173. Preparation of Chiral Building Blocks for Starburst Dendrimer Synthesis

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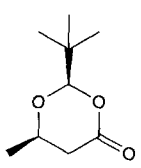
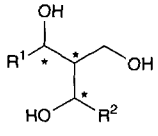
Double aldols, formally derived from acetic acid and two different aldehydes, as obtained by addition of the enolate of (*R*,*R*)-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one (**A**) to various aldehydes, are reduced to triols which are actually substituted chiral 'tris(hydroxymethyl)methanes' (see **B** and **3**–**8**). Etherifications of the three OH groups of these triols with functionalized halides (allyl, 4-(silyloxy)but-2-en-1-yl, 4-substituted benzyl) and esterifications with pent-4-enoic and 3,5-dinitrobenzyl chlorides, followed by functional group manipulations, lead to the potential center pieces **14**–**30** for the construction of chiral dendrimers: the building blocks prepared contain the required 'spacers' between the core unit, as well as three vinyl groups, three aryl bromide groups, three alcoholic or phenolic OH groups, three mesylate groups, three ester groups, or six arylamino groups at the terminus of their branches. The new compounds are all obtained on a preparative scale and are fully characterized (including elemental analysis).

Introduction. – One strategy for the synthesis of chiral dendrimers[3]) is the use of enantiomerically pure building blocks as central pieces [2] [3]. We have been working on the preparation of such central pieces in developing an easy access to chiral 'tris(hydroxymethyl)methanes' [4] (see **B**) from (2*R*,6*R*)-2-(*tert*-butyl)-6-methyl-1,3-dioxan-4-one (**A**) by aldol addition and reduction (from *ent*-**A**, the enantiomers of all products described below are likewise available).

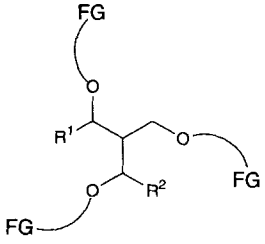
This simple procedure prompted us to investigate further the synthesis of potential core molecules for chiral dendrimers (see **C**), and here we report the results of this work. Besides being central cores for dendritic molecules, these building blocks might also serve as tripodal ligands in metal complexes [5] [6] and as partners in inclusion complexes [7].



A



B



C

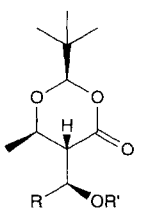
[1]) Postdoctoral research at ETH-Zürich 1991–1993, financed by a fellowship from the *Natural Sciences and Engineering Research Council of Canada*.

[2]) Postdoctoral research at ETH-Zürich 1992/93, financed by the *Deutsche Forschungsgemeinschaft (DFG)*, Bonn.

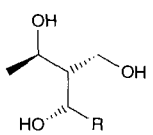
[3]) For recent reviews and highlights on dendrimers, see [1].

Results. – In addition to the triols **3**, **4**, **7**, and **8** described earlier [4], we have now prepared the two new chiral triols **5** and **6**, one possessing an especially bulky group (Ph_2CH) at C(1) and the other a styrene moiety.

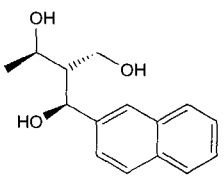
The Li-enolate of dioxanone **A** was allowed to react with diphenylacetaldehyde furnishing aldol adduct **1a** in 79% yield with a diastereoselectivity greater than 99:1. With phenylpropynal, the aldol addition gave **2a** as a mixture of diastereoisomers at C(1′) in a ratio of 1.2:1 with 57% yield. The major isomer was obtained in pure form by flash chromatography, while the minor one was not isolated in pure form. Without proof, we assign (5*R*,1′*S*)-configuration to **1a** and (5*R*,1′*R*)-configuration (see *Formula*) to the major isomer **2a** formed with the acetylenic aldehyde – in analogy with the configuration determined previously for the major products isolated from reactions of the enolate from **A** and aldehydes [4]. Acetylation of the aldol adducts **1a** and **2a** afforded the corresponding protected aldols **1b** and **2b** in good yields (> 85%). The reduction of **1b** with $LiAlH_4$ furnished triol **5** (73%), while in the case of **2b**, $LiAlH_4$ not only reduced the dioxanone part and removed the Ac group reductively, but also converted the acetylene to a *trans*-olefin moiety (→**6**) [8], with an excellent yield of 93%.



1a R = Ph_2CH, R′ = H
b R = Ph_2CH, R′ = $COCH_3$
2a R = PhC≡C, R′ = H
b R = PhC≡C, R′ = $COCH_3$



3 R = i-Pr
4 R = *t*-Bu
5 R = Ph_2CH
6 R = (*E*)-PhCH=CH
7 R = naphth-2-yl



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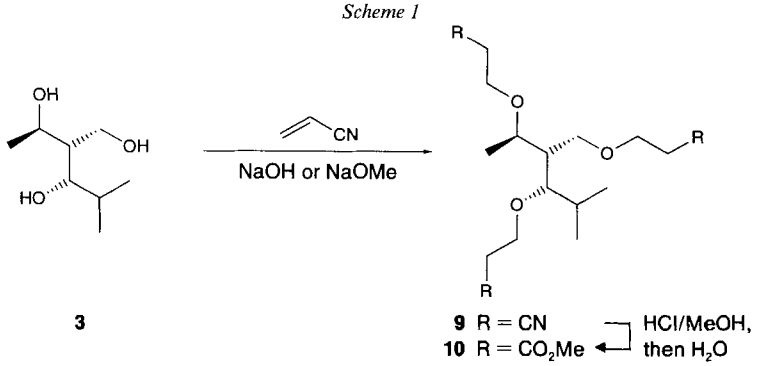
Our plan was to elongate the three branches of the center pieces by attaching so-called spacers, in order to avoid excessive steric hindrance between the three dendrimer subunits to be attached. The first idea was to *O*-alkylate the triols to obtain tri-ethers. Methylation with iodomethane did indeed work very well in a model study, but other alkyl halides, bearing functional groups, failed completely. The use of α-bromo- or α-chloroacetic acid [9] also did not give the corresponding trioxa-tricarboxylates.

One solution to the problem was found when we subjected triol **3** to acrylonitrile in the presence of a catalytic amount of base such as NaOH or NaOMe [10] (*Scheme 1*); unfortunately, the *Michael* addition gave erratic yields of the trinitril **9**, the best being 40%. On the other hand, compound **9**, when treated with methanolic HCl and then with H_2O gave the trioxa-tricarboxylate **10** in nearly quantitative yield. The major difficulty with trinitril **9** was its purification, *i.e.* its separation from mono- and di-ether impurities; we were not able to fine-tune the conditions such that the *Michael* addition would go to completion. Still, trinitril **9** and triester **10** are possible building blocks for chiral dendrimer synthesis, since **9** could be reduced to a trioxa-triamine and **10** to a trioxa-triol[4]).

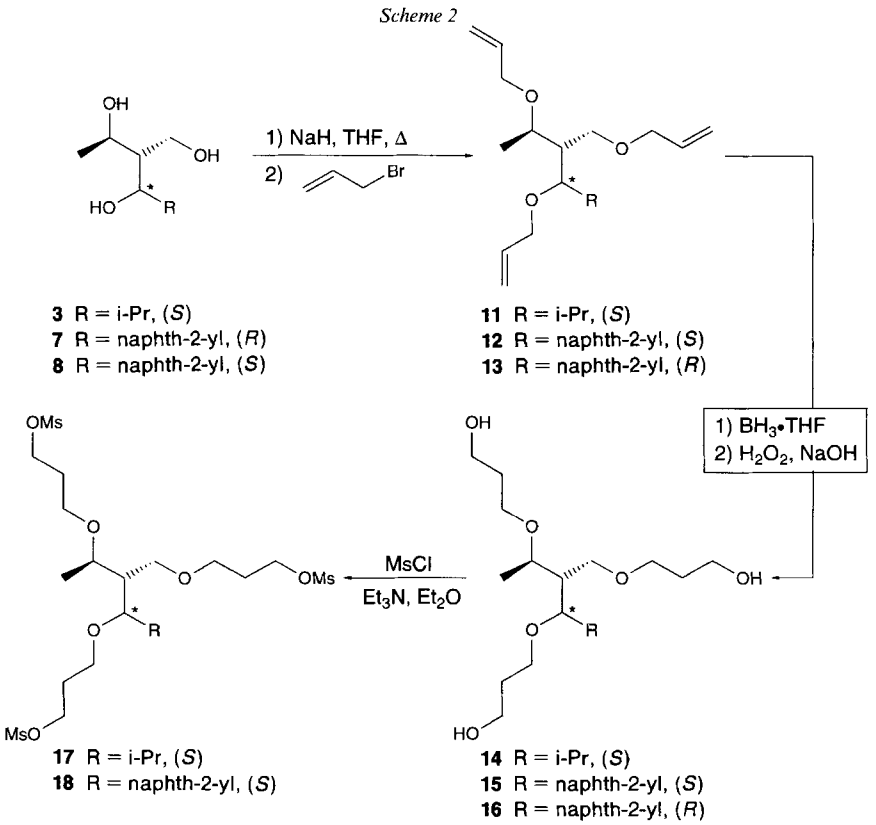
[4]) The compound that would result from the reduction of **10** can, however, be prepared by a simpler procedure, see *Scheme 2*.

Scheme 1



With allyl bromide as electrophile, the etherification of the triols worked very well: by first treating **3**, **7**, or **8** with excess NaH (9 equiv.) then with allyl bromide, the corresponding triallyl tri-ethers **11**–**13** were obtained in good yields (> 80%, *Scheme 2*). Compounds **11**–**13** were subsequently subjected to hydroboration with $BH_3 \cdot THF$ complex, followed by an oxidative treatment to afford the elongated triols **14**–**16**. The yields of the

Scheme 2



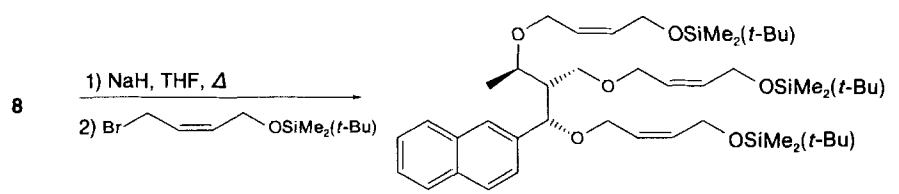
[a]) The configurational descriptors refer to the starred center.

hydroboration reaction were somewhat low, despite all our attempts to optimize them; the reaction required 1 equiv. of BH_3 per double bond, and the yields were in the order of 40–45%[5][6]).

The sequence of allylation/hydroboration shown in *Scheme 2* provides a good route to 'elongated' triols, keeping the original OH functionality after introduction of a C_3 spacer (it was demonstrated before that problems in the coupling reactions leading to higher dendrimer generations are caused by too small distances between the reactive sites and that the introduction of a spacer unit is often necessary [11]). The 'elongated' triols **14** and **15** were converted to the corresponding trimesylates **17** and **18**, central pieces ready for subsequent branching steps. Thus, compound **18** was employed in a branching reaction using triethyl sodiomethanetricarboxylate in toluene/DMF at 110° [9] to give a nonaester (by ^{1}H-NMR spectroscopy), purification of which proved to be difficult.

The allylation procedure was also applied with a functionalized allyl bromide, partially to illustrate the generality of the method and partially to avoid the hydroboration step (*Scheme 3*): triol **8** was etherified with (*Z*)-1-bromo-4-[(*tert*-butyl)dimethylsilyloxy]-but-2-ene, giving the expected product **19** in 52% yield[7]).

