o*rtho*-Lithiation of Tetrahydroquinoline Derivatives and Its Use for the Facile Construction of Polymerization Catalysts

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Supporting Information

General Remarks. All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Diethyl ether, THF, and C_6D_6 were distilled from benzophenone ketyl. Toluene (anhydrous grade) and 1-octene used for the polymerization reaction were purchased from Aldrich and purified over Na/K alloy. Ethylene was purchased from Conley gas (99.0%) and purified by contacting with molecular sieves and copper for several days under the pressure of 200 psig. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Mercury plus 400. Elemental analyses were carried out at the Analytical Center, Kyunghee University. Mass spectra were obtained on a Micromass VG Autospec. Gel permeation chromatograms (GPC) were obtained at 140 ^{o}C in trichlorobenzene using Waters Model 150-C+ GPC and the data were analyzed using a polystyrene analyzing curve. Tetrahydroquinoline and 2-methyltetrahydroquinoline are commercially available and 2-n-butyltetrahydroquinoline and 2-*tert*-butyltetrahydroquinoline were prepared according to the literature method.[1]

2-(6-*tert*-Butoxyhexyl)tetrahydroquinoline. Freshly cut lithium (0.17 g, 25 mmol) was added to a Schlenk flask containing diethyl ether (8 mL). After the flask was cooled to -25^{o}C, 1-*tert*-butoxy-6-

chlorohexane (2.38 g, 12.4 mmol) was added using a syringe pump over a period of one hour. The solution was stirred for one hour at -20 ~ -15 ^{o}C. Then, the temperature was raised to 0^{o}C, and the solution was stirred for another hour. After a solution of quinoline (1.60 g, 12.4 mmol) in THF (5 mL) was added at 0^{o}C, the cooling bath was removed. After stirring for two hours, water (15 mL) was added. The reaction mixture was extracted using diethyl ether (3 × 25 ml), and the organic phases were combined and dried over anhydrous $MgSO_4$. The removal of the solvent using a rotary evaporator gave an oily residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 10:1). The obtained product was dissolved in anhydrous ethanol (40 mL). Then, freshly cut sodium metal (3.4 g, 150 mmol) was added and the solution was refluxed for 2 hours. After the solution was cooled to 0^{o}C, cold water (50 mL) was added. The product was then extracted using toluene (3 × 20 mL). After the collected organic phase was washed with water, it was dried over anhydrous $MgSO_4$. The solvent was removed using a 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). The product was obtained as a pale yellow oil (1.97 g, 55%). ^{1}H NMR (C_6D_6): δ 7.05 (t, *J* = 7.2 Hz, 1H, Ph-H), 6.97 (d, *J* = 7.2 Hz, 1H, Ph-H), 6.72 (t, *J* = 7.2 Hz, 1H, Ph-H), 6.36 (d, *J* = 7.6 Hz, 1H, Ph-H), 3.34 (br s, 1H, N-H), 3.31 (t, *J* = 6.4 Hz, 2H, OCH_2), 2.96-2.88 (m, 1H, CH), 2.64 (ddd, *J* = 16, 11, 5.6 Hz, 1H, benzyl-CH_2), 2.56 (dt, *J* = 16, 8.0 Hz, 1H, benzyl-CH_2), 1.68-1.56 (m, 4H, CH_2), 1.44-1.36 (m, 4H, CH_2), 1.31-1.12(m, 4H), 1.18 (s, 9H, $C(CH_3)_3$) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 145.16, 129.52, 127.04, 121.23, 117.17, 114.43, 72.17, 61.70, 51.86, 37.13, 31.35, 30.34, 28.50, 27.95, 27.06, 27.03, 26.14 ppm. HRMS (EI): *m/z* calcd for ($[M]^+$ $C_{19}H_{31}NO$) 289.2406, found 289.2404.

***Ortho*-lithiation (Preparation of 1).** At -78^{o}C, *n*-BuLi (3.0 mL, 7.5 mmol, 2.5 M solution in hexane) was added dropwise to a solution of 1,2,3,4-tetrahydroquinoline (1.00 g, 7.51 mmol) in diethyl ether (16 mL). After the solution was stirred for one hour at -78^{o}C, it was allowed to warm to room temperature. White solid precipitated and the butane gas was evolved, which was removed through a bubbler. The solution was cooled again to -78^{o}C and CO_2 gas was added. The white solid disappeared immediately. After the solution was stirred for 40 minutes at -78^{o}C, the temperature was slowly raised to -20^{o}C while

excess CO_2 gas was removed through a bubbler. White solid again precipitated. Then, THF (0.60 g, 8.3 mmol) and *tert*-BuLi (4.9 mL, 8.3 mmol, 1.7 M solution in pentane) were successively added to the slurry at -20 ^oC, and the solution was stirred for two hours. The lithiated compound was quenched by the addition of D_2O. The ^1H NMR spectrum of the organic phase shows a decrease in the intensity of the *ortho*-proton signal from 1.0 to 0.14, indicating 86% *ortho*-lithiation yield. Various conditions were screened to reach a complete *ortho*-lithiation (See Table S1), but they failed. The 86% *ortho*-lithiation yield is the best we achieved. When excess *t*BuLi (1.3 equivalent) was employed, the *ortho*-lithiation yield was not improved. We did not observe any intensity decrease of the other signals except the *ortho*-proton signal in the ^1H NMR spectrum of the D_2O-quenched product. These results indicate the rest of the added reactant (14%) remained intact. Furthermore, when we used excess *t*BuLi (1.3 equivalent) and added an electrophilic of 2,3,4,5-tetramethylcyclopenenone to the lithiated compound, we observed some side product of the cyclopentadiene compound which was prepared by the nucleophilic attack of the *t*BuLi to the tetramethylcyclopentenone. We presume that some lithium carbamate group loses CO_2 to become just lithium amide group or the *t*BuLi attacks the carbonyl carbon on the lithium carbamate to bring the lithium carbamate group to lithium amide group. The lithium amide group cannot work as an *ortho*-directing group, but is intact by the treatment to give the reactant after the work-up. The lithiated compounds **2**-**5** were also prepared by the same conditions and procedure as for **1** using the corresponding substituted tetrahydroquinoline.

Table S1. The *ortho*-Lithiation Yield by Variation of the Condition

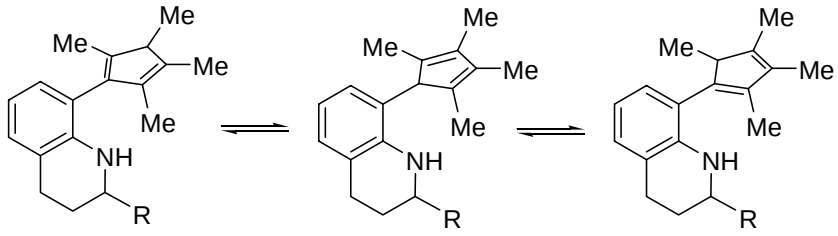
Solvent	RLi (eq)	Additive (eq)	Temp (^oC)	Time (hr)	Yield (%)
THF	*t*-BuLi (1.1)	None	-78	4	60
THF	*t*-BuLi (1.1)	None	-78	6	60
Dimethoxyethane (DME)	*t*-BuLi (1.1)	None	-78	4	30
THF	*s*-BuLi (1.1)	None	-78	4	60
Diethyl ether	*t*-BuLi (1.1)	None	-20	6	50

Diethyl ether	*t-BuLi (1.1)*	*THF (1.1)*	*-20*	*2*	*86*
Diethyl ether	*t*-BuLi (1.0)	THF (1.0)	-20	2	80
Diethyl ether	*t*-BuLi (1.2)	THF (1.2)	-20	2	86
Diethyl ether	*t*-BuLi (1.3)	THF (1.3)	-20	2	85
Diethyl ether	*t*-BuLi (1.1)	THF (1.1)	-20	4, 6, or 8	86
Diethyl ether	*t*-BuLi (1.1)	THF (1.1)	-5	4	85
Diethyl ether	*t*-BuLi (1.1)	TMEDA[a](1.1)	-20	2	62
Methyl *t*-butyl ether (MTBE)	*t*-BuLi (1.1)	THF (1.1)	-20	2	73
Methyl *t*-butyl ether (MTBE)	*t*-BuLi (1.1)	Dioxane (1.1)	-20	2	42

[a]Tetramethylethylenediamine

8-(Tetramethylcyclopentadienyl)tetrahydroquinoline (ligand for 6). At -78°C, *n*-BuLi (3.0 mL, 7.5 mmol, 2.5 M solution in hexane) was added dropwise to a solution of 1,2,3,4-tetrahydroquinoline (1.00 g, 7.51 mmol) in diethyl ether (16 mL). After the solution was stirred for one hour at -78°C, it was allowed to warm to room temperature. White solid precipitated and the butane gas was evolved, which was removed through a bubbler. The solution was cooled again to -78°C and CO_2 gas was added. The white solid disappeared immediately. After the solution was stirred for 40 minutes at -78°C, the temperature was slowly raised to -20°C while excess CO_2 gas was removed through a bubbler. White solid again precipitated. Then, THF (0.60 g, 8.3 mmol) and *tert*-BuLi (4.9 mL, 8.3 mmol, 1.7 M solution in pentane) were successively added to the slurry at -20 °C, and the solution was stirred for two hours. The 2,3,4,5-tetramethyl-2-cyclopentenone (0.88 g, 6.38 mmol) dissolved in THF containing $CeCl_3$-2LiCl (19 mL, 0.33 M) was added using a syringe. The solution was stirred for one hour at -20°C. After the solution was slowly warmed to room temperature for one hour, water (15 mL) was added. With the addition of water, a white gel was formed, which was filtered over Celite. The filtrate was extracted using ethyl acetate (3 × 15 mL). Then, the organic phases were combined and transferred to a separatory funnel. After aqueous HCl (2N, 40 mL) was added, the separatory funnel was shaken vigorously for two minutes. Aqueous saturated $NaHCO_3$ (60 mL) was carefully added to neutralize the water phase. The organic phase was collected and dried over anhydrous $MgSO_4$. The solvent was

removed with a rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). The product was obtained as yellow oil (0.69 g, 43%). The moderate yield is consistent with those (40 - 50%) observed for the reactions of other lithiated compounds with the tetramethylcyclopentenone.[2] Because the 1,5-sigmatropic rearrangement is a facile process in the cyclopentadiene system[3], the ^{1}H and ^{13}C NMR signals are complicate. Furthermore, the signals are very broad possibly due to the rotational barrier around (phenylene)C-C(Cp) bond. Deprotonation of the Cp-H and N-H protons by the treatment of two equivalents of n-BuLi to the compound showing the complicate NMR signals provides readily assignable ^{1}H and ^{13}C NMR spectra (see the spectra below). IR (neat): 3415 (N-H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.96-6.90 (m, 2H, Ph-H), 6.77 (t, J = 7.6 Hz, 1H, Ph-H), 3.72-3.54 (br, 1H, N-H), 3.20-2.54 (br m, 5H, Cp-H, NCH_2, and benzyl-CH_2), 1.85 (s, 3H, Cp-CH_3), 1.81 (s, 3H, Cp-CH_3), 1.79 (s, 3H, Cp-CH_3), 1.72-1.57 (m, 2H, CH_2), 1.07-0.95 (br, 3H, Cp-CH_3) ppm. HRMS (EI): *m/z* calcd for ($[M]^+$ $C_{18}H_{23}N$) 253.1830, found 253.1830.



Scalable synthesis of 8-(tetramethylcyclopentadienyl)tetrahydroquinoline (ligand for 6). The *ortho*-lithiation was carried out using the same procedure and conditions with tetrahydroquinoline (20.0 g, 150 mmol), diethyl ether (240 mL), *n*-BuLi (60.0 mL, 150 mmol, 2.5 M solution in hexane), THF (14.1 g, 195 mmol), and *tert*-BuLi (115 mL, 195 mmol, 1.7 M solution in pentane). *Because the preparation of THF-soluble $CeCl_3$-2LiCl solution is painful (reference 8 in the main text), we tried carbonyl-attack reaction in the presence of LiCl only. A purification method which avoids the column chromatography was devised.* Thus, a THF solution (200 mL) containing 2,3,4,5-tetramethyl-2-cyclopentenone (17.6 g, 128 mmol) and LiCl (10.8 g, 255 mmol) was added to the *ortho*-lithiated compound using a syringe at -20°C. After the solution was stirred for one hour at -20°C, it was slowly warmed to room temperature for another hour. Water (300 mL) was added, and the product was

extracted with ethyl acetate (3 × 100 mL). The organic phases were collected, and the solvent was removed with a rotary evaporator. The residue was dissolved in diethyl ether (500 mL) and then was transferred to a separatory funnel. Aqueous 2N HCl (500 mL) was added, and the separatory funnel was shaken vigorously for two minutes. A white solid precipitated, which was collected by filtration. *The unreacted 2,3,4,5-tetramethyl-2-cyclopentenone, which is soluble in diethyl ether, and the unreacted tetrahydroquinoline, which is soluble as a HCl salt in water, were removed by filtration. The HCl salt of the product is soluble neither in water nor in diethyl ether, and it precipitated.* After the solid was washed with diethyl ether, it was suspended in ethyl acetate, and aqueous saturated $NaHCO_3$ solution was added. While the mixture was stirred, triethylamine was added dropwise until the solid completely dissolved. Then the organic phase was collected and dried over anhydrous $MgSO_4$. The removal of the solvent with a rotary evaporator gave the desired compound (14.9 g, 46%). The analysis of the ^{1}H NMR spectrum showed that the product obtained this way was pure to be used for the next step without further purifications. (See the ^{1}H NMR spectrum below).

