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Tetrahedron: *Asymmetry* 16 (2005) 1157–1165

Organocatalytic kinetic resolution of racemic primary alcohols using a chiral 1,2-diamine derived from (*S*)-proline

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Received 26 November 2004; revised 22 January 2005; accepted 24 January 2005

Abstract—A highly efficient and good enantioselective organocatalytic asymmetric acylation of racemic primary alcohols with acyl chlorides has been achieved catalyzed by a chiral 1,2-diamine derived from (*S*)-proline.

1. Introduction

The kinetic resolution of racemic alcohols via asymmetric acylation has been widely used to construct various useful chiral building blocks in the synthesis of complex natural products.[1] Most methods reported so far have employed enzymes, such as a lipase or esterase.[2] The asymmetric acylation of alcohols using molecular catalysts has emerged as a viable alternative to the well-established enzyme-catalyzed acylation. For example, Vedejs et al. have reported the kinetic resolution of racemic secondary alcohols using a highly modified chiral phosphine catalyst.[3] Fu et al. achieved the asymmetric acylation of racemic secondary aryl carbinols using acetic anhydride catalyzed by chiral dimethylaminopyridine derivatives having a ferrocene unit.[4] Miller et al. have reported the asymmetric acylation of racemic secondary hydroxy amides catalyzed by oligopeptide,[5] while Spivey et al. reported the kinetic resolution of racemic secondary aryl carbinols catalyzed by atropisomeric dimethylaminopyridine derivatives, which contain a chiral axis *meta*-position to the pyridyl nitrogen.[6] Others have also reported the kinetic resolution of racemic secondary alcohol using chiral dimethylaminopyridine derivatives[7] or organocopper reagent[8] and so on. Recent disclosures from our laboratories have demonstrated the synthetic potential of a simple 1,2-diamine as an efficient chiral organocatalyst for asymmetric acylation of alcohols.[9] As part of these investigations, we presented a highly efficient and enantioselective kinetic resolution of racemic secondary alcohols catalyzed by a chiral 1,2-diamine derived from (*S*)-proline (Scheme 1).[10] This reaction has advantages, such as high efficiency and excellent enantioselectivity, extensive substrate generality, and very low catalyst loading. On the other hand, the kinetic resolution of racemic primary alcohols is supposed to be very difficult because the reactive site and the asymmetric carbon center are far apart. In fact, the enantioselectivity obtained by an enzymatic method is hardly satisfactory ($E = \sim 50$).[11] Therefore, we extended the kinetic resolution of racemic primary alcohols using a chiral organocatalyst.

Herein, we report a kinetic resolution of various racemic primary alcohols catalyzed by a chiral 1,2-diamine derived from (*S*)-proline.

2. Results and discussion

2.1. Kinetic resolution of various glycerol derivatives

Initially, we investigated the kinetic resolution of glycerol derivatives having two protected hydroxy functions as a model substrate of racemic primary alcohols due to the pioneering work of desymmetrization of glycerol derivatives using chiral 1,2-diamine was reported by Mukaiyama and co-workers.[12] The treatment of 2,3-*O*-(isopropylidene)glycerol with benzoyl chloride (0.75 equiv)

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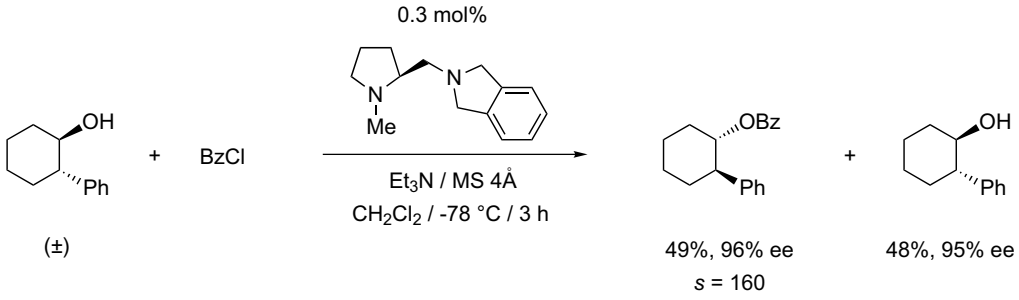
doi:10.1016/j.tetasy.2005.01.034



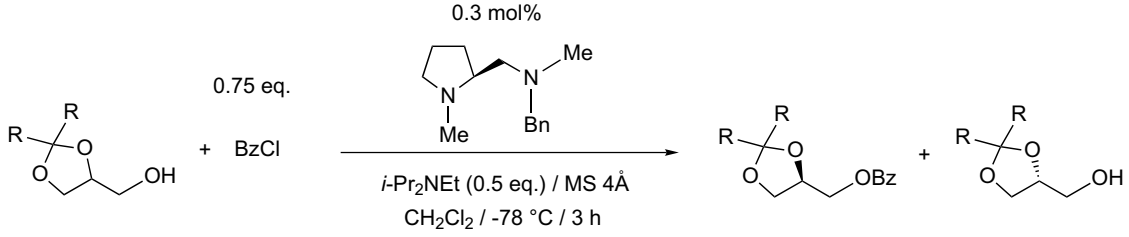
Scheme 1. Non-enzymatic kinetic resolution of a racemic secondary alcohol catalyzed by a chiral 1,2-diamine.

under the influence of (*S*)-1-methyl-2-[(benzylmethylamino)methyl]pyrrolidine (0.3 mol %) combined with diisopropylethylamine (0.5 equiv) at −78 °C in dichloromethane for 3 h gave the corresponding benzoate in 44% yield with 56% ee and the unreacted alcohol in 33% isolated yield with 69% ee (Table 1, run 1). The absolute configuration of 4-benzoyloxymethyl-2,2-dimethyl-1,3-dioxolane was assigned to be (*R*)- by comparison of optical rotation with reported value.[13] The enantiomeric excess was determined by HPLC analysis with a chiral column. The kinetic resolution of the glycerol derivative protected by di-*n*-propyl acetal gave $s = 7.0$ selectivity (run 2). Substrates with *n*-Bu or cyclohexylidene substituents showed moderate selectivity (runs 3 and 4). When sterically hindered 1,3-dioxolane having two isopropyl groups was used, comparatively high *s* value ($s = 7.3$) was acquired (run 5). 1,3-Dioxolanes having cyclohexyl and phenyl groups gave also comparable results from the standpoint of selectivity (runs 6 and 8). The enantioselectivity was decreased by the use of benzyl groups (run 7).

2.2. Kinetic resolution of glycerol derivatives with various acylating agent

Next, we tested the acylating agent (Table 2). When the substituent on the aromatic ring of benzoyl chloride was explored (*ortho*-Me, *meta*-Me, *para*-Me), it was found that the *para*-substituted benzoate showed a higher selectivity than the *ortho*- and *meta*-substituted ones (runs 2–4). Among the *para*-substituents tested, such as the electron-donating and electron-withdrawing groups (runs 4–7), the *para*-Me group gave an $s = 9.8$ selectivity (run 4). α-Naphthoyl chloride gave a low chemical yield and selectivity because of its insolubility with methylene chloride at −78 °C (run 8). When mixed

