

# Development of effective Lewis acids for the catalytic Diels–Alder reaction of $\alpha,\beta$ -unsaturated lactones with cyclopentadiene

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**Abstract**—We found that ‘ $\text{Tf}_2\text{CH}_2 + \text{Me}_3\text{Al}$ ’ systems are effective catalytic systems for the DA reaction of less reactive  $\alpha,\beta$ -unsaturated lactone derivatives, compared to  $\alpha,\beta$ -unsaturated ester derivatives, with cyclopentadiene. Mononuclear aluminum methide complex,  $\text{Tf}_2\text{CHAlMe}_2$ , as an active species is formed in these catalytic systems. Effects of lactone ring-size on the reactivity and stereoselectivity were also examined. By expanding ring-size, reactivity of  $\alpha,\beta$ -unsaturated lactones reduced but *endo*-selectivity notably increased.

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Lactone derivatives are one of the most popular compounds in nature and their clinically interesting bioactivities such as antibacterial,<sup>1</sup> cytotoxic<sup>2</sup> and immunosuppressive activities<sup>3</sup> have been reported. From a viewpoint of organic synthesis, lactone derivatives have also been used as useful building blocks toward efficient preparations of hydroxylated carbonyl compounds,<sup>4</sup> more complex polycyclic lactone derivatives,<sup>5</sup> or other type of compounds,<sup>6</sup> because a variety of lactones is readily available either by simple procedures or by commercial route. Although Diels–Alder (DA) reactions of  $\alpha,\beta$ -unsaturated lactones with 1,3-dienes have many advantages for the construction of polycyclic lactone frameworks,<sup>7,8</sup> it is known that the reactivity of  $\alpha,\beta$ -unsaturated lactones as dienophiles is lower than that of the corresponding acyclic  $\alpha,\beta$ -unsaturated esters.<sup>9</sup> Thus, drastic reaction conditions, such as high reaction temperature and/or high pressure, are required for smooth reaction.<sup>10</sup>

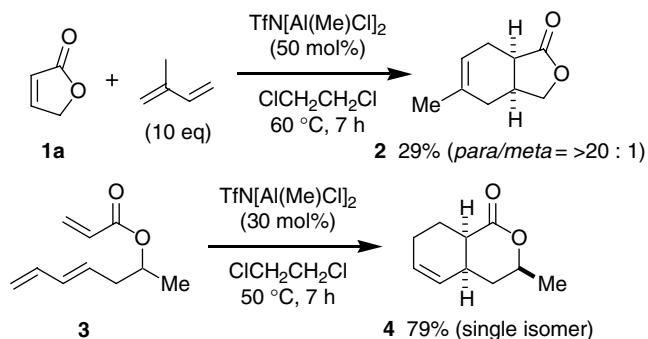
To solve such a low reactivity of  $\alpha,\beta$ -unsaturated lactones as dienophiles, we have reported that bis-aluminated triflic amides  $[\text{TfN}(\text{AlR}^1\text{R}^2)_2]$ ,  $\text{Tf} = \text{CF}_3\text{SO}_2$ , as bidentate Lewis acids, highly activate  $\alpha,\beta$ -unsaturated

lactones to efficiently promote the DA reactions under mild conditions.<sup>11,12</sup> Generally, Lewis basicity of a lactone conformationally locked in cisoid form is stronger than that of the corresponding acyclic ester. This enhanced basicity of lactones often causes high catalyst loading (generally, more than a stoichiometric amount) in the Lewis acid-mediated reactions.<sup>13</sup> Similar tendency was also observed in our previous work. Thus, the *intermolecular* DA reaction of  $\gamma$ -crotonolactone **1a** with isoprene in the presence of sub-stoichiometric amount (50 mol %) of  $\text{TfN}[\text{Al}(\text{Me})\text{Cl}]_2$  gave DA product **2** in poor yield, although catalytic amount (30 mol %) of  $\text{TfN}[\text{Al}(\text{Me})\text{Cl}]_2$  could efficiently promote the *intramolecular* DA reaction of ester-tethered 1,7,9-triene **3** to give cyclized product **4** in good yield under mild conditions (Scheme 1).<sup>14,15</sup>

