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Stereochemical study on an oxygen-directed olefin oxidation and subsequent oxygen cyclization: Differences between peracid and metal oxide-catalyzed hydroperoxide in oxidation reactions

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ABSTRACT

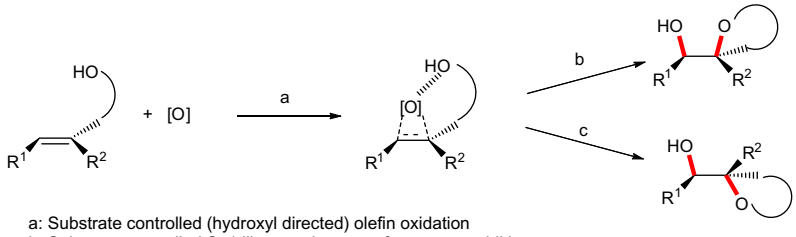
Optically active (2*S*,4*R*)-2-hydroxy-4-pentyl enol ether was prepared for the first time and subjected to hydroxy-directed oxidations at the olefinic group. Treatment with *m*-chloroperbenzoic acid and *tert*-butyl hydroperoxide/vanadium acetylacetonate resulted in the same stereoface differentiation at the olefin, with diastereomeric excesses as high as 79% and 92%, respectively, whereas the stereochemistry of the products of subsequent nucleophilic additions of the hydroxy group was opposite.

1. Introduction

Electrophilic oxidation of an olefin can be directed to a certain stereoface by a neighboring intramolecular hydroxy group.[1,2] A typical example is the epoxidation of olefins, where an intramolecular hydroxy group, mostly at the vicinal position, directs oxidants to one face of the olefin, resulting in stereoselective epoxidation. As the oxidant, both *m*-chloroperbenzoic acid (MCPBA) and *tert*-butyl hydroperoxide (TBHP)/metal oxide catalyst are often employed.[3] When the hydroxy group exists in an appropriate geometry to react further with the oxidized olefinic carbon, a cyclic ether bond can form in two different ways: addition from the same face as the oxidation and addition from the opposite direction with Warden inversion (Scheme 1, new C–O bonds are shown in red). The former reaction is classified as a substrate-controlled nucleophilic addition, and is uncommon, while the latter is classified as a reaction mechanism-controlled nucleophilic addition.[4]

The oxidation–cyclization sequence requires a remote and conformationally regulated hydroxy group to sufficiently direct the initial oxidation and to promote an effective cyclization. A typical example is the oxidation of (2*R*,4*R*)-2-hydroxy-4-pentyl enol ethers, such as **1** (Scheme 2).[5]

The treatment of **1** with MCPBA gives quantitatively (7*R*)-**2** with up to 99% diastereomeric excess (de) (CH_2Cl_2, −78 °C), while the oxidation of **1** with TBHP resulted in up to 97% de (40% yield with $Ti(OiPr)_4$ as a catalyst). The two different oxidants can be stereocontrolled by a common directing effect, similar to the case of the epoxidation of allylic alcohols, although the presence of an



a: Substrate controlled (hydroxyl directed) olefin oxidation
b: Substrate controlled S_N1 like reaction to perform a *syn*-addition
c: Reaction mechanism controlled S_N2 like reaction to perform an *anti*-addition

Scheme 1.

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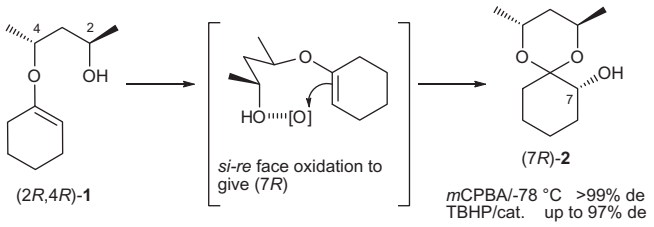


Scheme 2.

