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Facial Stereoselective Diels–Alder Cycloadditions of a Sesquibicyclo[2.2.2]octadiene-fused Maleic Anhydride with Exocyclic 1,3-Butadienes

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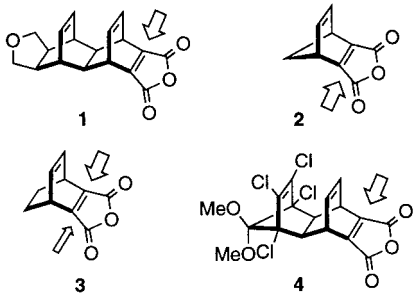
Abstract—The Diels–Alder cycloadditions of facially dissymmetric sesquibicyclo[2.2.2]octadiene-fused maleic anhydride **1** with exocyclic 1,3-butadienes have been studied. The reactions proceeded via *syn*-side (relative to the etheno-bridge in **1**) attack of the diene upon **1**.

Rigid polycyclic molecules having isolated double bonds located in the laticyclic topology[1] and spatially in close proximity have provided suitable frameworks for study of orbital interactions[2] and transannular reactions.[3] As our interest in the synthesis and transannular reactions of polycyclic hydrocarbons continues, we recently have reported the preparation and the Diels–Alder cycloadditions of 11-oxapentacyclo[6.5.2.2^{3,6}.0^{2,7}.0^{9,13}]heptadeca-4,14,16-trien-4,5-dicarboxylic anhydride (**1**).[4] Compound **1** has facial dissymmetry about the anhydride double bond, and is expected to display facial selectivity in the Diels–Alder cycloaddition. We observed that the Diels–Alder cycloaddition of **1** with cyclopentadiene proceeded via *syn*-side (relative to the etheno-bridge in **1**) attack of the diene upon the activated double bond of **1** to produce Alder and anti-Alder adducts in a ratio of 1:1.[4] This result was contrary to the behavior of bicyclo[2.2.1]hepta-2,5-dien-2,3-dicarboxylic anhdride (**2**) which is known to undergo the Diels–Alder cycloadditions with dienes exclusively on the face *anti* to the etheno-bridge of **2**.[5] However, the cycloaddition of cyclopentadiene onto bicyclo[2.2.2]octa-2,5-dien-2,3-dicarboxylic anhydride (**3**) takes place preferentially at its *syn*-face.[6] In the Diels–Alder cycloadditions of more elaborated analogous anhydride **4** with cyclic dienes, exclusive *syn*-facial selectivity was also observed.[7] In continuation of the study, we undertook an extended study on the Diels–Alder cycloadditions of **1** with exocyclic 1,3-butadienes and the results of this study is described in this paper.



Results and Discussion

The preparation of maleic anhydride **1** was previously reported.[4] The anhydride **1** is thermally unstable and decomposes to phthalic anhydride, 2,5-dihydrofuran and benzene when heating at 80°C for three days. Therefore, the Diels–Alder reactions of **1** with dienes were operated at 40°C in dichloromethane in a sealed glass tube (0.8 mm OD, 10 cm length).

Cycloaddition with 2,3-dimethyl-1,3-butadiene

To test the reactivity of anhydride **1** in Diels–Alder cycloaddition with exocyclic 1,3-butadienes, we first performed the reaction of **1** with acyclic conjugated diene, 2,3-dimethyl-1,3-butadiene. The reaction afforded cycloadduct **5** in 94% yield as sole product (Scheme 1). The stereochemical assignment of cycloadduct **5** as a result of *syn*-facial attack of diene upon **1** was elucidated on the basis of the NOE difference experiment. An enhancement (2.78%) of signal displayed by one of the methylene protons in the

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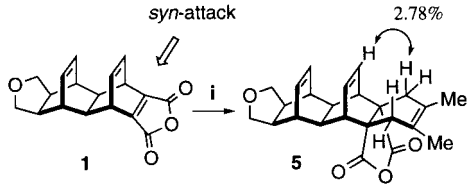


Scheme 1. Cycloaddition of **1** with 2,3-dimethyl-2,4-butadiene: (i) $CH_2{=}C(CH_3){-}C(CH_3){=}CH_2$, CH_2Cl_2, 40°C, two days, 94%.

newly formed cyclohexene ring was observed, when one of the olefinic protons (δ 5.77) was irradiated.

Cycloaddition with exocyclic 1,3-butadienes

The Diels–Alder cycloadditions of anhydride **1** with exocyclic dienes **8**, **15**, and **16**, in which the 1,3-butadiene moiety is grafted on the bicyclo[2.2.2]octene ring system, were subsequently examined. Exocyclic dienes **8** was prepared from the known compound **6**[8] in two steps (tosylation/elimination) as shown in Scheme 2. The analogous diene **15** was prepared from the cycloaddct of dienone **9** with maleic anhydride followed by a reduction/tosylation/elimination process (Scheme 2).[9] A minor product **13** resulting from dehydration was isolated during the conversion of diol **12** to ditosylate **14**. The preparation of exocyclic diene **16** was previously reported.[3e]

Like anhydride **1**, the exocyclic 1,3-butadienes **8**, **15**, and **16**, are facially dissymmetric and expected to show stereoselectivity. Obviously, Diels–Alder cycloadditions of anhydride **1** with exocyclic dienes to afford the anti-Alder adducts are not expected to occur easily due to the steric interaction in transition state (Fig. 1). However, these anti-Alder additions of anhydride **1** to the exocyclic 1,3-butadienes can not be identified experimentally, unless the 1,3-butadiene component has substituents at the terminal C1 and

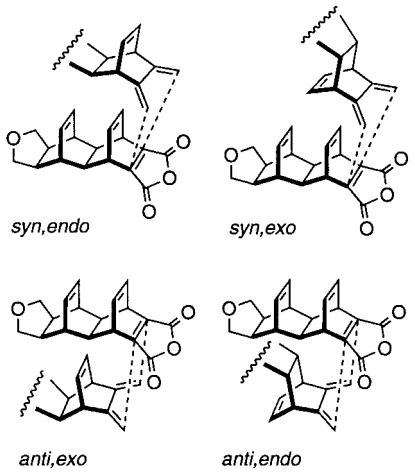
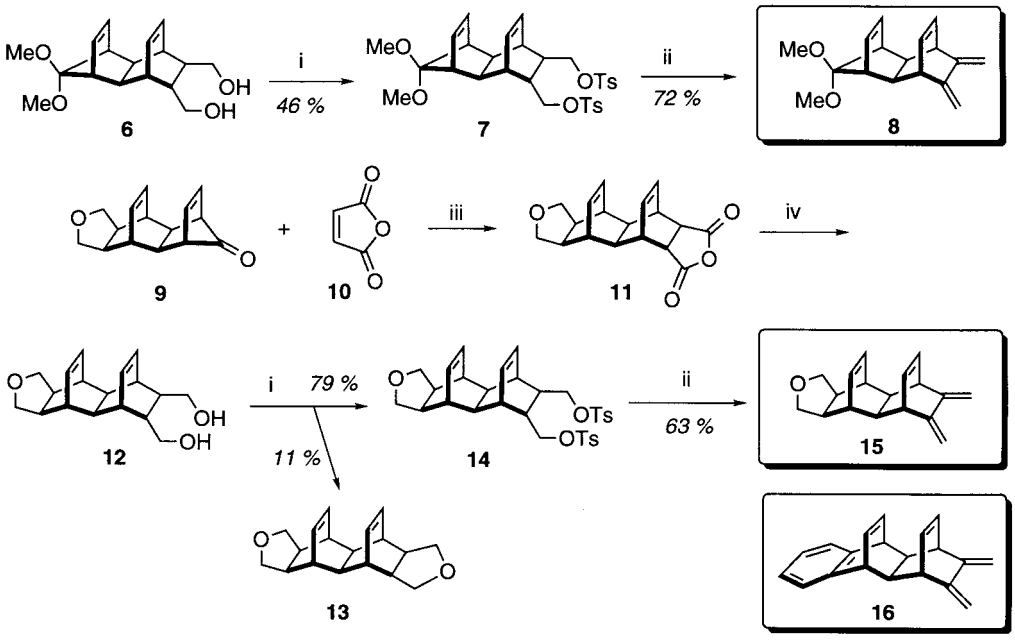


Figure 1. Sterically disfavoured anti-Alder additions of anhydride **1** on exocyclic butadienes. The π-faces relative to the etheno-bridge in **1** are denoted by *syn* and *anti* and in exocyclic dienes by *exo* and *endo*.

