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Intramolecular [3+2] cycloaddition reaction of α,β-enoate derivatives having allylsilane parts: 1,1′-biphenyl-2,2′-di(triflyl)amide (BIPAM)+2Me$_2$AlCl as a novel Lewis acid

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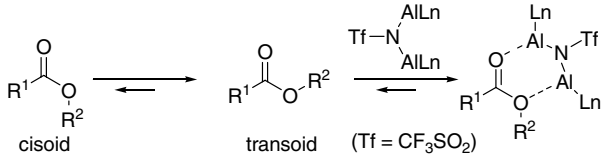
Abstract—The bidentate Lewis acid generated by mixing 1,1′-biphenyl-2,2′-di(triflyl)amide (BIPAM) and 2 M equiv of Me$_2$AlCl can efficiently promote the intramolecular [3+2] cycloaddition reaction of α,β-enoate derivatives having ester tether linking α,β-unsaturated ester and allylsilane parts.

Allylsilanes are widely used as very powerful synthons for the formation of carbon–carbon bonds in organic synthesis, since 1,2- or 1,4-additions of allylsilanes to aldehydes and α,β-unsaturated carbonyl compounds have found many applications in stereoselective synthesis.[1] In addition to such simple 1,2- and 1,4-additions, the Lewis acid mediated cycloaddition reactions of allylsilanes with electron deficient olefins have shown their potential efficiency to construct a variety of four- and five-membered carbocycles.[2–4] For example, the reaction with α,β-enone derivatives provided cyclopentane compounds in good yields and high stereoselectivities through [3+2] cycloaddition.[2] In contrast, the use of acrylate derivatives as substrates brought about competitive [2+2] and [3+2] cycloaddition.[3] Although these reactions have been well known as intermolecular reactions, as far as we know, no successful example of intramolecular version, which would be potentially efficient procedures for the preparation of bicyclic and polycyclic compounds, has been reported.[5]

As one of the straightforward procedures for the preparation of bicyclic lactones, which are important constituents of many biologically active natural products,[6,7] we have reported the intramolecular Diels–Alder (IMDA) reactions of ester-tethered ene-diene systems. It should be noted that such ester compounds, compared to the corresponding amide tethered compounds, show lower reactivity in the IMDA reaction due to the difficulty in adopting a cisoid form, in which the diene and the dienophile are in close proximity.[8,9] The fact is attributed to the steric repulsion between two alkyl substituents (R^1 and R^2) and the dipole–dipole repulsion between carbonyl and ethereal oxygen functions (Scheme 1).[10] To overcome the conformational disadvantage of the ester-tethered compounds for the IMDA reactions, we have developed the efficient IMDA reactions of 3,5-hexadienyl acrylates catalyzed by a bis-aluminated triflic amide TfN[Al(Me)Cl]$_2$. The coordination of both oxygen atoms of the ester group to the bidentate Lewis acid would be expected to control the geometry of the ester moiety to be a cisoid structure and strongly enhance the reactivity of the dienophile (Scheme 1).[11,12]



Scheme 1.

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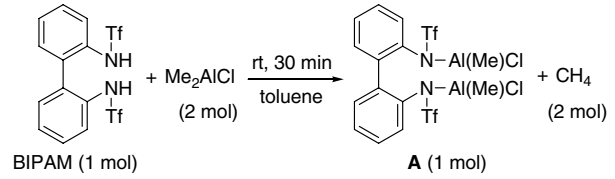
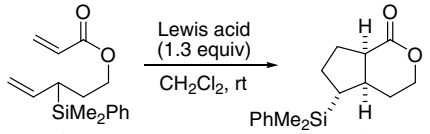
As an extension of our projects, we have examined the cycloaddition reaction of 3-trialkylsilyl-4-pentenyl α,β-enoate derivatives **1**. We found that the [3+2] cycloaddition reaction of **1** was effectively promoted by a novel bidentate Lewis acid **A** generated in situ by mixing 1,1′-biphenyl-2,2′-di(triflyl)amide (BIPAM) and 2 M equiv of Me_2AlCl (Scheme 2), and report the detail in this letter.

