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Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 17 (2006) 750–755

Effective and recyclable dendritic ligands for the enantioselective epoxidation of enones

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Received 5 December 2005; revised 15 February 2006; accepted 17 February 2006
Available online 23 March 2006

Abstract—An operationally simple and mild protocol for the catalytic enantioselective epoxidation of enones has been established using a series of chiral pyrrolidinylmethanol-based dendritic catalysts and *tert*-butyl hydroperoxide (TBHP) as an oxidant. The epoxides have been obtained in good yields and ee up to 78%.

1. Introduction

Catalytic asymmetric epoxidation of C–C double bonds provides access to enantiomerically enriched epoxides, which are of fundamental importance in organic chemistry.[1] In recent years, we have seen the dramatic development of methods for this purpose. In the field of metal-catalyzed epoxidations, in particular the Sharpless epoxidation of allylic alcohols, using catalytic amounts of titanium and tartrate, represents a reaction of great importance.[2] Similarly, the asymmetric epoxidation of non-functionalized olefins catalyzed by the manganese-salen complexes (Jacobsen–Katsuki epoxidation) has provided an easy approach to unfunctionalized epoxides.[3] For metal-free asymmetric epoxidation of olefins using chiral ketones as catalysts, typically, preparatively useful ees have been achieved for the first time by Yang et al. using the binaphthyl-derived chiral ketones as catalysts.[4] On the other hand, the asymmetric epoxidation of α,β-unsaturated carbonyl compounds is another important functionalization in organic chemistry[5] because of the usefulness of the corresponding α,β-epoxy carbonyl compounds. Shibasaki et al. have, via the use of chiral Lewis acid complexes, developed the catalytic asymmetric epoxidation of α,β-unsaturated ketones, esters, and amides applying *tert*-butyl hydroperoxide as the terminal oxidant.[6] Very recently, Ding et al. reported the highly enantioselective epoxidation of enones by employing the self-supported heterogeneous Shibasaki's catalysts prepared in situ.[7] The catalytic asymmetric epoxidation of enones applying sodium hypochlorite has also been achieved using chiral phase-transfer catalysis, and the enantioenriched epoxides were generally obtained with high enantioselectivities.[8] Furthermore, the use of chiral ketones as catalysts for the asymmetric epoxidation of a broad range of olefins has also been demonstrated.[9]

Dendrimers are well-defined macromolecules with controllable structures. Their applications in catalysis have caused increasing attention, since dendritic catalysts have the advantages of complete solubility and can be analyzed with routine spectroscopic techniques.[10] Moreover, the globular shapes of higher generation dendritic catalysts are suitable for membrane filtration[11] or selective precipitation under specific conditions.[12]

Recently, we reported the synthesis of a series of new polyether dendritic chiral pyrrolidinylmethanol derivatives and their application in catalytic, highly enantioselective aryl transfer reactions to aldehydes.[13] High catalytic activity and enantioselectivity were observed, and the higher generation catalysts could be recovered through solvent precipitation and reused several times without any apparent loss of activity. We also reported their applications in the highly enantioselective reduction of ketones and their derivatives.[14] Very recently, Lattanzi et al. reported a

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0957-4166/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.tetasy.2006.02.019