To develop a sterically bulky and strong Lewis acid effective for both high activation of  $\alpha,\beta$ -unsaturated lactones and low catalyst loading, we planned to use bis(trifluoromethanesulfonyl)methane ( $\text{Tf}_2\text{CH}_2$ ,  $\text{p}K_{\text{a}} = -1$ ) as a Lewis acid ligand.<sup>16</sup> It was reported that compared to  $\text{Me}_3\text{SiOTf}$ , trimethylsilylated analogues of  $\text{Tf}_2\text{NH}$  and  $\text{Tf}_2\text{CHC}_6\text{F}_5$  activate  $\alpha,\beta$ -unsaturated aldehydes more strongly due to the steric bulk of these ligands.<sup>17</sup> However, to the best of our knowledge, the reaction of  $\text{Tf}_2\text{CH}_2$  with alkylaluminums and synthetic application of the resultant aluminum methide complexes have not been reported. Herein, we disclose that in the presence of excess of  $\text{Me}_3\text{Al}$  mononuclear

**Keywords:** Lewis acid; Bis(trifluoromethanesulfonyl)methane; Diels–Alder reaction;  $\alpha,\beta$ -Unsaturated lactones.

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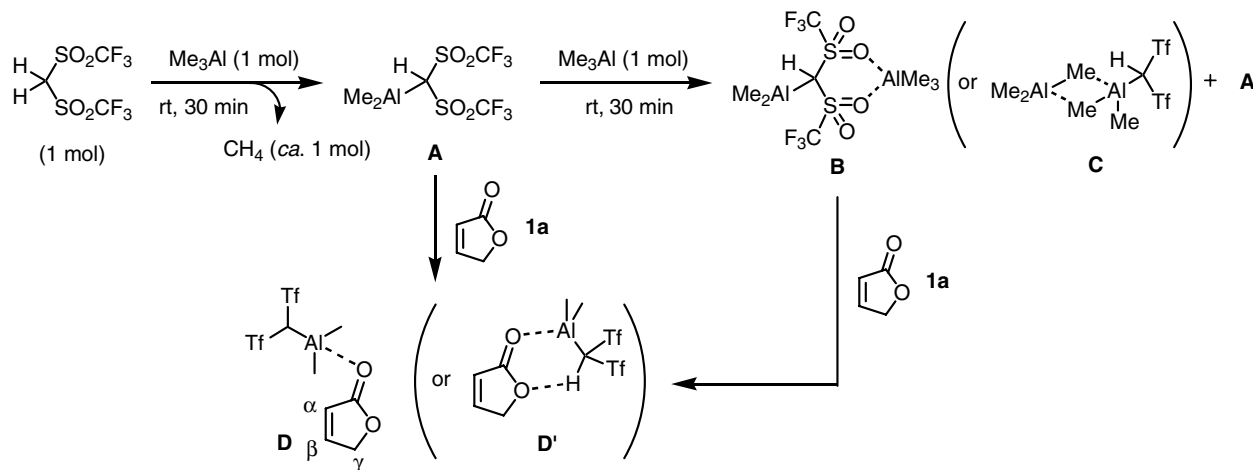
Scheme 1.

aluminum methide,  $\text{Tf}_2\text{CHAlMe}_2$ , generated by simply mixing  $\text{Tf}_2\text{CH}_2$  and  $\text{Me}_3\text{Al}$  can efficiently catalyze the DA reaction of  $\alpha,\beta$ -unsaturated lactones with cyclopentadiene (CP).

