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A New Synthetic Route to Enantiomerically Pure Axially Chiral 2,2′-Bipyridine *N*,*N*′-Dioxides. Highly Efficient Catalysts for Asymmetric Allylation of Aldehydes with Allyl(trichloro)silanes

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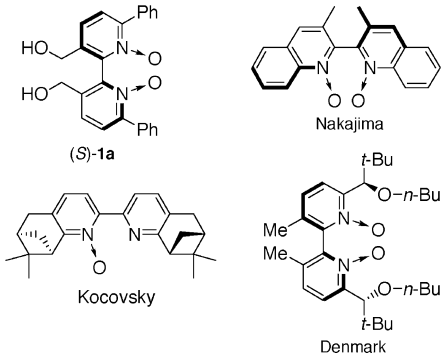
New axially chiral 2,2′-bipyridine *N*,*N*′-dioxides **1** were obtained in an enantiomerically pure form by way of cyclic diesters **6** or **7** which were formed by the esterification of diols **2** with (*R*)-2,2′-bis-(chlorocarbonyl)-1,1′-binaphthalene (**5**). Epimerization of the kinetic products at the ester formation (R_{nap},S_{pyr})-**6** to the thermodynamically stable isomers (R_{nap},R_{pyr})-**7** was observed in refluxing toluene or in the presence of trifluoroacetic acid. One of the *N*,*N*′-dioxides **1a** which is substituted with phenyl groups at the 6 and 6′ positions was found to be highly catalytically active and enantioselective for the asymmetric allylation of aldehydes with allyl(trichloro)silane giving homoallyl alcohols.

Introduction

Some of the enantiomerically pure molecules based on the axially chiral biaryl skeleton have been used successfully as powerful chiral ligands or catalysts in catalytic asymmetric reactions,[1] and the development of their preparation method has been one of the recent topics in the chiral technology because of the great utility of the enantiomerically pure axially chiral compounds.[1] The method for the preparation so far reported involves their asymmetric synthesis by enantioselective[2] and diastereoselective[3] coupling between two aryl groups, desymmetrization of symmetrically substituted biaryls,[4,5] and enantioselective ring-opening of cyclic substrates fixing axial chirality.[6,7] Of the axially chiral compounds, 2,2′-bipyridine *N*,*N*′-dioxide derivatives have recently attracted considerable attention due to their high ability as a chiral Lewis base which catalyzes the asymmetric allylation of aldehydes with allyl(trichloro)silanes,[8,9] asymmetric aldol reaction with trichlorosilyl enol ethers,[10] asymmetric conjugate addition of thiols,[11] and asymmetric ring-opening of epoxides.[12] The first example of the axially chiral 2,2′-bipyridine *N*,*N*′-dioxide reported by Nakajima was prepared by optical resolution of the racemate (Chart 1).[13] Other *N*-oxides used by Kocovsky[9] and Denmark[10] are substituted with chiral moieties other than bipyridine axial chirality. In a preliminary communication, we have reported[14] a new, efficient method

CHART 1



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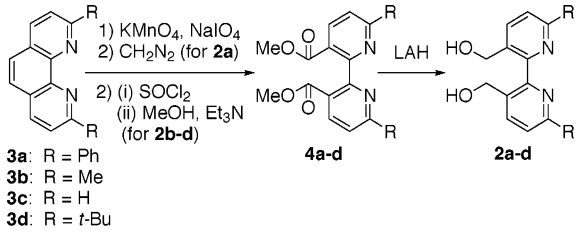
SCHEME 1



of obtaining enantiomerically pure 2,2′-bipyridine *N*,*N*′-dioxides **1**. The chiral axis of configurationally labile 2,2′-bipyridinediol **2** is fixed by the formation of cyclic diesters with (*R*)-1,1′-binaphthalene-2,2′-dicarboxylic acid and oxidation of bipyridine nitrogens giving *N*,*N*′-dioxides followed by hydrolysis to remove the dicarboxylic acid give axially chiral 2,2′-bipyridine *N*,*N*′-dioxides **1** whose axis is not labile. At the cyclic diester formation, we observed an interesting phenomenon that the kinetic product can be isomerized into the thermodynamically more stable epimeric isomer by heating. Taking advantage of this epimerization, both enantiomers of *N*,*N*′-dioxide **1** were obtained in an enantiomerically pure form using a single enantiomer of the dicarboxylic acid. Here, we wish to report a full description of the experiments on the epimerization including its kinetic studies and the results obtained for the asymmetric allylation of aldehydes catalyzed by the 2,2′-bipyridine *N*,*N*′-dioxides **1**.

Results and Discussion

Preparation of Axially Chiral 2,2′-Bipyridine *N*,*N*′-Dioxides. The bipyridinediols **2a**−**d**, which contain substituents at the 6 and 6′ positions, were readily prepared from the corresponding 2,9-disubstituted 1,10-phenanthrolines **3**[15] by a sequence of reactions consisting of oxidation with potassium permanganate and sodium periodate, esterification of the carboxylic acids, and reduction of esters **4** with lithium aluminum hydride (Scheme 1). The formation of cyclic diesters of 1,1′-binaphthalene-2,2′-dicarboxylate proceeded at room temperature with high selectivity to give one of the two possible diastereomeric isomers in a ratio of over 5:1 for all the bipyridinediols **2** (Scheme 2, upper equation). Thus, treatment of 3,3′-bis(hydroxymethyl)-6,6′-diphenyl-2,2′-bipyridine (**2a**) with an excess of (*R*)-2,2′-bis(chlorocarbonyl)-1,1′-binaphthalene (**5**)[16] in the presence of triethylamine in chloroform at room temperature for 8 h gave a high yield of cyclic diester which consists of diastereomeric isomers (R_{nap},S_{pyr})-**6a** and (R_{nap},R_{pyr})-**7a** in a ratio of 17:1, which was determined by ^{1}H NMR studies. Isomerically pure (R_{nap},S_{pyr})-**6a** was obtained in 67% isolated yield by a chromatography on silica gel followed by GPC purification. The preferential formation of the isomer (R_{nap},S_{pyr})-**6** was also observed in the esterification of other diols with (*R*)-**5**, the ratio of (R_{nap},S_{pyr})-**6** to (R_{nap},R_{pyr})-**7** being 24/1, 20/1, and 5/1 for the diols **2b**, **2c**, and **2d**, which are substituted with methyl, hydrogen, and *tert*-butyl, respectively.

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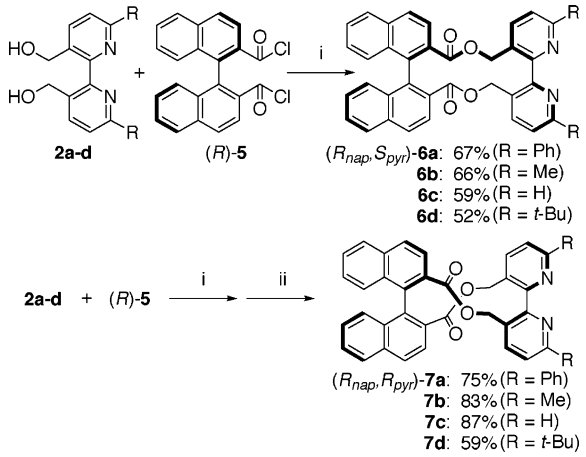
SCHEME 2[a]



[a] Reaction conditions: (i) Et_3N, $CHCl_3$, rt, 8 h; (ii) PhMe, reflux, 48 h.

An interesting epimerization was observed on heating the crude product obtained by the esterification of diol **2a** (Scheme 2, lower equation). Thus, the crude mixture consisting of (R_{nap},S_{pyr})-**6a** and (R_{nap},R_{pyr})-**7a** in a ratio of 17:1 was heated in refluxing toluene for 48 h. ^{1}H NMR studies showed that there was no detectable amount of the isomer **6a** and all of **6a** was isomerized into its epimer **7a**. It follows that the isomer **6a** is the kinetic product formed at the esterification and it can be isomerized into thermodynamically more stable isomer **7a** upon heating in toluene. After this isomerization procedure, the isomerically pure **7a** was isolated in 75% yield. The absolute configuration of the bipyridine axis of these isomers was determined by X-ray crystallography of the esters **6a** and **7a**. As can be seen from the ORTEP drawings shown in Figure 1, the kinetic product **6a** has the *S* configuration on its bipyridine axis while thermodynamically stable isomer **7a** has the *R* configuration. The complete epimerization of bipyridine axis from *S* to *R* on heating was also observed for the cyclic diesters **6b**, **6c**, and **6d**, which gave (R_{nap},R_{pyr})-**7b**−**d** in 83%, 87%, and 59% isolated yields, respectively. This epimerization will be discussed in detail in the next section.

