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TETRAHEDRON: *ASYMMETRY*

Syntheses of new C_2-symmetric, optically active 1,2-diols bearing tertiary alkyl groups

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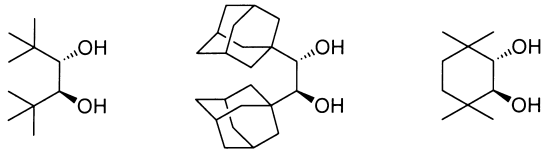
Abstract

New C_2-symmetric chiral 1,2-diols, 1,2-bis(1-adamantyl)-1,2-ethanediol and 3,3,6,6-tetramethyl-1,2-cyclohexanediol, were synthesized by the use of a new resolution method.

1. Introduction

Optically active 1,2-diols play important roles as chiral auxiliaries and ligands in asymmetric syntheses,[1] and a number of diols of this class have been reported so far.[2] Among them, the 1,2-diols bearing tertiary alkyl groups at the stereogenic centers have been rarely described, despite the potentially high utility.[3] Previously the enantiomerically pure 2,2,5,5-tetramethyl-3,4-hexanediol **1** was prepared, and we demonstrated that it exhibited high enantioselectivity in catalytic asymmetric oxidations of sulfides.[4] We considered that this selectivity might be due to a steric contrast between the *tert*-butyl group and the hydrogen atom at the stereogenic center. This consideration has led us to explore 1,2-bis-(1-adamantyl)-1,2-ethanediol **2** and 3,3,6,6-tetramethyl-1,2-cyclohexanediol **3**, which might create more effective asymmetric environments owing to the bulkier alkyl groups or more rigid structure. In this paper we report the syntheses of these compounds together with a new resolution method.



1 **2** **3**

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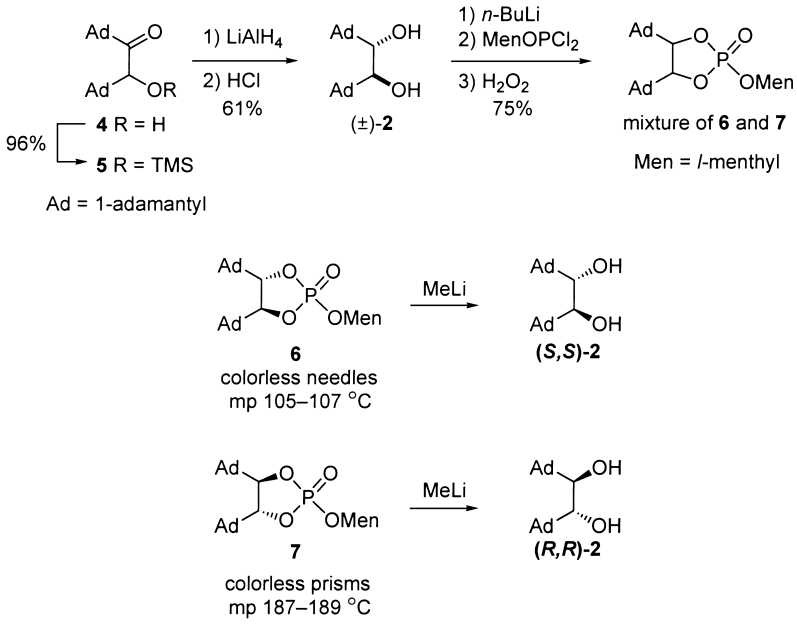
2. Results and discussion

2.1. Synthesis of optically active 1,2-bis(1-adamantyl)-1,2-ethanediol

Optically active 1,2-bis(1-adamantyl)-1,2-ethanediol **2** was synthesized according to the reaction sequences shown in Scheme 1. The protection of acyloin **4**[5] as the trimethylsilyl ether, followed by the reduction of the carbonyl group with $LiAlH_4$, produced the key intermediate (±)-**2** in good yield and with high stereoselectivity.[6] The racemic diol **2** was transformed into the cyclic phosphates possessing a *l*-menthyl group.[4,7] The resulting diastereomer mixture was separated by recycling preparative HPLC to give colorless needles (mp 105–107°C) and colorless prisms (mp 187–189°C), respectively. In order to determine the absolute configurations of these diastereomers, the molecular structure of the latter crystal was analyzed by X-ray crystallography. The ORTEP drawing is shown in Fig. 1, which apparently indicates that the compound possesses the (*R,R*) configuration. This diastereomer **7** was treated with MeLi to give (−)-**2**. In a similar manner, (+)-**2** was also prepared from the other diastereomer **6**.[8]



Scheme 1.

