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Chiral Molecular Recognition of α,β-Unsaturated Ester Using Aluminum Tris(2,6-diphenylphenoxide) (ATPH): Molecular Design for Asymmetric 1,4-Addition

Hirotsugu Ito, Takashi Nagahara, Kazuaki Ishihara, Susumu Saito,* Hisashi Yamamoto*

[*] **Prof. Dr. S. Saito**

Institute for Advanced Research & Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602 (Japan)
FAX: 81-52-789-5945; E-mail: susumu@chem.nagoya-u.ac.jp

[*] **Prof. Dr. H. Yamamoto**

Department of Chemistry, the University of Chicago, 5735 South Ellis Ave, Chicago, IL 60637 (USA)
FAX: 1-773-702-0805; E-mail: yamamoto@uchicago.edu

H. Ito, T. Nagahara, Prof. Dr. K. Ishihara
Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603 (Japan)

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Hirotsugu Ito, Takashi Nagahara, Kazuaki Ishihara, Susumu Saito,*[†] Hisashi Yamamoto*[‡]

Graduate School of Engineering, Nagoya University, SORST, Japan Science and Technology Corporation (JST), Chikusa Nagoya 464-8603, Japan

[†]Institute for Advanced Research and Graduate School of Science, Nagoya University

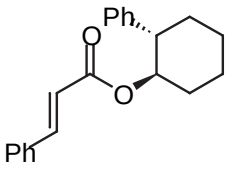
[‡]Department of Chemistry, University of Chicago, 5735 South Ellis Avenue, Chicago 60637, U. S. A.

General. Infrared (IR) spectra were recorded on a Shimazu FTIR-8100 spectrometer. ^{1}H-NMR spectra were measured on a Varian Gemini-300 spectrameter (300MHz) at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s=singlet d=doublet t=triplet, and m=multiplet), coupling constant (Hz), integration, and assignment. ^{13}C-NMR spectra were measured on Varian Gemini-300 (75MHz) spectrometer. Chemical shift were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform ar 77.07 ppm). Chiral high-performance liquid chromatography (chiral HPLC) analysis were conducted using Shimazu LC-10 AD coupled diode array-detector SPD-MA-10A-VP and chiral column of CHIRALCEL OD-H (Daicel chemical industries, LTD.). All experiments were carried out under an atmosphere of dry argon. For tin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254 0.25 mm) were used. The products were purified by column chromatography on silica gel (E. Merck Art. 9385). Microanalyses were conducted at the Faculty of Agriculture, Nagoya University.

In experiments that required dry solvent toluene was distilled from calcium hydride , and tetrahydrofuran (THF) and 1,2-dimethoxyethane were freshly distilled from sodium metal using benzophenone ketyl as indicator.

Preparation of Chiral Ester 1. The following procedure for the reaction of (1*R*,2*S*)-2-phenylcyclohexanol and cinnamoyl chloride is representative. To a solution of cinnamoyl chloride (1.99 g 12.0 mmol), (1*R*,2*S*)-2-phenylcyclohexanol (1.76 g 10.0 mol), and 4-dimethylaminopyridine (61 mg 0.5 mmol) in dichloroethane (20 mL) was added pyridine (1.21 mL 15 mmol) at 0 ˚C under Ar. The reaction mixture was stirred at room temperature for 16 h and quenched with aqueous hydrogen chloride (1.0N, 15 mL). Organic compounds were extracted with ether, dried over Na_2SO_4 and concentrated. The residue was purified column chromatography on silica gel (ether/hexane = 1/15 to 1/8 as the eluent) to give (1*R*,2*S*)-2-phenylcyclohexyl cinnamate (97 % yield) as white solid.

Spectral and Analytical Data of chiral ester 1.



(1*R*,2*S*)-2-phenylcyclohexyl cinnamate (**1**); Known compound:[1)] ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.25 (m, 11H), 6.19 (d, 1H, 15.9 Hz), 5.11 (td, 1H, *J* = 10.8, 4.5 Hz), 2.76 (td, 1H, *J* = 4.5, 11.5 Hz), 2.23 (m, 1H), 1.90 (m, 3H), 1.50 (m, 4H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 166.2, 144.2, 143.2, 134.4, 130.1, 128.8, 128.3, 128.0, 127.5, 126.4, 118.4, 76.0, 49.8, 34.1, 32.5, 25.9, 24.8; IR (KBr) 2861, 2878, 1709, 1640, 1497, 1449, 1327, 1306, 1285, 1206, 1175, 1022, 980, 766, 704 cm^{-1}. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32, H, 7.24. Found: C, 82.20; H, 7.43.

