Syntheses of Acetylenic Oligophenylene Macrocycles Based on a Novel Dewar Benzene Building Block Approach

Masakazu Ohkita, Kohta Ando, Takanori Suzuki, and Takashi Tsuji*

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

tsuji@science.hokudai.ac.jp

Received February 24, 2000

A general synthetic approach to strained *p*-phenylene-based acetylenic macrocycles is described. A key feature in this approach is exploitation of Dewar benzene as an angular *p*-phenylene synthon. Thus, 1,4-acetal-bridged 2,5-dichloro(Dewar benzene) **5**, prepared in four steps from dimethyl acetylenedicarboxylate and 1,2-dichloroethylene, is applied as such a building block in the syntheses of strained macrocycles **13** and *anti*-**20**. For the synthesis of **13**, *m*-phenylene units are used as spacers and modified Eglington−Glaser coupling is applied for the macrocyclization step. For the synthesis of *anti*-**20**, on the other hand, *o*-phenylene units are used as spacers and Sonogashira coupling is applied for the macrocyclization step. Macrocycles **13** and *anti*-**20** are characterized crystallographically, and their strained nature is reflected mainly in the deviation of the acetylene units from linearity; the C≡C−C angles range from 168.7(3)° to 179.9(3)° in **13** and from 168.0(5)° to 171.4(4)° in *anti*-**20**. Macrocycle **13** shows unique conformational property, namely, the *p*-phenylene units arranged in parallel in the rectangular framework rotate freely about the long axes, as evidenced by the ^{1}H NMR studies. Macrocycle *anti*-**20** exhibits a Stokes shift of 179 nm, which is exceptionally large for phenylacetylene macrocycles, presumably owing to the characteristic stacking structure.

Introduction

Macrocycles consisting of benzene cores linked by acetylenic units have attracted considerable recent attention in supramolecular chemistry and materials science.[1] Owing to the rigid and directional characteristics of the subunits, they have provided well-defined, shape-persistent structural motives that show unique association behavior[2] as well as conformational properties.[3] They have been also regarded as attractive precursors for novel carbon allotropes and carbon-rich materials.[4] Despite the extensive studies, however, *p*-phenylene-based, and thus strained, acetylenic macrocycles are so rare that their chemistry has not been well developed.[5]

Valence-bond isomerization of Dewar derivatives is a useful reaction for generating structurally distorted benzene derivatives and has been successfully applied for the preparation of small [*n*]paracyclophanes.[6] Despite the high potential, however, only little attention has been focused on the application of this transformation for more complex cyclophane systems so far,[7] probably because the oligo(Dewar benzene) precursors are rather laborious to prepare.

We were interested in exploiting a Dewar structure for the preparation of *p*-phenylene-based strained macrocycles. Since the bent shape of Dewar benzene is expected to provide a unique template effect on the cyclization, novel macrocyclic systems that are difficult to access from planar benzene derivatives may well become available from the Dewar benzene approach. To investigate these possibilities, we designed Dewar benzene **5**, possessing a 1,4-acetal bridge that prevents an undesired aromatization of the Dewar form before macrocyclization, as a building block. In this paper we describe the rational and efficient syntheses of *p*-phenylene-based strained macrocycles **13** and *anti*-**20** based on the Dewar benzene approach using **5**.[8] Structures and properties of these novel macrocycles will be also reported.

Results and Discussion

Preparation of 5. Dewar benzene **5** was readily prepared in four steps and on a gram scale from dimethyl

(1) Hally, M. M.; Pak, J. J.; Brand, S. C. In *Topics in Current Chemistry*; de Meijere, A., Ed.; Springer-Verlag: Heidelberg, 2000; Vol. 201, p 81.

(2) (a) Zhang, J.; Pesak, D. J.; Ludwick, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4227. (b) Shetty, A. S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019. (c) Tobe, Y.; Utsumi, N.; Kawabata, K.; Naemura, K. *Tetrahedron Lett.* **1996**, *37*, 9325. (d) Tobe, Y.; Utsumi, N.; Kawabata, K.; Naemura, K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1285.

(3) (a) Bedard, T. C.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 10662. (b) Höger, S.; Meckenstock, A.-D.; Muller, S. *Chem. Eur. J.* **1998**, *4*, 2423. (c) Romero, M. A.; Fallis, A. G. *Tetrahedron Lett.* **1994**, *35*, 4711.

(4) Reviews: (a) Faust, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2825. (b) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, *28*, 107.

(5) (a) Kawase, T.; Darabi, H. R.; Oda, M. *Angew. Chem., Int. Ed.* **1996**, *35*, 2664. (b) Haley, M. M.; Langsdorf, B. L. *J. Chem. Soc., Chem. Commun.* **1997**, 1121. (c) Collins, S. K.; Yap, G. P. A.; Fallis, A. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 385.

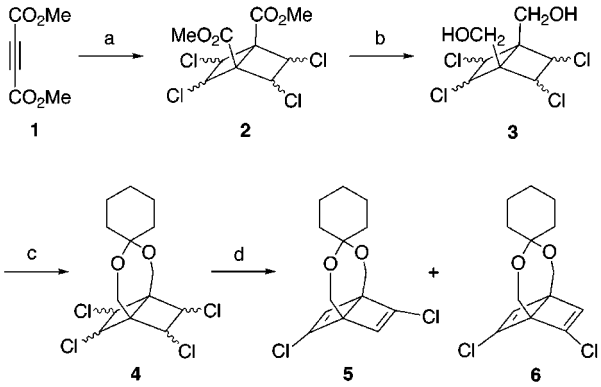
(6) Tsuji, T. *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI Press: Greenwich, 1999; Vol. 7, p 103 and references therein.

(7) (a) Tsuji, T.; Ohkita, M.; Nishida, S. *J. Am. Chem. Soc.* **1993**, *115*, 5284. (b) Tsuji, T.; Ohkita, M.; Konno, T.; Nishida, S. *J. Am. Chem. Soc.* **1997**, *119*, 8425. (c) Kawai, H.; Suzuki, T.; Ohkita, M.; Tsuji, T. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 817. (d) Kawai, H.; Suzuki, T.; Ohkita, M.; Tsuji, T. *Chem. Eur. J.*, in press. (e) Wijsman, G. W.; van Es, D. S.; de Wolf, W. H.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 726.

(8) Part of the results have been published in preliminary form: Ohkita, M.; Ando, K.; Yamamoto, K.; Suzuki, T.; Tsuji, T. *J. Chem. Soc., Chem. Commun.* **2000**, 83.