The cycloaddition reaction of 3-trialkylsilyl-4-pentenyl acrylate derivative **1a** as a model substrate was conducted under the various Lewis acid mediated conditions (Table 1). At the outset, treatment of **1a** with 1.3 equiv of triflic amide-based aluminated Lewis acid $TfN[Al(Me)Cl]_2$, which showed the best efficiency as the mediator for the IMDA reactions of 3,5-hexadienyl acrylates, promoted the [3+2] cycloaddition reaction in dichloromethane at room temperature for 19 h to give bicyclic lactone **2a** in 61% yield (entry 1). The reaction proceeded with high *endo* selectivity and cis-fused cycloadduct was obtained as a single isomer. As shown in entry 2, toluene was also a suitable solvent (**2a**; 66% yield). However, the use of $TfN(AlMe_2)_2$ brought about recovery of **1a** in 25% at room temperature for 22 h (entry 3) and the use of $TfN(AlCl_2)_2$ lowered the yield of adduct **2a** due to the isolation of undesirable compound (entry 4). It turned out that Me_2AlCl and $TiCl_4$ (2.6 equiv), which have been well documented as efficient Lewis acids for intermolecular cycloaddition reaction of allylsilanes,[10–12] were ineffective for the cycloaddition of **1a** (entries 5 and 6).



Scheme 2.

Table 1. Effect of Lewis acid on [3+2] cycloaddition reaction of **1a**



1a **2a**

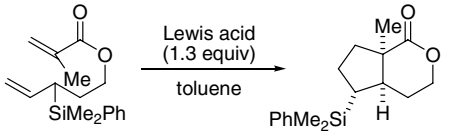
Entry	Lewis acid	Time (h)	**2a** Yield (%)[a]	Recovery of **1a** (%)[a]
1	$TfN[Al(Me)Cl]_2$	19	61	—
2[b]	$TfN[Al(Me)Cl]_2$	20	66	—
3	$TfN(AlMe_2)_2$	22	48[c]	25
4	$TfN(AlCl_2)_2$	17	38[d]	—
5[e]	Me_2AlCl	22	14[c,d]	27
6[e]	$TiCl_4$	17	23	—

[a] Isolated yield.
[b] Solvent; toluene.
[c] A considerable amount of 3-dimethylphenylsilyl-4-penten-1-ol was detected.
[d] A considerable amount of $PhMe_2SiOH$ was detected.
[e] 2.6 equiv of Lewis acid was employed.

Based on the aforementioned results of **1a**, bidentate Lewis acid $TfN[Al(Me)Cl]_2$ was applied to the [3+2] cycloaddition reaction of methacrylate **1b** (Table 2, entry 1). When the reaction of **1b** was carried out even at 50 °C for 24 h in toluene, the corresponding lactone **2b** was obtained in only 31% yield along with the recovery of **1b** (29%). Since a considerable amount of $PhMe_2SiOH$ was also detected in this reaction, it turned out that $TfN[Al(Me)Cl]_2$ is not necessarily optimal Lewis acid for the cyclization of **1b**. Further efforts to search an effective promoter made us find out 1,1′-biphenyl-2,2′-di(triflyl)amide (BIPAM) as the basic ligand in employable Lewis acid. That is, in the presence of Lewis acid **A** (Scheme 2) derived from BIPAM (1 mol) and Me_2AlCl (2 mol), the reaction of **1b** under similar conditions (50 °C, 20 h) gave lactone **2b** in 37% yield and the recovery of **1b** was good as shown in entry 2 (52% yield). Furthermore, by treatment of **1b** with 1.3 equiv of Lewis acid **A** at 80 °C, the reaction completed within 5 h to give bicyclic lactone **2a** in 65% yield with complete *endo* selectivity (entry 3). Recently, Maruoka et al. reported the utility of Lewis acid **C** derived from BIPAM and Me_3Al in a ratio of 1:1 (Scheme 3) for a synthetic example.[13] Therefore, we examined the use of Lewis acid **B** derived from BIPAM and Me_2AlCl instead of Me_3Al under the same condition. In the presence of 1.3 equiv of Lewis acid **B**, the [3+2] cycloaddition of **1b** was incomplete even at 80 °C for 22 h and the corresponding lactone **2b** was obtained in only 34% yield (Table 2, entry 4). It turned out that the use of Lewis acid **A** rather than Lewis acid **B**, a combination of BIPAM and Me_2AlCl in a ratio of 1:2, provided better results.

