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Syntheses and Properties of Enantiomerically Pure Higher ($n \geq 7$) [$n-2$]Triangulanedimethanols and σ-[n]Helicenes**

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Dedicated to Professor Nikolai S. Zefirov on the occasion of his 70th birthday

Abstract: (*P*)-(+)-Hexaspiro[2.0.0.0.0.0.2.1.1.1.1.1.1]pentadecane [(*P*)-**17**] as well as (*M*)-(−)- and (*P*)-(+)-octaspiro-[2.0.0.0.0.0.0.0.2.1.1.1.1.1.1.1.1]nonadecanes [(*M*)- and (*P*)-**25**]—enantiomerically pure unbranched [7]- and [9]triangulanes—have been prepared starting from racemic THP-protected (methylenecyclopropyl)methanol **6**. The relative configurations of all important intermediates as well as the absolute configurations of the key intermediates were established by X-ray crystal structure analyses. This new convergent approach to enantiomerically pure linear [*n*]triangulanes for $n=7$, 9 was also tested in two variants towards [15]triangulane. Some of the most prominent and unexpected features of the newly prepared compounds are the remarkable modes of self-assembly of the diols (*P*)-**14**, (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21**, (*P*)-(+)-**22**, and (*E*)-**31** in the solid state through frameworks of intermolecular hydrogen bonds leading to, depending on the respective structure, nanotube- [(*P*)-**14**, (*P*)-(+)-**22**, and (*E*)-**31**], honeycomb-like structures [(*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21**] or a supramolecular double helix [(*P*)-(+)- and (*M*)-(−)-**22**]. Liquid crystalline properties of the esters and ethers of the diols (*P*)-**14**, (*P*)-, and (*M*)-**22** have also been tested. Although all of these [*n*]triangulanes have no chromophore which would lead to significant absorptions above 200 nm, they exhibit surprisingly high specific rotations even at 589 nm with $[\alpha]_D^{20}=+672.9$ ($c=0.814$ in $CHCl_3$) for (*P*)-(+)-**17**, +909.9 ($c=0.96$ in $CHCl_3$) for (*P*)-(+)-**25**, −890.5 ($c=1.01$ in $CHCl_3$) for (*M*)-(−)-**25**, and −1302.5 ($c=0.36$ in $CHCl_3$) for (*M*)-(−)-**39**, and the specific rotations increase drastically on going to shorter wavelengths. This outstanding rotatory power is in line with their rather rigid helical arrangement of σ bonds, and accordingly these helically shaped unbranched [*n*]triangulanes may be termed "σ-[*n*]helicenes", as they represent the σ-bond analogues of the aromatic π-[*n*]helicenes. Density functional theory (DFT) computations at the B3LYP/6-31+G(d,p) level of theory for the geometry optimization and time-dependent DFT for determining optical rotations with a triplet-ζ basis set (B3LYP/TZVP) reproduce the optical rotatory dispersions (ORD) very well for the lower members ($n=4$, 5) of the σ-[*n*]helicenes. For the higher ones ($n=7$, 9, 15) the computed specific rotations turn out increasingly larger than the experimental values. The remarkable increase of the specific rotation with an increasing number of three-membered rings is proportional neither to the molecular weight nor to the number of cyclopropane rings in these σ-[*n*]helicenes.

Keywords: chirality · helical structures · optical rotations · self-assembly · small ring systems

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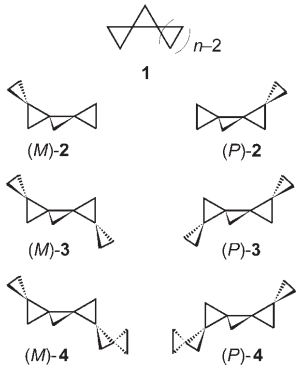
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Syntheses of the diol (1*S*,3*S*,4*S*,5*R*,6*R*,7*S*,8*S*,9*S*)-**22** and of the liquid crystalline compounds **43a–f**, **44a–f** and **45a–f**.

Introduction

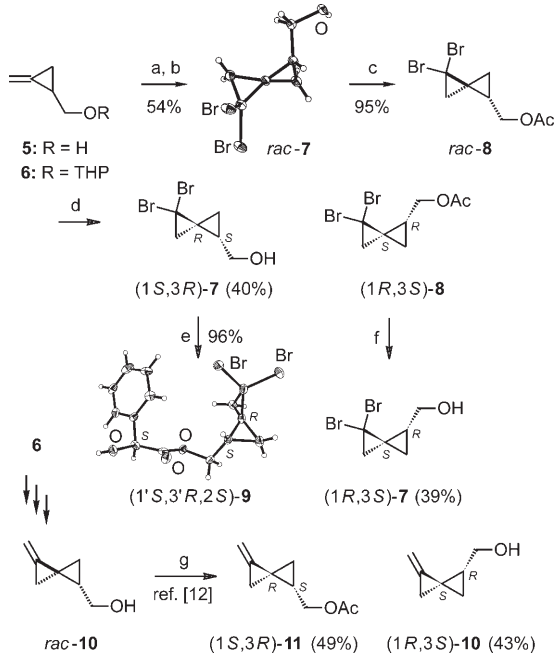
Although the so-called [*n*]triangulanes **1**,[1] hydrocarbons which consist of spiroannelated cyclopropane rings only, have no chromophore that would lead to any significant absorption above 200 nm, the [4]- (**2**) and [5]triangulanes (**3**) in enantiomerically pure form have been found to exhibit remarkably high specific rotations even at 589 nm with $[\alpha]_D^{20} = -192.7$ [(*M*)-**2**, *c* = 1.18, $CHCl_3$)] or +373.0 [(*P*)-**3**, *c* = 1.18, $CHCl_3$)].[2] This outstanding rotatory power is in line with their completely rigid helical arrangement of sigma bonds, as the C_2-symmetric molecules of (*M*)- and (*P*)-**2**–**4** are sections of a helix, and therefore the stereochemical descriptors for helicenes[3] should best be applied to **2** as well as higher unbranched [*n*]triangulanes **1**.[4]



As predicted by DFT calculations at a reasonably high level of theory,[2b] the rotatory strengths of the [5]triangulanes (*M*)-**3** and (*P*)-**3** turned out to be about twice as large as those of the [4]triangulanes (*M*)-**2** and (*P*)-**2**. However, it remained an open question whether this good agreement would also hold for the higher (*M*)- and (*P*)-σ-[*n*]helicenes. Thus, for the unbranched [6]triangulanes (*M*)-**4** and (*P*)-**4** the computed specific rotations at 589 nm ($[\alpha]_D^{20} = 509.7$) are only 29% larger than those for (*M*)-**3** and (*P*)-**3**. Whether or not this may be attributed to the fact that the sum of all interplanar angles between pairs of adjacent spiroannelated cyclopropane rings reaches 360° in the [5]triangulanes (*M*)-**3** and (*P*)-**3**, while it is 450° in [6]triangulanes (*M*)-**4** and (*P*)-**4**, may only be speculated about. In comparison to the [*n*]triangulanes, the recently reported helical hydrocarbons consisting of spiroannelated four-membered rings, which are conformationally flexible, not only disclosed significantly smaller specific rotations, but their values also decrease with an increasing number of spirocyclobutanes in the helix.[5] To systematically address the question, whether the specific rotations of higher σ-[*n*]helicenes keep increasing significantly with increasing *n*, we set out to prepare several such higher [*n*]triangulanes with $n \geq 7$ in enantiomerically pure form.

Results and Discussion

Preparation of higher triangulanes and their derivatives in enantiomerically pure form: Because of the rapidly growing number of possible stereoisomers of higher [*n*]triangulanes with increasing *n*,[6] and the fact that upon each addition of a monosubstituted cyclopropanating reagent onto a methylene[*n*]triangulane, two new stereogenic centers are created, any linear synthesis such as the previously elaborated approaches to the enantiomerically pure [4]- and [5]triangulanes,[2] would face severe problems of separation en route to higher [*n*]triangulanes. Therefore new, more convergent routes to (*M*)-(−)- and (*P*)-(+)-[*n*]triangulanes with $n \geq 7$ starting from the known α,ω-difunctional chiral building blocks (2-methylenecyclopropyl)methanol (**5**) and (4-methylenespiropentyl)methanol (**10**)[7] were taken into account. The plan was to prepare from these the enantiomerically pure (4,4-dibromospiropentyl)methanol [(1*S*,3*R*)-**7**] and (5,5-dibromodispiro[2.0.2.1]heptyl)methanol [(1*R*,3*S*,4*S*)-**19**], respectively, and apply the dehalogenative coupling of the 1-bromo-1-lithiocyclopropanes generated from them in the presence of cupric chloride according to the method of Neuenschwander et al.[8] by an improved protocol.[8f] The actual starting material was the previously described 2-[(2-methylenecyclopropyl)methoxy]tetrahydropyran (**6**),[7] to which dibromocarbene was added under phase-transfer catalysis using KOH pellets according to a well-established protocol (Scheme 1).[9] This cyclopropanation proceeded highly stereoselectively and, after cleavage of the THP ether, afforded dibromoalcohol *rac*-**7** (54% overall yield) with an *anti*-arrangement of its hydroxymethyl and dibromomethylene groups, as confirmed by X-ray crystal structure analysis.[10]



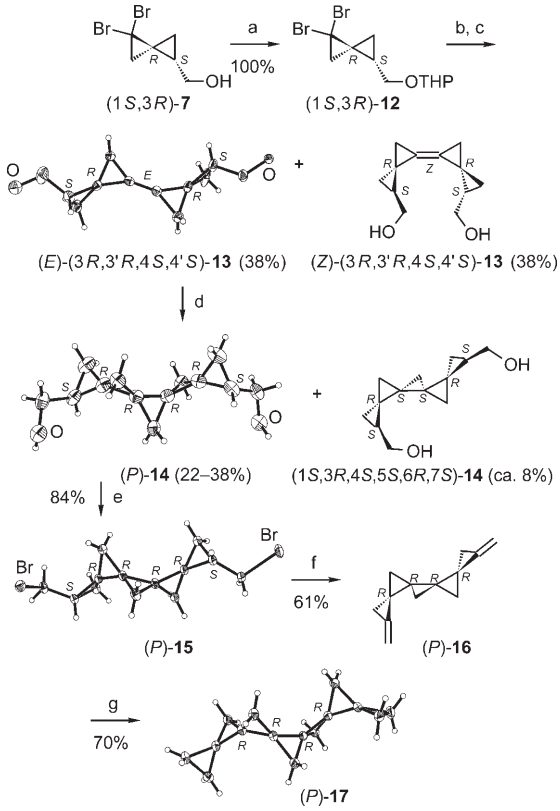
Scheme 1. Preparation of enantiomerically pure starting materials (1*S*,3*R*)-**7**, (1*R*,3*S*)-**8**, (1*R*,3*S*)-**10**, and (1*S*,3*R*)-**11**. a) $CHBr_3$, KOH (pellets), TEBACl, CH_2Cl_2, 20–25 °C, 3 h; b) MeOH, PPTS, 65 °C, 3 h; c) Ac_2O, Py, 0–20 °C, 6 h; d) lipase CES, CH_2Cl_2, phosphate buffer solution (pH 7), 50 °C, 6 d; e) (*S*)-mandelic acid, *p*TsOH·H_2O, benzene, molecular sieves 4 Å, 80 °C, 6 h; f) MeOH, H_2SO_4, 65 °C, 4 h; g) vinyl acetate, lipase PS, Et_2O, 0–20 °C, 6 h.

The alcohol *rac*-**7** was acetylated with acetic anhydride in pyridine, and the acetate *rac*-**8** was kinetically resolved by means of enantioselective enzymatic deacylation with lipase CES[11] to furnish (1*S*,3*R*)- and [(1*R*,3*S*)-4,4-dibromospiropent-1-yl]methanol [(1*S*,3*R*)-**7** and (1*R*,3*S*)-**7**] in 40 and 39% yield, the latter after hydrolysis of the [(1*R*,3*S*)-4,4-dibromospiropent-1-yl]methyl acetate [(1*R*,3*S*)-**8**], respectively. The absolute configuration of the former was assigned on the basis of the relative configuration of its ester with (*S*)-(+)-mandelic acid (1′*S*,3′*R*,2*S*)-**9** as determined by X-ray diffraction[10] (Scheme 1).

On the other hand, the methylenecyclopropane derivative **6** was converted in three steps into (4-methylenespiropent-1-yl)methanol *rac*-**10** according to the published procedure,[7a] and *rac*-**10** was kinetically resolved in $\geq$100 g quantities by means of an enantioselective enzymatic acylation catalyzed by lipase PS (*Pseudomonas* sp.), applying the previously published protocol[2b,12] to afford the alcohol (1*R*,3*S*)-**10** and the acetate (1*S*,3*R*)-**11**.

Applying an improved protocol of the original one by Neuenschwander et al.[8f] for the reductive dimerization of a dibromocyclopropane via a copper carbenoid generated by treatment of the dibromocyclopropane with *n*-butyllithium in the presence of copper(II) chloride, to the tetrahydropyranyl ether (1*S*,3*R*)-**12**, prepared from the corresponding alcohol (1*S*,3*R*)-**7** with an *anti*-arrangement of its hydroxymethyl and dibromomethylene groups, yielded a mixture of the diastereomeric bicyclopropylidene[13] derivatives (*E*)-**13** and (*Z*)-**13** as diols after cleavage of the THP ethers (Scheme 2). After chromatographic separation, (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** and (*Z*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** with appropriate configurations of the former towards the target continuously helical [7]triangulane were obtained in 38% yield each. The assigned *E* configuration of (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** was confirmed by an X-ray crystal structure analysis.[10]

Among several attempted cyclopropanations of the diol (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** (e. g. with CH_2N_2/$Pd(OAc)_2$[14] or with CH_2I_2/$AlMe_3$[15]) only the old and nowadays rarely applied Müller's modification[16c] of the Müller–Gaspar–Roth cyclopropanation protocol (with CH_2N_2/CuCl),[16] albeit with a tremendous excess of diazomethane and cuprous chloride, gave the target [5]triangulane-1,7-dimethanol (1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-**14** [(*P*)-(+)-**14**] (assigned on the basis of its relative configuration as disclosed by X-ray crystal structure analysis[10]) in 22–38% isolated yield on a 7 mmol scale,[17] along with the corresponding diastereomer (1*S*,3*R*,4*S*,5*S*,6*R*,7*S*)-**14** in about 8% yield. The enantiomerically pure diol (*P*)-(+)-**14** was transformed to the enantiomerically pure (*P*)-[7]triangulane [(*P*)-(+)-**17**] in three routine steps as established for the preparation of triangulanes.[2] First, it was converted to the bis(bromomethyl)[5]triangulane (*P*)-**15** by treatment with the triphenylphosphane/bromine reagent, subsequent dehydrobromination of (*P*)-**15** with potassium *tert*-butoxide gave 1,7-dimethylene[5]triangulane (*P*)-**16**, and cyclopropanation of the latter with diazomethane under $Pd(OAc)_2$ catalysis[14] furnished the enantiomerically pure (*P*)-[7]triangulane [(*P*)-(+)-**17**] with enantiomeric excesses of $\geq$99% in

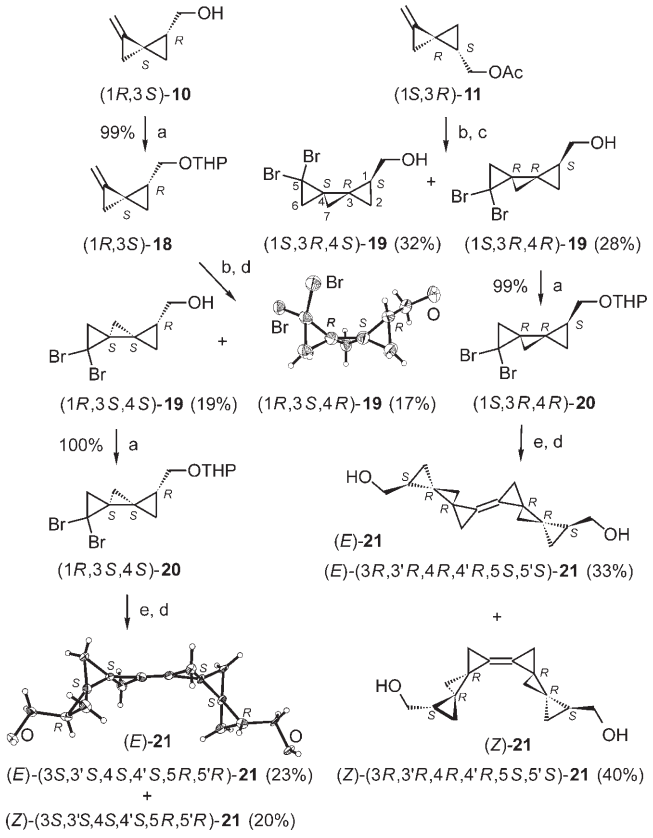


Scheme 2. Preparation of enantiomerically pure (3*R*,3′*R*,4*S*,4′*S*)-{4′-hydroxymethyl-[1,1′-bi(spiropentylidene)]-4-yl}methanols (*Z*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** and (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13**, cyclopropanation of the latter and synthesis of enantiomerically pure (*P*)-[7]triangulane [(*P*)-(+)-**17**. a) DHP, PPTS, CH_2Cl_2, 20°C, 3.5 h; b) *n*BuLi, $CuCl_2$, THF/Et_2O 10:1, −105 to −95°C, 1 h, then −78 → 20°C, 2 h; c) MeOH, PPTS, 65°C, 6 h; d) CH_2N_2 (26.3 equiv), CuCl (23.4 equiv) (22% yield) or CH_2N_2 (21 equiv), CuCl (19.4 equiv), $Cu(OTf)_2$ (0.14 equiv), 20°C, 3 h (38% yield); e) $Ph_3P{\cdot}Br_2$, Py, CH_2Cl_2, −30 → 20°C, 5.5 h; f) *t*BuOK, DMSO, 20°C, 25 min; g) CH_2N_2, $Pd(OAc)_2$, Et_2O, −5°C.

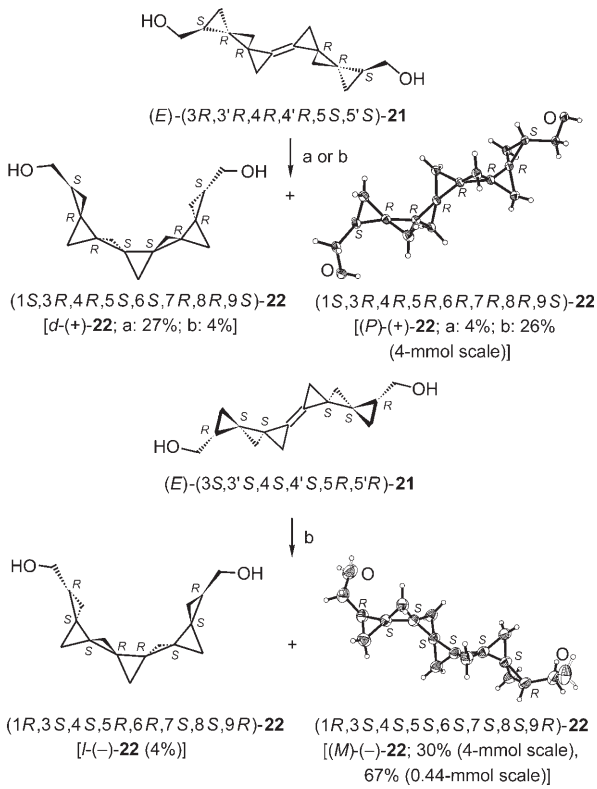
36% overall yield after chromatographic purification in the last step (Scheme 2).

The preparation of enantiomerically pure [9]triangulanes applying this same strategy started with dibromocarbene addition onto the double bond in the tetrahydropyranyl ether (1*R*,3*S*)-**18** from the alcohol (1*R*,3*S*)-**10** or in the acetate (1*S*,3*R*)-**11**, adopting the protocol mentioned above; subsequent deprotection and chromatographic separation furnished (5,5-dibromodispiro[2.0.2.1]heptyl)methanols (1*R*,3*S*,4*S*)-, (1*R*,3*S*,4*R*)-, (1*S*,3*R*,4*S*)-, and (1*S*,3*R*,4*R*)-**19** in 19, 17, 32, and 28% yield, respectively (Scheme 3). The absolute configuration of all four diastereomers was assigned on the basis of the X-ray crystal structure analysis[10] of an arbitrarily selected dibromocyclopropane derivative of type **19**, prepared from (1*R*,3*S*)-**11**, the known absolute configuration of the starting materials,[12] and comparison of the NMR spectra.

Reductive dimerization of the tetrahydropyranyl ethers (1*R*,3*S*,4*S*)-**20** and (1*S*,3*R*,4*R*)-**20** prepared from the corresponding alcohols (1*R*,3*S*,4*S*)-**19** and (1*S*,3*R*,4*R*)-**19** with an



Scheme 3. Preparation of enantiomerically pure 5,5′-bis(dispiro-[2.0.2.1]heptylidene-methanols) (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-, (*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-, and (*Z*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-**21**. a) DHP, PPTS, CH_2Cl_2, 20 °C, 1.5–5 h; b) $CHBr_3$, KOH (pellets), TEBACl, CH_2Cl_2, 20–25 °C, 1–3 h; c) MeOH, H_2SO_4, 65 °C, 4 h; d) MeOH, PPTS, 50–65 °C, 2–18 h; e) *n*BuLi, $CuCl_2$, THF/Et_2O 10:1, −105 to −95 °C, 1 h, then −78 → 20 °C, 2 h; 2 h.



Scheme 4. Cyclopropanation of enantiomerically pure 1,1′-bis(dispiro-[2.0.2.1]heptylidene-methanols) (*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)- and (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21** under two different conditions. a) $ZnEt_2$, CH_2I_2, TFA, CH_2Cl_2, 0 → 20 °C, 5.5 h; b) CH_2N_2 (120–160 equiv), CuCl (43–50 equiv), 20 °C, 3 h.

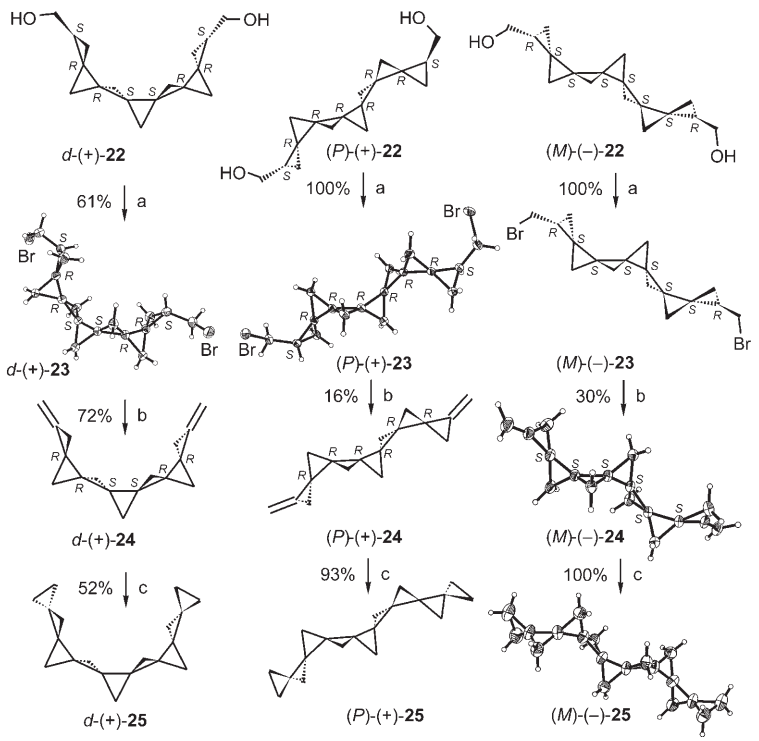
anti-arrangement of their hydroxymethyl and dibromomethylene groups, yielded mixtures of the diastereomeric bicyclopropylidene derivatives (*E*)-**21** and (*Z*)-**21** after cleavage of the THP ethers (Scheme 3). After chromatographic separation, diols (*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-**21** and (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21** with appropriate configurations towards the target continuously helical [9]triangulanes were obtained in 33 and 23 % yield, respectively. The assigned *E* configuration of the latter was confirmed by an X-ray crystal structure analysis.[10]

As was mentioned above for the attempted cyclopropanations of bis(spiropentylidene)dimethanol (*E*)-**13** with CH_2N_2/$Pd(OAc)_2$ or CH_2I_2/$AlMe_3$ reagents, those of the analogous **21** proceeded with very low conversions. Surprisingly, the modified Simmons–Smith type cyclopropanation[18] according to Shi et al. (with CH_2I_2/$ZnEt_2$/TFA)[19] applied to (*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-**21** gave a moderate yield (27 %) of a [7]triangulanedimethanol which, disappointingly, turned out to be the inappropriately configured (1*S*,3*R*,4*R*,5*S*,6*S*,7*R*,8*R*,9*S*)-**22** [*d*-(+)-**22**] with a horseshoe shape (Scheme 4). Apparently, the cyclopropanation of (*E*)-**21** under these conditions occurs on the sterically less congested face of the bicyclopropylidene moiety.

Like (*P*)-**14** from (*E*)-**13**, the target diols (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*,8*R*,9*S*)-**22** [(*P*)-(+)-**22**] and (1*R*,3*S*,4*S*,5*S*,6*S*,7*S*,8*S*,9*R*)-**22** [(*M*)-(−)-**22**] (assigned on the basis of their relative configurations as disclosed by X-ray crystal structure analyses[10]) were eventually prepared in 26 and 30 % isolated yield, respectively, on a 4-mmol scale applying the Müller–Gaspar–Roth cyclopropanation protocol again (Scheme 4). It is conceived that the bicyclopropylidenediols (*E*)-**13** and (*E*)-**21** under these conditions with excesses of copper(I) salts present, initially form alkenecopper(I) complexes in which the copper sits on the *exo*-face,[20] and these copper(I) complexes then undergo cyclopropanation with attack of the carbenoid on the originally more congested *endo*-face.