2.2. Synthesis of enantiomerically pure 3,3,6,6-tetramethyl-1,2-cyclohexanediol

Synthesis of *cis*- and *trans*-3,3,6,6-tetramethyl-1,2-cyclohexanediol **3** was reported by Applequist and co-workers,[9] but their synthetic route gave the *cis*-diol as a major product. Therefore, we devised an alternative route to diol **3** (Scheme 2). The dimethylester **9**[10] was subjected to intramolecular acyloin condensation by sodium metal,[11] followed by reduction with sodium metal in the presence of 2-propanol,[12] to give *trans*-diol **3** in 52% yield.[13] It should be noted that these reaction sequences were carried out in one pot, and that only trace amounts of undesired *cis*-diol were produced.

The observed high stereoselectivity can be explained by considering the stable conformation of the intermediate **A** (Fig. 2). The two oxygen atoms occupy the equatorial positions to avoid the 1,3-diaxial

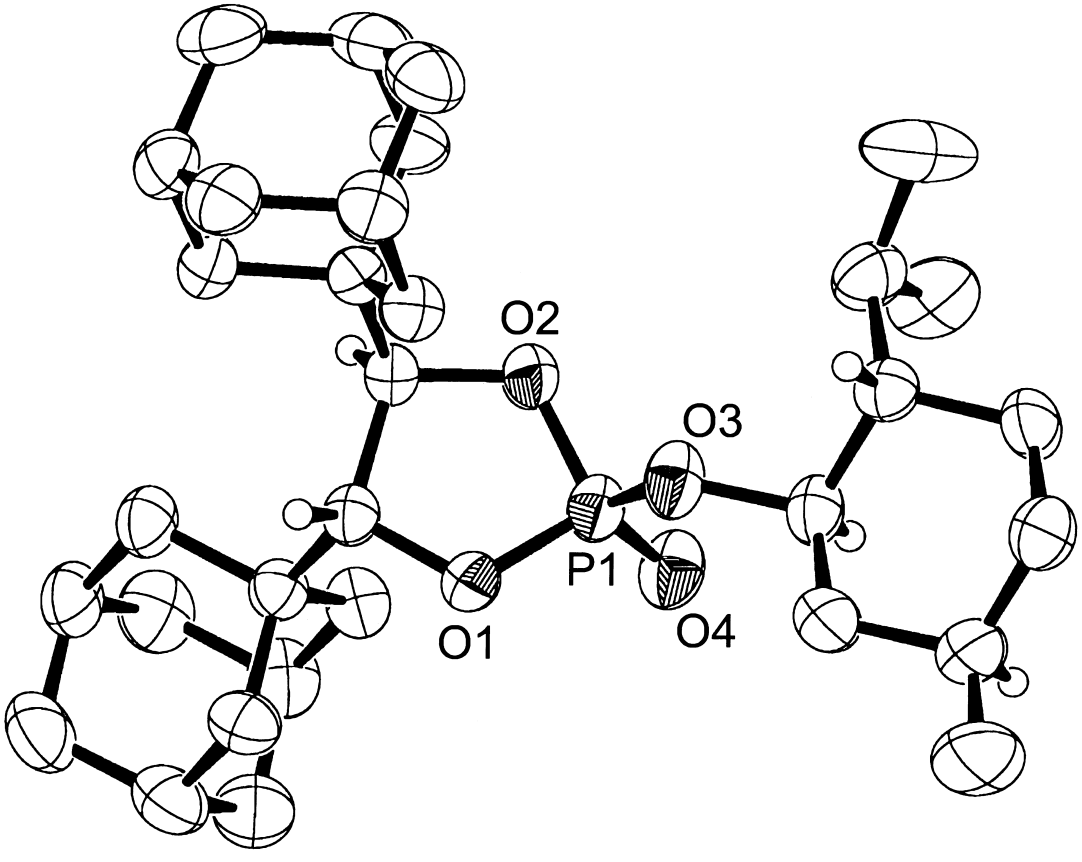
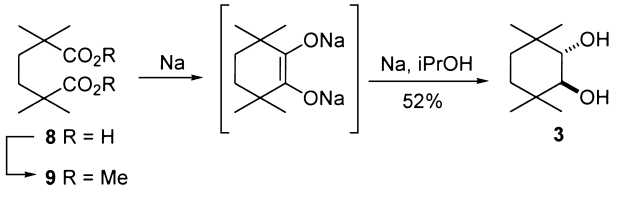