Scheme 3



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We also investigated benzylation with our triols, since benzylic coupling is an important tool in dendrimer synthesis [12]. The chiral triol **4** was benzylated using 9 equiv. of NaH and a small excess (3.5 equiv.) of a benzyl bromide, affording the corresponding tris(benzyl ethers) **20**–**22**. The yields were generally high (> 70%), and the purification of the products was readily accomplished by simple flash chromatography or by short-path distillation. The tris(benzyl ethers) **21** and **22** could be useful building blocks for dendrimer synthesis: the phenolic OH groups generated by deprotection, would serve for coupling reactions, thus, in fact, the benzylation step represents another 'elongation' of

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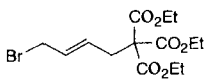
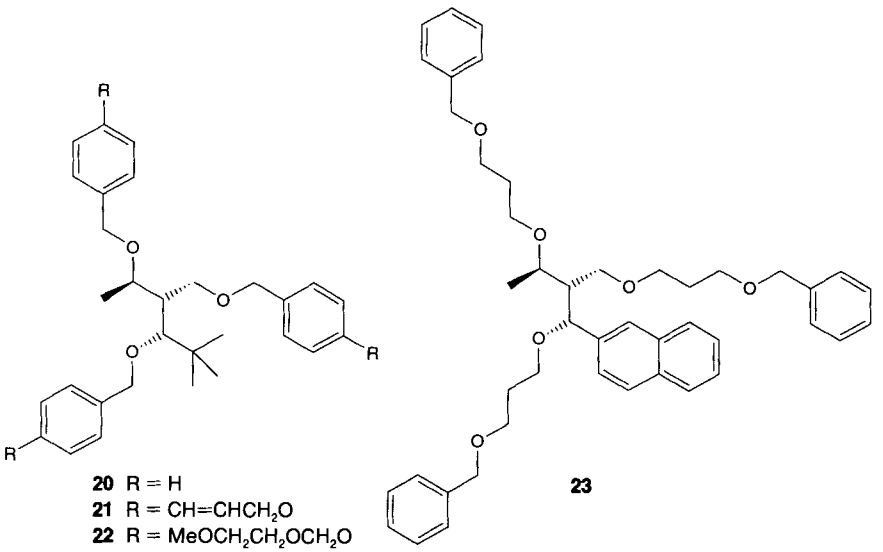
[5]) In view of the fact that three hydroboration reactions were performed, a 42% total yield, corresponding to *ca.* 75% per hydroboration step, is probably acceptable.

[6]) The necessity for, in fact, using 200% excess BH_3 instead of only 0.33 equiv. per C=C bond, is probably caused by the fact that a cross-linked polyborane is formed with stoichiometric BH_3 amounts.

[7]) We tried the same coupling reaction with **i**, looking for an expeditious synthesis of a dendrimer of generation 1. The result was a mixture of mono- and di-alkylated products.



i



20 R = H
21 R = $CH{=}CHCH_2O$
22 R = $MeOCH_2CH_2OCH_2O$

23

the starting chiral triol. The benzylation was also performed with the trioxa-triol **16**, affording compound **23** in 82% yield[8]).

Two other benzylic coupling reactions were realized under the same conditions. The chiral triol **3** was coupled with the 4-(bromomethyl)benzoic acid and the crude product esterified with diazomethane to the trimethyl ester **24** in an overall yield of 30% (*Scheme 4*). Reduction of the latter with $LiAlH_4$ provided the 'elongated' triol **25** (81%) in which the spacer unit is a benzene ring instead of an aliphatic chain[9]). The coupling of triol **6**, containing the (*E*)-olefinic bond, with 1-bromo-4-(bromomethyl)benzene gave the corresponding bromobenzyl ether **26** (91%). The chiral triol **25** provides another central piece with large enough distance between the reactive sites so that we believe it could be used for high-generation dendrimer synthesis. Compound **26**, bearing the bromophenyl moiety, on the other hand, constitutes a chiral core for introducing branches *via* a metal-mediated coupling reaction with vinylic [13] or acetylenic reagents [14] [15].

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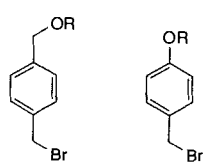
[8]) The demonstration that benzylation worked fine for 'elongating' the triols paves the way to the preparation of less-hindered central-piece dendrimers in which larger holes will be present to accomodate larger host molecules in host-guest complexes [1].

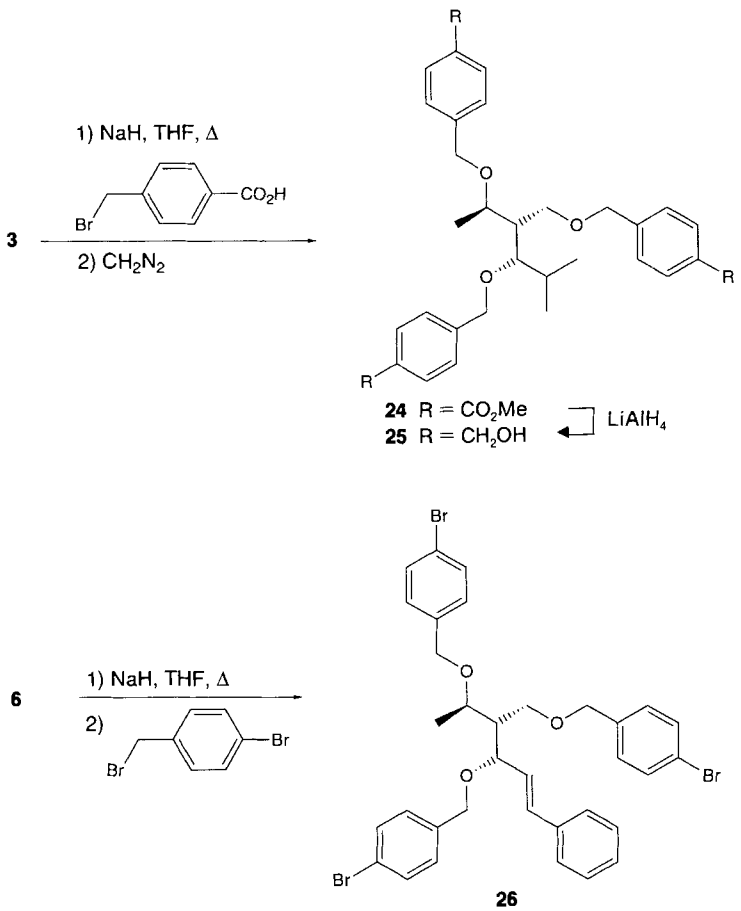
[9]) We tried to incorporate this spacer by another method, using **ii** bearing different silyl protective groups, but the result, surprisingly, was a complex mixture (by ^{1}H-NMR) which we did not try to seperate. We observed similar mixtures in an attempt to incorporate phenol-protected spacers, using **iii**.



ii **iii**

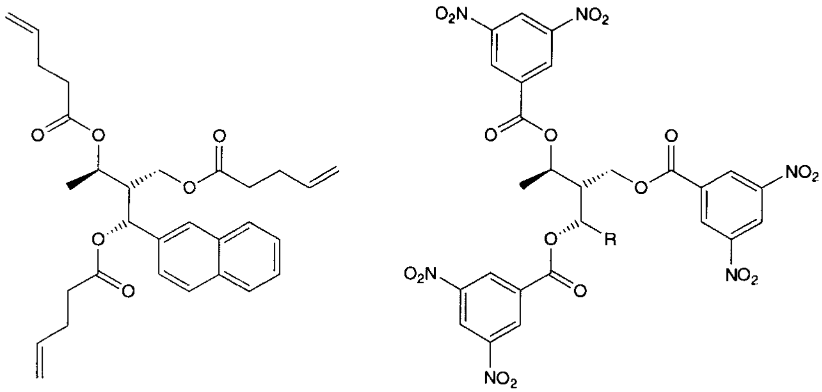
R = (*t*-Bu)Me_2Si or (*t*-Bu)Ph_2Si

Scheme 4



In *Schemes 1–4*, we described only reactions of our chiral triols with formation of ether bonds. Another type of coupling which was used in dendrimer synthesis is esterification [16]. Thus, we also carried out this type of reaction in pyridine at 80°: from triol **7** and pent-4-enoyl chloride, triester **27** was obtained in 52% yield, and the triols **3** and **5** were esterified with 3,5-dinitrobenzoyl chloride to produce **28** and **29**, respectively, in high yields (> 95%, after purification; *Scheme 5*). The former compound was then subjected to hydrogenation with *Adam*'s catalyst in dioxane, affording in quantitative yield the hexamine **30**. After purification and careful removal of the volatiles *in vacuo* at 25°, we found that the solid we isolated consisted of an inclusion compound, in a ratio of 1:1, of **30** and dioxane. Heating this solid at 100°/0.31 Torr for 6 h led to another inclusion complex of **30** and dioxane in a ratio of 2:1; even after 24 h at high temperature, some dioxane remained (6:1), showing the stability of the complex. Both dioxane clathrates were isolated in pure form.

Scheme 5



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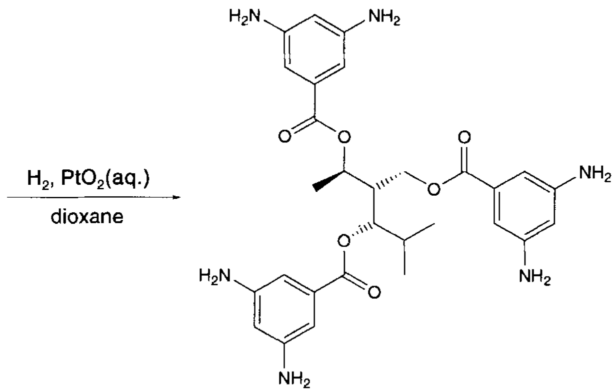
28 R = i-Pr
29 R = Ph_2CH

28



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All new compounds **1–30** reported herein were fully characterized by their IR, ^1H-NMR, ^{13}C-NMR, and mass spectra, as well as by elemental analysis.

Conclusion. – We have shown that chiral 'tris(hydroxymethyl)methane' derivatives can be used to construct interesting building blocks which are potential central pieces for dendrimer synthesis. The compounds prepared may also serve for more conventional synthetic target molecules, and some of them showed the ability of clathrating small molecules to form inclusion complexes. This last mentioned observation demonstrates that it is reasonable to expect that the resulting dendrimers are chiral endoreceptors. Some of the building blocks described herein have actually been used as center pieces of chiral dendrimers, in an investigation the results of which will be reported in due course.

We are grateful for postdoctoral stipends given to *J.-M. Lapierre* by the *Natural Sciences and Engineering Research Council of Canada* and to *K. Skobridis* by the *Deutsche Forschungsgemeinschaft (DFG)*. Continuous support by the *Sandoz AG*, Basel, is greatfully acknowledged.

