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Lanthanide Triflates as Water-Tolerant Lewis Acids. Activation of Commercial Formaldehyde Solution and Use in the Aldol Reaction of Silyl Enol Ethers with Aldehydes in Aqueous Media

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Lanthanide trifluoromethanesulfonates (triflates), especially ytterbium triflate ($Yb(OTf)_3$), were found to be stable Lewis acids in water. In the presence of a catalytic amount of lanthanide triflate, formaldehyde in water solution (commercial formaldehyde solution) was activated and the hydroxymethylation reaction of silyl enol ethers proceeded smoothly. Lanthanide triflates were also quite effective in the aldol reaction of silyl enol ethers with aldehydes in aqueous media, and water-soluble aldehydes such as acetaldehyde, acrolein, and chloroacetaldehyde could be employed for direct use. Moreover, in all these reactions, lanthanide triflates were quantitatively recovered after the reactions were completed and could be reused.

Introduction

The utility of aqueous reactions is now generally recognized.[1] It is desirable to perform the reactions of compounds containing water of crystallization or other water-soluble compounds in aqueous media, because tedious procedures to remove water are necessary when the reactions are carried out in organic solvents. Moreover, aqueous reactions of organic compounds avoid the use of harmful organic solvents.[2]

However, water often interferes with desired reactions, especially those using Lewis acids[3] or organometallic reagents.[4] Recently, Lewis acid-catalyzed carbon−carbon bond-forming reactions have been of great interest in organic synthesis because of their unique reactivity and selectivity and for the mild conditions used.[3] While various kinds of Lewis acid-promoted reactions were developed and many of them have been applied in industry, these reactions must be carried out under strict anhydrous conditions. The presence of even a small amount of water stops the reaction, because most Lewis acids immediately react with water rather than the substrates and decompose or deactivate.

Our goal is to develop versatile Lewis acid-promoted reactions that can be carried out in aqueous media. In order to realize these aqueous reactions, we thought that a new type of Lewis acid which can be used in water was necessary. Recently, we have studied the chemistry of metal trifluoromethanesulfonates (triflates),[5] which have stronger Lewis acidity than the corresponding metal halides because of the electron-withdrawing trifluoromethanesulfonyl group. In the course of our investigations to develop new synthetic reactions using metal triflates, we focused on lanthanide triflates.[6,7] Lanthanide triflates are expected to act as stronger Lewis acids because of the hard character and to have strong affinity toward carbonyl oxygens. On the other hand, their hydrolysis was postulated to be slow from their hydration energies and hydrolysis constants.[8] In fact, while most metal triflates are prepared under strict anhydrous conditions, lanthanide triflates are reported to be prepared in aqueous solution.[9] The large radius of lanthanide(III) and the specific coordination number also attracted us, and we investigated the use of lanthanide triflate as a Lewis acid catalyst in aqueous media and first tried to activate formaldehyde water solution.[10]

Results and Discussion

Activation of Formaldehyde in Water Solution (Commercial Formaldehyde Solution). Hydroxymethylation Reaction of Silyl Enol Ethers. Formaldehyde is a versatile reagent as one of the most highly reactive C1 electrophiles in organic synthesis.[11] Dry

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Table 1. Effect of Lanthanide Triflates in the Reaction of 1 with Commercial Formaldehyde Solution at rt

	yield/%		
	100 mol %		
$Ln(OTf)_3$	24 h	1 h	20 mol % 36 h
$La(OTf)_3$	90	23	88
$Pr(OTf)_3$	92	40	80
$Nd(OTf)_3$	74	6	89
$Sm(OTf)_3$	92	51	91
$Eu(OTf)_3$	92	28	93
$Gd(OTf)_3$	92	20	79
$Dy(OTf)_3$	89	20	85
$Ho(OTf)_3$	91	38	86
$Er(OTf)_3$	90	44	83
$Yb(OTf)_3$	94	5	94

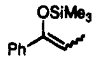
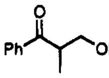
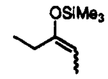
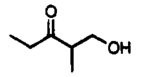
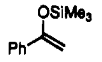
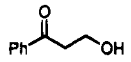
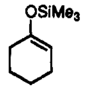
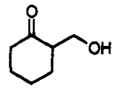
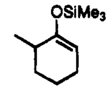
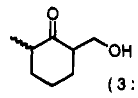
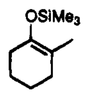
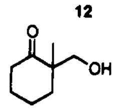
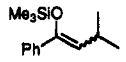
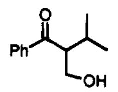
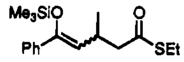
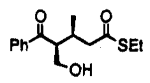
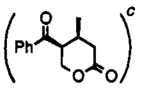
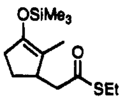
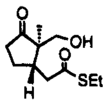
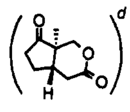
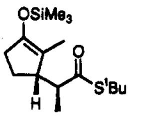
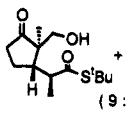
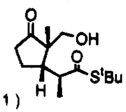
gaseous formaldehyde required for many reactions has some disadvantages because it must be generated before use from solid polymer paraformaldehyde by way of thermal depolymerization and it self-polymerizes easily.[12] On the other hand, commercial formaldehyde solution, which is an aqueous solution containing 37% formaldehyde and 8–10% methanol, is cheap, easy to handle, and stable even at room temperature. However, the use of this reagent is strongly restricted due to the existence of a large amount of water. For example, the titanium tetrachloride ($TiCl_4$)-promoted hydroxymethylation reaction of silyl enol ethers was carried out by using trioxane as a HCHO source under strict anhydrous conditions.[13] Formaldehyde water solution could not be used because $TiCl_4$ and the silyl enol ether reacted with water rather than HCHO in that water solution.

First, we attempted the hydroxymethylation reaction of silyl enol ethers with commercial formaldehyde solution by using $Ln(OTf)_3$. The effects of some selected lanthanide triflates in the reaction of the silyl enol ether of propiophenone (**1**) with commercial formaldehyde solution are shown in Table 1. In most cases, the reactions proceeded smoothly to give the corresponding adduct in high yields. The reaction was most effectively carried out in commercial formaldehyde solution–THF media[14] under the influence of a catalytic amount of $Yb(OTf)_3$.