10.1021/jo0002590 CCC: $19.00
Published on Web 06/08/2000

Scheme 1[a]



[a] (a) *hν*, 1,2-dichloroethylene, −70 °C, 12 h, 27%; (b) $LiAlH_4$, Et_2O, 89%; (c) 1,1-dimethoxycyclohexane, TsOH, benzene, 68%; (d) *t*-BuOK, THF, 45% of **5** and 35% of **6**.

acetylenedicarboxylate (**1**) and 1,2-dichloroethylene (Scheme 1).[9] Thus, irradiation of **1** in a 1:1 mixture of 1,2-dichloroethylene and dichloromethane with a high-pressure mercury lamp afforded bicyclo[2.2.0]hexane derivatives **2** in 27% yield as a mixture of five stereoisomers with regard to the chlorine substituents. $LiAlH_4$ reduction of the esters **2** followed by treatment of the resulting diols **3** with 1,1-dimethoxycyclohexane under the influence of a catalytic amount of TsOH provided **4** in 61% yield. Cyclohexylidene was an acetal of choice because of its adequate stability toward acid hydrolysis. Dehydrochlorination of **4** with *t*-BuOK in THF at room temperature afforded desired **5** (45%) together with its regioisomer **6** (35%), which were separated by conventional column chromatography. Differentiation between **5** and **6** was readily made by examining their ^{1}H NMR spectra; acetal methylene protons in **5** appear as a pair of AB doublets (δ 3.95 and 3.98, J = 13.2 Hz), whereas those in **6** appear as two singlets (δ 3.98 and 4.00). Furthermore, the structure of crystalline **5** was unambiguously determined by X-ray crystallography. The structural analysis also revealed that a dihedral angle of the Dewar benzene is 116°. We thus evaluated that an angle of about 120°, similar to a *m*-phenylene unit, may be applicable for the macrocyclization using **5**.

Synthesis of 13. The synthesis of **13** was carried out as outlined in Scheme 2. In the synthesis, *m*-phenylene units were used as spacers and modified Eglington−Glaser coupling[10] was applied for the crucial macrocyclization step. Singly protected 1,3-diethynylbenzene **8** was prepared in 43% yield by partial desilylation of 1,3-bis[(trimethylsilyl)ethynyl]benzene (**7**)[11] with aqueous KOH in MeOH followed by purification by distillation. Palladium-catalyzed coupling of **5** with **8** afforded diethynylation product **9** in 55% yield, which was then deprotected to the terminal acetylene **10** in 76% yield. Copper-mediated oxidative coupling of **10** with CuCl/$Cu(OAc)_2$[10] in pyridine under pseudo-high-dilution conditions produced cyclic dimer **11** in 70% yield.[12] Acid hydrolysis of the acetal **11** followed by silylation of the resulting tetraol afforded **12** in 68% yield. Photochemical isomerization of **12** proceeded smoothly by irradiation with a high-pressure mercury lamp through Pyrex at 12 °C to afford **13** in quantitative yield. The clean and quantitative conversion of **12** into **13** was further supported by the UV monitoring of the reaction, which showed an isosbestic point at 295 nm. The less symmetrical product resulting from the rearrangement of only one of the Dewar benzene units was not detected in the ^{1}H NMR monitoring of the reaction.

It is interesting to note that, in the ^{1}H NMR spectra, the benzylic methylene protons of **13** appear as a singlet (δ 4.95) whereas those of **12** appear as a pair of AB doublets (δ 4.10 and 4.12, J = 11.0 Hz), indicating that these protons are diastereotopic in **12** and operationally enantiotopic in **13**. These observations would be most reasonably explained by postulating fast interconversion of **13a** with the rotamer **13b**, namely, fast rotation of the *p*-phenylene unit(s) in **13** on the NMR time scale (Scheme 3). Molecular modeling shows, in fact, that such rotation requires no serious deformation of the macrocyclic framework.[13] Further elaboration of **13** would provide an interesting structural motif with unique conformational properties; for example, transmission-type combined rotation could be achieved if the residues R in **13** interact sterically with each other.

X-ray Crystallographic Study on 13. Crystals of **13** suitable for X-ray structure determination (see Supporting Information) were obtained by slow diffusion of ethanol into a solution of **13** in chloroform at room temperature. The molecule adopts a nearly planar conformation in the crystal, and the dimension of the framework is 7.32 Å × 11.54 Å, as defined by the four inner *m*-phenylene carbon atoms. Interestingly, the framework appears to be distorted to a parallelogram to accommodate two $SiMe_2OCH_2$ moieties inside the cavity. The twist angles of the benzene rings from the least-square plane formed by the acetylenic carbon atoms are 3.7° and 0.4° in the *m*-phenylene units and 3.4° in the *p*-phenylene units. The benzene rings are essentially planar (deviation < 0.01 Å), while the acetylene units show deviation from linearity with the C≡C−C angles ranging from 168.7(3)° to 179.9(3)°.

Synthesis of *anti*-20. To explore the scope of the present Dewar benzene building block approach, the synthesis of *anti*-**20** was next carried out as outlined in Scheme 4. In the synthesis, *o*-phenylene units were used as spacers and Sonogashira coupling[14] was applied for the crucial macrocyclization step. Macrocycle *anti*-**20** would also be regarded as a novel example of alkynyl-based fully unsaturated paracyclophanes.[15] Singly protected 1,2-diethynylbenzene **16** was prepared in 63% yield by the successive coupling of 1-bromo-2-iodobenzene (**14**) with (trimethylsilyl)acetylene and 2-methyl-3-butyn-2-ol followed by desilylation of the diethynylation product **15** with Bu_4NF. Palladium-catalyzed coupling of **5** with **16** gave monoethynylated product **17** in 57% yield.

(9) Tsuji, T.; Watanabe, H.; Tanaka, J.; Inada, M.; Nishida, S. *Chem. Lett*. **1990**, 1193.

(10) (a) O'Krongly, D.; Denmade, S. R.; Chiang, M. Y.; Breslow, R. *J. Am. Chem. Soc.* **1985**, *107*, 5544. (b) De Meijere, A.; Kozhushkov, S.; Haumann, T.; Boese, R.; Puls, C.; Cooney, M. J.; Scott, L. T. *Chem. Eur. J*. **1995**, *1*, 124.

(11) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem*. **1988**, *53*, 2489.