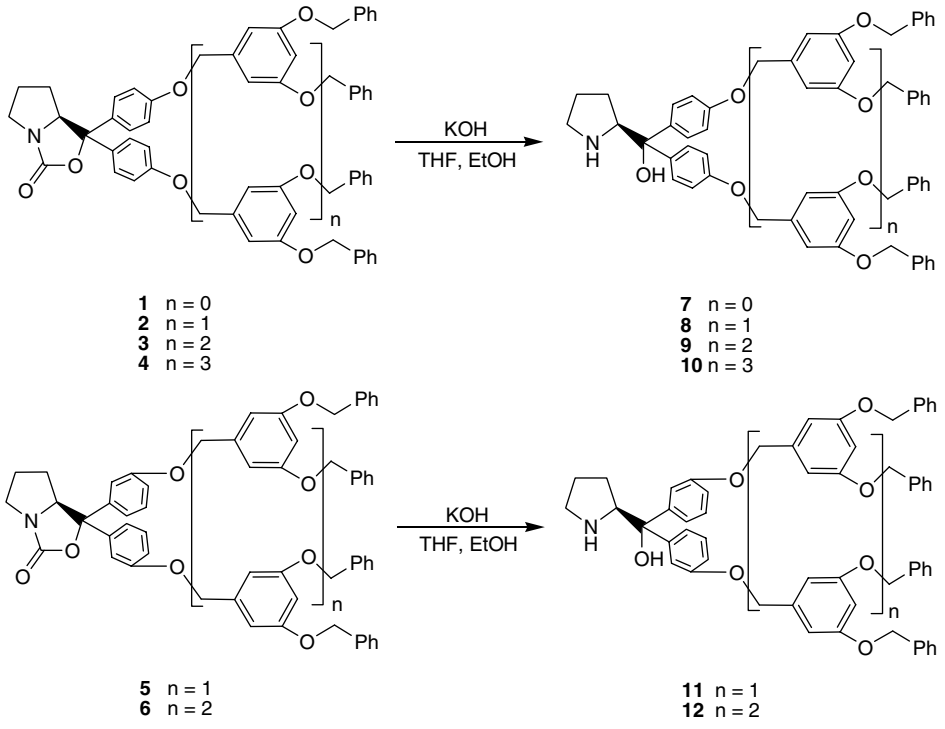
new methodology for the catalytic asymmetric epoxidation of a broad range of enones catalyzed by the bifunctional organocatalyst α,α-diphenyl-L-pyrrolidinemethanol. The epoxides have been obtained in good yields and with up to 80% ee.[15] Jørgensen et al. also reported the first asymmetric organocatalytic epoxidation of α,β-unsaturated aldehydes using a pyrrolidine derivative as the catalyst with good to high yields and enantioselectivities.[16] Being interested in the development of mild and convenient methodologies of asymmetric reactions using recyclable catalysts, we herein report the enantioselective epoxidation of enones using the polyether dendritic chiral pyrrolidinylmethanol derivatives and *tert*-butyl hydroperoxide (TBHP) as an oxidant.

2. Results and discussion

The chiral dendrimers were synthesized as shown in Scheme 1. The pyrrolidinylmethanol ligands **1**–**6** were firstly synthesized according to the published method.[13] Hydrolysis of the ester moieties with KOH afforded the corresponding alcohols **7**–**12** in 61–96% yields. These ligands were purified by flash column chromatography and characterized by ^{1}H and ^{13}C NMR spectra, MALDI mass spectrometry and elemental analysis.

A preliminary study was performed to test the catalytic property of these reagents in the asymmetric organocatalytic epoxidation of enones **13a** with TBHP (Table 1). The reaction was performed using 30 mol % of dendritic catalysts in different solvents. When employing catalyst **8**, in hexane at room temperature according to Lattanzi's protocol, no reaction of **13a** with TBHP occurred to give the corresponding epoxide, probably due to poor solubility of the dendritic catalyst in the reaction media (Table 1, entry 1). Since apolar and non-coordinating solvents furnished better results in Lattanzi's report, the reaction was performed in CCl_4. When using **8** (30 mol %) as catalyst, we found that the reaction proceeded well to give (2*R*,3*S*)-**14a** as the sole product in 60% yield and 66% ee (Table 1, entry 2). To investigate the effect of dendritic branches on the catalytic activity and stereoselectivity of the pyrrolidinylmethanol, we tested dendrimers **7**–**12** in the enantioselective epoxidation under the same conditions. In general, good conversion of enone **13a** was achieved, and the corresponding optically active epoxide was obtained in good yields. The enantioselectivities were moderate to good (41–71%), with the (2*R*,3*S*)-configured product **14a** was formed predominantly (Table 1, entries 2–7). Among all the dendritic chiral catalysts evaluated in this reaction, the second-generation ligand **12** was the best one in terms of yield and ee (Table 1, entry 7).

