Tetrahedron 67 (2011) 6474–6478

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Asymmetric epoxidation of (*Z*)-enol esters catalyzed by titanium(salalen) complex with aqueous hydrogen peroxide

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ARTICLE INFO

Article history:
Received 30 April 2011
Accepted 8 June 2011
Available online 16 June 2011

This paper is dedicated to Professor Satoshi Ōmura on the occasion of his receipt of the Tetrahedron Prize for Creativity in Organic Chemistry for 2010

Keywords:
Asymmetric reaction
Epoxidation
Hydrogen peroxide
Titanium
Enol ester

ABSTRACT

Titanium(salalen) complex **1** was an effective catalyst for asymmetric epoxidation of enol esters. Although (*E*)-enol esters were reluctant to proceed, (*Z*)-enol esters underwent asymmetric epoxidation to give the epoxides in high yields with high enantioselectivity ranging from 86 to >99% ee in the presence of aqueous hydrogen peroxide as the stoichiometric oxidant. Complete enantioselectivity was observed in the reaction of (*Z*)-3,3-dimethylbut-1-en-1-yl 4-methoxybenzoate. The obtained epoxide was readily transformed into the corresponding 1,2-diol by reduction with lithium borohydride without erosion of the high enantiomeric excess.

1. Introduction

Enantioenriched epoxides are one of the most versatile chiral building blocks in organic transformations, and thus many efficient asymmetric epoxidation methods using chiral transition metal-based catalysts and organocatalysts have been developed in the last three decades.[1–3] Epoxides prepared from enol esters and ethers are also synthetically useful compounds, because these epoxides can be readily transformed into the corresponding α-hydroxy carbonyl compounds and 1,2-diols, which are prevalent structural motifs in natural products and biologically active compounds.[4–12] Thus, the development of asymmetric epoxidation of enol esters and ethers has attracted attention. Chiral manganese(salen) complexes can be applied to asymmetric epoxidation of enol esters and ethers.[4] For example, Fukuda and Katsuki reported that cyclic enol ethers undergo enantioselective epoxidation and subsequent epoxide ring opening in alcoholic solvent to give α-hydroxy acetals with high enantioselectivity.[4c] A fructose-derived ketone catalyst also shows high enantioselectivity in the epoxidation of enol esters and ethers, in which enol esters and ethers are transformed into the corresponding epoxides and α-hydroxy ketones with high enantioselectivity, respectively.[5] In addition, Shi and co-workers demonstrated that enol ester epoxides can rearrange to α-acyloxy ketones in a highly stereoselective manner.[5c] In this way, efficient epoxidation reactions of enol esters and ethers have been reported and high enantioselectivity has been achieved. However, no examples of asymmetric epoxidation of aldehyde enol esters and ethers have yet been reported.

On the other hand, we have reported that Ti(salalen) complex **1** is an effective catalyst for asymmetric epoxidation of various simple olefins using aqueous hydrogen peroxide as the stoichiometric oxidant.[13,14] In particular, *cis*-disubstituted olefins exhibited high reactivity and enantioselectivity. On the basis of our preceding studies, we envisioned that the Ti(salalen) system shows high enantioselectivity in the epoxidation of aldehyde enol esters, which correspond to *cis*-disubstituted olefins. Here, we demonstrate highly enantioselective epoxidation of aldehyde (*Z*)-enol esters (Scheme 1).

2. Result and discussion

We first conducted asymmetric epoxidation of an *E*/*Z* mixture of oct-1-enyl benzoate (*E*/*Z*=4:5) with 2 mol % of Ti(salalen) complex

