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Activation of ether functionality of allyl vinyl ethers by chiral bis(organoaluminum) Lewis acids: application to asymmetric Claisen rearrangement

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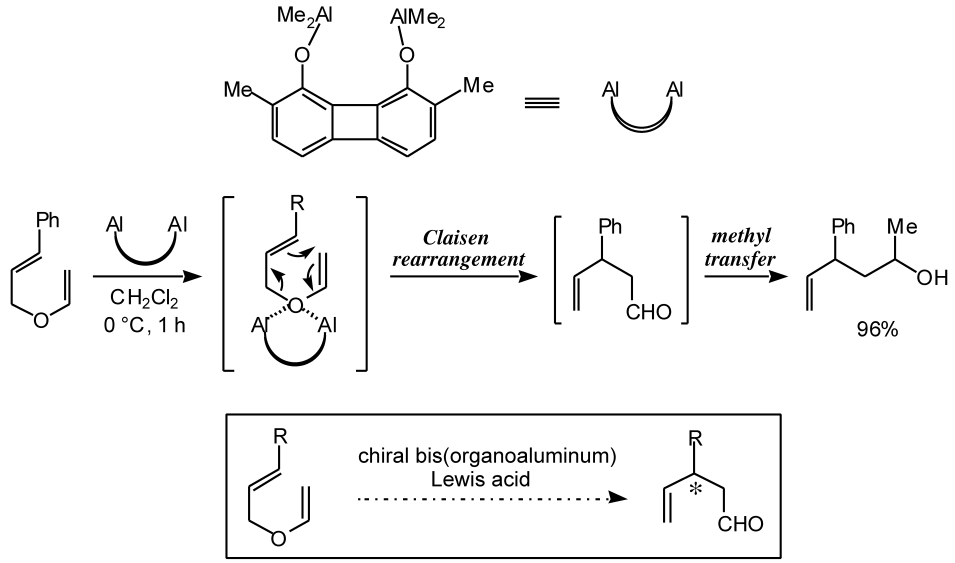
Abstract—Chiral bis(organoaluminum) Lewis acids have been newly designed and synthetic utility of their eminent activation ability of an ether functionality has been successfully demonstrated by the application to asymmetric Claisen rearrangement of allyl vinyl ethers.

Apparently, the Claisen rearrangement serves as an excellent stereoselective route to α,β-unsaturated carbonyl compounds from allylic alcohols, and offers a crucial step in the stereo- and regiochemically defined synthesis of a wide variety of natural products along with numerous recent developments of new variants of the [3,3]-sigmatropic rearrangement.[1] However, studies regarding its asymmetric version, especially using chiral Lewis acids, have been limited despite the potential mechanistic and synthetic importance.[2] Recently, we reported that (2,7-dimethyl-1,8-biphenylenedioxy)bis(dimethylaluminum) was capable of strongly activating not only carbonyl compounds but also substrates possessing ether moiety such as allyl vinyl ethers via double coordination as shown in Scheme 1.[3a] This finding prompted us to pursue the design of a new chiral bis(organoaluminum) Lewis acid, which could promote facile Claisen rearrangement of allyl vinyl ethers in an asymmetric fashion via eminent activation of the ether functionality. In this article, we wish to describe the results of this study.



Scheme 1.

Keywords: Claisen rearrangement; carbonyl compounds; chiral Lewis acids.

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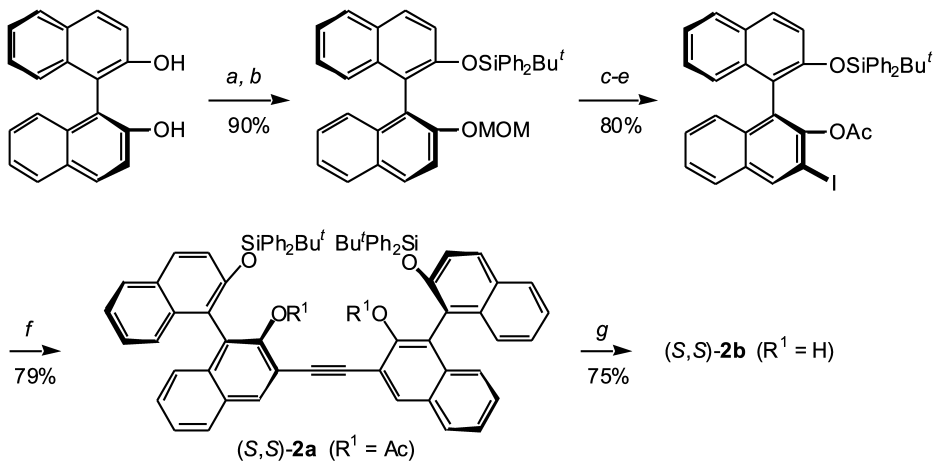