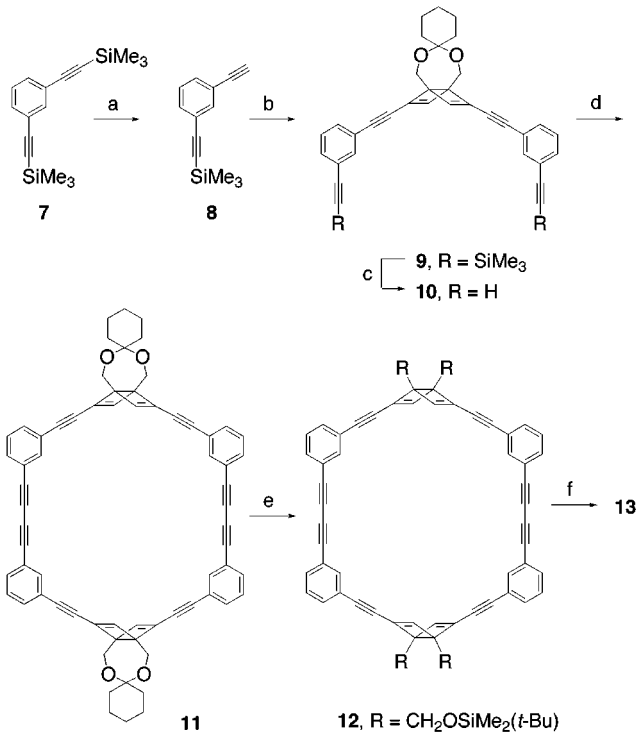
(12) The isolated **11** was spectroscopically homogeneous although two stereoisomers arising from relative orientation of the Dewar units are possible. Compound **12** was also spectroscopically homogeneous.

(13) Similar rotation of spindles in phenylacetylene macrocycles, see ref 3.

(14) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

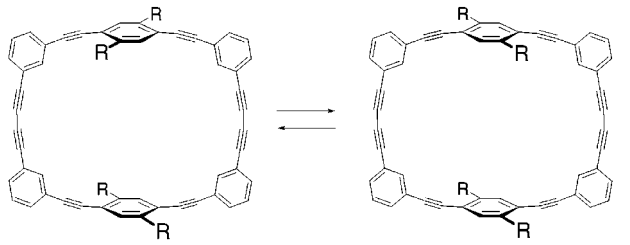
(15) Examples of alkynyl-based paracyclophanes, see (a) Hopf, H.; Jones, P. G.; Bubenitschek, P.; Werner, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2367. (b) Bauer, M.; Nieger, M.; Vögtle, F. *Chem. Ber.* **1992**, *125*, 2533.

Scheme 2[a]



[a] (a) 1 N KOH, MeOH, 30 min, 43%; (b) **5**, $Pd(PPh_3)_4$, CuI, Et_3N, 55%; (c) Bu_4NF, THF, 76%; (d) $Cu(OAc)_2$, CuCl, Py, 60 °C, syringe-pump (over 2 h), 70%; (e) (i) 1 N HCl, THF, (ii) *t*-$BuMe_2SiOTf$, Et_3N, 68%; (f) *hν*, CH_2Cl_2, 12 °C, 100%.

Scheme 3

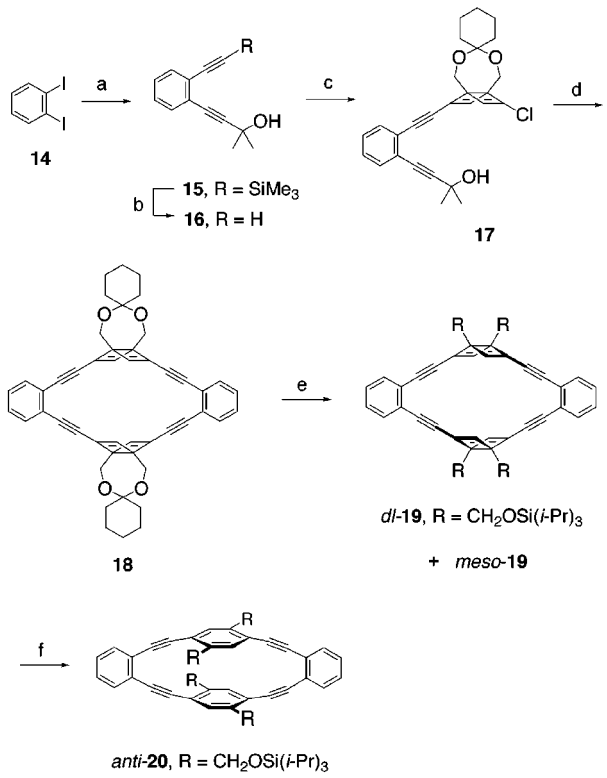


Cyclodimerization of **17** to **18** was achieved by an in situ deprotection/alkynylation sequence under phase-transfer conditions.[16] We found that tricaprylylmethylammonium choride was a superior catalyst to conventional benzyltriethylammonium choride[16] for this reaction; the latter gave only a trace amount of **18**, whereas the former afforded **18** in 22% yield as an inseparable mixture of *meso*- and *dl*-isomers (4:6). Acid hydrolysis of **18** followed by silylation of the resulting tetraols afforded **19** in 72% yield, which was then separated into the *meso*- and *dl*-isomers by preparative HPLC. Photochemical isomerization of *dl*-**19** by irradiation with a high-pressure mercury lamp through Pyrex in CH_2Cl_2 at 12 °C afforded *anti*-**20** in 74% yield. Unexpectedly, *meso*-**19** decomposed under the same photolysis conditions and produced no identifiable product; the reason is not clear at the present.[17]

X-ray Structure and Spectroscopic Properties of *anti*-20. Crystals of *anti*-**20** suitable for X-ray structure determination (see Supporting Information) were grown by vapor diffusion of methanol into a chloroform solution of *anti*-**20** at room temperature. The *p*-phenylene units are almost parallel with the interplanar distance of 3.48 Å, and the angles between the macrocyclic plane and the *p*-phenylene benzene rings are 62.5° and 64.2°. The acetylene units show deviation from linearity with the C≡C−C angles ranging from 168.0(5)° to 171.4(4)°. The transannular distances between the acetylenic carbon atoms are 2.75 and 2.76 Å.

