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Dimethylaluminum methide complex $Tf_2CHAlMe_2$: an effective catalyst for Diels–Alder reaction of α,β-unsaturated lactone derivatives with cyclopentadiene

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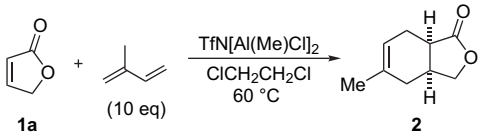
Abstract—Lewis acid derived by mixing Tf_2CH_2 and Me_3Al was found to be an effective catalyst system for the catalytic DA reaction of less reactive α,β-unsaturated lactone derivative with cyclopentadiene (CP). In this catalyst system, $Tf_2CHAlMe_2$ is an active species and an excess amount of Me_3Al plays an important role to lower the catalyst loading. Substituent effect of the lactone framework on π-facial selectivity was also examined. In the reactions of both γ-substituted 5-membered lactone derivatives and γ- or δ-methylated 6-membered lactone derivatives with CP, selective attack on the *anti* face of γ- or δ-substituent was observed. On the other hand, in the cases of γ- or ε-methylated 7-membered lactone derivatives, CP favorably attacked on the *syn* face.

1. Introduction

Diels–Alder (DA) reaction is one of the most powerful synthetic reactions to construct complex polycyclic systems.[1] It is well known that as a dienophile electron-deficient alkene derivatives are more reactive than electron-neutral and electron-rich alkene derivatives. For example, acyclic α,β-unsaturated ester derivatives are used for the synthesis of natural products and functional molecules.[1] α,β-Unsaturated lactone derivatives, which are cyclic analogues of α,β-unsaturated ester derivatives, can also be used as dienophiles. α,β-Unsaturated lactone derivatives are less reactive than acyclic ester derivatives, and thus the DA reaction of α,β-unsaturated lactone derivatives is not necessarily general approach to polycyclic lactone derivatives.[2–5] For instance, Ortuño and co-workers have reported the DA reaction of γ-substituted γ-crotonolactone derivatives with 1,3-dienes under various conditions including simply thermal or high-pressure reactions, but, compared to 6- and 7-membered α,β-unsaturated lactone derivatives, only relatively reactive 5-membered lactone derivatives were used as substrates.

Related to our ongoing study on the development of Lewis acids having unique properties,[6–8] we have reported that bis-aluminated triflic amides [$TfN(AlR^1R^2)_2$, $Tf{=}CF_3SO_2$], as bidentate Lewis acids, highly promote the DA reaction of 5- and 6-membered lactone derivatives not only with cyclopentadiene (CP) but also with acyclic dienes, such as isoprene and 2,3-dimethyl-1,3-butadiene, under mild conditions.[9] By the bidentate Lewis acids, a significant activation of α,β-unsaturated lactone derivatives was realized, but high catalyst loading (110 mol %) remained a serious problem.[10] In general, since Lewis basicity of lactone derivatives conformationally locked in cisoid form is higher than that of the corresponding acyclic ester derivatives, the dissociation of Lewis acid from Lewis acid–product complex is difficult. Thereby, high catalyst loading is needed for the smooth reaction. In fact, we observed that in the presence of substoichiometric amount (50 mol %) of $TfN[Al(Me)Cl]_2$ the DA reaction of γ-crotonolactone **1a** with isoprene in 1,2-dichloroethane gave DA product **2** in only 29% yield (Scheme 1).



Scheme 1.

To solve these synthetic problems, development of an efficient Lewis acid catalyst for the catalytic DA reaction of α,β-unsaturated lactone derivatives is an important task. However, there have been only a few studies on this issue.[11] Recently, Corey et al. reported catalytic enantioselective DA reaction of γ-crotonolactone with CP using chiral cationic

Keywords: Lewis acid; Bis(trifluoromethanesulfonyl)methane; Diels–Alder reaction; α,β-Unsaturated lactones.
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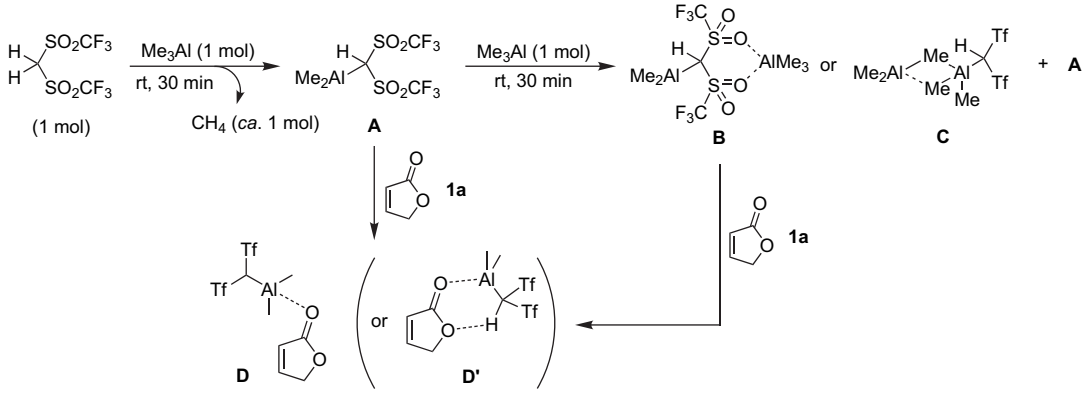
oxazaborolidine catalyst, but scope and limitations with respect to a structural variation of unsaturated lactones and 1,3-dienes are not clear.[12]

We have also reported an effective Lewis acid system derived from bis(trifluoromethanesulfonyl)methane (Tf_2CH_2) and Me_3Al for the catalytic DA reaction of less reactive 6- and 7-membered lactonic dienophiles with CP.[13] It is likely that the following two characteristics of this Lewis acid system contribute to realize catalytic activation of α,β-unsaturated lactone derivatives: (1) high Lewis acidity for high activation of less reactive α,β-unsaturated lactones[14] and (2) steric bulk of Lewis acid having sterically hindered bis(trifluoromethanesulfonyl)methide ligand for catalyst loading.[15] In this paper, we would like to report a full detail on this Lewis acid system and the application to the catalytic DA reaction of α,β-unsaturated lactone derivatives with CP.

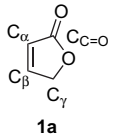
2. Results and discussions

Since the formation of aluminum methide through the reaction of carbon acids with alkylaluminum reagents was not reported, we examined the reaction of Tf_2CH_2 with Me_3Al. As shown in Scheme 2, treatment of Tf_2CH_2 (1 mol) with Me_3Al (1 mol) in CH_2Cl_2 at room temperature for 30 min liberated 1 mol of methane gas. Further addition of Me_3Al (1 mol) to this reaction mixture resulted in no liberation of gas. In a separate experiment, when to a solution of 1 mol of Tf_2CH_2 in CH_2Cl_2, 2 mol of Me_3Al was added in one-portion at room temperature, almost the same result, namely, only 1 mol of methane liberation, was observed.[16] ^{13}C NMR spectrum (100 MHz) of a 1:1.1 mixture of Tf_2CH_2 and Me_3Al in $CDCl_3$ at room temperature showed clean formation of the single complex (−10.9, 47.9, and 119.6 ppm) with complete consumption of Tf_2CH_2.[17] On the other hand, ^{13}C NMR spectrum of a 1:2 mixture of Tf_2CH_2 and Me_3Al showed two kinds of the complexes, that is, major one is the same as above and the other newly formed complex has a signal of CF_3 moiety at 119.8 ppm. In ^1H NMR spectrum, a 1:1.1 mixture of Tf_2CH_2 and Me_3Al showed two sharp peaks at 4.42 ppm (Tf_2CH) and −0.53 ppm ($AlCH_3$). Up-field shifts of Tf_2C carbon by 16.3 ppm and Tf_2CH proton by 0.54 ppm possibly indicate the formation of $Tf_2CHAlMe_2$ **A** having a carbon–aluminum bond. NMR study of the complex derived from the present aluminum methide **A** and γ-crotonolactone **1a** would provide further information on the structure of the complex and the qualitative Lewis acidity of **A** (Table 1). Thus, a mixture of **1a** and the aluminum methide **A** (1.0 equiv) in $CDCl_3$ brought about new signals presumably due to the formation of a complex such as **D** (simple Lewis acid coordination model) or **D′** (a bidentate model for Lewis acid coordination with hydrogen bonding), although the exact structure was not clear at this moment.[18] Compared to crotonolactone **1a**, complex **D** (or **D′**) showed down-field shifts of carbonyl, β- and γ-carbons by 9.6, 11.3, and 7.2 ppm, respectively, and up-field shift of α-carbon by 1.4 ppm in ^{13}C NMR spectrum (entry 2). In the case of a mixture of **1a** and 'Tf_2CH_2+2.0Me_3Al' system, essentially the same peaks were observed in ^{13}C NMR



Scheme 2.

