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Syntheses and reactions of (*R*)-$(C_{10}H_6)_2M_2$ (M = $SnMeCl_2$, $SnMe_2Cl$, $SnMe(OTf)_2$, $SnMe_2OTf$, $SiMe_2I$) as novel chiral 2,2′-bis-metallic-1,1′-binaphthyl catalysts

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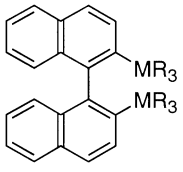
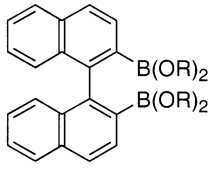
Abstract—(*R*)-$(C_{10}H_6)_2M_2$ (M = $SnMeCl_2$, $SnMe_2Cl$, $SnMe(OTf)_2$, $SnMe_2OTf$, $SiMe_2I$) were synthesized as novel chiral 2,2′-bis-metallic-1,1′-binaphthyl catalysts. The catalytic activities were evaluated in the Diels–Alder reaction of methacrolein and cyclopentadiene and the asymmetric acylation reaction of racemic 1-phenyl-1,2-ethanediol. © 2002 Published by Elsevier Science Ltd.

1. Introduction

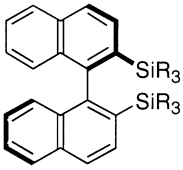
Chiral 2,2′-bis-metallic-1,1′-binaphthyl catalysts have recently attracted growing attention as a new class of multifunctional chiral catalysts from several viewpoints: firstly, the corresponding chiral binaphthyl ligands such as BINAP have achieved remarkable success in asymmetric syntheses; secondly, the metal catalytic centres are directly attached to the binaphthyl framework so that the substrate is activated in closer proximity to the asymmetric environment than conventional metal–BINOL complexes, and thirdly, the bimetallic centre is expected to be an active site for bidentate Lewis acid catalysts. The first example of bis-metallic binaphthyl compounds was reported by Kuivila et al.[1] They synthesized the Lewis acidic bis-stannyl derivatives (±)-**1** and investigated the complexation behavior of (±)-**1a** with DMSO both in solution and the solid state. Since then, major efforts have focused on the development of Lewis acid catalysts based on the bis-metallic binaphthyls (Fig. 1). Though early studies reported only the racemic binaphthyls (±)-**1**,[1,2] (±)-**2**,[3,4] (±)-**3**,[2] and (±)-**4**[2] due in part to the lack of an efficient method for the introduction of metal groups to the optically active binaphthyl framework, we demonstrated that dilithiation of (*R*)-2,2′-dibromo-1,1′-binaphthyl **5** followed by bis-silylation of the resulting dilithio-intermediate **6** gave (*R*)-2,2′-bis(silyl)-1,1′-binaphthyls **7** as the first optically active bis-metallic binaphthyl compounds (Eq. (1)).[5] As an extension of this study, novel chiral bis-metallic binaphthyl catalysts were successively prepared according to our protocol. (*R*)-2,2′-Dimercurio-1,1′-



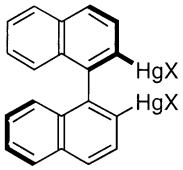
(±)-**1a**: $MR_3 = SnMeCl_2$
(±)-**1b**: $MR_3 = SnMe_2Cl$
(±)-**1c**: $MR_3 = SnMe(OTf)_2$
(±)-**1d**: $MR_3 = SnMe_2OTf$
(±)-**2a**: $MR_3 = SiMe_2F$
(±)-**2b**: $MR_3 = SiMe_2Cl$
(±)-**2c**: $MR_3 = SiMe_2Br$
(±)-**3** : $MR_3 = GeMe_2Cl$



(±)-**4a**: $B(OR)_2 = B(OH)_2$
(±)-**4b**: $B(OR)_2 = B(OCMe_2CMe_2O)$



7a: $SiR_3 = SiMe_3$
7b: $SiR_3 = SiMe_2Ph$



8a: HgX = HgCl
8b: $HgX = HgO_2CCF_3$
8c: HgX = HgOTf

Figure 1.

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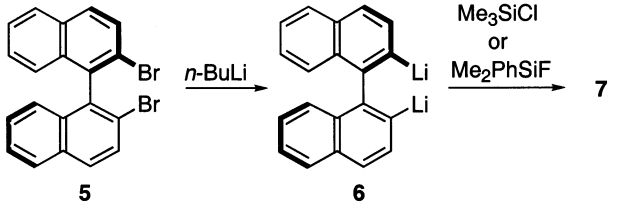
binaphthyls **8** are the first chiral bis-metallic binaphthyl catalysts reported by Oh et al.[6] They evaluated the catalytic activity in the Diels–Alder reaction of compounds **8**. We also reported syntheses of (*R*)-2,2′-bis-(dichloromethylstannyl)-1,1′-binaphthyl **1a** and its triflate **1c** and the evaluation of these two optically active bis-stannyl binaphthyls as chiral Lewis acid catalysts in the Diels–Alder reaction and the asymmetric acylation reaction of a racemic alcohol.[7] In the study we report herein, the full details of our development of the syntheses and reactions of chiral bis-metallic binaphthyl catalysts are presented.