Several examples of the hydroxymethylation reaction of silyl enol ethers with commercial formaldehyde solution are listed in Table 2, and the following characteristic features of this reaction are noted. (1) In every case, the reactions proceeded smoothly under extremely mild conditions (almost neutral) to give the corresponding hydroxymethylated adducts in high yields. Sterically hindered silyl enol ethers (entries 6–10) also worked well and the diastereoselectivities were high. (2) Di- and polyhydroxymethylated products were not observed.[15] (3) The absence of equilibrium (double bond migration) in silyl enol ethers allowed for a regiospecific hydroxymethylation reaction (entry 5). (4) Only a catalytic amount of $Yb(OTf)_3$ was required to complete the reaction. The amount of the catalyst was examined by taking the reaction of silyl enol ether **1** with commercial formaldehyde solution as a model, and the reaction was found to be catalyzed by even 1 mol % of $Yb(OTf)_3$: 1 mol % (90% yield); 5 mol % (90% yield); 10 mol % (94% yield); 20 mol % (94% yield); 100 mol % (94% yield).

Lanthanide triflates are more soluble in water than in organic solvents such as dichloromethane. Very interest-

Table 2. Reaction of Silyl Enol Ethers with Commercial Formaldehyde Solution Catalyzed by $Yb(OTf)_3$ (10 mol %)

entry	silyl enol ether	product	yield/%
1	 **1**^{a}	 **8**	94
2	 **2E**^{b}	 **9**	85
3	 **3**	 **10**	77
4	 **4**	 **11**	82
5		 (3:2) **12**	86
6		 **13**	92
7	 ^{a}	 **14**	92
8	 **5**^{a}	 **15**  (**16**)^{c}	88
9	 **6**	 **17**  (**18**)^{d}	83
10	 **7**	 **19** +  **20** (9:1)	90

^{a} Z/E = >98/2. ^{b} Z/E = 1/4. ^{c} The mixture of the hydroxy thioester and the lactone (2:1) was obtained. The other diastereomers were not observed. ^{d} The mixture of the hydroxy thioester and the lactone (3:1) was obtained. Less than 3% yield of the other diastereomers were observed.

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[13] (a) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503. TMSOTf-mediated aldol-type reaction of silyl enol ethers with dialkoxymethanes was also reported. (b) Murata, S.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 2527.

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ingly, almost 100% of $Yb(OTf)_3$ was quite easily recovered from the aqueous layer after the reaction was completed and it could be reused. First use (20 mol %) in the reaction of **1** (94% yield); second use (91% yield); third use (93% yield). It is also noteworthy that the present reaction could be carried out smoothly in aqueous media (water does not interfere with this reaction).[16]

Activation of Other Aldehydes. The Aldol Reaction of Silyl Enol Ethers with Aldehydes in Aqueous Media. Next, we examined the use of lanthanide triflates in the activation of aldehydes other than formaldehyde, and intended to develop a lanthanide triflate-catalyzed aldol reaction of silyl enol ethers with aldehydes in aqueous media.[17]

The titanium tetrachloride-mediated aldol reaction of silyl enol ethers with aldehydes was first reported in 1973.[13a,18] The reaction is notably distinguished from the conventional aldol reactions carried out under basic conditions; it proceeds in a highly regioselective manner to afford cross aldols in high yields.[19] Since this pioneering effort, several efficient activators such as trityl salts,[20] Cray montmorillonite,[21] fluoride anions,[22] etc.[23] have been developed to realize high yields and selectivities, and now the reaction is considered to be one of the most important carbon–carbon bond forming reactions in organic synthesis. These reactions are usually carried out under strictly nonaqueous conditions. The presence of even a small amount of water causes lower yields probably due to the rapid decomposition or deactivation of the promoters and the hydrolysis of the silyl enol ethers. Furthermore, the promoters cannot be recovered and reused because they decompose under usual quenching conditions. Lubineau reported the water-promoted aldol reaction of silyl enol ethers with aldehydes;[14] however, the yields and the substrate scope were not yet satisfactory.

First, we examined the model reaction of 1-(trimethylsiloxy)cyclohexene (**4**) with benzaldehyde under the influence of a catalytic amount of $Yb(OTf)_3$ (10 mol %). The reaction proceeded smoothly in H_2O–THF (1:4), but the yields were low when water or THF was used alone. Among several lanthanide triflates screened, neodymium triflate ($Nd(OTf)_3$), gadolinium triflate ($Gd(OTf)_3$), $Yb(OTf)_3$, and lutetium triflate ($Lu(OTf)_3$) were quite effective, while the yield of the desired aldol adduct was lower in the presence of lanthanum triflate ($La(OTf)_3$), praseodymium triflate ($Pr(OTf)_3$), or thulium triflate ($Tm(OTf)_3$) (Table 3).

Table 3. Effect of Lanthanide Triflates in the Reaction of 4 with Benzaldehyde at rt for 20 h in H_2O–THF (1:4)

$Ln(OTf)_3$	yield/%	$Ln(OTf)_3$	yield/%
$La(OTf)_3$	8	$Dy(OTf)_3$	73
$Pr(OTf)_3$	28	$Ho(OTf)_3$	47
$Nd(OTf)_3$	83	$Er(OTf)_3$	52
$Sm(OTf)_3$	46	$Tm(OTf)_3$	20
$Eu(OTf)_3$	34	$Yb(OTf)_3$	91
$Gd(OTf)_3$	89	$Lu(OTf)_3$	88

Table 4. Lanthanide Triflate-Catalyzed Aqueous Aldol Reaction by Using $Yb(OTf)_3$ (10 mol %)[a]

entry	aldehyde	silyl enol ether	product	yield/%
1	PhCHO	**4**	**22**[b]	91
2	PhCHO	**2Z**	**23**[c]	89
3	PhCHO	**2E**	**23**[d]	93
4	PhCHO	**1**	**24**[e]	81
5	PhCHO	$EtSC(OSiMe_3)=CMe_2$ **18**	**25**	90
6	*p*-Cl-PhCHO	**4**	**26**[f]	89
7	*p*-MeO-PhCHO	**4**	**27**[g]	77
8	(*E*)-$CH_3(CH_2)_2$-CH=CHCHO	**4**	**28**[h]	90
9	$Ph(CH_2)_2CHO$	**2Z**	**29**[f]	79
10	$Ph(CH_2)_2CHO$	**2E**	**29**[i]	72
11	CH_3CHO	**1**	**30**[j]	93
12	$CH_2=CHCHO$	**1**	**31**[k]	82
13	$ClCH_2CHO$	**1**	**32**[l]	95
14	$ClCH_2CHO$	**3**	**33**	67
15	$ClCH_2CHO$	**18**	**34**	66
16	$PhCOCHO{\cdot}H_2O$	**1**	**35**[m]	67
17	*o*-HO-PhCHO	**1**	**36**[h]	81
18	2-pyridinecarboxaldehyde	**1**	**37**[n]	97

[a] $Gd(OTf)_3$ was used in entries 11 and 12. In entry 17, $Lu(OTf)_3$ was used. [b] *syn*/*anti* = 73/27. [c] 63/37. [d] 71/29. [e] 53/47. [f] 65/35. [g] 61/39. [h] 55/45. [i] 68/32. [j] 46/54. [k] 60/40. [l] 45/55. [m] 27/73. [n] 42/58.

