Bidirectional and Convergent Routes to Oligo(tetrahydrofurans)

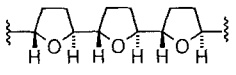
Ulrich Koert,* Matthias Stein and Holger Wagner

Abstract: Oligo(tetrahydrofurans) (oligo-THFs) **8**–**12** have been synthesised stereoselectively. Multiple Williamson reactions were used as key steps. While oligo-THFs with an even number of THF rings like the bi-THFs **8** and **9** as well as the tetra-THFs **10** and **11** were obtained by a bidirectional strategy, the penta-THF **12** with an odd number of THF rings was prepared by a convergent strategy with a sulfone–aldehyde coupling as connecting step. The oligo-THF products are important structural features of natural (Annonaceae acetogenins) and non-natural (artificial ion channels) products.

Keywords
oligomers · polyethers · tetrahydrofurans · Williamson reaction

Introduction

2,5-Connected oligo(tetrahydrofurans) (oligo-THFs) of type **1** are key structural features of natural and non-natural products.[1] The annonaceous acetogenins, a class of natural products with remarkable antitumor, immunosuppressive, antimalarial and pesticidal properties, include a large number of compounds with a bi-THF skeleton.[2] Recently the isolation of goniocin **2**, the first tri-THF acetogenin, has been reported.[3] Of the non-natural products, oligo-THFs and oligo-THF amino acids such as **3** are important building blocks for oligo-THF



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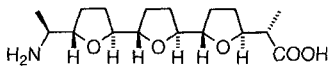

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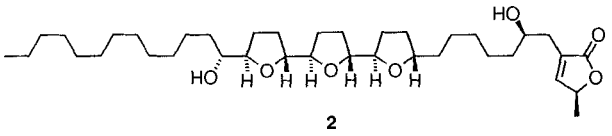

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peptides, which can be inserted into membranes and show channel-like cation-transport behaviour.[4] The key to the bioactivity of the oligo-THF compounds lies in their stereostructure. For example, one of the preferred conformations in the all-*trans*-*threo*-*trans* series is helical.[4]

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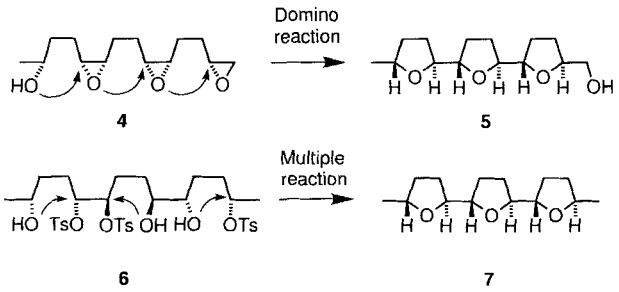
While several synthetic approaches to bi-THFs are already known,[5] routes to larger oligo-THFs are rare. Domino-type[6] intramolecular openings of epoxides[7] (**4** → **5**) or cyclic sulfates[8] have been reported (Scheme 1). Direct oxidative cyclisation routes are a useful approach to oligo-THFs.[9]



4 **5** **6** **7**

Scheme 1. Domino-type epoxide opening and multiple Williamson reaction: two alternative approaches to oligo-THFs.

We envisioned the intramolecular multiple Williamson ether reaction (**6** → **7**) as a key reaction for the construction of the oligo-THF framework.[10] Here we provide a full account of the use of the intramolecular Williamson reaction in bidirectional and convergent strategies that lead stereoselectively to oligo-THFs of type **8**–**12**.[11]

Results and Discussion

Target molecules **8**–**11** with an even number of THF rings were chosen to test the bidirectional strategy, while compound **12** with an odd number of THF rings was adressed by the convergent strategy. Starting point for the bidirectional approach was the enantiomerically pure bromide **13**.[12] Alkylation of dilithium diacetylide, prepared from the ethylenediamine complex of lithium actetylide and lithium amide, with two equiva-

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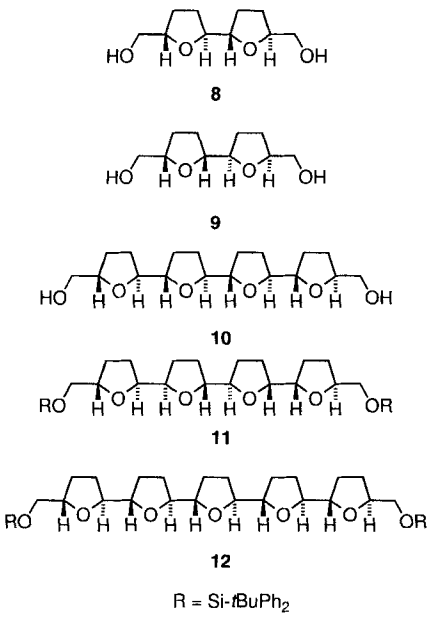
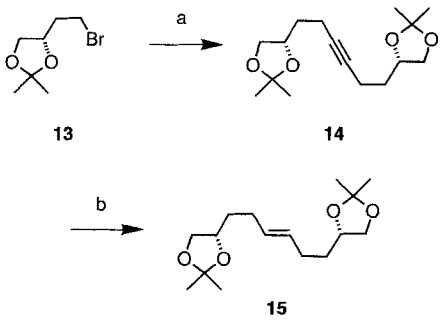


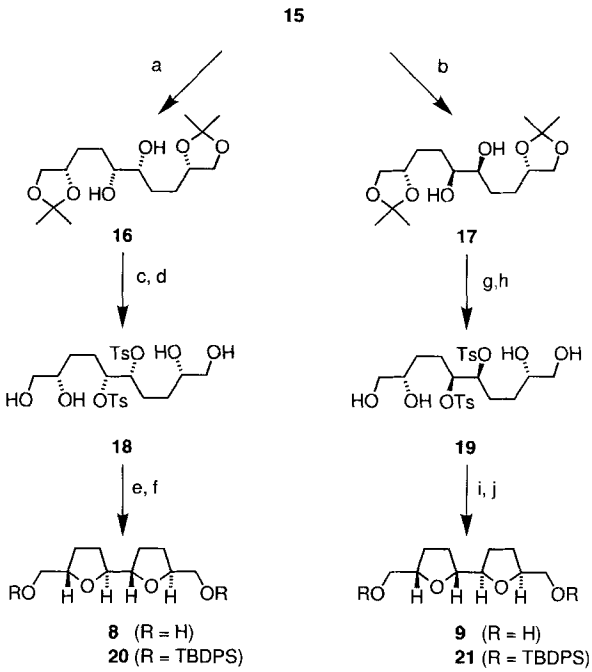
lents of **13** gave the disubstituted acetylene **14** in 41% yield (Scheme 2). A subsequent reduction with sodium in liquid NH_3[13] provided the (*E*)-alkene **15** in 90% yield.



Scheme 2. Synthesis of the olefin **15**. a) 1.2 equiv $LiNH_2$, NH_3, −33 °C, then 1.0 equiv lithium actetylide ethylenediamine complex, then 2.0 equiv **13**, −33 °C, 3 h (41%); b) 2.4 equiv Na, NH_3/THF (1/1), −33 °C, 2 h (90%).

By a diastereoselective Sharpless dihydroxylation,[14] the olefin **15** was converted with AD-mix-β (asymmetric dihydroxylation) to diol **16** and, with the corresponding AD-mix-α, to the diol **17** (Scheme 3). In both reactions a stereoselectivity of 9:1 was observed. These complementary results show that reagent control by the Sharpless catalyst is solely responsible for the stereoselectivity. This observation was supported by a control experiment in which the olefin **15** was dihydroxylated in the absence of a chiral ligand: use of OsO_4/*N*-methylmorpholine-*N*-oxide gave a 1:1 ratio of **16** and **17**. The two chiral centres of **15**, therefore, had no stereocontrolling influence on the dihydroxylation process.

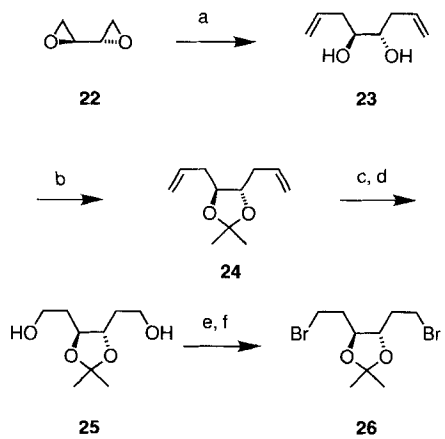
Ditosylation of the diol **16** followed by double acetonide cleavage gave the tetrahydroxyditosylate **18**, which was subjected to a multiple Williamson reaction with NaH as base. The resulting hydrophilic bi-THF-diol **8** was isolated as its lipophilic bis(*tert*-butyldiphenylsilyl) ether **20**. The overall yield from **16** to **20** was 52%. By the same route, the diol **17** was transformed into the bi-THF **21** via the tetrahydroxyditosylate **19**. The rela-



Scheme 3. Multiple Williamson routes to the bi-THFs **20** and **21**. a) 1 equiv AD-mix-β, *t*BuOH/H_2O 1/1, 0–20 °C, 12 h (98%); b) 1 equiv AD-mix-α, *t*BuOH/H_2O 1/1, 0–20 °C, 12 h (84%); c) 8 equiv *p*-TsCl, pyridine (83%); d) AcOH/H_2O 10/1, 40 °C, 8 h; e) 8 equiv NaH, THF, 3 h, 40 °C (71%, from **16**); f) TBDPSCl, imidazole, DMF (89%); g) 8 equiv *p*TsCl, pyridine (86%); h) AcOH/H_2O 10/1, 40 °C, 6 h; i) 8 equiv NaH, THF, 3 h, 40 °C (58%, from **17**); j) TBDPSCl, imidazole, DMF (92%). TBDPS = *t*$BuPh_2Si$.

tive configurations of the bi-THFs **8** and **9** correspond to the bi-THF core of several annonaceous acetogenins.[2] For example, the *trans-threo-trans* pattern of **8** is found in bullatacin, while the *cis-threo-cis* pattern of **9** corresponds to rolliniastatin 1. Since both initial bromide enantiomers **13** and *ent*-**13** can be combined with AD-mix-α and AD-mix-β, a wide variety of bi-THFs can be synthesised by this modular approach.

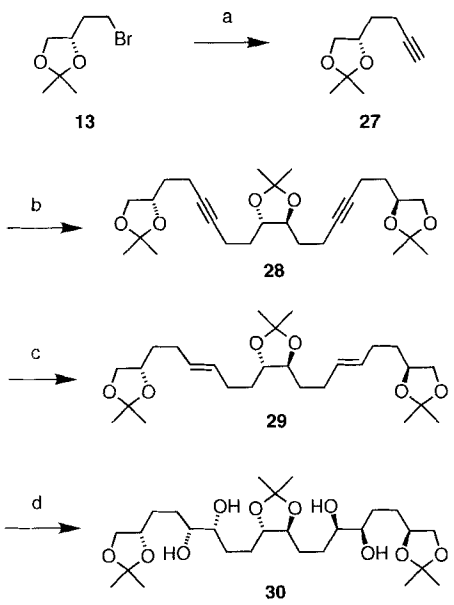
For a bidirectional synthesis of the tetra-THF **10**, a central bifunctional dibromide **26** was required. Starting from the enantiomerically pure bisepoxide **22**,[15] a Cu^I-catalyzed, regioselective epoxide opening by vinylmagnesium chloride gave the diol **23** (Scheme 4). After acetonide protection of the diol function,



Scheme 4. Synthesis of the dibromide **26**: a) vinylmagnesium chloride, cat. CuBr·Me_2S, THF, −30–0 °C (85%); b) 2,2-dimethoxypropane, *p*TsOH (98%); c) O_3, CH_2Cl_2, −78 °C, then Me_2S; d) $NaBH_4$, MeOH (56%); e) *p*-TsCl, pyridine; f) LiBr, THF (66% from **25**).

24 was obtained. Subsequent ozonolysis and $NaBH_4$ work-up gave the diol **25**, which was transformed via the corresponding ditosylate into the dibromide **26**.

