Supporting Information for:

(π-Allyl)palladium Complexes Bearing Diphosphinidenecyclobutene Ligands (DPCB): Highly Active Catalysts for Direct Conversion of Allylic Alcohols

Fumiyuki Ozawa,* Hideyuki Okamoto, Seiji Kawagishi, Shogo Yamamoto,
Tatsuya Minami, and Masaaki Yoshifuji
Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Osaka 558-8585, Japan and Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
(ozawa@a-chem.eng.osaka-cu.ac.jp)

Experimental Section

Materials and Instrumentation. Complexes **1a–c**, **6**, and **7** were prepared as previously reported.[1,2] (*R*)-1-Phenyl-3-hydroxybutene (**2g**, 98.5% ee) was provided by Dr. Kunihiko Murata at Kanto Chemicals. All other chemicals were obtained from commercial suppliers and used without purification.

NMR spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts are reported in δ (ppm), referred to ^{1}H (of residual protons) and ^{13}C signals of the deuterated solvents or to the ^{31}P signal of an external 85% H_3PO_4 standard. GLC analysis was performed on a Shimadzu GC-14B instrument equipped with a FID detector and a capillary column (Shimadzu CBP-1, 25 m × 0.25 mm). Mass spectra were measured with a Shimadzu QP-5000 GC-mass spectrometer (EI, 70 eV). Preparative MPLC was performed with a prepacked silica gel column (Kusano CGI Si-10, 22 mm × 30 cm, hexane/AcOEt = 10/1). Enantiomeric purity of optically active compounds was determined by HPLC (Shimadzu LC-10, UV 254 nm) using a chiral column (Daicel CHIRALCEL OJ, *i*-PrOH/hexane = 5/95, 1.0 mL/min). Optical rotations were measured on a JASCO DIP-370 polarimeter.

Catalytic Allylation of Aniline (Table 1). A typical procedure (run 1) is as follows. To a Schlenk tube containing **1a** (1.2 mg, 1.1 μmol) were added toluene (1 mL), 2-propenyl alcohol (70 μL, 1.03 mmol), $MgSO_4$ (0.25 g), and aniline (180 μL, 1.98 mmol) successively at room temperature. The mixture was stirred at room temperature for 2 h. GLC analysis revealed disappearance of the starting alcohol. The white solid of $MgSO_4$ was removed by filtration and washed with Et_2O (2 mL × 2). The combined filtrate was concentrated to dryness and purified

by MPLC to give *N*-(2-propenyl)aniline (131 mg, 96%) and *N*,*N*-di(2-propenyl)aniline (2.7 mg, 3%).

***N*-(2-Propenyl)aniline.** ^{1}H NMR ($CDCl_3$): δ 3.79 (dt, *J* = 5.4 and 1.5 Hz, 2H, NCH_2), 4.07 (br, 1H, NH), 5.18 (dq, *J* = 10.2 and 1.5 Hz, 1H, CH=C*H*H), 5.30 (dq, *J* = 17.1 and 1.5 Hz, 1H, CH=CH*H*), 5.97 (ddt, *J* = 17.1, 10.2 and 5.4 Hz, 1H, C*H*=CH_2), 6.66 (m, *J* = 8.7 and 0.9 Hz, 2H, *o*-Ph), 6.74 (m, *J* = 7.4 and 0.9 Hz, 1H, *p*-Ph), 7.19 (m, *J* = 8.7 and 7.4 Hz, 2H, *m*-Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 47.6 (NCH_2), 113.2 (*o*-Ph), 116.4 (CH=*C*H_2), 117.8 (*p*-Ph), 129.2 (*m*-Ph), 135.2 (*C*H=CH_2), 147.7 (*ipso*-Ph). MS, m/z (relative intensity): 133 (M^+, 89), 117 (25), 106 (100), 91 (12), 77 (63), 65 (15).

***N*,*N*-Di(2-propenyl)aniline.** ^{1}H NMR ($CDCl_3$): δ 3.93 (m, 4H, NCH_2), 5.15–5.22 (m, 4H, CH=CH_2), 5.81–5.94 (m, 2H, C*H*=CH_2), 6.60–6.85 (m, 3H, *o*- and *p*-Ph), 7.21 (m, 2H, *m*-Ph). MS, m/z (relative intensity): 173 (M^+, 53), 158 (12), 146 (60), 130 (35), 117 (18), 104 (54), 91 (11), 77 (84), 65 (12).

Runs 2–9 in Table 1 were similarly examined. Monoallylation products in runs 4–7 were obtained as a mixture of stereo- and/or regio-isomers; the product yields and the (*E*)/(*Z*) ratios listed in the table were based on GLC analysis of the products separated from the reaction solutions by MPLC.

