Catalytic Asymmetric Allylation of Prochiral Nucleophiles, α-Acetamido-β-ketoesters

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Supporting Information

General and Materials. Specific rotations were measured with a JASCO P-1020 polarimeter. NMR spectra were obtained with a Varian GEMINI-2000 spectrometer. Toluene and THF were distilled from Na–benzophenone ketyl under nitrogen. α-Acetamido-β-ketoesters **1**[1] and $[Pd(\pi\text{-allyl})Cl]_2$[2] were prepared according to the literature procedures. Other materials were purchased and used without further purification.

General Procedure of Asymmetric Allylation of 1. A mixture of $[Pd(\pi\text{-allyl})Cl]_2$ (0.9 mg, 2.5 μmol) and (*R*)-BINAP (3.3 mg, 5.3 μmol) in toluene (0.5 ml) was stirred for 10 min at room temperature. Allyl acetate **2** (0.75 mmol) was added to the solution. After 10 min, the solution was added to a suspension of **1** (0.50 mmol) and *t*-BuOK (67.3 mg, 0.60 mmol) in toluene (2.0 ml) at –30 °C. The reaction was monitored by TLC. After complete consumption of **1**, the reaction was quenched by 1 N HCl aq (3.0 ml). The mixture was extracted three times with EtOAc. The organic layer was washed with brine, dried with Na_2SO_4, and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc), giving **3**.

Methyl 2-(*N*-Acetylamino)-3-oxo-2-(2-propenyl)pentanoate (3a). The enantiomeric excess was determined to be 72% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OD-H (hexane/2-propanol = 96/4): White solid; $[\alpha]^{20}_D$ = +6.3 (*c* 1.07, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.06 (t, *J* = 7.3 Hz, 3H), 2.05 (s, 3H), 2.49 (q, *J* = 7.3 Hz, 2H), 3.03 (dd, *J* = 7.7, 14.6 Hz, 1H), 3.19 (dd, *J* = 7.1, 14.6 Hz, 1H), 3.77 (s, 3H), 5.05–5.15 (m, 2H), 5.40–5.55 (m, 1H), 6.94 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.7, 22.9, 30.1, 36.4, 53.4, 71.3, 119.9, 131.1, 169.0, 169.2, 202.3; Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16. Found: C, 57.99; H, 7.33; N, 6.14.

Methyl (*R*)-2-(*N*-Acetylamino)-3-oxo-2-(2-propenyl)butanoate (3b). The enantiomeric excess was determined to be 76% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OD-H (hexane/2-propanol = 96/4): White solid; $[\alpha]^{20}_D$ = +9.7 (*c* 1.01, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.05 (s, 3H), 2.18 (s, 3H), 3.01 (dd, *J* = 7.7, 14.7 Hz, 1H), 3.19 (dd, *J* = 6.8, 14.7 Hz, 1H), 3.78 (s, 3H), 5.09 (s, 1H), 5.09–5.17 (m, 1H), 5.41–5.57 (m, 1H), 6.92 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9,

24.4, 36.2, 53.4, 71.7, 119.9, 131.0, 168.8, 169.2, 199.2; Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33; H, 7.09; N, 6.57. Found: C, 56.06; H, 6.99; N, 6.59.

Methyl 2-(*N*-Acetylamino)-3-oxo-3-phenyl-2-(2-propenyl)propionate (3c). The enantiomeric excess was determined to be 80% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OB-H (hexane/2-propanol = 8/2): White solid; $[\alpha]^{20}_D$ = –11.2 (*c* 1.09, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.91 (s, 3H), 3.15–3.30 (m, 2H), 3.78 (s, 3H), 5.02–5.16 (m, 2H), 5.58 (ddt, *J* = 10.2, 16.8, 7.5 Hz, 1H), 7.10 (br s, 1H), 7.36–7.44 (m, 2H), 7.48–7.56 (m, 1H), 7.84–7.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8, 37.8, 53.6, 69.8, 120.2, 128.3, 128.5, 131.3, 133.0, 134.9, 168.6, 170.1, 191.3; Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.51; H, 6.23; N, 4.89.

Methyl (*R*)-2-(*N*-Acetylamino)-2-{(*E*)-2-hexenyl}-3-oxobutanoate (3d). The enantiomeric excess was determined to be 87% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OD-H (hexane/2-propanol = 96/4): White solid; $[\alpha]^{20}_D$ = +5.4 (*c* 1.30, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 0.85 (t, *J* = 7.3 Hz, 3H), 1.33 (sextet, *J* = 7.3 Hz, 2H), 1.93 (q, *J* = 6.9 Hz, 2H), 2.04 (s, 3H), 2.17 (s, 3H), 2.95 (dd, *J* = 7.8, 14.6 Hz, 1H), 3.12 (dd, *J* = 7.1, 14.6 Hz, 1H), 3.77 (s, 3H), 5.00–5.14 (m, 1H), 5.51 (dt, *J* = 14.9, 6.9 Hz, 1H), 6.89 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 22.3, 22.9, 24.4, 34.5, 35.1, 53.3, 72.0, 122.2, 136.3, 168.9, 169.1, 199.4; Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.16; H, 8.29; N, 5.49. Found: C, 61.13; H, 8.23; N, 5.26.

Methyl 2-(*N*-Acetylamino)-2-{(*E*)-2-hexenyl}-3-oxo-3-phenylpropionate (3e). The enantiomeric excess was determined to be 89% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OF (hexane/2-propanol = 8/2): White solid; $[\alpha]^{20}_D$ = +10.8 (*c* 1.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 0.86 (t, *J* = 7.3 Hz, 3H), 1.32 (sextet, *J* = 7.3 Hz, 2H), 1.91 (s, 3H), 1.94 (q, *J* = 6.9 Hz, 2H), 3.14 (dd, *J* = 7.5, 14.6 Hz, 1H), 3.17 (dd, *J* = 7.5, 14.6 Hz, 1H), 3.76 (s, 3H), 5.16 (dtt, *J* = 15.3, 1.5, 7.5 Hz, 1H), 5.45 (dt, *J* = 15.3, 6.9 Hz, 1H), 7.09 (br s, 1H), 7.36–7.43 (m, 2H), 7.48–7.55 (m, 1H), 7.84–7.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 22.4, 22.8, 34.6, 36.6, 53.5, 70.1, 122.3, 128.4, 128.5, 133.0, 135.0, 136.5, 168.5, 170.2, 191.6; HRMS (FAB) Calcd for $C_{18}H_{24}NO_4$: 318.1705. Found: 318.1702 (M + H^+).

Methyl 2-(*N*-Acetylamino)-3-oxo-2-{(*E*)-3-phenyl-2-propenyl}pentanoate (3f). The enantiomeric excess was determined to be 91% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OD-H (hexane/2-propanol = 9/1): White solid; $[\alpha]^{20}_D$ = –11.4 (*c* 1.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.08 (t, *J* = 7.1 Hz, 3H), 2.05 (s, 3H), 2.53 (q, *J* = 7.1 Hz, 2H), 3.19 (ddd, *J* = 1.2, 7.8, 14.7 Hz, 1H), 3.35 (ddd, *J* = 1.2, 7.4, 14.7 Hz, 1H), 3.79 (s, 3H), 5.82 (dt, *J* = 15.6, 7.8 Hz, 1H), 6.43 (dt, *J* = 15.6, 1.2 Hz, 1H), 6.97 (br s, 1H), 7.19–7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.8, 23.0, 30.2, 35.7, 53.4, 71.6, 122.4, 126.3, 127.7, 128.6, 134.8,

136.8, 169.0, 169.3, 202.4; Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.30; H, 7.13; N, 4.59.

Methyl (*R*)-2-(*N*-Acetylamino)-3-oxo-2-{(*E*)-3-phenyl-2-propenyl}butanoate (3g). The enantiomeric excess was determined to be 94% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OD-H (hexane/2-propanol = 85/15): White solid; $[\alpha]^{20}_D = -11.7$ (*c* 1.56, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.06 (s, 3H), 2.22 (s, 3H), 3.18 (ddd, *J* = 1.2, 7.8, 14.7 Hz, 1H), 3.34 (ddd, *J* = 1.2, 7.5, 14.7 Hz, 1H), 3.80 (s, 3H), 5.84 (dt, *J* = 15.6, 7.5 Hz, 1H), 6.45 (dt, *J* = 15.6, 1.2 Hz, 1H), 6.94 (br s, 1H), 7.19–7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 24.4, 35.5, 53.5, 71.9, 122.2, 126.3, 127.7, 128.6, 134.9, 136.8, 168.8, 169.3, 199.2; Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.15; H, 6.64; N, 4.90.

