Reactivity of 2-Methylene-1,3-dicarbonyl Compounds. Stereoselective and Asymmetric Diels−Alder Reactions

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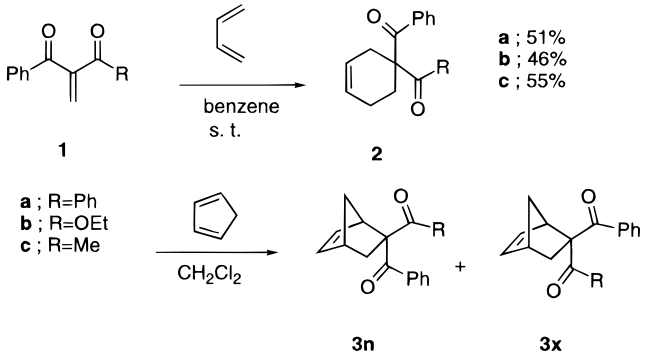
The Diels−Alder reaction of 1,1-dicarbonylethenes **1** with dienes was investigated. The adduct of the reaction of **1**, whose two carbonyl groups were different, with cyclopentadiene showed moderate stereoselectivity and this was explained by FMO theory. However, in the Lewis acid-catalyzed addition, the reaction proceeded with high stereoselectivity to give the exo adduct **3x**. This might be due to steric hindrance because the benzene ring cannot orient in the plane of the conjugated system in the metal-chelated enedione **6**. Applying this principle to (1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-benzoylacrylate (**1d**), we achieved a diastereomeric Diels−Alder reaction to afford **3x-R**, whose structure was confirmed by the X-ray crystal analysis.

In the Diels−Alder reaction, the effect of a functional group attached directly to the diene or dienophile has been extensively studied.[1] The introduction of an electron-withdrawing group into the dienophile lowers the LUMO energy level and increases its reactivity toward a diene having an electron-rich substituent.[2] α,β-Unsaturated carbonyl compounds,[3] as reactive dienophiles, have been employed widely, and endo adducts are produced under kinetically-controlled reaction conditions. The remarkable stereoselectivity and regioselectivity of the reaction are well explained by frontier molecular orbital (FMO) theory.[4] Lewis acid catalysis influences the rate of reaction as well as regioselectivity and stereoselectivity.[4] Based on these principles, asymmetric Diels−Alder reactions have been investigated widely in both diastereometric[5] and enantiomeric[6] versions. Still lacking among the excellent studies reported so far is a study of a dienophile having two electron-withdrawing groups at the same olefinic carbon. Because of the instability of 1,1-dicarbonylethenes,[7] they can be used as reaction intermediates in a normal electron-demand Diels−Alder reaction.[8] We reported the synthesis of the 1,1-dicarbonylethenes **1**,[9] in which at least one of the carbonyls was a benzoyl group, and their use in regioselective hetero-Diels−Alder reactions.[10] When the two carbonyl groups on the ethene are of different types, an interesting problem arises; namely, which substituent would orient endo in the normal electron-demand Diels−Alder reaction. If endo/exo stereoselectivity is achieved, an asymmetric reaction might be expected when one carbonyl group is an ester of a chiral alcohol. In the present paper we report a study of the reactions of **1** with 1,3-butadiene and cyclopentadiene and the diastereomeric Diels−Alder reaction of (1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-benzoylacrylate **1d** with cyclopentadiene.[11]

Scheme 1



Diels−Alder Reaction of 2-Methylene-1,3-dicarbonyl Compounds 1a−c. First, the reaction with butadiene was examined by using 1,1-dibenzoylethene (**1a**) (Scheme 1). Whereas the Diels−Alder adduct was not formed at ambient temperature after 10 h, the adduct was obtained after 10 h at 70 °C in a sealed tube. Thus the reaction of 2-methylene-1,3-dicarbonyl compounds **1** with butadiene was carried out in a sealed tube at 100 °C for 15 h. The low yield of this reaction might be due to polymerization of **1** under the reaction conditions. On the other hand the reaction with cyclopentadiene proceeded smoothly even at ambient temperature to yield

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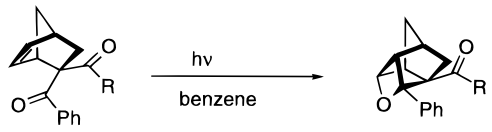
0022-3263/96/1961-2719$12.00/0

Table 1. Reactions of 1 with Cyclopentadiene

entry	reactant	reaction conditions: catalyst	*T*, °C	*t*, h	total yield (%)	product ratio[a] **3n:3x**
1	**1a**	none	rt[b]	5	70	
2	**1b**	none	rt	5	67	79:21
3	**1b**	BF_3·OEt_2[c]	0	1	30	25:75
4	**1b**	BF_3·OEt_2	−40	3	54	17:83
5	**1b**	BF_3·OEt_2	−78	7	50	9:91
6	**1b**	$ZnCl_2$[d]	rt	0.2	47	12:88
7	**1b**	$ZnCl_2$	−40	3	75	5:95
8	**1b**	$ZnCl_2$	−78	7	73	4:96
9	**1c**	none	rt	0.5	80	32:68
10	**1c**	$ZnCl_2$	0	1	80	15:85
11	**1c**	$ZnCl_2$	−15	1.5	80	14:86
12	**1c**	$ZnCl_2$	−40	3	80	11:89
13	**1c**	$ZnCl_2$	−78	7	81	6:94

[a] Ratios were determined by ^{1}H NMR (olefinic protons). [b] rt = room temperature. [c] 1 equiv of BF_3·OEt_2 was used with respect to **1**. [d] 1.5 equiv of $ZnCl_2$ was used with respect to **1**.

Scheme 2



3n **4**

the corresponding adduct (Table 1).[12] 1-Benzoyl-1-(ethoxycarbonyl)ethene (**1b**) gave an inseparable mixture of exo/endo adducts[13] in which the endo product was predominant (entry 2). In the ^{1}H NMR spectrum two olefinic protons of the adduct appear as a pair of double doublets at δ 6.00 and δ 6.15 for the endo isomer and at δ 5.96 and δ 6.39 for the exo isomer. Compared with the higher field signals of the 6-Hs, the lower field signals of the 5-Hs are sufficiently separated to determine the endo/exo ratio. The exo or endo relationship of the benzoyl to the bicyclo[2.2.1] system was determined through a Paterno−Büchi reaction[14] of the product (Scheme 2). Irradiation of the product at 300 nm through Pyrex gave the isomer **4b** formed from the endo product **3bn** and unreacted exo isomer **3bx**. Interestingly, the stereochemistry of the product was reversed when the reaction was carried out in the presence of a Lewis acid. The reaction was performed by the initial addition of the Lewis acid to the dienophile followed by addition of cyclopentadiene at various temperatures as shown in Table 1. When boron trifluoride etherate was added to the dienophile in CH_2Cl_2, the temperature of the reaction mixture increased and the solution turned dark. The yield of adducts was lower than that obtained in the presence of $ZnCl_2$.

