Synthesis of a Variety of Bichromophoric "Ball-and-Chain" Systems Based on Buckminsterfullerene (C_{60}) for the Study of Intramolecular Electron and Energy Transfer Processes

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Diels−Alder reaction of C_{60} with the 1,3-dienes **7e**−**h**, **8a**, **8b**, and **8d**−**h** affords the "ball-and-chain" systems **2e**−**h**, **3a**, **3b**, and **3d**−**h** bearing two chromophores linked *via* a rigid, hybrid saturated polynorbornane−bicyclo[2.2.0]hexane ("norbornylogous") hydrocarbon bridge. Analogous reaction with the bis(diene) **9** affords the soluble dumbbell system **4** bearing two C_{60} chromophores. The norbornylogous bridge is a strong mediator of electron and energy transfer *via* a through-bond coupling mechanism. The norbornylogous donor−bridge−diene units **7d**−**h**, **8a**, **8b**, and **8d**−**h** were prepared in a straightforward manner from bicyclo[2.2.2]octane precursors by extending the bridges with linearly fused norbornane−bicyclo[2.2.0]hexane moieties through execution of the tandem Mitsudo−Smith series of reactions. The X-ray structure of the dimethoxybenzene−bridge−C_{60} system **3a** reveals favorable self-complementarity manifested by the unusual packing structure of **3a** in the crystal. Molecular mechanics, semiempirical, and *ab initio* conformational analyses of compounds **2e**, **3a**, **3b**, **3e**, **3f**, **3h**, **68**, and **70** (MM2, Sybyl, CVFF, AM1, HF/3-21G) were performed to quantify their ability to adopt two nondegenerate boat conformations, i.e., extended and folded conformers, as well as their kinetic barrier of interconversion. A similar treatment of the C_{60}−bridge−C_{60} system **4** revealed unusual preference for the folded−folded conformer (18.9 kcal/mol at CVFF level), which was not reproduced by the AM1 method (0.11 kcal/mol). The reduction potentials of the systems **2e**, **3a**, and **3e** were about 0.1−0.5 V more negative than C_{60}, and the third reduction potential (E^3) of the 6-bond system **2e** was 0.14 V more negative than the corresponding wave for the 10-bond system **3e**. This shift was attributed to the closer proximity of the dimethylaniline donor group to the C_{60} surface for **2e** *vs* **3e**.

Introduction

The functionalization of buckminsterfullerene (C_{60}) is a burgeoning area of research, and a number of recent studies have demonstrated the ease by which this fascinating molecule undergoes a wide range of addition reactions with unsaturated systems.[1,2] We have exploited the Diels−Alder reaction between C_{60} and 1,3-dienes to obtain a variety of highly stable adducts which have properties similar to those of C_{60}.[2−4] A major reason for the intense interest in functionalized fullerenes lies in the exceptional electronic structure of the C_{60} cage, reflected by its rich redox chemistry, its magnetic and electronic properties, and its photophysical behavior.[1a] In particular, the characteristic electronic properties of fullerenes suggest that suitably functionalized derivatives may have important applications in fields as diverse as conductive materials[5] and biological chemistry.[3d,6]

Furthermore, the unusual photophysical and redox properties of C_{60} have made it the focus of many studies of energy and electron transfer between this framework and other chromophores.[7,8] An important issue to be resolved in such studies is how the dynamics of energy and electron transfer depend on the distance and relative orientation between the C_{60} group and the electron-donating chromophore. This problem is best handled using rigid covalently linked donor−bridge−acceptor systems in which the two chromophores can be held at well-defined distances and orientations with respect to each other by a rigid bridge, which is generally either a

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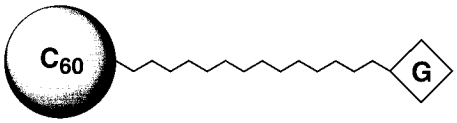
saturated hydrocarbon or a protein.[9] To date, there are only a few reported studies of intramolecular electron transfer in *rigid* covalently linked dyads in which one of the chromophores is the C_{60} cage.[10,11]

We have been studying intramolecular energy and electron transfer processes in rigid, covalently linked, multichromophoric systems such as **1(m,n)** in which the bridge is a polynorbornane−bicyclo[2.2.0]hexane hybrid ("norbornylogous") saturated hydrocarbon oligomer.[12−14] These studies have revealed that the norbornylogous bridge strongly mediates both electron and energy transfer over distances exceeding 12 Å by a through-bond coupling mechanism.[14]

The ease with which we are able to alter systematically both the length and configuration of our norbornylogous bridge, together with the efficacy with which this type of bridge mediates long-range intramolecular electron and energy transfer, makes it an ideal unit for studying the distance and orientation dependence of energy transfer and electron transfer dynamics involving the C_{60} system.

1(m,n)

We report herein full details of our successful strategy for synthesizing a variety of bichromophoric "ball-and-chain" systems[3b] **2e**−**h**, **3a**, **3b**, and **3d**−**h** shown in Chart 1, in which the C_{60} group is tethered to several different chromophores by our norbornylogous bridge of varying length, ranging from the 6-bond systems **2e**,**g**,**h**, to the 7-bond molecule **2f**, to the 10-bond bichromophores **3a**, **3b**, and **3d**−**g**.[15]



Ball-and-Chain System

Results and Discussion

Synthetic Strategy for Bridge Construction. It was decided to use the 2,3-bis(methylene)bicyclo[2.2.2]-octane unit as the diene component in the Diels−Alder reactions with C_{60}, rather than the 2,3-bis(methylene)-bicyclo[2.2.1]heptane group, on account of the comparative ease with which bridges containing the former group can be constructed. This methodology led ultimately to the synthesis of the donor−bridge−dienes **7d**−**h**, **8a**, **8b**, and **8d**−**h** and the tetraene **9** (Chart 2).

The key part of the synthesis is depicted in Scheme 1 and involves Diels−Alder reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene to the terminal double bond of the bridge to give the Diels−Alder adduct possessing the stereochemistry depicted. Reductive dechlorination of this material followed by deketalization will lead to the formation of the 7-norbornenone system. The 7-norbornenone group is known to be thermally labile, readily losing carbon monoxide by a cheletropic reaction to give the 1,3-cyclohexadiene system **5**. Diels−Alder reaction of **5** with dimethyl fumarate will form the adduct **6**, from which the bis(methylene) functionality may be obtained *via* reduction of the ester groups, bistosylation of the resulting bis(hydroxymethylene) groups, and subsequent bisdehydrotosylation.

Synthesis of the extended bridges containing linearly fused norbornane−bicyclo[2.2.0]hexane groups was achieved through execution of the tandem Mitsudo[16]−Smith[17] series of reactions as illustrated in Scheme 2. This methodology has been well described in previous papers.[13c,18,19] Specific details of the bridge syntheses are

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(15) An *n*-bond ball-and-chain system is one in which the two chromophores are connected by a bridge which has *n* σ-bonds separating them.

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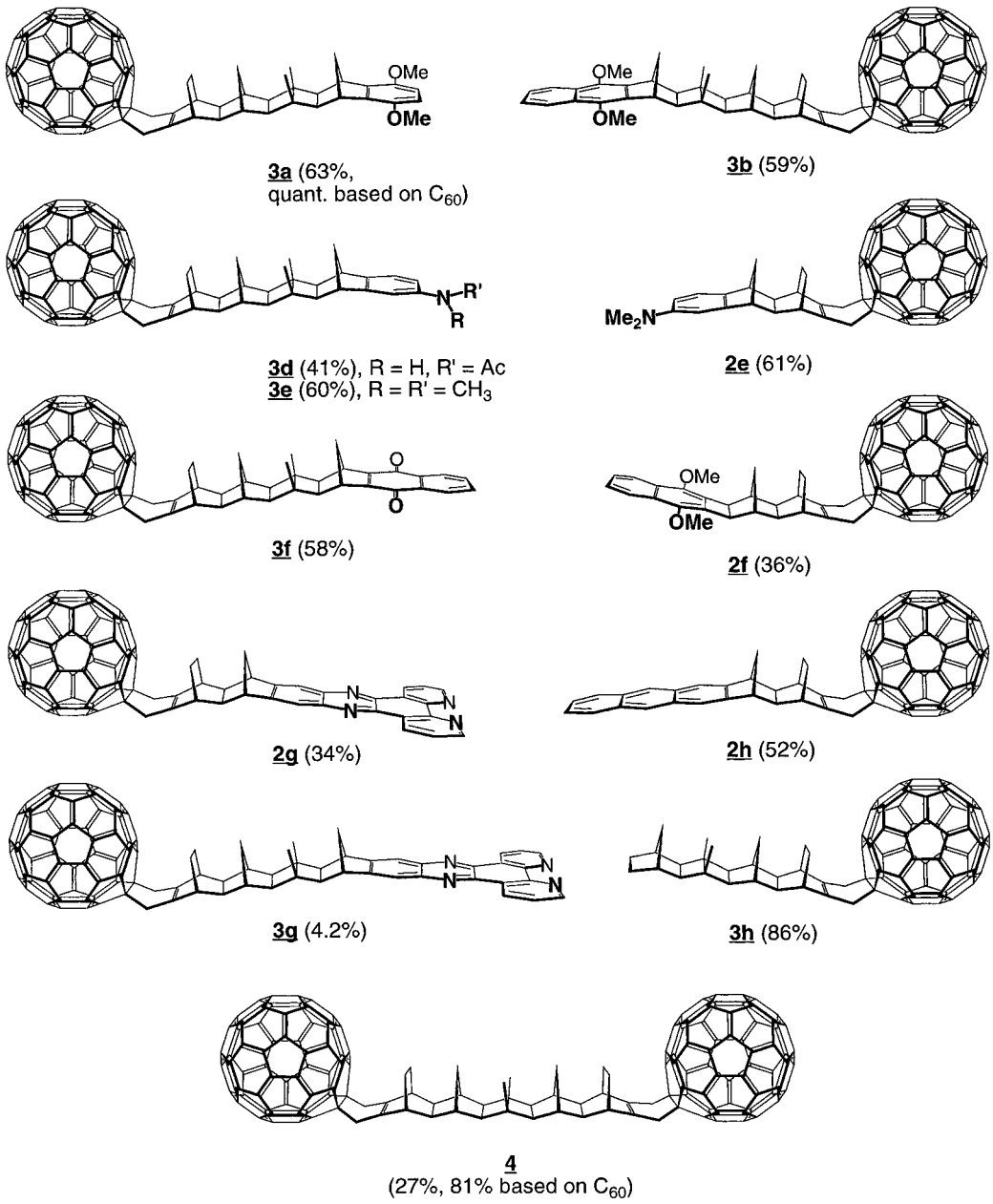
Chart 1



presented in Schemes 3−7, most of which involve fairly standard procedures and so will not be discussed in great depth.

The bridge dienes **7f**, **7h**, **8a**, **8b**, and **8h** were readily synthesized from the respective accessible norbornene derivatives **10a**,**b**,**f**,**h** which already contain the chromophore (either 1,4-dimethoxybenzene, 1,4-dimethoxynaphthalene, or anthracene) in its final form. These chromophores are able to withstand the chemical reactions used in the construction of the dienes (Schemes 3 and 4). The naphthoquinone−diene **8f** was obtained in good yield by treatment of the 1,4-dimethoxynaphthalene−diene **8b** with cerium(IV) ammonium nitrate (CAN) under standard conditions.[20]

The *N*,*N*-dimethylaniline−dienes **7e** and **8e**, and their respective acetanilide derivatives **7d** and **8d**, were obtained in the manner depicted in Scheme 5. The acetanilides **7d** and **8d** were best prepared from the corresponding bis(hydroxymethyl) systems **17c** (Scheme 3) and **30c** (Scheme 4), respectively. Protective acetylation of the hydroxy groups in **17c** and **30c** followed by nitration ($Cu(NO_3)_2$, Ac_2O) gave the nitro diacetates **34** and **35**, which were converted into the bis(hydroxymethyl)acetanilides **38** and **39** by catalytic hydrogenation of the nitro group, followed by protective acetylation of the formed NH_2 functionality, and subsequent reduction of the acetoxy groups with $LiBH_4$. Bistosylation, followed by base-induced bisdehydrotosylation gave the acetanilide−dienes **7d** and **8d**. Basic hydrolysis of the acetanilide **7d** gave the aniline **42** which was exhaustively methylated (MeI, $NaHCO_3$) to yield the quaternary ammonium iodide **43**. Reductive demethylation of this compound with $LiAlH_4$ completed the synthesis of the *N*,*N*-dimethylaniline **7e** which was obtained in an overall yield of 9% from **17c**.

The disappointingly low yield for the synthesis of **7e** by way of the acetanilide **7d** prompted us to devise an alternative, shorter synthesis of the *N*,*N*-dimethylaniline−diene **8e** bearing a longer bridge. Instead of

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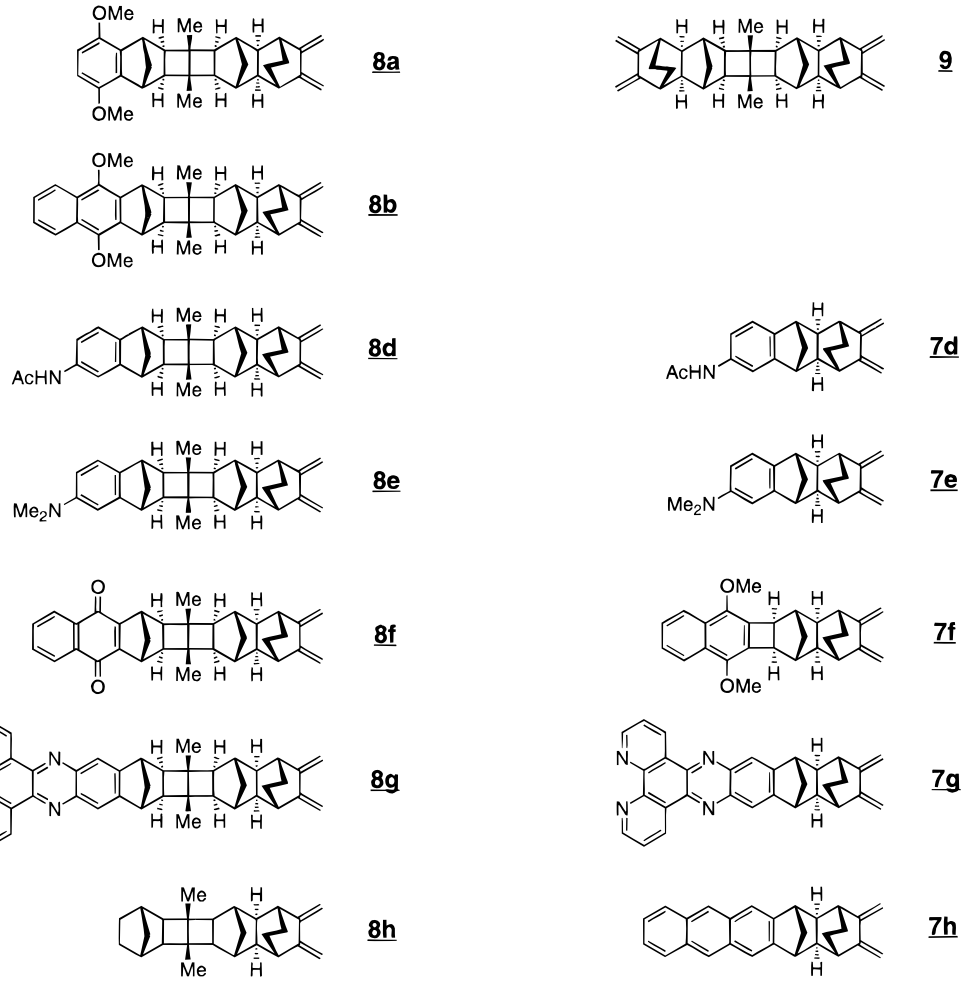
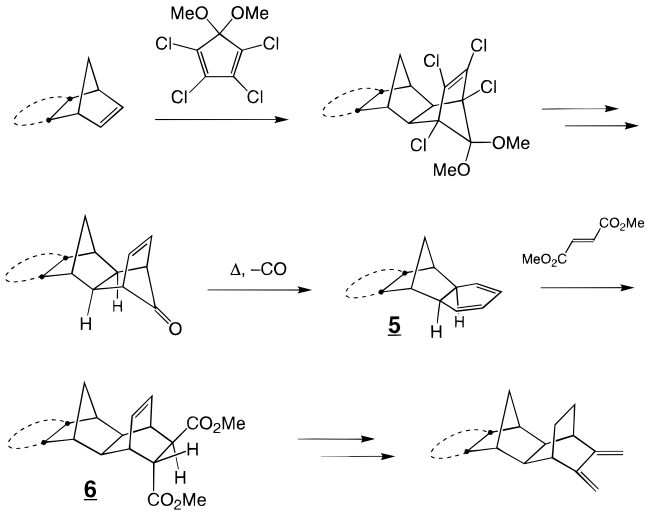
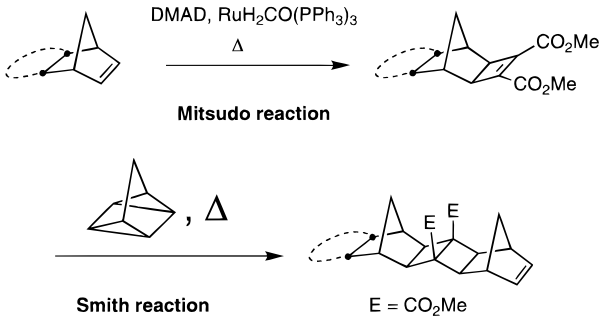
Chart 2



Scheme 1



Scheme 2

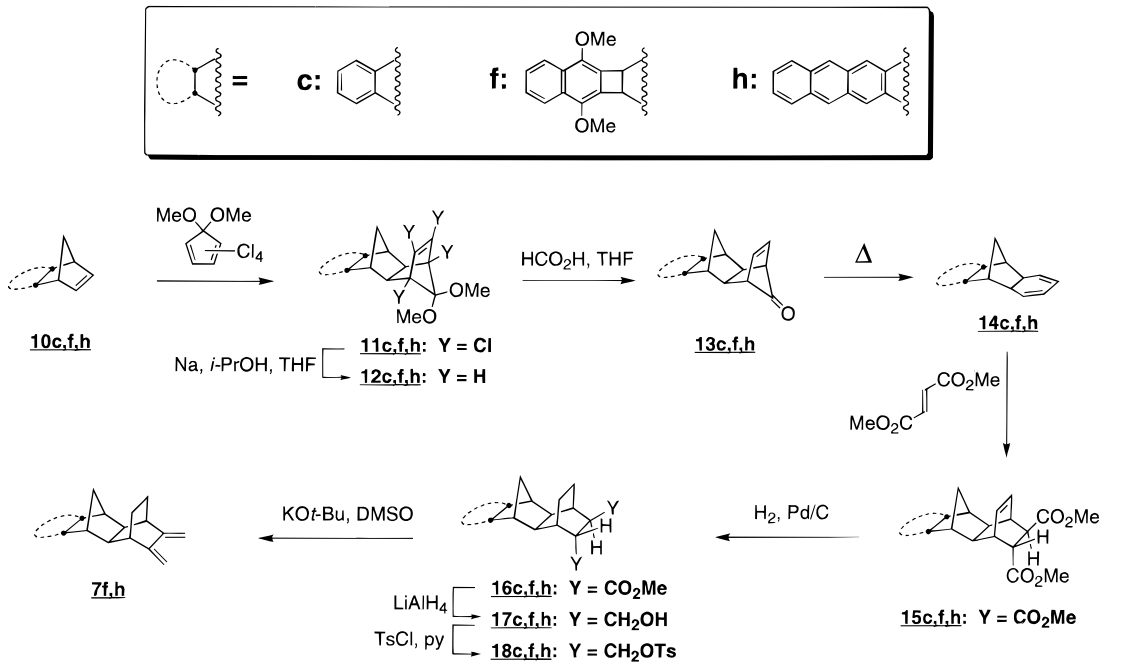


procuring this compound *via* the acetanilide−diene **8d** which, in turn, was obtained from the bis(hydroxymethyl) compound **30c** in low yield, the diester **29c**, whose synthesis is outlined in Scheme 4, was directly nitrated to give **44**. Catalytic hydrogenation of this material gave a good yield of the aniline **45**. Reductive methylation of **45** ($H_2C{=}O$, $NaBH_4$, dilute H_2SO_4) led to the formation of the *N*,*N*-dimethylaniline **46** (80% yield), which was then converted into the diene **8e** using standard reactions. The overall yield of **8e** from the diester **29c** was 27.5% as opposed to the 8.5% yield for **7e** prepared from the corresponding diester **16c**.

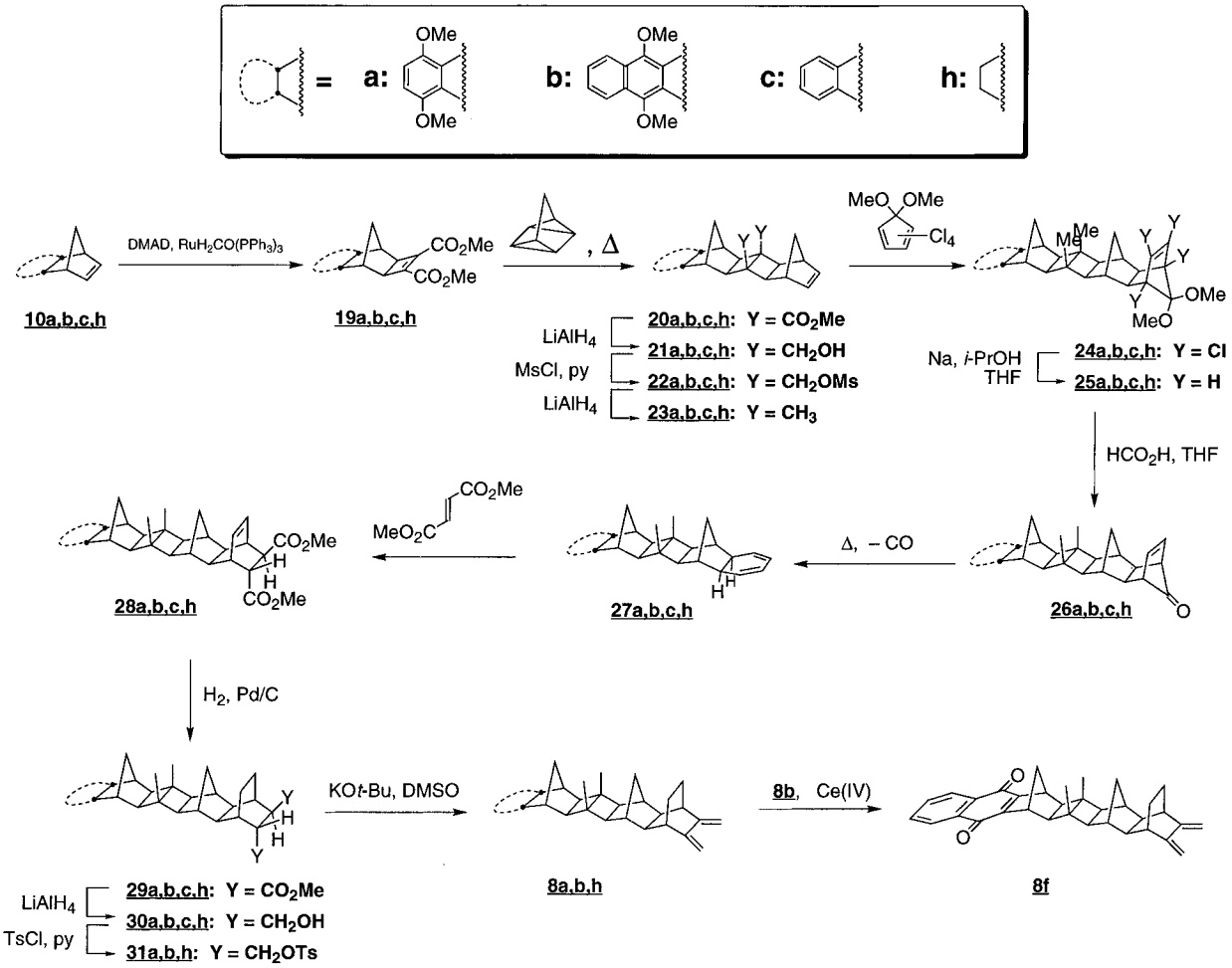
Access to the dipyridophenazine−dienes **7g** and **8g** was achieved using reactions which are outlined in Scheme 6. Nitration ($Cu(NO_3)_2$, Ac_2O) of bis(acetoxymethyl)-acetanilides **36** and **37** gave the respective *o*-nitroacetanilide derivatives **49** and **50**. Treatment of the acetanilides with hydrazine hydrate effected the smooth removal of the acetyl groups to give **51** and **52**. Reduction of **51** and **52** using hydrazine hydrate and Pd/C led to the formation of the respective *o*-phenylenediamines **53** and **54**. Condensation of **53** and **54** with 1,10-phenanthroline-5,6-dione (**55**) gave the dipyridophenazinediols **56** and **57**, and these materials were readily converted into the corresponding dienes **7g** and **8g** through sequential deployment of the bistosylation and bisdehydrotosylation reactions.