Experimental Part

General. Solvents used were *Fluka puriss.* grade, except for THF which was distilled over K/benzophenone. Commercially available aldehydes and acyl chlorides were used as received without any further purification. The *(2R,6R)-2-(tert-butyl)-6-methyl-1,3-dioxan-4-one* (**A**) was prepared as described in [17]. Thin layer chromatography (TLC): glass plated TLC silica gel *60* F_{254} (*Merck*). Flash chromatography (FC): Kieselgel *60* (*Merck*) 40–60 μm. M.p.: *Büchi 510*, uncorrected. Optical rotations: *Perkin-Elmer-241* polarimeter; 1-dm cells. IR: *Perkin-Elmer 983* or *Perkin-Elmer 297*; in cm^{-1}. NMR: *Bruker-AMX400, Varian-XL-300, Bruker-WM-300,* or *Varian-Gemini-200* spectrometers; $CDCl_3$ solns., unless mentioned otherwise; chemical shifts δ in ppm downfield from internal Me_4Si (= 0 ppm), coupling constants J in Hz. MS: *Hitachi-Perkin-Elmer RMU-6M*; *m/z* (rel. intensities in %). Microanalyses were performed by Mikroanalytisches Laboratorium der ETH-Zürich. Abbreviations: THF = tetrahydrofuran, LDA = lithium diisopropylamide, h.v. = high vacuum.

(1'S,2R,5R,6R)-2-(tert-Butyl)-5-(1'-hydroxy-2',2'-diphenylethyl)-6-methyl-1,3-dioxan-4-one (**1a**). An ice-cold soln. of $(i\text{-}Pr)_2NH$ (7.6 ml, 54.2 mmol, 1.08 equiv.) in THF (150 ml) was treated with BuLi (1.5M in hexanes; 36.1 ml, 54.2 mmol, 1.08 equiv.), stirred at 0° for 15 min, and then cooled to −78°. To this soln. of LDA was added **A** (8.6 g, 50 mmol) in THF (50 ml) at such a rate that the temp. never exceeded −70°. Then the mixture was maintained at −78° for 45 min. To the resulting enolate soln. was added diphenylacetaldehyde (9.8 g, 50 mmol, 1.0 equiv.) in THF (20 ml), maintaining the temp. below −75°. The mixture was stirred at −78° for 3 h, then quenched by the addition of sat. aq. NH_4Cl soln. (200 ml) followed by Et_2O (200 ml). The aq. phase was extracted with Et_2O (2 × 200 ml) and the combined extract dried ($MgSO_4$) and evaporated. The crude product contained practically only one diastereoisomer. Recrystallization from hexanes gave 14.6 g (79%) of pure **1a**. M.p. 128–129°. $[\alpha]_D = +97.7$ ($c = 2.0$, $CHCl_3$). IR ($CHCl_3$): 3580*w*, 2980*w*, 1730*s*, 1595*w*, 1485*m*, 1450*m*, 1365*m*, 1355*s*, 1285*m*, 1210*s*, 1155*w*, 1070*w*, 1030*w*, 1000*s*, 970*m*. ^{1}H-NMR (400 MHz): 0.92 (*s*, *t*-Bu); 1.17 (*d*, $J = 6.14$, Me); 1.88 (*d*, $J = 4.06$, OH); 2.36 (*d*, $J = 9.60$, H–C(5)); 4.07 (*dq*, $J = 9.68, 6.13$, H–C(6)); 4.35 (*dd*, $J = 10.93, 3.89$, H–C(1')); 4.90 (*d*, $J = 10.92$, H–C(2')); 4.94 (*s*, H–C(2)); 7.15–7.45 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz): 19.81; 23.87; 34.95; 50.13; 55.72; 73.55; 74.02; 107.73; 127.02; 127.19; 128.43; 128.90; 129.08; 140.73; 141.37; 168.58. MS: 311 (< 1), 265 (12), 238 (29), 220 (32), 201 (53), 196 (31), 168 (38), 167 (81), 165 (33), 115 (14), 105 (14), 91 (16), 87 (100), 69 (39), 27 (25). Anal. calc. for $C_{23}H_{28}O_4$: C 74.97, H 7.66; found: C 75.15, H 7.82.

(1'S,2R,5S,6R)-5-(1'-Acetoxy-2',2'-diphenylethyl)-2-(tert-butyl)-6-methyl-1,3-dioxan-4-one (**1b**). To an ice-cold soln. of **1a** (10.0 g, 27.1 mmol) in pyridine (50 ml), acetyl chloride (3 ml, 41.6 mmol, 1.5 equiv.) was added dropwise. The mixture was kept at 0° for 15 min, allowed to warm up to r.t. for 3 h, then treated with ice and acidified with 10% HCl soln. The precipitate was filtered off and washed with H_2O. FC (CH_2Cl_2/hexane 4:1) gave 9.5 g (85%) of pure **1b**. M.p. 172–173°. $[\alpha]_D = -13.5$ ($c = 2.75$, $CHCl_3$). IR ($CHCl_3$): 3040*w*, 3000*w*, 2990*w*, 2875*w*, 1740*s*, 1600*w*, 1495*w*, 1450*w*, 1410*w*, 1370*s*, 1355*m*, 1280*m*, 1220*s*, 1155*w*, 1065*w*, 1035*m*, 1000*s*, 975*w*, 620*w*. ^{1}H-NMR (300 MHz): 0.90 (*s*, *t*-Bu); 1.28 (*d*, $J = 6.06$, Me); 1.74 (*s*, AcO); 2.51 (*dd*, $J = 10.13, 0.79$, H–C(5)); 3.76 (*dq*, $J = 10.29, 6.06$, H–C(6)); 4.70 (*s*, H–C(2)); 5.15 (*d*, $J = 11.48$, H–C(2')); 5.81 (*dd*, $J = 11.46, 0.83$, H–C(1')); 7.1–7.5 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz): 19.61; 20.65; 23.82; 35.11; 49.62; 53.83; 73.38; 73.50; 108.17; 126.77; 127.28; 128.34; 128.61; 129.06; 140.59; 140.68; 166.93; 170.78. MS: 411 (< 1, $[M + 1]^+$), 353 (< 1), 265 (14), 248 (21), 247 (10), 221 (21), 220 (100), 219 (27), 197 (10), 196 (67), 167 (63), 165 (22), 152 (10), 87 (10), 57 (10), 43 (24). Anal. calc. for $C_{25}H_{30}O_5$: C 73.15, H 7.37; found: C 73.12, H 7.20.

(1'R,2R,5R,6R)-2-(tert-Butyl)-5-(1'-hydroxy-3'-phenylprop-2'-ynyl)-6-methyl-1,3-dioxan-4-one (**2a**). As described for **1a**, from **A** (5.75 g, 33.5 mmol), $(i\text{-}Pr)_2NH$ (5 ml, 35.7 mmol, 1.06 equiv.), BuLi (1.5M in hexane; 23.8 ml, 35.7 mmol, 1.06 equiv.), and 3-phenylprop-2-ynal (4.5 g, 34.5 mmol, 1.02 equiv.). The crude product was a 1.2:1 epimer mixture (at C(1')). FC (hexane/Et_2O 1:1) gave 3.1 g (31%) of pure **2a** and 2.6 g (26%) of the 1'-epimer containing some of the diastereoisomer. *Data of* **2a**: m.p. 96°. $[\alpha]_D = -1.3$ ($c = 1.90$, $CHCl_3$). IR ($CHCl_3$): 3500*w*, 2995*m*, 2985*m*, 2230*w*, 1720*s*, 1490*m*, 1445*w*, 1415*w*, 1385*m*, 1370*s*, 1355*s*, 1285*m*, 1230*s*, 1155*m*, 1130*w*, 1030*s*, 995*s*, 970*m*, 940*w*. ^{1}H-NMR (300 MHz): 0.91 (*s*, *t*-Bu); 1.48 (*d*, $J = 6.15$, Me); 1.60 (*s*, OH); 2.80 (*dd*, $J = 9.92, 3.57$, H–C(5)); 4.12 (*m*, H–C(6)); 4.81 (*dd*, $J = 9.33, 3.57$, H–C(1')); 5.02 (*s*, H–C(2)); 7.3–7.45 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz): 20.32; 23.88; 35.15; 53.92; 61.37; 72.45; 86.85; 86.91; 108.63; 121.84; 128.41; 128.96; 131.78; 170.49. MS: 302 (2, M^+), 216 (39), 200 (34), 199 (100), 173 (38), 172 (35), 171 (39), 157 (41), 150 (40), 143 (26), 131 (95), 130 (99), 129 (59), 102 (67), 87 (30), 77 (34), 69 (96), 57 (38), 41 (25). Anal. calc. for $C_{18}H_{22}O_4$: C 71.50, H 7.33; found: C 71.39, H 7.24.

(1'R,2R,5S,6R)-5-(1'-Acetoxy-3'-phenylprop-2'-ynyl)-2-(tert-butyl)-6-methyl-1,3-dioxan-4-one (**2b**). As described for **1b**, from **2a** (2.3 g, 7.6 mmol) and acetyl chloride (1.1 ml, 15.2 mmol, 2 equiv.). FC (CH_2Cl_2) gave 2.45 g (94%) of pure **2b**. Colourless oil. $[\alpha]_D = -133.5$ ($c = 2.15$, $CHCl_3$). IR ($CHCl_3$): 3010*w*, 2980*m*, 2965*m*, 2910*w*, 2875*w*, 2235*w*, 1750*s*, 1490*m*, 1485*m*, 1370*s*, 1350*s*, 1280*m*, 1220*s*, 1155*m*, 1030*m*, 990*s*, 960*m*, 925*w*, 835*w*.

^{1}H-NMR (300 MHz): 0.99 (*s*, *t*-Bu); 1.62 (*d*, *J* = 6.14, Me); 2.12 (*s*, AcO); 2.87 (*dd*, *J* = 9.20, 2.79, H–C(5)); 4.31 (*dq*, *J* = 9.16, 6.13, H–C(6)); 4.99 (*s*, H–C(2)); 6.14 (*d*, *J* = 2.79, H–C(1′)); 7.3–7.45 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz): 20.81; 21.72; 23.88; 35.09; 52.21; 62.96; 73.45; 84.00; 87.95; 108.02; 121.48; 128.44; 129.22; 131.84; 167.61; 168.81. MS: 344 (1, M^+), 245 (19), 227 (27), 216 (54), 201 (18), 200 (36), 199 (49), 198 (100), 181 (21), 172 (32), 155 (52), 131 (22), 129 (37), 105 (74), 77 (22), 69 (28), 43 (70). Anal. calc. for $C_{20}H_{24}O_5$: C 69.75, H 7.02; found: C 69.58, H 6.93.

(2S,3S,4R)-3-(Hydroxymethyl)-1,1-diphenylpentane-2,4-diol (**5**). To **1b** (5.0 g, 12.2 mmol) in THF (140 ml) at 0° was added $LiAlH_4$ (3.3 g, 61 mmol, 5 equiv.). The mixture was stirred at r.t. for 30 min and then at 40° for 20 h. After cooling to 0°, H_2O (6 ml), 15% NaOH soln. (5 ml), and H_2O (10 ml) were added consecutively, and the resulting mixture was stirred vigourously until a white precipitate formed. The precipitate was filtered off and the filtrate diluted with Et_2O (200 ml), dried ($MgSO_4$), and evaporated: colourless liquid. FC (Et_2O) afforded 2.55 g (73%) of pure **5**. M.p. 73°. $[\alpha]_D$ = +5.9 (*c* = 2.30, $CHCl_3$). IR ($CHCl_3$): 3505*s*, 3065*w*, 3005*s*, 2915*w*, 1600*w*, 1495*s*, 1450*s*, 1420*m*, 1140*m*, 1070*s*, 1035*w*, 990*w*, 920*w*. ^{1}H-NMR (400 MHz): 1.24 (*d*, *J* = 6.39, H–C(5)); 1.38 (*m*, H–C(3)); 2.80 (*d*, *J* = 4.03, OH); 3.03 (*m*, 2 OH); 4.01 (*m*, H–C(4)); 4.1–4.2 (*m*, 2 H–C(1′)); 4.21 (*d*, *J* = 10.19, H–C(1)); 4.70 (*ddd*, *J* = 10.19, 3.88, 2.56, H–C(2)); 7.15–7.45 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz): 21.51; 45.89; 56.52; 59.69; 70.30; 76.90; 126.83; 126.99; 128.06; 128.45; 128.92; 128.93; 141.42; 141.67. MS: 287 (2, $[M + 1]^+$), 206 (5), 169 (37), 168 (100), 167 (93), 166 (31), 165 (68), 153 (12), 152 (32), 119 (60), 101 (32), 91 (22), 71 (20), 57 (67), 55 (47), 45 (24), 43 (13). Anal. calc. for $C_{18}H_{22}O_3$: C 75.50, H 7.74; found: C 75.55, H 7.99.

