intermediate **39** (71% yield) and the fully deprotected tetrol **40** (11%). Diol **39** gave perbenzoate **41** in convenient chemical yield. All these compounds showed excellent analytical and spectroscopic data, in good agreement with these structures (Scheme 14).

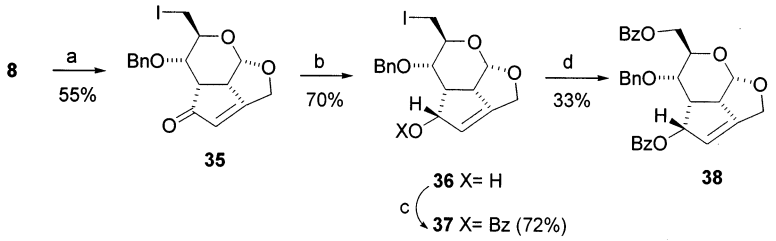
The HH reaction of compound **41** gave the expected benzoate/bromide **42** in moderate yield (Scheme 15). We then submitted benzoate **42** to the elimination conditions described by Chrétien (sodium hydride in DMF),[25] but a complex reaction resulted. The use of silver fluoride[23] for the same purpose gave a mixture of product **44** (18%) and the desired molecule **45** in very poor yield (3%). The use of iodide **43** in the same experimental conditions gave enol-ether **45** in 30% yield (Scheme 15). The reaction of this compound with mercuric chloride in acetone at reflux[12] gave compound **46** in 34% yield. In the ^{1}H NMR spectrum of compound **46**, we could observe signals for a methylene group [$C(6)H_2$] at 2.93 and 2.84 ppm, as doublets of doublets, a signal at 4.52–4.49 ppm for H–C(7)–OH (m) and H-7a, at 3.37 ppm showing a vicinal coupling constant with H-7 equal to 4.0 Hz, a typical value for an axial–equatorial orientation of protons, suggesting that the hydroxyl group at C-7 is α located. In the ^{13}C



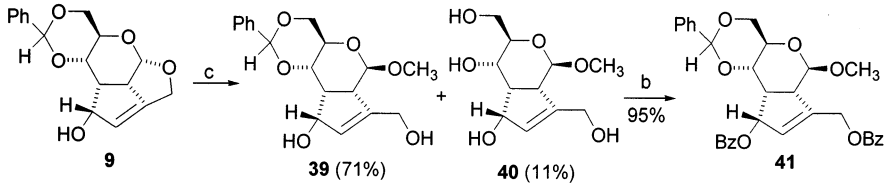
Scheme 11. Reduction of intermediate **30**. Reagents: (a) DIBALH, −78 °C, THF; (b) ClBz, py, rt; (c) AgF, py, 100 °C.



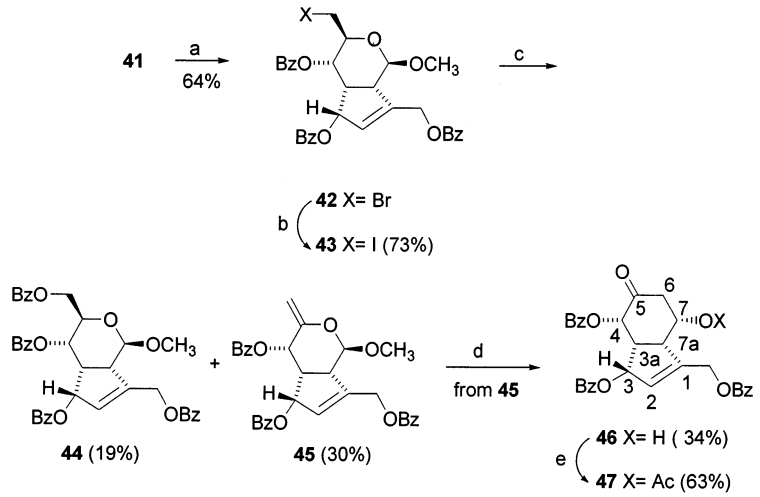
Scheme 12. Synthesis and PK reaction of precursor **7**. Reagents: (a) Bu_4NF, THF; (b) I_2, Ph_3P, imidazole, (c) (i) $Co_2(CO)_8$; (ii) $NMO{\cdot}H_2O$.



Scheme 13. Pauson–Khand reaction of precursor **8**. Reagents: (a) (i) $Co_2(CO)_8$; (ii) $NMO{\cdot}H_2O$; (b) DIBALH, −78 °C, toluene; (c) ClBz, py; (d) AgF, py.



Scheme 14. Transformations of precursor **9**. Reagents: (a) MeOH, *p*-TsOH; (b) (from **39**) ClBz, py, rt.



Scheme 15. Synthesis and Ferrier-II reaction of intermediate **45**. Reagents: (a) NBS, $BaCO_3$, CCl_4; (b) NaI, ethylmethylketone; (c) AgF, py [from **42**:**44** (18%) and **45** (3%); from **43**:**44** (19%) and **45** (30%)]; (d) (from **45**) $HgCl_2$, acetone, reflux; (e) Ac_2O, py, rt.

NMR spectrum, we observed signals for CO (201.7 ppm), C-6 (42.6 ppm) and C-7 (68.4 ppm). The formation of product **46** is noteworthy because this is the first example of a Ferrier-II type reaction on a cyclopentaneannulated methyl 5,6-enopyranoside.

In summary, we conclude that the synthesis of hydrindene derivatives from carbohydrates following the HH protocol plus Ferrier-II reaction is possible, but the yields were low. Work is now in progress in our laboratory in order to improve these results, and will be reported in due course.

3. Experimental

General methods.—Reactions were monitored by TLC using precoated silica gel aluminum plates containing a fluorescent indicator (E. Merck, 5539). Detection was done by UV (254 nm) followed by charring with H_2SO_4–AcOH spray, 1% aq $KMnO_4$ solution or 0.5% phosphomolybdic acid in 95% EtOH. Anhydrous Na_2SO_4 was used to dry organic solutions during work-ups and the removal of solvents was carried out under vacuum with a rotary evaporator. Flash-

column chromatography was performed using Silica Gel 60 (230–400 mesh, E. Merck) and hexane–EtOAc mixtures as eluent unless otherwise stated. ^1H spectra were recorded with a Varian VXR-300(400)S spectrometers, using tetramethylsilane as internal standard and ^{13}C NMR spectra were recorded with a Bruker WP-200-SY. Values with (*) can be interchanged.

General method for the Pauson–Khand reaction.—To a solution of the corresponding precursor in dry CH_2Cl_2 (0.025 M), under Ar and at rt, Co_2CO_8 (1.1 equiv) was added and the mixture was stirred until complete reaction ($\sim$30 min). Then the mixture was cooled at 0 °C and commercially available $NMO{\cdot}H_2O$ (6.3 equiv) was added in one pot. After 3 h at rt, the crude was filtered over Celite 545, washed with CH_2Cl_2, and the solvent was evaporated under diminished pressure. The residue was purified by flash chromatography eluting with hexane–EtOAc mixtures.

General method for acetylation.—The compound was treated with a mixture of 1:1 Ac_2O–pyridine at rt overnight. The solvent was evaporated and the residue was submitted to chromatography.

General method for benzoylation.—The compound was dissolved in dry pyridine (0.1 M), cooled in an ice bath, under Ar and stirring. Recently distilled BzCl (1.1 equiv) was slowly added. The mixture was stirred at rt overnight. The solvent was evaporated and the residue was diluted with EtOAc, washed with diluted HCl, brine, dried, filtered, evaporated, and the residue was submitted to chromatography.

General method for oxidation (Dess–Martin).—To a solution of the alcohol, in dry CH_2Cl_2 (0.28 M), a commercially available solution of the Dess–Martin reagent (1.1 equiv) in CH_2Cl_2 (0.06 M) was added, and the mixture was stirred at rt for 6 h. Then the reaction was diluted with Et_2O and aq NaOH (1.3 M) was incorporated. The mixture was stirred for 10 min, and the organic phase was separated, washed with brine, dried, filtered, evaporated, and the residue was submitted to chromatography.

General method for desilylation reactions.—The compound was dissolved in dry THF (0.14 M) and treated with tetrabutylammonium fluoride (3 equiv) at rt for 24 h. The solvent was eliminated and the residue submitted to chromatography to give the product.

General method for the synthesis of iodides from tosylates/bromides.—The compound was dissolved in dry DMF, treated with NaI (12 equiv) and warmed at 80 °C for 6 h. The mixture was diluted with EtOAc, washed with a 10% aq sodium thiosulfate solution and brine. The organic layer was dried, filtered, evaporated and the residue was submitted to chromatography.

General method for the iodination of alcohols.—To a solution of the alcohol in dry toluene, triphenylphosphine (3 equiv), imidazole (3 equiv) and iodine (2 equiv) were added, and the mixture was heated at reflux for 10 min. Then, the mixture was diluted with an aq satd $NaHCO_3$ solution and a 5% aq $Na_2S_2O_3$ solution. The organic layer was dried, filtered and evaporated. The residue was submitted to chromatography.

General method for tosylation.—The compound, dissolved in dry pyridine, cooled in an ice bath, under Ar, was treated with *p*-toluenesulfonyl chloride (1.1 equiv) and a catalytic amount of DMAP. The mixture was stirred for 6 h until complete reaction. The solvent was removed and the residue was dissolved in EtOAc, washed with brine, dried, filtered, evaporated, and the residue was submitted to chromatography.

General method for acetal mediated acid hydrolysis.—The compound was dissolved in MeOH (0.093 M), cooled at −78 °C and treated with *p*-TsOH (cat.). The reaction was warmed at 0 °C, and after complete reaction, solid $NaHCO_3$ was added, the suspension was filtered, the solvent was eliminated and the residue was submitted to chromatography.

General method for O-benzylation.—The compound, dissolved in dry THF or DMF (0.2 M), under Ar and at 0 °C, was treated with sodium hydride (1.5 equiv, 60% dispersion in oil), a catalytic amount of tetrabutylammonium iodide and BnBr (1.1 equiv). After stirring at rt for 15 h, the reaction was complete and some drops of AcOH were added. Then the mass was filtered over Celite. The solvent was evaporated, diluted with wa-

ter, extracted with CH_2Cl_2 several times, and washed with brine. The organic layer was dried, filtered, and evaporated. Flash chromatography gave the benzylated compound.

General method for the reduction with DIBALH.—The ketone was dissolved in dry THF or in toluene (0.092 M) and cooled at −78 °C under Ar. DIBALH (1.1 equiv, 1.0 M in toluene) was added and stirred at this temperature. After 3 h, more DIBALH (1.9 equiv) was added. When the reaction was complete (TLC), MeOH was added to destroy the excess of reagent and the mixture was warmed at rt. The suspension was filtered, washed with toluene and evaporated. The crude reaction mixture was submitted to chromatography.

General method for the elimination of halides (Br/I) with AgF.—To a solution of the compound in dry pyridine (0.15 M), AgF (1.5 equiv) was added and the mixture was heated at 100 °C. After complete reaction, the mixture was cooled, diluted with CH_2Cl_2, filtered, concentrated, and purified by chromatography.

General method for the Hanessian–Hullar reaction.—To a solution of compound in dry CCl_4 (0.055 M) at reflux, NBS (1.1 equiv) and $BaCO_3$ (0.42 equiv) were added. After 90 min, the mixture was cooled, filtered, diluted with CH_2Cl_2, and extracted with brine. The organic phase was separated, dried (Na_2SO_4), filtered, evaporated, and submitted to chromatography to give the product.

