Aldehydes vs Aldimines. Unprecedented Aldimine-Selective Nucleophilic Additions in the Coexistence of Aldehydes Using a Lanthanide Salt as a Lewis Acid Catalyst

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Abstract: It is well-recognized that aldimines are less reactive than aldehydes toward nucleophilic additions. In this paper, an unprecedented change in the reactivity is described: preferential reactions of aldimines over aldehydes in nucleophilic additions using a lanthanide salt as a Lewis acid catalyst. In the presence of a catalytic amount of ytterbium triflate (Yb(OTf)$_3$), only aldimines reacted with silyl enol ethers, ketene silyl acetals, allyltributylstannane, or cyanotrimethylsilane to afford the corresponding adducts in high yields, even in the coexistence of aldehydes. Selective formation of an aldimine−Yb(OTf)$_3$ complex rather than an aldehyde−Yb(OTf)$_3$ complex was indicated by ^{13}C NMR analyses. While this report demonstrates the effective use of Lewis acids in organic synthesis, the basic idea of changing reactivity as shown here will be widely applied to many other nucleophilic additions.

Introduction

Nucleophilic additions to carbonyl and related compounds are among the most fundamental and important reactions in organic chemistry. It is well-recognized that aldimines are less reactive than aldehydes. For example, activators are needed in some nucleophilic additions to aldimines, while aldehydes react with the nucleophiles smoothly without any activators.[1] These low reactivities of aldimines are explained by the difference in electronegativity between oxygen and nitrogen, the steric hindrance of aldimines, etc. In this paper, we describe an unprecedented change in the reactivity: preferential reactions of aldimines over aldehydes with nucleophiles such as enolates, allylation, and cyanation reagents using a lanthanide salt as a Lewis acid.[2]

Our basic idea to change reactivity is shown in Scheme 1. A Lewis acid activates an aldehyde[3] or an aldimine,[4] and nucleophilic additions are accelerated by the Lewis acid. When a large excess of a Lewis acid is used and both aldehyde and aldimine are activated, the aldehyde is more reactive than the aldimine. On the other hand, the formation of aldehyde−Lewis acid or aldimine−Lewis acid complexes takes place under equilibrium conditions in the presence of a small amount of a Lewis acid,

Scheme 1
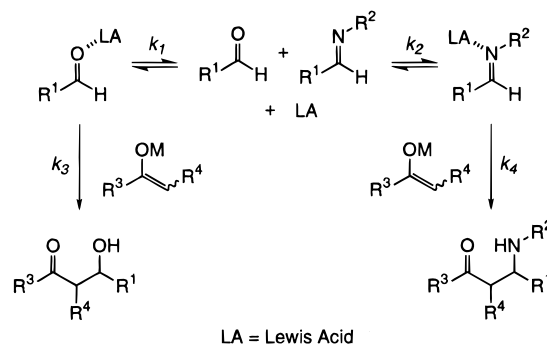
LA = Lewis Acid

and if a Lewis acid could coordinate an aldimine preferentially and nucleophilic addition could occur under such conditions, preferential reactions of aldimines over aldehydes could be achieved.

Enolate Addition

Based on this idea, we first examined enolate addition reactions (aldol-type reactions).[5] It was found that propiophenone lithium enolate attacked benzaldehyde exclusively. On the other hand, propiophenone trimethylsilyl enolate (the silyl enol ether derived from propiophenone) attacked neither benzaldehyde nor *N*-benzylideneaniline without a Lewis acid. We then screened various Lewis acids in the model reaction. Selective reactions of the aldehyde were found to take place using typical Lewis acids such as TiCl$_4$, SnCl$_4$, TMSOTf, etc., even when catalytic amounts of the Lewis acids were used (Table 1). Recently, we found that lanthanide triflates (Ln(OTf)$_3$) are unique Lewis acids which are stable in water and catalyze several useful synthetic reactions.[6] It was found that

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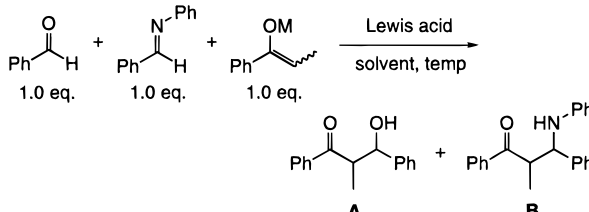
[‡] Japan Science and Technology Corporation.

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(1) For example, Yamaguchi, M. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 1, Chapter 1.11.
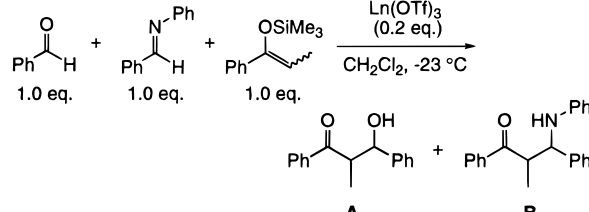
(2) Very recently, Yamamoto et al. reported imine-selective allylation via a palladium catalyzed allylstannane reaction. Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 1459; *J. Am. Chem. Soc.* **1996**, *118*, 6641.

