DOI: 10.1002/cjoc.201200697

Enantioselective Synthesis of Terminal 1,2-Diols from Acyl Chlorides

Shao, Panlin(邵攀霖) Shen, Litao(申理滔) Ye, Song*(叶松)

Beijing National Laboratory for Molecular Sciences, *CAS Key Laboratory of Molecular Recognition and Function*, *Institute of Chemistry*, *Chinese Academy of Sciences*, *Beijing 100190*, *China*

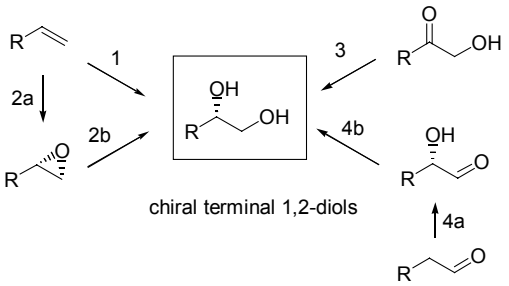
Optically active terminal 1,2-diols were prepared with high enantiopurity via the TMS-quinidine-catalyzed enantioselective cyclization of acyl chlorides and oxaziridine, followed by reductive ring-opening of the cycloadducts.

Keywords 1,2-diols, acyl chlorides, enantioselective synthesis, cinchona alkaloids, oxidation

Introduction

The 1,2-diol motif occurs frequently in many natural products and bioactive compounds.[1] In addition, optically active 1,2-diols are useful chiral reagents or ligands in asymmetric synthesis.[2] Thus, many methods have been developed for the preparation of chiral 1,2-diols. However, the preparation of chiral terminal 1,2-diols remains relative less developed (Scheme 1).

Scheme 1 Typical routes to chiral terminal 1,2-diols



(1) asymmetric dihydroxylation of terminal alkenes
(2) asymmetric epoxidation followed by hydrolysis
(3) asymmetric reduction of α-hydroxyl carbonyl ketones
(4) asymmetric α-oxylation of aldehydes followed by reduction

The OsO_4-catalyzed dihydroxylation of alkenes is a straightforward approach to 1,2-diols (Route 1, Scheme 1).[3] However, the toxicity of osmium hinders its application. The hydrolysis of epoxides represents an important method for diols (Route 2, Scheme 1). Despite the significant advance in catalytic asymmetric epoxidation of alkenes, the corresponding reaction of terminal alkenes remains most challenging.[4] In 2002, Jacobsen *et al*.[5] reported the Co(Salen)-catalyzed kinetic resolution of racemic terminal 1,2-diol. In 2009, Li *et al*.[6] reported the synthesis of 1,2-diols from aryl olefins by tandem biocatalysts with monooxygenase and epoxide hydrolase. The asymmetric hydrogenation of α-hydroxyl ketones is an alternative approach to chiral terminal 1,2-diols (Route 3, Scheme 1). Chiral Ir and Ru complexes have been successfully applied to this transformation.[7] Recently, the asymmetric α-hydroxylation of aldehydes followed by reduction becomes a powerful tool for the preparation of chiral 1,2-diols (Route 4, Scheme 1). In 2003, MacMillan *et al*.[8] reported the *L*-proline-catalyzed enantioselective α-hydroxylation of aldehydes, and followed reduction to give chiral 1,2-diols.

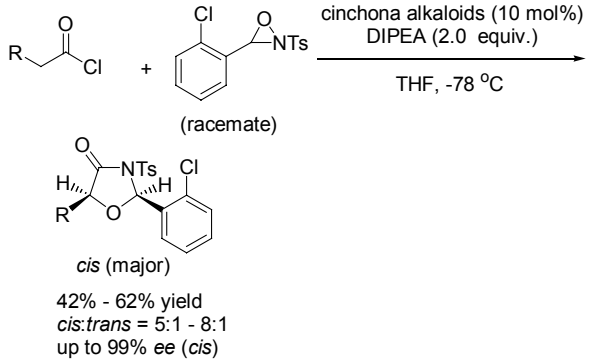
The cinchona alkaloids-catalyzed cyclization of acyl chlorides have been well established for a variety of heterocycles.[9] In 1982, Wynberg *et al*.[10] reported the first cinchona alkaloids-catalyzed enantioselective cyclization of acyl chlorides with aldehydes. In 2000, Lectka *et al*.[11] reported the pioneering cinchona alkaloids-catalyzed cyclization of acyl chlorides with imines.

