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Syntheses and Structural Properties of Distellenes

Rolf Gleiter,* Gerd Fritzsche, Oliver Borzyk, Thomas Oeser, Frank Rominger, and
Hermann Irngartinger

Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270,
D-69120 Heidelberg, Germany

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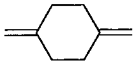
The syntheses of a mixture of the racemic (**a**) and the meso form (**b**) of several derivatives of 2,2′-bi(tricyclo[3.3.0.0^{3,7}]octylidene) are described: The 6,6′-diisopropylidene- (**4**), 6,6′-dimethylidene- (**5**), 6,6′-dione- (**6**), *syn*-4,4′-dione- (**7**), *anti*-4,4′-dione- (**8**), *syn*-4-methylidene-4′-one- (**9**), *anti*-4-methylidene-4′-one- (**10**), *syn*-4,4′-dimethylidene- (**11**), and *anti*-4,4′-dimethylidene- (**12**) derivatives. Starting materials for all compounds were tricyclo[3.3.0.0^{3,7}]octane-2,4-diol (**19**) and its 2,6-isomer **20**. Key reaction was the McMurry coupling of 6-isopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-one (**23**) or 6-methylidenetricyclo[3.3.0.0^{3,7}]octan-2-one (**24**) to yield **4** or **5**, respectively. The McMurry coupling of the ketone **26** yielded **7** and **8**. From the latter, species **9**−**12** could be generated via the Wittig reaction. In most cases only the racemates could be isolated. X-ray investigations on **4a** revealed a separation of the isopropylidene groups by 10.3 Å. The central C−C bridging bonds of the stellane units in **4a**, **7a**, **8a**, **12a**, and **30** C(1)−C(5), C(3)−C(7), C(1)−C(5′), C(3′)−C(7′) were found to be between 1.596(2) and 1.616(3) Å. In **4a** we found a twisting between the terminal isopropylidene groups by a torsion ($(CH_3)_2C{=}C\cdots C{=}C(CH_3)_2$) of 74° and 83°, respectively, in both independent molecules. The twist angle between the CO groups in **7a** amounts to 53°, and in **8a** to 118°. The same twist angle was found between the *exo*-methylidene groups in **12a**.

Electron-transfer reactions play important roles in chemistry and biology.[1,2] There are different approaches to study such reactions: either one uses complex models which are close to nature or very simple ones which capture the essence only. In the latter approach donor and acceptor units are connected to a rigid σ-scaffold. In the models investigated so far the distance and orientation of the π-system have been varied. In those compounds where both π-systems are separated by more than 3 Å the through-bond coupling should dominate, therefore the nature of the σ-system should be important. To test this we have started a program in which one varies not only the distance between two π-moieties but also increases the bridging.[3] If the bridges are small the angle strain within the scaffold is increased which usually leads to an increase of the p-character of the C−C bonds.[4] A series of simple model compounds are 1,4-cyclohexylidene (**1**), 2,5-dimethylidenebicyclo[2.2.1]heptane (**2**), and 2,6-dimethylidenetricyclo[3.3.0.0^{3,7}]octane (2,6-stelladiene, **3**). In these series the number of methylidene bridges and the angle strain within the central scaffold increase. Investigations by means of PE spectroscopy on **1**[5] and **3**[6] have shown that the energy difference between the π-ionization energies increases from **1** ($\Delta I_\pi = 0.5$ eV) to **3** ($\Delta I_\pi = 0.9$ eV).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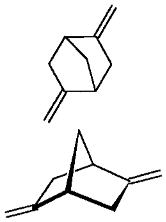
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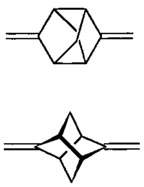
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In continuation of this work we have prepared stelladienes with donor and acceptor groups on opposite sides and have made efforts to extend the central stellane skeleton to two stellane units. In this paper we report on our synthesis of 6,6′-diisopropylidene-2,2′-bi(tricyclo-[3.3.0.0^{3,7}]octylidene) (**4**), 6,6′-dimethylidene-2,2′-bi(tricyclo[3.3.0.0^{3,7}]octylidene (**5**), 2,2′-bi(tricyclo[3.3.0.0^{3,7}]-octylidene)-6,6′-dione (**6**), *syn*-2,2′-bi(tricyclo[3.3.0.0^{3,7}]-octylidene)-4,4′-dione (**7**), *anti*-2,2′-bi(tricyclo[3.3.0.0^{3,7}] octylidene)-4,4′-dione (**8**), *syn*-4-methylidene-2,2′-bi(tricyclo[3.3.0.0^{3,7}]octylidene)-4′-one (**9**), *anti*-4-methylidene-2,2′bi(tricyclo[3.3.0.0^{3,7}]octylidene)-4′-one (**10**), *syn*-4,4′-dimethylidene-2,2′-bi(tricyclo[3.3.0.0^{3,7}]octylidene) (**11**), and *anti*-4,4′-dimethylidene-2,2′-bi(tricyclo[3.3.0.0^{3,7}]-octylidene) (**12**). Common to all of them are two stellane units and, for the racemic forms **a**, a helical arrangement of the three π-systems.

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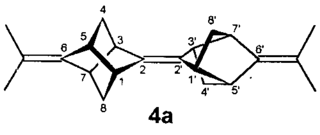
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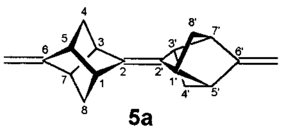
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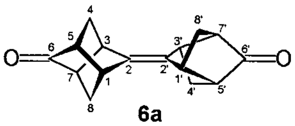
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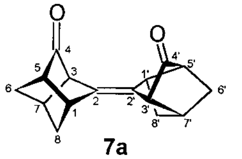
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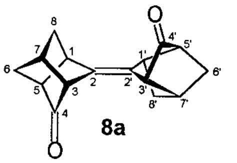
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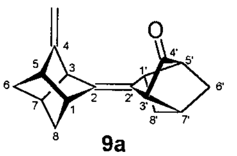
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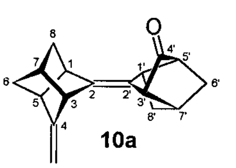
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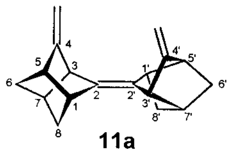
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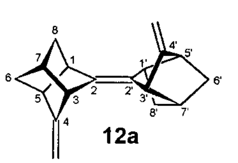
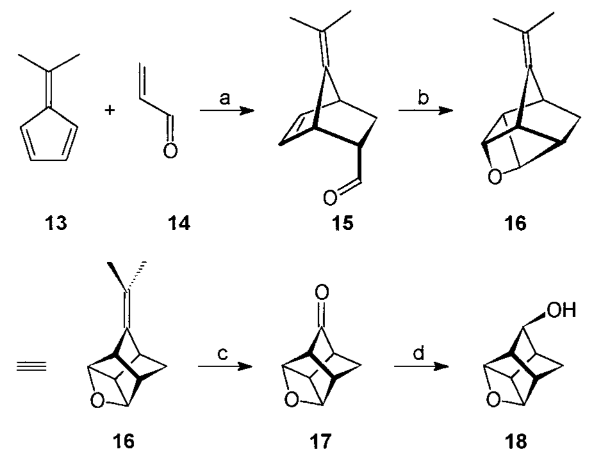

12a

Syntheses of Distellenes

The stellane systems needed for our purposes could be prepared by using protocols developed by Sauers et al.[7,8] and Nakazaki et al.[9,10] As an example we show in Scheme 1 the synthesis of 4-oxatetracyclo[4.2.1.0.^{2,5}0^{3,7}]nonan-8-one (**17**),[11-13] a key compound in our further syntheses. The reaction between 6,6-dimethylfulvene[13] and acrolein afforded *endo*-2-formyl-7-isopropylidene-bicyclo[2.2.1]hept-5-ene (**15**), which could be transformed to 8-isopropylidene-4-oxatetracyclo[4.2.1.0.^{2,5}0^{3,7}]nonane (**16**) upon irradiation. Ozonolysis of **16** yielded **17** which could be reduced by $LiEt_3BH$[14] to 4-oxatetracyclo-[4.2.1.^{2,5}0^{3,7}]nonan-8-ol (**18**).

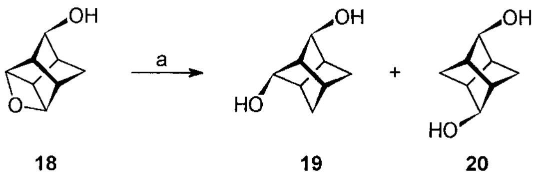
Starting from **18** we followed different routes. Our first route is summarized in Schemes 2 and 3. To cleave the oxetane ring of **18** it was treated with lithium in EDA.[7] This gave a 1:1 mixture of 2,4- and 2,6-dihydroxystellane **19** and **20**, respectively, in 89% yield: no side products could be isolated. These alcohols could be separated and further reactions were carried out with the individual isomers.

Scheme 1[a]



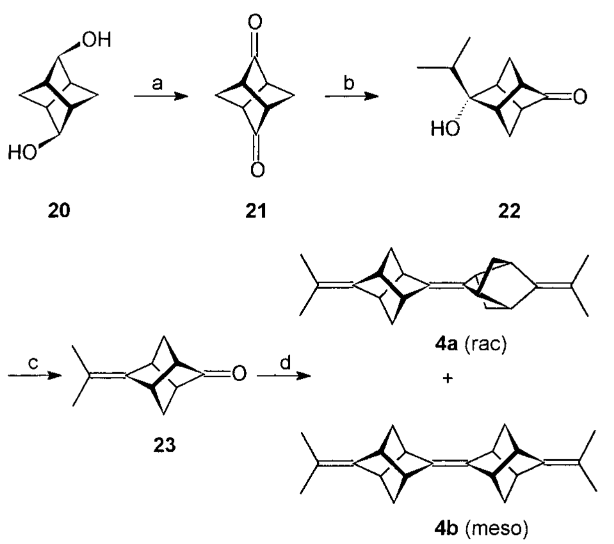
[a] Reagents, conditions, and yields: (a) 2 d, rt; (b) *hν* (250 nm), Et_2O, 2 d, 43% (steps a and b); (c) O_3, CH_2Cl_2/DMS, 62%; (d) $LiEt_3BH$, THF, 0 °C, 17 h, 94%.