Figure 1. ORTEP drawing of compound **7**



Scheme 2.

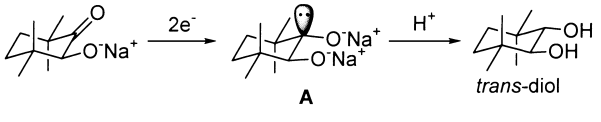
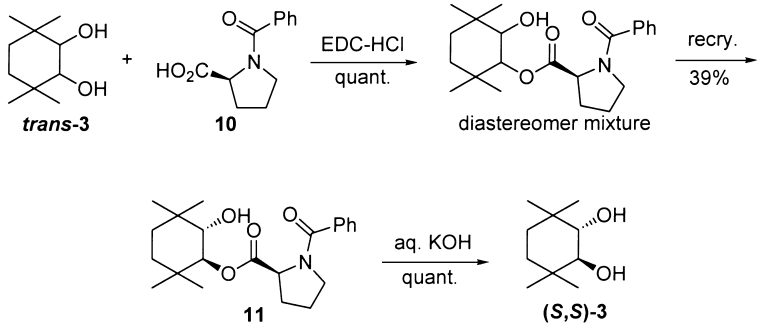


Figure 2.

interactions. The lone pair at the axial position as well as the oxygen anions abstracts protons to form the *trans*-diol.[14,15]

The resolution of (±)-*trans*-diol **3** was attempted by the methods used for the diol **1** or **2**,[4] but the desired products were not obtained. After the various attempts at resolution, we found that efficient resolution was achieved by converting *trans*-diol **3** into the amino acid ester (Scheme 3). Thus, (±)-*trans*-diol **3** and *N*-benzoyl *l*-proline **10** were treated with 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) to give a mixture of two diastereomeric amino acid esters in quantitative yield.[16] Diastereomerically pure **11** was isolated by recrystallization of the mixture from cyclohexane:EtOAc

(5:1). Enantiomerically pure (+)-**3** was furnished by the subsequent hydrolysis of this diastereomer in 39% yield from (±)-*trans*-diol **3**. Unfortunately, the other diastereomer was not obtained as a good crystalline solid.



Scheme 3.

The absolute configuration of diol (+)-**3** was unequivocally determined as (*S*,*S*) on the basis of X-ray structural analysis of amino acid ester **11** (Fig. 3). The ORTEP drawing apparently indicates the existence of the hydrogen bond between O(1) and O(4). We consider that this hydrogen bond may serve for the formation of the rigid structure, which may be one of the factors of easy crystallization.