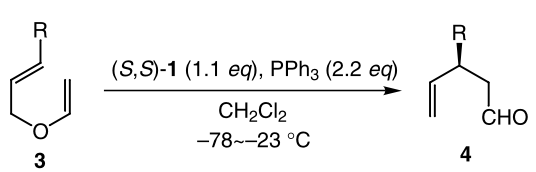
Scheme 2. (a) ^{t}BuPh$_2$SiCl, Imidazole, DMF. (b) NaH, MOMCl, THF. (c) BuLi, ether, then I_2, THF. (d) conc. HCl, dioxane. (e) Ac_2O, pyridine, cat DMAP, CH_2Cl_2. (f) bis(tributylstannyl)acetylene, Pd(OAc)$_2$, PPh$_3$, BHT, LiCl, dioxane. (g) MeLi, THF-ether.

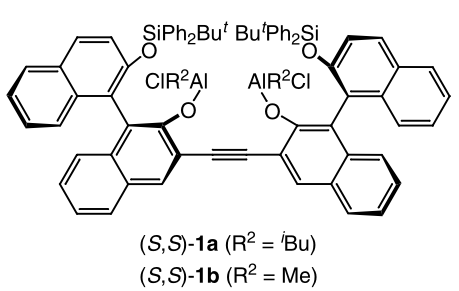
Table 1. Asymmetric Claisen rearrangement of allyl vinyl ether **3** with chiral bis(organoaluminum) Lewis acid (*S*,*S*)-**1**

Entry	Substrate **3**	Bis-Al Lewis acid	Condition (°C, h)	Product	% Yield[a]	% ee[b] (configuration)[c]
1	R=*c*-C_6H_{11} (**3a**)	**1a**	−78, 0.1; −45, 4	**4a**	82	62 (*S*)
2		**1b**	−78, 0.1; −45, 4	**4a**	66	71 (*S*)
3	R=*t*-Bu (**3b**)	**1a**	−78, 1.5; −45, 4	**4b**	75	80 (*S*)
4		**1b**	−78, 1.5; −45, 4	**4b**	70	85 (*S*)
5	R=Ph (**3c**)	**1a**	−78, 0.1; −45, 1	**4c**	92	51 (*S*)
6		**1b**	−78, 0.1; −45, 1	**4c**	50	57 (*S*)
7	R=$SiMe_3$ (**3d**)	**1b**	−78, 0.1; −45, 2 −35, 1; −23, 1	**4d**	63	83

The reaction was carried out in CH_2Cl_2 with (*S*,*S*)-**1** (1.1 equiv.) in the presence of PPh_3 (2.2 equiv.) under the given reaction conditions.
[a] Isolated yield.
[b] Determined by capillary GLC analysis after conversion to its acetal of (2*R*,4*R*)-pentanediol.
[c] Determined by the comparison with the reported one.[2c,d]

The requisite optically pure bis(binaphthol) (*S*,*S*)-**2b**[4] can be synthesized from commercially available (*S*)-binaphthol in 7-step sequences, as illustrated in Scheme 2. Treatment of (*S*,*S*)-**2b** in CH_2Cl_2 with ^{i}Bu$_2$AlCl (2 equiv.) in hexane at 25°C for 30 min generated a chiral bis(organoaluminum) reagent (*S*,*S*)-**1a** (R^2=^{i}Bu). In evaluating the potential of (*S*,*S*)-**1a** as a chiral activator in the asymmetric Claisen rearrangement, we employed PPh_3 as an additive according to Nozaki's protocol to avoid the fragmentation of **3** prior to the desired rearrangement.[5] Thus, reaction of (*S*,*S*)-**1a**



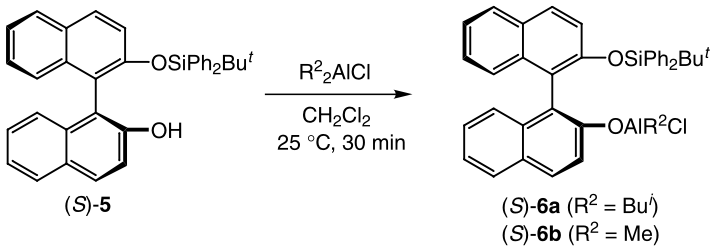


Scheme 3.