Preparation of ATPH. To a degassed solution of 2,6-diphenylphenol (3.0 equiv.) in toluene at room temperature a 1.0 M hexane solution of Me_3Al (1.0 equiv.) Methane gas(~3.0 equiv.) evolved immediately. The resulting pale yellow solution was stirred at room temperature for 0.5 h and used without further purification.

Typical Procedure for the Diastereoselective Michael Addition to α,β–Unsaturared Chiral Ester Complexed with ATPH Using Lithium Reagent. The following procedure for the reaction of (1*R*,2*S*)-2-phenylcyclohexyl cinnamate and *n*-butyllithium is representative. To a solution of ATPH (0.33 mmol) in toluene (3.0 mL) was added (1*R*,2*S*)-2-phenylcyclohexyl cinnamate (91.9 mg, 0.30 mmol) in toluene (0.5 mL) at room

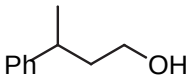
temperature under argon atmosphere. After stirring for 5 min, the mixture was cooled to –78 ˚C, then THF (3.0 mL) was added dropwise and stirred for 1h. To the mixture was added *n*-butyllithium (1.55 M, 290 μL, 0.45 mmol) dropwise at the same temperature. The reaction mixture was stirred for 1 h and quenched with aqueous hydrogen chloride (1.0M, 5 mL). Organic compounds were extracted with ether, dried over Na_2SO_4 and concentrated. The residue was dissolved in THF (9.0 mL) and reduced with lithium aluminum hydride (92%, 63 mg, 1.5 mmol) under Ar at 0 ˚C, and stirred for 1h at room temperature. The reaction mixture was quenched by a dropwise addition of methanol, and was neutralized with a 1N aqueous hydrogen chloride. The organic layer was extracted with ether, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (ether/hexane = 1/3 to 1/2 as the eluent) to give 3-phenylheptanol (99% yield, 97% de) as the reduced 1,4-adduct.

Availability of Other Lithium Reagents: Methyllithium in diethyl ether (1.4 M, halide content < 0.05M) was purchased from Aldrich. 2-propenyllithium, allyllithium, methallyllithium, prenyllithium, benzyllithium were prepared by treatment of the corresponding organotin reagents with *n*-butyllithium at 0 ˚C under Ar in THF. Vinyllithium was prepared from tetravinyltin and phenyllithium at 0 ˚C under Ar in THF.

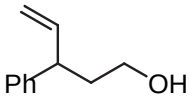
The reaction of (1*R*,2*S*)-2-phenylcyclohexyl cinnamate and lithium enolate of *t*-butyl acetate. To a solution of ATPH (0.33 mmol) was added (1*R*,2*S*)-2-phenylcyclohexyl cinnamate (91.9 mg, 0.30 mmol) dissolved in toluene (3.0 mL) at –78 ˚C under Ar. After stirring for 5 min, lithium enolate of *t*-butyl acetate (0.45 mmol) in TMEDA (1.5 equiv)-THF {prepared by treatment of *t*-butyl acetate (60.7 μL, 0.45 mmol) with a THF solution of LDA [generated by treatment of diisopropylamine (63.1 μL, 0.45 mmol) in THF (3.0 mL) with *n*-butyl lithium (1.55 M, 290 μL, 0.45 mmol) at –50˚C for 1h] at –50 ˚C for 30 min, followed by subsequent addition of TMEDA (0.68 mmol)} was transferred by a cannula to the toluene solution of the ATPH-chiral ester complex. This total mixture was stirred for 1 h at –78 ˚C. The reaction was quenched with aqueous hydrogen chloride (1M, 5.0 mL). The organic layer was extracted with ether, dried over Na_2SO_4 and concentrated. The residue was purified with column chromatography on silica gel (ether/hexane=1/8 to 1/4 as the eluent) to give (1*R*,2*S*)-2-phenylcyclohexyl *t*-butyl 4-phenylpenta-1,5-dicarboxylate (**3f**)

(90% yield, 93 % de) as the 1,4-adduct.