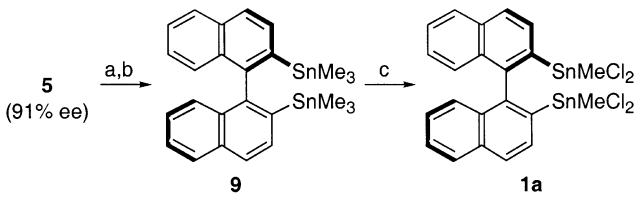


(1)

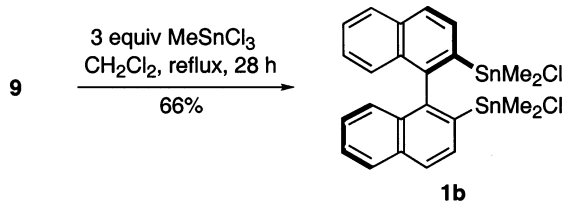
2. Results and discussion

2.1. Synthetic study of (*R*)-2,2′-bis(stannyl)-1,1′-binaphthyls

The synthetic pathway for the preparation of optically active (*R*)-2,2′-bis(stannyl)-1,1′-binaphthyls is shown in Scheme 1. Dilithiation of (*R*)-2,2′-dibromo-1,1′-binaphthyl **5** (91% ee[8]) was carried out using 2.4 equiv. of *n*-BuLi at −73°C for 1 h. The mixture was then cooled to −90°C. To the resulting dilithio-intermediate **6** was slowly added a 3-fold excess of Me_3SnCl and after this addition, the reaction mixture was gradually warmed to −50°C and stirred for an additional 4 h to give (*R*)-2,2′-bis(trimethylstannyl)-1,1′-binaphthyl **9** in 51% yield as a white powder. In order to suppress racemization (i.e. loss of the axial chirality), it is crucial to control the reaction temperature below −50°C during the bis-stannylation reaction.[5,8] The preparation of (*R*)-2,2′-bis-(dichloromethylstannyl)-1,1′-binaphthyl **1a** was accomplished by Kuivila's method.[1] The redistribution reaction of **9** with $SnCl_4$ in CH_2Cl_2 at room temperature for 25 h gave the desired Lewis acid catalyst **1a** in 77% yield as a white powder. Analogously, the reaction of **9** with $MeSnCl_3$ gave (*R*)-2,2′-bis(chlorodimethylstannyl)-1,1′-binaphthyl **1b** in 66% yield (Eq. (2)).



Scheme 1. *Reagents and conditions*: (a) *n*-BuLi (2.4 equiv.), THF, −73°C, 1 h; (b) Me_3SnCl (3 equiv.), −90 to −50°C, 4 h, 51% for two steps; (c) $SnCl_4$ (6 equiv.), CH_2Cl_2, rt, 25 h, 77%.



(2)

The enantiomeric excess of the bis-stannane **1a** was determined by alkylation with enantiomerically pure (*S*)-2-methylbutylmagnesium chloride, conversion to 2,2′-bis(methyldi((*S*)-2-methylbutyl)stannyl)-1,1′-binaphthyl **10a**, and ^1H NMR analysis of its diastereomeric ratio (Eq. (3) and Fig. 2). Fig. 2 shows the ^1H NMR spectra of the Sn–Me resonance of **10a** and **10a′** derived from the racemic dibromide (±)-**5**. Two equivalent singlet signals assigned to two diastereomers due to axial chirality were observed in the ^1H NMR spectrum of **10a′**. In contrast, one signal

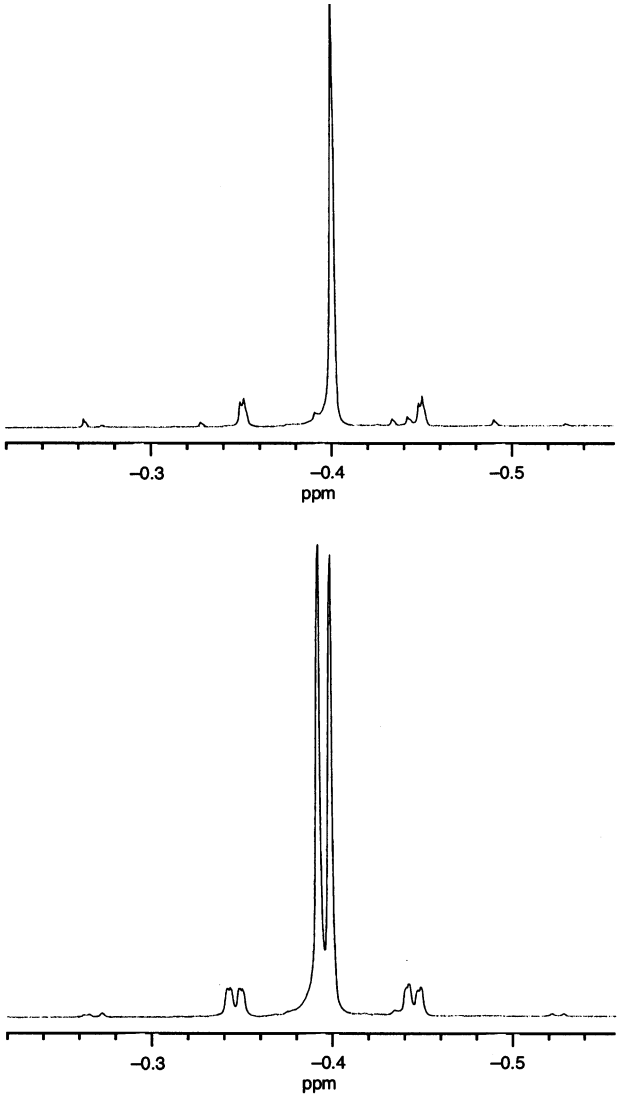
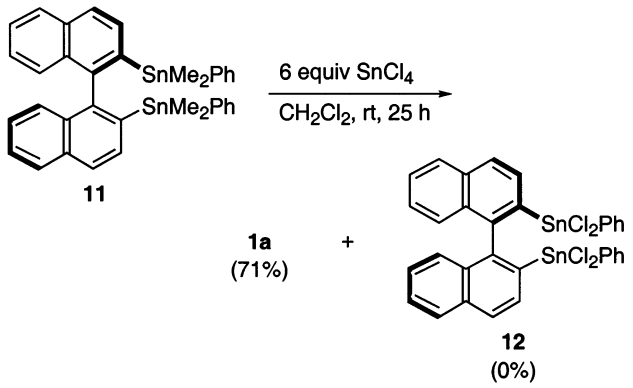


Figure 2. ^1H NMR spectra of Sn–methyl resonance of **10a** (top) and **10a′** (bottom).

