4 H), 5.88 (s, 4 H), 6.89 (m, 8 H), 7.02 (m, 8 H), 7.31 (m, 4 H), 7.41 (m, 4 H), 7.53 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 49.87, 50.21, 51.03, 111.46, 123.61, 123.81, 125.04, 125.52, 133.01, 135.13, 135.56, 136.57, 144.15, 144.49, 144.90, 145.01; HRMS calcd for $C_{72}H_{42}Cl_2$ 976.2663, found 976.2628.

Attempted Cycloaddition of 25 and 4. A solution of 0.49 g (0.5 mmol) of **25** and 0.3 g (excess) of **4** were heated at reflux for 24 h. Removal of the solvent (vacuum distillation) and chromatography of the remaining residue over silica gel using 2:1 CH_2Cl_2/hexanes as eluent gave only a small amount of the starting materials.

Alkene 26. To a solution of dichloride **22** (1.96 g, 2 mmol) in 100 mL of anhydrous THF under Ar was added 0.28 g (40 mmol) of Li wire, and the mixture was heated at reflux for 72 h. Excess Li was removed with tweezers, solvent was evaporated, and the residue was taken up in 100 mL of CH_2Cl_2, washed with water and saturated NaCl solution, and dried ($MgSO_4$). Solvent was removed, and the slightly yellow residue was triturated with 60 mL of 2:1 hexanes/ether to give 1.67 g (92%) of **26** as a white powder: mp dec >350 °C; ^{1}H NMR ($CDCl_3$) δ 5.82 (s, 4 H), 5.87 (s, 4 H), 5.98 (dd, J = 3.7, <1 Hz, 2 H), 6.76 (dd, J = 3.7, <1 Hz, 2 H), 6.80–7.01 (m, 16 H), 7.25–7.54 (m, 16 H); ^{13}C NMR (CD_2Cl_2) δ 42.77, 50.12, 50.32, 123.77, 123.93, 124.11, 125.22, 125.64, 125.69, 135.02, 135.95, 140.01, 144.89, 145.13, 145.66, 145.72; HRMS calcd for $C_{72}H_{44}$ 908.3442, found 908.3471.

Cycloadduct 27. A suspension of alkene **26** (910 mg, 1.0 mmol) and diene **4** (450 mg, 1.1 mmol) in decalin (50 mL) was heated at reflux for 8 h. The cooled mixture was diluted with 45 mL of 1:2 CH_2Cl_2/hexanes. Filtration and vacuum drying gave 1.17 g (89%) of **27** as a fine white powder: mp dec >450 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (br d, J = 8 Hz, 2 H), 1.48 (br d, J = 8 Hz, 2 H), 4.55 (d, J = 1 Hz, 2 H), 4.97 (s, 2 H), 5.18 (s, 2 H), 5.66 (s, 2 H), 5.70 (s, 2 H), 5.75 (s, 2 H), 5.81 (s, 2 H), 6.60–7.58 (m, 48 H); ^{13}C NMR ($CDCl_3$) δ 38.50, 45.02, 46.78, 48.52, 48.89, 50.43, 50.61, 50.91, 123.13, 123.44, 123.74, 124.15, 124.34, 124.64, 124.94, 125.19, 125.64, 125.84, 126.07, 126.41, 127.10, 130.57, 132.46, 134.33, 134.87, 135.73, 136.27, 137.07, 141.24, 142.27, 142.51, 143.69, 145.37, 145.62, 146.03; HRMS calcd for $C_{104}H_{66}$ 1314.5164, found 1314.5180.

Aromatization of 27. Supertriptycene (2). To a solution of cycloadduct **27** (1.0 g, 0.76 mmol) in 200 mL of 1,1,2,2-tetrachloroethane at reflux was added 3 mL of bromine, and the mixture was heated at reflux for 4 h. Removal of the solvent (rotavap) and trituration of the residue with 40 mL of 3:1 CH_2Cl_2/ethyl acetate gave, on filtration, 850 mg (85%) of **2** as a white powder: mp >500 °C; ^{1}H NMR (tetrachloroethene) δ 5.63 (s, 6 H), 5.90 (s, 6 H), 6.60 (s, 2 H), 6.73–6.79 (m, 24 H), 7.16 (m, 12 H), 7.50 (m, 12 H); ^{13}C NMR (tetrachloroethene) δ 43.46, 52.55, 53.01, 125.46, 126.06, 126.90, 127.14, 136.74, 136.93, 137.48, 146.76, 146.96; HRMS calcd for $C_{104}H_{62}$ 1311.4930 (MH^+), found 1311.4890.

Cycloadduct 29. A solution of 0.91 g (1 mmol) of **26** and 0.92 g (4 mmol) of **28** in 25 mL of decalin was heated at reflux for 24 h. Removal of the solvent (vacuum distillation) and chromatography of the residue over silica gel using 3:2 CH_2Cl_2/hexanes as eluent gave 0.66 g (58%) of **29**: mp 305–308 °C; ^{1}H NMR ($CDCl_3$) δ 1.32 (ddd, J = 14.7, 6.0, 2.1 Hz, 2 H), 1.76 (dd, J = 6.0, 5.3 Hz, 2 H), 2.41 (dd, J = 14.7, 5.3 Hz, 2 H), 4.61 (s, 2 H), 4.91 (br s, 2 H), 5.801 (s, 2 H), 5.808 (s, 2 H), 5.81 (s, 2 H), 5.82 (s, 2 H), 6.71–7.09 (m, 24 H), 7.22–7.49 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 30.91, 40.53, 40.84, 49.92 (4), 55.55, 122.21, 122.38, 123.07, 123.23, 123.31, 123.37, 123.47, 123.53, 123.64, 123.73, 123.82, 123.91, 124.07, 124.65, 124.75, 124.90, 124.99, 125.12, 125.19, 125.24, 125.45, 131.47, 134.02, 134.31, 135.48, 135.72, 136.75, 143.05, 144.77, 144.82, 145.01, 145.08, 145.19, 145.43, 145.50, 145.55, 145.90, 146.46; HRMS calcd for $C_{90}H_{58}$ 1138.4571, found 1138.4532.

