Pergamon

Tetrahedron: *Asymmetry* 11 (2000) 2347–2357

TETRAHEDRON: *ASYMMETRY*

Asymmetric glyoxylate-ene reaction catalyzed by C_2-symmetric chiral bis(oxazoline)–lanthanide complexes

Changtao Qian* and Longcheng Wang

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

Received 24 March 2000; accepted 20 April 2000

Abstract

Efficient C_2-symmetric chiral bis(oxazoline)–lanthanide catalysts are developed for the glyoxylate-ene reaction to afford the α-hydroxy esters in 85% yield and up to 54% ee. An enhanced level of diastereoselectivity (81% de) was obtained in the reaction between menthyl glyoxylate and alkenes catalyzed by bis(oxazoline)–$Ln(OTf)_3$ complex.

1. Introduction

Glyoxylate-ene reactions produce α-hydroxy esters, which are a class of compounds of synthetic and biological importance.[1] The reactions take place at high temperature or are catalyzed by Lewis acids.[2] Many papers have been published for the asymmetric glyoxylate-ene reaction. They may be divided into two categories: substrate based induction and catalytic promotion. Some recent examples of metal mediated enantioselective ene reactions with prochiral glyoxylate include the use of Ti complexes,[3] Cu complexes[4] and ytterbium trifluoromethanesulfonate ($Yb(OTf)_3$)–binaphthol complexes.[5] However, the asymmetric glyoxylate-ene reaction catalyzed by bis(oxazoline)–$Ln(OTf)_3$ complex has so far not been reported to our knowledge. This paper describes the ene reaction of alkyl glyoxylate and menthyl glyoxylate with alkenes catalyzed by bis(oxazoline)–lanthanide triflate complexes.

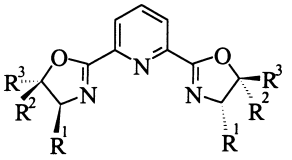
2. Results and discussion

Bisoxazoline ligand **1** and **2** were prepared according to the literature and have been used with great success in enantioselective catalysis by transition metal complexes,[4,6–12] but there were a few

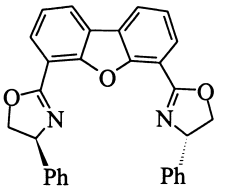
* Corresponding author. E-mail: qianct@pub.sioc.ac.cn

0957-4166/00/$ - see front matter
PII: S0957-4166(00)00166-X

reports of the use of this class of ligand in lanthanide catalysis.[13–15] We began our investigations with $Yb(OTf)_3$ and the readily prepared ^{i}Pr-pybox ligand (**1a**: $R_1 = {}^i$Pr, $R_2 = R_3 = H$). The product was isolated in 31% yield and 46% ee.

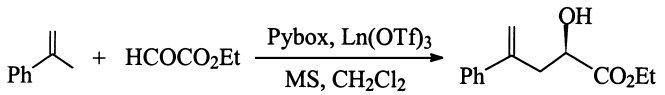


1a $R^1 = {}^i$Pr, $R^2 = R^3 = H$
1b $R^1 = {}^t$Bu, $R^2 = R^3 = H$
1c $R^1 = Ph$, $R^2 = R^3 = H$
1d $R^1 = R^2 = Ph$, $R^3 = H$
1e $R^1 = R^2 = R^3 = Ph$



2

In the absence of $Yb(OTf)_3$, there was no reaction and in the absence of pybox the reaction proceeded much faster (5 h) to give racemic product in 86% isolated yield. The deceleration of the reaction in the presence of pybox can be explained by the formation of a soluble pybox–$Yb(OTf)_3$ complex which has lower Lewis acidity. This result is consistent with the fact that $EtAlCl_2$, a stronger Lewis acid than Me_2AlCl, successfully promotes ene reactions with mono-substituted alkenes.[16]



3a **5a** (1)

With this promising result, we then investigated the effect of solvent, amount of pybox and character of pybox on the reaction.

The optimum ratio of pybox: $Ln(OTf)_3$ was found to be 1:1. The effect of solvent is summarized in Table 1, which shows that methylene chloride is the best solvent tested, consistent with the case of glyoxylate-ene reaction catalyzed by bis(oxazoline)–$Cu(OTf)_2$ complex.[4] In the case of strong coordinating solvents such as CH_3CN and CH_3NO_2, the asymmetric catalyst lost its activity. The result is in sharp contrast to that of glyoxylate-ene reaction catalyzed by $Ln(OTf)_3$ in which acetonitrile is the best solvent.[5]

The effects of varying Ln and the substituents on the bis(oxazoline) ligand are summarized in Table 2. Ph-pybox was found to give the best enantioselectivity, ^{i}Pr-pybox a little lower, but the ^{t}Bu-pybox gave substantially lower ee's than other pybox ligands. For (*S*,*S*)-4,6-dibenzofurandiyl-2′,2′-bis(4-phenyloxazoline), due to its small box space for coordination, Yb^{3+} could not enter, thus the result was not satisfactory compared to ligands **1**. It is not surprising that there is a variation in enantioselectivity on varying Ln, and thus the radius of Ln^{3+}. Of the Ln investigated, $Yb(OTf)_3$ has the most appropriate ionic radius and shows the best enantioselectivity.