(2R,3S,4S,5E)-3-(Hydroxymethyl)-6-phenylhex-5-ene-2,4-diol (**6**). As described for **5**, from **2b** (2.1 g, 6.1 mmol) and $LiAlH_4$ (1.65 g, 30.5 mmol, 5 equiv.). FC (CH_2Cl_2/MeOH) gave 1.25 g (93%) of pure **6**. Colourless oil. $[\alpha]_D$ = –7.5 (*c* = 2.08, $CHCl_3$). IR ($CHCl_3$): 3410*s*, 3005*m*, 2900*w*, 1600*w*, 1495*w*, 1450*w*, 1415*w*, 1295*w*, 1070*m*, 970*s*, 850*w*. ^{1}H-NMR (300 MHz): 1.31 (*d*, *J* = 6.57, H–C(1)); 1.62 (*m*, H–C(3)); 2.80 (br. *s*, OH); 3.09 (br. *s*, OH); 3.33 (br. *s*, OH); 3.90 ('*dd*', *AB*, *J* = 11.47, 5.01, 1 H–C(1′)); 4.15 ('*dd*', *AB*, *J* = 11.47, 5.01, 1 H–C(1′)); 4.39 (*dq*, *J* = 15.92, 6.04, H–C(5)); 6.70 (*dd*, *J* = 15.94, 1.22, H–C(6)); 7.2–7.4 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz): 21.46; 49.91; 61.59; 67.75; 73.83; 126.53; 127.80; 128.65; 130.49; 131.10; 136.60. MS: 222 (2, M^+), 186 (16), 173 (11), 160 (34), 143 (34), 133 (100), 131 (69), 115 (41), 105 (34), 104 (73), 77 (21), 55 (27). Anal. calc. for $C_{13}H_{18}O_3$: C 70.23, H 8.16; found: C 69.82, H 7.80.

3-{(2R,3S,4S)-4-(2-Cyanoethoxy)-3-[(2-cyanoethoxy)methyl]-5-methylhexan-2-yloxy}propanenitrile (**9**). To a stirred mixture of triol **3** [4] (2.0 g, 12.3 mmol) and 5% NaOH soln. (1.0 ml) was added dropwise freshly distilled acrylonitrile (2.65 ml, 40 mmol). After the addition, the temp. was raised to 40–50° for 5 h and then maintained at r.t. for 20 h. H_2O was added and the resulting mixture extracted with Et_2O. The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated. FC (Et_2O) gave 1.58 g (40%) of pure **9**. Colourless oil. $[\alpha]_D$ = +11.0 (*c* = 0.30, $CHCl_3$). IR ($CHCl_3$): 2965*m*, 2875*m*, 2255*w*, 1465*w*, 1415*w*, 1365*w*, 1105*s*, 850*w*. ^{1}H-NMR (300 MHz): 0.94 (*d*, *J* = 7.18, Me); 0.96 (*d*, *J* = 7.46, Me); 1.24 (*d*, *J* = 6.39, Me); 1.9–2.05 (*m*, 2 H); 2.5–2.6 (*m*, 3 CH_2CN); 3.29 (*dd*, *J* = 5.09, 3.99, H–C(2′)); 3.5–3.8 (*m*, 8 H). ^{13}C-NMR (75 MHz): 16.50; 17.86; 18.96; 19.26; 31.49; 45.64; 63.25; 65.48; 65.77; 68.48; 75.71; 83.21; 118.17; 118.28. MS: 279 (5), 166 (10), 148 (23), 126 (16), 125 (14), 110 (36), 98 (100), 72 (15), 71 (12), 57 (13), 55 (18), 54 (18), 43 (13). Anal. calc. for $C_{17}H_{27}N_3O_3$: C 63.53, H 8.47; N 13.07; found: C 63.70, H 8.27, N 12.80.

Methyl 3-{(2R,3S,4S)-4-[2-(Methoxycarbonyl)ethoxy]-3-{[2-(methoxycarbonyl)ethoxy]methyl}-5-methylhexan-2-yloxy}propanoate (**10**). Through an ice-cold soln. of **9** (1.0 g, 3.1 mmol) in MeOH (20 ml) was bubbled dry HCl gas for 1 h. Then the flask was stoppered and let to stand at r.t. overnight. H_2O was added and the mixture stirred for 30 min at 50° and then at r.t. for 1 h. The resulting mixture was extracted with Et_2O and the combined extract washed with 10% Na_2CO_3 soln., dried ($MgSO_4$), and evaporated. FC (Et_2O) gave 1.28 g (98%) of pure **10**. Colourless oil. $[\alpha]_D$ = +11.0 (*c* = 1.60, $CHCl_3$). IR ($CHCl_3$): 2955*m*, 2875*w*, 1735*s*, 1440*m*, 1365*w*, 1180*s*, 1100*s*, 1020*w*, 850*w*. ^{1}H-NMR (300 MHz): 0.86 (*d*, *J* = 6.77, Me); 0.90 (*d*, *J* = 6.83, Me); 1.13 (*d*, *J* = 6.40, Me); 1.85–2.0 (*m*, 1 H); 2.5–2.6 (*m*, 3 CH_2CO_2); 3.14 (*m*, 1 H); 3.42 (*m*, 1 H); 3.5–3.8 (*m*, 8 H); 3.68 (*s*, MeO). ^{13}C-NMR (75 MHz): 16.15; 17.99; 19.16; 31.23; 35.07; 35.34; 35.54; 44.91; 51.57; 64.03; 66.26; 66.55; 68.72; 75.32; 82.60; 172.24. MS: 421 (< 1, M^+), 273 (6), 219 (5), 213 (3), 199 (5), 185 (3), 159 (35), 158 (5), 143 (30), 131 (51), 117 (7), 109 (7), 105 (3), 87 (100), 59 (23), 55 (11), 45 (7), 43 (7). Anal. calc. for $C_{20}H_{36}O_9$: C 57.13, H 8.63; found: C 57.35, H 8.72.

3-{(2R,3S,4S)-5-Methyl-4-(prop-2-enyloxy)-3-[(prop-2-enyloxy)methyl]hexan-2-yloxy}prop-1-ene (**11**). To NaH (2.9 g, 121 mmol, 9 equiv.) in THF (100 ml) was added **3** [4] (2.19 g, 13.5 mmol) in THF (50 ml). The mixture was stirred under reflux for 30 min, then 3-bromoprop-1-ene (10.5 ml, 121 mmol, 9 equiv.) was added at once. The reflux was maintained for 24 h. H_2O (100 ml) was carefully added, the resulting mixture extracted 3 times with Et_2O (150 ml), the combined extract dried ($MgSO_4$) and evaporated, and the yellow liquid purified by FC (hexane/Et_2O 10:1): 3.43 g (90%) of pure **11**. An anal. pure sample was obtained from a short-path distillation. B.p. 92°/0.1 Torr. $[\alpha]_D$ = +16.7 (*c* = 1.81, $CHCl_3$). IR ($CHCl_3$): 3080*w*, 3000*s*, 2980*s*, 2965*s*, 2890*s*, 1645*w*, 1460*m*, 1425*m*, 1380*m*,

1345*m*, 1075*s*, 995*s*, 930*s*. ^{1}H-NMR (300 MHz): 0.93 (*d*, *J* = 6.70, Me); 0.95 (*d*, *J* = 6.76, Me); 1.20 (*d*, *J* = 6.46, Me); 1.9–2.1 (*m*, H–C(5′)); 2.1–2.2 (*m*, H–C(3′)); 3.29 (*dd*, *J* = 5.38, 3.55, H–C(4′)); 3.50 ('*dd*', *AB*, *J* = 9.89, 7.80, 1 H, OCH_2–C(3′)); 3.65 ('*dd*', *AB*, *J* = 10.08, 4.19, 1 H, OCH_2–C(3′)); 3.6–3.8 (*m*, H–C(2′)); 3.9–4.1 (*m*, 6 H); 5.0–5.3 (*m*, 6 H); 5.8–6.0 (*m*, 3 H). ^{13}C-NMR (75 MHz): 16.36; 18.22; 19.29; 31.47; 44.77; 68.32; 69.50; 71.87; 72.41; 74.78; 82.67; 115.49; 115.92; 116.27; 135.28; 135.52; 135.60. MS: 283 (10, $[M + 1]^+$), 261 (3), 239 (60), 205 (2), 183 (55), 167 (9), 153 (56), 139 (63), 127 (85), 113 (22), 97 (60), 85 (35), 71 (25), 55 (16), 41 (100). Anal. calc. for $C_{17}H_{30}O_3$: C 72.30, H 10.71; found: C 72.36, H 10.95.

3-{(1S,2S,3R)-1-(Naphth-2-yl)-3-(prop-2-enyloxy)-2-[(prop-2-enyloxy)methyl]butyloxy}prop-1-ene (**12**). As described for **11**, with **8** [4] (0.5 g, 2.0 mmol), NaH (0.24 g, 10.2 mmol, 5 equiv.), and allyl bromide (0.9 ml, 10.2 mmol, 5 equiv.). FC (hexane/Et_2O 10:1) gave 0.58 g (77%) of pure **12**. $[\alpha]_D = -25.1$ (*c* = 2.96, $CHCl_3$). IR ($CHCl_3$): 3080*m*, 3060*m*, 3005*s*, 2920*s*, 2860*s*, 1645*w*, 1600*w*, 1510*w*, 1480*w*, 1455*m*, 1420*m*, 1375*m*, 1350*m*, 1325*m*, 1070*s*, 995*s*, 930*s*, 895*m*, 860*m*, 820*m*. ^{1}H-NMR (300 MHz): 1.27 (*d*, *J* = 6.53, Me); 2.0–2.2 (*m*, H–C(2′)); 3.21 ('*dd*', *AB*, *J* = 9.87, 4.59, 1 H, OCH_2–C(2′)); 3.44 ('*dd*', *AB*, *J* = 9.84, 4.85, 1 H, OCH_2–C(2′)); 3.49 ('*ddt*', *AB*, *J* = 12.76, 5.53, 1.38, 1 H, $CH_2CH{=}CH_2$); 3.58 ('*ddt*', *AB*, *J* = 12.77, 5.55, 1.37, 1 H, $CH_2CH{=}CH_2$); 3.73 ('*ddt*', *AB*, *J* = 12.58, 5.99, 1.34, 1 H, $CH_2CH{=}CH_2$); 3.86 ('*ddt*', *AB*, *J* = 12.60, 5.28, 1.38, 1 H, $CH_2CH{=}CH_2$); 3.97 ('*ddt*', *AB*, *J* = 12.85, 5.56, 1.47, 1 H, $CH_2CH{=}CH_2$); 4.1–4.2 (*m*, 2 H); 4.54 (*d*, *J* = 9.14, H–C(1′)); 4.9–5.0 (*m*, 2 H); 5.1–5.4 (*m*, 4 H); 5.5–5.7 (*m*, 1 H); 5.8–6.1 (*m*, 2 H); 7.4–7.6 (*m*, 3 arom. H); 7.7–7.9 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 18.42; 51.31; 67.17; 69.72; 70.30; 71.60; 73.06; 80.76; 116.05; 116.21; 116.63; 125.47; 125.73; 125.96; 127.15; 127.70; 127.83; 128.06; 133.11; 133.20; 134.82; 135.02; 135.89; 138.65. MS: 366 (5, M^+), 325 (18), 309 (10), 267 (8), 252 (9), 235 (8), 223 (12), 207 (7), 197 (95), 181 (28), 167 (100), 155 (83), 141 (66), 128 (28), 115 (6), 97 (6), 85 (50), 69 (4), 55 (7), 41 (62). Anal. calc. for $C_{24}H_{30}O_3$: C 78.65, H 8.25; found: C 78.50, H 8.39.

