Development of Chiral Pincer Palladium Complexes Bearing a Pyrroloimidazolone Unit. Catalytic Use for Asymmetric Michael Addition

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SUPPORTING INFORMATION

General: All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. NMR spectra were recorded on a JEOL JNM-AL400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P), JEOL JNM-AL500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C), or JEOL JNM-LA500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are given relative to $CDCl_3$ as an internal standard (*d* 77.0). The ^{31}P NMR data are reported relative to external 85 % H_3PO_4. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted. FAB mass spectra were recorded on a JEOL JMS-777V spectrometer; 3-nitrobenzyl alcohol was used as the matrix. Melting points were determined using a Yanaco micro melting point apparatus MP-J3 and are uncorrected. Optical rotations were measured on a JASCO P-1020 polarimeter. GC analysis was carried out on a Hewlett Packard 4890 system with a chiral stationary phase column, Cyclodex CB. Commercially available reagents were used without any purification. 5-*tert*-Butyl-1,3-diformyl-2-hydroxybenzene[1] and $Pd_2(dba)_3{\cdot}CHCl_3$[2] were prepared by the literature methods. Anilides **6** and **7** were prepared by the methods reported by our laboratory.[3] Isopropyl 2-cyanopropionate (**9a**) and diisopropylmethyl 2-cyanopropionate (**9c**) were prepared according to procedures in the literature. [4]

4-*tert*-Butyl-2,6-diformylphenyl trifluoromethanesulfonate. To a solution of 5-*tert*-butyl-1,3-diformyl-2-hydroxybenzene[1] (1.72 g, 8.34 mmol) and pyridine (1.20 mL, 14.8 mmol) in 50 mL of CH_2Cl_2 was added trifluoromethanesulfonic anhydride (1.80 ml, 10.7 mmol) dropwise at 0 °C over 10 min. The reaction mixture was warmed to room temperature and stirred for 30 min. The solution was cooled to 0 °C and quenched with 40 mL of 1.5 M HCl. After separation, the aqueous phase was extracted twice with CH_2Cl_2 (30 mL) and the combined extract was dried over Na_2SO_4. The organic phase was passed through a short plug of silica gel, which was then washed with CH_2Cl_2 (100 mL). The filtrates were concentrated under reduced pressure and the crude product was recrystallized from hexane to give the title compound (2.63 g, 93%) as a white crystalline solid. Mp: 69–70 °C. MS (EI): *m/z* 338 ($[M]^+$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.35 (s, 9H, C*H*$_3$), 8.22 (s, 2H, Ar*H*), 10.24 (s, 2H, C*H*O); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 31.1 (C(*C*H$_3$)$_3$), 35.5 (*C*(CH$_3$)$_3$), 118.4 (q, $^1J_{CF}$ = 320 Hz, O$_3$S*C*F$_3$), 129.2 (Ar*C* attached to CHO), 132.4 (Ar*C*), 147.0 (Ar*C* attached to *t*-Bu), 153.2 (Ar*C* attached to OTf), 185.3 (*C*HO). Anal. Calcd for $C_{13}H_{13}F_3O_5S$: C, 46.15; H, 3.87; S, 9.48. Found: C, 45.89; H, 3.87; S, 9.64.