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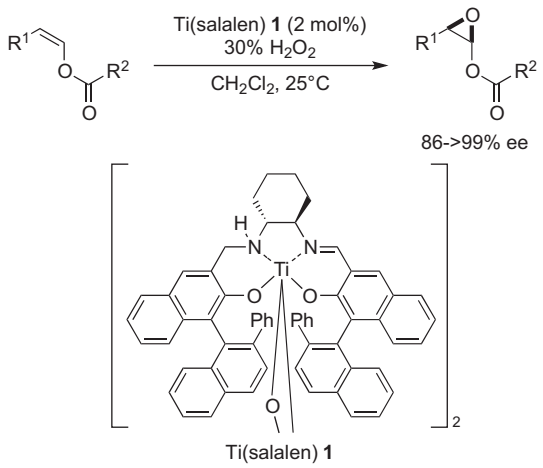
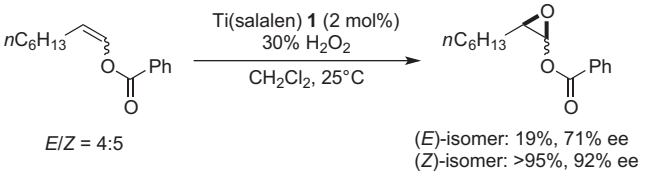
doi:10.1016/j.tet.2011.06.022



Scheme 1. Ti(salalen)-catalyzed asymmetric epoxidation of (*Z*)-enol esters.

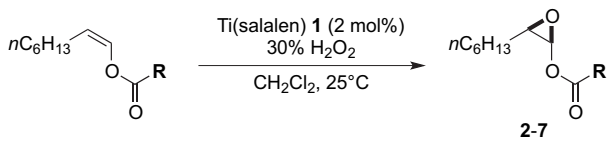
1 at 25 °C (Scheme 2). As is the case with other olefin substrates in Ti(salalen)-catalyzed asymmetric epoxidation, high reactivity, and enantioselectivity were observed for (*Z*)-oct-1-enyl benzoate, and the (*E*)-isomer gave poor yield and diminished enantioselectivity. Thus, we focused on the asymmetric epoxidation of (*Z*)-enol esters, which can be readily prepared in a highly stereoselective manner by ruthenium-catalyzed *anti*-Markovnikov addition of carboxylic acids to terminal alkynes reported by Goossen and co-workers.[15]



Scheme 2. Asymmetric epoxidation of (*Z*)- and (*E*)-oct-1-enyl benzoate.

The effect of the ester moiety on reactivity and enantioselectivity was investigated in the reaction of (*Z*)-oct-1-enyl esters (Table 1). The epoxidation of geometrically pure (*Z*)-oct-1-enyl benzoate furnished the epoxide **2** in high yield with high enantioselectivity of 92% ee (entry 1). The epoxidation proceeds in a stereospecific manner, thus no *trans*-epoxide was observed. While the introduction of an electron-withdrawing trifluoromethyl group at the *para*-position resulted in loss of the enantiomeric excess, the substitution with an electron-donating methoxy group at the *para*-position slightly improved enantioselectivity (entries 2 and 3). Introduction of the *ortho*-methoxy group had no effect on the enantioselectivity (entry 4). The reaction of 2,4-dimethoxybenzoate also gave the epoxide **6** with 93% ee, but lower epoxide yield was observed (entry 5). Aliphatic 3-phenylpropanoate showed inferior reactivity and enantioselectivity (entry 6). Consequently, we chose 4-methoxyphenyl benzoate for further exploration. It is of note that no products other than the desired epoxides were detected by ^{1}H NMR analysis of the crude reaction mixture.

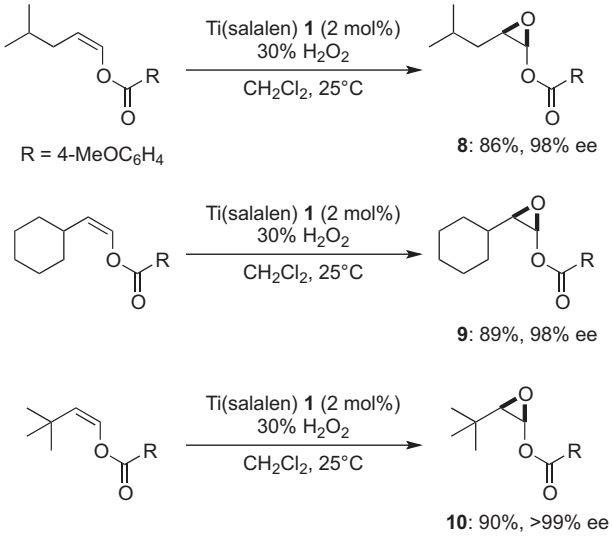
Table 1
Effect of ester moiety[a]



