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Design of Optically Active Hydroxamic Acids as Ligands in Vanadium-Catalyzed Asymmetric Epoxidation

Yujiro Hoshino, Noriaki Murase, Masataka Oishi, and Hisashi Yamamoto*

Graduate School of Engineering, Nagoya University, CREST, Japan Science and Technology Corporation (JST), Chikusa-ku, Nagoya 464-8603

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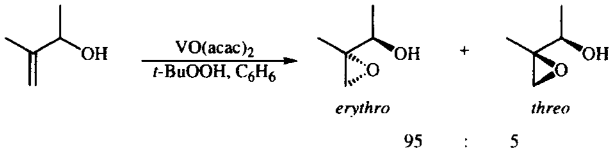
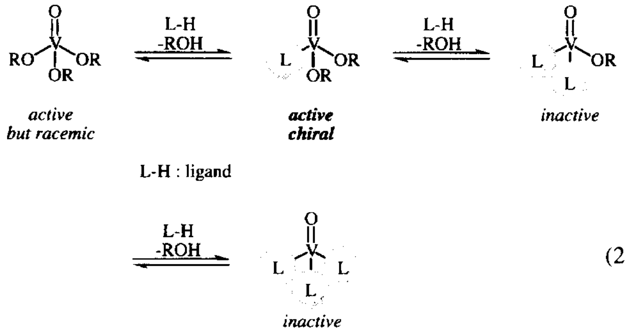
New optically active hydroxamic acids bearing a 1,1′-binaphthyl group were prepared as ligands in a vanadium-catalyzed asymmetric epoxidation. The feature of these hydroxamic acids is a sterically hindered ligand. The asymmetric epoxidation with good selectivity and reactivity can be established by using VO(O-*i*-Pr)$_3$ (5 mol%) and a small excess amount of ligand (7.5 mol%) with triphenylmethyl hydroperoxide (TrOOH) in toluene at −20 °C. Disubstituted allyl alcohols were epoxidized more rapidly than mono- or tri-substituted allyl alcohols, and were obtained in good to high enantioselectivities (48—94%ee). The transition state based on X-ray crystal structure of **1e** is discussed.

Since its discovery by Sharpless in 1986, the metal-catalyzed asymmetric epoxidation of olefins has been viewed as a powerful method for preparing synthetically useful chiral building blocks as well as optically active oxiranes.[1] The epoxidation can be carried out with a wide variety of olefins and metals such as Ti, Mn, Fe, Mo, etc., and vanadium catalyst is one of the most active catalysts in the transition metal-catalyzed epoxidation. The regio- and stereoselective epoxidation of allyl alcohols using VO(acac)$_2$ has been extensively investigated and has become a synthetically useful method.[2] For example, the epoxidation of 3-methyl-3-buten-2-ol by *t*-BuOOH occurs erythro selectively (Eq. 1).[2b] To the best of our knowledge, however, there have been few reports on chiral vanadium catalysts for asymmetric epoxidation.[3] Sharpless and co-workers proposed a mechanism in which the alcohol coordinates to vanadium (V) and oxygen-atom transfer occurs from coordinated alkyl peroxide. They suggested that the control of the complexation mode of vanadium (V) is important (Eq. 2).[4] Recently, we showed that a chiral vanadium catalyst prepared in situ from VO(O-*i*-Pr)$_3$ and sterically hindered hydroxamic acid **1e** can achieve the asymmetric epoxidation of allylic alcohols with good selectivities, and some allylic alcohols gave a higher ee value than one reported previously using chiral vanadium catalysts.[5] In this paper, we report the design of such ligands as well as the scope and limitations of the asymmetric epoxidation of allylic alcohols.



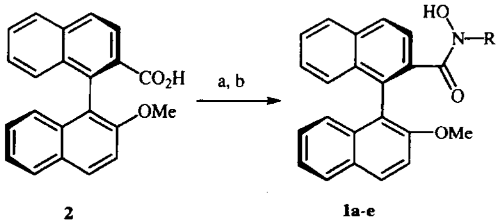
(1)



(2)

Results and Discussion

1. Preparation of Optically Active Hydroxamic Acids. We first discuss the synthesis of hydroxamic acids **1a—e** starting from carboxylic acids **2**, as shown in Scheme 1. Carboxylic acid **2** was prepared from (*R*)-1,1′-bi-2-naphthol in several steps as described in the literature.[6] The carboxylic acid was converted to acid chloride by treatment with (COCl)$_2$ and a catalytic amount of DMF in CH$_2$Cl$_2$. Then, hydroxamic acids **1a—e** were synthesized via condensation of the intermediary acid chloride and various hydroxylamines **3** in the usual manner (Table 1). In the case of **1e**, the *O*-acylated by-product **1e′** was obtained at the same time.



