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Synthesis and Structure of C_2-Symmetric, Doubly Bridged Bis(indenyl)titanium and -zirconium Dichlorides

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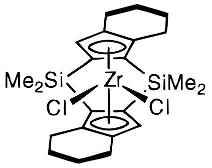
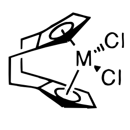
The synthesis of the new C_{2h}-symmetric doubly bridged 1,2′-(ethane-1,2-diyl)-2,1′-(ethane-1,2-diyl)bis(indene) ligand **9** from 1,5-dimethyl-1,5-cyclooctadiene via a selenium-catalyzed oxidation reaction and a double Nazarov π-cyclization reaction is reported. Only one bridged C_2-symmetric metallocene diastereomer was formed in the metalation of **9** because the geometry of the double bridge precluded formation of a meso isomer. The C_2-symmetric [1,2′-(ethane-1,2-diyl)-2,1′-(ethane-1,2-diyl)bis(indenyl)]titanium and -zirconium dichlorides **10** and **11** were prepared in good (63 and 67%) yields, with no evidence of oligomeric metallocene products. The solid-state structure of **11** was determined by X-ray crystallography. The related bis(indene) **19**, containing a bicyclo[3.3.1]nonane bridging moiety, was synthesized from Meerwein's diketone but could not be efficiently metalated.

C_2-symmetric *ansa*-metallocenes of group 4 transition metals are among the most prominent catalysts[2] for a number of organic transformations such as: epoxidation,[3] hydrogenation,[4] and carbomagnesation[5] of alkenes, reduction of imines[6] and carbonyls,[7] and diene cyclization.[8] Several synthetic groups have demonstrated that C_2-symmetrical *ansa*-metallocenes with reduced flexibility and enhanced availability of the active metal center for the approaching monomer molecule are considered to be the best organometallic catalysts for the stereoregular polymerization of alkenes.[9] A synthetic challenge in this area has been to avoid the formation of undesired *meso* side products to give a selective synthesis of *dl*-*ansa*-metallocenes with well-defined geometries. Although the tethering of ligands at an unsymmetrical site (e.g. the 1-position of indenyl) has in some cases led selectively to C_2-symmetrical *ansa*-metallocenes, these complexes are often conformationally too mobile to provide a well-defined geometry.[2,10] One successful approach for the selective formation of conformationally well-defined, C_2-symmetric *ansa*-metallocenes has been the use of a biaryl bridge to link cyclopentadienyl or indenyl ligands at a symmetrical site (e.g. the 2-position of indenyl).[11] Another recent approach has been to use doubly bridged bis(cyclopentadienyl) ligands to give conformationally well-defined complexes.[12−14] Compounds **1**−**3** are recently reported doubly bridged "cyclopentadienylphane" type metallocene dihalides.



1[12]



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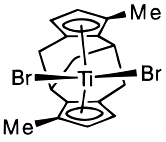

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In an effort to develop a facile, possibly general, and large-scale route to bis(ethanediyl)-bridged *ansa*-bis(indenes), we have investigated the Nazarov cycliza-

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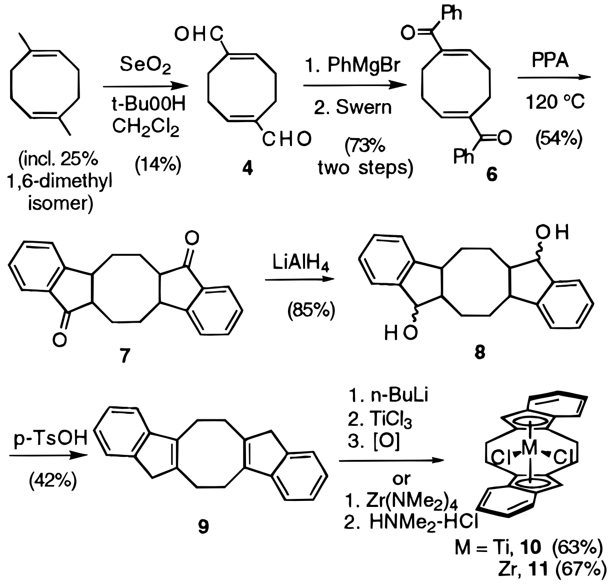
Scheme 1. Synthesis of Doubly Bridged Bis(indenyl)metal Complexes 10 and 11

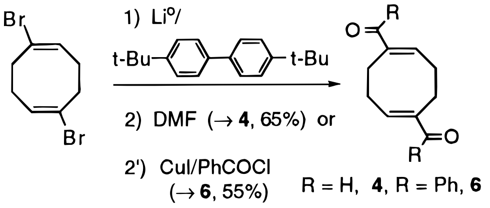


tion[15,16] of aryl vinyl ketones of 1,5-cyclooctadiene. In this paper we report the application of the Nazarov strategy toward the preparation of novel, rigid, doubly bridged bis(indene) **9**. In this achiral ligand with C_{2h} symmetry, the synfacial indenyl faces are related by C_2 symmetry and, thus, metalation can lead only to one conformationally well-defined C_2-symmetric *ansa*-metallocene diastereomer. The formation of a *meso*-metallocene isomer is inherently prevented by the symmetry of the double bridge.

Results and Discussion

As shown in Scheme 1, our successful approach to the synthesis of doubly bridged bis(indene) **9** required access to the C_{2h}-symmetric 1,5-diformyl-1,5-cyclooctadiene (**4**). On the basis of a report by Brown[17] on the selective oxidation of the allylic methyl group in (+)-α-pinene to form (1*S*)-(+)-myrtenal using catalytic selenium dioxide and *tert*-butyl hydroperoxide (TBHP) as a reoxidant, we applied this method to our ligand synthesis. 1,5-Dimethyl-1,5-cyclooctadiene has methyl groups appropriately situated to give the desired 1,5-diformyl species **4** through methyl group oxidation. Given the low cost and ready availability of the ca. 75:25 mixture of 1,5- and 1,6-dimethyl-1,5-cyclooctadienes, we utilized the direct oxidation of this mixture to a product mixture containing the desired dialdehyde **4** using catalytic SeO_2 in the presence of TBHP in methylene chloride.[18] Under all conditions studied, oxidation of the methylene groups was a competing side reaction. When the oxidation was run slowly in dilute dichloromethane solution at room temperature, some selectivity for the formation of the desired dialdehyde was obtained. ^1H NMR analysis of the crude product mixture indicated dialdehyde **4** was present in about 25% yield. After purification by column chromatography, C_{2h}-symmetric **4** was isolated in 14% yield. Although the yield was low, the reaction was simple to perform, the product was easy to isolate, and a single run could deliver over 12 g of pure dialdehyde **4** in one step from an inexpensive starting material.