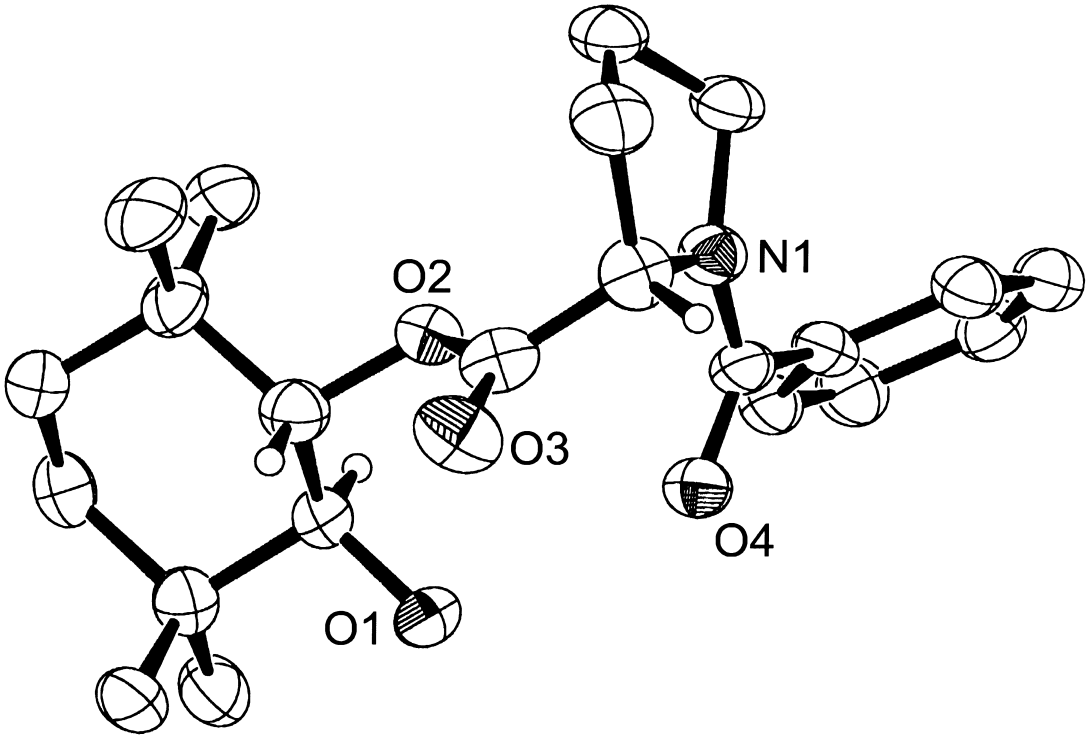
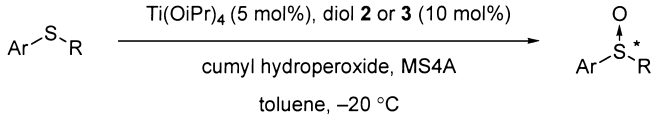


Figure 3. ORTEP drawing of compound **11**. Distance of O(1)–O(4): 2.841(5) Å

2.3. Catalytic asymmetric oxidation of sulfides

To test the catalytic efficiency of diols **2** and **3**, the asymmetric oxidation of sulfides using Ti(IV)–diol complex was examined (Scheme 4).[4,17] Under the same conditions as the reaction using diol **1**, the reactions proceeded sluggishly to produce the corresponding sulfoxides with quite low enantioselectivities (Table 1). These low selectivities may be attributed to the formation of the non-effective Ti(IV)–diol complexes.



Scheme 4.

Table 1
Catalytic asymmetric oxidation of sulfides

entry	Ar	R	diol	time (h)	sulfoxide	
					yield (%)[a]	ee (%)
1	*p*-tolyl	Me	**2**	42	68	7[b,c]
2	*p*-tolyl	Me	**3**	84	36	0
3	Ph	$PhCH_2$	**2**	66	76	14[d]
4	Ph	$PhCH_2$	**3**	96	65	0

[a]Isolated yield. [b]Determined by HPLC analysis using Daicel CHIRALCEL OD-H column (9:1 hexanen2-propanol). [c]The reaction using diol **1** afforded the corresponding sulfoxide in 42% yield, 95% ee. [d]Daicel CHIRALCEL OJ column (5:1 hexane:2-propanol).

3. Conclusion

We have synthesized two new optically active 1,2-diols, and developed a new method for their resolution via amino acid esters. Further studies directed towards application of these diols in various asymmetric reactions are under way.