Prop-2-ynyl 2,3-dideoxy-6-O-[(1,1-dimethylethyl)dimethylsilyl]-α-D-erythro-hex-2-enopyranoside (**1**).—To a solution of diol **11**[8] (2.03 g, 0.011 mmol) in dry CH_2Cl_2 (0.12 M), cooled at 0 °C, under Ar, *t*-butyldimethylsilyl chloride (1 equiv), imidazole (1.1 equiv) and 4-dimethylaminopyridine (cat.) were added. The mixture was warmed at rt and stirred for 8 h, diluted with CH_2Cl_2, washed with an aq satd solution of $NaHCO_3$ and brine. The organic phase was dried, filtered, and the solvent was removed. The crude product was submitted to chromatography (4:1 hexane–EtOAc) to give product **1** (3.08 g, 94%), which showed physical and spectroscopic data identical to those described for this compound in literature.[13]

Pauson–Khand reaction of precursor **1**.—Following the 'General method for the Pauson–Khand reaction', enyne **1** (170 mg, 0.57 mmol) afforded products **12** (10 mg, 5%) and **13** (28 mg, 15%) after chromatography (from hexane to 3/2 hexane–EtOAc). Following the 'General method for acetylation', **12** (3 mg, 0.009 mmol), gave product (1*R*,3*R*,4*S*,4a*S*,7a*S*)-1,4-bis-acetoxy-3-[((1,1-dimethylethyl)dimethylsilyloxy)methyl]-7-methyl-3,4,4a,7a-tetrahydro-cyclopenta[*c*]pyran-5(1*H*)-one (**14**, 3 mg, 90%) after chromatography (17:3 hexane–EtOAc): oil; $[\alpha]_D^{25}$ +5° (*c* 0.06, $CHCl_3$); IR (film) *ν* 2930, 2857, 1747, 1700, 1625, 1372, 1234, 837 cm^{-1}; ^1H NMR ($CDCl_3$): *δ* 6.18 (s, 1 H, H-1), 5.95 (t, *J* 1.6 Hz, 1 H, H-6), 5.10 (ddd, $J_{3,4}$ 7.9, $J_{3,3a}$ 5.5, $J_{3,3a'}$ 3.3 Hz, 1 H, H-3), 4.44 (dd, $J_{4,3}$ 7.9, $J_{4,4a}$ 2.1 Hz, 1 H, H-4), 3.83 (dd, $J_{3a',3a}$ 11.2, $J_{3a',3}$ 3.3 Hz, 1 H, H-3a′), 3.72 (dd, $J_{3a,3a'}$ 11.2, $J_{3a,3}$ 5.5 Hz, 1 H, H-3a), 3.46 (br d, $J_{7a,4a}$ 6.0 Hz, 1 H, H-7a), 3.06 (dd, $J_{4a,7a}$ 6.0, $J_{4a,4}$ 2.1 Hz, 1 H, H-4a), 2.25 (s, 3 H, CH_3), 2.18, 2.15 (2 × $OCOCH_3$), 0.88 [s, 9 H, $(CH_3)_2SiC(CH_3)_3$], 0.07 [s, 6 H, $(CH_3)_2SiC(CH_3)_3$]; MS (70 eV): *m/z* 355 (50), 295 (64), 253 (100), 235 (49), 161 (64), 117 (87), 75 (50). Anal. Calcd for $C_{20}H_{32}O_7Si$: C, 58.23; H, 7.82. Found: C, 58.35; H, 7.53. Following the 'General method for acetylation', **13**[13] (17.6 mg, 0.054 mmol) gave (4a*S*,5*S*,6*R*,7a*S*,7b*S*)-5-(acetoxy)-6-[((1,1-dimethylethyl)dimethylsilyloxy)-methyl]-5,6,7a,7b-tetrahydro-2*H*-1,7-dioxacyclopent[cd]inden-4(4aH)-one (**15**, 13 mg, 63%) after chromatography (4:1 hexane–EtOAc): oil; $[\alpha]_D^{25}$ −67° (*c* 0.75, $CHCl_3$); IR (KBr) *ν* 2930, 2857, 1748, 1720, 1651, 1372, 1233, 1137, 1044, 1015 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 6.21 (br s, 1 H, H-3), 5.63 (d, $J_{7a,7b}$ 6.5 Hz, 1 H, H-7a), 5.11 (dd, $J_{5,6} = J_{5,4a}$ 9.4 Hz, 1 H, H-5), 4.85 (dt, $J_{2',2}$ 15.3, *J* 1.4 Hz, 1 H, H-2′), 4.67 (dt, $J_{2,2'}$ 15.3, *J* 2.0 Hz, 1 H, H-2), 3.76 (dd, $J_{6a,6a'}$ 11.4, $J_{6a',6}$ 2.5 Hz, 1 H, H-6a′), 3.70 (dd, $J_{6a,6a'}$ 11.4, $J_{6a,6}$ 2.5 Hz, 1 H, H-6a), 3.64 (dt, $J_{6,5}$ 9.4, $J_{6,6a} = J_{6,6a'}$ 2.5 Hz, 1 H, H-6), 3.52 (dd, 1 H, $J_{7b,4a}$ 8.9, $J_{7b,7a}$ 6.5 Hz, 1 H, H-7b), 3.45–3.40 (m, 1 H, H-4a), 2.07 (s, 3 H, $OCOCH_3$), 0.86 [s, 9 H, $(CH_3)_2SiC(CH_3)_3$], 0.03 [s, 6 H, $(CH_3)_2SiC(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 206.2 (C-4), 181.0 (C-2a), 169.9 ($OCOCH_3$), 126.1 (C-3), 96.5

(C-7a), 70.1 (C-6), 65.9 (C-2), 65.8 (C-5), 62.4 (C-6a), 47.9 (C-4a), 46.3 (C-7b), 25.8 [$(CH_3)_2SiC(CH_3)_3$], 20.8 ($OCOCH_3$), 18.2 [$(CH_3)_2SiC(CH_3)_3$], −5.5, −5.6 [2 C, $(CH_3)_2SiC(CH_3)_3$]; MS (70 eV): *m*/*z* 309 (45), 251 (87), 223 (50), 195 (44), 177 (46), 129 (46), 117 (100), 75 (97), 43(77). Anal. Calcd for $C_{18}H_{28}O_6Si$: C, 58.67; H, 7.66. Found: C, 58.55; H, 7.43.

*Prop-2-ynyl 4-*O*-acetyl-2,3-dideoxy-6-*O*-[(1,1-dimethylethyl)dimethylsilyl]-α-*D*-erythro-hex-2-enopyranoside* (**2**).—Following the 'General method for acetylation', **1** (1.23 g, 4.12 mmol) afforded acetate **2** (1.40 g, 99%) after chromatography (9:1 hexane–EtOAc): oil; $[\alpha]_D^{25}$ +158° (*c* 2.44, $CHCl_3$); IR (KBr) *ν* 1742, 1372, 1235, 1127, 1094, 1038, 837, 778 cm^{-1}; MS (70 eV): *m*/*z* 223 (16), 117(100), 89 (16), 75 (25), 43(24). Anal. Calcd for $C_{17}H_{28}O_5Si$: C, 59.97; H, 8.29. Found: C, 59.73; H, 8.14.

Pauson–Khand reaction of precursor **2**.—Following the 'General method for the Pauson–Khand reaction', enyne **2** (475 mg, 1.4 mmol) afforded product **15** (325 mg, 63%) after chromatography (4:1 hexane–EtOAc), a compound identical in all the physical and spectroscopic data to the compound obtained by acetylation of the PK reaction product **13**.

*(4*S*,4a*R*,5*S*,6*R*,7a*S*,7b*S*)-6-[((1,1-Dimethylethyl)dimethylsilyoxy)methy] - 4,4a,5,6,7a,7b-hexahydro - 2*H* - 1,7 - dioxacyclopent[*cd*]indene-4,5-diol* (**16**).—Following the 'General method for the reduction with DIBALH in toluene', ketone **15** (127 mg, 0.34 mmol) gave diol **16** (50 mg, 45%) after flash chromatography (13:9 hexane–EtOAc): mp 69–72 °C; $[\alpha]_D^{25}$ −105° (*c* 0.48, $CHCl_3$); IR (KBr) *ν* 3307, 1255, 1080, 1063, 1038, 838, 775 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 5.78 (br s, 1 H, H-3), 5.40 (d, $J_{7a,7b}$ 4.8 Hz, 1 H, H-7a), 5.30 (br s, 1 H, H-4), 4.31 (dm, $J_{2',2}$ 13.6 Hz, 1 H, H-2′), 4.02–3.89 (m, 2 H, H-6, H-5), 3.84 (dd, $J_{6a,6a'}$ 10.7, $J_{6a,6}$ 4.4 Hz, 1 H, H-6a), 3.79 (dd, $J_{6a',6a}$ 10.7, $J_{6a',6}$ 6.3 Hz, 1 H, H-6a′), 3.08 (q, $J_{4a,4} = J_{4a,5} = J_{4a,7b}$ 6.2 Hz, 1 H, H-4a), 0.89 [s, 9 H, $(CH_3)_2SiC(CH_3)_3$], 0.072 [s, 6 H, $(CH_3)_2SiC(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 144.3 (C-2a), 127.8 (C-3), 95.4 (C-7a), 84.9 (C-4), 77.2 (C-6), 66.9 (C-5), 64.9 (C-2), 62.9 (C-6a), 49.6 (C-7b), 44.6 (C-4a), 25.7 [$(CH_3)_2SiC(CH_3)_3$], 18.1 [$(CH_3)_2SiC(CH_3)_3$], −5.6 [2 C, $(CH_3)_2SiC(CH_3)_3$]; MS (70 eV): *m*/*z* 175 (39), 129 (24), 117 (38), 107 (92), 89 (19), 79 (100), 59 (17), 41(17). Anal. Calcd for $C_{16}H_{28}O_5Si$: C, 58.50; H, 8.59. Found: C, 58.65; H, 8.72.

*Prop-2-ynyl 2,3-dideoxy-4-*O*-(methoxymethyl) - 6 - O - [(1,1 - dimethyllethyl)dimethylsilyl)]-α-*D*-erythro-hex-2-enopyranoside* (**3**).—To a solution of compound **1** (2.0 g, 6.7 mmol) in dry DMF (0.18 M) cooled at a 0 °C under Ar, sodium hydride (402 mg, 10.05 mmol, 1.5 equiv, 60% dispersion in oil) and MOMCl (0.76 mL, 10.05 mmol, 1.5 equiv) were added. The mixture was stirred at rt. After 90 min, some drops of AcOH were added, the solvent was removed, and the crude product was submitted to chromatography (9:1 hexane–EtOAc) to give **3** (1.69 g, 74%): oil; $[\alpha]_D^{25}$ +107° (*c* 2.64, $CHCl_3$); IR (KBr) *ν* 2150, 1255, 1097, 1036, 963, 837, 777 cm^{-1}; MS (70 eV): *m*/*z* 168 (24), 118 (24), 117 (100), 89 (36), 81 (23), 45 (70). Anal. Calcd for $C_{17}H_{30}O_5Si$: C, 59.62; H, 8.83. Found: C, 59.55; H, 8.92.

Pauson–Khand reaction of precursor (**3**).—Following the 'General method for the Pauson–Khand reaction', enyne **3** (235 mg, 0.69 mmol) gave enone (4a*S*,5*S*,6*R*,7a*S*,7b*S*) 5-(methoxymethyl) - 6 - [((1,1 - dimethylethyl)dimethylsilyloxy)methyl] - 5,6,7a,7b - tetrahydro-2*H* - 1,7 - dioxacyclopent[cd]inden - 4(4aH) - one (**17**, 137 mg, 54%) after chromatography (from 4:1 to 3:2 hexane–EtOAc): oil; IR (film) *ν* 2930, 2857, 1750, 1717, 1471, 1254, 1110, 1029, 836 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 6.21 (br s, 1 H, H-3), 5.56 (d, $J_{7a,7b}$ 4.9 Hz, 1 H, H-7a), 4.83 (d, *J* 7.0 Hz, 1 H, OCH_2O), 4.82 (dm, $J_{2',2}$ 15.4 Hz, 1 H, H-2′), 4.72 (d, *J* 7.0 Hz, 1 H, OCH_2O), 4.66 (dm, $J_{2,2'}$ 15.4 Hz, 1 H, H-2), 4.17 (t, $J_{5,6} = J_{5,4a}$ 8.7 Hz, 1 H, H-5), 3.78 (dd, $J_{6a,6a'}$ 11.7, $J_{6a',6}$ 2.4 Hz, 1 H, H-6a′), 3.74 (dd, $J_{6a,6a'}$ 11.7, $J_{6a,6}$ 2.4 Hz, 1 H, H-6a), 3.58 (dt, $J_{6,5}$ 9.0, $J_{6,6a} = J_{6,6a'}$ 2.4 Hz, 1 H, H-6), 3.48 (s, 3 H, OCH_3), 3.47–3.31 (m, 2 H, H-4a, H-7b), 0.88 [s, 9 H, $(CH_3)_2SiC(CH_3)_3$], 0.06 [s, 6 H, $(CH_3)_2SiC(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 207.1 (C-4), 180.1 (C-2a), 126.4 (C-3), 96.3 (OCH_2O)*, 95.9 (C-7a)*, 72.2 (C-6), 68.6 (C-4), 65.5 (C-2), 62.6 (C-6a), 56.3 (OCH_3), 48.5 (C-4a)*, 48.1 (C-7b)*, 25.9 [$(CH_3)_2SiC(CH_3)_3$], 18.3

[$(CH_3)_2SiC(CH_3)_3$], −5.4, −5.2 [2 C, $(CH_3)_2SiC(CH_3)_3$]; MS (70 eV): *m/z* 313 (29), 251 (47), 197 (90), 89 (42), 75 (38), 45 (100). Anal. Calcd for $C_{18}H_{30}O_6Si$: C, 58.35; H, 8.16. Found: C, 58.44; H, 8.02.