2 **1a-e**

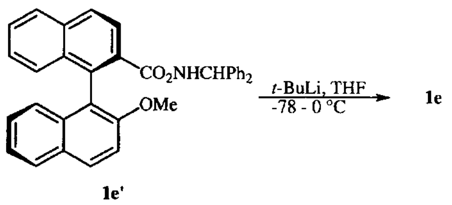
Scheme 1. Conditions: (a) (COCl)$_2$,cat. DMF, CH$_2$Cl$_2$; (b) **3**, NEt$_3$, CH$_2$Cl$_2$.

Table 1. Preparation of Hydroxamic Acid **1a**—**e**

	R	Yield of **1** from **2** %
1a	Cyclohexyl	84
1b	$CH(i\text{-}Pr)_2$	50
1c	Bn	72
1d	9-Fluorenyl	26
1e	$CHPh_2$	89[a)]

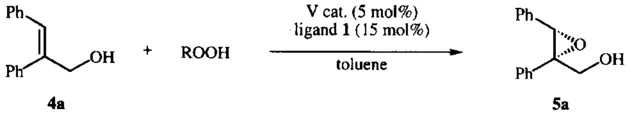
a) Combined yield after rearrangement of **1e**′.

Fortunately, **1e**′ was easily isomerized to **1e** through *t*-BuLi-promoted 1,2-rearrangement (Eq. 3).



(3)

2. Asymmetric Epoxidation Catalyzed by Chiral Vanadium Catalysts: Optimization of Reaction Conditions. We chose (*E*)-2,3-diphenyl-2-propen-1-ol as a standard substrate for optimization of the reaction conditions (Eq. 4).



(4)

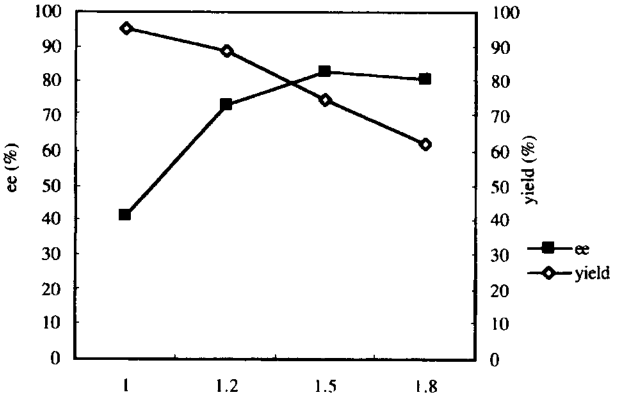
The results of asymmetric epoxidation in the presence of 5 mol% of vanadium complex and 15 mol% of optically active hydroxamic acids are shown in Table 2. First, we performed the epoxidation using a variety of *N*-substituted hydroxamic acids, and found that phenyl groups and steric hindrance affect the reactivity and selectivity of the epoxidation considerably. Interestingly, a much shorter period of reaction time and higher enantioselectivity were observed using hydroxamic acid **1e** with *N*-diphenylmethyl group (Entry 5). Furthermore, replacement of the vanadium precatalyst of $VO(acac)_2$ to $VO(O\text{-}i\text{-}Pr)_3$ resulted in a remarkable increase of reaction rate. Seeking higher enantioselectivity, we then performed epoxidation at lower temperature. As anticipated from the Sharpless epoxidation, sterical hindrance of alkyl hydroperoxides required prolongation of reaction time with higher enantioselectivity. Epoxidation reaction proceeded very rapidly but with lower selectivity when TBHP was employed, while the sterically hindered oxidant having phenyl group produced higher selectivity with decreasing reaction rate. The combination of sterically hindered ligand **1e** and triphenylmethyl hydroperoxide at −20 °C gave high selectivity (86%ee) (Entry 7). We next examined the relationship between selectivity and reactivity with varying mole ratio of ligand to vanadium (Fig. 1). As noted by Sharpless, the reactivity decreased with increase in this ratio. It is a characteristic feature of our hydroxamic acid ligand that higher selectivity of 73%ee was obtained without any deleterious effect on reactivity even when there was a 1.2 molar amount of ligand over vanadium.