Entry	R	Yield/%[b]	% ee[c]
1	Ph (**2**)	>95 (94)	92
2	4-$CF_3C_6H_4$ (**3**)	>95 (94)	87
3	4-$MeOC_6H_4$ (**4**)	>95 (91)	93
4	2-$MeOC_6H_4$ (**5**)	>95 (86)	92
5	2,4-$(MeO)_2C_6H_3$ (**6**)	82 (72)	93
6	$PhCH_2CH_2$ (**7**)	36 (27)	63

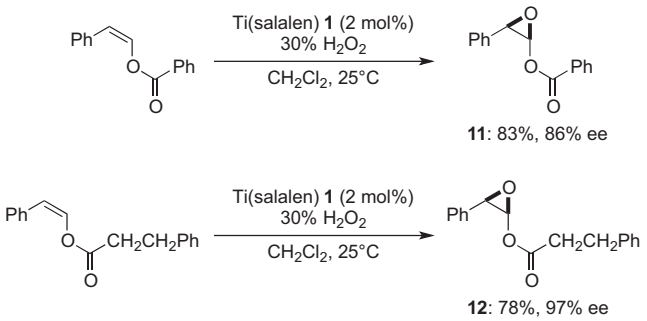
[a] The reaction was carried out with enol ester (0.5 mmol), 30% H_2O_2 (0.6 mmol), and Ti(salalen) complex (2 mol %) in CH_2Cl_2 at 25 °C.
[b] Determined by ^{1}H NMR (400 MHz). The number in parentheses is isolated yield.
[c] Determined by chiral HPLC analysis, see the Experimental section for details.

Other (*Z*)-enol esters bearing a 4-methoxybenzoate group also displayed high enantioselectivity in the titanium(salalen)-catalyzed asymmetric epoxidation (Scheme 3). The enol ester bearing an isobutyl group showed high enantioselectivity of 98%. The reaction of cyclohexyl-substituted enol ester also furnished the epoxide **9** with 98% ee. Excellent enantioselectivity of >99% ee was observed with *tert*-butyl group. Irrespective of the steric hindrance, the epoxide **10** was obtained in high yield.



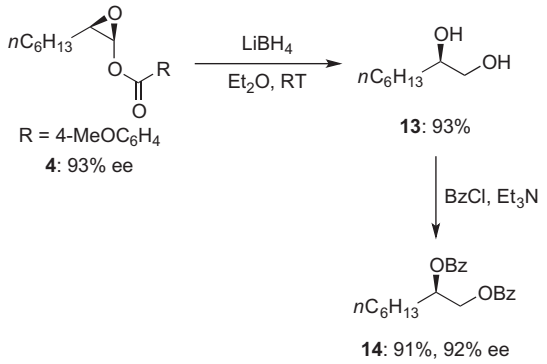
Scheme 3. Asymmetric epoxidation of aliphatic (*Z*)-enol esters.

Both aliphatic enol esters and aromatic esters underwent epoxidation effectively (Scheme 4). While the reaction of (*Z*)-styryl benzoate gave the epoxide with somewhat lower enantiomeric excess of 86%, replacement of the benzoyl moiety with a 3-phenylpropanoyl group led to the significant improvement of the enantioselectivity to afford the epoxide **12** with 97% ee. It is of interest that the ester moieties had the reverse effect on the asymmetric induction in epoxidation of aromatic- and aliphatic-substituted enol esters.



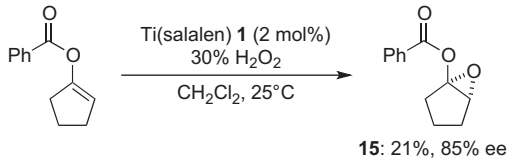
Scheme 4. Asymmetric epoxidation of aromatic (*Z*)-enol esters.

