# Structure and Asymmetric Diels−Alder Reactions of Optically Active Allene-1,3-dicarboxylates

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Optically active allene-1,3-dicarboxylates (**1a** and **2a**), which contain the axial asymmetry of the allene moiety, were prepared. The Diels−Alder reaction of **1a** and **2a** with cyclopentadiene afforded the 1:1 (**1a** or **2a** to cyclopentadiene) *endo* adducts **3a** and **4a** through the combination of the sterically favorable approach of the diene and the dienophile owing to the axial asymmetry of the allene moiety and the effective secondary orbital interaction. The absolute configurations of **3a** and **4a** were determined by chemical transformation and X-ray analysis. The absolute configuration of the axial asymmetry of **1a** was also determined to be *R* by X-ray analysis.

## Introduction

As early as in 1875, van't Hoff predicted that unsymmetrically substituted allenes should exist in two enantiomeric forms.[1] Since the synthesis of the enantiomeric 1,3-diphenyl-1,3-di-α-naphthylallenes after 60 years,[2] several general methods have been developed for the synthesis of optically active allenes,[3,4] and an evergrowing volume of publications is unfolding their interesting properties.[5]

The cycloaddition reactions of optically active allenes which involve the transfer of the axial chiral element of allenes to products is a powerful tool for the enantioselective synthesis. In recent years, enantioselective intramolecular Diels−Alder reactions[5a] and intramolecular [2 + 2] photocycloadditions[5b] of optically active allenes have been reported. On the other hand, the *intermolecular* Diels−Alder reaction of allene-1,3-dicarboxylic derivative was reported by Agosta in 1964 to establish the absolute configuration of partially resolved (−)-allene-1,3-dicarboxylic acid.[6] However, the definitive examples of the Diels−Alder reactions of this type have not been reported up to now.

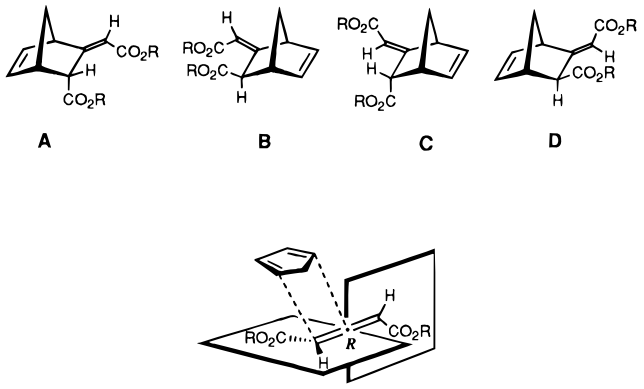


**Figure 1.**

As a part of systematic studies on pericyclic reactions, we have studied the asymmetric Diels−Alder reactions of allene-1,3-dicarboxylates with the aim of π-face selective reactions owing to the axial asymmetry of the allene moiety. The activating influence that a carboxylate function exerts upon the allene framework makes these compounds excellent dienophiles in Diels−Alder reactions.[7] It was predicted that the Diels−Alder reaction of the optically active allene-1,3-dicarboxylate proceeds with high stereoselectivity derived from the axial asymmetry of the allene moiety. From this point of view, it is expected that the *endo* adduct **A** would be preferentially obtained through the combination of the sterically favorable approach of the diene and the dienophile (the *re* face attack of the (*R*)-allene-1,3-dicarboxylate) owing to the axial asymmetry of the allene moiety and the effective secondary orbital interaction (Figure 1). While the adduct **B** would be formed without secondary orbital interaction of carboxylate moiety, the adduct **C** must be

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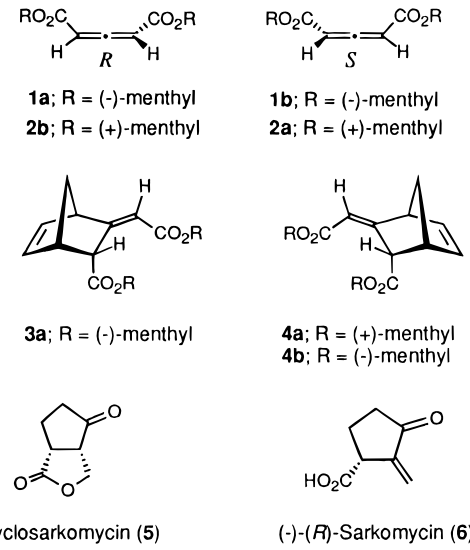
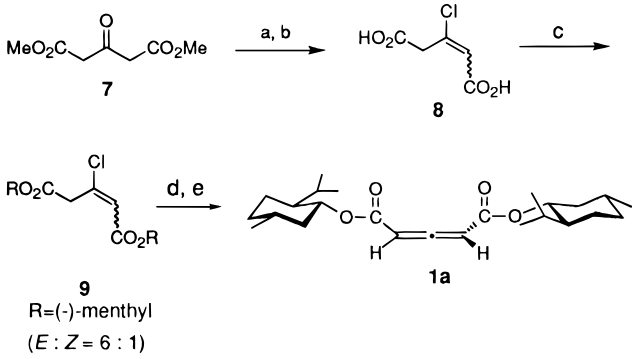



**Figure 2.**

**Scheme 1**[a]




[a] *Reagents and conditions*: (a) $PCl_5$; (b) 20% HCl, reflux (37%, 2 steps); (c) (-)-menthol, conc. $H_2SO_4$, benzene, reflux (93%); (d) $Et_3N$, THF, 0° C (98%); (e) recrystallized from pentane (23%).

formed against the steric hindrance. The adduct **D** would be scarcely formed because of two disadvantageous factors.

Moreover, the major adducts obtained by the asymmetric Diels−Alder reactions of (*R*)- and (*S*)-allene-1,3-dicarboxylates are considered to be useful chiral synthons for the synthesis of optically active natural products such as (−)-cyclosarkomycin (**5**), a synthetic precursor of antitumor antibiotic sarkomycin (**6**) (Figure 2).[8]

## Results

**Preparation of Optically Pure Allene-1,3-dicarboxylate.** Optically pure di-(−)-menthyl allene-1,3-dicarboxylate (**1a**) was prepared by the modification of Smith's procedure[9] of allene-1,3-dicarboxylate (Scheme 1). Menthol was used as a chiral auxiliary of choice with the aim of preparation of (*R*)- or (*S*)-allene-1,3-dicarboxylate, because both optically pure (−)- and (+)-menthols are readily available and comparatively inexpensive. 3-Chloroglutaconic acid (**8**) was obtained from dimethyl 1,3-acetonedicarboxylate (**7**) by treatment with phosphorus pentachloride (1.05 equiv) followed by hydrolysis with

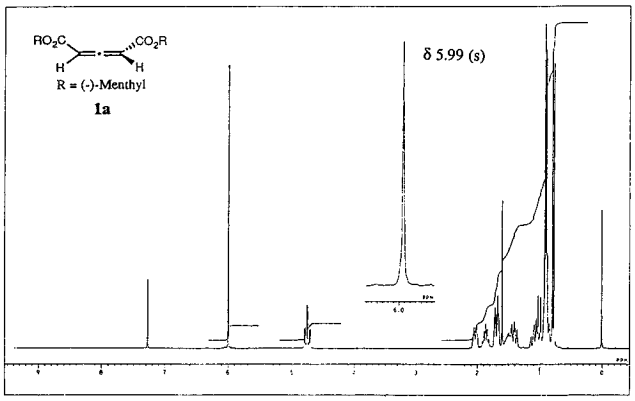



**Figure 3.** The $^1$H NMR spectrum of **1a**.

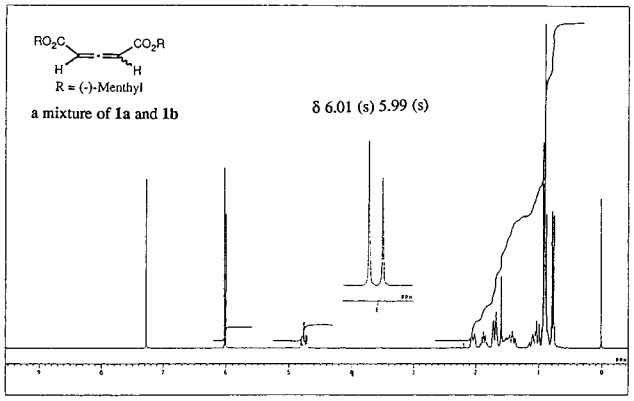



**Figure 4.** The $^1$H NMR spectrum of a mixture of **1a** and **1b**.

20% hydrochloric acid. Esterification of **8** with (−)-menthol (concd sulfuric acid, benzene, reflux) proceeded to give the chloro di-(−)-menthyl ester **9** as a mixture of geometrical isomers in high yield. The ratio of isomers **9** was determined by $^1$H NMR spectrum inspection (*E*:*Z* = 6:1). Dehydrochlorination of **9** with triethylamine (1.2 equiv) in dry tetrahydrofuran at 0 °C gave a mixture of diastereomers, which was recrystallized from pentane to afford one of the diastereomers, **1a**, in optically pure form; mp 83 °C, $[\alpha]^{20}_D$ −251.1° (*c* 1.00, $CHCl_3$). Although it was presumed that the other diastereomer **1b** was enriched in the mother liquor, attempts to isolate **1b** were not successful.