Several examples of the present aldol reaction of silyl enol ethers with aldehydes are listed in Table 4. In every case, the aldol adducts were obtained in high yields in the presence of a catalytic amount of $Yb(OTf)_3$, $Gd(OTf)_3$, or $Lu(OTf)_3$ in aqueous media. Diastereoselectivities were generally good to moderate. One feature in the present reaction is that water-soluble aldehydes, for instance, acetaldehyde, acrolein, and chloroacetaldehyde, can be reacted with silyl enol ethers to afford the corresponding cross aldol adducts in high yields (entries 11–15). Some of these aldehydes are commercially supplied as water solutions and are appropriate for direct use. Phenylglyoxal monohydrate also worked well (entry 16). It is known that water often interferes with the aldol reaction of metal enolates with aldehydes and that in the cases where such water-soluble aldehydes are employed, some troublesome purifications including dehydration are necessary. Moreover, salicylaldehyde (entry 17) and 2-pyridinecarboxaldehyde (entry 18) could be successfully employed. The former has a free hydroxy group which is incompatible with metal enolates or Lewis acids, and the latter is generally difficult to use under the influence of Lewis acids because of the coordination of the nitrogen atom to the Lewis acids resulting in the deactivation of the acids. While a silyl enol ether derived from a thioester worked well (entries 5 and 15), no desired aldol adduct was obtained when silyl enol ethers derived from esters (ketene silyl acetals) were employed.[24]

It is noted that in all these reactions the catalyst could be easily recovered from the aqueous layer after the reaction was completed and could be reused.

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[16] Lithium enolates prepared from simple ketones react with gaseous formaldehyde to give the corresponding hydroxymethylation adducts. Stork, G.; d'Angelo, J. *J. Am. Chem. Soc.* **1974**, *96*, 7114. See also, Grieco, P. A.; Hiroi, K.; *J. Chem. Soc., Chem. Commun.* **1972**, 1317.

[17] Preliminary communication, Kobayashi, S.; Hachiya, I. *Tetrahedron Lett.* **1992**, 1625.

[18] Mukaiyama, T.; Narasaka, K.; Banno, T. *Chem. Lett.* **1973**, 1011.

[19] Mukaiyama, T. *Org. React.* **1982**, *28*, 203.

[20] Kobayashi, S.; Murakami, M.; Mukaiyama, T. *Chem. Lett.* **1985**, 1535.

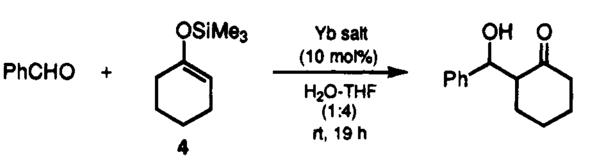
[21] Kawai, M.; Onaka, M.; Izumi, Y. *Chem. Lett.* **1986**, 1581. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1237.

[22] Noyori, R.; Yokoyama, K.; Sakata, J.; Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1977**, *99*, 1265. Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, *48*, 932.

[23] Lanthanide(III) chlorides or some organolanthanide compounds catalyzed aldol reactions of ketene silyl acetals with aldehydes: (a) Takai, K.; Heathcock, C. H. *J. Org. Chem.* **1985**, *50*, 3247. (b) Vougioukas, A. E.; Kagan, H. B. *Tetrahedron Lett.* **1987**, *28*, 5513. (c) Gong, L.; Streitwieser, A. *J. Org. Chem.* **1990**, *55*, 6235. (d) Mikami, K.; Terada, M.; Nakai, T. *Ibid.* **1991**, *56*, 5456. (e) Mikami, K.; Terada, M.; Nakai, T. *J. Chem. Soc., Chem. Commun.* **1993**, 343, and references cited therein.

[24] For use of lanthanide triflates in organic solvents, see Kobayashi, S. Hachiya, I.; Takahori, T. *Synthesis* **1993**, 371.

Table 5. Effect of Yb Salts



Yb salt	yield/%
$Yb(OTf)_3$	91[a]
$Yb(ClO_4)_3$	88[b]
$YbCl_3$	3
$Yb(OAc)_3{\cdot}8H_2O$	14
$Yb(NO_3)_3{\cdot}5H_2O$	7
$Yb_2(SO_4)_3{\cdot}5H_2O$	trace

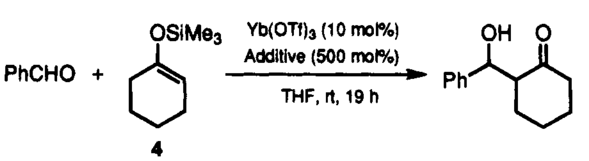
[a] *syn*/*anti* = 73/27. [b] 76/24.

Mechanistic Study. Although hydrolysis of lanthanide compounds is expected to be very slow,[8] there still remains a possibility that a small amount of protons exists in the aqueous media according to the following equation (eq 1). We independently prepared various pH aqueous solutions (pH = 1−6) of trifluoromethanesulfonic acid and tested the model reaction of silyl enol ether **4** with benzaldehyde. In the pH 5 and 6 solutions, only a trace amount of the product was detected on TLC, the yields were less than 5%, and hydrolysis of **4** was also observed. In the pH 1−4 solutions, the silyl enol ether immediately hydrolyzed to give the original ketone, and no aldol adduct was obtained. From these experiments, the protons which may be produced from the hydrolysis of the lanthanide triflates were found not to be an active catalytic species in the present aldol reaction of silyl enol ethers with aldehydes.[25]

$$\begin{array}{ccc} Yb(OTf)_3 + m\,H_2O & \rightleftharpoons & Yb(H_2O)_m^{3+} + 3OTf^- \\ & & \downarrow\uparrow \\ & & Yb(H_2O)_{m-1}(OH)^{2+} + H^+ \end{array} \qquad \text{(Eq. 1)}$$

Next, we investigated the effect of ytterbium salts. The aldol reaction of silyl enol ether **4** with benzaldehyde was carried out under the influence of a catalytic amount of $Yb(OTf)_3$, $Yb(ClO_4)_3$, $YbCl_3$, $Yb(OAc)_3$, $Yb(NO_3)_3$, or $Yb_2(SO_4)_3$ in THF−H_2O (4:1). The results are summarized in Table 5. It is presumed from the dissociation equilibrium equation (eq 1) that these ytterbium salts form a large amount of ytterbium(III) ions in aqueous media. From Table 5, it is suggested that not only the cations but also the counter anions are very important for the catalytic activity. While the Yb salts with less-nucleophlic counter anions such as OTf^- or ClO_4^- effectively catalyzed the reaction, only low yields of the product were obtained when the Yb salts with more-nucleophilic counter anions such as Cl^-, OAc^-, NO_3^-, and SO_4^{2-} were employed. The Yb salts with less-nucleophilic counter anions are more cationic and the high Lewis acidity promotes the desired reaction.

