Ortho-Phenylene-Bridged Cp/Amido Titanium Complexes for Ethylene/1-Hexene Copolymerization

Dae Joon Cho,[a] *Chun Ji Wu,*[a] *Sujith S,*[a] *Won-Sik Han,*[b] *Sang Ook Kang,*[b] *and Bun Yeoul Lee**[a]

[a]Department of Molecular Science and Technology, Ajou University, Suwon 443-749 Korea and
[b]Department of Chemistry, Korea University, 208 Seochang, Chochiwon, Chung-nam, 339-700, Korea

Supporting Information

General Remarks. All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Toluene, pentane, hexane, THF, and C_6D_6 were distilled from benzophenone ketyl. Toluene used for polymerization reactions was purchased from Aldrich (anhydrous grade) and purified further over Na/K alloy. Water used for the Suzuki-coupling was degassed by bubbling of nitrogen gas for 30 minutes. Dimethoxyethane (DME) used for the Suzuki-coupling was degassed by repeating the evacuation at -78 ^oC and the warming to room temperature three times. Ethylene was purchased from Conley Gas (99.9 %) and purified by contacting with molecular sieves and copper. NMR spectra were recorded on a Varian Mercury plus 400 or Bruker spectrometer. Elemental analyses were carried out at the Inter-University Center Natural Science Facilities, Seoul National University. Gel permeation chromatograms (GPC) were obtained at 140 ^oC in trichlorobenzene using Waters Model 150-C+ GPC and the data were analyzed using a polystyrene analyzing curve. 3,4-Dimethyl-2-cyclopenten-1-one,[1] compound **4f**,[2] 4,4'-methylenebis(2-bromoaniline),[3] and 4,4"-diamino-*o*-terphenyl[4] were prepared by the literature methods.

2-Bromo-3,4-dimethyl-2-cyclopenten-1-one (1). 3,4-Dimethyl-2-cyclopenten-1-one (56.0 g, 0.507 mol) was dissolved in CH_2Cl_2 (500 mL) in 2.0 L three neck flask. The solution was cooled to 0 ^oC with an ice bath. Bromine (81.2 g, 0.507 mol) dissolved in CH_2Cl_2 (500 mL) was added dropwise for 2 hours while keeping the temperature below 5 ^oC. The solution was stirred until its color became pale yellow from light red (~2 hours). Triethylamine (61.7 g, 0.610 mol) was added dropwise while keeping the temperature below 5 ^oC. The solution was allowed to warm to room temperature and stirred overnight. Aqueous HCl solution (1.0 N, 320 mL) was added and the mixture was stirred for 30 min. The mixture was transferred to a separatory funnel and the aqueous layer was removed. The organic layer was washed with saturated aqueous $NaHCO_3$ solution (300 mL). Solvent was removed by rotary evaporator to give a residue which was dissolved in diethyl ether (300 mL). The etheral solution was washed with water (300 mL × 2) to remove any residual HBr salt of triethylamine. After the etheral solution was dried over anhydrous $MgSO_4$, solvent was removed with rotary evaporator to give a residue, which was distilled under reduced pressure (64 ^oC/0.5 torr) to give colorless oil (60.1 g, 63 %). ^1H NMR ($CDCl_3$): δ 1.25 (d, J = 6.8 Hz, 3H, CH_3), 2.15 (dd, J = 18.8, 8.8 Hz, 1H, CH_2), 2.16 (s, 3H, CH_3), 2.78 (dd, J = 18.8, 2.0 Hz, 1H, CH_2), 2.87–2.94 (m, 1H, CH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.03, 19.04, 38.45, 41.80, 122.82 (C=C), 177.06 (C=C), 200.15 (C=O) ppm.

2-Bromo-3,4-dimethyl-2-cyclopenten-1-one ethylene ketal (2). 2-Bromo-3,4-dimethyl-2-cyclopenten-1-one (60.0 g, 0.317 mol), ethylene glycol (138 g, 2.22 mol), and triethyl orthoformate (142 g, 0.952 mol) were mixed in 1.0 L flask. *p*-Toluenesulfonic acid monohydrate (3.02 g, 15.9 mmol) was added and the solution was stirred overnight at room temperature. Saturated aqueous $NaHCO_3$ (300

mL) was added and the product was extracted with hexane (300 mL × 4). The hexane phase was washed with water (300 mL × 3) and dried over anhydrous $MgSO_4$. Solvent was removed by rotary evaporator to give a residue which was distilled under full vacuum (0.5 torr). Unreacted triethyl orthoformate was distilled off at ~ 42 ^oC and the product was collected at ~ 62 ^oC (57.0 g, 77 %). In some cases, abrupt decomposition of the product to black shoot was observed during distillation. Addition of solid K_2CO_3 (0.8 g) to the distillation pot consistently blocked the decomposition. ^1H NMR ($CDCl_3$): δ 1.13 (d, J = 6.8 Hz, 3H, CH_3), 1.76. (dd, J = 13.6, 4.4 Hz, 1H, CH_2), 1.79 (s, 3H, CH_3), 2.41 (dd, J = 13.6, 8.0 Hz, 1H, CH_2), 2.60–2.68 (m, 1 H, CH), 3.94-4.01 (m, 2H, CH_2O), 4.16-4.21 (m, 2H, CH_2O) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.14, 19.11, 38.74, 42.91, 65.24 (C-O), 65.43 (C-O), 116.37 (C=C), 118.93 (C=C), 147.72 (OCO) ppm.

2-(Dihydroxyboryl)-3,4-dimethyl-2-cyclopenten-1-one (3). To a Schlenk flask containing 2-bromo-3,4-dimethyl-2-cyclopenten-1-one ethylene ketal (57.3 g, 0.246 mol) was added THF (300 ml). After the solution was cooled to -78 ^oC, n-BuLi (98.3 mL, 2.5 M in hexane, 0.245 mol) was added via syringe. The solution was stirred for 1 hour at -78 ^oC. A cooled solution of $B(OiPr)_3$ (50.9 g, 0.270 mol) in THF (50 ml) at -78 ^oC was added to the flask containing the lithiated compound via a cannula. After the solution was stirred for 1.5 hour at -78 ^oC, it was slowly warmed to -30 ^oC for 30 minutes. Aqueous HCl solution (2 N, 300 mL) was added and the reaction mixture was transferred to a separatory funnel containing ethyl acetate (300 mL). Organic phase was collected and the aqueous phase was extracted with additional ethyl acetate (300 mL). After the combined organic phase was dried over anhydrous $MgSO_4$, solvent was removed with rotary evaporator to give a yellow residue, which was triturated in hexane to give a white solid. The solid was collected by filtration (20.3 g). The filtrate was collected and solvent was removed by rotary evaporator to give an oily residue to which aqueous HCl solution (2 N, 40 mL) and hexane (20 mL) were added. Additional white solid was obtained by stirring the mixture for several hours. The solid was collected by filtration and washed with cold hexane (7.6 g). From the filtrate, organic phase was collected and stored in a freezer to give additional crops which was collected by decantation (3.6 g). The combined yield was 85 % (31.5 g). M.p. 79 ^oC. IR (neat): 3301 (O-H), 1650 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.24 (d, J = 3.6 Hz, 3H, CH_3), 2.09 (dd, J = 19, 2.0 Hz, 1H, CH_2), 2.39 (s, 3H, CH_3), 2.72 (dd, J = 19, 6.8 Hz, 1H, CH_2), 2.84-2.86 (m, 1H, CH), 7.29 (s, 2H, OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.01, 18.90, 40.76, 44.22, 197.08, 216.12 ppm. Anal. Calc. ($C_7H_{11}BO_3$): C: 54.60; H, 7.20 %. Found: C, 54.40; H, 7.42 %.

Compound 4a. 2-Bromoaniline (1.65 g, 9.56 mmol) and cyclohexanone (4.693 g, 47.81 mmol) were dissolved in benzene (9 ml) and molecular sieves (4 A, 2.0 g) was added. The flask was connected with a Dean-Stark apparatus and the solution was refluxed for 4 days. After the solution was cooled to room

temperature, the molecular sieves were filtered off. All volatiles were removed under vacuum at 60 ^{o}C to give a crude imine compound. The imine compound was dissolved in degassed methanol (28 ml). Sodium borohydride (1.08 g , 28.7 mmol) was added slowly under weak stream of nitrogen and the mixture was stirred at room temperature for 2 hours. Aqueous 1 N KOH (20 mL) was added and the product was extracted with methylene chloride (30 mL × 2). The combined organic layer was dried over $MgSO_4$ and solvent was removed by rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane. Colorless oil was obtained (1.43 g, 59 %). IR (neat): 3401 (N-H) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.99 (t, *J* = Hz, 2H, Cy), 1.29-1.53 (m, 3H, Cy), 1.72-1.75 (m, 1H, Cy), 1.88-1.84 (m, 2H, Cy), 2.11-2.14 (m, 2H, Cy), 3.36-3.40 (m, 1H, N-CH), 4.34 (br s, 1H, NH), 6.58 (td, *J* = 7.6, 0.8 Hz, 1H, C_6H_4), 6.71 (d, *J* = 7.6 Hz, 1H, C_6H_4), 7.20 (td, *J* = 7.6, 0.8 Hz, 1H, C_6H_4), 7.47 (dd, *J* = 7.6, 1.2 Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR($CDCl_3$): δ 24.91, 25.94, 33.13, 51.53, 109.62, 111.58, 116.92, 128.16, 132.33, 143.83 ppm. Anal. Calc. ($C_{12}H_{16}BrN$): C, 56.71; H, 6.35; N, 5.51 %. Found: C, 56.67; H, 6.58; N, 5.82 %.