(1.1 equiv.) with allyl vinyl ether **3a** (R=*c*-C_6H_{11}) in the presence of PPh_3 (2.2 equiv.) in CH_2Cl_2 at −78 to −45°C for 4 h gave rise to a rearrangement product **4a** (R=*c*-C_6H_{11}) (82% yield), whose enantiomeric purity was determined to be 62% ee by capillary GLC analysis after conversion to its acetal of (2*R*,4*R*)-pentanediol (entry 1, Table 1, Scheme 3).[6]

Switching the bis(organoaluminum) Lewis acid from (*S*,*S*)-**1a** to (*S*,*S*)-**1b** brought the increase of enantioselectivity to 71% ee for this substrate, though the chemical yield turned out to be moderate (entry 2). Use of toluene in place of CH_2Cl_2 decreased the enantioselectivity (58% ee). It should be emphasized that preparation of mono(organoaluminum) counterpart (*S*)-**6a** from monosilylated (*S*)-binaphthol **5** and ^{i}Bu$_2$AlCl, and subsequent treatment with PPh_3 and allyl vinyl ether **3a** (R=*c*-C_6H_{11}) under similar reaction conditions resulted in the Claisen product **4a** (R=*c*-C_6H_{11}) in only 9% yield with the enantiomeric excess (ee) of 22% ee, indicating that the strong activation ability of chiral bis(organoaluminum) Lewis acid of type **1** is responsible for obtaining a synthetically useful level of chemical yield and enantioselectivity (Scheme 4).

Other selected examples are summarized in Table 1. Generally, (*S*,*S*)-**1a** and (*S*,*S*)-**1b** seemed to be complements of each other in terms of reactivity and selectivity. Higher enantioselectivity was observed in the rearrangement of the



Scheme 4.

substrate with more sterically hindered substituent R (entries 3, 4 vs. 1, 2). Notably, a facile asymmetric synthesis of functionalized allylic silanes **4d** (R=$SiMe_3$) appears feasible by the present method (entry 7).

In conclusion, we have designed new chiral bis(organoaluminum) Lewis acid of type **1** whose effectiveness as an efficient chiral activator for the substrates having ether functionality has been investigated by conducting asymmetric Claisen rearrangement of allyl vinyl ethers in comparison with **6** as a corresponding mono(organoaluminum) Lewis acid. Scope and limitations of this unique system have also been revealed.

1. Experimental

1.1. General

Infrared (IR) spectra were recorded on a Shimazu FT-IR 8200A spectrometer. ^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometers. Tetramethylsilane was used as internal standard of ^{1}H NMR (δ=0). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. Analytical gas–liquid phase chromatography (GLC) was performed on Shimazu GC-14B instruments equipped with a flame ionization detector and a capillary column of PEG-HT (0.25×25,000 mm) using nitrogen as carrier gas. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel 60 E, Merck Art 9385. The high-resolution mass spectra (HRMS) analysis were accomplished at the Graduate School of Engineering, Kyoto University. Reaction involving air- or moisture-sensitive compounds were conducted in appropriate round-bottomed flask with magnetic stirring bars under an atmosphere of dry argon. In experiments requiring dry solvents, ether and tetrahydrofuran (THF) were purchased from KANTO Chemical Co., Inc., Japan as anhydrous solvent. Methylene chloride, 1,4-dioxane and DMF were stored over 4 Å molecular sieves. Pyridine was stored over KOH pellets. In the asymmetric Claisen process, methylene chloride as solvent was freshly distilled from calcium hydride before use. Diisobutylaluminum chloride (*i*-Bu_2AlCl) and dimethylaluminum chloride (Me_2AlCl) were kindly supplied from Tosoh-Finechem. Co. Ltd, Japan. Other simple chemicals were purchased and used as such.

1.2. Preparation of allyl vinyl ethers

(*E*)-3-Cyclohexenyl-2-propenyl vinyl ether (**3a**), (*E*)-3-*tert*-butyl-2-propenyl vinyl ether (**3b**), (*E*)-cinnamyl vinyl ether (**3c**) and (*E*)-3-trimethylsilyl-2-propenyl vinyl ether (**3d**) were known compounds and synthesized according to the literature procedure.[2b]

1.2.1. (*E*)-3-Cyclohexyl-2-propenyl vinyl ether (3a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (1H, dd, *J*=14.4, 6.8 Hz, CH_2=C*H*), 5.71 (1H, dd, *J*=15.6, 6.6 Hz, *c*-Hex-C*H*=CH), 5.55 (1H, dtd, *J*=15.6, 6.0, 1.2 Hz, *c*-Hex-CH=C*H*), 4.21 (1H, dd, *J*=14.4, 2.0 Hz, *cis*-CH_2=CH), 4.17 (2H, d, *J*=6.0 Hz, CH_2O), 4.00 (1H, dd, *J*=6.8, 2.0 Hz, *trans*-CH_2=CH), 2.04–1.94 (1H, m, CH), 1.77–1.62 (5H, m, *equatorial*-CH_2), 1.33–1.03 (5H, m, *axial*-CH_2); IR (liquid film) 3117, 2926, 2853, 1636, 1611, 1448, 1379, 1319, 1198, 1053, 970, 812 cm^{-1}.

