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A new approach to helical primary structures of four-membered rings: (*P*)- and (*M*)-tetraspiro[3.0.0.0.3.2.2.2]hexadecane☆

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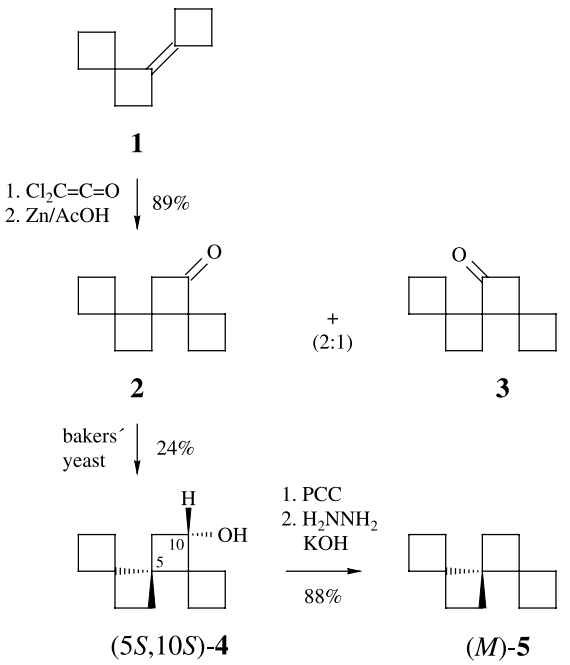
Abstract—A new approach to helical primary structures of four-membered rings uses a cycloaddition of a trimethylenketeniminium salt to suitable tailored methylenecyclobutanes to assemble the desired carbon framework. The results are short and effective syntheses of (*M*)-trispiro[3.0.0.3.2.2]tridecane [(*M*)-**5**], and (*P*)- and (*M*)-tetraspiro[3.0.0.0.3.2.2.2]hexadecane [(*P*)- and (*M*)-**24**]. Unlike helices of three-membered rings, the specific rotation decreases, as the length of the helix increases.

1. Introduction

The interesting quest, whether and to what extent the chiroptical properties of helical hydrocarbons of spiro-annelated rings are governed by static parameters like the identity period and the diameter and length of the helix, and/or by dynamic phenomena like conformational changes may best be answered experimentally in conjunction with an appropriate theoretical treatment. Towards this end, helical structures of rings of different size, and, for five-membered and larger rings, with different location of the spiro-centers should be considered. However, until now only three examples exist,[1,2] and methods with a general applicability for a synthesis of such compounds are rare.[3]

We recently described the synthesis of (*M*)-trispiro-[3.0.0.3.2.2]tridecane [(*M*)-**5**],[1] the first helical hydrocarbon of spiroannelated four-membered rings,[4] via a substance-, diastereo- and enantioselective enzymatic reduction of an inseparable 2:1-mixture of the trispiroketones **2** and **3** [**2**/**3**–(5*S*,10*S*)-**4**], itself obtained from bicyclobutylidene **1** by an addition of dichloroketene and a reductive dehalogenation. Oxidation with pyridinium chlorochromat followed by Wolff–Kishner reduction then yielded (*M*)-**5** (Scheme 1).



Scheme 1.

To improve the synthesis of **5**, and to make it suitable for a synthesis of higher analogues as well, we thought it necessary to prevent the formation of regioisomers and to establish the spiro[3.3]heptan-1-one subunit in **2** regio-specifically in a single step. Towards this end, we envisaged a cycloaddition of a trimethylenketeniminium salt **10**[5] to 1-methylenespiro[3.3]heptane (**8**), readily obtained by methylenation of **6**. As will be shown below, this approach proved successful, and therefore, a synthesis of the next higher analogue via a homologization of **6**, followed by the same set of reactions as used for the synthesis of **2** [**6**–**7**–**9**–**11**(**12**)] seemed feasible (Scheme 2). Stereochemically, a large preference for a formation of (5*R**,6*R**)-**11** with the desired helical carbon framework could be expected, and

☆ Polyspiranes, Part 28. For Part 27, see Ref. 1.

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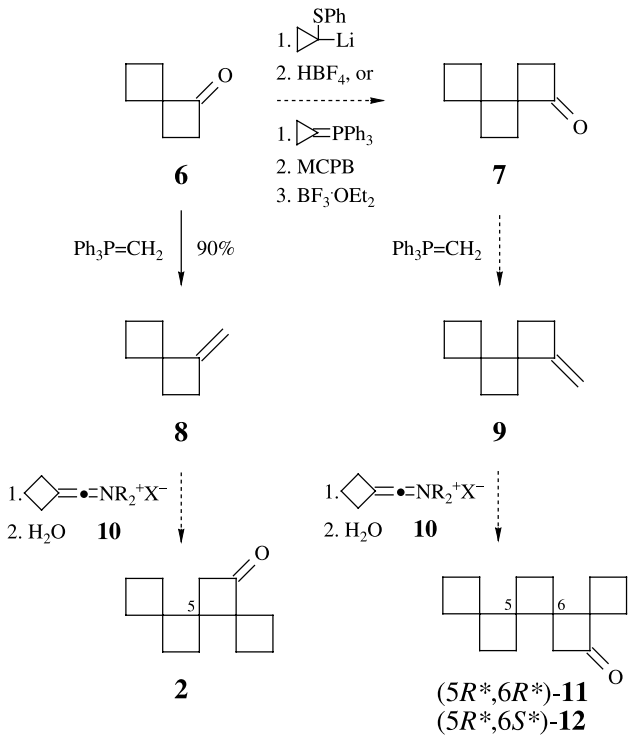
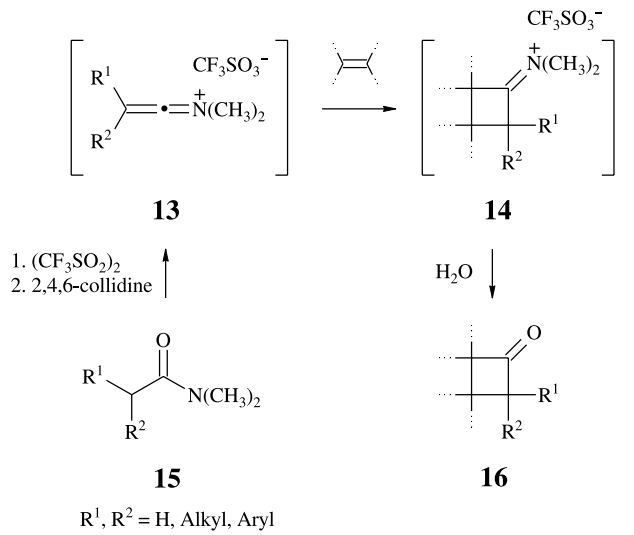


Scheme 2.

concerning its resolution, alternative possibilities to an enzymatic reduction were available. Of these, a use of (−)-diisopinocampheylchloroborane [(−)-DIP-Cl][6] as *S*-selective reducing agent for α-tertiary cycloalkanones and/or a use of (*S*)-(−)-2-hydrazino-2-oxo-*N*-(1-phenylethyl)-acetamide[7] as ketone resolving reagent seemed most promising. Research following these lines not only shortened the synthesis of (*M*)-trispiro[3.0.0.3.2.2]tridecane (**5**), but also enabled the first synthesis of (*P*)- and (*M*)-tetraspiro[3.0.0.0.3.2.2.2]hexadecane **24** as next higher analogues.