Scheme 2. Alternate Synthesis of 4 and 6



Phenylmagnesium chloride was added to dialdehyde **4** to produce the phenylmethanol derivative **5**, which was oxidized under Swern conditions[19] (oxalyl chloride, dimethyl sulfoxide (DMSO), Et_3N) to diketone **6** in 73% yield for the two steps. The desired C_{2h}-symmetry of **6** was confirmed through the observed ^1H NMR coupling between the cyclooctadiene ethylene hydrogens. The potential 1,6-dibenzoyl-1,5-cyclooctadiene isomer would possess C_{2v} symmetry and would have only homotopic hydrogens in each ethylene group, and thus, no mutual coupling would be observed.

Alternate syntheses of **6** going through the known 1,5-dibromo-1,5-cyclooctadiene were also investigated (Scheme 2). Two methods for the formation of the dibromide have been reported; both rely on recrystallization to remove the isomeric 1,6-dibromo-1,5-cyclooctadiene formed in the elimination of a 1,2,5,6-tetrabromocyclooctane.[20] While direct metal−halogen exchange of the vinyl bromides was not successful, the use of a lithium/4,4′-di-*tert*-butylbiphenyl solution[21] enabled dilithiation of 1,5-dibromo-1,5-cyclooctadiene. The treatment of the intermediate dilithio species with DMF followed by aqueous workup produced dialdehyde **4** in 65% yield, while treatment with copper iodide/benzoyl chloride[22] gave diketone **6** directly in 55% yield. While these lithiation/carbonylation reactions worked fine on small scales (100 mg of dibromide), they could not be readily scaled up without greatly diminished yields. The direct oxidation of 1,5-dimethylcyclooctadiene remained the most favorable route for producing larger quantities of dialdehyde **4**. Cyanide couplings were also examined but were found to be overall less satisfactory than the oxidation of the dimethylcyclooctadiene.

With the bis(aryl vinyl ketone) **6** available in good quantities, the Nazarov cyclization reaction[15] was successfully applied to give the doubly bridged diketone **7**. Diketone **6** was mixed with polyphosphoric acid,[15] and the resulting mixture was kept at 120 °C for 3 h with stirring. The course of the reaction was followed by TLC. When the reaction was judged complete, the hot

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[15] For a review of the Nazarov reaction see: Denmark, S. E. Nazarov and Related Cationic Cyclizations In *Comprehensive Organic Synthesis*; Paquette, L. A., Ed.; Pergamon: New York, 1991; Vol. 5, pp 751−784.

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reaction mixture was poured into cold water and extracted with ether. Column chromatography furnished doubly bridged bis(indanone) **7** as a yellow solid as a mixture of stereoisomers in 54% yield. In this cyclization reaction the desired orientation of the indanone moieties was firmly established. Reduction of diketone **7** with lithium aluminum hydride gave after purification a stereoisomeric mixture of diol **8** in 85% yield as a viscous oil. Diol **8** was dehydrated in boiling benzene with a catalytic amount of *p*-TsOH in 2 h. Aqueous workup and silica gel purification furnished the desired doubly bridged bis(indene) as a clear viscous oil in 42% yield as a mixture of double-bond isomers and stereoisomers. Conversion of this mixture into the dilithium salt with *n*-BuLi at 0 °C and the subsequent quenching with water resulted in the predominant formation of bis(indene) **9** as the thermodynamically more stable tetrasubstituted double-bond isomer. While this removal of the stereocenters facilitated the characterization of C_{2h}-symmetric **9**, the isomeric bis(indene) mixture was used in the subsequent metalation reactions.

The new C_{2h}-symmetric ligand **9** was cleanly metalated to doubly bridged bis(indenyl)titanium and -zirconium dichloride complexes **10** and **11**. For the titanium complex, bis(indene) **9** was deprotonated with *n*-butyllithium in THF at 0 °C under nitrogen and the solution of the dilithium salt was transferred to a −78 °C solution of $TiCl_3$ in THF. The resulting dark greenish brown solution was gradually warmed to room temperature and then heated under reflux for 8 h. Oxidation with HCl in air[23] and subsequent workup provided a single racemic diastereomer of **10** as a dark green powder in 63% yield. For the zirconium complex, a chlorobenzene solution of bis(indene) **9** and tetrakis(dimethylamido)zirconium was heated under reflux for 24 h to give a clear yellow-orange solution of presumably a bis(indenyl)zirconium diamido complex.[24] The amido groups where exchanged with chlorides through the 0 °C addition of $HNMe_2-HCl$ in dichloromethane followed by stirring at room temperature for 2 h. The reaction mixture was concentrated, and addition of hexane resulted in the precipitation of bis(indenyl)zirconium dichloride **11** as a yellow powder in 67% yield. In both cases, the bis(indenyl)metal dichloride was isolated as a single racemic diastereomer in good yield, since the formation of the meso isomer was prevented through the constraints imposed by the double bridge. The initial product mixtures exhibited clean NMR spectra with no evidence for any oligomeric products often formed in the metalation of bis(indenyl) ligands. This selectivity for forming the single isomer of the metallocene is attrributed to the flexibility of the double bridge and the exposure of only a single diastereotopic face of the second indenyl moiety to the coordinated metal.

Table 1. Crystal Data and Structure Refinement for 11

identification code	rh03c
empirical formula	$C_{22}H_{18}C_{12}Zr$
fw	444.48
temp	218(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	*P*2/*c*
unit cell dimens	$a = 13.656(3)$ Å
	$b = 11.374(2)$ Å
	$c = 12.085(2)$ Å
	$\alpha = 90°$
	$\beta = 109.44(3)°$
	$\gamma = 90°$
V, *Z*	1770.1(6) Å^3, 4
density (calcd)	1.668 Mg/m^3
abs coeff	0.924 mm^{-1}
F(000)	896
cryst size	0.14 × 0.16 × 0.42 mm
θ range for data collection	1.58−25.00°
limiting indices	$-16 \le h \le 15, -13 \le k \le 13, -1 \le l \le 14$
no. of reflns collected	3743
no. of indep rflns	3112 (R(int) = 0.0386)
abs corr	semiempirical from ψ scans
max and min transmissn	0.3231 and 0.1933
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	3105/0/299
goodness of fit on F^2	1.057
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0294, wR2 = 0.0667
R indices (all data)	R1 = 0.0446, wR2 = 0.0774
largest diff peak and hole	+0.373 and −0.476 e/Å^3

