Syntheses of Rigid and Semirigid Molecules for Investigations of Photoinduced Electron Transfer Reactions

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Investigations of electron transfer reactions in donor–spacer–acceptor (DSA) molecules posessing small numbers of reactive conformations have significantly increased understanding of factors that control transfer rate constants. The syntheses of polynorbornane-based DSA molecules **12**, **16**, **20**, **26**, **30**, and **34** and heptacyclotetradecane-based DSA molecules **40**, **47**, **51**, and **60** are described. These molecules have been used to explore the effects of electronic symmetry, solvent electronic structure, and temperature on photoinduced electron transfer reactions.

Introduction

Photoinduced long-range electron transfer (eT) reactions have been the focus of extensive theoretical and experimental investigation in recent years.[1,2] The essential role of photoinduced eT in photosynthesis[3] and potential uses of systems undergoing efficient charge separation have resulted in a multidisciplinary effort at understanding these processes in detail. Though the photosynthetic reaction center is perhaps nature's most intriguing and important model for comparisons between theory and experiment, much of the physical understanding of the factors governing eT has come from work on smaller molecules. The effects of distance, orientation, driving force, solvent, temperature, and electric and magnetic fields on the rate constants of electron transfer in model systems have been investigated. These investigations have benefited from the use of rigid donor–spacer–acceptor (DSA) complexes, which has brought the problem into the realm of organic chemistry. Elegant molecules have originated in the laboratories of Closs,[4] Wasielewski,[5] Michel-Beyerle,[6] Dervan,[7] Verhoeven,[8] Paddon-Row,[9] Gust and Moore,[10] McLendon,[11] Sakata,[12] Osuka,[13] and elsewhere. During the past several years, we have designed and synthesized numerous DSA molecules to probe the influence of orbital symmetry, temperature, and solvent electronic structure on the rate constants of intramolecular electron transfer. We outline here the synthetic strategies involved in the construction of these molecules and their desired design characteristics.

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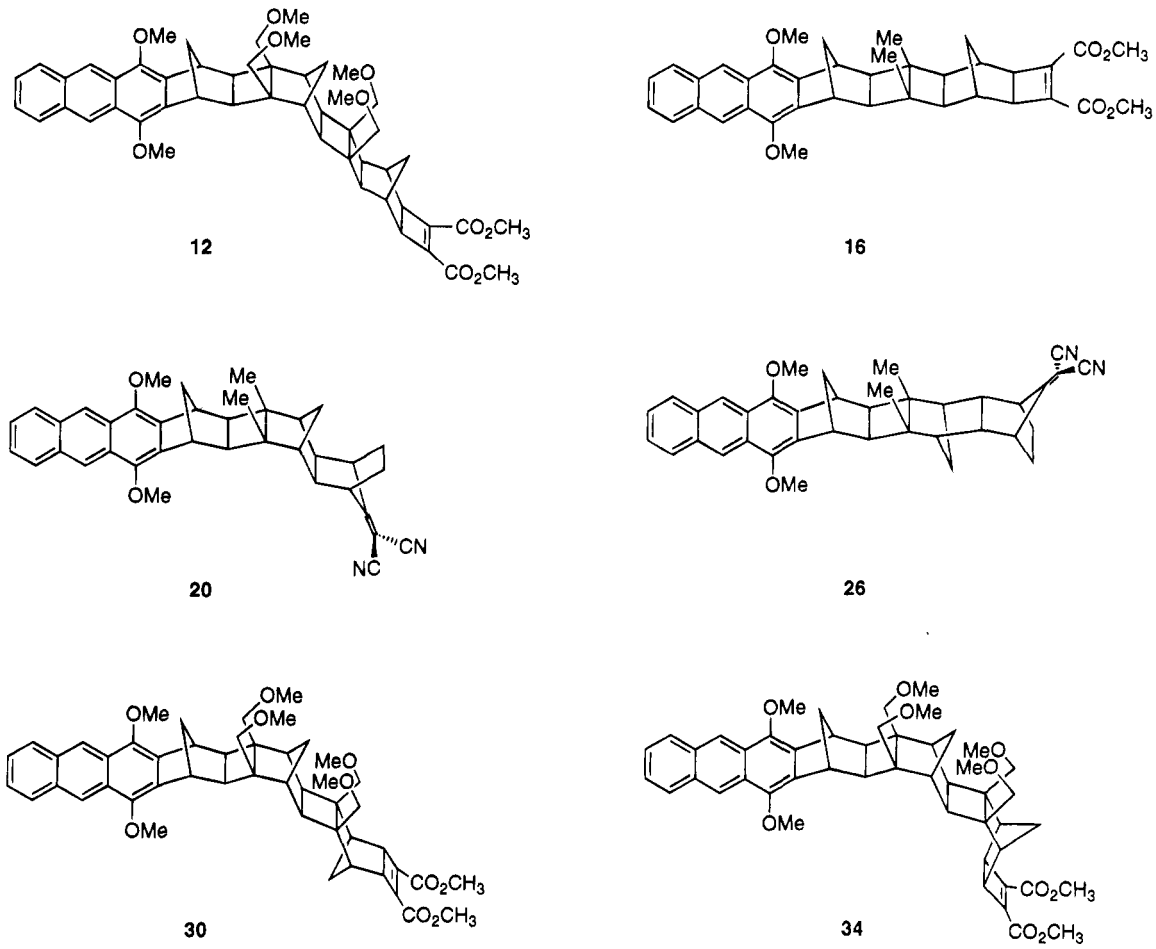

Figure 1. Donor–spacer–acceptor (DSA) molecules containing dimethoxyanthracene donor and polynorbornyl spacers.

Motivation and Strategy

The synthetic strategies leading to the donor–spacer–acceptor (DSA) molecules **12, 16, 20, 26, 30**, and **34** (Figure 1) containing the dimethoxy anthracene donor utilizes cycloaddition methodology that has been extensively developed by Paddon-Row and co-workers[9,14] for investigations of photoelectron spectroscopy[15] and photoinduced intramolecular eT.[9] The key steps in these sequences are the Diels–Alder reaction, to construct the [2.2.1] cycloheptane moieties, and the transition metal-catalyzed $[2\pi_s + 2\pi_s]$ reaction to afford the cyclobutanes. The combination of these reactions creates a relatively rigid spacer and provides facile regulation of the through space distance and the number of bonds separating the donor and the acceptor.

The spacers in DSA molecules **16, 20**, and **26** contain seven saturated covalent bonds as the shortest connection between the donor and the acceptor. In **16** and **26**, the seven-bond path contains an all s-*trans* arrangement, whereas the shortest path spanning the spacer in **20** contains a single s-*cis* link. This series of compounds has been used to demonstrate orbital symmetry effects on eT.[16] All three polycyclic DSA complexes exhibit approximate C_s symmetry. The LUMOs of the 1,1-dicyanoethylene acceptors in **26** and **20** are symmetric (a′) and the LUMO of the 1,2-dicarbomethoxyethylene acceptor in **16** is antisymmetric (a″) with respect to the mirror plane symmetry element in these molecules. Thus, eT from the symmetric (a′) LUMO of the locally excited dimethoxyanthracene donor to the acceptor LUMO is formally symmetry allowed in **20** and **26** and formally symmetry forbidden in **16**. Although eT in **16** is more exothermic than in **20** and **26**, the eT rate constants in **16** are 3–10 times slower than those in **20** and **26**. We have attributed this difference in eT rate constants to symmetry modulation of the electronic coupling between the donor and acceptor. In a previous report, we have discussed the factors affecting the relative magnitudes of the eT rate constants in the above molecules.[16b]

Symmetry effects on eT rate constants have also been explored in DSAs derived from a heptacyclotetradecane spacer. Metal-catalyzed dimerization of 7-oxy-substituted norbornadienes generates the rigid spacer **35** in a single step.[17] Subsequent functional group transformations and addition reactions produce the desired DSA

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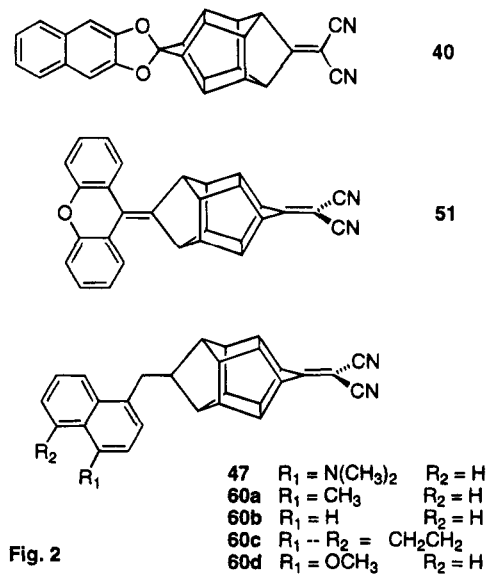

Figure 2. DSA molecules containing the heptacyclotetradecane spacer.

structure **51** (Figure 2). In this molecule, the ethylenic portions of the donor and acceptor π systems are rotated, relative to each other, by 90° around the approximate C_2 molecular axis. In principle, electronic coupling and electron transfer between these two π systems should also be symmetry forbidden. The nonplanar conformation of the xanthenylidene group and its rapid twisting upon excitation[18] relax the symmetry constraint on coupling and results in subnanosecond transfer rate constants.

The importance of *solvent-mediated electronic coupling* in intramolecular electron transfer is currently being explored in our laboratory. Prior evidence for such coupling has been obtained from investigations of electron transfer reactions between randomly distributed donors and acceptors in rigid glasses[19] and from studies of solvent-separated ion pairs.[20] There is little definitive evidence demonstrating significant contributions of through solvent electronic coupling in covalently linked, rigid DSA molecules.[21] In order to determine whether solvent-mediated electronic coupling can compare in magnitude to through bond electronic coupling in intramolecular electron transfer reactions, a series of rigid "C-clamp" DSA molecules **12, 30,** and **34** (Figure 1) have been constructed. These molecules were designed (1) to minimize through bond coupling by employing a symmetry-forbidden DSA topology and a minimum of nine σ bonds in the spacer and (2) to maximize through solvent coupling by positioning the donor and acceptor such that the shortest path between them passes entirely through the solvent.

Table 1. Parameters Highlighting the Structural Features of Various DSAs

compound	s-*cis* links	no. of bonds	distance (Å)[a]
12	1	10	10.1
16	0	7	9.7
30	1	9	9.1
34	2	9	6.9

[a] Donor–acceptor distances, defined as the distance from the center of the aromatic ring with the methoxy substituents to the acceptor ethylene, were calculated after geometry optimization utilizing MM2 force field by Molecular Mechanics running on CAChe, Version 3.0 (CAChe Scientific, 1992).

The synthetic strategy employed in these syntheses relies heavily on the stereochemical control provided by the key Diels–Alder reactions. *Endo* Diels–Alder cycloadditions linearly extend the spacers by addition of s-*trans* bonds, whereas *exo* additions generate the s-*cis* bonds needed to introduce bends in the C-clamps.[22] The three C-clamp DSA molecules, **12, 30,** and **34,** along with DSA **16,** provide a range of shapes and donor acceptor separations. Table 1 lists the number of *cis* links in the spacer, the minimum number of spacer bonds separating the donor and acceptor, and the donor–acceptor separation for each of the four DSA molecules.

Finally, analysis of the temperature dependence of eT rate constants provides information about the free energy barrier which impedes formation of the transition state and the donor–acceptor interaction encountered in the transition state. For long distance electron transfer reactions, the intercept of an Arrhenius plot may be related to the donor–acceptor electronic coupling matrix element.[1] However, the analysis of electron transfer rate constants as a function of temperature can be complicated by significant temperature dependences of both the driving force and the intrinsic barriers to reaction.[4d,6d,23] Independent characterization of these temperature dependences are required in order to effect a proper analysis of rate constant variation with temperature. Fortunately, the shape and position of charge transfer emission spectra are determined by the same quantities; the intrinsic barriers and the reaction driving force.[20] Their variation with temperature may be extracted from the behavior of the emission band. Thus, a proper analysis of electron transfer kinetics temperature dependence can be achieved if accompanied by a simultaneous analysis of charge transfer emission spectra. Compounds **40, 47,** and **60a–d** (Figure 2) exhibit rapid photoinduced electron transfer in solvents ranging from ether to ethanol. The resulting charge transfer states have significant emission quantum yields in solvents with dielectric constants of 10 or less. Thus, a full analysis of the electron transfer kinetics and spectroscopy can be effected in these solvents. The electron donors are incorporated into these compounds using a Suzuki coupling reaction[24] on the alkenes in **44** and **56** or by ketal formation from diketone **38.** Subsequent functional group modifications generate the desired electron acceptors.

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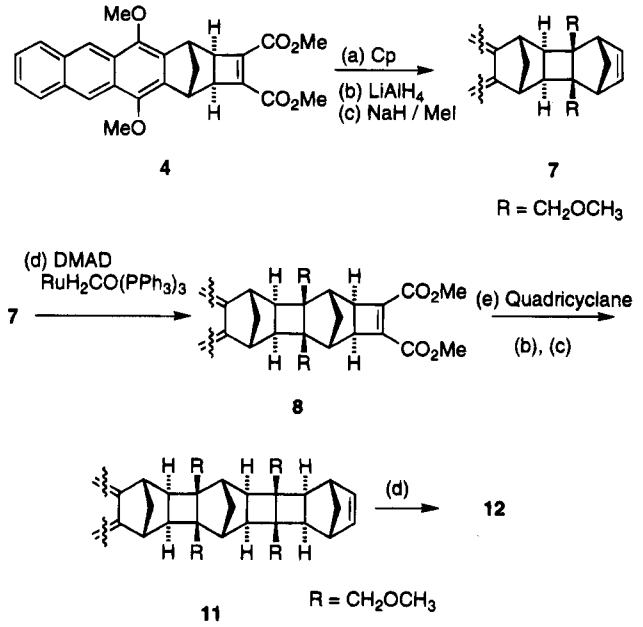
Scheme 1



Results and Discussion

The synthesis of all compounds containing the dimethoxyanthracene donor diverges from the common intermediate **4** (Scheme 1). A Diels–Alder reaction of dienophile 1,4 anthraquinone (**1**) with cyclopentadiene gave the adduct **2** in 80% yield.[25] The cycloadduct **2** was treated with sodium hydride and O-methlyated with methyl iodide[26] or dimethyl sulfate to give dimethoxyanthracenonorbornadiene (**3**) in 70–90% yield. These reactions establish the dimethoxyanthracene nucleus. Reaction of **3** with dimethyl acetylenedicarboxylate (DMAD) in the presence of catalytic amounts of $RuH_2CO(PPh_3)_3$ afforded **4** in 84% yield via a [2 + 2] reaction.[9a,27] The catalyst $RuH_2CO(PPh_3)_3$ was prepared according to literature procedures.[28]

The symmetry-forbidden, 10 Å C-clamp structure **12** was obtained as follows (Scheme 1). Reaction of cyclopentadiene with dienophile **4** at 0 °C produces the Diels–Alder adduct **5** in a quantitative yield. Only the *exo* adduct is obtained under these conditions.[29] The exclusive formation of the *exo* adduct was previously explained as the result of unfavorable nonbonded interactions between the methylene hydrogens of the cyclopentadiene and the methyne (ring junction) hydrogens on the cyclobutene in the *endo* transition state.[30] This interaction is missing in the *exo* transition state. A significant alteration of the addition stereochemistry is achieved by a change in the substitution pattern on the dienophile. Reaction of the diacid ($-CO_2Me \rightarrow -CO_2H$) results in a higher proportion of the *endo* adduct (*endo*:*exo* ≥ 2.5). An intramolecular hydrogen bond between the two carboxylic acids on the dienophile was advanced as the cause of this reversal in stereochemical preference.[31] The hydrogen bond creates unfavorable nonbonded interactions in the *exo* transition state in that the methylene hydrogens on the cyclopentadiene cannot easily bisect the two acid groups. This result was employed in the construction of the straight compound **26** and will be discussed later.

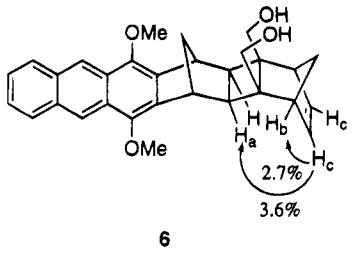


Figure 3. NOE enhancements from the vinyl proton (H_c) to the cyclobutane bridgehead (H_a) and norbornane bridgehead (H_b) protons in diol **6**. The H_c to H_a NOEs confirm the *exo* addition of Cp to **4**.