Methyl 2-(*N*-Acetylamino)-3-oxo-3-phenyl-2-{(*E*)-3-phenyl-2-propenyl}propionate (3h). The enantiomeric excess was determined to be 95% ee by HPLC analysis with a chiral stationary phase column, SUMICHIRAL OA-2000 (hexane/1,2-dichloroethane/ethanol = 100/20/1): White solid; $[\alpha]^{20}_D = +67.1$ (*c* 1.18, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.91 (s, 3H), 3.36 (ddd, *J* = 1.4, 7.6, 14.4 Hz, 1H), 3.40 (ddd, *J* = 1.3, 7.6, 14.4 Hz, 1H), 3.79 (s, 3H), 5.93 (dt, *J* = 15.6, 7.6 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 7.13 (br s, 1H), 7.19–7.34 (m, 5H), 7.38–7.45 (m, 2H), 7.49–7.57 (m, 1H), 7.86–7.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 37.2, 53.7, 70.1, 122.6, 126.3, 127.6, 128.4, 128.6, 133.1, 134.9, 135.1, 137.0, 168.8, 170.1, 191.4; Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.76; H, 6.01; N, 3.92.

Methyl 2-(*N*-Acetylamino)-5-methyl-3-oxo-2-{(*E*)-3-phenyl-2-propenyl}hexanoate (3i). The enantiomeric excess was determined to be 92% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OD-H (hexane/2-propanol = 9/1): White solid; $[\alpha]^{20}_D = +1.7$ (*c* 1.19, EtOH); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 0.87 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 2.05 (s, 3H), 2.20 (nonet, *J* = 6.6 Hz, 1H), 2.36 (dd, *J* = 6.6, 17.1 Hz, 1H), 2.41 (dd, *J* = 6.6, 17.1 Hz, 1H), 3.17 (ddd, *J* = 1.2, 7.8, 14.9 Hz, 1H), 3.37 (ddd, *J* = 1.5, 7.2, 14.9 Hz, 1H), 3.78 (s, 3H), 5.81 (dt, *J* = 15.6, 7.5 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.98 (br s, 1H), 7.19–7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 22.3, 23.0, 24.0, 35.3, 45.5, 53.3, 72.1, 122.3, 126.3, 127.7, 128.6, 134.8, 136.8, 168.8, 169.3, 200.9; Anal. Calcd for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60; N, 4.23. Found: C, 68.80; H, 7.64; N, 4.19.

Methyl 2-(*N*-Acetylamino)-4-methyl-3-oxo-2-{(*E*)-3-phenyl-2-propenyl}pentanoate (3j). The enantiomeric excess was determined to be 91% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OF (hexane/2-propanol = 7/3): White solid; $[\alpha]^{20}_D = -9.1$ (*c* 1.06, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.04 (d, *J* = 6.7 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 3H), 2.05 (s, 3H), 3.08 (septet, *J* = 6.7 Hz, 1H), 3.20 (ddd, *J* = 1.3, 7.7, 14.9 Hz, 1H), 3.40 (ddd, *J* = 1.4, 7.7, 14.9 Hz, 1H), 3.79 (s, 3H),

5.78 (dt, J = 15.6, 7.7 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 7.00 (br s, 1H), 7.19–7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5, 20.0, 23.0, 34.8, 35.4, 53.2, 71.5, 122.4, 126.3, 127.7, 128.6, 134.9, 136.8, 168.9, 169.2, 206.5; Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.30; N, 4.41. Found: C, 67.98; H, 7.38; N, 4.36.

Conversion 3g into Methyl (2*R*,3*S*)-2-(*N*-Acetylamino)-3-hydroxy-2-{(*E*)-3-phenyl-2-propenyl}butanoate (5g). To a solution of **3g** (58.0 mg, 0.20 mmol) in THF (1.0 ml) was added 0.3 ml (0.3 mmol) of L-Selecride® (1.0 M solution in THF) at –78 °C. The solution was stirred for 2 h at –78 °C. After water (0.1 ml), EtOH (0.1 ml), 15% NaOH aq (0.1 ml), and 30% H_2O_2 aq (0.1 ml) were added, the mixture was stirred for 10 min at room temperature. After excess of H_2O_2 was carefully decomposed with saturated $Na_2S_2O_3$ aq, the mixture was diluted with water, and extracted three times with EtOAc. The organic layer was washed with brine, dried with Na_2SO_4, and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc), giving **5g** (55.8 mg, 96%): Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.22 (d, J = 6.6 Hz, 3H), 2.06 (s, 3H), 2.80 (dd, J = 9.2, 14.1 Hz, 1H), 2.95 (ddd, J = 1.5, 5.7, 14.1 Hz, 1H), 3.84 (s, 3H), 4.21 (dq, J = 9.9, 6.6 Hz, 1H), 4.71 (d, J = 9.9 Hz, 1H), 5.94 (ddd, J = 5.7, 9.2, 15.9 Hz, 1H), 5.98 (br s, 1H), 6.54 (d, J = 15.9 Hz, 1H), 7.23–7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.3, 23.8, 37.5, 52.9, 69.3, 71.2, 122.9, 126.4, 128.0, 128.7, 135.5, 136.4, 171.6, 172.0; HRMS (FAB) Calcd for $C_{16}H_{22}NO_4$: 292.1548. Found: 292.1556 (M + H$^+$).

Methyl (2*R*,3*S*)-2-(*N*-Acetylamino)-3-hydroxy-2-(2-propenyl)butanoate (5b) was obtained from **3b** in 83 % yield: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.19 (d, J = 6.6 Hz, 3H), 2.08 (s, 3H), 2.58 (dd, J = 9.0, 13.8 Hz, 1H), 2.80 (ddt, J = 5.6, 13.8, 1.5 Hz, 1H), 3.80 (s, 3H), 4.15 (q, J = 6.6 Hz, 1H), 4.87 (br s, 1H), 5.17–5.28 (m, 2H), 5.53–5.68 (m, 1H), 5.94 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.2, 23.6, 38.5, 52.7, 68.9, 71.2, 120.8, 132.1, 171.6, 171.8; HRMS (FAB) Calcd for $C_{10}H_{18}NO_4$: 216.1236. Found: 216.1239 (M + H$^+$).

Relative configuration between 2- and 3-position was determined to be (2*R**,3*S**) by X-ray crystal structure analysis of racemic **5b** obtained from racemic **3b** in similar manner.

X-ray Crystal Structure Analysis of Racemic 5b. Suitable crystals for a diffraction study were grown by the slow diffusion of hexane into a EtOAc solution of racemic **5b** at room temperature. The data were collected at 20 °C on a Mac Science MXC3 diffractometer with graphite monochromated Cu Kα radiation. The cell constants and orientation matrix for data collection were obtained from a least-square refinement using the setting angles of 22 carefully centered reflections in the range of $47.40 < 2\theta < 59.34°$. The intensities of three standard reflections monitored every 150 reflections showed no serious decay. An empirical absorption correction based on azimuthal scans of a reflection was

applied. All data were corrected for Lorentz and polarization effects. A summary of the cell parameters, data collection conditions, and refinement results are given in Table S-1.

The structure was solved by direct methods (SIR-92).[3] All non-hydrogen atoms were refined anisotropically by a full-matrix least-squares method on |*F*|. Hydrogen atoms were located at calculated positions (d(C–H) = 0.96 Å), and their isotropic temperature factors U_{iso} were set 0.05. Though all hydrogen atoms were included in the calculations, their positions were not refined except for hydrogen atoms on nitrogen and oxygen atoms; the isotropic U values were refined. All of the calculations were performed using the program package Crystan 6.3.3.

Methyl (2*R*,3*S*)-2-(*N*-Acetylamino)-3-hydroxy-2-{(*E*)-2-hexenyl}butanoate (5d) was obtained from **3d** in 75 % yield: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.90 (t, J = 7.5 Hz, 3H), 1.18 (d, J = 6.6 Hz, 3H), 1.39 (sextet, J = 7.5 Hz, 2H), 2.02 (q, J = 7.5 Hz, 2H), 2.08 (s, 3H), 2.40 (dd, J = 9.6, 14.1 Hz, 1H), 2.72 (ddd, J = 1.1, 5.3, 14.1 Hz, 1H), 3.80 (s, 3H), 4.10 (q, J = 6.6 Hz, 1H), 5.11–5.24 (m, 1H), 5.24 (br s, 1H), 5.63 (dt, J = 6.9, 15.3 Hz, 1H), 5.89 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 18.1, 22.4, 23.6, 34.5, 38.1, 52.6, 69.2, 71.1, 123.1, 137.6, 171.8; HRMS (FAB) Calcd for $C_{13}H_{24}NO_4$: 258.1705. Found: 258.1696 (M + H$^+$).

General Procedure of Preparation of MTPA Esters of 5 and Assignment of their Absolute Configurations. DCC (12.4 mg, 60 μmol) was added to a solution of **5** (30 μmol), (*S*)- or (*R*)-MTPA (14.1 mg, 60 μmol), and DMAP (1 piece) in CH_2Cl_2 (0.2 ml). After stirring for 1 h, the mixture was diluted with 1 N HCl aq, filtered through Celite pad, and extracted with EtOAc. The organic layer was washed with brine, dried with Na_2SO_4, and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc), giving the corresponding MTPA ester.