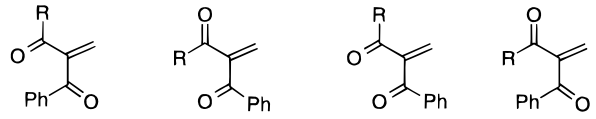
In the case of 1-acetyl-1-benzoylethene (**1c**), the stereoselectivity was somewhat lower than that of **1b** in the absence of a Lewis acid, and the exo isomer was predominant. In the presence of a Lewis acid, however, exo selectivity was observed, similar to the reaction of **1b**. In this case the ratios of endo to exo were also determined by the olefinic proton signals (5-Hs) in the ^{1}H NMR spectra. The stereochemistry of the adduct was also confirmed by the Paterno−Büchi reaction. Thus irradiation of the product, prepared in the absence of Lewis acid, at 300 nm through Pyrex gave the oxetane derived from [2 + 2] cyclization between the C−C double bond and the benzoyl carbonyl group. Under these conditions the acetyl carbonyl group did not react with the double bond and the endo isomer was recovered.

Table 2. Computed Data for 1b

1	total energy (eV)	LUMO energy (eV)	LUMO coefficients: Cbz[a]	Ces[b] or Cac[c]
1b-A	−2669.33280	−0.581	0.283	0.260
1b-B	−2669.33605	−0.591	0.288	0.232
1b-C	−2669.32602	−0.573	0.286	0.236
1b-D	−2669.23242	−0.605	0.289	0.248
1c-A	−2190.45442	−0.611	0.257	0.316
1c-B	−2190.47647	−0.576	0.316	0.267
1c-C	−2190.46117	−0.577	0.265	0.284
1c-D	−2190.29849	−0.524	0.292	0.299

[a] Cbz = benzoyl carbonyl carbon. [b] Ces = ester carbonyl carbon. [c] Cac = acetyl carbonyl carbon.

Chart 1



Generally, the endo isomer is kinetically preferred in the Diels−Alder reaction of electron-poor dienophiles, such as α,β-unsaturated carbonyl compounds or maleic anhydride. In the case of 2-methylene-1,3-dicarbonyl compounds **1**, it is interesting to speculate as to which carbonyl group would facilitate an endo approach to the diene. FMO theory which employs secondary attractive interactions[4,15] clarifys the problem. MNDO[16] calculations were carried out for four possible conformers **A**−**D** (Chart 1). Brief calculations show that the most stable form is one in which the plane of the benzene ring of the benzoyl group is situated perpendicular to the conjugated enedione system in each conformer (**A**−**D**). This is presumably due to the steric hindrance between the ortho hydrogen of benzoyl benzene and the carbonyl oxygen (in **A**), the *cis*-oriented vinyl hydrogen (in **B** and **C**), or the R group (in **D**). The optimized total energies and LUMO energies and coefficients for the most stable conformers (**A**−**D**) were listed in Table 2. The total energies of conformers **A**−**C** are almost the same (energy differences <0.5 kcal/mol in **1b** and <0.3 kcal/mol in **1c**). Since the total energies of both **D** conformers are ca. 2.5 kcal/mol and ca. 4 kcal/mol higher than that of the others in **1b** and **1c,** respectively, the contribution of the conformer **D** to the reaction might be neglected.

In the case of 1-(ethoxycarbonyl)-1-benzoylethene (**1b**) the coefficients of the benzoyl carbonyl carbons are larger than that of the ester carbonyl carbons in the **A**−**C** conformers. In the transition state the orientation (see **5**) giving the endo-benzoyl adduct has a larger secondary interaction than that leading to the endo-ester adduct.

(12) The rection times have been reported as 5−7 h in ref 11. We reexamined the reaction throughout and found the reactions were completed within the times shown.

(13) Since all of the ethenes have at least one benzoyl group, exo and endo are defined by the relationship of the benzoyl group and the bicyclo[2.2.1]heptene to unify and easily understand the reaction series.

(14) (a) Jones, G., II. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1981; Vol. 5, ch. 1. (b) Sauers, R. R.; Henderson, T. R. *J. Org. Chem.* **1974**, *39*, 1850. (c) Sauers, R. R.; Rousseau, A. D.; Byrne, B. *J. Am. Chem. Soc.* **1975**, *97*, 4947. (d) Smith, A. B., III, ; Dieter, R. K. *Tetrahedron Lett.* **1976**, 327.

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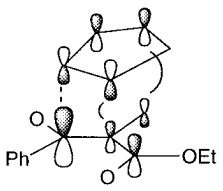
(16) QCPE 353, modified by Osawa and Buda, which converted to PC version by Tokiwa.

Chart 2



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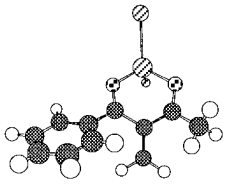

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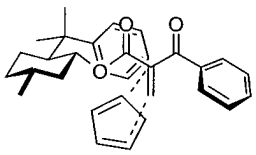


7

Taking the conformation of the benzoyl benzene ring into consideration with the approaching diene, the conformer **A** might be preferable to the others.

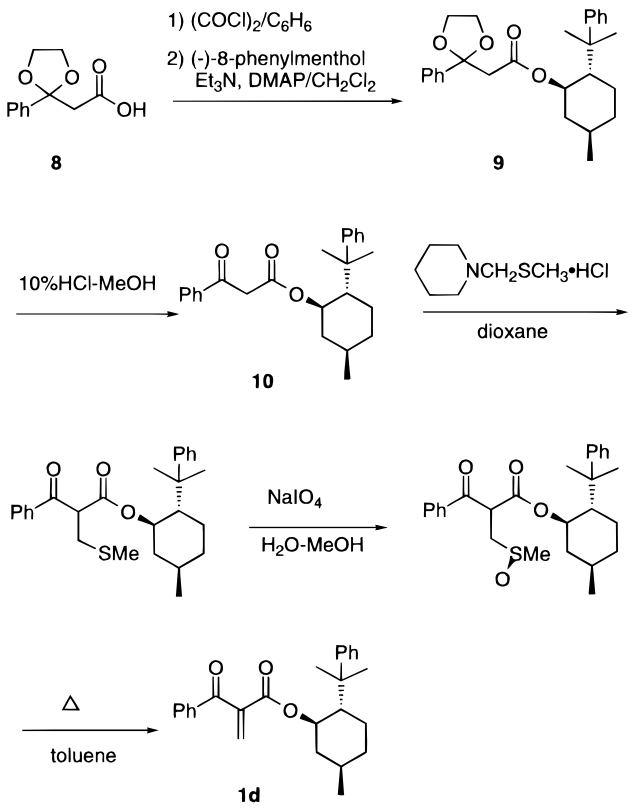
In the case of 1-acetyl-1-benzoylethene (**1c**), the situation is more complex. As shown in Table 2 the coefficients of the acetyl carbonyl carbons are not always larger than that of benzoyl carbonyl carbons. The conformer (**B** or **C**), in which the benzoyl carbonyl and the methylene group are in an *s-trans* relationship, is less important because the benzene ring, situated perpendicular to the conjugated enedione system, causes a large steric hindrance to the approaching diene in the transition state. Furthermore the energy level in the LUMO of **1c-A** is lower than that of the others. Thus the most important conformer is **A**, and the coefficient of the acetyl carbonyl carbon is larger than that of the benzoyl carbonyl carbon in **A**. As a result, the exo-adduct is formed preferentially over the endo-adduct.