Table 1. Kinetic resolution of various glycerol derivatives

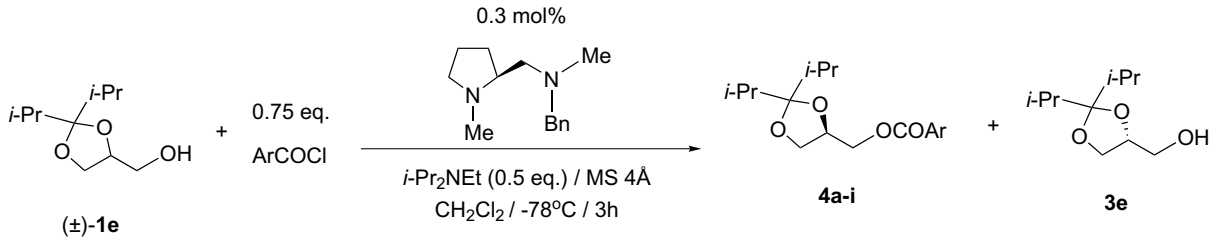


(±)-**1a-h** **2a-h** **3a-h**

Run	R	Ester **2a–h**		Alcohol **3a–h**		*s*[c]
		Yield/%	Ee[a]/%	Yield/%	Ee[b]/%	
1	Me (**1a**)	44	56	33	69	5.4
2[d,e]	*n*-Pr (**1b**)	49	60	37	64	7.0
3	*n*-Bu (**1c**)	52	54	41	71	5.9
4[d]	–$(CH_2)_5$– (**1d**)	49	53	41	65	5.3
5	*i*-Pr (**1e**)	52	59	39	75	7.3
6	*cyclo*-Hex (**1f**)	54	51	43	82	5.5
7	Bn (**1g**)	53	23	47	29	2.0
8	Ph (**1h**)	51	54	45	62	5.8

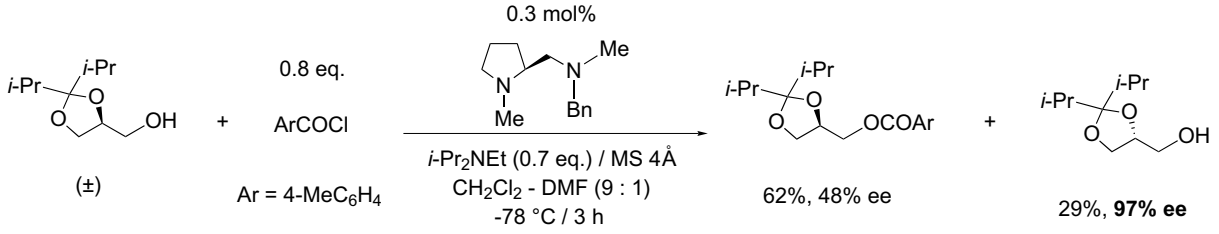
[a] Determined by HPLC analysis with a chiral column.
[b] Determined by HPLC analysis with a chiral column after converted to the corresponding benzoate.
[c] *s* Value was calculated by the equation. See Ref. 19. In this place, conversion of products adopts chemical yield of acylated esters as an expedient.
[d] 0.5 mol % of chiral diamine was used.
[e] When 0.5 mol % of (*S*)-1-methyl-2-[(dihydroisoindol-2-yl)methyl]pyrrolidine was used, 51%, 6% ee of ester and 46%, 8% ee of unreacted alcohol were obtained, respectively.

Table 2. The effect of acyl chloride



Run	ArCOCl	Ester **4a–i**		Alcohol **3e**		*s*
		Yield/%	Ee[a]/%	Yield/%	Ee[b]/%	
1	PhCOCl	52 (**4a**)	59	39	75	7.3
2	2-MeC_6H_4COCl	21 (**4b**)	61	44	15	4.8
3	3-MeC_6H_4COCl	54 (**4c**)	51	37	79	5.5
4	4-MeC_6H_4COCl	48 (**4d**)	68	43	81	9.8
5	4-*t*-BuC_6H_4COCl	55 (**4e**)	57	36	84	7.4
6	4-$MeOC_6H_4COCl$	39 (**4f**)	70	32	44	8.7
7	4-ClC_6H_4COCl	53 (**4g**)	51	41	76	5.4
8	α-Naphthoyl chloride	20 (**4h**)	67	57	23	6.0
9[c]	α-Naphthoyl chloride	38 (**4h**)	81	50	48	16
10[c,d]	α-Naphthoyl chloride	47 (**4h**)	77	46	68	16
11[c]	β-Naphthoyl chloride	13 (**4i**)	78	77	10	9.1

[a] Determined by HPLC analysis with a chiral column.
[b] Determined by HPLC analysis with a chiral column after converted to the corresponding benzoate.
[c] CH_2Cl_2–DMF (9:1) was used as a solvent.
[d] The reaction was performed in 30 mmol scale.



Scheme 2. Kinetic resolution of glycerol derivatives.

solvents [CH_2Cl_2–DMF (9:1)] were used, $s = 16$ selectivity was obtained (run 9). In addition, we demonstrated that the reaction proceeds efficiently on a 30 mmol scale (run 10).

We succeeded in increasing the enantiomeric excess of the unreacted alcohol by up to 97% ee by progressing acylation over 60% using 0.8 equiv of 4-methylbenzoyl chloride and 0.7 equiv of diisopropylethylamine (Scheme 2).

2.3. Kinetic resolution of various racemic primary alcohols

The reactions of various racemic primary alcohols, having heterocycles and a cyclopropane ring, were examined. The results are summarized in Scheme 3 and Table 3. The kinetic resolution of glycidol was performed by successive acylation and silylation in order to isolate unreacted alcohol. Consequently, the corresponding benzoate and silyl ether were directly obtained in 36% chemical yield and 64% ee and 59% chemical yield and 46% ee, respectively (Scheme 3). When 2-oxiranylethanol, which is far away between the reactive site and the asymmetric carbon center, was used, the selectivity was very poor (run 1). Other various racemic primary alcohols having oxirane, aziridine, tetrahydrofuran, and tetrahydropyran showed moderate selectivities (runs 2–6). 2-Phenylcyclopropane-1-methanol, which does not contain a heteroatom except for a hydroxyl group in the molecule, was ineffective from the standpoint of enantioselectivity (run 7).

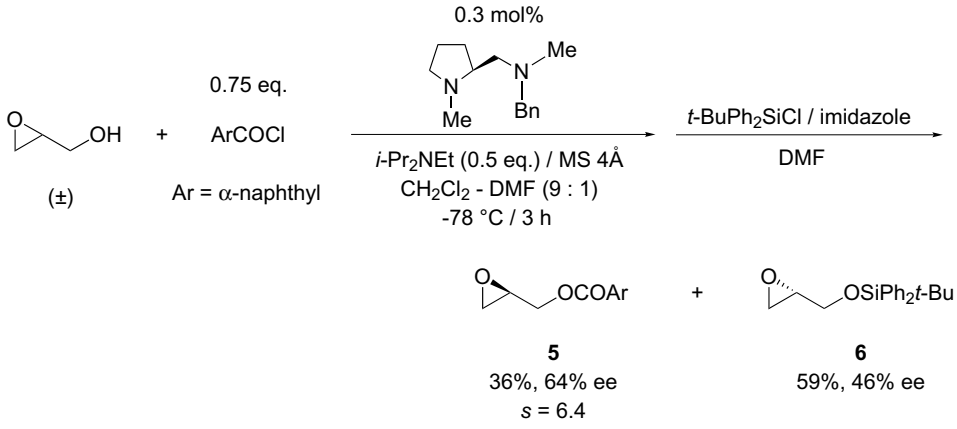
3. Conclusion

In summary, we have demonstrated the kinetic resolution of racemic primary alcohols catalyzed by a chiral 1,2-diamine. To the best of our knowledge, this is the first example of a non-enzymatic catalytic kinetic resolution of racemic primary alcohols attaining high selectivities.

