mixture was stirred at -78 °C for 15 min. A solution of the arenesulfonyl fluoride (0.57 mmol, *p*-toluenesulfonyl fluoride unless otherwise noted) in anhydrous THF (2 mL) was then added slowly. The mixture was allowed to warm to rt and stirred for the given period of time. Normal workup was followed.

General procedure E was followed for the following reactions.

Methyl *p*-Tolyl Sulfone (3a, Table I, Entry 35). Reaction time: 18 h. Sulfone **3a** was obtained in 86% yield.

***n*-Butyl *p*-Tolyl Sulfone (3b, Table I, Entry 36).** Reaction time: 18 h. Sulfone **3b** was obtained in 88% yield.

***sec*-Butyl *p*-Tolyl Sulfone (3d, Table I, Entry 37).** Reaction time: 36 h. Sulfone **3d** was obtained in 34% yield.

***tert*-Butyl *p*-Tolyl Sulfone (3e, Table I, Entry 38).** Reaction time: 18 h. Sulfone **3e** was obtained in 17% yield.

Phenyl *p*-Tolyl Sulfone (3f, Table I, Entry 39). Reaction time: 24 h. Sulfone **3f** was obtained in 94% yield.

Preparation of 2-Pentyl *p*-Tolyl Sulfone (5) via Treatment of *p*-Toluenesulfonyl Fluoride (1a) with *n*-BuLi (2 equiv) Followed by Methyl Iodide. *n*-Butyllithium (0.60 mL, 1.21 mmol) was added dropwise over 5 min to a rapidly stirred solution of *p*-toluenesulfonyl fluoride **1a** (0.10 g, 0.57 mmol) in anhydrous THF (10 mL) at -78 °C. The solution was stirred at -78 °C for 20 min and then alkylated with a solution of MeI (0.20 mL, 2.87 mmol) and HMPA (0.20 mL, 1.15 mmol) in anhydrous THF and stirred for 30 min. The normal workup was followed giving sulfone **5** (0.109 g, 84%) as a pale yellow oil: IR ($CHCl_3$, lit.[25]) 1289, 1136 cm^{-1}.

Preparation of 2-(2-Methylpentyl) *p*-Sulfone (6) via Treatment of *p*-Toluenesulfonyl Fluoride (1a) with *n*-BuLi (3 equiv) Followed by Methyl Iodide. *n*-Butyllithium (0.80 mL, 1.72 mmol) was added dropwise over 5 min to a rapidly stirred solution of *p*-toluenesulfonyl fluoride **1a** (0.10 g, 0.57 mmol) in anhydrous THF (10 mL) at -78 °C. The solution was stirred at -78 °C for 20 min and then alkylated with a solution of MeI (0.20 mL, 2.87 mmol) and HMPA (0.20 mL, 1.15 mmol) in anhydrous THF and stirred for 30 min. The normal workup was followed giving sulfone **6** (0.115 g, 89%) as a pale yellow oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.81 (d, 2 H, J = 8.2 Hz), 7.41 (d, 2 H, J = 8.2 Hz), 2.51 (s, 3 H), 1.70-1.68 (m, 2 H), 1.37-1.02 (m, 2 H), 1.34 (s, 6 H), 0.98 (t, 3 H, J = 7.3 Hz).

[(*p*-Tolylsulfonyl)methylene]cyclohexane (7) via Treatment of *p*-Toluenesulfonyl Fluoride (1a) and (Trimethylsilyl)methyllithium Followed by Cyclohexanone. (Trimethylsilyl)methyllithium (1.6 mL, 1.14 mmol) was added dropwise over 5 min to a rapidly stirred solution of *p*-toluenesulfonyl fluoride (**1a**) (0.1 g, 0.57 mmol) in anhydrous THF (10 mL) at -78 °C and stirred for 2 h. Distilled cyclohexanone (0.06 mL, 0.63 mmol) was added dropwise over 5 min at -78 °C, and the reaction was allowed to warm to rt over 2 h. The normal workup was followed giving sulfone **7** (0.0844 g, 54%) as an oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.74 (d, 2 H, J = 8.0 Hz), 7.28 (d, 2 H, J = 8.0 Hz), 6.11 (s, 1 H), 2.71 (br s, 2 H), 2.39 (s, 3 H), 2.10 (br s, 2 H), 1.53 (br s, 6 H).

Registry No. **2a**, 15310-28-8; **2b**, 94265-66-4; **2k**, 72834-71-0; **3a**, 3185-99-7; **3b**, 7569-36-0; **3c**, 136828-00-7; **3d**, 91968-80-8; **3e**, 5324-90-3; **3f**, 640-57-3; **3g**, 127-63-9; **3h**, 42756-18-3; **3i**, 13894-21-8; **3j**, 67963-06-8; **3k**, 91358-89-3; **3l**, 3112-87-6; **3m**, 5535-52-4; **5**, 29182-78-3; **6**, 136828-01-8; **7**, 136828-02-9; 1 (Ar = *p*-Tol), 455-16-3; 1 (Ar = Ph), 368-43-4; MeLi, 917-54-4; *n*-BuLi, 109-72-8; $TMSCH_2Li$, 1822-00-0; *s*-BuLi, 598-30-1; *t*-BuLi, 594-19-4; PhLi, 591-51-5; Ph_3CLi, 733-90-4; TMSC≡CLi, 54655-07-1; MeMgCl, 676-58-4; *n*-BuMgCl, 693-04-9; PhMgBr, 100-58-3; HC≡CMgBr, 4301-14-8; cyclo-$C_6H_{11}MgCl$, 931-51-1; *i*-BuMgCl, 5674-02-2; allylMgCl, 2622-05-1; vinylMgBr, 1826-67-1; Me_2CuLi, 15681-48-8; *n*-Bu_2CuLi, 24406-16-4; $(TMSCH_2)_2CuLi$, 40988-97-4; *s*-Bu_2CuLi, 23402-73-5; *t*-Bu_2CuLi, 23402-75-7; Ph_2CuLi, 23402-69-9; *n*-BuCuSPhLi, 53128-68-0; $Me_2CuMgCl$, 67234-12-2; *n*-$Bu_2CuMgCl$, 60101-92-0; $Ph_2CuMgBr$, 58938-91-3; $(cyclo\text{-}C_6H_{11})_2CuMgCl$, 62280-27-7; *i*-$Bu_2CuMgCl$, 136828-04-1; $(allyl)_2CuMgCl$, 91550-88-8; *n*-BuPhSCuMgCl, 90384-66-0; MeCu, 1184-53-8; *n*-BuCu, 34948-25-9; *s*-BuCu, 89828-30-8; *t*-BuCu, 56583-96-1; PhCu, 3220-49-3; allylCu, 37974-18-8; *n*-BuCuP(*n*-Bu)$_3$, 26679-41-4; copper(I) iodide, 7681-65-4; cyclohexanone, 108-94-1.

Supplementary Material Available: Elemental analysis results and spectral data on compounds **2a,b**, **2k**, **3a-g**, **3i,j**, **3l**, and **5-7** (3 pages). Ordering information is given on any current masthead page.

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Branched Triangulanes: General Strategy of Synthesis

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A general synthetic strategy for the construction of *branched triangulanes* (BTs) (spirocondensed polycyclopropanes) has been elaborated. The synthetic utility of the method is illustrated by the synthesis of some members of the [5]- and [6]BT families, especially **13a,b** and **14**. An independent synthesis of the perspirocyclopropanated spiropentane **14** is also presented.

The so-called *triangulanes*, hydrocarbons consisting exclusively of spiro-attached three-membered rings,[1] have interesting stereochemical implications, as elaborated for their simplest subclass, that of *unbranched* triangulanes (UTs) **1**.[1-3] UTs can be prepared by the addition of chloromethylcarbene to methylenecyclopropanes,[2,4-6] subsequent dehydrochlorination with potassium *tert*-butoxide in DMSO,[2,4,6-8] and final cyclopropanation of the