The absolute configurations of **5** were assigned by comparison between ^{1}H NMR spectra of the (*S*)- and (*R*)-MTPA esters according to Kakisawa's manner.[4] The results are summarized in Figure S-1, revealing the absolute configurations of **5** to be (2*R*,3*S*).

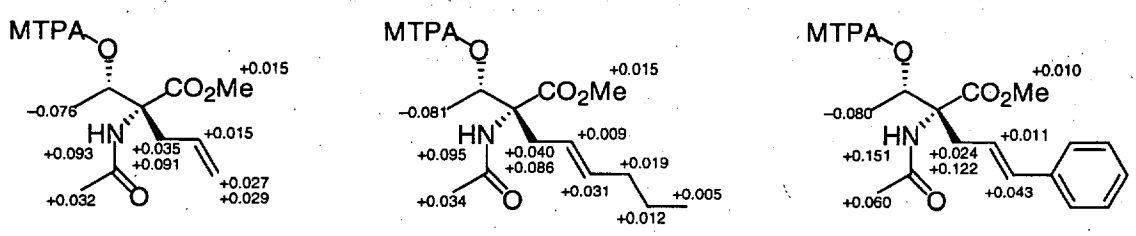

Figure S-1. List of Δδ values of MTPA esters of **5b**, **5d**, and **5g**. $\Delta\delta = \delta_S - \delta_R$.

Conversion of 3g into 6. RuO_2 (1.3 mg, 10 μmol) was added to a two-phase solution of **3g** (145 mg, 0.50 mmol) and $NaIO_4$ (439 mg, 2.05 mmol) in CCl_4 (1.0 ml), MeCN (1.0 ml) and water (1.5 ml). The mixture was vigorously stirred for 2 h at room

temperature, diluted with water and 1 ml of 1 N HCl aq, extracted five times with EtOAc. The organic layer was dried with $MgSO_4$, and evaporated under reduced pressure. To a suspension of the residue in Et_2O (2 ml) was carefully added diazomethane (ca. 0.7 M) in Et_2O until evolution of nitrogen ceased. After stirring for 5 min, the mixture was evaporated under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc), giving dimethyl (*R*)-2-acetyl-2-(*N*-acetylamino)succinate (**6**) (101 mg, 82%). The enantiomeric excess was determined to be 94% ee by HPLC analysis with a chiral stationary phase column, CHIRALCEL OF (hexane/2-propanol = 6/4): Colorless oil; $[\alpha]^{20}_D = -18.2$ (*c* 1.03, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.06 (s, 3H), 2.18 (s, 3H), 3.44 (d, *J* = 17.6 Hz, 1H), 3.64 (d, *J* = 17.6 Hz, 1 H), 3.66 (s, 3H), 3.79 (s, 3H), 7.16 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8, 23.8, 37.1, 51.9, 53.9, 69.8, 168.0, 169.7, 171.2, 197.8; Anal. Calcd for $C_{10}H_{15}NO_6$: C, 48.98; H, 6.17; N, 5.71. Found: C, 49.01; H, 6.21; N, 5.79.

[Pd(π-allyl){(*R*)-BINAP)}]ClO$_4$. A mixture of [Pd(π-allyl)Cl]$_2$ (18.3 mg, 50 μmol) and (*R*)-BINAP (62.3 mg, 100 μmol) in MeOH (2.0 ml) was stirred at room temperature. The solids dissolved after 10 min and gave yellow solution. After 2 h, $LiClO_4 \cdot 3H_2O$ in MeOH (2.0 ml) was added to the mixture. White precipitates generated immediately. After stirring for 2 h, water was added to the suspension. [Pd(π-allyl){(*R*)-BINAP)}]ClO_4 (84.5 mg, 97%) was obtained by filtration, washed with water and dried in vacuo. Analytical pure sample was obtained by recrystallization from acetone/MeOH giving colorless crystal as acetone adduct; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 3.11 (pseudo t, 1H), 3.93–4.15 (m, 3H), 5.86–6.04 (m, 1H), 6.53–7.70 (m, 32H); ^{31}P NMR (121.5 MHz, CDCl3, 85% H_3PO_4) δ 22.1 (d, *J* = 50 Hz), 23.5 (d, *J* = 50 Hz); Anal. Calcd for $C_{47}H_{37}O_4ClP_2Pd \cdot C_3H_6O$: C, 64.73; H, 4.67. Found: C, 64.31; H, 4.71.

X-ray Crystal Structure Analysis of [Pd(π-allyl){(*R*)-BINAP}]ClO$_4$·(CH$_3$COCH$_3$). Suitable crystals for a diffraction study were grown by the slow diffusion of methanol into a acetone solution of [Pd(π-allyl){(*R*)-BINAP}]ClO_4 at room temperature. The data were collected at 20 °C on a Mac Science MXC3 diffractometer with graphite monochromated Cu Kα radiation. The cell constants and orientation matrix for data collection were obtained from a least-square refinement using the setting angles of 22 carefully centered reflections in the range of $56.20 < 2\theta < 59.31°$. The intensities of three standard reflections monitored every 250 reflections showed no serious decay. An empirical absorption correction based on azimuthal scans of a reflection was applied. All data were corrected for Lorentz and polarization effects. A summary of the cell parameters, data collection conditions, and refinement results are given in Table S-1.

The structure was solved by direct methods (SIR-92),[3] and expanded using a Fourier technique (DIRDIF).[5] All non-hydrogen atoms were refined anisotropically by a full-matrix least-squares method on |*F*|. Hydrogen atoms were located at calculated positions (*d*(C–H) =

0.96 Å), and their isotropic temperature factors U_{iso} were set equal to 0.02 + U_{iso} of the carbon atoms to which they are attached. Though all hydrogen atoms were included in the calculations, their positions were not refined; the isotropic U values were refined except for hydrogen atoms in the allyl ligand and the acetone molecule. All of the calculations were performed using the program package Crystan 6.3.3.

References

(1) Genet, J. P.; Pinel, C.; Mallart, S.; Juge, S.; Thorimbert, S.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1991**, *2*, 555.

(2) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorganic Synthesis* **1979**, *19*, 220.

(3) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Cryst.* **1994**, *27*, 435.

(4) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092.

(5) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system, Technical Report of the Crystallography Laboratory*; University of Nijmegen: The Netherlands, 1992.

Table S-1. Summary of crystal data and detail of data collection and refinement parameters for **5b** and [Pd(π-allyl){(*R*)-BINAP}]ClO_4·(CH_3COCH_3).

Compound	**5b** (racemic)	[Pd(π-allyl){(*R*)-BINAP}]ClO_4
Formula	$C_{10}H_{17}NO_4$	$C_{47}H_{37}O_4ClP_2Pd·C_3H_6O$
M	215.25	927.69
Crystal System	orthorhombic	orthorhombic
Space Group	*Pbca*	$P2_12_12_1$
a (Å)	13.298(2)	18.447(4)
b (Å)	20.659(5)	20.194(4)
c (Å)	8.599(2)	11.571(3)
α (deg)	90.00	90.00
β (deg)	90.00	90.00
γ (deg)	90.00	90.00
V (Å^3)	2362.4(8)	4310.2(17)
Z	8	4
D (calcd) (g/cm^3)	1.21	1.419
Crystal Size (mm)	0.15 × 0.15 × 0.15	0.25 × 0.30 × 0.45
μ (CuKα) (mm^{-1})	7.42	52.24
Radiation	CuKα (λ=1.54178 Å)	CuKα (λ=1.54178 Å)
Scan Type	$\theta/2\theta$	$\theta/2\theta$
Scan Rate (deg/min)	6.0	6.0
Scan Width (deg)	1.20 + 0.20 tan θ	1.28 + 0.20 tan θ
$2\theta_{max}$ (deg)	130	130
No. of Measd Reflns	2337	4087
Obsd Reflns	1220 ($I > 3.00\sigma(I)$)	3513 ($I > 3.00\sigma(I)$)
No. of Variables	160	565
R	0.053	0.039
R_w	0.060	0.051
GOF	1.47	1.26
Max Shift/Error in Final Cycle	0.05	0.03
Max Peak in Diff Fourier Map (*e*/Å^3)	0.54	0.68
Min Peak in Diff Fourier Map (*e*/Å^3)	–0.26	–0.56

Table S-2. Fractional Atomic Coordinates and U_{iso} (Å^2) of Racemic **5b**.