Asymmetric Epoxidation of Various Substituted Allyl Alcohols. Epoxidation of a variety of substituted allyl alcohols was examined under the aforementioned optimized reaction conditions to learn the scope and limitation of the $VO(O\text{-}i\text{-}Pr)_3$–**1e** system (Eq. 5). As can be seen from Table 3, both types of 2,3- and 3,3-disubstituted allyl alcohols were epoxidized in high yields and with good enantioselectivities. In particular, high ee's of approximately 90% were obtained with 2,3-disubstituted allyl alcohols; mono- and trisubstituted allyl alcohols gave less satisfactory results, and these data are shown in Tables 3 and 4. It should be noted that 1-cyclopentnylmethanol was effectively epoxidized without loss of selectivity compared with the titanium(IV) tartrate[7] (Table 3, Entry 8).

Table 2. Catalytic Enantioselective Epoxidation of (*E*)-2,3-Diphenyl-2-propen-1-ol[a)]

Entry	Catalyst	ROOH[b)]	Conditions (°C, h)	Ee(%)[c)]
1	$VO(acac)_2$/**1a**	CHP	0, 6 days	25
2	**1b**	CHP	0, 2 days	24
3	**1c**	CHP	0, 8 days	54
4	**1d**	CHP	0, 24	47
5	**1e**	CHP	0, 19	65
6	$VO(O\text{-}i\text{-}Pr)_3$/**1e**	CHP	−20, 3	68
7		TrOOH	−20, 68	86
8[d)]		TrOOH	−20, 24	83
9		TBHP	−40, 10	40

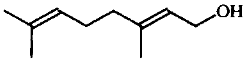
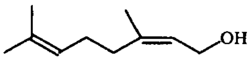
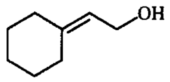
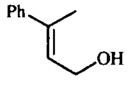
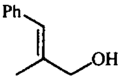
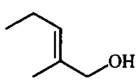
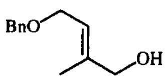
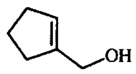
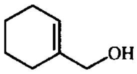
a) Unless otherwise noted, the reaction was carried out in toluene in the presence of vanadium complex (5 mol%) and **1** (15 mol%). Isolated yield in each entry was around 80%. b) CHP = 1-methyl-1-phenylethyl hydroperoxide, TrOOH = triphenylmethyl hydroperoxide, TBHP = *t*-butylhydroperoxide. c) Absolute configuration of the major enantiomer in each run was 2*S*, 3*S* and the ee values were determined by chiral HPLC (column,OD-H) analysis. d) 7.5 mol% of **1e**.



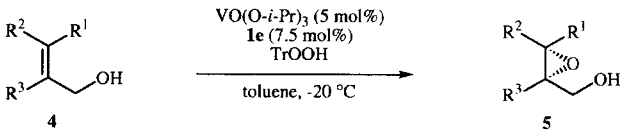
a) The reaction was carried out as follows: 5 mol% of $VO(O\text{-}i\text{-}Pr)_3$, 1.5 mol amt. of TrOOH in toluene at -20 °C for 1 day.

Fig. 1. Reactivity and selectivity of $VO(O\text{-}i\text{-}Pr)_3$/**1e** catalyst in the asymmetric epoxidation of (*E*)-2,3-diphenyl-2-propen-1-ol.[a)]

Table 3. Catalytic Epoxidation of Disubstituted Allyl Alcohols in the Presence of VO(O-*i*-Pr)$_3$/**1e**[a]

Entry	Allylic alcohol	Yield(%)[b]	Ee(%)[c]	Config.(2,3)[d]
1		80	66	(*S*,*S*)
2		87	41	(*S*,*R*)
3		88	48	(2*S*)
4		70	78[e]	(*S*,*S*)
5		96	91[e]	(*S*,*S*)
6		69	75	(*S*,*S*)
7		88	81[e]	(*S*,*S*)
8		59	94	(*S*,*S*)
9		61	87	(*S*,*S*)

a) The epoxidation was conducted at −20 °C for 2—3 d in toluene in the presence of VO(O-*i*-Pr)$_3$ (5 mol%) and **1e** (7.5 mol%). b) Isolated yield. c) Determined by chiral GLC (column, *β*-TA) analysis. d) Determined by comparison of reported optical rotation. e) Determined by chiral HPLC (column, OD-H) analysis.