The IR spectrum of **1a** suggested the existence of an allenic central carbon atom (1960 $cm^{-1}$) and a carbonyl group (1700 $cm^{-1}$). The $^1$H NMR spectrum indicated two equivalent olefinic protons of the allene at $\delta$ 5.99 (s) (Figure 3). The $^{13}$C NMR spectrum exhibited the signal for the allenic central carbon atom at $\delta$ 219.56 (s). In contrast, the $^1$H NMR spectrum of the mixture of diastereomers **1a** and **1b** indicated two signals of olefinic protons of the allene at $\delta$ 6.01 (s) and 5.99 (s) (Figure 4). In addition, two signals of the allenic central carbon atoms were observed at $\delta$ 219.52 (s) and 219.17 (s), respectively, in the $^{13}$C NMR spectrum.

On the other hand, the optically active di-(+)-menthyl allene-1,3-dicarboxylate (**2a**) (mp 83 °C, $[\alpha]^{22}_D$ +262.7° (*c* 0.99, $CHCl_3$)) was isolated in a similar manner to the preparation of **1a** (Scheme 2). Spectral and physical data of **2a** were identical with those of **1a** except for antipodal optical rotation.

**Asymmetric Cycloaddition Reactions of 1a and 2a with Cyclopentadiene.** The Diels−Alder reaction of **1a** with cyclopentadiene in the presence of aluminum

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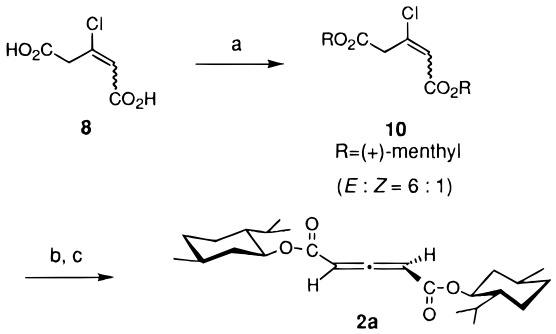
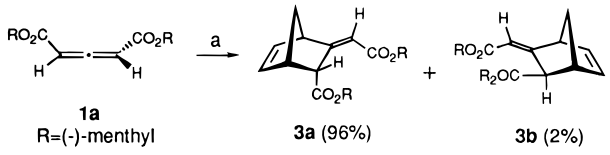
**Scheme 2**[a]



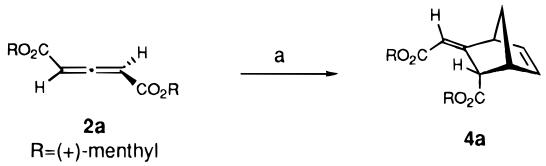

[a]*Reagents and conditions*: (a) (-)-menthol, conc. $H_2SO_4$, benzene, reflux (94%); (b) $Et_3N$, THF, 0° C (75%); (c) recrystallized from pentane (25%).

**Scheme 3**[a]




[a]*Reagents and conditions*: (a) cyclopentadiene, $AlCl_3$, $CH_2Cl_2$, -78 °C, 5 h.

**Scheme 4**[a]




[a]*Reagents and conditions*: (a) cyclopentadiene, $AlCl_3$, $CH_2Cl_2$, -78 °C, 2 h (95%).

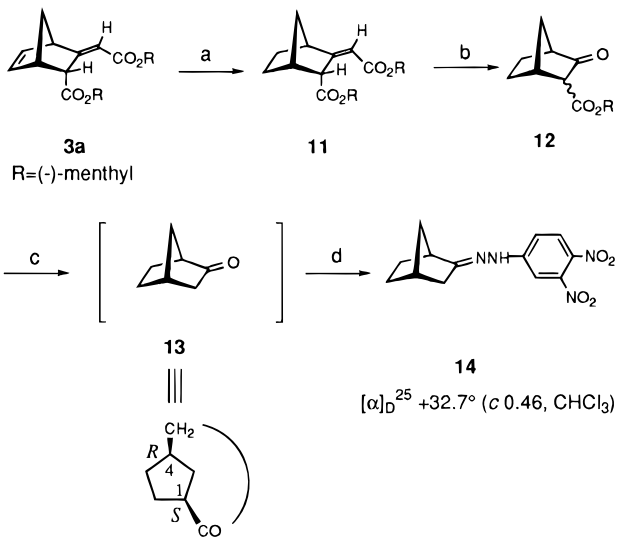
chloride ($AlCl_3$) proceeded with high diastereoselectivity to afford a mixture of two 1:1 adducts in high yield. No evidence for other adducts besides two adducts was found by TLC and $^1$H NMR inspection. The ratio of adducts (major (**3a**)/minor (**3b**) = 98:2) was determined by HPLC analysis. The major adduct **3a** was isolated in 96% yield (Scheme 3).

The relative configuration of adducts **3a** and **3b** was established on the basis of $^1$H NMR and other spectral data. First, each 1:1 adduct showed two olefinic protons ($H_5$ and $H_6$) [**3a**: $\delta$ 6.18−6.11 (m, 2H); **3b** $\delta$ 6.33 (dd, $J$ = 5.3, 3.0 Hz, 1H) and 6.12 (dd, $J$ = 5.3, 3.0 Hz, 1H)] and the *exo*-olefinic proton (Ha) [**3a**: $\delta$ 5.98 (d, $J$ = 2.0 Hz, 1H); **3b**: $\delta$ 5.99 (d, $J$ = 2.0 Hz, 1H)]. The major isomer **3a** showed a characteristic signal of an *exo*-$H_2$ at $\delta$ 3.87 as a doublet of doublet with coupling constants 3.5 and 2.0 Hz, which indicated that **3a** was the *endo* adduct. Detailed inspection of $^1$H NMR showed that the minor isomer **3b** was the *exo* adduct (Scheme 3).

On the other hand, the reaction of the (*S*)-allene-1,3-dicarboxylate **2a** with cyclopentadiene in the presence of $AlCl_3$ proceeded similarly to that of **1a** to afford the 1:1 adduct **4a** in 95% yield (Scheme 4). Physical and spectral data of **4a** were identical with those of **3a** except for antipodal optical rotation.

The absolute configuration of **3a** was determined by Agosta's procedure,[6] the chemical transformation into (+)-norcamphor 2,4-dinitrophenylhydrazone (Scheme 5).[10]

**Scheme 5**[a]




[a]*Reagents and conditions*: (a) $H_2$, Pd-C, AcOEt (quant.); (b) $O_3$, $CH_2Cl_2$, -78°C; $Me_2S$, -78 °C (quant.); (c) conc. HCl, reflux; (d) 2,4-dinitrophenylhydrazine, conc. HCl, MeOH (52% from **12**).

