Optically Pure C_2-Symmetric Transition Metal Complexes. Steric Consequences of Flanking the Cyclopentadienyl Anion with a Pair of Bridged Bicyclic Terpene-Derived Hydrocarbon Subunits

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The method developed by Erker for the preparation of "dibornacyclopentadiene" **1** has been generalized to encompass two related cyclopentadienes flanked by bridged bicyclic subunits derived from (1*R*)-(+)-verbenone (**4**). Whereas lithium dimethylcuprate addition to **4** leads to **5a**, reaction with diisobutylaluminum hydride and methylcopper affords the less substituted analog **5b**. Both saturated ketones undergo the Shapiro reaction and subsequent in situ condensation with ethyl formate to deliver the dienols **7a**,**b**, respectively. The dehydrative cyclization of these intemediates proved to be more difficult to accomplish than in the earlier work involving **1**. Exposure of **7a** to camphorsulfonic acid in benzene at 25 °C gives rise to **8** in 82% yield. These conditions proved much too harsh for **7b**, which however undergoes ring closure to give **9** (68%) with iodine in ether. Following deprotonation, **8** can be silylated to give **11**, but neither the lithium cyclopentadienide nor the silane can be coaxed into forming a variety of titanocene or zirconocene complexes. These reactants must consequently be more sterically crowded than **1**, which does react with MCl_4 (Erker) and $CpTiCl_3$ (this work). Remarkably, hydrocarbon **9** completely resists deprotonation, a direct reflection of the extreme nonbonded congestion in the vicinity of its sp^3-bound cyclopentadienyl proton.

The demand for chiral, nonracemic complexes based on group 4 transition metals has increased enormously in recent years[1] because of their perceived effectiveness as efficient catalysts in a wide range of asymmetric organic reactions. Several research groups, including our own,[2] have spearheaded the campaign to synthesize cyclopentadienyl complexes of this type[3−13] and to exploit their latent chemistry.[14−18] Despite the success of this enterprise, efforts to link the absolute configuration of the organometallic reagents to the stereochemical outcome of the promoted transformations continue to dominate the field presently.[19] It was in this context

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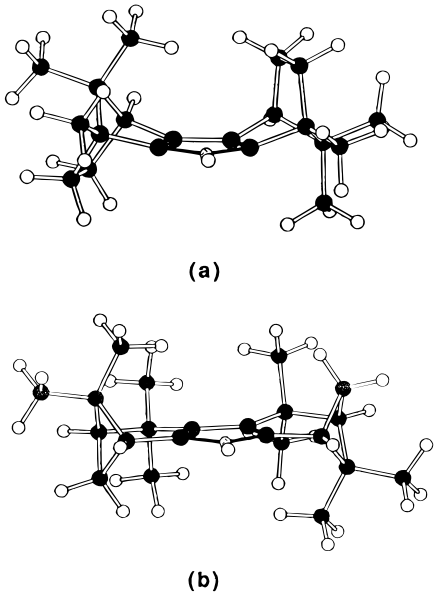
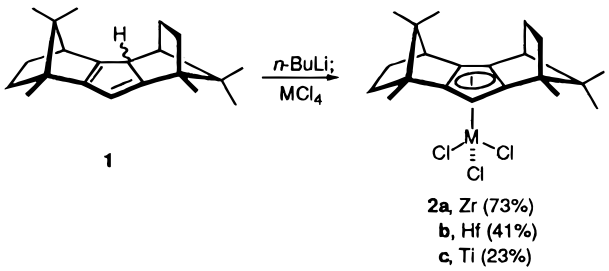


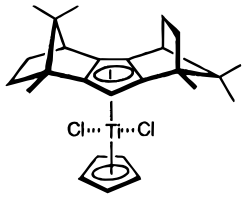
Figure 1. Energy-minimized conformations of (a) $\mathbf{1}^-$ and (b) $\mathbf{8}^-$ showing the steric congestion associated with π-complexation to either face of the cyclopentadienide core.

that Erker pursued the fascinating concept of preparing the "dibornacyclopentadiene" **1** and of generating from



this hydrocarbon the triad of complexes **2a**−**c**.[20] The flanking of a cyclopentadienyl anion with two bornyl ring systems introduces a significant level of steric congestion in the areas above and below the planar five-membered cyclic core (see Figure 1a), whose two faces are identically compromised because of the prevailing C_2 symmetry. The very modest yield of titanocene trichloride **2c** could be construed to be an indicator of the limited volume for metal occupancy existent in $\mathbf{1}^-$.

The present study began by investigating whether a somewhat more bulky titanium-based electrophile could be accommodated by $\mathbf{1}^-$. Generation of the anion from **1** proved to be a sluggish process, requiring 3 days of stirring with *n*-butyllithium in ether−hexanes at room temperature. Exposure of $\mathbf{1}^-$ in dry THF to $CpTiCl_3$ for an equivalent period of time at 25 °C allowed for the isolation of **3** in 49% yield. The structural features of **3**



3

follow directly from its spectroscopic properties and, especially, from NOE and DEPT data. In particular, the enhancement observed between the singlets attributable to the upper (1 H) and lower Cp rings (5 H) suggests that the bridgehead methyl groups face the "back" of the catalyst. Unfortunately, all attempts to obtain adequate single crystals of **3** for X-ray crystallographic analysis proved unsuccessful.