epoxy intermediate is not certain. Due to the symmetry of the chiral tether (the 2,4-pentanediol moiety), the stereochemistry of the cyclization step is unknown. The selectivity can be determined with **3** containing a (2*S*,4*R*)-tether (Scheme 3). The oxidation of **3** is interesting in the initial oxidation step because it is unknown whether the influences of the two stereogenic centers on the tether for the oxidation work cooperatively or competitively.[6]

The stereocontrol ability of the (2*S*,4*R*) tether has been tested in several different reactions; however, an enol ether-type substrate such as **3** has not been investigated in an optically active form because the production of such a substrate is difficult. The selectivity has been studied with racemic **3** [7] prepared from the acetal of *meso*-PD and cyclohexanone; however, the chiral information was partially lost, and considering its synthetic value, when **3** is used in a stereo-directing oxidation reaction, it must be enantiomerically pure. Herein we reported a method for making optically active **3** from **1** using a modified Mitsunobu reaction. The successful preparation of this substrate would allow a comparison between (2*R*,4*R*)-**1** and (2*S*,4*R*)-**3** and thus determine the stereocontrol ability of the tether. The stereochemistry of the acetal forming steps is also reported.

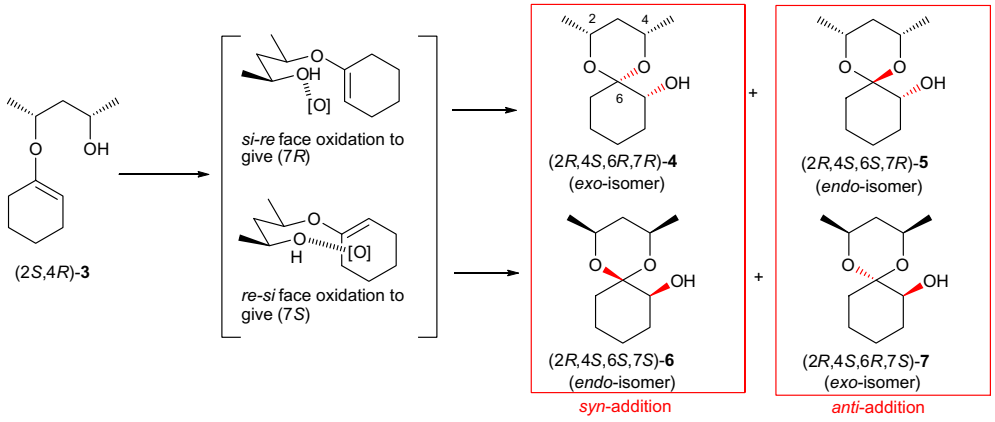
2. Results and discussion

2.1. Preparation of 3

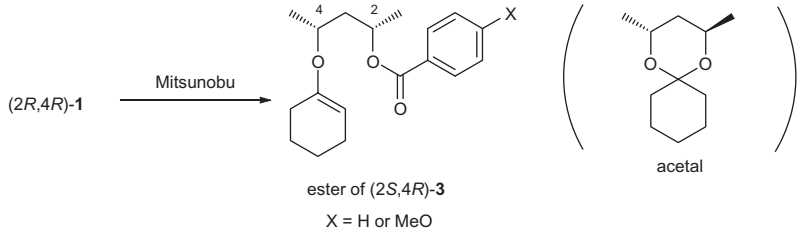
Although **1** could be prepared in enantiomerically, diastereomerically, and chemically pure form on a large scale, it is fragile and is especially unstable under acidic conditions. A racemic mixture of **3** could be prepared by the isomerization of achiral *meso*-2,4-pentanediol cyclohexanone acetal with Al(*i*Bu)$_3$; however, the *rac*-**3** produced was much less stable than **1**, which necessitated careful operation. When the Mitsunobu inversion of **1** was performed to obtain the chiral ester analogue of **3**, synthesis under conventional conditions was not successful and only gave the acetal (see Scheme 4). The Mitsunobu reaction is usually considered to be a neutral reaction;[8] however, in practice, the benzoic acid of the initially employed pro-nucleophile could serve as a proton source during the reaction. In order to reduce the acidity of the reaction media, we used anisic acid in place of benzoic acid.[9] Here the presence of trace (5%) amounts of pyridine in the reaction media was also a key factor (it most likely protects the reactant from acidic side products). With this modification, the anisic ester of **3** was obtained in 63% yield after performing Al_2O_3 column chromatography, with complete stereoinversion (Scheme 4). The higher nucleophilicity, due to the stronger conjugate base of anisic acid is an additional benefit.[6] The basic hydrolysis reaction of the ester obtained afforded stereochemically pure (2*S*,4*R*)-**3** in 84% yield.