***N*-Cyclohexyl-4-methylaniline.** *p*-Toluidine (3.85 g, 35.9 mmol) and cyclohexanone (21.2 g, 0.216 mol) were dissolved in toluene (25 ml) and molecular sieves (4A, 7.0 g) was added. The flask was sealed with screw-cap and heated at 100 ^{o}C for 2 days. After the molecular sieves were filtered off, all volatiles were removed under vacuum at 60 ^{o}C to give a crude imine compound. The imine compound was reduced with sodium borohydride (4.08 g, 108 mmol) by the same conditions and procedures as for **4a**. The product was purified by column chromatography on silica eluting with hexane and ethyl acetate (10 : 1). A white solid was obtained (5.16 g, 76 %). M.p. 39 ^{o}C. IR (neat): 3460 (N-H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.88-0.94 (m, 2H, Cy), 1.04-1.09 (m, 1H, Cy), 1.12-1.21 (m, 2H, Cy), 1.46-1.50 (m, 1H, Cy), 1.55-1.60 (m, 2H, Cy), 1.90-1.93 (m, 2H, Cy), 2.23 (s, 3H, CH_3), 3.03 (br s, 1H, NH), 3.04-3.10 (m, 1H, N-CH), 6.45 (d, *J* = 8.0 Hz, 2H, C_6H_4), 7.00 (d, *J* = 8.0 Hz, 2H, C_6H_4) ppm. ^{13}C{^{1}H} NMR(C_6D_6): δ 20.85, 25.50, 26.50, 33.82, 52.04, 113.82, 125.78, 130.03, 145.60 ppm. Anal. Calc. ($C_{13}H_{19}N$): C, 82.48; H, 10.12; N, 7.40 %. Found: C, 82.26; H, 10.27; N, 7.19 %.

Compound 4b. *N*-Cyclohexyl-4-methylaniline (2.00 g, 10.6 mmol) was dissolved in methylene chloride (20 mL) and Br_2 (1.69 g, 10.6 mmol) in methylene chloride (16 ml) was added at 0 ^{o}C for 30 minutes. The solution was stirred further for 2 hours. After an aqueous 1N KOH (20 ml) was added, the product was extracted with methylene chloride (40 mL × 2). The combined organic layer was dried over $MgSO_4$ and solvent was removed by rotary evaporator to give an residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (10 : 1). Colorless oil was obtained (2.67 g, 94 %). IR (neat): 3401 (N-H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.98-1.03 (m, 3H, Cy), 1.10-1.16 (m, 3H, Cy), 1.39-1.42 (m, 1H, Cy), 1.53-1.56 (m, 2H, Cy), 1.82-1.85 (m, 2H, Cy), 2.03 (s, 3H, CH_3), 3.06-3.08 (m, 1H, N-CH), 4.16 (br d, *J* = 7.2 Hz, 1H, NH), 6.46 (d, *J* = 7.6 Hz, 1H, C_6H_3), 6.84 (dd, *J* = 1.6, 7.6

Hz, 1H, C_6H_3), 7.23 (d, *J* = 1.6 Hz, 1H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 20.25, 25.21, 26.29, 33.37, 51.90, 110.25, 112.29, 126.71, 129.24, 133.29, 142.34 ppm. Anal. Calc. ($C_{13}H_{18}BrN$): C, 58.22; H, 6.76; N, 5.22 %. Found: C, 58.05; H, 6.84; N, 4.96 %.

***N*-Cyclohexyl-4-phenylaniline**. The compound was prepared by the same conditions and procedures as for *N*-cyclohexyl-4-methylaniline using benzidine. A light yellow solid was obtained (65 %). M.p. 75 ^oC. IR (neat): 3385 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 0.84-0.94 (m, 2H, Cy), 1.02-1.21 (m, 3H, Cy), 1.46-1.59 (m, 3H, Cy), 1.88-1.91 (m, 2H, Cy), 3.06-3.11 (m, 1H, N-CH), 3.18 (br s, 1H, NH), 6.49 (d, *J* = 8.0 Hz, 2H, C_6H_4), 7.14 (t, *J* = 8.0 Hz, 1H, C_6H_5), 7.28 (t, *J* = 8.0 Hz, 2H, C_6H_5), 7.49 (d, *J* = 8.0 Hz, 2H, C_6H_4), 7.60 (d, *J* = 8.0 Hz, 2H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 25.43, 26.41, 33.66, 51.70, 113.78, 126.15, 126.59, 128.27, 129.00, 130.10, 142.03, 147.14 ppm. Anal. Calc. ($C_{18}H_{21}N$): C, 86.01; H, 8.42; N, 5.57 %. Found: C, 85.95; H, 8.26; N, 5.32 %.

Compound 4c. The compound was synthesized by the same conditions and procedures as for **4b** using *N*-cyclohexyl-4-phenylaniline. It was purified by column chromatography on silica gel eluting with hexane and methylene chloride (4 : 1). Colorless oil was obtained (73 %). IR (neat): 3401 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 0.96-1.05 (m, 2H, Cy), 1.06-1.18 (m, 2H, Cy), 1.23-1.31 (m, 1H, Cy), 1.39-1.44 (m, 1H, Cy), 1.52-1.56 (m, 2H, Cy), 1.79-1.83 (m, 2H, Cy), 3.02-3.11 (m, 1H, N-CH), 4.35 (br d, *J* = 7.2 Hz, 1H, NH), 6.52 (d, *J* = 8.0 Hz, 1H, C_6H_3), 7.11 (tt, *J* = 1.6, 8.0 Hz, 1H, C_6H_5), 7.21 (t, *J* = 8.0 Hz, 2H, C_6H_5), 7.34 (dd, *J* = 2.4, 8.4 Hz, 1H, C_6H_3), 7.37 (dd, *J* = 1.2, 8.0 Hz, 2H, C_6H_5), 7.78 (d, *J* = 2.4 Hz, 1H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 25.13, 26.20, 33.22, 51.70, 110.72, 112.28, 126.56, 126.62, 127.36, 129.02, 130.93, 131.42, 140.42, 143.67 ppm. Anal. Calc. ($C_{18}H_{20}BrN$): C, 65.46; H, 6.10; N, 4.24 %. Found: C, 65.29; H, 5.85; N, 4.36 %.

4-Chloro-*N*-cyclohexylaniline. The compound was prepared by the same conditions and procedures as for *N*-cyclohexyl-4-methylaniline using 4-chloroaniline. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (10 : 1). A white solid was obtained (71 %). M.p. 41 ^oC. IR (neat): 3408 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 0.77-0.85 (m, 2H, Cy), 1.01-1.17 (m, 3H, Cy), 1.45-1.56 (m, 3H, Cy), 1.76-1.79 (m, 2H, Cy), 2.85-2.90 (m, 1H, N-CH), 3.03 (br s, 1H, NH), 6.15 (d, *J* = 8.8 Hz, 2H, C_6H_4), 7.09 (d, *J* = 8.8 Hz, 2H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 25.36, 26.34, 33.44, 51.70, 114.42, 121.31, 129.30, 146.21 ppm. Anal. Calc. ($C_{12}H_{16}ClN$): C, 68.73; H, 7.69; N, 6.68 %. Found: C, 68.52; H, 7.37; N, 6.84 %.

Compound 4d. The compound was synthesized by the same conditions and procedures as for **4b** using 4-chloro-*N*-cyclohexylaniline. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (10 : 1). Colorless oil was obtained (90 %). IR (neat): 3401 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 0.82-0.93 (m, 2H, Cy), 0.96-0.98 (m, 1H, Cy), 1.00-1.11 (m, 2H, Cy), 1.37-1.41 (m,

1H, Cy), 1.36-1.41 (m, 2H, Cy), 1.66-1.69 (m, 2H, Cy), 2.79-2.90 (m, 1H, N-CH), 4.14 (br d, J = 7.2 Hz, 1H, NH), 6.16 (d, J = 8.8 Hz, 1H, C_6H_3), 6.98 (dd, J = 2.8, 8.8 Hz, 1H, C_6H_3), 7.38 (d, J = 2.8 Hz, 1H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 25.06, 26.15, 33.03, 51.68, 109.87, 112.42, 121.04, 128.57, 132.16, 143.12 ppm. Anal. Calc. ($C_{12}H_{15}BrClN$): C, 49.94; H, 5.24; N, 4.85 %. Found: C, 50.12; H, 5.39; N, 4.94 %.

