

Use of 8,8'-dihydroxy-1,1'-binaphthalene as a chiral auxiliary for asymmetric Diels–Alder cycloadditions

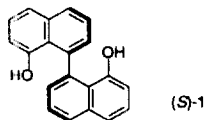
Kiyoshi Tanaka, Naoyuki Asakawa, Mohammad Nuruzzaman and Kaoru Fuji*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

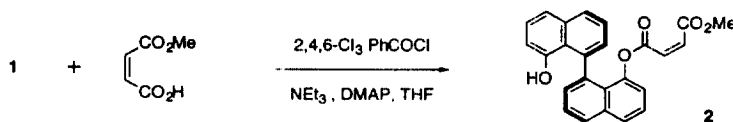
Abstract: The Diels–Alder reactions of unsymmetrical maleate **2** and fumarate **10** possessing axially chiral 8,8'-dihydroxy-1,1'-binaphthalene **1** with cyclopentadiene were investigated under various conditions in the presence of a Lewis acid. Both the diastereo- and *endo/exo*-selectivities depended on the Lewis acid used. A notably high level of diastereoselection was achieved with $\text{TiCl}(\text{O}^i\text{Pr})_3$ for the *endo* adduct of the maleate, and with SnCl_4 for that of the fumarate. The results suggest that the free hydroxyl group of the auxiliary plays a crucial role in inducing the high level of diastereoselectivity in these cycloadditions. © 1997 Elsevier Science Ltd

Introduction

The use of axially chiral C_2 symmetrical 1,1'-binaphthalene-2,2'-diol (BINOL) and related compounds has been extensively investigated in the field of asymmetric reactions¹ as well as in molecular recognition.^{2,3} In contrast, compared to 1,1'-binaphthalene-2,2'-diol derivatives, the corresponding 8,8'-diols^{2a,3} have received little attention and their efficiency in asymmetric transformations is still unclear. Recently, we demonstrated that the 1,1'-binaphthalene-8,8'-diol unit provides a highly asymmetric microenvironment for the protonation of enolates⁴ and that α,β -unsaturated half esters of 8,8'-diol undergo successive 1,4- and 1,2-additions with dialkyl cuprates to give β -substituted ketones with extremely high enantioselectivity.⁵ Asymmetric cycloaddition, such as in the Diels–Alder reaction, is one of the most efficient carbon–carbon bond-forming reactions involving the simultaneous creation of multiple asymmetric centers,⁶ and is often used to elaborate the skeletons of natural products. In the asymmetric Diels–Alder reaction, chirality can be introduced to the Lewis acid catalyst, the dienophile, or the diene.⁶ As part of our ongoing studies of asymmetric transformation using 8,8'-dihydroxy-1,1'-binaphthalene **1** as a stereo-controller, we examined the Diels–Alder reaction of the unsymmetrical maleate and fumarate of 8,8'-BINOL as dienophiles with cyclopentadiene in the presence of a Lewis acid.



Results and discussion



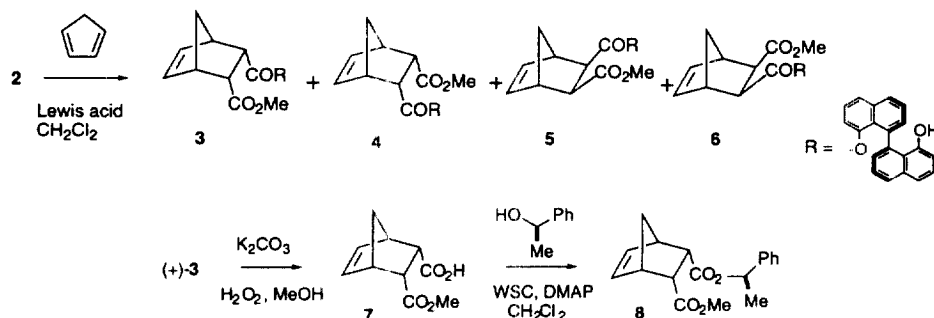
The half ester of 8,8'-dihydroxy-1,1'-binaphthalene **2** was easily prepared in 63% yield by condensation of **1**^{2a,3,7} with maleic acid monomethyl ester based on a mixed anhydride method.⁸ Prior to the asymmetric Diels–Alder reaction using chiral dienophiles, the Diels–Alder reactions of