4. Experimental

4.1. General procedure

All melting points were measured on Yamato micro melting point apparatus and were uncorrected. Optical rotations were measured with JASCO DIP-370 polarimeter. IR spectra were performed with a Hitachi IR 215 spectrophotometer. NMR spectra were measured with JEOL JMN-LA-400 (400 MHz) spectrometer in $CDCl_3$. Chemical shifts were reported by δ ppm. HRMS (FAB) spectra were measured with JEOL HX-110 spectrometer in Chemical Analysis Center, Chiba University. Organic solvents used

were dried by standard methods. Commercially available reagents were used without further purification. Silica gel (Wakogel, C-200) was used for column chromatography. HPLC analyses were performed on a Hitachi L-6000 pump, L-7490 RI detector, and L-4000 UV detector with an appropriate chiral column. Recycling preparative HPLC was performed on JAIGEL-ODS 345-15 column, JAI LC-908 pump and RI detector RI-5.

*4.2. 1,2-Bis(1-adamantyl)-2-(trimethylsilyl)oxyethanone **5***

To a solution of 1,2-bis(1-adamantyl)-2-hydroxyethanone **4** (37 g, 0.11 mol) and 4-(*N*,*N*-dimethylamino)pyridine (1.2 g, 0.01 mol) in pyridine was added TMSCl (43.1 mL, 0.34 mol) at rt under Ar atmosphere. After the mixture was stirred for 2 h, the reaction was quenched with water. The organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined extracts were washed with brine and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and washed with hexane to give **5** (43 g, 96%) as a white powder: mp 132–134°C; IR (KBr) 2905, 2850, 1705, 1450, 1250, 1100, 880, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.16 (9H, s), 1.22–2.05 (30H, m), 4.16 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.03, 27.7, 28.0, 28.3, 36.4, 36.5, 37.0, 37.6, 37.8, 38.4, 38.5, 38.8, 46.9, 214.9; FAB MS m/z 401 (M^++1H); HRMS calcd for $C_{25}H_{41}O_2Si$ (M^++1H) 401.2876, found 401.2871.

*4.3. (±)-1,2-Bis(1-adamantyl)-1,2-ethanediol **2***

To the suspension of lithium aluminum hydride (4.1 g, 0.11 mol) in THF was slowly added a solution of **5** (43 g, 0.11 mol) in THF at rt under Ar atmosphere, and the mixture was refluxed for 5 h. The reaction mixture was carefully poured into concentrated HCl at 0°C. After the mixture was diluted with water, the organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the residue was recrystallized from DME to give **2** (22.4 g, 61%) as colorless needles: mp 277–279°C; IR (KBr) 3400, 2900, 2850, 1450, 1080, 605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.51–1.73 (30H, m), 2.25 (2H, d, *J*=6.8 Hz), 3.20 (2H, d, *J*=6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2, 36.7, 37.2, 38.0, 74.0; FAB MS m/z 331 (M^++1H). Anal. calcd for $C_{22}H_{34}O_2$: C, 9.95; H, 10.37. Found: C, 80.17; H, 10.58.

*4.4. Preparation of diastereomerically pure phosphates **6** and **7***

To a solution of (±)-**2** (4.7 g, 14 mmol) in THF was added *n*-BuLi (18.2 mL of 1.54 M hexane solution, 28 mmol) at 0°C under Ar atmosphere. The mixture was added to a solution of dichloro(*l*-menthyloxy)phosphine (3.8 g, 14 mmol) in THF at −78°C, and the reaction mixture was allowed to warm to rt. The reaction was quenched with water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The combined extracts were washed with brine and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the residue was added to H_2O_2 (1.6 mL of 30% water solution, 14 mmol) at rt. After the mixture was stirred for 3 h, the reaction was quenched with saturated aqueous $Na_2S_2O_3$. The mixture was extracted with hexane five times. The combined extracts were washed with brine and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the residue was purified by chromatography on silica gel (hexane:EtOAc, 50:1) to give **6** and **7** (5.6 g, 75%) as colorless solids. This mixture of two diastereomers was separated by

recycling HPLC (MeOH). The compounds **6** (1.6 g, 29%) and **7** (1.5 g, 27%) were obtained from the first and second fraction, respectively.