2-Methyl-8-(tetramethylcyclopentadienyl)tetrahydroquinoline (ligand for 7). The compound was synthesized using the same conditions and procedure as those for 8-(tetramethylcyclopentadienyl)tetrahydroquinoline with 2-methyltetrahydroqunoline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). Yellow oil was obtained in 42% yield. The compound was also prepared in 13 g-scale according to the same procedure and conditions as those for 8-(tetramethylcyclopentadienyl)tetrahydroquinoline with 2-methyltetrahydroquinoline (20.0 g, 136 mmol), diethyl ether (220 mL), *n*-BuLi (54.4 mL, 136 mmol, 2.5 M solution in hexane), THF (12.7 g, 177 mmol), *tert*-BuLi (104 mL, 177 mmol, 1.7 M solution in pentane), and THF solution (180 mL) containing 2,3,4,5-tetramethyl-2-cyclopentenone (16.0 g, 116 mmol) and LiCl (9.79 g, 231 mmol). Because the HCl salt of the product did not precipitate by the work-up procedure described in the scalable synthesis of 8-(tetramethylcyclopentadienyl)tetrahydroquinoline, the work-up procedure was modified. Thus, the crude carbonyl-attacked product was dissolved in diethyl ether (400 mL) and then HCl solution in

dioxane (48 mL, 192 mmol, 4 M) was added. The resulting slurry was stirred vigorously for 75 minutes. The precipitates were collected by filtration and washed thoroughly with diethyl ether. The solid was dispersed in water (100 ml) and the resulting slurry was stirred vigorously for 10 minutes. The solid was colleted by filtration and washed with water (50 mL). The solid was dispersed in a flask containing saturated aqueous $NaHCO_3$ solution (70 mL) and ethyl acetate (90 mL). While the two phase mixture was stirred vigorously, triethylamine was added dropwise until all solid was dissolved. The organic phase was collected and dried over anhydrous $MgSO_4$. Removal of solvent gave light yellow oil (12.6 g, 41%). The analysis of the ^1H NMR spectrum showed that the product obtained this way was pure to be used for the next step without further purifications. IR (neat): 3406 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 6.95-6.90 (m, 2H, Ph-H), 6.76 (m, 1H, Ph-H), 3.95-3.70 (m, 1H, N-H), 3.31-2.59 (br m, 4H, Cp-H, NCH, and benzyl-CH_2), 1.88-1.76 (m, 9H, Cp-CH_3), 1.71-1.58 (m, 1H, CH_2), 1.48-1.34 (m, 1H, CH_2), 1.10-0.98 (m, 3H, Cp-CH_3), 0.92-0.82 (m, 3H, CH_3) ppm. HRMS (EI): *m/z* calcd for ($[M]^+$ $C_{19}H_{25}N$) 267.1987, found 267.1990.

2-n-Butyl-8-(tetramethylcyclopentadienyl)tetrahydroquinoline (ligand for 8). The compound was synthesized using the same conditions and procedure as those for 8-(tetramethylcyclopentadienyl)tetrahydroquinoline with 2-n-butyltetrahydroquinoline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 50:1). Light yellow oil was obtained in 47% yield. IR (neat): 3415 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.01-6.89 (m, 2H, Ph-H), 6.79-6.72 (m, 1H, Ph-H), 4.18-3.86 (br, 1H, N-H), 3.21-2.56 (br m, 4H, Cp-H, NCH, and benzyl-CH_2), 1.90-1.76 (m, 9H, Cp-CH_3), 1.82-1.66 (m, 1H, CH_2), 1.58-1.42 (m, 1H, CH_2), 1.36-1.08 (m, 6H, CH_2), 1.10-0.98 (m, 3H, Cp-CH_3), 0.88-0.78 (m, 3H, CH_3) ppm. HRMS (EI): *m/z* calcd for ($[M]^+$ $C_{22}H_{31}N$) 309.2456, found 309.2457.

2-(6-*tert*-Butoxyhexyl)-8-(tetramethylcyclopentadienyl)tetrahydroquinoline (ligand for 9). The compound was synthesized using the same conditions and procedure as those for 8-(tetramethylcyclopentadienyl)tetrahydroquinoline with 2-(6-*tert*-butoxyhexyl)tetrahydroquinoline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v,

50:1). Yellow oil was obtained in 42% yield. IR (neat): 3415 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.04-6.94 (m, 2H, Ph-H), 6.84-6.76 (m, 1H, Ph-H), 4.22-3.98 (br, 1H, N-H), 3.32-3.22 (m, 2H, OCH_2), 3.22-2.64 (br m, 4H, Cp-H, NCH, and benzyl-CH_2), 1.92-1.78 (m, 9H, Cp-CH_3), 1.82-1.66 (m, 1H, CH_2), 1.60-1.51 (m, 3H), 1.42-1.01 (m, 11H), 1.16 (s, 9H, $C(CH_3)_3$) ppm. HRMS (EI): *m/z* calcd for ($[M]^+$ $C_{28}H_{43}NO$) 409.3345, found 409.3347.

Complex 6. The MeLi (0.760 g, 1.68 mmol, 2.21 g/mmol in diethyl ether) was added dropwise to a stirred solution of 8-(tetramethylcyclopentadienyl)tetrahydroquinoline (0.10 g, 0.40 mmol) in cold diethyl ether (-30°C). The solution was stirred overnight at room temperature. The resulting solution was cooled to -30°C, and $TiCl_4$·DME (0.11 g, 0.40 mmol) was added in one portion. After the solution was stirred for three hours at room temperature, the solvent was removed under vacuum. Pentane was then added, and the solution was filtered over Celite. The removal of the solvent results in a red solid (0.087 g, 67%). The crude product was tolerably pure with the analysis of the ^1H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. The single crystals were obtained by recrystallization in pentane at -30°C. ^1H NMR (C_6D_6): δ 7.00 (d, *J* = 7.2 Hz, 1H, Ph-H), 6.92 (d, *J* = 7.2 Hz, 1H, Ph-H), 6.84 (t, *J* = 7.6 Hz, 1H, Ph-H), 4.58-4.50 (m, 2H, NCH_2), 2.47 (t, *J* = 6.4 Hz, 2H, CH_2), 2.05 (s, 6H, Cp-CH_3), 1.74-1.58 (m, 2H, CH_2), 1.66 (s, 6H, Cp-CH_3), 0.58 (s, 6H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 160.76, 136.20, 131.68, 128.73, 127.76, 126.99, 120.95, 119.97, 119.69, 51.03, 48.85, 27.32, 23.09, 12.14 ppm. Anal. Calc. ($C_{20}H_{27}NTi$): C, 72.95; H, 8.26; N, 4.25%. Found: C, 73.31; H, 7.88; N, 4.43%.

Complex 7. The complex was synthesized using the same conditions and procedure as those for **6** with 2-methyl-8-(tetramethylcyclopentadienyl)tetrahydroquinoline. The product was obtained as a red solid in 82% yield. The crude product was tolerably pure with the analysis of the ^1H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. ^1H NMR (C_6D_6): δ 7.02 (d, *J* = 7.2 Hz, 1H, Ph-H), 6.97 (d, *J* = 7.2 Hz, 1H, Ph-H), 6.86 (t, *J* = 7.6 Hz, 1H, Ph-H), 5.54-5.46 (m, 1H, NCH), 2.69 (ddd, *J* = 16, 13, 6.0 Hz, 1H, benzyl-CH_2), 2.37 (dd, *J* = 16, 4.0 Hz, 1H, benzyl-CH_2), 2.05 (s, 3H, Cp-CH_3), 2.03 (s, 3H, Cp-CH_3), 1.80-1.54 (m, 2H, CH_2), 1.69 (s, 3H,

Cp-CH_3), 1.62 (s, 3H, Cp-CH_3), 1.16 (d, J = 6.8 Hz, 3H, CH_3), 0.63 (s, 3H, TiCH_3), 0.57 (s, 3H, TiCH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 159.16, 135.93, 135.66, 131.48, 128.84, 128.23, 126.97, 122.61, 119.76, 119.41, 118.47, 52.96, 50.19, 49.65, 27.45, 21.94, 20.10, 12.24, 12.17, 12.15, 11.99 ppm. Anal. Calc. ($C_{21}H_{29}NTi$): C, 73.46; H, 8.51; N, 4.08%. Found: C, 73.69; H, 8.20; N, 4.21%.

Complex 8. The complex was synthesized using the same conditions and procedure as those for **6** with 2-n-butyl-8-(tetramethylcyclopentadienyl)tetrahydroquinoline. The product was obtained as a red solid in 82% yield. The crude product was tolerably pure with the analysis of the ^1H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. ^1H NMR (C_6D_6): δ 7.00 (d, J = 7.2 Hz, 1H, Ph-H), 6.95 (d, J = 7.2 Hz, 1H, Ph-H), 6.84 (t, J = 7.2 Hz, 1H, Ph-H), 5.46-5.37 (m, 1H, NCH), 2.65 (ddd, J = 17, 14, 6.0 Hz, 1H, benzyl-CH_2), 2.37 (dd, J = 17, 4.0 Hz, 1H, benzyl-CH_2), 2.09 (s, 3H, Cp-CH_3), 2.05 (s, 3H, Cp-CH_3), 1.87-1.56 (m, 4H, CH_2), 1.71 (s, 3H, Cp-CH_3), 1.62 (s, 3H, Cp-CH_3), 1.38-1.21 (m, 4H, CH_2), 0.90 (t, J = 7.2 Hz, 3H, CH_3), 0.62 (s, 3H, TiCH_3), 0.54 (s, 3H, TiCH_3) ppm. $^{13}C\{^1H\}$NMR(C_6D_6): δ 159.50, 135.94, 135.59, 131.47, 128.84, 128.05, 126.94, 122.88, 119.73, 119.26, 118.62, 54.94, 53.06, 49.70, 33.64, 29.20, 23.55, 23.26, 21.89, 14.73, 12.31, 12.23, 12.16, 12.08 ppm. Anal. Calc. ($C_{24}H_{35}NTi$): C, 74.79; H, 9.15; N, 3.63%. Found: C, 74.69; H, 8.79; N, 3.84%.

Complex 9. The complex was synthesized using the same conditions and procedure as those for **6** with 2-(6-*tert*-butoxyhexyl)-8-(tetramethylcyclopentadienyl)tetrahydroquinoline. The product was obtained as red oil in 53% yield. The crude product was pure with the analysis of the ^1H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. ^1H NMR (C_6D_6): δ 7.01 (d, J = 6.8 Hz, 1H, Ph-H), 6.96 (d, J = 7.2 Hz, 1H, Ph-H), 6.84 (t, J = 7.6 Hz, 1H, Ph-H), 5.44-5.39 (m, 1H, NCH), 3.27 (t, J = 6.4 Hz, 2H, OCH_2), 2.65 (ddd, J = 17, 14, 5.6 Hz, 1H, CH_2), 2.36 (dd, J = 17, 4.4 Hz, 1H, CH_2), 2.07 (s, 3H, Cp-CH_3), 2.04 (s, 3H, Cp-CH_3), 1.99-1.88 (m, 2H, CH_2), 1.72 (s, 3H, Cp-CH_3), 1.62 (s, 3H, Cp-CH_3), 1.80-1.56 (m, 4H, CH_2), 1.46-1.28 (m, 6H, CH_2), 1.15 (s, 9H, $C(CH_3)_3$), 0.63 (s, 3H, TiCH_3), 0.55 (s, 3H, TiCH_3) ppm. $^{13}C\{^1H\}$NMR (C_6D_6): δ 159.53, 135.95,

135.59, 131.47, 128.86, 128.07, 126.94, 122.90, 119.73, 119.27, 118.68, 72.11, 61.68, 55.00, 53.05, 49.63, 33.95, 31.30, 30.10, 27.97, 27.09, 27.04, 23.55, 21.89, 12.30, 12.19, 12.13, 12.07 ppm.