Palladium-catalyzed hydrogenation of **3a** produced **11** in quantitative yield. Ozonolysis of the double bond of **11** proceeded to give the $\beta$-keto ester **12** in quantitative yield. Compound **12** was hydrolyzed and decarboxylated directly by heating with concentrated hydrochloric acid to give volatile norcamphor **13**, which was treated with 2,4-dinitrophenylhydrazine without purification to give **14**, (+)-norcamphor dinitrophenylhydrazone [mp 132 °C, $[\alpha]^{25}_D$ +32.7° (*c* 0.46, $CHCl_3$)]. Spectral data were identical in all respects with the Agosta's data of (+)-norcamphor dinitrophenylhydrazone [mp 129−130 °C, $[\alpha]^{28}_D$ +30° ($CHCl_3$)] derived from the authentic (1*S*,4*R*)-norcamphor. Judging from these results, the absolute configuration of **3a** was determined to be (1*S*,2*R*,4*R*)-form. Similarly, **4a** was converted into (−)-norcamphor dinitrophenylhydrazone **18** [mp 131 °C, $[\alpha]^{23}_D$ −28.0° (*c* 1.03, $CHCl_3$)] (Scheme 6).

The bridgehead structure and the *exo*-olefin geometry of the *endo* adduct **4a** derived from (*S*)-allene-1,3-dicarboxylate **2a** was completely confirmed by X-ray analysis as depicted in Figure 5, and thus the *exo*-olefin geometry of **4a** was determined to be *Z*.

**Determination of the Absolute Configurations of 1a and 2a.** The absolute configurations of the Diels−Alder adducts **3a** and **4a**[19] were determined by chemical transformation and X-ray analysis. The stereochemistry of the *endo* adduct **3a** can only be derived by the reaction of **1a** from the *re* face and that suggested the absolute configuration of the axial asymmetry of **1a** was *R*.

An unequivocal support for the structure of **1a** was obtained by single-crystal X-ray analysis,[19] and the axial asymmetry of the allene moiety of **1a** was determined to be *R* (Figure 6). Crystallographic data are listed in Tables 1−3. Interestingly, the X-ray analysis of **1a** showed that the two allenic double bonds retain their linear arrangements (178.4°) and that the bond length (1.298 Å) is somewhat shorter than the standard allenic bond length (1.31 Å).[11] The structure and the frontier molecular orbitals of the allene portion of **1a** were studied

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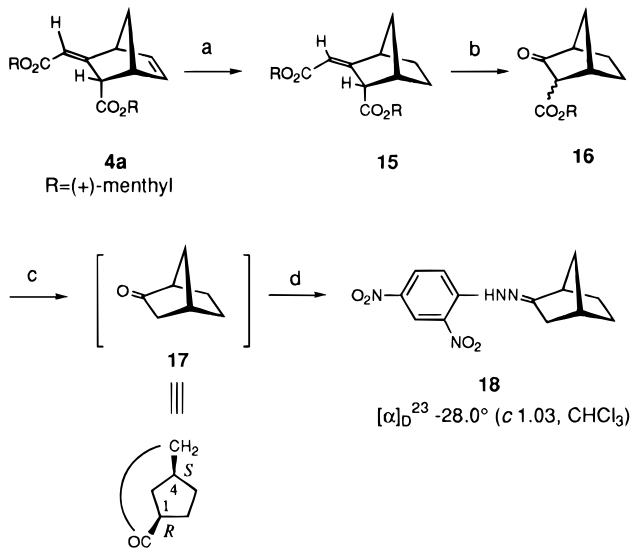
**Scheme 6**[a]




[a] *Reagents and conditions*: (a) $H_2$, Pd-C, AcOEt (98%); (b) $O_3$, $CH_2Cl_2$, -78°C; $Me_2S$, -78 °C (98%); (c) conc. HCl, reflux; (d) 2,4-dinitrophenylhydrazine, conc. HCl, MeOH (39% from **16**).

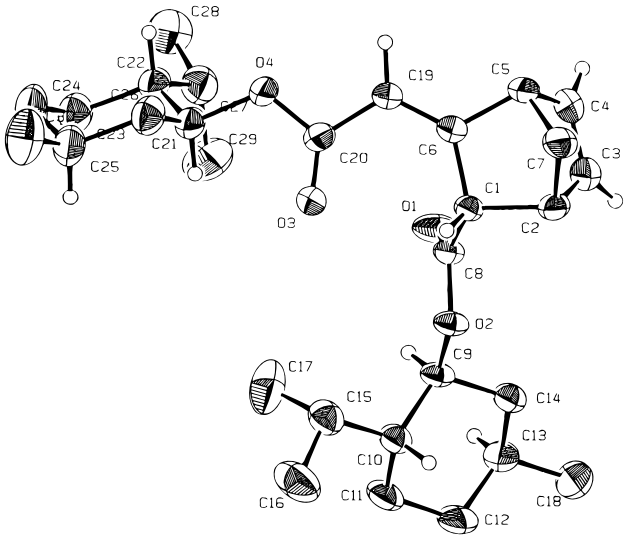



**Figure 5.** Computer-generated perspective drawing of **4a** as determined by X-ray analysis. The atom numbering is arbitrary.

by *ab initio* calculations of model structures with Gaussian 92[12] employing the 6-31G basis set.[13] The X-ray structure of the central portion of **1a** was almost superimposable with the optimized geometry of dimethyl allenedicarboxylate (DMAD). In our previous study,[14] AM1 revealed a remarkable decrease in the LUMO level of allene upon the introduction of carboxylate groups at 1,3-positions (1.74 eV). This trend has been confirmed and accentuated by *ab initio* calculations which produced a larger decrease in the LUMO level (2.44 eV); LUMO: allene 4.85 eV, DMAD 2.41 eV).

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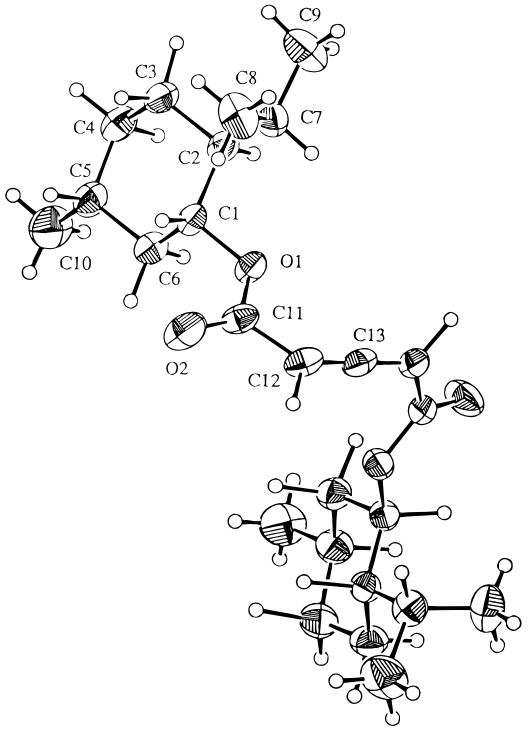


**Figure 6.** Computer-generated perspective drawing of **1a** as determined by X-ray analysis. The atom numbering is arbitrary.