***N*-Cyclohexyl-4-fluoroaniline.** The compound was prepared by the same conditions and procedures as for *N*-cyclohexyl-4-methylaniline using 4-fluoroaniline. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (50 : 1). Brown oil was obtained (92 %). IR (neat): 3413 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 0.83-0.92 (m, 2H, Cy), 1.00-1.22 (m, 3H, Cy), 1.47-1.52 (m, 1H, Cy), 1.56-1.60 (m, 2H, Cy), 1.82-1.85 (m, 2H, Cy), 2.89-2.95 (m, 1H, N-CH), 3.00 (br s, 1H, NH), 6.22 (dd, J = 4.4, 8.8 Hz, 2H, C_6H_4), 6.79 (t, J = 8.8 Hz, 2H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 25.45, 26.43, 33.64, 52.33, 114.13 (d, $^3J_{CF}$ = 6.8 Hz, C_6H_4F), 155.78 (d, $^2J_{CF}$ = 22 Hz, C_6H_4F), 144.18 (d, $^4J_{CF}$ = 1.5 Hz, C_6H_4F-C), 155.66 (d, $^1J_{CF}$ = 231.3 Hz, C_6H_4F-C) ppm. Anal. Calc. ($C_{12}H_{16}FN$): C, 74.58; H, 8.34; N, 7.25 %. Found: C, 74.35; H, 8.27; N, 7.42 %.

Compound 4e. The compound was synthesized by the same conditions and procedures as for **4b** using *N*-cyclohexyl-4-fluoroaniline. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (50 : 1). Colorless oil was obtained (92 %). IR (neat): 3401 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 0.90-0.99 (m, 2H, Cy), 1.03-1.19 (m, 3H, Cy), 1.42-1.46 (m, 1H, Cy), 1.53-1.57 (m, 2H, Cy), 1.75-1.78 (m, 2H, Cy), 2.87-2.96 (m, 1H, N-CH), 3.97 (d, J = 7.2 Hz, 1H, NH), 6.23 (dd, J = 4.4, 8.8 Hz, 1H, C_6H_3), 6.72 (td, J = 2.8, 8.8 Hz, 1H, C_6H_3), 7.09 (dd, J = 2.8, 8.0 Hz, 1H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 25.20, 26.28, 33.29, 52.15, 109.14 (d, $^3J_{CF}$ = 9.9 Hz, C_6H_3), 111.99 (d, $^3J_{CF}$ = 7.6 Hz, C_6H_3), 115.21 (d, $^2J_{CF}$ = 21.2 Hz, C_6H_3), 119.71 (d, $^2J_{CF}$ = 25 Hz, C_6H_3), 141.26 (d, $^4J_{CF}$ = 2.3 Hz, C_6H_3), 154.32 (d, J_{CF} = 236 Hz, C_6H_3) ppm. Anal. Calc. ($C_{12}H_{15}BrFN$): C, 52.96; H, 5.56; N, 5.15 %. Found: C, 53.15; H, 5.92; N, 5.37 %.

Compound 4g. The compound was prepared by the same conditions and procedures as for **4a** using 2-bromoaniline and 3-pentanone. It was purified by column chromatography on silica gel eluting with hexane. Colorless oil was obtained (61 %). IR (neat): 3407 (N-H) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.01 (t, J = 7.6 Hz, 6H, CH_3), 1.54-1.74 (m, 4H, CH_2), 3.34 (quintet, J = 6.0 Hz, 1H, N-CH), 4.25 (s, 1H, NH), 6.56 (td, J = 7.6, 1.2 Hz, 1H, C_6H_4), 6.67 (dd, J = 8.0, 1.2 Hz, 1H, C_6H_4), 7.18 (td, J = 7.6, 1.6 Hz, 1H, C_6H_4), 7.45 (dd, J = 8.0, 1.6 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 10.22, 26.73, 55.60, 109.65, 111.55, 116.74, 128.19, 132.30, 144.54 ppm. Anal. Calc. ($C_{11}H_{16}BrN$): C, 54.56; H, 6.66; N, 5.78 %. Found: C, 54.36; H, 6.48; N, 5.48 %.

Compound 5a. Compound **3** (1.27 g, 8.26 mmol), Na_2CO_3 (1.25 g, 11.8 mmol), $Pd(PPh_3)_4$ (0.182 g, 0.157 mmol) and **4a** (2.00 g, 7.87 mmol) were added into a Schlenk flask inside a glovebox. The flask was brought out and degassed DME (21 mL) and degassed water (7 mL) were added. The flask was sealed with screw-cap and heated at 95 ^oC overnight. The solution was cooled to room temperature and the product was extracted with ethyl acetate (50 ml × 2). The combined organic layer was dried over anhydrous $MgSO_4$ and solvent was removed by rotary evaporator to give a residue which was purified by column chromatography eluting with hexane and ethyl acetate (5 : 1). Yellow oil was obtained (2.06 g, 92 %). IR (neat): 3379 (N-H), 1697 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.13-1.28 (m, 4H, Cy), 1.32 (d, J = 6.8 Hz, 3H, CH_3), 1.35-1.41 (m, 2H, Cy), 1.62-1.65 (m, 1H, Cy), 1.71-1.75 (m, 2H, Cy), 2.03 (s, 3H, CH_3), 1.98-2.07 (m, 1H, Cy), 2.19 (d, J = 18.4 Hz, 1H, CH_2), 2.83 (dd, J = 18.8, 6.8 Hz, 1H, CH_2), 2.95 (quintet, J = 6.8 Hz, 1H, CH), 3.24-3.29 (m, 1H, N-CH), 3.48 (s, 1H, NH), 6.71 (t, J = 8.8 Hz, 1H, C_6H_4), 6.74 (d, J = 8.8 Hz, 1H, C_6H_4), 6.88 (d, J = 8.8 Hz, 1H, C_6H_4), 7.20 (t, J = 8.8 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 16.31, 19.54, 24.82, 25.88, 33.13, 37.59, 43.52, 51.43, 111.34, 116.13, 117.19, 128.89, 129.44, 130.39, 144.72, 178.62, 206.65 ppm. Anal. Calc. ($C_{19}H_{25}NO$): C, 80.52; H, 8.89; N, 4.94 %. Found: C, 80.68; H, 9.05; N, 5.12 %.

Compound 5b. The compound was synthesized by the same conditions and procedures as for **5a** using **4b**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (3 : 1). Yellow oil was obtained (98 %). IR (neat): 3378 (N-H), 1697 (C=O) cm^{-1}. ^1H NMR (C_6D_6): δ 0.77 (d, J = 6.8 Hz, 3H, CH_3), 1.10-1.22 (m, 4H, Cy), 1.42-1.48 (m, 2H, Cy), 1.54-1.62 (m, 2H, Cy), 1.63 (s, 3H, CH_3), 1.86 (dd, J = 2.4, 18.4 Hz, 1H, CH_2), 1.96-2.06 (m, 2H, Cy), 2.18-2.23 (m, 1H, CH), 2.25 (s, 3H, C_6H_3-CH_3), 2.46 (dd, J = 6.8, 18.4 Hz, 1H, CH_2), 3.14-3.24 (m, 1H, N-CH), 3.84 (br s, 1H, NH), 6.73 (d, J = 8.4 Hz, 1H, C_6H_3), 6.86 (br s, 1H, C_6H_3), 7.08 (dd, J = 2.4, 8.4 Hz, 1H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 16.19, 19.50, 20.81, 25.32, 26.53, 33.75, 37.67, 43.78, 52.02, 112.29, 119.07, 125.25, 129.85, 131.90, 139.93, 143.96, 176.77, 205.26 ppm. Anal. Calc. ($C_{20}H_{27}NO$): C, 80.76; H, 9.15; N, 4.71 %. Found: C, 80.86; H, 8.89; N, 4.52 %.

Compound 5c. The compound was synthesized by the same conditions and procedures as for **5a** using **4c**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (3 : 1). Light yellow solid was obtained (98 %). M.p. 51-52 ^oC, IR (neat): 3444 (N-H), 1637 (C=O) cm^{-1}. ^1H NMR (C_6D_6): δ 0.75 (d, J = 6.8 Hz, 3H, CH_3), 1.11-1.25 (m, 4H, Cy), 1.42-1.47 (m, 2H, Cy), 1.56-1.62 (m, 2H, Cy), 1.61 (s, 3H, CH_3), 1.87 (dd, J = 2.0, 18.4 Hz, 1H, CH_2), 1.97-2.06 (m, 2H, Cy), 2.16-2.26 (m, 1H, CH), 2.46 (dd, J = 6.4, 18.4 Hz, 1H, CH_2), 3.17-3.29 (m, 1H, N-CH), 4.14 (br s, 1H, NH), 6.79 (d, J = 8.0 Hz, 1H, C_6H_3), 7.14 (tt, J = 1.2, 7.2 Hz, 1H, C_6H_5), 7.27 (t, J = 8.0 Hz, 2H, C_6H_5), 7.36 (d, J = 2.0 Hz, 1H, C_6H_3), 7.55 (dd, J = 2.0, 8.4 Hz, 1H, C_6H_3), 7.62 (dd, J = 1.2, 8.0 Hz, 2H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 16.19, 19.39, 25.23, 26.45, 33.59, 37.80, 43.73, 51.81, 112.53, 119.36, 126.29,

126.76, 128.18, 129.02, 129.81, 130.25, 141.92, 145.76, 177.41, 205.30 ppm. Anal. Calc. ($C_{25}H_{29}NO$): C, 83.52; H, 8.13; N, 3.90 %. Found: C, 83.46; H, 7.95; N, 3.69 %.