Electronic absorption and emission spectra of *anti*-**20** are shown in Figure 1. It is interesting to note that *anti*-**20** exhibits a large Stokes shift (179 nm), which is not commonly observed for phenylacetylene macrocycles[19] or linear *p*-phenylene ethynylenes.[20] Since the suitable overlap of the *p*-phenylene units is found for *anti*-**20** in the X-ray structure, the observed long-wavelength fluorescence might be attributable to the intramolecular excimer-like emission resulting from the stacking structure.

Scheme 4[a]



[a] (a) (i) (trimethylsilyl)acetylene, $Pd(PPh_3)_4$, CuI, Et_3N, 95%, (ii) 2-methyl-3-butyne-2-ol, $Pd(PPh_3)_4$, CuI, Et_3N, 72%; (b) Bu_4NF, THF, 92%; (c) **5**, $Pd(PPh_3)_4$, CuI, Et_3N, 57%; (d) tricaprylylmethylammonium chloride, 5 N NaOH, benzene, $Pd(PPh_3)_4$, CuI, 80 °C, 22%; (e) (i) 1 N HCl, THF, (ii) *i*-Pr_3SiOTf, Et_3N, 72%; (f) *hν*, CH_2Cl_2, 12 °C, 74%.

(16) (a) Huynh, C.; Linstrumelle, G. *Tetrahedron* **1988**, *44*, 6337. (b) Tobe, Y.; Matsumoto, H.; Naemura, K.; Achiba, Y.; Wakabayashi, T. *Angew. Chem., Int. Ed.* **1996**, *35*, 1800. (c) Nishinaga, T.; Kawamura, T.; Komatsu, K. *J. Org. Chem.* **1997**, *62*, 5354.

(17) The isomerization of **19** into **20** must result in shortening of the distance between the acetylenic groups, which has been proposed as the crucial geometrical change triggering the Bergman cyclization of some enediyne antitumor antibiotics (ref 18), so that the possible Bergman cyclizations of **19** as well as **20** in 1,4-cyclohexadiene were examined. However, no information about the intermediacy of the cycloaromatization products was obtained under thermal or photochemical reaction conditions.

(18) Reviews: (a) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25. (b) Nicolaou, K. C.; Dai, W.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387.

(19) Exceptionaly large Stokes shift (121 nm) has been reported for cyclic [6]paraphenylacetylene (ref 5a).

(20) Davey, A. P.; Elliott, S.; O'Connor, O.; Blau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433.

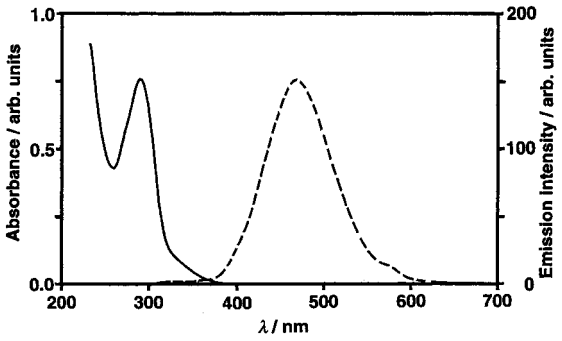


Figure 1. Electronic absorption (line) and fluorescence emission (dotted line) spectra of *anti*-**20** in dichloromethane (5×10^{-6} M); λ_{max} 290 nm, λ_{em} 469 nm.

Conclusion

In conclusion, we have successfully synthesized and characterized novel *p*-phenylene-based strained macrocycles **13** and *anti*-**20** through a macrocyclization−deprotection−aromatization sequence by using Dewar benzene **5** as a building block. The present results demonstrate that a Dewar benzene unit can be exploited as a masked *p*-phenylene unit for the construction of strained macrocyclic systems. By using other spacers and/or connection modes, a variety of *p*-phenylene-containing strained macrocycles with unique structures and properties may well become available on the basis of the present building block approach.

Experimental Section

General. 1,3-Bis[(trimethylsilyl)ethynyl]benzene (**7**)[11] was prepared following the known procedure. Other reagents and solvents were obtained from commercial sources and purified prior to use.

1,3-Bis(methoxycarbonyl)-2,3,5,6-tetrachlorobicyclo-[2.2.0]hexanes (2). A solution of **1** (8.0 g, 56.3 mmol) in a 1:1 mixture of 1,2-dichloroethylene (a mixture of *cis* and *trans* isomers) and dichloromethane (220 mL) was distributed in eight quartz tubes (18 mm × 23 cm), bubbled with argon for 10 min, and irradiated with a high-pressure Hg lamp at −70 °C. The reaction was monitored by GLC (10% Silicon SE-30, 0.5 m, 100−270 °C), and the irradiation was terminated after 12 h (35% GLC conversion). The combined reaction mixture was concentrated to recover the unreacted 1,2-dichloroethylene and **1**. The distillation of the residue in vacuo gave 5.20 g (27%) of **2**, from which five stereoisomers were isolated by preparative GLC (5% Silicon XE-60, 2 m, 100−200 °C). **2a**: mp 74−74.5 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.83 (s, 6 H), 4.75 (d, J = 7.6 Hz, 2 H), 4.97 (d, J = 7.6 Hz, 2 H). **2b**: mp 112−112.5 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.80 (s, 3 H), 3.91 (s, 3 H), 4.70 (d, J = 5.8 Hz, 2 H), 5.32 (d, J = 5.8 Hz, 2 H). **2c**: mp 110−110.5 °C; ^{1}H NMR (90 MHz, C_6D_6) δ 3.13 (s, 6 H), 4.68 (d, J = 9.1 Hz, 1 H), 4.71 (d, J = 9.1 Hz, 1 H), 5.41 (s, 2 H). **2d**: mp 88−89.5 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.81 (s, 3 H), 3.85 (s, 3 H), 4.46 (d, J = 7.3 Hz, 1 H), 4.81 (d, J = 5.9 Hz, 1 H), 4.89 (d, J = 7.3 Hz, 1 H), 5.26 (d, J = 5.9 Hz, 1 H). **2e**: mp 85−85.5 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.82 (s, 6 H), 5.10 (s, 2 H), 5.24 (s, 2 H); IR (KBr) 1746, 1440, 1334, 1264, 1220 cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_4Cl_4$: C, 35.75; H, 3.00; Cl, 42.21. Found: C, 35.77; H, 2.90; Cl, 42.22.