Crystals of the zirconium complex **11** suitable for X-ray diffraction were grown at 0 °C by diffusion of hexane into a methylene chloride solution of **11**. The solid-state structure of **11** was solved as described in Table 1. Two independent molecules of **11** having slightly different conformations were found in the unit cell. Each molecule contained a C_2 axis of symmetry going through the zirconium atom and bisecting the Cl−Zr−Cl angle. ORTEP views of **11** are shown in Figure 1. The cyclopentadienyl rings were not quite eclipsed with the meridional C(3a)−C(4) indenyl bonds, exhibiting dihedral angles of 24.8 and 28.0° for the two molecules. At 120.4 and 120.8°, the $Cp_{cent}-Zr-Cp_{cent}$ angles are at the lower end of the usual range for bis(indenyl)zirconium dichlorides. The $Cp_{cent}-Zr$ distances are 2.219 and 2.218 Å. The Zr−C bond distances are not very uniform, varying from 2.47 Å for the unsubstituted carbons to 2.60 Å for the carbons at the benzo annelation. Selected bond lengths are in Table 2.

Meerwein's Diketone-Derived Bis(indene) 19. The doubly bridged cyclooctane-derived bis(indene) **9** is achiral, and its metalation leads to the formation of a racemic set of C_2-symmetric metal complexes. By incorporation of an additional bridging methylene group as in Meerwein's[25] diketone-derived bis(indene) **19**, only a single C_2-symmetric stereoisomer of *ansa*-bis(indenyl)metal complexes could be formed due to the bicyclic nature of the bridging unit. An added incentive to undertake this study was that bis(indene) **19** could be prepared in nonracemic form since the resolution of Meerwein's diketone **12** is known.[26] By extending the selective chemistry seen with doubly bridged bis(indene) **9** to a nonracemic variant, we hoped we could avoid the need for resolutions at the metal complex stage.

We based our successful synthesis of the bicyclic-bridged **19** on the bis-Nazarov approach applied above for the preparation of **9**. We prepared racemic Meer-

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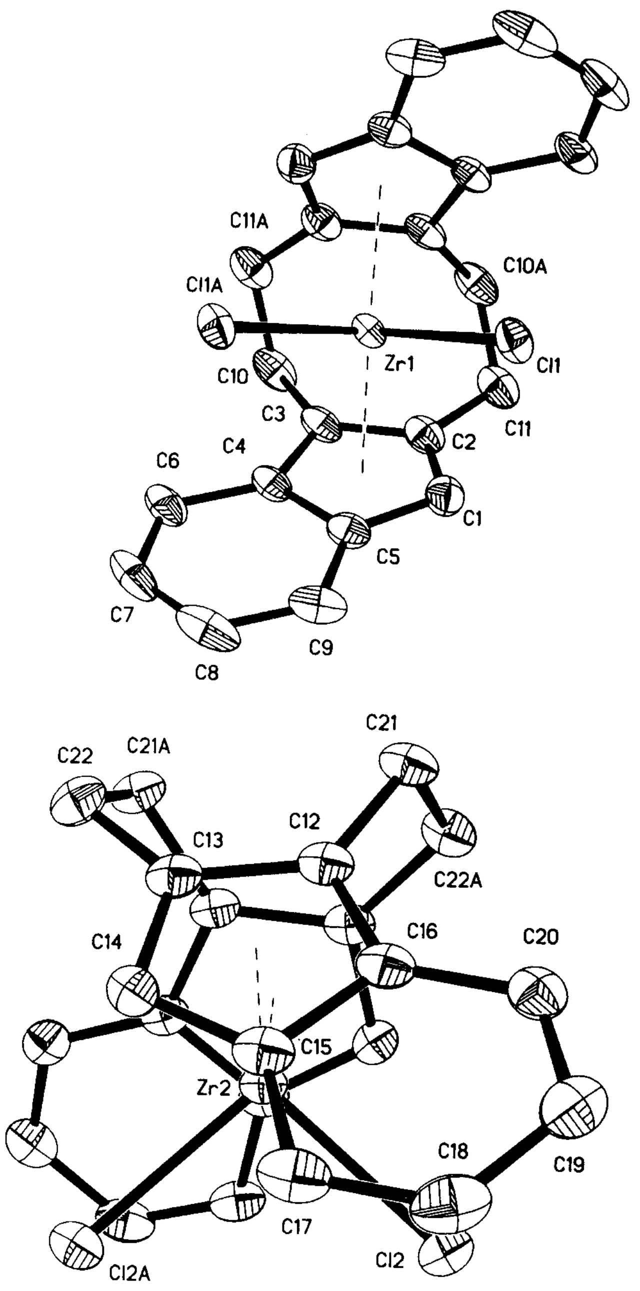


Figure 1. ORTEP drawings of **11** (40% thermal ellipsoids): (a, top) front view of molecule 1; (b, bottom) top view of molecule 2.

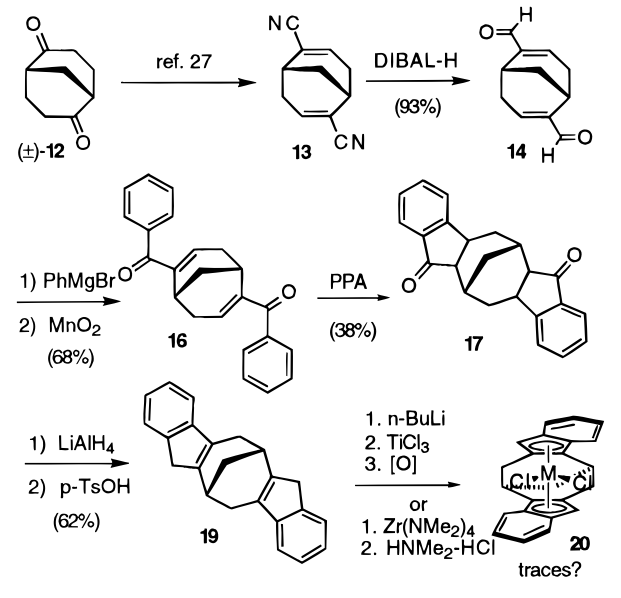
Table 2. Selected Bond Lengths (Å) and Angles (deg) for 11[a]