8-(Indenyl)tetrahydroquinoline (ligand for 10). *Ortho*-lithiation was carried out using the same procedure and condition with 1,2,3,4-tetrahydroquinoline (1.21 g, 9.08 mmol), diethyl ether (19 mL), n-BuLi (3.6 mL, 9.1 mmol, 2.5 M solution in hexane), THF (0.72 g, 10 mmol), and *tert*-BuLi (5.9 mL, 10 mmol, 1.7 M solution in pentane). Then 1-indanone (1.02 g, 7.72 mmol) dissolved in THF containing $CeCl_3$-2LiCl (23 mL, 0.33 M) was added to the slurry of **1** in diethyl ether using a syringe. The solution was stirred for one hour at -20^{o}C. After the solution was slowly warmed to room temperature for one hour, water (15 mL) was added. This then results in the formation of a gel which was filtered over Celite. The filtrate was extracted using ethyl acetate (3 × 15 mL). The organic phases were then combined and transferred to a separatory funnel. After aqueous HCl (6 N, 20 mL) was added, the separatory funnel was shaken vigorously for two minutes. Aqueous saturated NaOH (5 M, 25 mL) was carefully added to neutralize the water phase, then the organic phase was collected and dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). The product was obtained as a yellow solid (0.94 g, 49%). M.p.: 68-69^{o}C. IR (neat): 3426 (N-H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.45 (dd, *J* = 6.8, 1.2 Hz , 1H), 7.34 (d, *J* = 6.4 Hz, 1H,), 7.20 (td, *J* = 7.2, 1.6 Hz, 2H,), 7.17-7.14 (m, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.35 (t, *J* = 2.0 Hz, 1H), 3.85 (s, 1H, N-H), 3.17 (d, *J* = 2.4 Hz, 2H, indenyl-H), 2.79-2.72 (m, 2H, CH_2), 2.63 (t, *J* = 6.8 Hz, 2H, benzyl-CH_2), 1.71- 1.54 (m, 2H, CH_2) ppm. ^{13}C{^{1}H}NMR (C_6D_6): δ 144.97, 144.51, 143.68, 142.76, 132.04, 129.43, 128.13, 126.61, 125.31, 124.16, 121.49, 121.18, 120.40, 116.43, 42.11, 38.73, 28.09, 22.53 ppm. Anal. Calc. ($C_{18}H_{17}N$): C, 87.41; H, 6.93; N, 5.66%. Found: C, 87.26; H, 7.31; N, 5.81%.

2-Methyl-8-(indenyl)tetrahydroquinoline (**ligand for 11).** The compound was synthesized using the same conditions and procedure as those for 8-(indenyl)tetrahydroquinoline with 2-methyltetrahydroquinoline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 40:1). Yellow oil was obtained in 45% yield. IR (neat): 3418 (N-H)

cm^{-1}. ^1H NMR (C_6D_6): δ 7.50 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.33 (dd, *J* = 6.8, 0.8 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.22-7.13 (m, 2H), 7.03 (dd, *J* = 7.2, 0.8 Hz, 1H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.43 (t, *J* = 2.4 Hz, 1H), 3.98 (br s, 1H, N-H), 3.18 (d, *J* = 2.0 Hz, 2H, indenyl-CH_2), 3.09-3.01 (m, 1H, NCH), 2.74 (ddd, *J* = 16, 11, 5.2 Hz, 1H, benzyl-CH_2), 2.65 (dt, *J* = 16, 4.8 Hz, 1H, benzyl-CH_2), 1.62-1.54 (m, 1H, CH_2), 1.49-1.38 (m, 1H, CH_2), 0.76 (d, *J* = 6.0 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR(C_6D_6): δ 144.84, 144.59, 143.70, 142.71, 132.06, 129.25, 128.18, 126.55, 125.34, 124.22, 121.49, 121.00, 120.28, 116.60, 47.42, 38.74, 30.35, 27.45, 22.61 ppm. HRMS (EI): *m/z* calcd for ($[M]^+$ $C_{19}H_{19}N$) 261.1517, found 261.1516.

2-n-Butyl-8-(indenyl)tetrahydroquinoline (ligand for 12). The compound was synthesized using same conditions and procedure as for 8-(indenyl)tetrahydroquinoline using 2-n-butyltetrahydroqunoline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 40:1). Yellow oil was obtained in 41% yield. IR (neat): 3418 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.47 (d, *J* = 6.8 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 7.24 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.18 (td, *J* = 7.2, 0.8 Hz, 1H), 7.14 (td, *J* = 7.2, 1.2 Hz, 1H), 7.03 (d, *J* = 6.8 Hz, 1H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.44 (t, *J* = 2.0 Hz, 1H), 4.12 (s, 1H, N-H), 3.20 (d, *J* = 2.0 Hz, 2H, indenyl-CH_2), 3.25-2.94 (m, 1H, NCH), 2.77 (ddd, *J* = 16, 10, 5.2 Hz, 1H, benzyl-CH_2), 2.70 (dt, *J* = 16, 4.8 Hz, 1H, benzyl-CH_2), 1.74-1.66 (m, 1H, CH_2), 1.56-1.44 (m, 1H, CH_2), 1.22-0.96 (m, 6H, CH_2), 0.77 (t, *J* = 6.8 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 144.68, 144.56, 143.81, 142.65, 132.01, 129.23, 128.17, 126.49, 125.32, 124.22, 121.53, 121.25, 120.30, 116.50, 51.93, 38.76, 36.74, 28.39, 28.31, 27.39, 23.20, 14.48 ppm. HRMS (EI): *m/z* calcd for ($[M]^+$ $C_{22}H_{25}N$) 303.1987, found 303.1990.

2-(6-*tert*-Butoxyhexyl)-8-(indenyl)tetrahydroquinoline (ligand for 13). The compound was synthesized using same conditions and procedure as for 8-(indenyl)tetrahydroquinoline using 2-(6-*tert*-butoxyhexyl)tetrahydroqunoline. The product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 40:1). Yellow oil was obtained in 40% yield. IR (neat): 3424 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.47 (dd, *J* = 0.8, 6.8 Hz, 1H), 7.32 (dd, *J* = 0.8, 6.8 Hz, 1H), 7.24 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.19 (td, *J* = 7.2, 0.8 Hz, 1H), 7.17-7.12 (m, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.44 (t, *J* = 2.0 Hz, 1H), 4.13 (br s, 1H, N-H), 3.25 (t, *J* = 6.0 Hz, 2H, OCH_2), 3.20 (d, *J*

= 1.6 Hz, 2H, indenyl-CH_2), 3.02-2.94 (m, 1H, NCH), 2.77 (ddd, *J* = 16, 11, 5.2 Hz, 1H, benzyl-CH_2), 2.69 (dt, *J* = 16, 4.8 Hz, 1H, benzyl-CH_2), 1.74-1.66 (m, 2H, CH_2), 1.58-1.44 (m, 4H, CH_2), 1.32-1.02 (m, 6H, CH_2), 1.16 (s, 9H, $C(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 144.72, 144.57, 143.83, 142.68, 132.04, 129.24, 128.18, 126.54, 125.34, 124.22, 121.55, 121.28, 120.33, 116.51, 72.11, 61.66, 51.92, 38.77, 37.00, 31.23, 30.05, 28.38, 27.94, 27.40, 26.90, 26.13 ppm. HRMS (EI): *m/z* calcd for ($[M]^+$ $C_{28}H_{37}NO$) 403.2875, found 403.2879.

Complex 10. The complex was synthesized using same conditions and procedure as for **6** using 8-(indenyl)tetrahydroquinoline. The product was obtained as a red solid in 47% yield. The crude product was tolerably pure with the analysis of the ^1H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. ^1H NMR (C_6D_6): δ 7.48 (dt, *J* = 8.4, 0.8 Hz, 1H), 7.16 (d, *J* = 6.8 Hz, 1H), 7.04-6.94 (m, 3H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.70 (ddd, *J* = 8.8, 6.4, 0.8 Hz, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 6.30 (d, *J* = 3.2 Hz, 1H), 4.57 (ddd, *J* = 13, 6.4, 3.2Hz, 1H, NCH_2), 4.32 (ddd, *J* = 13, 7.6, 3.6 Hz, 1H, NCH_2), 2.43 (t, *J* = 6.0 Hz, 2H, CH_2), 1.72-1.58 (m, 2H, CH_2), 0.83 (s, 3H, $TiCH_3$), -0.02 (s, 3H, $TiCH_3$) ppm. $^{13}C\{^1H\}$NMR (C_6D_6): δ 161.76, 135.10, 129.56, 129.13, 127.83, 127.36, 127.18, 125.60, 125.42, 125.26, 123.18, 120.30, 119.63, 103.36, 58.74, 55.11, 49.34, 27.15, 22.82 ppm. Anal. Calc. ($C_{20}H_{21}NTi$): C, 74.31; H, 6.55; N, 4.33%. Found: 74.43; H, 6.26; N, 4.68%.

Complex 11. The complex was synthesized using the same conditions and procedure as those for **6** with 2-methyl-8-(indenyl)tetrahydroquinoline. The product was obtained as a red solid in 66% yield. The crude product was tolerably pure with the analysis of the ^1H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. The compound was obtained as a mixture of two diastereomers in 0.67:0.33 ratio and hence two sets of signals were observed in the ^1H and ^{13}C NMR spectra. Signals from the minor isomer were marked as *italic*. Single crystals of an isomer were deposited when the pentane solution was stored at -30°C. ^1H NMR (C_6D_6): δ 7.47 (ddt, *J* = 8.4, 6.0, 0.8 Hz, 1H), *7.17* (d, *J* = 8.8 Hz, 0.33H), 7.06-6.96 (m, 3H), 6.93 (d, *J* = 8.4 Hz, 0.67H,), 6.87 (t, *J* = 7.6 Hz, 0.67H), *6.86* (t, *J* = 7.2 Hz, 0.33H), 6.71-6.67 (m, 1.67H), *6.54* (d, *J* = 3.2 Hz, 0.33H, indenyl-H), *6.45* (d, *J* = 3.2 Hz, 0.33H, indenyl-H), 6.16 (d, *J* = 3.2 Hz, 0.67H), 5.50-5.36 (m, 1H,

NCH), 2.79-2.59 (m, 1H, benzyl-CH_2), 2.42-2.26 (m, 1H, benzyl-CH_2), 1.85-1.50 (m, 2H, CH_2), *1.22* (d, *J* = 6.4 Hz, 1H, CH_3), 1.03 (d, *J* = 6.4 Hz, 2H, CH_3), 0.89 (s, 2H, $TiCH_3$), *0.86* (s, 1H, $TiCH_3$), *0.01* (s, 1H, $TiCH_3$), -0.04 (s, 2H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 160.39, 160.01, 135.43, 134.18, 129.49, 129.31, 129.25, 128.62, 127.42, 127.36, 127.04, 126.66, 125.78, 125.74, 125.35, 125.33, 125.20, 124.26, 123.45, 122.73, 120.20, 120.02, 118.60, 118.27, 105.17, 102.09, 60.31, 57.18, 56.61, 54.10, 50.74, 50.58, 27.24, 27.19, 21.86, 21.76, 19.97, 19.39 ppm. Anal. Calc. ($C_{21}H_{23}NTi$): C, 74.78; H, 6.87; N, 4.15%. Found: C, 74.62; H, 7.05; N, 4.38%.

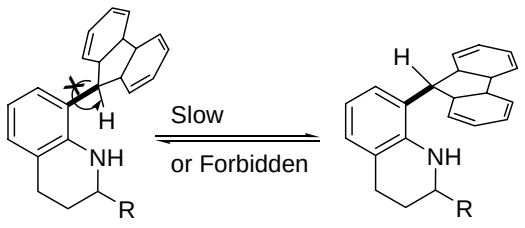
Complex 12. The complex was synthesized using the same conditions and procedure as those for **6** with 2-n-butyl-8-(indenyl)tetrahydroquinoline. The product was obtained as a red solid in 57% yield. The crude product was tolerably pure with the analysis of the ^1H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. The compound was obtained as a mixture of two diastereomers in 0.64:0.36 ratio and two sets of signals were observed in the ^1H and ^{13}C NMR spectra. Signals from the minor isomer were marked as *italic*. ^1H NMR (C_6D_6): δ 7.49 (t, *J* = 8.8 Hz, 1H), *7.17* (d, *J* = 7.6 Hz, 0.36H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.04-6.96 (m, 2H), 6.94 (d, *J* = 8.4 Hz, 0.64H), 6.87 (t, *J* = 7.6 Hz, 0.64H), *6.87* (t, *J* = 7.6 Hz, 0.36H), 6.75 (d, *J* = 3.2 Hz, 0.64H), 6.71 (d, *J* = 8.4 Hz, 1H), *6.55* (d, *J* = 3.2 Hz, 0.36H), *6.50* (d, *J* = 3.6 Hz, 0.36H), 6.17 (d, *J* = 3.2 Hz, 0.64H, indenyl-H), 5.38-5.29 (m, 1H, NCH), 2.70-2.61 (m, 1H, benzyl-CH_2), 2.40-2.28 (m, 1H, benzyl-CH_2), 1.94-1.71 (m, 2H, CH_2), 1.70-1.11 (m, 6H, CH_2), 0.92 (s, 1.92H, $TiCH_3$), *0.90* (t, *J* = 2.4 Hz, 1.08H, CH_3), *0.85* (s, 1.08H, $TiCH_3$), 0.82 (t, *J* = 2.4 Hz, 1.92H, CH_3), *0.03* (s, 1.08H, $TiCH_3$), -0.04 (s, 1.92H, $TiCH_3$) ppm. $^{13}C\{^1H\}$NMR (C_6D_6): δ 160.73, 160.26, 135.39, 134.08, 129.52, 129.31, 129.25, 128.55, 127.42, 127.35, 127.30, 127.02, 126.81, 125.81, 125.66, 125.35, 125.29, 125.19, 124.55, 124.12, 123.54, 122.74, 120.17, 120.00, 118.69, 118.38, 105.40, 101.84, 60.57, 57.10, 56.69, 55.42, 55.32, 54.31, 33.50, 32.96, 29.18, 29.14, 23.45, 23.24, 23.13, 21.71, 14.70, 14.67 ppm. Anal. Calc. ($C_{24}H_{29}NTi$): C, 75.98; H, 7.71; N, 3.69%. Found: C, 76.31; H, 7.33; N, 3.98%.