Table 6. Effect of Additives



additive	yield/%
none	10
DMF	21[a]
DMSO	trace
Et_3N	trace
pyridine	23[b]
Et_2O	14
H_2O	80[c]

[a] *syn*/*anti* = 66/34. [b] 73/27. [c] 76/24.

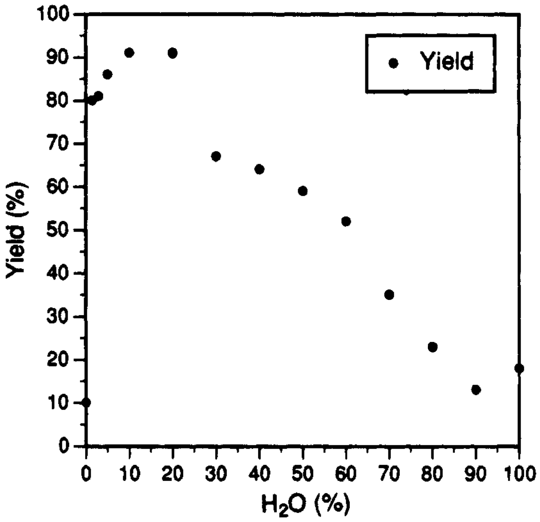


Figure 1. Effect of water (yield).

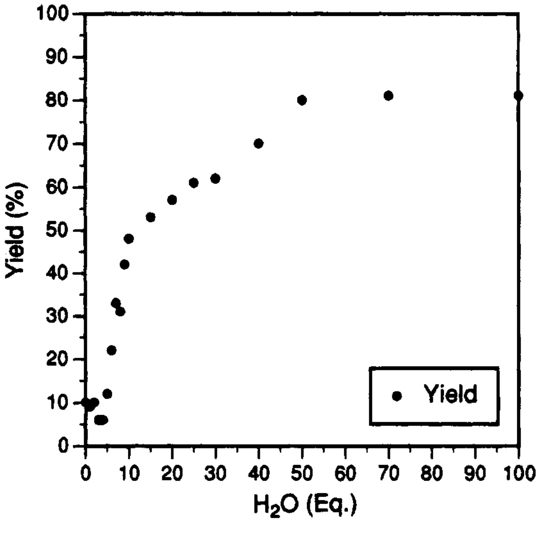


Figure 2. Effect of water (yield).

In aqueous media, water coordinates to ytterbium to form active Yb cations. Are there any effective ligands other than water? Several additives as ligands were screened and the results are summarized in Table 6. Very interestingly, only water was effective. In the presence of other polar molecules such as Et_2O, ROH, DMF,[26] or DMSO, the reaction proceeded very slowly.

The amount of water also influenced yields and diastereoselectivities strongly. The effect of the amount of water on the yield in the model reaction of silyl enol ether **4** with benzaldehyde in the presence of 10 mol % of $Yb(OTf)_3$ in THF are shown in Figures 1 and 2. The best

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(25) The pHs of $Yb(OTf)_3$ solutions were measured. 5.90 (1.6×10^{-2} M, THF−H_2O (4:1)); 6.40 (8.0×10^{-2} M, H_2O).

(26) Pisaniello, D.; Helm, L.; Meier, P.; Merbach, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 4528.

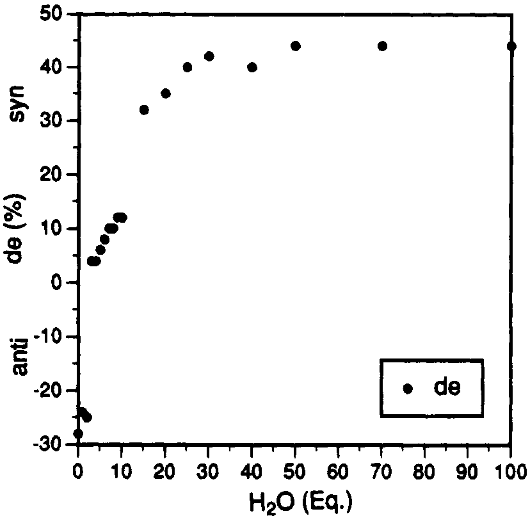

Figure 3. Effect of water (de).

yields were obtained when the ratios of water were 10–20%. When the amount of water increased, the yield began to decrease. The reaction system became two phases when the amount of water increased, and the yield decreased. Only 18% of the product was isolated in 100% water solution. On the other hand, when water was not added or 1–5 equiv of water was added to Yb(OTf)$_3$, the yield of the desired aldol adducts was also low (ca. 10% yield). The yield improved as water was increased to 6–10 equiv, and when more than 50 equiv of water was added, the yield improved to more than 80%.

As for the diastereoselectivities, the amount of water also has an important role in deciding the course of the reactions (Figure 3). In the absence of water, the reaction proceeded with *anti* preference. The selectivity changed as the amount of water increased and the *syn* aldol began to be obtained when more than 3 equiv of water to Yb(OTf)$_3$ was added. The selectivity improved in accordance with the amount of water, and almost the same selectivities were obtained when more than 15 equiv of water was added.

At present we can explain these phenomena as follows. First, in the absence of water or in the presence of a small amount of water, THF predominantly coordinates to Yb(OTf)$_3$ and the activity of THF-coordinated Yb(OTf)$_3$ as a Lewis acid is low. The reaction proceeds slowly via the cyclic six-membered transition state with *anti* preference.[27] On the other hand, when the equivalents of water are gradually increased, water is prone to coordinate to Yb(OTf)$_3$ instead of THF, and Yb(OTf)$_3$ dissociates to form the active Yb cation.[28] At this stage, the intramolecular and intermolecular exchange reactions of water molecules frequently occur. There is a chance for an aldehyde to coordinate to Yb^{3+} instead of water molecules, and the aldehyde is activated. A silyl enol ether attacks this activated aldehyde to produce the aldol adduct. This ytterbium-catalyzed aldol reaction would proceed via the acyclic transition state to give *syn* aldols.[29] When the amount of water is further increased, a competitive reaction, hydrolysis of the silyl enol ether, precedes the desired aldol reaction.