The enantiomerically pure diols *d*-(+)-**22**, (*P*)-(+)-**22**, and (*M*)-(−)-**22** were transformed to the enantiomerically pure *d*- [*d*-(+)-**25**], (*M*)- [(*M*)-(−)-**25**] and (*P*)-[9]triangulanes [(*P*)-(+)-**25**], respectively, as described above for (*P*)-**14**, by initial conversion to the corresponding bis(bromomethyl)[7]-triangulanes **23**, subsequent twofold dehydrobromination of **23** with potassium *tert*-butoxide to 1,9-dimethylene[7]triangulanes **24**, and final twofold cyclopropanation of the latter with diazomethane under $Pd(OAc)_2$ catalysis. The enantio-

merically pure *d*- [*d*-(+)-**25**], (*M*)- [(*M*)-(−)-**25**], and (*P*)-[9]triangulanes [(*P*)-(+)-**25**] were obtained from **22** in 23, 30, and 15% overall yield, respectively, with enantiomeric excesses of ≥99%, after chromatographic separation in the last step (Scheme 5). The relative configurations of (*M*)-(−)-**24** and (*M*)-(−)-**25** were confirmed by X-ray crystal structure analyses.[10]



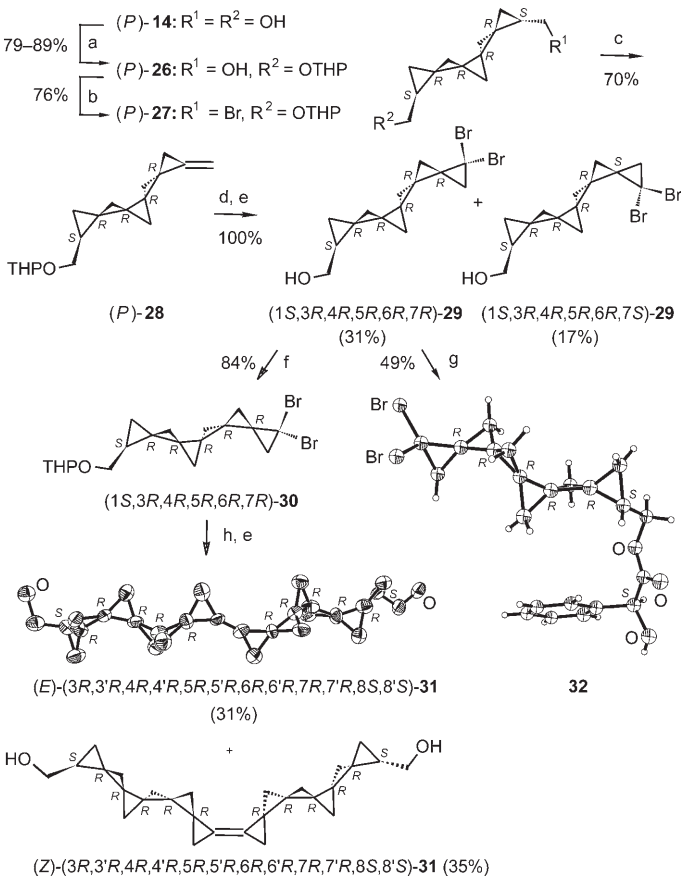
Scheme 5. Preparation of enantiomerically pure *d*- [*d*-(+)-**25**], (*M*)- [(*M*)-(−)-**25**] and (*P*)-[9]triangulanes [(*P*)-(+)-**25**]. a) $Ph_3P{\cdot}Br_2$, Py, CH_2Cl_2, −30 → 20 °C, 5 h; b) *t*BuOK, DMSO, 55 °C, 20 min; c) CH_2N_2, $Pd(OAc)_2$, Et_2O, −5 °C.

This new approach to enantiomerically pure linear triangulanes with an odd number of three-membered rings was also tested in two variants towards [15]triangulane (Scheme 6). According to the first variant, the enantiomerically pure diol (*P*)-**14** was selectively protected as a THP ether on one hydroxy group applying wet Dowex 50WX2-100 resin as a catalyst (cf. ref. [21]), the free hydroxymethyl moiety was converted to a bromomethyl group according to a published protocol,[22] and then the monobromide was dehydrobrominated to give THP-protected methylene[5]triangulanylmethanol (*P*)-**28** in 47% overall yield. Dibromocyclopropanation of the latter followed by deprotection furnished a 3:2 mixture of two diastereomeric dibromo[6]triangulanylmethanols **29** in virtually quantitative yield; however, upon HPLC separation the yield dropped to 31 and 17%, respectively. The absolute configuration of the major diastereomer was assigned on the basis of the relative configuration of its ester **32** with (*S*)-(+)-mandelic acid (Scheme 6) according to an X-ray crystal structure determination[10] and appeared to be (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*), thus appropriate for the reductive dimerization towards the target molecule. Therefore, (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-**29** was converted in three routine steps into a mixture of bicyclopropylidene derivatives (*E*)- and (*Z*)-**31**, from which the diol (*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*R*,5′*R*,6*R*,6′*R*,7*R*,7′*R*,8*S*,8′*S*)-**31** with appropriate configuration towards [15]triangulane, as established by X-ray crystal structure analysis,[10] was isolated in 31% yield. The corresponding diastereomer (*Z*)-**31** was obtained in 35% yield.[23]

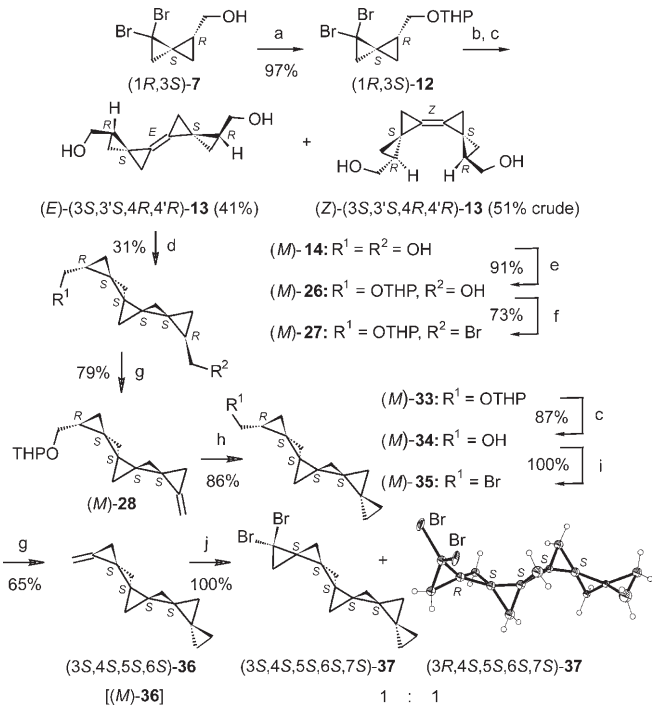
However, cyclopropanation of (*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*R*,5′*R*,6*R*,6′*R*,7*R*,7′*R*,8*S*,8′*S*)-**31** turned out to be the road-block in this synthetic sequence, as none of the cyclopropanation methods discussed above was successful in this particular case. Even the reaction with diazomethane under $CuCl/Cu(OTf)_2$ catalysis gave only traces of the cyclopropanation products without any stereoselectivity; a number of unidentified by-products was also formed. This peculiar behavior is not at all understood in view of the above described results for the successful cyclopropanation of (*E*)-**13** or (*E*)-**21**.

The second possible approach to an enantiomerically pure [15]triangulane was conceived to apply the reductive dimerization of an enantiomerically pure dibromo[7]triangulane **37** as a key step, followed by final cyclopropanation of the central bicyclopropylidene double bond. The preparation of the appropriate building block (3*S*,4*S*,5*S*,6*S*,7*S*)-**37** started with the enantiomerically pure [(1*R*,3*S*)-4,4-dibromospiropentyl]methanol [(1*R*,3*S*)-**7**] (see Scheme 7).

Applying the new standard set of transformations, the dibromoalcohol (1*R*,3*S*)-**7** was converted in four steps with 12% overall yield into [5]triangulane-1,7-dimethanol (*M*)-(−)-**14**, and this was then transformed to the methylene[5]-triangulane derivative (*M*)-**28** in three further steps (52% overall yield). The terminal double bond in the latter was cyclopropanated, and transformation of the second cyclopropylmethanol terminus in the resulting (*M*)-**33** into a methylenecyclopropane moiety in three successive steps with 57% overall yield afforded the methylene[6]triangulane (*M*)-**36** (Scheme 7). Dibromocyclopropanation of the latter furnished a 1:1 mixture of diastereomeric dibromo[7]-triangulanes (3*R*,4*S*,5*S*,6*S*,7*S*)-**37** and (3*S*,4*S*,5*S*,6*S*,7*S*)-**37** in quantitative yield. The pure dibromides (3*R*,4*S*,5*S*,6*S*,7*S*)- and (3*S*,4*S*,5*S*,6*S*,7*S*)-**37** were isolated by HPLC separation,



Scheme 6. Attempted preparation of enantiomerically pure (*P*)-(+)-[15]triangulane. a) DHP, Dowex 50WX2-100, toluene, DMF, 25 °C, 11–41 h; b) CBr_4, Ph_3P, Im-H, CH_2Cl_2, 0–20 °C, 1.5 h; c) *t*BuOK, DMSO, 20 °C, 20 min; d) $CHBr_3$, KOH (pellets), TEBACl, CH_2Cl_2, 0–25 °C, 3 h; e) MeOH, PPTS, 65 °C, 3–10 h; f) DHP, PPTS, CH_2Cl_2, 20 °C, 4 h; g) (*S*)-mandelic acid, *p*-TsOH·H_2O, benzene, molecular sieves 4 Å, 80 °C, 2.5 h; h) *n*BuLi, $CuCl_2$, THF/Et_2O 25:1, −105 to −95 °C, 1 h, then −78 → 20 °C, 2 h.

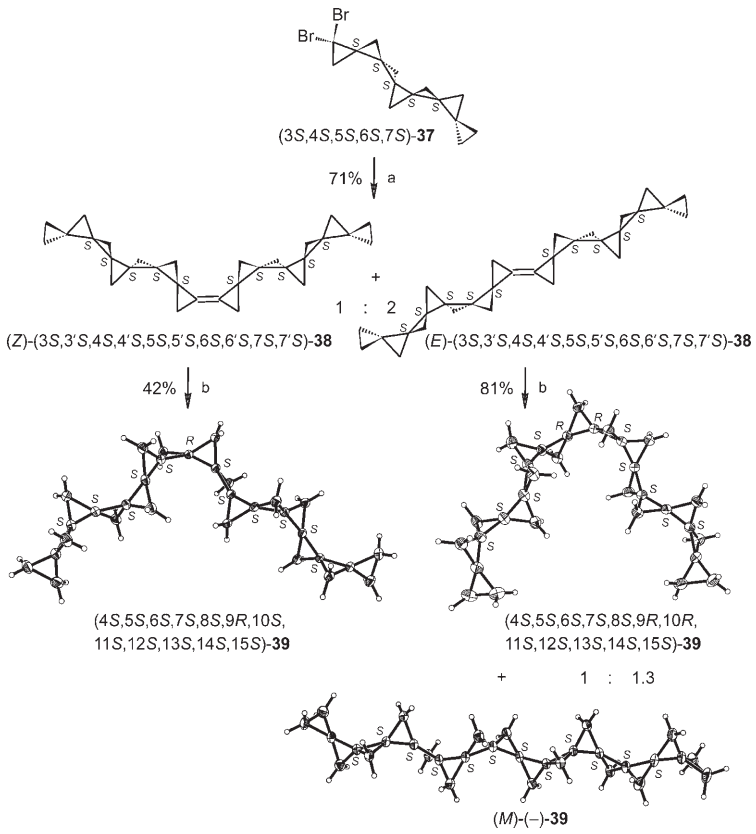


Scheme 7. Preparation of enantiomerically pure building blocks (3*S*,4*S*,5*S*,6*S*,7*S*)-**37** and (3*R*,4*S*,5*S*,6*S*,7*S*)-**37**. a) DHP, PPTS, CH_2Cl_2, 20 °C, 26 h; b) *n*BuLi, $CuCl_2$, THF/Et_2O 14:1, −105 to −95 °C, 1 h, then −78 → 20 °C, 2 h; c) MeOH, PPTS, 65 °C, 2 h; d) CH_2N_2 (21 equiv), CuCl (19.4 equiv), $Cu(OTf)_2$ (0.14 equiv), 20 °C, 3 h; e) DHP, Dowex 50WX2-100, toluene, DMF, 25 °C, 16 h; f) CBr_4, Ph_3P, Im-H, CH_2Cl_2, 0–20 °C, 1.5 h; g) *t*AmOK, DMSO, 20 °C, 40 min; h) CH_2N_2, $Pd(OAc)_2$, Et_2O, −5 °C; i) $Ph_3P{\cdot}Br_2$, Py, CH_2Cl_2, −30 → 20 °C, 5 h; j) $CHBr_3$, KOH (powder), TEBACl, CH_2Cl_2, 0–25 °C, 14 h.

however, with significant loss of material, so that the final yields were only 16 and 20%, respectively. Their absolute configurations were assigned on the basis of an X-ray crystal structure analysis[10] of the arbitrarily selected dibromo[7]-triangulane (3*R*,4*S*,5*S*,6*S*,7*S*)-**37**, and the known absolute configuration of the starting material. While an attempted reductive dimerization of the dibromide (3*R*,4*S*,5*S*,6*S*,7*S*)-**37** furnished only trace amounts of bicyclopropylidene derivatives along with a number of unidentified products, reductive dimerization of its diastereomer (3*S*,4*S*,5*S*,6*S*,7*S*)-**37** gave a 1:2 mixture of diastereomeric bicyclopropylidenes (*Z*)- and (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*S*,5′*S*,6*S*,6′*S*,7*S*,7′*S*)-**38** in 71% yield (Scheme 8). After HPLC separation these compounds were isolated in 20 and 33% yield, respectively, and exhibited specific rotations $[\alpha]_D^{20} = -1110.1$ ($c = 0.525$ in $CHCl_3$) and −1446.1 ($c = 0.525$ in $CHCl_3$), respectively.

Both the (*Z*)- and (*E*)-**38** were almost resistant towards cyclopropanation; however, applying a tremendous excess of diazomethane and cuprous chloride and repeating the cyclopropanation protocol four times, a single diastereomer of [15]triangulane with $[\alpha]_D^{20} = -868.5$ ($c = 0.931$ in $CHCl_3$) was obtained from (*Z*)-**38** in 42% yield, X-ray crystal structure analysis of which indeed disclosed the expected (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*) configuration.[10] Under the same conditions, bicyclopropylidene (*E*)-**38** gave a 1:1.3 mixture of two diastereomers in 81% yield. After HPLC separation these compounds were isolated in 19 and 23% yield, respectively; the X-ray crystal structure analyses revealed the horseshoe-shaped (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39** and the continuously helical (*M*)-**39** configuration, respectively, with specific rotations $[\alpha]_D^{20} = -721.8$ ($c = 0.257$ in $CHCl_3$) and −1302.5 ($c = 0.362$ in $CHCl_3$), respectively (Scheme 8).

These newly prepared two bent and one straight rod-like [15]triangulanes (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*S*11*S*,12*S*,13*S*,14*S*,15*S*)-**39**, (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39** and the continuously helical (*M*)-**39**, essentially set the new record for unbranched [*n*]triangulanes. By the sheer number of spiroannelated three-membered rings, this record had previously only been achieved for a highly branched [15]triangulane (cf. ref. [8f]). The widths between the outermost hydrogen atoms in (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39**, (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39**, and (*M*)-**39** were found to be 17.3, 13.5, and 21.1 Å, respectively, and



Scheme 8. Preparation of enantiomerically pure (−)-[15]triangulanes. a) *n*BuLi, $CuCl_2$, THF/Et_2O 10:1, −105 to −95 °C, 1 h, then −78 → 20 °C, 2 h; b) CH_2N_2 (290–350 equiv), CuCl (313–400 equiv), $Cu(OTf)_2$ (2.2–3.6 equiv), 20 °C, 3 h, and this procedure was repeated three more times.

the widths between the outermost carbon atoms are 16.4, 11.6, and 19.5 Å, respectively (see Figure 1).

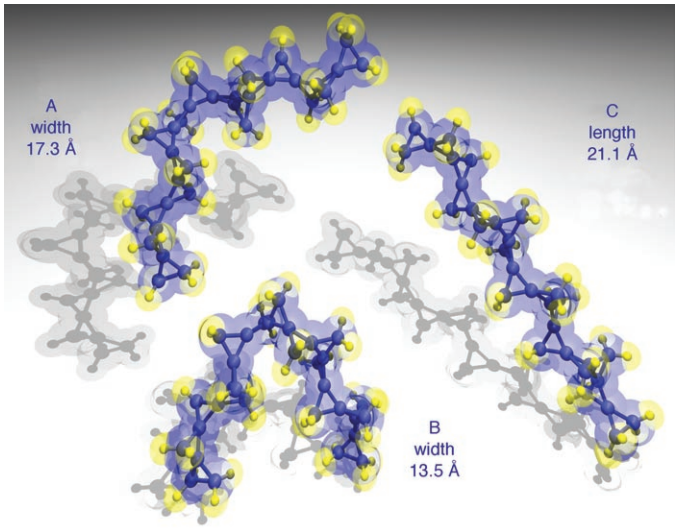


Figure 1. Space-filling models of enantiomerically pure bent [15]triangulanes (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39** (A), (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39** (B) and the continuously helical σ-[15]helicene (M)-(−)-**39** (C) according to their X-ray crystal structures.

Rotatory powers of higher [*n*]triangulanes and methylenetriangulanes: As expected, enantiomerically pure [*n*]triangulanes do not display any absorption in the ordinarily accessible Vis/UV spectral range (800–200 nm, Figure 2). Their CD curves are very intense below 200 nm and differ in intensity and shape (thus, a shoulder is observed around 192 nm in the case of (*P*)-**3** and (*P*)-**4**). Their intensities grow with a growing number of cyclopropane units in the molecules (Figure 2).

However, the newly prepared σ-[7]helicene (*P*)-(+)-**17** as well as both the σ-[9]helicenes (*P*)-(+)-**25** and (*M*)-(−)-**25** and [15]helicene (*M*)-(−)-**39** have remarkably high specific rotations even at 589 nm with $[\alpha]_D^{20} = +672.9$ ($c = 0.814$ in $CHCl_3$) [(*P*)-(+)-**17**], +909.9 ($c = 0.96$ in $CHCl_3$) [(*P*)-(+)-**25**], −890.5 ($c = 1.01$ in $CHCl_3$) [(*M*)-(−)-**25**], and −1302.5 ($c = 0.362$ in $CHCl_3$) [(*M*)-(−)-**39**]. The specific rotations increase drastically on going to shorter wavelengths with $[\alpha]_{436}^{20} = +1404.5$ and $[\alpha]_{365}^{20} = +2290.8$ [(*P*)-(+)-**17**], $[\alpha]_{436}^{20} = +1907.0$ and $[\alpha]_{365}^{20} = +3119.4$ [(*P*)-(+)-**25**], $[\alpha]_{436}^{20} = -1866.2$ and $[\alpha]_{365}^{20} = -3051.1$ [(*M*)-(−)-**25**] and $[\alpha]_{436}^{20} = -2738.7$ and $[\alpha]_{365}^{20} = -4493.4$ [(*M*)-(−)-**39**] indicating that these compounds must have Cotton effects with extremely large amplitudes in the ORD below 200 nm.

Density functional theory (DFT) computations at the level B3LYP/6-31+G(d,p)[25–30] for the geometry optimization and time-dependent DFT for determining optical rotations with a triplet-ζ basis set (B3LYP/TZVP)[31] in the gas phase predicted specific rotations which are in remarkably good agreement with the experimental values over the whole range of wavelengths (Table 1) for the [4]- (**2**), [5]- (**3**), and [7]triangulanes (**17**). This confirms strong positive or negative Cotton effects in the ORDs going along with large ellipticities in the circular dichroisms below 200 nm. This good agreement between experiment and theory not only provides confidence in the general applicability of this computational approach to the simulation of ORD and CD spectra,[32] but also confirms that the rotatory powers of **2**, **3**, and **17** are an outflow of their helical arrangements of sigma bonds. In contrast, the enantiomerically pure, but not continuously helical, horse-shoe shaped *d*-[9]triangulane *d*-(+)-**25**, showed specific rotations of $[\alpha]_D^{20} = +244.9$ ($c = 1.13$ in $CHCl_3$), $[\alpha]_{436}^{20} = +511.2$, and $[\alpha]_{365}^{20} = +832.0$ only. Starting

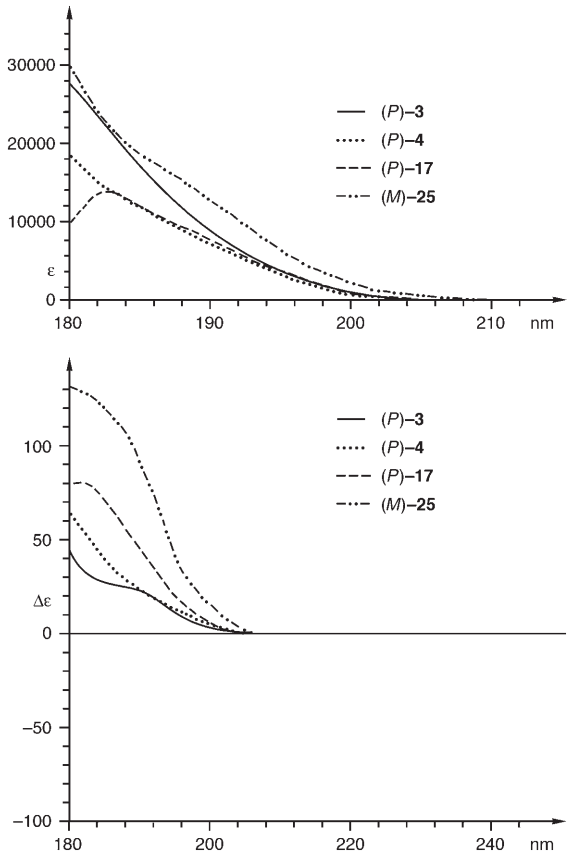


Figure 2. UV (top) and CD (bottom) spectra of enantiomerically pure [*n*]triangulanes (*P*)-**3**, (*P*)-**4**, (*P*)-**17**, and (*M*)-**25** in cyclohexane, path length 0.01 cm. For (*M*)-**25**, the CD spectrum was multiplied by −1 for comparison.[24]

with the [7]triangulane, the computed specific rotations for the higher [*n*]triangulanes with $n=9$ and 15 (as well as for the higher π-[*n*]helicenes) increasingly exceed the experimentally determined ones (Figure 3 and Tables 1 and 2). Most probably, this is due to an increasing flexibility with increasing length of the [*n*]triangulanes,[33] which is not taken into account by the computations. This interpretation is particularly feasible in view of the fact that recently prepared helical [*n*]tetrangulanes do not exhibit increasing specific rotations at all with an increasing number of four-membered rings.[5] It is also supported by the observation that the specific rotations of for example (*M*)-**39** increase with decreasing temperature to a significantly larger extent than would correspond to the increasing density.[34]

Obviously, the inherent helicity of the [*n*]triangulanes also is an essential contributor to the overall rotatory power of the methylene[*n*−1]triangulanes and dimethylene-[*n*−2]triangulanes, which are the synthetic precursors of the [*n*]triangulanes. However, when comparing the specific rotations of methylene[6]triangulane [(*M*)-(−)-**36**], dimethylene[5]triangulane [(*P*)-(+)-**16**], [7]triangulane [(*P*)-(+)-**17**], dimethylene[7]triangulane [(*P*)-(+)-**24**] and [9]triangulane [(*P*)-(+)-**25**] (912.4, 926.2, 672.9, 1302.1, and 909.9°, respectively), it is noted that, in contrast to [4]- and [5]triangulanes, for which the specific rotations of their synthetic precursors were lower ($[\alpha]^{20}_{D\ \text{dimethylenespiropentane}}/[\alpha]^{20}_{D\ [4]\text{triangulane}}=0.65$) or similar,[2b] the rotatory strengths of the dienes **16**, **24** turned out to be 1.37 and 1.43 times as large as those of the triangulanes **17**, **25**, respectively.

Table 1. Comparison of the measured (in $CHCl_3$) and DFT/SCI-computed specific rotations of enantiomerically pure methylenetriangulanes and triangulanes.

Compound	λ [nm]	$[\alpha]^{20}_D$ Measured	$[\alpha]^{20}_D$ Computed[a]
(*M*)-(−)-**2**[b]	589	−192.7	−217.9
	546	−229.7	−264.0
	436	−400.2	−407.8
	365	−648.2	−576.7
(*P*)-(+)-**3**[b]	589	+373.0	+394.9
	546	+445.2	+508.1
	436	+777.4	+791.9
	365	+1264.0	+1080.3
(*M*)-(−)-**3**[b]	589	−334.2	−394.9
	546	−398.7	−508.1
	436	−696.3	−791.9
	365	−1033.1	−1080.3
(*M*)-(−)-**36**	589	−912.4	−1138.5
(*P*)-(+)-**16**	589	+926.2	+1068.3
	546	+1118.3	+1266.1
	436	+2060.2	+2134.3
	365	+3612.6	+3340.6
(*P*)-(+)-**17**	589	+672.9	+879.5
	546	+802.8	+1054.4
	436	+1404.5	+1873.1
	365	+2290.8	+3165.2
(*M*)-(−)-**24**	589	−1285.4	−1623.9
	546	−1556.4	−1946.7
	436	−2863.4	−3397.8
	365	−4971.5	−5623.5
(*P*)-(+)-**24**	589	+1302.1	+1623.9
	546	+1570.2	+1946.7
	436	+2872.5	+3397.8
	365	+4989.7	+5623.5
(*M*)-(−)-**25**	589	−890.5	−1006.5
	546	−1058.0	−1192.8
	436	−1866.2	−2010.7
	365	−3051.1	−3145.5
(*P*)-(+)-**25**	589	+909.9	+1006.5
	546	+1087.1	+1192.8
	436	+1907.0	+2010.7
	365	+3119.4	+3145.5
(*M*)-(−)-**39**	589	−1302.5	−2419.9
	546	−1556.6	−2875.5
	436	−2738.7	−4904.8
	365	−4493.4	−7804.1

[a] All computed values were adjusted by subtracting a constant value to account for effects of solvent–solute interactions, which currently cannot be taken into account computationally (see Computational Methods). [b] From ref. [2b].

Comparison of the values of $[\alpha]^{20}_D$ for the now known five enantiomerically pure σ-[*n*]helicenes (*M*)-(−)-**2** (−192.7),[2a,b] (*P*)-(+)-**3** (+373.0),[2b] (*P*)-(+)-**17** (+672.9), (*P*)-(+)-**25** (+909.9), and (*M*)-(−)-**39** (−1302.5) indicates a drastic and continuous increase of the specific rotation with an increasing number of three-membered rings (cf. ref. [5]).