* Corresponding author. Email: fuji@sun.scl.kyoto-u.ac.jp

Table 1. The Diels–Alder reactions of **2** with cyclopentadiene

entry	Lewis acid	conditions (°C, h)	isolated yield (%)	endo/exo ratio	endo (3/4)	exo (5/6)
1	none	r. temp., 18	100	77/23	38/62	62/38
2	AlEt ₂ Cl	-78, 3	92	100/0	23/77	-
3	AlMe ₃	-78, 26	12	90/10	15/85	100/0
4	SnCl ₄	-78, 1	100	93/7	74/26	0/100
5	TiCl ₄	-78, 4	22	88/12	91/9	0/100
6	TiCl ₄	-78, 42	32	72/28	89/11	0/100
7	TiCl(O ^{<i>i</i>} Pr) ₃	-78, 48	43	73/27	100/0	0/100
8	TiCl(O ^{<i>i</i>} Pr) ₃	0, 46	96	86/14	100/0	0/100
9	BF ₃ •Et ₂ O	-78, 1	87	93/7	72/28	0/100
10	ZnCl ₂	-78, 29	38	75/25	64/36	28/72

racemic **2** with cyclopentadiene were first carried out with or without a Lewis acid under several different reaction conditions, and the diastereomeric excesses of the adducts **3–6** were determined by HPLC analysis. Alternatively, to identify the adducts, standard samples of the diastereomeric *endo*-adducts **3** and **4** were prepared by condensation of racemic **1** and **7**. The results of the Diels–Alder reactions are summarized in Table 1. As shown, poor selectivity was observed in the absence of a Lewis acid (entry 1). Among the Lewis acids employed, boron, zinc, aluminum and tin catalysts gave poor to moderate diastereoselectivity, while titanium catalysts, especially TiCl(O^{*i*}Pr)₃ induced a high level of diastereoselection (entry 7) and an increased chemical yield was obtained when the reaction temperature was raised to 0°C (entry 8). The complexation pattern of the substrate with Lewis acids may reflect the observed diastereoselectivities (*vide infra*).



Starting from the non-racemic (*S*)-**2**, asymmetric cycloaddition with cyclopentadiene provided (+)-**3** as a major adduct, whose absolute stereostructure was ascertained by chemical transformation to the known compound **8**,⁹ as shown above. Thus, selective hydrolysis of the binaphthyl ester to **7** and successive condensation with (*R*)-(+)-phenylethanol gave the known diester **8**. The absolute structure of the minor adduct is temporarily assumed to be **5** based on mechanistic considerations.

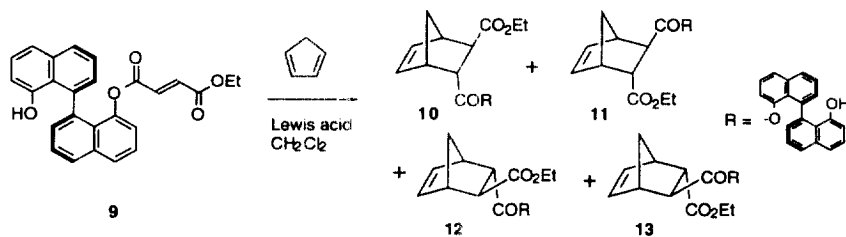
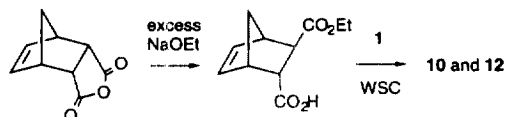


Table 2. The Diels–Alder reactions of **9** with cyclopentadiene

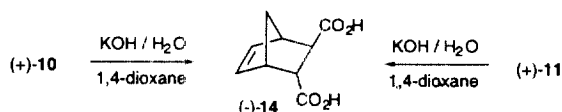
entry	Lewis acid	conditions (°C, h)	isolated yield (%)	endo/exo ratio	endo (10/12)	exo (11/13)
1	none	r. temp., 12	100	54 / 46	50 / 50	47 / 53
2	AlEt ₂ Cl	-78, 1	100	32 / 68	46 / 54	74 / 26
3	AlMe ₃	-78, 8	100	78 / 22	25 / 75	63 / 37
4	AlCl ₃	-78, 3	100	39 / 61	72 / 28	55 / 45
5	SnCl ₄	-78, 24	56 (69) ^a	62 / 38	99 / 1	89 / 11
6	TiCl ₄	-78, 24	0 ^b			
7	TiCl(O ⁱ Pr) ₃	0, 16	100	53 / 47	56 / 44	59 / 41
8	BF ₃ ·Et ₂ O	-78, 23	96	0 / 100	-	85 / 15
9	ZnCl ₂	-78, 24	0			
10	ZnCl ₂	0, 6	100	43 / 57	34 / 66	57 / 43

^a Isolated yield based on consumed starting material. ^b Heterogeneous mixture.