(3) (a) Chan, T.-H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 2, Chapter 2.3. (b) Mukaiyama, T.; Banno, K.; Narasaka, K. *Chem. Lett.* **1973**, 357. (c) Mukaiyama, T. *Org. React.* **1982**, *28*, 203.

(4) (a) Kleinman, E. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 2, Chapter 4.1. (b) Ojima I.; Inaba, S.; Yoshida, K. *Tetrahedron Lett.* **1977**, 3643. (c) Guanti, G.; Narisano, E.; Banfi, L. *Tetrahedron Lett.* **1987**, *28*, 4331. (d) Mukaiyama, T.; Kashiwagi, K.; Matsui, S. *Chem. Lett.* **1989**, 1397. (e) Mukaiyama, T.; Akamatsu, H.; Han, J. S. *Chem Lett.* **1990**, 889. (f) Onaka, M.; Ohno, R.; Yanagiya, N.; Izumi, Y. *Synlett* **1993**, 141. (g) Ishihara, K.; Funahashi, M.; Hanaki, N.; Miyata, M.; Yamamoto, H. *Synlett* **1994**, 963.

(5) Kobayashi, S.; Nagayama, S. *J. Org. Chem.* **1997**, *62*, 232.

(6) Kobayashi, S. *Synlett* **1994**, 689.

(7) We have already found that lanthanide triflates are effective catalysts for the reactions of aldehydes or aldimines with silyl enol ethers or ketene silyl acetals. (a) Aldehyde: Kobayashi, S.; Hachiya, I. *Tetrahedron Lett.* **1992**, *33*, 1625. (b) Aldimine: Kobayashi, S.; Araki, M.; Ishitani, H.; Nagayama, S.; Hachiya, I. *Synlett* **1995**, 233. See, also: (c) Kobayashi, S.; Hachiya, I.; Suzuki, S.; Moriwaki, M. *Tetrahedron Lett.* **1996**, *37*, 2809.

Table 1. Effect of Lewis Acids

M	Lewis acid/ equiv	solvent	temp (°C)	yield (%)[a] A	B	A/B
Li		THF	−78	97	trace	>99/1
Me$_3$Si		CH$_2$Cl$_2$	−78	0	0	
Me$_3$Si	SnCl$_4$/1.0	CH$_2$Cl$_2$	−78	93	1	99/1
Me$_3$Si	TiCl$_4$/1.0	CH$_2$Cl$_2$	−78	86	1	99/1
Me$_3$Si	Me$_3$SiOTf/1.0	CH$_2$Cl$_2$	−23	87	trace	>99/1
Me$_3$Si	SnCl$_4$/0.2	CH$_2$Cl$_2$	−78	18	trace	>99/1
Me$_3$Si	TiCl$_4$/0.2	CH$_2$Cl$_2$	−78	12	trace	>99/1
Me$_3$Si	BF$_3$·OEt$_2$/0.2	CH$_2$Cl$_2$	−78	26	7	79/21
Me$_3$Si	Me$_3$SiOTf/0.2	CH$_2$Cl$_2$	−23	52	12	81/19
Me$_3$Si	Yb(OTf)$_3$/2.0	CH$_2$Cl$_2$	−23	49	31	61/39
Me$_3$Si	Yb(OTf)$_3$/1.0	CH$_2$Cl$_2$	−23	40	31	56/44
Me$_3$Si	Yb(OTf)$_3$/0.2	CH$_2$Cl$_2$	−23	2	92	2/98
Me$_3$Si	Yb(OTf)$_3$/0.2	CH$_2$Cl$_2$	−45	trace	69	<1/>99
Me$_3$Si	Yb(OTf)$_3$/0.2	CH$_2$Cl$_2$	0	39	55	41/59
Me$_3$Si	Yb(OTf)$_3$/0.2	CH$_2$Cl$_2$	rt[b]	41	48	46/54
Me$_3$Si	Yb(OTf)$_3$/0.2	CH$_3$CN	−23	2	92	2/98
Me$_3$Si	Yb(OTf)$_3$/0.2	C$_2$H$_5$CN	−45	trace	83	<1/>99

[a] Isolated yield. [b] Room temperature = rt.

Table 2. Effect of Ln(OTf)$_3$
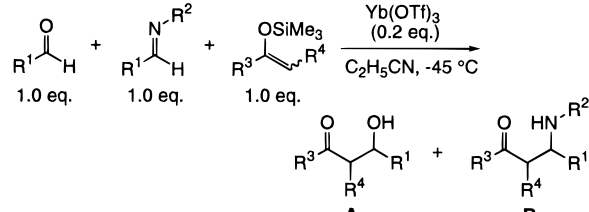
Ln	yield (%)[a] A	B	A/B	Ln	A	B	A/B
Sc	24	65	27/73	Gd	3	81	4/96
Y	19	64	23/77	Dy	12	46	21/79
La	3	82	4/96	Ho	2	78	3/97
Ce	2	77	3/97	Er	22	63	26/74
Pr	1	55	2/98	Tm	3	82	4/96
Nd	5	72	6/94	Yb	2	92	2/98
Sm	10	34	23/77	Lu	trace	70	<1/>99
Eu	2	78	3/97				