Buoyed by the acquisition of **3**, we next proceeded to synthesize two cyclopentadienes doubly fused with bicyclic terpenoid subunits structurally based on (1*R*)-(+)-verbenone (**4**).[21] Whereas lithium dimethylcuprate addition to **4** gave rise to **5a**,[19b] alternate recourse to diisobutylaluminum hydride in combination with methylcopper[22] proceeded stereoselectively to deliver the less substituted analog **5b** (Scheme 1). Once the respective 2,4,6-triisopropylbenzenesulfonyl hydrazones **6a**,**b** had been generated, independent Shapiro degradation[23] and direct condensation of the cycloalkenyl anion with ethyl formate in a stoichiometric ratio of 2:1 afforded the alcohols **7a**,**b** in good yield.

The subsequent processing of **7a** under the conditions reported to be effective for providing **1** (cat. $KHSO_4$, 110−120 °C, neat, in vacuo)[20] led to a complex mixture of products, the major component of which has been identified as **12**.[24] Evidently, the reaction pathway involving methyl migration in tandem with the elimination of water is competitive under these circumstances. This is not surprising in view of the harshness of the conditions involved. Since **8** was recognized to be present as well in this mixture, we simply made recourse to milder acidic reagents. Indeed, suitable means for effecting the smooth conversion of **7a** to **8** consists of stirring the dienol with H_2SO_4 in THF or with camphorsulfonic acid in benzene at room temperature. In the latter case, **7a** is consumed within 5 h and the colorless oily cyclopentadiene is isolated in 82% yield after chromatography. As expected, **8** exhibits only 12 carbon signals. In its high-field ^{1}H NMR spectrum, the two-proton singlet located at δ 2.66 (in $CDCl_3$) is attributed to the geminal methylene hydrogens of the five-membered ring.

Attempts to perform a Nazarov cyclization[25] on the ketone derived from **7a** were unsuccessful.[24]

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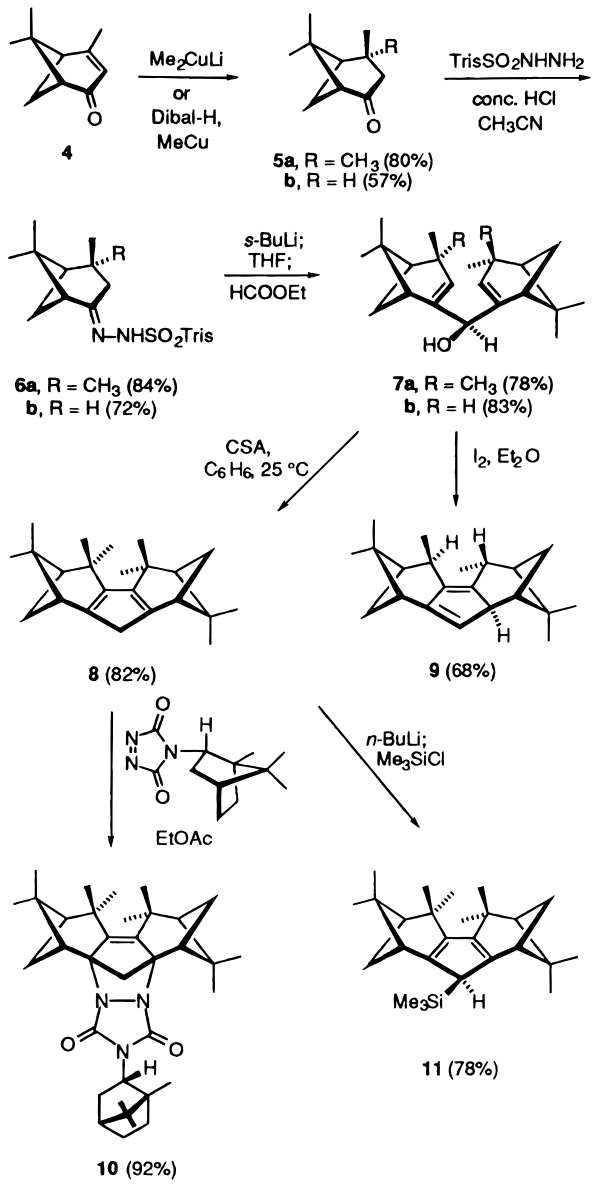
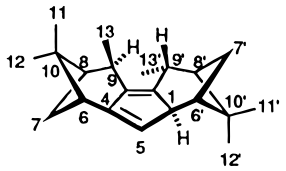
(25) For analogy, see: Halterman, R. L.; Tretyakov, A. *Tetrahedron* **1995**, *51*, 4371.