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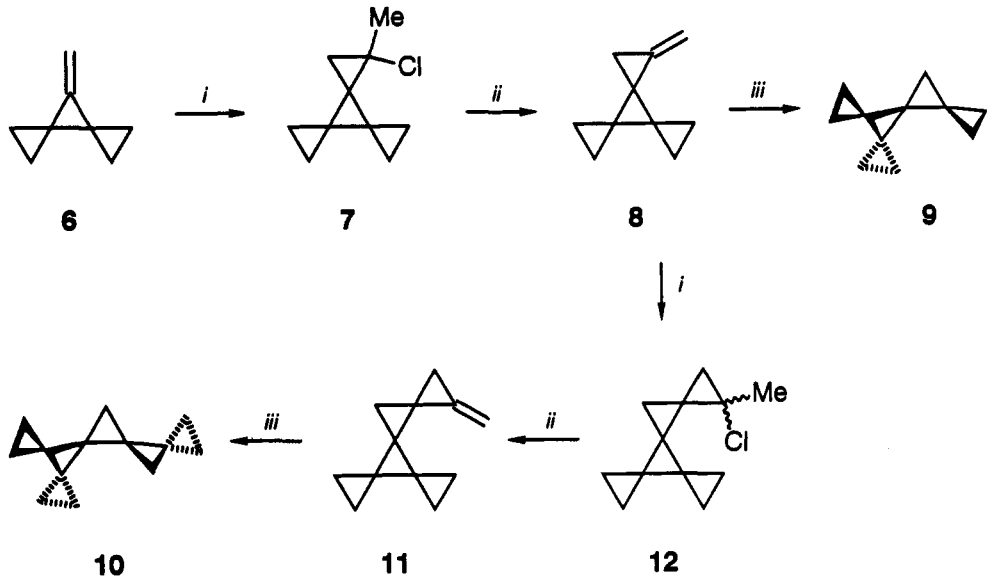
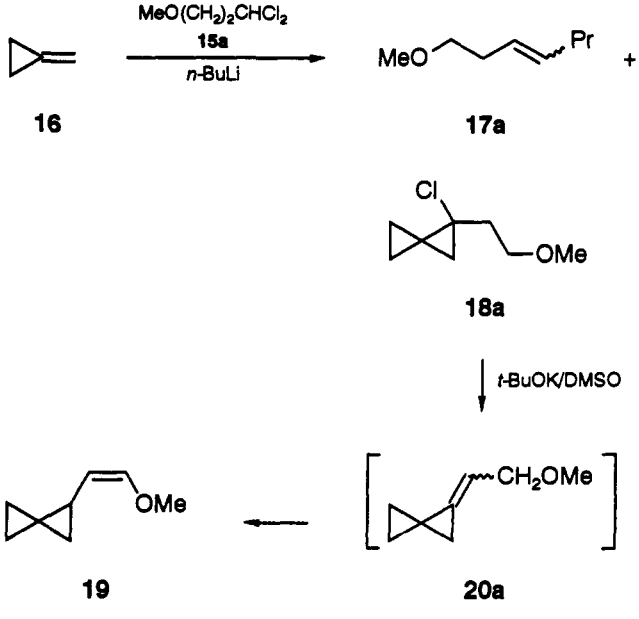
0022-3263/92/1957-0701$03.00/0

Scheme I[a]

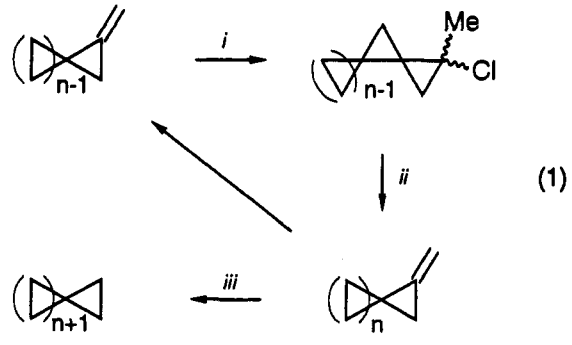


[a] (i) CH_3CHCl_2/BuLi, (ii) *t*-BuOK/DMSO, (iii) CH_2N_2/$Pd(OAc)_2$.

Scheme II

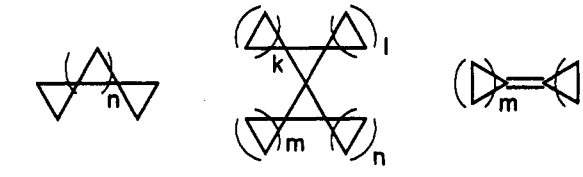


resulting methylenetriangulane with diazomethane in the presence of palladium(II) acetate[2,9,10] (eq 1).



(i) CH_3CHCl_2/BuLi, (ii) *t*-BuOK/DMSO, (iii) CH_2N_2/$Pd(OAc)_2$

This sequence may also be applied to the synthesis of *branched triangulanes* (BTs) **2**, provided that alkenes of type **3** are available. Starting from bicyclopropylidene **5**,[11] the simplest BT–[3]rotane **4**[12]–was prepared in this manner.[2,5] More recently, this approach has been applied to the synthesis of triangulane **9**, a member of the [5]BT family, and hydrocarbon **10**, a member of the [6]BT family,



1 **2** **3**

4 **5**

starting from methylene[4]UT **6**[2,5] (Scheme I). The structures of triangulanes **9** and **10** and methylenetriangulanes **8** and **11** were confirmed by their spectral characteristics as outlined in the Experimental Section.

In this paper a general strategy is proposed for the preparation of BTs based upon the addition of substituted chloroethylcarbenes to methylenecyclopropanes as de-

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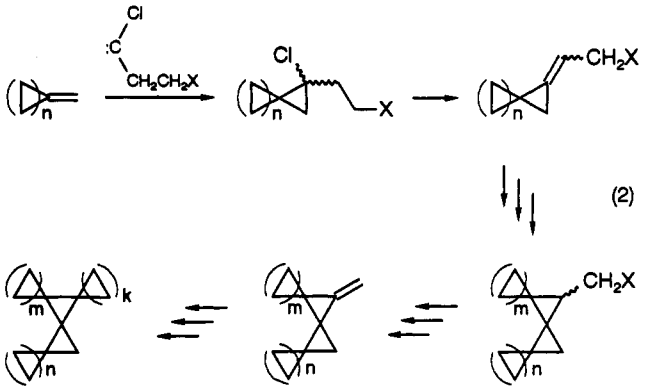
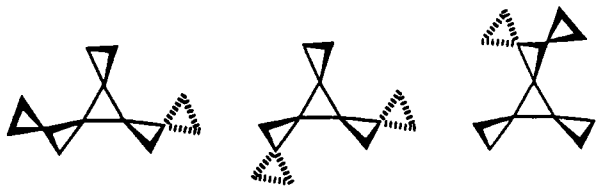
picted in eq 2. The synthetic potential of this approach



is demonstrated by the preparation of some members of the [5]- and [6]BT families, namely, hydrocarbons **13a,b** and **14**.



13a **13b** **14**

Results and Discussion

1,1-Dichloro-3-R-oxypropanes **15a,b** (R = Me, tetrahydropyran-2-yl) have been prepared from known precursors by standard methods (see Experimental Section) and examined as potential carbenoid precursors for the [1 + 2] cycloaddition to methylenecyclopropanes. In fact the carbenoid generated by the action of sodium bis(trimethylsilyl)amide[4] on **15a** adds to the double bond of methylenecyclopropane (**16**) to give the desired spiropentane derivative **18a** in good yield, whereas *n*-BuLi reacts with the carbenoid[13] to give **17a** (Scheme II). Dehydrochlorination of chloride **18a** with potassium *tert*-butoxide in DMSO at 60 °C was accompanied by allylic rearrangement[14] to afford enol ether **19**; but at ambient temperature within 15 h a *Z*/*E* mixture of olefin **20a** is obtained.

Schemes III and IV illustrate the application of this strategy to the synthesis of the novel branched triangulanes **13a,b** and **14**. Note that the method is successful only when R in the carbenoid precursor and its products **18–25** is a THP (tetrahydropyranyl) group. When R is a methyl group, efforts to remove the protecting group in compound **25a** with $FeCl_3/Ac_2O$,[15] $POCl_3/DMF$[16] (20 °C, 24 h), and Me_3SiCl/NaI[17] (20 °C) were unsuccessful; with pure Me_3SiI[18] (−30 °C) a 5.8% total yield of olefins **28a,b** was isolated by column chromatography on silica gel after dehydroiodination of the resulting mixture of iodides with *t*-BuOK/DMSO. Chlorination of alcohol **26** (CCl_4/PPh_3, 20 °C, 96 h[19]) was incomplete (~10%), but bromination with subsequent dehydrobromination gave the desired olefins **28a,b** (2.2:1 mixture of *anti* and *syn* isomers), which partially decomposed upon distillation.

Cyclopropanation of this substance afforded a mixture of hydrocarbons **13a,b** in a ratio of 1.4:1. The stereoisomers **13a,b** were identified on the basis of their ^{13}C NMR spectra, taking into consideration the total symmetry of the molecules. Triangulane **13a** has a C_2 axis, and the isomer **13b** possesses a symmetry plane. Thus, carbon atoms C^{11} and C^{12} are to be equivalent in the ^{13}C NMR spectrum of the anti isomer **13a** and nonequivalent in that of the syn isomer **13b**. Based on the fact that compound **13a** was produced from olefin **28a** (**13b** from **28b**) and that the major isomer in the mixture was **13a**, spectral assignments for the mixture of *anti*- and *syn*-methylenetriangulanes **28a,b** were made. The consideration of the molecular symmetry (C_2 axis in **28a** and symmetry plane in **28b**) leads to the same spectroscopic results in this case.

This same methodology was used for the synthesis of the branched triangulane **14** starting from bicyclopropylidene **5**[12] (Scheme IV). All compounds depicted in Scheme IV were obtained in satisfactory yields. As in the previous sequence the methyl group in ether **33a** could not be removed without destruction of the skeleton, but the acetal **33b** could smoothly be converted to alcohol **34**.

The highly symmetrical (symmetry point group D_{2d}) triangulane **14** shows only three signals in its ^{13}C NMR spectrum and a few signals in the ^1H NMR spectrum.

The [6]BT **14**, a fully spirocyclopropanated spiropentane, was independently synthesized by reaction of in situ generated diazocyclopropane[20] with the known bi-

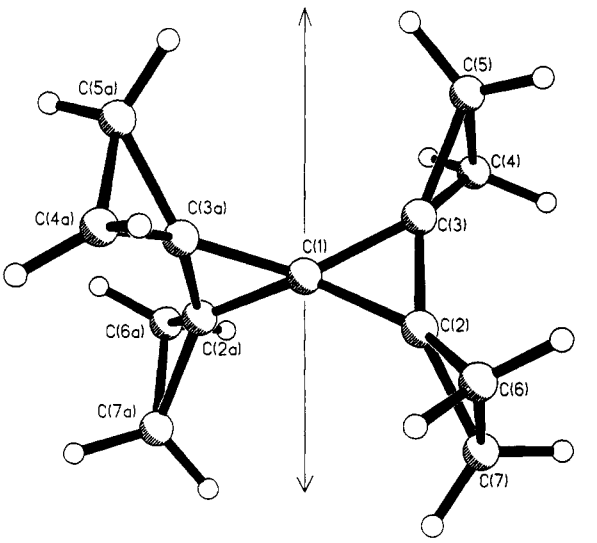


Figure 1. General view of the molecule **14**.