[a] Isolated yield.

use of these lanthanide triflates changed the reaction course dramatically.[7] Effects of lanthanide salts are summarized in Table 2. In all cases, the aldimine reacted selectively in the coexistence of the aldehyde. In particular, La, Ce, Pr, Nd, Eu, Gd, Ho, Tm, Yb, and Lu(OTf)$_3$ gave reasonable yields with excellent selectivities. When 0.2 equiv of ytterbium triflate (Yb-(OTf)$_3$, a representative of the lanthanide triflates) was used in dichloromethane, selective reaction of the aldimine over the aldehyde took place at −23 °C or −45 °C.[8] Both aldimine and aldehyde reacted at 0 °C or room temperature. When propionitrile was used as a solvent, only the aldimine reacted at −45 °C to afford the corresponding adduct in an 83% yield.

We then examined other combinations of aldehydes and aldimines and the results are shown in Table 3. In all cases,

(8) The high catalytic activity of Yb(OTf)$_3$ should also be noted. While high yields of **A** + **B** were obtained using 20 mol % Yb(OTf)$_3$, much lower yields were observed when 20 mol % of SnCl$_4$ or TiCl$_4$ was used.

Table 3. Enolate Addition

entry	R^1	R^2	R^3	R^4	yield (%)[a] A	B[b]	A/B
1	Ph	Ph	Ph	Me[c]	trace	83	<1/>99
2	Ph	p-MeO-Ph	Ph	Me	trace	81	<1/>99[f]
3	Ph	p-Cl-Ph	Ph	Me	trace	87	<1/>99
4	Ph	Ph	Ph	H	trace	92	<1/>99
5	Ph	Ph	^{t}Bu	H	trace	88	<1/>99[f]
6	Ph	Ph	Et	Me[d]	trace	81	<1/>99[f]
7	2-furyl	Ph	Ph	Me	trace	91	<1/>99
8	c-C$_6$H$_{11}$	Ph	Ph	Me	trace	85	<1/>99
9	Ph	Ph	−(CH$_2$)$_4$−		trace	83	<1/>99[g]
10	Ph	Ph	SEt	Me[e]	trace	93	<1/>99[g]
11	Ph	PhCH$_2$	SEt	Me	trace	82	<1/>99[g]
12	CH$_3$(CH$_2$)$_7$	Ph$_2$CH	OMe	Me$_2$	trace	86	<1/>99[h]

[a] Isolated yield. [b] Diastereomer ratios were 9/1−1.3/1. [c] E/Z = <1/>99. [d] E/Z = 4/1. [e] E/Z = 1/15. [f] The reaction was carried out at −23 °C. [g] −78 °C. [h] 0 °C.

aldimines reacted with ketone enolates exclusively, and the corresponding aldehydes reacted sluggishly under these conditions. It is noted that not only ketone enolates (silyl enol ethers) but also thioester and ester enolates (ketene silyl acetals) reacted only with an aldimine.

Syn/Anti Assignment of Aldimine Adducts

Relative stereochemical assignments of the aldimine adducts were tentatively performed by comparison of the methyl resonance in the ^{13}C NMR spectrum. Chemical shifts of the methyl carbons of *syn* isomers were 2.5−5.5 ppm higher than those of *anti* isomers (see the Supporting Information).[9] These assignments were confirmed in the cases of entries 10 and 11: the adducts were converted to the β-lactams according to the following equations,[10,11] and the proton−proton coupling constants were compared with those in the literatures.[12] In the case of entry 9, relative stereochemical assignment was not made.
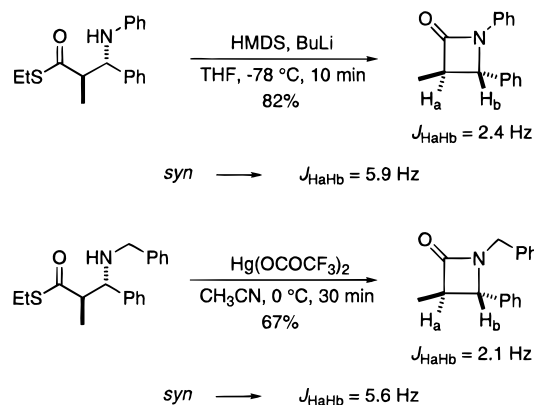
(9) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: Orlando, FL, 1984; Vol. 3, Chapter 2.

(10) Masamune, S.; Kamata, S.; Schilling, W. *J. Am. Chem. Soc.* **1975**, *97*, 3515.

(11) Gennari, C.; Verturini, I.; Gislon, G.; Schimperna, G. *Tetrahedron Lett.* **1987**, *28*, 227.

(12) (a) Mukaiyama, T.; Suzuki, H.; Yamada, T. *Chem. Lett.* **1986**, 915. (b) Yamasaki, N.; Murakami, M.; Mukaiyama, T. *Chem. Lett.* **1986**, 1013.