With these promising results, attention was then turned to modifying the above protocol in anticipation of obtaining better results. Inspired by Shibasaki et al.'s report in which the catalytic asymmetric epoxidation of enones was greatly improved by carrying out the reaction in the presence of 4 Å MS,[5] we found that after optimizing the reaction conditions, a slightly higher enantioselectivity and substantial improvement in the yield could be observed under the same conditions when **9**, **11** and **12** were used as the catalysts (Table 1, entries 8–10). Carrying out the epoxidation with 30 mol % of **12** at 0 °C had a deleterious effect on the level of selectivity, even though good conversion was



1 n = 0
2 n = 1
3 n = 2
4 n = 3

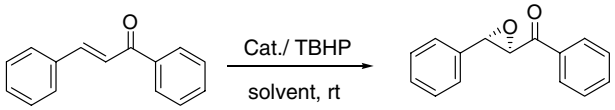
7 n = 0
8 n = 1
9 n = 2
10 n = 3

5 n = 1
6 n = 2

11 n = 1
12 n = 2

Scheme 1.

Table 1. Screening reaction conditions for the epoxidation of **13a**[a]



13a **14a**

Entry	Catalyst	Solvent	Oxidant	T (°C)	T (h)	Yield (%)[b]	ee (%)[c] (config)[d]
1	**8**	Hexane	TBHP	rt	48	Trace	nd[e]
2	**8**	CCl_4	TBHP	rt	144	60	66
3	**7**	CCl_4	TBHP	rt	120	59	41
4	**9**	CCl_4	TBHP	rt	144	64	67
5	**10**	CCl_4	TBHP	rt	144	73	68
6	**11**	CCl_4	TBHP	rt	144	67	69
7	**12**	CCl_4	TBHP	rt	144	70	71
8	**9** + 4 Å MS	CCl_4	TBHP	rt	144	85	69
9	**10** + 4 Å MS	CCl_4	TBHP	rt	144	86	73
10	**12** + 4 Å MS	CCl_4	TBHP	rt	144	84	74
11	**12** + 4 Å MS	CCl_4	TBHP	0	144	80	13
12	**11** + 4 Å MS	CCl_4/hexane = 1:1	TBHP	rt	96	65	66
13	**11** + 4 Å MS	Benzene	TBHP	rt	96	66	69
14	**11** + 4 Å MS	CH_2Cl_2	TBHP	rt	144	20	54
15	**11**	CCl_4	H_2O_2	rt	48	0	—

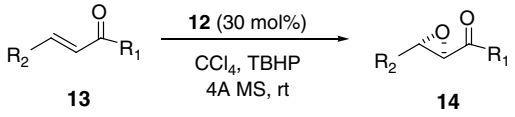
[a] Unless otherwise specified, the reaction was carried out with 1.2 equiv of TBHP in the presence of 30 mol % of catalyst.
[b] After column chromatography.
[c] Enantiomeric excess was determined by the HPLC analysis by using a chiral Daicel Chiralcel OD column.
[d] The absolute configuration of **14a** was determined to be (2*R*,3*S*) by comparison of the HPLC retention time with known data.
[e] Not determined.

achieved (Table 1, entry 11). When the reaction was carried out in benzene, hexane/CCl_4 = 1:1 (v/v), and CH_2Cl_2, the reaction yield was lowered (compared with entry 9, Table 1) and the enantioselectivity moderately reduced (Table 1, entries 12–14). Notably, when the epoxidation was performed with hydrogen peroxide (H_2O_2) as an oxidant, no reaction occurred under conditions otherwise identical to those reports in entry 9 (Table 1, entry 15). From these results, we concluded that using catalyst **12**, TBHP in CCl_4 in the presence of 4 Å MS at room temperature was the most effective protocol for the epoxidation of chalcone **13a**.