assigned to a minor diastereomer almost vanished in the ^{1}H NMR spectrum of **10a**. The diastereomeric ratio (91% de) based on the integration of the peak areas is comparable to the enantiomeric purity of the starting material **5** (91% ee).[9] The ^{1}H NMR analysis of **10b** disclosed that the enantiomeric excess of **1b** was also equivalent to **5**. The Sn–Me cleavage reactions of **9** with $SnCl_4$ and $MeSnCl_3$ were disclosed by Kuivila and co-workers. However, they used only racemic mixtures so that the enantiospecificity of this process was unexplored prior to this work. Our present study reveals that both the bis-stannylation and the subsequent redistribution reaction are enantiofacial with retention of the axial chirality of the binaphthyl moieties. Because chlorostannanes are versatile intermediates in syntheses of organotin compounds, the enantiofacial chlorination reactions of **9** with tin chlorides suggest that the trimethylstannyl precursor **9** is the prospective equivalent for various optically active bis-stannyl binaphthyl derivatives. In addition, we were encouraged by the high selectivity of the Sn–Me cleavage in the preparation of **1a**. Thus, we attempted to prepare the bis-dichlorophenylstannyl catalyst **12** via Sn–Me cleavage reaction of **11**. However, in this case, the formation of the desired catalyst **12** was not confirmed and **1a** was predominately obtained in 71% yield (Eq. (4)).



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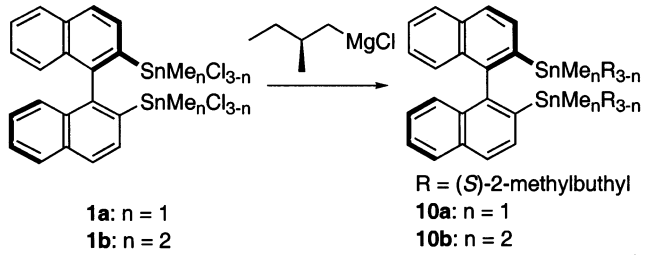


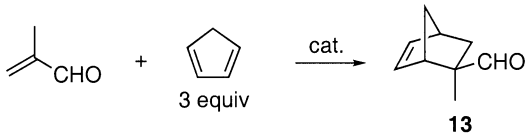
(3)

2.2. Diels–Alder reaction of methacrolein and cyclopentadiene

Our initial evaluation of the novel optically active bis-stannyl binaphthyls as chiral Lewis acid catalysts was based on the asymmetric Diels–Alder reaction of methacrolein with cyclopentadiene (Table 1). In the presence of the bis-dichlorostannyl binaphthyl **1a** (100 mol%), the Diels–Alder reaction was completed at 20°C after 10 h to give the cycloadducts **13** (*exo*/*endo* = 88/12) in 57% yield and 12% ee for the major *exo*-isomer (entry 1). The enantiomeric excess and the absolute configuration of the *exo*-adduct was determined by conversion to the acetal of (2*R*,4*R*)-(−)-2,4-pentanediol, whose ^{1}H NMR spectrum was compared to that reported in the literature.[10] After the reaction, **1a** was recovered in 61% yield. However, the catalytic activity was so modest that stoichiometric amounts of **1a** had to be employed in order to effect full conversion. The bis-monochlorostannyl binaphthyl **1b** (100 mol%) was so inert that the cycloaddition was incomplete after stirring at 20°C for 29 h, and at the end of the reaction compound **13** (*exo*/*endo* = 87/13) was obtained in only 20% yield and no enantioselectivity was found in the major *exo*-isomer (entry 2).

Thus, we turned our attention to the triflate derivatives, **1c** and **1d**, with the expectation that the triflate ligands would either dissociate or be readily displaced by methacrolein so that the stannyl triflates would offer the advantages of a much higher catalytic activity than

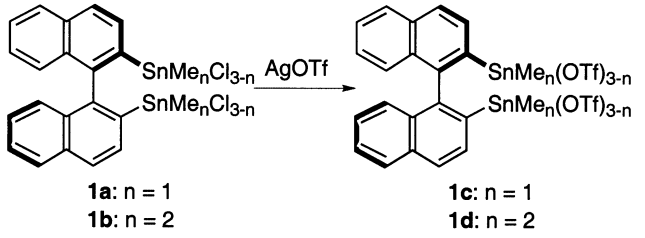
Table 1. Diels–Alder reaction of methacrolein and cyclopentadiene catalyzed by **1a–d**



Entry	Catalyst[a] (mol%)	Temp. (°C)	Time (h)	Yield (%)	*exo*/*endo*[b]	*exo* ee (%)[c] [config.]
1[d]	**1a** (100)	20	10	57	88/12	12 [*R*]
2[d]	**1b** (100)	20	29	20	87/13	0
3[e]	**1c** (10)	−60	1	51	86/14	0
4[f]	**1d** (10)	−78	16	54	90/10	2 [*R*]

[a] The enantiomeric purity of the catalyst is 91% ee.
[b] *exo*/*endo* ratios were determined by ^{1}H NMR analysis.
[c] The ee of major isomer and the absolute configuration of its carbonyl α-carbon are indicated.
[d] Solvent: CH_2Cl_2.
[e] Solvent: CH_2Cl_2–CH_3NO_2, 3:1 v/v.
[f] Solvent: CH_2Cl_2–CH_3CN, 3:1 v/v.

the parent stannyl chlorides. The catalysts, **1c** and **1d**, were prepared by the metathetic reaction of the stannyl chloride precursors with the appropriate amount of AgOTf according to the previously reported procedures (Eq. (5)).[1] At this point, the resulting catalyst suspension was diluted with CH_2Cl_2, cooled for the execution of the cycloaddition reaction, and then methacrolein followed by cyclopentadiene was added. As expected, the reactions were accelerated markedly in the presence of only 10 mol% catalyst. However, the enantioselectivity was found to be very low for the major *exo*-isomer in both cases (entries 3 and 4).