The symmetrical 10-bond tetraene **9** was synthesized from the known[19] 6-bond diene **60** (Scheme 7). Thus, compound **60** was reacted with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene to give the bisadduct **61**.

Scheme 3



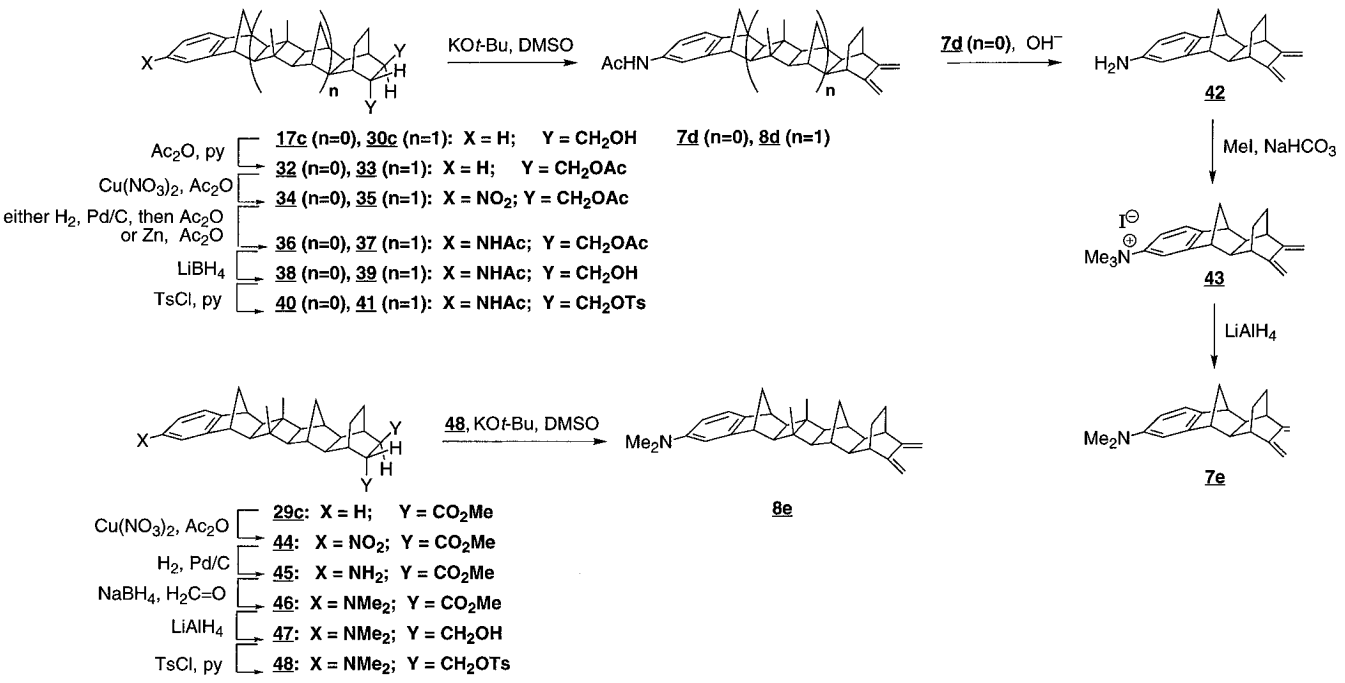
Scheme 4



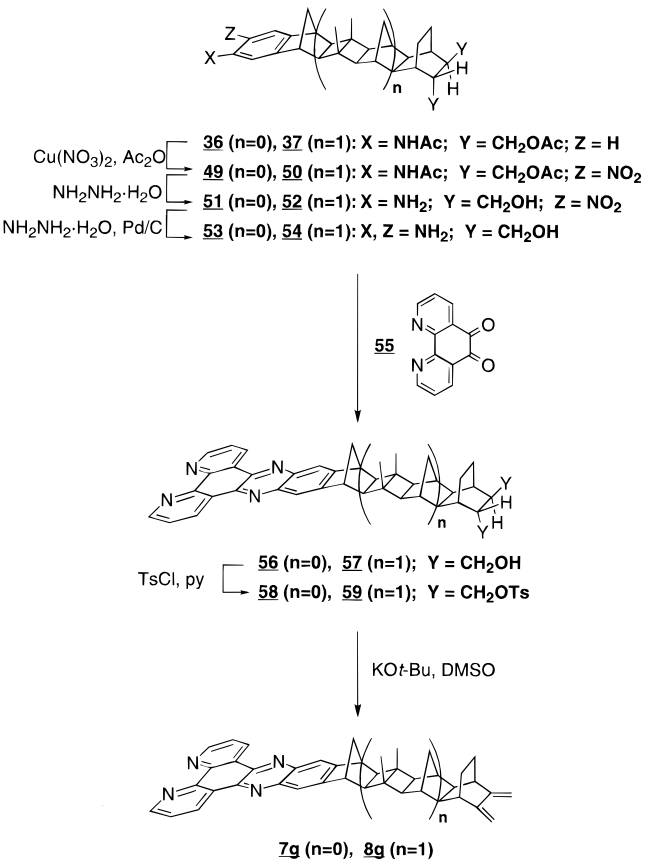
Reductive dechlorination of this compound (Na, *i*-PrOH)[21] led to the formation of **62**, which was deprotected (HCO_2H) to give the thermally labile bis-7-norbornenone compound **63**. Thermolysis of **63** in the presence of dimethyl fumarate in refluxing toluene led to the direct formation of the bisadduct **64** in excellent yield (94%). Conversion of **64** into the required tetraene **9** was effected in a straightforward manner.

Diels–Alder Cycloadditions with C_{60}. The first "ball-and-chain" system to be synthesized in our laboratory was compound **3a** which bears a 1,4-dimethoxybenzene donor group (Chart 1).[3b] Compound **3a**, as well as

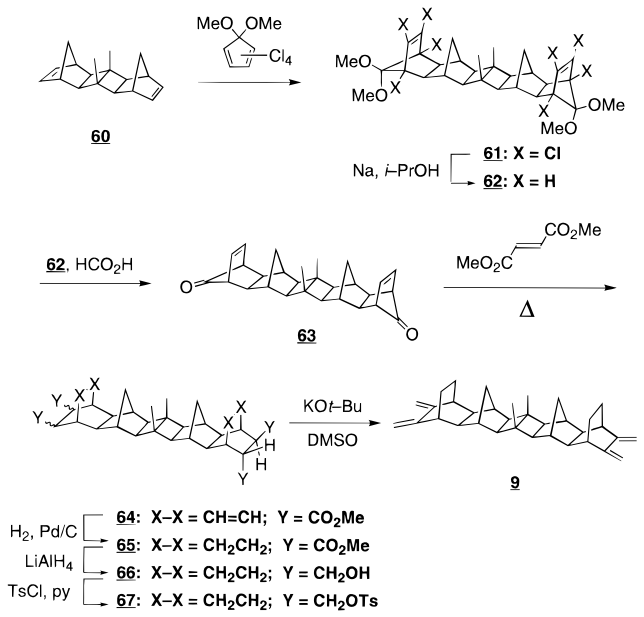
Scheme 5



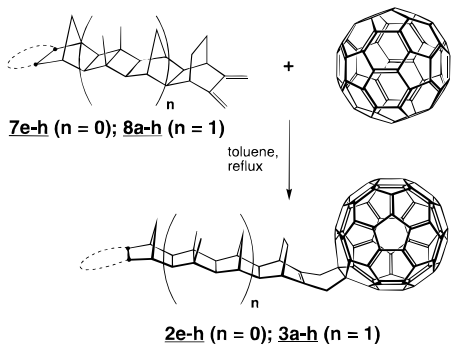
Scheme 6



Scheme 7



all Diels–Alder adducts except **4**, was prepared by addition of 1–1.5 equiv of diene *via* syringe pump (2–6 h) to a toluene solution of C_{60} maintained under reflux to minimize the formation of bis and higher adducts. Purification by flash chromatography over silica gel was performed very conveniently by following the elution of the brown-colored band(s). Most products obtained were remarkably stable in the solid state and could be handled without special precautions. However, we recently became aware of the remarkable reactivity of C_{60}-fused cyclohexene derivatives toward self-sensitized formation of singlet oxygen, which leads to ene reaction products.[2,22] This problem is particularly critical in solution, as found for compounds **2g** and **3g** (see below).



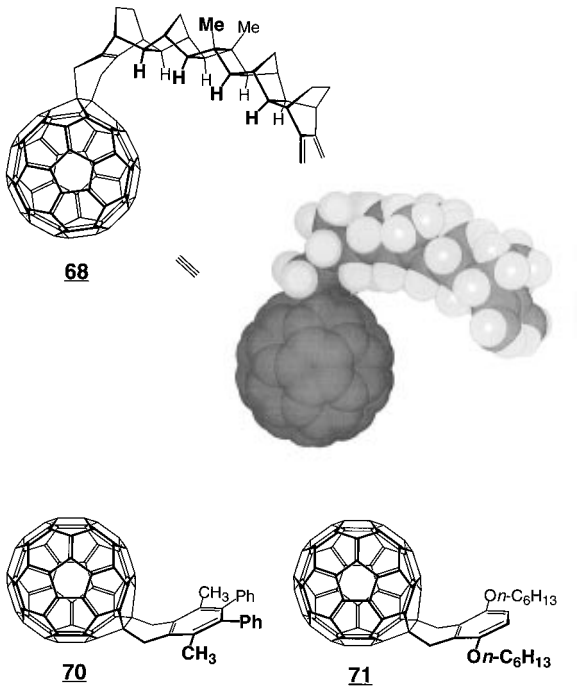
The entire series of "ball-and-chain" systems obtained by cycloaddition of the corresponding bridge dienes to C_{60}

is displayed in Chart 1. The model bridge compound **3h** lacks a donor group and was prepared for comparison purposes. Besides the dimethoxybenzene ball-and-chain system **3a**, we prepared the analogous 1,4-dimethoxynaphthalene systems **3b** and **2f**, the latter having a shorter bridge to C_{60}. The dimethylanilino systems **2e** and **3e** should lend themselves better than **3a**, **3b**, and **2f** to photoinduced electron transfer studies, because of the lower oxidation potential of this type of donor.[7c,10a,11] The naphthoquinone system **3f** was prepared to study both the electron correlation properties of its dianion diradical and also the dynamics of the intramolecular charge−shift process in the monoanion radical.[23] The most exciting compounds in this series are, perhaps, the two dipyridophenazines **2g** and **3g**. Their complexation with bis(bipyridine)ruthenium(II) moieties should give systems prone to undergo photoinduced electron transfer from ruthenium(II) to the C_{60} moiety.[24] The large distance between the donor and acceptor moieties should prevent fast electron back-transfer, which is one of the main problems encountered in systems designed to effect the photochemical decomposition of water.[11,25,26]

However, both dipyridophenazines **2g** and **3g** are relatively unstable in solution, unlike the other systems in this series. We believe that this effect is related to the $^1O_2$-generating properties of fullerenes as mentioned earlier, resulting in the oxidation of the dipyridophenazines system either by endoperoxide or *N*-oxide formation.[22] We are currently working on the preparation of simpler 1,10-phenanthroline-substituted bridges, which when complexed to a transition metal should be much more robust systems.[24]

It seemed interesting to prepare a bis-C_{60} adduct such as **4**, as there are only a few examples of derivatives with multiple C_{60} moieties connected by a rigid spacer.[27] In addition, there was a challenge in preparing this type of system because the low solubility of compounds bearing more than one fullerene moiety poses serious technical problems.[2] This fact was observed in recent work by Paquette *et al.* who describe the preparation of an insoluble dumbbell system tied by a flexible bridge comprising linearly fused 1,4-cyclohexadiene moieties.[27c] When tetraene **9** became available, we immediately set out to prepare compound **4** using the general conditions described above (toluene solvent). However, only products arising from the coupling of Diels−Alder intermediates were obtained in the form of a black insoluble polymer (**69**). This material was insoluble in solvents such as 1,2-dichlorobenzene, CS_2, or 1-methylnaphthalene, which are excellent solvents for fullerenes. Fortunately, we found that this reaction proceeded surprisingly well in 1,2-dichlorobenzene at 135 °C, leading to a remarkably high yield of compound **4** (81% based on recovered C_{60}) which is *soluble* in 1,2-dichlorobenzene and CS_2, albeit sparingly in the latter. Attempts to grow crystals of **4** suitable for X-ray diffraction have so far led to plates too thin to be usable. We are actively pursuing this aspect of our work since we expect the packing of this dumbbell molecule to be as interesting as that of compound **3a** (see below).

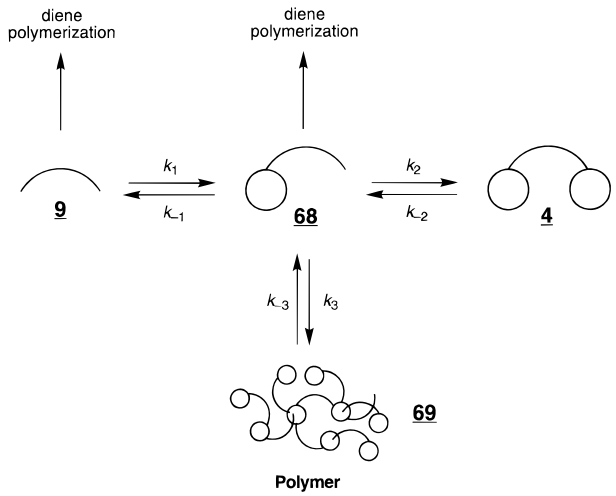
Chart 3



It is perhaps surprising that the different conditions used for the preparation of **4** should give such dramatically different experimental results. In particular, the aspect of polymer formation is important because it could lead to misinterpretation of limited available experimental data (e.g., CPMAS ^{13}C NMR or IR) due to insolubility. Calculations (see next section) on the two possible conformations available for the mono-addition product **68** show that the folded conformation is marginally preferred (1.02−2.80 kcal/mol, Chart 3). Given the small energy difference between the two conformations, it seems likely that either conformation may play some role in lowering the reactivity of the fullerene core of **68** (monoadduct) toward further attack by another diene moiety, as compared to unsubstituted C_{60}, by sterically shielding a number of the reactive sites on the fullerene surface (see space-filling model for the folded conformation of **68**, Chart 3). This would favor further intermolecular reaction between **68** and C_{60} producing **4**, and not between **68** and another molecule of **68** to ultimately form polymeric material **69** (i.e., $k_1 \gg k_2 > k_3$). In addition, the reactivity of the fullerene double bonds (at the 6,6-ring junctions) is in general lowered by a significant amount after the first addition of a group on C_{60}, which permits, for example, the obtention of high yields of monoadducts (up to ∼100% yield of **3a**, based on recovered C_{60}). However, this fact does not explain the different course of the reaction taken in the two experimental conditions. It seems most likely that the key factor in the successful experiment using 1,2-dichlorobenzene is higher temperature and perhaps better solubility. If the polymerization reaction leading to polymer **69** is reversible at >130 °C ($k_{-3} \neq 0$ and $k_{-2} <$

(21) Lap, B. V.; Paddon-Row, M. N. *J. Org. Chem.* **1979**, *44*, 4979−4981.
(22) An, Y.-Z.; Viado, A. L.; Arce, M.-J.; Rubin, Y. *J. Org. Chem.* **1995**, *60*, 8330−8331.
(23) For ESR studies on intramolecular charge shift processes in anion radicals, see, for example: Gerson, F.; Wellauer, T.; Oliver, A. M.; Paddon-Row, M. N. *Helv. Chim. Acta* **1990**, *73*, 1586−1601.
(24) Maggini, M.; Dono, A.; Scorrano, G.; Prato, M. *J. Chem. Soc., Chem. Commun.* **1995**, 845−846.
(25) Igarashi, M.; Fukuda, M.; Taki, M.; Tago, T.; Minowa, T.; Okada, Y.; Nishimura, J. *Fullerene Sci. Technol.* **1995**, *3*, 37−43.
(26) Yonemoto, E. H.; Riley, R. L.; Kim, Y. I.; Atherton, S. J.; Schmehl, R. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 8081−8087 and references cited therein.
(27) (a) Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 78−80. (b) Isaacs, L.; Seiler, P.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1466−1469. (c) Paquette, L. A.; Graham, R. J. *J. Org. Chem.* **1995**, *60*, 2958−2959.

k_{-3}),[28] the reaction equilibrium will lead to the formation of **4** *via* **68**. The reaction essentially stops when the concentrations of both **9** or **68** become negligible. It is also possible that the formation of **69** is simply avoided in 1,2-dichlorobenzene by the faster trapping of **68** with excess C_{60} due to the higher temperature used. Finally, solubility may affect the outcome of the reaction by keeping **68** and especially **4** in solution as they are produced. Coprecipitation of **4** and **68** would induce solid state polymerization leading to **69**. Meanwhile, there are competing radical or ionic polymerization processes owing to the reactive nature of the diene units in either **9** or **68**, which explains the large discrepancy between isolated and C_{60}-based yields of **4** (27 *vs* 81%).



Characterization of the C_{60}−bridge−donor systems was generally performed with relative ease. The ^{1}H and ^{13}C NMR spectra of compounds **2e**−**h**, **3a**, **3b**, **3d**−**h**, and **4** immediately confirmed their structure. In particular, all the allylic CH_2 groups in direct proximity to the C_{60} cage appeared as characteristic AB quartets in the ^{1}H NMR spectra. Owing to the C_s symmetry of these compounds, a total of 32 lines in the ^{13}C NMR spectra are expected for the fullerene framework. These were not always observed in totality since electronic differentiation from the first bicyclo[2.2.2]octene moiety in the norbornylogous bridges is not very large and some spectra appear to be a compromise between C_s and pseudo-C_{2v} symmetries. Mass spectral characterization was the most challenging part of this work. A general tendency for all C_{60} derivatives, especially those studied here, is to give fragmentation where C_{60} is the only recognizable ion. FAB MS was successful in many cases, and matrix-assisted laser desorption ionization (MALDI) mass spectroscopy also led to positive results for some compounds. So far, however, dumbbell compound **4** has resisted all mass spectrometric attempts, even using Wilson's mild electrospray technique.[29] As it stands, this problem is likely to be a major stumbling block on the road to large fullerene-based structures, at least until a general solution for mass spectroscopy can be found. It is fortunate that **4** is soluble and could be characterized by ^{1}H and ^{13}C NMR spectroscopy, as well as FT-IR.

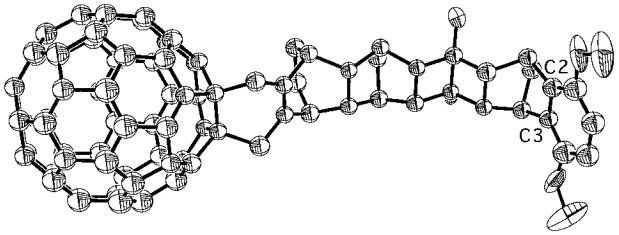


Figure 1. ORTEP representation of the X-ray structure of adduct **3a**.

X-ray Crystallographic Characterization. Compound **3a** was characterized by X-ray crystallography (Figure 1).[3b,30] The addition of diene **8a** to C_{60} occurs at the reactive 6,6-ring junction of C_{60}, which is always the case for this type of reaction.[1] The bond between the sp^3-hybridized carbons of C_{60} is elongated to 1.62(2) Å as was also observed for the Diels−Alder adduct **70**.[3a] The distance between the center of the 1,4-dimethoxybenzene unit to the median of the C_{60} sp^3−sp^3 bond is 12.34 Å and the shortest distances (R) between the two C_{60} sp^3 carbons and C2 or C3 of the donor unit are 11.79 and 11.85 Å, respectively, in good agreement with the calculated values (11.814 and 11.822 Å, Figure 4). The rigid norbornylogous bridge has a regular curvature, which is an important feature in the ability of **3a** to form dimeric pairs in the crystal (Figure 2).

One of the most unusual and beautiful crystal-packing arrangements we have observed is displayed in Figure 2. There is perfect but coincidental self-complementarity of compound **3a** in the crystal. This effect is reflected by the arrangement of **3a** in the lattice into head-to-tail pairs, which may originate from the combination of crystal-packing forces and electrostatic or π-stacking interactions between the donor units and the C_{60} moiety. Inspection of the space-filling model generated from the coordinates for pairs of **3a** (Biosym, Insight II) reveals close contacts that are essentially within van der Waals distances (Figure 3). The average of the C−H contact distances between the norbornylogous axial hydrogens pointing inward and the corresponding carbons on C_{60} is 3.09 Å. The shortest H−H distance between axial hydrogens of paired units is 2.59 Å. The coincidental self-complementarity of compound **3a** is also reflected in its unusual ability to form well-developed platelets, a property which we were unable so far to reproduce for the other compounds prepared in this study.

Conformational Analysis. The ball-and-chain molecules are not totally rigid since the cyclohexene ring that connects the bridge to the fullerene cage is able to adopt two nondegenerate boat conformations, namely, an ex-

(28) (a) Rotello, V. M.; Howard, J. B.; Yadav, T.; Conn, M. M.; Viani, E.; Giovane, L. M.; Lafleur, A. L. *Tetrahedron Lett.* **1993**, *34*, 1561−1562. (b) Giovane, L. M.; Barco, J. W.; Yadav, T.; Lafleur, A. L.; Marr, J. A.; Howard, J. B.; Rotello, V. M. *J. Phys. Chem.* **1993**, *97*, 8560−8561. (c) Guhr, K. I.; Greaves, M. D.; Rotello, V. M. *J. Am. Chem. Soc.* **1994**, *116*, 5997−5998. (d) Nie, B.; Hasan, K.; Greaves, M. D.; Rotello, V. M. *Tetrahedron Lett.* **1995**, *36*, 3617−3618. (e) Schlueter, J. A.; Seaman, J. M.; Taha, S.; Cohen, H.; Lykke, K. R.; Wang, H. H.; Williams, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 972−974. (f) Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1296−1298. (g) Komatsu, K.; Murata, Y.; Sugita, N.; Takeuchi, K.; Wan, T. S. M. *Tetrahedron Lett.* **1993**, *34*, 8473−8476. (h) Gonzalez, R.; Knight, B. W.; Wudl, F.; Semones, M. A.; Padwa, A. *J. Org. Chem.* **1994**, *59*, 7949−7951.

(29) (a) Wilson, S. R.; Lu, Q. Y. *Tetrahedron Lett.* **1993**, *34*, 8043−8046. (b) Wilson, S. R.; Wu, Y. H. *J. Chem. Soc., Chem. Commun.* **1993**, 784−786.

(30) Compound **3a** ($C_{92}H_{38}O_2$·1.5C_6H_5Cl; M_r = 1344.17) crystallized in the monoclinic space group $P21/n$ with cell dimensions of a = 25.180(5) Å, b = 10.136(2) Å, c = 25.241(5) Å, β = 112.35(1)°, V = 5958(2) Å^3, and an occupation of Z = 4 in the unit cell. Data were collected at 20 °C on a Rigaku AFC5R diffractometer using graphite-monochromated Cu Kα radiation, to a maximum 2θ = 115°, giving 8615 unique reflections; the structure was solved by direct methods (SHELX86), yielding R = 0.116, R_w = 0.136 for 2604 independent reflections with $F > 6\sigma(F)$.

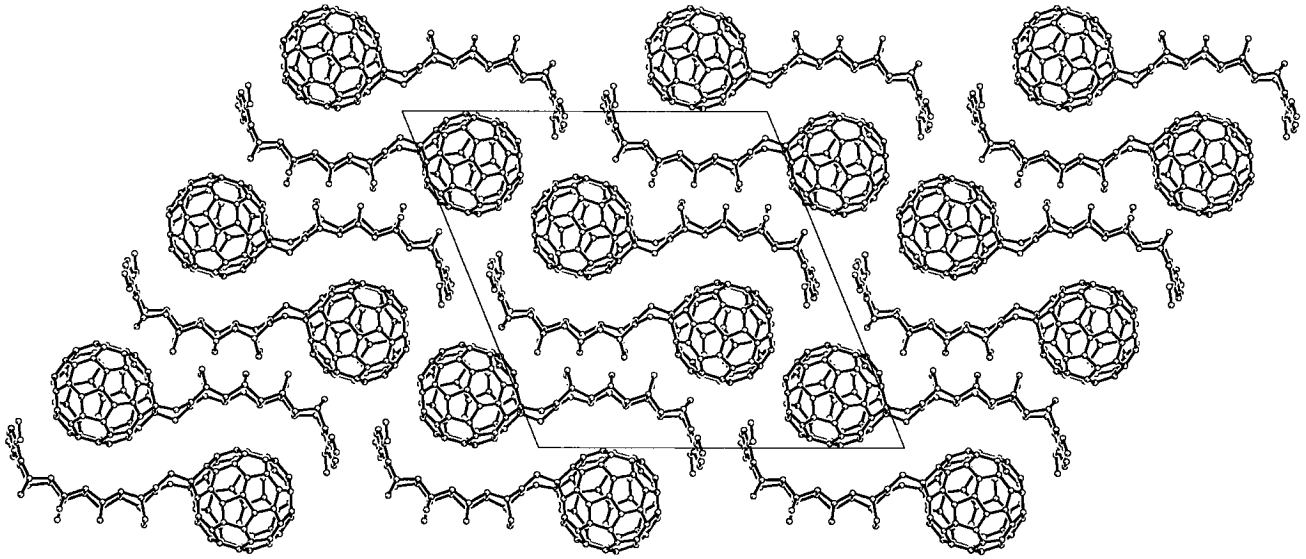


Figure 2. Crystal packing structure of the "ball-and-chain" system **3a**.