Scheme 1



Alcohol **7b** was seen to be still more sensitive than **7a**. As a consequence of our inability to realize its cyclization under those conditions previously found effective for delivering **1** and **8**, attention was directed to the use of a catalytic quantity of iodine in ether at 20 °C on the strength of a report by Garner and Prince.[26] These mild conditions, applied here in a reverse addition mode, caused reaction to proceed rapidly to completion, resulting in the formation of **9** as a single stereoisomer. The structural features of **9** were established by a combination of long-range DEPT,[27] HETCOR,[28] and NOE studies[29] (Chart 1). Particularly diagnostic of the stereochemistry of this hydrocarbon are the very disparate chemical shifts of the two interior apical methylene protons (δ 1.58 and 1.16). The strong upfield shift

Chart 1

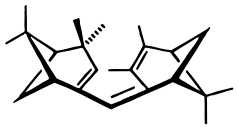


9

Irradiate	Observe	% n.O.e.
H_1 (δ 3.3)	H_6'	5
	H_{12}'	4
	H_5	6
	H_9	8
H_{11} (δ 0.97)	H_{12}	8
	endo-H_7'	6
	H_9'	3
	H_6	3
	H_8	2
H_{12}' (δ 1.01)	H_1	15
	H_{11}'	8
	H_{13}'	7
	H_9	14

associated with the *endo*-H_7' signal reflects its projection well into the shielding zone above the cyclopentadiene ring. This geometric arrangement is possible only when H-1 is oriented endo.

Admixture of **8** with enantiopure *endo*-bornyltriazolinedione[30] in ethyl acetate resulted in efficient operation of a Diels–Alder cycloaddition and formation of **10**. The structure of this adduct and hence of its precursor **7a** was confirmed by X-ray diffraction analysis of a single crystal of the urazole (Figure 2).



12

Studies related to the deprotonation of **8** involved the initial preliminary screening of *n*-butyllithium in hexanes, methyllithium in THF, methyllithium in ether, and *tert*-butyllithium in hexanes at room temperature. All of these conditions resulted in little, if any, deprotonation. Use of the stronger base, *n*-butyllithium/TMEDA in hexanes, resulted in 38% conversion to silane **11** after quenching with chlorotrimethylsilane. Finally, it was discovered that refluxing **8** with an excess of *n*-butyllithium in hexanes for 22–24 h gave the desired anion efficiently, as reflected in the essentially quantitative production (^{1}H NMR analysis) of **11**. Subsequent chromatographic purification delivered the silane as a colorless solid in 78% isolated yield. Crystals of **11** were well-suited to X-ray crystallographic analysis (Figure 3). In contrast to structurally simpler cyclopentadienylsilanes which are responsive to $TiCl_4$

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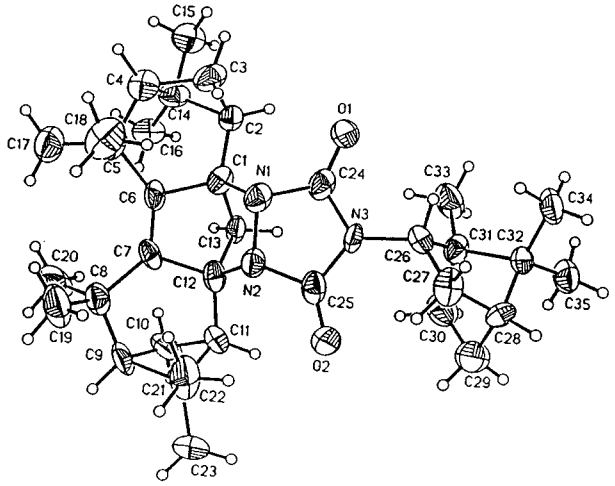

Figure 2. Crystallographically determined molecular structure of **10** as drawn with 50% thermal ellipsoids.

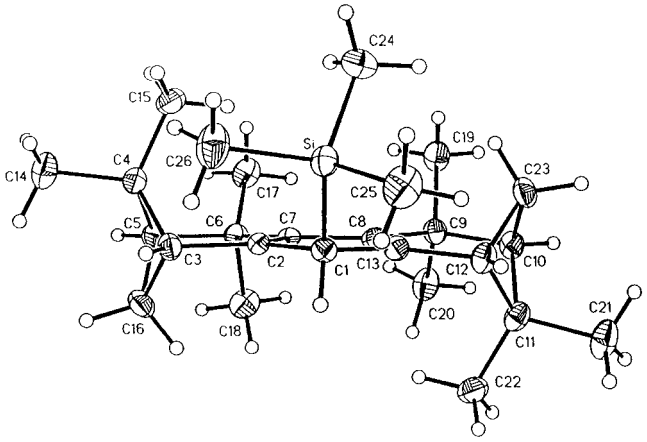

Figure 3. Crystallographically determined molecular structure of **11** as drawn with 50% thermal ellipsoids.

and $ZrCl_4$,[2f] **11** proved inert to these reagents under a variety of rather forcing conditions. More remarkable yet, reaction of $\mathbf{8}^-$ with these same tetrachlorides as well as $CpTiCl_3$ and $CpZrCl_3$ did not give rise to detectable metallocene formation ($TiCl_3$ was not examined). This lack of reactivity can be reasonably attributed to the considerable steric congestion resident on either face of $\mathbf{8}^-$ (see Figure 1b) as well as on the conjugated π surface anti to the C−Si bond in **11**. Simply stated, there appears to be insufficient room in **8** and **11** to allow for titanocene or zirconocene formation. We are unaware of a related complication in any other cyclopentadiene reported heretofore.