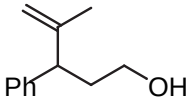
Spectral and Analytical Data of Diols Derived by Reduction of 1,4-Adducts.



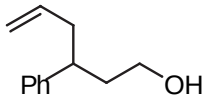
3-Phenylbutan-1-ol; Known compound:[2), 5)] $[\alpha]_D^{20}$ = +13.67 (*c*1.02, $CHCl_3$, for 93% ee); ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.22 (m, 5H), 3.56 (m, 2H), 2.89 (sextet, 1H, *J* = 6.9 Hz), 1.87 (q, 2H, *J* = 6.9 Hz), 1.28 (d, 3H, 6.9 Hz). HPLC analysis: OD-H, 1.0 mL/min flow rate, hexane/2-propanol = 40/1 as eluent, t_R = 17.5 (minor) and 20.7 (major; *S*, determined by comparing the value in ref. 5a) min.



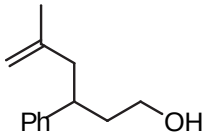
3-Phenyl-4-penten-1-ol; Known compound:[3)] $[\alpha]_D^{20}$ = -22.08 (*c*1.00, $CHCl_3$, for 97% ee); ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.25 (m, 5H), 5.98 (ddd, 1H, *J* = 7.5, 10.5, 17.7 Hz), 5.10 (m 2H), 3.63 (m, 2H), 3.48 (q, 1H, *J* = 7.8 Hz), 2.01 (m, 2H). HPLC analysis: OD-H, 1.0 mL/min flow rate, hexane/2-propanol = 40/1 as eluent, t_R = 17.8 (minor) and 22.5 (major; *R*, determined by comparing the value in ref. 3) min.



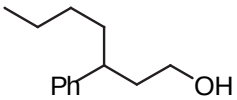
4-Methyl-3-phenyl-4-penten-1-ol; Known compound:[6)] $[\alpha]_D^{20}$ = +28.49 (*c*0.99, $CHCl_3$, for 96% ee); ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.23 (m, 5H), 4.96 (m, 1H), 4.86 (m, 1H), 3.59 (m, 2H), 3.41 (t, 1H, *J* = 7.8 Hz), 2.12 (m 1H), 1.99 (m, 1H), 1.59 (s, 3H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 147.8, 143.0, 128.3, 127.8, 126.4, 110.5, 61.2, 48.9, 35.7, 21.0; IR (neat) 3335, 2941, 2880, 1645, 1601, 1493, 1453, 1374, 1046, 893, 770, 749, 700 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.93; H, 9.35. HRMS (FAB): Exact Mass Calcd for $C_{12}H_{16}O$: 176.1200, found 176.1228. HPLC analysis: OD-H, 1.0 mL/min flow rate, hexane/2-propanol = 80/1 as eluent, t_R = 35.0 (minor) and 37.3 (major) min.



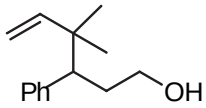
3-Phenyl-5-hexen-1-ol; Known compound:[4), 5)] $[\alpha]_D^{20}$ = -1.21 (*c*1.00, $CHCl_3$, for 94% ee); ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.25 (m, 5H), 5.64 (m, 1H), 4.98 (m, 1H), 4.93 (m, 1H), 3.50 (m, 2H), 2.80 (m, 1H), 2.39 (t, 2H, *J* = 7.0 Hz), 1.98 (m, 1H), 1.80 (m, 1H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 144.4, 136.7, 128.4, 127.6, 126.3, 116.2, 60.9, 42.2, 41.3, 38.5; IR (neat) 3340, 2930, 1640, 1495, 1455, 1048, 1028, 995, 912, 762, 700 cm^{-1}. HPLC analysis: OD-H, 1.0 mL/min flow rate, hexane/2-propanol = 40/1 as eluent, t_R = 16.6 (minor) and 20.4 (major; *S*, determined by comparing the value in ref. 4b) min.