A mixture of (*E*)- and (*Z*)-*N*-(2-butenyl)aniline (A, B) and *N*-(1-methyl-2-propenyl)aniline (C) (A/B/C = 78/11/11). ^{1}H NMR ($CDCl_3$): δ 1.32 (d, *J* = 6.9 Hz, 0.33H, NCHCH_3 (**C**)), 1.71 (dd, *J* = 6.2 and 1.3 Hz, 2.67H, CH=CHCH_3 (**A**)),[3] 3.69 (dd, *J* = 5.7 and 1.3 Hz, 1.56H, NCH_2 (**A**)), 3.78 (d, *J* = 6.3 Hz, 0.22H, NCH_2 (**B**)), 3.90 (br, 1H, NH (**A**–**C**)), 3.99 (qdt, *J* = 6.9, 5.7 and 1.3 Hz, 0.11H, NC*H*CH_3 (**C**)), 5.09 (dt, *J* = 10.2 and 1.3, 0.11H, CH=C*H*H (**C**)), 5.22 (dt, *J* = 17.4 and 1.3 Hz, 0.11H, CH=CH*H* (**C**)), 5.60 (dtq, *J* = 15.6, 5.7 and 1.3 Hz, 0.89H, CH=C*H*NCH_2 (**A**)),[3] 5.73 (dqt, *J* = 15.6, 6.2 and 1.3 Hz, 0.89H, CH_3C*H*=CH (**A**)),[3] 5.84 (ddd, *J* = 17.4, 10.2 and 5.7 Hz, 0.11H, CHC*H*=CH_2 (**C**)), 6.64 (m, 2H, *o*-Ph (**A**–**C**)), 6.72 (m, 1H, *p*-Ph (**A**–**C**)), 7.18 (m, 2H, *m*-Ph (**A**–**C**)). ^{13}C{^{1}H} NMR ($CDCl_3$): (**A**) δ 17.8 (CH_3), 46.0 (NCH_2), 113.0 (*o*-Ph), 117.4 (*p*-Ph), 123.0 (CH=*C*H), 127.9 (*C*H=CH), 129.1 (*m*-Ph), 148.1 (*ipso*-Ph); (**B**) δ 21.6 (CH_3), 40.9 (NCH_2), 113.4 (*o*-Ph), 117.5 (*p*-Ph), 127.2 (*C*H=CH), 127.5 (CH=*C*H), 129.1 (*m*-Ph), 148.1 (*ipso*-Ph); (**C**) δ 13.1 (CH_3), 51.1 (NCH), 113.3 (*o*-Ph), 114.1 (CH=*C*H_2), 117.3 (*p*-Ph), 129.1 (*m*-Ph), 141.1 (*C*H=CH_2), 147.2 (*ipso*-Ph). MS, m/z (relative intensity): (**A**) 147 (M^+, 69), 132 (63), 117 (22), 106 (44), 93 (100), 77 (54), 55 (65); (**B**) 147 (M^+, 58), 132 (51), 117 (18), 106 (42), 93 (100), 77 (45), 55 (40); (**C**) 147 (M^+, 38), 132 (100), 117 (28), 93 (25), 77 (29), 65 (38), 51 (25).

***N*,*N*-Di(2-butenyl)aniline.** ^{1}H NMR ($CDCl_3$): δ 1.68 (dd, *J* = 6.3 and 1.3 Hz 6H CH=CHCH_3), 3.82 (brd, *J* = 5.1 Hz, 4H, NCH_2), 5.46 (dt, *J* = 15.6 and 5.1 Hz, 2H, CH=C*H*NCH_2), 5.56 (dq, *J* = 15.6 and 6.3 Hz, 2H, CH_3C*H*=CH), 6.65 (t, *J* = 7.2 Hz, 1H, *p*-Ph),

6.70 (d, J = 8.1 Hz, 2H, *o*-Ph), 7.19 (dd, J = 8.1 and 7.2 Hz, *m*-Ph). MS, m/z (relative intensity): 201 (M^+, 31), 186 (7), 158 (11), 147 (17), 132 (20), 118 (9), 106 (53), 93 (11), 77 (48), 55 (100).

A mixture of (*E*)- and (*Z*)-*N*-(2-hexenyl)aniline (D/E = 90/10). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, J = 7.5 Hz, 2.7H, CH_3 (**D**)), 0.94 (t, J = 7.5 Hz, 0.3H, CH_3 (**E**)), 1.41 (sextet, J = 7.5 Hz, 2H, CH_2CH$_3$ (**D**, **E**)), 2.03 (m, 1.8H, CH_2CH$_2$CH$_3$ (**D**)), 2.11 (m, 0.2H, CH_2CH$_2$CH$_3$ (**E**)), 3.71 (dd, J = 5.7 and 0.9 Hz, 1.8H, NCH$_2$ (**D**)), 3.72 (br, 1H, NH), 3.77 (d, J = 5.4 Hz, 0.2H, NCH$_2$ (**E**)), 5.58 (dtt, J = 15.6, 5.7 and 1.2 Hz, 0.9H, CH=C*H*CH$_2$N (**D**)),[3] 5.71 (dtt, J = 15.6, 6.6 and 1.2 Hz, 0.9H, C*H*=CHCH$_2$N (**D**)),[3] 6.64 (m, 2H, *o*-Ph), 6.72 (m, 1H, *p*-Ph), 7.19 (m, 2H, *m*-Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): (**D**) δ 13.7 (CH_3), 22.4 (CH_2), 34.4 (CH_2), 46.1 (NCH$_2$), 113.0 (*o*-Ph), 117.4 (*p*-Ph), 126.8 (*C*H=CH), 129.1 (*m*-Ph), 133.3 (CH=*C*H), 148.1 (*ipso*-Ph); (**E**) δ 13.8 (CH_3), 22.7 (CH_2), 29.6 (CH_2), 41.2 (NCH$_2$), 113.3 (*o*-Ph), 117.5 (*p*-Ph), 126.7 (*C*H=CH), 129.2 (*m*-Ph), 133.1 (CH=*C*H), 148.1 (*ipso*-Ph). MS, m/z (relative intensity): major isomer, 175 (M^+, 23), 146 (5), 132 (56), 106 (18), 93 (100), 77 (24), 55 (34).