Acknowledgment. We are indebted to the National Science Foundation (Grants CHE 87-12118 and CHE 90-08503) and the National Aeronautics and Space Administration (Grant NAG 3-670) for financial support of this research and to Dr. Mary Ann Meador (NASA, Cleveland, OH) for the thermogravimetric analyses).

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of compounds **2**, **3**, **9**, **12**, **14–16**, **23–27**, and **29** (39 pages). Ordering information is given on any current masthead page.

Synthesis of Three Helically Chiral Iptycenes

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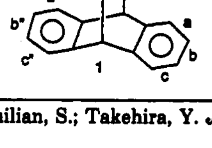
Received April 8, 1991

The synthesis of iptycenes **2–4**, each of which is helically chiral and has a C_2 symmetry axis, is described. Key intermediates are diene **7**, prepared in two steps and 44% yield from known ketone **5**, and anthracene **11**, prepared in four steps and 48% yield from diene **7**. A noteworthy step in the latter sequence is the aluminum chloride catalyzed, room-temperature, regio- and stereoselective cycloaddition of naphthoquinone **8** to diene **7** to give a single isomer of **9**. Anthracene **11** was converted in one step to **2** and in four steps to **3** (Scheme II). Bicycloalkene **15**, an intermediate in the latter synthesis, was converted to **4** in two steps (Scheme III). Cycloaddition of unactivated dienophile **15** to unactivated dienes **17** and **18** proceeds in good yields. Hydrocarbon **3** could be resolved on several chiral columns.

Twenty-four iptycenes[1] can be generated by fusing from zero to six 9,10-anthradiyl moieties to the benzenoid rings of triptycene **1**.[2] Of these, six are chiral, three with C_1 and three with C_2 symmetry. We describe here the first synthesis of three of these chiral iptycenes, the heptiptycene **2**, the noniptycene **3**, and the undecaiptycene **4**, the three that have C_2 symmetry. They are formally derived from triptycene by fusing 9,10-anthradiyl moieties to the ac′, ab′c″ and aca′c″ bonds, respectively.[3]



1

These iptycenes are interesting for at least two reasons. First, they have cavities that might be useful for resolving nonpolar guest molecules. Second, they present a synthetic challenge that is quite different from previously synthesized iptycenes[1,2,4] in that two of the 9,10-anthradiyl moieties are angularly[5] rather than linearly fused to the central triptycene portion of the molecule.

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[1] Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427–4432.

[2] Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641–1654.

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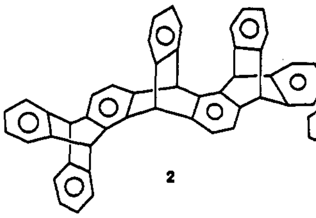
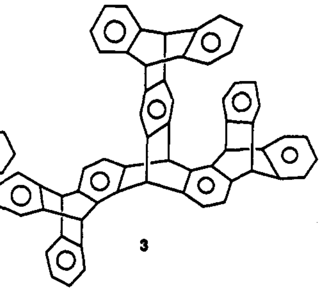


2



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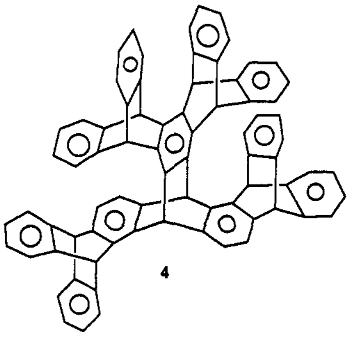
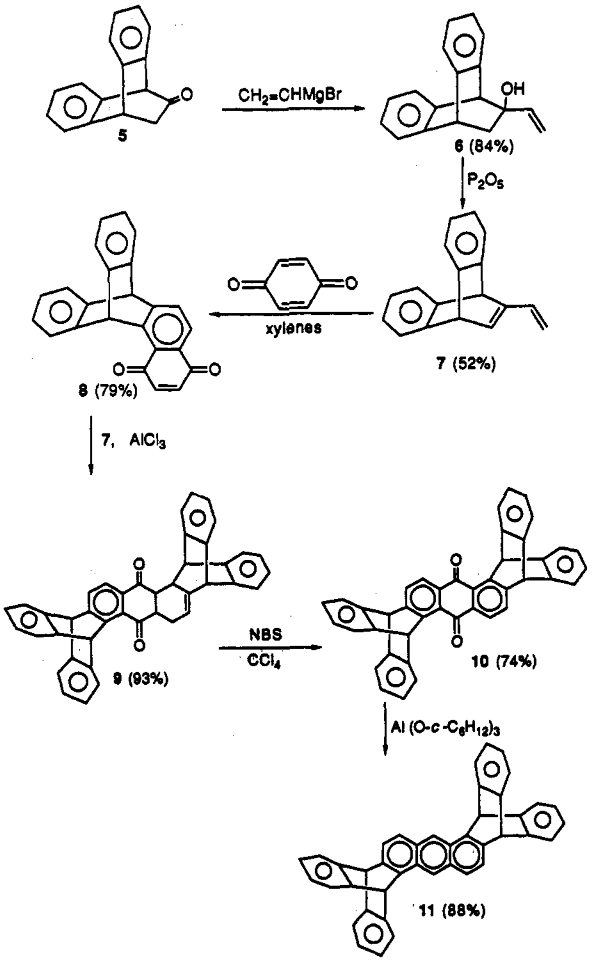