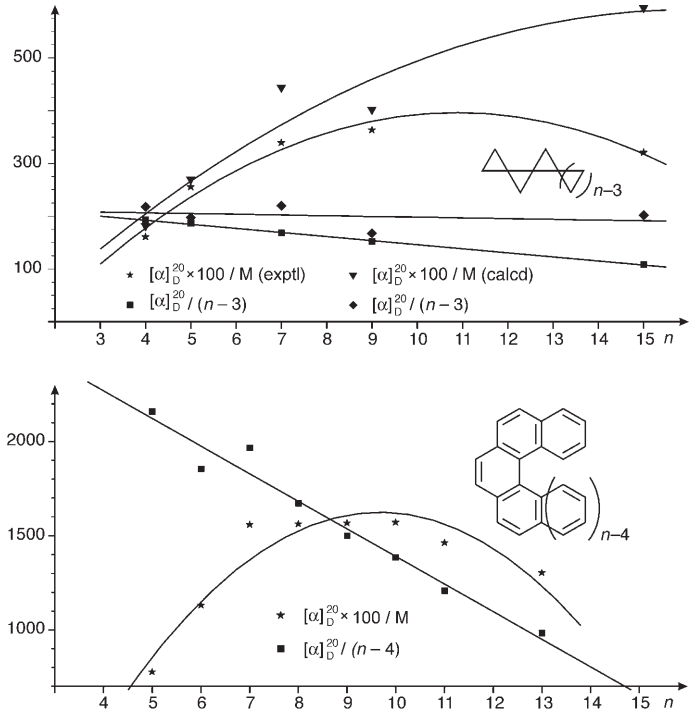


Figure 3. Dependence of specific rotations $[\alpha]_D^{20}$ of enantiomerically pure helical [*n*]triangulanes ("σ-[*n*]helicenes") normalized with respect to molecular weights (■: experimentally determined values, ◆: computed values) and to the number of spiroannelated cyclopropanes (*: experimentally determined values, ▼: computed values) on the number of spiroannelated cyclopropane rings (top) in comparison with analogous experimentally determined values for π-[*n*]helicenes (bottom).[35]

This increase goes beyond that to be expected with increasing molecular weights (Figure 3). Interestingly, the values of $[\alpha]_D^{20}$ normalized with respect to the number of spiroannelated cyclopropanes exceeding $n=3$ for the achiral [3]triangulane ($n-3$) decrease steadily with an increasing number n.

The decreasing incremental value $[\alpha]_D^{20}/(n-3)$ ($\Delta[\alpha]$) for each added spirocyclopropane ring starting from the achiral [3]triangulane (dispiro[2.0.2.1]heptane) exhibits virtually a linear dependence on the number of the rings with a regression line $\Delta[\alpha]=223.32-7.72\times n$ and a correlation coefficient $r=0.999$. The extrapolation of this line intersects the base line at $n=29$, which means that the specific rotation, normalized with respect to the number ($n-3$) of three-membered rings added to the achiral [3]triangulane, for higher enantiomerically pure helical [*n*]triangulanes ($n \geq 29$) would not increase any more. Although it has never been interpreted in this way, the same phenomenon can be observed for the π-[*n*]helicenes, for which the intersection with the base line already occurs around $n=15$ (Figure 3).

It will also be quite interesting to investigate the Raman optical activities (ROA) of the whole series of enantiomerically pure methylene[$n-2$]triangulanes and [*n*]triangulanes, since the ROA of (*M*)-(−)-[4]triangulane (*M*)-(−)-**3** has been shown to disclose spectacular effects with Δ values close to 0.5 % in the 900 cm^{-1} region.[37]

Crystal engineering and molecular architectures of newly prepared compounds: formation of unique supramolecular aggregates: On top of the extraordinarily high specific rotations, several of the newly prepared helical [*n*]triangulane derivatives exhibit additional remarkable features in that the diols (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13**, (*P*)-**14**, (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21**, (*P*)-(+)-**22**, (1*S*,3*R*,4*S*,5*S*,6*S*,7*S*,8*R*,9*S*)-**22** (see below), and (*E*)-**31** self-assemble in very specific ways in the solid state. The remarkably variable packing modes of diols in general and, therefore, their potential use as assembly units in crystal engineering, attracted significant attention in several recent publications.[38] The most common intermolecular interactions in these compounds are, not surprisingly, hydrogen bonds, and they frequently form linear chains of the type O-H···O-H···O-H···; however, hydrogen bridging between diol molecules can also lead to various types of supramolecular aggregates such as different ladders, sheets, rings. Diols also eagerly form inclusion compounds with a large variety of the guest mol-

Table 2. Experimentally determined and computed specific and normalized rotations for [*n*]triangulanes (σ-[*n*]helicenes) and π-[*n*]helicenes.

σ-[*n*]helicenes							
		Experimentally found[a]			Computed		
n	*M*	$[\alpha]_D^{20}$	$([\alpha]_D^{20}/M)\times 100$	$[\alpha]_D^{20}/(n-3)$	$[\alpha]_D^{20}$	$([\alpha]_D^{20}/M)\times 100$	$[\alpha]_D^{20}/(n-3)$
4	120.2	192.7	160.3	192.7	217.9	181.3	217.9
5	146.2	373.0	255.1	186.5	394.9	270.1	197.5
7	198.3	672.9	339.4	168.2	879.5	443.5	219.9
9	250.4	909.9	363.4	151.6	1006.5	402.0	167.8
15	406.6	1302.5	320.4	108.6	2419.9	595.2	201.7
π-[*n*]helicenes							
		Experimentally found[b,c]			Computed[d]		
n	*M*	$[\alpha]_D^{20}$	$([\alpha]_D^{20}/M)\times 100$	$[\alpha]_D^{20}/(n-4)$	$[\alpha]_D^{20}$	$([\alpha]_D^{20}/M)\times 100$	$[\alpha]_D^{20}/(n-4)$
5	278.4	2160[35a]	776.0	2160.0	2116.1	760.1	2116.1
6	328.4	3709[35b]	1129.4	1854.5	3695.1	1125.2	1847.6
7	378.5	5900[35c]	1558.9	1966.7	9577.0	2530.3	3192.3
8	428.5	6690[35d]	1561.2	1672.5	–[e]	–	–
9	478.6	7500[35d]	1567.1	1500.0	–	–	–
10	528.7	8300[35d]	1570.0	1383.3	–	–	–
11	578.7	8460[35d]	1461.8	1208.6	–	–	–
13	678.8	8840[35d]	1302.2	982.2	–	–	–

[a] Correlations for experimentally determined values: $[\alpha]_D^{20}/(n-3)=223.32-7.72\times n$ ($r=0.999$). [b] Correlations for experimentally determined values: $[\alpha]_D^{20}/(n-4)=2854.62-146.51\times n$ ($r=0.982$). [c] The experimentally determined values of specific rotations for π-[*n*]helicenes were taken from ref. [35]. [d] For other computations of specific rotations for π-[*n*]helicenes see ref. [36]. [e] Attempted computations for the higher ($n > 7$) π-[*n*]helicenes were not successful.

ecules. Yet, the crystal packings of the newly prepared triangulanedimethanols show some peculiar arrangements of the molecules as a result of their unique geometries. Since the linear triangulanes virtually are relatively long rigid rods, the spatial arrangement of these "rods", resulting from hydrogen bonds bridging only at their ends, can lead to the formation of polymorphs and pseudo-polymorphs. The conformational mobility of the terminal hydroxymethyl groups can also lead to conformational isomorphism, that is, the co-existence of several conformers in the same crystal.

In all cases except one [diol (*P*)-**22**, see below], the OH groups of the studied diols are linked to each other with the most common motif: an O-H···O-H···O-H··· chain; however, the arrangement of the molecules is different. Thus, a crystal of the diol (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** contains three crystallographically independent molecules, with different orientations of the hydroxymethyl groups (conformational isomorphism). The molecules form layers, and there are zigzag chains of hydrogen bonds between the layers. The OH groups in these chains alternatingly belong to the molecules in adjacent layers. The chains are shifted relative to each other and interlinked by the molecular "rods", which create an elaborate 3-D framework (Figure 4A). One might describe the resulting pattern as a "rope-ladder" aggregate.

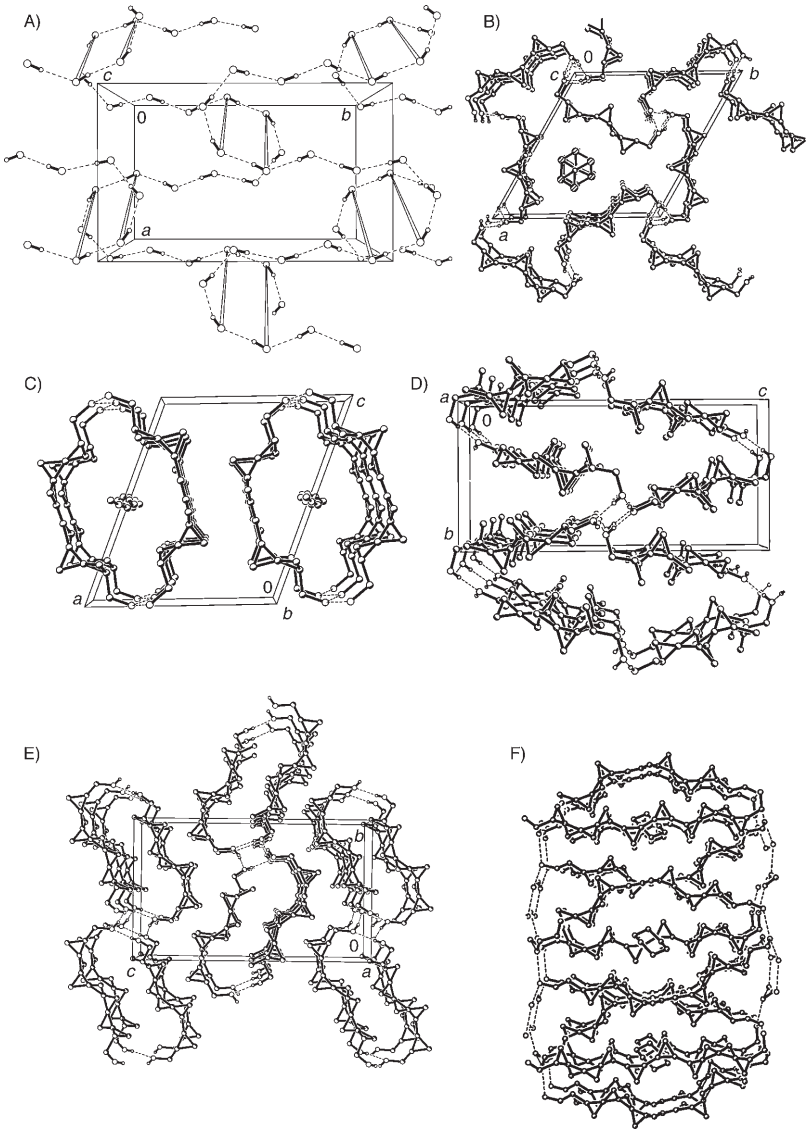


Figure 4. Sections from the crystal packing of the molecules of diols (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** (A), (*P*)-**14** (B), (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21** (C), (*P*)-(+)-**22** (D), (1*S*,3*R*,4*S*,5*S*,6*S*,7*S*,8*R*,9*S*)-**22** (E) and (*E*)-**31** (F). For (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** (A), two layers of the O-H···O-H···O-H··· chains of hydrogen bonds are shown, while the molecules which link these chains with each other are shown as long sticks; only the OH groups of other participating molecules are presented around the edges. For (1*S*,3*R*,4*S*,5*S*,6*S*,7*S*,8*R*,9*S*)-**22** (E): view along the *a* axis. Hydrogen atoms of methylene groups are omitted for clarity, hydrogen bonds are shown as dotted lines.

The replacement of the double bond in (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** with a three-membered ring as in (*P*)-**14** changes the general shape of the molecule, and subsequently leads to a dramatic change in the packing. The molecules are still linked by chains of hydrogen bonds, but these chains form spirals around a threefold axis. As a result, the molecules form wide channels with a peculiar three-bladed propeller shape (Figure 4B). Interestingly enough, the shape of the channels is close to the one found for the packing of one of the "helical tubuland" diols,[39] which is also conformationally rigid and possesses a vaguely similar molecular shape. The walls of each tube or channel are built from a "double tread" of molecules, and each full step of the spiral consists of six molecules. The channels are filled with disordered guest molecules of dichloromethane.

Chains of O-H···O-H··· hydrogen bonds also link molecules in the packing of (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21**. Topologically this pattern can be described as a simple "ladder"; however, the unique horseshoe shape of the molecules transforms this ladder into a channel or sort of a nanotube, which contains disordered guest molecules of diethyl ether (Figure 4C).

The two structure determinations of diols **22** demonstrate the variability of packing modes in crystals of different triangulanedimethanols. Thus, in crystals of (*P*)-(+)-**22**, ob-

tained from EtOH or from hexane/Et_2O, the molecules are also linked by spiral chains (around a twofold screw axis, parallel to the *a* direction) of usual O-H···O-H··· hydrogen bonds. The resulting three-dimensional network of molecules can be described as a set of elliptic channels or nanotubes (Figure 4D), linked in a honeycomb-like arrangement which, however, does not contain any solvent (cf. ref. [40]). Each tube consists of spirals of molecules with four molecules per each turn of the spiral.

The molecules of (1*S*,3*R*,4*S*,5*S*,6*S*,7*S*,8*R*,9*S*)-**22** are also linked by helices of O-H···O-H···O-H hydrogen bonds. The packing of the molecules in the crystal resembles the one of (*P*)-(+)-**22**: the molecules are also arranged in tubes (Figure 4E). Each tube is formed by a single spiral of molecules. However, as each turn of the spiral consists of just two molecules, the tubes are connected in layers (perpendicular to the *c* axis), rather than in a three-dimensional network as it was found in the crystal of (*P*)-(+)-**22**. The channels in the packing of (1*S*,3*R*,4*S*,5*S*,6*S*,7*S*,8*R*,9*S*)-**22** are very narrow and do not contain any guest molecules, which is not unexpected, taking into account the essentially linear shape of the molecules. Recrystallization of (*P*)-(+)-**22** from THF/heptane or of (*M*)-(−)-**22** from hexane/Et_2O in the presence of THF led to the formation of two types of crystals, the first of which was identical with the previously discussed one and did not contain any solvent. In the second type of crystals, however, the packing contained disordered solvent molecules, and they were the only crystals of triangulanedimethanols, in which a cyclic $(OH)_4$···H bond system (common for other diols according to ref. [38b]) was found. These cyclic arrangements create channels in the aggregate, in which solvent molecules are located. The channel walls consist of pairs of molecules, which embrace each other (Figure 5), resulting in a supramolecular helical arrangement, and two such helices each form a supramolecular double helix (Figure 5).

In spite of being severely disordered in their respective locations, these solvent molecules apparently play an important role in gluing the two helices together: upon exposing the crystals to the open air, they rapidly disintegrate into powder, most probably because the Et_2O evaporates from the channels.[41] Single, double and even triple helical structures do play very important roles in biology and in polymer chemistry;[42] however, for relatively small non-biological objects this is not a common phenomenon[43] in that they rarely form single helices,[44] even less frequently double and triple ones.[45] The hydroxymethyl end groups in (*P*)- and (*M*)-**22** apparently are also essential for the supramolecular double helix formation, as the hydrocarbons (*P*)-**17**, (*M*)-**24**, and (*M*)-**25** do not pack in such arrangements in their crystals. On the other hand, in the crystal of [7]triangulanedicarboxylic acid (*M*)-(−)-**40** (see below) the molecules are linked in infinitive chains by a pair of hydrogen bonds typical for carboxylic acids[46] at each end of the molecule (Figure 5C). These chains are packed in layers, which are perpendicular to the *b* axis, and short intermolecular CH···O interactions connect the molecules of adjacent layers.

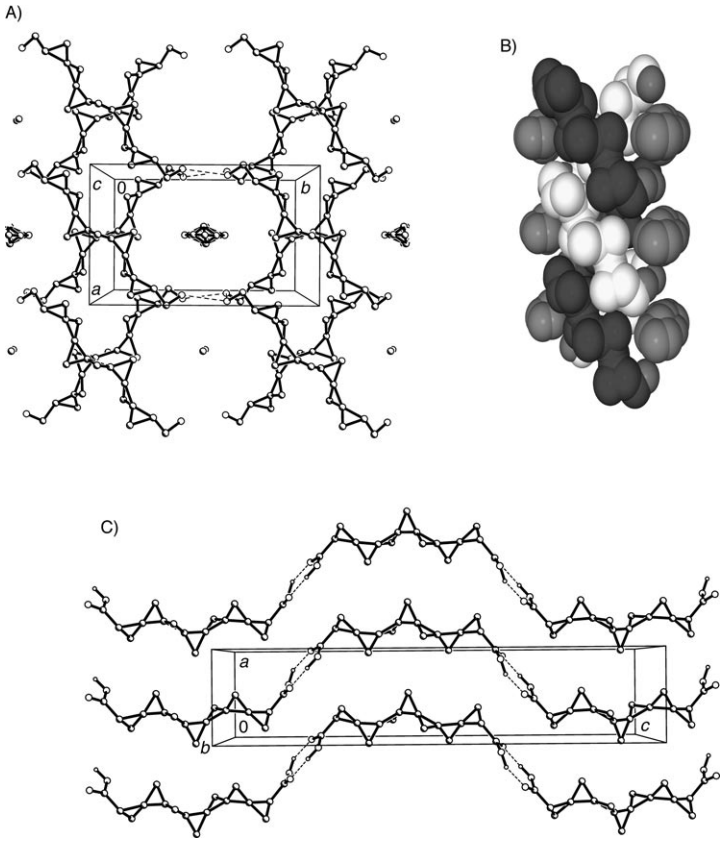


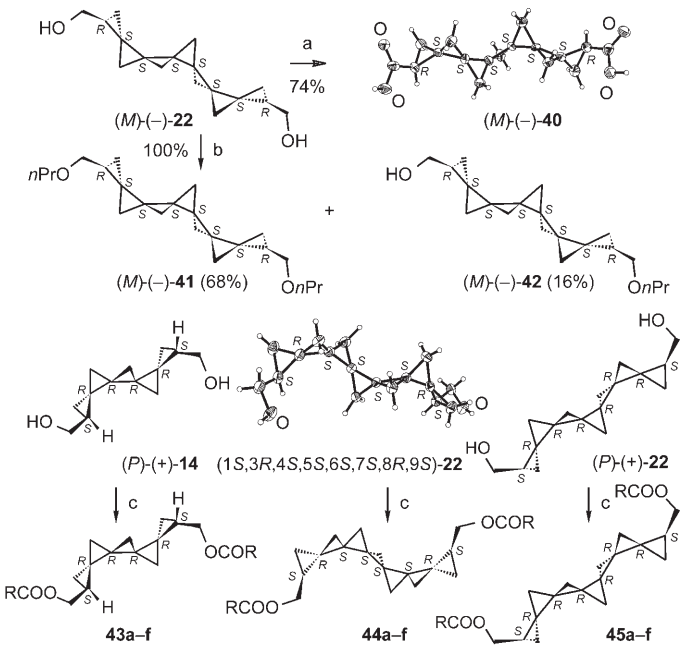
Figure 5. Sections from the crystal packings of (*M*)-(−)-**22** (crystals from Et_2O/hexane) with a supramolecular double-helical arrangement of hydrogen-bridged molecules as ball-and-stick (A) and space-filling models (B) and of [7]triangulanedicarboxylic acid (*M*)-(−)-**40** (C).

In order to test, whether there is chiral recognition of the enantiomers of **22**, crystals of *rac*-**22** were grown from a solution of a 1:1 mixture of (*P*)-(+)-**22** and (*M*)-(−)-**22** in chloroform and subjected to X-ray crystal structure analysis. These crystals turned out to be of a single type, in which severely corrugated layers of molecules, connected by usual O-H···O-H chains of hydrogen bonds, were observed. In the centrosymmetrical unit cell, there are two crystallographically independent molecules, which differ by the orientations of their OH bonds. Somewhat similar corrugated layers were also found in the crystals of the so far largest triangulanedimethanol (*E*)-**31** (Figure 4F). The unit cell contains three crystallographically independent molecules. The slightly bent overall shape of the molecules creates the cavities in the aggregate, in which the guest solvent molecules are enclosed.

Liquid crystalline physical properties of enantiomerically pure triangulanes and their derivatives: Starting from the first observations of the phenomenon of liquid crystallinity by Reinitzer in 1888[47a] and by Lehmann in 1889,[47b] the design and preparation of molecules possessing liquid crystalline properties has been of interest to physical-organic chemists for a long time, and it is difficult to name any

other branch of synthetic organic chemistry which develops as rapidly.[48] Among the liquid crystalline compounds, cyclopropane derivatives, especially 1,2-disubstituted cyclopropanes, provide more rigid conformations than those with similar alkyl groups that are widely used as fragments in liquid crystalline compounds. The first example of a liquid crystalline compound with a cyclopropane ring appeared as early as 1971[49] and, according to the database LiqCryst 4.4,[50] more than 85000 such compounds have been synthesized up to now. However, liquid crystalline properties only of functionally substituted [2]- and [3]triangulanes[12,51] are listed among them. To fill this gap, some of the newly prepared triangulane derivatives were tested for possible liquid crystalline properties.

To begin with, [7]triangulanedimethanol (*M*)-**22** was oxidized under Jones conditions applying a published procedure[52] to give the diacid (*M*)-**40**, the relative configuration of which was determined by X-ray crystal structure analysis (Figure 5C and Scheme 9). Unfortunately, neither (*M*)-**22** nor (*M*)-**40** were sufficiently soluble in the base nematic mixture. Therefore, (*M*)-**22** was converted into its di-*n*-propyl ether (*M*)-**41** according to a published protocol,[53] and a number of esters was prepared from its enantiomer (*P*)-(+)-**22** as well as from its non-helical diastereomer (1*S*,3*R*,4*S*,5*S*,6*S*,7*S*,8*R*,9*S*)-**22** [prepared from the dibromide (1*S*,3*R*,4*S*)-**19** according to the elaborated procedure, see Supporting Information] and from [5]triangulanedimethanol (*P*)-(+)-**14** (Scheme 9).



	a	b	c	d	e	f
R	nC_5H_{11}	nC_5H_{11}	nC_3H_7	nC_3H_7	OnC_5H_{11}	nC_5H_{11}
Yield of **43** (%)	47	63	40	69	34	40
Yield of **44** (%)	31	39	28	34	58	65
Yield of **45** (%)	52	58	50	70	61	49

Scheme 9. Preparation of enantiomerically pure difunctionalized [5]- and [7]triangulanes for testing their liquid crystalline properties. a) Jones reagent, acetone, 0°C, 2 h, then 20°C, 15 min, then *i*PrOH; b) NaH (10 equiv), DMF, 20°C, 0.5 h, then *n*PrI (20 equiv), 20°C, 14 h; c) RCO_2H, DMAP, DCC, 0–20°C, 12 h.

Unfortunately, none of the synthesized compounds exhibited any mesophase, but only showed melting points, in spite of their having extended longitudinal structures. Most probably, the strong intermolecular interactions going along with the particular packing, decreases the mesogenic potential and increases the crystallinity.

Helical twisting powers (HTPs, Table 3) of the synthesized compounds were measured applying Cano's wedged cell method.[54] Each compound was dissolved in the base nematic mixture ZLI-1132 comprising benzonitrile derivatives (clearing point = 71.7°C) available from Merck KGaA in Darmstadt (Germany). The HTPs of the compounds range from 0.82 to 17.7 μm^{-1}. A significant number of the synthesized compounds showed a two to three times larger HTP value than (*S*)-4-cyano-4′-(2-methybutyl)-1,1′-biphenyl (CB-15), which is commonly used in the flat panel display industry (HTP = 6.6 μm^{-1}).

Table 3. Phase transition temperatures and helical twisting powers (HTP) of the newly synthesized triangulane derivatives (*P*)-(+)-**25**, (*M*)-**22**, (*M*)-(−)-**41**, **43a–f**, **44a–f** and **45a–f** in comparison with CB-15 (**X1**).

Entry	Compound	Phase transition temperatures [°C]	HTP [μm^{-1}]
1	(*P*)-(+)-**25**	91.1	5.7
2	(*M*)-**22**	123.9	13.0
3	(*M*)-(−)-**41**	oil	17.7
4	**43a**	49.0	3.1
5	**43b**	77.3	6.2
6	**43c**	72.7	5.2
7	**43d**	90.0	7.9
8	**43e**	86.3	3.5
9	**43f**	oil	12.2
10	**44a**	68.3	12.6
11	**44b**	63.1	4.5
12	**44c**	73.7	5.0
13	**44d**	79.3	2.8
14	**44e**	69.1	9.8
15	**44f**	oil	0.8
16	**45a**	71.3	10.2
17	**45b**	65.3	5.3
18	**45c**	72.1	10.6
19	**45d**	101.4	5.5
20	**45e**	81.9	10.7
21	**45f**	oil	11.1
22	**X1**	oil	6.6

Figure 6 shows the temperature dependence of the HTPs for the three representative compounds **43c**, **44c**, and **45c**.

It is noteworthy that the three series of the diesters **43**, **44** and **45** displayed different dependences of their HTPs on the temperature, the first one being positive, the second slightly negative and the third negative, respectively.

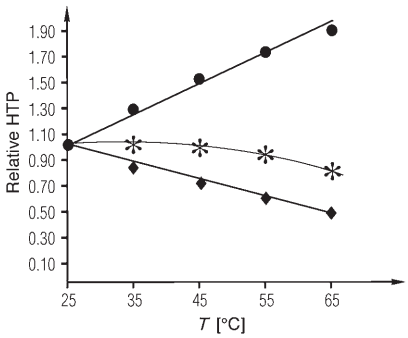


Figure 6. Temperature (T) dependence of the helical twisting powers (HTPs) for the three representative compounds **43c** (●), **44c** (*), and **45c** (◆).

The HTP values at 25 °C were all adjusted as being 1 on the vertical axis, thus, only relative values are compared.

Attempts were made to obtain spontaneous polarization (Ps) values for **43a**, **44a**, and **45a** by extrapolation from the Ps values of SmC* mixtures containing 5% by weight of each compound **43a**, **44a**, and **45a** in an SmC base mixture exhibiting the phase sequence Cr 4 SmC 65 SmA 79 N 90 I, and comprising pyrimidines. The magnitude of Ps for these mixtures was measured according to the established method,[55a] and the sign of Ps was determined according to the convention of Lagerwall[55b] in the filed reversal method by optical observation of the director motion. Unfortunately, the Ps values for the compounds **43a**, **44a**, and **45a** were so small that they could not even be detected in any of the three SmC* mixtures containing them.