C4 carbons. For example, the *syn*,*endo*-adduct that formed by the mode of anti-Alder addition would be identical to the *syn*,*exo*-adduct resulting from the addition by the course in accordance with the Alder rule (Fig. 2).

Therefore, four cycloadducts are possible from the Diels–Alder reactions of anhydride **1** with the exocyclic 1,3-butadienes via modes of addition in accordance with the Alder rule. The transition states leading to the four possible cycloadducts are shown in Fig. 2.

When a solution of maleic anhydride **1** and exocyclic butadiene **8** in CH_2Cl_2 was heated at 40°C for six days, the reaction produced two out of four possible cycloadducts in a ratio of 1:1. These two products, **17a** and **17b**, were isolated by flash chromatography in a total yield of 95%.



Scheme 2. Synthesis of exocyclic 1,3-butadienes: (i) TsCl, pyridine, 0°C; (ii) *t*-BuOK, DMSO, 50°C. (iii) benzene, reflux; 8 h, 88%; (iv) $LiAlH_4$, THF, 6 h, 70%.

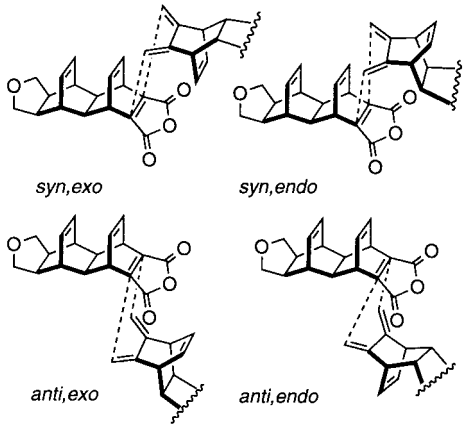


Figure 2. Four sterically more favoured transition states in the Diels–Alder reactions of anhydride **1** with exocyclic butadienes leading to four possible cycloadducts in accordance with the Alder rule.

The NOE difference spectra of **17a** and **17b** that show through-space interaction between the methylene protons of newly formed cyclohexene ring and the olefinic protons of dienophilic unit, suggest the cycloadditions have occurred with exclusive attack of exocyclic 1,3-butadiene **8** upon the *syn*-side of dienophile **1** to produce adducts **17a** (*syn*,*endo*) and **17b** (*syn*,*exo*) as shown in Scheme 3. Another two possible 1:1 cycloadducts are of *anti*,*endo* and *anti*,*exo* connections (Fig. 2), with structures that are not expected to show the respect NOE as **17a** and **17b** do. The spectral data, however, did not allow each structure of cycloadducts **17a** and **17b** to be unambiguously established. Thus, the structural assignment of the cycloadducts was unequivocally achieved by the X-ray crystallographic analysis for the *syn–exo* cycloadduct **17b** (Fig. 3).[10]

Similarly, as shown in Scheme 3, when a solution of maleic anhydride **1** and exocyclic butadiene **15** in CH_2Cl_2 was heated at 40°C for two days, the reaction provided only

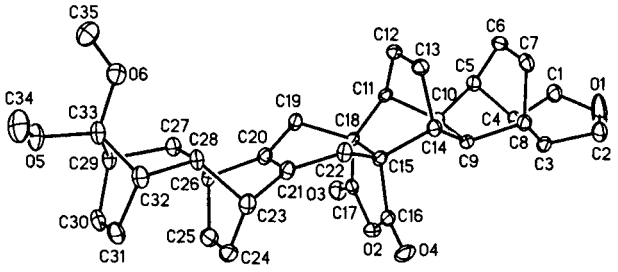
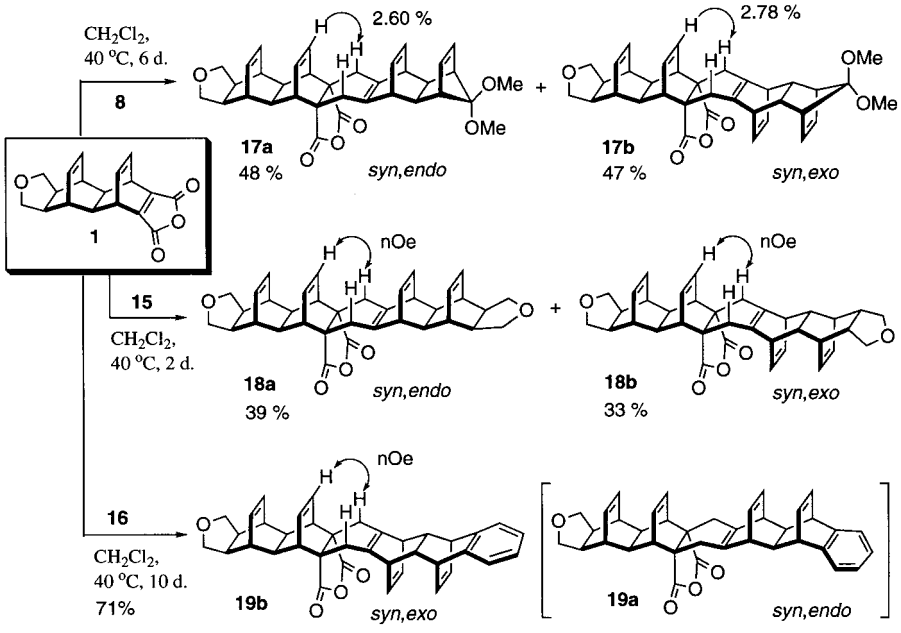


Figure 3. ORTEP drawing of X-ray crystallographic structure of **17b**.

