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Enantioselective Diels–Alder Reaction of α-Acyloxyacroleins Catalyzed by Chiral 1,1′-Binaphthyl-2,2′-diammonium Salts

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Abstract: A diammonium salt of chiral 1,1′-binaphthyl-2,2′-diamine (**2a**) and trifluoromethanesulfonimide (Tf_2NH) shows excellent catalytic activity and enantioselectivity for the Diels–Alder reaction of α-acyloxyacroleins. For example, in the presence of 5 mol% of **2a** and 9.5 mol% of Tf_2NH, the Diels–Alder reaction of α-(cyclohexanecarbonyloxy)acrolein with cyclopentadiene proceeded in EtCN at −75 °C to give the adducts in 88% yield with 92% *exo* and 91% *ee*. The electron-donating property of the acyl group of the α-acyloxyacroleins increases the enantioselectivity due to the formation of strong intramolecular hydrogen bonding of the acyl group with a proton of the ammonium group in the transition state. This catalyst can be easily prepared *in situ* by mixing the commercially available chiral diamine and Tf_2NH.

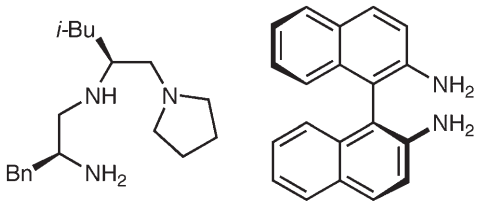
Keywords: α-acyloxyacrolein; ammonium salts; 1,1′-binaphthyl-2,2′-diamine; cycloaddition; Diels–Alder reaction

Introduction

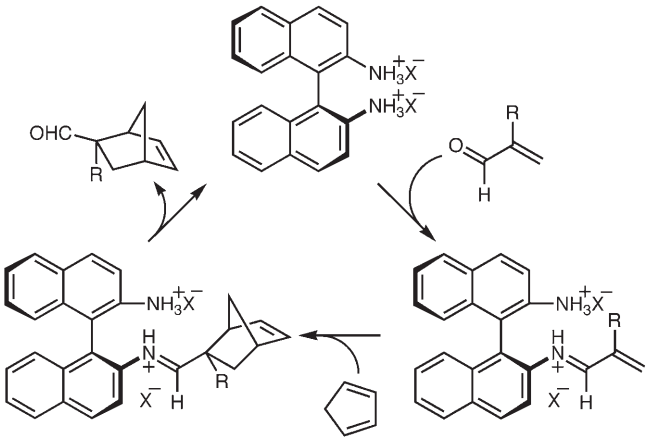
The enantioselective Diels–Alder reaction is one of the most powerful organic transformations, and is a versatile method for the synthesis of many important chiral building blocks for the total synthesis of bioactive natural products.[1] Recently, the use of organocatalysts for the enantioselective Diels–Alder reaction has attracted great attention and has been extensively studied with great success.[2–4] Most of the reported organocatalysts for the enantioselective Diels–Alder reaction are ammonium salts of *secondary* amines, and their general mode of catalysis is the generation of iminium cations as active intermediates. While these organocatalysts give good results for the Diels–Alder reaction of α-*unsubstituted* acroleins, it is difficult to activate α-*substituted* acroleins, probably because of poor generation of the corresponding iminium cations. The greater bulkiness of the secondary amines has been considered to be unfavorable for generating an iminium ion with an α-substituted acrolein.[5]

α-Acyloxyacrolein is an important alternative to α-haloacrolein,[6] and is very versatile in synthesis as a dienophile.[7] For example, the adducts of cyclopentadiene with α-acyloxyacrolein can be converted to bicyclo[2.2.1]hept-5-en-2-one, which is a promising synthetic intermediate for the total synthesis of several bioactive compounds,[8] and the development of a practical method for the synthesis of this compound in an enantiomerically pure form is strongly needed. Recently, we reported the enantioselective organocatalytic Diels–Alder reaction with α-acyloxyacrolein.[9] Our catalyst is the chiral ammonium salt of the chiral triamine **1** bearing a *primary* aliphatic amino group with pentafluorobenzenesulfonic acid ($C_6F_5SO_3H$).[10] The Diels–Alder reactions of acyclic dienes and cyclohexadiene with α-(*p*-methoxybenzoyloxy)acrolein give the adducts with high enantioselectivities. Unfortunately, however, the enantioselectivity for the reaction of cyclopentadiene is up to 83% *ee*. In addition, the catalytic activity is not so high (10–20 mol% of catalyst is loaded at −20 °C to room temperature) because of its relatively weak acidity.

To improve the catalytic activity and enantioselectivity for the Diels–Alder reaction of cyclopentadiene, we planned to use the ammonium salt of a weakly basic aromatic amine with a super Brønsted acid[10] as a catalyst at a lower reaction temperature. The strong-



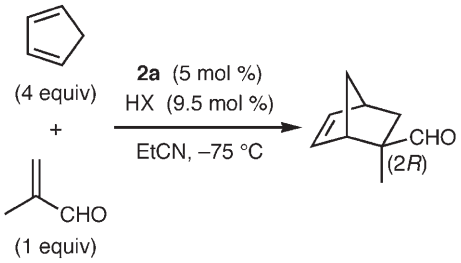
1 2a



Scheme 1. Chiral 1,1′-binaphthyl-2,2′-diammonium salt catalysts for the enantioselective Diels–Alder reaction of cyclopentadiene with α-substituted acroleins.

ly acidic ammonium salt of chiral aromatic diamine **2a** was thought to react easily with an α-substituted acrolein to form an iminium cation as an active intermediate, which would smoothly react with cyclopentadiene even at lower temperature (Scheme 1). We describe here chiral 1,1′-binaphthyl-2,2′-diammonium salt catalysts for the enantioselective Diels–Alder reactions of α-substituted acroleins.[11]

Table 1. Diels–Alder reaction of cyclopentadiene with methacrolein.[a]



Entry	HX	Time [h]	Yield [%][b]	*exo*/*endo*[b]	ee [%][c]
1	$C_6F_5SO_3H$	6	8	90:10	45
2	TfOH	6	27	97:3	39
3	$C_6F_{13}SO_3H$	6	99	93:7	0
4[d]	(+)-CSA	3	99	87:13	13
5[d]	2,4,6-(*i*-Pr)$_3$C$_6$H$_2$SO$_3$H	3	85	88:12	13
6	Tf_2NH	6	13	97:3	61
7	$(C_4F_9SO_2)_2NH$	6	30	97:3	60

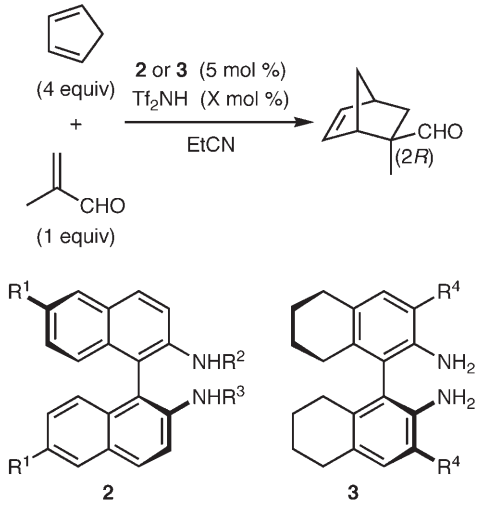
[a] Unless otherwise noted, the Diels–Alder reaction of cyclopentadiene (4 mmol) with methacrolein (1 mmol) in EtCN (2 mL) was carried out at −75 °C.
[b] Determined by ^{1}H NMR analysis.
[c] Enantiomeric excess of the *exo*-adduct.
[d] The reaction was conducted at 0 °C.