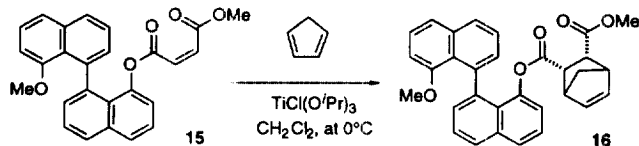
The unsymmetrical fumarate of 8,8'-dihydroxy-1,1'-binaphthalene **9** was prepared by condensation of **1** with fumaric acid monoethyl ester, and subjected to Diels–Alder cycloaddition with cyclopentadiene. The diastereo- and *endo/exo*-selectivities, as well as the reaction conditions, are shown in Table 2. Standard samples for comparison, **10** and **12**, were also prepared as described below. Again, no significant selectivity was observed without a Lewis acid (entry 1). Interestingly, in this case titanium catalysts gave poor results with respect to chemical yield and diastereoselectivity (entries 6 and 7). High diastereoselection of 98% *de* was achieved for the *endo*-adduct **10** when SnCl₄ was used as a Lewis acid catalyst (entry 5).



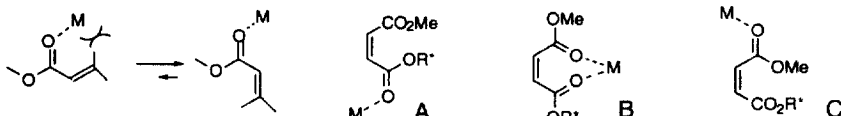
The optically active dienophile (*S*)-(+)-**9** gave (+)-**10** and (+)-**11**, whose absolute stereostructures were deduced from comparison with the known diacid (–)-**14**¹⁰ obtained by an alkaline hydrolysis of (+)-**10** and (+)-**11**.



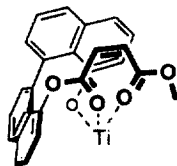
We anticipated that the structure of the reactive species toward the dienophile in the transition state of the Diels–Alder reaction is sterically constrained by rigid chelation of the titanium catalyst through bonding between the free hydroxyl group of the auxiliary and the ester carbonyl groups. This contribution of the free hydroxyl group of the auxiliary to stereoselection was suggested by the following experiment. When the dienophile **15**, which has a weakly ligating methoxyl group in place of OH at the 8' position, was used for the Diels–Alder reaction with cyclopentadiene, a remarkable decrease in diastereoselectivity as well as in the reaction yield (26% *de* and 25% yield, respectively) was observed under the same reaction conditions as those for **2**.



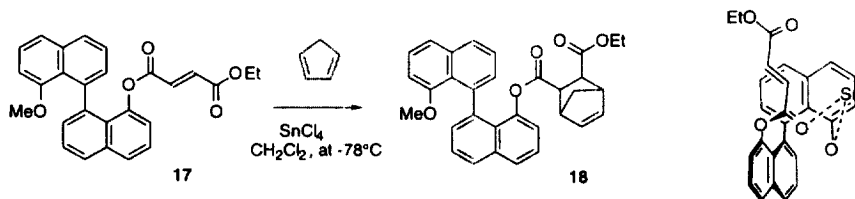
The predominant conformation of α,β -unsaturated esters in the ground state is *s-cis*. However, the *s-trans* conformer is favored in the presence of a Lewis acid. Since a Lewis acid coordinates so as to minimize the interaction between the alkoxy oxygen¹¹ and the β -substituent,¹² the *s-trans* conformation plays a major role in Diels–Alder cycloaddition in preference to the *s-cis* conformation.^{13,14} However, if the ester bears another functional group, the Lewis acid can chelate both groups and favor the *s-cis* conformation.¹⁵ As a consequence, three possible complexation patterns, A, B and C, are feasible.^{9,16} To elucidate the actual species for the reaction, the ¹³C NMR spectrum of a unimolecular equivalent mixture of **2** and TiCl(O^{*i*}Pr)₃ was taken in CDCl₃ at 0°C. The down-field shift of two ester carbonyls, from δ 165.15 and 163.92 to δ 165.67 and 165.08 ppm, was probably due to complexation with the Lewis acid, which supports structure B.⁹ A down-field shift of the complexed carbonyl and an up-field shift or no shift of the uncomplexed carbonyl are expected from complexes type A and C.



Considering these experimental results and the above discussion, the structure depicted below for the reactive species of the dienophile might be feasible. Three-point binding by the titanium atom between the dienophile and the likelihood of attractive π – π interaction between the maleate double bond and the naphthalene ring make the complex so rigid that one of the π -faces is strongly shielded by the naphthalene ring of the auxiliary.