Zr(1)−Cl (1)	2.4283(8)	Zr(2)−Cl (2)	2.4355(9)
Zr(1)−Cp_{cent}(1)	2.219(3)	Zr(2)−Cp_{cent}(2)	2.218(3)
Zr(1)−C(1)	2.481(3)	Zr(2)−C(12)	2.493(3)
Zr(1)−C(2)	2.470(3)	Zr(2)−C(13)	2.472(3)
Zr(1)−C(3)	2.500(3)	Zr(2)−C(14)	2.493(3)
Zr(1)−C(4)	2.601(3)	Zr(2)−C(15)	2.586(3)
Zr(1)−C(5)	2.423(4)	Zr(2)−C(16)	2.593(3)

Cl(1)−Zr(1)−Cl (1′)	93.88(4)
Cp_{cent}(1)−Zr(1)−Cp_{cent}(1′)	120.2(1)
Cl(2)−Zr(2)−Cl (2′)	96.43(4)
Cp_{cent}(2)−Zr(2)−Cp_{cent}(2′)	120.4(1)

[a] Symmetry transformations used to generate equivalent atoms: (molecule 1) $-x + 1, y, -z + 1/2$; (molecule 2) $-x + 2, y, -z + 1/2$.

Scheme 3. Synthesis of Doubly Bridged Bis(indene) from Meerwein's Diketone



wein's diketone **12** and converted it into the dinitrile **13** according to literature procedures.[27] We were unable to get good yields of the desired dibenzoyl compound **15** by the direct addition of phenyllithium or phenylmagnesium halides to the nitriles. Apparently, poor solubility after the first addition was at least partially to blame. We were able to effect an efficient three-step procedure by first reducing dinitrile **13** to dialdehyde **14** with DIBAL-H and then adding phenyl Grignard to give a stereoisomeric mixture of diols **15**, which underwent oxidation of the allylic diols with MnO_2 to give dibenzoyl **16** in 63% yield for the three steps. Treating diketone with polyphosphoric acid induced the two desired Nazarov cyclizations to yield bis(indanone) **17** in 38% yield. Reduction of **17** with $LiAlH_4$ gave bis(indenol) **18**, which could be dehydrated to give the desired bis(indene) **19** in 62% yield for the two steps. The NMR spectra of **19** indicated that a mixture of indenyl double-bond isomers was present. The isomer of **19** with the more substituted position could be isolated by chromatography and characterized.

Attempts to metalate bis(indene) **19** under the conditions successfully used to metalate **9** did not produce isolable bis(indenyl)metal dichloride complexes. The addition of $ZrCl_4$ to the dilithium salt of **19** was also unsuccessfully attempted. In each case, new ^1H NMR signals from the crude reaction product mixtures could be seen in the range of 6−7 ppm, but signals corresponding to recovered ligand were the major peaks. Since we were never able to isolate any of the metal complexes, we do not know if some of these initial signals were arising from the desired *ansa*-metallocenes or if all were due to complexation of metals on the more accessible convex π-faces of the ligands. During the course of our metalation study, Buchwald and coworkers published results with the same bridging group for bis(cyclopentadienes)[14] rather than the indenes in our ligand **19**. Our lack of success in obtaining isolable metal complexes is mirrored by poor yields obtained in Buchwald's metalation of the bicyclic bridged bis(cyclopentadienes).

Summary. The new C_{2h}-symmetric doubly bridged bis(indene) **9** was prepared from 1,5-dimethyl-1,5-cyclo-

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octadiene via selenium-catalyzed oxidation reaction and a double Nazarov π-cyclization reaction. The first C_2-symmetric doubly bridged bis(indenyl)titanium and -zirconium dichlorides containing ethylene bridges were prepared. Through the addition of substituted phenylmetal reagents to dialdehyde **4**, the extension of this method to the preparation of substituted C_2-symmetric doubly bridged bis(indenyl)metal complexes should be possible. The solid-state structure of zirconium complex **11** and the ability of **11** to promote isotactic polymerization of propene were also determined.

Experimental Section

General Considerations. For a description of standard synthetic techniques used in our laboratory, see ref 28.

1,5-Cyclooctadiene-1,5-dicarboxaldehyde (4). To a *tert*-butyl hydroperoxide (TBHP) solution in dichloromethane (5.0 M, 550 mL, 2.65 mol) diluted with additional dichloromethane (2.0 L)[18] was added a commercial mixture of 1,5-dimethyl-1,5-cyclooctadiene and 1,6-dimethyl-1,5-cyclooctadiene (75:25 ratio) (100 g, 0.73 mol), followed by addition of SeO_2 (2.4 g, 21.6 mmol). Every 5 days the same amount of SeO_2 was added to the solution and the progress of the reaction was followed by NMR spectroscopy. On this large scale, the reaction mixture was stirred for 62 days, during which time the solution turned orange and a selenium-based precipitate deposited along the side of the flask. Dimethyl sulfide (200 mL) was added to the reaction mixture to quench the excess TBHP, and the solution was stirred at room temperature for 6 h. The volatiles were removed *in vacuo*, and the residual oil was dissolved in ether (500 mL) and treated with aqueous 1 N NaOH solution (3 × 50 mL). The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified (SiO_2, 20% ethyl acetate/80% petroleum ether) to furnish **4** as a white solid (12.65 g, 14%): mp 112−115 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 9.34 (s, 2 H), 6.59 (dd, $J = 5.0$ Hz, 2 H), 2.85 (dd, $J = 6.0$ Hz, 4 H), 2.66 (dd, $J = 6.0$, 5.0 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.9, 154.3, 142.1, 30.2, 20.8. IR (thin film): 2888, 1671, 1636, 1481, 1442, 1404, 1276, 1140 cm^{-1}. MS (EI, 12 eV: *m/e* (relative intensity)): 164 (43), 146 (14), 136 (53), 117 (60), 107 (69), 91 (64), 81 (40), 79 (100), 77 (66), 67 (35), 53 (48), 43 (30).

1,5-Dibenzoyl-1,5-cyclooctadiene (6). Phenylmagnesium chloride (2.0 M in THF, 27.5 mL, 54.8 mmol) was added dropwise to a THF (150 mL) solution of **4** (3 g, 18.3 mmol) at −78 °C. The resulting solution was warmed to room temperature over 4 h. The reaction mixture was cooled to 0 °C and carefully quenched with water (25 mL) and 1 M HCl (30 mL). After separation of the organic phase, the aqueous layer was extracted with dichloromethane (2 × 80 mL). The combined organic layers were dried with $MgSO_4$ and concentrated *in vacuo*. The crude product was purified (SiO_2, 30% ethyl acetate/70% petroleum ether) to yield 1,5-bis(hydroxyphenylmethyl)-1,5-cyclooctadiene (**5**) as a viscous oil (5.8 g, 99%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.34 (bs, 10 H), 5.65 (dd, $J = 6.0$, 6.0 Hz, 2 H), 5.09 (s, 2 H), 2.33−2.12 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.5, 141.2, 128.2, 128.1, 127.3, 126.2, 126.1, 126.0, 79.6, 79.5, 29.7, 26.8, 26.7, 26.6. IR (thin film) 3479, 3301, 2950, 2851, 1634, 1497, 1448, 1238, 1016 cm^{-1}. MS (EI, 12 eV); *m/e* (relative intensity)): 320 (6), 316 (6), 302 (23), 300 (34), 284 (32), 274 (20), 211 (60), 196 (47), 182 (100), 170 (37), 156 (23), 146 (20), 133 (40), 105 (67).