***trans*-(4-*tert*-Butyl-2,6-diformylphenyl)chloro-bis(triphenylphosphine)palladium (5).** 4-*tert*-Butyl-2,6-diformylphenyl trifluoromethanesulfonate (2.03 g, 6.00 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$[2] (3.11 g, 3.00 mmol), and triphenylphosphine (3.15 g, 12.0 mmol) were dissolved in 60 mL of CH_2Cl_2, which was stirred at room temperature for 4 h. After removal of the solvent, the residue and LiCl (2.73 g, 64 mmol) were suspended in a mixture of acetone (50 mL) and water (10 mL). The reaction mixture was stirred at room temperature for 10 h and then concentrated under reduced pressure. The residue was dissolved in 100 mL of $CHCl_3$, which was washed with water (50 mL x 2) and brine (50 mL), and dried over Na_2SO_4. After evaporation of the solvent, the resulting solid was recrystallized from MeCN to afford **5** (4.71 g, 92%) as a yellow crystal. Mp: 226–229 °C (dec.). MS (FAB): *m/z* 819 ($[M - Cl]^+$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.16 (s, 9H, C*H*$_3$), 7.15 (s, 2H, Ar*H*), 7.22 (t, 12H, $^3J_{HH}$ = 7.6 Hz, *m*-Ph*H*), 7.30 (t, 6H, $^3J_{HH}$ = 7.2 Hz, *p*-Ph*H*), 7.50 (dd, 12H, *o*-Ph*H*), 10.40 (s, 2H, C*H*O); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 31.3 (C(*C*H$_3$)$_3$), 34.1 (*C*(CH$_3$)$_3$), 127.9 (virtual t, $|^2J_{CP} + {}^4J_{CP}|$= 5.3 Hz, *o*-Ph*C*), 129.7 (virtual t, $|^1J_{CP} + {}^3J_{CP}|$= 23.9 Hz, *ipso*-Ph*C*), 129.9 (*p*-Ph*C*), 132.4 (Ar*C*), 134.1 (virtual t, $|^3J_{CP} + {}^5J_{CP}|$= 6.3 Hz, *m*-Ph*C*), 140.9 (Ar*C*

attached to CHO), 146.7 (Ar*C* attached to *t*-Bu), 172.4 (t, $^2J_{CP}$ = 6.2 Hz, Ar*C* attached to Pd), 194.7 (*C*HO); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 22.5 (s). Anal. Calcd for $C_{48}H_{43}ClO_2P_2Pd{\cdot}CH_3CN$: C, 66.97; H, 5.17; N, 1.56. Found: C, 67.04; H, 5.17; N, 1.53.

[4-*tert*-Butyl-2,6-bis{(3*R*,7a*S*)-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*]imidazole-1-on-3-yl}phenyl]chloro-palladium (1-Cl). The palladium complex **5** (1.71 g, 2.00 mmol) and the anilide **6**[3] (3.80 g, 20 mmol) were suspended in 60 mL of MeCN. The suspension was refluxed under an O_2 atmosphere for 94 h (until it turned to a clear solution) and then allowed to cool to room temperature. After removal of the solvent, the crude product was treated with MeOH and ether. The resulting yellow powder was filtered, washed with ether, and dried in vacuo to give **1-Cl** (1.33 g, 98%). Mp: 263–265 °C (dec.). MS (FAB): *m/z* 639 ($[M - Cl]^+$). $[\alpha]_D^{24}$ –161 (*c* 1.0, CH_2Cl_2). ^1H NMR ($CDCl_3$, 500 MHz): δ 0.70 (s, 9H, C*H*$_3$), 1.81 (m, 2H), 2.17 (m, 2H), 2.39 (m, 2H), 2.60 (m, 2H), 3.56 (m, 2H), 4.23 (m, 2H), 5.13 (dd, 2H, $^3J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 1.9 Hz, bridge-head C*H*), 5.87 (s, 2H), 6.15 (s, 2H), 7.20 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *o*-Ph*H*), 7.32 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph*H*), 7.41 (t, 4H, $^3J_{HH}$ = 7.8 Hz, *m*-Ph*H*); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 23.5 (*C*H$_2$ in pyrroloimidazolone ring), 29.2 (*C*H$_2$ in pyrroloimidazolone ring), 30.7 (C(*C*H$_3$)$_3$), 34.2 (*C*(CH$_3$)$_3$), 63.6 (N-*C*H$_2$), 71.3 (bridge-head *C*H), 94.4 (N-*C*H-N), 121.5 (*p*-Ph*C*), 126.6 (*o*-Ph*C*), 128.0 (Ar*C*), 129.5 (*m*-Ph*C*), 134.9 (*ipso*-Ph*C*), 144.6 (Ar*C* attached to pyrroloimidazolone ring), 146.7 (Ar*C* attached to *t*-Bu), 150.0 (Ar*C* attached to Pd), 170.2 (*C*=O). Anal. Calcd for $C_{34}H_{37}ClN_4O_2Pd$: C, 60.45; H, 5.52; N, 8.29. Found: C, 60.30; H, 5.74; N, 8.03.