(4S,4aR,5S,6R,7aS,7bS)-5-(Methoxymethyl)-6-[((1,1-dimethylethyl)dimethylsilyloxy)methyl]-4,4a,5,6,7a,7b-hexahydro-2H-1,7-dioxacyclopent[cd]indene (**18**).—Following the 'General method for reduction with DIBALH, **17** (343 mg, 0.9 mmol) afforded alcohol **18** (182 mg, 53%) after chromatography (from 4:1 to 7:3 hexane–EtOAc): oil; $[\alpha]_D^{25}$ −93° (*c* 1.23, $CHCl_3$); IR (film) *ν* 3494, 2930, 2855, 1471, 1274, 1025, 948, 836, 777 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 5.73 (s, 1 H, H-7), 5.40 (m, 1 H, H-4), 5.37 (d, $J_{7a,7b}$ 4.9 Hz, 1 H, H-7a), 4.77 (d, *J* 6.4, Hz, 1 H, OCH_2O), 4.70 (d, *J* 6.4 Hz, 1 H, OCH_2O), 4.61 (d, $J_{-OH,4}$ 7.1 Hz, 1 H, OH), 4.54 (dd, $J_{2',2}$ 12.8, *J* 1.6 Hz, 1 H, H-2′), 4.24 (dm, $J_{2,2'}$ 12.8 Hz, 1 H, H-2), 4.13 (dt, $J_{6,5}$ 6.7, $J_{6,6a} = J_{6,6a'}$ 3.2 Hz, 1 H, H-6), 4.05 (t, $J_{5,6} = J_{5,4a}$ 6.7 Hz, 1 H, H-5), 3.78 (dd, $J_{6a,6a'}$ 11.2, $J_{6a',6}$ 3.2 Hz, 1 H, H-6a′), 3.73 (dd, $J_{6a,6a'}$ 11.2, $J_{6a,6}$ 3.2 Hz, 1 H, H-6a), 3.45 (s, 3 H, OCH_3), 3.23 (dt, $J_{4a,7b}$ 7.7, $J_{4a,5} = J_{4a,4}$ 6.6 Hz, 1 H, H-4a), 3.12–3.07 (m, 1 H, H-7b), 0.88 [s, 9 H, $(CH_3)_2SiC(CH_3)_3$], 0.06 [s, 6 H, $(CH_3)_2SiC(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 143.9 (C-2a), 126.8 (C-3), 96.8 (OCH_2O), 95.3 (C-7a), 85.3 (C-4), 73.5 (C-6), 72.8 (C-5), 64.0 (C-2), 62.4 (C-6a), 56.1 (OCH_3), 51.6 (C-7b), 41.7 (C-4a), 25.7 [$(CH_3)_2SiC(CH_3)_3$], 18.0 [$(CH_3)_2SiC(CH_3)_3$], −5.7, −5.4 [2 C, $(CH_3)_2SiC(CH_3)_3$]; MS (70 eV): *m/z* 253 (16), 207 (64), 137 (26), 117 (57), 91 (38), 89 (32), 75 (46), 45 (100). Anal. Calcd for $C_{18}H_{32}O_6Si$: C, 58.03; H, 8.66. Found: C, 58.23; H, 8.42.

Prop-2-ynyl 4-O-benzyl-2,3-dideoxy-6-O-[(1,1-dimethylethyl)dimethylsilyl]-α-D-erythro-hex-2-enopyranoside (**4**).—Following the 'General method for O-benzylation', **1** (285 mg, 0.96 mmol) gave **4** (364 mg, 98%) after chromatography (9:1 hexane–EtOAc): oil; $[\alpha]_D^{25}$ +133° (*c* 1.8, $CHCl_3$); IR (KBr) *ν* 2150, 1254, 1095, 1044, 837, 778, 698 cm^{-1}; MS (70 eV): *m/z* 214 (13), 185 (23), 117 (92), 91 (100), 89 (17), 79 (15), 39 (13). Anal. Calcd for $C_{22}H_{32}O_4Si$: C, 68.00; H, 8.30. Found: C, 67.85; H, 8.42.

(4aS,5S,6R,7aS,7bS)-6-[((1,1-Dimethylethyl)dimethylsilyloxy)methyl]-5-phenylmethoxy-5,6,7a,7b-tetrahydro-2H-1,7-dioxacyclopent[cd]inden-4(4aH)-one (**19**).—Following the 'General method for the Pauson–Khand reaction', precursor **4** (474 mg, 1.22 mmol) gave **19** (208 mg, 39%) after chromatography (7:3 hexane–EtOAc): oil; $[\alpha]_D^{25}$ −20° (*c* 4.14, $CHCl_3$); IR (film) *ν* 2928, 2856, 1716, 1652, 1462, 1114, 1015, 836, 778 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.44–7.26 (m, 5 H, C_6H_5), 6.21 (br s, 1 H, H-3), 5.55 (d, $J_{7a,7b}$ 6.4 Hz, 1 H, H-7a), 4.98 (d, *J* 10.6 Hz, 1 H, OCH_2Ph), 4.81 (d, $J_{2',2}$ 15 Hz, 1 H, H-2′), 4.64 (dt, $J_{2,2'}$ 15.3, *J* 1.8 Hz, 1 H, H-2), 4.49 (d, *J* 10.6 Hz, 1 H, $OCH_2C_6H_5$), 4.00 (t, $J_{5,6} = J_{5,4a}$ 8.9 Hz, 1 H, H-5), 3.81 (dd, $J_{6a,6a'}$ 11.2, $J_{6a',6}$ 2.5 Hz, 1 H, H-6a′), 3.74 (dd, $J_{6a,6a'}$ 11.2, $J_{6a,6}$ 2.5 Hz, 1 H, H-6a), 3.56 (dt, $J_{6,5}$ 8.9, $J_{6,6a} = J_{6,6a'}$ 2.5 Hz, 1 H, H-6), 3.43 (dd, $J_{4a,5}$ 8.9, $J_{4a,7b}$ 6.6 Hz, 1 H, H-4a), 3.40–3.35 (m, 1 H, H-7b), 0.90 [s, 9 H, $(CH_3)_2SiC(CH_3)_3$], 0.06 [s, 6 H, $(CH_3)_2SiC(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 206.6 (C-4), 179.7 (C-2a), 137.7-127.6 ($OCH_2C_6H_5$), 126.0 (C-3), 96.3 (C-7a), 72.4 ($OCH_2C_6H_5$), 71.4 (C-5)*, 71.2 (C-6)*, 65.5 (C-2), 62.6 (C-6a), 8.1 (C-7b)*, 48.0 (C-4a)*, 25.8 [$(CH_3)_2SiC(CH_3)_3$], 18.2 [$(CH_3)_2SiC(CH_3)_3$], −5.5, −5.3 [2 C, $(CH_3)_2SiC(CH_3)_3$]; MS (70 eV): *m/z* 359 (25), 243 (40), 91 (100), 75 (31), 73 (31), 65 (22). Anal. Calcd for $C_{23}H_{32}O_5Si$: C, 66.31; H, 7.74. Found: C, 66.42; H, 7.53.

(4S,4aR,5S,6R,7aS,7bS)-6-[((1,1-Dimethylethyl)dimethylsilyloxy)methyl]-5-(phenylmethoxy)-4,4a,5,6,7a,7b-hexahydro-2H-1,7-dioxacyclopent[cd]indene-4-ol (**20**).—Following the 'General method for DIBALH reduction', ketone **19** (223 mg, 0.54 mmol) gave alcohol **20** (173 mg, 77%) after chromatography (4:1 hexane–EtOAc): oil; $[\alpha]_D^{25}$ +2° (*c* 0.42, $CHCl_3$); IR (film) *ν* 3467, 2929, 2856, 1462, 1254, 1070, 1015, 836, 778 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): *δ* 7.36–7.33 (m, 5 H, C_6H_5), 5.70 (br s, 1 H, H-3), 5.37 (d, $J_{7a,7b}$ 5.0 Hz, 1 H, H-7a), 5.36–5.32 (m, 1 H, H-4), 4.81 (d, $J_{OH,4}$ 7.8 Hz, 1 H, OH), 4.72 (d, *J* 11.1 Hz, 1 H, $OCH_2C_6H_5$), 4.56 (d, *J* 10.6 Hz, 1 H, $OCH_2C_6H_5$), 4.56 (dm, $J_{2',2}$ 13.0 Hz, 1 H, H-2′), 4.25 (ddt, $J_{2,2'}$ 13.0, *J* 3.7, *J* 2.1 Hz, 1 H, H-2), 4.18 (dt, $J_{6,5}$ 6.8, $J_{6,6a} = J_{6,6a'}$ 3.7 Hz, 1

H, H-6), 3.96 (t, $J_{5,6} = J_{5,6'}$ 6.8 Hz, 1 H, H-5), 3.87 (dd, $J_{6a,6a'}$ 11.0, $J_{6a',6}$ 3.7 Hz, 1 H, H-6a′), 3.78 (dd, $J_{6a,6a'}$ 11.0, $J_{6a,6}$ 3.7 Hz, 1 H, H-6a), 3.17 (q, $J_{4a,5} = J_{4a,7b} = J_{4a,4}$ 6.8 Hz, 1 H, H-4a), 3.10–3.04 (m, 1 H, H-7b), 0.91 [s, 9 H, $(CH_3)_2SiC(CH_3)_3$], 0.08 [s, 6 H, $(CH_3)_2SiC(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.1 (C-2a), 137.1–127.8 ($OCH_2C_6H_5$), 126.7 (C-3), 95.5 (C-7a), 85.6 (C-4), 74.2 (C-5), 72.6 (C-6), 72.3 ($OCH_2C_6H_5$), 64.2 (C-2), 62.5 (C-6a), 51.2 (C-7b), 41.0 (C-4a), 25.8 [$(CH_3)_2SiC(CH_3)_3$], 18.2 [$(CH_3)_2SiC(CH_3)_3$], −5.5, −5.3 [2 C, $(CH_3)_2SiC(CH_3)_3$]; MS (70 eV): *m/z* 207 (25), 137 (16), 117 (28), 92 (21), 91 (100), 79 (20), 75 (23), 73 (19). Anal. Calcd for $C_{23}H_{34}O_5Si$: C, 65.99; H, 8.19. Found: C, 65.73; H, 8.01.

*(4*S*,4a*R*,5*S*,6*R*,7a*S*,7b*S*)-6-[((1,1-Dimethylethyl)silyloxy)methyl]-5-(phenylmethoxy)-4,4a,5,6,7a,7b-hexahydro-2*H*-1,7-dioxacyclopent[cd]indene-4-ol benzoate* (**21**).—Following the 'General method for benzoylation', **20** (102 mg, 0.24 mmol) afforded benzoate **21** (72 mg, 60%) after chromatography (9:1 hexane–EtOAc): oil; $[\alpha]_D^{25}$ +85° (*c* 0.59, $CHCl_3$); IR (film) *v* 2929, 2856, 1719, 1272, 1114, 1026, 836, 711 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.82–7.27 (m, 5 H, $OCOC_6H_5$), 7.18–7.12 (m, 5 H, $OCH_2C_6H_5$); 6.69 (br d, $J_{4,4a}$ 6.0 Hz, 1 H, H-4), 5.79 (br s, 1 H, H-3), 5.47 (d, $J_{7a,7b}$ 4.0 Hz, 1 H, H-7a), 4.62 (d, *J* 11.4 Hz, 1 H, $OCH_2C_6H_5$), 4.58 (d, $J_{2',2}$ 13.6 Hz, 1 H, H-2′), 4.37 (d, *J* 11.4 Hz, 1 H, $OCH_2C_6H_5$), 4.29 (dd, $J_{2,2'}$ 13.6, *J* 1.2 Hz, 1 H, H-2), 4.20 (d, $J_{6,5}$ 9.4 Hz, 1 H, H-6), 3.96 (dd, $J_{5,6}$ 9.4, $J_{5,4a}$ 6.0 Hz, 1 H, H-5), 3.75 (s, 2 H, 2 H-6a), 3.51 (q, $J_{4a,5} = J_{4a,7b} = J_{4a,4}$ 6.0 Hz, 1 H, H-4a), 3.29–3.27 (m, 1 H, H-7b), 0.89 [s, 9 H, $(CH_3)_2SiC(CH_3)_3$], 0.07 [s, 6 H, $(CH_3)_2SiC(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0 ($OCOC_6H_5$), 147.7 (C-2a), 138.0–127.1 ($OCH_2C_6H_5$, $OCOC_6H_5$), 123.9 (C-3), 95.6 (C-7a), 84.6 (C-4), 74.9 (C-6), 72.1 (2 C, $OCH_2C_6H_5$, C-5), 63.8 (C-2)*, 63.5 (C-6a)*, 54.5 (C-7b), 37.8 (C-4a), 25.9 [$(CH_3)_2SiC(CH_3)_3$], 18.2 [$(CH_3)_2SiC(CH_3)_3$], −5.5, −5.3 [2 C, $(CH_3)_2SiC(CH_3)_3$]; MS (70 eV): *m/z* 253 (19), 227 (33), 207 (24), 137 (20), 117 (25), 105 (85), 91 (100), 77 (28). Anal. Calcd for $C_{30}H_{38}O_6Si$: C, 68.93; H, 7.33. Found: C, 68.75; H, 7.41.