Complex 13. The complex was synthesized using the same conditions and procedures as those for **6** with 2-(6-*tert*-butoxyhexyl)-8-(indenyl)tetrahydroquinoline. The product was obtained as red oil in 71%

yield. The crude product was tolerably pure with the analysis of the ^{1}H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. The compound was obtained as a mixture of two diastereomers in 0.60:0.40 ratio and two sets of signals were observed in the ^{1}H and ^{13}C NMR spectra. Signals from the minor isomer were marked as *italic*. ^{1}H NMR (C_6D_6): δ 7.49 (t, *J* = 8.4 Hz, 1H), *7.17* (d, *J* = 7.6 Hz, 0.40H), 7.06 (d, *J* = 8.8 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 0.60H), 6.98 (d, *J* = 6.8 Hz, 1.20H), 6.93 (d, *J* = 8.8 Hz, 0.80H), 6.87 (t, *J* = 7.2 Hz, 0.60H), *6.86* (t, *J* = 7.6 Hz, 0.40H), 6.75 (d, *J* = 2.8 Hz, 0.60H), 6.74-6.68 (m, 1H), *6.55* (d, *J* = 3.6 Hz, 0.40H), *6.50* (d, *J* = 3.6 Hz, 0.40H), 6.16 (d, *J* = 3.2 Hz, 0.60H), 5.39-5.24 (m, 1H, NCH), *3.27* (t, *J* = 6.8 Hz, 0.80H, OCH_2), 3.22 (t, *J* = 6.4 Hz, 1.20H, OCH_2), 2.70-2.28 (m, 2H, benzyl-CH_2), 1.90-1.72 (m, 2H, CH_2), 1.64-1.16 (m, 10H, CH_2), *1.15* (s, 3.6H, $C(CH_3)_3$), 1.13 (s, 5.4H, $C(CH_3)_3$), 0.90 (s, 1.8H, $TiCH_3$), *0.84* (s, 1.2H, $TiCH_3$), *0.01* (s, 1.2H, $TiCH_3$), -0.05 (s, 1.8H, $TiCH_3$) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 160.74, 160.26, 135.38, 134.08, 129.50, 129.32, 129.26, 128.54, 127.43, 127.33, 127.28, 127.02, 126.83, 125.81, 125.66, 125.38, 125.27, 125.19, 124.56, 124.13, 123.55, 122.75, 120.17, 119.98, 118.73, 118.42, 105.41, 101.83, 72.11, 72.08, 61.68, 61.62, 60.59, 57.07, 56.67, 55.50, 55.38, 54.28, 33.78, 33.26, 31.30, 31.22, 30.08, 29.98, 27.95, 27.03, 23.51, 23.17, 21.74 ppm.

8-(Fluorenyl)tetrahydroquinoline (ligand for 14). The *ortho*-lithiation was carried out using the same procedure and conditions with 1,2,3,4-tetrahydroquinoline (1.00 g, 7.51 mmol), diethyl ether (16 mL), n-BuLi (3.0 mL, 7.5 mmol, 2.5 M solution in hexane), THF (0.60 g, 8.3 mmol), and *tert*-BuLi (4.9 mL, 8.3 mmol, 1.7 M solution in pentane). A THF solution (10 mL) of 9-fluorenone (1.15 g, 6.38 mmol) was added to the slurry of **1** in diethyl ether using a syringe. After the solution was stirred for one hour at -20°C, it was slowly warmed to room temperature for another hour. After water (15 mL) was added, the mixture was transferred to a separatory funnel containing ethyl acetate (20 mL). The organic phase was collected, and the aqueous phase was extracted with additional ethyl acetate (3 × 15 mL). The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was removed with a rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). Yellow solid was obtained (1.42 g, 71%). The solid

was dissolved in glacial acetic acid (90 mL), and hydroiodic acid (5.27 g, 22.7 mmol, 55 wt-%) was added. After the solution was refluxed for 2 hours, it was cooled to room temperature. Aqueous $Na_2S_2O_3$ solution was added to reduce the generated I_2. Then the solution was extracted with diethyl ether (3 × 60 mL). The collected organic phase was washed with aqueous KOH solution (1 N) and dried over anhydrous $MgSO_4$. This was followed by the removal of the solvent using a rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). White solid was obtained (0.76 g, 56%). In the ^1H and ^{13}C NMR spectra, two sets of broad signals were observed in 0.68:0.32 ratio, but in the ^1H and ^{13}C NMR spectra of the dilithiated compound, which was generated by the treatment of two equivalents of n-BuLi to the compound showing two sets of signals, only a set of signals was cleanly observed (see the spectra below). Observation of the two sets of signals can be attributed to a rotational barrier around (phenylene)C-C(fluorenyl). M.p.: 110-112°C. IR (neat): 3421 (N-H) cm^{-1}. ^1H NMR (C_6D_6): δ 7.67 (d, *J* = 8.0 Hz, 2H, fluorenyl-H), *7.41* (br d, *J* = 6.4 Hz, 0.64H, fluorenyl-H), 7.32 (br d, *J* = 7.6 Hz, 1.36H, fluorenyl-H), 7.23 (t, *J* = 7.2 Hz, 2H, fluorenyl-H), 7.21 (d, *J* = 7.6 Hz, 0.68H, Ph-H), 7.09 (t, *J* = 7.6 Hz, 2H, fluorenyl-H), 6.94 (br d, *J* = 6.8 Hz, 0.68H, Ph-H), 6.82 (br t, *J* = 7.2 Hz, 0.68H, Ph-H), *6.77* (br d, *J* = 7.6 Hz, 0.32H, Ph-H), *6.44* (br d, *J* = 7.6 Hz, 0.32H, Ph-H), *6.40* (br t, *J* = 7.6 Hz , 0.32H, Ph-H), 4.81 (s, 0.68H, fluorenyl-CH), 4.78 (s, 0.32H, fluorenyl-CH), 3.83 (br s, 0.32H, N-H), 3.01 (br s, 0.68H, N-H), 2.71 (br, 0.64H, CH_2), 2.65 (br, 0.64H, CH_2), 2.39 (br, 1.36H, CH_2), 2.30 (br, 1.36H, CH_2), 1.71 (br, 0.64H, CH_2), 1.22 (br, 1.36H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 148.33, 146.43, 143.06, 141.57, 140.48, 131.53, 129.34, 128.54, 127.83, 127.51, 127.43, 125.88, 125.66, 125.34, 122.61, 122.04, 120.19, 117.53, 116.25, 55.35, 48.23, 42.81, 41.68, 28.33, 27.88, 22.75, 21.95 ppm. Anal. Calc. ($C_{22}H_{19}N$): C, 88.85; H, 6.44; N, 4.71%. Found: C, 88.55; H, 6.68; N, 5.01%.



2-Methyl-8-(fluorenyl)tetrahydroquinoline (ligand for 15). The compound was synthesized using the same conditions and procedure as those for 8-(fluorenyl)tetrahydroquinoline with 2-methyltetrahydroquinoline. The intermediate tertiary alcohol was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The yield for the intermediate tertiary alcohol was 63 %. Then, the final product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). The yield for the second reduction step was 75%. Two sets of broad signals were observed in 0.74:0.26 ratio in the ^{1}H and ^{13}C NMR spectra. M.p.: 101-103^{o}C. IR (neat): 3421 (N-H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.66 (d, *J* = 7.2 Hz, 2H, fluorenyl-H), *7.52* (br s, 0.26H, fluorenyl-H), *7.39* (br s, 0.26H, fluorenyl-H), 7.33 (d, *J* =7.2 Hz, 0.74H, fluorenyl-H), 7.29 (d, *J* = 7.2 Hz, 0.74H, fluorenyl-H), 7.26-7.18 (br m, 2.74H), 7.08 (t, *J* = 7.2 Hz, 2H, fluorenyl-H), 6.97(d, *J* = 7.2 Hz, 0.74H, Ph-H), *6.84* (d, *J* = 7.2 Hz, 0.26H, Ph-H), 6.83 (t, *J* = 7.2 Hz, 0.74H, Ph-H), 6.48 (br, 0.26H, Ph-H), 6.42 (br, 0.26H, Ph-H), 4.89 (s, 0.26H, fluorenyl-CH), 4.83 (s, 0.74H, fluorenyl-CH), 3.96 (br s, 0.26H, N-H), 3.22 (br s, 0.26H, NCH), 2.81-2.32 (br m, 3.48H, NCH, NH, benzyl-CH_2), 1.75-1.60 (br, 0.26H, CH_2), 1.60-1.42 (br, 0.26H, CH_2), 1.32-1.16 (br, 0.74H, CH_2), 1.11-0.92 (br, 0.74H, CH_2), 0.35 (d, *J* = 5.6 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 146.60, 146.45, 142.89, 140.70, 140.63, 131.31, 128.86, 127.57, 125.88, 125.46, 122.43, 121.75, 120.02, 117.70, 116.12, 55.22, 48.28, 48.01, 46.82, 30.44, 29.76, 27.67, 27.46, 23.02, 22.09 ppm. Anal. Calc. ($C_{23}H_{21}N$): C, 88.71; H, 6.80; N, 4.50%. Found: C, 88.52; H, 7.19; N, 4.38%.

2-n-Butyl-8-(fluorenyl)tetrahydroquinoline (ligand for 16). The compound was synthesized using the same conditions and procedure as those for 8-(fluorenyl)tetrahydroquinoline with 2-n-butyltetrahydroqunoline. The intermediate tertiary alcohol was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The yield for the intermediate tertiary alcohol was 55 %. The final product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The yield for the second reduction step was 73%. Two sets of broad signals were observed in 0.85:0.15 ratio in the ^{1}H and ^{13}C NMR spectra. M.p.: 66-67^{o}C. IR (neat): 3432 (N-H) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.68 (m, 2H, fluorenyl-H), *7.54* (br, 0.15H, fluorenyl-H), *7.43* (br,

0.15H, fluorenyl-H), 7.32 (d, *J* = 7.2 Hz, 0.85H, fluorenyl-H), 7.29 (d, *J* = 7.2 Hz, 0.85H, fluorenyl -H), 7.23 (t, *J* =7.2 Hz, 2H, fluorenyl-H), 7.22 (d, *J* = 7.2 Hz, 0.85H, Ph-H), 7.07 (t, *J* = 7.6 Hz, 2H, fluorenyl-H), 7.00 (d, *J* = 7.2 Hz, 0.85H, Ph-H), 6.83 (t, *J* = 7.2 Hz, 0.85H, Ph-H), *6.74* (br t, *J* = 8.0 Hz, 0.15H, Ph-H), *6.50* (br, 0.15H, Ph-H), 6.44 (br, 0.15H, Ph-H), *5.03* (br s, 0.15H, fluorenyl-CH), 4.82 (s, 0.85H, fluorenyl-CH), *4.16* (br s, 0.15H, NH), *3.14* (br s, 0.15H, NCH), 2.76 (s, 0.85H, NH), 2.59-2.35 (m, 2.85H, NCH and CH_2), 1.89-0.42 (m, 8H) 0.82 (t, *J* = 6.8 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.58, 146.52, 142.87, 140.70, 140.61, 131.41, 128.98, 127.85, 127.55, 125.49, 125.39, 122.52, 121.90, 120.17, 119.95, 116.05, 55.31, 51.14, 36.48, 28.46, 27.54, 27.46, 23.18, 14.54 ppm. Anal. Calc. ($C_{26}H_{27}N$): C, 88.34; H, 7.70; N, 3.96%. Found: C, 87.98; H, 7.91; N, 4.32%.

2-*tert*-Butyl-8-(fluorenyl)tetrahydroquinoline (ligand for 17). The compound was synthesized using the same conditions and procedure as those for 8-(fluorenyl)tetrahydroquinoline with 2-*tert*-butyltetrahydroqunoline. The intermediate tertiary alcohol was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 30:1). The yield for the intermediate tertiary alcohol was 72 %. The final product was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 20:1). The yield for the second reduction step was 62%. A set of relatively sharp signals was observed in the ^1H and ^{13}C NMR spectra. M.p.: 111-112^oC. IR (neat): 3434 (N-H) cm^{-1}.^1H NMR (C_6D_6) : δ 7.66 (t, *J* = 6.4 Hz, 2H, fluorenyl-H), 7.32 (d, *J* = 7.6 Hz, 1H, fluorenyl-H), 7.28 (d, *J* = 7.6 Hz, 1H, fluorenyl-H), 7.26-7.19 (m, 3H, fluorenyl-H and Ph-H), 7.10 (td, *J* = 7.6, 0.8 Hz, 1H, fluorenyl-H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1H, fluorenyl-H), 7.01 (d, *J* = 7.2 Hz, 1H, Ph-H), 6.83 (t, *J* = 7.2 Hz, 1H, Ph-H), 4.81 (s, 1H, fluorenyl-CH), 2.68 (s, 1H, NH), 2.55 (ddd, *J* = 16, 12, 5.2 Hz, 1H, benzyl-CH_2), 2.45 (ddd, *J* = 16, 4.8, 2.0 Hz, 1H, benzyl-CH_2), 2.32 (dd, *J* = 11, 2.4 Hz, 1H, NCH), 1.41-1.32 (m, 1H, CH_2), 1.10 (ddd, *J* = 24, 12, 4.8 Hz, 1H, CH_2), 0.29 (s, 9H, $C(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.70, 146.39, 143.21, 140.86, 140.56, 131.57, 128.78, 127.82, 127.72, 127.51, 125.46, 125.31, 122.65, 121.96, 120.36, 120.14, 115.95, 61.09, 55.35, 33.15, 28.48, 25.62, 22.92 ppm. Anal. Calc. ($C_{26}H_{27}N$): C, 88.34; H, 7.70; N, 3.96%. Found: C, 87.98; H, 7.80; N, 4.29%.