[4-*tert*-Butyl-2,6-bis{(3*R*,6*R*,7a*S*)-6-hydroxy-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*]imidazole-1-on-3-yl}phenyl]chloropalladium (2-Cl). Following the procedure described for the preparation of **3**, the reaction of the palladium complex **5** (855 mg, 1.00 mmol) with the anilide **7**[3] (2.83 g, 9.84 mmol) in 40 mL of MeCN under an O_2 atmosphere for 136 h gave **2-Cl** (617 mg, 87%) as yellow needles after trituration of the crude product with EtOAc and hexane. Mp: 204–205 °C (dec.). MS (FAB): *m/z* 671 ($[M - Cl]^+$). $[\alpha]_D^{22}$ –180 (*c* 1.0, CH_2Cl_2). ^1H NMR (DMSO-d_6, 500 MHz): δ 0.70 (s, 9H, C*H*$_3$), 2.59 (m, 2H), 3.72 (dd, 2H, $^3J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 6.9 Hz), 4.06 (dd, 2H, $^3J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 6.9 Hz), 4.50 (m, 2H), 5.13 (dd, 2H, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 3.4 Hz), 5.22 (d, 2H, $^3J_{HH}$ = 8.1 Hz), 6.03 (s, 2H), 6.17 (s, 2H), 7.23 (d, 4H, $^3J_{HH}$ = 8.1 Hz, *o*-Ph*H*), 7.33 (t, 2H, $^3J_{HH}$ = 7.6 Hz, *p*-Ph*H*), 7.41 (t, 4H, $^3J_{HH}$ = 7.6 Hz, *m*-Ph*H*); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 125 MHz): δ 30.3 (C(*C*H$_3$)$_3$), 33.8 (*C*(CH$_3$)$_3$), 36.4 (*C*H$_2$ in pyrroloimidazolone ring), 67.7 (N-*C*H$_2$), 68.1 (*C*H in pyrroloimidazolone ring), 69.7 (*C*H in pyrroloimidazolone ring), 93.8 (N-*C*H-N), 121.3 (*p*-Ph*C*), 126.1 (*o*-Ph*C*), 127.6 (Ar*C*), 129.0 (*m*-Ph*C*), 134.3 (*ipso*-Ph*C*), 143.3 (Ar*C* attached to pyrroloimidazolone ring), 146.4 (Ar*C* attached to *t*-Bu), 149.7 (Ar*C* attached to Pd), 168.9 (*C*=O). Anal. Calcd for $C_{34}H_{37}ClN_4O_4Pd{\cdot}H_2O$: C, 56.28; H, 5.42; N, 7.72. Found: C, 56.12; H, 5.37; N, 7.69.