3-{(1R,2S,3R)-1-(Naphth-2-yl)-3-(prop-2-enyloxy)-2-[(prop-2-enyloxy)methyl]butyloxy}prop-1-ene (**13**). As described for **11**, with **7** [4] (1.18 g, 4.8 mmol), NaH (1.04 g, 43.2 mmol, 9 equiv.), and 3-bromoprop-1-ene (3.75 ml, 43.2 mmol, 9 equiv.). FC (hexane/Et_2O 10:1) gave 1.38 g (78%) of pure **13**. $[\alpha]_D = +42.6$ (*c* = 4.93, $CHCl_3$). IR ($CHCl_3$): 3080*m*, 3060*m*, 3005*s*, 2920*m*, 2860*s*, 1645*m*, 1600*w*, 1510*m*, 1480*w*, 1460*m*, 1425*m*, 1410*w*, 1380*m*, 1330*m*, 1270*m*, 1125*s*, 1080*s*, 1025*m*, 995*s*, 930*s*, 895*m*, 860*m*, 825*s*. ^{1}H-NMR (300 MHz): 1.20 (*d*, *J* = 6.44, Me); 2.1–2.3 (*m*, H–C(6)); 3.39 (*qd*, *J* = 6.45, 3.38, H–C(5)); 3.6–3.7 (*m*, 1 H); 3.7–3.85 (*m*, 3 H); 3.9–4.05 (*m*, 4 H); 4.68 (*d*, *J* = 6.42, H–C(1′)); 5.1–5.3 (*m*, 6 H); 5.8–6.0 (*m*, 3 H); 7.4–7.5 (*m*, 3 arom. H); 7.7–7.9 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 17.00; 50.92; 67.17; 69.37; 69.86; 71.80; 73.93; 115.74; 116.13; 116.28; 125.15; 125.70; 125.83; 126.02; 126.28; 127.70; 127.83; 128.06; 133.02; 133.22; 135.08; 135.25; 135.57; 138.97. MS: 366 (12, M^+), 325 (40), 308 (7), 267 (18), 252 (33), 237 (25), 223 (97), 197 (100), 181 (7), 169 (30), 155 (36), 141 (18), 128 (12), 115 (2), 85 (10), 71 (2), 55 (5), 41 (86). Anal. calc. for $C_{24}H_{30}O_3$: C 78.65, H 8.25; found: C 78.35, H 8.38.

3-{(2R,3S,4S)-4-(3-Hydroxypropyloxy)-3-[(3-hydroxypropyloxy)methyl]-5-methylhexan-2-yloxy}propan-1-ol (**14**). To **11** (5.9 g, 20.9 mmol) in THF (100 ml) was added BH_3·THF complex (63 ml, 62.7 mmol, 1.0M, 3 equiv.). The mixture was kept at r.t. for 5 h and then cooled to 0° for the addition of H_2O (7.8 ml), 3M NaOH (11.7 ml), and 30% H_2O_2 soln. (11.7 ml). The mixture was vigourously stirred at r.t. for 2 h and then diluted with H_2O (50 ml) and extracted with Et_2O (3 × 200 ml). Drying ($MgSO_4$) and evaporation gave a colourless oil. FC (Et_2O/MeOH 19:1) yielded 2.55 g (36%) of pure **14**. $[\alpha]_D = +0.2$ (*c* = 3.78, $CHCl_3$). IR ($CHCl_3$): 3440*s*, 3005*s*, 2965*s*, 2875*s*, 1470*m*, 1425*m*, 1380*m*, 1345*w*, 1260*w*, 1075*s*, 970*w*. ^{1}H-NMR (300 MHz): 0.91 (*d*, *J* = 6.76, Me); 0.97 (*d*, *J* = 6.84, Me); 1.24 (*d*, *J* = 6.28, Me); 1.65–1.75 (*m*, H–C(6)); 1.75–1.85 (*m*, 3 CH_2CH_2OH); 1.8–2.0 (*m*, H–C(5′)); 3.15–3.3 (*m*, 2 H); 3.4–3.5 (*m*, 2 H); 2.15 (br. *s*, OH); 2.98 (br. *s*, OH); 3.5–3.9 (*m*, 13 H). ^{13}C-NMR (75 MHz): 17.16; 17.32; 19.94; 30.82; 31.88; 32.37; 32.53; 46.65; 61.25; 61.63; 62.21; 67.75; 68.04; 69.89; 72.22; 75.52; 83.48. MS: 337 (14, $[M + 1]^+$), 293 (26), 279 (5), 261 (6), 245 (8), 235 (6), 217 (59), 199 (10), 184 (47), 171 (10), 158 (6), 141 (9), 131 (26), 115 (100), 103 (47), 83 (4), 73 (21), 59 (75), 45 (13), 31 (16). Anal. calc. for $C_{17}H_{36}O_6$: C 60.69, H 10.78; found: C 60.60, H 10.49.

3-{(1S,2S,3R)-3-(3-Hydroxypropyloxy)-2-[(3-hydroxypropyloxy)methyl]-1-(naphth-2-yl)butyloxy}propan-1-ol (**15**). As described for **14**, with **12** (1.07 g, 2.9 mmol) and BH_3·THF complex (8.7 ml, 8.7 mmol, 1.0M, 3 equiv.). FC (Et_2O/MeOH 19:1) gave 0.53 g (44%) of pure **15**. $[\alpha]_D = -29.0$ (*c* = 1.30, $CHCl_3$). IR ($CHCl_3$): 3620*w*, 3440*m*, 3060*w*, 3005*s*, 2940*s*, 2880*s*, 1600*w*, 1510*w*, 1470*w*, 1425*m*, 1375*m*, 1325*m*, 1270*w*, 1210*m*, 1070*s*, 1025*m*, 950*m*, 895*w*, 860*m*, 825*m*. ^{1}H-NMR (300 MHz): 1.26 (*d*, *J* = 6.45, Me); 1.6–2.0 (*m*, H–C(6), 3 CH_2CH_2OH); 2.93 ('*dd*', *AB*, *J* = 9.87, 4.15, 1 H, OCH_2–C(2′)); 3.2–3.4 (*m*, 2 H); 3.4–3.6 (*m*, 5 H); 3.7–3.9 (*m*, 6 H); 4.02 (*qd*, *J* = 6.46, 2.57, H–C(3)); 4.72 (*d*, *J* = 9.22, H–C(1)); 7.4–7.55 (*m*, 3 arom. H); 7.75–7.9 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 17.48; 31.78; 32.35; 50.96; 61.44; 61.54; 61.89; 67.31; 67.88; 68.50; 70.02; 73.94; 81.05; 124.79; 125.99; 126.25; 126.99; 127.74; 127.87; 128.38; 128.47; 133.23; 138.32. MS: 420 (11, M^+), 397 (2), 361 (3), 344 (25), 285 (17), 268 (36), 255 (80), 241 (16), 215 (100), 197 (3), 181 (4), 167 (7), 157 (49), 141 (10), 129 (22), 115 (2), 103 (5), 71 (3), 59 (23), 45 (10), 31 (27). Anal. calc. for $C_{24}H_{36}O_6$: C 68.55, H 8.63; found: C 68.62, H 8.46.

3-{(1R,2S,3R)-3-(3-Hydroxypropyloxy)-2-[(3-hydroxypropyloxy)methyl]-1-(naphth-2-yl)butyloxy}-propan-1-ol (**16**). As described for **14**, with **13** (1.18 g, 3.2 mmol) and BH_3·THF complex (9.7 ml, 9.7 mmol, 1.0M, 3 equiv.). FC (Et_2O/MeOH 19:1) gave 0.61 g (45%) of pure **16**. $[\alpha]_D = +27.3$ ($c = 1.90$, $CHCl_3$). IR ($CHCl_3$): 3620*w*, *3460m*, 3060*w*, 3005*s*, 2950*s*, 2880*s*, 1600*w*, 1520*w*, 1475*w*, 1425*m*, 1375*m*, 1340*w*, 1325*w*, 1270*w*, 1230*m*, 1170*w*, 1070*s*, 955*w*, 895*w*, 860*m*, 825*m*. ^{1}H-NMR (300 MHz): 1.16 (*d*, $J = 6.33$, Me); 1.7–1.95 (*m*, 7 H); 2.11 (br. *s*, OH); 2.65 (br. *s*, OH); 2.89 (br. *s*, OH); 3.1–3.35 (*m*, 2 H); 3.4–3.5 (*m*, 2 H); 3.55–3.7 (*m*, 2 H); 3.7–4.0 (*m*, 9 H); 4.71 (*d*, $J = 8.49$, H–C(1)); 7.4–7.6 (*m*, 3 arom. H); 7.75–7.9 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 17.09; 31.79; 32.24; 51.34; 60.63; 61.03; 61.61; 62.19; 66.89; 68.08; 68.17; 69.89; 74.16; 81.48; 124.75; 126.02; 126.28; 126.99; 127.09; 127.74; 128.44; 128.61; 133.17; 138.18. MS: 421 (1, $[M + 1]^+$), 420 (1, M^+), 361 (7), 344 (50), 299 (2), 285 (31), 268 (70), 255 (82), 241 (49), 228 (6), 215 (100), 197 (3), 181 (5), 167 (6), 157 (40), 141 (6), 129 (15), 115 (2), 103 (4), 87 (3), 59 (11), 45 (5). Anal. calc. for $C_{24}H_{36}O_6$: C 68.55, H 8.63; found: C 68.51, H 8.72.