A solution of oxalyl chloride (5.74 g, 45.3 mmol) in anhydrous methylene chloride (100 mL) was cooled to −78 °C under nitrogen. Dimethyl sulfoxide (7.35 g, 6.68 mL, 94.1 mmol) was added dropwise at a rapid rate, with stirring. After 15 min, the CH_2Cl_2 solution (50 mL) of the above 1,5-bis(phenylhydroxymethyl)-1,5-cyclooctadiene (5.8 g, 18.1 mmol) was added dropwise over 10 min. After 15 min of stirring, triethylamine (25 mL, 181 mmol) was added dropwise, with the temperature kept below −50 °C. Stirring was then continued for 15 min. The mixture was warmed to room temperature, and water (100 mL) was added. The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 80 mL). The organic phases were washed with saturated NaCl solution (75 mL) and dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue purified (SiO_2, 15% ethyl acetate/85% petroleum ether) to yield **6** as a clear colorless oil (4.23 g, 74%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, $J = 8.0$ Hz, 4 H), 7.49 (dd, $J = 7.0$, 7.0 Hz, 2 H), 7.40 (dd, $J = 8.0$, 7.0 Hz, 4 H), 6.53 (dd, $J = 6.0$ Hz, 2 H), 2.99 (dd, $J = 6.0$, 6.0 Hz, 4 H), 2.73 (ddd, $J = 6.0$, 6.0, 6.0 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 145.8, 139.9, 138.7, 131.5, 129.2, 128.1, 29.6, 25.3. IR (neat): 2924, 2890, 1644, 1450, 1209 cm^{-1}. MS (EI 70 eV; *m/e* (rel intensity)): 316 (29), 288 (3), 211 (8), 183 (8), 105 (100), 77 (60), 51 (7).

Alternate Synthesis of 4. Li metal (0.016 g, 2.25 mmol) was cut and quickly added to a solution of 4,4′-di-*tert*-butylbiphenyl (0.72 g, 2.7 mmol) in THF (10 mL) at room temperature.[21] After a few minutes an intense deep blue color developed, and the mixture was cooled to 0 °C and stirred rapidly for 3 h. After the mixture was cooled to −78 °C, a solution of 1,5-dibromo-1,5-cyclooctadiene[20] (0.10 g, 0.37 mmol) in THF (2 mL) was added dropwise. After 1 h a solution of dimethylformamide (0.17 mL, 2.25 mmol) in THF (2 mL) was added at −78 °C by syringe. The color of the reaction mixture changed from dark blue to dark red. After it was stirred at −78 °C for an additional 1 h, the mixture was stirred at room temperature overnight. Water (5 mL) was added, the layers separated, and the aqueous portion was extracted with dichloromethane (2 × 10 mL). The combined organic portion was dried with $MgSO_4$ and concentrated and the crude product purified (SiO_2, 20% ethyl acetate/80% petroleum ether) to furnish **4** as a white solid (0.040 g, 65%). The ^1H NMR and ^{13}C NMR spectral data of this product were identical with those collected above.

Alternate Synthesis of 6. Copper(I) iodide (0.215 g, 1.13 mmol) was placed in a 25 mL round-bottom flask under a nitrogen atmosphere in a glovebox. A solution of benzoyl chloride (0.16 g, 1.13 mmol) in THF (5 mL) was added via syringe and this "mixture A" was stirred at room temperature for 3 h.[22] Li metal (0.012 g, 1.73 mmol) was cut and quickly added to a solution of 4,4′-di-*tert*-butylbiphenyl (0.50 g, 1.88 mmol) in THF (10 mL) at room temperature.[21] After a few minutes an intense deep blue color developed and the mixture was cooled to 0 °C and stirred rapidly for 3 h. After the mixture was cooled to −78 °C, a solution of 1,5-dibromo-1,5-cyclooctadiene[20] (0.10 g, 0.37 mmol) in THF (2 mL) was added dropwise. The solution was stirred for 1 h and then slowly transferred via cannula into a precooled (−78 °C) solution of mixture A. The resulting dark brown-green mixture was stirred at −78 °C for 1 h and then warmed to 0 °C, at which point saturated NH_4Cl (10 mL) was added. The mixture was extracted with methylene chloride (3 × 15 mL), and the combined organic portions were dried over $MgSO_4$ and evaporated. The crude product was purified (SiO_2, 15% ethyl acetate/85% petroleum ether) to yield **6** as a clear pale yellow oil (0.065 g, 55%). The ^1H NMR and ^{13}C NMR spectral data of this product were identical with those collected above.

2,3′-(Ethane-1,2-diyl)-3,2′-(ethane-1,2-diyl)bis(indanone) (7). 1,5-dibenzoyl-1,5-cyclooctadiene (**6**; 0.46 g, 1.45 mmol) was mixed with polyphosphoric acid (PPA; 10 mL), and the resulting mixture was kept at 120 °C for 3 h with stirring. While hot, the reaction mixture was poured into cold water (40 mL) and extracted with ether (3 × 40 mL). The ether extracts were dried with $MgSO_4$ and concentrated in *vacuo*. The crude product was purified (SiO_2, 20% ethyl acetate/80% petroleum ether) to furnish **7** as a yellow solid (0.25 g, 54%) as a mixture of isomers. ^1H NMR (300 MHz, $CDCl_3$): δ 7.76

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(28) Halterman, R. L.; Ramsey, T. M.; Pailes, N. A. *J. Organomet. Chem.* **1995**, *497*, 43−53.

