A New, Non-Iterative Asymmetric Synthesis of Long-Chain 1,3-Polyols

Marc-Etienne Schwenter and Pierre Vogel*[a]

Abstract: A new approach to the asymmetric synthesis of pentadeca-1,3,5,7,9,11,13,15-octols and their derivatives is presented. It is based on the Sharpless asymmetric dihydroxylation (AD) of 4,4′-methylene[(1*R*,1′*S*,6*R*,6′*S*)-6-acetoxycyclohept-3-en-1-yl]bis(4-methoxybenzoate) (**9**), derived from a double [3+4] cycloaddition of the 1,1,3-trichloro-2-oxyallyl cation with 2,2′-methylenedifuran (**1**). The diol (−)-**10**, obtained in 98.4% *ee* from **9** with "AD-mix-β($5\times$), was oxidised into (2*R* and 2*S*,4*S*,6*R*)-tetrahydro-2-hydroxy-6-{(4*S*,6*S*)-{6-hydroxy-4-[(4-methoxybenzoyl)oxy]cyclohept-1-en-1-yl}-2-oxopropyl}-2*H*-pyran-4-yl 4-methoxybenzoates ((−)-**18**). By the combinations of Evans' *anti* and Nasaraka's *syn* reductions of aldol (−)-**18** with the double Mitsunobu reaction, 16 diastereomeric pentadeca-1,3,5,7,9,11,13,15-octols and analogues can be obtained, in principle, with high enantio- and diastereoselectivities.

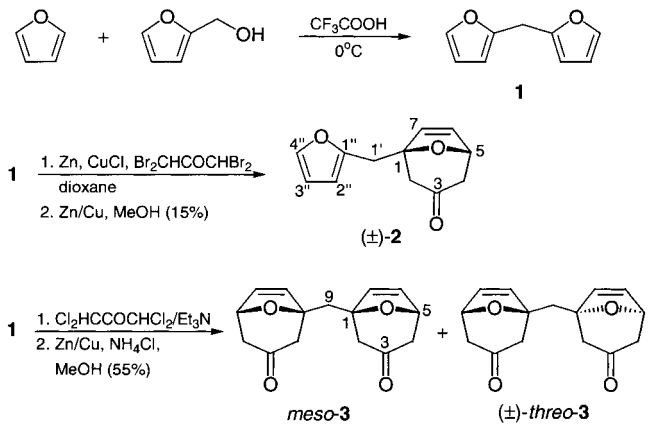
Keywords: aldols · cycloadditions · cycloheptenes · polyketides · polyols

Introduction

A great variety of natural products of biological interest includes polyketides (1,3-polyoxo, 1,3-polyols, aldols).[1] Several approaches for their synthesis have been proposed.[2, 3] We disclose a new, non-iterative approach based on the double [4+3] cycloaddition of 1,1,3-trichloro-2-oxyallyl cation, engendered by HCl elimination from 1,1,3,3-tetrachloroacetone,[4] to 2,2′-methylenedifuran (**1**). The double adducts so-obtained are converted into *meso*-1,1-methylene-bis(4,6-dihydroxycyclohept-1-ene) derivatives that can be desymmetrised and transformed into pentadeca-1,3,5,7,9,11,13,15-octols and other long-chain polyketides with high stereo- and enantioselectivity. The method was inspired by the work of Lautens[5a] and Hoffmann and co-workers[5b] who have converted 8-oxabicyclo[3.2.1]oct-6-en-3-one into 7-carbon-1,3-polyols and analogues[5c] and by that of Kaku et al.[6] who have transformed cyclohept-3-ene-1,6-diol into 1,3-polyols and their derivatives.

Results and Discussion

All the published procedures to prepare 2,2′-methylenedifuran (**1**)[7–10] led to low yields in our hands. A new and improved method was developed that starts with inexpensive furfuryl alcohol and furan (Scheme 1). A stirred 0.9 molar solution of furfuryl alcohol in furan that contained CF_3COOH (0 °C, 24 h) produced **1** in 65% yield. Several well-established methods have been employed to convert furan and substituted furans into 8-oxabicyclo[3.2.1]oct-6-en-3-one[11–14] and its derivatives.[15] Under the conditions developed by Noyori et al.,[11] a low yield of monoketone (±)-**2** was isolated after reductive work-up with zinc/copper (Scheme 1); [16] the major product was polymeric material. The best yield of (±)-**2** (13%) was obtained when a two-fold excess of a 1:1 mixture of $[Fe_2(CO)_9]$/1,1,3,3-tetrabromoacetone was treated with **1** in benzene (50 °C, 22 h). Similar results were obtained in MeCN as the solvent (−78 to 20 °C, 40 h). Under the conditions developed by Hoffmann et al.,[12] (±)-**2** was obtained in 15% yield in the best case (dioxane, 1,1,3,3-tetrabromoacetone, Zn/CuCl, ultrasonification, 20 °C, 15 h). Traces of [4+3] bis-adducts were found on application of Shimizu's method[13]



Scheme 1.

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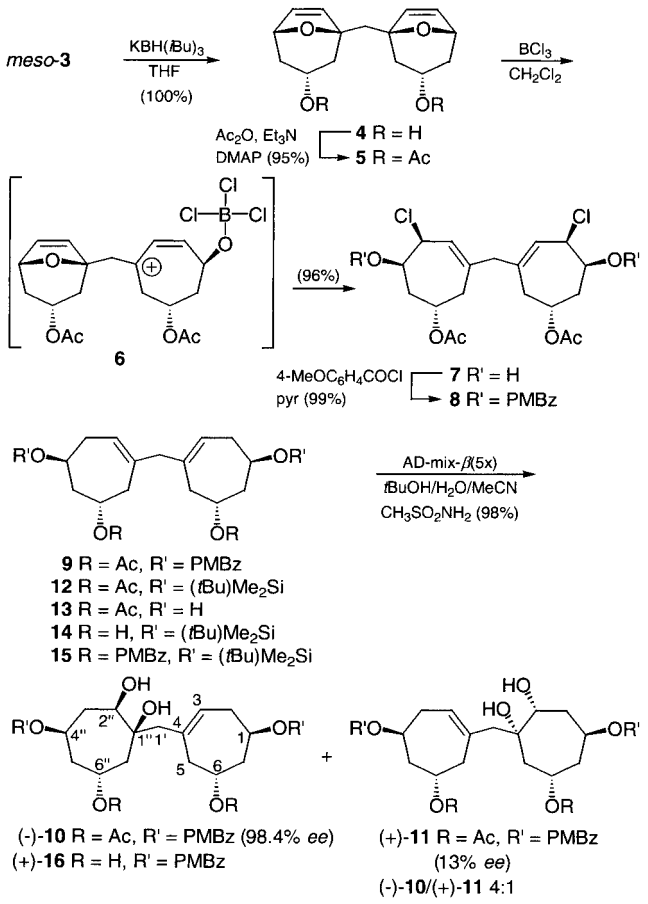
(1,3-dichloro-2-(trimethylsilyloxy)propene, $AgClO_4$, $CaCO_3$, $MeNO_2$, 0–20 °C, 24 h). Finally, the best results were obtained by the use of Föhlisch's method:[14] treatment of **1** with 2.6 equivalents of 1,1,3,3-tetrachloroacetone[17] and Et_3N in $CF_3CH(OH)CF_3$ afforded a mixture of products that was not isolated but directly reduced with zinc/copper couple[16] in MeOH saturated with NH_4Cl. This produced a 45:55 mixture (55% based on **1**) of *meso*-**3** and (±)-*threo*-**3** that was separated by fractional crystallisation from furan and finally H_2O (Scheme 1). The yield of **3** was lower if solvents other than $CF_3CH(OH)CF_3$ (i.e. CF_3CH_2OH, MeCN, CH_2Cl_2, CH_3NO_2, $CHF_2CF_2CH_2OH$, THF) were used for the elimination of HCl and the [4+3] cycloaddition. The *meso*-**3**/(±)-*threo*-**3** product ratio was not affected on changing solvent and/or the base (tetramethylethylenediamine (TMEDA), $Me_2N(CH_2)_4NMe_2$, $Et_2N(CH_2)_2NEt_2$, 1,10-bis(dimethylamino)napthhalene) (Scheme 1).

The differentiation between *meso*-**3** and (±)-*threo*-**3** was based on their ^1H NMR spectra (two doublets at $\delta_H = 2.36$ and 2.25, $^2J = 15.2$ Hz for the methylene linker of *meso*-**3**; one singlet at $\delta_H = 2.30$ for (±)-*threo*-**3**) and by their conversion into bis(1,3-dioxolanes) derived from (*R*,*R*)-butane-2,3-diol (^{13}C NMR). The reduction of *meso*-**3** with K-selectride ($KBH(iBu)_3$) in THF[17] gave diol **4** that was acetylated (Ac_2O, Et_3N, CH_2Cl_2, DMAP) into **5** (95%, 2 steps). Attempts to induce reductive ethereal-ring opening of the two 8-oxabicyclo[3.2.1]oct-6-ene moieties of **4** and **5** following Lautens' methods[18] were not met with success. Protection of diol **4** as dibenzyl, bis(methoxymethyl) or disilyl ethers gave products that refused to undergo ethereal-ring opening. However, the treatment of **5** with BCl_3 in CH_2Cl_2 afforded the dichloride **7** in 96% yield. The high stereo- and regioselectivity of this double S_N2'-type 8-oxa bridge cleavage can be interpreted in terms of the formation of zwitterionic intermediate **6** (Scheme 2) that arises from the Lewis acid promoted heterolysis of the tertiary C1–O8 bonds. Dichlorodiol **7** was esterified with 4-methoxybenzoyl chloride in pyridine to give **8** (99%). Reductive dechlorination of **8** with Bu_3SnH (toluene, 2,2′-azobisisobutronitrile (AIBN), 80 °C)[19] provided **9** (84%). Attempts to dechlorinate **8** with $(Me_3Si)_3SiH$/AIBN[20] (toluene, 80 °C) led to a maximum yield of 10% only.

Abstract in French: *Une nouvelle méthode est proposée pour la synthèse asymétrique de pentadeca-1,3,5,7,9,11,13,15-octols et de leurs dérivés. Elle exploite la dihydroxylation asymétrique selon Sharpless appliquée au bis(4-méthoxybenzoate) de 4,4′-méthylène[(1R,1′S,6R,6′S)-6-acétoxycyclohept-3-en-1-yle] (**9**) dérivant de la double cycloaddition [3+4] du cation 1,1,3-trichloro-2-oxyallyle sur le 2,2′-méthylènedifurane (**1**). Le diol (−)-**10** obtenu avec un ee de 98.4% par oxydation de **9** au moyen de l'"AD-mix-β(5x)" est oxydé en 4-méthoxybenzoate de (2R et 2S,4S,6R)-tetrahydro-2-hydroxy-6-{(4S,6S)-{6-hydroxy-4-[(4-méthoxybenzoyl)oxy]cyclohept-1-en-1-yl}-2-oxopropyl}-2H-pyran-4-yle ((−)-**18**). En combinant les réductions anti-sélectives selon Evans, ou syn-sélectives selon Nasaraka, avec la double substitution selon Mitsunobu, 16 diastéréomères et leurs dérivés peuvent être préparés, en principe, avec hautes énantio- et diastéréosélectivités.*



Scheme 2.

Desymmetrisation of the methylenebis(heptenyl) system **9** was realized by means of the Sharpless asymmetric dihydroxylation.[21] This led to a 4:1 mixture of diols (−)-**10** and (+)-**11** which were then separated by column chromatography on silica gel (Scheme 2). Pure diol (−)-**10** was isolated in 72% yield. Less than 2% of tetrols were formed when the reaction mixture was quenched after disappearance of **9**. ^{19}F NMR spectroscopy (^{13}C–^{19}F satellites) of Mosher's esters (−)-**10M** and (+)-**11M**, derived from (*S*)-α-methoxy-α-trifluoromethylphenylacetyl chloride,[22] showed (−)-**10** to have 98.4% *ee* and (+)-**11** 13.0% *ee*. The relative configurations of C1″ and C2″ in (−)-**10** and (+)-**11** were assigned by NOE analysis of acetonides (−)-**10ac** and (+)-**11ac**, respectively. A strong NOE effect has been detected between the ^1H NMR signals of $Me_2C(OR)_2$ and H-C6″ in (−)-**10ac**, whereas no such effect was found in (+)-**11ac**. This result is in accordance with predictions that the *para*-methoxybenzoate group can enhance the enantioselectivity of the *syn* osmylation (to yield (−)-**10**).[23] The *para*-methoxybenzoate moiety is a necessity for a good yield in the Sharpless dihydroxylation and a high enantiomeric excess. Derivatives **12**–**15** have been prepared and submitted to the above desymmetrisation reaction with AD-mix-β (10-fold excess). With **12**, the yield of the expected diol never surpassed 50% and the highest *ee* value obtained only reached 13%! With **13**, a mixture of diols (55%) and tetrols (36%) was obtained. With the bis(*para*-methoxybenzoate) **15**, a diol was isolated in 28% yield and in 25% *ee*. The

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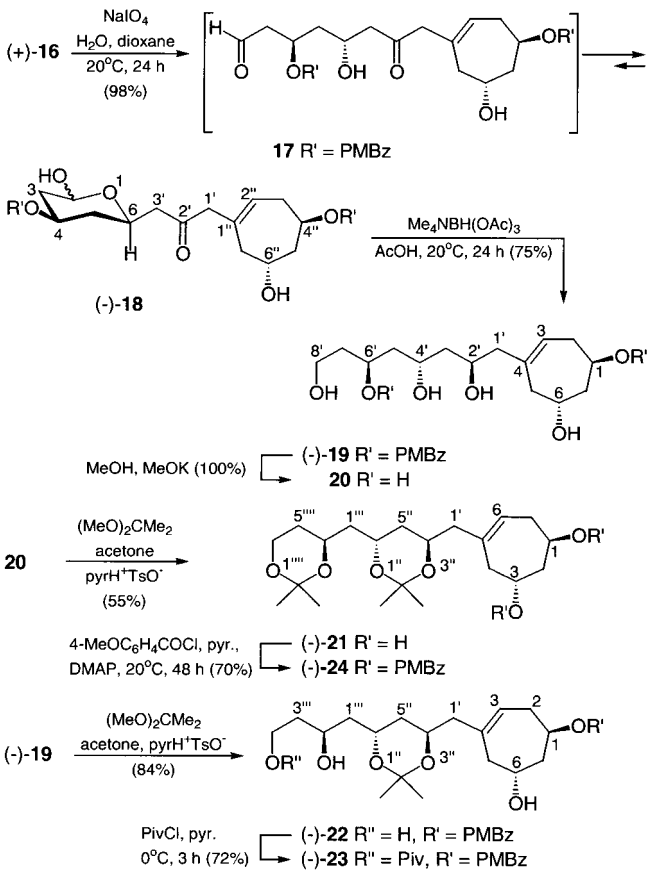
absolute configuration of (−)-**10** was established by circular dichroism of a derivative (see below).

Oxidative cleavage of diol (−)-**10** with $NaIO_4$ or with $Pb(OAc)_4$ led to mixtures of unstable products that probably arise from the elimination of acetic acid. Selective methanolysis of the acetate was possible on treating (−)-**10** with $Mg(OMe)_2$ in methanol.[24] This generated tetrol (+)-**16** in 70% yield, the oxidation of which with $NaIO_4$ in aqueous dioxane afforded a 3:2 mixture of α- and β-pyranose (−)-**18** in 98% yield (Scheme 3). The 2D NOESY ^{1}H MNR spectrum of (−)-**18** proved that the H4 and H6 protons are axial, thus demonstrating that epimerisation had not occurred at C4 and C6. Hemiacetal (−)-**18** equilibrates with the corresponding oxoaldehyde **17** that was reduced selectively under Evans' conditions[25] ($Me_4NBH(OAc)_3$, AcOH, 20 °C) to give (−)-**19** in 75% yield (Scheme 3). Methanolysis of (−)-**19** (MeOK, MeOH) liberated the hexol **20** that was converted into bis-



Scheme 3.

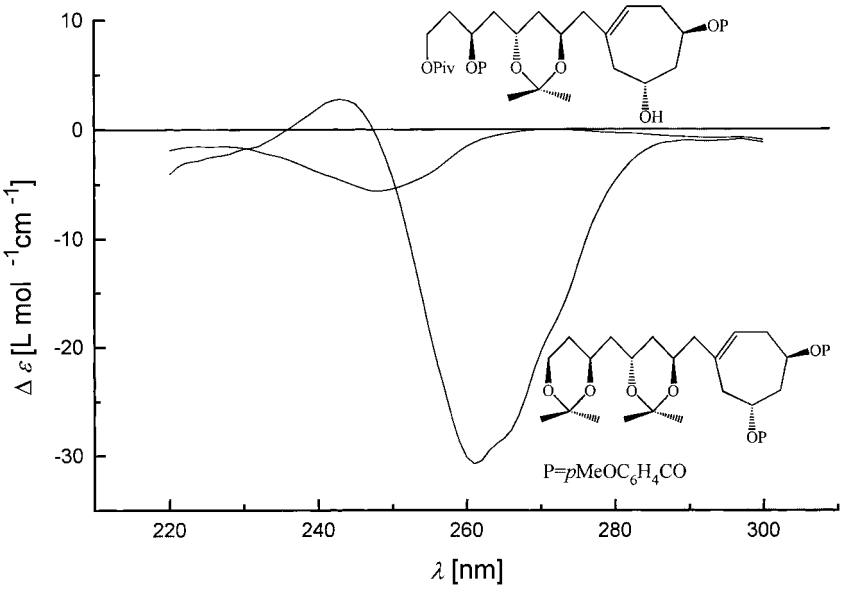
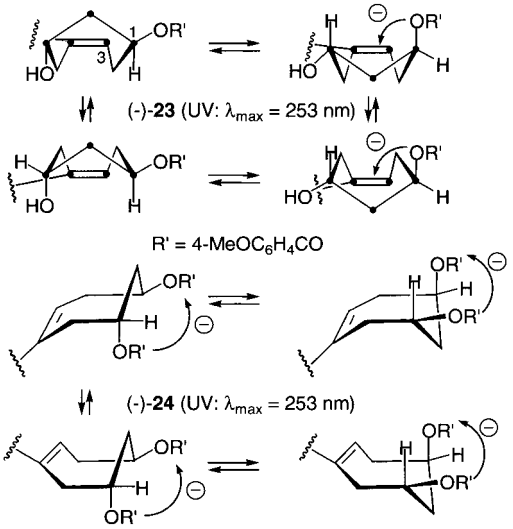


Figure 1. CD spectra (MeCN) of (−)-**23** and (−)**24**. See Scheme 4.

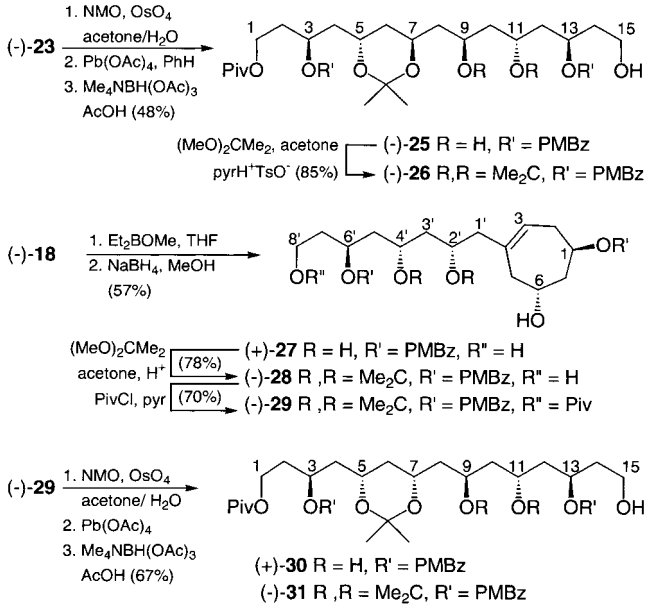


Scheme 4. Equilibria of (−)-**23** and (−)**4** in the CD spectra (MeCN) given in Figure 1.

acetonide (−)-**21** (55%, two steps). Its ^{13}C NMR spectrum (δ_C(Me) = 30.0, 24.7, 24.6, 19.2)[26] confirmed the *anti*-2′,4′ relative configuration (Scheme 3). Treatment of tetrol (−)-**19** with $(MeO)_2CMe_2$/acetone/pyridinium *para*-toluenesulfonate, followed by esterification with pivaloyl chloride afforded (−)-**23** in 60% yield (two steps). Its circular dichroism (CD) spectrum (Figure 1 and Scheme 4) showed a negative Cotton effect ($\Delta\varepsilon_{248} = -5$) that results from the coupling of the electric transition moments of the alkene moiety at C3, C4 and the *para*-methoxybenzoate chromophore at C1 of the cycloheptene group. For all possible conformations of this ring, negative chirality is expected, in agreement with the proposed configuration. In order to confirm this assignment, diester (−)-**24** was prepared by the treatment of diol (−)-**21** with *para*-methoxybenzoyl chloride. The CD spectrum of (−)-**24** (Figure 1 and Scheme 4) showed, as expected for all possible conformations of the cyclohept-5-en-1,3-diyl bis(*p*-

methoxybenzoate) system, a double Cotton effect ($\Delta\varepsilon_{262} = -30$, $\Delta\varepsilon_{243} = +3$) that results from the exiton coupling between the two aromatic chromophores to produce a negative couplet.[24] This interpretation is consistent with the fact that the point of inflection of the CD curve is close to $\lambda =$ 253 nm, the wavelength of maximum absorption in the UV spectrum of (−)-**24**.