Spiro[cyclohexane-1,4′-3′,5′-dioxa-8′,10′-dichlorobicyclo-[2.2.0]hexa-8′,10′-diene] (5). To a suspension of lithium aluminum hydride (2.68 g, 70.7 mmol) in dry ether (420 mL) was added dropwise a solution of **2** (11.88 g, 35.4 mmol, a mixture of stereoisomers) in dry ether (220 mL) over 90 min under argon. After the addition, the mixture was refluxed for 2 h, cooled, and treated successively with water (2.7 mL), 15% aqueous sodium hydroxide (2.7 mL), and water (8.1 mL) with vigorous stirring. The precipitate was filtered off, and the ethereal solution was dried with Na_2SO_4. Evaporation of the solvent gave crude alcohol **3** (8.78 g, 89%), which was used for the next step without purification. IR (neat) 3324, 1044 cm^{-1}.

A mixture of **3** (8.78 g, 31.4 mmol), 1,1-dimethoxycyclohexane (9.46 g, 65.6 mmol), and TsOH (0.60 g, 3.1 mmol) in benzene (280 mL) was heated to reflux, and MeOH generated was azeotopically distilled off through Vigreux column (30 cm). After 3 h, the mixture was cooled to room temperature, washed successively with 5% aqueous $NaHCO_3$ (150 mL) and brine (150 mL), dried with Na_2CO_3/Na_2SO_4 (1:1), concentrated, and chromatographed on silica gel eluted with ether/hexane (2:98) to afford 4.77 g (68%) of stereoisomeric acetals **4**. IR (KBr) 2936, 2856, 1448, 1100, 1044 cm^{-1}.

To a stirred solution of **4** (8.88 g, 24.7 mmol) in dry THF (160 mL) was added a solution of *t*-BuOK (13.87 g, 123.8 mmol) in dry THF (200 mL) over 40 min at 0 °C under argon. The mixture was stirred at room temperature for 2.5 h, evaporated to remove THF, diluted with ether (600 mL), washed successively with water (300 mL) and brine (300 mL), dried with Na_2SO_4, concentrated, and chromatographed on silica gel eluted with ether/hexane (3:97) to give 3.20 g (45%) of **5** as crystals and 2.45 g (35%) of **6** as an oil. **5**: mp 93.5−94 °C (hexane); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.40−1.73 (m, 10 H), 3.95 (d, J = 13.2 Hz, 2 H), 3.98 (d, J = 13.2 Hz, 2 H), 6.31 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.72, 25.64, 33.07, 57.44, 64.50, 103.80, 133.08, 140.56; IR (KBr) 1564, 1098 cm^{-1}; MS (FD) m/z 290 (M^+ + 4, 13), 286 (M^+ + 2, 65), 286 (M^+, 100). Anal. Calcd for $C_{14}H_{16}O_2Cl_2$: C, 58.55; H, 5.62; Cl, 24.69. Found: C, 58.28; H, 5.72; Cl, 24.74. **6**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.40−1.73 (m, 10 H), 3.98 (s, 2 H), 4.00 (s, 2 H), 6.28 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.75, 25.66, 32.92, 55.69, 57.88, 59.57, 70.25, 103.80, 134.45, 139.59; IR (neat) 1580, 1104 cm^{-1}; MS (FD) m/z 290 (M^+ + 4, 17), 286 (M^+ + 2, 71), 286 (M^+, 100). Anal. Calcd for $C_{14}H_{16}O_2Cl_2$: C, 58.55; H, 5.62; Cl, 24.69. Found: C, 58.21; H, 5.79; Cl, 24.75.

1-(Trimethylsilyl)ethynyl-3-ethynylbenzene (8). To a degassed solution of **7**[11] (2.7 g, 10 mmol) in MeOH (100 mL) was added 1 N aqueous KOH (0.03 mL), and the mixture was stirred at room temperature under argon. After 30 min, the mixture was poured into pentane (300 mL), washed successively with water (300 mL) and brine (100 mL), dried with Na_2SO_4, concentrated, and distilled to give 0.85 g (43%) of **8** as a colorless liquid, whose purity was >95% by GLC analysis (10% Silicon SE-30, 0.5 m, 80−180 °C). **8**: bp 55−60 °C (10^{-3} Torr); ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.24 (s, 9 H), 3.06 (s, 1 H), 7.20−7.50 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.11, 77.73, 82.79, 95.15, 103.91, 122.37, 123.52, 128.31, 132.00, 132.15, 135.52; IR (neat) 3304, 2152 cm^{-1}; MS (EI) m/z 198 (M^+, 24), 183 (M^+ − 15, 100); HRMS calcd for $C_{13}H_{14}Si$ 198.0864, found 198.0877.

Palladium-Catalyzed Coupling of 5 with 8. To a degassed suspension of **5** (360 mg, 1.25 mmol), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol), and CuI (12 mg, 0.06 mmol) in dry triethylamine (40 mL) was added a degassed solution of **8** (600 mg, 3.0 mmol) in degassed triethylamine (5 mL). The mixture was stirred at 70 °C under argon for 12 h, cooled, evaporated to remove triethylamine, taken up in ether (200 mL), and washed with 1 N aqueous HCl (3 × 100 mL). The aqueous solution was extracted with ether (2 × 100 mL). The organic extracts were combined, washed successively with aqueous $NaHCO_3$ (200 mL) and brine (200 mL), dried with Na_2SO_4, concentrated, and chromatographed on silica gel eluted with ether/hexane (2:98) to give 421 mg (55%) of **9** as colorless amorphous: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41−1.75 (m, 10 H), 0.25 (s, 18 H), 4.07 (d, J = 13.2 Hz, 2 H), 4.13 (d, J = 13.2 Hz, 2 H), 6.79 (s, 2 H), 7.25 (t, J = 7.8 Hz, 2 H), 7.38 (dt, J = 7.8, 1.5 Hz, 2 H), 7.40 (dt, J = 7.8, 1.5 Hz, 2 H), 7.57 (t, J = 1.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.09, 22.81, 25.73, 33.30, 58.71, 64.52, 83.54, 95.12, 103.18, 103.64, 103.97, 122.97, 123.12, 128.33, 131.47, 131.93, 135.04, 135.06, 144.28; IR (neat) 2156, 1598, 1476, 1250 cm^{-1}; MS (FD) m/z 610 (M^+, 100).