4

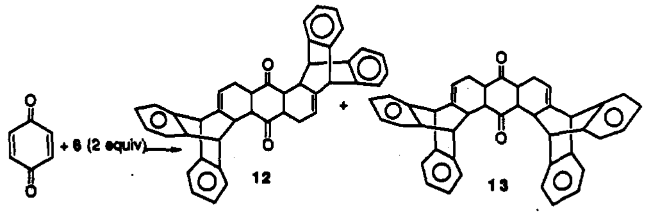
Results and Discussion

Synthesis of Anthracene 11. Retrosynthetic analysis of 2-4 leads directly to anthracene 11, and this became our initial target (Scheme I). Treatment of ketone 5[6] with vinylmagnesium bromide in tetrahydrofuran (THF) gave tertiary allylic alcohol 6 in 84% yield. The first critical step was to bring about the dehydration of 6 without rearrangement, since such systems are notoriously susceptible to arrangement.[7] The best procedure for obtaining pure 7 involved heating a solution of 6 in 1:1 heptane/THF with powdered phosphorus pentoxide for 36-48 h, in which case 7 was obtained, after chromatography, as a white solid, mp 115-116 °C. Other dehydration procedures, such as $CuSO_4$ in refluxing benzene, also gave mainly 7 but as a viscous oil that was difficult to purify. The ^1H NMR spectrum of 7 showed six peaks for the four vinyl and two bridgehead protons, as well appropriate aromatic proton signals.[8]

Scheme I



Double cycloaddition of diene 7 to benzoquinone gave an inseparable mixture of adducts 12 and 13 (88% total yield). Although this mixture could be aromatized to quinone 10 and its regioisomer (also inseparable), which could then be reduced to a mixture of anthracene 11 and its regioisomer (difficultly separable), it became essential as the second critical task to develop a regioselective route to 11.



Treatment of diene 7 with excess benzoquinone (10 equiv) gave naphthoquinone 8 as a bright yellow solid, mp 259-260 °C, in 79% yield, excess quinone having oxidized the intermediate cycloadduct. Consistent with this structure, one bridgehead proton appeared in the usual region (δ 5.55) whereas the other was substantially deshielded (δ 7.42) by the nearby carbonyl oxygen.

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[3] Chiral triptycenes and their absolute configurations have been investigated by several groups. For examples, see: Sonoda, A.; Ogura, F.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 853-857. Ogura, F.; Nakagawa, M. *Ibid.* **1965**, *38*, 155-156. Kuritani, M.; Sakata, Y.; Ogura, F.; Nakagawa, M. *Chimia* **1972**, *26*, 470-471. Tanaka, J.; Ogura, F.; Kuritani, M.; Nakagawa, M. *Ibid.* **1972**, *26*, 471-473. Sakate, N.; Sakabe, K.; Ozeki-Minakata, K.; Tanaka, J. *Acta Crystallogr. B* **1972**, *28*, 3441-3446. Ogura, F.; Sakata, Y.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3646-3651. Shimizu, Y.; Tatemitsu, H.; Ogura, F.; Nakagawa, M. *J. Chem. Soc., Chem. Commun.* **1973**, 22-23. Kuritani, M.; Sakata, Y.; Ogura, F.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 605-610. Sakata, Y.; Ogura, F.; Nakagawa, M. *Ibid.* **1973**, *46*, 611-617. Ogura, F.; Nakagawa, M. *Ibid.* **1973**, *46*, 651-653. Shimizu, Y.; Naito, T.; Ogura, F.; Nakagawa, M. *Ibid.* **1973**, *46*, 1520-1525. Hashimoto, M.; Shimizu, Y.; Ogura, F.; Nakagawa, M. *Ibid.* **1974**, *47*, 1761-1766. Harada, N.; Tamai, Y.; Takuma, Y.; Uda, H. *J. Am. Chem. Soc.* **1980**, *102*, 501-506. Harada, N.; Tamai, Y.; Uda, H. *Ibid.* **1980**, *102*, 506-511. Harada, N.; Tamai, Y.; Uda, H. *J. Org. Chem.* **1984**, *49*, 4266-4271. Daub, J.; Jakob, L.; Salbeck, J.; Okamoto, Y. *Chimia* **1985**, *39*, 393-395. Daub, J.; Jakob, L.; Salbeck, J. *Chem. Ber.* **1988**, *121*, 2187-2194. For a discussion of the desymmetrization of triptycene, see: Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319-3328.

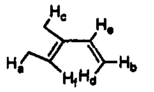
[4] Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. *J. Org. Chem.* **1983**, *48*, 4357-4360. Bashir-Hashemi, A.; Hart, H.; Ward, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 6675-6679. Luo, J.; Hart, H. *J. Org. Chem.* **1987**, *52*, 3631-3636. Chen, Y-S.; Hart, H. *J. Org. Chem.* **1989**, *54*, 2612-2615. Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1990**, *112*, 3687-3688.

[5] Shahlai, K.; Hart, H. *J. Org. Chem.* **1989**, *54*, 2615-2620.

[6] Miettinen, T. *Acta Chem. Scand.* **1977**, *B31*, 818-822.

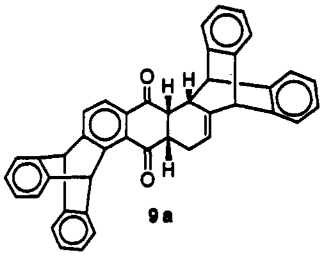
[7] Cristol, S. J.; Bly, R. K. *J. Am. Chem. Soc.* **1960**, *82*, 6155-6162. Cristol, S. J.; Arganbright, R. P.; Tanner, D. D. *J. Org. Chem.* **1963**, *28*, 1374-1377.

[8] The aliphatic proton signals are assigned as follows:



H_a δ 5.06, d, J_{af} = 6.3 Hz; H_b δ 5.09; d, J_{be} = 10.7 Hz; H_c δ 5.36, d, J_{cf} = 1.0 Hz; H_d δ 5.58, d, J_{de} = 17.0 Hz; H_e δ 6.39, dd, J = 10.7, 17.0 Hz; H_f δ 6.74, dd, J = 1.0, 6.3 Hz.

Thermal cycloaddition of 8 to diene 7 gave, as expected, a mixture of regioisomeric adducts, with 9 predominating. However, reaction of 8 with 7 in methylene chloride containing a catalytic amount of anhydrous aluminum chloride gave, *after 1 h at room temperature*, a 93% yield of pure 9, mp 214–216 °C, as a single regio- and stereoisomer, thought to be **9a**.[9]



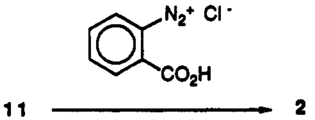
9a

Aromatization of 9 to give anthraquinone 10, mp 453–454 °C, was accomplished in 74% yield by bromination–dehydrobromination with *N*-bromosuccinimide (NBS) in refluxing CCl$_4$. The key features of the ^{1}H NMR spectrum confirm the C_{2v} symmetry. Noteworthy are singlets at δ 5.57 and 7.50 for the two sets of bridgehead protons, exceptional deshielding of one of these peaks being due to the adjacent carbonyl oxygens. Also, the protons on the internal aryl rings appear as two doublets (J = 7.7 Hz) at δ 7.74 and 8.11.