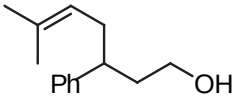
5-Methyl-3-phenyl-5-hexen-1-ol; New compound: $[\alpha]_D^{20}$ = +5.99 (*c*0.98, $CHCl_3$, for 96% ee); ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.23 (m, 5H), 4.69 (s, 1H), 4.62 (s, 1H), 3.50 (m, 2H), 2.9 (m, 1H), 2.35 (d, 2H, *J* = 7.8 Hz), 1.95 (m, 2H), 1.75 (m, 1H), 1.67 (s, 3H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 144.7, 143.6, 128.4, 127.5, 126.2, 112.3, 61.0, 45.6, 40.3, 38.8, 22.3; IR (neat) 3320, 2932, 1647, 1495, 1454, 1375, 1047, 889, 760, 700 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.99; H, 9.73. High-resolution mass spectrum for $C_{13}H_{18}O$ calcd190.14, found 190.1376. HPLC analysis: OD-H, 1.0 mL/min flow rate, hexane/2-propanol = 40/1 as eluent, t_R = 14.5 (minor) and 19.8 (major) min.



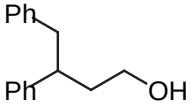
3-Phenylheptan-1-ol; Known compound:[5)] $[\alpha]_D^{20}$ = -1.28 (*c*1.02, $CHCl_3$, for 94% ee); ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.50 (m, 5H), 3.50 (m, 2H), 2.67 (m, 1H,), 1.83 (m, 2H), 1.61 (m, 2H), 1.22 (m, 4H), 0.83 (t, 3H, *J* = 6.9 Hz). HPLC analysis: OD-H, 1.0 mL/min flow rate, hexane/2-propanol = 40/1 as eluent, t_R = 12.8 (minor) and 15.4 (major; *S*, determined by comparing the value in ref. 5b) after converting to the corresponding acid: $[\alpha]_D^{20}$ = +6.42 (*c*1.04, $CHCl_3$)) min.



4,4-Dimethyl-3-phenyl-5-hexen-1-ol; New compound: $[\alpha]_D^{20}$ = +7.85 (*c*1.05, $CHCl_3$, for 89% ee); ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.20 (m, 5H), 5.86 (dd, 1H, *J* = 10.8, 17.7 Hz), 5.00 (d, 1H, *J* = 10.8 Hz), 4.93 (d, 1H, *J* = 17.7 Hz), 3.36 (m, 2H), 2.55 (dd, *J* = 12.3, 3.0 Hz), 1.95 (m, 2H), 0.94 (s, 3H), 0.92 (s, 3H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 144.0, 141.4, 129.6, 127.7, 126.3, 111.8, 61.8, 52.1, 39.9, 32.9, 27.1, 23.2; IR (neat) 3350, 2965, 1636, 1601, 1495, 1455, 1414, 1379, 1364, 1044, 912, 783, 723, 702 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.32; H, 9.93. HPLC analysis: OD-H, 1.0 mL/min flow rate, hexane/2-propanol = 40/1 as eluent, t_R = 14.2 (minor) and 17.8 (major) min.



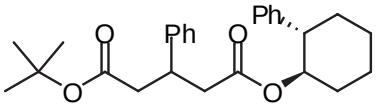
6-Methyl-3-phenyl-6-hepten-1-ol; New compound: ^{1}H-NMR (300MHz, C_6D_6) δ 7.10 (m, 5H), 5.12 (m, 1H), 3.28 (m, 2H), 2.71 (m, 1H), 2.27 (m, 2H), 1.82 (m, 1H), 1.62 (m, 1H), 1.57 (s, 3H), 1.45 (s, 3H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 145.1, 132.7, 127.7, 126.1, 122.4, 61.2, 42.9, 38.4, 35.6, 25.7, 17.8; IR (neat) <α/γ = 8.5/1> 3325, 2930, 1603, 1495, 1453, 1377, 1111, 1046, 912, 758, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O$ <α/γ = 8.5/1>: C, 82.30; H, 9.87. Found: C, 82.29; H, 9.97. HPLC analysis: OD-H, 1.0 mL/min flow rate, hexane/2-propanol = 40/1 as eluent, t_R = 13.8 (minor) and 17.2 (major) min.