Compound 5d. The compound was synthesized by the same conditions and procedures as for **5a** using **4d**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (3 : 1). A light yellow solid was obtained (1.07 g, 97 %). M.p. 47 ^{o}C, IR (neat): 3378 (N-H), 1698 (C=O) cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.68 (d, *J* = 7.2 Hz, 3H, CH_3), 1.03-1.17 (m, 4H, Cy), 1.40-1.46 (m, 2H, Cy), 1.47 (s, 3H, CH_3), 1.53-1.55 (m, 2H, Cy), 1.78 (dd, *J* = 2.0, 18.4 Hz, 1H, CH_2), 1.84-1.94 (m, 2H, Cy), 2.08-2.12 (m, 1H, CH), 2.36 (dd, *J* = 7.2, 18.4 Hz, 1H, CH_2), 2.97-3.08 (m, 1H, N-CH), 4.00 (br s, 1H, NH), 6.47 (d, *J* = 8.8 Hz, 1H, C_6H_3), 7.01 (d, *J* = 2.4 Hz, 1H, C_6H_3), 7.21 (dd, *J* = 2.4, 8.8 Hz, 1H, C_6H_3) ppm. ^{13}C{^{1}H} NMR(C_6D_6): δ 16.02, 19.30, 21.15, 26.37, 33.32, 37.80, 43.61, 51.76, 113.08, 120.46, 120.98, 129.05, 130.94, 138.63, 144.87, 178.02, 204.82 ppm. Anal. Calc. ($C_{19}H_{24}ClNO$): C, 71.80; H, 7.61; N, 4.41 %. Found: C, 71.92; H, 7.46; N, 4.34 %.

Compound 5e. The compound was synthesized by the same conditions and procedures as for **5a** using **4e**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (10 : 1). Light yellow oil was obtained (90 %). IR (neat): 3378 (N-H), 1698 (C=O) cm^{-1}. ^{1}H NMR (C_6D_6): δ 0.76 (d, *J* = 7.2 Hz, 3H, CH_3), 1.06-1.20 (m, 4H, Cy), 1.43-1.48 (m, 2H, Cy), 1.56 (s, 3H, CH_3), 1.54-1.62 (m, 2H, Cy), 1.81 (dd, *J* = 2.0, 18.4 Hz, 1H, CH_2), 1.86-1.96 (m, 2H, Cy), 2.18-2.22 (m, 1H, CH), 2.40 (dd, *J* = 6.8, 18.4 Hz, 1H, CH_2), 2.99-3.08 (m, 1H, N-CH), 3.78 (br s, 1H, NH), 6.48 (dd, *J* = 4.8, 8.8 Hz, 1H, C_6H_3), 6.77 (dd, *J* = 3.2, 8.8 Hz, 1H, C_6H_3), 6.91 (td, *J* = 3.2, 8.8 Hz, 1H, C_6H_3) ppm. ^{13}C{^{1}H} NMR(C_6D_6): δ 16.06, 19.30, 25.24, 26.45, 33.53, 37.77, 43.63, 52.21, 112.81 (d, J_{CF} = 7.6 Hz, C_6H_3), 115.51 (d, $^{2}J_{CF}$ = 21.2 Hz, C_6H_3), 117.84 (d, $^{2}J_{CF}$ = 21.2 Hz, C_6H_3), 120.15 (d, J_{CF} = 7.6 Hz, C_6H_3), 142.66, 154.01, 156.33, 177.80, 204.84 ppm. Anal. Calc. ($C_{19}H_{24}FNO$): C, 75.71; H, 8.03; N, 4.65 %. Found: C, 75.84; H, 8.25; N, 4.48 %.

Compound 5f. The compound was synthesized by the same conditions and procedures as for **5a** using **4f**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (5 : 1). Light yellow oil was obtained (96 %). IR (neat): 3407 (N-H), 1697 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.30 (d, *J* = 6.8 Hz, 3H, CH_3), 1.31 (s, 9H, $C(CH_3)_3$), 2.01 (s, 3H, CH_3), 2.17 (dd, *J* = 2.0, 18.4 Hz, 1H, CH_2), 2.80 (dd, *J* = 6.4, 18.4 Hz, 1H, CH_2), 2.93 (br quintet, *J* = 6.4 Hz, 1H, CH), 3.44 (s, 1H, NH), 6.75 (td, *J* = 1.2, 7.2 Hz, 1H, C_6H_4), 6.87 (d, *J* = 6.8 Hz, 1H, C_6H_4), 6.98 (d, *J* = 8.4 Hz, 1H, C_6H_4) 7.17 (td, *J* = 1.6, 7.6 Hz, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR($CDCl_3$): δ 16.16, 19.55, 29.94, 37.50, 43.52, 51.26, 115.50, 117.20, 119.71, 127.46, 128.34, 130.29, 144.48, 178.44, 206.44 ppm. Anal. Calc. ($C_{17}H_{23}NO$): C, 79.33; H, 9.01; N, 5.44 %. Found: C, 79.59; H, 9.35; N, 5.16 %.

Compound 5g. The compound was synthesized by the same conditions and procedures as for **5a** using **4g**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (10 : 1). Light yellow oil was obtained (88 %). IR (neat): 3407 (N-H), 1697 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.91 (t, *J* = 7.6 Hz, 6H, CH_3), 1.32 (d, *J* = 7.6 Hz, 3H, CH_3), 1.43-1.61 (m, 4H, CH_2), 2.02 (s, 3H, CH_3), 2.19 (dd, *J* = 18.4, 2.0 Hz, 1H, CH_2), 2.83 (dd, *J* = 18.4, 6.8 Hz, 1H, CH_2), 2.95 (br quintet, *J* = 6.8 Hz, 1H, CH), 3.25 (quintet, *J* = 5.6 Hz, 1H, N-CH), 3.34 (s, 1H, NH), 6.67 (d, *J* = 7.6 Hz, 1H, C_6H_4), 6.68 (t, *J* = 7.6 Hz, 1H, C_6H_4), 6.86 (d, *J* = 6.4 Hz, 1H, C_6H_4), 7.12 (td, *J* = 1.2, 7.6 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 10.09, 16.28, 19.67, 26.42, 37.62, 43.59, 55.05, 110.98, 115.91, 127.49, 128.96, 129.51, 130.36, 134.49, 178.76, 206.66 ppm. Anal. Calc. ($C_{18}H_{25}NO$): C, 79.66; H, 9.28; N, 5.16 %. Found: C, 79.84; H, 9.42; N, 5.38 %.

Compound 6a. Anhydrous $CeCl_3$ (5.27 g, 21.4 mmol) and THF (24 ml) were added into a Schlenk flask inside a glovebox. The flask was brought out and the slurry was cooled to -78 °C. MeLi (13.4 mL, 21.4 mmol, 1.6 M solution in diethyl ether w/o LiBr) was added with syringe. The mixture was stirred for 1 hour at -78 °C. Compound **5a** (2.02 g, 7.13 mmol) was added as a solid under weak stream of nitrogen gas. After the mixture was stirred for 2 hours at -78 °C, it was transferred to a separatory funnel containing water (20 ml) and ethyl acetate (40 mL). The organic phase was collected and the water phase was further extracted with additional ethyl acetate (10 mL × 2). The combined organic phase was shaken vigorously with aqueous HCl (2 N, 20 mL) for 2 minutes. Aqueous saturated $NaHCO_3$ (20 mL) was added carefully to neutralize the solution. The collected organic phase was dried with anhydrous $MgSO_4$ and solvent was removed with rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 10:1). Colorless oil was obtained (1.66 g, 83 %). The cyclopentadiene compound is unstable and slowly decomposes even in a freezer under N_2 atmosphere. So, the compound is used for the next reaction as soon as it is prepared. ^1H NMR ($CDCl_3$): δ 1.06-1.20 (m, 2H, Cy), 1.21-1.30 (m, 1H, Cy), 1.34-1.46 (m, 2H, Cy), 1.68 (d, *J* = 1.2 Hz, 3H, CH_3), 1.74-1.81 (m, 3H, Cy), 1.87 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.03-2.10 (m, 2H, Cy), 2.94 (AB, *J* = 22.8 H_Z, 1H, CH_2), 3.01 (AB, *J* = 22.8 H_Z, 1H, CH_2), 3.29-3.34 (m, 1H, N-CH), 3.67 (br s, 1H, NH), 6.69 (td, *J* = 1.2, 7.2 Hz, 1H, C_6H_4), 6.71 (d, *J* = 8.0 Hz, 1H, C_6H_4), 6.93 (dd, *J* = 1.6, 7.2 Hz, 1H, C_6H_4), 7.20 (ddd, *J* = 1.6, 7.2, 8.0 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 11.70, 13.73, 14.47, 25.13, 25.17, 26.05, 33.17, 33.50, 48.81, 51.50, 110.18, 115.50, 122.53, 127.76, 130.01, 133.11, 135.64, 136.80, 139.66, 144.86 ppm.