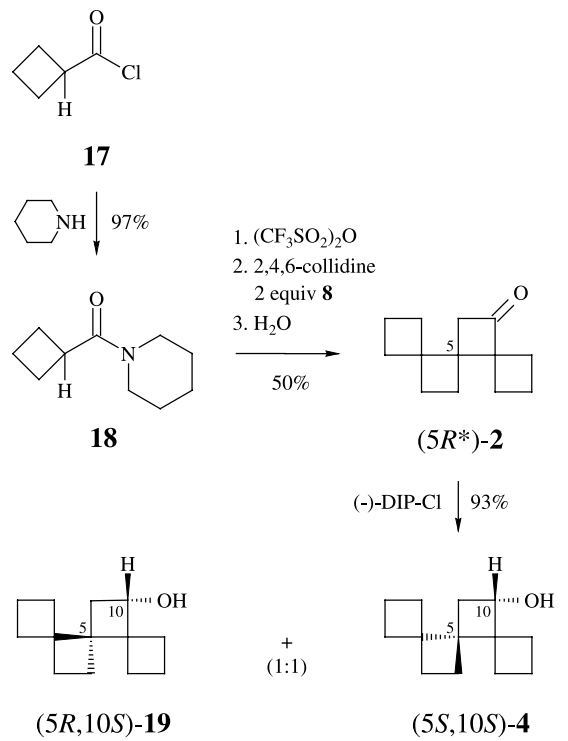
Scheme 3.

2. Results

Due to the pioneering work of Ghosez and co-workers[5] it is well known that keteniminium salts **13** may conveniently be generated by treatment of carboxylic acid amides **15** with trifluromethanesulfonic acid anhydride followed by 2,4,6-collidine, and that these salts effectively add to olefins yielding cyclobutylidene ammonium salts **14**, and, after hydrolysis, cyclobutanones **16** (Scheme 3). However, keteniminium salts derived from cycloalkanecarboxylic acid amides, representing a promising source for a variety of spiranes, have never been explored.

With this knowledge in mind, we reacted cyclobutanecarboxylic acid chloride (**17**) with piperidine and treated a solution of the resulting amide **18**[8] in dichloromethane first with trifluoromethanesulfonic acid anhydride, and then, in the presence of an excess of **8**, with 2,4,6-collidine. After 24 h of reflux and subsequent hydrolysis, the desired trispiroketone **2** was isolated in 50% yield (Scheme 4). This indicates that trimethylenketeniminium salts may offer distinct advantages over trimethylenketene itself,[9] at least in [2+2] cycloadditions with electron-poor olefins.

Having established a short and effective route to **2**, we next investigated its reduction with (−)-DIP-Cl. No reduction of an α-tertiary cyclobutanone had been described before, but spiro[4.4]nonan-1-one as an α-tertiary cyclopentanone had been transformed to the corresponding *S*-configurated alcohol within 12 h in 65% yield and 95% ee.[6] In any case, we were pleased to learn that (−)-DIP-Cl and **2** reacted almost instantaneously, and that the 1:1-mixture of alcohols formed consisted of (5*S*,10*S*)-**4** and a diastereoisomer, tentatively assigned as (5*R*,10*S*)-**19** (Scheme 4). Both alcohols were known from the reduction of **2** with

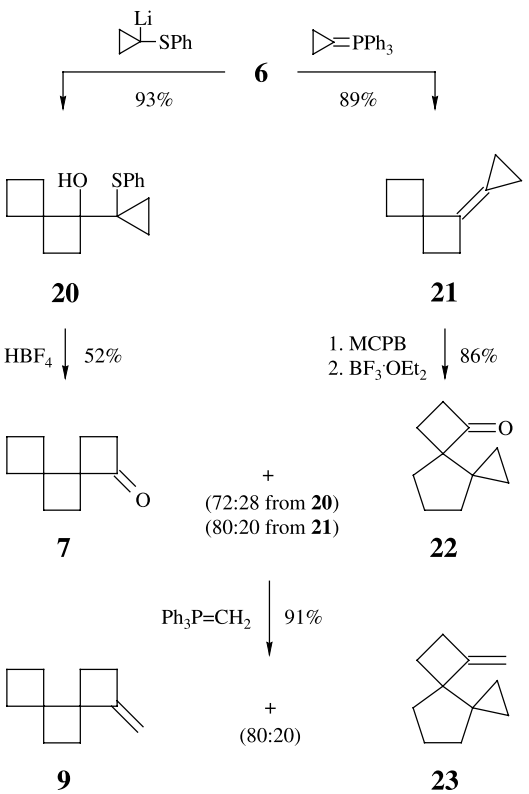


Scheme 4.

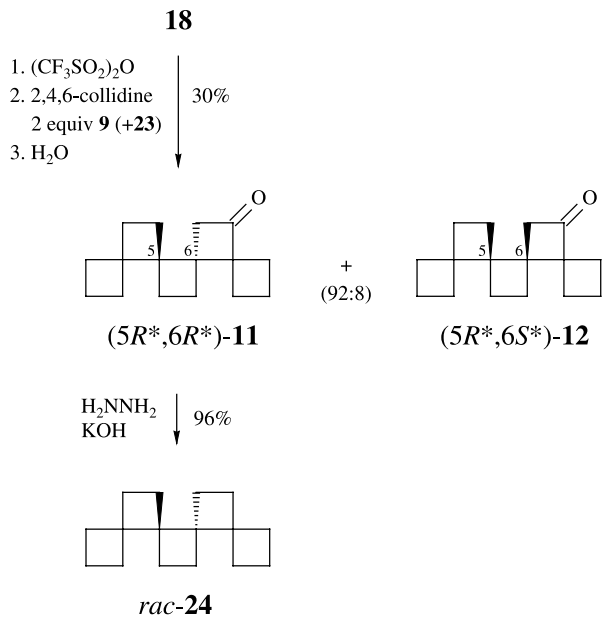
bakers' yeast,[1] and both were enantiomerically pure (>99% ee) according to capillary gas chromatography on a γ-cyclodextrin as chiral phase. As (5*S*,10*S*)-**4** had already been transformed to (*M*)-**5** by oxidation with pyridinium chlorochromate followed by Wolff–Kishner reduction[1] (Scheme 1), no efforts were made to repeat these reactions with (5*R*,10*S*)-**19**.

For the synthesis of tetraspiro[3.0.0.0.3.2.2.2]hexadecane (**24**), we first explored two routes to ketone **7** as precursor of olefin **9**, itself needed for a cycloaddition to the keteniminium salt derived from **18**: (a) an addition of 1-lithiocyclopropylphenyl sulphide to **6**, and a subsequent rearrangement with tetrafluoroboric acid [**6**–**20**–**7**(**22**)],[10] and (b) a cyclopropylidenation of **6**, and a subsequent epoxidation and rearrangement with boron trifluoride etherate [**6**–**21**–**7**(**22**)] (Scheme 5). In both cases, the C_3–C_4 ring enlargement leading to **7** was accompanied by a C_4–C_5 ring enlargement followed by a C_4–C_3 ring contraction and another C_4–C_5 ring enlargement leading to **22**, yielding the two ketones in a ratio of 72:28 from **20**, and 80:20 from **21**. Unfortunately, the two ketones were inseparable on a preparative scale, and the same was true for the two olefins **9** and **23** derived therefrom. However, no complications were met during the next step.