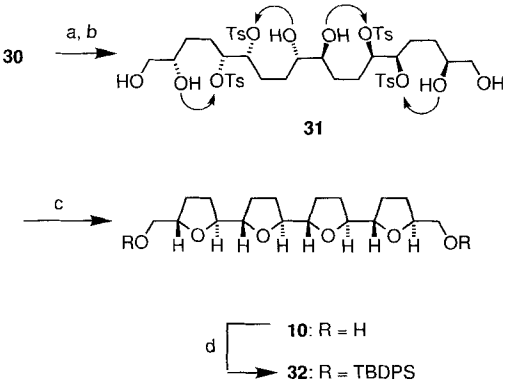
Monoalkylation of acetylene with the bromide **13** afforded the monosubstituted alkyne **27** (Scheme 5). The latter was allowed to react with the dibromide **26** to yield the dialkyne **28**,



Scheme 5. Synthesis of the tetraol **30**. a) 1.3 equiv lithium actetylide ethylenediamine complex, NH_3/THF (10/1), then 1.0 equiv **13**, −33 °C, 3 h (81%); b) 4.3 equiv $LiNH_2$, NH_3, −33 °C, then 4.3 equiv **27**, 15 min, then 1.0 equiv bromide **26**, −33 °C, 3 h (67%); c) 4.4 equiv Na, NH_3/THF 1.5/1, −33 °C, 1.5 h (70%); d) 2.2 equiv AD-mix-β, tBuOH/H_2O (1/1), 0–20 °C, 12 h (98%).

which was reduced to the dialkene **29**. With the carbon backbone of the tetra-THF in place, the introduction of the remaining stereocentres was addressed next. Diastereoselective double-Sharpless dihydroxylation gave the tetraol **30** with a stereoselectivity of 9:1 per double bond.

Prior to the multiple Williamson reaction, the tetraol **30** was converted to the hexahydroxytetratosylate **31** by quadruple tosylation and subsequent triple acidic acetonide cleavage (Scheme 6). Heating the cyclisation precursor **31** in dry THF with 2.5 equiv NaH per hydroxy function to 40 °C for 4 h produced the tetra-THF **10** in 56% yield.

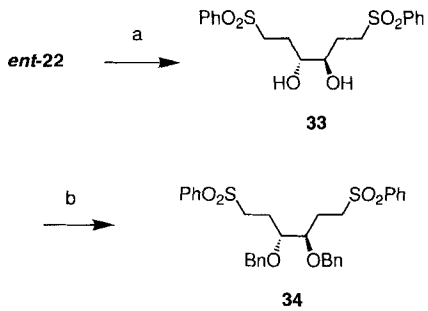


Scheme 6. Synthesis of the tetra-THF **32**. a) 16 equiv p-TsCl, pyridine; b) AcOH/H_2O (10/1), 40 °C, 8 h; c) 12 equiv NaH, THF, 3 h, 40 °C (56% from **30**); d) TBDPSCl, imidazole, DMF (95%). TBDPS = tBuPh$_2$Si.

The ^1H and ^{13}C NMR spectra of **10** show the characteristic half set of signals reflecting its C_2 symmetry. Four rings were closed in a single step in a predictable manner. Two points are noteworthy in this quadruple Williamson reaction. First, it exhibits strict selectivity for five-membered rings. No formation of six-membered or larger ethers occurred. Second, this multiple Williamson reaction shows cooperative behavior. When the reaction **31** → **10** was followed by thin layer chromatography, the highly polar spot of the starting material slowly disappeared while just one spot slowly appeared with increasing activity: the product spot with all four THF rings closed. Intermediates with one, two or three THF rings could not be detected. This indicates that the formation of the first THF ring helps the formation of the second, the third, and the fourth THF ring. Such a process is reminiscent of haemoglobin,[16] a tetrameric protein that binds four molecules of O_2. It consists of four subunits, each with a haem molecule capable of binding one O_2 molecule. In the haemoglobin case, binding of O_2 to the first haem molecule helps to bind O_2 to the second, the third and the fourth haem molecule. While cooperative phenomena are well known in biochemistry,[17] physical chemistry[18] and supramolecular chemistry,[19] they may deserve more attention in organic synthesis.[20]

For the stereoselective synthesis of tri-THFs, a convergent strategy was developed[21] which allowed the coupling of building blocks containing one THF ring. The reaction of an α-lithiated sulfone with an aldehyde was found to be a suitable for connecting the left and right parts of the molecule.

In order to apply this sulfone–aldehyde coupling to the bidirectional strategy, we focussed on the disulfone **34** (Scheme 7).



Scheme 7. Synthesis of the bis(sulfone) **34**: a) 2 equiv methyl phenyl sulfone, nBu-Li, THF/hexane, −78–0 °C, 12 h (95%); b) BnBr, NaH, THF (91%).

As a central building block, **34** should allow one to elaborate the molecule simultaneously to the left and to the right. Therefore, a short and efficient synthesis of the enantiomerically pure disulfone **34** was necessary. Towards this end the diepoxide *ent*-**22** was treated with an excess of α-lithiated methyl phenyl sulfone. The resulting dihydroxydisulfone **33** was dibenzylated to yield the disulfone **34**.

With the disulfone **34** in hand we turned our attention to the bidirectional sulfone–aldehyde coupling (Scheme 8). Dilithiation of **34** was accomplished with lithium diisopropyl amide at −78 °C in THF. Addition of 2.2 equiv of the mono-THF aldehyde **35**[21] produced a dihydroxydisulfone as the direct coupling product. Without further purification, the latter was Swern oxidised to the corresponding diketodisulfone, which was

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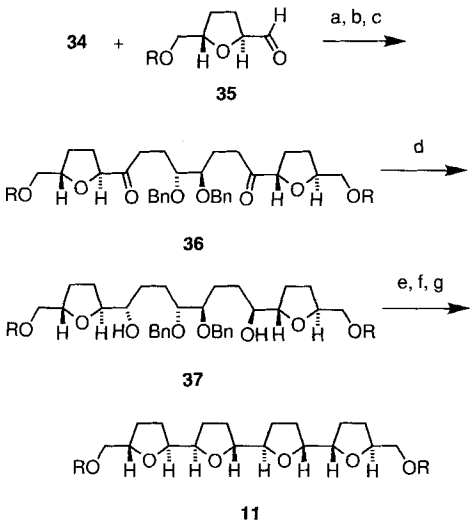
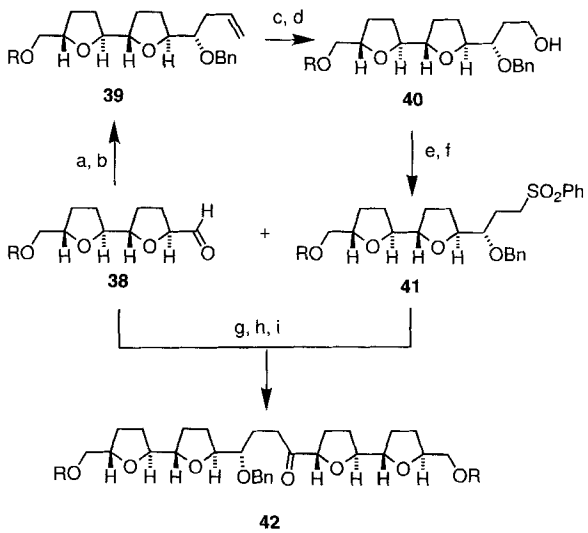


Scheme 8. Synthesis of the tetra-THF **11** (R = TBDPS = tBuPh$_2$Si). a) **34**, 2.4 equiv LDA, THF, −78 °C, then 2.2 equiv **35**, −78–0 °C; b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; c) Al/Hg, THF/nPrOH (5/1) (42% from **34**); d) L-selectride, THF, −78 °C, 5 min (99%); e) p-TsCl, pyridine (50%); f) H_2, Pd/C, MeOH, 20 °C, 6 h (85%); g) NaH, THF, 40 °C, 2 h (74%).



Scheme 9. Synthesis of the ketone **42** (R = TBDPS = tBuPh$_2$Si). a) (−)-B-Allyldiisopinocampheylborane, THF, −78 °C (75%); b) BnBr, NaH, THF, 72%; c) O_3, CH_2Cl_2, Ph_3P (97%); d) $NaBH_4$, MeOH (99%); e) PhSSPh, Bu_3P, CH_2Cl_2 (90%); f) MMPP, EtOH, 20 °C, 30 min (76%); g) LDA, THF, −78 °C; h) $(COCl)_2$, DMSO, CH_2Cl_2, −50 °C, then Et_3N; i) Al/Hg, THF/nPrOH (73% from **41**).

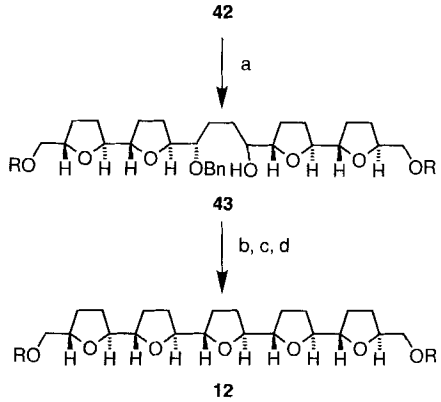
desulfonised with aluminium amalgam to the diketone **36** (42% yield from **34**).

L-Selectride reduction of **36** gave the diol **37**. The ^{13}C NMR spectrum of **37** showed the signal for the new stereocentre at $\delta = 74.3$, as expected[21] for the *threo* reduction product. In contrast, the *erythro* epimer[21] would have been seen at $\delta = 72$. The stereoselectivity in the formation of **37** was >95:5, as determined by inspection of the ^1H and ^{13}C NMR spectra. In preparation for a multiple Williamson reaction to close the remaining two THF rings simultaneously, diol **37** was first ditosylated. Next, the two benzyl ethers were cleaved by hydrogenolysis. Finally, double intramolecular Williamson reaction afforded the tetra-THF **11** with *trans-erythro-trans-threo-trans-erythro-trans* relative configuration in a stereocontrolled manner.

For the synthesis of membrane-bound ion channels longer oligo-THFs are desirable. To test the scope of the synthetic methodology developed so far, the assembly of the penta-THF **12** was investigated. Along the convergent route a bis-THF aldehyde should be connected to a bis-THF sulfone, after which ring closure of the new central THF ring gives the pentacyclic target structure. Beginning with the bis-THF aldehyde **38**,[21] the bis-THF sulfone **41** was synthesised first (Scheme 9). Reagent-controlled allyl boration[22] of **38** with (−)-B-allyl diisopinocampheylborane lead stereoselectively (*threo*/*erythro* = 85/15) to a homoallylic alcohol, which was converted into the corresponding benzyl ether **39**. The 85/15 mixture was separated by chromatography at the benzyl ether stage. Attempts to use a substrate-controlled reaction for the allylation of the aldehyde **38** failed. For example, an $SnCl_4$-catalysed Sakurai reaction with allyltrimethylsilane gave a 1:1 mixture of both epimers. Reaction of **38** with allylmagnesium bromide/CuBr afforded only a 3/2 epimeric mixture.

The terminal double bond of compound **39** was ozonised. After $NaBH_4$ reduction the alcohol **40** was obtained. The latter was transformed via its phenyl thioether[23] into the phenyl sulfone **41**. Magnesium monoperoxophthalate (MMPP) proved to be the reagent of choice for the thioether to sulfone oxidation.[24]

When the lithiated bis-THF sulfone **41** was allowed to react with the bis-THF aldehyde **38**, a coupling product resulted, which was directly Swern oxidised and desulfonised with aluminium amalgam to yield the ketone **42** in 73% overall yield. The final steps to the penta-THF **12** are shown in Scheme 10.



Scheme 10. Synthesis of the penta-THF **12** (R = TBDPS = tBuPh$_2$Si): a) $NaBH_4$, MeOH, ds: 50/50, 99%; b) p-TsCl, py, 20 °C, 81%; c) H_2, Pd/C, MeOH; d) NaH, THF, 50 °C, 2 h, two steps, 23%.

$NaBH_4$ reduction (**42** → **43**) followed by tosylation of the resulting alcohols (1:1 epimeric mixture) gave the corresponding tosylates. A subsequent benzyl ether cleavage provided the starting materials for the key Williamson reaction, the corresponding hydroxytosylates. Reaction of the latter with NaH in THF gave, after chromatography, the pentacylic product **12**. The ^1H and ^{13}C NMR spectra of **12** showed the characteristic half set of signals reflecting its C_2 symmetry. Unfortunately, no stereoselective reaction could be accomplished in the first ketone reduction step. The epimeric by-product had to be separated from the final product by chromatography.

Conclusions

An efficient synthetic approach to bis-, tetra- and penta-THFs has been described. The combination of Sharpless dihydroxylation and multiple Williamson reaction has been developed as a key sequence for the construction of the oligo-THF skeleton. The coupling of a THF aldehyde with a THF sulfone is suitable for the synthesis of larger oligo-THFs. The concept of substrate control, which worked well in the di-, and tri-THF systems,[21] has unfortunately failed so far in the penta-THF case. Reagent control was necessary to direct the introduction of new stereocentres (e.g., **38** → **39**). The work presented here should have great impact on the synthesis of annonaceous acetogenins and other polyether natural products with an oligo-THF structure. The field of artificial ion channels based on polyether structures should benefit from these results in the same way.