4.5. *(1′S,2′S)-(1′,2′-Diadamantyl-1′,2′-ethanediyl)* l-*menthyl phosphate* ***6***

Colorless needles: mp 105–107°C; $[\alpha]_D^{21}$ −64.2 (*c* 1.02, $CHCl_3$); IR (KBr) 2900, 2860, 1450, 1280, 1060, 1030, 985, 960, 870 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83–2.28 (48H, m), 3.91 (1H, dd, *J*=18.5, 3.1 Hz), 3.95 (1H, dd, *J*=17.3, 3.1 Hz), 4.25–4.35 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.1, 20.8, 22.0, 23.2, 25.9, 27.8 (d, *J*=16.4 Hz), 31.5, 34.1, 36.4 (d, *J*=4.9 Hz), 36.8 (d, *J*=11.5 Hz), 37.2 (d, *J*=16.4 Hz), 42.8, 48.3 (d, *J*=8.2 Hz), 80.4 (d, *J*=6.6 Hz), 84.8 (d, *J*=2.5 Hz), 85.1 (d, *J*=1.6 Hz); FAB MS m/z 529 (M^+−1H); HRMS calcd for $C_{32}H_{52}O_4P$ (M^++1H) 531.3603, found 531.3600.

4.6. *(1′R,2′R)-(1′,2′-Diadamantyl-1′,2′-ethanediyl)* l-*menthyl phosphate* ***7***

Colorless prisms: mp 187–189°C; $[\alpha]_D^{21}$ +12.5 (*c* 1.01, $CHCl_3$); IR (KBr) 2900, 2860, 1450, 1280, 1060, 1030, 985, 960, 870 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83–2.25 (48H, m), 3.91 (1H, dd, *J*=11.4, 2.9 Hz), 3.92 (1H, dd, *J*=9.9, 2.9 Hz), 4.30–4.39 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 20.9, 21.9, 23.0, 26.3, 27.8, 31.5, 34.1, 36.4 (d, *J*=4.9 Hz), 36.8 (d, *J*=5.7 Hz), 37.2 (d, *J*=3.3 Hz), 42.9, 48.3 (d, *J*=6.6 Hz), 81.0 (d, *J*=7.4 Hz), 84.9 (d, *J*=1.6 Hz), 85.1 (d, *J*=2.5 Hz); FAB MS m/z 529 (M^+−1H); HRMS calcd for $C_{32}H_{52}O_4P$ (M^++1H) 531.3603, found 531.3617.

4.7. *X-Ray crystallographic analysis of compound* ***7***

A well-shaped monoclinic crystal of **7** was obtained by recrystallization from Et_2O: $C_{32}H_{51}O_4P$; space group $P2_1$ (#4); *a*=10.877(7) Å, *b*=12.474(8) Å, *c*=12.474(8) Å; *V*=1507(1) $Å^3$; *Z*=2, *D*=1.169 g/cm^3; F(000)=580; μ(Mo Kα)=1.25 cm^{-1}; λ(Mo Kα)=0.71070 Å; temperature of data collection 300 K; 2669 reflections measured, 2603 observed ($I > 3.00\sigma(I)$); 335 variables; R=0.055, R_W=0.080, GOF=1.36. Selected bond distance (Å) and angles (deg): P(1)–O(1) 1.584(3), P(1)–O(2) 1.589(3), P(1)–O(3) 1.562(3), P(1)–O(4) 1.462(3), O(1)–P(1)–O(2) 97.6(1), O(1)–P(1)–O(3) 104.6(2), O(1)–P(1)–O(4) 117.4(2), O(2)–P(1)–O(3) 105.4(2), O(2)–P(1)–O(4) 116.1(4), O(3)–P(1)–O(4) 113.7(1).