2.2. Stereochemical assignment of 4–7

Racemic **3**[10] was first prepared and treated with MCPBA at 0 °C. The product was a stereoisomeric mixture obtained in 77% yield. The isomeric ratio was *endo*/*exo* = 74:26, where the isolated minor isomer was assigned as the *exo* isomer as deduced by NOE between 2H–7H and 4H–7H. Oxidation with another oxidant, [TBHP



Scheme 3. Hydroxy-directing oxidation–cyclization with **3** containing the (2*S*,4*R*)-tether.



Scheme 4.

($Ti(OiPr)_4$) molecular sieves 4 Å, 0 °C] primarily gave the acetal (50%); however, the oxidized product obtained in low yield (21%) was the *exo*-rich product, which suggests an unexpected reversal in the stereochemistry between the oxidation reactions.

Next, we oxidized optically active (2*S*,4*R*)-**3** with MCPBA or TBHP/metal catalyst. According to the gas–liquid chromatographic (GLC) analysis using a chiral column (β-DEX-325, 120 °C), all four stereoisomers of **4**–**7** were observed as separate peaks, accompanied by a peak corresponding to the cyclohexanone acetal of *meso*-PD in some cases. The configuration at C7 was determined by chemical correlation; that is, (*R*,*R*)-1,2-cyclohexanediol was monoacetylated with Ac_2O/pyridine/DMAP (23% yield) and oxidized with PCC to give (2*R*)-2-acetoxycyclohexanone (79%). Acetal formation with *meso*-2,4-pentanediol in the presence of Py·TsOH at benzene reflux resulted in 49% yield, and the subsequent basic hydrolysis should give the (7*R*)-product; GLC analysis was used to identify the product as *endo*-acetal **5**. The corresponding *exo*-isomer was also produced as *exo*-(7*R*)-acetal **4** (**4**:**5** = 1:15.7). From these results, the other enantiomer of the *endo*-(2*S*)-product was assigned as **6**; **7** should represent the *exo*-(2*S*)-product.

In order to confirm the above assignments, additional experiments with Mosher's ester were performed.[11] A small amount of the reaction mixture was treated with (*R*)-MTPACl to give the (*S*)-MTPA esters of **4**–**7**. The ^1H NMR spectra of the reaction mixture indicated the presence of impurities and decomposed compounds, whereas H-7 was observed as four separate peaks at isolated positions of δ 5.00–5.05 for the *endo*-products **5** and **6** and at δ 5.95–6.00 for the *exo*-products **4** and **7**. From Mosher's method rule, H-8,8′ of the (7*R*)-product should appear at a higher field than that of the (7*S*)-product. Although H-8,8′ was among many unidentified peaks, the COSY spectrum provided the necessary information, as shown in Figure 1 (*y*-axis). The stereochemistry determined by this method is identical to that obtained by chemical correlation using 1,2-cyclohexanediol.

