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Catalyzed Diels−Alder Reaction of Alkylidene- or Arylideneacetoacetates and Danishefsky's Dienes with Lanthanide Salts Aimed at Selective Synthesis of *cis*-4,5-Dimethyl-2-cyclohexenone Derivatives[†]

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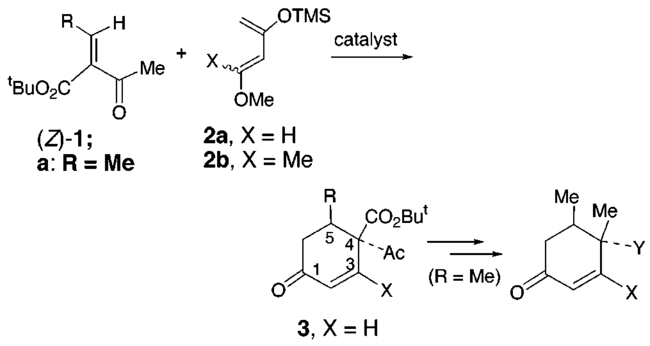
The first successful example of the catalyzed Diels−Alder reaction of 1-methoxy-3-trimethylsiloxy-1,3-diene (Danishefsky's diene, **2a**), giving the corresponding carbocyclic adducts, is described. The reaction of (*Z*)-ethylideneacetoacetate **1a** with **2a** is catalyzed with lanthanide salts such as Yb(OTf)$_3$ at 0 °C, affording the corresponding 2-cyclohexenone **3a** in good yield with complete integrity of the starting geometry of **1a**. The thermal version of the same cycloaddition results in a decrease in the cis arrangement of the 5-methyl and the 4-alkoxycarbonyl groups on 2-cyclohexenone. The catalyzed reaction of (*E*)-**1a** unexpectedly affords the cis-arranged **3a**. The reaction path for the catalyzed Diels−Alder reaction is postulated on the basis of these results.

Introduction

The Diels−Alder reaction, usually performed by heating, is one of the pivotal strategies for the syntheses of the cyclohexane structure with many possibilities for control of stereochemistry and introduction of functional groups.[1] Furthermore, the Diels−Alder reactions with acid catalysts expand their scope by allowing reactions with heat sensitive compounds and applications in chiral syntheses.[1,2] Recently, lanthanide compounds have been employed as catalysts for various transformations including Diels−Alder reactions and others.[3]

In a program aimed at the stereoselective introduction of cis-arranged vicinal dimethyl groups onto cyclohexane rings,[4] we have studied Lewis acid-catalyzed Diels−Alder reactions of ethylideneacetoacetates **1a** and the siloxy dienes such as 1-methoxy-3-trimethylsiloxy-1,3-diene[5,6] (Danishefsky's diene, **2a**); these diene and dienophiles are highly reactive but are acid or heat sensitive.

Scheme 1



Although catalyzed hetero-Diels−Alder reactions using this diene **2a** have been intensively studied,[7] few are successful for "normal" Diels−Alder reactions of **2a** under catalyzed conditions with a Lewis acid, giving the carbocyclic adducts. This may be due to the instability of **2a** to conventionally used Lewis acids such as ZnCl$_2$ and AlCl$_3$.[5b] We now report the lanthanide-catalyzed Diels−Alder reaction of alkylideneacetoacetates **1** and **2a** achieved with high stereoselectivity (Scheme 1).

Results and Discussion

Alkylideneacetoacetates **1**, easily accessible from aldehydes and acetoacetates by Knoevenagel's condensation,[8−10] are amenable to *Z*/*E* isomerization by heating.

[†] Dedicated to the memory of Wolfgang Oppolzer.

(1) (a) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Tetrahedron Organic Chemistry Series; Pergamon: Oxford, 1990; Vol. 8. (b) Oppolzer, W. *Comprehensive Organic Synthesis*; Pergamon: New York, 1991; Vol. 5, pp 315−399. (b) Dell, C. P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3873−3905.

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(4) Cis-arranged dimethyl cyclohexanes assembled in a bicyclo[3.3.1] nonane system: (a) Hashimoto, T.; Koyama, H.; Tori, M.; Takaoka, S.; Asakawa, Y. *Phytochemistry* **1995**, *40*, 171−176. (b) Butler, M. S.; Capon, R. J. *Aust. J. Chem.* **1993**, *46*, 1363−1374. (c) Schulte, G.; Scheuer, P. J.; McConnell, O. J. *J. Org. Chem.* **1980**, *45*, 552−554. In a bicyclo[9.3.1]pentadecane system: (d) Foote, K. M.; John, M.; Pattenden, G. *Synlett* **2001**, 365−368.