As was to be expected, the cycloaddition of the keteniminium salt derived from **18** to 1-methylene-dispiro[3.0.3.2]-decane (**9**) proceeded regio- and stereoselectively and delivered the desired tetraspiroketone (5*R**,6*R**)-**11** as major product of a 92:8-mixture with (5*R**,6*S**)-**12**, in 30% combined yield. Separation from (5*R**,6*S**)-**12** and products derived from **23** was achieved by column chromatography, and Wolff–Kishner reduction then yielded tetraspiro[3.0.0.0.3.2.2.2]hexadecane [*rac*-**24**] (Scheme 6). As the number and multiplicities of the resonance lines in the ^{13}C NMR spectrum [15.74 (t), 26.43 (t), 26.51 (t), 30.70 (t), 31.31 (t), 32.37 (t), 49.21 (s), 52.34 (s)] could account for both *rac*-**24** (symmetry C_2) and its achiral counterpart derived from (5*R**,6*S**)-**12** (symmetry C_s), a capillary gas chromatographic analysis on a γ-cyclodextrin as chiral phase proved necessary. This analysis revealed that the hydrocarbon in question was a racemic mixture of two enantiomers, and hence *rac*-**24**.

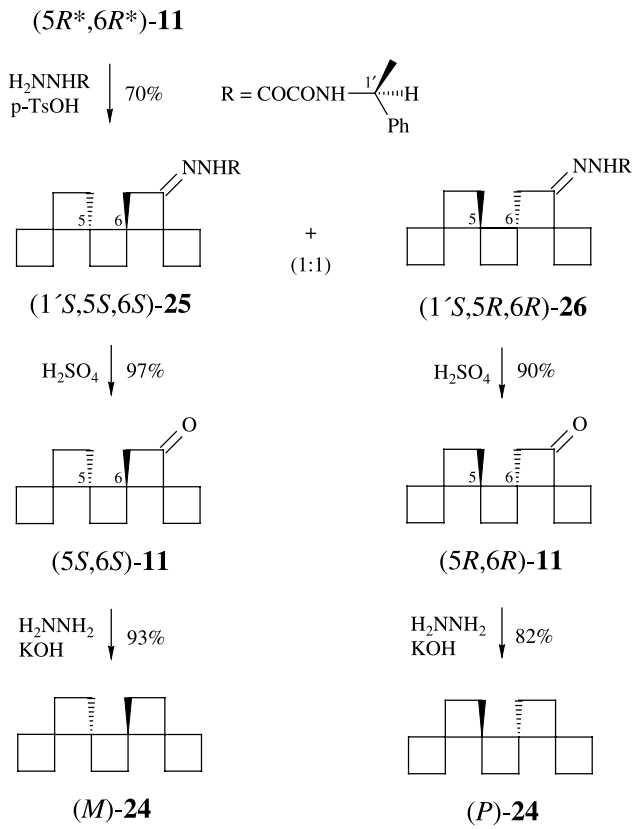


Scheme 5.



Scheme 6.

For the resolution of (5*R**,6*R**)-**11**, we first tried an enantioselective reduction with (−)-DIP-Cl[6] as already applied to the resolution of (5*R**)-**2** (Scheme 4). Unfortunately, this time the two diastereoisomeric alcohols formed were not separable on a preparative scale, neither by column nor by gas chromatography. We therefore investigated the usefulness of (*S*)-(−)-2-hydrazino-2-oxo-*N*-(1-phenylethyl)-acetamide[7] as ketone resolving reagent (Scheme 7). Catalyzed by *p*-toluenesulfonic acid, this reagent yielded a 1:1-mixture of two diastereoisomeric hydrazones, which could be separated by column chromatography on silica gel in pentane/ether (1:1), albeit partial hydrolysis was observed. As a consequence, both the first (R_f=0.33) and the second eluted hydrazone (R_f=0.28) contained ketone (R_f=0.77): the former more (10%) than the latter (3%) (^1H NMR). As the second eluted hydrazone could only contain ketone originating from itself, we hoped that its hydrolysis would deliver an enantiomerically pure ketone. However, due to an incomplete separation from the first eluted hydrazone, the optical purity was slightly diminished (94% ee, $[\alpha]_D^{20}=-46.3°$, c=1.09, acetone), as evidenced by capillary gas chromatography of the corresponding hydrocarbon obtained by Wolff–Kishner reduction (94% ee, $[\alpha]_D^{20}=-24.2°$, c=1.17, $CHCl_3$). The identity of the ketone as (5*S*,6*S*)-**11**, the hydrocarbon as (*M*)-**24** and the hydrazone as (1′*S*,5*S*,6*S*)-**25** followed from the fact, that in the CD



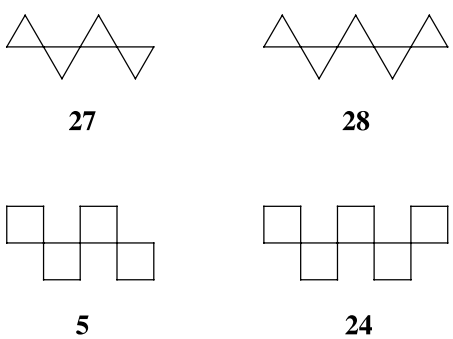
Scheme 7.

spectrum of the ketone ($[\theta]_{302}$=+1967, CH_3OH) a net positive Cotton effect[11] was observed.

For the synthesis of (*P*)-**24**, we used the same set of reactions as for (*M*)-**24**. This time, the starting hydrazone (1′*S*,5*R*,6*R*)-**26** was contaminated with 10% ketone originating from both (1′*S*,5*S*,6*S*)-**25** and (1′*S*,5*R*,6*R*)-**26**. Consequently, its hydrolysis to (5*R*,6*R*)-**11** delivered a product of lower optical purity (92% ee, $[\alpha]_D^{20}$=+45.9°, *c*=1.09, acetone), which translated to (*P*)-**24** (92% ee, $[\alpha]_D^{20}$=+23.9°, *c*=1.18, $CHCl_3$) through Wolff–Kishner reduction.

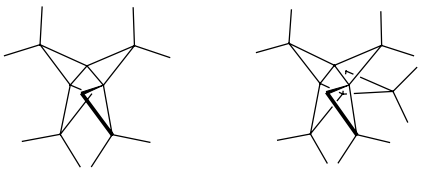
3. Discussion

Until now, only three examples for hydrocarbons with a helical primary structure were known: trispiro[2.0.0.2.1.1]-nonane (**27**),[2a,b] tetraspiro[2.0.0.0.2.1.1.1]undecane (**28**)[2b] and trispiro[3.0.0.3.2.2]tridecane (**5**).[1] The present contribution describes the synthesis of tetraspiro[3.0.0.0.3.2.2.2]-hexadecane (**24**) and thereby allows a first comparison of two pairs of helical primary structures of spiroannelated three and four-membered rings (Scheme 8).

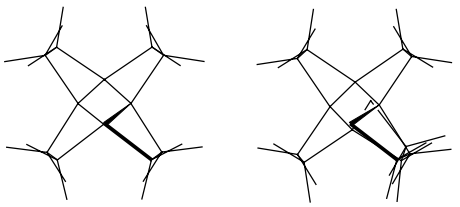


Scheme 8.