**Table 1. Atomic Coordinates and $B_{iso}/B_{eq}$ of 1a**

| atom | *x* | *y* | *z* | $B_{eq}$[a] |
|---|---|---|---|---|
| O(1) | 0.0749(2) | 0.3468(1) | 0.0379(2) | 5.15(6) |
| O(2) | −0.0597(2) | 0.3642(2) | −0.0739(3) | 9.1(1) |
| C(1) | 0.1118(2) | 0.3002(2) | −0.0704(3) | 4.64(8) |
| C(2) | 0.2178(2) | 0.3114(2) | −0.0736(4) | 5.11(8) |
| C(3) | 0.2565(4) | 0.2600(3) | −0.1846(4) | 6.2(1) |
| C(4) | 0.2310(3) | 0.1787(3) | −0.1591(5) | 6.7(1) |
| C(5) | 0.1240(3) | 0.1669(2) | −0.1483(4) | 6.3(1) |
| C(6) | 0.0843(3) | 0.2204(2) | −0.0425(4) | 5.74(9) |
| C(7) | 0.2491(3) | 0.3929(2) | −0.0881(4) | 6.1(1) |
| C(8) | 0.2107(4) | 0.4325(3) | −0.2086(5) | 8.4(1) |
| C(9) | 0.3542(4) | 0.3998(3) | −0.0791(7) | 9.8(2) |
| C(10) | 0.0983(4) | 0.0875(3) | −0.1164(6) | 9.1(2) |
| C(11) | −0.0099(3) | 0.3756(2) | 0.0209(4) | 5.45(9) |
| C(12) | −0.0391(3) | 0.4235(2) | 0.1325(4) | 5.58(10) |
| C(13) | 0.0000 | 0.4245(3) | 0.2500 | 5.0(1) |
| H(1) | 0.0772 | 0.3260 | −0.1657 | 4.6000 |
| H(2) | 0.2436 | 0.2847 | 0.0288 | 5.2000 |
| H(3a) | 0.3340 | 0.2606 | −0.1956 | 6.2000 |
| H(3b) | 0.2247 | 0.2662 | −0.2783 | 6.2000 |
| H(4a) | 0.2579 | 0.1432 | −0.2354 | 6.7000 |
| H(4b) | 0.2543 | 0.1584 | −0.0425 | 6.7000 |
| H(5) | 0.0927 | 0.1843 | −0.2580 | 6.3000 |
| H(6a) | 0.0039 | 0.2210 | −0.0454 | 5.8000 |
| H(6b) | 0.1071 | 0.1976 | 0.0610 | 5.8000 |
| H(7) | 0.2242 | 0.4200 | −0.0102 | 6.1000 |
| H(8a) | 0.2326 | 0.4818 | −0.2169 | 8.5000 |
| H(8b) | 0.2357 | 0.4057 | −0.2904 | 8.5000 |
| H(8c) | 0.1450 | 0.4300 | −0.2154 | 8.5000 |
| H(9a) | 0.3843 | 0.3812 | −0.0023 | 9.9000 |
| H(9b) | 0.3862 | 0.3753 | −0.1573 | 9.9000 |
| H(9c) | 0.3770 | 0.4527 | −0.0892 | 9.9000 |
| H(10a) | 0.0319 | 0.0777 | −0.1144 | 9.0000 |
| H(10b) | 0.1263 | 0.0522 | −0.1781 | 9.0000 |
| H(10c) | 0.1227 | 0.0744 | −0.0280 | 9.0000 |
| H(12) | −0.1089 | 0.4470 | 0.1160 | 5.5000 |

[a] $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

## Discussion

Optically active dimenthyl allenedicarboxylates **1a** and **2a** were prepared, and the absolute configurations were

**Table 2. Bond Lengths of 1a in Angstroms**

| | | | |
|---|---|---|---|
| O(1)−C(1) | 1.464(4) | O(1)−C(11) | 1.320(4) |
| O(2)−C(11) | 1.200(5) | C(1)−C(2) | 1.518(5) |
| C(1)−C(6) | 1.509(5) | C(2)−C(3) | 1.542(5) |
| C(2)−C(7) | 1.535(5) | C(3)−C(4) | 1.523(7) |
| C(4)−C(5) | 1.537(6) | C(5)−C(6) | 1.535(6) |
| C(5)−C(10) | 1.504(7) | C(7)−C(8) | 1.500(6) |
| C(7)−C(9) | 1.498(7) | C(11)−C(12) | 1.466(6) |
| C(12)−C(13) | 1.298(5) | | |
| C(1)−H(1) | 1.17 | C(2)−H(2) | 1.19 |
| C(3)−H(3a) | 1.10 | C(3)−H(3b) | 1.05 |
| C(4)−H(4a) | 1.06 | C(4)−H(4b) | 1.26 |
| C(5)−H(5) | 1.22 | C(6)−H(6a) | 1.14 |
| C(6)−H(6b) | 1.16 | C(7)−H(7) | 0.98 |
| C(8)−H(8a) | 0.94 | C(8)−H(8b) | 1.01 |
| C(8)−H(8c) | 0.94 | C(9)−H(9a) | 0.94 |
| C(9)−H(9b) | 1.00 | C(9)−H(9c) | 1.01 |
| C(10)−H(10a) | 0.96 | C(10)−H(10b) | 0.97 |
| C(10)−H(10c) | 0.98 | C(12)−H(12) | 1.09 |

**Table 3. Bond Angles of 1a in Degrees**

| | | | |
|---|---|---|---|
| C(1)−O(1)−C(11) | 117.1(3) | O(1)−C(1)−C(2) | 107.2(3) |
| O(1)−C(1)−C(6) | 108.2(3) | C(2)−C(1)−C(6) | 112.7(3) |
| C(1)−C(2)−C(3) | 106.8(3) | C(1)−C(2)−C(7) | 114.5(3) |
| C(3)−C(2)−C(7) | 113.5(3) | C(2)−C(3)−C(4) | 111.6(3) |
| C(3)−C(4)−C(5) | 112.2(4) | C(4)−C(5)−C(6) | 109.0(4) |
| C(4)−C(5)−C(10) | 112.6(4) | C(6)−C(5)−C(10) | 110.9(4) |
| C(1)−C(6)−C(5) | 111.7(3) | C(2)−C(7)−C(8) | 115.0(4) |
| C(2)−C(7)−C(9) | 111.2(4) | C(8)−C(7)−C(9) | 111.7(5) |
| O(1)−C(11)−O(2) | 124.8(4) | O(1)−C(11)−C(12) | 112.9(4) |
| O(2)−C(11)−C(12) | 122.2(4) | C(11)−C(12)−C(13) | 125.0(3) |
| C(12)−C(13)−C(12)* | 178.4(6) | | |
| O(1)−C(1)−H(1) | 103.0 | C(2)−C(1)−H(1) | 110.3 |
| C(6)−C(1)−H(1) | 114.7 | C(1)−C(2)−H(2) | 103.5 |
| C(3)−C(2)−H(2) | 105.6 | C(7)−C(2)−H(2) | 112.1 |
| C(2)−C(3)−H(3a) | 114.8 | C(2)−C(3)−H(3b) | 115.2 |
| C(4)−C(3)−H(3a) | 105.2 | C(4)−C(3)−H(3b) | 98.6 |
| H(3a)−C(3)−H(3b) | 109.8 | C(3)−C(4)−H(4a) | 111.6 |
| C(3)−C(4)−H(4b) | 111.6 | C(5)−C(4)−H(4a) | 108.8 |
| C(5)−C(4)−H(4b) | 98.8 | H(4a)−C(4)−H(4b) | 113.2 |
| C(4)−C(5)−H(5) | 105.1 | C(6)−C(5)−H(5) | 108.9 |
| C(10)−C(5)−H(5) | 110.1 | C(1)−C(6)−H(6a) | 104.2 |
| C(1)−C(6)−H(6b) | 115.3 | C(5)−C(6)−H(6a) | 110.8 |
| C(5)−C(6)−H(6b) | 106.9 | H(6a)−C(6)−H(6b) | 107.8 |
| C(2)−C(7)−H(7) | 107.0 | C(8)−C(7)−H(7) | 105.6 |
| C(9)−C(7)−H(7) | 105.6 | C(7)−C(8)−H(8a) | 113.4 |
| C(7)−C(8)−H(8b) | 107.1 | C(7)−C(8)−H(8c) | 113.4 |
| H(8a)−C(8)−H(8b) | 105.2 | H(8a)−C(8)−H(8c) | 111.5 |
| H(8b)−C(8)−H(8c) | 105.5 | C(7)−C(9)−H(9a) | 118.2 |
| C(7)−C(9)−H(9b) | 111.5 | C(7)−C(9)−H(9c) | 113.1 |
| H(9a)−C(9)−H(9b) | 105.8 | H(9a)−C(9)−H(9c) | 105.6 |
| H(9b)−C(9)−H(9c) | 101.0 | C(5)−C(10)−H(10a) | 114.6 |
| C(5)−C(10)−H(10b) | 112.7 | C(5)−C(10)−H(10c) | 109.5 |
| H(10a)−C(10)−H(10b) | 107.2 | H(10a)−C(10)−H(10c) | 106.5 |
| H(10b)−C(10)−H(10c) | 105.8 | C(11)−C(12)−H(12) | 111.7 |
| C(13)−C(12)−H(12) | 121.3 | | |

determined by chemical transformation and X-ray analysis. The Diels−Alder reactions of **1a** and **2a** proceeded with ease under Lewis acid-catalyzed conditions. Optically pure **1a**, the axial asymmetry of which was determined to be *R*, afforded the *endo* adduct **3a** (96%), accompanied by the *exo* adduct **3b** (2%).