Scheme 2[a]



[a] Reagents, conditions, and yields: (a) Li, EDA, 45% (**19**), 44% (**20**).

Scheme 3[a]



[a] Reagents, conditions, and yields: (a) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, −60 °C, 82%; (b) isopropyllithium (pentane), THF, 0 °C, 65%; (c) $POCl_3$, pyridine, 0 °C, 76%; (d) $TiCl_3 \cdot (DME)_{1.5}$, Zn/Cu, DME, 45 °C, 16.5 h, 1.3%.

The main difference of our approach of the syntheses of **21**[13] to that of Nakazaki et al.[12] was that we reduced the ketone **17** to **18**. In the latter compound the cleavage of the oxetane was possible while in **17** all efforts were in vain.[12] This difference in reactivity of **17** and **18** allowed us to produce larger amounts of **19** and **20**.

The oxidation of **20** to 2,6-stelladione (**21**)[12,13] could be accomplished in 82% yield with a mixture of oxalyl chloride/DMSO/triethylamine following a protocol pro-

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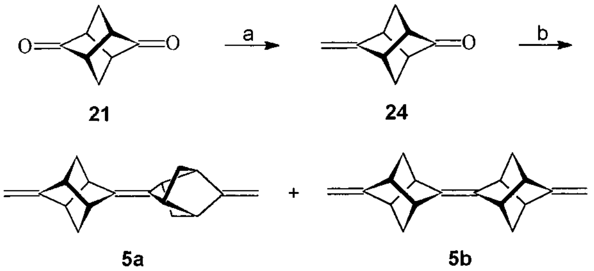
Scheme 4[a]



[a] Reagent, conditions, and yields: (a) $(C_6H_5)_3PCH_3Br$, $NaNH_2$, Et_2O, 54%; (b) $TiCl_3$·$(DME)_{1.5}$, Zn(Cu), DME, 40 °C, 12%.

posed by Swern et al.[16] The reaction of **21** with 1 equiv of isopropyllithium[17] gave in 65% yield the alcohol **22** (Scheme 3), which could be dehydrated to 6-isopropylidenetricyclo[3.3.0.0^{3,7}]octan-2-one (**23**). Treatment of the latter with low valent titanium[18] yielded the racemic mixture of 6,6′-diisopropylidene-2,2′-bi(tricyclo[3.3.0.0^{3,7}]-octylidene) (**4a**) and its meso isomer **4b** in the ratio of 98:2. In the case of **4a** we were able to isolate single crystals which have been investigated by means of the X-ray technique (see below).

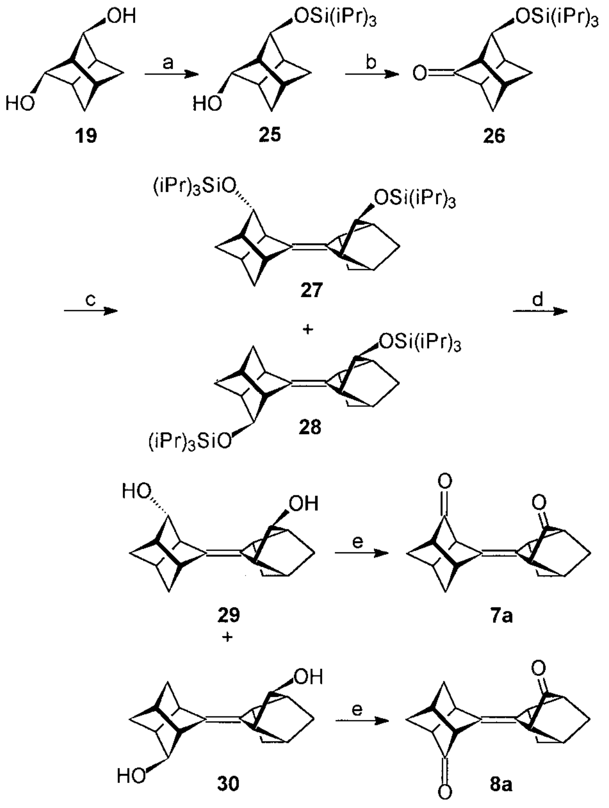
The diketone **21** can be transformed to 6-methylidenetricyclo[3.3.0.0^{3,7}]octan-2-one (**24**)[19] by treating **21** with triphenylmethylphosphonium bromide and sodium amide (instant ylide) in ether. Two equivalents of **24** could be coupled[18] to 6,6′-dimethylidene-2,2′-bi(tricyclo[3.3.0.0^{3,7}]-octylidene) (distella-2,2′,6,6′-triene) obtained as a mixture of the racemic (**5a**) and the meso (**5b**) form.

Treatment of the 2,4-diol **19** with 0.56 equiv of triisopropylsilyl (TIPS) triflate yielded the monosubstitution product **25** in 47% yield. Subsequent oxidation of **25** by the Swern reagent[16] gave in good yield the ketone **26** (Scheme 5).

Coupling of two units of **26** could be achieved with low valent titanium[18] to yield a mixture of **27** and **28**. Treatment of this mixture with a solution of tetrabutylammonium fluoride in THF gave an 1:1 mixture of the diastereomeric alcohols **29** and **30** in 99% yield. Structures of these alcohols are assigned on spectroscopic data and X-ray investigations on single crystals of **30** which clearly reveal the *anti*-arrangement of the OH-groups. Our findings show that the McMurry coupling of **26** favors the racemic form of the distellene nucleus probably because of steric reasons. The alcohols **29** and **30** could be separated by chromatography. Their oxidation yielded *syn*-2,2′-bi(tricyclo[3.3.0.0^{3,7}]octylidene)-4,4′-dione (**7a**) and *anti*-2,2′-bi(tricyclo[3.3.0.0^{3,7}] octylidene)-4,4′-dione (**8a**). We were able to grow single crystals of both diketones suitable for X-ray investigations (see below).

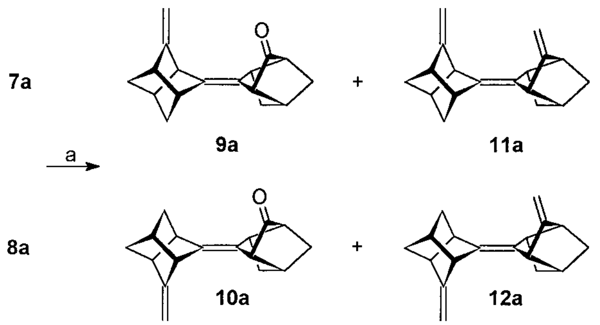
Treatment of **7a** with a mixture of methyltriphenylphosphonium bromide and sodium amide in THF yielded **9a** and **11a**. Analogously **10a** and **12a** could be obtained from **8a** via a Wittig reaction (see Scheme 6).

Scheme 5[a]



[a] Reagents, conditions, and yields: (a) TIPS-triflate, lutidine, CH_2Cl_2, THF, rt, 47%; (b) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, −60 °C, 78%; (c) $TiCl_3$·$(DME)_{1.5}$, Zn(Cu), DME, 45 °C, 40%; (d) Bu_4NF, THF, 0 °C, 99%; (e) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, −60 °C, 72% (**7a**), 47% (**8a**).

Scheme 6[a]



[a] Reagents, conditions, and yields: (a) $(C_6H_5)_3PCH_3Br$, $NaNH_2$, THF, 14% (**9a**), 31% (**10a**), 2,2% (**11a**), 15% (**12a**).

In the case of **12a** we were able to grow single crystals suitable for X-ray investigations (see below).

6,6′-Bis(tricyclo[3.3.0.0.^{3,7}]octylidene)-2,2′-dione (**6**) represents an isomer of **7** and **8**; two diastereomers, one belonging to point group D_2 (**6a**) and one to C_{2h} (**6b**), are possible. The protocol for the synthesis of both isomers is shown in Scheme 7. The starting material for synthesizing **6** was **31** which could be obtained from **18** by reaction with triisopropylsilyl triflate in the presence of lutidine as base. We chose this protecting group because the trimethylsilyl group was not stable under the reaction conditions. The oxetane ring of **31** could be cleaved by treating the latter with Li in ethylenediamine (EDA). In addition to the anticipated alcohols **25** and **32** we found as side products **36** and **37**. The mechanism for the

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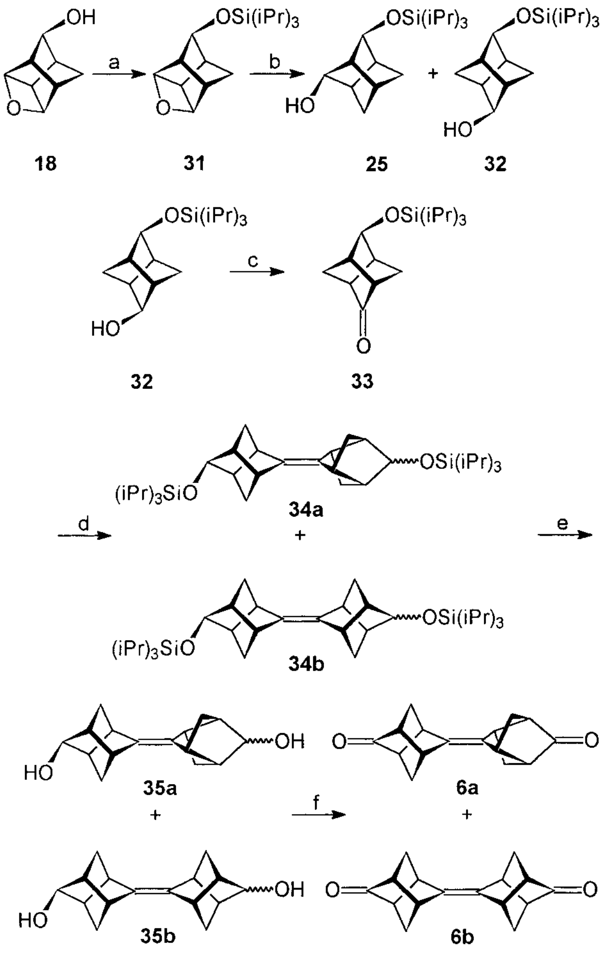
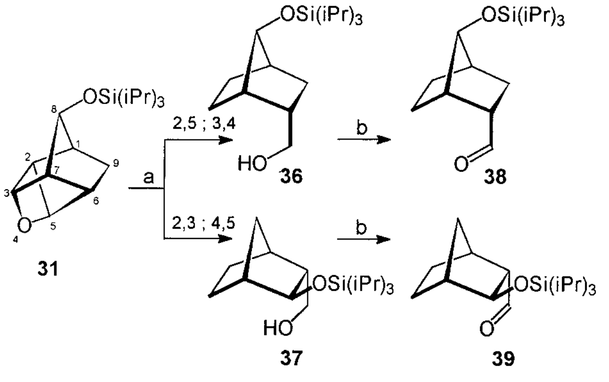
Scheme 7[a]



[a] Reagents, conditions, and yields: (a) TIPS-triflate, lutidine, CH_2Cl_2, 0 °C, 85%; (b) Li, EDA, 39% (**21**), 38% (**28**); (c) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, −60 °C, 65%; (d) $TiCl_3\cdot(DME)_{1.5}$, Zn(Cu), DME, 40 °C, 59%; (e) Bu_4NF, THF, 0 °C, 86%; (f) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, −60 °C, 75%.