3-{(2R,3S,4S)-5-Methyl-4-[3-(methylsulfonyloxy)propyloxy]-3-{[3-(methylsulfonyloxy)propyloxy]-methyl}hexan-2-yloxy}propyl Methanesulfonate (**17**). To **14** (0.5 g, 1.49 mmol) in EtO (10 ml) at 0° was added Et_3N (4.2 ml, 30 mmol, 20 equiv.) and methanesulfonyl chloride (0.7 ml, 8.9 mmol, 2 equiv./OH). The mixture was stirred at r.t. for 16 h, then poured in H_2O (10 ml) and extracted with Et_2O (3 × 20 ml). The combined extract was washed with 10% HCl soln. (10 ml), sat. $NaHCO_3$ soln. (10 ml), and brine (10 ml), dried ($MgSO_4$), and evaporated and the pale yellow oil purified by FC (Et_2O/MeOH 19:1): 0.57 g (67%) of pure **17**. $[\alpha]_D = +5.0$ ($c = 2.83$, $CHCl_3$). IR ($CHCl_3$): 3010*m*, 2965*m*, 2930*m*, 2875*m*, 1470*w*, 1415*w*, 1360*s*, 1175*s*, 1100*s*, 970*s*, 950*s*, 840*m*. ^{1}H-NMR (300 MHz): 0.90 (*d*, $J = 6.86$, Me); 0.93 (*d*, $J = 6.93$, Me); 1.16 (*d*, $J = 6.37$, Me); 1.9–2.05 (*m*, 8 H); 3.02 (*s*, 3 $MeSO_2$); 3.17 (*dd*, *AB*, $J = 5.20, 3.76$, 1 H, OCH_2–C(3′)); 3.4–3.7 (*m*, 9 H); 4.33 (*t*, $J = 6.40$, CH_2OSO_2Me). ^{13}C-NMR (75 MHz): 16.28; 18.10; 19.20; 29.59; 29.95; 30.20; 31.27; 37.30; 45.28; 63.83; 66.23; 66.46; 67.44; 68.78; 75.34; 82.61. MS: 571 (< 1, $[M + 1]^+$), 527 (3), 401 (3), 373 (25), 359 (2), 373 (25), 359 (2), 345 (25), 319 (20), 279 (3), 262 (21), 249 (56), 236 (19), 223 (55), 193 (67), 167 (3), 137 (100), 109 (7), 82 (5), 59 (12), 41 (15). Anal. calc. for $C_{20}H_{42}O_{12}S_3$: C 42.09, H 7.42; found: C 42.29, H 7.42.

3-{(1S,2S,3R)-3-[3-(Methylsulfonyloxy)propyloxy]-2-{[3-(methylsulfonyloxy)propyloxy]methyl}-1-(naphth-2-yl)butyloxy}propyl Methanesulfonate (**18**). As described for **17**, with **15** (0.49 g, 1.16 mmol), Et_3N (3.2 ml, 23 mmol, 20 equiv.) and methanesulfonyl chloride (0.54 ml, 6.9 mmol, 2 equiv./OH). FC (Et_2O/MeOH 19:1) gave 0.51 g (68%) of pure **18**. Colourless oil. $[\alpha]_D = -19.4$ ($c = 1.49$, $CHCl_3$). IR ($CHCl_3$): 3010*m*, 2980*w*, 2920*w*, 2900*w*, 2890*w*, 1470*w*, 1415*w*, 1360*s*, 1340*s*, 1175*s*, 1105*m*, 970*s*, 950*s*, 890*w*, 820*m*. ^{1}H-NMR (300 MHz): 1.24 (*d*, $J = 6.47$, Me); 1.6–1.75 (*m*, 3 H); 1.9–2.1 (*m*, 4 H); 2.83 (*s*, $MeSO_2$); 2.89 (*s*, $MeSO_2$); 2.95–3.1 (*m*, 1 H); 3.04 (*s*, $MeSO_2$); 3.1–3.25 (*m*, 2 H); 3.35–3.45 (*m*, 3 H); 3.47 (*dt*, $J = 9.42, 6.02$, 1 H); 3.70 (*dt*, $J = 9.44, 5.78$, 1 H); 3.9–4.1 (*m*, 3 H); 4.25–4.5 (*m*, 5 H); 7.4–7.55 (*m*, 3 arom. H); 7.72 (br. *s*, 1 arom. H); 7.8–7.9 (*m*, 3 arom. H). ^{13}C-NMR (75 MHz): 18.16; 29.27; 29.72; 30.04; 37.03; 37.25; 37.36; 51.10; 64.09; 64.35; 65.84; 67.26; 67.37; 67.58; 67.72; 73.52; 81.58; 125.15; 125.98; 126.22; 127.02; 127.70; 127.83; 128.19; 133.04; 133.17; 138.39. MS (FAB): 654 (42, M^+), 587 (7), 529 (6), 501 (25), 399 (5), 333 (24), 293 (39), 181 (40), 137 (100), 109 (8), 78 (13). Anal. calc. for $C_{27}H_{42}O_{12}S_3$: C 49.52, H 6.46; found: C 49.47, H 6.57.

*(2Z)-1-[(*tert*-Butyl)dimethylsilyloxy]-4-{(1S,2S,3R)-3-{(2Z)-4-[(*tert*-butyl)dimethylsilyloxy]but-2-enyloxy}-2-{3-{(2Z)-4-[(*tert*-butyl)dimethylsilyloxy]but-2-enyloxy}methyl}-1-(naphth-2-yl)butyloxy}but-2-ene* (**19**). As described for **11**, with **8** [4] (0.18 g, 0.71 mmol), NaH (85 mg, 3.6 mmol, 5 equiv.), and (*Z*)-1-bromo-4-[(*tert*-butyl)dimethylsilyloxy]but-2-ene (0.84 g, 3.6 mmol, 5 equiv.). FC (hexane/Et_2O 10:1) gave 0.30 g (52%) of pure **19**. Pale yellow oil. $[\alpha]_D = -13.4$ ($c = 1.95$, $CHCl_3$). IR ($CHCl_3$): 3000*m*, 2980*s*, 2965*s*, 2880*s*, 2860*s*, 1470*m*, 1460*m*, 1410*w*, 1390*w*, 1375*w*, 1360*m*, 1330*w*, 1255*s*, 1075*s*, 1010*m*, 890*s*. ^{1}H-NMR (300 MHz): −0.65 (*s*, MeSi); −0.13 (*s*, MeSi); 0.10 (*s*, MeSi); 0.81 (*s*, *t*-BuSi); 0.85 (*s*, *t*-BuSi); 0.92 (*s*, *t*-BuSi); 1.26 (*d*, $J = 6.50$, Me); 2.0–2.1 (*m*, H–C(2′)); 3.14 (*dd*, $J = 9.79, 4.49$, 1 H); 3.39 (*dd*, $J = 9.77, 4.87$, 1 H); 3.5–3.7 (*m*, 2 H); 3.75–3.95 (*m*, 2 H); 3.95–4.1 (*m*, 7 H); 4.21 (*dd*, $J = 12.74, 4.80$, 1 H); 4.29 (*d*, $J = 4.15$, 1 H); 4.47 (*d*, $J = 9.14$, H–C(8)); 5.1–5.25 (*m*, 1 H); 5.35–5.5 (*m*, 1 H); 5.55–5.7 (*m*, 4 H); 7.45–7.55 (*m*, 3 arom. H); 7.72 (br. *s*, 1 arom. H); 7.75–7.9 (*m*, 3 arom. H). ^{13}C-NMR (75 MHz): −5.33; −5.15; 18.25; 25.86; 51.18; 59.34; 59.43; 59.66; 64.39; 64.94; 66.39; 67.23; 73.00; 80.74; 125.37; 125.75; 125.98; 126.88; 127.05; 127.19; 127.65; 127.80; 127.96; 128.06; 131.62; 131.69; 132.37; 133.04; 133.17; 138.42. MS: 798 (10, $[M - 1]^+$), 742 (3), 613 (17), 539 (14), 464 (8), 421 (4), 395 (20), 341 (4), 285 (19), 259 (85), 219 (3), 185 (100), 141 (7), 115 (11), 73 (29), 41 (5). Anal. calc. for $C_{45}H_{72}O_6Si_3$: C 67.62, H 9.84; found: C 67.74, H 9.71.

1-{{(2R,3S,4R)-4-(Benzyloxy)-3-[(benzyloxy)methyl]-5,5-dimethylhexan-2-yloxy}methyl}benzene (= *(3R,4S,5R)-3,5-Bis(benzyloxy)-4-[(benzyloxy)methyl]-2,2-dimethylhexane*; **20**). As described for **11** with **4** [4] (0.59 g, 3.35 mmol) NaH (0.72 g, 30 mmol, 9 equiv.) and benzyl bromide (3.6 ml, 30 mmol, 9 equiv.). FC (hexane/Et_2O 19:1) gave 1.22 g (82%) of pure **20**. An anal. pure sample was obtained from a short-path distillation. B.p. 250°/0.1 Torr. $[\alpha]_D = +10.7$ ($c = 2.66$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3060*m*, 3030*m*, 2960*s*, 2870*s*, 1605*w*,

1495*m*, 1455*s*, 1360*s*, 1305*w*, 1245*w*, 1205*w*, 1155*w*, 1100*s*, 1030*m*, 905*w*, 735*s*, 695*s*. ^{1}H-NMR (300 MHz): 0.95 (*s*, *t*-Bu); 1.28 (*d*, *J* = 6.44, Me); 2.25–2.35 (*m*, H–C(3′)); 3.20 (*d*, *J* = 2.12, H–C(4′)); 3.57 (*'dd'*, *AB*, *J* = 10.11, 8.60, 1 H, OCH_2–C(3′)); 3.72 (*qd*, *J* = 6.51, 3.80, H–C(2′)); 3.79 (*'dd'*, *AB*, *J* = 10.13, 3.58, 1 H, OCH_2–C(3′)); 4.3–4.7 (*m*, 3 PhCH_2); 7.1–7.4 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz): 16.64; 26.35; 37.45; 44.87; 68.30; 70.82; 72.16; 73.09; 73.86; 76.27; 86.30; 126.94; 127.32; 127.61; 127.77; 128.10; 128.25; 128.42; 138.97; 139.10; 139.66. MS: 447 (3, $[M + 1]^+$), 389 (5), 355 (1), 338 (0.5), 281 (2), 259 (2), 247 (2), 203 (2), 181 (15), 161 (3), 147 (12), 135 (3), 107 (4), 91 (100), 57 (3). Anal. calc. for $C_{30}H_{38}O_3$: C 80.68, H 8.58; found: C 80.69, H 8.52.

*3-{4-{{(2*R*,3*S*,4*R*)-5,5-Dimethyl-4-[4-(prop-2-enyloxy)benzyloxy]-3-{[4-(prop-2-enyloxy)benzyloxy]methyl}hexan-2-yloxy}methyl}phenyloxy}prop-1-ene* (**21**). As described for **11** with **4** [4] (0.50 g, 2.84 mmol), NaH (0.61 g, 26 mmol, 9 equiv.), and 4-(prop-2-enyloxy)benzyl bromide (2.25 g, 9.9 mmol, 3.5 equiv.). FC (hexane/Et_2O 4:1) gave 1.21 g (70%) of pure **21**. Pale yellow oil. $[\alpha]_D$ = +18.0 (*c* = 2.34, $CHCl_3$). IR ($CHCl_3$): 3005*m*, 2965*s*, 2870*s*, 1880*w*, 1650*w*, 1610*s*, 1585*m*, 1510*s*, 1465*m*, 1425*m*, 1365*m*, 1300*m*, 1250*s*, 1175*s*, 1100*s*, 1025*s*, 1000*s*, 930*s*, 830*s*. ^{1}H-NMR (300 MHz): 0.92 (*s*, *t*-Bu); 1.25 (*d*, *J* = 6.41, Me); 2.2–2.3 (*m*, H–C(3′)); 3.15 (*d*, *J* = 1.92, H–C(4′)); 3.52 (*'dd'*, *AB*, *J* = 10.03, 8.61, 1 H, OCH_2–C(3′)); 3.6–3.8 (*m*, H–C(2′), 1 H of OCH_2–C(3′)); 4.25–4.5 (*m*, 4 H); 4.5–4.6 (*m*, 8 H); 5.2–5.5 (*m*, 6 H); 5.9–6.2 (*m*, 3 H); 6.8–6.95 (*m*, 6 arom. H); 7.1–7.3 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz): 16.70; 26.36; 37.39; 44.77; 68.07; 68.85; 70.38; 71.53; 72.67; 73.55; 75.91; 86.09; 114.40; 114.53; 114.69; 117.55; 128.50; 129.12; 129.26; 129.38; 130.71; 131.34; 131.43; 132.04; 133.40; 157.78; 158.02; 158.23. MS: 614 (< 1, M^+), 585 (1), 564 (2), 507 (1), 467 (4), 381 (1), 319 (8), 293 (3), 263 (2), 247 (1), 187 (20), 147 (100), 107 (11), 91 (4), 41 (23). Anal. calc. for $C_{39}H_{50}O_6$: C 76.19, H 8.20; found: C 76.31, H 8.19.