4. Experimental

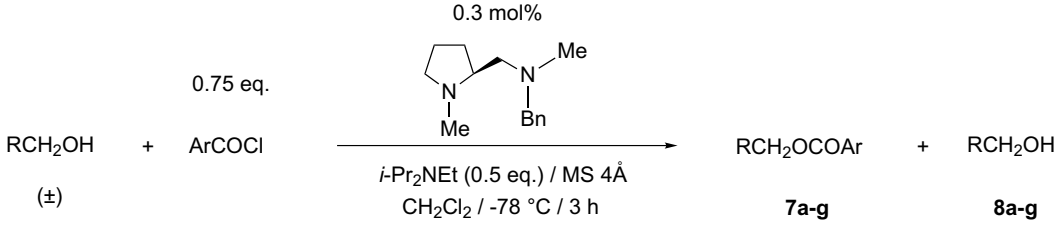
4.1. General

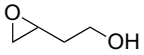
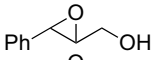
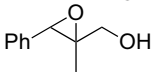
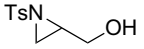
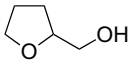
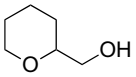
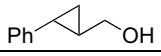
^1H NMR data were collected on a JEOL NMR GSX-400 (399.6 MHz) spectrometer in deuteriochloroform with tetramethylsilane used as an internal standard. The



Scheme 3. Kinetic resolution of glycidol.

Table 3. Kinetic resolution of various racemic primary alcohols



Run	Alcohol	Ar	Ester **7a–g**		Alcohol **8a–g**		*s*
			Yield/%	Ee[a]/%	Yield/%	Ee[a]/%	
1		4-MeC_6H_4	49 (**7a**)	11	42 (**8a**)[b]	12	1.4
2[c]		4-*t*-BuC_6H_4	52 (**7b**)	44	40 (**8b**)	47	4.0
3[c]		Ph	50 (**7c**)	43	45 (**8c**)	48	3.7
4[c]		Ph	42 (**7d**)	32	31 (**8d**)	32[d]	2.4
5		4-MeC_6H_4	48 (**7e**)	50	47 (**8e**)[b]	46	4.6
6		4-MeC_6H_4	50 (**7f**)	41	37 (**8f**)[b]	41	3.5
7[c]		Ph	51 (**7g**)	2	49 (**8g**)	3	1.1

[a] Determined by HPLC analysis with a chiral column.
[b] Unreacted alcohol was isolated as a corresponding *t*-butyldiphenylsilyl ether.
[c] 0.6 equiv of acyl chloride was used.
[d] Determined by HPLC analysis with a chiral column after converted to the corresponding benzoate.

enantiomeric ratios of the esters were determined using HPLC through Daicel Chiralpak AD or Daicel Chiralcel OD column (1.0 mL/min, 254 nm). Optical rotations were measured by JASCO DIP-1000 polarimeter using a sodium lamp (589 nm). CH_2Cl_2 was distilled over CaH_2 after dried up with P_2O_5. DMF was distilled over P_2O_5. MS 4 Å was used as a powder.

4.2. Chiral 1,2-diamine[9]

4.2.1. (*S*)-1-Methyl-2-[(benzylmethylamino)methyl]pyrrolidine. $[\alpha]_D = -83$ (*c* 1.0, EtOH), ^{1}H NMR: δ 1.55 (m, 1H), 1.67–1.74 (m, 2H), 1.98–2.03 (m, 1H), 2.16 (dt, 1H, $J = 8.0$, 9.6 Hz), 2.20 (s, 3H), 2.29–2.35 (m, 2H), 2.38 (s, 3H), 2.51–2.55 (m, 1H), 3.01–3.05 (m, 1H), 3.43 (d, 1H, $J = 13.2$ Hz), 3.56 (d, 1H, $J = 13.2$ Hz), 7.22–7.32 (m, 5H); ^{13}C NMR: δ 22.43 (CH_2), 30.70 (CH_2), 41.35 (CH_3), 43.01 (CH_3), 57.74 (CH_2), 62.56 (CH_2), 63.15 (CH), 63.69 (CH_2), 126.84 (CH), 128.10 (CH), 128.99 (CH), 139.19 (C).

4.3. Typical procedure for the preparation of glycerol derivatives

To a solution of glycerol (9.17 g, 99.6 mmol) and imidazole (40.9 g, 600 mmol) in DMF (120 mL) was added

trimethylsilyl chloride (60 mL, 500 mmol) at 0 °C under argon atmosphere. After being stirred for 5 h at room temperature, it was quenched with satd $NaHCO_3$ aq at 0 °C. The organic materials were extracted with ether and the combined extracts washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude products were purified by distillation under reduced pressure to yield 23.9 g of tris(trimethylsilyl)glycerol (78%).

To a solution of tris(trimethylsilyl)glycerol (2.36 g, 7.64 mmol) and dibenzyl ketone (1.34 g, 6.37 mmol) in dichloromethane (7 mL) was added trimethylsilyl trifluoromethanesulfonate (72.2 mg, 0.32 mmol) in dichloromethane (3 mL) at −78 °C under an argon atmosphere. After being stirred for 2 h at −78 °C and then additionally stirred for 6 h at −20 °C and at room temperature for 14 h, triethylamine (1.2 mL) was added and quenched with 10% aq NaOH. The organic materials were extracted with ether and the combined extracts washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. To a solution of crude products in THF was added TBAF in THF (1 M, 7 mL) and stirred for 30 min. The organic materials were extracted with ether and the combined extracts were washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude products were purified by silica gel column chromatography to yield 1.57 g of (2,2-dibenzyl-[1,3]dioxolan-4-yl)methanol (87%).

(2,2-Dicyclohexyl-[1,3]dioxolan-4-yl)-methanol and (2,2-diphenyl-[1,3]dioxolan-4-yl)methanol were prepared similarly as mentioned above using the corresponding ketones, respectively. Other glycerol derivatives were prepared from glycerol and the corresponding ketones under classical acidic conditions.[14]

4.3.1. (2,2-Di-*n*-propyl-[1,3]dioxolan-4-yl)-methanol 1b. ^{1}H NMR: δ 0.92 (t, 3H, J = 7.3 Hz), 0.92 (t, 3H, J = 7.3 Hz), 1.32–1.45 (m, 4H), 1.56–1.65 (m, 4H), 1.89 (br, 1H), 3.56–3.62 (m, 1H), 3.71–3.78 (m, 2H), 4.03 (dd, 1H, J = 6.6, 8.1 Hz), 4.19–4.25 (m, 1H); ^{13}C NMR: δ 14.41 (CH_3), 17.03 (CH_2), 17.33 (CH_2), 39.19 (CH_2), 39.67 (CH_2), 62.99 (CH_2), 65.97 (CH_2), 76.24 (CH), 112.59 (C).

4.3.2. (2,2-Di-*n*-butyl-[1,3]dioxolan-4-yl)-methanol 1c. ^{1}H NMR: δ 0.91 (t, 6H, J = 6.6 Hz), 1.26–1.39 (m, 8H), 1.58–1.66 (m, 4H), 1.87 (br, 1H), 3.60 (dd, 1H, J = 5.1, 11.7 Hz), 3.72–3.78 (m, 2H), 4.03 (dd, 1H, J = 6.6, 8.1 Hz), 4.20–4.25 (m, 1H); ^{13}C NMR: δ 14.11 (CH_3), 23.02 (CH_2), 25.92 (CH_2), 26.22 (CH_2), 36.61 (CH_2), 37.16 (CH_2), 62.99 (CH_2), 65.90 (CH_2), 76.21 (CH), 112.76 (C).

4.3.3. (2,2-Diisopropyl-[1,3]dioxolan-4-yl)-methanol 1e. ^{1}H NMR: δ 0.92–0.95 (m, 12H), 1.88 (br, 1H), 2.04–2.13 (m, 2H), 3.64 (dd, 1H, J = 7.3, 8.8 Hz), 3.65–3.76 (m, 2H), 4.12 (t, 1H, J = 7.3 Hz), 4.30–4.36 (m, 1H); ^{13}C NMR: δ 17.42 (CH_3), 33.58 (CH), 34.67 (CH), 63.45 (CH_2), 68.40 (CH_2), 78.12 (CH), 116.97 (C).