We have applied our catalytic system to a range of alkenes. The 2-aryl alkene reacted with alkyl glyoxylate to afford α-hydroxy esters in reasonable yield and moderate stereoselectivity as shown in Table 3. However, the glyoxylate-ene reaction between dialkyl alkene such as isobutene and methylene cyclohexane and alkyl glyoxylate cannot be carried out.

Table 1
Effect of solvent on the reaction catalyzed by ^{i}Pr-pybox–Yb(OTf)$_3$[a]

Entry	Solvent	Time(h)	Yield(%)[b]	ee(%)[c]
1	$C_6H_5CH_3$	40	4	31
2	CH_2Cl_2	8	31	46
3	THF	40	6	48
4	CH_3CN	40	/	/
5	CH_3NO_2	40	/	/

a: conditions: 10 mol % catalyst, rt, α-methyl styrene:ethyl glyoxylate(1:1)

b: isolated yield

c: determined by HPLC analysis with chiral column OJ.

Table 2
Effect of bis(oxazoline) substituents and Ln^{3+} on the glyoxylate-ene reaction[a]

Entry	Pybox	Ln(OTf)$_3$	Time(h)	Yield(%)[b]	ee(%)[c]
1	**1a**	Sc(OTf)$_3$	40	26	27
2	**1a**	Dy(OTf)$_3$	40	44	20
3	**1a**	Sm(OTf)$_3$	40	42	16
4	**1a**	Yb(OTf)$_3$	8	31	46
5	**1b**	Yb(OTf)$_3$	36	75	1
6	**1c**	Yb(OTf)$_3$	36	71	50
7	**1d**	Yb(OTf)$_3$	36	73	37
8	**1e**	Yb(OTf)$_3$	36	81	5
9	**2**	Yb(OTf)$_3$	36	68	1

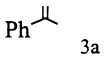
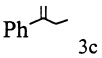
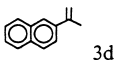
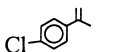
a: conditions: 10 mol % catalyst, rt, α-methyl styrene:ethyl glyoxylate(1.2:1)

b: isolated yield

c: determined by HPLC analysis with chiral column OJ.

As shown in Table 3, the reaction between ethyl glyoxylate and α-methyl styrene catalyzed by Ph-pybox–Yb(OTf)$_3$ complex has a better enantioselectivity and chemical yield than that of methyl glyoxylate and butyl glyoxylate. The enantiomeric excess was determined by HPLC analysis by using chiral column. The configuration of **5a** was assigned to be *R* by measuring the optical rotation which shows that (*S*)-stereochemistry in the ligand leads to (*R*)-stereochemistry in the product.

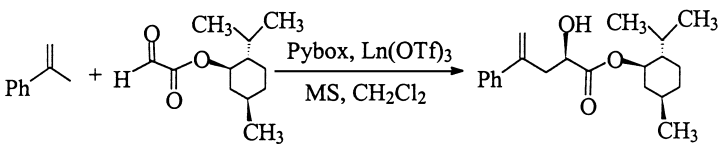
Table 3
The glyoxylate-ene reaction catalyzed by Ph-pybox–Yb(OTf)$_3$ complex[a]

Entry	Alkene	$HCOCO_2R$	Time(h)	Product	Yield(%)[b]	ee(%)[c]
1	 3a	Me	36	5aa	43	46
2	3a	Et	36	5ab	71	49
3	3a	Bu	36	5ac	60	18
4	 3b	Et	30	5b	60	16
5	 3c	Et	40	5c	85	41
6	 3d	Et	36	5d	78	38
7	 3e	Et	45	5e	69	54

a: conditions: 10 mol% catalyst, rt, in CH_2Cl_2

b: isolated yield

c: determined by HPLC analysis with chiral column OJ.



3a **6a** (2)

We further investigated the glyoxylate-ene reaction between menthyl glyoxylate and alkenes catalyzed by Ph-pybox–Yb(OTf)$_3$ complex, as summarized in Table 4. We found that the reaction of menthyl glyoxylate and alkenes has higher stereoselectivity than that of alkyl glyoxylate and the correspondent alkenes. Evidently, the substrate and asymmetric catalyst have the same effect of induction. The percentage of the isomer that accounts for 53% (de = 6%) in the reaction catalyzed by Yb(OTf)$_3$ rose remarkably to 90.5% (de = 81%) in the case of catalyzed by Ph-pybox–Yb(OTf)$_3$. To determine the absolute configuration of the new stereogenic center predominantly formed in adduct **6**, **6a** (de = 81%) was subjected to esterification in anhydrous methanol catalyzed by sodium methoxide to afford methyl 2-hydroxy 4-phenyl-4-pentenoate with $[\alpha]_D^{20} = -27$. Comparing to the literature, the configuration of the new stereogenic center is *R*.