Recently, we developed a cinchona alkaloids-catalyzed enantioselective formal [3+2] cycloaddition of ketenes and oxaziridines (Eq. 1).[12] The cycloadduct could be easily transformed to chiral 1,2-diols by reduction. However the moderate yields and diastereoselectivities limit its usage. In this paper, we wish to report the optimization of the process to give 1,2-diols in good yields with high enantiopurities.

Results and Discussion

Initially, the cyclization of phenylacetyl chloride (**1a**) and oxaziridine (**2**) was investigated under varied reaction conditions (Table 1). The yield was improved to 62% when 2 equiv. of DIPEA was used (Entry 1 vs. 2). Slow addition of acetyl chloride and oxaziridine led

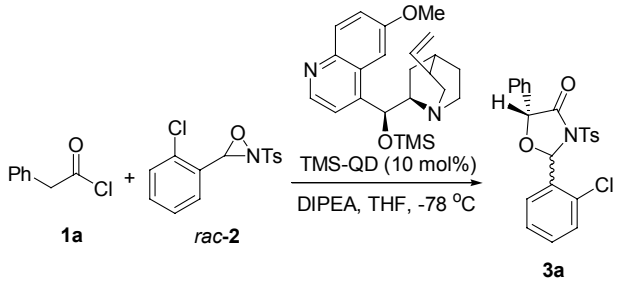
* E-mail: songye@iccas.ac.cn
Received July 9, 2012; accepted August 27, 2012; published online XXXX, 2012.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201200697 or from the author.



(1)

to decreased yield (Entry 3). Reaction with excess of acetyl chloride gave the desired cycloaddition in good yield but with decreased diastereoselectivity (Entries 4 and 5).

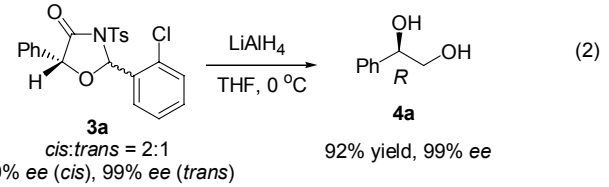
Table 1 Cyclization of phenylacetyl chloride (**1a**) and oxaziridine **2** under varied reaction conditions



Entry	n(**1a**) : n(DIPEA) : n(*rac*-**2**)	Yield[a]/%	*cis* : *trans*[b]	*ee*/% *cis*	*ee*/% *trans*
1	1 : 1 : 1	51	5 : 1	99	99
2	1 : 2 : 1	62	5 : 1	99	99
3	1 : 2 : 1[c]	24	4 : 1	99	99
4	2 : 4 : 1	66	2 : 1	99	99
5	4 : 4 : 1	81	2 : 1	99	99

[a] Isolated yield. [b] Determined by ^{1}H NMR (300 MHz) of the reaction mixture. [c] Both the solution of **1a** and *rac*-**2** were added over 5 h via a syringe pump separately. DIPEA = *N*,*N*-diisopropylethylamine.

However, the enantioselectivities are high (99% *ee*) for both diastereomers. We envisioned that both diastereomers could be transformed to the same enantiomer of 1,2-diols via reduction if they have same absolute configuration at the α-position of the carbonyl group. We are happy to find that reduction of the mixture of two diastereomers **3a** (*cis* : *trans* = 2 : 1) gave the corresponding 1,2-diol in 72% yield (two steps) with 99% *ee* (Eq. 2). Thus, the synthesis of chiral terminal 1,2-diol

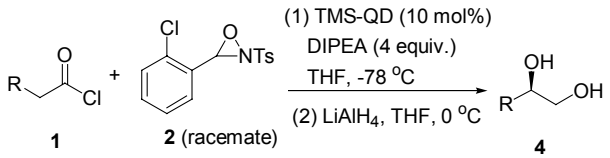


(2)

from acyl chloride via a two steps cyclization/ring-opened reduction process without separation of two diastereoisomers of the cycloadduct **3a** was established.