4.3.4. (2,2-Dicyclohexyl-[1,3]dioxolan-4-yl)-methanol 1f. ^{1}H NMR: δ 1.04–1.23 (m, 10H), 1.64–1.77 (m, 13H), 3.57 (dd, 1H, J = 7.3, 8.8 Hz), 3.65–3.73 (m, 2H), 4.08 (t, 1H, J = 7.3 Hz), 4.26–4.33 (m, 1H); ^{13}C NMR: δ 26.54 (CH_2), 27.25 (CH_2), 43.31 (CH_2), 44.55 (CH), 63.49 (CH_2), 68.38 (CH_2), 78.16 (CH), 116.27 (C).

4.3.5. (2,2-Dibenzyl-[1,3]dioxolan-4-yl)-methanol 1g. ^{1}H NMR: δ 2.94–3.04 (m, 5H), 3.33 (t, 1H, J = 7.3 Hz), 3.40 (dd, 1H, J = 2.6, 12.1 Hz), 3.67 (t, 1H, J = 7.3 Hz), 3.70–3.76 (m, 1H), 7.22–7.32 (m, 10H); ^{13}C NMR: δ 44.08 (CH_2), 45.17 (CH_2), 62.06 (CH_2), 66.04 (CH_2), 76.76 (CH), 111.33 (C), 126.52 (CH), 126.70 (CH), 127.96 (CH), 128.04 (CH), 130.62 (CH), 130.98 (CH), 136.09 (C), 136.41 (C).

4.4. Chiral esters of primary alcohol

4.4.1. (*R*)-4-Benzoyloxymethyl-2,2-dimethyl-1,3-dioxolane 2a. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 9.6 min (−), 10.9 min (+)), 56% ee, $[\alpha]_D$ = +4.0 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 1.39 (s, 3H), 1.46 (s, 3H), 3.88 (dd, 1H, J = 5.9, 8.4 Hz), 4.15 (dd, 1H, J = 6.6, 8.4 Hz), 4.36 (dd, 1H, J = 5.5, 11.4 Hz), 4.41 (dd, 1H, J = 4.8, 11.4 Hz), 4.43–4.57 (m, 1H), 7.43–7.46 (m, 2H), 7.55–7.59 (m, 1H), 8.05–8.07 (m, 2H); ^{13}C NMR: δ 25.42 (CH_3), 26.76 (CH_3), 65.03 (CH_2), 66.41 (CH_2), 73.67 (CH), 109.80 (C), 128.32 (CH), 129.60 (CH), 129.65 (CH), 133.04 (C), 166.20 (C).

4.4.2. 4-Benzoyloxymethyl-2,2-di-*n*-propyl-1,3-dioxolane 2b. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 6.6 min (−), 7.5 min (+)), 60% ee, $[\alpha]_D$ = +11.9 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 0.88 (td, 3H, J = 1.1, 7.3 Hz), 0.93 (td, 3H, J = 1.1, 7.3 Hz), 1.34–1.46 (m, 4H), 1.58–1.66 (m, 4H), 3.82 (td, 1H, J = 1.5, 6.6 Hz), 4.14 (td, 1H, J = 1.5, 6.2 Hz), 4.35–4.47 (m, 3H), 7.43–7.47 (m, 2H), 7.55–7.59 (m, 1H), 8.08 (dt, 2H, J = 1.3, 8.4 Hz); ^{13}C NMR: δ 14.32 (CH_3), 16.96 (CH_2), 17.23 (CH_2), 39.34 (CH_2), 39.75 (CH_2), 64.78 (CH_2), 66.79 (CH_2), 73.85 (CH), 113.13 (C), 128.37 (CH), 129.70 (CH), 129.83 (CH), 133.13 (C), 166.35 (C).

4.4.3. 4-Benzoyloxymethyl-2,2-di-*n*-butyl-1,3-dioxolane 2c. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 6.4 min (−), 7.0 min (+)), 54% ee, $[\alpha]_D$ = +10.7 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 0.84–0.93 (m, 6H), 1.23–1.40 (m, 8H), 1.59–1.68 (m, 4H), 3.84 (dd, 1H, J = 6.2, 8.1 Hz), 4.14 (dd, 1H, J = 6.2, 8.1 Hz), 4.36–4.48 (m, 3H), 7.44 (t, 2H, J = 7.5 Hz), 7.57 (tt, 1H, J = 1.5, 7.3 Hz), 8.06 (dt, 2H, J = 1.5, 8.4 Hz); ^{13}C NMR: δ 14.10 (CH_3), 23.02 (CH_2), 25.86 (CH_2), 26.18 (CH_2), 36.83 (CH_2), 37.27 (CH_2), 64.65 (CH_2), 66.73 (CH_2), 73.81 (CH), 113.18 (C), 128.30 (CH), 129.62 (CH), 129.66 (CH), 133.06 (C), 166.22 (C).

4.4.4. (*R*)-2-Benzoyloxymethyl-1,4-dioxa-spiro[4.5]decane 2d. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 8.5 min (−), 9.8 min (+)), 53% ee, $[\alpha]_D$ = +6.5 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 1.34–1.48 (m, 2H), 1.58–1.68 (m, 8H), 3.88 (dd, 1H, J = 5.9, 8.4 Hz), 4.14 (dd, 1H, J = 6.2, 8.4 Hz), 4.38 (d, 2H, J = 4.8 Hz), 4.41–4.48 (m, 1H), 7.43–7.47 (m, 2H), 7.55–7.59 (m,

1H), 8.06 (dt, 2H, J = 1.5, 8.4 Hz); ^{13}C NMR: δ 23.79 (CH_2), 23.93 (CH_2), 25.07 (CH_2), 34.89 (CH_2), 36.36 (CH_2), 65.11 (CH_2), 66.11 (CH_2), 73.27 (CH), 110.39 (C), 128.41 (CH), 129.68 (CH), 129.84 (CH), 133.10 (C), 166.32 (C).

4.4.5. (*R*)-4-Benzoyloxymethyl-2,2-diisopropyl-1,3-dioxolane 2e. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 6.3 min (−), 7.8 min (+)), 59% ee, $[\alpha]_D$ = +8.9 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 0.93–0.97 (m, 12H), 2.07–2.14 (m, 2H), 3.77 (t, 1H, J = 7.7 Hz), 4.24 (dd, 1H, J = 6.6, 7.7 Hz), 4.39–4.57 (m, 3H), 7.43–7.47 (m, 2H), 7.55–7.59 (m, 1H), 8.04–8.07 (m, 2H); ^{13}C NMR: δ 17.34 (CH_3), 17.42 (CH_3), 33.64 (CH_2), 34.63 (CH_2), 64.90 (CH_2), 69.28 (CH_2), 75.40 (CH), 117.35 (C), 128.37 (CH), 129.72 (CH), 133.13 (C), 166.35 (C).

4.4.6. 4-Benzoyloxymethyl-2,2-dicyclohexyl-1,3-dioxolane 2f. HPLC: Daicel Chiralpak AD (*i*-PrOH/hexane = 1/20, t_R = 8.3 min (−), 11.0 min (+)), 51% ee, $[\alpha]_D$ = +7.5 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 1.04–1.23 (m, 10H), 1.61–1.84 (m, 12H), 3.73 (t, 1H, J = 8.1 Hz), 4.19 (t, 1H, J = 7.1 Hz), 4.44–4.52 (m, 3H), 7.43–7.47 (m, 2H), 7.55–7.60 (m, 1H), 8.04–8.07 (m, 2H); ^{13}C NMR: δ 26.48 (CH_2), 27.14 (CH_2), 43.33 (CH_2), 44.39 (CH), 64.54 (CH_2), 69.03 (CH_2), 75.45 (CH), 116.57 (C), 128.27 (CH), 129.58 (CH), 129.70 (CH), 133.04 (C), 166.25 (C).