Reduction of 10 to anthracene 11 was accomplished by aluminum cyclohexoxide in cyclohexanol in 88% yield. Anthracene 11 is a pale yellow solid, mp 443–445 °C. The bridgehead protons appear at δ 5.62 and 6.33, the protons on the central ring of the anthracene moiety appear at lowest field (δ 8.84), and appropriate peaks are present for the remaining sets of aryl protons.

To summarize, the construction of 11 from ketone 5 required six steps and proceeded in 21% overall yield, the worst step being the dehydration of tertiary allylic alcohol 6.

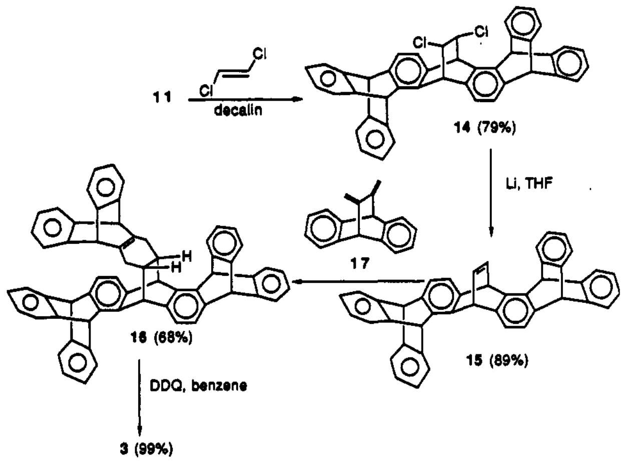
Synthesis of Iptycene 2. Addition of benzyne to 11 gave heptiptycene 2 in 60% yield, mp 420 °C. Consistent with the C_2 symmetry of this $C_{48}H_{30}$ hydrocarbon, the bridgehead protons appeared as three singlets at δ 5.27, 5.85, and 5.86.



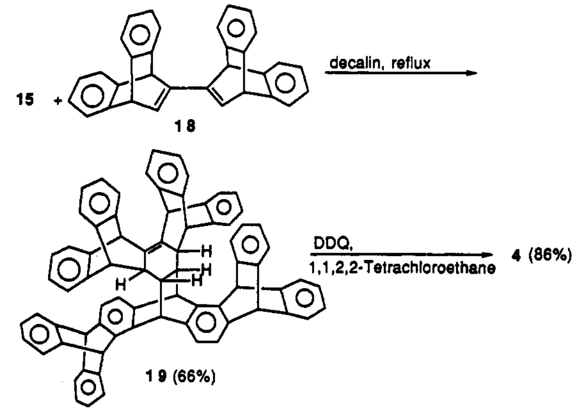
Synthesis of Noniptycene 3. Conversion of anthracene 11 to 3 is outlined in Scheme II. The Diels–Alder addition of *trans*-1,2-dichloroethene to 11 proceeded (sealed tube, 195–200 °C, 48 h) to give adduct 14, mp 384–385 °C, in 79% yield. Elimination of the chlorines with lithium in THF gave alkene 15 in 89% yield. Both 14 and 15 exhibited ^{1}H NMR spectra consistent with their C_2 symmetry.

To build the final triptycene moiety on to the double bond, 15 was heated with excess diene 17[2,10] in refluxing decalin (24 h) to give cycloadduct 16, mp 274–276 °C, in 68% yield. The ^{1}H NMR spectrum showed six sharp one-proton singlets for the (outer) bridgehead protons (δ 4.58, 4.65, 5.24, 5.25, 5.65, 5.66), whereas the central bridgehead protons were doublets as required at δ 4.34 and 4.44.[9]

Scheme II



Scheme III



Cyclohexene 16 was aromatized quantitatively by DDQ in refluxing benzene to give 3, mp >500 °C. As required by the C_2 symmetry, the bridgehead protons in 3 appeared as four sharp 2-proton singlets (δ 5.24, 5.29, 5.74, 5.82), and the ^{13}C NMR spectrum showed four aliphatic carbon peaks (δ 49.64, 49.71, 53.78, 53.83).

Dilute solutions of 3 in ethanol could be resolved through chromatography on triacetylcellulose columns[11] or on (−)-poly(triphenylmethyl methacrylate) or (−)-poly(diphenyl-2-pyridylmethyl methacrylate) columns.[11]

Synthesis of Undecaiptycene 4. This chiral iptycene was synthesized from alkene 15 using the same technology as was developed for the synthesis of supertriptycene (last citation in ref 4), as shown in Scheme III.

The cycloaddition of bicycloalkene 15 to diene 18,[5] though neither partner is particularly activated, proceeded readily in refluxing decalin to give adduct 19 in 66% yield. As required, this adduct showed only six one-proton singlets for bridgehead protons lacking an adjacent C–H group. It also showed the expected 14 sp^3 carbon signals in its ^{13}C NMR spectrum (between δ 29.70 and 54.06). Dehydrogenation of 19 with DDQ gave the desired 4, whose C_2 symmetry was apparent from its NMR spectra. For example, the bridgehead protons appeared as five two-proton singlets (δ 5.22, 5.83, 5.99, 6.00, and 6.27) and there were just five signals for the bridgehead carbons (sp^3).

Experimental Section[12]

1,4[1′,2′]-Benzeno-1,2,3,4-tetrahydro-2-ethenylnaphthalen-2-ol (6). A solution of ketone 5[6] (22 g, 0.1 mol) in

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[9] For a discussion of the interesting features of its ^{1}H NMR spectrum which supports this conclusion, see the supplemental material.