Table 1. Chemical shifts of Lewis acid–**1a** complexes in ^{13}C NMR[a]



1a

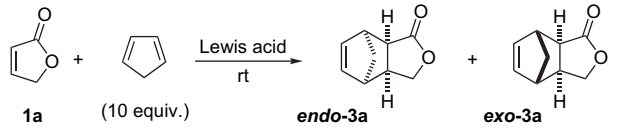
Entry	Lewis acid (1.0 equiv)	Chemical shifts								
		$C_{C=O}$	$\Delta C_{C=O}$	C_α	ΔC_α	C_β	ΔC_β	C_γ	ΔC_γ	$\Delta C_\beta - C_\alpha$
1	None	173.6	—	121.5	—	152.7	—	72.1	—	31.2
2	Tf_2CH_2+1.1 Me_3Al	183.2	+9.6	120.1	−1.4	164.0	+11.3	79.3	+7.2	43.9
3	Tf_2CH_2+2.0 Me_3Al	183.2	+9.6	120.4	−1.1	163.5	+10.8	79.1	+7.0	43.1
4	Me_3Al[b]	180.9	+7.3	120.9	−0.6	158.9	+6.2	76.5	+4.4	38.0

[a] In $CDCl_3$, rt (100 MHz, ppm).
[b] 1.1 equiv of Me_3Al was used.

spectrum (entry 3). These data may indicate that the dissociation of Me_3Al from the complex possibly such as **B** or **C** by Lewis basic γ-crotonolactone **1a** easily takes place. Since the chemical shift difference between C_β and C_α reflects the reactivity as a dienophile, the observed $\Delta C_\beta - C_\alpha$ value (43.9 ppm) in $Tf_2CHAlMe_2$–**1a** complex also means significantly high activation of **1a** by $Tf_2CHAlMe_2$, compared to the use of 1.1 equiv of Me_3Al ($\Delta C_\beta - C_\alpha$=38.0 ppm).

To find out the efficiency of $Tf_2CHAlMe_2$, in the presence of a mixture of Tf_2CH_2 and Me_3Al in various ratios, reaction of γ-crotonolactone **1a** with CP was conducted. These results are summarized in Table 2. As shown in entry 1, catalytic amount of $Tf_2CHAlMe_2$ (20 mol %), which was generated by a 1:1 reaction of Tf_2CH_2 and Me_3Al, catalyzed the reaction of **1a** with CP (10 equiv) in CH_2Cl_2 for 8 h at room temperature to give cycloadduct **3a** in 52% yield as an *endo*/*exo* mixture in a ratio of 6.8:1. A 1:1 mixture of Tf_2CH_2 and *i*-Bu_2AlH instead of Me_3Al did not promote the DA reaction (entry 2). The use of a 1:2 mixture of Tf_2CH_2 and Me_3Al dramatically increased the yield of **3a** to 89% only after 4 h without an appreciable change in *endo*/*exo* selectivity (entry 3). Catalyst loading of 'Tf_2CH_2+2.0Me_3Al' system could be reduced to 10 mol % without significant decrease in the yield of **3a** (entries 4, 5).[19] To check effects of an excess amount of Me_3Al over Tf_2CH_2, the DA reaction of **1a** was conducted in the presence of only Me_3Al (40 mol %) for 8 h, but the yield of **3a** was only 21% (entry 9, *endo*/*exo*=9.7:1). This result indicates that catalytic amount of Me_3Al does not effectively catalyze the DA reaction of **1a** under the present conditions. Without addition of Lewis acid DA product **3a** was not obtained after stirring for 14 h at room temperature (entry 7). While we have reported that bidentate Lewis acid, TfN(Al*i*-Bu_2)$_2$, promoted the DA reaction of **1a** with CP, compared with the present 'Tf_2CH_2+2.0Me_3Al' system, the use of stoichiometric amount of this sulfonamide-based Lewis acid (110 mol %) and longer reaction time (13 h) were needed for the smooth reaction (entry 8).[9]

Table 2. Effects of Lewis acids on DA reaction of **1a** with CP



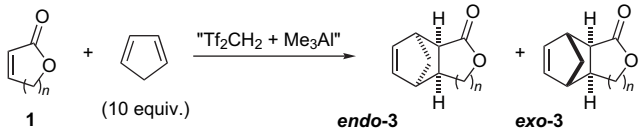
Entry	Lewis acid (mol %)	Solvent	Time (h)	Yield[a] (%)	Ratio[b] (*endo*/*exo*)
1	Tf_2CH_2+1.0 Me_3Al (20)	CH_2Cl_2	8	52	6.8:1
2	Tf_2CH_2+1.0 DIBAL–H (20)	CH_2Cl_2	12	Trace	nd[c]
3	Tf_2CH_2+2.0 Me_3Al (20)	CH_2Cl_2	4	89	6.8:1
4	Tf_2CH_2+2.0 Me_3Al (10)	CH_2Cl_2	5	83	7.8:1
5	Tf_2CH_2+1.3 Me_3Al (20)	CH_2Cl_2	3	88	8.3:1
6	Tf_2CHMe+1.3 Me_3Al (20)	CH_2Cl_2	3	76	8.1:1
7	None	Toluene	14	0	—
8[d]	TfN(Al*i*-Bu_2)$_2$ (110)	Toluene	13	97	5.5:1
9	Me_3Al (40)	CH_2Cl_2	8	21	9.7:1

[a] Isolated yield.
[b] Determined by ^{1}H NMR.
[c] Not determined.
[d] Ref. 9.

To see the influence of lactone ring-size to the reactivity and the *endo*/*exo* selectivity, we examined the reaction of various α,β-unsaturated lactone derivatives with CP (Table 3).[20] We found that by expanding lactone ring-size, reactivity of α,β-unsaturated lactones as dienophiles reduces but *endo*-selectivity notably increases. The reaction of 6-membered lactone **1b** in the presence of 20 mol % of 'Tf_2CH_2+1.3Me_3Al' system required higher reaction temperature (60 °C) for the smooth reaction to give DA adduct **3b** in 76% yield as a 14:1 mixture of *endo*/*exo* isomers (entry 1). The use of 'Tf_2CH_2+2.0Me_3Al' system in place of 'Tf_2CH_2+1.3Me_3Al' system increased the product yield to 81% with a small decrease in *endo*/*exo* selectivity (entry 2, *endo*/*exo*=9.4:1). The reactivity of 7-membered lactone derivative **1c** was lower than that of 5- and 6-membered lactone substrates, that is, in the presence of 30 mol % of 'Tf_2CH_2+1.3Me_3Al' system the reaction with 20 equiv of CP yielded **3c** in only 56% yield with fairly high *endo*/*exo* selectivity (entry 3, *endo*/*exo*=17:1). On the other hand, the use of 'Tf_2CH_2+2.0Me_3Al' system improved both the product yield and *endo*/*exo* selectivity (entry 4, 85% yield, *endo*/*exo*=21:1).

Next, we examined the substituent effects of the lactone ring systems on the stereochemical outcomes. Results are summarized in Table 4. It is well known that in the DA reaction of γ-substituted 5-membered lactones, 1,3-dienes perfectly attack on the opposite face to the γ-substituents under both simply thermal conditions and Lewis acid mediated conditions (*anti* addition).[3,9] Under 'Tf_2CH_2+1.3Me_3Al' catalyzed conditions, the reaction of γ-methyl-γ-butenolide

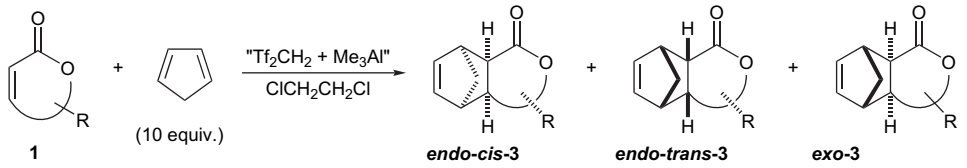
Table 3. Effect of lactone ring-size on DA reaction with CP

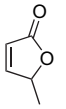
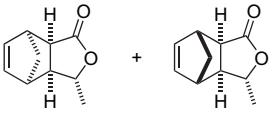
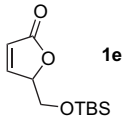
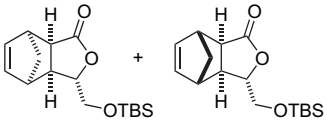
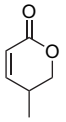
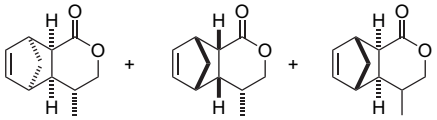
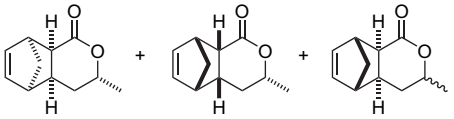
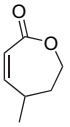
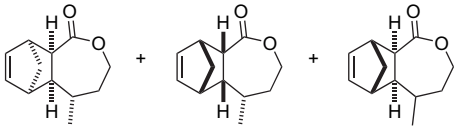
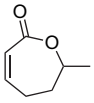
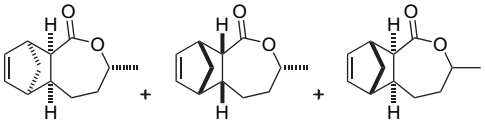