To demonstrate the scope and potential for the organocatalytic epoxidation, a series of different substituted enones **13** were reacted with TBHP at room temperature in the presence of **12** (30 mol %) as the catalyst. The results are summarized in Table 2. As shown, almost all reactions proceeded in reasonable reaction times when 30 mol % of **12** was used at room temperature and diastereoisomerically pure *trans*-(2*R*,3*S*)-epoxides **14** were obtained. Different types of electronic substitution on the phenyl ring of the carbonyl group furnished results comparable to those achieved in the epoxidation of **13** (Table 2, entries 2–5). It was found that 4-nitro chalcone could be transformed to the epoxide in 93% yield with 73% ee (Table 2, entry 4). However, the *p*-C_6H_5-C_6H_4 derivative was converted slowly to the epoxide in 77% ee, which can be attributed to the poor solubility of the enone in the reaction media (Table 2, entry 5). Enones with *para* electron-withdrawing substituents in the β-phenyl group were all converted to the corresponding optically active epoxides in good yields and enantioselectivities (Table 2, entries 6 and 7). However, under the same reaction conditions, an electron-donating substituent did not react with TBHP, due to its low reactivity (Table 2, entry 8). Specifically, when an enone bearing an *ortho*-chloro substituent on the β-phenyl group was used as a substrate, it was found that corresponding product was obtained in 90% yield with 57% ee (Table 2, entry 9). In contrast, the product was obtained in 85% yield with 37% ee when using α,α-diphenyl-L-pyrrolidinemethanol as a bifunctional organocatalyst (Table 2, entry 10). The result in entry 11 shows that the protocol can be successfully extended to a substrate having an alkyl substituent. Specifically, when (*E*)-4-methyl-1-phenylpent-1-en-3-one, bearing a strong steric bulk at the β-position was used as a substrate, it was found that no reaction occurred under the same reaction conditions (Table 2, entry 12). As the mechanism of this reaction is similar to Lattanzi's results,[15] we suggest that the chiral pyrrolidinylmethanol-based dendritic catalysts also serve as bifunctional catalysts giving rise to the simultaneous activation of the enone and the alkyl hydroperoxide by the hydroxy and amino groups, respectively.

A significant advantage of dendritic catalysts is that they can be easily separated from substrates and products through precipitation, due to the different solubilities in methanol. Therefore, these dendritic catalysts were tested by the precipitation method. After the completion of the reaction, dry methanol was added to the reaction mixture, and catalyst **12** was almost quantitatively precipitated and recovered via filtration. The recovered catalyst was reused at least five times with little or no loss of activity and enantioselectivity (Table 3).

Table 2. Catalytic enantioselective epoxidation of enones promoted by **12** and TBHP[a]



Entry	R_1	R_2	T (h)	Yield (%)[b]	ee (%)[c] (config.)[d]
1	Ph	Ph	144	84	74 (2*R*,3*S*)
2	*p*-Cl–C_6H_4	Ph	144	90	73 (2*R*,3*S*)
3	*p*-F–C_6H_4	Ph	144	92	74 (2*R*,3*S*)
4	*p*-NO_2–C_6H_4	Ph	120	93	73 (2*R*,3*S*)
5	*p*-C_6H_5–C_6H_4	Ph	144	60	77 (2*R*,3*S*)
6	Ph	*p*-Cl–C_6H_4	120	90	73 (2*R*,3*S*)
7	*p*-F–C_6H_4	*p*-Cl–C_6H_4	120	90	78 (2*R*,3*S*)
8	Ph	*p*-MeO–C_6H_4	200	Trace	nd
9	Ph	*o*-Cl–C_6H_4	120	90	56 (2*R*,3*S*)
10[e]	Ph	*o*-Cl–C_6H_4	120	85	37 (2*R*,3*S*)
11[f]	CH_3	Ph	144	70	69 (2*R*,3*S*)
12	*i*-Pr	Ph	120	Trace	nd[g]