As an X-ray crystal structure of the catalyst–substrate complex was not available, we speculate the catalyst coordinated to ethyl glyoxylate should have the structure of a distorted trigonal

Table 4
The ene reaction of menthyl glyoxylate with alkenes catalyzed by Ph-pybox–Yb(OTf)$_3$ complex[a]

Entry	Alkene	Time(h)	Product	Yield(%)[b]	D.e.(%)[c]
1		20	6a	88	6[d]
2		30	6a	76	81
3		20	6b	93	10[d]
4		36	6b	84	13
5		22	6c	84	10[d]
6		40	6c	73	40
7		16	6d	96	3[d]
8		42	6d	94	62
9		15	6e	65	1[d]
10		50	6e	60	66

a: conditions: 10 mol% catalyst, rt, in CH_2Cl_2

b: isolated yield

c: determined by HPLC analysis with chiral column OJ.

d: in the absence of pybox.

bipyramidal[17] as shown in Fig. 1. The *R* selectivity can be rationalized by attack of alkenes to the proposed distorted trigonal bipyramidal Yb(III)–glyoxylate complex via an open transition state, which minimizes the number of repulsive *gauche* between alkene and the phenyl group.

As has been noticed before (–)-menthyl glyoxylate takes the conformation depicted in Fig. 2, where ϕ is a dihedral angle approaching 90°. We assume that the olefin approaches the aldehydic carbonyl group preferentially from the less shielded side and attained *R* configuration in the new

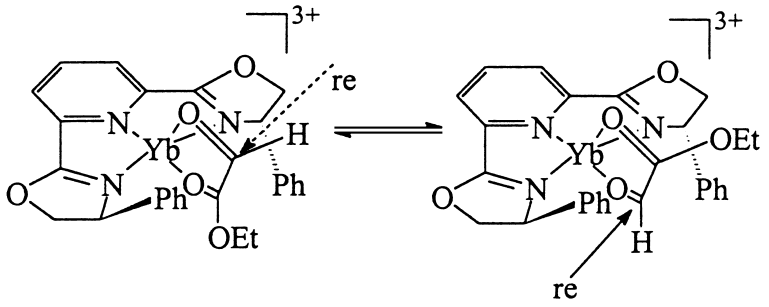


Figure 1.

stereogenic center in the ene reaction of glyoxylate and alkenes catalyzed by $Yb(OTf)_3$. In the reaction of menthyl glyoxylate with alkenes catalyzed by bis(oxazoline)–$Yb(OTf)_3$, the complex could not take the conformation **a** shown in Fig. 3 in which there is strong interaction between isopropyl in menthyl and phenyl group. However, due to the bond rotation of C–O, the menthyl group turns away from the phenyl group, which is beneficial to the stereoselection of the product. This can be ascertained by MM (Molecular Mechanics) calculation using Merck force field, and SPARTAN 5.0 program on a SGI O_2 workstation. It shows that the configuration in Fig. 4b has lower energy than that in Fig. 4a by 15 kcal/mol.

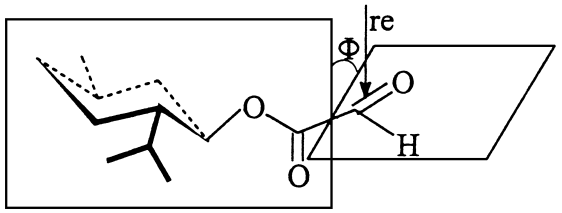


Figure 2.