Compound 6b. The compound was synthesized by the same conditions and procedures as for **6a** using **5b**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (30 : 1). A light yellow solid was obtained (70 %). M.p. 62-63 °C. ^1H NMR (C_6D_6): δ 0.92-1.04 (m, 3H, Cy), 1.12-1.22 (m, 2H, Cy), 1.40-1.48 (m, 1H, Cy), 1.50-1.57 (m, 2H, Cy), 1.81 (s, 3H, CH_3), 1.88 (s,

3H, CH_3), 1.90 (s, 3H, CH_3), 1.93-2.01 (m, 2H, Cy), 2.28 (s, 3H, CH_3), 2.72 (AB, J = 22.8 H_Z, 1H, CH_2), 2.80 (AB, J = 22.8 H_Z, 1H, CH_2), 3.16-3.25 (m, 1H, N-CH), 3.65 (br d, J = 8.0 Hz, 1H, NH), 6.70 (d, J = 8.0 Hz, 1H, C_6H_3), 6.93 (d, J = 2.0 Hz, 1H, C_6H_3), 7.07 (dd, J = 2.0, 8.0 Hz, 1H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 12.19, 13.90, 14.76, 20.95, 25.53, 26.46, 33.97, 49.07, 51.96, 111.28, 123.27, 124.94, 129.02, 131.14, 133.11, 136.46, 136.62, 141.11, 143.40 ppm.

Compound 6c. The compound was synthesized by the same conditions and procedures as for **6a** using **5c**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (10 : 1). A light yellow oil was obtained (75 %). ^1H NMR (C_6D6_6): δ 0.87-1.04 (m, 3H, Cy), 1.11-1.23 (m, 2H, Cy), 1.41-1.47 (m, 1H, Cy), 1.50-1.58 (m, 2H, Cy), 1.80 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.93-2.00 (m, 2H, Cy), 2.72 (AB, J = 22.8 H_Z, 1H, CH_2), 2.80 (AB, J = 22.8 H_Z, 1H, CH_2), 3.17-3.28 (m, 1H, N-CH), 3.86 (br d, J = 8.0 Hz, 1H, NH), 6.77 (d, J = 8.0 Hz, 1H, C_6H_3), 7.13 (t, J = 8.0 Hz, 1H, C_6H_5), 7.27 (t, J = 8.0 Hz, 2H, C_6H_5), 7.48 (d, J = 2.4 Hz, 1H, C_6H_3), 7.59 (dd, J = 2.4, 8.0 Hz, 1H, C_6H_3), 7.64 (d, J = 8.0 Hz, 2H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 12.21, 13.90, 14.78, 25.42, 25.45, 26.35, 33.78, 33.81, 49.13, 51.67, 111.22, 123.43, 126.09, 126.60, 127.22, 128.98, 129.23, 129.35, 133.45, 136.29, 137.15, 140.73, 142.05, 145.00 ppm.

Compound 6d. The compound was synthesized by the same conditions and procedures as for **6a** using **5d**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (10 : 1). A light yellow solid was obtained (60 %). M.p. 69 ^oC. ^1H NMR (C_6D_6): δ 0.80-0.90 (m, 2H, Cy), 0.94-1.01 (m, 1H, Cy), 1.08-1.18 (m, 3H, Cy), 1.40-1.51 (m, 4H, Cy), 1.67 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 2.61 (AB, J = 22.8 H_Z, 1H, CH_2), 2.71 (AB, J = 22.8 H_Z, 1H, CH_2), 2.99-3.07 (m, 1H, N-CH), 3.68 (br d, J = 8.0 Hz, 1H, NH), 6.44 (d, J = 8.8 Hz, 1H, C_6H_3), 7.07 (d, J = 2.4 Hz, 1H, C_6H_3), 7.17 (dd, J = 2.4, 8.8 Hz, 1H, C_6H_3) ppm, $^{13}C\{^1H\}$ NMR(C_6D_6): δ 11.93, 13.82, 14.54, 25.36, 25.39, 26.29, 33.56, 33.59, 49.10, 51.65, 111.77, 120.79, 124.66, 128.24, 130.18, 133.70, 135.67, 137.73, 139.52, 144.15 ppm.

Compound 6e. The compound was synthesized by the same conditions and procedures as for **6a** using **5e**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (10 : 1). A yellow oil was obtained (41 %). ^1H NMR (C_6D_6): δ 0.85-0.92 (m, 2H, Cy), 0.95-1.01 (m, 1H, Cy), 1.08-1.18 (m, 2H, Cy), 1.41-1.46 (m, 1H, Cy), 1.48-1.54 (m, 2H, Cy), 1.71 (d, J = 0.4 Hz, 3H, CH_3), 1.80 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.84-1.90 (m, 2H, Cy), 2.62 (AB, J = 22.8 H_Z, 1H, CH_2), 2.72 (AB, J = 22.8 H_Z, 1H, CH_2), 3.01-3.09 (m, 1H, N-CH), 3.57 (br d, J = 8.0 Hz, 1H, NH), 6.45 (dd, J = 4.8, 9.2 Hz, 1H, C_6H_3), 6.88 (dd, J = 3.2, 9.2 Hz, 1H, C_6H_3), 6.94 (td, J = 3.2, 8.4 Hz, 1H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 11.96, 13.78, 14.54, 25.40, 25.43, 26.34, 33.75, 33.78, 49.05, 52.14, 111.50 (d,

J_{CF} = 7.6 Hz, C_6H_3), 114.64 (d, $^2J_{CF}$ = 21.2 Hz, C_6H_3), 117.15 (d, $^2J_{CF}$ = 21.2 Hz, C_6H_3), 133.59, 135.78, 137.50, 139.85, 142.02, 154.21, 156.45 ppm.

Compound 6f. The compound was synthesized by the same conditions and procedures as for **6a** using **5f**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (20 : 1). A colorless oil was obtained (0.461 g, 58 %). ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 9H, $C(CH_3)_3$), 1.71 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.96 (AB, *J* = 22.8 H_Z, 1H, CH_2), 3.03 (AB, *J* = 22.8 H_Z, 1H, CH_2), 3.83 (br s, 1H, NH), 6.77 (t, *J* = 7.2 Hz, 1H, C_6H_4), 6.97 (d, *J* = 7.6 Hz, 1H, C_6H_4), 7.01 (d, *J* = 8.0 Hz, 1H, C_6H_4), 7.21 (t, *J* = 7.2 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 11.71, 13.70, 14.46, 30.09, 48.75, 50.96, 113.93, 116.31, 124.62, 127.24, 129.99, 133.25, 135.44, 136.62, 140.01, 144.70 ppm.

Compound 6g. The compound was synthesized by the same conditions and procedures as for **6a** using **5g**. It was purified by column chromatography on silica gel eluting with hexane and triethylamine (v/v, 50:1). A colorless oil was obtained (60 %). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, *J* = 7.6 Hz, 6H, CH_3), 1.45-1.63 (m, 4H, CH_2), 1.68 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.95 (AB, *J* = 22.4 Hz, 1H, CH_2), 3.02 (AB, *J* = 22.4 Hz, 1H, CH_2), 3.30 (br quintet, *J* = 6.0 Hz, 1H, N-CH), 3.56 (br s, 1H, NH), 6.67 (d, *J* = 7.6 H_Z, 1H, C_6H_4), 6.68 (t, *J* = 7.6 Hz, 1H, C_6H_4), 6.92 (dd, *J* = 1.6, 7.6 Hz, 1H, C_6H_4), 7.20 (td, *J* = 1.6, 7.6 Hz, 1H, C_6H_4) ppm, $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 10.15, 10.23, 13.69, 14.36, 26.73, 26.83, 48.78, 54.95, 109.66, 115.10, 122.42, 127.75, 129.88, 132.94, 135.75, 136.97, 139.76, 145.66 ppm.

Complex 7a. Compound **6a** (0.196 g, 0.696 mmol) and $Ti(NMe_2)_4$ (0.156 g, 0.696 mmol) were dissolved in toluene (2 mL) and the flask was sealed. The solution was heated for 2 days at 80 ^oC. Removal of solvent gave red solid. The NMR data for the intermediate bis(dimethylamido)titanium complex: ^{1}H NMR (C_6D_6): δ 0.86-1.01 (m, 1H, Cy), 1.10-1.25 (m, 2H, Cy), 1.34-1.49 (m, 3H, Cy), 1.64-1.74 (m, 2H, Cy), 1.77 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.99-2.09 (m, 2H, Cy), 2.89 (s, 6H, NCH_3), 3.07 (br s, 6H, NCH_3), 5.65 (br s, 1H, Cp-H), 6.68-6.84 (br s, 1H, C_6H_4), 6.86 (td, *J* = 0.8, 7.2 Hz, 1H, C_6H_4), 7.18 (dd, *J* = 1.6, 7.2 Hz, 1H, C_6H_4), 7.24 (td, *J* = 1.6, 7.2 Hz, 1H, C_6H_4) ppm. To the flask containing the bis(dimethylamido)titanium complex was added toluene (2 mL) and Me_2SiCl_2 (0.269 g, 2.09 mmol) successively at room temperature. After the solution was stirred for 4 hours at room temperature, solvent was removed by vacuum. Analytically pure red crystals were isolated by recrystallization in hexane at -30 ^oC (0.183 g, overall yield, 66 %). ^{1}H NMR (C_6D_6): δ 0.83-1.00 (m, 2H, Cy), 1.35-1.51 (m, 3H, Cy), 1.64 (s, 3H, CH_3), 1.66-1.74 (m, 3H, Cy), 1.75 (s, 3H, CH_3), 1.81-1.95 (m, 2H, Cy), 2.09 (s, 3H, CH_3), 5.46-5.58(m, 1H, N-CH), 6.06 (s, 1H, Cp-H), 6.65 (d, *J* = 7.2 Hz, 1H, C_6H_4), 6.95 (td, *J* = 0.8, 7.2 Hz, 1H, C_6H_4), 7.07 (dd, *J* = 2.0, 7.2 Hz, 1H, C_6H_4), 7.11 (td, *J* =

2.0, 7.2 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.38, 14.48, 14.82, 25.81, 27.08, 27.51, 59.57, 111.11, 118.50, 123.05, 128.49, 128.99, 131.56, 132.17, 142.13, 142.93, 143.42, 164.02 ppm. Anal. Calc. ($C_{20}H_{25}Cl_2NTi$): C, 60.33; H, 6.33; N, 3.52 %. Found: C, 60.19; H, 6.52; N, 3.29 %.