Table 4. Allylation

R[1]	R[2]	Lewis acid/ equiv	yield (%)[a] A	B	A/B
Ph	Ph	Yb(OTf)$_3$/0.2	trace	81	<1/>99
Ph	*p*-MeO-Ph	Yb(OTf)$_3$/0.2	trace	83	<1/>99
Ph	*p*-Cl-Ph	Yb(OTf)$_3$/0.2	trace	89	<1/>99
Ph	PhCH$_2$	Yb(OTf)$_3$/0.2	trace	31	<1/>99
2-furyl	Ph	Yb(OTf)$_3$/0.2	trace	92	<1/>99[b]
2-thiophene	Ph	Yb(OTf)$_3$/0.2	trace	86	<1/>99[b]
c-C$_6$H$_{11}$	Ph	Yb(OTf)$_3$/0.2	trace	94	<1/>99
Ph	Ph	SnCl$_4$/4.0	77	trace	>99/<1[c]

[a] Isolated yield. [b] The reaction was carried out at −23 °C. [c] −78 °C.

Allylation

We then examined allylation reactions, which are also one of the most basic and versatile carbon−carbon bond-forming reactions. Among several allylation reagents, allyltributylstannane, which is one of the most useful and popular reagents, was chosen. While more than a stoichiometric amount of a Lewis acid such as BF$_3$·OEt$_2$, TiCl$_4$, or SnCl$_4$ is needed in the allylation reactions of aldehydes[13,14] or aldimines[13,15] with allyltributylstannane, the reactions were reported very recently to proceed catalytically by using ytterbium triflate (Yb(OTf)$_3$).[16] In the Yb(OTf)$_3$-catalyzed allylations of aldehydes or aldimines, the reactions were carried out in dichloromethane at room temperature for 24 h in both cases, and the difference in reactivity between aldehydes and aldimines was not mentioned at all. We set benzaldehyde and *N*-benzylideneaniline as models for the competition reaction with allyltributylstannane. When 400 mol % of SnCl$_4$ was used, only the aldehyde reacted, and no addition adduct of the aldimine was obtained. Contrarily, it was found that when 0.2 equiv of Yb(OTf)$_3$ was used in propionitrile (C$_2$H$_5$CN) at −45 °C, the aldimine reacted with allyltributylstannane selectively, and the coexisting aldehyde remained unreacted. We then examined other aldehydes and aldimines, and the results are shown in Table 4. In all cases, aldimines reacted with allyltributylstannane exclusively,[17] and the corresponding aldehydes reacted sluggishly under these conditions.

Cyanation

We also examined cyanations using cyanotrimethylsilane (TMSCN). When benzaldehyde, *N*-benzylideneaniline, TM-

(13) Review: Yamamoto, Y; Asao. N. *Chem. Rev.* **1993**, *93*, 2207.

(14) (a) Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.* **1979**, 919. (b) Hosomi, A.; Iguchi, H.; Endo, M.; Sakurai, H. *Chem. Lett.* **1979**, 977. Recently, chiral titanium catalysts were shown to be effective in the enantioselective reactions of aldehydes with allyltributylstannane. (c) Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Tromboni, C.; Umani-Rouchi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7001. (d) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467.

(15) (a) Keck, G. E.; Enholm, E. J. *J. Org. Chem.* **1985**, *50*, 146. (b) Trost, B. M.; Bonk, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 1778.

(16) (a) Aspinall, H. C.; Browning, A. F.; Greeves, N.; Ravenscroft, P. *Tetrahedron Lett.* **1994**, *35*, 4639. (b) Bellucci, C.; Cozzi, P. G.; Umani-Ronchi, A. *Tetrahedron Lett.* **1995**, *36*, 7289. See, also: (c) Kobayashi, S.; Ishitani, H.; Hachiya, I. *The 64th Annual Meeting of Chemical Society of Japan*; Tokyo, 1993; 3E306.

(17) It is noted that the yields are much improved compared to those shown in ref 16b.

Table 5. Cyanation

R[1]	R[2]	Lewis acid/ equiv	yield (%)[a] A	B	A/B
Ph	Ph	Yb(OTf)$_3$/0.2	trace	83	<1/>99
Ph	*p*-MeO-Ph	Yb(OTf)$_3$/0.2	trace	84	<1/>99
Ph	*p*-Cl-Ph	Yb(OTf)$_3$/0.2	trace	91	<1/>99
Ph	Ph$_2$CH	Yb(OTf)$_3$/0.2	trace	65	<1/>99[b]
CH$_3$(CH$_2$)$_7$	Ph$_2$CH	Yb(OTf)$_3$/0.2	trace	94	<1/>99[b]
c-C$_6$H$_{11}$	Ph	Yb(OTf)$_3$/0.2	trace	quant	<1/>99
c-C$_6$H$_{11}$	Ph	SnCl$_4$/4.0	91	trace	>99/<1[c]

[a] Isolated yield. [b] The reaction was carried out at −23 °C. [c] −78 °C.