1.2.2. (*E*)-3-*tert*-Butyl-2-propenyl vinyl ether (3b). ^{1}H NMR (400 MHz, $CDCl_3$, 6:4 mixture of rotamers) δ 6.47 (1H, dd, *J*=14.4, 6.8 Hz, CH_2=C*H*), 5.778 (0.4H, dt, *J*=15.6, 2.4 Hz, *t*-Bu–C*H*=CH), 5.775 (0.6H, dt, *J*=15.6, 2.4 Hz, *t*-Bu–C*H*=CH), 5.515 (0.6H, dt, *J*=15.6, 6.2 Hz, *t*-Bu–CH=C*H*), 5.512 (0.4H, dt, *J*=15.6, 6.2 Hz, *t*-Bu–CH=C*H*), 4.24–4.17 (3H, m, *cis*-CH_2=CH and CH_2O), 4.011 (0.6H, dd, *J*=6.4, 2.0 Hz, *trans*-CH_2=CH), 4.008 (0.4H, dd, *J*=6.4, 2.0 Hz, *trans*-CH_2=CH), 1.031 (5.4H, s, *t*-Bu), 1.028 (3.6H, s, *t*-Bu); IR (liquid film) 3119, 3036, 2961, 2905, 2868, 1636, 1612, 1475, 1464, 1364, 1321, 1200, 1153, 1059, 974, 814 cm^{-1}.

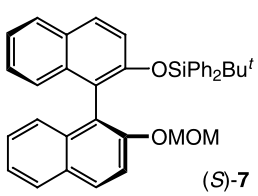
1.2.3. (*E*)-Cinnamyl vinyl ether (3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, d, *J*=7.6 Hz, Ph), 7.32 (2H, t, *J*=7.6 Hz, Ph), 7.27–7.23 (1H, m, Ph), 6.66 (1H, d, *J*=16.0 Hz, Ph–C*H*=CH), 6.52 (1H, dd, *J*=14.4, 6.8 Hz, CH_2=C*H*), 6.32 (1H, dt, *J*=16.0, 6.0 Hz, Ph–CH=C*H*), 4.40 (2H, d, *J*=6.0 Hz, CH_2O), 4.28 (1H, d, *J*=14.4 Hz, *cis*-CH_2=CH), 4.07 (1H, d, *J*=6.8 Hz, *trans*-CH_2=CH); IR (liquid film) 3028, 2912, 2860, 1636, 1614, 1495, 1450, 1373, 1319, 1194, 1153, 1055, 966, 822, 743, 692 cm^{-1}.

1.2.4. (*E*)-3-Trimethylsilyl-2-propenyl vinyl ether (3d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (1H, dd, *J*=14.4, 6.8 Hz, CH_2=C*H*), 6.12 (1H, dt, *J*=18.8, 4.8 Hz, Me_3Si–CH=C*H*), 5.98 (1H, dt, *J*=18.8, 1.4 Hz, Me_3Si–C*H*=CH), 4.25 (2H, dd, *J*=4.8, 1.4 Hz, CH_2O), 4.22 (1H, dd, *J*=14.4, 2.0 Hz, *cis*-CH_2=CH), 4.03 (1H, dd, *J*=4.8, 2.0 Hz, *trans*-CH_2=CH), 0.08 (9H, s, $SiMe_3$); IR (liquid film) 2957, 2899, 1636, 1614, 1366, 1319, 1250, 1200, 989, 962, 864, 839, 770, 694 cm^{-1}.