4.4.7. 4-Benzoyloxymethyl-2,2-dibenzyl-1,3-dioxolane 2g. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 13.7 min (−), 15.4 min (+)), 23% ee, $[\alpha]_D$ = +1.0 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 2.96 (m, 2H), 2.99 (s, 2H), 3.22–3.27 (m, 1H), 3.67–3.72 (m, 1H), 3.82–3.92 (m, 3H), 7.21–7.30 (m, 10H), 7.41–7.45 (m, 2H), 7.54–7.58 (m, 1H), 7.98–8.00 (m, 2H); ^{13}C NMR: δ 44.79 (CH_2), 44.89 (CH_2), 64.62 (CH_2), 67.53 (CH_2), 74.34 (CH), 112.20 (C), 126.49 (CH), 126.55 (CH), 127.82 (CH), 127.96 (CH), 128.36 (CH), 129.62 (CH), 129.78 (CH), 130.76 (CH), 131.01 (CH), 133.07 (CH), 136.04 (C), 136.37 (C), 166.08 (C).

4.4.8. (*R*)-4-Benzoyloxymethyl-2,2-diphenyl-1,3-dioxolane 2h. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 9.0 min (−), 10.1 min (+)), 54% ee, $[\alpha]_D$ = +16.7 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 4.04 (dd, 1H, J = 6.2, 8.1 Hz), 4.17 (dd, 1H, J = 6.6, 8.4 Hz), 4.47 (d, 2H, J = 4.8 Hz), 4.56 (qui, 1H, J = 6.2 Hz), 7.23–7.42 (m, 8H), 7.49–7.57 (m, 5H), 7.95–7.97 (m, 2H); ^{13}C NMR: δ 64.59 (CH_2), 66.94 (CH_2), 74.32 (CH), 110.30 (C), 126.13 (CH), 127.97 (CH), 128.06 (CH), 128.11 (CH), 128.25 (CH), 129.61 (CH), 133.00 (CH), 141.81 (CH), 166.14 (C).

4.4.9. (*R*)-4-(*o*-Toluoyl)oxymethyl-2,2-diisopropyl-1,3-dioxolane 4b. HPLC: Daicel Chiralpak AD (*i*-PrOH/hexane = 1/1000, t_R = 9.5 min (−), 10.4 min (+)), 61% ee, $[\alpha]_D$ = +6.1 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 0.93–0.96 (m, 12H), 2.04–2.14 (m, 2H), 2.60 (s, 3H), 3.74 (dd, 1H, J = 7.9, 8.6 Hz), 4.24 (dd, 1H, J = 7.0, 7.7 Hz), 4.36 (dd, 1H, J = 5.1, 11.4 Hz), 4.44 (dd, 1H, J = 5.9, 11.4 Hz), 4.49–4.56 (m, 1H), 7.23–7.24 (m, 2H), 7.39–7.43 (m, 1H), 7.90–7.92 (m, 1H); ^{13}C NMR: δ 17.38 (CH_3), 17.49 (CH_3), 21.72 (CH_3), 33.65 (CH), 34.64 (CH), 64.87 (CH_2), 69.49 (CH_2), 75.39 (CH), 117.14 (CH), 125.70 (CH), 130.68 (CH), 131.71 (CH), 132.15 (C), 140.33 (C), 167.27 (C).

4.4.10. (*R*)-4-(*m*-Toluoyl)oxymethyl-2,2-diisopropyl-1,3-dioxolane 4c. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 6.0 min (−), 7.0 min (+)), 51% ee, $[\alpha]_D$ = +8.6 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 0.94–0.97 (m, 12H), 2.05–2.31 (m, 2H), 3.77 (dd, 1H, J = 7.7, 8.4 Hz), 4.24 (dd, 1H, J = 6.6, 7.7 Hz), 4.40 (dd, 1H, J = 5.0, 11.4 Hz), 4.47 (dd, 1H, J = 5.1, 11.4 Hz), 4.50–4.56 (m, 1H), 7.31–7.52 (m, 2H), 7.83–8.06 (m, 2H); ^{13}C NMR: δ 17.36 (CH_3), 17.39 (CH_3), 17.47 (CH_3), 21.23 (CH_3), 33.68 (CH), 34.66 (CH), 64.83 (CH_2), 69.30 (CH_2), 75.44 (CH), 117.32 (CH), 126.87 (CH), 128.26 (CH), 130.25 (CH), 133.89 (C), 138.18 (C), 166.56 (C).

4.4.11. (*R*)-4-(*p*-Toluoyl)oxymethyl-2,2-diisopropyl-1,3-dioxolane 4d. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 5.3 min (−), 9.4 min (+)), 68% ee, $[\alpha]_D$ = +10.4 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 0.90–0.99 (m, 12H), 2.07–2.14 (m, 2H), 2.41 (s, 3H), 3.76 (t, 1H, J = 8.2 Hz), 4.23 (dd, 1H, J = 6.8, 7.5 Hz), 4.37–4.49 (m, 1H), 4.50–4.55 (m, 1H), 7.24 (d, 2H, J = 8.1 Hz), 7.94 (dt, 2H, J = 1.8, 8.4 Hz); ^{13}C NMR: δ 17.36 (CH_3), 17.39 (CH_3), 17.47 (CH_3), 18.51 (CH_3), 21.68 (CH_3), 33.68 (CH), 34.66 (CH), 64.71 (CH_2), 69.33 (CH_2), 75.47 (CH), 117.30 (CH), 127.03 (CH), 129.10 (CH), 129.19 (CH), 129.76 (C), 143.87 (C), 166.45 (C).

4.4.12. (*R*)-4-(*p*-*t*-Butylbenzoyl)oxymethyl-2,2-diisopropyl-1,3-dioxolane 4e. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 5.4 min (−), 7.1 min (+)), 57% ee, $[\alpha]_D$ = +7.7 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 0.94–0.96 (m, 12H), 1.34 (s, 9H), 2.05–2.16 (m, 2H), 3.76 (t, 1H, J = 8.1 Hz), 4.23 (t, 1H, J = 7.1 Hz), 4.39 (dd, 1H, J = 4.8, 11.4 Hz), 4.67 (dd, 1H, J = 5.1, 11.4 Hz), 4.50–4.55 (m, 1H), 7.46 (dt, 2H, J = 1.8, 8.8 Hz), 7.98 (dt, 2H, J = 1.8, 8.8 Hz); ^{13}C NMR: δ 17.36 (CH_3), 17.41 (CH_3), 17.49 (CH_3), 31.10 (CH_3), 33.68 (CH), 34.64 (CH), 35.10 (C), 64.73 (CH_2), 69.35 (CH_2), 75.47 (CH), 117.30 (CH), 125.37 (C), 126.96 (CH), 129.61 (CH), 156.85 (C), 166.38 (C).