Complex 7b. The compound was synthesized by the same conditions and procedures as for **7a** using **6b**. It was purified by recrystallization in hexane at -30 °C. Red crystals were isolated in 59 %. The ^1H NMR datum for the intermediate bis(dimethylamido)titanium complex: ^1H NMR (C_6D_6): δ 0.88-1.01 (m, 1H, Cy), 1.15-1.26 (m, 2H, Cy), 1.36-1.50 (m, 3H, Cy), 1.65-1.75 (m, 2H, Cy), 1.81 (s, 3H, CH_3), 1.82-1.88 (m, 2H, Cy), 1.89 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.92 (s, 6H, NCH_3), 3.04 (br s, 6H, NCH_3), 5.67 (br s, 1H, Cp-H), 6.64-6.76 (br s, 1H, C_6H_3), 7.02 (s, 1H, C_6H_3), 7.11 (d, J = 7.6 Hz, 1H, C_6H_3) ppm. The analytical data for **7b**: ^1H NMR (C_6D_6): δ 0.84-1.00 (m, 2H, Cy), 1.37-1.53 (m, 3H, Cy), 1.69 (s, 3H, CH_3), 1.71-1.76 (m, 2H, Cy), 1.80 (s, 3H, CH_3), 1.85-1.97 (m, 2H, Cy), 2.10-2.18 (m, 1H, Cy), 2.11 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 5.57 (m, 1H, N-CH), 6.09 (s, 1H, Cp-H), 6.60 (d, J = 8.4 Hz, 1H, C_6H_3), 6.91 (s, 1H, C_6H_3), 6.94 (d, J = 8.4 Hz, 1H, C_6H_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.45, 14.50, 14.89, 20.69, 25.85, 27.10, 27.58, 59.59, 110.77, 118.38, 128.87, 129.68, 131.37, 132.55, 132.75, 142.06, 142.64, 143.11, 161.82 ppm. Anal. Calc. ($C_{21}H_{27}Cl_2NTi$): C, 61.19; H, 6.60; N, 3.40 %. Found: C, 60.94; H, 6.54; N, 3.61 %.

Complex 7c. The compound was synthesized by the same conditions and procedures as for **7a** using **6c**. It was purified by trituration in pentane. Red powder was isolated in 87 % yield. The ^1H NMR datum for the intermediate bis(dimethylamido)titanium complex: ^1H NMR (C_6D_6): δ 0.84-0.98 (m, 1H, Cy), 1.14-1.29 (m, 2H, Cy), 1.37-1.52 (m, 3H, Cy), 1.68-1.77 (m, 2H, Cy), 1.79 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 2.04-2.16 (m, 2H, Cy), 2.91 (s, 6H, NCH_3), 3.13 (s, 6H, NCH_3), 5.68 (s, 1H, Cp-H), 6.84 (br s, 1H, C_6H_3), 7.13 (t, J = 8.0 Hz, 1H, C_6H_5), 7.29 (t, J = 8.0 Hz, 2H, C_6H_5), 7.51 (d, J = 2.0 Hz, 1H, C_6H_3), 7.58 (dd, J = 2.0, 8.0 Hz, 1H, C_6H_3), 7.69 (dd, J = 2.0, 8.0 Hz, 2H, C_6H_5) ppm. The analytical data for **7c**: ^1H NMR (C_6D_6): δ 0.93-1.06 (m, 2H, Cy), 1.38-1.56 (m, 4H, Cy), 1.70 (s, 3H, CH_3), 1.72-1.80 (m, 2H, Cy), 1.81 (s, 3H, CH_3), 1.88-2.03 (m, 2H, Cy), 2.13 (s, 3H, CH_3), 5.54 (m, 1H, N-CH), 6.10 (s, 1H, Cp-H), 6.71 (d, J = 8.0 Hz, 1H, C_6H_3), 7.20 (d, J = 8.0 Hz, 1H, C_6H_5), 7.31 (t, J = 8.0 Hz, 2H, C_6H_5), 7.38 (d, J = 2.0 Hz, 1H, C_6H_3), 7.44 (dd, J = 2.0, 8.0 Hz, 1H, C_6H_3), 7.58 (dd, J = 2.0, 8.0 Hz, 2H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.58, 14.63, 15.03, 25.95, 27.17, 27.68, 59.73, 111.22, 118.40, 126.81, 126.99, 127.27, 128.79, 129.05, 131.50, 132.68, 136.14, 140.46, 141.77, 142.72, 143.20, 163.14 ppm. Anal. Calc. ($C_{26}H_{29}Cl_2NTi$): C, 65.84; H, 6.16; N, 2.95 %. Found: C, 65.92; H, 6.05; N, 3.13 %.

Complex 7d. The compound was synthesized by the same conditions and procedures as for **7a** using **6d**. It was purified by recrystallization in hexane at -30 °C. Red crystals were isolated in 73 % yield.

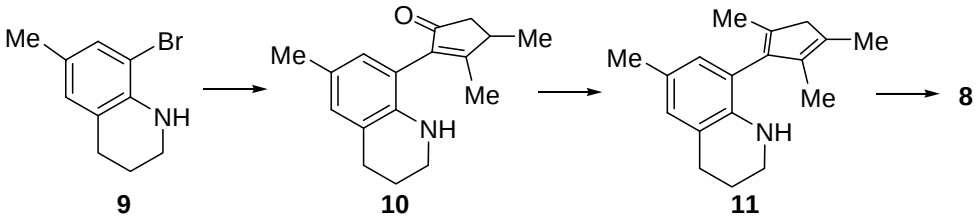
The ^{1}H NMR datum for the intermediate bis(dimethylamido)titanium complex: ^{1}H NMR (C_6D_6): δ 0.84-0.95 (m, 1H, Cy), 1.13-1.22 (m, 2H, Cy), 1.32-1.43 (m, 3H, Cy), 1.67 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.79-1.84 (m, 2H, Cy), 1.92-2.03 (m, 2H, Cy), 1.90 (s, 3H, CH_3), 2.84 (s, 6H, NCH_3), 3.03 (br s, 6H, NCH_3), 5.60 (s, 1H, Cp-H), 6.52 (br s, 1H, C_6H_3), 7.16 (d, J = 2.4 Hz, 1H, C_6H_3), 7.20 (dd, J = 2.4, 8.8 Hz, 1H, C_6H_3) ppm. The analytical data for **7d**: ^{1}H NMR (C_6D_6): δ 0.82-0.96 (m, 2H, Cy), 1.31-1.50 (m, 4H, Cy), 1.56 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.68-1.78 (m, 2H, Cy), 1.91-2.03 (m, 2H, Cy), 2.04 (s, 3H, CH_3), 5.39 (m, 1H, N-CH), 6.00 (s, 1H, Cp-H), 6.40 (d, J = 8.8 Hz, 1H, C_6H_3), 7.04 (d, J = 2.8 Hz, 1H, C_6H_3), 7.10 (dd, J = 2.8, 8.8 Hz, 1H, C_6H_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 12.30, 14.44, 14.74, 25.72, 26.97, 27.28, 59.67, 111.71, 118.64, 128.33, 128.45, 129.05, 131.85, 133.38, 140.29, 142.78, 143.28, 162.54 ppm. Anal. Calc. ($C_{20}H_{24}Cl_3NTi$): C, 55.52; H, 5.59; N, 3.24 %. Found: C, 55.38; H, 5.79; N, 3.34 %.