(5)

2.3. Asymmetric acylation of 1-phenyl-1,2-ethanediol

Organotin catalysts have been gradually employed for the acylation of alcohols in view of their high reactivity and selectivity (Fig. 3). For example, Otera and Matsumura recently reported that asymmetric acylation reactions catalyzed by the optically active organotin ditriflate **14** and the bromide derivative **15** are effective

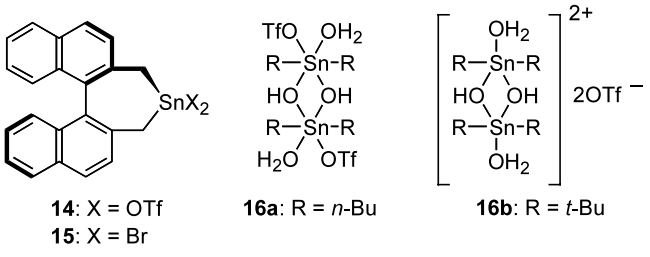


Figure 3.

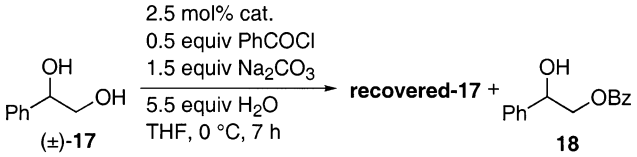
for the kinetic resolution of *meso*- and racemic diols.[11,12] While with achiral catalysts, Otera also demonstrated that dimeric organotin triflates **16**, the hydrolysis products of $R_2Sn(OTf)_2$, have much higher catalytic activity due to the increased Lewis acidity than the monomeric analogues.[13] Thus, we investigated the catalytic properties of the bis-dichlorostannyl catalyst **1a** and its triflate **1c** in the asymmetric acylation of racemic 1-phenyl-1,2-ethanediol **17** with 0.5 equiv. of benzoyl chloride in the presence of Na_2CO_3 and H_2O (Table 2).

Both catalysts **1a** and **1c** (2.5 mol%, 91% ee) induced high yields and regioselectivities. However, a distinct difference was found in the enantioselectivities: when the tin chloride **1a** was used to catalyze the acylation reaction, the product (1*S*)-**18** was obtained in 43% yield and 6% ee with a selectivity factor[14] of 1.2 (entry 1). In contrast, the tin triflate **1c** functioned as a reverse enantiofacial catalyst to give (1*R*)-**18** in 41% yield and 33% ee with a selectivity factor of 2.6 (entry 2). The reactivity and the selectivity of **1c** were not affected by both the presence of AgCl (entry 3) and the reaction temperature (entry 4). In parallel with the investigation of catalysts, metal carbonate effects were also evaluated with 2.5 mol% of catalyst **1c**.[15] Li_2CO_3, K_2CO_3, and $MgCO_3$ showed high yields and regioselectivities. However, no enantioselectivity was found in both the acylation product **18** and the recovered diol **17**. In the presence of Ag_2CO_3, the catalyst **1c** was deactivated. Thus, Na_2CO_3 was found to be a particularly efficient metal carbonate in this asymmetric acylation reaction. Though the precise structure of the hygroscopic tin triflate catalyst **1c** is not yet clear,[16] we have assumed that two stannyl groups were intramolecularly hydrolyzed into the binuclear complex similar to **16**. In fact, the catalytic activity of **1c** drastically decreased in the absence of H_2O and the acylation product **18** was obtained in only 10% yield.

2.4. (*R*)-2,2′-Bis(silyl)-1,1′-binaphthyls

Optically active bis-halosilyl binaphthyls have also been expected to be novel chiral Lewis acid catalysts based

Table 2. Asymmetric acylation of 1-phenyl-1,2-ethanediol **17** catalyzed by **1a** and **1c**



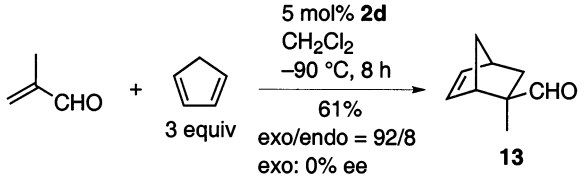
Entry	Catalyst	Yield (%) of **18**	(*s*)[a]	ee (%) of **17**[b] [config.]	ee (%) of **18**[c] [config.]
1	**1a**	43	1.2	12 [*R*]	6 [*S*]
2	**1b**	41	2.6	28 [*S*]	33 [*R*]
3[d]	**1c**	50	1.6	18 [*S*]	15 [*R*]
4[e]	**1d**	35	1.9	22 [*S*]	21 [*R*]

[a] Ratio of rate constants for the more reactive to the less reactive enantiomer calculated according to Ref. 14.
[b] Determined by HPLC using a Chiralcel OB-H column.
[c] Determined by HPLC using a Chiralcel OB-H column after conversion to **17**.
[d] AgCl was removed by filtration before the acylation reaction.
[e] –40°C.

on the 2,2′-bis-metallic-1,1′-binaphthyls. Lucchi and coworkers reported the pioneering synthetic study.[3] They demonstrated that 2,2′-bis(chlorodimethylsilyl)-1,1′-binaphthyl (±)-**2b** and its bromide derivative (±)-**2c** were obtained quantitatively via Si–Si bond cleavage of 3,4-disila-3,3,4,4-tetramethyl-3,4-dihydrodibenzo[*c*,*g*]-phenanthrene (±)-**19** using X_2 (X = Cl, Br). Because iodosilanes have proven to be excellent Lewis acid catalysts,[17] we synthesized the enantiomerically pure precursor **19**, prepared (*R*)-2,2′-bis(iododimethylsilyl)-1,1′-binaphthyl **2d** via iodinative Si–Si cleavage of **19**, and then evaluated **2d** as the chiral Lewis acid catalyst in the Diels–Alder reaction of methacrolein and cyclopentadiene.

The pathway developed for the synthesis of the optically active (*R*)-2,2′-bis(silyl)-1,1′-binaphthyls is shown in Scheme 2. Dilithiation followed by the cyclization with $ClMe_2SiSiMe_2Cl$ of **5** gave the optically active **19** in 70% yield with retention of the axial chirality. After two recrystallizations, enantiomerically pure crystals of **19** were obtained. The X-ray structural analysis also supports the enantiomeric purity of **19** (Fig. 4).[18] The space group $I4_1$ (#80) suggests that the unit cell has chirality (Fig. 5) and the absolute configuration based on the Flack parameter of 0.18(8) is consistent with the starting material **5**. Iodinative Si–Si cleavage of **19** proceeded very rapidly to give **2d** in high yield as verified by the ^1H NMR analysis.