In Table 3, we have demonstrated the results of the [3+2] cycloaddition reactions of substituted substrates

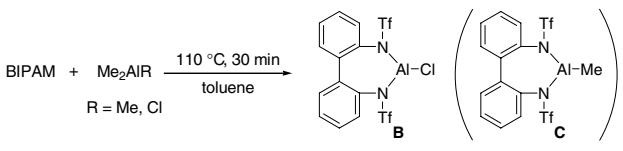
Table 2. Effect of Lewis acid on [3+2] cycloaddition reaction of **1b**



1b **2b**

Entry	Lewis acid	Temp (°C)	Time (h)	**2b** Yield (%)[a]
1	$TfN[Al(Me)Cl]_2$	50	24	31[b,c]
2	BIPAM+2Me_2AlCl (**A**)	50	20	37[d]
3	BIPAM+2Me_2AlCl (**A**)	80	5	65
4	BIPAM+Me_2AlCl (**B**)	80	22	34

[a] Isolated yield.
[b] A considerable amount of $PhMe_2SiOH$ was detected.
[c] Recovery of **1b**, 29%.
[d] Recovery of **1b**, 52%.

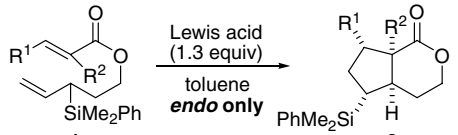


Scheme 3.

1a–**f** promoted by Lewis acid **A**. The reaction of acrylate **1a** proceeded at 50 °C giving rise to the corresponding adduct **2a** in 73% yield (entry 1) and the yield of **2a** slightly increased, compared with the use of TfN[Al(Me)Cl]$_2$ (**2a**; 66% yield, Table 1, entry 2). α-CF$_3$-substituted acrylate **1c** was consumed at room temperature to give adduct **2c** in 76% yield (entry 3), showing higher reactivity than **1a**. It is interesting to note that fumarate **1d** having the electron-withdrawing CO$_2$Et group at β-position of acrylate moiety showed lower reactivity than **1a**, although **2d** was obtained in 72% yield on heating at 80 °C for 10 h (entry 4). Furthermore, crotonate **1e** having the electron-donating group at β-position required prolonged reaction time (40 h) at 80 °C to provide adduct **2e** in 72% yield (entry 5). Unfortunately, the reaction of cinnamate **1f** as β-substituted acrylate did not afford the cyclized product even at 110 °C and recovery of the starting material was 27% (entry 6).

In all cases shown in Table 3, cis-fused adducts **2a**–**e** were obtained as a single isomer with the illustrated relative configuration.[14] The observed diastereoselectivity indicated that the [3+2] cycloaddition reaction would proceed via polar *endo*-boatlike transition state **A** (Fig. 1). This conformational preference is in accord with our previous results in the IMDA reactions of 3,5-hexadienyl acrylates affording similar cis-fused bicyclic lactone structure.[11] Since the stereochemistry between the silyl group and the carbonyl group in the cyclized product **2** is trans relationship as in the case of the intermolecular reaction of allylsilanes with α,β-enone derivatives,[2] one of the factors for *endo* selectivity could be explained by considering the polar transition state having positive charge on the silyl group and negative charge on the neighboring carbonyl group arised from coordination of Lewis acid with ester group. That is, when silyl group occupies *endo* rather than *exo* orientation toward carbonyl group, such an arrangement would minimize charge separation in polar transition state.[2a]