As pointed out elsewhere,[1] helical hydrocarbons of spiroannelated three- and four-membered rings form regular helices, but their identity periods differ: that of the former comprises eight three-membered rings within two helical turns, that of the latter five four-membered rings within one helical turn. This means, that in **24** a helical turn is just complete, while in **28** it goes about 50° beyond (Fig. 1). A second difference concerns the fact, that helices of three-membered rings form rigid structures, while those of four-membered rings may adopt different conformations. Thus, within 3 kcal above the global minimum, our conformational search routine HUNTER[12] in connection with MM3[13] located seven additional minima for **5**, and three for **24**. Only the global minimum conformations represent regular helices (Fig. 1), while all other conformations contain non-regular sections. We therefore believe, that the large difference in the specific rotations of (*M*)-**27** ($[\alpha]_D^{20}$=−192.7°, *c*=1.2, $CHCl_3$)[2] and (*M*)-**5** ($[\alpha]_D^{20}$=−63.3°, *c*=1.09, $CHCl_3$)[1] is due to the conformational mobility of



	(*M*)-**27**	(*M*)-**28**
$[\alpha]_D^{20}$ ($CDCl_3$)	- 192.7°	- 381.2°



	(*M*)-**5**		(*M*)-**24**
$[\alpha]_D^{20}$ ($CDCl_3$)	- 63.3°		- 24.2°
ΔH_f^0 (kcal/mol)	**79.3**	81.5	**104.3**
	80.1	81.9	106.1
	80.7	82.0	106.3
	80.7	82.2	106.5

Figure 1. Global minimum structures of (*M*)-**27**, (*M*)-**28**, (*M*)-**5** and (*M*)-**24**: views along the helical axis. The structure of (*M*)-**28** was generated using the crystal structure data of *rac*-**28**.[2b] The remaining structures were determined by molecular mechanics using PC-model[14] [(*M*)-**27**] and the conformational search routine HUNTER[12] in connection with MM3[13] [(*M*)-**5**, (*M*)-**24**], respectively. All carbon–hydrogen bonds within the inner spheres have been omitted for clarity. For (*M*)-**5** and (*M*)-**24**, the heats of formation (in kcal/mol) of all minimum conformations up to 3 kcal/mol above the global minimum (in bold) are given. For views of their structures, see Ref. 1.

(*M*)-**5**, not present in (*M*)-**27**, and to the fact, that (*M*)-**5** describes a distinctly shorter section of a helix than (*M*)-**27**.

As mentioned above, the number of conformations within 3 kcal/mol above the global minimum is reduced from eight in (*M*)-**5** to four in (*M*)-**24**. This indicates that the conformational mobility of a helix of four-membered rings decreases, as the length of the helix increases. It was therefore tempting to speculate,[1] that the large difference between the specific rotations of (*M*)-**27** and (*M*)-**5** for (*M*)-**28** ($[\alpha]_D^{20}=-381.2°$, $c=1.2$, $CHCl_3$)[2] and (*M*)-**24** ($[\alpha]_D^{20}=-24.2°$, $c=1.17$, $CHCl_3$) could diminish. However, the contrary is true: while the specific rotation of (*M*)-**27** doubles, the specific rotation of (*M*)-**5** is cut in three. The reason for this unexpected result is not yet clear, but ab initio calculations on a sufficiently large set of potentially low-lying conformers with subsequent calculation of Boltzmann-averaged CD or ORD spectra should help to clarify the matter.[15]

4. Experimental

4.1. General

IR-spectra were obtained with a Perkin–Elmer 298 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 or a Varian VXR 500 or VXR 600 spectrometer. For standards other than TMS the following chemical shifts were used: δ_H (C_2HDCl_4)=5.99, δ_H ($CHCl_3$)=7.24, δ_H (C_6D_5H)=7.15, δ_C ($C_2D_2Cl_4$)=73.71, δ_C ($CDCl_3$)=77.00, δ_C (C_6D_6)=128.00. ^{13}C multiplicities were studied by APT and/or DEPT measurements. Mass spectra were obtained with a Varian CH 5 (CI) or a Finnegan MAT 95 spectrometer (EI und HR-EI) operated at 70 eV. Optical rotations were measured on a Perkin–Elmer 241 digital polarimeter in a 1 dm cell. UV and CD spectra were obtained with a JASCO J-710/720 spektropolarimeter. Preparative GC was carried out on a Carlo-Erba GC 6000 Vega series 2 instrument employing a thermal conductivity detector, and hydrogen as carrier gas. Analytical GC was performed on a Carlo-Erba GC 6000 Vega series 2 instrument employing a split/splitless injector, a FID 40 detector, and hydrogen (0.6 bar) as carrier gas. The following columns were used: (A): 3 m×1/4″ all-glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh; (B) 25 m×0.25 mm i.d. deactivated fused-silica capillary column coated with oktakis-(2,6-di-*O*-pentyl-3-*O*-butyryl)-γ-cyclodextrin (Lipodex® E); (C) 25 m×0.25 mm i.d. deactivated fused-silica capillary column coated with oktakis-(2,3-di-*O*-pentyl-6-*O*-methyl)-γ-cyclodextrin (Lipodex® G). Product ratios were not corrected for relative response. R_f values are quoted for Macherey & Nagel Polygram SIL G/UV254 plates. Colorless substances were detected by oxidation with 3.5% alcoholic 12-molybdophosphoric acid and subsequent warming. Melting points were observed on a Reichert microhotstage and are not corrected. Microanalytical determinations were done at the Microanalytical Laboratory of the Institute of Organic Chemistry, Göttingen. (*S*)-(−)-1-phenyl-ethylamine, 98%, used for the preparation of (*S*)-(−)-2-hydrazino-2-oxo-*N*-(1-phenyl-ethyl)-acetamide [(*S*)-(−)-**9**],[7] was purchased from Aldrich Chemical Company, Inc.

4.1.1. 1-Methylene-spiro[3.3]heptane (8). To a suspension of methyltriphenylphosphonium bromide (46.4 g, 130 mmol) in anhydrous ether (250 ml) was added under argon with stirring potassium-*t*-butoxide (14.6 g, 130 mmol) and the mixture heated to reflux. After 15 min, most of the ether was distilled off (bath temperature up to 60 °C), **6** (12.1 g, 110 mmol) was added dropwise, and after additional 30 min at 60 °C the reaction was complete according to GC [column A, 120 °C; retention times (min): 1.03 (**8**), 4.63 (**6**)]. The mixture was diluted with pentane (100 ml) and hydrolyzed with water (11 ml). The organic layer was decanted, the residue was extracted with pentane (2×70 ml), and the combined organic phases were washed with water (3×70 ml) and dried ($MgSO_4$). The solvent was distilled off through a 20 cm vigreux column (bath temperature up to 130 °C) and the remaining material fractionated to yield 10.7 g (90%) of **8** as colorless liquid, bp 116–118 °C (purity 97% GC). IR (neat): 1670 cm^{-1} (C=C); ^1H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.73–1.87 (m, 2H), 1.95 (t, J=8 Hz, 2H), 1.95–2.03 (m, 2H), 2.10–2.17 (m, 2H), 2.51 (tt, J=8, 2 Hz, 2H), 4.67 (t, J=2 Hz, 1H), 4.88 (t, J=2 Hz, 1H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=16.15 (t), 27.30 (t), 32.01 (t), 34.41 (t), 50.80 (s), 101.40 (t), 159.10 (s); MS (EI): m/e=108 (3, M^+), 79 (100); C_8H_{12} requires C, 88.82; H, 11.18. Found: C, 88.96; H, 10.98.