Results and Discussion

First, we examined the Diels–Alder reaction of cyclopentadiene (4 equivs.) with methacrolein using chiral ammonium salts of commercially available **2a** (5 mol%) and a variety of Brønsted acids (HX, 9.5 mol%) in propionitrile (EtCN) at −75 °C (Table 1). The ammonium salt of **2a** and $C_6F_5SO_3H$ gave the (2*R*)-*exo*-adduct as a major diastereomer in a conversion yield of 8% with 45% *ee* (entry 1). The use of trifluoromethanesulfonic acid (TfOH) gave an enantioselectivity (39% *ee*) similar to that with $C_6F_5SO_3H$ (entry 2). The ammonium salt of the much stronger perfluorohexanesulfonic acid ($C_6F_{13}SO_3H$) gave the adduct in quantitative yield with no enantioselectivity, since the acidity of the ammonium salt was too strong to control the reaction (entry 3). Since the catalytic activities of the ammonium salts of (+)-10-camphorsulfonic acid [(+)-CSA] and 2,4,6-triisopropylbenzenesulfonic acid [2,4,6-(*i*-Pr)$_3$C$_6$H$_2$SO$_3$H], which were weaker sulfonic acids than TfOH, were quite low, the reactions catalyzed by them required an increased reaction temperature (0 °C) and gave the *exo*-adduct with quite low enantioselectivities (13% *ee*) (entries 4 and 5). Importantly, ammonium salts of trifluoromethanesulfonimide (Tf_2NH) and perfluorobutanesulfonimide [$(C_4F_9SO_2)_2NH$] gave the (2*R*)-*exo*-adduct with better enantioselectivities (61 and 60% *ee*, respectively) (entries 7 and 8). The suitably strong acidities of the ammonium catalysts promoted the reactions well, and the bulkiness of the counter anions of the ammonium catalysts might increase the enantioselectivities. Therefore, we considered that commercially available Tf_2NH was the most suitable Brønsted acid for the present Diels–Alder reaction.

Next, we investigated the catalytic activities of ammonium salts of the binaphthyldiamines **2** and octahydrobinaphthyldiamines **3** with Tf_2NH (Table 2). The ammonium salt of 6,6′-dibromo derivative **2b** showed good catalytic activity (82% yield) with an enantioselectivity similar to that with **2a** (62% *ee*) (entry 1). The introduction of bromo substituents at the 6,6′-positions would enhance the acidity of the ammonium salt to result in higher catalytic activity. The ammonium salts of *N*-monosubstituted or *N,N*′-disubstituted binaphthyldiamines **2c–g** all gave the adduct with quite lower enantioselectivities (< 13% *ee*) (entries 2–6). The *N*-substituents might hinder the formation of the aldimine intermediate. The ammonium salt of octahydrobinaphthyldiamine **3a** showed moderate catalytic activity (52% yield) with low enantioselectivity (33% *ee*) (entry 7). The introduction of bromo substituents at the 3,3′-positions led to the opposite enantioselectivity with low enantiomeric excess (18%) (entry 8). Among the chiral diamines we examined,

Table 2. Substituent effect of binaphthyldiamines **2** and octahydrobinaphthyldiamines **3** on the Diels–Alder reaction.[a]



Entry	**2** [R^1, R^2, R^3] or **3** [R^4]	X [mol %]	Conditions [°C, h]	Yield [%][b]	*exo*/*endo*[b]	ee [%][c] (config)
1	**2b** [Br, H, H]	9.5	−75, 22	82	99:1	62 (2*R*)
2	**2c** [H, Me, Me]	9.5	−20, 2	93	82:18	0
3	**2d** [H, Bn, H]	9.5	−45, 4.5	99	90:10	0
4	**2e** [H, Ph, H]	4.8	−75, 20	59	91:9	0
5	**2f** [H, Bz, H]	4.8	−40, 72	29	97:3	13 (2*R*)
6	**2g** [H, Ts, H]	4.8	−45, 15	20	99:1	0
7	**3a** [H]	9.5	−40, 10	52	90:10	33 (2*R*)
8	**3b** [Br]	9.5	−75, 25	19	96:4	18 (2*S*)

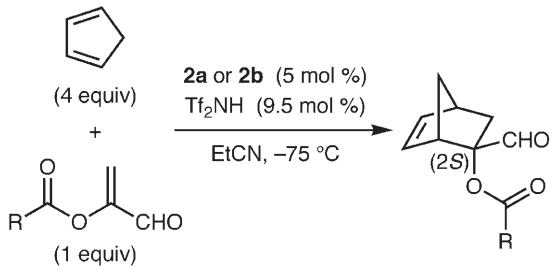
[a] The Diels–Alder reaction of cyclopentadiene (4 mmol) with methacrolein (1 mmol) in EtCN (2 mL) was carried out.
[b] Determined by ^{1}H NMR analysis.
[c] Enantiomeric excess of the *exo*-adduct.

2a and **2b** were found to be quite effective for the present Diels–Alder reaction.

With these results in hand, we examined the Diels–Alder reaction of cyclopentadiene (4 equivs.) with α-acyloxyacroleins catalyzed by the ammonium salt of **2a** or **2b** (5 mol %) with Tf_2NH (9.5 mol %) (Table 3). In the presence of the ammonium salt of **2a**, the Diels–Alder reaction with α-(*p*-methoxybenzoyloxy)-acrolein, which gave the highest enantiomeric excess (83 %) in the Diels–Alder reaction of cyclopentadiene catalyzed by the ammonium salt of **1** and $C_6F_5SO_3H$, gave the corresponding (2*S*)-*exo*-adduct as a major diastereomer with remarkably high enantiomeric excess (94 %) in moderate yield (48 %) (entry 1). The electron-donating property of the *p*-methoxybenzoyloxy group was thought to increase the enantioselectivity (see Figure 1). However, the poor solubility of α-(*p*-methoxybenzoyloxy)acrolein in EtCN at −75 °C resulted in poor reactivity. The use of the ammonium salt of **2b** as a catalyst gave the (2*S*)-*exo*-adduct in quantitative yield, although the enantioselectivity was slightly decreased (87 % *ee*) (entry 2). The stronger acidity of the ammonium salt of **2b** would result in a higher reaction rate but lower enantioselectivity than that of **2a**.