Table 3. Lewis acid **A** promoted [3+2] cycloaddition reaction of **1**



1 **2**

Entry	1	R^1	R^2	Temp (°C)	Time (h)	2	Yield (%)[a]
1	**1a**	H	H	50	7	**2a**	73
2	**1b**	H	Me	80	5	**2b**	65
3	**1c**	H	CF$_3$	rt	20	**2c**	76
4	**1d**	CO$_2$Et	H	80	10	**2d**	72
5	**1e**	Me	H	80	40	**2e**	72
6	**1f**	Ph	H	110	22	**2f**	—[b]

[a] Isolated yield.
[b] Recovery of **1f**, 27%.

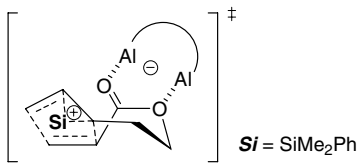


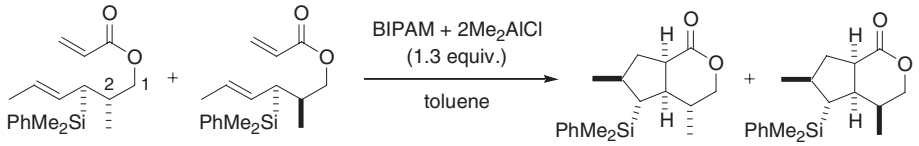
Figure 1. *endo*-Boatlike transition state **A**.

Next, by the [3+2] cycloaddition reactions of *syn*-ester **1g** and *anti*-ester **1h** having methyl group at 2-position of 4-pentenyl alcohol moiety, including allylsilane unit, we examined the substituent effect on stereospecificity and the reactivity between each diastereomer (Table 4). In the presence of Lewis acid (1.3 equiv), the reaction of a 6:1 mixture of *syn*-ester **1g** and *anti*-ester **1h** at 50 °C for 40 h was incomplete, and *syn* isomer was recovered in 22% while complete consumption of *anti* isomer (entry 1). However, at 80 °C the reaction of the same mixture smoothly proceeded to give adduct **2g** as a major isomer (entry 2, **2g** 70%, **2h** 14%). Compound **2g** was *endo*-cis isomer, which has cis relationship between Me group at 2-position and hydrogen on the ring-junction and the ratio of **2g**:**2h** (5:1) was nearly equal to the *syn*:*anti* ratio of the starting ester (6:1). On the other hand, the reaction of *anti*-ester **1h** completed at 80 °C within 3 h giving rise to *endo*-trans isomer **2h** in 76% yield as a single isomer (entry 3). Thus, the [3+2] cycloaddition reactions of **1g** and **1h** proceeded in stereospecific manner.[14] As shown in entries 4 and 5, difference of the reactivity of *syn*- and *anti*-ester was obvious. Treatment of 1:1 mixture of *syn*- and *anti*-ester at 50 °C for 26 h afforded *endo*-trans **2h** derived from *anti*-ester in 14% yield, which was 2-fold higher than that of *endo*-cis **2g** (7%), while the recovery of *syn*-ester was 24%, which was 2-fold the amount of recovered *anti*-ester (entry 4). Furthermore, when the ratio of *anti*-isomer **1h** was higher than *syn*-isomer **1g** (*syn*:*anti* = 1:4), a considerable amount of *syn*-isomer was recovered and it turned out that *anti*-isomer reacted more rapidly than *syn*-isomer (entry 5).