The obtained epoxides could be transformed into useful compounds without eroding enantiomeric excess. Reduction of epoxide **4** with lithium borohydride in diethyl ether afforded the corresponding 1,2-diol **13** in high yield (Scheme 5).[16] No decrease of the high enantiomeric excess was observed during this transformation.



Scheme 5. Reduction of enol ester-derived epoxide **4** to 1,2-diol **13**.

We further investigated asymmetric epoxidation of ketone enol esters under the titanium-catalyzed conditions. Although cyclopent-1-en-1-yl benzoate underwent epoxidation with good enantioselectivity of 85%, a low yield of epoxide **15** was observed (Scheme 6).[5a,c]



Scheme 6. Asymmetric epoxidation of ketone enol esters.

3. Conclusions

We have demonstrated that titanium(salalen) complex **1** effectively catalyzes asymmetric epoxidation of aldehyde (*Z*)-enol esters in the presence of aqueous hydrogen peroxide as the stoichiometric oxidant. A range of (*Z*)-enol esters gave the epoxides in high yield with high enantioselectivity ranging from 86 to >99% ee. Ketone enol esters also underwent epoxidation with good enantioselectivity albeit with low epoxide yield. The obtained epoxides were transformed into the corresponding 1,2-diols with no erosion of high enantiomeric excess.

4. Experimental section

4.1. General

All reactions were carried out in an oven-dried glassware with magnetic stirring under air. ^{1}H and ^{13}C NMR spectra were measured on a JEOL AL-400 spectrometer. Tetramethylsilane (TMS) served as internal standard (0 ppm) for ^{1}H NMR and $CDCl_3$ was used as internal standard (77.0 ppm) for ^{13}C NMR. Optical rotations were measured on a JASCO P-1020 polarimeter. Infrared spectra were measured using disposal polyethylene or polytetrafluoroethylene IR cards on a SHIMADZU FTIR-8600 spectrophotometer. High-performance liquid chromatography was carried out using SHIMADZU LC-10AT-VP equipped with a variable wavelength detector on chiral stationary columns from Daicel Chemical Industries, Ltd. Hydrogen peroxide (30%, Cat. No. 18084-00) was purchased from Kanto Chemical Co., Inc. and used as received. All enol esters were prepared by the procedure reported by Goossen co-workers.[14]

4.2. Asymmetric epoxidation: general procedure

To a solution of Ti(salalen) complex **1** (17.8 mg, 2 mol %) in dichloromethane (0.5 mL) was added enol ester (0.5 mmol). Aqueous hydrogen peroxide (61.9 μL) was added to the solution, and then the resulting mixture was stirred at 25 °C. After 12 h, the reaction was quenched with saturated $Na_2S_2O_3$. The reaction mixture was extracted with dichloromethane, and the extracts was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel (*n*-hexane/ether) to give the desired epoxide. The enantiomeric excess was determined by HPLC analysis on a chiral stationary phase.

*4.2.1. cis-3-Hexyloxiran-2-yl benzoate (**2**).* Colorless oil; 116.5 mg, 94%; 92% ee (CHIRALPAK IC, *n*-hexane/*i*-PrOH 95/5); $[\alpha]_D^{19}$ −26.8 (*c* 1.50, $CHCl_3$); FTIR (neat): 2926, 2855, 1732, 1601, 1583, 1454, 1375, 1315, 1263, 1177, 1094, 1069, 1026, 978, 831, 710, 687, 673, 536 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.04 (d, *J*=7.3 Hz, 2H), 7.62−7.58 (m, 1H), 7.48−7.44 (m, 2H), 5.79 (d, *J*=2.4 Hz, 1H), 3.10 (ddd, *J*=2.4, 5.9, 6.3 Hz, 1H), 1.86−1.72 (m, 2H), 1.61−1.48 (m, 2H), 1.43−1.37 (m, 6H), 0.88 (t, *J*=6.3 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 166.1, 133.6, 129.8, 129.1, 128.5, 76.5, 56.8, 31.6, 29.0, 27.0, 26.0, 22.5, 14.0 ppm; elemental analysis: calcd (%) for $C_{15}H_{20}O_3$: C 72.55, H 8.12; found: C 72.73, H 8.14.