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10.1021/jo010575u CCC: $20.00

Scheme 2

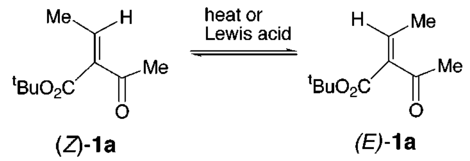
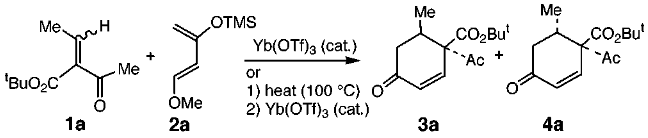


Table 1. The Diels–Alder Reactions of 1a with 2a under Thermal and Catalyzed Conditions



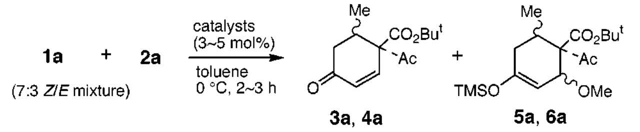
entry	conditions[a]	substrate **1a**[b]	yield, %[c]	**3a**/**4a**[d]
1	A	(*Z*)	87	4.1/1
2	B	(*Z*)	87	44/1
3	A	(*E*)	94	1/5.3
4	B	(*E*)	92	9.5/1

[a] Conditions for the Diels–Alder reaction. A: (1) **1a** and **2a** (1.5–2.0 equiv) were heated at 100 °C for 24–40 h in toluene, (2) treated with $\mathrm{Yb(OTf)_3}$ (3–5 mol%) at 0 °C for 2–7 h. B: **1a** and **2a** (1.5–2.0 equiv) were stirred with $\mathrm{Yb(OTf)_3}$ (3–5 mol%) at 0 °C for 12–20 h in toluene. [b] Purity of the substrates: (*E*)-**1a**, 93%; (*Z*)-**1a**, 99%. [e] Yields are based on isolated products. [d] Ratios of **3a**/**4a** were determined by GC (MS, 100 °C).

For example, the pure (*Z*)-**1a** underwent isomerization to give an ca. 1:1 mixture of (*Z*)- and (*E*)-**1a** by heating at 100 °C in toluene for about 12 h. Furthermore, *Z*/*E* isomerization of **1a** proceeded by treatment with $\mathrm{Yb(OTf)_3}$ (10 mol %) and MeOTMS (20 mol %) in toluene, where the diene **2a** (ca. 3 mol %) was presented to ensure dissolution of $\mathrm{Yb(OTf)_3}$ by making a complex with these substrates; otherwise, no geometric isomerization of **1a** has occurred (Scheme 2).

The Diels–Alder reaction of (*Z*)-**1a** with the diene **2a** under thermal conditions needed heating at 100 °C for 24–40 h, with inevitable competitive formation of the Diels–Alder adducts from (*E*)-**1a**. Indeed, as shown in Table 1, the reaction of (*Z*)-**1a** and the diene **2a** at 100 °C for 40 h and the subsequent treatment of the adducts with $\mathrm{Yb(OTf)_3}$ for elimination of TMSOMe[11] afforded the desired enones **3a** and **4a** in 87% as a 4.1:1 mixture, inseparable by usual chromatography on silica gel (entry 1). Similarly, the Diels–Alder reaction of (*E*)-**1a** with **2a** at 100 °C and the subsequent treatment with $\mathrm{Yb(OTf)_3}$ afforded a 1:5.3 mixture of **3a** and **4a** in 87% yields (entry 3). These results indicate that the thermal Diels–Alder reactions of **1a** and **2a** are stereospecific, though selectivity is moderate presumably due to *Z*/*E* isomerization of the dienophile **1a**.