Desilylation of 9. To a degassed suspension of **9** (400 mg, 0.66 mmol) in THF (10 mL) was added Bu_4NF (2 mL, 1 M solution in THF, 2.0 mmol) dropwise, and the reaction was

stirred at room temperature for 30 min. The mixture was evaporated to remove THF, taken up in ether (150 mL), washed successively with water (50 mL) and brine (50 mL), dried with Na_2SO_4, concentrated, and chromatographed on silica gel eluted with ether/hexane (5:95) to give 233 mg (76%) of colorless amorphous **10**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.4−1.8 (m, 10 H), 3.08 (s, 2 H), 4.07 (d, J = 13.2 Hz, 2 H), 4.13 (d, J = 13.2 Hz, 2 H), 6.81 (s, 2 H), 7.28 (t, J = 7.8 Hz, 2 H), 7.42 (dt, J = 7.8, 1.5 Hz, 2 H), 7.43 (dt, J = 7.8, 1.5 Hz, 2 H), 7.58 (t, J = 1.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.81, 25.73, 33.23, 58.71, 64.59, 77.91, 82.63, 83.67, 95.39, 103.68, 122.53, 123.12, 128.46, 131.86, 132.17, 135.13, 139.58, 144.53; IR (neat) 3300, 2936, 1600, 1476, 1096, 758 cm^{-1}; MS (FD) m/z 466 (M^+, 100).

Cyclodimerization of 10. To a degassed slurry of CuCl (930 mg, 9.4 mmol) and $Cu(OAc)_2$ (2.3 g, 12.5 mmol) in dry pyridine (300 mL) was added dropwise a degassed solution of **10** (146 mg, 0.31 mmol) in dry pyridine (30 mL) over 2 h at 60 °C. The mixture was stirred for an additional 1 h at the same temperature, cooled, evaporated to remove pyridine, taken up in EtOAc (200 mL), and washed with ice-cooled 1 N aqueous HCl (200 mL). The aqueous solution was extracted with EtOAc (3 × 100 mL). The organic extracts were combined, washed successively with aqueous $NaHCO_3$ (200 mL) and brine (200 mL), dried with Na_2SO_4, concentrated, and chromatographed on silica gel eluted with chloroform to give 102 mg (70%) of colorless amorphous **11**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.4−1.8 (m, 20 H), 4.08 (d, J = 13.2 Hz, 4 H), 4.15 (d, J = 13.2 Hz, 4 H), 6.86 (s, 4 H), 7.31 (t, J = 7.8 Hz, 4 H), 7.42 (dt, J = 7.8, 1.5 Hz, 4 H), 7.43 (dt, J = 7.8, 1.5 Hz, 4 H), 7.71 (t, J = 1.5 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) 22.84, 25.73, 33.50, 58.76, 65.00, 74.54, 80.98, 84.05, 95.04, 103.71, 122.15, 123.35, 128.64, 131.42, 131.55, 136.98, 136.99, 145.26; IR (neat) 1596, 1474, 1156, 1098 cm^{-1}; MS (FD) m/z 929 (M^+ + 1, 100), 928 (M^+, 100).

Bis(Dewar benzene) Precursor 12. To a solution of **11** (102 mg, 0.11 mmol) in THF (40 mL) was added 1 N aqueous HCl (4 mL), and the reaction was stirred at room temperature for 14 h. The mixture was evaporated to remove THF, treated with saturated aqueous $NaHCO_3$ (50 mL), and extracted with EtOAc (3 × 50 mL). The organic extracts were combined, washed with brine (50 mL), dried with Na_2SO_4, and concentrated to give a solid (126 mg), which was dissolved in dry dichloromethane (50 mL). To the dichloromethane solution was added successively triethylamine (167 mg, 1.65 mmol) and *t*-$BuMe_2SiOTf$ (175 mg, 0.66 mmol), and the mixture was stirred at room temperature under argon for 6 h. The mixture was diluted with 1 N aqueous HCl (50 mL) and extracted with dichloromethane (2 × 50 mL). The extracts were combined, washed successively with saturated aqueous $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4, concentrated, and purified by preparative GPC (JAIGEL-1H, 2 × 20 mm ϕ × 600 mm, chloroform) to give 92 mg (68%, two steps) of colorless amorphous **12**: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.08 (s, 24 H), 0.92 (s, 36 H), 4.10 (d, J = 11.0 Hz, 4 H), 4.12 (d, J = 11.0 Hz, 4 H), 6.83 (s, 4 H), 7.29 (t, J = 7.8 Hz, 4 H), 7.38 (dt, J = 7.8, 1.5 Hz, 4 H), 7.52 (dt, J = 7.8, 1.5 Hz, 4 H), 7.70 (t, J = 1.5 Hz, 4 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ −5.36, −5.23, 18.61, 26.05, 60.93, 66.42, 74.62, 81.31, 85.05, 94.77, 122.42, 124.11, 129.12, 131.75, 131.85, 136.18, 137.14, 146.02; IR (KBr) 1258, 1104, 838 cm^{-1}; MS (FD) m/z 1224 (M^+, 100).

Macrocycle 13. A solution of **12** (11.0 mg, 0.009 mmol) in dichloromethane (25 mL) was placed in a Pyrex test tube (18 mm × 18 cm), bubbled with argon for 15 min at 0 °C, and irradiated with a high-pressure Hg lamp at 12 °C. The reaction was monitored by HPLC, which showed the formation of a single product. After 30 min (100% conversion), the irradiation was terminated, and the mixture was evaporated to give 11.0 mg (100%) of **13** as colorless powder: mp >280 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.15 (S, 24 H), 0.96 (s, 36 H), 4.95 (s, 8 H), 7.36 (t, J = 7.8 Hz, 4 H), 7.41 (dt, J = 7.8, 1.5 Hz, 4 H), 7.49 (dt, J = 7.8, 1.5 Hz, 4 H), 7.66 (s, 4 H), 7.88 (t, J = 1.5 Hz, 4 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ −5.07, 18.82, 26.24, 63.56, 75.37, 82.73, 89.08, 95.11, 120.79, 122.62, 124.36, 129.32, 130.13, 130.34, 130.92, 139.73, 142.36; IR (KBr) 1258, 1104, 838 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) = 262.5 (4.68), 277.5 (4.51), 293.5 (4.63), 312 (4.72), 334 (4.60), 354 nm (3.44); fluorescence (CH_2Cl_2, λ_{ex} = 313 nm) λ_{em} = 365, 383 nm; MS (FD) m/z 1225 (M^+ + 1, 100), 1224 (M^+, 94); HRMS calcd for $C_{80}H_{88}O_4Si_4$ 1224.5800, found 1224.5780.

