# Ytterbium Trifluoromethanesulfonate Mediated Cross-Aldol Reaction between Ketones and Aldehydes

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The cross-aldol reaction between a ketone and an aldehyde proceeded smoothly with *threo* diastereoselection favorably mediated by ytterbium trifluoromethanesulfonate and tertiary amine in diethyl ether or in dichloromethane. A ytterbium enolate was trapped with chlorotrimethylsilane to afford a silyl enol ether.

The past decade has seen an explosive growth in the applications of lanthanoid reagents to organic synthesis.[1,2] The utilization of this class of reagents now has become one of the standard procedures for selective organic synthesis. In early studies in this research area, we and other research groups challenged the utilization of trivalent lanthanoid halide as a hard Lewis acid for functional-group transformation and carbon–carbon bond formation.[3—7] Although some studies were successful, there seemed to be a limitation in organic synthesis, because of its much weaker Lewis acidity, compared to that of strong Lewis acids, such as zinc chloride and titanium chloride. Among trivalent lanthanoid compounds, we are interested in lanthanoid trifluoromethanesulfonate (triflate) [$Ln(OTf)_3$], which appeared in a pyrimidine synthesis from the reaction of acetonitrile and a secondary amine.[8] Recent communications have dealt with $Ln(OTf)_3$ as a catalyst for the Mukaiyama aldol reaction of silyl enol ethers in aqueous media, where $Ln(OTf)_3$ works as a Lewis acid.[9] We would like to report here on the first ytterbium triflate [$Yb(OTf)_3$] mediated cross-aldol reaction via ytterbium enolate in the presence of a tertiary amine. Although the efficiency of lanthanoid enolate for a cross-aldol reaction was first reported by Imamoto et al.,[10] its chemistry has not been fully studied to date.

## Results and Discussion

The present work began with a condensation reaction of 3-pentanone with benzaldehyde in diethyl ether. Table 1 summarizes the results of the reaction under various conditions. The ytterbium enolate was generated by the sequential addition of the ketone and a tertiary amine to $Yb(OTf)_3$ in diethyl ether at 0 °C to room temperature.[11] Upon quenching with benzaldehyde (1 equiv) after the indicated reaction time, a mixture of *erythro* and *threo* aldols was produced in good yield in a ratio of the *erythro*: *threo*=65 : 35—70 : 30 (Scheme 1). It is impressive that the isomer ratio depended on the reaction time; *erythro* selectivity increased up to 90% when the reaction was carried out for 48 h (Run 4). The reaction could be carried out in dichloromethane under indicated conditions, and a similar tendency of diastereoselectivity (*erythro* favored) was observed (Runs 6—10); however, a longer reaction time (24—48 h) hardly affected the diastereoselectivity. No aldol adduct was produced in $CS_2$ or in THF (Runs 12 and 13).

In following studies we found that 3-pentanone also reacts with isobutyraldehyde or pivalaldehyde under the shown conditions to give the aldol adduct in moderate to good yields. The results are also given in Table 1. Quite interestingly, the diastereoselectivity in either case sharply contrasted with that of the reaction with benzaldehyde; the *threo* aldol adduct was primarily produced (*erythro*: *threo*=30 : 70—1 : 99). Runs 20—23 in Table 1 illustrate that the increase of an aldehyde steric hindrance completed the high *threo* selectivity (*threo*: *erythro*=96 : 4—99 : 1). An amine steric hindrance slightly influenced the diastereoselectivity. Thus, *N*,*N*-diisopropylethylamine was somewhat effective in achieving a better diastereoselectivity (Runs 3 and 5, 6 and 9, 23 and 24); however, usually *N*,*N*-diisopropylethylamine, triethylamine, and *N*-ethylpiperidine gave essentially the same selectivities. The aldol diastereoselection in dichloromethane is comparable to that observed in diethyl ether.

Experiments were conducted to determine the tendency of the diastereoselection in the aldol reaction via the ytterbium enolate of various ethyl ketones, such as 2-methyl-3-pentanone, 2,2-dimethyl-3-pentanone, propiophenone, and 2,4,6-trimethylpropiophenone. The results of the examples given in Table 2 show that the stereochemical result showed a uniform tendency of diastereoselection, with each case favoring the *threo* aldol isomer in either diethyl ether or dichloromethane. A high *threo* selectivity (98—100%) was again accomplished in a reaction with 2,2-dimethyl-3-pentanone (Table 2, Run 5) and each reaction with pivalaldehyde (Table 2, Runs 3,4 and 10).