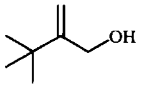
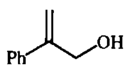
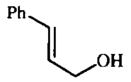
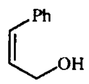
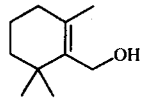


(5)

Crystal Structure of Ligand 1e. Noting an unusual observation in the ^{1}H NMR experiment on the structure of ligand **1e**, we performed an X-ray crystallographic analysis of hydroxamic acid **1e**. A crystal of **1e** suitable for X-ray analysis was obtained by recrystallization from ether. Selected bond lengths, bond angles, and torsional angles for **1e** are compiled in Table 5. Figure 2 shows an ORTEP drawing of **1e**. Usual five-membered hydrogen bonding within hydroxamic acid functionality was no longer observable due to the steric repulsion between binaphthyl and diphenyl group. Labile hydrogen bonding between a methoxy group and the hydroxamic acid was estimated from the bond length of 1.84(8) Å. The solid state structure of **1e** suggests that ancillary coordination of the methoxy group plays an important role in making the vanadium complex comformationally more rigid and suitable for the asymmetric reaction.

Possible Transition State Structures for Asymmetric Epoxidation. To explain our results, we proposed the transition state structure, based on the structure of X-ray crystal structure of ligand, in the present epoxidation reaction illustrated in Fig. 3, since the square bipyramidal geometry

Table 4. Catalytic Epoxidation of Mono- or Trisubstituted Allyl Alcohols in the Presence of VO(O-*i*-Pr)$_3$/**1e**[a]

Entry	Allylic alcohol	Yield(%)[b]	Ee(%)[c]	Config.(2,3)[d]
1		16	40	(2*S*)
2		53	39	(2*S*)
3		14	71[e]	(*S*, *S*)
4		19	38[f]	(*S*, *R*)
5		61	50	(*S*, *S*)

a) The epoxidation was conducted at −20 °C for 2—3 d in toluene in the presence of VO(O-*i*-Pr)$_3$ (5 mol%) and **1e** (7.5 mol%). b) Isolated yield. c) Determined by chiral GLC (column, *β*-TA) analysis. d) Determined by comparison of reported optical rotation. e) Determined by chiral HPLC (column, OD-H) analysis. f) Determined by chiral GLC (column, *γ*-TA) analysis.

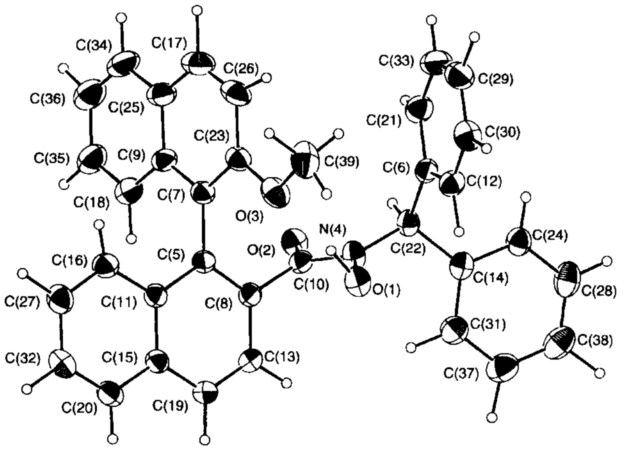


Fig. 2. ORTEP drawing of ligand **1e**.

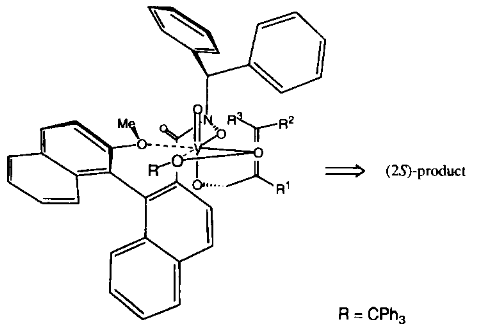


Fig. 3. Proposed transition states of asymmetric epoxidation.