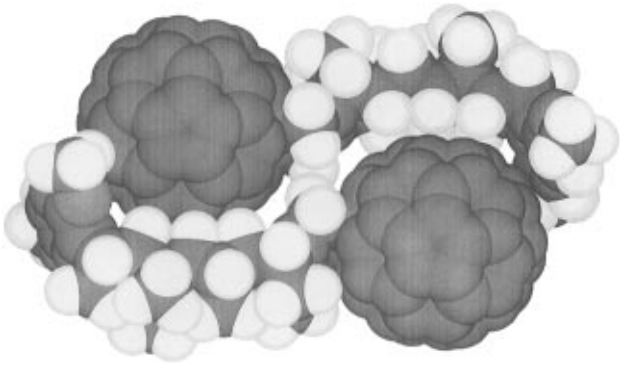


Figure 3. Space-filling model of the dimeric units in the crystal for system **3a**.

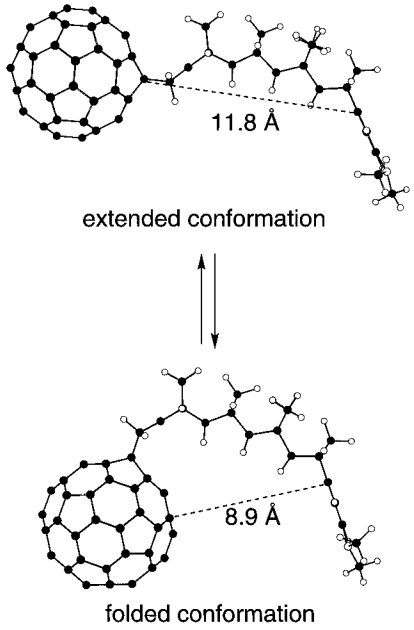


Figure 4. Calculated conformations for the dimethylaniline–C_{60} system **3e**. Distances *R* are AM1-optimized geometries.

tended conformer and a folded conformer. These conformations are shown in Figure 4 for the case of the 10-bond dimethylaniline system **3e**. As may be clearly seen from this figure, the direct, spatial inter-chromophore separation, *R*, the closest distance between the surface of the fullerene cage and the point of attachment of the non-C_{60} chromophore to the bridge, is quite different in the two conformations, amounting to a difference of about 2.9 Å for the 10-bond system **3e** and 2.75 Å for the 6-bond system **2e**.

Consequently, the dynamics of electron transfer and energy transfer between the chromophores could well be different for the two conformers. It is therefore necessary to determine both the relative energies of the two conformations and the energy barrier separating them and to ascertain how these quantities depend on bridge length and the nature of the non-C_{60} chromophore. The last point is important since one, for example, might envisage weak intramolecular attractive interactions existing between the strong dimethylaniline donor group and the C_{60} acceptor group in **3e**, which may slightly stabilize the folded conformer over the extended one.

There are limited experimental data that bear on this issue. The X-ray crystal structure of **3a** (Figure 1) reveals that, in the solid state, this compound adopts the extended conformation. However this preference is most likely due to the presence of favorable intermolecular interactions operating within the crystal structure. Line shape analysis (^{1}H NMR) of the CH_2–allylic absorptions of **3a** indicate that both isomers are present in solution and that one isomer is *ca*. 0.65 kcal/mol higher in energy than the other (at −110 °C).[3b] The barrier to interconversion of the conformers has been determined in the related benzannulated system **70**,[3a] in which the two conformations are energetically degenerate. The free energy barrier for this system was found to be *ca*. 14.6 kcal/mol.[3a] However, the benzannulation of the cyclohexene ring in **70** is expected to raise significantly the barrier to cyclohexene ring inversion.

We have carried out a preliminary theoretical study of the C_{60}–benzene system **70**, the dimethylaniline 6-bond system **2e**, the unsubstituted 10-bond system **3h**, and a series of 10-bond systems bearing a variety of chromophores (**3a**, **3b**, **3e**, and **3f**). The molecular geometries were fully optimized at the AM1 level of theory,[31,32] and single-point energies were obtained at the Hartree–Fock level with the 3-21G basis set (HF/3-21G//AM1).[33]

A fully optimized transition structure (TS) for the interconversion between the extended and folded conformers was located at the AM1 level for **3e**. As it was

Table 1. HF/3-21G//AM1 Energy Differences, ΔE_C (kcal/mol), between the Folded and Extended Conformers and the Activation Energies, $\Delta E^{\ddagger}$ (kcal/mol), of the Transition Structures Separating the Two Conformers for a Series of C_{60} Adducts

compd	ΔE_C[a]	$\Delta E^{\ddagger}$ [b]
3h	−3.50	7.79 (11.30)
3a	−0.42	9.89 (10.31)
3b	−0.03	9.20 (9.24)
3e	0.10	9.88 (9.78)
3f	−0.02	9.89 (9.91)
2e	−0.42	9.62 (10.04)
68	−1.02 (−2.80)[c]	2.65 (3.67)
70	*d*	17.61[d]

[a] A positive value indicates that the extended conformer is favored. [b] The activation energy with respect to the folded conformer is given in parentheses. [c] Biosym Insight II CVFF force field.[35c] [d] The folded conformer is degenerate with the extended conformer.

not feasible to locate the conformational transition structures for the other molecules, approximate transition structures were obtained by fixing the "flap angle" (the angle between the two mean planes of the cyclohexene ring) equal to that of the TS of **3e** and optimizing all other degrees of freedom. In the case of **70**, where the folded and extended conformers are identical, the TS was located by fixing the flap angle at 180°.

It was found that the conformational energy difference, ΔE_C, between the extended and folded conformations is small in these molecules, with a slight preference for the folded conformation (Table 1). For the dimethoxybenzene molecule **3a**, the folded conformation is slightly favored by 0.51 kcal/mol which is in reasonable agreement with the experimental value for this system (0.65 kcal/mol), although it is uncertain which of the folded or extended conformations is preferred in the NMR. In the case of the 6-bond dimethylaniline system **2e**, the folded conformation is slightly favored by *ca*. 0.42 kcal/mol, whereas the extended conformation is favored for the 10-bond analog **3e**, but by only *ca*. 0.1 kcal/mol. Both conformations are isoenergetic for the dimethoxynaphthalene and naphthoquinone molecules **3b** and **3f**, respectively. Interestingly, the unsubstituted system **3h** exhibits the largest conformational preference, with a ΔE_C value of 3.50 kcal/mol, favoring the folded conformer. Clearly, the remote electron-donating chromophores in these systems are attenuating the natural preference of the unsubstituted hydrocarbon bridge, as in **3h**, to adopt the folded conformation. We have no ready explanation why this should be so. However, we point out that a proper treatment of long-range electronic and electrostatic interactions that might exist between the chromophores in **3a**, **3b**, **3e**, and **3f** requires the use of large basis sets containing diffuse functions, together with inclusion of electron correlation effects (neither of which has been considered here, for purely technical reasons). Consequently, the observed trends in the HF/3-21G//AM1 ΔE_C values for these molecules should be treated with caution.

The calculated conformational activation barrier, $\Delta E^{\ddagger}$, for **70** is 17.61 kcal/mol (Table 1) which is in reasonable accord with the experimental value of 14.6 kcal/mol. Therefore, the HF/3-21G//AM1 theoretical model should give meaningful barrier heights for the ball-and-chain molecules. The calculated $\Delta E^{\ddagger}$ values for the other systems are *ca*. 50% lower than that for **70**, and this is probably due to increased steric congestion between the C_{60} moiety and the bridge attached to the cyclohexene ring in the ground state conformations of these systems, compared to **70**. However, the smaller inversion barriers calculated for the ball-and-chain molecules, compared to **70**, may also be related to the observation that the degree of ring planarity and the size of the inversion barriers along the series 1,4-cyclohexadiene, 1,4-dihydronaphthalene, and 9,10-dihydroanthracene show strong influence of benzannulation.[34] The $\Delta E^{\ddagger}$ values are not noticeably affected by the bridge length (*cf.* **2e** and **3e**) or by the nature of the non-C_{60} chromophore (*cf.* **3a**, **3b**, **3e**, and **3f**).

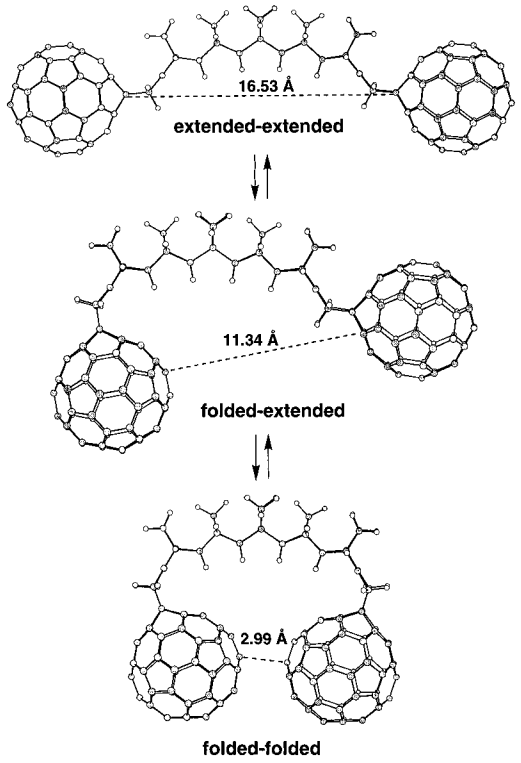


Figure 5. Three unique conformations for dumbbell system **4**. Distances are MM2-optimized geometries.

Finally, we examined the dumbbell system **4** because it is an interesting system for conformational and dynamic reasons. This molecule has two C_{60} moieties connected by a 14-bond norbornylogous saturated hydrocarbon bridge and can flex at the "hinges" formed by the cyclohexene rings in a process somewhat similar to a pair of *bolas* used by the *gauchos* (Figure 5). There are three possible nondegenerate conformations that the dumbbell can adopt: *extended-extended*, *extended-folded*, and *folded-folded*. As with the preceding systems, the molecular geometries were fully optimized at the AM1 level of theory with no symmetry constraints (Table 2). Molecular geometries were also optimized using three different force fields,[35] namely MM2,[35b] Sybyl,[35b] and CVFF.[35c]

(31) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.
(32) Spartan version 4.0, Wavefunction, Inc., 18401 Von Karman Ave. 370, Irvine, CA 92715.
(33) Gaussian 92, Revision A: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1992.
(34) Rabideau, P. W.; Lipkowitz, K. B.; Nachbar, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 3119−3123.
(35) (a) Burkert, U.; Allinger, N. L. in *Molecular Mechanics*, ACS Monograph 177; American Chemical Society: Washington, DC, 1982. (b) As implemented in Spartan, ref 32. (c) Biosym Insight II molecular modeling package.

Table 2. Energy Differences, ΔE_C (kcal/mol), and Closest C_{60}/C_{60} Separations for the Conformers of Dumbbell System 4

	distance (Å)			
conformer	ΔE_C(MM2)[a]	ΔE_C(Sybyl)[a]	ΔE_C(CVFF)[b]	ΔE_C(AM1)[c]
extended-extended	+9.32 *16.53*	+8.43 *16.07*	+18.85 *16.56*	+0.11 *15.78*
folded-extended	+7.30 *11.34*	+7.96 *10.66*	+14.66 *8.83*	+0.05 *11.22*
folded-folded	0 (rel.) *2.99*	0 (rel.) *2.83*	0 (rel.) *3.38*	0 (rel.) *4.74*

[a] From Spartan 4.0. [b] Biosym Insight II molecular modeling program. [c] Mopac 93.00, Stewart, J. J. P., Fujitsu Limited, Tokyo, 1993; the PRECISE keyword was used for all geometry optimizations.

At the AM1 level of theory, the energy differences between the three conformations are small (0.05−0.11 kcal/mol), although there is a slight preference for the folded-folded conformation. Since the AM1 method marginally favors the *extended* conformation over the *folded* conformation in ball-and-chain diene **68** possessing a single C_{60} moiety (by 0.01 kcal/mol), the predicted preferred folded-folded conformation for **4** is most likely due to the presence of weak, attractive $\pi-\pi$ or van der Waals interactions.[36] The AM1 method severely underestimates these types of interactions, and this is consistent with the fairly large calculated closest separation of 4.5 Å between the two C_{60} groups in the folded-folded conformation.

In contrast, all three force field models, which have been parametrized to take into account long-range interactions between unsaturated groups,[35a] predict a much stronger preference for the folded-folded conformation, by 7.3−14.7 kcal/mol, relative to the extended-folded conformation, and by 8.4−18.9 kcal/mol, relative to the extended-extended conformation. These methods also predict the folded conformation to be preferred over the extended conformation in **68**, but only by *ca.* 1 kcal/mol. The closest separation between the two C_{60} spheres in the folded-folded conformation of the force field optimized geometries is only *ca.* 2.8−3.4 Å, which clearly reflects the strength of the attractive interactions between the two C_{60} cages predicted by the force field methods. Such interactions are probably exaggerated by the force field calculations,[37] but it does seem likely that the folded-folded conformation is the genuine minimum energy conformation for **4**. One should note that shortest intermolecular contacts as small as 3.13 Å have been observed between C_{60} molecules in the X-ray structures of C_{60} itself and its derivatives.[38]

In summary, we conclude from the HF/3-21G//AM1 calculations that the bridge length and the nature of the non-C_{60} chromophore have little effect on the relative conformational energetics of these ball-and-chain molecules. However, this conclusion is subject to confirmation using a higher level of theory that includes electron correlation effects.

Table 3. Reduction Potentials (*vs* Ag/AgCl) of C_{60} and Adducts 2e, 3a, and 3e (25 °C, THF, Fc/Fc^+ internal reference, scan rate 100 mV s^{-1})

compd	E^1	E^2	E^3
C_{60}	−0.86	−1.38	−1.97
3a	−1.04	−1.62	−2.26
2e	−1.10	−1.69	−2.50
3e	−1.08	−1.72	−2.36

Electrochemistry. Diels−Alder adducts **2e**, **3a**, and **3e** were reduced at more negative potentials than C_{60} by about 0.1−0.3 V, which is reflective of the general trend seen in 1,2-dihydrofullerene derivatives (Table 3).[39,40] With one exception, the nature of the non-C_{60} chromophore has little effect on the reduction potentials. The exception involves the third reduction potential of the 6-bond and 10-bond dimethylaniline systems **2e** and **3e**; the former is 0.14 V more negative. This result suggests a proximity effect, namely, greater electron repulsion between the electron-rich system of the more proximate aniline ring in the 6-bond system **2e** and the C_{60} trianion, as has been observed for the 1,4-dialkoxybenzene system **71**.[40] The closest contacts between $sp^2_{(C_{60})}$ and $sp^2_{(donor)}$ carbons are 4.48 Å for **3e** and 3.10 Å for **71** (MM2).

Preliminary Photophysical Studies. Verhoeven and Williams have carried out a preliminary photophysical study of the 6-bond anthracene system **2h** and the 10-bond dimethylaniline molecule **3e** in order to ascertain whether intramolecular energy transfer and electron transfer (ET) processes take place in these types of molecules.[11] The results are very exciting. Singlet−singlet intramolecular energy transfer does, indeed, take place in the anthracene 6-bond system **2h** with a rate constant of *ca.* 5×10^7 s^{-1}.

Flash photolysis of the 10-bond aniline ball-and-chain molecule **3e** (benzonitrile solvent) results in rapid and efficient intramolecular ET from the dimethylaniline (DMA) donor to the C_{60} acceptor, to form the charge-separated state, C_{60}^-−bridge−DMA^+. The rate constant for this process is *ca.* 5.5×10^9 s^{-1}. The photoinduced ET rate for **3e** is comparable to that observed for the 10-bond dimethylnaphthalene−dicyanovinyl system **1(1,1)**.[13c] This is unexpected since the driving force for photoinduced ET in **1(1,1)** is greater than that for **3e**. Clearly, the electronic coupling between the C_{60} group and the hydrocarbon bridge must be very strong in order to compensate for the smaller driving force in **3e**. Intriguingly, the lifetime of the C_{60}^-−bridge−DMA^+ charge-separated state is 250 ns (benzonitrile solvent), which is quite long for bichromophoric charge-separated states.[41]

Conclusion. The ball-and-chain systems **2e**−**h**, **3a**, **3b**, and **3d**−**h** bearing the C_{60} and donor-substituted aryl chromophores linked *via* a rigid norbornylogous hydrocarbon bridge have been prepared and characterized. Various calculations on compounds **2e**, **3a**, **3b**, **3e**, **3f**, **3h**, **68**, and **70** using molecular mechanics, semiempirical, and *ab initio* methods show that there is little preference between the folded and extended conformations, while the activation barriers between the two conformers have relatively consistent values (7.79−9.89 kcal/mol).

Preliminary photophysical studies clearly demonstrate that rapid long-range intramolecular electron transfer

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processes can take place in the ball-and-chain systems and that the electronic coupling between the C_{60} chromophore and the hydrocarbon bridge is unusually strong. These molecules therefore offer considerable scope for probing systematically the effect of distance, driving force, and bridge configuration on the dynamics of intramolecular energy and electron transfer processes in C_{60}-based multichromophoric systems.[14]

Experimental Section

General. All reactions were performed under argon and, for $^1O_2$-sensitive compounds, in absence of light. The matrix used for FAB mass spectra was *m*-nitrobenzyl alcohol. Matrix-assisted laser desorption mass spectra (matrix: 9-nitroanthracene or 3,5-dihydroxybenzoic acid) were recorded in the negative ion mode with relatively low laser power on a PerSeptive Biosystems Voyager RP instrument (MALDI-TOF-MS) or in the negative or positive ion modes by the group of Charles L. Wilkins[42] at the University of California, Riverside, on a Waters-Extrel FTMS-2000 instrument (MALDI-FTMS). Elemental microanalyses for **3a** were carried out by Desert Analytics, Tucson, AZ; microanalyses for all other compounds were performed by Dr. H. P. Pham of the School of Chemistry, UNSW. Column chromatography was performed on silica gel 70−230 mesh or 230−400 mesh (flash) from E. Merck or Scientific Absorbents; thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F_{254} from E. Merck.

Materials. The C_{60}/C_{70} soluble extract was obtained from Texas Fullerene Corporation, Houston, TX, or from MER Corporation, Tucson, AZ. Pure C_{60} was isolated using the convenient procedure described by Tour *et al*.[43] Reagents and solvents were purchased reagent grade and used as received. Anhydrous $MgSO_4$ or Na_2SO_4 was used as the drying agent after workup in all the experiments. Solvent and other impurities in the C_{60} derivatives were removed as described earlier.[2]

Electrochemistry. Cyclic voltammetry measurements were performed on a BAS 100 electrochemical analyzer. Experiments were conducted at 25 °C in a one-compartment cell containing a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl quasi-reference electrode. As internal reference redox system the Fc/Fc^+ couple was used with a redox potential measured to 0.45 V (*vs* Ag/AgCl). Measurements were made on solutions of each sample in THF (distilled from potassium/benzophenone) containing $Bu_4N^+BF_4^-$ (0.1 M, Aldrich) as supporting electrolyte with a scan rate of 100 mV s^{-1}.

Synthesis. (1α,4α,4aα,9β,9aα,10β)-1,4,4a,9,9a,10-Hexahydro-1,4:9,10-dimethano-12,12-dimethoxyanthracene (12c). Sodium metal (127.0 g, 5.61 mol) was added piecewise to a stirred, refluxing solution of **11c**[44] (48.3 g, 0.120 mol) in 2-propanol (800 mL) and THF (400 mL) over 5 h. After the addition was completed, the resulting mixture was refluxed for a further 12 h and then cooled to 25 °C. The reaction was quenched by the addition of methanol (20 mL) and then water (50 mL). The solvent was evaporated under reduced pressure to give an off-white precipitate in an aqueous solution. Water (500 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (3 × 200 mL). The organic layers were combined, washed successively with water (500 mL), saturated $NaHCO_3$ (2 × 500 mL), and brine (500 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give clear oil which was crystallized from methanol to give **12c** as a white solid (29.1 g, 91%), whose spectral properties are identical to those previously reported:[44] ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.22 (d, J = 9.7 Hz, 1H), 2.29 (t, J = 1.8 Hz, 2H), 2.89 (dt, J = 1.8, 9.7 Hz, 1H), 2.97 (m, 2H), 3.08 (s, 3H), 3.10 (s, 3H), 3.11 (m, 2H), 6.15 (m, 2H), 7.02 (dd, J = 3.0, 5.5 Hz, 2H), 7.10 (dd, J = 3.0, 5.5 Hz, 2H).

(1α,4α,4aα,9β,9aα,10β)-1,4,4a,9,9a,10-Hexahydro-1,4:9,10-dimethanoanthracen-12-one (13c). 12c (22.5 g, 83.1 mmol) was dissolved in THF (200 mL) and formic acid (100 mL) and stirred for 18 h at 25 °C. The resulting solution was poured onto water (100 mL) and extracted with CH_2Cl_2 (2 × 100 mL). The organic layers were combined, washed with water (2 × 200 mL), saturated $NaHCO_3$ (2 × 200 mL), brine (200 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give an off-white oil which was crystallized from methanol to give **13c** as a white solid (16.2 g, 87%), whose spectral properties are identical to those previously reported:[44] ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.27 (dt, J = 1.2, 9.8 Hz, 1H), 2.28 (m, 2H), 2.71 (dt, J = 1.8, 9.8 Hz, 1H), 3.18 (m, 2H), 3.37 (t, J = 1.6 Hz, 2H), 6.48 (t, J = 2.5 Hz, 2H), 7.08 (dd, J = 3.0, 5.5 Hz, 2H), 7.12 (dd, J = 3.0, 5.5 Hz, 2H).

Dimethyl (1α,4α,4aβ,9α,9aβ,10α)-1,2,3,4,4a,9,9a,10-Octahydro-1,4-etheno-9,10-methanoanthracene-2,3-*trans*-dicarboxylate (15c). A mixture of **13c** (20.6 g, 92.4 mmol) and dimethyl fumarate (13.6 g, 94.7 mmol) in toluene (10 mL) was heated at reflux for 14 h. The solvent was evaporated under reduced pressure to give a brown oil which was crystallized from methanol (100 mL) to give **15c** as a white powder (30.0 g, 96%): mp 124 °C; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.21 (d, J = 9.5 Hz, 1H), 1.68 (dd, J = 2.5, 8.3 Hz, 1H), 1.88 (dd, J = 2.7, 8.3 Hz, 1H), 2.73 (dt, J = 1.7, 9.5 Hz, 1H), 2.83 (dd, J = 2.8, 5.8 Hz, 1H), 3.07 (dd, J = 2.2, 5.8 Hz, 1H), 3.08 (br s, 1H), 3.10 (br s, 1H), 3.26 (m, 2H), 3.65 (s, 3H), 3.66 (s, 3H), 6.19 (t, J = 7.2 Hz, 1H), 6.39 (dd, J = 7.2 Hz, 1H), 7.00 (m, 2H), 7.08 (m, 2H); IR ν_{max} (Nujol) 3030, 3005, 1725, 1455, 1215, 1200, 1185, 1270, 1030, 740 cm^{-1}. Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55. Found: C, 74.31; H, 6.78.