Scheme 8[a]



[a] Reagents and conditions: (a) Li, EDA; (b) $(COCl)_2$, DMSO, NEt_3, $CHCl_2$, −60 °C.

formation of these species requires that for **36** the 2,5 and 3,4 bonds of **31** have to be broken while for **37** it is the 2,3 and 4,5 bonds (Scheme 8). A related cleavage was reported by Sauers et al.[8] for the reaction of 4-oxatetracyclo[4.2.1.0.^{2,5}0.^{3,7}]nonane. Since both side products, **36** and **37**, exhibit properties similar to **25** and **32**, their separation proved to be very inefficient. A better procedure was achieved by oxidation of the mixture followed by separation. The better way of obtaining the pure monosilylated alcohol **25**, however, was the reaction of **19** (Scheme 2) with the silylating reagent. After oxidation of the mixture of the four alcohols **25**, **32**, **36**, and **37** with the Swern reagent[16] we obtained a mixture of the ketones **26** and **33** together with **38** and **39**. The pure ketones **26** and **33** were obtained according to the sequence in Schemes 5 and 7, respectively. At this stage we were able to separate all four products without much loss. The treatment of **33** with low valent titanium led to the desired coupling products **34a** and **34b** in 60% yield. This reaction had to be carried out at 40 °C or below in DME. At higher temperatures no defined products could be isolated, while at 40° the main product was the alcohol **32**. The diastereomeric mixture (**34a**, **34b**) could not be separated. Treatment of the mixture with tetrabutylammonium fluoride in THF gave in high yields a mixture of the diastereomeric alcohols **35a**[21] and **35b**[21] which could not be separated. The oxidation of the mixture by the Swern procedure finally led to **6a** and **6b** in 75% yield. Our efforts to separate this mixture were in vain. Chromatographic evidence suggests that the racemic product **6a** was the main compound.

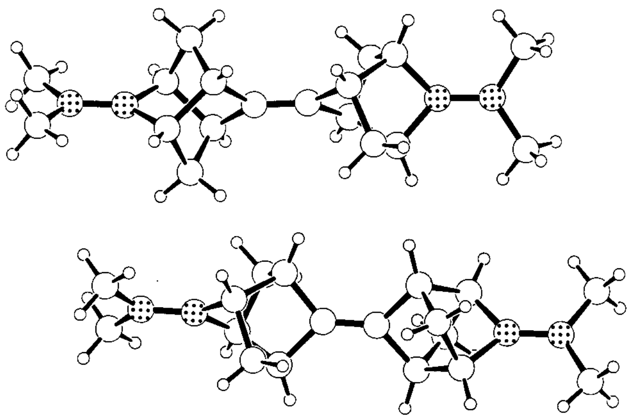


Figure 1. Molecular structure of **4a**. The two independent molecules in the unit cell are shown. The sp^2-hybridized carbon atoms of the isopropylidene groups are stipled.

X-ray Diffraction Analysis of 4a, 7a, 8a, 12a, and 30. Single crystals of **4a**, **7a**, **8a**, **12a** and **30** could be obtained. The molecular structures of **4a**, **7a**, **8a**, **12a**, and **30** are shown in Figures 1−3. In the case of **4a** two independent molecules are found in the unit cell. In accordance to former studies on stelladienes[20] and 2,6-stelladienone[13] we find long central bonds in the stellane fragments of all five species, i.e., bonds C(1)−C(5), C(3)−C(7), C(1′)−C(5′), and C(3′)−C(7′). In **4a** the central distances between the bridgehead carbon atoms of each stellane unit vary between 1.605(4) and 1.616(3) Å; in **7a** the central C−C distances of each stellane unit alternate between 1.596(2) and 1.601(2) Å, in **8a** between 1.600(2) and 1.604(2), in **12a** between 1.606(3) and 1.616(3), and in **30** between 1.605(2) and 1.611(2) Å. The distance between the sp^2 centers of the isopropylidene groups amounts to 10.33 Å in **4a**. In **7a** and **8a** the distances between the oxygen atoms were measured to be 5.025 and 6.552 Å, respectively.

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(21) The proposed structure of this compound is based solely on NMR data.

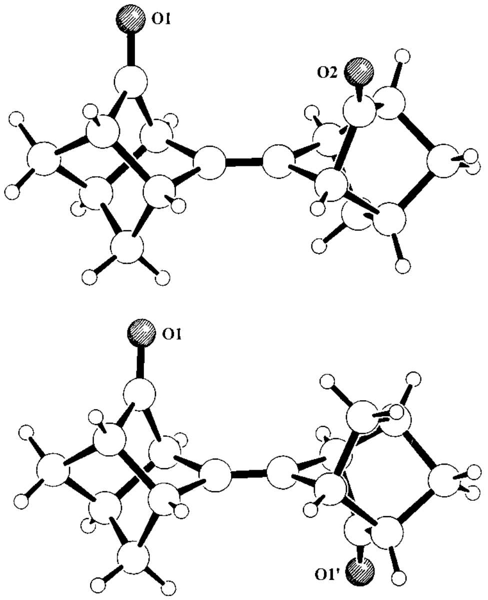

Figure 2. Molecular structures of **7a** (top) and **8a** (bottom). The oxygen atoms are indicated with shaded circles.

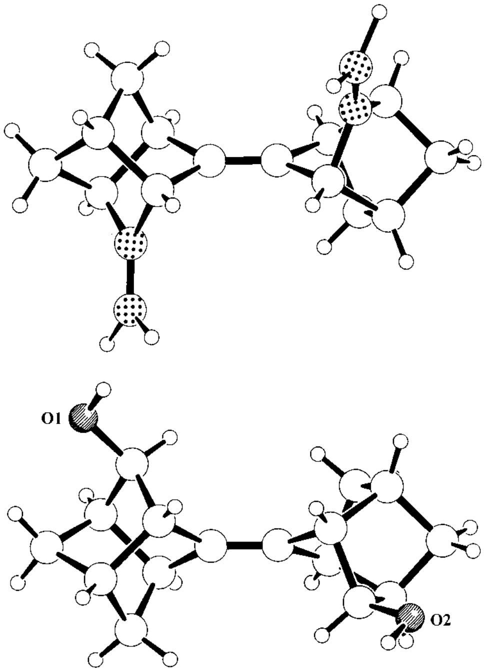

Figure 3. Molecular structures of **12a** (top) and **30** (bottom). The sp^2-hybridized carbon atoms of the *exo*-methylidene groups in **12a** are stipled.

The length of the central C−C double bond remains essentially constant. **4a**: 1.320(3) Å and 1.318(3) Å in both independent molecules, **7a**: 1.319(1) Å, **8a**: 1.318(2) Å, **12a**: 1.318(4) Å, and **30**: 1.315(2) Å.

The twist angle between the terminal isopropylidene groups of both independent molecules **4a** in the unit cell defined by a torsion ($(CH_3)_2C{=}C\cdots C{=}C(CH_3)_2$) amounts to 74° and 83°, respectively. It is interesting to note that the central double bond in **4a** is slightly twisted by 10° and 14.5°, respectively, for both molecules in the unit cell. The twist angle between the CO groups in **7a** amounts to 53° and to 118.5° in **8a**. The same twist angle (118.5°) was found between the *exo*-methylidene groups of **12a**. We anticipate for **4a**, **7a**, **8a**, and **12a** high optical rotatory power.

We ascribe the elongation of the central bonds in each of the stellane units C(1)−C(5), C(3)−C(7), C(1′)−C(5′), C(3′)−C(7′) to strain energy. The strain is mostly due to a reduction of the angles at the sp^2 and sp^3 centers. In the case of the central bonds of each stellane unit the eclipsed conformation along the central bond adds additional strain (C−C−C−C torsional angles in the range of 0.2(1)−4.4(1)°). Especially large is the angle deformation at the sp^2 centers in the stellane units. The angles vary. **4a**: 95.3(2)−96.1(2), **7a**: 96.81(8)−97.44(8), **8a**: 96.97(8)−97.30(8), **12a**: 96.1(2)−96.4(2).

Experimental Section

General procedures and characterization methods are as described elsewhere.[15] To determine the R_f values on TLC we use anisaldehyde for detection. Microanalyses were carried out at the analytical laboratory of the "Chemisches Institut der Universität Heidelberg".

General Procedure for the McMurry Coupling.[18] All reactions were carried out under argon atmosphere in dry and oxygen free solvents. The complex between dimethoxyethane (DME) and $TiCl_3$ as well as the zinc−copper couple were prepared as follows: To 100 g $TiCl_3$ (0.65 mol) was added by distillation 1.5 L DME. After refluxing 2 d, the suspension was filtered off, washed with dry pentane, and dried under vacuum at rt.

To 19.6 g of zinc dust was added 80 mL of oxygen free water under argon. Subsequently 1.5 g of dry $CuSO_4$ was added by bubbling argon through the solution. The dark colored suspension was filtered off and washed with 80 mL of dry and oxygen free acetone followed by 80 mL of dry and oxygen free ether. The powder was dried under vacuum at rt. The McMurry coupling was carried out in a glovebox under argon with less than 0.8 ppm oxygen.