In contrast to the cycloaddition of **2**, type B complexation is impossible for the Diels–Alder reaction with **9** in the presence of a Lewis acid. In this case, complexation with a Lewis acid of type A is considered. In the ¹³C NMR experiment with a unimolecular equivalent mixture at –60°C, the shift from δ 164.53 and 163.48 to δ 165.75 and 163.80 ppm suggested one-point chelation between the ester carbonyl. Furthermore, using a substrate with a protected 8'-hydroxyl, **17**, a decrease was observed in both the yield and selectivity of the adduct (27% yield, 34% de for **18**) under the same reaction conditions as for **9**. These results suggest the two-point binding by the tin atom between one of the ester carbonyls and the hydroxyl group, leading to the rather rigid complex depicted below.



Conclusion

In this study of Diels–Alder reactions of dienophiles with 8,8'-BINOL as a chiral auxiliary, we have demonstrated that a high level of diastereoselectivity could be obtained by the appropriate choice of reaction conditions, and the stereochemical outcome of the reaction can be explained by considering a transition state involving the dienophile and the Lewis acid. We have demonstrated that 8,8'-dihydroxy-1,1'-binaphthalene can provide an efficient diastereomeric space with a Lewis acid, and acts as an effective asymmetric inducer in Diels–Alder cycloaddition to give 1,2-dicarboxylates. The optically active asymmetric *cis*-cyclohexene-1,2-dicarboxylates and their *trans* derivatives are versatile chiral

building blocks for preparing numerous useful compounds. The present study provides an alternative to the enzymatic approach to these kinds of optically active compounds.⁹ To determine any latent abilities of 8,8'-dihydroxy-1,1'-binaphthalene derivatives in asymmetric chemical transformations, their use in other types of reactions, including non- σ -bonding systems, is now being investigated.

Experimental

Unless otherwise specified, all ¹H NMR spectra were taken at 200 MHz or 400 MHz in CDCl₃ with chemical shifts being reported as δ ppm from tetramethylsilane as an internal standard, and couplings are expressed in hertz. Infrared (IR) spectra were measured in CHCl₃. THF, ether, and toluene were distilled from sodium benzophenone ketyl, CH₂Cl₂ was from calcium hydride and MeOH was from magnesium. Unless otherwise noted, all reactions were run under an argon or nitrogen atmosphere. All extractive organic solutions were dried over anhydrous MgSO₄. Flash column chromatography was carried out with silica gel 60 spherical (150–325 mesh) and silica gel 60 F254 plates (Merck) were used for preparative TLC (pTLC). Diastereomeric excesses (de) of Diels–Alder adducts were determined by HPLC on CHEMCOSORB Si-5 column (Chemco Co.) with hexane:EtOAc (92:8) and/or ¹H NMR (400 MHz).

Preparation of methyl 8'-hydroxy-1,1'-binaphthalene-8-yl maleate 2

To a stirred solution of maleic acid monomethyl ester (364 mg, 2.8 mmol) and NEt₃ (283 mg, 2.8 mmol) in THF (100 mL) was added 2,4,6-trichlorobenzoyl chloride (683 mg, 2.8 mmol). After being stirred for 2 h at room temperature, the precipitated NEt₃·HCl was filtered off and the filtrate was added to a solution of (*S*)-1 (400 mg, 1.4 mmol) and DMAP (1026 mg, 8.4 mmol) in THF (300 mL) at –78°C. After 20 min, the reaction was stopped by addition of 2 N HCl aqueous solution. The mixture was extracted with EtOAc, dried, concentrated, and subjected to flash chromatography with EtOAc:hexane (1:3) to furnish **2** (350 mg, 63% yield) which was recrystallized from CHCl₃/hexane.

2 (optically active): reddish prisms; mp 131–134°C; [α]_D¹⁷ +239.2 (c 0.78, CHCl₃, 100% ee); IR 3520, 1737, 1150 cm⁻¹; ¹H NMR δ 3.69 (s, 3H), 4.64 (d, *J*=12.0, 1H), 5.30 (s, 1H), 5.75 (d, *J*=11.8, 1H), 6.82 (d, *J*=7.5, 1H), 7.13 (d, *J*=7.0, 1H), 7.36–7.62 (m, 7H), 7.84–7.94 (m, 2H), 8.03 (d, *J*=8.1, 1H); Anal. Calcd. for C₂₅H₁₈O₅: C, 75.37; H, 4.55. Found: C, 75.42; H, 4.48.