Experimental Section

General aspects: Racemic 1-methylene-2-tetrahydropyranyloxymethylcyclopropane (**6**),[7a] (4-methylenespiropent-1-yl)methanol (*rac*-**10**),[7a] enantiomerically pure (4-methylenespiropent-1-yl)methanol [(1*R*,3*S*)-**10**], and (4-methylenespiropent-1-yl)methyl acetate [(1*S*,3*R*)-**11**][12] were prepared according to the previously published procedures. All operations in anhydrous solvents were performed under argon in flame-dried glassware. Diethyl ether, THF, benzene and 1,2-dimethoxyethane were dried by distillation from sodium/benzophenone, pyridine, DMF and DMSO from calcium hydride, pentane and CH_2Cl_2 from P_2O_5, MeOH from magnesium methoxide. CuCl and $CuCl_2$ were dried at 100 °C in vacuo 0.01 Torr overnight. All other chemicals were used as commercially available; lipase PS (*Pseudomonas* sp., from Amano Pharmaceutical Co., Ltd) as well as lipases CES, 300, AK and EC3.1.1.3 were kindly provided by Chisso Petrochemical Corporation. Organic extracts were dried over $MgSO_4$. NMR spectra were recorded on a Bruker AM 250 (250 MHz for ^{1}H and 62.9 MHz for ^{13}C NMR) and a Varian Inova 600 (599.8 MHz for ^{1}H and 150 MHz for ^{13}C NMR) instrument in $CDCl_3$, if not otherwise specified. Multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer) measurements. Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual $CHCl_3$ signals. IR spectra were recorded on a Bruker IFS 66 FT-IR as KBr pellets or oils between NaCl plates. Mass spectra were measured with a Finnigan MAT 95 (EI and HR-EI, at 70 eV, preselected ion peak matching at $R \geqslant 10000$ to be within ±2 ppm of the exact masses) spectrometer. Enantiomeric excesses were determined by HPLC using a Chiracel OD column, hexane/isopropanol 98:2 (0.9 mL min^{-1}). The HPLC analysis of (*M*)-**39** and its diastereomer (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39** formed from (*E*)-**38** was performed on a JASCO PU-986 chromatograph equipped with a refractive index (JASCO RI-2031) and a polarimetric (JASCO OR-990) detector using a 25 × 0.46 cm column with Chiralcel OD, methanol/water 98:2, 0.5 mL min^{-1}, and their preparative separation was conducted on the same HPLC system using a 25 × 2 cm column with Chiralcel OD, methanol/water 98:2, 6 mL min^{-1}, detector JASCO OR-990. Preparative HPLC separations of compounds **37** and **38** were performed using a column with Kromasil RP18 under conditions specified below. Optical rotations were measured on a Perkin–Elmer 241 digital polarimeter in a 1 dm cell. Melting points were determined on a Büchi 510 capillary melting point apparatus, values are uncorrected. Transition temperatures have been measured by a DSC Perkin–Elmer DSC 7 (10 °C min^{-1}) and a microscopic (Nikon Optiphot polarization microscope with Mettler FP82 hot stage) observation (3 °C min^{-1}). TLC analyses were performed on precoated sheets, 0.25 mm Sil G/UV$_{254}$ (Macherey-Nagel). Silica gel grade 60 (230–400 mesh) (Merck) was used for column chromatography.

Crystal structure determinations: Suitable crystals of the compounds were grown by slowly concentrating their diluted solutions in hexane/Et_2O [*rac*-**7**, (1′*S*,3′*R*,2*S*)-**9**, (1*R*,3*S*,4*R*)-**19**, (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*,8*R*,9*S*)-**22**, (1*S*,3*R*,4*S*,5*S*,6*S*,7*S*,8*R*,9*S*)-**22**, (*M*)-(−)-**22**, (*P*)-(+)-**23**], in THF/octane [(*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13**], in Et_2O [(*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21**, (*M*)-(−)-**40**], in CH_2Cl_2 [(*P*)-**14**], in MeOH [(*P*)-**15**], in MeCN [(*P*)-**17**], in EtOH [*rac*-**22**], in THF/heptane [(*P*)-(+)-**22**], in MeOH/Et_2O [*d*-(+)-**23**, (*M*)-(−)-**24**, (*M*)-(−)-**25**], in cyclohexane/dioxane [(*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*R*,5′*R*,6*R*,6′*R*,7*R*,7′*R*,8*S*,8′*S*)-**31**], in C_6H_{12}/Et_2O [(*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*R*,5′*R*,6*R*,6′*R*,7*R*,7′*R*,8*S*,8′*S*)-**31**], in MeOH/H_2O (**32**), in acetone/acetonitrile [(4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39**,], and in toluene [(4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39** and (*M*)-**39**]. The data were collected on a Bruker Apex Proteum-M [(*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** and [(*P*)-**14**], a Stoe IPDS II [(1*R*,3*S*,4*R*)-**19**] and a Bruker SMART CCD 6000 (other compounds) diffractometer (graphite monochromator, $Mo_{K\alpha}$ radiation, ω scan), equipped with Oxford Cryostream low-temperature devices. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. The treatment of H atoms varied for the different structures, but in most cases the H atoms were located in the difference Fourier map and refined isotropically. Absolute configurations of the bromine-substituted molecules were determined on the basis of X-ray data; absolute configurations of other molecules were assigned on the basis of additional chemical information. The parameters of crystal data collections and structure refinements are presented in Table 4.[10]

Preparation of *gem*-dibromo[*n*]triangulanylmethanols

General procedure GP 1: $CHBr_3$ (379.12 g, 131.0 mL, 1.50 mol) and benzyltriethylammonium chloride (TEBACl, 31.6 mmol) in anhydrous CH_2Cl_2 (850 mL) were added in one portion KOH (pellets, 454.5 g, 8.10 mol) to a vigorously stirred pre-cooled (−10 °C) solution of the respective protected (methylenetriangulanyl)methanol (500 mmol), and the resulting mixture was stirred with TLC monitoring for the indicated time maintaining the temperature at 20–25 °C by external cooling. Pentane (2.5 L) was added and, after stirring for an additional 0.5 h, the mixture was filtered through a pad of Celite (0.5 cm) and silica gel (1 cm), then concentrated under reduced pressure. The excess bromoform was distilled off at 40 °C under reduced pressure 0.001 Torr. The residue was used without further purification (GP 1a) or taken up with methanol (400 mL) and stirred with pyridinium *p*-toluenesulfonate (PPTS, 6.5 mmol) at 50–65 °C for the indicated time (for THP-protected alcohols, GP 1b). The reaction mixture was cooled to ambient temperature and, after addition of 2% H_2O v/v, concentrated under reduced pressure. The products were isolated by column chromatography on silica gel followed by recrystallization. In the case of acetylated alcohols (GP 1c), the crude dibromocarbene adduct was stirred under reflux in MeOH in the presence of sulfuric acid (0.5 g, 0.27 mL) for the indicated time and, after cooling to ambient temperature, neutralized with sodium methoxide (1 g), concentrated under reduced pressure and purified by column chromatography on silica gel followed by recrystallization.

***rac*-(*anti*-4,4-Dibromospiropent-1-yl)methanol (*rac*-7)**: The residue obtained from *rac*-1-methylene-2-tetrahydropyranyloxymethylcyclopropane

Table 4. Crystal and data collection parameters for compounds *rac*-**7**, (1′*S*,3′*R*,2*S*)-**9**, (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13**, (*P*)-**14**, (*P*)-**15**, (*P*)-**17**, (1*R*,3*S*,4*R*)-**19**, (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21**, *rac*-**22**, (1*R*,3*S*,4*S*,5*S*,6*S*,7*S*,8*S*,9*R*)-**22**, (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*,8*R*,9*S*)-**22**, (1*S*,3*R*,4*S*,5*S*,6*S*,7*S*,8*R*,9*S*)-**22**, *d*-(+)-**23**, (*P*)-(+)-**23**, (*M*)-(−)-**24**, (*M*)-(−)-**25**, (*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*R*,5′*R*,6*R*,6′*R*,7*R*,7′*R*,8*S*,8′*S*)-**31**, (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39**, (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39**, (*M*)-**39**, and diacid (*M*)-(−)-**40**.

Compound	*rac*-**7**	(1′*S*,3′*R*,2*S*)-**9**	(*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13**	(*P*)-**14**	(*P*)-**15**	(*P*)-**17**	(1*R*,3*S*,4*R*)-**19**	(*E*)-**21**
formula	$C_6H_8Br_2O$	$C_{14}H_{14}Br_2O_3$	$C_{12}H_{16}O_2$	$C_{13}H_{18}O_2 \times 0.25\,CH_2Cl_2$	$C_{13}H_{16}Br_2$	$C_{15}H_{18}$	$C_8H_{10}Br_2O$	$C_{16}H_{20}O_2 \times 0.5\,C_4H_{10}O$
molecular mass	255.94	390.07	192.25	227.51	332.08	198.29	281.98	281.38
crystals	monoclinic	orthorhombic	orthorhombic	hexagonal	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$P3_2$	$P2_12_12_1$	$P2_1$	$P2_1$	$P2_1$
crystal size [mm]	0.56×0.10×0.08	0.58×0.04×0.02	0.38×0.30×0.04	0.52×0.16×0.14	0.46×0.18×0.12	0.24×0.18×0.08	0.25×0.20×0.15	1.30×0.04×0.03
a [Å]	6.3458(1)	5.4644(2)	9.6596(5)	14.263(1)	5.3216(1)	7.3275(2)	11.811(2)	11.498(2)
b [Å]	17.3413(4)	14.1592(4)	16.004(1)	14.263(1)	15.2548(3)	9.6053(2)	6.5023(13)	5.067(1)
c [Å]	22.0989(4)	37.116(1)	20.295(2)	5.6131(5)	16.0135(3)	8.9956(2)	12.682(3)	13.351(3)
α [°]	90	90	90	90	90	90	90	90
β [°]	96.27(1)	90	90	90	90	109.82(1)	95.67(3)	110.99(6)
γ [°]	90	90	90	120	90	90	90	90
V [Å^3]	2417.30(8)	2871.7(2)	3137.5(3)	988.9(1)	1299.97(4)	595.62(2)	969.1(3)	726.2(3)
Z	12	8	12	3	4	2	2	2
F(000)	1464	1536	1248	368	656	216	544	306
ρ [g cm^{-3}]	2.110	1.804	1.221	1.146	1.697	1.106	1.933	1.287
μ [mm^{-1}]	9.981	5.646	0.081	0.172	6.203	0.062	8.309	0.084
T [K]	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	133(2)	120(2)
Θ_{max} [°]	29.50	27.50	29.50	26.99	29.00	29.00	24.73	25.99
refl. collected	26948	25788	32447	9033	16029	6505	4549	2424
refl. independent	6691	6586	8729	2823	3446	3118	2916	2201
R_{int}	0.0284	0.0773	0.1026	0.0261	0.0205	0.0366	0.0567	0.0231
R_1 [$I=2\sigma(I)$]	0.0241	0.0354	0.0468	0.0759	0.0143	0.0323	0.0494	0.0629
wR_2 (all data)	0.0542	0.0649	0.0.866	0.2114	0.0365	0.0827	0.1320	0.1733
no. of parameters refined	340	351	403	172	200	208	199	255
GOOF	1.024	0.969	0.915	1.117	1.067	0.0872	1.091	1.130
largest diff. peak and hole [e Å^{-3}]	1.033, −0.647	0.719, −0.643	0.265, −0.201	0.559, −0.264	0.414, −0.345	0.185, −0.162	0.553, −0.813	0.446, −0.315

Compound	(*P*)-(+)-**22** (from EtOH)	(*M*)-(−)-**22** (from hexane/Et_2O)	(*P*)-(+)-**22** (from heptane/THF)	*rac*-**22**	(1*S*,3*R*,4*S*,5*S*,6*S*,7*S*,8*R*,9*S*)-**22**	(*P*)-(+)-**23**	*d*-(+)-**23**	(*M*)-(−)-**24**
formula	$C_{17}H_{22}O_2$	$C_{17}H_{22}O_2 \times 0.5\,C_4H_{10}O$	$C_{17}H_{22}O_2 \times 0.5\,C_4H_8O$	$C_{17}H_{22}O_2$	$C_{17}H_{22}O_2$	$C_{17}H_{20}Br_2$	$C_{17}H_{20}Br_2$	$C_{17}H_{18}$
molecular mass	258.35	295.42	294.4	258.35	258.35	384.15	384.15	222.31
crystals	orthorhombic	orthorhombic	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$I222$	$I222$	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$C2$	$P2_1$
crystal size [mm]	0.44×0.28×0.24	0.31×0.14×0.11	0.60×0.12×0.04	0.32×0.08×0.02	0.31×0.18×0.04	0.32×0.20×0.14	0.22×0.20×0.10	0.32×0.29×0.03
a [Å]	7.9640(1)	7.6776(4)	7.5264(5)	13.3211(8)	6.3064(3)	5.5575(1)	23.9536(5)	9.9639(2)
b [Å]	9.6434(1)	12.5642(6)	12.6120(8)	19.416(1)	11.8894(6)	16.2902(3)	6.5749(1)	10.6100(2)
c [Å]	19.8564(3)	18.6416(9)	17.784(1)	11.6168(7)	19.934 (1)	18.1928(3)	16.7246(4)	13.6195(3)
α [°]	90	90	90	90	90	90	90	90
β [°]	90	90	90	104.43(2)	90	90	110.67(1)	110.46(1)
γ [°]	90	90	90	90	90	90	90	90
V [Å^3]	1524.97(3)	1798.22(15)	1688.1(2)	2909.8(3)	1494.65(13)	1647.04(5)	2464.45(9)	1348.94(5)
Z	4	4	4	8	4	4	6	4
F(000)	560	632	640	1120	560	768	1152	480
ρ [g cm^{-3}]	1.125	1.080	1.158	1.179	1.148	1.549	1.553	1.095
μ [mm^{-1}]	0.072	0.070	0.075	0.075	0.073	4.908	4.920	0.061
T [K]	120(2)	250(2)	120(2)	120(2)	120(2)	120(2)	150(2)	120(2)
Θ_{max} [°]	29.50	25.99	29.00	26.00	28.49	30.00	29.00	29.00
refl. collected	17249	5790	7990	20640	12389	23084	8833	16685
refl. independent	4249	1773	2266	5721	2188	4795	6407	7160
R_{int}	0.0460	0.0177	0.0522	0.1148	0.0640	0.0198	0.0154	0.0278
R_1 [$I=2\sigma(I)$]	0.0309	0.0492	0.0550	0.0470	0.0455	0.0162	0.0323	0.0371
wR_2 (all data)	0.0837	0.1603	0.1576	0.0695	0.1229	0.0425	0.0755	0.0806
no. of parameters refined	260	103	135	519	260	252	378	451
GOOF	1.036	1.036	1.056	0.815	1.121	0.988	1.046	1.195
largest diff. peak and hole [e Å^{-3}]	0.221, −0.173	0.182, −0.194	0.450, −0.440	0.183, −0.188	0.244, −0.171	0.355, −0.264	0.587, −0.811	0.185, −0.152

Compound	(*M*)-(−)-**25**	(*E*)-**31** (from C_6H_{12}/Et_2O)	(*E*)-**31** (from dioxane/C_6H_{12})	(4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39**	(4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39**	(*M*)-**39**	(*M*)-(−)-**40**
formula	$C_{19}H_{22}$	$C_{28}H_{32}O_2 \times {}^1/_6C_6H_{12}$	$C_{28}H_{32}O_2 \times {}^1/_3C_6H_{12}$	$C_{31}H_{34}$	$C_{31}H_{34}$	$C_{31}H_{34}$	$C_{17}H_{18}O_4$
molecular mass	250.37	414.56	428.59	406.58	406.58	406.58	286.31
crystals	trigonal	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$P3_121$	$P2_1$	$P2_1$	$P2_12_12_1$	$C2$	$P2_1$	$P2_12_12_1$
crystal size [mm]	0.13×0.12×0.11	0.20×0.10×0.01	0.28×0.19×0.07	0.56×0.20×0.14	0.32×0.28×0.12	0.36×0.12×0.06	0.32×0.12×0.01
a [Å]	9.183(1)	9.870(2)	9.9247(8)	7.4015(1)	27.2928(7)	10.2656(3)	5.6750(15)
b [Å]	9.183(1)	40.010(8)	40.112(3)	16.3396(3)	10.6234(3)	6.0517(2)	10.029(3)
c [Å]	46.985(9)	11.097(2)	11.0939(9)	20.8063(4)	14.0357(4)	20.0823(6)	26.637(7)
α [°]	90	90	90	90	90	90	90
β [°]	90	115.5(3)	115.832(4)	90	112.18(1)	94.55(1)	90
γ [°]	120	90	90	90	90	90	90
V [Å^3]	3431.4(10)	3955.0(14)	3975.2(6)	2516.26(8)	3768.4(2)	1243.7(1)	1516.0(7)
Z	9	6	6	4	6	2	4
F(000)	1224	1344	1302	880	1320	440	608
ρ [g cm^{-3}]	1.090	1.044	1.074	1.073	1.075	1.086	1.254
μ [mm^{-1}]	0.061	0.064	0.065	0.060	0.060	0.061	0.089
T [K]	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Θ_{max} [°]	25.49	22.50	25.00	29.00	28.99	29.50	25.35
refl. collected	29160	13430	29839	19912	20699	14198	9520
refl. independent	4249	7505	7095	3775	5261	3785	2749
R_{int}	0.1146	0.2375	0.0892	0.0286	0.0691	0.0553	0.2355
R_1 [$I=2\sigma(I)$]	0.0470	0.0936	0.0825	0.0328	0.0372	0.0376	0.0658
wR_2 (all data)	0.0595	0.2604	0.2238	0.0885	0.0913	0.0843	0.1316
no. of parameters refined	262	845	877	416	624	416	196
GOOF	0.940	0.794	1.114	1.118	0.917	0.972	0.884
largest diff. peak and hole [e Å^{-3}]	0.127, −0.143	0.090, −0.067	0.312, −0.352	0.221, −0.125	0.239, −0.177	0.174, −0.193	0.246, −0.258

(**6**) (88.0 g, 524 mmol), $CHBr_3$ (388.2 g, 137.3 mL, 1.536 mol), KOH (476.31 g, 8.49 mol) and TEBACl (7.54 g, 33.1 mmol) in CH_2Cl_2 (880 mL) according to GP 1a (3 h of stirring), was treated with MeOH (1.4 L) and PPTS (4.80 g, 19.1 mmol) according to GP 1b (65 °C, 3 h). Column chromatography of the residue (500 g silica gel, 7×30 cm column, pentane/Et_2O 10:1 → 2:1) followed by recrystallization from hexane/Et_2O furnished *rac*-**7** (72.9 g, 54 %) as a colorless solid. M.p. 57–59 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.59 (dd, J = 6.5, 11.4 Hz, 1H; CH_2O), 3.51 (dd, J = 6.8, 11.4 Hz, 1H; CH_2O), 2.01 (d, J = 6.7 Hz, 1H; *c*Pr-H), 1.92 (d, J = 6.7 Hz, 1H; *c*Pr-H), 1.83–1.72 (m, 1H; *c*Pr-H), 1.61 (s, 1H; OH), 1.40 (dd, J = 5.1, 8.6 Hz, 1H; *c*Pr-H), 1.16 (dd, J = 5.1, 5.3 Hz, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 64.1 (CH_2), 31.3 (C), 28.9 (C), 26.9 (CH_2), 25.1 (CH), 15.7 (CH_2). The structure of *rac*-**7** was confirmed by X-ray crystal structure analysis.[10]

{(1*R*,3*S*,4*R*)- and {(1*R*,3*S*,4*S*)-5,5-Dibromodispiro[2.0.2.1]hept-1-yl}methanol [(1*R*,3*S*,4*R*)-19 and (1*R*,3*S*,4*S*)-19]: The crude 2-{(1*R*,3*S*)-4-methylenespiro[2.2]pent-1-ylmethoxy}-tetrahydropyran [(1*R*,3*S*)-**18**], which was prepared from [(1*R*,3*S*)-4-methylenespiropentyl]-methanol [(1*R*,3*S*)-**10**] (7.76 g, 70.4 mmol), DHP (8.90 g, 106 mmol) and PPTS (1.76 g, 7.0 mmol) in CH_2Cl_2 (150 mL) according to GP 2 (see below, 5 h of stirring), was treated with $CHBr_3$ (53.40 g, 211.3 mmol, 18.9 mL), KOH (65.0 g, 1.158 mol) and TEBACl (1.10 g, 4.83 mmol) in CH_2Cl_2 (100 mL) according to GP 1a. The resulting mixture of crude {[(1*R*,3*S*,4*R*)- and {[(1*R*,3*S*,4*S*)-5,5-dibromodispiro[2.0.2.1]hept-1-yl]methoxy}tetrahydropyrans was treated with methanol (400 mL) and PPTS (1.70 g, 6.76 mmol) according to GP 1b (50 °C, 18 h). Column chromatography of the residue (500 g silica gel, 7×30 cm column, pentane/Et_2O 4:1 → 1:2) followed by recrystallization from pentane/Et_2O 4:1 furnished (1*R*,3*S*,4*R*)-**19** (3.45 g, 17 % over three steps) and (1*R*,3*S*,4*S*)-**19** (3.68 g, 19 % over three steps) as colorless solids.

Compound (1*R*,3*S*,4*R*)-**19**: R_f = 0.43 (pentane/Et_2O 1:2); m.p. 69–70 °C; $[\alpha]_D^{20}$ = +41.4 (c = 1.18 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.80 (dd, J = 6.3, 11.3 Hz, 1H; CH_2O), 3.59 (dd, J = 7.3, 11.3 Hz, 1H; CH_2O), 2.06–1.96 (m, 2H; *c*Pr-H, OH), 1.89 (d, J = 6.7 Hz, 2H; *c*Pr-H), 1.57 (d, J = 4.6 Hz, 1H; *c*Pr-H), 1.45 (d, J = 4.6 Hz, 1H; *c*Pr-H), 0.96 (dd, J = 4.8, 8.1 Hz, 1H; *c*Pr-H), 0.82 (t, J = 4.8 Hz, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 65.4 (CH_2), 30.5 (C), 29.3 (C), 28.6 (CH_2), 24.7 (C), 16.6 (CH), 14.2 (CH_2), 10.1 (CH_2). Its relative configuration was confirmed by X-ray crystal structure analysis.[10]

Compound (1*R*,3*S*,4*S*)-**19**: R_f = 0.30 (pentane/Et_2O 1:2); m.p. 63–64 °C; $[\alpha]_D^{20}$ = −165.4 (c = 1.09 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.64 (dd, J = 6.7, 6.7 Hz, 2H; CH_2O), 2.07 (d, J = 6.7 Hz, 1H; *c*Pr-H), 1.89 (d, J = 6.7 Hz, 1H; *c*Pr-H), 1.61–1.50 (m, 4H; *c*Pr-H, OH), 1.47–1.35 (m, 1H; *c*Pr-H), 0.82 (t, J = 4.9 Hz, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 65.4 (CH_2), 30.4 (C), 29.2 (C), 28.7 (CH_2), 24.9 (C), 19.1 (CH), 14.0 (CH_2), 7.8 (CH_2).

[(1*S*,3*R*,4*S*)- and [(1*S*,3*R*,4*R*)-5,5-Dibromodispiro[2.0.2.1]hept-1-yl]methanol [(1*S*,3*R*,4*S*)-19 and (1*S*,3*R*,4*R*)-19]: The residue obtained from (1*S*,3*R*)-4-methylenespiropentylmethyl acetate [(1*S*,3*R*)-**11**] (17.72 g, 116.4 mmol), $CHBr_3$ (147.1 g, 52.0 mL, 582 mmol), KOH (26.54 g, 473 mmol) and TEBACl (1.70 g, 7.46 mmol) in CH_2Cl_2 (200 mL) according to GP 1a (2 h of stirring), was treated with MeOH (600 mL) and H_2SO_4 (0.5 g, 0.27 mL) according to GP 1c (65 °C, 4 h). Column chromatography of the residue (1000 g silica gel, 9×35 cm column, pentane/Et_2O 4:1 → 1:1) followed by recrystallization from hexane/Et_2O afforded (1*S*,3*R*,4*S*)-**19** (10.41 g, 32 %) and (1*S*,3*R*,4*R*)-**19** (9.33 g, 28 %) as color-

less solids. Their ^{1}H- and ^{13}C NMR spectra were identical with those obtained for the enantiomers (1*R*,3*S*,4*R*)-**19** and (1*R*,3*S*,4*S*)-**19**, respectively (see above).

Compound (1*S*,3*R*,4*S*)-**19**: m.p. 69–70 °C; $[\alpha]_D^{20} = -41.3$ ($c = 0.925$ in $CHCl_3$).

Compound (1*S*,3*R*,4*R*)-**19**: m.p. 63–64 °C; $[\alpha]_D^{20} = +164.8$ ($c = 1.17$ in $CHCl_3$).

(1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-(8,8-Dibromopentaspiro[2.0.0.0.0.2.1.1.1.1]tridec-1-yl)methanol and (1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-(8,8-dibromopentaspiro[2.0.0.0.0.2.1.1.1.1]tridec-1-yl)methanol [(1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-29 and (1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-29]: The residue obtained from (1*S*,3*R*,4*R*,5*R*,6*R*)-2-{(7-methylenetetraspiro[2.0.0.0.2.1.1.1]undec-1-yl)methoxy}tetrahydro-2*H*-pyran [(*P*)-**28**] (3.41 g, 12.52 mmol), $CHBr_3$ (15.8 g, 5.6 mL, 62.7 mmol), KOH (3.88 g, 69.15 mmol) and TEBACl (200 mg, 0.88 mmol) in CH_2Cl_2 (30 mL) according to GP 1a (3 h of stirring), was treated with MeOH (100 mL) and PPTS (180 mg, 0.72 mmol) according to GP 1b (65 °C, 10 h). Column chromatography of the oily residue (6.0 g) (850 g silica gel, 9×35 cm column, pentane/Et_2O 2:1) furnished a 3:2 mixture (4.55 g, 100 %) of (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-**29** and (1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-**29** (according to HPLC analysis) which were separated by preparative HPLC (Kromasil RP18, MeCN/H_2O 75:25, 12 mL min^{-1}) to give (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-**29** (1.390 g, 31 %) and (1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-**29** (762 mg, 17 %) as colorless semisolids.