[4-*tert*-Butyl-2,6-bis{(3*R*,7a*S*)-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*]imidazole-1-on-3-yl}phenyl](tri-fluoromethanesulfonato)palladium (1-OTf). A suspension of the chloride complex **1-Cl** (338 mg, 0.500 mmol) and silver trifluoromethanesulfonate (188 mg, 0.732 mmol) in a mixture of CH_2Cl_2 (19.8 mL) and water (0.2 mL) was stirred at room temperature for 16 h. The resulting white precipitate (silver chloride) was removed by filtration through Celite and washed with additional CH_2Cl_2. The combined filtrate and washings were evaporated in vacuo to give a yellow powder. The crude product was purified by re-precipitation from $CHCl_3$ and hexane to afford **1-OTf** (375 mg, 95%) as a white powder. Mp: 245–246 °C (dec.). MS (FAB): *m/z* 639 ($[M - OTf]^+$). $[\alpha]_D^{25}$ –130 (*c* 0.52, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.68 (s, 9H, C*H*$_3$), 1.83 (m, 2H), 2.14 (m, 2H), 2.38 (m, 2H), 2.59 (m, 2H), 3.63 (m, 2H), 3.99 (m, 2H), 4.94 (dd, 2H, $^3J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 2.0 Hz, bridge-head C*H*), 5.74 (s, 2H), 6.10 (s, 2H), 7.12 (dd, 4H, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 1.2 Hz, *o*-Ph*H*), 7.34 (tt, 2H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 1.2 Hz, *p*-Ph*H*), 7.40 (tt, 4H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 1.2 Hz, *m*-Ph*H*); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 23.4 (*C*H$_2$ in pyrroloimidazolone ring), 29.2 (*C*H$_2$ in pyrroloimidazolone ring), 30.6 (C(*C*H$_3$)$_3$), 34.2 (*C*(CH$_3$)$_3$), 62.7 (N-*C*H$_2$), 70.4 (bridge-head *C*H), 93.4 (N-*C*H-N), 119.9 (q, $^1J_{CF}$ = 318 Hz, O_3SCF_3), 122.1 (*p*-Ph*C*), 127.1 (*o*-Ph*C*), 128.4 (Ar*C*), 129.5 (*m*-Ph*C*), 134.1 (*ipso*-Ph*C*), 143.8 (Ar*C* attached to Pd), 144.6 (Ar*C* attached to pyrroloimidazolone ring), 147.2 (Ar*C* attached to *t*-Bu), 169.6 (*C*=O). Anal. Calcd for $C_{35}H_{37}F_3N_4O_5PdS$: C, 53.27; H, 4.73; N, 7.10. Found: C, 53.23; H, 4.72; N, 6.99.

[4-*tert*-Butyl-2,6-bis{(3*R*,6*R*,7a*S*)-6-hydroxy-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*]imidazole-1-on-3-yl}phenyl](trifluoromethanesulfonato)palladium (2-OTf). Following the procedure described for the preparation of **1-OTf**, reaction of the chloride complex **2-Cl** (177 mg, 0.250 mmol) with silver trifluoromethanesulfonate (81.2 mg, 0.316 mmol) in a mixture of CH_2Cl_2 (19.8 mL) and water (0.2 mL) at room temperature for 15 h gave **2-OTf** (198 mg, 94%) as an off-white powder after trituration of the crude product with EtOAc and ether. Mp: 197–198 °C (dec.). MS (FAB): *m/z* 671 ($[M - OTf]^+$). $[\alpha]_D^{25}$ –178 (*c* 0.52, MeOH). ^1H NMR (CD_3OD, 400 MHz): δ 0.71 (s, 9H, C*H*$_3$), 2.35 (m, 2H), 2.58 (m, 2H), 3.87 (m, 4H), 4.72 (m, 2H), 4.80 (dd, 2H, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 7.2 Hz), 6.23 (s, 2H), 6.31 (s, 2H), 7.22 (dd, 4H, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 1.6 Hz, *o*-Ph*H*), 7.34 (tt, 2H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 1.2 Hz, *p*-Ph*H*), 7.41 (tt, 4H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 1.2 Hz, *m*-Ph*H*); $^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): δ 31.2 (C(*C*H$_3$)$_3$), 35.2 (*C*(CH$_3$)$_3$), 37.2 (*C*H$_2$ in pyrroloimidazolone ring), 68.9 (N-*C*H$_2$), 70.6 (*C*H in pyrroloimidazolone ring), 70.9 (*C*H in pyrroloimidazolone ring), 94.5 (N-*C*H-N), 121.7 (q, $^1J_{CF}$ = 318 Hz, O_3SCF_3), 123.6 (*p*-Ph*C*), 128.0 (*o*-Ph*C*), 129.3 (Ar*C*), 130.4 (*m*-Ph*C*), 135.6 (*ipso*-Ph*C*), 145.3 (Ar*C* attached to pyrroloimidazolone ring), 146.9 (Ar*C* attached to Pd), 148.8 (Ar*C* attached to *t*-Bu), 170.5 (*C*=O). Anal. Calcd for $C_{35}H_{37}F_3N_4O_7PdS{\cdot}H_2O$: C, 50.09; H, 4.68; N, 6.68. Found: C, 50.23; H, 4.75; N, 6.48.