*4.2.2. cis-3-Hexyloxiran-2-yl 4-trifluoromethylbenzoate (**3**).* Colorless oil; 148 mg, 94%; 87% ee (CHIRALPAK IC, *n*-hexane/*i*-PrOH 95/5); $[\alpha]_D^{19}$ −18.1 (*c* 2.29, $CHCl_3$); FTIR (neat): 2930, 2912, 2856, 1746, 1514, 1458, 1412, 1327, 1267, 1171, 1096, 1067, 1018, 862, 831, 773, 702, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.15 (d, *J*=7.8 Hz, 2H), 7.74 (d, *J*=7.8 Hz, 2H), 5.82 (d, *J*=2.4 Hz, 1H), 3.12 (ddd, *J*=2.4, 5.9, 6.3 Hz, 1H), 1.86−1.71 (m, 2H), 1.64−1.26 (m, 8H), 0.88 (t, *J*=6.3 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 165.0, 135.1 (q, J_{C-F}=33 Hz), 132.3, 130.2, 125.6 (q, J_{C-F}=3 Hz), 123.5 (q, J_{C-F}=273 Hz), 77.0, 56.8, 31.7, 29.0, 27.0, 26.0, 22.5, 14.0 ppm; elemental analysis: calcd (%) for $C_{16}H_{19}F_3O_3$: C 60.75, H 6.05; found: C 60.90, H 6.12.

*4.2.3. cis-3-Hexyloxiran-2-yl 4-methoxybenzoate (**4**).* Colorless oil; 127 mg, 91%; 93% ee (CHIRALPAK IC, *n*-hexane/*i*-PrOH 90/10); $[\alpha]_D^{19}$ −30.0 (*c* 2.20, $CHCl_3$); FTIR (neat): 2932, 2909, 2856, 2841, 1728, 1607, 1582, 1512, 1460, 1421, 1317, 1256, 1169, 1090, 1028, 847, 768, 694, 611 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.99 (d, *J*=8.8 Hz, 2H), 6.94 (d, *J*=8.8 Hz, 2H), 5.77 (d, *J*=2.4 Hz, 1H), 3.87 (s, 3H), 3.09 (ddd, *J*=2.4, 5.9, 6.3 Hz, 1H), 1.85−1.71 (m, 2H), 1.63−1.26 (m, 8H), 0.89 (t, *J*=6.3 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 166.1, 164.3, 132.2, 121.7, 114.1, 76.7, 57.1, 55.8, 32.0, 29.3, 27.4, 26.3, 22.8, 14.3 ppm; elemental analysis: calcd (%) for $C_{16}H_{22}O_4$: C 69.04, H 7.97; found: C 69.02, H 7.97.

*4.2.4. cis-3-Hexyloxiran-2-yl 2-methoxybenzoate (**5**).* Colorless oil; 120 mg, 86%; 92% ee (CHIRALPAK AD-H, *n*-hexane/*i*-PrOH 99/1); $[\alpha]_D^{20}$ −23.0 (*c* 1.16, $CHCl_3$); FTIR (neat): 2932, 2908, 2856, 1717, 1601, 1582, 1491, 1466, 1437, 1375, 1298, 1238, 1128, 1051, 1024, 976, 870, 833, 756, 702, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.84 (dd, *J*=1.5, 7.8 Hz, 1H), 7.54−7.49 (m, 1H), 7.01−6.97 (m, 2H), 5.78 (d, *J*=2.4 Hz, 1H), 3.91 (s, 3H), 3.08 (ddd, *J*=2.4, 5.9, 6.3 Hz, 1H), 1.86−1.70 (m, 2H), 1.61−1.26 (m, 8H), 0.88 (t, *J*=6.8 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 165.8, 160.1, 134.7, 132.4, 120.4, 118.8, 112.4, 76.7, 57.1, 56.2, 32.0, 29.4, 27.3, 26.3, 22.8, 14.3 ppm; elemental analysis: calcd (%) for $C_{16}H_{22}O_4$: C 69.04, H 7.97; found: C 69.10, H 7.95.