The reaction scope was then briefly investigated (Table 2). It was found that both phenylacetyl chlorides with electron-donating group (4-MeC_6H_4) and with electron-withdrawing group (4-ClC_6H_4, 4-BrC_6H_4) worked well to give the corresponding 1,2-diols **4b**—**4d** in good yields with high eantioselectivities. Reactions of 2-(3-chlorophenyl)acetyl chloride (**1e**) afforded the diol **4e** in 73% with 84% *ee*, while 2-(2-chlorophenyl)acetyl chloride (**1f**) resulted in low yield (34%) but high enantioselectivity (93% *ee*). In addition, both acyl chlorides with 1- and 2-naphthyl group furnished diols **4g** and **4h** in good yields with high enantioselectivities. 3-Phenylpropanoyl chloride (**1i**) afforded the diol **4i** in moderate yield but with 99% *ee*. Reactions of aliphatic acyl chloride (**1j** and **1k**) gave the desired chiral 1,2-diols **4j** and **4k** in good yields with good to high enantioselectivities.

Table 2 Asymmetric synthesis of terminal 1,2-diols from acyl chlorides



Compd.	R	Yield[a]/%	*ee*[b]/%
4a	Ph	72	99
4b	4-Me-C_6H_4	74	99
4c	4-Cl-C_6H_4	73	99
4d	4-Br-C_6H_4	65	92
4e	3-Cl-C_6H_4	73	84
4f	2-Cl-C_6H_4	34	93
4g	1-Naphthyl	70	97
4h	2-Naphthyl	69	98
4i	$PhCH_2$	47	99
4j[c]	C_2H_5	56	75
4k[c]	*n*-C_6H_{13}	52	86

[a] Overall yields of **4a**—**4k** of two steps. [b] Determined by HPLC on chiral column. [c] Determined by the analysis of its bistrifluoroacetate (**4j**) or dibenzoate (**4k**).

Conclusions

In summary, a series of chiral terminal 1,2-diols was successfully prepared by a process of cinchona alkaloids-catalyzed formal [3+2] cyclization of acyl chlorides and oxaziridines, followed by reduction. Although only moderate diastereoselectivities were observed for the [3+2] cyclization, the reduction of the mixture of two diastereomers gave the corresponding chiral terminal 1,2-diols in good overall yields with good to high enantiopurities.

CHINESE JOURNAL OF CHEMISTRY

Experimental

Unless otherwise indicated, all reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. Anhydrous THF was distilled from sodium and benzophenone. Column chromatograph was performed on silica gel (200—300 mesh). All ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) spectra were recorded on a Bruker-DMX 300 spectrometer in $CDCl_3$ or $(CD_3)_2CO$, with tetramethylsilane as an internal standard. Infrared spectra were recorded on a JASCO FT/IR-480 spectrophotometer and reported as wavenumber (cm^{-1}). Optical rotations were measured on Perkin Elmer/ Model-343 digital polarimeter operating at the sodium D line with a 100 mm path cell, and reported as follows: $[\alpha]_D^T$ (concentration/(g/100 mL), solvent).

General procedure for the enantioselective synthesis of 1,2-diols from acyl chlorides

To a solution of oxaziridine *rac*-**2** (155 mg, 0.5 mmol), TMS-quinidine (20 mg, 0.05 mmol) and *N*,*N*-diisopropylethylamine (700 μL, 4 mmol) in THF (3 mL) at −78 ℃ was added the solution of acyl chloride (2 mmol) in 2 mL of THF over 5 h via a syringe pump. After stirring at −78 ℃ for 19 h, the reaction mixture was quenched with 5 mL of ethyl acetate. The mixture was filtered through a plug of silica gel; the plug was flushed thoroughly with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, V∶V=15∶1) on silica gel to give the desired cycloadduct **3** as a *cis/trans* mixture.

To a solution of the cycloadduct **3** in THF (5 mL) was added $LiAlH_4$ (38 mg, 1 mmol) at 0 ℃. The reaction mixture was stirred at 0 ℃ overnight, and then the reaction was carefully quenched with HCl/MeOH (2.5 mol•L^{-1}, 5 mL). The resulting mixture was concentrated, and purified by flash chromatography (petroleum ether/ethyl acetate, V∶V=2∶1) on silica gel to give the desired optically active 1,2-diols **4**.