[4-*tert*-Butyl-2,6-bis{(3*R*,6*R*,7a*S*)-6-methoxy-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*]imidazole-1-on-3-yl}phenyl](trifluoromethanesulfonato)palladium (3-OTf). To a solution of the chloride complex **2-Cl** (70.8 mg, 0.100 mmol) in 10 mL of THF cooled to 0 °C was added potassium *tert*-butoxide (45.0 mg, 0.401 mmol), which was warmed to room temperature and stirred for 1.5 h. The solution was again cooled to 0 °C and quenched with methyl iodide (0.15 mL, 2.4 mmol). After stirring at room temperature for 3 h, the solvent and an excess of methyl iodide were removed by evaporation. The resulting residue was dissolved in CH_2Cl_2 (20 mL), which was washed with water (20 mL). After separation, the aqueous phase was extracted twice with CH_2Cl_2 (20 mL) and the combined extract was dried over Na_2SO_4 and $Na_2S_2O_3$. The solution was evaporated to give a yellow sludge. The residue and silver trifluoromethanesulfonate (40.9 mg, 0.159 mmol) were suspended in a mixture of CH_2Cl_2 (9.9 mL) and water (0.1 mL), which was stirred at room temperature for 12 h. The resulting yellow precipitate (silver iodide) was removed by filtration through Celite and washed with additional CH_2Cl_2. After evaporation of the solvent, the crude product was chromatographed on silica gel (eluent: CH_2Cl_2/MeOH = 200/1) and then triturated with hexane to afford **3-OTf** (64.8 mg, 76% for 2 steps) as a yellow powder. Mp: 176–178 °C (dec.). MS (FAB): *m/z* 699 ($[M - OTf]^+$). $[\alpha]_D^{25}$ –132 (*c* 0.53, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.77 (s, 9H, C(C*H*$_3$)$_3$), 2.59 (m, 2H), 2.89 (m, 2H), 3.42 (s, 6H, OC*H*$_3$), 3.57 (dd, 2H, $^3J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7.5 Hz), 4.16 (m, 2H), 4.23 (d, 2H, $^3J_{HH}$ = 14.0 Hz), 4.88 (d, 2H, $^3J_{HH}$ = 8.5 Hz), 6.30 (s, 2H), 6.43 (br s, 2H), 7.31 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph*H*), 7.45 (t, 4H, $^3J_{HH}$ = 8.0 Hz, *m*-Ph*H*), 7.50 (d, 4H, $^3J_{HH}$ = 8.0 Hz, *o*-Ph*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 30.8 (C(*C*H$_3$)$_3$), 33.1 (*C*H$_2$ in pyrroloimidazolone ring), 34.5 (*C*(CH$_3$)$_3$), 57.8 (OCH$_3$), 65.0 (N-*C*H$_2$), 70.6 (*C*H in pyrroloimidazolone ring), 78.6 (*C*H in pyrroloimidazolone ring), 90.0 (N-*C*H-N), 120.5 (q, $^1J_{CF}$ = 319 Hz, O$_3$S*C*F$_3$), 121.0 (*p*-Ph*C*), 123.5 (Ar*C*), 127.1 (*o*-Ph*C*), 129.4 (*m*-Ph*C*), 135.3 (*ipso*-Ph*C*), 141.9 (Ar*C* attached to pyrroloimidazolone ring), 148.8 (Ar*C* attached to *t*-Bu), 168.3 (*C*=O); Ar*C* attached to Pd was not observed. Anal. Calcd for $C_{37}H_{41}F_3N_4O_7PdS$: C, 52.33; H, 4.87; N, 6.60. Found: C, 52.01; H, 5.27; N, 6.31.