4.8. *(1*S,*2*S*) and (1*R,*2*R*)-1,2-Bis(1-adamantyl)-1,2-ethanediol* ***2***

Diastereomerically pure **6** (0.82 g, 1.6 mmol) in toluene was treated with MeLi (5.3 mL of 1.5 M Et_2O solution, 8 mmol) at rt under Ar atmosphere, and the mixture was stirred for 5 h. The reaction mixture was poured into vigorously stirred water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The combined extracts were washed with brine and dried (Na_2SO_4). The solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (hexane:EtOAc, 15:1), and recrystallized from DME to give optically active (1*S*,2*S*)-**2** (185 mg, 35%) as colorless needles: mp 270–272°C; $[\alpha]_D^{25}$ +14.5 (*c* 0.77, $CHCl_3$).

In a similar manner, optically active (1*R*,2*R*)-**2** was obtained from **7** (195 mg, 37%): mp 271–273°C; $[\alpha]_D^{25}$ −13.7 (*c* 1.01, $CHCl_3$).

4.9. *Dimethyl 2,2,5,5-tetramethylhexanedioate* **9**

To a solution of 2,2,5,5-tetramethylhexanedioic acid **8** (17.7 g, 88 mmol) and KOH (11.8 g, 210 mmol) in MeOH was added iodomethane (20 mL, 320 mmol) at rt, and the mixture was refluxed for 3 h. The reaction was quenched with water, and the mixture was extracted with Et_2O three times. The combined extracts were washed with brine and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the residue was purified by chromatography on silica gel (hexane) to give **9**[18] (12.6 g, 61%) as a colorless solid: mp 35–36°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (12H, s), 1.44 (4H, s), 3.66 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 35.6, 42.0, 51.6, 178.2.

4.10. trans-*3,3,6,6-Tetramethyl-1,2-cyclohexanediol* ***3***

Metallic sodium (7.4 g, 0.32 mol) in xylene was refluxed until the sodium melted under Ar atmosphere. The oil bath was removed and the mixture was cooled to rt with very vigorous stirring. The solvent was removed with a syringe, and to the powdered sodium was added the solution of diester **9** (4.6 g, 0.02 mol) in Et_2O. The mixture was refluxed for 3 days, and then slowly added 2-propanol (25 mL, 0.32 mol). After additional reflux for 2 h, the reaction was quenched with water. The organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined extracts were washed with 1 M HCl, saturated aqueous $NaHCO_3$ and brine, and dried (Na_2SO_4). The solvent was evaporated under reduced pressure. The residue was purified by chromatography on silica gel (hexane:EtOAc 5:1), and recrystallized from *n*-Bu_2O to give racemic **3** (1.8 g, 52%) as colorless needles: mp 150–152°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (6H, s), 1.01 (6H, s), 1.34 (4H, dd, *J*=83.4, 9.7 Hz), 2.51 (2H, s), 3.22 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4 (d, 4.1 Hz), 29.5 (d, 4.1 Hz), 34.6, 36.3, 78.0.

4.11. *(1′*S*,2′*S*)-(2′-Hydroxy-3′,3′,6′,6′-tetramethyl)cyclohexyl (*S*)-1-benzoyl-2-pyrrolidine-carboxylate* ***11***