4.4.13. (*R*)-4-(*p*-Methoxybenzoyl)oxymethyl-2,2-diisopropyl-1,3-dioxolane 4f. HPLC: Daicel Chiralpak AD (*i*-PrOH/hexane = 1/50, t_R = 8.0 min (+), 8.7 min (−)), 70% ee, $[\alpha]_D$ = +9.6 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 0.88–0.96 (m, 12H), 2.06–2.14 (m, 2H), 3.76 (dd, 1H, J = 7.9, 8.6 Hz), 3.87 (s, 3H), 4.23 (t, 1H, J = 7.3 Hz), 4.38 (dd, 1H, J = 4.9, 11.5 Hz), 4.44 (dd, 1H, J = 5.3, 11.5 Hz), 4.48–4.55 (m, 1H), 6.90–6.94 (m, 2H), 7.98–8.02 (m, 2H); ^{13}C NMR: δ 17.44 (CH_3), 17.53 (CH_3), 33.69 (CH), 33.72 (CH), 34.66 (CH), 34.69 (CH), 65.44 (CH_2), 69.60 (CH_2), 75.49 (CH), 113.56 (CH), 117.20 (CH), 122.09 (CH), 131.71 (C), 163.38 (C), 165.95 (C).

4.4.14. (*R*)-4-(*p*-Chlorobenzoyl)oxymethyl-2,2-diisopropyl-1,3-dioxolane 4g. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 4.8 min (−), 7.4 min (+)), 51% ee, $[\alpha]_D$ = +5.4 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 0.93–

0.96 (m, 12H), 2.06–2.14 (m, 2H), 3.75 (t, 1H, $J = 8.2$ Hz), 4.23 (t, 1H, $J = 7.3$ Hz), 4.41 (dd, 1H, $J = 4.8$, 11.4 Hz), 4.47 (dd, 1H, $J = 6.2$, 11.4 Hz), 4.50–4.55 (m, 1H), 7.40–7.44 (m, 2H), 7.97–8.00 (m, 2H); ^{13}C NMR: δ 17.34 (CH_3), 17.38 (CH_3), 17.46 (CH_3), 17.49 (CH_3), 33.65 (CH), 33.64 (CH), 65.09 (CH_2), 69.14 (CH_2), 75.36 (CH), 117.45 (CH), 128.23 (CH), 128.75 (CH), 131.11 (C), 139.65 (C), 165.51 (C).

4.4.15. (*R*)-4-α-Naphthoyloxymethyl-2,2-diisopropyl-1,3-dioxolane 4h. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 12.0 min (−), 13.2 min (+)), 81% ee, $[\alpha]_D$ = +5.9 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 0.93–0.98 (m, 12H), 2.09–2.17 (m, 2H), 3.79 (t, 1H, $J = 8.1$ Hz), 4.27 (t, 1H, $J = 7.1$ Hz), 4.48 (dd, 1H, $J = 4.6$, 11.2 Hz), 4.53–4.63 (m, 2H), 7.47–7.55 (m, 2H), 7.88 (d, 1H, $J = 7.7$ Hz), 8.02 (d, 1H, $J = 8.1$ Hz), 8.19 (dd, 1H, $J = 1.5$, 7.3 Hz), 8.91 (d, 1H, $J = 8.8$ Hz); ^{13}C NMR: δ 17.47 (CH_3), 17.58 (CH_3), 33.71 (CH), 33.74 (CH), 65.15 (CH_2), 69.42 (CH_2), 75.43 (CH), 117.44 (CH), 124.37 (CH), 125.72 (C), 126.19 (CH), 126.64 (CH), 127.79 (CH), 128.51 (CH), 130.31 (CH), 131.30 (C), 133.55 (C), 133.75 (C), 167.12 (C). Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.26; H, 7.66.

4.4.16. (*R*)-4-β-Naphthoyloxymethyl-2,2-diisopropyl-1,3-dioxolane 4i. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 40.1 min (−), 71.0 min (+)), 78% ee, $[\alpha]_D$ = +10.3 (*c* 1.2, $CHCl_3$), ^{1}H NMR: δ 0.96–0.98 (m, 12H), 2.09–2.18 (m, 2H), 3.82 (t, 1H, $J = 8.1$ Hz), 4.27 (t, 1H, $J = 7.1$ Hz), 4.48 (dd, 1H, $J = 4.8$, 11.4 Hz), 4.52–4.61 (m, 2H), 7.52–7.62 (m, 2H), 7.88 (d, 1H, $J = 8.4$ Hz), 7.95 (d, 1H, $J = 8.1$ Hz), 8.06 (dd, 1H, $J = 1.5$, 8.4 Hz), 8.62 (s, 1H); ^{13}C NMR: δ 17.47 (CH_3), 17.57 (CH_3), 33.72 (CH), 33.77 (CH), 34.69 (CH), 34.74 (CH), 64.97 (CH_2), 69.28 (CH_2), 75.48 (CH), 117.31 (CH), 125.13 (CH), 126.62 (CH), 126.90 (CH), 127.71 (CH), 128.28 (CH), 129.33 (CH), 131.20 (C), 132.36 (C), 135.51 (C), 166.41 (C).

4.4.17. (*R*)-α-Naphthoyloxymethyloxirane 5. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 12.8 min (*S*), 14.3 min (*R*)), 64% ee, $[\alpha]_D$ = −18.7 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 2.77 (dd, 1H, $J = 2.7$, 4.9 Hz), 2.92 (d, 1H, $J = 4.4$ Hz), 3.38–3.42 (m, 1H), 4.27 (dd, 1H, $J = 6.0$, 12.3 Hz), 4.74 (dd, 1H, $J = 3.1$, 12.3 Hz), 7.48–7.55 (m, 2H), 7.62 (td, 1H, $J = 1.5$, 7.0 Hz), 7.88 (d, 1H, $J = 8.1$ Hz), 8.03 (d, 1H, $J = 8.1$ Hz), 8.24 (dd, 1H, $J = 1.1$, 7.0 Hz), 8.92 (dd, 1H, $J = 0.7$, 8.8 Hz); ^{13}C NMR: δ 44.82 (CH_2), 49.51 (CH), 65.52 (CH_2), 124.42 (CH), 125.64 (CH), 126.19 (CH), 126.32 (CH), 127.84 (CH), 128.54 (CH), 130.55 (CH), 131.30 (C), 133.59 (CH), 133.69 (CH), 166.92 (C).

4.4.18. *p*-Toluoyloxyethyloxirane 7a. HPLC: Daicel Chiralpak AD (*i*-PrOH/hexane = 1/100, t_R = 18.7 min (−), 20.8 min (+)), 11% ee, $[\alpha]_D$ = −6.6 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 1.91–2.09 (m, 2H), 2.40 (s, 3H), 2.56 (dd, 1H, $J = 2.6$, 4.8 Hz), 2.81 (t, 1H, $J = 4.4$ Hz), 3.08–3.13 (m, 1H), 4.45–4.48 (m, 2H), 7.22–7.24 (m, 2H), 7.91–7.94 (m, 2H); ^{13}C NMR: δ 21.65 (CH_3), 32.06 (CH_2), 46.87 (CH), 49.65 (CH_2), 61.61 (CH_2), 127.21 (C), 128.98 (CH), 129.45 (CH), 143.56 (C), 166.33 (C).

4.4.19. (*S*)-2-(4-*t*-Butylbenzoyloxymethyl)-3-phenyloxirane 7b. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/10, t_R = 6.3 min (+), 23.9 min (−)), 44% ee, $[\alpha]_D$ = −13.7 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 1.33 (s, 9H), 3.37 (ddd, 1H, $J = 2.2$, 3.3, 5.5 Hz), 3.87 (d, 1H, $J = 1.8$ Hz), 4.33 (dd, 1H, $J = 5.9$, 12.5 Hz), 4.71 (dd, 1H, $J = 3.3$, 12.5 Hz), 7.26–7.35 (m, 5H), 7.45 (dt, 2H, $J = 2.2$, 8.8 Hz), 8.01 (dt, 2H, $J = 2.2$, 8.8 Hz); ^{13}C NMR: δ 31.05 (CH_3), 35.04 (C), 56.37 (CH), 59.43 (CH), 64.33 (CH_2), 125.24 (CH), 125.56 (CH), 126.69 (C), 128.28 (CH), 128.37 (CH), 129.50 (CH), 136.14 (C), 156.72 (C), 166.00 (C).