Dimethyl (1α,4α,4aβ,9α,9aβ,10α)-1,2,3,4,4a,9,9a,10-Octahydro-1,4-ethano-9,10-methanoanthracene-2,3-*trans*-dicarboxylate (16c). Compound **15c** (29.5 g, 86.7 mmol) in ethyl acetate (600 mL) was hydrogenated at 1 atm and 25 °C using 10% Pd/C (0.30 g) until uptake of H_2 had ceased. The catalyst was removed by suction filtration, and the solvent was evaporated under reduced pressure to give a clear oil. The product was crystallized with methanol to give **16c** as a white solid (28.4 g, 96%): mp 110 °C; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.31−1.52 (m, 3H), 1.54−1.66 (m, 3H), 1.75−1.86 (m, 1H), 2.18 (br d, J = 10.0 Hz, 1H), 2.35 (br s, 1H), 2.40 (br s, 1H), 3.02 (br d, J = 6.4 Hz, 1H), 3.15−3.20 (m, 3H), 3.62 (s, 3H), 3.71 (s, 3H), 7.02 (m, 2H), 7.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 17.53, 22.23, 31.59, 32.01, 38.59, 43.72, 44.78, 46.44, 46.58, 46.78, 47.10, 52.10, 120.19, 120.38, 125.25, 150.22, 174.56, 174.90; IR ν_{max} (Nujol) 3030, 1725, 1490, 1210, 1195, 1180, 1030, 740 cm^{-1}. Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.06; H, 7.08.

(1α,4α,4aβ,9α,9aβ,10α)-1,2,3,4,4a,9,9a,10-Octahydro-1,4-ethano-2,3-*trans*-bis(hydroxymethyl)-9,10-methanoanthracene (17c). $LiAlH_4$ (3.0 g, 79 mmol) was added portionwise to an ice cold, stirred solution of **16c** (10.0 g, 29.4 mmol) in dry THF (200 mL). After the addition was complete, the reaction mixture was heated at reflux for 2 h. The reaction mixture was cooled to 0 °C, and the excess reagent was quenched by the sequential addition of water (12 mL), 15% NaOH (12 mL), and then water (36 mL). The mixture was filtered and the solvent evaporated under reduced pressure to give a white solid which was recrystallized from CH_2Cl_2 to give **17c** as a white powder (8.02 g, 96%): mp 163−164 °C; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.30−1.70 (m, 8H), 1.77−1.86 (m, 3H), 2.27 (d, J = 10.1 Hz, 1H), 2.31 (br s, 2H) 3.13 (s, 1H), 3.18 (s, 1H), 3.40 (t, J = 9.4 Hz, 1H), 3.55 (dd, J = 5.3, 9.4 Hz, 1H), 3.62 (d, J = 4.1 Hz, 1H), 3.65 (d, J = 1.5 Hz, 1H), 7.03 (dd, J = 3.1, 5.4 Hz, 2H), 7.14 (dd, 3.1, J = 5.4 Hz, 2H); IR ν_{max} (Nujol) 3250 cm^{-1}. Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.18; H, 8.46.

(1α,4α,4aβ,5α,5aβ,11bβ,12α,12aβ)-1,2,3,4,4a,5,5a,11b,12,-12a-Decahydro-1,4-ethano-5,12-methano-6,11-dimethoxy-2,3-bis(methylene)dibenzo[*b*,*h*]biphenylene (7f). A solution of **10f** (14.0 g, 51 mmol)[18e] and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (14.5 g, 55 mmol) in xylene (bp

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138−141 °C) (50 mL) was refluxed for 18 h. Azeotropic removal of the xylene, through addition of ethanol (75 mL), gave a solid residue which was assumed to be **11f** (25.0 g, 89%) since its 300 MHz ^{1}H NMR spectrum revealed the complete absence of the peak at 6.25 ppm due to the double-bond protons of **10f**.

Sodium metal (17.0 g, 0.74 mol) was added piecewise to a refluxing solution of **11f** (10.0 g, 18 mmol) in THF (200 mL) and 2-propanol (400 mL), and the resulting mixture was refluxed for a further 17 h. Methanol (50 mL) was added to the cooled reaction mixture followed by crushed ice (200 g). Extraction with CH_2Cl_2 (3 × 150 mL) and evaporation of the organic extracts (after washing with water and drying) gave a solid whose ^{1}H NMR spectrum revealed the presence of **12f**, together with compounds resulting from partial reduction of the naphthalene ring. Rearomatization was achieved by treating this material with DDQ (8.3 g, 34 mmol) in benzene (100 mL) at 25 °C for 18 h. The reaction mixture was filtered, and the filtrate was washed with 1 M NaOH (100 mL). Evaporation of the dried filtrate gave a brownish solid which was subjected to column chromatography (silica, EtOAc: hexane 30:70). Although the eluted solid (5.6 g, 76%) was not further purified, its identity as **12f** was proven by ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.86 (d, J = 11.2 Hz, 1H), 2.14 (d, J = 11.4 Hz, 1H), 2.22 (s, 2H), 2.28 (s, 2H), 2.98 (m, 2H), 3.12 (s, 3H), 3.24 (s, 3H), 3.44 (s, 2H), 4.07 (s, 6H), 6.06 (t, J = 2.3 Hz, 2H), 7.37 (m, 2H), 8.07 (m, 2H).

A solution of the ketal **12f** (5.6 g, 14 mmol) in formic acid (100 mL) and THF (75 mL) was stirred for 18 h at 25 °C. The formic acid was removed by extraction with water and saturated $NaHCO_3$. Evaporation of the organic extracts gave the ketone **13f** as a fine white powder (4.5 g, 89%). This material was unstable at elevated temperatures and could not be fully characterized. **12f**: IR ν_{max} (Nujol) 1770 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.97 (d, J = 11.5 Hz, 1H), 1.98 (dt, J = 1.7, 11.7 Hz, 1H), 2.27 (m, 2H), 2.51 (s, 2H), 3.18 (m, 2H), 3.46 (d, J = 1.1 Hz, 2H), 4.07 (s, 6H), 6.42 (t, J = 2.5 Hz, 2H), 7.38 (m, 2H), 8.09 (m, 2H).

The synthesis of **15f** from **13f** was effected without isolation of the intermediate diene **14f**. Thus, a solution of the ketone **13f** (4.25 g, 12 mmol) and dimethyl fumarate (1.8 g, 12.5 mmol) in toluene (50 mL) was refluxed for 18 h. The solvent was then removed under reduced pressure to give the diester **15f** (4.8 g, 85%) which was not purified further: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.88 (d, J = 11.2 Hz, 1H), 1.68 (d, J = 10.9 Hz, 1H), 1.87 (d, J = 10.9 Hz, 1H), 2.06 (d, J = 11.2 Hz, 1H), 2.24 (m, 2H), 2.84−3.43 (m, 6H), 3.66 (s, 3H), 3.79 (s, 3H), 4.04 (s, 6H), 6.12 (t, J = 7.1 Hz, 1H), 6.30 (t, J = 7.1 Hz, 1H), 7.37 (m, 2H), 8.07 (m, 2H).

Compound **15f** (4.1 g, 8.7 mmol) in ethyl acetate (200 mL) was hydrogenated at 1 atm and 25 °C using 10% Pd/C (200 mg) until uptake of H_2 had ceased. Standard workup procedures gave the saturated diester **16f** as colorless needles (3.65 g, 91%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.25−1.78 (overlapping multiplets, 8H), 2.21−2.33 (m, 4H), 3.17 (m, 2H), 3.46 (m, 2H), 3.72 (s, 3H), 3.76 (s, 3H), 4.07(s, 6H), 7.37 (m, 2H), 8.08 (m, 2H).

To a suspension of $LiAlH_4$ (0.48 g, 12.6 mmol) in anhydrous THF (30 mL) was added a solution of **16f** (3.0 g, 6.3 mmol) in THF (100 mL), and the mixture was refluxed for 18 h. To the chilled reaction mixture were added water (0.5 mL), 15% NaOH (0.5 mL), and more water (1.5 mL) successively. The mixture was then filtered, and the filtrate was dried over Na_2SO_4 and evaporated under reduced pressure to give the diol **17f** (2.5 g, 95%) which was not further purified.

To a cooled (−5 °C) solution of the diol **17f** (2.1 g, 5.0 mmol) in dry pyridine (50 mL) was added *p*-toluenesulfonyl chloride (2.0 g, 10.5 mmol), and the resulting mixture was maintained at −5 °C for 36 h. The reaction was then quenched with crushed ice, and the solution was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed successively with 1 M HCl (3 × 100 mL) and saturated $NaHCO_3$ (100 mL), before being dried and concentrated under reduced pressure to give the ditosylate **18f** (3.1 g, 85%) which was not purified.

To a solution of the ditosylate **18f** (2.0 g, 2.7 mmol) in dry DMSO (50 mL) was added *t*-BuOK (1.0 g, 9.0 mmol). The mixture was then stirred at 25 °C for 18 h. Ice water was added, and the product was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extracts were washed with water (2 × 100 mL) and brine (3 × 50 mL) to remove all traces of DMSO and dried, and the solvent was removed under reduced pressure. The residue was then chromatographed (silica, EtOAc:hexane 30:70) to give the pure diene **7f** (0.75 g, 71%): mp 182−183 °C (from EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$ δ 1.48−1.52 (m, 2H), 1.72 (br s, 2H), 1.78−1.83 (overlapping multiplets, J = 2 Hz, 4H), 2.37 (br s, 2H), 2.46 (br s, 2H), 3.46 (s, 2H), 4.10 (s, 6H), 4.77 (s, 2H), 5.31 (d, J = 1.2 Hz, 2H), 7.39 (m, 2H), 8.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 22.15, 28.22, 40.72, 43.19, 45.02, 51.55, 57.62, 103.04, 121.85, 122.51, 124.62, 126.82, 142.27, 150.44. Anal. Calcd for $C_{27}H_{28}O_2$: C, 84.34; H, 7.34. Found: C, 84.08; H, 7.07.

(1α,4α,4aβ,5α,14α,14aβ)-1,4,4a,5,14,14a-Hexahydro-1,4-ethano-5,14-methano-2,3-bis(methylene)pentacene (7h). A solution of **10h** (1.0 g, 4.13 mmol)[18b] and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (1.18 g, 4.45 mmol) in toluene (20 mL) was refluxed for 18 h. The solvent was removed under reduced pressure to give a solid residue which was assumed to be **11h** (2.0 g, 94%), since its 300 MHz ^{1}H NMR spectrum revealed the complete absence of the peak at 6.71 ppm due to the double-bond protons of **10h**.

Sodium metal (3.5 g, 0.15 mol) was added piecewise to a refluxing solution of **11h** (1.9 g, 3.85 mmol) in THF (50 mL) and 2-propanol (200 mL). The resulting mixture was refluxed for 17 h. Methanol (20 mL) was added to the cooled reaction mixture followed by crushed ice (100 g). Extraction with CH_2Cl_2 (3 × 100 mL) and evaporation of the organic extracts (after washing with water and drying) gave a semisolid whose ^{1}H NMR spectrum revealed the presence of **12h** (1.15 g, 81%) together with compounds resulting from partial reduction of the naphthalene ring. Rearomatization was not performed on this step.

A solution of the ketal **12h** (1.15 g, 3.1 mmol) in formic acid (50 mL) and THF (25 mL) was stirred for 18 h at 25 °C. The formic acid was removed by extraction with water and saturated $NaHCO_3$. Evaporation of the organic extracts gave the ketone **13h** (0.85 g, 84%). This material was unstable at elevated temperatures and could not be fully characterized: IR ν_{max} (Nujol) 1770 cm^{-1}.

The synthesis of **15h** from **13h** was effected without isolation of the intermediate diene **14h**. Thus, a solution of the ketone **13h** (0.8 g, 2.5 mmol) and dimethyl fumarate (0.4 g, 2.8 mmol) in toluene (20 mL) was refluxed for 18 h. The solvent was then removed under reduced pressure to give the diester **15h** (0.9 g, 83%) which was not purified further.

Compound **15h** (0.9 g, 2.05 mmol) in ethyl acetate (50 mL) was hydrogenated at 1 atm and 25 °C using 10% Pd/C (50 mg) until uptake of H_2 had ceased. Standard workup procedures gave the saturated diester **16h** (0.8 g, 89%) whose ^{1}H NMR spectrum revealed the absence of two peaks (triplets) at 6.17 and 6.38 ppm due to the double-bond protons and complete reduction of the anthracene ring in the 9,10 positions. Rearomatization was achieved by treating this material with DDQ (0.08 g, 0.35 mmol) in dry benzene (20 mL) at 25 °C for 5 h. The reaction mixture was filtered, and the filtrate was washed with a 1 M solution of NaOH (50 mL). Evaporation of the dried filtrate gave a solid which was subjected to column chromatography (silica, EtOAc:hexane 30:70) to obtain a brown solid (0.50 g) which was not further purified. Its identity as **16h** was proven by ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.45 (d, J = 9.9 Hz, 1H), 1.47−1.61 (overlapping multiplets, 4H), 1.66 (d, J = 9.9 Hz, 1H), 1.70 (d, J = 10.3 Hz, 1H), 2.40 (d, J = 10.1 Hz, 1H), 2.44 (dt, J = 2.3, 9.6 Hz, 2H), 3.17 (d, J = 10.4 Hz, 1H), 3.34 (d, J = 9.7 Hz, 1H), 3.52 (d, J = 9.7 Hz, 2H), 3.61 (s, 3H), 3.73 (s, 3H), 7.42 (m, 2H,), 7.59 (d, J = 3.2 Hz, 2H), 7.94 (m, 2H), 8.28 (d, J = 2.9 Hz, 2H).

To a suspension of $LiAlH_4$ (0.10 g, 2.6 mmol) in anhydrous THF (20 mL) was added a solution of **16h** (0.5 g, 1.25 mmol) in THF (50 mL), and the mixture was refluxed for 18 h. To the chilled reaction mixture were added water (0.1 mL), 15% NaOH (0.1 mL), and more water (0.3 mL) successively. The mixture was then filtered, and the filtrate was dried over Na_2-

SO_4 and evaporated under reduced pressure to give the diol **17h** (0.35 g, 80%) which was not further purified.

To a cooled (−5 °C) solution of the diol **17h** (0.35 g, 0.9 mmol) in dry pyridine (20 mL) was added *p*-toluenesulfonyl chloride (0.3 g, 1.55 mmol), and the resulting mixture was maintained at −5 °C for 36 h. The reaction was then quenched with crushed ice, and the solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed successively with 1 M HCl (3 × 50 mL) and saturated $NaHCO_3$ (50 mL) before being dried and concentrated under reduced pressure to give the ditosylate **18h** (0.45 g, 71%) which was not purified.

To the solution of the ditosylate **18h** (0.4 g, 0.6 mmol) in dry DMSO (20 mL) was added *t*-BuOK (0.23 g, 2 mmol). The mixture was then stirred at 25 °C for 18 h. Ice water was added, and the product was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were washed with water (2 × 50 mL) and brine (3 × 50 mL) to remove all traces of DMSO and dried, and the solvent was removed under reduced pressure to give the diene **7h** (0.13 g, 61%): mp 245−246 °C (from EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.53 (s, 2H), 1.73 (d, J = 10.4 Hz, 1H), 1.85 (s, 2H), 1.95 (dq, J = 2.5, 10.2 Hz, 2H), 2.46 (d, J = 10.3 Hz, 1H), 2.62 (br s, 2H), 3.40 (s, 2H), 4.74 (s, 2H), 5.22 (d, J = 0.6 Hz, 2H), 7.40 (m, 2H), 7.63 (s, 2H), 7.94 (m, 2H), 8.27 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 22.10, 40.90, 42.66, 43.90, 46.49, 103.23, 117.16, 124.70, 125.61, 127.92, 131.25, 131.42, 148.78, 150.17. Anal. Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94. Found: C, 92.83; H, 7.06.

Dimethyl (1α,4α,4a*β*,4bα,4c*β*,5α,8α,8aα,8b*β*,8cα)-1,4,4a,-4b,4c,5,6,7,8,8a,8b,8c-Dodecahydro-1,4:5,8-dimethanobenzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2]benzene-4b,-8b-dicarboxylate (20h). A solution of **19h** (20.0 g, 84.7 mmol)[16] in quadricyclane (8.30g, 90 mmol) was refluxed for 18 h. Acetone (25 mL) was added to the cooled solution, and the resulting precipitate was collected and recrystallized from acetone to give **20h** (24.0 g, 86.6%): mp 137−138 °C (from EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.05 (m, J = 1.5 Hz, 1H), 1.07 (m, J = 1.07 Hz, 1H), 1.08 (d, J = 2.5 Hz, 1H), 1.10 (d, J = 2.5 Hz, 1H), 1.12 (m, J = 1.6 Hz, 1H), 1.15 (m, J = 1.5 Hz, 1H), 1.46 (m, J = 3.0 Hz, 1H), 1.48 (m, J = 3.0 Hz, 1H), 2.10 (m, J = 1.8 Hz, 1H), 2.12 (s, 2H), 2.14 (m, J = 1.8 Hz, 1H), 2.31 (s, 2H), 2.79 (m, J = 1.6 Hz, 2H), 3.79 (s, 6H), 6.04 (t, J = 1.8 Hz, 2H). Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 72.95; H, 7.30.

(1α,4α,4a*β*,4bα,4c*β*,5α,8α,8aα,8b*β*,8cα)-1,4,4a,4b,4c,5,6,7,8,-8a,8b,8c-Dodecahydro-1,4:5,8-dimethano-4b,8b-dimethylbenzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2]benzene (23h). To a solution of **20h** (20.0 g, 61.9 mmol) in dry THF (300 mL) was added $LiAlH_4$ (4.5 g, 0.120 mol) in small portions. The mixture was refluxed for 18 h. To the cooled reaction mixture were added successively water (4.5 mL), 15% NaOH (4.5 mL), and water (13.5 mL). The mixture was then filtered, and the filtrate was dried and evaporated under reduced pressure to give the diol **21h** (15.2 g, 91%) which was not purified further: IR ν_{max} (Nujol) 3250 cm^{-1}.

To a cooled solution (−5 °C) of the diol **21h** (15.0 g, 55.1 mmol) in dry pyridine (100 mL) was added slowly methanesulfonyl chloride (12.6 g, 0.110 mol). The resulting solution was maintained at −5 °C for 72 h, after which it was poured onto crushed ice and then extracted with CH_2Cl_2 (3 × 150 mL). The organic extract was washed successively with 1 M HCl (750 mL) and saturated $NaHCO_3$, then dried, and evaporated to give the dimesylate **22h** (16.5 g, 76%) which was not purified.

A magnetically stirred mixture of the dimesylate **22h** (16.5 g, 41.66 mmol) and $LiAlH_4$ (3.0 g, 80 mmol) in dry THF (300 mL) was refluxed for 48 h. Use of a workup procedure that was identical to that described above for the synthesis of the diol gave **23h** (9.1 g, 91%): mp 101−102 °C (from EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.76 (s, 6H), 1.07 (dm, J = 9.3 Hz, 2H), 1.13 (dt, J = 1.5, 8.6 Hz, 1H), 1.21 (dt, J = 1.8, 10.0 Hz, 1H), 1.31 (br d J = 8.7 Hz, 1H), 1.48 (dm, J = 9.3 Hz, 2H), 1.57 (dt, J = 1.9, 10.1 Hz, 1H), 1.73 (s, 2H), 1.89 (s, 2H), 2.12 (m, J = 2.3 Hz, 2H), 2.69 (m, J = 2.1 Hz, 2H), 5.99 (t, J = 1.9 Hz, 2H). Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 89.84; H, 10.03.

(1α,4α,4a*β*,4bα,4c*β*,5α,5a*β*,9a*β*,10α,10aα,10bα,10cα)-1,2,3,4,4a,4b,4c,5,5a,9a,10,10a,10b,10c-Tetradecahydro-1,4:5,8-dimethano-4b,8b-dimethylbenzo[3′,4′]cyclobuta-[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene (27h). A solution of **23h** (5.0 g, 20.8 mmol) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (5.8 g, 22.0 mmol) in toluene (20 mL) was refluxed for 18 h. The solvent was removed under reduced pressure to give a solid residue which was assumed to be **24h** (9.5 g, 91%) since its 300 MHz ^{1}H NMR spectrum revealed the complete absence of the peak at 5.99 ppm due to the double-bond protons of **23h**.

Sodium metal (15.0 g, 0.65 mol) was added piecewise to a refluxing solution of **24h** (9.5 g, 18.4 mmol) in THF (50 mL) and 2-propanol (150 mL). The resulting mixture was refluxed for 17 h. Methanol (20 mL) was added to the cooled reaction mixture followed by crushed ice (100 g). Extraction with CH_2Cl_2 (3 × 100 mL) and evaporation of the organic extracts (after washing with water and drying) gave a solid whose ^{1}H NMR spectrum revealed the presence of **25h** (6.0 g, 87%).

A solution of the ketal **25h** (6.0 g, 16.3 mmol) in formic acid (50 mL) and THF (25 mL) was stirred for 18 h at 25 °C. The formic acid was removed by extraction with water and saturated $NaHCO_3$. Evaporation of the organic extracts gave the ketone **26h** (4.5 g, 86%). This material was unstable at elevated temperatures and could not be fully characterized: IR ν_{max} (Nujol) 1770 cm^{-1}.

A solution of the ketone **26h** (4.5 g, 14.2 mmol) in toluene (50 mL) was refluxed for 1 h. The solvent was then removed under reduced pressure to give **27h** (3.5 g, 85%): mp 159−160 °C (from EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.74 (s, 6H), 1.06 (d, J = 2.4 Hz, 1H), 1.08 (d, J = 2.4 Hz, 1H), 1.18 (dt, J = 1.6, 10.2 Hz, 1H), 1.48 (overlapping multiplets, 2H), 1.57 (dt, J = 1.7, 10.1 Hz, 1H), 1.61 (dt, J = 1.5, 10.2 Hz, 1H), 1.64 (dt, J = 10.2 Hz, 1H), 1.81 (dt, J = 1.5, 10.2 Hz, 1H), 1.87 (m, J = 2.1 Hz, 2H), 1.97 (br s, 2H), 2.04 (m, J = 2.1 Hz, 2H), 2.16 (br s, 2H), 2.42 (m, J = 2.1 Hz, 2H), 5.35 (overlapping multiplets, 2H), 5.56 (overlapping multiplets, 2H). Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.01; H, 9.25.

(1α,4α,4a*β*,4bα,4c*β*,5α,5a*β*,6α,9α,9a*β*,10α,10aα,10bα,10cα)-1,2,3,4,4a,4b,4c,5,5a,6,9,9a,10,10a,10b,10c-Hexadecahydro-6,9-ethano-1,4:5,8-dimethano-4b,8b-dimethyl-7,8-bis-(methylene)benzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene (8h). A solution of **27h** (3.0 g, 10.3 mmol) and dimethyl fumarate (1.57 g, 11.0 mmol) in benzene (20 mL) was refluxed for 18 h. The solvent was then removed under reduced pressure to give the diester **28h** (3.6 g, 81%) which was not purified further.

Compound **28h** (3.6 g, 8.07 mmol) in ethyl acetate (50 mL) was hydrogenated at 1 atm and 25 °C using 10% Pd/C (50 mg) until uptake of H_2 had ceased. Standard workup procedures gave the saturated diester **29h** (3.5 g, 97%) whose ^{1}H NMR spectrum revealed the absence of two peaks (triplets) at 6.12 and 6.32 ppm due to the double-bond protons.

To a suspension of $LiAlH_4$ (0.57 g, 15 mmol) in anhydrous THF (20 mL) was added a solution of **29h** (3.5 g, 7.8 mmol) in THF (50 mL), and the mixture refluxed for 18 h. To the chilled reaction mixture were added water (0.5 mL), 15% NaOH (0.5 mL), and more water (1.5 mL) successively. The mixture was then filtered, and the filtrate was dried over Na_2SO_4 and evaporated under reduced pressure to give the diol **30h** (2.6 g, 84%) which was not further purified.

To a cooled (−5 °C) solution of the diol **30h** (2.6 g, 6.6 mmol) in dry pyridine (20 mL) was added *p*-toluenesulfonyl chloride (3.0 g, 15.5 mmol), and the resulting mixture was maintained at −5 °C for 36 h. The reaction was then quenched with crushed ice, and the solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed successively with 1 M HCl (3 × 50 mL) and saturated $NaHCO_3$ before being dried and concentrated under reduced pressure to give the ditosylate **31h** (4.5 g, 83%) which was not purified.

To a solution of the ditosylate **31h** (4.0g, 5.7 mmol) in dry DMSO (20 mL) was added *t*-BuOK (2.3 g, 2 mmol). The mixture was then stirred at 25 °C for 18 h. Ice water was added, and the product was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were washed with water (2 × 50 mL) and brine (3 × 50 mL) to remove all traces of

DMSO and dried, and the solvent was removed under reduced pressure to give the diene **8h** (1.55 g, 74%): mp 168−170 °C (from EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.75 (s, 6H), 1.09 (dq, J = 2.3, 5.4 Hz, 2H), 1.16 (dt, J = 1.3, 9.9 Hz, 1H), 1.46 (overlapping multiplets, 5H), 1.52 (s, 2H), 1.56 (partially hidden d, 1H), 1.82−1.90 (m, 3H), 1.94 (br s, 4H), 2.01 (s, 2H), 2.04 (m, 2H), 2.30 (br s, 2H), 4.69 (s, 2H), 5.23 (d, J = 1.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 9.73, 22.32, 28.62, 31.13, 35.07, 36.12, 39.18, 40.76, 45.17, 45.19, 52.70, 54.20, 102.45, 151.05. Anal. Calcd for $C_{26}H_{34}$: C, 90.11; H, 9.89. Found: C, 90.30; H, 9.64.