Table I. Bond Lengths (Å) in Structure 14

C(1)–C(2)	1.481 (2)	C(2)–C(6)	1.486 (3)	C(3)–C(5)	1.484 (3)
C(1)–C(3)	1.480 (2)	C(2)–C(7)	1.482 (3)	C(4)–C(5)	1.532 (3)
C(2)–C(3)	1.477 (3)	C(3)–C(4)	1.480 (3)	C(6)–C(7)	1.532 (3)

Table II. Bond Lengths (Å) in Structure 32 (Mean Values for Four Independent Molecules)

O(1)–C(12)	1.431 (4)	C(2)–C(6)	1.485 (6)	C(8)–C(9)	1.506 (6)
C(1)–C(2)	1.482 (5)	C(2)–C(7)	1.481 (6)	C(8)–C(12)	1.512 (6)
C(1)–C(3)	1.478 (5)	C(3)–C(4)	1.485 (6)	C(9)–C(10)	1.487 (6)
C(1)–C(8)	1.515 (5)	C(3)–C(5)	1.483 (6)	C(9)–C(11)	1.491 (6)
C(1)–C(9)	1.465 (5)	C(4)–C(5)	1.542 (6)	C(10)–C(11)	1.540 (6)
C(2)–C(3)	1.476 (5)	C(6)–C(7)	1.541 (6)		

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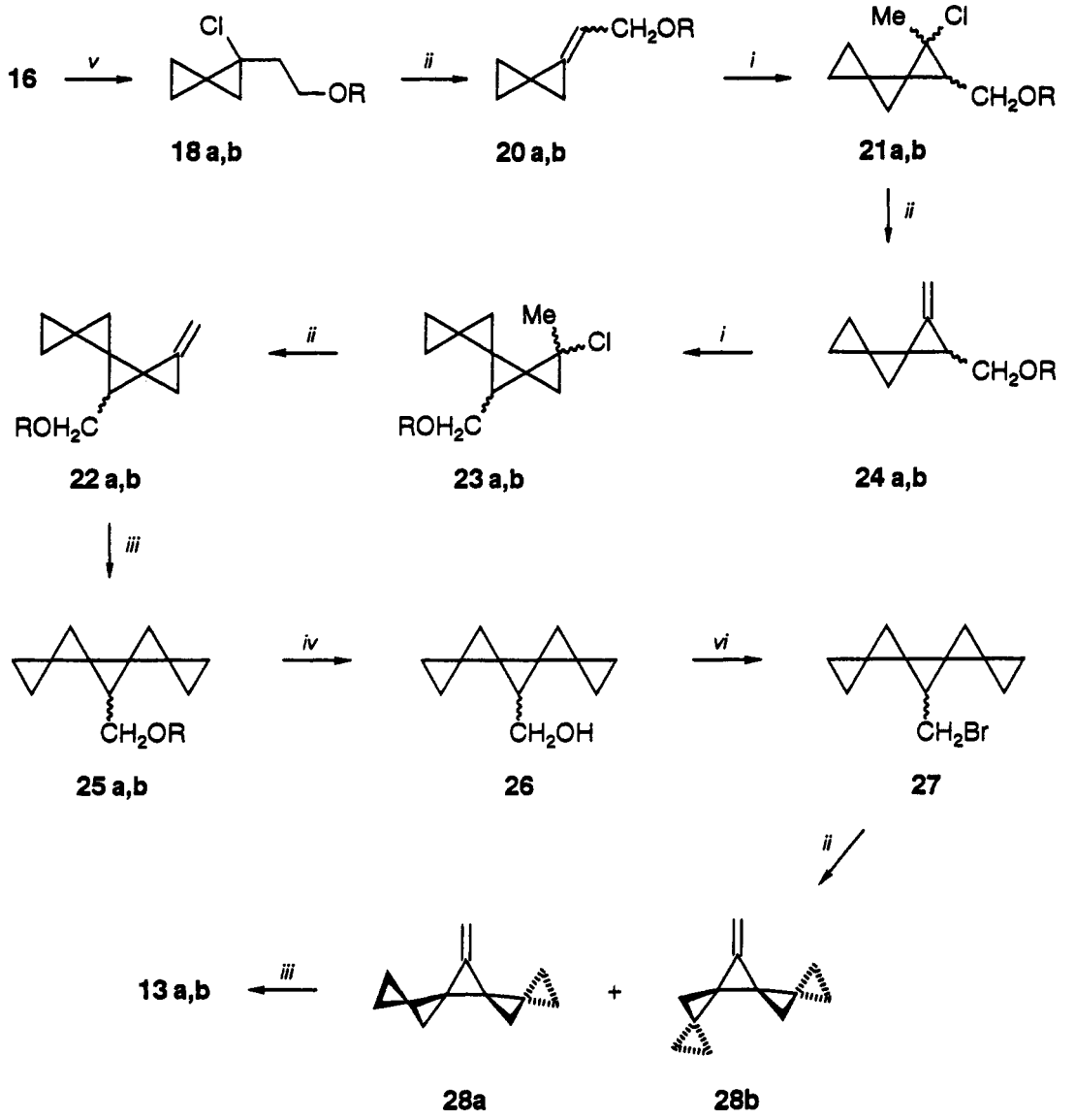
(20) Cf. (a) Fitjer, L.; Conia, J.-M. *Angew. Chem.* **1973**, *85*, 349; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 334. (b) Kirmse, W.; Schütte, H. *Chem. Ber.* **1968**, *101*, 1674.

Scheme III[a,b]



[a] (a) R = Me; (b) R = $-\overline{CH(CH_2)_4O}$. [b] (i) CH_3CHCl_2/BuLi, (ii) *t*-BuOK/DMSO, (iii) $CH_2N_2/Pd(OAc)_2$, (iv) HCl, (v) $RO(CH_2)_2CHCl_2$ (**15a,b**)/$NaN(SiMe_3)_2$, (vi) Ph_3PBr_2/Py.

cyclopropylidene derivative **37**[21] (Scheme V). Except for unreacted starting material (51%), **14** was isolated as the sole product (23% yield). The same approach has been used to prepare the [8]BT heptaspiro-[2.0.0.2.0.2.0.0.0.2.0.2.0.0]heptadecane (**41**) along with 11-cyclopropylidenetetraspiro[2.0.0.2.0.2.0.1]undecane (**40**) and bi(trispiro[2.0.2.1]heptylidene) (**39**).[22]

The molecular geometries of compounds **14** and **32** were confirmed by X-ray crystal structure analyses (Figures 1 and 2). The most interesting features of these molecules are the lengthening of distal bonds opposite the four external spiro carbon atoms of the central spiropentane unit and the shortening of bonds involving these atoms (Tables I and II). This difference in bond distances is the same as observed for spiropentane[23] and [3]rotane[24] and in agreement with ab initio calculations at the STO-3G level.[25]

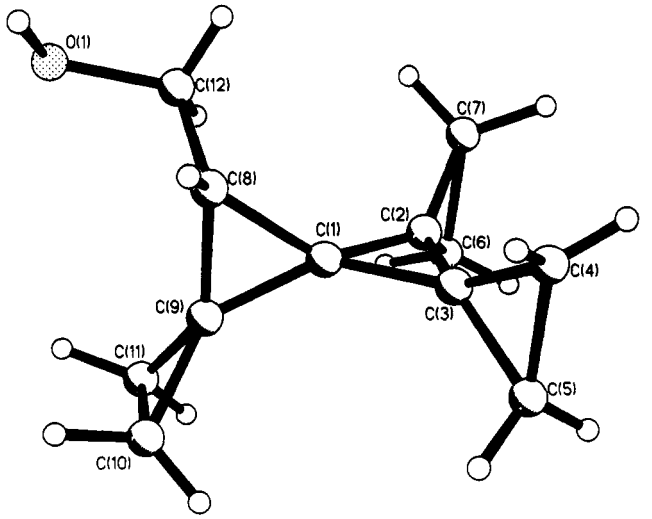


Figure 2. General view of one independent molecule **34**.