[4-*tert*-Butyl-2,6-bis{(3*R*,6*R*,7a*S*)-6-*tert*-butyldimethylsilyloxy-2-phenylhexahydro-1*H*-pyrrolo[1,2-*c*]imidazole-1-on-3-yl}phenyl](trifluoromethanesulfonato)palladium (4-OTf). To a solution of the complex **2-Cl** (283 mg, 0.399 mmol) and imidazole (223 mg, 3.28 mmol) in 4.0 mL of DMF was added *tert*-butyldimethylsilyl chloride (306 mg, 2.03 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and then quenched with 40 mL of saturated aqueous $NaHCO_3$. The reaction mixture was extracted three times with $CHCl_3$ (40 mL) and the combined extract was dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (eluent: CH_2Cl_2/MeOH = 200/1), followed by recrystallization from a EtOAc–hexane mixture to give the corresponding chloride complex (321 mg, 86%) as a pale-yellow crystalline solid. Mp: 254–256 °C (dec.). MS (FAB): *m/z* 899 ($[M - Cl]^+$). $[\alpha]_D^{22}$ –105 (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.10 (s, 6H, SiC*H*$_3$), 0.11 (s, 6H, SiC*H*$_3$), 0.68 (s, 9H, C(C*H*$_3$)$_3$), 0.90 (s, 18H, SiC(C*H*$_3$)$_3$), 2.53 (t, 4H, $^3J_{HH}$ = 8.0 Hz), 3.62 (dd, 2H, $^3J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 6.0 Hz), 4.02 (t, 2H, $^3J_{HH}$ = 11.6 Hz), 4.41 (m, 2H), 5.36 (t, 2H, $^3J_{HH}$ = 6.4 Hz), 5.66 (s, 2H), 6.12 (s, 2H), 7.06 (d, 4H, $^3J_{HH}$ = 7.2 Hz, *o*-Ph*H*), 7.33 (t, 2H, $^3J_{HH}$ = 7.2 Hz, *p*-Ph*H*), 7.39 (t, 4H, $^3J_{HH}$ = 7.2 Hz, *m*-Ph*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ –4.8 (SiCH$_3$), –4.5 (SiCH$_3$), 18.1 (Si*C*(CH$_3$)$_3$), 25.7 (SiC(*C*H$_3$)$_3$), 30.7 (C(*C*H$_3$)$_3$), 34.2 (*C*(CH$_3$)$_3$), 37.4 (*C*H$_2$ in pyrroloimidazolone ring), 67.1 (N-*C*H$_2$), 68.2 (*C*H in pyrroloimidazolone ring), 69.3 (*C*H in pyrroloimidazolone ring), 95.6 (N-*C*H-N), 121.9 (*p*-Ph*C*), 127.5 (*o*-Ph*C*), 128.3 (Ar*C*), 129.4 (*m*-Ph*C*), 134.0 (*ipso*-Ph*C*), 144.2 (Ar*C* attached to pyrroloimidazolone ring), 146.0 (Ar*C* attached to *t*-Bu), 152.0 (Ar*C* attached to Pd), 169.6 (*C*=O). Anal. Calcd for $C_{46}H_{65}ClN_4O_4PdSi_2$: C, 59.02; H, 7.00; N, 5.99. Found: C, 59.04; H, 7.07; N, 5.97; Following the procedure described for the preparation of **1-OTf**, reaction of the chloride complex (187 mg, 0.200 mmol) with silver trifluoromethanesulfonate (62.4 mg, 0.243 mmol) in a mixture of CH_2Cl_2 (19.8 mL) and water (0.2 mL) at room temperature for 24 h gave **4-OTf** (206 mg, 97%) as a white powder after trituration of the crude product with ether and hexane. Mp: 201–203 °C (dec.). MS (FAB): *m/z* 899 ($[M - OTf]^+$). $[\alpha]_D^{25}$ –97 (*c* 0.52, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.12 (s, 12H, SiC*H*$_3$), 0.73 (s, 9H, C(C*H*$_3$)$_3$), 0.89 (s, 18H, SiC(C*H*$_3$)$_3$), 2.55 (m, 2H), 2.87 (dd, 2H, $^3J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 8.2 Hz), 3.56 (dd, 2H, $^3J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7.7 Hz), 4.05 (dd, 4H, $^3J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 3.2 Hz), 4.91 (d, 2H, $^3J_{HH}$ = 9.0 Hz), 6.26 (s, 2H), 6.29 (br s, 2H), 7.29 (br m, 2H, *p*-Ph*H*), 7.43 (br m, 8H, *o*- and *m*-Ph*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ –4.7 (SiCH$_3$), –4.6 (SiCH$_3$), 18.4 (Si*C*(CH$_3$)$_3$), 25.9 (SiC(*C*H$_3$)$_3$), 30.8 (C(*C*H$_3$)$_3$), 34.5 (*C*(CH$_3$)$_3$), 36.4 (*C*H$_2$ in pyrroloimidazolone ring), 67.2 (N-*C*H$_2$), 70.1 (*C*H in pyrroloimidazolone ring), 70.5 (*C*H in pyrroloimidazolone ring), 90.2 (N-*C*H-N), 120.4 (q, $^1J_{CF}$ = 319 Hz, O$_3$S*C*F$_3$), 121.2 (*p*-Ph*C*), 123.6 (Ar*C*), 127.2 (*o*-Ph*C*), 129.4 (*m*-Ph*C*), 135.2 (*ipso*-Ph*C*), 141.2 (Ar*C* attached to Pd), 142.1 (Ar*C* attached to pyrroloimidazolone ring), 148.7 (Ar*C* attached to *t*-Bu), 168.5 (*C*=O). Anal. Calcd for $C_{47}H_{65}F_3N_4O_7PdSSi_2 \cdot H_2O$: C, 52.87; H, 6.32; N, 5.25. Found: C, 53.02; H, 6.30; N, 5.31.