*(4*S*,4a*R*,5*S*,6*R*,7a*S*,7b*S*) - 4,4a,5,6,7a,7b-Hexahydro-5-phenylmethoxy-2*H*-1,7-dioxacyclopent[cd]indene-4-ol benzoate* (**22**).—Following the 'General method for desilylation', **21** (626 mg, 1.27 mmol) afforded alcohol **22** (411 mg, 80%) after chromatography (7:3 hexane–EtOAc): mp 82–85 °C; $[\alpha]_D^{25}$ +104° (*c* 0.31, $CHCl_3$); IR (KBr) *v* 2929, 2856, 1719, 1272, 1114, 1026, 836, 711 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.85 (dd, *J* 7.0, *J* 1.7 Hz, 2 H, $OCOC_6H_5$), 7.46 (t, *J* 7.5, *J* 1.3 Hz, 1 H, $OCOC_6H_5$), 7.07–7.32 (m, 7 H, $OCH_2C_6H_5$, $OCOC_6H_5$), 6.66 (dq, $J_{4,4a}$ 7.5, *J* 1.7 Hz, 1 H, H-4), 5.82 (br s, 1 H, H-3), 5.41 (d, $J_{7a,7b}$ 4.6 Hz, 1 H, H-7a), 4.59 (dd, $J_{2',2}$ 12.6, *J* 1.3 Hz, 1 H, H-2′), 4.64 (d, *J* 11.4 Hz, 1 H, $OCH_2C_6H_5$), 4,39 (dt, $J_{6,5}$ 9.6, $J_{6,2H6a}$ 4.3 Hz, 1 H, H-6), 4.34 (d, *J* 11.4 Hz, 1 H, $OCH_2C_6H_5$), 4.30 (ddt, $J_{2,2'}$ 12.6, *J* 3.4, *J* 2.0 Hz, 1 H, H-2), 3.70–3.64 (m, 3 H, H-5, 2 H6a), 3.56 (ddd, $J_{4a,7b}$ 8.9, $J_{4a,4}$ 7.5, $J_{4a,5}$ 5.9 Hz, 1 H, H-4a), 3.39 (dm, $J_{7b,4a}$ 8.9 Hz, 1 H, H-7b), 2.17–2.04 (br s, 1 H, OH)]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2 ($OCOC_6H_5$), 147.9 (C-2a), 137.1–1276 ($OCH_2C_6H_5$, $OCH_2C_6H_5$), 123.4 (C-3), 95.2 (C-7a), 84.7 (C-4), 75.3 (C-5), 72.7 (C-6), 72.2 ($OCH_2C_6H_5$), 63.6 (C-2)*, 63.3 (C-6a)*, 54.2 (C-7b), 37.4 (C-4a); MS (70 eV): *m/z* 286 (9), 168 (45), 105 (100), 91 (98), 77 (55), 65 (14). Anal. Calcd for $C_{24}H_{24}O_6$: C, 70.58; H, 5.92. Found: C, 70.66; H, 6.23.

Oxidation of intermediate **22**.—Compound **22** (132 mg, 0.32 mmol) was oxidized according to the Dess–Martin protocol to give (4*S*,4a*R*,5*S*,6*RS*,7a*S*,7b*S*) - 4 - (benzoyloxy) - 4,4a,5,6,7a,7b - hexahydro - 5 - (phenylmethoxy)-2*H* - 1,7 - dioxacyclopent[cd]inden - 6 - carbaldehyde (**23**, 109 mg, 83%) (as a mixture of epimers at C-6 in 2:1 ratio) after chromatography (1:1 hexane–EtOAc) [IR (KBr) *v* 3436, 2927, 1716, 1450, 1273, 1112 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.74 and 9.65 (s, 1 H, CHO), 8.00–7.20 (m, 10 H, $OCH_2C_6H_5$, $OCOC_6H_5$), 6.60 and 6.20 (m, 1 H, H-4), 5.90–5.80 (m, 2 H, H-3), 5.52 (d, $J_{7a,7b}$ 4.6 Hz, 1 H, H-7a), 5.51 (m, 1 H, H-7a), 4.80–4.20 (m, 5 H, $OCH_2C_6H_5$, 2 H-2, H-5), 4.85 (dm, $J_{2',2}$ 11.5 Hz, 1 H, H-2′), 4.60 (m, 1 H, H-5), 4.52 (dm, $J_{2,2'}$ 11.7 Hz, 1 H, H-2), 4.42 (d, *J* 11.8 Hz, 1 H, $OCH_2C_6H_5$), 4,28 (d, *J* 11.8 Hz, 1 H, $OCH_2C_6H_5$), 4.02 (d, $J_{6,5}$ 5.7 Hz, 1 H,

H-6), 4.00–3.98 (m, 1 H, H-6), 3.49 (q, *J* 5.9 Hz, 1 H, H-4a), 3.60–3.40 (m, 1 H, H-4a), 3.40–3.00 (m, 2 H, H-7b); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.8, 199.0 (CHO), 166.1 ($2 \times OCOC_6H_5$), 147.0–126.0 (10 C, $OCOC_6H_5$, $OCH_2C_6H_5$), 124.0 and 122.1 (C-3), 98.1 and 95.2 (C-7a), 84.4 and 84.2 (C-6), 78.7 and 77.9 (C-4), 74.0 and 71.9 ($OCH_2C_6H_5$), 72.6 and 72.1 (C-5), 66.0 and 64.4 (C-2), 52.9 and 50.2 (C-7b), 48.6 and 39.0 (C-4a); MS (70 eV): *m*/*z* 377 (4), 257 (20), 165 (14), 105 (100), 91 (98), 79 (43), 77 (64)]. Compound **23** (58 mg, 0,14 mmol) was dissolved in dry toluene (4.8 mL, 0.03 M) and $RhCl(PPh_3)_3$ (132 mg, 0.14 mmol, 1 equiv) was added. The mixture was stirred at rt for 24 h, EtOH was added, the mixture was filtered, evaporated and the crude was submitted to chromatography (4:1 hexane–EtOAc) to give (4a*S*,5*S*,7a*S*,7b*S*)-5,6,7a,7b-tetrahydro-5-(phenylmethoxy)-2*H*-1,7-dioxacyclopent[cd]inden-4-ol benzoate (**24**, 3.4 mg, 6%) [^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (dd, *J* 7.9, *J* 1.5 Hz, 2 H, $OCOC_6H_5$), 7.50 (tm, *J* 7.5 Hz, 1 H, $OCOC_6H_5$), 7.37–7.24 (m, 7 H, $OCH_2C_6H_5$, $OCOC_6H_5$), 6.33–6.31 (m, 1 H, H-4), 5.85 (m, 1 H, H-3), 5,32 (d, $J_{7a,7b}$ 5.1 Hz, 1 H, H-7a), 4.71 (dq, $J_{2',2}$ 13.4, *J* 2.0 Hz, 1 H, H-2′), 4.55 (d, *J* 11.8 Hz, 1 H, $OCH_2C_6H_5$), 4.41 (ddt, $J_{2,2'}$ 13.8, *J* 3.8, *J* 1.8 Hz, 1 H, H-2), 4.30 (d, *J* 11.8 Hz, 1 H, $OCH_2C_6H_5$), 4.03 (dd, $J_{6,6'}$ 12.2, $J_{6,5}$ 4.2 Hz, 1 H, H-6), 3.54 (ddd, $J_{5,4a}$ 6.4, $J_{5,6}$ 4.2, $J_{5,6'}$ 1.2 Hz, 1 H, H-5), 3.43 (q, *J* 6.4 Hz, 1 H, H-4a), 3.36 (dd, $J_{6',6}$ 12.2, $J_{6',5}$ 1.2 Hz, 1 H, H-6′), 3.13–3.11 (m, 1 H, H-7b)] whose decomposition prevented additional analysis.

Decarbonylation of intermediate **23**.—Compound **23** (25 mg, 0,062 mmol) was dissolved in dry toluene (2 mL, 0.03 M), heated at reflux and *t*-Bu_2O_2 (2,3 μL, 0.012 mmol, 20% mol) was added. After 2 h, the solvent was removed and the crude was submitted to chromatography (1:1 hexane–EtOAc) giving (4*S*,4a*R*,5*S*,6*RS*,7a*S*,7b*S*) - 4 - benzoyloxy - 4,4a,5,6,7a,7b-hexahydro-5-phenylmethoxy-2*H*-1,7-dioxacyclopent[cd]inden-6-formate (**25**, 4.5 mg, 17%): oil; $[\alpha]_D^{25}$ +44° (*c* 0.17, $CHCl_3$); IR (KBr) *v* 3435, 2920, 1718, 1631, 1270, 1113 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (s, 1 H, HCOO), 8.00 (dm, *J* 7.5 Hz, 2 H, $OCOC_6H_5$), 7.52 (tm, *J* 7.5 Hz, 1 H, $OCOC_6H_5$), 7.37 (t, *J* 7.5 Hz, 2 H, $OCOC_6H_5$), 7.28–7.27 (m, 5 H, $OCH_2C_6H_5$), 6.51 (dq, $J_{4,4a}$ 7.1, *J* 1.5 Hz, 1 H, H-4), 6.35 (d, $J_{6,5}$ 6.0 Hz, 1 H, H-6), 5.85 (br s, 1 H, H-3), 5.45 (d, $J_{7a,7b}$ 4.0 Hz, 1 H, H-7a), 4.63 (ddm, $J_{2',2}$ 12.0, *J* 1.3 Hz, 1 H, H-2′), 4.56 (d, *J* 11.8 Hz, 1 H, $OCH_2C_6H_5$), 4.49 (d, *J* 11.8 Hz, 1 H, $OCH_2C_6H_5$), 4.37 (ddt, $J_{2,2'}$ 12.0, *J* 3.1, *J* 1.8 Hz, 1 H, H-2), 3.75 (t, $J_{5,4a} = J_{5,6}$ 6.0 Hz, 1 H, H-5), 3.49 (ddd, $J_{4a,7b}$ 8.3, $J_{4a,4}$ 7.1, $J_{4a,5}$ 6.0 Hz, 1 H, H-4a), 3.33–3.28 (m, 1 H, H-7b); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1 ($OCOC_6H_5$), 145.8 (C-2a), 133.2–127.5 (12 C, $OCOC_6H_5$, $OCH_2C_6H_5$), 125.4 (C-3), 97.7 (C-7a), 94.9 (C-6), 83.9 (C-4), 74.0 (C-5), 72.6 ($OCH_2C_6H_5$), 65.3 (C-2), 53.2 (C-7b), 39.1 (C-4a); MS (70 eV): *m*/*z* 227 (19), 164 (29), 105 (100), 91 (98), 77 (60).

*Prop-2-ynyl 2,3-dideoxy-6-*O-p-*toluenesulfonyl-α-*D-erythro-*hex-2-enopyranoside* (**26**).—Following the 'General method for acetylaton', diol **11** (1.02 g, 5.55 mmol) gave product **26** (1.22 g, 65%) after chromatography (1:1 hexane–EtOAc): oil; $[\alpha]_D^{25}$ +60° (*c* 0.43, $CHCl_3$); IR (KBr) *v* 3450, 3230, 2060, 1570, 1325, 1160, 1145, 1010, 920 cm^{-1}; MS (70 eV): *m*/*z* 283 (14), 155 (25), 124 (100), 91 (74), 85 (96), 57 (41), 39 (38). Anal. Calcd for $C_{16}H_{18}O_6S$: C, 56.79; H, 5.36; S, 9.48. Found: C, 56.88; H, 5.39; S, 9.23.

*Prop-2-ynyl 4-*O-*acetyl-2,3-dideoxy-6-*O-p-*toluenesulfonyl-α-*D-erythro-*hex-enopyranoside* (**27**).—Following the 'General method for acetylation', **26** (986 mg, 2.9 mmol) gave acetate **27** (952 mg, 86%) after chromatography (7:3 hexane–EtOAc): mp 53–54 °C; $[\alpha]_D^{25}$ +132° (*c* 0.45, $CHCl_3$); IR (KBr) *v* 3210, 2070, 1705, 1330, 1210, 1165, 1150, 1015, 920 cm^{-1}; MS (70 eV): *m*/*z* 166 (40), 155 (24), 124 (100), 91 (32), 85 (23), 43 (29). Anal. Calcd for $C_{18}H_{20}O_7S$: C, 56.83; H, 5.30, S, 8.43. Found: C, 57.14; H, 5.62; S, 8.21.

*Prop-2-ynyl 4-*O-*acetyl-2,3,6-trideoxy-6-iodo-α-*D-erythro-*hex-2-enopyranoside* (**5**).—Following the 'General method for the synthesis of iodides from tosylates', **27** (517 mg, 1.36 mmol) gave iodide **5** (422 mg, 92%) after chromatography (9:1 hexane–EtOAc): mp 27–30 °C; $[\alpha]_D^{25}$ +161° (*c* 1.66, $CHCl_3$); IR (KBr) *v* 3230, 2060, 1715, 1340, 1200, 1000 cm^{-1}; MS (70 eV): *m*/*z* 166 (35), 124 (100), 85

(33), 43 (54), 39 (20). Anal. Calcd for $C_{11}H_{13}O_4I$: C, 39.30; H, 3.90. Found: C, 39.16; H, 4.12.