Lewis acid catalysis resulted in the high *endo* selectivity in this reaction. Agosta studied the Diels−Alder reaction of allene-1,3-dicarboxylic acid.[6] According to his result, the Diels−Alder reaction of racemic allene-1,3-dicarboxylic acid with cyclopentadiene (ether, room temperature) afforded approximately equal amounts of isomeric adducts, the *endo* adduct **A** and the *exo* adduct **B** (R = H, Figure 1). It is also reported that the reaction of partially resolved (−)-allene-1,3-dicarboxylic acid with cyclopentadiene under similar conditions gave a mixture from which the adduct **B** was separated, but the adduct **A** could not be purified without total loss in optical activity. Lewis acid catalysis in the Diels−Alder reactions of **1a** and **2a** with furan also effected the higher *endo*/*exo* selectivity (the *endo* adduct analogous to **A**:the *exo* adduct analogous to **B** = 53:47 (uncatalyzed; 40 °C) and 81:19 (2 equiv of $TiCl_4$; −78 °C) although the selectivity was not as high as that in the reaction with cyclopentadiene.[15,16]

The adducts **3a** and **3b** both formed by the reaction of **1a** from the *re* face, which suggests that the $\pi$-face selectivity of the reaction is completely controlled. The axial asymmetry of the allene moiety and the two (−)-menthyl groups could contribute to the asymmetric Diels−Alder reaction of **1a**.

Yamamoto et al. reported that the diastereoselectivity in the asymmetric Diels−Alder reaction of fumarate using menthol as a chiral auxiliary was improved dramatically by switching catalyst from $AlCl_3$ to homogeneous organoaluminum reagent such as diethylaluminum chloride.[17] They described that the Lewis acid coordinated fumarate was considered to exist in the *s-trans* form predominantly and that the two (−)-menthyl groups should cooperatively cover the *re* face of the double bond. Consequently, a diene approached from the *si* face of the double bond of the fumarate for cycloaddition.

In marked contrast to their result, the asymmetric Diels−Alder reaction of optically pure di-(−)-menthyl (*R*)-allene-1,3-dicarboxylate proceeded from the *re* face of the double bond of **1a** under Lewis acid-catalyzed conditions.

It is presumed that high $\pi$-facial selectivity of the optically pure allene-1,3-dicarboxylate in the Diels−Alder reaction is elicited from the axial asymmetry of the allene moiety and not from the topological feature of the (−)-menthyl group. It is assumed that the asymmetry of the (−)-menthyl group of the carboxylate which was attached to the reacting double bond of the allene may have rather a disadvantageous effect in approach of diene under Lewis acid-catalyzed conditions. The other (−)-menthyl group which is attached to the unreacting double bond of allene-1,3-dicarboxylate increases the influence of the axial asymmetry of the allene moiety in the Diels−Alder reaction.

## Experimental Section

Melting points are uncorrected. Optical rotations were measured using a 5 cm path length cell. Analytical thin layer chromatography (TLC) was carried out on precoated TLC plates (Kieselgel 60 $F_{254}$, 0.2 mm). Nuclear magnetic resonance spectra ($^1$H NMR and $^{13}$C NMR) were taken in $CDCl_3$ unless otherwise noted. Chemical shifts are reported as $\delta$ values with respect to tetramethylsilane (TMS) as an internal standard. Signal multiplicities are represented by s (singlet), d (doublet), t (triplet), q (quartet), br (broad), and m (multiplet). Column chromatography was performed by using silica gel (70−230 mesh) as the stationary phase. Flash column chromatography was performed by using silica gel (230−400 mesh) as the stationary phase.

**3-Chloro-2-pentenedioic acid (8)** was prepared according to the method of Smith et al.[9,18] To well-stirred dimethyl acetone-1,3-dicarboxylate (**7**) (25.0 g, 0.143 mol) was added

(15) Ikeda, I.; Gondo, A.; Shiro, M.; Kanematsu, K. *Heterocycles* **1993**, *36*, 2669.

(16) The Lewis acid-catalyzed Diels−Alder reaction of **1a** with diphenylfulvene only led to polymerization although the uncatalyzed reaction (benzene, 60 °C) gave the *exo* adduct (68 %) and the *endo* adduct (32%).

(17) (a) Furuta, K.; Iwanaga, K.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 4507. (b) Maruoka, K.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1992**, *114*, 1089.

(18) Malachowski, R.; Kalinski, T. *Roczniki. Chem.* **1926**, *6*, 768.

phosphorus pentachloride (31.4 g, 0.151 mol) in ten portions during 30 min when the mixture turned red. The mixture was heated at 40 °C for 40 min and then cooled in an ice-bath, carefully poured onto ice (100 g), and stirred for 30 min. The reaction vessel was rinsed with dichloromethane/water. The combined two-phase mixture was separated, and the aqueous layer was extracted with dichloromethane. The organic layer and the extract were combined, washed with brine, and evaporated to give a red oil. This red oil was used in the subsequent reaction without further purification. This oil was suspended in 20% hydrochloric acid (100 mL), and the mixture was boiled for 5 h. The mixture was cooled to room temperature and was extracted with ether. The organic layer was dried over $Na_2SO_4$ and evaporated to give an orange-brown solid. Recrystallization from benzene afforded **8** (8.77 g, 37% for two steps) as a colorless solid: mp 127.5−128.5 °C (recrystallized from benzene) (lit.,[28] mp 129 °C); IR (KBr) 3000 (m), 1720 (s), 1705 (s), 1640 (s) $cm^{-1}$; $^1H$ NMR (60 MHz, DMSO-$d_6$) $\delta$ 6.18 (s, 1H), 3.94 (s, 2H).

**[2*E*(1*R*,2*S*,5*R*)]-Bis[5-methyl-2-(1-methylethyl)cyclohexyl] 3-Chloro-2-pentenedioate ((*E*)-9) and [2*Z*(1*R*,2*S*,5*R*)]-Bis[5-methyl-2-(1-methylethyl)cyclohexyl] 3-Chloro-2-pentenedioate ((*Z*)-9).** (−)-Menthol used was determined to be optically pure from optical rotation. To a mixture of (−)-menthol (4.75 g, 30.4 mmol) and **8** (1.00 g, 6.08 mmol) in dry benzene (30 mL) was added concentrated sulfuric acid (3 drops) and the solution was boiled at reflux with a Dean-Stark separator for 12 h. After cooling, ether was added, the solution was washed with saturated aqueous $NaHCO_3$ solution and brine, and the organic layer was dried over $Na_2SO_4$. After evaporation, the residue was chromatographed on silica gel eluting with ethyl acetate/hexane (1:80) to give a mixture of (*E*)- and (*Z*)-**9** (2.48 g, 93%) as a yellow oil. Analytical samples of two isomers were prepared by flash column chromatography: **Major**: $R_f$ 0.42 (ethyl acetate/hexane, 1:10); IR (neat) 1745 (s), 1710 (s), 1635 (m) $cm^{-1}$; $^1H$ NMR (60 MHz) $\delta$ 6.23 (s, 1H), 4.96−4.51 (m, 2H), 4.08 (s, 2H), 2.23−0.96 (m, 18H), 0.96−0.62 (m, 18H); LRMS (FD) *m*/*z* (rel inten) 440 ($M^+$, base). **Minor**: $R_f$ 0.31 (ethyl acetate/hexane, 1:10); IR (neat) 1745 (s), 1710 (s), 1635 (m) $cm^{-1}$; $^1H$ NMR (60 MHz) $\delta$ 6.17 (s, 1H), 4.96−4.51 (m, 2H), 3.42 (s, 2H), 2.23−0.96 (m, 18H), 0.96−0.62 (m, 18H); LRMS (FD) *m*/*z* (rel inten) 440 ($M^+$, base).