4.4.20. (*S*)-2-Benzoyloxymethyl-2-methyl-3-phenyloxirane 7c. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 10.9 min (+), 11.6 min (−)), 43% ee, $[\alpha]_D$ = −11.8 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 1.20 (s, 3H), 4.15 (s, 1H), 4.37 (d, 1H, $J = 11.7$ Hz), 4.59 (d, 1H, $J = 11.7$ Hz), 7.29–7.38 (m, 5H), 7.43–7.47 (m, 2H), 7.55–7.59 (m, 1H), 8.08–8.11 (m, 2H); ^{13}C NMR: δ 13.87 (CH_3), 61.24 (C), 61.66 (C), 68.34 (CH_2), 126.40 (CH), 127.68 (CH), 128.08 (CH), 128.36 (CH), 129.60 (CH), 129.68 (C), 133.10 (CH), 134.99 (C), 166.01 (C).

4.4.21. (*S*)-2-Benzoyloxymethyl-1-tosylaziridine 7d. HPLC: Daicel Chiralpak AD (*i*-PrOH/hexane = 1/10, t_R = 19.7 min (+), 21.5 min (−)), 32% ee, $[\alpha]_D$ = −8.2 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 2.32 (s, 1H), 2.33 (s, 3H), 2.84 (d, 1H, $J = 6.6$ Hz), 3.11–3.17 (m, 1H), 4.00 (dd, 1H, $J = 7.3$, 12.1 Hz), 4.52 (dd, 1H, $J = 4.0$, 12.1 Hz), 7.22 (d, 2H, $J = 8.1$ Hz), 7.37–7.41 (m, 2H), 7.55–7.58 (m, 1H), 7.80–7.81 (m, 2H), 7.82–7.84 (m, 2H); ^{13}C NMR: δ 21.61 (CH_3), 30.56 (CH_2), 37.75 (CH), 64.02 (CH_2), 127.90 (CH), 127.95 (CH), 128.17 (CH), 129.22 (CH), 129.60 (C), 133.07 (CH), 134.53 (C), 144.55 (C), 165.70 (C).

4.4.22. 2-(*p*-Toluoyloxymethyl)tetrahydrofuran 7e. HPLC: Daicel Chiralpak AD (*i*-PrOH/hexane = 1/100, t_R = 25.5 min (−), 30.7 min (+)), 50% ee, $[\alpha]_D$ = −13.3 (*c* 1.2, $CHCl_3$), ^{1}H NMR: δ 1.68–1.77 (m, 2H), 1.87–2.01 (m, 2H), 2.03–2.11 (m, 1H), 2.41 (s, 3H), 3.81–3.86 (m, 1H), 3.91–3.96 (m, 1H), 4.24–4.30 (m, 2H), 4.34–4.40 (m, 1H), 7.23 (d, 2H, $J = 8.1$ Hz), 7.95 (dt, 2H, $J = 1.8$, 8.1 Hz); ^{13}C NMR: δ 21.63 (CH_3), 25.74 (CH_2), 28.10 (CH_2), 66.75 (CH_2), 68.53 (CH_2), 129.02 (CH), 129.70 (CH), 143.63 (C), 166.62 (C).

4.4.23. 2-(*p*-Toluoyloxymethyl)tetrahydropyran 7f. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 10.7 min (+), 12.4 min (−)), 41% ee, $[\alpha]_D$ = −1.3 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 1.37–1.68 (m, 5H), 1.88–1.91 (m, 1H), 2.40 (s, 3H), 3.47 (dt, 1H, $J = 2.6$, 11.4 Hz), 3.64–3.70 (m, 1H), 4.01–4.05 (m, 1H), 4.26 (dd, 1H, $J = 5.8$, 11.4 Hz), 4.29 (dd, 1H, $J = 4.4$, 11.4 Hz), 7.23 (d, 2H, $J = 8.4$ Hz), 7.95 (dt, 2H, $J = 2.2$, 4.4 Hz); ^{13}C NMR: δ 21.71 (CH_3), 23.07 (CH_2), 25.86 (CH_2), 28.12 (CH_2), 67.68 (CH_2), 68.43 (CH_2), 75.57 (CH), 127.31 (C), 128.91 (CH), 129.67 (CH), 143.47 (C), 166.52 (C).

4.4.24. (2*S*,3*S*)-1-Benzoyloxymethyl-2-phenylcyclopropane 7g. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 6.2 min (+), 12.4 min (−)), 2% ee, $[\alpha]_D$ = +2.0 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 1.06 (t, 2H, *J* = 7.0 Hz), 1.58–1.65 (m, 2H), 1.97–2.01 (m, 1H), 4.28–4.37 (m, 2H), 7.08–7.11 (m, 2H), 7.14–7.18 (m, 1H), 7.24–7.28 (m, 2H), 7.42–7.45 (m, 2H), 7.53–7.57 (m, 1H), 8.04–8.07 (m, 2H); ^{13}C NMR: δ 13.95 (CH_2), 21.56 (CH), 21.88 (CH), 68.42 (CH_2), 125.75 (CH), 125.99 (CH), 128.28 (CH), 129.49 (CH), 129.62 (CH), 130.30 (C), 132.82 (CH), 141.89 (C), 166.58 (C).

4.5. Chiral primary alcohols

4.5.1. (*R*)-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-methanol 3a. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 9.6 min (−), 11.0 min (+)), 69% ee (measured after converted to benzoate), $[\alpha]_D$ = −6.6 (*c* 1.32, MeOH) {lit.[13] (*S*)-configuration; $[\alpha]_D$ = +6.7 (*c* 0.0025, hexane)}.

4.5.2. (2,2-Di-*n*-propyl-[1,3]dioxolan-4-yl)-methanol 3b. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 6.5 min (−), 7.4 min (+)), 64% ee (measured after converted to benzoate), $[\alpha]_D$ = −3.3 (*c* 1.01, $CHCl_3$).

4.5.3. (2,2-Di-*n*-butyl-[1,3]dioxolan-4-yl)-methanol 3c. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 6.5 min (−), 7.1 min (+)), 71% ee (measured after converted to benzoate), $[\alpha]_D$ = −3.2 (*c* 0.99, $CHCl_3$).

4.5.4. (*R*)-(1,4-Dioxa-spiro[4.5]dec-2-yl)-methanol 3d. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 8.6 min (−), 9.8 min (+)), 65% ee (measured after converted to benzoate), $[\alpha]_D$ = −3.8 (*c* 0.09, MeOH) {lit.[13] (*S*)-configuration $[\alpha]_D$ = +6.8 (*c* 0.0118, MeOH)}.

4.5.5. (*R*)-(2,2-Diisopropyl-[1,3]dioxolan-4-yl)-methanol 3e. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 6.1 min (−), 7.3 min (+)), 75% ee (measured after converted to benzoate), $[\alpha]_D$ = −13.7 (*c* 1.02, $CHCl_3$) {lit.[15] (*S*)-configuration $[\alpha]_D$ = +0.4 (*c* 1.5, MeOH)}.

4.5.6. (2,2-Dicyclohexyl-[1,3]dioxolan-4-yl)-methanol 3f. HPLC: Daicel Chiralpak AD (*i*-PrOH/hexane = 1/20, t_R = 8.0 min (−), 11.2 min (+)), 82% ee (measured after converted to benzoate), $[\alpha]_D$ = −5.9 (*c* 1.05, $CHCl_3$).