(m, 2 H), 7.64 (m, 2 H), 7.55 (m, 2 H), 7.40 (m, 2 H), 3.54 (m, 0.5 H), 3.26−3.12 (m, 1.5 H), 2.79−2.22 (m, 6 H), 1.84−1.62 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.1, 200.3, 158.3, 136.6, 135.5, 135.3, 135.2, 127.9, 127.7, 125.6, 124.9, 123.9, 123.8, 123.6, 55.7, 53.2, 51.7, 48.1, 43.8, 38.1, 33.0, 30.6, 23.1. IR (thin film): 2917, 1704, 1596, 1464, 1288, 1224 cm^{-1}. MS (EI, 12 eV; *m/e* (relative intensity)): 316 (100), 298 (68), 280 (11), 270 (23), 158 (22), 144 (12).

2,3′-(Ethane-1,2-diyl)-3,2′-(ethane-1,2-diyl)bis(indanol) (8). To a THF suspension (50 mL) of $LiAlH_4$ (0.044 g, 1.2 mmol) at 0 °C under nitrogen was slowly added a THF solution (5 mL) of **7** (0.19 g, 0.6 mmol), and the solution was gradually warmed to room temperature. After it was stirred for 1 h at room temperature, the solution was cooled to 0 °C and the reaction was slowly quenched with Rochelle's salt (2 mL), the mixture was then stirred for 0.5 h and filtered. The solution was concentrated and the crude product was purified (SiO_2, 35% ethyl acetate/65% petroleum ether) to furnish diol **8** as a colorless viscous oil (0.163 g, 85%) as a mixture of isomers. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42−7.22 (m, 8 H), 5.19 (d, J = 7.0 Hz, 0.2 H), 4.99 (d, J = 7.0 Hz, 0.2 H), 4.85 (m, 0.8 H), 4.74 (d, J = 7.0 Hz, 0.8 H), 3.32 (m, 0.4 H), 3.08 (m, 0.8 H), 2.77−2.15 (m, 3.6 H), 2.05−1.54 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.4, 146.8, 146.0, 143.4, 143.0, 142.8, 128.7, 128.6, 128.5, 128.4, 128.1, 127.2, 127.1, 127.0, 124.6, 124.2, 123.8, 123.6, 123.2, 83.9, 83.6, 83.1, 81.5, 61.7, 55.2, 53.9, 49.8, 47.4, 45.2, 37.4, 36.9, 35.9, 34.5, 32.1, 29.7, 29.6, 24.8. IR (thin film): 3298, 2921, 2851, 1638, 1459, 1376, 1259, 1019 cm^{-1}. MS (EI, 12 eV; *m/e* (relative intensity)): 320 (60), 302 (100), 284 (63), 269 (12), 256 (34), 156 (25), 143 (13), 130 (10).

1,2′-(Ethane-1,2-diyl)-2,1′-(ethane-1,2-diyl)bis(indene) (9). To a benzene solution (20 mL) of **8** (0.16 g, 0.49 mmol) was added the catalytic amount of *p*-TsOH·×H_2O (10 mg, 0.053 mmol), and the solution was heated under reflux. After 2 h the reaction was judged complete by TLC analysis (SiO_2, 30% ethyl acetate/70% petroleum ether). Sodium carbonate (1 g, 9.4 mmol) was added to quench the reaction. Filtration and evaporation of the solvent afforded the crude mixture, which was purified (SiO_2, petroleum ether) to furnish **9** as a clear viscous oil (0.06 g, 42%) as a mixture of isomers. Conversion of this mixture into the dilithium salt, and subsequent quenching with water, resulted in the formation of a mixture of isomers where **9** was a predominant compound as a thermodynamically more stable isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37−7.04 (m, 8H), 3.28 (bs, 4H), 3.02 (bs, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5, 148.7, 147.8, 144.1, 142.2, 141.6, 135.1, 128.6, 128.5, 126.5, 126.4, 126.1, 126.0, 124.1, 123.8, 123.7, 123.0, 122.4, 122.1, 119.8, 119.8, 117.5, 50.7, 50.2, 43.3, 43.1, 30.1, 29.7, 29.6, 29.6, 28.6, 27.9, 26.2, 25.4, 24.7. IR (thin film): 3063, 3012, 2923, 2877, 2823, 1603, 1464, 1425, 1390 cm^{-1}. MS (EI, 12 eV: *m/e* (relative intensity)): 284 (100), 269 (6), 256 (9), 155 (8), 142 (22).

[1,2′-(Ethane-1,2-diyl)-2,1′-(ethane-1,2-diyl)bis(indenyl)]dichlorotitanium (10). Into a solution of bis(indene) **9** (0.09 g, 0.31 mmol) in THF (2 mL) at 0 °C was injected *n*-butyllithium (0.26 mL, 2.7 M in hexane, 0.69 mmol) via syringe under nitrogen. After it was stirred for 30 min at 0 °C, the solution was transferred to a previously cooled (−78 °C) solution of $TiCl_3$ (0.059 g, 0.38 mmol) in THF (1 mL). The resulting dark greenish brown solution was gradually warmed to room temperature and then heated under reflux for 8 h. The solvent was removed *in vacuo,* the residue was taken up in $CHCl_3$ (4 mL), 6 M HCl (1 mL) was added, and the solution was stirred for 2 h. The organic layer was separated and the water layer extracted with CH_2Cl_2 (2 × 5 mL), dried over $MgSO_4$, and concentrated to provide a dark green solid. The solid was rinsed with hexanes, filtered, and dried *in vacuo* to give a single diastereomer of bis(indenyl)titanium dichloride **10** (0.08 g, 63%) as a dark green powder: mp >190 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, J = 2 H), 7.35 (dd, J = 8.0, 7.0 Hz, 2 H), 7.15 (m, 4 H), 6.89 (s, 2 H), 3.75 (m, 4 H), 3.61 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.4, 131.1, 129.8, 127.4, 126.8, 125.9, 123.3, 122.7, 117.8, 30.8, 28.2. IR (thin film): 2991, 2921, 1605, 1471, 1455, 1299, 1259, 1087 cm^{-1}. MS (EI, 12 eV; *m/e* (relative intensity)): 406 ($M^+ + 6$, 1), 405 ($M^+ + 5$, 3), 404 ($M^+ + 4$, 7), 403 ($M^+ + 3$, 12), 402 ($M^+ + 2$, 80), 401 ($M^+ + 1$, 30), 400 (M^+, 100), 366 (21), 365 (10), 364 (43), 362 (10), 328 (12), 310 (8), 282 (7), 168 (6), 142 (7), 84 (7).