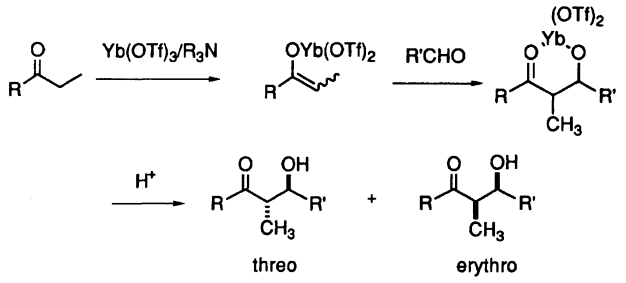
Because cyclopentanone and cyclohexanone produce the ***E*** ytterbium enolate, we expected a higher *threo* diastereoselection of the cyclic ***E*** enolate than that of the acyclic enolate, which should be a mixture of ***E*** and ***Z*** isomers. This expectation was based upon Zimmerman and Traxler's aldol diastereoselection model.[12] Indeed, *threo* diastereoselection with cyclohexanone was superior to that observed in the acyclic enolate; *threo*: *erythro*=80 : 20—94 : 6 (Table 2, Runs 14—16).

We also examined the reactivity of the other lan-

Table 1. Reaction of 3-Pentanone with Aldehydes Promoted by $Yb(OTf)_3$ and Tertiary Amine[a)]

| Run | Aldehyde | Amine | Solv. | Temp (°C) | Time (h) | Yield (%)[b)] | *threo* : *erythro*[c)] |
|---|---|---|---|---|---|---|---|
| 1 | PhCHO | $Pr^i_2NEt$ | $Et_2O$ | 0 | 3 | 92 | 34 : 66 |
| 2 | PhCHO | $Pr^i_2NEt$ | $Et_2O$ | 25 | 3 | 97 | 28 : 72 |
| 3 | PhCHO | $Pr^i_2NEt$ | $Et_2O$ | 25 | 24 | 72 | 17 : 83 |
| 4 | PhCHO | $Pr^i_2NEt$ | $Et_2O$ | 25 | 48 | 97 | 9 : 91 |
| 5 | PhCHO | $Et_3N$ | $Et_2O$ | 25 | 24 | 45 | 25 : 75 |
| 6 | PhCHO | $Pr^i_2NEt$ | $CH_2Cl_2$ | 0 | 3 | 88 | 30 : 70 |
| 7 | PhCHO | $Pr^i_2NEt$ | $CH_2Cl_2$ | 25 | 24 | 78 | 26 : 74 |
| 8 | PhCHO | $Pr^i_2NEt$ | $CH_2Cl_2$ | 25 | 48 | 84 | 33 : 67 |
| 9 | PhCHO | $Et_3N$ | $CH_2Cl_2$ | 0 | 3 | 81 | 35 : 65 |
| 10 | PhCHO | EtNpip[d)] | $CH_2Cl_2$ | 0 | 3 | 81 | 35 : 65 |
| 11 | PhCHO | $Et_3N$ | $CHCl_3$ | 0 | 3 | 68 | 35 : 65 |
| 12 | PhCHO | $Et_3N$ | THF | 0 | 3 | — | — |
| 13 | PhCHO | $Et_3N$ | $CS_2$ | 0 | 3 | — | — |
| 14 | $Pr^i$CHO | $Pr^i_2NEt$ | $Et_2O$ | 25 | 24 | 66 | 77 : 23 |
| 15 | $Pr^i$CHO | $Pr^i_2NEt$ | $Et_2O$ | 25 | 48 | 87 | 70 : 30 |
| 16 | $Pr^i$CHO | EtNpip[d)] | $CH_2Cl_2$ | 0 | 3 | 73 | 70 : 30 |
| 17 | $Pr^i$CHO | $Et_3N$ | $CH_2Cl_2$ | 0 | 3 | 73 | 70 : 30 |
| 18 | $Pr^i$CHO | $Pr^i_2NEt$ | $CH_2Cl_2$ | 0 | 3 | 78 | 70 : 30 |
| 19 | $Pr^i$CHO | $Pr^i_2NEt$ | $CH_2Cl_2$ | 25 | 48 | 76 | 84 : 16 |
| 20 | $Bu^t$CHO | $Pr^i_2NEt$ | $Et_2O$ | 25 | 24 | 89 | 97 : 3 |
| 21 | $Bu^t$CHO | $Et_3N$ | $Et_2O$ | 25 | 24 | 52 | 96 : 4 |
| 22 | $Bu^t$CHO | EtNpip[d)] | $Et_2O$ | 25 | 24 | 49 | 97 : 3 |
| 23 | $Bu^t$CHO | $Pr^i_2NEt$ | $CH_2Cl_2$ | 0 | 3 | 55 | 99 : 1 |
| 24 | $Bu^t$CHO | $Et_3N$ | $CH_2Cl_2$ | 0 | 3 | 42 | 90 : 10 |