Entry	**1**	Lewis acid (mol %)	Temp (°C)	Time (h)	Solvent	**3**	Yield[a] (%)	Ratio of **3**[b] (*endo*/*exo*)
1	**1b** (*n*=2)	Tf_2CH_2+1.3 Me_3Al (20)	60	4	$ClCH_2CH_2Cl$	**3b**	76	14:1
2	**1b** (*n*=2)	Tf_2CH_2+2.0 Me_3Al (20)	60	4	$ClCH_2CH_2Cl$	**3b**	81	9.4:1
3[c]	**1c** (*n*=3)	Tf_2CH_2+1.3 Me_3Al (30)	60	4	$ClCH_2CH_2Cl$	**3c**	56	17:1[d]
4[c]	**1c** (*n*=3)	Tf_2CH_2+2.0 Me_3Al (30)	60	4	$ClCH_2CH_2Cl$	**3c**	85	21:1[d]
5	**1a** (*n*=1)	Tf_2CH_2+1.3 Me_3Al (20)	rt	3	CH_2Cl_2	**3a**	88	8.3:1

[a] Isolated yield.
[b] Determined by ^{1}H NMR.
[c] CP of 20 equiv was used.
[d] Determined by isolated yield.

Table 4. Diastereoselective DA reaction of various α,β-unsaturated lactones with CP



Entry	1	Lewis acid (mol %)	Temp (°C)	Time (h)	Products 3	Yield[a] (%)	*endo*/*exo*[b,c] (*endo*-cis/*endo*-trans)
1[d]		Tf_2CH_2+1.3 Me_3Al (20)	rt	4		80	6.7:1
2[d]	**1d**	Tf_2CH_2+2.0 Me_3Al (20)	rt	4		90	5.9:1
3		Tf_2CH_2+2.0 Me_3Al (30)	60	24		63	5.9:1
4		Tf_2CH_2+1.3 Me_3Al (20)	60	7		84	9.9:1 (2.3:1)
5	**1f**	Tf_2CH_2+2.0 Me_3Al (20)	60	7		93	13:1 (2.4:1)
6[e]		Tf_2CH_2+1.3 Me_3Al (30)	60	4		92	25:1 (11:1)
7[e]	**1g**	Tf_2CH_2+2.0 Me_3Al (30)	60	4		92	25:1 (14:1)
8[f]		Tf_2CH_2+1.3 Me_3Al (50)	60	8		80	17:1 (1:1.8)
9[f]	**1h**	Tf_2CH_2+2.0 Me_3Al (50)	60	8		80	12:1 (1:1.7)
10[g,h]		Tf_2CH_2+1.3 Me_3Al (30)	60	4		70	19:1 (1:3.8)
11[g,h]	**1i**	Tf_2CH_2+2.0 Me_3Al (30)	60	4		70	>20:1 (1:5.5)

endo-3d *exo*-3d; *endo*-3e *exo*-3e; *endo*-cis-3f *endo*-trans-3f *exo*-3f; *endo*-cis-3g *endo*-trans-3g *exo*-3g; *endo*-cis-3h *endo*-trans-3h *exo*-3h; *endo*-cis-3i *endo*-trans-3i *exo*-3i

[a] Isolated yield.
[b] Determined by ^1H NMR.
[c] A ratio of *endo*-cis/*endo*-trans isomers is shown in parentheses.
[d] Solvent: CH_2Cl_2.
[e] CP of 20 equiv was used.
[f] CP of 30 equiv of was used.
[g] CP of 40 equiv was used.
[h] Solvent; toluene (0.5 M).

1d with 10 equiv of CP gave an *endo*/*exo* mixture of *anti* adducts **3d** in 80% yield (entry 1, *endo*/*exo*=6.7:1). As shown in entry 2, the use of 'Tf_2CH_2+2.0Me_3Al' system instead of 'Tf_2CH_2+1.3Me_3Al' system improved the product yield to 90%, although *endo*/*exo* selectivity was decreased to 5.9:1. The reaction of silyloxymethylated γ-butenolide **1e** also proceeded in the presence of 20 mol % of 'Tf_2CH_2+2.0Me_3Al' system for 24 h at 60 °C to give the desired cycloadduct **3e** in reasonable yield with the perfect π-facial selectivity (entry 3, 63% yield, *endo*/*exo*=5.9: 1). Compared to 5-membered lactone derivatives, there have been reported only a few studies on the reactivity and on the π-facial selectivity of substituted 6- or 7-membered lactone derivatives.[21] In the presence of 20 mol % of 'Tf_2CH_2+1.3Me_3Al' the reaction of γ-methylated 6-membered lactone derivative **1f** with CP for 7 h at 60 °C gave the desired adduct **3f** in 84% yield as a mixture of three isomers (entry 4). Based on NOESY data or X-ray crystallographic analysis, structures of these products were determined as two *endo* isomers and one *exo* isomer (*endo*/*exo*=9.9:1, *endo*-cis/*endo*-trans=2.3:1).[22,23] Under the similar conditions, the use of 'Tf_2CH_2+2.0Me_3Al' system gave a better result in both the product yield and the *endo*/*exo* selectivity (entry 5, 93% yield, *endo*/*exo*=13:1, *endo*-cis/*endo*-trans=2.4:1). Compared to γ-methyl group on the δ-pentenolide structure, δ-methyl group dramatically improved not only the reactivity and the

endo/*exo* selectivity but also the *endo*-cis/*endo*-trans selectivity. As shown in entry 6, in the presence of 'Tf_2CH_2+1.3Me_3Al' system (30 mol %) the reaction of δ-methylated 6-membered substrate **1g** with 20 equiv of CP gave DA product **3g** in 92% yield as a mixture of four isomers with excellent *endo*/*exo* selectivity (*endo*/*exo*=25:1) and high π-facial selectivity between two *endo* isomers (*endo*-cis/*endo*-trans=11:1). Furthermore, in the reaction using 'Tf_2CH_2+2.0Me_3Al' system instead of 'Tf_2CH_2+1.3Me_3Al' system, the π-facial selectivity between two *endo* isomers improved to 14:1 without decrease in both the product yield and the *endo*/*exo* selectivity (entry 7). In the presence of 50 mol % of 'Tf_2CH_2+1.3Me_3Al' system γ-methyl-7-membered lactone **1h** reacted with 40 equiv of CP to give the cycloadduct **3h** in 80% yield as a mixture of two *endo* adducts and one *exo*-adduct (*endo*/*exo*=17:1, entry 8). The major *endo* adduct had *endo*-trans structure (*endo*-cis/*endo*-trans=1:1.8), which was determined by X-ray crystallographic analysis.[22] This result on the π-facial selectivity is a sharp contrast to those in the reactions of methylated 5- and 6-membered lactone substrates with CP. The use of 'Tf_2CH_2+2.0Me_3Al' system instead of 'Tf_2CH_2+1.3Me_3Al' system decreased the *endo*/*exo* selectivity to 12:1 without any change of the yield and *endo*-cis/*endo*-trans selectivity (entry 9). The similar tendency on the *endo*-cis/*endo*-trans selectivity was also observed in the case of ε-methylated 7-membered substrate **1i**. That is, the reaction of **1i** with 30 equiv of CP in the presence of 30 mol % of 'Tf_2CH_2+1.3Me_3Al' system gave a mixture of two *endo* adducts and one *exo*-adduct in 70% yield (*endo*/*exo*=19:1, entry 10). Interestingly, compared to the case of **1h** having γ-methyl group, *endo*-cis/*endo*-trans selectivity in the reaction of **1i** was increased to 1:3.8. The reaction using 30 mol % of 'Tf_2CH_2+2.0Me_3Al' improved the stereoselectivity without loss of the yield (70% yield, *endo*/*exo*= >20:1, *endo*-cis/*endo*-trans=1:5.5, entry 11).

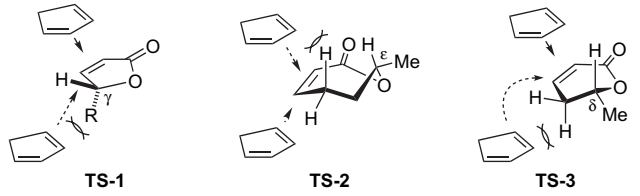


Figure 1. Proposed transition models of DA reactions of α,β-unsaturated lactones with CP. **TS-1** and **TS-3** show that CP attacks on the opposite face from γ-methyl group on 5-membered lactone structure or δ-methyl group on 6-membered lactone structure (*anti* addition), respectively. On the other hand, in the case of 7-membered lactone **1i**, CP attacks on the same face (*syn* addition) to ε-methyl group as shown in **TS-2**.