Therefore, we investigated the Diels–Alder reaction of cyclopentadiene with several α-acyloxyacroleins, which had an acyloxy group with electron-donating substituents and could be dissolved in EtCN at −75 °C. As a result, we found that the reaction with α-(cyclohexanecarbonyloxy)acrolein catalyzed by the ammonium salt of **2a** gave the corresponding (2*S*)-*exo*-adduct with good enantioselectivity (86 % *ee*) and in good yield (80 %) (entry 3). Moreover, when the reaction was conducted in the presence of 10 mol % of water, the yield and enantioselectivity were increased[12] (88 % yield and 91 % *ee*) (entry 4). Water might promote the hydrolysis of the aldimine intermediate to increase the catalytic turnover rate. The use of the ammonium salt of **2a** (5 mol %) and Tf_2NH (4.8 mol %) as a catalyst gave a lower yield (72 %) and enantioselectivity (71 %) (entry 5). α-(Cyclopentanecarbonyloxy)acrolein and α-(diphenylacetyloxy)-acrolein also gave good results (entries 7 and 8). Importantly, α-[*p*-(triisopropylsilyloxy)benzoyloxy]acrolein, which had good electron-donating ability and could be dissolved in EtCN, exhibited reactivity higher than α-(*p*-methoxybenzoyloxy)acrolein (76 % yield) with excellent enantioselectivity (94 % *ee*) (entry 9).

Table 3. Diels–Alder reaction of cyclopentadiene with α-acyloxyacroleins.[a]



Entry	R	Diamine	Time [h]	Yield [%][b]	*exo*/*endo*[b]	ee [%][c]
1	*p*-$MeOC_6H_4$	**2a**	28	48	93:7	94
2	*p*-$MeOC_6H_4$	**2b**	21	99	87:13	87
3	*c*-C_6H_{11}	**2a**	24	80	94:6	86
4[d]	*c*-C_6H_{11}	**2a**	24	88	92:8	91
5[e]	*c*-C_6H_{11}	**2a**	24	72	91:9	71
6	*c*-C_6H_{11}	**2b**	25	78	86:14	83
7[d]	*c*-C_5H_9	**2a**	24	95	92:8	88
8[f]	Ph_2CH	**2a**	24	99	95:5	91
9	*p*-$TIPSOC_6H_4$	**2a**	24	76	93:7	94

[a] Unless otherwise noted, the Diels–Alder reaction of cyclopentadiene (1.6 mmol) with α-acyloxyacrolein (0.4 mmol) in EtCN (0.8 mL) was carried out at −75 °C.
[b] Determined by ^1H NMR analysis.
[c] Enantiomeric excess of the *exo*-adduct.
[d] The reaction was conducted in the presence of H_2O (10 mol %).
[e] The reaction was conducted in the presence of **2a** (5 mol %) and Tf_2NH (4.8 mol %).
[f] The reaction was carried out at −40 °C.

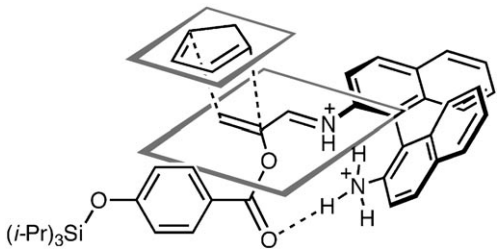
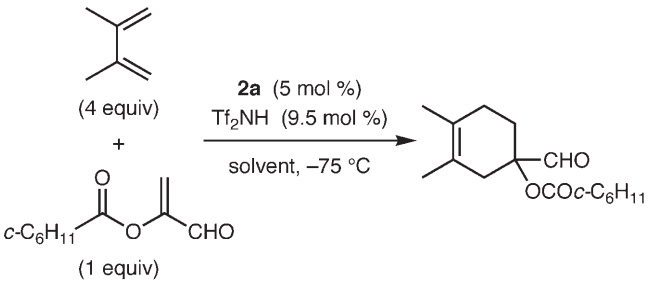


Figure 1. Proposed transition-state assembly. Counter anions (Tf_2N^-) are omitted for clarity.

As described above, we succeeded in the Diels–Alder reaction of cyclopentadiene with high enantioselectivity. However, when the reaction of acyclic 2,3-dimethylbutadiene with α-(cyclohexanecarbonyloxy)-acrolein was conducted under the same reaction conditions, the yield and enantioselectivity of the corresponding Diels–Alder adduct were moderate (52 % yield and 54 % *ee*) (Table 4, entry 2). Therefore, we screened a variety of solvents (Table 4), and found that the use of more polar nitroethane ($EtNO_2$) as a solvent resulted in a higher enantioselectivity (60 % yield and 71 % *ee*) (entry 1).[13] Dichloromethane (CH_2Cl_2) gave an enantioselectivity (49 % *ee*) that was slightly lower than that with EtCN (entry 3). The use of a less polar solvent such as dieth yl ether (Et_2O) or toluene resulted in low reactivity (entries 4 and 5).

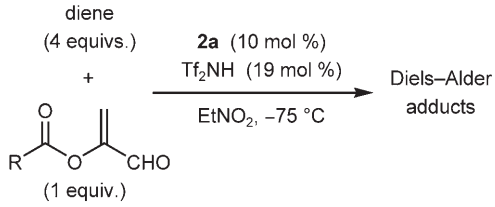
Table 4. Diels–Alder reaction of 2,3-dimethylbutadiene with α-acyloxyacroleins.[a]

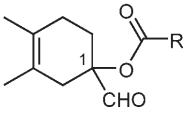
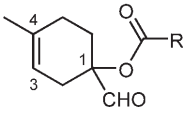
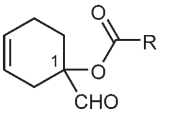
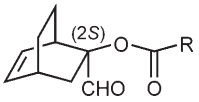


Entry	Solvent	Time [h]	Yield [%][b]	*ee* [%][c]
1	$EtNO_2$	72	60	71
2	EtCN	65	52	54
3	CH_2Cl_2	72	59	49
4	Et_2O	15	3	ND
5	Toluene	15	3	ND

[a] The Diels–Alder reaction of cyclopentadiene (1.6 mmol) with α-acyloxyacrolein (0.4 mmol) in solvent (0.8 mL) was carried out at −75 °C.
[b] Determined by ^1H NMR analysis.
[c] Enantiomeric excess of the *exo*-adduct.