a) 3-Pentanone (2.3 mmol), $Yb(OTf)_3$ (2.0 mmol), tertiary amine (2.5 mmol), aldehyde (2.0 mmol), solvent (20 ml). b) Isolated yield of the aldol. c) Isomer ratio was determined by 400 MHz, $^1H$ NMR. d) *N*-Ethylpiperidine.




Scheme 1.

thanoid triflates, including scandium and yttrium triflates, in the reaction of 3-pentanone with isobutyraldehyde. We chose neodymium, samarium, and lutetium as typical lanthanoid elements. Neodymium and samarium triflates were inactive for the reaction, a trace of the aldol product being formed. Scandium, yttrium, and lutetium triflates gave the aldol product in as good yields as $Yb(OTf)_3$. The results are shown in Table 3. The diastereoselectivity of the reaction was almost the same as that with $Yb(OTf)_3$.

The formation of the ytterbium enolate was confirmed by derivatization with chlorotrimethylsilane to the corresponding trimethylsilyl enol ethers. The stereochemistry of the derived trimethylsilyl enol ethers was revealed to be mainly ***E***, which was determined by $^1H$ NMR; ***E***:***Z*** = 82:18 and 86:14 in R=Ph and $Pr^i$, respectively (Scheme 2).[13)]

The *erythro* aldol (R=Et, R′=$Pr^i$) (90% de) isomerized to the corresponding *threo* aldol (*threo*: *erythro* = 72:28) upon a treatment with one equivalent each of $Yb(OTf)_3$ and *N*,*N*-diisopropylethylamine in dichloromethane under the conditions of the aldol reaction. The stereochemistry of this isomerization experiment was quite consistent with the results of Runs 16—18 in Table 1. This results suggest that the stereochemistry of the $Yb(OTf)_3$ mediated aldol reaction is thermodynamically controlled.[14)] At the transition state of the reaction, the ytterbium chelate permits isomerization around the $C_2$–$C_3$ bond with or without dissociation of the adduct from the metal. Scheme 3 illustrates the equilibrium between *threo* and *erythro* chelates. When R′ is sterically demanding, such as *t*-butyl, the equilibrium favors the normal preference for the formation of the *threo* ytterbium chelate in which R′ and the methyl group are both equatorial; then, excellent diastereoselection could be attained.[15)] However, for a less bulky aldehyde (R′=phenyl, isopropyl), the diastereoselection has been observed to be diminished. The sterically crowded ketone (2,2-dimethyl-3-pentanone, R=*t*-Bu) favors the *threo* ytterbium chelate, resulting in a high *threo* diastereoselection. The question why the reaction of 3-pentanone with benzaldehyde exceptionally afforded *erythro* favored diastereoselection has remained unanswered.

Table 2. $Yb(OTf)_3$ Promoted Cross Aldol Reaction of Several Ethyl Ketones with Aldehydes[a)]