Complex 7e. The compound was synthesized by the same conditions and procedures as for **7a** using **6e**. It is oily and could not be purified by recrystallization. Extraction with pentane gave clean compound (90 %). The ^{1}H NMR datum for the intermediate bis(dimethylamido)titanium complex: ^{1}H NMR (C_6D_6): δ 0.82-0.96 (m, 1H, Cy), 1.08-1.23 (m, 2H, Cy), 1.32-1.45 (m, 3H, Cy), 1.70 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 1.82-1.88 (m, 2H, Cy), 1.92 (s, 3H, CH_3), 1.97-2.08 (m, 2H, Cy), 2.86 (s, 6H, NCH_3), 3.03 (s, 6H, NCH_3), 5.60 (s, 1H, Cp-H), 6.49 (br s, 1H, C_6H_3), 6.89-6.95 (m, 2H, C_6H_3) ppm. The analytical data for **7e**: ^{1}H NMR (C_6D_6): δ 0.88-1.03 (m, 2H, Cy), 1.32-1.47 (m, 2H, Cy), 1.47-1.56 (m, 1H, Cy), 1.61 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 1.72-1.84 (m, 3H, Cy), 1.93-2.05 (m, 2H, Cy), 2.09 (s, 3H, CH_3), 5.38-5.47 (m, 1H, N-CH), 6.05 (s, 1H, Cp-H), 6.43 (dd, J = 4.8, 8.8 Hz, 1H, C_6H_3), 6.79-6.85 (m, 2H, C_6H_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 12.61, 14.75, 15.04, 26.03, 27.29, 27.58, 27.66, 59.74, 111.38 (d, $^3J_{CF}$ = 8.3 Hz, C_6H_3), 114.80 (d, $^2J_{CF}$ = 22.8 Hz, C_6H_3), 116.49 (d, $^2J_{CF}$ = 23.5 Hz, C_6H_3), 118.62, 131.69, 133.42 (d, $^3J_{CF}$ = 8.3 Hz, C_6H_3), 140.02, 142.53, 143.00, 159.74 (d, $^1J_{CF}$ = 240.4 Hz, C_6H_3), 160.02 ppm. ^{19}F NMR (C_6D_6): δ -28.83 (dd, J = 7.8 , 12.4 Hz) ppm.

Complex 7f. The compound was synthesized by the same conditions and procedures as for **7a** using **6f**. The reaction between $Ti(NMe_2)_4$ and **6f** was so slow that complete conversion to the intermediate bis(dimethylamido)titanium complex was achieved by heating for 10 days at 80 ^{o}C. Overall yield was 56 %. The ^{1}H NMR datum for the intermediate bis(dimethylamido)titanium complex: ^{1}H NMR (C_6D_6): δ 1.56 (s, 9H, $C(CH_3)_3$), 1.71 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.82 (s, 6H, NCH_3), 3.00 (s, 6H, NCH_3), 5.68 (s, 1H, Cp-H), 6.84 (t, J = 8.0 Hz, 1H, C_6H_4), 6.93 (d, J = 8.0 Hz, 1H, C_6H_4), 7.15 (dd, J = 2.0, 8.0 Hz, 1H, C_6H_4), 7.22 (td, J = 2.0, 8.0 Hz, 1H, C_6H_4) ppm. The analytical data for **7f**: ^{1}H NMR (C_6D_6): δ 1.68 (s, 3H, CH_3), 1.80 (s, 12H, $C(CH_3)_3$ and CH_3), 2.12 (s, 3H, CH_3), 6.21 (s, 1H, Cp-H), 6.71 (d, J = 8.4 Hz, 1H, C_6H_4), 6.93 (d, J = 8.4 Hz, 1H, C_6H_4), 6.95 (t, J = 8.4 Hz, 1H, C_6H_4),

7.10 (t, J = 8.4 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.65, 14.98, 15.04, 29.98, 60.64, 115.18, 122.08, 122.46, 128.14, 128.58, 129.89, 134.47, 141.17, 143.41, 143.91, 163.84 ppm. Anal. Calc. ($C_{18}H_{23}Cl_2NTi$): C, 58.09; H, 6.23; N, 3.76 %. Found: C, 58.24; H, 6.54; N, 3.51 %.

Complex 7g. The compound was synthesized by the same conditions and procedures as for **7a** using **6g**. Analytically pure crystals were isolated in 67 % yield by recrystallization in pentane at -30 ^oC. The ^1H NMR datum for the intermediate bis(dimethylamido)titanium complex: ^1H NMR (C_6D_6): δ 0.89 (br t, J =6.8 Hz, 3H, pentyl-CH_3), 1.07 (br t, J =6.8 Hz, 3H, pentyl-CH_3), 1.74 (s, 3H, CH_3), 1.76-2.01 (m, 4H, pentyl-CH_2), 1.87 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 2.89 (s, 6H, NCH_3), 3.16 (br s, 6H, NCH_3), 4.20 (br s, 1H, pentyl-CH), 5.75 (s, 1H, Cp-H), 6.65 (d, J = 8.0 Hz, 1H, C_6H_4), 6.86 (td, J = 1.2, 8.0 Hz, 1H, C_6H_4), 7.18 (d, J = 8.0 Hz, 1H, C_6H_4), 7.19 (t, J = 8.0 Hz, 1H, C_6H_4) ppm. The analytical data for **7g**: ^1H NMR (C_6D_6): δ 1.01 (t, J = 7.6 Hz, 6H, pentyl-CH_3), 1.66 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 1.79-1.93 (m, 4H, pentyl-CH_2), 2.10 (s, 3H, CH_3), 5.43-5.50 (m, 1H, pentyl-CH), 6.07 (s, 1H, Cp-H), 6.43 (d, J = 8.0 Hz, 1H, C_6H_4-CH), 6.95 (t, J = 8.0 Hz, 1H, C_6H_4-CH), 7.07 (d, J = 8.0 Hz, 1H, C_6H_4), 7.08 (t, J = 8.0 Hz, 1H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.45, 12.63, 14.74, 14.90, 26.58, 62.63, 111.27, 118.62, 122.99, 128.47, 128.74, 131.36, 131.73, 142.16, 142.76, 143.32, 163.92 ppm. Anal. Calc. ($C_{19}H_{25}Cl_2NTi$): C, 59.09; H, 6.53; N, 3.63 %. Found: C, 59.16; H, 6.76; N, 3.49 %.



9 **10** **11**

Compound 9. 6-Methyl-1,2,3,4-tetrahydroquinoline (1.16 g, 7.90 mmol) was dissolved in CCl_4 (4 mL) and the solution was cooled to -20 ^oC. N-Bromosuccinimide (1.41 g, 7.90 mmol) was added slowly as a solid.[5] The solution was warmed to room temperature and stirred for 5 hours. The crude mixture was loaded on silica pad and the column chromatography was conducted eluting with methylene chloride and hexane (1 : 1). Light yellow oil was obtained (0.710 g, 40 %). IR (neat): 3413 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 1.42-1.52 (m, 2H, CH_2), 2.00 (s, 3H, CH_3), 2.39 (t, J = 6.4 Hz, 2H, CH_2), 2.75 (dt, J = 2.8, 8.4 Hz, 2H, N-CH_2), 4.04 (br s, 1H, NH), 6.51 (s, 1H, C_6H_2), 7.09 (s, 1H, C_6H_2) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 20.06, 22.04, 27.60, 41.91, 108.84, 122.59, 126.16, 129.48, 130.67, 139.79 ppm. Anal. Calc. ($C_{10}H_{12}BrN$): C, 53.12; H, 5.35; N, 6.19 %. Found: C, 53.30; H, 5.13; N, 6.51 %.

Compound 10. The compound was synthesized by the same conditions and procedures as for **5a** using **9**. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (2 : 1). A light yellow solid was obtained (90 %). M.p. 67-69 ^oC. IR (neat): 3375 (N-H), 1700 (C=O)