The stereochemistry of the Diels–Alder adduct **5** was confirmed from an analysis of NOE experiments on the diol **6**. Irradiation of the vinyl protons (H_c) in **6** resulted in NOE enhancements in protons H_a and H_b, consistent with the *exo* geometry of **6** and **5** (Figure 3). The diol **6** was obtained in 96% yield by reduction of the diester **5** with $LiAlH_4$. The instability of the Diels–Alder adduct **5** to the high temperatures[32] (75–85 °C) needed for the subsequent cycloaddition step renders this reduction step essential. Although the diol **6** is stable to retro Diels–Alder reactions, it did not produce satisfactory yields in the subsequent [2 + 2] cycloaddition step. The diol was converted to the corresponding diether, which produces higher yields in the cycloaddition. Treatment of the diol **6** with NaH and CH_3I[33] furnished the diether **7** in quantitative yield. Reaction of **7** with DMAD and $RuH_2CO(PPh_3)_3$ at 80 °C in a sealed tube resulted in the formation of **8** in 82% yield. The [2 + 2] cycloadduct **8** was refluxed in neat quadricyclane to give **9** in 66% yield via a $[2\pi + 2\sigma + 2\sigma]$ cycloaddition.[9a,34] The diester **9** was converted to the corresponding diol **10** using LAH and was subsequently methylated using NaH/CH_3I to generate diether **11**. Two-dimensional NMR investigations on **11** established both the connectivity and the stereochemistry of the spacer. The proton connectivities were derived from a LR-COSY (long-range homonuclear correlation) experiment which included a delay period to

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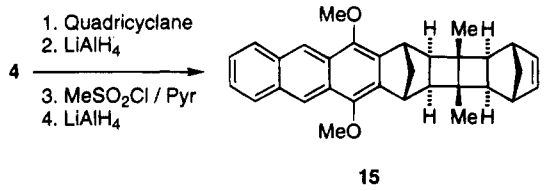
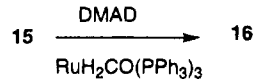
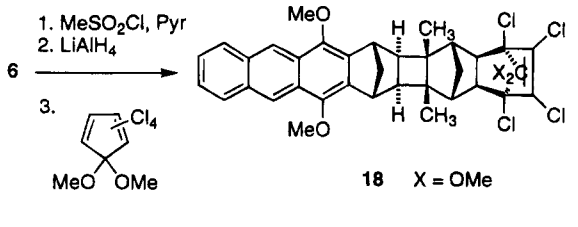
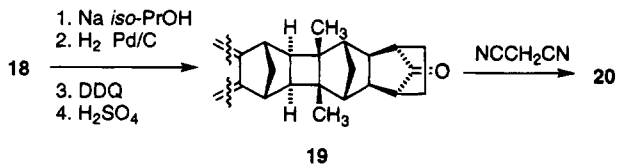
Scheme 2





Scheme 3



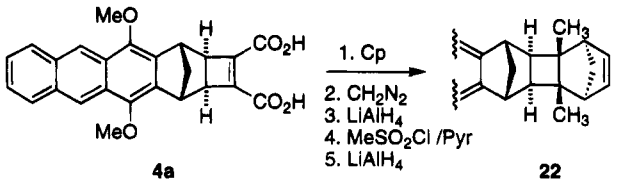


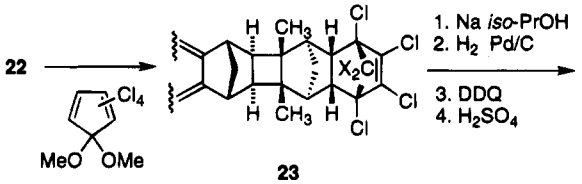
emphasize long-range and small couplings.[35] Once the proton connectivities were established, the $^1H-^{13}C$ connectivities were easily obtained from a HETCORR[36] experiment, utilizing polarization transfer from ^1H to ^{13}C. The desired DSA molecule **12** was obtained from **11** by reaction with DMAD and catalyst $RuH_2CO(PPh_3)_3$ at 80 °C in a 68% yield.

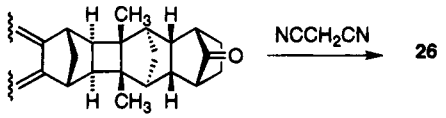
The symmetry-forbidden, 10 Å linear structure **16** was obtained as follows (Scheme 2). Diester **4** was refluxed with quadricyclane at 110 °C for 3 days, resulting in formation of the $[2\pi + 2\sigma + 2\sigma]$ adduct **13** in a quantitative yield. The diester **13** was transformed to the diol **14** by treatment with LAH. The diol **14** was converted to the dimesylate and reduced ($LiAlH_4$)[9a,37] to deliver **15** in 79% overall yield from the diester. The construction of the electron acceptor was accomplished by treatment of **15** with DMAD and $RuH_2CO(PPh_3)_3$, yielding the [2 + 2] cycloadduct **16** in 18% yield.

The synthesis of the symmetry-allowed, 9 Å C-clamp structure **20** was initiated from **6**. The diol (Scheme 3) was converted to the bis-mesylate by treatment with pyridine and methanesulfonyl chloride and was subsequently reduced with LAH to provide **17** in 93% yield. An inverse electron demand Diels–Alder reaction[9a,38] with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene produced **18** in 63% yield. The adduct **18** was subjected to reductive dechlorination[39] followed by reduction of the ene using Pd on C and hydrogen. The anthracene nucleus, reduced in the latter reaction, was regenerated by oxidation with DDQ[40] (55% overall yield from **18**).

Scheme 4







Treatment of the ketal with 40% H_2SO_4 for 24 h delivered the ketone **19** in 76% yield. The ketone in **19** was reacted with malononitrile in toluene in the presence of ammonium acetate and acetic acid[9a] to produce the desired compound **20** in 39% yield as the only detectable product.

The synthesis of the symmetry-allowed, linear compound **26** required an *endo* addition of cyclopentadiene in the elongation of **4**. Thus, the diester **4** was hydrolyzed to the corresponding diacid **4a** in 95% yield by refluxing with 2 N aqueous NaOH. The diacid dienophile **4a** underwent a Diels–Alder reaction with cyclopentadiene (Scheme 4), producing cycloadduct **4b** in a quantitative yield and with an *endo*:*exo* ratio of 2.5:1. As described above, the stereochemical preference for formation of the *exo* product is reversed through use of the diacid dienophile. This enabled assembly of straight (all *trans*) or bent (containing one or more s-*cis* links) spacers by choice of the dienophile substituent. The diacids (*endo* and *exo*) were converted to the respective diesters by treatment with diazomethane[41] at 0 °C. The two diesters were separated by silica gel chromatography at this stage.

Reduction of the diester **21** with LAH, mesylation, and reduction (LAH) afforded **22** in 58% overall yield. The alkene **22** underwent an inverse electron demand Diels–Alder reaction when heated with the electron-poor diene 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene at 140 °C in a sealed tube to furnish the adduct **23** in 38% yield. Reductive dechlorination of **23** followed by reduction of the cyclopentene using Pd/C and hydrogen produced **24**. Once again, the anthracene nucleus, reduced during these reactions, was immediately oxidized using DDQ (dichlorodicyanoquinone) at room temperature for 24 h to give **24a** in 66% yield. Treatment of the ketal **24a** with 40% aqueous H_2SO_4 produced **25**. Refluxing **25** in toluene with malononitrile in the presence of ammonium acetate/water and acetic acid gave the DSA **26** as the only detectable product. The structural characterization and unambiguous assignment of stereochemistry for **26** was achieved by X-ray diffraction. The results of this study will be documented elsewhere.

The two structural isomers **30** and **34** were both obtained from the common advanced intermediate **8**

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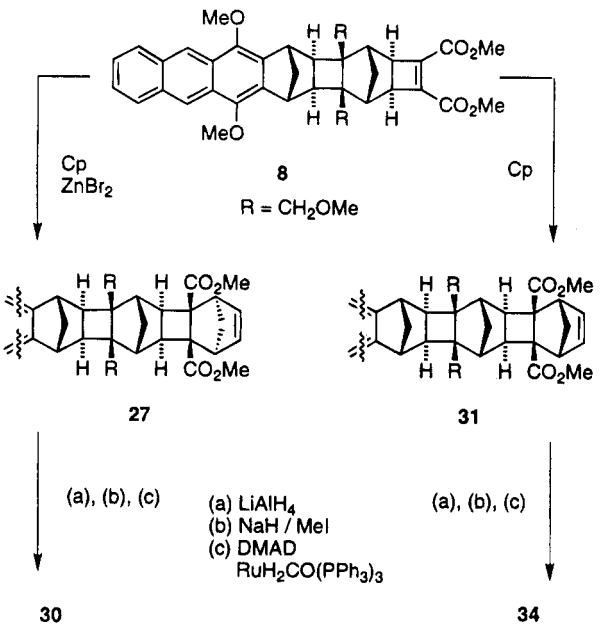
(41) Black, T. H. *Aldrichimica Acta* **1983**, *16*, 3.

Scheme 5



(Scheme 5). Given the predominance of *exo* cycloaddition for the reaction of cyclopentadiene with **4**, we were confident of achieving similar results with **8**. Although the dienophile **8** is structurally similar to the diester dienophile **4**, room temperature reaction of **8** with cyclopentadiene did not result in the formation of the [4 + 2] cycloadduct in any appreciable yield. The highest yield at room temperature was obtained by running the reaction in neat cyclopentadiene (~15%). Several other approaches were explored, but for the most part, these foundered as a result of cyclopentadiene dimerization and problems associated with the chromatographic separation of **8** and cycloadduct **31**. High temperatures (>140 °C) resulted in decomposition of the dimethoxyanthracene moiety. In order to simultaneously maximize diastereomeric selectivity and the extent of reaction, we explored running these reactions at intermediate temperatures. Heating the dienophile **8** at 72 °C with excess cyclopentadiene produced the Diels–Alder adducts **31** and **27** in a quantitative yield with a diastereomeric ratio of 4:1 (*exo*:*endo*). The two diastereomers were separated by flash column chromatography at this stage. With reasonable yields for the second *exo* addition achieved, the pure *exo* diester **31** was reduced to the corresponding diol **32** by LAH in 94% yield. The diol **32** was bis-methylated using NaH and methyl iodide to afford the diether **33** in 89% yield. A metal-catalyzed [2 + 2] reaction of the ene **33** with DMAD furnished the required DSA **34** as the only detectable product in 77% yield.

Although the uncatalyzed reaction of the diester dienophile **8** at moderately high temperatures with cyclopentadiene resulted in the formation of both the *endo* and *exo* diastereomers, we endeavored to find a method which would provide a higher ratio of the *endo* product. Lewis acid catalysis of Diels–Alder reactions is known to favor the *endo* adduct.[42] Indeed, upon exposure to cyclopentadiene in the presence of excess $ZnBr_2$,[43] the dienophile **8** engaged in a Diels–Alder reaction to produce solely the *endo* adduct in 95% yield. This accomplished the required reversal of stereochemistry from that observed in the uncatalyzed reaction. By analogy to the explanation for the reversal of stereochemistry when the diacid reacts, this preference can be explained if coordination of the $ZnBr_2$ to the esters generates unfavorable nonbonded interactions with the cyclopentadiene methylene hydrogens in the *exo* transition state. Alternatively, the *endo* stereochemistry may result from more favorable secondary orbital overlap with the more electron deficient ester. Irrespective of the mechanism, these reactions allow the bridge to be configured to the desired shape in the norbornylogous series. The *endo* diester **27** was converted to the corresponding diether **29** by reduction with LAH (to afford the diol **28**) followed by bis-methylation using NaH/CH_3I. The *endo* diether ene **29** was subjected to a transition metal-catalyzed [2 + 2] reaction with DMAD to afford the required DSA **30**.

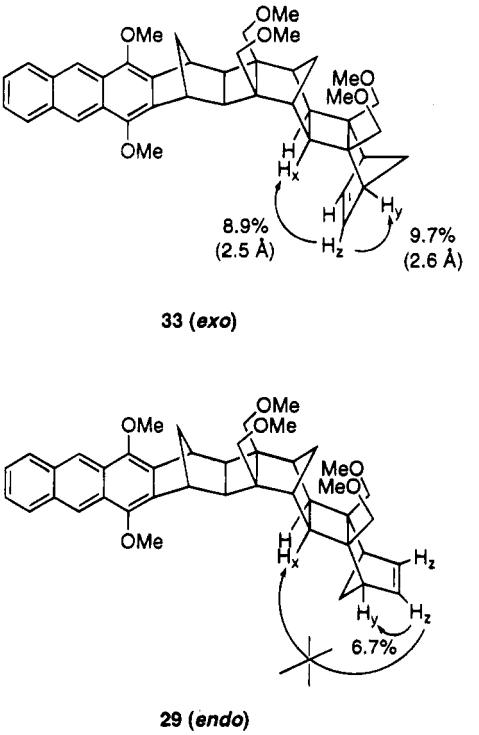


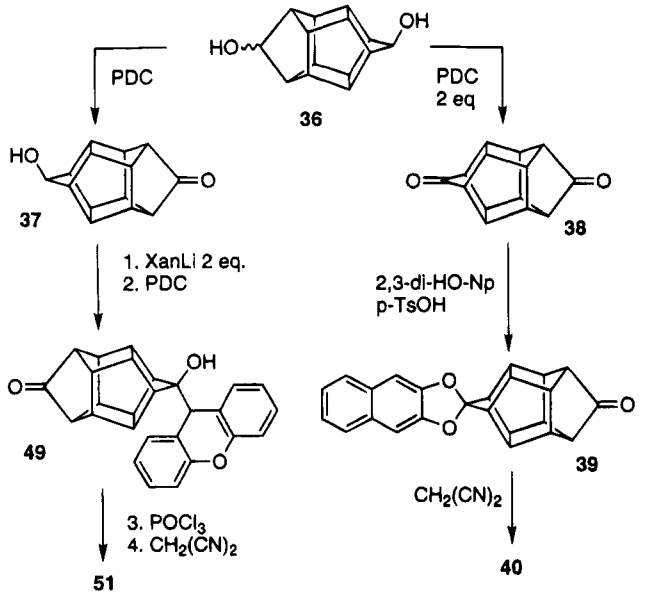
Figure 4. Comparison of NOE enhancements from the vinyl proton (H_z) to the cyclobutane bridgehead (H_x) and norbornane bridgehead (H_y) protons in **33** and **29**. The significant H_z to H_x NOE in **33**, and its absence in **29**, confirm *exo* Cp addition stereochemistry for 33 and *endo* stereochemistry in **29**.

The stereochemical identity of the two diastereomers was ascertained unambiguously by NOE difference spectroscopy (Figure 4). Irradiation of the vinyl protons (H_z) in the *exo* diastereomer (diether derivative **33**) resulted in positive NOE enhancements for the the ring-junction protons (H_x) and the adjoining bridgehead protons (H_y). In a similar experiment with the *endo* diastereomer (diether derivative **29**), no enhancement in the ring-junction protons was detectable, whereas the NOE enhancement to the adjoining bridgehead protons was maintained.

(42) (a) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070. (b) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436. (c) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16–33. (d) Corey, E. J.; Weinshenker, N. M.; Schaaf, T. K.; Huber, W. *J. Am. Chem. Soc.* **1969**, *91*, 5675.

(43) Many Lewis acid induced Diels–Alder reactions require 20–200 mol % of the Lewis acid; see for instance: (a) Roush, W. R.; Gillis, H. R. *J. Org. Chem.* **1980**, *45*, 4267–4268. (b) Cohen, T.; Kosarych, Z. *J. Org. Chem.* **1982**, *47*, 4005–4008. (c) Oppolzer, W. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 876–889. (d) Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **1987**, *70*, 436–440.

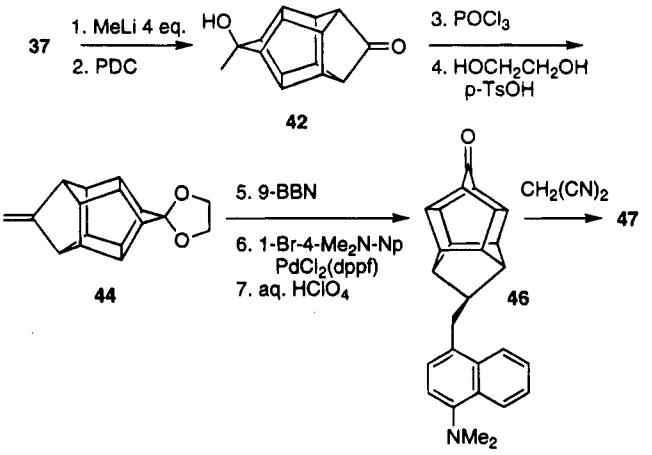
Scheme 6



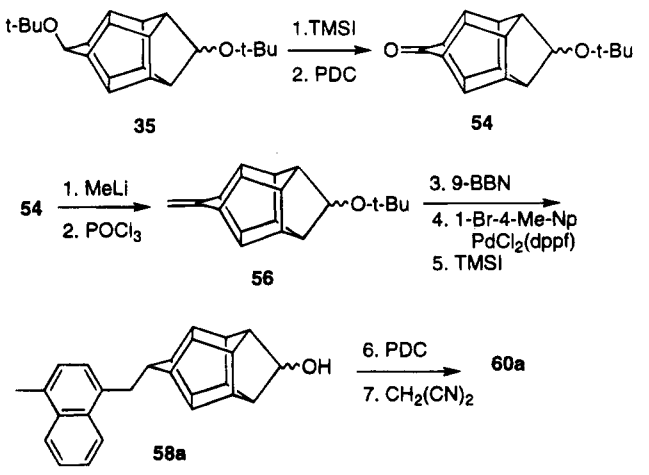
The syntheses of the DSA compounds **40**, **47**, **51**, and **60a–d** (Figure 2) containing the heptacyclotetradecane spacer originated from the 7-*tert*-butoxynorbornadiene dimer.[17] The dicyanoethylene acceptor was used in all of these DSA molecules. Incorporation of the donors required various levels of deprotection and oxidation of the bridge carbons. Treatment of the di-*tert*-butyl ether **35** with more than 2 equiv of TMSI[44] yielded the diol **36** in good yield (Scheme 6). Oxidation of the diol with excess pyridinium dichromate[45] followed by chromatography yielded the diketone **38** in 81% yield. *p*-TSA-catalyzed reaction of **38** with 2,3-dihydroxynaphthalene produced a mixture of monoketal **39** and bis-ketal products. Although this method of attaching the naphthalene donor did not selectively produce the desired, monoketal product, the amount of bis-ketal could be minimized by use of a small (naphthalene:**38**) ratio. Furthermore, **38** and mono- and bis-ketal products were readily separated by chromatography. A modified Knoevenagel reaction[46] of **39** with malononitrile yielded the rigid naphthalene ketal/dicyanoethylene DSA **40**.