4.5.7. (2,2-Dibenzyl-[1,3]dioxolan-4-yl)-methanol 3g. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 14.2 min (−), 15.9 min (+)), 29% ee, $[\alpha]_D$ = −2.4 (*c* 1.03, $CHCl_3$).

4.5.8. (*R*)-(2,2-Diphenyl-[1,3]dioxolan-4-yl)-methanol 3h. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 14.8 min (−), 16.1 min (+)), 62% ee, $[\alpha]_D$ = −24.5 (*c* 0.95, $CHCl_3$) {lit.[13] (*S*)-configuration $[\alpha]_D$ = +22.5 (*c* 0.0036, MeOH)}.

4.5.9. (*R*)-*trans*-3-Phenylglycidol 8b. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 21.4 min (−), 24.3 min (+)), 47% ee, $[\alpha]_D$ = +24.1 (*c* 1.8, $CHCl_3$) {lit.[16] (*R*)-configuration $[\alpha]_D$ = +45.9 (*c* 1.5, EtOH)}.

4.5.10. (*R*)-*trans*-2-Methyl-3-phenylglycidol 8c. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 10.2 min (−), 13.5 min (+)), 48% ee, $[\alpha]_D$ = +9.1 (*c* 1.8, $CHCl_3$) {lit.[16] (*S*)-configuration $[\alpha]_D$ = −16.9 (*c* 2.0, $CHCl_3$)}.

4.5.11. (*S*)-1-Tosylaziridine-2-methanol 8d. HPLC: Daicel Chiralpak AD (*i*-PrOH/hexane = 1/10, t_R = 20.9 min (+), 22.8 min (−)), 32% ee, $[\alpha]_D$ = −10.9 (*c* 1.0, $CHCl_3$) {lit.[17] (*R*)-configuration $[\alpha]_D$ = +29.9 (*c* 9.9, EtOAc)}.

4.5.12. (2*R*,3*R*)-2-Phenylcyclopropane-1-methanol 8g. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/20, t_R = 13.1 min (+), 19.0 min (−)), 3% ee, $[\alpha]_D$ = −2.2 (*c* 2.1, EtOH) {lit.[18] (2*R*,3*R*)-configuration $[\alpha]_D$ = +92.0 (*c* 1.23, EtOH)}.

4.6. Chiral silyl ethers of primary alcohol

4.6.1. (*S*)-*t*-Butyldiphenylsilyloxymethyloxirane 6. HPLC: Daicel Chiralpak AD (*i*-PrOH/hexane = 1/1000, t_R = 6.2 min (−), 7.8 min (+)), 46% ee, $[\alpha]_D$ = −1.4 (*c* 1.0, $CHCl_3$) {lit.[16] (*S*)-configuration $[\alpha]_D$ = −2.3 (*c* 9.07, $CHCl_3$)}.

4.6.2. *t*-Butyldiphenylsilyloxyethyloxirane 8a. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/100, t_R = 5.1 min (+), 6.2 min (−)), 12% ee, $[\alpha]_D$ = +1.6 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 1.06 (s, 9H), 1.77 (q, 2H, *J* = 5.9 Hz), 2.51 (dd, 1H, *J* = 2.6, 5.1 Hz), 2.78 (t, 1H, *J* = 4.8 Hz), 3.08–3.12 (m, 1H), 3.79 (dd, 1H, *J* = 5.9, 10.6 Hz), 3.85 (dd, 1H, *J* = 6.2, 10.3 Hz), 7.36–7.44 (m, 6H), 7.66–7.67 (m, 4H); ^{13}C NMR: δ 19.23 (C), 26.85 (CH_3), 35.72 (CH_2), 47.28 (CH), 50.13 (CH_2), 60.89 (CH_2), 127.59 (CH), 129.57 (CH), 133.51 (C), 133.57 (C), 135.43 (CH), 135.45 (CH).

4.6.3. 2-(*t*-Butyldiphenylsilyloxymethyl)tetrahydrofuran 8e. HPLC: Daicel Chiralpak AD (*i*-PrOH/hexane = 1/1000, t_R = 6.2 min (+), 7.3 min (−)), 46% ee, $[\alpha]_D$ = +2.6 (*c* 1.4, $CHCl_3$), ^{1}H NMR: δ 1.06 (s, 9H), 1.74–1.98 (m, 4H), 3.62 (dd, 1H, *J* = 4.9, 10.4 Hz), 3.67 (dd, 1H, *J* = 4.9, 10.4 Hz), 3.75–3.80 (m, 1H), 3.82–3.87 (m, 1H), 4.01–4.07 (m, 1H), 7.35–7.42 (m, 6H), 7.67–7.70 (m, 4H); ^{13}C NMR: δ 19.24 (C), 25.82 (CH_2), 26.83 (CH_3), 27.86 (CH_2), 66.42 (CH_2), 68.43 (CH_2), 79.29 (CH), 127.61 (CH), 129.56 (CH), 133.70 (C), 135.63 (CH).

4.6.4. 2-(*t*-Butyldiphenylsilyloxymethyl)tetrahydropyran 8f. HPLC: Daicel Chiralcel OD (*i*-PrOH/hexane = 1/1000, t_R = 7.6 min (+), 9.5 min (−)), 41% ee, $[\alpha]_D$ = −3.0 (*c* 1.0, $CHCl_3$), ^{1}H NMR: δ 1.05 (s, 9H), 1.21–1.32 (m, 1H), 1.41–1.62 (m, 3H), 1.71 (d, 1H, *J* = 12.8 Hz), 1.84 (d, 1H, *J* = 11.7 Hz), 3.38–3.44 (m, 2H), 3.52 (dd, 1H, *J* = 5.9, 10.3 Hz), 3.71 (dd, 1H, *J* = 5.5, 10.3 Hz), 3.94–3.97 (m, 1H), 7.35–7.43 (m, 6H), 7.66–7.68 (m, 4H); ^{13}C NMR: δ 19.35 (C), 23.19

(CH_2), 26.25 (CH_2), 26.92 (CH_3), 28.65 (CH_2), 67.42 (CH_2), 68.34 (CH_2), 78.16 (CH), 127.50 (CH), 129.46 (CH), 133.65 (C), 133.69 (C), 135.54 (CH).

4.7. Typical procedure of the kinetic resolution of racemic primary alcohol

To molecular sieves 4 Å (40 mg) were added a solution of (*S*)-1-methyl-2-[(benzylmethylamino)methyl]pyrrolidine (0.2 mg, 0.92 μmol) in CH_2Cl_2 (0.2 mL), a solution of diisopropylethylamine (19.7 mg, 0.152 mmol) in CH_2Cl_2 (0.5 mL), a solution of (2,2-diisopropyl-[1,3]-dioxolane-4-yl)-methanol (57.2 mg, 0.304 mmol) in CH_2Cl_2 (0.8 mL) and a solution of α-naphthoyl chloride (43.4 mg, 0.228 mmol) in CH_2Cl_2 (0.3 mL) and DMF (0.2 mL) sequentially at −78 °C under an argon atmosphere. The reaction was quenched after 3 h at −78 °C by the addition of a phosphate buffer (pH 7). The organic materials were extracted with ether and the combined extracts were washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude products were purified by TLC to yield 37.7 mg of 4-α-naphthoyloxymethyl-2,2-diisopropyl-1,3-dioxolane {38%, 81% ee, $[\alpha]_D = +5.2$ (*c* 1.0, $CHCl_3$)} and 28.5 mg of (2,2-diisopropyl-[1,3]-dioxolane-4-yl)-methanol {50%, 48% ee, $[\alpha]_D = -10.3$ (*c* 0.9, MeOH)}.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (A) 'Exploitation of Multi-Element Cyclic Molecules' from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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