[a] Unless otherwise specified, the reaction was carried out with 1.2 equiv of TBHP in the presence of 30 mol % of catalyst **12**.
[b] After column chromatography.
[c] Enantiomeric excess was determined by the HPLC analysis by using the chiral column.
[d] The absolute configuration of **14** was determined to be (2*R*,3*S*) by comparison of the HPLC retention times with known data.
[e] Using α,α-diphenyl-L-pyrrolidinemethanol as the bifunctional organocatalyst.
[f] 50 mol % catalyst was used in this reaction.
[g] Not determined.

Table 3. Recycling use of dendritic catalyst in asymmetric epoxidation of chalcone **13a**[a]

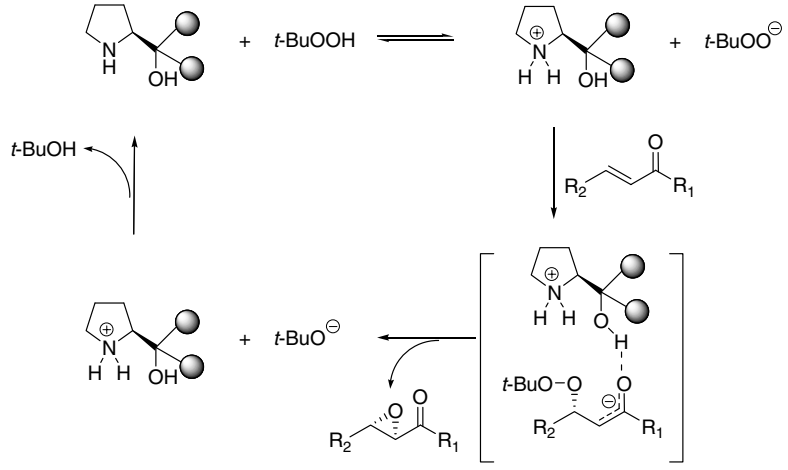
Entry	Catalyst	T (h)	Yield (%)[b]	ee (%)[c]
1	**12**	144	84	74
2	**12** (second)	144	84	73
3	**12** (third)	144	80	72
4	**12** (fourth)	144	81	73
5	**12** (fifth)	144	83	72

[a] Unless otherwise specified, the reaction was carried out with 1.2 equiv of TBHP in the presence of 30 mol % of catalyst.
[b] After column chromatography.
[c] Enantiomeric excess was determined by the HPLC analysis using a chiral Daicel Chiralcel OD column.

Although the reaction mechanism is not clear, a possible mechanism for this epoxidation of enones was proposed according to the catalytic cycle by Lattanzi (Scheme 2).[15]

3. Conclusion

In conclusion, a series of new dendritic chiral pyrrolidinylmethanol derivatives were synthesized and proven to be highly effective bifunctional organocatalysts for the asymmetric catalytic epoxidation with *tert*-butyl hydroperoxide (TBHP) as an oxidant. This study opens up a new frontier for the development of highly effective and easily separable



Scheme 2.

chiral bifunctional organocatalyst. Work is currently being focused on gaining detailed insight into the nature of the dendritic effect and the exploration of these catalysts in other reactions.

4. Experimental

General: All reactions were carried out under a dry Ar atmosphere. CCl_4 was freshly distilled from CaH_2 before use. Enones were prepared according to the reported procedures and further purified by silica gel column.[17] All NMR spectra were recorded in $CDCl_3$ as the solvent unless otherwise stated.