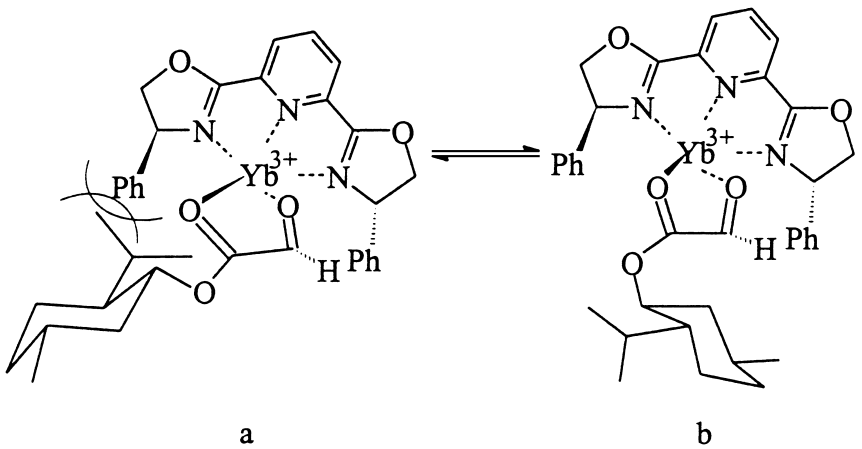
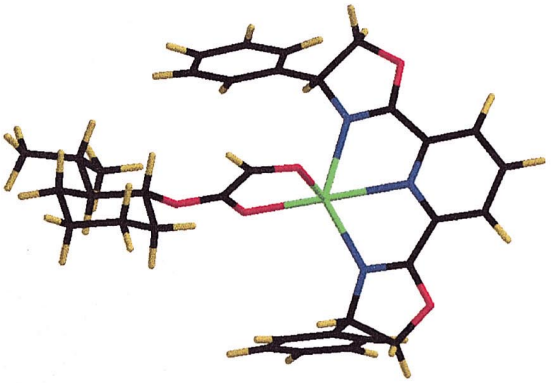
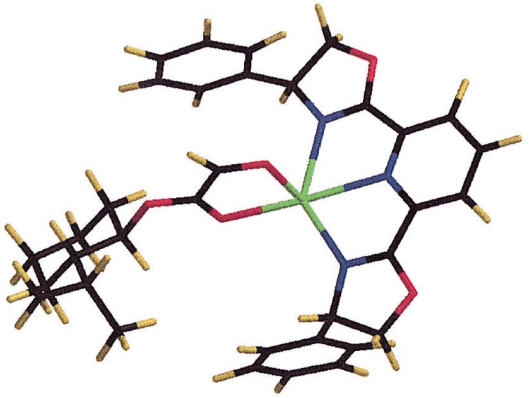


Figure 3.



a



b

Figure 4.

The combination of $Yb(OTf)_3$, Ph-pybox and solvent has achieved an enantioselectivity of 54% for the addition of ethyl glyoxylate to α-methyl 4-chlorostyrene and a diastereoselectivity of 81% for the addition of menthyl glyoxylate to α-methyl styrene in a reaction conducted at room temperature. This is a better stereoselectivity than that reported with Ln catalyzed system.

3. Experimental

3.1. General method

All reactions were performed under a nitrogen atmosphere using oven-dried glassware. Solvents were treated prior to use according to the standard method. ^1H NMR spectra were recorded on a Brucker AMX-300 (300 MHz) spectrometer in $CDCl_3$ using TMS as internal standard. IR spectra

were obtained on a Shimadzu IR-440 infrared spectrophotometer. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Elemental analyses were performed on a Foss-Heraeus Vario EL instrument. Optical rotation was measured on a Perkin–Elmer polarimeter 341 with a thermally jacketed 10 cm cell at 20°C (concentration c given as g/100 ml). The ee and de values were determined by HPLC analysis on a Chiralcel OJ column with isopropanol/hexane as eluent.

Methyl glyoxylate, ethyl glyoxylate, butyl glyoxylate, menthyl glyoxylate, alkenes **3b**, **3c**, **3d**, **3e** and ligands **1a**, **1b**, **1c**, **1e** and **2** were prepared by known methods.

3.2. The synthesis of *1d*

Pyridine-2,6-dicarboxylic acid (0.53 g, 3.2 mmol) was treated with $SOCl_2$ (5 ml) at reflux temperature for 18 h. Excess $SOCl_2$ was then removed under reduced pressure to give the acid chloride as a white solid. To a solution of (1*S*,2*R*)-2-amino-1,2-diphenylethanol (1.48 g, 6.9 mmol) and triethylamine (2.66 ml, 19.1 mmol) in chloroform (12.5 ml) was slowly added a solution of the acid chloride in chloroform (10 ml) at 0°C. The mixture was stirred for 1 day at room temperature, then $SOCl_2$ (2.35 ml, 32.2 mmol) was added, and the mixture was stirred at 0°C for 2 h and room temperature for 8 h. The mixture was slowly poured into ice water. The organic layer was collected, washed with brine (10 ml) and aqueous K_2CO_3 (0.1 M, 10 ml), and dried over anhydrous Na_2SO_4. After column chromatography, a white solid was obtained (0.71 g, 43% yield). The solid was treated with NaH (115 mg, 4.8 mmol) in THF (10 ml) at room temperature for 12 h. The mixture was cooled to –78°C and wet THF (5 ml) was added dropwise after the reaction was completed. The solvent was removed under reduced pressure and to the residue was added 10 ml CH_2Cl_2. The mixture was washed with aqueous NH_4Cl and brine, respectively, dried with anhydrous Na_2SO_4, concentrated to give the brown solid, which was purified by column chromatography with silica gel to give the white solid 0.46 g (74% yield). Mp: 196–198°C; $[\alpha]_D^{20} = +38.6$ (*c*, 2.27, $CHCl_3$). ^{1}H NMR δ (ppm): 8.37 (d, J = 7.83 Hz, 2H), 7.96 (t, J = 7.93 Hz, 1H), 7.44–7.31 (m, 20H), 5.54 (d, 8.42 Hz, 2H), 5.32 (d, J = 8.42 Hz, 2H). MS: 521 (M^+, 5.46), 416 (5.67), 248 (32.25), 194 (22.5), 180 (base), 179 (27.12), 90 (10.28). IR (KBr pellet, cm^{-1}): 3028, 1636, 1602, 1571, 1495, 1452, 1383, 1110, 1011, 969, 700. Anal. calcd for $C_{35}H_{27}N_3O_2$: C, 80.59, H, 5.21, N, 8.06. Found: C, 80.31, H, 5.09, N, 8.10.