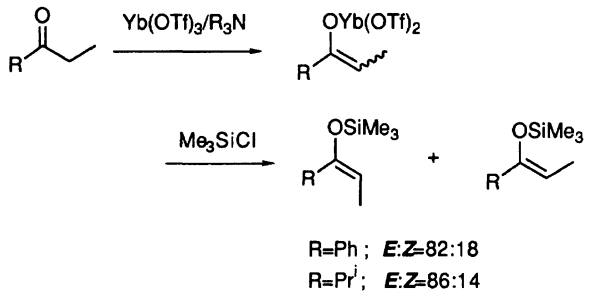
| Run | Ketone | Aldehyde | Amine | Solv. | Temp (°C) | Time (h) | Yield (%)[b)] | *threo* : *erythro*[c)] |
|---|---|---|---|---|---|---|---|---|
| 1 | 2-Methyl-3-pentanone (R=$Pr^i$) | PhCHO | $Et_3N$ | $Et_2O$ | 25 | 24 | 83 | 65 : 35 |
| 2 | | PhCHO | $Et_3N$ | $CH_2Cl_2$ | 0 | 3 | 83 | 65 : 35 |
| 3 | | $Bu^tCHO$ | $Pr^i{}_2NEt$ | $Et_2O$ | 25 | 24 | 60 | 98 : 2 |
| 4 | | $Bu^tCHO$ | $Pr^i{}_2NEt$ | $CH_2Cl_2$ | 25 | 24 | 50 | 99 : 1 |
| 5 | 2,2-Dimethyl-3-pentanone (R=$Bu^t$) | PhCHO | $Pr^i{}_2NEt$ | $CH_2Cl_2$ | 25 | 24 | 68 | 96 : 4 |
| 6 | Propiophenone (R=Ph) | PhCHO | $Pr^i{}_2NEt$ | $Et_2O$ | 25 | 24 | 30 | 65 : 35 |
| 7 | | PhCHO | $Pr^i{}_2NEt$ | $Et_2O$ | 25 | 48 | 86 | 56 : 44 |
| 8 | | PhCHO | $Et_3N$ | $CH_2Cl_2$ | 0 | 3 | 68 | 84 : 16 |
| 9 | | PhCHO | $Pr^i{}_2NEt$ | $CH_2Cl_2$ | 25 | 24 | 83 | 80 : 20 |
| 10 | | $Bu^tCHO$ | $Pr^i{}_2NEt$ | $CH_2Cl_2$ | 25 | 24 | 80 | 100 : 0 |
| 11 | 2,4,6-Trimethylpropiophenone | PhCHO | $Pr^i{}_2NEt$ | $Et_2O$ | 25 | 24 | 28 | 82 : 18 |
| 12 | | PhCHO | $Pr^i{}_2NEt$ | $CH_2Cl_2$ | 25 | 24 | 31 | 70 : 30 |
| 13 | Cyclopentanone | PhCHO | $Et_3N$ | $CH_2Cl_2$ | 0 | 3 | 75 | 70 : 30 |
| 14 | Cyclohexanone | PhCHO | $Pr^i{}_2NEt$ | $CH_2Cl_2$ | 0 | 3 | 65 | 94 : 6 |
| 15 | | $Pr^iCHO$ | $Et_3N$ | $CH_2Cl_2$ | 0 | 3 | 77 | 89 : 11 |
| 16 | | $Bu^tCHO$ | $Pr^i{}_2NEt$ | $CH_2Cl_2$ | 0 | 3 | 71 | 90 : 10 |

a) Ketone (2.2 mmol), aldehyde (2.0 mmol), tertiary amine (2.5 mmol), $Yb(OTf)_3$ (2.0 mmol). b) Isolated yield of the aldol. c) Isomer ratio was determined by 400 MHz, $^1H$ NMR.

Table 3. Reaction of 3-Pentanone with Aldehydes Promoted by $Ln(OTf)_3$[a)]

| Run | Ln in $Ln(OTf)_3$ | Aldehyde | Yield(%)[b)] | Isomer ratio[c)] (*threo* : *erythro*) |
|---|---|---|---|---|
| 1 | Sc | Isobutyraldehyde | 82 | 85 : 15 |
| 2 | Sc | Benzaldehyde | 54 | 14 : 86 |
| 3 | Y | Isobutyraldehyde | 71 | 80 : 20 |
| 4 | Y | Benzaldehyde | 62 | 27 : 73 |
| 5 | Nd | Isobutyraldehyde | Trace | — |
| 6 | Sm | Isobutyraldehyde | Trace | — |
| 7 | Lu | Isobutyraldehyde | 65 | 58 : 42 |

a) 3-Pentanone (2.0 mmol), $Ln(OTf)_3$ (2.0 mmol), *N*,*N*-diisopropylethylamine (2.5 mmol), aldehyde (2.0 mmol), $CH_2Cl_2$ (20 ml); r.t., 24 h. b) Isolated yield of the aldol. c) Isomer ratio was determined by 400 MHz, $^1H$ NMR.




Scheme 2.