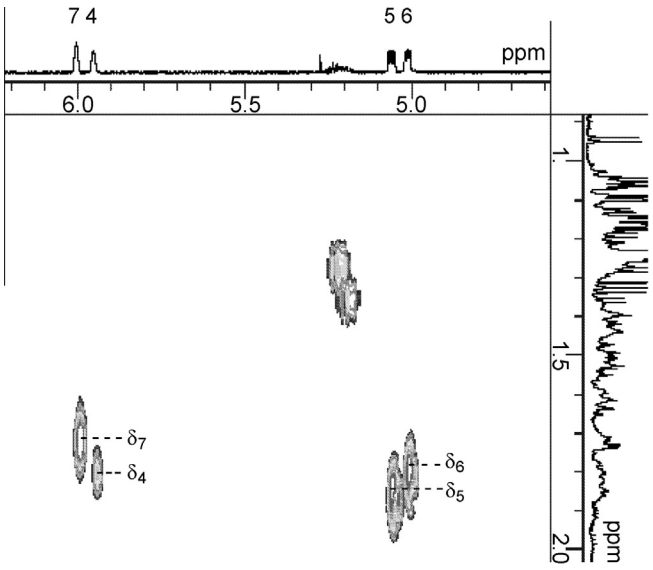


Fig. 1. COSY spectrum of the (*S*)-MTPA ester of *rac*-**4**.

2.3. Stereoselectivity in the oxidation of (2*S*,4*R*)-3

The isomeric ratios of **4**–**7** obtained by the oxidation of (2*S*,4*R*)-**3** were determined by GLC analysis;[12] the results are summarized in Table 1. The major isomer produced by the MCPBA oxidation in dichloromethane was (7*R*)-*endo*-**5**. The calculated (7*R*)-selectivity versus (7*S*) was 52% de at room temperature, which increased to 70% de at −78 °C (entries 1–3). The acetal formation step was mainly via an *anti* addition in the (7*R*)-product, whereas the minor (7*S*)-product showed a high *syn*-selectivity. The presence of a weak inorganic base did not affect the selectivity (entry 4),[13] whereas a less-directed reaction in polar THF resulted in *anti*-cyclization and poor 7-selectivity. Overall, the MCPBA oxidation is less stereoselective with **3** (70% de at −78 °C) than with **1** (99% de at −78 °C), while a *syn*-cyclization preference resulted in an *endo*-rich product.

The TBHP oxidation of (2*S*,4*R*)-**3** with $Ti(Oi\text{-}Pr)_4$ in dichloromethane also gave a (7*R*)-rich product in 56% enantiomeric excess (ee), but differed from the peracid oxidation, where the *syn*-cyclization of the (7*R*)-product to give *exo*-**4** was predominant (entry 6). The low face-selectivity was a disappointing issue, and poor selectivity was also found with the $Mo(CO)_6$-catalyzed reaction (entry 7). However, the selectivity of the vanadium acetylacetonate ($VO(acac)_2$)-catalyzed reaction was not poor, and the reaction in toluene at −20 °C gave the best results with 92% de and 18/1 *syn*-cyclization selectivity (entry 10, 93% *exo*, 94.8% ee). The *exo*-(7*R*)-selectivity with TBHP is clearly attributable to *syn*-cyclization. The observed stereoselectivity at C7 is higher than the oxidation of **1** with the same catalyst (87% de).

Nucleophilic addition to an epoxide usually occurs through an S_N2 mechanism.[14] The *anti*-selectivity with MCPBA oxidation may indicate the formation of an epoxide intermediate, whereas the TBHP oxidation tends to induce cyclization, which interrupts the epoxide formation process. The generality of these tendencies was confirmed with cycloheptanone derivative **9**.[15] The Mitsunobu reaction of **8** to **9** was not as smooth as that of **1** to **3**, and a mixture of **9** and cycloheptanone acetal was obtained. Compound **9** did not exceed 50% of the contents, and could not be isolated. The oxidation of the mixture gave four peaks, which were temporarily assigned to be **4**′–**7**′ the same as **4**–**7** as shown in Table 2. As

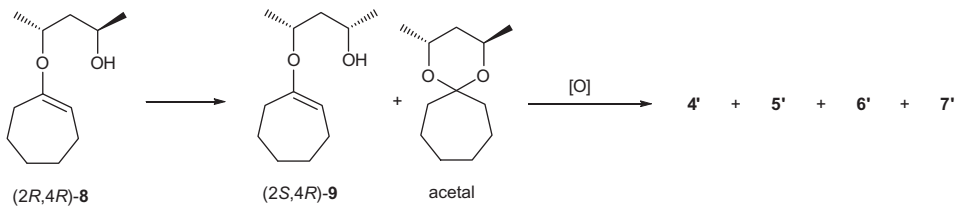
Table 1
Yields and isomeric compositions in the oxidation of **3** under various conditions