6-Hydroxy-6-isopropyltricyclo[3.3.0.0^{3,7}]octan-2-one (22). Freshly prepared isopropyllithium[17] (88.2 mL of a 0.5 M solution in *n*-pentane) was added dropwise over a period of 2 h to a magnetically stirred solution of dione **21**[13] (4 g, 29.4 mmol) in dry THF (100 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and allowed to warm to room temperature before being poured into cold 2% aqueous HCl and extracted twice with ethyl acetate. The combined organic layers were washed with 5% aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated. Purification of the residue by silica gel chromatography, elution with pentane−ether (1/1) gave **22** (3.45 g, 65%) as a colorless liquid: R_f (silica gel, pentane−ether (1/1)) = 0.16; ^{1}H NMR (300 MHz) δ 0.93−0.95 (d, ^3J = 6.8 Hz, 3H), 0.99−1.01 (d, ^3J = 6.7 Hz, 3H), 1.30−1.35 (dd, ^2J = 12.6 Hz, ^3J = 2.1 Hz, 1H), 1.39−1.43 (dd, ^2J = 11.7 Hz, ^3J = 2.0 Hz, 1H), 1.71 (s, br, 1H), 1.80−1.93 (hept, ^3J = 6.8 Hz, 1H), 1.97−2.02 (dd, ^2J = 12.6 Hz, ^3J = 2.9 Hz, 1H), 2.15−2.17 (m, br, 1H), 2.19−2.21 (m, br, 1H), 2.25−2.29 (m, br, 1H), 2.37−2.40 (m, br, 1H), 2.67−2.71 (dd, ^2J = 11.7 Hz, ^3J = 3.0 Hz, 1H); ^{13}C NMR (75.47 MHz) δ 14.9 (q), 17.1 (q), 31.2 (d), 32.4 (t), 34.2 (t), 40.6 (d), 43.3 (d), 46.0 (d), 46.4 (d), 87.3 (s), 210.0 (s), MS(GC) *m*/*z* 180 (0.1) [M$^+$], 162 (1), 137 (18), 119 (11), 109 (56), 95 (13), 93 (17), 91 (24), 82 (20), 81 (100), 80 (16), 79 (47), 77 (15); HRMS calcd for $C_{11}H_{16}O_2$ 180.11504, found 180.11499; IR (neat film) 3467, 3013, 2966, 2932, 2876, 1756, 1490, 1469, 1369, 1261, 12207 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ϵ) = 278 (1.64). Anal. Calcd for $C_{11}H_{18}O$ (180.11): C, 73.30; H, 8.95. Found C. 73.00; H, 9.16.

6-Isopropylidenetricyclo[3.3.0.0^{3,7}]octane-2-one (23). Phosphorus oxychloride (1.45 mL, 15.6 mmol) was added dropwise to a magnetically stirred solution of alcohol **22** (644 mg, 3.57 mmol) and 24.9 mL of dry pyridine at 0 °C. The reaction was stirred for 72 h at room temperature. The reaction mixture was poured into ice−water. Extraction was effected with ether (3×), and the combined ether solutions were washed with 5% aqueous HCl and brine. The separated organic layer was evaporated and after purification of the residue by silica gel chromatography (elution with pentane−ether (20/1), 527.3 mg (91%) of product was obtained as a colorless liquid: R_f (silica gel, pentane−ether (20/1)) = 0.19; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.43−1.48 (dd, ^2J = 10.8 Hz, ^3J = 2.5 Hz, 2H), 1.57−1.62 (m, 2H), 1.65 (s, 6H), 2.15−2.17 (m, 2H), 2.91−2.93 (m, 2H); ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 19.8 (q), 37.2 (d), 38.2 (t), 44.1 (d), 113.3 (s), 143.7 (s), 213.1 (s); MS(GC) *m/z* 162 (32) [M$^+$], 134 (19), 119 (67), 107 (100), 106 (39); IR (neat film) 3011, 2974, 2929, 2865, 1771, 1451, 1372 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ϵ) = 232 (3.02). Anal. Calcd for $C_{11}H_{14}O$ (162.23): C, 81.44; H, 8.70. Found: C, 81.38; H, 8.99.

***rac*-6,6′-Diisopropylidene-2,2′-bi(tricyclo[3.3.0.0^{3,7}]-octylidene) (4a) and *meso*-6,6′-Diisopropylidene-2,2′-bi(tricyclo[3.3.0.0^{3,7}]octylidene) (4b).** $TiCl_3{\cdot}(DME)_{1.5}$ (11.63 g, 35.8 mmol) and Zn(Cu) (9.34 g, 143 mmol) in dry DME (120 mL) were refluxed for 3 h to yield a black suspension. The mixture was cooled to 45 °C, and ketone **23** (1.392 g, 8.57 mmol) in 10 mL of DME was added. The mixture was stirred at 45−50 °C for 16.5 h. After being cooled to room temperature, the reaction mixture was diluted with pentane (120 mL), filtered through a pad of florisil, and evaporated. Further purification of the residue by silica gel chromatography (elution with pentane) gave 16 mg (1.3%) of products **4a** and **4b** (98:2) as colorless crystals (from pentane at −30 °C): **4a**: mp 138 °C; R_f (silica gel, pentane) = 0.65; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.28 (m, 8H), 1.57 (s, 12H), 2.54 (s, br, 4H), 2.65 (s, br, 4H); ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 19.6 (q), 38.6 (d), 39.8 (d), 44.0 (t), 107.9 (s), 132.0 (s), 148.7 (s); MS(GC) *m/z* 292 (100) [M$^+$], 277 (36), 249 (19); HRMS calcd for $C_{22}H_{28}$ 292.2191, found 292.2174; IR (KBr) 2994, 2926, 2859, 1709, 1449, 1369, 1277, 1254 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ϵ) = 226 (3.93), **4b**: ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 19.6 (q), 39.3 (d), 39.9 (d), 44.1 (t), 107.9 (s), 132.0 (s), 148.7 (s).

6-Methylidenetricyclo[3.3.0.0^{3,7}]octan-2-one (24).[19] At 0 °C a mixture of 6.2 g of methyltriphenylphosphonium bromide/$NaNH_2$ (instant ylide, 14.9 mmol phosphonium salt) in dry ether (120 mL) was stirred for 0.5 h. A solution of dione **21**[12,13] (1.35 g, 10 mmol) in dry ether (60 mL) was added, and the reaction was stirred for 23 h at room temperature. After addition of pentane (160 mL), the mixture was filtered on silica gel. The filtrate was evaporated, and the residue was chromatographed on silica gel (elution with pentane−ether (2/1), to yield **24** (724 mg, 54%) as a colorless solid: mp: 32 °C; R_f (silica gel, pentane−ether (2/1)) = 0.29; ^{1}H NMR (300 MHz) δ 1.64 (ddd, ^1J = 24.7 Hz, $^3J_1$ = 11.3 Hz, $^3J_2$ = 1.1 Hz, 4H), 2.25 (dd, ^4J = 5.1 Hz, ^3J = 2.6 Hz, 2H), 2.72 (s, 2H), 4.64 (s, 2H); ^{13}C NMR (75.47 MHz) δ 38.2 (t), 40.1 (d), 44.0 (d), 96.5 (t), 158.5 (s), 212.0 (s); MS(GC) *m/z* 134 (31) [M$^+$], 133 (13), 105 (34), 92 (13), 91 (100), 79 (42; IR (KBr) 3075, 1770, 860 cm^{-1}; UV/vis (isooctane) λ_{max} [nm] (log ϵ) = 286 (24.1). Anal. Calcd for $C_9H_{10}O$ (134.18): C, 80.56; H, 7.51. Found:: C, 80.56; H, 7.52.

***rac,meso*-6,6′-Dimethylidene-2,2′-bi(tricyclo-[3.3.0.0^{3,7}]octylidene) (5a, 5b).** $TiCl_3{\cdot}(DME)_{1.5}$ (5.2 g, 17.9 mmol) and Zn(Cu) (4.9 g, 69 mmol) in dry DME (100 mL) were refluxed for 6 h to yield a black suspension. The mixture was cooled to 40 °C, and enone **24** (323 mg, 2.4 mmol) in 12 mL of DME was added. The mixture was stirred at 40 °C for 19 h. After being cooled to room temperature, the reaction mixture was diluted with pentane (100 mL), filtered through a pad of florisil, and evaporated. Further purification of the residue by silica gel chromatography (elution with pentane) gave 31 mg (12%) of product **5a** and **5b** (98:2) as a white solid: mp 111 °C; R_f (silica gel, pentane) = 0.53; ^{1}H NMR (300 MHz) δ 1.33−1.47 (m, 8H), 2.47−2.48 (m, 4H); 2.57−2.59 (m, 4H), 4.34 (s, 4H); ^{13}C NMR (75.47 MHz) δ 38.7 (d), 41.9 (d), 44.4 (t), 91.8 (t), 131.5 (s), 163.8 (s); MS(GC) *m/z* 237 (29) [M$^+$ + 1], 236 (100) [M$^+$], 181 (22), 180 (38); IR ($CDCl_3$) 2992, 2950, 2930, 2858, 1690, 1676, 1662, 1462 cm^{-1}; UV/vis (CH_3CN) λ_{max} [nm] (log ϵ) = 254 (2.21). Anal. Calcd for $C_{18}H_{20}$ (236.35): C, 91.47; H, 8.53. Found: C, 91.33; H, 8.76.