Table 5. Selected Bond Lengths, Bond Angles, and Torsional Angles of Ligand **1e**[a)]

	Bond lengths		
O(1)–N(4)	1.411(2)	O(2)–C(10)	1.230(2)
O(3)–C(23)	1.384(2)	O(3)–C(39)	1.447(3)
N(4)–C(10)	1.355(2)	C(5)–C(7)	1.512(2)
C(5)–C(8)	1.386(2)	C(7)–C(23)	1.385(3)
C(8)–C(10)	1.510(2)	O(1)–H(1)	1.04(3)
C(22)–H(22)	1.06(2)	O(3)–H(1)	1.848
	Bond angles		
C(23)–O(3)–C(39)	117.9(2)	O(1)–N(4)–C(10)	117.6(1)
O(1)–N(4)–C(22)	116.8(2)	C(10)–N(4)–C(22)	125.5(2)
O(2)–C(10)–N(4)	121.4(2)	O(2)–C(10)–C(8)	122.5(2)
N(4)–C(10)–C(8)	116.1(2)	N(4)–O(1)–H(1)	100.8(13)
O(3)–C(23)–C(7)	116.2(2)	C(5)–C(7)–C(23)	120.4(2)
C(7)–C(5)–C(8)	120.6(2)	C(5)–C(8)–C(10)	121.5(2)
	Torsional angles		
O(1)–N(4)–C(10)–O(2)	−177.7(2)	C(5)–C(8)–C(10)–O(2)	−80.7(2)
C(39)–O(3)–C(23)–C(7)	−169.7(3)	C(5)–C(7)–C(23)–O(3)	2.8(2)
C(8)–C(5)–C(7)–C(23)	−81.8(2)		

a) Bond lengths are giben in Å, and angles in °. See Fig. 2 for the numbering.

of vanadium complexes involving hydroxamate or peroxo ligands is the most acceptable to date.[8] Trans orientation over the vanadium center between the bulky hydroxamate and trityl peroxide and apically bound allylic alkoxide could be essential and lead to a favorable oxygen transfer to the *Si*-face of a carbon-carbon double bond.

Conclusion. In the presence of chiral vanadium catalysts prepared in situ from VO(O-*i*-Pr)$_3$ and sterically hindered hydroxamic acid having an optically active binaphthyl group, disubstituted allyl alcohols were epoxidized in good ee's (up to 94%ee). The asymmetric epoxidation of allyl alcohols in good enantioselectivities was achieved using a slight excess (50%) of ligand and did not decrease the reactivity.

Experimental

General. Infrared (IR) spectra were measured on a Shimadzu FTIR-9100 spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini-300 (300 MHz) spectrometer. Chemical shifts of ^{1}H NMR are expressed in ppm downfield relative to internal standard (tetramethylsilane at 0 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. ^{13}C NMR spectra were measured on a Varian Gemini-300 (75 MHz) spectrometer and are reported in ppm using solvent as the internal standard (CDCl$_3$ at 77.0 ppm). Analytical gas-liquid chromatography (GLC) was performed on a Shimadzu GC-17A instrument equipped with a flame ionization detector and a capillary column of β-TA (0.25 mm × 25 m) using nitrogen as carrier gas. High-performance liquid chromatography (HPLC) analyses were carried out on a Shimadzu LC-10AD instrument with a SPD-M10A UV detector using a chiral stationary column (Daicel, OD-H). Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. Reaction products were purified by flash chromatography on silica gel E. Merck 9385 or silica gel 60 extra pure. Analytical thin-layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm).

In experiments requiring dry solvents, toluene and CH$_2$Cl$_2$ were freshly distilled from calcium hydride. Triethylamine was stored over KOH pellets. VO(acac)$_2$ and VO(O-*i*-Pr)$_3$ were purchased from Wako Pure Chem. Ind., Ltd. and High Purity Chemicals, respectively. Carboxylic acid **2a**, hydroxylamines **3**, and triphenylmethyl hydroperoxide (TrOOH) were prepared according to the literature procedure.[9,10] Other hydroperoxides and simple chemicals were purchased.