Both the kinetic products (R_{nap},S_{pyr})-**6a**−**d** and the thermodynamic products (R_{nap},R_{pyr})-**7a**−**d** were readily converted into the axially chiral bipyridine *N*,*N*′-dioxides **1a**−**d** without loss of the axial chirality of the bipyridine moiety (Scheme 3). For example, oxidation of the bipyridine moiety in (R_{nap},S_{pyr})-**6a** with *m*-chloroperbenzoic acid gave *N*,*N*′-dioxide (R_{nap},S_{pyr})-**8a** in 63% yield. The formation of *N*,*N*′-dioxide fixes the axial chirality of bipyridine moiety and does not allow the rotation about the bipyridine axis even after the removal of the chiral diacid. Alkaline hydrolysis of **8a** gave 85% yield of (*S*)-3,3′-bis(hydroxymethyl)-6,6′-diphenyl-2,2′-bipyridine *N*,*N*′-dioxide (**1a**), whose enantiomeric purity determined by HPLC analysis was >99% ee. The chiral source, 1,1′-binaphthalene-2,2′-dicarboxylic acid, was recovered quantitatively. Starting from the thermodynamic isomer (R_{nap},R_{pyr})-**7a**, the oxidation and alkaline hydrolysis gave (*R*) isomer of the bipyridine *N*,*N*′-dioxide **1a**. Thus, the achiral bipyridine diol **2a** can be converted into either enantiomer of the axially chiral *N*,*N*′-dioxide **1a** in an enantiomerically pure form simply by choosing the reac-

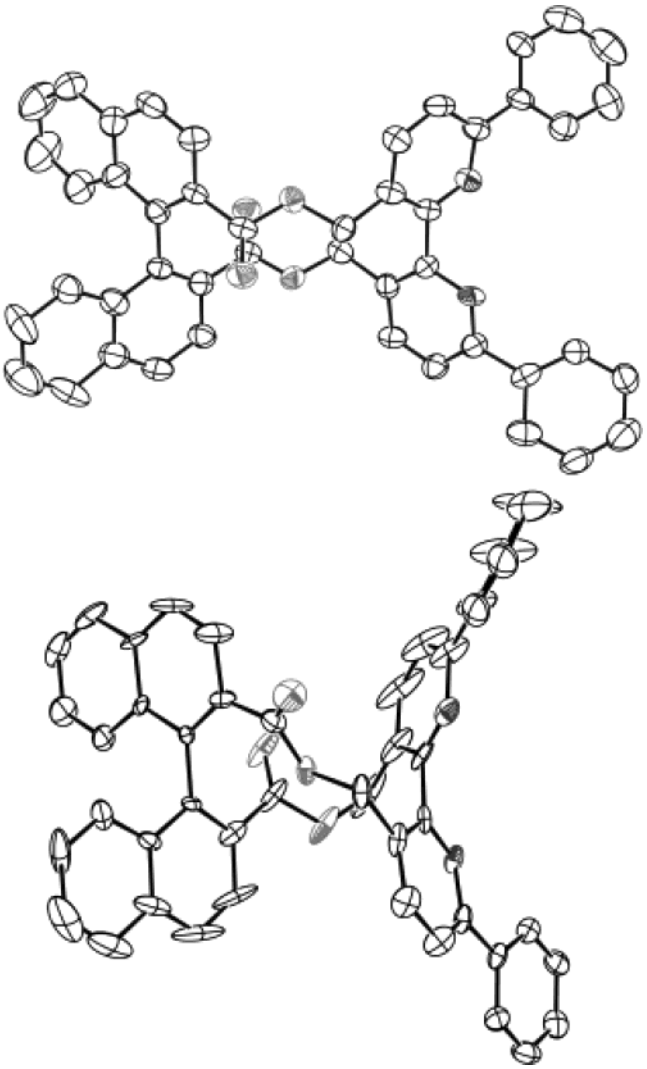


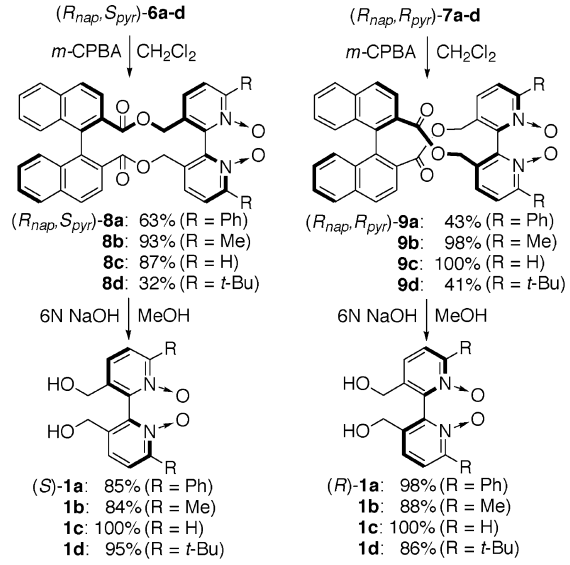
FIGURE 1. Ortep drawings for (R_{nap},S_{pyr})-**6a** (upper) and (R_{nap},R_{pyr})-**7a** (lower). Thermal ellipsoids are shown at the 30% probability level. The solvent molecules and all hydrogens are omitted for simplicity.

tion procedures, oxidation of the bipyridine moiety before or after the epimerization. Similarly, cyclic diesters (R_{nap},S_{pyr})-**6b**−**d** and (R_{nap},R_{pyr})-**7b**−**d** gave the corresponding bipyridine *N*,*N*′-dioxides (*S*)-**1b**−**d** and (*R*)-**1b**−**d**, respectively.

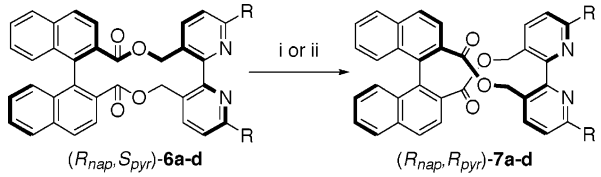
Kinetic Studies on the Epimerization of Cyclic Diesters. Epimerization of (R_{nap},S_{pyr})-**6a** to (R_{nap},R_{pyr})-**7a** proceeded thermally, and the activation parameters were determined to be $\Delta G^{\ddagger}_{103°C} = 104$ kJ·mol^{-1}, $\Delta H^{\ddagger}_{103°C} = 111$ kJ·mol^{-1}, and $\Delta S^{\ddagger}_{103°C} = 19$ J·mol^{-1}K^{-1}, which were measured by monitoring the ratio of (R_{nap},S_{pyr})-**6a** to (R_{nap},R_{pyr})-**7a** by use of ^{1}H NMR spectroscopy (Scheme 4, Table 1). Plotting ln([(R_{nap},S_{pyr})-**6a**]/[(R_{nap},S_{pyr})-**6a**]$_0$) versus time gave a straight line ($R^2 \geq 0.99$), indicating that the epimerization is first order in [(R_{nap},S_{pyr})-**6a**]. The rate constant of epimerization at 103 °C is 2.91×10^{-2} h^{-1}. Other species were not detected during the epimerization reaction. The isomer (R_{nap},R_{pyr})-**7a** is much more stable than its epimer (R_{nap},S_{pyr})-**6a**, because a detectable amount of (R_{nap},S_{pyr})-**6a** was not observed after heating the isomerically pure (R_{nap},R_{pyr})-**7a** in refluxing toluene. The activation parameters of (R_{nap},S_{pyr})-**6b**−**d** were determined in a similar manner (Table 1). The activation free energy for all the derivatives (R_{nap},S_{pyr})-**6a**−**d** are almost the same irrespective of the substituents at 6 and 6′ positions. It is likely that the epimerization proceeds via a transition state which involves a bipyridine of planar conformation. Activation barrier is considered to be determined by the repulsion between methylene protons, the repulsion between lone pairs of pyridine nitrogens, and the stabilization of bipyridine by π-conjugation. The repulsion between methylene protons is probably the most decisive factor, because the substituents at the 6 and 6′ positions did not affect the activation free energy of epimerization.

Addition of trifluoroacetic acid greatly accelerated the epimerization (Table 2). The rate constant of epimerization of (R_{nap},S_{pyr})-**6a** in the presence of 1 equiv of trifluoroacetic acid at 33 °C was 0.23 h^{-1}, much larger than that in the absence of trifluoroacetic acid. Comparing this rate constant with the value estimated by the extrapolation of the Arrhenius plot in the absence of acid to 33 °C, the epimerization in the presence of acid is 23 000 times faster than that in the absence of acid. It is known

SCHEME 3



SCHEME 4[a]



[a] Reaction conditions: (i) PhMe, reflux; (ii) trifluoroacetic acid, PhMe.

TABLE 1. Activation Parameters for Thermal Isomerization of (R_{nap},S_{pyr})-6a−d Calculated from Arrhenius Plot

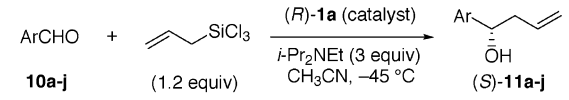
ligand	$\Delta G^{\ddagger}_{103°C}$ (kJ·mol^{-1})	$k_{103°C}$ (h^{-1})	$\Delta H^{\ddagger}_{103°C}$ (kJ·mol^{-1})	$\Delta S^{\ddagger}_{103°C}$ (J·K^{-1}mol^{-1})
(R_{nap},S_{pyr})-**6a**	104	2.91×10^{-2}	111	18.6
(R_{nap},S_{pyr})-**6b**	104	2.29×10^{-2}	162	154
(R_{nap},S_{pyr})-**6c**	102	5.87×10^{-2}	141	104
(R_{nap},S_{pyr})-**6d**	102	5.43×10^{-2}	116	37.2

TABLE 2. Rate Constant and Activation Free Energy for Proton-Promoted Isomerization of (R_{nap},S_{pyr})-6a−d

ligand	$\Delta G^{\ddagger}_{H^+ 33°C}$ (kJ·mol^{-1})	$k_{H^+ 33°C}$ (h^{-1})	$\Delta G^{\ddagger}_{33°C}$[a] (kJ·mol^{-1})	$k_{33°C}$[a] (h^{-1})	$k_{H^+ 33°C}/k_{33°C}$
(R_{nap},S_{pyr})-**6a**	79	0.23	1.0×10^2	1.0×10^{-5}	2.3×10^4
(R_{nap},S_{pyr})-**6b**	89	0.0042	1.2×10^2	1.7×10^{-7}	2.5×10^4
(R_{nap},S_{pyr})-**6c**	81	0.11	1.1×10^2	1.9×10^{-6}	5.5×10^4
(R_{nap},S_{pyr})-**6d**	77	0.40	1.0×10^2	1.3×10^{-5}	3.1×10^4

[a] These values are estimated by the extrapolation of the Arrhenius plot in the absence of acid to 33 °C.