In order to obtain a better understanding of the preponderance of the exo-isomer in the Lewis acid-catalyzed reaction, we carried out molecular mechanics calculations[17] of the metal-chelated enedione. Although the tetrahedral zinc-complex **6** is more stable than the planar one, the conformation of the enedione is almost identical in both complexes. In conformer **6** the benzene ring is situated nearly perpendicular to the ene. Hence cyclopentadiene approaches from the side leading to the exo-isomer because of the steric hindrance of the benzene ring in the fixed metal-chelated enedione. The reason that the same stereoselectivity is observed with monovalent boron trifluoride is not obvious but the similarity between boron and divalent metals has been noted.[18]

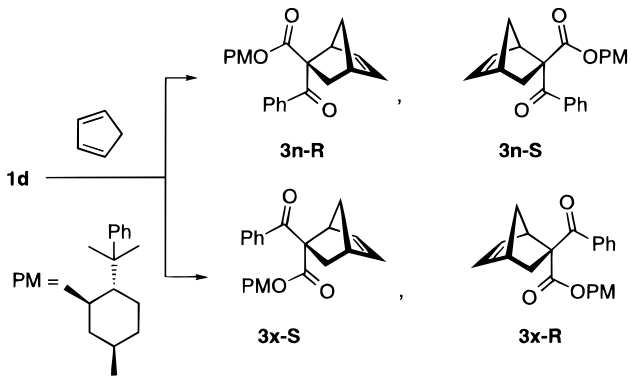
From these results it was expected that the Diels–Alder reaction of (1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-benzoylacrylate (**1d**) in the presence of a Lewis acid would proceed *via* transition state **7** stereoselectively. The π-stacking[19] of the chelated conjugated system and the benzene ring of the phenylmenthyl group restricts the attack of diene from the back side, and the steric hindrance of benzoyl benzene blocks the approach of the diene from the benzoyl group.

Diels–Alder Reaction of 1d with Cyclopentadiene in the Absence of Lewis Acid. (1′*R*,2′*S*,5′*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-benzoylacrylate (**1d**) was synthesized as follows (Scheme 3). The acid chloride, obtained by treatment of 2-phenyl-1,3-dioxolan-2-ylacetic acid (**8**) with oxalyl chloride, was treated with (−)-8-phenylmenthol[20] to yield chiral ester **9**. Selective hydrolysis was achieved by treatment of **10** with 10% HCl(aq)−MeOH (1:6) at ambient temperature. The resulting dione **10** was converted into **1d** by the method previously developed in our laboratory.[9] The reaction of **1d** with cyclopentadiene in the absence of a Lewis acid gave all four possible stereoisomers (Scheme 4), which showed one spot on TLC but partially separated on HPLC. Repeated preparative HPLC separated the adducts into four fractions. Fractions 1, 2, and 4 contained almost pure isomers but not fraction 3. The signals of the olefinic protons (5-Hs and 6-Hs) and the proton (1′-H) attached to the carbon bearing the oxycarbonyl group of the mixture and each isomer and the

Scheme 3



Scheme 4



(17) Molecular mechanics calculations were carried out with IBM PC/2 using MMX program (v. 3.3, Serena Software).

(18) Smith, A. B., III; Leahy, J. W.; Node, I.; Remiszewski, S. W.; Liverton, N. J.; Zibuck, R. *J. Am. Chem. Soc.* **1992**, *114*, 2995.

(19) For review, see: Jones, G. B.; Chapman, B. J. *Synthesis* **1995**, 475.

(20) (a) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908. (b) Ort, O. *Organic Synthesis*; Wiley: Tokyo, 1993; Coll. Vol. VIII, p 522.

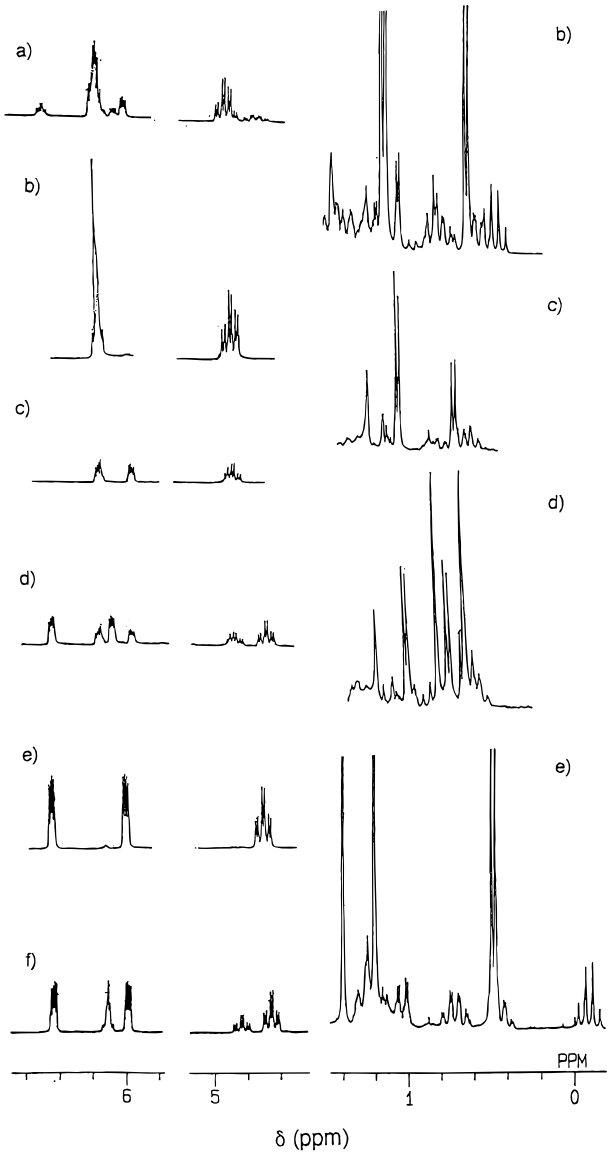
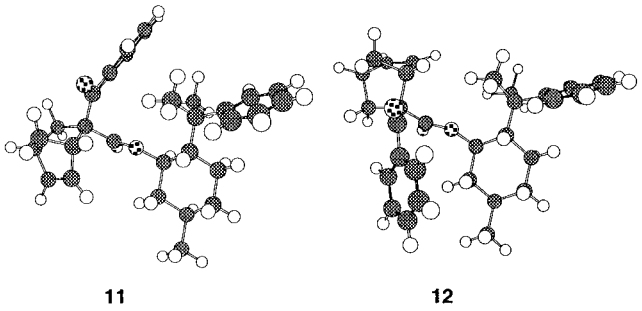


Figure 1. ^{1}H NMR spectra (270 MHz) of (a) the adduct of no catalyst, (b) fraction 1, (c) fraction 2, (d) fraction 3, (e) fraction 4, and (f) the adduct under $FeCl_2$ at ambient temperature.