For the other heptacyclotetradecane-containing DSA molecules, differentiation between the donor and acceptor ends was established prior to their introduction. Oxidation of the diol **36** with 1.5 equiv of PDC produced the ketone/alcohol, monooxidation product **37** in a 19% isolated yield, the diketone **38** in a 50% isolated yield, and recovered starting material (Scheme 6). Additional **37** was obtained by incomplete $NaBH_4$ reduction of the diketone. Treatment of **37** with 4 equiv of MeLi, followed by PDC oxidation, produced the 3° alcohol/ketone **42** (Scheme 7). Phosphorus oxychloride[47] induced elimination followed by *p*-TSA-catalyzed protection of the ketone yielded the ethylene/ketal **44**. Reaction of **44** with

Scheme 7



Scheme 8



1-bromo-4-(dimethylamino)naphthalene via a Pd-catalyzed Suzuki coupling[24] introduced the donor group. Hydrolysis of the ketal and condensation with malononitrile yielded the desired (dimethylamino)naphthalene/dicyanoethylene DSA **47**. In this synthesis, the acceptor carbonyl group was introduced prior to attachment of the (dimethylamino)naphthalene donor as the latter was oxidized by reagents capable of converting the alcohol to the ketone. The use of 9-BBN in the Suzuki coupling required the ketone's protection as the ketal.

The synthesis of the symmetry probe, DSA **51**, also originated with the ketone/alcohol **37** (Scheme 6). Addition of more than 2 equiv of xanthenyllithium to **37** followed by PDC oxidation produced the 3°-alcohol/ketone **49**. $POCl_3$-induced dehydration of the alcohol followed by condensation of the ketone with malononitrile yielded the symmetry probe **51**. This sequence of functional group transformations was necessary, as attempts to generate the acceptor ketone after formation of the xanthenylidene chromophore resulted in cleavage of the xanthenylidene attachment to the spacer.

The syntheses of the semirigid naphthalene DSAs **60a–d** employed the *tert*-butyl ether/ketone **54** (Scheme 8). This was obtained by partial deprotection of the *tert*-butyl ether groups in **35** and subsequent PDC oxidation. Reaction of the carbonyl with methyllithium followed by $POCl_3$ dehydration generated the ether/methylene **56** in 85% yield. The substituted naphthalene donors were introduced via Pd-catalyzed Suzuki reactions, with yields ranging from 77 to 93%. TMSI deprotection of the *tert*-

(44) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761.
(45) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, *5*, 399–402.
(46) (a) Knoevenagel, E. *Ber.* **1898**, *31*, 2585. (b) Knoevenagel, E. *Ber.* **1904**, *37*, 4502. (c) Patai, S.; Zabicky, J.; Israeli, Y. *J. Chem. Soc.* **1960**, 2039. (d) For excellent reviews on this reaction, see: (i) Freeman, F. *Chem. Rev.* **1980**, *80*, 329. (ii) Fatiadi, A. J. *Synthesis* **1978**, *165*, 241. (e) For an example of catalysis by β-alanine, see: Prout, F. S. *J. Org. Chem.* **1953**, *18*, 928.
(47) Bernstein, S.; Littell, R.; Williams, J. H. *J. Am. Chem. Soc.* **1953**, *75*, 4830.

butyl ether followed by PDC oxidation and condensation with malononitrile generated the desired DSA molecules, **60a–d**.

Conclusions

A variety of polycyclic donor–spacer–acceptor molecules have been synthesized for use in investigations of photoinduced electron transfer reactions. The incorporation of polycyclic spacers into these molecules provides considerable rigidity, fixes the orientation of the donor and acceptor, and provides control over the overall molecular topology. This, in turn, enables meaningful investigations of the structural dependences of electron transfer rate constants. These molecules have been used to (i) demonstrate electronic symmetry effects on eT, (ii) investigate the dependence of donor–acceptor interactions on solvent electronic structure, and (iii) probe the temperature dependence of electron transfer rate constants and thermodynamics. This work documents the synthetic details for all DSA molecules synthesized, to date, in our laboratory for which we have reported or will soon report eT dynamics to address a variety of mechanistic questions.

Experimental Section

General. All ^{1}H NMR spectra were recorded at room temperature in standard deuterated solvents at either 250 or 400 MHz. ^{1}H NMR spectra are expressed in parts per million (ppm) downfield from internal standard tetramethylsilane (δ 0.00). ^{13}C NMR spectra were obtained at room temperature using a Bruker AM400 NMR spectrometer operating at 100.614 MHz using a 5 mm, low-frequency broad-band proton-decoupled probe. Infrared spectra were recorded using an FTIR spectrometer with a 4 cm^{-1} bandpass. Spectra of solid samples were obtained as solid thin films or dissolved in thin layers of organic solvents between NaCl plates. Flash column chromatography was performed using Kieselgel 60 SiO_2 gel into glass columns using standard literature procedures. Analytical thin layer chromatography was performed on precoated silica gel TLC plates 60 F-254. Mass spectra were obtained on a Kratos MS-50 double-focusing spectrometer. All solvents were distilled under N_2 or argon, utilizing standard literature procedures.

Anthracenonorbornadiene (3). A solution of the cycloadduct **2** (6.2 g, 22.6 mmol) in 45 mL of dry THF was continually stirred and maintained in an ice bath at 0 °C. A magnetically stirred solution of NaH (3.8 g, 158 mmol) in 10 mL of dry THF was added to the solution of **2**. The solution gradually turned dark blue. The reaction was stirred at 0 °C for 1 h. Iodomethane (16 mL, 258 mmol) was added dropwise to the blue solution. The ice water bath was removed after 30 min, and the reaction vessel was allowed to warm to room temperature. The reaction was further stirred at room temperature for 17 h, following which it was quenched with 100 mL of ice water. The aqueous layer was extracted with Et_2O (6 × 30 mL). The organic layers were subsequently combined and dried over $MgSO_4$. The solution was concentrated to about 10 mL using a rotary evaporator, and 20 mL of hexane was added. The solution was cooled to crystallize the product. The product was recrystallized from ethanol. The yield of **3** was 5.69 g (83%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.55 (s, 2H), 8.01–7.97 (m, 2H), 7.45–7.41 (m, 2H), 6.74 (t, 2H, J = 2.5 Hz), 4.35 (triplet, 2H, J = 2.5 Hz), 4.07 (s, 6H), 2.29–2.16 (m, 2H). FTIR (CH_2Cl_2, ν, cm^{-1}): 3054, 2933, 2833, 1652, 1453, 1344, 1323, 1300, 1210, 1140, 1118, 1084, 1027, 977. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 144.66, 140.92, 133.12, 131.46, 128.31, 127.20, 125.17, 120.63, 62.87, 62.01, 46.45. EI-HRMS: calcd for $C_{21}H_{18}O_2$, 302.1306; found, 302.1305.

C_{27} Cyclobutene–Diester 4. Method A. A solution of **3** (3.2 g, 10.5 mmol), catalyst $RuH_2CO(PPh_3)_3$ (0.25 g, 0.27 mmol), and dimethyl acetylenedicarboxylate (DMAD) (1.4 mL, 11.4 mmol) in 15 mL of benzene was maintained under argon for 15 min in a high-pressure tube. The tube was subsequently sealed and lowered into a preheated oil bath maintained at 80 °C. After 17 h, the tube was cooled to room temperature. The product **4** was purified using flash column chromatography (25% EtOAc/hexane). The fractions with R_f = 0.33 in 30% ethyl acetate in hexane were collected. The solvents were evaporated. The yield of **4** was 3.76 g (80%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.62 (s, 2H), 8.05–8.01 (m, 2H), 7.48–7.44 (m, 2H), 4.11 (s, 6H), 3.88 (s, 6H), 3.78 (s, 2H), 3.01 (s, 2H), 1.93 (d, 1H, J = 10.5 Hz), 1.84 (d, 1H, J = 10.5 Hz). FTIR (CCl_4, ν, cm^{-1}): 3650, 3434, 2955, 2839, 1724, 1698, 1436, 1323, 1260. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 161.5, 145.0, 142.7, 131.3, 131.0, 128.3, 127.3, 125.4, 120.8, 61.9, 52.1, 46.3, 38.4, 37.5. FAB-MS (m/z): calcd for $C_{27}H_{24}O_6$, 444; found, 444.

***exo*-C_{32} Diels–Alder adduct 5.**[48] A solution of the dienophile **4** (65.3 mg, 0.14 mmol) in dichloromethane (4–5 mL) was maintained at 0 °C. Freshly distilled cyclopentadiene (0.09 mL, 1.0 mmol) was added to the same. The reaction was allowed to proceed at 0 °C or below for 2 h and subsequently at room temperature for 24 h. The reaction mixture was dried ($MgSO_4$), and solvents and excess cyclopentadiene were removed using a rotary evaporator. The product **5** was obtained in quantitative yield (75 mg). The R_f of the product was 0.33 in 30% ethyl acetate in hexane, UV active, blue fluorescence. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.59 (s, 2H), 8.01–7.98 (m, 2H), 7.46–7.42 (m, 2H), 6.36–6.34 (m, 2H), 4.08 (s, 2H), 4.06 (s, 6H), 3.82 (s, 6H), 3.23 (t, 2H, J = 2.0 Hz), 2.44 (d, 1H, J =10.5 Hz), 2.32 (d, 1H, J = 8.8 Hz), 1.83 (d, 1H, J = 10.5 Hz), 1.74 (s, 2H), 1.67 ppm (d, 1H, J = 8.9 Hz). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 173.02, 143.76, 137.78, 133.05, 131.11, 128.27, 127.19, 125.21, 120.70, 61.84, 59.86, 53.15, 51.80, 46.34, 44.55, 41.98, 34.65. FTIR (CH_2Cl_2, ν, cm^{-1}): 3055, 2988, 2951, 2837, 1726, 1651, 1454, 1434, 1325, 1265, 1225, 1154, 1090, 1030. FAB-HRMS (NBA matrix): calcd for $C_{32}H_{30}O_6$, 510.2042; found, 510.2037.

C_{30} Ene–Diol 6. Method B. A magnetically stirred solution of **5** (55.3 mg, 0.10 mmol) in dry diethyl ether was maintained under argon. In a flame-dried reaction vessel, 29.1 mg (0.76 mmol) of LAH in 100 mL of dry diethyl ether was refluxed under argon. To this refluxing LAH suspension was slowly added the diethyl ether solution of **5** dropwise. The addition produced white solids. The solution was continually refluxed for 1 h, following which the reaction was quenched with 0.05 mL of water, 0.05 mL of 15% NaOH/H_2O, and 0.15 mL of H_2O. The white solids were removed by filtration. The products were dried over $MgSO_4$, and the solvents were removed by evaporation. The product obtained was purified using flash column chromatography (43% ethyl acetate in hexane). Fractions with R_f = 0.41 in neat ethyl acetate were collected. The product was a light ochre-colored solid. The yield of the reaction was 58.4 mg (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 2H), 8.00–7.98 (m, 2H), 7.44–7.42 (m, 2H), 6.29–6.28 (m, 2H), 4.17 (d, 2H, J = 11.06 Hz), 4.04 (s, 6H), 3.83 (s, 2H), 3.73 (d, 2H, J = 11.05 Hz), 2.95 (s, broad, 2H), 2.55 (d, 1H, J = 9.73 Hz), 1.89 (d, 1H, J = 10.62 Hz), 1.86 (broad, 2H, alc protons), 1.60–1.57 (m, 3H), 1.51 (d, 1H, J = 9.24 Hz). FTIR (CCl_4, ν, cm^{-1}): 3402, 2925, 1731, 1651, 1454, 1322, 1141, 1028, 886. ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 143.3, 137.4, 134.0, 131.2, 128.3, 127.1, 125.2, 120.7, 62.6, 61.8, 53.8, 51.0, 49.5, 45.0, 44.3, 40.0. FAB-HRMS (thioglycerol matrix): calcd for $C_{30}H_{30}O_4$, 454.2144; found, 454.2147.

C_{32} Ene–Diether 7. Method C. To 25 mL of freshly distilled THF, diol **6** (15.8 mg, 0.034 mmol), methyl iodide (0.12 mL, 1.9 mmol), and NaH (100 mg, 4.16 mmol) were sequentially added. The reaction was stirred at room temperature for 24 h and was then quenched by adding 10 mL of water. The water layer was extracted with diethyl ether (3 × 30 mL), and subsequently the ether layer was washed with 3 × 10 mL of saturated NH_4Cl. The organic layers were combined, dried

(48) *Exo* and *endo* in the compound titles refer to the stereochemistry of the addition of the last cyclopentadiene unit. The stereochemistry of the addition of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene in the inverse electron demand Diels–Alder reactions is well known and is not distinguished here by use of a prefix.

($MgSO_4$), and evaporated. The reaction mixture was purified by flash column chromatography (30% ether/hexane/10% EtOAc). The spot with $R_f = 0.25$ in 40% EtOAc/ether was the required diether **7**. ^1H NMR (250 MHz, $CDCl_3$): δ 8.58 (s, 2H), 8.00–7.96 (m, 2H), 7.44–7.40 (m, 2H), 6.26 (s, 2H), 4.08 (s, 6H), 3.92 (d, 2H), 3.81 (s, broad, 2H), 3.45 (s, 6H), 3.27 (d, 2H), 2.98 (s, broad, 2H), 2.55 (d, 1H), 1.89 (d, 1H), 1.62–1.58 (m, 4H). FT-IR (CH_2Cl_2, ν, cm^{-1}): 3054, 2986, 1421, 1324, 1265, 1100, 1032, 895. ^{13}C NMR (100.614 MHz , $CDCl_3$): δ 143.31, 136.84, 131.08, 128.28, 127.08, 125.06, 120.63, 112.80, 72.94, 61.66, 59.28, 52.61, 51.04, 49.21, 44.99, 44.79, 40.25. EI-HRMS: calcd for $C_{32}H_{34}O_4$, 482.2457; found, 482.2452.

C_{38} Cyclobutene–Diester 8. A metal-catalyzed [2 + 2] reaction of **7** (49 mg, 0.102 mmol) with DMAD (14 μL, 0.113 mmol) following method A (see the experimental procedure for **4**) in benzene (0.6 mL) using catalyst $RuH_2CO(PPh_3)_3$ [10.3 mg] afforded **8**. The product was purified by flash column chromatography (20% EtOAc/hexane). The compound with R_f = 0.3 in 40% EtOAc/hexane was collected. The yield of the reaction was 52.0 mg (82%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.60 (s, 2H), 8.01–7.98 (m, 2H), 7.44–7.42 (m, 2H), 4.08 (s, 6H), 3.86 (s, broad, 2H), 3.78 (d, 2H), 3.74 (s, 6H), 3.41 (s, 6H), 3.30 (s, broad, 2H), 3.20 (d, 2H), 2.48 (s, broad, 2H), 2.42 (s, broad at base, 3H), 1.86 (d, 1H), 1.50 (d, 1H), 1.40 (d, 1H). FTIR ($CDCl_3$, ν, cm^{-1}): 2952, 2895, 2834, 1738, 1716, 1652, 1558, 1455, 1436, 1346, 1324, 1258, 1217, 1144, 1099, 1034, 967, 909, 731. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 161.25, 143.45, 142.14, 133.82, 131.15, 128.29, 127.11, 125.13, 120.75, 72.40 , 61.75, 59.20, 53.41, 51.72, 50.08, 43.77, 42.71, 42.03, 40.76, 40.69, 30.53. FAB-HRMS: calcd for $C_{38}H_{40}O_8$, 624.2723; found, 624.2717.