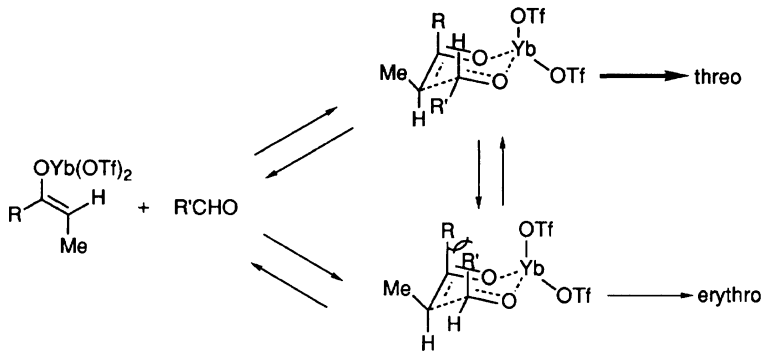
## Experimental

**General.** $^1H$ NMR spectra were recorded on a JEOL JNM A-400 NMR (400 MHz) spectrometer as solutions in $CDCl_3$. The chemical shifts are reported in $\delta$ units downfield from the internal reference, $Me_4Si$. Infrared spectra were obtained from solutions in chloroform with a Shimadzu FT IR-810 spectrometer. GLC analyses were carried out on a Shimadzu GC-14A gas chromatography equipped with a capillary column (CBPl-25) (0.25 μm, 25 m) (Helium as carrier gas). Elemental analyses were carried out using Yanaco CHN CORDER MT-5. Column chromatography was performed on a Yamazen YFLC-540 and a Michael Miller column equipped with a UV detector by using a Wakogel C-300. Preparative TLC was conducted using a 20×20 cm glass sheet coated with a 2 mm thick layer of Merck Kieselgel 60 $PF_{254}$.

**Materials.** Ytterbium trifluoromethanesulfonate [$Yb(OTf)_3$] was prepared from ytterbium oxide (Nippon Yttrium Co., Ltd., 99.9%) and trifluoromethanesulfonic acid (Central Glass Co., Ltd.) in water; the resulting hydrate was dried by heating under a vacuum at 200 °C for 48 h.[16] Diethyl ether was distilled under nitrogen from sodium benzophenone ketyl just before use. Dichloromethane was dried by $P_2O_5$, and then distilled before use. Triethylamine, *N*,*N*-diisopropylethylamine, and *N*-ethylpiperidine were distilled from $CaH_2$ and kept over KOH. All organic compounds were commercially available and used without purification, unless otherwise noted.

**Warning:** $Yb(OTf)_3$ is quite hygroscopic, and must be strictly dried before use. The reaction will not occur or give a low yield of the desired product, even if a slight amount of moisture contaminates.

**Reaction of Ethyl Ketones with Aldehyde by Yb-**




Scheme 3.

**$(OTf)_3$ and Tertiary Amine.** All of the reactions were carried out under nitrogen in order to prevent any contamination from atmospheric moisture. The following example provides a general procedure for the reaction of the ethyl ketone with the aldehyde. $Yb(OTf)_3$ (1.2 g, 2.0 mmol) was placed in a 50 $cm^3$ schlenk tube. The tube was heated at 200 °C in vacuo for 2 h. After the tube had been cooled down to room temperature, a magnetic stirring bar was placed in the flask, which was flushed with nitrogen. Dry diethyl ether (20 $cm^3$) was added by a syringe through a rubber septum with stirring. After the mixture had been stirred at room temperature for 1 h, the tube was cooled in an ice bath and 3-pentanone (0.20 g, 2.3 mmol) was injected at 0 °C into the suspension and then *N,N*-diisopropylethylamine (0.32 g, 2.5 mmol) was added. The resulting mixture was stirred at 0 °C for 1 h, during which time a yellow precipitate (ammonium triflate) settled on the bottom of the tube and the supernatant solution became clear. Benzaldehyde (0.20 g, 2.0 mmol) was added to the solution, and the mixture was stirred under the indicated conditions (0 °C or room temperature, for 3—48 h). The solution was treated with dilute HCl (3%, 20 $cm^3$), and then extracted with diethyl ether (20 $cm^3 \times 3$). The extracts were combined and washed with brine and dried over $MgSO_4$. The solvent was evaporated and a pale-yellow residue was subjected to column chromatography on silica gel (3 cm×20 cm) or preparative TLC ($SiO_2$): Hexane/diethyl ether (5 : 1) eluted the desired ethyl 1-hydroxy-2-methyl-1-phenyl-3-pentanone.[13] $^1H$ NMR spectrum showed that the *erythro* adduct was a major isomer with a small amount of *threo* adduct: The ratio of *threo*: *erythro* adducts in the crude product was determined by $^1H$ NMR integration of the proton of CHOH. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta$=0.90 (3H, t, $CH_2CH_3$), 0.98 (3H, d, $CHCH_3$), 2.3—2.4 (1H, m, one of $COCH_2$), 2.4—2.5 (1H, m, one of $COCH_2$), 2.85 (0.9H, dq, *erythro* COCH, $J$=4.0 and 8.0 Hz), 2.91 (0.1H, dq, $J$=8.0 and 8.0 Hz, *threo* COCH), 4.75 (0.1H, d, $J$=8.0 Hz, *threo* CHOH), 5.04 (0.9H, d, $J$=4.1 Hz, *erythro* CHOH), 7.2 (5H, s, Ph). IR ($CHCl_3$) 1703 (C=O), 3500 $cm^{-1}$ (OH). Found: C, 74.83; H, 8.28%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