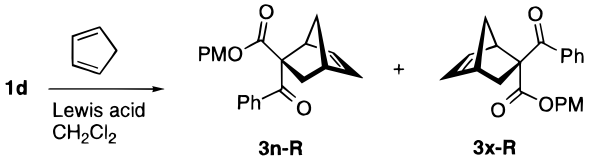
upper field signals of each isomer are shown in Figure 1. Considering the reaction of **1b** with cyclopentadiene, we should assign a pair of double triplets (ca. 4.8 ppm in a) to a pair of endo isomers, **3n-S** and **3n-R**, since these should be predominant in the absence of Lewis acid as well as in the case of **1b**. Therefore fractions 1 and 2 should be the endo isomers, and fractions 3 and 4 the exo isomers. Olefinic protons (5-H and 6-H) of fraction 1 appeared as a broad singlet (b), and that of fraction 2 were split as two double doublets (c). No significant differences were observed in the signals of the secondary and tertiary dimethyl groups. At this point we could not determine which fraction was **3n-R** or **3n-S**. However, we could determine that fractions 1 and 2 were **3n-R** and **3n-S**, respectively, from the results of the reaction catalyzed by Lewis acid (*vide infra*.). The signals of tertiary dimethyl group of fractions 3 appeared at considerable upfield shift compared with the other. This is because the dimethyl groups are situated over the plane of the benzene ring of the benzoyl group, consistent with the most stable conformer **11** of **3x-S** calculated by MMX (Chart 3). Therefore fraction 4 should be **3x-R** and

Chart 3



11 **12**

Table 3. Reactions of 1d with Cyclopentadiene



	reaction conditions			total	product ratio[a]
entry	catalyst	*T*, °C	*t*, h	yield (%)	**3n-R**:**3x-R**
1	BF_3·OEt_2[b]	−40	3	57	13:87
2	BF_3·OEt_2	−78	7	49	8:92
3	$ZnCl_2$[c]	rt[d]	0.5	46	14:86
4	$ZnCl_2$	−40	3	91	10:90
5	$ZnCl_2$	−78	7	88	4:96
6	$FeCl_2$	rt	0.5	86	29:71
7	$FeCl_2$	−40	3	86	24:76
8	$FeCl_2I$[b]	rt	0.5	81	<1:>99
9	$FeCl_2I$	0	1	80	<1:>99
10	$FeCl_2I$	−40	3	80	0:100
11	$FeCl_2I$	−78	7	78	0:100

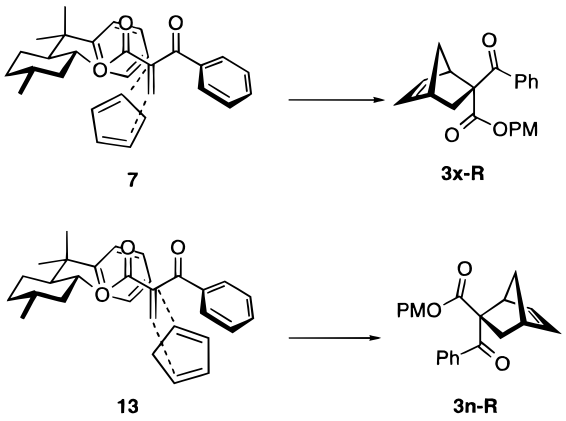
[a] Ratios were determined by ^{1}H NMR (olefinic protons). [b] 1 equiv of Lewis acid was used with respect to **1d**. [c] 1.5 equiv of $ZnCl_2$ was used with respect to **1d**. [d] rt = room temperature.

the unusual upfield shift of 2′-H_{ax} (−0.09 ppm) is because this proton is over the plane of the benzene ring of the benzoyl group of the most stable conformer **12**.

Diels−Alder Reaction of 1d with Cyclopentadiene in the Presence of Lewis Acid. The reactions in the presence of Lewis acid are shown in Table 3.[12] In the presence of BF_3·OEt_2 or $ZnCl_2$, a detectable amount of a minor isomer was obtained. Each endo or exo product was a single isomer and corresponded to fraction 1 or fraction 4, which implied that the reaction proceeded with perfect diasteroselectivity. The signals of the olefinic protons and 1′-H of the product obtained under $FeCl_2$ catalysis are shown in Figure 1f. Provided π-stacking occurs in the metal-chelated transition state, cyclopentadiene attacks only from the front side to afford **3x-R** from **7**, and **3n-R** from **13** (Chart 4). As the reaction temperature is lowered, the plane of the benzene ring of the benzoyl group is fixed perpendiculer to the conjugated system, which increases the exo/endo selectivity. A single recrystallization (entry 5) from ethanol gave pure **3x-R** [mp 135−136 °C; $[\alpha]^{30}_D$ +135° (*c*, 0.38, $CHCl_3$)] whose X-ray crystal structure[21] confirmed the assignment of stereochemistry. The conformation, as shown by the X-ray data is very similar to the most stable conformation

(21) An X-ray crystal structure analysis indicated the space group $P2_12_12_1$, a = 12.404(25) Å, b = 28.961(18) Å, c = 7.193(18) Å, U = 2583.9(α 77) Å^3, Z = 4, r = 1.174 g/mL, m(Cu Kα) = 0.586 mm^{-1}. Final R and RW were 0.0498 and 0.1488 for 2539 reflections. The atomic coordinates of **3x-R** have been deposited with the Cambridge Crystallographic Data Centre. They can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Chart 4



12 of **3x-R** calculated by MMX. In order to obtain higher exo/endo selectivity, we carried out the reaction under $FeCl_2I$ catalysis.[22] The addition product obtained was almost single isomer **3x-R** even at ambient temperature (entry 8).

Experimental Section

General. Melting points are uncorrected. $MgSO_4$ was used to dry organic layers after extraction. Column chromatography was performed with silica gel (Micro Bead 4B, Fuji-Davison Chemical Ltd.). HPLC was carried out with a column, Megapak SIL (10 μm), 1.0 × 25 cm. NMR spectra were recorded in chloroform-*d* at 270 MHz for ^{1}H and 67.89 MHz for ^{13}C using tetramethylsilane (TMS) as the internal reference. IR spectra were determined either neat or in KBr pellets. Mass spectra were recorded at 70 eV.