4.1.2. 1-(Cyclobutylcarbonyl)-piperidine (18). To a solution of piperidine (34.0 g, 0.40 mol) in dichloromethane (150 ml) was added under argon with stirring cyclobutyryl chloride (23.6 g, 0.20 mol) such that, the internal temperature did not exceed 25 °C. After the addition was complete, the mixture was stirred for 30 min at room temperature and then washed with water (80 ml), 2 N HCl (80 ml), saturated sodium bicarbonate (80 ml) and dried ($MgSO_4$). The solvent was distilled off and the residue fractionated to yield 32.6 g (97%) of **18** as colorless liquid, bp 147 °C/16 Torr (purity 99% GC) (lit.[8] bp 89–91 °C/1 Torr). IR (neat): 1640 cm^{-1} (C=O); ^1H NMR (600 MHz, symm $C_2D_2Cl_4$, C_2DHCl_4 int, 120 °C): δ=1.47–1.54 (m, 4H), 1.58–1.65 (m, 2H), 1.83–1.98 (m, 2H), 2.09–2.17 (m, 2H), 2.28–2.37 (m, 2H), 3.18–3.26 (m, 1H), 3.37 (br s, 4H); ^{13}C NMR (150.8 MHz, symm $C_2D_2Cl_4$, $C_2D_2Cl_4$ int, 120 °C): δ=17.70 (t), 24.28 (t), 24.92 (t), 25.74 (t), 37.11 (d), 44.10 (br t), 172.38 (s); MS (EI): m/e=167 (42, M^+), 84 (100); $C_{10}H_{17}NO$ requires C, 71.81; H, 10.24; N, 8.55. Found: C, 71.75; H, 10.18; N, 8.60.

4.1.3. (5*R)-Trispiro[3.0.0.3.2.2]tridecan-10-one (2).** To a solution of **18** (1.68 g, 10 mmol) in 1,2-dichloroethane (10 ml) was added at −15 °C under argon with stirring trifluoromethanesulfonic acid anhydride (3.38 g, 12 mmol), and, within 20 min, a solution of 2,4,6-collidine (1.46 g, 12 mmol) and **8** (2.16 g, 20 mmol). The mixture was heated for 24 h to reflux and then concentrated on a rotary evaporator (bath temperature 35 °C/15 Torr). The residual black oil was extracted with anhydrous ether (3×20 ml), and the remaining material hydrolyzed in a two-phase system of dichloromethane (15 ml) and water (15 ml). After 2 h of reflux, GC analysis [column A, 230 °C; retention times (min): 2.58 (**2**), 4.49 (**18**)] indicated the presence of a 76:24-mixture of **2** and **18**. The organic phase was washed with 2 N H_2SO_4 (10 ml), dried ($MgSO_4/K_2CO_3$) and concentrated on a rotary evaporator (bath temperature 35 °C/15 Torr), and the residual brown oil (2.50 g)

chromatographed on silica gel (0.05–0.20 mm) in pentane/ether [8:2, R_f=0.62 (**2**); column 75×5 cm] yielding 950 mg (50%) of **2** as colorless liquid (purity 96% GC). The ^{1}H and ^{13}C NMR data reported[1] are data from spectra of a 2:1-mixture with **3** in C_6D_6. The data for pure **2** in $CDCl_3$ are as follows: ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.65–1.82 (m, 5H), 1.82–1.92 (m, 1H), 1.95–2.15 (m, 7H), 2.15–2.30 (m, 4H), 2.60 (d, J=17 Hz, 1H), 2.92 (d, J=17 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$, $CDCl_3$ int): δ=16.29 (t), 16.77 (t), 24.87 (t), 27.23 (t), 27.92 (t), 30.91 (t), 32.01 (t), 32.73 (t), 43.77 (s), 48.85 (s), 49.57 (t), 67.23 (s), 213.22 (s).

4.1.4. (5*S*,10*S*)-(+)-Trispiro[3.0.0.3.2.2]tridecan-10-ol [(5*S*,10*S*)-4] and (5*R*,10*S*)-(−)-trispiro[3.0.0.3.2.2]tridecan-10-ol [(5*R*,10*S*)-19]. To (−)-diisopinocampheylchloroborane [(−)-DIP-Cl] (642 mg, 2.00 mmol) was added under argon with stirring (*R**)-**2** (380 mg, 2.00 mmol) via a syringe. A slightly exothermic reaction was observed, and, within a few minutes, a clear solution had formed. After 45 min at room temperature, the solution was diluted with ether (4 ml), and diethanolamine (210 mg, 2.0 mmol) was added, causing a heavy precipitate. After 1 h the mixture was filtrated and the residue washed with pentane (2×4 ml). The combined organic phases were washed with saturated sodium carbonate (4 ml) and water (4 ml), and dried ($MgSO_4$). The solvents were evaporated and the residue chromatographed on silica gel (0.05–0.20 mm) in pentane/ether[7:3; R_f=0.32 (**4**/**19**); column 60×4.5 cm] to give 356 mg (93%) of a 1:1-mixture of **4** and **19**. According to capillary gas chromatography on a chiral phase [column B, 120 °C, retention times (min): 24.68 (**4**), 28.86 (**19**)] both alcohols were enantiomerically pure (>99% ee). Analytically pure samples were obtained by preparative GC [column A, 210 °C; retention times (min): 9.75 (**4**), 10.65 (**19**)]. Their ^{1}H NMR data were identical with those of racemic samples.[1]

4.1.5. 1-(1-Phenylsulfanyl-cyclopropyl)-spiro[3.3]heptan-1-ol (20). To a stirred solution of cyclopropyl phenyl sulphide (21.6 g, 144 mmol) in anhydrous tetrahydrofuran (300 ml) under argon at 0 °C was added within 45 min a 1.60 M solution of *n*-butyllithium in hexane (90 ml, 144 mmol). After 1.5 h at 0 °C, a solution of **6** (13.2 g, 120 mmol) in tetrahydrofuran (40 ml) was added within 30 min and the temperature maintained for additional 1.5 h at 0 °C. The mixture was hydrolyzed with saturated ammonium chloride (15 ml), the liquid phase was decanted, and the residue was extracted with ether (3×50 ml). The organic phases were concentrated on a rotary evaporator (bath temperature 50 °C/15 Torr), and the residual oil (36 g) was chromatographed on silica gel (0.05–0.20 mm) first using pentane (column 70×3 cm) to yield 5.0 g of unreacted cyclopropyl phenyl sulphide, and then ether to yield 29.0 g (93%) of **20** as slightly yellowish oil. IR (neat): 3600–3300 cm^{-1} (OH_{ass}); ^{1}H NMR (600 MHz, symm $C_2D_2Cl_4$, C_2DHCl_4 int, 120 °C): δ=0.85–0.90 (m, 1H), 1.04–1.09 (m, 1H), 1.13–1.18 (m, 2H), 1.70–1.95 (m, 7H), 2.07–2.14 (m, 1H), 2.26 (br s, 1H), 2.45 (ddd, J=10, 10, 10 Hz, 1H), 2.54 (ddd, J=10, 10, 10 Hz, 1H), 7.21 (tt, J=8, 1 Hz, 1H), 7.30 (dd, J=8, 8 Hz, 2H), 7.56 (dd, J=8, 1 Hz, 2H); ^{13}C NMR (150.8 MHz, symm $C_2D_2Cl_4$, $C_2D_2Cl_4$ int, 120 °C): δ=10.79 (t), 14.67 (t), 14.88 (t), 27.16 (t), 29.87 (t), 29.90 (t), 31.41 (t), 31.54 (s), 51.08 (s), 80.73 (s), 125.92 (d), 128.30 (d), 129.94 (d), 136.79 (s); MS (EI): *m*/*e*=260 (85, M^+), 192 (100); $C_{16}H_{20}SO$ requires C, 73.80; H, 7.74; S, 12.31. Found: C, 73.85; H, 7.87.