***N*,*N*-Di(2-hexenyl)aniline.** ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 7.5 Hz, 6H, CH_3), 1.37 (sextet, J = 7.5 Hz, 4H, CH_2CH$_3$), 2.00 (q, J = 7.2 Hz, 4H, CH_2CH$_2$CH$_3$), 3.84 (d, J = 5.1 Hz, 4H, NCH$_2$), 5.45 (dt, J = 15.6 and 5.1 Hz, 2H, CH=C*H*CH$_2$N), 5.57 (dt, J = 15.6 and 6.6 Hz, 2H, C*H*=CHCH$_2$N), 6.65 (t, J = 7.2 Hz, 2H, *o*-Ph), 6.71 (d, J = 8.4 Hz, 1H, *p*-Ph), 7.18 (m, 2H, *m*-Ph). MS, m/z (relative intensity): 257 (M^+, 22), 228 (7), 214 (19), 175 (24), 144 (17), 132 (41), 106 (38), 93 (84), 77 (36), 55 (93), 41 (100).

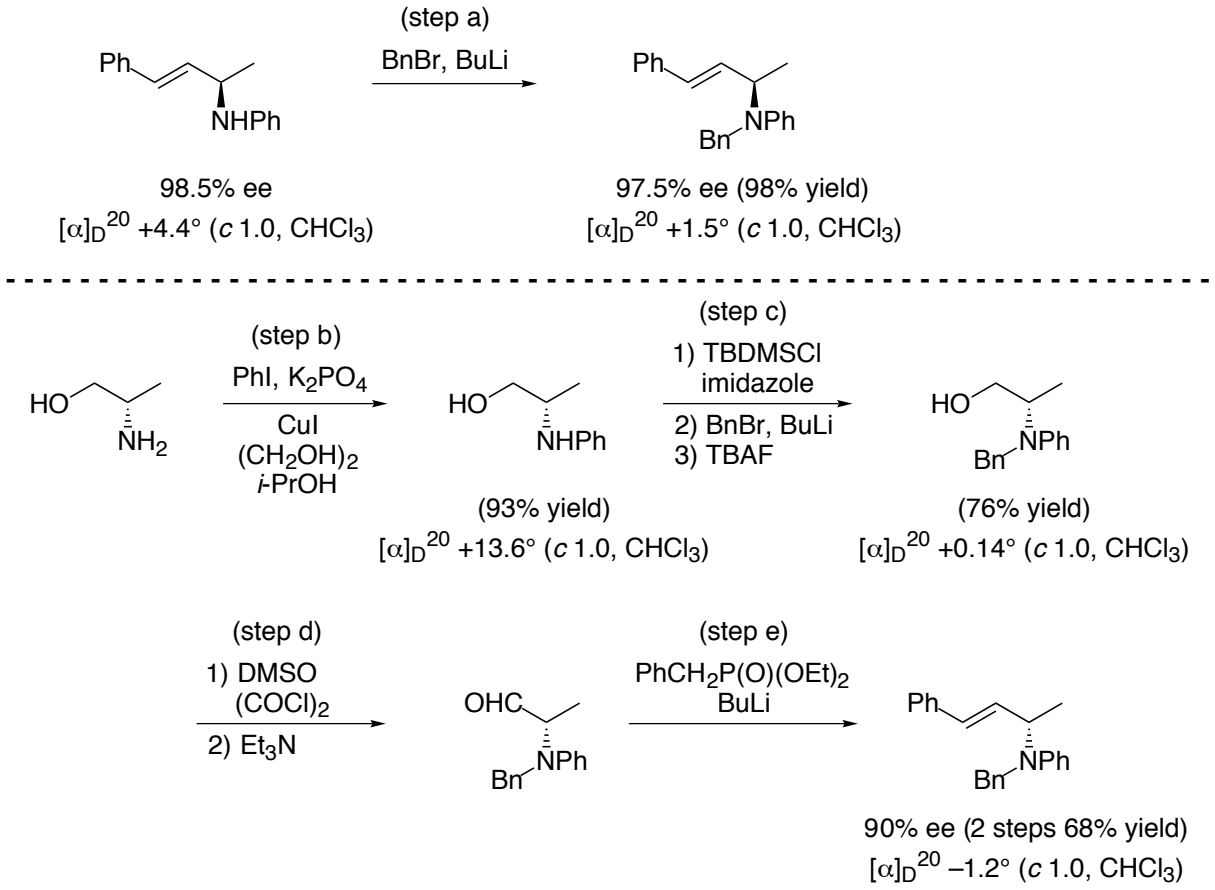
***N*-(3-Phenyl-2-propenyl)aniline.** ^{1}H NMR ($CDCl_3$): δ 3.96 (dd, J = 5.7 and 1.5 Hz, 2H, NCH$_2$), 3.95 (br, 1H, NH), 6.35 (dt, J = 15.9 and 5.7 Hz, 1H, PhCH=C*H*), 6.65 (d, J = 15.9 Hz, 1H, PhC*H*=CH), 6.68–6.78 (m, 3H, *o*-PhN), 7.18–7.41 (m, 7H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 46.2 (NCH$_2$), 113.1 (*o*-PhN), 117.7 (*p*-PhN), 126.3 (*o*-Ph), 126,9 (PhCH=*C*H), 127.5 (*m*-PhN) 128.5 (*p*-Ph), 129.3 (*m*-Ph), 131.5 (Ph*C*H=CH), 136.8 (*ipso*-Ph), 147.9 (*ipso*-PhN). MS, m/z (relative intensity): 209 (M^+, 32), 192 (3), 132 (7), 117 (100), 104 (7), 91 (25), 77 (23), 65 (11).