1.3. Preparation of optically pure bis(binaphthol) (*S*,*S*)-2b (R′=H)

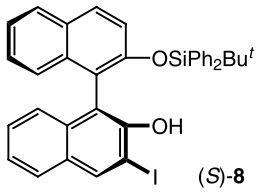
1.3.1. (*S*)-2-*tert*-Butyldiphenylsilyloxy-2′-hydroxy-1,1′-binaphthyl [(*S*)-5].[7] To a solution of (*S*)-binaphthol (4.29 g, 15.0 mmol) and imidazole (2.04 g, 30 mmol) in DMF (30 mL) was added *tert*-butyldiphenylsilyl chloride (4.1 mL, 16 mmol) and the mixture was stirred at 50°C for 4 h under argon. After the resulting mixture was cooled to room temperature, saturated NH_4Cl was added and extractive workup was performed with Et_2O. The combined extracts were washed with brine and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography on silica gel (hexane/CH_2Cl_2=2:1 as eluent) gave (*S*)-**5** (7.27 g, 13.9 mmol, 92% yield) as colorless crystal. $[\alpha]_D^{20}$=+36.4° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (1H, d, *J*=9.2 Hz, Ar–H), 7.88 (1H, dd, *J*=8.4, 1.6 Hz, Ar–H), 7.77 (1H, dt, *J*=7.6, 1.6 Hz, Ar–H), 7.64–7.60 (3H, m, Ar–H), 7.54–7.51 (2H, m, Ar–H), 7.44–7.26 (12H, m, Ar–H), 7.20 (1H, m, Ar–H), 6.89 (1H, d, *J*=8.8 Hz, Ar–H), 5.02 (1H, s, OH), 0.49 (9H, s, *t*-Bu); IR (KBr) 3531, 3055, 2957, 2930, 2891, 2856, 1620, 1591, 1504, 1472, 1460, 1429, 1362, 1339, 1277, 1263, 1248, 1207, 1148, 1115, 1005, 814, 745, 700 cm^{-1}.

1.3.2. (*S*)-2-*tert*-Butyldiphenylsilyloxy-2′-methoxymethoxy-1,1′-binaphthyl [(*S*)-7]. To a solution of (*S*)-**5** (849 mg, 1.62 mmol) in THF (8 mL) was added NaH (60 wt% in oil, 84 mg, 2.1 mmol) at 0°C and the mixture was warmed to room temperature and stirred there for 0.5 h. It was then cooled again to 0°C and chloromethyl methyl ether (0.14 mL, 1.9 mmol) was added. After stirring at room temperature for 12 h, saturated NH_4Cl was added slowly at 0°C and then extractive workup was conducted with Et_2O. The combined extracts were washed with brine and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by silica gel column chromatography (hexane/CH_2Cl_2=4:1–1:1 as eluent) gave (*S*)-**7** (833 mg, 1.46 mmol, 90% yield) as colorless crystal. $[\alpha]_D^{23}$=−55.2° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (1H, d, *J*=9.2 Hz, Ar–H), 7.89 (1H, d, *J*=8.0 Hz, Ar–H), 7.76–7.73 (1H, m, Ar–H), 7.64–7.61 (3H, m, Ar–H), 7.57–7.53 (3H, m, Ar–H), 7.42–7.20 (12H, m, Ar–H), 6.84 (1H, d, *J*=9.2 Hz, Ar–H), 5.11 (1H, d, *J*=6.8 Hz, CH), 5.04 (1H, d, *J*=6.8 Hz, CH), 3.19 (3H, s, Me), 0.45 (9H, s, *t*-Bu); IR (KBr) 3053, 2957, 2930, 2893, 2856, 1622, 1591, 1506, 1474, 1460, 1429, 1356, 1339, 1279, 1265, 1250, 1240, 1150, 1115, 1074, 1034, 1005, 812, 746, 702 cm^{-1}. HRMS (FAB) calcd for $C_{38}H_{36}O_3Si$ (M^+): 568.2434, found: 568.2435.



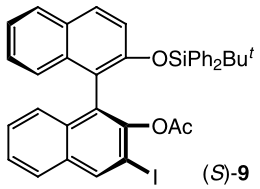
(*S*)-**7**

1.3.3. (*S*)-2-*tert*-Butyldiphenylsilyloxy-2′-hydroxy-3′-iodo-1,1′-binaphthyl [(*S*)-8]. To a solution of (*S*)-**7** (791 mg, 1.39 mmol) in Et_2O (4.5 mL) was added a 1.6 M hexane solution of *n*-BuLi (1.1 mL, 1.8 mmol) at room temperature under argon and the mixture was stirred for 3 h. The resulting pale-brown suspension was cooled to −78°C and a solution of iodine (323 mg, 2.1 mmol) in THF (2 mL) was added dropwise slowly. The mixture was warmed to room temperature and stirring was continued for 3 h. The excess iodine was reduced by addition of saturated Na_2SO_3 and the mixture was extracted with Et_2O. The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was dissolved into 1,4-dioxane (4.6 mL) and conc. HCl (2.3 mL) was added. After stirring at 50°C for 15 h, the resulting mixture was diluted with H_2O and extracted with Et_2O. The combined extracts were washed with brine and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography on silica gel (hexane/CH_2Cl_2=2:1 as eluent) gave (*S*)-**8** (692 mg, 1.06 mmol, 77% yield) as colorless crystal. $[\alpha]_D^{25}$=+31.4° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (1H, s, Ar–H), 7.77 (2H, d, *J*=7.2 Hz, Ar–H), 7.64–7.60 (3H, m, Ar–H), 7.50 (2H, dd, *J*=7.2, 1.6 Hz, Ar–H), 7.43 (1H, tt, *J*=7.2, 1.6 Hz, Ar–H), 7.38–7.25 (10H, m, Ar–H), 7.14 (1H, dd, *J*=8.4, 0.8 Hz, Ar–H), 6.88 (1H, d, *J*=8.8 Hz, Ar–H), 5.49 (1H, s, OH), 0.52 (9H, s, *t*-Bu); IR (KBr) 3504, 3051, 2963, 2932, 2856, 1620, 1591, 1502, 1466, 1427, 1356, 1340, 1279, 1261, 1246, 1202, 1146, 1115, 1078, 1034, 1003, 816, 746, 702 cm^{-1}. HRMS (FAB) calcd for $C_{36}H_{31}IO_2Si$ (M^+): 650.1138, found: 650.1133.