atom	x	y	z	Uiso
O(1)	-0.79844(15)	-0.15138(9)	-0.48531(25)	0.057(1)
O(2)	-0.85989(18)	-0.22149(10)	-0.31109(31)	0.075(2)
O(3)	-1.07166(15)	-0.05690(9)	-0.46033(25)	0.047(1)
O(4)	-0.75083(14)	-0.08882(9)	-0.18154(24)	0.055(1)
N(1)	-0.88456(16)	-0.05304(11)	-0.31844(29)	0.039(1)
C(1)	-0.7257(3)	-0.1996(2)	-0.5341(6)	0.085(3)
C(2)	-0.8594(2)	-0.1688(1)	-0.3703(4)	0.049(2)
C(3)	-0.93475(18)	-0.11533(12)	-0.33342(32)	0.038(1)
C(4)	-1.00368(19)	-0.10884(13)	-0.47973(32)	0.042(2)
C(5)	-1.0576(3)	-0.1707(2)	-0.5241(5)	0.067(2)
C(6)	-0.7964(2)	-0.0442(1)	-0.2443(3)	0.043(2)
C(7)	-0.7569(3)	0.0240(2)	-0.2443(5)	0.067(2)
C(8)	-0.9980(3)	-0.1318(2)	-0.1890(4)	0.059(2)
C(9)	-0.9514(4)	-0.1293(3)	-0.0384(6)	0.122(4)
C(10)	-0.9784(5)	-0.0921(4)	0.0764(6)	0.159(5)
H(1)	-0.9101(19)	-0.0196(12)	-0.3687(32)	0.040(8)
H(1A)	-0.682(3)	-0.187(1)	-0.618(4)	0.17(2)
H(1B)	-0.68430	-0.21053	-0.44653	0.16(2)
H(1C)	-0.76200	-0.23753	-0.56673	0.11(1)
H(3)	-1.123(2)	-0.071(1)	-0.418(3)	0.05(1)
H(4)	-0.96248	-0.10084	-0.56933	0.045(8)
H(5A)	-1.01132	-0.20594	-0.53783	0.09(1)
H(5B)	-1.10452	-0.18174	-0.44353	0.11(2)
H(5C)	-1.09372	-0.16404	-0.61943	0.07(1)
H(7A)	-0.79190	0.05889	-0.29409	0.12(2)
H(7B)	-0.74960	0.03609	-0.13709	0.15(2)
H(7C)	-0.69150	0.02219	-0.29159	0.20(3)
H(8A)	-1.05345	-0.10202	-0.18584	0.12(2)
H(8B)	-1.02355	-0.17482	-0.20374	0.09(1)
H(9)	-0.89522	-0.15757	-0.02135	0.2(2)
H(10A)	-0.94354	-0.09344	0.17418	0.27(4)
H(10B)	-1.03404	-0.06324	0.06228	0.34(6)

Table S-3. Anisotropic Thermal Parameters of Racemic **5b**.

atom	U11	U22	U33	U12	U13	U23
O(1)	0.046(1)	0.056(1)	0.071(1)	0.011(1)	0.007(1)	-0.010(1)
O(2)	0.079(2)	0.047(1)	0.100(2)	0.006(1)	-0.015(2)	0.018(1)
O(3)	0.029(1)	0.049(1)	0.062(1)	-0.001(1)	-0.001(1)	0.010(1)
O(4)	0.038(1)	0.059(1)	0.068(1)	0.000(1)	-0.017(1)	0.004(1)
N(1)	0.031(1)	0.039(1)	0.046(1)	-0.001(1)	-0.005(1)	0.003(1)
C(1)	0.057(2)	0.080(3)	0.119(4)	0.021(2)	0.003(3)	-0.040(3)
C(2)	0.042(2)	0.043(2)	0.062(2)	-0.002(1)	-0.014(2)	0.001(2)
C(3)	0.031(1)	0.042(1)	0.040(2)	-0.003(1)	-0.001(1)	0.001(1)
C(4)	0.031(1)	0.051(2)	0.044(2)	-0.004(1)	-0.001(1)	0.002(1)
C(5)	0.062(2)	0.064(2)	0.075(3)	-0.008(2)	-0.023(2)	-0.008(2)
C(6)	0.031(1)	0.050(2)	0.046(2)	-0.003(1)	-0.001(1)	-0.004(1)
C(7)	0.062(2)	0.053(2)	0.086(3)	-0.015(2)	-0.018(2)	0.000(2)
C(8)	0.060(2)	0.070(2)	0.048(2)	-0.015(2)	0.001(2)	0.012(2)
C(9)	0.093(3)	0.204(6)	0.070(3)	-0.070(4)	0.001(3)	0.028(4)
C(10)	0.130(5)	0.291(9)	0.055(3)	-0.099(5)	0.032(3)	-0.053(4)

Table S-4. Intramolecular Bond Lengths (Å) of Racemic **5b**.

atom - atom	distance	atom - atom	distance
O(1) - C(1)	1.451(5)	O(1) - C(2)	1.329(4)
O(2) - C(2)	1.201(4)	O(3) - C(4)	1.413(4)
O(4) - C(6)	1.229(4)	N(1) - C(3)	1.455(4)
N(1) - C(6)	1.346(4)	C(2) - C(3)	1.525(4)
C(3) - C(4)	1.562(4)	C(3) - C(8)	1.539(5)
C(4) - C(5)	1.515(5)	C(6) - C(7)	1.503(5)
C(8) - C(9)	1.437(6)	C(9) - C(10)	1.300(9)
O(3) - H(3)	0.83(3)	N(1) - H(1)	0.88(3)
C(1) - H(1A)	0.96(4)	C(1) - H(1B)	0.960(5)
C(1) - H(1C)	0.961(5)	C(4) - H(4)	0.960(3)
C(5) - H(5A)	0.960(4)	C(5) - H(5B)	0.960(4)
C(5) - H(5C)	0.960(4)	C(7) - H(7A)	0.959(4)
C(7) - H(7B)	0.960(5)	C(7) - H(7C)	0.961(4)
C(8) - H(8A)	0.961(4)	C(8) - H(8B)	0.959(4)
C(9) - H(9)	0.960(6)	C(10) - H(10A)	0.961(6)
C(10) - H(10B)	0.958(8)		

Table S-5. Intramolecular Bond Angles (°) of Racemic **5b**.

atom - atom - atom	angle	atom - atom - atom	angle
C(1) - O(1) - C(2)	115.8(3)	C(3) - N(1) - C(6)	124.1(3)
O(1) - C(2) - O(2)	124.3(3)	O(1) - C(2) - C(3)	111.0(3)
O(2) - C(2) - C(3)	124.4(3)	N(1) - C(3) - C(2)	111.0(3)
N(1) - C(3) - C(4)	105.3(3)	N(1) - C(3) - C(8)	112.1(3)
C(2) - C(3) - C(4)	106.3(3)	C(2) - C(3) - C(8)	111.5(3)
C(4) - C(3) - C(8)	110.4(3)	O(3) - C(4) - C(3)	110.2(3)
O(3) - C(4) - C(5)	111.6(3)	C(3) - C(4) - C(5)	114.1(3)
O(4) - C(6) - N(1)	122.4(3)	O(4) - C(6) - C(7)	122.1(3)
N(1) - C(6) - C(7)	115.5(3)	C(3) - C(8) - C(9)	118.9(4)
C(8) - C(9) - C(10)	125.9(6)	C(4) - O(3) - H(3)	108.0(20)
C(3) - N(1) - H(1)	118.2(17)	C(6) - N(1) - H(1)	117.4(17)
O(1) - C(1) - H(1A)	115.5(19)	O(1) - C(1) - H(1B)	108.5(5)
O(1) - C(1) - H(1C)	108.0(4)	H(1A) - C(1) - H(1B)	107.9(20)
H(1A) - C(1) - H(1C)	107.9(20)	H(1B) - C(1) - H(1C)	109.0(5)
O(3) - C(4) - H(4)	109.2(3)	C(3) - C(4) - H(4)	109.1(3)
C(5) - C(4) - H(4)	102.3(3)	C(4) - C(5) - H(5A)	111.5(4)
C(4) - C(5) - H(5B)	109.0(4)	C(4) - C(5) - H(5C)	109.2(3)
H(5A) - C(5) - H(5B)	109.0(4)	H(5A) - C(5) - H(5C)	109.0(4)
H(5B) - C(5) - H(5C)	109.0(4)	C(6) - C(7) - H(7A)	122.3(4)
C(6) - C(7) - H(7B)	106.2(4)	C(6) - C(7) - H(7C)	106.3(3)
H(7A) - C(7) - H(7B)	106.4(4)	H(7A) - C(7) - H(7C)	106.2(4)
H(7B) - C(7) - H(7C)	109.0(4)	C(3) - C(8) - H(8A)	107.5(3)
C(3) - C(8) - H(8B)	107.0(3)	C(9) - C(8) - H(8A)	106.4(4)
C(9) - C(8) - H(8B)	107.7(4)	H(8A) - C(8) - H(8B)	109.1(4)
C(8) - C(9) - H(9)	116.8(5)	C(10) - C(9) - H(9)	117.3(6)
C(9) - C(10) - H(10A)	120.9(8)	C(9) - C(10) - H(10B)	119.0(6)
H(10A) - C(10) - H(10B)	120.1(8)		

Table S-6. Fractional Atomic Coordinates and U_{iso} (Å^2) of [Pd(π-allyl){(*R*)-BINAP}]ClO_4.