***N*,*N*-Bis(3-phenyl-2-propenyl)aniline.** ^{1}H NMR ($CDCl_3$): δ 4.15 (dd, J = 5.1 and 1.5 Hz, 4H, NCH$_2$), 6.29 (dt, J = 16.2 and 5.1 Hz, 2H, PhCH=C*H*), 6.55 (d, J = 16.2 Hz, 2H, PhC*H*=CH), 6.73 (t, J = 7.2 Hz, 1H *p*-Ph), 6.83 (d, J = 8.1 Hz, 2H, *o*-PhN), 7.20–7.39 (m, 12H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 52.2 (NCH$_2$), 112.5 (*o*-PhN), 116.5 (*p*-PhN), 125.8 (PhCH=*C*H), 126.3 (*o*-Ph), 127.4 (*m*-PhN), 128.5 (*p*-Ph), 129.3 (*m*-Ph), 131.1 (Ph*C*H=CH), 136.8 (*ipso*-Ph), 148.8 (*ipso*-PhN). MS, m/z (relative intensity): 325 (M^+, 32), 220 (14), 144 (15), 117 (100), 104 (40), 91 (51), 77 (31), 65 (11).

***(R)*-(+)-*N*-(1-Methyl-3-phenyl-2-propenyl)aniline (98.5% ee).** ^{1}H NMR ($CDCl_3$): δ 1.42 (d, J = 6.6 Hz, 3H, CH_3), 3.94 (br, 1H, NH), 4.16 (qd, J = 6.6 and 5.9 Hz, 1H, NCH), 6.24 (dd, J = 15.9, 5.9 Hz, 1H, PhCH=C*H*), 6.59 (d, J = 15.9 Hz, 1H, PhC*H*=CH), 6.67–6.75 (m, 3H,

o,p-PhN), 7.15–7.39 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.0 (CH_3), 51.0 (NCH), 113.6 (*o*-PhN), 117.5 (*p*-PhN), 126.3 (Ph), 127.3 (Ph) 128.5 (Ph), 129.2 (*m*-PhN), 129.4 (PhCH=*C*H), 133.0 (Ph*C*H=CH), 136.9 (*ipso*-Ph), 147.1 (*ipso*-PhN). MS, m/z (relative intensity): 223 (M^+, 25), 208 (13), 131 (100), 115 (16), 91 (53), 77 (23), 65 (12), 51 (19). $[\alpha]_D^{20}$ +4.4° (*c* 1.0, $CHCl_3$). HPLC (retention time, min): *S* (11.0), *R* (12.8). Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.96; H, 7.61; N, 6.32.

Determination of Absolute Configuration. The absolute configuration of the reaction product in run 9 in Table 1 was determined by chemical correlation, outlined in Scheme 4.



Scheme 4

Step a. A hexane solution of *n*-BuLi (1.6 M, 0.15 mL, 0.24 mmol) was added to a solution of (+)-*N*-(1-methyl-3-phenyl-2-propenyl)aniline (98.5% ee, 45 mg, 0.20 mmol) in THF (2.0 mL) at –78 °C. After 30 min, benzylbromide (30 μL, 0.25 mmol) was added. The mixture was gradually warmed to room temperature, and stirred for 30 min. Water was added, and the reaction mixture was extracted with Et_2O (20 mL × 2). The combined extract was washed with brine and dried over $MgSO_4$. After concentration, column chromatography (SiO_2,

hexane/AcOEt = 100/1 to 50/1) was performed to give a colorless solid of (*R*)-(+)-*N*-benzyl-*N*-(1-methyl-3-phenyl-2-propenyl)aniline (97.5% ee) (62 mg, 98%). ^{1}H NMR ($CDCl_3$): δ 1.41 (d, *J* = 6.9 Hz, 3H, CH_3), 4.48 (s, 2H, CH_2Ph), 4.80–4.87 (m, 1H, CH), 6.33 (dd, *J* = 16.0 and 4.6 Hz, 1H, PhCH=C*H*), 6.49 (d, *J* = 16.0 Hz, 1H, PhC*H*=CH), 6.71 (t, *J* = 7.3 Hz, 1H, *p*-Ph), 6.78 (d, *J* = 8.2 Hz, 2H, *o*-Ph), 7.16–7.30 (m, 12H, Ph). $[\alpha]_D^{20}$ +1.5 (*c* 1.0, $CHCl_3$). HPLC (retention time, min): *S* (9.1), *R* (10.1). Anal. Calcd for $C_{23}H_{23}N$: C, 88.14; H, 7.40; N, 4.47. Found: C, 88.12; H, 7.22; N, 4.32.

Step b. This step was based on Ref 4. Copper (I) iodide (100 mg, 0.50 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were placed in a Schlenk tube, and the system was replaced with N_2 gas. 2-Propanol (10 mL), ethylene glycol (1.10 mL, 20.0 mmol), (*S*)-alaninol (>99% ee) (750 mg, 10.0 mmol), and PhI (1.10 mL, 10.0 mmol) were successively added at room temperature. The mixture was heated at 80 °C for 24 h to give a pale yellow suspension. After cooling the solution at room temperature, water was added, and the mixture was extracted with Et_2O (20 mL × 3). The combined organic extract was washed with brine and dried over $MgSO_4$. The solvent was removed by evaporation, and the residue was purified by column chromatography (SiO_2, hexane/AcOEt = 4/1), to give a colorless oil of (*S*)-(+)-*N*-(1-methyl-2-hydroxyethyl)aniline (1.41 g, 93%). ^{1}H NMR ($CDCl_3$): δ 1.21 (d, *J* = 6.4 Hz, 3H, CH_3), 3.53 (dd, *J* = 10.5 and 6.0 Hz, 1H, CH*H*), 3.60–3.70 (m, 1H, CH), 3.74 (dd, *J* = 10.5 and 4.1 Hz, C*H*H), 6.72 (dd, *J* = 7.5 and 1.1 Hz, 2H, *o*-Ph), 6.76 (td, *J* = 7.3 and 1.0 Hz, 1H, *p*-Ph), 7.20 (td, *J* = 7.3 and 1.2 Hz, 2H, *m*-Ph). $[\alpha]_D^{20}$ +13.6 (*c* 1.0, $CHCl_3$).