Reaction of 2-Methylene-1,3-dicarbonyl Compound 1 with Butadiene. A solution of 2-methylene-1,3-dicarbonyl compound **1** (1 mmol) and butadiene (ca. 5 mmol) in benzene (5 mL) was heated at 100 °C in a sealed tube for 15 h. The reaction mixture was evaporated off at reduced pressure, and the residue was subjected to column chromatography to yield the corresponding adduct.

1,1-Dibenzoylethene (**1a**) gave (1-benzoylcyclohex-3-enyl)-phenylmethanone (**2a**): mp 107−108 °C (from MeOH); IR (KBr) 1660, 1600, 1580 cm^{-1}; ^{1}H NMR δ 1.94 (br s, 2H), 2.45 (t, J = 6.5 Hz, 2H), 2.71 (br s, 2H), 5.72 (m, 2H), 7.34 (t, J = 7.3 Hz, 4H), 7.45 (t, J = 7.3 Hz, 2H), 7.88 (d, J = 7.3 Hz, 4H); ^{13}C NMR δ 21.7, 29.6, 33.1, 62.8, 124.3, 125.4, 128.7, 129.1, 133.0, 136.0, 199.0. Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.49; H, 6.35.

1-Benzoyl-1-(ethoxycarbonyl)ethene (**1b**) gave ethyl 1-benzoylcyclohex-3-enecarboxylate (**2b**): viscous oil; IR (neat) 1735, 1685, 1600, 1580 cm^{-1}; ^{1}H NMR δ 1.10 (t, J = 7.3 Hz, 3H), 2.03 (m, 2H), 2.28 (m, 2H), 2.63 (br s, 2H), 4.15 (q, J = 7.3 Hz, 2H), 5.69 (br s, 2H), 7.3−7.5 (m, 3H), 7.84 (d, J = 6.6 Hz, 2H). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.16; H, 7.31.

1-Acetyl-1-benzoylethene (**1c**) gave 1-(benzoylcyclohex-3-enyl)ethanone (**2c**): viscous oil; IR (neat) 1715, 1670, 780, 700 cm^{-1}; ^{1}H NMR δ 1.96 (m, 2H), 2.15 (s, 3H), 2.27 (tABq, J = 17.0, 7.0 Hz, 2H), 2.57 (ABq, J = 17.0 Hz, 2H), 5.67 (br s, 2H), 7.41 (t, J = 7.3 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.77 (d, J = 7.3 Hz, 2H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.41; H, 7.14. HRMS Calcd for $C_{15}H_{16}O_2$: 228.1150. Found: 228.1145.

Reaction of 2-Methylene-1,3-dicarbonyl Compound 1 with Cyclopentadiene in the Absence of Lewis Acid. A 1.0 M solution of cyclopentadiene in CH_2Cl_2 (3 mL) was added to a solution of 2-methylene-1,3-dicarbonyl compound **1** (1.0 mmol) in CH_2Cl_2 (3 mL) at ambient temperature. The reaction mixture was stirred for 5 h and evaporated off at reduced pressure. The residue was subjected to column chromatography to give the corresponding adducts.

1,1-Dibenzoylethene (**1a**) gave (2-benzoylbicyclo[2.2.1]hept-5-en-2-yl)phenylmethanone (**3a**): mp 109−110 °C (from hexane); IR (KBr) 1660, 1600, 1585, 1575 cm^{-1}, ^{1}H NMR δ 1.59 (br d, J = 8.8 Hz, 1H), 1.73 (br d, J = 8.8 Hz, 1H), 2.18 (dd, J = 12.5, 3.6 Hz, 1H), 2.82 (dd, J = 12.5, 2.9 Hz, 1H), 2.98 (br s, 1H), 3.91 (br s, 1H), 5.74 (dd, J = 5.1, 2.9 Hz, 1H), 6.28 (dd, J = 5.1, 2.9 Hz, 1H), 7.33 (t, J = 7.3 Hz, 4H), 7.43 (t, J = 7.3 Hz, 2H), 7.90 (d, J = 7.3 Hz, 2H), 7.94 (d, J = 7.3 Hz, 2H); ^{13}C NMR δ 36.8, 42.9, 49.2, 51.6, 71.8, 128.4, 128.5, 129.1, 129.8, 132.6, 132.8, 133.0, 136.5, 137.4, 140.0, 196.9, 200.0. Anal. Calcd for $C_{12}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.41; H, 6.00.

1-Benzoyl-1-(ethoxycarbonyl)ethene (**1b**) gave endo/exo ethyl 2-benzoylbicyclo[2.2.1]hept-5-ene-2-carboxylate **3bn**/**3bx** (3.8:1) mixture. HRMS Calcd for $C_{17}H_{18}O_3$: 270.1256. Found: 270.1229. Major component **3bn**: ^{1}H NMR δ 1.06 (t, J = 7.3Hz, 3H), 1.50 (br d J = 8.8 Hz, 1H), 1.79 (br d, J = 8.8 Hz, 1H), 2.03 (dd, J = 12.5, 2.9 Hz, 1H), 2.49 (dd, J = 12.5, 3.7 Hz, 1H), 2.94 (br s, 1H), 3.54 (br s, 1H), 4.12 (q, J = 7.3 Hz, 2H), 6.00 (dd, J = 5.1, 2.9 Hz, 1H), 6.12 (dd, J = 5.1, 2.9 Hz, 1H), 7.41 (t, J = 7.3 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.87 (d, J = 7.3 Hz, 2H); ^{13}C NMR δ 13.8, 36.6, 42.1, 47.7, 51.0, 61.7, 65.6, 128.3, 128.5, 132.7, 134.7, 136.2, 138.4, 174.0, 195.5. The minor component **3bx** was obtained in pure form after irradiation of the mixture or from the reaction in the presence of Lewis acid, and its spectral data are described below.

1-Acetyl-1-benzoylethene (**1c**) gave endo/exo 1-(2-benzoylbicyclo[2.2.1]hept-5-en-2-yl)ethanone **3cn**/**3cx** (1:2.1) mixture. HRMS Calcd for $C_{16}H_{16}O_2$: 240.1149. Found: 240.1146. The major component **3cx** was obtained in pure form after irradiation of the mixture, and the spectral data are listed below. Minor component **3cn**: ^{1}H NMR δ 1.46 (m, 2H), 1.98 (dd, J = 12.5, 3.5 Hz, 1H), 2.15 (s, 3H), 2.49 (dd, J = 12.5, 3.6 Hz, 1H), 2.90 (br s, 1H), 3.57 (br s, 1H), 5.98 (dd, J = 5.9, 2.2 Hz, 1H), 6.12 (dd, J = 5.9, 2.9 Hz, 1H), 7.41 (t, J = 7.3 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.81 (d, J = 7.3 Hz, 2H).