3.3. General procedure

To a stirred solution of Ph-pybox (26 mg, 0.07 mmol) in CH_2Cl_2 (4 ml) under nitrogen was added $Yb(OTf)_3$ (43 mg, 0.069 mmol) and MS 4 Å. The resulting mixture was stirred at room temperature for 0.5 h, and alkyl glyoxylate (0.69 mmol) was added. After being stirred for another 0.5 h, alkene (1.38 mmol) was introduced and stirred for about 35 h. The reaction mixture was filtered, washed with water and dried with anhydrous Na_2SO_4 after completion of the reaction. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to furnish the corresponding product. The enantiomeric purity and distereoselectivity was determined by HPLC analysis on a Chiralcel column.

3.3.1. (R)-Methyl 2-hydroxy-4-phenyl-4-pentenoate *5aa*[3]

Colorless oil; yield: 43%; 46% ee; $[\alpha]_D^{20} = -11.2$ (*c*, 2.70, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.43–7.27 (m, 5H), 5.40 (s, 1H), 5.21 (s, 1H), 3.61 (s, 3H), 3.10–3.03 (m, 1H), 2.85

(s, broad, 1H), 3.22–2.81 (m, 1H). MS (m/z): 206 (M^+, 20.03), 188 (40.77), 147 (35.22), 129 (base), 128 (44.21), 117 (37.25), 91 (64.61), 77 (29.45). IR (neat, cm^{-1}): 3466, 3082, 2952, 1734, 1624, 1572, 1492, 1438, 1272, 1032, 910, 710.

*3.3.2. (*R*)-Ethyl 2-hydroxy-4-phenyl-4-pentenoate* ***5ab***[4]

Colorless oil; yield: 71%; 49% ee; $[\alpha]_D^{20} = -18.6$ (*c*, 0.945, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.44–7.27 (m, 5H), 5.40 (d, J = 1.34 Hz, 1H), 5.22 (q, J = 1.16 Hz, 1H), 4.28 (q, J = 4.55 Hz, 1H), 4.08 (m, 2H), 3.07 (ddd, J = 1.01, 4.55, 14.49 Hz, 1H), 2.85 (ddd, J = 1.01, 7.56, 14.49 Hz, 1H), 2.63 (s, broad, 1H), 1.25 (m, 3H).

*3.3.3. (*R*)-Butyl 2-hydroxy-4-phenyl-4-pentenoate* ***5ac***

Colorless oil; yield: 60%; 18.0% ee; $[\alpha]_D^{20} = -7.8$ (*c*, 2.78, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.34–7.15 (m, 5H), 5.30 (s, 1H), 5.12 (s, 1H), 4.18 (dd, J = 4.57, 7.59 Hz, 1H), 3.93 (m, 2H), 2.97 (ddd, J = 0.97, 4.57, 14.45 Hz, 1H), 2.78–2.70 (s, broad, 1H), 2.74 (ddd, J = 0.79, 7.59, 14.45 Hz, 1H), 1.49 (m, 2H), 1.26 (m, 2H), 0.84 (7, J = 7.34 Hz, 3H). MS (m/z): 286 (M^+, 6.32), 231 (20.50), 175 (61.13), 147 (46.55), 129 (base), 91 (61.36). IR (neat, cm^{-1}): 3462, 2957, 2871, 1731, 1627, 1495, 1448, 1200, 906, 708.