SCHEME 5



Ar = 4-MeOC$_6$H$_4$ (**a**)

(*R*)-**1a**	time (h)	yield (%)	% ee
0.1	2.5	96	94
0.01	12	68	94

Ar = 3,4-(MeO)$_2$C$_6$H$_3$ (**b**), 4-*n*-BuOC$_6$H$_4$ (**c**), 4-*t*-BuC$_6$H$_4$ (**d**), 4-MeC$_6$H$_4$ (**e**), Ph (**f**), 1-Nap (**g**), 2-MeOC$_6$H$_4$ (**h**), 4-CF$_3$C$_6$H$_4$ (**i**), (*E*)-PhCH=CH (**j**).

that unsubstituted 2,2′-bipyridine exists in a trans conformation in organic solvent, and it takes a stable cis conformation in an acidic solution.[17] The protonation of pyridine nitrogen is proposed to accelerate the epimerization by stabilizing the planar transition state.

Application of Axially Chiral 2,2′-Bipyridine *N*,*N*′-Dioxides 1 to Asymmetric Allylation with Allyl(trichloro)silanes. As reported in our previous paper,[14] the bipyridine dioxide (*R*)-**1a** which contains two phenyl groups at the 6 and 6′ positions has high catalytic activity as well as high enantioselectivity for the asymmetric allylation with allyl(trichloro)silanes. For example, the reaction of 4-methoxybenzaldehyde (**10a**) with allyl(trichloro)silanes (1.2 equiv) in acetonitrile at −45 °C was completed within 2.5 h even in the presence of 0.1 mol % of (*R*)-**1a** to give 96% yield of the corresponding homoallyl alcohol **11a**, which is an (*S*) isomer of 94% ee (Scheme 5). The high catalytic activity of (*R*)-**1a** observed here makes a remarkable contrast to the much lower catalytic activity of other chiral Lewis acid and base catalysts used so far in the asymmetric reactions,[18] where 1−10 mol % of the catalyst is usually required for a reasonable reaction rate. The other bipyridine oxides **1b**−**d** were not so effective as **1a** for the asymmetric allylation of aldehydes.[14]

It has been proposed that bidentate *N*-oxide attaches to the silicon atom to generate a pentacoordinate cationic silicate, which activates the carbonyl moiety of aldehyde as Lewis acid[8,12,19] and the nucleophilic attack to carbonyl carbon takes place at the γ position of allyl group via six-membered cyclic chairlike transition structure to give the corresponding homoallyl alcohol.[20] Our catalyst system is consistent with the proposed mechanism. Crotylation catalyzed by (*R*)-**1a** gave only γ-allylated homoallyl alcohol, whose relative configuration is syn from *Z*-crotyl(trichloro)silane while anti from *E*-crotyl(trichloro)silane, both in perfect regio- and diastereoselectivity (Scheme 6). These results support the six-membered ring chairlike transition states.

SCHEME 6

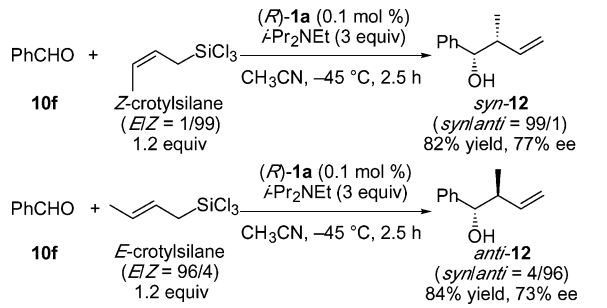


TABLE 3. Asymmetric Allylation of Aldehydes 10 with Allyl(trichloro)silane Catalyzed by 0.1 mol % of (*R*)-1a[a]

entry	aldehyde **10**	yield[b] (%) of **11**	% ee[c] of **11** (config)	$[\alpha]^{20}_D$ of **11** (*c* in C$_6$H$_6$)
1	4-MeOC$_6$H$_4$CHO (**10a**)	96 (**11a**)	94 (*S*)	−32.7 (1.0)
2	3,4-(MeO)$_2$C$_6$H$_3$CHO (**10b**)	95 (**11b**)	98 (*S*)	−37.8 (1.9)
3	4-*n*-BuOC$_6$H$_4$CHO (**10c**)	93 (**11c**)	94 (*S*)	−23.2 (2.6)[d]
4	4-*t*-BuC$_6$H$_4$CHO (**10d**)	93 (**11d**)	89 (*S*)	−24.1 (1.0)[d]
5	4-MeC$_6$H$_4$CHO (**10e**)	94 (**11e**)	89 (*S*)	−43.4 (1.1)
6	PhCHO (**10f**)	95 (**11f**)	84 (*S*)	−48.9 (1.0)
7	1-NapCHO (**10g**)	90 (**11g**)	81 (*S*)	−84.1 (1.0)
8	2-MeOC$_6$H$_4$CHO (**10h**)	93 (**11h**)	76 (*S*)	−68.4 (1.0)
9	4-CF$_3$C$_6$H$_4$CHO (**10i**)	83 (**11i**)	56 (*S*)	−18.1 (1.9)
10	(*E*)-PhCH=CHCHO (**10j**)	95 (**11j**)	60 (*S*)	+10.9 (1.0)[d]

[a] The allylation was carried out with (*R*)-**1a** (0.1 mol %), allyl(trichloro)silane (1.2 equiv), and diisopropylethylamine (3 equiv) in 1.0 M acetonitrile solution at −45 °C for 2.5 h. [b] Isolated yield. [c] Determined by GLC analysis with CP-Chirasil-Dex for **11a**,**b**,**d**,**e**, by HPLC analysis with Chiralcel OD-H for **11c**,**f**,**g**,**h**,**j**, and by HPLC analysis with Chiralcel OJ for **11i**. [d] Specific rotation in Et$_2$O.

In the presence of 0.1 mol % of (*R*)-**1a**, Lewis base-catalyzed allylation of various aromatic aldehydes proceeded smoothly in acetonitrile at −45 °C to give the corresponding homoallyl alcohols in high yield (Table 3). The enantioselectivity was strongly dependent on the substituents on the phenyl ring, being higher with more electron donating groups. The highest enantioselectivity (98% ee) was observed in the reaction of 3,4-dimethoxybenzaldehyde (**10b**). High catalytic activity was also observed for an α,β-unsaturated aldehyde, although aliphatic aldehydes were not good substrates, showing poor reactivity and enantioselectivity.

Conclusion

New axially chiral 2,2′-bipyridine *N*,*N*′-dioxides **1** were obtained by a new method which does not require any procedures for the separation of enantiomers or diastereoisomers. The present method involves the formation of a diastereomeric chiral cyclic diester as a key step, where an interesting epimerization from the kinetic product to the thermodynamically stable isomer was observed. Either enantiomer of the dioxides, (*R*)-**1** or (*S*)-**1**, can be obtained in an enantiomerically pure form by choosing the reaction procedures. One of the dioxides, which is substituted with phenyl groups at 6 and 6′ positions, exhibited extremely high catalytic activity for

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the asymmetric allylation of aldehydes with allyl(trichloro)silane giving homoallyl alcohols. The low catalyst loading realized here (0.01−0.1 mol %) is unprecedented for the Lewis base-catalyzed asymmetric reactions.

Experimental Section

General Methods. All moisture-sensitive manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard or residual peak of toluene-d_8 (δ 2.32 of methyl proton) for ^{1}H NMR and chloroform-*d* (δ 77.0 ppm) for ^{13}C NMR.

Materials. 2,9-Diphenyl-1,10-phenanthroline (**3a**),[15] 2,9-di-*tert*-butyl-1,10-phenanthroline (**3d**),[15] 3,3′-bis(methoxycarbonyl)-6,6′-dimethyl-2,2′-bipyridine (**4b**),[21] and 3,3′-bis(hydroxymethyl)-2,2′-bipyridine (**2c**)[22] were prepared according to the reported procedures.

3,3′-Bis(methoxycarbonyl)-6,6′-diphenyl-2,2′-bipyridine (4a). A mixture of 2,9-diphenyl-1,10-phenanthroline (**3a**) (4.43 g, 13.3 mmol), potassium carbonate (5.3 g, 38 mmol), sodium periodate (22 g, 0.10 mol), potassium permanganate (2.7 g, 17 mmol), *tert*-butyl alcohol (340 mL), and water (510 mL) was refluxed vigorously for 14 h. The black precipitate was removed from the resulting mixture by filtration, and the filter cake was washed with chloroform (ca. 100 mL). The filtrate was concentrated to ca. 200 mL under reduced pressure, and the starting material was recovered by filtration in 39% (1.72 g). The filtrate was acidified with concentrated hydrochloric acid to give white precipitate by filtration. After the precipitate was dried under reduced pressure at 40 °C for 3 h, the suspension of bipyridine derivative in diethyl ether (300 mL) was treated with diazomethane, quenched with acetic acid, and adjusted to pH 8 with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with chloroform three times. The combined organic layer was washed with aqueous sodium chloride, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give 3,3′-bis(methoxycarbonyl)-6,6′-diphenyl-2,2′-bipyridine (**4a**) (1.99 g, 35% yield): ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 6H), 7.45 (m, 6H), 7.87 (d, J = 8.3 Hz, 2H), 8.06 (d, J = 8.7 Hz, 4H), 8.33 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 52.3, 118.9, 125.1, 127.3, 128.8, 129.8, 138.0, 138.8, 158.1, 167.5. Anal. Calcd for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75. Found: C, 73.39; H, 4.69.