*(4a*S,*5*S,*6*R,*7a*S,*7b*S*)-5-Acetyloxy-5,6,7a,7b-tetrahydro-6-iodomethyl-2*H*-1,7-dioxacyclopent[cd]inden-4(4aH)-one* (**28**).—Following the 'General method for the Pauson–Khand reaction', **5** (114 mg, 0.34 mmol) afforded **28** (54 mg, 44%) after chromatography (3:2 hexane–EtOAc): mp > 230 °C; $[\alpha]_D^{25}$ −108° (*c* 0.20, $CHCl_3$); IR (KBr) *v* 1715, 1680, 1620, 1355, 1205, 1195, 955, 845 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.21 (s, 1 H, H-3), 5.62 (d, $J_{7a,7b}$ 5.9 Hz, 1 H, H-7a), 4.85 (d, $J_{2',2}$ 15.3 Hz, 1 H, H-2′), 4.82 (t, $J_{5,6} = J_{5,4a}$ 9.1 Hz, 1 H, H-5), 4.65 (d, $J_{2,2'}$ 15.3 Hz, 1 H, H-2), 3.54–3.46 (m, 2 H, H-4a, H-7b), 3.32 (dd, $J_{6a,6a'}$ 11.1, $J_{6a',6}$ 2.6 Hz, 1 H, H-6a′), 3.37–3.29 (m, 1 H, H-6), 3.19 (dd, $J_{6a,6a'}$ 11.1, $J_{6a,6}$ 5.3 Hz, 1 H, H-6a), 2.09 (s, 3 H, $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.1 (C-4), 180.6 (C-2a), 169.6 ($OCOCH_3$), 126.1 (C-3), 96.4 (C-7a), 70.4 (C-5), 66.8 (C-6), 65.9 (C-2), 48.0 (C-7b)*, 45.7 (C-4a)*, 20.6 ($OCOCH_3$), 6.7 (C-6a); MS (70 eV): *m*/*z* 237 (41), 177 (32), 152 (22), 95 (19), 43 (100), 39 (15). Anal.Calcd for $C_{12}H_{13}O_5I$: C, 39.58; H, 3.60. Found: C, 39.91; H, 3.90.

Prop-2-ynyl 4-O-*benzoyl-2,3-dideoxy-6*-O-p-*toluenesulfonyl-α*-D-erythro-*hex-2-enopyranoside* (**29**).—Following the 'General method for benzoylation', tosylate **26** (1 g, 2.96 mmol) gave **29** (1.23 g, 94%) after chromatography (9:1 hexane–EtOAc): mp 70–73 °C; $[\alpha]_D^{25}$ + 194° (*c* 1.12, $CHCl_3$); IR (KBr) *v* 1690, 1570, 1420, 1335, 1235, 1160, 1145, 1075, 1065, 1015, 995 cm^{-1}; MS (70 eV): *m*/*z* 228 (63), 105 (100), 91 (19), 77 (27). Anal. Calcd for $C_{23}H_{22}O_7S$: C, 62.43; H, 5.01; S, 7.25. Found: C, 62.50; H, 5.23; S, 7.40.

Prop-2-ynyl 4-O-*benzoyl-2,3,6-trideoxy-6-iodo-α*-D-erythro-*hex-2-enopyranoside* (**6**).—Following the 'General method for the synthesis of iodides from tosylates', **29** (196 mg, 0.44 mmol) gave iodide **6** (145 mg, 82%) after chromatography (19:1 hexane–EtOAc): oil; $[\alpha]_D^{25}$ + 178° (*c* 1.52, $CHCl_3$); IR (KBr) *v* 3293, 2118, 1721, 1451, 1316, 1261, 1108, 1026, 958, 711 cm^{-1}; MS (70 eV): *m*/*z* 150 (51), 149 (81), 132 (52), 115 (48), 107 (45), 105 (100), 91 (61), 43 (73). Anal. Calcd for $C_{16}H_{15}O_4I$: C, 48.26; H, 3.80. Found: C, 48.34; H, 3.56.

*(4a*S,*5*S,*6*R,*7a*S,*7b*S*)-5-Benzoyloxy-5,6,7a,7b-tetrahydro-6-iodomethyl-2*H*-1,7-dioxacyclopent[cd]inden-4(4aH)-one* (**30**).—Following the 'General method for the Pauson–Khand reaction', **6** (465 mg, 1.17 mmol) gave **30** (277 mg, 55%) after chromatography (7:3 hexane–EtOAc): oil; ^1H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, *J* 7.3 Hz, 2 H, $OCOC_6H_5$), 7.55 (t, *J* 7.3 Hz, 1 H, $OCOC_6H_5$), 7.42 (t, *J* 7.7 Hz, 2 H, $OCOC_6H_5$), 6.23 (s, 1 H, H-3), 5.65 (d, $J_{7a,7b}$ 6.1 Hz, 1 H, H-7a), 5.11 (t, $J_{5,6} = J_{5,4a}$ 9.2 Hz, 1 H, H-5), 4.86 (d, $J_{2',2}$ 15.3 Hz, 1 H, H-2′), 4.65 (d, $J_{2,2'}$ 15.3 Hz, 1 H, H-2), 3.61–3.49 (m, 3 H, H-6, H-4a, H-7b), 3.26 (dd, $J_{6a,6a'}$ 10.9, $J_{6a',6}$ 2.7 Hz, 1 H, H-6a′), 3.23 (dd, $J_{6a,6a'}$ 10.9, $J_{6a,6}$ 5.3 Hz, 1 H, H-6a); ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.9 (C-4), 180.6 (C-2a), 165.2 ($OCOC_6H_5$), 133.3–128.4 ($OCOC_6H_5$), 126.1 (C-3), 96.3 (C-7a), 70.6 (C-5), 67.1 (C-6), 65.9 (C-2), 48.0 (C-7b)*, 45.9 (C-4a)*, 6.8 (C-6a). Anal. Calcd for $C_{17}H_{15}O_5I$: C, 47.91; H, 3.55. Found: C, 47.83; H, 3.41.

*(4*S,*4a*R,*5*S,*6*R,*7a*S,*7b*S*)-4,4a,5,6,7a,7b-Hexahydro-6-iodomethyl-2*H*-1,7-dioxacyclopent[cd]inden-4,5-diol dibenzoate* (**32**).—Following the 'General method for the reduction with DIBALH', **30** (117 mg, 0.27 mmol) in THF gave alcohol **31** (32 mg, 27%) after chromatography (7:3 hexane–EtOAc). Compound **31** (26 mg, 0.061 mmol) gave dibenzoate **32** (11.5 mg, 35%) Following the 'General method for benzoylation', after chromatography (7:3 hexane–EtOAc): oil; IR (KBr) *v* 2926, 1717, 1280, 1113, 1027 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77–7.25 (m, 10 H, 2 × $OCOC_6H_5$), 6.46 (dm, $J_{4,4a}$ 6.4 Hz, 1 H, H-4), 5.88 (br s, 1 H, H-3), 5.58 (d, $J_{7a,7b}$ 4.8 Hz, 1 H, H-7a), 5.35 (t, $J_{5,6} = J_{5,4a}$ 6.4 Hz, 1 H, H-5), 4.78 (dq, $J_{2',2}$ 13.4, *J* 1.8 Hz, 1 H, H-2′), 4.48 (ddt, $J_{2,2'}$ 13.4, *J* 3.5, *J* 2.2 Hz, 1 H, H-2), 4.26 (dt, $J_{6,5}$ 6.4, $J_{6,6a}$ 5.5 Hz, 1 H, H-6), 3.73 (q, $J_{4a,4}$ $J_{4a,5}$ $J_{4a,7b}$ 6.4 Hz, 1 H, H-4a), 3.39 (dd, $J_{6a,6a'}$ 10.9, $J_{6a',6}$ 5.5 Hz, 1 H, H-6a′), 3.34 (dd, $J_{6a,6a'}$ 10.9, $J_{6a,6}$ 5.5 Hz, 1 H, H-6a), 3.38–3.31 (m, 1 H, H-7b); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8, 165.78 (2 × $OCOC_6H_5$), 146.6 (C-2a), 133.1–128.16 (10 C, 2 × $OCOC_6H_5$), 122.3 (C-3), 94.2 (C-7a), 84.3 (C-4), 73.4 (C-6), 67.9 (C-5), 64.7 (C-2), 51.0

(C-7b), 40.7 (C-4a), 3.9 (C-6a); MS (70 eV): *m/z* 532 (5), 410 (12), 405 (9), 287 (47), 133 (28), 105 (100), 77 (71). Anal. Calcd for $C_{24}H_{21}O_6I$: C, 54.15; H, 3.98. Found: C, 54.27; H, 3.77.

*(4*S,*4a*R,*5*S,*6*R,*7a*S,*7b*S*)-6-[(Benzoyloxy)-methyl]-4,4a,5,6,7a,7b-hexahydro-2*H*-1,7-dioxa-cyclopent[cd]indene-4,5-diol dibenzoate* (**33**).—Following the 'General method for the reaction of silver fluoride', **32** (5 mg, 0.009 mmol) in anhyd pyridine (0.5 mL, 0.01 M) with silver fluoride (2 mg, 0.014 mmol, 1.5 equiv) afforded **33** (2 mg, 36%): oil; $[\alpha]_D^{25}$ −5° (*c* 0.3, $CHCl_3$); IR (KBr) *v* 2927, 1719, 1271, 1113, 1026, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 (dm, *J* 7.1 Hz, 2 H), 7.75 (dm, *J* 7.1 Hz, 2 H), 7.55 (t, *J* 7.5 Hz, 1 H), 7.49 (t, *J* 7.3 Hz, 1 H), 7.45–7.21 (m, 10 H) [3 × C_6H_5], 6.47–6.45 (m, 1 H, H-4), 5.88 (br s, 1 H, H-3), 5.62 (d, $J_{7a,7b}$ 4.8 Hz, 1 H, H-7a), 5.45 (t, $J_{5,4a} = J_{5,6}$ 5.7 Hz, 1 H, H-5), 4.78 (dd, $J_{2,2'}$ 13.2, *J* 1.5 Hz, 1 H, H-2), 4.61 (q, $J_{6,5} = J_{6,6a} = J_{6,6a'}$ 5.7 Hz, 1 H, H-6), 4.54 (dd, $J_{6a',6a}$ 11.9, $J_{6a',6}$ 5.7 Hz, 1 H, H-6a′), 4.49 (dd, $J_{6a,6a'}$ 11.9, $J_{6a,6}$ 5.7 Hz, 1 H, H-6a), 4.47 (m, 1 H, H-2), 3.73 (q, $J_{4a,7b} = J_{4a,5} = J_{4a,4}$ 5.7 Hz, 1 H, H-4a), 3.41–3.36 (m, 1 H, H-7b); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 165.7 (3 C, 3 × $OCOC_6H_5$), 146.6 (C-2a), 133.2–128.2 (15 C, 3 × C_6H_5), 122.7 (C-3), 95.0 (C-7a), 84.4 (C-4), 72.6 (C-6), 66.3 (C-5), 64.8 (C-2), 63.2 (C-6a), 51.5 (C-7b), 41.6 (C-4a); MS (70 eV): *m/z* 526 (1), 282 (7), 254 (6), 160 (50), 132 17), 105 (100). Anal. Calcd for $C_{31}H_{26}O_8$: C, 70.71; H, 4.98. Found: C, 70.59; H, 4.73.

*Prop-2-ynyl 4-*O*-benzyl-2,3-dideoxy-α-*D*-*erythro*-hex-2-enopyranoside* (**7**).—Following the 'General method for desilylation', **4** (990 mg, 2.55 mmol) gave alcohol **7** (720 mg, 90%) after chromatography (7:3 hexane–EtOAc): oil; $[\alpha]_D^{25}$ +158° (*c* 0.69, $CHCl_3$); IR (film) *v* 3400, 3289, 2916, 2200, 1454, 1398, 1138, 1042, 957, 699 cm^{-1}; MS (70 eV): *m/z* 214 (91), 185 (65), 123 (66), 95 (57), 91(100), 67 (53), 39 (78). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.06; H, 5.88. Found: C, 69.94; H, 5.81.