atom	x	y	z	Uiso
Pd(1)	0.36601(4)	0.22012(4)	-0.14159(6)	0.0355(4)
Cl(1)	0.5583(3)	0.1826(3)	-0.4328(4)	0.080(3)
P(1)	0.43463(14)	0.19969(12)	0.02219(24)	0.032(1)
P(2)	0.35581(14)	0.33313(13)	-0.11119(21)	0.033(1)
O(1)	0.5940(11)	0.1248(10)	-0.4092(22)	0.15(2)
O(2)	0.4938(11)	0.1921(16)	-0.3704(18)	0.21(2)
O(3)	0.5436(15)	0.1895(22)	-0.5372(17)	0.32(4)
O(4)	0.6029(17)	0.2236(13)	-0.4012(52)	0.38(4)
O(5)	0.6921(12)	0.4712(12)	-0.4473(16)	0.16(2)
C(1)	0.3577(10)	0.1183(7)	-0.2006(15)	0.069(9)
C(2)	0.3055(14)	0.1562(10)	-0.2536(19)	0.10(1)
C(3)	0.3146(9)	0.2108(8)	-0.3134(13)	0.070(9)
C(4)	0.4984(5)	0.2673(5)	0.0533(8)	0.031(4)
C(5)	0.5715(6)	0.2589(6)	0.0274(11)	0.045(6)
C(6)	0.6191(6)	0.3102(7)	0.0327(13)	0.052(6)
C(7)	0.5960(6)	0.3753(6)	0.0642(10)	0.044(6)
C(8)	0.6443(8)	0.4290(7)	0.0650(12)	0.059(8)
C(9)	0.6188(8)	0.4914(7)	0.0942(13)	0.059(7)
C(10)	0.5470(8)	0.5004(6)	0.1234(12)	0.053(7)
C(11)	0.5008(7)	0.4489(6)	0.1283(11)	0.047(6)
C(12)	0.5228(6)	0.3841(5)	0.0962(9)	0.034(5)
C(13)	0.4739(6)	0.3293(5)	0.0882(9)	0.032(5)
C(14)	0.3958(5)	0.3411(5)	0.1237(9)	0.033(5)
C(15)	0.3804(6)	0.3451(5)	0.2448(10)	0.037(5)
C(16)	0.4346(7)	0.3385(6)	0.3304(10)	0.045(6)
C(17)	0.4169(9)	0.3396(7)	0.4482(11)	0.059(8)
C(18)	0.3453(9)	0.3489(7)	0.4811(11)	0.060(8)
C(19)	0.2924(9)	0.3560(7)	0.4020(13)	0.059(8)
C(20)	0.3070(7)	0.3529(6)	0.2819(11)	0.045(6)
C(21)	0.2532(8)	0.3590(7)	0.1985(13)	0.055(7)
C(22)	0.2688(6)	0.3586(6)	0.0825(11)	0.042(6)
C(23)	0.3410(6)	0.3488(5)	0.0440(9)	0.034(5)
C(24)	0.4923(6)	0.1267(5)	0.0035(10)	0.039(5)
C(25)	0.4990(9)	0.0783(7)	0.0873(13)	0.061(8)
C(26)	0.5445(11)	0.0249(7)	0.0674(16)	0.08(1)
C(27)	0.5824(9)	0.0197(7)	-0.0364(17)	0.072(9)
C(28)	0.5747(7)	0.0658(6)	-0.1176(12)	0.053(7)
C(29)	0.5301(7)	0.1211(6)	-0.0985(11)	0.044(6)
C(30)	0.3817(6)	0.1866(5)	0.1506(11)	0.037(5)
C(31)	0.3069(7)	0.1819(7)	0.1415(15)	0.059(8)
C(32)	0.2644(9)	0.1764(10)	0.2347(18)	0.08(1)
C(33)	0.2958(10)	0.1726(8)	0.3469(15)	0.07(1)
C(34)	0.3687(9)	0.1762(7)	0.3587(12)	0.060(8)
C(35)	0.4123(6)	0.1837(5)	0.2587(11)	0.042(6)
C(36)	0.2788(6)	0.3705(6)	-0.1856(11)	0.044(6)
C(37)	0.2792(8)	0.4327(6)	-0.2364(14)	0.060(8)
C(38)	0.2207(10)	0.4546(8)	-0.2965(17)	0.08(1)
C(39)	0.1600(9)	0.4162(9)	-0.3113(15)	0.07(1)
C(40)	0.1576(9)	0.3555(9)	-0.2608(16)	0.073(9)
C(41)	0.2162(7)	0.3326(6)	-0.1995(13)	0.052(7)
C(42)	0.4343(6)	0.3792(6)	-0.1574(10)	0.040(6)
C(43)	0.4854(7)	0.3456(7)	-0.2262(12)	0.051(7)
C(44)	0.5465(8)	0.3790(9)	-0.2652(13)	0.065(8)
C(45)	0.5582(9)	0.4456(9)	-0.2349(15)	0.071(9)
C(46)	0.5083(8)	0.4781(7)	-0.1650(13)	0.060(8)
C(47)	0.4462(7)	0.4462(6)	-0.1300(11)	0.049(6)
C(48)	0.7142(19)	0.4986(15)	-0.6416(25)	0.14(2)
C(49)	0.6778(11)	0.4597(12)	-0.5437(16)	0.09(1)
C(50)	0.6289(15)	0.4036(17)	-0.5793(27)	0.14(2)

Table S-6. (Continued)

atom	x	y	z	Uiso
H(1A)	0.34554	0.07866	-0.15899	0.1(4)
H(1B)	0.40744	0.13196	-0.20639	0.1(5)
H(2)	0.25636	0.14092	-0.24666	0.1(13)
H(3A)	0.36273	0.22814	-0.32347	0.1(8)
H(3B)	0.27393	0.23364	-0.34647	0.09(6)
H(5)	0.58904	0.21597	0.00494	0.04(3)
H(6)	0.66923	0.30260	0.01477	0.12(8)
H(8)	0.69436	0.42236	0.04562	0.06(4)
H(9)	0.65103	0.52883	0.09302	0.05(4)
H(10)	0.52912	0.54393	0.14097	0.2(1)
H(11)	0.45195	0.45567	0.15464	0.06(4)
H(16)	0.48417	0.33214	0.30781	0.06(4)
H(17)	0.45417	0.33458	0.50533	0.04(3)
H(18)	0.33365	0.34988	0.56199	0.08(5)
H(19)	0.24352	0.36288	0.42750	0.07(5)
H(21)	0.20389	0.36470	0.22319	0.2(1)
H(22)	0.23071	0.36423	0.02687	0.03(3)
H(25)	0.47142	0.08089	0.15749	0.05(4)
H(26)	0.55044	-0.00845	0.12549	0.10(7)
H(27)	0.61447	-0.01711	-0.04875	0.08(5)
H(28)	0.60031	0.06125	-0.18944	0.07(5)
H(29)	0.52546	0.15484	-0.15651	0.06(4)
H(31)	0.28447	0.18334	0.06671	0.07(5)
H(32)	0.21261	0.17570	0.22666	0.04(3)
H(33)	0.26457	0.16781	0.41268	0.09(5)
H(34)	0.39057	0.17259	0.43373	0.08(5)
H(35)	0.46414	0.18621	0.26565	0.01(2)
H(37)	0.32204	0.45962	-0.23043	0.07(4)
H(38)	0.22144	0.49894	-0.32674	0.5(3)
H(39)	0.11979	0.43125	-0.35690	0.09(5)
H(40)	0.11573	0.32774	-0.26900	0.05(4)
H(41)	0.21376	0.28984	-0.16371	0.02(2)
H(43)	0.47791	0.29981	-0.24546	0.01(2)
H(44)	0.58197	0.35660	-0.31175	0.09(6)
H(45)	0.59927	0.46909	-0.26448	0.12(8)
H(46)	0.51846	0.52236	-0.13994	0.05(4)
H(47)	0.41025	0.47005	-0.08683	0.09(6)
H(48A)	0.70364	0.48862	-0.72103	0.2(4)
H(48B)	0.76574	0.49392	-0.63243	0.2(2)
H(48C)	0.70114	0.54412	-0.62953	0.2(2)
H(50A)	0.61819	0.39375	-0.65871	0.2(2)
H(50B)	0.58329	0.41415	-0.54361	0.2(2)
H(50C)	0.64749	0.36355	-0.54621	0.2(2)

Table S-7. Anisotropic Thermal Parameters of [Pd(π-allyl){(*R*)-BINAP}]ClO_4.