SCN, and 4 equiv of SnCl$_4$ were combined, TMSCN reacted only with the aldehyde to afford the corresponding cyanohydrin after hydrolysis,[18] and no addition adduct of the aldimine was obtained under these conditions. On the other hand, the aldimine reacted with TMSCN exclusively to give the corresponding α-amino nitrile by using 0.2 equiv of Yb(OTf)$_3$ instead of SnCl$_4$.[19] We examined other substrates, and the results are summarized in Table 5. In all cases, TMSCN reacted with aldimines selectively in the presence of 0.2 equiv of Yb(OTf)$_3$ to produce the corresponding α-amino nitriles in high yields.

Nuclear Magnetic Resonance (NMR) Studies

As for the mechanism of these reactions, selective formation of an aldimine−Yb(OTf)$_3$ complex rather than an aldehyde−Yb(OTf)$_3$ complex is postulated. ^{13}C NMR analyses were performed using a CD$_3$CN solution of a mixture of 1 equiv of benzaldehyde, 1 equiv of *N*-benzylideneaniline, and Yb(OTf)$_3$ (*x* equiv).[20] Control experiments of ^{13}C NMR analysis using benzaldehyde and *N*-benzylideneaniline, respectively, were also carried out, and the results are shown in Figure 1. A lower field shift was observed at the aldimine carbons in accordance with the amount of Yb(OTf)$_3$, while a higher field shift at the carbonyl carbons was observed.[21] It is noted that almost no shift was observed at the carbonyl carbon when 0.2 equiv of Yb(OTf)$_3$ was used, while almost the same large shift was measured between the aldimine carbon in the absence and presence of the aldehyde. These results indicate selective formation of the aldimine−Yb(OTf)$_3$ complex in the coexistence of the aldehyde[21] and can explain the excellent aldimine-selectivities obtained in the nucleophilic additions when 0.2 equiv of Yb(OTf)$_3$ was used.

Conclusions

In summary, preferential reactions of aldimines over aldehydes with enolates, allylation, and cyanation reagents have been achieved. These results have turned generally accepted common

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(19) Very recently, we have found that Ln(OTf)$_3$ was an excellent catalyst in the reactions of aldimines with TMSCN. Kobayashi, S.; Ishitani, H.; Ueno, M. *Synlett* **1997**, 115.

(20) (a) Shambayati, S.; Schreiber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 1, Chapter 1.10. (b) Santelli, M.; Pons, J.-M. *Lewis Acids and Selectivity in Organic Synthesis*; CRC Press: Boca Raton, FL, 1995; Chapter 1.

(21) Morrill, T. C. In *Lanthanide Shift Reagents in Stereochemical Analysis*; Morrill, T. C., Ed.; VCH: New York, 1986; Chapter 1.
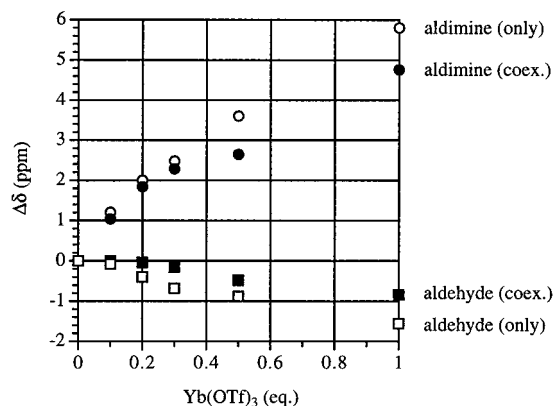
Figure 1. Correlation between the amount of Yb(OTf)$_3$ and ^{13}C NMR chemical shift (Δ). The average values of the three independent experiments are shown.

sense of reactivity between aldehydes and aldimines in organic chemistry. Use of a lanthanide salt as a Lewis acid is key in these reactions.[22,23] ^{13}C NMR analyses in CD$_3$CN showed selective formation of an aldimine–Yb(OTf)$_3$ complex rather than an aldehyde–Yb(OTf)$_3$ complex. While this report demonstrates the effective use of Lewis acids, the basic idea of changing reactivity as shown here will be applied to many other nucleophilic reactions.

Experimental Section

General Methods. IR spectra were recorded on a Horiba FT-300. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNR-EX270L or a JNM-LA400 spectrometer in CDCl$_3$ unless otherwise noted. Tetramethylsilane (TMS) served as internal standard ($\delta = 0$) for ^{1}H NMR, and CDCl$_3$ was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. Mass spectra were measured on a JEOL DX-303HF spectrometer.

^{13}C NMR analyses of an aldimine–Yb(OTf)$_3$ complex and an aldehyde–Yb(OTf)$_3$ complex were performed at 20 °C using CD$_3$CN as a solvent. CD$_3$CN was used as internal standard ($\delta = 118.2$).

In all cases shown in Tables 1–5, the aldehyde adducts and the aldimine adducts were prepared independently according to the literatures' methods,[16,18,19,24–28] and they were used as authentic samples. 1-Phenyl-3-butene-1-ol[29] and 1-cyclohexyl-3-butene-1-ol[30] are known compounds.