[10] Anantanarayan, A.; Hart, H. *J. Org. Chem.* **1991**, *56*, 991–996.

[11] We are indebted to Professors Albrecht Mannschreck and Yoshio Okamoto, respectively, for these results.

[12] For general procedures, see: Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1988**, *110*, 7136–7140.

150 mL of anhydrous THF was added dropwise to a solution of vinylmagnesium bromide (0.15 mol) in THF (300 mL) under Ar at 0–5 °C. The mixture was stirred at rt for 4 h then quenched with 100 mL of saturated NH_4Cl solution. The organic layer was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated. The oily residue was chromatographed on silica gel using 6:3:1 hexanes/CH_2Cl_2/ether as eluent to give 21 g (84%) of **6** as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.56 (br s, 1 H), 1.78 (dd, J = 13.3, 2.7 Hz, 1 H), 2.13 (dd, J = 13.3, 2.6 Hz, 1 H), 4.13 (s, 1 H), 4.34 (dd, J = 2.7, 2.6 Hz, 1 H), 4.98 (dd, J = 10.7, 1.1 Hz, 1 H), 5.18 (dd, J = 17.1, 1.1 Hz, 1 H), 5.59 (dd, J = 17.1, 10.7 Hz, 1 H), 7.13 (m, 2 H), 7.21 (m, 2 H), 7.29 (m, 2 H), 7.38 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 43.81, 44.49, 57.00, 75.94, 111.64, 122.76, 123.31, 125.35, 125.43, 125.68, 125.97, 126.05, 126.33, 139.73, 140.09, 142.77, 142.84, 143.23; MS *m/e* (relative intensity) 230 (0.4), 215 (1), 191 (2), 189 (2), 179 (15), 178 (100). Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.99; H, 6.58.

1,4[1′,2′]-Benzeno-1,4-dihydro-2-ethenylnaphthalene (7). To a solution of alcohol **6** (17.4 g, 70 mmol) in 1000 mL of 1:1 heptane/THF was added 19.9 g (140 mmol) of powdered P_2O_5, and the mixture was stirred mechanically at reflux under Ar for 36–48 h. The mixture was cooled and filtered, and the solid was washed (2 × 100 mL) with anhydrous THF. Liquid layers were combined and evaporated, and the oily residue was chromatographed using 7:1 hexanes/CH_2Cl_2 as eluent, to give 8.4 g (52%) of **7**[13] as a white solid: mp 115–116 °C; ^1H NMR ($CDCl_3$) 5.06 (d, J = 6.3 Hz, 1 H), 5.09 (d, J = 10.7 Hz, 1 H), 5.36 (d, J = 1.0 Hz, 1 H), 5.58 (d, J = 17.0 Hz, 1 H), 6.39 (dd, J = 17.0, 10.7 Hz, 1 H), 6.74 (dd, J = 6.3, 1.0 Hz, 1 H), 6.94 (m, 4 H), 7.25 (m, 2 H), 7.31 (m, 2 H); ^{13}C NMR ($CDCl_3$) 49.14, 50.21, 111.42, 122.44, 124.17, 124.32, 132.80, 136.61, 145.08, 145.78, 150.46 (one arom overlapped); MS *m/e* (relative intensity) 231 (18), 230 (100), 229 (91), 228 (42), 227 (19), 226 (22), 215 (67), 202 (31), 178 (63). Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.95; H, 6.07.

7,12[1′,2′]-Benzeno-1,4,7,12-tetrahydrobenz[*a*]anthracene-1,4-dione (8). A solution of **7** (5.76 g, 25 mmol) and 27 g (0.25 mol) of 1,4-benzoquinone in 500 mL of xylenes was heated at reflux for 72 h, cooled, and filtered. The solid was washed (2 × 100 mL) with 1:1 CH_2Cl_2/hexanes, and the combined organic solutions were evaporated (rotavap) to remove the solvent and excess benzoquinone. Chromatography of the residue on silica gel with 3:1 CH_2Cl_2/hexanes as eluent gave 6.6 g (79%) of **8** as a bright yellow solid: mp 259–260 °C; ^1H NMR ($CDCl_3$) δ 5.55 (s, 1 H), 6.83 (d, J = 10.5 Hz, 1 H), 6.90 (d, J = 10.5 Hz, 1 H), 7.06 (m, 4 H), 7.42 (s, 1 H), 7.44 (m, 2 H), 7.54 (m, 2 H), 7.68 (d, J = 7.8 Hz, 1 H), 7.82 (d, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 48.90, 54.44, 123.82, 124.78, 125.19, 125.82, 125.84, 126.20, 128.30, 129.52, 137.62, 140.01, 143.87, 144.10, 147.38, 153.71, 184.54, 187.39; MS *m/e* (relative intensity) 335 (3), 334 (16), 305 (4), 252 (7), 229 (7), 215 (5), 179 (12), 178 (100), 152 (8), 149 (9). Anal. Calcd for $C_{24}H_{14}O_2$: C, 86.21; H, 4.22. Found: C, 86.27; H, 4.01.