Dihydroxylation of the cycloheptene moiety of (−)-**23** with *N*-methylmorpholine *N*-oxide and OsO_4 (cat.) provided a mixture of 1,2-diols that were cleaved oxidatively with $Pb(OAc)_4$ in benzene and AcOH (5 °C, 2.5 h). This produced a mixture of hemiacetals that was reduced under Evans conditions[25] to give (−)-**25** (48%) (Scheme 5). Its bis-

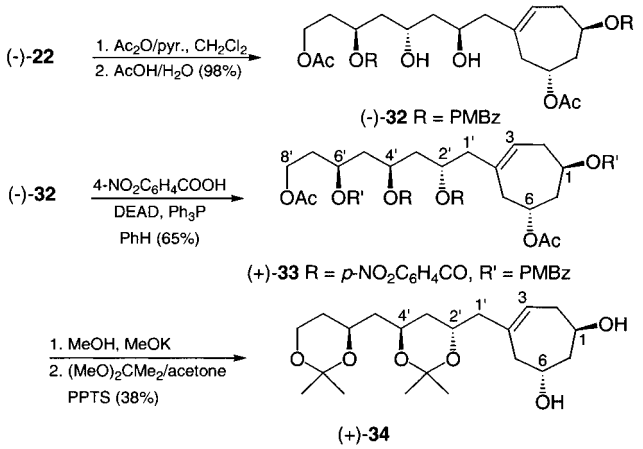


Scheme 5.

acetonide (−)-**26** (85%), obtained on treatment with $Me_2C(OMe)_2$/acetone and $pyrH^+TsO^-$ showed $\delta(Me) = 24.5$, 24.4, 24.3 and 24.2, typical of *anti*-5,7 and *anti*-9,11 relative configurations.[26]

Selective *syn* reduction of (−)-**18** under Nasaraka's conditions[28] gave (+)-**27** (57%). Its acetonide (−)-**28** (78%) showed $\delta(Me) = 29.9$ and 19.3.[26] Selective esterification of (−)-**28** with PivCl/pyridine afforded pivalate (−)-**29** (70%) that was oxidised with *N*-methyl *N*-morpholine oxide and OsO_4 (cat.) in acetone/water to give a mixture of 1,2-diols. The latter were cleaved with $Pb(OAc)_4$ into an oxo-aldehyde that was directly reduced under Evans' conditions to produce triol (+)-**30** (67%). Treatment of (+)-**30** with $Me_2C(OMe)_2$/acetone/$pyrH^+TsO^-$ provided the bis-acetonide (−)-**31** for which $\delta(Me) = 30.1$, 24.2, 24.1 and 19.5 proved the *anti*-9,11 relative configuration[26].

Esterification of (−)-**22** with Ac_2O/pyridine/4-dimethylaminopyridine (cat.) afforded a diacetate that was treated with AcOH/H_2O to produce diol (−)-**32** (98%) (Scheme 6). Double Mitsunobu displacement with *para*-nitrobenzoic acid (EtOOCN=NCOOEt, Ph_3P, PhH) afforded (+)-**33** (65%). Saponification of (+)-**33** (MeOH/MeOK) gave an hexol that



Scheme 6.

was treated with $(MeO)_2CMe_2$/acetone/$pyrH^+TsO^-$ to afford bis-acetonide (−)-**34** (38%). Its ^{13}C NMR spectrum showed $\delta(Me) = 29.9$, 25.1, 25.0 and 19.2 which is consistent with the *anti*-2′,4′ relative configuration.[26] This product is different from the isomeric bis-acetonide derived in a similar way from (−)-**19**, and thus confirms that double inversion had occurred during the Mitsunobu displacement reaction (Scheme 6).

Conclusions

The combinations of Evans' *anti*[25] and Nasaraka's[28] *syn* reductions of aldols with the double Mitsunobu reaction[29] on our intermediates, 16 diastereomeric pentadeca-1,3,5,7,9,11,13,15-octols and analogues, can be obtained, in principle. If the *syn* relationship between the 4-methoxybenzoates at C3 and C13 could be changed into a *anti* relative configuration, all possible stereomeric pentadeca-1,3,5,7,9,11,13,15-octols could be reached in both enantiomeric forms (Sharpless asymmetric dihydroxylation[21]). Furthermore, because of our ability to differentiate between the reactivity of alcohols on aliphatic and on cycloheptene systems, selective semi-protection of the polyols is possible and should allow the introduction of functions other than alcohols on the fifteen-carbon chain.

Experimental Section

General methods: see Ref. [30]. All the ^1H NMR and ^{13}C NMR assignments were confirmed by 2D NMR (COSY, NOESY, HMQC spectra).

2,2′-Methylenedifuran (1): Furfuryl alcohol (10.9 g, 0.12 mol) and furan (136 g, 2 mol) were mixed and cooled to 0 °C. CF_3COOH (10.3 g, 0.09 mol) was added dropwise. Stirring was continued at 0 °C for 24 h. The mixture was washed with a saturated aqueous solution of $NaHCO_3$ (200 mL, 2 ×), then with H_2O (200 mL, 2 ×). Drying (Na_2SO_4) and distillation afforded furan (95 g), followed by **1** (b.p. 45 °C, 3 Torr) as a pungent, colourless oil. Yield: 12.0 g (65%).[9]

(±)-(1*RS*,5*SR*)-1-Furfuryl-8-oxabicyclo[3.2.1]oct-6-en-3-one (2): Zinc powder (3.92 g, 60 mmol) was dried under a flow of N_2 and under heating (150–200 °C). After the mixture had been cooled to 20 °C under N_2 atmosphere, CuCl (0.6 g, 6 mmol) and **1** (1.48 g, 10 mmol) were added. The mixture was subjected to ultrasonification at 0 °C for 5 min, then 1,1,3,3-tetrabromoacetone (7.4 g, 20 mmol) in anhydrous dioxane (11 mL) was added over a period of 15 min. The mixture was ultrasonicated

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(plunging cylinder) for 15 h at 15–20 °C. The solid was filtered off and the solvent evaporated in vacuo. The residue was taken up in MeOH (20 mL) and stirred with freshly prepared zinc/copper couple[16] (2 g) for 20 min at 20 °C (controlled by TLC on silica gel, R_f (**2**) = 0.13, EtOAc/light petroleum ether 1:10). The solid was filtered off on Celite and a saturated aqueous solution of Na_2EDTA (50 mL; EDTA = ethylenediaminetetraacetate) was added. The mixture was extracted with CH_2Cl_2 (30 mL, 3 ×, then 10 mL, 4 ×). The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by flash chromatography on silica gel (EtOAc/light petroleum ether 1:10) to give **2**. Yield: 306 mg (15 %); colourless crystals, m.p. 53–54 °C (CH_2Cl_2/hexane); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 7.34 (dd, ^3J(H,H) = 1.8, ^4J(H,H) = 0.5 Hz, 1H; H4″), 6.31 (dd, ^3J(H,H) = 3.1, 1.8 Hz, 1H; H3″), 6.18 (dd, ^3J(H,H) = 5.9, 1.7 Hz, 1H; H6), 6.16 (d, ^3J(H,H) = 3.1 Hz, 1H; H2″), 6.15 (d, ^3J(H,H) = 5.9 Hz, 1H; H7), 5.08 (br d, ^3J(H,H) = 5.1 Hz, 1H; H5), 3.12 (s, 2H; H1′), 2.68 (dd, ^2J(H,H) = 16.3, ^3J(H,H) = 5.1 Hz, 1H; H4$_{exo}$), 2.57 (d, ^2J(H,H) = 16.2 Hz, 1H; H2$_{exo}$), 2.38 (d, ^2J(H,H) = 16.3 Hz, 1H; H2$_{endo}$), 2.28 (d, ^2J(H,H) = 16.2 Hz, 1H; H4$_{endo}$); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 205.9 (s; C3), 150.2 (s; C1″), 141.9 (d, ^1J(C,H) = 202 Hz; C4″), 134.9 (d, ^1J(C,H) = 169 Hz; C7), 133.4 (d, ^1J(C,H) = 166 Hz; C6), 110.3 (d, ^1J(C,H) = 175 Hz; C3″), 108.2 (d, ^1J(C,H) = 174 Hz; C2″), 85.2 (s; C1), 77.6 (d, ^1J(C,H) = 170 Hz; C5), 50.5 (t, ^1J(C,H) = 129 Hz; C2), 45.1 (t, ^1J(C,H) = 130, C4), 35.3 (t, ^1J(C,H) = 129, C1′); IR (KBr): $\tilde{\nu}$ = 3135, 2980, 1710, 1600, 1420, 1345, 1325, 1235, 1205, 1190, 1155, 1090, 1065, 1045, 1015, 940, 920, 855, 830, 815, 775, 760, 745, 730, 605, 480 cm^{-1}; UV (MeCN): λ_{max} (ε) = 217 nm (8650 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m/z* (%): 204 (44) [*M*+NH_4]$^+$, 176 (2), 162 (13), 147 (28), 123 (5), 94 (15), 81 (100); elemental analysis calcd for $C_{12}H_{12}O_3$ (204.2) (%): C 70.57, H 5.92; found C 70.54, H 5.89.

1,1′-Methylenedi[(1*R*,1′*S*,5*S*,5′*R*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-ene] (*meso*-3) and (±)-1,1′-methylenedi[(1*RS*,1′*RS*,5*SR*,5′*SR*)-3-oxo-8-oxabicyclo[3.2.1]oct-6-ene] ((±)-*threo*-3): Et_3N (4.0 g, 39.5 mmol), then 1,1,3,3-tetrachloroacetone (7.0 g, 35.7 mmol) were added slowly to a vigourously stirred solution of **1** (2.25 g, 15.2 mmol) in $CF_3CH(OH)CF_3$ (35 mL) cooled to 0 °C. After the mixture had been stirred at 20 °C overnight, $CF_3CH(OH)CF_3$ was recovered by distillation under vacuum and the residue was taken up in a solution of MeOH saturated with NH_4Cl (100 mL). Zn/Cu couple (7 g) was added portionwise to the vigourously stirred mixture. After the mixture had been stirred at 20 °C for 5 d, the precipitate was filtered off on Celite and the solvent evaporated. CH_2Cl_2 (100 mL) was added and the solution washed with 5 % aqueous HCl (100 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL, 3 ×). The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The residue was taken up in CH_2Cl_2 (10 mL) and Et_2O (90 mL) was added under stirring. Silica gel (20 g) was then added and the mixture stirred for 20 min. Filtration, rinsing with Et_2O (50 mL), and evaporation of the solvent afforded *meso*-**3** + (±)-*threo*-**3** (2.85 g, 72 %) that was recrystallised from furan (7.2 g) to give pure (±)-*threo*-**3** (0.94 g; 33 %). The mother liquor contained a 8:2 mixture of *meso*-**3**/(±)-*threo*-**3** that was purified by filtration though a pad of silica gel (Et_2O/light petroleum 9:1) and used as such for the next step. Pure *meso*-**3** was obtained by recrystallisation from H_2O at 4 °C. Yield: 0.88 g (55 %).

meso-**3**: Colourless crystals; m.p. 112–113 °C (H_2O); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.24 (d, ^3J(H,H) = 5.9 Hz, 2H; H7), 6.16 (dd, ^3J(H,H) = 5.9, 1.7 Hz, 2H; H6), 5.06 (br d, ^3J(H,H) = 5.0 Hz, 2H; H5), 2.68 (dd, ^2J(H,H) = 16.2 Hz, ^3J(H,H) = 5.0 Hz, 2H; H4$_{exo}$), 2.65 (d, ^2J(H,H) = 16.2 Hz, 2H; H2$_{exdo}$), 2.45 (d, ^2J(H,H) = 16.2 Hz, 2H; H2$_{endo}$), 2.36 (d, ^2J(H,H) = 15.2 Hz, 1H of methylene), 2.30 (d, ^2J(H,H) = 16.2 Hz, 2H; H4$_{endo}$), 2.25 (d, ^2J(H,H) = 15.2 Hz, other H of methylene); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 206.9 (s; C3), 137.0 (d, ^1J(C,H) = 174 Hz; C7), 133.1 (d, ^1J(C,H) = 180 Hz; C6), 85.2 (s; C1), 77.6 (d, ^1J(C,H) = 170 Hz; C5), 52.1 (t, ^1J(C,H) = 130 Hz; C2), 45.6 (t, ^1J(C,H) = 130 Hz; C4), 42.5, (t, ^1J(C,H) = 126 Hz; C9); IR (KBr): $\tilde{\nu}$ = 1710, 1335, 1215, 1095, 1020, 925, 855, 830, 765, 730, 695 cm^{-1}; MS (CI/NH_3): *m/z* (%): 260 (12) [*M*+H]$^+$, 242 (6), 217 (9), 203 (2), 175 (9), 137 (31), 123 (8), 81 (100); elemental analysis calcd for $C_{15}H_{16}O_4$ (260.3) (%): C 69.22, H 6.20; found C 68.46, H 6.11.

(±)-*threo*-**3**: Colourless needles; m.p. 160 °C (furan, decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.20 (d, ^3J(H,H) = 5.9 Hz, 2H; H7), 6.09 (dd, ^3J(H,H) = 5.9, 1.7 Hz, 2H; H6), 5.03 (br d, ^3J(H,H) = 5.0 Hz, 2H; H5), 2.68 (dd, ^2J(H,H) = 16.2 Hz, ^3J(H,H) = 5.0 Hz, 2H; H4$_{exo}$), 2.61 (d, ^2J(H,H) = 16.2 Hz, 2H; H2$_{exo}$), 2.47 (d, ^2J(H,H) = 16.2 Hz, 2H; H2$_{endo}$), 2.29 (d, ^2J(H,H) = 16.2 Hz, 2H; H4$_{endo}$), 2.30 (s, 2H; CH_2(methylene)); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 205.8 (s; C3), 135.5 (d, ^1J(C,H) = 175 Hz; C7), 131.9 (^1J(C,H) = 174 Hz; C6), 84.7 (s; C1), 77.0 (d, ^1J(C,H) = 160 Hz; C5), 52.3 (t, ^1J(C,H) = 130 Hz; C2), 45.4 (t, ^1J(C,H) = 130 Hz; C4), 42.3 (t, ^1J(C,H) = 126, CH_2); IR (KBr): $\tilde{\nu}$ = 3110, 2965, 2925, 1710, 1595, 1560, 1545, 1510, 1460, 1430, 1400, 1355, 1340, 1320, 1280, 1225, 1200, 1100, 1060, 1030, 925, 860, 835, 810, 765, 735, 700, 670, 645, 505, 485, 435, 420 cm^{-1}; MS (CI/NH_3): *m/z* (%): 260 (12) [*M*+H]$^+$, 242 (6), 217 (9), 175 (9), 137 (31), 123 (8), 81 (100); elemental analysis calcd for $C_{15}H_{16}O_4$ (260.3) (%): C 69.22, H 6.20; found C 68.62, H 6.09.

1,1′-Methylenedi[(1*R*,1′*S*,3*S*,3′*R*,5*S*,5′*R*)-8-oxabicyclo[3.2.1]oct-6-en-3-ol] (4): A 1 M solution of K-selectride in THF (114 mL) was added dropwise to a stirred solution of *meso*-**3** (13.4 g, 51.8 mmol) in anhydrous THF (700 mL) cooled to −78 °C. The temperature was allowed to reach 20 °C in 3 h and the mixture stirred at 20 °C for 12 h. MeOH (60 mL), then MeOH saturated in NH_4Cl (60 mL) were added. After the mixture had been stirred at 20 °C for 30 min, the precipitate was filtered off on Celite. Concentration by evaporation (40 mL), flash chromatography on silica gel (CH_2Cl_2/MeOH 96:4) and precipitation from CH_2Cl_2 (200 mL) and light petroleum (400 mL) gave diol **4** (13.4 g; 98 %) as colourless crystals. M.p. 136–137 °C (CH_2Cl_2/light petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.45 (d, ^3J(H,H) = 5.9 Hz, 2H; H7), 6.35 (dd, ^3J(H,H) = 5.9, 1.7 Hz, 2H; H6), 4.79 (m, 2H; H5), 3.97 (dddd, ^3J(H,H) = 5.7, 5.6, 4.7, 4.6 Hz, 2H; H3), 2.24 (d, ^3J(H,H) = 10.2 Hz, 2H; OH), 2.17 (ddd, ^2J(H,H) = 14.7, ^3J(H,H) = 5.7, 4.0 Hz, 2H; H4$_{exo}$), 2.08 (br d, ^2J(H,H) = 14.7 Hz, H2$_{exo}$), 2.05 (m, ^2J(H,H) = 14.8 Hz, 2H(AB); CH_2), 1.87 (br d, ^2J(H,H) = 14.7 Hz, 2H; H2$_{endo}$), 1.68 (d, ^2J(H,H) = 14.7 Hz, 2H; H4$_{endo}$); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 138.7 (d, ^1J(C,H) = 169 Hz; C7), 134.7 (d, ^1J(C,H) = 177 Hz; C6), 84.2 (s; C1), 78.1 (d, ^1J(C,H) = 137 Hz; C5), 65.6 (d, ^1J(C,H) = 154 Hz; C3), 44.5 (t, ^1J(C,H) = 125 Hz; CH_2), 42.0 (t, ^1J(C,H) = 125 Hz; C2), 35.5 (t, ^1J(C,H) = 127 Hz; C4); IR (KBr): $\tilde{\nu}$ = 3345, 2920, 2585, 1655, 1460, 1400, 1345, 1285, 1260, 1205, 1180, 1135, 1115, 1075, 1060, 1040, 1020, 880, 745, 705, 620 cm^{-1}; MS (CI/NH_3): *m/z* (%): 264 (2) [*M*+H]$^+$, 246 (3), 203 (3), 167 (11), 140 (33), 125 (32), 107 (30), 95 (44), 81 (100); elemental analysis calcd for $C_{15}H_{20}O_4$ (264.3) (%): C 68.16, H 7.63; found C 68.15, H 7.52.