*(4a*S,*5*S,*6*R,*7a*S,*7b*S*)-5,6,7a,7b-Tetrahydro-6-hydroxymethyl-2*H*-1,7-5-phenylmethoxydi-oxacyclopent[cd]inden-4(4aH)-one* (**34**).—Following the 'General method for the Pauson–Khand reaction', **7** (88 mg, 0.32 mmol) afforded ketone **34** (45 mg, 47%) after chromatography (1:4 hexane–EtOAc): mp 131–134 °C; $[\alpha]_D^{25}$ +2° (*c* 0.09, $CHCl_3$); IR (KBr) *v* 3452, 1712, 1656, 1123, 1019, 977, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.41–7.30 (m, 5 H, $OCH_2C_6H_5$), 6.24 (s, 1 H, H-3), 5.53 (d, $J_{7a,7b}$ 5.9 Hz, 1 H, H-7a), 5.01 (d, *J* 10.9 Hz, 1 H, $OCH_2C_6H_5$), 4.84 (d, $J_{2',2}$ 15.4 Hz, 1 H, H-2′), 4.64 (d, $J_{2,2'}$ 15.4 Hz, 1 H, H-2), 4.51 (d, *J* 10.9 Hz, 1 H, $OCH_2C_6H_5$), 3.83 (t, $J_{5,6} = J_{5,4a}$ 8.9 Hz, 1 H, H-5), 3.72 (dd, $J_{6a,6a'}$ 11.6, $J_{6a',6}$ 3.3 Hz, 1 H, H-6a′), 3.64–3.57 (m, 2 H, H-6, H-6a), 3.50–3.42 (m, 2 H, H-4a, H-7b), 2.09 (br s, 1 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.0 (C-4), 179.8 (C-2a), 137.1–128.0 ($OCH_2C_6H_5$), 126.2 (C-3), 96.2 (C-7a), 72.5 (C-5), 72.0 ($OCH_2C_6H_5$), 69.7 (C-6), 65.7 (C-2), 62.6 (C-6a), 47.9 (C-7b)*, 4780 (C-4a)*; MS (70 eV): *m/z* 196 (43), 132 (27), 108 (34), 91 (100), 65 (35). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.25; H, 6.28.

*Prop-2-ynyl 4-*O*-benzyl-2,3,6-trideoxy-6-iodo-α-*D*-*erythro*-hex-2-enopyranoside* (**8**).—Following the 'General method for iodination of alcohols', **7** (1.28 g, 4.7 mmol) gave iodide **8** (1.51 g, 84%) after chromatography (19:1 hexane–EtOAc): oil; $[\alpha]_D^{25}$ +162°° (*c* 5.39, $CHCl_3$); IR (film) *v* 3290, 2920, 2863, 2220, 1123, 1075, 1027, 956, 698 cm^{-1}; MS (70 eV): *m/z* 214 (76), 185 (29), 123 (31), 95 (29), 91 (100), 65 (29), 39 (34). Anal. Calcd for $C_{16}H_{17}O_2I$: C, 52.19; H, 4.65. Found: C, 52.36; H, 4.72.

*(4a*S,*5*S,*6*R,*7a*S,*7b*S*)-5,6,7a,7b-Tetrahydro-6-iodomethyl-5-phenylmethoxy-2*H*-1,7-dioxa-cyclopent[cd]inden-4(4aH)-one* (**35**).—Following the 'General method for the Pauson–Khand reaction', iodide **8** (1.44 g, 3.75 mmol) gave ketone **35** (847 mg, 55%) after chromatography (1:1 hexane–EtOAc): mp 113–116 °C; $[\alpha]_D^{25}$ +17° (*c* 1.35, $CHCl_3$); IR (film) *v* 2965, 1708, 1650, 1221, 1125, 1107, 1012, 971, 874, 766, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.45–7.26 (m, 5 H, $OCH_2C_6H_5$), 6.23 (s, 1 H, H-3), 5.59 (d, $J_{7a,7b}$ 5.6 Hz, 1 H, H-7a), 5.07 (d, *J* 10.0 Hz, 1 H, $OCH_2C_6H_5$), 4.83 (d, $J_{2',2}$ 15.4 Hz, 1 H, H-2′), 4.65 (dt, $J_{2,2'}$ 15.4, *J* 1.6 Hz, 1 H, H-2), 4.50 (d, *J* 10.0 Hz, 1 H, $OCH_2C_6H_5$), 3.78 (t, $J_{5,6} = J_{5,4a}$ 8.5 Hz, 1 H, H-5), 3.53–3.45 (m, 2 H, H-4a, H-7b), 3.41

(dd, $J_{6a,6a'}$ 10.6, $J_{6a',6}$ 3.0 Hz, 1 H, H-6a′), 3.36 (dd, $J_{6a,6a'}$ 10.6, $J_{6a,6}$ 3.0 Hz, 1 H, H-6a), 3.20 (dt, $J_{6,5}$ 8.5, $J_{6,6a} = J_{6,6a'}$ 3.0 Hz, 1 H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.8 (C-4), 179.6 (C-2a), 137.0–128.1 ($OCH_2C_6H_5$), 126.1 (C-3), 96.4 (C-7a), 75.7 (C-5), 72.6 ($OCH_2C_6H_5$), 67.8 (C-6), 65.8 (C-2), 48.1 (C-7b)*, 47.5 (C-4a)*, 9.6 (C-6a); MS (70 eV): *m*/*z* 306 (61), 179 (21), 151 (17), 133 (31), 107 (32), 91 (100), 65 (29). Anal. Calcd for $C_{17}H_{17}O_4I$: C, 49.53; H, 4.16. Found: C, 49.80; H, 4.45.

*(4*S*,4a*R*,5*S*,6*R*,7a*S*,7b*S*) - 4,4a,5,6,7a,7b-Hexahydro - 6 - iodomethyl - 2*H*- 5 - phenylmethoxy - 1,7 - dioxacyclopent[cd]inden - 4 - ol* (**36**).—Following the 'General method for with DIBALH reduction', **35** (770 mg, 1.87 mmol) afforded **36** (542 mg, 70%) after chromatography (7:3 hexane–EtOAc): oil; $[\alpha]_D^{25}$ +8° (*c* 0.95, $CHCl_3$); IR (KBr) *v* 3447, 1010, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38–7.29 (m, 5 H, $OCH_2C_6H_5$), 5.72 (br s, 1 H, H-3), 5.39 (d, $J_{7a,7b}$ 4.5 Hz, 1 H, H-7a), 5.40–5.37 (m, 1 H, H-4), 4.75 (d, $J_{OH,4}$ 6.7 Hz, 1 H, OH), 4.73 (d, *J* 10.7 Hz, 1 H, $OCH_2C_6H_5$), 4.68 (d, *J* 10.7 Hz, 1 H, $OCH_2C_6H_5$), 4.52 (dd, $J_{2',2}$ 11.0, *J* 1.3 Hz, 1 H, H-2′), 4.21 (dm, $J_{2,2'}$ 11.0 Hz, 1 H, H-2), 3.95 (dt, $J_{6,5}$ 7.9, $J_{6,2H6a}$ 4.0 Hz, 1 H, H-6), 3.81 (t, $J_{5,4a} = J_{5,6}$ 7.9 Hz, 1 H, H-5), 3.47 (dd, $J_{6a',6a}$ 10.6, $J_{6a',6}$ 4.2 Hz, 1 H, H-6a′), 3.34 (dd, $J_{6a,6a'}$ 10.6, $J_{6a,6}$ 4.0 Hz, 1 H, H-6a), 3.25–3.15 (m, 2 H, H-4a, H-7b); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.2 (C-2a), 136.2-128.2 ($OCH_2C_6H_5$), 126.7 (C-3), 95.1 (C-7a), 85.7 (C-4), 77.8 (C-5), 73.0 ($OCH_2C_6H_5$), 69.5 (C-6), 63.9 (C-2), 51.5 (C-7b), 38.7 (C-4a), 9.2 (C-6a); MS (70 eV): *m*/*z* 153 (14), 107 (17), 91 (100), 79 (26), 65 (16). Anal. Calcd for $C_{17}H_{19}O_4I$: C, 49.29; H, 4.62. Found: C, 49.34; H, 4.32.

*(4*S*,4a*R*,5*S*,6*R*,7a*S*,7b*S*) - 4,4a,5,6,7a,7b-Hexahydro - 6 - iodomethyl - 5 - phenylmethoxy - 2*H*-1,7-dioxacyclopent[cd]inden - 4 - ol benzoate* (**37**).—Following the 'General method for benzoylation', alcohol **36** (61mg, 0.15 mmol) gave benzoate **37** (60 mg, 72%) after chromatography (7:3 hexane–EtOAc): mp 105–108 °C; $[\alpha]_D^{25}$ +125° (*c* 0.95, $CHCl_3$); IR (KBr) *v* 2921, 1712, 1265, 1116, 1014, 717 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (dd, *J* 8.2, *J* 1.1 Hz, 2 H), 7.43 (tm, *J* 7.5 Hz, 1 H), 7.25 (d, *J* 7.7 Hz, 1 H) [$OCOC_6H_5$], 7.09–7.20 (m, 5 H, $OCH_2C_6H_5$), 6.63 (ddt, $J_{4,4a}$ 5.7, $J_{4,2}$ 3.5, $J_{4,2'} = J_{4,3}$ 1.7 Hz, 1 H, H-4), 5.80 (br s, 1 H, H-3), 5.54 (d, $J_{7a,7b}$ 4.4 Hz, 1 H, H-7a), 4.70 (d, *J* 10.5 Hz, 1 H, $OCH_2C_6H_5$), 4.60 (dd, $J_{2',2}$ 12.5, $J_{2',4}$ 1.5 Hz, 1 H, H-2′), 4.40 (d, *J* 10.5 Hz, 1 H, $OCH_2C_6H_5$), 4.32 (ddt, $J_{2,2'}$ 12.5, $J_{2,4}$ 3.5, *J* 1.7 Hz, 1 H, H-2), 4.04 (dt, $J_{6,5}$ 9.0, $J_{6,6a}$ 3.3 Hz, 1 H, H-6), 3.68 (dd, $J_{5,6}$ 9.0, $J_{5,4a}$ 5.7 Hz, 1 H, H-5), 3.59 (dt, $J_{4a,7b}$ 8.9, $J_{4a,4} = J_{4a,5}$ 5.7 Hz, 1 H, H-4a), 3.48 (dd, $J_{6a',6a}$ 10.5, $J_{6a',6}$ 3.3 Hz, 1 H, H-6a′), 3.42–3.37 (m, 1 H, H-7b), 3.40 (dd, $J_{6a,6a'}$ 10.5, $J_{6a,6}$ 3.3 Hz, 1 H, H-6a); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9 ($OCOC_6H_5$), 148.1 (C-2a), 137.2-127.4 ($OCOC_6H_5$, $OCH_2C_6H_5$), 123.2 (C-3), 95.3 (C-7a), 84.7 (C-4), 77.0 (C-5), 72.6 ($OCH_2C_6H_5$), 71.0 (C-6), 63.6 (C-2), 54.6 (C-7b), 36.7 (C-4a), 12.2 (C-6a); MS (70 eV): *m*/*z* 269 (31), 227 (12), 197 (19), 168 (32), 105 (100), 91(100), 79 (45), 77 (62). Anal. Calcd for $C_{24}H_{23}O_5I$: C, 55.61; H, 4.47. Found: C, 55.81; H, 4.67.

Reaction of intermediate **37** *with silver fluoride.*—Following the 'General method for the elimination reaction with this reagent', **37** (35 mg, 0.068 mmol) gave (4*S*,4a*R*,5*S*,6*R*,7a*S*,7b*S*) - 6 - (benzoyloxy)methyl - 4,4a,5,6,7a,7b-hexahydro-5-phenylmethoxy-2*H*-1,7-dioxacyclopent[cd]inden-4-ol benzoate (**38**, 11.5 mg, 33%) after chromatography (7:3 hexane–EtOAc): oil; IR (KBr) *v* 2920, 1717, 1274, 1113 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* 8.4 Hz, 2 H), 7.78 (d, *J* 8.4 Hz, 2 H), 7.47 (t, *J* 7.4 Hz, 2 H), 7.40 (t, *J* 7.4 Hz, 1 H), 7.33 (t, *J* 7.7 Hz, 2 H), 7.23 (t, *J* 7.7 Hz, 2 H) [2 × $OCOC_6H_5$], 6,99 (s, 5 H, $OCH_2C_6H_5$), 6.60 (dm, $J_{4,4a}$ 7.6 Hz, 1 H, H-4), 5.77 (br s, 1 H, H-3), 5.41 (d, $J_{7a,7b}$ 4.2 Hz, 1 H, H-7a), 4.64–4.52 (m, 1 H, H-6), 4.53 (dm, $J_{2',2}$ 12.5 Hz, 1 H, H-2′), 4.49 (d, *J* 11.4 Hz, 1 H, $OCH_2C_6H_5$), 4.36 (d, $J_{2H6a,6}$ 2.9 Hz, 2 H, 2 H-6a), 4.27 (d, *J* 11.4 Hz, 1 H, $OCH_2C_6H_5$), 4.25 (dm, $J_{2,2'}$ 12.5 Hz, 1 H, H-2), 3.80 (dd, $J_{5,6}$ 9.0, $J_{5,4a}$ 5.9 Hz, 1 H, H-5), 3.53 (dt, $J_{4a,7b}$ 8.9, $J_{4a,4} = J_{4a,5}$ 7.6 Hz, 1 H, H-4a), 3.33–3.30 (m, 1 H, H-7b); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2 (2 × $OCOC_6H_5$), 147.8 (C-2a), 132.9-127.5 (15 C, 2 × $OCOC_6H_5$, $OCH_2C_6H_5$), 123.9 (C-3), 95.2 (C-7a), 84.7 (C-4), 73.0 (C-5), 72.0 (2 C, $OCH_2C_6H_5$, C-6), 64.8 (C-6a), 63.8 (C-2), 54.4 (C-7b), 37.4 (C-4a); MS (70

eV): *m*/*z* 390 (7), 105 (100), 91 (91), 77 (44). Anal. Calcd for $C_{31}H_{28}O_7$: C, 72.64; H, 5.51. Found: C, 72.77; H, 5.34.