Dimethyl (2aα,3*β*,8*β*,8aα)-2a,3,8,8a-Tetrahydro-3,8-methano-4,7-dimethoxycyclobuta[*b*]naphthalene-1,2-dicarboxylate (19a). A magnetically stirred solution of **10a** (38.5 g, 0.19 mol),[45] DMAD (27.5 g, 0.193 mol), and $RuH_2CO(PPh_3)_3$ (0.6 g, 0.5 mmol)[16] in benzene (200 mL) was refluxed under an argon atmosphere for 18 h. Ethanol was added to the cooled reaction mixture, and the precipitated material was collected and recrystallized from ethanol to give the ester **19a** (56.1 g, 86%): mp 168−169 °C (from ethanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.73 (s, 2H), 2.76 (s, 2H), 3.50 (s, 2H), 3.79 (s, 6H), 3.83 (s, 6H), 6.62 (s, 2H). Anal. Calcd for $C_{19}H_{20}O_6$: C, 66.27; H, 5.85. Found: C, 66.15; H, 6.03.

Dimethyl (1α,4α,4a*β*,4bα,4c*β*,5α,10α,10a*β*,10bα,10c*β*)-1,4,4a,4b,4c,5,10,10a,10b,10c-Decahydro-1,4:5,10-dimethano-6,9-dimethoxybenzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene-4b,10b-dicarboxylate (20a). A solution of **19a** (56.0 g, 0.163 mol) in quadricyclane (20.0 g, 0.217 mol) was refluxed under an argon atmosphere for 18 h. Acetone (25 mL) was added to the cooled solution, and the resulting precipitate was collected and recrystallized from acetone to give **20a** (51.2 g, 71.7%): mp 176−179 °C (from acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.14 (d, J = 10.3 Hz, 1H), 1.51 (d, J = 10.2 Hz, 1H), 1.88 (d, J = 9.7 Hz, 1H), 2.07 (s, 2H), 2.30 (s, 2H), 2.32 (d, J = 9.5 Hz, 1H), 2.86 (s, 2H), 3.56 (s, 2H,), 3.77 (s, 6H), 3.79 (s, 6H), 6.04 (t, J = 1.6 Hz, 2H), 6.60 (s, 2H). Anal. Calcd for $C_{26}H_{28}O_6$: C, 71.54; H, 6.46. Found: C, 71.76; H, 6.72.

(1α,4α,4a*β*,4bα,4c*β*,5α,10α,10a*β*,10bα,10c*β*)-1,4,4a,4b,4c,5,10,10a,10b,10c-Decahydro-1,4:5,10-dimethano-6,9-dimethoxy-4b,10b-dimethylbenzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene (23a). To a solution of **20a** (51.2 g, 0.117 mol) in dry THF (300 mL) was added $LiAlH_4$ (9.2 g, 0.245 mol) in small portions. The mixture was refluxed for 18 h. To the cooled reaction mixture were added successively water (9.2 mL), 15% NaOH (9.2 mL), and water (27.6 mL). The mixture was then filtered, and the filtrate was dried and evaporated under reduced pressure to give the diol **21a** (42.3 g, 95%) which was not purified further: IR ν_{max} (Nujol) 3250 cm^{-1}.

To a cooled solution (−5 °C) of the diol **21a** (42.0 g, 110 mmol) in dry pyridine (200 mL) was added slowly methanesulfonyl chloride (27.0 g, 0.236 mol). The resulting solution was kept at −5 °C for 72 h, after which it was poured onto crushed ice and then extracted with CH_2Cl_2 (3 × 150 mL). The organic extract was washed successively with 1 M HCl (750 mL) and saturated $NaHCO_3$ (100 mL), then dried, and evaporated to give the dimesylate **22a** (53.0 g, 95%) which was not purified.

A magnetically stirred mixture of the dimesylate **22a** (53.0 g, 0.105 mol) and $LiAlH_4$ (8.0 g, 0.22 mol) in dry THF (350 mL) was refluxed for 48 h. Use of a workup procedure that was identical to that described above for the synthesis of the diol gave **23a** (32.5 g, 89%): mp 210−211 °C (from EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.90 (s, 6H), 1.17 (d, J = 8.7 Hz, 1H), 1.38 (d, J = 8.7 Hz, 1H), 1.57 (d, J = 9.6 Hz, 1H), 1.67 (s, 2H), 1.77 (d, J = 9.4 Hz, 1H), 1.91 (s, 2H), 2.74 (s, 2H), 3.52 (s, 2H), 3.79 (s, 6H), 5.98 (t, J = 1.8 Hz, 2H), 6.60 (s, 2H). Anal. Calcd for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.44; H, 8.29.

(1α,4α,4aα,5*β*,5aα,5b*β*,5cα,6*β*,11*β*,11aα,11b*β*,11cα,12*β*,12aα)-1,4,4a,5,5a,5b,5c,6,11,11a,11b,11c,12,12a-Tetradecahydro-1,4:5,12:6,11-trimethano-7,10,15,15-tetramethoxy-5b,11b-dimethylnaphtho[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene (25a). A solution of **23a** (5.0 g, 14.4 mmol) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (4.0 g, 15 mmol) in xylene (bp 138−141 °C) (30 mL) was refluxed for 18 h. Azeotropic removal of the xylene, through addition of ethanol (50 mL), gave a solid residue which was assumed to be **24a** (7.7 g, 87%) since its 300 MHz ^{1}H NMR spectrum revealed the complete absence of the peak at 5.98 ppm due to the double-bond protons of **23a**.

Sodium metal (14.0 g, 0.61 mol) was added piecewise to a refluxing solution of **24a** (7.7 g, 12.6 mmol) in THF (100 mL) and 2-propanol (400 mL). The resulting mixture was refluxed for 17 h. Methanol (20 mL) was added to the cooled reaction mixture followed by crushed ice (100 g). Extraction with CH_2Cl_2 (3 × 150 mL) and evaporation of the organic extracts (after washing with water and drying) gave a solid (4.8 g, 80.5%) whose ^{1}H NMR spectrum revealed the presence of **25a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.79 (s, 6H), 1.00 (d, J = 10.9 Hz, 1H), 1.49 (d, J = 9.5 Hz, 1H), 1.67 (d, J = 9.4 Hz, 1H), 1.86 (s, 2H), 1.93 (br s, 4H), 1.99 (s, 2H), 2.28 (d, J = 11.0 Hz, 1H), 3.06 (s, 3H), 3.13 (s, 3H), 3.45 (s, 2H), 3.79 (s, 6H), 6.03 (t, J = 2.3 Hz, 2H), 6.58 (s, 2H).

(1α,4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,11α,11a*β*,11bα,11c*β*,12α,12a*β*)-1,4,4a,5,5a,5b,5c,6,11,11a,11b,11c,12,12a-Tetradecahydro-1,4-ethano-5,12:6,11-dimethano-7,10-dimethoxy-5b,11b-dimethyl-2,3-bis(methylene)naphtho[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene (8a). A solution of the ketal **25a** (3.0 g, 6.33 mmol) in formic acid (50 mL) and THF (20 mL) was stirred for 18 h at 25 °C. The formic acid was removed by extraction with water (3 × 100 mL) and saturated $NaHCO_3$ (100 mL). Evaporation of the organic extracts gave the ketone **26a** as a fine white powder (2.5 g, 91%). This material was unstable at elevated temperatures and could not be fully characterized: IR ν_{max} (Nujol) 1780 cm^{-1}.

A solution of the ketone **26a** (2.5 g, 5.84 mmol) and dimethyl fumarate (0.90 g, 6 mmol) in toluene (20 mL) was refluxed for 18 h. The solvent was then removed under reduced pressure to give the diester **28a** (3.0 g, 95%) which was not purified further.

Compound **28a** (3.0 g, 5.5 mmol) in ethyl acetate (200 mL) was hydrogenated at 1 atm and 25 °C using 10% Pd/C (200 mg) until uptake of H_2 had ceased. Standard workup procedures gave the saturated diester **29a** as colorless needles (2.9 g, 98%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.85 (s, 3H), 0.86 (s, 3H), 1.19−1.89 (overlapping multiplets, 12H), 1.92 (s, 2H), 1.99 (d, J = 11.6 Hz, 2H), 2.04 (br d, J = 11.4 Hz, 2H), 2.10 (dt, J = 2.2, 12.5 Hz, 2H), 3.08 (s, 2H), 3.65 (s, 3H), 3.68 (s, 3H), 3.77(s, 3H), 3.79 (s, 3H), 6.58 (s, 2H).

To a suspension of $LiAlH_4$ (0.38 g, 10 mmol) in anhydrous THF (20 mL) was added a solution of **29a** (3.0 g, 5.5 mmol) in THF (100 mL), and the mixture was refluxed for 18 h. To the chilled reaction mixture were added water (0.4 mL), 15% NaOH (0.4 mL), and more water (1.2 mL) successively. The mixture was then filtered, and the filtrate was dried over Na_2SO_4 and evaporated under reduced pressure to give the diol **30a** (2.5 g, 93%) which was not further purified.

To a cooled (−5 °C) solution of the diol **30a** (2.5 g, 5.10 mmol) in dry pyridine (50 mL) was added *p*-toluenesulfonyl chloride (2.0 g, 10.5 mmol), and the resulting mixture was maintained at −5 °C for 36 h. The reaction was then quenched with crushed ice, and the solution was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed successively with 1 M HCl (3 × 100 mL) and saturated $NaHCO_3$ before being dried and concentrated under reduced pressure to give the ditosylate **31a** (4.0 g, 97%) which was not purified.

To a solution of the ditosylate **31a** (4.0 g, 5.0 mmol) in dry DMSO (50 mL) was added *t*-BuOK (2.0 g, 18.4 mmol). The mixture was then stirred at 25 °C for 18 h. Ice water was added, and the product was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extracts were washed with water (2 × 100 mL) and brine (3 × 50 mL) to remove all traces of DMSO and dried, and the solvent was removed under reduced pressure. The residue was then chromatographed (silica, EtOAc:hexane 30:70) to give pure diene **8a** (1.4 g, 62%): mp 212−213 °C (from EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.89 (s, 6H), 1.43 (d, J = 9.0 Hz, 2H), 1.45 (br s, 2H), 1.52 (dt, J = 1.5, 9.2 Hz, 2H), 1.72 (br d, J = 9.2 Hz, 1H), 1.86

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(br d, J = 9.3 Hz, 2H), 1.88 (s, 2H), 1.94 (s, 2H), 1.98 (d, J = 9.2 Hz, 1H), 2.07 (br s, 2H), 2.31 (br s, 2H), 3.47 (s, 2H), 3.79 (s, 6H), 4.69 (s, 2H), 5.23 (d, J = 1.1 Hz, 2H), 6.60 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 9.60, 22.31, 31.12, 39.31, 40.24, 40.70, 43.60, 43.69, 45.04, 49.74, 53.82, 56.10, 102.55, 109.00, 136.79, 147.80, 150.93. Anal. Calcd for $C_{32}H_{38}O_2$: C, 84.54; H, 8.42. Found: C, 84.03; H, 8.67.

Dimethyl (1α,4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,13α,13a*β*,13bα,-13c*β*,14α,14a*β*)-1,2,3,4,4a,5,5a,5b,5c,6,13,13a,13b,13c,14,-14a-Hexadecahydro-1,4-etheno-5,14:6,13-dimethano-7,12-dimethoxy-5b,13b-dimethylnaphtho[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobut[1,2-*b*]anthracene-2,3-*trans*-dicarboxylate (28b). A solution of ketal **25b** (4.61 g, 8.77 mmol)[18a] in formic acid (30 mL) and THF (40 mL) was stirred for 18 h at 25 °C. The formic acid was removed by extraction with water and saturated $NaHCO_3$. Evaporation of the organic extracts gave ketone **26b** (3.87 g, 92%). This material was unstable at elevated temperatures and could not be fully characterized: IR ν_{max} (Nujol) 1770 cm^{-1}.

A solution of the ketone **26b** (3.81 g, 7.97 mmol) and dimethyl fumarate (1.18 g, 8.21 mmol) in dry toluene (14.0 mL) was refluxed for 18 h. Removal of the solvent under reduced pressure and recrystallization of the residue from hot MeOH gave pure **28b** (4.38 g, 93%): mp 250−251 °C (from MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.84 (d, J = 2.6 Hz, 6H), 1.07 (d, J = 10.8 Hz, 1H), 1.41 (dd, J = 2.3, 8.5 Hz, 1H), 1.62 (d, J = 9.0 Hz, 2H), 1.84 (d, J = 9.5 Hz, 1H), 1.89 (s, 2H), 1.97 (s, 2H), 2.01 (s, 2H), 2.13 (s, 2H), 2.24 (d, J = 10.8 Hz, 1H), 2.70 (dd, J = 3.1, 5.4 Hz, 1H), 3.03−3.05 (m, 1H), 3.08−3.10 (m, 2H), 3.59 (d, J = 3.1 Hz, 2H), 3.62 (s, 3H), 3.68 (s, 3H), 3.95 (d, J = 5.1 Hz, 6H), 6.08 (br t, J = 7.2 Hz, 1H), 6.26 (br t, J = 7.4 Hz, 1H), 7.41−7.45 (m, 2H), 8.06−8.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 9.68, 31.01, 37.15, 37.22, 40.56, 41.07, 41.50, 42.57, 42.79, 43.93, 43.96, 46.13, 46.88, 47.27, 50.61, 52.05, 52.18, 54.16, 61.81, 61.93, 121.98, 124.63, 127.79, 132.13, 134.35, 135.25, 135.32, 144.14, 173.95, 174.43. Anal. Calcd for $C_{38}H_{42}O_6$: C, 76.74; H, 7.12. Found: C, 76.47; H, 7.25.

(1α,4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,13α,13a*β*,13bα,13c*β*,14α,-14a*β*)-1,4,4a,5,5a,5b,5c,6,13,13a,13b,13c,14,14a-Tetradecahydro-1,4-ethano-5,14:6,13-dimethano-7,12-dimethoxy-5b,13b-dimethyl-2,3-bis(methylene)naphtho-[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobut[1,2-*b*]anthracene (8b). A solution of **28b** (4.3 g, 7.25 mmol) in EtOAc (150 mL) was catalytically hydrogenated at 1 atm and 25 °C using 5% Pd/C (300 mg) until the uptake of hydrogen had ceased. Filtration and evaporation under reduced pressure gave the saturated diester **29b** (4.2 g, 96%), which was not purified further: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.93 (d, J = 2.3 Hz, 6H), 1.23−1.65 (overlapping multiplets, 8H), 1.88 (d, J = 9.8 Hz, 2H), 1.96 (s, 2H), 2.03 (d, J = 11.0 Hz, 2H), 2.05 (d, J = 12.1 Hz, 2H), 2.16 (s, 2H), 3.08 (br s, 2H), 3.62 (d, J = 3.3 Hz, 2H), 3.65 (s, 3H), 3.68 (s, 3H), 3.95 (s, 3H), 3.98 (s, 3H), 7.42−7.45 (m, 2H), 8.06−8.09 (m, 2H).

To an ice cold slurry of $LiAlH_4$ (600 mg, 15.5 mmol) in anhydrous THF (25 mL) was added **29b** (4.2 g, 7.05 mmol) in THF (125 mL), and the resulting reaction mixture was refluxed for 24 h. Successive additions of water (0.7 mL), 15% NaOH (0.7 mL), and more water (2.1 mL) to the cooled reaction mixture, followed by filtration and evaporation under reduced pressure, gave the diol **30b** (3.5 g, 92%) which was not purified further: IR, ν_{max} (Nujol) 3250 (br, OH) cm^{-1}.

To a solution of **30b** (3.5 g, 6.47 mmol) in anhydrous pyridine (60 mL) cooled to −5 °C was added *p*-toluenesulfonyl chloride (3.43 g, 17.97 mmol) in pyridine (25 mL). After addition was completed the reaction mixture was stored at −5 °C for 3.5 d and then poured on to ice and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed with 1 M HCl (5 × 75 mL) and saturated $NaHCO_3$ and dried, and the solvent was removed under reduced pressure to give the ditosylate **31b** (5.3 g, 97%) which was not purified further.

To a solution of **31b** (5.3 g, 6.24 mmol) in anhydrous DMSO was carefully added *t*-BuOK (2.5 g, 20.35 mmol). After being stirred at 25 °C for 19 h, the reaction mixture was poured onto ice and extracted with CH_2Cl_2 (3 × 120 mL). The organic extracts were successively washed with water (2 × 75 mL) and brine (6 × 75 mL), to remove the DMSO. The combined organic phases were dried and filtered, and the solvent was removed under reduced pressure. The residue was chromatographed (silica, EtOAc:hexane 20:80) to give pure **8b** (2.68 g, 85%): mp decomposed above 250 °C (from hot hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.96 (s, 6H), 1.44 (d, J = 8.7 Hz, 2H), 1.48 (br s, 2H), 1.50 (d, J = 10.4 Hz, 1H), 1.66 (d, J = 9.5 Hz, 1H), 1.86 (d, J = 8.2 Hz, 2H), 1.91 (d, J = 10.4 Hz, 2H), 1.98 (d, J = 11.3 Hz, 1H), 2.11 (s, 2H), 2.16 (s, 2H), 2.32 (br s, 2H), 3.65 (s, 2H), 3.98 (s, 6H), 4.68 (s, 2H), 5.22 (s, 2H), 7.41−7.46 (m, 2H), 8.05−8.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 9.79, 22.26, 31.14, 39.26, 40.50, 40.64, 42.79, 44.27, 44.98, 50.68, 53.93, 61.86, 102.62, 121.96, 124.94, 127.77, 135.31, 144.17, 150.77. Anal. Calcd for $C_{36}H_{40}O_2$: C, 85.67; H, 7.99. Found: C, 85.86; H, 8.15.

(1α,4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,13α,13a*β*,13bα,13c*β*,14α,-14a*β*)-1,4,4a,5,5a,5b,5c,6,13,13a,13b,13c,14,14a-Tetradecahydro-1,4-ethano-5,14:6,13-dimethano-5b,13b-dimethyl-2,3-bis(methylene)naphtho[2″,3″:3′,4′]cyclobuta-[1′,2′:3,4]cyclobut[1,2-*b*]anthracene-7,12-dione (8f). To a stirred solution of **8b** (151 mg, 0.299 mmol) in THF/MeCN (6:8) was added, dropwise over 5 min, CAN (491 mg, 0.9 mmol) in water (3 mL). The reaction mixture was then stirred for a further 25 min at 25 °C, during which time **8f** precipitated as a yellow solid. After filtration, the filtrate was extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic extracts were washed with water (2 × 20 mL), dried, filtered, and evaporated under reduced pressure to give a second crop of **8f** (total combined yield 135 mg, 95%) which was further purified by chromatography (silica, EtOAc:hexane 20:80): mp decomposed above 220 °C (from hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.88 (s, 6H), 1.43−1.50 (overlapping multiplets, 6H), 1.62 (d, J = 10.0 Hz, 1H), 1.84 (d, J = 8.7 Hz, 2H), 1.88 (s, 2H), 1.97 (d, J = 9.3 Hz, 1H), 2.11 (s, 2H), 2.32 (br s, 2H), 3.53 (s, 2H), 4.68 (s, 2H), 5.22 (s, 2H), 7.65−7.69 (m, 2H, 8.03−8.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 9.53, 22.26, 31.06, 39.41, 40.62, 41.43, 43.88, 44.99, 48.59, 53.81, 102.68, 126.24, 133.12, 133.25, 150.77, 154.05, 181.92. Anal. Calcd for $C_{34}H_{24}O_2$: C, 86.04; H, 7.22. Found: C, 85.90; H, 7.35.

Dimethyl (2aα,3*β*,8*β*,8aα)-2a,3,8,8a-Tetrahydro-3,8-methanocyclobuta[*b*]naphthalene-1,2-dicarboxylate (19c). A magnetically stirred solution of benzonorbornadiene, **10c** (27.0 g, 0.19 mol), DMAD (27.5 g, 0.193 mol), and $RuH_2CO(PPh_3)_3$ (0.6 g, 0.5 mmol) in benzene (200 mL) was refluxed under an argon atmosphere for 18 h. Ethanol was added to the cooled reaction mixture, and the precipitated material was collected and recrystallized from ethanol to give the ester **19c** (50.3 g, 90%): mp 94−95 °C (from methanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.77 (s, 2H), 2.75 (s, 2H), 3.27 (s, 2H), 3.85 (s, 6H), 7.10 (m, 2H), 7.24 (m, 2H). Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 72.06; H, 5.78.

Dimethyl (1α,4α,4a*β*,4bα,4c*β*,5α,10α,10a*β*,10bα,10c*β*)-1,4,4a,4b,4c,5,10,10a,10b,10c-Decahydro-1,4:5,10-dimethanobenzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]-naphthalene-4b,10b-dicarboxylate (20c). A solution of **19c** (50.0 g, 0.176 mol) in quadricyclane (20.0 g, 0.217 mol) was refluxed under an argon atmosphere for 18 h. Acetone (25 mL) was added to the cooled solution, and the resulting precipitate was collected and recrystallized from acetone to give **20c** (57.2 g, 86.4%): mp 156−157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.15 (d, J = 9.9 Hz, 1H), 1.57 (d, J = 10.6 Hz, 1H), 1.92 (d, J = 9.8 Hz, 1H), 2.07 (s, 2H), 2.30 (s, 2H), 2.35 (d, J = 10.4 Hz, 1H), 2.86 (s, 2H), 3.32 (s, 2H), 3.80 (s, 6H), 6.05 (t, J = 1.6 Hz, 2H), 7.09 (m, 2H), 7.20 (m, 2H). Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.78; H, 6.60.

(1α,4α,4a*β*,4bα,4c*β*,5α,10α,10a*β*,10bα,10c*β*)-1,4,4a,4b,-4c,5,10,10a,10b,10c-Decahydro-1,4:5,10-dimethano-4b,-10b-dimethylbenzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene (23c). To a solution of **20c** (40.0 g, 0.106 mol) in dry THF (300 mL) was added $LiAlH_4$ (9.0 g, 0.240 mol) in small portions. The mixture was refluxed for 18 h. To the cooled reaction mixture were added successively water (9.0 mL), 15% NaOH (9.0 mL), and water (27.0 mL). The mixture was then filtered, and the filtrate was dried and evaporated under reduced pressure to give the diol **21c** (30.5 g, 89%) which was not purified further: IR ν_{max} (Nujol) 3250 cm^{-1}.

To a cooled solution (−5 °C) of the diol **21c** (30.0 g, 80.0 mmol) in dry pyridine (150 mL) was added slowly methanesulfonyl chloride (21.8 g, 0.190 mol). The resulting solution was kept at −5 °C for 72 h, after which it was poured onto crushed ice and then extracted with CH_2Cl_2 (3 × 150 mL). The organic extract was washed successively with 1 M HCl (750 mL) and saturated $NaHCO_3$ (100 mL), then dried, and evaporated to give the dimesylate **22c** (31.0 g, 73%) which was not purified.

A magnetically stirred mixture of the dimesylate **22c** (30.0 g, 56.39 mmol) and $LiAlH_4$ (4.5 g, 0.120 mol) in dry THF (300 mL) was refluxed for 48 h. Use of a workup procedure that was identical to that described above for the synthesis of the diol gave **23c** (15.2 g, 93%): mp 113 °C (from EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.90 (s, 6H), 1.19 (d, J = 8.9 Hz, 1H), 1.40 (d, J = 8.8 Hz, 1H), 1.64 (d, J = 8.9 Hz, 1H), 1.65 (s, 2H), 1.82 (d, J = 8.9 Hz, 1H), 1.89 (s, 2H), 2.76 (br s, 2H), 3.27 (s, 2H), 5.98 (t, J = 1.8 Hz, 2H), 7.05 (m, 2H), 7.15 (m, 2H). Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.52; H, 8.52.

(1α,4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,11α,11a*β*,11bα,11c*β*,12α,12a*β*)-1,4,4a,5, 5a,5b,5c,6,11,11a,11b,11c,12,12a-Tetradecahydro-8-acetamido-1,4-ethano-5,12:6,11-dimethano-5b,11b-dimethyl-2,3-bis(methylene)naphtho[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene (8d). A solution of **23c** (14.0 g, 48.6 mmol) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (13.0 g, 50 mmol) in xylene (bp 138−141 °C) (50 mL) was refluxed for 18 h. Azeotropic removal of the xylene, through addition of ethanol (75 mL), gave a solid residue which was assumed to be **24c** (22.5 g, 84%) since its 300 MHz ^{1}H NMR spectrum revealed the complete absence of the peak at 5.98 ppm due to the double-bond protons of **23c**.