C_{45} Quadricyclane Adduct 9. A magnetically stirred solution of **8** (151.1 mg, 0.242 mmol) in quadricyclane (1 mL, 9.973 mmol) was heated in a sealed pressure tube at 110 °C for 3 days. The reaction was cooled, and some solvent was removed on a rotary evaporator. The R_f value of the product was 0.3 in 27% ethyl acetate/36% ethyl ether/pentane. The product was isolated from the reaction mixture using flash column chromatography (15% ethyl ether/15% ethyl acetate/pentane). The isolated yield of the product was 111.6 mg (≈66%). FTIR (CH_2Cl_2, ν, cm^{-1}): 3040, 2950, 2864, 1749, 1711, 1651, 1624, 1454, 1379, 1325, 1265, 1218, 1093, 1041, 964, 931, 890. ^1H NMR (250 MHz, $CDCl_3$): δ 8.62 (s, 2H), 8.02–7.98 (m, 2H), 7.45–7.41 (m, 2H), 5.91 (s, 2H), 4.08 (s, 6H), 3.84 (bs, 2H), 3.70–3.67 (m, 8H), 3.37 (s, 6H), 3.11 (d, 2H, J = 9.35 Hz), 2.87 (bs, 2H), 2.73 (bs, 2H), 2.43–2.34 (m, 6H), 2.04 (bs, 2H), 1.83 (d, J = 10.18 Hz, 1H), 1.75 (d, J = 9.35 Hz, 1H), 1.43 (d, J = 11.28 Hz, 1H), 1.01 (d, J = 9.62 Hz, 1H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 170.62, 143.41, 135.91, 134.02, 131.14, 128.26, 127.08, 125.12, 120.74, 71.99, 61.78, 59.13, 53.42, 51.11, 50.82, 47.19, 46.83, 46.53, 43.82, 43.52, 40.83, 40.70, 40.55, 32.60. FAB-HRMS (NBA matrix): calcd for $C_{45}H_{48}O_8$, 716.3349; found, 716.3389.

C_{43} Ene–Diol 10. The diester **9** was reduced using $LiAlH_4$ to give the diol **10** in 95% yield (Method B, see experimental procedure for **6**). The product had an R_f of 0.38 in neat ethyl acetate. FTIR (CH_2Cl_2, ν, cm^{-1}): 3471, 2930, 1651, 1455, 1346, 1324, 1264, 1209, 1091, 1034, 923, 888, 736. ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 2H), 8.01–7.98 (m, 2H), 7.44- 7.42 (m, 2H), 5.94 (bs, 2H), 4.07 (s, 6H), 3.82 (bs, 2H), 3.75–3.68 (m, 4H), 3.52 (d, J = 10.83 Hz, 2H), 3.40 (s, 6H), 3.21 (d, J = 9.07 Hz, 2H), 2.84 (bs, 2H), 2.61 (bs, 2H), 2.46–2.41 (m, 5H), 1.84–1.64 (m, 5H), 1.33 (d, J = 8.62 Hz, 1H), 1.18 (d, J = 8.85 Hz, 1H), 1.00 (bs, 2H, alc protons). ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 143.41, 136.22, 134.13, 131.16, 128.29, 127.11, 125.10, 120.74, 72.33, 61.78, 59.17, 57.02, 51.32, 46.73, 45.59, 44.58, 43.63, 43.13, 43.12, 42.15, 40.82, 40.72, 34.91. FAB-HRMS (NBA matrix): calcd for $C_{43}H_{48}O_6$, 660.3450; found, 660.3452.

C_{45} Diether–Ene 11. Diol **10** (28.0 mg, 0.0424 mmol) was easily bis-methylated by use of methyl iodide (1 mL, 16.06 mmol) and sodium hydride (316.1 mg, 13.16 mmol) under conditions similar to those of method C (see experimental procedure for **7**). The product **11** was a light yellow oily solid and had R_f = 0.66 in neat ethyl acetate. The isolated yield of the reaction was 28.9 mg (99.3%). FTIR ($CDCl_3$, ν, cm^{-1}): 2961, 2924, 1647, 1449, 1377, 1325, 1259, 1188, 1141, 1100, 1035, 910. ^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 2H), 8.00–7.97 (m, 2H), 7.43–7.40 (m, 2H), 5.92 (s, 2H), 4.05 (s, 6H), 3.80 (bs, 2H), 3.72 (d, J = 9.28 Hz, 2H), 3.40–3.38 (m, 8H), 3.28–3.23 (m, 10H), 2.78 (bs, 2H), 2.59 (bs, 2H), 2.42–2.40 (m, 5H), 1.79–1.77 (m, 4H), 1.60 (d, J = 10.39 Hz, 1H), 1.43 (d, J = 7.96 Hz, 1H), 1.12 (d, J = 9.07 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 143.35, 136.28, 134.30, 131.12, 128.29, 127.11, 125.00, 120.70, 72.59, 67.36, 61.81, 59.14, 58.87, 51.36, 45.86, 45.84, 45.61, 44.42, 43.69, 42.32, 42.03, 40.85, 40.75, 34.51. FAB-HRMS (NBA matrix): calcd for $C_{45}H_{52}O_6$, 688.3763; found, 688.3763.

10 Å C-Clamp DSA 12. A thermal [2 + 2] reaction of **11** (50 mg, 0.072 mmol) with dimethyl acetylenedicarboxylate (9 μL, 0.075 mmol) (Method A; see experimental procedure for **4**) in the presence of catalyst $RuH_2CO(PPh_3)_3$ [15 mg] and subsequent flash column chromatographic (20% ethyl acetate/20% ethyl ether/hexane) purification of the reaction mixture afforded **12** (68%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 2H), 8.01–7.99 (m, 2H), 7.44–7.42 (m, 2H), 4.08 (s, 6H), 3.82 (bs, 2H), 3.73–3.70 (m, 8H), 3.39–3.30 (m, 10H), 3.25–3.22 (m, 8H), 2.65 (bs, 2H), 2.49 (bs, 2H), 2.44–2.41 (m, 3H), 2.36 (bs, 2H), 2.23 (bs, 2H), 2.04 (bs, 2H), 1.82 (d, J = 10.12 Hz, 1H), 1.75 (d, J = 10.64 Hz, 1H), 1.62 (d, 1H), 1.59 (d, J = 11.2 Hz, 1H), 1.29 (d, J = 9.6 Hz, 1H). FTIR ($CDCl_3$, ν, cm^{-1}): 2950, 2922, 2807, 1737, 1721, 1645, 1631, 1478, 1451, 1434, 1324, 1206, 1141, 1099. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 161.59, 143.35, 141.64, 134.32, 131.14, 128.28, 127.09, 125.13, 120.73, 72.53, 67.44, 61.81, 59.15, 58.88, 51.73, 51.33, 49.78, 48.59, 45.99, 45.67, 44.45,43.64, 40.89, 40.77, 34.47, 29.68, 26.90. FAB-HRMS (NBA matrix): calcd for $C_{51}H_{58}O_{10}$, 830.4029; found, 830.4026.

C_{34} Quadricyclane Diester Adduct 13. A solution of **4** (500 mg, 1.1 mmol) in 3 mL of quadricyclane (2.8 g, 30 mmol) was refluxed (110 °C) for 3 days. After cooling, the reaction mixture was loaded onto a SiO_2 column and eluted with 10% ethyl acetate in hexane to remove quadricyclane. The cycloadduct **13** was obtained as a light-yellow oily solid in a quantitative yield [(603 mg), R_f = 0.3 (25% EtOAc/hexane)]. ^1H NMR (250 MHz, $CDCl_3$): δ 8.62 (s, 2H), 8.03–7.99 (m, 2H), 7.47–7.43 (m, 2H), 6.06 (s, 2H), 4.08 (s, 6H), 3.85 (s, 6H), 3.79 (s, 2H), 2.89 (s, 2H), 2.60–2.53 (m, 3H), 2.15 (s, 2H), 1.94 (d, 1H, J = 10.1 Hz), 1.71 (d, 1H, J = 10.3 Hz), 1.17 (d, 1H, J = 10.3 Hz).

C_{32} Terminal-Ene 15. A solution of the diester **13** (220 mg, 0.41 mmol) in 20 mL of dry THF was maintained under N_2 in an ice water bath. $LiAlH_4$ (370 mg, 9.7 mmol) was added, and the reaction was warmed to room temperature over 15 min and then stirred for 48 h. The reaction was quenched with 50 mL of wet THF. Cold 4 N H_2SO_4 (2 mL) was added to react with the LiOH and $Al(OH)_3$ formed. The aqueous phase was extracted with 3 × 30 mL of Et_2O. The organic layers were combined and dried over $MgSO_4$. The solvents were evaporated. The diol **14** (R_f = 0.17, 50% EtOAc/hexane) was purified by flash column chromatography. The yield of the reaction was 95.3 mg (48.4%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 2H), 8.02–8.00 (m, 2H), 7.43 (m, 2H), 6.08 (s, 2H), 4.09 (s, 6H), 3.96 (s, 2H), 3.84–3.72 (m, 4H), 2.96 (s, 2H), 2.36 (s, 2H), 2.11 (d, lH, J = 9.9 Hz), 1.91 (s, 2H), 1.87 (d, 1H, J =10.0 Hz), 1.48 (d, 1H, J = 9.5 Hz), 1.33 (d, 1H, J = 8.6 Hz).

A solution of the diol **14** (166 mg, 0.35 mmol) in 2 mL of pyridine was cooled to −24 °C (CCl_4/dry ice). To this solution was added methanesulfonyl chloride (0.08 mL, 1 mmol). After 10 min of stirring, the reaction flask was moved quickly to a freezer (−5 °C). The reaction was quenched with crushed ice 18 h later. The reaction mixture was extracted with 3 × 30 mL of Et_2O. The organic layers were combined and dried ($MgSO_4$), and the solvents were evaporated. The crude residue was taken up in 10 mL of dry THF under argon and cooled to 0 °C. To this solution was added $LiAlH_4$ (300 mg, 7.9 mmol), and the reaction was warmed to rt after 15 min. The reaction was quenched 48 h later with 40 mL of wet THF followed by 3 mL of cold 4 N H_2SO_4. The aqueous phase was extracted with 3 × 40 mL of ether. The organic layers were combined and dried ($MgSO_4$), and the solvents were evaporated. The residue was loaded onto a SiO_2 column and eluted with EtOAc/hexanes. The band with R_f = 0.46 (10% EtOAc/hexane) was

the desired compound **15** (light yellow solid). The yield of the reaction was 99 mg (79% from **13**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 2H), 8.02–7.99 (m, 2H), 7.45–7.42 (m, 2H), 5.99 (s, broad, 2H), 4.07 (s, 6H), 3.74 (s, 2H), 2.79 (s, 2H), 2.21 (s, 2H), 2.01 (d, 1H, J = 9.8 Hz), 1.78–1.75 (m, 3H), 1.41 (d, 1H, J = 7.6 Hz), 1.21 (d, 1H, J = 8.6 Hz), 0.98 (s, 6H). FT-IR ($CHCl_3$, ν, cm^{-1}): 2922, 2852, 1654, 1462, 1377, 1326, 1261, 1210, 1139, 1088, 1038. ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 143.6, 136.0, 133.7, 131.0, 128.3, 127.2, 125.1, 120.6, 61.8, 50.9, 47.9, 42.4, 42.3, 42.1, 41.9, 40.6, 9.4. MS (FAB): M^+ = 448.

10 Å Linear DSA 16. Ene **15** (99 mg, 0.22 mmol), 5 mg of $RuH_2CO(PPh_3)_3$, and DMAD (0.13 mL, 1.1 mmol) in 1.5 mL of benzene were reacted according to Method A (see experimental procedure for **4**). The residue from the reaction was loaded onto a silica gel column and eluted with 25% EtOAc/hexane. The band with R_f = 0.29 (25% EtOAc/hexane) was the desired DSA **16** (23 mg, 18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 2H), 8.03–8.00 (m, 2H), 7.46–7.43 (m, 2H), 4.07 (s, 6H), 3.79 (s, 6H), 3.70 (s, 2H), 2.58 (s, 2H), 2.28(s, 2H), 2.26(s, 2H), 1.99–1.97 (m, 3H), 1.75 (d, 1H, J = 9.6 Hz), 1.51 (d, 1H, J = 11.2 Hz), 1.36 (d, 1H, J = 11.5 Hz), 0.98 (s, 6H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 161.5, 143.6, 141.8, 133.5, 131.1, 128.3, 127.1, 125.2, 120.6, 61.8, 51.9, 51.6, 50.8, 46.1, 45.4, 42.0, 40.4, 34.2, 26.9, 9.8. MS (FAB): M^+ = 590. HRMS (FAB, NBA matrix): calcd for $C_{38}H_{38}O_6$, 590.2668; found, 590.2658. FTIR (CCl_4, ν, cm^{-1}): 2992, 2947, 1738, 1719, 1454, 1433, 1323.

***exo*-C_{30} Terminal-Ene 17.** A solution of the diol **6** (274 mg, 0.6 mmol) in 2 mL of pyridine was cooled to −24 °C (CCl_4/dry ice). Methanesulfonyl chloride (0.224 mL, 0.33 g, 3 mmol) was added to the solution. After 10 min of stirring, the reaction flask was stored in a freezer (−5 °C). The reaction was quenched with crushed ice 18 h later, which resulted in the formation of white-yellow solids. The reaction mixture was extracted with 3 × 30 mL of Et_2O. The organic layers were combined and dried ($MgSO_4$), and the solvents were evaporated. The product **6a** was obtained in 93% yield [345 mg, R_f = 0.73 (EtOAc)]. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.59 (s, 2H), 8.01–7.97 (m, 2H), 7.46–7.42 (m, 2H), 6.31–6.30 (m, 2H), 4.81 (d, 2H, J = 10.0 Hz), 4.22 (d, 2H, J =10.0 Hz), 4.05 (s, 6H), 3.89 (s, 2H), 3.13 (s, 6H), 3.04 (s, 2H), 2.39 (d, 1H, J =10.5 Hz), 2.01 (d, 1H, J =10.8 Hz), 1.62 (d, 1H, J = 8 Hz), 1.51 (d, 1H, J = 9 Hz).

The crude residue **6a** (103 mg, 0.17 mmol) was taken up in 20 mL of dry THF under argon and cooled to 0 °C. $LiAlH_4$ (200 mg, 5 mmol) was added to the solution, and the mixture was warmed to rt after 15 min. The reaction was quenched 24 h later with 30 mL of wet THF followed by 2 mL of cold 4 N H_2SO_4. The aqueous phase was extracted with 3 × 40 mL of ether. The organic layers were combined and dried ($MgSO_4$), and the solvents were evaporated. The residue was loaded onto a SiO_2 column and eluted with EtOAc/hexanes. The product **17** was obtained as a light yellow solid in 67% yield [47 mg, R_f = 0.36 (10% EtOAc/hexanes)]. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.57 (s, 2H), 8.00–7.97 (m, 2H), 7.44–7.41 (m, 2H), 6.23 (s, 2H), 4.03 (s, 6H), 3.60 (s, 2H), 2.50 (s, 2H), 2.43 (d, 1H, J = 9.9 Hz), 1.80 (d, 1H, J = 9.9 Hz), 1.54 (s, 2H), 1.47–1.41 (m, 2H), 1.21 (s, 6H). MS (FAB, NBA matrix): M^+ = 422.

***exo*-C_{37} Inverse Diels–Alder Adduct 18.** To the dienophile **17** (130 mg, 0.31 mmol) in a high-pressure tube was added the electron-poor diene 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (244 mg, 0.93 mmol). The tube was flushed with argon for 15 min, sealed, and heated at 120 °C for 48 h. The reaction mixture was cooled to rt, and the product was purified using flash column chromatography. Unreacted 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene was flushed out using 5% EtOAc/hexanes. The cycloadduct **18** was obtained in 63% yield (113 mg) and had a R_f of 0.27 (10% EtOAc/hexanes). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.62 (s, 2H), 8.05–8.01 (m, 2H), 7.49–7.45 (m, 2H), 4.09 (s, 6H), 3.66 (s, 2H), 3.42 (s, 3H), 3.35 (s, 3H), 3.07 (s, 2H), 2.40 (s, 2H), 2.32 (d, 1H, J =10.2 Hz), 2.01 (s, 2H), 1.82 (d, 1H, J = 10.2 Hz), 1.52 (d, 1H, J = 12.3 Hz), 1.18 (d, 1H, J = 12.2 Hz), 1.11 (s, 6H).

***exo*-C_{35} Ketone 19.** 2-Propanol (2.8 mL) was added to a solution of the cycloadduct **18** (113 mg, 0.27 mmol) in 25 mL of dry THF, and the solution was brought to reflux. Over a period of 3 h, 5 lots of sodium pellets were added (each lot weighing approximately 200 mg) to this refluxing mixture. After 17 h, the reaction flask was cooled in an ice water bath and methanol was added to react excess Na. The reaction mixture was diluted with 40 mL of water. The aqueous layer was extracted with 3 × 30 mL of hexane. The organic layers were combined and dried with $MgSO_4$, and the solvents were evaporated.

The crude residue **18a** was immediately taken up in 3 mL of methyl acetate and hydrogenated with H_2 (1 atm) and 43 mg of 5% Pd/C for 17 h. The reaction was filtered through a plug of glass wool/silica gel, and the solvents were removed. The central ring of the anthracene nucleus was also reduced in this process. Thus, the crude residue was dissolved in benzene and dichlorodicyanoquinone (25 mg) was added. After 17 h, the product mixture was loaded onto a silica gel column. On elution with 10% EtOAc/hexanes, the band with R_f = 0.27 afforded **18b** as a light yellow solid (50 mg, 55% from **18**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 2H), 8.03–8.00 (m, 2H), 7.46–7.43 (m, 2H), 4.06 (s, 6H), 3.61 (s, 2H), 3.15 (s, 3H), 3.04 (s, 3H), 2.53 (s, 2H), 2.44 (s, 2H), 2.32 (d, 1H, J =10 Hz), 2.06 (d, 1H, J = 9.35 Hz), 1.95 (s, 2H), 1.82 (s, 2H), 1.75 (d, 1H, J = 9.24 Hz), 1.59 (s, broad, 4H), 1.33 (d, 1H, J = 10 Hz), 1.11 (s, 6H).