The catalyst **2d** for the execution of the cycloaddition reaction was prepared by stirring a solution of **19** and I_2 in CH_2Cl_2 at 0°C for 1 h. At this point, the resulting catalyst solution was cooled to −90°C, and methacrolein was added, followed by cyclopentadiene. The mixture was stirred at this temperature for 8 h to give the Diels–Alder cycloadducts **13** (*exo*/*endo* = 92/8) in 61% yield (Eq. (6)). However, no enantioselectivity was found in the major *exo*-isomer.



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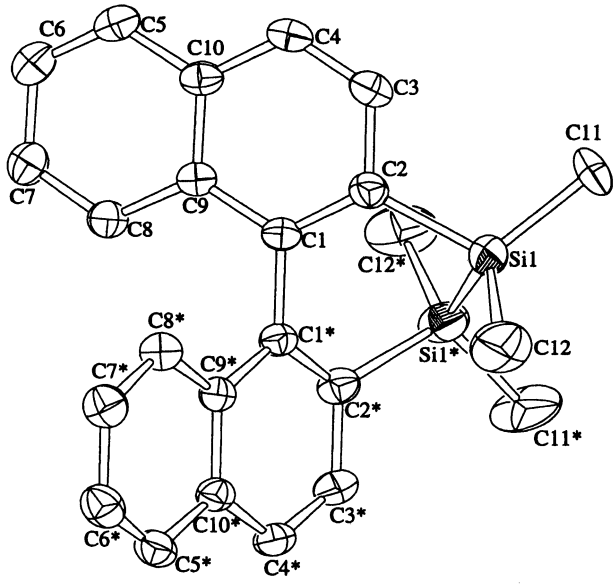
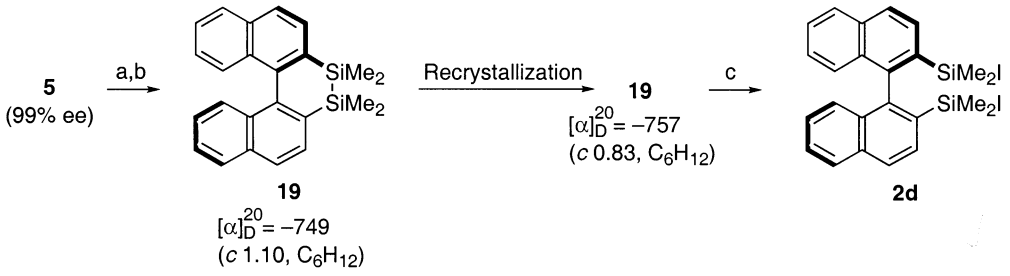


Figure 4. Molecular structure of **19** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

3. Experimental

3.1. General

Nuclear magnetic resonance (NMR) spectra were obtained with a Varian Gemini 200H instrument operating at 200 MHz for the ^1H NMR and 50 MHz for the ^{13}C NMR or a Varian Unity 500 plus instrument operating at 499.9 MHz for the ^1H NMR in $CDCl_3$. The ^1H and ^{13}C chemical shifts were referenced to internal $CDCl_3$ (^1H δ 7.24 ppm; ^{13}C δ 77.0 ppm) relative to Me_4Si at δ 0.00 ppm. Optical rotations were measured with a Horiba Sepa-200 polarimeter. Analytical high performance liquid chromatography (HPLC) was performed on a Hitachi L-7100 with a Hitachi L-7400 UV detector using Daicel Chiralcel OB-H (0.46 cm ϕ×25 cm). Melting points are uncorrected and were measured on a Yanaco MP-500D melting point apparatus. The microanalytical determinations were performed by the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University, Sendai, Japan. Tetrahydrofuran (THF) and Et_2O were dried over and distilled from sodium–



Scheme 2. *Reagents and conditions*: (a) *n*-BuLi (2.4 equiv.), THF, −70°C, 30 min; (b) $ClMe_2SiSiMe_2Cl$ (1.2 equiv.), −90 to −70°C, 3 h, 70% for two steps; (c) I_2, $CDCl_3$, 100%.

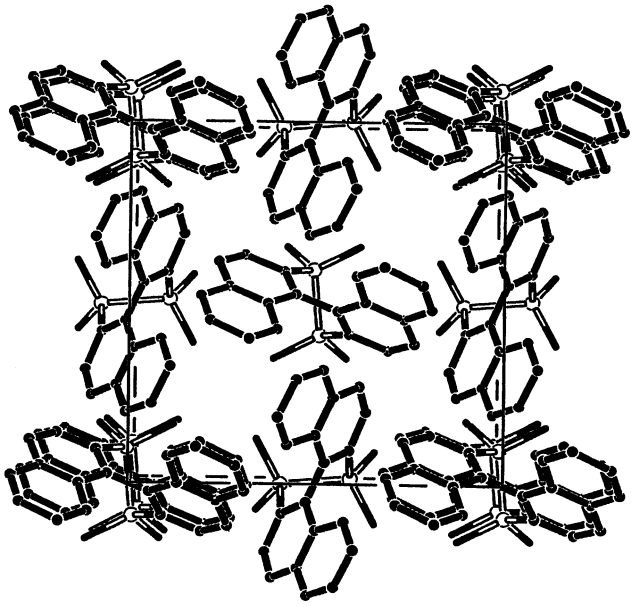


Figure 5. Packing of enantiomerically pure **19** in the unit cell. Hydrogen atoms are omitted for clarity.

benzophenone ketyl prior to use. CH_2Cl_2, CH_3NO_2, and CH_3CN were dried over and distilled from CaH_2 prior to use. (*R*)-2,2′-Dibromo-1,1′-binaphthyl (**5**) was prepared according to the published procedure.[5] All other chemicals were commercially obtained and used as received. All reactions were carried out under a nitrogen atmosphere.