Concerning the observed π-facial selectivity, we propose the transition state models as shown in Figure 1.[24] In the DA reaction of γ-substituted 5-membered lactone derivatives with CP under simply thermal conditions, it is known that CP attacks on the opposite π-face to avoid steric repulsion of γ-substituents.[3a] Under the present Lewis acid-catalyzed conditions, similar selectivity was also observed (Fig. 1, **TS-1**). On the other hand, in the case of ε-methylated 7-membered lactone **1i** the π-facial selectivity was inversed to that of γ-methylated 5-membered lactone **1d**. This result can be explained by considering transition state model **TS-2**. Since in **TS-2**, sterically bulky ε-methyl group occupies pseudo-equatorial position and thus the *anti* face to ε-methyl group is sterically shielded by ε-proton and γ-axial proton, CP favorably attacks on the *syn* face of lactone substrate leading *endo*-trans isomer as a major product. Sammakia and co-workers reported a similar stereoselectivity in the cationic intramolecular DA reaction of 7-membered oxocarbenium species.[25] In contrast, *anti* addition of nitrile oxide to ε-methyl lactone **1i** was also reported.[26] The observed π-facial selectivity controlled by the remote substituent effect in the 7-membered cyclic system is the first example of kinetically controlled *syn* addition in the *intermolecular* cycloadditions. Regarding the reactivity and stereoselectivity, 6-membered lactone derivatives showed intermediate nature between 5-membered lactones and 7-membered lactones. The DA reaction of δ-methylated lactone derivative **1g** should proceed via **TS-3**, in which δ-methyl group occupies a pseudo-equatorial position and γ-axial proton shields the *syn* face to δ-methyl group, that is, the moderate *anti*-selectivity was observed.[27]

In the present Lewis acid system, the ratio of Tf_2CH_2 and Me_3Al affected notably the yield of DA adducts. Concerning these results, we propose the catalytic cycle as shown in Figure 2. Based on the above NMR studies, the reaction of Tf_2CH_2 and Me_3Al gave $Tf_2CHAlMe_2$ **A**, which highly activates α,β-unsaturated lactone derivatives, compared to Me_3Al. While, complexation of aluminum methide **A** with α,β-unsaturated lactone derivatives promotes the DA

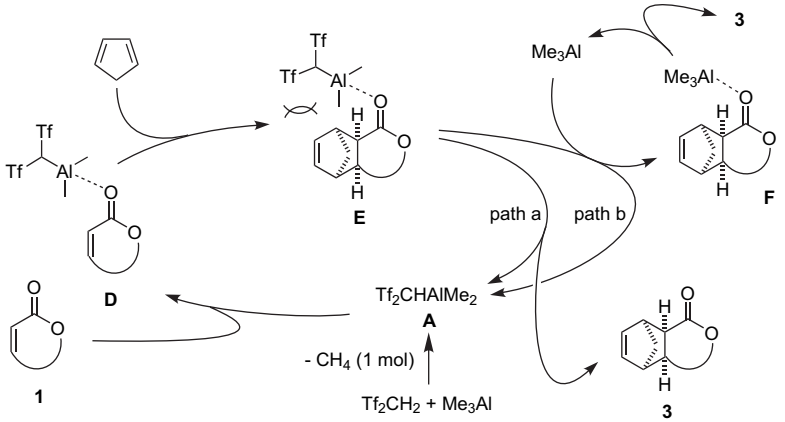
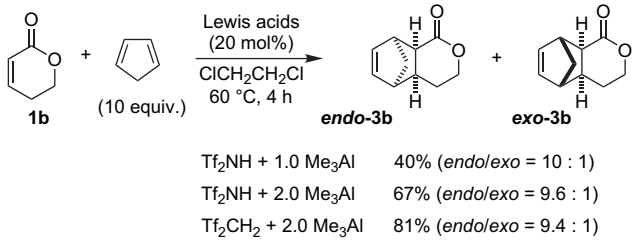


Figure 2. Proposed catalytic cycle on the catalytic DA reaction of α,β-unsaturated lactones.

reaction with CP to give complex **E**. Since complex **E**, which have sterically bulky bis(trifluoromethanesulfonyl)methide ligand and DA adduct part, is thermodynamically less stable, both direct dissociation of **A** (path a) and Lewis acid exchange reaction with Me_3Al (path b), which provides thermodynamically more stable complex **F**, result in regeneration of **A** with formation of DA product **3**. That is, excess amount of Me_3Al in the present Lewis acid systems should improve the turnover of complex **A**.

According to this concept laying in the use of combination of a catalytic amount of bulky ligand and catalytic/substoichiometric amount of alkylaluminum, we examined the efficiency of other mononuclear aluminum Lewis acid catalyst. For example, in the presence of 20 mol % of Tf_2NAlMe_2 generated in situ by mixing Tf_2NH and 1 M equivalent of Me_3Al, the reaction of **1b** with CP gave DA adduct **3b** in only 40% yield, but the use of 20 mol % of 'Tf_2NH+2.0Me_3Al' system significantly improved the product yield to 67% (Scheme 3).[28]



Scheme 3.

In summary, we found efficient catalytic systems derived by mixing Tf_2CH_2 and Me_3Al for the DA reactions of α,β-unsaturated lactone derivatives with CP. Aluminum methide complex, $Tf_2CHAlMe_2$, is an active species in these catalytic systems and a small excess of Me_3Al plays an important role to improve catalyst loading. The present catalytic systems activate not only relatively reactive 5-membered lactone derivatives but also less reactive 6- and 7-membered lactone derivatives. Lactone ring-size influences both reactivity and the *endo*/*exo* selectivity. Thus, by expanding ring-size, reactivity of α,β-unsaturated lactone derivatives reduced but *endo*-selectivity notably increased. Furthermore, substituent effects of the lactone framework on π-facial selectivity were also examined. In the reactions of both γ-substituted 5-membered lactone derivatives and γ- or δ-methylated 6-membered lactone derivatives with CP, CP attacked on *anti* face of γ- or δ-substituted groups. On the other hand, in the cases of γ- or ε-methylated 7-membered lactone derivatives, CP favorably attacked on the *syn* face.

3. Experimental

3.1. General and materials

All reactions were carried out under Ar atmosphere. ^1H and ^{13}C NMR spectra were taken on a Varian Mercury 300, Bruker DPX400 or Brucker AV600 spectrometers, and chemical shifts were reported in parts per million (ppm) using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^1H NMR, and $CDCl_3$ (77.01 ppm) for ^{13}C NMR as an internal standard, respectively. ^{19}F NMR spectra were taken on a Bruker dpx400 spectrometer, and chemical shifts were reported in parts per million using benzotrifluoride (0 ppm) as a standard. Infrared (IR) spectra were recorded on a JASCO FT/IR-620 infrared spectrophotometer. Mass spectra (MS) were obtained on a Micromass LCT (ESI) or Micromass AutoSpec (EI). Medium pressure liquid chromatography (MPLC) was performed using prepacked column (KUSANO Prepacked column Si-10, 40×300 mm I.D., silica gel, 50 μm) with RI detector.

3.1.1. Preparation of bis(trifluoromethanesulfonyl)methane. To a solution of trimethylsilylmethyllithium (1.0 M in pentane, 100 mL, 100 mmol), trifluoromethanesulfonic anhydride (18.6 g, 67 mmol) was added dropwise at 0 °C over 2 h. Reaction mixture was stirred at the same temperature for 30 min, then quenched with saturated aqueous $NaHCO_3$ solution (100 mL) at 0 °C. After being washed with CH_2Cl_2 (100 mL×2), the pH of the aqueous layer was adjusted to 2–3 by careful addition of concd HCl, and the resulting mixture was extracted with CH_2Cl_2 (150 mL×3). The organic layer was dried over $MaSO_4$ and evaporated. To remove impurities, additional extractive work-up using H_2O (20 mL), concd HCl (20 mL), and CH_2Cl_2 (50 mL×3) and evaporation were carried out to give bis(trifluoromethanesulfonyl)methane as colorless crystals. The structure was confirmed by comparison of spectrum data reported in the literature.[14] ^1H NMR (400 MHz, $CDCl_3$) δ: 4.96 (2H, s). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 64.2, 118.8 (q, J=327.8 Hz). ^{19}F NMR (386 MHz, $CDCl_3$) δ: −13.0 (6F, s).

3.1.2. NMR data of dimethylaluminum bis(trifluoromethanesulfonyl)methide complex. For $Tf_2CHAlMe_2$: ^1H NMR (400 MHz, $CDCl_3$) δ: −0.53 (6H, s), 4.42 (1H, s). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: −10.9 (br), 47.9, 119.6 (q, J=319.0 Hz).