The present results shown in Table 4 could be explained by considering the *endo*-boatlike transition state. That is, since both **2g** and **2h** were cis-fused lactones having trans relationship between the silyl group and carbonyl group as in the cases of **2a**–**e**, the [3+2] cycloaddition reactions of **1g** and **1h** would proceed via *endo*-boatlike transition state. Taking the stereochemistry of methyl group at 2-position into account, *endo*-cis isomer **2g** would be derived from *syn*-ester **1g** via *endo*-boatlike transition state **B**, in which methyl substituent occupies a pseudo-equatorial position. On the other hand, *endo*-trans isomer **2h** would be derived from *anti*-ester **1h** via *endo*-boatlike transition state **C**, in which methyl substituent occupies a pseudo-axial position. The difference of the reactivity between *syn*- and *anti*-ester would be attributed to the steric repulsion between silyl substituent and methyl substituent at a pseudo-equatorial position in transition state **B**. In transition state **C**, since such a steric repulsion between silyl and methyl substituent would become relatively tiny, *anti*-isomer should be more reactive than *syn*-isomer.

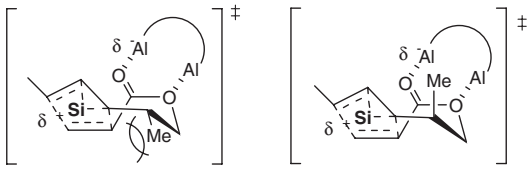
To understand the structure of Lewis acid **A**, we have examined the following experiment. As shown in

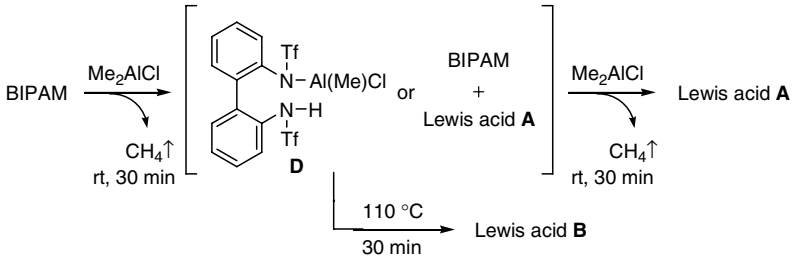
Table 4. Lewis acid **A** promoted [3+2] cycloaddition reaction of **1g**,**h**



syn **1g** ***anti*** **1h** ***endo-cis*** **2g** ***endo-trans*** **2h**

Entry	**1** (*syn* : *anti*)	Temp (°C)	Time (h)	Yield (%)[a]		Recovery (%)[a]	
				2g	**2h**	***syn***	***anti***
1	**1g** + **1h** (6 : 1)	50	40	28	9	22	0
2	**1g** + **1h** (6 : 1)	80	5	70	14	-	-
3	**1h** (*anti* only)	80	3	0	76	-	-
4	**1g** + **1h** (1 : 1)	50	26	7	14	24	12
5	**1g** + **1h** (1 : 4)	80	3	4	42	10	10



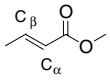


Scheme 4.

Scheme 2, treatment of BIPAM with 2 M equiv of Me_2AlCl for 30 min liberated 2 mol of gas. By the addition of 1 M equiv of Me_2AlCl to BIPAM, 1 mol of gas was detected at room temperature within 30 min, and the addition of another 1 M equiv of Me_2AlCl liberated 1 mol of gas after 30 min (Scheme 4). These results suggested that the reaction of BIPAM and Me_2AlCl in a ratio of 1:1 at room temperature for 30 min would provide mono-aluminated Lewis acid **D** or a mixture of bis-aluminated Lewis acid **A** and original BIPAM. Further treatment with another 1 M equiv of Me_2AlCl would lead to bis-aluminated Lewis acid **A**. On the other hand, generation of cyclic diamide type Lewis acid **B** required the thermal condition as in the case of cyclic Lewis acid **C** reported by Maruoka et al. (Scheme 3), since the peaks of methyl ligand of aluminum metal disappeared in ^1H NMR spectrum after a mixture of BIPAM and Me_2AlCl in a ratio of 1:1 reacted at 110 °C for 30 min in toluene-d_8.