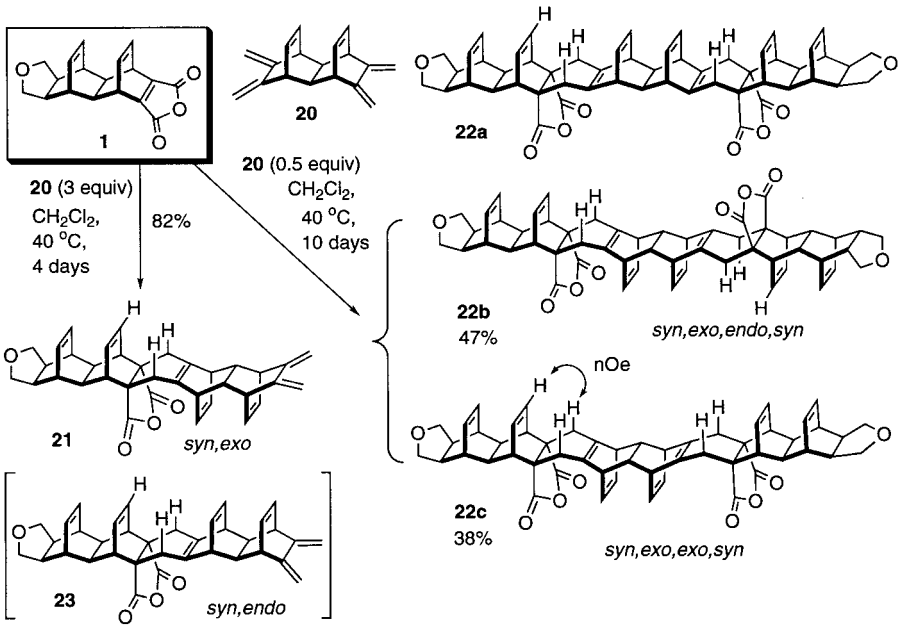
two cycloadducts, *syn*,*endo*-**18a** (39%) and *syn*,*exo*-**18b** (33%). Both adducts **18a** and **18b** were formed via the addition of diene on the *syn*-side anhydride **1** as indicated by the NOE experiment that showed signal enhancement as that observed for **17a** and **17b**. The assignment of relative stereochemistry of **18a** and **18b** was made possible by the chemical shifts of carbonyl carbons of anhydride moiety in their ^{13}C NMR spectra (Table 1). The ^{13}C NMR spectrum of *syn*,*exo* **18b** shows absorption of carbonyl carbon at 177.15 ppm which is close to that (177.14 ppm) of *syn*,*exo*-**17b**, while the corresponding carbon of *syn*,*endo*-**18a** appears at 177.81 ppm which is close to that of the corresponding carbon (177.80 ppm) of *syn*,*endo*-**17a**. The maleic anhydride ring facing the distant etheno-bridge on the opposite side across the cyclohexene ring (*syn*-orientation) displays the absorption of carbonyl carbon at higher field (smaller δ value), possibly due to being more shielded by the double bond of etheno-bridge, as compared to the

Table 1. Chemical shifts of carbonyl carbons in the cycloadducts

syn–endo	**17a**	**18a**	**22b**		
(ppm)	177.80	177.81	177.80		
syn–exo	**17b**	**18b**	**19b**	**21**	**22b**
(ppm)	177.14	177.15	177.18	177.18	177.21



Scheme 3. Cycloaddition of **1** with exocyclic 1,3-butadienes **8**,**15**,**16**.



Scheme 4. Cycloaddition of **1** with bis-exocylic-1,3,-butadiene **20**.

maleic anhydride ring that is oriented *anti* to the double bond of distant etheno-bridge.[11]

The Diels–Alder cycloaddition of **1** with exocyclic butadiene **16**[3e] in dichloromethane at 40°C for 10 days, however, furnished *syn*,*exo*-adduct **19b** as the only detectable product in 71% yield after chromatography (Scheme 3). The corresponding *syn*,*endo*-adduct **19a** was not observed. The *syn*-facial selectivity of anhydride **1** resulting in the formation of cycloadduct **19b** was again deduced on the basis of ^{1}H NOE experiment. The *syn*,*exo* configuration was determined on the basis of the chemical shift of carbonyl carbon in the ^{13}C NMR spectrum that absorbed at 117.18 ppm, very close to those of the corresponding carbons in *syn*,*exo*-adducts **17b** and **18b** (Table 1).

Cycloaddition with bis-exocyclic 1,3-butadiene

We next focused our attention on the bis-exocyclic butadiene **20**.[8] As shown in Scheme 4, Diels–Alder cycloaddition of anhydride **1** with 3 equiv. of bis-butadiene **20** gave a 1:1 cycloadduct **21** as sole product. The *syn*,*exo* stereochemistry was immediately apparent from the ^{13}C NMR spectrum that showed chemical shift of carbonyl carbon at 117.18 ppm, almost equal to those shown by the *syn–exo* configuration of **17b**, **18b** and **19b** (Table 1). Additional confirmation of the indicated stereochemistry was secured from the following repeated cycloaddition. The reaction of **1** with half equimolar amount of bis-exocyclic diene **20** in dichloromethane at 40°C for 10 days yielded two 1:2 cycloadducts **22b** and **22c** in yields of 47 and 38%, respectively. Three different stereoisomers **22a–c** were expected from the four distinctive cycloadditions as *syn*-oriented π-facial selectivity controlled by dienophile **1**. The diagnostic twenty-seven-line ^{13}C NMR resonances for the cycloadduct **22b** clearly illustrated the formation of *syn–exo–endo–syn* arrangement. The chemical shift of its two nonequivalent carbonyl carbons are shown in Table 1 that carbon shielded by ethylene bridges absorbs at 177.21 ppm and the other absorbs at 177.80 ppm. Stereoisomers *syn–exo–exo–syn*-**22c** and *syn–exo–endo–syn*-**22a** could be structurally inferred from the cycloaddition of **1** with **21** and **23** respectively. The observed chemical shift of carbonyl carbons from the isolated product **22c** showing absorption at 177.45 ppm was rationalized by decreasing shielding effect of C=C bonds of etheno-bridges lined between two carboxylic anhydride moieties. Namely, the second maleic anhydride projected *syn* position toward two parallel etheno-bridges diminished the shielding effect toward carbonyl carbons (Table 1). To gain additional insight into the mechanism of the tandem cycloaddition of **20**, reaction of **1** with an equivalent of **21** under identical conditions, gradually gave rise to a mixture of cycloadducts **22b** and **22c**.

The cycloadducts obtained in this report were stable in dichloromethane solution in a sealed tube at 45°C during 10 days. These results indicate that products are kinetically controlled. In summary, we demonstrated that the Diels–Alder reactions between sesquibicycl[2.2.2]octadienyl maleic anhydride **1** with exocyclic butadienes produced exclusively *syn*-facial selective addition. The chemical shifts of carbonyl carbons in cycloadducts are similar in the same stereochemistry.

Experimental

General

Melting points were determined in open capillaries (Thomas Hoover) and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on E. Merk silica gel 60F_{254} plate (0.25 mm). Flash chromatography was performed on E. Merk silica gel (230–400 mesh). ^{1}H NMR spectra were measured at 300 MHz and ^{13}C NMR at 75 MHz,

respectively. Chemical shifts are referenced to TMS or to the residual H in perdeuterated solvents (7.26 ppm for $CDCl_3$). ^{13}C NMR multiplicities were determined using DEPT pulse sequences. NOE difference experiments were performed with compounds **5**, **17a**, **17b**, **18a**, **18b**, **19b** and **22c**. MS spectra were determined at 70 eV in the EI mode unless otherwise stated. IR spectra in KBr were determined by FT-IR. Microanalyses were performed by Analytical Centers of National Cheng Kung and Taiwan Universities, Taiwan.