Complex 14. The complex was synthesized using the same conditions and procedure as those for **6** with 8-(fluorenyl)tetrahydroquinoline. A red solid was obtained in 31% yield. The crude product was tolerably pure with the analysis of the ^{1}H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. Single crystals were obtained by recrystallization in pentane at -30°C. ^{1}H NMR (C_6D_6): δ 7.94 (d, *J* = 8.4 Hz, 2H, fluorenyl-H), 7.27 (d, *J* = 7.6 Hz, 1H, Ph-H), 7.17 (dt, *J* = 8.4, 0.8 Hz, 2H, fluorenyl-H), 7.09 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 2H, fluorenyl-H), 7.04 (d, *J* = 7.6 Hz, 1H, Ph-H), 6.92 (t, *J* = 7.6 Hz, 1H, Ph-H), 6.91 (ddd, *J* = 8.4, 6.8, 0.8 Hz, 2H, fluorenyl-H), 4.25-4.20 (m, 2H, NCH_2), 2.47 (t, *J* = 6.4 Hz, 2H, benzyl-CH_2), 1.62-1.57 (m, 2H, CH_2), 0.14 (s, 6H, Ti-CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 160.64, 137.28, 129.42, 129.30, 127.79, 126.43, 126.17, 123.68, 123.35, 120.18, 118.99, 118.69, 111.22, 59.66, 48.59, 27.27, 22.76 ppm. Anal. Calc. ($C_{24}H_{23}NTi$): C, 77.22; H, 6.21; N, 3.75%. Found: C, 77.58; H, 5.95; N, 3.93%.

Complex 15. The complex was synthesized using same condition and procedure as those for **6** with 2-methyl-8-(fluorenyl)tetrahydroquinoline. The crude product was tolerably pure with the analysis of the ^{1}H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. A red solid was obtained in 40% yield. ^{1}H NMR (C_6D_6): δ 7.92 (t, *J* = 8.0 Hz, 2H, fluorenyl-H), 7.28 (d, *J* = 6.8 Hz, 1H, fluorenyl-H), 7.17 (d, *J* = 7.6 Hz, 1H, fluorenyl-H), 7.12-7.02 (m, 4H, fluorenyl-H and Ph-H), 6.93 (t, *J* = 7.6 Hz, 1H, Ph-H) 6.96-6.89 (m, 2H, fluorenyl-H), 5.11-4.98 (m, 1H, NCH), 2.71 (ddd, *J* = 17, 14, 5.6 Hz, 1H, benzyl-CH_2), 2.40 (dd, *J* = 17, 4.4 Hz, 1H, benzyl-CH_2), 1.76-1.64 (m, 1H, CH_2), 1.54-1.46 (m, 1H, CH_2), 1.05 (d, *J* = 6.4 Hz, 3H, CH_3), 0.18 (s, 3H, $TiCH_3$), 0.09 (s, 3H, $TiCH_3$) ppm. $^{13}C\{^{1}H\}$ NMR(C_6D_6): δ 158.95, 136.70, 136.46, 129.55, 129.27, 127.83, 127.70, 126.69, 126.42, 125.81,123.96, 123.79, 123.41, 122.82, 120.49, 120.05, 117.73, 117.06, 110.04, 61.88, 57.23, 49.83, 27.08, 21.94, 19.55 ppm. Anal. Calc. ($C_{25}H_{25}NTi$): C, 77.52; H, 6.51; N, 3.62%. Found: C, 77.23; H, 6.84; N, 3.98%.

Complex 16. The complex was synthesized using the same conditions and procedure as those for **6** with 2-n-butyl-8-(fluorenyl)tetrahydroquinoline. A red solid was obtained in 50% yield. The crude product was tolerably pure with the analysis of the ^{1}H and ^{13}C NMR spectra (see the spectra below) and

was used for the polymerization without further purification. ^{1}H NMR (C_6D_6): δ 7.94 (dt, *J* = 8.8, 0.8 Hz, 1H, fluorenyl-H), 7.91 (dt, *J* = 8.8, 1.2 Hz, 1H, fluorenyl-H), 7.28 (d, *J* = 7.2 Hz, 1H, fluorenyl-H), 7.20 (dt, *J* = 8.4, 0.8 Hz, 1H, fluorenyl-H), 7.14-7.04 (m, 4H, Ph-H and fluorenyl-H), 6.93 (t, *J* = 7.6 Hz, 1H, Ph-H), 6.93 (ddd, *J* = 8.4, 6.4, 0.8 Hz, 2H, fluorenyl-H), 4.99-4.89 (m, 1H, NCH), 2.67 (ddd, *J* = 18, 13.6, 6.0 Hz, 1H, benzyl-CH_2), 2.38 (dd, *J* = 17, 4.4 Hz, 1H, benzyl-CH_2), 1.84-1.04 (m, 8H, CH_2), 0.82 (t, *J* = 6.4 Hz, 3H, CH_3), 0.21 (s, 3H, $TiCH_3$), 0.09 (s, 3H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 159.26, 136.65, 136.39, 129.55, 129.22, 127.81, 127.70, 126.53, 126.42, 125.76, 124.00, 123.90, 123.37, 122.83, 120.72, 120.03, 117.88, 116.92, 110.98, 62.09, 57.16, 54.50, 33.07, 29.09, 23.29, 23.11, 21.88, 14.62 ppm. Anal. Calc. ($C_{28}H_{31}NTi$): C, 78.31; H, 7.28; N, 3.26%. Found: C, 78.69; H, 7.44; N, 3.48%.

Complex 17. The complex was synthesized using the same conditions and procedures as those for **6** with 2-*tert*-butyl-8-(fluorenyl)tetrahydroquinoline. A red solid was obtained in 86% yield. The crude product was tolerably pure with the analysis of the ^{1}H and ^{13}C NMR spectra (see the spectra below) and was used for the polymerization without further purification. ^{1}H NMR (C_6D_6): δ 7.89 (t, *J* = 8.4 Hz, 2H, fluorenyl-H), 7.40 (d, *J* = 8.4 Hz, 1H, fluorenyl-H), 7.27 (d, *J* = 6.8 Hz, 1H, fluorenyl-H), 7.15-7.06 (m, 3H), 7.00-6.94 (m, 3H), 6.86 (t, *J* = 8.0 Hz, 1H, Ph-H), 4.53 (t, *J* = 7.6 Hz, 1H, NCH), 2.74 (ddd, *J* = 17, 14, 6.4 Hz, 1H, CH_2), 2.37 (dd, *J* = 17, 6.0 Hz, 1H, CH_2), 2.06-2.01 (m, 1H, CH_2), 1.83-1.74 (m, 1H, CH_2), 0.83 (s, 9H, $C(CH_3)_3$), 0.23 (s, 3H, $TiCH_3$), 0.12 (s, 3H, $TiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.75, 133.81, 133.74, 129.51, 129.18, 127.61, 127.43, 126.35, 125.60, 124.75, 124.50, 124.46, 123.44, 122.87, 119.79, 118.44, 115.65, 109.86, 66.12, 62.99, 58.61, 39.54, 29.72, 24.49, 23.83 ppm. Anal. Calc. ($C_{28}H_{31}NTi$): C, 78.31; H, 7.28; N, 3.26%. Found: C, 78.05; H, 7.53; N, 2.93%.

Ethylene/1-octene copolymerization. In a glove box, 30 mL of toluene solution of 1-octene (1.0 g, 0.30 M) was added to a dried 60 mL glass reactor. The reactor was assembled and brought out from the glove box. The reactor was then heated to 70^{o}C by a mantle. After an activated catalyst, which was prepared by mixing the complex [0.50 (or 0.2) μmol], $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ [2.0 (or 0.80) μmol], and $(iBu)_3Al$ [0.20 (or 0.080) mmol] for 5 minutes, was added via a syringe, the ethylene gas (60 psig) was fed immediately. In the case of highly active catalysts (entries 1-2, 13-14, and 16), the mantle was

removed immediately after the injection of the activated catalyst to remove the generated heat. After polymerization was conducted for 5 (or 2) minutes, the ethylene gas was vented. Acetone was added to the reactor to give white precipitates which were collected by filtration, and then they were dried under vacuum at 60 ^{o}C. The 1-octene contents were calculated by the analysis of the ^{1}H NMR spectra of the copolymers. In the ^{1}H NMR spectra, the methyl (CH_3) signals (0.93-1.02 ppm) are well isolated from the methine (CH) and methylene (CH_2) signals (1.30-1.50 ppm), and the 1-octene contents can be calculated from the integration values of the two regions (See the typical ^{1}H NMR spectrum of the copolymer). The integration values were rather sensitively changeable depending on the conditions of the instrument shimming, signal phase, or integration phase. However, cutting with scissors and weighing the two signals after printing the spectrum on a paper in the 0.5-2.0 ppm region gave consistently invariable values. The copolymer (5 mg) was dissolved in C_6D_6, and the ^{1}H NMR spectra were recorded at 80 ^{o}C. The polymer prepared by **7** (entry 13) was transparent while the polymer prepared by CGC (entry 16) was opaque (See the picture below).

X-Ray Crystallography. Crystals of **6**, **11**, and **14** coated with grease (Apiezon N) were mounted onto a thin glass fiber with epoxy glue and placed in a cold nitrogen stream at 150(2) K on Rigaku single crystal X-ray diffractometer. The structures were solved by direct methods (SHELXL-97) and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results are summarized in Table S2 and the Ortep drawings are shown in Figure S1-S3.

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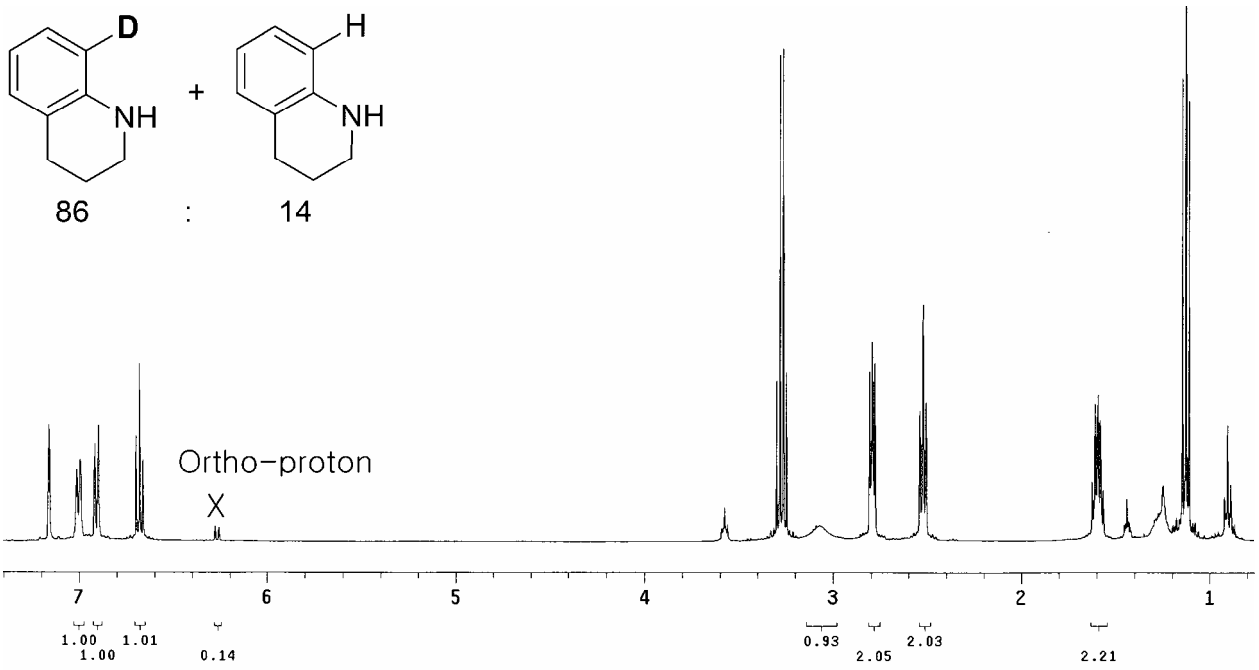
Table S2. Crystallographic Parameters of 14, 15, 24, and 26

	14	**15**	**24**
formula	$C_{20}H_{27}NTi$	$C_{21}H_{23}NTi$	$C_{24}H_{23}NTi$
Fw	329.31	337.29	373.32
size, mm^3	0.15×0.1×0.05	0.5×0.5×0.6	0.5×0.3×0.3
a, Å	14.465(5)	15.4701(17)	12.4129(3)
b, Å	8.585(2)	14.6775(14)	12.4500(3)
c, Å	16.138(4)	15.8899(14)	14.4623(4)
α, deg	90	90	68.4935(7)
β, deg	116.824(11)	103.832(3)	68.3872(7)
γ, deg	90	90	73.8696(7)
V, $Å^3$	1788.3(9)	3503.4(6)	1906.69(8)
crystal system	monoclinic	monoclinic	triclinic
space group	P21/a	C2/c	P-1
D(calc), gcm^{-1}	1.223	3503.4(6)	1.301
Z	4	8	4
μ, mm^{-1}	0.476	0.488	0.460
no. of data collected	16978	3990	18879
no. of unique data [R(int)]	4103 [0.0538]	3990 [0]	8633 [0.0233]
no. of variables	307	300	653
R(%)	0.0407	0.0679	0.0380
R_w(%)	0.0891	0.1692	0.1066
Goodness of fit	1.030	1.053	1.109

[a]Data collected at 150(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 $F_o > 2.0\sigma(I)$.