3,4-Diphenylbutan-1-ol; Known compound:[7] $[\alpha]_D^{20}$ = -34.96 (c1.02, $CHCl_3$, for 98% ee); ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.20 (m, 10H), 3.4 (m, 2H), 2.95 (m, 3H), 1.9 (m, 2H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 144.3, 140.3, 129.2, 128.4, 128.1, 127.7, 126.3, 125.9, 60.98, 44.4, 43.8, 38.1; IR (neat) 3340, 2932, 1495, 1452, 1044, 760, 733, 700 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found C, 84.91; H, 8.15. HPLC analysis: OD-H, 0.5

mL/min flow rate, hexane/2-propanol = 20/1 as eluent, t_R = 29.4 (minor) and 31.8 (major) min.

Spectral and Analytical Data of the 1,4-Adduct Derived from the Lithium Enolate of *t*-Butyl Acetate.

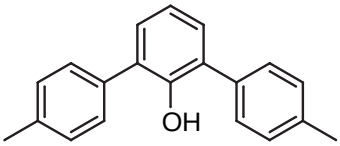


(1*R*,2*S*)-2-Phenylcyclohexyl *t*-butyl 3-phenylpentan-1,5-dicarboxylate (**3f**); New compound: ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.20 (m, 10H), 4.93 (td, 1H, *J* = 10.8, 3,9 Hz), 3.31 (quintet, 1H, *J* = 7.2 Hz), 2.61 (td, 1H, *J* = 12.3, 2.4 Hz), 2.30 (m, 2H), 2.16 (m, 2H), 1.80 (m, 4H), 1.40 (m, 4H), 1.24 (s, 9H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 170.9, 170.6, 143.0, 142.3, 128.3, 128.2, 127.5, 127.3, 126.6, 126.4, 80.1, 76.0, 49.6, 41.25, 41.17, 38.8, 33.8, 32.0, 27.8, 25.7, 24.6; IR (KBr) 2978, 1725, 1603, 1495, 1453, 1435, 1366, 1340, 1294, 1240, 1140, 1080, 1016, 961, 851, 762, 698 cm^{-1}. Anal. Calcd for $C_{27}H_{34}O_4$: C, 76.74; H, 8.11. Found: C, 76.74, H, 8.37. HPLC analysis: OD-H, 1.0 mL/min flow rate, hexane/2-propanol = 40/1 as eluent, t_R = 7.2 (minor) and 8.1 (major) min.

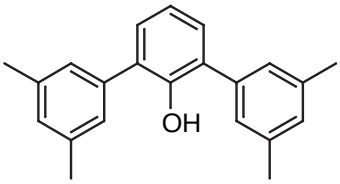
Preparation of 2,6-diphenylphenol analogues. The following procedure for the synthesis of 2,6-bis(4-ethylphenyl)phenol is representative. 2,6-Dibromophenyl methyl ether (1.01 mL 7.0 mmol), 4-ethylphenylboric acid (3.15 g 21.0 mmol), palladium(II) acetate (80 mg 0.36 mmol), tri-*o*-tolylphosphine (218 mg 0.72 mmol), and barium hydoxide octahydrate (6.63 g 21.0 mmol) were mixed in DME/H_2O (24 mL/5 mL) at room temperature. The mixture should be well degassed and was heated to reflux for 2 h. The reaction mixture was cooled to room temperature, quenched with aqueous NH_4Cl, filtered through a pad of celite, extracted with ether, and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified column chromatography on silica gel to yield 2,6-bis(4-ethylphenyl)phenyl methyl ether (96 % yield) as a color less viscous liquid. The obtained methyl ether was demethylated by BBr_3 as following. To a solution of 2,6-bis(4-ethylphenyl)phenyl methyl ether (6.6 mmol) in dichloroethane (12 mL) was added excess BBr_3 (~1.0 ml) at 0˚C under Ar, and the mixture was stirred at room temperature. After

ether spot disappearing on TLC, the reaction mixture was quenched by adding H_2O very slowly at 0 ˚C, then neutralized with aqueous $NaHCO_3$, extracted with ether, washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to yield 2,6-bis(4-ethylphenyl)phenol (97% yield) as a colorless viscous oil.

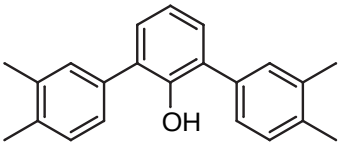
Spectral and Analytical Data of Phenols



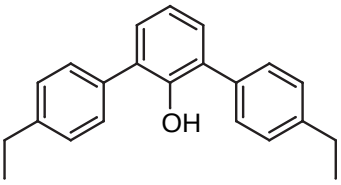
2,6-Bis(4-mehtylphenyl)phenol; Known compound:[8] ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.45 (d, 4H, 8.1 Hz), 7.26 (m, 6H), 7.04 (t, 1H), 5.41 (s, 1H), 2.41 (s, 6H).