Reaction of 2-Methylene-1,3-dicarbonyl Compound 1 with Cyclopentadiene in the Presence of Lewis Acid. The following procedure was carried out at the temperature listed in Table 1. Boron trifluoride etherate (1.0 mmol) or zinc chloride (1.5 mmol) was added to a solution of 2-methylene-1,3-dicarbonyl compound **1** (1.0 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 min. A 1.0 M solution of cyclopentadiene in CH_2Cl_2 (3 mL) was added dropwise, and the mixture was stirred for 7 h. The reaction mixture was washed with water, $NaHCO_3$ solution, brine, and dried. Evaporation of the mixture gave an oily residue which was subjected to column chromatography to yield the corresponding adducts in the ratio listed in Table 1. A single recrystallization of the product (entry 8) gave pure **3bx**: mp 60−62 °C (from benzene−hexane); IR 1735, 1680, 1595, 1580 cm^{-1}; ^{1}H NMR δ 0.98 (t, J = 7.3 Hz, 3H), 1.53 (m, 2H), 2.01 (dd, J = 11.7, 3.6 Hz, 1H), 2.43 (dd, J = 11.7, 2.2 Hz, 1H), 2.97 (br s, 1H), 3.67 (br s, 1H), 3.96 (dq J = 7.3, 2.2 Hz, 2H), 5.96 (dd, J = 5.9, 2.9 Hz, 1H), 6.39 (dd, J = 5.9, 2.9 Hz, 1H), 7.41 (t, J = 7.3 Hz, 2H), 7.52 (t, J = 7.3 Hz,1H), 7.93 (d, J = 7.3 Hz, 2H); ^{13}C NMR δ 13.8, 36.2, 43.1, 49.7, 50.2, 61.3, 64.0, 128.4, 129.1, 132.6, 132.9, 135.8, 140.5, 172.3, 197.1. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.28; H, 6.61. HRMS Calcd for $C_{17}H_{18}O_3$: 270.1255. Found: 270.1257.

Irradiation of the Adducts. A Diels−Alder adduct was dissolved in benzene in a Pyrex tube, which was then flushed with nitrogen and irradiated for 10 h. The reaction mixture was evaporated off, and the residue was subjected to column chromatography to remove a more polar unidentified product. The less polar mixture of products was further subjected to preparative centrifugal TLC.

(a) (2-Benzoylbicyclo[2.2.1]hept-5-en-2-yl)phenylmethanone (**3a**) (90 mg) gave (1-phenyl-9-oxapentacyclo[5.2.1.0.^{2,6}0^{4,8}]-nonyl)phenylmethanone (**4a**) (82 mg, 91%): mp 118 °C (from benzene−hexane); IR (KBr): 1650, 1595, 1575 cm^{-1}; ^{1}H NMR δ 1.84 (br s, 2H), 1.95 (d, J = 11.0 Hz, 1H), 2.21 (br s, 1H), 2.54 (br d, J = 11.0 Hz, 1H), 3.44 (br s, 1H), 3.65 (m, 1H), 5.01 (m, 1H), 7.1−7.6 (m, 8H), 8.05 (d, J = 7.0 Hz, 2H); ^{13}C NMR

(22) Corey, E. J.; Imai, N.; Zhang, H.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 728.

δ 33.8, 42.4, 46.4, 50.9, 62.7, 67.5, 86.3, 104.1, 126.4, 128.1, 128.2, 128.5, 129.5, 132.0, 135.9, 138.3, 202.1. Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.21; H, 5.87.

(b) A mixture of the adducts **3bn** and **3bx** (150 mg ratio 3.8:1) gave the less polar, recovered **3bx** (25 mg, 17%) and ethyl 1-phenyl-9-oxapentacyclo[5.2.1.0.^{2,6}0^{4,8}]nonane-2-carboxylate (**4b**) (106 mg 71% (89% from **3bn**)): $bp_{0.1}$ 140 °C; IR (neat) 1720, 760, 700 cm^{-1}; ^{1}H NMR δ 1.22 (t, J = 7.0 H, 3H), 1.82 (br s, 2H), 1.84 (d, J = 11.0 Hz, 1H), 2.18 (br s, 1H), 2.27 (br d, J = 11.0 Hz, 1H), 3.22 (br s, 1H), 3.47 (dd, J = 3.6, 2.2 Hz, 1H), 4.09 (q, J = 7.0 Hz, 2H), 4.86 (dd, J = 3.6, 2.2 Hz, 1H), 7.2−7.4 (m, 5H); ^{13}C NMR δ 14.2, 34.7, 42.0, 44.0, 50.4, 60.3, 60.5, 61.4, 86.0, 102.4, 126.0, 128.0, 128.4, 136.2, 172.6. HRMS Calcd for $C_{17}H_{18}O_3$: 270.1256. Found: 270.1258.

(c) A mixture of the adducts **3cn** and **3cx** (130 mg ratio 1:2.1) gave the less polar, unreacted **3cx** (63 mg, 48%): IR (neat) 1715, 1670, 1600, 1580 cm^{-1}; ^{1}H NMR δ 1.45 (br d, J = 8.8 Hz, 1H), 1.57 (br d, J = 8.8 Hz, 1H), 1.89 (dd, J = 11.7, 3.7 Hz, 1H), 2.03 (s, 3H), 2.59 (dd, J = 11.7, 2.9 Hz, 1H), 2.93 (br s, 1H), 3.82 (br s, 1H), 5.88 (dd, J = 5.9, 2.9 Hz, 1H), 6.34 (dd, J = 5.9, 2.9 Hz, 1H), 7.41 (t, J = 7.3 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.87 (d, J = 7.3 Hz, 2H); ^{13}C NMR δ 27.7, 34.3, 43.2, 49.7, 49.9, 73.8, 128.5, 129.6, 131.3, 133.2, 136.0, 140.8, 198.8, 204.3. Also formed was 1-(1-phenyl-9-oxapentacyclo[5.2.1.0.^{2,6}0^{4,8}]nonyl)ethanone (**4c**) {38 mg, 29% (91% from **3cn**)}: IR (neat) 1700, 1600, 750, 700 cm^{-1}; ^{1}H NMR δ 1.80 (m, 2H), 1.89 (d, J = 11.0 Hz, 1H), 2.06 (s, 3H), 2.18 (br s, 1H), 2.29 (br d, J = 11.0 Hz,1H), 3.17 (br s, 1H), 3.50 (m, 1H), 4.89 (m, 1H), 7.2−7.4 (m, 5H). HRMS Calcd for $C_{16}H_{16}O_2$: 240.1150. Found: 240.1161.