3,3′-Bis(hydroxymethyl)-6,6′-diphenyl-2,2′-bipyridine (2a). To a solution of 3,3′-bis(methoxycarbonyl)-6,6′-diphenyl-2,2′-bipyridine (**4a**) (2.36 g, 5.55 mmol) in tetrahydrofuran (55 mL) under nitrogen atmosphere was added lithium aluminum hydride (347 mg, 9.15 mmol) at −78 °C. The reaction mixture was stirred at room temperature for 2 h, quenched with water (0.42 mL), stirred for additional 30 min, and filtered through Celite. The filtrate was dried over anhydrous sodium sulfate and evaporated, and the residue was chromatographed on silica gel (ethyl acetate/hexane/chloroform = 1/1/1) to give 3,3′-bis(hydroxymethyl)-6,6′-diphenyl-2,2′-bipyridine (**2a**) (1.79 g, 88% yield): ^{1}H NMR ($CDCl_3$) δ 4.49 (d, J = 7.1 Hz, 4H), 5.56 (t, J = 7.1 Hz, 2H), 7.45 (t, J = 7.3 Hz, 2H), 7.50 (t, J = 7.3 Hz, 4H), 7.83 (d, J = 8.1 Hz, 2H), 7.89 (d, J = 8.7 Hz, 4H), 8.02 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 62.9, 121.6, 127.1, 129.1, 129.4, 135.2, 138.6, 140.6, 156.0, 157.1. Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47. Found: C, 78.03; H, 5.31.

3,3′-Bis(hydroxymethyl)-6,6′-dimethyl-2,2′-bipyridine (2b): 76% yield; ^{1}H NMR ($CDCl_3$) δ 2.60 (s, 6H), 4.40 (s, 4H), 6.13 (b, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 23.8, 62.9, 123.4, 133.8, 140.1, 155.8, 156.3. Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60. Found: C, 68.59; H, 6.81.

3,3′-Bis(hydroxymethyl)-6,6′-di-*tert*-butyl-2,2′-bipyridine (2d). A mixture of 2,9-di-*tert*-butyl-1,10-phenanthroline (**3d**) (1.79 g, 6.13 mmol), potassium carbonate (2.5 g, 18 mmol), sodium periodate (10 g, 49 mmol), potassium permanganate (1.3 g, 8.5 mmol), *tert*-butyl alcohol (200 mL), and water (300 mL) was refluxed vigorously for 9.5 h. The black precipitate was removed from the resulting mixture by filtration, and the filter cake was washed with chloroform (ca. 100 mL). *tert*-Butyl alcohol was removed from the filtrate, and the resulting solution was acidified with concentrated hydrochloric acid and extracted with chloroform three times. The combined organic layer was washed with aqueous sodium chloride, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. To the residue was added thionyl chloride (13 mL, 0.18 mol); the reaction mixture was refluxed for 7 h. Thionyl chloride was evaporated under reduced pressure. To the residue was added methanol (10 mL, 0.25 mol), followed by triethylamine dropwise at 0 °C. The reaction mixture was stirred at room temperature for 8 h. Methanol was removed from the mixture. The residue was dissolved to chloroform, the mixture was washed with 0.5 N hydrochloric acid, saturated aqueous $NaHCO_3$, aqueous sodium chloride, dried over anhydrous sodium sulfate, and evaporated under reduced pressure, and the residue was passed through silica gel column to give the mixture of starting material **3d** and 3,3′-bis(methoxycarbonyl)-6,6′-di-*tert*-butyl-2,2′-bipyridine (**4d**) (1.76 g, **3d**/**4d** = 0.6/1), which was used for the next reaction immediately. **3d**: ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 18H), 7.70 (s, 2H), 7.71 (d, J = 8.5 Hz, 2H), 8.13 (d, J = 8.5 Hz, 2H). **4d**: ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 18H), 3.72 (s, 6H), 7.38 (d, J = 8.0 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H).

To the mixture (1.76 g) in tetrahydrofuran (46 mL) under nitrogen atmosphere was added lithium aluminum hydride (176 mg, 4.63 mmol) at −78 °C. The reaction mixture was stirred at room temperature for 2 h, quenched with water (0.34 mL), stirred for additional 30 min, and filtered through Celite. The filtrate was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was chromatographed on silica gel (hexane/ethyl acetate = 1/1) to give starting material (**3d**) (422 mg, 24% recovery) and 3,3′-bis(hydroxymethyl)-6,6′-dimethyl-2,2′-bipyridine (**2d**) (634 mg, 43% yield): ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 18H), 4.37 (d, J = 6.9 Hz, 4H), 5.43 (t, J = 6.9 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 30.1, 37.3, 62.8, 119.8, 133.5, 139.7, 156.1, 167.4. Anal. Calcd for $C_{20}H_{28}N_2O_2$: C, 73.14; H, 8.59. Found: C, 73.42; H, 8.42.

Cyclic diester ((R_{nap},S_{pyr})-6a). To a solution of (*R*)-2,2′-bis(chlorocarbonyl)-1,1′-binaphthalene ((*R*)-**5**) (1.08 g, 2.85 mmol) in chloroform (19 mL) under nitrogen atmosphere was added dropwise a solution of **2a** (700 mg, 1.90 mmol) and triethylamine (1.1 mL, 7.6 mmol) in chloroform (19 mL) at 0 °C. The reaction mixture was stirred at room temperature for 21 h. It was diluted with chloroform and washed with water, 0.1 N hydrochloric acid, saturated aqueous $NaHCO_3$, and aqueous sodium chloride. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was chromatographed on silica gel (benzene/ethyl acetate = 20/1) and purified by GPC to give (R_{nap},S_{pyr})-**6a** (860 mg, 67% yield): $[\alpha]^{20}_D$ +115.1 (*c* 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.89 (d, J = 12.0 Hz, 2H), 5.19 (d, J = 12.0 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 7.27 (t, J = 8.5 Hz, 2H), 7.40 (t, J = 7.3 Hz, 2H), 7.46 (t, J = 7.3 Hz, 4H), 7.51 (t, J = 7.5 Hz, 2H), 7.84 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H), 8.00 (m, 6H), 8.09 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 63.8, 120.8, 124.5, 127.0, 127.2, 127.3, 127.5, 127.5, 127.9, 128.5, 128.6, 129.1, 129.9, 132.7, 133.9, 135.7, 138.6, 139.5, 155.9, 158.0, 167.8.

Cyclic diester ((R_{nap},S_{pyr})-6b): 66% yield; $[\alpha]^{20}_D$ +0.4 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.61 (s, 6H), 4.70 (d, J = 11.9 Hz, 2H), 5.12 (d, J = 11.9 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 7.27 (t, J = 7.5 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 7.88 (d, J = 8.1 Hz, 2H),

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7.91 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 24.5, 63.8, 123.8, 124.6, 126.2, 127.1, 127.4, 127.6, 128.0, 128.5, 130.2, 132.8, 134.0, 135.6, 139.1, 155.3, 159.6, 168.1.

Cyclic diester ((R_{nap},S_{pyr})-6c): 59% yield; $[\alpha]^{20}_D$ −27.7 (c 0.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.76 (d, J = 12.1 Hz, 2H), 5.16 (d, J = 12.1 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 7.27 (t, J = 8.1 Hz, 2H), 7.48 (dd, J = 7.7, 4.8 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.98 (d, J = 8.6 Hz, 2H), 8.02 (d, J = 7.7 Hz, 2H), 8.76 (b, 2H); ^{13}C NMR ($CDCl_3$) δ 63.8, 123.9, 124.5, 127.2, 127.5, 127.6, 128.0, 128.6, 129.2, 130.0, 132.8, 134.1, 135.7, 139.0, 150.5, 155.8, 168.0.

Cyclic diester ((R_{nap},S_{pyr})-6d): 52% yield; $[\alpha]^{20}_D$ +1.7 (c 2.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 18H), 4.78 (d, J = 12.0 Hz, 2H), 5.09 (d, J = 12.0 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H), 7.25 (t, J = 7.6 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 30.0, 37.6, 64.0, 118.9, 124.6, 125.5, 127.0, 127.4, 127.6, 128.0, 128.5, 130.2, 132.8, 134.0, 135.8, 138.6, 155.4, 168.1, 169.7.

Cyclic Diester ((R_{nap},R_{pyr})-7a). To a solution of (*R*)-2,2′-bis(chlorocarbonyl)-1,1′-binaphthalene (*R*)-**5** (185 mg, 0.489 mmol) in chloroform (3.3 mL) under nitrogen atmosphere was added dropwise a solution of **4a** (120 mg, 0.326 mmol) and triethylamine (0.18 mL, 1.3 mmol) in chloroform (3.3 mL) at 0 °C. The reaction mixture was stirred at room temperature for 24 h, and the solvent was removed. Toluene (6.6 mL) was added, and the mixture was refluxed for 48 h. It was diluted with chloroform and washed with water, 0.1 N hydrochloric acid, saturated aqueous $NaHCO_3$, and aqueous sodium chloride. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was chromatographed on silica gel (benzene/ethyl acetate = 20/1) and purified by GPC to give (R_{nap},R_{pyr})-**7a** (171 mg, 75% yield): $[\alpha]^{20}_D$ +617 (c 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.83 (d, J = 12.0 Hz, 2H), 5.86 (d, J = 12.0 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 7.18 (t, J = 7.6 Hz, 2H), 7.36 (m, 12H), 7.65 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.7 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 8.05 (d, J = 7.6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 64.7, 119.2, 125.4, 126.8, 127.0, 127.4, 127.5, 127.6, 127.9, 128.0, 128.8, 129.1, 132.8, 134.4, 138.5, 138.9, 139.7, 156.3, 156.9, 166.7. Anal. Calcd for $C_{46}H_{30}N_2O_4$: C, 81.88; H, 4.48. Found: C, 81.99; H, 4.71.