Cycloaddition of 1 with 2,3-dimethyl-1,3-butadiene. Formation of (1α, 2β, 3α, 4β, 8β, 9α, 10β, 11α, 12β, 17β)-14,15-Dimethyl-6-oxahexacyclo[9.6.2.2^{3,9}.0^{2,10}.0^{4,8}.0^{12,17}]-heneicosa-14,18,20-trien-12,17-dicarboxylic anhydride (5). A solution of dicarboxylic anhydride **1** (0.10 g, 0.34 mmol) and 2,3-dimethyl-1,3-butadiene (60.0 mg, 0.73 mmol) in CH_2Cl_2(1.0 mL) was sealed under vacuum in a glass tube (0.8 mm OD, 10 cm length), then heated at 40°C for two days. The solvent was removed under reduced pressure and the residue was recrystalized from CH_2Cl_2/hexane to give pure cycloadduct **5** (0.12 g, 94%) as a white solid: mp 240–242°C (hexane/CH_2Cl_2); R_f 0.59 (CH_2Cl_2); IR (KBr) 2937, 2854, 1838, 1780, 1443, 1237, 1190, 961, 738, 688 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.56 (d, 6H, *J*=1.5 Hz), 2.06–2.14 (m, 4H), 2.26 (s, 1H), 2.31 (s, 1H), 2.43–2.48 (m, 4H), 2.75 (dd, 2H, *J*=3.6, 3.9 Hz), 3.26 (dd, 2H, *J*=5.1, 9.0 Hz), 3.70–3.76 (m, 2H), 5.77 (dd, 2H *J*=3.3, 4.5 Hz), 5.85 (dd, 2H, *J*=3.0, 4.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.83 (q), 37.72 (d), 38.06 (t), 39.26 (d), 42.15 (d), 46.71 (d), 59.10 (s), 71.98 (t), 126.04 (s), 131.99 (d), 132.34 (d),177.01 (s); MS(EI, 70 eV) *m/z* (relative intensity) 378 (M^+, 35), 350 (69), 305 (100), 291 (7), 275 (2), 235 (3), 195 (4), 183 (14), 157 (10), 143 (32), 128 (20), 91 (37), 69 (20); HRMS *m/z* calcd for $C_{24}H_{26}O_4$ (M^+) 378.1831, obsd 378.1823. Anal calcd for $C_{24}H_{26}O_4$: C, 76.17, H. 6.92. Found: C, 76.10, H. 7.05.

(1α, 2β, 3α, 6α 7β, 8α,)-11,12-Bis[(*p*-toluenesulfonyl)-oxymethyl]-13,13-dimethoxyltetracyclo[6.2.2.1^{3,6}.0^{2,7}]trideca-4,9-diene (7). To a stirred solution of *p*-toluenesulfonyl chloride (7.53 g, 39.50 mmol) in dry pyridine (30 mL) was added dropwise a solution of diol **6** (1.00 g, 3.42 mmol) in dry pyridine (25 mL) at 0°C. After stirring for 6 h, pyridine was removed in vacuo, the resulting residue was partitioned between cold water (40 mL) and CH_2Cl_2 (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were washed with water (2×30 mL), brine (30 mL) and then dried ($MgSO_4$). After removal of the solvents in vacuum, the residue was purified by silica gel column chromatography with 20% CH_2Cl_2 in hexane as eluent. Recrystallization from CH_2Cl_2/hexane gave an analytical sample of ditosylate **7** (0.95 g, 46%) as a white solid: mp 120–121°C; R_f 0.21 (1:1 CH_2Cl_2/hexane); IR (KBr) 2952, 1365, 1262, 1178, 1097, 950, 864, 814, 714, 666, 555 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.24 (m, 2H), 2.36–2.37 (m, 2H), 2.46 (s, 6H), 2.55–2.57 (m, 2H), 2.76–2.78 (m, 2H), 3.03 (s, 3H), 3.16 (s, 3H), 3.55–3.58 (m, 2H), 3.70–3.73 (m, 2H), 5.44–5.48 (m, 4H), 7.33–7.37 (m, 4H), 7.71–7.75 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.63 (q), 35.12 (d), 38.83 (d), 42.78 (d), 48.70 (d), 49.68 (q), 51.91 (q), 69.46 (t), 119.91 (s), 127.84 (d), 129.95 (d), 130.57 (d), 131.17 (d), 132.75 (s), 144.95 (s); MS (EI, 70 eV) *m/z* 428 (M^+−TsOH, 8), 414 (3), 256 (21), 242 (19), 155 (79), 91 (100), 65 (48), 39 (21); Anal. calcd for $C_{31}H_{36}O_8S_2$: C, 61.98; H, 6.04; S, 10.67. Found: C, 61.92; H, 6.07; S, 10.62.

(1α, 2β, 3α, 6α 7β, 8α,)-13,13-Dimethoxy-11,12-dimethylidenetetracyclo[6.2.2.1^{3,6}.0^{2,7}]trideca-4,9-diene (8). Potassium *t*-butoxide (7.06 g, 62.92 mmol) was dissolved in dry dimethyl sulfoxide (75 mL). The mixture was stirred at room temperature for 15 min under nitrogen, and then added dropwise a solution of **7** (5.40 g, 8.99 mmol) in 50 mL of dimethyl sulfoxide in 30 min and 75 mL of hexane. The resulting solution was vigorously stirred at 50°C for 8 h. The upper layer of hexane was separated and the dimethyl sulfoxide solution was poured into ice-water (150 mL), extracted with CH_2Cl_2 (3×60 mL). The combined organic layers were washed with water (2×60 mL), brine (60 mL) and dried over $MgSO_4$. The solvent was evaporated in vacuo, and the residue was purified by flash chromatography (10% CH_2Cl_2 in hexane). Recrystallization from CH_2Cl_2/hexane gave an analytical sample of **8** (1.89 g, 72%) as a white solid: mp 91–92°C; R_f 0.32 (1:4 CH_2Cl_2/hexane); IR (KBr) 2935, 2908, 2831, 1273, 1210, 1113, 1079, 1050, 907, 884, 740, 693, 679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.62–2.63 (m, 2H), 2.86–2.89 (m, 2H), 3.07 (s, 3H), 3.13–3.14 (m, 2H), 3.19 (s, 3H), 4.78 (s, 2H), 5.14 (d, 2H, *J*=0.6 Hz), 5.55 (dd, 2H, *J*=2.1, 2.1 Hz), 5.68 (dd, 2H, *J*=3.6, 4.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.27 (d), 44.85 (d), 48.80 (d), 49.76 (q), 51.89 (q), 102.43 (t), 120.51 (s), 130.13 (d), 130.39 (d), 147.69 (s); MS(EI, 70 eV) *m/z* 292(M^+, 37), 261 (88), 242 (17), 228 (22), 210 (4), 151 (100), 121 (64), 105 (13), 91 (56), 74 (65), 59 (49); HRMS *m/z* calcd for $C_{17}H_{24}O_4$: (M^+) 292.1675, obsd 292.1679; Anal. calcd for $C_{17}H_{24}O_4$: C, 79.65; H, 7.86. Found: C, 79.49; H, 7.92.