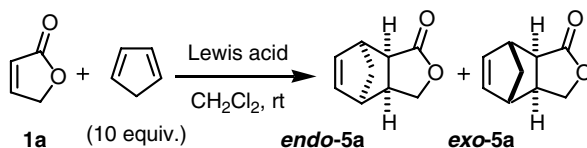
Since the formation of aluminum methide through the reaction of carbon acids with alkylaluminum reagents was not reported, we examined the reaction of  $\text{Tf}_2\text{CH}_2$  with  $\text{Me}_3\text{Al}$ . As shown in Scheme 2, treatment of  $\text{Tf}_2\text{CH}_2$  (1 mol) with  $\text{Me}_3\text{Al}$  (1 mol) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 30 min liberated 1 mol of methane gas. Further addition of  $\text{Me}_3\text{Al}$  (1 mol) to this reaction mixture resulted in no liberation of gas. In a separate experiment, when to a solution of 1 mol of  $\text{Tf}_2\text{CH}_2$  in  $\text{CH}_2\text{Cl}_2$ , 2 moles of  $\text{Me}_3\text{Al}$  were added in one-portion at room temperature, almost the same result, namely, only 1 mol of methane liberation, was obtained.<sup>18</sup>  $^{13}\text{C}$  NMR spectrum (100 MHz) of a 1:1.1 mixture of  $\text{Tf}_2\text{CH}_2$  and  $\text{Me}_3\text{Al}$  in  $\text{CDCl}_3$  at room temperature showed clean formation of the single complex (−10.9 ppm, 47.9 ppm and 119.6 ppm) with complete consumption of  $\text{Tf}_2\text{CH}_2$ .<sup>19</sup> On the other hand,  $^{13}\text{C}$  NMR spectrum of a 1:2 mixture of  $\text{Tf}_2\text{CH}_2$  and  $\text{Me}_3\text{Al}$  showed two kinds of the complexes, that is, major one is the same as above and the other newly formed complex has the signal of  $\text{CF}_3$  moiety at 119.8 ppm. In  $^1\text{H}$  NMR spectrum, a 1:1.1 mixture of  $\text{Tf}_2\text{CH}_2$  and  $\text{Me}_3\text{Al}$  showed two sharp peaks at 4.42 ppm ( $\text{Tf}_2\text{CH}$ ) and −0.53 ppm ( $\text{AlCH}_3$ ).

Up-field shifts of  $\text{Tf}_2\text{C}$  carbon by 16.3 ppm and  $\text{Tf}_2\text{CH}$  proton by 0.54 ppm possibly indicate the formation of  $\text{Tf}_2\text{CHAlMe}_2$  **A** having a carbon–aluminum bond.<sup>20</sup> NMR study of the complex derived from the present aluminum methide **A** and  $\gamma$ -crotonolactone **1a** would provide further information of the structure of the complex and Lewis acidity of **A**. Thus, a mixture of **1a** and aluminum methide **A** (1.0 equiv) in  $\text{CDCl}_3$  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.<sup>21</sup> Compared to crotonolactone **1a**, complex **D** (or **D'**) showed down-field shifts of carbonyl,  $\beta$ - and  $\gamma$ -carbons by 9.6, 11.3, and 7.2 ppm, respectively, and up-field shift of  $\alpha$ -carbon by 1.4 ppm in  $^{13}\text{C}$  NMR spectrum.<sup>22</sup> In the case of a mixture of **1a** and ' $\text{Tf}_2\text{CH}_2 + 2.0\text{Me}_3\text{Al}$ ' system, essentially the same peaks were observed in  $^{13}\text{C}$  NMR spectrum. These data may indicate the dissociation of  $\text{Me}_3\text{Al}$  from the complex possibly such as **B** or **C** by Lewis basic  $\gamma$ -crotonolactone **1a**. Since the chemical shift difference between  $\text{C}\beta$  and  $\text{C}\alpha$  reflects the reactivity as a dienophile, the observed  $\Delta\text{C}\beta\text{-C}\alpha$  value (43.9 ppm) in  $\text{Tf}_2\text{CHAlMe}_2\text{-1a}$  complex also means significantly high activation of **1a** by  $\text{Tf}_2\text{CHAlMe}_2$ , compared to the use of 1.1 equiv of  $\text{Me}_3\text{Al}$  ( $\Delta\text{C}\beta\text{-C}\alpha = 38.0$  ppm).

To find out the efficiency of  $\text{Tf}_2\text{CHAlMe}_2$ , reaction of  $\gamma$ -crotonolactone **1a** with CP was conducted in the presence of a mixture of  $\text{Tf}_2\text{CH}_2$  and  $\text{Me}_3\text{Al}$  in a various ratio. These results are summarized in Table 1. As shown in entry 1, catalytic amount of  $\text{Tf}_2\text{CHAlMe}_2$  (20 mol %), which was generated from a 1:1 mixture of  $\text{Tf}_2\text{CH}_2$  and  $\text{Me}_3\text{Al}$ , catalyzed the reaction to give cycloadduct **5a** in 52% yield after 8 h. A 1:1 mixture of  $\text{Tf}_2\text{CH}_2$  and  $i\text{-Bu}_2\text{AlH}$  instead of  $\text{Me}_3\text{Al}$  did not promote the DA reaction (entry 2). The use of a 1:2 mixture of  $\text{Tf}_2\text{CH}_2$  and  $\text{Me}_3\text{Al}$  remarkably increased the yield of **5a** to 89% only after 4 h (entry 3). Catalyst loading of ' $\text{Tf}_2\text{CH}_2 + 2.0\text{Me}_3\text{Al}$ ' system could be reduced to 10 mol % without significant decrease in the yield of **5a** (entries 6, 7).