2,6-Bis(3,5-dimethylphenyl)phenol; New compound: ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.16 (m, 6H), 7.00 (m, 3H), 2.37 (s, 12H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 149.5, 138.5, 137.7, 129.8, 129.4, 128.9, 127.2, 120.6, 21.52; IR (KBr) 3525, 2915, 1603, 1453, 1412, 1379, 1337, 1235, 1208, 1163, 1117, 1073, 1040, 849, 799, 754, 704 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.37; H, 7.25.



2,6-Bis(3,4-dimethylphenyl)phenol; New compound: ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.24 (m, 8H), 7.02 (t, 1H, *J* = 7.8 Hz), 5.44 (s, 1H), 2.32 (s, 12H); ^{13}C-NMR (75MHz, $CDCl_3$) δ 149.4, 137.1, 136.1, 135.2, 130.5, 130.1, 129.6, 128.7, 126.7, 19.9, 19.6; IR (KBr) 2918, 1505, 1441, 1391, 1325, 1229, 1217, 1182, 1132, 1020, 881, 823, 783, 749, 741, 716 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.39; H, 7.39.



2,6-Bis(4-ethylphenyl)phenol; New compound: ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.48 (d, 4H, *J* = 6.3 Hz), 7.28 (m, 6H), 7.03 (t, 1H, *J* = 7.8 Hz), 5.44 (s, 1H), 2.71 (q, 4H, *J* = 7.8 Hz), 1.29 (t, 6H, *J* = 7.8 Hz); ^{13}C-NMR (75MHz, $CDCl_3$) δ 149.6, 143.8, 135.1, 129.9, 129.5, 128.8, 128.5, 120.8, 28.8, 15.7; IR (neat) 3542, 2965, 1514, 1449, 1402, 1329, 1225, 1167, 1098, 841, 830, 793, 743 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.22; H, 7.59.

^{1}H NMR measurement of ATPH Complex of (1*R*,2*S*)-2-Phenylcyclohexyl Cinnamate (1) at Room Temperature.

Ester **1** (before complexation): ^{1}H-NMR (300MHz,, toluene-d_8) δ 7.48 (d, 1H, *J* = 15.9 Hz), 7.13 (m, 4H), 6.84 (m, 6H), 6.11 (d, 1H, *J* = 15.9 Hz), 5.23 (td, 1H, *J* = 10.2, 3.7 Hz), 2.64 (td, 1H, *J* = 12.0, 3.9 Hz), 2.25 (m, 1H), 1.73 (m,1H), 1.57 (m, 1H), 1.46 (m, 1H), 1.30 (m, 2H), 1.10 (m, 1H).

ATPH-**1** complex **2** (after complexation): ^{1}H-NMR (300MHz,, toluene-d_8) δ 7.80 ~ 6.40 (m, 50H), 5.16 (d, 1H, *J* = 15.9 Hz), 3.57 (td, 1H, *J* = 10.0, 4.0 Hz), 2.21 (td, 1H, *J* = 11.1, 3.9 Hz), 1.50 ~ 0.60 (m, 7H), 0.22 (m, 1H).

Single Crystal of the ATPH–1 Complex 2. To a solution of ATPH (0.5 mmol) in CH_2Cl_2 (4.0 mL) was added **1** (0.5 mmol) at rt under argon atmosphere. After 30 min, the addition of hexane (1.4~1.6 mL) resulted in precipitation of yellow-orange crops, which were subsequently entirely redissolved by heating. The mixture was allowed to stand at rt for 1~2 days with rigorous exclusion of air and moisture to give colorless crystals.