All allylic alcohols and products in Tables 3 and 4 have been previously isolated and characterized. References can be found elsewhere.[11]

Preparation of Hydroxamic Acid Ligand 1a. To a stirred solution of *N*-cyclohexylhydroxylamine (127 mg, 1.1 mmol) and Et$_3$N (0.35 mL, 2.5 mmol) in CH$_2$Cl$_2$ (10 mL) at 0 °C was added dropwise a CH$_2$Cl$_2$ solution of 2′-methoxy-1,1′-binaphthyl-2-carbonyl chloride, which was prepared from **2a**[6] (328 mg, 2.5 mmol) with oxalyl chloride (10 mL, 0.1 M, 1 mmol). After being stirred for 30 min, the reaction mixture was poured into 1 M HCl (10 mL, 1 M = 1 mol dm^{-3}) and extracted with Et$_2$O three times. The combined organic phase was washed with water and brine, and dried over Na$_2$SO$_4$. Evaporation of solvents followed by chromatographic purification (EtOAc/hexane = 1 : 2) gave the title compound as a powdered solid (359 mg, 84%). Hydroxamic acid **1a** can be further purified by recrystallization from chloroform/hexane: $R_f = 0.37$ (EtOAc/hexane = 1 : 1, FeCl$_3$ stain); $[\alpha]_D^{27}$+50.3° (*c* 0.59, CHCl$_3$); ^{1}H NMR (THF-d_8) δ = 8.44 (1H, br s, OH), 7.92—7.98 (3H, m, Ar-H), 7.79 (1H, d, J = 8.1 Hz, Ar-H), 7.43—7.54 (3H, m, Ar-H), 7.12—7.30 (5H, m, Ar-H), 3.74 (3H, s, CH$_3$), 3.51 (1H, br s, N-CH), 1.00—1.63 (10H, m, 5CH$_2$); ^{13}C NMR (CDCl$_3$) δ = 168.7 (C=O), 164.4 (C=O), 154.8 (2-Ar), 154.0 (2-Ar), 135.8, 134.1, 133.7, 133.2, 132.7, 132.6, 132.5, 131.8, 130.4, 130.3, 129.5, 128.6, 128.3, 128.2, 128.0, 127.6, 126.9, 126.7, 126.5, 126.4, 126.2, 125.9, 124.5, 124.2, 123.4, 121.2, 119.1, 113.8 (2′-Ar), 112.8 (2′-Ar), 77.2, 58.4, 57.8, 56.2, 53.7, 29.7 (CH$_2$), 28.5 (CH$_2$), 28.3 (CH$_2$), 25.1 (CH$_2$), 25.0 (CH$_2$), 24.7 (CH$_2$); IR (KBr) 3100, 2856, 1625, 1599, 1558, 1508, 1468, 1310, 1250, 810, 752 cm^{-1}. Found: C, 78.91; H, 6.51; N, 3.39%. Calcd for C$_{28}$H$_{27}$NO$_3$: C, 79.03; H, 6.40; N, 3.29%.

Hydroxamic Acid 1b. **1b** was prepared in the manner described above (50% yield): $R_f = 0.35$ (EtOAc/hexane = 1 : 3, $FeCl_3$ stain); $[\alpha]_D^{29}+105.9^\circ$ (c 1.06, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.94$—8.05 (3H, m, Ar-H), 7.37 (1H, d, $J = 8.4$ Hz, Ar-H), 7.60 (1H, d, $J = 8.4$ Hz, Ar-H), 7.24—7.49 (5H, m, Ar-H), 7.13 (2H, dd, $J = 8.4$, 12.3 Hz, Ar-H), 3.87 (1H, dd, $J = 7.8$, 9.6 Hz, NCH), 3.77 (3H, s, OCH_3), 2.05 (1H, br, $^iPr_2CH$), 1.91 (1H, m, $^iPr_2CH$), 0.92 (6H, br, $C(CH_3)_2$), 0.67 (3H, d, $J = 6.6$ Hz, CCH_3), 0.43 (3H, br, CCH_3); IR (KBr) 3058, 2963, 1646, 1624, 1593, 1509, 1468, 1356, 1246, 822, 752 cm^{-1}. Found: C, 78.86; H, 7.20; N, 3.39%. Calcd for $C_{29}H_{31}NO_3$: C, 78.88; H, 7.08; N, 3.17%.