Scheme 2.

**Table 1.** Effects of Lewis acids on DA reaction of  $\gamma$ -crotonolactone **1a** with CP

Entry	Lewis acid (mol %)	Solvent	Time (h)	Yield <sup>a</sup> (%)	Ratio <sup>b</sup> ( <i>endo/exo</i> )
1	Tf <sub>2</sub> CH <sub>2</sub> + 1.0Me <sub>3</sub> Al (20)	CH <sub>2</sub> Cl <sub>2</sub>	8	52	6.8:1
2	Tf <sub>2</sub> CH <sub>2</sub> + 1.0DIBAL-H (20)	CH <sub>2</sub> Cl <sub>2</sub>	12	Trace	Nd <sup>c</sup>
3	Tf <sub>2</sub> CH <sub>2</sub> + 2.0Me <sub>3</sub> Al (20)	CH <sub>2</sub> Cl <sub>2</sub>	4	89	6.8:1
4	Tf <sub>2</sub> CH <sub>2</sub> + 2.0Me <sub>3</sub> Al (20)	Toluene	5	85	6.3:1
5	Tf <sub>2</sub> CH <sub>2</sub> + 3.0Me <sub>3</sub> Al (20)	CH <sub>2</sub> Cl <sub>2</sub>	4	77	7.1:1
6	Tf <sub>2</sub> CH <sub>2</sub> + 2.0Me <sub>3</sub> Al (10)	CH <sub>2</sub> Cl <sub>2</sub>	5	83	7.8:1
7	Tf <sub>2</sub> CH <sub>2</sub> + 2.0Me <sub>3</sub> Al (5)	CH <sub>2</sub> Cl <sub>2</sub>	5	33	7.9:1
8	None	Toluene	14	0	—
9 <sup>d</sup>	TfN(Al <i>i</i> -Bu) <sub>2</sub> (110)	Toluene	13	97	5.5:1
10	Me <sub>3</sub> Al (40)	CH <sub>2</sub> Cl <sub>2</sub>	8	21	9.7:1

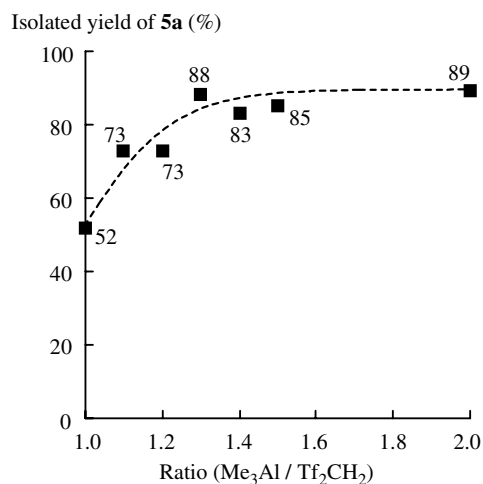
<sup>a</sup> Isolated yield.<sup>b</sup> Determined by <sup>1</sup>H NMR.<sup>c</sup> Not determined.<sup>d</sup> Ref. 12.

To check the effects of an excess amount of Me<sub>3</sub>Al over Tf<sub>2</sub>CH<sub>2</sub>, the DA reaction of **1a** was conducted in the presence of only Me<sub>3</sub>Al (40 mol %) for 8 h, but the yield of **5a** was only 21% (entry 10, *endo/exo* = 9.7:1). This result indicated that catalytic amount of Me<sub>3</sub>Al does not effectively catalyze the DA reaction of **1a**. Without an addition of Lewis acid DA product **5a** was not obtained after stirring for 14 h (entry 8). While we have reported that bidentate Lewis acid, TfN(Al*i*-Bu)<sub>2</sub>, promoted the DA reaction of **1a** with CP, 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 9).<sup>12</sup>

Further study was made to examine the effect of a ratio of Tf<sub>2</sub>CH<sub>2</sub> (20 mol %) and Me<sub>3</sub>Al on the yield of **5a**. Results are shown in Figure 1 by plotting the yield of **5a** on *y* axis and the molar ratio of Tf<sub>2</sub>CH<sub>2</sub> and Me<sub>3</sub>Al on the *x* axis. Interestingly, when the ratio of Tf<sub>2</sub>CH<sub>2</sub> and Me<sub>3</sub>Al was between 1.3 and 2.0, very little difference in the product yield was observed keeping in a range of 83–89% yield. As a ratio of Tf<sub>2</sub>CH<sub>2</sub> and Me<sub>3</sub>Al decreased to 1.2 and 1.0, the yield of **5a** was gradually lowered to 73% and 52%, respectively.