Sodium metal (33.0 g, 1.45 mol) was added piecewise to a refluxing solution of **24c** (20.0 g, 36.2 mmol) in THF (100 mL) and 2-propanol (400 mL). The resulting mixture was refluxed for 17 h. Methanol (20 mL) was added to the cooled reaction mixture followed by crushed ice (100 g). Extraction with CH_2Cl_2 (3 × 150 mL) and evaporation of the organic extracts (after washing with water and drying) gave a solid (12.5 g, 83%) whose ^{1}H NMR spectrum revealed the presence of **25c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.80 (s, 6H), 1.02 (d, J = 10.7 Hz, 1H), 1.54 (d, J = 9.2 Hz, 1H), 1.72 (d, J = 9.2 Hz, 1H), 1.86 (s, 2H), 1.91 (s, 2H), 1.95 (br s, 2H), 2.01 (s, 2H), 2.28 (d, J = 10.7 Hz, 1H), 2.86 (br s, 2H), 3.06 (s, 3H), 3.13 (s, 3H), 3.20 (s, 2H), 6.03 (t, J = 1.8 Hz, 2H), 7.06 (m, 2H), 7.14 (m, 2H).

A solution of the ketal **25c** (12.0 g, 28.8 mmol) in formic acid (100 mL) and THF (50 mL) was stirred for 18 h at 25 °C. The formic acid was removed by extraction with water and saturated $NaHCO_3$. Evaporation of the organic extracts gave the ketone **26c** as a fine white powder (9.6 g, 90%). This material was unstable at elevated temperatures and could not be fully characterized: IR ν_{max} (Nujol) 1780 cm^{-1}.

The preparation of **28c** was achieved directly from **26c**, without isolation of the intermediate diene **27c**. Thus, a solution of the ketone **26c** (9.5 g, 25.84 mmol) and dimethyl fumarate (4.0 g, 26.6 mmol) in toluene (50 mL) was refluxed for 18 h. The solvent was then removed under reduced pressure to give the diester **28c** (11.8 g, 94%) which was not purified further: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.78 (s, 3H), 0.79 (s, 3H), 1.07 (d, J = 10.8 Hz, 1H), 1.58−1.71 (overlapping multiplets, 6H), 1.85 (s, 2H), 1.88 (s, 2H), 1.96 (d, J = 14.8 Hz, 2H), 2.24 (d, J = 10.5 Hz, 1H), 3.09 (s, 2H), 3.18 (d, J = 2.8 Hz, 2H), 3.62 (s, 3H), 3.69 (s, 3H), 6.09 (t, J = 7.2 Hz, 1H), 6.27 (t, J = 7.4 Hz, 1H), 7.05 (m, 2H), 7.13 (m, 2H).

Compound **28c** (11.0 g, 22.7 mmol) in ethyl acetate (200 mL) was hydrogenated at 1 atm and 25 °C using 10% Pd/C (200 mg) until uptake of H_2 had ceased. Standard workup procedures gave the saturated diester **29c** as colorless needles (10.5 g, 95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.86 (s, 3H), 0.87 (s, 3H), 1.43 (d, J = 11.8 Hz, 1H), 1.24−1.76 (overlapping multiplets, 8H), 1.89 (s, 2H), 1.91 (s, 2H), 2.03 (d, J = 11.4 Hz, 2H), 2.08 (d, J = 12.7 Hz, 1H), 3.08 (s, 2H), 3.20 (d, J = 2.6 Hz, 2H), 3.66 (s, 3H), 3.68 (s, 3H), 7.05 (m, 2H), 7.13 (m, 2H).

To a suspension of $LiAlH_4$ (1.52 g, 40 mmol) in anhydrous THF (50 mL) was added a solution of **29c** (10.0 g, 20.7 mmol) in THF (100 mL), and the mixture was refluxed for 18 h. To the chilled reaction mixture were added water (1.5 mL), 15% NaOH (1.5 mL), and more water (4.5 mL) successively. The mixture was then filtered, and the filtrate was dried over Na_2SO_4 and evaporated under reduced pressure to give the diol **30c** (8.6 g, 91%) which was not further purified.

To a cooled solution (−5 °C) of the diol **30c** (8.5 g, 19.8 mmol) in dry pyridine (120 mL) was added acetic anhydride (90 mL). The resulting solution was stirred at 25 °C for 18 h and then for 1 h at 60 °C. To the chilled reaction mixture was added methanol (50 mL). The solution was evaporated, and the residue was extracted with CH_2Cl_2 (3 × 150 mL). The organic extract was washed successively with 1 M HCl (750 mL) and saturated $NaHCO_3$ (100 mL), then dried, and evaporated to give the diacetate **33** (9.86 g, 97%) which was not purified.

$Cu(NO_3)_2 \cdot 2.5H_2O$ (3.0 g, 12.4 mmol) was added to a solution of **33** (9.86 g, 19.2 mmol) in CH_2Cl_2 (30 mL) and acetic anhydride (40 mL). The reaction mixture was magnetically stirred for 18 h at 25 °C. The mixture was poured into ice (50 g) and ammonia (15 M, 60 mL). The resulting dark blue solution was extracted with CH_2Cl_2 (3 × 150 mL), washed with water (3 × 50 mL), dried over anhydrous Na_2SO_4, and filtered and the solvent was evaporated to give crude **35** (10.2 g, 81%).

Compound **35** (10.2 g, 18.2 mmol) and zinc powder (12.0 g, 0.185 mol) in acetic acid (17 M, 50 mL) and acetic anhydride (6 mL) were refluxed for 18 h under an argon atmosphere. The resulting white mixture was cooled to 25 °C, neutralized with ammonia (15 M, 60 mL), extracted with CH_2Cl_2 (2 × 100 mL), washed with water (2 × 100 mL), and dried, and the solvent was evaporated to give the crude amide **37** (9.5 g, 91%).

A solution of **37** (9.5 g, 16.6 mmol) and $LiBH_4$ (0.8 g, 34 mmol) in dry THF (75 mL) was stirred at 25 °C for 5 d. Acetic acid (5 M) was then carefully added until foaming had ceased. The solution was extracted with CH_2Cl_2 (3 × 100 mL), washed with saturated $NaHCO_3$ (3 × 100 mL), and dried, and the solvent was removed under reduced pressure to give crude **39** (5.8 g, 72%).

To a cooled (−5 °C) solution of the diol **39** (5.8 g, 11.9 mmol) in dry pyridine (50 mL) was added *p*-toluenesulfonyl chloride (4.0 g, 21 mmol), and the resulting mixture was maintained at −5 °C for 36 h. The reaction was then quenched with crushed ice, and the solution was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed successively with 1 M HCl (3 × 100 mL) and saturated $NaHCO_3$ (100 mL) before being dried and concentrated under reduced pressure to give the ditosylate **41** (8.3 g, 88%) which was not purified.

To a solution of the ditosylate **41** (8.3 g, 10.4 mmol) in dry DMSO (75 mL) was added *t*-BuOK (3.4 g, 30 mmol). The mixture was then stirred at 25 °C for 18 h. Ice water was added, and the product was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed with water (2 × 100 mL) and brine (3 × 50 mL) to remove all traces of DMSO and dried, and the solvent was removed under reduced pressure. The residue was then chromatographed (silica, EtOAc/hexane 30:70) to give the pure diene **8d** (3.2 g, 68%): mp 210 °C (from EtOAc/pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.87 (s, 6H), 1.44 (br d, J = 11.6 Hz, 2H), 1.46 (s, 2H), 1.50−1.55 (m, 2H), 1.72 (d, J = 9.2 Hz, 1H), 1.85 (s, 2H), 1.87 (br d, J = 11.6 Hz, 2H), 1.91 (s, 2H), 1.96 (d, J = 11.0 Hz, 1H), 2.09 (s, 2H), 2.12 (s, 3H), 2.30 (s, 2H), 3.16 (br s, 2H), 4.67 (s, 2H), 5.22 (s, 2H), 7.05 (br s, 2H), 7.12 (br s, 1H), 7.39 (br s, 1H); ^{13}C NMR (125 MHz, CS_2:acetone-d_6 1:1) δ (ppm) 10.25, 23.18, 24.27, 28.58, 30.01, 30.44, 31.04, 31.93, 40.10, 41.53, 43.34, 44.30, 44.38, 44.75, 45.87, 45.89, 51.51, 51.77, 103.37, 113.44, 116.89, 121.04, 137.74, 142.95, 148.48, 151.02, 167.47. Anal. Calcd for $C_{32}H_{37}NO \cdot H_2O$: C, 91.61; H, 8.39. Found: C, 91.52; H, 8.52.

(1α,4α,4a*β*,9α,9a*β*,10α)-1,2,3,4,4a,9,9a,10-Octahydro-1,4-ethano-2,3-*trans*-bis(acetoxymethyl)-9,10-methanoanthracene (32). A solution of **17c** (7.27 g, 27.1 mmol) in acetic anhydride (90 mL) and pyridine (180 mL) was stirred at 25 °C for 22 h and then heated at 80 °C for 2 h. The reaction mixture was cooled to 0 °C, and the excess acetic anhydride was quenched by the slow addition of methanol (40 mL) over

40 min. The solvent volume was reduced *in vacuo* to ~100 mL, and the resulting solution was poured onto ice (300 g) and 1 M HCl (200 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The organic extracts were combined, washed with 1 M HCl (6 × 200 mL), water (200 mL), and saturated $NaHCO_3$ (2 × 200 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and then under high vacuum to give **32** as a clear oil (9.85 g, 98%) which was recrystallized from hexane: mp 80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.20−1.52 (m, 4H), 1.55−1.67 (m, 4H), 1.78−1.90 (m, 3H), 2.03 (s, 3H), 2.06 (s, 3H), 2.26 (d, J = 10.0 Hz, 1H), 3.15 (br s, 1H), 3.20 (br s, 1H), 3.82 (dd, J = 8.7, 10.9 Hz, 1H), 3.97 (dd, J = 6.7, 10.9 Hz, 1H), 4.01−4.15 (m, 2H), 7.03 (dd, J = 3.1, 5.1 Hz, 2H), 7.12 (m, 2H); IR ν_{max} (Nujol) 3030, 1735, 1490, 1250, 1245, 1230, 1030, 740 cm^{-1}. Anal. Calcd for $C_{19}H_{24}O_2$: C, 74.97; H, 7.66. Found: C, 75.23; H, 7.85.

(1α,4α,4a*β*,9α,9a*β*,10α)-1,2,3,4,4a,9,9a,10-Octahydro-2,3-*trans*-bis(acetoxymethyl)-1,4-ethano-9,10-methano-6-nitroanthracene (34). $Cu(NO_3)_2 \cdot 2.5H_2O$ (8.40 g, 34.7 mmol) was added to a stirred solution of **32** (8.40 g, 22.8 mmol) in acetic anhydride (80 mL) and CH_2Cl_2 (40 mL) at 0 °C, and the reaction mixture was stirred at 20 °C for 17 h. The reaction mixture was poured onto a mixture of ice (300 g) and 15 M NH_3 (150 mL) and stirred for 30 min. The resulting solution was extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were combined and washed with saturated $NaHCO_3$ (2 × 200 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give a yellow oil which was subjected to column chromatography (silica, benzene/ethyl acetate 80:20) to give **34** as a light yellow oil (9.30 g, 89%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.28−1.38 (m, 2H), 1.40 (m, 1H), 1.50 (m, 1H), 1.58−1.66 (m, 4H), 1.80 (m, 1H), 1.88 (m, 2H), 2.03 (s, 3H), 2.05 (s, 3H), 2.35 (d, J = 10.5 Hz, 1H), 3.27 (s, 1H), 3.32 (s, 1H), 3.80 (m, 1H), 3.91−4.13 (m, 3H), 7.25 (m, 1H), 7.96 (m, 1H), 7.99 (s, 1H).

(1α,4α,4a*β*,9α,9a*β*,10α)-1,2,3,4,4a,9,9a,10-Octahydro-6-acetamido-2,3-*trans*-bis(acetoxymethyl)-1,4-ethano-9,10-methanoanthracene (36). Compound **34** (26.5 g, 64.1 mmol) in ethyl acetate (250 mL) and ethanol (50 mL) was hydrogenated at 1 atm and 25 °C using 10% Pd/C (0.40 g) until uptake of H_2 had ceased. The catalyst was removed, and the filtrate was evaporated under reduced pressure to give crude amine as a brown oil (23.9 g, 97%). The crude product was used in the next reaction: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.31−1.46 (m, 3H), 1.53−1.63 (m, 5H), 1.73−1.85 (m, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.20 (d, J = 10.0 Hz, 1H), 3.03 (s, 1H), 3.08 (s, 1H), 3.46 (br s, 2H), 3.81−3.86 (m, 1H), 3.94−4.13 (m, 3H), 6.34 (dd, J = 1.9, 7.9 Hz, 1H), 6.54−6.57 (m, 1H), 6.86−6.92 (m, 1H); IR ν_{max} (thin film) 3440, 3360, 3210, 3010, 2940, 1835, 1615, 1595, 1240, 1030, 905, 730 cm^{-1}.

Acetic anhydride (7.0 mL, 74.0 mmol) was added to a stirred solution of the crude amine (23.9 g, 62.3 mmol) in CH_2Cl_2 (50 mL), and stirring was continued for 30 min. Saturated $NaHCO_3$ (250 mL) was added, and the resulting mixture was stirred for a further 2 h. The layers were separated, and the aqueous layer was extracted with a further portion of CH_2Cl_2 (50 mL). The organic layers were combined, washed with brine (200 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give a brown oil. The crude product was subjected to column chromatography (silica, benzene/ethyl acetate 60:40) to give **36** as a white solid (24.9 g, 94%): mp 84−85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.21−1.50 (m, 4H), 1.52−1.59 (m, 4H), 1.77−1.83 (m, 3H), 2.02 (s, 3H), 2.04 (s, 3H), 2.09 (s, 3H), 2.22 (d, J = 9.9 Hz, 1H), 3.09 (s, 1H), 3.12 (s, 1H), 3.72−3.83 (m, 1H), 3.91−4.13 (m, 3H), 6.88−7.04 (m, 2H), 7.48 (br d, J = 3.0 Hz, 1H), 7.80 (br s, 1H); IR ν_{max} (Nujol) 3280, 3030, 1735, 1670, 1600, 1230 cm^{-1}. Anal. Calcd for $C_{25}H_{31}NO_5$: C, 70.57; H, 7.34; N, 3.29. Found: C, 70.34; H, 7.60; N, 3.35.

(1α,4α,4a*β*,9α,9a*β*,10α)-1,4,4a,9,9a,10-Hexahydro-6-acetamido-1,4-ethano-9,10-methano-2,3-bis(methylene)anthracene (7d). $LiBH_4$ (3.00 g, 0.160 mol) was added to a stirred solution of **36** (24.9 g, 58.6 mmol) in dry THF (580 mL) at 0 °C. The reaction mixture was allowed to warm to 25 °C and stirred for 6.5 d. The 5% acetic acid (150 mL) was added, and the solvent was evaporated under reduced pressure to give a white viscous oil which was dried under high vacuum over P_2O_5. The dried solid was dissolved in dry THF (100 mL) and filtered through dry silica. The silica was washed with a further portion of THF (200 mL). The solutions were combined and evaporated under reduced pressure to give **38** as a clear oil (19.9 g, 99%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.20−1.70 (m, 8H), 1.78−1.84 (m, 3H), 2.04 (m, 2H), 2.14 (s, 3H), 2.23 (d, J = 10.1 Hz, 1H), 3.07 (br s, 2H), 3.10 (s, 1H), 3.14 (s, 1H), 3.31−3.55 (m, 2H), 3.60−3.65 (m, 2H), 6.93−6.99 (m, 1H), 7.05 (d, J = 7.8 Hz, 1H), 7.30−7.42 (m, 2H).

p-Toluenesulfonyl chloride (38.0 g, 0.200 mmol) was added to an ice cold solution of **38** (19.9 g, 58.7 mmol) in pyridine (150 mL). The reaction mixture was maintained at −5 °C for 36 h and then poured onto ice (500 g). The resulting mixture was extracted with CH_2Cl_2 (3 × 150 mL). The extracts were combined, washed with 1 M HCl (5 × 250 mL) and saturated $NaHCO_3$ (2 × 250 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give **40** as a yellow solid (33.5 g, 88%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.07−1.53 (m, 8H), 1.68−1.85 (m, 3H), 2.11 (s, 3H), 2.42 (s, 3H), 2.44 (s, 3H), 3.00 (s, 1H), 3.08 (s, 1H), 3.72 (br d, J = 7.8 Hz, 2H), 3.91 (br d, J = 7.8 Hz, 2H), 6.93−6.99 (m, 1H), 7.05 (d, J = 8.2 Hz, 1H), 7.29−7.40 (m, 5H), 7.64−7.77 (m, 5H); IR ν_{max} (Nujol) 3280, 3030, 1660, 1595, 1350, 1170, 950, 760, 660 cm^{-1}.

t-BuOK (23.0 g, 0.205 mol) was added to a stirred solution of **40** (33.5 g, 51.3 mmol) in DMSO (400 mL). The reaction mixture was stirred for 14 h and then poured onto ice (500 g) and brine (500 mL). The resulting precipitate was filtered, dissolved in CH_2Cl_2 (200 mL), and washed with saturated $NaHCO_3$ (2 × 200 mL). The solution was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give a brown solid. This was subjected to column chromatography (silica, chloroform/ethyl acetate/benzene 50:25:25) to give an off-white solid (8.5 g) which was recrystallized from benzene to give **7d** as a white solid (6.50 g, 41%): mp 175 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.53 (br d, J = 8.8 Hz, 2H), 1.61 (d, J = 10.0 Hz, 1H), 1.62 (s, 2H), 1.86 (br d, J = 8.8 Hz, 2H), 2.13 (s, 3H), 2.26 (d, J = 10.0 Hz, 1H), 2.54 (s, 2H), 3.18 (s, 1H), 3.20 (s, 1H), 4.71 (s, 2H), 5.21 (s, 2H), 6.96 (dd, J = 2.0, 7.7 Hz, 1H), 7.05 (d, J = 7.7 Hz, 1H), 7.08 (br s, 1H), 7.42 (d, J = 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.90, 21.96, 24.58, 40.80, 43.06, 43.31, 44.16, 46.24, 46.92, 103.04, 103.16, 113.28, 116.67, 120.36, 135.09, 146.84, 150.21, 150.32, 151.42, 168.10. Anal. Calcd for $C_{21}H_{23}NO$: C, 82.59; H, 7.59; N, 4.59. Found: C, 82.80; H, 7.72; N, 4.34.

(1α,4α,4a*β*,9α,9a*β*,10α)-1,4,4a,9,9a,10-Hexahydro-6-amino-1,4-ethano-9,10-methano-2,3-bis(methylene)anthracene (42). A suspension of **7d** (1.00 g, 3.27 mmol) and KOH (5.30 g, 94 mmol) in methanol (28 mL) and water (5 mL) was refluxed, under an argon atmosphere, for 24 h. The reaction mixture was cooled to 25 °C, and water (50 mL) was added. The resulting precipitate was filtered off and washed with water. The precipitate was dissolved in CH_2Cl_2 (100 mL), washed with saturated $NaHCO_3$ (100 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give a white solid which was extracted into boiling hexane (8 × 100 mL) and filtered. The filtrate fractions were combined, and the solvent volume was reduced under reduced pressure to *ca.* 20 mL. The resulting white precipitate was collected as **42** (0.46 g, 53%): mp 120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.52 (br d, J = 8.2 Hz, 2H), 1.59 (d, J = 9.8 Hz, 1H), 1.63 (s, 2H), 1.87 (br d, J = 8.2 Hz, 2H), 2.24 (d, J = 9.8 Hz, 1H), 2.54 (s, 2H), 3.12 (s, 2H), 3.33 (br s, 2H), 4.72 (s, 2H), 5.22 (s, 2H), 6.34 (dd, J = 2.2, 7.8 Hz, 1H), 6.56 (d, J = 2.2 Hz, 1H), 6.90 (d, J = 6.90 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.97, 40.90, 40.96, 43.37, 43.90, 43.99, 45.89, 46.98, 102.86, 102.92, 108.77, 111.32, 120.65, 141.36, 143.77, 150.47, 151.91. Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.65; H, 8.13; N, 5.28.

(1α,4α,4a*β*,9α,9a*β*,10α)-1,4,4a,9,9a,10-Hexahydro-1,4-ethano-9,10-methano-6-(*N*,*N*,*N*-trimethylamino)-2,3-bis(methylene)anthracene Iodide (43). A suspension of **42** (0.72 g, 2.73 mmol) and $NaHCO_3$ (0.88 g, 10.5 mmol) in methanol (30 mL) and methyl iodide (1 mL, 16 mmol) was refluxed for 21 h. A further portion of methyl iodide (1 mL, 16 mmol) was then added, and refluxing was continued for a further 24 h. The solvent was evaporated under reduced pressure and the

resulting white solid was dissolved in CH_2Cl_2 (200 mL), washed with saturated $NaHCO_3$ (2 × 100 mL), and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to give a white solid which was recrystallized from CH_2Cl_2/hexane to give **43** as a white solid (0.92 g, 78%): mp 156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.55 (br d, J = 8.3 Hz, 2H), 1.64 (d, J = 10.3 Hz, 1H), 1.70 (s, 2H), 1.84 (br d, J = 8.3 Hz, 2H), 2.33 (d, J = 10.3 Hz, 1H), 2.57 (s, 1H), 2.60 (s, 1H), 3.29 (s, 1H), 3.43 (s, 1H), 3.93 (s, 9H), 4.72 (s, 1H), 4.73 (s, 1H), 5.21 (s, 2H), 7.28 (d, J = 8.3 Hz, 1H), 7.45 (dd, J = 2.7, 8.3 Hz, 1H), 7.76 (d, J = 2.7 Hz, 1H). Anal. Calcd for $C_{22}H_{28}NI \cdot {}^1/_2H_2O$: C, 59.73; H, 6.60; N, 3.17. Found: C, 59.73; H, 6.70; N, 3.15.

(1α,4α,4a*β*,9α,9a*β*,10α)-1,4,4a,9,9a,10-Hexahydro-1,4-ethano-9,10-methano-6-(*N*,*N*-dimethylamino)-2,3-bis(methylene)anthracene (7e). 43 (0.82 g, 1.89 mmol) was added portionwise to a stirred, ice cold suspension of $LiAlH_4$ (0.53 g, 14 mmol) in THF (20 mL). The reaction mixture was heated at reflux for 80 min and then cooled to 0 °C. The excess reagent was quenched by the sequential addition of water (0.5 mL), 15% NaOH (0.5 mL), and then water (1.5 mL). The mixture was filtered, and the solvent was evaporated under reduced pressure to give a white solid which was crystallized from methanol to give **7e** as a white powder (0.417 g, 76%): mp 152 °C; ^{1}H NMR (300 MHz) δ (ppm) 1.51 (br d, J = 8.1 Hz, 2H), 1.60 (br d, J = 9.7 Hz, 1H), 1.64 (s, 2H), 1.87 (br d, J = 8.1 Hz, 2H), 2.25 (br d, J = 9.7 Hz, 1H), 2.54 (br s, 2H), 2.88 (s, 6H), 3.14 (s, 1H), 3.15 (s, 1H), 4.70 (s, 2H), 5.20 (s, 2H), 6.40 (dd, J = 2.4, 8.0 Hz, 1H), 6.70 (d, J = 2.4 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 22.00, 40.96, 41.03, 41.42, 43.52, 43.96, 44.13, 45.81, 47.35, 102.81, 106.69, 109.33, 120.46, 139.61, 149.15, 150.54, 151.64. Anal. Calcd for $C_{21}H_{25}N$: C, 86.55; H, 8.65; N, 4.81. Found: C, 86.28; H, 8.52; N, 4.77.

Dimethyl (1α,4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,11α,11a*β*,11bα,-11c*β*,12α,12a*β*)-1,2,3,4,4a,5,5a,5b,5c,6,11,11a,11b,11c,12,-12a-Hexadecahydro-1,4-ethano-5,12:6,11-dimethano-5b,-11b-dimethyl-8-nitronaphtho[2″,3″:3′,4′]cyclobuta-[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene-2,3-*trans*-dicarboxylate (44). The nitration of **29c** (4.65 g, 9.55 mmol) with $Cu(NO_3)_2 \cdot 2.5H_2O$ (2.40 g, 10.3 mmol) in acetic anhydride (95 mL) and CH_2Cl_2 (40 mL) was performed according to the procedure for **34** (see above). The crude product was subjected to column chromatography (silica, benzene) and recrystallized from hexane to give **44** as a white solid (4.63 g, 91%): mp 141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.85 (s, 3H), 0.87 (s, 3H), 1.19−1.24 (m, 2H), 1.40−1.47 (m, 3H), 1.56−1.59 (m, 1H), 1.62 (s, 1H), 1.75 (m, 1H), 1.82 (d, J = 9.8 Hz, 1H), 1.86 (s, 1H), 1.89 (s, 4H), 2.01 (s, 1H), 2.04 (s, 1H), 2.05 (d, J = 6.3 Hz, 1H), 2.11(m, 1H), 3.07 (m, 2H), 3.31 (br t, J = 3.4 Hz, 2H), 3.64 (s, 3H), 3.67 (s, 3H), 7.23 (d, J = 8 Hz, 1H), 7.97 (s, 1H), 7.98 (br d, J = 8 Hz, 1H). Anal. Calcd for $C_{32}H_{37}NO_6$: C, 72.29; H, 7.01; N, 2.63. Found: C, 72.55; H, 7.26; N, 2.58.