Experimental Section

General methods: All temperatures quoted are uncorrected. Melting points: Tottoli apparatus (Büchi). Elemental analyses: Analytik-Servicelabor Marburg, CHN-Rapid (Heracus). Thin-layer chromatography (TLC): Merck silica gel 60 on glass plates with fluorescence indicator F-254; detection by UV irradiation and/or heat-gun treatment with 5% phosphomolybdic acid in ethanol. HPLC: Merck LiChroGraph L-6200, L-4200 UV/Vis detector ($\lambda = 254$ nm), D-2500 chromato-integrator, column: Merck Supersphere Si 60 (250-4). Optical rotations: Polarimeter 241 (Perkin Elmer). IR: Interferometer Bruker IFS88. NMR: Bruker AT200, AC-300, WH400, AMX-500. Column chromatography (CC): Merck silica gel 60 (70–200 mesh, ASTM). Dry solvents [petroleum ether (PE), diethyl ether (Et_2O), ethyl acetate (AcOEt), methyl *tert*-butyl ether (MTBE)]: all solvents used for the Grignard reactions were dried and handled under argon; THF was predried with KOH, distilled from $LiAlH_4$, then from sodium/benzophenone; Et_2O was predried with $CaCl_2$ and distilled from sodium/benzophenone; CH_2Cl_2 was distilled from CaH_2, MeOH from $Mg(OMe)_2$, acetone from P_4O_{10}, and toluene from sodium/benzophenone. Boiling range of PE: 40–60 °C.

(2*S*,9*S*)-1,2-9,10-Bis-*O*-isopropylidene-5-decyne-1,2,9,10-tetraol (14): A solution of *n*BuLi in hexane (1.4 M, 21.4 mL, 30.0 mmol) was added at −78 °C to NH_3 (*100 mL*). *The reaction mixture was warmed to* −33 °C and lithium acetylide ethylenediamine complex (2.3 g, 25.0 mmol) was added. After stirring for 5 min bromide **13** (11.0 g; 52.6 mmol) was added. The reaction mixture was stirred for 3 h and the NH_3 was allowed to evaporate. MTBE (70 mL) and saturated aqueous NH_4Cl solution (60 mL) were successively added to the residue. The aqueous phase was extracted with MTBE (2 × 50 mL). The combined organic layers were washed with a saturated aqueous NaCl solution (80 mL) and dried with $MgSO_4$. The solvent was evaporated in vacuo. The residue was purified by CC (50 g of silica gel) with petroleum ether/MTBE (6/1) to give alkyne **14** (2.89 g, 10.3 mmol, 41%) as a colourless liquid. TLC (petroleum ether/MTBE, 10/1): $R_f = 0.13$; $[\alpha]_D^{20} = -9.9$, $[\alpha]_{578}^{20} = -10.3$, $[\alpha]_{546}^{20} = -11.1$, $[\alpha]_{436}^{20} = -15.3$, $[\alpha]_{365}^{20} = -16.7$ ($c = 2.13$, $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2986, 2937, 2871, 1380, 1369, 1245, 1215, 1157, 1074 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.34$ (s, 6H, acetonide CH_3), 1.39 (s, 6H, acetonide CH_3), 1.63–1.84 [m, 4H, C(3) and C(8)], 2.22–2.28 [m, 4H, C(4) and C(7)], 3.56 [t, $J = 7.4$, 2H, C(1) and C(10)], 4.07 [dd, $J = 7.8$ and 6.1, 2H, C(1) and C(10)], 4.13–4.22 [m, 2H, C(2) and C(9)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.3$ [C(4) and C(7)], 25.6 and 26.9 (acetonide CH_3), 33.0 [C(3) and C(8)], 69.1 [C(1) and C(10)], 74.9 [C(2) and C(9)], 79.5 [C(5) and C(6)], 108.6 (acetal); $C_{16}H_{26}O_4$ (282.38): calcd C 68.06, H 9.28; found C 67.96, H 8.99.

(2*S*,9*S*)-1,2-9,10-Bis-*O*-isopropylidene-5-decene-1,2,9,10-tetraol (15): Na in small pieces (200 mg, 8.7 mmol) was added to a stirred solution of alkyne **14** (2.0 g, 7.1 mmol) in NH_3 (20 mL) and THF (20 mL) at −33 °C. After 20 min, more Na (200 mg) was added and the colour of the solution turned deep blue. Solid NH_4Cl was added cautiously until the blue colour disappeared. The NH_3 was allowed to evaporate and a saturated aqueous NH_4Cl solution (30 mL) was added. The aqueous phase was extracted with MTBE (2 × 30 mL). The combined organic layers were washed with a saturated aqueous NaCl solution (50 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by CC (40 g of silica gel) with petroleum ether/MTBE (5/1) to yield alkene **15** (1.8 g, 6.3 mmol, 90%) as a colourless liquid. TLC (petroleum ether/MTBE, 5:1): $R_f = 0.50$; $[\alpha]_D^{20} = +22.1$, $[\alpha]_{578}^{20} = +23.0$, $[\alpha]_{546}^{20} = +25.7$, $[\alpha]_{436}^{20} = +46.0$, $[\alpha]_{365}^{20} = +72.8$ ($c = 3.35$, $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2986, 2935, 2867, 1378, 1369, 1249, 1215, 1157, 1066 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.28$ (s, 6H, acetonide CH_3), 1.34 (s, 6H, acetonide CH_3), 1.41–1.71 [m, 4H, C(3) and C(8)], 1.90–2.11 [m, 4H, C(4) and C(7)], 3.38–3.46 [m, 2H, C(1) and C(10)], 3.93–4.05 [m, 4H, C(1), C(10), C(2) and C(9)], 5.36–5.40 [m, 2H, C(5) and C(6)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.8$ and 26.9 (acetonide CH_3), 28.7 [C(4) and C(7)], 33.6 [C(3) and C(8)], 69.4 [C(1) and C(10)], 75.6 [C(2) and C(9)], 108.6 (acetal), 129.9 [C(5) and C(6)]; $C_{16}H_{28}O_4$ (284.40): calcd C 67.57, H 9.92; found C 67.67, H 10.21.

(2*S*,5*R*,6*R*,9*S*)-1,2-9,10-Bis-*O*-isopropylidenedecane-1,2,5,6,9,10-hexaol (16): Methanesulfonamide (100 mg, 1.0 mmol) and alkene **15** (284 mg, 1.0 mmol) were successively added to a magnetically stirred suspension of AD-mix-β (1.40 g) in *t*BuOH (5 mL) and H_2O (5 mL) at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. After this time, $Na_2S_2O_3$ (1.5 g) was added. The reaction mixture was stirred for 0.5 h, AcOEt (10 mL) was added and the phases were separated. The aqueous phase was extracted with AcOEt (2 × 10 mL). The combined organic layers were washed with dilute aqueous NaOH (20 mL) and with a saturated aqueous NaCl solution (20 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by CC (15 g of silica gel) with petroleum ether/AcOEt (1/3) to give a 9:1 mixture of diols **16** and **17** (310 mg, 0.97 mmol, 97%). TLC (petroleum ether/AcOEt, 1/3): $R_f = 0.11$; $[\alpha]_D^{20} = +26.8$, $[\alpha]_{578}^{20} = +28.1$, $[\alpha]_{546}^{20} = +32.2$, $[\alpha]_{436}^{20} = +55.6$, $[\alpha]_{365}^{20} = +86.0$ ($c = 1.065$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.29$ (s, 6H, acetonide CH_3), 1.34 (s, 6H, acetonide CH_3), 1.38–1.78 [m, 8H, C(3), C(4), C(7) and C(8)], 3.36 (d, $J = 8.3$, 2H, OH), 3.46 [t, $J = 7.1$, 2H, C(1) and C(10)], 3.97–4.10 [m, 6H, C(1), C(2), C(5), C(6), C(9) and C(10)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.6$ (acetonide CH_3), 26.8 (acetonide CH_3), 29.5 and 29.8 [C(3), C(4), C(7) and C(8)], 69.3 [C(1) and C(10)], 74.1 [C(2) and C(9)], 76.1 [C(5) and C(6)], 108.9 (acetal); $C_{16}H_{30}O_6$ (318.41): calcd C 60.35, H 9.50; found C 60.48, H 9.72.

(2*S*,5*S*,6*S*,9*S*)-1,2-9,10-Bis-*O*-isopropylidenedecane-1,2,5,6,9,10-hexaol (17): Methanesulfonamide (*100 mg, 1.0 mmol*) and alkene **15** (284 mg, 1.0 mmol) were successively added to a magnetically stirred suspension of AD-mix-α (1.40 g) in *t*BuOH (5 mL) and H_2O (5 mL) at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. $Na_2S_2O_3$ (1.5 g) was added. The reaction mixture was stirred for 0.5 h, AcOEt (10 mL) was added and the phases were separated. The aqueous phase was extracted with AcOEt (2 × 10 mL). The combined organic layers were washed with dilute aqueous NaOH (20 mL) and with saturated aqueous NaCl (20 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by CC (15 g of silica gel) with petroleum ether/AcOEt (1/3) to give a 9:1 mixture of diols **17** and **16** (269 mg, 0.84 mmol, 84%). TLC (petroleum ether/AcOEt, 1/3): $R_f = 0.11$; $[\alpha]_D^{20} = -2.3$, $[\alpha]_{578}^{20} = -2.2$, $[\alpha]_{546}^{20} = -2.2$, $[\alpha]_{436}^{20} = -1.1$, $[\alpha]_{365}^{20} = +2.2$ ($c = 1.43$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.29$ (s, 6H, acetonide CH_3), 1.35 (s, 6H, acetonide CH_3), 1.50–1.72 [m, 8H, C(3), C(4), C(7) and C(8)], 3.35–3.41 (m, 2H, OH), 3.47 [t, $J = 7.4$, 2H, C(1) and C(10)], 3.95–4.11 [m, 6H, C(1), C(2), C(5), C(6), C(9) and C(10)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.6$ and 26.9 (acetonide CH_3), 29.9 and 30.0 [C(3), C(4), C(7) and C(8)], 69.4 [C(1) and C(10)], 74.2 [C(2) and C(9)], 76.0 [C(5) and C(6)], 108.9 (acetal); $C_{16}H_{30}O_6$ (318.41): calcd C 60.35, H 9.50; found C 60.63, H 9.68.

1:1 Mixture of 16 and 17: NMO (400 mg, 3.4 mmol) and K_2OsO_4 (10 mg, 0.03 mmol) were added successively to a magnetically stirred solution of alkene **15** (284 mg, 1.0 mmol) in acetone (4 mL) and H_2O (2 mL). After stirring for 12 h the solution was diluted with H_2O (10 mL) and extracted with AcOEt (3 × 10 mL). The combined organic layers were washed with saturated $NaHSO_3$ solution (10 mL) and with saturated aqueous NaCl (10 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by CC (15 g of silica gel) with petroleum ether/AcOEt (1/3) to give a 1:1 mixture of diols **16** and **17** (318 mg, 1.0 mmol, 99%). TLC (petroleum ether/AcOEt, 1/3): $R_f = 0.11$; ^1H NMR (300 MHz, $CDCl_3$):

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$\delta = 1.28$ (s, 6H, acetonide CH_3), 1.34 (s, 6H, acetonide CH_3), 1.38–1.74 [m, 8H, C(3), C(4), C(7) and C(8)], 3.34–3.40 (m, 2H, OH), 3.43–3.52 [m, 2H, C(1) and C(10)], 3.95–4.10 [m, 6H, C(1), C(2), C(5), C(6), C(9), and C(10)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.6$ and 26.8 (acetonide CH_3), 29.6, 29.8 and 29.9 [C(3), C(4), C(7) and C(8)], 69.2 and 69.3 [C(1) and C(10)], 74.1 [C(2) and C(9)], 75.9 and 76.1 [C(5) and C(6)], 108.9 (acetal); $C_{16}H_{30}O_6$ (318.41): calcd C 60.35, H 9.50; found C 60.26, H 9.50.