Concerning the activation of ester-tethered substrate by Lewis acid **A**, we have carried out NMR studies using methyl crotonate (Table 5). The ^{13}C NMR spectrum (100 MHz) of a mixture of methyl crotonate and Lewis acid **A** in $CDCl_3$ at room temperature showed two kinds of complexes in a ratio of 1.3:1. Down-field shift of the β-carbon of the major complex was found to be 15.0 ppm, while upper-field shift of the α-carbon was 3.2 ppm (entry 4 vs entry 1). Thus, the chemical shift difference between the β-carbon and the α-carbon was 40.5 ppm, indicating a significant electronic activation of the double bond of the enoate moiety. In the case of the minor complex, the chemical shift difference between the β-carbon and the α-carbon was 42.8 ppm, larger than that of the major isomer. These differences in chemical shifts were larger than those observed with 2 M equiv of monodentate Lewis acid Me_2AlCl (entry 2) or bidentate Lewis acid $TfN[Al(Me)Cl]_2$ (entry 3), supporting the fact that Lewis acid **A** is more effective.

Table 5. ^{13}C NMR (100 MHz, $CDCl_3$, rt) of methyl crotonate with/without Lewis acid



Entry	Lewis acid		Chemical shift (ppm)		
			C_β	C_α	C_β–C_α[a]
1	N		144.7	122.4	22.3
2[b,c]	Me_2AlCl	Major	157.5	119.4	38.1
		Minor	159.4	119.2	40.2
3	$TfN[Al(Me)Cl]_2$		159.8	119.0	40.8
4[d]	BIPAM+2Me_2AlCl (**A**)	Major	159.7	119.2	40.5
		Minor	161.9	119.1	42.8

[a] Chemical shift difference between C_β and C_α.
[b] 2 equiv of Lewis acid was added.
[c] Major:minor = 2:1.
[d] Major:minor = 1.3:1.

In conclusion, we have demonstrated that a novel bidentate Lewis acid in situ generated from 1,1′-biphenyl-2,2′-di(triflyl)amide (BIPAM) and 2 M equiv of Me_2AlCl can promote the intramolecular [3+2] cycloaddition reaction of acrylate derivatives having allylsilane moiety to give the cycloadduct in good yield and with excellent stereoselectivity. Further studies on the structure of the bidentate complexes, and application to the synthesis of natural products are underway.