Cyclic diester ((R_{nap},R_{pyr})-7b): 83% yield; $[\alpha]^{20}_D$ +404 (c 0.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.59 (s, 6H), 4.63 (d, J = 11.9 Hz, 2H), 5.58 (d, J = 11.9 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 7.9 Hz, 2H), 7.14 (t, J = 7.5 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.54 (d, J = 8.7 Hz, 2H), 7.78 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 24.1, 64.3, 121.9, 125.3, 126.7, 127.0, 127.3, 127.5, 127.5, 127.8, 127.9, 132.7, 134.3, 138.5, 139.2, 156.3, 157.5, 166.6. Anal. Calcd for $C_{36}H_{26}N_2O_4$: C, 78.50; H, 4.76. Found: C, 78.53; H, 4.64.

Cyclic diester ((R_{nap},R_{pyr})-7c): 87% yield; $[\alpha]^{20}_D$ +315 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.70 (d, J = 12.2 Hz, 2H), 5.69 (d, J = 12.2 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 7.17 (td, J = 7.8, 1.5 Hz, 2H), 7.22 (dd, J = 7.4, 4.9 Hz, 2H), 7.37 (dd, J = 7.8, 2.0 Hz, 2H), 7.46 (td, J = 7.6, 1.5 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 7.9 Hz, 2H), 8.63 (dd, J = 4.9, 1.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 64.6, 122.7, 125.3, 126.8, 127.4, 127.6, 127.6, 127.8, 130.4, 132.8, 134.4, 138.6, 138.9, 148.5, 156.9, 166.6. Anal. Calcd for $C_{34}H_{22}N_2O_4$: C, 78.15; H, 4.24. Found: C, 78.40; H, 4.46.

Cyclic diester ((R_{nap},R_{pyr})-7d): 59% yield; $[\alpha]^{20}_D$ +418 (c 0.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 18H), 4.63 (d, J = 11.4 Hz, 2H), 5.80 (d, J = 11.4 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 7.15 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 30.2, 37.5, 65.1, 117.5, 125.2, 126.7, 127.2, 127.3, 127.4, 127.5, 127.8, 128.0, 132.8, 134.3, 138.5, 139.1, 155.9, 166.6, 168.1. Anal. Calcd for $C_{42}H_{38}N_2O_4$: C, 79.47; H, 6.03. Found: C, 79.64; H, 6.11.

Cyclic Diester *N*,*N*′-Dioxide ((R_{nap},S_{pyr})-8a). To a solution of (R_{nap},S_{pyr})-**6a** (393 mg, 0.583 mmol) in dichloromethane (5.8 mL) was added *m*-chloroperbenzoic acid (502 mg, 2.04 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 64 h, before water was added. It was extracted with chloroform three times. The combined organic layer was washed with saturated aqueous $NaHCO_3$ and aqueous sodium chloride and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel (ethyl acetate/hexane/chloroform = 2/1/1) to give (R_{nap},S_{pyr})-**8a** (261 mg, 63% yield) and a mixture of substrate and the monoxide (132 mg). (R_{nap},S_{pyr})-**8a**: $[\alpha]^{20}_D$ +190.9 (c 0.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.74 (d, J = 12.0 Hz, 2H), 5.21 (d, J = 12.0 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 7.26 (t, J = 7.4 Hz, 2H), 7.41 (m, 6H), 7.52 (t, J = 7.1 Hz, 2H), 7.62 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 8.9 Hz, 2H), 7.84 (m, 6H), 7.93 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 63.3, 124.6, 126.7, 127.2, 127.5, 127.6, 128.0, 128.0, 128.6, 129.2, 129.5, 129.7, 131.8, 132.8, 133.4, 134.2, 136.0, 142.4, 149.3, 167.4.

Cyclic Diester *N*,*N*′-Dioxide ((R_{nap},S_{pyr})-8b). The above-mentioned procedure was performed with a smaller amount of *m*-chloroperbenzoic acid (2.5 equiv) and shorter reaction time (8 h), because (R_{nap},S_{pyr})-**6b** had higher reactivity. Cyclic diester *N*,*N*′-dioxide (R_{nap},S_{pyr})-**8b** was obtained in 93% yield: $[\alpha]^{20}_D$ +73.5 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 6H), 4.53 (d, J = 12.0 Hz, 2H), 5.15 (d, J = 12.0 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 7.26 (td, J = 7.6, 1.1 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.52 (td, J = 7.6, 1.1 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 17.9, 63.3, 124.5, 126.9, 127.2, 127.2, 127.5, 127.6, 128.0, 128.7, 129.5, 132.4, 132.8, 134.1, 135.7, 141.6, 149.9, 167.5.

Cyclic Diester *N*,*N*′-Dioxide ((R_{nap},S_{pyr})-8c). The title compound was prepared according to the procedure described for (R_{nap},S_{pyr})-**8b**: 87% yield; $[\alpha]^{20}_D$ +46.5 (c 0.50, $CHCl_3$/MeOH = 1/1); ^{1}H NMR ($CDCl_3$) δ 4.58 (d, J = 12.1 Hz, 2H), 5.17 (d, J = 12.1 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 7.27 (td, J = 7.6, 1.1 Hz, 2H), 7.47 (dd, J = 8.1, 6.5 Hz, 2H), 7.52 (td, J = 7.6, 1.1 Hz, 2H), 7.61 (d, J = 7.7 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.93 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.6 Hz, 2H), 8.34 (dd, J = 6.5, 1.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 63.0, 124.5, 126.7, 127.2, 127.3, 127.5, 127.7, 128.0, 128.7, 129.2, 132.8, 134.2, 135.3, 136.0, 139.7, 141.3, 167.4.

Cyclic Diester *N*,*N*′-Dioxide ((R_{nap},S_{pyr})-8d). The title compound was prepared according to the procedure described for (R_{nap},S_{pyr})-**8a**: 32% yield; $[\alpha]^{20}_D$ +76.9 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 18H), 4.58 (d, J = 12.1 Hz, 2H), 5.17 (d, J = 12.1 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.48 (s, 4H), 7.50 (t, J = 7.6 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.7, 36.4, 63.5, 124.1, 124.7, 125.9, 127.2, 127.6, 127.6, 128.0, 128.6, 129.5, 132.2, 132.9, 134.2, 136.1, 143.8, 158.0, 167.6.

Cyclic Diester *N*,*N*′-Dioxide ((R_{nap},R_{pyr})-9a). The procedure described above for compound (R_{nap},S_{pyr})-**8a** was followed starting from (R_{nap},R_{pyr})-**7a** (1.10 g, 1.56 mmol), *m*-chloroperbenzoic acid (1.2 g, 4.8 mmol), and dichloromethane (16 mL). The mixture was purified as described for (R_{nap},S_{pyr})-**8a** to give (R_{nap},R_{pyr})-**9a** (491 mg, 43% yield) and a mixture of substrate and the monoxide (537 mg). The mixture was oxidized according to the same procedure to give (R_{nap},R_{pyr})-**9a** (316 mg, 28% yield). The combined (R_{nap},R_{pyr})-**9a** was 806 mg (71% yield). (R_{nap},R_{pyr})-**9a**: $[\alpha]^{20}_D$ +875 (c 0.50 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.99 (d, J = 12.0 Hz, 2H), 5.27 (d, J = 12.0 Hz, 2H), 6.90 (t, J = 7.8 Hz, 4H), 7.22 (t, J = 7.3 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.50 (m, 8H), 7.71 (d, J = 8.8 Hz, 2H), 7.91 (m, 8H); ^{13}C

NMR ($CDCl_3$) δ 63.9, 125.4, 126.6, 126.8, 127.1, 127.5, 127.7, 127.9, 128.0, 128.3, 129.5, 129.8, 132.5, 132.9, 134.6, 135.5, 138.9, 143.0, 149.4, 166.4. Anal. Calcd for $C_{46}H_{30}N_2O_6$: C, 78.17; H, 4.28. Found: C, 78.15; H, 4.20.

Cyclic Diester *N,N′*-Dioxide ((*R*$_{nap}$,*R*$_{pyr}$)-9b). The title compound was prepared according to the procedure described for (R_{nap},S_{pyr})-**8b**: 98% yield; $[\alpha]^{20}_D$ +780 (*c* 0.35, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.57 (s, 6H), 4.85 (d, J = 12 Hz, 2H), 5.14 (d, J = 12 Hz, 2H), 6.67 (d, J = 7.9 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 7.18 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.0, 63.7, 125.3, 125.7, 126.2, 126.9, 127.4, 127.6, 127.7, 127.8, 127.9, 132.7, 134.1, 134.5, 138.7, 142.2, 149.2, 166.4. Anal. Calcd for $C_{36}H_{26}N_2O_6$: C, 74.22; H, 4.50. Found: C, 74.29; H, 4.55.