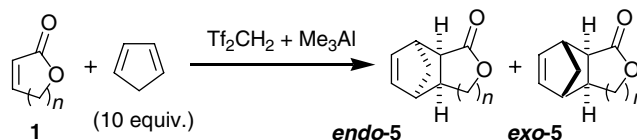
As shown above, in the presence of 20 mol % of 'Tf<sub>2</sub>CH<sub>2</sub> + 1.3Me<sub>3</sub>Al' system,  $\gamma$ -crotonolactone **1a** smoothly reacted with CP to give cycloadduct **5a** in 88% yield with high *endo* selectivity (*endo/exo* = 8.3:1, see also Table 2, entry 1). Under the similar conditions, the use of Tf<sub>2</sub>CHMe instead of Tf<sub>2</sub>CH<sub>2</sub> reduced the yield of **5a** to 76% (*endo/exo* = 8.1:1, entry 2).<sup>21</sup>

Next, to see the scope of the present Lewis acid systems for the catalytic DA reaction of  $\alpha,\beta$ -unsaturated lactones, we examined the reaction of various lactone substrates. Reactivity and *endo/exo* selectivity were found to depend on the ring size of the lactone used (Table 2). Compared to  $\gamma$ -butenolide **1a**, the reactivity of  $\delta$ -

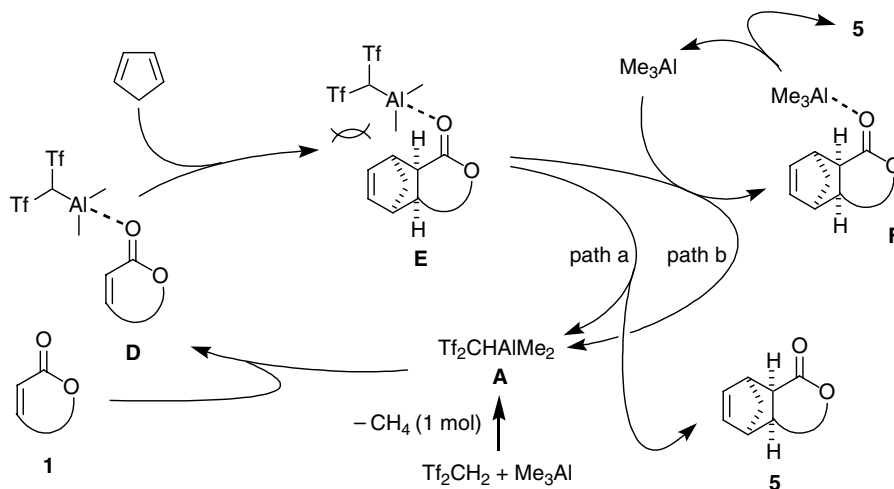


**Figure 1.** The plots of the yield and the composition of Lewis acid (molar ratio of Me<sub>3</sub>Al and Tf<sub>2</sub>CH<sub>2</sub>) in the DA reaction of **1a** with CP. In the presence of 20 mol % Lewis acid generated by mixing Tf<sub>2</sub>CH<sub>2</sub> and Me<sub>3</sub>Al,  $\gamma$ -crotonolactone **1a** (0.5 mmol scale) was treated with CP (10 equiv) at room temperature for 2–4 h.

pentenolide **1b** decreased so much that a higher reaction temperature was needed to obtain the DA adduct **5b** within a short reaction time. Thus, in the presence of 20 mol % of 'Tf<sub>2</sub>CH<sub>2</sub> + 1.3Me<sub>3</sub>Al' system, the reaction of **1b** with CP (10 eq) for 4 h at 60 °C afforded DA product **5b** in 76% yield with high *endo* selectivity (*endo/exo* = 14:1, entry 3). The use of 'Tf<sub>2</sub>CH<sub>2</sub> + 2.0Me<sub>3</sub>Al' system resulted in a better yield of product **5b**, but lower *endo/exo* selectivity was observed (81% yield, *endo/exo* = 9.4, entry 4). Furthermore, 7-membered  $\alpha,\beta$ -unsaturated lactone **1c** was less reactive than 6-membered lactone **1b**. Thus, the reaction of **1c** with 20 molar equivalent of CP was not fully promoted by the use of 30 mol % of 'Tf<sub>2</sub>CH<sub>2</sub> + 1.3Me<sub>3</sub>Al' system to give the desired adduct **5c** in only 56% yield, but with high *endo*