Dimethyl (1α,4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,11α,11a*β*,11bα,-11c*β*,12α,12a*β*)-1,2,3,4,4a,5,5a,5b,5c,6,11,11a,11b,11c,12,-12a-Hexadecahydro-1,4-ethano-5,12:6,11-dimethano-5b,-11b-dimethyl-8-(*N*,*N*-dimethylamino)naphtho[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene-2,3-*trans*-dicarboxylate (46). Compound **44** (4.63 g, 8.71 mmol) in a mixture of ethyl acetate (150 mL) and ethanol (30 mL) was hydrogenated at 1 atm and 25 °C using 5% Pd/C (100 mg) until uptake of H_2 had ceased. The catalyst was removed, and the filtrate was evaporated under reduced pressure to give crude **45** as a brown oil (4.27 g, 98%). The crude product was used in the next reaction: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.83 (s, 3H), 0.84 (s, 3H), 1.20−1.31 (m, 3H), 1.35−1.65 (m, 4H), 1.68−1.93 (m, 6H), 1.97−2.12 (m, 5H), 3.08 (s, 2H), 3.11 (br s, 2H), 3.66 (s, 3H), 3.68 (s, 3H), 4.40 (br s, 2H), 6.50−6.54 (m, 1H), 6.68 (br s, 1H,), 6.91−6.96 (m, 1H); IR ν_{max} (Nujol) 3460, 3380, 1740 cm^{-1}.

A slurry of **45** (1.30 g, 2.59 mmol) and $NaBH_4$ (2.00 g, 31 mmol) in THF (16 mL) and ethanol (4 mL) was added dropwise to an ice cooled, stirring solution consisting of 35% formaldehyde (4.0 mL, 22 mmol), 3 M H_2SO_4 (6 mL), and THF (8 mL). The dropping rate was controlled so that the reaction temperature remained between 15 and 20 °C. After the addition was complete, 2.5 M KOH (20 mL) was added and the solution stirred for 30 min. Water (100 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, washed with water (100 mL), saturated $NaHCO_3$ (100 mL), and brine (100 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give a brown solid which was subjected to column chromatography (silica, 60−80 °C, light petroleum ether/ethyl acetate 70:30) to give **46** as a white powder (1.10 g, 80%) which was recrystallized from hexane: mp 166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.83 (s, 3H), 0.84 (s, 3H), 1.20−1.31 (m, 3H), 1.35−1.65 (m, 4H), 1.68−1.93 (m, 6H), 1.97−2.12 (m, 5H), 2.88 (s, 6H), 3.08 (s, 2H), 3.13 (br s, 2H), 3.66 (s, 3H), 3.68 (s, 3H), 6.43−6.48 (m, 1H), 6.70 (br s, 1H), 6.99−7.03 (m, 1H); IR ν_{max} (Nujol) 1740, 1620, 1580 cm^{-1}. Anal. Calcd for $C_{34}H_{43}NO_4$: C, 77.09; H, 8.14; N, 2.64. Found: C, 77.20; H, 8.44; N, 2.55.

(1α,4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,11α,11a*β*,11bα,11c*β*,12α,-12a*β*)-1,4,4a,5,5a,5b,5c,6,11,11a,11b,11c,12,12a-Tetradecahydro-1,4-ethano-5,12:6,11-dimethano-5b,11b-dimethyl-8-(*N*,*N*-dimethylamino)-2,3-bis(methylene)naphtho[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene (8e). The reduction of **46** (1.00 g, 1.89 mmol) with $LiAlH_4$ (0.50 g, 13 mmol) in THF (20 mL) was performed according to the procedure for **17c** (see above). The crude product **47** (0.86 g, 96%) was dried over P_2O_5, under vacuum, and used in the next reaction: ^{1}H NMR (60 MHz, $CDCl_3$) δ (ppm) 0.9 (s, 6H), 1.3−1.8 (m, 10H), 1.85−2.2 (m, 10H), 2.9 (s, 6H), 3.2 (br s, 4H), 3.3−3.7 (m, 6H), 6.5 (br d, lH), 6.7 (br d, 1H), 7.0 (br d, 1H); IR ν_{max} (Nujol) 3320, 1620, 1580 cm^{-1}.

The bistosylation of **47** (0.86 g, 1.82 mmol) with *p*-toluenesulfonyl chloride (1.12 g, 5.89 mmol) in pyridine (20 mL) was performed according to the procedure for **40** (see above). The crude product **48** (1.20 g, 84%) was dried over P_2O_5, under vacuum, and used in the next reaction: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.83 (s, 3H), 0.84 (s, 3H), 1.13−1.29 (m, 4H), 1.44−1.65 (m, 6H), 1.69−1.83 (m, 4H), 1.85−2.00 (m, 4H), 2.42 (s, 3H), 2.45 (s, 3H), 2.91 (s, 6H), 3.13 (s, 1H), 3.15 (s, 1H), 3.80−3.88 (m, 4H), 6.47 (dd, J = 2.4, 8.0 Hz, 1H), 6.73 (d, J = 2.4 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 7.30−7.36 (m, 4H), 7.71−7.77 (m, 4H).

The bisdehydrotosylation of **48** (1.10 g, 1.40 mmol) with *t*-BuOK (1.0 g, 8.9 mmol) in DMSO (15 mL) was performed according to the procedure for **7d** (see above). The crude product was subjected to column chromatography (silica, benzene) and recrystallized from hexane to give **8e** as a white solid (0.296 g, 48%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.87 (s, 6H), 1.44 (br d, J = 11.6 Hz, 2H), 1.46 (s, 2H), 1.48 (d, J = 11.0 Hz, 1H), 1.54 (d, J = 9.2 Hz, 1H), 1.74 (d, J = 9.2 Hz, 1H), 1.86 (s, 2H), 1.87 (d, J = 11.6 Hz, 1H), 1.91 (s, 2H), 1.95 (d, J = 11.0 Hz, 1H), 2.07 (s, 2H), 2.31 (s, 2H), 2.90 (s, 6H), 3.13 (s, 1H), 3.15 (s, 1H), 4.68 (s, 2H), 5.23 (s, 2H), 6.45 (dd, J = 2.4, 8.0 Hz, 1H), 6.70 (d, J = 2.4 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 9.73, 9.78, 22.32, 31.13, 39.30, 40.71, 41.30, 42.74, 43.59, 43.88, 43.97, 44.39, 45.03, 50.80, 51.30, 53.89, 102.55, 106.91, 109.45, 120.87, 136.71, 149.06, 149.33, 150.93. Anal. Calcd for $C_{32}H_{39}N \cdot H_2O$: C, 84.43; H, 9.07; N, 3.07. Found: C, 84.70; H, 9.22; N, 3.12.

(1α4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,6a*β*,7α,10α,10*β*,11α,11a*β*,-11bα,11c*β*,12α,12a*β*)-1,4,4a,5,5a,5b,5c,6,6a,7,10,10a,11,11a,-11b,11c,12,12a-Octadecahydro-1,4:7,10-diethano-5,12:6,-11-dimethano-5b,11b-dimethyl-2,3,8,9-tetrakis-(methylene)naphtho[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]naphthalene (9). A solution of **60** (10.0 g, 42.0 mmol)[19] and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (25.0 g, 94.7 mmol) in xylene (bp 138−141 °C) (100 mL) was refluxed for 18 h. Azeotropic removal of the xylene, through addition of ethanol (100 mL), gave a solid residue which was assumed to be **61** (32.1 g, 94%) since its 300 MHz ^{1}H NMR spectrum revealed the complete absence of the peak at 6.01 ppm due to the double-bond protons of **60**.

Sodium metal (25.0 g, 1.1 mol) was added piecewise to a refluxing solution of **61** (10.0 g, 13.1 mmol) in THF (200 mL) and 2-propanol (400 mL). The resulting mixture was refluxed for 18 h. Methanol (50 mL) was added to the cooled reaction mixture, followed by crushed ice (100 mL). Extraction with CH_2Cl_2 (3 × 150 mL) and evaporation of the organic extracts

(after washing with water and drying) gave the bisketal **62** (5.4 g, 85%) which was not purified further.

A solution of bisketal **62** (5.2 g, 10.6 mmol) in formic acid (50 mL) and THF (20 mL) was stirred for 18 h at 25 °C. The formic acid was removed by extraction with water and saturated $NaHCO_3$. Evaporation of the organic extracts gave diketone **63** (3.85 g, 91%). This material was unstable at elevated temperatures and could not be fully characterized: IR ν_{max} (Nujol) 1770 cm^{-1}.

A solution of the diketone **63** (3.5 g, 8.8 mmol) and dimethyl fumarate (3.0 g, 20.8 mmol) in toluene (30 mL) was refluxed for 18 h. The solvent was then removed under reduced pressure to give the tetraester **64** (5.9 g, 94%) which was not purified further.

The tetraester **64** (5.5 g, 8.7 mmol) in ethyl acetate (100 mL) was hydrogenated at 1 atm and 25 °C using 10% Pd/C (100 mg) until uptake of H_2 had ceased. Standard workup procedures gave the saturated tetraester **65** (5.5 g, 98%) whose ^{1}H NMR spectrum revealed the absence of two peaks (triplets) at 6.14 and 6.38 ppm due to the double-bond protons.

A solution of **65** (5.5 g, 8.7 mmol) in THF (100 mL) was added to a suspension of $LiAlH_4$ (1.5 g, 39.5 mmol) in THF (50 mL), and the mixture was refluxed for 18 h. To the chilled reaction mixture were added water (1.5 mL), 15% NaOH (1.5 mL), and more water (4.5 mL) successively. The mixture was then filtered, and the filtrate was evaporated under reduced pressure to give the tetrol **66** (3.9 g, 86%) which was not further purified: IR ν_{max} (Nujol) 3254 cm^{-1}.

To a cooled (−5 °C) solution of the tetrol **66** (3.8 g, 7.3 mmol) in dry pyridine (50 mL) was added *p*-toluenesulfonyl chloride (5.6 g, 29.4 mmol). The resulting mixture was maintained at −5 °C for 36 h. The reaction was then quenched with crushed ice, and the solution was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed successively with 1 M HCl (3 × 100 mL) and saturated $NaHCO_3$ (100 mL) before being dried and concentrated under reduced pressure to give the tetratosylate **67** (7.5 g, 91%) which was not purified.

To a solution of the tetratosylate **67** (7.0 g, 6.2 mmol) in dry DMSO (50 mL) was added *t*-BuOK (4.0 g, 36.8 mmol). The mixture was then stirred at 25 °C for 18 h. Ice water was added, and the product was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extracts were washed with water (3 × 100 mL) and brine (3 × 50 mL) to remove all traces of DMSO and dried, and the solvent was removed under reduced pressure. The residue was then chromatographed (silica, EtOAc:hexane 30:70) to give pure tetraene **9** (1.4 g, 66%): mp 225 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.76 (s, 6H), 1.42 (br d, J = 9.9 Hz, 6H), 1.51 (s, 4H), 1.85 (m, 4H), 1.89 (d, J = 10.1 Hz, 2H), 1.91 (s, 4H), 2.01 (s 4H), 2.30 (s, 4H), 4.67 (s, 4H), 5.22 (s 4H). Anal. Calcd for $C_{34}H_{42}$: C, 90.61; H, 9.39. Found: C, 90.38; H, 9.51.

(1α,4α,4a*β*,9α,9a*β*,10α)-1,2,3,4,4a,9,9a,10-Octahydro-7-acetamido-2,3-bis(acetoxymethyl)-6-nitro-1,4-ethano-9,-10-methanoanthracene (49). The nitration of **36** (7.60 g, 17.8 mmol) with $Cu(NO_3)_2 \cdot 2.5H_2O$ (5.30 g, 22.8 mmol) in acetic anhydride (100 mL) was performed according to the procedure for **34** (see above). The crude product was subjected to column chromatography (silica, light petroleum ether/ethyl acetate 70:30) and recrystallized from hexane to give the diasereometric mixture of **49** as a yellow solid (6.93 g, 83%): mp 62−63 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.25−1.53 (m, 4H), 1.55−1.67 (m, 4H), 1.80−1.91 (m, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.25 (s, 3H), 2.33 (d, J = 10.5 Hz, 1H), 3.22 and 3.27 (s, 1H), 3.27 and 3.31 (s, 1H), 3.70−3.83 (m, 1H), 3.94−4.10 (m, 3H), 7.95 and 7.98 (s, 1H), 8.55 and 8.59 (s, 1H), 10.53 and 10.56 (s, 1H). Anal. Calcd for $C_{25}H_{30}N_2O_7 \cdot {}^1/_2C_6H_{14}$: C, 65.47; H, 7.26; N, 5.45. Found: C, 65.72; H, 7.05; N, 5.50.

(1α,4α,4a*β*,5α,18α,18a*β*)-1,2,3,4,4a,5,18,18a-Octahydro-2,3-bis(hydroxymethyl)-1,4-ethano-5,18-methanonaphtho-[2″,3″-*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine (56). A stirred suspension of **49** (1.89 g, 4.02 mmol) in hydrazine hydrate (40 mL) was heated at 100 °C for 13 h under argon atmosphere. The solvent was evaporated under high vacuum to give **51** as a yellow solid. The crude product was used in the next reaction. ^{1}H NMR indicated complete loss of acetyl groups.

A solution of the crude **51** in hydrazine hydrate (11 mL, 0.23 mol) and ethanol (50 mL) over 5% Pd/C (0.10 g) was heated at reflux for 2 h under an argon atmosphere. The catalyst was remove by suction filtration, and the solvent was evaporated under reduced pressure to give a yellow oil. Water (50 mL) was added, and the resulting suspension was extracted with $CHCl_3$ (7 × 100 mL). The organic extracts were combined and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give **53** as an off-white solid (0.70 g, 55% from **49**): ^{1}H NMR (300 MHz, d_6-DMSO) δ (ppm) 0.89−0.93 (m, 1H), 1.03−1.15 (m, 4H), 1.33 (d, J = 9.0 Hz, 1H), 1.46 (s, 1H), 1.47 (s, 1H), 1.62−1.73 (m, 1H), 1.77 (br s, 2H), 2.12 (d, J = 9.0 Hz, 1H), 2.83 (s, 1H), 2.88 (s, 1H), 3.05−3.40 (m, 4H), 4.10 (br s, 4H), 4.46 (br s, 2H), 6.38 (s, 2H).

A stirred solution of **53** (0.70 g, 2.23 mmol) and 1,10-phenanthroline-5,6-dione (**55**) (0.42 g, 2.00 mmol) in THF (100 mL) was heated at reflux, under an argon atmosphere for 10 h. The solvent was evaporated under reduced pressure to give a yellow solid which was recrystallized from ethyl acetate to give **56** as a yellow solid (0.89 g, 91%): mp 224 °C; ^{1}H NMR (300 MHz, d_6-DMSO) δ (ppm) 1.30−1.70 (m, 8H), 1.77−1.86 (m, 3H), 2.42 (d, J = 11.2 Hz, 1H), 2.60 (br s, 2H), 3.15−3.49 (m, 6H), 7.68 (dd, J = 4.4, 8.2 Hz, 2H), 7.86 (s, 2H), 9.10 (d, J = 4.4 Hz, 2H), 9.52 (d, J = 8.2 Hz, 2H). Anal. Calcd for $C_{31}H_{28}N_4O_2 \cdot {}^3/_2H_2O$: C, 72.21; H, 6.06; N, 10.87. Found: C, 72.28; H, 6.16; N, 11.02.

(1α,4α,4a*β*,5α,18α,18a*β*)-1,4,4a,5,18,18a-Hexahydro-2,3-bis(methylene)-1,4-ethano-5,18-methanonaphtho[2″,3″-*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine (7g). The bistosylation of **56** (0.87 g, 1.78 mmol) with *p*-toluenesulfonyl chloride (3.00 g, 15.7 mmol) in pyridine (50 mL) was performed according to the procedure for **40** (see above). The reaction mixture was poured onto ice (200 g), resulting in the formation of a white precipitate. This was isolated by suction filtration and washed with water (3 × 50 mL). The crude bistosylate **58** (1.26 g, 89%) was dried over P_2O_5, under vacuum, and used in the next reaction: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.24−1.30 (m, 2H), 1.41−1.51 (m, 2H), 1.60 (s, 1H), 1.63 (s, 1H), 1.77−1.85 (m, 3H), 2.01 (s, 2H), 2.36 (s, 3H), 2.42 (d, J = 11.2 Hz, 1H), 2.44 (s, 3H), 3.42 (s, 1H), 3.50 (s, 1H), 3.70−3.76 (m, 2H), 3.92−3.97 (m, 2H), 7.23−7.36 (m, 4H), 7.59−7.67 (m, 4H), 7.76 (dd, J = 4.4, 8.2 Hz, 2H), 7.91 (s, 2H), 9.23 (d, J = 4.4 Hz, 2H), 9.58 (d, J = 8.2 Hz, 2H).

The bisdehydrotosylation of **58** (1.26 g, 1.57 mmol) with *t*-BuOK (1.1 g, 9.8 mmol) in DMSO (10 mL) was performed according to the procedure for **7e** (see above). The crude product was subjected to column chromatography (silica, CH_2Cl_2/methanol 98:2) and recrystallized from hexane to give **7g** as an orange solid (0.12 g, 17%): mp 208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.63 (d, J = 8.3 Hz, 2H), 1.84 (d, J = 10.5 Hz, 1H), 1.89 (s, 2H), 1.97 (d, J = 8.3 Hz, 2H), 2.56 (d, J = 10.5 Hz, 1H), 2.69 (s, 2H), 3.58 (s, 2H), 4.78 (s, 2H), 5.25 (s, 2H), 7.79 (dd, J = 4.4, 8.2 Hz, 2H), 7.98 (s, 2H), 9.26 (d, J = 4.4 Hz, 2H), 9.63 (d, J = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 22.05, 40.77, 43.10, 43.28, 46.88, 103.70, 119.02, 124.15, 128.00, 129.90, 133.87, 139.42, 142.80, 150.79, 151.77, 152.84; HRMS calcd for $C_{31}H_{24}N_4$ 452.2001, found 452.2032.

(1α,4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,11α,11a*β*,11bα,11c*β*,12α,-12a*β*)-1,2,3,4,4a,5,5a,5b,5c,6,11,11a,11b,11c,12,12a-Hexadecahydro-9-acetamido-2,3-*trans*-bis(acetoxymethyl)-5b,11b-dimethyl-8-nitro-1,4-ethano-5,12:6,11-dimethanonaphtho[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta-[1,2-*b*]naphthalene (50). The nitration of **37** (2.32 g, 4.06 mmol) with $Cu(NO_3)_2 \cdot 2.5H_2O$ (1.08 g, 4.64 mmol) in acetic anhydride (30 mL) and CH_2Cl_2 (10 mL) was performed according to the procedure for **34** (see above). The crude product was subjected to column chromatography (silica, light petroleum ether/ethyl acetate 50:50) and recrystallized from CH_2Cl_2/ hexane to give **50** as a yellow solid (2.03 g, 81%): mp 170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.87 (s, 6H), 1.15−1.27 (m, 2H), 1.36−1.40 (m, 2H), 1.46 (s, 1H), 1.50 (s, 1H), 1.56−1.63 (m, 5H), 1.82 (s, 1H), 1.85−1.92 (m, 4H), 1.94 (s, 2H), 2.00 (s, 1H), 2.04 (s, 6H), 2.06 (s, 1H), 2.27 (s, 3H), 3.26 (s, 1H), 3.32 (s, 1H), 3.96−4.10 (m, 4H), 7.96 (s, 1H), 8.55 (s, 1H), 10.53 (br s, 1H). Anal. Calcd for $C_{36}H_{44}N_2O_7 \cdot {}^1/_2H_2O$: C, 69.10; H, 7.25; N, 4.48. Found: C, 69.19; H, 7.50; N, 4.28.

(1α,4α,4a*β*,5α,5a*β*,5bα,5c*β*,6α,19α,19a*β*,19bα,19c*β*,20α,-20a*β*)-1,2,3,4,4a,5,5a,5b,5c,6,19,19a,19b,19c,20,20a-Hexa-

decahydro-2,3-bis(methylene)-5b,19b-dimethyl-1,4-ethano-5,20:6,19-dimethanonaphtho[2′′′′,3′′′′:3′′′,4′′′]-cyclobuta[1′′′,2′′′:3′′,4′′]cyclobuta[1′′,2′′-*i*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine (8g). The hydrolysis of **50** (2.53 g, 4.10 mmol) with hydrazine hydrate (50 mL) was performed according to the procedure for **51** (see above). The crude product **52** was isolated as a yellow solid and not purified further. ^{1}H NMR showed no acetyl groups.

The reduction of the crude **52** with hydrazine hydrate (10 mL, 21 mmol) in ethanol (50 mL) over 5% Pd/C (0.10 g) was performed according to the procedure for **53** (see above). The crude product **54** was isolated as a yellow solid (1.31 g, 69% from **50**) and not purified further: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.87 (s, 6H), 1.19−1.46 (m, 7H), 1.50−1.60 (m, 4H), 1.82−1.87 (m, 2H), 1.96 (s, 2H), 2.02−2.09 (m, 5H), 2.32 (br s, 4H), 2.71 (br s, 2H), 3.08 (br s, 2H), 3.52−3.61 (m, 4H), 6.52 (s, 2H).

The condensation of **54** (1.31 g, 2.82 mmol) and 1,10-phenanthroline-5,6-dione (**55**) (0.59 g, 2.81 mmol) in THF (100 mL) was performed according to the procedure for **56** (see above). The crude product was crystallized from ethyl acetate to give **57** as a yellow solid (1.72 g, 96%) and not purified further: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.97 (s, 3H), 0.98 (s, 3H), 1.21−1.46 (m, 7H), 1.50−1.60 (m, 4H), 1.82−1.87 (m, 2H), 1.96 (s, 2H), 2.02 (s, 1H), 2.05−2.07 (m, 2H), 2.16 (s, 2H), 2.00−2.50 (br s, 2H), 3.52−3.61 (m, 6H), 7.78 (dd, J = 4.4, 8.2 Hz, 2H), 8.01 (s, 2H), 9.25 (d, J = 4.4 Hz, 2H), 9.64 (d, J = 8.2 Hz, 2H).

The bistosylation of **57** (1.70 g, 2.67 mmol) with *p*-toluenesulfonyl chloride (2.00 g, 10.5 mmol) in pyridine (20 mL) was performed according to the procedure for **58** (see above). The crude product **59** (2.13 g, 84%) was dried over P_2O_5, under vacuum, and used in the next reaction: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.95 (s, 3H), 0.96 (s, 3H), 1.21−1.46 (m, 7H), 1.50−1.60 (m, 4H), 1.82−1.87 (m, 2H), 1.96 (s, 2H), 2.02 (s, 1H), 2.05−2.07 (m, 2H), 2.16 (s, 2H), 2.40 (s, 3H), 2.44 (s, 3H), 3.57 (s, 2H), 3.77−3.87 (m, 4H), 7.30 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.79 (dd, J = 4.4, 8.2 Hz, 2H), 8.00 (s, 2H), 9.23 (d, J = 4.4 Hz, 2H), 9.66 (d, J = 8.2 Hz, 2H).

The bisdehydrotosylation of **59** (2.13 g, 2.25 mmol) with *t*-BuOK (0.80 g, 7.1 mmol) in DMSO (10 mL) was performed according to the procedure for **7e** (see above). The crude product was subjected to column chromatography (silica, CH_2Cl_2/methanol 98:2) and recrystallized from hexane to give **8g** as an orange solid (0.31 g, 23%): mp 270 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 0.99 (s, 6H), 1.44−1.55 (m, 6H), 1.94 (s, 2H), 2.01 (d, J = 10.3 Hz, 1H), 2.07−2.17 (m, 5H), 2.32 (s, 2H), 3.56 (s, 2H), 4.67 (s, 2H), 5.20 (s, 2H), 7.79 (dd, J = 4.4, 8.2 Hz, 2H), 8.00 (s, 2H), 9.23 (d, J = 4.4 Hz, 2H), 9.66 (d, J = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 9.84, 22.29, 31.20, 39.33, 40.68, 42.62, 43.81, 44.40, 45.05, 50.36, 54.25, 102.67, 119.52, 124.20, 127.31, 128.04, 133.91, 139.31, 142.80, 150.79, 151.77, 152.84; MALDI MS m/z (rel intensity) 599 (M + 1, 100).