(*R*)-1-Phenylethane-1,2-diol (**4a**): Yield 49.7 mg (72%). White solid, m.p. 66—68 ℃; R_f=0.15 (petroleum ether/ethyl acetate, V∶V=2∶1). $[\alpha]_D^{20}$ −18.0 (*c* 0.5, EtOH) [Ref:[13] $[\alpha]_D^{21}$ −38.1 (*c* 1.25, EtOH)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.35—7.24 (m, 5H), 4.78—4.74 (m, 1H), 3.71—3.56 (m, 2H), 3.50 (br s, 1H), 3.11 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.5, 128.5, 127.9, 126.1, 74.7, 68.0; HPLC analysis: 99% *ee* [Daicel CHIRALPAK OD-H column; 20 ℃, 210 nm, 1.0 mL/min; solvent system: 2-propanol/hexane, V∶V=10∶90; retention times: 18.7 min (major), 21.1 (minor)].

(*R*)-1-*p*-Tolylethane-1,2-diol (**4b**): Yield 56.3 mg (74%). White solid, m.p. 75—77 ℃; R_f=0.15 (petroleum ether/ethyl acetate, V∶V=2∶1). $[\alpha]_D^{20}$ −28.6 (*c* 1, EtOH) [Ref:[14] $[\alpha]_D^{27}$ −48.1 (*c* 1.1, EtOH)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.25—7.13 (m, 4H), 4.73 (dd, J=3.4, 8.1 Hz, 1H), 3.71—3.55 (m, 2H), 3.02 (br s, 2H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.7, 137.5, 129.2, 126.0, 74.6, 68.1, 21.1; HPLC analysis: 99% *ee* [Daicel CHIRALPAK OD-H column; 20 ℃, 210 nm, 1.0 mL/min; solvent system: 2-propanol/hexane, V∶V=5∶95; retention times: 17.6 min (major), 19.8 (minor)].

(*R*)-1-(4-Chlorophenyl)ethane-1,2-diol (**4c**): Yield 62.8 mg (73%). White solid, m.p. 84—86 ℃; R_f=0.15 (petroleum ether/ethyl acetate, V∶V=2∶1). $[\alpha]_D^{20}$ −28.4 (*c* 0.35, EtOH) [Ref:[15] $[\alpha]_D^{20}$ −27.6 (*c* 0.96, EtOH)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.33—7.26 (m, 4H), 4.78 (d, J=5.3 Hz, 1H), 3.74—3.56 (m, 2H), 3.03 (br s, 1H), 2.56 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.9, 133.8, 128.7, 127.5, 74.0, 67.9; HPLC analysis: 99% *ee* [Daicel CHIRALPAK OD-H column; 20 ℃, 210 nm, 1.0 mL/min; solvent system: 2-propanol/hexane, V∶V=5∶95; retention times: 20.7 min (major), 22.7 (minor)].

(*R*)-1-(4-Bromophenyl)ethane-1,2-diol (**4d**): Yield 70.2 mg (65%). White solid, m.p. 98—99 ℃; R_f=0.15 (petroleum ether/ethyl acetate, V∶V=2∶1). $[\alpha]_D^{20}$ −32.2 (*c* 1, EtOH) [Ref:[14] $[\alpha]_D^{23}$ −41.4 (*c* 1.2, EtOH)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51—7.48 (m, 2H), 7.25 (d, J=7.5 Hz, 2H), 4.79 (dd, J=3.1, 8.0 Hz, 1H), 3.77—3.74 (m, 1H), 3.65—3.58 (m, 1H), 2.66 (br s, 1H), 2.12 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.4, 131.7,127.8, 121.9, 74.1, 67.9; HPLC analysis: 92% *ee* [Daicel CHIRALPAK OD-H column; 20 ℃, 210 nm, 1.0 mL/min; solvent system: 2-propanol/hexane, V∶V=5∶95; retention times: 22.3 min (major), 25.2 min (minor)].