Compound (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-**29**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 3.78 (dd, $J = 6.7$, 11.1 Hz, 1H; CH_2O), 3.65 (dd, $J = 7.1$, 11.1 Hz, 1H; CH_2O), 3.14 (s, 1H; OH), 2.05–1.99 (m, 2H; *c*Pr-H), 1.71 (d, $J = 4.3$ Hz, 1H; *c*Pr-H), 1.55 (d, $J = 4.5$ Hz, 1H; *c*Pr-H), 1.47 (d, $J = 4.6$ Hz; 1H, *c*Pr-H), 1.42–1.34 (m, 1H; *c*Pr-H), 1.25–1.19 (m, 3H; *c*Pr-H), 1.13 (d, $J =$ 4.0 Hz, 1H; *c*Pr-H), 1.07 (d, $J = 4.3$ Hz, 1H; *c*Pr-H), 1.08–1.03 (m, 1H, *c*Pr-H), 0.71 (t, $J = 4.5$ Hz, 1H; *c*Pr-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 66.1 (CH_2), 30.5 (C), 29.0 (C), 27.7 (CH_2), 24.3 (C), 18.5 (CH), 18.3 (C), 18.0 (C), 17.4 (C), 14.5 (CH_2), 10.2 (CH_2), 9.1 (CH_2), 8.8 (CH_2), 7.8 (CH_2). Its absolute configuration was derived from the relative configuration of its ester with (*S*)-(+)-mandelic acid **32**, as determined by X-ray crystal structure analysis.[10]

Compound (1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-**29**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 3.78 (dd, $J = 7.3$, 11.1 Hz, 1H; CH_2O), 3.63 (dd, $J = 6.5$, 11.1 Hz, 1H; CH_2O), 2.52 (s, 1H; OH), 2.08 (d, $J = 6.6$ Hz, 1H; *c*Pr-H), 1.97 (d, $J =$ 6.6 Hz, 1H; *c*Pr-H), 1.70 (d, $J = 4.5$ Hz, 1H; *c*Pr-H), 1.55 (d, $J = 4.5$ Hz, 1H; *c*Pr-H), 1.41 (d, $J = 4.5$ Hz, 1H; *c*Pr-H), 1.29–1.21 (m, 4H; *c*Pr-H), 1.17 (d, $J = 4.3$ Hz, 1H; *c*Pr-H), 1.11 (d, $J = 4.1$ Hz, 1H; *c*Pr-H), 1.03 (dd, $J = 4.4$, 7.7 Hz, 1H; *c*Pr-H), 0.70 (t, $J = 4.4$ Hz, 1H; *c*Pr-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 66.3$ (CH_2), 31.7 (C), 29.7 (C), 25.5 (C), 18.3 (CH), 18.2 (C), 17.99 (C), 17.98 (C), 29.7 (CH_2), 14.9 (CH_2), 14.0 (CH_2), 11.0 (CH_2), 8.9 (CH_2), 8.8 (CH_2).

(3*R*,4*S*,5*S*,6*S*,7*S*)-1,1-Dibromohexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadecane and (3*S*,4*S*,5*S*,6*S*,7*S*)-1,1-dibromohexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]-pentadecane [(3*R*,4*S*,5*S*,6*S*,7*S*)-37 and (3*S*,4*S*,5*S*,6*S*,7*S*)-37]: Column chromatography (300 g silica gel, 4.4×40 cm column, hexane, $R_f = 0.47$) of the residue obtained from the methylene[6]triangulane (3*S*,4*S*,5*S*,6*S*)-**36** (1.05 g, 5.70 mmol), $CHBr_3$ (5.761 g, 2.04 mL, 22.79 mmol), KOH (15.986 g, 284.9 mmol, powder) and TEBACl (100 mg, 0.44 mmol) in CH_2Cl_2 (50 mL) according to GP 1a (14 h of stirring) furnished a 1:1 mixture (2.029 g, 100 %) of (3*R*,4*S*,5*S*,6*S*,7*S*)-**37** and (3*S*,4*S*,5*S*,6*S*,7*S*)-**37** (according to HPLC analysis). Attempted preparative HPLC separation (Kromasil RP18, MeCN/H_2O 75:25 + 0.5 % CF_3CO_2H, 0.8 mL min^{-1}) gave the same 1:1 mixture (1.154 g, 57 %). Repeated separation of this mixture (Kromasil RP18, MeCN/H_2O 90:10 + 0.5 % CF_3CO_2H, 1.5 mL min^{-1}) furnished two fractions (3*R*,4*S*,5*S*,6*S*,7*S*)-**37** (397 mg, 20 %) and (3*S*,4*S*,5*S*,6*S*,7*S*)-**37** (329 mg, 16 %).

Compound (3*R*,4*S*,5*S*,6*S*,7*S*)-**37**: colorless solid; m.p. 60–61 °C; $[\alpha]_D^{20} =$ -464.9 ($c = 1.401$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.08$ (d, $J =$ 6.7 Hz, 1H), 1.98 (d, $J = 6.7$ Hz, 1H), 1.56 (d, $J = 4.3$ Hz, 1H), 1.42 (d, $J =$ 4.3 Hz, 1H), 1.35 (d, $J = 4.3$ Hz, 1H), 1.29 (d, $J = 4.0$ Hz, 1H), 1.22–1.17 (m, 3H), 1.14 (d, $J = 4.0$ Hz, 1H), 1.09 (d, $J = 3.8$ Hz, 1H), 1.00 (d, $J =$ 4.0 Hz, 1H), 0.90–0.84 (m, 1H), 0.83–0.69 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 31.8$ (C), 29.8 (CH_2), 25.6 (C), 23.5 (C), 18.6 (C), 18.0 (C), 17.4 (C), 15.2 (CH_2), 13.5 (C), 11.2 (CH_2), 10.4 (CH_2), 10.3 (CH_2), 8.9 (CH_2), 4.8 (CH_2), 4.3 (CH_2). Its relative configuration was determined by X-ray crystal structure analysis.[10]

Compound (3*S*,4*S*,5*S*,6*S*,7*S*)-**37**: colorless oil; $[\alpha]_D^{20} = -516.0$ ($c = 1.446$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.03$ (d, $J = 6.5$ Hz, 1H), 1.99 (d, $J = 6.5$ Hz, 1H), 1.73 (d, $J = 4.3$ Hz, 1H), 1.56 (d, $J = 4.5$ Hz, 1H), 1.48 (d, $J = 4.5$ Hz, 1H), 1.30 (d, $J = 4.3$ Hz, 1H), 1.21–1.17 (m, 3H), 1.13 (d, $J = 4.0$ Hz, 1H), 1.05 (d, $J = 3.8$ Hz, 1H), 1.00 (d, $J = 3.8$ Hz, 1H), 0.90–0.84 (m, 1H), 0.82–0.66 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 30.7$ (C), 29.0 (C), 27.7 (CH_2), 24.3 (C), 18.03 (C), 17.99 (C), 17.94 (C), 14.6 (CH_2), 13.6 (C), 11.1 (CH_2), 10.3 (CH_2), 8.8 (CH_2), 8.0 (CH_2), 4.8 (CH_2), 4.3 (CH_2).

***rac*-(4,4-Dibromospiropent-1-yl)methyl acetate (*rac*-8)**: Acetic anhydride (38.4 g, 35.5 mL, 376.1 mmol) was added in one portion at 0 °C to a stirred solution of *rac*-(4,4-dibromospiropent-1-yl)methanol (*rac*-**7**) (80.0 g, 312.6 mmol) in pyridine (67 mL). After additional stirring at this temperature for 2 h and at ambient temperature for 4 h, the reaction mixture was diluted with water (200 mL), then extracted with diethyl ether (2× 100 mL) and pentane (2×100 mL); the combined organic layers were washed with water (4×100 mL), dried, filtered through a 1 cm pad of silica gel and a 0.5 cm pad of Celite and concentrated under reduced pressure. The residue was distilled in vacuo to give acetate *rac*-**8** (88.2 g, 95 %). B.p. 92–94 °C (2 mbar); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 4.20$ (dd, $J = 6.4$, 11.5 Hz, 1H; CH_2O), 3.88 (dd, $J = 7.7$, 11.5 Hz, 1H; CH_2O), 2.03 (d, $J = 6.6$ Hz, 1H; *c*Pr-H), 2.04 (s, 3H; CH_3), 1.97 (d, $J = 6.6$ Hz, 1H; *c*Pr-H), 1.92–1.84 (m, 1H; *c*Pr-H), 1.49 (dd, $J = 5.5$, 8.6 Hz, 1H; *c*Pr-H), 1.23 (t, $J = 5.4$, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 170.7$ (C), 65.6 (CH_2), 31.9 (C), 28.2 (C), 27.1 (CH_2), 21.9 (CH), 20.8 (CH_3), 16.1 (CH_2).

Deracemization of *rac*-(4,4-dibromospiropent-1-yl)methyl acetate (*rac*-8): A mixture of *rac*-**8** (88.0 g, 295.3 mmol), lipase CES (4.62 g), concentrated aq. buffer solution (400 mL, pH 7) [prepared from K_2PO_4 (29.1 g), $Na_2HPO_4{\cdot}12H_2O$ (76.6 g) and water to 1 L], and dichloromethane (770 mL) was stirred with heating under reflux (bath temperature 50 °C) for 6 d with GC monitoring. After cooling to ambient temperature, the reaction mixture was filtered through a pad of Celite, the layers were separated, the aqueous one was extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed with water (50 mL), dried and concentrated under reduced pressure. Column chromatography of the residue [300 g silica gel, 5×35 cm column, pentane/Et_2O 1:8 (3 L), then 1:4 (2 L), then Et_2O (2 L)] gave [(1*R*,3*S*)-4,4-dibromospiropent-1-yl]methyl acetate [(1*R*,3*S*)-**8**, first fraction] and [(1*S*,3*R*)-4,4-dibromospiropent-1-yl]methanol [(1*S*,3*R*)-**7**, second fraction]. The former was treated with MeOH (600 mL) and H_2SO_4 (0.5 g, 0.27 mL) according to GP 1c (65 °C, 4 h) and, after recrystallization of the residue from pentane, furnished [(1*R*,3*S*)-4,4-dibromospiropent-1-yl]methanol [(1*R*,3*S*)-**7**] (29.3 g, 39 %) as a colorless solid. M.p. 44–45 °C; $[\alpha]_D^{20} = -72.4$ ($c = 1.05$ in $CHCl_3$); *ee* $\geq$ 95 %. The second fraction was recrystallized from pentane to afford [(1*S*,3*R*)-**7**] (30.02 g, 40 %) as a colorless solid. M.p. 47 °C; $[\alpha]_D^{20} = +74.0$ ($c = 1.11$ in $CHCl_3$); *ee* $\geq$ 97 %. Their NMR spectra were identical to those of *rac*-**7**.

Preparation of THP-protected *gem*-dibromo[*n*]triangulanylmethanols

General procedure GP 2: A solution of the respective *gem*-dibromotriangulanylmethanol (10 mmol), 3,4-dihydro-2*H*-pyran (DHP, 17 mmol) and pyridinium *p*-toluenesulfonate (PPTS, 0.8 mmol) in anhydrous dichloromethane (50 mL) was stirred at ambient temperature for the indicated time and then concentrated under reduced pressure. The residue was taken up with Et_2O (100 mL), the solution washed with sat. aq. $NaHCO_3$ solution (2×50 mL), water (50 mL), dried and concentrated again. The products were isolated by column chromatography on silica gel or used without further purification.

2-{[(1*S*,3*R*)-4,4-Dibromospiropent-1-yl]methoxy}tetrahydro-2*H*-pyran [(1*S*,3*R*)-12]: Column chromatography (500 g silica gel, 7×30 cm column, pentane/Et_2O 10:1) of the residue obtained from [(1*S*,3*R*)-4,4-dibromospiropent-1-yl]methanol [(1*S*,3*R*)-**7**] (19.5 g, 76.2 mmol), DHP (10.90 g, 11.77 mL, 129.6 mmol) and PPTS (1.40 g, 5.57 mmol) in CH_2Cl_2 (200 mL) according to GP 2 (20 °C, 3.5 h) afforded (1*S*,3*R*)-**12** (25.9 g, 100 %) as a colorless oil.

2-{[(1*R*,3*S*)-4,4-Dibromospiropent-1-yl]methoxy}tetrahydro-2*H*-pyran [(1*R*,3*S*)-12]: This compound (161.1 g, 97%) was obtained from [(1*R*,3*S*)-4,4-dibromospiropent-1-yl]methanol [(1*R*,3*S*)-**7**] (125.0 g, 488.4 mmol), DHP (62.0 g, 66.95 mL, 737.0 mmol) and PPTS (5.0 g, 19.9 mmol) in CH_2Cl_2 (500 mL) according to GP 2 (20 °C, 26 h) as a colorless oil and used without further purification. Its IR and NMR spectra were identical to those of the enantiomer (1*S*,3*R*)-**12** (see above).

2-{[(1*R*,3*S*,4*S*)-5,5-Dibromodispiro[2.0.2.1]hept-1-yl]methoxy}tetrahydro-2*H*-pyran [(1*R*,3*S*,4*S*)-20]: Column chromatography (100 g silica gel, 4× 20 cm column, pentane/Et_2O 5:1, R_f = 0.38) of the crude product obtained from (1*R*,3*S*,4*S*)-**19** (3.14 g, 11.14 mmol), DHP (1.60 g, 1.73 mL, 19.0 mmol) and PPTS (209 mg, 0.83 mmol) in CH_2Cl_2 (60 mL) according to GP 2 (20 °C, 3 h) afforded (1*R*,3*S*,4*S*)-**20** (4.08 g, 100%) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.62 (t, *J* = 3.0 Hz, 0.5 H; OCHO), 4.57 (t, *J* = 3.0 Hz, 0.5 H; OCHO), 3.72–3.64 (m, 1 H; CH_2O), 3.84–3.79 (m, 1 H; CH_2O), 3.50–3.42 (m, 2 H; CH_2O), 2.08–2.03 (m, 1 H), 1.91–1.37 (m, 11 H), 0.83 (t, *J* = 4.9 Hz, 1 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 98.6 (CH), 98.5 (CH), 70.12 (CH_2), 70.06 (CH_2), 62.24 (CH_2), 62.16 (CH_2), 30.64 (C), 30.6 (CH_2), 29.3 (C), 28.72 (CH), 28.68 (CH), 25.4 (CH_2), 25.1 (C), 24.9 (C), 19.5 (CH_2), 19.4 (CH_2), 16.63 (CH_2), 16.60 (CH_2), 14.22 (CH), 14.16 (CH), 8.5 (CH_2), 8.3 (CH_2); IR (film): $\tilde{\nu}$ = 3065, 2941, 2868, 1440, 1336, 1201, 1163, 1119, 1077, 1057, 1027, 903, 815, 683 cm^{-1}; MS (CI): *m*/*z* (%): 752/750/748 (9/16/9) [$2M^+ + NH_4$], 470/468/466 (52/100/52), 386/384/382 (25/49/25) [$M^+ + NH_4$].

2-{[(1*S*,3*R*,4*R*)-5,5-Dibromodispiro[2.0.2.1]hept-1-yl]methoxy}tetrahydro-2*H*-pyran [(1*S*,3*R*,4*R*)-20]: Column chromatography (500 g silica gel, 7× 30 cm column, pentane/Et_2O 5:1, R_f = 0.38) of the residue obtained from [(1*S*,3*R*,4*R*)-5,5-dibromodispiro[2.0.2.1]hept-1-yl]methanol [(1*S*,3*R*,4*R*)-**19**] (20.7 g, 73.4 mmol), DHP (11.0 g, 11.9 mL, 130.8 mmol) and PPTS (1.40 g, 5.6 mmol) in CH_2Cl_2 (150 mL) according to GP 2 (20 °C, 1.5 h) furnished crude (1*S*,3*R*,4*R*)-**20** (26.5 g, 99%) as a colorless oil which was used without further purification.

(1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-2-{(8,8-Dibromopentaspiro[2.0.0.0.0.2.1.1.1.1]tridec-1-yl)methoxy}tetrahydro-2*H*-pyran [(1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-30]: The crude compound (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-**30** (1.447 g, 84%) was obtained from the dibromotriangulanemethanol (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-**29** (1.390 g, 3.86 mmol), DHP (741 mg, 0.8 mL, 8.81 mmol) and PPTS (100 mg, 0.40 mmol) in CH_2Cl_2 (10 mL) according to GP 2 (20 °C, 4 h) and used without further purification.

Preparation of bis([*n*]triangulanylidenemethanols)

General procedure GP 3: Anhydrous $CuCl_2$ (2 mmol) was added in one portion at −100 °C to a stirred solution of the respective THP-protected *gem*-dibromotriangulanylmethanol (10 mmol) in an anhydrous THF/Et_2O mixture (30 mL), and the resulting slurry was stirred at this temperature for an additional 0.5 h. *n*BuLi (10.8 mmol, a solution in hexane) was added dropwise at −105 to −95 °C over a period of 1 h, the resulting mixture was stirred at this temperature for an additional 1 h, allowed to warm up to room temperature over 2 h, and then poured into an ice-cold mixture of sat. aq. NH_4Cl solution and diethyl ether (50 mL each). The aqueous layer was extracted with Et_2O (2×30 mL), the combined organic phases were dried and concentrated under reduced pressure. The oily residue was taken up with methanol (300 mL) and stirred with pyridinium *p*-toluenesulfonate (PPTS, 1.6 mmol) at 50–65 °C for the indicated time. The reaction mixture was cooled to ambient temperature and, after addition of water (6 mL), concentrated under reduced pressure. The product was isolated by column chromatography on silica gel followed by recrystallization.

(*E*)-(3*R*,3′*R*,4*S*,4′*S*)-{4′-Hydroxymethyl-[1,1′]bi(spiropentylidene)-4-yl}-methanol [(*E*)-(3*R*,3′*R*,4*S*,4′*S*)-13] and (*Z*)-(3*R*,3′*R*,4*S*,4′*S*)-{4′-hydroxymethyl-[1,1′]bi(spiropentylidene)-4-yl}methanol [(*Z*)-(3*R*,3′*R*,4*S*,4′*S*)-13]: The oily residue obtained from {[(1*S*,3*R*)-4,4-dibromospiropent-1-yl]methoxy}tetrahydropyran [(1*S*,3*R*)-**12**] (25.9 g, 76.2 mmol), *n*BuLi (92.0 mmol, 38 mL of a 2.42 M solution in hexane) and $CuCl_2$ (2.05 g, 15.25 mmol) in THF/Et_2O 10:1 (290 mL) was treated with MeOH (1000 mL) and PPTS (1.50 g, 6.0 mmol) according to GP 3 (65 °C, 6 h). Column chromatography of the residue (300 g silica gel, 5×35 cm column, hexane/Et_2O 1:1, then Et_2O, R_f = 0.22 in Et_2O) followed by recrystallization from hexane/Et_2O furnished (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** (2.83 g, 38% over two steps) as a colorless solid. Evaporation of the mother liquor gave (*Z*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** (2.87 g, 38%) as a colorless solid which, however, contained an impurity of the (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** isomer (ca. 20%).

Compound (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13**: m.p. 129–130 °C; $[\alpha]_D^{20}$ = +302.2, $[\alpha]_{578}^{20}$ = +315.7, $[\alpha]_{546}^{20}$ = +363.2, $[\alpha]_{436}^{20}$ = +665.9, $[\alpha]_{365}^{20}$ = +1165.5 (*c* = 1.10 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.68 (d, *J* = 6.8 Hz, 4 H; 2 CH_2O), 1.72 (s, 2 H; 2 OH), 1.77–1.67 (m, 2 H; *c*Pr-H), 1.47 (d, *J* = 5.9 Hz, 2 H; *c*Pr-H), 1.38 (d, *J* = 5.9 Hz, 2 H; *c*Pr-H), 1.29 (dd, *J* = 4.3, 7.8 Hz, 2 H; *c*Pr-H), 1.03 (t, *J* = 4.6 Hz, 2 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 111.1 (2 C), 65.7 (2 CH_2), 22.3 (2 CH), 15.4 (2 C), 13.5 (2 CH_2), 7.8 (2 CH_2). Its relative configuration was established by X-ray crystal structure analysis.[10]

Compound (*Z*)-(3*R*,3′*R*,4*S*,4′*S*)-**13**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.71–3.58 (m, 4 H; 2 CH_2O), 2.10 (brs, 2 H; 2×OH), 1.61–1.51 (m, 2 H; *c*Pr-H), 1.54 (d, *J* = 6.0 Hz, 2 H; *c*Pr-H), 1.44 (d, *J* = 6.0 Hz, 2 H; *c*Pr-H), 1.13 (dd, *J* = 4.3, 7.9 Hz, 2 H; *c*Pr-H), 1.02 (t, *J* = 4.6 Hz, 2 H; cPr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 111.5 (2 C), 65.6 (2 CH_2), 22.5 (2 CH), 16.0 (2 C), 13.8 (2 CH_2), 7.9 (2 CH_2).

(*E*)-(3*S*,3′*S*,4*R*,4′*R*)-{4′-Hydroxymethyl-[1,1′]bi(spiropentylidene)-4-yl}-methanol [(*E*)-(3*S*,3′*S*,4*R*,4′*R*)-13] and (*Z*)-(3*S*,3′*S*,4*R*,4′*R*)-{4′-hydroxymethyl-[1,1′]bi(spiropentylidene)-4-yl}methanol [(*Z*)-(3*S*,3′*S*,4*R*,4′*R*)-13]: {[(1*R*,3*S*)-4,4-Dibromospiropent-1-yl]methoxy}tetrahydropyran [(1*R*,3*S*)-**12**] (40.0 g, 117.6 mmol) was treated with *n*BuLi (145.0 mmol, 54 mL of a 2.685 M solution in hexane) and $CuCl_2$ (3.17 g, 23.6 mmol) in THF/Et_2O 14:1 mixture (250 mL) according to GP 3. The combined oily residues collected from four such preparations were deprotected with MeOH (3 L) and PPTS (8.0 g, 31.8 mmol) according to GP 3 (65 °C, 2 h). Column chromatography (1000 g silica gel, 9×35 cm column, hexane/Et_2O 1:1, then Et_2O, R_f = 0.22 in Et_2O) followed by twice repeated recrystallization from hexane/Et_2O/THF furnished (*E*)-(3*S*,3′*S*,4*R*,4′*R*)-**13** (18.57 g, 41%) as a colorless solid. Evaporation of the mother liquor gave (*Z*)-(3*S*,3′*S*,4*R*,4′*R*)-**13** (23.10 g, 51%) as a colorless solid which, however, contained an impurity of the (*E*)-(3*S*,3′*S*,4*R*,4′*SR*)-**13** isomer (ca. 20%).

Compound (*E*)-(3*S*,3′*S*,4*R*,4′*R*)-**13**: m.p. 129.0 °C; $[\alpha]_D^{20}$ = −302.3, $[\alpha]_{578}^{20}$ = −317.0, $[\alpha]_{546}^{20}$ = −365.1, $[\alpha]_{436}^{20}$ = −670.1, $[\alpha]_{365}^{20}$ = −1174.3 (*c* = 0.80). Its NMR spectra were identical to those of the enantiomer (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** (see above).

(*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-{5′-Hydroxymethyl-[1,1′]bi(dispiro[2.0.2.1]-heptylidene)-5-yl}-methanol [(*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-21]: The oily residue obtained from (1*R*,3*S*,4*S*)-**20** (4.08 g, 11.14 mmol), *n*BuLi (12.3 mmol, 7.7 mL of a 1.59 M solution in hexane) and $CuCl_2$ (300 mg, 2.23 mmol) in THF/Et_2O 10:1 mixture (33 mL) was treated with MeOH (500 mL) and PPTS (460 mg, 1.83 mmol) according to GP 3 (50 °C, 2 h). Column chromatography of the residue (100 g silica gel, 3×30 cm column, pentane/Et_2O 1:2, R_f = 0.33 in Et_2O) followed by recrystallization from hexane/Et_2O furnished (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21** (308 mg, 23%) as a colorless solid. M.p. 142–143 °C; $[\alpha]_D^{20}$ = −424.0 (*c* = 0.90 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.72 (dd, *J* = 6.6, 11.1 Hz, 2 H; CH_2O), 3.61 (dd, *J* = 7.2, 11.1 Hz, 2 H; CH_2O), 1.60–1.52 (m, 6 H; 4 *c*Pr-H, 2 OH), 1.48–1.38 (m, 4 H; *c*Pr-H), 1.29 (d, *J* = 5.9 Hz, 2 H; *c*Pr-H), 0.97 (dd, *J* = 4.6, 7.8 Hz, 2 H; *c*Pr-H), 0.80 (t, *J* = 4.6 Hz, 2 H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 112.3 (2 C), 66.0 (2 CH_2), 21.9 (2 C), 19.1 (2 CH), 16.4 (2 C), 13.7 (2 CH_2), 10.9 (2 CH_2), 10.0 (2 CH_2). Its relative configuration was confirmed by X-ray crystal structure analysis.[10] The corresponding *Z* isomer was also formed, but not isolated from the mother liquor.

(*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-{5′-Hydroxymethyl-[1,1′]bi(dispiro[2.0.2.1]-heptylidene)-5-yl}methanol [(*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-21] and (*Z*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-{5′-hydroxymethyl-[1,1′]bi(dispiro[2.0.2.1]heptylidene)-5-yl}methanol [(*Z*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-21]: Compound (1*S*,3*R*,4*R*)-**20** (26.5 g, 72.4 mmol) was treated with *n*BuLi (86.88 mmol, 57.9 mL of a 1.50 M solution in hexane) and $CuCl_2$ (1.930 g, 14.35 mmol) in THF/Et_2O 10:1 (220 mL), and the oily residue was worked up with MeOH (1100 mL) and PPTS (2.30 g, 9.15 mmol) according to GP 3 (65 °C, 12 h). Column chromatography of the residue (500 g silica gel, 7×30 cm column, pentane/Et_2O 1:2, R_f = 0.33 in Et_2O) followed by recrystallization from hexane/Et_2O furnished (*E*)-

(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-**21** (2.92 g, 33 % over three steps) as a colorless solid. M.p. 142–143 °C; $[\alpha]_D^{20} = +423.2$ ($c = 0.98$ in $CHCl_3$). Its NMR spectra were identical to those of the enantiomer (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21** (see above). Evaporation of the mother liquor gave (*Z*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-**21** (3.51 g, 40 %) as a colorless solid which, however, contained an impurity of the (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21** isomer (ca. 20 %).

Compound (*Z*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.68$ (dd, $J = 6.5$, 11.1 Hz, 2H; CH_2O), 3.65 (dd, $J = 7.1$, 11.1 Hz, 2H; CH_2O), 2.01 (br s, 2H; 2OH), 1.60–1.19 (m, overlapping signals of *Z*- and *E* isomers), 0.85 (dd, $J = 4.5$, 7.9 Hz, 2H; *c*Pr-H), 0.72 (t, $J = 4.5$ Hz, 2H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 112.5$ (2C), 66.8 ($2CH_2$), 22.1 (2C), 19.3 (2CH), 16.9 (2C), 14.4 ($2CH_2$), 10.5 ($2CH_2$), 9.9 ($2CH_2$).