(All-*S*)-5,5′-bis-[(*tert*-butyldiphenylsiloxy)-methyl]-octahydro-[2,2′]-bisfuran (20): TsCl (1.52 g, 8.0 mmol) and pyridine (3 mL) were added to a magnetically stirred solution of diol **16** (309 mg, 0.97 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After stirring for 1 h the reaction mixture was warmed to room temperature, stirred for a further 12 h and then diluted with CH_2Cl_2 (10 mL). H_2O (1 mL) was added and the mixture was stirred until TsCl could no longer be detected by TLC. To this mixture was added H_2O (10 mL). The mixture was acidified with diluted HCl to pH 4. The phases were separated and the aqueous phase was extracted with MTBE (2 × 20 mL). The combined organic layers were washed with a saturated aqueous $NaHCO_3$ (20 mL) solution and with a saturated aqueous NaCl solution (20 mL). After drying with $MgSO_4$ the solvent was evaporated and the residue was purified by CC (15 g of silica gel) with PE/MTBE (1/1) to give the corresponding ditosylate as a colourless liquid (508 mg, 0.81 mmol, 83%). This was dissolved in HOAc (20 mL) and H_2O (2 mL). After stirring for 5 h at room temperature the solvents were evaporated in vacuo. The crude tetrahydroxy ditosylate **18** was taken up in THF (10 mL) and a suspension of 80% NaH in paraffin (120 mg) was added at 0 °C. The reaction mixture was warmed to 45 °C and stirred for 2 h. After cooling to room temperature HOAc (15 mL) was added cautiously. The solvents were evaporated in vacuo. The residue was azeotropically distilled twice with toluene (10 mL) to remove the traces of HOAc. CC (10 g of silica gel) with $CHCl_3$/MeOH 5/1 yielded the hydrophilic di-THF **8** (140 mg, 0.69 mmol, 71%), which was transformed to the lipophilic bis-TBDPS ether **20** for characterisation: di-THF **8** (77 mg, 0.17 mmol) was dissolved in DMF (3 mL). To this solution was added imidazole (30 mg, 0.44 mmol) and TBDPSCl (0.15 mL, 0.55 mmol). The reaction mixture was stirred for 3 h and diluted with MTBE (10 mL) and a saturated aqueous NH_4Cl solution (10 mL). The aqueous phase was extracted with MTBE (2 × 10 mL), and the combined organic layers were washed with saturated aqueous NaCl (15 mL). After drying with $MgSO_4$, the solvent was evaporated. The residue was purified by CC (15 g of silica gel) with petroleum ether/MTBE (10/1) to give the bis-TBDPS ether **20** (104 mg, 0.15 mmol, 89%) as a colourless oil. TLC (petroleum ether/MTBE, 10/1): $R_f = 0.33$; $[\alpha]_D^{20} = -3.2$, $[\alpha]_{578}^{20} = -3.2$, $[\alpha]_{546}^{20} = -4.3$, $[\alpha]_{436}^{20} = -8.6$, $[\alpha]_{365}^{20} = -12.8$ ($c = 0.93$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2957$, 2930, 2857, 1472, 1427, 1111, 1007, 999, 823, 741, 702, 611, 505 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.01$ (s, 18H, $C(CH_3)_3$), 1.60–2.07 [m, 8H, C(3), C(3′), C(4) and C(4′)], 3.58 (dd, $J = 10.3$ and 5.9, 2H, C*H*H-OTBDPS), 3.69 (dd, $J = 10.3$ and 4.3, 2H, CH*H*-OTBDPS), 3.83–3.90 [m, 2H, C(2), C(2′)], 4.06–4.12 [m, 2H, C(5) and C(5′)], 7.30–7.40 (m, 12H, Ph), 7.62–7.70 (m, 8H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.1$ ($C(CH_3)_3$), 26.7 ($C(CH_3)_3$), 28.2 and 28.4 [C(3), C(3′), C(4) and C(4′)], 66.5 (CH_2OTBDPS), 79.6 [C(5) and C(5′)], 81.8 [C(2) and C(2′)], 127.5, 129.4, 133.7 and 135.6 (Ph); $C_{42}H_{54}O_4Si_2$ (679.06): calcd C 74.29, H 8.02; found C 74.18, H 8.13.

(2*R*,2′*R*,5*S*,5′*S*)-5,5′-Bis-[(*tert*-butyldiphenylsiloxy)methyl]-octahydro-[2,2′]-bisfuran (21): TsCl (1.00 g, 5.5 mmol) and pyridine (5 mL) were added to a magnetically stirred solution of diol **17** (138 mg, 0.43 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After stirring for 1 h the reaction mixture was warmed to room temperature. The reaction mixture was stirred for 12 h and then diluted with CH_2Cl_2 (10 mL). H_2O (1 mL) was added and the reaction mixture was stirred until the TsCl could no longer be detected by TLC. To this mixture was added H_2O (10 mL). The mixture was acidified with dilute HCl to pH 4. The phases were separated and the aqueous phase was extracted with MTBE (2 × 30 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (30 mL) and with saturated aqueous NaCl (30 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by CC (15 g of silica gel) with petroleum ether/MTBE (1/1) to give the corresponding ditosylate (234 mg, 0.37 mmol, 86%) as a colourless liquid. This was dissolved in HOAc (10 mL) and H_2O (2 mL). After stirring for 12 h at room temperature the solvents were evaporated in vacuo. The resulting tetrahydroxy ditosylate **19** was redissolved in THF (10 mL), and a suspension of 80% NaH in paraffin (100 mg) was added at 0 °C. The reaction mixture was warmed to 45 °C and stirred for 3 h. After cooling to room temperature, HOAc (8 mL) was added cautiously. The solvents were evaporated in vacuo. The residue was twice redissolved in toluene (10 mL) and concentrated in vacuo. CC (10 g of silica gel) with $CHCl_3$/MeOH 5/1 yielded the hydrophilic di-THF **9** (51 mg, 0.25 mmol, 68%), which was transformed to the lipophilic bis-TBDPS ether **21** for characterisation: di-THF **9** (51 mg, 0.25 mmol) was dissolved in DMF (3 mL). To this solution were added imidazole (255 mg, 3.75 mmol) and TBDPSCl (0.41 mL, 1.5 mmol). The reaction mixture was stirred for 4 h and diluted with MTBE (20 mL) and a saturated aqueous NH_4Cl solution (20 mL). The aqueous phase was extracted with MTBE (2 × 15 mL) and the combined organic layers were washed with a saturated aqueous NaCl solution (20 mL). After drying with $MgSO_4$, the solvent was evaporated. The residue was purified by CC (30 g of silica gel) with petroleum ether/MTBE (10/1) to give the bis-TBDPS ether **21** (153 mg, 0.23 mmol, 92%) as a colourless oil. TLC (petroleum ether/MTBE, 10/1): $R_f = 0.33$; $[\alpha]_D^{20} = -8.5$, $[\alpha]_{578}^{20} = -11.0$, $[\alpha]_{546}^{20} = -12.5$, $[\alpha]_{436}^{20} = -15.5$, $[\alpha]_{365}^{20} = -19.0$ ($c = 2.00$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2997$, 2930, 2860, 1472, 1463, 1427, 1106, 1007, 999, 804, 741, 705, 505 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.00$ (s, 18H, $C(CH_3)_3$), 1.46–1.59 (m, 4H) and 1.73–1.99 [m, 4H, C(3), C(3′), C(4) and C(4′)], 3.51 (dd, $J = 10.2$ and 6.6, 2H, C*H*H-OTBDPS), 3.68 (dd, $J = 10.2$ and 4.0, 2H, CH*H*-OTBDPS), 3.68-3.76 [m, 2H, C(2), C(2′)], 3.99–4.07 [m, 2H (C(5) and C(5′)], 7.28–7.36 (m, 12H, Ph), 7.59–7.65 (m, 8H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.2$ ($C(CH_3)_3$), 26.8 ($C(CH_3)_3$), 27.5 and 28.1 [C(3), C(3′), C(4) and C(4′)], 66.2 (CH_2OTBDPS), 79.6 [C(5) and C(5′)], 82.7 [C(2) and C(2′)], 127.5, 129.5, 133.7 and 135.6 (Ph); $C_{42}H_{54}O_4Si_2$ (679.06): calcd C 74.29, H 8.02; found C 74.36, H 8.23.

(4*S*,5*S*)-4,5-*O*-Isopropylidene-1,7-octadiene-4,5-diol (24): $CuBr \cdot SMe_2$ (310 mg, 1.55 mmol) was added to a stirred solution of vinylmagnesium chloride in THF (1 M, 155 mL, 155 mmol) at −30 °C. A deep black colour of the reaction mixture resulted. After 5 min a solution of the bisepoxide **22** (4.6 g, 53.4 mmol) in THF (70 mL) was added over 20 min. Further $CuBr \cdot SMe_2$ (310 mg) was added, the temperature was raised to −20 °C and the reaction mixture was stirred for 15 min. Then another portion of $CuBr \cdot SMe_2$ (310 mg) was added, the temperature was raised to 0 °C for 30 min and then to room temperature for 2 h. The reaction mixture was recooled to 0 °C, and a saturated aqueous NH_4Cl solution (150 mL) was added cautiously. The aqueous phase was extracted with MTBE (3 × 150 mL). The combined organic layers were washed with saturated aqueous NaCl (200 mL) and dried with $MgSO_4$. The solvent was evaporated, and the residue was purified by CC (150 g of silica gel) with petroleum ether/MTBE (1/1) to give the diol **23** (6.45 g, 45.4 mmol, 85%), which was directly redissolved in DMF (80 mL). 2,2-Dimethoxypropane (15.0 mL, 122 mmol) and *p*-toluenesulfonic acid (190 mg) were added successively at 0 °C. The reaction mixture was stirred for 12 h and then partitioned between saturated aqueous NH_4Cl (300 mL) and H_2O (200 mL). The aqueous phase was extracted twice with MTBE (200 mL) each. The combined organic layers were washed with saturated aqueous NaCl (150 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by CC (100 g of silica gel) with petroleum ether/MTBE 30/1 to give the acetonide **24** (8.10 g, 44.5 mmol, 98%) as a colourless oil. TLC (petroleum ether/MTBE, 30/1): $R_f = 0.30$; $[\alpha]_D^{20} = -3.2$, $[\alpha]_{578}^{20} = -3.3$, $[\alpha]_{546}^{20} = -3.8$, $[\alpha]_{436}^{20} = -6.2$, $[\alpha]_{365}^{20} = -9.9$ ($c = 1.86$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2986$, 2934, 2866, 1643, 1432, 1378, 1371, 1170, 1096, 1057, 995, 915, 867, 838 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.39$ (s, 6H, acetonide CH_3), 2.29–2.38 [m, 4H, C(3) and C(6)], 3.69–3.77 [m, 2H, C(4) and C(5)], 5.07–5.16 [m, 4H, C(1) and C(8)], 5.78–5.92 [m, 2H, C(2) and C(7)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.0$ (acetonide CH_3), 36.9 [C(3) and C(6)], 79.3 [C(4) and C(5)], 108.0 (acetal), 117.2 [C(1) and C(8)], 133.8 [C(2) and C(7)]; $C_{11}H_{18}O_2$ (182.26): calcd C 72.49, H 9.95; found C 72.39, H 9.86.

(3*S*,4*S*)-1,6-Dibromo-3,4-*O*-isopropylidenehexane-3,4-diol (26): A solution of the diolefin **24** (8.55 g, 46.9 mmol) in CH_2Cl_2 (80 mL) was cooled to −78 °C. Ozone-containing oxygen was bubbled through the solution until it turned blue. The reaction mixture was purged with Ar until the blue colour disappeared, Me_2S (15 mL) was added and the mixture was allowed to warm to room temperature. After stirring for 12 h, the solvent was evaporated in vacuo. The residue was dissolved in MeOH (60 mL) and $NaBH_4$ (12 g) was added in portions over a period of 2 h. The reaction mixture was stirred for 4 h and was then cooled to 0 °C. A saturated aqueous NH_4Cl solution (80 mL) was added, and most of the MeOH was evaporated in vacuo. The aqueous phase was extracted with AcOEt (5 × 100 mL), and the combined organic layers were dried with $MgSO_4$. Concentration in vacuo was followed by CC (90 g of silica gel) with AcOEt to give the diol **25** (5.03 g, 26.5 mmol,

56%). This was dissolved in CH_2Cl_2 (100 mL) and the solution was cooled to 0 °C. TsCl (30.2 g,158 mmol) and pyridine (45 mL) were added. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Then the mixture was cooled to 0 °C, H_2O (10 mL) was added and the reaction mixture was stirred until TsCl could no longer be detected by TLC. H_2O (80 mL) was added and the mixture was acidified with 1 M HCl to pH 4. The aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL) each and the combined organic layers were washed with a saturated $NaHCO_3$ solution (150 mL) and a saturated NaCl solution (150 mL). After drying with $MgSO_4$ the solvent was evaporated in vacuo. The residue was dissolved in THF (100 mL). LiBr (13.7 g, 158 mmol) was added and the reaction mixture was heated to reflux for 2 h. Then it was cooled to room temperature and partitioned between a semi-saturated NH_4Cl solution (300 mL) and MTBE (200 mL). The aqueous phase was extracted with MTBE (2 × 150 mL), and the combined organic layers were washed with a saturated NaCl solution (150 mL). Drying with $MgSO_4$, concentration in vacuo and CC (120 g of silica gel) with petroleum ether/MTBE (10/1) yielded the dibromide **26** (5.52 g, 17.5 mmol, 66%) as a colourless oil. TLC (petroleum ether/MTBE, 10/1): $R_f = 0.58$; $[\alpha]_D^{20} = -60.4$, $[\alpha]_{578}^{20} = -62.7$, $[\alpha]_{546}^{20} = -70.4$, $[\alpha]_{436}^{20} = -115.4$, $[\alpha]_{365}^{20} = -169.3$ ($c = 1.32$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2985, 2934, 1380, 1255, 1241, 1220, 1090, 1054, 985\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.36$ (s, 6H, acetonide CH_3), 2.03–2.11 [m, 4H, C(2) and C(5)], 3.44–3.58 [m, 4H, C(1) and C(6)], 3.80–3.84 [m, 2H, C(3) and C(4)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.2$ (acetonide CH_3), 29.3 [C(1) and C(6)], 36.1 [C(2) and C(5)], 78.2 [C(3) and C(4)], 108.9 (acetal); $C_9H_{16}Br_2O_2$ (316.05): calcd C 34.20, H 5.10; found C 34.50, H 5.16.