The lengthening of the distal bonds is apparently due to increased angular strain at the spiro carbons and the

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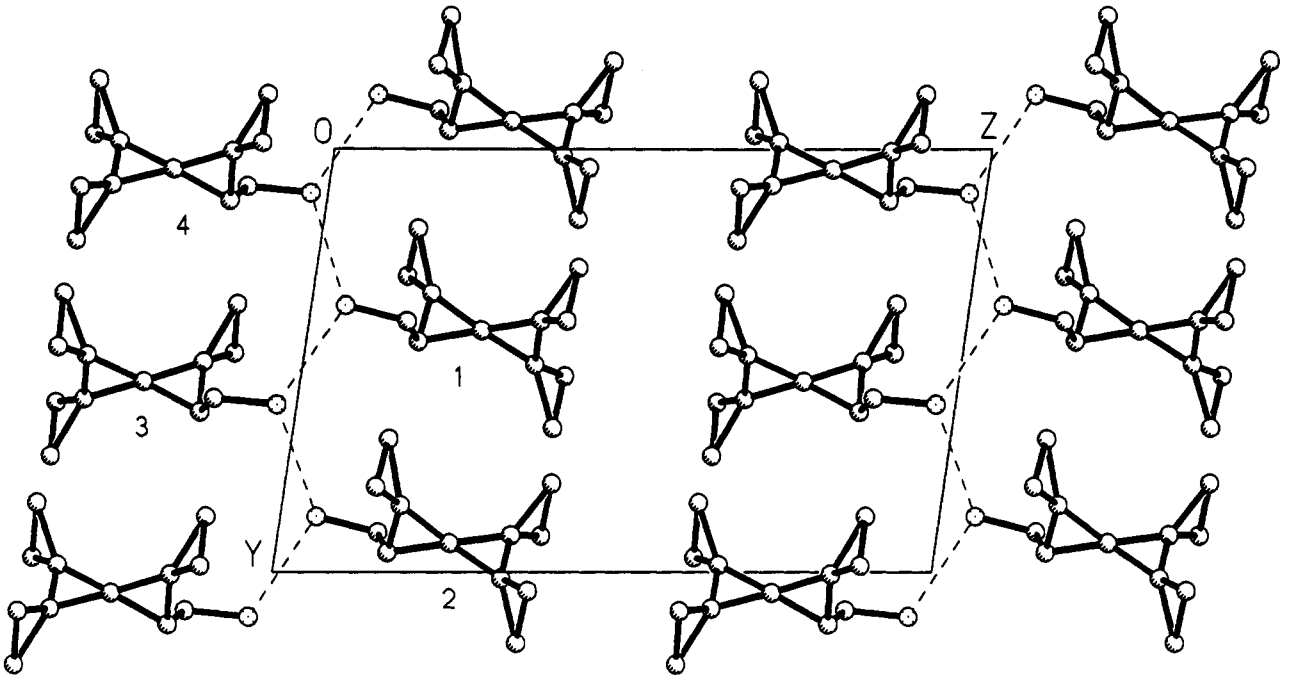
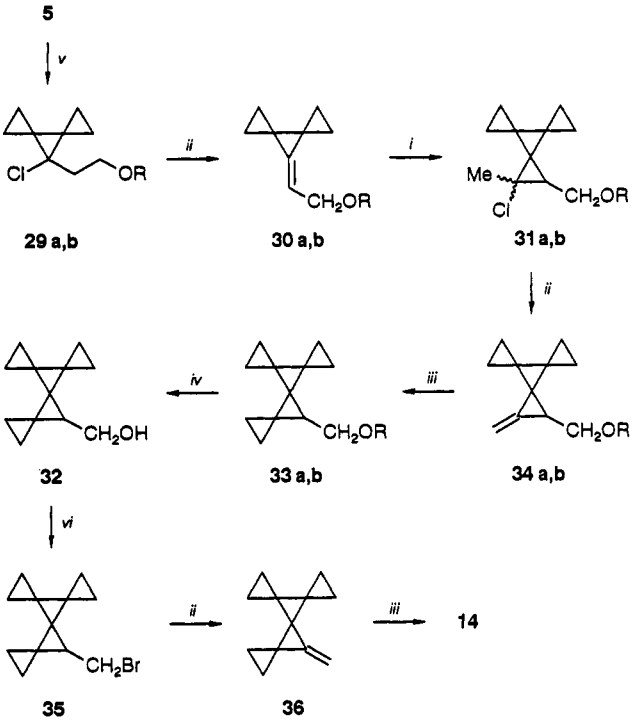


Figure 3. Packing in crystal of **32** projected along *a*. Four independent molecules are numbered 1, 2, 3, and 4.

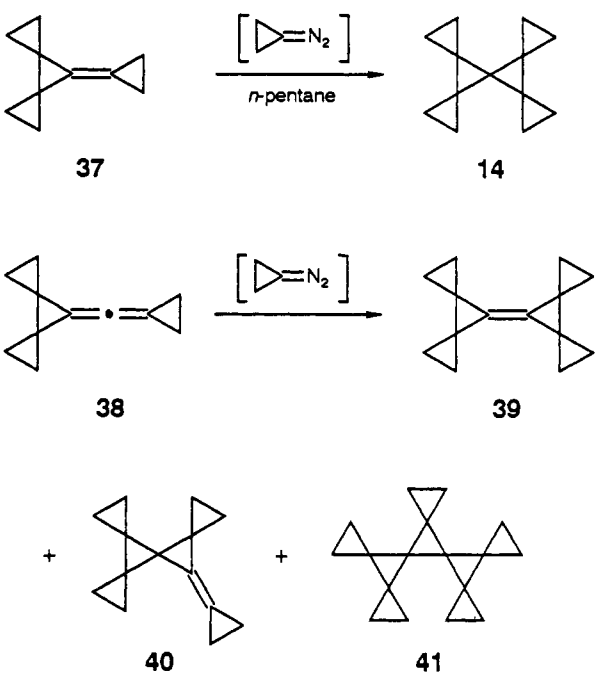
Scheme IV[a,b]



[a] (i) (a) R = Me; (b) R = $-\overline{CH(CH_2)_4O}$. [b] (i) CH_3CHCl_2/BuLi, (ii) *t*-BuOK/DMSO, (iii) CH_2N_2/$Pd(OAc)_2$, (iv) HCl, (v) RO-$(CH_2)_2CHCl_2$/$NaN(SiMe_3)_2$, (vi) Ph_3PBr_2/Py.

shortening of all bonds in the central spiropentane unit of **14** is an effect of hybridization changes.[26,27] It is also noteworthy that the molecules of **32** in the crystal form infinite chains with hydrogen bonds along the *b* direction (Figure 3).

Scheme V



Conclusion

The results presented in this paper illustrate that application of the suggested general strategy for the synthesis of BTs can give really good results. Moreover, using the combination of these four reactions—[2 + 1] addition of substituted chloroethylcarbene to alkenes, addition of chloromethylcarbene to methylenetriangulanes, dehydrohalogenation, and cyclopropanation—one can imagine the construction of branched triangulanes of any degree of complexity.

Experimental Section

General. ^{13}C and ^1H NMR spectra were obtained in CD_2Cl_2 solutions for compounds **13a,b** and **28a,b** and in $CDCl_3$ solutions

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for the other ones. GLC analyses and separations were performed using silicone SE-30, OV-225, or DSFS on Chromatone N-AW-DMCS. All solvents and reagents were purified and dried by standard techniques. Extracts were dried over $MgSO_4$ unless otherwise stated. 7-Methylenedispiro[2.0.2.1]heptane (**6**),[2,5] 3-methoxypropanal,[28,29] 3,3-dichloropropanol,[30,31] bicyclopropylidene (**5**),[12d] and 7-cyclopropylidenedispiro[2.0.2.1]heptane (**37**)[21] were prepared using literature procedures.

Crystal structure determinations: intensities of 2198 (for **14**) and 5053 (for **32**) unique reflections were measured with a Siemens P3/PE diffractometer (Mo Kα radiation, graphite monochromator, $\theta/2\theta$-scan, $\theta < 35°$ and 30° for **14** and **32**). Both structures were solved by direct methods and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms in **14** were located from a difference Fourier map and refined anisotropically. In **32** H-atoms of CH_2 groups were geometrically positioned and refined with the fixed $U = 0.05$ Å^2 and only one hydrogen atom of the OH group was located objectively. The structure **14** was refined to $R = 0.064$, $R_W = 0.061$ on 1020 reflections with $I > 4\sigma$; the structure **32** was refined to $R = 0.047$, $R_W = 0.049$ on 4034 reflections with $I > 4\sigma$. All calculations were carried out using the SHELXTL PC program package.

Crystal data for **14**: $C_{13}H_{16}$, orthorhombic, space group *Pbcn*; at 138 °C $a = 9.466$ (3), $b = 7.601$ (3), and $c = 14.440$ (4) Å, $V = 1039$ (1) Å^3, $Z = 4$ (molecule in the special position on the 2-fold axis passing through the central C(1) atom), $D_{calcd} = 1.10$ g/cm^3, μ(Mo Kα) = 0.57 cm^{-1}.

Crystal data for **32**: $C_{12}H_{15}O$, triclinic, space group *P*1, at −150 °C $a = 7.458$ (2), $b = 9.414$ (3), and $c = 14.775$ (5) Å, $\alpha = 98.28$ (3)°, $\beta = 96.71$ (3)°, $\gamma = 90.05$ (3)°, $V = 1019$ (1) Å^3, $Z = 4$ (4 independent molecules in the unit cell with the same matrix parameters but with inverted configuration of one molecular pair), $D_{calcd} = 1.14$ g/cm^3, μ(Mo Kα) = 0.66 cm^{-1}.

1,1-Dichloro-3-methoxypropane (15a).[32] To a well-stirred solution of 3-methoxypropanal (27.9 g, 0.317 mol) and dry pyridine (2.6 mL) in dry dichloromethane (40 mL) was added a solution of phosphorus pentachloride (70.6 g, 0.34 mol) in dry dichloromethane (700 mL) dropwise over 3 h at 0 to −5 °C. The reaction mixture was allowed to warm to rt and was stirred for an additional 10 h. Then it was cooled to 0 °C and sodium bicarbonate (158.5 g) was added in small portions over a period of 2 h. The mixture was stirred for 15 h. The organic phase was separated, washed with water, and dried. Evaporation of the solvent and distillation gave dichloride **15a** in 55% yield: bp 73–77 °C (90 mm), n^{20}_D 1.4367; ^{1}H NMR (60 MHz) δ 2.0–2.43 (m, 2 H), 3.23 (s, 3 H), 3.43 (t, 2 H, $J = 6$ Hz), 5.83 (t, 1 H, $J = 7$ Hz).