General procedure for asymmetric Diels–Alder reaction of maleate 2, fumarate 9 and related compounds

To a solution of the dienophile (0.126 mmol) in CH₂Cl₂ (0.6 mL) was added a Lewis acid (0.126 mmol) followed by cyclopentadiene (0.25 mmol) at –78°C. The resulting mixture was stirred under the conditions indicated in Tables 1 and 2. The mixture was then added to cold 2 N HCl and extracted with EtOAc. The organic layer was washed with water, dried, concentrated, and purified by GPC column chromatography on direct connection of JAIGEL 1H–2H (each 20×600 mm) columns with CHCl₃ to give adducts **3–6**, **10–13**, **16** and **18**.

3 (optically active): white powder; mp 192–194°C; [α]_D¹⁷ +192.9 (c 1.45, CHCl₃, 100% ee); IR 2980, 1730, 1250, 780 cm⁻¹; ¹H NMR δ 0.84 (d, *J*=8.4, 1H), 0.95 (dd, *J*=10.2, 3.7, 1H), 1.30 (m, 1H), 2.47 (dd, *J*=10.1, 3.7, 1H), 2.58 (brs, 1H), 2.95 (brs, 1H), 3.49 (s, 3H), 5.52 (s, 1H), 5.89 (dd, *J*=5.5, 2.9, 1H), 6.31 (dd, *J*=5.4, 2.9, 1H), 6.84 (d, *J*=7.4, 1H), 7.08 (d, *J*=7.0, 1H), 7.35–7.55 (m, 7H), 7.81 (brd, *J*=8.1, 2H), 7.97 (d, *J*=8.1, 1H); Anal. Calcd for C₃₀H₂₄O₅·1/2H₂O: C, 76.10; H, 5.32. Found: C, 76.48; H, 5.21; HRMS (*m/z*) Calcd 464.1624 (M⁺), Found 464.1647; MS (*m/z*) 464 (M⁺), 286.

4 (racemic): colorless crystals; mp 203–205°C; IR 2980, 1730, 1250, 1215, 780 cm⁻¹; ¹H NMR δ 0.79 (d, *J*=8.8, 1H), 1.17 (m, 2H), 1.70 (brs, 1H), 2.87 (dd, *J*=10.0, 3.5, 1H), 2.98 (brs, 1H), 3.57 (s, 3H), 5.34 (s, 1H), 5.97 (dd, *J*=5.5, 2.9, 1H), 6.07 (dd, *J*=5.5, 2.9, 1H), 6.90 (dd, *J*=7.4, 1.3, 1H), 7.19 (dd, *J*=7.1, 1.3, 1H), 7.25–7.59 (m, 7H), 7.86 (m, 2H), 8.01 (dd, *J*=8.2, 1.4, 1H); Anal. Calcd for C₃₀H₂₄O₅: C, 77.57; H, 5.21. Found: C, 77.25; H, 5.19.

5 (racemic): amorphous; IR 2980, 1730, 1250, 1215, 780 cm⁻¹; ¹H NMR δ 0.63 (dd, *J*=9.5, 1.8,

1H), 1.06 (dd, $J=9.1, 1.5$, 1H), 1.68 (d, $J=9.6$, 1H), 1.98 (brs, 1H), 2.24 (d, $J=9.6$, 1H), 2.75 (brs, 1H), 3.57 (s, 3H), 5.18 (s, 1H), 5.65 (m, 1H), 5.93 (m, 1H), 6.81 (dd, $J=7.4, 1.4$, 1H), 7.12 (m, 2H), 7.32–7.52 (m, 6H), 7.80 (m, 2H), 7.93 (d, $J=8.3$, 1H); HRMS (m/z) Calcd 464.1624 (M^+), Found 464.1637; MS (m/z) 464 (M^+), 286; Anal. Calcd for $C_{30}H_{24}O_5$: C, 77.57; H, 5.03. Found: C, 69.15; H, 5.03.

6 was not isolated in pure form. Since this compound did not correspond to either of *endo* products, prepared from racemic **1** and **7**, on HPLC, **6** can be assigned as an alternative *exo* product.

10 (optically active): white powder; mp 178–181°C; $[\alpha]_D^{17} +122.6$ (c 1.04, $CHCl_3$, 100% ee); IR 3520, 3000, 1750, 1720, 1180, 1160, 820 cm^{-1} ; 1H NMR δ 1.10 (m, 1H), 1.18 (m, 1H), 1.30 (t, $J=7.2$, 3H), 1.62 (m, 1H), 1.76 (brs, 1H), 2.35 (dd, $J=4.3, 1.6$, 1H), 2.88 (brs, 1H), 4.17 (q, $J=7.1$, 2H), 5.38 (s, 1H), 5.93 (dd, $J=5.5, 2.9$, 1H), 6.12 (dd, $J=5.8, 2.9$, 1H), 6.92 (m, 2H), 7.06 (dd, $J=7.0, 1.2$, 1H), 7.37–7.60 (m, 6H), 7.90 (m, 2H), 8.01 (dd, $J=8.1, 1.5$, 1H); Anal. Calcd for $C_{31}H_{26}O_5$: C, 77.81; H, 5.48. Found: C, 77.76; H, 5.42.