*1-(Methoxyethoxymethoxy)-4-{{(2*R*,3*S*,4*R*)-4-[4-(methoxyethoxymethoxy)benzyloxy]-3-{[4-(methoxyethoxymethoxy)benzyloxy]methyl}-5,5-dimethylhexan-2-yloxy}methyl}benzene* (= *(3*R*,4*S*,5*R*)-3,5-Bis[4-(methoxyethoxymethoxy)benzyloxy]-4-{[4-(methoxyethoxymethoxy)benzyloxy]methyl}-2,2-dimethylhexane*; **22**). As described for **11**, with **4** (0.35 g, 1.96 mmol), NaH (0.42 g, 17.7 mmol, 9 equiv.), and 4-(methoxyethoxymethoxy benzyl bromide (1.89 g, 6.9 mmol, 3.5 equiv.). FC (hexane/Et_2O 1:3) gave 1.45 g (99%) of pure **22**. Colourless oil. $[\alpha]_D$ = +13.1 (*c* = 2.34, $CHCl_3$). IR ($CHCl_3$): 3005*m*, 2930*m*, 2895*m*, 1610*m*, 1590*w*, 1510*s*, 1455*w*, 1365*w*, 1305*w*, 1250*m*, 1165*m*, 1100*s*, 1010*s*, 850*m*. ^{1}H-NMR (300 MHz): 0.92 (*s*, *t*-Bu); 1.26 (*d*, *J* = 6.41, Me); 2.2–2.3 (*m*, H–C(3′)); 3.16 (*d*, *J* = 1.92, H–C(4′)); 3.37 (*s*, 6 H); 3.38 (*s*, 3 H); 3.5–3.6 (*m*, 7 H); 3.65–3.8 (*m*, 2 H); 3.8–3.9 (*m*, 6 H); 4.3–4.6 (*m*, 3 ArCH_2); 5.26 (*s*, 6 H); 6.9–7.05 (*m*, 6 arom. H); 7.1–7.3 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz): 16.67; 26.34; 37.39; 44.73; 58.98; 67.59; 68.14; 70.37; 71.64; 72.64; 73.48; 76.00; 86.04; 93.56; 115.95; 116.05; 128.42; 129.03; 129.19; 132.40; 132.49; 133.10; 156.41; 156.67. MS: 757 (< 1, $[M - 1]^+$), 697 (< 1), 651 (< 1), 563 (5), 457 (5), 367 (13), 311 (4), 263 (1), 195 (100), 107 (13), 89 (94), 59 (52). Anal. calc. for $C_{42}H_{62}O_{12}$: C 66.47, H 8.23; found: C 66.49, H 8.28.

*(7*R*,8*S*,9*R*)-8-{[3-(Benzyloxy)propyloxy]methyl}-7-methyl-9-(naphth-2-yl)-1,15-diphenyl-2,6,10,14-tetraoxapentadecan* (**23**). As described for **11**, with **16** (0.51 g, 1.22 mmol), NaH (0.26 g, 11 mmol, 9 equiv.), and benzyl bromide (0.51 ml, 4.3 mmol, 3.5 equiv.). FC (hexane/Et_2O 3:1) gave 0.69 g (82%) of pure **23**. Colourless oil. $[\alpha]_D$ = +18.4 (*c* = 3.68, $CHCl_3$). IR ($CHCl_3$): 3065*w*, 3005*m*, 2925*m*, 2865*s*, 1495*w*, 1455*m*, 1365*m*, 1095*s*, 1025*w*, 950*w*, 860*w*, 825*w*. ^{1}H-NMR (300 MHz): 1.13 (*d*, *J* = 6.43, Me); 1.75–1.9 (*m*, 6 H); 2.05–2.15 (*m*, H–C(8)); 3.15–3.2 (*m*, H–C(7)); 3.25–3.75 (*m*, 14 H); 4.45–4.5 (*m*, 3 PhCH_2); 4.52 (*d*, *J* = 6.36, H–C(9)); 7.2–7.35 (*m*, 15 arom. H); 7.35–7.5 (*m*, 3 arom. H); 7.68 (*s*, 1 arom. H); 7.7–7.85 (*m*, 3 arom. H). ^{13}C-NMR (75 MHz): 16.90; 30.20; 30.37; 30.59; 50.70; 65.03; 65.97; 67.59; 67.67; 72.94; 73.87; 80.51; 125.16; 125.60; 125.96; 126.06; 127.46; 127.60; 127.84; 127.93; 128.08; 128.33; 128.46; 132.92; 133.20; 138.55; 138.65; 139.41. MS: 690 (< 1, M^+), 524 (< 1), 433 (< 1), 417 (1), 391 (< 1), 375 (1), 359 (1), 345 (3), 331 (4), 305 (17), 231 (10), 215 (6), 193 (35), 165 (12), 141 (28), 107 (13), 91 (100), 71 (19). Anal. calc. for $C_{45}H_{54}O_6$: C 78.23, H 7.88; found: C 78.01, H 7.79.

*Methyl 4-{{(2*R*,3*S*,4*S*)-4-[4-(Methoxycarbonyl)benzyloxy]-3-{[4-(methoxycarbonyl)benzyloxy]methyl}-5-methylhexan-2-yloxy}methyl}benzoate* (**24**). As for **11**, with **3** [4] (0.5 g, 3.1 mmol), NaH (0.48 g, 20 mmol, 6.5 equiv.), and 4-bromobenzoic acid (1.95 g, 20 mmol, 6.5 equiv.). The crude product obtained was diluted in Et_2O (50 ml), and treated with a diazomethane soln. until the soln. turned yellow. The mixture was allowed to stand overnight and then carefully evaporated. FC (hexane/Et_2O 2:1) gave 0.56 g (30%) of pure **24**. Pale yellow oil. $[\alpha]_D$ = +16.6 (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 2955*w*, 1720*s*, 1615*w*, 1600*w*, 1435*m*, 1415*w*, 1285*s*, 1175*w*, 1110*s*, 1020*m*, 965*w*, 850*w*. ^{1}H-NMR (300 MHz): 0.97 (*d*, *J* = 6.80, 2 Me–C(5′)); 1.25 (*d*, *J* = 6.39, Me(1′)); 2.07 (*m*, H–C(5′)); 2.24 (*m*, H–C(3′)); 3.48 (*dd*, *J* = 5.10, 3.59, H–C(4′)); 3.63 (*dd*, *J* = 9.75, 7.51, 1 H, OCH_2–C(3′)); 3.75–3.85 (*m*, 3 H); 3.91 (*s*, 3 MeO); 4.45–4.65 (*m*, 3 ArCH_2); 7.25–7.4 (*m*, 6 arom. H); 7.9–8.1 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz): 16.48; 18.16; 19.29; 31.46; 45.36; 52.02; 68.62; 70.01; 72.51; 72.66; 75.29; 83.09; 126.66; 126.79; 127.04; 129.09; 129.28; 129.57; 129.64; 144.01; 144.33; 144.47; 166.97. MS: 607 (< 1, $[M + 1]^+$), 575 (2), 297 (2), 221 (4), 165 (5), 150 (18), 149 (100), 121 (9), 90 (5), 27 (9). Anal. calc. for $C_{35}H_{42}O_9$: C 69.29, H 6.98; found: C 68.94, H 7.02.

4-{{(2R,3S,4S)-4-[4-(Hydroxymethyl)benzyloxy]-3-{[4-(hydroxymethyl)benzyloxy]methyl}-5-methylhexan-2-yloxy}methyl}benzyl Alcohol (**25**). As for **5**, with **24** (0.15 g, 0.25 mmol) and $LiAlH_4$ (0.95 g, 2.5 mmol, 10 equiv.). FC (CH_2Cl_2/MeOH 9:1) gave 0.105 g (81%) of pure **25**. Colourless oil. $[\alpha]_D = +11.1$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3600*m*, 3405*m*, 3005*m*, 2960*m*, 2930*m*, 2875*m*, 1670*m*, 1515*w*, 1465*w*, 1420*m*, 1385*m*, 1275*w*, 1085*s*, 1015*s*, 720*s*. ^{1}H-NMR (300 MHz): 0.97 (*d*, $J = 6.80$, 2 Me–C(5′)); 1.24 (*d*, $J = 6.40$, Me(1′)); 1.6–2.0 (br. *s*, 3 OH); 2.05 (*m*, H–C(5′)); 2.22 (*m*, H–C(3′)); 3.43 (*dd*, $J = 5.17$, 3.82, H–C(4′)); 3.60 (*dd*, $J = 9.79$, 7.44, 1 H, OCH_2–C(3′)); 3.76 (*m*, 3 H); 4.4–4.6 (*m*, 3 ArCH_2); 4.65 (*s*, 1 ArCH_2); 4.66 (*s*, 2 ArCH_2); 7.2–7.4 (*m*, 12 arom. H). ^{13}C-NMR (75 MHz): 16.63; 18.22; 19.45; 31.49; 45.28; 65.16; 68.40; 70.18; 72.73; 73.02; 74.77; 82.86; 126.93; 127.41; 127.52; 127.77; 127.88; 138.28; 138.58; 138.80; 139.84; 140.00. MS: 523 (11, $[M + 1]^+$), 263 (3), 241 (6), 155 (6), 154 (19), 137 (21), 136 (19), 122 (21), 121 (100), 120 (13), 119 (15), 107 (11), 105 (21), 104 (25), 93 (13), 90 (26), 76 (19). Anal. calc. for $C_{32}H_{42}O_6$: C 73.53, H 8.10; found: C 73.39, H 7.88.