(1α, 2β, 3α, 4β, 5β, 6α, 7β, 8α, 9β, 13β)-11-Oxapentacyclo[6.5.2.2^{3,6}.0^{2,7}0^{9,13}]heptadeca-14,16-diene-4,5-dicarboxylic anhydride (11). A mixture of **9**[9] (14.22 g, 62.28 mmol) and maleic anhydride (6.32 g, 64.45 mmol) in dry benzene (150 mL) was refluxed for 6 h under a nitrogen atmosphere. The reaction mixture was cooled, and the crystallized, pure cycloadduct **11** was collected by filtration. The filtrate was concentrated, and the residue remaining was chromatographed on silica gel using 3:1 of ethyl acetate in hexane as eluent to afford an additional crop of **11**. The total yield was 16.35 g (88%). Recrystallization from 1,2-dimethoxyethane/hexane (5:1) gave white crystals; mp 275–278°C (dec.); R_f 0.62 (EtOAc); IR(KBr) 3076, 2997, 2877, 1855, 1790, 1242, 1043, 933, 833, 689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 2H), 2.47–2.51 (m, 2H), 2.57 (s, 2H), 3.11 (s, 2H,), 3.17 (dd, 2H, *J*=1.8, 1.7 Hz), 3.30 (dd, 2H, *J*=3.9, 5.4 Hz), 3.38–3.83 (m, 2H), 5.79 (dd, 2H, *J*=3.3, 4.5 Hz), 5.91 (dd, 2H, *J*=3.0, 4.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.04 (d), 37.54 (d), 41.06 (d), 46.30 (d), 46.97 (d), 71.91 (t), 131.43 (d), 131.97 (d), 172.18 (s); MS(EI, 70 eV) *m/z* 298 (M^+, 88.4), 270 (24), 268 (40), 117 (23), 92 (44), 91 (59), 78 (100), 69 (63); HRMS *m/z* calcd for $C_{18}H_{18}O_4$: (M^+) 298.1205, obsd 298.1200; Anal. calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.44; H, 6.16.

(1α, 2β, 3α, 4β, 5β,6α, 7β, 8α, 9β, 13β)-4,5-Bis(hydroxymethyl)-11-oxapentacyclo[6.5.2.2^{3,6}.0^{2,7}0^{9,13}]heptadeca-14,16-diene (12). A solution of **11** (0.56 g, 1.88 mmol) in 50 mL of anhydrous THF was added slowly under a nitrogen atmosphere to a well-stirred slurry of lithium aluminum hydride (0.35 g, 9.22 mmol) in 20 mL of THF at 0°C. The reaction mixture was stirred at room temperature for 4 h and refluxed for another 1 h before quenching with water (0.6 mL) and then 1 g of sodium hydrogen carbonate. The reaction mixture was stirred for 2 h and filtered the white precipitate. The filtrate was dried, concentrated and chromatographed on silica gel using gradient 20–60% EtOAc in hexane as eluent to give **12** (0.38 g, 70%); mp 223–225°C (CH_2Cl_2/hexane); R_f 0.37 (EtOAc); IR(KBr) 3410, 2928, 2865, 1656(w), 1440, 915, 724 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (s, 2H), 2.24–2.28(m, 2H), 2.38 (m, 2H), 2.46–2.48 (m, 4H), 3.27 (dd, 2H, J=5.4, 8.7 Hz), 3.02–3.35 (br, 2H, OH), 3.47 (dd, 2H, J=3.9, 11.1 Hz), 3.57 (m, 2H), 3.77 (m, 2H), 5.69 (dd, 2H, J=3.6, 4.5 Hz), 5.73 (dd, 2H, J=3.6, 4.5 Hz); 5.73 (2G-HC, 2H, J=3.6, 4.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.05 (d), 40.15 (d), 43.27 (d), 47.15 (d), 47.44 (d), 64.55 (t), 72.06 (t), 131.50 (d), 132.20 (d); MS(EI, 70 eV) m/z 288 (M^+, 32), 274(20), 258(35), 240(48), 210(25), 91(100), 79(61); HRMS m/z calcd for $C_{18}H_{24}O_3$: (M^+) 288.1726, obsd 288.1719; Anal. calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.00; H, 8.44.

(1α, 2β, 3α, 6α, 7β, 8α, 9α, 13α, 17α, 17α)-16,17-Bis[(*p*-toluenesulfonyl)oxymethyl]-11-oxapentacyclo[6.5.2.2^{3,6}.0^{2,7}.0^{9,13}]hepta-4,14-diene (14) and **(1α, 2β, 3α, 4α, 8α, 9α, 10β, 11α, 12α, 16α)-6,14-Dioxahexacyclo-[9.5.2.2^{3,9}.0^{2,10}.0^{4,8}.0^{12,16}]eicosa-17,19-diene (13).** A solution of *p*-toluenesulfonyl chloride (7.68 g, 40.28 mmol) in anhydrous pyridine (10 mL) was added dropwise to the solution of diol **12** (1.70 g, 5.90 mmol) in anhydrous pyridine (23 mL) at 0°C. After 4 h, pyridine was removed in vacuo, the resulting residue was partitioned between cold water (40 mL) and CH_2Cl_2 (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were washed with water (2×30 mL), brine (30 mL) and then dried ($MgSO_4$), concentrated, chromatographed (silica gel, 10% EtOAc/hexane) to afford **13** (0.18 g, 11%) as a white solid: mp 175–176°C (EtOAc/hexane); R_f 0.23 (1:2 EtOAc/hexane); IR (KBr) 3048, 2915, 2867, 1264, 1122, 1042, 920, 688 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (s, 2H), 2.46–2.50 (m, 8H), 3.28 (dd, 4H, J=5.4, 8.6 Hz), 3.78 (dd, 4H, J=5.1, 9.8 Hz), 5.76 (dd, 4H, J=3.3, 4.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.14 (d), 43.13 (d), 47.40 (d), 72.09 (t), 132.25 (d); MS(EI, 70 eV) m/z (relative intensity) 270 (M^+, 100), 240 (24), 92 (69), 91 (78), 69 (36); HRMS m/z calcd for $C_{18}H_{22}O_2$: (M^+) 270.1620, obsd 270.1615; Anal. calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.90; H, 8.30.

Further elution gave the pure ditosylate **14** (2.78 g,79%) as a pale yellow solid: mp 145–147°C (hexane/CH_2Cl_2); R_f 0.16 (2:1 hexane/EtOAc); IR (KBr) 1360, 1176, 958, 655 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.93 (s, 2H). 2.24 (m, 2H), 2.40–2.50 (m, 12H), 3.24 (dd, 2H, J=3.0, 9.5 Hz), 3.53 (dd, 2H, J=9.0, 9.3 Hz), 3.69–3.74 (m, 4H), 5.57 (dd, 2H, J=3.0, 4.5 Hz), 5.69 (dd, 2H, J=3.6, 3.9 Hz), 7.33 (d, 4H, J=7.8 Hz), 7.74–7.70 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.62 (q), 37.49 (d), 37.78 (d), 42.15 (d), 42.35 (d), 46.94 (d), 69.51 (t),71.98 (t), 127.82 (d), 129.94 (d),131.60 (d), 132.10 (d), 132.68 (s), 144.96 (s); MS (EI, 70 eV) m/z (relative intensity) 424 (M^+−TsOH, 10), 252 (61), 172 (20), 55(23), 91(100), 65(22); HRMS m/z calcd for $C_{25}H_{28}O_4S$ (M^+−TsOH) 424.1709, obsd 424.1708; Anal calcd for $C_{32}H_{36}O_7S_2$: C, 64.41; H, 6.08. Found: C, 64.37; H, 6.10.