**Table 2.** Effects of lactone ring-size on DA reaction with cyclopentadiene


Entry	<b>1</b>	Lewis acid (mol %)	Temperature (°C)	Time (h)	Solvent	<b>5</b>	Yield <sup>a</sup> (%)	ratio <sup>b</sup> ( <i>endo/exo</i> )
1	<b>1a</b> ( <i>n</i> = 1)	Tf <sub>2</sub> CH <sub>2</sub> + 1.3Me <sub>3</sub> Al (20)	rt	3	CH <sub>2</sub> Cl <sub>2</sub>	<b>5a</b>	88	8.3:1
2	<b>1a</b> ( <i>n</i> = 1)	Tf <sub>2</sub> CHMe + 1.3Me <sub>3</sub> Al (20)	rt	3	CH <sub>2</sub> Cl <sub>2</sub>	<b>5a</b>	76	8.1:1
3	<b>1b</b> ( <i>n</i> = 2)	Tf <sub>2</sub> CH <sub>2</sub> + 1.3Me <sub>3</sub> Al (20)	60	4	ClCH <sub>2</sub> CH <sub>2</sub> Cl	<b>5b</b>	76	14:1
4	<b>1b</b> ( <i>n</i> = 2)	Tf <sub>2</sub> CH <sub>2</sub> + 2.0Me <sub>3</sub> Al (20)	60	4	ClCH <sub>2</sub> CH <sub>2</sub> Cl	<b>5b</b>	81	9.4:1
5 <sup>c</sup>	<b>1c</b> ( <i>n</i> = 3)	Tf <sub>2</sub> CH <sub>2</sub> + 1.3Me <sub>3</sub> Al (30)	60	4	ClCH <sub>2</sub> CH <sub>2</sub> Cl	<b>5c</b>	56	17:1 <sup>d</sup>
6 <sup>c</sup>	<b>1c</b> ( <i>n</i> = 3)	Tf <sub>2</sub> CH <sub>2</sub> + 2.0Me <sub>3</sub> Al (30)	60	4	ClCH <sub>2</sub> CH <sub>2</sub> Cl	<b>5c</b>	85	21:1 <sup>d</sup>

<sup>a</sup> Isolated yield.<sup>b</sup> Determined by <sup>1</sup>H NMR.<sup>c</sup> 20 equiv of CP was used.<sup>d</sup> Determined by isolated yield.**Figure 2.** Proposed catalytic cycle on the catalytic DA reaction of  $\alpha,\beta$ -unsaturated lactones **1**.

selectivity (*endo/exo* = 17:1, entry 5). Both chemical yield and *endo/exo* selectivity were improved under ‘Tf<sub>2</sub>CH<sub>2</sub> + 2.0Me<sub>3</sub>Al’ catalyzed conditions (**5c** 85% yield, *endo/exo* = 21:1, entry 6).

Regarding the effects of a ratio of Tf<sub>2</sub>CH<sub>2</sub> and Me<sub>3</sub>Al on the efficiency of the DA reaction, we propose a catalytic cycle shown in Figure 2. Since Tf<sub>2</sub>CHAlMe<sub>2</sub> **A** readily generated by the 1:1 reaction of Tf<sub>2</sub>CH<sub>2</sub> with Me<sub>3</sub>Al would be more active than Me<sub>3</sub>Al existing together in the reaction mixture (see Table 1, entry 10), complexation between Tf<sub>2</sub>CHAlMe<sub>2</sub> **A** and  $\alpha,\beta$ -unsaturated lactone **1** promotes the DA reaction with CP to give a DA adduct **E**. Since Tf<sub>2</sub>CHAlMe<sub>2</sub> **A** has sterically bulky Tf<sub>2</sub>CH moiety as a ligand, I-strain assisted dissociation of **A** from complex **E** proceeds to give the uncomplexed product **5** directly (path a). Alternatively, dissociation of **A** from complex **E** would be promoted by the formation of thermodynamically stable complex **F** through the ligand exchange reaction, in particular in the cases where ‘Tf<sub>2</sub>CH<sub>2</sub> + 2.0Me<sub>3</sub>Al’ rather than ‘Tf<sub>2</sub>CH<sub>2</sub> + 1.3Me<sub>3</sub>Al’ worked more efficiently (path b). Thus, co-existence of Me<sub>3</sub>Al in the reaction mixture would be essential for

the efficient catalytic cycle of Tf<sub>2</sub>CHAlMe<sub>2</sub> **A** as in the cases of **1b** and **1c**.