*4.2.5. cis-3-Hexyloxiran-2-yl 2,4-dimethoxybenzoate (**6**).* White solid; 111 mg, 72%; 93% ee (CHIRALPAK AD-3, *n*-hexane/*i*-PrOH 95/

5); $[\alpha]_D^{21}$ −28.1 (*c* 2.06, $CHCl_3$); FTIR (KBr): 2910, 2845, 1711, 1609, 1574, 1505, 1462, 1418, 1373, 1213, 1136, 1105, 1069, 1030, 928, 835, 768, 729, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.87 (d, *J*=8.3 Hz, 1H), 6.52–6.48 (m, 2H), 5.76 (d, *J*=2.4 Hz, 1H), 3.89 (s, 3H), 2.86 (s, 3H), 3.06 (ddd, *J*=2.4, 5.9, 6.3 Hz, 1H), 1.85–1.70 (m, 2H), 1.61–1.26 (m, 8H), 0.88 (t, *J*=6.8, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 165.0, 164.9, 162.1, 134.3, 110.9, 104.7, 98.9, 76.1, 56.8, 55.9, 55.5, 31.7, 29.1, 27.1, 26.0, 22.5, 14.0 ppm; elemental analysis: calcd (%) for $C_{17}H_{24}O_5$: C 66.21, H 7.84; found: C 66.25, H 7.64.

*4.2.6. cis-3-Hexyloxiran-2-yl 3-phenylpropanoate (**7**).* Colorless oil; 37 mg, 27%; 63% ee (CHIRALPAK IC, *n*-hexane/*i*-PrOH 90/10); $[\alpha]_D^{20}$ −13.1 (*c* 0.62, $CHCl_3$); FTIR (neat): 2910, 2856, 1757, 1497, 1454, 1358, 1136, 1109, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.31–7.19 (m, 5H), 5.55 (d, *J*=2.4, 1H), 2.99–2.95 (m, 3H), 2.73–2.69 (m, 2H), 1.68–1.24 (m, 10H), 0.89 (t, *J*=6.3 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 172.6, 140.0, 128.5, 128.2, 126.4, 76.1, 56.6, 35.7, 31.6, 30.5, 29.0, 26.8, 25.9, 22.5, 14.0 ppm; elemental analysis: calcd (%) for; $C_{17}H_{24}O_3$: C 73.88, H 8.75; found: C 74.04, H 8.78.

*4.2.7. cis-3-Isobutyloxiran-2-yl 4-methoxybenzoate (**8**).* Colorless oil; 107 mg, 86%, 98% ee (DAICEL CHIRALPAK IC, hexane/*i*-PrOH 80:20); $[\alpha]_D^{20}$ −28.6 (*c* 2.43, $CHCl_3$); FTIR (neat): 2957, 1730, 1605, 1512, 1466, 1317, 1261, 1165, 1142, 1099, 1024, 843, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.01–7.97 (m, 2H), 6.96–6.92 (m, 2H), 5.77 (d, *J*=2.4, 1H), 3.87 (s, 3H), 3.14–3.10 (m, 1H), 1.96–1.86 (m, 1H), 1.75–1.61 (m, 2H), 1.03 (d, *J*=6.8 Hz, 3H), 1.02 ppm (d, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 163.9, 131.9, 121.4, 113.8, 76.1, 55.7, 55.4, 35.7, 26.3, 22.8, 22.4 ppm; elemental analysis: calcd (%) for $C_{14}H_{18}O_4$:C 67.18, H 7.25; found: C 67.13, H 7.25.