Table 2. Survey of Lanthanide Catalysts for Diels–Alder Reaction of 1a and 2a



entry[a]	lanthanide catalysts	product ratio[b] **3a** + **4a**	**5a** + **6a**	recovery, **1a**	ratio **3a**/**4a**
1	$\mathrm{Sc(OTf)_3}$	42.3	9.7	46.3	27/1
2	$\mathrm{Y(OTf)_3}$	81	3.8	12.6	15/1
3	$\mathrm{Y(OCOCF_3)_3}$	1.1	29.9	69	
4	$\mathrm{Nd(OTf)_3}$	5.9	36.5	54.8	9/1
5	$\mathrm{Sm(OTf)_3}$		59.4	38.6	
6	$\mathrm{Eu(OTf)_3}$	36.8	46	15	21/1
7[c]	$\mathrm{Eu(fod)_3}$		91.7	8.3	
8	$\mathrm{Gd(OTf)_3}$	35	46	15	17/1
9	$\mathrm{Ho(OTf)_3}$	88	4	5	12/1
10	$\mathrm{Yb(OTf)_3}$	86	11	2.8	24/1

[a] The reactions were carried out using **1a** (ca. 7/3 mixture of (*Z*)- and (*E*)-**1a**, 1–2 mmol), **2a** (2 equiv), and Lewis acid catalysts (3–5 mol%) in toluene (5 mL) at 0 °C for 2–3 h. After the reactions, the crude products were conventionally worked up. [b] Analyzed by GC (MS, 100 °C). Conditions are same as those noted in Experimental Section. [c] Carried out at room temperature for 44 h. The ratio of **3a**/**4a** was determined as 4:1 after $\mathrm{Yb(OTf)_3}$ treatment of the reaction mixture. $\mathrm{Eu(fod)_3}$: europium tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate).

Alternatively, we examined the catalyzed procedure to perform the reaction at a lower temperature (Table 1). To our delight, the cycloaddition of (*Z*)-**1a** and **2a** and the subsequent elimination of TMSOMe from the adducts were cleanly effected in a one-pot sequence by the reaction at 0 °C in the presence of a catalytic amount of $\mathrm{Yb(OTf)_3}$, affording a 44:1 mixture of **3a** and **4a** in 86% yield (entry 2). Unexpectedly, a similar reaction of (*E*)-**1a** and **2a** with $\mathrm{Yb(OTf)_3}$ formed **3a** as a major product (entry 4). This result means that the compound (*E*)-**1a** has isomerized to (*Z*)-**1a** under the catalyzed conditions with $\mathrm{Yb(OTf)_3}$, and the *Z*-isomer thus formed reacted more quickly with **2a** than did the *E*-isomer to give the corresponding enone **3a**, preferentially.

To search for efficient catalysts, we applied different lanthanide compounds to the Diels–Alder reaction of **1a**, a 7:3 *Z*/*E* mixture being used, and **2a**. As shown in Table 2, entries 2, 9, and 10, efficient conversions are achieved by using $\mathrm{Y(OTf)_3}$, $\mathrm{Ho(OTf)_3}$, and $\mathrm{Yb(OTf)_3}$. Interestingly, the catalyzed reaction of **1a** is convergent in forming **3a** in every run starting from a 7:3 mixture of (*Z*)-**1a** and (*E*)-**1a**; the highest selectivity of **3a** over **4a** is achieved in the run with $\mathrm{Yb(OTf)_3}$ (entry 10). This means that the separation of *Z* and *E* isomers **1a** prior to the reaction is not necessary for the preparation of the desired **3a**. The use of $\mathrm{Sc(OTf)_3}$ might have caused the decomposition of the diene **2a** at the early stage of the reaction, since the reaction gave mainly the enone **3a** along with the recovery of the starting **1a** (entry 1). The reactions with weaker Lewis acids such as $\mathrm{Y(OCOCF_3)_3}$ and $\mathrm{Eu(fod)_3}$ terminated at the stage forming the enol silyl ethers **5a** and **6a**, but these compounds are easily convertible into the enones **3a** and **4a** by treatment with $\mathrm{Yb(OTf)_3}$.[11]

Lewis acids other than lanthanide compounds such as $\mathrm{Zn(OTf)_2}$, $\mathrm{Cu(OTf)_2}$, $\mathrm{Sn(OTf)_2}$, and $\mathrm{ZnCl_2}$ have also been examined in the cycloaddition of **1a** (a 7:3 *Z*/*E* mixture) and **2a**. Although the desired cycloaddition, giving a mixture of **3a** and **4a**, was induced at 0–14 °C for 17 h by using these acid catalysts (10 mol %), the reaction terminated at the stage when 7–21% of the starting **1a** had been consumed, and the combined yields of **3a** and

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(9) *E* and *Z* geometry of the alkylideneacetoacetates **1** were assigned on the basis of line separations due to coupling of the ^{13}C NMR between the ester C=O carbon and the vinylic ^{1}H nucleus. The major components of the alkylideneacetoacetates showed a large line separation of 11.7–12.3 Hz for the ester carbonyl carbons, and their geometry was assigned to be *Z* (relationship between R and ester groups). The minor component showed reverse results with line separation of 7.4–8.3 Hz and was assigned to *E* geometry.