Hydroxamic Acid 1c. **1c** was prepared in the manner described above (72% yield): $R_f = 0.39$ (EtOAc/hexane = 1 : 1, $FeCl_3$ stain); $[\alpha]_D^{27}+131.8^\circ$ (c 0.50, $CHCl_3$); ^1H NMR (THF-d^8) $\delta = 8.82$, 8.11 (1H, br s, OH), 7.91—8.02 (3H, m, Ar-H), 7.84 (1H, d, $J = 8.4$ Hz, Ar-H), 7.57 (1H, br s, Ar-H), 7.42—7.47 (2H, m, Ar-H), 7.13—7.28 (9H, m, Ar-H), 6.82 (1H, br s, Ar-H), 4.68 (1H, d, $J = 15.0$ Hz, NCH2), 4.43 (1H, br s, NCH_2), 3.59 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) $\delta = 169.4$ (C=O), 165.5 (C=O), 154.1 (2-Ar), 153.7 (2-Ar), 135.5, 134.9, 134.8, 133.9, 133.7, 133.6, 133.2, 132.4, 131.1, 130.2, 130.0, 129.8, 129.1, 128.3, 128.2, 128.0, 127.6, 127.5, 127.3, 127.1, 126.9, 126.8, 126.7, 126.4, 126.2, 125.8, 125.6, 125.3, 124.2, 123.5, 123.3, 120.1, 118.7, 113.4 (2′-Ar), 112.5 (2′-Ar), 56.5 (OCH_3), 55.5 (OCH_3), 53.0 ($PhCH_2$), 50.4 ($PhCH_2$); IR (KBr) 3061, 3010, 1624, 1598, 1510, 1433, 1356, 1250, 812, 750 cm^{-1}. Found: C, 80.08; H, 5.52; N, 3.25%. Calcd for $C_{29}H_{23}NO_3$: C, 80.35; H, 5.35; N, 3.23%.

Hydroxamic Acid 1d. **1d** was prepared in the manner described above (26% yield): $R_f = 0.39$ (EtOAc/hexane = 1 : 1, $FeCl_3$ stain); $[\alpha]_D^{29}+39.9^\circ$ (c 1.08, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 8.17$ (1H, d, $J = 3.0$ Hz, Ar-H), 8.06 (1H, d, $J = 8.1$ Hz, Ar-H), 7.96 (2H, d, $J = 8.1$ Hz, Ar-H), 7.74 (1H, d, $J = 8.4$ Hz, Ar-H), 7.67 (2H, d, $J = 7.8$ Hz, Ar-H), 7.18—7.52 (12H, m, Ar-H), 7.10 (1H, d, $J = 8.4$ Hz, Ar-H), 6.59 (1H, br, NCH), 3.46 (3H, s, CH_3); IR (KBr) 3048, 2940, 1640, 1625, 1509, 1451, 1355, 1250, 811, 745 cm^{-1}. Found: C, 82.81; H, 4.94; N, 2.91%. Calcd for $C_{35}H_{25}NO_3$: C, 82.82; H, 4.96; N, 2.76%.

Hydroxamic Acid 1e. **1e** was also prepared in the manner described for **1a**. In this case, **1e** was obtained in 70% yield together with a significant amount of *O*-acylated by-product **1e′** (22% yield). Rearrangement of **1e′** to **1e** was carried out by treatment of *t*-BuLi (2 mol amt.) in THF, while raising the temperature from −78 to 0 °C. Acidic work-up and purification of column chromatography on silica gel furnished **1e** in 86% yield: $R_f = 0.38$ (EtOAc/hexane = 1 : 2, $FeCl_3$ stain); $[\alpha]_D^{27}+121.5^\circ$ (c 1.52, $CHCl_3$); ^1H NMR (C_6D_6) $\delta = 8.40$ (1H, br s, OH), 7.70—7.74 (4H, m, Ar-H), 7.62 (2H, d, $J = 8.4$ Hz, Ar-H), 7.36—7.48 (4H, m, Ar-H), 6.89—7.24 (12H, m, Ar-H), 6.68 (1H, d, $J = 9.0$ Hz, Ar-H), 2.59 (3H, br s, CH_3); ^{13}C NMR ($CDCl_3$) $\delta = 169.5$ (C=O), 166.7 (C=O), 154.0 (2-Ar), 153.6 (2-Ar), 138.3, 135.2, 134.1, 133.9, 133.5, 133.3, 133.0, 132.5, 131.4, 130.1, 129.9, 129.7, 129.3, 128.6, 128.5, 128.2, 127.7, 127.6, 127.4, 127.1, 126.8, 126.6, 126.3, 124.9, 124.5, 123.7, 123.5, 120.2, 118.4, 113.3 (2′-Ar), 122.3 (2′-Ar), 66.4 (Ph-*C*H), 61.3 (Ph-*C*H), 56.5 (OCH_3), 54.8 (OCH_3); IR (KBr) 3300, 3025, 1650, 1625, 1598, 1503, 1460, 1250, 708, 650 cm^{-1}. Found: C, 82.49; H, 5.41; N, 2.81%. Calcd for $C_{35}H_{27}NO_3$: C, 82.49; H, 5.34; N, 2.75%.