The steric constraints in cyclopentadiene **9** are equally striking in that they disallow deprotonation even under extreme conditions. For example, **9** is unreactive toward sodium amide in liquid ammonia as well as *tert*-butyllithium/TMEDA in hexanes. Molecular models of this hydrocarbon show its purportedly acidic methine proton to be well imbedded into the interior of the carbocyclic superstructure (Figure 4), thus causing it to be unreachable for abstraction by a base of sufficient strength. Unlike **8**, **9** does not enter into Diels−Alder cycloaddition with *endo*-bornyltriazolinedione.

In conclusion, we have come to realize that **8** and **9** are "overdesigned" enantiomerically pure cyclopentadienes in that these molecules are too sterically congested for conversion into group 4 metallocenes of any type. While structural rigidity and other potentially attractive structural features are resident in these molecules, other outlets must be opened to take advantage of these properties.

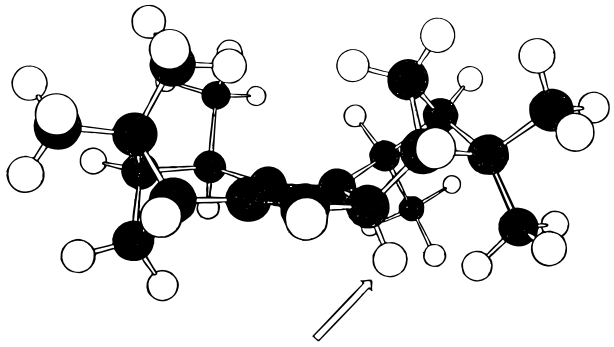

Figure 4. Energy-minimized conformation of **9** showing the steric hindrance to deprotonation (see arrow).

Experimental Section

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at the indicated field strengths. High-resolution mass spectra were obtained at The Ohio State University Chemical Instrumentation Center. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and at Atlantic Microlab, Inc., Norcross, GA. All reactions were carried out under a nitrogen or argon atmosphere, and the ensuing separations were effected under flash chromatography conditions on Merck silica gel HG_{254}. The organic extracts were dried over anhydrous magnesium sulfate. Solvents were reagent grade and in many cases dried before use.

Dichloro(η^5-1,4-cyclopentadien-1-yl)[(1*R*,4*S*,5*S*,8*R*)-(4a,4b,8a,9,9a-η)-1,2,3,4,5,6,7,8-octahydro-1,8,10,10,11,11-hexamethyl-1,4:5,8-dimethanofluoren-9-yl]titanium (3). Cyclopentadienes **1** (974 mg, 3.45 mmol) were dissolved in a mixture of ether (8 mL) and hexanes (4 mL), cooled to −78 °C, and treated dropwise with *n*-butyllithium in hexanes (2.50 mL, 4.00 mmol). The yellow solution was stirred at rt (room temperature) for 3 days, the solvent was removed in vacuo, and the residue was taken up in dry THF (35 mL), cooled to −78 °C, and added to a cold (−78 °C) solution of $CpTiCl_3$ (720 mg, 3.28 mmol) in dry THF (20 mL). A color change from yellow to red to violet was observed. After 2 days at 25 °C, the dark, green-brown solution was concentrated in vacuo, diluted with acidic (HCl) $CHCl_3$, and filtered through Celite. Solvent removal from the filtrate left a dark violet residue which was dissolved in toluene, filtered, and cooled to −10 °C to yield 422 mg of green crystals. Concentration of the mother liquor and further cooling provided an additional 328 mg of **3** (total 49%): Mp 160−162 °C dec; ^1H NMR (300 MHz, $CDCl_3$) δ 6.57 (s, 5 H), 6.43 (s, 1 H), 3.03 (d, J = 3.7 Hz, 1 H), 2.83 (d, J = 4.2 Hz, 1 H), 2.16−1.95 (m, 2 H), 1.79−1.51 (m, 4 H), 1.41 (s, 3 H), 1.14 (s, 3 H), 0.902 (s, 3 H), 0.899 (s, 3 H), 0.86−0.71 (m, 2 H), 0.61 (s, 3 H), 0.31 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 173.0, 161.0, 142.9, 120.2, 110.6, 109.0, 71.0, 56.6, 56.4, 54.1, 51.6, 50.7, 38.1, 33.6, 29.1, 26.5, 23.0, 21.9, 21.6, 20.8, 12.5, 10.7 ppm; MS m/z (M^+ − Cl) calcd 429.1829, obsd 429.1822; $[\alpha]_D^{25}$ +1163 (*c* 0.16, $CHCl_3$).

Anal. Calcd for $C_{26}H_{34}Cl_2Ti$: C, 67.11; H, 7.36. Found: C, 67.74; H, 7.40.