(*S*)-**8**

1.3.4. (*S*)-2-Acetoxy-2′-*tert*-butyldiphenylsilyloxy-3-iodo-1,1′-binaphthyl [(*S*)-9]. To a solution of (*S*)-**8** (634 mg, 0.974 mmol) in CH_2Cl_2 (2 mL) was added 4-dimethylaminopyridine (2 mg, 0.002 mmol), pyridine (0.12 mL, 1.5 mmol) and acetic anhydride (0.14 mL, 1.5 mmol) sequentially, and the solution was stirred for 6 h at room temperature. The resulting solution was concentrated and purification of the residue by column chromatography on silica gel (hexane/CH_2Cl_2=3:1–1.5:1 as eluent) afforded (*S*)-**9** (634 mg, 0.915 mmol, 94% yield) as colorless crystal. $[\alpha]_D^{25}$=+39.4° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (1H, s, Ar–H), 7.84 (1H, d, *J*=8.4 Hz, Ar–H), 7.74–7.69 (3H, m, Ar–H), 7.54–7.24 (15H, m, Ar–H), 6.78 (1H, d, *J*=9.2 Hz, Ar–H), 1.85 (3H, s, CH_3CO), 0.52 (9H, s, *t*-Bu); IR (KBr) 3071, 2955, 2930, 2856, 1774, 1624, 1593, 1508, 1470, 1429, 1360, 1354, 1340, 1279, 1261, 1248, 1182, 1115, 1082, 1036, 1009, 824, 748, 702 cm^{-1}. HRMS (FAB) calcd for $C_{38}H_{33}IO_3Si$ (M^+): 692.1244, found: 692.1252.



(*S*)-**9**

1.3.5. (*S*,*S*)-3-Bis(2-acetoxy-2′-*tert*-butyldiphenylsilyloxy-1,1′-binaphthyl)acetylene [(*S*,*S*)-2a (R′=Ac)]. To a solution of (*S*)-**9** (7.44 g, 10.7 mmol) in dry 1,4-dioxane (53 mL) was added triphenylphosphine (0.59 g, 2.3 mmol), lithium chloride (2.72 g, 64 mmol), BHT (a few crystals) and palladium diacetate (0.24 g, 1.1 mmol) at room temperature. The mixture was degassed and filled with argon quickly and then refluxed for 4 h. The resulting mixture was cooled to room temperature and filtered through a pad of Celite. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2=2:1–1:1 as eluent) to give (*S*,*S*)-**2a** (R′=Ac) (4.85 g, 4.20 mmol, 79% yield) as yellow solid. $[\alpha]_D^{25}=-43.6°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (2H, s, Ar–H), 7.94 (2H, d, *J*=8.0 Hz, Ar–H), 7.71–7.68 (6H, m, Ar–H), 7.56–7.46 (8H, m, Ar–H), 7.42–7.21 (22H, m, Ar–H), 6.78 (2H, d, *J*=8.8 Hz, Ar–H), 1.77 (6H, s, CH_3CO), 0.48 (18H, s, *t*-Bu); IR (KBr) 3051, 2957, 2932, 2893, 2858, 1774, 1622, 1593, 1508, 1470, 1429, 1362, 1340, 1273, 1250, 1210, 1195, 1184, 1115, 997, 824, 746, 700 cm^{-1}. HRMS (FAB) calcd for $C_{78}H_{67}O_6Si_2$ ($[M+H]^+$): 1155.4476, found: 1155.4480.