Conclusion

Lanthanide triflates are able to work as Lewis acids in aqueous media. They could successfully activate formaldehyde in water solution (commercial formaldehyde solution) and realize the hydroxymethylation reaction of silyl enol ethers. Lanthanide triflates could also activate other aldehydes, and the aqueous aldol reactions of silyl enol ethers with aldehydes proceeded to afford the aldol adducts in high yields. Water-soluble aldehydes such as acetaldehyde, acrolein, and chloroacetaldehyde could be employed for direct use in these reactions. This is the first example of Lewis acid-promoted reactions in aqueous media. Moreover, the reaction was completed by using only a catalytic amount of lanthanide triflate, and the catalyst could be easily recovered after the reaction was completed and could be reused. There are many kinds of Lewis acid-promoted reactions in industrial chemistry, and treatment of large amounts of the acids left after the reactions has induced some important and severe environmental problems. From the standpoint of catalytic use and reusability, lanthanide triflates are expected to be new types of catalysts providing some solutions for these problems.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a Horiba FT-300. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270LFT-NMR system (270 MHz). Tetramethylsilane (TMS) served as an internal standard. Low- and high-resolution mass spectra were recorded on a JEOL DX-303HF mass spectrometer. Column chromatography was performed on silica gel 60 (Merck) or Wakogel B5F. Formaldehyde-water solution was purchased from Kokusan Kagaku Co., Ltd., and chloroacetaldehyde (40% water solution) and phenylglyoxal monohydrate were purchased from Tokyo Kasei Kogyo Co., Ltd. These reagents were used without further purification. All other reagents and solvents were used after purification according to usual methods. Silyl enol ether **5–7** were prepared by using the trityl salt-catalyzed Michael reaction.[30] All lanthanide triflates (Ln(OTf)$_3$) were prepared by the modification method based on the literature.[9a,b]

Preparation of Lanthanide Triflates (Ln(OTf)$_3$). Lanthanide oxide (30 mmol) was mixed with TfOH–H$_2$O (v/v = 1/1, 21.2 mL), and the suspension was heated at 100 °C for 2 h. Unreacted oxide was removed by filtration and the filtrate was concentrated under reduced pressure. The hydrate thus prepared was dried *in vacuo* (200 °C/0.5 mmHg for 40 h) to give anhydrous lanthanide triflate. The triflate thus prepared was pure enough to use in the following experiments.

Yb(OTf)$_3$: IR (KBr) 3650, 3350, 2300, 1650, 1300, 1040 cm^{-1}; ^{13}C NMR (D$_2$O) δ 122.4 (q, J = 317 Hz) (sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) served as an internal standard). Recrystallization from CH$_3$CN/CH$_2$Cl$_2$ was possible.

Typical Procedure of the Hydroxymethylation Reaction. To commercial formaldehyde solution (1 mL) and THF (3 mL) were successively added Yb(OTf)$_3$ (0.04 mmol, 10 mol%) and silyl enol ether (0.4 mmol) in THF (1 mL) at rt. The mixture was stirred for 24 h at this temperature and then THF was removed under reduced pressure. Water was added and the product was extracted with dichloromethane. After the usual workup, the crude product was chromatographed on silica gel to give the pure adduct. Yb(OTf)$_3$ was almost quantitatively

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(27) Heathcock, C. H. In *Asymmetric Synthesis, Vol. 3, Part B*; Morrison, J. D., Ed.; Academic Press: New York, 1984; p 111.

(28) The solid-state structure of Yb(OTf)$_3$·9H$_2$O was investigated. Harrowfield, J. M.; Kepert, D. L.; Patrick, J. M.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 483. When Yb(OTf)$_3$·9H$_2$O, which was prepared according to the literature, was used, the aldol reactions proceeded, but faster hydrolysis of the silyl enol ethers was observed.

(29) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248.

(30) Mukaiyama, T.; Tamura, M.; Kobayashi, S. *Chem. Lett.* **1986**, 1817; **1987**, 743.

recovered from the aqueous layer after removing water and could be reused.

Typical Procedure of the Aqueous Aldol Reaction. To a Yb(OTf)$_3$ (0.04 mmol, 10 mol %) solution (THF:H$_2$O = 2:1, 1.5 mL) was added a mixture of a silyl enol ether (0.44 mmol) and an aldehyde (0.4 mmol) in THF (1 mL) at rt. The mixture was stirred for an appropriate time at this temperature (checked by TLC, 3–12 h) and then THF was removed under reduced pressure. Water was added and the product was extracted with dichloromethane. After the usual workup, the crude product was chromatographed on silica gel to yield the pure aldol adduct. Yb(OTf)$_3$ was almost quantitatively recovered from the aqueous layer after removing water and could be reused.

The Aqueous Aldol Reaction Using Chloroacetaldehyde–Water Solution. Yb(OTf)$_3$ (0.04 mmol, 10 mol %), chloroacetaldehyde–water solution (40%) (0.3 mL), and THF (0.9 mL) were mixed at room temperature. A silyl enol ether (0.4 mmol) in THF (0.7 mL) was then added and the mixture was stirred for 30 h at this temperature. THF was removed under reduced pressure, and water was added. The product was extracted with dichloromethane and after the usual workup, the crude product was chromatographed on silica gel to yield the pure aldol adduct.

3-Hydroxy-2-methyl-1-phenyl-1-propanone (8): IR (neat) 3420, 1674 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.24 (d, 3H, J = 7.6 Hz), 2.38 (brs, 1H), 3.63–4.02 (m, 3H), 7.45–7.62 (m, 3H), 7.95–7.99 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 14.5, 42.9, 64.5, 128.3, 128.6, 133.2, 136.0, 204.4; Anal. Calcd for C$_{10}$H$_{12}$O$_2$: C, 73.15; H, 7.37. Found: C, 72.50; H, 7.41.

1-Hydroxy-2-methyl-3-pentanone (9):[31] IR (neat) 3420, 1730 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.06 (t, 3H, J = 7.3 Hz), 1.13 (d, 3H, J = 7.3 Hz), 2.40–2.63 (m, 3H), 2.72–2.83 (m, 1H), 3.66 (dd, 1H, J = 11.0, 5.3 Hz), 3.75 (dd, 1H, J = 11.0, 5.3 Hz).