Table 5. Diels–Alder reaction of dienes with α-acyloxyacroleins.[a]



Entry	Diene	Product	R	Time [h]	Yield [%][b]	*eo*/*endo*[b]	*ee* [%][c] (config)
1			*c*-C_6H_{11}	48	88	-	70 (ND)
2			*c*-C_5H_9	48	98	-	65 (ND)
3[d]			Ph_2CH	10	99	-	70 (ND)
4			*p*-$TIPSOC_6H_4$	48	85	-	85 (ND)
5			*c*-C_6H_{11}	48	67	>99:<1[e]	71 (ND)
6[d]			Ph_2CH	16	99	>99:<1[e]	67 (ND)
7			*p*-$TIPSOC_6H_4$	48	85	>99:<1[e]	82 (ND)
8			*c*-C_6H_{11}	48	65	-	68 (ND)
9			*p*-$TIPSOC_6H_4$	48	77	-	82 (ND)
10[f]			*c*-C_6H_{11}	48	90	<1:>99	91 (2*S*)
11[f]			*c*-C_5H_9	48	97	<1:>99	87 (2*S*)

[a] Unless otherwise noted, the Diels–Alder reaction of dienes (1.6 mmol) with α-acyloxyacrolein (0.4 mmol) in $EtNO_2$ (0.8 mL) was carried out at −75 °C.
[b] Determined by ^1H NMR analysis.
[c] Enantiomeric excess of the major diastereomer.
[d] The reaction was carried out at −40 °C.
[e] The molar ratio of 4-methyl and 3-methyl isomers is indicated.
[f] The reaction was conducted in the presence of **2a** (5 mol %) and Tf_2NH (9.5 mol %).

With the optimized reaction conditions in hand, the reaction of various dienes was examined to explore the generality and scope of the present Diels–Alder reaction (Table 5). Since acyclic dienes such as 2,3-dimethylbutadiene, isoprene and butadiene were less reactive, 10 mol % of the catalyst was used for the reaction of acyclic dienes. For the Diels–Alder reaction of 2,3-dimethylbutadiene and isoprene, the use of α-(diphenylacetyloxy)acrolein resulted in an enantioselectivity similar to that with α-(cyclohexanecarbonyloxy)acrolein and α-(cyclopentanecarbonyloxy)acrolein (entries 1–3, 5 and 6). As expected, the reaction of 2,3-dimethylbutadiene with α-[*p*-(triisopropylsilyloxy)benzoyl]acrolein gave much better results (85 % yield, 85 % *ee*) (entry 4).[14]

The Diels–Alder reaction of cyclohexadiene with α-(cyclohexanecarbonyloxy)acrolein was conducted in the presence of 5 mol % of the ammonium catalyst and gave the corresponding (2*S*)-*endo*-adduct as a single diastereomer in 90 % yield with 91 % *ee* (entry 10). α-(Cyclopentanecarbonyloxy)acrolein also gave good results (97 % yield, 87 % *ee*) (entry 11). In general, the Diels–Alder reaction of cyclohexadiene with α-substituted acroleins is highly *endo*-selective, while the reaction of cyclopentadiene is *exo*-selective.[6i,j] The Diels–Alder adducts of cyclohexadiene with α-acyloxyacrolein can be converted to bicyclo-[2.2.2]oct-5-en-2-one, which is also useful as a common intermediate for the total syntheses of several bioactive compounds.[15]

The sense of asymmetric induction observed in the present Diels–Alder reaction is considered to be as follows (Figure 1).[11] The aldimine would be formed from an α-acyloxyacrolein and the ammonium salt of **2a** as an active intermediate. In the active intermediate, the aldimine moiety is activated by Tf_2NH and the acyloxy group forms an intramolecular hydrogen bonding with a proton of the ammonium group. The diene should approach the *si*-face of the *s-trans* acrolein moiety of the active intermediate from the less-hindered side, to give the (2*S*)-adduct.

α-[*p*-(Triisopropylsilyloxy)benzoyl]acrolein bearing a good electron-donating *p*-(triisopropylsilyloxy)-phenyl group exhibited very high enantioselectivity, which would be attributed to the formation of the strong intramolecular hydrogen bonding in the transition state, due to the higher basicity of the carbonyl oxygen of the acyloxy group.

Conclusions

In conclusion, we have developed the enantioselective Diels–Alder reaction with α-acyloxyacroleins catalyzed by the chiral ammonium salt of binaphthyl-based diamine **2a** with Tf_2NH. The use of a small amount (5–10 mol%) of this chiral ammonium catalyst at a low reaction temperature (−75 °C) gave excellent reactivity and enantioselectivity in the Diels–Alder reaction with α-acyloxyacroleins. The electron-donating property of the acyl group of the α-acyloxyacroleins increased the enantioselectivity due to the formation of strong intramolecular hydrogen bonding between the acyl group and a proton of the ammonium group in the transition state. The ammonium catalyst could be easily prepared *in situ* by mixing commercially available 2,2′-diamino-1,1′-binaphthyl (**2a**) and Tf_2NH.

Experimental Section

General Remarks

IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. ^{1}H NMR spectra were measured on a Varian Gemini-2000 spectrometer (300 MHz) at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethysilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR spectra were measured on a Varian Gemini-2000 spectrometer (75 MHz). Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm). Analytical HPLC was performed on a Shimadzu LC-10 coupled diode array-detector SPD-MA-10 A-VP and column of Daicel CHIRALCEL OD-H, AD-H or OJ-H (Ø 4.6 mm × 250 mm). Optical rotations were measured on a RUDOLPH AUTOPOL IV digital polarimeter. GC analysis was performed with Shimadzu 17 A instruments with a flame-ionization detector and a capillary column of PEG-HT Bonded (25 m × 0.25 mm) using nitrogen as carrier gas. All experiments were carried out under an atmosphere of dry nitrogen. For TLC analysis, Merck precoated TLC plates (silica gel 60 F_{254} 0.25 mm) were used. For preparative column chromatography, Merck silica gel 60 (0.040–0.063 mm) was used. High resolution mass spectral analysis (HR-MS) was performed at Chemical Instrument Room, Research Center for Materials Science, Nagoya University. Dry toluene and THF was purchased from Wako as "anhydrous" and stored under nitrogen. CH_2Cl_2, EtCN and $EtNO_2$ were freshly distilled from calcium hydride. Other materials were obtained from commercial supplies and used without further purification. (*S*)-2,2′-diamino-1,1′-binaphthyl (**2a**) was purchased from Wako. Tf_2NH was purchased from Aldrich. Diamines **2c**,[16] **2d**,[17] **2e**,[18] **3a**[19] were prepared according to the reported procedure. α-(*p*-Methoxybenzoyloxy)-acrolein (Table 3),[9,11] α-(cyclohexanecarbonyloxy)acrolein (Tables 3–5),[9] α-(cyclopentanecarbonyloxy)acrolein (Tables 3 and 5),[11] (1*S*,2*R*,4*S*)-2-formyl-2-methylbicyclo[2.2.1]hept-5-ene (Tables 1 and 2),[9,11] (−)-(1*S*,2*S*,4*S*)-2-formylbicyclo-[2.2.1]hept-5-ene-2-yl *p*-methoxybenzoate (Table 3),[9,11] (−)-(1*S*,2*S*,4*S*)-2-formylbicyclo[2.2.1]hept-5-ene-2-yl cyclohexanecarboxylate (Tables 3),[11] (−)-(1*S*,2*S*,4*S*)-2-formylbicyclo-[2.2.1]hept-5-ene-2-yl cyclopentanecarboxylate (Table 3),[11] (+)-(1*R*,2*S*,4*R*)-2-formylbicyclo[2.2.2]oct-5-ene-2-yl cyclohexanecarboxylate (Table 5),[11] (+)-(1*R*,2*S*,4*R*)-2-formylbicyclo[2.2.2]oct-5-ene-2-yl cyclopentanecarboxylate (Table 5),[11] 1-formyl-3,4-dimethylcyclohex-3-enyl cyclohexanecarboxylate (Table 4),[11] 1-formyl-3,4-dimethylcyclohex-3-enyl cyclopentanecarboxylate (Table 5)[11] were previously known.