Reaction of intermediate **9** *with MeOH.*—Following the 'General method for the hydrolysis with MeOH in acidic conditions', **9** (70 mg, 0.23 mmol) gave (1*R*,2a*R*,6a*S*,6b*R*,7*S*,9a*S*) - 1,2a,3,5,6a,6b,9a - octahydro - 7-hydroxy-1-methoxy-6-phenyl-4,6-dioxacyclohexa[e]cyclopenta[*c*]pyran-9-MeOH (**39**, 57.4 mg, 71%) and (1*R*,3*R*,4*S*,4a*R*,5*S*,7a*S*)-1,3,4,4a,5,7a-hexahydro-4,5-dihydroxy-cyclopenta-[cd]pyran-3,7-dimethanol (**40**, 6 mg, 11%) after chromatography (from hexane to EtOAc). Compound **39**: oil; IR (KBr) *ν* 3414, 1380, 1101, 1084, 1025, 761, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.38 (m, 5 H, C_6H_5), 5.81 (d, $J_{8,7}$ 2.3 Hz, 1 H, H-8), 5.61 (s, 1 H, H-5), 4.92 (br t, $J_{7,8} = J_{7,OH}$ 2.3 Hz, 1 H, H-7), 4.56 (d, $J_{1,9a}$ 7.8 Hz, 1 H, H-1), 4.38 (dd, $J_{3',3}$ 10.0, $J_{3',2a}$ 4.4 Hz, 1 H, H-3′), 4.31 (br dd, $J_{9'',9'}$ 14.8, $J_{9'',OH}$ 6.0 Hz, 1 H, H-9″), 4.25 (br dd, $J_{9',9''}$ 14.8, $J_{9',OH}$ 6.0 Hz, 1 H, H-9′), 4.15–4.04 (m, 2 H, H-2a, H-6a), 3.77 (t, $J_{3,3'} = J_{3,2a}$ 10.0 Hz, 1 H, H-3), 3.54 (s, 3 H, OCH_3), 2.78–2.74 (m, 2 H, H-6b, H-9a), 2.45 (d, $J_{OH,7}$ 2.3, Hz, 1 H, OH), 2.34 (t, $J_{OH,9'}$ 6.0 Hz, 1 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.0 (C-9), 137.5–126.3 (C_6H_5), 128.1 (C-8), 107.2 (C-1), 102.7 (C-5), 79.2 (C-6a), 75.7 (C-7), 70.3 (C-3), 67.8 (C-2a), 61.5 (C-9′), 57.0 (OCH_3), 50.2 (C-9a)*, 43.3 (C-6b)*; MS (70 eV): *m*/*z* 256 (75), 179 (31), 134 (25), 121 (36), 107 (95), 105 (100), 91 (63), 79 (78), 78 (86), 77 (52). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.32; H, 6.56. Compound **40**: oil; $[\alpha]_D^{25}$ +41° (*c* 0.95, MeOH); IR (KBr) *ν* 3429, 3250, 1375, 1097, 1056, 1031, 989, 890 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.08 (d, $J_{6,7'}$ 1.8 Hz, 1 H, H-6), 5.03–4.80 (m, 1 H, H-5), 4.67 (d, $J_{1,7a}$ 8.4 Hz, 1 H, H-1), 4.44 (dd, $J_{7,7''}$ 15.8, $J_{7',6}$ 1.8 Hz, 1 H, H-7′), 4.29 (br d, $J_{7'',7'}$ 15.8 Hz, 1 H, H-7″), 4.10–3.99 (m, 3 H, H-3a, H-4, H-3), 3.81 (dd, $J_{3a,3a'}$ 11.4, $J_{3a',3}$ 5.5 Hz, 1 H, H-3a′), 3.67 (s, 3 H, OCH_3), 2.79 (q, $J_{4a,7a} = J_{4a,4} = J_{4a,5}$ 7.0 Hz, 1 H, H-4a), 2.67 (dd, $J_{7a,1}$ 8.4, $J_{7a,4a}$ 7.0 Hz, 1 H, H-7a); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.5 (C-7), 128.4 (C-6), 108.0 (C-1), 79.8 (C-3)*, 76.6 (C-5), 68.0 (C-4)*, 63.6 (C-3a), 61.6 (C-7′), 56.7 (OCH_3), 50.6 (C-7a), 46.9 (C-4a); MS (70 eV): *m*/*z* 107 (21), 95 (37), 94 (22), 91 (21), 79 (50), 78 (100), 77 (24), 67 (28), 66 (20), 61 (20). Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.36; H, 7.39.

*(1*R*,2a*R*,6a*S*,6b*R*,7*S*,9a*S*) - 7 - Benzoyloxy - 1,2a,3,5,6a,6b,7,9a - octahydro - 1 - methoxy - 5-phenyl - 4,6 - dioxacyclohexa[e]cyclopenta[c]-pyran-9-methanol benzoate* (**41**).—Following the 'General method for the benzoylation reaction', **39** (185 mg, 0.55 mmol) afforded **41** (285 mg, 95%) after chromatography (9:1 hexane–EtOAc): mp 60–63 °C; $[\alpha]_D^{25}$ +107° (*c* 0.25, $CHCl_3$); IR (KBr) *ν* 1719, 1269, 1103, 1026, 712 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.10–7.20 (m, 15 H, 2 × $OCOC_6H_5$, C_6H_5), 6.23 (d, $J_{8,7}$ 1.8 Hz, 1 H, H-8), 6.09 (dd, $J_{7,6b}$ 7.1, $J_{7,8}$ 1.8 Hz, 1 H, H-7), 5.54 (s, 1 H, H-5), 5.08 (dd, $J_{9',9''}$ 16.0, $J_{9'',8}$ 1.3 Hz, 1 H, H-9″), 4.97 (d, $J_{9',9''}$ 16.0 Hz, 1 H, H-9′), 4.62 (d, $J_{1,9a}$ 8.3 Hz, 1 H, H-1), 4.37 (dd, $J_{3',3}$ 9.9, $J_{3',2a}$ 4.9 Hz, 1 H, H-3′), 4.20 (td, $J_{2a,6a} = J_{2a,3}$ 9.9, $J_{2a,3'}$ 4.9 Hz, 1 H, H-2a), 4.05 (dd, $J_{6a,2a}$ 9.9, $J_{6a,6b}$ 7.1 Hz, 1 H, H-6a), 3.75 (t, $J_{3,3'} = J_{3,2a}$ 9.9 Hz, 1 H, H-3a), 3.59 (s, 3 H, OCH_3), 3.10 (q, $J_{6b,9a} = J_{6b,7} = J_{6b,9a}$ 7.1 Hz, 1 H, H-6b), 2.90 (dd, $J_{9a,1}$ 8.3, $J_{9a,6b}$ 7.1 Hz, 1 H, H-9a); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 165.9 (2 × $OCOC_6H_5$), 147.7 (C-9), 137.1–126.2 (2 × $OCOC_6H_5$, C_6H_5), 126.9 (C-8), 106.4 (C-1), 102.8 (C-5), 77.9 (C-6a), 77.0 (C-7), 69.8 (C-3), 67.0 (C-2a), 62.5 (C-9′), 56.9 (OCH_3), 50.5 (C-9a), 42.1 (C-6b); MS (70 eV): *m*/*z* 149 (16), 132 (15), 105 (100), 77 (24). Anal. Calcd for $C_{32}H_{30}O_8$: C, 70.84; H, 5.57. Found: C, 70.98; H, 5.80.

Hanessian–Hullar reaction of intermediate **41**.—Following the 'General method for the Hanessian–Hullar reaction', **41** (285 mg, 0.53 mmol) gave (1*R*,3*R*,4*S*,4a*R*,5*S*,7a*S*)-4,5-dibenzoyloxy - 3 - bromomethyl - 1,3,4,4a,5,7a-hexahydro - 1 - methoxy - cyclopenta[*c*]pyran - 7-methanol benzoate (**42**, 208.6 mg, 64%) after chromatography (9:1 hexane–EtOAc): mp 41–44 °C; $[\alpha]_D^{25}$ +72° (*c* 0.8, $CHCl_3$); IR (film) *ν* 1721, 1451, 1270, 1095, 1069, 1026, 709 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.07–7.28 (m, 15 H, 3 × $OCOC_6H_5$), 6.13 (d, $J_{6,5}$ 1.8 Hz, 1 H, H-6), 5.98 (dd, $J_{5,4a}$ 7.7, $J_{5,6}$ 1.8 Hz, 1 H, H-5), 5.28 (dd, $J_{4,3}$ 10.0, $J_{4,4a}$ 7.7 Hz, 1 H, H-4), 5.10 (dd, $J_{7',7''}$ 15.8, $J_{7'',6}$ 1.5 Hz, 1 H, H-7″), 4.94 (d, $J_{7',7''}$ 15.8 Hz, 1 H, H-7′), 4.71

(d, $J_{1,7a}$ 8.4 Hz, 1 H, H-1), 4.46 (ddd, $J_{3,4}$ 10.0, $J_{3,3a}$ 7.7, $J_{3,3a'}$ 2.3 Hz, 1 H, H-3), 3.64 (s, 3 H, OCH_3), 3.56 (dd, $J_{3a',3a}$ 11.0, $J_{3a',3}$ 2.3 Hz, 1 H, H-3a′), 3.42 (dd, $J_{3a,3a'}$ 11.0, $J_{3a,3}$ 7.7 Hz, 1 H, H-3a), 3.36 (q, $J_{4a,7a} = J_{4a,4} = J_{4a,5}$ 7.7 Hz, 1 H, H-4a), 2.80 (dd, $J_{7a,1}$ 8.4, $J_{7a,4a}$ 7.7 Hz, 1 H, H-7a); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9, 165.6, 165.6 ($3 \times OCOC_6H_5$), 147.9 (C-7); 133.5–128.4 (18 C, $3 \times OCOC_6H_5$), 126.1 (C-6), 106.2 (C-1), 77.3 (C-5), 75.3 (C-3), 70.4 (C-4), 62.4 (C-7′), 56.8 (OCH_3), 49.9 (C-7a), 42.0 (C-4a), 32.1 (C-3a); MS (70 eV): m/z 297 (11), 258 (10), 106 (10), 105 (100), 77 (21). Anal. Calcd for $C_{32}H_{29}BrO_8$: C, 61.85; H, 4.70. Found: C, 62.05; H, 4.63.

*(1*R*,3*R*,4*S*,4a*R*,5*S*,7a*S*)-4,5-Dibenzoyloxy-1,3,4,4a,5,7a-hexahydro-3-iodomethyl-1-methoxy-cyclopenta[c]pyran-7-methanol benzoate* (**43**).—Following the 'General method for the iodination', bromide **42** (345 mg, 0.56 mmol) gave **43** (272 mg, 73%) after chromatography (17: 3 hexane–EtOAc,): oil; IR (KBr) ν 1720, 1631, 1270, 1093, 710 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08–7.51 (m, 15 H, $3 \times OCOC_6H_5$), 6.15 (d, $J_{6,5}$ 1.8 Hz, 1 H, H-6), 5.99 (dd, $J_{5,4a}$ 7.5, $J_{5,6}$ 1.8 Hz, 1 H, H-5), 5.21 (dd, $J_{4,3}$ 9.4, $J_{4,4a}$ 7.8 Hz, 1 H, H-4), 5.12 (dd, $J_{7',7''}$ 15.9, $J_{7'',6}$ 1.6 Hz, 1 H, H-7″), 4.96 (br d, $J_{7',7''}$ 15.9 Hz, 1 H, H-7′), 4.73 (d, $J_{1,7a}$ 8.4 Hz, 1 H, H-1), 4.39 (td, $J_{3,4} = J_{3,3a}$ 9.4, $J_{3,3a'}$ 2.4 Hz, 1 H, H-3), 3.69 (s, 3 H, OCH_3), 3.40 (dd, $J_{3a',3a}$ 10.9, $J_{3a',3}$ 2.4 Hz, 1 H, H-3a′), 3.37 (q, $J_{4a,7a} = J_{4a,4} = J_{4a,5}$ 7.5 Hz, 1 H, H-4a), 3.20 (dd, $J_{3a,3a'}$ 10.9, $J_{3a,3}$ 9.4 Hz, 1 H, H-3a), 2.98 (dd, $J_{7a,1}$ 8.4, $J_{7a,4a}$ 7.5 Hz, 1 H, H-7a); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9, 165.9, 165.6 ($3 \times OCOC_6H_5$), 147.9 (C-8), 133.5–128.4 (15 C, $3 \times OCOC_6H_5$), 126.0 (C-6), 106.3 (C-1), 77.3 (C-5), 75.7 (C-3), 71.8 (C-4), 62.5 (C-7′), 56.9 (OCH_3), 50.1 (C-7a), 42.3 (C-4a), 4.8 (C-3a); MS (70 eV): m/z 481 (24), 259 (12), 237 (24), 106 (28), 105 (100), 77 (62), 51 (14). Anal. Calcd for $C_{32}H_{29}IO_8$: C, 57.50; H, 4.37. Found: C, 57.62; H, 4.59.