Entry	Conditions (reagent/(catalyst)/solvent/temp)	Yield[a]	Composition of the four isomers/%				(7*R*)/(7*S*)	*syn* versus *anti* additions	
			4	**5**	**6**	**7**		(7*R*)-Product (**4**/**5**)	(7*S*)-Product (**6**/**7**)
1	MCPBA/CH_2Cl_2/22 °C	100	24	52	22	2.3	76/24	1/2.2	9.6/1
2	MCPBA/CH_2Cl_2/0 °C	93	21	56	18	4.7	77/23	1/2.7	3.8/1
3	MCPBA/CH_2Cl_2/−76 °C	100	21	64	13	1.7	85/15	1/3.1	7.6/1
4	MCPBA/CH_2Cl_2+$NaHCO_3$ aq/0 °C	87	23	54	19	3.9	77/23	1/2.4	4.9/1
5	MCPBA/THF/0 °C	99	14	24	22	40	38/62	1/1.7	1/1.8
6	TBHP/$Ti(Oi\text{-}Pr)_4$/CH_2Cl_2/0 °C	89	63	15	16	6.3	78/22	4.2/1	2.5/1
7	TBHP/$Mo(CO)_6$/CH_2Cl_2/0 °C	53	45	20	17	18	65/35	2.3/1	1/1.1
8	TBHP/$VO(acac)_2$/CH_2Cl_2/0 °C	100	76	19	3.8	1.5	95/5	4/1	2.5/1
9	TBHP/$VO(acac)_2$/toluene/0 °C	93	87	7.3	3.0	2.7	94/5	12/1	1.1/1
10	TBHP/$VO(acac)_2$/toluene/−20 °C	100	91	5.1	2.2	1.9	96/4	18/1	1.2/1

[a] The yields of **4**–**7** were determined by GLC analysis. Most of the side product was the unoxidized cyclohexanone acetal of PD.

Table 2
Yields and isomeric compositions in the oxidation of **9** under various conditions

Entry	Conditions (reagent/(catalyst)/solvent/temp)	Yield[a]	Composition of four isomers/%				(7*R*)/(7*S*)	*Syn* versus *anti* additions	
			4′	**5′**	**6′**	**7′**		(7*R*-product (**4′**/**5′**)	(7*S*)-product (**6′**/**7′**)
1	MCPBA/CH_2Cl_2/−76 °C	—	44	39	14	2.8	83/17	1.1/1	4.9/1
2	MCPBA/CH_2Cl_2/0 °C	—	51	26	17	6.3	77/23	1.9/1	2.7/1
3	TBHP/$VO(acac)_2$/CH_2Cl_2/0 °C	—	77	19	2.8	1.3	95/5	3.9/1	2.5/1



Scheme 5. Hydroxy-directing oxidation–cyclization with **9** containing the (2*S*,4*R*) tether.

expected, compounds **3** and **9** showed little difference in the selective oxidations to give (7*S*). In the case of the MCPBA oxidation, **9** gave the thermodynamically stable *endo*-product more than **3**. In the case of TBHP/$VO(acac)_2$ oxidation, **9** gave the four products with the same (Scheme 5) selectivity as **3** (Table 1, entry 8).

3. Conclusion

A Mitsunobu inversion reaction for acid-sensitive compounds was developed. Using this reaction, we prepared optically active **3**. In order to assign the configuration of the secondary alcohol with a complex NMR spectrum, the Mosher's ester rule was used in conjunction with 2D COSY spectra. The best oxidant dealing with the stereoface selectivity between (2*R*,4*R*)-**1** and (2*S*,4*R*)-**3** differed: MCPBA was the best oxidant for **1**, whereas TBHP was the best oxidant for **3**. The *syn*/*anti*-cyclization selectivity with **3** was found to be opposite between the oxidants. Herein we have reported on our attempts to clarify the stereochemistry of the oxidation–cyclization process with the chiral PD-tethered reactions.