(1α, 2β, 3α, 4α, 6α, 7β, 8α, 9α, 13α)-11-Oxa-16,17-dimethylidenepentacyclo[6.5.2.2^{3,6}.0^{2,7}.0^{9,13}]heptadeca-4,14-diene (15). A solution of **14** (1.50 g, 2.51 mmol) in 15 mL of dimethyl sulfoxide was treated with potassium *t*-butoxide (4.50 g, 40.10 mmol) and 5 mL of hexane. The mixture was stirred at 50°C for 10 h under nitrogen. After cooling to room temperature, the hexane layer was separated, and the dimethyl sulfoxide solution was poured into cold water (80 mL) and diethyl ether (40 mL) at 0°C. The aqueous phase was extracted with diethyl ether (3×50 mL), and the organic extracts and hexane solution were combined, washed with water (30 mL) and brine (30 mL), and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel using hexane as eluent to afford **15** (0.40 g, 63%) as a white solid: mp 120–123°C (hexane/Et_2O); R_f 0.69 (2:1 hexane/EtOAc); IR(KBr) 3040, 2931, 2867, 1741, 1617, 1473, 1383, 1263, 1216, 1107, 1031, 923, 878, 741, 687 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17 (dd, 2H, J=1.2, 1.5 Hz), 2.44–2.47 (m, 2H), 2.53–2.56 (m, 2H), 3.08–3.11 (m, 2H), 3.30 (dd, 2H, J=5.1, 5.7 Hz), 3.75–3.80 (m, 2H), 4.77 (s, 2H), 5.13 (s, 2H), 5.77–5.82 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.82 (d), 42.74 (d), 47.12 (d), 47.31 (d), 72.01 (t),102.24 (t), 130.70 (d), 132.05 (d), 147.56 (s); MS(EI, 70 eV) m/z (relative intensity) 252 (M^+, 78), 237 (2), 221 (3), 207 (3), 181 (6), 165 (15), 141 (9), 129 (20), 115 (22), 104 (100), 78 (44), 69 (22), 65 (10), 52 (9); HRMS m/z calcd for $C_{18}H_{20}O$ (M^+) 252.1515, obsd 252.1523; Anal. calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.56; H, 8.08.

Cycloaddition of 1 with exocyclic *cis*-1,3-butadiene 8 to afford dicarboxylic anhydrides 17a and 17b. A solution of dienophile **1** (0.63 g, 2.13 mmol) in CH_2Cl_2 (5 mL) was treated with **8** (0.50 g,1.71 mmol) using the procedure described for **1** with 2,3-dimethyl-1,3-butadiene. After six days, the solvent was removed at reduced pressure, and the pale yellow residue was purified by flash chromatography (silica gel, 5% EtOAc in hexane) to give **17a** (0.45 g, 48%) as a white solid: mp 189–192°C (hexane/CH_2CI_2); R_f 0.31 (2:1 hexane/EtOAc); IR(KBr) 2936, 1841, 1773, 1271, 1112, 963, 735 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17–2.26 (m, 6H), 2.44–2.49 (m, 4H), 2.63–2.68 (m, 4H), 2.75 (dd, 2H, J=3.6, 3.6 Hz), 2.97–2.99 (m, 2H), 3.02 (s, 3H), 3.17 (s, 3H), 3.25 (dd, 2H, J=5.1, 8.6 Hz), 3.71–3.76 (m, 2H), 5.39 (dd, 2H, J=2.1, 2.4 Hz), 5.65 (dd, 2H, J=3.3, 4.2 Hz), 5.75 (dd, 2H, J=3.6, 4.4 Hz), 5.83 (dd, 2H, J=3.3, 4.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 5.43 (t), 37.69 (d), 39.34 (d), 40.95 (d), 42.72 (d), 43.83 (d), 46.67 (d), 47.60 (d), 49.56 (q), 51.52 (q), 60.50 (s), 71.96 (t), 121.44 (s), 129.38 (d), 132.26 (d), 132.41 (d), 132.49 (d), 140.98 (s), 177.80 (s); MS(EI, 70 eV) m/z (relative intensity) 552 (M^+, 2), 400 (33), 372 (16), 328 (100),

179 (46), 91 (43), 78 (50); HRMS *m/z* calcd for $C_{35}H_{36}O_6$ (M^+) 552.2513, obsd 552.2519; Anal. calcd for $C_{35}H_{36}O_6$: C, 76.06; H, 6.57. Found: C, 75.85; H, 6.61.

Further elution gave stereoisomeric **17b** (0.44 g, 47%) as a white solid: mp 189–191°C (hexane/CH_2C1_2); R_f 0.22 (2:1 hexane/EtOAc); IR(KBr) 2938, 1841, 1778, 1273, 1111, 966, 737, 693 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.11 (s, 2H), 2.29–2.35 (m, 4H), 2.41–2.46 (m, 4H), 2.54–2.59 (m, 2H), 2.63–2.65 (m, 2H), 2.73–2.76 (m, 2H), 2.92–2.95 (m, 2H), 3.02 (s, 3H), 3.14 (s, 3H), 3.25 (dd, 2H, *J*=5.1, 8.9 Hz), 3.72 (dd, 2H, *J*=7.5, 8.1 Hz), 5.39 (dd, 2H, *J*=2.1, 2.4 Hz), 5.63 (dd, 2H, *J*=3.3, 3.3 Hz), 5.76 (dd, 2H, *J*=3.3, 4.5 Hz), 5.90 (dd, 2H, *J*=2.7, 4.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.59 (t), 37.69 (d), 39.13 (d), 41.38 (d), 42.76 (d), 43.81 (d), 46.61 (d), 47.63 (d), 49.63 (q), 51.57 (q), 59.40 (s), 71.95 (t), 121.45 (s), 129.42 (d), 132.24 (d), 132.70 (d), 132.78 (d), 141.11 (s), 177.14 (s); MS(EI, 70 eV) *m/z* (relative intensity) 552 (M^+, 1), 400 (36), 328 (100), 179 (31), 121 (38), 84 (60), 59 (70); HRMS *m/z* calcd for $C_{35}H_{36}O_6$ (M^+) 552.2513, obsd 552.2515.

Cycloaddition of 1 with exocyclic *cis*-1,3-butadiene 15 to afford dicarboxylic anhydrides 18a and 18b. A solution of dienophile **1** (0.12 g, 0.41 mmol) in 1 mL of CH_2Cl_2 was treated with **15** (90.0 mg, 0.36 mmol) using the procedure described for **1** with 2,3-dimethy-1,3-butadiene. After heating at 40°C for two days, the mixture was concentrated and chromatographed (silica gel, 5% EtOAc in hexane) to give **18b** (65.3 mg, 33%) as a white solid: mp 187–189°C (hexane/CH_2Cl_2); R_f 0.37 (2:1 hexane/EtOAc); IR (KBr): 3043, 2926, 1836, 1770, 1240, 1111, 1035, 960, 968 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.81 (s, 2H), 2.13 (s, 2H), 2.27 (d, 2H, *J*=13.8 Hz), 2.36–2.47 (m, 8H), 2.61 (d, 2H, *J*=14.1 Hz), 2.74–2.77 (m, 2H), 2.95–2.98 (m, 2H), 3.25 (dd, 4H, *J*=5.1, 8.6 Hz), 3.69–3.73 (m, 4H), 5.64–5.67 (m, 2H), 5.76 (dd, 4H, *J*=3.9, 7.5 Hz), 5.90 (dd, 2H, *J*=3.3, 4.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.51 (t), 37.81 (d), 37.96 (d), 39.21 (d), 42.92 (d), 44.15 (d), 46.50 (d), 46.75 (d), 47.87 (d), 59.36 (s), 71.86 (t), 72.03 (t),131.46 (d), 132.32 (d), 132.81 (d), 132.96 (d), 139.39 (s), 177.15 (s); MS (FAB) *m/z* (relative intensity) 549 (MH^+, 15), 535 (9), 491 (12), 425 (23), 391 (10), 342 (22), 307 (90), 289 (65), 252 (100), 215 (26), 165 (40); HRMS (FAB^+) *m/z* for $C_{36}H_{37}O_5$ (MH^+) 549.2642, obsd: 549.2630.