***threo*- and *erythro*-5-Hydroxy-4,6-dimethyl-3-heptanone.**[13] The title compound was prepared by the reaction of 3-pentanone with isobutyraldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta$=0.7—1.2 (12H, several peaks, four $CH_3$), 1.6—1.7 (m, 1H, $CH(CH_3)_2$), 2.5—2.6 (m, 2H, $COCH_2$), 2.71 (dq, 1H, $J$=4.0 and 8.0 Hz, COCH), 3.44 (dd, 0.7H, $J$=1.4 and 6.6 Hz, *threo* CHOH), 3.51 (dd, 0.3H, $J$=2.9 and 8.5 Hz, *erythro* CHOH). IR ($CHCl_3$) 1700 (C=O), 3500 $cm^{-1}$ (OH). Anal. Found: C, 68.27; H, 11.25%. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47%.

***threo*- and *erythro*-5-Hydroxy-4,6,6-trimethyl-3-heptanone.** The title compound was prepared by the reaction of 3-pentanone with pivalaldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta$=0.91 (9H, s, $(CH_3)_3C$), 1.05 (3H, t, $J$=7.0 Hz, $CH_2CH_3$), 1.23 (3H, d, $J$=8.0 Hz, $CH_3CH$), 2.56 (2H, q, $J$=7.0 Hz, $COCH_2$), 2.89 (1H, dq, $J$=2.0 and 8.0 Hz, COCH), 3.25 (0.99H, d, $J$=2.2 Hz, *threo* CHOH), 3.59 (0.01H, d, $J$=3.1 Hz, *erythro* CHOH), 4.15 (1H, s, OH). The authentic *erythro* adduct was prepared by the titanium enolate.[12] IR ($CHCl_3$) 1699 (C=O), 3450 $cm^{-1}$ (OH). Anal. Found: C, 69.64; H, 11.73%. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70%.

***threo*- and *erythro*-1-Hydroxy-2,4-dimethyl-1-phenyl-3-pentanone.**[13] The title compound was prepared by the reaction of 2-methyl-3-pentanone with benzaldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta$=0.9—1.2 (9H, several peaks, three $CH_3$), 2.5—2.6 (1H, m, $COCH(CH_3)_2$), 3.00 (0.35H, q, $J$=4.0 Hz, *erythro* $COCHCH_3$), 3.07 (0.65H, q, $J$=8 Hz, *threo* $COCHCH_3$), 4.76 (0.65H, d, $J$=7.6 Hz, *threo* CHOH), 4.98 (0.35H, d, $J$=4.4 Hz, *erythro* CHOH), 7.3 (5H, s, Ph). IR ($CHCl_3$) 1700 (C=O), 3600 $cm^{-1}$ (OH).

***threo*-5-Hydroxy-2,4,6,6-tetramethyl-3-heptanone.** The title compound was prepared by the reaction of 2-methyl-3-pentanone with pivalaldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta$=0.91 (9H, s, $(CH_3)_3C$), 1.12 (3H, d, $(CH_3)_2CH$, $J$=6.8 Hz), 1.14 (3H, d $(CH_3)_2CH$, $J$=6.8 Hz), 1.31 (3H, d, $CH_3CH$, $J$=7.1 Hz), 2.78 (1H, sept, $J$=6.8 Hz, $(CH_3)_2CH$), 3.03 (1H, dq, $J$=2.5, 7.1 Hz, $CH_3CH$), 3.24 (1H, d, $J$=2.0 Hz, *threo* CHOH). Authentic *erythro* adduct caused an additional signal at $\delta$=3.49 (d, $J$=2.2 Hz, CHOH). IR ($CHCl_3$) 1700 (C=O), 3400 $cm^{-1}$ (OH). Anal. Found: C, 70.88; H, 11.87%. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90%.