Step c. The (*S*)-(+)-*N*-(1-methyl-2-hydroxyethyl)aniline (1.50 g, 10.0 mmol) thus obtained was dissolved in DMF (5.0 mL), and imidazole (750 mg, 11.0 mmol) and *t*-butyldimethylsilyl chloride (1.65 g, 11.0 mmol) were added at room temperature. The mixture was stirred for 6 h at 50 °C, and then poured into water and extracted with Et_2O (20 mL × 2). The combined extract was washed with brine and dried over $MgSO_4$. Evaporation of the solvent followed by bulb-to-bulb distillation of the residue (150–160 °C at 0.1 mmHg) gave (*S*)-*N*-(1-methyl-2-*t*-butyldimethylsiloxyethyl)aniline (2.41 g, 91%) as a colorless oily material. ^{1}H NMR ($CDCl_3$): δ –0.04 (s, 3H, SiMe), –0.53 (s, 3H, SiMe), 0.91 (s, 9H, *t*-Bu), 1.21 (d, *J* = 6.2 Hz, CH_3), 3.50–3.67 (m, 3H, CH_2CH), 6.65 (d, *J* = 7.7 Hz, 2H, *o*-Ph), 6.71 (t, *J* = 7.3 Hz, 1H, *p*-Ph), 7.14 (t, *J* = 7.3 Hz, 2H, *m*-Ph).

n-Butyllithium (1.6 M, 6.5 mL, 10.4 mmol) was added to a solution of (*S*)-*N*-(1-methyl-2-*t*-butyldimethylsiloxyethyl)aniline (2.38 g, 9.00 mmol) in THF (20 mL) at –78 °C. After 30 min, benzylbromide (1.50 mL, 12.7 mmol) was added. The system was then gradually warmed to room temperature, and stirred for 30 min. Water was added, and the resulting mixture was extracted with Et_2O (20 mL × 2). The combined extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was dissolved in

THF (20 mL). Tetrabutylammonium fluoride (2.50 g, 9.60 mmol) was added at room temperature, and the system was stirred for 2 h. The reaction mixture was poured into water, and extracted with Et_2O (20 mL × 2). The combined extract was washed with brine and dried over $MgSO_4$. The resulting product was purified by column chromatography (SiO_2, hexane/AcOEt = 10/1 to 5/1) to afford a colorless solid of (*S*)-*N*-benzyl-*N*-(1-methyl-2-hydroxyethyl)aniline (1.83 g, 84%). ^{1}H NMR ($CDCl_3$): δ 1.16 (d, *J* = 6.3 Hz, 3H, CH_3), 1.83 (br, 1H, OH), 3.54–3.70 (m, 2H, CH_2), 4.13–4.22 (m, 1H, CH), 4.43 (s, 2H, CH_2Ph), 6.77 (t, *J* = 7.3 Hz, 1H, *p*-Ph), 6.86 (d, *J* = 7.3 Hz, 2H, *o*-Ph), 7.17–7.34 (m, 8H).

Step d. This step was based on Ref 5. To a CH_2Cl_2 (20 mL) solution of oxalyl chloride (0.31 g, 2.41 mmol) was added dimethyl sulfoxide (0.32 g, 4.00 mmol) at –78 °C. After 5 min, (*S*)-*N*-benzyl-*N*-(1-methyl-2-hydroxyethyl)aniline (480 mg, 2.00 mmol) was added in one portion. The reaction system was gradually warmed to 0 °C over 30 min, and then cooled to –78 °C. Triethylamine (2.50 mL, 8.00 mmol) was added, and the mixture was warmed to room temperature. Water was added, and the organic phase was separated. The aqueous phase was extracted repeatedly with CH_2Cl_2. The combined organic phase was washed successively with dilute hydrochloric acid (ca. HCl), water, an aqueous $NaHCO_3$ solution, and brine. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure, to provide a crude product of (*S*)-*N*-benzyl-*N*-(1-formylethyl)aniline, which was subjected to the next reaction (step e) without purification.

Step e. To a solution of $PhCH_2P(O)(OEt)_2$ (550 mg, 2.41 mmol) in THF (15 mL) was added *n*-BuLi (1.60 M solution in hexane, 1.50 mL, 2.40 mmol) at –78 °C. The mixture was warmed to 0 °C over 30 min, and then cooled to –78 °C. A THF solution (5.0 mL) of the aldehyde prepared by step d was added dropwise, and the mixture was stirred for 15 min at –78 °C and then at room temperature for 12 h. The reaction was quenched with water and extracted with Et_2O (20 mL × 2). The combined extract was washed with brine and dried over $MgSO_4$. The resulting product was purified by column chromatography (SiO_2, hexane/AcOEt = 100/1 to 50/1) to give (*S*)-(–)-*N*-benzyl-*N*-(1-methyl-3-phenyl-2-propenyl)aniline (89.8% ee) (426 mg, 68%). $[\alpha]_D^{20}$ –1.2 (*c* 1.0, $CHCl_3$). The product exhibited the same ^{1}H NMR spectrum as (*R*)-(+)-*N*-benzyl-*N*-(1-methyl-3-phenyl-2-propenyl)aniline, prepared by step a.