3.2. (*R*)-2,2′-Bis(trimethylstannyl)-1,1′-binaphthyl, 9

To a solution of **5** (91% ee) (4.35 g, 10.6 mmol) in THF (5 mL) was added a hexane solution of *n*-BuLi (16.0 mL, 1.59 M, 25.4 mmol) at −73°C, and then the reaction mixture was stirred for 1 h. After the reaction mixture was cooled to −90°C, a solution of Me_3SnCl (6.3 g, 32 mmol) in THF (10 mL) was slowly added. After the addition was complete, the reaction mixture was gradually warmed to −50°C and stirred for an additional 4 h until the dark red dilithio-dianion completely faded. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was subjected to flash chromatography (silica gel, hexane) to afford **9** (3.1 g, 5.4 mmol) in 51% yield and 91% ee as a white powder: mp 77–80°C; $[\alpha]_D^{20}$ +10.2 (*c* 1.04, cyclohexane); ^{1}H NMR ($CDCl_3$, 200 MHz): δ −0.36 (s, 18H), 7.2–7.3 (m, 4H), 7.42 (ddd, J=8.3, 5.5, 2.4 Hz, 2H), 7.70 (d, J=8.1 Hz, 2H), 7.86–7.92 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ −8.7, 125.8, 125.9, 126.8, 126.9, 127.9, 132.1, 133.2, 133.7, 142.5, 147.5. Anal. calcd for $C_{26}H_{30}Sn_2$: C, 53.85; H, 5.21. Found: C, 54.30; H, 5.43%.

3.3. (*R*)-2,2′-Bis(dichloromethylstannyl)-1,1′-binaphthyl, 1a

To a solution of **9** (2.5 g, 4.3 mmol) derived from **5** (91% ee) in CH_2Cl_2 (35 mL) was slowly added $SnCl_4$ (3.0 mL, 26 mmol) at −70°C, and the reaction mixture was then allowed to warm to room temperature and stirred for an additional 25 h. The solution was concentrated under reduced pressure, chromatographed (silica gel, CH_2Cl_2), and recrystallized from CH_2Cl_2 to give **1a** (2.2 g, 3.3 mmol) in 77% yield and 91% ee as a white powder: mp 235–238°C; $[\alpha]_D^{20}$ −9.20 (*c* 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.06 (s, 6H), 7.29 (d, J=8.4 Hz, 2H), 7.45 (ddd, J=8.4, 6.7, 1.4 Hz, 2H), 7.64 (ddd, J=8.4, 6.7, 1.1 Hz, 2H), 8.03 (d, J=8.5 Hz, 2H), 8.13 (d, J=8.4 Hz, 2H), 8.21 (d, J=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 5.6, 126.6, 128.4, 128.6, 128.8, 129.5, 130.6, 132.7, 134.8, 142.9, 144.1. Anal. calcd for $C_{22}H_{18}Sn_2Cl_4$: C, 39.94; H, 2.74. Found: C, 40.10; H, 2.88%.

3.4. (*R*)-2,2′-Bis(chlorodimethylstannyl)-1,1′-binaphthyl, 1b

To a solution of **9** (350 mg, 0.604 mmol) derived from **5** (91% ee) in CH_2Cl_2 (7 mL) was slowly added a solution of $MeSnCl_3$ (392 mg, 1.65 mmol) in CH_2Cl_2 (3 mL) at 0°C. The reaction mixture was then heated to reflux for 28 h. The solution was cooled to room temperature, concentrated under reduced pressure, chromatographed (silica gel, Et_2O), and recrystallized from CH_2Cl_2–hexane to give **1b** (248 mg, 0.400 mmol) in 66% yield and 91% ee as a white powder: mp 124–127°C; $[\alpha]_D^{20}$ +13.5 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.05 (s, 12H), 7.26 (d, J=8.4 Hz, 2H), 7.36 (ddd, J=8.4, 6.7, 1.2 Hz, 2H), 7.55 (ddd, J=8.2, 6.7, 1.2 Hz, 2H), 7.99 (d, J=8.2 Hz, 2H), 8.00 (d, J=8.4 Hz, 2H), 8.09 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ −0.8, 1.0, 126.5, 127.2, 127.4, 128.4, 128.8, 131.1, 132.9, 134.3, 142.6, 145.5. Anal. calcd for $C_{24}H_{24}Sn_2Cl_2$: C, 46.44; H, 3.90. Found: C, 46.00; H, 3.86.

3.5. (*R*)-2,2′-Bis(methyldi((*S*)-2-methylbutyl)stannyl)-1,1′-binaphthyl, 10a

To a solution of (*S*)-2-methylbutylmagnesium chloride (2.8 mmol) in Et_2O (5 mL) was slowly added a solution of **1a** (50 mg, 76 μmol) derived from **5** (91% ee) in THF (3 mL). The reaction mixture was then stirred for 1 h. Water was added, and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was subjected to flash chromatography (silica gel, hexane) to afford **10a** (55 mg, 68 μmol) in 90% yield and 91% de determined by ^{1}H NMR analysis: ^{1}H NMR ($CDCl_3$, 499.9 MHz): δ −0.40 (s, 6H, SnMe, major isomer), −0.39 (s, 6H, SnMe, minor isomer)) as a colorless oil: $[\alpha]_D^{20}$ +7.33 (*c* 0.586, cyclohexane); ^{1}H NMR ($CDCl_3$, 499.9 MHz): δ −0.40 (s, 6H), 0.12 (dd, J=13.5, 8.5 Hz, 2H), 0.34 (dd, J=13.0, 8.5 Hz, 2H), 0.48 (dd, J=13.0, 6.0 Hz, 2H), 0.61 (d, J=6.5 Hz, 6H), 0.69–0.80 (m, 20H), 0.92–1.46 (m, 12H), 7.18–7.22 (m, 4H), 7.40 (ddd, J=8.5, 4.5, 2.5 Hz, 2H), 7.69 (d, J=8.5 Hz, 2H), 7.86–7.90 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ −9.2, 11.55, 11.56, 21.0, 21.1, 22.8, 23.0, 32.8, 32.9, 33.2, 33.3, 125.68, 125.73, 126.6, 127.1, 127.8, 132.7, 133.3, 133.6, 143.5, 147.6. Anal. calcd for $C_{42}H_{62}Sn_2$: C, 62.72; H, 7.77. Found: C, 62.94; H, 7.61%. A mixture of equal portions of two diastereomers **10a**′ was prepared according to a similar procedure using racemic (±)-**1a**.