Typical Procedure. A typical experimental procedure for the competition reaction between an aldehyde and an aldimine with a silyl enol ether (Table 3): To Yb(OTf)$_3$ (0.2 equiv) in C$_2$H$_5$CN (1 mL) was added a mixture of an aldehyde (0.5 mmol) and an aldimine (0.5 mmol) in C$_2$H$_5$CN (1 mL). The mixture was cooled to −45 °C, and a silyl enol ether (0.5 mmol) in C$_2$H$_5$CN (1 mL) was added. The reaction was monitored by TLC, and less than a trace amount of an aldehyde

adduct was detected after 12 h (carefully compared with an authentic sample). Water was added to quench the reaction, and the mixture was warmed to room temperature. After extraction of the aqueous layer with CH$_2$Cl$_2$, the crude adduct was treated with THF−1 N HCl (10:1) for 30 min at 0 °C. After usual workup, the crude product was chromatographed on silica gel to afford the corresponding aldimine adduct.

Physical data of selected compounds are shown below. Others are included in Supporting Information.

1,3-Diphenyl-2-methyl-3-(*N*-phenyl)amino-1-propanone: (*syn/anti* = 1/2) ^{1}H NMR δ = 1.21 (minor, d, 3H, *J* = 6.9 Hz), 1.27 (major, d, 3H, *J* = 6.9 Hz), 3.22 (brs, 1H), 3.90−4.00 (m, 1H), 4.71 (major, d, 1H, *J* = 5.9 Hz), 4.75 (minor, d, 1H, *J* = 5.0 Hz), 6.44−6.64 (m, 3H), 6.98−7.52 (m, 10H), 7.70−7.92 (m, 2H). ^{13}C NMR δ = 11.5, 16.6, 46.3, 46.8, 59.1, 61.0, 113.3, 113.7, 117.1, 117.5, 126.72, 126.75, 127.1, 128.1, 128.16, 128.23, 128.4, 128.5, 128.7, 128.8, 129.0, 129.2, 133.1, 133.2, 136.1, 137.0, 141.4, 141.7, 147.06, 147.13, 202.6, 204.0. HRMS: Calcd for C$_{22}$H$_{21}$NO: 315.1623, found 315.1631.

1-(2′-Furyl)-2-methyl-3-phenyl-3-(*N*-phenyl)amino-1-propanone: (*syn/anti* = 1/2) ^{1}H NMR δ = 1.22 (minor, d, 3H, *J* = 7.3 Hz), 1.30 (major, d, 3H, *J* = 6.9 Hz), 4.07−4.66 (m, 2H), 4.86 (minor, d, 1H, *J* = 6.6 Hz), 4.94 (major, d, 1H, *J* = 6.6 Hz), 6.10−6.17 (m, 2H), 6.50−6.70 (m, 3H), 7.06−7.61 (m, 6H), 7.87−7.92 (m, 2H); ^{13}C NMR δ = 13.2, 15.7, 43.9, 44.7, 54.0, 55.0, 107.17, 107.22, 110.2, 112.1, 113.6, 113.8, 116.2, 117.9, 118.0, 120.9, 126.2, 127.7, 128.1, 128.2, 128.4, 128.5, 128.6, 129.0, 133.1, 136.1, 136.8, 141.5, 145.6, 146.99, 147.0, 147.7, 154.0, 154.1, 202.0, 203.3. HRMS: Calcd for C$_{20}$H$_{19}$NO$_2$: 305.1416, found 305.1422. Anal. Calcd for C$_{20}$H$_{19}$NO$_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.81; H, 6.25; N, 4.64.

2-[1′-Phenyl-1′-(*N*-phenyl)amino]methylcyclohexanone: (*syn/anti* = 1/1.3) ^{1}H NMR δ = 1.55−2.01 (m, 6H), 2.20−2.40 (m, 2H), 2.74−2.78 (m, 1H), 4.10−4.90 (brs, 1H), 4.78 (major, d, 1H, *J* = 4.3 Hz), 4.60 (minor, d, 1H, *J* = 6.9 Hz), 6.41−6.64 (m, 4H), 6.64−7.33 (m, 6H); ^{13}C NMR δ = 23.6, 24.8, 26.9, 27.8, 28.6, 31.2, 41.7, 42.3, 56.5, 57.1, 57.3, 57.9, 113.5, 114.0, 117.4, 117.6, 126.3, 126.6, 126.9, 127.1, 127.2, 127.4, 128.3, 128.4, 128.9, 129.0, 141.5, 141.6, 147.1, 147.4, 211.3, 212.8. HRMS: Calcd for C$_{19}$H$_{21}$NO: 279.1623, found 279.1644.