4.1.6. 1-Cyclopropylidenspiro[3.3]heptane (21). To a suspension of potassium-*t*-butoxide (44.8 g, 0.40 mol) in dry benzene (700 ml) was added under argon with stirring cyclopropyltriphenylphosphonium bromide (153 g, 0.40 mmol) and the mixture heated for 2 h to 55 °C. **6** (22.0 g, 0.20 mol) was added, and after additional 2 h at 70 °C the reaction was complete according to GC [column A, 140 °C; retention times (min): 1.97 (**21**), 2.37 (**6**)]. The mixture was diluted with pentane (700 ml) and hydrolyzed with water (30 ml). The liquid phase was decanted and the residue extracted with pentane (2×100 ml). The combined organic phases were concentrated through a 40 cm vigreux column (bath temperature up to 130 °C), and the residue was diluted with pentane (600 ml), causing a heavy precipitate. The mixture was filtered and the residue washed with pentane (2×100 ml). The combined filtrates were concentrated through a 40 cm vigreux column (bath temperature up to 135 °C) and the residue was fractionated through a microdistillation apparatus to yield 23.8 g (89%) of **21** as colorless liquid, bp 67–68 °C/15 Torr (purity 97% GC). IR (neat): 1788 cm^{-1} (C=C); ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=0.90–0.95 (m, 2H), 1.09–1.14 (m, 2H), 1.76–1.91 (m, 2H), 1.95–2.02 (m, 2H), 2.03 (t, J=8 Hz, 2H), 2.20–2.27 (m, 2H), 2.58 (ttt, J=8, 2.5, 2.5 Hz, 2H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=0.04 (t), 1.04 (t), 16.51 (t), 26.38 (t), 32.46 (t), 34.03 (t), 50.83 (s), 107.99 (s), 136.37 (s); MS (EI): *m*/*e*=134 (5, M^+), 91 (100); $C_{10}H_{14}$ requires C, 89.49; H, 10.51. Found: C, 89.51; H, 10.53.

4.1.7. Dispiro[3.0.3.2]decan-1-one (7) and dispiro[2.0.3.3]decan-5-one (22). *A. From* **20**. To a stirred solution of **20** (26.0 g, 0.10 mol) in ether (300 ml) was added at 5–7 °C within 30 min 50% aqueous tetrafluoroboric acid (60 ml). The mixture was allowed to warm to room temperature and the reaction progress was monitored by GC [column A, 245 °C; retention time (min): 18.8 (**20**)]. After 6 h, more tetrafluoroboric acid (10 ml) was added, and after 22 h the reaction was complete. Sodium bicarbonate (50 g, 0.60 mol) was added in portions, and the organic phase was separated, washed with 5% aqueous potassium hydroxide (2×150 ml), water (2×150 ml) and dried ($MgSO_4$). The solvent was distilled off and the residue fractionated to yield 7.8 g (52%) of a 72:28-mixture of **7** and **22** as colorless liquid, bp 78–80 °C/13 Torr. Analytically pure samples were obtained by preparative GC [3 m×1/4″ all-glass system, 15% FFAP on Chromosorb W AW/DMCS 60/80 mesh, 180 °C; retention times (min): 3.11 (**7**), 3.44 (**22**)]. **7**: IR (neat): 1770 cm^{-1} (C=O); ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.65–1.74 (m, 1H), 1.74–1.90 (m, 6H), 1.90–1.98 (m, 1H), 1.99–2.06 (m, 1H), 2.13–2.23 (m, 3H), 2.83 (m_c, 2H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=16.05 (t), 19.82 (t), 25.23 (t), 30.87 (t), 31.04 (t), 31.16 (t), 43.28 (t), 48.23 (s), 70.80 (s), 213.42 (s); MS (EI): *m*/*e*=150 (17, M^+), 79 (100); $C_{10}H_{14}O$ requires C, 79.96; H, 9.39. Found: C, 80.10; H, 9.46. **22**: IR (neat): 1765 cm^{-1} (C=O); ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=0.31–0.37 (m, 1H), 0.43–0.56 (m, 3H), 1.52–1.60 (m, 1H),

1.64–1.84 (m, 6H), 2.10–2.16 (m, 1H), 2.61 (m_c, 1H), 2.85 (m_c, 1H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=8.55 (t), 9.14 (t), 20.76 (t), 22.51 (t), 26.98 (s), 35.10 (t), 35.97 (t), 42.59 (t), 72.72 (s), 215.52 (s); MS (EI): *m/e*=150 (6, M^+), 79 (100); $C_{10}H_{14}O$ requires C, 79.96; H, 9.39. Found: C, 80.14; H, 9.55.

B. From **21**. To a vigorously stirred solution of **21** (26.8 g, 200 mol) in dichloromethane (350 ml) was added a 0.7 M aqueous solution of sodium bicarbonate (500 ml), and, within 2.5 h at 5 °C, a solution of 3-chloro-peroxybenzoic acid (54.3 g, 70% w/w, 220 mol) in dichloromethane (500 ml). After 1 h, the reaction was complete according to GC [column A, 160 °C; retention times (min): 1.45 (**21**), 3.00 (epoxide), 4.51 (**7**), 5.08 (**22**)]. The organic layer was washed with 1 N NaOH (200 ml), dried (K_2CO_3/$MgSO_4$), and concentrated to approximately 500 ml by distillation over a 40 cm vigreux column. Solid potassium carbonate (1.0 g) was added to the remaining solution, until it was cooled to 5 °C and borontrifluoride etherate (300 mg, 2.1 mmol) was added drop by drop, causing an exothermic reaction, which with the last drops subsided. After the addition was complete, the mixture was stirred for 30 min at room temperature, until it was washed with 1 N NaOH (50 ml), water (150 ml), and dried (K_2CO_3/$MgSO_4$). The solvent was distilled off over a 40 cm vigreux column and the residue fractionated to yield 25.9 g (86%) of a 80:20-mixture of **7** and **22** as colorless liquid, bp 85–88 °C/13 Torr (purity 97% GC). Analytically pure samples were obtained by preparative GC. Their NMR data were identical with those of authentic samples.

4.1.8. 1-Methylene-dispiro[3.0.3.2]decane (9) and 5-methylene-dispiro[2.0.3.3]decane (23). To a suspension of methyltriphenylphosphonium bromide (78.5 g, 220 mmol) in anhydrous ether (450 ml) was added under argon with stirring potassium-*t*-butoxide (24.6 g, 220 mmol) and the mixture heated to reflux. After 1 h, a 80:20-mixture of **7** and **22** (25.5 g, 170 mmol) was added dropwise, and after additional 1 h of reflux the reaction was complete according to GC [column A, 160 °C; retention times (min): 1.39 (**9**), 1.54 (**23**), 4.51 (**7**), 5.08 (**22**)]. The mixture was hydrolyzed with saturated aqueous ammonium chloride (15 ml), the liquid phase was decanted, the residue was extracted with pentane (3×200 ml), and the combined organic phases were filtrated, washed with water (3×200 ml) and dried ($MgSO_4$). Most of the solvents were distilled off over a 40 cm vigreux column (bath temperature up to 70 °C), the residue was diluted with pentane (200 ml), and, after filtration, first concentrated by distillation over a 20 cm vigreux column (bath temperature up to 135 °C) and then fractionated over a microdistillation apparatus to yield 22.9 g (91%) of a 80:20-mixture of **9** and **23** as colorless liquid, bp 95 °C/55 Torr. Analytically pure samples were obtained by preparative GC. **9**: IR (neat): 1669 cm^{-1} (C=C); ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.61–1.69 (m, 1H), 1.69–1.85 (m, 7H), 1.91–1.97 (m, 1H), 2.05–2.14 (m, 3H), 2.41–2.53 (m, 2H), 4.73 (t, *J*=2.5 Hz, 1H), 4.75 (t, *J*=2.0 Hz, 1H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=15.48 (t), 26.42 (t), 27.92 (t), 29.28 (t), 30.35 (t), 30.36 (t), 31.37 (t), 49.02 (s), 56.02 (s), 103.29 (t), 155.55 (s); MS (EI): *m/e*=148 (14, M^+), 79 (100); $C_{11}H_{16}$ requires C, 89.12; H, 10.88. Found: C, 89.24; H, 10.88. **23**: IR (neat): 1670 cm^{-1} (C=C); ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=0.27–0.34 (m, 2H), 0.40–0.48 (m, 1H), 0.48–0.56 (m, 1H), 1.52–1.60 (m, 1H), 1.62–1.82 (m, 8H), 1.87–1.94 (m, 1H), 2.29 (m_c, 1H), 2.48 (m_c, 1H), 4.67 (t, *J*=2.5 Hz, 1H), 4.70 (t, *J*=2.0 Hz, 1H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=8.29 (t), 10.21 (t), 21.55 (t), 27.17 (t), 28.39 (t), 28.46 (s), 34.68 (t), 39.70 (t), 57.16 (s), 104.42 (t), 156.36 (s); MS (EI): *m/e*=148 (1, M^+), 120 (100); $C_{11}H_{16}$ requires C, 89.12; H, 10.88. Found: C, 89.06; H, 10.86.