atom	U11	U22	U33	U12	U13	U23
Pd(1)	0.0386(4)	0.0331(4)	0.0347(4)	-.0006(3)	-.0049(3)	-.0012(3)
Cl(1)	0.074(2)	0.103(3)	0.064(2)	0.023(2)	0.008(2)	0.006(2)
P(1)	0.032(1)	0.030(1)	0.035(1)	0.000(1)	-0.001(1)	0.003(1)
P(2)	0.031(1)	0.034(1)	0.034(1)	0.000(1)	0.000(1)	0.004(1)
O(1)	0.15(2)	0.13(1)	0.19(2)	0.03(1)	0.02(2)	0.00(1)
O(2)	0.12(1)	0.39(4)	0.11(1)	0.09(2)	0.04(1)	0.01(2)
O(3)	0.22(3)	0.67(7)	0.08(1)	0.26(4)	0.03(1)	0.09(2)
O(4)	0.20(3)	0.15(2)	0.80(13)	-0.01(2)	-0.13(5)	-0.10(4)
O(5)	0.14(1)	0.23(3)	0.10(1)	-0.03(2)	0.01(1)	0.00(1)
C(1)	0.09(1)	0.05(1)	0.07(1)	0.00(1)	-0.02(1)	-0.01(1)
C(2)	0.15(2)	0.07(1)	0.10(1)	-0.02(1)	-0.06(1)	-0.02(1)
C(3)	0.09(1)	0.08(1)	0.05(1)	0.00(1)	-0.03(1)	-0.01(1)
C(4)	0.032(5)	0.030(5)	0.030(5)	-0.002(4)	0.005(4)	0.003(4)
C(5)	0.033(5)	0.045(6)	0.057(7)	0.005(5)	-0.002(5)	-0.007(5)
C(6)	0.028(6)	0.057(7)	0.070(8)	0.001(5)	0.005(5)	0.002(6)
C(7)	0.039(6)	0.054(6)	0.040(6)	-0.008(5)	-0.005(5)	0.000(5)
C(8)	0.056(8)	0.062(8)	0.059(8)	-0.018(7)	0.007(7)	0.010(6)
C(9)	0.062(8)	0.056(7)	0.058(7)	-0.020(6)	-0.006(7)	-0.004(6)
C(10)	0.067(8)	0.041(6)	0.052(8)	-0.012(6)	0.000(6)	-0.007(5)
C(11)	0.057(7)	0.043(6)	0.042(6)	-0.001(5)	-0.003(6)	-0.005(5)
C(12)	0.037(5)	0.035(5)	0.031(5)	-0.005(4)	-0.001(5)	-0.004(4)
C(13)	0.032(5)	0.038(5)	0.028(5)	0.001(4)	-0.002(4)	0.003(4)
C(14)	0.031(5)	0.029(5)	0.039(6)	-0.001(4)	0.006(4)	0.000(4)
C(15)	0.037(6)	0.029(5)	0.045(6)	-0.001(4)	0.009(5)	0.001(4)
C(16)	0.049(6)	0.048(6)	0.036(6)	-0.007(5)	0.002(5)	0.001(5)
C(17)	0.09(1)	0.06(1)	0.03(1)	-0.02(1)	0.00(1)	-0.01(1)
C(18)	0.09(1)	0.05(1)	0.04(1)	-0.03(1)	0.02(1)	0.00(1)
C(19)	0.066(9)	0.054(7)	0.058(8)	-0.001(7)	0.029(8)	-0.011(6)
C(20)	0.050(7)	0.037(5)	0.048(7)	0.001(5)	0.014(6)	0.009(5)
C(21)	0.050(7)	0.057(7)	0.058(8)	0.003(6)	0.009(7)	0.004(6)
C(22)	0.032(5)	0.051(6)	0.044(6)	0.006(5)	-0.001(5)	0.007(5)
C(23)	0.033(5)	0.029(5)	0.039(5)	0.000(4)	-0.001(4)	0.000(4)
C(24)	0.039(6)	0.028(5)	0.051(7)	0.002(4)	-0.006(5)	0.002(5)
C(25)	0.08(1)	0.05(1)	0.05(1)	0.02(1)	0.01(1)	0.00(1)
C(26)	0.11(1)	0.05(1)	0.08(1)	0.04(1)	0.00(1)	0.02(1)
C(27)	0.066(9)	0.048(7)	0.102(13)	0.025(7)	0.016(9)	-0.009(8)
C(28)	0.049(7)	0.048(6)	0.063(8)	0.006(5)	0.007(6)	-0.009(6)
C(29)	0.051(7)	0.039(6)	0.043(6)	-0.003(5)	0.004(5)	-0.005(5)
C(30)	0.037(5)	0.029(4)	0.045(6)	-0.005(4)	0.000(5)	-0.001(5)
C(31)	0.041(6)	0.063(8)	0.073(9)	-0.007(6)	0.007(8)	0.002(8)
C(32)	0.054(9)	0.091(12)	0.099(14)	-0.009(9)	0.025(9)	-0.001(11)
C(33)	0.08(1)	0.08(1)	0.07(1)	-0.01(1)	0.04(1)	0.01(1)
C(34)	0.080(9)	0.056(7)	0.045(6)	-0.007(7)	0.006(8)	0.007(6)
C(35)	0.042(6)	0.034(5)	0.049(7)	0.007(5)	0.001(5)	0.000(5)
C(36)	0.031(5)	0.054(7)	0.046(6)	0.009(5)	-0.005(5)	0.002(5)
C(37)	0.067(9)	0.041(6)	0.072(9)	-0.002(6)	-0.013(8)	0.018(6)
C(38)	0.09(1)	0.05(1)	0.09(1)	0.02(1)	-0.02(1)	0.02(1)
C(39)	0.066(9)	0.078(10)	0.078(10)	0.023(8)	-0.025(8)	0.010(9)
C(40)	0.053(8)	0.082(10)	0.085(11)	0.009(8)	-0.027(8)	-0.014(9)
C(41)	0.049(7)	0.043(6)	0.065(8)	-0.002(5)	-0.009(6)	0.012(6)
C(42)	0.037(5)	0.048(6)	0.034(5)	0.001(5)	0.005(5)	0.012(5)
C(43)	0.050(7)	0.053(7)	0.050(7)	0.001(6)	0.004(6)	0.009(6)
C(44)	0.053(8)	0.082(10)	0.059(8)	0.002(7)	0.018(7)	0.008(8)
C(45)	0.063(9)	0.082(10)	0.068(9)	-0.021(8)	0.004(8)	0.032(9)
C(46)	0.069(9)	0.053(7)	0.057(8)	-0.019(6)	-0.017(7)	0.020(6)
C(47)	0.052(7)	0.046(6)	0.048(7)	0.000(5)	-0.009(6)	0.007(6)
C(48)	0.20(3)	0.13(2)	0.10(2)	-0.03(2)	-0.06(2)	0.00(2)
C(49)	0.07(1)	0.13(2)	0.07(1)	0.03(1)	-0.01(1)	-0.03(1)
C(50)	0.10(2)	0.18(3)	0.13(2)	-0.01(2)	0.01(2)	0.02(2)

Table S-8. Intramolecular Bond Lengths (Å) of [Pd(π-allyl){(*R*)-BINAP}]ClO_4.

atom - atom	distance	atom - atom	distance
Pd(1)- P(1)	2.317(3)	Pd(1)- P(2)	2.316(3)
Pd(1)- C(1)	2.172(15)	Pd(1)- C(2)	2.14(3)
Pd(1)- C(3)	2.210(16)	P(1) - C(4)	1.837(10)
P(1) - C(24)	1.831(11)	P(1) - C(30)	1.798(12)
P(2) - C(23)	1.844(12)	P(2) - C(36)	1.825(13)
P(2) - C(42)	1.802(12)	C(1) - C(2)	1.38(3)
C(2) - C(3)	1.31(3)	C(4) - C(5)	1.392(15)
C(4) - C(13)	1.392(15)	C(5) - C(6)	1.360(17)
C(6) - C(7)	1.430(18)	C(7) - C(8)	1.401(19)
C(7) - C(12)	1.411(16)	C(8) - C(9)	1.39(2)
C(9) - C(10)	1.38(3)	C(10)- C(11)	1.348(19)
C(11)- C(12)	1.418(17)	C(12)- C(13)	1.431(15)
C(13)- C(14)	1.516(15)	C(14)- C(15)	1.433(16)
C(14)- C(23)	1.378(15)	C(15)- C(16)	1.414(17)
C(15)- C(20)	1.428(18)	C(16)- C(17)	1.402(18)
C(17)- C(18)	1.39(3)	C(18)- C(19)	1.35(3)
C(19)- C(20)	1.42(2)	C(20)- C(21)	1.39(2)
C(21)- C(22)	1.37(2)	C(22)- C(23)	1.417(16)
C(24)- C(25)	1.383(19)	C(24)- C(29)	1.374(18)
C(25)- C(26)	1.38(3)	C(26)- C(27)	1.39(3)
C(27)- C(28)	1.33(3)	C(28)- C(29)	1.406(18)
C(30)- C(31)	1.387(17)	C(30)- C(35)	1.374(18)
C(31)- C(32)	1.34(3)	C(32)- C(33)	1.42(3)
C(33)- C(34)	1.35(3)	C(34)- C(35)	1.419(19)
C(36)- C(37)	1.388(19)	C(36)- C(41)	1.394(18)
C(37)- C(38)	1.36(3)	C(38)- C(39)	1.37(3)
C(39)- C(40)	1.36(3)	C(40)- C(41)	1.37(3)
C(42)- C(43)	1.407(18)	C(42)- C(47)	1.406(17)
C(43)- C(44)	1.39(3)	C(44)- C(45)	1.41(3)
C(45)- C(46)	1.39(3)	C(46)- C(47)	1.38(2)
Cl(1)- O(1)	1.37(3)	Cl(1)- O(2)	1.40(3)
Cl(1)- O(3)	1.25(3)	Cl(1)- O(4)	1.22(4)
O(5) - C(49)	1.17(3)	C(48)- C(49)	1.53(4)
C(49)- C(50)	1.50(4)		