To a solution of **18b** (50 mg, 0.12 mmol) in 8 mL of THF was added 4 mL of 40% H_2SO_4. The solution was stirred at room temperature for 24 h. The reaction mixture was extracted with Et_2O (3×). The ether layers were combined, washed with 20 mL of saturated $NaHCO_3$, and dried ($MgSO_4$), and the solvents were removed. The residue was developed on a preparative TLC plate using 10% EtOAc/hexanes. The ketone **19** [R_f = 0.14 (10% EtOAc/hexanes)] was obtained as a light-yellow solid (35 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 2H), 8.02–7.99 (m, 2H), 7.45–7.42 (m, 2H), 4.06 (s, 6H), 3.63 (s, 2H), 2.57 (s, 2H), 2.39 (s, 2H), 2.30 (d, 1H, J = 10.1 Hz), 2.18 (d, 1H, J = 11.3 Hz), 2.03 (s, 2H), 1.94–1.91 (m, 2H) 1.86 (s, 2H), 1.79, 1.77 (d, 1H, J = 10.4 Hz), 1.70 (d, 2H, J = 9.67 Hz), 1.52 (d, 1H, J =11.4 Hz), 1.14 (s, 6H). FTIR (ν, cm^{-1}) (unsaturated ketone absorption): 1760 cm^{-1}, other major IR bands 2977, 2932, 1650, 1454, 1324. MS (FAB, NBA matrix): M^+ = 504.

***exo*-Symmetry-Allowed 9 Å C-Clamp DSA 20.** To a solution of **19** (35 mg, 0.07 mmol) in 9.5 mL of toluene was added a mixture containing ammonium acetate (catalyst, 146 mg), acetic acid (0.38 mL), and malononitrile (14 mg, 0.22 mmol). The solution was refluxed for 10 h in a Dean–Stark apparatus. The reaction mixture was loaded onto a preparative TLC plate and developed in benzene. This afforded the DSA **20** (15 mg, 39%) as a light-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 2H), 8.02–8.00 (m, 2H), 7.47–7.44 (m, 2H), 4.08 (s, 6H), 3.64 (s, 2H), 2.92 (s, broad, 2H), 2.47 (s, broad, 2H), 2.29–2.27 (m, 3H), 2.04–2.00 (m, 5H), 1.82 (d, 1H, J = 10.5 Hz), 1.62 (d, 2H, J = 8.9 Hz), 1.49 (d, 1H, J = 10.8 Hz), 1.14 (s, 6H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 191.9, 143.4, 134.2, 131.2, 128.3, 127.0, 125.3, 120.8, 111.3, 73.9, 62.0, 51.9, 49.0, 45.5, 43.3, 43.1, 40.2, 38.2, 35.4, 21.9, 17.3. MS (FAB, NBA matrix): M^+ = 552. FTIR (acetone, ν, cm^{-1}): 2966, 2943, 2226, 1637, 1455, 1320. FAB-HRMS (NBA matrix): calcd for $C_{38}H_{36}O_2N_2$, 552.2776; found, 552.2778.

***endo*-C_{32} Diels–Alder Adduct 21.** Diester **4** (471 mg, 1.06 mmol) was hydrolyzed by refluxing with NaOH (84.8 mg) in 12 mL of a 1:1 mixture of EtOH/H_2O for 15 min. The reaction mixture was cooled to 0 °C. Upon addition of cold 4 N H_2SO_4 to the solution, the diacid **4a** precipitated. The aqueous phase was then extracted with 30 mL of Et_2O (3×). The organic layers were combined and dried ($MgSO_4$), and the solvents were evaporated. The diacid **4a** was obtained as a light-yellow solid in 95% yield (419.5 mg), R_f = 0.05 (5% MeOH/EtOAc). ^{1}H NMR (400 MHz, CD_3OD): δ 8.60 (s, 2H), 8.03–8.00 (m, 2H), 7.47–7.44 (m, 2H), 4.12 (s, 6H), 3.77 (s, 2H), 3.03 (s, 2H), 1.89 (d, 1H, J = 8.0 Hz), 1.81 (d, 2H, J = 8.0 Hz). IR (solid thin layer, ν, cm^{-1}): 1741, 1727.

To a solution of the diacid dienophile **4a** (604 mg, 1.44 mmol) in 1,2-dimethoxyethane was added cyclopentadiene (8 mL, 97 mmol). The reaction was stirred at rt for 24 h, following which a NaOH/H_2O (200 mL, 0.3 M) mixture was added to separate the unreacted cyclopentadiene from the sodium salt of the

diacid mixture **4b**. The aqueous layer was washed with 30 mL (3×) of hexanes to remove cyclopentadiene. Upon addition of cold 4 N H_2SO_4 to the solution, the diacid adducts **4b** (both isomers) precipitated out of solution. The aqueous phase was extracted with 50 mL of Et_2O (3×). The organic layers were combined and dried ($MgSO_4$), and the solvents were evaporated. The *endo/exo* ratio (*endo/exo*, 2.5/1) was ascertained by ^1H NMR.

For ease of separation, the diacid mixture **4b** was converted to the corresponding diester mixture using diazomethane. The crude residue of the diacids (2 g) was dissolved in 300 mL of Et_2O and cooled to 0 °C. To this was added ethereal diazomethane (generated by the addition of *N*-nitrosomethylurea (3.3 g) to a KOH (3 mL, 40%)/Et_2O (30 mL) suspension) and the reaction was stirred at 0 °C for 1 h. Acetic acid was added to quench the reaction and react with any leftover diazomethane. The solvents were evaporated. The two diesters (*endo/exo*) generated were separated by flash column chromatography (10% EtOAc/hexanes) which afforded the *endo* diester adduct **21** (518 mg, 24.5% from the diacid **4a**) as a light-yellow solid. ^1H NMR (250 MHz, $CDCl_3$): δ 8.62 (s, 2H), 8.03–7.99 (m, 2H), 7.47–7.43 (m, 2H), 6.21 (s, 2H), 4.10 (s, 6H), 3.95 (s, 2H), 3.77 (s, 6H), 3.07 (s, 2H), 2.55 (d, 1H, J = 10.6 Hz), 2.16 (s, 2H), 1.91 (d, 1H, J = 9.56 Hz), 1.81 (d, 1H, J =10.7 Hz), 1.32 (d, 1H, J = 9.72 Hz).

***endo*-C_{30} Terminal-Ene 22.** The diester **21** (488 mg, 0.96 mmol) was reduced to the diol **21a** by the use of $LiAlH_4$ (370 mg, 9.7 mmol) following method B (see procedure for the preparation of **6**). The diol **21a** was obtained as a light-yellow solid in quantitative yield [433 mg, R_f = 0.32 (EtOAc)]. ^1H NMR (250 MHz, $CDCl_3$): δ 8.61 (s, 2H), 8.03–7.99 (m, 2H), 7.47–7.43 (m, 2H), 6.33 (s, broad, 2H), 4.09 (s, 6H), 3.97 (d, 2H, J = 10.9 Hz), 3.89 (s, 2H); 3.30 (d, 2H, J = 11.0 Hz), 2.93 (s, 2H), 2.38 (d, 1H, J = 10.22 Hz), 2.00 (s, 2H), 1.92 (d, 1H, J = 10.4 Hz), 1.86 (d, 1H, J = 9.4 Hz), 1.35 (d, 1H, J = 9.8 Hz).

A solution of the diol **21a** (433 mg, 0.95 mmol) in 9 mL of pyridine was cooled to −24 °C (CCl_4/dry ice). To this solution was added methanesulfonyl chloride (1.2 mL, 1.8 g, 15 mmol). After 10 min of stirring, the reaction flask was moved to a freezer (−5 °C). The reaction was quenched with crushed ice 24 h later, which resulted in the formation of white-yellow solids. The reaction mixture was extracted with 3 × 100 mL of Et_2O. The organic layers were combined and dried ($MgSO_4$), and the solvents were evaporated. The product **21b** was obtained in 93% yield [R_f = 0.44 (50% EtOAc/hexanes)]. The crude residue **21b** (517 mg) was taken up in 10 mL of dry THF under argon and cooled to 0 °C. $LiAlH_4$ (600 mg, 16 mmol) was added to this solution, and the reaction was warmed to rt after 30 min. The reaction was quenched 48 h later with 50 mL of wet THF and 6 mL of cold 4 N H_2SO_4. The aqueous phase was extracted with 4 × 50 mL of ether. The organic layers were combined and dried ($MgSO_4$), and the solvents were evaporated. The residue was loaded onto a SiO_2 column and eluted with EtOAc/hexanes. The product **22** was obtained as a light-yellow solid in 58% yield [234 mg, R_f = 0.42 (10% EtOAc/hexanes)]. ^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 2H), 8.02–7.99 (m, 2H), 7.45–7.43 (m, 2H), 6.19 (s, 2H), 4.08 (s, 6H), 3.64 (s, 2H), 2.46 (s, 2H), 2.28 (d, 1H, J = 9.02 Hz), 1.90 (s, 2H), 1.86 (d, 1H, J = 9.2 Hz), 1.82 (d, 1H, J = 10.0 Hz), 1.14 (d, 1H, J = 9.12 Hz), 0.94 (s, 6H). MS (FAB, NBA matrix): M^+ = 422.

***endo*-C_{37} Inverse Diels–Alder Adduct 23.** The dienophile **22** (203 mg, 0.48 mmol) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (635 mg, 2.4 mmol) were flushed with Ar for 20 min in a pressure tube. After 24 h at 140 °C, the reaction mixture was cooled to rt, and the product was purified using flash column chromatography. Unreacted 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene was flushed out using 5% EtOAc/hexanes. The cycloadduct **23** was obtained in 38% yield [125 mg, R_f = 0.2 (10% EtOAc/hexanes)]. ^1H NMR (250 MHz, $CDCl_3$): δ 8.59 (s, 2H), 8.02–7.98 (m, 2H), 7.46–7.42 (m, 2H), 4.03 (s, 6H), 3.61 (s, broad, 5H), 3.52 (s, 3H), 2.76 (s, 2H), 2.24 (d, 1H, J = 10.8 Hz), 1.95–1.90 (m, 3H), 1.87 (s, 2H), 1.81 (d, 1H, J = 10.6 Hz), 1.32–1.28 (m, 1H), 1.10 (s, 6H).

***endo*-C_{35} Ketone 25.** A solution of the cycloadduct **23** (125 mg, 0.18 mmol) in 30 mL of dry THF and 25.6 mL of 2-propanol was brought to reflux. Over a period of 3 h, 4 lots of sodium pellets were added (each lot weighing approximately 200 mg). After 24 h, the reaction flask was cooled in an ice water bath and methanol was added to react with excess Na. The reaction mixture was diluted with 50 mL of water. The aqueous layer was extracted with 3 × 30 mL of hexanes. The organic layers were combined, dried with $MgSO_4$, and concentrated. The reductively dechlorinated product **23a** [R_f = 0.17 (10% EtOAc/hexanes)] was obtained in 77% yield (76 mg) after purification by flash column chromatography (EtOAc/hexanes). ^1H NMR (250 MHz, $CDCl_3$): δ 7.31–7.28 (m, 2H), 7.20–7.15 (m, 2H), 6.05–6.03 (m, 2H), 3.93 (s, 2H), 3.88 (d, 2H, J = 12.5 Hz), 3.01 (s, 6H), 3.38 (s, 2H), 3.20 (s, 3H), 3.08 (s, 3H), 2.86 (s, broad, 2H), 2.43 (s, broad, 2H), 2.31 (d, 1H, J = 12.1 Hz), 2.08 (d, 1H, J = 9.75 Hz), 1.62 (m, 3H), 1.53 (s, 2H), 1.46 (d, 1H, J = 12.0 Hz), 1.02 (s, 6H).

The crude residue **23a** was dissolved in 2 mL of methyl acetate and hydrogenated with H_2 (1 atm) and 42 mg of 5% Pd/C for 12 h. The reaction was filtered through a plug of glass wool and silica gel, following which the solvents were removed. The crude residue was dissolved in benzene (3 mL) and reacted with DDQ (36 mg, 0.16 mmol)] for 18 h. The product mixture was purified on a silica gel column. On elution with 10% EtOAc/hexanes, the band with R_f = 0.20 afforded **24a** as a light-yellow solid (50 mg, 66%). ^1H NMR (250 MHz, $CDCl_3$): δ 8.60 (s, 2H), 8.03–7.97 (m, 2H), 7.46–7.42 (m, 2H), 4.06 (s, 6H), 3.60 (s, 2H), 3.20 (s, 3H), 3.25 (s, 3H), 2.28 (d, 1H, J = 9.8 Hz), 2.20 (s, broad, 2H), 2.05–1.97 (m, 3H), 1.87 (s, 2H), 1.82–1.77 (m, 2H), 1.68–1.59 (m, 6H), 1.03 (s, 6H).

H_2SO_4 (40%, 5 mL) was added to a solution of **24a** (50 mg, 0.09 mmol) in 15 mL of THF. The solution was stirred at room temperature for 15 h. The reaction mixture was cooled in an ice bath and extracted with Et_2O (3×) and saturated aqueous $NaHCO_3$. The ether layers were combined and dried ($MgSO_4$), and the solvents were removed. The residue was purified by flash column chromatography using 10% EtOAc/hexanes. The ketone **25** [R_f = 0.35 (25% EtOAc/hexanes)] was obtained as a light-yellow solid (35 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 2H), 8.01–7.99 (m, 2H), 7.45–7.42 (m, 2H), 4.06 (s, 6H), 3.62 (s, 2H), 2.57 (s, 2H), 2.39 (s, 2H), 2.29 (d, 1H, J = 10.1 Hz), 2.18 (d, 1H, J = 11.32 Hz), 1.93–1.90 (m, 2H), 1.86 (s, 2H), 1.78 (d, 1H, J = 10.36 Hz), 1.70–1.68 (m, 2H), 1.51 (d, 1H, J = 11.4 Hz), 1.14 (s, 6H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 212.9, 143.4, 134.1, 131.1, 128.3, 127.1, 125.2, 120.6, 61.8, 49.4, 48.3, 45.4, 43.9, 43.0, 40.1, 33.8, 29.5, 18.7, 11.3. MS (FAB): M^+ = 504.

***endo*-Symmetry Allowed Linear DSA 26.** A mixture containing ammonium acetate (catalyst, 100 mg), acetic acid (0.5 mL), and malononitrile (17 mg, 0.27 mmol) was added to a solution of ketone **25** (25 mg, 0.05 mmol) in 5 mL of toluene. The solution was refluxed for 3 h in a Dean–Stark apparatus. The reaction mixture was loaded onto a silica gel column and eluted with EtOAc/hexanes. This afforded the DSA **26** [(25 mg, 91%), R_f = 0.46 (25% EtOAc/hexanes)] as a light-yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 2H), 8.02–8.00 (m, 2H), 7.46–7.44 (m, 2H), 4.06 (s, 6H), 3.62 (s, 2H), 3.00 (s, 2H), 2.25 (d, 1H, J = 10.0 Hz), 2.16–2.13 (m, 3H), 2.02–1.99 (m, 2H), 1.93 (s, 2H), 1.90 (s, 2H), 1.82 (d, 1H, J = 10.0 Hz), 1.76 (d, 1H, J = 12.6 Hz), 1.65 (s, broad, 2H), 1.01 (s, 6H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 192.8, 143.5, 133.8, 131.1, 128.3, 127.1, 125.2, 120.6, 111.5, 73.4, 61.9, 49.2, 48.3, 45.6, 45.4, 43.9, 40.1, 37.5, 28.8, 22.0, 11.3. MS (FAB): M^+= 552. FTIR (CCl_4, ν, cm^{-1}): 2964, 2926, 2236, 1994, 1637, 1464, 1323. FAB-HRMS (NBA matrix): calcd for $C_{38}H_{36}O_2N_2$, 552.2776; found, 552.2792.