4.1.9. (5*R,6*R**)-Tetraspiro[3.0.0.0.3.2.2.2]hexadecan-11-one [(5*R**,6*R**)-11] and (5*R**,6*S**)-tetraspiro-[3.0.0.0.3.2.2.2]hexadecan-11-one [(5*R**,6*S**)-12].** To a solution of **18** (8.40 g, 50 mmol) in dichloromethane (50 ml) was added at −15 °C under argon with stirring trifluoromethanesulfonic acid anhydride (16.9 g, 60 mmol), and, within 20 min, a solution of 2,4,6-collidine (7.26 g, 60 mmol) in a 78:22-mixture of **9** and **23** (14.8 g, 100 mmol). The mixture was heated for 44 to reflux and then concentrated on a rotary evaporator (bath temperature 35 °C/15 Torr). The residual black oil was extracted with anhydrous ether (4×70 ml), and the remaining material hydrolyzed in a two-phase system of dichloromethane (70 ml) and water (70 ml). After 2 h of reflux, GC analysis [column A, 230 °C; retention times (min): 4.48 (**18**), 5.76 (**11/12**)] indicated the presence of a 60:40-mixture of **11/12** and **18**. The organic phase was washed with 2 N H_2SO_4 (60 ml), dried ($MgSO_4$/K_2CO_3) and concentrated on a rotary evaporator (bath temperature 35 °C/15 Torr). The residual brown oil (21.5 g) was extracted with pentane/ether (1:1; 2×100 ml), the combined extracts were concentrated on a rotary evaporator (bath temperature 35 °C/15 Torr), and the remaining oil (10.7 g) was chromatographed first on silica gel (0.05–0.20 mm) in pentane/ether [95:5, column 70×5 cm, R_f=0.36–0.39 (**11/12**)] yielding 3.43 g (30%) of a 92:8-mixture of **11** and **12** (^{1}H NMR), and then on silica gel (0.040–0.063 mm) in pentane/ether [97:3, column 70×5 cm, R_f=0.21 (**11**), 0.19 (**12**)] yielding 2.42 g (21%) of pure **11** and 0.50 g (4%) of a 2:1-mixture of **11** and **12** (^{1}H NMR) as colorless oils. **12** could not be obtained pure. **12**: ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): only the protons neighboring the carbonyl group could be assigned: δ=2.60 (*J*=17 Hz, 1H), 2.88 (*J*=17 Hz, 1H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): all resonances could be assigned: δ=15.33 (t), 16.28 (t), 25.46 (t), 27.14 (t), 27.80 (t), 28.27 (t), 28.96 (t), 31.21 (t), 31.21 (t), 31.94 (t), 46.60 (s), 47.42 (s), 50.64 (t), 54.28 (s), 66.13 (s) 213.17 (s). **11**: ^{1}H NMR (600 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.55–1.90 (m, 10H), 1.95–2.25 (m, 9H), 2.36–2.43 (m, 1H), 2.71 (d, *J*=17 Hz, 1H), 3.31 (d, *J*=17 Hz, 1H); ^{13}C NMR (150.8 MHz, $CDCl_3$, $CDCl_3$ int): δ=15.46 (t), 16.56 (t), 26.26 (t), 26.60 (t), 26.90 (t), 26.97 (t), 27.09 (t), 30.48 (t), 31.34 (t), 32.08 (t), 43.81 (s), 48.91 (s), 50.61 (t), 52.57 (s), 67.76 (s), 213.17 (s); MS (EI): *m/e*=230 (<1, M^+), 120 (100); $C_{16}H_{22}O$ requires C, 83.43; H, 9.63. Found: C, 83.55; H, 9.67.

4.1.10. *rac*-Tetraspiro[3.0.0.0.3.2.2.2]hexadecane [*rac*-24]. To a solution of hydrazine hydrate (300 mg, 6.0 mmol) and powdered potassium hydroxide (450 mg, 8.0 mmol) in diethylene glycol (4.0 ml) was added under argon with stirring **11** (230 mg, 1.0 mmol). The mixture was heated for 2 h to 160 °C, until it was diluted with water (40 ml) and

extracted with pentane (3×20 ml). The combined extracts were washed with water (30 ml), dried ($MgSO_4$), and concentrated using a 20 cm vigreux column. Last traces of solvent were evaporized under reduced pressure yielding 207 mg (96%) of *rac*-**24** as colorless oil (purity 97% GC). The enantiomers could be resolved by capillary gas chromatography on a chiral phase [column C, 105 °C, retention times (min): 40.32/41.49 (*rac*-**24**)]. An analytically pure sample was obtained by preparative GC [column A, 200 °C; retention time (min): 3.01 (*rac*-**24**)]. ^{1}H NMR (500 MHz, $CDCl_3$, $CHCl_3$ int): δ=1.45 (m_c, 2H), 1.53–1.63 (m, 4H), 1.64–1.72 (m, 2H), 1.75–1.94 (m, 10H), 1.98–2.05 (m, 2H), 2.25 (m_c, 2H), 2.35–2.44 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$, $CDCl_3$ int): δ=15.74 (t), 26.43 (t), 26.51 (t), 30.70 (t), 31.31 (t), 32.37 (t), 49.21 (s), 52.34 (s); MS (EI): *m*/*e*=216 (<1, M^+), 120 (96), 79 (100); $C_{16}H_{24}$ requires C, 88.82; H, 11.18. Found: C, 88.71; H, 10.90.