1,1′-Methylenedi[(1*R*,1′*S*,3*S*,3′*R*,5*S*,5′*R*)-8-oxabicyclo[3.2.1]oct-6-en-3-yl] bisacetate (5): A mixture of **4** (6.0 g, 22.7 mmol), CH_2Cl_2 (170 mL), Ac_2O (9.3 g), Et_3N (15 g) and 4-dimethylaminopyridine (280 mg) was stirred at 20 °C for 2 h. The solution was washed with 3 % aqueous HCl, then with saturated aqueous solution of $NaHCO_3$. Evaporation of the solvent, flash chromatography on silica gel (MeOH/CH_2Cl_2 3:97) afforded **5** (7.7 g; 98 %) as colourless crystals. M.p. 98–99 °C (Et_2O/light petroleum). Compound **5** can also be obtained starting with the 7:3 mixture of *meso*-**3**/(±)-*threo*-**3** obtained above. A final flash chromatography on silica gel (EtOAc/CH_2Cl_2 15:85) afforded **5** (68 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.18 (d, ^3J(H,H) = 5.9 Hz, 2H; H7), 6.10 (dd, ^3J(H,H) = 5.9, 1.6 Hz, 2H; H6), 5.04 (dd, ^3J(H,H) = 6.0, 5.9 Hz, 2H; H3), 4.74 (br d, ^3J(H,H) = 3.5 Hz, 2H; H5), 2.16 (ddd, ^2J(H,H) = 15.1 Hz, ^3J(H,H) = 5.9, 4.1 Hz, 2H; H4$_{exo}$), 2.07 (dd, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 6.0 Hz, 2H; H2$_{exo}$), 2.06, 1.97 (2d, ^2J(H,H) = 15.0 Hz, 2H methylene), 1.97 (s, 6H; Ac), 1.73 (d, ^2J(H,H) = 15.0 Hz, 2H; H2$_{endo}$), 1.55 (d, ^2J(H,H) = 15.0 Hz, H4$_{endo}$); IR (KBr): $\tilde{\nu}$ = 3430, 3085, 2970, 2935, 2910, 1725, 1425, 1365, 1270, 1255, 1195, 1140, 1070, 1030, 970, 945, 885, 810, 745, 700 cm^{-1}; UV (MeCN): λ_{max} (ε) = 200 nm (9600 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m/z* (%): 348 (4) [*M*$^+$], 305 (9), 288 (18), 271 (3), 245 (8), 228 (25), 209 (4), 167 (12), 121 (79), 107 (100), 81 (79); elemental analysis calcd for $C_{19}H_{24}O_6$ (348.4) (%): C 65.50, H 6.94; found 65.58, H 6.88.

3,3′-Methylenedi[(1*R*,1′*S*,5*R*,5′*S*,6*S*,6′*R*)-5-chloro-6-hydroxycyclohept-3-en-1-yl] bisacetate (7): A 1.0 M solution of BCl_3 in CH_2Cl_2 (75 mL) was added slowly to a stirred solution of **5** (8.5 g, 24.4 mmol) in anhydrous CH_2Cl_2 (600 mL) cooled to −10 °C. After stirring at −10 °C for 4 h, the solution was gently allowed to reach 20 °C, and a saturated aqueous solution of $NaHCO_3$ (150 mL) cooled to 0 °C was added under vigourous stirring over a period of 15 min. The aqueous layer was extracted with CH_2Cl_2 (50 mL, 3 ×). The combined organic phases were dried ($MgSO_4$, charcoal), and the solvent was evaporated to afford 10 g (96 %) of **7**, an unstable compound used directly in the next step.

4,4′-Methylene-di[1*R*,1′*S*,2*S*,2′*R*,6*S*,6′*R*)-6-acetoxy-2-chlorocyclohept-3-en-1-yl] bis(*para*-methoxybenzoate) (8): Crude **7** (10 g, obtained above) was immediately taken up in dry pyridine (60 mL). *para*-Methoxybenzoyl

chloride (14.2 g, 83.2 mmol) and 4-dimethylaminopyridine (290 mg) were added and the mixture was stirred at 20 °C for 15 h. Dry MeOH (50 mL) was added and the solution stirred for an additional hour at 20 °C. The solvent was evaporated in vacuo, the residue taken up in CH_2Cl_2 (100 mL) and washed with 3% aqueous HCl (250 mL) at 0 °C, then with saturated aqueous solution of $NaHCO_3$ (250 mL, 2 ×). Drying ($MgSO_4$), evaporation of the solvent, flash chromatography on silica gel (Et_2O/light petroleum ether 1:1) afforded **8** (17.6 g; 96% based on **5**) as colourless crystals. M.p. 92–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.01$ (m, 4H), 6.94 (m, 4H), 5.83 (d, $^3J(H,H) = 7.4$ Hz, 2H; H3), 5.55 (ddd, $^2J(H,H) = 10.0$, $^3J(H,H) = 3.8$, 1.8 Hz, 2H; H1), 5.16 (m, 2H; H6), 4.85 (d, $^3J(H,H) = 7.4$ Hz, 2H; H2), 3.87 (s, 6H; 2MeO), 2.87, 2.73 (2d, $^2J(H,H) = 14.4$ Hz, 2H; CH_2-C(4)), 2.68 (ddd, $^2J(H,H) = 13.7$, $^3J(H,H) = 10.1$, 3.6 Hz, 2H; H7), 2.53 (m, 4H; H5), 2.26 (ddd, $^2J(H,H) = 13.7$, $^2J(H,H) = 6.8$, 4.0 Hz, 2H; H7), 2.08 (s, 6H; 2Ac); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 170.2$ (s, Ac), 165.3 (s; C_{arom}), 163.7 (s, Ac*C*OO), 140.7 (s; C4), 131.8 (d, $^1J(C,H) = 163$ Hz, HC_{arom}), 125.8 (d, $^1J(C,H) = 162$ Hz; C3), 122.1 (s; C_{arom}), 113.7 (d, $^1J(C,H) = 162$ Hz, HC_{arom}), 70.2 (d, $^1J(C,H) = 155$ Hz; C1), 68.2 (d, $^1J(C,H) = 147$ Hz; C6), 60.1 (d, $^1J(C,H) = 151$ Hz; C2), 55.5 (q, $^1J(C,H) = 144$ Hz, MeO), 51.9 (t, $^1J(C,H) = 126$ Hz; CH_2), 35.7 (t, $^1J(C,H) = 132$ Hz; C7), 35.3 (t, $^1J(C,H) = 127$ Hz; C5), 21.1 (q, $^1J(C,H) = 130$ Hz; CH_3COO); IR (KBr): $\tilde{\nu} = 3450$, 2955, 1735, 1715, 1655, 1605, 1580, 1510, 1460, 1440, 1420, 1260, 1170, 1115, 1100, 1030, 845, 770 cm^{-1}; MS (CI/NH_3): *m*/*z* (%): 706 (72) $[M+NH_3]^+$, 683 (3) $[M^{+\cdot}]$, 670 (10), 441 (9), 170 (42), 152 (23), 135 (100), 77 (7); elemental analysis calcd for $C_{35}H_{38}Cl_2O_{10}$ (689.6) (%): C 60.96, H 5.55, Cl 10.28; found C 60.98, H 5.67, Cl 10.29.

4,4-Methylene[(1*R*,1′*S*,6*R*,6′*S*)-6-acetoxycyclohept-3-en-1-yl] bis(4-methoxybenzoate) (9): A mixture of **8** (16.5 g, 24 mmol), toluene (100 mL), Bu_3SnH (24.5 g, 84 mmol) and AIBN (350 mg, 2.13 mmmol) was stirred at 85 °C for 4 h. The solvent was evaporated and the residue taken up in MeCN (150 mL). After extraction with pentane (50 mL, 4 ×) and evaporation of the solvent, the residue was taken up in Et_2O (150 mL). KF (100 mg) was added under vigourous stirring. Stirring was continued at 20 °C for 4 h then the mixture was filtered and the solvent evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (150 mL) and the solution washed with 3% aqueous HCl (50 mL), then with saturated aqueous solution of $NaHCO_3$ (50 mL). The organic phase was dried ($MgSO_4$). Solvent evaporation and flash chromatography on silica gel (Et_2O/light petroleum ether 7:3) afforded pure **9** (12.7 g; 84%) as a colourless oil that can be crystallised from Et_2O (140 mL) and light petroleum ether (130 mL). Colourless crystals. M.p. 92–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.98$, 6.92 (2m, 8H), 5.55 (t, $^3J(H,H) = 6.5$ Hz, 2H; H3), 5.26 (dddd, $^3J(H,H) = 8.4$, 7.0, 3.4, 2.8 Hz, 2H; H1), 5.04 (dddd, $^3J(H,H) = 9.4$, 8.6, 3.5, 2.0 Hz, 2H; H6), 3.90 (s, 6H; 2MeO), 2.85, 2.69 (2d, $^2J(H,H) = 14.1$ Hz, 2H; $H_2CC(4)$), 2.61 (ddd, $^2J(H,H) = 14.6$, $^3J(H,H) = 8.4$, 6.5 Hz, 2H), 2.52 (m, 2H), 2.48, 2.32 (2br d, $^2J(H,H) = 14.8$ Hz, 4H), 2.27 (ddd, $^2J(H,H) = 13.6$, $^3J(H,H) = 7.0$, 3.5 Hz, 2H), 2.19 (ddd, $^2J(H,H) = 13.6$, $^3J(H,H) = 8.6$, 3.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta =$ 170.2 (s, AcCO), 165.4 (s; C_{arom}), 163.3 (s, ArCOO), 137.2 (s; C4), 131.6 (d, $^1J(C,H) = 163$ Hz, HC_{arom}), 123.6 (d, $^1J(C,H) = 146$ Hz; C3), 122.9 (s; C_{arom}), 113.6 (d, $^1J(C,H) = 161$ Hz, HC_{arom}), 69.9 (d, $^1J(C,H) = 149$ Hz; C1), 68.2 (d, $^1J(C,H) = 154$ Hz; C6), 55.4 (q, $^1J(C,H) = 144$ Hz, MeO), 50.4 (t, $^1J(C,H) = 126$ Hz; C8), 41.5 (t, $^1J(C,H) = 125$ Hz; C7), 36.5 (t, $^1J(C,H) =$ 127 Hz; C5), 32.0 (t, $^1J(C,H) = 126$, C2), 21.2 (q, $^1J(C,H) = 130$ Hz; CH_3COO); IR (KBr): $\tilde{\nu} = 2955$, 1730, 1710, 1610, 1510, 1440, 1380, 1245, 1165, 1120, 1030, 985, 845, 770, 695, 610 cm^{-1}; UV (MeCN): λ_{max} (ε) = 254 (35500), 207 nm (36800 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 638 (100) $[M+NH_4]^+$, 561 (18), 469 (21), 409 (8), 349 (9), 256 (20), 196 (34), 135 (76), 91 (31); elemental analysis calcd for $C_{35}H_{40}O_{10}$ (620.7) (%): C 67.73, H 6.50; found C 67.82, H 6.44.

(1*R*,6*R*)-6-Acetoxy-4-{(1*R*,2*S*,4*S*,6*R*)-6-acetoxy-1,2-dihydroxy-4-[(4-methoxybenzoyl)oxy]cyclohept-1-yl}methylcyclohept-3-en-1-yl 4-methoxybenzoate ((−)-10): "AD-mix-β(5 ×)" was prepared by grinding $[K_3Fe(CN)_6]$ (700 mg), anhydrous K_2CO_3 (294 mg),$(DHQD)_2$-PHAL (DHQD = dihydroquinidine, PHAL = 1,3-phthalazinediyl; 27.6 mg) and $K_2OsO_4 \cdot 2H_2O$ (5.3 mg). Some of this mixture (478 mg) was added to a stirred solution of **9** (2.0 g, 3.22 mmol) and $MeSO_2NH_2$ (300 mg, 3.1 mmol) in *t*BuOH/H_2O/MeCN (47.5:47.5:5, 30 mL) cooled to 0 °C. After the mixture had been stirred at 0 °C for 24 h, Na_2SO_3 (0.5 g) was added and the mixture stirred for 1 h. The solid was filtered off (Celite) and the solution extracted with EtOAc (10 mL, 5 ×). Drying ($MgSO_4$), solvent evaporation in vacuo, and flash chromatography on silica gel (CH_2Cl_2/MeOH 98:2, R_f ((−)-**10**) = 0.18) afforded a first fraction: (−)-**10** (1.51 g, 72%) as a colourless foam. M.p. 69–72 °C; $[\alpha]_D^{25} = -73$, $[\alpha]_{577}^{25} = -75$, $[\alpha]_{546}^{25} = -86$, $[\alpha]_{435}^{25} = -161$, $[\alpha]_{405}^{25} = -202$ ($c = 1.0$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.98$ (m, 4H), 6.91 (m, 4H), 5.63 (t, $^3J(H,H) = 6.5$ Hz, 1H; H3), 5.38 (dddd, $^3J(H,H) = 10.5$, 8.7, 6.0, 1.8 Hz, 1H; H4″), 5.27 (m, H1), 5.19 (dddd, $^3J(H,H) = 10.7$, 9.0, 6.1, 2.6 Hz, 1H; H6″), 5.11 (m, 1H; H6), 3.85, 3.82 (2s, 6H; 2MeO), 3.72 (br d, $^3J(H,H) = 10.7$ Hz, 1H; H2″), 2.89, 2.74 (2s, 2 OH), 2.65 (m, 1H; H2), 2.64 (m, 2H; H7), 2.57, 2.27 (2d, $^2J(H,H) = 13.3$ Hz, 2H; H1′(CH_2)), 2.48 (dd, $^2J(H,H) = 15.0$, $^3J(H,H) =$ 5.9 Hz, 1H; H′-2), 2.30 (m, 3H; H3″, H5, H7″), 2.27 (d, $^2J(H,H) = 13.3$, H1′(CH_2)), 2.20 (m, 1H; H5), 2.10 (m, 1H; H7″), 2.03 (m, 2H; H5″, H3″), 1.81 (dd, $^2J(H,H) = 14.7$, $^3J(H,H) = 10.5$ Hz, H5″); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 170.6$, 170.2 (2s, 2AcO), 165.5 (2s; $2C_{arom}$), 163.4, 163.3 (2s, 2ArCOO), 136.9 (s; C4), 131.6 (d, $^1J(C,H) = 163$ Hz; $4C_{arom}$), 127.3 (d, $^1J(C,H) = 162$ Hz; C3), 122.6 (s; C_{arom}), 122.5 (s; C_{arom}), 113.6 (d, $^1J(C,H) =$ 161 Hz, $4HC_{arom}$), 74.3 (s; C1″), 73.0 (d, $^1J(C,H) = 141$ Hz; C2″), 68.7 (d, $^1J(C,H) = 154$ Hz; C1), 68.2 (d, $^1J(C,H) = 137$ Hz; C6), 68.1 (d, $^1J(C,H) =$ 149 Hz; C6″), 66.9 (d, $^1J(C,H) = 147$ Hz; C4″), 55.4 (q, $^1J(C,H) = 145$ Hz, MeO), 50.8 (t, $^1J(C,H) = 127$ Hz; C1′), 41.5, 40.9, 39.0, 38.6, 37.7 (5t, C3′,5,5′,7,7′), 32.3 (t, $^1J(C,H) = 127$ Hz; C2), 21.3 (q, $^1J(C,H) = 130$ Hz, $2CH_3COO$); IR (KBr): $\tilde{\nu} = 3490$, 2940, 1710, 1605, 1510, 1460, 1370, 1255, 1170, 1105, 1025, 850, 770, 700, 615 cm^{-1}; UV (MeCN): λ_{max} (ε) = 253 (47000), 206 nm (45400 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 672 (92) $[M+NH_4]^+$, 595 (5), 503 (10), 443 (6), 337 (28), 135 (100), 106 (93), 78 (38); elemental analysis calcd for $C_{35}H_{42}O_{12}$ (654.7) (%): C 64.21, H 6.47; found C 64.12, H 6.41.

(1*S,6*S**)-6-Acetoxy-4-{{(1*R**,2*S**,4*R**,6*R**)-6-acetoxy-1,2-dihydroxy-4-[(4-methoxybenzoyl)oxy]cyclohept-1-yl}methyl}cyclohept-3-en-1-yl 4-methoxybenzoate ((+)-11)**: The above flash chromatography afforded a second fraction (0.39 g, 19%) of **11** as a colourless foam. $[\alpha]_D^{25} = 1.2$, $[\alpha]_{546}^{25} = 0.6$, $[\alpha]_{435}^{25} = 0.6$, $[\alpha]_{405}^{25} = 0.7$ ($c = 1.1$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.99$, 6.92 (2m, 8H), 5.64 (t, $^3J(H,H) = 6.2$ Hz, 1H; H3), 5.47 (m, 1H; H4″), 5.31 (m, 1H; H1), 5.10 (br t, $^3J(H,H) = 9.4$ Hz, 1H; H6), 4.98 (br t, $^3J(H,H) = 9.4$ Hz, 1H; H6″), 3.87, 3.86 (2s, 6H; 2MeO), 3.85 (m, 1H; H2″), 2.74–2.56 (m, 4H; H2, H5, H7), 2.61 (d, $^2J(H,H) = 13.5$ Hz, H′-1′), 2.48–2.43 (m, 2H; H′-2, H′-7), 2.46 (d, $^2J(H,H) = 13.5$ Hz, H′-1′), 2.38–2.34 (m, 3H; H3″, H7″, H′-5), 2.23–1.97 (m, 7H), 2.04 (s, 3H; AcO), 1.91 (dd, $^2J(H,H) = 13.9$, $^3J(H,H) = 10.4$ Hz, 1H; H′-7″), 1.79 (s, 3H; AcO); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 171.1$, 170.0 (2s, 2AcO), 165.2, 163.4 (2s), 136.2 (s; C4), 131.7, 131.6 (2d, $^1J(C,H) = 163$ Hz, HC_{arom}), 127.8 (d, $^1J(C,H) = 159$ Hz; C3), 122.5 (s; C_{arom}), 113.6 (d, $^1J(C,H) = 161$ Hz, HC_{arom}), 113.5 (d, $^1J(C,H) = 161$ Hz, HC_{arom}), 73.8 (s; C1″), 71.1 (d, $^1J(C,H) = 141$ Hz; C2″), 68.8 (d, $^1J(C,H) = 149$ Hz; C1), 68.2 (d, $^1J(C,H) = 149$ Hz; C6), 67.6 (d, $^1J(C,H) = 149$ Hz; C4″), 66.4 (d, $^1J(C,H) = 149$ Hz; C6″), 55.4 (q, $^1J(C,H) = 143$ Hz, MeO), 47.7 (t, $^1J(C,H) = 125$ Hz; C1′), 43.1 (t, $^1J(C,H) = 133$ Hz; C7″), 41.5 (t, $^1J(C,H) =$ 130 Hz; C7), 41.1 (t, $^1J(C,H) = 130$ Hz; C5″), 39.6 (t, $^1J(C,H) = 125$ Hz; C5), 35.6 (t, $^1J(C,H) = 124$ Hz; C3″), 31.8 (t, $^1J(C,H) = 127$ Hz; C2), 21.3, 20.9 (q, $^1J(C,H) = 129$ Hz, $2CH_3COO$); IR (film): $\tilde{\nu} = 3420$, 2935, 1710, 1605, 1510, 1455, 1370, 1255, 1170, 1105, 1025, 915, 850, 770 cm^{-1}; UV (MeCN): λ_{max} (ε) = 254 (37500), 201 nm (44700 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 672 (1) $[M+NH_4]^+$, 595 (3), 318 (6), 135 (65), 106 (100), 91 (21).