4.1. Synthesis of catalysts

All the dendrimeric bromides,[18] prolinol cores and the linking of dendrimers with prolinol core were prepared according to the literature.[13,14] Hydrolysis of the carbonyl group with potassium hydroxide in dimethyl sulfoxide at 80 °C for 4 h and after purification by silica gel chromatography using CH_2Cl_2/acetone (1:1) as eluent gave the corresponding dendrimeric catalysts **7**–**12**:

4.1.1. Catalyst 7 (*n* = 0). 66% yield, colorless oil. $[\alpha]_D^{20} = -59.6$ (*c* 1.00, $CHCl_3$); IR (Film): 3358, 1607, 1507, 1454, 1241 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.50–1.71 (m, 4H), 2.85–3.02 (m, 2H), 4.19 (t, $J = 7.3$ Hz, 1H), 4.99 (s, 2H), 5.00 (s, 2H), 6.86–6.90 (m, 4H, Ar), 7.23–7.46 (m, 14H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.5, 26.3, 46.7, 64.7, 69.9, 70.0, 76.6, 114.1, 114.2, 114.4, 126.6, 127.0, 127.4, 127.5, 127.6, 127.9, 128.0, 128.5, 137.1, 137.2, 138.4, 140.9, 157.3, 157.4; MS (ESI) *m*/*z* 466.1 (M^++1, 100%) HRMS-ESI: *m*/*z* (M^++1) calcd for $C_{31}H_{32}NO_3$: 466.23829; found: 466.23767.

4.1.2. Catalyst 8 (*n* = 1). 95% yield, white foam, mp 45 °C; $[\alpha]_D^{20} = -32.3$ (*c* 0.93, $CHCl_3$). IR (Film) 3359, 1596, 1506, 1452, 1159 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.53–1.79 (m, 5H), 2.94–3.04 (m, 2H), 4.19 (t, $J = 6.3$ Hz, 1H), 4.95 (s, 4H), 5.03 (s, 8H), 6.56–6.57 (m, 2H, Ar), 6.66–6.67 (m, 4H, Ar), 6.86–6.93 (m, 4H, Ar), 7.25–7.47 (m, 24H, Ar). MALDI MS (IAA): *m*/*e* 872.4 $[M-H_2O+H]^+$; Anal. Calcd for $C_{59}H_{55}NO_7$: C, 79.62; H, 6.23; N, 1.57. Found: C, 79.58; H, 6.27; N, 1.45.

4.1.3. Catalyst 9 (*n* = 2). 83% yield, white foam, mp 57–59 °C; $[\alpha]_D^{20} = -25.8$ (*c* 1.25, $CHCl_3$); IR (Film): 3353, 2872, 1596, 1506, 1452, 1157 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.52–1.69 (m, 5H), 2.86–3.02 (m, 2H), 4.10 (t, $J = 7.5$ Hz, 1H), 4.93 (s, 12H), 5.00 (s, 16H), 6.51–6.56 (m, 6H, Ar), 6.63–6.67 (m, 12H, Ar), 6.85–6.87 (m, 4H, Ar), 7.29–7.41 (m, 44H, Ar); MALDI MS (IAA): *m*/*e* 1721.7 ($[M-H_2O+H]^+$); Anal. Calcd for $C_{115}H_{103}NO_{15}$: C, 79.42; H, 5.97; N, 0.81. Found: C, 79.40; H, 5.94; N, 0.76.

4.1.4. Catalyst 10 (*n* = 3). 61% yield, white foam, mp 61–63 °C; $[\alpha]_D^{20} = -5.3$ (*c* 0.8, $CHCl_3$); IR (Film): 3400, 2872, 1598, 1498, 1452, 1216 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.52–1.69 (m, 5H), 2.86–3.02 (m, 2H), 4.08 (t, $J = 7.8$ Hz, 1H), 4.93 (s, 28H), 4.99 (s, 32H), 6.52–6.55 (m, 14H, Ar), 6.63–6.66 (m, 28H, Ar), 6.82–6.85 (m, 4H, Ar), 7.26–7.37 (m, 84H, Ar); MALDI MS (IAA): *m*/*e* 3417.5 ($[M-H_2O+H]^+$); Anal. Calcd for $C_{227}H_{199}NO_{31}$: C, 79.33; H, 5.84; N, 0.41. Found: C, 79.41; H, 5.82; N, 0.40.