2-(Triisopropylsiloxy)tricyclo[3.3.0.0^{3,7}]octan-4-ol (25). To a magnetically stirred solution of diol (**19**)[13] (5.5 g, 39.2 mmol) in dry THF (500 mL) was added dropwise a solution of triisopropylsilyl triflate (5.86 mL, 21.8 mmol) and 2,6-lutidine (3.8 mL, 32.7 mmol) in CH_2Cl_2 (1 L) via syringe pump over a period of 30 h at room temperature. The reaction mixture was hydrolyzed with water (5 mL), evaporated, and directly chromatographed on silica gel (elution with pentane−ether (1/1)) to give **25** (5.5 g, 47.1%; selectivity: 86.8%), as a colorless liquid; further elution with ether gave diol **19** (2.5 g, 17.9 mmol): **25**: R_f (silica gel, pentane−ether (1/1)) = 0.63; ^{1}H NMR (300 MHz) δ 1.02−1.05 (m, 21 H), 1.29−1.38 (m, 2H), 1.69 (m 1H), 2.00−2.03 (m, 1H), 2.18−2.21 (m, 2H), 2.28−2.31 (m, 1H), 2.33−2.38 (m, 1H), 2.57−2.62 (m, 1H), 4.03 (m, 2H); ^{13}C NMR (50.32 MHz) δ 12.0 (d), 18.0 (q), 34.6 (d), 38.3 (t), 38.7 (t), 42.1 (d), 43.4 (d), 50.3 (d), 77.2 (d), 77.7 (d); MS(GC) *m/z* 296 (1) [M$^+$], 254 (19), 253 (90); IR (neat film) 3321, 2943, 2894, 2866, 1496, 1464 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ϵ) = 230 (1.7). Anal. Calcd for $C_{17}H_{32}O_2Si$ (296.52): C, 68.86; H, 10.88; Found: C, 68.63; H, 10.83.

2-(Triisopropylsiloxy)tricyclo[3.3.0.0^{3,7}]octan-4-one (26). To a stirred solution of oxalyl chloride (7.0 mL, 82.0 mmol) in dry CH_2Cl_2 (1.4 l) was added dry DMSO (11.6 mL, 164 mmol) at −50 to −60 °C.[16] After the mixture was stirred for 2 min, a solution of alcohol **25** (20.26 g, 68.3 mmol) in dry CH_2Cl_2 (200 mL) was added dropwise at −50 to −60 °C. The reaction mixture was stirred for 15 min, treated with triethylamine (57.1 mL, 410 mmol), and allowed to warm to room temperature before cold water was added. Extraction was effected with CH_2Cl_2 (3×), and the combined organic layers were washed with aqueous HCl (5%), aqueous $NaHCO_3$ (5%), water, and brine, dried ($MgSO_4$) and evaporated. Purification by silica gel chromatography (elution with pentane-ether (10/1) gave **26** (15.69 g, 78%) as a colorless liquid: R_f (silica gel, pentane−ether (10/1)) = 0.44; ^{1}H NMR (200 MHz) δ 0.98−0.99 (m, 21H), 1.41−1.52 (m, 2H), 1.65−1.72 (dd, ^2J = 11.0 Hz, ^3J = 2.9 Hz, 1H), 2.07−2.10 (m, 1H), 2.25 (m, br, 1H), 2.47 (m, 1H), 2.55−2.61 (m, 2H), 3.96−3.97 (d, ^3J = 2.5 Hz, 1H); ^{13}C NMR (50.32 MHz) δ 11.8 (d), 17.8 (q), 34.3 (d), 36.1 (t), 38.4 (t), 43.7 (d), 47.2 (d), 52.4 (d), 78.0 (d), 210.2 (s); MS(GC) *m/z* 294 (8) [M$^+$], 251 (17), 131 (34), 103 (95), 93 (12); IR (KBr) 2944, 2892, 2867, 1775, 1465, 1398, 1388 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ϵ) = 288 (1.83). Anal. Calcd for $C_{17}H_{30}SiO_2$ (294.53): C, 69.33; H, 10.27. Found: C, 69.33; H, 10.39.

***syn*-4,4′-Bis(triisopropylsiloxy)-2,2′-bi(tricyclo-[3.3.0.0^{3,7}]octylidene) (27) and *anti*-4,4′-Bis(triisopropylsiloxy)-2,2′-bi(tricyclo[3.3.0.0^{3,7}]octylidene) (28).** $TiCl_3{\cdot}(DME)_{1.5}$ (24.4 g, 75.0 mmol) and Zn(Cu) (19.6 g, 300 mmol) in dry DME (280 mL) were refluxed for 3 h to yield a black suspension. The mixture was cooled to 44 °C, and ketone **26** (5.3 g, 18.0 mmol) in 15 mL of DME was added. The mixture was stirred at 44 °C for 18 h. After being cooled to room temperature, the reaction mixture was diluted with pentane (200 mL), filtered through a pad of florisil (elution with ether), and evaporated. Further purification of the residue by silica gel chromatography (elution with pentane) gave 5.01 g (40.1%) of product **27**[21] and **28** (1:1) as a colorless solid: **27**: R_f (silica gel, pentane) = 0.46; ^{1}H NMR (200 MHz) δ 1.09 (s, 42H), 1.13−1.28 (m, 4H), 1.46−1.51 (dd, ^2J = 8.9 Hz, ^3J = 2.6 Hz, 2H), 2.03−2.04 (m, 2H), 2.26−2.34 (m, 4H), 2.43−2.49 (m, 4H), 3.73−3.75 (d, ^2J = 2.9 Hz, 2H); ^{13}C NMR (50.32 MHz) δ 11.9 (d), 17.7 (q), 17.8 (q), 35.0 (d), 37.5 (t), 39.8 (d), 41.1 (d), 44.5 (t), 46.6 (d), 81.7 (d), 128.0 (s); **28**: mp 85−86 °C; R_f (SiO_2, pentane) = 0.49; ^{1}H NMR (300 MHz) δ 1.01 (s, 42H), 1.13−1.16 (d, ^2J = 8.9 Hz, 2H), 1.22−1.24 (d, ^2J = 7.3 Hz, 2H), 1.46−1.50 (dd, ^2J = 8.9 Hz, ^3J = 2.5 Hz, 2H), 2,03 (m, 2H), 2.22 (m, 4H), 2.41−2.44 (m, 4H), 3.66−3.67 (d, ^2J = 2.9 Hz, 2H); ^{13}C NMR (75.47 MHz) δ 11.9 (d), 17.7 (q), 17.8 (q), 34.9 (d), 37.5 (t), 39.4 (d), 41.1 (d), 44.5 (t), 46.6 (d), 81.5 (d), 128.0 (s); MS *m/z* 556 (1) [M$^+$], 214 (19), 213 (100), 171 (43); IR (KBr) 2945, 2867, 1632, 1464, 1387 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ϵ) = 230 (2.75). Anal. Calcd for $C_{34}H_{60}O_2Si_2$ (557.02): C, 73.31; H, 10.86. Found: C, 73.14; H, 10.89.

***syn*-2,2′-Bi(tricyclo[3.3.0.0^{3,7}]octylidene)-4,4′-diol (29) and *anti*-2,2′-Bi(tricyclo[3.3.0.0^{3,7}]octylidene)-4,4′-diol (30).** To a solution of protected diols (**27**/**28**) (2.648 g, 4.75 mmol) in anhydrous THF (60 mL) was added a 0.1 M solution of (*n*-

Bu)$_4$NF (10.45 mL, 10.45 mmol) in THF at 0 °C. The mixture was stirred at 0 °C for 10 min and then allowed to warm to room temperature. After the mixture was stirred for 20 h at room temperature, it was hydrolyzed with water (1 mL), evaporated, and separated on silica gel (elution with pentane−ether (1/2)) to give the diols in a ratio of 1:1 (1.149 g, 99%) as colorless solids which could be crystallized from pentane−ether (1/2) at room temperature: **29**: mp 197 °C; R_f (silica gel, pentane-ether (1/2)) = 0.21; ^{1}H NMR (300 MHz, THF-d_8) δ 1.01−1.12 (m, 2H), 1.18−1.21 (m, 2H), 1.42−1.46 (dd, ^2J = 8.8 Hz, ^3J = 2.3 Hz, 2H), 2.00 (m, 2H), 2.18 (m, 2H), 2.23 (m, 2H), 2.40 (m, 2H), 2.44−2.47 (m, 2H), 3.65−3.66 (m, 2H), 4.07−4.08 (d, ^3J = 3.5 Hz, 2H); ^{13}C NMR (50.32 MHz, THF-d_8) δ 36.0(d), 38.1 (t), 40.8 (d), 41.4 (d), 45.0 (t), 46.6 (t), 81.6 (d), 129.4 (s); MS(GC) m/z 244 (0.2) [M$^+$], 200 (1), 187 (12), 169 (12), 144 (13), 143 (13), 132 (14), 131 (100); IR (KBr) 3390, 2982, 2927, 1632, 1484, 1346 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ϵ) = 230 (2.76). Anal. Calcd for $C_{16}H_{20}O_2$ (244.33): C, 78.65; H, 8.25. Found: C, 78.53; H, 8.31. **30**: mp: 236 °C, R_f (silica gel, pentane-ether (1/2)) = 0.29; ^{1}H NMR (300 MHz, THF-d_8) δ 1.16−1.22 (m, 4H), 1.45−1.49 (dd, ^2J = 8.9 Hz, ^3J = 2.5 Hz, 2H), 1.97−1.98 (m, 2H), 2.19 (m, 4H), 2.44−2.46 (m, 4H), 3.58−3.59 (m, 2H), 3.94−3.95 (d, ^3J = 3.5 Hz, 2H); ^{13}C NMR (50.32 MHz, THF-d_8) δ 36.1 (d), 38.2 (t), 40.6 (d), 41.5 (d), 45.2 (t), 47.0 (d), 81.6 (d), 129.6 (s); MS(GC) m/z 244 (0.2) [M$^+$], 187 (16), 143 (11), 132 (13), 131 (100), 129 (14), 128 (11), 115 (12), 91 (25), 79 (13), 77 (13), 57 (32); IR (KBr) 3411, 2980, 2927, 2877, 1637, 1484, 1329; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ϵ) = 230 (2.22). Anal. Calcd for $C_{16}H_{20}O_2$ (244.33): C, 78.65; H, 8.25. Found: C, 78.53; H, 8.25.