1-[(1-Methyl-1-hydroxyethyl)ethynyl]-3-[(trimethylsilyl)ethynyl]benzene (15). To a degassed suspension of **14** (5.62 g, 19.9 mmol), $Pd(PPh_3)_4$ (460 mg, 0.40 mmol), and CuI (37 mg, 0.19 mmol) in dry triethylamine (200 mL) was added (trimethylsilyl)acetylene (2.14 g, 21.9 mmol), and the mixture was stirred at 70 °C under argon. After 2 days, the mixture was cooled, evaporated to remove triethylamine, diluted with water (200 mL), and extracted with ether (2 × 200 mL). The extracts were combined, washed with brine (200 mL), dried with Na_2SO_4, concentrated, and chromatographed on silica gel eluted with hexane to give an oil (4.43 g, 95%), which was dissolved in dry triethylamine (90 mL). To the degassed solution was added $Pd(PPh_3)_4$ (204 mg, 0.18 mmol), CuI (17 mg, 0.09 mmol), and 2-methyl-3-butyne-2-ol (1.49 g, 17.7 mmol), and the mixture was stirred at 65 °C under argon. After 5 days, the mixture was cooled, evaporated to remove triethylamine, diluted with water (200 mL), and extracted with EtOAc (2 × 200 mL). The extracts were combined, washed with brine (200 mL), dried with Na_2SO_4, concentrated, and chromatographed on silica gel eluted with ether/hexane (2:8) to give **15** (1.63 g, 72%) as an oil: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.27 (s, 9 H), 1.64 (s, 6 H), 7.17−7.52 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.05, 31.52, 65.71, 80.90, 97.79, 98.20, 103.31, 125.33, 125.63, 127.89, 128.15, 131.82, 132.37; IR (neat) 3356, 2156, 1164 cm^{-1}; MS (FD) m/z 256 (M^+, 100); HRMS calcd for $C_{16}H_{20}OSi$ 256.1283, found 256.1297.

1-[(1-Methyl-1-hydroxyethyl)ethynyl]-3-ethynylbenzene (16). To a degassed solution of **15** (1.61 g, 6.3 mmol) in THF (400 mL) was added Bu_4NF (1 M solution in THF, 12.6 mL, 12.6 mmol), and the reaction was stirred at 0 °C under argon. After 3 h, the mixture was evaporated to remove THF, diluted with water (100 mL), and extracted with ether (2 × 150 mL). The extracts were combined, washed with brine (100 mL), dried with Na_2SO_4, concentrated, and chromatographed on silica gel eluted with ether/hexane (2:8) to give **16** (1.07 g, 92%) as an oil: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.64 (s, 6 H), 3.28 (s, 1 H), 7.21−7.55 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.40, 65.70, 80.63, 80.71, 82.11, 98.07, 124.78, 125.76, 127.95, 128.47, 131.72, 132.46; IR (neat) 3292, 1164 cm^{-1}; MS (FD) m/z 184 (M^+, 100); HRMS calcd for $C_{13}H_{12}O$ 184.0888, found 184.0895.

Palladium-Catalyzed Coupling of 5 with 16. To a degassed suspension of **5** (1.45 g, 5.0 mmol), $Pd(PPh_3)_4$ (117 mg, 0.10 mmol), and CuI (19 mg, 0.10 mmol) in dry triethylamine (80 mL) was added a degassed suspension of **16** (0.93 g, 5.0 mmol) in dry triethylamine (20 mL), and the mixture was stirred at 65 °C under argon. After 19 h, the mixture was cooled, evaporated to remove triethylamine, diluted with water (100 mL), and extracted with ether (2 × 100 mL). The extracts were combined, washed with brine (100 mL), dried with Na_2SO_4, concentrated, and chromatographed on silica gel eluted with ether/hexane (2:8) to give **17** (1.25 g, 57%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40−1.71 (m, 10 H), 3.96 (d, J = 13.2 Hz, 1 H), 4.04 (d, J = 13.2 Hz, 1 H), 4.06 (d, J = 13.2 Hz, 1 H), 4.17 (d, J = 13.2 Hz, 1 H), 6.37 (s, 1 H), 6.71 (s, 1 H), 7.25−7.44 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.02, 27.03, 31.36, 31.52, 42.00, 58.06, 58.58, 64.74, 65.61, 67.80, 77.23, 80.58, 85.83, 95.90, 98.55, 124.99, 125.46, 127.99, 128.56, 131.74, 13176, 134.20, 135.06, 139.95, 141.93; IR (neat) 3432 cm^{-1}; MS (FD) m/z 434 (M^+, 100).

Cyclodimerization of 17. To a degassed suspension of **17** (254 mg, 0.59 mmol), tricaprylylmethylammonium chloride (73 mg, 0.18 mmol), $Pd(PPh_3)_4$ (14 mg, 0.012 mmol), PPh_3 (3 mg, 0.011 mmol), and CuI (1 mg, 0.005 mmol) in benzene (12 mL) was added 5 N aqueous NaOH (4.5 mL), and the mixture was stirred at 80 °C under argon. After 38 h, the mixture was cooled, treated with 1 N aqueous HCl (25 mL), and extracted with benzene (3 × 30 mL). The extracts were combined, washed with brine (30 mL), dried with Na_2SO_4, concentrated, and chromatographed on silica gel eluted with EtOAc/benzene

(2:98) to give colorless amorphous **18** (43 mg, 22%, a 60:40 mixture of stereoisomers): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40−1.71 (m, 20 H), 4.07 (d, J = 13.2 Hz, 4 H of the *meso*-isomer), 4.08 (d, J = 13.2 Hz, 4 H of the *dl*-isomer), 4.14 (d, J = 13.2 Hz, 4 H of the *meso*-isomer), 4.15 (d, J = 13.2 Hz, 4 H of the *dl*-isomer), 6.80 (s, 4 H of the *dl*-isomer), 6.81 (s, 4 H of the *meso*-isomer), 7.27−7.30 (m, 4 H), 7.42−7.46 (m, 4 H); IR (KBr) 2936, 2860, 1100 cm^{-1}; MS (FD) *m*/*z* 680 (M^+, 83), 99 (100).