1-Bromo-4-{{(2R,3S,4S,5E)-4-(4-Bromobenzyloxy)-3-[(4-bromobenzyloxy)methyl]-6-phenylhex-5-en-2-yloxy}methyl}benzene (= *(3S,4S,5R,1E)-3,5-Bis(4-bromobenzyloxy)-4-[(4-bromobenzyloxy)methyl]-1-phenylhex-1-ene*; **26**). As for **11**, with **6** (0.5 g, 2.25 mmol), NaH (0.35 g, 15.0 mmol, 6.7 equiv.), and 4-bromobenzyl bromide (1.97 g, 7.9 mmol, 3.5 equiv.). FC (CH_2Cl_2/hexane 2:1) gave 1.5 g (91%) of pure **26**. Yellow oil. $[\alpha]_D = -44.5$ ($c = 2.30$, $CHCl_3$). IR ($CHCl_3$): 3010*w*, 2870*m*, 1700*w*, 1595*m*, 1480*s*, 1360*w*, 1070*s*, 1015*s*, 970*m*, 840*m*, 635*w*. ^{1}H-NMR (300 MHz): 1.28 (*d*, $J = 6.42$, H–C(1′)); 1.97 (*m*, H–C(3′)); 3.45 (*'dd'*, *AB*, $J = 9.69$, 5.62, 1 H, OCH_2–C(3′)); 3.73 (*'dd'*, *AB*, $J = 9.70$, 3.94, 1 H, OCH_2–C(3′)); 3.9–4.05 (*m*, H–C(2′), H–C(4′)); 4.17 (*d*, $J = 12.00$, 1 H, ArCH_2); 4.19 (*d*, $J = 11.90$, 1 H, ArCH_2); 4.26 (*d*, $J = 11.96$, 1 H, ArCH_2); 4.34 (*d*, $J = 11.98$, 1 H, ArCH_2); 4.49 (*d*, $J = 10.44$, 1 H, ArCH_2); 4.53 (*d*, $J = 11.84$, 1 H, ArCH_2); 6.18 (*dd*, $J = 15.94$, 8.71, H–C(5′)); 6.50 (*d*, $J = 15.95$, H–C(6′)); 7.05–7.15 (*m*, 6 arom. H); 7.25–7.45 (*m*, 11 arom. H). ^{13}C-NMR (75 MHz): 17.99; 50.29; 67.55; 69.37; 70.11; 72.31; 73.15; 80.02; 121.23; 121.36; 126.57; 127.86; 128.67; 129.12; 129.23; 129.45; 131.32; 131.45; 133.10; 136.54; 137.51; 137.67. MS: 729 (< 1, M^+), 563 (3), 559 (7), 373 (7), 303 (24), 187 (11), 185 (10), 172 (20), 171 (100), 169 (99), 143 (10), 131 (12), 90 (9). Anal. calc. for $C_{34}H_{33}Br_3O_3$: C 55.95, H 4.52; found: C 56.02, H 4.48.

(1R,2S,3R)-1-(Naphth-2-yl)-3-(pent-4-enoyloxy)-2-[(pent-4-enoyloxy)methyl]butyl Pent-4-enoate (**27**). To a soln. of **7** [4] (0.25 g, 1.02 mmol) in pyridine (25 ml) was added pent-4-enoyl chloride (1.2 g, 10.2 mmol, 10 equiv.). The mixture was kept at r.t. for 1 h, then heated at 80° for 6 h. After being cooled at 0°, H_2O (50 ml) was added slowly and then the mixture acidified to pH 1 with conc. HCl soln. A continuous extraction with Et_2O (500 ml) for 2 days gave an orange liquid. FC (hexane/Et_2O 2:1) yielded 0.26 g (52%) of pure **27**. B.p. *ca.* 250°/0.5 Torr (dec.). $[\alpha]_D = +17.9$ ($c = 2.00$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3070*w*, 3000*w*, 2990*w*, 2910*w*, 1730*s*, 1640*w*, 1570*w*, 1440*w*, 1415*w*, 1360*w*, 1230*m*, 1170*s*, 1125*m*, 1100*m*, 995*m*, 920*m*, 860*w*, 820*w*. ^{1}H-NMR (300 MHz): 1.26 (*d*, $J = 6.51$, Me); 2.05–2.25 (*m*, 4 H); 2.3–2.7 (*m*, 11 H); 4.36 (*m*, H–C(4)); 4.9–5.1 (*m*, 6 H); 5.6–5.9 (*m*, 3 H); 7.3–7.55 (*m*, 3 arom. H); 7.7–7.9 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 18.19; 28.62; 28.71; 33.49; 33.68; 47.81; 60.60; 68.55; 73.75; 115.28; 115.58; 115.76; 116.18; 116.35; 116.46; 124.08; 125.79; 126.31; 126.44; 127.67; 128.03; 128.42; 135.76; 136.38; 136.54; 171.76; 171.87; 172.80. MS: 492 (1, M^+), 409 (1), 392 (2), 309 (3), 293 (1), 266 (< 1), 239 (2), 210 (11), 193 (25), 167 (17), 155 (100), 127 (6), 100 (7), 83 (39), 55 (88). Anal. calc. for $C_{30}H_{36}O_6$: C 73.15, H 7.37; found: C 73.04, H 7.46.

(2S,3S,4R)-4-(3,5-Dinitrobenzyloxy)-3-[(3,5-dinitrobenzoyloxy)methyl]-1,1-diphenylpentan-2-yl 3,5-Dinitrobenzoate (**29**). To a soln. of **5** (0.40 g, 1.4 mmol) in pyridine (20 ml) was added 3,5-dinitrobenzoyl chloride (1.15 g, 4.9 mmol, 3.5 equiv.) at 0°. The mixture was kept at 0° for 2 h, then at r.t. for 18 h. The mixture was poured into ice and acidified with 10% HCl soln. The precipitate was filtered off, washed with H_2O and dried *in vacuo*. FC (CH_2Cl_2) gave, after drying at 100°/h.v. (dec. of the inclusion compound), 1.25 g (95%) of pure **29**. M.p. > 125° (→glassy solid slowly melting at 150–180°). $[\alpha]_D = -95.3$ ($c = 2.30$, acetone). IR ($CHCl_3$): 3100*m*, 3035*w*, 1735*s*, 1630*m*, 1600*w*, 1550*s*, 1495*w*, 1460*w*, 1345*s*, 1270*s*, 1160*s*, 1105*w*, 1075*m*, 980*w*, 925*m*. ^{1}H-NMR (400 MHz): 1.63 (*d*, $J = 6.40$, H–C(5)); 2.76 (*m*, H–C(3)); 4.70 (*d*, $J = 11.00$, H–C(1)); 4.85 (*'dd'*, *AB*, $J = 12.15$, 4.67, 1 H, OCH_2–C(3)); 5.03 (*'dd'*, *AB*, $J = 12.14$, 4.67, 1 H, OCH_2–C(3)); 5.56 (*quint.*, $J = 6.36$, H–C(4)); 6.44 (*dd*, $J = 11.02$, 1.84, H–C(2)); 7.0–7.5 (*m*, 10 arom. H); 8.65 (*d*, $J = 2.13$, 2 arom. H); 8.98 (*d*, $J = 2.13$, 2 arom. H); 9.05 (*d*, $J = 2.11$, 1 arom. H); 9.06 (*d*, $J = 2.12$, 1 arom. H); 9.09 (*m*, 1 arom. H); 9.18 (*m*, 1 arom. H); 9.22 (*m*, 1 arom. H). ^{13}C-NMR (75 MHz): 18.21; 44.90; 55.67; 62.29; 72.80; 76.59; 122.68; 122.89; 127.54; 128.01; 128.09; 128.15; 128.88; 128.92; 129.24; 129.28; 129.59; 132.54; 132.91; 133.35; 139.15; 139.44; 148.46; 148.63; 148.76; 161.74; 162.08; 162.42. MS: 701 (1), 233 (2), 232 (8), 195 (16), 168 (15), 167 (100), 152 (5), 119 (4). Anal. calc. for $C_{39}H_{28}N_6O_{18}$: C 53.92, H 3.25, N 9.67; found: C 53.97, H 3.46, N 9.49.

(2R,3S,4S)-4-(3,5-Dinitrobenzyloxy)-3-[(3,5-dinitrobenzoyloxy)methyl]-5-methylhexan-2-yl 3,5-Dinitrobenzoate (**28**). As described for **29** with **3** [4] (1.5 g, 9.2 mmol) and 3,5-dinitrobenzoyl chloride (7.4 g, 32 mmol, 3.5 equiv.). FC (CH_2Cl_2) gave, after drying at 100°/h.v., 6.55 g (96%) of pure **28**. White solid. M.p. 185–190°.

$[\alpha]_D = -16.7$ ($c = 3.05$, acetone). IR ($CHCl_3$): 3100*m*, 2970*w*, 2885*w*, 1735*s*, 1630*m*, 1550*s*, 1460*m*, 1345*s*, 1270*s*, 1265*s*, 1075*m*, 925*m*, 825*w*. ^{1}H-NMR (300 MHz): 1.08 (*d*, $J = 6.61$, 1 Me–C(5)); 1.14 (*d*, $J = 6.70$, 1 Me–C(5)); 1.65 (*d*, $J = 6.42$, Me(1)); 2.39 (*m*, H–C(5)); 2.81 (*quint.* $J = 4.90$, H–C(3)); 4.78 (*'dd'*, *AB*, $J = 12.03$, 5.01, 1 H, OCH_2–C(3)); 4.90 (*'dd'*, *AB*, $J = 12.00$, 4.52, 1 H, OCH_2–C(3)); 5.47 (*dd*, $J = 7.01$, 4.35, H–C(4)); 5.58 (*quint.*, $J = 6.22$, H–C(2)); 9.05–9.1 (*m*, 6 arom. H); 9.15–9.25 (*m*, 3 arom. H). ^{13}C-NMR (75 MHz): 17.87; 18.22; 19.48; 31.10; 44.51; 62.78; 72.57; 79.21; 122.78; 122.88; 129.27; 129.55; 132.99; 133.33; 148.87; 161.89; 162.27; 162.49. MS: 744 (< 1, M^+), 701 (6), 195 (12), 194 (100), 148 (19), 108 (4), 102 (4), 75 (17), 48 (12), 27 (14). Anal. calc. for $C_{29}H_{24}N_6O_{18}$: C 46.78, H 3.25, N 11.29; found: C 46.97, H 3.18, N 11.21.

*(2*R*,3*S*,4*S*)-4-(3,5-Diaminobenzoyloxy)-3-[(3,5-diaminobenzoyloxy)methyl]-5-methylhexan-2-yl 3,5-Diaminobenzoate* (**30**). A mixture of **28** (1.2 g, 1.6 mmol) and PtO_2(aq) (*Adam*'s catalyst, 0.14 g) in dioxane (40 ml) was vigourously stirred under a static H_2 atmosphere at r.t. for 16 h. Filtration and evaporation of the filtrate gave, after drying at 100°/h.v. for 6 h, an inclusion compound (clathrate) of pure **30** with 1,4-dioxane in a ratio of 2:1 in quant. yield. M.p. > 185° (dec.). $[\alpha]_D = 0$ ($c = 1.25$, $CHCl_3$). IR (KBr): 3435*s*, 3360*s*, 3235*w*, 2975*w*, 1700*s*, 1620*s*, 1600*s*, 1465*m*, 1370*s*, 1230*s*, 1195*m*, 1100*m*, 985*w*, 850*w*, 765*m*, 705*w*. ^{1}H-NMR (300 MHz, (D_6)acetone): 0.95 (*d*, $J = 6.27$, 1 Me–C(5)); 1.00 (*d*, $J = 6.66$, 1 Me–C(5)); 1.41 (*d*, $J = 6.41$, H–C(1)); 2.22 (*m*, H–C(5)); 2.56 (*quint.*, $J = 5.12$, H–C(3)); 4.4–4.7 (*m*, 15 H); 5.25–5.35 (*m*, H–C(2), H–C(4)); 6.2–6.25 (*m*, 3 arom. H); 6.65 (*d*, $J = 1.96$, 2 arom. H); 6.67 (*d*, $J = 1.97$, 2 arom. H); 6.70 (*d*, $J = 1.90$, 2 arom. H). ^{13}C-NMR (75 MHz): 17.70; 18.22; 19.86; 31.75; 45.31; 62.31; 70.79; 76.84; 105.53; 106.01; 132.55; 132.74; 150.04; 167.01; 167.39; 167.60. MS: 565 (4, $[M + 1]^+$), 564 (11, M^+), 412 (9), 153 (18), 152 (100), 136 (8), 135 (44), 124 (5), 108 (12), 107 (31), 80 (12). Anal. calc. for $C_{29}H_{36}N_6O_6 \cdot$ dioxane (2:1): C 61.17, H 6.62, N 13.81; found: C 60.87, H 6.99, N 13.33.

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