11 (optically active): colorless oil; $[\alpha]_D^{17} +19.5$ (c 1.01, $CHCl_3$, 100% ee); IR 3520, 2920, 1730, 1230, 1220, 780 cm^{-1} ; 1H NMR δ 1.18 (m, 1H), 1.30 (t, $J=7.2$, 3H), 1.62 (m, 1H), 1.76 (brs, 1H), 2.35 (dd, $J=4.3, 1.6$, 1H), 2.88 (brs, 1H), 4.17 (q, $J=7.1$, 2H), 5.38 (s, 1H), 5.93 (dd, $J=5.5, 2.9$, 1H), 6.12 (dd, $J=5.8, 2.9$, 1H), 6.92 (m, 2H), 7.06 (dd, $J=7.0, 1.2$, 1H), 7.37–7.60 (m, 6H), 7.90 (m, 2H), 8.01 (dd, $J=8.1, 1.5$, 1H); Anal. Calcd for $C_{31}H_{26}O_5 \cdot 1/3H_2O$: C, 76.85; H, 5.55. Found: C, 76.86; H, 5.46; HRMS (m/z) Calcd 478.1781 (M^+). Found 478.1752; MS (m/z) 478 (M^+), 286.

12 was not isolated in pure form.

13 was not isolated in pure form.

16 (mixture of four diastereomers): IR 1750, 1730, 1260, 780, 770 cm^{-1} ; 1H NMR δ 0.80 (m, 2H), 1.15 (m, 4H), 1.66 (brs, 2H), 1.81 (brs, 2H), 2.35 (m, 0.6H), 2.50 (brs, 0.6H), 2.75 (m, 1H), 2.92 (brs, 1.5H), 3.08 (m, 4.9H), 3.51 (s, 3H), 5.88 (m, 0.6H), 6.01 (m, 1H), 6.09 (m, 1H), 6.28 (m, 0.6H), 6.73 (m, 1.7H), 7.20 (m, 3H), 7.48 (m, 6H), 7.82 (m, 3H); HRMS (m/z) Calcd 478.1780 (M^+), Found 478.1775; MS (m/z) 478 (M^+), 300, 179.

18 (mixture of four diastereomers): IR 1750–1720, 1260, 780, 770 cm^{-1} ; 1H NMR δ 1.20 (m, 7.4H), 1.50 (m, 0.6H), 1.68 (brs, 0.6H), 1.92 (brs, 1H), 2.25 (brs, 0.5H), 2.35 (m, 0.5H), 2.70 (m, 0.7H), 2.87 (brs, 0.5H), 2.98 (t, $J=3.8, 0.5H$), 3.02 (brs, 1H), 4.08 (m, 2.5H), 5.79 (m, 0.5H), 5.88 (m, 1H), 5.96 (m, 1H), 6.11 (m, 0.5H), 6.75 (m, 1.7H), 6.98 (m, 1H), 7.20 (m, 3H), 7.48 (m, 6.6H), 7.85 (m, 3.7H); HRMS (m/z) Calcd 492.1937 (M^+), Found 492.1915; MS (m/z) 492 (M^+), 300.

5-Norbornene 2,3-dicarboxylic acid monomethyl ester **7**

To a stirred solution of 5-norbornene 2,3-dicarboxylic anhydride (4.93 g, 30 mmol) in THF (13 mL), NaOMe (30 mmol in 30 mL of MeOH) was added dropwise at 0°C, and the reaction mixture was stirred for a few minutes. The mixture was made acidic by pouring into aq. 2 N HCl at 0°C and extracted with EtOAc. The organic phase was washed with water, dried, concentrated, and finally subjected to chromatography on silica gel with EtOAc:hexane (2:3) to furnish **7** (3.06 g, 52% yield).

7: colorless oil; IR (neat) 3700–2800, 1750, 1730, 1710, 1200 cm^{-1} ; 1H NMR δ 1.34 (d, $J=8.7$, 1H), 1.50 (m, 1H), 3.19 (m, 2H), 3.32 (m, 2H), 3.61 (s, 3H), 6.23 (dd, $J=5.5, 2.9$, 1H), 6.33 (dd, $J=5.6, 2.9$, 1H).