*4.2.8. cis-3-Cyclohexyloxiran-2-yl 4-methoxybenzoate (**9**).* Colorless oil; 123 mg, 89%; 98% ee (CHIRALPAK IC, *n*-hexane/*i*-PrOH 80/20); $[\alpha]_D^{20}$ −31.5 (*c* 1.60, $CHCl_3$); FTIR (neat): 2910, 2857, 1726, 1607, 1582, 1512, 1450, 1421, 1252, 1169, 1094, 1028, 970, 879, 831, 799, 768, 696, 613, 554, 509 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.99–7.96 (m, 2H), 6.96–6.92 (m, 2H), 5.78 (d, *J*=2.4 Hz, 1H), 3.87 (s, 3H), 2.81 (dd, *J*=2.4, 8.8 Hz, 1H), 2.03–2.01 (m, 1H), 1.77–1.55 (m, 5H), 1.36–1.11 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$): δ 166.2, 164.3, 132.2, 121.7, 114.1, 76.7, 60.9, 55.8, 36.5, 30.6, 28.9, 26.5, 25.8, 25.6 ppm; elemental analysis: calcd (%) for $C_{16}H_{20}O_4$: C 69.54, H 7.30; found: C 69.80, H 7.28.

*4.2.9. cis-3-tert-Butyloxiran-2-yl 4-methoxybenzoate (**10**).* Colorless oil; 113 mg, 90%; >99% ee (CHIRALPAK IC, *n*-hexane/*i*-PrOH 80/20); $[\alpha]_D^{19}$ −26.3 (*c* 1.89, $CHCl_3$); FTIR (neat): 2950, 1728, 1607, 1582, 1512, 1421, 1367, 1256, 1090, 1007, 959, 930, 847, 806, 768, 696, 617, 554 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.00–7.96 (m, 2H), 6.96–6.92 (m, 2H), 5.72 (d, *J*=2.4 Hz, 1H), 3.87 (s, 3H), 2.81 (d, *J*=2.4, 1H), 1.13 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$): δ 165.9, 164.0, 131.9, 121.4, 113.9, 77.6, 64.0, 55.5, 31.2, 27.3 ppm; elemental analysis: calcd (%) for $C_{14}H_{18}O_4$: C 67.18, H 7.25; found: C 67.19, H 7.23.

*4.2.10. cis-3-Phenyloxiran-2-yl benzoate (**11**).* Colorless oil; 100 mg, 83%; 86% ee (CHIRALPAK IC, *n*-hexane/*i*-PrOH 95/5); $[\alpha]_D^{21}$ +42.5 (*c* 1.15, $CHCl_3$); FTIR (neat): 2924, 2852, 1734, 1601, 1495, 1454, 1360, 1315, 1252, 1205, 1177, 1094, 1069, 1026, 904, 862, 756, 710, 583, 521 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.86–7.84 (m, 2H), 7.56–7.32 (m, 8H), 6.01 (d, *J*=2.4 Hz, 1H), 4.16 (d, *J*=2.4 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 165.9, 133.7, 132.5, 129.8, 128.7, 128.5, 128.5, 128.1, 127.3, 77.0, 57.3 ppm; elemental analysis: calcd (%) for $C_{15}H_{12}O_3$: C 74.99, H 5.03; found: C 75.17, H 5.04.

*4.2.11. cis-3-Phenyloxiran-2-yl 3-phenylpropanoate (**12**).* Colorless oil; 105 mg, 78%; 97% ee (CHIRALPAK IC, *n*-hexane/*i*-PrOH 95/5); $[\alpha]_D^{21}$ +18.0 (*c* 1.02, $CHCl_3$); FTIR (neat): 3028, 2924, 1755, 1497, 1454, 1416, 1352, 1134, 1078, 897, 872, 754, 698, 567 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.35–7.32 (m, 5H), 7.27–7.23 (m, 2H), 7.19–7.16 (m, 1H), 7.08–7.06 (m, 2H), 5.73 (d, *J*=2.4 Hz, 1H), 4.04 (d, *J*=2.4 Hz, 1H), 2.80 (t, *J*=7.81 Hz, 2H), 2.61–2.47 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 172.3, 139.8, 132.4, 128.5, 128.4, 128.1, 128.0, 127.2, 126.3, 76.8, 57.2, 35.5, 30.3 ppm; elemental analysis: calcd (%) for $C_{17}H_{16}O_3$: C 76.10, H 6.01; found: C 76.20, H 5.92.