2,4,6-Triisopropylbenzenesulfonic Acid, [(1*R*,5*R*)-4,4,6,6-tetramethylbicyclo[3.1.1]hept-2-ylidene]hydrazide (6a). Ketone **5a** (10.0 g, 60.1 mmol) and 1,3,5-triisopropylbenzenesulfonyl hydrazide (19.73 g, 66.1 mmol) were suspended in acetonitrile (30 mL) and treated with concentrated HCl, which caused the hydrazide to dissolve. After 24 h at rt, the yellow solution was stored at −20 °C for 3 days, during which time

crystals of **6a** were deposited. Filtration of the reaction mixture afforded 11.20 g of **6a** as cubelike crystals. The mother liquor was concentrated in vacuo, diluted with CH_2Cl_2, washed twice with saturated $NaHCO_3$ solution and brine, and then dried. Removal of solvent gave an additional 11.35 g of **6a** (total yield of 84%), an analytical sample of which was obtained as colorless crystals from methanol: Mp 132.5−133.5 °C; IR ($CHCl_3$, cm^{-1}) 1386, 1166, 1154, 666; ^1H NMR (300 MHz, $CDCl_3$) δ 7.14 (s, 2 H), 4.24 (heptet, J = 6.7 Hz, 2 H), 2.89 (heptet, J = 6.9 Hz, 1 H), 2.53 (t, J = 5.4 Hz, 1 H), 2.42−2.34 (m, 1 H), 2.20 (two overlapping d, J = 7.8 Hz, 2 H), 1.80−1.69 (m, 2 H), 1.31 (d, J = 10.8 Hz, 1 H), 1.27−1.23 (m, 20 H), 1.12 (s, 3 H), 1.02 (s, 3 H), 0.73 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 163.8, 153.0, 151.2, 131.5, 123.6, 53.5, 51.4, 41.2, 35.8, 34.1, 32.7, 32.5, 29.84, 29.78, 27.2, 27.0, 25.4, 24.82, 24.75, 23.53, 23.49 ppm; MS m/z (M^+) calcd 446.2967, obsd 446.2995; $[\alpha]_D^{25}$ +31.8 (c 2.2, $CHCl_3$).

Anal. Calcd for $C_{26}H_{42}N_2O_2S$: C, 69.91; H, 9.48. Found: C, 69.85; H, 9.46.

Bis[(1*R*,5*R*)-4,4,6,6-tetramethylbicyclo[3.1.1]-2-en-2-yl]-methanol (7a). A solution of **6a** (5.0 g, 11.19 mmol) in dry THF (70 mL) and anhydrous hexanes (1.5 mL) was cooled to −78 °C and treated dropwise during 20 min with a solution of *sec*-butyllithium in cyclohexane (16.7 mL, 24.6 mmol). The second 1 equiv of base was accompanied by formation of a red-orange color. After 2.5 h, the reaction mixture was warmed to 0 °C, during which time nitrogen evolution occurred. Twenty minutes later, recooling to −78 °C was carried out and a THF solution of ethyl formate (0.45 mL, 5.57 mmol) was introduced during 10 min. The mixture was allowed to warm to rt overnight, quenched with water (2 mL), and concentrated in vacuo. The residue was partitioned between water and hexanes, and the separated aqueous phase was further extracted with hexanes. The combined organic layers were dried and concentrated to leave a solid that was purified by chromatography on silica gel (elution with 5% ethyl acetate in hexanes) to give **7a** (1.43 g, 78%) as a colorless solid: Mp 83.5−84.5 °C; IR ($CHCl_3$, cm^{-1}) 3603, 1474, 1264, 1252, 1038; ^1H NMR (300 MHz, C_6D_6) δ 5.53 (dd, J = 3.2, 1.9 Hz, 1 H), 5.15 (s, 1 H), 4.28 (d, J = 1.8 Hz, 1 H), 2.41−2.25 (m, 3 H), 2.07−2.03 (m, 1 H), 1.79−1.66 (m, 2 H), 1.41−1.23 (m, 2 H), 1.28 (s, 6 H), 1.10 (s, 3 H), 1.08 (s, 3 H), 1.06 (s, 3 H), 1.03 (s, 3 H), 1.02 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) 145.7, 145.5, 130.3, 125.4, 77.2, 54.1, 54.0, 44.9, 42.4, 42.1, 41.7, 38.6, 38.4, 32.0, 31.8, 30.8, 30.5, 27.9, 27.7, 26.3, 26.2, 25.4, 24.9 ppm; MS m/z (M^+) calcd 328.2766, obsd 328.2753; $[\alpha]_D^{25}$ −108.9 (c 1.57, $CHCl_3$).

Anal. Calcd for $C_{23}H_{36}O$: C, 84.09; H, 11.04. Found: C, 84.13; H, 11.02.