***endo*-C_{43} Diels–Alder Adduct 27.** Freshly distilled cyclopentadiene (33 μL, 0.493 mmol) was added to a solution of **8** (154 mg, 0.246 mmol) and zinc bromide (383 mg, 1.7 mmol) in methylene chloride. The reaction vessel was sealed and heated at 85 °C for 14 h. The reaction was cooled to room temperature and quenched with 0.5 mL of water, and then the mixture was washed with 3 × 10 mL of 0.1 M sodium thiosulfate ($Na_2S_2O_3$). The organic layer was dried (Na_2SO_4)

and evaporated. The product was further dried *in vacuo*. The product had $R_f = 0.47$ (4.6:3.6:1.8, EtOAc:ethyl-ether:hexane). The reaction yield was 161.1 mg (94.6%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.61 (s, 2H), 8.01–7.98 (m, 2H), 7.45–7.42 (m, 2H), 6.05 (s, 2H), 4.08 (s, 6H), 3.85 (bs, 2H), 3.73 (d, 2H, J = 8.95 Hz), 3.64 (s, 6H), 3.39 (s, 6H), 3.12 (d, 2H, J = 8.98 Hz), 2.89 (bs, 2H), 2.50 (bs, 2H), 2.45–2.42 (m, 3H), 2.33 (bs, 2H), 2.29 (d, 1H, J = 11.23 Hz), 1.96 (d, 1H, J = 9.55 Hz), 1.83 (d, 1H, J = 10.39 Hz), 1.43 (d, 1H, J = 10.15 Hz), 1.14 (d, 1H, J = 9.78 Hz). FTIR (CH_2Cl_2, ν, cm^{-1}): 2981, 2949, 2833, 1741, 1712, 1653, 1454, 1440, 1324, 1242, 1104, 1035. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 171.57, 143.37, 135.90, 133.99, 131.14, 128.27, 127.18, 125.17, 120.70, 72.28, 61.76, 59.18, 58.88, 51.55, 51.16, 51.11, 46.61, 43.64, 43.36, 42.12, 40.90, 40.87, 34.67. FAB-HRMS (NBA matrix): calcd for $C_{43}H_{46}O_8$, 690.3192; found, 690.3217.

***endo*-C_{41} Ene–Diol 28.** Diester **27** (161.3 mg, 0.233 mmol) was reduced without event by $LiAlH_4$ (70 mg, 1.84 mmol) under conditions similar to method B (see procedure for **6**). The product was obtained as light-yellow solid (R_f = 0.23 in neat EtOAc) after flash column chromatography (40% EtOAc/20% ethyl ether/40% pentane) in 73% yield (107.1 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.62 (s, 2H), 8.01–7.98 (m, 2H), 7.45–7.42 (m, 2H), 6.18 (s, 2H), 4.10 (s, 6H), 3.87–3.83 (m, 4H), 3.75 (d, 2H, J = 9.02 Hz), 3.39 (s, 6H), 3.17 (d, 2H, J = 8.92 Hz), 3.13 (d, 2H, J = 10.95 Hz), 2.77 (bs, 2H), 2.43 (bs, 2H), 2.40 (s, 2H), 2.28 (bs, 2H), 2.04 (s, 2H), 2.05 (d, 1H), 1.91 (d, 1H, J = 9.13 Hz), 1.82 (d, 1H, J = 9.82 Hz), 1.65 (d, 1H, J = 11.04 Hz), 1.25 (d, 1H, J = 11.80 Hz), 1.16 (d, 1H, J = 8.80 Hz). FTIR (ν, cm^{-1}, CH_2Cl_2): 3411, 2966, 2942, 2892, 1653, 1558, 1456, 1324, 1096, 1032. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 143.26, 136.67, 133.95, 131.07, 128.21, 127.11, 125.11, 120.63, 72.43, 61.68, 60.98, 59.10, 54.03, 51.61, 48.82, 44.89, 43.65, 42.69, 41.19, 40.80, 40.17, 36.92. FAB-HRMS (NBA matrix): calcd for $C_{41}H_{46}O_6$, 634.3294; found, 634.3299.

***endo*-C_{43} Diether–Ene 29.** Sodium hydride powder (581 mg, 22.99 mmol) and methyl iodide (1.5 mL, 24.09 mmol) easily bis-methylated the diol **28** (105.1 mg, 0.165 mmol) under reaction conditions similar to method C (see the experimental procedure for **7**). The product had a R_f of 0.71 in 50% EtOAc/ethyl ether. The reaction mixture was subjected to flash column chromatography (EtOAc/pentane), and the product was recovered as a light-yellow solid in 81% yield (88.9 mg). ^{1}H NMR (C_6D_6, 400 MHz): δ 8.82 (s, 2H), 7.86–7.83 (m, 2H), 7.22–7.19 (s, 2H), 6.08 (s, 2H), 4.03 (s, 2H), 3.80 (s, 6H), 3.63 (d, 2H, J = 9.29 Hz), 3.59 (d, 2H, J = 9.07 Hz), 3.19–3.16 (m, 8H), 3.05 (s, 6H), 2.97 (s, 2H), 2.81 (bs, 2H), 2.78 (bs, 2H), 2.75–2.72 (m, 3H), 2.54 (s, 2H), 2.39 (d, 1H, J = 9.95 Hz), 2.23 (d, 1H, J = 11.28 Hz), 1.83 (d, 1H, J = 11.03 Hz), 1.75 (d, 1H, J = 10.17 Hz), 0.96 (d, 1H, J = 9.51 Hz). FTIR (CH_2Cl_2, ν, cm^{-1}): 2976, 2923, 2829, 1643, 1448, 1324, 1194, 1100, 1035. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 143.24, 136.69, 134.13, 131.08, 128.25, 127.15, 125.04, 120.63, 72.68, 71.06, 61.73, 59.10, 58.99, 52.31, 51.62, 48.90, 45.16, 43.71, 42.20, 41.97, 40.90, 40.84, 36.79. FAB-HRMS (NBA matrix): calcd for $C_{43}H_{50}O_6$, 662.3607; found, 662.3609.

9 Å C-Clamp DSA 30. DMAD, diether–ene **29**, and catalyst $RuH_2CO(PPh_3)_3$ were added to benzene and reacted in a fashion similar to method A (see the experimental procedure for **4**). The reaction mixture was purified using flash column chromatography (40% EtOAc/20% ether/pentane) to afford the cycloadduct **30** in 42.1% yield (24.5 mg, 98% based on starting material consumed). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.60 (s, 2H), 8.00–7.98 (m, 2H), 7.44–7.41 (m, 2H), 4.05 (s, 6H), 3.80 (s, 2H), 3.72 (d, 2H, J = 8.84 Hz), 3.68 (s, 6H), 3.58 (d, 2H, J = 10.62 Hz), 3.39 (s, 6H), 3.30–3.28 (m, 8H), 3.21 (d, 2H, J = 9.51 Hz), 2.92 (bs, 2H), 2.42–2.39 (m, 3H), 2.33 (s, 2H), 2.27 (bs, 2H), 2.09 (s, 2H), 2.03 (d, 1H, J = 11.06 Hz), 1.91 (d, 1H, J = 11.94 Hz), 1.79 (d, 1H, J = 10.4 Hz), 1.66 (d, 1H, J = 11.06 Hz), 1.16 (d, 1H, J = 11.27 Hz). FTIR (CH_2Cl_2, ν, cm^{-1}): 2972, 2945, 2924, 2824, 2805, 1736, 1718, 1648, 1457, 1436, 1324, 1256, 1203, 1141, 1096, 1036. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 161.50, 143.30, 142.11, 133.99, 131.13, 128.28, 127.15, 125.06, 120.69, 72.54, 68.25, 61.72, 59.14, 58.99, 51.96, 51.67, 50.22, 45.59, 43.68, 42.72, 41.68, 41.42, 40.93, 40.81, 36.57, 24.92. FAB-HRMS (NBA matrix): calcd for $C_{49}H_{56}O_{10}$, 804.3873; found, 804.3870.

***exo*-C_{43} Diels–Alder Adduct 31.** Freshly distilled cyclopentadiene (200 μL, 2.989 mmol) was added to a solution of **8** (159.6 mg, 0.255 mmol) in methylene chloride. The reaction vessel was sealed and heated at 72 °C for 14 h. The reaction was subsequently cooled to room temperature and diluted. The crude material (mixture of diastereomers) was subjected to ^{1}H NMR analysis (the *exo*:*endo* ratio was 4.2:1). The *exo* product **31** had R_f = 0.70 in neat ethyl acetate. The two diastereomers were separated by flash column chromatography (20% EtOAc/20% Et_2O/pentane). The reaction yielded 118.3 mg (68%) of the *exo* adduct. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.60 (s, 2H), 8.03–8.00 (m, 2H), 7.46–7.44 (m, 2H), 6.26 (t, 2H, J = 2.13 Hz), 4.04 (s, 6H), 3.76 (bs, 2H), 3.70 (d, 2H, J = 9.17 Hz), 3.66 (s, 6H), 3.38 (s, 6H), 3.08 (d, 2H, J = 9.2 Hz), 3.03 (t, 2H, J = 2.11 Hz), 2.60 (bs, 2H), 2.42 (d, 1H, J = 10.3 Hz), 2.12 (bs, 2H), 2.08 (s, 2H), 2.04 (d, 1H, J = 11.4 Hz), 1.96 (d, 1H, J = 8.95 Hz), 1.75 (d, 1H, J = 10.5 Hz), 1.46–1.42 (m, 2H). FTIR (CH_2Cl_2, ν, cm^{-1}): 2950, 2918, 2847, 2827, 1737, 1715, 1650, 1454, 1429, 1324, 1253, 1229, 1148, 1095, 1034, 888. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 172.98, 143.35, 137.72, 134.22, 131.06, 128.25, 127.22, 125.21, 120.65, 72.35, 61.68, 60.53, 59.18, 51.48, 51.32, 50.79, 46.68, 43.72, 42.84, 42.63, 40.81, 40.61, 36.81. FAB-HRMS (NBA matrix): calcd for $C_{43}H_{46}O_8$, 690.3192; found, 690.3193.

***exo*-C_{41} Ene–Diol 32.** The diester **31** (115.0 mg, 0.166 mmol) was easily reduced by LAH (56 mg, 1.47 mmol) to the bis-diol **32** under conditions similar to those of method B (see procedure for the synthesis of **6**). The product was obtained as light-yellow solid (R_f = 0.34 in neat EtOAc) after flash column chromatography (20% EtOAc/20% ethyl ether/60% pentane) in 94% yield (99.2 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.63 (s, 2H), 8.02–8.00 (s, 2H), 7.45–7.43 (m, 2H), 6.20 (bs, 2H), 4.05–4.03 (m, 8H), 3.76 (s, 2H), 3.70 (d, 2H, J = 9.11 Hz), 3.58 (d, 2H, J = 11.22 Hz), 3.37 (s, 6H), 3.11 (d, 2H, J = 9.17 Hz), 2.82 (bs, 2H), 2.39–2.36 (m, 3H), 2.27 (d, 1H, J = 11.14 Hz), 2.21 (bs, 2H), 1.96 (s, 2H), 1.88 (alc protons, broad, 2H), 1.74 (d, 1H, J = 9.97 Hz), 1.60 (d, 1H, J = 10.95 Hz), 1.41 (d, 1H, J = 8.67 Hz), 1.33 (d, 1H, J = 8.71 Hz). FT-IR (CH_2Cl_2, ν, cm^{-1}): 3409, 2970, 2932, 2897, 2826, 1653, 1485, 1454, 1323, 1265, 1204, 1142, 1092, 1033, 966. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 143.30, 137.11, 134.22, 131.03, 128.21, 127.16, 125.18, 120.61, 72.43, 62.63, 61.69, 59.09, 54.82, 51.90, 51.26, 48.75, 44.70, 43.75, 40.69, 40.57, 39.95, 37.95. FAB-HRMS (NBA matrix): calcd for $C_{41}H_{46}O_6$, 634.3294; found, 634.3299.

***exo*-C_{41} Diether–Ene 33.** Diol **32** (90.1 mg, 0.142 mmol) was bis-methylated without event by use of NaH powder (400 mg, 16.66 mmol) and methyl iodide (1.25 mL, 20.07 mmol) in THF in a fashion similar to method C (see the experimental procedure for **7**). The product was recovered as a light-yellow solid in 89% yield (83.2 mg) [R_f of 0.70 in neat EtOAc]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.63 (s, 2H), 8.02–8.00 (m, 2H), 7.45–7.42 (s, 2H), 6.19 (s, 2H), 4.03 (s, 6H), 3.83 (d, 2H, J = 9.29 Hz), 3.75 (bs, 2H), 3.68 (d, 2H, J = 9.06 Hz), 3..37 (s, 6H), 3.33 (s, 6H), 3.17 (d, 2H, J = 9.29 Hz), 3.16 (d, 2H, J = 9.28 Hz), 2.85 (bs, 2H), 2.40–2.37 (m, 3H), 2.24 (d, 1H, J = 11.5 Hz), 2.20 (bs, 2H), 1.94 (bs, 2H), 1.73 (d, 1H, J = 9.95 Hz), 1.60 (d, 1H, J = 10.62 Hz), 1.36 (d, 1H, J = 9.21 Hz), 1.31 (d, 1H, J = 9.07 Hz). FTIR (CH_2Cl_2, ν, cm^{-1}): 2966, 2922, 2898, 2824, 2807, 1650, 1481, 1448, 1377, 1324, 1186, 1100, 1033. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 143.25, 136.96, 134.39, 131.00, 128.22, 127.18, 125.09, 120.57, 72.96, 72.69, 61.71, 59.16, 59.05, 53.59, 51.88, 51.25, 48.49, 45.00, 43.76, 40.76, 40.67, 40.49, 37.86. FAB-HRMS (NBA matrix): calcd for $C_{43}H_{50}O_6$, 662.3607; found, 662.3597.

7 Å C-Clamp DSA 34. DMAD (24 μL, 0.195 mmol), **33** (63.0 mg, 0.095 mmol), and catalyst $RuH_2CO(PPh_3)_3$ (13.2 mg) in benzene were reacted according to method A (see the experimental procedure for **4**). The reaction mixture was purified using flash column chromatography (15% EtOAc/5% pentane/hexanes) to afford the cycloadduct **34** in 77% yield (based on starting material consumed). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.62 (s, 2H), 7.99–7.97 (m, 2H), 7.43–7.40 (m, 2H), 4.06 (s, 6H), 3.79 (s, 2H), 3.72–3.68 (m, 4H), 3.62 (s, 6H), 3.37

(s, 6H), 3.30 (s, 6H), 3.24 (bs, 2H), 3.17 (d, 2H, J = 9.29 Hz), 3.10 (d, 2H, J = 9.29 Hz), 2.79 (bs, 2H), 2.44 (s, 2H), 2.40 (d, 1H, J = 11.17 Hz), 2.35 (broad, s, 4H), 2.10 (d, 1H, J = 11.28 Hz), 1.77 (d, 1H, J = 10.4 Hz), 1.59 (d, 1H, J = 11.28 Hz), 1.36 (d, 1H, J = 11.94 Hz), 1.25 (d, 1H, J = 10.84 Hz). FT-IR (CH_2Cl_2, ν, cm^{-1}): 2962, 2923, 2849, 2807, 1734, 1718, 1654, 1636, 1457, 1324, 1212, 1101, 1035, 967. ^{13}C NMR ($CDCl_3$, 100.614 MHz): δ 160.99, 143.38, 142.39, 134.06, 131.08, 128.23, 127.25, 125.12, 120.67, 72.63, 72.58, 61.78, 59.15, 59.08, 53.77, 52.25, 51.55, 50.94, 45.40, 43.76, 42.70, 42.14, 40.98, 40.83, 36.52, 35.92. FAB-HRMS (NBA matrix): calcd for $C_{49}H_{56}O_{10}$, 804.3873; found, 804.3882.

C_{14} Diol 36. A solution of 7-*tert*-butoxynorbornadiene dimer **35** (400 mg, 1.22 mmol) in $CHCl_3$ (4 mL) was maintained under argon. TMSI (0.4 mL, 2.8 mmol, 2.3 equiv) was added. After the reaction was stirred at room temperature for 10 min, the reaction mixture was transferred to a second flask containing 300 mg of $NaHCO_3$ in CH_3OH (1 mL). The liquid was decanted from the $NaHCO_3$, and the solvents were removed. The residue was purified by flash column chromatography (70% EtOAc/hexanes). The crude reaction yield was 235 mg (89%). ^1H NMR (250 MHz, $CDCl_3$): δ 4.53 (s, 2H), 2.83 (s, 4H), 2.45 (s, 6H), 2.28 (s, 2H), 1.54 (s, 2H). FTIR (CCl_4, ν, cm^{-1}): 3308, 2952. EI-HRMS: calcd for $C_{14}H_{16}O_2$, 216.1150; found, 216.1151.