S-Ethyl 2-methyl-3-phenyl-3-(*N*-phenyl)aminopropanethioate: (*syn/anti* = 1/3) ^{1}H NMR δ = 1.12−1.24 (m, 9H), 2.74−2.88 (m, 2H), 2.92−3.10 (m, 1H), 4.51 (minor, d, 1H, *J* = 7.6 Hz), 4.60 (brs, 1H), 4.71 (major, d, 1H, *J* = 5.0 Hz), 6.48−6.66 (m, 3H), 7.02−7.08 (m, 2H), 7.21−7.47 (m, 5H); ^{13}C NMR δ = 11.8, 14.4, 14.5, 16.0, 23.3, 23.4, 54.3, 54.7, 60.0, 60.9, 113.3, 113.7, 117.3, 117.6, 126.85, 126.92, 127.3, 127.4, 128.5, 129.0, 130.0, 140.6, 141.1, 146.8, 147.1, 201.9, 202.4. HRMS: Calcd for C$_{18}$H$_{21}$NOS: 299.1344, found 299.1351. Anal. Calcd for C$_{18}$H$_{21}$NOS: C, 72.20; H, 7.07; N, 4.68; S, 10.71. Found: C, 72.48; H, 6.89; N, 4.90; S, 10.54.

S-Ethyl 3-(*N*-benzyl)amino-2-methyl-3-phenylpropanethioate: (*syn/anti* = 1/9) ^{1}H NMR δ = 0.89 (minor, d, 3H, *J* = 2.4 Hz), 1.07−1.30 (major, m, 3H), 1.86 (brs, 1H), 2.68−2.95 (m, 3H), 3.44 (major, d, 1H, *J* = 13.5 Hz), 3.58 (major, d, 1H, *J* = 13.5 Hz), 3.47 (minor, d, 1H, *J* = 13.5 Hz), 3.67 (minor, d, 1H, *J* = 13.5 Hz), 3.83 (d, 1H, *J* = 9.9 Hz), 3.98 (d, 1H, *J* = 5.6 Hz), 7.18−7.36 (m, 10H); ^{13}C NMR δ = 12.7, 12.5, 14.7, 15.9, 23.1, 23.3, 51.2, 51.3, 55.1, 55.3, 63.7, 65.2, 126.7, 126.8, 127.2, 127.5, 127.7, 127.85, 127.94, 128.0, 128.1, 128.2, 128.4, 128.6, 140.2, 140.3, 141.0, 141.1, 202.3, 202.9. HRMS: Calcd for C$_{19}$H$_{23}$NOS: 313.1500, found 313.1512.

Methyl 2,2-dimethyl-3-(*N*-diphenylmethyl)aminoundecanate: ^{1}H NMR δ = 0.89 (t, 3H, *J* = 6.7 Hz), 1.09−1.49 (m, 20H), 2.72 (dd, 1H, *J* = 4.0, 6.3 Hz), 3.55 (s, 3H), 4.90 (s, 1H), 7.13−7.45 (m, 10H); ^{13}C NMR δ = 14.1, 22.0, 22.6, 27.9, 29.2, 29.4, 29.9, 31.8, 32.7, 47.8, 51.4, 60.7, 65.7, 126.7, 126.8, 127.3, 127.8, 128.1, 128.4, 144.1, 145.4, 178.2. HRMS: Calcd for C$_{27}$H$_{39}$NO$_2$: 409.2981, found 409.2988.

4-Phenyl-4-(*N*-phenyl)amino-1-butene: IR (neat) 3410, 3224, 1601 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 2.42−2.66 (m, 2H), 4.15 (brs, 1H), 4.35−4.41 (m, 1H), 5.12−5.23 (m, 2H), 5.68−5.84 (m, 1H), 6.46−6.67 (m, 3H), 7.01−7.39 (m, 7H). ^{13}C NMR (CDCl$_3$): δ = 43.3, 57.1, 113.4, 117.3, 118.3, 126.2, 126.9, 128.6, 129.0, 134.6, 143.5, 147.3. HRMS: Calcd for C$_{16}$H$_{17}$N: 223.1289, found 223.1325.

4-(*N*-Benzyl)amino-4-phenyl-1-butene: ^{1}H NMR (CDCl$_3$): δ = 1.77 (brs, 1H), 2.41−2.46 (m, 3H), 3.53 (d, 1H, *J* = 13.4 Hz), 3.67 (d, 1H, *J* = 13.7 Hz), 5.02−5.11 (m, 2H), 5.65−5.75 (m, 1H), 7.20−7.37

(22) Recently, it was reported that a Lewis acidic silicon species was an active catalyst in the Lewis acid (including Yb(OTf)$_3$)-mediated aldol reactions of ketene silyl acetals with aldehydes (the Mukaiyama aldol reaction).[23] We have several contrary experimental results concerning this proposal, and the present paper is thought to be one of them. Precise discussion will be reported in due course. In addition, these results may open a door to develop chiral Lewis acid catalysis in enantioselective reactions of aldimines with silylated nucleophiles, which is one of the most difficult and challenging themes. Cf.: Ishitani, H.; Ueno, M.; Kobayashi, S. *J. Am. Chem. Soc.* **1997**, *119*, 7153.

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(m, 10H). ^{13}C NMR (CDCl$_3$): δ = 43.1, 51.1, 61.6, 117.5, 126.8, 127.0, 127.3, 128.1, 128.2, 128.3, 135.4, 140.6, 143.8. HRMS: Calcd for C$_{17}$H$_{19}$N 237.1499, found 237.1483.