(All-*S*)-1,2-9,10-17,18-tris-*O*-isopropylideneoctadecane-5,13-diyne-1,2,9,10,17,18-hexaol (28): Bromide **13** (8.0 g, 38.3 mmol) was added to a magnetically stirred solution of lithium acetylide ethylenediamine complex (4.6 g, 50.0 mmol) in NH_3 (80 mL) at −33 °C. The reaction mixture was stirred for 3 h and then the solvent was allowed to evaporate. MTBE (50 mL) and a saturated aqueous NH_4Cl solution (30 mL) were successively added to the residue. The aqueous phase was extracted with MTBE (2 × 30 mL). The combined organic layers were washed with saturated aqueous NaCl (50 mL) and dried with $MgSO_4$. Evaporation of the solvent yielded an oily residue. This was purified by CC (120 g of silica gel) with petroleum ether/MTBE (10/1) to yield alkyne **27** (4.77 g, 31.0 mmol, 81%) as a colourless liquid. Alkyne **27** was dissolved in NH_3 (100 mL) and the mixture was cooled to −78 °C. A solution of *n*BuLi in hexane (1.5 M, 20 mL) was added with magnetic stirring. The reaction mixture was allowed to warm to −33 °C and THF (30 mL) and DMSO (30 mL) were added. After addition of the dibromide **26** (2.21 g, 7.0 mmol) the reaction mixture was stirred for 3 h. The NH_3 was allowed to evaporate and then MTBE (80 mL) and a saturated NH_4Cl solution (80 mL) were added. The aqueous phase was extracted with MTBE (2 × 50 mL), and the combined organic layers were washed with a saturated NaCl solution (80 mL). After drying with $MgSO_4$, the solvent was evaporated in vacuo and the residue was purified by CC (100 g of silica gel) with petroleum ether/MTBE 4/1. The dialkyne **28** was obtained as a colourless liquid (2.20 g, 4.7 mmol, 67%). TLC (petroleum ether/MTBE, 4/1): $R_f = 0.15$; $[\alpha]_D^{20} = -24.6$, $[\alpha]_{578}^{20} = -25.4$, $[\alpha]_{546}^{20} = -27.8$, $[\alpha]_{436}^{20} = -42.3$, $[\alpha]_{365}^{20} = -55.5$ ($c = 1.36$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2985, 2935, 2871, 1378, 1369, 1243, 1216, 1072\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.29$ (s, 6H, acetonide CH_3), 1.30 (s, 6H, acetonide CH_3), 1.34 (s, 6H, acetonide CH_3), 1.54–1.79 [m, 8H, C(3), C(8), C(11) and C(16)], 2.16–2.34 [m, 8H, C(4), C(7), C(12) and C(15)], 3.51 [dd, $J = 7.0$ and 7.8, 2H, C(1) and C(18)], 3.62–3.70 [m, 2H, C(9) and C(10)], 4.01 [dd, $J = 6.0$ and 7.9, 2H, C(1) and C(18)], 4.08–4.16 [m, 2H, C(2) and C(17)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.2$ and 15.5 [C(5), C(7), C(12) and C(15)], 25.5, 26.8 and 27.1 (acetonide CH_3), 32.4 and 33.0 [C(3), C(8), C(11) and C(17)], 69.0 [C(1) and C(18)], 74.8 [C(2) and C(17)], 79.2 [C(9) and C(10)], 79.4 and 79.6 [C(5), C(6), C(13) and C(14)], 108.2 and 108.6 (acetal); $C_{27}H_{42}O_6$ (462.63): calcd C 70.10, H 9.15; found C 69.93, H 9.31.

(2*S*,5*E*,9*S*,10*S*,13*E*,17*S*)-1,2-9,10-17,18-Tris-*O*-isopropylideneoctadeca-5,13-diene-1,2,9,10,17,18-hexaol (29): Small portions of Na (126 mg, 5.48 mmol) were added to a magnetically stirred solution of dialkyne **28** (1.16 g, 2.5 mmol) in THF (20 mL) and NH_3 (30 mL) at −33 °C. After stirring for 10 min another portion of Na (126 mg, 5.48 mmol) was added and the colour of the reaction mixture turned deep blue. After 5 min NH_4Cl was added cautiously until the blue colour of the mixture disappeared. MTBE (20 mL) was added and the NH_3 was allowed to evaporate. The residue was partitioned between a saturated NH_4Cl solution (30 mL) and MTBE (30 mL). The aqueous phase was extracted with MTBE (2 × 20 mL). The combined organic layers were washed with a saturated NaCl solution (20 mL) and dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by CC (25 g of silica gel) with PE/MTBE to give the diene **29** (817 mg, 1.75 mmol, 70%). TLC (PE/MTBE, 4/1): $R_f = 0.44$; $[\alpha]_D^{20} = -5.3$, $[\alpha]_{578}^{20} = -5.3$, $[\alpha]_{546}^{20} = -6.0$, $[\alpha]_{436}^{20} = -6.7$, $[\alpha]_{365}^{20} = -4.0$ ($c = 1.50$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2986, 2934, 2865, 1378, 1369, 1242, 1216, 1067\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.28$ (s, 6H), 1.30 (s, 6H) and 1.33 (s, 6H, acetonide CH_3), 1.42–1.53 (m, 6H) and 1.59–1.71 [m, 2H, (C(3), C(8), C(11) and C(16)], 1.93–2.20 [m, 8H, C(4), C(7), C(12) and C(15)], 3.43 [t, $J = 7.1$, 2H, C(1) and C(18)], 3.49–3.57 [m, 2H, C(2) and C(17)], 3.91–4.05 [m, 4H, C(1), C(9), C(10) and C(18)], 5.36–5.41 [m, 4H, C(5), C(6), C(13) and C(14)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.6$, 26.8, 27.2, 28.6, 28.9 [C(3), C(8), C(11), C(16) and acetonide CH_3], 32.7, 33.3 [C(4), C(7), C(12) and C(15)], 69.3 [C(1) and C(18)], 75.5 [C(2) and C(17)], 80.1 [C(9) and C(10)], 107.8 (acetal), 108.5 (acetal), 129.7 and 130.0 [C(5), C(6), C(13) and C(14)]; $C_{27}H_{46}O_6$ (462.63): calcd C 69.49, H 9.49; found C 69.67, H 9.85.

(2*S*,5*R*,6*R*,9*S*,10*S*,13*R*,14*R*,17*S*)-1,2-9,10-17,18-Tris-*O*-isopropylideneoctadeca-1,2,5,6,9,10,13,14,17,18-decaol (30): AD-mix-β (5.93 g) and methanesulfonamide (371 mg, 3.9 mmol) were added consecutively to a magnetically stirred solution of the dialkene **29** (817 mg, 1.75 mmol) in *t*BuOH (20 mL) and H_2O (20 mL) at 0 °C. The temperature was slowly warmed to room temperature and the mixture was stirred for 12 h. $Na_2S_2O_3$ (5.90 g) was added. The reaction mixture was stirred for 3 h, AcOEt (30 mL) was added and the phases were separated. The aqueous phase was extracted with AcOEt (3 × 30 mL). The combined organic layers were washed with dilute aqueous NaOH (40 mL) and with saturated aqueous NaCl (40 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue was purified by CC (30 g of silica gel) with petroleum ether/AcOEt 1/5 to give the tetraol **30** (917 mg, 1.72 mmol, 98%) as a colourless oil. TLC (petroleum ether/AcOEt, 1/5): $R_f = 0.31$; $[\alpha]_D^{20} = -5.3$ ($c = 1.50$, $CHCl_3$); IR (neat): $\tilde{\nu} = 3432, 2986, 2935, 1404, 1381, 1211, 1092, 850, 627\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.29$ (s, 6H, acetonide CH_3), 1.32 (s, 6H, acetonide CH_3), 1.35 (s, 6H, acetonide CH_3), 1.38–1.82 [m, 16H, C(3), C(4), C(7), C(8), C(11), C(12), C(15) and C(16)], 3.35–3.57 [m, 10H, C(1), C(5), C(6), C(13), C(14), C(18) and OH], 3.96–4.09 [m, 6H, C(1), C(2), C(9), C(10), C(17) and C(18)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.6$, 26.8, 27.1, 28.4, 29.4, 29.7 and 30.1 [C(3), C(4), C(7), C(8), C(11), C(12), C(15), C(16) and 6 × acetonide CH_3], 69.3 [C(1) and C(18)], 74.0 and 74.1 [C(5), C(6), C(13) and C(14)], 76.0 [C(2) and C(17)], 81.0 [C(9) and C(10)], 108.2 and 108.9 (double intensity, acetal); $C_{27}H_{50}O_{10}$ (534.69): calcd C 60.65, H 9.43; found C 60.50, H 9.24.

(All-*S*)-5,5‴-bis(hydroxymethyl)hexadecahydro-[2,2′;5′,2″;5″,2‴]-tetrafuran (10): TsCl (3.42 g, 17.9 mmol) and pyridine (5 mL) were added consecutively to a magnetically stirred solution of the tetraol **30** (600 mg, 1.12 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Then the mixture was diluted with CH_2Cl_2 (50 mL). H_2O (3 mL) was added and the reaction mixture was stirred until the TsCl could no longer be detected by TLC. The mixture was acidified with diluted HCl to pH 4. A saturated solution of $NaHCO_3$ (20 mL) was added and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 30 mL), and the combined organic layers were washed with a saturated NaCl solution (30 mL). After drying with $MgSO_4$ the solvent was evaporated in vacuo and the residue was purified by CC (30 g of silica gel) with MTBE. The tetratosylate thus obtained was dissolved in HOAc (25 mL) and H_2O (2 mL). The mixture was warmed to 45 °C and stirred for 3 h. It was then cooled to room temperature and stirred for 12 h. The solvent was evaporated in vacuo to yield the crude hexahydroxy tetratosylate **31**. This was twice dissolved in toluene (10 mL) and concentrated in vacuo. Then it was dissolved in THF (30 mL) and a 80% suspension of NaH (280 mg) in paraffin was added. The reaction mixture was warmed to 40 °C and stirred for 4 h. After cooling to room temperature, HOAc (20 mL) was added cautiously. The solvent was evaporated in vacuo. The residue was twice dissolved in toluene (10 mL), concentrated in vacuo and purified by CC (30 g of silica gel) with $CHCl_3$/MeOH 5/1 to give the tetra-THF **10** (191 mg, 0.56 mmol, 56%) as a colourless oil. TLC ($CHCl_3$/MeOH, 5/1): $R_f = 0.30$; $[\alpha]_D^{20} = +10.6$, $[\alpha]_{578}^{20} = +11.0$, $[\alpha]_{546}^{20} = +11.9$, $[\alpha]_{436}^{20} = +12.4$, $[\alpha]_{365}^{20} = +4.1$ ($c = 0.70$, $CHCl_3$); IR (neat): $\tilde{\nu} = 3400, 2932, 2872, 1369, 1260, 1213, 1189, 1177, 1060, 957, 854\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.49–1.71$ (m, 8H) and 1.84–1.95 (m, 8H) [C(3), C(4), C(3′), C(4′), C(3″), C(4″), C(3‴) and C(4‴)],

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3.15 (brs, 2H OH), 3.42 (dd, $J = 5.7$ and 11.6, 2H, C*H*H–OH), 3.60 (dd, $J = 3.5$ and 11.5, 2H, CH*H*–OH), 3.79–3.95 [m, 6H, C(5), C(2′), C(5′), C(2″), C(5″), and C(2‴)], 4.02–4.10 [m, 2H, C(2) and C(5‴)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 27.5$, 28.1, 28.4 and 28.6 [C(3), C(4), C(3′), C(4′), C(3″), C(4″), C(3‴) and C(4‴)], 64.7 (CH_2OH), 79.9 [C(2) and C(5‴)], 81.6, 81.9 and 82.1 [C(5), C(2′), C(5′), C(2″), C(5″) and C(2‴)]; HRMS (EI −70 eV): the molecular formula was verified by checking the calculated precise mass $M = 342.2042$ for $C_{18}H_{30}O_6$ (±2 ppm; $R = 10000$).