5,18:9,14-Di[1′,2′]benzeno-5,6,6a,7,9,14,14a,14b,15,18-decahydronaphtho[2,3-*c*]pentaphene-6,15-dione (9). To a solution of quinone **8** (5.0 g, 15 mmol) and a catalytic amount (~0.4 g) of anhydrous $AlCl_3$ in 100 mL of CH_2Cl_2 was added 3.7 g (16 mmol) of diene **7**. The mixture was stirred for 1 h at room temperature, then washed with water (50 mL) and saturated NaCl solution (50 mL), and dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue on silica gel using 2:1 CH_2Cl_2/hexanes as eluent gave 7.9 g (93%) of **9** as a white solid: mp 214–216 °C; ^1H NMR ($CDCl_3$)[9] δ 1.94 (ddd, J = 15.6, 6.6, 4.2 Hz, 1 H), 2.76 (ddd, J = 15.6, 6.1, 4.1 Hz, 1 H), 2.78 (dd, J = 9.3, 3.3 Hz, 1 H), 3.18, (ddd, J = 7.8, 4.2, 4.1 Hz, 1 H), 3.72 (dd, J = 9.3, 7.8 Hz, 1 H), 4.41 (br s, 1 H), 4.65 (s, 1 H), 5.45 (s, 1 H), 5.71 (t, J = 7.5, 1 H), 5.90 (t, J = 7.5 Hz, 1 H), 6.10 (ddd, J = 6.6, 6.6, 3.3 Hz, 1 H), 6.29 (d, J = 7.5 Hz, 1 H), 6.77 (d, J = 7.5 Hz, 1 H), 6.96 (s, 1 H), 6.99 (m, 2 H), 7.05 (m, 2 H), 7.12 (m, 2 H), 7.24 (m, 2 H), 7.39 (m, 3 H), 7.50 (m, 1 H), 7.59 (d, J = 7.7 Hz, 1 H), 7.80 (d, J = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.95, 40.88, 46.25, 47.94, 48.08, 48.91, 52.62, 53.86, 120.72, 121.05, 122.53, 123.00, 123.34, 123.41, 124.17, 124.25, 124.85, 124.95, 125.15, 125.19, 125.26, 125.48, 125.53, 125.63, 125.67, 127.76, 128.25, 133.17, 137.87, 138.49, 140.93, 142.88, 143.78, 144.01, 144.08, 144.67, 146.19, 153.43, (two arom overlapped); 196.58, 198.74; MS, (FAB) *m/e* (relative intensity) 565 (100, MH^+), 564 (100), 563 (25), 387 (53), 335 (45), 307 (40), 289 (31), 252 (34), 178 (69); HRMS calcd for $C_{42}H_{28}O_2$ 565.2167 (MH^+), found 565.2137. Anal. Calcd for $C_{42}H_{28}O_2$: C, 89.33; H, 4.99. Found: C, 89.41; H, 4.95.

5,18:9,14-Di[1′,2′]benzeno-5,6,9,14,15,18-hexahydronaphtho[2,3-*c*]pentaphene-6,15-dione (10). A solution of adduct **9** (5.65 g, 10 mmol) and 4.0 g (22.5 mmol) of NBS in CCl_4 (250 mL) was heated at reflux for 24 h. Removal of the solvent and chromatography of the crude solid on silica gel using 2:1 CH_2Cl_2/hexanes as eluent gave 4.15 g (74%) of **10** as a yellow solid: mp 453–454 °C; ^1H NMR ($CDCl_3$) δ 5.57 (s, 2 H), 7.06 (m, 8 H), 7.44 (m, 4 H), 7.50 (s, 2 H), 7.56 (m, 4 H), 7.74 (d, J = 7.7 Hz, 2 H), 8.11 (d, J = 7.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 49.16, 54.41, 123.88, 124.95, 125.81, 125.91, 125.98, 127.96, 128.70, 132.44, 144.41, 144.46, 147.86, 153.75 (one arom overlapped), 185.87; MS *m/e* (relative intensity) 560 (3), 252 (2), 206 (4), 179 (14), 178 (100), 111 (5), 109 (4). Anal. Calcd for $C_{42}H_{24}O_2$: C, 89.87; H, 4.31. Found: C, 89.79; H, 4.12.

5,18:9,14-Di(1′,2′)benzeno-5,9,14,18-tetrahydronaphtho[2,3-*c*]pentaphene (11). To a solution of aluminum cyclohexoxide, prepared by dissolving 2.7 g (0.1 mol) of Al in 60 mL of cyclohexanol, was added 5.6 g (10 mmol) of anthraquinone **10** and 30 mL of cyclohexanol. After the mixture was heated at reflux for 24 h, the solvent was removed and the residue was extracted with CH_2Cl_2 (2 × 100 mL). The extract was washed with water (50 mL), saturated NaCl solution (50 mL), and dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue on silica gel using 2:1 hexanes/CH_2Cl_2 gave 4.66 g (88%) of **11** as a pale yellow solid: mp 443–445 °C; ^1H NMR ($CDCl_3$) δ 5.62 (s, 2 H), 6.33 (s, 2 H), 6.96 (m, 8 H), 7.44 (m, 4 H), 7.50 (m, 4 H), 7.66 (d, J = 8.5 Hz, 2 H), 7.86 (d, J = 8.5 Hz, 2 H), 8.84 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 49.33, 54.62, 120.77, 122.97, 123.03, 123.15, 124.39, 124.48, 125.33, 126.46, 130.18, 141.77, 142.74, 145.03, 145.95; MS *m/e* (relative intensity) 532 (7), 531 (4), 530 (6), 265 (13), 263 (13), 252 (13), 179 (13), 178 (60), 87 (73), 85 (100), 83 (38); UV (CH_2Cl_2) λ_{max} 419 nm (ϵ 5265), 396 (5700), 376 (4000), 349 (2900), 282 (103 000). Anal. Calcd for $C_{42}H_{26}$: C, 95.06; H, 4.94. Found: C, 95.13; H, 5.04.

Bis-Adducts 12 and 13 from Diene 6 and 1,4-Benzoquinone. A solution of diene **6** (920 mg, 4 mmol) and 1,4-benzoquinone (216 mg, 2 mmol) in 120 mL of xylenes was heated at reflux for 48 h. The solvent was evaporated and the residue was chromatographed over silica gel with 1:1 CH_2Cl_2/hexanes to give 1.0 g (88%) of an inseparable mixture of **12** and **13** with virtually identical ^1H NMR [($CDCl_3$) δ 2.43 (m, 4 H), 3.16 (m, 4 H), 3.62 (m, 2 H), 4.42 (m, 2 H), 4.70 (s, 2 H), 5.73 (m, 2 H), 7.08 (m, 8 H), 7.14 (m, 4 H), 7.22 (m, 4 H)]: MS *m/e* (relative intensity) 568 (M^+, 3), 539 (1), 338 (1), 317 (3), 284 (1), 282 (4), 255 (10), 215 (10), 178 (100). Aromatization and reduction of this mixture (as with **9** and **10**) gave **11** (identical by ^1H NMR and mass spectrum with authentic material prepared as above) and its regioisomer **5,18:11,16-di[1′,2′]benzeno-5,11,16,18-tetrahydronaphtho[2,3-*a*]pentaphene** which, though not fully characterized, was isolated as pale yellow crystals: mp 410 °C; ^1H NMR ($CDCl_3$) δ 5.63 (s, 2 H), 6.59 (s, 2 H), 7.03 (m, 8 H), 7.46 (m, 4 H), 7.61 (m, 4 H), 7.67 (m, 4 H), 8.34 (s, 1 H), 9.29 (s, 1 H); UV (CH_2Cl_2) λ_{max} 419 nm (ϵ 5260), 395 (6000), 375 (5600), 277 (49 000).