Acknowledgements

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References and notes

1. Reviews: (a) Fleming, I. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 2, p 563; (b) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375; (c) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063; (d) Laurent, C.; Philippe, J.; Yannick, L. *Eur. J. Chem.* **2004**, 3173.
2. (a) Danheiser, R. L.; Takahashi, T.; Bertok, B.; Dixon, B. R. *Tetrahedron Lett.* **1993**, *34*, 3845; (b) Knölker, H. J.; Foitzik, N.; Goesmann, H.; Graf, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1081; (c) Knölker, H. J.; Jones, P. G.; Graf, R. *Synlett* **1996**, 1155; (d) Groaning, M. D.; Brengel, G. P.; Meyers, A. I. *J. Org. Chem.* **1998**, *63*, 5517; (e) Akiyama, T.; Hoshi, E.; Fujiyoshi, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2121; (f) Peng, Z. H.; Woerpel, K. A. *Org. Lett.* **2000**, *2*, 1379.
3. (a) Knölker, H. J.; Baum, G.; Graf, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1612; (b) Knölker, H. J. *J. Prakt. Chem.* **1997**, *339*, 304; (c) Knölker, H. J.; Baum, G.; Schmitt, O.; Wanzl, G. *Chem. Commun.* **1999**, 1737; (d) Organ, M. G.; Dragan, V.; Miller, M.; Froese, R. D. J.; Goddard, J. D. *J. Org. Chem.* **2000**, *65*, 3666.
4. (a) Brengel, G. P.; Rithner, C.; Meyers, A. I. *J. Org. Chem.* **1994**, *59*, 5144; (b) Groaning, M. D.; Brengel, G. P.; Meyers, A. I. *Tetrahedron* **2001**, *57*, 2635; (c) Murphy, W. S.; Neville, D. *Tetrahedron Lett.* **1997**, *38*, 7933.
5. Photochemical [2+2]-cycloaddition reaction of acrylate and acrylamide derivatives was reported, see: Fature, S.; Blanc, S. P.; Piva, O. *Tetrahedron Lett.* **1999**, *40*, 6001.
6. (a) Fallis, A. G. *Acc. Chem. Res.* **1999**, *32*, 464; (b) Suzuki, Y.; Murata, T.; Takao, K.; Tadano, K. *J. Synth. Org. Chem., Jpn.* **2002**, *60*, 679.
7. (a) Chackalamannil, S.; Davies, R. J.; Wang, Y.; Asberom, T.; Doller, D.; Wong, J.; Leon, D. *J. Org. Chem.* **1999**, *64*, 1932; (b) Jauch, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2764; (c) Padwa, A.; Brodney, M. A.; Dimitroff, M.; Liu, B.; Wu, T. *J. Org. Chem.* **2001**, *66*, 3119; (d) Suzuki, Y.; Ohara, A.; Sugaya, K.; Takao, K.; Tadano, K. *Tetrahedron* **2001**, *57*, 7291; (e) Wong, L. S.-M.; Sherburn, M. S. *Org. Lett.* **2003**, *5*, 3603; (f) Inoue, M.; Sato, T.; Hirama, M. *J. Am. Chem. Soc.* **2003**, *125*, 10772.
8. Reviews on the intramolecular Diels–Alder reaction: (a) Ciganek, E. In *Organic Reactions*; Dauben, W. G., Ed.; John Wiley & Sons: New York, 1984; Vol. 32, pp 1–374; (b) Craig, D. *Chem. Soc. Rev.* **1987**, *16*, 187; (c) Roush, W. R. In *Advances in Cycliaddition*; Curran, D. P., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 2, pp 91–146; (d) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 5, pp 513–550.
9. (a) Boeckman, R. K., Jr.; Demko, D. M. *J. Org. Chem.* **1982**, *47*, 1789; (b) Martin, S. F.; Williamson, S. A.; Gist, R. P.; Smith, K. M. *J. Org. Chem.* **1983**, *48*, 5170.
10. (a) Cain, D.; Pawar, D. M.; Stewart, M.; Billings, H., Jr.; Noe, E. A. *J. Org. Chem.* **2001**, *66*, 6092; Review on the conformation and stereoelectronic effect of ester compounds, see: (b) Deslongchamps, P. In *Stereoelectric Effects in Organic Chemistry*; Pergamon Press: Oxford, 1983; pp 54–100.
11. (a) Saito, A.; Ito, H.; Taguchi, T. *Org. Lett.* **2002**, *4*, 4619; (b) Saito, A.; Yanai, H.; Taguchi, T. *Tetrahedron* **2004**, *60*, 12239; (c) Saito, A.; Yanai, H.; Sakamoto, W.; Takahashi, K.; Taguchi, T. *J. Fluorine Chem.* **2005**, *126*, 709.
12. Example of intermolecular Diel–Alder reaction: Saito, A.; Yanai, H.; Taguchi, T. *Tetrahedron Lett.* **2004**, *45*, 9439.
13. Ooi, T.; Ohmatsu, K.; Ishii, H.; Saito, A.; Maruoka, K. *Tetrahedron Lett.* **2004**, *45*, 9315.
14. Structures of the crystalline compounds **2b**, **2c**, and **2e** were determined by their X-ray analyses, and the relative stereochemistries of compounds **2a**, **2d**, **2g**, and **2h** were determined by the NOESY spectra data. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 604006 (**2b**), 604007 (**2c**), and 607008 (**2e**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.