<The ^{1}H NMR spectrum of the D_2O-quenched 1>



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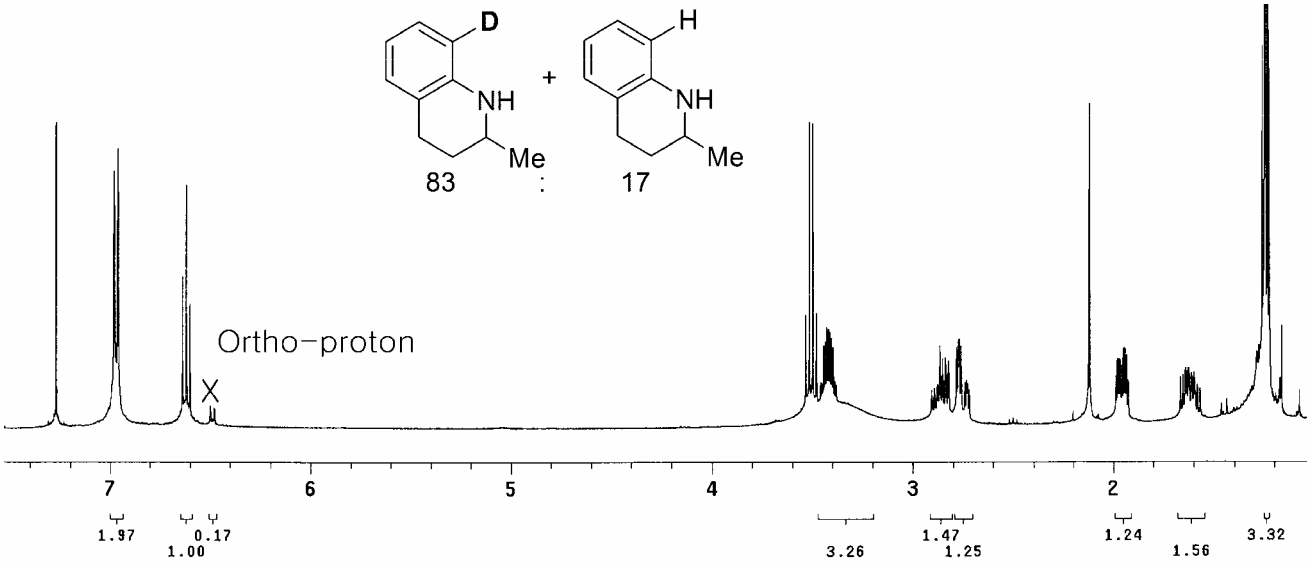
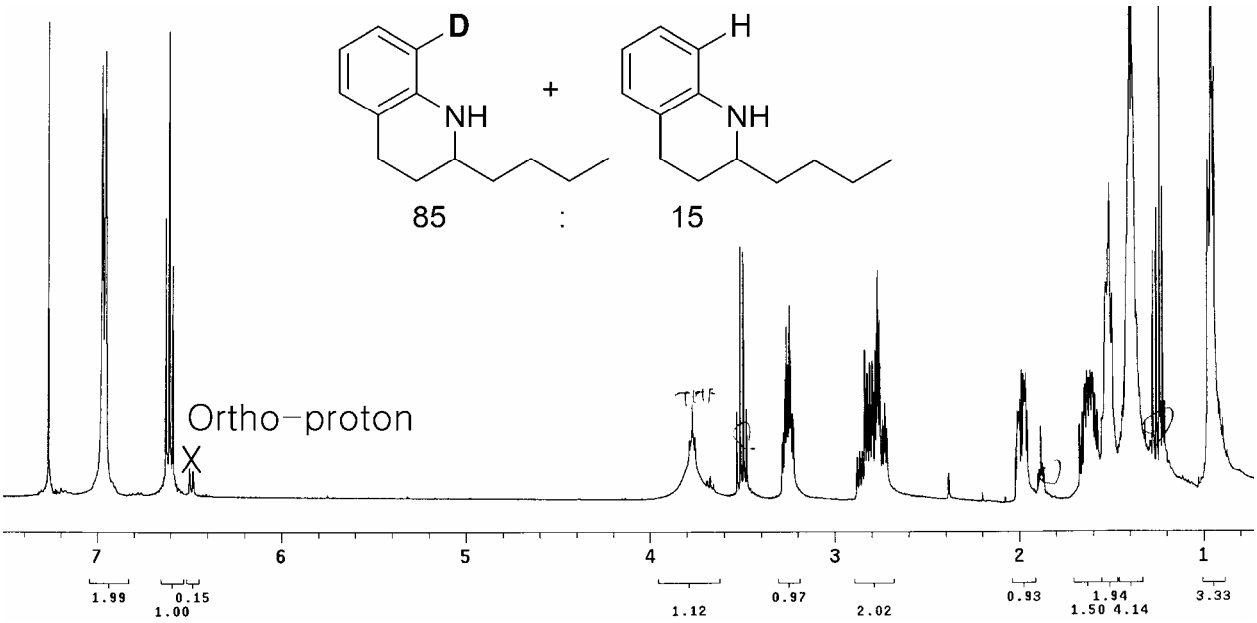


<The ^{1}H NMR spectrum of the D_2O-quenched 3>



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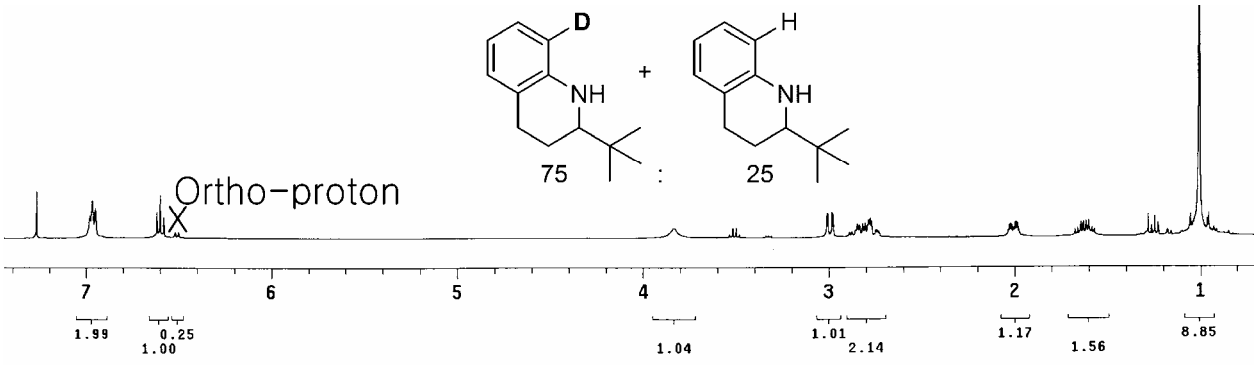
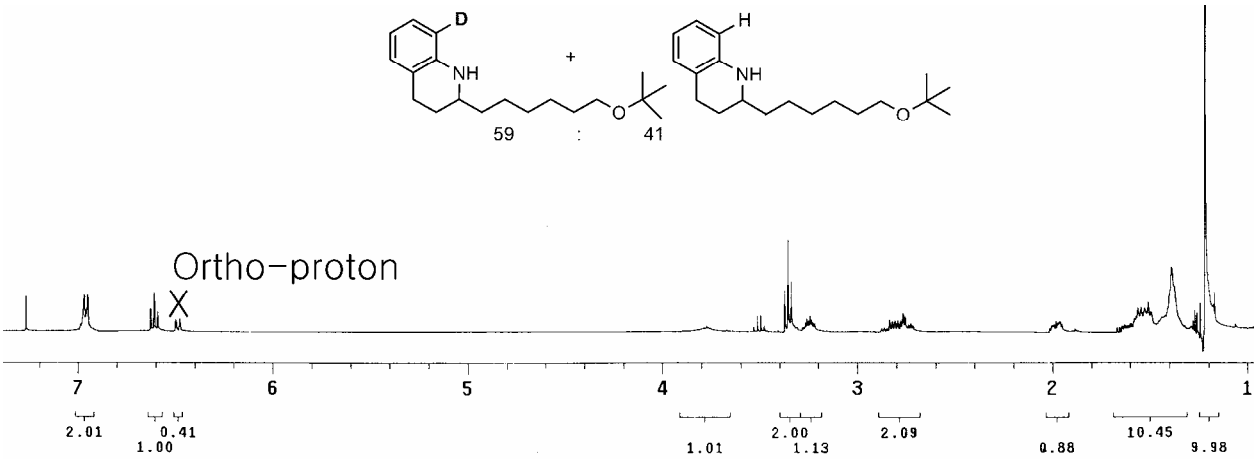
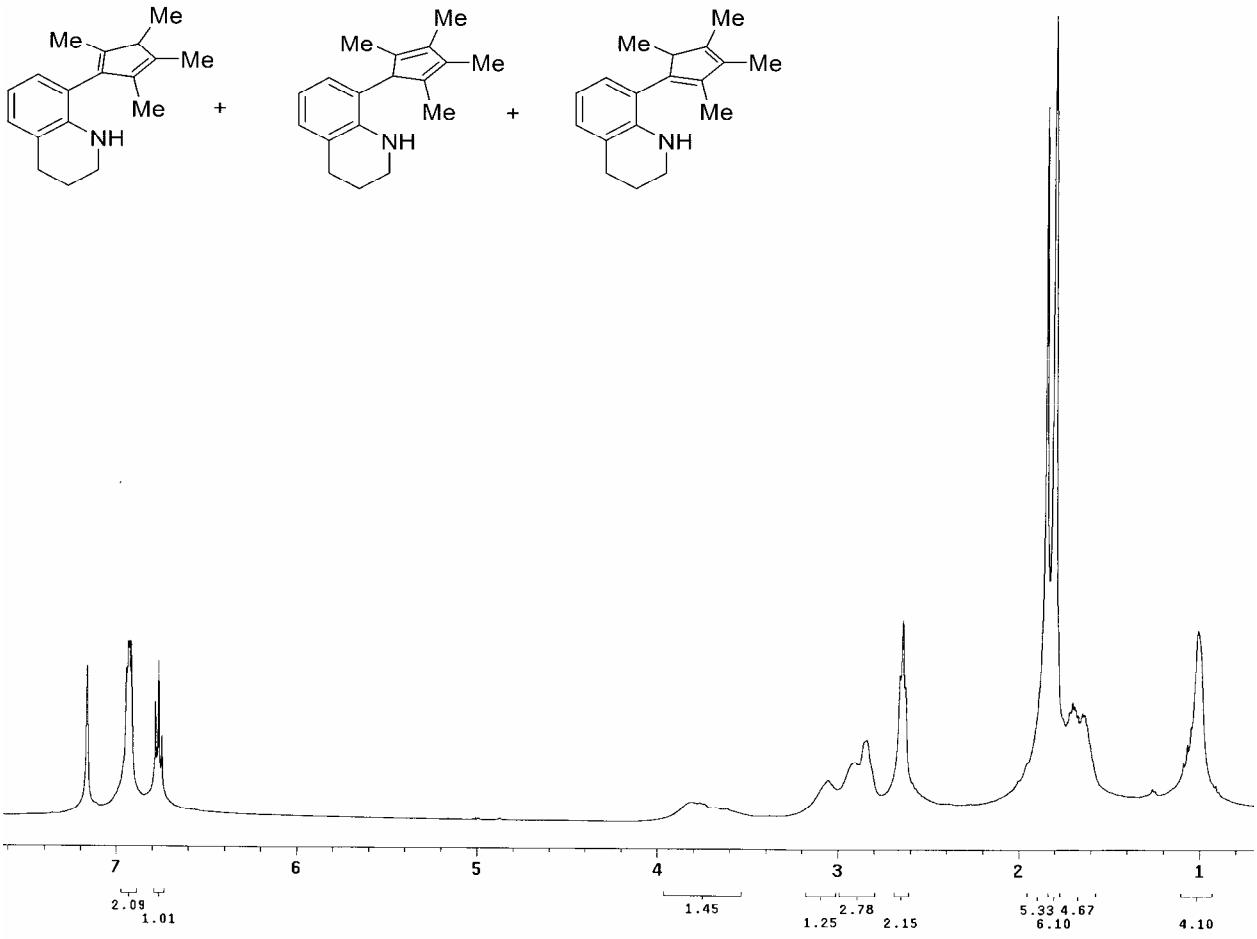