1.3.6. (*S*,*S*)-3-Bis(2′-*tert*-butyldiphenylsilyloxy-2-hydroxy-1,1′-binaphthyl)acetylene [(*S*,*S*)-2b (R′=H)]. To a solution of (*S*,*S*)-**2a** (R′=Ac) (4.85 g, 4.20 mmol) in THF (24 mL) was added a 1.4 M ether solution of MeLi (24 mL, 34 mmol) at −78°C and the mixture was allowed to warm to room temperature. After stirring for 1 h, it was cooled to 0°C and the excess MeLi was quenched by the slow addition of saturated NH_4Cl. Then, 1N HCl was added at room temperature and the mixture was extracted with Et_2O. The combined extracts were washed with brine and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by silica gel column chromatography (hexane/CH_2Cl_2=2:1 to 1:1 as eluent) furnished (*S*,*S*)-**2b** (R′=H) (3.28 g, 3.10 mmol, 73% yield) as colorless crystal. $[\alpha]_D^{22}=+36.4°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (2H, s, Ar–H), 7.88 (2H, d, *J*=8.0 Hz, Ar–H), 7.75 (2H, d, *J*=8.4 Hz, Ar–H), 7.58–7.54 (10H, m, Ar–H), 7.39–7.15 (24H, m, Ar–H), 6.86 (2H, d, *J*=8.8 Hz, Ar–H), 6.27 (2H, s, OH), 0.48 (18H, s, *t*-Bu); IR (KBr) 3510, 3443, 3055, 2957, 2932, 2858, 1622, 1593, 1502, 1468, 1427, 1340, 1273, 1246, 1115, 997, 824, 746, 700 cm^{-1}. HRMS (FAB) calcd for $C_{74}H_{62}O_4Si_2$ (M^+): 1070.4187, found: 1070.4189.

1.4. Preparation of chiral bis(organoaluminum) reagent (*S*,*S*)-1a or (*S*,*S*)-1b

To a degassed solution of (*S*,*S*)-**2b** (R′=H) (589 mg, 0.55 mmol) and triphenylphosphine (315 mg, 1.2 mmol) in CH_2Cl_2 (5 mL) was added a 2.0 M hexane solution of *i*-Bu_2AlCl or Me_2AlCl (0.55 mL, 1.1 mmol) at room temperature. Isobutane or methane gas evolved immediately. The resulting pale-yellow solution was stirred for 0.5–1.0 h at the same temperature and used as a solution of chiral bis(organoaluminum) reagent (*S*,*S*)-**1a** or **1b** in CH_2Cl_2 without any purification.

1.5. Preparation of chiral mono(organoaluminum) reagent (*S*)-6a or (*S*)-6b

To a degassed solution of (*S*)-**5** (577 mg, 1.1 mmol) and triphenylphosphine (315 mg, 1.2 mmol) in CH_2Cl_2 (5 mL) was added a 2.0 M hexane solution of *i*-Bu_2AlCl or Me_2AlCl (0.55 mL, 1.1 mmol) at room temperature and, after 0.5 h of stirring, the solution was used as described above.

1.6. General procedure for the asymmetric Claisen rearrangement of allyl vinyl ethers with chiral bis(organoaluminum) reagent (*S*,*S*)-1a or 1b

To a solution of the chiral bis(organoaluminum) reagent (*S*,*S*)-**1a** or **1b** (0.55 mmol) in degassed CH_2Cl_2 (5 mL) was added an allyl vinyl ether (0.50 mmol) at −78°C. After a few minutes, the mixture was warmed up to −45°C and stirred under the conditions indicated in Table 1. The reaction mixture was poured into 1N HCl, extracted with CH_2Cl_2 and dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography on silica gel (hexane or pentane/CH_2Cl_2 as eluent) gave Claisen product in the yields shown in Table 1. The Claisen products, 3-cyclohexyl-4-pentenal (**4a**), 3-*tert*-butyl-4-pentenal (**4b**), 3-phenyl-4-pentenal (**4c**) and 3-trimethylsilyl-4-pentanal (**4d**) are all known compounds. The ee was determined by the following procedure. The Claisen product was converted to the acetal of (−)-(2*R*,4*R*)-pentanediol (1.5 equiv.) with triethylorthoformate (2.0 equiv.) and catalytic *p*-toluenesulfonic acid monohydrate in benzene (0.1–0.2 M) at room temperature. Its ee was established by capillary GLC analysis based on separated two peaks. The absolute configuration was also determined by GLC analysis based on the retention time under reported conditions.[2d]

1.7. General method for the asymmetric Claisen rearrangement of allyl vinyl ethers with chiral mono(organoaluminum) reagent (*S*)-6a or 6b

Chiral mono(organoaluminum) reagent (*S*)-**6a** or **6b** (1.1 mmol) was used instead of chiral bis(organoaluminum) reagent (*S*,*S*)-**1a** or **1b** in the procedure described above.