**[3*R*(1*R*,2*S*,5*R*)]-Bis[5-methyl-2-(1-methylethyl)cyclohexyl] 2,3-Pentadienedioate (1a).** To a stirred, ice-cooled solution of **9** (4.00 g, 9.08 mmol) in dry tetrahydrofuran was added dropwise dry triethylamine (1.5 mL, 10.8 mmol). The resultant solution was stored at −5 °C until precipitates had appeared. The solid was filtered off and washed with dry ether. The combined filtrates and washings were washed with 0.2 N hydrochloric acid (×4), water (×1), and brine (×3) and dried over $Na_2SO_4$. The solution was evaporated in vacuo, the residue was chromatographed on silica gel eluting with ethyl acetate/hexane (1:50) to give a mixture of **1a** and **1b** (3.60 g, 98%) as a pale yellow oil: $R_f$ 0.33 (ethyl acetate/hexane, 1:10); IR ($CHCl_3$) 1945 (m), 1685 (s) $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta$ 6.01 (s, 1.07H), 5.99 (s, 0.93H), 4.74 (ddd, $J$ = 10.9, 10.9, 4.3 Hz, 2H), 2.03 (dm, $J$ = 11.9 Hz, 2H), 1.87, 1.84 (qd, $J$ = 6.9, 2.6 Hz, total 2H), 1.77−1.63 (m, 4H), 1.63−1.34 (m, 6H), 1.18−0.81 (m, 16H), 0.78, 0.77 (d, $J$ = 6.9 Hz, total 6H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) $\delta$ 219.52 (s), 219.17 (s), 162.96 (s), 92.68 (d), 92.61 (d), 75.72 (d), 75.64 (d), 46.99 (d), 46.92 (d), 40.72 (t), 34.19 (t), 31.43 (d), 31.36 (d), 26.48 (d), 26.41 (d), 23.71 (t), 23.67 (t), 21.95 (q), 20.63 (q), 16.59 (q), 16.52 (q).

This oil was crystallized and repeatedly recrystallized from pentane to give **1a** (0.84 g, 23%) as colorless needles: $R_f$ 0.33 (ethyl acetate/hexane, 1:10); mp 83 °C; $[\alpha]^{20}_D$ −251.1° (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 1945 (m), 1685 (s) $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta$ 5.99 (s, 2H), 4.74 (ddd, $J$ = 10.9, 10.9, 4.3 Hz, 2H), 2.03 (dm, $J$ = 11.9, 2H), 1.87, 1.84 (qd, $J$ = 6.9, 2.6 Hz, total 2H), 1.77−1.63 (m, 4H), 1.63−1.34 (m, 6H), 1.18−0.91 (m, 16H), 0.78, 0.77 (d, $J$ = 6.9 Hz, total 6H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) $\delta$ 219.56 (s), 163.07 (s), 92.66 (d), 75.68 (d), 47.01 (d), 40.74 (t), 34.21 (t), 31.39 (d), 26.47 (d), 23.70 (t), 22.01 (q), 20.66 (q), 16.60 (q); LRMS (EI, 30 eV) *m*/*z* (rel inten) 404 ($M^+$, 1), 403 (2), 390 (5), 389 (18), 267 (55), 266 (40), 251 (20), 249 (26), 248 (40), 223 (90), 222 (29), 200 (base). Anal. Calcd for $C_{25}H_{40}O_4$: C, 74.22; H, 9.97. Found: C, 74.08; H, 9.90. Further attempts at isolation and purification of **1b** from the mother liquor was failed.

**[2*E*(1*S*,2*R*,5*S*)]-Bis[5-methyl-2-(1-methylethyl)cyclohexyl] 3-Chloro-2-pentenedioate ((*E*)-10) and [2*Z*(1*S*,2*R*,5*S*)]-Bis[5-methyl-2-(1-methylethyl)cyclohexyl] 3-Chloro-2-pentenedioate ((*Z*)-10).** In a similar manner to the synthesis of **9**, **10** (34.7 g, 94%) was obtained as a yellow oil from **8** (13.9 g, 84.2 mmol) and (+)-menthol (30.6 g, 196 mmol): **Major**: $R_f$ 0.42 (ethyl acetate/hexane, 1:10); IR (neat) 1745 (s), 1710 (s), 1635 (m) $cm^{-1}$; $^1H$ NMR (60 MHz) $\delta$ 6.23 (s, 1H), 4.80−4.40 (m, 2H), 4.09 (s, 2H), 2.20−1.30 (m, 18H), 1.30−0.50 (m, 18H); LRMS (FD) *m*/*z* (rel inten) 440 ($M^+$, base). **Minor**: $R_f$ 0.31 (ethyl acetate/hexane, 1:10); IR (neat) 1745 (s), 1710 (s) $cm^{-1}$; $^1H$ NMR (60 MHz) $\delta$ 6.14 (s, 1H), 4.80−4.40 (m, 2H), 3.41 (s, 2H), 2.40−1.10 (m, 18H), 1.10−0.60 (m, 18H); LRMS (FD) *m*/*z* (rel inten) 440 ($M^+$, base).

**[3*S*(1*S*,2*R*,5*S*)]-Bis[5-methyl-2-(1-methylethyl)cyclohexyl] 2,3-Pentadienedioate (2a).** In a similar manner to the synthesis of **1a**, a mixture of **2a** and **2b** (1.03 g, 75%) was obtained as a yellow oil from a mixture of (*E*)- and (*Z*)-**10** (1.48 g, 3.36 mmol): $R_f$ 0.33 (ethyl acetate/hexane, 1:10); IR ($CHCl_3$) 1945 (m), 1685 (s) $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta$ 6.01 (s, 1H), 5.99 (s, 1H), 4.74 (ddd, $J$ = 10.9, 10.9, 4.3 Hz, 2H), 2.03 (dm, $J$ = 11.9, 2H), 1.87, 1.84 (qd, $J$ = 6.9, 2.6 Hz, total 2H), 1.77−1.63 (m, 4H), 1.63−1.34 (m, 6H), 1.18−0.91 (m, 16H), 0.78, 0.77 (d, $J$ = 6.9 Hz, total 6H). This oil was crystallized and repeatly recrystallized from pentane to give **2a** (0.212 g, 25%) as colorless needles: $R_f$ 0.33 (ethyl acetate/hexane, 1:10); mp 83 °C; $[\alpha]^{22}_D$ +262.7° (*c* 0.99, $CHCl_3$); IR ($CHCl_3$) 1945 (m), 1685 (s) $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta$ 5.99 (s, 2H), 4.74 (ddd, $J$ = 10.9, 10.9, 4.3 Hz, 2H), 2.03 (dm, $J$ = 11.9 Hz, 2H), 1.87, 1.84 (qd, $J$ = 6.9, 2.6 Hz, total 2H), 1.77−1.63 (m, 4H), 1.63−1.34 (m, 6H), 1.18−0.91 (m, 16H), 0.78, 0.77 (d, $J$ = 6.9 Hz, total 6H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) $\delta$ 219.56 (s), 163.07 (s), 92.66 (d), 75.68 (d), 47.01 (d), 40.74 (t), 34.21 (t), 31.40 (d), 26.47 (d), 23.70 (t), 22.01 (q), 20.66 (q), 16.60 (q); LRMS (EI, 30 eV) *m*/*z* (rel inten) 404 ($M^+$, 1), 403 (2), 390 (5), 389 (18), 267 (55), 266 (40), 251 (20), 249 (26), 248 (40), 223 (90), 222 (29), 200 (base). Anal. Calcd for $C_{25}H_{40}O_4$: C, 74.22; H, 9.97. Found: C, 74.14; H, 9.95. In this case, further attempts at isolation and purification of **2b** from the mother liquior was failed.