For $Tf_2CHAlMe_2$–**1a** complex: ^1H NMR (400 MHz, $CDCl_3$) δ: −0.62 (6H, s, $AlCH_3$), 4.09 (1H, s, Tf_2CH), 5.47 (2H, s, $C_\gamma H_2$), 6.52 (1H, dt, J=5.7, 1.8 Hz, $C_\alpha H$), 8.26 (br d, J=5.7 Hz, $C_\beta H$). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: −10.9, 51.3, 79.3, 120.1, 120.2 (q, J=323.8), 164.0, 183.2.

3.1.3. Preparation of α,β-unsaturated lactones (1). 5*H*-Furan-2-one **1a** and 5,6-dihydro-2*H*-pyran-2-one **1b** are available commercially. 6,7-Dihydro-5*H*-oxepin-2-one **1c**,[29] 5-methyl-5*H*-furan-2-one **1d**,[30] 5-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)-5*H*-furan-2-one **1e**,[31] 6-methyl-5,6-dihydro-2*H*-pyran-2-one **1g**,[32] and 7-methyl-6,7-dihydro-5*H*-oxepin-2-one **1i**[33] were prepared by the reported procedure.

3.1.4. 5-Methyl-5,6-dihydro-2*H*-pyran-2-one (1f). This compound was prepared by extending a method described in the literature.[34] To a solution of 2-methyl-3-buten-1-ol (1.0 mL, 10.0 mmol) in CH_2Cl_2 (30 mL), acryloyl chloride (2.2 mL, 11.0 mmol) and Et_3N (1.8 mL, 12.0 mmol) were added at 0 °C. After being stirred at the same temperature for 3 h, extractive work-up and purification by silica gel column chromatography (pentane/Et_2O=50:1) gave 2-methyl-3-butenyl acrylate (953 mg, 6.8 mmol, 68% yield) as colorless oil. IR (neat) ν cm^{-1}: 1730. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.06 (3H, d, J=6.9 Hz), 2.50–2.64 (1H, m), 4.03 (1H, dd,

J=10.8, 6.6 Hz), 4.08 (1H, dd, J=10.8, 6.9 Hz), 5.04 (1H, d, J=10.4 Hz), 5.08 (1H, br d, J=17.4 Hz), 5.76 (1H, ddd, J=17.4, 10.4, 6.9 Hz), 5.81 (1H, dd, J=10.3, 1.3 Hz), 6.12 (1H, dd, J=17.3, 10.4 Hz), 6.39 (1H, dd, J=17.3, 1.3 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 16.4, 37.0, 68.4, 115.0, 128.5, 130.6, 139.9, 166.2. Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.38; H, 8.59. To a solution of the above acrylate (641 mg, 4.58 mmol) in CH_2Cl_2 (900 mL), Grubbs II catalyst (170 mg, 0.19 mmol) was added at room temperature. After being stirred at 40 °C for 2 h, evaporation of the reaction mixture followed by purification by column chromatography on silica gel (pentane/Et_2O=1:1) gave 5-methyl-5,6-dihydro-2*H*-pyran-2-one **1f** (370 mg, 3.30 mmol, 73% yield). The structure was confirmed by comparison of spectrum data with the authentic sample.[35]

3.1.5. 5-Methyl-6,7-dihydro-5*H*-oxepin-2-one (1h). To a solution of LDA prepared from *n*-BuLi (1.59 M in hexane, 6.3 mL, 10.0 mmol) and diisopropylamine (6.3 mL, 10.0 mmol) in THF (30 mL), 5-methyl-6,7-dihydro-5*H*-oxepin-2-one (1.28 g, 10.0 mmol) was added at −78 °C over 15 min. After being stirred at the same temperature for 30 min, the reaction mixture was treated with benzeneselenyl chloride (2.50 g, 13.0 mmol) at −78 °C for 3 h and quenched with H_2O (20 mL) at 0 °C. After usual extractive work-up and evaporation, purification of the resulting residue by silica gel column chromatography (hexane/EtOAc=3:1) gave 5-methyl-3-(phenylselenyl)-2-oxepanone (950 mg, 3.40 mmol). Light yellow oil. IR (neat) ν cm^{-1}: 1715. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.00 (3H, d, J=6.5 Hz), 1.44–1.57 (1H, m), 1.83 (1H, ddd, J=13.7, 11.1, 2.5 Hz), 1.90–2.07 (2H, m), 2.10–2.19 (1H, m), 4.20 (1H, dd, J=6.5, 2.5 Hz), 4.32 (1H, ddd, J=13.1, 5.9, 1.8 Hz), 4.75 (1H, dd, J=13.1, 10.1 Hz), 7.25–7.36 (3H, m), 7.58–7.62 (2H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 22.0, 32.1, 37.2, 37.4, 45.5, 68.1, 128.4, 128.7, 129.4, 134.3, 173.0. ESI-MS (*m*/*z*): 285 $[M+H]^+$. HRMS: calcd for $C_{13}H_{16}O_2Se$: 285.0394 $[M+H]^+$, found: 285.0390. Anal. Calcd for $C_{13}H_{16}O_2Se$: C, 55.13; H, 5.69. Found: C, 55.05; H, 5.67. The above phenylselenide was treated with 30% H_2O_2 (0.57 mL) in THF (24 mL) at room temperature for 4 h. Resulting mixture was quenched with saturated aqueous $Na_2S_2O_7$ solution (10 mL) at 0 °C and extracted with Et_2O (20 mL×3). The combined organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. Chromatographic purification (pentane/Et_2O=1:1) of resulting residue gave 5-methyl-6,7-dihydro-5*H*-oxepin-2-one **1h** as colorless oil. IR (neat) ν cm^{-1}: 1706. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.09 (3H, d, J=7.2 Hz), 1.66–1.78 (1H, m), 2.14–2.26 (1H, m), 2.56–2.68 (1H, m), 4.15–4.33 (1H, m), 5.83 (1H, dd, J=12.4, 2.3 Hz), 6.21 (1H, dd, J=12.4, 3.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 20.3, 34.7, 35.5, 66.0, 119.6, 149.2, 168.6. EIMS (*m*/*z*): 126 $[M]^+$. Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.49; H, 8.00.

3.2. General procedure of Tf_2CH_2+Me_3Al catalyzed Diels–Alder reaction of α,β-unsaturated lactones (1) with CP

3.2.1. (1*S,2*R**,6*S**,7*R**)-4-Oxatricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (*endo*-3a) and (1*R**,2*R**,6*S**,7*S**)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (*exo*-3a).** To a solution of Tf_2CH_2 (28.1 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL), Me_3Al (1.05 M in hexane, 0.12 mL, 0.13 mmol) was stirred for 1 h at room temperature. To this reaction mixture, a solution of 2(5*H*)-furan-2-one **1a** (42.0 mg, 0.50 mmol) in CH_2Cl_2 (1.0 mL) and freshly prepared CP were added. After being stirred for 3 h at same temperature, the resulting mixture was quenched with H_2O (10 mL), and extracted with Et_2O (10 mL×3). The organic layer was dried over $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography (silica gel, hexane/EtOAc=3:1) to give *endo*-**3a** (58.9 mg, 0.39 mmol, 78% yield) and *exo*-**3a** (7.1 mg, 0.05 mmol, 10% yield). The structure was confirmed by comparison of spectrum data with the literature.[36]

3.2.2. (1*S,2*S**,7*S**,8*R**)-4-Oxatricyclo[6.2.1.0^{2,7}]undec-9-en-3-one (*endo*-3b) and (1*R**,2*S**,7*S**,8*S**)-4-oxatricyclo[6.2.1.0^{2,7}]undec-9-en-3-one (*exo*-3b).** *endo*-**3b**: Colorless oil. IR (neat) ν cm^{-1}: 1726. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.12–1.21 (1H, m), 1.35 (1H, d, J=8.5 Hz), 1.52 (1H, dd, J=8.5, 1.5 Hz), 1.91–2.00 (1H, m), 2.63–2.74 (1H, m), 2.88–2.95 (1H, m), 3.32 (1H, br s), 4.06 (1H, td, J=11.7, 1.5), 4.20 (1H, dt, J=11.7, 3.1 Hz), 6.06 (1H, dd, J=5.5, 2.9 Hz), 6.28 (1H, dd, J=5.5, 2.6 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 27.8, 388.8, 43.4, 45.6, 45.6, 48.2, 67.7, 135.0, 138.1, 174.2. ESI-MS *m*/*z*: 165 $[M+H]^+$. HRMS: calcd for $C_{10}H_{13}O_2$: 165.0916 $[M+H]^+$, found: 165.0917.

exo-**3b**: Colorless oil. IR (neat) ν cm^{-1}: 1732. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.31 (1H, br s), 1.45 (2H, m), 2.01 (1H, m), 2.14 (1H, ddd, J=8.6, 5.4, 1.6 Hz), 2.47 (1H, br d, J=9.1 Hz), 2.71 (1H, br s), 3.47 (1H, br s), 4.08 (1H, ddd, J=12.4, 11.0, 1.4 Hz), 4.33 (1H, m), 6.14 (1H, dd, J=5.3, 2.8 Hz), 6.19 (1H, dd, J=5.3, 2.7 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 29.7, 40.0, 42.8, 44.5, 46.2, 46.3, 67.2, 135.4, 137.6, 174.4. EIMS *m*/*z*: 165 $[M]^+$. HRMS: calcd for $C_{10}H_{13}O_2$: 165.0916 $[M]^+$, found: 165.0917.