(1′*R*,2′*S*,5′*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (2-Phenyl-1,3-dioxolan-2-yl)acetate (9). Oxalyl chloride (3.0 mL, 34.4 mmol) was added dropwise to a solution of 2-phenyl-1,3-dioxolan-2-ylacetic acid (**8**) (3.0 g, 14.4 mmol) in benzene (40 mL), and the reaction mixture was stirred for 3 h at ambient temperature. The solvent was evaporated off. The resulting residue was dissolved in CH_2Cl_2 (5 mL) and added to a solution of (−)-8-phenylmenthol (2.32 g, 10.0 mmol), Et_3N (1.5 g, 14.9 mmol), and DMAP (10 mg, 0.082 mmol) in CH_2Cl_2 (40 mL) at 0 °C. After addition was completed, the reaction mixture was stirred for 10 h at ambient temperature. The reaction mixture was washed with water (30 mL × 3) and brine (20 mL), dried, and evaporated. The residue was subjected to column chromatography (8% AcOEt in hexane as eluent) to give (1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (2-phenyl-1,3-dioxolan-2-yl)acetate (3.50 g, 83% from the alcohol): IR (neat) 1735, 1500, 760, 700 cm^{-1}; ^{1}H NMR δ 0.81 (d, J = 6.6 Hz, 3H), 1.16 (s, 3H), 1.24 (s, 3H,), 2.38 (ABq, J = 14.7 Hz, 2H), 3.75 (m, 2H), 4.01 (m, 2H), 4.72 (dt, J = 10.5, 4.4 Hz, 1H), 7.10−7.43 (m, 5H); $[\alpha]_D^{26}$ = +2.1° (*c*, 2.4, $CHCl_3$). Anal. Calcd for $C_{27}H_{34}O_4$: C, 76.75; H, 8.11. Found: C, 76.99; H, 8.18.

(1′*R*,2′*S*,5′*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 3-Oxo-3-phenylpropionate (10). To a solution of (1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (2-phenyl-1,3-dioxolan-2-yl)acetate (**9**) (3.35 g, 7.94 mmol) in MeOH (120 mL) was added dropwise 10% HCl (18 mL), and the reaction mixture was stirred for 12 h at ambient temperature. A large part of MeOH was evaporated off under reduced pressure at ambient temperature, and water (50 mL) and ether (50 mL) were added to the residue. The organic layer was separated, and the aqueous layer was extracted with ether (40 mL × 2). The combined organic layer was washed with brine (50 mL × 2), dried, and evaporated. The residue was subjected to column chromatography to give **10** (2.90 g, 97%): IR (neat) 1735, 1685, 1600, 1580 cm^{-1}; ^{1}H NMR δ 0.86 (d, J = 6.6 Hz, 3H), 1.20 (s, 3H), 1.32 (s, 3H), 3.27 (ABq, J = 15.7 Hz, 2H), 4.86 (dt, J = 10.6, 4.4 Hz, 1H), 7.24−7.79 (m, 5H); $[\alpha]_D^{23}$ = +49.5° (*c*, 2.0, $CHCl_3$). Anal. Calcd for $C_{25}H_{30}O_3$: C,79.33; H, 7.99. Found: C, 79.05; H, 8.24.

(1′*R*,2′*S*,5′*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-[(Methylthio)methyl]-3-oxo-3-phenylpropionate. A mixture of **10** (2.00 g, 5.29 mmol) and *N*-[(methylthio)-methyl]piperidine hydrochloride (1.43 g, 7.88 mmol) in dioxane (110 mL) was stirred for 17 h at 90 °C. The solvent was evaporated off, and AcOEt (100 mL) and water (50 mL) were added to the residue. The organic layer separated was washed with water (50 mL × 2) and brine (50 mL), dried, and evaporated. The residue was subjected to column chromatography to give (1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-[(methylthio)methyl]-3-oxo-3-phenylpropionate (2.20 g, 96%): IR (neat) 1735, 1685, 1600, 1580 cm^{-1}; ^{1}H NMR δ 0.78 (d, J = 6.6 Hz, 3H), 1.16 (s, 3H), 1.29 (s, 3H), 2.08 (s, 3H), 2.95 (d, J = 7.0 Hz, 2H), 3.76 (t, J = 7.0 Hz, 1H), 4.81 (dt, J = 10.5, 4.4 Hz, 1H), 7.25−7.97 (m, 5H). Anal. Calcd for $C_{27}H_{34}O_3S$: C, 73.93; H, 7.81. Found: C, 73.68; H, 8.11. HRMS Calcd for $C_{27}H_{34}O_3S$: 438.2227. Found: 438.2224.

(1′*R*,2′*S*,5′*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-[(Methylsulfinyl)methyl]-3-oxo-3-phenylpropionate. A solution of $NaIO_4$ (8.7 g, 40.7 mmol) in water (100 mL) was slowly added to a solution of (1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-[(methylthio)methyl]-3-oxo-3-phenylpropionate (2.22 g, 5.07 mmol) in MeOH (300 mL) at 0 °C. The reaction mixture was stirred for 12 h at ambient temperature and evaporated to 1/5 of its original volume. The residue was diluted with water (100 mL) and extracted with AcOEt (100 mL × 3). The organic layer was washed with water (100 mL × 3) and brine (80 mL), dried, and evaporated. The residue was subjected to column chromatography to yield (1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-[(methylsulfinyl)methyl]-3-oxo-3-phenylpropionate (2.01 g, 92%): IR (neat) 1730, 1680, 1600, 1580 cm^{-1}.

(1′*R*,2′*S*,5′*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-Benzoylacrylate 1d. A solution of (1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-[(methylsulfinyl)-methyl]-3-oxo-3-phenylpropionate (2.01 g, 4.43 mmol) in toluene (2 mL) was refluxed for 12 h. The reaction mixture was diluted with benzene (30 mL), washed with water (20 mL × 3) and brine (15 mL), dried, and evaporated. The residue was subjected to column chromatography to yield (1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-benzoylacrylate (**1d**) (1.67 g, 97%): IR (neat) 1715, 1680, 1600, 1580 cm^{-1}; ^{1}H NMR δ 0.70−2.10 (m, 8H), 0.85 (d, J = 6.4 Hz, 3H), 1.20 (s, 3H), 1.26 (s, 3H), 4.91 (dt, J = 10.5, 4.5 Hz, 1H), 5.83 (s, 1H), 6.04 (s, 1H), 7.1−7.6 (m, 8H), 7.78 (dd, J = 8.5, 1.2 Hz, 2H); ^{13}C NMR δ 21.7, 26.4, 26.8, 26.9, 31.3, 34.4, 39.8, 41.3, 50.2, 76.0, 125.2, 125.5, 128.1, 128.4, 129.4, 131.3, 133.4, 136.5, 141.2, 151.2, 163.5, 193.2; $[\alpha]_D^{23}$ = −19.0° (*c*, 3.0, $CHCl_3$). Anal. Calcd for $C_{26}H_{30}O_3$: C, 79.97; H, 7.74. Found: C, 79.77; H, 7.97. HRMS Calcd for $C_{26}H_{30}O_3$: 390.2193. Found: 390.2211.