**[1*S*,2*R*(1*R*,2*S*,5*R*),3*Z*(1*R*,2*S*,5*R*),4*R*]-5-Methyl-2-(1-methylethyl)cyclohexyl 3-[2-[[5-Methyl-2-(1-methylethyl)cyclohexyl]oxy]-2-oxoethylidene]bicyclo [2.2.1]hept-5-ene-2-carboxylate (3a) and [1*R*,2*R*(1*R*,2*S*,5*R*),3*Z*(1*R*,2*S*,5*R*),4*S*]-5-Methyl-2-(1-methylethyl)cyclohexyl 3-[2-[[5-Methyl-2-(1-methylethyl)cyclohexyl]oxy]-2-oxoethylidene]-bicyclo[2.2.1]hept-5-ene-2-carboxylate (3b).** To a suspension of aluminum chloride ($AlCl_3$) (0.592 g, 4.44 mmol, 1.20 equiv) in 12 mL of dry dichloromethane at −78 °C under nitrogen was added a solution of **1a** (1.49 g, 3.69 mmol) in dry dichloromethane. After 30 min, cyclopentadiene (3 mL, excess) was added. The reaction mixture was stirred at −78 °C for 5 h, and the reaction was quenched with water. The resultant slurry was diluted with dichloromethane, and the two-phase mixture was separated. The aqueous layer was extracted with dichloromethane, and the combined organic layers were dried over $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel eluting with ethyl acetate/hexane (0:1 → 1:80) to afford the adduct **3a** (1.66 g, 96%) and **3b** (0.03 g, 2%); **3a**: $R_f$ 0.33 (ethyl acetate/hexane, 1:10); mp 97 °C (recrystallized from ether); $[\alpha]^{23}_D$ −48.2° (*c* 1.03, $CHCl_3$); IR ($CHCl_3$) 1710 (s), 1690 (s) $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta$ 6.18−6.11 (m, 2H), 5.98 (d, $J$ = 2.0 Hz, 1H), 4.62 (ddd, $J$ = 10.9, 10.9, 4.3 Hz, 1H), 4.55 (ddd, $J$ = 10.9, 10.9, 4.3 Hz, 1H), 3.87 (dd, $J$ = 3.5, 2.0 Hz, 1H), 3.41 (br s, 1H), 3.33 (br s, 1H), 2.15−1.81 (m, 4H), 1.77−1.57 (m, 5H), 1.57−1.20 (m, 6H), 1.17−0.62 (m, 23H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) $\delta$ 170.60 (s), 165.95 (s), 159.86 (s), 135.71 (d), 133.55 (d), 113.70 (d), 74.20 (d), 73.58 (d), 53.13 (d), 51.00 (d), 50.58 (t), 46.96 (d), 46.91

(19) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(d), 46.33 (d), 41.05 (t), 40.59 (t), 34,34 (t), 31.42 (d), 31.34 (d), 26.13 (d), 25.53 (d), 23.6 (t), 23.05 (t), 22.02 (q), 20.92 (q), 20.70 (q), 16.53 (q), 15.99 (q); LRMS (FAB) *m/z* (rel inten) 471 ([M + H]$^+$, 43), 333 (20), 195 (85), 177 (base). Anal. Calcd for $C_{30}H_{46}O_4$: C, 76.55; H, 9.85. Found: C, 76.45; H, 9.80. **3b** (a colorless syrup): $R_f$ 0.43 (ethyl acetate/hexane, 1:10); $[\alpha]^{23}_D$ −341.7° (*c* 1.03, $CHCl_3$); IR ($CHCl_3$) 1710 (s) cm$^{-1}$; $^1$H NMR (270 MHz) $\delta$ 6.33 (dd, $J$ = 5.3, 3.0 Hz, 1H), 6.12 (dd, $J$ = 5.3, 3.0 Hz, 1H), 5.99 (d, $J$ = 2.0 Hz, 1H), 4.69 (ddd, $J$ = 10.9, 10.9, 4.3 Hz, 1H), 4.62 (ddd, $J$ = 10.6, 10.6, 4.3 Hz, 1H), 3.43−3.36 (m, 2H), 3.18 (br s, 1H), 2.14−1.83 (m, 5H), 1.74−1.57 (m, 5H), 1.55−1.31 (m, 4H), 1.15−0.79 (m, 16H), 0.76 (d, $J$ = 6.9 Hz, 3H), 0.72 (d, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (67.8 MHz, $CDCl_3$) $\delta$ 171.34 (s), 165.81 (s), 161.28 (s), 138.95 (d), 135.58 (d), 113.80 (d), 74.27 (d), 73.66 (d), 51.63 (d), 51.31 (d), 47.73 (d), 47.07 (t), 46.95 (d), 41.08 (t), 40.66 (t), 34.35 (t), 31.42 (d), 26.28 (d), 25.69 (d), 23.70 (t), 23.04 (t), 22.04 (q), 21.98 (q), 21.04 (q), 20.67 (q), 16.57 (q), 15.98 (q); LRMS (FAB) *m/z* (rel inten) 471 ([M + H]$^+$, 29), 333 (21), 195 (90), 177 (base); HRMS (FAB) *m/z* calcd for $C_{30}H_{47}O_4$ ([M + H]$^+$) 471.3474, found 471.3484.

**[1*R*,2*S*(1*S*,2*R*,5*S*),3*Z*(1*S*,2*R*,5*S*),4*S*]-5-Methyl-2-(1-methylethyl)cyclohexyl 3-[2-[[5-Methyl-2-(1-methylethyl)cyclohexyl]oxy]-2-oxoethylidene]bicyclo[2.2.1]hept-5-ene-2-carboxylate (4a).** In a similar manner to the synthesis of **3a**, **4a** (5.53 g, 95%) was obtained from **2a** (5.00 g, 12.4 mmol), cyclopentadiene (5.7 mL), and $AlCl_3$ (1.89 g, 14.2 mmol). Purification of **4a** by recrystallization from ether to afford colorless prisms: $R_f$ 0.33 (ethyl acetate/hexane, 1:10); mp 104.5 °C (recrystallized from diethyl ether); $[\alpha]^{22}_D$ +47.1° (*c* 1.08, $CHCl_3$); IR ($CHCl_3$) 1710 (s), 1690 (s) cm$^{-1}$; $^1$H NMR (270 MHz) $\delta$ 6.18−6.11 (m, 2H), 5.98 (d, $J$ = 2.0 Hz, 1H), 4.62 (ddd, $J$ = 10.9, 10.9, 4.3 Hz, 1H), 4.55 (ddd, $J$ = 10.9, 10.9, 4.3 Hz, 1H), 3.87 (dd, $J$ = 3.5, 2.0 Hz, 1H), 3.41 (br s, 1H), 3.33 (br s, 1H), 2.11−1.28 (m, 20H), 1.10−0.70 (m, 18H); LRMS (EI, 30 eV) *m/z* (rel inten) 470 (M$^+$, 10), 455 (11), 33 (base). Anal. Calcd for $C_{30}H_{46}O_4$: C, 76.55; H, 9.85. Found: C, 76.48; H, 9.85.

**[1*R*,2*R*(1*R*,2*S*,5*R*),3*Z*(1*R*,2*S*,5*R*),4*S*]-5-Methyl-2-(1-methylethyl)cyclohexyl 3-[2-[(5-Methyl-2-(1-methylethyl)cyclohexyl)oxy]-2-oxoethylidene]bicyclo[2.2.1]heptane-2-carboxylate (11).** A mixture of **3a** (0.313 g, 0.665 mmol) and a catalytic amount of 5% Pd/C in ethyl acetate was stirred at room temperature under hydrogen atmosphere. The mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel eluting with ethyl acetate/hexane (1:10) to afford **11** (0.314 g, 100%) as a colorless syrup: $R_f$ 0.35 (ethyl acetate/hexane, 1:10); IR ($CHCl_3$) 1730 (s), 1700 (s) cm$^{-1}$;$^1$H NMR (60 MHz) $\delta$ 5.81 (d, $J$ = 2.4 Hz, 1H), 4.84−4.20 (m, 2H), 3.72 (dd, $J$ = 4.2, 2.4 Hz, 1H), 2.92−2.62 (m, 2H), 2.44−1.08 (m, 24H), 1.08−0.51 (m, 18H).