3.2.3. (1*S,2*S**,8*S**,9*R**)-4-Oxatricyclo[7.2.1.0^{2,8}]dodec-10-en-3-one (*endo*-3c) and (1*R**,2*S**,8*S**,9*S**)-4-oxatricyclo[7.2.1.0^{2,8}]dodec-10-en-3-one (*exo*-3c).** *endo*-**3c**: Colorless crystals. Mp 66.8–67.0 °C. IR (KBr) ν cm^{-1}: 1726. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.00 (1H, td, J=14.0, 6.5 Hz), 1.34 (1H, d, J=8.5 Hz), 1.49 (1H, d, J=8.5 Hz), 1.47–1.58 (1H, m), 1.75 (1H, dd, J=14.0, 7.2 Hz), 1.88–2.01 (1H, m), 2.26–2.38 (1H, m), 2.76 (1H, br s), 3.15 (1H, br s), 3.27 (1H, dd, J=10.0, 3.5 Hz), 4.15 (1H, dd, J=12.4, 6.6 Hz), 4.29 (1H, td, J=12.4, 3.9 Hz), 6.01 (1H, dd, J=5.6, 3.0 Hz), 6.39 (1H, dd, J=5.6, 2.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 25.6, 26.2, 40.2, 45.5, 47.2, 48.3, 49.3, 64.9, 133.2, 137.6, 174.9. ESI-MS (*m*/*z*): 179 $[M+H]^+$. HRMS: calcd for $C_{11}H_{15}O_2$: 179.1072 $[M+H]^+$, found: 179.1069. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.36; H, 8.16.

exo-**3c**: Colorless oil. IR (neat) ν cm^{-1}: 1730. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.29–1.48 (1H, m), 1.45 (1H, dt, J=9.4, 1.7 Hz), 1.54 (1H, d, J=9.4 Hz), 1.52–1.63 (1H, m), 1.64–1.73 (1H, m), 1.87–1.96 (1H, m), 2.02–2.14 (1H, m), 2.52–2.62 (2H, m), 3.32 (1H, br s), 4.16–4.30 (2H, m), 6.13 (1H, dd, J=5.7, 3.0 Hz), 6.28 (1H, dd, J=5.7, 3.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 25.9, 27.6,

39.9, 44.8, 45.1, 47.4, 48.2, 65.0, 135.5, 139.5, 176.1. ESI-MS (*m/z*): 179 $[M+H]^+$. HRMS: calcd for $C_{11}H_{15}O_2$: 179.1072 $[M+H]^+$, found: 179.1082.

3.2.4. (1*S,2*R**,5*R**,6*S**,7*R**)-5-Methyl-4-oxatricyclo-[5.2.1.0^{2,6}]dec-8-en-3-one (*endo*-3d) and (1*R**,2*R**,5*R**,6*S**,7*S**)-5-methyl-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (*exo*-3d).** The structure of these compounds was confirmed by comparison of spectrum data with the literature.[3d]

3.2.5. (1*S,2*R**,5*S**,6*S**,7*R**)-5-({[*tert*-Butyl(dimethyl)silyl]oxy}methyl)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (*endo*-3e) and (1*R**,2*R**,5*S**,6*S**,7*S**)-5-({[*tert*-butyl(dimethyl)silyl]oxy}methyl)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (*exo*-3e).** *endo*-**3e**: Colorless crystals. Mp 51.1–52.0 °C. IR (KBr) ν cm^{-1}: 1753. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.04 (6H, s), 0.88 (9H, s), 1.44 (1H, br d, J=8.4 Hz), 1.64 (1H, br d, J=8.4 Hz), 2.93–3.00 (1H, m), 3.07 (1H, br s), 3.20 (1H, dd, J=9.0, 4.6 Hz), 3.28 (1H, br s), 3.63 (1H, dd, J=11.0, 2.8 Hz), 3.72 (1H, dd, J=11.0, 3.4 Hz), 3.92–3.97 (1H, m), 6.22 (1H, dd, J=5.4, 2.9 Hz), 6.28 (1H, dd, J=5.5, 2.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: −5.6, −5.6, 18.1, 25.8, 42.9, 45.5, 45.8, 51.7, 65.0, 82.2, 134.5, 136.7, 177.9. ESI-MS (*m/z*): 295 $[M+H]^+$. HRMS: calcd for $C_{16}H_{27}O_3$: 295.1729 $[M+H]^+$, found: 295.1729.

exo-**3e**: Colorless crystals. Mp 52.0–53.2 °C. IR (KBr) ν cm^{-1}: 1766. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.06 (6H, s), 0.87 (9H, s), 1.50 (2H, br s), 2.40 (1H, dd, J=8.1, 2.2 Hz), 2.62 (1H, br d, J=8.1 Hz), 2.88 (1H, br s), 3.24 (1H, br s), 3.67 (1H, dd, J=11.0, 2.8 Hz), 3.82 (1H, dd, J=11.0, 3.2 Hz), 4.16–4.19 (1H, m), 6.18 (1H, dd, J=5.6, 3.0 Hz), 6.22 (1H, dd, J=5.6, 3.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: −5.5, −5.5, 18.2, 25.8, 43.6, 44.6, 46.5, 47.5, 49.1, 65.0, 83.5, 137.5, 137.8, 177.5. ESI-MS (*m/z*): 295 $[M+H]^+$. HRMS: calcd for $C_{16}H_{27}O_3$: 295.1729 $[M+H]^+$, found: 295.1715.

3.2.6. (1*S,2*R**,6*R**,7*R**,8*R**)-6-Methyl-4-oxatricyclo-[6.2.1.0^{2,7}]undec-9-en-3-one (*endo-cis*-3f), (1*R**,2*S**,6*R**,7*S**,8*S**)-6-methyl-4-oxatricyclo[6.2.1.0^{2,7}]undec-9-en-3-one (*endo-trans*-3f), and (1*R**,2*R**,7*R**,8*S**)-6-methyl-4-oxatricyclo[6.2.1.0^{2,7}]undec-9-en-3-one (*exo*-3f).** *endo-cis*-**3f**: Colorless crystals. Mp 68.9–69.0 °C. IR (neat) ν cm^{-1}: 1727. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.01 (3H, d, J=7.0 Hz), 1.23–1.35 (1H, m), 1.33 (1H, d, J=8.4 Hz), 1.55 (1H, dt, J=8.4, 1.8 Hz), 2.20 (1H, td, J=10.7, 3.9 Hz), 2.92 (1H, dd, J=6.5, 3.9 Hz), 3.01 (1H, br s), 3.34 (1H, br s), 3.81 (1H, dd, J=11.0, 10.8 Hz), 4.00 (1H, dd, J=10.8, 3.6 Hz), 6.05 (1H, dd, J=5.7, 3.0 Hz), 6.28 (1H, dd, J=5.7, 2.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 15.6, 33.2, 43.1, 44.0, 45.5, 46.9, 48.1, 73.0, 135.0, 138.0, 174.4. ESI-MS *m/z*: 179 $[M+H]^+$. HRMS: calcd for $C_{11}H_{15}O_2$: 179.1072 $[M+H]^+$, found: 179.1057.

endo-trans-**3f**: Colorless crystals. Mp 49.5–49.8 °C. IR (neat) ν cm^{-1}: 1735. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.00 (3H, d, J=7.0 Hz), 1.39 (1H, d, J=8.7 Hz), 1.53 (1H, dt, J=8.7, 1.7 Hz), 2.26–2.40 (1H, m), 2.60 (1H, ddd, J=9.4, 6.5, 3.1 Hz), 3.08 (1H, br s), 3.11 (1H, dd, J=9.4, 4.4 Hz), 3.33 (1H, br s), 3.88–3.99 (2H, m), 6.23 (2H, br s). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 14.2, 29.1, 42.3, 43.1, 45.4, 47.4, 51.1, 71.5, 135.7, 136.6, 173.4. ESI-MS (*m/z*): 179 $[M+H]^+$. HRMS: calcd for $C_{11}H_{15}O_2$: 179.1072 $[M+H]^+$, found: 179.1058.

exo-**3f**: Colorless crystals. Mp 31.1–33.1 °C. IR (neat) ν cm^{-1}: 1736. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.07 (3H, d, J=6.2 Hz), 1.26 (1H, d, J=8.9 Hz), 1.41 (1H, br d, J=8.9 Hz), 1.45–1.63 (2H, m), 2.25 (1H, dd, J=8.9, 1.7 Hz), 2.78 (1H, br s), 3.46 (1H, br s), 3.80 (1H, t, J=10.6 Hz), 4.12 (1H, dd, J=5.6, 3.1 Hz), 6.16 (1H, dd, J=5.6, 3.0 Hz), 6.19 (1H, dd, J=5.6, 2.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 16.2, 34.7, 42.3, 44.6, 45.0, 45.9, 46.0, 72.4, 135.4, 137.6, 174.5. ESI-MS (*m/z*): 179 $[M+H]^+$. HRMS: calcd for $C_{11}H_{15}O_2$: 179.1072 $[M+H]^+$, found: 179.1064.