5,18:8,17:9,14-Tri[1′,2′]benzeno-5,8,9,14,17,18-hexahydronaphtho[2,3-*c*]pentaphene (2). A solution of anthracene **11** (53 mg, 0.1 mmol), benzenediazonium 2-carboxylate hydrochloride[14] (90 mg, 0.5 mmol), and propylene oxide (0.5 mL) in 10 mL of 1,2-dichloroethane was heated at reflux for 12 h then cooled and concentrated. The residue was chromatographed over silica gel using 1:3 ether/hexanes as eluent to give 36 mg (60%) of **2**: mp 420 °C dec; ^1H NMR ($CDCl_3$) δ 5.27 (s, 2 H), 5.85 (s, 2 H), 5.86 (s, 2 H), 6.93 (m, 10 H), 7.00 (m, 4 H), 7.25 (m, 4 H), 7.36 (m, 6 H); MS, *m/e* (relative intensity) 606 (M^+, 47), 530 (2), 428 (22), 353 (11), 303 (12), 252 (15), 178 (8). Anal. Calcd for $C_{48}H_{30}$: C, 95.05; H, 4.95. Found: C, 95.16; H, 4.83.

Cycloadduct 14. A suspension of anthracene **11** (5.3 g, 10 mmol) in 80 mL of 1:1 *trans*-1,2-dichloroethene/cyclooctane (or

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[13] By eluting the column with polar solvents (ether, ethyl acetate), 10–20% of starting alcohol **6** can be recovered. Longer reflux times did not improve the yield, and varying the amount of P_2O_5 or the solvent ratios decreased the yield.

[14] Logullo, F. M., Ph.D. Thesis, Case Institute of Technology, Cleveland, OH, 1965.

decalin) was heated in a sealed tube at 195–200 °C for 48 h. Removal of the solvents by vacuum distillation and chromatography of the residue on silica gel using 1:2 CH_2Cl_2/hexanes as eluent gave 4.95 g (79%) of **14** as a white solid: mp 384–385 °C; ^{1}H NMR ($CDCl_3$) δ 4.12 (dd, *J* = 1.2, <1.0 Hz, 2 H), 4.95 (d, *J* = <1.0 Hz, 2 H), 5.37 (s, 2 H), 5.74 (s, 2 H), 6.89 (m, 4 H), 6.99 (m, 6 H), 7.20 (d, *J* = 7.3 Hz, 2 H), 7.29 (m, 4 H), 7.39 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 47.84, 49.09, 53.42, 64.90, 120.27, 121.50, 123.11, 123.24, 123.45, 124.79, 124.84, 131.65, 135.51, 141.90, 143.97, 144.41, 144.50, 144.73 (4 arom signals overlapped); HRMS calcd for $C_{44}H_{28}Cl_2$ 626.1568, found 626.1572.

5,18:9,14-Di[1,2′]benzeno-8,17-etheno-5,8,9,14,17,18-hexahydronaphtho[2,3-*c*]pentaphene (15). To a solution of dichloride **14** (3.14 g, 5 mmol) in 150 mL of anhydrous THF under Ar was added 0.35 g (50 g-atoms) of Li metal in small pieces. The mixture was heated at reflux for 72 h then cooled, and the excess Li was carefully destroyed (methanol). The solvent was removed, and the residue was taken up in 100 mL of CH_2Cl_2, washed with 50 mL each of water and saturated NaCl solution, and dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue over silica gel using 2:1 hexanes/CH_2Cl_2 as eluent gave 2.47 g (89%) of **15** as a white solid: mp 383–385 °C; ^{1}H NMR ($CDCl_3$) δ 5.31 (s, 2 H), 5.58 (dd, *J* = 4.0, 3.3 Hz, 2 H), 5.78 (s, 2 H), 6.89 (m, 4 H), 6.94 (dd, *J* = 4.0, 3.3 Hz, 2 H), 6.99 (m, 4 H), 7.26 (m, 4 H), 7.31 (m, 4 H), 7.34 (m, 2 H), 7.42 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 46.11, 49.12, 53.25, 118.77, 118.84, 123.04, 123.10, 123.18, 124.64, 124.69, 124.77, 137.98, 138.90, 139.50, 141.05, 142.22, 144.43, 144.71, 145.02, 145.32 (2 arom overlapped); HRMS calcd for $C_{44}H_{28}$ 556.2191, found 556.2205.