(*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*R*,5′*R*,6*R*,6′*R*,7*R*,7′*R*,8*S*,8′*S*)-{8′-Hydroxymethyl-[1,1′]bi(pentaspiro[2.0.0.0.0.2.1.1.1.1]tridecylidene)-8-yl}methanol [(*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*R*,5′*R*,6*R*,6′*R*,7*R*,7′*R*,8*S*,8′*S*)-31 [(*E*)-31] and (*Z*)-(3*R*,3′*R*,4*R*,4′*R*,5*R*,5′*R*,6*R*,6′*R*,7*R*,7′*R*,8*S*,8′*S*)-{8′-hydroxymethyl-[1,1′]bi(-pentaspiro[2.0.0.0.0.2.1.1.1.1]tridecylidene)-8-yl}methanol [(*Z*)-(3*R*,3′*R*,4*R*,4′*R*,5*R*,5′*R*,6*R*,6′*R*,7*R*,7′*R*,8*S*,8′*S*)-31 [(*Z*)-31]: The crude dibromide (1*S*,3*R*,4*R*,5*S*,6*R*,7*R*)-**30** (1.447 g, 3.26 mmol) was treated with *n*BuLi (4.04 mmol, 1.67 mL of a 2.42 M solution in hexane) and $CuCl_2$ (88 mg, 0.65 mmol) in THF/Et_2O 25:1 (26 mL), and the oily residue was worked up with MeOH (150 mL) and PPTS (100 mg, 0.40 mmol) according to GP 3 (65 °C, 3 h). Column chromatography of the residue (20 g silica gel, 2×15 cm column, $CHCl_3$/THF 15:1) followed by recrystallization from hexane/Et_2O furnished (*E*)-**31** (204 mg, 31 %) as a colorless solid. M.p. 172–173 °C; $[\alpha]_D^{20} = +1084.2$, $[\alpha]_{578}^{20} = +1135.2$, $[\alpha]_{546}^{20} = +1305.2$, $[\alpha]_{436}^{20} = +2372.5$, $[\alpha]_{365}^{20} = +4109.1$ ($c = 0.386$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 3.72$ (dd, $J = 6.6$, 11.1 Hz, 2H; CH_2O), 3.60 (dd, $J = 7.2$, 11.1 Hz, 2H; CH_2O), 1.52 (d, $J = 3.6$ Hz, 2H; *c*Pr-H), 1.48–1.45 (m, 4H; *c*Pr-H), 1.44 (d, $J = 3.6$ Hz, 2H; *c*Pr-H), 1.38–1.34 (m, 2H; *c*Pr-H), 1.26 (d, $J = 4.0$ Hz, 2H; *c*Pr-H), 1.21 (d, $J = 4.0$ Hz, 2H; *c*Pr-H), 1.18 (d, $J = 3.9$ Hz, 2H; *c*Pr-H), 1.15 (d, $J = 3.9$ Hz, 2H; *c*Pr-H), 1.13 (d, $J = 4.0$ Hz, 2H; *c*Pr-H), 1.11 (d, $J = 4.0$ Hz, 2H; *c*Pr-H), 1.09 (d, $J = 4.0$ Hz, 2H; *c*Pr-H), 1.00 (d, $J = 3.7$ Hz, 2H; *c*Pr-H), 0.67 (t, $J = 4.5$ Hz, 2H; *c*Pr-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 112.0$ (2C), 66.3 ($2CH_2$), 21.2 (2C), 18.9 (2C), 18.6 (2CH), 18.3 (2C), 17.4 (2C), 16.3 (2C), 14.3 ($2CH_2$), 10.8 ($2CH_2$), 10.2 ($2CH_2$), 9.1 ($2CH_2$), 8.9 ($2CH_2$), 8.8 ($2CH_2$). Its relative configuration was established by X-ray crystal structure analysis.[10]

Evaporation of the mother liquor gave (*Z*)-**31** (230 mg, 35 %) as a colorless solid which, however, contained an impurity of the (*E*)-**31** isomer (ca. 10 %); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 112.2$ (2C), 66.3 ($2CH_2$), 21.4 (2C), 19.1 (2C), 18.6 (2CH), 18.3 (2C), 17.4 (2C), 16.9 (2C), 15.5 ($2CH_2$), 10.5 ($2CH_2$), 10.3 ($2CH_2$), 9.0 ($2CH_2$), 8.8 ($2CH_2$), 8.6 ($2CH_2$).

(*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*S*,5′*S*,6*S*,6′*S*,7*S*,7′*S*)-(1,1′)bi(hexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadecylidene) [(*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*S*,5′*S*,6*S*,6′*S*,7*S*,7′*S*)-38] and (*Z*)-(3*S*,3′*S*,4*S*,4′*S*,5*S*,5′*S*,6*S*,6′*S*,7*S*,7′*S*)-(1,1′)bi(hexaspiro[2.0.0.0.0.0.0.2.1.1.1.1.1]pentadecylidene) [(*Z*)-(3*S*,3′*S*,4*S*,4′*S*,5*S*,5′*S*,6*S*,6′*S*,7*S*,7′*S*)-38]: The dibromotriangulane [(3*S*,4*S*,5*S*,6*S*,7*S*)-**37**] (330 mg, 0.927 mmol) was treated with *n*BuLi (1.15 mmol, 475 μL of a 2.42 M solution in hexane) and $CuCl_2$ (25 mg, 0.186 mmol) in THF/Et_2O 10:1 (11 mL) according to GP 3. Column chromatography of the residue (40 g silica gel, 2.6×20 cm column, hexane, $R_f = 0.45$) provided a 2:1 mixture of (*E*)-**38** and (*Z*)-**38** (130 mg, 71 %) as a wax. Preparative HPLC separation of the latter (Kromasil RP18, MeOH/H_2O 90:10 + 0.5 % CF_3CO_2H, 1.0 mL min^{-1}) furnished (*E*)-**38** (60 mg, 33 %) and (*Z*)-**38** (37 mg, 20 %) as foams.

Compound (*Z*)-**38**: $[\alpha]_D^{20} = -1110.1$ ($c = 0.525$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.59$ (d, $J = 4.0$ Hz, 2H), 1.58 (s, 4H), 1.29 (d, $J = 3.5$ Hz, 2H), 1.25 (d, $J = 3.5$ Hz, 2H), 1.22 (d, $J = 3.8$ Hz, 2H), 1.18 (d, $J = 3.8$ Hz, 2H), 1.15 (d, $J = 3.8$ Hz, 2H), 1.13 (d, $J = 3.8$ Hz, 2H), 1.08 (d, $J = 4.0$ Hz, 2H), 1.03 (d, $J = 4.5$ Hz, 2H), 1.01 (d, $J = 4.5$ Hz, 2H), 0.90–0.69 (m, 8H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 112.3$ (2C), 21.4 (2C), 18.4 (2C), 18.1 (2C), 18.0 (2C), 16.9 (2C), 15.2 ($2CH_2$), 13.6 (2C), 11.1 ($2CH_2$), 10.8 ($2CH_2$), 10.4 ($2CH_2$), 9.0 ($2CH_2$), 8.8 ($2CH_2$), 4.8 ($2CH_2$), 4.4 ($2CH_2$).

Compound (*E*)-**38**: $[\alpha]_D^{20} = -1446.1$ ($c = 0.525$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.55$ (d, $J = 3.5$ Hz, 2H), 1.49 (s, 4H), 1.48 (d, $J = 4.5$ Hz, 2H), 1.29 (d, $J = 4.0$ Hz, 2H), 1.25 (d, $J = 3.5$ Hz, 2H), 1.20 (d, $J = 4.0$ Hz, 2H), 1.17 (d, $J = 4.0$ Hz, 2H), 1.15 (d, $J = 4.0$ Hz, 2H), 1.14 (d, $J = 3.8$ Hz, 2H), 1.08 (d, $J = 3.8$ Hz, 2H), 1.01 (d, $J = 4.5$ Hz, 2H), 0.89–0.68 (m, 8H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 112.0$ (2C), 21.2 (2C), 18.1 (4C), 18.0 (2C), 16.3 (2C), 14.4 ($2CH_2$), 13.6 (2C), 11.2 ($2CH_2$), 11.0 ($2CH_2$), 10.3 ($2CH_2$), 8.9 ($2CH_2$), 8.8 ($2CH_2$), 4.8 ($2CH_2$), 4.4 ($2CH_2$).

(1*S*,3*R*,4*R*,5*S*,6*S*,7*R*,8*R*,9*S*)-(9-Hydroxymethylhexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadec-1-yl)methanol {*d*-(+)-[7]triangulane-1,9-dimethanol, *d*-22}: Diethylzinc (17.35 mmol, 6.94 mL of a 2.5 M solution in toluene) was added to freshly distilled anhydrous dichloromethane (10 mL). The solution was cooled in an ice bath, and a solution of trifluoroacetic acid (1.974 g, 1.33 mL, 17.3 mmol) in CH_2Cl_2 (8 mL) was added slowly dropwise. Under vigorous stirring, a solution of CH_2I_2 (3.09 g, 926 μL, 11.5 mmol) in CH_2Cl_2 (8 mL) was added dropwise over a period of 20 min. After stirring for an additional 20 min, a solution of (*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-**21** (1.41 g, 5.77 mmol) in CH_2Cl_2 (100 mL) was added, and the ice bath was removed. The mixture was stirred at ambient temperature for 5 h, and the reaction quenched with sat. aq. NH_4Cl solution (5 mL). The aqueous phase was extracted with Et_2O (100 mL). The combined organic phases were dried and concentrated under reduced pressure. Column chromatography of the residue (250 g silica gel, 5× 30 cm column, pentane/Et_2O 1:1 → 1:4, $R_f = 0.17$ in Et_2O) followed by recrystallization from hexane/Et_2O afforded the diol *d*-**22** (400 mg, 27 %) as a colorless solid. M.p. 114–115 °C; $[\alpha]_D^{20} = +16.8$ ($c = 0.358$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.67$ (dd, $J = 6.5$, 11.1 Hz, 2H; CH_2O), 3.54 (dd, $J = 7.2$, 11.1 Hz, 2H; CH_2O), 1.71 (br s, 2H; 2OH), 1.31–1.20 (m, 2H; *c*Pr-H), 1.30 (d, $J = 4.0$ Hz, 2H; *c*Pr-H), 1.23 (d, $J = 3.9$ Hz, 2H; *c*Pr-H), 1.16 (s, 2H; *c*Pr-H), 1.08 (d, $J = 3.8$ Hz, 2H; *c*Pr-H), 0.83–0.73 (m, 6H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 66.2$ ($2CH_2$), 20.2 (2C), 19.5 (2C), 18.7 (2C), 18.6 (2CH), 13.2 ($2CH_2$), 12.5 (CH_2), 10.8 ($2CH_2$), 10.3 ($2CH_2$).

Cyclopropanation of enantiomerically pure bis([*n*]triangulanylidenemethanols)

General procedure GP 4: A solution of CH_2N_2 in diethyl ether (20–100 equiv) was added dropwise at ambient temperature to the vigorously stirred suspension of the respective bis(triangulanylidenemethanol) (2–7 mmol) and CuCl (18–40 equiv) [or CuCl/$Cu(OTf)_2$ mixture] in Et_2O (150 mL) for a period of 3 h. The combined reaction mixtures obtained from several cyclopropanations were filtered through a pad of Celite (2 cm), concentrated under reduced pressure to about 100 mL and treated with CH_2N_2 and CuCl again with TLC monitoring (Et_2O). After filtration through a pad of Celite (2 cm) and concentration of the reaction mixture under reduced pressure, the product was isolated by column chromatography on silica gel followed by recrystallization from CH_2Cl_2/Et_2O/hexane, if not otherwise specified.

(1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-(7-Hydroxymethyltetraspiro[2.0.0.0.2.1.1.1]undec-1-yl)methanol {(*P*)-(+)-[5]triangulane-1,7-dimethanol, (*P*)-14}: Each of two equal portions of the diol (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** (1.287 g, 6.694 mmol) was treated with CH_2N_2 [prepared from 15.6 g (151 mmol) *N*-methyl-*N*-nitrosourea (NMU)] in the presence of CuCl (12.0 g, 121.2 mmol) according to GP 4, and the combined reaction mixtures were treated with CH_2N_2 [prepared from 5.20 g (50.44 mmol) NMU] in the presence of CuCl (7.0 g, 70.71 mmol) according to GP 4 again. Column chromatography of the residue (400 g silica gel, 7×25 cm column, Et_2O, $R_f = 0.33$) followed by recrystallization afforded (*P*)-**14** (607 mg, 22 %) as a colorless solid. M.p. 127–128 °C; $[\alpha]_D^{20} = +432.3$, $[\alpha]_{578}^{20} = +451.5$, $[\alpha]_{546}^{20} = +515.0$, $[\alpha]_{436}^{20} = +893.4$, $[\alpha]_{365}^{20} = +1439.6$ ($c = 8.00$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.70$ (dd, $J = 6.5$, 11.0 Hz, 2H; CH_2O), 3.58 (dd, $J = 7.2$, 11.0 Hz, 2H; CH_2O), 1.66 (s, 2H; 2OH), 1.40–1.31 (m, 2H; *c*Pr-H), 1.13 (d, $J = 3.8$ Hz, 2H; *c*Pr-H), 1.09 (s, 2H; *c*Pr-H), 1.06 (d, $J = 3.8$ Hz, 2H; *c*Pr-H), 0.98 (dd, $J = 4.3$, 7.7 Hz, 2H; *c*Pr-H), 0.64 (t, $J = 4.4$ Hz, 2H, *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 66.3$ ($2CH_2$), 18.5 (2CH), 18.2 (2C), 18.1 (2C), 11.6 (CH_2), 9.0 ($2CH_2$), 8.5 ($2CH_2$). Its relative configuration was determined by X-ray crystal structure analysis.[10] The corresponding diastereomer (1*S*,3*R*,4*S*,5*S*,6*R*,7*S*)-**14** was also isolated as a colorless oil in about 8 % yield, but was not obtained in pure form and not completely characterized. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.94$ (dd, $J = 4.5$, 11.0 Hz, 2H; CH_2O), 3.43 (br s, 2H; 2OH), 3.14 (dd, $J = 9.6$, 11.0 Hz, 2H; CH_2O), 1.42–1.32 (m, 4H, *c*Pr-H), 1.13 (s, 2H; *c*Pr-H), 0.97 (d, $J =$

3.6 Hz, 2H; *c*Pr-H), 0.92 (dd, $J=4.5$, 8.0 Hz, 2H; *c*Pr-H), 0.64 (dd, $J=4.5$, 4.5 Hz, 2H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=66.0$ ($2CH_2$), 19.1 (2CH), 18.1 (2C), 17.5 (2C), 11.3 (CH_2), 8.9 ($2CH_2$), 7.8 ($2CH_2$).

Under modified conditions in the presence of Cu^{II} triflate, the diol (*E*)-(3*R*,3′*R*,4*S*,4′*S*)-**13** (3.0 g, 15.6 mmol) was treated with CH_2N_2 [prepared from 34.0 g (329.8 mmol) NMU] in the presence of CuCl (30.0 g, 303 mmol) and $Cu(OTf)_2$ (800 mg, 2.21 mmol) in Et_2O (550 mL) according to GP 4. Column chromatography of the residue (400 g silica gel, 7×25 cm column, Et_2O, $R_f=0.33$) followed by recrystallization from hexane/Et_2O afforded (*P*)-**14** (1.22 g, 38%).

(1*R*,3*S*,4*S*,5*S*,6*S*,7*R*)-(7-Hydroxymethyltetraspiro[2.0.0.0.2.1.1.1]undec-1-yl)methanol {(*M*)-(−)-[5]triangulane-1,7-dimethanol, (*M*)-14}: Each of three equal portions of the diol (*E*)-(3*S*,3′*S*,4*R*,4′*R*)-**13** (3.0 g, 15.6 mmol) was treated with CH_2N_2 [prepared from 34.0 g (329.8 mmol) NMU] in the presence of CuCl (30.0 g, 303 mmol) and $Cu(OTf)_2$ (800 mg, 2.21 mmol) according to GP 4. Column chromatography (600 g silica gel, 7×35 cm column, Et_2O, $R_f=0.33$) of the combined residues followed by recrystallization from benzene afforded (*M*)-**14** (2.996 g, 31%) as a colorless solid. M.p. 126–128°C; $[\alpha]_D^{20}=-417.1$, $[\alpha]_{578}^{20}=-435.5$, $[\alpha]_{546}^{20}=-497.0$, $[\alpha]_{436}^{20}=-862.5$, $[\alpha]_{365}^{20}=-1391.4$ ($c=0.938$ in $CHCl_3$).

(1*S*,3*R*,4*R*,5*R*,6*R*,7*R*,8*R*,9*S*)-(9-Hydroxymethylhexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadec-1-yl)methanol {(*P*)-(+)-[7]triangulane-1,9-dimethanol, (*P*)-22} and (1*S*,3*R*,4*R*,5*S*,6*S*,7*R*,8*R*,9*S*)-(9-hydroxymethylhexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadec-1-yl)methanol {*d*-(+)-[7]triangulane-1,9-dimethanol, *d*-22}: Each of five equal portions of the diol (*E*)-(3*R*,3′*R*,4*R*,4′*R*,5*S*,5′*S*)-**21** (538 mg, 2.202 mmol) was treated with CH_2N_2 [prepared from 20.8 g (202 mmol) NMU] in the presence of CuCl (7.0 g, 70.7 mmol), and the combined reaction mixtures were treated with CH_2N_2 [prepared from 20.82 g (202 mmol) NMU] in the presence of CuCl (12.0 g, 121.2 mmol) again according to GP 4. Column chromatography of the residue (400 g silica gel, 7×25 cm column, Et_2O) followed by recrystallization afforded (*P*)-**22** (747 mg, 26%, $R_f=0.25$) and *d*-**22** (105 mg, 4%, $R_f=0.17$).

Compound (*P*)-**22**: colorless solid; m.p. 130–131°C; $[\alpha]_D^{20}=+691.2$, $[\alpha]_{578}^{20}=+721.9$, $[\alpha]_{546}^{20}=+824.1$, $[\alpha]_{436}^{20}=+1436.1$, $[\alpha]_{365}^{20}=+2330.1$ ($c=0.835$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=3.71$ (dd, $J=6.5$, 11.0 Hz, 2H; CH_2O), 3.58 (dd, $J=7.1$, 11.0 Hz, 2H; CH_2O), 1.70 (br s, 2H; 2 OH), 1.32–1.42 (m, 4H; cPr-H), 1.21 (d, $J=3.9$ Hz, 2H; cPr-H), 1.16 (dd, $J=3.9$, 11.0 Hz, 4H; cPr-H), 1.04 (s, 2H; cPr-H), 1.00 (d, $J=3.9$ Hz, 2H; cPr-H), 0.67 (dd, $J=4.4$ Hz, 2H; cPr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=66.3$ ($2CH_2$), 18.5 (2CH), 18.2 (2C), 18.0 (2C), 17.4 (2C), 10.4 ($2CH_2$), 9.0 ($2CH_2$), 8.8 (CH_2), 8.7 ($2CH_2$). Its relative configuration was determined by X-ray crystal structure analysis.[10]

(1*R*,3*S*,4*S*,5*S*,6*S*,7*S*,8*S*,9*R*)-(9-Hydroxymethylhexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadec-1-yl)methanol {(*M*)-(−)-[7]triangulane-1,9-dimethanol, (*M*)-22} and (1*R*,3*S*,4*S*,5*R*,6*R*,7*S*,8*S*,9*R*)-(9-hydroxymethylhexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadec-1-yl)methanol {*l*-(+)-[7]triangulane-1,9-dimethanol, *l*-22}: Each of three equal portions of the diol (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*R*,5′*R*)-**21** (977 mg, 4.0 mmol) was treated with CH_2N_2 [prepared from 41.2 g (400 mmol) NMU] in the presence of CuCl (15.0 g, 151.5 mmol), and the combined reaction mixtures were treated with CH_2N_2 [prepared from 75.0 g (728 mmol) NMU] in the presence of CuCl (15.0 g, 151.5 mmol) again according to GP 4. Column chromatography of the residue (400 g silica gel, 7×25 cm column, benzene/THF 2:1) followed by recrystallization afforded (*M*)-**22** (930 mg, 30%, $R_f=0.38$) and *l*-**22** (124 mg, 4%, $R_f=0.22$).

Compound (*M*)-**22**: colorless solid; m.p. 129–131°C; $[\alpha]_D^{20}=-660.0$ ($c=1.04$ in $CHCl_3$). Its NMR spectra were identical to those of its enantiomer (*P*)-**22**, and the relative configuration was determined by X-ray crystal structure analysis.[10]

Compound *l*-**22**: colorless solid; m.p. 113–114°C (hexane/Et_2O); $[\alpha]_D^{20}=-19.80$ ($c=0.555$ in $CHCl_3$). Its NMR spectra were identical to those of its enantiomer *d*-**22**.

(4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*)-Tetradecaspiro[2.0.0.0.0.0.0.0.0.0.0.0.0.2.1.1.1.1.1.1.1.1.1.1.1.1.1.1]untriacontane [(4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*)-39]: The bicyclopropylidene derivative (*Z*)-(3*S*,3′*S*,4*S*,4′*S*,5*S*,5′*S*,6*S*,6′*S*,7*S*,7′*S*)-**38** (30 mg, 0.076 mmol) was treated with CH_2N_2 [prepared from 2.28 g (22.1 mmol) NMU] in the presence of CuCl (3.0 g, 30.3 mmol) and $Cu(OTf)_2$ (100 mg, 0.276 mmol) in Et_2O (10 mL) according to GP 4. After concentration of the reaction mixture under reduced pressure, the residue was treated with the same quantities of reagents three more times. Column chromatography of the final residue (50 g silica gel, 2.6×20 cm column, hexane, $R_f=0.56$) afforded the title product as a foam (13 mg, 42%) which, was recrystallized from acetone/acetonitrile. M.p. 126–127°C; $[\alpha]_D^{20}=-868.5$ ($c=0.931$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=1.25$–1.09 (m, 23H), 1.06 (d, $J=4.0$ Hz, 2H), 0.98 (d, $J=3.5$ Hz, 1H), 0.87–0.65 (m, 8H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=20.3$ (2C), 18.7 (C), 18.5 (2C), 18.2 (2C), 18.1 (C), 18.0 (2C), 17.9 (C), 17.4 (C), 13.54 (C), 13.52 (C), 11.3 ($2CH_2$), 11.1 ($2CH_2$), 11.0 ($2CH_2$), 10.6 ($2CH_2$), 10.2 (CH_2), 10.1 (CH_2), 9.2 (CH_2), 9.0 (CH_2), 8.9 (CH_2), 4.7 ($2CH_2$), 4.3 ($2CH_2$). Its relative configuration was determined by X-ray crystal structure analysis.[10] Some of the starting material was also isolated (14 mg, 47%).

(4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-Tetradecaspiro[2.0.0.0.0.0.0.0.0.0.0.0.0.2.1.1.1.1.1.1.1.1.1.1.1.1.1.1]untriacontane [(4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-39] and (4*S*,5*S*,6*S*,7*S*,8*S*,9*S*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*)-tetradecaspiro[2.0.0.0.0.0.0.0.0.0.0.0.0.2.1.1.1.1.1.1.1.1.1.1.1.1.1.1]untriacontane [(4*S*,5*S*,6*S*,7*S*,8*S*,9*S*,10*S*,11*S*,12*S*,13*S*,14*S*,15*S*)-39 [(*M*)-(−)-39]: The bicyclopropylidene derivative (*E*)-(3*S*,3′*S*,4*S*,4′*S*,5*S*,5′*S*,6*S*,6′*S*,7*S*,7′*S*)-**38** (50 mg, 0.127 mmol) was treated with CH_2N_2 [prepared from 4.55 g (44.2 mmol) NMU] in the presence of CuCl (3.942 g, 39.82 mmol) and $Cu(OTf)_2$ (100 mg, 0.276 mmol) in Et_2O (10 mL) according to GP 4. After concentration of the reaction mixture under reduced pressure, the residue was treated with the same quantities of reagents three more times. Column chromatography of the final residue (50 g silica gel, 2.6×20 cm column, hexane, $R_f=0.56$) afforded the mixture of the title products (42 mg, 81%).

HPLC analysis on a Chiralcel OD column proved it to be a 1:1.3 mixture of (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39** and (*M*)-(−)-**39** diastereomers with $t_R=9.0$ and 10.42 min, respectively, and they were separated by preparative HPLC on a Chiralcel OD column to give (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39** (10 mg, 19%) and (*M*)-(−)-**39** (12 mg, 23%). Their relative configurations were determined by X-ray crystal structure analysis.[10] The analytical samples were obtained by recrystallization from MeOH.

Compound (4*S*,5*S*,6*S*,7*S*,8*S*,9*R*,10*R*,11*S*,12*S*,13*S*,14*S*,15*S*)-**39**: slowly sublimed above 136°C; m.p. 146°C; $[\alpha]_D^{20}=-721.8$, $[\alpha]_{578}^{20}=-753.7$, $[\alpha]_{546}^{20}=-859.5$, $[\alpha]_{436}^{20}=-1509.7$, and $[\alpha]_{365}^{20}=-2464.9$ ($c=0.257$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=1.29$ (d, $J=3.5$ Hz, 2H), 1.28 (s, 2H), 1.26 (d, $J=3.5$ Hz, 2H), 1.24 (d, $J=3.5$ Hz, 2H), 1.21 (d, $J=3.8$ Hz, 2H), 1.17 (d, $J=3.8$ Hz, 4H), 1.14 (d, $J=3.8$ Hz, 2H), 1.06 (d, $J=3.8$ Hz, 2H), 1.02 (d, $J=3.8$ Hz, 2H), 0.97 (d, $J=3.8$ Hz, 4H), 0.92 (d, $J=3.8$ Hz, 2H), 0.88–0.83 (m, 2H), 0.81–0.66 (m, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=19.7$ (2C), 19.5 (2C), 17.9 (4C), 17.8 (2C), 17.6 (2C), 13.6 (2C), 12.7 (CH_2), 12.3 ($2CH_2$), 12.2 ($2CH_2$), 11.2 ($2CH_2$), 10.9 ($2CH_2$), 10.2 ($2CH_2$), 8.5 ($2CH_2$), 4.8 ($2CH_2$), 4.3 ($2CH_2$).