(*R*)-1-(3-Chlorophenyl)ethane-1,2-diol (**4e**): Yield 62.8 mg (73%). Pale yellow oil, R_f=0.15 (petroleum ether/ethyl acetate, V∶V=2∶1). $[\alpha]_D^{20}$ −13.6 (*c* 0.9, EtOH) [Ref:[14] $[\alpha]_D^{24}$ −15.8 (*c* 1.1, EtOH)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32—7.22 (m, 4H), 4.81 (dd, J=3.4, 7.4 Hz, 1H), 3.81—3.74 (m, 1H), 3.67—3.59 (m, 1H), 2.64 (d, J=3.4, 1H), 2.10—2.06 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.6, 134.5, 129.8, 128.1, 126.3, 124.2, 74.0, 67.9; HPLC analysis: 84% *ee* [Daicel CHIRALPAK OD-H column; 20 ℃, 220 nm, 1.0 mL/min; solvent system: 2-propanol/hexane, V∶V=5∶95; retention times: 17.4 min (major), 21.0 min (minor)].

(*R*)-1-(2-Chlorophenyl)ethane-1,2-diol (**4f**): Yield 29.2 mg (34%). White solid, m.p. 101—104 ℃; R_f=0.15 (petroleum ether/ethyl acetate, V∶V=2∶1). $[\alpha]_D^{20}$ −37.5 (*c* 1, EtOH) [Ref:[16] $[\alpha]_D^{20}$ −56.5 (*c* 1.8, EtOH)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.61—7.58 (m, 1H), 7.36—7.23 (m, 3H), 5.24 (dd, J=2.2, 7.5 Hz, 1H), 3.90 (d, J=9.6 Hz, 1H), 3.58 (dd, J=7.9, 11.2 Hz, 1H), 2.77 (br s, 1H), 2.17 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.9, 132.0, 129.5, 129.0, 127.6, 127.1, 71.5, 66.3; HPLC analysis: 93% *ee* [Daicel CHIRALPAK OD-H column; 20 ℃, 210 nm, 1.0 mL/min; solvent system: 2-propanol/hexane, V∶V=5∶95; retention times: 15.3 min (major), 21.2 min (minor)].

(*R*)-1-(Naphthalen-1-yl)ethane-1,2-diol (**4g**): Yield

65.8 mg (70%). White solid, m.p. 123—125 ℃; R_f= 0.15 (petroleum ether/ethyl acetate, V∶V=2∶1); $[\alpha]_D^{20}$ −64.3 (*c* 1.1, MeOH) [Ref:[17] $[\alpha]_D^{20}$ −76.8 (*c* 1.0, MeOH)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.10—8.05 (m, 1H), 7.90—7.80 (m, 2H), 7.72—7.70 (m, 1H), 7.56—7.47 (m, 3H), 5.64 (d, J=5.7 Hz, 1H), 4.01—3.97 (m, 1H), 3.83—3.76 (m, 1H), 2.66 (br s, 1H), 2.21 (br s, 1H); ^{13}C NMR (75 MHz,$CDCl_3$) δ: 136.0, 133.6, 130.3, 128.9, 128.3, 126.3, 125.6, 125.4, 123.5, 122.6, 71.6, 67.5; HPLC analysis: 97% *ee* [Daicel CHIRALPAK OD-H column; 20 ℃, 210 nm, 1.0 mL/min; solvent system: 2-propanol/hexane, V∶V=10∶90; retention times: 13.4 min (major), 23.6 min (minor)].

(*R*)-1-(Naphthalen-2-yl)ethane-1,2-diol (**4h**): Yield 64.9 mg (69%). White solid, m.p. 136—138 ℃; R_f= 0.15 (petroleum ether/ethyl acetate, V∶V=2∶1). $[\alpha]_D^{20}$ −42.6 (*c* 1.4, EtOH) [Ref:[18] $[\alpha]_D^{23}$ −31.2 (*c* 0.997, EtOH)]; ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ: 7.90—7.84 (m, 4H), 7.57—7.45 (m, 3H), 4.89 (dd, J=3.9, 7.7 Hz, 1H), 4.45 (d, J=3.7 Hz, 1H), 3.88—3.84 (m, 1H), 3.78—3.68 (m, 1H), 3.66—3.60 (m, 1H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ: 141.3, 134.3, 133.9, 128.7, 128.4, 128.4, 126.7, 126.4, 125.7, 125.6, 75.4, 68.9; HPLC analysis: 98% *ee* [Daicel CHIRALPAK OD-H column; 20 ℃, 210 nm, 1.0 mL/min; solvent system: 2-propanol/hexane, V∶V=10∶90; retention times: 15.2 min (major), 19.2 min (minor)].