4-(*N*-Phenyl)amino-4-(2′-thiophene)-1-butene: ^{1}H NMR (CDCl$_3$): δ = 2.56−2.66 (m, 3H), 4.00−4.30 (brs, 1H), 4.69 (t, 1H, *J* = 6.4 Hz), 5.13−5.22 (m, 2H), 5.71−5.86 (m, 1H), 6.57−6.71 (d, 3H), 6.90−6.96 (m, 2H), 7.01−7.18 (m, 3H). ^{13}C NMR (CDCl$_3$): δ = 43.0, 53.3, 113.6, 117.9, 118.6, 123.4, 123.7, 126.7, 129.1, 134.0, 147.0, 148.6. HRMS: Calcd for C$_{14}$H$_{15}$NS: 229.0853, found 229.0889. Anal. Calcd for C$_{14}$H$_{15}$NS: C, 73.32; H, 6.59; N, 6.11; S, 13.98. Found: C, 73.57; H, 6.49; N, 6.12; Cl, 13.81.

4-Cyclohexyl-4-(*N*-phenyl)amino-1-butene: ^{1}H NMR (CDCl$_3$): δ = 0.84−1.85 (m, 1H), 2.14−2.39 (m, 2H), 3.24 (dd, 1H, *J* = 5.1, 6.9 Hz), 3.50 (brs, 1H), 5.00−5.08 (m, 2H), 5.72−5.87 (m, 1H), 6.53−6.65 (m, 3H), 7.10−7.19 (m, 2H). ^{13}C NMR (CDCl$_3$): δ = 26.3, 26.4, 26.5, 29.4, 35.8, 41.2, 57.2, 112.9, 116.5, 117.0, 129.2, 135.6, 148.3. HRMS: Calcd for C$_{16}$H$_{23}$N: 229.1877, found 229.1854.

1-Phenyl-1-(*N*-phenylamino)acetonitrile: ^{1}H NMR (CDCl$_3$): δ = 4.20 (d, 1H, *J* = 9.2 Hz), 5.61 (d, 1H, *J* = 9.2 Hz), 6.75−6.78 (m, 2H), 6.88−7.00 (m, 2H), 7.22−7.36 (m, 6H). ^{13}C NMR (CDCl$_3$): δ = 46.0, 104.6, 114.5, 117.5, 120.7, 127.2, 129.5, 136.7, 144.0. HRMS: Calcd for C$_{14}$H$_{12}$N$_2$: 208.1000, found 208.1021.

1-(*N*-*p*-Chlorophenyl)amino-1-phenylacetonitrile: IR (neat) 3369, 3060, 2235, 1599 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 4.16 (d, 1H, *J* = 8.2 Hz), 5.35 (d, 1H, *J* =8.2 Hz), 6.66−6.86 (m, 2H), 7.17−7.21 (m, 2H), 7.39−7.47 (m, 3H), 7.51−7.62 (m, 2H). ^{13}C NMR (CDCl$_3$): δ = 50.1, 115.3, 117.9, 124.9, 127.1, 129.3, 129.3, 129.5, 133.4, 143.1. HRMS: Calcd for C$_{14}$H$_{11}$N$_2$Cl: 242.0614, found 242.0611. Anal. Calcd for C$_{14}$H$_{11}$N$_2$Cl: C, 69.28; H, 4.57; N, 11.54; Cl, 14.61. Found: C, 69.47; H, 4.49; N, 11.62; Cl, 14.84.

1-Phenyl-1-(*N*-Diphenylmethyl)aminoacetonitrile: IR (neat) 3301, 3030, 2229, 1599 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 2.14 (brs, 1H), 4.58 (s, 1H), 5.18 (s, 1H), 7.19−7.58 (m, 15H). ^{13}C NMR (CDCl$_3$): δ = 52.5, 65.6, 118.7, 127.1, 127.2, 127.4, 127.7, 127.9, 128.7, 129.0, 134.9, 141.0, 142.7. HRMS: Calcd for C$_{21}$H$_{18}$N$_2$: 298.1444, found 298.1457.

1-(*N*-Diphenylmethyl)amino-1-decanonitrile: IR (neat) 3317, 2924, 2227, 1599 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.88 (t, 3H, *J* = 6.6 Hz), 1.26−1.82 (m, 15H), 3.36 (dt, 1H, *J* = 6.9, 12.5 Hz), 5.13 (s, 1H), 7.17−7.50 (m, 10H). ^{13}C NMR (CDCl$_3$): δ = 14.1, 22.6, 25.5, 29.0, 29.1, 29.2, 31.7, 33.7, 48.3, 65.5, 120.3, 127.0, 127.3, 127.5, 127.6, 128.7, 128.8, 141.3, 143.2. HRMS: Calcd for 334.2403, found 334.2406. Anal. Calcd for C$_{23}$H$_{30}$N$_2$: C, 82.59; H, 9.04; N, 8.37. Found: C, 82.79; H, 9.11; N, 8.31.

Supporting Information Available: Table of ^{13}C NMR chemical shifts and all physical data of the products (3 pages). See any current masthead page for ordering and Internet access instructions.

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