3.2.7. (1*S,2*R**,7*R**,8*R**)-5-Methyl-4-oxatricyclo-[6.2.1.0^{2,7}]undec-9-en-3-one (*endo*-3g), (1*S**,2*R**,5*R**,7*R**,8*S**)-5-methyl-4-oxatricyclo[6.2.1.0^{2,7}]undec-9-en-3-one (*exo-cis*-3g), and (1*R**,2*S**,5*R**,7*S**,8*R**)-5-methyl-4-oxatricyclo[6.2.1.0^{2,7}]undec-9-en-3-one (*exo-trans*-3g).** *endo*-**3g** (as an mixture of two diastereomers): IR (neat) ν cm^{-1}: 1721. ^1H NMR (400 MHz, $CDCl_3$) δ: for *endo-cis*-**3g** 1.30–1.45 (2H, m), 1.36 (3H, d, J=6.7 Hz), 1.46–1.62 (1H, m), 1.87 (1H, ddd, J=14.0, 7.0, 3.2 Hz), 2.65–2.78 (1H, m), 2.93 (1H, br s), 2.85–3.00 (1H, dd, J=10.0, 4.0 Hz), 3.38 (1H, br s), 4.47–4.59 (1H, m), 6.13 (1H, dd, J=5.6 Hz), 6.28 (1H, dd, J=5.6 Hz); for *endo-trans*-**3g** 1.25 (3H, d, J=6.3 Hz), 1.94 (1H, dd, J=13.7, 6.9 Hz), 4.20–4.30 (1H, m), 6.04 (1H, dd, J=5.6, 3.0 Hz). Other signals could not be assigned through peak overlapping. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: for *endo-cis*-**3g** 20.7, 32.0, 34.9, 42.8, 46.1, 46.2, 48.6, 74.7, 135.4, 137.6, 173.7; for *endo-trans*-**3g** 21.0, 35.1, 38.6, 42.9, 45.4, 45.4., 48.3, 75.1, 134.9, 138.2, 174.5. ESI-MS (*m/z*): 179 $[M+H]^+$. HRMS: calcd for $C_{11}H_{15}O_2$: 179.1072 $[M+H]^+$, found: 179.1051. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.03; H, 7.83.

exo-trans-**3g**: Colorless oil. IR (neat) ν cm^{-1}: 1724. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.36 (3H, d, J=6.8 Hz), 1.40 (1H, d, J=9.4 Hz), 1.32–1.43 (1H, m), 1.55–1.68 (1H, m), 1.98–2.12 (1H, m), 2.22–2.30 (1H, m), 2.66 (1H, br s), 3.47 (1H, br s), 4.65–4.74 (1H, m), 6.17 (1H, dd, J=5.6, 2.9 Hz), 6.21 (1H, dd, J=5.6, 3.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 19.6, 33.7, 33.8, 42.4, 44.4, 46.4, 46.6, 74.3, 135.7, 137.6, 173.9. ESI-MS (*m/z*): 179 $[M+H]^+$. HRMS: calcd for $C_{11}H_{15}O_2$: 179.1072 $[M+H]^+$, found: 179.1069.

exo-cis-**3g**: Colorless crystals. Mp 30.0–30.5 °C. IR (KBr) ν cm^{-1}: 1723. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.36 (3H, d, J=6.3 Hz), 1.10–1.44 (3H, m), 1.95–2.06 (1H, m), 2.12 (1H, dd, J=13.8, 7.2 Hz), 2.22 (1H, dd, J=9.4, 1.6 Hz), 2.67 (1H, br s), 3.47 (1H, br s), 4.22–4.33 (1H, m), 6.15 (1H, dd, J=5.5, 3.0 Hz), 6.19 (1H, dd, J=5.5, 2.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.1, 36.9, 37.9, 42.3, 44.5, 46.1, 46.2, 74.6, 135.5, 137.7, 174.7. ESI-MS (*m/z*): 179 $[M+H]^+$. HRMS: calcd for $C_{11}H_{15}O_2$: 179.1072 $[M+H]^+$, found: 179.1063.

3.2.8. (1*S,2*S**,7*S**,8*S**,9*R**)-7-Methyl-4-oxatricyclo-[7.2.1.0^{2,8}]dodec-10-en-3-one (*endo-cis*-3h), (1*R**,2*R**,**

7*S,8*R**,9*S**)-7-methyl-4-oxatricyclo[7.2.1.0^{2,8}]dodec-10-en-3-one (*endo-trans*-3h), and (1*R**,2*S**,8*S**,9*S**)-7-methyl-4-oxatricyclo[7.2.1.0^{2,8}]dodec-10-en-3-one (*exo*-3h).** *endo-cis*-**3h**: Colorless crystals. Mp 50.0–50.9 °C. IR (KBr) ν cm^{-1}: 1725. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (3H, d, J=6.1 Hz), 1.09–1.23 (2H, m), 1.30 (1H, d, J=8.5 Hz), 1.51 (1H, d, J=8.5 Hz), 1.97–2.11 (2H, m), 2.92 (1H, br s), 3.15 (1H, br s), 3.30 (1H, dd, J=9.9, 3.5 Hz), 4.14 (1H, dd, J=12.5, 6.6 Hz), 4.32 (1H, td, J=12.5, 3.3 Hz), 6.04 (1H, dd, J=5.7, 2.9 Hz), 6.42 (1H, dd, J=5.7, 2.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 19.8, 31.4, 35.0, 45.0, 45.2, 46.8, 47.5, 49.1, 64.5, 132.2, 138.1, 175.0. ESI-MS (*m*/*z*): 193 $[M+H]^+$. HRMS: calcd for $C_{12}H_{17}O_2$: 193.1229 $[M+H]^+$, found: 193.1235. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.71; H, 8.39.

endo-trans-**3h**: Colorless crystals. Mp 119.5–120.2 °C. IR (KBr) ν cm^{-1}: 1723. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81 (3H, d, J=7.7 Hz), 1.40 (1H, d, J=8.3 Hz), 1.52 (1H, br d, J=8.5 Hz), 1.84–1.95 (2H, m), 2.37–2.44 (1H, m), 2.73 (1H, dt, J=11.1, 3.5 Hz), 2.82 (1H, br s), 3.12 (1H, br s), 3.34 (1H, dd, J=11.1, 3.5 Hz), 4.26 (1H, dd, J=12.8, 6.8 Hz), 4.47 (1H, td, J=12.8, 5.1 Hz), 6.08 (1H, dd, J=5.6, 3.0 Hz), 6.37 (1H, dd, J=5.6, 3.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.3, 31.4, 35.3, 44.8, 45.0, 46.6, 47.8, 50.9, 66.2, 135.2, 135.7, 176.1. ESI-MS (*m*/*z*): 193 $[M+H]^+$. HRMS: calcd for $C_{12}H_{17}O_2$: 193.1229 $[M+H]^+$, found: 193.1210. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.72; H, 8.42.

exo-**3h**: Colorless oil. IR (neat) ν cm^{-1}: 1732. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.05 (3H, d, J=6.2 Hz), 1.19 (1H, ddd, J=13.9, 10.2, 4.0 Hz), 1.37–1.48 (2H, m), 1.49 (1H, d, J=8.9 Hz), 1.49–1.62 (1H, m), 2.12–2.23 (1H, m), 2.59 (1H, d, J=10.2 Hz), 2.91 (1H, br s), 3.31 (1H, br s), 4.15 (1H, dd, J=12.5, 6.9 Hz), 4.27 (1H, td, J=12.5, 4.0 Hz), 6.16 (1H, dd, J=5.6, 3.0 Hz), 6.23 (1H, dd, J=5.6, 3.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 19.8, 31.4, 35.9, 43.7, 44.0, 44.7, 46.5, 47.4, 64.3, 136.3, 139.3, 176.3. ESI-MS (*m*/*z*): 193 $[M+H]^+$. HRMS: calcd for $C_{12}H_{17}O_2$: 193.1229 $[M+H]^+$, found: 193.1229.