General Procedure for the Michael Reactions. To a solution of the catalyst (0.005 equiv.) in either toluene or benzene (2.0 mL) were added the cyano ester (1.0 equiv.), the Michael acceptor (1.5 equiv.), and finally Hünig's base (0.1 equiv.). The reaction mixture was stirred at 25 °C for an appropriate time. After removal of the solvent, the residue was purified by Kugelrohr distillation to give the desired product.

Ethyl 2-cyano-2-methyl-5-oxohexanoate (10a). Colorless oil. $[\alpha]_D^{25}$ –3.71 (*c* 1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.34 (t, 3H, $^3J_{HH}$ = 7.2 Hz, C*H*$_3$), 1.61 (s, 3H, –C(CN)C*H*$_3$), 2.02–2.28 (m, 2H, –C*H*$_2$–), 2.19 (s, 3H, –C(O)C*H*$_3$), 2.56–2.75 (m, 2H, –C*H*$_2$–), 4.27 (q, 2H,

$^3J_{HH}$ = 7.2 Hz, –OCH_2CH$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 14.0, 23.5, 30.0, 31.5, 39.1, 43.0, 62.9, 119.4, 168.7, 205.6. The enantiomeric excess was determined by GC analysis using a chiral stationary phase column (Cyclodex CB) to be 81% ee. The absolute configuration was assigned on the basis of the optical rotation.[4]