Cyclic Diester *N,N′*-Dioxide ((*R*$_{nap}$,*R*$_{pyr}$)-9c). The title compound was prepared according to the procedure described for (R_{nap},S_{pyr})-**8b**: 100% yield; $[\alpha]^{20}_D$ +810 (*c* 1.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.95 (d, J = 12.5 Hz, 2H), 5.24 (d, J = 12.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 7.6 Hz, 2H), 7.20 (t, J = 7.7 Hz, 2H), 7.26 (t, J = 7.1 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 8.31 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 63.8, 125.2, 125.8, 127.0, 127.1, 127.4, 127.5, 127.9, 127.9, 132.7, 134.5, 137.1, 138.7, 139.5, 141.8, 166.4. Anal. Calcd for $C_{34}H_{22}N_2O_6$: C, 73.64; H, 4.00. Found: C, 73.61; H, 4.28.

Cyclic Diester *N,N′*-Dioxide ((*R*$_{nap}$,*R*$_{pyr}$)-9d). The title compound was prepared according to the procedure described for (R_{nap},S_{pyr})-**8a**: 41% yield; $[\alpha]^{20}_D$ +94.0 (*c* 0.73, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 18H), 4.83 (d, J = 12.1 Hz, 2H), 5.13 (d, J = 12.1 Hz, 2H), 6.78 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 27.2, 36.6, 63.9, 122.9, 125.4, 126.6, 127.0, 127.4, 127.7, 127.7, 127.8, 127.9, 132.8, 133.8, 134.5, 138.6, 144.5, 158.1, 166.4. Anal. Calcd for $C_{42}H_{38}N_2O_6$: C, 75.66; H, 5.74. Found: C, 75.25; H, 5.70.

(*S*)-3,3′-Bis(hydroxymethyl)-6,6′-diphenyl-2,2′-bipyridine *N,N′*-Dioxide ((*S*)-1a). To a suspension of (R_{nap},S_{pyr})-**8a** (265 mg, 0.375 mmol) in methanol (12 mL) was added 6 N aqueous sodium hydroxide (3.1 mL). After the mixture was stirred at room temperature for 31 h, methanol was removed to give a white precipitate. It was filtered, and the filter cake was washed with 15% aqueous sodium hydroxide to give 127 mg (85% yield) of (*R*)-3,3′-bis(hydroxymethyl)-6,6′-diphenyl-2,2′-bipyridine *N,N′*-dioxide ((*S*)-**1a**). The aqueous layer was acidified with concentrated hydrochloric acid and extracted with chloroform three times. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure to give (*R*)-1,1′-binaphthalene 2,2′-dicarboxylic acid (129 mg, 100% yield). (*S*)-**1a**: $[\alpha]^{20}_D$ +67.1 (*c* 0.25, $CHCl_3$); the enantiomeric excess is >99% ee, which was determined by HPLC analysis with a chiral column (Daicel Chiralcel OD-H, hexane/2-propanol = 1/1, 0.30 mL/min), t_R (*S*)-(+), 26.7 min; (*R*)-(−), 66.7 min; ^{1}H NMR ($CDCl_3$) δ 4.32 (d, J = 11.4 Hz, 2H), 4.43 (t, J = 11.4 Hz, 2H), 4.85 (d, J = 8.8 Hz, 2H), 7.48 (m, 6H), 7.65 (d, J = 7.9 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 7.9 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 60.1, 127.4, 127.7, 128.0, 129.2, 129.6, 131.6, 139.8, 140.5, 148.5. Anal. Calcd for $C_{24}H_{20}N_2O_4$: C, 71.99; H, 5.03. Found: C, 71.72; H, 5.14. (*R*)-1,1′-Binaphthalene 2,2′-dicarboxylic acid: ^{1}H NMR ($CDCl_3$) δ 6.90 (d, J = 8.6 Hz, 2H), 7.15 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.91 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 126.0, 126.3, 126.6, 127.3, 127.8, 128.2, 129.5, 132.8, 135.2, 141.2, 171.6.

(*R*)-3,3′-Bis(hydroxymethyl)-6,6′-diphenyl-2,2′-bipyridine *N,N′*-Dioxide ((*R*)-1a). 98% yield: $[\alpha]^{20}_D$ −69.2 (*c* 0.25, $CHCl_3$), and recovery of (*R*)-1,1′-binaphthalene 2,2′-dicarboxylic acid: 100% yield.

(*S*)-3,3′-Bis(hydroxymethyl)-6,6′-dimethyl-2,2′-bipyridine *N,N′*-Dioxide ((*S*)-1b). To a suspension of (R_{nap},S_{pyr})-**8b** (212 mg, 0.363 mmol) in methanol (7.6 mL) was added 6 N aqueous sodium hydroxide (0.5 mL). After the mixture was stirred at room temperature for 37 h, sodium salt was removed using ion-exchange resin (DOWEX 50WX8-400). The methanol was evaporated under reduced pressure from the resulting mixture. After the mixture was acidified with concentrated hydrochloric acid, the mixture was extracted with chloroform three times. The combined organic layer was dried over anhydrous sodium sulfate and then evaporated under reduced pressure to give recovery of (*R*)-1,1′-binaphthalene 2,2′-dicarboxylic acid (113 mg, 91% yield). The aqueous layer was evaporated to give (*S*)-3,3′-bis(hydroxymethyl)-6,6′-dimethyl-2,2′-bipyridine *N,N′*-dioxide ((*S*)-**1b**) (92.5 mg, 84% yield): $[\alpha]^{20}_D$ −88.8 (*c* 1.49, EtOH); the enantiomeric excess is >99% ee, which was determined by HPLC analysis with a chiral column (Daicel Chiralcel OD-H, hexane/ethanol = 1/1, 0.30 mL/min), t_R (*R*)-(+), 15.7 min; (*S*)-(−), 21.1 min; ^{1}H NMR (CD_3OD) δ 2.54 (s, 6H), 4.20 (d, J = 13.8 Hz, 2H), 4.32 (d, J = 13.8 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H); ^{13}C NMR (CD_3OD) δ 17.7, 60.9, 128.4, 128.6, 140.4, 141.3, 149.7. Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84. Found: C, 60.57; H, 5.77.

(*R*)-3,3′-Bis(hydroxymethyl)-6,6′-dimethyl-2,2′-bipyridine *N,N′*-dioxide ((*R*)-1b): 88% yield; $[\alpha]^{20}_D$ +91.8 (*c* 1.49, EtOH). Recovery of (*R*)-1,1′-binaphthalene 2,2′-dicarboxylic acid: 100% yield.

(*S*)-3,3′-Bis(hydroxymethyl)-2,2′-bipyridine *N,N′*-Dioxide ((*S*)-1c). The procedure described above for compound (*S*)-**1b** was followed starting from (R_{nap},S_{pyr})-**8c** (166 mg, 0.318 mmol) and methanol (6.4 mL), and 6 N aqueous sodium hydroxide (0.4 mL) was addded. The mixture was purified as described for (*S*)-**1b** to give (*S*)-**1c** (86.5 mg, 100% yield) and recovery of (*R*)-1,1′-binaphthalene 2,2′-dicarboxylic acid (108 mg, 100% yield). (*S*)-**1c**: $[\alpha]^{20}_D$ −184 (*c* 0.33, MeOH); the enantiomeric excess is >99% ee, which was determined by HPLC analysis with a chiral column (Daicel Chiralcel OD-H, ethanol, 0.20 mL/min), t_R (*S*)-(−), 38.4 min; (*R*)-(+), 41.7 min; ^{1}H NMR (D_2O) δ 4.22 (d, J = 14.5 Hz, 2H), 4.31 (d, J = 14.5 Hz, 2H), 7.66 (dd, J = 8.0, 6.5 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 8.31 (d, J = 6.5 Hz, 2H); ^{13}C NMR (D_2O) δ 60.2, 129.1, 131.3, 139.4, 139.5, 142.1. Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87. Found: C, 57.90; H, 4.77.

(*R*)-3,3′-Bis(hydroxymethyl)-2,2′-bipyridine *N,N′*-dioxide ((*R*)-1c): 100% yield; $[\alpha]^{20}_D$ +184 (*c* 0.27, MeOH). Recovery of (*R*)-1,1′-binaphthalene 2,2′-dicarboxylic acid: 92% yield.

(*S*)-3,3′-Bis(hydroxymethyl)-6,6′-di-*tert*-butyl-2,2′-bipyridine *N,N′*-Dioxide ((*S*)-1d). To a solution of (R_{nap},S_{pyr})-**8d** (60.1 mg, 0.090 mmol) in methanol (6 mL) was added 6 N aqueous sodium hydroxide (3 mL), and the mixture was stirred at room temperature for 48 h. After the removal of methanol, the aqueous layer was extracted with chloroform three times. The combined organic layer was washed with aqueous sodium chloride, dried over anhydrous sodium sulfate, and evaporated to give (*R*)-3,3′-bis(hydroxymethyl)-6,6′-di-*tert*-butyl-2,2′-bipyridine *N,N′*-dioxide ((*S*)-**8d**) (30.8 mg, 95% yield). The aqueous layer was acidified with concentrated hydrochloric acid and extracted with chloroform three times. The combined organic layer was washed with aqueous sodium chloride, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give recovery of (*R*)-1,1′-binaphthalene 2,2′-dicarboxylic acid (32.0 mg, 100% yield): $[\alpha]^{20}_D$ −537 (*c* 0.30, $CHCl_3$). The enantiomeric excess is >99% ee, which was determined by HPLC analysis with a chiral column (Daicel Chiralpak AD, hexane/ethanol = 1/1, 0.50 mL/min), t_R (*S*)-(−), 7.3 min; (*R*)-(+), 8.9 min; ^{1}H NMR ($CDCl_3$) δ 1.54 (s, 18H), 4.08 (d, J = 11.9 Hz, 2H), 4.31 (d, J = 11.9 Hz, 2H), 5.06 (b, 2H), 7.55 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 27.3, 36.6, 63.1, 124.7, 129.2, 137.9, 144.1, 158.9. Anal. Calcd for $C_{20}H_{28}N_2O_4$: C, 66.64; H, 7.83. Found: C, 66.38; H, 7.66.