1,1-Dichloro-3-(tetrahydropyran-2-yloxy)propane (15b). A solution of 3,3-dichloropropanol (59 g, 0.457 mol), 3,4-dihydropyran (71.7 g, 0.854 mol), and pyridinium *p*-toluenesulfonate[33] (12.5 g) in dry dichloromethane (400 mL) was stirred for 5 h at rt. The reaction mixture was washed with brine, dried, concentrated, and diluted with ether (400 mL). The solution was washed with water, dried, and concentrated. The product was used without further purification: yield 98%; ^{1}H NMR (CCl_4, 60 MHz) δ 1.0–1.8 (m, 6 H), 2.2–2.8 (q, 2 H, $J = 6$ Hz), 3.1–3.4 (m, 4 H), 4.4 (t, 1 H, $J = 3.5$ Hz), 5.8 (t, 1 H, $J = 7$ Hz).

General Procedure for the Preparation of 1-Chloro-1-(2-R-oxyethyl)triangulanes 18a,b and 29a,b. To a well-stirred suspension of olefin (0.48 mol for methylenecyclopropane **16** or 0.16 mol for bicyclopropylidene **5**), pentane (30 mL), and sodium bis(trimethylsilyl)amide (0.17 mol) were added dichlorides **15a,b** (0.16 mol) dropwise over a period of 6 h at −5 to −10 °C under argon. The reaction mixture was stirred for 10 h at −10 °C, quenched with methanol, and carefully warmed to 50 °C. The solution was cooled to rt, washed with water, dried, carefully concentrated, and distilled in vacuo.

1-Chloro-1-(2-methoxyethyl)spiropentane (18a) was obtained in 53% yield: bp 72 °C (20 mm), n^{20}_D 1.4558; ^{1}H NMR (250 MHz) δ 0.7–1.05 (m, 4 H), 1.2 (d, 1 H, $J = 6$ Hz), 1.37 (d, 1 H, $J = 6$ Hz), 2.0 (t, 2 H, $J = 7$ Hz), 3.33 (s, 3 H), 3.58 (t, 2 H, $J = 7$ Hz); ^{13}C–^{1}H NMR δ 7.10 (t, $J = 163.9$ Hz), 7.71 (t, $J = 163.2$ Hz), 21.63 (t, $J = 162.7$ Hz), 22.14 (s), 39.0 (t, $J = 127.9$ Hz), 47.31 (s), 58.82 (q, $J = 140.7$ Hz), 70.14 (t, $J = 141.9$ Hz). Anal. Calcd for $C_8H_{13}ClO$: C, 59.81; H, 8.16. Found: C, 59.56; H, 7.91.

1-Chloro-1-[2-(tetrahydropyran-2-yloxy)ethyl]spiropentane (18b) was obtained in 60% yield as 1:1.5 mixture of diastereomers: bp 103–105 °C (2 mm), n^{21}_D 1.4800; ^{1}H NMR (250 MHz) δ 0.75–1.5 (m, 4 H), 1.17, 1.19, 1.33, 1.35 (d, 2 H, $J = 2.8$ Hz), 1.40–1.85 (m, 6 H), 1.90–2.10 (m, 2 H), 3.42–3.61 (m, 2 H), 3.67–3.96 (m, 2 H), 4.54, 4.59 (t, 1 H, $J = 3.3$ Hz); ^{13}C NMR δ 6.96 (t, 2 C), 7.70 (t), 7.76 (t), 21.36 (t), 21.43 (t), 22.05 (s), 22.13 (s), 47.19 (s), 47.25 (s) (spiropentane moiety); 19.27 (t), 19.39 (t), 25.36 (t, 2 C), 30.50 (t), 30.52 (t), 61.68 (t), 61.89 (t), 64.55 (t), 65.55 (t), 98.60 (d), 98.72 (d). Anal. Calcd for $C_{12}H_{19}ClO_2$: C, 62.46; H, 8.28. Found: C, 62.82; H, 8.26.

7-Chloro-7-(2-methoxyethyl)dispiro[2.0.2.1]heptane (29a) was obtained in 54.5% yield: bp 67–68 °C (6 mm), n^{20}_D 1.4730; ^{1}H NMR (250 MHz) δ 0.68–0.83 and 0.97–1.18 (m, 8 H), 2.04 (t, 2 H, $J = 7.2$ Hz), 3.31 (s, 3 H), 3.51 (t, 2 H, $J = 7.2$ Hz); ^{13}C–^{1}H NMR δ 6.56 (t, 2 C, $J = 166.4$ Hz), 7.08 (t, 2 C, $J = 163.5$ Hz), 25.74 (s, 2 C), 37.61 (t, $J = 128.3$ Hz), 52.43 (s), 59.76 (q, $J = 140.6$ Hz), 69.72 (t, $J = 141.1$ Hz). Anal. Calcd for $C_{10}H_{15}ClO$: C, 64.34; H, 8.10. Found: C, 64.01; H, 8.32.

7-Chloro-7-[2-(tetrahydropyran-2-yloxy)ethyl]dispiro[2.0.2.1]heptane (29b) was obtained in 55% yield: bp 135–140 °C (3 mm), mp 48–49 °C; ^{1}H NMR (250 MHz) δ 0.67–0.85 (m, 4 H), 0.95–1.20 (m, 4 H), 1.45–1.85 (m, 6 H), 2.04 (t, 2 H, $J = 5.5$ Hz), 3.44–3.55 (m, 2 H), 3.80–3.97 (m, 2 H), 3.58 (t, 1 H, $J = 3.8$ Hz); ^{13}C–^{1}H NMR δ 6.18 (t, 2 C, $J = 161.4$ Hz), 6.79 (t, 2 C, $J = 161.6$ Hz), 19.27 (t, $J = 128.5$ Hz), 25.31 (t, $J = 125.4$ Hz), 25.46 (s, 2 C), 30.47 (t, $J = 128.5$ Hz), 37.40 (t, $J = 128.1$ Hz), 52.67 (s), 61.52 (t, $J = 142.8$ Hz), 64.05 (t, $J = 142.7$ Hz), 98.56 (d, $J = 160.8$ Hz). Anal. Calcd for $C_{14}H_{21}ClO_2$: C, 65.48; H, 8.24. Found: C, 65.06; H, 8.32.

General Procedure for the Cycloaddition of Chloromethylcarbene to Olefins 8, 10, 20a,b, 24a,b, and 30a,b. Preparation of Chloromethyltriangulanes 7, 12, 21a,b, 23a,b, and 31a,b and Olefin 17a. To a solution of an olefin (50 mmol) and 1,1-dichloroethane (100 mmol, 8.4 mL) in dry ether (15 mL) was added *n*-butyllithium (100 mmol, 62.5 mL of 1.6 N solution in pentane) dropwise over 2 h at −35 to −40 °C under argon. The reaction mixture was allowed to warm to rt and quenched with cold water. The organic layer was separated, washed with water, dried, carefully concentrated, and distilled in vacuo.

1-Chloro-1-methyltrispiro[2.0.2.0.2.0]nonane (7) was obtained in 80% yield: bp 88 °C (30 mm), n^{20}_D 1.4835; ^{1}H NMR (250 MHz) δ 0.67–0.84 and 0.90–0.97 (m, 8 H), 1.03 (d, 1 H, $J = 5.9$ Hz), 1.28 (d, 1 H, $J = 5.9$ Hz), 1.59 (s, 3 H); ^{13}C NMR δ 3.15, 4.09, 4.44, 4.54, 21.23 (CH_2), 19.29, 20.04, 25.85, 47.60 (C), 25.28 (CH_3). Anal. Calcd for $C_{10}H_{13}Cl$: C, 71.21; H, 7.77. Found: C, 71.70; H, 8.03.

1-Chloro-1-methyltetraspiro[2.0.0.2.0.2.0.1]undecane (12) was obtained as 1:1 mixture of stereoisomers in 61% yield: bp 77.5 °C (1 mm), n^{20}_D 1.4935; ^{1}H NMR (250 MHz) δ 0.57–1.27 (m, 12 H), 1.60 and 1.66 (s, 3 H). Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.02; H, 7.77. Found: C, 73.83; H, 8.21.

1-Methoxyhept-2-ene (17a) was obtained in 48% yield together with chlorides **10a** and **13a** (11% and 20%, isolated by preparative GLC): bp 76 °C (80 mm), n^{20}_D 1.4915; ^{1}H NMR (250 MHz) δ 0.83 (t, 3 H, $J = 7$ Hz), 1.1–1.57 (m, 2 H), 1.77–2.37 (m, 4 H), 3.30 (s, 3 H), 3.35 (t, 2 H, $J = 7$ Hz), 5.30 (m, 2 H). Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.75; H, 12.31.

1-Chloro-1-methyl-2-(methoxymethyl)dispiro[2.0.2.1]heptane (21a) was obtained in 95.5% yield as 2.5:2.2:1:2.7 mixture of stereoisomers: bp 53–58 °C (2 mm), n^{20}_D 1.4732; ^{1}H NMR (250 MHz) δ 0.6–0.94 (m, 4 H), 1.1–1.37 (m, 3 H), 1.50, 1.52, 1.64 and 1.70 (s, 3 H), 3.30, 3.32, 3.34 and 3.36 (s, 3 H), 3.37–3.63 (m, 2 H). Anal. Calcd for $C_{10}H_{15}ClO$: C, 64.34; H, 8.10. Found: C, 64.01; H, 7.85.