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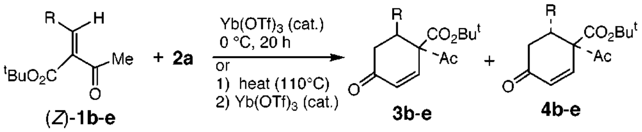
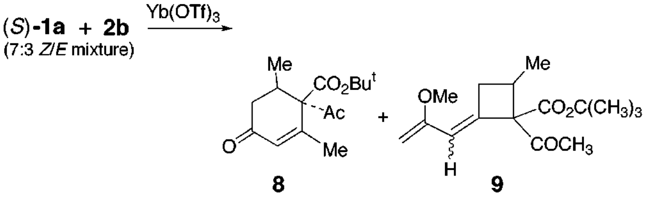
Table 3. Diels−Alder Reactions of (*Z*)-1b−e and 2a under Catalyzed (0 °C to Room Temperature) or Thermal Conditions (100−110 °C)



(*Z*)-**1**		catalyzed with Yb(OTf)_3 [a,b]			thermal[b,c]	
	R	mol%/ temperature	**3**, %	ratio **3**/**4**	**3**, %	ratio **3**/**4**
b	Ph	20/0 °C	86	36 (A)	76	6.5
c	2-furyl	3.2/0 °C	86	24 (B)	84	7.3
d	$(\text{CH}_3)_2\text{CH}$	10/0 °C	78	55 (A)	63[d]	23
e	$(\text{CH}_3)_2\text{C}{=}\text{CH}$	15/room temp	80	23 (B)	97	11

[a] Carried out by using (*Z*)-**1b**−**e** (1.0 mmol), **2a** (2.0 mmol), Yb(OTf)_3 (3.2−20 mol %) at 0 °C to room temperature in toluene (18 mL) for 20−44 h. [b] Yields are based on isolated products, and ratios of **3**/**4** were determined by GC (A) or based on isolated products (B). [c] Carried out by using (*Z*)-**1b**−**e** (1.0 mmol) and **2a** (1.5 mmol) in toluene (9 mL) at 110 °C for 40 h, and the adducts were treated with YB(OTf)_3 (3−4 mol %) at 0 °C for 7 h. [d] Carried out at 100 °C.

Scheme 3



4a were 5−16% (based on GC analyses) with a **3a**/**4a** ratio of ca. 2−3:1 which was lower than that with lanthanide catalysts. Incompleteness of the reactions using these Lewis acids might be ascribable to the decomposition of the diene **2a** in the early stage of the reactions.[5b]

As shown in Table 3, the catalyzed Diels−Alder reactions of other arylidene- and alkylideneacetoacetates **1b**−**e** with **2a**, giving the corresponding 2-cyclohexenones **3b**−**e**, are performed by using Yb(OTf)_3 as a catalyst; the results are compared with the thermal ones. It turned out that the catalyzed method using Yb(OTf)_3 is generally favorable in producing **3b**−**e** in a **3b**−**e**/**4b**−**e** ratio of 23−55:1. This value is much better than the ratio of 6.5−23:1 obtained under the thermal conditions. These high selectivities are useful for the purification of the products whose chromatographic purification is difficult. For examples, the enones **3b** and **3c** can be easily purified by simple recrystallization of the crude products.

A similar reaction of (*S*)-**1a** (7:3 *Z*/*E* mixture) and the methylated diene **2b** with Yb(OTf)_3 (10 mol %) produced the corresponding enone **8** in 28% yield, which was accompanied by formation of the cyclobutane derivative **9** and 1,4-adducts (Scheme 3).