Further elution gave stereoisomeric **18a** (76.7 mg, 39%) as a white solid: mp 249–25°C (dec., hexane/CH_2Cl_2); R_f 0.21 (hexane/EtOAc); IR (KBr): 3036, 2928, 1840, 1772, 1246, 966, 726 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 72 (s, 2H), 2.16 (dd, 4H, *J*=7.2, 7.5 Hz), 2.34 (m, 2H), 2.44–2.48 (m, 6H), 2.61–2.66 (m, 2H), 2.76–2.78 (m, 2H), 3.00 (m, 2H), 3.25–3.29 (m, 4H), 3.69–3.76 (m, 4H), 5.65 (dd, 2H, *J*=3.0, 4.6 Hz), 5.74–5.77 (m, 4H), 5.83 (dd, 2H, *J*=3.3, 4.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.24 (t), 37.73 (d), 38.17 (d), 39.36 (d), 42.78 (d), 43.31 (d), 46.38 (d), 46.67 (d), 47.48 (d), 60.29 (s), 71.97 (t, two peaks),131.28 (d), 132.27 (d), 132.57 (d), 132.80 (d), 139.33 (s),177.81 (s); MS (FAB) *m/z* (relative intensity) 549 (MH^+, 20), 535 (15), 491 (20), 414 (11), 342 (41), 307 (66), 289 (57), 239 (24), 202 (43), 165 (100); HRMS (FAB^+) *m/z* for $C_{36}H_{37}O_5$ (MH^+) 549.2642, obsd 549.2641. Anal. calcd for $C_{36}H_{36}O_5$: C, 78.81; H, 6.61. Found: C, 78.55; H, 6.74.

Cycloaddition of 1 with *exo-cis*-1,3-butadiene 16 to afford dicarboxylic anhydride 19b. A solution of dienophile **1** (100.2 mg, 0.34 mmol) in 1.20 mL of CH_2Cl_2 was treated with **16** (96.0 mg, 0.37 mmol) using the procedure described for **1** with 2,3-dimethy1-1,3-butadiene. After heating at 40°C for 10 days, the mixture was concentrated and the residue was subjected to chromatography (silica gel, gradient 0–15% EtOAc/hexane) to give cycloadduct **19b** (145.7 mg, 71%) as a white solid: mp 240°C (dec., hexane/CH_2CI_2); R_f 0.43 (2:1 hexane/EtOAc); IR(KBr) 2932, 1841, 1775, 1043, 1034, 957, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.01 (s, 2H), 2.11 (s, 2H), 2.40–2.43 (m, 4H), 2.57 (d, 2H *J*=14.0 Hz), 2.72 (dd, 2H, *J*=3.6, 3.6 Hz), 3.00–3.02 (m, 2H), 3.25 (dd, 2H, *J*=4.5, 8.9 Hz), 3.50–3.52 (m, 2H), 3.72 (dd, 2H, *J*=7.2, 7.8 Hz), 5.73 (dd, 2H, *J*=3.3, 3.3 Hz), 5.80 (dd, 2H, *J*=3.0, 4.5 Hz), 5.88 (dd, 2H, *J*=3.0, 3.3 Hz), 6.01 (dd, 2H, *J*=3.3, 4.5 Hz), 6.96–6.98 (m, 2H), 7.04–7.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.32 (t), 37.70 (d), 39.09 (d), 42.94 (d), 44.99 (d), 45.94 (d), 46.64 (d, two peaks), 58.94 (s), 71.97 (t), 122.41 (d), 124.90(d), 132.25(d), 132.60 (d), 132.78 (d, two peaks), 139.89 (s), 146.85 (s), 177.18 (s); MS(EI, 70 eV) *m/z* (relative intensity) 554 (M^+, 1), 400 (21), 328 (100), 205 (6), 179 (47), 91 (46), 69 (33); HRMS *m/z* calcd for $C_{38}H_{34}O_4$ (M^+) 554.2458, obsd 554.2458.

Cycloaddition of 1 with 3 equiv. of 3,4,8,9-tetramethylidene-*endo*-2,5:*endo*-7,10-dietheno-*cis*-decalin (20) at 40°C for four days to afford dicarboxylic anhydride 21. Dienophile **1** (0.050 g, 0.17 mmol) in 1.0 mL of CH_2Cl_2 was treated with **20** (0.12 g, 0.51 mmol) at 40°C for four days in a sealed tube. Standard workup and purification by flash chromatography (silica gel, 10% EtOAc in hexane) gave 1:1 cycloadduct **21** 0.074 g, 82%) as a white solid: mp 189–193°C (dec., CH_2Cl_2/hexane); R_f 0.64 (2:3 EtOAc/hexane); IR (KBr) 3049, 2930, 1840, 1773, 1241, 953, 922, 680 cm; ^1H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 2H), 2.12 (s, 2H), 2.22 (d, 2H, *J*=14.1 Hz), 2.44–2.47 (m, 4H), 2.58 (d, 2H, *J*=13.8 Hz), δ 2.74 (dd, 2H, *J*=3.0, 3.6 Hz), 2.99 (m, 2H), 3.06 (m, 2H), 3.26 (dd, 2H, *J*=5.1, 8.6 Hz), 3.72–3.75 (m, 2H), 4.74 (s, 2H), 5.09 (s, 2H), 5.70 (dd, 2H, *J*=3.3, 4.5 Hz), 5.74–5.79 (m, 4H), 5.85 (dd, 2H, *J*=3.3, 4.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.36 (t), 37.73 (d), 39.13 (d), 42.94 (d), 43.70 (d), 46.15 (d), 46.65 (d), 46.93 (d), 59.06 (s), 71.99 (t), 102.59 (t), 129.86 (d), 132.27 (d), 132.70 (d), 132.78 (d), 139.29 (s), 147.54 (s), 177.18 (s); HRMS *m/z* calcd for $C_{36}H_{35}O_4$ (MH^+) 531.2536, obsd 531.2532; Anal. calcd for $C_{36}H_{34}O_4{\cdot}H_2O$: C, 78.81; H, 6.61. Found: C, 78.53; H, 6.42.