(*S*)-6,6′-Dibromo-1,1′-binaphthyl-2,2′-diamine (2b)

To a solution of **2a** (284 mg, 1.0 mmol) in 1,4-dioxane (10 mL) was added *N*-bromosuccinimide (534 mg, 3.0 mmol), and the mixture was stirred at ambient temperature for 5 h. The reaction was quenched with 10% aqueous $Na_2S_2O_3$ (10 mL), and the aqueous layer extracted with EtOAc (50 mL × 3). The combined organic layer and extracts were washed with H_2O and brine, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography on silica gel using hexane-EtOAc as the eluent, to give **2b**; yield: 173 mg (41%). $[\alpha]_D^{26}$: 0.400 (*c* 1.0, $CHCl_3$); IR (KBr): ν = 1617, 1492, 1383, 1350, 1068 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 4H), 6.90 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.26 (dd, *J* = 2.1, 8.7 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.94 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 111.9, 116.2, 119.4, 125.7, 128.9, 129.6, 130.2, 130.3, 132.2, 143.2; HR-MS (FAB): *m/z* = 442.9568, calcd. for $C_{20}H_{15}Br_2N_2$ $[M+H]^+$: 442.9583.

(*S*)-*N*-Benzoyl-1,1′-binaphthyl-2,2′-diamine (2f)

To a solution of **2a** (100 mg, 0.35 mmol) and pyridine (85 μL, 1.05 mmol) in acetnitrile (3.5 mL) was added benzoyl chloride (45 μL, 0.39 mmol), and the mixture was refluxed for 12 h. After cooling to ambient temperature, the reaction was quenched with brine (10 mL) and extracted with EtOAc (15 mL × 3). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel using hexane-EtOAc as the eluent, to give **2f**; yield: 26 mg (19%);. $[\alpha]_D^{26}$: −103.7 (*c* 1.00, $CHCl_3$); IR (KBr): ν = 1619, 1596, 1500, 1426, 1080 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.19–7.48 (m, 10H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.94 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 8.91 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 110.3, 118.2, 120.4, 120.7, 123.0, 123.8, 125.3, 125.6, 126.9, 127.1, 127.7, 128.3, 128.4, 128.5, 128.7, 129.6, 130.7, 131.4, 131.7, 132.5, 133.6, 134.9, 135.3, 143.0, 165.4; HR-MS (FAB): *m/z* = 389.1656, calcd for $C_{27}H_{21}ON_2$ $[M+H]^+$: 389.1654.

(*S*)-*N*-(*p*-Toluenesulfonyl)-1,1′-binaphthyl-2,2′-diamine (2g)

To a solution of **2a** (100 mg, 0.35 mmol) and pyridine (85 μL, 1.05 mmol) in acetnitrile (3.5 mL) was added *p*-toluenesulfonyl chloride (73 mg, 0.38 mmol), and the mixture was refluxed for 12 h. After cooling to ambient temperature, the reaction was quenched with brine (10 mL) and extracted

with EtOAc (15 mL × 3). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel using hexane-EtOAc as the eluent, to give **2g**; yield: 130 mg (85%); $[\alpha]_D^{27}$: 9.61 (*c* 1.00, $CHCl_3$); IR (KBr): ν = 1620, 1596, 1509, 1401, 1318, 1163, 1091 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 3.40 (s, 2H), 6.40 (d, *J* = 8.4 Hz, 1H), 6.67 (s, 1H), 6.94 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 7.03 (m, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 7.21 (m, 2H), 7.34–7.45 (m, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.7 Hz, 1H), 8.12 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 109.6, 118.1, 119.6, 121.7, 122.5, 123.4, 125.5, 125.8, 127.2, 127.3, 128.2, 128.2, 129.5, 129.8, 130.8, 131.4, 132.8, 133.6, 133.7, 136.2, 142.8, 143.8; HR-MS (FAB): *m/z* = 439.1450, calcd. for $C_{27}H_{23}O_2N_2S$ $[M+H]^+$: 439.1480.

(*S*)-3,3′-Dibromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diamine (3b)

Compound **3b** was prepared according to the same manner as **2b** using (*S*)-**3a** instead of (*S*)-**2a**. $[\alpha]_D^{27}$: −26.8 (*c* 1.00, $CHCl_3$); IR (KBr): ν = 2928, 1602, 1458, 1094 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.50–1.80 (m, 8H), 2.00–2.30 (m, 4H), 2.70 (t, *J* = 6.0 Hz, 4H), 3.72 (s, 4H), 7.21 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.1, 23.3, 26.9, 29.2, 107.2, 122.5, 129.2, 132.4, 135.8, 139.3; HR-MS (FAB): *m/z* = 451.0217, calcd. for $C_{20}H_{23}Br_2N_2$ $[M+H]^+$: 451.0209.

α-(Diphenylacetyloxy)acrolein (Tables 3 and 5)

This compound was prepared according to the reported procedure.[9,11] IR (KBr): ν = 2880, 1766, 1687, 1644, 1496, 1455, 1347, 1272, 1191, 1142, 1084 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 5.24 (s, 1H), 5.94 (d, *J* = 2.4 Hz, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 7.25–7.41 (m, 10H), 9.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.6, 121.8, 127.7, 128.8, 128.8, 137.9, 152.7, 170.1, 185.1; HR-MS (FAB): *m/z* = 267.1025, calcd. for $C_{17}H_{15}O_3$ $[M+H]^+$: 267.1021.

α-[*p*-(Triisopropylsilyloxy)benzoyloxy]acrolein (Tables 3 and 5)

This compound was prepared according to the reported procedure.[9,11] IR (neat): ν = 2869, 1741, 1602, 1509, 1464, 1252, 1164, 1077 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 6.9 Hz, 18H), 1.22–1.35 (m, 3H), 6.03 (d, *J* = 2.1 Hz, 1H), 6.19 (d, *J* = 2.1 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 8.02 (d, *J* = 8.7 Hz, 2H), 9.48 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 17.9, 120.0, 120.9, 121.5, 132.6, 153.0, 161.5, 163.7, 185.7; HR-MS (FAB): *m/z* = 349.1832, calcd for $C_{19}H_{29}O_4Si$ $[M+H]^+$: 349.1835.