We postulated the reaction path for the Lewis acid-catalyzed reaction of (*Z*)-**1** and **2a** as shown in Figure 1, in which the chelated structures **A** and **B** were involved.[12] The complex **A** bearing an R group anti to the acetyl group is considered to be more favorable than its stereoisomer **B**, because the R group in **A** can allow a resonance structure **C** by hyperconjugative (R = alkyl) or conjugative (R = aryl) interaction. Contribution of this kind of resonance to the structure can be inferred from the IR spectra pattern of the enones **1**; (*Z*)-**1**'s show three absorptions in the double bond region due to the hyperconjugated or conjugated structure, while (*E*)-**1**'s show two absorptions, which implies no such conjugation.[10b] It is conceived that addition of the diene **2a** to the dienophiles in an endo mode with respect to the acetyl group is favorable and that the methoxy oxygen of **2a** might coordinate to the metallic center owing to the high coordination ability of lanthanide compounds,[13] thus forming the chelated structure **E**, route a.[14] Indeed, the catalyzed reaction of (*Z*)-**1b** with the diene **2a** by use of a weak Lewis acid such as Eu(fod)_3 produced the adduct **5b**, selectively. The structure of **5b** was confirmed by its conversion to the methoxy ketone **7b** on treatment with Florisil or triethylamine in methanol and the subsequent X-ray crystallographic analysis of **7b** (Scheme 4).

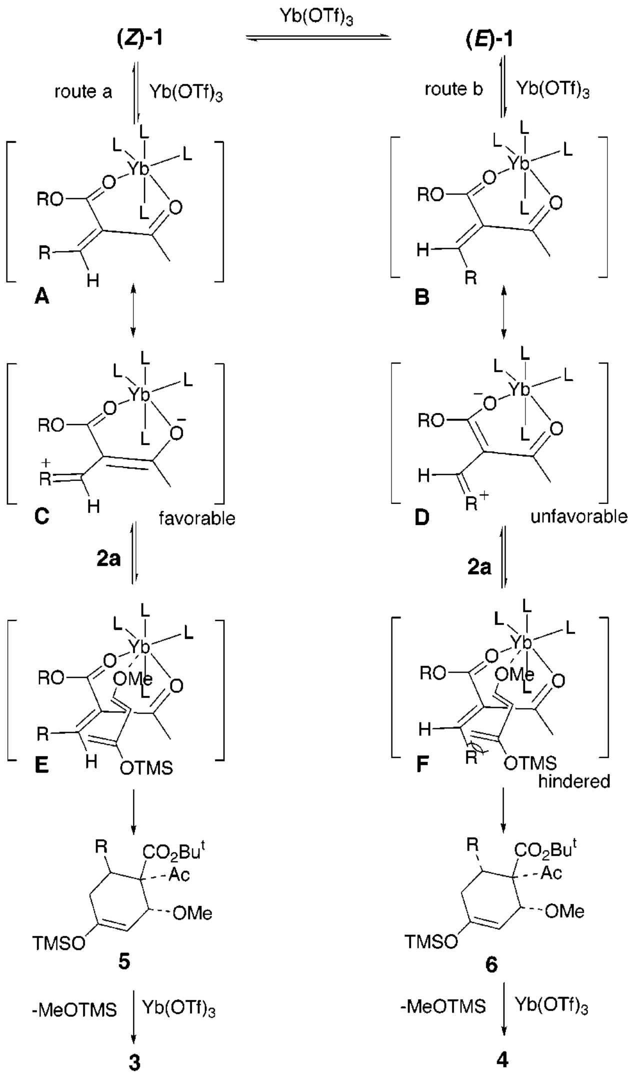


Figure 1. Probable transition states leading to either **3** or **4**.

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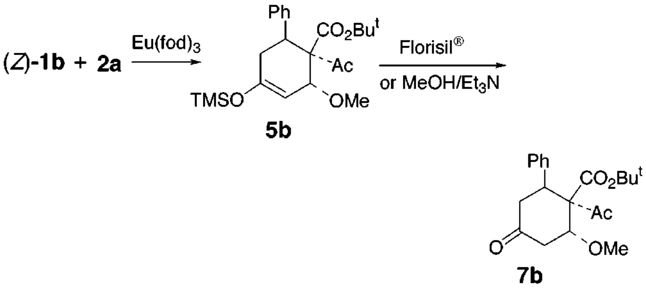
[12] Six-membered chelated structure with Ti in a similar system, see: Schultz, A. G.; Lee, H. *Tetrahedron Lett.* **1992**, *33*, 4397−4400.

[13] Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2466−2488.

[14] Diels−Alder reactions catalyzed with highly coordinated lanthanide compounds: (a) Kobayashi, S.; Araki, M.; Hachiya, I. *J. Org. Chem.* **1994**, *59*, 3758−3759. (b) Markó, I. E.; Evans, G. R.; Declercq, J.-P. *Tetrahedron* **1994**, *50*, 4557−4574. (c) Kobayashi, S.; Ishitani, H.; Hachiya, I.; Araki, M. *Tetrahedron* **1994**, *50*, 11623−11636. (d) Nishida, A.; Yamanaka, M.; Nakagawa, M. *Tetrahedron Lett.* **1999**, *40*, 1555−1558.