Catalytic Allylation of Active Methylene Compounds (Table 2). A typical procedure (run 1) is as follows. The complex **1a** (22.5 mg, 20 μmol) was placed in a Schlenk tube, and 2-propenyl alcohol (70 μL, 1.0 mmol), ethyl acetoacetate (255 μL, 2.0 mmol), $MgSO_4$ (0.25 g), and pyridine (8 μL, 0.1 mmol) were added successively at room temperature. The mixture was stirred at 50 °C for 4 h. GLC analysis revealed complete conversion of 2-propenyl alcohol.

After removal of $MgSO_4$ by filtration, the reaction mixture was subjected to MPLC, giving the monoallylation product in 92% yield (156 mg) and the diallylation product in 7% yield (7.6 mg).

Ethyl 2-Acethyl-4-pentenoate. ^{1}H NMR ($CDCl_3$): δ 1.26 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 2.22 (s, 3H, $COCH_3$), 2.58 (m, 2H, CH_2), 3.51 (t, *J* = 7.5 Hz, 1H, CH), 4.18 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 5.03 (ddt, *J* = 10.2, 1.5 and 1.1 Hz, 1H, *cis*-CH=CH*H*), 5.08 (dq, *J* = 17.1 and 1.5 Hz, 1H, *trans*-CH=C*H*H), 5.73 (ddt, *J* = 17.1, 10.2 and 6.9 Hz, 1H, C*H*=CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.1 (OCH_2CH_3), 29.1 (CH_3CO), 32.1 (CH_2), 59.2 (CH), 61.4 (OCH_2CH_3), 117.4 (CH=CH_2), 134.2 (CH=CH_2), 169.2 (CO_2Et), 202.5 (CO). MS, m/z (relative intensity): 170 (M^+, 0.4), 152 (0.5), 127 (20), 112 (0.2), 99 (11), 81 (13), 55 (21), 43 (100).

Ethyl 2-Acetyl-2-(2-propenyl)-4-pentenoate. ^{1}H NMR ($CDCl_3$): δ 1.26 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 2.13 (s, 3H, $COCH_3$), 2.57 (ddt, *J* = 14.4, 7.2 and 1.2 Hz, 2H, CH*H*), 2.64 (ddt, *J* = 14.4, 7.2 and 1.2 Hz, 2H, C*H*H), 4.20 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 5.06–5.14 (m, 4H, CH=CH_2), 5.52–5.66 (m, 2H, C*H*=CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.1 (OCH_2CH_3), 26.9 (CH_3CO), 35.9 (CH_2), 61.4 (OCH_2CH_3), 63.2 (CO*C*CO), 119.2 (CH=CH_2), 132.1 (CH=CH_2), 171.5 (CO_2Et). MS, m/z (relative intensity): 210 (M^+, 0.1), 181 (0.5), 168 (6), 137 (2), 123 (14), 95 (14), 79(13), 67(8), 43(100).

Ethyl 2-Acetyl-4-octenoate. ^{1}H NMR ($CDCl_3$): δ 0.84 (t, *J* = 7.5 Hz, 3H, CH_3), 1.25 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 1.33 (sextet, *J* = 7.4 Hz, 2H, CH_2), 1.92 (brq, *J* = 7.0 Hz, 2H, CH_2), 2.21 (s, 3H, $COCH_3$), 2.52 (m, *J* = 7.2 Hz, 2H, CH_2), 3.45 (t, *J* = 7.5 Hz, 1H, CH), 4.17 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 5.31 (dtt, *J* = 15.3, 6.9 and 1.2 Hz, 1H, C*H*=CH), 5.49 (ddt, *J* = 15.3, 6.6 and 1.2 Hz, 1H, CH=C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.5 (CH_3), 14.1 (OCH_2CH_3), 22.4 (CH_2), 29.1 (CH_3CO), 31.3 (CH_2), 34.5 (CH_2), 59.9 (CH), 61.3 (OCH_2CH_3), 125.4 (CH=CH), 133.7 (CH=CH), 169.4 (CO_2Et), 202.9 (CO). MS, m/z (relative intensity): 212 (M^+, 0.4), 169 (21), 139 (8), 95 (42), 81 (14), 55 (24), 43 (100).

Ethyl 2-Acetyl-5-phenyl-4-pentenoate. ^{1}H NMR ($CDCl_3$): δ 1.26 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 2.26 (s, 3H, $COCH_3$), 2.75 (t, *J* = 7.2 Hz, 1H, CH*H*), 2.75 (t, *J* = 7.2 Hz, 2H, C*H*H), 3.59 (t, *J* = 7.2 Hz, 1H, CH), 4.20 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 6.12 (dt, *J* = 15.6 and 7.2 Hz, 1H, PhCH=C*H*), 6.46 (d, *J* = 15.6 Hz, 1H, PhC*H*=CH), 7.18–7.34 (m, 5H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.1 (OCH_2CH_3), 29.2 (CH_3CO), 31.5 (CH_2), 59.5 (CH), 61.4 (OCH_2CH_3), 125.6 (Ph), 126.1 (Ph), 127.3 (Ph), 128.5 (PhCH=CH), 132.7 (PhCH=CH), 136.9 (Ph), 169.2 (CO_2Et), 202.4 (CO). MS, m/z (relative intensity): 246 (M^+, 8), 228 (6), 203 (14), 172 (12), 157 (49), 129 (24), 117 (22), 104 (5), 91 (33), 77 (7), 43 (100).