Mosher's ester of (−)-10: (+)-(1*R*,3*R*,5*R*,7*S*)-5-acetoxy-7-{{(4*R*,6*R*)-6-acetoxy-4-[(4-methoxybenzoyl)oxy]cyclohept-1-en-1-yl}methyl}-3-[(4-methoxybenzoyl)oxy]-7-hydroxycyclohept-1-yl (*R*)-α-methoxy-α-trifluoromethylphenylacetate ((−)-10M): A mixture of (−)-**10** (100 mg, 0.15 mmol), (+)-*S*-α-methoxy-α-trifluoromethylphenylacetyl chloride (0.1 g), anhydrous CH_2Cl_2 (10 mL), Et_3N (0.2 mL) and 4-dimethylaminopyridine (30 mg) was stirred at 20 °C overnight. A saturated aqueous solution of $NaHCO_3$ (0.5 mL) was added and the organic phase was collected. The aqueous phase was extracted with Et_2O (2 mL, 2 ×) and the combined organic extracts were dried ($MgSO_4$). After filtration though a pad of silica gel, the solvent was evaporated to give 104 mg (78%) of **10M** as a colourless foam. $R_f = 0.14$ (silica gel 230–400 mesh, Et_2O/light petroleum 7:3); $[\alpha]_D^{25} = -14$, $[\alpha]_{577}^{25} = -19$, $[\alpha]_{546}^{25} = -19$, $[\alpha]_{435}^{25} = -35$, $[\alpha]_{405}^{25} = -44$ ($c = 0.6$, $CHCl_3$); ^{19}F NMR (376.5 MHz, $CDCl_3$, 25 °C, $CFCl_3$): $\delta = -71.37$ (s, 3F, CF_3, major), −71.55 (s, 3F, CF_3, minor); 98.4% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.97$ (m, 4H), 7.56 (m, 2H), 7.40 (m, 3H), 6.91 (m, 4H), 5.57 (t, $^3J(H,H) = 6.4$ Hz, H2″), 5.36–5.25 (m, 3H, H1, H3, H4″), 5.09–5.06 (m, 2H, H5, H6″), 3.87 (s, 3H, MeO), 3.83 (s, 3H,

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MeO), 3.54 (s, 3H, MeOH), 2.71–2.60 (m, 2H; H3″, H5″), 2.55–2.44 (m, 3H; H1′, H3″, H5″), 2.34–2.22 (m, 3H; H2, H6), 2.21–2.11 (m, 5H; H′-1′, H2, H4, H7″), 2.05, 2.04 (2s, 6H; 2AcO), 1.80 (dd, ^2J(H,H) = 14.9, ^3J(H,H) = 9.0 Hz, 1H; H′-4), 1.67 (br s, 1H; HO); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 170.4, 170.0 (2s; 2CH_3COO), 165.6, 165.5, 165.2 (3s), 163.5, 163,4 (2s, 2ArCOO), 135.4 (s; C1″), 131.7 (d, ^1J(C,H) = 163 Hz, HC_{arom}), 129.8 (d, ^1J(C,H) = 162 Hz, HC_{arom}), 128.8 (s; C_{arom}), 128.6 (d, ^1J(C,H) = 165 Hz, HC_{arom}), 128.4, 127.6 (2d, ^1J(C,H) = 162 Hz, 2HC_{arom}), 126.2 (q, ^1J(C,F) = 286 Hz; CF_3), 122.6, 122.5 (2s), 113.6 (d, ^1J(C,H) = 161 Hz), 78.3 (d, C5), 74.1 (s; C7), 68.6 (d, ^1J(C,H) = 142 Hz; C4″), 68.4 (d, ^1J(C,H) = 140 Hz; C6″), 68.0 (d, ^1J(C,H) = 151 Hz; C3), 66.9 (d, ^1J(C,H) = 149 Hz; C1), 55.4 (q, ^1J(C,H) = 140 Hz, 3MeO), 48.9 (t, ^1J(C,H) = 127 Hz; C1′), 41.5 (m, C6), 40.9 (m, C4), 38.7 (m, C5″), 38.1 (m, C7″), 33.6 (t, ^1J(C,H) = 130 Hz; C2), 32.3 (t, ^1J(C,H) = 129 Hz; C3″), 21.2 (q, ^1J(C,H) = 160 Hz, 2CH_3CO); IR (KBr): $\tilde{\nu}$ = 3450, 2360, 1710, 1605, 1510, 1455, 1255, 1170, 1105, 1025, 850, 770, 700 cm^{-1}; UV (MeCN): λ_{max} (ε) = 260 (44400), 254 (47700), 203 (65600), 198 nm (73700 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 888 (13) $[M+NH_4]^+$, 552 (17), 401 (6), 318 (5), 189 (25), 170 (15), 152 (19), 135 (100), 106 (70), 91 (34), 77 (30); elemental analysis calcd for $C_{45}H_{49}F_3O_{14}$ (870.9) (%): C 62.06, H 5.67; found C 62.17, H 5.77.

Mosher's ester of (+)-11: (+)-(1*R,3*S**,5*S**,7*S**)-5-acetoxy-7-{[(4*S**,6*S**)-6-acetoxy-4-[(4-methoxybenzoyl)oxy]cyclohept-1-en-1-yl}methyl}-3-[(4-methoxybenzoyl)oxy]-7-hydroxycyclohept-1-yl (*R*)-α-methoxy-α-trifluoromethylphenylacetate ((+)-11M)**: Same procedure as above, colourless foam. $[\alpha]_D^{25}$ = 24, $[\alpha]_{577}^{25}$ = 24, $[\alpha]_{546}^{25}$ = 25, $[\alpha]_{435}^{25}$ = 44, $[\alpha]_{405}^{25}$ = 55 (*c* = 0.5, $CHCl_3$); ^{19}F NMR (376.5, $CDCl_3$, 25 °C, $CFCl_3$): δ = −71.44 (s, major), −71.49 (s, minor): *ee* = 15%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.63, 5.53 (2t, ^3J(H,H) = 6.5 Hz, H2″), 3.58, 3.53 (2s, OMe (MTPA)); IR (film): $\tilde{\nu}$ = 3500, 2955, 1735, 1710, 1605, 1510, 1455, 1370, 1255, 1170, 1105, 1025, 850, 770, 700 cm^{-1}; UV (MeCN): λ_{max} (ε) = 260 (38000), 255 (40700), 207 (49300), 203 nm (53500 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 888 (26) $[M+NH_4]^+$, 811 (3), 552 (5), 401 (4), 318 (6), 189 (26), 170 (8), 166 (8), 152 (11), 135 (81), 107 (28), 106 (100), 105 (32), 91 (28), 77 (22).

(1*R*,6*R*)-6-Acetoxy-4{[(1*R*,2*S*,4*S*,6*R*)-6-acetoxy-1,2-(isopropylidenedioxy)-4-[(4-methoxybenzoyl)oxy]cyclohept-1-yl}methylcyclohept-3-en-1-yl 4-methoxybenzoate ((−)-10ac) and (1*S,6*S**)-6-acetoxy-4-{{1*R**,2*S**,4*R**,6*R**)-6-acetoxy-1,2-(isopropylidenedioxy)-4-[(4-methoxybenzoyl)oxy]cyclohept-1-yl}methyl}cyclohept-3-en-1-yl 4-methoxybenzoate ((+)-11ac)**: (−)-**10ac** and (+)-**11ac** were prepared by treatment of (−)-**10** and (+)-**11** (50 mg) at 20 °C for 12 h in acetone (1.0 mL), dimethoxypropane (0.5 mL) and pyridinium *para*-toluenesulfonate (5 mg). Neutralisation (saturated solution of aqueous $NaHCO_3$, 1.0 mL), and evaporation of the solvent followed by extraction (CH_2Cl_2) afforded the acetonide (49 mg, 93%) as a colourless oil.

(−)-10ac: $[\alpha]_D^{25}$ = −1, $[\alpha]_{546}^{25}$ = −2, $[\alpha]_{435}^{25}$ = −5, (*c* = 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.08 (m, 4H), 7.97 (m, 4H), 5.60 (t, ^3J(H,H) = 6.8 Hz, 1H; H3), 5.50 (br t, *J*(H,H) = 10.1 Hz, 1H; H6″), 5.35 (m, 1H; H4″), 5.26 (tt, ^3J(H,H) = 7.7, 4.0 Hz, 1H; H1), 5.14 (m, 1H; H6), 4.15 (br d, ^3J(H,H) = 6.2 Hz, 1H; H2″), 3.87, 3.85 (2s, 6H; 2MeO), 2.74 (m, 2H; H5, H3″), 2.58 (m, 3H; 2H2, H′-5), 2.44 (d, ^2J(H,H) = 13.5 Hz, 1H; H1′(CH_2)), 2.36 (br d, ^2J(H,H) = 13.8 Hz, 1H; H5″), 2.25 (m, 2H; H7), 2.19 (d, ^2J(H,H) = 13.5 Hz, 1H; H′-1′(CH_2)), 2.15 (d, ^2J(H,H) = 14.9 Hz, 1H; H7″), 2.02 (s, 6H, 2AcO), 1.89 (m, 2H; H′-5″, H′-3″), 1.77 (dd, ^2J(H,H) = 14.9, ^3J(H,H) = 10.1 Hz, 1H; H′-7″), 1.58, 1.35 (2s, 6H; acetonide); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 170.3, 169.8 (2s, 2AcO), 165.7 (2s; 2C_{arom}), 163.3 (2s, 2ArCOO), 136.7 (s; C4), 131.9, 131.6 (2d, ^1J(C,H) = 163 Hz; 4C_{arom}), 126.2 (d, ^1J(C,H) = 153 Hz; C3), 123.1 (2s; 2C_{arom}), 113.6, 113.5 (2d, ^1J(C,H) = 160 Hz; 4C_{arom}), 107.4 (s, acetonide), 82.4 (s; C1″), 81.4 (d, ^1J(C,H) = 145 Hz; C2″), 68.8 (d, ^1J(C,H) = 145 Hz; C1), 67.9 (d, ^1J(C,H) = 152 Hz; C6), 67.7 (d, ^1J(C,H) = 147 Hz; C4″), 66.6 (d, ^1J(C,H) = 147 Hz; C6″), 55.4 (q, ^1J(C,H) = 145 Hz, 2MeO), 51.2 (t, ^1J(C,H) = 128 Hz; C1′), 44.7 (t, ^1J(C,H) = 126 Hz; C7″), 37.9 (2t, ^1J(C,H) = 128 Hz; C7,5″), 32.9 (t, ^1J(C,H) = 128 Hz; C5), 31.0 (t, ^1J(C,H) = 129 Hz; C2), 27.6, 25.6 (2q, ^1J(C,H) = 128 Hz, acetonide), 21.4 (q, ^1J(C,H) = 129 Hz, 2AcO); IR (film): $\tilde{\nu}$ = 2940, 2840, 1735, 1710, 1605, 1510, 1460, 1370, 1280, 1255, 1170, 1115, 1025, 915, 850, 770, 730, 695 cm^{-1}; MS (CI/NH_3): *m*/*z* (%): 712 (1) $[M+NH_4]^+$, 662 (2), 317 (3), 165 (45), 135 (100), 107 (15), 83 (10).

(+)-11ac: $[\alpha]_D^{25}$ = 4, $[\alpha]_{577}^{25}$ = 4, $[\alpha]_{546}^{25}$ = 6, $[\alpha]_{435}^{25}$ = 10, $[\alpha]_{405}^{25}$ = 12 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.98 (m, 4H), 6.93 (m, 4H), 5.59 (t, ^3J(H,H) = 6.5 Hz, H3), 5.49 (m, 1H; H4″), 5.24 (m, 1H; H1), 5.18 (m, 1H; H6), 5.05 (m, 1H; H6″), 4.13 (dd, ^3J(H,H) = 8.9, 3.5 Hz, 1H; H2″), 3.87, 3.84 (2s, 6H; 2MeO), 2.80 (dd, ^2J(H,H) = 14.8, ^3J(H,H) = 9.2 Hz, 1H; H5), 2.67–2.37 (m, 6H; 2H1′, 2H2, H′-5, H3″), 2.31–2.04 (m, 6H; 2H7″, 2H7, H5″, H′-3″), 2.03 (s, 3H; AcO), 1.96 (m, 1H; H′-5″), 1.90 (s, 3H; AcO), 1.46, 1.37 (2s, 6H; acetonide); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 170.1, 169.9 (2s; 2AcO), 165.5, 165.2 (2s; 2C_{arom}), 163.4 (2s; 2ArCOO), 136.7 (s; C4), 131.7, 131.6 (2d, ^1J(C,H) = 163 Hz; 4C_{arom}), 126.6 (d, ^1J(C,H) = 153 Hz; C3), 122.8, 122.4 (2s; 2C_{arom}), 113.7, 113.6 (2d, ^1J(C,H) = 161 Hz; 4C_{arom}), 108.7 (s, acetonide), 83.2 (s; C1″), 79.4 (d, ^1J(C,H) = 144 Hz; C2″), 68.8 (d, ^1J(C,H) = 149 Hz; C1), 68.2 (d, ^1J(C,H) = 148 Hz; C6), 67.0 (d, ^1J(C,H) = 148 Hz; C4″), 66.6 (d, ^1J(C,H) = 148 Hz; C6″), 55.4 (q, ^1J(C,H) = 145 Hz, 2MeO), 47.3 (t, ^1J(C,H) = 126 Hz; C1′), 41.5, 40.4 (2t, ^1J(C,H) = 130 Hz; C7,7″), 40.0 (t, ^1J(C,H) = 131 Hz; C5″), 38.6 (t, ^1J(C,H) = 131 Hz; C5), 34.2 (t, ^1J(C,H) = 131 Hz; C3″), 32.3 (t, ^1J(C,H) = 131 Hz; C2), 29.4, 27.6 (2q, ^1J(C,H) = 127 Hz, acetonide), 21.3, 21.0 (2q, ^1J(C,H) = 129 Hz, 2AcO); IR (film): $\tilde{\nu}$ = 2940, 2845, 1730, 1715, 1605, 1580, 1510, 1460, 1370, 1315, 1255, 1170, 1100, 1025, 915, 850, 770, 735, 695 cm^{-1}; MS (CI/NH_3): *m*/*z* (%): 712 (1) $[M+NH_4]^+$, 679 (2), 635 (4), 429 (2), 319 (6), 225 (14), 165 (100), 135 (71), 83 (89).

(1*R*,1′*S*,6*R*,6′*S*)-3,3-Methylenebis{6-{[(*tert*-butyl)dimethylsilyl]oxy}cyclohept-3-en-1-yl} diacetate (12): 2,6-Lutidine (5 mL, 4.6 g, 43 mmol) was added dropwise to a stirred solution of **7** (2.42 g, 5.7 mmol) in anhydrous CH_2Cl_2 (350 mL) cooled to −78 °C under N_2 atmosphere. Then (*tert*-butyl)dimethylsilyl trifluoromethanesulfonate (5 mL, 5.7 g, 21.8 mmol) was added dropwise. The mixture was allowed to warm to 20 °C overnight under stirring and N_2 atmosphere (TLC, R_f (bis-silyl ether) = 0.79, MeOH/CH_2Cl_2 5:95). 3% HCl in H_2O (100 mL) was added and the phases were separated. The aqueous layer was extracted with CH_2Cl_2 (30 mL, 2×). The combined organic extracts were washed with saturated aqueous solution of $NaHCO_3$ (50 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue filtered though a pad of silica gel (light petroleum ether/Et_2O) to give bis-silyl ether of **7** (3.67 g; 97%) as a colourless oil. A mixture of this oil (0.5 g, 0.77 mmol), anhydrous toluene (2 mL), Bu_3SnH (0.7 g, 2.41 mmol) and AIBN (20 mg, 0.12 mmol) was heated to 80 °C for 4 h. The solvent was evaporated and the residue was subjected to flash chromatography on silica gel (230–400 mesh, i) pentane, ii) Et_2O/pentane 5:95, R_f (**12**) = 0.18) gave **12** (400 mg, 90%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.46 (dd, ^3J(H,H) = 6.4, 6.3 Hz, 2H; H4), 4.99 (dddd, ^3J(H,H) = 9.3, 9.2, 3.2, 2.4 Hz, 2H; H1), 3.98 (dddd, ^3J(H,H) = 7.3, 7.2, 3.7, 3.1, 2H; H6), 2.74, 2.56 (2d, ^2J(H,H) = 13.9 Hz; CH_2), 2.35 (dd, ^2J(H,H) = 14.6, ^3J(H,H) = 9.4 Hz, 2H; H2), 2.33–2.23 (m, 4H; H5), 2.21 (dd, ^2J(H,H) = 14.6, ^3J(H,H) = 1.1 Hz, 2H; H′-2), 2.06–1.93 (m, 4H; H7), 2.01 (s, 6H; 2AcO), 0.88 (s, 18H; 2*t*Bu), 0.05, 0.04 (2s, 12H; 2Me_2Si); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 170.0 (s; CH_3COO), 136.2 (s; C3), 124.3 (d, ^1J(C,H) = 155 Hz; C4), 69.0 (d, ^1J(C,H) = 153 Hz; C1), 66.7 (d, ^1J(C,H) = 141 Hz; C6), 51.0 (t, ^1J(C,H) = 126 Hz; CH_2(methylene)), 45.2 (t, ^1J(C,H) = 127 Hz; C7), 36.2 (2t, ^1J(C,H) = 127 Hz; C2, C5), 25.8 (q, ^1J(C,H) = 125 Hz, *t*Bu), 21.3 (q, ^1J(C,H) = 129 Hz; CH_3COO), 18.1 (s), −4.9 (q, ^1J(C,H) = 118 Hz, Me_2Si); IR (film): $\tilde{\nu}$ = 2955, 2940, 2885, 1735, 1470, 1465, 1365, 1190, 1090, 1065, 1025, 990, 935, 905, 840, 775, 740 cm^{-1}; UV (MeCN): λ_{max} (ε) = 206 nm (21600 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 598 (1) $[M+NH_4]^+$, 523 (2), 449 (6), 331 (23), 289 (7), 197 (75), 117 (58), 75 (86), 73 (100); elemental analysis calcd for $C_{31}H_{56}O_6Si_2$ (581.0) (%): C 64.09, H 9.72; found C 64.14, H 9.67.

(1*R*,1′*S*,6*R*,6′*S*)-3,3′-Methylenebis(6-hydroxycyclohept-3-en-1-yl) diacetate (13): A mixture of **12** (0.5 g, 0.86 mmol), THF (50 mL) and a 1M solution of Bu_4NF in THF (3.0 mL, 3 mmol) was stirred at 20 °C for 15 h (R_f (**13**) = 0.30, 1:9 MeOH/CH_2Cl_2). Solvent evaporation and filtration on silica gel (MeOH/CH_2Cl_2 5:95) yielded **13** (302 mg, 99%) as a colourless oil that crystallised from toluene. M.p. 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.51 (dd, ^3J(H,H) = 6.3, 6.2 Hz, 2H; H4), 4.94 (dddd, ^3J(H,H) = 9.3, 9.2, 3.4, 2.0 Hz, 2H; H1), 4.03 (dddd, ^3J(H,H) = 7.0, 6.9, 2.9, 2.8 Hz, 2H; H6), 2.80, 2.66 (2d, ^2J(H,H) = 14.4 Hz; CH_2 of methylene), 2.46–2.35 (m, 6H), 2.22 (br d, ^2J(H,H) = 14.2 Hz, 2H; H2), 2.12–1.98 (m, 4H; H7), 2.01 (s, 6H; 2AcO), 1.91 (s, 2OH); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 170.3 (s, AcO), 137.7 (s; C3), 123.7 (d, ^1J(C,H) = 156 Hz; C4), 68.1 (d, ^1J(C,H) = 153 Hz; C1), 66.1 (d, ^1J(C,H) = 145 Hz; C6), 50.5 (t, ^1J(C,H) = 128 Hz; CH_2 of methylene), 44.4 (t, ^1J(C,H) = 128 Hz; C7), 36.7 (t, ^1J(C,H) = 128 Hz; C2), 35.0 (t, ^1J(C,H) = 128 Hz; C5), 21.3 (q, ^1J(C,H) = 130 Hz; CH_3COO); IR (KBr): $\tilde{\nu}$ = 3345, 2940, 2910, 2865, 1740, 1725, 1655,

1435, 1370, 1240, 1080, 1045, 1030, 985, 885, 685 cm^{-1}; UV (MeCN): λ_{max} (ε) = 207 nm (14600 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 370 (5) $[M+NH_4]^+$, 335 (2), 293 (9), 233 (23), 214 (9), 188 (9), 129 (10), 105 (11), 91 (32), 85 (76), 83 (100); elemental analysis calcd for $C_{19}H_{28}O_6$ (352.4) (%): C 64.75, H 8.01; found C 64.68, H 7.92.