Scheme 4



On the other hand, the similar reaction of the *E* isomers **1** with **2a** did not proceed as expected, and *E* isomers such as **1a** and **1b**, for example, produced cis-arranged enones **3a** (92% yield with the **3a**/**4a** ratio of 9.5:1, see Table 1, entry 4) and **3b** (22% conversion with the **3a**/**4a** ratio of 99:1), respectively. The formation of cis isomers **3a** and **3b** from (*E*)-**1a** and (*E*)-**1b** rather than the expected trans isomers **4a** and **4b** may be ascribed to the *E*/*Z* isomerization of the dienophiles **1a** and **1b** with Lewis acid and the subsequent cycloaddition of (*Z*)-isomers **1a** and **1b** with **2a** through the chelated structure **A**. The highly selective formation of **3a** and **3b** over the trans isomers **4a** and **4b** should be ascribed to the difference in reaction rates between the chelated structures **E** and **F**. Slow reaction of the chelated structure **F** can be rationalized by invoking the steric repulsion of the alkyl or the aryl substituent of the dienophiles (*E*)-**1** against the diene **2a** (route b).

In conclusion, the Diels–Alder reaction of alkylideneacetoacetates **1** and Danishefsky's diene **2a** can be catalyzed with lanthanide triflates such as Yb(OTf)$_3$. The corresponding 2-cyclohexenones **3** bearing cis arrangement of 5-alkyl or -aryl and 4-alkoxycarbonyl groups are produced in a highly product selective way, even starting from a mixture of (*E*)- and (*Z*)-**1**. A mechanistic pathway involving coordination of the methoxy oxygen of **2a** and high endo-selectivity, with respect to the acetyl group, is proposed.

Experimental Section

General Procedure for Preparation of Alkylideneacetoacetates. To a cooled (0 °C) mixture of acetaldehyde (44 g, 1.0 mol) and *tert*-butyl acetoacetate (23.6 g, 149 mmol) was added a mixture of piperidine (0.3 mL) and EtOH (0.25 mL). The mixture was stirred at 0 °C for 12 h, and the reaction was quenched with cold aqueous 20% tartaric acid. The products were extracted with AcOEt, and the extracts were washed with brine, dried (MgSO$_4$), and concentrated. The crude product was distilled, and a fraction of the boiling range 90–94 °C/8 Torr was collected to give 22.3 g (81%) of a 46:54 mixture of (*E*)-**1a** (5.99 min) and (*Z*)-**1a** (7.03 min), analyzed by GC (MS, 100 °C). Pure *Z* and *E* isomers were obtained by separation by column chromatography (SiO$_2$, hexane–AcOEt 10:1).

***tert*-Butyl Ethylideneacetoacetate. (*E*)-1a.** (R_f 0.52, hexane–AcOEt 5:1). IR (neat): 1720, 1700, 1643 cm^{-1}. ^{1}H NMR (200 MHz): δ 1.48 (s, 9H), 1.85 (d, J = 7.3 Hz, 3H), 2.33 (s, 3H), 6.89 (q, J = 7.3, 1H). ^{13}C NMR (50 MHz): δ 15.1, 28.0 (3C), 30.9, 81.8, 138.1, 142.7, 163.6, 201.4.

(Z)-1a. (R_f 0.32). IR (neat): 1727, 1699, 1673, 1641 cm^{-1}. ^{1}H NMR (200 MHz): δ 1.51 (s, 9H), 1.92 (d, J = 7.3 Hz, 3H), 2.57 (s, 3H), 6.82 (q, J = 7.3, 1H). ^{13}C NMR (50 MHz): δ 15.4, 26.9, 28.1 (3C), 82.2, 139.3, 142.0, 165.8, 195.1.

General Procedure for Yb(OTf)$_3$-Catalyzed Diels–Alder Reaction. To a cooled (0 °C) mixture of (*Z*)-**1a** (184 mg, 1.0 mmol) and **2a** (351 mg, 2 mmol) in toluene (18 mL) was added Yb(OTf)$_3$ (62 mg, 0.1 mmol). The mixture was stirred at the same temperature for 12 h, during which insoluble materials precipitated in the flask as stirring was continued. The reaction was quenched with cold aqueous NaCl, and the products were extracted with AcOEt. The usual workup and the subsequent purification of the crude products by column chromatography (SiO$_2$, hexane–AcOEt 7:1) gave 219 mg of pure cis-isomer **3a** (R_f 0.23, hexane–AcOEt 5:1). GC analysis (MS, 150 °C) of the crude product showed the ratio of cis-isomer **3a** (9.88 min) to trans-isomer **4a** (8.68 min) was 44:1.