Table S-9. Intramolecular Bond Angles (°) of [Pd(π-allyl){(*R*)-BINAP}]ClO_4.

atom - atom - atom	angle	atom - atom - atom	angle
P(1) - Pd(1)- P(2)	95.5(1)	P(1) - Pd(1)- C(1)	97.2(5)
P(1) - Pd(1)- C(2)	132.2(6)	P(1) - Pd(1)- C(3)	162.8(5)
P(2) - Pd(1)- C(1)	167.1(5)	P(2) - Pd(1)- C(2)	130.0(6)
P(2) - Pd(1)- C(3)	100.6(5)	C(1) - Pd(1)- C(2)	37.2(8)
C(1) - Pd(1)- C(3)	66.9(7)	C(2) - Pd(1)- C(3)	35.1(8)
Pd(1)- P(1) - C(4)	112.2(4)	Pd(1)- P(1) - C(24)	111.4(4)
Pd(1)- P(1) - C(30)	113.9(4)	C(4) - P(1) - C(24)	104.4(5)
C(4) - P(1) - C(30)	107.2(5)	C(24)- P(1) - C(30)	107.1(5)
Pd(1)- P(2) - C(23)	109.2(4)	Pd(1)- P(2) - C(36)	113.5(5)
Pd(1)- P(2) - C(42)	113.5(4)	C(23)- P(2) - C(36)	105.9(6)
C(23)- P(2) - C(42)	108.6(5)	C(36)- P(2) - C(42)	105.8(6)
Pd(1)- C(1) - C(2)	70.2(11)	Pd(1)- C(2) - C(1)	72.6(13)
Pd(1)- C(2) - C(3)	75.3(12)	C(1) - C(2) - C(3)	127.8(23)
Pd(1)- C(3) - C(2)	69.6(12)	P(1) - C(4) - C(5)	119.3(8)
P(1) - C(4) - C(13)	121.1(8)	C(5) - C(4) - C(13)	119.1(10)
C(4) - C(5) - C(6)	121.6(11)	C(5) - C(6) - C(7)	121.3(11)
C(6) - C(7) - C(8)	121.5(11)	C(6) - C(7) - C(12)	117.9(11)
C(8) - C(7) - C(12)	120.6(12)	C(7) - C(8) - C(9)	119.3(13)
C(8) - C(9) - C(10)	120.3(13)	C(9) - C(10)- C(11)	121.1(13)
C(10)- C(11)- C(12)	121.3(12)	C(7) - C(12)- C(11)	117.3(11)
C(7) - C(12)- C(13)	119.3(10)	C(11)- C(12)- C(13)	123.3(11)
C(4) - C(13)- C(12)	120.7(10)	C(4) - C(13)- C(14)	121.9(9)
C(12)- C(13)- C(14)	117.4(9)	C(13)- C(14)- C(15)	117.5(9)
C(13)- C(14)- C(23)	122.3(10)	C(15)- C(14)- C(23)	120.2(10)
C(14)- C(15)- C(16)	122.7(11)	C(14)- C(15)- C(20)	119.2(11)
C(16)- C(15)- C(20)	118.0(11)	C(15)- C(16)- C(17)	121.0(13)
C(16)- C(17)- C(18)	119.3(14)	C(17)- C(18)- C(19)	121.2(13)
C(18)- C(19)- C(20)	121.6(15)	C(15)- C(20)- C(19)	118.6(12)
C(15)- C(20)- C(21)	118.5(12)	C(19)- C(20)- C(21)	122.8(13)
C(20)- C(21)- C(22)	121.9(13)	C(21)- C(22)- C(23)	120.3(12)
P(2) - C(23)- C(14)	121.6(8)	P(2) - C(23)- C(22)	117.9(9)
C(14)- C(23)- C(22)	119.7(11)	P(1) - C(24)- C(25)	122.6(10)
P(1) - C(24)- C(29)	117.4(9)	C(25)- C(24)- C(29)	120.0(12)
C(24)- C(25)- C(26)	119.2(14)	C(25)- C(26)- C(27)	120.4(15)
C(26)- C(27)- C(28)	120.2(14)	C(27)- C(28)- C(29)	120.5(14)
C(24)- C(29)- C(28)	119.7(12)	P(1) - C(30)- C(31)	119.2(11)
P(1) - C(30)- C(35)	122.3(9)	C(31)- C(30)- C(35)	118.4(12)
C(30)- C(31)- C(32)	121.8(16)	C(31)- C(32)- C(33)	120.1(16)
C(32)- C(33)- C(34)	119.6(16)	C(33)- C(34)- C(35)	119.1(14)
C(30)- C(35)- C(34)	120.9(12)	P(2) - C(36)- C(37)	124.8(10)
P(2) - C(36)- C(41)	118.2(10)	C(37)- C(36)- C(41)	116.9(12)
C(36)- C(37)- C(38)	120.5(14)	C(37)- C(38)- C(39)	121.8(16)
C(38)- C(39)- C(40)	118.8(16)	C(39)- C(40)- C(41)	120.1(15)
C(36)- C(41)- C(40)	121.8(13)	P(2) - C(42)- C(43)	117.2(9)
P(2) - C(42)- C(47)	123.7(9)	C(43)- C(42)- C(47)	119.1(11)
C(42)- C(43)- C(44)	119.6(13)	C(43)- C(44)- C(45)	120.6(15)
C(44)- C(45)- C(46)	119.6(15)	C(45)- C(46)- C(47)	120.1(14)
C(42)- C(47)- C(46)	120.9(12)		
O(1) - Cl(1)- O(2)	114.9(17)	O(1) - Cl(1)- O(3)	113.2(23)
O(1) - Cl(1)- O(4)	101.1(18)	O(2) - Cl(1)- O(3)	107.4(16)
O(2) - Cl(1)- O(4)	109.0(25)	O(3) - Cl(1)- O(4)	111.1(33)
O(5) - C(49)- C(48)	120.3(23)	O(5) - C(49)- C(50)	123.1(24)
C(48)- C(49)- C(50)	116.5(21)		

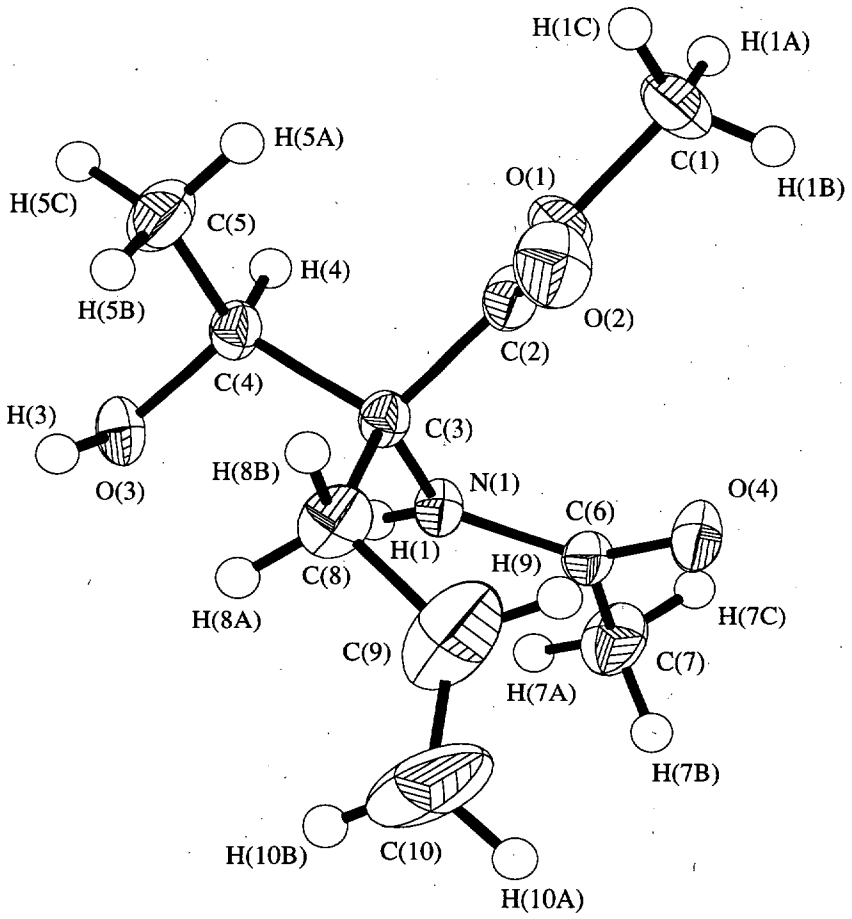

Figure S-2. ORTEP Drawing (50% Probability Level) with Atom-Labeling Scheme for Methyl ($2R^*$,$3S^*$)-2-(*N*-Acetylamino)-3-hydroxy-2-(2-propenyl)butanoate (**5b**).