Transformation of (+)-**3** to **8**

To a solution of (+)-**3** (153 mg, 0.33 mmol) in MeOH (14 mL), was added K_2CO_3 (60 mg, 0.43 mmol) followed by H_2O_2 (2.88 mmol of 31% aqueous solution). After being stirred for 7 h at room temperature, the reaction was terminated by the addition of 2 N HCl at 0°C. The mixture was extracted with EtOAc, and the organic phase was washed with water, dried, concentrated, and chromatographed (EtOAc:hexane=1:3) to furnish **7** (28 mg, 43% yield). All spectral data of **7** were identical with the reported values.⁹ To a solution of **7** (16 mg, 0.082 mmol) in CH_2Cl_2 (3 mL) was added (*R*)-(+)-phenethyl alcohol (20 μ L, 0.163 mmol), WSC (32 mg, 0.163 mmol), DMAP (2 mg, 0.01 mmol) and

the mixture was stirred for 131 h at room temperature. The reaction was quenched by adding 2 N HCl at 0°C. The mixture was extracted with EtOAc, and the organic phase was washed with water, dried, concentrated to leave the residue, which was chromatographed on silica gel (EtOAc:hexane=1:5) to furnish **8** (5 mg, 19% yield). **8** was identical with that reported.⁹

8 (optically active): colorless oil; $[\alpha]_D^{17} +85.3$ (c 0.25, THF, 100% ee); IR 3000, 1775, 1735, 1200, 1170 cm^{-1} ; $^1\text{H NMR}$ δ 1.50 (d, $J=6.6$, 3H), 3.16 (brs, 2H), 3.32 (m, 2H), 3.60 (s, 3H), 5.82 (q, $J=6.6$, 1H), 6.06 (m, 1H), 6.28 (m, 1H), 7.35 (m, 5H).

Preparation of ethyl 8'-hydroxy-1,1'-binaphthalene-8-yl fumarate **9**

Racemic **9** was synthesized in 89% yield (731 mg) from **1** (572 mg, 2 mmol), fumaric acid monoethyl ester (346 mg, 2.4 mmol), WSC (575 mg, 3 mmol), DMAP (25 mg, 0.2 mmol) and dry CH_2Cl_2 (30 mL) according to the procedure described for the preparation of **2**.

9 (racemic): white powder; mp 121–122°C.

9 (optically active): white powder; mp 145–150°C; $[\alpha]_D^{17} +250.7$ (c 2.02, CHCl_3 , 100% ee); IR 3520, 3020, 2360, 1720, 1290, 1230, 1140, 820 cm^{-1} ; $^1\text{H NMR}$ δ 1.35 (t, $J=7.2$, 3H), 4.20 (q, $J=7.2$, 2H), 5.28 (s, 1H), 5.57 (d, $J=15.8$, 1H), 5.84 (d, $J=15.8$, 1H), 6.78 (dd, $J=6.4$, 2.3, 1H), 7.09 (m, 2H), 7.26–7.60 (m, 6H), 7.70 (dd, $J=8.3$, 1.3, 1H), 7.89 (dd, $J=8.3$, 1.2, 1H), 8.00 (dd, $J=8.2$, 1.4, 1H); Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_5$: C, 75.72; H, 4.89. Found: C, 75.64; H, 4.85.

Hydrolysis of **10** and **11** to (–)-**14**

To a solution of **10** (58 mg, 0.11 mmol) in 1,4-dioxane (5 mL), was added aq. KOH (204 mg, 3.64 mmol) and the mixture was refluxed for 12 h. The reaction was terminated by adding 2 N HCl at 0°C. The mixture was extracted with EtOAc, and organic phase was washed with water, dried over MgSO_4 , concentrated, and chromatographed (CHCl_3 :MeOH=20:1) to furnish (–)-**14**⁸ (18 mg, 89% yield). A similar treatment of **12** also furnished (–)-**14** in 90% yield.

14 (optically active): amorphous; $[\alpha]_D^{19} -150.0$ (c 0.52, MeOH, 100% ee); IR (KBr) 3400–2800, 1690, 1425 cm^{-1} ; $^1\text{H NMR}$ (MeOH- d_4) δ 1.42 (d, $J=8.1$, 1H), 1.60 (d, $J=8.0$, 1H), 2.49 (brs, 1H), 3.06 (brs, 1H), 3.17 (brs, 1H), 3.32 (brs, 1H), 6.11 (brs, 1H), 6.25 (brs, 1H).

Preparation of methyl 8'-methoxyl-1,1'-binaphthalene-8-yl maleate **15**

To a stirred solution of **2** (30 mg, 0.075 mmol) in acetone (1 mL), was added MeI (47 μL , 0.75 mmol) and K_2CO_3 (52 mg, 0.375 mmol) and the mixture was stirred for 4 h with reflux. The reaction was terminated by addition of aq. 2 N HCl at 0°C. The mixture was extracted with EtOAc, and organic phase was washed with water, dried, concentrated, and chromatographed (EtOAc:hexane=1:4) to furnish **15** (22 mg, 71% yield) as a colorless oil.