(1*R*,3*R*,6*S*,8*R*)-1,2,3,4,5,6,7,8-Octahydro-2,2,4,4,5,5,7,7-octamethyl-1,3:6,8-dimethanofluorene (8). A solution of **7a** (1.28 g, 3.90 mmol) in dry benzene (75 mL) was treated with camphorsulfonic acid (50 mg, 0.22 mmol) and stirred at rt for 4 h. After dilution with ether (75 mL), the mixture was extracted with saturated $NaHCO_3$ solution, dried, and concentrated. Chromatography of the residue on neutral alumina (elution with hexanes) afforded 890 mg (73%) of **8** as a colorless oil that crystallized slowly in the refrigerator: IR ($CHCl_3$, cm^{-1}) 1474, 1380, 1364; ^1H NMR (300 MHz, C_6D_6) δ 2.66 (s, 2 H), 2.39−2.27 (m, 4 H), 1.77 (t, J = 6.1 Hz, 2 H), 1.58 (d, J = 8.7 Hz, 2 H), 1.39 (s, 6 H), 1.34 (s, 6 H), 1.33 (s, 6 H), 0.91 (s, 6 H); ^{13}C NMR (75 MHz, C_6D_6) 145.9, 141.6, 59.4, 44.3, 43.9, 42.9, 38.5, 32.1, 31.9, 28.6, 27.5, 24.7 ppm; MS m/z (M^+) calcd 310.2661, obsd 310.2660; $[\alpha]_D^{25}$ −17.9 (c 1.97, $CHCl_3$).

Anal. Calcd for $C_{23}H_{34}$: C, 88.96; H, 11.04. Found: C, 88.43; H, 11.00.

(1*R*,3*R*,4*R*,5*R*,6*R*,8*R*,8a*R*)-2,3,4,5,6,7,8,8a-Octahydro-2,2,4,5,7,7-hexamethyl-1,3:6,8-dimethano-1*H*-fluorene (5b). Anhydrous copper(I) iodide (2.24 g, 11.8 mmol) was dissolved in dry THF (750 mL), cooled to 0 °C, and treated dropwise via syringe with halide-free methyllithium (7.70 mL of 1.4 M in ether, 10.8 mmol). After 15 min, the magnetically stirred mixture was cooled to −60 °C and treated sequentially with HMPA (56 mL) during 10 min and with diisobutylaluminum hydride (258 mL of 1 M in hexanes, 258 mmol) during 1 h. After an additional 1 hour at −60 °C, a solution of **4** (30.4 g, 202 mmol) in dry THF (100 mL) was introduced followed 2 h later by a small amount of methyllithium (0.80 mL of 1.4 M in ether, 1.12 mmol). The reaction mixture was then stirred at −20 °C for 90 min and quenched with sodium potassium tartrate solution. The separated aqueous phase was extracted with ether (3 × 200 mL), and the combined organic layers were washed with sodium potassium tartrate solution and brine prior to drying and solvent evaporation. The residue was purified by chromatography on silica gel (elution with 10% ethyl acetate in hexanes) to give 17.5 g (57%) of **5b** and 6.96 g of a 1:1 mixture of unreacted **4** and the corresponding alcohol.

Data for **5b**: colorless oil; bp 39 °C/0.1 mmHg; IR ($CHCl_3$, cm^{-1}) 1712, 1691, 1471, 1457, 1412, 1387, 1378, 1370, 1306, 1287, 1248, 1235, 1200, 1102; ^1H NMR (300 MHz, $CDCl_3$) δ 2.83 (dd, J = 19.9, 10.7 Hz, 1H), 2.62−2.51 (m, 2 H), 2.40−2.28 (m, 1 H), 2.18−2.08 (m, 2 H), 1.38 (d, J = 9.9 Hz, 1 H), 1.31 (s, 3 H), 1.14 (d, J = 7.4 Hz, 3 H), 0.98 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 214.4, 58.0, 47.4, 41.4, 40.2, 31.1, 28.4, 27.0, 24.5, 21.0 ppm; MS m/z (M^+) calcd 152.1201, obsd 152.1196; $[\alpha]_D^{25}$ +61.6 (c 2.38, $CHCl_3$).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.27; H, 10.85.

2,4,6-Triisopropylbenzenesulfonic Acid, [(1*R*,2*S*,5*R*)-4,6,6-trimethylbicyclo[3.1.1]hept-2-ylidene]hydrazide (6b). Reaction of **5b** (3.50 g, 23.0 mmol) with 2,4,6-triisopropylbenzenesulfonyl hydrazide (7.67 g, 25.7 mmol) and concentrated HCl (2.3 mL) in freshly distilled acetonitrile (12 mL) in the predescribed manner yielded 7.17 g (72%) of **6b** as a colorless solid: Mp 147.0−148.5 °C (from methanol); IR ($CHCl_3$, cm^{-1}) 3248, 1599, 1463, 1384, 1165, 1154; ^1H NMR (300 MHz, $CDCl_3$) δ 7.15 (s, 2 H), 4.26 (heptet, J = 6.8 Hz, 2 H), 2.89 (heptet, J = 6.9 Hz, 1 H), 2.73 (dd, J = 19.0, 10.4 Hz, 1 H), 2.57 (t, J = 5.4 Hz, 1 H), 2.47 (dt, J = 10.2, 6.0 Hz, 1 H), 2.33−2.22 (m, 1 H), 2.01 (dd, J = 19.1, 4.9 Hz, 1 H), 1.98−1.91 (m, 1 H), 1.28−1.22 (m, 21 H), 1.13−1.09 (m, 1 H), 1.09 (d, J = 7.4 Hz, 3 H), 0.71 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 163.6, 152.9, 151.2, 131.6, 123.6, 51.2, 47.2, 40.3, 34.1, 31.9, 30.5, 29.9, 29.2, 26.7, 24.82, 24.75, 24.1, 23.52, 23.49, 21.6 ppm; MS m/z (M^+) calcd 432.2811, obsd 432.2812; $[\alpha]_D^{25}$ +22.4 (c 2.94, $CHCl_3$).