***syn*-2,2′-Bi(tricyclo[3.3.0.0^{3,7}]octylidene)-4,4′-dione (7a).** The Swern oxidation[16] of diol **29** was accomplished in the same way as the oxidation of alcohol **25**. Thus, **29** (0.733 g, 3.00 mmol) yielded **7a** (530 mg, 72%) as a colorless crystalline solid which could be crystallized from pentane-ether (1/1) at room temperature: mp 156 °C, R_f (silica gel, pentane−ether (1/1)) = 0.39; ^{1}H NMR (300 MHz) δ 1.54−1.58 (m, 2H), 1.62−1.73 (m, 6H), 2.42 (m, 2H), 2.69 (m, 2H), 2.75−2.77 (m, 2H), 2.86−2.88 (m, 2H); ^{13}C NMR (75.47 MHz) δ 36.3 (d), 38.4 (t), 39.4 (d), 40.8 (t), 46.7 (d), 49.1 (d), 129.5 (s), 203.2 (s); MS(GC) m/z 240 (7) [M$^+$], 185 (19), 157 (18), 130 (15), 129 (19), 128 (13), 115 (19), 91 (27), 79 (13), 77 (14), 65 (13), 55 (100), 51 (11); IR (KBr) 3003, 2977, 2883, 1769, 1479, 1450 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ϵ) = 232 (4.15), 306 (3.64), 316 (3.76). Anal. Calcd for $C_{16}H_{16}O_2$ (240.30): C, 79.97; H, 6.71. Found: C, 79.82; H, 6.89.

***anti*-2,2′-Bi(tricyclo[3.3.0.0^{3,7}]octylidene)-4,4′-dione (8a).** The Swern oxidation[16] of diol **30** was accomplished in the same way as the oxidation of alcohol **25**. Thus, **30** (0.744 g, 3.04 mmol) yielded **8a** (263 mg, 36%) as a colorless crystalline solid which could be crystallized from pentane−ether (1/1) at room temperature: mp 143 °C, R_f (silica gel, pentane−ether (1/1)) = 0.48; ^{1}H NMR (300 MHz) δ 1.59−1.72 (m, 8H), 2.41 (m, 2H), 2.62−2.64 (m, 2H), 2.69 (m, 2H), 3.01−3.03 (m, 2H); ^{13}C NMR (75.47 MHz) δ 36.4 (d), 38.4(t), 39.5 (d), 40.7 (t), 46.7 (d), 49.3 (d), 129.8 (s), 204.3 (s); MS(GC) m/z 240 (22) [M$^+$], 213 (10), 212 (54), 206 (15), 204 (45), 202 (48), 186 (11), 185 (64), 184 (14), 171 (15), 169 (22), 167 (14), 158 (14), 157 (75), 156 (17), 155 (31), 153 (10), 143 (32), 142 (34), 141 (31), 131 (14), 130 (64), 129 (66), 128 (46), 127 (15), 118 (11), 117 (30), 116 (23), 115 (69), 105 (10), 103 (14), 102 (10), 92 (18), 91 (100), 89 (15); IR (KBr) 3044, 3019, 3995, 2984, 2955, 2885, 1759, 1636, 1481 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} [nm] (logϵ) = 232 (4.14), 282 (3.04), 316 (3.73). Anal. Calcd for $C_{16}H_{16}O_2$ (240.30): C, 79.97; H, 6.71. Found: C, 79.79; H, 6.72.

4-Oxa-8-(triisopropylsiloxy)tetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (31). To a solution of 960 mg (7 mmol) of **18** in 20 mL of dry CH_2Cl_2 was added dropwise at 0 °C 2.1 mL (17 mmol) of freshly distilled 2,6-lutidine and 2.4 mL (9 mmol) of triisopropylsilyl triflate. After stirring for 2 h at 0 °C, 20 mL of H_2O was added. The water phase was extracted with CH_2Cl_2. After separation the organic phase was dried with $MgSO_4$ and the solvent removed. The pink colored residue was purified by column chromatography on silica gel (pentane/ether 8:1) to yield 1.74 g (85%) of **27** as colorless oil. R_f (silica gel, pentane/ether (8/1)) = 0.27. ^{1}H NMR (300 MHz) δ 4.68−4.65 (1H, m), 4.60−4.56 (1H, m), 3.85 (1H, d, J = 2.6 Hz), 3.15−3.14 (1H, m), 2.65 (1H, d, J = 1.9 Hz), 2.56 (1H, d, J = 2.1 Hz), 2.48 ((1H, dd, J_1 = 10.5 Hz, J_2 = 2.4 Hz), 1.88 (1H, S), 1.44 (1H, dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz), 1.04−1.05 (m, 21H); ^{13}C NMR (75.47 MHz) δ 90.61 (d), 85.85 (d), 78.77 (d), 55.32 (d), 49.64 (d), 41.88 (d), 41.84 (d), 35.80 (t), 18.14 (q), 12.23 (d); MS m/z 294 (1) [M$^+$], 251 (29), 229 (50), 185 (60), 179 (17), 157 (14), 151 (13), 143 (30), 131 (23), 115 (100) 105 (21), 103 (48), 101 (12), 99 (15), 93 (11), 91 (41), 87 (15), 79 (30); IR (neat) 2936, 2858, 2848, 1461; UV/vis (CH_3CN) λ_{max} [nm] (log ϵ) 230 (2.01). Anal. Calcd for $C_{17}H_{30}SiO_2$ (294.51): C, 69.33; H, 10.27. Found: C 69.21; H, 10.27.

Cleavage of the Oxetane Ring of 31. To a magnetically stirred solution of 13.14 g (45 mmol) of **31** in 15 mL of anhydrous ethylenediamine (EDA) was added 312 mg (145 mmol) of lithium powder under an Ar atmosphere together with a few mL of a blue solution of Li in EDA. The reaction mixture turned blue under vigorous and exothermic reaction cooling. As the blue color disintegrates, 1.249 g (180 mmol) of lithium was added under cooling. After stirring the mixture at room temperature for 30 min, the reaction mixture was cooled and first ether and then water were added to destroy excess reagent. The aqueous layer was percolated with ether for 2 d. The organic phase was separated and dried ($MgSO_4$), and the solvent was removed. The residue was chromatographed on silica gel (pentane/ether (2/1)) to yield 5.97 g (39%) of **25** and 3.04 g (38%) of **32** as colorless oils. R_f **25** (silica gel, pentane/ether (2/1)) = 0.22; R_f **32** (silica gel, pentane/ether (2/1)) 0.14. Further products which could be isolated were a mixture of **36**[21] and **37**.[21] **32**: ^{1}H NMR (300 MHz) δ 4.08 (1H, s), 4.03 (1H, d, J = 2.8 Hz), 2.44−2.41 (1H, m), 2.20−2.17 (1H, m), 2.10 (3H, s), 2.05−2.03 (1H, m), 1.74 (1H, s), 1.36−1.29 (2H, m), 1.03 (21H, m); ^{13}C NMR (75.47 MHz) δ 82.89 (d), 82.61 (d), 42.49 (d), 42.33 (d), 42.33 (d), 40.77 (d), 39.34 (d), 32.64 (t), 31.99 (t), 18.00 (t), 12.08 (d); MS(GC) m/z 296 (1) [M$^+$], 255 (11) 253 (35), 211 (32), 157 (10), 151 (13), 145 (11), 131 (66), 122 (10), 119 (18), 115 (15), 107 (10), 105 (74), 103 (98), 91 (22), 87 (18), 79 (33), 77 (32), 75 (100), 73 (28), 67 (15); IR (neat) ν 3362, 2936, 2884, 2858, 1460; UV (CH_3CN) λ_{max} [nm] (log ϵ) 260 (1.75). Anal. Calcd for $C_{17}H_{32}SiO_2$ (296.53); C, 68.86, H, 10.88. Found: C, 68.68, H, 10.58. **36**: ^{1}H NMR (300 MHz) δ 4.09 (1H, s), 3.97−3.71 (1H, m), 3.67−3.60 (1H, m), 2.59−2.53 (1H, m), 2.10−1.08 (2H, m), 1.89−1.87 (1H, m), 1.61 (1H, s), 1.45−1.25 (3H, m), 1.04 (21H, s + 1H, m), 0.75−0.70 (1H, m); ^{13}C NMR (75.47 MHz) δ 81.19 (d), 64.75 (t), 42.57 (d), 41.17 (d), 39.25 (d), 31.53 (t), 26.65 (t), 19.64 (t), 18.02 (q), 2.27 (d). **37**: ^{13}C NMR (75.47 MHz) δ 78.41 (d), 63.08 (t), 55.52 (d), 45.01 (d), 36.76 (d), 35.97 (t), 24.59 (t), 21.70 (t), 18.09 (q), 12.27 (d)

Oxidation of a Mixture of 25, 32, 36, and 37. The Swern oxidation[16] of the mixture was accomplished in the same way as the oxidation of the pure alcohol **25**. Starting materials: 3.41 g (11.5 mmol) of **25** in 40 mL of CH_2Cl_2 containing small amounts of **36** and **37**, 3.41 g (11.5 mmol) of **32** in 46 mL of CH_2Cl_2 containing small amounts of **36** and **37**. Both **25** and **32** were oxidized separately with 1.6 mL (38 mmol) of DMSO in 20 mL of CH_2Cl_2 and 9 mL (64 mmol) of triethylamine to yield 1.9 g (56%) of **26** and 2.2 g (65%) of **33** as colorless oils. R_f **33** (silica gel, pentane/ether (10/1)) = 0.48; R_f **26** (silica gel, pentane/ether (10/1)) = 0.44. As side products we isolated two products for which we propose structures **38** and **39**. Only 5 mg of each could be isolated therefore only NMR data could be collected. **33**: ^{1}H NMR (300 MHz) δ 4.25 (1H, d, J = 2.8 Hz), 2.77 (1H, dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz), 2.38 (1H, m), 2.29 (1H, m), 2.27−2.23 (2H, m), 1,70 (1H, dd, J_1 = 2.0 Hz), 1.47 (1H, dd, J_1 = 11.4 Hz, J_2 = 2.0 Hz), 1.34 (1H, dd, J_1 = 11.7 Hz, J_2 = 2.5 Hz),1.06 (21H, s); ^{13}C NMR (75.47 MHz) δ 24.0 (s), 81.04 (d), 44.5 (d), 42.5 (d), 42.1 (d), 37,72 (d), 34.51 (t), 32.39 (t), 17.46 (q), 12.02 (d); IR ($CDCl_3$) 2938, 2860, 1758, 1150 cm^{-1}; UV/vis λ_{max} (CH_2CN) [nm] (log ϵ) 274 (2.1); MS(GC) m/z 294 (24) [M$^+$], 251 (50), 223 (19), 221 (13), 209 (12), 145 (12), 131 (43), 103 (100), 91 (11), 92 (13), 91 (57), 87 (12), 79 (13), 77 (28), 76 (11). Anal. Calcd for $C_{17}H_{30}SiO_2$ (294.53): C, 69.33; H, 10.27. Found: C, 69.23; H, 10.40. **38**:[21] ^{1}H NMR (300 MHz)

δ 9.87 (1H, d, J = 0.9 Hz), 4.15 (1H, s), 3.25−3.20 (1H, m), 2.39 (1H, m), 1.98 (1H, d, J = 3.3 Hz), 1.95−1.89 (1H, m), 1.75 (1H, dd, J_1 = 12.1 Hz, J_2 = 4.4 Hz), 1.58−1.31 (1H, m), 1.50−1.95 (1H, m), 1.27−1.20 (2H, m); 1.60 (21H, s); ^{13}C NMR (75.47 MHz) δ 205.96 (d), 81.04 (d), 52.02 (d), 43.41 (d), 41.78 (d), 26.67 (t), 26.19 (t), 21.34 (t), 17.97 (q), 12.06 (d). **39**:[21] ^{1}H NMR (300 MHz) δ 9.78 (1H, s), 4.13 (1H, s), 2.68 (1H, s), 2.64 (1H, s), 2.21 (1H, d, J = 4.9 Hz), 1.86 (1H, d, J = 9.7 Hz), 1.55−1.45 (1H, m), 1.31−1.26 (2H, m), 1.13−1.08 (2H, m), 1.03 (21H, s). ^{13}C NMR (75.47 MHz) δ 203.15 (d), 73,64 (d), 66.84 (d), 45. 58 (d), 37.63 (d), 36. 45 (t), 23.85 (t), 27.7 (t), 17.97 (q), 12.07 (d).