(All-*S*)-5,5‴-bis[(*tert*-butyldiphenylsiloxy)methyl]hexadecahydro-[2,2′;5′,2″;5″,2‴]-tetrafuran (32): The tetra-THF **10** (50 mg, 0.4 mmol) was dissolved in DMF (4 mL). TBDPSCl (250 mg, 0.91 mmol) and imidazole (100 mg, 1.47 mmol) were added successively and the mixture was stirred for 8 h. Then the mixture was partitioned between a half-saturated NH_4Cl solution (15 mL) and MTBE (10 mL). The aqueous phase was extracted with MTBE (2 × 10 mL). The combined organic layers were washed with a saturated NaCl solution (10 mL) and dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by CC (20 g of silica gel) with PE/MTBE 4/1 to give the bis-TBDPS ether **32** (109 mg, 0.13 mmol, 95%) as a colourless oil. TLC (PE/MTBE, 4/1): $R_f = 0.37$; $[\alpha]_D^{20} = -5.2$, $[\alpha]_{578}^{20} = -5.4$, $[\alpha]_{546}^{20} = -6.7$, $[\alpha]_{436}^{20} = -14.3$, $[\alpha]_{365}^{20} = -26.4$ ($c = 4.05$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2959$, 2930, 2858, 1112, 1085, 703 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.03$ (s, 18H, C(CH_3)$_3$), 1.60–2.09 [m, 16H, C(3), C(4), C(3′), C(4′), C(3″), C(4″), C(3‴) and C(4‴)], 3.59 (dd, $J = 5.7$ and 10.3, 2H, C*H*H–OH), 3.69 (dd, $J = 4.4$ and 10.3, 2H, CH*H*–OH), 3.85-4.00 [m, 6H, C(5), C(2′), C(5′), C(2″), C(5″) and C(2‴)], 4.08–4.16 [m, 2H, C(2) and C(5‴)], 7.31–7.39 (m, 12H, Ph), 7.64–7.69 (m, 8H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.2$ (*C*(CH_3)$_3$), 26.8 (C(*C*H_3)$_3$), 27.9, 28.2, 28.4 and 28.4 [C(3), C(4), C(3′), C(4′), C(3″), C(4″), C(3‴) and C(4‴)], 66.6 (CH_2–OH), 79.7 [C(2) and C(5‴)], 81.5, 81.8 and 81.9 [C(5), C(2′), C(5′), C(2″), C(5″) and C(2‴)], 127.6, 129.5, 133.8 and 135.6 (Ph); $C_{50}H_{66}O_6Si_2$ (819.24): calcd C 73.30, H 8.12; found C 73.14, H 8.10.

(3*R*,4*R*)-1,6-Bis(benzenesulfonyl)hexane-3,4-diol (33): A magnetically stirred solution of methyl phenyl sulfone (7.20 g, 46.0 mmol) in THF (200 mL) was cooled to −78 °C and a solution of *n*BuLi (1.4 M, 50 mL, 69 mmol) in hexane was added. Then the diepoxide *ent*-**22** (2.00 g, 23.0 mmol) was added and the mixture was allowed to warm to room temperature over 12 h. The mixture was partitioned between a saturated aqueous NH_4Cl solution (100 mL) and AcOEt (150 mL). The aqueous phase was extracted with AcOEt (3 × 70 mL). The combined organic layers were washed with a saturated aqueous NaCl solution (100 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue was recrystallised from AcOEt to yield the disulfone **33** (8.70 g, 21.9 mmol, 95%). M.p.: 146–147 °C; TLC (AcOEt): $R_f = 0.53$; $[\alpha]_D^{20} = +22.7$, $[\alpha]_{578}^{20} = +24.0$, $[\alpha]_{546}^{20} = +27.0$, $[\alpha]_{436}^{20} = +45.3$, $[\alpha]_{365}^{20} = +67.7$ ($c = 3.00$, acetone); IR (neat): $\tilde{\nu} = 3445$, 1850, 1320, 1290, 1140, 1050, 755, 725, 600 cm^{-1}; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 1.56–1.63$ [m, 4H, C(2) and C(5)], 2.85–2.99 [m, 2H, C(1) and C(6)], 3.07–3.21 [m, 4H, C(1), C(6) and OH], 3.97 [d, $J = 6.4$, 2H, C(3) and C(4)], 7.29–7.45 (m, 6H, Ph), 7.64–7.67 (m, 4H, Ph); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 26.5$ [C(2) and C(5)], 53.1 [C(1) and C(6)], 71.8 [C(3) and C(4)], 127.8, 129.2, 133.6 and 139.1 (Ph); $C_{18}H_{22}O_6S_2$ (398.48): calcd C 54.25, H 5.58; found C 54.20, H 5.63.

(3*R*,4*R*)-1,6-Bis(benzenesulfonyl)-3,4-bis(benzyloxy)hexane (34): The diol **33** (7.00 g, 17.6 mmol) was dissolved in THF (100 mL). To this solution were successively added at room temperature NaH (1.70 g, 70.0 mmol) and benzyl bromide (9.00 g, 53.0 mmol). After stirring for 12 h H_2O (20 mL) was added dropwise with caution. The mixture was partitioned between a saturated aqueous NH_4Cl solution (100 mL) and Et_2O (100 mL). The aqueous phase was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with saturated aqueous NaCl (50 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue was recrystallised from Et_2O (30 mL) to afford the disulfone **34** (9.20 g, 16.0 mmol, 91%). M.p. (Et_2O): 130 °C; TLC (petroleum ether/Et_2O, 1:1): $R_f = 0.20$; $[\alpha]_D^{20} = +33.9$, $[\alpha]_{578}^{20} = +36.1$, $[\alpha]_{546}^{20} = +40.8$, $[\alpha]_{436}^{20} = +68.4$, $[\alpha]_{365}^{20} = +101.9$ ($c = 1.30$, $CHCl_3$); IR (neat): $\tilde{\nu} = 1450$, 1300, 1290, 1150, 1140, 1120, 1100, 1085, 1070, 1055, 1030, 1020, 745, 685 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.73–1.78$ [m, 2H, C(2) and C(5)], 1.99–2.06 [m, 2H, C(2) and C(5)], 2.94–3.04 [m, 2H, C(1) and C(6)], 3.11–3.20 [m, 2H, C(1) and C(6)], 3.65–3.68 [m, 2H, C(3) and C(4)], 4.45 (d, $J = 11.6$, 2H, OCH_2Ph), 4.55 (d, $J = 11.6$, 2H, OCH_2Ph), 7.22–7.36 (m, 11H, Ph), 7.53–7.70 (m, 5H, Ph), 7.83–7.86 (m, 4H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 22.7$ [C(2) and C(5)], 52.5 [C(1) and C(6)], 72.6 (OCH_2Ph), 76.7 [C(3) and C(4)], 127.9, 128.5, 129.2, 133.6, 137.6 and 139.0 (Ph); $C_{32}H_{34}O_6S_2$ (578.74): calcd C 66.41, H 5.93; found C 66.70, H 5.86.

(4*R*,5*R*,2′*S*,5′*S*)-4,5-Bis(benzyloxy)-1,8-bis(5′-*tert*-butyldiphenylsiloxymethyltetrahydrofuran-2′-yl]-octan-1,8-dione (36): A solution of *n*BuLi (1.4 M, 4.40 mL, 6.3 mmol) in hexane was added to a magnetically stirred solution of *i*Pr_2NH (0.51 mL, 3.6 mmol) in THF (10 mL) at −78 °C . After 15 min a solution of the disulfone **34** (1.50 g, 2.6 mmol) in THF (50 mL) was added. Then a solution of the aldehyde **35** (2.10 g, 5.7 mmol) in THF (50 mL) was added and the reaction mixture was allowed to warm to 0 °C over 5 h. A saturated aqueous NH_4Cl solution (100 mL) was added, the aqueous phase was extracted with Et_2O (3 × 50 mL), and the combined organic layers were washed with a saturated aqueous NaCl solution (100 mL). After drying with $MgSO_4$, the solvent was evaporated in vacuo. The crude dihydroxydisulfone thus obtained was subjected to Swern oxidation: DMSO (1.10 mL) was added at −78 °C to a solution of $(COCl)_2$ (0.68 mL) in CH_2Cl_2 (20 mL). After 15 min the mixture was warmed to −50 °C and a solution of the dihydroxydisulfone in CH_2Cl_2 (30 mL) was added. After 30 min Et_3N (3.60 mL, 26.0 mmol) was added and the mixture was allowed to warm to 0 °C over 30 min. Then H_2O (20 mL) and a saturated aqueous NH_4Cl solution (50 mL) were added successively. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with a saturated aqueous NaCl solution (50 mL) and dried with $MgSO_4$. The solvent was evaporated to yield the crude diketodisulfone. This was dissolved in THF/*n*PrOH (5/1, 60 mL), and freshly prepared aluminium amalgam was added until TLC indicated full conversion of the starting material. The reaction mixture was filtered over Celite. The Celite plug was washed with Et_2O (100 mL) and the combined filtrates were concentrated in vacuo. CC (20 g of silica gel) with petroleum ether/Et_2O 2/1 afforded the diketone **36** (1.10 g, 1.10 mmol, 42%) as a colourless oil. TLC (petroleum ether/AcOEt, 4/1): $R_f = 0.62$; $[\alpha]_D^{20} = -0.8$, $[\alpha]_{578}^{20} = -1.2$, $[\alpha]_{546}^{20} = -1.6$, $[\alpha]_{436}^{20} = -6.0$, $[\alpha]_{365}^{20} = -18.0$ ($c = 2.50$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2955$, 2930, 2890, 1715, 1430, 1115, 1085, 1005, 740, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.08$ (s, 18H, C(CH_3)$_3$), 1.72–1.99 [m, 12H, C(3), C(6), C(3′) and C(4′)], 2.49–2.60 [m, 2H, C(2)], 2.65–2.74 [m, 2H, C(2) and C(7)], 3.55–3.58 [m, 2H, C(4) and C(5)], 3.66–3.72 (m, 4H, CH_2OTBDPS), 4.20–4.23 [m, 2H, C(5′)], 4.34 [t, $J = 7.2$, 2H, C(2′)], 4.49 (d, $J = 11.6$, 2H, OCH_2Ph), 4.65 (d, $J = 11.6$, 2H, OCH_2Ph), 7.16–7.40 (m, 24H, Ph), 7.69–7.70 (m, 6H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.4$ [*C*(CH_3)$_3$), 23.4 (C(3) and C(6)], 26.9 (C(*C*H_3)$_3$), 27.6 and 29.3 [C(3′) and C(4′)], 34.2 [C(2) and C(7)], 66.2 (CH_2OTBDPS), 72.6 (OCH_2Ph), 79.0, 80.9 and 84.0 [C(4), C(5), C(2′) and C(5′)], 125.4, 127.7, 127.8, 128.0, 128.3, 128.4, 129.1, 129.8, 133.6, 133.7, 135.7, 135.8 and 138.8 (Ph), 212.3 (C=O); $C_{64}H_{78}O_8Si_2$ (1031.52): calcd C 74.52, H 7.64; found C 74.36, H 7.66.