Representative Procedure for the Enantioselective Diels–Alder Reaction:[11]

To a solution of (*S*)-**2a** (5.7 mg, 0.02 mmol) and trifluoromethanesulfonimide (10.7 mg, 0.038 mmol) in propionitrile or nitroethane (0.8 mL) was added α-acyloxyacrolein (0.4 mmol). After cooling to −75 °C, diene (1.6 mmol) was added to the solution, and the reaction mixture was stirred at −75 °C for several hours. Upon consumption of α-acyloxyacrolein, the reaction was quenched with Et_3N, and concentrated under vacuum. The crude product was purified by silica gel chromatography using hexane-EtOAc as the eluent.

(−)-(1*S*,2*S*,4*S*)-2-Formylbicyclo[2.2.1]hept-5-ene-2-yl diphenylacetate (*exo* isomer) (Table 3): $[\alpha]_D^{27}$: −66.1 (*c* 1.00, $CHCl_3$) for 91% ee; IR (neat): ν = 2818, 1733, 1600, 1496, 1454, 1335, 1192, 1153, 1138, 1046 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.17 (dd, *J* = 3.9, 12.9 Hz, 1H), 1.41 (m, 1H), 1.67 (d, *J* = 9.6 Hz, 1H), 2.48 (dd, *J* = 3.9, 12.9 Hz, 1H), 2.93 (s, 1H), 3.15 (s, 1H), 5.00 (s, 1H), 5.90 (dd, *J* = 3.0, 5.4 Hz, 1H), 6.31 (dd, *J* = 3.0, 5.7 Hz, 1H), 7.20–7.40 (m, 10H), 9.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.0, 42.2, 45.8, 48.7, 56.6, 92.2, 127.5, 128.7, 128.8, 132.5, 138.0, 140.7, 172.7, 198.6; HR-MS (FAB): *m/z* = 333.1494, calcd. for $C_{22}H_{21}O_3$ $[M+H]^+$: 333.1491. The *exo-endo* ratio was determined by ^1H NMR analysis: δ = 9.39 [s, 1H, C*H*O (*endo*-isomer)] and 9.60 [s, 1H, C*H*O (*exo*-isomer)]. The *ee* and the absolute configuration of major enantiomer were established according to the reported procedure[9,11] by HPLC analysis (Daicel Chiralcel OJ-H column, hexane-*i*-PrOH = 40:1, flow rate = 1 mL min^{-1}) after conversion to (2-hydroxybicyclo-[2.2.1]hept-5-en-2-yl)methyl benzoate by reduction with $LiAlH_4$ (2 equivs.) in THF at ambient temperature and subsequent selective benzoylation of the primary hydroxy group of the corresponding 1,2-diol with benzoyl chloride (1.3 equivs.) in the presence of *N,N*-diisopropylethylamine (2 equivs.) in chloroform at 0 °C: t_R = 15.9 (minor *endo*-enantiomer), 17.6 (minor *endo*-isomer), 20.9 min (minor *exo*-isomer), and 23.4 (major *exo*-isomer) min.

(−)-(1*S*,2*S*,4*S*)-2-Formylbicyclo[2.2.1]hept-5-ene-2-yl *p*-(triisopropylsilyloxy)benzoate (*exo* isomer) (Table 3): $[\alpha]_D^{27}$: −55.3 (*c* 1.00, $CHCl_3$) for 94% *ee*; IR (neat): ν = 2868, 1736, 1710, 1603, 1509, 1463, 1272, 1162, 1111, 1095 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 7.2 Hz, 1H), 1.20–1.37 (m, 4H), 1.48 (m, 1H), 1.76 (d, *J* = 9.0 Hz, 1H), 2.64 (d, *J* = 3.6, 12.9 Hz, 1H), 6.22 (dd, *J* = 3.0, 5.4 Hz, 1H), 6.47 (dd, *J* = 3.0, 5.7 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 7.87 (d, *J* = 8.7 Hz, 2H), 9.73 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 18.0, 38.1, 42.4, 45.7, 48.8, 91.7, 119.9, 121.9, 132.0, 132.5, 140.1, 161.2, 166.5, 198.9; HR-MS (FAB): *m/z* = 415.2309, calcd for $C_{24}H_{35}O_4Si$ $[M+H]^+$: 415.2305. The *exo-endo* ratio was determined by ^1H NMR analysis: δ = 9.53 [s, 1H, C*H*O (*endo*-isomer)] and 9.73 [s, 1H, C*H*O (*exo*-isomer)]. The *ee* and the absolute configuration of major enantiomer were established by the same procedure as described above for (−)-(1*S*,2*S*,4*S*)-2-formylbicyclo-[2.2.1]hept-5-ene-2-yl diphenylacetate.

(−)-1-Formyl-3,4-dimethylcyclohex-3-enyl diphenylacetate (Table 5): $[\alpha]_D^{27}$: −3.60 (*c* 1.00, $CHCl_3$) for 70% *ee*; IR (neat): ν = 2915, 1734, 1601, 1496, 1452, 1227, 1188, 1150, 1068 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 6H), 1.63–1.74 (m, 1H), 1.85–2.05 (m, 3H), 2.19 (br d, *J* = 17.7 Hz, 1H), 2.55 (br d, *J* = 17.7 Hz, 1H), 5.05 (s, 1H), 7.20–7.40 (m, 10H), 9.53 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7, 18.9, 26.8, 27.6, 34.9, 56.9, 84.2, 121.1, 125.0, 127.5, 127.5, 128.6, 128.7, 128.8, 138.1, 138.2, 172.2, 198.5; HRMS (FAB): *m/z* = 349.1809, calcd. for $C_{23}H_{25}O_3$ $[M+H]^+$: 349.1804. The *ee* was determined, according to the reported procedure[9,11] by chiral HPLC (Daicel OD-H, hexane-*i*-PrOH = 40:1, flow rate 0.5 mL min^{-1}) after conversion to (1-hydroxy-3,4-dimethylcyclohex-3-enyl)methyl benzoate by reduction with $LiAlH_4$ (2 equivs.) in THF at ambi-

ent temperature and subsequent selective benzoylation of the primary hydroxy group of the corresponding 1,2-diol with benzoyl chloride (1.3 equivs.) in the presence of *N,N*-diisopropylethylamine (2 equivs.) in chloroform at 0 °C: t_R = 31.2 (major) and 35.7 (minor) min. The absolute configuration was not established.

(−)-1-Formyl-3,4-dimethylcyclohex-3-enyl *p*-(triisopropylsilyloxy)benzoate (Table 5): $[\alpha]_D^{27}$: −8.81 (*c* 1.00, $CHCl_3$) for 85% *ee*; IR (neat): ν = 2868, 1737, 1708, 1602, 1509, 1464, 1289, 1248, 1163, 1112, 1096, 1069 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 7.2 Hz, 18H), 1.20–1.37 (m, 3H), 1.65 (s, 3H), 1.67 (s, 3H), 1.75–1.87 (m, 1H), 1.98–2.30 (m, 3H), 2.34 (br d, *J* = 18.6 Hz, 1H), 2.69 (br d, *J* = 18.6 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 9.64 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 18.0, 18.8, 19.0, 27.2, 27.8, 35.4, 83.4, 119.9, 121.5, 122.0, 124.9, 132.0, 161.2, 165.9, 198.8; HR-MS (FAB): *m/z* = 431.2604, calcd. for $C_{25}H_{39}O_4Si$ $[M+H]^+$: 431.2618. The *ee* and the absolute configuration of major enantiomer were established by the same procedure as described above for (−)-1-formyl-3,4-dimethylcyclohex-3-enyl diphenylacetate. The absolute configuration was not established.