Compound (*M*)-(−)-**39**: slowly sublimed above 136°C; m.p. 149°C; $[\alpha]_D^{20}=-1302.5$, $[\alpha]_{578}^{20}=-1360.8$, $[\alpha]_{546}^{20}=-1556.6$, $[\alpha]_{436}^{20}=-2738.7$, and $[\alpha]_{365}^{20}=-4493.4$ ($c=0.362$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=1.25$ (s, 2H), 1.23 (d, $J=4.0$ Hz, 2H), 1.20 (d, $J=3.5$ Hz, 2H), 1.19–1.12 (m, 14H), 1.10 (d, $J=3.5$ Hz, 2H), 1.08 (d, $J=3.5$ Hz, 2H), 1.00 (d, $J=3.8$ Hz, 2H), 0.88–0.77 (m, 6H), 0.75–0.63 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=18.05$ (2C), 17.99 (2C), 17.4 (8C), 13.6 (2C), 12.1 (CH_2), 11.2 ($2CH_2$), 10.3 ($2CH_2$), 9.3 ($6CH_2$), 9.1 ($2CH_2$), 4.8 ($2CH_2$), 4.4 ($2CH_2$). Some of the starting material was also isolated (5 mg, 10%).

Conversion of enantiomerically pure [*n*]triangulanemethanols and 1,*n*-[*n*]triangulanedimethanols to the corresponding bromides and dibromides

General procedures GP 5

GP 5a: Bromine (2.10 equiv) was added as a solution in CH_2Cl_2 at −30 to −15°C over a period of 10 min to a stirred solution of triphenylphosphane (2.10 equiv) in anhydrous dichloromethane (30 mL). After an additional 15 min of stirring, a mixture of the respective alcohol (1–3 mmol) and anhydrous pyridine (2 equiv) in CH_2Cl_2 (3 mL) was added dropwise at −30°C. The mixture was stirred at −10°C for 1.5 h, and then at ambi-

ent temperature for the indicated time. After evaporation of the solvent under reduced pressure, pentane (100 mL) was added, the mixture was stirred for 3 h at ambient temperature and then filtered. The precipitate was thoroughly washed with pentane (3×50 mL), and the combined pentane extracts were filtered through a 0.5 cm pad of silica gel. After concentration of the filtrate under reduced pressure, the product was purified as indicated below.

GP 5b: Tetrabromomethane was added in three portions to a stirred solution of the respective THP-monoprotected diol **26**, imidazole (Im-H) and triphenylphosphane in anhydrous methylene chloride (250 mL) maintaining the temperature around 0 °C with external cooling. After stirring for an additional 5 min, the reaction mixture was allowed to warm up to ambient temperature, stirred at this temperature for an additional 1.5 h, and the reaction was quenched by adding 10 % aq. Na_2SO_3 solution (100 mL). The organic phase was separated, dried and concentrated under reduced pressure. The product was purified by column chromatography on silica gel.

(1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-1,7-Bis(bromomethyl)tetraspiro[2.0.0.0.2.1.1.1]undecane {1,7-bis(bromomethyl)-(*P*)-(+)-[5]triangulane, (*P*)-15}: From the diol (*P*)-**14** (495 mg, 2.40 mmol) and pyridine (380 mg, 388 μL, 4.80 mmol) in CH_2Cl_2 (3 mL), Ph_3P (1.340 g, 5.11 mmol) and Br_2 (816 mg, 262 μL, 5.1 mmol) in CH_2Cl_2 (1 mL), essentially pure dibromide (*P*)-**15** (673 mg, 84 %) was obtained as a slightly yellow solid according to GP 5a (5.5 h of stirring at ambient temperature) after evaporation of the filtered pentane extract. An analytical sample was prepared by recrystallization from MeOH. M.p. 88 °C; $[\alpha]_D^{20}=+351.7$, $[\alpha]_{578}^{20}=+368.1$, $[\alpha]_{546}^{20}=+421.8$, $[\alpha]_{436}^{20}=+742.0$, $[\alpha]_{365}^{20}=+1222.2$ ($c=1.20$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=3.50$ (s, 2H; CH_2Br), 3.47 (s, 2H; CH_2Br), 1.61–1.50 (m, 2H; *c*Pr-H), 1.28 (d, $J=3.9$ Hz, 2H; *c*Pr-H), 1.18 (dd, $J=4.6$, 7.9 Hz, 2H; cPr-H), 1.14 (s, 2H; *c*Pr-H), 1.05 (d, $J=3.8$ Hz, 2H; *c*Pr-H), 0.74 (t, $J=4.5$ Hz, 2H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): $\delta=38.3$ (2CH_2), 22.5 (2C), 19.1 (2CH), 18.8 (2C), 13.3 (2CH_2), 11.5 (CH_2), 7.8 (2CH_2). Its relative configuration was determined by X-ray crystal structure analysis.[10]

(1*S*,3*R*,4*R*,5*R*,6*R*,7*R*,8*R*,9*S*)-1,9-Bis(bromomethyl)hexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadecane {1,9-bis(bromomethyl)-(*P*)-(+)-[7]triangulane, (*P*)-23}: From the diol (*P*)-**22** (597 mg, 2.31 mmol) and pyridine (353 mg, 361 μL, 4.46 mmol) in CH_2Cl_2 (3 mL), Ph_3P (1.272 g, 4.85 mmol) and Br_2 (775 mg, 249 μL, 4.85 mmol) in CH_2Cl_2 (1 mL), essentially pure dibromide (*P*)-**23** (877 mg, 100 %) was obtained as a slightly yellow solid according to GP 5a (5 h of stirring at ambient temperature) after evaporation of the filtered pentane extract. An analytical sample was prepared by recrystallization from MeOH. M.p. 88–89 °C; $[\alpha]_D^{20}=+527.7$, $[\alpha]_{578}^{20}=+552.2$, $[\alpha]_{546}^{20}=+631.9$, $[\alpha]_{436}^{20}=+1113.8$, $[\alpha]_{365}^{20}=+1833.7$ ($c=1.245$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=3.50$ (s, 2H; CH_2Br), 3.47 (s, 2H; CH_2Br), 1.60–1.51 (m, 2H; *c*Pr-H), 1.31 (d, $J=3.9$ Hz, 2H; *c*Pr-H), 1.25 (d, $J=4.0$ Hz, 2H; *c*Pr-H), 1.18 (dd, $J=4.7$, 7.7 Hz, 2H; *c*Pr-H), 1.12 (d, $J=3.8$ Hz, 2H; *c*Pr-H), 1.03 (s, 2H; *c*Pr-H), 1.01 (d, $J=4.1$ Hz, 2H; *c*Pr-H), 0.75 (t, $J=4.5$ Hz, 2H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=38.3$ (2CH_2), 22.5 (2C), 19.1 (2CH), 18.2 (2C), 18.1 (2C), 13.3 (2CH_2), 10.4 (2CH_2), 9.0 (CH_2), 8.1 (2CH_2). Its relative configuration was determined by X-ray crystal structure analysis.[10]

(1*R*,3*S*,4*S*,5*S*,6*S*,7*S*,8*S*,9*R*)-1,9-Bis(bromomethyl)hexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadecane {1,9-bis(bromomethyl)-(*M*)-(−)-[7]triangulane, (*M*)-23}: From the diol (*M*)-**22** (415 mg, 1.606 mmol) and pyridine (254 mg, 260 μL, 3.21 mmol) in CH_2Cl_2 (3 mL), Ph_3P (876 mg, 3.34 mmol) and Br_2 (534 mg, 172 μL, 3.34 mmol) in CH_2Cl_2 (1 mL), almost pure dibromide (*M*)-**23** (617 mg, 100 %) was obtained as a slightly yellow solid according to GP 5a (5 h of stirring at ambient temperature). M.p. 87–88 °C (MeOH); $[\alpha]_D^{20}=-519.1$ ($c=0.71$ in $CHCl_3$). Its NMR spectra were identical to those of its enantiomer (*P*)-**23**.

(1*S*,3*R*,4*R*,5*S*,6*S*,7*R*,8*R*,9*S*)-1,9-Bis(bromomethyl)hexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadecane {1,9-bis(bromomethyl)-*d*-(+)-[7]triangulane, *d*-23}: The residue obtained from the diol *d*-**22** (387 mg, 1.498 mmol) and pyridine (237 mg, 242 μL, 3.0 mmol) in CH_2Cl_2 (3 mL), Ph_3P (825 mg, 3.145 mmol) and Br_2 (503 mg, 161 μL, 3.145 mmol) in CH_2Cl_2 (1 mL) according to GP 5a (5 h of stirring at ambient temperature), was recrystallized from MeOH/Et_2O to give the dibromide *d*-**23** (350 mg, 61 %) as a slightly yellow solid. M.p. 73–74 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=3.46$ (d, $J=7.6$ Hz, 4H; 2CH_2Br), 1.46 (dq, $J=4.6$, 7.6, Hz, 2H; *c*Pr-H), 1.38 (d, $J=3.9$ Hz, 2H; *c*Pr-H), 1.34 (d, $J=4.1$ Hz, 2H; *c*Pr-H), 1.19 (s, 2H; *c*Pr-H), 1.09 (d, $J=3.9$ Hz, 2H; *c*Pr-H), 0.96 (dd, $J=4.8$, 7.6 Hz, 2H; *c*Pr-H), 0.87 (d, $J=4.7$ Hz, 2H; *c*Pr-H), 0.83 (d, $J=4.1$ Hz, 2H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=38.2$ (2CH_2), 23.0 (2C), 20.3 (2C), 20.2 (2C), 19.2 (2CH), 15.9 (2CH_2), 13.2 (2CH_2), 12.5 (CH_2), 9.7 (2CH_2).

(1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-2-{[7-(Bromomethyl)tetraspiro[2.0.0.0.2.1.1.1]undec-1-yl]methoxy}tetrahydro-2*H*-pyran [(*P*)-27]: Column chromatography (450 g silica gel, 7×30 cm column, hexane/THF 20:1) of the residue obtained from (*P*)-**26** (5.560 g, 19.15 mmol), Im-H (2.518 g, 37.0 mmol), Ph_3P (10.365 g, 39.52 mmol) and CBr_4 (12.32 g, 37.13 mmol) in CH_2Cl_2 (250 mL) according to GP 5b furnished the bromide (*P*)-**27** (5.14 g, 76 %) as a colorless wax. $R_f=0.23$ (hexane/THF 20:1); ^{13}C NMR (62.9 MHz, CDC_3): $\delta=98.40/98.36$ (CH), 70.9 (CH_2), 62.2/62.1 (CH_2), 38.2 (CH_2), 30.68/30.62 (CH_2), 25.4 (CH_2), 22.5 (C), 19.6/19.5 (CH_2), 19.0 (CH), 18.7 (C), 18.28/18.23 (C), 18.2/17.9 (C), 15.7 (CH), 13.2 (CH_2), 11.4 (CH_2), 9.9/9.6 (CH_2), 8.7/8.6 (CH_2), 7.9 (CH_2).

(1*R*,3*S*,4*S*,5*S*,6*S*,7*R*)-2-{[7-(Bromomethyl)tetraspiro[2.0.0.0.2.1.1.1]undec-1-yl]methoxy}tetrahydro-2*H*-pyran [(*M*)-27]: Column chromatography (500 g silica gel, 7×30 cm column, hexane/THF 20:1) of the residue obtained from (*M*)-**26** (7.017 g, 24.17 mmol), Im-H (2.889 g, 42.42 mmol), Ph_3P (11.893 g, 45.34 mmol) and CBr_4 (14.076 g, 42.44 mmol) in CH_2Cl_2 (250 mL) according to GP 5b furnished the bromide (*M*)-**27** (6.23 g, 73 %) as a colorless wax. Its ^{13}C NMR spectrum was identical to that of its enantiomer (*P*)-**27**.

(1*R*,3*S*,4*S*,5*S*,6*S*)-1-(Bromomethyl)pentaspiro[2.0.0.0.0.2.1.1.1.1]tridecane [(*M*)-35]: From the alcohol (*M*)-**34** (1.788 g, 8.839 mmol) and pyridine (734 mg, 751 μL, 9.281 mmol) in CH_2Cl_2 (3 mL), Ph_3P (2.434 g, 9.281 mmol) and Br_2 (1.483 g, 476 μL, 9.281 mmol) in CH_2Cl_2 (10 mL), almost pure dibromide (*M*)-**35** (2.344 g, 100 %) was obtained as a slightly yellow oil according to GP 5a (5 h of stirring at ambient temperature) and used without further purification. $R_f=0.33$ (hexane, decomp.); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=3.50$ (dd, $J=1.3$, 7.5 Hz, 2H; CH_2Br), 1.60–1.49 (m, 1H; *c*Pr-H), 1.29 (d, $J=3.9$ Hz, 1H; *c*Pr-H), 1.21 (d, $J=3.3$ Hz, 1H; *c*Pr-H), 1.19 (d, $J=4.0$ Hz, 1H; *c*Pr-H), 1.16 (d, $J=4.8$ Hz, 1H; *c*Pr-H), 1.15–1.11 (m, 3H; *c*Pr-H), 0.96 (t, $J=3.9$ Hz, 2H; *c*Pr-H), 0.90–0.66 (m, 4H; *c*Pr-H), 0.76 (d, $J=4.8$ Hz, 1H; *c*Pr-H).

Dehydrobromination of enantiomerically pure 1,*n*-bis(bromomethyl)[*n*]-triangulanes

General procedure GP 6: A solution of potassium *tert*-butoxide or *tert*-amyloxide (*t*BuOK or *t*AmOK) (7.5 mmol) in anhydrous DMSO (25 mL) was added over a period of 5 min to a solution of the respective dibromide (2.5 mmol) in anhydrous DMSO (10 mL) maintaining the temperature around 20 °C with external water cooling. The reaction mixture was stirred at 20 °C for an additional 15–20 min, poured into ice-cold water (50 mL), the mixture was extracted with pentane (2×30 mL) and diethyl ether (2×30 mL). The combined organic extracts were washed with water (3×30 mL), brine (30 mL), dried and carefully concentrated under ambient pressure. The product was purified by column chromatography on silica gel, if not otherwise specified.

(3*R*,4*R*,5*R*,6*R*)-1,7-Dimethylenetetraspiro[2.0.0.0.2.1.1.1]undecane {1,7-dimethylene-(*P*)-(+)-[5]triangulane, (*P*)-16}: The pentane solution obtained from the dibromide (*P*)-**15** (540 mg, 1.626 mmol) in DMSO (7 mL) and *t*BuOK (540 mg, 4.81 mmol) in DMSO (4 mL) according to GP 6 was filtered through a 1 cm pad of silica gel and concentrated under reduced pressure to give (*P*)-**16** (170 mg, 61 %) as a colorless oil. $[\alpha]_D^{20}=+926.2$, $[\alpha]_{578}^{20}=+970.5$, $[\alpha]_{546}^{20}=+1118.3$, $[\alpha]_{436}^{20}=+2060.2$, $[\alpha]_{365}^{20}=+3612.6$ ($c=0.87$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=5.34$ (s, 2H; 2 =CH), 5.25 (t, $J=2.2$ Hz, 2H; 2 =CH), 1.60 (d, $J=3.8$ Hz, 2H; *c*Pr-H), 1.43–1.40 (m, 6H; *c*Pr-H), 1.18 (s, 2H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=135.4$ (2C), 99.4 (2CH_2), 22.5 (2C), 15.6 (2C), 14.5 (2CH_2), 11.9 (CH_2), 8.6 (2CH_2).

(3*S*,4*S*,5*S*,6*S*,7*S*,8*S*)-1,9-Dimethylenehexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadecane {1,9-dimethylene-(*M*)-(−)-[7]triangulane, (*M*)-24}: Column chromatography (20 g silica gel, 2.6×12 cm column, hexane, $R_f=0.47$) of the residue obtained from the dibromide (*M*)-**23** (631 mg, 1.642 mmol) in DMSO (7 mL) and *t*BuOK (540 mg, 4.81 mmol) in DMSO (4 mL) ac-

cording to GP 6 afforded (*M*)-**24** (109 mg, 30%) as a colorless oil, which crystallized upon standing at 0°C overnight. An analytical sample was prepared by recrystallization from MeOH. M.p. 59–61°C; $[\alpha]_D^{20}=-1285.4$, $[\alpha]_{578}^{20}=-1348.5$, $[\alpha]_{546}^{20}=-1556.4$, $[\alpha]_{436}^{20}=-2863.4$, $[\alpha]_{365}^{20}=-4971.5$ ($c=0.60$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=5.31$ (s, 2H; $=CH_2$), 5.23 (t, $J=1.9$ Hz, 2H; $=CH_2$), 1.56 (d, $J=3.7$ Hz, 2H; *c*Pr-H), 1.43 (d, $J=3.7$ Hz, 2H; *c*Pr-H), 1.39 (d, $J=7.7$ Hz, 2H; *c*Pr-H), 1.37 (dt, $J=1.9$, 7.7 Hz, 2H; *c*Pr-H), 1.25 (d, $J=4.0$ Hz, 2H; *c*Pr-H), 1.15 (s, 2H; *c*Pr-H), 1.08 (d, $J=4.0$ Hz, 2H; *c*Pr-H); ^{13}C NMR (150.8 MHz, $CDCl_3$): $\delta=135.7$ (2C), 99.3 ($2CH_2$), 21.9 (2C), 18.1 (2C), 15.9 (2C), 15.0 ($2CH_2$), 10.7 ($2CH_2$), 8.6 (3 CH_2). Its relative configuration was determined by X-ray crystal structure analysis.[10]

(3*R*,4*R*,5*R*,6*R*,7*R*,8*R*)-1,9-Dimethylenehexaspiro[2.0.0.0.0.0.2.1.1.1.1.1.1]pentadecane {1,9-dimethylene-(*P*)-(+)-[7]triangulane, (*P*)-24}: Column chromatography (20 g silica gel, 2.6×12 cm column, hexane, $R_f=0.47$) of the residue obtained from the dibromide (*P*)-**23** (0.877 g, 2.28 mmol) in DMSO (10 mL) and *t*BuOK (760 mg, 6.77 mmol) in DMSO (4 mL) according to GP 6 afforded (*P*)-**24** (80 mg, 16%) as a colorless oil, which crystallized upon standing at 0°C overnight. An analytical sample was prepared by recrystallization from MeOH. M.p. 62°C; $[\alpha]_D^{20}=+1302.1$, $[\alpha]_{578}^{20}=+1364.4$, $[\alpha]_{546}^{20}=+1570.2$, $[\alpha]_{436}^{20}=+2872.5$, $[\alpha]_{365}^{20}=+4989.7$ ($c=1.165$ in $CHCl_3$). Its NMR spectra were identical to those of its enantiomer (*M*)-**24**.

(3*R*,4*R*,5*S*,6*S*,7*R*,8*R*)-1,9-Dimethylenehexaspiro[2.0.0.0.0.0.2.1.1.1.1.1.1]pentadecane {1,9-dimethylene-*d*-(+)-[7]triangulane, *d*-24}: The pentane solution obtained from the dibromide *d*-**23** (300 mg, 0.78 mmol) in DMSO (2 mL) and *t*BuOK (260 mg, 2.32 mmol) in DMSO (2 mL) according to GP 6 was filtered through a 0.5 cm pad of silica gel and concentrated under reduced pressure to give *d*-**24** (125 mg, 72%) as a colorless oil. ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=135.9$ (2C), 99.2 ($2CH_2$), 24.2 (2C), 20.7 (2C), 16.4 (2C), 16.5 ($2CH_2$), 13.9 ($2CH_2$), 12.5 (CH_2), 11.2 ($2CH_2$).

(1*S*,3*R*,4*R*,5*R*,6*R*)-2-{(7-Methylenetetraspiro[2.0.0.0.2.1.1.1]undec-1-yl)-methoxy}tetrahydro-2*H*-pyran [(*P*)-28]: Column chromatography (300 g silica gel, 5×35 cm column, pentane/Et_2O 20:1, then 10:1) of the residue obtained from (*P*)-**27** (6.23 g, 17.6 mmol) in DMSO (50 mL) and *t*BuOK (2.930 g, 26.11 mmol) in DMSO (15 mL) according to GP 6 afforded (*P*)-**28** (3.38 g, 70%) as a colorless wax. $R_f=0.33$ (hexane/THF 15:1); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=125.4$ (C), 99.1 (CH_2), 98.29/98.25 (CH), 70.8/70.7 (CH_2), 62.1/61.9 (CH_2), 30.61/30.55 (CH_2), 25.4 (CH_2), 22.25/22.22 (C), 19.5/19.4 (CH_2), 18.24 (C), 18.18 (C), 18.1 (C), 17.7 (C), 15.7 (CH), 14.6 (CH_2), 11.6 (CH_2), 9.9 (CH_2), 9.6 (CH_2), 8.43/8.36 (CH_2). The product of nucleophilic substitution, (1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-2-{[7-[(1,1-dimethylethoxy)methyl]tetraspiro[2.0.0.0.2.1.1.1]undec-1-yl]methoxy}tetrahydro-2*H*-pyran (1.240 g, 20%) was also isolated as a colorless wax. ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=98.42/98.36$ (CH), 72.4 (C), 71.0 (CH_2), 65.3 (CH_2), 62.3/62.1 (CH_2), 30.71/30.64 (CH_2), 27.6 ($3CH_3$), 25.4 (CH_2), 19.6/19.5 (CH_2), 18.3 (C), 18.12 (C), 18.06 (C), 17.9 (C), 16.4 (CH), 15.7 (CH), 11.5 (CH_2), 9.9 (CH_2), 9.6 (CH_2), 8.6/8.5 (CH_2), 8.3 (CH_2).

(1*R*,3*S*,4*S*,5*S*,6*S*)-2-{(7-Methylenetetraspiro[2.0.0.0.2.1.1.1]undec-1-yl)methoxy}tetrahydro-2*H*-pyran [(*M*)-28]: Column chromatography (350 g silica gel, 7×25 cm column, hexane/THF 15:1, $R_f=0.33$) of the residue obtained from (*M*)-**27** (5.248 g, 14.86 mmol) in DMSO (80 mL) and *t*AmOK (2.439 g, 19.32 mmol) in DMSO (15 mL) according to GP 6 afforded (*M*)-**28** (3.21 g, 79%) as a colorless wax. Its ^{13}C NMR spectrum was identical to that of its enantiomer (*P*)-**28**.

(3*S*,4*S*,5*S*,6*S*)-1-Methylenepentaspiro[2.0.0.0.0.2.1.1.1.1]tridecane [(3*S*,4*S*,5*S*,6*S*)-36, (*M*)-36]: Column chromatography (120 g silica gel, 3.6×25 cm column, hexane, $R_f=0.49$) of the residue obtained from (*M*)-**35** (2.344 g, 8.84 mmol) in DMSO (30 mL) and *t*AmOK (1.523 g, 12.06 mmol) in DMSO (10 mL) according to GP 6 afforded (*M*)-**36** (1.059 g, 65%) as a colorless oil. $[\alpha]_D^{20}=-912.4$ ($c=1.184$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=5.31$ (m, 1H; =CH), 5.23 (td, $J=0.8$, 2.0 Hz, 1H; =CH), 1.57 (d, $J=3.8$ Hz, 1H, *c*Pr-H), 1.43 (d, $J=3.3$ Hz, 1H, *c*Pr-H), 1.43–1.34 (m, 2H; cPr-H), 1.24 (d, $J=4.0$ Hz, 1H, *c*Pr-H), 1.20–1.16 (m, 3H, cPr-H), 1.02 (d, $J=4.0$ Hz, 1H, *c*Pr-H), 0.98 (d, $J=4.0$ Hz, 1H, *c*Pr-H), 0.90–0.65 (m, 4H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=135.8$ (C), 99.1 (CH_2), 21.9 (C), 18.8 (C), 17.9 (C), 15.9 (C), 15.3 (CH_2), 13.6 (C), 11.2 (CH_2), 10.4 (CH_2), 9.9 (CH_2), 8.5 (CH_2), 4.8 (CH_2), 4.3 (CH_2).

Cyclopropanation of enantiomerically pure 1,*n*-dimethylene[*n*]triangulanes

General procedure GP 7: A solution of diazomethane [prepared from 3.00 g (29.1 mmol) of *N*-methyl-*N*-nitrosourea (NMU)] in diethyl ether (30 mL) was added dropwise at −5°C to a solution of the respective dimethylenetriangulane (0.3–1 mmol) and palladium acetate (35 mg) in diethyl ether (10 mL). The reaction mixture was filtered through a 3 cm pad of Celite and carefully concentrated at ambient pressure. The product was isolated by column chromatography on silica gel and then purified as indicated individually below.