3.2.9. (1*S,2*S**,5*R**,8*S**,9*R**)-5-Methyl-4-oxatricyclo-[7.2.1.0^{2,8}]dodec-10-en-3-one (*endo-cis*-3i), (1*R**,2*R**,5*R**,8*R**,9*S**)-5-methyl-4-oxatricyclo[7.2.1.0^{2,8}]dodec-10-en-3-one (*endo-trans*-3i), and (1*R**,2*S**,8*S**,9*S**)-5-methyl-4-oxatricyclo[7.2.1.0^{2,8}]dodec-10-en-3-one (*exo*-3i).** *endo-cis*-**3i**: Colorless crystals. Mp 60.0–60.6 °C. IR (KBr) ν cm^{-1}: 1712. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.03–1.17 (1H, m), 1.34 (1H, d, J=8.4 Hz), 1.51 (3H, d, J=7.2 Hz), 1.49–1.59 (2H, m), 1.75–1.84 (1H, m), 1.96–2.06 (1H, m), 2.42 (1H, ddt, J=13.0, 10.2, 2.9 Hz), 2.74 (1H, br s), 3.13 (1H, br s), 3.25 (1H, dd, J=10.2, 3.5 Hz), 4.49 (1H, qdd, J=7.2, 7.0, 4.0 Hz), 6.05 (1H, dd, J=5.6, 3.0 Hz), 6.40 (1H, J=5.6, 2.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 22.6, 29.0, 32.9, 41.3, 45.5, 47.7, 48.7, 51.9, 75.3, 133.6, 137.7, 176.3. ESI-MS (*m*/*z*): 193 $[M+H]^+$. HRMS: calcd for $C_{12}H_{17}O_2$: 193.1229 $[M+H]^+$, found: 193.1222.

endo-trans-**3i**: Colorless crystals. Mp 104.5–105.2 °C. IR (KBr) ν cm^{-1}: 1725. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02–1.04 (1H, m), 1.32 (3H, d,J=6.2 Hz), 1.30–1.36 (1H, m), 1.49 (1H, br d, J=8.4 Hz), 1.58–1.74 (3H, m), 2.26–2.36 (1H, m), 2.75 (1H, br s), 3.16 (1H, br s), 3.26 (1H, dd, J=10.0, 3.6 Hz), 4.49–4.62 (1H, m), 6.00 (1H, dd, J=5.6, 3.0 Hz), 6.41 (1H, dd, J=5.6, 2.9 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 20.9, 26.8, 33.8, 40.6, 45.5, 47.3, 48.3, 49.9, 72.3, 133.0, 137.8, 174.5. ESI-MS (*m*/*z*): 193 $[M+H]^+$. HRMS: calcd for $C_{12}H_{17}O_2$: 193.1229 $[M+H]^+$, found: 193.1214.

exo-**3i**: Colorless crystals. Mp 30.0–31.0 °C. IR (KBr) ν cm^{-1}: 1728. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.29–1.42 (1H, m), 1.34 (3H, d, J=6.2 Hz), 1.44 (1H, dt, J=9.2, 1.7 Hz), 1.52–1.58 (1H, m), 1.62–1.82 (3H, m), 1.83–1.89 (1H, m), 2.51–2.59 (1H, m), 2.56 (1H, br s), 3.32 (1H, br s), 4.47–4.56 (1H, m), 6.12 (1H, dd, J=5.7, 3.0 Hz), 6.27 (1H, dd, J=5.7, 3.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 20.7, 28.1, 34.1, 40.2, 44.8, 45.0, 47.9, 48.3, 72.4, 135.5, 139.5, 175.8. ESI-MS (*m*/*z*): 193 $[M+H]^+$. HRMS: calcd for $C_{12}H_{17}O_2$: 193.1229 $[M+H]^+$, found: 193.1239.

3.3. The structure determination of *endo*/*exo*-3e and *endo-cis*-3h

3.3.1. (1*S,2*R**,5*S**,6*S**,7*R**)-5-(Hydroxymethyl)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-en-3-one and (1*R**,2*R**,5*S**,6*S**,7*S**)-5-(hydroxymethyl)-4-oxatricyclo[5.2.1.0^{2,6}]-dec-8-en-3-one.** To a solution of pure *endo*-**3e** (88.7 mg, 0.30 mmol) in THF (0.4 mL), tetrabutylammonium fluoride (TBAF, 0.62 mL, 1.0 M solution in THF, 0.62 mmol) was added dropwise at 0 °C, and then stirred for 3 h at the same temperature. The reaction mixture was poured into H_2O (5 mL), and extracted with EtOAc (10 mL×3). The organic layer was dried over anhydrous $MgSO_4$, and the filtrate was evaporated. The residue was purified by column chromatography (hexane/EtOAc=2:1) to give (1*S**,2*R**,5*S**,6*S**,7*R**)-5-(hydroxymethyl)-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (41.1 mg, 0.23 mmol, 76% yield) as a single diastereomer. Under the same conditions, (1*R**,2*R**,5*S**,6*S**,7*S**)-isomer was also obtained from pure *exo*-**3e** in 84% yield. The structures both (1*S**,2*R**,5*S**,6*S**,7*R**)-isomer and (1*R**,2*R**,5*S**,6*S**,7*S**)-isomer were confirmed by comparison of spectrum data with the authentic samples, respectively.[3d]

3.3.2. (1*S,2*S**,3*S**,4*R**)-*N*-(4-Bromophenyl)-3-[(2*R**)-2-hydroxypropyl]bicyclo[2.2.1]hept-5-ene-2-carboxamide.** To a solution of *p*-bromoaniline (119 mg, 0.69 mmol) in toluene (0.3 mL), Me_3Al (1.05 M in hexane, 0.66 mL, 0.69 mmol) was added at 0 °C. After being stirred at room temperature for 30 min, this mixture was treated with a solution of *endo-cis*-**3h** (40.0 mg, 0.23 mmol) in toluene (0.5 mL) at room temperature for 3 h. Reaction mixture was quenched with 1 M HCl (10 mL), extracted with EtOAc (10 mL×3), and dried over $MgSO_4$. After evaporation of the combined organic layers, the residue was purified by silica gel column chromatography (hexane/EtOAc=2:1) and additional recrystallization to give (1*S**,2*S**,3*S**,4*R**)-*N*-(4-bromophenyl)-3-[(2*R**)-2-hydroxypropyl]bicyclo[2.2.1]-hept-5-ene-2-carboxamide (77.0 mg, 0.22 mmol, 96% yield) as colorless crystals. To determine relative stereochemistry of *endo-cis*-**3h**, this compound was submitted to the X-ray crystallographic analysis.[21] Mp 174.8 °C. IR (KBr) ν cm^{-1}: 3451, 1668. ^{1}H NMR (400 MHz, methanol-d_4) δ: 1.17 (3H, d, J=6.2 Hz), 1.29–1.52 (4H, m), 2.64–2.74 (1H, m), 2.89

(1H, br s), 3.04 (1H, br s), 3.17 (1H, dd, J=10.1, 3.1 Hz), 3.73 (1H, sex., J=6.2 Hz), 6.15 (1H, dd, J=5.6, 3.0 Hz), 6.40 (1H, dd, J=5.6, 3.0 Hz), 7.42–7.52 (4H, m). ^{13}C NMR (100.6 MHz, methanol-d_4) δ: 23.7, 41.0, 43.5, 48.7, 48.7, 50.5, 51.6, 68.1, 117.4, 123.0, 133.0, 134.3, 137.8, 139.6, 174.7. ESI-MS (m/z): 350 $[M+H]^+$. HRMS: calcd for $C_{17}H_{20}BrNO_2$: 350.0756 $[M+H]^+$, found: 350.0764. Anal. Calcd for $C_{17}H_{20}BrNO_2$: C, 58.13; H, 5.76; N, 4.00. Found: C, 57.95; H, 5.86; N, 3.71.

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19. In this paper, composition and catalyst loading of Lewis acid was generally showed as 'Tf_2CH_2+$x$$Me_3Al$' ($y$ mol %), which means the use of Lewis acid system derived from the reaction of y mol % of Tf_2CH_2 and xy mol % of Me_3Al.
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23. In this paper, *endo*-cis isomers mean *endo* adducts having relative cis-relationship between angular hydrogen and pendant methyl group on lactone structure; *endo*-trans isomers mean the *endo* adducts having trans-relationship between angular hydrogen and pendant methyl group.
24. To check interposition of the retro DA reaction and the direct epimerization reaction of chiral center, *endo-cis*-**3i**, *endo-trans*-**3i**, and *endo-cis*-**3g** were treated by 30 mol % of 'Tf_2CH_2+2.0Me_3Al' at 60 °C, respectively. According to the results, retro DA reaction and the direct epimerization reaction were not observed in each reaction. These results strongly indicated that the *endo* adducts are kinetically favored products in the present DA reaction.
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