Preparation of *rac,meso*-6,6′-Bis(triisopropylsiloxy)-2,2′-bi(tricyclo[3.3.0.0^{3,7}]octylidene) (34a, 34b). The McMurry coupling[18] of **33** was carried out analogous to **26**. Starting materials: 3.80 g (13 mmol) of **33** in 30 mL of dry DME, 40 °C; 25.0 g (86 mmol) of TiCl$_3$·DME complex in 500 mL of DME, 17.4 g (245 mmol) of Zn(Cu) couple. This mixture was stirred at 40 °C for 19 h. After workup the product was chromatographed with silica gel (pentane) to afford 2.12 g (59%) of a mixture of **34a** and **34b** as a colorless solid; R_f (silica gel, pentane) = 0.29. ^{1}H NMR (300 MHz) δ 4.00−3.99 (2H, d, ^{3}J = 1.8 Hz), 2.58−2.54 (2H, m), 2.49−2.39 (4H, m), 2.06−2.03 (4H, m), 1.51−1.47 (2H, m), 1.26 (2H, m), 1.17−1.09 (2H, m), 1.05−1.04 (42H, m); ^{13}C NMR (75.47 MHz) δ 130.7 (s), 82.5 (d), 44.1 (d), 43.2 (d), 40.5 (d), 39.7 (d), 39.6 (d), 39.5 (d), 39.0 (t), 38.6 (t), 38.5 (t), 38.4 (t), 37.9 (d), 37.8 (d), 18.0 (q), 12.1 (d); IR (CDCl$_3$) 2934, 2880, 2856, 1276, 1268; MS(GC) *m*/*z* 557 (5) [M$^+$], 237 (20), 207 (14), 195 (100), 167 (14), 157 (11), 131 (47), 105 (14), 103 (50), 98 (15), 91 (11), 87 (14), 79 (20), 77 (10). Anal. Calcd for C$_{34}$H$_{60}$Si$_2$O$_2$ (557.02): C, 73.32; H, 10.86. Found: C, 72.99, H, 11.03

***rac,meso*-2,2′-Bi(tricyclo[3.3.0.0^{3,7}]octylidene)-6,6′-diol (35a and 35b).** To a solution of 2.2 g of a mixture of **34a** and **34b** (4 mmol) in 50 mL of dry THF was added at room temperature a 1 M solution of tetrabutylammonium fluoride in THF. The solution was stirred for 16 h at room temperature and hydrolyzed. The raw material was chromatographed on silica gel (pentane/ether (1/1)) to yield 0.82 g (86%) of a mixture of **35a**[21] and **35b**[21] as a colorless white material, mp 105 °C; R_f (silica gel, pentane/ether (1/1)) = 0.12. ^{1}H NMR (300 MHz, acetone-d_6) δ 3.97 (4H, s), 2.54 (2H, dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz), 2.47−2.41 (6H, m), 1.53 (2H, dd, J_1 = 9.5 Hz, J_2 = 2.4 Hz), 1.13−0.96 (6H, m); ^{13}C NMR (75.47 MHz, acetone-d_6) δ 131.2 (s), 43.3 (d), 43.3 (d), 43.3 (d), 39.7 (d), 39.3 (t), 38.9 (t), 38.2 (d); MS (70 eV) *m*/*z* 245 (1) [M$^+$ + 1], 244 (4) [M$^+$], 226 (9), 208 (4), 187 (37), 170 (22), 169 (41), 147 (41), 131 (100), 129 (63), 117 (37), 105 (44), 91 (79), 79 (53), 57 (66).

***rac,meso*-6,6′-Bi(tricyclo[3.3.0.0^{3,7}]octylidene)-2,2′-dione (6a, 6b).** To a stirred solution of oxalyl chloride (22 mL), 24.7 mmol) in 100 mL of dry CH$_2$Cl$_2$ was added dry DMSO (1.4 mL. 20.2 mmol) in 20 mL of dry CH$_2$Cl$_2$ at −50 to −60 °C.[16] After stirring for 2 min a solution of the mixture **35a** and **35b** (1.025 g, 4.2 mmol) in 300 mL of dry CH$_2$Cl$_2$ was added dropwise at −50 to −60 °C. The reaction mixture was stirred for 15 min, treated with 5 mL (36.1 mmol) of triethylamine, and allowed to warm to room temperature before cold water was added. Extraction was effected with CH$_2$Cl$_2$ (3×), and the combined organic phases were washed with aqueous HCl (5%), aqueous NaHCO$_3$ (5%), water, and brine, dried (MgSO$_4$), and evaporated. Purification by silica gel chromatography (pentane/ether (1/1)) yielded 758 mg (75%) of a mixture of **6a** and **6b** as colorless crystals, mp 177 °C. R_f (silica gel, pentane/ether (1/1)) = 0.18. ^{1}H NMR (300 MHz) δ 2.86 (4H, dd, J_1 = 11.1 Hz, J_2 = 1.5 Hz) 2.28 (4H, dd, J_1 = 5.4 Hz, J_2 = 2.6 Hz), 1.74 (4H, dd, J_1 = 11.1 Hz, J_2 = 1.5 Hz), 1.53 (4H, dd, J_1 = 11.1 Hz, J_2 = 2.5 Hz); ^{13}C NMR (75.47 MHz) δ 212.1 (s), 131.6 (s), 43.1 (d), 38.6 (t), 37.7 (d); IR (CDCl$_3$) 3014, 2956, 2930, 2862, 1751, 1721, 1256; UV/vis (CH$_3$CN) $\lambda_{\max}$ (log ϵ) = 280 nm (2.22); MS(GC) *m*/*z* 240 (3) [M$^+$], 212 (22), 184 (15), 155 (21), 141 (23). Anal. Calcd for C$_{16}$H$_{16}$O$_2$ (240.30): C, 79.97; H, 6.71. Found: C, 80.05; H, 6.77.

***syn*-4-Methylidene-2,2′-bi(tricyclo[3.3.0.0^{3,7}]octylidene)-4′-one (9a) and *syn*-4,4′-Dimethylidene-2,2′-bi(tricyclo-[3.3.0.0^{3,7}]octylidene) (11a).** At 0 °C a mixture of 2.2 g of methyltriphenylphosphonium bromide/NaNH$_2$ (Instant Ylide, 5.2 mmol phosphonium salt) in dry THF (130 mL) was stirred for 0.5 h. A solution of dione **7a** (414 mg, 1.7 mmol) in dry THF (30 mL) was added, and the reaction was stirred for 46 h at room temperature. After addition of pentane (160 mL), the mixture was filtered on silica gel. The filtrate was evaporated, and the residue was chromatographed on silica gel (elution with pentane−ether (4/1), to yield **9a** (56 mg, 13.8%) and **11a** (9 mg, 2.2%) as colorless solids: **9a**: mp: 72 °C; R_f (SiO$_2$, pentane−ether (4/1), *p*-anisaldehyde) = 0.39; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 1.33−1.71 (m, 8H), 2.25−2.27 (m, 1H), 2.44 (m, 1H), 2.57−2.59 (m, 1H), 2.60−2.87 (m, 3H), 2.92−2.93 (m, 1H), 2.94−2.95 (m, 1H), 4.17 (s, 1H), 4.22 (s, 1H); ^{13}C NMR (75.47 MHz, CD$_2$Cl$_2$) δ 36.7 (d), 37.5 (d), 38.9 (t), 39.5 (d), 40.8 (d), 41.0 (t), 43.4 (t), 43.4 (d), 43.8 (t), 46.5 (d), 46.8 (d), 49.2 (d), 91.9 (t), 121.6 (s), 137.3 (s), 159.2 (s), 203.8 (s); MS *m*/*z* 238 (28) [M$^+$], 210 (11), 209 (11), 196 (15), 195 (67), 184 (15), 183 (78), 182 (17), 181 (32), 180 (10), 179 (13), 169 (48), 168 (58), 167 (91), 166 (22), 165 (30), 154 (42), 153 (75), 152 (21), 144 (11), 142 (44), 141 (93), 131 (13), 130 (24), 129 (90), 128 (70), 127 (19), 118 (11), 117 (55), 116 (27), 115 (79), 105 (29), 103 (18), 102 (10), 92 (15), 91 (100), 89 (14), 79 (52), 78 (18), 77 (58), 67 (36), 65 (36), 63 (20), 55 (77), 53 (20), 51 (29); IR (KBr) 3086, 2984, 2946, 2878, 1886, 1760, 1674, 1477, 1448, 1276, 1201, 1171, 1113, 1015, 958, 892, 820, 784 cm^{-1}; UV/vis (CH$_2$Cl$_2$) $\lambda_{\max}$ [nm] (log ϵ) = 222 (3.87), 240 (4.09), 300 (3.46); HRMS *m*/*z* calcd (M$^+$) 238.1358, obsd 238.1360. **11a**: R_f (SiO$_2$, pentane−ether (4/1), *p*-anisaldehyde) = 0.82; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 1.31−1.52 (m, 8H), 2.39 (m, 2H), 2.47 (m, 2H), 2.56−2.59 (m, 2H), 2.74−2.79 (m, 2H), 4.06 (s, 2H), 4.14 (s, 2H); ^{13}C NMR (50.32 MHz, CD$_2$Cl$_2$) δ 37.3 (d), 40.2 (d), 43.3 (t), 43.9 (d), 45.2 (t), 45.8 (d), 90.1 (t), 128.5 (s), 159.7 (s); MS *m*/*z* 237 (12) [M$^+$ + 1], 236 (56) [M$^+$], 235 (15), 221 (26), 209 (10), 208 (38), 207 (50), 206 (10), 197 (12), 196 (11), 195 (56), 194 (21), 193 (73), 192 (19), 191 (16), 184 (18), 183 (15), 182 (20), 181 (48), 180 (64), 179 (71), 178 (41), 170 (15), 169 (37), 168 (23), 167 (100), 166 (36), 165 (83), 157 (31), 156 (52), 155 (80), 154 (43), 153 (55), 152 (41), 151 (37), 144 (14), 143 (42), 142 (52), 141 (83), 131 (25), 130 (29), 129 (97), 128 (89), 127 (20), 119 (10), 118 (13), 117 (60), 116 (29), 115 (73), 105 (29), 103 (18), 93 (13), 92 (14), 91 (50), 79 (20), 78 (14), 77 (42), 65 (14); IR (neat film) 3071, 2981, 2958, 2919, 2875, 2122, 1671, 1274, 857, 788 cm^{-1}; UV/vis (CH$_2$Cl$_2$) $\lambda_{\max}$ [nm] (log ϵ) = 244 (3.96); HRMS *m*/*z* calcd (M$^+$) 236.1565, obsd 236.1555.