(*R*)-3-Phenylpropane-1,2-diol (**4i**): Yield 35.7 mg (47%). Colorless oil; R_f=0.15 (petroleum ether/ethyl acetate, V∶V=2∶1); $[\alpha]_D^{20}$ 18.5 (*c* 0.5, EtOH) [Ref:[8] $[\alpha]_D^{20}$ 25.5 (*c* 1.0, EtOH)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.35—7.21 (m, 5H), 4.00—3.92 (m, 1H), 3.70 (dd, J=3.2, 11.1 Hz, 1H), 3.53 (dd, J=7.0, 11.1 Hz, 1H), 2.85—2.71 (m, 2H), 2.04 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.8, 129.4, 128.7, 126.7, 73.1, 66.1, 39.8; HPLC analysis: 99% *ee* [Daicel CHIRALPAK OD-H column; 20 ℃, 210 nm, 1.0 mL/min; solvent system: 2-propanol/hexane, V∶V=5∶95; retention times: 18.9 min (major), 20.7 (minor)].

(*R*)-Butane-1,2-diol (**4j**): Yield 25.2 mg (56%). Colorless oil; R_f=0.15 (petroleum ether/ethyl acetate, V∶V=2∶1). $[\alpha]_D^{20}$ 12.0 (*c* 0.1, EtOH) [Ref:[19] $[\alpha]_D^{20}$ 15.0 (*c* 1.7, EtOH)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.90 (br s, 2H), 3.64—3.61 (m, 2H), 3.45—3.38 (m, 1H), 1.50—1.41 (m, 2H), 0.96 (t, J=7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 73.8, 66.4, 26.0, 9.9; GC analysis of its bistrifluoroacetate derivative: 75% *ee* [CHIRALDEX G-TA column, 30 m×0.25 mm×0.12 μm, 7 psi, 60 ℃, 2 min, 1 ℃/min, retention times: 11.6 min (major), 11.9 min (minor)].

(*R*)-Octane-1,2-diol (**4k**): Yield 37.9 mg (52%). Colorless oil; R_f=0.15 (petroleum ether/ethyl acetate, V∶V=2∶1). $[\alpha]_D^{20}$ 13.6 (*c* 1.2, MeOH) [Ref:[20] $[\alpha]_D^{24}$ +12.8 (*c* 0.95, MeOH)], ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.67—3.62 (m, 2H), 3.44—3.38 (m, 1H), 2.80 (br s, 2H), 1.42—1.28 (m, 10H), 0.86 (t, J=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 72.4, 66.9, 33.2, 31.8, 29.4, 25.6, 22.7, 14.1; HPLC analysis of its dibenzoate derivative: 86% *ee* [Daicel CHIRALPAK AD-H column, 20 ℃, 254 nm, 1.0 mL/min, solvent system: 2-propanol/hexane, V∶V=5∶95; retention times: 12.7 min (minor), 16.4 min (major)].

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 21072195) and the Major State Basic Research Development Program (No. 2011CB808600).

References

[1] (a) Hanessian, H. *Total Synthesis of Natural Products*: *The* "*Chiron*" *Approach*, Pergamon, Oxford, **1983**; (b) Bianchi, D.; Bosetti, A.; Cesti, P.; Golini, P. *Tetrahedron Lett*. **1992**, *33*, 3231; (c) Wang, Z.-M.; Zhang, X.-L.; Sharpless, K. B. *Tetrahedron Lett*. **1993**, *34*, 2267; (d) Fürstner, A.; Bogdanović, B. *Angew*. *Chem*., *Int*. *Ed*. **1996**, *35*, 2442; (e) Cho, B. T.; Chun, Y. S. *Tetrahedron*: *Asymmetry* **1999**, *10*, 1843; (f) Duchek, J.; Adams, D. R.; Hudlicky, T. *Chem*. *Rev*. **2011**, *111*, 4223.