*3.3.4. (*R*)-Ethyl 2-hydroxy-3-[1-(3,4-dihydro)naphthyl]-4-propionate* ***5b***

Colorless oil; yield: 60%; 16% ee; $[\alpha]_D^{20} = +7.0$ (*c*, 0.25, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.22–7.05 (m, 4H), 5.91 (t, J = 4.56 Hz, 1H), 4.29 (dd, J = 4.53, 7.66 Hz, 1H), 4.15 (dq, J = 2.79, 7.12 Hz, 1H), 4.05 (dq, J = 3.62, 7.12 Hz, 1H), 3.25 (s, broad, 1H), 2.94 (ddd, J = 1.26, 4.53, 14.46 Hz, 1H), 2.70–2.63 (m, 3H), 2.23–2.16 (m, 2H), 1.18 (t, J = 7.12 Hz, 3H). MS (m/z): 247 (M^++1, 6.38), 246 (M^+, 35.43), 228 (12.67), 199 (7.32), 155 (31.80), 143 (base), 128 (99.37), 115 (33.65), 104 (32.17), 91 (17.13), 76 (30.04). IR (neat, cm^{-1}): 3446, 2960, 1731, 1449, 1214, 1099, 867, 766, 741. Anal. calcd for $C_{15}H_{18}O_3$: C, 73.15, H, 7.37; found: C, 72.96, H, 7.42.

*3.3.5. (*R*)-Ethyl 2-hydroxy-4-phenyl-4-hexenoate* ***5c***

Colorless oil; yield: 85%; 41% ee; $[\alpha]_D^{20} = -7.6$ (*c*, 0.72, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.40–7.19 (m, 5H), 5.90 (q, J = 6.92 Hz, 1H), 4.20 (dd, J = 5.44, 6.92 Hz, 1H), 4.11–4.00 (m, 1H), 3.95–3.83 (m, 1H), 3.04 (dd, J = 5.28, 14.15 Hz, 1H), 2.95 (dd, J = 7.12, 14.15 Hz, 1H), 2.75 (s, broad, 1H), 1.84 (d, J = 6.92 Hz, 3H), 1.19 (t, J = 7.21 Hz, 3H). MS (m/z): 234 (M^+, 14.02), 216 (28.24), 201 (7.30), 187 (8.04), 173 (7.33), 161 (13.79), 143 (base), 131 (57.77), 115 (56.43), 91 (94.56). IR (neat, cm^{-1}): 3450, 2978, 1730, 1597, 1443, 1210, 1099, 1034, 762, 703. Anal. calcd for $C_{14}H_{18}O_3$: C, 71.77, H, 7.74. Found: C, 71.67, H, 7.62.

*3.3.6. (*R*)-Ethyl 2-hydroxy-4-(β)-naphthylpent-4-enoate* ***5d***

Colorless oil; yield: 78%; 38% ee; $[\alpha]_D^{20} = -45$ (*c*, 1.035, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.88–7.81 (m, 4H), 7.60 (dd, J = 1.67, 8.60 Hz, 1H), 7.53–7.44 (m, 2H), 5.57 (s, 1H), 5.34 (s, 1H), 4.33 (dd, J = 4.59, 7.54 Hz, 1H), 4.16–3.96 (m, 2H), 3.2 (dd, J = 4.36, 14.44 Hz, 1H), 2.98 (dd, J = 7.59, 14.43 Hz, 1H), 2.87 (s, broad, 1H), 1.22 (t, 7.11 Hz, 3H). MS (m/z): 270 (M^+, 52.1), 252 (37.74), 223 (15.4), 197 (32.12), 179 (base), 165 (34.84), 155 (70.53), 141 (41.95), 128 (42). IR (neat, cm^{-1}): 3473, 3061, 2980, 2940, 2870, 1720, 1625, 1600, 1500, 1450, 1380, 1270, 1210, 1100, 1040, 900, 860, 824, 762. Anal. calcd for $C_{17}H_{18}O_3$: C, 75.53, H, 6.71. Found: C, 75.56, H, 6.99.

*3.3.7. (*R*)-Ethyl 2-hydroxy-4-(4′-chlorophenyl)-4-pentenoate* ***5e***

Colorless oil; yield: 69%; 54% ee; $[\alpha]_D^{20} = -6.3$ (*c*, 1.44, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.41–7.26 (m, 4H), 5.38 (d, J = 0.89 Hz, 1H), 5.22 (d, J = 0.89 Hz, 1H), 4.25 (dd, J = 4.51, 7.56 Hz, 1H), 4.20–4.01 (m, 2H), 3.02 (dd, J = 4.40, 14.67 Hz, 1H), 2.84–2.76 (s, broad, 1H), 2.80 (dd, J = 7.61, 14.67 Hz, 1H), 1.24 (t, J = 7.24 Hz, 3H); MS (m/z): 256 (M^++2, 10.51), 254 (M^+, 29.51), 236 (M^+–18, 25.25), 208 (11.63), 181 (48.33), 163 (100). IR (neat): 3462, 2980, 1731, 1491, 1211, 1115, 1015, 840. Anal. calcd for $C_{13}H_{15}ClO_3$: C, 61.30, H, 5.94. Found: C, 61.58, H, 6.06.