Cycloadduct 16. A solution of **15** (1.67 g, 3 mmol) and diene **17**[2,10] (2.3 g, 10 mmol) in 50 mL of decalin was heated at reflux for 24 h. Vacuum distillation of the solvent and chromatography of the residue on silica gel using 2:1 hexanes/CH_2Cl_2 as eluent gave 1.59 g (68%) of **16** as a white solid: mp 274–276 °C; ^{1}H NMR ($CDCl_3$)[9] δ 1.29 (ddd, *J* = 14.6, 10.2, 2.5 Hz, 1 H), 1.67 (ddd, *J* = 14.4, 9.8, 2.1 Hz, 1 H), 1.90 (ddddd, *J* = 14.5, 10.5, 6.3, 2.1, 1.8 Hz, 1 H), 1.99 (ddddd, *J* = 14.2, 10.5, 6.3, 2.5, 2.3 Hz, 1 H), 2.45 (dd, *J* = 15.4, 14.9 Hz, 1 H), 2.49 (dd, *J* = 15.4, 15.0 Hz, 1 H), 4.34 (d, *J* = 1.7 Hz, 1 H), 4.44 (d, *J* = 2.3 Hz, 1 H), 4.58 (s, 1 H), 4.65 (s, 1 H), 5.24 (s, 1 H), 5.25 (s, 1 H), 5.65 (s, 1 H), 5.66 (s, 1 H), 6.80 (m, 10 H), 6.96 (m, 8 H), 7.11 (m, 2 H), 7.21 (m, 4 H), 7.31 (m, 2 H), 7.37 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.04, 30.31, 39.33, 39.65, 44.71, 44.78, 48.95, 53.42, 53.49, 54.98, 55.06 (one aliph overlapped), 119.02, 119.90, 120.12, 121.40, 121.79, 121.86, 121.90, 122.04, 122.69, 123.03, 123.17, 123.39, 123.56, 123.62, 123.74, 124.50, 124.56, 124.64, 124.71, 124.84, 135.95, 137.66, 137.98, 140.20, 142.24, 142.45, 142.78, 144.55, 144.63, 144.71, 144.91, 145.03, 145.13, 145.49, 145.57, 145.78, 145.88, 145.21 (12 arom overlapped). Anal. Calcd for $C_{62}H_{42}$: C, 94.66; H, 5.34. Found: C, 94.88; H, 5.16.

Chiral Noniptycene 3. A solution of adduct **16** (937 mg, 1.2 mmol) and DDQ (700 mg, 3 mmol) in 50 mL of benzene was heated at reflux for 24 h. Removal of the solvent and chromatography of the residue on silica gel using 3:2 hexanes/CH_2Cl_2 as eluent gave 930 mg (99%) of **3** as a white solid: mp >500 °C; ^{1}H NMR ($CDCl_3$) δ 5.24 (s, 2 H), 5.29 (s, 2 H), 5.74 (s, 2 H), 5.82 (s, 2 H), 6.90 (m, 16 H), 7.28 (m, 10 H), 7.40 (m, 4 H); ^{13}C NMR ($CDCl_3$) 49.64, 49.71, 53.78, 53.83, 119.67, 119.75, 119.90, 123.41, 123.57, 123.65, 125.10, 125.20, 138.79, 139.41, 142.01, 142.15, 142.33, 142.73, 144.91, 145.02, 145.51, 145.57, 145.63 (6 arom overlapped). Anal. Calcd for $C_{62}H_{38}$: C, 95.14; H, 4.86. Found: C, 95.24; H, 4.48.

Cycloadduct 19. A solution of alkene **15** (56 mg, 0.1 mmol) and diene **18**[5] (61 mg, 0.15 mmol) in 10 mL of decalin was heated at reflux for 12 h. Removal of the solvent (rotavap) and chromatography of the residue on a silica gel glass plate using 3:2 hexanes/CH_2Cl_2 as eluent gave 64 mg (66%) of **19** as a white solid: mp 289–291 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (ddd, *J* = 11.0, 10.5, 2.5 Hz, 1 H), 1.15 (ddd, *J* = 11.0, 10.5, 1.9 Hz, 1 H), 1.64 (ddd, *J* = 11.0, 10.5, 1.7 Hz, 2 H), 4.67 (d, *J* = 2.2 Hz, 1 H), 4.70 (d, *J* = 2.4 Hz, 1 H), 4.79 (d, *J* = 1.9 Hz, 1 H), 4.84 (d, *J* = 2.4 Hz, 1 H), 5.14 (s, 1 H), 5.19 (s, 1 H), 5.22 (s, 1 H), 5.25 (s, 1 H), 5.77 (s, 1 H), 5.83 (s, 1 H), 6.79–7.63 (m, 36 H); ^{13}C NMR ($CDCl_3$) δ 29.70, 42.12, 42.84, 45.03, 45.74, 46.69, 47.29, 47.58, 47.96, 48.06, 48.46, 49.70, 49.90, 54.06, 119.82, 120.47, 120.75, 120.92, 122.53, 122.85, 123.35, 123.47, 123.53, 123.57, 123.64, 123.87, 124.12, 124.89, 124.97, 125.03, 125.14, 125.24, 125.28, 125.35, 125.46, 125.50, 125.63, 125.86, 125.91, 126.40, 126.57, 129.74, 130.18, 135.25, 137.27, 138.63, 138.92, 140.59, 140.89, 141.06, 141.38, 141.41, 141.84, 141.91, 142.02, 142.34, 142.87, 143.28, 143.61, 144.39, 144.82, 144.88, 145.13, 145.29, 145.39, 145.54, 145.70 (9 arom protons overlapped); HRMS calcd for $C_{76}H_{50}$ 962.3912 found: 962.3890.

Undecaiptycene 4. A solution of cycloadduct **19** (49 mg, 0.05 mmol) and 45 mg (excess) of DDQ in 2 mL of 1,1,2,2-tetrachloroethane was heated at 100 °C for 3 h. Removal of the solvent (rotavap) and chromatography of the residue on a silica gel glass plate using 3:2 CH_2Cl_2/hexanes as eluent gave 41 mg (86%) of **4** as a white solid, mp >470 °C; ^{1}H NMR ($CDCl_3$) δ 5.22 (s, 2 H), 5.83 (s, 2 H), 5.99 (s, 2 H), 6.00 (s, 2 H), 6.27 (s, 2 H), 6.94 (m, 20 H), 7.23 (m, 4 H), 7.30 (m, 4 H), 7.44 (m, 4 H), 7.61 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 45.71, 49.91, 49.99, 50.15, 53.93, 119.60, 120.05, 123.46, 123.58, 123.74, 124.77, 124.87, 125.09, 125.22, 125.28, 125.47, 134.56, 134.88, 135.04, 138.69, 138.94, 141.58, 142.01, 144.30, 144.83, 144.89, 144.99, 145.04, 145.13, 145.51 (8 arom protons overlapped); HRMS calcd for $C_{76}H_{46}$ 958.3599, found 958.3577.

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Supplementary Material Available: ^{1}H NMR assignments and stereochemistry of **9** and **16** and ^{1}H and ^{13}C NMR spectra of **4**, **14**, **15**, and **19** (15 pages). Ordering information is given on any current masthead page.