3-Hydroxy-1-phenyl-1-propanone (10):[32] IR (neat) 3420, 1674 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.73 (brs, 1H), 3.23 (t, 2H, J = 5.3 Hz), 4.04 (t, 2H, J = 5.3 Hz), 7.44–7.62 (m, 3H), 7.95–7.99 (m, 2H).

2-(Hydroxymethyl)cyclohexanone (11):[14b] IR (neat) 3420, 1705 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.40–2.17 (m, 6H), 2.26–2.65 (m, 3H), 2.73 (brs, 1H), 3.55–3.63 (m, 1H), 3.73 (dd, 1H, J = 11.5, 7.3 Hz).

2-(Hydroxymethyl)-6-methylcyclohexanone (12):[12d] isomer ratio = 3:2; IR (neat) 3420, 1705 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.18 (d, 3H, J = 7.3 Hz), 1.51–1.98 (m, 6H), 2.49–2.73 (m, 3H), 3.61–3.80 (m, 2H).

2-(Hydroxymethyl)-2-methylcyclohexanone (13):[12d] IR (neat) 3460, 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.19 (s, 3H), 1.36–2.77 (m, 9H), 3.50 (brs, 2H).

3-Hydroxy-2-(1-methylethyl)-1-phenyl-1-propanone (14): IR (neat) 3420, 1674 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.95 (d, 6H, J = 6.6 Hz), 2.19 (dq, 1H, J = 7.6, 6.6 Hz), 2.19 (brs, 1H), 3.48 (ddd, 1H, J = 7.6, 7.6, 3.3 Hz), 3.83 (dd, 1H, J = 10.9, 3.3 Hz), 4.06 (dd, 1H, J = 10.9, 7.6 Hz), 7.41–7.59 (m, 3H), 7.94–7.98 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 19.7, 21.4, 28.6, 54.1, 61.3, 128.4, 128.7, 133.3, 137.8, 205.3; HRMS calcd for C$_{12}$H$_{16}$O$_2$ (M$^+$) 192.1148, found 192.1145.

Hydroxymethylation product 15 from silyl enol ether 5 (Table 2, entry 8): IR (neat) 3475, 1732, 1674 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.96 (d, 3H, J = 6.9 Hz), 1.25 (t, 3H, J = 7.4 Hz), 2.26 (brs, 1H), 2.46–2.57 (m, 1H), 2.62–2.80 (m, 2H), 2.89 (q, 2H, J = 7.4 Hz), 3.73 (ddd, 1H, J = 6.9, 4.3, 4.0 Hz), 3.83 (dd, 1H, J = 11.2, 4.0 Hz), 4.08 (dd, 1H, J = 11.2, 6.9 Hz), 7.42–7.62 (m, 3H), 7.98–8.01 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 14.8, 16.5, 23.5, 30.8, 48.5, 51.2, 60.2, 128.5, 128.8, 133.5, 136.7, 198.8, 203.6; HRMS calcd for C$_{15}$H$_{20}$O$_3$S (M$^+$) 280.1131, found 280.1130.

Lactone 16 from silyl enol ether 5 (Table 2, entry 8): IR (neat) 1741, 1674 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.07 (d, 3H, J = 6.6 Hz), 2.31 (dd, 1H, J = 16.8, 8.3 Hz), 2.58–2.74 (m, 1H), 2.86 (dd, 1H, J = 16.8, 7.6 Hz), 3.63 (ddd, 1H, J = 9.6, 8.1, 5.3 Hz), 4.36 (dd, 1H, J = 11.5, 9.6 Hz), 4.49 (dd, 1H, J = 11.5, 5.3 Hz), 7.49–7.67 (m, 3H), 7.95–7.99 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 20.8, 29.6, 36.7, 47.7, 69.2, 128.4, 129.1, 134.1, 136.2, 170.6, 198.9; HRMS calcd for C$_{13}$H$_{14}$O$_3$ (M$^+$) 218.0942, found 218.0945.

Hydroxymethylation product 17 from silyl enol ether 6 (Table 2, entry 9): IR (neat) 3460, 1734, 1687 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.84 (s, 3H), 1.27 (t, 3H, J = 7.4 Hz), 2.11–2.85 (m, 8H), 2.91 (q, 2H, J = 7.4 Hz), 3.39 (d, 1H, J = 11.2 Hz), 3.70 (d, 1H, J = 11.2 Hz); ^{13}C NMR (CDCl$_3$) δ 13.7, 14.6, 23.5, 24.9, 37.2, 37.3, 44.4, 52.8, 65.2, 198.8, 222.0; HRMS calcd for C$_{11}$H$_{18}$O$_3$S (M$^+$) 230.0974, found 230.0965.

Lactone 18 from silyl enol ether 6 (Table 2, entry 9): IR (neat) 1741, 1737 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.13 (s, 3H), 1.57–1.67 (m, 1H), 2.28–2.59 (m, 5H), 2.74–2.83 (m, 1H), 3.93 (d, 1H, J = 11.5 Hz), 4.39 (d, 1H, J = 11.5 Hz); ^{13}C NMR (CDCl$_3$) δ 21.2, 26.4, 34.0, 36.8, 39.1, 47.2, 71.7, 172.1, 218.9; HRMS calcd for C$_9$H$_{12}$O$_3$ (M$^+$) 168.0785, found 168.0787.

Hydroxymethylation product 19 from silyl enol ether 7 (Table 2, entry 10): IR (neat) 3465, 1734, 1678 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.84 (s, 3H), 1.25 (d, 3H, J = 6.8 Hz), 1.48 (s, 9H), 2.11–2.22 (m, 2H), 2.35–2.45 (m, 1H), 2.58–2.67 (m, 4H), 3.22 (d, 1H, J = 9.9 Hz), 3.77 (dd, 1H, J = 10.2, 9.9 Hz); ^{13}C NMR (CDCl$_3$) δ 14.1, 17.8, 22.8, 29.5, 36.7, 41.1, 48.4, 49.3, 53.6, 65.0, 205.5, 221.3. Anal. Calcd for C$_{14}$H$_{24}$O$_3$S: C, 61.73; H, 8.88; S, 11.77. Found: C, 61.92; H, 8.94; S, 11.59.