TABLE 4. Crystallographic Data for (R_{nap},S_{pyr})-6a and (R_{nap},R_{pyr})-7a[a]

	(R_{nap},S_{pyr})-**6a**	(R_{nap},R_{pyr})-**7a**
formula	$C_{53}H_{38}N_2O_4$	$C_{58}H_{42}N_2O_4$
fw	766.89	830.98
space group	$P2_12_12_1$(#19)	$P2_12_12_1$(#19)
cell dimensions		
Å	34.2(1)	8.9674(1)
Å	11.82(3)	20.8342(2)
Å	10.60(2)	23.2481(3)
Å^3	4280.2(2)	4343.41(7)
Z	4	4
d_{calcd}, g·cm^{-3}	1.19	1.27
crystal shape	platelet	block
crystal size, mm	0.40 × 0.30 × 0.10	0.40 × 0.20 × 0.10
radiation	Mo Kα (λ = 0.710 75 Å)	Mo Kα (λ = 0.710 75 Å)
cm^{-1}	0.75	0.79
max 2θ, deg	−55.0	−55.0
no. of unique data	4320	5463
no. of data used	3709 ($I > 0.01\sigma(I)$)	5116 ($I > 0.20\sigma(I)$)
R indices	R1 = 0.089	R = 0.072
	wR2 = 0.220	Rw = 0.044
GOF	1.27	1.13
max shift/err	0.03	0.00

(*R*)-3,3′-Bis(hydroxymethyl)-6,6′-di-*tert*-butyl-2,2′-bipyridine *N*,*N*′-dioxide ((*R*)-1d): 86% yield; $[\alpha]^{20}_D$ +545 (*c* 0.40, $CHCl_3$). Recovery of (*R*)-1,1′-binaphthalene 2,2′-dicarboxylic acid: 91% yield.

X-ray Structure Determination of (R_{nap},S_{pyr})-6a and (R_{nap},R_{pyr})-7a. A suitable crystal of (R_{nap},S_{pyr})-**6a** was obtained by recrystalization from toluene, (R_{nap},R_{pyr})-**7a** from benzene. Crystal data are summarized in Table 4.

Determination of the Rate Constant (*k*) of Thermal Epimerization of Kinetic Products (R_{nap},S_{pyr})-6a−d. The following treatment was carried out in order to remove the small amount of proton of (R_{nap},S_{pyr})-**6a**−**d**. To a solution of (R_{nap},S_{pyr})-**6a**−**d** (0.14 mmol) in $CHCl_3$ (3.5 mL) was added potassium carbonate 3.8 mg (0.028 mmol). The suspension was stirred vigorously at room temperature for 12 h and passed through Celite pad for removal of the salt, and the solvent was evaporated.

The treated (R_{nap},S_{pyr})-**6a** (7.4 μmol) was weighed into an NMR tube. Toluene-d_8 (0.5 mL) was added to it, followed by sealing quickly under air atmosphere. The content of a NMR tube was heated with oil bath at constant temperature between each accumulation. The reaction temperature was determined by the average of temperature collected at 30 s for 5 min. NMR spectra were collected at appropriate intervals until nine points. From the NMR spectra, the integral ratio of (R_{nap},S_{pyr})-**6a** to (R_{nap},R_{pyr})-**7a** could be obtained. Thus, the ratio of [(R_{nap},S_{pyr})-**6a**]/[(R_{nap},S_{pyr})-**6a**]$_0$ was equal to (R_{nap},S_{pyr})-**6a**/((R_{nap},S_{pyr})-**6a**+(R_{nap},R_{pyr})-**7a**) (integral ratio in NMR charts). The observed rate constant was determined by plotting [(R_{nap},S_{pyr})-**6a**]/[(R_{nap},S_{pyr})-**6a**]$_0$ versus time, the slope of the curve is the observed rate constant ($R^2 \geq 0.99$).

The above-mentioned procedure was exceptionally performed with less amount of (R_{nap},S_{pyr})-**6c** (2.9 μmol), because (R_{nap},S_{pyr})-**6c** had poor solubility.

Determination of the Rate Constant (k_{H^+}) of Proton-Promoted Epimerization of Kinetic Products (R_{nap},S_{pyr})-6a−d. Kinetic product (R_{nap},S_{pyr})-**6a** (7.4 μmol) was weighed into an NMR tube. Toluene-d_8 (0.5 mL), trifluoroacetic acid (7.4 μmol, 17 μL of the solution of trifluoroacetic acid (10 μL, 0.13 mmol) in toluene-d_8 (0.3 mL)) was added to it. The NMR tube was kept at 33 °C and spinning at 10−16 Hz. NMR spectra were collected at appropriate intervals until nine points.

The above-mentioned procedure was performed with a smaller amount of (R_{nap},S_{pyr})-**6c** (2.9 μmol), toluene-d_8 (0.5 mL), trifluoroacetic acid (7.4 μmol, 17 μL of the solution of trifluoroacetic acid (10 μL, 0.13 mmol) in toluene-d_8 (0.3 mL)), because (R_{nap},S_{pyr})-**6c** had poor solubility.

Catalytic Enantioselective Allylation of 4-Methoxybenzaldehyde with Allyl(trichloro)silane. To a solution of (*R*)-**1a** (0.4 mg, 0.001 mmol, 0.1 mol %), 4-methoxybenzaldehyde (**10a**) (136 mg, 1.00 mmol), and diisopropylethylamine (0.522 mL, 3.00 mmol) in acetonitrile (1 mL) was added dropwise allyl(trichloro)silane (0.173 mL, 1.20 mmol) at −45 °C. The reaction mixture was stirred at −45 °C for 2.5 h, before 1 mL of 3 N sodium hydroxide was added. The reaction mixture was stirred at room temperature for an additional 10 min, and it was extracted with diethyl ether three times. The combined organic layer was washed with aqueous sodium chloride, dried over anhydrous sodium sulfate, and evaporated under reduced pressure, and the residue was purified by flash column chromatography (ethyl acetate/hexane = 1/5) to give (*S*)-1-(4-methoxyphenyl)-3-buten-1-ol ((*S*)-**11a**) (172 mg, 96% yield): $[\alpha]^{20}_D$ −37.8 (*c* 1.9, C_6H_6). The enantiomeric excess of this sample was determined to be 94% ee by GLC analysis with a chiral stationary phase column (CP-Chiralsil-Dex CB, column temperature 125 °C): t_R (*R*)-(+), 41.2 min; (*S*)-(−) (lit.[23] 43.5 min for (*S*)-**11a** of 88% ee); $[\alpha]^{24}_D$ −35.6 (*c* 1.07, C_6H_6); ^{1}H NMR ($CDCl_3$) δ 1.96 (s, 1H), 2.50 (t, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 4.69 (t, *J* = 6.3 Hz, 1H), 5.13 (d, *J* = 11.2 Hz, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 5.81 (ddt, *J* = 17.1, 11.2, 7.1 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 43.6, 55.2, 72.9, 113.7, 118.0, 127.0, 134.6, 136.0, 158.9.

(*S*)-1-(3,4-Dimethoxyphenyl)-3-buten-1-ol ((*S*)-11b):[24] $[\alpha]^{20}_D$ −32.7 (*c* 1.0, C_6H_6); 98% ee by GLC analysis: t_R (*R*)-(+), 71.5 min; (*S*)-(−), 76.2 min, (CP-Chiralsil-Dex CB, column temperature 125 °C) (lit.[24] for (*S*)-**11b** of 65% ee: $[\alpha]^{20}_D$ −10.1); ^{1}H NMR ($CDCl_3$) δ 2.03 (d, *J* = 3.1 Hz, 1H), 2.51 (t, *J* = 7.9 Hz, 2H), 3.87 (s, 3H), 3.90 (s, 3H), 4.69 (t, *J* = 7.2 Hz, 1H), 5.14 (d, *J* = 10.3 Hz, 1H), 5.17 (d, *J* = 17.8 Hz, 1H), 5.81 (ddt, *J* = 17.8, 10.3, 7.2 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 43.8, 55.8, 55.9, 73.2, 108.9, 110.9, 118.0, 118.3, 134.5, 136.5, 148.4, 149.0.

(*S*)-1-(4-Butoxyphenyl)-3-buten-1-ol ((*S*)-11c): $[\alpha]^{20}_D$ −23.2 (*c* 2.6, Et_2O); 94% ee by HPLC analysis: t_R (*R*)-(+), 23.8 min; (*S*)-(−), 26.0 min (Daicel Chiralcel OD-H, hexane/2-propanol = 98/2, 0.50 mL/min); ^{1}H NMR ($CDCl_3$) δ 0.97 (t, *J* = 7.5 Hz, 3H), 1.48 (tq, *J* = 7.7, 7.5 Hz, 2H), 1.75 (tt, *J* = 7.7, 6.5 Hz, 2H), 2.12 (b, 1H), 2.47 (t, *J* = 6.7 Hz, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 4.65 (t, *J* = 6.2 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 5.78 (ddt, *J* = 17.2, 10.3, 6.2 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8, 19.2, 31.3, 43.6, 67.6, 73.0, 114.3, 118.0, 127.0, 134.6, 135.8, 158.6. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.49; H, 9.31.