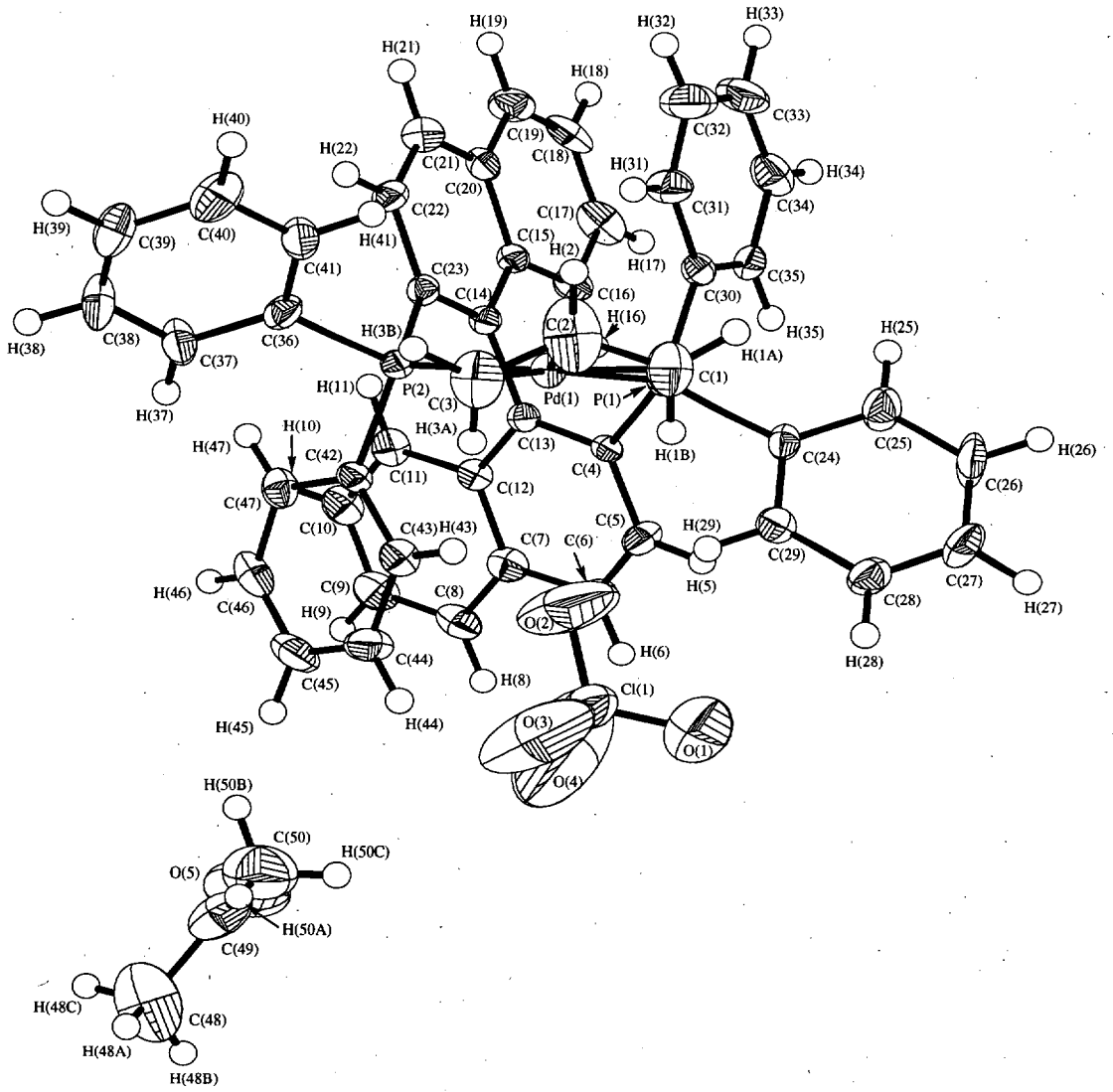

Figure S-3. ORTEP Drawing (30% Probability Level) with Atom-Labeling Scheme for [Pd(π-allyl){(*R*)-BINAP}]ClO_4·(CH_3COCH_3).

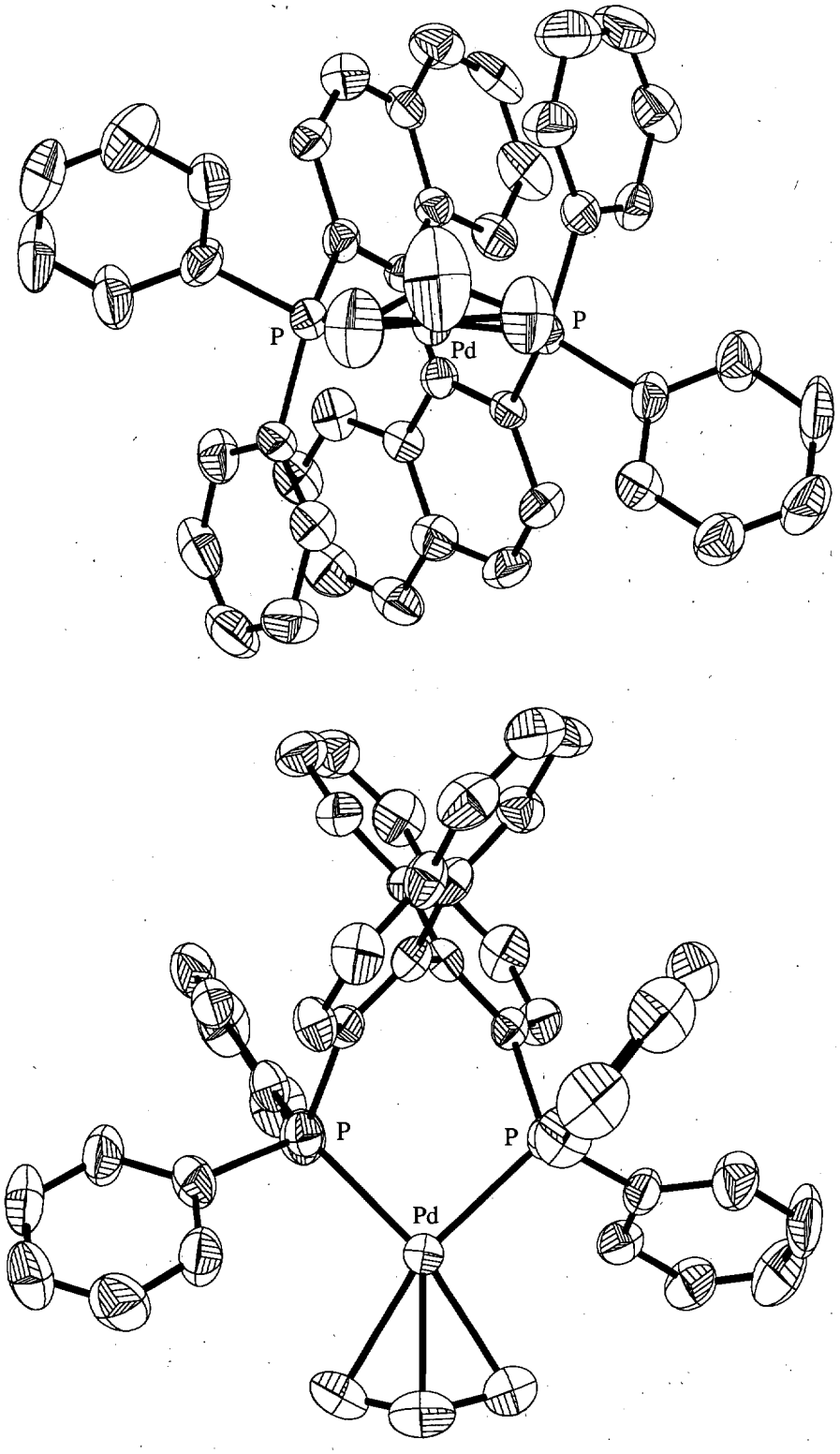

Figure S-4. ORTEP drawing (50% probability level) for [Pd(π-allyl){(*R*)-BINAP}]ClO_4·(CH_3COCH_3). Hydrogen atoms, perchlorate anion, and acetone are omitted for clarity.