C_{14} Ketone/Alcohol 37. PDC (1.157 g, 3.075 mmol) was added to a solution of the diol **36** (443 mg, 2.050 mmol) in 10 mL of CH_2Cl_2. After being stirred for 21 h, the reaction was filtered through a short plug of silica gel using EtOAc as eluant. The material was then purified by flash column chromatography (50% EtOAc/hexanes to elute the diketone **38** followed by 60% EtOAc/hexanes to elute the diol **36** and the desired ketone/alcohol **37**). The reaction produced 219 mg of the diketone **38** (50%) and 123 mg of the ketone/alcohol **37** (19%). Some unreacted starting diol **36** (66 mg, 10%) was also recovered. Additional **37** was obtained by addition of the diketone **38** (171 mg, 0.806 mmol) in THF (3 mL) to $NaBH_4$ (9 mg, 0.238 mmol, 0.29 eq.) in THF (17 mL). After 10–15 min, the solution became cloudy. After 4.5 h, the reaction was quenched by addition of 10 mL of water. The aqueous layer was extracted with EtOAc (3 × 25 mL). The material was purified by flash column chromatography [40% EtOAc/hexanes was used to elute the diketone **38** (35 mg, 20%). Subsequently, 50% EtOAc/hexanes was used to elute the ketone/alcohol **37** (93 mg, 54%) and finally 70% EtOAc/hexanes was used to elute the diol **36** (25 mg, 14%)]. ^1H NMR (ketone/alcohol **37**, 400 MHz, $CDCl_3$): δ 4.69 (s, 1H), 3.11 (s, 2H), 2.70 (s, 2H), 2.64 (s, 4H), 2.46 (m, 1H), 2.35 (m, 2H), 2.29 (m, 1H), 1.65 (d, 1H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 217.6, 88.1, 53.9, 53.5, 51.9, 51.4, 50.9, 46.9, 46.1. FTIR (CCl_4, ν, cm^{-1}): 3565, 2961, 1737. EI-MS (m/z): 214. EI-HRMS: calcd for $C_{14}H_{14}O_2$, 214.0994; found, 214.0996.

C_{14} Diketone 38. A round-bottomed flask equipped with an argon inlet adapter was charged with a solution of diol **36** (220 mg, 1.017), PDC (2.30 g, 6.11 mmol, 6.0 equiv), CH_2Cl_2 (3 mL, distilled from P_2O_5), and DMF (3 mL, distilled under reduced pressure from $MgSO_4$). The reaction was stirred for 7 h and then poured into a separatory funnel containing water (40 mL) and Et_2O (125 mL). After extraction, the organic layer was dried over $MgSO_4$ and concentrated with a rotary evaporator. The diketone **38** was obtained in 81% yield (176 mg). ^1H NMR (diketone **38**, 250 MHz, $CDCl_3$): δ 2.82 (s, 8H), 2.42 (s, 4H). FTIR (CCl_4, ν, cm^{-1}): 1778, 1752, 2973. EI-HRMS: calcd for $C_{14}H_{12}O_2$, 212.0387; found, 212.0387.

C_{24} Naphthalene Ketal/Ketone 39. A round-bottomed flask equipped with an argon inlet adapter was connected to a Dean–Stark apparatus and charged with diketone **38** (48 mg, 0.226 mmol), 2,3-dihydroxynaphthalene (36 mg, 0.224 mmol, 1.0 equivalent), *p*-toluenesulfonic acid (15 mg, 0.087 mmol), and 15 mL of toluene. The reaction was refluxed for 37 h. The organic layer was extracted with aqueous solutions of NaCl and Na_2CO_3. The organic layer was dried over $MgSO_4$ and concentrated with a rotary evaporator. The naphthalene ketal/ketone **39** was isolated by flash column chromatography. ^1H NMR (naphthalene ketal/ketone, 250 MHz, $CDCl_3$): δ 7.65 (m, 2H), 7.30 (m, 2H), 7.05 (s, 2H), 3.09 (s, 4H), 2.76 (s, 4H), 2.56 (m, 2H), 2.43 (m, 2H). FTIR (CCl_4, ν, cm^{-1}): 2969, 1767, 1551, 1472, 1082. EI-HRMS: calcd for $C_{24}H_{18}O_3$, 354.1256; found, 354.1247.

Naphthalene Ketal/Dicyanoethylene DSA 40. A 25-mL three-necked round-bottomed flask equipped with an argon inlet adapter, a glass stopper, and a Dean–Stark apparatus was charged with a mixture of naphthalene ketal/ketone **39** (19 mg, 0.053 mmol), malononitrile (25 mg, 0.377 mmol, 7.1 equiv), 61 μL of glacial AcOH, β-alanine (13 mg, 0.145 mmol), and 15 mL of benzene. The solution was refluxed for 23 h. It was then transferred to a separatory funnel containing EtOAc and aqueous K_2CO_3. After the organic layer was washed with aqueous K_2CO_3 and saturated NaCl, it was dried ($MgSO_4$) and concentrated with a rotary evaporator. The product was purified by rinsing with acetone, which removed the excess malononitrile. This produced the desired product with the naphthalene ketal donor and the dicyanoethylene acceptor. ^1H NMR (250 MHz, $CDCl_3$): δ 7.65 (m, 2H), 7.31 (m, 2H), 7.05 (s, 2H), 3.27 (m, 2H), 3.12 (s, 4H), 2.90 (s, 4H), 2.68 (m, 2H). FTIR (CCl_4, ν, cm^{-1}): 3057, 2954, 2228, 1627, 1082. ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 195.86, 147.57, 135.32, 130.32, 126.94, 124.31, 111.47, 103.53, 74.92, 53.44, 51.92, 51.82, 51.48. MS m/z (EI): 402. EI-HRMS: calcd for $C_{27}H_{18}N_2O_2$, 402.1368; found, 402.1375.

C_{15} Diol 41. A solution of ketone/alcohol **37** (100 mg, 0.467 mmol) in 20 mL of THF was maintained in a dry ice/acetone (−78 °C) bath under argon. Methyllithium (1.33 mL of a 1.4 M solution in Et_2O, 4.0 equiv) was added dropwise. After 25 min, the flask was removed from the dry ice bath and placed in an ice water bath for 15 min. The reaction mixture was transferred to a separatory funnel containing brine and EtOAc. After the aqueous layer was extracted with 350 mL of EtOAc, the organic layer was dried over $MgSO_4$ and concentrated with a rotary evaporator. ^1H NMR (methanol/alcohol, 250 MHz, $CDCl_3$): δ 4.52 (s, 1H), 2.84 (s, 4H), 2.65–2.20 (m, 7H), 2.08 (s, 1H), 1.38 (s, 3H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 92.81, 86.22, 60.01, 57.40, 55.35, 53.95, 52.59, 52.10, 51.39, 51.10, 50.90, 50.57, 49.86, 49.34, 23.24. FTIR (CCl_4, ν, cm^{-1}): 3284, 2937. CI-HRMS (isobutane): calcd for $C_{15}H_{18}O_2$ $[M - H]^+$, 229.1229; found, 229.1228.

C_{15} Alcohol/Ketone 42. A 50-mL round-bottomed flask was charged with methanol/alcohol **41** (104 mg, 0.452 mmol), PDC (1.504 g, 3.99 mmol, 8.8 equiv), and 7 mL of CH_2Cl_2. After being stirred for 19 h, the reaction was filtered through silica gel (30% EtOAc/hexanes was used as the eluant). The product was obtained in 86% yield (89 mg). ^1H NMR (250 MHz, $CDCl_3$): δ 3.12 (s, 2H), 2.79 (s, 2H), 2.64 (s, 4H), 2.41 (m, 1H), 2.32 (m, 1H), 2.14 (m, 2H), 1.45 (s, 3H). FTIR (CCl_4, ν, cm^{-1}): 3284, 2943, 1749. EI-HRMS: calcd for $C_{15}H_{16}O_2$, 228.1150; found, 228.1157.

C_{15} Methylene/Ketone 43. A suspension of methanol/ketone **42** (80 mg, 0.3506 mmol) in 1.74 mL of pyridine was placed in an ice water bath under argon. Addition of phosphorus oxychloride (138 μL, 1.47 mmol, 4.3 equiv) to this suspension resulted in the formation of a white precipitate. The reaction was removed from the ice bath after 20 min and stirred for a total of 141 h. The solution was then transferred to a separatory funnel containing EtOAc and dilute HCl. The aqueous layer was extracted with 4 × 75 mL of EtOAc. The aqueous layer was neutralized with 30% NaOH and re-extracted with Et_2O (3 × 50 mL). The organic layers were combined and filtered through silica gel [30% EtOAc/hexanes was used as eluant]. The combined organic layers were dried (MgSO4), and the solvents were removed. This gave a total of 64 mg of the methylene/ketone **43** (87%). ^1H NMR (methylene/ketone, 250 MHz, $CDCl_3$): δ 4.56 (s, 2H), 2.80 (s, 4H), 2.65 (m, 6H), 2.39 (m, 2H). FTIR (CCl_4, ν, cm^{-1}): 2922, 1763.

C_{17} Methylene/Ketal 44. A 50-mL round-bottomed flask attached to a Dean–Stark apparatus was charged with methylene/ketone **43** (66 mg, 0.314 mmol), ethylene glycol (20 μL, 0.358 mmol, 1.8 equiv), a few small crystals of *p*-toluenesulfonic acid, and benzene (20 mL). The reaction was refluxed for 4 h, and the contents from the flask were transferred to a separatory funnel containing a saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with several hundred milliliters of ethyl acetate. The organic layer was dried over $MgSO_4$, and the solvents were removed with a

rotary evaporator. The product was purified by column chromatography (5% EtOAc/hexanes). The methylene/ketal **44** was obtained in 70% (56 mg) yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.48 (s, 2H), 3.93 (s, 4H), 2.67 (s, 4H), 2.58 (s, 6H), 2.21 (m, 2H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 165.09, 127.65, 96.61, 64.76, 52.80, 52.71, 51.80, 50.83. FTIR (methylene/ketal, CCl_4, ν, cm^{-1}): 3066 (weak), 2957 (strong). EI-HRMS: calcd for $C_{17}H_{18}O_2$, 254.1307; found, 254.1312.

C_{29} (Dimethylamino)naphthalene/Ketal 45. A 25-mL round-bottomed, flame-dried and argon-flushed flask was charged with methylene/ketal **44** (35 mg, 0.1377 mmol), THF (2.5 mL), and 9-BBN (0.275 mL of 0.5 M solution in THF, 1.0 equiv). The flask was immediately placed in an ice water bath. After 40 min, the flask was removed from the ice bath and stirred at room temperature for 5 h. At this point, catalyst $PdCl_2$(dppf)[49] (3mg), 1-bromo-4-(dimethylamino)naphthalene (**52**) (31 mg, 0.124 mmol, 0.90 equiv), 125 μL of 3 M aqueous NaOH, and THF (2 mL) were added to the flask. Upon addition of the NaOH solution, the solution immediately turned dark brown/black. After refluxing for 14 h, the contents of the flask were transferred to a separatory funnel containing brine and hexanes. After the aqueous layer was extracted with several hundred milliliters of hexanes, the organic layer was dried over $MgSO_4$ and concentrated with a rotary evaporator. The compound was further purified by flash column chromatography [EtOAc/hexanes]. The (dimethylamino)naphthalene/ketal **45** was obtained in 61% yield (32 mg). ^{1}H NMR ((dimethylamino)naphthalene/ketal, 250 MHz, $CDCl_3$): δ 8.29 (m, 1H), 8.03 (m, 1H), 7.49 (m, 2H), 7.21 (d, 1H), 7.03 (d, 1H), 3.93 (s, 4H), 3.02 (d, 2H), 2.94 (s, 2H), 2.86 (s, 6H), 2.79 (t, 1H), 2.63 (m, 2H), 2.60–2.45 (m, 4H), 2.30 (t, 1H), 2.24 (s, 2H), 2.15 (t, 1H). EI-HRMS: calcd for $C_{29}H_{31}NO_2$, 425.2355; found, 425.2347.

C_{27} (Dimethylamino)naphthalene/Ketone 46. (Dimethylamino)naphthalene/ketal **45** (30 mg, 0.070 mmol) was added to a solution containing perchloric acid (0.6 mL), water (1.8 mL), and THF (2.8 mL). After 4 h, 10 mL of water was added to the reaction mixture, and this solution was transferred to a separatory funnel containing aqueous K_2CO_3. The aqueous layer was extracted with EtOAc (3 × 50 mL). The organic layers were combined, washed with aqueous NaOH (pH 10–11), dried ($MgSO_4$), and concentrated with a rotary evaporator. The compound was purified by flash column chromatography (EtOAc/hexanes). The product (dimethylamino)naphthalene/ketone **46** was obtained in 80% yield (22 mg). ^{1}H NMR ((dimethylamino)naphthalene/ketone, 250 MHz, $CDCl_3$): δ 8.30 (m, 1H), 8.02 (m, 1H), 7.50 (m, 2H), 7.22 (d, 1H), 7.01 (d, 1H), 3.17 (s, 2H), 3.08 (d, 2H), 3.00 (t, 1H), 2.87 (s, 6H), 2.72 (s, 2H) 2.61 (m, 2H), 2.54 (m, 2H), 2.45 (t, 1H), 2.31 (t, 1H), 2.24 (s, 2H). MS *m/z* (EI): 381. FTIR ($CHCl_3$, ν, cm^{-1}): 2951, 2861, 2826, 1760, 1044. EI-HRMS: calcd for $C_{27}H_{27}NO$, 381.2093; found, 381.2097.

(Dimethylamino)naphthalene/Dicyanoethylene DSA 47. A 25-mL round-bottomed, flame-dried, argon-flushed flask was charged with (dimethylamino)naphthalene/ketone **46** (14 mg, 0.036 mmol), malononitrile (11 mg, 0.166 mmol, 4.5 equiv), β-alanine (11 mg, 0.123 mmol), 4 mL of benzene, and 61 μL of glacial AcOH. After the reaction mixture was refluxed for several hours, the contents of the flask were transferred to a separatory funnel containing EtOAc. The organic layer was washed with 10% $NaHCO_3$, dried ($MgSO_4$), and concentrated with a rotary evaporator. Purification on silica gel yielded the desired (dimethylamino)naphthalene-containing DSA. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.30 (m, 1H), 7.98 (m, 1H), 7.50 (m, 2H), 7.19 (d, 1H), 7.00 (d, 1H), 3.30 (t, 1H), 3.17 (m, 3H), 3.05 (d, 2H), 2.96 (t, 1H), 2.88 (s, 6H), 2.74 (m, 4H), 2.65 (m, 2H), 2.39 (s, 2H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 196.89, 149.59, 132.76, 132.13, 129.26, 126.01 125.55, 124.83, 124.71, 124.19, 113.62, 111.66, 111.61, 73.73, 61.30, 55.14, 53.88, 53.66, 52.85, 52.73, 50.77, 50.54, 45.28, 33.80. MS *m/z* (EI): 429. EI-HRMS: calcd for $C_{30}H_{27}N_3$, 429.2205; found, 429.2208.

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Xanthene Alcohol/Alcohol 48. *n*-BuLi [1.19 mL (1.6 M)] was added to a solution of xanthene (303 mg, 1.663 mmol, 2.3 equiv) in 30 mL of THF maintained under argon at −78 °C. The solution rapidly turned bright red, indicating the formation of xanthenyllithium. This xanthenyllithium solution was transferred to a solution of the ketone/alcohol **37** (155 mg, 0.723 mmol) in 30 mL of THF at −78 °C (dry ice/acetone). The red color of the xanthenyllithium solution faded on initial addition to solution of the ketone/alcohol **37**. However, the solution eventually became red as additional xanthenyllithium was added. After 30 min, the reaction was removed from the dry ice bath. The reaction was quenched after 4 h by transferring the solution into an aqueous NH_4Cl solution. The aqueous layer was extracted with diethyl ether (3 × 100 mL) and dried ($MgSO_4$), and the solvents were removed. The product was purified using flash column chromatography (10% EtOAc/hexanes to remove xanthene and then 50% EtOAc/hexanes to elute the desired product). The yield of the reaction was 265 mg (92%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.35–7.00 (m, 8H), 4.48 (s, 1H), 4.17 (s, 1H), 2.96 (m, 3H), 2.70 (m, 3H), 2.56 (m, 1H), 2.45–2.25 (m, 4H), 2.21 (m, 1H). FTIR (CCl_4, ν, cm^{-1}): 3395, 2958. EI-HRMS: calcd for $C_{27}H_{23}O_3$ [M −H]$^+$, 395.1647; found, 395.1655.

Xanthene Alcohol/Ketone 49. A round-bottomed flask was charged with a solution of xanthene alcohol/alcohol **48** (232 mg, 0.525 mmol) in 30 mL of CH_2Cl_2 under argon. PDC (1.63 g, 4.332 mmol) was added to the solution. The reaction was stirred for 18 h and then filtered through a silica gel column (eluant: 50% EtOAc/hexanes) to produce the desired xanthene alcohol/ketone **49** (180 mg, 78%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.35–6.95 (m, 8H), 4.20 (s, 1H), 3.20 (s, 2H), 2.93 (s, 2H), 2.77 (m, 2H), 2.59 (m, 2H), 2.41 (m, 2H), 2.27 (s, 2H), 1.67 (s, broad, 1H). FTIR (CCl_4, ν, cm^{-1}): 3464, 2958, 1763. EI-HRMS: calcd for $C_{27}H_{23}O_3$ [M + H]$^+$, 395.1647; found, 395.1639.