(*S*)-1-(4-*tert*-Butylphenyl)-3-buten-1-ol ((*S*)-11d):[25] $[\alpha]^{20}_D$ −24.1 (*c* 1.0, Et_2O); 89% ee by GLC analysis: t_R (*R*)-(+), 49.8 min; (*S*)-(−), 53.0 min, (CP-Chirasil-Dex CB, column temperature 125 °C); ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 9H), 2.17 (b, 1H), 2.51 (m, 2H), 4.68 (t, *J* = 6.5 Hz, 1H), 5.13 (d, *J* = 11.4 Hz, 1H), 5.16 (d, *J* = 17.3 Hz, 1H), 5.82 (ddt, *J* = 17.3, 11.4, 6.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 31.3, 34.4, 43.6, 73.1, 118.1, 125.2, 125.5, 134.7, 140.9, 150.4.

(*S*)-1-(4-Methylphenyl)-3-buten-1-ol ((*S*)-11e):[26] $[\alpha]^{20}_D$ −43.4 (*c* 1.1, C_6H_6); 89% ee by GLC analysis: t_R (*R*)-(+), 56.4 min; (*S*)-(−), 63.5 min, (CP-Chiralsil-Dex CB, column temperature 105 °C) (lit.[26] for (*S*)-**11e** of 82% ee: $[\alpha]^{25}_D$ −37.3 (*c* 2.0, C_6H_6)); ^{1}H NMR ($CDCl_3$) δ 2.51 (s, 3H), 2.65 (t, *J* = 6.8 Hz, 2H), 4.81 (t, *J* = 6.4 Hz, 1H), 5.27 (d, *J* = 8.4 Hz, 1H), 5.29 (d,

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J = 16.0 Hz, 1H), 5.95 (ddt, J = 16.0, 8.4, 6.4 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.1, 43.8, 73.2, 118.3, 125.8, 129.1, 134.6, 137.2, 140.9.

(*S*)-1-Phenyl-3-buten-1-ol ((*S*)-11f):[23] $[\alpha]^{20}_D$ −48.9 (*c* 1.0, C_6H_6); 84% ee by HPLC analysis: t_R (*R*)-(+), 15.2 min; (*S*)-(−), 16.5 min, (Daicel Chiralcel OD-H, hexane/2-propanol = 19/1, 0.50 mL/min) (lit.[23] for (*S*)-**11f** of 87% ee: $[\alpha]^{24}_D$ −48.1 (*c* 1.05, C_6H_6)); ^{1}H NMR ($CDCl_3$) δ 2.08 (b, 1H), 2.48 (m, 2H), 4.63 (t, J = 6.5 Hz, 1H), 5.13 (d, J = 10.2 Hz, 1H), 5.16 (d, J = 16.8 Hz, 1H), 5.75 (m, 1H), 7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 43.8, 73.3, 118.3, 125.8, 127.5, 128.4, 134.4, 143.8.

(*S*)-1-(1-Naphthyl)-3-buten-1-ol ((*S*)-11g):[26] $[\alpha]^{20}_D$ −84.1 (*c* 1.0, C_6H_6); 81% ee by HPLC analysis: t_R (*S*)-(−), 16.5 min; (*R*)-(+), 27.5 min, (Daicel Chiralcel OD-H, hexane/2-propanol = 9/1, 0.50 mL/min) (lit.[26] for (*S*)-**11g** of 80% ee: $[\alpha]^{24}_D$ −77.5 (*c* 2.9, C_6H_6)); ^{1}H NMR ($CDCl_3$) δ 2.19 (b, 1H), 2.70 (m, 2H), 5.18 (d, J = 10.1 Hz, 1H), 5.22 (d, J = 17.2 Hz, 1H), 5.53 (b, 1H), 5.93 (ddt, J = 17.2, 10.1, 7.1 Hz, 1H), 7.50 (m, 3H), 7.66 (d, J = 7.3 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 42.9, 69.9, 118.4, 122.8, 122.9, 125.4, 125.5, 126.0, 128.0, 128.9, 130.2, 133.8, 134.7, 139.4.

(*S*)-1-(2-Methoxyphenyl)-3-buten-1-ol ((*S*)-11h):[26] $[\alpha]^{20}_D$ −68.4 (*c* 1.0, C_6H_6); 76% ee by HPLC analysis: t_R (*S*)-(−), 15.6 min; (*R*)-(+), 16.7 min, (Daicel Chiralcel OD-H, hexane/2-propanol = 9/1, 0.50 mL/min) (lit.[26] for (*S*)-**11h** of 80% ee: $[\alpha]^{23}_D$ −65.8 (*c* 3.56, C_6H_6)); ^{1}H NMR ($CDCl_3$) δ 2.56 (m, 3H), 3.85 (s, 3H), 4.96 (dd, J = 8.1, 5.0 Hz, 1H), 5.10 (d, J = 10.1 Hz, 1H), 5.13 (d, J = 17.6 Hz, 1H), 5.85 (ddt, J = 17.6, 10.1, 6.8 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 41.8, 55.3, 69.7, 110.4, 117.6, 120.7, 126.8, 128.3, 131.7, 135.2, 156.4.

(*S*)-1-(4-Trifluoromethylphenyl)-3-buten-1-ol ((*S*)-11i):[23] $[\alpha]^{20}_D$ −18.1 (*c* 1.9, C_6H_6); 56% ee by HPLC analysis: t_R (*S*)-(−), 48.0 min; (*R*)-(+), 51.9 min, (Daicel Chiralcel OJ, hexane/2-propanol = 100/1, 0.40 mL/min) (lit.[23] for (*S*)-**11i** of 80% ee: $[\alpha]^{24}_D$ −25.5 (*c* 1.50, C_6H_6)); ^{1}H NMR ($CDCl_3$) δ 2.22 (b, 1H), 2.50 (m, 2H), 4.80 (dd, J = 7.8, 4.8 Hz, 1H), 5.18 (m, 2H), 5.79 (dddd, J = 17.7, 9.7, 7.9, 6.5 Hz, 1H), 7.48 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 43.9, 72.5, 119.2, 124.2 (q, J = 271.0 Hz), 125.3 (q, J = 3.7 Hz), 126.1, 129.6 (q, J = 32.3 Hz), 133.7, 147.8.

(*S*)-1-Phenyl-1,5-hexadien-3-ol ((*S*)-11j):[8] $[\alpha]^{20}_D$ +10.9 (*c* 1.0, Et_2O); 60% ee by HPLC analysis: t_R (*R*)-(−), 14.5 min; (*S*)-(+), 21.4 min, (Daicel Chiralcel OD-H, hexane/2-propanol = 9/1, 0.50 mL/min) (lit.[8] for (*R*)-**11j** of 80% ee: $[\alpha]_D$ −11.3 (Et_2O)); ^{1}H NMR ($CDCl_3$) δ 1.90 (b, 1H), 2.42 (m, 2H), 4.36 (b, 1H), 5.16 (d, J = 10.2 Hz, 1H), 5.18 (d, J = 17.3 Hz, 1H), 5.85 (ddt, J = 17.3, 10.2, 7.2 Hz, 1H), 6.23 (dd, J = 16.0, 6.4 Hz, 1H), 6.60 (d, J = 16.0 Hz, 1H), 7.23 (t, J = 7.3 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 41.9, 71.7, 118.5, 126.4, 127.6, 128.5, 130.3, 131.5, 134.0, 136.6.

(1*S*,2*R*)-2-Methyl-1-phenyl-3-buten-1-ol ((1*S*,2*R*)-12):[8] $[\alpha]^{20}_D$ −21.1 (*c* 2.2, $CHCl_3$); 77% ee by HPLC analysis: t_R (1*S*,2*R*)-(−), 14.4 min; (1*R*,2*S*)-(+), 16.5 min, (Daicel Chiralcel OD-H, hexane/2-propanol = 95/5, 0.50 mL/min) (lit.[8] for (1*R*,2*S*)-**12** of 84% ee: $[\alpha]_D$ +22.6 ($CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ 1.00 (d, J = 6.9 Hz, 3H), 2.03 (b, 1H), 2.57 (m, 1H), 4.59 (d, J = 8.9 Hz, 1H), 5.03 (m, 2H), 5.80 (m, 1H), 7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.2, 44.7, 77.3, 115.5, 126.6, 127.4, 128.1, 140.3, 142.6.

(1*S*,2*S*)-2-Methyl-1-phenyl-3-buten-1-ol ((1*S*,2*S*)-12):[8] $[\alpha]^{20}_D$ −88.1 (*c* 2.3, $CHCl_3$); 73% ee by HPLC analysis: t_R (1*R*,2*R*)-(+), 15.5 min; (1*S*,2*S*)-(−), 16.5 min, (Daicel Chiralcel OD-H, hexane/2-propanol = 95/5, 0.50 mL/min) (lit.[8] for (1*R*,2*R*)-**12** of 86% ee: $[\alpha]_D$ +94.6 ($CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ 0.87 (d, J = 6.9 Hz, 3H), 2.17 (b, 1H), 2.48 (m, 1H), 4.35 (d, J = 8.0 Hz, 1H), 5.17 (d, J = 10.3 Hz, 1H), 5.20 (d, J = 17.5 Hz, 1H), 5.80 (ddd, J = 17.5, 10.3, 8.3 Hz, 1H), 7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.5, 46.2, 77.7, 116.8, 126.8, 127.6, 128.2, 140.6, 142.4.

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Supporting Information Available: X-ray crystallographic data for (R_{nap},S_{pyr})-**6a** and (R_{nap},R_{pyr})-**7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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