Ethyl 2-Acetyl-2-(3-phenyl-2-propenyl)-5-phenyl-4-pentenoate. ^{1}H NMR ($CDCl_3$): δ 1.27 (td, *J* = 7.2 Hz, 3H, OCH_2CH_3), 2.21 (s, 3H, $COCH_3$), 2.78 (dd, *J* = 14.4 and 7.5 Hz, 2H, CH*H*), 2.85 (dd, *J* = 14.4 and 7.5 Hz, 2H, C*H*H), 4.23 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 6.01 (dt, *J* = 15.6 and 7.5 Hz, 2H, PhCH=C*H*), 6.46 (d, *J* = 15.6 Hz, 2H, PhC*H*=CH) 7.18–7.34 (m, 10H,

Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.1 (OCH_2CH_3), 26.9 (CH_3CO), 35.7 (CH_2), 61.4 (OCH_2CH_3), 63.8 (COCCO), 123.7 (Ph), 126.2 (Ph), 127.5 (Ph), 128.5 (PhCH=CH), 134.1 (PhCH=CH), 136.9 (Ph), 171.5 (CO_2Et), 204.2 (CO). MS, m/z (relative intensity): 362 (M^+, 0.1), 344 (6), 288 (10), 245 (7), 199 (60), 171 (7), 157 (32), 141 (12), 128 (11), 117 (39), 91 (43), 43(100).

Ethyl 2-Ethoxycarbonyl-4-pentenoate. ^1H NMR ($CDCl_3$): δ 1.26 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 2.63 (tt, J = 7.0 and 1.5 Hz, 2H, CH_2) 3.41 (t, J = 7.5 Hz, 1H, CH), 4.19 (q, J = 7.2 Hz, 4H, OCH_2CH_3), 5.05 (ddt, J = 10.2, 1.5 and 1.5 Hz, 1H, *cis*-CH=CH*H*), 5.11 (ddt, J = 17.1, 1.5 and 1.5 Hz, 1H, *trans*-CH=C*H*H), 5.77 (ddt, J = 17.1, 10.2 and 6.8 Hz, 1H, C*H*=CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.1 (OCH_2CH_3), 32.8 (CH_2), 51.6 (CH), 61.4 (OCH_2CH_3), 117.5 (CH=CH_2), 134.0 (CH=CH_2), 168.9 (CO_2Et). MS, m/z (relative intensity): 200 (M^+, 0.4), 155 (8), 127 (100), 109 (95), 81 (83), 55 (65).

Ethyl 2-(2-propenyl)-2-cyclohexanonecarboxylate. ^1H NMR ($CDCl_3$): δ 1.23 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 1.37–2.67 (m, 10H, CH_2), 4.17 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 4.97–5.07 (m, 2H, CH=CH_2), 5.73 (m, 1H, C*H*=CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.1 (OCH_2CH_3), 22.4, 27.5, 35.7, 39.3, 41.1, 60.8 (COCCO), 61.2 (OCH_2CH_3), 118.2 (CH=CH_2), 133.3 (CH=CH_2), 171.4 (CO_2Et), 207.5 (CO). MS, m/z (relative intensity): 210 (M^+, 3), 182 (3), 164 (6), 141 (7), 137 (41), 119 (32), 108 (23), 93 (27), 79 (31), 67 (65), 41 (100).

Preparation of $[Pt_2(\mu\text{-}H)_2(DPCB)_2]^{2+}(OTf^-)_2$ (5'). The complex PtMe(OTf)(DPCB) (**7**)[2] (312 mg, 0.28 mmol) was dissolved in CH_2Cl_2 (10 mL; pretreated with water), and $HSiMe_2Ph$ (44 mL, 0.29 mmol) was added at room temperature. The color of the solution instantly changed from orange to dark red. GLC analysis revealed the formation of $PhMe_2SiOSiMe_2Ph$ (0.15 mmol) and methane (qualitative). The $^{31}P\{^1H\}$ NMR spectrum exhibited a set of signals assignable to the title compound. The solvent was removed by pumping, and the dark red solid was washed repeatedly with pentane, and dried under vacuum (160 mg, 52%). This product was spectroscopically pure, but satisfactory elemental analysis data was not obtained. Attempts to perform recrystallization were unsuccessful. ^1H NMR (CD_2Cl_2): δ –8.10 (quintet, $^1J_{PtH}$ = 521 Hz, $^2J_{PH}$ = 60 Hz, 2H, PtH), 1.45 (s, 36H, *t*-Bu(*p*)), 1.53 (s, 72H, *t*-Bu(*o*)), 6.88 (d, J = 8.2 Hz, 8H, *o*-Ph), 6.94 (t, J = 8.0 Hz, *m*-Ph), 7.22 (t, J = 6.6 Hz, 4H, *p*-Ph), 7.62 (br, 8H, PAr). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 152.4 (m, $^1J_{PtP}$ = 3455 Hz, $^3J_{PtP}$ = 342 Hz; see Figure 1).