In conclusion, we found that ‘Tf<sub>2</sub>CH<sub>2</sub> + Me<sub>3</sub>Al’ systems are effective catalysts for the DA reaction of less reactive  $\alpha,\beta$ -unsaturated lactone derivatives with CP. Mononuclear aluminum methide complex, Tf<sub>2</sub>CHAlMe<sub>2</sub>, was determined as an active species in this catalytic systems by NMR study. Effects of lactone ring-size on the reactivity and stereoselectivity were also examined. Interestingly, by increasing ring-size, reactivity of  $\alpha,\beta$ -unsaturated lactones reduced but *endo*-selectivity was notably increased. Further study on synthetic application of these small and reactive lactone derivatives is proceeding in our laboratory.

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18. For Tf<sub>2</sub>CH<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 4.96 (2H, s). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, δ ppm): 64.2, 118.8 (q, *J* = 327.8 Hz). <sup>19</sup>F NMR (386 MHz, CDCl<sub>3</sub>, δ ppm): –13.0 (6F, s). For Tf<sub>2</sub>CHAlMe<sub>2</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): –0.53 (6H, s), 4.42 (1H, s). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, δ ppm): –10.9 (br), 47.9, 119.6 (q, *J* = 319.0 Hz).
19. This is a sharp contrast to TfNH<sub>2</sub>, since reaction of TfNH<sub>2</sub> (1 mol) with Me<sub>3</sub>Al (2 mol) gave TfN(AlMe<sub>2</sub>)<sub>2</sub> with liberation of 2 moles of methane gas.
20. Previously, in the 1:2 reaction of TfNH<sub>2</sub> and Me<sub>2</sub>AlCl in CDCl<sub>3</sub>, we observed the formation of three kinds of complexes in <sup>13</sup>C NMR study.<sup>14a</sup> Jonas and co-workers also reported a rapid equilibrium of bis-silylated triflic amide between *N,N*-bis-silylated form and *N,O*-bis-silylated form. Jonas, S.; Westerhausen, M.; Simchen, G. *J. Organomet. Chem.* **1997**, *548*, 131–137.
21. Concerning this observed difference of these two Lewis acids derived from Tf<sub>2</sub>CH<sub>2</sub> or Tf<sub>2</sub>CHMe, although detail is not clear, we assume that acidic hydrogen of Tf<sub>2</sub>CHAlMe<sub>2</sub> would act as a hydrogen bond donor to form complex **D'** as shown in Figure 1. In our previous works, we have proposed double coordination manner of α,β-unsaturated lactones and esters to bidentate Lewis acids, TfN[AlR<sup>1</sup>R<sup>2</sup>]<sub>2</sub>, to explain high activation of these substrates by TfN[AlR<sup>1</sup>R<sup>2</sup>]<sub>2</sub>.<sup>12</sup>
22. For γ-crotonolactone **1a**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 4.91 (2H, m), 6.17 (1H, dt, *J* = 5.8, 2.2 Hz), 7.58 (1H, dt, *J* = 5.8, 1.6 Hz). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, δ ppm): 72.1, 121.5, 152.7, 173.6. For Tf<sub>2</sub>CHAlMe<sub>2</sub>-**1a** complex. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm, rt): –0.62 (6H, s, AlCH<sub>3</sub>), 4.09 (1H, s, Tf<sub>2</sub>CH), 5.47 (2H, s, C<sub>γ</sub>H<sub>2</sub>), 6.52 (1H, dt, *J* = 5.7, 1.8 Hz, C<sub>α</sub>H), 8.26 (br d, *J* = 5.7 Hz, C<sub>β</sub>H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, δ ppm, rt): –10.9, 51.3, 79.3, 120.1, 120.2 (q, *J* = 323.8), 164.0, 183.2.