Isopropyl 2-cyano-2-methyl-5-oxohexanoate (10b). Colorless oil. $[\alpha]_D^{25}$ –4.07 (*c* 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.31 (d, 3H, $^3J_{HH}$ = 6.0 Hz, –OCH(CH_3)$_2$), 1.32 (d, 3H, $^3J_{HH}$ = 6.0 Hz, –OCH(CH_3)$_2$), 1.56 (s, 3H, –C(CN)CH_3), 2.02–2.25 (m, 2H, –CH_2–), 2.19 (s, 3H, –C(O)CH_3), 2.56–2.73 (m, 2H, –CH_2–), 5.07 (sept, 1H, $^3J_{HH}$ = 6.0 Hz, –OCH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 21.6, 21.7, 23.6, 30.1, 31.5, 39.2, 43.3, 70.9, 119.3, 167.9, 205.3. The enantiomeric excess was determined by GC analysis using a chiral stationary phase column (Cyclodex CB) to be 80% ee. The absolute configuration was assigned on the basis of the optical rotation.[4]

Diisopropylmethyl 2-cyano-2-methyl-5-oxohexanoate (10c). Colorless oil. $[\alpha]_D^{26}$ –0.43 (*c* 1.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.83–0.88 (m, 12H, –OCH(CH(CH_3)$_2$)$_2$), 1.56 (s, 3H, –C(CN)CH_3), 1.91–1.95 (m, 2H, –OCH(CH(CH$_3$)$_2$)$_2$), 1.96–2.20 (m, 2H, –CH_2–), 2.12 (s, 3H, –C(O)CH_3), 2.52–2.67 (m, 2H, –CH_2–), 4.59 (t, 1H, $^3J_{HH}$ = 6.0 Hz, –OCH(CH(CH$_3$)$_2$)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 17.1. 17.2, 19.6, 19.7, 24.0, 29.4, 29.5, 30.0, 31.3, 39.3, 43.4, 86.0, 119.3, 168.5, 205.2. The enantiomeric excess was determined by GC analysis using a chiral stationary phase column (Cyclodex CB) to be 82% ee. The absolute configuration was assigned on the basis of the optical rotation.[4]

Isopropyl 2-cyano-2-methyl-5-oxoheptanoate (12). Colorless oil. $[\alpha]_D^{26}$ –4.13 (*c* 1.06, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.07 (t, 3H, $^3J_{HH}$ = 7.3 Hz, –C(O)CH$_2$CH_3), 1.31 (d, 3H, $^3J_{HH}$ = 6.0 Hz, –OCH(CH_3)$_2$), 1.32 (d, 3H, $^3J_{HH}$ = 6.0 Hz, –OCH(CH_3)$_2$), 1.60 (s, 3H, –C(CN)CH_3), 2.03–2.26 (m, 2H, –CH_2–), 2.47 (q, 3H, $^3J_{HH}$ = 7.3 Hz, –C(O)CH_2CH$_3$), 2.52–2.67 (m, 2H, –CH_2–), 5.07 (sept, 1H, $^3J_{HH}$ = 6.0 Hz, –OCH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 7.87, 21.5, 21.6, 23.5, 31.6, 36.1, 37.9, 43.3, 70.9, 119.3, 167.9, 208.0. The enantiomeric excess was determined by GC analysis using a chiral stationary phase column (Cyclodex CB) to be 83% ee. The absolute configuration was assigned on the basis of the optical rotation.[4]

X-ray structure determination. A single crystal suitable for X-ray structure analysis was obtained by cooling a hot solution of **1**-Cl in toluene. The data were collected on a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71070 Å) at a temperature of 173 K. The structure was solved by direct methods (SIR97[5]) and expanded using Fourier techniques (DIRDIF99). The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using the riding model. Neutral atom scattering factors were taken from Cromer and Waber.[6] Anomalous dispersion effects were included in Fcalc.[7] All calculations were performed using the CrystalStructure[8] crystallographic software package. Crystal data of **1**-Cl•toluene: $C_{41}H_{45}ClN_4O_2Pd$, orthorhombic, $P2_12_12_1$ (No. 19), *a*= 12.2613 (5) Å, *b* = 12.4185 (5) Å, *c* = 23.9133 (11) Å, *V* = 3641.2 (3) Å^3, *Z* = 4, *R*1 = 0.023, *wR*2 = 0.060, GOF = 0.94.

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