To a solution of racemic **3** (0.34 g, 2 mmol), *N*-benzoyl *l*-proline **10** (0.53 g, 2.4 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (0.12 g, 1 mmol) in CH_2Cl_2 was added EDC-HCl (0.7 g, 3.6 mmol) and Et_3N (0.5 mL, 3.6 mmol) at rt under Ar atmosphere, and the mixture was stirred for 2 h. The reaction was quenched with 1 M HCl (50 mL), and the mixture was added to Et_2O (50 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined extracts were washed with saturated aqueous $NaHCO_3$ twice and brine, and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the residue was dried in vacuo to give the mixture of diastereomers (0.75 g, 100%). The mixture was recrystallized from cyclohexane–EtOAc to give amino acid ester **11** (0.29 g, 39%) as colorless plates: mp 171°C (dec.); $[\alpha]_D^{20}$ −3.47 (*c* 0.99, $CHCl_3$); IR (KBr) 3450, 2930, 1735, 1620, 1600, 1580, 1455, 1300, 1085, 1045, 980, 800, 740, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (3H, s), 0.94 (3H, s), 0.97 (3H, s), 1.04 (3H, s), 1.23–1.30 (2H, m), 1.45 (1H, dt, *J*=4.0, 14.3 Hz), 1.57 (1H, dt, *J*=4.9, 13.7 Hz), 1.92–2.08 (2H, m), 2.10–2.18 (1H, m), 2.38–2.47 (1H, m), 3.25–3.30 (2H, m), 3.56–3.66 (2H, m), 4.68 (1H, dd, *J*=8.5, 4.9 Hz), 4.84 (1H, d, *J*=9.5 Hz), 7.40–7.47 (3H, m), 7.51–7.54 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 19.8, 25.4, 29.3, 29.6, 29.8, 34.7, 36.3, 36.8, 50.3, 60.1, 75.7, 81.6, 127.0, 128.5, 130.4, 136.1, 170.6, 171.6; FAB MS m/z 374 (M^++1H). Anal. calcd for $C_{22}H_{31}NO_4$: C, 70.75; H, 8.37; N, 3.75. Found: C, 70.84; H, 8.52; N, 3.84.

4.12. X-Ray crystallographic analysis of compound **11**

A well-shaped monoclinic crystal of **11** was obtained by recrystallization from toluene: $C_{22}H_{31}NO_4$; space group $P2_12_12_1$ (#19); a=9.158(4) Å, b=34.678(9) Å, c=6.730(4) Å; V=2137(1) Å^3; Z=4, D=1.161 g/cm^3; F(000)=808.00; μ(Mo Kα)=0.79 cm^{-1}; λ(Mo Kα)=0.71070 Å; temperature of data collection 173 K; 1950 reflections measured, 1853 observed (I >1.50σ(I)); 245 variables; R=0.089, R_W=0.109, GOF=1.91. Selected distance (Å): O(1)–O(2) 2.838(5), O(1)–O(4) 2.841(5), O(2)–O(4) 2.948(4).

4.13. (1S,2S)-3,3,6,6-Tetramethyl-1,2-cyclohexanediol **3**

A solution of amino acid ester **11** (0.8 g, 2.14 mmol) and KOH (14 g) in H_2O (50 mL) was refluxed for 6 h. The mixture was extracted with Et_2O three times. The combined extracts were washed with 1 M HCl, saturated aqueous $NaHCO_3$ and brine, and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the residue was dried in vacuo to give (*S*,*S*)-**3** (366 mg, 100%) as colorless needles: mp 152–153°C; $[\alpha]_D^{25}$ +27.2 (*c* 1.04, $CHCl_3$).

The enantiomeric excess was determined to be 100% ee by chiral HPLC analysis: Daicel Chiralpak AD (hexane:2-propanol 9:1, flow rate=1.0 mL/min): t_r(*S*,*S*)=5.9 min, t_r(*R*,*R*)=8.0 min.

4.14. Asymmetric oxidation of sulfides

The solution of Ti(O*i*Pr)$_4$ (7.4 μL, 0.025 mmol), MS4A (100 mg), and diol (0.05 mmol) in toluene (1 mL) was stirred for 1 h at rt, and then sulfide (0.5 mmol) was added. The solution was cooled to −20°C, and 80% cumyl hydroperoxide (190 μL, 1 mmol) was added. The mixture was stirred at same temperature by monitoring the reaction by TLC until sulfide disappeared. The reaction was quenched with ca. 10% aqueous solution of sodium sulfite. The aqueous layer was extracted with EtOAc three times. The combined organic layer was washed with brine and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (EtOAc) on silica gel to give sulfoxide. The enantiomeric excess of sulfoxide was determined by chiral HPLC analysis: Daicel Chiralcel OD-H (hexane:2-propanol 9:1, flow rate=0.5 mL/min) for methyl *p*-tolyl sulfoxide, and Daicel Chiralcel OJ (hexane:2-propanol 5:1, flow rate=0.8 mL/min) for benzyl phenyl sulfoxide.

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