Hydroxymethylation product 20 from silyl enol ether 7 (Table 2, entry 10): IR (neat) 3465, 1734, 1678 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.98 (s, 3H), 1.23 (d, 3H, J = 6.6 Hz), 1.48 (s, 9H), 1.67–1.78 (m, 3H), 2.04–2.46 (m, 3H), 2.84–2.92 (m, 1H), 3.76 (dd, 1H, J = 8.9, 5.0 Hz), 3.82 (d, 1H, J = 8.9 Hz); ^{13}C NMR (CDCl$_3$) δ 17.7, 20.5, 24.7, 29.7, 37.4, 48.2, 48.7, 49.2, 52.5, 66.1, 204.0, 223.9; HRMS calcd for C$_{14}$H$_{24}$O$_3$S (M$^+$) 272.1444, found 272.1442.

2-[Hydroxy(phenyl)methyl]cyclohexanone (22).[33] *Syn*: mp 104.8–105.2 °C; IR (KBr) 3552, 1699 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.47–1.88 (m, 5H), 2.04–2.13 (m, 1H), 2.31–2.49 (m, 2H), 2.56–2.64 (m, 1H), 3.03 (d, 1H, J = 3.3 Hz), 5.40 (t, 1H, J = 2.6 Hz), 7.22–7.38 (m, 5H). *Anti*: IR (neat) 3510, 1699 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.23–1.37 (m, 1H), 1,47–1.83 (m, 4H), 2.04–2.13 (m, 1H), 2.30–2.54 (m, 2H), 2.57–2.67 (m, 1H), 3.97 (s, 1H), 4.79 (d, 1H, J = 8.9 Hz), 7.20–7.39 (m, 5H).

1-Hydroxy-2-methyl-1-phenyl-3-pentanone (23): *syn/anti* = 63/37; IR (neat) 3462, 1707 cm^{-1}; ^{1}H NMR (CDCl$_3$) 0.90–1.09 (m, 6H), 2.26–2.61 (m, 2H), 2.79–3.22 (m, 2H), 4.74 (d, 0.37H, J = 8.3 Hz), 5.03 (d, 0.63H, J = 4.0 Hz), 7.22–7.37 (m, 5H). Anal. Calcd for C$_{12}$H$_{16}$O$_2$: C, 74.97; H, 8.39. Found: C, 74.60; H, 8.40.

3-Hydroxy-2-methyl-3-phenyl-1-propanone (24):[33] *syn/anti* = 53/47; IR (neat) 3467, 1678 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.02 (d, 1.41H, J = 7.3 Hz), 1.17 (d, 1.59H, J = 7.3 Hz), 3.20 (brs, 0.53H), 3.64–3.87 (m, 1.47H), 4.96 (dd, 0.47H, J = 3.3, 7.9 Hz), 5.19 (d, 0.53H, J = 2.3 Hz), 7.20–7.57 (m, 8H), 7.88–7.97 (m, 2H).

***S*-Ethyl 3-hydroxy-2,2-dimethyl-3-phenylpropanethioate (25):** IR (neat) 3508, 1664 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.09 (s, 3 H), 1.20–1.26 (m, 6 H), 2.86 (q, 2 H, J = 7.3 Hz), 3.12 (s, 1 H), 4.92 (s, 1 H), 7.25–7.31 (m, 5 H); HRMS calcd for C$_{13}$H$_{18}$O$_2$S (M$^+$) 238.1027, found 238.1031.

2-[Hydroxy(4-chlorophenyl)methyl]cyclohexanone (26).[33] *Syn*: mp 114.8–115.5 °C; IR (KBr) 3225, 1701 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.46–1.74 (m, 4H), 1.79–1.89 (m, 1H), 2.05–2.13 (m, 1H), 2.31–2.60 (m, 3H), 3.07 (d, 1H, J = 3.0 Hz), 5.36 (s, 1H), 7.22–7.33 (m, 4H). *Anti*: mp 94.0–94.8 °C; IR (KBr) 3421, 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.23–1.36 (m, 1H), 1.47–1.83 (m, 4H), 2.05–2.14 (m, 1H), 2.29–2.61 (m, 3H), 4.00 (d, 1H, J = 2.6 Hz), 4.76 (dd, 1H, J = 2.3, 8.6 Hz), 7.23–7.25 (m, 4H).

2-[Hydroxy(4-methoxyphenyl)methyl]cyclohexane (27).[34] *Syn*: mp 125.5–126.3 °C; IR (KBr) 3442, 1695 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.49–1.89 (m, 4H), 2.04–2.13 (m, 1H), 2.30–2.49 (m, 3H), 2.53–2.60 (m, 1H), 3.00 (d, 1H, J = 3.0 Hz), 3.80 (s, 3H), 5.33 (s, 1H), 6.85–6.90 (m, 2H), 7.20–7.26 (m, 2H). *Anti*: mp 78.6–79.2 °C; IR (KBr) 3462, 1705 cm^{-1}; ^{1}H NMR

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($CDCl_3$) 1.23−1.35 (m, 1H), 1.47−1.81 (m, 4H), 2.04−2.13 (m, 1H), 2.30−2.64 (m, 3H), 3.80 (s, 3H), 3.94 (s, 1H), 4.74 (d, 1H, *J* = 8.9 Hz), 6.85−6.90 (m, 2H), 7.21−7.27 (m, 2H).

2-(1-Hydroxy-2-hexenyl)cyclohexane (28). *Syn*: IR (neat) 3464, 1703 cm^{-1}; ^1H NMR ($CDCl_3$) 0.90 (t, 3H, *J* = 7.3 Hz), 1.23−2.50 (m, 13H), 2.60−3.00 (brs, 1H), 4.47−4.51 (m, 1H), 5.43−5.51 (m, 1H), 5.63−5.74 (m, 1H). *Anti*: IR (neat) 3442, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) 0.90 (t, 3H, *J* = 7.3 Hz), 1.23−2.46 (m, 14H), 4.19 (t, 1H, *J* = 7.9 Hz), 5.36−5.45 (m, 1H), 5.63−5.74 (m, 1H). Anal. (*syn/anti* = 55/45) Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.10; H, 10.50.

5-Hydroxy-4-methyl-7-phenyl-3-heptanone (29): *syn/anti* = 65/35; IR (neat) 3458, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) 0.99−1.15 (m, 6H), 1.53−1.91 (m, 2H), 2.35−2.94 (m, 6H), 3.63−3.69 (m, 0.35H), 3.90−3.93 (m, 0.65H), 7.17−7.30 (m, 5H); Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.50; H, 9.43.