(4*R*,5*R*,6*R*,7*R*)-Hexaspiro[2.0.0.0.0.0.2.1.1.1.1.1.1]pentadecane {(*P*)-(+)-[7]triangulane, (*P*)-17}: Column chromatography (20 g silica gel, 2.6×12 cm column, hexane, $R_f=0.60$) of the residue obtained from the diene (*P*)-**16** (168 mg, 0.987 mmol), diazomethane [prepared from 3.0 g (29.1 mmol) NMU] and $Pd(OAc)_2$ (35 mg, 156 μmol, 15.8 mol%) according to GP 7 afforded (*P*)-**17** (137 mg, 70%) as a colorless oil which crystallized upon standing at 0°C overnight and had m.p. 50–51°C. An analytical sample was prepared by recrystallization from MeCN. M.p. 52–53°C; $[\alpha]_D^{20}=+672.9$, $[\alpha]_{578}^{20}=+703.1$, $[\alpha]_{546}^{20}=+802.8$, $[\alpha]_{436}^{20}=+1404.5$, $[\alpha]_{365}^{20}=+2290.8$ ($c=0.814$ in $CHCl_3$); UV (cyclohexane): no absorbtion $\lambda > 200$ nm; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=1.21$ (d, $J=3.8$ Hz, 2H), 1.18 (d, $J=3.9$ Hz, 2H), 1.15 (d, $J=4.0$ Hz, 2H), 1.02 (s, 2H), 0.97 (d, $J=3.9$ Hz, 2H), 0.89–0.65 (m, 8H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=18.1$ (2C), 18.0 (2C), 13.6 (2C), 11.2 ($2CH_2$), 10.2 ($2CH_2$), 8.8 (CH_2), 4.8 ($2CH_2$), 4.3 ($2CH_2$). Its relative configuration was determined by X-ray crystal structure analysis.[10]

(3*S*,4*S*,5*S*,6*S*,7*S*,8*S*)-Octaspiro[2.0.0.0.0.0.0.0.2.1.1.1.1.1.1.1.1]nonadecane {(*M*)-(−)-[9]triangulane, (*M*)-25}: Column chromatography (20 g silica gel, 2.6×12 cm column, hexane, $R_f=0.58$) of the residue obtained from the diene (*M*)-**24** (90 mg, 0.405 mmol), diazomethane [prepared from 3.0 g (29.1 mmol) NMU] and $Pd(OAc)_2$ (20 mg, 89 μmol, 22 mol%) according to GP 7 afforded (*M*)-**25** (101 mg, 100%) as a colorless solid. An analytical sample was prepared by sublimation at 110°C (0.1 Torr) followed by recrystallization from EtOH. M.p. 85–87°C; $[\alpha]_D^{20}=-890.5$, $[\alpha]_{578}^{20}=-930.6$, $[\alpha]_{546}^{20}=-1058.0$, $[\alpha]_{436}^{20}=-1866.2$, $[\alpha]_{365}^{20}=-3051.1$ ($c=1.01$ in $CHCl_3$); UV (pentane and cyclohexane): no absorption $\lambda > 200$ nm; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.20$ (d, $J=3.8$ Hz, 2H), 1.17 (d, $J=3.8$ Hz, 2H), 1.13 (d, $J=3.8$ Hz, 2H), 1.11 (s, 2H), 1.08 (d, $J=3.7$ Hz, 2H), 1.06 (d, $J=3.7$ Hz, 2H), 0.97 (d, $J=3.8$, 2H), 0.86–0.83 (m, 2H), 0.79–0.74 (m, 4H), 0.70–0.67 (m, 2H); ^{13}C NMR (150.8 MHz, $CDCl_3$): $\delta=18.1$ (2C), 18.0 (2C), 17.4 (2C), 13.6 (2C), 11.2 ($2CH_2$), 10.3 ($2CH_2$), 9.2 (CH_2), 9.1 ($2CH_2$), 4.8 ($2CH_2$), 4.6 ($2CH_2$). Its relative configuration was determined by X-ray crystal structure analysis.[10]

(3*R*,4*R*,5*R*,6*R*,7*R*,8*R*)-Octaspiro[2.0.0.0.0.0.0.0.2.1.1.1.1.1.1.1.1]nonadecane {(*P*)-(+)-[9]triangulane, (*P*)-25}: Column chromatography (20 g silica gel, 2.6×12 cm column, hexane, $R_f=0.58$) of the residue obtained from the diene (*P*)-**24** (70 mg, 0.315 mmol), diazomethane [prepared from 3.0 g (29.1 mmol) NMU] and $Pd(OAc)_2$ (20 mg, 89 μmol, 28.3 mol%) according to GP 7 afforded (*P*)-**25** (73 mg, 93%) as a colorless solid. An analytical sample was prepared by sublimation at 110°C (0.1 Torr) followed by recrystallization from EtOH. M.p. 85–86°C; $[\alpha]_D^{20}=+909.9$, $[\alpha]_{578}^{20}=+951.2$, $[\alpha]_{546}^{20}=+1087.1$, $[\alpha]_{436}^{20}=+1907.0$, $[\alpha]_{365}^{20}=+3119.4$ ($c=0.96$ in $CHCl_3$). Its NMR spectra were identical to those of its enantiomer (*M*)-**25**.

(3*R*,4*R*,5*S*,6*S*,7*R*,8*R*)-Octaspiro[2.0.0.0.0.0.0.0.2.1.1.1.1.1.1.1.1]nonadecane {*d*-(+)-[9]triangulane, *d*-25}: Column chromatography (20 g silica gel, 2.6×12 cm column, hexane) of the residue obtained from the diene *d*-**24** (125 mg, 0.562 mmol), diazomethane [prepared from 1.50 g (14.55 mmol) NMU] and $Pd(OAc)_2$ (20 mg, 89 μmol, 16 mol%) according to GP 7 afforded *d*-**25** (73 mg, 52%) as a colorless oil. $[\alpha]_D^{20}=+244.9$, $[\alpha]_{578}^{20}=+255.3$, $[\alpha]_{546}^{20}=+292.3$, $[\alpha]_{436}^{20}=+511.2$, $[\alpha]_{365}^{20}=+832.0$ ($c=1.13$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=1.30$ (d, $J=3.7$ Hz, 2H), 1.28 (s, 2H), 1.23 (d, $J=3.9$ Hz, 2H), 1.17 (d, $J=3.7$ Hz, 2H), 1.13 (d, $J=4.3$ Hz, 2H), 1.09 (d, $J=3.9$ Hz, 2H), 1.02 (d, $J=3.8$ Hz, 2H), 0.99 (d, $J=3.7$, 2H), 0.95 (d, $J=3.7$ Hz, 2H), 0.90–0.83 (m, 4H); ^{13}C NMR (62.9 MHz,

$CDCl_3$): $\delta = 20.1$ (2C), 19.6 (2C), 18.4 (2C), 13.8 (2C), 14.2 ($2CH_2$), 12.7 (CH_2), 11.9 ($4CH_2$), 4.7 ($2CH_2$), 3.8 ($2CH_2$).

(1*R*,3*S*,4*S*,5*S*,6*S*)-2-{(Pentaspiro[2.0.0.0.0.2.1.1.1.1]tridec-1-yl)methoxy}tetrahydro-2*H*-pyran [(*M*)-33] and (pentaspiro[2.0.0.0.0.2.1.1.1.1]tridec-1-yl)methanol [(*M*)-34]: Column chromatography (350 g silica gel, 7 × 25 cm column, hexane/THF 15:1, $R_f = 0.33$) of the residue obtained from the methylene[5]triangulane (*M*)-**28** (3.210 g, 11.79 mmol), diazomethane [prepared from 18.22 g (176.8 mmol) NMU] and $Pd(OAc)_2$ (132 mg, 588 μmol, 5 mol %) according to GP 7 afforded (*M*)-**33** (2.913 g, 86 %) as a colorless oil. The latter was taken up with MeOH (50 mL) and deprotected by treatment of the solution with PPTS (100 mg, 0.4 mmol) according to GP 1b (65 °C, 1 h). Column chromatography (150 g silica gel, 3.6 × 35 cm column, hexane/THF 5:2, $R_f = 0.32$) furnished (*M*)-**34** (1.788 g, 87 %) as a colorless oil. $[\alpha]_D^{20} = -501.8$ ($c = 0.80$ in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.73$ (dd, $J = 6.5$, 11.0 Hz, 1H; CH_2O), 3.60 (dd, $J = 7.3$, 11.0 Hz, 1H; CH_2O), 1.44 (s, 1H; OH), 1.42–1.31 (m, 1H; *c*Pr-H), 1.20–1.09 (m, 4H; *c*Pr-H), 1.27 (d, $J = 4.3$ Hz, 1H; *c*Pr-H), 1.00 (d, $J = 4.3$ Hz, 1H; *c*Pr-H), 0.95 (d, $J = 3.0$ Hz, 1H; *c*Pr-H), 0.92 (d, $J = 3.0$ Hz, 1H; *c*Pr-H), 0.88–0.65 (m, 6H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta =$ 66.2 (CH_2), 18.6 (C), 18.4 (CH), 18.2 (C), 17.9 (C), 17.4 (C), 13.5 (C), 11.0 (CH_2), 10.1 (CH_2), 9.9 (CH_2), 9.0 (CH_2), 8.6 (CH_2), 4.7 (CH_2), 4.3 (CH_2).

Selective THP-monoprotection of enantiomerically pure [5]triangulane-1,7-dimethanols (*P*)-(+)-14 and (*M*)-(−)-14

General procedure GP 8: The respective diol **14** and DHP were stirred in a 20:1 toluene/DMF mixture in the presence of wet Dowex 50WX2-100 resin at ambient temperature for the indicated time. The resin was filtered off, and the solvent was removed under reduced pressure. The product was isolated by column chromatography on silica gel deactivated with triethylamine, a drop of which was also added to each collected fraction. Several crumbs of imidazole were added to the combined fractions of each product before evaporation. The product was used immediately without further purification, as it was found to disproportionate slowly giving a mixture of the starting material **14** and bisprotected diol even at +4 °C.

(1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-7-{[(Tetrahydro-2*H*-pyran-2-yl)oxymethyl]tetraspiro[2.0.0.0.2.1.1.1]undec-1-yl}methanol [(*P*)-26]: Column chromatography (180 g silica gel, 5 × 25 cm column, pentane/Et_2O 1:1, then Et_2O) of the residue obtained from (*P*)-**14** (290 mg, 1.406 mmol), DHP (463 mg, 0.5 mL, 5.50 mmol) and Dowex 50WX2-100 resin (210 mg) in toluene/DMF (6 mL + 0.3 mL) according to GP 8 (41 h) gave (*P*)-**26** (362 mg, 89 %) as a colorless wax. $R_f = 0.40$ (Et_2O); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 98.42/98.37$ (CH), 71.0 (CH_2), 66.2 (CH_2), 62.3/62.1 (CH_2), 30.7/30.6 (CH_2), 25.4 (CH_2), 19.6/19.5 (CH_2), 18.4 (CH), 18.3 (C), 18.2 (C), 18.12/18.05 (C), 17.97/17.90 (C), 15.7 (CH), 11.5 (CH_2), 9.9/9.6 (CH_2), 9.0 (CH_2), 8.6 (CH_2), 8.4 (CH_2); MS (CI): *m*/*z* (%): 308 (100) [$M^+ + NH_4$].

THP-bisprotected (1*S*,3*R*,4*R*,5*R*,6*R*,7*S*)-2-{7-[(tetrahydro-2*H*-pyran-2-yl)oxymethyl]tetraspiro[2.0.0.0.2.1.1.1]undec-1-yl]methoxy}tetrahydro-2*H*-pyran (60 mg, 11 %) was also isolated as a colorless wax. $R_f = 0.65$ (Et_2O); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 98.29/98.26$ (2CH), 70.9 ($2CH_2$), 62.1/61.9 ($2CH_2$), 30.63/30.56 ($2CH_2$), 25.4 ($2CH_2$), 19.5/19.4 ($2CH_2$), 18.21/18.05 (2C), 17.96/17.85 (2C), 15.6 (2CH), 11.4 (CH_2), 9.8/9.5 ($2CH_2$), 8.6/8.4 ($2CH_2$); MS (CI): *m*/*z* (%): 392 (100) [$M^+ + NH_4$].

In a repeated preparation, from (*P*)-**14** (5.0 g, 24.24 mmol), DHP (13.16 g, 8.62 mL, 156.4 mmol) and Dowex 50WX2-100 resin (3.621 g) in toluene/DMF (100 mL + 5 mL), (*P*)-**26** (5.555 g, 79 %) and starting material (*P*)-**14** (1.050 g, 21 %) were obtained according to GP 8 (11 h).

(1*R*,3*S*,4*S*,5*S*,6*S*,7*R*)-7-{[(Tetrahydro-2*H*-pyran-2-yl)oxymethyl]tetraspiro[2.0.0.0.2.1.1.1]undec-1-yl}methanol [(*M*)-26]: Column chromatography (500 g silica gel, 7 × 30 cm column, hexane/THF 2:1) of the residue obtained from (*M*)-**14** (5.44 g, 26.4 mmol), DHP (8.704 g, 9.40 mL, 103.5 mmol) and Dowex 50WX2-100 resin (3.942 g) in toluene/DMF (250 mL + 11 mL) according to GP 8 (16 h) gave (*M*)-**26** (6.987 g, 91 %) as a colorless wax, $R_f = 0.30$ (hexane/THF 2:1). Its ^{13}C NMR spectrum was identical to that of its enantiomer (*P*)-**26**.

Esterification of triangulanylmethanols with (*S*)-(+)-mandelic acid

General procedure GP 9: A solution of the respective triangulanylmethanol, (*S*)-mandelic acid and *p*-TsOH·H_2O in anhydrous benzene was stirred with heating under reflux attached to a Dean–Stark apparatus filled with molecular sieves 4 Å for the indicated time. After cooling, the reaction mixture was diluted with Et_2O (20 mL), washed with sat. aq. $NaHCO_3$ solution and brine (15 mL each), dried and concentrated under reduced pressure. The product was purified by column chromatography.

(1*S*,3*R*)-(4,4-Dibromospiro[2.2]pent-1-yl)methyl (*S*)-2-hydroxy-2-phenylacetate [(1′*S*,3′*R*,2*S*)-(+)-9]: Column chromatography (20 g silica gel, 2.6 × 12 cm column, hexane/Et_2O 3:2) of the residue obtained from (4,4-dibromospiropent-1-yl)methanol [(1*S*,3*R*)-**7**] (256 mg, 1.0 mmol), (*S*)-mandelic acid (304 mg, 2.0 mmol) and *p*-TsOH·H_2O (40 mg) in C_6H_6 (10 mL) according to GP 9 (6 h of heating) afforded (1′*S*,3′*R*,2*S*)-(+)-**9** (375 mg, 96 %) as a colorless solid. M.p. 61–63 °C (hexane/Et_2O); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.42$–7.32 (m, 5H; Ph-H), 5.17 (d, $J =$ 5.6 Hz, 1H; HCO), 4.37 (dd, $J = 5.8$, 11.5 Hz, 1H; CH_2O), 3.93 (dd, $J =$ 8.0, 11.5 Hz, 1H; CH_2O), 3.40 (d, $J = 5.6$ Hz, 1H; OH), 1.89–1.78 (m, 3H; *c*Pr-H), 1.42 (dd, $J = 5.4$, 8.8 Hz, 1H; *c*Pr-H), 1.17 (t, $J = 5.4$, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 173.4$ (C), 156.4 (C), 137.9 (CH), 128.4 (2CH), 126.5 (2CH), 72.7 (CH), 67.0 (CH_2), 31.6 (C), 27.7 (C), 26.8 (CH_2), 21.5 (CH), 15.7 (CH_2). Its relative configuration was confirmed by X-ray crystal structure analysis.[10]

(1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-(8,8-Dibromopentaspiro[2.0.0.0.0.2.1.1.1.1]tridec-1-yl)methyl (*S*)-2-hydroxy-2-phenylacetate (32): Column chromatography (25 g silica gel, 2.6 × 12 cm column, hexane/Et_2O 2:1, $R_f = 0.32$) of the residue obtained from (1*S*,3*R*,4*R*,5*R*,6*R*,7*R*)-**29** (140 mg, 0.39 mmol), (*S*)-mandelic acid (118 mg, 0.78 mmol) and *p*-TsOH·H_2O (10 mg) in C_6H_6 (10 mL) according to GP 9 (2.5 h of heating) afforded **32** (94 mg, 49 %) as a colorless solid. M.p. 51–53 °C (hexane/Et_2O); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.44$–7.25 (m, 5H; Ph-H), 5.18 (s 1H; HCO), 4.29 (dd, $J =$ 7.0, 11.3 Hz, 1H; CH_2O), 4.12 (dd, $J = 7.5$, 11.3 Hz, 1H; CH_2O), 3.08 (s, 1H; OH), 2.03 (d, $J = 6.5$ Hz, 1H; *c*Pr-H), 1.98 (d, $J = 6.5$ Hz, 1H; *c*Pr-H), 1.68 (d, $J = 4.3$ Hz, 1H; *c*Pr-H), 1.52 (d, $J = 4.8$ Hz, 1H; *c*Pr-H), 1.44 (d, $J = 4.8$ Hz, 1H; *c*Pr-H), 1.42–1.39 (m, 1H; *c*Pr-H), 1.25–1.17 (m, 2H; *c*Pr-H), 1.10 (d, $J = 4.3$ Hz, 1H; *c*Pr-H), 1.06 (d, $J = 4.8$ Hz, 1H; *c*Pr-H), 1.03 (d, $J = 4.8$ Hz, 1H; *c*Pr-H), 0.95 (d, $J = 4.3$ Hz, 1H; *c*Pr-H), 0.69 (t, $J = 3.4$, 1H; *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 173.7$ (C), 138.4 (C), 128.5 (2CH), 128.3 (CH), 126.4 (2CH), 72.8 (CH), 69.6 (CH_2), 30.4 (C), 28.9 (C), 27.6 (CH_2), 24.2 (C), 18.5 (C), 18.4 (C), 17.4 (C), 14.7 (CH), 14.5 (CH_2), 10.1 (CH_2), 9.5 (CH_2), 8.7 (CH_2), 7.8 (CH_2). Its relative configuration was confirmed by X-ray crystal structure analysis.[10]

(1*R*,3*S*,4*S*,5*S*,6*S*,7*S*,8*S*,9*R*)-Hexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadecane-1,9-dicarboxylic acid {(*M*)-(−)-[7]triangulane-1,9-dicarboxylic acid, (*M*)-40}: This dicarboxylic acid was prepared adopting a published Jones oxidation protocol.[52] An 8 M solution of chromium trioxide in 5 M aq. sulfuric acid (1.0 mL) was added dropwise at 0 °C to a solution of [7]triangulanedimethanol (*M*)-**22** (168 mg, 0.65 mmol) in acetone (30 mL). The reaction mixture was stirred at this temperature for 2 h and at ambient temperature for 15 min, the reaction was quenched with isopropanol (1.0 mL), and the mixture poured into a 1:1 THF/brine mixture (50 mL). The aqueous layer was extracted with THF (3 × 20 mL), and, after evaporation of the combined organic extracts under reduced pressure, the residue was taken up with 1 N aq. NaOH solution (10 mL) and washed with THF (2 × 10 mL). The aqueous solution was acidified by addition of 1 N aq. HCl solution (13 mL) and extracted with THF (3 × 20 mL). The combined organic extracts were dried and evaporated under reduced pressure. Recrystallization of the residue from hexane/THF afforded (*M*)-**40** (137 mg, 74 %) as a colorless solid. M.p. 257–259 °C (decomp.); $[\alpha]_D^{20} = -743.7$ ($c = 0.941$ in THF); ^{1}H NMR (600 MHz, [D_8]THF): $\delta = 9.28$ (br s, 2H; 2OH), 1.80 (dd, $J = 4.0$, 7.5 Hz, 2H; 2CH), 1.39 (t, $J = 4.0$ Hz, 2H), 1.31 (d, $J = 4.5$ Hz, 2H), 1.29–1.27 (m, 4H), 1.22 (d, $J = 4.5$ Hz, 2H), 1.09 (s, 2H), 1.07 (d, $J = 4.0$ Hz, 2H); ^{13}C NMR (150.8 MHz, [D_8]THF): $\delta =$ 174.3 (2C), 23.6 (2CH), 19.5 (2C), 19.4 (2C), 19.2 (2C), 13.3 ($4CH_2$), 10.9 ($2CH_2$), 9.6 (CH_2). Its relative configuration was determined by X-ray crystal structure analysis.[10]

(1*R*,3*S*,4*S*,5*S*,6*S*,7*S*,8*S*,9*R*)-1,9-Bis(*n*-propyloxymethyl)hexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadecane {(*M*)-(−)-bis(*n*-propyloxymethyl)[7]triangulane, (*M*)-41} and (1*R*,3*S*,4*S*,5*S*,6*S*,7*S*,8*S*,9*R*)-9-(*n*-propyloxymethyl)hexaspiro[2.0.0.0.0.0.2.1.1.1.1.1]pentadecane-1-methanol {(*M*)-(−)-9-(*n*-propyloxymethyl)[7]triangulane-1-methanol, (*M*)-42}: The compounds were

prepared adopting a published protocol.[53] Sodium hydride (46.3 mg.1.93 mmol, 10 equiv, prepared from a 60% suspension in mineral oil by washing with anhydrous pentane) was added to the stirred solution of [7]triangulanedimethanol (*M*)-**22** (50 mg, 0.193 mmol) in anhydrous DMF (10 mL). After stirring at ambient temperature for an additional 30 min, *n*-propyl iodide (656 mg, 376 μL, 3.86 mmol, 20 equiv) was added, and the resulting suspension was stirred at the same temperature overnight. The resulting clear solution was poured into ice-cold water (30 mL) and extracted with Et_2O (3×20 mL). The combined organic extracts were washed with H_2O (4×10 mL), brine (15 mL), dried and evaporated under reduced pressure. Column chromatography of the residue (20 g silica gel, 2×15 cm column) furnished diether (*M*)-**41** (45 mg, 68%, R_f=0.68) and monoether (*M*)-**42** (9 mg, 15.5%) as colorless oils.

Compound (*M*)-**41**: ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.49 (dd, J=6.3, 10.3 Hz, 2H; CH_2O), 3.41–3.34 (m, 6H; $3CH_2O$), 1.59 (sext, J=7.3 Hz, 4H; $2CH_2$), 1.39–1.29 (m, 2H; *c*Pr-H), 1.20 (d, J=3.9 Hz, 2H; *c*Pr-H), 1.13 (d, J=3.6 Hz, 2H; *c*Pr-H), 1.07 (d, J=3.6 Hz, 2H; *c*Pr-H), 1.06–1.02 (m, 2H; *c*Pr-H), 1.01 (s, 2H; *c*Pr-H), 0.97 (d, J=3.9 Hz, 2H; *c*Pr-H), 0.91 (t, J=7.3 Hz, 6H; $2CH_3$), 0.64 (t, J=4.4 Hz, 2H, *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=74.1 ($2CH_2$), 72.3 ($2CH_2$), 22.9 ($2CH_2$), 18.2 (2C), 18.0 (2C), 17.5 (2C), 15.8 (2CH), 10.6 ($2CH_3$), 10.3 ($2CH_2$), 9.7 ($2CH_2$), 8.9 (CH_2), 8.8 ($2CH_2$).

Compound (*M*)-**42**: ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.72 (dd, J=6.3, 10.9 Hz, 1H; CH_2O), 3.59 (dd, J=6.9, 10.9 Hz, 1H; CH_2O), 3.51 (dd, J=6.5, 10.3 Hz, 1H; CH_2O), 3.40 (t, J=6.7 Hz, 2H; CH_2O), 3.38 (dd, J=6.8, 10.3 Hz, 1H; CH_2O), 1.58 (sext, J=6.7 Hz, 4H; $2CH_2$), 1.42–1.31 (m, 2H; *c*Pr-H), 1.25 (br s, 1H; OH), 1.21 (d, J=3.8 Hz, 1H; *c*Pr-H), 1.18 (d, J=3.9 Hz, 1H; *c*Pr-H), 1.13 (d, J=4.6 Hz, 1H; *c*Pr-H), 1.09 (d, J=3.6 Hz, 1H; *c*Pr-H), 1.05–0.97 (m, 2H; *c*Pr-H), 1.03 (s, 2H; *c*Pr-H), 0.92 (t, J=6.7 Hz, 3H; CH_3), 0.91–0.84 (m, 1H; *c*Pr-H), 0.67 (t, J=3.6 Hz, 1H, *c*Pr-H), 0.65 (t, J=3.7 Hz, 2H, *c*Pr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=74.1 (CH_2), 72.3 (CH_2), 66.4 (CH_2), 23.0 (CH_2), 18.5 (CH), 18.21 (C), 18.17 (C), 18.1 (C), 18.0 (C), 17.6 (C), 17.4 (C), 15.8 (CH), 10.6 (CH_3), 10.4 ($2CH_2$), 9.7 (CH_2), 9.1 (CH_2), 8.85 (CH_2), 8.81 (CH_2),8.7 (CH_2).

Computational studies: Geometries were optimized by density functional theory (DFT) computations employing Becke's three-parameter functional with the Lee–Yang–Parr correlation functional (B3LYP)[27–30] utilizing the 6-31+G(d) basis set[30,55] as implemented in Gaussian 98.[26] All optimized structures were characterized as minima by computing analytical second energy derivatives.[57] The optical rotations ORs were computed by the sum-over-states method from the circular dichroism data:

$$\beta = \frac{c}{3\pi h} \mathrm{Im} \sum_{n\neq 0} \frac{\langle 0|\mu|n\rangle\langle n|\mathbf{m}|0\rangle}{\omega_{n_0}^2 - \omega^2}$$

where μ and **m** are the electric dipole and magnetic dipole operators, respectively; the summation runs over all excitations, and β is the trace of the frequency-dependent electric-dipole magnetic-dipole polarizability tensor.[58]

Only the single excitations of the valence electrons were computed at the time-dependent (TD) DFT level of theory using the B3LYP functional at the respective optimized geometries with the 6-31+G(d,p) basis set[30,56] as implemented in Gaussian 03. The thus obtained ORs apply to the gas phase while the experimental ORs are measured in solution. In general, computations of the gas phase overshoot the values for solvated molecules[59] due to interactions with the solvent, sometimes considerably so. Currently the solvent cannot be taken into account explicitly, but for non-interacting or weakly interacting solvents (i.e., van der Waals and small dipole interactions only) the gas phase computations are a decent approximation.

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[4] Adopting the [4]triangulanes to possess an axis of chirality that bisects the two central cyclopropane rings and considering the two other spiroannelated cyclopropane rings as substituents, (*M*)-**3** according to the IUPAC rules may also be termed (*R*)-**3**, and (*P*)-**3** would be (*S*)-**3**. See: *IUPAC Tentative Rules for the Nomenclature in Organic Chemistry. Section E. Fundamental Stereochemistry*, *J. Org. Chem.* **1970**, *35*, 2849–2867.

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[6] The stereochemical features of unbranched [*n*]triangulanes **1** have been thoroughly analyzed, e.g. the families of [7]- and [9]triangulanes consists of 4 and 16 pairs of enantiomers, respectively, plus 2 and 4 *meso*-diastereomers, respectively. Compare N. S. Zefirov, S. I. Kozhushkov, T. S. Kuznetsova, O. V. Kokoreva, K. A. Lukin, B. I. Ugrak, S. S. Tratch, *J. Am. Chem. Soc.* **1990**, *112*, 7702–7707.

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[11] After several unsuccessful attempts of either acylate the alcohol *rac*-**7** or deacylate the acetate *rac*-**8** catalyzed by lipases PS, 300, AK (*Pseudomonas* sp, from Amano Pharmaceutical Co., Ltd) as well as lipases EC3.1.1.3 (*Procine pancreas*) and CES, the latter was found to be the only appropriate one for this deracemization.

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[17] For reasons unknown, this cyclopropanation on a 7 mmol scale ceased after about 50% conversion irrespective of the quantity of diazomethane and CuCl applied. The product and the starting material had to be isolated as a mixture and together subjected to repeated cyclopropanations until the starting bicyclopropylidene had disappeared, as (*P*)-(+)-**14** is very well separable from *d*-(+)-**11**, but not from the starting material. These required repeated cyclopropanations followed by recrystallization from hexane/Et_2O/CH_2Cl_2 decreased the yield significantly. However, the yield can be improved by scaling the reaction down or (in this particular case) applying Cu^{II} triflate as a co-catalyst, see Experimental Section.

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