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1-Chloro-1-methyl-2-[(tetrahydropyran-2-yloxy)methyl]-dispiro[2.0.2.1]heptane (21b) was obtained in 82% yield as 3:1:3:1:1:1 mixture of stereoisomers: bp 118–122 °C (1 mm), n^{22}_D 1.4910; ^{1}H NMR (250 MHz) δ 0.70–0.95 (m, 4 H), 1.10–1.38 (m, 2 H), 1.45–2.10 (m, 7 H), 1.54, 1.55, 1.56, 1.67, 1.70, 1.73 (s, 3 H), 3.40–3.65 (m, 2 H), 3.75–4.0 (m, 2 H), 4.58–4.67 (m, 1 H). Anal. Calcd for $C_{14}H_{21}ClO_2$: C, 65.48; H, 8.24. Found: C, 64.92; H, 7.91.

1-Chloro-1-methyl-9-(methoxymethyl)trispiro-[2.0.0.2.1.1]nonane (23a) was obtained in 63.6% yield as 1:2.7:1:1.9 mixture of stereoisomers: bp 73–76 °C (2 mm), n^{20}_D 1.4820; ^{1}H NMR (250 MHz) δ 0.65–1.1 (m, 4 H), 1.18–1.38 (m, 5 H), 1.53, 1.57, 1.64 and 1.69 (s, 3 H), 3.26, 3.29, 3.30 and 3.33 (s, 3 H), 3.30–3.50 (m, 2 H). Anal. Calcd for $C_{12}H_{17}ClO$: C, 67.75; H, 8.06. Found: C, 67.43; H, 8.25.

1-Chloro-1-methyl-9-[(tetrahydropyran-2-yloxy)methyl]-trispiro[2.0.0.2.1.1]nonane (23b) was obtained as 1:1.3:2.3:1.8 mixture of stereoisomers in 97% yield and used without purification: ^{1}H NMR (250 MHz) δ 0.55–1.0 (m, 4 H), 1.0–1.25 (m, 4 H), 1.30–1.85 (m, 7 H), 1.59, 1.61, 1.63, 1.66 (s, 3 H), 3.35–3.55 (m, 2 H), 3.65–3.85 (m, 2 H), 4.42, 4.48, 4.55, 4.59 (t, 1 H, J = 3.5 Hz).

1-Chloro-1-methyl-2-(methoxymethyl)trispiro-[2.0.2.0.2.0]nonane (31a) was obtained in 83.4% yield as 1:1.3 mixture of stereoisomers: bp 71–73 °C (2 mm), n^{20}_D 1.4920; ^{1}H NMR (250 MHz) δ 0.60–0.98 (m, 8 H), 1.60 and 1.62 (s, 3 H), 1.66–1.82 (m, 1 H), 3.34 and 3.37 (s, 3 H), 3.40–3.65 (m, 2 H). Anal. Calcd for $C_{12}H_{17}ClO$: C, 67.75; H, 8.06. Found: C, 67.48; H, 7.95.

1-Chloro-1-methyl-2-[(tetrahydropyran-2-yloxy)methyl]-trispiro[2.0.2.0.2.0]nonane (31b) was obtained as 1:1.4 mixture of stereoisomers in 90% yield and dehalogenated without further purification: ^{1}H NMR (250 MHz) δ 0.58–1.28 (m, 8 H), 1.40–1.86 (m, 7 H), 1.54 and 1.57 (s, 3 H), 3.37–3.52 (m, 2 H), 3.73–3.91 (m, 2 H), 4.54 and 4.59 (t, 1 H, J = 3.5 Hz).

General Procedure for Dehydrohalogenation of Halides 7, 12, 18a,b, 21a,b, 23a,b, 27, 29a,b, 31a,b, and 35 to the Olefins 8, 11, 20a,b, 19, 22a,b, 24a,b, 28a,b, 30a,b, 34a,b, and 36. To sublimed potassium *tert*-butoxide (3.35 g, 30 mmol) in dry DMSO (20 mL) was added halide (20 mmol) dropwise at 20 °C. The reaction mixture was stirred for 15 h (3 h for bromides **27** and **35**) and then quenched with cold water (30 mL). Pentane (30 mL) was added, and the organic layer was separated, washed with water, and dried. The pentane solution was carefully concentrated and distilled in vacuo or separated by preparative GLC.

1-Methylenetrispiro[2.0.2.0.2.0]nonane (8) was obtained in 85% yield: bp 82 °C (60 mm), n^{20}_D 1.4905; ^{1}H NMR (250 MHz) δ 0.70–0.95 (m, 8 H), 1.25–1.37 (m, 2 H), 5.23 (m, 1 H), 5.30 (m, 1 H); ^{13}C–^{1}H NMR δ 5.11 (t, 2 C, J = 162.1 Hz), 5.50 (t, 2 H, J = 162.2 Hz), 9.09 (t, J = 162.1 Hz), 14.24 (s), 22.63 (s, 2 C), 99.75 (t, J = 161.4 Hz), 135.51 (s). Anal. Calcd for $C_{10}H_{12}$: C, 90.91; H, 9.09. Found: C, 90.55; H, 9.68.

1-Methylenetetraspiro[2.0.0.2.0.2.0.1]undecane (11) was obtained in 82% yield (isolated by preparative GLC): n^{20}_D 1.5000; ^{1}H NMR (250 MHz) δ 0.61–1.09 (m, 8 H), 1.35 (dt, 1 H, J = 2.3, 7.5 Hz), 1.38 (d, 1 H, J = 3.9 Hz), 1.43 (dt, 1 H, J = 1.8, 7.5 Hz), 1.48 (d, 1 H, J = 3.9 Hz), 5.13 (t, 1 H, J = 2.3 Hz), 5.33 (t, 1 H, J = 1.8 Hz); ^{13}C NMR δ 3.70, 4.32, 4.32, 4.81, 8.86, 15.06, 99.71 (CH_2); 17.0, 18.13, 18.77, 25.86, 135.3 (C). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.96; H, 8.68.

[2-(Methoxymethyl)ethylidene]spiropentane (20a) was obtained in 64% yield as a 5:3 mixture of isomers: bp 68–70 °C (35 mm), n^{20}_D 1.4705; ^{1}H NMR (250 MHz) δ 1.0–1.21 (m, 4 H), 1.36–1.45 (m, 2 H), 3.29, 3.35 (s, 3 H), 3.87, 4.07 (d, 2 H, J = 6.7 Hz), 5.65, 5.8 (t, 1 H, J = 6.7 Hz); ^{13}C NMR δ 9.13 (t), 9.97 (t), 10.10 (t, 2 C), 10.39 (s), 10.91 (s) (spiropentane moiety), 57.63 (q), 71.92 (t), 72.34 (t), 109.76 (d), 111.90 (d), 132.77 (s), 133.50 (s). Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.02, H, 9.55.

[2-(Tetrahydropyran-2-yloxy)ethylidene]spiropentane (20b) was obtained as 1.5:1 mixture of isomers in 84% yield: bp 89–92 °C (2 mm), n^{20}_D 1.4920; ^{1}H NMR (250 MHz) δ 1.0–1.25 (m, 4 H), 1.40 (s, 2 H), 1.50–1.95 (m, 6 H), 3.43–3.56 (m, 1 H), 3.80–3.98 (m, 2 H), 4.14–4.24 (dt, 1 H, J = 6, 1.5 Hz), 4.63, 4.68 (t, 1 H, J = 3.7 Hz), 5.68, 5.83 (t, 1 H, J = 6 Hz); ^{13}C NMR δ 8.98 (t), 9.72 (t), 9.87 (t), 10.12 (t), 10.27 (s), 10.68 (s) (spiropentane moiety), 19.37 (t), 19.59 (t), 25.36 (t), 30.55 (t), 61.84 (t), 61.97 (t), 66.37 (t), 66.94 (t), 97.37 (d), 97.64 (d), 109.77 (d), 111.57 (d), 131.99 (s), 133.11 (s). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.24; H, 8.91.

***cis*-(2-Methoxyvinyl)spiropentane (19)** was obtained in 72% yield at 60 °C (isolated by preparative GLC): n^{20}_D 1.4720; ^{1}H NMR (250 MHz) δ 0.5–0.8 (m, 4 H), 1.0–1.2 (m, 2 H), 1.7–2.2 (m, 1 H), 3.45 (s, 3 H), 3.7–4.0 (dd, 1 H, J = 9, 7 Hz), 5.7 (d, 1 H, J = 7 Hz); ^{13}C–^{1}H NMR δ 3.86 (t, J = 161.1 Hz), 6.02 (t, J = 161.9 Hz), 13.98 (d, J = 162.7 Hz), 14.5 (t, J = 160.38 Hz), 15.86 (s), 59.56 (q, J = 143 Hz), 109.38 (d, J = 157.2 Hz), 146.1 (d, J = 178.8 Hz). Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.11; H, 9.59.