Reaction of intermediate **43** *with AgF.*—Following the 'General method for the elimination with this reagent', **43** (403 mg, 0.6 mmol) afforded **44** (75 mg, 19%) and (1*R*,4*S*,4a*R*,5*S*,7a*S*)-4,5-dibenzoyloxy-1,4,4a,5,7a-pentahydro-1-methoxy-3-methylene-cyclopenta[*c*]pyran-7-methanol benzoate (**45**, 99 mg, 30%) after chromatography (4:1 hexane–EtOAc). Compound **44**: mp 37–40 °C; $[\alpha]_D^{25}$ + 89° (*c* 0.11, $CHCl_3$); IR (KBr) ν 1721, 1272, 1097, 1069, 1026, 709 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13–7.23 (m, 20 H, $4 \times C_6H_5$), 6.19 (br d, $J_{6,5}$ 2.0 Hz, 1 H, H-6), 6.01 (dd, $J_{5,4a}$ 7.8, $J_{6,6}$ 2.0 Hz, 1 H, H-5), 5.52 (dd, $J_{4,3}$ 9.8, $J_{4,4a}$ 7.8 Hz, 1 H, H-4), 5.14 (dd, $J_{7',7''}$ 15.8, $J_{7'',6}$ 1.4 Hz, 1 H, H-7″), 4.98 (d, $J_{7',7''}$ 15.8 Hz, 1 H, H-7′), 4.74 (d, $J_{1,7a}$ 8.4 Hz, 1 H, H-1), 4.68–4.59 (m, 2 H, H-3a′, H-3), 4.45 (dd, $J_{3a,3a'}$ 12.7, $J_{3a,3}$ 6.5 Hz, 1 H, H-3a), 3.61 (s, 3 H, OCH_3), 3.43 (q, $J_{4a,7a} = J_{4a,4} = J_{4a,5}$ 7.8 Hz, 1 H, H-4a), 3.01 (dd, $J_{7a,1}$ 8.4, $J_{7a,4a}$ 7.8 Hz, 1 H, H-7a); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1–165.7 ($4 \times OCOC_6H_5$), 147.8 (C-7), 133.3–128.3 (24 C, $4 \times OCOC_6H_5$), 126.3 (C-6), 106.2 (C-1), 77.6 (C-5), 73.5 (C-3), 68.8 (C-4), 64.4 (C-3a), 62.5 (C-7′), 56.8 (OCH_3), 49.8 (C-7a), 43.0 (C-4a); MS (70 eV): m/z 149 (16), 132 (15), 105 (100), 77 (24). Anal. Calcd for $C_{39}H_{34}O_{10}$: C, 70.69; H, 5.17. Found: C, 70.52; H, 5.13. Compound **45**: oil; IR (KBr) ν 2920, 1720, 1451, 1268, 1109, 1026, 709 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10–7.29 (m, 15 H, $3 \times OCOC_6H_5$), 6.20 (dm, $J_{5,4a}$ 8.0 Hz, 1 H, H-5), 6.06 (q, J 1.6 Hz, 1 H, H-6), 6.03 (d, $J_{4,5}$ 4.6 Hz, 1 H, H-4), 5.19 (d, $J_{1,7a}$ 5.6 Hz, 1 H, H-1), 5.13 (dq, $J_{7'',7'}$ 14.8, $J_{7'',6}$ 1.2 Hz, 1 H, H-7″), 4.99 (dm, $J_{7',7''}$ 14.8 Hz, 1 H, H-7′), 4.58 (d, $J_{3a',3a}$ 0.8 Hz, 1 H, H-3a′), 4.58 (d, $J_{3a,3a'}$ 0.8 Hz, 1 H, H-3a), 3.54 (s, 3 H, OCH_3), 3.36 (ddd, $J_{4a,7a}$ 9.2, $J_{4a,5}$ 8.0, $J_{4a,4}$ 4.6 Hz, 1 H, H-4a), 3.27–3.22 (m, 1 H, H-7a); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 166.0, 165.1 ($3 \times OCOC_6H_5$), 142.9 (C-7), 153.5 (C-3), 133.3–128.1 (18 C, $OCOC_6H_5$), 129.0 (C-6), 101.3 (C-1), 92.1 (C-3a), 77.6 (C-5), 67.4 (C-4), 61.8 (C-7′), 56.8 (OCH_3), 49.7 (C-7a), 40.7 (C-4a); MS (70 eV): m/z 192 (6), 105 (100), 77 (22). Anal. Calcd for $C_{32}H_{30}O_8$: C, 70.84; H, 5.57. Found: C, 70.72; H, 5.41.

Ferrier reaction of intermediate **45**.—Compound **45** (43 mg, 0.08 mmol) was dissolved in dry acetone (2.6 mL, 0.03M), $HgCl_2$ (24 mg, 0.08 mmol, 1 equiv) was added, and the mixture was refluxed for 2 h 30 min; then, more $HgCl_2$ (24 mg, 0.08 mmol, 1 equiv) was added, and the reaction was warmed for 2 h. The mixture was cooled, water was added and the

mass was extracted with EtOAc. The organic phase was washed with an aq $NaHCO_3$ solution, brine, dried with Na_2SO_4, filtered and the solvent was evaporated. The residue was submitted to chromatography (from 3:2 hexane to hexane–EtOAc) affording (3*S*,3a*S*,7a*S*)-1-benzoyloxymethyl-3,4-bis-(benzoyloxy)-3,3a,4,6,7,7a-hexahydro-7-hydroxy-5*H*-inden-5-one (**46**, 15.7 mg, 34%): oil; $[\alpha]_D^{25}$ +161° (*c* 0.29, $CHCl_3$); IR (film) *v* 3444, 2929, 2869, 1715, 1671, 1601, 1451, 1315, 1267, 1108, 1070, 1026, 711 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.07 (dd, *J* 7.8, *J* 0.8 Hz, 2 H), 7.92 (dd, *J* 7.2, *J* 1.2 Hz, 2 H), 7.87 (dd, *J* 7.2, *J* 1.3 Hz, 2 H), 7,60 (tm, *J* 7.5 Hz, 1 H), 7.56–7.40 (m, 6 H), 7.32 (br t, *J* 7.7 Hz, 2 H), 6.21–6.19 (m, 2 H, H-4, H-2), 6.16 (d, $J_{3,3a}$ 7.7, $J_{3,2}$ 2.5 Hz, 1 H, H-3), 5.10 (br s, 2 H, 2 H-1a), 4.52–4.49 (m, 1 H, H-7), 3.32 (q, $J_{3a,3} = J_{3a,7a} = J_{3a,4}$ 7.7 Hz, 1 H, H-3a), 3.37 (dd, $J_{7a,3a}$ 7.7, $J_{7a,7}$ 4.0 Hz, 1 H, H-7a), 2.93 (dd, $J_{6,6'}$ 16.2, $J_{6,7}$ 3.3 Hz, 1 H, H-6), 2,84 (dd, $J_{6',6}$ 16.2, $J_{6',7}$ 6.1 Hz, 1 H, H-6′), 2.71 (d, $J_{-OH,7}$ 3.2 Hz, 1 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.7 (C-5), 166.3 ($3 \times OCO\ C_6H_5$), 147.4 (C-1), 133.5–128.3 (18 C, $3 \times OCOC_6H_5$), 127.9 (C-2), 77.2 (C-3), 72.6 (C-4), 68.4 (C-7), 61.9 (C-1a), 52.2 (C-7a), 43.2 (C-3a), 42.6 (C-6); MS (70 eV): *m*/*z* 404 (3), 282 (15), 160 (57), 106 (309, 105 (100), 77 (62). Anal. Calcd for $C_{30}H_{26}O_8$: C, 70.03; H, 5.09. Found: C, 69.94; H, 4.92.

*(3*S*,3a*S*,7a*S*)-7-Acetyloxy-3,4-bis(benzoyloxy)-1-benzoyloxymethyl-3,3a,4,6,7,7a-hexahydro-5*H*-inden-5-one* (**47**).—Following the 'General method for acetylation', **46** (10 mg, 0,019 mmol) gave acetate **47** (6.6 mg, 63%) after purification by chromatography (7:3 hexane–EtOAc): oil; IR (KBr) *v* 3436, 1721, 1451, 1265, 1096, 1070, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, *J* 7.1 Hz, 2 H), 7.93 (d, *J* 7.1 Hz, 2 H), 7.87 (d, *J* 7.2 Hz, 2 H), 7.63–7.42 (m, 7 H), 7.34 (t, *J* 7.8 Hz, 2 H), 6.26 (dm, $J_{3,3a}$ 7.4 Hz, 1 H, H-3), 6.19 (s, 1 H, H-2), 6.14 (d, $J_{4,3a}$ 7.4 Hz, 1 H, H-4), 5.55 (m, 1 H, H-7), 5.14 (br d, *J* 16.2 Hz, 1 H, H-1a), 5.09 (br d, *J* 16.2 Hz, 1 H, H-1a′), 3.59 (q, $J_{3a,3} = J_{3a,7a} = J_{3a,4}$ 7.4 Hz, 1 H, H-3a), 3.49 (dd, $J_{7a,3a}$ 8.5 Hz, 1 H, H-7a), 3.00 (dd, $J_{6,6'}$ 17.8, $J_{6,7}$ 3.2 Hz, 1 H, H-6), 2.87 (ddm, $J_{6',6}$ 17.8, $J_{6',7}$ 3.0 Hz, 1 H, H-6′), 2.17 (s, 3 H, $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.5 (C-5), 169.9 (2 C), 165.9, 165.6 ($3 \times OCOC_6H_5$, $OCOCH_3$), 145.3 (C-1), 133.4–128,3 (18 C, $3 \times OCOC_6H_5$), 129.0 (C-2), 77.2 (C-3), 71.9 (C-4), 68.4 (C-7), 61.3 (C-1a), 49.7 (C-3a), 42.0 (C-7a), 40.3 (C-6), 21.3 ($OCOCH_3$); MS (70 eV): *m*/*z* 387 (7), 264 (42), 160 (23), 105 (100), 77 (53). Anal. Calcd for $C_{32}H_{28}O_9$: C, 69.06; H, 5.07. Found: C, 69.19; H, 5.31.

Acknowledgements

J.R.C. is a fellow of the CAM.

References

1. Martínez-Grau, A.; Marco-Contelles, J. *Chem. Soc. Rev.* **1998**, *27*, 155–162.
2. Marco-Contelles, J.; Alhambra, C.; Martínez-Grau, A. *Synlett* **1998**, 693–699 (Corrigendum: *Synlett* **1999**, 376).
3. Schore, N. E. *Org. React.* **1991**, *40*, 1–90.
4. Marco-Contelles, J.; Ingate, S. *Org. Prep. Proc. Int.* **1998**, *30*, 121–143.
5. Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263–3283.
6. Marco-Contelles, J.; Ruiz, J. *Tetrahedron Lett.* **1998**, *39*, 6393–6394.
7. Marco-Contelles, J.; Ruiz, J. *J. Chem. Res. (S)* **1999**, 260–261.
8. Marco-Contelles, J.; Ruiz, J. *J. Org. Chem.* **1999**, *64*, 8302–8310.
9. Marco-Contelles, J.; Ruiz-Caro, J. *Tetrahedron Lett.* **2001**, *42*, 1515–1517.
10. El-Naggar, L. J.; Beil, J. L. *J. Nat. Prod.* **1980**, *42*, 649–707.
11. Zhu, G. D.; Okamura, W. H. *Chem. Rev.* **1995**, *95*, 1877–1952.
12. Ferrier, R. J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1455–1458.
13. Kelly, D. R.; Picton, M. R. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1559–1569.
14. Smit, W. A.; Simonyan, S. O.; Shashkov, A. S.; Mamyan, S. S.; Tarasov, V; Ibragimov, I. *Izv. Akad. SSSR. Ser. Khim.* **1987**, 234–235.
15. Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277–7287.
16. Eschinazi, H. E. *J. Am. Chem. Soc.* **1959**, *81*, 2905–2906.
17. Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, J. *J. Chem. Soc. (A)* **1966**, 1711–1732.
18. Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99–107.
19. Walborsky, H. M.; Allen, L. E. *J. Am. Chem. Soc.* **1971**, *93*, 5645–5648.
20. Schubert, W. M.; Kintner, R. R. In *The Chemistry of the Carbonyl Group*; Patai, S., Ed.; Interscience: New York, 1966 Chap. 14.
21. Hasall, C. H. *Org. React.* **1967**, *9*, 73–106.

22. Hanessian, S.; Plessas, N. R. *J. Org. Chem.* **1969**, *34*, 1045–1053.
23. Picq, D.; Anker, D. *J. Carbohydr. Chem.* **1985**, *4*, 113–123.
24. Garegg, P. J.; Samuelson, B. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2866–2869.
25. Chrétien, F. *Synth. Commun.* **1989**, *19*, 1015–1024.