Cycloaddition of 1 with 0.5 equiv. of 3,4,8,9-tetramethylidene-*endo*-2,5:*endo*-7,10-dietheno-*cis*-decalin (20) at 40°C for eight days to afford cycloadducts 22b and 22c. According to the procedure for the reaction of **1** with **8** at 40°C for four days in a sealed glass tube. A solution of dicarboxylic anhydride **1** (0.14 g, 0.47 mmol) in 1.0 mL of CH_2Cl_2 was treated with tetracyclic hexaene **20** (53.0 mg, 0.23 mmol) in 1 mL of CH_2Cl_2. After heating at 40°C for eight days, the mixture was concentrated and the resulting residue was purified by chromatography (silica gel, gradient elution with 0–15% EtOAc in hexane) to give **22b** (88.2 mg, 47%) as a white solid: mp 200°C (dec.) (hexane/CH_2Cl_2); R_f 0.41 (2:3 hexane/EtOAc); ^1H NMR (300 MHz,

$CDCl_3$) δ 1.79 (s, 2H), 2.06–2.14 (m, 6H), 2.28 (d, 2H, J=14.1 Hz), 2.41–2.61 (m, 12H), 2.71–2.76 (m, 8H), 3.23–3.27 (m, 4H), 3.71–3.75 (m, 4H), 5.69–5.78 (m, 8H), 5.82 (dd, 2H, J=3.0, 4.5 Hz), 5.92 (dd, 2H, J=3.0, 4.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.71 (t), 35.02 (t), 37.68 (d), 37.71 (d), 39.34 (d), 39.18 (d), 42.86 (d), 42.91 (d), 45.73 (d), 45.76 (d), 46.34 (d), 46.67 (d), 46.71 (d), 59.48 (s), 59.87 (s), 71.95 (t), 71.98 (t), 132.28 (d, two peaks), 132.38 (d), 132.65 (d, three peaks), 140.39 (s), 140.77 (s), 177.21 (s), 177.80 (s); MS (FAB^+) m/z (relative intensity) 827 (MH^+, 36), 799 (18), 753 (15), 625 (9), 581 (8), 531 (14), 441 (21), 426 (100), 353 (84), 327 (79); HRMS (FAB^+) m/z calcd for $C_{54}H_{50}O_8$ (M^+) 826.3507, obsd: 826.3510.

Further elution gave stereoisomeric **22c** (72.0 mg, 38%) as a white solid: mp 200°C (dec.) (hexane/ CH_2Cl_2); R_f 0.30 (2:3 hexane/EtOAc); IR(KBr) 3051, 1842, 1776, 1243, 1108, 1036, 964, 728, 698 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.88 (s, 2H), 2.08 (s, 4H), 2.22 (d, 4H, J=14.1 Hz), 2.50 (d, 4H, J=14.1 Hz), 2.39–2.50 (m, 8H), 2.53 (s, 2H), 2.71–2.77 (m, 8H), 3.19 (dd, 4H, J=5.1, 8.4 Hz), 3.67 (dd, 4H, J=7.8, 7.8 Hz), 5.71–5.75 (m, 8H), 5.85 (dd, 4H, J=3.0, 4.5 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 34.84 (t), 38.13 (d), 39.65 (d), 43,33 (d), 46,13 (d), 47,16 (d), 47,91 (d), 59.61 (s), 72.18 (t), 132.70 (d), 132.84 (d), 133.14 (d), 140.92 (s), 177.45 (s); MS(FAB) m/z (relative intensity), 827 (MH^+, 12), 799 (5), 753 (3), 613 (2), 528 (2), 460 (10), 426 (7), 307 (100), 289 (61), 220 (21); HRMS(FAB^+) m/z calcd for $C_{54}H_{51}O_8$ (MH^+) 827.3584, obsd: 827.3583; Anal. calcd for $C_{54}H_{50}O_8$: C, 78.43; H, 6.09. Found: C, 78.41; H, 6.14.

Crystal structure of 17b. Space group and cell dimensions: monoclinic $C2/c$, a=26.9717 (11) Å, b=9.7680 (4) Å, β=96.504 (1)°, c=22.1409 (9) Å, and V=5795.7 (14) Å^3, empirical formula: $C_{71}H_{74}Cl_2O_{12}$ (2×**17b**, CH_2Cl_2). Crystal dimensions: 0.45×0.30×0.18 mm, F_W=1190.2, Z=8, $F(000)$=520, D_{calc}=1.364 g/cm^3, λ=0.71073 Å, $2\theta_{(max)}$=50.0°. The intensity data were collected on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source. The hkl ranges were $-31<h<30$, $0<k<11$, $0<l<26$. There were 4095 independent reflections ($3131>\sigma(I)$) (R_{int}=3.90%) collected above background measured at 296 K. Intensity data were collected in 1271 frames with increasing ωwidth of 0.3° per frame). Unit cell dimensions were determined by a least-squares fit of 5303 reflections with $5<2\theta<50°$. Absorption correction was based on 2944 symmetry-equivalent reflections using the SHELXTL-PC program package ($T_{min,max}$= 0.798, 0.946). The final R indices was 0.0739 with R_w=0.0951. GoF=1.52. In the last density map, the deepest hole was −0.57 eÅ^{-3}, and the highest peak 0.70 eÅ^{-3}. Tables of atomic co-ordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center.

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References

1. (a) Goldstein, M. J.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6193–6204. (b) Berning, W.; Hünig, S.; Prokschy, F. *Chem. Ber.* **1984**, *117*, 1455–1464. (c) Grimme, W.; Gossel, J.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 473–475. (d) Grimme, W.; Wortmann, J.; Frowein, D.; Lex, J.; Chen, G.; Gleiter, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1893–1900.

2. Hünig, S.; Martin, H.-D.; Mayer, B.; Peters, K.; Prokschy, F.; Schmitt, M.; von Schnering, H. G. *Chem. Ber.* **1987**, *120*, 195–202.

3. (a) Osawa, E.; Aigami, K.; Inamoto, Y. *Tetrahedron* **1978**, *34*, 509–515. (b) Abert, B.; Berning, W.; Burschka, C.; Hünig, S.; Prokschy, F. *Chem. Ber.* **1984**, *117*, 1465–1475. (c) Grimme, W.; Pohl, K.; Wortmann, J.; Frowein, D. *Liebigs Ann.* **1996**, 1905–1916. (d) Hünig, S.; Brand, U.; Peters, K.; Prokschy, F.; von Schnering, H. G. *Liebig Ann. Recl.* **1977**, 785–790. (e) Lin, C. T.; Wang, N. J.; Yeh, Y. L.; Chou, T. C. *Tetrahedron* **1995**, *51*, 2907–2928.

4. Lin, C. T.; Hsu, H. C.; Chou, T. C. *J. Org. Chem.* **1999**, *64*, 7260–7264.

5. (a) Edman, J. R.; Simmons, H. E. *J. Org. Chem.* **1968**, *33*, 3808–3816. (b) Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383–1390. (c) Bartlett, P. D.; Combs, Jr., G. L.; Le, A.-X. T.; Watson, W. H.; Galloy, J.; Kimura, M. *J. Am. Chem. Soc.* **1982**, *104*, 3131–3138. (d) Williams, R. V.; Sung, C. L. A.; Kurtz, H. A.; Harris, T. M. *Teterahedron Lett.* **1988**, *29*, 19–20. (e) AbouGharbia, M.; Patel, U. R.; Webb, M. B.; Moyer, J. A.; Andree, T. H.; Muth, E. A. *J. Med. Chem.* **1988**, *31*, 1382–1392.

6. Williams, R. V.; Todime, M. M. R.; Enemark, P.; van der Helm, D.; Rizvi, S. K. *J. Org. Chem.* **1993**, *58*, 6740–6744.

7. Chou, T. C.; Jiang, T. S.; Hwang, J. T.; Lin, C. T. *Tetrahedron Lett.* **1994**, *35*, 4165–4168.

8. Lin, C. T.; Chou, T. C. *Org. Chem.* **1990**, *55*, 2252–2254.

9. Lin, C. T.; Wang, N. J.; Tseng, H. Z.; Chou, T. C. *J. Org. Chem.* **1997**, *62*, 4857–4861.

10. The authors have deposited X-ray data with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

11. Chou, T. C.; Jiang, T. S.; Hwang, J. T.; Lin, K. J.; Lin, C. T. *J. Org. Chem* **1999**, *64*, 4874–4883.