1.7.1. 3-Cyclohexyl-4-pentenal (4a). ^1H NMR (400 MHz, $CDCl_3$) δ 9.69 (1H, dd, *J*=2.6, 1.8 Hz, CHO), 5.67 (1H, ddd, *J*=17.2, 10.4, 8.4 Hz, CH_2=C*H*), 5.06 (1H, dd, *J*=10.4, 1.4 Hz, *trans*-CH_2=CH), 5.00 (1H, d, *J*=17.2 Hz, *cis*-CH_2=CH), 2.52–2.35 (3H, m, C*H*CH_2CHO), 1.78–1.62 (5H, m, CH and *equatorial*-CH_2), 1.34–0.89 (6H, m, *axial*-CH_2); IR (liquid film) 3078, 2926, 2853, 2718, 1726, 1639, 1450, 1410, 1267, 1028, 1001, 918 cm^{-1}; GLC retention times: t_R=16.9 min [(*R*)-**4a**-(2*R*,4*R*)-acetal], 20.5 min [(*S*)-**4a**-(2*R*,4*R*)-acetal] at the column temperature of 130°C.

1.7.2. 3-*tert*-Butyl-4-pentenal (4b). ^1H NMR (400 MHz, $CDCl_3$) δ 9.65 (1H, dd, *J*=3.4, 1.4 Hz, CHO), 5.69 (1H, ddd, *J*=17.0, 10.2, 9.2 Hz, CH_2=C*H*), 5.10 (1H, dd, *J*=10.2, 1.8 Hz, *trans*-CH_2=CH), 5.03 (1H, ddd, *J*=17.0, 1.8 Hz, *cis*-CH_2=CH), 2.55–2.50 (1H, m, *t*-BuCH), 2.42–2.29 (2H, m, CH_2), 0.90 (9H, s, *t*-Bu); IR (liquid film) 3080, 3020, 2963, 2930, 2872, 1726, 1638, 1468, 1367, 1217, 920, 758, 669 cm^{-1}; GLC retention times: t_R=3.7 min [(*R*)-**4b**-(2*R*,4*R*)-acetal], 4.5 min [(*S*)-**4b**-(2*R*,4*R*)-acetal] at the column temperature of 130°C.

1.7.3. 3-Phenyl-4-pentenal (4c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (1H, t, J=2.0 Hz, CHO), 7.32 (2H, t, J=7.4 Hz, Ph), 7.25–7.20 (3H, m, Ph), 5.99 (1H, ddd, J=17.0, 10.4, 6.8 Hz, CH_2=C*H*), 5.12 (1H, dd, J=10.4, 0.8 Hz, *trans*-C*H*$_2$=CH), 5.07 (1H, dd, J=17.0, 0.8 Hz, *cis*-C*H*$_2$=CH), 3.96 (1H, dt, J=7.6, 6.8 Hz, CHPh), 2.87 (1H, ddd, J=16.6, 7.6, 2.0 Hz, CH), 2.81 (1H, ddd, J=16.6, 7.6, 2.0 Hz, CH); IR (liquid film) 3084, 3063, 3030, 2826, 2727, 1724, 1638, 1601, 1493, 1452, 1408, 1030, 997, 922, 762, 702 cm^{-1}; GLC retention times: t_R=35.4 min [(*S*)-**4c**-(2*R*,4*R*)-acetal], 36.7 min [(*R*)-**4c**-(2*R*,4*R*)-acetal] at the column temperature of 130°C.

1.7.4. 3-Trimethylsilyl-4-pentenal (4d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (1H, dd, J=2.8, 1.8 Hz, CHO), 5.77 (1H, ddd, J=17.2, 10.4, 8.4 Hz, CH_2=C*H*), 4.96 (1H, ddd, J=10.4, 1.2, 1.2 Hz, *trans*-C*H*$_2$=CH), 4.86 (1H, ddd, J=17.2, 1.2, 1.2 Hz, *cis*-C*H*$_2$=CH), 2.50 (1H, ddd, J=16.4, 11.2, 2.8 Hz, CH_2), 2.41 (1H, ddd, J=16.4, 4.0, 1.8 Hz, CH_2), 2.13 (1H, ddddd, J=11.2, 8.4, 4.0, 1.2, 1.2 Hz, $CHSiMe_3$), 0.03 (9H, s, $SiMe_3$); IR (liquid film) 3080, 2957, 2899, 2812, 2716, 1726, 1628, 1408, 1250, 1136, 1105, 1036, 1001, 899, 841, 752, 692 cm^{-1}; GLC retention times: t_R=5.8 min (major isomer), 7.2 min (minor isomer) at the column temperature of 110°C.

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