3.6. (*R*)-2,2′-Bis(dimethyl((*S*)-2-methylbutyl)stannyl)-1,1′-binaphthyl, 10b

To a solution of (*S*)-2-methylbutylmagnesium chloride (1.0 mmol) in Et_2O (3 mL) was slowly added a solution of **1b** (50 mg, 80 μmol) derived from **5** (91% ee) in THF (5 mL). The reaction mixture was then stirred for 1 h. Water was added, and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was subjected to flash chromatography (silica gel, hexane) to afford **10b** (46 mg, 67 μmol) in 83% yield and 91% de determined by ^{1}H NMR analysis (^{1}H NMR ($CDCl_3$, 499.9 MHz): δ −0.43 (s, 6H, SnMe, major isomer), −0.42 (s, 6H, SnMe, minor isomer), −0.27 (s, 6H, SnMe, minor isomer), −0.26 (s, 6H, SnMe, major isomer)) as a colorless oil: $[\alpha]_D^{20}$ +6.15 (*c* 0.682, cyclohexane); ^{1}H NMR ($CDCl_3$, 499.9 MHz): δ −0.43 (s, 6H), −0.26 (s, 6H), 0.26 (dd, J=13.0, 8.0 Hz, 2H), 0.54 (dd, J=13.0, 5.5, 2H), 0.63 (d, J=6.5 Hz, 6H), 0.70 (t, J=7.5 Hz, 6H), 0.96–1.12 (m, 4H), 1.24–1.40 (m, 2H), 7.20–7.26 (m, 4H), 7.41 (ddd, J=8.5, 6.5, 2.0 Hz, 2H), 7.70 (d, J=8.5 Hz, 2H), 7.88–7.93 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ −9.0, −8.5, 11.5, 20.9, 22.7, 32.9, 33.0, 125.7, 125.8, 126.7, 127.0, 127.8, 132.3, 133.2, 133.6, 143.1, 147.5. Anal. calcd for $C_{34}H_{46}Sn_2$: C, 59.00; H, 6.70. Found: C, 58.80; H, 6.57%.

3.7. (*R*)-2,2′-Bis(dimethylphenylstannyl)-1,1′-binaphthyl, 11

To a solution of phenylmagnesium chloride (80 mmol) in THF (15 mL) was slowly added a solution of **1b** (91% ee) (1.77 g, 2.85 mmol) in THF (5 mL). The reaction mixture was then stirred for 1 h. Water was added, and the mixture was extracted with AcOEt. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was subjected to flash chromatography (silica gel, hexane) to afford **11** (1.79 g, 2.54 mmol) in 89% yield as a white powder: mp 95–98°C; $[\alpha]_D^{20}$ −7.79 (*c* 1.48, cyclohexane); ^{1}H NMR ($CDCl_3$, 200 MHz): δ −0.34 (s, 6H), −0.17 (s, 6H), 7.03–7.23 (m, 14H), 7.39 (ddd, J=8.1, 5.9, 2.2 Hz, 2H), 7.65 (d, J=8.1 Hz, 2H), 7.80–7.89 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ −9.5, −9.0, 125.9, 126.2, 127.0, 127.1, 127.8, 127.9, 128.1, 132.4, 133.2, 133.8, 136.0, 141.5, 141.6, 147.6. Anal. calcd for $C_{36}H_{34}Sn_2$: C, 61.41; H, 4.87. Found: C, 61.78; H, 4.94%.

3.8. Redistribution reaction of 11 with $SnCl_4$

To a solution of **11** (120 mg, 0.170 mmol) in CH_2Cl_2 (5 mL) was slowly added $SnCl_4$ (120 μL, 1.02 mmol) at −77°C. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 25 h. The solution was concentrated under reduced pressure, chromatographed (silica gel, CH_2Cl_2), and recrystallized from CH_2Cl_2 to give **1a** (77 mg, 0.12 mmol) in 71% yield as a white powder.

3.9. Diels–Alder reaction of methacrolein and cyclopentadiene catalyzed by 1a and 1b

To a solution of **1a** (91% ee) (662 mg, 1.00 mmol) in CH_2Cl_2 (5 mL) was added methacrolein (84 μL, 1.0 mmol) followed by cyclopentadiene (0.26 mL, 3.0 mmol) at 20°C. The reaction mixture was then stirred for 10 h. Saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated to afford the crude products. Purification by silica gel chromatography eluting with 10:1 hexane–Et_2O provided the pure Diels–Alder adduct **13** (77 mg, 0.57 mmol) in 57% yield. The *exo*/*endo* ratio of **13** was determined by ^{1}H NMR analysis: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 9.37 (s, 1H, CHO, *endo*), 9.66 (s, 1H, CHO, *exo*). Enantioselectivity was determined by ^{1}H NMR analysis after conversion to the acetal of (2*R*,4*R*)-(−)-2,4-pentanediol: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.66 (s, 1H, CHO_2, major *exo*-isomer), 4.68 (s, 1H, CHO_2, minor *exo*-isomer). The reaction catalyzed by **1b** was carried out according to a similar procedure.

3.10. Diels–Alder reaction of methacrolein and cyclopentadiene catalyzed by 1c

A mixture of **1a** (91% ee) (67.0 mg, 0.10 mmol) and AgOTf (100 mg, 0.389 mmol) in CH_3NO_2 (1.5 mL) was stirred at room temperature for 2 h,[1] then diluted with CH_2Cl_2 (4.5 mL). After the resulting suspension including the catalyst **1c** was cooled to −60°C, methacrolein (84 μL, 1.0 mmol) followed by cyclopentadiene (0.26 mL, 3.0 mmol) was added. The reaction mixture was then stirred for 1 h. Saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with pentane. Further work-up provided **13** (69 mg, 0.51 mmol) in 51% yield.