*3.3.8. (1*R*,2*S*,5*R*)-Menthyl (2*R*)-2-hydroxy-4-phenyl-4-pentenoate* ***6a***

Colorless oil; yield: 76%; 81% de; $[\alpha]_D^{20} = -71.2$ (*c*, 1.88, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.46–7.26 (m, 5H), 5.41 (d, J = 0.95 Hz, 1H), 5.23 (d, J = 0.95 Hz, 1H), 4.81–4.73 (m, 1H), 4.27–4.21 (m, 1H), 3.12 (ddd, J = 0.86, 4.05, 14.65 Hz, 1H), 2.72 (ddd, J = 0.78, 8.81, 14.65 Hz, 1H), 2.60 (s, broad, 1H), 2.01–1.89 (m, 2H), 1.74–1.67 (m, 2H), 1.49–1.41 (m, 2H), 1.05–0.75 (m, 12H). MS (m/z): 331 (M^++1, 0.63), 193 (67.12), 175 (31.26), 139 (base), 138 (51.34), 83 (97.3). IR (neat, cm^{-1}): 3450, 2954, 2867, 1724, 1627, 1572, 1451, 1388, 1098, 1042, 985, 908, 706. Anal. calcd for $C_{21}H_{30}O_3$: C, 76.32, H, 9.15. Found: C, 76.09, H, 9.36.

*3.3.9. (1*R*,2*S*,5*R*)-Menthyl (2*R*)-2-hydroxy-3-[1-(3,4-dihydro)naphthyl]propionate* ***6b***

Colorless oil; yield: 84%; 13% de; $[\alpha]_D^{20} = -32$ (*c*, 2.48, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.20–7.05 (m, 4H), 5.92 (m, 1H), 4.74–4.65 (m, 1H), 4.28–4.24 (m, 1H), 3.03–2.97 (m, 1H), 2.71–2.49 (m, 4H), 2.22–2.18 (m, 2H), 1.92–1.83 (m, 2H), 1.64–1.58 (m, 2H), 1.41–1.32 (m, 2H), 0.96–0.65 (m, 12H). MS (m/z): 356 (M^+, 12.63), 336 (3.31), 219 (38.52), 218 (92.15), 143 (98.26), 129 (54.94), 128 (59.03), 83 (base). IR (neat, cm^{-1}): 3474, 3058, 2956, 2870, 1728, 1456, 1370, 1265, 1211, 1102, 751. Anal. calcd for $C_{23}H_{32}O_3$: C, 77.49, H, 9.05. Found: C, 77.29, H, 9.09.

*3.3.10. (1*R*,2*S*,5*R*)-Menthyl (2*R*)-2-hydroxy-4-phenyl-4-hexenoate* ***6c***

Colorless oil; yield: 73%; 40% de; $[\alpha]_D^{20} = -37.8$ (*c*, 1.23, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.38–7.21 (m, 5H), 5.90 (m, 1H), 4.75–4.68 (m, 1H), 4.14–4.11 (m, 1H), 2.98–2.87 (m, 2H), 2.70 (s, broad, 1H), 1.95–1.90 (m, 1H), 1.84 (dd, J = 1.65, 6.97 Hz, 3H), 1.68–1.65 (m, 2H), 1.55–1.50 (d, J = 7.2 Hz, 1H), 1.49–1.30 (m, 2H), 1.10–0.90 (m, 3H), 0.89 (2d, J = 7.03 Hz, 6H), 0.74 (2d, J = 6.98 Hz, 3H). MS (m/z): 344 (M^+, 0.7), 206 (69.43), 189 (17.54), 188 (15.81), 161 (12.52), 139 (49.63), 83 (base). IR (neat, cm^{-1}): 3482, 3028, 2957, 2929, 2871, 1727, 1456, 1371, 1265, 1210, 1098, 758, 699. Anal. calcd for $C_{22}H_{32}O_3$: C, 76.7, H, 9.36. Found: C, 76.98, H, 9.59.

*3.3.11. (1*R*,2*S*,5*R*)-Menthyl (2*R*)-2-hydroxy-4-(β)-naphthyl-4-pentenoate* ***6d***