Bis(Dewar benzene) Precursors 19. To a solution of **18** (37 mg, 0.054 mmol) in THF (5 mL) was added 1 N aqueous HCl (0.5 mL), and the reaction was stirred at room temperature for 13 h. The mixture was evaporated to remove THF, treated with saturated aqueous $NaHCO_3$ (50 mL), and extracted with EtOAc (2 × 30 mL). The extracts were combined, washed with brine (30 mL), dried with Na_2SO_4, and concentrated to give a solid (28 mg), which was dissolved in dry dichloromethane (10 mL). To the dichloromethane solution was added successively triethylamine (220 mg, 2.17 mmol) and *i*-Pr_3SiOTf (267 mg, 0.87 mmol), and the mixture was stirred at room temperature under argon. After 14 h, the mixture was diluted with 1 N aqueous HCl (30 mL) and extracted with ether (2 × 30 mL). The extracts were combined, washed successively with saturated aqueous $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4, concentrated, and purified by preparative GPC (JAIGEL-1H, 2 × 20 mm ϕ × 600 mm, chloroform) to give 44 mg (72%, two steps) of **19** as a 60:40 mixture of stereoisomers, which was further purified by preparative HPLC (LiChrosorb Si60, 10 mm ϕ × 250 mm, ether/hexane) to afford colorless amorphous *dl*-**19** and *meso*-**19**. *dl*-**19**: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.09 (br s, 84 H), 4.20 (d, J = 10.4 Hz, 4 H), 4.28 (d, J = 10.4 Hz, 4 H), 6.87 (s, 4 H), 7.26−7.30 (m, 4 H), 7.35−7.39 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.50, 18.35, 61.83, 66.35, 88.85, 94.47, 126.62, 128.45, 131.03, 136.76, 145.99; IR (KBr) 2936, 2860, 1102 cm^{-1}; MS (FD) *m*/*z* 1144 (M^+, 100). *meso*-**19**: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.10 (br s, 84 H), 4.20 (d, J = 10.4 Hz, 4 H), 4.26 (d, J = 10.4 Hz, 4 H), 6.90 (s, 4 H), 7.26−7.30 (m, 4 H), 7.35−7.39 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.50, 18.35, 61.83, 66.34, 88.60, 94.58, 126.54, 128.45, 131.02, 136.83, 146.32; IR (KBr) 2936, 2860, 1102 cm^{-1}; MS (FD) *m*/*z* 1144 (M^+, 100).

Macrocycle *anti*-20. A solution of *dl*-**19** (16.2 mg, 0.014 mmol) in dichloromethane (14 mL) was placed in a Pyrex test tube (18 mm × 18 cm), bubbled with argon for 15 min at 0 °C, and irradiated with a high-pressure Hg lamp at 12 °C. The reaction was monitored by HPLC, which showed the formation of a single product. After 55 min (100% conversion), the irradiation was terminated. The mixture was evaporated and purified by preparative GPC (JAIGEL-1H, 2 × 20 mm ϕ × 600 mm, chloroform) to give 12.0 mg (74%) of *anti*-**20** as a colorless powder: mp 152 °C (dec); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.14 (m, 84 H), 4.62 (d, J = 13.2 Hz, 4 H), 4.95 (d, J = 13.2 Hz, 4 H), 7.25 (s, 4 H), 7.34−7.37 (m, 4 H), 7.46−7.50 (m, 4 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 12.51, 18.27, 18.30, 64.02, 94.57, 95.86, 121.58, 128.60, 128.63, 129.50, 130.14, 142.01; IR (KBr) 2936, 2860, 1102 cm^{-1}; UV (CH_2Cl_2) λ_{max} 291 nm (ϵ 33 000); fluorescence (CH_2Cl_2, λ_{ex} = 290 nm) λ_{em} = 469 nm; MS (FD) *m*/*z* 1144 (M^+, 100); HRMS calcd for $C_{72}H_{104}O_4Si_4$ 1144.7012, found 1144.6997.

X-ray structure determination for 5: $C_{14}H_{16}O_2Cl_2$, M_r = 287.2, colorless cube (0.40 × 0.40 × 0.40 mm^3), orthorhombic, space group *Pbca*, a = 16.093(5), b = 20.07(1), c = 8.587(3) Å, V = 2773(1) Å^3, D_c = 1.375 g cm^{-3}, Z = 8, Mo Kα radiation (λ = 0.71069 Å), T = 296 K, μ = 4.59 cm^{-1}, F(000) = 1200. A total of 3605 unique reflections were collected, of which 2200 observed reflections [$I > 2\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares with 163 parameters) to give final R = 0.086 and wR = 0.080. Residual electron density is 0.79 e Å^{-3}.

X-ray structure determination for 13: $C_{80}H_{88}O_4Si_4$, M_r = 1225.9, colorless plate (0.60 × 0.30 × 0.05 mm^3), triclinic, space group *P*1 bar, a = 12.926(1), b = 17.570(2), c = 8.074(1) Å, α = 93.356(4)°, β = 97.690(3)°, γ = 79.755(4)°, V = 1787.1(3) Å^3, D_c = 1.14 g cm^{-3}, Z = 1, Mo Kα radiation (λ = 0.71069 Å), T = 203 K, μ = 1.31 cm^{-1}, F(000) = 656. A total of 7513 unique reflections were collected, of which 5339 observed reflections [$I > 3\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares with 398 parameters) to give final R = 0.063 and wR = 0.069. Residual electron density is 0.45 e Å^{-3}.

X-ray structure determination for *anti*-20: $C_{72}H_{104}O_4Si_4$, M_r = 1144.7, colorless block (0.50 × 0.25 × 0.25 mm^3), triclinic, space group *P*1 bar, a = 14.1929(4), b = 20.3494(5), c = 13.1721(4) Å, α = 105.252(1)°, β = 100.2988(6)°, γ = 79.896(2)°, V = 3578.0(2) Å^3, D_c = 1.064 g cm^{-3}, Z = 2, Mo Kα radiation (λ = 0.71069 Å), T = 203 K, μ = 1.26 cm^{-1}, F(000) = 1248. A total of 15541 unique reflections were collected, of which 10152 observed reflections [$I > 2\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares with 721 parameters) to give final R = 0.083 and wR = 0.080. Residual electron density is 0.40 e Å^{-3}.

Acknowledgment. We thank Professor Tamotsu Inabe (Hokkaido University) for the use of X-ray analytical facilities. This work was supported in part by a Grant-in-Aid for Scientific Research (09640620) from the Ministry of Education, Science, Sports, and Culture of Japan.

Supporting Information Available: Copies of ^{1}H NMR spectra of compounds **9**−**13** and **17**−**20** and X-ray crystallographic reports for **5**, **13**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0002590