[1,2′-(Ethane-1,2-diyl)-2,1′-(ethane-1,2-diyl)bis(indenyl)]dichlorozirconium (11). To bis(indene) **9** (0.550 g, 1.93 mmol) and tetrakis(dimethylamido)zirconium (0.518 g, 1.93 mmol) was added chlorobenzene dropwise at 0 °C, and the resulting solution was warmed to reflux for 24 h. The resulting clear yellow-orange solution was cooled to 0 °C, and a solution of $HNMe_2$−HCl (0.316 g, 3.88 mmol) in dichloromethane (50 mL) was added dropwise. The mixture was warmed to room temperature and stirred for 2 h. After it was concentrated to approximately 1 mL, hexanes were slowly added to the solution until a fine yellow precipitate formed. The precipitate was filtered in a Schlenk frit and rinsed with hexanes (2 × 10 mL) to yield bis(indenyl)zirconium dichloride as a yellow powder in 67% yield (0.573 g, 1.29 mmol): mp >225 °C dec. Anal. Calcd for $C_{22}H_{18}ZrCl_2$: C, 59.45; H, 4.08. Found: C, 59.69; H, 4.08. ^{13}C NMR (75 MHz, $CDCl_3$): δ.138.6, 128.2, 127.2, 125.6, 124.4, 122.4, 117.8, 108.2, 104.8, 30.5, 26.8. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (2H, d, J = 8.5 Hz), 7.40 (2H, d, J = 8.5 Hz), 7.28 (2H, dd, J = 8.5, 7.5 Hz), 7.08 (2H, dd, J = 8.5, 7.5 Hz), 6.56 (2H, s), 3.70 (4H, m), 3.55 (4H, m). MS (EI, 12 eV; *m/e* (relative intensity)): 450 ($M^+ + 8$, 2.5), 449 ($M^+ + 7$, 6.2), 448 ($M^+ + 6$, 32), 446 ($M^+ + 4$, 66), 444 ($M^+ + 2$, 98), 443 ($M^+ + 1$, 58), 442 (M^+, 100) 406 (11).

X-ray Structure of 11. The data were collected at −55 °C on a Siemens P4 diffractometer. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scans was applied. The structure was solved by direct methods using SHELXTL (Siemens systems) and refined by full-matrix least-squares on F^2 using all reflections. Two independent molecules were located in the unit cell, with each molecule possessing a crystallographically imposed C_2 axis. All the hydrogen atoms were located and refined isotropically. For 2416 observed reflections ($I > 2\sigma(I)$), the final R1 value was 0.029. Details of the crystal data and refinement are given in Table 1. The ORTEP figures are drawn with 40% thermal ellipsoids.

Bicyclo[3.3.1]nona-2,6-diene-2,6-dicarboxaldehyde (14). Bicyclo[3.3.1]nona-2,6-diene-2,6-dicarbonitrile (**13**) was prepared according to the literature from Meerwein's diketone **12**.[27] To a solution of **13** (8.6 g, 50.5 mmol) in benzene (500 mL) at −78 °C was added diisobutylaluminum hydride (1.5 M in toluene, 86 mL, 129 mmol) dropwise. The resulting solution was warmed to 0 °C during 2 h. The reaction was quenched with saturated Rochelle's salt solution (100 mL) and the mixture extracted with dichloromethane (2 × 200 mL). The combined organic layers were dried with $MgSO_4$ and evaporated at room temperature to give **14** (8.3 g, 93%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 2H), 6.73 (dd, J = 5.0, 2.0 Hz, 2H), 3.20 (m, 2H), 2.60 (m, 2H), 2.30 (dd, J = 10.0, 5.0 Hz, 2H), 1.69 (dd, J = 3.0, 3.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.5, 150.4, 144.3, 32.3, 27.1, 24.9. IR (thin film): 2923, 2815, 1677, 1631, 1418, 1159 cm^{-1}. (EI, 12 eV; *m/z* (relative intensity)): 176 (100), 147 (30), 129 (27), 117 (11), 94 (17), 91 (12), 78 (10).

2,6-Bis(hydroxyphenylmethyl)bicyclo[3.3.1]nona-2,6-diene (15). Phenylmagnesium chloride (2.0 M in THF, 60 mL, 120 mmol) was added to a solution of **14** (8.3 g, 47.1 mmol) in THF (150 mL) at −78 °C. The resulting solution was warmed to room temperature over 4 h. The reaction mixture was quenched with water (25 mL) and 5% H_2SO_4 (30 mL) and extracted with ether (2 × 80 mL). The combined organic portion was dried with $MgSO_4$ and concentrated *in vacuo*. The crude product was purified (SiO_2, petroleum ether followed by 30% ethyl acetate/70% petroleum ether) to yield **15** (15.2 g, 97%) as a colorless viscous oil. ^{1}H NMR (mixture of isomers;

300 MHz, $CDCl_3$): δ 7.50−7.20 (m, 10H), 6.95−5.95 (m, 2H), 5.30−5.00 (m, 2H), 2.50 (m, 2H), 2.40−2.10 (m, 4H), 2.00−1.80 (m, J = 3.0 Hz, 2H), 1.60−1.50 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.8, 142.7, 128.5, 127.8, 127.2, 127.0, 126.3, 78.1, 31.7, 31.4, 31.1, 30.1, 29.7, 28.0, 27.8. IR (thin film): 3417, 3025, 2922, 2828, 1653, 1600, 1491, 1449, 1019 cm^{-1}. MS (EI, 12 eV; m/z (relative intensity)): 314 (8), 244 (26), 227 (14), 226 (100), 208 (14), 185 (26), 148 (12), 107 (25), 106 (12), 105 (41).

2,6-Dibenzoylbicyclo[3.3.1]nona-2,6-diene (16). A mixture of **15** (15.2 g, 45.7 mmol) and MnO_2 (40 g, 460 mmol) in CH_2Cl_2 (250 mL) was stirred for 8 h at room temperature. The mixture was filtered through Celite and concentrated. The residue was purified by column chromatography (SiO_2, 20% ethyl acetate in petroleum ether) to provide **16** (10.5 g, 70%) s a viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70−7.40 (m, 10H), 6.61 (dd, J = 5.0, 2.0 Hz, 2H), 3.34 (m, 2H), 2.60 (ddd, J = 20.0, 5.0, 2.0 Hz, 2H), 2.42 (dd, J = 20.0, 5.0 Hz, 2H), 1.85 (dd, J = 3.0, 3.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 143.5, 141.3, 138.9, 131.5, 139.1, 128.1, 32.8, 28.1, 26.3. IR (thin film): 2927, 2871, 1642, 1596, 1445, 1419, 1267 cm^{-1}. MS (EI, 12 eV; m/z, (relative intensity)): 329 (9), 328 (100), 223 (13), 183 (8), 105 (22).