4.1.11. (1′*S*,5*S*,6*S*)-2-(*N*′-Tetraspiro[3.0.0.0.3.2.2.2]hexadec-11-ylidene-hydrazino)-2-oxo-*N*-(1-phenyl-ethyl)-acetamide [(1′*S*,5*R*,6*S*)-25] and (1′*S*,5*R*,6*R*)-2-(*N*′-tetraspiro[3.0.0.0.3.2.2.2]hexadec-11-ylidene-hydrazino)-2-oxo-*N*-(1-phenyl-ethyl)-acetamide [(1′*S*,5*S*,6*R*)-26]. To a suspension of (*S*)-(−)-2-hydrazino-2-oxo-*N*-(1-phenyl-ethyl)-acetamide[7] (2.59 g, 12.5 mmol) in benzene (200 ml) was added under argon with stirring **11** (1.15 g, 5.0 mmol) and a 0.74 M solution of anhydrous *p*-toluenesulfonic acid in benzene (10 ml, 7.4 mmol). The mixture was heated to reflux and the reaction progress monitored by TLC in pentane/ether [1:1; R_f=0.77 (**11**), 0.33 (**26**), 0.28 (**25**)]. After 2 h more acetamide (0.52 g, 2.5 mmol) was added, and after an additional hour the reaction was complete. The mixture was filtrated, the residue was washed with ether (2×50 ml), and the combined filtrates were washed with saturated sodium carbonate (50 ml), water (100 ml), and dried ($MgSO_4$). The solvents were distilled off (bath temperature 60 °C/15 Torr), and the remaining material (2.70 g) was chromatographed on silica gel (0.05–0.20 mm) in pentane/ether [1:1, column 100×6.5 cm; R_f=0.77 (**11**), 0.33 (**26**), 0.28 (**25**)] yielding 690 mg (33%) of **26** as sticky oil, 290 mg (14%) of a 3:1-mixture of **25** and **26** as waxy solid, and 480 mg (23%) of **25** as amorphous solid, mp 116–117 °C. **25**: ^{1}H NMR (300 MHz, C_6D_6, C_6D_5H int): δ=1.08–1.18 (m, 1H), 1.13 (d, *J*=7 Hz, 3H), 1.32–1.42 (m, 1H), 1.45–1.80 (m, 10H), 1.80–2.00 (m, 3H), 1.90 (d, *J*=16 Hz, 1H), 2.04–2.32 (m, 5H), 2.66 (d, *J*=16 Hz, 1H), 5.10 (dq, *J*=9, 7 Hz, 1H), 6.96–7.14 (m, 5H), 8.10 (d, *J*=9 Hz, 1H), 9.84 (s, 1H); ^{13}C NMR (150.8 MHz, C_6D_6, C_6D_6 int): δ=16.02 (t), 16.85 (t), 21.80 (q), 26.87 (t), 26.91 (t), 27.05 (t), 28.67 (t), 29.79 (t), 30.98 (t), 31.73 (t), 32.45 (t), 37.10 (t), 47.37 (s), 48.99 (s), 50.03 (d), 52.86 (s), 58.64 (s), 126.83 (d), 127.63 (d), 128.97 (d), 143.44 (s), 155.75 (s), 159.79 (s), 167.95 (s). **26**: ^{1}H NMR (300 MHz, C_6D_6, C_6D_5H int): δ=1.12–1.20 (m, 1H), 1.20 (d, *J*=7 Hz, 3H), 1.32–1.44 (m, 1H), 1.46–1.82 (m, 10H), 1.82–2.00 (m, 3H), 1.92 (d, *J*=16 Hz, 1H), 2.00–2.30 (m, 5H), 2.69 (d, *J*=16 Hz, 1H), 5.12 (dq, *J*=9, 7 Hz, 1H), 6.98–7.12 (m, 3H), 7.16–7.22 (m, 2H), 8.34 (d, *J*=9 Hz, 1H), 9.87 (s, 1H); ^{13}C NMR (150.8 MHz, C_6D_6, C_6D_6 int): δ=15.87 (t), 16.72 (t), 21.57 (q), 26.69 (t), 26.76 (t), 26.89 (t), 28.55 (t), 29.54 (t), 30.81 (t), 31.56 (t), 32.30 (t), 36.90 (t), 47.21 (s), 48.84 (s), 49.83 (d), 52.72 (s), 58.51 (s), 126.62 (d), 127.50 (d), 128.83 (d), 143.22 (s), 155.53 (s), 159.63 (s), 167.79 (s).

4.1.12. (5*S*,6*S*)-(−)-Tetraspiro[3.0.0.0.3.2.2.2]hexadecan-11-one [(5*S*,6*S*)-11]. To a solution of (1′*S*,5*S*,6*S*)-**25** (356 mg, 0.85 mmol) in benzene (25 ml) was added 60% H_2SO_4 (4.0 ml). The resulting two-phase system was vigorously stirred at room temperature. According to TLC [pentane/ether (1:1); R_f=0.77 (**11**), 0.28 (**25**)], after 1 h the hydrolysis was complete. The organic phase was decanted, the heterogeneous residue was extracted with benzene (10 ml), and the combined organic phases were washed with water (10 ml) and dried ($MgSO_4$). Evaporation of the solvent (bath temperature 55 °C/15 Torr) yielded 190 mg (97%) of crude (5*S*,6*S*)-**11** (purity 97% GC). Preparative GC [column A, 230 °C; retention time (min): 5.76 (**11**)] yielded an analytically pure sample as colorless oil (94% ee; $[\alpha]_D^{20}$=−46.3, *c*=1.09, acetone). For the preparation of (*M*)-**24**, the crude material was used. The ^{1}H NMR data were identical with those of racemic **11**. UV (CH_3OH): λ_{max}=292 nm, ε=14; CD (CH_3OH): $[\theta]_{302}$=+1964.

4.1.13. (5*R*,6*R*)-(+)-Tetraspiro[3.0.0.0.3.2.2.2]hexadecan-11-one [(5*R*,6*R*)-11]. (1′*S*,5*R*,6*R*)-**26** (587 mg, 1.40 mmol) was hydrolyzed as described for (1′*S*,5*S*,6*S*)-**25** yielding 292 mg (90%) of crude (5*R*,6*R*)-**11** (purity 97% GC). Preparative GC [column A, 230 °C; retention time (min): 5.76 (**11**)] yielded an analytically pure sample as colorless oil (92% ee; $[\alpha]_D^{20}$=+45.9°, *c*=1.09, acetone). For the preparation of (*P*)-**24**, the crude material was used. The ^{1}H NMR data were identical with those of racemic **11**.

4.1.14. (*M*)-(−)-Tetraspiro[3.0.0.0.3.2.2.2]hexadecane [(*M*)-24]. To a solution of hydrazine hydrate (150 mg, 3.0 mmol) and powdered potassium hydroxide (224 mg, 4.0 mmol) in diethylene glycol (2 ml) was added under argon with stirring (5*S*,6*S*)-**11** (99 mg, 0.43 mmol) and the mixture heated to 160 °C. After 1 h, the mixture was diluted with water (20 ml) and extracted with pentane (3×15 ml). The extracts were washed with water (20 ml), dried ($MgSO_4$) and concentrated on a rotary evaporator (bath temperature 40 °C/15 Torr) to yield 87 mg (93%) of crude (*M*)-**24** (purity 97% GC). Preparative GC [column A, 200 °C; retention time (min): 3.01 (*M*)-**24**)] yielded 40 mg of analytically pure (*M*)-**24** as colorless oil ($[\alpha]_D^{20}$=−24.2°, *c*=1.17, $CHCl_3$). According to capillary chromatography on a chiral phase [column C, 105 °C, retention times (min): 40.68 (*M*)-**24**, 41.13 (*P*)-**24**], the material contained 3% (*P*)-**24** (94% ee). The ^{1}H NMR data were identical with those of racemic **24**.

4.1.15. (*P*)-(+)-Tetraspiro[3.0.0.0.3.2.2.2]hexadecane [(*P*)-24]. (5*R*,6*R*)-**11** (150 mg, 0.65 mmol) was reduced as described for (5*S*,6*S*)-**11** yielding 110 mg (79%) of crude (*P*)-**24** (purity 97% GC). Preparative GC [column A, 200 °C; retention time (min): 3.01 (*M*)-**24**)] yielded 56 mg of analytically pure (*P*)-**24** as colorless oil ($[\alpha]_D^{20}$=+23.9°, *c*=1.18, $CHCl_3$). According to capillary chromatography on a chiral phase [column C, 105 °C, retention times (min): 39.70 (*M*)-**24**, 41.49 (*P*)-**24**], the material contained 4% (*M*)-**24** (92% ee). The ^{1}H NMR data were identical with those of racemic **24**.

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