(−)-1-Formyl-4-methylcyclohex-3-enyl cyclohexanecarboxylate (Table 5): $[\alpha]_D^{26}$: −8.01 (*c* 1.00, $CHCl_3$) for 71% *ee*; IR (neat): ν = 2856, 1728, 1450, 1379, 1315, 1244, 1167, 1134, 1071, 1026 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.14–1.53 (m, 6H), 1.53–2.21 (m, 8H), 1.69 (s, 3H), 2.27 (br d, *J* = 18.0 Hz, 1H), 2.36 (tt, *J* = 3.6, 11.1 Hz, 1H), 2.57 (br d, *J* = 18.0 Hz, 1H), 5.30 (s, 1H), 9.52 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.3, 25.4, 25.4, 25.8, 26.2, 26.6, 28.9, 29.0, 29.7, 42.8, 81.8, 116.4, 133.5, 175.9, 199.0; HR-MS (FAB): *m/z* = 251.1637, calcd for $C_{15}H_{23}O_3$ $[M+H]^+$: 251.1647. The *ee* was determined, according to the reported procedure,[9,11] by chiral HPLC (Daicel AD-H, hexane-*i*-PrOH = 40:1, flow rate 1 mL min^{-1}) after conversion to (1-hydroxy-4-methylcyclohex-3-enyl)methyl benzoate by reduction with $LiAlH_4$ (2 equivs.) in THF at ambient temperature and subsequent selective benzoylation of the primary hydroxy group of the corresponding 1,2-diol with benzoyl chloride (1.3 equivs.) in the presence of *N,N*-diisopropylethylamine (2 equivs.) in chloroform at 0 °C: t_R = 37.8 (major) and 42.7 (minor) min. The absolute configuration was not established.

(−)-1-Formyl-4-methylcyclohex-3-enyl diphenylacetate (Table 5): $[\alpha]_D^{26}$: −15.2 (*c* 1.00, $CHCl_3$) for 67% *ee*; IR (neat): ν = 2829, 1732, 1720, 1598, 1496, 1454, 1312, 1238, 1187, 1162, 1074, 1026 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 3H), 1.69–1.96 (m, 3H), 1.96–2.10 (m, 1H), 2.31 (br d, *J* = 18.3 Hz, 1H), 2.55 (br d, *J* = 18.3 Hz, 1H), 5.06 (s, 1H), 5.24 (s, 1H), 7.20–7.40 (m, 10H), 9.56 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.2, 26.1, 26.5, 29.6, 56.9, 83.1, 116.1, 127.5, 127.6, 128.7, 128.7, 128.8, 128.8, 133.6, 138.2, 138.2, 172.3, 198.6; HR-MS (FAB): *m/z* = 335.1646, calcd. for $C_{22}H_{23}O_3$ $[M+H]^+$: 335.1647. The *ee* and the absolute configuration of major enantiomer were established by the same procedure described above for (−)-1-formyl-4-methylcyclohex-3-enyl cyclohexanecarboxylate. The absolute configuration was not established.

(−)-1-Formyl-4-methylcyclohex-3-enyl *p*-(triisopropylsilyloxy)benzoate (Table 5): $[\alpha]_D^{26}$: −25.6 (*c* 1.00, $CHCl_3$) for 85% *ee*; IR (neat): ν = 2868, 1738, 1708, 1603, 1509, 1464, 1280, 1244, 1163, 1112, 1096, 1069 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 7.2 Hz, 18H), 1.20–1.37 (m, 3H), 1.72 (s, 3H), 1.79–1.92 (m, 1H), 1.98–2.13 (m, 1H), 2.13–2.33 (m, 2H), 2.44 (br d, *J* = 18.0 Hz, 1H), 2.69 (br d, *J* = 18.0 Hz, 1H), 5.35 (s, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 9.67 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 18.0, 23.4, 26.4, 26.9, 29.8, 82.4, 116.7, 119.9, 122.0, 132.0, 133.4, 161.2, 165.9, 198.9; HR-MS (FAB): *m/z* = 417.2442, calcd. for $C_{24}H_{37}O_4Si$ $[M+H]^+$: 417.2461. The *ee* and the absolute configuration of major enantiomer were established by the same procedure as described above for (−)-1-formyl-4-methylcyclohex-3-enyl cyclohexanecarboxylate. The absolute configuration was not established.

(−)-1-Formylcyclohex-3-enyl cyclohexanecarboxylate (Table 5): $[\alpha]_D^{23}$: −5.21 (*c* 1.00, $CHCl_3$) for 68% *ee*; IR (neat): ν = 2855, 1732, 1451, 1375, 1362, 1309, 1216, 1164, 1096 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.14–1.53 (m, 6H), 1.54–1.81 (m, 4H), 1.91 (br d, *J* = 12.3 Hz, 2H), 1.97–2.42 (m, 4H), 2.62 (br d, *J* = 18.0 Hz, 1H), 5.63 (d, *J* = 9.6 Hz, 1H), 5.75 (d, *J* = 9.6 Hz, 1H), 9.51 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 25.4, 25.8, 26.2, 29.0, 29.3, 42.9, 81.8, 122.5, 126.2, 175.9, 198.7; HR-MS (FAB): *m/z* = 237.1494, calcd. for $C_{14}H_{21}O_3$ $[M+H]^+$: 237.1491. The *ee* was determined, according to the reported procedure[9,11] by chiral HPLC (Daicel AD-H, hexane-*i*-PrOH = 40:1, flow rate 1 mL min^{-1}) after conversion to (1-hydroxycyclohex-3-enyl)methyl benzoate by reduction with $LiAlH_4$ (2 equivs.) in THF at ambient temperature and subsequent selective benzoylation of the primary hydroxy group of the corresponding 1,2-diol with benzoyl chloride (1.3 equivs.) in the presence of *N,N*-diisopropylethylamine (2 equivs.) in chloroform at 0 °C: t_R = 38.3 (major) and 40.9 (minor) min. The absolute configuration was not established.