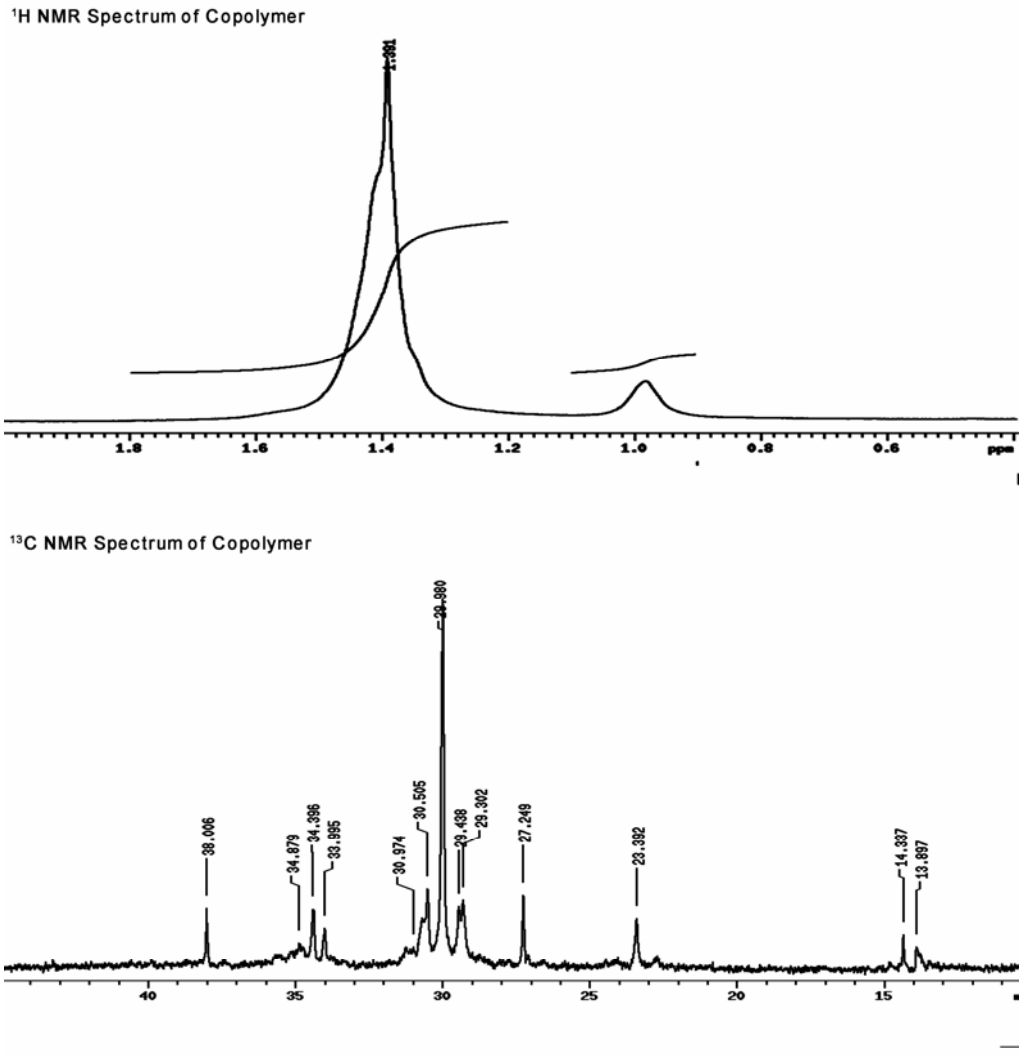
cm^{-1}.^{1}H NMR (C_6D_6): δ 0.77 (d, *J* = 7.2 Hz, 3H, CH_3), 1.59-1.70 (m, 2H, $CH_2CH_2CH_2$), 1.65 (s, 3H, CH_3), 1.84 (dd, *J* = 2.4, 18.4 Hz, 1H, $OCCH_2$), 2.21 (s, 3H, CH_3), 2.20-2.30 (m, 1H, CH), 2.44 (dd, *J* = 6.4, 18.4 Hz, 1H, $OCCH_2$), 2.60 (br t, *J* = 6 Hz, 2H, CH_2), 2.97 (br t, *J* = 5.6 Hz, 2H, N-CH_2), 4.06 (s, 1H, NH), 6.66 (s, 1H, CH, C_6H_2), 6.74 (s, 1H, C_6H_2) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 15.83, 19.06, 20.58, 22.51, 27.92, 37.52, 42.48, 43.55 ppm**.** Anal. Calc. ($C_{17}H_{21}NO$): C, 79.96; H, 8.29; N, 5.49 **%.** Found: C, 80.17; H, 8.44; N, 5.75 %.

Compound 11. The compound was synthesized by the similar conditions and procedures as for **6a** using **10**. $La(OTf)_3$ was used instead of $CeCl_3$. Light yellow solid was obtained in 42 % yield. ^{1}H NMR (C_6D_6): δ 1.66-1.71 (m, 2H, $CH_2CH_2CH_2$), 1.80 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.64 (br t, *J* = 6.4 Hz, 2H, CH_2), 2.74 (d, *J* = 2 Hz, 2H, CH_2), 2.86-2.92 (m, 2H, N-CH_2), 3.62 (br s, 1H, NH), 6.75 (s, 1H, C_6H_2), 6.77 (s, 1H, C_6H_2) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 11.85 , 13.61, 14.39, 20.74, 22.86, 27.70, 42.20, 48.88, 120.81, 122.01, 124.78, 128.68, 129.36, 132.87, 136.36, 136.65, 140.75, 141.15 ppm.

Complex 8. It was synthesized by the same conditions and procedures as for **7a** using **20**. It was purified by trituration in pentane. Overall yield from **20** was 63 %. The ^{1}H NMR datum for the intermediate bis(dimethylamido)titanium complex: ^{1}H NMR (C_6D_6): δ 1.69-1.74 (m, 2H, $CH_2CH_2CH_2$), 1.86 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 2.31(s, 3H, CH_3), 2.57 (t, *J* = 5.6 Hz, 2H, CH_2), 2.95 (s, 6H, NCH_3), 3.27 (s, 6H, NCH_3), 4.02 (ddd, *J* = 5.2, 7.2, 12.0 Hz, 1H, NCH_2), 4.24 (dt, *J*= 5.2, 12.4Hz, 1H, NCH_2), 5.78 (s, 1H, Cp-H), 6.77 (s, 1H, C_6H_2), 6.91 (s, 1H, C_6H_2) ppm. The analytical data for **10**: ^{1}H NMR (C_6D_6): δ 1.36 - 1.44 (m, 2H, $CH_2CH_2CH_2$), 1.76 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.12 (t, *J* = 4Hz, 2H, CH_2), 4.50-4.70 (m, 2H, N-CH_2), 6.02 (s, 1H, Cp-H), 6.59 (s, 1H, C_6H_2), 6.78 (s, 1H, C_6H_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.76, 14.87, 15.06, 21.14, 22.39, 26.32, 54.18, 117.49, 120.40, 126.98, 129.53, 130.96, 131.05, 133.19, 143.22, 143.60, 160.82 ppm. Anal. Calc. ($C_{18}H_{21}Cl_2NTi$): C, 58.41; H, 5.72; N, 3.78%. Found: C, 58.19; H, 5.93; N, 3.89 %.

Polymerizations. Inside a dry box, to a dried 70 mL glass reactor was added 30 mL of toluene solution of 1-hexene (0.30 M). The reactor was assembled and brought out from the dry box. The reactor was heated to 90 ^{o}C by mantle. After an activated catalyst, which was prepared by mixing the complex (0.50 μmol Ti), $[CPh_3]^+[B(C_6F_5)_4]^-$ (2.0 μmol), and $(iBu)_3Al$ (0.200 mmol) for 5 minutes, was added via a syringe, ethylene (100 psig) was fed immediately. After polymerization was conducted for 5 minutes, the ethylene was vented and the acetone was added to the reactor to give white precipitates which were collected by filtration and dried under vacuum at 88-100 ^{o}C for 5 hours. In the ^{1}H NMR spectra of the copolymers, the methyl (CH_3) signals (0.93-1.02 ppm) was well isolated from the methine (CH) and methylene (CH_2) signals (1.30-1.50 ppm) and the 1-hexene contents were calculated from the

integration values of the methyl signal and the combined signal of methine and methylene (See the typical ^{1}H NMR spectrum of the copolymer below). The copolymer (10 mg) was dissolved in C_6D_6 and the ^{1}H NMR spectra were obtained at 78 ^{o}C. The copolymer (20 mg) was dissolved in C_6D_6 and the ^{13}C NMR spectrum was obtained (100 MHz, 90^o pulse angle, 10 second relaxation delay time, 4000 acquisition number). The 1-hexene content calculated roughly from the ^{13}C NMR spectrum[6] was in agreement with that calculated from the ^{1}H NMR spectrum.



Crystallographic Studies. Crystals of **7a** and **7d** were mounted in thin-walled glass capillaries and sealed under argon. The data sets were collected on a Bruker Smart CCD detector single diffractometer. Mo-Kα radiation (λ = 0.7107 Å) was used for all structures. Structure of **7a** was solved by the application of Patterson method and the structure of **7d** was solved by the direct methods using the SHELX-96 program and least-squares refinement using the SHELXL-Plus (5.1) software package. All

non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the calculated positions. The crystal data and refinement results are summarized below in Table 1.

Table 1. Crystallographic Parameters of 7a and 7d

	7a	**7d**
formula	$[C_{20}H_{25}Cl_2NTi]_2$	$C_{20}H_{24}Cl_3NTi$
Fw	796.42	432.65
color	red	red
size, mm^3	0.42×0.29×0.19	0.33×0.24×0.06
a, Å	8.7730(18)	8.3533(10)
b, Å	13.301(3)	11.2763(13)
c, Å	17.470(4)	11.9066(14)
α, deg	82.526(4)	99.884(2)
β, deg	82.582(4)	98.641(2)
γ, deg	87.424(4)	106.940(2)
V, $Å^3$	2003.6(7)	1032.8(2)
crystal system	triclinic	triclinic
space group	P-1	P-1
D(calc), gcm^{-1}	1.320	1.391
Z	2	2
μ, mm^{-1}	0.695	0.805
no. of data collected	27027	13924
no. of unique data	9883	5066
no. of variables	439	229
R(%)	0.0336	0.0607
R_w(%)	0.0890	0.2040
Goodness of fit	1.046	1.134

[a]Data collected at 293(2) K with Mo-Kα radiation (λ(Kα) = 0.7107Å), $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o > 2.0\sigma(I)$, $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$.

---

[1] Conia, J. M.; Leriverend, M. L. *Bull. Soc. Chim. Fr.* **1970**, 2981.

[2] Gage, J. R.; Wagner, J. M. *J. Org. Chem*, **1995**, *60*, 2613.

[3] Ma, H.; Shen, Y.-Q.; Chen, P.; Wang, Y.-M. Meng, J.-B. *Eur. Polym. J.* **1998**, *34*, 1125.

[4] Kasashima, Y.; Kumada, H.; Yamamoto, K.; Akutsu, F.; Naruchi, K.; Miura, M. *Polymer* **1995**, *36*, 645.

[5] Marchand, P.; Puget, A.; Le Baut, G.; Emig, P.; Czech, M.; Günther, E. *Tetrahedron* **2005**, *61*, 4034.

[6] Cheng, H. N. *Polym. Bull.* **1991**, *26*, 325.