4. Experimental

4.1. General

NMR spectra were recorded on a JEOL JNM-ECA600 spectrometer operating at 600 MHz for ^{1}H NMR and at 150 MHz for ^{13}C NMR. The chemical shifts (δ ppm) for the ^{1}H NMR spectra of samples dissolved in $CDCl_3$ are downfield from TMS (=0). In the ^{13}C NMR spectra, the chemical shifts are reported on a scale relative to $CDCl_3$ (77.0 ppm), which was used as an internal reference. IR spectra were recorded on a JASCO FT/IR-410 spectrophotometer. Optical rotations were measured on a Perkin Elmer 241 polarimeter. ESI mass spectra were recorded on a JEOL JMS-T100LC spectrometer.

4.2. Oxidation of (2*R**,4*S**)-3 with MCPBA to give racemic *endo*-5/6 and *exo*-4/7

To a solution of *rac*-**3** (192.4 mg, 1.04 mmol) in dichloromethane (5 ml), MCPBA (210.6 mg, 1.22 mmol) was added at 0 °C with stirring. After 10 min, the mixture was allowed to warm to room temperature and was stirred for 5 h. The reaction mixture was extracted and purified by silica gel column chromatography (5 g, elution with 20% ethyl acetate in hexane) to give an *endo*/*exo* mixture (161 mg, 77.4%). The mixture was further purified to give partially separated **5**/**6** and **4**/**7**. Racemic *endo*-product **5/6**: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.04–3.90 (2H, m), 3.44 (1H, dd, J = 8.2 Hz, 4.1 Hz), 2.20 (1H,br), 1.80 (1H, m), 1.65–1.50 (3H, m),1.49 (2H, dt, J = 13.1 Hz, 2.6 Hz), 1.44 (1H, m), 1.39 (1H, m), 1.28 (1H, m), 1.16 (3H, d, J = 6.2 Hz), 1.15 (3H, d, J = 6.2 Hz), 1.13 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 98.98, 73.99, 65.83, 64.58, 40.66, 30.88, 29.53, 26.46, 25.75, 22.13, 15.24; IR (neat): 3479, 2932, 2663, 1722, 1446, 1382, 1233, 1042, 1011, 949, 920, 856, 825, 795, 754, 704, 678 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{20}NaO_3$ [M+Na]$^+$: 223.131, found: 223.131. *exo*-product **4/7**: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.48 (1H, m), 4.06 (1H, m), 4.00 (1H, m), 2.15 (1H, s), 1.81 (1H, m), 1.75 (1H, m), 1.56–1.48 (8H, m), 1.19 (3H, d, J = 6.2 Hz), 1.14 (3H, d, J = 6.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 98.74, 64.91, 64.33, 62.70, 39.81, 33.65, 27.98, 22.01, 21.99, 21.69, 18.69; IR (neat): 3466, 2936, 1713, 1446, 1382, 1238, 1175, 1116, 1081, 1041, 1011, 894, 856 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{20}NaO_3$ [M+Na]$^+$: 223.131, found: 223.131.

4.3. (2*S*,4*R*)-4-(Cyclohex-1-en-1-yloxy)pentan-2-yl 4-methoxybenzoate (ester of 3)

A solution of DIAD (103 mg, 0.51 mol) in THF (3.0 ml) was added dropwise over a period of 2 min to a stirred solution of (2*R*,4*R*)-4-(cyclohex-1-en-1-yloxy)pentan-2-ol **1** (98.0 mg, 0.53 mmol), *p*-anisic acid (79.3 mg, 0.52 mmol), PPh_3 (143.3 mg, 0.55 mmol), and a few drops of pyridine in THF (1.0 ml) at room temperature. After being stirred for 4 h, the reaction mixture was concentrated and purified by Al_2O_3 column chromatography (hexane/EtOAc = 6:1) to give the ester of **3** (106.2 mg, 0.33 mmol, 63% yield).

Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (2H, d, J = 8.9 Hz), 6.89 (2H, d, J = 8.9 Hz), 5.22 (1H, m), 4.62 (1H, t, J = 3.8 Hz), 4.18 (1H, m), 3.83 (3H, s), 2.19 (1H, m), 2.01–2.00 (2H, m), 1.97–1.95 (2H, m),1.67–1.50 (3H, m), 1.49 (2H, dt, J = 8.9 Hz, 5.3 Hz), 1.33 (3H, d, J = 6.2 Hz), 1.22 (3H, d, J = 6.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.53, 163.05, 152.36, 131.30, 122.98, 113.38, 113.32, 94.81, 68.61, 67.70, 55.17, 42.27, 29.94, 26.77, 23.36, 22.74, 22.53, 20.32, 19.49; IR (neat): 3403, 2928, 2042, 1917, 1714, 1606, 1512, 1455, 1256, 848, 770, 696, 664, 613 cm^{-1}; $[\alpha]_D^{20} = +23.0$ (c 1.02, CH_2Cl_2); HRMS (ESI-TOF) calcd for $C_{19}H_{26}NaO_4$ [M+Na]$^+$: 341.173, found: 341.173.

4.4. (2*S*,4*R*)-4-(Cyclohex-1-en-1-yloxy)pentan-2-ol 3

A 1.0 M NaOH aqueous solution (300 μl) was added dropwise to a stirred solution of (2*S*,4*R*)-4-(cyclohex-1-en-1-yloxy)pentan-2-yl 4-methoxybenzoate (ester of **3**) (51.1 mg, 0.16 mmol) in MeOH

(1.0 ml) at room temperature. After being stirred at 65 °C until the substrate could not be detected by silica gel TLC analysis, the reaction mixture was cooled to room temperature. The mixture was extracted four times with CH_2Cl_2, and the combined organic phase was washed with H_2O and dried (K_2CO_3). After 10 drops of Et_3N were added, the solution was concentrated and purified by Al_2O_3 column chromatography (hexane/EtOAc = 4:1) to give the product **3** (24.6 mg, 0.13 mmol, 84% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.70 (1H, t, J = 4.1 Hz), 4.25 (1H, m), 3.94 (1H, m), 2.92 (1H, s), 2.04–2.01 (2H, m), 2.00–1.98 (2H, m), 1.74 (1H, dt, J = 17.2 Hz, 7.2 Hz), 1.63 (2H, m), 1.57 (1H, dt, J = 14.2 Hz, 3.1 Hz), 1.52–1.49 (2H, m), 1.19 (3H, d, J = 6.2 Hz), 1.16 (3H, d, J = 6.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.17, 96.65, 71.57, 67.28, 64.20, 45.59, 28.28, 23.64, 23.01, 22.73, 19.93; IR (neat) 3389, 2929, 1664, 1446, 1374, 1334, 1267, 1183, 1041, 1007, 918, 828, 769 cm^{-1}; $[\alpha]_D^{20} = +51.0$ (c 0.52, CH_2Cl_2); HRMS (ESI-TOF) calcd for $C_{11}H_{20}NaO_2$ $[M+Na]^+$: 207.136, found: 207.153.

4.5. Oxidations of (2*S*,4*R*)-9

Compound (2*R*,4*R*)-**8** was prepared from the cycloheptanone acetal as reported, and then converted into (2*S*,4*R*)-**9** by the same procedure for **1**–**3** (85–90% crude yield). The mixture of **9** and the acetal was oxidized as above, and analyzed by a GLC (β-DEX325, 120 °C, 25 cm/s) to give four peaks at 26.5, 26.9, 27.2, and 27.7 min (by the same conditions, the oxidation mixture of **3** gave peaks at 27.2 min for **4**, 27.8 min for **7**, 28.6 min for **6**, and 29.4 min for **5**).

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