General Procedure for the Preparation of the Ball-and-Chain C_{60} Diels−Alder Adducts 2e−h and 3a,b,d−h. A solution of the diene **7e**−**h** or **8a**,**b**,**d**−**h** in 5−10 mL of toluene was added *via* syringe pump (2−6 h) to a solution of C_{60} in toluene under reflux. After the addition was completed, the reaction was maintained at reflux for an additional 1−2 h. The reaction mixture was cooled to 25 °C, concentrated to a small volume, and purified by flash chromatography on silica gel. Yields of adducts are based on isolated material, except when the yield based on recovered C_{60} is also indicated. Elemental analyses were generally unsatisfactory due to the strong solvent inclusion properties and/or incomplete combustion of these C_{60} derivatives.

***N*,*N*-Dimethylaniline 6-Bond C_{60} Adduct 2e.** Following the general procedure, C_{60} (137.8 mg, 0.19 mmol), diene **7e** (87.4 mg, 0.3 mmol), and toluene (50 mL) were used. Flash chromatography on silica gel (toluene) afforded the product **2e** as dark brown crystals (118.1 mg, 61%): ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.77 (d, J = 9.0 Hz, 2H), 1.80 (d, J = 10.0 Hz, 1H), 2.01 (s, 2H), 2.04 (d, J = 9.0 Hz, 2H), 2.44 (d, J = 10.0 Hz, 1H), 2.89 (s, 6H), 2.97 (br s, 2H), 3.07 (br s, 1H), 3.09 (s, 1H), 4.0−4.2 (AB q, J = 14.0 Hz, 4H), 6.32 (d, J = 8.0 Hz, 1H), 6.67 (br s, 1H), 6.97 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ (ppm) 22.31, 22.34, 39.14, 39.20, 41.1, 43.8, 44.0, 44.02, 45.5, 46.5, 47.3, 66.2, 106.7, 109.0, 120.5, 135.1, 135.3, 139.7, 139.90, 139.94, 141.34, 141.39, 141.8, 141.9, 142.1, 142.32, 142.38, 142.41, 142.89, 142.93, 143.4, 143.7, 144.49, 144.51, 144.54, 145.11, 145.18, 145.20, 145.27, 145.36, 145.56, 145.63, 146.01, 146.03, 146.28, 146.30, 147.43, 148.7, 151.9, 156.9, 158.4; FAB MS m/z (rel intensity) 1012 (100, MH^+), 720 (90, C_{60}^+); MALDI FTMS[41] m/z (rel intensity) 1012 (MH^+, 100), 720 (C_{60}^+, 7); HRMS (FAB) calcd for $C_{81}H_{25}N{\cdot}H^+$ 1012.2065, found 1012.2046.

1,4-Dimethoxynaphthalene 7-Bond C_{60} Adduct 2f. Following the general procedure, C_{60} (36 mg, 0.05 mmol), diene **7f** (19.2 mg, 0.05 mmol), and toluene (10 mL) were used. Flash chromatography (CS_2/toluene 9:1) gave the cycloadduct **2f** as dark brown crystals (20 mg, 36%): ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 1.43 (br d, J = 11.6 Hz, 1H), 1.66 (br d, J = 8.4 Hz, 2H), 1.95 (d, J = 11.6 Hz, 1H), 1.99 (d, J = 8.4 Hz, 2H), 2.02 (br s, 2H), 2.36 (s, 2H), 2.95 (br s, 2H), 3.47 (s, 2H), 4.06 (s, 6H), 4.18 (s, 4H), 7.25 (dd, J = 6.4, 3.4 Hz, 2H), 7.92 (dd, J = 6.4, 3.4 Hz, 2H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ (ppm) 22.6, 23.6, 39.1, 41.8, 44.0, 46.5, 51.9, 56.9, 66.2, 121.3, 121.8, 124.4, 126.7, 135.09, 135.12, 139.9 (2C), 141.29, 141.31, 141.76, 141.78, 142.95, 142.03, 142.14, 142.3, 142.8, 142.9, 144.41, 144.43, 145.08, 145.10, 145.15, 145.17, 145.23, 145.46, 145.50, 146.0 (2C), 146.22, 146.24, 147.34; FAB MS m/z (rel intensity) 1105 (20, MH^+), 720 (100, C_{60}^+).

Dipyridophenazine 6-Bond C_{60} Adduct 2g. Method A. Following the general procedure, C_{60} (14.4 mg, 0.02 mmol), diene **7g** (9.04 mg, 0.024 mmol), and toluene (15 mL) were used. Flash chromatography (toluene/chloroform 1:3) gave the product **2g** as dark brown crystals (5.6 mg, 24%). Compound **2g** slowly decomposes during chromatography and on standing in air and light in solution: ^{1}H NMR (500 MHz, $CDCl_3/CS_2$ 1:1) δ (ppm) 1.86 (d, J = 8.8 Hz, 2H), 2.06 (d, J = 10.4 Hz, 1H), 2.13 (d, J = 8.8 Hz, 2H), 2.22 (s, 2H), 2.76 (d, J = 10.4 Hz, 1H), 3.17 (s, 2H), 3.60 (s, 2H), 4.0−4.2 (AB q, J = 14.1 Hz, 4H), 7.80 (dd, J = 8.2, 4.4 Hz, 2H), 8.06 (s, 2H), 9.27 (dd, J = 4.4, 1.7 Hz, 2H), 9.65 (dd, J = 8.2, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3/CS_2$ 1:1) δ (ppm) 38.93, 42.92, 45.31, 45.62, 66.19, 119.22, 123.8, 127.71, 133.26, 135.04, 135.26, 139.52, 140.02, 141.39, 141.45, 141.87, 141.94, 142.12, 142.35, 142.46, 142.54, 142.9, 143.69, 144.50, 144.60, 145.13, 145.25, 145.29, 145.35, 145.64, 146.10, 146.30, 146.40, 147.50, 147.92, 151.90, 154.91, 156.99, 158.26; FAB MS m/z (rel intensity) 1173 (28, MH^+), 720 (100, C_{60}^+); HRMS calcd for $C_{91}H_{24}N_4{\cdot}H^+$ 1173.2079, found 1173.2089.

Method B. To a solution of C_{60} (69.3 mg, 0.09 mmol) in 15 mL of *o*-dichlorobenzene in a pressure tube was added diene **7g** (29 mg, 0.064 mmol) in 5 mL of *o*-dichlorobenzene. The solution was deoxygenated and the tube heated in an oil bath at 120−125 °C for 17 h. After being cooled to 25 °C, the reaction mixture was diluted by adding 20 mL of light petroleum ether. After 1 h, the precipitate was collected by filtration. The residue was dissolved in chloroform (25 mL), and cyclohexane (50 mL) was added. The mixture was filtered, and the filtrate was evaporated to give a brown solid. The solid was further purified by being dissolved in a minimum amount of chloroform (1 mL), followed by precipitation with light petroleum ether, to give a brown solid. The yield was 25 mg (34%) of **2g** identical to material prepared above.

Anthracene 6-Bond C_{60} Adduct 2h. Following the general procedure, C_{60} (72 mg, 0.1 mmol), diene **7h** (43.5 mg, 0.125 mmol), and toluene (65 mL) were used. Flash chromatography (cyclohexane/chloroform 4:1) gave the cycloadduct **2h** as dark brown crystals (55.3 mg, 52%), which were somewhat light-sensitive ($^1O_2$ formation): ^{1}H NMR (500 MHz, $CDCl_2CDCl_2/CS_2$ 2:1) δ (ppm) 1.90 (d, J = 8.9 Hz, 2H), 2.00 (d, J = 10.4 Hz, 1H), 2.18 (d, J = 8.9 Hz, 2H), 2.25 (s, 2H), 2.71 (d, J = 10.4 Hz, 1H), 3.17 (s, 2H), 3.46 (s, 2H), 4.10 (d, J = 14.1 Hz, 2H), 4.28 (d, J = 14.1 Hz, 2H), 7.46 (dd, J = 6.4, 3.2 Hz, 2H), 7.72 (s, 2H), 7.98 (dd, J = 6.4, 3.2 Hz, 2H), 8.29 (s, 2H); ^{13}C NMR (125.8 MHz, $CDCl_2CDCl_2/CS_2$ 2:1) δ (ppm) 22.5, 39.2, 42.6, 44.0, 45.0, 46.2, 66.2, 117.5, 124.9, 125.7, 127.9, 131.1, 131.3, 135.1, 135.3, 139.97, 140.03, 141.40, 141.45, 141.85, 141.97, 142.17, 142.38, 142.44, 142.45, 142.93, 142.98, 143.45, 144.52, 144.59, 145.14, 145.25, 145.31, 145.40, 145.61, 145.63,

146.07, 146.32, 146.35, 147.5, 148.9, 156.9, 158.5; FAB MS *m/z* (rel intensity) 1069 (30, MH^+) 720 (100, C_{60}^+); HRMS calcd for $C_{87}H_{24}{\cdot}H^+$ 1069.1956, found 1069.1949.

1,4-Dimethoxybenzene 10-Bond C_{60} Adduct 3a. Following the general procedure, C_{60} (72.1 mg, 0.1 mmol), diene **8a** (44.7 mg, 0.098 mmol), and toluene (50 mL) were used. Flash chromatography (toluene/hexanes 1:9) gave C_{60} (29.9 mg, 41%). Further elution with toluene/hexanes (1:1) gave the product **3a** as dark brown crystals (73.0 mg, 63%, quantitative based on consumed C_{60}): ^{1}H NMR (360 MHz, $CS_2/CDCl_3$ 2:1) δ (ppm) 0.92 (s, 6H), 1.45 (dt, J = 1.6, 9.3 Hz, 1H), 1.56 (br d, J = 11.1 Hz, 1H), 1.61 (br d, J = 7.6 Hz, 2H), 1.69 (br d, J = 9.3 Hz, 1H), 1.72 (br s, 2H), 1.89 (s, 2H), 1.92 (s, 2H), 1.96 (br d, J = 7.5 Hz, 2H), 2.07 (br d, J = 11.5 Hz, 1H), 2.11 (s, 2H), 2.82 (br s, 2H), 3.41 (s, 2H), 3.72 (s, 6H), 4.0−4.15 (AB q, J = 14.0 Hz, 4H), 6.46 (s, 2H); ^{13}C NMR (125.8 MHz, $CS_2/CDCl_3$ 2:1) δ (ppm) 9.63, 22.66, 30.64, 37.74, 38.97, 40.14, 43.36, 43.41, 43.95, 46.27, 49.81, 54.21, 55.33, 66.21, 108.46, 135.14, 135.16, 136.27, 139.88, 139.90, 141.31, 141.33, 141.80, 141.85, 142.12, 142.22, 142.34, 142.54, 142.83, 142.89, 144.47, 144.49, 145.16, 145.17, 145.19, 145.20, 145.25, 145.52, 145.71, 145.97, 145.98, 146.23, 146.27, 147.37, 147.47, 157.48, 158.00. Anal. Calcd for $C_{92}H_{38}O_2$ (1175.33): C, 94.02; H, 3.26. Found: C, 94.08; H, 2.94.

1,4-Dimethoxynaphthalene 10-Bond C_{60} Adduct 3b. Following the general procedure, C_{60} (14.4 mg, 0.02 mmol), diene **8b** (12.1 mg, 0.024 mmol), and toluene (13 mL) were used. Flash chromatography (toluene/cyclohexane 1:1) gave the adduct **3b** as dark brown crystals (13.9 mg, 59%): ^{1}H NMR (360 MHz, $CDCl_2{-}CDCl_2$) δ (ppm) 1.02 (s, 6H), 1.53−1.63 (m, 2H), 1.65−1.68 (m, 2H), 1.74 (s, 2H), 1.90−1.98 (m, 2H), 1.98 (s, 2H), 2.08−2.12 (m, 2H), 2.13 (s, 2H), 2.19 (s, 2H), 2.83 (s, 2H), 3.67 (s, 2H), 3.99 (s, 6H), 4.05−4.2 (AB q, J = 14.1 Hz, 2H), 7.46 (dd, J = 6.3, 3.3 Hz, 2H), 8.09 (dd, J = 6.3, 3.3 Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3/CS_2$ 1:1) δ (ppm) 10.0, 22.7, 29.8, 30.8, 37.8, 38.9, 40.7, 44.1, 44.3, 46.3, 50.8, 54.3, 61.9, 66.6, 121.5, 125.2, 127.7, 135.36, 135.42, 140.03, 140.07, 141.5, 142.05, 142.09, 142.47, 142.54, 142.57, 142.9, 143.1, 144.0, 144.74, 144.76, 145.3, 145.4, 145.64, 145.66, 145.9, 146.2, 146.47, 146.51, 147.7, 158.2, 158.5. No parent ion could be observed either by FAB or MALDI mass spectroscopy.

Acetanilide 10-Bond C_{60} Adduct 3d. Following the general procedure, C_{60} (244 mg, 0.339 mmol), diene **8d** (226 mg, 0.5 mmol), and toluene (50 mL) were used. Flash chromatography with toluene first gave C_{60} (144.6 mg, 59%). Further elution with toluene/ethyl acetate (3:2) gave the cycloadduct **3d** as dark brown crystals (65.8 mg, 41%): ^{1}H NMR (500 MHz, CS_2/acetone-d_6 1:1) δ (ppm) 0.98 (s, 3H), 0.99 (s, 3H), 1.54 (br d, J = 9.3 Hz, 2H), 1.62 (br d, J = 11.4 Hz, 2H), 1.68 (br d, J = 8.6 Hz, 2H), 1.79 (m, 3H), 1.94 (br s, 2H), 1.95−1.98 (m, 1H), 1.98 (s, 3H), 2.12 (s, 2H), 2.43 (br s, 2H), 2.90 (br s, 2H), 3.17 (br s, 2H), 4.15−4.3 (AB q, J = 14.0 Hz, 4H), 6.93 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 7.46 (s, 1H), 8.68 (br s, 1H); ^{13}C NMR (125.8 MHz, CS_2/acetone-d_6 1:1) δ (ppm) 10.4, 23.5, 24.3, 31.5, 38.7, 39.8, 44.0, 44.31, 44.32, 44.44, 44.67, 44.82, 47.19, 47.20, 51.6, 51.9, 55.3, 67.2, 113.5, 116.7, 121.1, 136.07, 136.09, 137.8, 140.71, 140.74, 142.17, 142.19, 142.66, 142.72, 142.92, 143.02, 143.14, 143.19, 143.47, 143.49, 143.70, 143.73, 145.33, 145.37, 146.01, 146.04, 146.18, 146.28, 146.44, 146.53, 146.8, 147.1, 148.2, 148.4, 158.5, 159.2, 167.3; FT-IR (KBr) ν (cm^{-1}) 3421 m br (N−H), 1671 s (C=O), 527 s (C_{60}). No parent ion could be observed either by FAB or MALDI mass spectroscopy.

***N,N*-Dimethylaniline 10-Bond C_{60} Adduct 3e.** Following the general procedure, C_{60} (72 mg, 0.1 mmol), diene **8e** (43.7 mg, 0.1 mmol), and toluene (30 mL) were used. Flash chromatography (toluene) gave the product **3e** as dark brown crystals (69.3 mg, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.91 (s, 3H), 0.92 (s, 3H), 1.53 (d, J = 9.2 Hz, 1H), 1.55 (d, J = 11.2 Hz, 1H), 1.61 (d, J = 8.4 Hz, 2H), 1.71 (s, 2H), 1.74 (d, J = 9.2 Hz, 1H), 1.92 (s, 4H), 1.95 (d, J = 8.4 Hz, 2H), 2.05 (d, J = 11.2 Hz, 1H), 2.10 (s, 2H), 2.82 (s, 2H), 2.88 (s, 6H), 3.10 (s, 1H), 3.13 (s, 1H), 4.05−4.2 (AB q, J = 13.9 Hz, 4H), 6.37 (dd, J = 8.0, 2.3 Hz, 1H), 6.61 (d, J = 2.3 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ (ppm) 9.74, 9.80, 22.6, 30.7, 37.69, 37.72, 39.0, 41.0, 42.7, 43.45, 43.58, 43.94, 44.3, 46.3, 50.9, 51.5, 54.3, 66.2, 106.8, 109.5, 120.8, 135.1, 135.2, 136.2, 139.85, 139.90, 141.3, 141.77, 141.83, 142.11, 142.22, 142.33, 142.52, 142.84, 142.87, 144.44, 144.48, 145.14, 145.20, 145.23, 145.5, 145.7, 146.0, 146.22, 146.26, 147.4, 148.3, 148.8, 157.4, 158.0; FAB MS *m/z* (rel intensity) 1158 (75, MH^+), 720 (100, C_{60}^+); HRMS calcd for $C_{92}H_{39}N{\cdot}H^+$ 1158.3161, found 1158.3121.

1,4-Naphthoquinone 10-Bond C_{60} Adduct 3f. Following the general procedure, C_{60} (72 mg, 0.1 mmol), diene **8f** (47.4 mg, 0.1 mmol), and toluene (75 mL) were used. Flash chromatography (toluene/cyclohexane 1:1) gave the product **3f** as dark brown crystals (68.8 mg, 58%): ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 0.94 (s, 6H), 1.50−1.72 (m, 6H), 1.74 (s, 2H), 1.96 (s, 2H), 1.95−2.0 (m, 1H), 2.05 (s, 2H), 2.11−2.16 (m, 1H), 2.16 (s, 2H), 2.86 (s, 2H), 3.57 (s, 2H), 4.05−4.2 (AB q, J = 14.1 Hz, 4H), 7.69 (dd, J = 5.7, 3.3 Hz, 2H), 8.06 (dd, J = 5.7, 3.3 Hz, 2H); ^{13}C NMR (125.8 MHz, toluene-d_8) δ (ppm) 9.4, 22.7, 30.6, 37.9, 38.9, 41.2, 41.3, 43.5, 43.9, 46.2, 48.7, 54.2, 66.2, 125.8, 127.8, 128.7, 132.5, 133.0, 135.16, 135.18, 139.97, 140.00, 141.4, 141.8, 141.9, 142.2, 142.3, 142.41, 142.42, 142.6, 142.9, 143.0, 144.49, 144.54, 145.16, 145.23, 145.6, 145.7, 146.0, 146.3, 147.4, 153.2, 157.5, 157.9, 180.3; FT-IR (KBr) ν (cm^{-1}) 1656 s (C=O), 1587 s, 1489 m, 1460 m, 1430 m (C=C), 523 s (C_{60}); FAB MS *m/z* (rel intensity) 1195 (20, MH^+), 720 (100, C_{60}^+); HRMS calcd for $C_{94}H_{34}O_2{\cdot}H^+$ 1195.2637, found 1195.2646.

Dipyridophenazine 10-Bond C_{60} Adduct 3g. Following the general procedure, C_{60} (36.0 mg, 0.05 mmol), diene **8g** (29.8 mg, 0.05 mmol), BHT (5.0 mg, 0.023 mmol), and toluene (18 mL) were used. Flash chromatography (toluene) gave the product **3g** as dark brown crystals (2.8 mg, 4.2%). Compound **3g** decomposes during chromatography and on standing in air and light in solution: ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.910 (s, 3H), 0.914 (s, 3H), 1.74 (s, 2H), 1.78 (d, J = 9.3 Hz, 1H), 1.85 (d, J = 5.8 Hz, 1H), 1.89 (d, J = 5.8 Hz, 1H), 1.92 (s, 2H), 1.97 (d, J = 9.3 Hz, 2H), 2.09 (s, 1H), 2.12 (s, 2H), 2.39 (br s, 5H), 2.85 (s, 2H), 3.17 (s, 2H), 4.09 (AB d, J = 14.1 Hz, 2H), 4.15 (AB d, J = 14.1 Hz, 2H), 6.25 (s, 1H), 6.65 (dd, J = 7.7, 2.0 Hz, 1H), 6.90 (d, J = 1.8 Hz, 1H), 6.99 (d, J = 7.7 Hz, 1H), 7.21 (br d, J = 8.3 Hz, 2H), 7.59 (br d, J = 8.3); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ (ppm) 9.8, 21.6, 22.6, 30.6, 37.7, 38.8, 43.8, 44.1, 46.2, 50.2, 50.3, 54.1, 66.5, 116.2, 119.9, 121.1, 127.3, 129.5, 133.5, 135.4, 136.4, 140.1, 141.5, 142.0, 142.1, 142.40, 142.42, 142.48, 142.6, 142.84, 142.86, 143.08, 143.11, 143.6, 144.73, 144.76, 145.33, 145.35, 145.44, 145.46, 145.53, 145.57, 145.81, 145.86, 145.99, 146.23, 146.27, 146.29, 146.51, 147.7, 149.1, 149.2, 158.1, 158.3; FT-IR (KBr) ν (cm^{-1}) 1459 m, 1425 m, 1381 m, 1337 m (C=C/C=N), 1155 s, 729 s, 528 s (C_{60}); HRMS calcd for $C_{102}H_{38}N_4$ 1318.3096, found 1318.2996.

10-Bond C_{60} Adduct 3h. Following the general procedure, C_{60} (14.4 mg, 0.02 mmol), diene **8h** (8.7 mg, 0.025 mmol), and toluene (15 mL) were used. Flash chromatography (cyclohexane/chloroform 9:1) gave the product **3h** as dark brown crystals (18.3 mg, 86%): ^{1}H NMR (400 MHz, $CDCl_2{-}CDCl_2$) δ (ppm) 0.82 (s, 6H), 1.22−1.26 (m, 4H), 1.42−1.65 (m, 6H), 1.75 (s, 2H), 1.94−2.09 (m, 10H), 2.84 (s, 2H), 4.05−4.2 (AB q, J = 14.0 Hz, 4H); ^{13}C NMR (100.6 MHz, $CDCl_2{-}CDCl_2$) δ (ppm) 10.0, 22.7, 28.8, 30.7, 35.2, 36.2, 37.6, 38.9, 44.1, 45.0, 46.4, 52.7, 54.5, 66.6, 135.44, 135.46, 140.0, 140.1, 141.51, 141.54, 142.06, 142.11, 142.5, 142.55, 142.57, 142.8, 143.1, 144.8, 145.3, 145.38, 145.42, 145.45, 145.6, 145.7, 145.9, 146.0, 146.22, 146.24, 146.49, 146.50, 147.7, 158.1, 158.7; FAB MS *m/z* (rel intensity) 1067 (13, MH^+), 720 (100, C_{60}^+); HRMS calcd for $C_{86}H_{34}{\cdot}H^+$ 1067.2739, found 1067.2742.

Dumbbell 14-Bond Bis-C_{60} Adduct 4. A solution of 26.0 mg (0.058 mmol) of tetraene **9** and 70.0 mg (0.097 mmol) of C_{60} in 25 mL of oxygen-free *o*-dichlorobenzene was heated in the dark under argon at 135 °C for 7.5 h. The crude mixture was then filtered through a pad of silica gel with cyclohexane. After evaporation of the solvent *in vacuo*, the crude solid was dissolved in a minimum of CS_2. Flash chromatography on silica gel (a ratio of 100g SiO_2/1 mg material is necessary to obtain good solubility and separation) with cyclohexane afforded two fractions from which the compounds were obtained by partial evaporation and precipitation from methanol.

Fraction 1 afforded recovered C_{60} (47 mg, 0.065 mmol).

Fraction 2 afforded 25 mg (27%, 81% based on recovered C_{60}) of compound **4** as a dark brown crystalline material: ^{1}H

NMR (400 MHz, $CS_2/CDCl_3$ 5:1) δ (ppm) 0.91 (s, 6H), 1.55 (br d, J = 10.4 Hz, 2H), 1.63 (br d, J = 9.2 Hz, 4H), 1.79 (s, 2H), 1.95 (br s, 8H), 2.04 (br s, 8H), 2.84 (br s, 4H), 4.05−4.2 (AB q, J = 14.0 Hz, 8H); ^{13}C NMR (500 MHz, *o*-dichlorobenzene-d_4/$CDCl_3$ 5:1) δ (ppm) 9.8, 22.5, 26.8, 37.5, 38.8, 43.9, 44.7, 46.1, 54.2, 66.3, 119.7, 134.7, 135.2, 139.74, 139.79, 141.14, 141.17, 141.66, 141.70, 142.10, 142.18, 142.55, 142.60, 142.68, 142.86, 144.35, 144.37, 144.98, 145.04, 145.06, 145.15, 145.27, 145.47, 145.52, 145.82, 145.87, 146.13, 146.19, 147.26, 157.7, 158.2; FT-IR (KBr) ν (cm^{-1}) 1422 m (C=C), 524 s (C_{60}). No parent ion could be observed by FAB, MALDI, or electrospray[29] mass spectroscopy.

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