[2] (a) Schmidt, M.; Amstutz, R.; Crass, G.; Seebach, D. *Chem*. *Ber*. **1980**, *113*, 1691; (b) Kagan, H. B.; Dang, T.-P. *J*. *Am*. *Chem*. *Soc*. **1972**, *94*, 6429; (c) Hoffmann, R. W. *Pure*. *Appl*. *Chem*. **1988**, *60*, 123; (d) Hasegawa, K.; Matsuda, F.; Yanagiya, M.; Matsumoto, T. *Tetrahedron Lett*. **1987**, *28*, 1671; (e) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J*. *Am*. *Chem*. *Soc*. **1989**, *111*, 5345; (f) Kang, S. H.; Jeong, J. W.; Hwang, Y. S.; Lee, S. B. *Angew*. *Chem*., *Int*. *Ed*. **2002**, *41*, 1392; (g) Smith III, A. B.; Chen, S. S.-Y.; Nelson, F. C.; Reichert, J. M.; Salvatore, B. A. *J*. *Am*. *Chem*. *Soc*. **1995**, *117*, 12013; (h) Haukaas, M. H.; O'Doherty, G. A. *Org*. *Lett*. **2002**, *4*, 1771.

[3] (a) Choi, D. S.; Han, S. S.; Kwueon, E. K.; Choi, H. Y.; Hwang, S. H.; Park, Y. S.; Song, C. E. *Adv*. *Synth*. *Catal*. **2006**, *348*, 2560; (b) Jin, Y.; Yao, Z.-J.; Zhang, S.-Y.; Jiang, R.; Sun, X.-L. *Chin*. *J*. *Org*. *Chem*. **2007**, *27*, 602 (in Chinese); (c) Liu, W.-M.; Liu, X.-Y.; Song, R.-J.; Zhang, S.-Y. *Chin*. *J*. *Org*. *Chem*. **2006**, *26*, 341 (in Chinese).

[4] (a) Palucki, M.; Pospisil, P. J.; Zhang, W.; Jacobsen, E. N. *J*. *Am*. *Chem*. *Soc*. **1994**, *116*, 9333; (b) Collman, J. P.; Wang, Z.; Straumanis, A.; Quelquejeu, M.; Rose, E. *J*. *Am*. *Chem*. *Soc*. **1999**, *121*, 460; (c) Botes, A. L.; Weijers, C. A. G. M.; Botes, P. J.; van Dyk, M. S. *Tetrahedron*: *Asymmetry* **1999**, *10*, 3327; (d) Goswami, A.; Totleben, M. J.; Singh, A. K.; Patel, R. N. *Tetrahedron*: *Asymmetry* **1999**, *10*, 3167.

[5] Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J*. *Am*. *Chem*. *Soc*. **2002**, *124*, 1307.

[6] Xu, Y.; Jia, X.; Panke, S.; Li, Z. *Chem*. *Commun*. **2009**, 1481.

[7] (a) Ohkuma, T.; Utsumi, N.; Watanabe, M.; Tsutsumi, K.; Arai, N.; Murata, K. *Org*. *Lett*. **2007**, *9*, 2565; (b) Kadyrov, R.; Koenigs, R. M.; Brinkmann, C.; Voigtlaender, D.; Rueping, M. *Angew*. *Chem*., *Int*. *Ed*. **2009**, *48*, 7556; (c) Touge, T.; Hakamata, T.; Nara, H.; Kobayashi, T.; Sayo, N.; Saito, T.; Kayaki, Y.; Ikariya, T. *J*. *Am*. *Chem*. *Soc*. **2011**, *133*, 14960; (d) Xu, H.; Meng, Q.-H.; Zhang, Z.-G. *Chin*. *J*. *Chem*. **2008**, *26*, 1656.

[8] Brown, S. P.; Brochu, M. P.; Sinz, C. J.; MacMillan, D. W. C. *J*. *Am*. *Chem*. *Soc*. **2003**, *125*, 10808.

[9] (a) Zhu, C.; Shen, X.; Nelson, S. G. *J*. *Am*. *Chem*. *Soc*. **2004**, *126*, 5352; (b) Chandra, B.; Fu, D.; Nelson, S. G. *Angew*. *Chem*., *Int*. *Ed*. **2010**, *49*, 2591; (c) Vargo, T. R.; Hale, J. S.; Nelson, S. G. *Angew*. *Chem*., *Int*. *Ed*. **2010**, *49*, 8678; (d) Xu, X.; Wang, K.; Nelson, S. G. *J*. *Am*. *Chem*. *Soc*. **2007**, *129*, 11690; (e) Tseni, P. S.; Peters, R.