(1*R*,1′*S*,6*R*,6′*S*)-3,3′-Methylenebis{6-{[(*tert*-butyl)dimethylsilyl]oxy}cyclohept-3-en-1-ol} (14): A mixture of **12** (200 mg, 0.34 mmol), MeOH (15 mL) and K_2CO_3 (0.5 g) was stirred at 20 °C for 15 h. After filtration on Celite, NH_4Cl (0.5 g) was added and the mixture filtered (Celite). The solvent was evaporated and the residue taken up in ether (20 mL). After filtration (Celite), the solvent was evaporated to give **14** (171 mg, 100%) as a colourless oil that solidified slowly. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.53 (t, ^3J(H,H) = 6.5 Hz, 2H; H4), 4.00 (m, 1H; H1), 3.93 (m, 1H; H6), 2.74 (d, ^2J(H,H) = 14.1 Hz, 1H; CH_2 of methylene), 2.66 (d, ^2J(H,H) = 14.1 Hz, 1H; CH_2 of methylene), 2.30 (m, 8H; 4H5, 4H2), 1.97 (m, 4H; H7), 1.45 (br s, 2H; OH), 0.88 (s, 18H; TBDMS), 0.06 (s, 12H; TBDMS); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 137.1 (s; C3), 124.3 (d, ^1J(C,H) = 157 Hz; C4), 66.4 (d, ^1J(C,H) = 141 Hz; C6), 66.1 (d, ^1J(C,H) = 146 Hz; C1), 51.5 (t, ^1J(C,H) = 127 Hz; CH_2 of methylene), 48.7 (t, ^1J(C,H) = 127 Hz; C7), 39.6 (t, ^1J(C,H) = 126 Hz; C2), 36.7 (t, ^1J(C,H) = 126 Hz; C5), 25.8 (q, ^1J(C,H) = 125 Hz, TBDMS), 18.1 (s, TBDMS), −4.8 (q, ^1J(C,H) = 118 Hz, TBDMS); IR (KBr): $\tilde{\nu}$ = 3345, 2930, 2855, 1470, 1465, 1360, 1255, 1085, 1060, 990, 900, 865, 835, 775 cm^{-1}; UV (MeCN): λ_{max} (ε) = 208 (13500), 197 nm (13800 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 479 (2), 421 (2), 347 (18), 289 (16), 197 (79), 155 (17), 129 (25), 91 (45), 73 (100); elemental analysis calcd for $C_{27}H_{54}Si_2O_4$ (496.9) (%): C 65.27, H 10.55, Si 11.30; found C 65.35, H 10.56, Si 11.34.

(1*R*,1′*S*,6*R*,6′*S*)-3,3′-Methylenebis{6-{[(*tert*-butyl)dimethylsilyl]oxy}cyclohept-3-en-1-yl} bis(4-methoxybenzoate) (15): A mixture of **14** (50 mg, 0.1 mmol), anhydrous CH_2Cl_2 (3 mL), pyridine (1 mL), 4-methoxybenzoyl chloride (0.1 g, 0.59 mmol) and DMAP (20 mg) was stirred at 50 °C (closed flask) for 1 day (TLC, R_f (**14**) = 0.56, R_f (**15**) = 0.70, Et_2O/light petroleum ether 9:1). After cooling to 20 °C, a saturated aqueous solution of $NaHCO_3$ (2 mL) was added and the mixture stirred at 20 °C for 1 h. The mixture was extracted with Et_2O (2 mL, 3 ×). The combined organic extracts were dried ($MgSO_4$), the solvent was evaporated and the residue purified by flash chromatography on silica gel (Et_2O/light petroleum ether 1:1) to give **15** (67 mg, 87%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.99 (m, 4H), 6.93 (m, 4H), 5.50 (t, ^3J(H,H) = 6.5 Hz, 2H; H4), 5.22 (m, 2H; H1), 3.99 (tt, ^3J(H,H) = 7.3, 3.8 Hz, 2H; H6), 3.86 (s, 6H; MeO), 2.73 (d, ^2J(H,H) = 14.0 Hz, 1H; CH_2 of methylene), 2.56 (d, ^2J(H,H) = 14.0 Hz, 1H; CH_2 of methylene), 2.47 (dd, ^2J(H,H) = 14.8 Hz, ^3J(H,H) = 8.5 Hz, 2H; H2), 2.29 (m, 6H; H5, H′-2), 2.16 (ddd, ^2J(H,H) = 13.6 Hz, ^3J(H,H) = 7.6, 3.3 Hz, 2H; H7), 1.97 (ddd, ^2J(H,H) = 13.6, ^3J(H,H) = 8.2, 3.1 Hz, 2H; H′-7), 0.85 (s, 18H; TBDMS), 0.03 (s, 6H; TBDMS), 0.02 (s, 6H; TBDMS); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 165.3 (s, 2ArCOO), 163.2 (s; 2C_{arom}), 136.6 (s; C3), 131.5 (d, ^1J(C,H) = 163 Hz; 4C_{arom}), 124.1 (d, ^1J(C,H) = 160 Hz; C4), 123.2 (s; 2C_{arom}), 113.5 (d, ^1J(C,H) = 162 Hz; 4C_{arom}), 69.4 (d, ^1J(C,H) = 151 Hz; C1), 66.5 (d, ^1J(C,H) = 145 Hz; C6), 55.4 (q, ^1J(C,H) = 144 Hz, 2MeO), 51.2 (t, ^1J(C,H) = 127 Hz; CH_2 of methylene), 45.5 (t, ^1J(C,H) = 127 Hz; C7), 36.8 (t, ^1J(C,H) = 126 Hz; C5), 35.7 (t, ^1J(C,H) = 127 Hz; C2), 25.8 (q, ^1J(C,H) = 125 Hz, TBDMS), 18.1 (s, TBDMS), −4.9 (q, ^1J(C,H) = 118 Hz, TBDMS); IR (KBr): $\tilde{\nu}$ = 2930, 2855, 1710, 1610, 1510, 1465, 1320, 1255, 1165, 1100, 1065, 1035, 835, 770 cm^{-1}; UV (MeCN): λ_{max} (ε) = 260 (33600), 254 (37400), 207 (43600), 201 nm (48000 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 782 (1) $[M+NH_4]^+$, 707 (10), 633 (27), 555 (21), 423 (42), 329 (43), 197 (86), 135 (100), 73 (55); elemental analysis calcd for $C_{43}H_{64}O_8Si_2$ (765.1) (%): C 67.50, H 8.43, Si 7.34; found C 67.49, H 8.53, Si 7.34.

(1*R*,6*R*)-6-Hydroxy-4-{(1*R*,2*S*,4*S*,6*S*)-1,2,6-trihydroxy-4-[(4-methoxybenzoyl)oxy]cyclohept-1′-yl}methyl}cyclohept-3-en-1-yl 4-methoxybenzoate ((+)-16): A mixture of (−)-**10** (4.0 g, 6.1 mmol), anhydrous MeOH (210 mL) and of 0.7 M solution of $Mg(OMe)_2$ in MeOH (Aldrich No. 33, 565–567, 72 mL, 50 mmol) was stirred at 20 °C under Ar atmosphere for 3.5 h (TLC, MeOH/CH_2Cl_2 5:95, R_f ((−)-**10**) = 0.48, R_f (monoacetate) = 0.30, R_f ((+)-**16**) = 0.20). After acidification with 2.5 M oxalic acid in anhydrous MeOH (bromothymol blue) and stirring at 20 °C for 1 h, the solution was filtered (Celite). Evaporation of the solvent and flash chromatography on silica gel (MeOH/CH_2Cl_2 5:95) afforded (+)-**16** (2.6 g, 74%) as a colourless solid. M.p. 155–156 °C; $[\alpha]_D^{25}$ = 13, $[\alpha]_{577}^{25}$ = 14, $[\alpha]_{546}^{25}$ = 17, $[\alpha]_{435}^{25}$ = 32, $[\alpha]_{405}^{25}$ = 41 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, CD_3OD, 25 °C, TMS): δ = 7.95 (m, 4H), 6.98 (m, 4H), 5.67 (t, ^3J(H,H) = 6.7 Hz, 1H; H3), 5.25–5.19 (m, 2H; H1, H4″), 4.25 (dddd, ^3J(H,H) = 9.5, 5.0, 4.9, 2.7 Hz, H6), 4.15–4.10 (m, 1H; H6″), 3.86, 3.84 (2s, 6H; 2MeO), 3.53 (dd, ^3J(H,H) = 10.9 Hz, ^3J(H,H) = 2.5 Hz, 1H; H2″), 2.69 (dd, ^2J(H,H) = 14.8, ^3J(H,H) = 7.6 Hz, 1H; H5), 2.66, 2.21 (2d, ^2J(H,H) = 12.7 Hz, 2H; H1′), 2.61–2.51 (m, 3H), 2.34 (ddd, ^2J(H,H) = 13.3, ^3J(H,H) = 10.9, 10.8 Hz, 1H; H3″), 2.26–2.14 (m, 5H), 2.03 (dd, ^2J(H,H) = 8.2, ^3J(H,H) = 6.2 Hz, 1H; H7″), 2.01–1.94 (m, 1H; H′-3″), 1.61 (dd, ^2J(H,H) = 14.5, ^3J(H,H) = 10.5 Hz, 1H; H5″); ^{13}C NMR (100.6 MHz, CD_3OD, 25 °C): δ = 167.2 (s), 165.1 (s), 139.6 (s; C4), 132.5 (d, ^1J(C,H) = 170 Hz, HC_{arom}), 127.6 (d, ^1J(C,H) = 158 Hz; C3), 124.1 (s; C_{arom}), 114.8 (d, ^1J(C,H) = 162 Hz, HC_{arom}), 76.0 (s; C1″), 74.0 (d, ^1J(C,H) = 138 Hz; C2″), 70.5, 70.4 (2d, ^1J(C,H) = 159 Hz; C1, C4″), 67.1 (d, ^1J(C,H) = 139 Hz; C6″), 64.4 (d, ^1J(C,H) = 143 Hz; C6), 56.0 (q, ^1J(C,H) = 144 Hz, MeO), 50.8 (t, ^1J(C,H) = 128 Hz; C1′), 45.8 (t, ^1J(C,H) = 127 Hz; C7), 45.0 (m, C5″), 43.5 (t, ^1J(C,H) = 126 Hz; C7″), 41.6 (m, C5), 38.5 (t, ^1J(C,H) = 127 Hz; C3″), 34.4 (t, ^1J(C,H) = 127 Hz; C2); IR (KBr): $\tilde{\nu}$ = 3360, 2940, 1695, 1605, 1510, 1460, 1420, 1255, 1170, 1105, 1030, 965, 845, 770, 695, 610 cm^{-1}; UV (MeCN): λ_{max} (ε) = 252 (30900), 208 nm (23600 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 588 (41) $[M+NH_4]^+$, 571 (14), 419 (7), 295 (23), 249 (7), 170 (25), 153 (15), 152 (40), 135 (100), 107 (40); elemental analysis calcd for $C_{31}H_{38}O_{10}$ (570.6) (%): C 65.25, H 6.71; found C 65.24, H 6.69.

(2*R* and 2*S*,4*S*,6*R*)-Tetrahydro-2-hydroxy-6{(4*S*,6*S*)-{6-hydroxy-4-[(4-methoxybenzoyl)oxy]cylohept-1-en-1-yl}-2-oxopropyl}-2*H*pyran-4-yl 4-methoxybenzoates ((−)-18): A mixture of (+)-**16** (2.20 g, 3.85 mmol), dioxane (40 mL), H_2O (16 mL), $NaIO_4$ (2.11 g, 9.9 mmol) was stirred at 20 °C for 15 h (TLC, MeOH/CH_2Cl_2 5:95, R_f ((+)-**16**) = 0.28, R_f ((−)-**18**) = 0.32). EtOAc (50 mL) was added and the phases allowed to separate. The aqueous phase was extracted with EtOAc (30 mL, 2 ×) and the combined organic extracts were dried ($MgSO_4$). Solvent evaporation and flash chromatography on silica gel (MeOH/CH_2Cl_2 3:97) afforded (−)-**18** (2.15 g, 98%) as a colourless foam. M.p. 67–70 °C; $[\alpha]_D^{25}$ = −59, $[\alpha]_{577}^{25}$ = −62, $[\alpha]_{546}^{25}$ = −71, $[\alpha]_{435}^{25}$ = −122, $[\alpha]_{405}^{25}$ = −147 (*c* = 0.6 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): mixture of α- and β-pyranose (α/β 60:40) δ = 7.99, 6.92 (2m, 8H), 5.71 (t, ^3J(H,H) = 6.6 Hz, H2″), 5.50 (m, 1.2H; 0.6, H4, 0.6 H2), 5.25 (m, H4″), 5.16 (tt, ^3J(H,H) = 11.5, 4.6 Hz, 0.4H; H4), 4.89 (br d, ^3J(H,H) = 9.3 Hz, 0.4H; $H2_{axial}$ of β-anomer), 4.65 (m, 0.6H; H6), 4.16 (m, H6″), 4.06 (m, 0.4H; H6), 3.87, 3.85 (2s, 2MeO), 3.37, 3.19 (2d, ^2J(H,H) = 16.2 Hz), 3.32, 3.22 (2d, ^2J(H,H) = 16.3 Hz, $H_2C(1')$), 2.94 (dd, ^2J(H,H) = 15.5, ^3J(H,H) = 9.1 Hz, 0.4H; H3′), 2.81 (dd, ^2J(H,H) = 15.3, ^3J(H,H) = 9.5 Hz, 0.6H; H3′), 2.60–2.44 (m, 5H; H3′, $H_2C(3'')$, $H_2C(7'')$), 2.43–2.36 (m, 0.5H), 2.34–2.07 (m, 3.5H), 1.74 (ddd, ^2J(H,H) = 11.8, ^3J(H,H) = 3.4, 3.3 Hz, 0.6H; H5), 1.61–1.43 (m, 1.4H; H5, H3); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): of 2 isomers δ = 208.5, 208.3 (s; C2′), 165.6, 165.5, 163.3 (3s), 133.7 (s; C1″), 131.6 (d, ^1J(C,H) = 163 Hz, HC_{arom}), 127.0 (d, ^1J(C,H) = 156 Hz; C2″), 123.0, 122.7, 122.4 (3s; C_{arom}), 113.6 (d, ^1J(C,H) = 162 Hz, HC_{arom}), 94.2 (d, ^1J(C,H) = 189 Hz; C2 of β-pyranose), 92.3 (d, ^1J(C,H) = 167 Hz; C2 of α-pyranose), 68.7 (C4), 68.5 (C4″), 68.4 (C6 of β-pyranose), 66.7 (C4), 65.7 (C6″), 64.3 (C6 of α-pyranose), 55.4 (q, ^1J(C,H) = 145 Hz, MeO), 55.0, 54.6 (C1′), 47.9, 47.4 (2t, ^1J(C,H) = 128 Hz; C3′), 44.6 (t, ^1J(C,H) = 127 Hz; C5″), 39.6 (t, ^1J(C,H) = 125 Hz; C7″), 38.1, 37.2 (C3), 36.2, 35.6 (C5), 33.3 (t, ^1J(C,H) = 128 Hz; C3″); IR (KBr): $\tilde{\nu}$ = 3425, 2935, 1710, 1605, 1510, 1420, 1260, 1170, 1105, 1030, 850, 770, 700, 615 cm^{-1}; UV (MeCN): λ_{max} (ε) = 254 (29200), 200 (36500), 196 nm (36500 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 586 (12) $[M+NH_4]^+$, 434 (46), 399 (53), 336 (20), 301 (10), 229 (10), 170 (100), 153 (53), 152 (87), 135 (74), 116 (12), 92 (22), 81 (53); elemental analysis calcd for $C_{31}H_{36}O_{10}$ (568.6) (%): C 65.48, H 6.38; found C 65.42, H 6.48.

(1*R*,6*R*)-6-Hydroxy-4-{(2*R*,4*S*,6*S*)-2,4,8-trihydroxy-6-[(4-methoxybenzoyl)oxy]octyl}cyclohept-3-en-1-yl 4-methoxybenzoate ((−)-19): A solution of (−)-**18** (1.10 g, 1.93 mmol) in anhydrous AcOH (10 mL) was added to a solution of $Me_4NBH(OAc)_3$ (7.0 g, 26.6 mmol) in anhydrous AcOH (16 mL). The mixture was stirred at 20 °C for 15 h, then crushed ice (20 g) was added and the solvents were evaporated in vacuo. CH_2Cl_2 (100 mL), H_2O (20 mL) then $NaHCO_3$ (5 g) were added under vigourous stirring. After 4 h at 20 °C, the aqueous layer was extracted with EtOAc (20 mL, 3 ×) and the combined organic extracts were dried ($MgSO_4$). Solvent evaporation and flash chromatography on silica gel (5% MeOH in CH_2Cl_2) afforded (−)-**19** (773 mg; 70%) as a colourless solid. M.p. 98–102 °C; $[\alpha]_D^{25}$ = −4, $[\alpha]_{546}^{25}$ = −4, $[\alpha]_{435}^{25}$ = −14, $[\alpha]_{405}^{25}$ = −21 (*c* = 0.5 in

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$CHCl_3$); ^1H NMR (400 MHz, CD_3OD, 25 °C): $\delta = 7.96$, 6.90 (2m, 8H), 5.65 (t, $^3J(H,H) = 6.7$ Hz, 1H; H3), 5.48 (dddd, $^3J(H,H) = 8.6$, 8.5, 4.3, 4.2 Hz, 1H; H6′), 5.17 (m, 1H; H1), 4.68 (m, 1H; H6), 4.09 (m, 1H; H2′), 3.98 (m, 1H; H4′), 3.85, 3.83 (2s, 6H; 2MeO), 3.76–3.62 (m, 2H), 2.59 (dd, $^2J(H,H) = 14.8$, $^3J(H,H) = 7.5$ Hz, 1H; H_a-5), 2.50–2.46 (m, 3H; H_b-5, $H_2C(2)$), 2.29 (ddd, $^2J(H,H) = 13.6$, $^3J(H,H) = 6.2$, 3.4 Hz, 1H), 2.18 (dd, $^2J(H,H) = 13.1$, $^3J(H,H) = 2.7$ Hz, 1H; H_a-1′), 2.07 (br d, $^2J(H,H) = 13.3$ Hz, 1H; H_b-1′), 2.11–2.03 (m, 2H), 1.94 (dddd, $^2J(H,H) = 7.9$, $^3J(H,H) = 5.3$, 5.2, 5.1 Hz, 1H; $H_2C(7')$), 1.86–1.83 (m, $H_2C(5)$), 1.64–1.61 (m, $H_2C(3')$); ^{13}C NMR (100.6 MHz, CD_3OD_3, 25 °C): $\delta = 167.4$, 165.6, 163.6, 163.3 (4s), 139.2 (s; C4), 131.8 (d, $^1J(C,H) = 165$ Hz, HC_{arom}), 131.5 (d, $^1J(C,H) = 164$ Hz, HC_{arom}), 124.2 (d, $^1J(C,H) = 155$ Hz; C3), 122.9, 122.1 (2s; C_{arom}), 113.7, 113.5 (2d, $^1J(C,H) = 161$ Hz, HC_{arom}), 69.5 (d, $^1J(C,H) = 145$ Hz; C2′), 69.4 (d, $^1J(C,H) = 140$ Hz; C6′), 68.6 (d, $^1J(C,H) = 151$ Hz; C1), 66.2 (d, $^1J(C,H) = 149$ Hz; C6), 65.2 (d, $^1J(C,H) = 140$ Hz; C4′), 58.6 (t, $^1J(C,H) = 140$ Hz; C8′), 55.4 (q, $^1J(C,H) = 145$ Hz, MeO), 48.4 (t, $^1J(C,H) = 126$ Hz; C1′), 44.7 (t, $^1J(C,H) = 126$ Hz; C7), 42.8 (t, $^1J(C,H) = 126$ Hz; C3′), 42.7 (t, $^1J(C,H) = 126$ Hz; C5′), 39.6 (t, $^1J(C,H) = 126$ Hz; C5), 38.0 (t, $^1J(C,H) = 125$ Hz; C7′), 33.5 (t, $^1J(C,H) = 127$ Hz; C2); IR (KBr): $\tilde{\nu} = 3360$, 2940, 1685, 1605, 1501, 1460, 1420, 1255, 1170, 1120, 1025, 845, 770, 695 cm^{-1}; UV (MeCN): λ_{max} (ε) = 254 (45300), 201 nm (53000 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 590 (36, $[M+NH_4]^+$), 573 (78) $[M^+]$, 555 (15), 421 (13), 385 (7), 297 (36), 279 (40), 233 (16), 170 (41), 135 (100); elemental analysis calcd for $C_{31}H_{40}O_{10}$ (572.7) (%): C 65.02, H 7.07; found C 64.91, H 7.01.