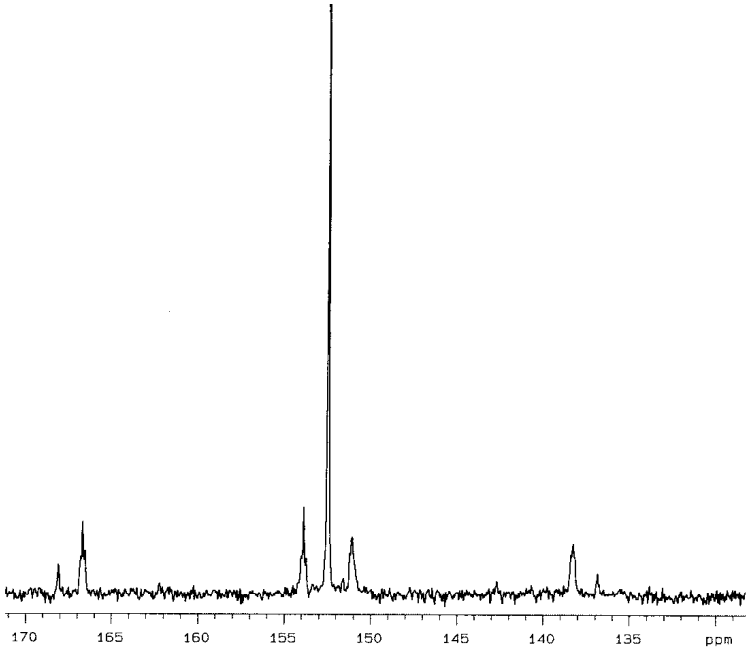


Figure 1. $^{31}P\{^{1}H\}$ NMR (121.49 MHz) spectrum of **5'** in CD_2Cl_2.

Preparation of [Pt(η^3-C_3H_5)(DPCB)]$^+$OTf$^-$ (8). Complex **7** (250 mg, 0.22 mmol) was dissolved in $ClCH_2CH_2Cl$ (5 mL; pretreated with water) at room temperature. 2-Propenyl alcohol (150 mL, 2.2 mmol) was added. Dimethylphenylsilane (35 mL, 0.23 mmol) was added to generate the hydridoplatinum complex. The resulting solution was stirred at 50 °C for 5 h. Volatile materials were removed by pumping at room temperature, and the residue was washed with Et_2O (3 mL) to give an orange precipitate. The crude product was dissolved in a minimum amount of CH_2Cl_2, layered with Et_2O (3 mL), and allowed to stand at room temperature to give a crystalline solid of **8** (168 mg, 67%). ^{1}H NMR (CD_2Cl_2): δ 1.45 (s, 18H, *t*-Bu(*p*)), 1.55 (s, 18H, *t*-Bu(*o*)), 1.64 (s, 18H, *t*-Bu(*o*)), 3.24 (t, J = 12.6 Hz, $^{2}J_{PtH}$ = 47.4 Hz, 2H, allylH(*anti*)), 4.71 (br, ^{2}JPtH = 10.1 Hz, 2H, allylH(*syn*)), 5.33 (tt, J = 12.6 and 6.8 Hz, $^{2}J_{PtH}$ = 66.6 Hz, 1H, allylH(*central*)), 6.88 (d, J = 8.2 Hz, 4H, *o*-Ph), 7.03 (t, J = 7.7 Hz, 4H, *m*-Ph), 7.32 (t, J = 7.3 Hz, 2H, *p*-Ph), 7.71 (d, J = 3.5 Hz, 2H, PAr), 7.72 (d, J = 3.5 Hz, 2H, PAr). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 31.4 (s, C*Me*$_3$), 33.8 (t, J = 4 Hz, C*Me*$_3$), 34.0 (t, J = 4 Hz, C*Me*$_3$), 36.0 (s, *C*Me$_3$), 39.0 (s, *C*Me$_3$), 39.2 (s, *C*Me$_3$), 64.8 (m, J = 37 Hz, $^{1}J_{PtC}$ = 125 Hz, allylC(1, 3)), 115.5 (t, J = 5 Hz, $^{1}J_{PtC}$ = 39 Hz, allylC(2)), 121.3 (q, $^{1}J_{FC}$ = 321 Hz, CF_3), 124.2 (d, J = 5 Hz, PAr), 124.2 (d, J = 5 Hz, PAr), 128.5 (t, J = 9 Hz, PAr), 128.5 (s, Ph), 129.2 (s, Ph), 129.2 (s, Ph), 132.0 (s, Ph), 152.9 (m, J = 57 and 32 Hz, P=C), 156.3 (s, PAr), 157.6 (s, $^{2}J_{PtC}$ = 16 Hz, PAr), 158.0 (s, $^{2}J_{PtC}$ = 14 Hz, PAr), 174.2 (dd, J = 67 and 12 Hz, P=C–*C*). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 133.6 (s, $^{1}J_{PtP}$ = 4549 Hz). Anal. Calcd for $C_{56}H_{73}F_3O_3P_2SPt$: C, 58.98 ; H, 6.45. Found: C, 58.35 ; H, 6.49

Preparation of [Pd(η^3-C_3H_5)(DPCB)]$^+$OTf$^-$ (1b). The complex PdMe(OTf)(DPCB) (**6**)[2] (51.3 mg, 50 mmol) was placed in a Schlenk tube and dissolved in CH_2Cl_2 (2 mL; pretreated with water) at room temperature. 2-Propenyl alcohol (4.1 mL, 60 mmol) and dimethylphenylsilane (7.7 mL, 50 mmol) were successively added. The color of the solution instantly changed from orange to red. GLC analysis revealed the formation of methane (qualitative) and $PhMe_2SiOSiMe_2Ph$ (25 mmol) in the system. The reaction solution was filtered through a filter-paper-tipped cannula and concentrated to dryness to give a yellow powder of **1b** (32.6 mg, 62%), which showed the NMR data identical with the authentic sample.[1]

References and Notes

(1) Minami, T.; Okamoto, H.; Ikeda, S.; Tanaka, R.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 4501.

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(3) The vinylic proton signals of the (*Z*)-isomer were obscured due to overlap with those of the (*E*)-isomer. However, the presence of the (*Z*)-isomer was clearly indicated by GLC and $^{13}C\{^1H\}$ NMR spectroscopy.

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