3.11. Diels–Alder reaction of methacrolein and cyclopentadiene catalyzed by 1d

A mixture of **1b** (91% ee) (64.0 mg, 0.10 mmol) and AgOTf (48 mg, 0.19 mmol) in CH_3CN (1.5 mL) was stirred at ambient temperature for 2 h,[1] and diluted with CH_2Cl_2 (4.5 mL). After the resulting suspension including the catalyst **1d** was cooled to −78°C, methacrolein (84 μL, 1.0 mmol) followed by cyclopentadiene (0.26 mL, 3.0 mmol) was added. The reaction mixture was then stirred for 16 h. Saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with pentane. Further work-up provided **13** (73 mg, 0.54 mmol) in 54% yield.

3.12. Representative procedure for asymmetric acylation of racemic 1-phenyl-1,2-ethanediol

A mixture of **1a** (33 mg, 0.05 mmol) and AgOTf (51 mg, 0.20 mmol) in THF (10 mL) was stirred at ambient temperature for 1 h, and then cooled to 0°C. To the resulting suspension including the catalyst **1c** was added Na_2CO_3 (319 mg, 3.01 mmol), H_2O (200 μL, 11.1 mmol), and 1-phenyl-1,2-ethanediol **17** (279 mg, 2.02 mmol) at this temperature. After the addition was

completed, the reaction mixture was stirred for 30 min at this temperature. Benzoyl chloride (116 μL, 1.00 mmol) was then added and stirred for an additional 7 h. Water was added, and the mixture was extracted with AcOEt. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated to afford the crude products. Purification by silica gel chromatography eluting with 1:1 hexane–AcOEt provided pure 2-benzoyloxy-1-phenylethanol **18** and recovered **17**. The enantiomeric excess of **17** was determined by HPLC using a Chiralcel OB-H column. The enantiomeric excess of **18** was determined after conversion to **17**.

3.13. 1-Phenyl-1,2-ethanediol, 17

Daicel Chiralcel OB-H (0.46 cm ϕ×25 cm), hexane:*i*-PrOH = 9:1, wavelength: 254 nm, flow rate: 0.5 mL/min, retention time: 15.5 min (1*R*), 19.3 min (1*S*).

3.14. (*R*)-3,4-Disila-3,3,4,4-tetramethyl-3,4-dihydrodibenzo[*c*,*g*]phenanthrene, 19

To a solution of **5** (99% ee) (752 mg, 1.82 mmol) in THF (10 mL) was added a hexane solution of *n*-BuLi (3.0 mL, 1.50 M, 4.5 mmol) at −73°C, and the reaction mixture was stirred for 1 h. After the reaction mixture was cooled to −90°C, a solution of $ClMe_2SiSiMe_2Cl$ (451 mg, 2.41 mmol) in THF (10 mL) was slowly added. After the addition was complete, the reaction mixture was gradually warmed to −70°C and stirred for an additional 3 h until the dark red dilithio-dianion completely faded. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was subjected to flash chromatography (silica gel, hexane) to afford **19** (467 mg, 1.27 mmol) in 70% yield as a white powder: $[\alpha]_D^{20}$ −757 (*c* 1.10, C_6H_{12}). After two cycles of recrystallization from an *i*-Pr_2O solution, optically pure crystals were obtained as colorless crystals: mp 200–204°C; $[\alpha]_D^{20}$ −757 (*c* 0.83, C_6H_{12}); ^1H NMR ($CDCl_3$, 200 MHz): δ −0.35 (s, 6H), 0.48 (s, 6H), 6.90 (d, J = 8.6 Hz, 2H), 7.10 (ddd, J = 8.6, 6.5, 1.3 Hz, 2H), 7.39 (ddd, J = 8.2, 6.5, 1.3 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.82–7.92 (m, 4H). Anal. calcd for $C_{24}H_{24}Si_2$: C, 78.20; H, 6.56. Found: C, 78.26; H, 6.38. Crystal data for **19** (23°C): colorless crystals; formula $C_{24}H_{24}Si_2$, F_w = 368.62; tetragonal, space group $I4_1$ (#80), $a = b = 12.3189(9)$, $c = 14.090(1)$ Å; V = 2138.3(3) Å^3, Z = 4, D_{calcd} = 1.145 g/cm^3, μ(Cu Kα) = 1.518 mm^{-1}. A total of reflections 1183, 1113 ($I > 3.00\sigma(I)$) were used in refinement: R = 0.089, R_w = 0.119. The reflection intensities were collected on a Rigaku AFC7S diffractometer with a rotating anode (50 kV, 30 mA) using graphite monochromated Cu Kα (λ = 1.54178 Å). Full lists of atomic coordinates, bond lengths and angles, thermal parameters have been deposited with the Cambridge Crystallographic Data Center (CCDC 190338).

3.15. (*R*)-2,2′-Bis(iododimethylsilyl)-1,1′-binaphthyl, 2d

Iodine was added to a $CDCl_3$ solution of **19**. The yield (NMR) was virtually quantitative. ^1H NMR ($CDCl_3$, 499.9 MHz): δ 0.32 (s, 12H), 7.14 (d, J = 8.0 Hz, 2H), 7.28 (ddd, J = 8.5, 6.8, 1.3 Hz, 2H), 7.50 (ddd, J = 8.0, 7.0, 1.5 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H), 7.9–8.1 (m, 4H). However, isolation was failed due to its highly hygroscopic nature.

3.16. Diels–Alder reaction of methacrolein and cyclopentadiene catalyzed by 2d

A mixture of **19** (45 mg, 0.12 mmol) and I_2 (25 mg, 99 μmol) in CH_2Cl_2 (5 mL) was stirred at 0°C for 1 h, and then cooled to −90°C. To the resulting catalyst **2d** was added methacrolein (165 μL, 1.97 mmol) followed by cyclopentadiene (0.46 mL, 5.3 mmol). The reaction mixture was then stirred for 8 h at this temperature. Saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated to afford the crude products. Purification by silica gel chromatography eluting with 10:1 hexane–Et_2O provided **13** (163 mg, 1.20 mmol) in 61% yield.

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