***threo*- and *erythro*-1-Hydroxy-2,4,4-trimethyl-1-phenyl-3-pentanone.**[12] The title compound was prepared by the reaction of 2,2-dimethyl-3-pentanone with benzaldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta$=1.03 (9H, s, $(CH_3)_3C$), 1.10 (3H, d, $J$=7.1 Hz, $CH_3$), 3.33 (1H, dq, $J$=7.1 and 7.1, $CH_3CH$), 4.79 (0.96H, d, $J$=7.1 Hz, *threo* CHOH), 4.90 (0.04H, d, $J$=4.1 Hz, *erythro* CHOH), 7.30 (5H, m, Ph). IR ($CHCl_3$) 1705 (C=O), 3500 $cm^{-1}$ (OH).

***threo*- and *erythro*-3-Hydroxy-2-methyl-1,3-diphenyl-1-propanone.**[13] The title compound was prepared by the reaction of propiophenone with benzaldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta$=1.00 (2.58H, d, $J$=7.0 Hz,

*threo* $CH_3$), 1.13 (0.42H, d, $J=7.0$ Hz, *erythro* $CH_3$), 2.9 (1H, br s, OH), 3.53 (0.14H, dq, $J=2.9$ and 7.0 Hz, *erythro* COCH), 3.80 (0.86H, dq, $J=7.8$ and 7.0 Hz, *threo* COCH), 4.92 (0.86H, d, $J=7.8$ Hz, *threo* C*H*OH), 5.17 (0.14H, d, $J=2.9$ Hz, *erythro* C*H*OH). IR ($CHCl_3$) 1680 (C=O), 3500 $cm^{-1}$ (OH).

***threo*-3-Hydroxy-2,4,4-trimethyl-1-phenyl-1-pentanone.** The title compound was prepared by the reaction of propiophenone with pivalaldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta=0.88$ (9H, s, $(CH_3)_3C$), 1.45 (3H, d, $J=8.0$ Hz, C*H*$_3$CH), 3.43 (1H, d, $J=4.0$ Hz, *threo* C*H*OH), 3.79 (1H, dq, $CH_3CH$, $J=4.0$ and 8.0 Hz), 4.70 (1H, s, OH), 7.4—7.6 (3H, m, Ph), 7.9—8.0 (2H, m, Ph). Authentic *erythro* adduct caused an additional signal at $\delta=3.77$ (d, $J=1.0$ Hz, C*H*OH). IR ($CHCl_3$) 1710 (C=O), 3500 $cm^{-1}$ (OH). Anal. Found: C, 76.47; H, 9.20%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

***threo*- and *erythro*-3-Hydroxy-3-phenyl-2,2′,4′,6′-tetramethylpropiophenone.**[13] The title compound was prepared by the reaction of 2,4,6-trimethylpropiophenone with benzaldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta=0.90$ (2.46H, d, $J=7.0$ Hz, *threo*-C*H*$_3$CH), 1.11 (0.54 H, d, $J=7.0$ Hz, *erythro* C*H*$_3$CH), 2.10 (6H, s, two $CH_3$), 2.67 (3H, s, $CH_3$), 3.31 (1H, m, COCH), 4.90 (0.82H, d, $J=8.6$ Hz, *threo* C*H*OH), 5.40 (0.18H, d, $J=2.2$ Hz, *erythro* C*H*OH), 6.8—7.5 (m, 7H, aromatic H). IR ($CHCl_3$) 1703 (C=O), 3500 $cm^{-1}$ (OH).

***threo*- and *erythro*-2-(Phenylhydroxymethyl)cyclohexanone.**[13] The title compound was prepared by the reaction of cyclohexanone with benzaldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta=1.1$—2.6 (9H, m, cyclohexyl-H), 4.78 (0.7H, d, $J=8.8$ Hz, *threo* C*H*OH), 5.38 (0.3H, d, $J=2.2$ Hz, *erythro* C*H*OH), 7.4 (5H, s, Ph). IR ($CHCl_3$) 1700 (C=O), 3510 $cm^{-1}$ (OH).