***O*-Acylated By-Product 1e′:** $R_f = 0.57$ (EtOAc/hexane = 1 : 2); $[\alpha]_D^{28}+12.0^\circ$ (c 1.27, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.85$—7.95 (5H, m, Ar-H), 7.68 (1H, d, $J = 3.6$ Hz, NH), 7.49—7.55 (1H, m, Ar-H), 7.14—7.35 (13H, m, Ar-H), 6.90 (1H, d, $J = 8.4$ Hz, Ar-H), 4.51 (1H, d, $J = 3.6$ Hz, CH), 3.56 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) $\delta = 168.0$ (C=O), 154.2, 139.7, 139.6, 137.0, 135.1, 133.7, 132.7, 129.6, 128.7, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.2, 126.7, 126.6, 125.7, 124.6, 123.5, 120.9 113.4 (2′-Ar), 68.6 (N-CH), 56.4 (CH_3); IR (KBr) 3061, 1728, 1622, 1595, 1510, 1460, 1335, 1271, 1252, 828, 754 cm^{-1}. Found: C, 82.28; H, 5.49; N, 2.81%. Calcd for $C_{35}H_{27}NO_3$: C, 82.49; H, 5.34, N, 2.75%.

Table 6. Crystallographic Data for **1e**

Formula	$C_{35}H_{27}N_1O_3$
Formula weight	$M_r = 509.60$
Crystal color, habit	Colorless, plate
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	12.4420(13)
b/Å	8.2220(4)
c/Å	13.6680(14)
β/°	102.624(4)
V/Å^3	1364.4(2)
Z	2
D_X/Mg m^{-3}	1.240
$F(000)$	536
Radiation type	Mo $K\alpha$
Wave length/Å	0.7107
μ/mm^{-1}	0.0785
T/°C	25
θ_{max}/°	25.45
Limiting indices	$0 \leq h \leq 15, 0 \leq k \leq 10, -17 \leq l \leq 16$
No.of independent reflections	2919
No.of observed reflections	2193
R; wR	0.036; 0.038
S	0.916

General Procedure for the Asymmetric Epoxidation of Allylic Alcohols. To a solution of the chiral vanadium catalyst (9.8 mM, 12.7 µmol) readily prepared from **1** (19.1 µmol) and VO(O-*i*-Pr)$_3$ (3.0 µL, 12.7 µmol) in dry toluene (25 °C, 1 h) were added an allylic alcohol (0.254 mmol) and trityl hydroperoxide (105 mg, 0.381 mmol) at −20 °C under argon atmosphere. After the solution was stirred for 2—7 d at this temperature, the reaction was quenched by addition of sat. Na_2SO_3 aq (2 mL). Extraction of the product with ether, evaporation of solvents and chromatographic purification on silica gel afforded the corresponding 2,3-epoxy alcohol in a yield of 14—96%.

X-Ray Analysis. A crystal of hydroxamic acid **1e** was grown from ether and mounted on a glass fiber. The crystal data and the parameters for data collection, structure determination and refinement are summarized in Table 6. All diagrams and calculations were performed using maXus (MacScience, Japan). The structure was solved by direct methods followed by full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic. Reflection data with $|I| > 3\sigma(I)$ were used. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1.0/[\sigma^2(F_o)+0.03[F_o]^2]$.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC NO. 143098. The details of structure have been deposited as Document No. 73037 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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