3-Hydroxy-2-methyl-1-phenyl-1-butanone (30):[35] *syn/anti* = 46/54; IR (neat) 3460, 1676 cm^{-1}; ^1H NMR ($CDCl_3$) 1.21−1.29 (m, 6H), 2.95 (brs, 0.54H), 3.18 (brs, 0.46H), 3.38−3.54 (m, 1H), 4.06−4.14 (m, 0.54H), 4.20−4.29 (m, 0.46H), 7.44−7.62 (m, 3H), 7.93−7.99 (m, 2H).

3-Hydroxy-2-methyl-1-phenyl-4-penten-1-one (31): *syn/anti* = 60/40; IR (neat) 3454, 1676 cm^{-1}; ^1H NMR ($CDCl_3$) 1.22 (d, 1.20H, *J* = 7.3 Hz), 1.26 (d, 1.80 H, *J* = 6.9 Hz), 3.01 (brs, 0.40H), 3.23 (brs, 0.60H), 3.50−3.66 (m, 1H), 4.38−4.43 (m, 0.40H), 4.58−4.60 (m, 0.60H), 5.17−5.40 (m, 2H), 5.82−5.99 (m, 1H), 7.43−7.61 (m, 3H), 7.90−7.97 (m, 2H). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.50; H, 7.40.

4-Chloro-3-hydroxy-2-methyl-1-phenyl-1-butanone (32): *syn/anti* = 45/55; IR (neat) 3423, 1676 cm^{-1}; ^1H NMR ($CDCl_3$) 1.27−1.32 (m, 3H), 3.16 (brs, 1H), 3.61−3.96 (m, 3H), 4.11−4.17 (m, 0.55H), 4.22−4.29 (m, 0.45H), 7.46−7.63 (m, 3H), 7.95−8.00 (m, 2H); HRMS calcd for $C_{11}H_{13}O_2Cl$ (M^+) 212.0602, found 212.0594.

4-Chloro-3-hydroxy-1-phenyl-1-butanone (33): IR (neat) 3454, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) 3.29 (d, 1H, *J* = 3.3 Hz), 3.32 (d, 1H, *J* = 1.3 Hz), 3.49 (brs, 1 H), 3.69−3.71 (dd, 2H, *J* = 1.3, 4.6 Hz), 4.44−4.52 (m, 1H), 7.46−7.63 (m, 3H), 7.95−7.98 (m, 2H); HRMS calcd for $C_{10}H_{11}O_2Cl$ (M^+) 198.0446, found 198.0425.

***S*-Ethyl 4-chloro-2-dimethyl-3-butanethioate (34):** IR (neat) 3507, 1666 cm^{-1}; ^1H NMR ($CDCl_3$) 1.22−1.31 (m, 9H), 2.83−2.92 (m, 3H), 3.49 (dd, 1H, *J* = 9.6, 11.2 Hz), 3.68 (dd, 1H, *J* = 2.3, 11.2 Hz), 3.97 (dd, 1H, *J* = 1.7, 9.6 Hz); HRMS calcd for $C_8H_{16}O_2ClS$ ($M + 1^+$) 211.0558, found 211.0556.

2-Hydroxy-3-methyl-1,4-diphenyl-1,4-butanedione (35). *Syn*: IR (neat) 3462, 1682, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) 1.12 (d, 3H, *J* =7.3 Hz), 3.74 (d, 1H, *J* = 6.3 Hz), 3.79−3.88 (m, 1H), 5.47 (dd, 1H, *J* = 3.5, 6.1 Hz), 7.46−7.68 (m, 6H), 7.87−7.96 (m, 4H). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.70; H, 6.09. *Anti*: IR (neat) 3464, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) 1.35 (d, 3H, *J* = 7.3 Hz), 3.95−4.05 (m, 1H), 4.38 (d, 1H, *J* = 9.2 Hz), 5.22 (dd, 1H, *J* = 4.6, 9.2 Hz), 7.44−7.63 (m, 6H), 7.90−8.00 (m, 4H). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.90; H, 6.00.

3-[Hydroxy(2-hydroxyphenyl)]-2-methyl-1-phenyl-1-propanone (36): *syn/anti* = 55/45; IR (neat) 3332, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) 1.03 (d, 1.35H, *J* = 7.3 Hz), 1.30 (d, 1.65H, *J* = 7.3 Hz), 3.73−3.82 (m, 0.45H), 4.00−4.11 (m, 0.55H), 4.82 (brs, 1H), 5.11 (d, 0.45H, *J* = 8.9 Hz), 5.39 (d, 0.55H, *J* = 3.3 Hz), 6.79−7.69 (m, 7H), 7.90−7.99 (m, 2H), 8.13 (brs, 0.47H), 8.77 (brs, 0.53H). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.21; H, 6.30.

3-Hydroxy-3-(2-pyridyl)-2-methyl-1-phenyl-1-propanone (37). *Syn*: mp 95.0−95.2 °C; IR (KBr) 3128, 1676 cm^{-1}; ^1H NMR ($CDCl_3$) 1.16 (d, 3H, *J* = 7.3 Hz), 4.04−4.13 (m, 1 H), 4.23 (brs, 1H), 5.23 (d, 1H, *J* = 4.0 Hz), 7.15−7.19 (m, 1H), 7.42−7.70 (m, 5H), 7.96 (d, 2H, *J* = 7.6 Hz), 8.53−8.55 (m, 1H). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.90; H, 6.27; N, 5.68. *Anti*: IR (neat) 3433, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) 1.22 (d, 3H, *J* = 6.9 Hz), 4.14−4.24 (m, 1H), 4.36 (brs, 1H), 5.02 (d, 1H, *J* = 6.0 Hz), 7.12−7.17 (m, 1H), 7.40−7.68 (m, 5H), 7.93−7.97 (m, 2H), 8.50−8.52 (m, 1H). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.60; H, 6.47; N, 5.68.

Effect of Water. A typical experimental procedure is described for the reaction using 50 equiv of water: $Yb(OTf)_3$ (0.04 mmol, 10 mol %) was dried at 200 °C (0.5 mmHg) for 2 h, and 2 N H_2O−THF solution (1 mL) was added. Then a mixture of 1-(trimethylsiloxy)cyclohexene (4, 0.44 mmol) and benzaldehyde (0.4 mmol) in THF (1.5 mL) was added at rt. The mixture was stirred for 19 h at this temperature and then water was added. The product was extracted with dichloromethane and dried, and the organic solvent was removed under reduced pressure. The residue was treated with THF:1 N HCl (20:1) for 0.5 h at 0 °C. After dilution with hexane, saturated aqueous $NaHCO_3$ was added and the product was extracted with dichloromethane. The organic extract was purified by thin-layer chromatography (silica gel) to give the pure aldol adduct (80% yield, *syn/anti* = 72/28).

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