(1*R*,3*R*)-5-[{(4*R*,6*S*)-6-[(4*S*)-(2,2-Dimethyl-1,3-dioxan-4-yl)methyl]-2,2-dimethyl-1,3-dioxan-4-yl}methyl]cyclohept-5-ene-1,3-diol ((−)-21): A mixture of (−)-**19** (44 mg, 0.077 mmol) and 4% MeOK in MeOH (20 mL) was stirred at 20 °C for 5 h. Neutralisation with anhydrous HCl in Et_2O (phenophthalein), then addition of solid $NaHCO_3$ under stirring filtration (Celite) and evaporation of the solvent gave hexol **20** as a white solid which was taken up in acetone (0.9 mL) and 2,2-dimethoxypropane (0.1 mL). After the addition of pyridinium *para*-toluenesulfonate (5 mg), the mixture was stirred at 20 °C for 24 h. Solid $NaHCO_3$ (10 mg) was added and the mixture stirred for 5 min. Evaporation of the solvent (without filtration) and flash chromatography on silica gel (MeOH/CH_2Cl_2 5:95) afforded (−)-**21** (16.2 mg; 55%) as a colourless oil. $[\alpha]_D^{25} = -5$, $[\alpha]_{546}^{25} = -6$, $[\alpha]_{435}^{25} = -14$, $[\alpha]_{405}^{25} = -20$ ($c = 0.8$ in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta =$ 5.60 (t, $^3J(H,H) = 6.7$ Hz, 1H; H6), 4.06–4.01 (m, 2H), 4.00–3.90 (m, 4H), 3.81 (ddd, $^2J(H,H) = 11.8$, $^3J(H,H) = 5.4$, 1.3 Hz, 1H, H6′′′′), 2.46 (dd, $^2J(H,H) = 14.5$, $^3J(H,H) = 8.1$ Hz, 1H; H_a-4), 2.41 (dd, $^2J(H,H) = 14.5$, $^3J(H,H) = 2.4$ Hz, 1H; H_b-4), 2.36 (m, 2H), 2.24 (dd, $^2J(H,H) = 13.9$, $^3J(H,H) = 4.0$ Hz, 1H; H_a-1′), 2.15 (dd, $^2J(H,H) = 13.9$, $^3J(H,H) = 9.2$ Hz, 1H; H_b-1′), 2.01 (t, $^3J(H,H) = 5.5$ Hz, $H_2C(2)$), 1.64–1.48 (m, 5H), 1.42 (s), 1.41 (m), 1.40, 1.34, 1.32 (3s). ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta =$ 138.0 (s; C5), 124.2 (d, $^1J(C,H) = 149$ Hz; C6), 100.6 (s; C2′′), 98.3 (s; C2′′′′), 66.7 (d, $^1J(C,H) = 143$ Hz; C4′′), 65.7 (d, $^1J(C,H) = 145$ Hz; C3), 65.5 (d, $^1J(C,H) = 143$ Hz; C1), 64.9 (d, $^1J(C,H) = 139$ Hz; C4′′′′), 62.1 (d, $^1J(C,H) = 143$ Hz; C6′′), 60.0 (t, $^1J(C,H) = 141$ Hz; C6′′′′), 48.5 (t, $^1J(C,H) = 124$ Hz; C2), 46.6 (t, $^1J(C,H) = 126$ Hz; C1′), 42.2 (t, $^1J(C,H) = 124$ Hz; C1′′′), 41.0 (t, $^1J(C,H) = 125$ Hz; C4), 38.7 (t, $^1J(C,H) = 127$ Hz; C5′′), 35.6 (t, $^1J(C,H) = 125$ Hz; C7), 31.6 (t, $^1J(C,H) = 128$ Hz; C5′′′′), 30.0 (q, $^1J(C,H) = 127$ Hz, Me-C(2′′′′)), 24.7 (q, $^1J(C,H) = 125$ Hz, Me-C(2′′)), 24.6 (q, $^1J(C,H) = 125$ Hz, Me-C(2′′)), 19.2 (q, $^1J(C,H) = 127$ Hz, Me-C(2′′′′)); IR (film): $\tilde{\nu} =$ 3390, 2990, 2925, 1455, 1380, 1225, 1200, 1165, 1100, 1040, 975, 935, 910, 870, 815, 740 cm^{-1}; UV (MeCN): λ_{max} (ε) = 201 nm (5700 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 402 (79) $[M+NH_4]^+$, 385 (100) $[M^+]$, 345 (18), 327 (96), 269 (41), 243 (13), 185 (11), 115 (10), 81 (14).

(1*R*,6*R*)-6-Hydroxy-4-{(4*R*,6*S*)-6-{(2*S*)-4-hydroxy-2-[(4-methoxybenzoyl)oxy]butyl}-2,2-dimethyl-1,3-dioxan-4-yl}methylcyclohept-3-en-1-yl 4-methoxybenzoate ((−)-22): A mixture of (−)-**19** (950 mg, 1.66 mmol), acetone (28 mL), $(MeO)_2CMe_2$ (2 mL) and $PyrH^+TsO^-$ (10 mg) was stirred at 0 °C for 4 h. Evaporation of the solvent, addition of wet CH_2Cl_2 and $PyrH^+TsO^-$ (5 mg). After the mixture had been stirred at 20 °C for 2 h, $NaHCO_3$ (100 mg) was added. Flash chromatography on silica gel (MeOH/CH_2Cl_2 3:97) afforded (−)-**22** (854 mg, 84%) as a white foam. $[\alpha]_D^{25} = -17$, $[\alpha]_{577}^{25} = -17$, $[\alpha]_{546}^{25} = -20$, $[\alpha]_{435}^{25} = -36$, $[\alpha]_{405}^{25} = -44$ ($c = 1.0$ in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.97$ (m, 4H), 6.91 (m 4H), 5.63 (t, $^3J(H,H) = 6.6$ Hz, 1H; H3), 5.46 (dddd, $^3J(H,H) = 9.8$, 9.7, 3.2, 3.1 Hz, 1H; H2′′′), 5.16 (dddd, $^3J(H,H) = 9.7$, 9.6, 3.9, 3.8 Hz, 1H; H1), 4.06 (m, 1H; H6), 3.99 (m, 1H; H4′′), 3.91 (m, 1H; H6′′), 3.86, 3.84 (2s, 6H; 2MeO), 3.79–3.55 (m, 2H; H4′′′), 2.91, 2.53 (2br s, 2 OH), 2.51–2.42 (m, 4H; H2, H5), 2.26–2.09 (m, 4H; H7, H1′), 1.98–1.87 & 1.81–1.72 (2m, 4H; H1′′′, H3′′′), 1.64 (ddd, $^2J(H,H) = 21.7$, $^3J(H,H) = 12.8$, 8.9 Hz, 1H; H_a-5′′), 1.63 (ddd, $^2J(H,H) = 21.7$, $^3J(H,H) = 12.8$, 9.0 Hz, 1H; H_b-5′′), 1.31, 1.14 (2s, M_2C); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 167.0$, 165.5, 163.5, 163.2 (4s), 137.5 (s; C4), 131.6, 131.5 (2d, $^1J(C,H) = 164$ Hz, HC_{arom}), 123.9 (d, $^1J(C,H) = 167$ Hz; C3), 123.1, 122.2 (2s; C_{arom}), 113.7, 113.5 (2d, $^1J(C,H) = 161$ Hz, HC_{arom}), 100.8 (s; C2′′), 68.7 (d, $^1J(C,H) = 151$ Hz; C1), 68.3 (d, $^1J(C,H) = 149$ Hz; C2′′′), 66.9 (d, $^1J(C,H) = 143$ Hz; C4′′), 65.9 (d, $^1J(C,H) = 143$ Hz; C6), 63.0 (d, $^1J(C,H) = 145$ Hz; C6′′), 58.2 (t, $^1J(C,H) = 140$ Hz; C4′′′), 55.4 (q, $^1J(C,H) = 145$ Hz, MeO), 45.9 (t, $^1J(C,H) = 126$ Hz; C1′), 44.8 (t, $^1J(C,H) = 126$ Hz; C7), 40.9 (t, $^1J(C,H) = 131$ Hz; C1′′′), 40.6 (t, $^1J(C,H) = 128$ Hz; C5), 38.4 (t, $^1J(C,H) = 126$ Hz; C5′′), 38.2 (t, $^1J(C,H) = 126$ Hz; C3′′′), 33.1 (t, $^1J(C,H) = 128$ Hz; C2), 24.4 (q, $^1J(C,H) = 128$ Hz, Me-C(2′′)), 24.3 (q, $^1J(C,H) = 128$ Hz, Me-C(2′′)); IR (KBr): $\tilde{\nu} = 3450$, 2935, 1705, 1605, 1510, 1260, 1170, 1105, 1030, 850, 770, 695, 610 cm^{-1}; UV (MeCN): λ_{max} (ε) = 252 (45500), 203 nm (43600 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 630 (8) $[M+NH_4]^+$, 613 (18) $[M^+]$, 555 (57), 403 (5), 279 (67), 135 (100), 83 (48); elemental analysis calcd for $C_{34}H_{44}O_{10}$ (612.7) (%): C 66.65, H 7.24; found C 66.51, H 7.36.

(1*R*,6*R*)-6-Hydroxy-4-{(4*R*,6*S*)-6-{(2*S*)-4-[(2,2-dimethyl-1-oxopropyl)oxy]-2-[(4-methoxybenzoyl)oxy]butyl}-2,2-dimethyl-1,3-dioxan-4-yl]methyl}cyclohept-3-en-1-yl 4-methoxybenzoate ((−)-23): A mixture of (−)-**22** (0.5 g, 0.082 mmol), anhydrous CH_2Cl_2 (7 mL), anhydrous pyridine (3 mL) and pivaloyl chloride (0.2 mL, 196 mg, 1.62 mmol) was stirred at 0 °C for 3 h (TLC, MeOH/CH_2Cl_2 5:95, R_f ((−)-**23**) = 0.31). A saturated aqueous solution of $NaHCO_3$ (0.5 mL) was added under stirring and the mixture was extracted with CH_2Cl_2 (10 mL, 3×). Evaporation of the solvent, flash chromatography on silica gel (MeOH/CH_2Cl_2 2:98) afforded (−)-**23** (410 mg, 72%) as a colourless oil. $[\alpha]_D^{25} = -34$, $[\alpha]_{577}^{25} = -34$, $[\alpha]_{546}^{25} = -41$, $[\alpha]_{435}^{25} = -74$, $[\alpha]_{405}^{25} = -93$ ($c = 0.9$ in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.96$, 6.90 (2m, 8H), 5.63 (t, $^3J(H,H) = 6.7$ Hz, 1H; H3), 5.40 (m), 5.16 (dddd, $^2J(H,H) = 8.0$, $^3J(H,H) = 7.9$, 4.0, 3.9 Hz, 1H; H1), 4.15 (ddd, $^2J(H,H) = 17.5$, $^3J(H,H) = 11.2$, 6.3 Hz, 1H), 4.13 (ddd, $^2J(H,H) = 17.5$, $^3J(H,H) = 11.2$, 6.9 Hz, 1H), 4.06 (m, 1H; H6), 3.99 (m, 1H), 3.91 (m, 1H), 3.85, 3.83 (2s, 6H; 2MeO), 2.48 (m, 4H), 2.26–2.08 (m, 4H), 2.04 (m, 2H), 1.87 (ddd, $^2J(H,H) = 14.2$, $^3J(H,H) = 9.0$, 3.2 Hz, 1H), 1.78 (ddd, $^2J(H,H) = 14.2$, $^3J(H,H) = 9.5$, 3.9 Hz, 1H), 1.62 (m, 2H), 1.31, 1.21 (2s, Me_2C), 1.18 (*t*Bu); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 178.3$, 165.5, 165.4, 163.3, 163.2 (5s), 137.4 (s; C4), 131.4 (d, $^1J(C,H) = 163$ Hz, HC_{arom}), 123.7 (d, $^1J(C,H) = 169$ Hz; C3), 123.0, 122.6 (2s; C_{arom}), 113.5, 113.5 (2d, $^1J(C,H) = 161$ Hz; C_{arom}), 100.6 (s; C2′′), 68.8 (d, $^1J(C,H) = 148$ Hz; C1), 68.4 (d, $^1J(C,H) = 149$ Hz; C2′′′), 66.7 (d, $^1J(C,H) = 143$ Hz; C4′′), 65.7 (d, $^1J(C,H) = 143$ Hz; C6), 63.0 (d, $^1J(C,H) = 144$ Hz; C6′′), 60.7 (t, $^1J(C,H) = 148$ Hz; C4′′′), 55.3 (q, $^1J(C,H) = 144$ Hz, MeO), 45.9 (t, $^1J(C,H) = 128$ Hz; C1′), 44.7 (t, $^1J(C,H) = 127$ Hz; C7), 40.6, 40.5 (2t, $^1J(C,H) = 127$ Hz; C1′′′, C5), 38.5 (s), 38.4 (t, $^1J(C,H) = 126$ Hz; C5′′), 33.8 (t, $^1J(C,H) = 128$ Hz; C3′′′), 32.9 (t, $^1J(C,H) = 128$ Hz; C2), 27.0 (q, $^1J(C,H) = 127$ Hz, *t*Bu), 24.4 (q, $^1J(C,H) = 125$ Hz, Me_2C); IR (film): $\tilde{\nu} = 2940$, 1710, 1605, 1510, 1460, 1365, 1260, 1170, 1100, 1030, 850, 770, 735, 700 cm^{-1}; UV (MeCN): λ_{max} (ε) = 253 (79000), 199 (100500), 194 nm (88700 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 714 (66) $[M+NH_4]^+$, 697 (4) $[M^+]$, 639 (100), 487 (4), 363 (61), 317 (8), 211 (22), 135 (87), 109 (44), 83 (79); elemental analysis calcd for $C_{39}H_{52}O_{11}$ (696.8) (%): C 67.22, H 7.52; found C 67.23, H 7.49.

(1*R*,3*R*)-5-[(4*R*,6*R*)-6-[(4*S*)-(2,2-dimethyl-1,3-dioxan-4-yl)methyl]-2,2-dimethyl-1,3-dioxan-4-yl)methyl}cyclohept-5-ene-1,3-diyl bis(4-methoxybenzoate) ((−)-24): A mixture of (−)-**21** (16 mg, 0.042 mmol), anhydrous pyridine (0.5 mL), *para*-methoxybenzoyl chloride (42 mg, 0.25 mmol) and 4-dimethylaminopyridine (2 mg) was stirred at 20 °C for 18 h. A saturated aqueous solution of $NaHCO_3$ (1 mL) was added. The organic phase was washed with 2% aqueous HCl (7 mL) at 0 °C. The combined organic phases were washed with H_2O (5 mL), then with saturated aqueous solution of $NaHCO_3$ (3 mL) and dried ($MgSO_4$). Evaporation of the solvent and flash chromatography on silica gel (Et_2O/light petroleum ether 3:2) afforded pure (−)-**24** (19 mg, 70%) as a colourless foam. $[\alpha]_D^{25} = -101$ $[\alpha]_{577}^{25} = -105$, $[\alpha]_{546}^{25} = -125$, $[\alpha]_{435}^{25} = -250$, $[\alpha]_{405}^{25} = -325$ ($c = 0.8$ in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.00$, 6.93 (2m, 8H), 5.62 (t, $^3J(H,H) = 6.6$ Hz, 1H; H6), 5.32 (m, 2H), 4.03–3.90 (m, 4H), 3.87, 3.86 (2s, 6H; 2MeO), 3.81 (ddd, $^2J(H,H) = 11.8$, $^3J(H,H) = 5.4$, 1.5 Hz, 1H), 2.71 (dd, $^2J(H,H) = 14.9$, $^3J(H,H) = 8.8$ Hz, 1H), 2.66–2.50 (m, 3H), 2.37 (t, $J(H,H) = 5.8$ Hz, 2H), 2.32 (dd, $^2J(H,H) = 14.2$, $^3J(H,H) = 7.0$ Hz, 1H), 2.15 (dd, $^2J(H,H) = 14.2$, $^3J(H,H) = 5.6$ Hz, 1H), 1.61–1.33 (m, 6H), 1.43,

1.37, 1.32, 1.30 (4s, 12H; 2 Me_2C); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 165.5, 163.3, 136.7 (3s), 131.7, 131.6 (2d, $^1J(C,H)$ = 163 Hz, HC_{arom}), 123.3 (d, $^1J(C,H)$ = 157 Hz; C6), 122.9 (s; C_{arom}), 113.6 (d, $^1J(C,H)$ = 161 Hz, HC_{arom}), 100.4 (s; C2″), 98.3 (s; C2‴), 69.0, 68.6 (2d, $^1J(C,H) \approx 152$ Hz; C1, C3), 64.9 (d, $^1J(C,H)$ = 144 Hz; C4″, C4‴), 62.1 (d, $^1J(C,H)$ = 145 Hz; C6″), 60.1 (t, $^1J(C,H)$ = 146 Hz; C6‴), 55.4 (q, $^1J(C,H)$ = 145 Hz, MeO), 46.1, 42.1 (2t, $^1J(C,H)$ = 127 Hz; C1′, C1‴), 41.6 (t, $^1J(C,H)$ = 131 Hz; C2), 38.5 (t, $^1J(C,H)$ = 128 Hz; C5″), 37.2 (t, $^1J(C,H)$ = 131 Hz; C4), 32.7 (t, $^1J(C,H)$ = 128 Hz; C7), 31.6 (t, $^1J(C,H)$ = 126 Hz; C5‴), 30.0 (q, $^1J(C,H)$ = 126 Hz, Me-C(2‴)), 24.6 (q, $^1J(C,H)$ = 127 Hz, Me_2C(2″)), 19.2 (q, $^1J(C,H)$ = 129 Hz, Me-C(2‴)); IR (film): $\tilde{\nu}$ = 3585, 2940, 1710, 1605, 1510, 1455, 1380, 1315, 1255, 1170, 1100, 1030, 990, 910, 850, 815, 770, 735, 695 cm^{-1}; UV (MeCN): λ_{max} (ε) = 254 (25700), 201 nm (31300 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m/z* (%): 670 (73) $[M+NH_4]^+$, 653 (100) $[M^+]$, 595 (48), 537 (10), 443 (5), 385 (5), 243 (28), 185 (15), 135 (25); elemental analysis calcd for $C_{37}H_{48}O_{10}$ (652.8) (%): C 68.08, H 7.41; found C 67.07, H 7.42.