Xanthenylidene/Ketone 50. Phosphorus oxychloride (0.24 mL, 2.575 mmol) was added to a solution of xanthene alcohol/ketone **49** (233 mg, 0.590 mmol) and 3 mL of pyridine (distilled from BaO) at 0 °C. The addition of $POCl_3$ resulted in the formation of precipitate after several minutes. The reaction was stirred for 90 h at room temperature. The material in the flask was then transferred to a separatory funnel containing ice water and ethyl acetate. After extraction, the ethyl acetate solution was washed with aqueous $NaHCO_3$ and aqueous NaCl in succession. The organic layer was dried (MgSO4) and filtered, and the solvents were removed. After purification by flash column chromatography, 147 mg of product was obtained (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.43 (d, 2H), 7.26–7.08 (m, 6H), 3.45 (s, 2H), 2.91 (s, 4H), 2.70 (s, 4H), 2.44 (s, 2H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 210.99, 154.81, 153.63, 127.55, 126.97, 125.72, 123.08, 116.43, 114.63, 54.73, 52.36, 47.30, 47.26. FTIR (CCl_4, ν, cm^{-1}): 2970, 1770, 1755. EI-HRMS: calcd for $C_{27}H_{20}O_2$, 376.1463; found, 376.1461.

Xanthenylidene/Dicyanoethylene DSA 51. The final step to the desired DSA molecule **51** was accomplished by adapting a modified Knoevenagel condensation. A solution containing xanthenylidene/ketone **50** (50 mg, 0.133 mmol), malononitrile (35 mg, 0.530 mmol, 4 equiv), β-alanine (12 mg, 0.134 mmol), and 67 μL of glacial AcOH in 1.4 mL of benzene was refluxed for 2.5 h in a Dean–Stark apparatus. The solution was transferred to a separatory funnel containing EtOAc. The EtOAc solution was washed in succession with 10% $KHCO_3$, water, and aqueous NaCl solution. The organic layer was dried ($MgSO_4$), and the solvents were removed. The product was purified by flash column chromatography (15% $CHCl_3$/5% EtOAc/hexanes). The compound was purified further by rinsing with pentane and acetone, in which the product was not soluble. This produced the desired product, with the xanthenylidene functionality separated from the dicyanoethylene group by the rigid norbornane dimer spacer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, 2H), 7.30–7.07 (m, 6H), 3.57 (s, 2H), 3.29 (s, 2H), 2.93 (s, 4H), 2.83 (s, 4H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 196.79, 153.61, 153.45, 127.79, 126.90, 125.34, 123.15, 116.52, 114.94, 111.55, 74.41, 54.16, 52.47, 51.79,

49.97. FTIR (CCl_4, ν, cm^{-1}): 2957, 2232. MS *m/z* (EI): 424. EI-HRMS: calcd for $C_{30}H_{20}N_2O$, 424.1576; found, 424.1578.

1-Bromo-4-(*N,N*-dimethylamino)naphthalene 52. To a round-bottomed, argon-flushed, and flame-dried flask attached to a condenser was added a mixture containing 1-bromo-4-aminonaphthalene[50] (500 mg, 2.262 mmol), anhydrous K_2CO_3 (465 mg, 3.364 mmol, 1.5 equiv), and 3 mL of distilled DMF. To this mixture was added methyl iodide (0.6 mL, 9.639 mmol, 4.2 equiv), and the reaction was refluxed at 65 °C for 25 h. The solution turned golden brown after 1 h. The temperature was increased to 120 °C, and the reaction was refluxed for an additional 3 h. The heat was discontinued at this point, and the reaction was stirred for an additional 16 h. The reaction was thereafter transferred to a separatory funnel containing 75 mL of $CHCl_3$. The organic layer was washed with approximately 400 mL of water and then with brine. The organic layer was dried ($MgSO_4$) and concentrated with a rotary evaporator. The solution was placed in a vacuum desiccator overnight, giving 560 mg of 1-bromo-4-(*N,N*-dimethylamino)-naphthalene (99%). ^1H NMR (1-bromo-4-(*N,N*-dimethylamino)naphthalene, 250 MHz, $CDCl_3$): δ 8.22 (m, 2H), 7.66 (d, 1H), 7.54 (m, 2H), 6.91 (d, 1H), 2.86 (s, 6H).

Ether/Alcohol 53. 7-*tert*-butoxynorbornadiene dimer **35** (1.0 g, 3.04 mmol) was added to a small round-bottomed flask containing dry $CHCl_3$ (10 mL) under a stream of argon. After TMSI (0.22 mL, 0.5 equiv) was added, the solution was stirred at room temperature for 30 min. The reaction was quenched by addition of 0.5 mL of CH_3OH. The solvents were evaporated to give a dark green residue. The residue was taken up in Et_2O (25 mL) and washed with 10% $NaHSO_3$, 10% $NaHCO_3$, and brine. The organic layer was dried (Na_2SO_4), and the solvents were removed. The mixture of diether **35**, ether/alcohol **53**, and diol **36** was separated by flash column chromatography (7% EtOAc/hexanes was used until the diether **35** eluted and then 40% EtOAc/hexanes was used to elute the ether/alcohol **53** and finally 100% ethyl acetate was used to elute the diol **36**). The ether/alcohol **53** was obtained in 49% yield (406 mg). FTIR (CCl_4, ν, cm^{-1}): 3260, 2955. ^1H NMR (250 MHz, $CDCl_3$): δ 4.50 (d, 1H), 4.29 (s, 1H), 2.78 (s, 4H), 2.39 (s, 6H), 2.25 (s, 1H), 2.19 (s, 1H), 1.47 (d, 1H), 1.18 (s, 9H). EI-HRMS: calcd for $C_{17}H_{21}O_2$ $(M - CH_3)^+$, 257.1542; found, 257.1546.

Ether/Ketone 54. Pyridinium dichromate (874 mg, 2.323 mmol) was added to a methylene chloride solution of the ether/alcohol **53** (422 mg, 1.55 mmol). The reaction was stirred at room temperature for 17 h and then filtered through a short silica gel column. The product was separated from residual starting ether/alcohol **53** by flash column chromatography (EtOAc/hexanes). The ether/ketone **54** was obtained in 85% yield (356 mg). FTIR (CCl_4, ν, cm^{-1}): 2972, 1747. ^1H NMR (250 MHz, $CDCl_3$): δ 4.44 (m, 1H), 3.06 (s, 2H), 2.7–2.5 (m, 6H), 2.40 (m, 1H), 2.25 (s, 3H), 1.19 (s, 9H). EI-HRMS: calcd for $C_{18}H_{22}O_2$, 270.1620; found, 270.1612.

Ether/Alcohol 55. A flame-dried, argon-flushed, round-bottomed flask was charged with ether/ketone **54** (150 mg, 0.55 mmol) and 15 mL of distilled THF. The flask was cooled to −78 °C in a dry ice/acetone bath. Methyllithium (0.57 mL of a 1.4 M solution, 1.4 equiv) was added to the flask. After 30 min at −78 °C, the reaction was warmed to room temperature and was stirred for an additional 10 min. The contents of the flask were transferred to a separatory funnel containing brine and ethyl acetate. After extraction, the organic phase was dried over $MgSO_4$, and the solvents were removed. This gave 142 mg of ether/methanol **55** (89%). ^1H NMR (250 MHz, $CDCl_3$): δ 4.28 (m, 1H), 2.80 (s, 4H), 2.49 (s, 2H), 2.39 (s, 2H), 2.32 (s, 1H), 2.19 (s, 2H), 2.03 (s, 1H), 1.61 (s, broad, 1H), 1.37 (s, 3H), 1.18 (s, 9H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 92.77, 85.94, 72.80, 59.88, 57.35, 55.14, 53.72, 52.50, 52.10, 51.87, 51.59, 51.03, 50.41, 49.11, 48.68, 28.61, 23.15. FTIR (CCl_4, ν, cm^{-1}): 3446, 2961. EI-HRMS: calcd for $C_{19}H_{26}O_2$, 286.1933; found, 286.1926.

Ether/Methylene 56. A solution of ether/methanol **55** (142 mg, 0.496 mmol) in pyridine (2.5 mL) was maintained in an ice water bath under argon. After the addition of phosphorus oxychloride (0.196 mL, 2.103 mmol, 4.3 equiv), the reaction was stirred at 0 °C for 4–5 h. It was then warmed to room temperature and stirred for a total of 91 h. The reaction material was then transferred to an Erlenmeyer flask containing pentane, 2.5 mL of concentrated HCl, and 100 mL of water. After stirring, the organic layer was washed with water and 10% $KHCO_3$. The acid solution was washed with 4 × 25 mL of pentane, which was then washed with water. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated with a rotary evaporator, giving 126 mg of ether/methylene **56** (95%). ^1H NMR (250 MHz, $CDCl_3$): δ 4.46 (s, 2H), 4.29 (m, 1H), 2.83 (s, 2H), 2.67 (s, 1H), 2.50 (s, 5H), 2.41 (s, 2H), 2.28 (s, 2H), 1.18 (s, 9H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 165.18, 96.13, 86.37, 72.80, 54.37, 54.16, 52.47, 52.43, 51.79, 51.62, 49.45, 28.60. FTIR (CCl_4, ν, cm^{-1}): 3069, 2957. EI-HRMS: calcd for $C_{19}H_{24}O$, 268.1827; found, 268.1833.

Methylnaphthalene/Ether 57a. Ether/methylene **56** (94 mg, 0.35 mmol) was added to a round-bottomed flask containing 2.5 mL of THF. The flask was placed in an ice bath and was charged with 9-borabicyclo[3.3.1]nonane (0.70 mL of a 0.5 M solution in THF). After being stirred for 5 h in the ice bath, the reaction mixture was warmed to room temperature. Catalyst, $PdCl_2$(dppf) [6.9 mg], 1-bromo-4-methylnaphthalene (50 μL, 0.319 mmol), 3 M aqueous NaOH (319 μL), and THF (2 mL) were added rapidly and in succession. The solution was then refluxed for 14 h. The organic layer was transferred to a separatory funnel containing EtOAc and an aqueous NaCl solution. After several wash cycles, the organic layer was dried over $MgSO_4$ and concentrated with a rotary evaporator. The resulting residue was purified by flash column chromatography (5% EtOAc/ hexanes), giving 101 mg of methylnaphthalene/ether **57a** (77%). ^1H NMR (250 MHz, $CDCl_3$): δ 8.03 (m, 2H), 7.50 (m, 2H), 7.20 (m, 2H), 4.24 (s, 1H), 3.04 (d, 2H), 2.95–2.10 (m, 16H), 1.18 (s, 9H).

The coupling yields achieved with the other bromoaromatics are as follows:

bromoaromatic	yield of Pd coupling reaction (product)
bromonaphthalene	80 (**57b**)
4-bromoacenaphthene	93 (**57c**)
1-bromo-4-methoxynaphthalene	79 (**57d**)

Methylnaphthalene/Alcohol 58a. A solution of methylnaphthalene/ether **57a** (101 mg, 0.246 mmol) in 7 mL of $CHCl_3$ was maintained in an ice water bath under argon. TMSI (88 μL, 0.618 mmol, 2.5 equiv) was added to the solution. After 5 min, the reaction flask was warmed to room temperature and the solution was stirred for 1 h. The flask contents were transferred to a round-bottomed flask containing 5 mL of CH_3OH, and the solvents were removed with a rotary evaporator. The residue obtained was taken up in EtOAc and transferred to a separatory funnel containing aqueous $NaHSO_3$ and EtOAc. The aqueous layer was extracted with EtOAc (3 × 25 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated with a rotary evaporator, giving the methylnaphthalene/alcohol **58a**. ^1H NMR (250 MHz, $CDCl_3$): δ 8.05 (m, 2H), 7.51 (m, 2H), 7.21 (m, 2H), 4.47 (s, 1H), 3.06 (d, 2H), 3.00–2.14 (m, 16H), 1.61 (s, br, 1H). FTIR (trace acetone, ν, cm^{-1}): 3361, 3070, 1072. EI-HRMS: calcd for $C_{26}H_{26}O$, 354.1984; found, 354.1980.

Methylnaphthalene/Ketone 59a. A round-bottomed flask was charged with methylnaphthalene/alcohol **58a** (87 mg, 0.245 mmol), 5 mL of CH_2Cl_2, and PDC (804 mg, 2.137 mmol, 8.7 equiv). The reaction was stirred for 40 h. The chromium salts were removed from the reaction by filtering the methylene chloride solution through a silica gel column using Et_2O as eluant. This yielded the methylnaphthalene/ketone **59a**. ^1H NMR (250 MHz, $CDCl_3$): δ 8.05 (m, 2H), 7.53 (m, 2H), 7.21 (m, 2H), 3.17 (s, 2H), 3.12 (d, 2H), 2.98 (t, 1H), 2.80–2.20 (m, 13H). FTIR ($CHCl_3$, ν, cm^{-1}): 2951, 1762, 1150. EI-HRMS: calcd for $C_{26}H_{24}O$, 352.1827; found, 352.1824.

Methylnaphthalene/Dicyanoethylene DSA 60a. A round-bottomed flask was charged with methylnaphthalene/ketone **59a** (18 mg, 0.051 mmol), malononitrile (17 mg, 0.257

(50) Bacon, R. G. R.; Hill, H. A. O. *J. Chem. Soc.* **1964**, 1108.

mmol, 5 equiv), β-alanine (11 mg, 0.123 mmol), 10 mL of benzene, and 61 μL of glacial AcOH. The flask was attached to a Dean–Stark apparatus and refluxed for 7 h. The solution was then transferred to a separatory funnel containing EtOAc, and the organic layer was washed with 10% $KHCO_3$, H_2O, and finally with brine. After the organic layer was dried over $MgSO_4$ and the solvent was removed with a rotary evaporator, the DSA **60a** was obtained as the only detectable product. ^1H NMR (250 MHz, $CDCl_3$): δ 8.04 (m, 2H), 7.53 (m, 2H), 7.21 (m, 2H), 3.31 (t, 1H), 3.17 (m, 3H), 3.10 (d, 2H), 2.96 (t, 1H), 2.72 (m, 4H), 2.67 (m, 5H), 2.37 (s, 2H). FTIR ($CHCl_3$, ν, cm^{-1}): 2955, 2232, 1631, 1295. ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 196.93, 135.77, 133.06, 132.72, 131.78, 126.22, 125.94, 125.42, 125.33, 124.96, 124.36, 111.71, 111.66, 73.80, 61.36, 55.18, 53.94, 53.71, 52.89, 52.79, 50.82, 50.59, 34.06, 19.42. MS *m/z* (EI): 400. EI-HRMS: calcd for $C_{29}H_{24}N_2$, 400.1939; found, 400.1940.

Spectroscopic Data. The spectroscopic data for the remaining compounds in the series are listed below.

Naphthalene/Dicyanoethylene DSA 60b. ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, 1H, J = 8.4 Hz), 7.87 (d, 1H, J = 7.5 Hz), 7.73 (d, 1H, J = 8.2 Hz), 7.50 (m, 2H), 7.39 (m, 1H), 7.29 (d, 1H, J = 6.8 Hz), 3.31 (t, 1H, J = 4.5 Hz), 3.17 (m, 3H), 3.13 (d, 2H, J = 7.6 Hz), 2.97 (t, 1H, J = 7.6 Hz), 2.74 (m, 4H), 2.66 (m, 2H), 2.38 (s, 2H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 196.87, 137.65, 133.99, 131.75, 128.87, 126.75, 126.23, 125.79, 125.50, 125.47, 123.81, 111.71, 111.66, 73.83, 61.24, 55.17, 53.94, 53.71, 52.90, 52.79, 50.82, 50.60, 34.10. MS: *m/z* (EI): 386.

Acenaphthene/Dicyanoethylene DSA 60c. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, 1H, J = 8.2 Hz), 7.47 (m, 1H), 7.29 (d, 1H, J = 6.7 Hz), 7.21 (m, 2H), 3.39 (m, 2H), 3.38 (m, 2H), 3.31 (t, 1H, J = 4.2 Hz), 3.17 (m, 3H), 3.05 (d, 2H, J = 7.7 Hz), 2.95 (t, 1H, J = 7.5 Hz), 2.73 (m, 4H), 2.65 (m, 2H), 2.37 (s, 2H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 197.01, 146.63, 144.23, 139.62, 133.46, 130.29, 127.59, 127.55, 119.23, 119.07, 118.97, 111.72, 111.68, 73.76, 61.57, 55.21, 53.93, 53.72, 52.90, 52.77, 50.82, 50.60, 33.15, 30.55, 29.85. MS: *m/z* (EI): 412.

Methoxynaphthalene/dicyanoethylene DSA 60d. ^1H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, 1H, J = 8.4 Hz), 7.95 (d, 1H, J = 8.2 Hz), 7.51 (m, 2H), 7.18 (d, 1H, J = 7.7 Hz), 6.74 (d, 1H, J = 7.7 Hz), 3.99 (s, 3H), 3.31 (t, 1H, J = 4.4 Hz), 3.17 (m, 3H), 3.04 (d, 2H, J = 7.7 Hz), 2.94 (t, 1H, J = 7.6 Hz), 2.73 (m, 4H), 2.65 (m, 2H), 2.37 (s, 2H). ^{13}C NMR (100.614 MHz, $CDCl_3$): δ 197.02, 154.22, 132.51, 129.56, 126.31, 126.03, 125.92, 124.84, 123.68, 122.73, 111.75, 111.69, 103.33, 73.79, 61.43, 55.49, 55.21, 53.96, 53.73, 52.92, 52.76, 50.83, 50.60, 33.66. MS: *m/z* (EI): 416.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of **3–18**, **20–22**, **23**, **25–34**, **36–56**, **58a–59a**, and **60a–d** (88 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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