Anal. Calcd for $C_{25}H_{40}N_2O_2S$: C, 69.40; H, 9.32. Found: C, 69.30; H, 9.30.

Bis[(1*R*,4*S*,5*R*)-4,6,6-trimethylbicyclo[3.1.1]hept-2-en-2-yl]methanol (7b). Reaction of hydrazone **6b** (38.5 g, 89.0 mmol) with *sec*-butyllithium (150 mL of 1.3 M in cyclohexane, 195 mmol) and ethyl formate (3.30 g, 44.6 mmol) in the predescribed manner afforded **7b** (8.36 g, 63%) as an off-white solid: Mp 71.0−72.0 °C, after chromatography on silica gel (elution with 5% ethyl acetate in hexanes); IR ($CHCl_3$, cm^{-1}) 3603, 1473, 1364, 1248, 1085; ^1H NMR (300 MHz, C_6D_6) δ 5.67 (t, J = 2.0 Hz, 1 H), 5.29 (s, 1 H), 4.32 (s, 1 H), 2.65−2.35 (m, 5 H), 2.09−2.04 (m, 1 H), 2.00−1.92 (m, 2 H), 1.27 (s, 6 H), 1.25 (d, J = 8.6 Hz, 1 H), 1.19 (d, J = 8.4 Hz, 1 H), 1.10 (d, J = 7.6 Hz, 3 H), 1.06 (s, 3 H), 1.05 (d, J = 7.5 Hz, 3 H), 1.01 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 146.6, 146.5, 126.3, 121.4, 77.2, 48.4, 48.3, 44.2, 41.8, 39.4, 39.3, 38.1, 37.9, 35.2, 35.1, 27.4, 27.2, 24.1, 23.7, 18.7, 18.5 ppm; MS m/z (M^+) calcd 300.2453, obsd 300.2446; $[\alpha]_D^{25}$ +13.5 (c 0.605, $CHCl_3$).

Anal. Calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73. Found: C, 84.02; H, 10.82.

(1*R*,3*R*,4*R*,5*R*,6*R*,8*S*,8a*R*)-2,3,4,5,6,7,8,8a-Octahydro-2,2,4,5,7,7-hexamethyl-1,3:6,8-dimethano-1*H*-fluorene (9). A cold (0 °C), magnetically stirred solution of alcohol **7b** (1.60 g, 5.32 mmol) in ether (100 mL) was treated dropwise during 5 h with a solution of iodine (62.4 mg, 0.246 mmol) in ether (100 mL). After 10 min at rt, the reaction mixture was quenched with saturated $Na_2S_2O_3$ solution and stirred for 10 min. The separated aqueous phase was extracted twice with

ether, and the combined organic layers were washed with $Na_2S_2O_3$ solution, dried, and concentrated. The residue, purified by chromatography on silica gel (elution with hexanes), furnished 1.02 g (68%) of **9** as a colorless oil: IR ($CHCl_3$, cm^{-1}) 2985, 2932, 1470, 1383, 1366; ^1H NMR (300 MHz, C_6D_6) δ 5.24 (d, $J = 2.2$ Hz, 1 H), 3.33−3.27 (m, 1 H), 2.75 (t, $J = 5.6$ Hz, 1 H), 2.70−2.64 (m, 1 H), 2.50 (dt, $J = 8.3$, 5.4 Hz, 1 H), 2.20−2.14 (m, 1 H), 2.08 (ddt, $J = 9.8$, 6.2, 1.3 Hz, 1 H), 2.00 (t, $J = 5.6$ Hz, 1 H), 1.90−1.84 (m, 1 H), 1.80 (d, $J = 1.9$ Hz, 3 H), 1.79−1.72 (m, 1 H), 1.58 (d, $J = 8.3$ Hz, 1 H), 1.30 (s, 3 H), 1.26 (d, $J = 7.3$ Hz, 3 H), 1.24 (s, 3 H), 1.16 (d, $J = 9.9$ Hz, 1 H), 1.01 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 148.5, 144.0, 130.7, 124.6, 50.34, 50.29, 48.4, 45.8, 44.9, 43.2, 43.1, 42.0, 39.9, 36.2, 28.0, 27.9, 26.5, 23.4, 23.3, 22.8, 20.3; MS *m/z* (M^+) calcd 282.2348, obsd 282.2347; [α]S(22,D) +14.0 (*c* 1.45, $CHCl_3$).

Anal. Calcd for $C_{21}H_{30}$: C, 89.30; H, 10.70. Found: C, 89.29; H, 10.71.