(1*S*,4*R*,5*R*,8*S*,2′*S*,5′*S*)-4,5-bis(benzyloxy)-1,8-bis(5′-*tert*-butyldiphenylsiloxymethyltetrahydrofuran-2′-yl)octan-1,8-diol (37): A solution of L-selectride (1 M, 1.10 mL, 1.10 mmol) in THF was added to a magnetically stirred solution of the diketone **36** (0.37 g, 0.36 mmol) in THF (20 mL) at −78 °C. After 5 min a saturated aqueous NH_4Cl solution (30 mL) and Et_2O (50 mL) were added. The aqueous phase was extracted with Et_2O (2 × 30 mL). The combined organic layers were washed with a saturated aqueous NaCl solution (30 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by CC (15 g of silica gel) with petroleum ether/Et_2O (1/1) to yield the diol **37** (0.37 g, 0.35 mmol, 99%) as a colourless oil. TLC (petroleum ether/AcOEt, 2/1): $R_f = 0.49$; $[\alpha]_D^{20} = 0$, $[\alpha]_{578}^{20} = 0$, $[\alpha]_{546}^{20} = 0$, $[\alpha]_{436}^{20} = -0.8$, $[\alpha]_{365}^{20} = -36.0$ ($c = 2.50$, $CHCl_3$); IR (neat): $\tilde{\nu} = 3404$, 2960, 2930, 2860, 1470, 1455, 1430, 1360, 1335, 1200, 1115, 1030, 1005, 995, 740, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.09$ (s, 18H, C(CH_3)$_3$), 1.22–2.03 [m, 16H, C(2), C(3), C(6), C(7), C(3′) and C(4′)], 2.40 (brs, 2H, OH), 3.32–3.42 (m, 2H) and 3.50–3.58 (m, 2H) [C(1), C(4), C(5) and C(8)], 3.69 (d, 4H, CH_2OTBDPS), 3.78–3.84 (m, 2H) and 4.11–4.14 [m, 2H, C(2′) and C(5′)], 4.57 (d, $J = 11.5$, 2H; OCH_2Ph), 4.68 (d, $J = 11.5$, 2H, OCH_2Ph), 7.28–7.47 (m, 22H, Ph), 7.68–7.76 (m, 8H, Ph); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 19.3$ (*C*(CH_3)$_3$), 26.8 (C(*C*H_3)$_3$), 27.0, 28.2, 28.5, and 30.1 [C(2), C(3), C(6), C(7), C(3′) and C(4′)], 66.4 (CH_2OTBDPS), 72.8 (OCH_2Ph), 74.3 [C(1) and C(8)], 79.5, 80.8 and 82.8 [C(4), C(5), C(2′) and C(5′)], 127.5, 127.6, 128.0, 128.3, 129.6, 133.6, 133.7, 135.6, 135.7 and 138.8 (Ph); $C_{64}H_{82}O_8Si_2$ (1035.65): calcd C 74.22, H 8.00; found C 74.32, H 8.14.

(2*S*,5*S*,2′*R*,5′*R*,2″*R*,5″*R*,2‴*S*,5‴*S*)-5,5‴-bis(*tert*-butyldiphenylsiloxymethyl)-hexadecahydro-[2,2′;5′,2″;5″,2‴]-tetrafuran (11): TsCl (0.70 g, 3.7 mmol) and pyridine (0.45 mL) were added to a solution of the diol **37** (0.95 g, 0.90 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 12 h and then H_2O (10 mL) was added. After stirring for 10 min the mixture was partitioned between a saturated aqueous NH_4Cl solution (30 mL) and Et_2O (50 mL). The aqueous phase was extracted with Et_2O (2 × 30 mL). The combined organic layers were washed with a saturated aqueous NaCl solution (30 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by CC (15 g of silica gel) with petroleum ether/Et_2O (2/1) to afford the corresponding ditosylate (0.62 g, 0.46 mmol, 50%). This ditosylate (0.15 g, 0.11 mmol) was dissolved in THF (5 mL) and MeOH (25 mL). Palladium on carbon (10%, 10 mg) was added. The flask was evaporated and filled with hydrogen gas (a balloon was fixed to the apparatus to maintain hydrogen atmosphere). The reaction mixture was stirred for 6 h. The Pd/C was removed by filtration through a pad of Celite. Evaporation of the solvent from the filtrate gave the crude dihydroxy ditosylate, which was purified by CC (10 g of silica gel) with petroleum ether/Et_2O (1/1) to give the dihydroxy ditosylate (0.11 g, 0.093 mmol, 85%). This product (50 mg, 0.043 mmol) was dissolved in THF (15 mL). NaH (5.0 mg, 0.22 mmol) was added and the mixture was stirred for 2 h at 40 °C. After cooling to 0 °C H_2O (5 mL) was added. The mixture was partitioned between a saturated aqueous NH_4Cl solution (10 mL) and Et_2O (10 mL). The aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with a saturated aqueous NaCl solution (30 mL) and dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by CC (10 g of silica gel) with petroleum ether/Et_2O 2:1 to afford the tetra-THF **11** (35 mg, 0.032 mmol, 74%) as a colourless oil. TLC (petroleum ether/AcOEt, 4/1): $R_f = 0.51$; $[\alpha]_D^{20} = +2.5$, $[\alpha]_{578}^{20} = +2.5$, $[\alpha]_{546}^{20} = +3.1$, $[\alpha]_{436}^{20} = +7.5$, $[\alpha]_{365}^{20} = +12.5$ ($c = 1.60$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2960$, 2930, 2860, 1430, 1110, 1065, 800, 740, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.03$ (s, 18H, C(CH_3)$_3$), 1.63–2.07 [m, 16H, C(3), C(4), C(3′), C(4′), C(3″), C(4″), C(3‴) and C(4‴)], 3.58 (dd, $J = 5.4$ and 10.4, 2H, CH_2OTBDPS), 3.64 (dd, $J = 4.6$ and 10.5, 2H, CH_2OTBDPS), 3.82–3.91 [m, 6H, C(2), C(2′), C(5′), C(2″), C(5″) and C(2‴)], 4.06-4.12 [m, 2H, C(5) and C(5‴)], 7.32–7.42 (m, 12H, Ph), 7.64–7.69 (m, 8H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.2$ (C(CH$_3$)$_3$), 26.8 (C(CH_3)$_3$), 27.8, 28.2, 28.7, 29.0, and 29.6 [C(3), C(4), C(3′), C(4′), C(3″), C(4″), C(3‴) and C(4‴)], 66.4 (CH_2OTBDPS), 79.6, 81.6, 81.8 and 81.9 [C(2), C(5), C(2′), C(5′), C(2″), C(5″), C(2‴) and C(5‴)], 127.5, 129.5, 133.7 and 135.6 (Ph); $C_{50}H_{66}O_6Si_2$ (819.28): calcd C 73.30, H 8.14; found C 73.13, H 8.18.

(All-*S*)-[5-(5′-*tert*-butyldiphenylsiloxymethyltetrahydrofuran-2′-yl)-2-(1″-benzyloxy-3″-buten-1″-yl)]-tetrahydrofuran (39): A solution of allylmagnesium bromide (1 M, 3.24 mL, 3.24 mmol) in Et_2O was added to a solution of (−)-*B*-methoxydiisopinocampheylborane (1.00 g, 3.24 mmol) in THF (30 mL) at −78 °C. After stirring for 15 min, the reaction mixture was warmed to room temperature over 1 h. Then the reaction mixture was cooled to −78 °C and a solution of the aldehyde **38** (1.20 g, 2.70 mmol) in THF (20 mL) was added dropwise. The mixture was stirred for 2 h and then warmed to room temperature. Aqueous solutions of NaOH (3 M, 2.70 mL, 8.00 mmol) and H_2O_2 (30%, 1.50 mL) were added successively. The resulting mixture was stirred for 15 min and then partitioned between a saturated NH_4Cl solution (60 mL) and Et_2O (60 mL). The aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with a saturated NaCl solution (80 mL) and dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by CC (20 g of silica gel) with petroleum ether/ Et_2O 2/1 to give a 85:15 mixture of the diastereomeric homoallylic alcohols (0.95 g, 2.00 mmol, 75%). These were dissolved in THF (30 mL). NaH (0.19 g, 7.90 mmol) and benzyl bromide (0.69 g, 4.00 mmol) were added and the mixture was stirred for 6 h at 45 °C. After cooling to 0 °C, H_2O (5 mL) was added cautiously and the mixture was partitioned between a saturated NH_4Cl solution (30 mL) and Et_2O (40 mL). The aqueous phase was extracted with Et_2O (3 × 30 mL) and the combined organic layers were washed with a saturated NaCl solution (40 mL). After drying with $MgSO_4$ the solvent was evaporated and the residue was purified by CC (50 g of silica gel) with petroleum ether/Et_2O (10/1) to yield the benzyl ether **39** (0.82 g, 1.43 mmol, 72%) as a colourless oil. TLC (petroleum ether/Et_2O, 10/1): $R_f = 0.08$; $[\alpha]_D^{20} = -9.5$, $[\alpha]_{578}^{20} = -10.2$, $[\alpha]_{546}^{20} = -11.7$, $[\alpha]_{436}^{20} = -22.2$, $[\alpha]_{365}^{20} = -38.5$ ($c = 1.20$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2960$, 2930, 2890, 1430, 1115, 1070, 740, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.04$ (s, 9H, C(CH_3)$_3$), 1.64–1.94 [m, 8H, C(3), C(4), C(3′) and C(4′)], 2.22–2.40 [m, 2H, C(2″)], 3.42–3.48 [m, 1H, C(1″)], 3.62 (dd, $J = 5.5$ and 10.3, 1H) and 3.70 (dd, 4.4 and 10.3, 1H) (CH_2OTBDPS), 3.89–3.95 (m, 2H) and 4.07–4.19 (m, 2H) [C(2), C(5), C(2′) and C(5′)], 4.62 (d, $J = 11.8$, 1H) and 4.68 (d, $J = 11.8$, 1H) (OCH_2Ph), 5.00–5.12 [m, 2H, C(4″)], 5.82–5.96 [m, 1H, C(3″)], 7.29–7.37 (m, 11H, Ph), 7.65–7.69 (m, 4H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.4$ (C(CH$_3$)$_3$), 27.0 (C(CH_3)$_3$), 28.1, 28.5 (2C), 28.6 [C(3), C(4), C(3′) and C(4′)], 35.6 [C(2″)], 66.8 (CH_2OTBDPS), 72.7 (OCH_2Ph), 80.0, 81.0, 81.4, 81.8 and 81.9 [C(2), C(5), C(2′), C(5′) and C(1″)], 116.7 [C(3″)], 134.0 (C(4″)], 127.5, 127.8, 128.0, 128.3, 129.7, 133.8, 135.7, 135.8 and 139.3 (Ph); $C_{36}H_{46}O_4Si$ (819.24): calcd C 75.74, H 8.14; found C 75.85, H 7.92.

(All-*S*)-Phenyl-[3-benzyloxy-3-{5′-(5″-*tert*-butyldiphenylsiloxymethyltetrahydrofuran-2″-yl)-tetrahydrofuran-2′-yl}propyl]sulfone (41): A solution of the alkene **39** (0.21 g, 0.36 mmol) in CH_2Cl_2 (20 mL) was cooled to −78 °C. Ozone-containing oxygen was bubbled through the solution until its colour turned to blue. The reaction mixture was purged with N_2, PPh_3 (0.15 g, 0.57 mmol) was added, and the mixture was allowed to warm to room temperature over 1 h. The solvent was evaporated and the residue purified by CC (55 g of silica gel) with petroleum ether/Et_2O to afford the corresponding aldehyde (0.20 g, 0.35 mmol, 97%). This aldehyde (0.57 g, 1.0 mmol) was dissolved in MeOH (40 mL), $NaBH_4$ (40 mg, 1.0 mmol) was added and the reaction mixture was stirred for 30 min. Then H_2O (20 mL) and Et_2O (60 mL) were added. The aqueous phase was extracted twice with Et_2O (20 mL) each. The combined organic layers were washed with a saturated NaCl solution (20 mL) and dried with $MgSO_4$. Evaporation of the solvent and CC (10 g of silica gel) with petroleum ether/Et_2O (1/1) yielded the alcohol **40** (0.57 g, 1.0 mmol, 99%) as a colourless oil. This was dissolved in CH_2Cl_2 (20 mL) and pyridine (0.47 g, 6.0 mmol), tri-*n*-butylphosphine (0.60 g, 3.0 mmol) and diphenyl disulfide (0.26 g, 1.2 mmol) were added. The mixture was stirred for 1 h and then partitioned between a saturated NH_4Cl solution (20 mL) and Et_2O (30 mL). The aqueous phase was extracted with Et_2O (2 × 20 mL), and the combined organic layers were washed with a saturated NaCl solution (50 mL). After drying with $MgSO_4$, the solvent was evaporated and the residue purified by CC (25 g of silica gel) with petroleum ether/ Et_2O 6:1 to afford the corresponding phenyl sulfide (0.60 g, 0.90 mmol, 90%). This (0.16 g, 0.25 mmol) was dissolved in EtOH (20 mL). MMPP (0.20 g, 0.50 mmol) was added and the mixture was stirred for 30 min. The reaction mixture was partitioned between H_2O (20 mL) and Et_2O (30 mL). The aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with a saturated NaCl solution (30 mL) and dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue purified by CC (15 g of silica gel) with petroleum ether/Et_2O (2/1) to give the sulfone **41** (0.13 g, 0.19 mmol, 76%) as a colourless oil. TLC (petroleum ether/ AcOEt, 4/1): $R_f = 0.33$; $[\alpha]_D^{20} = -14.5$, $[\alpha]_{578}^{20} = -15.4$, $[\alpha]_{546}^{20} = -17.4$, $[\alpha]_{436}^{20} = -31.1$, $[\alpha]_{365}^{20} = -50.1$ ($c = 4.00$, $CHCl_3$); IR (neat): $\tilde{\nu} = 2960$, 2930, 2860, 1470, 1460, 1430, 1300, 1150, 1080, 1030, 1000, 940, 825, 740, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.01$ (s, 9H, C(CH_3)$_3$), 1.66–2.00 [m, 10H, C(2), C(3′), C(4′), C(3″) and C(4″)], 3.02–3.10 [m, 1H, C(1)], 3.19–3.29 [m, 1H, C(1)], 3.41–3.47 [m, 1H, C(3)], 3.59 [dd, $J = 5.3$ and 10.4, 1H) and 3.66 (dd, $J = 4.5$ and 10.4, 1H) (CH_2–OTBDPS), 3.82–3.90 (m, 2H), 3.98–4.04 (m, 1H) and 4.05–4.13 (m, 1H), [C(2′), C(5′), C(2″) and C(5″)], 4.47 (d, $J = 11.7$, 1H) and 4.66 (d, $J = 11.7$, 1H) (OCH_2Ph), 7.20–7.37 (m, 10H, Ph), 7.46–7.67 (m, 8H, Ph), 7.81–7.84 (m, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.3$ (C(CH$_3$)$_3$), 24.1 [C(2), 26.9 (C(CH_3)$_3$], 28.1, 28.2, 28.4 (2C) [C(3′), C(4′), C(3″) and C(4″)], 52.9 (C(1)], 66.7 (CH_2–OTBDPS), 72.7 (OCH_2Ph), 78.8, 79.9, 81.6 (2C) and 81.8 [C(3), C(2′), C(5′), C(2″) and C(5″)], 127.7, 127.8, 127.9, 128.0, 128.4, 129.3, 129.6, 129.7, 133.6, 133.8, 135.7, 138.5 and 139.3 (Ph); $C_{41}H_{50}O_6SSi$ (699.01): calcd C 70.44, H 7.22; found C 70.27, H 6.98.