1-Methylene-2-(methoxymethyl)dispiro[2.0.2.1]heptane (24a) was obtained as 1:1 mixture of stereoisomers in 78% yield: bp 82–87 °C (25 mm), n^{20}_D 1.4750; ^{1}H NMR (250 MHz) δ 0.87–1.30 (m, 4 H), 1.59–2.0 (m, 3 H), 3.54, 3.58 (s, 3 H), 3.67, 3.71 (d, 2 H, J = 7 Hz), 5.40 (m, 1 H), 5.55 (m, 1 H); ^{13}C–^{1}H NMR δ 5.52 (t, J = 164.2 Hz), 5.63 (t, 2 C, J = 164.2 Hz), 5.87 (t, J = 162.3 Hz), 14.73 (t, J = 162.8 Hz), 17.09 (t, J = 162.5 Hz), 18.6, 19.3, 20.2, 20.6 (s), 19.55 (d, J = 156.4 Hz), 21.95 (d, J = 162.6 Hz), 58.07 (q, J = 140.5 Hz), 58.15 (q, J = 140.5 Hz), 73.17 (t, J = 141.7 Hz), 74.38 (t, J = 142 Hz), 99.79 (t, J = 161.7 Hz), 139.1, 139.32 (s). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.61; H, 9.15.

1-Methylene-2-[(tetrahydropyran-2-yloxy)methyl]dispiro[2.0.2.1]heptane (24b) was obtained in 82% yield as a mixture of stereoisomers: bp 108–111 °C (2 mm), n^{24}_D 1.4940; ^{1}H NMR (250 MHz) δ 0.7–1.0 (m, 4 H), 1.1–1.42 (m, 2 H), 1.45–1.90 (m, 7 H), 3.21–3.93 (m, 4 H), 4.58, 4.62 and 4.70 (t, 1 H, J = 3.8 Hz), 5.18 (m, 1 H), 5.34 (m, 1 H). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.28; H, 8.81.

1-Methylene-9-(methoxymethyl)trispiro[2.0.0.2.1.1]nonane (22a) was obtained as 2:1 mixture of stereoisomers in 81% yield: bp 72–77 °C (8 mm), n^{20}_D 1.4930; ^{1}H NMR (250 MHz) δ 0.65–1.0 (m, 4 H), 1.05–2.20 (m, 5 H), 3.30, 3.35 (s, 3 H), 3.35–3.70 (m, 2 H), 5.0–5.35 (m, 2 H); ^{13}C NMR δ 3.79, 4.63, 4.83, 5.48, 6.22, 7.88, 10.0, 12.55, 73.52, 74.41, 99.46, 99.87 (CH_2), 13.38, 14.5, 17.15, 20.42, 22.0, 25.27, 134.06, 134.08 (C), 24.08, 26.44 (CH), 58.33, 58.40 (CH_3). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.49; H, 9.31.

1-Methylene-9-[(tetrahydropyran-2-yloxy)methyl]trispiro[2.0.0.2.1.1]nonane (22b) was obtained as 1:2.2:1.7 mixture of stereoisomers in 76% yield: bp 108–111 °C (3 mm), n^{23}_D 1.5015; ^{1}H NMR (250 MHz) δ 0.6–0.95 (m, 4 H), 1.0–1.40 (m, 4 H), 1.42–1.88 (m, 7 H), 3.20–3.93 (m, 4 H), 4.50, 4.55 and 4.65 (t, 1 H, J = 3.8 Hz), 5.05, 5.16, 5.20 (t, 1 H, J = 2.5 Hz), 5.26, 5.30, 5.32 (m, 1 H). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.91; H, 8.79.

10-Methylenetetraspiro[2.0.0.0.2.1.1.1]undecane (28a,b) was obtained in 55% yield as a mixture of **28a** and **28b** (2.2:1): bp 62 °C (8 mm), n^{20}_D 1.5080. Olefin **28a**: ^{1}H NMR (250 MHz) δ 0.68–0.95 (m, 8 H), 1.32 (d, 2 H, J = 3.5 Hz), 1.49 (d, 2 H, J = 3.5 Hz), 5.07 (s, 2 H); ^{13}C NMR δ 4.66 (t, 2 C), 5.38 (t, 2 C), 14.39 (t, 2 C), 17.73 (s, 2 C), 20.22 (s, 2 C), 95.30 (t, 1 C), 140.76 (s, 1 C). Olefin **28b**: ^{1}H NMR (250 MHz) δ 0.68–0.95 (m, 8 H), 1.42 (d, 2 H, J = 3.5 Hz), 1.47 (d, 2 H, J = 3.5 Hz), 5.08 (s, 2 H); ^{13}C NMR δ 5.63 (t, 2 C), 7.67 (t, 2 C), 16.70 (t, 2 C), 17.99 (s, 2 C), 22.04 (s, 2 C), 95.21 (t, 1 C), 140.31 (s, 1 C). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.75; H, 8.82.

7-[2-(Methoxymethyl)ethylidene]dispiro[2.0.2.1]heptane (30a) was obtained in 81% yield: bp 83–85 °C (12 mm), n^{20}_D 1.4915; ^{1}H NMR (250 MHz) δ 0.92–1.15 (m, 8 H), 3.28 (s, 3 H), 3.88 (d, 2 H, J = 6.5 Hz), 5.06 (t, 1 H, J = 6.5 Hz); ^{13}C–^{1}H NMR δ 9.07 (t, 2 C, J = 163.7 Hz), 9.15 (t, 2 C, J = 163.7 Hz), 15.30 (s), 15.41 (s), 57.53 (q, J = 141.8 Hz), 71.6 (t, J = 142.9 Hz), 107.7 (d, J = 161.2 Hz), 137.56 (s). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.23; H, 9.08.

7-[2-(Tetrahydropyran-2-yloxy)ethylidene]dispiro-[2.0.2.1]heptane (30b) was obtained in 67% yield: bp 115–118 °C, n^{22}_D 1.5020; ^{1}H NMR (250 MHz) δ 0.88–1.20 (m, 8 H), 1.45–1.88 (m, 6 H), 3.80–3.92 (m, 2 H), 3.94–4.0 (dd, 1 H, J = 12, 7 Hz), 4.22–4.28 (dd, 1 H, J = 12, 5.8 Hz), 4.66 (t, 1 H, J = 3.5 Hz), 5.61 (t, 1 H, J = 6.4 Hz); ^{13}C–^{1}H NMR δ 9.16 (t, 2 C, J = 163.6 Hz), 9.45 (t, 2 C, J = 164.3 Hz), 15.36 (s), 15.55 (s), 19.58 (t, J = 127.7 Hz), 25.56 (t, J = 125.8 Hz), 30.77 (t, J = 127.1 Hz), 62.11 (t, J = 141.1 Hz), 66.41 (t, J = 140.8 Hz), 97.65 (d, J = 161.4 Hz), 107.7 (d, J = 159.54 Hz), 137.08 (s). Anal. Calcd for $C_{14}H_{20}O_2$:

C, 76.32; H, 9.15. Found: C, 75.98; H, 8.72.

1-Methylene-2-(methoxymethyl)dispiro[2.0.2.0.2.0]nonane (34a) was obtained in 78% yield: bp 60–63 °C (6 mm), n^{20}_D 1.4930; ^{1}H NMR (250 MHz) δ 0.68–1.05 (m, 8 H), 1.52–1.70 (m, 1 H), 3.36 (s, 3 H), 3.25–3.50 (m, 2 H), 5.25 (m, 1 H), 5.36 (m, 1 H); ^{13}C NMR δ 4.42, 5.12, 5.29, 5.37, 73.12, 100.46 (CH_2); 14.79, 16.13, 25.82 (C), 21.42 (CH), 58.08 (CH_3). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.63; H, 9.00.

1-Methylene-2-[(tetrahydropyran-2-yloxy)methyl]trispiro[2.0.2.0.2.0]nonane (34b) was obtained as 1:1.5 mixture of diastereomers in 63% yield: bp 113–117 °C (1 mm), n^{20}_D 1.5015; ^{1}H NMR (250 MHz) δ 0.70–0.90 (m, 4 H), 0.95–1.20 (m, 4 H), 1.35–1.95 (m, 7 H), 3.45–3.58 (m, 2 H), 3.78–4.0 (m, 2 H), 4.60, 4.65 (t, 1 H, J = 3.8 Hz), 5.23 (m, 1 H), 5.35 (m, 1 H). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.85; H, 8.73.

11-Methylenetetraspiro[2.0.0.2.0.2.0.1]undecane (36) was obtained in 56% yield: bp 64–67 °C (10 mm), n^{20}_D 1.5230; ^{1}H NMR (250 MHz) δ 0.63–1.20 (m, 12 H), 4.33 (m, 1 H), 4.45 (m, 1 H). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.81; H, 8.95.

General Procedure for Deprotection of Acetals 25b and 33b to the Alcohols 26 and 32. A solution of the acetal (10 mmol) and hydrochloric acid (0.5 mL of 0.1 N solution) in ethanol (50 mL) was refluxed until all the acetal had reacted according to TLC (20–40 min). After evaporation of the solvent, alcohols were isolated by distillation or column chromatography (eluent ether/pentane 4:6).

10-(Hydroxymethyl)tetraspiro[2.0.0.0.2.1.1.1]undecane (26) was obtained in 78% yield as a mixture of stereoisomers: bp 73–77 °C (2 mm), n^{25}_D 1.5040; ^{1}H NMR (250 MHz) δ 0.5–0.95 (m, 8 H), 1.0–1.28 (m, 4 H), 1.5–1.75 (m, 1 H), 1.65 (s, 1 H), 3.5–3.8 (m, 2 H). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.63; H, 8.77.