X-ray Crystallographic Determinations. A single crystal of ATPH complex **2** suitable for X-ray diffraction analysis was transferred to a glass capillary tube as quickly as possible under air atmosphere, and the glass capillary was mounted with a sticky compound on a goniometer for measurement. Diffraction data were obtained with graphite-monochromated Mo Kα radiation on a MAC Science DIP2030 diffractometer. Standard

reflections for each data set showed no significant decrease in intensity throughout acquisition. All non-hydrogen atoms were located from the direct method, where the full-matrix was used for least-squares data. All non-hydrogen atoms were refined anisotropically. The hydrogens of all the methyl groups were refined from an initial idealized position (0.96 Å), and the other hydrogens were found by Fourier synthesis, using isotropic temperature factors. Crystallographic computations were performed on a Silicon Graphics INDY computer using the maXus program for data reduction, determining the structure, refining the structure, and molecular graphics. MAC DENZO software was used for cell refinement.

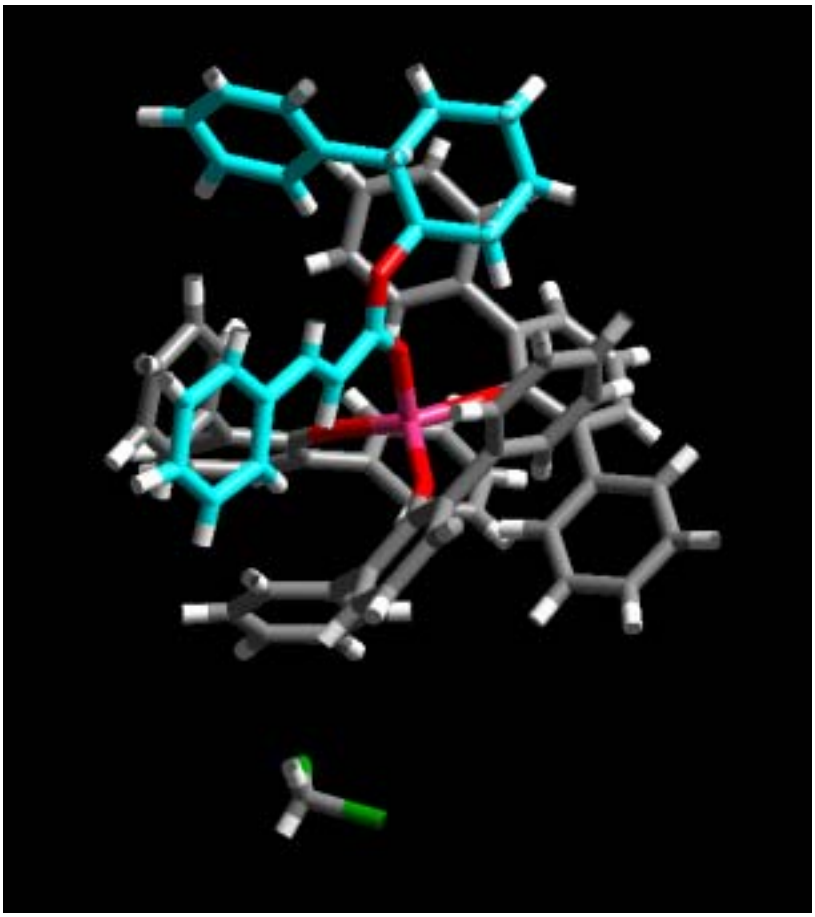


Figure. Cylinder model of ATPH-**1** Complex **2**.