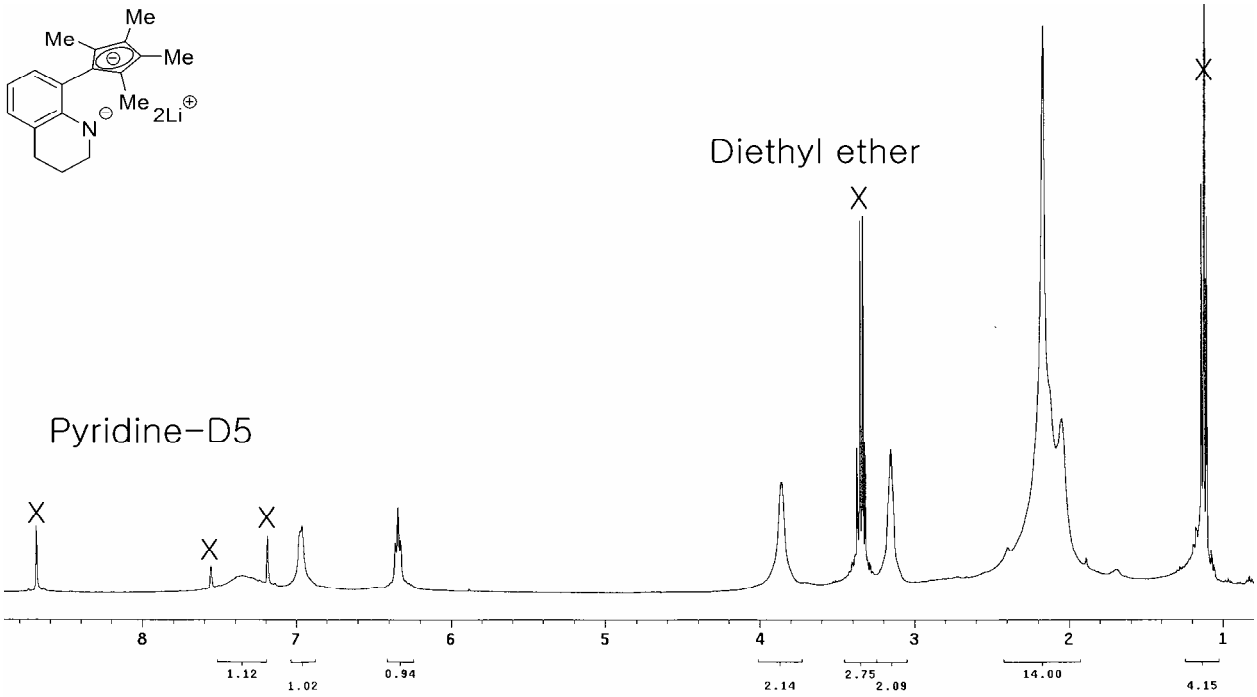
<The ^{1}H NMR spectrum of the D_2O-quenched 5>



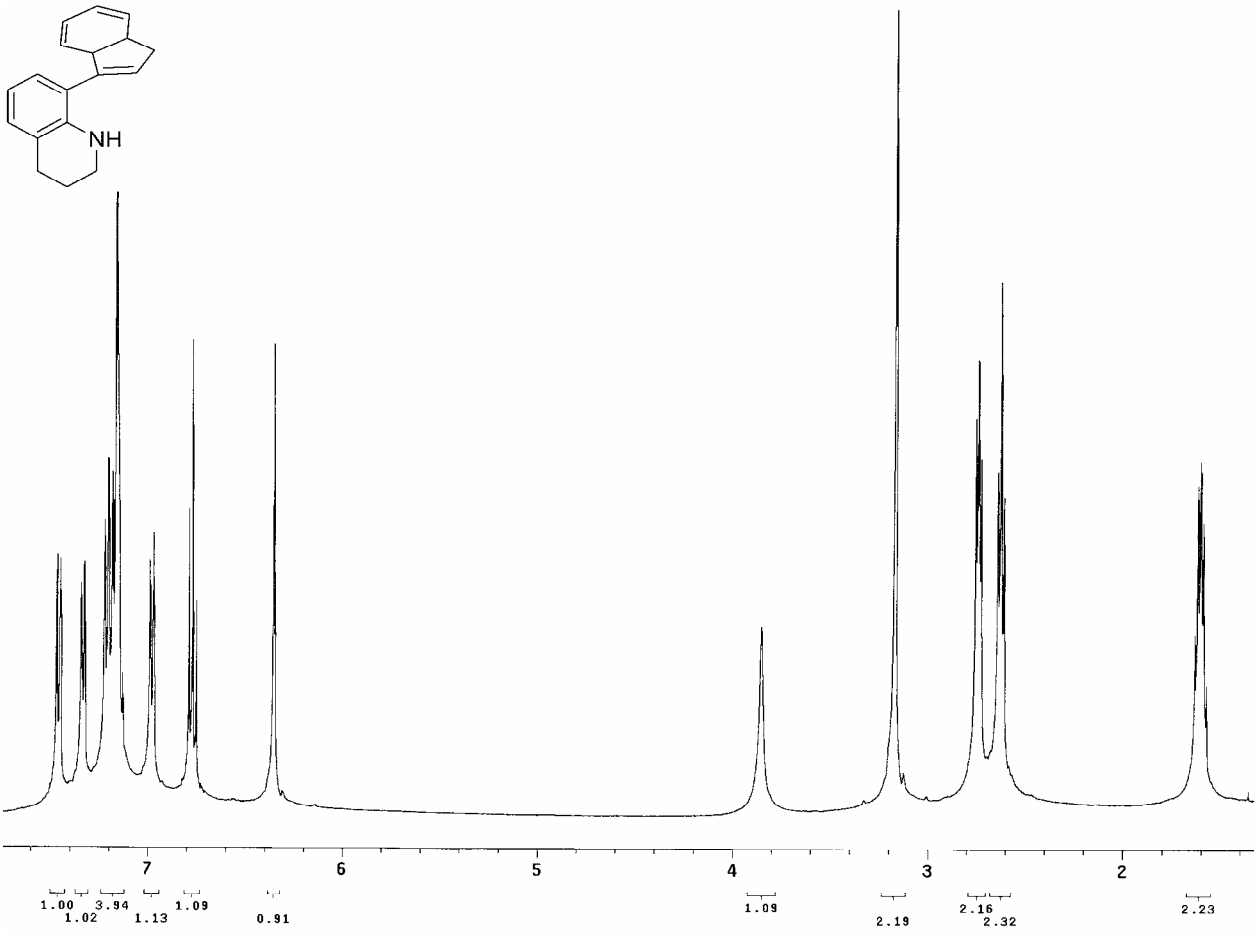
<The ^{1}H NMR spectrum of 8-(tetramethylcyclopentadienyl)tetrahydroquinoline (ligand for 6) prepared in large scale without the column chromatography>



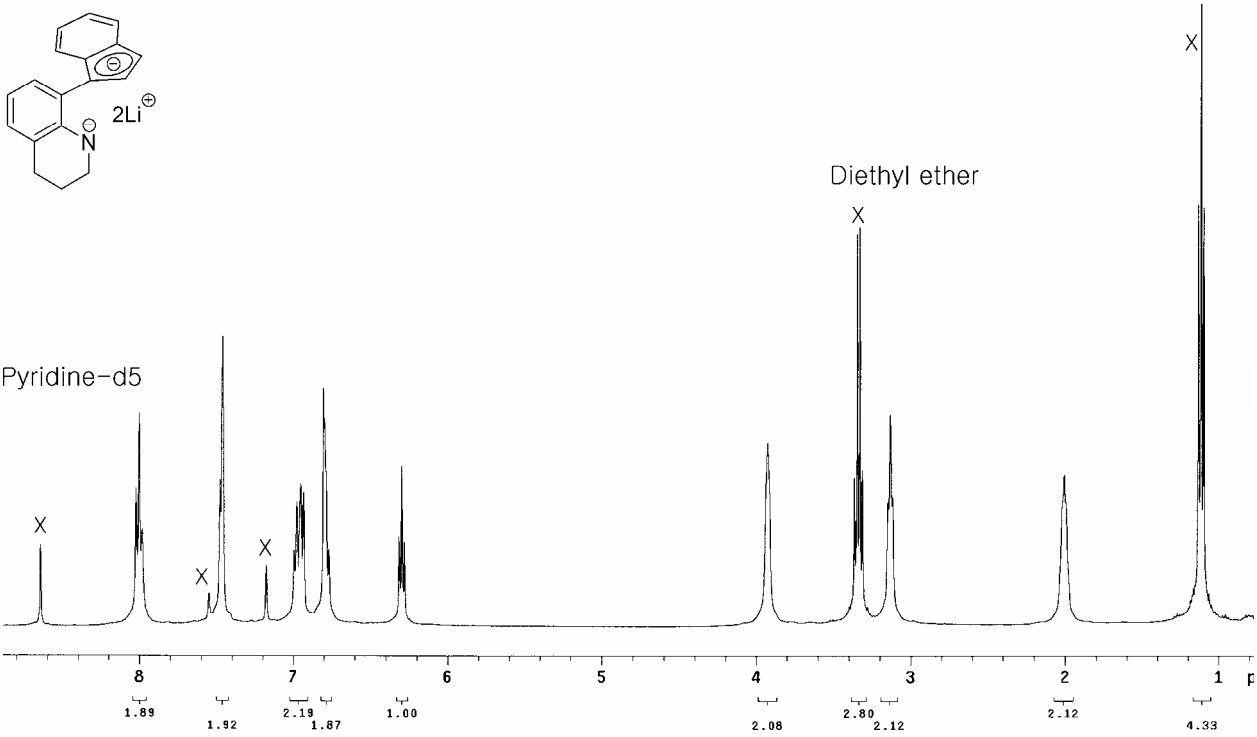
<The ^{1}H NMR spectrum of dilithium salt of 8-(tetramethylcyclopentadienyl)tetrahydroquinoline>



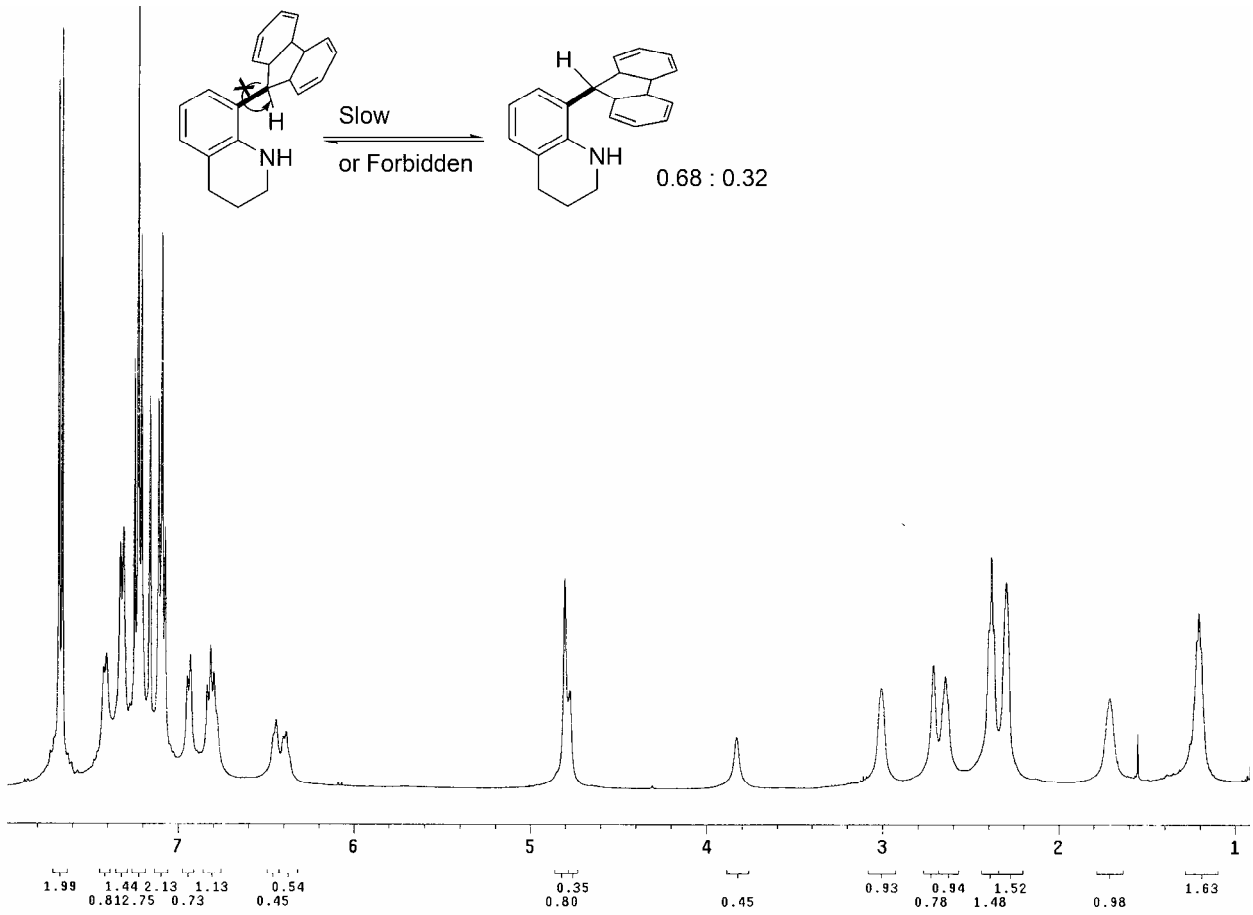
<The ^{1}H NMR spectrum of 8-(indenyl)tetrahydroquinoline (ligand for 10)>