1,6-*cis*-1-Acetyl-6-methyl-4-oxocyclohex-2-enecarboxylic Acid *tert*-Butyl Ester (3a). bp 145–150 °C/0.005 Torr (bath temperature). IR (neat): 1716 (C=O), 1685 (C=O), 1619 (C=C), 1371, 1222, 1147, 1076, 840, 767 cm^{-1}. ^{1}H NMR (500 MHz): δ 1.00 (d, J = 7.3 Hz, 3H), 1.49 (s, 9H), 2.21 (s, 3H), 2.27 (d,d,d, J = 17.1, 4.0, 0.9 Hz, 1H), 2.82 (d,d, J = 17.1, 4.9 Hz, 1H), 3.12 (m, 1H), 6.11 (d,d, J = 10.4, 0.9 Hz, 1H), 7.11 (d,d J = 10.4, 1.8 Hz, 1H). ^{13}C NMR (50 MHz): δ 16.1, 27.3, 27.6 (3C), 32.9, 42.2, 66.5, 83.4, 130.4, 142.4, 167.6, 197.5, 198.5. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 65.89; H, 7.89.

Similar reaction of (*E*)-**1a** (30 mg, 0.163 mmol), **2a** (60 mg, 0.34 mmol), and Yb(OTf)$_3$ (5 mg, 0.008 mmol) in toluene (5 mL) at 0 °C for 12 h afforded 38 mg (92%) of a 9.5:1 mixture of **3a** and **4a**, determined by GC (MS, 100 °C).

General Procedure for Diels–Alder Reaction under Thermal Conditions and the Subsequent Treatment with Yb(OTf)$_3$. A mixture of (*Z*)-**1a** (184 mg, 1.0 mmol) and **2a** (258 mg, 1.5 mmol) in toluene (9 mL) was heated at 100 °C for 40 h. To the mixture, after being cooled to 0 °C, was added Yb(OTf)$_3$ (20 mg, 0.03 mmol), and the resulting mixture was stirred at the same temperature for 7 h. The reaction was quenched with cold aqueous NaCl, and products were extracted with AcOEt. Workup of the extracts in the usual manner followed by column chromatography (SiO$_2$, hexane–AcOEt, 7:1) of the crude products gave 220 mg (87%) of an inseparable 4.1:1 mixture of **3a** and **4a**, determined by GC analysis (MS, 150 °C).

Similarly, a mixture of (*E*)-**1a** (93% pure, 17 mg, 0.09 mmol) and **2a** (33 mg, 0.19 mmol) in toluene (5 mL) was heated at 100 °C for 24 h, and then the adducts were treated with Yb(OTf)$_3$ (5 mg, 0.008 mmol) in toluene (5 mL) at 0 °C for 12 h. The usual workup followed by the column chromatography as above gave 22 mg (94%) of a 1:5.3 mixture of **3a** (22.7 min) and **4a** (22.5 min), determined by GC analysis (MS, 100 °C). **4a** (contaminated with 11% of cis-isomer **3a**). IR (neat): 1714 (C=O), 1685 (C=O), 1371, 1251, 1149, 1072, 838 cm^{-1}. ^{1}H NMR (300 MHz): δ 0.91 (d, J = 7.1 Hz, 3H), 1.45 (s, 9H), 2.21 (s, 3H), 2.31 (d,d, J = 16.9, 4.1 Hz, 1H), 2.96 (d,d, J = 16.9, 4.9 Hz, 1H), 3.12 (m, 1H), 6.08 (d, J = 10.3 Hz, 1H), 7.02 (d,d, J = 10.4, 1.8 Hz, 1H). ^{13}C NMR (75.5 MHz): δ 15.9, 26.1, 27.7 (3C), 33.6, 42.3, 65.5, 83.6, 129.2, 143.8, 167.4, 197.7, 201.5.