**[1*R*,2*R*(1*R*,2*S*,5*R*),4*S*]-5-Methyl-2-(1-methylethyl)cyclohexyl 3-Oxobicyclo[2.2.1]heptane-2-carboxylate (12).** Compound **11** (0.314 g, 0.665 mmol) in dichloromethane (15 mL) was treated with ozone at −78 °C until the blue color persisted. The excess ozone was removed by bubbling of dry nitrogen gas, and then dimethyl sulfide (1 mL) was added dropwise at −78 °C. The reaction mixture was then allowed to warm up to room temperature with stirring and was evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with ethyl acetate/hexane (1:25) to afford the ketone **12** (0.195 g, 100%) as a colorless syrup: $R_f$ 0.23 (ethyl acetate/hexane, 1:10); IR ($CHCl_3$) 1760 (s), 1720 (s) cm$^{-1}$; $^1$H NMR (60 MHz) $\delta$ 5.08−4.40 (m, 2H), 3.05−2.86 (m, 1H), 2.61 (m, 1H), 2.28−1.06 (m, 15H), 1.06−0.56 (m, 9H).

**(1*S*,4*R*)-Bicyclo[2.2.1]heptan-2-one [(1*S*,4*R*)-Norcamphor] (13) and (1*S*,4*R*)-Bicyclo[2.2.1]heptan-2-one 2,4-Dinitrophenylhydrazone [(+)-Norcamphor 2,4-Dinitrophenylhydrazone] (14).** A suspension of **12** (0.195 g, 0.665 mmol) in concd hydrochloric acid (5.6 mL) was refluxed for 5 h. After cooling to room temperature, the reaction mixture was diluted with water. The resulting mixture was extracted with diethyl ether. The organic layer was washed with 5% aqueous NaOH solution, water, and brine and dried over $Na_2SO_4$. The solvent was removed under reduced pressure, and the residue was used for the subsequent reaction without further purification. A solution of the crude **13** ($R_f$ 0.23 (ethyl acetate/hexane, 1:10)), 2,4-dinitrophenylhydrazine (0.132 g, 0.665 mmol), and concd hydrochloric acid (0.7 mL) in dry methanol was heated at 40 °C for 3 h. After cooling, the solvent was concentrated under reduced pressure, and the residue was diluted with diethyl ether. After addition of water, the resulting mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated *in vacuo*. After flash column chromatography on silica gel eluting with ethyl acetate/hexane (1:20), recrystallization of the crude hydrazone **14** from methanol gave **14** (46.8 mg, 52% for two steps) as yellow crystals: $R_f$ 0.48 (ethyl acetate/hexane, 1:1); mp 132 °C (recrystallized from methanol); $[\alpha]^{25}_D$ +32.7° (*c* 0.46, $CHCl_3$); IR ($CHCl_3$) 1615 (s) cm$^{-1}$; $^1$H NMR (60 MHz) $\delta$ 10.73 (br s, 1H), 9.11 (d, $J$ = 2.4 Hz, 1H), 8.29 (dd, $J$ = 9.6, 2.4 Hz, 1H), 7.89 (d, $J$ = 9.6 Hz, 1H), 3.16−2.92 (m, 1H), 2.92−2.50 (m, 2H), 1.82−0.82 (m, 7H).

**[1*S*,2*S*(1*S*,2*R*,5*S*),3*Z*(1*S*,2*R*,5*S*),4*R*]-5-Methyl-2-(1-methylethyl)cyclohexyl 3-[2-[(5-Methyl-2-(1-methylethyl)cyclohexyl)oxy]-2-oxoethylidene]bicyclo[2.2.1]heptane-2-carboxylate (15).** A similar manner to the synthesis of **11**, **15** (0.297 g, 98%) was obtained as colorless crystals from **4a** (0.301 g, 0.641 mmol): $R_f$ 0.35 (ethyl acetate/hexane, 1:10); mp 142.5−143 °C (recrystallized from diethyl ether); IR ($CHCl_3$) 1730 (s), 1700 (s) cm$^{-1}$;$^1$H NMR (270 MHz) $\delta$ 5.81 (d, $J$ = 2.6 Hz, 1H), 4.63 (ddd, $J$ = 10.7, 10.7, 4.6 Hz, 1H), 4.61 (ddd, $J$ = 10.8, 10.8, 4.3 Hz, 1H), 3.76−3.69 (m, 1H), 2.84 (d, $J$ = 4.3 Hz, 1H), 2.72 (br s, 1H), 2.25−2.08 (m, 1H), 2.08−1.84 (m, 3H), 1.84−1.29 (m, 14H), 1.14−0.63 (m, 6H), 0.91, 0.88 (each d, $J$ = 6.9 Hz, 12H), 0.78 (d, $J$ = 6.9 Hz, 3H), 0.74 (d, $J$ = 6.9 Hz, 3H); LRMS (FAB) *m/z* (rel inten) 473 (M$^+$, 85), 179 (base). Anal. Calcd for $C_{30}H_{48}O_4$: C, 76.23; H, 10.24. Found: C, 76.34; H, 10.25.

**[1*S*,2*S*(1*S*,2*R*,5*S*),4*R*]-5-Methyl-2-(1-methylethyl)cyclohexyl 3-Oxobicyclo[2.2.1]heptane-2-carboxylate (16).** A similar manner to the synthesis of **12**, **16** (0.209 g, 98%) was obtained as a colorless syrup from **15** (0.346 g, 0.773 mmol): $R_f$ 0.23 (ethyl acetate/hexane, 1:10); IR ($CHCl_3$) 1755 (s), 1720 (s) cm$^{-1}$; $^1$H NMR (270 MHz) $\delta$ 4.72 (ddd, $J$ = 10.9, 10.9, 4.6 Hz, 0.21H), 4.70 (ddd, $J$ = 10.9, 10.9, 4.6, 0.79H), 3.03 (br d, $J$ = 3.7 Hz, 0.21 H), 2.93−2.99 (m, 0.21H), 2.89 (t, $J$ = 1.7 Hz, 0.79H), 2.82 (d, $J$ = 3.3 Hz, 0.79H), 2.70 (br d, $J$ = 4.6 Hz, 0.21H), 2.65 (br d, $J$ = 3.3 Hz, 0.79H), 2.21 (dm, $J$ = 10.8 Hz, 0.79H), 2.06−1.33 (m, 10.21H), 1.16−0.64 (m, 4H), 0.90, 0.89 (each d, $J$ = 6.9 Hz, 6H), 0.75 (d, $J$ = 6.9 Hz, 3H); LRMS (FAB) *m/z* (rel inten) 293 ([M + H]$^+$, 51), 155 (base); HRMS (FAB) *m/z* calcd for $C_{18}H_{29}O_3$ ([M + H]$^+$) 293.2118, found 293.2112.

**(1*R*,4*S*)-Bicyclo[2.2.1]heptan-2-one [(1*R*,4*S*)-Norcamphor] (17) and (1*R*,4*S*)-Bicyclo[2.2.1]heptan-2-one 2,4-Dinitrophenylhydrazone [(−)-Norcamphor 2,4-Dinitrophenylhydrazone] (18).** In a similar manner to the synthesis of **14**, **18** (76.1 mg, 39% for two steps) was obtained as colorless crystals from **16** (0.195 g, 0.668 mmol) $R_f$ 0.48 (ethyl acetate/hexane, 1:1); mp 131 °C (recrystallized from methanol); $[\alpha]^{23}_D$ −28.0° (*c* 1.03, $CHCl_3$); IR ($CHCl_3$) 1615 (s) cm$^{-1}$; $^1$H NMR (270 MHz) $\delta$ 10.73 (br s, 1H), 9.12 (d, $J$ = 2.6 Hz, 1H), 8.28 (ddd, $J$ = 9.6, 2.6, 0.7 Hz, 1H), 7.91 (d, $J$ = 9.6 Hz, 1H), 3.03 (d, $J$ = 3.3 Hz, 1H), 2.74 (br s, 1H), 2.37 (ddd, $J$ = 16.7, 4.4, 2.3 Hz, 1H), 2.12 (dd, $J$ = 16.7, 3.3 Hz, 1H), 1.97−1.74 (m, 2H), 1.69−1.49 (m, 3H), 1.46−1.33 (m, 1H); LRMS (EI, 30eV) *m/z* (rel inten) 290 (M$^+$, 86), 67 (base).

**Supporting Information Available:** $^1$H NMR spectra of compounds (8 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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