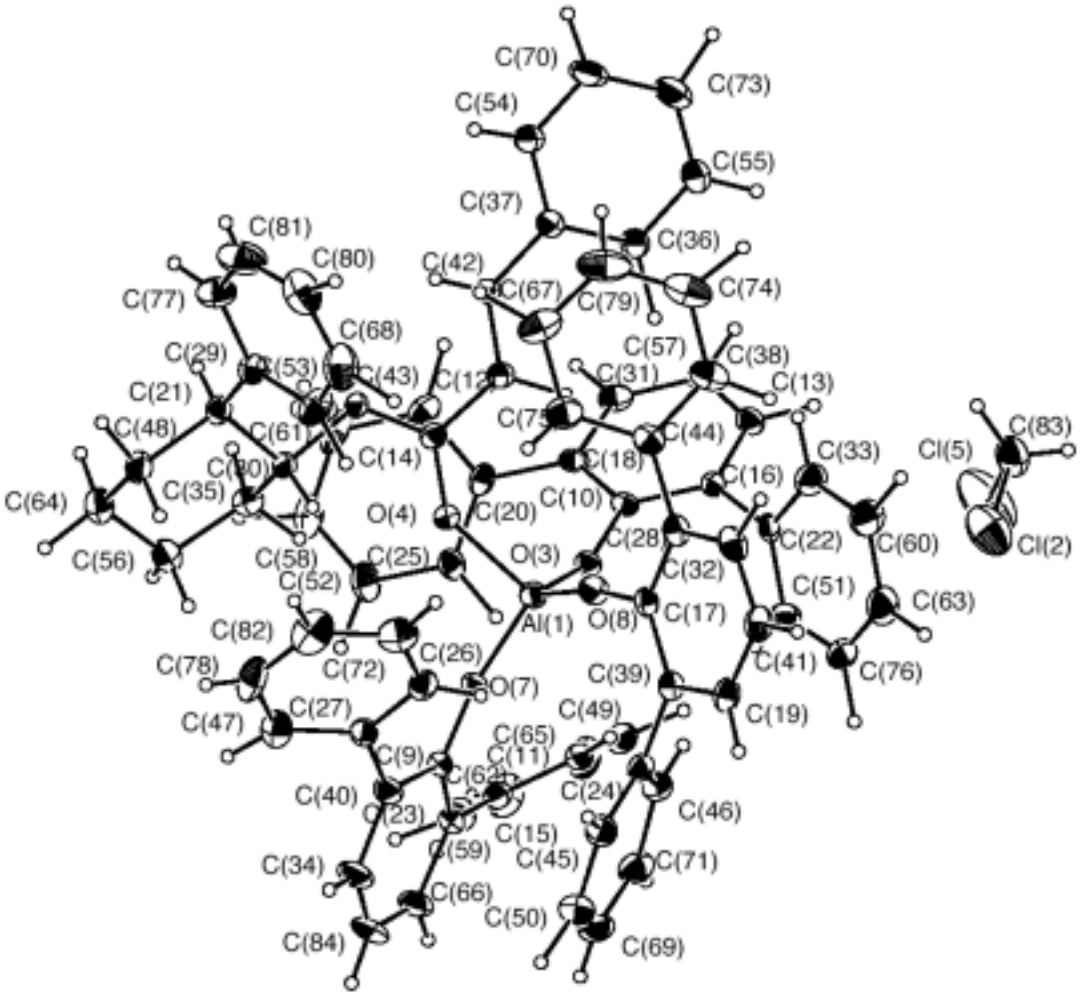
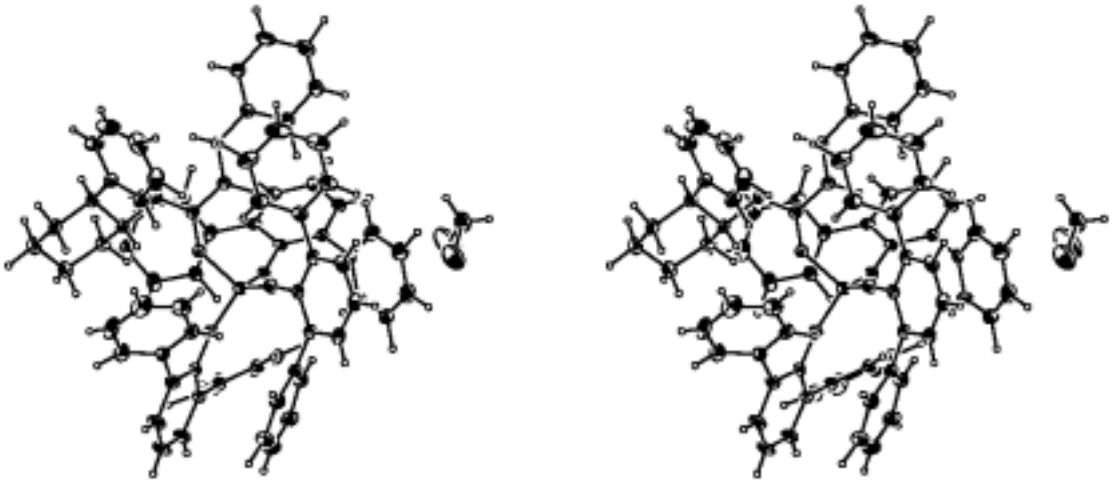


Figure. ORTEP representation of ATPH-**1** Complex **2**.



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