Diels−Alder Reaction of (1′*R*,2′*S*,5′*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 2-Benzoylacrylate (1d). (a) In the Absence of Lewis Acid. A solution of cyclopentadiene in CH_2Cl_2 (2.1 M solution, 1.0 mL) was added to a solution of **1d** (100 mg, 0.256 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 6 h at ambient temperature. The mixture was diluted with CH_2Cl_2 (20 mL), washed with water (10 mL × 2) and brine (5 mL), dried, and evaporated. The residue was subjected to column chromatography to yield a mixture of four stereoisomers. The preparative HPLC of the mixture gave *endo*-(1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (1*S*,2*R*,4*S*)-2-benzoylbicylo[2.2.1]hept-5-ene-2-carboxylate (**3n-R**) (as first fraction): ^{1}H NMR δ 0.47 (q, J = 11.3 Hz, 1H), 0.57 (dq, J = 11.7, 3.0 Hz, 1H), 0.64 (d, J = 6.6 Hz, 3H), 0.80 (dq, J = 13.2, 2.5 Hz, 1H), 1.13 (s, 3H), 1.16 (s, 3H), 1.19−1.53 (m, 5H), 1.68−1.83 (m, 2H), 1.89 (dd, J = 12.1, 2.5 Hz, 1H), 2.66 (dd, J = 12.1, 3.7 Hz, 1H), 2.93 (br s, 1H), 3.46 (br s, 1H), 4.82 (dt, J = 10.6, 4.7 Hz, 1H), 6.12 (m, 2H), 7.08−7.53 (m, 8H), 7.90 (dd, J = 7.3, 1.5 Hz, 2H), *endo*-(1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (1*R*,2*S*,4*R*)-2-benzoylbicylo[2.2.1]hept-5-ene-2-carboxylate (**3n-S**) (as second fraction): ^{1}H NMR δ 0.64 (q, J = 10.0 Hz, 1H), 0.73 (d, J = 6.2 Hz, 3H), 0.78−0.92 (m, 2H), 1.06 (s, 3H), 1.08 (s, 3H), 1.11−1.54 (m, 5H), 1.70−1.79 (m, 3H), 2.09 (dd, J = 12.1, 2.9 Hz, 1H), 2.39 (dd, J = 12.1, 3.7 1H), 2.93 (br s, 1H), 3.57 (br s, 1H), 4.80 (dt, J = 10.5, 4.4 Hz, 1H), 5.93 (dd, J = 15.5, 2.9 Hz, 1H), 6.14 (dd, J = 15.5, 2.9 Hz, 1H), 7.09−7.54 (m, 8H), 7.92 (dd, J = 7.0, 1.5 Hz, 2H), *exo*-(1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (1*S*,2*S*,4*S*)-2-benzoylbicylo[2.2.1]hept-5-ene-2-carboxylate (**3x-S**) (as major component of third fraction): ^{1}H NMR δ 0.65 (q, J = 10.5 Hz,

1H), 0.71 (s, 3H), 0.81 (d, J = 6.2 Hz, 3H), 0.88 (s, 3H), 0.91−1.97 (m, 10H), 2.10 (dd, J = 12.1, 3.7 Hz, 1H), 2.53 (dd, J = 12.1, 2.6 Hz, 1H), 2.96 (br s, 1H), 3.78 (br s, 1H), 4.61 (dt, J = 10.6, 4.0 Hz, 1H), 6.06 (dd, J = 15.5, 2.9 Hz, 1H), 6.42 (dd, J = 15.5, 2.9 Hz, 1H), 7.02−7.54 (m, 8H), 8.02 (dd, J = 7.3, 1.5 Hz, 2H), and **3x-R** (as fourth fraction), whose spectral data are shown below.

(b) In the Presence of Lewis Acid. A equimolar amount of Lewis acids (BF_3·OEt_2, $FeCl_2$, $FeCl_2I$) and 1.5 equiv of $ZnCl_2$ were used. A solution of **1d** (100 mg, 0.256 mmol) in CH_2Cl_2 (5 mL) was added to a solution or suspension of Lewis acids in CH_2Cl_2 (5 mL) and stirred for 30 min at the temperatures shown in Table 3. Then a solution of cyclopentadiene in CH_2Cl_2 (2.1 M solution, 1.0 mL) was added to the above mixture and stirred under the reaction conditions shown in Table 3. After the reaction was completed, water (5 mL) was added to the mixture and the resulting solution was stirred for 5 min at ambient temperature, washed with water (15 mL × 2) and brine (5 mL), dried, and evaporated. The residue was subjected to column chromatography to yield the adduct (yields and exo/endo ratios were shown in Table 3). A single recrystallization of the product under $ZnCl_2$ catalyst at −78 °C gave pure *exo*-(1′*R*,2′*S*,5′*R*)-5-methyl-2-(1-methyl-1-phenylethyl)cyclohexyl (1*R*,2*R*,4*R*)-2-benzoylbicylo[2.2.1]hept-5-ene-2-carboxylate (**3x-R**): mp 135−136 °C (from EtOH); IR (KBr) 1730, 1680 cm^{-1}; ^1H NMR δ −0.09 (q, J = 11.5 Hz, 1H), 0.45 (dq, J = 12.5, 3.5 Hz, 1H), 0.49 (d, J = 6.8 Hz, 3H), 0.72 (dq, J = 13.2, 3.3 Hz, 1H), 1.04 (dq, J = 12.6, 3.3 Hz, 1H), 1.14 (dq, J = 11.5, 4.0 Hz, 1H), 1.21 (s, 3H), 1.26 (m, 1H), 1.30 (m, 1H), 1.40 (s, 3H), 1.56 (m, 2H), 1.69 (dt, J = 12.0, 3.3 Hz, 1H), 2.05 (dd, J = 12.0, 3.6 Hz, 1H), 2.43 (dd, J = 12.0, 1.8 Hz, 1H), 2.98 (br s, 1H), 3.57 (br s, 1H), 4.66 (dt, J = 10.6, 4.0 Hz, 1H), 5.99 (dd, J = 5.5, 2.9 Hz, 1H), 6.43 (dd, J = 5.5, 2.9 Hz, 1H), 7.10−7.60 (m, 8H), 7.91 (dd, J = 7.0, 1.8 Hz, 2H); ^{13}C NMR δ 21.4, 27.4, 30.87, 30.91, 34.1, 36.6, 39.9, 40.3, 43.2, 49.3, 49.8, 50.1, 63.4, 77.1, 125.4, 125.7, 128.0, 128.3, 129.2, 132.3, 132.8, 136.0, 140.5, 150.4, 171.8, 197.2; $[\alpha]^{30}_D$ = +135° (*c*, 0.35, $CHCl_3$). Anal. Calcd for $C_{31}H_{36}O_3$: C, 81.54; H, 7.95. Found: C, 81.54; H, 8.13. HRMS Calcd for $C_{31}H_{36}O_3$: 456.2663. Found: 456.2653.

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