*4.2.12. 6-Oxabicyclo[3.1.0]hexan-1-yl benzoate (**15**).* Colorless oil; 21%, 85% ee (DAICEL CHIRALPAK AD-H, *n*-hexane/*i*-PrOH 99:1); $[\alpha]_D^{20}$ −29.5 (*c* 0.66, $CHCl_3$) [lit.[5c] $[\alpha]_D^{25}$ −26.8 (*c* 0.41, $CHCl_3$), 80% ee]; FTIR (neat): 2937, 2855, 1730, 1601, 1421, 1275, 1252, 1202, 1067, 1024, 941, 903, 708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06–8.04 (m, 2H), 7.61–7.57 (m, 1H), 7.47–7.43 (m, 2H), 3.80 (s, 1H), 2.46 (dd, *J*=8.8, 13.2 Hz, 1H), 2.18–2.10 (m, 1H), 2.01–1.88 (m, 2H), 1.81–1.73 (m, 1H), 1.62–1.52 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 133.6, 129.9, 129.2, 128.5, 89.8, 62.6, 28.2, 26.0, 20.0 ppm; elemental analysis: calcd (%) for $C_{12}H_{12}O_3$:C 70.57, H 5.92; found: C 70.51, H 6.00.

4.3. Reduction of epoxide 4

To a solution of epoxide **4** (100.0 mg) in diethyl ether (3.0 mL) was added lithium borohydride (23.5 mg) at 0 °C and the resulting mixture was stirred at room temperature. After 30 min, the reaction was quenched with saturated NH_4Cl aq. The reaction mixture was extracted with ether, and the extracts were washed with water and brine and then dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on basic silica gel (*n*-hexane/ether=4:1) to give the 1,2-diol **13** (48.9 mg, 93%). To a solution of diol **13** (30.0 mg) in CH_2Cl_2 (1.0 mL) was added triethylamine (85.4 μL) and benzoylchloride (72.6 μL). After stirring overnight, the reaction was quenched with saturated $NaHCO_3$ aq. The reaction mixture was extracted with CH_2Cl_2, and the extracts were washed with brine and then dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on basic silica gel (*n*-hexane/ether=20:1) to give the dibenzoate **14** (66.2 mg, 91%); 92% ee (CHIRALPAK AD-H, *n*-hexane/*i*-PrOH 99/1); $[\alpha]_D^{25}$ +4.97 (*c* 0.71, $CHCl_3$) [lit.[17] $[\alpha]_D^{24}$ +5.4 (*c* 0.63, $CHCl_3$), >99% ee]; FTIR (neat): 2920, 2851, 1715, 1684, 1649, 1583, 1458, 1261, 1177, 1069, 1026, 849, 716, 689 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.06–8.00 (m, 4H), 7.57–7.52 (m, 2H), 7.45–7.39 (m, 4H), 5.53–5.47 (m, 1H), 4.56 (dd, *J*=3.4, 11.7 Hz, 1H), 4.47 (dd, *J*=6.3, 11.7 Hz, 1H), 1.89–1.74 (m, 2H), 1.52–1.26 (m, 8H), 0.87 (t, *J*=6.8 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$): δ 166.3, 166.1, 133.0, 133.0, 130.2, 129.9, 129.7, 128.4, 72.2, 65.7, 31.6, 31.0, 29.1, 25.1, 22.5, 14.0 ppm; elemental analysis: calcd (%) for $C_{22}H_{26}O_4$: C 74.55, H 7.39; found: C 74.48, H 7.32.

Acknowledgements

We are grateful to Nissan Chemical Industries and the Global COE program 'Science for Future Molecular Systems' from MEXT (Japan) for generous financial support. T.O. is grateful for JSPS Research Fellowship for Young Scientists.

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