(3*R*,5*S*,7*R*,9*S*,11*R*,13*R*)-9,11,15-Trihydroxy-5,7-(isopropylidenedioxy)-3,13-di[(4-methoxybenzoyl)oxy]pentadec-1-yl pivalate ((−)-25): A mixture of (−)-**23** (366 mg, 0.52 mmol) in acetone/H_2O (8:1, 3.6 mL), *N*-methylmorpholine *N*-oxide (NMO, 140 mg, 1.04 mmol) and 0.1M OsO_4 in CCl_4 (0.25 mL) was stirred at 20 °C for 15 h. $Na_2S_2O_5$ (100 mg) was added and the mixture extracted with EtOAc (10 mL, 5×). The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The residue was dissolved in benzene (9 mL). After the mixture had been cooled to 5 °C [$Pb(OAc)_4$] (containing 15% of AcOH) (185 mg, 0.35 mmol) was added portionwise in 2 h under stirring. After stirring at 20 °C for 30 min a saturated aqueous solution of $NaHCO_3$ (5 mL) was added and the mixture extracted with EtOAc (10 mL, 3×). Drying ($MgSO_4$), evaporation of the solvent and flash chromatography on silica gel (MeOH/CH_2Cl_2 3:97) afforded a mixture of hemiacetals (328 mg; 87%) that were dissolved in MeCN (5.5 mL) and AcOH (1.9 mL). $Me_4NBH(OAc)_3$ (2.7 g, 10.7 mmol) was added under stirring at −20 °C. The mixture was left at 2 °C for 7 days. It was poured on ice, then $NaHCO_3$ (5.4 g) and CH_2Cl_2 (8 mL) were added. After stirring at 20 °C for 20 min, the mixture was extracted with EtOAc (15 mL, 3×). Drying ($MgSO_4$), evaporation of the solvent, flash chromatography on silica gel (MeOH/CH_2Cl_2 3:97) afforded (−)-**25** (158 mg, 48%) as a colourless oil. $[\alpha]_D^{25} = -8$, $[\alpha]_{577}^{25} = -9$, $[\alpha]_{546}^{25} = -9$, $[\alpha]_{435}^{25} = -14$, $[\alpha]_{405}^{25} = -16$ (c = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.99, 6.90 (2m, 8H), 5.49 (tdd, $^3J(H,H)$ = 8.6, 4.2, 4.1 Hz, 1H; H13), 5.38 (m, H3), 4.20–4.01 (m, 4H), 3.98–3.87 (m, 2H), 3.86 (s, 6H; 2MeO), 3.74–3.61 (m, 2H; H_2C(15)), 2.06–2.00 (m, H_2C(2)), 1.97–1.88 (m, 2H; H_2C(14)), 1.88–1.74 (m, 4H), 1.70–1.52 (m, 6H), 1.32, 1.18 (2s, 6H; Me_2C), 1.17 (s, 9H; *t*Bu). ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 178.4, 167.3, 165.5, 163.6, 163.3 (5s), 131.8, 131.4 (2d, $^1J(C,H)$ = 163 Hz, HC_{arom}), 122.5, 122.0 (2s; C_{arom}), 113.6 (d, $^1J(C,H)$ = 162 Hz; C_{arom}), 100.8 (s, Me_2C), 69.2 (d, $^1J(C,H)$ = 150 Hz; C9), 69.0 (d, $^1J(C,H)$ = 140 Hz; C13), 68.3 (d, $^1J(C,H)$ = 151 Hz; C3), 67.6 (d, $^1J(C,H)$ = 143 Hz; C7), 64.6 (d, $^1J(C,H)$ = 144 Hz; C11), 62.9 (d, $^1J(C,H)$ = 146 Hz; C5), 60.7 (t, $^1J(C,H)$ = 151 Hz; C1), 58.2 (t, $^1J(C,H)$ = 142 Hz; C15), 55.4 (q, $^1J(C,H)$ = 144 Hz, MeO), 43.5, 42.3 (2t, $^1J(C,H)$ = 125 Hz; C8, C10), 43.0, 40.4 (2t, $^1J(C,H)$ = 130 Hz; C4, C12), 38.7, 38.0 (2t, $^1J(C,H)$ = 125 Hz; C6, C14), 33.8 (t, $^1J(C,H)$ = 127 Hz; C2), 27.0 (q, $^1J(C,H)$ = 128 Hz, *t*Bu), 24.6, 24.2 (2q, $^1J(C,H)$ = 125 Hz, Me_2C); IR (film): $\tilde{\nu}$ = 3420, 2940, 1710, 1610, 1510, 1260, 1170, 1100, 1030, 850, 770, 735, 700 cm^{-1}; UV (MeCN): λ_{max} (ε) = 253 (49500), 208 nm (38200 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m/z* (%): 699 (3), 657 (3), 153 (11), 152 (29), 136 (12), 135 (100), 83 (63); MS (electrospray, H_2O/MeCN/AcOH 50:50:1): *m/z* (%): 755 (40) $[M+Na]^+$, 734 (100) $[M+H]^+$, 676 (82); elemental analysis calcd for $C_{39}H_{56}O_{13}$ (732.9) (%): C 63.92, H, 7.70; found C 63.87, H 7.83.

(3*R*,5*S*,7*R*,9*S*,11*R*,13*R*)-15-Hydroxy-5,7:9,11-bis(isopropylidenedioxy)-3,13-di[(4-methoxybenzoyl)oxy]pentadec-1-yl pivalate ((−)-26): To pivalate (−)-**25** (30 mg, 0.041 mmol) was added dry acetone (240 μL) and propanone dimethylacetal (60 μL). Then pyridine *para*-toluenesulfonate (10 mg) was added at 20 °C and the mixture allowed to react under stirring for 2 h. A aqueous saturated solution of $NaHCO_3$ (2 mL) was poured and the volatile solvents evaporated in vacuo. Crude (−)-**26** was extracted with CH_2Cl_2 (15 mL, 3×), dried ($MgSO_4$) and purified by flash chromatography (MeOH/CH_2Cl_2 3%) to afford pure (−)-**26** (27 mg; 85%). $[\alpha]_D^{25} = -10$, $[\alpha]_{577}^{25} = -11$, $[\alpha]_{546}^{25} = -13$, $[\alpha]_{435}^{25} = -24$, $[\alpha]_{405}^{25} = -31$ (c = 1.2 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.98 (m, 4H), 6.92 (m, 4H), 5.46 (m, 1H; H13), 5.38 (m, 1H; H3), 4.16 (ddd, $^2J(H,H)$ = 17.6, $^3J(H,H)$ = 11.3, 6.5 Hz, 1H; H_a-1), 4.13 (ddd, $^2J(H,H)$ = 17.6, $^3J(H,H)$ = 11.2, 6.9 Hz, 1H; H_b-1), 3.90 (m, 4H), 3.87, 3.86 (2s, 6H; 2MeO), 3.65, 3.59 (2m, 2H; H15), 2.08–1.72 (m, 9H), 1.59 (m, 4H), 1.45 (m, 1H; H5), 1.27 (s, 6H, Me_2C), 1.18 (s, 3Me), 1.17 (s, 9H; *t*Bu), 1.11 (s, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 178.4, 167.0, 165.5, 163.6, 163.3 (5s), 131.6, 131.5 (2d, $^1J(C,H)$ = 163 Hz, HC_{arom}), 122.7, 122.2 (2s; C_{arom}), 113.7, 113.6 (2d, $^1J(C,H)$ = 161 Hz, HC_{arom}), 100.5, 100.4 (2s, 2 Me_2C), 68.5, 68.3 (2d, $^1J(C,H)$ = 150 Hz; C3, C13), 63.0, 62.9 (2d, $^1J(C,H)$ = 146 Hz; C5, C7, C9, C11), 60.7 (t, $^1J(C,H)$ = 152 Hz; C1), 58.3 (t, $^1J(C,H)$ = 141 Hz; C15), 55.4 (q, $^1J(C,H)$ = 145 Hz, MeO), 41.5 (t, $^1J(C,H)$ = 124 Hz; C8), 41.0, 40.6 (2t, $^1J(C,H) \approx 126$ Hz; C4, C12), 38.6, 37.6 (2t, $^1J(C,H)$ = 126 Hz; C6, C10, C14), 33.8 (t, $^1J(C,H)$ = 127 Hz; C2), 27.1 (q, $^1J(C,H)$ = 126 Hz, *t*Bu), 24.5, 24.4, 24.3, 24.2 (4q, $^1J(C,H)$ = 126 Hz, 2 Me_2C); IR (film): $\tilde{\nu}$ = 3475, 2940, 1710, 1605, 1510, 1380, 1260, 1225, 1170, 1100, 1030, 850, 770 cm^{-1}; UV (MeCN): λ_{max} (ε) = 254 (74300), 198 nm (91200 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m/z* (%): 757 (14), 715 (14), 657 (4), 486 (4), 334 (4), 135 (100), 81 (24); MS (electrospray, H_2O/MeCN/AcOH 50:50:1): 795 (30) $[M+Na]^+$, 791 (90) $[M+H_2O]^+$, 773 (10) $[M^+]$; elemental analysis calcd for $C_{42}H_{60}O_{13}$ (772.9) (%): C 65.27, H 7.82; found C 65.16, H 7.75.

(1*R*,6*R*)-6-Hydroxy-4-{(2*S*,4*S*,6*S*)-2,4,8-trihydroxy-6-[(4-methoxybenzoyl)oxy]octyl}cyclohept-3-en-1-yl 4-methoxybenzoate ((+)-27): 1M Et_2BOMe in THF (5.3 mL) was added to a solution of (−)-**18** (1 g, 1.78 mmol) in anhydrous THF (15 mL) stirred in a Schlenk tube under N_2 atmosphere at −78 °C. The mixture was allowed to reach 20 °C in 1 h. After the mixture had been cooled to −10 °C, anhydrous MeOH (5 mL) and $NaBH_4$ (133 mg, 3.52 mmol) were added portionwise. After the mixture had been stirred at −10 °C for 1 h, $B(OH)_3$ (300 mg) and $NaBH_4$ (133 mg, 3.52 mmol) were added and the mixture was then stirred at −10 °C for 2 h, followed by addition of more $NaBH_4$ (133 mg, 3.52 mmol). This mixture was then stirred at −10 °C for a further 2 h, and then EtOAc (40 mL), AcOH (1.5 mL), and H_2O (40 mL) were added. The mixture was neutralised with $NaHCO_3$ and the aqueous layer was extracted with EtOAc (10 mL, twice), then with CH_2Cl_2 (10 mL, twice). The combined organic extracts were dried ($MgSO_4$). Evaporation of the solvent and flash chromatography on silica gel (5:95 MeOH/CH_2Cl_2) afforded pure (+)-**27** (580 mg, 57%) as a colourless gum. $[\alpha]_D^{25} = 15$, $[\alpha]_{577}^{25} = 17$, $[\alpha]_{546}^{25} = 19$, $[\alpha]_{435}^{25} = 33$, $[\alpha]_{405}^{25} = 41$ (c = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.97, 6.91 (2m, 8H), 5.70 (dd, $^3J(H,H)$ = 7.7, 5.9 Hz, 1H; H3), 5.48 (m, H6′), 5.12 (tt, $^3J(H,H)$ = 10.3, 2.8 Hz, 1H; H1), 4.20 (brs, 1H; H6), 4.05 (m, 1H; H2′), 3.91 (m, 1H; H4′), 3.86, 3.85 (2s, 6H; 2MeO), 3.70 (m, 2H; H_2C(8′)), 2.45 (m, 5H), 2.10 (d, $J(H,H)$ = 6.7 Hz, 2H), 1.98–1.93 (m, 3H), 1.81 (t, $^3J(H,H)$ = 6.3 Hz, 1H), 1.57 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 167.1, 165.5, 163.5, 163.2 (4s), 137.4 (s; C4), 131.8, 131.5 (2d, $^1J(C,H)$ = 163 Hz, HC_{arom}), 124.9 (d, $^1J(C,H)$ = 154 Hz; C3), 122.9, 122.2 (2s; C_{arom}), 113.6, 113.4 (2d, $^1J(C,H)$ = 166 Hz, HC_{arom}), 69.2 (d, $^1J(C,H)$ = 147 Hz; C6′), 68.5 (d, $^1J(C,H)$ = 141 Hz; C2′, C4′), 68.2 (d, $^1J(C,H)$ = 152 Hz; C1), 65.9 (d, $^1J(C,H)$ = 143 Hz; C6), 58.5 (t, $^1J(C,H)$ = 143 Hz; C8′), 55.4, 55.3 (2q, $^1J(C,H)$ = 144 Hz, 2MeO), 48.4 (t, $^1J(C,H)$ = 128 Hz; C1′), 44.9 (t, $^1J(C,H)$ = 133 Hz; C7), 43.1, 42.5, 38.0, 36.5, 34.1 (5t, $^1J(C,H)$ = 126–127 Hz; C5′, C3′, C7′, C5, C2); IR (film): $\tilde{\nu}$ = 3390, 2940, 1705, 1605, 1510, 1420, 1260, 1170, 1120, 1030, 975, 850, 770, 735, 700 cm^{-1}; UV (MeCN): λ_{max} (ε) = 253 (107100), 201 nm (119500 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m/z* (%): 590 (9) $[M+NH_4]^+$, 574 (42) $[M+H]^+$, 573 (54) $[M^+]$, 555 (11), 421 (11), 297 (18), 279 (13), 215 (12), 170 (65), 135 (100), 124 (11), 92 (18); elemental analysis calcd for $C_{31}H_{40}O_{10}$ (572.7) (%): C 65.02, H 7.04; found C 64.62, H 6.93.

(1*R*,6*R*)-6-Hydroxy-4-{(2*S*,4*S*,6*S*)-8-hydroxy-2,4-isopropylidenedioxy-6-[(4-methoxybenzoyl)oxy]octyl}cyclohept-3-en-1-yl 4-methoxybenzoate ((−)-28): This acetonide was prepared according to the procedure presented for the preparation of (−)-**26** starting from (+)-**27** (400 mg). Yield of (−)-**28**: 78%; colourless solid. m.p. 50–54 °C; $[\alpha]_D^{25} = -8$, $[\alpha]_{577}^{25} = -9$, $[\alpha]_{546}^{25} = -10$, $[\alpha]_{435}^{25} = -20$, $[\alpha]_{405}^{25} = -25$ (c = 0.9 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.97, 6.92 (2m, 8H), 5.64 (dd, $^3J(H,H)$ = 6.6, 6.5 Hz, 1H; H3), 5.48 (m, 1H; H6′), 5.16 (dddd, $^3J(H,H)$ = 8.8, 8.7, 3.4, 3.3 Hz, 1H; H1), 4.06 (m, 1H; H6), 3.99 (m, 2H; H2′, H4′), 3.86, 3.84 (2s, 6H; 2MeO), 3.69–3.57 (m, 2H; H8′), 2.45 (m, 2H; H2, H5), 2.29 (ddd, $^2J(H,H)$ = 13.3, $^3J(H,H)$ = 6.2, 3.3 Hz, 1H; H_a-7), 2.21 (dd, $^2J(H,H)$ = 13.9, $^3J(H,H)$ = 7.3 Hz, 1H; H_a-1′), 2.15 (dd, $^2J(H,H)$ = 13.9, $^3J(H,H)$ = 4.8 Hz, H_b-1′), 2.05 (ddd, $^2J(H,H)$ = 13.3, $^3J(H,H)$ = 9.4, 2.8 Hz, H_b-7), 1.95 (dddd, $^2J(H,H)$ = 14.4, $^3J(H,H)$ = 9.3, 5.6, 3.6 Hz, 1H; H_a-7′), 1.88–1.74 (m, 3H;

0947-6539/00/0622-4100 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 22

H_b-5′, H7′), 1.45 (ddd, ^2J(H,H) = 12.9, ^3J(H,H) = 2.5, 2.4 Hz, 1H; H3′), 1.36, 1.27 (2s, Me_2C), 1.30 (m, H3′); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 166.9, 165.4, 163.6, 163.2 (4s), 136.4 (s; C4), 131.7, 131.5 (2d, ^1J(C,H) = 164 Hz, HC_{arom}), 125.3 (d, ^1J(C,H) = 161 Hz; C3), 123.1, 122.2 (2s; C_{arom}), 113.7, 113.5 (2d, ^1J(C,H) = 161 Hz, HC_{arom}), 99.1 (s, Me_2C), 68.4 (d, ^1J(C,H) = 152 Hz; C1), 68.3, 67.1 (2d, ^1J(C,H) = 132 Hz; C4′, C6′), 65.8 (d, ^1J(C,H) = 135 Hz; C6), 65.5 (d, ^1J(C,H) = 141 Hz; C4′), 58.3 (t, ^1J(C,H) = 140 Hz; C8′), 55.4 (q, ^1J(C,H) = 145 Hz, MeO), 46.8 (t, ^1J(C,H) = 125 Hz; C1′), 44.8 (t, ^1J(C,H) = 126, C7), 41.6, 38.8, 38.2, 36.8 (4t, ^1J(C,H) = 126–128 Hz; C5′, C5, C7′, C3′), 33.6 (t, ^1J(C,H) = 126 Hz; C2), 29.9, 19.3 (2q, ^1J(C,H) = 125 Hz, Me_2C); IR (film): $\tilde{\nu}$ = 3450, 2940, 1705, 1605, 1510, 1420, 1380, 1315, 1260, 1170, 1105, 1030, 975, 850, 770, 735, 700 cm^{-1}; UV (MeCN): λ_{max} (ε) = 254 (14700), 197 (22800 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 630 (57) $[M+NH_4]^+$, 613 (51) $[M^{+}]$, 555 (48), 443 (12), 385 (26), 338 (8), 279 (100), 135 (84), 83 (30); elemental analysis calcd for $C_{34}H_{44}O_{10}$ (612.7) (%): C 66.65, H 7.24; found C 66.38, H 7.37.

(1*R*,6*R*)-6-Hydroxy-4-{(2*S*,4*S*,6*S*)-8-[(2,2-dimethylpropanoyl)oxy]-2,4-isopropylidenedioxy-6-[(4-methoxybenzoyl)oxy]octyl}cyclohept-3-en-1-yl 4-methoxybenzoate ((−)-29): A mixture of (−)-**28** (0.5 g, 0.816 mmol), anhydrous CH_2Cl_2 (7 mL), pyridine (3 mL) and pivaloyl chloride (0.2 mL, 196 mg, 1.62 mmol) was stirred at 0 °C for 3 h. After the addition of a saturated aqueous solution of $NaHCO_3$ (0.5 mL), the mixture was extracted with CH_2Cl_2 (10 mL, 3 ×). Evaporation of the solvent and flash chromatography on silica gel (MeOH/CH_2Cl_2 2:98) gave (−)-**29** (645 mg, 70%) as a slightly yellow gum. $[\alpha]_D^{25} = -22$, $[\alpha]_{577}^{25} = -23$, $[\alpha]_{546}^{25} = -29$, $[\alpha]_{435}^{25} = -55$, $[\alpha]_{405}^{25} = -70$ (*c* = 0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.97, 6.91 (2m, 8H), 5.66 (t, ^3J(H,H) = 6.3 Hz, 1H; H3), 5.44 (m, 1H; H6′), 5.15 (tt, ^3J(H,H) = 9.4, 3.0 Hz, 1H; H1), 4.15 (m, 2H; H8′), 4.04–3.92 (m, 3H; H6, H4′, H2′), 3.87, 3.85 (2s, 6H; 2MeO), 2.50–2.43 (m, 4H; H2, H5), 2.33 (ddd, ^2J(H,H) = 13.2, ^3J(H,H) = 5.3, 3.0 Hz, 1H; H_a-7), 2.23 (dd, ^2J(H,H) = 13.7, ^3J(H,H) = 7.5 Hz, 1H; H_a-1′), 2.16 (dd, ^2J(H,H) = 13.7, ^3J(H,H) = 4.6 Hz, 1H; H_b-1′), 2.08–2.01 (m, 3H; H_b-7, H7′), 1.81 (m, 2H; H5′), 1.44 (ddd, ^2J(H,H) = 12.9, ^3J(H,H) = 2.4, 2.3 Hz, 1H; H_a-3′), 1.38, 1.35 (2s, 6H; Me_2C), 1.29 (m, 1H; H_b-3′), 1.18 (s, 9H; *t*Bu); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 178.5, 165.5, 165.4, 163.3, 163.2 (5s), 136.4 (s; C4), 131.5, 131.45 (2d, ^1J(C,H) = 164 Hz, HC_{arom}), 125.4 (d, ^1J(C,H) = 157 Hz; C3), 123.1, 122.7 (2s; C_{arom}), 113.6, 113.5 (2d, ^1J(C,H) = 161 Hz, HC_{arom}), 99.1 (s, Me_2C), 68.4 (d, ^1J(C,H) = 148 Hz; C1, C6′), 67.0, 65.8 (2d, ^1J(C,H) = 128 Hz; C2′, C6), 65.4 (d, ^1J(C,H) = 140 Hz; C4′), 60.8 (t, ^1J(C,H) = 148 Hz; C8′), 55.4 (q, ^1J(C,H) = 145 Hz, MeO), 46.9, 44.9 (2t, ^1J(C,H) = 125 Hz; C1′, C2), 41.4, 38.7, 36.8, 34.0, 33.7 (5t, ^1J(C,H) = 128–130 Hz; C5′, C5, C3′, C7′, C7), 29.9, 19.3 (2q, ^1J(C,H) = 126 Hz, Me_2C(acetonide)), 27.1 (q, ^1J(C,H) = 131 Hz, Me_3C); IR (film): $\tilde{\nu}$ = 3460, 2940, 1710, 1605, 1510, 1460, 1380, 1315, 1255, 1165, 1100, 1030, 980, 850, 770, 735, 695 cm^{-1}; UV (MeCN): λ_{max} (ε) = 253 (30000), 199 nm (38500 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 714 (90) $[M+NH_4]^+$, 697 (11) $[M^{+}]$, 639 (38), 469 (5), 363 (47), 211 (36), 135 (100), 109 (51), 81 (48); elemental analysis calcd for $C_{38}H_{52}O_{11}$ (696.5) (%): C 67.22, H 7.52; found C 67.37, H 7.39.