11-(Hydroxymethyl)tetraspiro[2.0.0.2.0.2.0.1]undecane (32) was obtained in 84% yield: mp 93–95 °C; ^{1}H NMR (250 MHz) δ 0.55–0.63 (m, 2 H), 0.69–0.85 (m, 10 H), 1.72 (t, 1 H, J = 7 Hz), 2.10 (s, 1 H), 3.55–3.68 (m, 2 H, J = 7, 11 Hz); ^{13}C NMR δ 1.31, 3.15, 3.55, 3.79, 4.23, 4.58, 64.79 (CH_2); 24.73 (CH); 6.79, 7.33, 16.91, 18.04 (C). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.66; H, 9.06.

General Procedure for Bromination of Alcohols 26 and 32 to the Bromides 27 and 35. To a cooled to −15 °C well-stirred solution of triphenylphosphine (1.38 g, 5.25 mmol) in dry dichloromethane (20 mL) was added bromine (0.27 mL, 5.25 mmol) in dry dichloromethane (2 mL) dropwise over 15 min. After additional stirring for 15 min, a solution of alcohol (5 mmol) and pyridine (0.43 mL, 5.25 mmol) in dry dichloromethane (5 mL) was added dropwise at −30 °C. The reaction mixture was stirred for 2 h at −10 °C and for 1 h at rt. After the evaporation of the solvent, the residue was throughly washed with pentane and filtered. The filtrate obtained was washed with water, dried, and after evaporation of the solvent dehydrohalogenated without further purification.

10-(Bromomethyl)tetraspiro[2.0.0.0.2.1.1.1]undecane (27) was obtained in 91% yield: bp 67–72 °C (1 mm), n^{23}_D 1.5230; ^{1}H NMR (60 MHz) δ 0.5–2.1 (m, 13 H), 3.2–3.7 (m, 2 H).

11-(Bromomethyl)tetraspiro[2.0.0.2.0.2.0.1]undecane (35) was obtained in 80% yield: n^{20}_D 1.5280; ^{1}H NMR (60 MHz) δ 0.5–1.8 (m, 13 H), 3.17–3.76 (m, 2 H).

General Procedure for the Cyclopropanation of Olefins 8, 11, 22a,b, 28a,b, 34a,b, and 36 to Triangulanes 9, 10, 13a,b, 14, 25a,b, and 33a,b. To a solution of olefin (5 mmol) and $Pd(OAc)_2$ (50 mg) in ether (15 mL), was added a solution of diazomethane (prepared from 5 g of *N*-nitroso-*N*-methylurea) in ether (50 mL) dropwise at −5 to 0 °C. The mixture was filtered through silica gel, concentrated, and distilled in vacuo or purified by preparative GLC.

Tetraspiro[2.0.0.2.0.2.0.1]undecane (9) was obtained in 76% yield: n^{20}_D 1.4910; ^{1}H NMR (250 MHz) δ 0.55–0.62 (m, 2 H), 0.68–0.84 (m, 10 H), 1.08 (s, 2 H); ^{13}C–^{1}H NMR δ 3.64 (t, 4 C, J = 161.6 Hz), 4.32 (t, 2 C, J = 161.5 Hz), 11.39 (t, 1 C, J = 161.2 Hz), 14.18 (s, 1 C), 18.06 (s, 2 C), 21.62 (s, 1 C). Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.02; H, 9.30.

Pentaspiro[2.0.0.0.2.0.2.0.1.1]tridecane (10) was obtained in 91% yield: n^{20}_D 1.5020; ^{1}H NMR (250 MHz) δ 0.60–0.96 (m, 12 H), 0.97 (d, 1 H, J = 3.8 Hz), 1.1 (d, 2 H, J = 3.8 Hz), 1.23 (d, 1 H, J = 3.8 Hz); ^{13}C NMR δ 3.93, 4.39, 4.59, 5.14, 6.57, 7.38, 10.59, 11.66 (CH_2); 13.55, 17.91, 18.65, 20.53, 23.41 (C). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.90; H, 9.66.

Pentaspiro[2.0.0.2.0.0.2.1.0.1]tridecanes 13a,b were obtained in 77% yield as a mixture of **13a** and **13b** (1.4:1): bp 60–64 °C (4 mm), n^{21}_D 1.5075. Triangulane **13a**: ^{1}H NMR (250 MHz) δ 0.56–0.90 (m, 12 H), 0.95 (d, 2 H, J = 3.7 Hz), 1.15 (d, 2 H, J = 3.7 Hz); ^{13}C NMR δ 3.19 (t, 2 C), 3.78 (t, 2 C), 3.90 (t, 2 C), 10.31 (t, 2 C), 13.85 (s, 2 C), 17.88 (s, 1 C), 21.53 (s, 2 C). Triangulane **13b**: ^{1}H NMR (250 MHz) δ 0.55–0.90 (m, 12 H), 1.06 (d, 2 H, J = 3.8 Hz), 1.16 (d, 2 H, J = 3.8 Hz); ^{13}C NMR δ 2.55 (t, 1 C), 3.86 (t, 1 C), 3.99 (t, 2 C), 6.66 (t, 2 C), 12.07 (t, 2 C), 14.22 (s, 2 C), 17.86 (s, 1 C), 23.28 (s, 2 C). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.32; H, 9.22.

Pentaspiro[2.0.0.2.0.2.0.0.2.0]tridecane (14) was obtained in 79% yield: mp 79–81 °C (hexane–ethanol); ^{1}H NMR (250 MHz) δ 0.57–0.76 (dd, 8 H, J = 3.76, 5.46 Hz), 0.81–0.84 (dd, 8 H, J = 4.05, 5.72 Hz); ^{13}C–^{1}H NMR δ 3.15 (t, 8 C, J = 162.2 Hz), 17.58 (s, 4 C), 24.62 (s, 1 C). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.23; H, 9.17.

10-(Methoxymethyl)tetraspiro[2.0.0.0.2.1.1.1]undecane (25a) was obtained in 83% yield as 2:1 mixture of stereoisomers: bp 73–78 °C (6 mm), n^{20}_D 1.4875; ^{1}H NMR (250 MHz) δ 0.50–0.95 (m, 8 H), 1.02, 1.04, 1.12, 1.22 (d, J = 4.3 Hz), 1.08, 1.16 (d, 4 H, J = 3.8 Hz), 1.35, 1.68 (t, 1 H, J = 6.5 Hz), 3.29, 3.33 (s, 3 H), 3.36, 3.52 (d, 2 H, J = 6.5 Hz). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.75; H, 9.32.

10-[(Tetrahydropyran-2-yloxy)methyl]tetraspiro[2.0.0.0.2.1.1.1]undecane (25b) was obtained in 82% yield as a mixture of stereoisomers: bp 108–110 °C (1 mm), n^{25}_D 1.4940; ^{1}H NMR (250 MHz) δ 0.50–0.90 (m, 8 H), 0.95–1.25 (m, 4 H), 1.40–1.88 (m, 7 H), 3.25–3.90 (m, 4 H), 4.50–4.61 (m, 1 H). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.63; H 8.77.

11-(Methoxymethyl)tetraspiro[2.0.0.2.0.2.0.1]undecane (33a) was obtained in 83% yield: bp 74–76 °C (6 mm), n^{20}_D 1.4875; ^{1}H NMR (250 MHz) δ 0.53–1.00 (m, 12 H), 1.65–1.81 (m, 1 H), 3.37 (s, 3 H), 3.25–3.63 (m, 2 H); ^{13}C NMR δ 1.36 (1 C), 3.37 (2 C), 3.60 (1 C), 4.20 (1 C), 4.50 (1 C), 74.22 (1 C, CH_2), 6.61 (1 C), 7.13 (1 C), 18.05 (1 C), 18.46 (1 C, C_{quart}); 22.27 (CH), 58.30 (CH_3). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.89; H, 9.41.

11-[(Tetrahydropyran-2-yloxy)methyl]tetraspiro[2.0.0.2.0.2.0.1]undecane (33b) was obtained in 74% yield as 2:1 mixture of diastereomers: bp 138–142 °C (2 mm), n^{20}_D 1.4965; ^{1}H NMR (250 MHz) δ 0.45–1.20 (m, 12 H), 1.40–1.85 (m, 7 H), 3.40–3.60 (m, 2 H), 3.75–3.92 (m 2 H), 4.49, 4.55 (t, 1 H, J = 4 Hz). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.11; H, 9.08.

Pentaspiro[2.0.0.2.0.2.0.0.2.0]tridecane (14) from 7-Cyclopropylidenedispiro[2.0.2.1]heptane (37). To a solution of **37** (156 mg, 1.2 mmol) in dry *n*-pentane (17 mL) were added in sequence at 0 °C *N*-nitroso-*N*-cyclopropylurea[20b] (320 mg, 2.5 mmol) and finely powdered sodium methoxide (2.0 g, 37 mmol), and the mixture was stirred at 0 °C for 8 h. Then the solution was filtered and the solid residue was washed with three portions of *n*-pentane (5 mL each); the combined pentane solutions were washed with water (2 × 5 mL) and dried over sodium sulfate. The solvent was trap-to-trap distilled in vacuo and the residue separated by preparative GLC. Yield: 80 mg (51%) starting material **37** (fraction I) and 49 mg (23%) **14** (fraction II). NMR spectroscopical data were identical with those of the sample obtained from **36**. MS (70 eV) m/z (rel intensity): 172 (0.3, M^+), 142 (41), 141 (46), 129 (72), 128 (100), 115 (67), 91 (66), 77 (34), 51 (22).

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Supplementary Material Available: X-ray crystallographic data, i.e., tables of atomic coordinates, temperature factors, and bond angles for compounds **14** and **32** (11 pages). Ordering information is given on any current masthead page.