Angew. *Chem*., *Int*. *Ed*. **2007**, *46*, 5325; (f) Shen, L.-T.; Sun, L.-H.; Ye, S. *J*. *Am*. *Chem*. *Soc*. **2011**, *133*, 15894.
[10] Wynberg, H.; Staring, E. G. J. *J*. *Am*. *Chem*. *Soc*. **1982**, *104*, 166.
[11] (a) Taggi, A. E.; Hafez, A. M.; Wack, H.; Young, B.; Drury, III, W. J.; Lectka, T. *J*. *Am*. *Chem*. *Soc*. **2000**, *122*, 7831; (b) Taggi, A. E.; Hafez, A. M.; Wack, H.; Young, B.; Ferraris, D.; Lectka, T. *J*. *Am*. *Chem*. *Soc*. **2002**, *124*, 6626; (c) Wack, H.; Taggi, A. E.; Hafez, A. M.; Drury, III, W. J.; Lectka, T. *J*. *Am*. *Chem*. *Soc*. **2001**, *123*, 1531; (d) France, S.; Wack, H.; Taggi, A. E.; Hafez, A. M.; Wagerle, T. R.; Shah, M. H.; Dusich, C. L.; Lectka, T. *J*. *Am*. *Chem*. *Soc*. **2004**, *126*, 4245; (e) Bekele, T.; Shah, M. H.; Wolfer, J.; Abraham, C. J.; Weatherwax, A.; Lectka, T. *J*. *Am*. *Chem*. *Soc*. **2006**, *128*, 1810; (f) Abraham, C. J.; Paull, D. H.; Bekele, T.; Scerba, M. T.; Dudding, T.; Lectka, T. *J*. *Am*. *Chem*. *Soc*. **2008**, *130*, 17085; (g) Wolfer, J.; Bekele, T.; Abraham, C. J.; Dogo-Isonagie, C.; Lectka, T. *Angew*. *Chem*., *Int*. *Ed*. **2006**, *45*, 7398; (h) Paull, D. H.; Scerba, M. T.; Alden-Danforth, E.; Widger, L. R.; Lectka, T. *J*. *Am*. *Chem*. *Soc*. **2008**, *130*, 17260; (i) Erb, J.; Paull, D. H.; Dudding, T.; Belding, L.; Lectka, T. *J*. *Am*. *Chem*. *Soc*. **2011**, *133*, 7536.
[12] Shao, P.-L.; Chen, X.-Y.; Ye, S. *Angew*. *Chem*., *Int*. *Ed*. **2010**, *49*, 8412.
[13] Uccello-Barretta, G.; Cuzzola, A.; Balzano, F.; Menicagli, R.; Iuliano, A.; Salvadori, P. *J*. *Org*. *Chem*. **1997**, *62*, 827.
[14] Jin, H.; Li, Z.-Y.; Dong, X.-W. *Org*. *Biomol*. *Chem*. **2004**, *2*, 408.
[15] Hudlicky, T.; Boros, E. E.; Boros, C. H. *Tetrahedron*: *Asymmetry* **1993**, *4*, 1365.
[16] Wei, Z.-L.; Li, Z.-Y.; Lin, G.-Q. *Tetrahedron* **1998**, *54*, 13059.
[17] Miao, G.; Rossiter, B. E. *J*. *Org*. *Chem*. **1995**, *60*, 8424.
[18] Becker, H.; King, S. B.; Taniguchi, M.; Vanhessche, K. P. M.; Sharpless, K. B. *J*. *Org*. *Chem*. **1995**, *60*, 3940.
[19] Hintzer, K.; Koppenhoefer, B.; Schurig, V. *J*. *Org*. *Chem*. **1982**, *47*, 3850.
[20] Weijers, C. A. G. M.; Botes, A. L.; van Dyk, M. S.; de Bont, J. A. M. *Tetrahedron*: *Asymmetry* **1998**, *9*, 467.

(Zhao, C.)