Colorless oil; yield: 94%; 62% de; $[\alpha]_D^{20} = -46.6$ (*c*, 0.535, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.80 (m, 4H), 7.67–7.60 (m, 1H), 7.49–7.45 (m, 2H), 5.56 (dd, J = 1.02, 4.72 Hz, 1H), 5.35 (s, 1H), 4.83–4.47 (m, 1H), 4.36–4.30 (m, 1H), 3.28–3.17 (m, 1H), 2.93 (dd, J = 7.46, 14.93 Hz, 1H), 2.87 (dd, J = 8.52, 14.63 Hz, 1H), 2.01–1.88 (m, 1H), 1.87–1.77 (m, 1H), 1.75–1.62 (m, 2H), 1.57–1.38 (m, 2H), 1.17–0.95 (m, 3H), 0.92 (2d, J = 7.06 Hz, 3H), 0.86 (2d, J = 6.53 Hz, 3H), 0.78 (2d, J = 6.98 Hz, 3H). MS (m/z): 380 (M^+, 3.83), 242 (85.88), 224 (57.28), 197 (269), 179 (32.4), 168 (44.86), 152 (59.85), 95 (42.83), 83 (base). IR (neat, cm^{-1}): 3474, 3058, 2956, 2870, 1728, 1456, 1370, 1265, 1211, 1102, 751. Anal. calcd for $C_{25}H_{32}O_3$: C, 79.02, H, 7.49. Found: C, 78.90, H, 7.21.

3.3.12. (1R,2S,5R)-Menthyl (2R)-2-hydroxy-4-(4′-chlorophenyl)-4-pentenoate **6e**

Colorless oil; yield: 60%; 66% de; $[\alpha]_D^{20} = -248$ (*c*, 0.65, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$/TMS) δ (ppm): 7.38–7.27 (m, 4H), 5.38 (m, 1H), 5.23 (m, 1H), 4.82–4.66 (m, 1H), 4.25–4.15 (m, 1H), 3.10–2.95 (m, 1H), 2.85 (s, broad, 1H), 2.80–2.62 (m, 1H), 2.05–1.92 (m, 1H), 1.91–1.78 (m, 1H), 1.72–1.64 (m, 2H), 1.52–1.21 (m, 2H), 1.03–0.92 (m, 3H), 0.88 (2d, J = 7.15 Hz, 6H), 0.73 (d, J = 7.18 Hz, 3H). MS (m/z): 226 (13.16), 208 (5.09), 181 (7.34), 139 (46.43), 83 (base). IR (neat, cm^{-1}): 3472, 3087, 2957, 2929, 2871, 1730, 1493, 1456, 1388, 1371, 1267, 1214, 1112, 1095, 1013, 836. Anal. calcd for $C_{21}H_{29}ClO_3$: C, 69.12, H, 8.01. Found: C, 69.10, H, 8.20.

Acknowledgements

We thank Dr. Xicheng Dong (Laboratory of Computer Chemistry) for calculation. Financial support from the National Natural Sciences Foundation of China and the Chinese Academy of Sciences is gratefully acknowledged.

References

1. (a) Morrison, J. D. *Asymmetric Synthesis*; Academic Press: New York, 1984; Vol. 3B. (b) Bosnich, B. *Asymmetric Catalysis*; Martinus Nijhoff Publishers: Dordrecht, 1986. (c) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1982; Vol. 8.
2. (a) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426. (b) Mikami, K.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021–1050.
3. Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 3949–3954.
4. Evans, D. A.; Burgey, C. S.; Paras, N. A.; Vojkovsky, T.; Tregay, S. W. *J. Am. Chem. Soc.* **1998**, *120*, 5824–5825.
5. Qian, C. T.; Huang, T. S. *Tetrahedron Lett.* **1997**, *38*, 6721–6724.
6. Ghosh, A. K.; Mathivanan, P.; Capiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1–45.
7. Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S. B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223–2224 and references cited therein.
8. Sekar, G.; DattaGupta, A.; Singh, V. K. *J. Org. Chem.* **1998**, *63*, 2961–2967.
9. Evans, D. A.; Olhava, E. J.; Johnson, J. S.; Janey, J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3372–3375.
10. Kanemasa, S.; Oderaotoshi, Y.; Sakaguchi, S.; Yamamoto, H.; Tanaka, J.; Wada, E.; Curran, D. P. *J. Am. Chem. Soc.* **1998**, *120*, 3074–3088.
11. Evans, D. A.; Burgey, C. S.; Kozlowski, M. C.; Tregay, S. W. *J. Am. Chem. Soc.* **1999**, *121*, 686–699.
12. (a) Evans, D. A.; Kozlowski, M. C.; Tedrow, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 1994–1995. (b) Evans, D. A.; Johnson, J. *J. Am. Chem. Soc.* **1998**, *120*, 4895–4896.
13. Sanchez-Blanco, A. I.; Gothelf, K. V.; Jorgensen, K. A. *Tetrahedron Lett.* **1997**, *38*, 7923–7926.
14. Aspinall, H. C.; Greeves, N.; Smith, P. M. *Tetrahedron Lett.* **1999**, *40*, 1763–1766.
15. Qian, C. T.; Wang, L. C. *Tetrahedron Lett.* **2000**, *41*, 2203–2206.
16. Snider, B. B.; Phillips, G. B. *J. Org. Chem.* **1983**, *48*, 464.
17. Barnhart, D. M. et al. *Inorg. Chem.* **1994**, *33(16)*, 3487–3497.