Hexacyclo[10.10.1.0^{2,10}.0^{4,9}.0^{13,21}.0^{15,30}]tricosa-4,6,8,15,17,19-hexaene-3,14-dione (17). Diketone **16** (3.50 g, 10.7 mmol) was mixed with polyphosphoric acid (PPA; 30 mL), and the resulting mixture was kept at 120 °C for 3 h with stirring. The reaction mixture was poured into cold water (80 mL) and extracted with ether (3 × 50 mL). The ether extracts were dried with $MgSO_4$ and concentrated *in vacuo*. The crude product was purified (SiO_2, 20% ethyl acetate/80% petroleum ether) to furnish **17** (1.36 g, 39%) as a pale yellow solid. Although the isomeric mixture could be used in the next step, careful chromatgraphy provided one of the isomers in a pure form. Mixture of isomers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95−6.90 (m, 8H), 4.90−3.40 (m, 1H), 3.20−2.70 (m, 3H), 2.60−2.0 (m, 3H), 2.10−1.60 (m, 2H), 1.50−1.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.3, 159.5, 158.9, 137.3, 135.1, 134.5, 134.1, 127.6, 127.3, 124.9, 123.9, 123.6, 53.8, 51.2, 35.0, 34.9, 34.1, 32.7, 29.6, 28.8, 25.7; MS (EI, 12 eV; m/z (relative intensity)) 329 (5), 328 (24), 311 (23), 310 (100), 292 (11), 197 (25), 184 (20), 183 (25), 182 (12), 181 (16), 179 (20), 167 (13), 166 (12), 165 (28), 152 (12), 146 (12), 145 (34), 133 (14), 132 (40), 131 (24), 128 (28), 115 (39), 77 (28). Single isomer: mp 269−270 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 7.5 Hz, 2H), 7.60 (dd, J = 7.5, 7.5 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 7.39 (dd, J = 7.5, 7.5 Hz, 2H), 3.80 (ddd, J = 14.5, 7.5, 7.5 Hz, 2H), 2.84 (m, 4H), 2.32 (m, 2H), 1.33 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.0, 159.2, 134.6, 134.5, 127.6, 125.0, 124.3, 53.7, 40.9, 37.8, 28.9, 26.8; IR (thin film) 2923, 2860, 1705, 1603, 1462 cm^{-1}; MS (EI, 70 eV; m/z (relative intensity)) 329 (9), 328 (87), 198 (100), 197 (79), 184 (30), 182 (47), 179 (93), 164 (35), 128 (51), 115 (48), 77 (27).

Hexacyclo[10.10.1.0^{2,10}.0^{4,9}.0^{13,21}.0^{15,30}]tricosa-4,6,8,15,17,19-hexaene-3,14-diol (18). To a THF suspension (20 mL) of $LiAlH_4$ (1.5 g, 39 mmol) at 0 °C under nitrogen was slowly added a THF solution (5 mL) of **17** (0.85 g, 2.6 mmol), and the solution was gradually warmed to room temperature. After it was stirred for 1 h at room temperature, the solution was cooled to 0 °C, the reaction was slowly quenched with Rochelle's salt (2 mL), and the mixture was stirred for 0.5 h and filtered. The solution was concentrated, and the crude product was purified (SiO_2, 35% ethyl acetate/65% petroleum ether) to furnish diol **18** as a white solid (0.163 g, 85%) as a mixture of isomers: mp 82−92 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45−6.50 (m, 8H), 5.40−4.90 (m, 2H), 3.80−2.80 (m, 2H), 2.50−1.0 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.6, 145.5, 145.3, 142.9, 128.8, 128.1, 127.9, 127.6, 126.9, 126.8, 126.5, 126.4, 123.7, 123.6, 122.2, 79.0, 68.0, 55.7, 50.1, 36.2, 34.1, 32.3, 29.1, 27.5, 26.4, 25.6. IR (thin film): 3484, 2019, 2916, 2951, 1695, 1602, 1458, 1263, 1056 cm^{-1}. MS (EI, 12 eV; m/z, (relative intensity)): 332 (1), 314 (100), 296 (19), 184 (10), 183 (10), 166 (11),117 (9).

Hexacyclo[10.10.1.0^{2,10}.0^{4,9}.0^{13,21}.0^{15,30}]tricosa-2(10),4,6,8,13(21),15,17,19-octaene (19). To a benzene solution (20 mL) of **18** (0.82 g, 2.5 mmol) was added a catalytic amount of p-TsOH·$x$$H_2O$ (10 mg, 0.053 mmol), and the solution was heated under reflux. After 5 h, sodium carbonate (2 g) was added to quench the reaction. Filtration and evaporation of the solvent afforded the crude mixture, which was purified (SiO_2, petroleum ether) to furnish **19** (0.475 g, 64%) as a white solid. Mixture of isomers: ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 156.2, 147.8, 147.0, 145.6, 144.6, 126.5, 126.3, 124.1, 123.8, 123.7, 122.6, 122.4, 120.4, 120.3, 120.1, 45.7, 43.3, 39.2, 34.2, 33.0, 30.9, 30.5, 30.2, 29.8, 22.7, 22.4, 14.1; MS (EI, 12 eV; m/z relative intensity)) 298 (5), 297 (26), 296 (100), 167 (58), 166 (24). Single double-bond isomer: mp 230−233 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 7.5 Hz, 2H), 7.20 (dd, J = 7.5, 7.0 Hz, 2H), 7.12 (d, J = 7.0 Hz, 2H), 7.07 (ddd, J = 7.5, 7.0, 1.5 Hz, 2H), 3.37 (ddd, J = 22.0, 3.0, 3.0 Hz, 2H), 3.23 (33, J = 22.0, 3.0 Hz, 2H), 2.75 (m, 2H), 2.52 (d, J = 17.0 Hz, 2H), 2.01 (dd, J = 3.0, 3.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.9, 144.3, 142.5, 134.2, 126.1, 123.9, 123.4, 117.6, 39.0, 30,8, 29.3, 28.7; IR (thin film) 2926, 2892, 1641, 1578, 1463, 1260, 1024 cm^{-1}; MS (EI, 12 eV; m/z (relative intensity)) 298 (5), 297 (14), 296 (90), 167 (100), 130 (18), 88 (6), 86 (41), 84 (60).

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Supporting Information Available: For *dl*-**11**, tables of X-ray crystal data atomic coordinates, anisotropic parameters, bond lengths, and angles (12 pages). Ordering information is given on any current masthead page.

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