(All-*S*)-4-benzyloxy-1,4-bis-5[′-(5″-*tert*-butyldiphenylsiloxymethyltetrahydrofuran-2″yl)-tetrahydrofuran-2′yl]butanone (42): A solution of *n*BuLi (1.4 M, 0.86 mL, 1.2 mmol) in hexane was added to a magnetically stirred solution of *i*Pr$_2$NH (0.23 mL, 1.6 mmol) in THF (2 mL) at −78 °C. After 15 min a solution of the sulfone **41** (0.51 g, 0.73 mmol) in THF (4 mL) was added. Then a solution of the aldehyde **38** (0.46 g, 1.0 mmol) in THF (10 mL) was added and the mixture was allowed to warm to 0 °C over 5 h. A saturated aqueous NH_4Cl solution (30 mL) was added, the aqueous phase was extracted with Et_2O (3 × 30 mL) and the combined organic layers were washed with a saturated aqueous NaCl solution (30 mL). After drying with $MgSO_4$, the solvent was evaporated in vacuo. The hydroxysulfone thus obtained was subjected to Swern oxidation: a solution of DMSO (0.23 mL) in CH_2Cl_2

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(20 mL) was added at −78 °C to a solution of $(COCl)_2$ (0.14 mL) in CH_2Cl_2 (10 mL). After 10 min the mixture was warmed to −50 °C and a solution of the hydroxysulfone (0.93 g) in CH_2Cl_2 (30 mL) was added. After 30 min Et_3N (2.3 mL) was added and the mixture was allowed to warm to 0 °C over 30 min. Then H_2O (30 mL) and a saturated aqueous NH_4Cl solution (50 mL) were added successively. The aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with a saturated aqueous NaCl solution (30 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by CC (15 g of silica gel) with petroleum ether/Et_2O (1/1) to yield the crude ketosulfone (0.90 g). This was dissolved in THF/*n*PrOH (5/1, 30 mL) and freshly prepared aluminium amalgam was added until TLC control showed complete consumption of the starting material. The reaction mixture was filtered over Celite. The Celite plug was washed with Et_2O (100 mL) and the combined filtrates were concentrated in vacuo. CC (20 g of silica gel) with petroleum ether/Et_2O (1/2) afforded the ketone **42** (0.53 g, 0.53 mmol, 73%) as a colourless oil. TLC (petroleum ether/AcOEt, 2/1): $R_f = 0.49$; $[\alpha]_D^{20} = -15.4$, $[\alpha]_{578}^{20} = -16.2$, $[\alpha]_{546}^{20} = -18.3$, $[\alpha]_{436}^{20} = -32.9$, $[\alpha]_{365}^{20} = -52.4$ ($c = 1.20$, $CHCl_3$); IR (neat): $\tilde{\nu}$ = 2960, 2930, 2860, 1710, 1430, 1215, 1115, 1070, 1005, 995, 760, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.01$ (s, 9H, $C(CH_3)_3$), 1.02 (s, 9H, $C(CH_3)_3$), 1.58–1.99 [m, 18H, C(3), C(3′), C(4′), C(3″) and C(4″)], 2.29–2.34 [m, 2H, C(2)], 3.32–3.36 [m, 1H, C(4)], 3.60–3.67 (m, 4H, CH_2OTBDPS), 3.71–3.77 (m, 2H), 3.87–3.91 (m, 2H) and 4.02–4.15 [m, 4H), C(2′), C(5′), C(2″) and C(5″)], 4.50 (d, $J = 11.7$, 1H) and 4.73 (d, $J = 11.7$, 1H) (OCH_2Ph), 7.29–7.36 (m, 17H, Ph), 7.63–7.65 (m, 8H, Ph), 7.81–7.84 (m, 8H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.4 ($C(CH_3)_3$), 20.0 ($C(CH_3)_3$), 26.9 ($C(CH_3)_3$), 27.1 [$C(CH_3)_3$], 28.4, 28.5, 28.6, 33.1 and 38.9 [C(3), C(3′), C(4′), C(3″) and C(4″)], 42.6 [C(2)], 66.5 and 66.7 (CH_2OTBDPS), 72.8 (CH_2OBn), 73.8, 79.7, 79.9, 80.5, 81.8, 82.1 and 82.6 [C(4), C(2′), C(5′), C(2″) and C(5″)], 127.5, 127.7, 127.8, 128.0, 128.1, 128.3, 128.4, 129.6, 129.7, 133.7, 133.8, 133.9, 135.7 and 139.2 (Ph), 210.9 (C=O); $C_{61}H_{78}O_8Si_2$ (995.49): calcd C 73.59, H 7.91; found C 73.51, H 7.93.

(1*θ*,4*S*,2′*S*,5′*S*,2″*S*,5″*S*)-4-Benzyloxy-1,4-bis-[5′-(5″-*tert*-butyldiphenylsiloxymethyltetrahydrofuran-2″-yl)-tetrahydrofuran-2′-yl]-1-butanol (43): $NaBH_4$ (5.0 mg, 0.14 mmol) was added to a magnetically stirred solution of the ketone **42** (0.14 g, 0.14 mmol) in EtOH (15 mL) at room temperature. The mixture was stirred until TLC control showed complete reaction. Then a saturated aqueous NH_4Cl solution (20 mL) was added and the aqueous phase was extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with a saturated aqueous NaCl solution (20 mL) and dried with $MgSO_4$. The solvent was evaporated and the residue purified by CC (10 g of silica gel) with petroleum ether/Et_2O (1/2) to afford **43** as a 1:1 epimeric mixture (0.14 g, 0.14 mmol, 98%). TLC (petroleum ether/AcOEt, 2/1): $R_f = 0.44$; IR (neat): $\tilde{\nu}$ = 3430, 2960, 2930, 2860, 1470, 1455, 1425, 1390, 1360, 1335, 1305, 1270, 1175, 1115, 1030, 1005, 995, 890, 825, 740, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.06$ (s, 18H, $C(CH_3)_3$), 1.42–2.07 [m, 20H, C(2), C(3), C(3′), C(4′), C(3″) and C(4″)]; 2.26 (br s) and 2.47–2.52 (m) (1H, OH); 3.62–3.74 (m, 4H, CH_2OTBDPS), 3.39–3.55 (m, 3H), 3.78–3.84 (m, 1H), 3.92–3.94 (m, 2H) and 4.07–4.22 (m, 4H) [C(1, C(4), C(2′), C(5′), C(2″) and C(5″)], 4.58 (d, $J = 2.9$), 4.62 (d, $J = 3.0$), 4.76 (d, $J = 4.1$) and 4.80 (d, $J = 4.0$) (2H, OCH_2Ph), 7.29–7.39 (m, 17H, Ph), 7.67–7.70 (m, 8H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 [$C(CH_3)_3$], 21.8 and 21.9 (C(2)], 26.9 ($C(CH_3)_3$), 28.2, 28.3, 28.4, 28.5, 33.5, 33.6, 34.0, 37.4 and 37.6 [C(3), C(3′), C(4′), C(3″) and C(4″)], 66.5 and 66.7 (CH_2OTBDPS), 72.6 and 72.8 (OCH_2Ph), 73.8 and 73.9 [C(1)], 71.6, 79.6, 79.8, 81.1, 81.6, 81.7, 82.6 and 82.7 [C(4), C(2′), C(5′), C(2″) and C(5″)], 127.5, 127.6, 127.7, 128.0, 128.1, 128.3, 129.6, 129.7, 133.6, 133.7, 133.8, 135.7 and 139.0 (Ph); $C_{61}H_{80}O_8Si_2$ (997.51): calcd C 73.44, H 8.10; found C 73.46, H 8.17.

(All-*S*)-5,5‴-bis(*tert*-butyldiphenylsiloxymethyl)eicosahydro-[2,2′;5′2″;5″,2‴;5‴,2⁗]-pentafuran (12): TsCl (80.0 mg, 0.40 mmol) was added to a solution of the alcohol **43** (0.14 g, 0.14 mmol) in pyridine (2 mL). After stirring for 12 h the mixture was cooled to 0 °C and H_2O (30 mL) was added. The mixture was stirred until TLC checks showed complete hydrolysis of TsCl. Then the aqueous phase was extracted with Et_2O (3 × 40 mL). The combined organic layers were dried with $MgSO_4$. Et_2O and pyridine were evaporated in vacuo. The residue was purified by CC (15 g of silica gel) to give the tosylate (0.13 g, 0.11 mmol, 81%). This was dissolved in AcOEt (20 mL), and palladium on carbon (10%, 20 mg) was added. The flask was evaporated and filled with hydrogen gas (a balloon was fixed to the apparatus to maintain hydrogen atmosphere). The reaction mixture was stirred for 3 h. The Pd/C was removed by filtration through a pad of Celite. Evaporation of the solvent from the filtrate gave the crude hydroxytosylate, which was redissolved in THF (20 mL). NaH (4 mg, 0.16 mmol) was added to the solution and the reaction mixture was heated at 50 °C for 2 h. It was subsequently cooled to 0 °C while H_2O (10 mL) and a saturated aqueous NH_4Cl solution (30 mL) were added. The aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic layers were dried with $MgSO_4$. CC (20 g of silica gel) with petroleum ether/Et_2O 2/1 afforded the penta-THF **12** (22 mg, 0.025 mmol, 23%) as a colourless oil. TLC (petroleum ether/AcOEt, 2/1): $R_f = 0.54$; $[\alpha]_D^{20} = -10.4$, $[\alpha]_{578}^{20} = -10.4$, $[\alpha]_{546}^{20} = -12.2$, $[\alpha]_{436}^{20} = -17.4$, $[\alpha]_{365}^{20} = -27.8$ ($c = 0.60$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.04$ (s, 18H, $C(CH_3)_3$), 1.60–2.03 [m, 20H, C(3), C(4), C(3′), C(4′), C(3″) and C(4″)], 3.60 (dd, $J = 5.7$ and 10.4, 2H, CH_2OTBDPS), 3.69 (dd, $J = 4.4$ and 10.4, 2H, CH_2OTBDPS), 3.85–3.97 [m, 8H, C(2), C(5″), C(2′), C(5′) and C(2″)], 4.10–4.15 [m, 2H, C(5)], 7.35–7.37 (m, 12H, Ph), 7.65–7.68 (m, 8H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 ($C(CH_3)_3$), 26.9 ($C(CH_3)_3$), 28.0, 28.1, 28.2, 28.3 and 28.5 [C(3), C(4), C(3′), C(4′), C(3″) and C(4″)], 66.6 (CH_2OTBDPS), 79.7, 81.6 (2C), 81.8 and 81.9 [C(2), C(5), C(2′), C(5′), C(2″) and C(5″)], 127.6, 129.5, 133.8, 135.6 and 135.7 (Ph); HRMS: calcd 888.4816; found 888.4951.

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