A similar reaction of **1a** (a 7:3 *Z*/*E* mixture, 92 mg, 0.5 mmol) and the diene **2b** (186 mg, 1.0 mmol) with Yb(OTf)$_3$ (31 mg) in toluene (9 mL) was stirred at 0 °C for 5 h and at room temperature overnight. Usual workup and the subsequent chromatography (SiO$_2$, hexane–AcOEt 5:1 and then 3:1) gave 67 mg of oil, which was composed of **8** (28% yield based on GC analysis at 150 °C), **9** (5%), and the 1,4-adducts (7%). Analytical samples were obtained by repeated chromatography (SiO$_2$).

1,6-*cis*-1-Acetyl-2,6-dimethyl-4-oxocyclohex-2-enecarboxylic Acid *tert*-Butyl Ester (8). bp 150–155 °C/0.005 Torr (bath temperature). IR (neat): 1712, 1670, 1623, 1369, 1249, 1149, 838 cm^{-1}. ^{1}H NMR (300 MHz): δ 1.14 (d, J = 6.9 Hz, 3H), 1.48 (s, 9H), 2.01 (s, 3H), 2.31 (s, 3H), 2.42 (brs, 1H), 2.45 (m, 1H), 2.71–2.83 (m, 1H), 6.00 (m, 1H). ^{13}C NMR (75.5 MHz): δ 17.1, 22.5, 27.9 (3C), 29.6, 36.6, 41.9, 69.7, 83.3, 129.8, 156.8, 167.1, 197.7, 204.3.

9. IR (neat): 1712, 1670, 1369, 1249, 1149, 838 cm^{-1}. ^{1}H NMR (300 MHz): δ 1.08 (d, J = 6.9 Hz, 3H), 1.46 (s, 9H), 1.99 (d,d, J = 17.3, 5.8 Hz, 1H), 2.21 (s, 3H), 2.47 (d,d, J = 17.3, 5.5 Hz, 1H), 2.47 (m, 1H), 3.57 (s, 3H), 4.94 (s, 1H), 5.10 (s, 1H), 5.34 (s, 1H). ^{13}C NMR (75.5 MHz): δ 17.1, 27.2, 27.9 (3C), 32.5, 33.7, 54.5, 69.1, 81.9, 98.8, 112.3, 139.7, 157.3, 168.6, 205.1.

Preparation of 1,2-*trans*-1,2-*cis*-1-Acetyl-6-phenyl-4-oxo-2-methoxycyclohexanecarboxylic Acid *tert*-Butyl Ester (7b). To a mixture of (*Z*)-**1b** (122 mg, 0.5 mmol) and the diene **2a** (198 mg, 1.15 mmol) in toluene (9 mL) was added at 0 °C Eu(fod)$_3$ (52 mg, 0.05 mmol). After being stirred at the same temperature for 20 h, the mixture was passed through a short silica gel column with AcOEt and then concentrated. To the crude oil were added hexane (200 mL), AcOEt (20 mL), MeOH (0.2 mL), and Florisil (10 g). The mixture was stirred at room temperature for 3 days, filtered, and concentrated. Purification of the crude oil by column chromatography (SiO$_2$, hexane−AcOEt 5:1) gave 128 mg (74%) of the methoxy ketone **7b** as solids. mp 59.5−60 °C (from hexane−AcOEt). IR (KBr): 2829, 1710, 1255, 1145, 1081, 835, 703 cm^{-1}. ^{1}H NMR (500 MHz): δ 1.24 (s, 9H), 2.22 (s, 3H), 2.62 (d,d, *J* = 15.6, 7.3 Hz, 1H), 2.73 (d,d, *J* = 15.6, 7.3 Hz, 1H), 2.95 (d,d, *J* = 15.6, 6.7 Hz, 1H), 3.22 (d,d, *J* = 15.6, 4.0 Hz, 1H), 3.36 (s, 3H), 4.09 (d,d, *J* = 7.3, 6.7 Hz, 1H), 4.32 (d,d, *J* = 7.3, 4.0 Hz, 1H), 7.14−7.17 (m, 2H, PhH), 7.20−7.26 (m, 3H, PhH). ^{13}C NMR (50 MHz): δ 27.5 (3C), 29.1, 41.3, 42.5, 44.7, 57.1, 67.4, 78.6, 83.2, 127.1, 128.0 (2C), 129.4 (2C), 140.7, 168.4, 202.4, 208.5. Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.56. Found: C, 69.31; H, 7.41.

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Supporting Information Available: Spectral data including IR, ^{1}H NMR, and ^{13}C NMR data of **3a**−**e**, **7b**, **8**, and **9**, and the crystallographic data of **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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