***threo*- and *erythro*-2-(1-Hydroxy-2,2-dimethylpropyl)cyclohexanone.** The title compound was prepared by the reaction of cyclohexanone with pivalaldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta=0.93$ (9H, s, $(CH_3)_3C$), 1.6—2.6 (9H, m, cyclohexyl-H), 3.10 (0.9H, d, $J=1.7$ Hz, *threo* C*H*OH), 3.38 (0.1H, d, $J=1.2$ Hz, *erythro* C*H*OH), 4.38 (1H, s, OH). IR ($CHCl_3$) 1700 (C=O), 3550 $cm^{-1}$ (OH). Anal. Found: C, 71.41; H, 10.92%. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94%.

***threo*- and *erythro*-2-(1-Hydroxy-2-methylpropyl)-cyclohexanone.**[17] The title compound was prepared by the reaction of cyclohexanone with isobutyraldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta=0.81$ (0.3H, d, $J=6.8$ Hz, *erythro* $CH_3$), 0.89 (2.7H, d, $J=6.8$ Hz, *threo* $CH_3$), 0.99 (2.7H, d, $J=6.8$ Hz, *threo* $CH_3$), 1.03 (0.3 H, d, $J=6.8$ Hz, *erythro* $CH_3$), 1.3—2.5 (10H, m, $(CH_3)_2CH$ and cyclohexyl-H), 3.52 (0.89H, dd, $J=3.9$ and 7.6 Hz, *threo* C*H*OH), 3.72 (0.11H, dd, $J=2.2$ and 9.3 Hz, *erythro* C*H*OH). IR ($CHCl_3$) 1699 (C=O), 3490 $cm^{-1}$ (OH).

***threo*- and *erythro*-2-Phenylhydroxymethylcyclopentanone.**[18] The title compound was prepared by the reaction of cyclopentanone with benzaldehyde. $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta=1.4$—2.6 (7H, m, cyclopentyl-H), 4.71 (0.67H, d, $J=9.0$ Hz, *threo* C*H*OH), 5.30 (0.33H, d, $J=3.0$ Hz, *erythro* C*H*OH), 7.3 (5H, s, Ph). IR ($CHCl_3$) 1722 (C=O), 3500 $cm^{-1}$ (OH).

**Trapping of Ytterbium Enolates with Chlorotrimethylsilane.** The following example provides a general procedure for the trapping of the ytterbium enolates with chlorotrimethylsilane. To a solution of $Yb(OTf)_3$ (3.0 g, 5.0 mmol) in dry dichloromethane (50 $cm^3$) at room temperature was added propiophenone (0.67 g, 5 mmol) and *N,N*-diisopropylethylamine (0.32 g, 2.5 mmol). After 1 h, chlorotrimethylsilane (1.0 g, 10.0 mmol) was added to the solution and the mixture was stirred at room temperature for 20 h, during which time a white to pale-yellow solid was precipitated. The solvent was removed by evaporation at reduced pressure and an organic product was extracted with hexane from the residue containing an inorganic solid. The $^1H$ NMR spectrum of the crude product was recorded and the ratio of ***E*** : ***Z*** in enol ethers was determined by integration of the alkene proton resonances.[13] $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta=0.05$ (9H, s, $(CH_3)_3Si$), 1.75 (1H, d, $J=6.8$ Hz, $CH_3C$=), 5.10 (0.18 H, q, $J=6.8$ Hz, ***Z***-CH=), 5.33 (0.82H, q, $J=6.8$ Hz, ***E***-CH=). Anal. Found: C, 69.90; H, 8.92%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

**(*E*)- and (*Z*)-3-[(Trimethylsilyl)oxy]-4-methyl-2-pentene.**[13] $^1H$ NMR ($CDCl_3$; 400 MHz) $\delta=0.05$ (9H, s, $(CH_3)_3Si$), 1.03 (6H, d, $J=7.2$ ($CH_3)_2CH$), 1.59 (3H, d, $J=6.9$ Hz, $CH_3C$=), 2.14 (1H, sept, $J=7.2$ $(CH_3)_2CH$), 4.47 (0.14 H, q, $J=6.9$ Hz, ***Z***-CH), 4.54 (0.86H, q, $J=6.9$ Hz, ***E***-CH=), 7.2—7.4 (5H, m, Ph). Anal. Found: C, 60.53 ; H, 11.45%. Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46%.

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