(2*S*,4*R*,4a*R*,6a*S*,7*R*,9*S*)-1,2,3,4,7,8,9,10-Octahydro-1,1,3,3,8,8, 10,10-octamethyl-*N*-[(1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]-2,4:4a,6a:7,9-trimethanobenzo[*c*]cinnoline-5,6-dicarboximide (10). A solution of **8** (60 mg, 0.193 mmol) in ethyl acetate (4 mL) was treated with freshly sublimed *endo*-bornyltriazolinedione (46 mg, 0.195 mmol) all at once. The pink color of the dienophile faded within seconds. After an additional 30 min, the solvent was removed under reduced pressure and the residue was purified by chromatography (silica gel, elution with 10% ethyl acetate in hexanes). There was isolated 96.9 mg (92%) of **10** as colorless crystals: Mp 242−244 °C dec (from ether−hexanes); ^1H NMR (300 MHz, C_6D_6) δ 4.48−4.42 (m, 1 H), 3.00 (dd, $J = 5.9$, 5.1 Hz, 1 H), 2.77−2.66 (m, 2 H), 2.58−2.49 (m, 2 H), 2.24 (dt, $J = 12.3$, 6.2 Hz, 1 H), 2.18−2.11 (m, 1 H), 2.02−1.93 (m, 1 H), 1.94 (d, $J = 8.8$ Hz, 1 H), 1.74−1.65 (m, 2 H), 1.64 (d, $J = 3.9$ Hz, 1 H), 1.62 (s, 3 H), 1.45 (s, 3 H), 1.47−1.39 (m, 3 H), 1.37 (s, 3 H), 1.27 (d, $J = 8.8$ Hz, 1 H), 1.26 (s, 3 H), 1.23 (s, 3 H), 1.21 (s, 3 H), 1.14 (s, 3 H), 0.99 (d, $J = 11.0$ Hz, 1 H), 0.95 (s, 3 H), 0.87 (s, 3 H), 0.84 (s, 3 H), 0.74 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) 158.7, 158.3, 149.5, 148.3, 84.54, 84.46, 59.2, 57.5, 55.7, 53.5, 51.9, 47.9, 45.9, 43.8, 42.1, 40.7, 40.1, 38.7, 38.5, 32.3, 31.6, 30.3, 30.2, 28.6, 28.4, 28.3, 28.2, 27.5, 26.3, 24.8, 24.4, 19.7, 18.7, 14.6 ppm; MS *m/z* (M^+) calcd 545.3981, obsd 545.3937; $[\alpha]_D^{25}$ −35.9 (*c* 0.92, $CHCl_3$).

Anal. Calcd for $C_{35}H_{51}N_3O_2$: C, 77.02; H, 9.42. Found: C, 77.29; H, 9.05.

Trimethyl[(1*R*,3*S*,6*S*,8*R*)-1,2,3,4,5,6,7,8-octahydro-2,2,4,4,5,5,7,7-octamethyl-1,3:6,8-dimethanofluoren-9-yl]-silane (11). A solution of **8** (112 mg, 0.36 mmol) in dry hexanes (6 mL) was treated with *n*-butyllithium in hexanes (0.68 mL, 1.09 mmol) via syringe and refluxed for 20 h, during which time a white precipitate formed. After cooling, dry THF (2 mL) was added to effect solubilization, and the reaction mixture was introduced via syringe into a cold (−78 °C) solution of chlorotrimethylsilane (0.16 mL, 1.26 mmol) in THF (5 mL). The solution was stirred overnight, diluted with water, and washed with water (2×) and brine. After drying and solvent removal, the residue was purified by chromatography on neutral alumina (hexane elution) to furnish 108 mg (78%) of **11** as a colorless oil that slowly crystallized. ^1H NMR analysis indicated the extent of silylation to be >98%. An analytical sample and colorless single crystals for X-ray analysis were obtained by recrystallization from methanol: Mp 81.5−82.5 °C; ^1H NMR (300 MHz, C_6D_6) δ 2.70 (s, 1 H), 2.51−2.42 (m, 2 H), 2.44−2.36 (m, 2 H), 1.78 (dt, $J = 6.0$, 6.1 Hz, 2 H), 1.65 (d, $J = 8.7$ Hz, 1 H), 1.46 (s, 3 H), 1.46 (d, $J = 8.6$ Hz, 1 H), 1.45 (s, 3 H), 1.38 (s, 3 H), 1.37 (s, 3 H), 1.33 (s, 3 H), 1.30 (s, 3 H), 1.07 (s, 3 H), 0.99 (s, 3 H), 0.17 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) 146.1, 145.9, 141.0, 140.2, 59.3, 58.8, 49.6, 45.0, 44.7, 43.4, 42.8, 38.8, 38.6, 33.0, 32.7, 31.9, 31.1, 29.6, 28.4, 27.9, 27.7, 26.0, 24.6, 0.23 ppm; MS *m/z* (M^+) calcd 382.3056, obsd 382.3075; $[\alpha]_D^{25}$ −0.40 (*c* 2.17, $CHCl_3$).

Anal. Calcd for $C_{26}H_{42}Si$: C, 81.60; H, 11.06. Found: C, 81.41; H, 10.93.

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Supporting Information Available: Tables of crystallographic details, atomic coordinates, bond lengths and bond angles, and anisotropic and isotropic displacement parameters for **10** and **11** (18 pages). Ordering information is given on any current masthead page.

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