15 (racemic): oil; IR 3000, 1730, 1580, 1220, 1150, 790, 730, 630 cm^{-1} ; $^1\text{H NMR}$ δ 3.06 (s, 3H), 3.68 (s, 3H), 4.49 (d, $J=11.8$, 1H), 5.68 (d, $J=11.8$, 1H), 6.67 (dd, $J=7.5$, 1.2, 1H), 7.17–7.27 (m, 3H), 7.35–7.52 (m, 5H), 7.77–7.89 (m, 3H); HRMS (m/z) Calcd 412.1311 (M^+), Found 412.1290; MS (m/z) 412 (M^+), 300, 284.

Preparation of ethyl 8'-methoxyl-1,1'-binaphthalene-8-yl fumarate **17**

To a solution of **9** (200 mg, 0.485 mmol) in acetone (7 mL), was added MeI (302 μL , 4.85 mmol) and K_2CO_3 (335 mg, 2.43 mmol) and the mixture was refluxed for 4 h with stirring. The reaction was terminated by an addition of 2 N HCl at 0°C. The mixture was extracted with EtOAc, and organic phase was washed with water, dried, concentrated, and chromatographed (EtOAc:hexane=1:5) to furnish **17** (166 mg, 80% yield).

17 (racemic): oil; IR 3020, 1720, 1260, 1220, 660 cm^{-1} ; $^1\text{H NMR}$ δ 1.38 (t, $J=7.2$, 3H), 3.08 (s, 3H), 4.24 (q, $J=7.2$, 2H), 5.50 (d, $J=16.0$, 1H), 5.80 (d, $J=16.0$, 1H), 6.66 (m, 1H), 7.03 (dd, $J=7.4$, 1.1, 1H), 7.17–7.53 (m, 7H), 7.77 (dd, $J=8.1$, 1.2, 1H), 7.88 (m, 2H); HRMS (m/z) Calcd 426.1467 (M^+), Found 426.1475; MS (m/z) 426 (M^+), 403, 328, 300.

The ¹³C NMR spectra of 2 and 2–TiCl(OⁱPr)₃ complex at low temperature

A solution of TiCl(OⁱPr)₃ (0.25 mmol, hexane solution) was added to the mixture of maleate **2** (100 mg, 0.25 mmol) and CDCl₃ (1.3 mL) in a tube for NMR (5 mm ϕ) at 0°C, and the ¹³C NMR spectra (at 100 MHz) were taken at the same temperature.

2: ¹³C NMR δ 165.16, 163.93, 153.01, 146.04, 137.29, 136.08, 135.31, 135.19, 130.01, 129.32, 129.08, 128.24, 127.75, 127.69, 127.22, 126.81, 126.20, 125.31, 125.19, 125.14, 122.51, 120.83, 120.58, 111.58, 52.10.

2–TiCl(OⁱPr)₃ (1:1) complex: ¹³C NMR δ 165.67, 165.52, 153.26, 146.21, 137.60, 136.55, 135.35, 135.31, 129.86, 129.69, 129.54, 128.89, 128.08, 127.69, 127.14, 126.78, 126.07, 125.38, 125.27, 125.12, 122.74, 120.76, 120.45, 111.53, 52.12.

The ¹³C NMR spectra of 9 and 9–SnCl₄ complex at low temperature

To a solution of the maleate **9** (100 mg, 0.25 mmol) in CDCl₃ (1.3 mL) in a 5 mm ϕ NMR tube was added SnCl₄ (0.25 mmol) at –78°C, and the ¹³C NMR spectra (at 100 MHz) were taken at the same temperature.

9: ¹³C NMR δ 164.53, 163.48, 152.55, 145.58, 136.64, 136.05, 135.99, 135.12, 135.02, 133.06, 132.64, 129.84, 128.96, 127.94, 127.82, 127.72, 127.51, 126.70, 125.87, 125.43, 125.00, 122.00, 120.58, 111.05, 61.34, 14.07.

9–SnCl₄ (1:1) complex: ¹³C NMR δ 165.75, 163.80, 152.18, 145.36, 136.58, 136.52, 135.94, 135.07, 135.00, 132.35, 132.02, 130.62, 129.79, 128.94, 127.91, 127.72, 126.84, 125.82, 125.50, 125.21, 124.83, 121.90, 120.68, 120.51, 111.24, 62.86, 13.96.

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