(−)-1-Formylcyclohex-3-enyl *p*-(triisopropylsilyloxy)benzoate (Table 5): $[\alpha]_D^{23}$: −12.4 (*c* 1.00, $CHCl_3$) for 82% *ee*; IR (neat): ν = 2869, 1735, 1701, 1603, 1509, 1228, 1171, 1133, 1064, 1036 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 7.2 Hz, 18H), 1.20–1.36 (m, 3H), 1.76–1.88 (m, 1H), 2.12–2.40 (m, 3H), 2.47 (br d, *J* = 18.3 Hz, 1H), 2.73 (br d, *J* = 18.6 Hz, 1H), 5.66 (d, *J* = 10.2 Hz, 1H), 5.80 (d, *J* = 10.2 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 9.0 Hz, 2H), 9.66 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 18.0, 21.6, 26.4, 29.4, 82.4, 119.9, 121.9, 122.8, 126.2, 132.1, 161.2, 165.9, 198.6; HR-MS (FAB): *m/z* = 403.2302, calcd. for $C_{23}H_{35}O_4Si$ $[M+H]^+$: 403.2305. The *ee* and the absolute configuration of major enantiomer were established by the same procedure as described above for (−)-1-formylcyclohex-3-enyl cyclohexanecarboxylate. The absolute configuration was not established.

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References

[1] For recent reviews, see: a) K. C. Nicolaou, S. A. Snyder, T. Montagnon, G. Vassilikogiannakis, *Angew.*

Chem. Int. Ed. **2002**, *41*, 1668–1698; b) E. J. Corey, *Angew. Chem. Int. Ed.* **2002**, *41*, 1650–1667.
[2] a) K. A. Ahrendt, C. J. Borths, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2000**, *122*, 4243–4244; b) A. B. Northrup, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2002**, *124*, 2458–2460; c) K. H. Kim, K. S. Lee, D.-W. Lee, D.-H. Ko, D.-C. Ha, *Tetrahedron Lett.* **2005**, *46*, 5991–5994; d) M. Lemay, W. W. Ogilvie, *Org. Lett.* **2005**, *7*, 4141–4144; e) T. Kano, Y. Tanaka, K. Maruoka, *Org. Lett.* **2006**, *8*, 2687–2689.
[3] For a hydrogen bonding catalysis for the Diels–Alder reaction, see: Y. Huang, A. K. Unni, A. N. Thadani, V. H. Rawal, *Nature* **2003**, *424*, 146.
[4] For a recent review of hydrogen bonding catalysis, see: M. S. Taylor, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **2006**, *45*, 1520–1543.
[5] MacMillan failed to activate methacrolein with a secondary ammonium salt: R. K. Kunz, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2005**, *127*, 3240–3241.
[6] a) E. J. Corey, T.-P. Loh, *J. Am. Chem. Soc.* **1991**, *113*, 8966–8967; b) J. A. Marshall, S. Xie, *J. Org. Chem.* **1992**, *57*, 2987–2989; c) E. J. Corey, C. L. Cywin, *J. Org. Chem.* **1992**, *57*, 7372–7373; d) E. J. Corey, T.-P. Loh, *Tetrahedron Lett.* **1993**, *34*, 3979–3982; e) K. Ishihara, Q. Gao, H. Yamamoto, *J. Org. Chem.* **1993**, *58*, 6917–6919; f) K. Ishihara, H. Yamamoto, *J. Am. Chem. Soc.* **1994**, *116*, 1561–1562; g) E. J. Corey, A. Guzman-Perez, T.-P. Loh, *J. Am. Chem. Soc.* **1994**, *116*, 3611–3612; h) K. Ishihara, H. Kurihara, H. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 3049–3050; i) K. Ishihara, H. Kurihara, M. Matsumoto, H. Yamamoto, *J. Am. Chem. Soc.* **1998**, *120*, 6920–6930; j) E. J. Corey, T. Shibata, T. W. Lee, *J. Am. Chem. Soc.* **2002**, *124*, 3808–3809.
[7] R. L. Funk, K. J. Yost, *J. Org. Chem.* **1996**, *61*, 2598–2599.
[8] a) A. E. Greene, C. Le Drian, P. Crabbé, *J. Am. Chem. Soc.* **1980**, *102*, 7583–7584; b) R. G. Salomon, N. D. Sachinvala, S. Roy, B. Basu, S. R. Raychaudhuri, D. B. Miller, R. B. Sharma, *J. Am. Chem. Soc.* **1991**, *113*, 3085–3095; c) C. Marschner, J. Baumgartner, H. Griengl, *J. Org. Chem.* **1995**, *60*, 5224–5235; d) G. T. Wang, S. Wang, Y. Chen, R. Gentles, T. Sowin, *J. Org. Chem.* **2001**, *66*, 2052; e) X.-F. Zhu, F. Nydegger, A. Gossauer, *Helv. Chim. Acta* **2004**, *87*, 2245–2265.
[9] K. Ishihara, K. Nakano, *J. Am. Chem. Soc.* **2005**, *127*, 10504–10505.
[10] $C_6F_5SO_3H$ is a weaker Brønsted acid than TsOH; a) K. Ishihara, S. Nakagawa, A. Sakakura, *J. Am. Chem. Soc.* **2005**, *127*, 4168–4169; b) A. Sakakura, S. Nakagawa, K. Ishihara, *Tetrahedron* **2006**, *62*, 422–433.
[11] Part of this work has been published as a preliminary communication, see: A. Sakakura, K. Suzuki, K. Nakano, K. Ishihara, *Org. Lett.* **2006**, *8*, 2229–2232.
[12] The reaction conducted in the presence of water (100 mol%) gave similar results. When the reaction was carried out in the presence of more than 500 mol% of water, the solvent was partially frozen and the reactivity was decreased.
[13] Unfortunately, when the Diels–Alder reaction of cyclopentadiene was conducted in $EtNO_2$, cyclopentadiene polymerized and the Diels–Alder adducts were obtained with low yield and enantioselectivity.
[14] The absolute stereochemistries of the Diels–Alder adducts of 2,3-dimethylbutadiene, isoprene and butadiene were proposed to be 1*S* by analogy with cyclopentadiene.[6a]
[15] a) D. A. Evans, A. M. Golob, N. S. Mandel, G. S. Mandel, *J. Am. Chem. Soc.* **1978**, *100*, 8170–8174; b) A. P. Kozikowski, R. J. Schmiesing, *J. Org. Chem.* **1983**, *48*, 1000–1007; c) M. Demuth, S. Chandrasekehar, K. Schaffner, *J. Am. Chem. Soc.* **1984**, *106*, 1092–1095; d) A. B. Smith III, J. R. Empfield, R. A. Rivero, H. A. Vaccaro, J. J.-W. Duan, M. M. Sulikowski, *J. Am. Chem. Soc.* **1992**, *114*, 9419–9434.
[16] S. Miyano, M. Nawa, A. Mori, H. Hashimoto, *Bull. Chem. Soc., Jpn.* **1984**, *57*, 2171–2176.
[17] M. Shi, W.-L. Duan, G.-B. Rong, *Chirality* **2004**, *16*, 642–651.
[18] S. Vyskocil, S. Jaracz, M. Smrcina, M. Stícha, V. Hanus, M. Polásek, P. Kocovsky, *J. Org. Chem.* **1998**, *63*, 7727–7737.
[19] M. Shi, C.-J. Wang, *Chirality* **2002**, *14*, 412–416.