***anti*-4-Methylidene-2,2′-bi(tricyclo[3.3.0.0^{3,7}]octylidene)-4′-one (10a) and *anti*-4,4′-Dimethylidene-2,2′-bi(tricyclo-[3.3.0.0^{3,7}]octylidene) (12a).** The Wittig reaction of dione **8a** was accomplished in the same way as the methylenation of dione **7a**. Thus, **8a** (211 mg, 0.9 mmol) yielded **10a** (107 mg, 51%) and **12a** (31 mg, 15%) as colorless solids. **10a**: mp: 106 °C, R_f (SiO$_2$, pentane−ether (4/1), *p*-anisaldehyde) = 0.42; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 1.38−1.61 (m, 8H), 2.29 (m, 1H), 2.44−2.45 (m, 1H), 2.56−2.58 (m, 2H), 2.62 (m, 1H), 2.76−2.78 (m, 2H), 2.90 (m, 1H), 4.17 (s, 1H), 4.20 (s, 1H); ^{13}C NMR (50.32 MHz, CD$_2$Cl$_2$) δ 36.6 (d), 37.5 (d), 38.9 (t), 39.3 (d),40.1 (t), 40.7 (d), 43.1 (t), 43.4 (d), 43.7 (t), 46.5 (d), 46.8 (d), 49.0 (d), 91.8 (t), 121.7 (s), 137.5 (s), 160.0 (s), 204.8 (s); MS *m*/*z* 238 (33) [M$^+$], 210 (22), 209 (12), 195 (39), 184 (13), 183 (78), 182 (32), 181 (42), 169 (48), 168 (42), 167 (71), 166 (19), 165 (25), 156 (22), 155 (70), 154 (35), 153 (45), 152 (17), 144 (20), 143 (39), 142 (42), 141 (80), 131 (21), 130 (31), 129 (85), 128 (64), 127 (16), 118 (18), 117 (59), 116 (28), 115 (71), 105 (27), 103 (16), 93 (13), 92 (18), 91 (100), 79 (50), 78 (17), 77 (48), 67 (41), 65 (33), 63 (15), 55 (87); IR (KBr) 3070, 3001, 2971, 2880, 1754, 1672, 1276, 1108, 890, 872, 598 cm^{-1}; UV/vis (CH$_2$Cl$_2$) $\lambda_{\max}$ [nm] (log ϵ) = 220 (3.77), 242 (4.08), 302 (3.44); HRMS *m*/*z* calcd (M$^+$) 238.1358, obsd 238.1364. **12a** mp: 82−84 °C, R_f (SiO$_2$, pentane−ether (4/1), *p*-anisaldehyde) = 0.85; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 1.27−1.46 (m, 8H), 2.38 (m, 2H), 2.50 (m, 2H), 2.62−2.64 (m, 2H), 2.73−2.76 (m, 2H), 4.13 (s, 2H), 4.15 (s, 2H); ^{13}C NMR (50.32 MHz, CD$_2$Cl$_2$) δ 37.2 (d), 40.1 (d), 42.3 (t), 43.4 (d), 43.8 (t), 45.9 (d), 90.4 (t), 129.0 (s), 161.1 (s); MS *m*/*z* 237 (17) [M$^+$ + 1], 236 (45) [M$^+$], 235 (12), 221 (41), 209 (11), 208 (28), 206 (11), 196 (13), 195 (69), 194 (17), 193 (46), 192 (16), 191 (16), 183 (13), 182 (36), 181 (59), 180

Table 1. Crystallographic Data of 4a, 7a, 8a, 12a, and 30

compound	**4a**	**7a**	**8a**	**12a**	**30**
empirical formula	$C_{22}H_{28}$	$C_{16}H_{16}O_2$	$C_{16}H_{16}O_2$	$C_{18}H_{20}$	$C_{16}H_{20}O_2$
molecular mass [g/mol]	292.4	240.3	240.3	236.3	244.3
crystal size [mm]	0.55 × 0.35 × 0.22	0.48 × 0.45 × 0.4	0.5 × 0.45 × 0.45	0.5 × 0.41 × 0.2	0.45 × 0.3 × 0.22
crystal color	colorless	colorless	colorless	colorless	colorless
crystal shape	fragment	polyhedron	polyhedron	fragment	polyhedron
space group	Cc	$P2_1/c$	$C2/c$	$C2/c$	$P4_2/n$
a [Å]	15.912(1)	10.507(1)	13.823(2)	13.7982(10)	20.055(3)
b [Å]	18.528(1)	11.506(2)	9.173(1)	9.7750(7)	20.055(3)
c [Å]	14.246(1]	11.110(2)	10.803(2)	11.0495(8)	6.128(1)
β [deg]	123.061(1)	115.80(1)	119.85(1)	116.28	90
V [A^3]	3519.8(2)	1209.2(3)	1188.1(3)	1336.2(2)	2464.7(7)
D_{calc} (mg/m^3]	1.104 g/cm^3	1.32	1.34	1.18	1.32
Z	8	4	4	4	8
F(000)	1280	512	512	512	1056
temp [K]	200	223	223	200	223
$h_{\mathrm{min}}/h_{\mathrm{max}}$	−18/19	0/13	0/18	−10/16	0/26
$k_{\mathrm{min}}/k_{\mathrm{max}}$	−20/21	0/15	0/12	−11/11	0/26
$l_{\mathrm{min}}/l_{\mathrm{max}}$	−17/8	−14/13	−14/12	−12/13	0/8
$(\sin \Theta/\lambda)_{\mathrm{max}}$ [Å^{-1}]	0.61	0.66	0.66	0.60	0.66
μ [mm^{-1}]	0.06	0.09	0.09	0.07	0.09
refl colld	16196	3066	1479	2968	3127
refl unique	3975	2916	1424	1132	2964
refl obsd [$I > 2\sigma(I)$]	3600	2354	1270	1005	2153
variables	533	227	114	116	243
$(\Delta/\sigma)_{\mathrm{max}}$	<0.01	<0.01	<0.01	<0.01	<0.01
R	0.038	0.039	0.039	0.063	0.040
R_{w}	0.089	0.107	0.103	0.173	0.102
S (Gof)	1.12	1.10	1.07	1.12	1.09
$(\Delta\rho)_{\mathrm{max}}$ [e Å^{-3}]	0.15	0.28	0.26	0.80	0.32
$(\Delta\rho)_{\mathrm{min}}$ [e Å^{-3}]	−0.15	−0.27	−0.32	−0.20	−0.22

(35), 179 (70), 178 (42), 170 (12), 169 (23), 168 (18), 167 (93), 166 (44), 165 (84), 158 (12), 157 (54), 156 (61), 155 (90), 154 (36), 153 (35), 152 (22), 149 (36), 144 (10), 143 (29), 142 (48), 141 (62), 131 (23), 130 (51), 129 (100), 128 (51), 127 (14), 119 (12), 118 (13), 117 (47), 116 (20), 115 (53), 105 (18), 104 (11), 103 (15), 93 (11), 92 (13), 91 (47), 89 (11), 81 (11), 79 (27), 78 (10), 77 (35), 71 (15), 67 (12), 65 (14), 57 (19), 55 (13);); IR (KBr): 3073, 2998, 2963, 2918, 2874, 1669, 1274, 1093, 853 (s) cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} [nm] (log ϵ) = 218 (3.98), 246 (4.19); HRMS m/z calcd (M$^+$) 236.1565, obsd 236.1550.

X-ray Diffraction Analysis of 4a, 7a, 8a, 12a, and 30. The reflections were collected with Siemens SMART (CCD) (**4a**, **12a**) and Nonius-CAD4-diffractometers (**7a**, **8a**, **30**) (Mo Kα-radiation graphite monochromator, $\omega-2\Theta$-scan). Intensities were corrected for Lorentz and polarization effects. All structures were solved by direct methods (SHELXS-86).[22] The structural parameters of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically with a full matrix least-squares technique (F^2). The hydrogen atoms of the methyl groups of **4a** and at C(8) and C(8′) of **12a** were calculated and fixed geometrically during refinement. Refinement was carried out with (SHELXL-93).[23] The crystallographic data and details of the refinement procedure are shown in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax. Int. Code +44(1223)336−033, e-mail: deposit@chemcrys.cam.ac.uk].

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **4a**, **5a**/**5b**, **9a**−**12a**, **22**, **24**, **36**/**37**, **38**, and **39** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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