4.1.5. Catalyst 11 (*n* = 1). 94% yield, white foam, mp 45–46 °C; $[\alpha]_D^{20} = -22.35$ (*c* 0.95, $CHCl_3$); IR (Film): 3358, 2871, 1596, 1496, 1451, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.19–1.73 (m, 5H), 2.86–3.01 (m, 2H), 4.15 (t, $J = 7.6$ Hz, 1H), 4.95 (s, 4H), 5.00 (s, 8H), 6.55 (m, 2H), 6.66–6.67 (m, 4H), 6.74–6.76 (m, 2H), 7.04–7.41 (m, 26H); Anal. Calcd for $C_{59}H_{55}NO_7$: C, 79.62; H, 6.23; N, 1.57. Found: C, 79.44; H, 6.29; N, 1.44.

4.1.6. Catalyst 12 (*n* = 2). 96% yield, white foam, mp 60–61 °C; $[\alpha]_D^{20} = -10.45$ (*c* 1.00, $CHCl_3$); IR (Film): 3359, 2872, 1597, 1507, 1452, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.90–1.12 (m, 2H), 1.70–1.96 (m, 2H), 3.11 (t, $J = 7.6$ Hz, 1H), 3.61–3.68 (m, 1H), 4.44 (m, 1H), 4.93 (s, 12H), 4.99 (s, 16H), 6.55 (m, 6H), 6.66 (m, 12H); 6.92–6.99 (m, 6H) 7.31–7.37 (m, 48H); MALDI MS (IAA): *m*/*e* 1721.7 ($[M-H_2O+H]^+$); Anal. Calcd for $C_{115}H_{103}NO_{15}$: C, 79.42; H, 5.97; N, 0.81. Found: C, 79.18; H, 5.91; N, 0.53.

4.2. Typical procedure for the asymmetric epoxidation of enones

To a solution of enone **13a** (20.8 mg, 0.1 mmol), catalyst **12** (30 mol %, 53 mg) and 4 Å MS (73 mg) in CCl_4 (0.4 mL) was added TBHP (0.13 mmol, 18 μL) at room temperature (23 °C) and stirring was maintained for the indicated time. Then, the 4 Å MS powder was filtered off and washed with CCl_4 (2 × 0.5 mL). The filtrate was then diluted with MeOH and the catalyst precipitated immediately to recover 50 mg (94.3%). After filtration, the organic layer was concentrated under vacuum to afford the crude epoxide, which was further purified by flash chromatography on silica gel (petroleum ether/diethyl ether 20:1) to yield product **14a** 18.8 mg (84%).

4.3. *trans*-(2*R*,3*S*)-Epoxy-1,3-diphenyl-propan-1-one 14a[6a]

The compound was obtained as a white solid; mp 88–90 °C; $[\alpha]_D^{23} = -116.3$ (*c* 0.40, $CHCl_3$) for 74% ee; ^1H NMR (300 MHz, $CDCl_3$) δ 4.01 (d, $J = 1.8$ Hz, 1H), 4.23 (d, $J = 1.8$ Hz, 1H), 7.32–7.45 (m, 7H), 7.54 (d, $J = 7.2$ Hz, 1H), 7.94 (d, $J = 7.8$ Hz, 2H); HPLC: Daicel Chiral OD column, hexane/*i*-PrOH = 9:1, 1.0 mL/min, $\lambda = 254$ nm, $t_R(2S,3R) = 14.7$ min, $t_R(2R,3S) = 15.6$ min.

Acknowledgements

We are grateful to the National Natural Science Foundation of China for financial support (Nos. 20172064, 203900502, 20532040, QT program), and Shanghai Natural Science Council.

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