(3*S*,5*S*,7*S*,9*R*,11*R*,13*R*)-9,11,15-Trihydroxy-5,7-(isopropylidenedioxy)-3,13-bis[(4-methoxybenzoyl)oxy]pentadec-1-yl pivalate ((+)-30): Same procedure as that used for the preparation of (−)-**25**, starting with (−)-**29** (166 mg, 67%); colourless gum. $[\alpha]_D^{25} = 12$, $[\alpha]_{577}^{25} = 11$, $[\alpha]_{546}^{25} = 10$, $[\alpha]_{435}^{25} = 8$, $[\alpha]_{405}^{25} = 13$ (*c* = 0.2 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.98, 6.92 (2m, 8H), 5.48 (m, 1H; H13), 5.43 (m, 1H; H3), 4.13 (m, 4H; H1, H5, H7), 3.94 (m, 2H; H9, H11), 3.86 (s, 6H; MeO), 3.69 (m, 2H; H15), 2.03 (m, 2H; H2), 1.93 (m, 2H; H14), 1.80 (m, 4H; H4, H12), 1.64 (ddd, ^2J(H,H) = 14.4, ^3J(H,H) = 8.9, 3.5 Hz, 1H; H_a-6), 1.56 (m, 2H; H10), 1.53 (ddd, ^2J(H,H) = 14.4, ^3J(H,H) = 7.1, 2.8 Hz, H_b-6), 1.36 (m, 2H; H8), 1.32, 1.29 (2s, 6H; Me_2C), 1.17 (s, 9H; Me_3C); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 178.5, 167.5, 165.5, 163.7, 163.4 (5s), 131.9, 131.5 (2d, ^1J(C,H) = 163 Hz, HC_{arom}), 122.7, 122.0 (2s; C_{arom}), 113.7, 113.6 (2d, ^1J(C,H) = 161 Hz, HC_{arom}), 98.8 (s, Me_2C), 69.2 (d, ^1J(C,H) = 145 Hz; C13), 68.2 (d, ^1J(C,H) = 150 Hz; C3), 67.1, 65.7 (2d, ^1J(C,H) = 144 Hz; C7, C5), 65.5, 64.9 (2d, ^1J(C,H) = 141 Hz; C9, C11), 60.8 (t, ^1J(C,H) = 150 Hz; C1), 58.7 (t, ^1J(C,H) = 140 Hz; C15), 55.5, 55.4 (2q, ^1J(C,H) = 145 Hz, 2MeO), 43.1, 41.3 (2t, ^1J(C,H) = 125–126 Hz; C4, C10, C12), 42.2 (t, ^1J(C,H) = 125 Hz; C6), 38.7 (s, Me_3C), 38.0, 36.6 (2t, ^1J(C,H) = 126 Hz; C14, C8), 33.9 (t, ^1J(C,H) = 127 Hz; C2), 30.0, 19.4 (2q, ^1J(C,H) = 126 Hz, Me_2C(acetonide)), 27.1 (q, ^1J(C,H) = 128 Hz, Me_3C); IR (film): $\tilde{\nu}$ = 3435, 2940, 1710, 1605, 1510, 1420, 1380, 1260, 1170, 1100, 1030, 850, 770, 735, 700 cm^{-1}; UV (MeCN): λ_{max} (ε) = 253 (46000), 206 nm (36800 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 699 (2), 657 (1), 135 (16), 85 (62), 83 (100), 77 (13); MS (electrospray H_2O/MeCN/AcOH 50:50:1): *m*/*z* (%): 756 (40) $[M+Na]^+$, 734 (100) $[M+H]^+$, 676 (85); elemental analysis calcd for $C_{39}H_{56}O_{13}$ (732.9) (%): C 63.92, H 7.70; found C 63.96, H 7.74.

(3*S*,5*S*,7*S*,9*R*,11*R*,13*R*)-15-Hydroxy-5,7:9,11-bis(isopropylidenedioxy)-3,13-bis[(4-methoxybenzoyl)oxy]pentadec-1-yl pivalate ((−)-31): Same procedure as that applied for the preparation of (−)-**26**, starting with (+)-**30** (35 mg, 0.048 mmol) to yield (−)-**31** (31 mg, 83%) as a colourless gum. $[\alpha]_D^{25} = -8$, $[\alpha]_{577}^{25} = -9$, $[\alpha]_{546}^{25} = -12$, $[\alpha]_{435}^{25} = -25$, $[\alpha]_{405}^{25} = -34$ (*c* = 0.6 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.97, 6.91 (2m, 8H), 5.44 (m, 2H; H3, H13), 4.14 (ddd, ^2J(H,H) = 17.5, ^3J(H,H) = 11.4, 6.3 Hz, 1H; H_a-1), 4.12 (ddd, ^2J(H,H) = 17.5, ^3J(H,H) = 11.1, 6.7 Hz, 1H; H_b-1), 4.07–3.87 (m, 4H; H5, H7, H9, H11), 3.86, 3.85 (2s, 2MeO), 3.65, 3.58 (2m, 2H; H15), 2.07–1.71 (m, 8H; H2, H4, H12, H14), 1.63–1.35 (m, 6H; H6, H8, H10), 1.32, 1.26 (2s, 6H; Me_2C), 1.24, 1.10 (2s, 6H; Me_2C), 1.17 (s, 9H; Me_3C); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 178.5, 167.1, 165.5, 163.6, 163.3 (5s), 131.7, 131.5 (2d, ^1J(C,H) = 163 Hz, HC_{arom}), 122.7, 122.2 (2s; C_{arom}), 113.7, 113.6 (2d, ^1J(C,H) = 165 Hz, HC_{arom}), 100.6, 98.6 (2s, 2Me_2C), 68.4, 68.3 (2d, ^1J(C,H) = 151 Hz; C13, C3), 65.6, 64.9 (2d, ^1J(C,H) = 138 Hz; C11, C9), 63.1, 62.2 (2d, ^1J(C,H) = 144–147 Hz; C7, C5), 60.8 (t, ^1J(C,H) = 151 Hz; C1), 58.3 (t, ^1J(C,H) = 141 Hz; C15), 55.4 (q, ^1J(C,H) = 145 Hz, MeO), 42.1, 41.3, 41.1 (3t, ^1J(C,H) = 126–128 Hz; C8, C12, C4), 38.9, 37.6 (2t, ^1J(C,H) = 130 Hz; C10, C6), 38.2 (t, ^1J(C,H) = 126 Hz; C14), 33.9 (t, ^1J(C,H) = 129 Hz; C2), 27.1 (q, ^1J(C,H) = 128 Hz, Me_3C), 30.1, 24.2, 24.1, 19.5 (4q, ^1J(C,H) = 128 Hz, 2Me_2C); IR (film): $\tilde{\nu}$ = 3505, 2940, 1710, 1605, 1510, 1460, 1380, 1260, 1170, 1100, 1030, 940, 850, 770, 735, 700 cm^{-1}; UV (MeCN): λ_{max} (ε) = 253 (34500), 207 (33000), 199 nm (40200 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 790 (11) $[M+NH_4]^+$, 773 (4) $[M^{+}]$, 757 (13), 715 (100), 657 (26), 544 (6), 135 (51), 81 (6); MS (electrospray, H_2O/MeCN/AcOH 50:50:1) *m*/*z* (%): 795 (92) $[M+Na]^+$, 791 (100) $[M+H_2O]^+$, 773 (35) $[M^{+}]$, 757 (30); elemental analysis calcd for $C_{42}H_{60}O_{13}$ (772.9) (%): C 65.27, H 7.82; found C 65.27, H 7.97.

(1*R*,6*R*)-6-Acetoxy-4-{(2*R*,4*S*,6*S*)-8-acetoxy-2,4-dihydroxy-6-[(4-methoxybenzoyl)oxy]octyl}cyclohept-3-en-1-yl 4-methoxybenzoate ((−)-32): A mixture of (−)-**22** (0.5 g, 0.816 mmol), CH_2Cl_2 (10 mL), Ac_2O (1 mL), pyridine (1 mL) and 4-dimethylaminopyridine (10 mg) was stirred at 20 °C for 1 h. The solvent was evaporated to dryness in vacuo. EtOH (0.5 mL), AcOH (3 mL) and H_2O (2 mL) were added and the mixture was stirred at 40 °C for 1 h. Evaporation of the solvent and flash chromatography on silica gel (3%, then 5% MeOH in CH_2Cl_2) afforded (−)-**32** (525 mg; 98%) as a colourless gum. $[\alpha]_D^{25} = -69$, $[\alpha]_{577}^{25} = -72$, $[\alpha]_{546}^{25} = -84$, $[\alpha]_{435}^{25} = -159$, $[\alpha]_{405}^{25} = -202$ (*c* = 0.8 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.97, 6.90 (2m, 8H), 5.57 (t, ^3J(H,H) = 6.5 Hz, 1H; H3), 5.44 (tdd, ^3J(H,H) = 7.8, 4.9, 4.7 Hz, 1H; H6′), 5.24 (m, 1H; H1), 5.04 (dddd, ^3J(H,H) = 8.8, 8.7, 3.6, 1.9 Hz, 1H; H6), 4.23–4.09 (m, 3H), 3.92 (dddd, ^3J(H,H) = 8.4, 8.0, 5.1, 2.8 Hz, 1H; H4′), 3.86, 3.83 (2s, 6H; 2MeO), 2.62–2.54 (m, 2H), 2.46–2.40 (m, 2H), 2.31–2.17 (m, 2H), 2.18 (br d, ^3J(H,H) = 6.3 Hz, 2H), 2.07 (m, 2H), 2.03, 1.99 (2s, 2AcO), 1.78 (m, 2H), 1.64, 1.57 (2ddd, ^2J(H,H) = 14.3, ^3J(H,H) = 8.4, 3.2 Hz, 2H; H3′); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 170.9, 170.3, 167.1, 165.5, 163.7, 163.4 (6s), 137.2 (s; C4), 131.8, 131.6 (2d, ^1J(C,H) = 163 Hz, HC_{arom}), 124.7 (d, ^1J(C,H) = 157 Hz; C3), 122.7, 122.1 (2s; C_{arom}), 113.7, 113.6 (2d, ^1J(C,H) = 161 Hz, HC_{arom}), 69.1 (d, ^1J(C,H) = 147 Hz; C6′), 68.8 (d, ^1J(C,H) = 151 Hz; C1), 68.4 (d, ^1J(C,H) = 145 Hz; C6), 66.1 (d, ^1J(C,H) = 142 Hz; C2′), 64.6 (d, ^1J(C,H) = 144 Hz; C4′), 60.9 (t, ^1J(C,H) = 147 Hz; C8′), 55.4 (q, ^1J(C,H) = 145 Hz, MeO), 48.2 (t, ^1J(C,H) = 126 Hz; C7), 43.2, 42.8 (2t, ^1J(C,H) = 126 Hz; C5′, C3′), 41.4 (t, ^1J(C,H) = 130 Hz; C7′), 37.2, 34.1, 32.1 (3t, ^1J(C,H) = 126–129 Hz; C1′, C5, C2), 21.2, 20.8 (2q, ^1J(C,H) = 130 Hz, 2CH_3CO); IR (film): $\tilde{\nu}$ = 3490, 2940, 1710, 1605, 1510, 1420, 1370, 1260, 1170, 1105, 1030, 850, 770, 735, 700 cm^{-1}; UV (MeCN): λ_{max} (ε) = 254 (35200), 199 nm (46100 mol^{-1} dm^3 cm^{-1}); MS (CI/NH_3): *m*/*z* (%): 674 (32) $[M+NH_4]^+$, 657 (92) $[M^{+}]$, 597 (10), 445 (5), 339 (40), 257 (13), 135 (100), 106 (41), 83 (35); elemental analysis calcd for $C_{35}H_{44}O_{12}$ (656.7) (%): C 64.01, H 6.75; found C 63.93, H 6.87.

(1*R*,6*R*)-6-Acetoxy-4-{(2*S*,4*R*,6*S*)-8-acetoxy-6-[(4-methoxybenzoyl)oxy]-2,4-bis[(4-nitrobenzoyl)oxy]octyl}cyclohept-3-en-1-yl 4-methoxybenzoate ((+)-33): EtOOC=NCOOEt (0.1 mL, 0.65 mmol) was added slowly to a stirred solution of (−)-**32** (428 mg, 0.65 mmol), Ph_3P (170 mg, 0.65 mmol) and *p*-$NO_2C_6H_4COOH$ (109 mg, 0.65 mmol) in anhydrous benzene cooled to 0 °C. After the mixture had been stirred at 0 °C for 4 h, Ph_3P (85 mg), *p*-

$NO_2C_6H_4COOH$ (55 mg) and EtOOCN=NCOOEt (50 μL) were added and the mixture was stirred at 0 °C for 2 h. The latter operation was repeated twice. Saturated aqueous solution of $NaHCO_3$ (5 mL) was added and the mixture stirred for 1 h. The aqueous layer was extracted with CH_2Cl_2 (10 mL, 3×) and the combined organic extracts were dried ($MgSO_4$). Evaporation of the solvent and flash chromatography on silica gel (3% MeOH in CH_2Cl_2) afforded pure (+)-**33** (403 mg, 65%) as a colourless gum. $[\alpha]_d^{25}=3$, $[\alpha]_{546}^{25}=4$, $[\alpha]_{435}^{25}=27$, $[\alpha]_{405}^{25}=32$ ($c=0.9$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=8.19-7.85$, 6.90–6.78 (2m, 16H), 5.56 (t, ^3J(H,H) = 6.3 Hz, 1H; H3), 5.37 (m, 3H), 5.20 (m, 1H; H1), 5.00 (m, 1H; H6), 4.11 (m, 2H), 3.83, 3.82 (2s, 6H; 2MeO), 2.62–1.82 (m, 20H), 1.82 (ddd, ^2J(H,H) = 14.2, ^3J(H,H) = 7.5, 3.6 Hz, 1H), 1.96, 1.95 (2s, 6H; 2AcO); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta=170.8$, 170.2, 165.7, 165.4, 164.0, 163.6, 163.4, 150.4, 150.2 (9s), 135.1 (s; C4, 131.5 (d, ^1J(C,H) = 163 Hz, HC_{arom}), 130.6, 130.3 (2d, ^1J(C,H) = 169 Hz, HC_{arom}), 125.8 (d, ^1J(C,H) = 157 Hz; C3), 123.3, 123.2 (2d, ^1J(C,H) = 175 Hz, HC_{arom}), 122.6, 121.8 (2s; C_{arom}), 113.6 (d, ^1J(C,H) = 160 Hz; C_{arom}), 69.5 (d, ^1J(C,H) = 145 Hz; C6′), 68.9 (d, ^1J(C,H) = 151 Hz; C1), 67.8 (d, ^1J(C,H) = 145 Hz; C6), 69.3, 68.2 (2d, ^1J(C,H) = 148 Hz; C2′, C4′), 60.5 (t, ^1J(C,H) = 146 Hz; C8′), 55.4 (q, ^1J(C,H) = 144 Hz, MeO), 45.3 (t, ^1J(C,H) = 126 Hz; C7), 41.2, 39.2, 37.8, 37.6, 33.8, 31.7 (6d, ^1J(C,H) = 126–128 Hz; C5, C5′, C3′, C1′, C7′, C2), 21.2, 20.8 (2q, ^1J(C,H) = 130 Hz, 2CH_3CO); IR (film): $\tilde{\nu}=2960$, 1725, 1605, 1530, 1455, 1350, 1260, 1170, 1100, 1030, 850, 770, 720 cm^{-1}; UV (MeCN): λ_{max} (ε) = 256 (36200), 200 nm (39700 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 971 (100), $[M+NH_4]^+$, 805 (12), 575 (2), 316 (8), 196 (5), 135 (24); elemental analysis calcd for $C_{49}H_{50}N_2O_{18}$ (954.3) (%): C 61.63, H 5.28, N 2.93; found C 61.55, H 5.18, N 2.85.

(1*R*,3*R*)-[(2*S*,4*R*,6*S*)-2,4:6,8-Bis(isopropylidenedioxy)octyl]cyclohept-5-ene-1,3-diol ((+)-34): MeOK (140 mg, 2 mmol) was added to a stirred solution of (+)-**33** in anhydrous MeOH (3.0 mL) and anhydrous toluene (0.1 mL) at 20 °C. The reaction was continued overnight (TLC, MeOH/CH_2Cl_2 15%, R_f (hexol) = 0.08) and neutralised with an anhydrous solution of HCl in Et_2O. MeOH (5 mL), then SiO_2 flash (2 g) were added and the solution was evaporated in vacuo. The residue was filtered off over a small pad of SiO_2 flash (MeOH/CH_2Cl_2 17%). After evaporation, the residue was diluted in dry acetone (4.0 mL) and allowed to react at 20 °C for 5 h by the adjunction of acetone dimethylacetal (0.5 mL) and pyridinium *para*-toluenesulfonate (7 mg) (TLC, MeOH/CH_2Cl_2 5%, R_f ((+)-**34**) = 0.16). $NaHCO_3$ (0.1 g) was added and the solvents evaporated in vacuo. Flash chromatography (MeOH/CH_2Cl_2 5%) afforded pure (+)-**34** as a colourless oil (28 mg, 38%). $[\alpha]_D^{25}=-1$, $[\alpha]_{546}^{25}=-2$, $[\alpha]_{435}^{25}=-8$, $[\alpha]_{405}^{25}=-11$ ($c=0.3$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=5.60$ (t, ^3J(H,H) = 7.0 Hz, H6), 4.06–3.90 (m, 6H), 3.82 (ddd, ^2J(H,H) = 11.7, ^3J(H,H) = 5.4, 1.6 Hz, 1H; H_a-8′), 2.46 (dd, ^2J(H,H) = 14.7, ^3J(H,H) = 7.0 Hz, H_a-4), 2.41 (dd, ^2J(H,H) = 14.7, ^3J(H,H) = 2.4 Hz, H_b-4), 2.34 (m, 2H; H7), 2.23 (m, 2H; H1′), 2.15 (ddd, ^2J(H,H) = 13.2, ^3J(H,H) = 6.9, 3.0 Hz, 1H; H_a-2), 1.89 (ddd, ^2J(H,H) = 13.2, ^3J(H,H) = 8.8, 3.0 Hz, 1H; H_b-2), 1.82 (ddd, ^2J(H,H) = 14.0, ^3J(H,H) = 8.1, 6.5 Hz, 1H; H_a-5′), 1.69 (ddd, ^2J(H,H) = 12.8, ^3J(H,H) = 9.0, 5.8 Hz, 1H; H_a-3′), 1.57 (m, 2H; H_a-7′, H_b-3′), 1.49 (ddd, ^2J(H,H) = 14.0, ^3J(H,H) = 6.5, 5.4 Hz, 1H; H_b-5′), 1.44, 1.37 (2s, 6H; Me_2C), 1.42 (m, 1H; H_b-7′), 1.34, 1.33 (2s, Me_2C); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta=137.2$ (s; C5), 124.8 (d, ^1J(C,H) = 157 Hz; C6), 100.4, 98.2 (2s, 2Me_2C), 65.6, 65.5, 65.4, 65.3 (4d, ^1J(C,H) = 144–147 Hz; C1, C3, C2′, C6′), 62.9 (d, ^1J(C,H) = 146 Hz; C4), 59.9 (t, ^1J(C,H) = 146 Hz; C8′), 48.2 (t, ^1J(C,H) = 128 Hz; C2), 45.9 (t, ^1J(C,H) = 125 Hz; C1′), 42.2 (t, ^1J(C,H) = 125 Hz; C5′), 39.4, 37.2 (2t, ^1J(C,H) = 128 Hz; C4, C3′), 36.4, 30.8 (2t, ^1J(C,H) = 130 Hz; C7, C7′), 29.9, 25.1, 25.0, 19.2 (4q, ^1J(C,H) = 126 Hz, 2Me_2C); IR (film): $\tilde{\nu}=3385$, 2990, 2935, 1445, 1380, 1225, 1200, 1165, 1100, 1040, 970, 870, 815 cm^{-1}; UV (MeCN): λ_{max} (ε) = 197 nm (75000 $mol^{-1}dm^3cm^{-1}$); MS (CI/NH_3): *m*/*z* (%): 402 (64) $[M+NH_4]^+$, 385 (80) $[M^+]$, 327 (100), 269 (37), 243 (14), 185 (15), 115 (13), 83 (10).

Acknowledgements

This work was supported by the Swiss National Science Foundation and the Fonds Herbette (Lausanne). We are grateful also to Messrs Martial Rey, Kai Meilert and Francisco Sepúlveda for technical assistance.

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Received: April 7, 2000 [F2410]