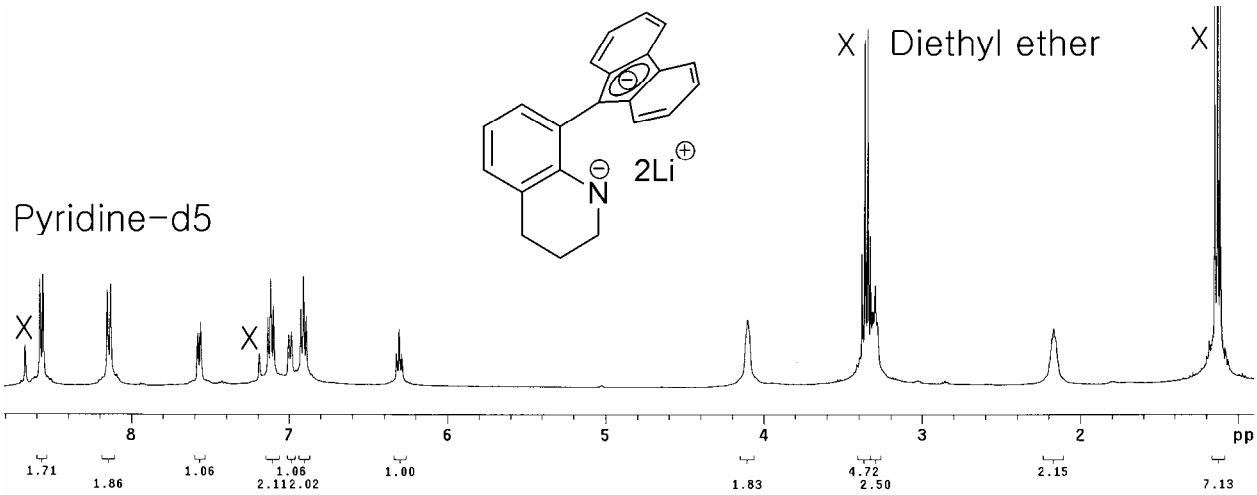
<The ^{1}H NMR spectrum of the dilithium salt of 8-(indenyl)tetrahydroquinoline>



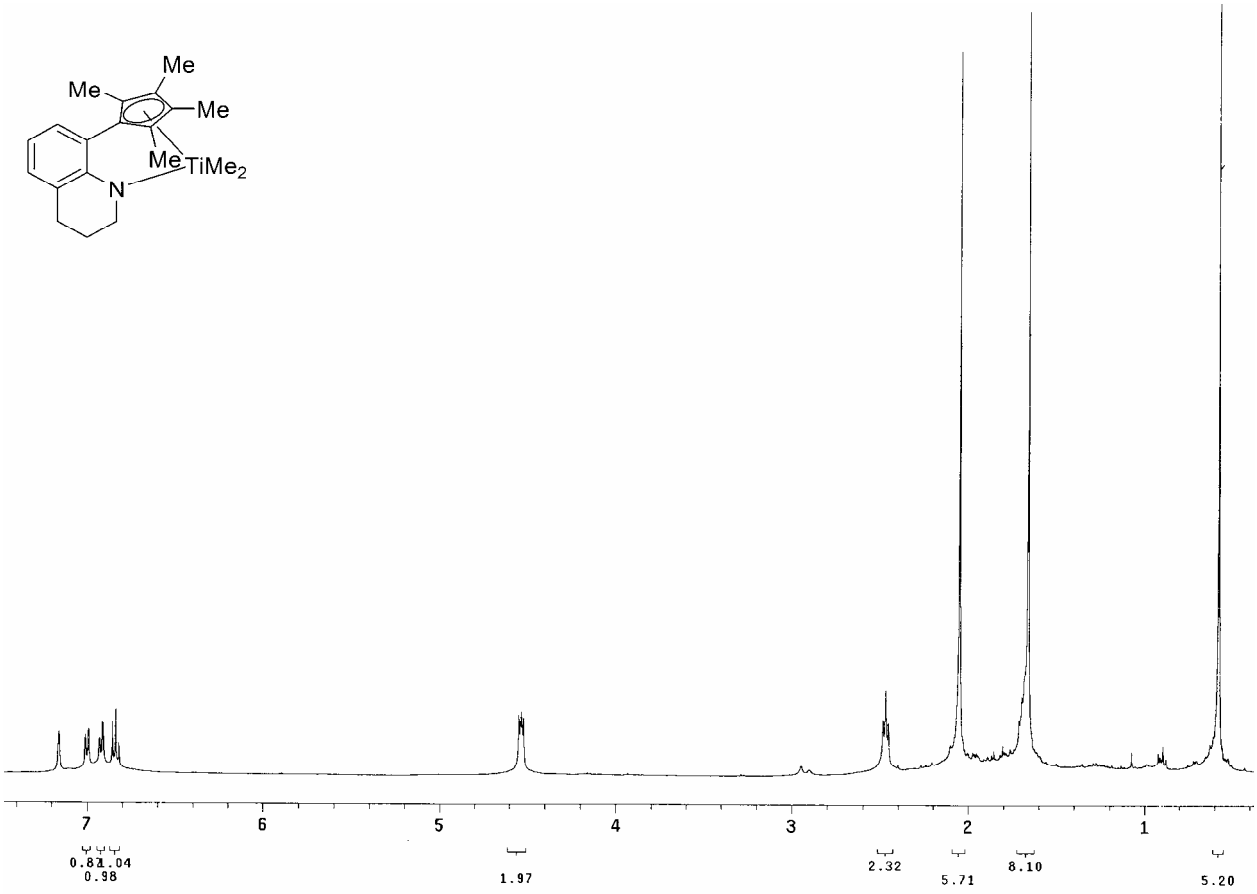
<The ^{1}H NMR spectrum of 8-(fluorenyl)tetrahydroquinoline (ligand for 14)>

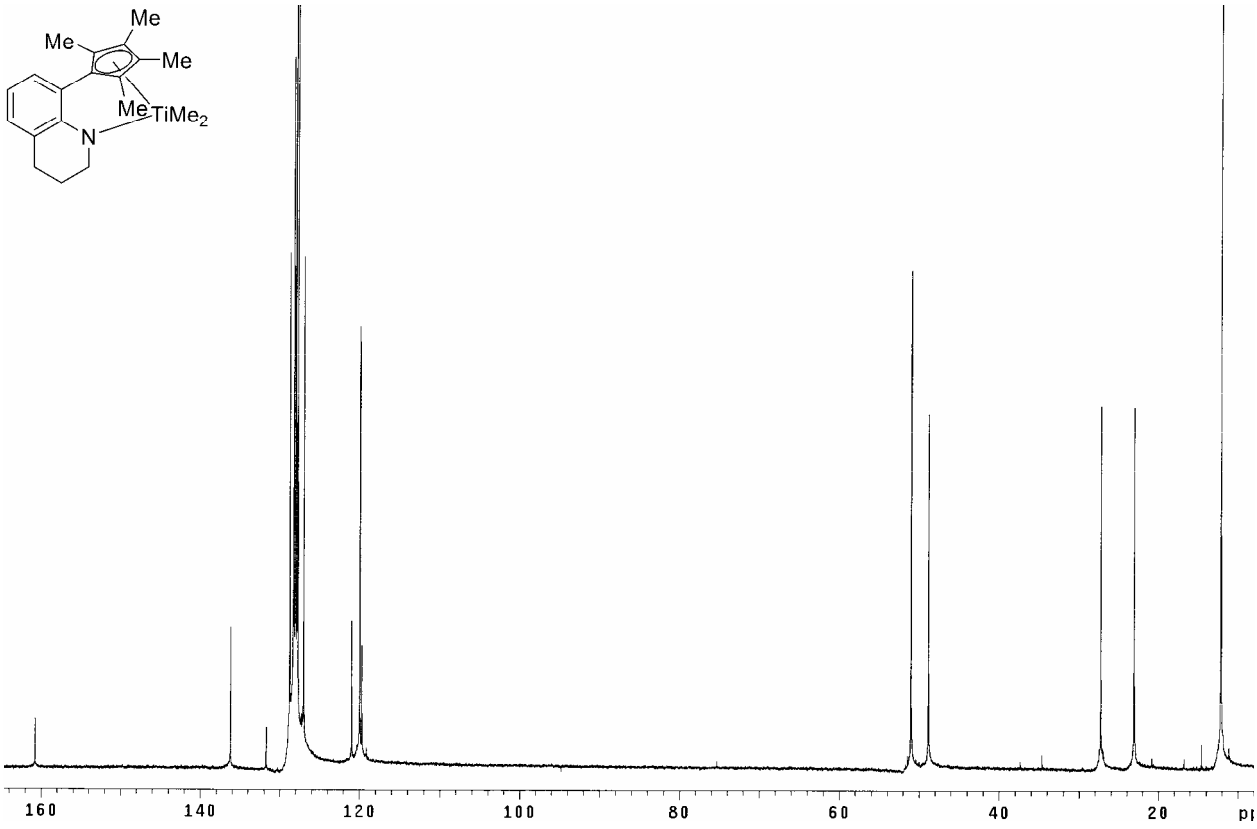


<The ^{1}H NMR spectrum of the dilithium salt of 8-(fluorenyl)tetrahydroquinoline>

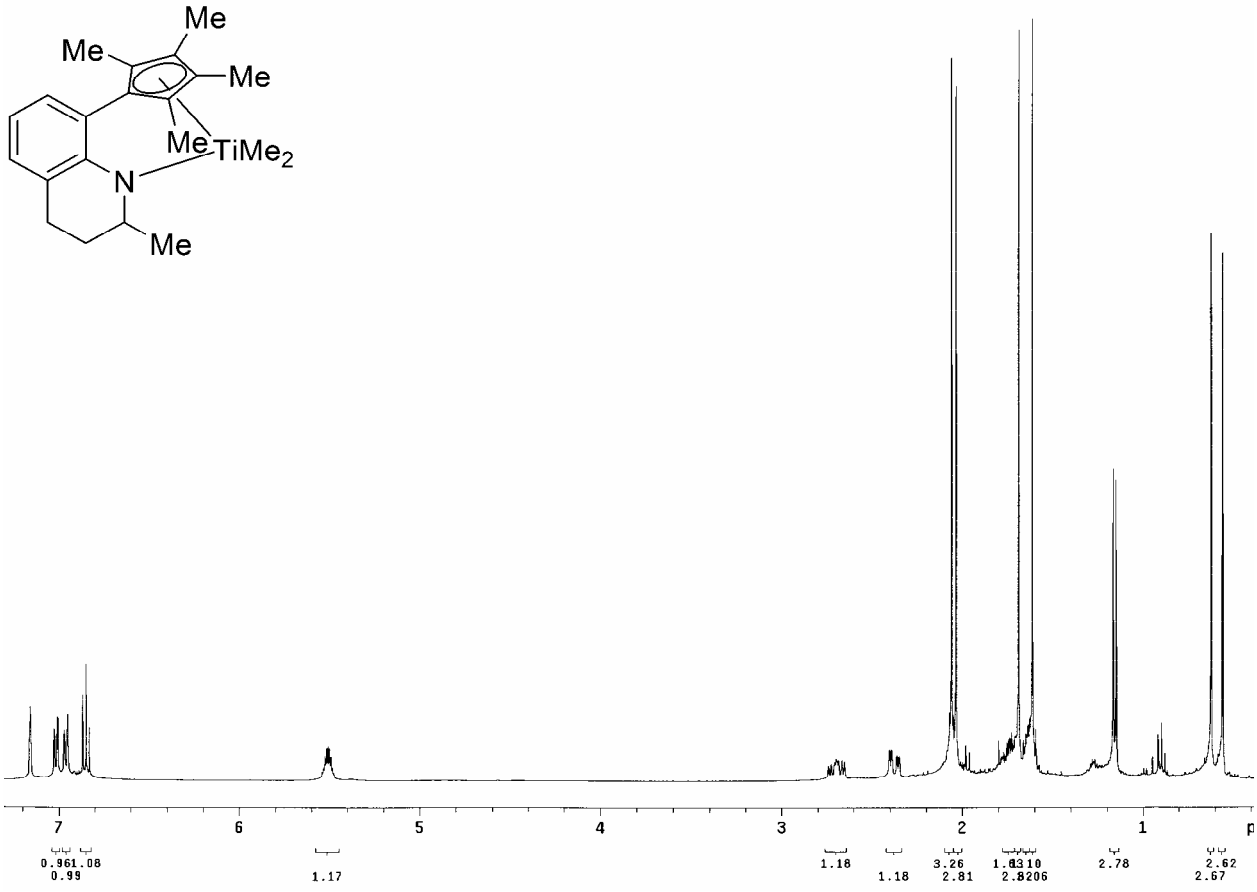


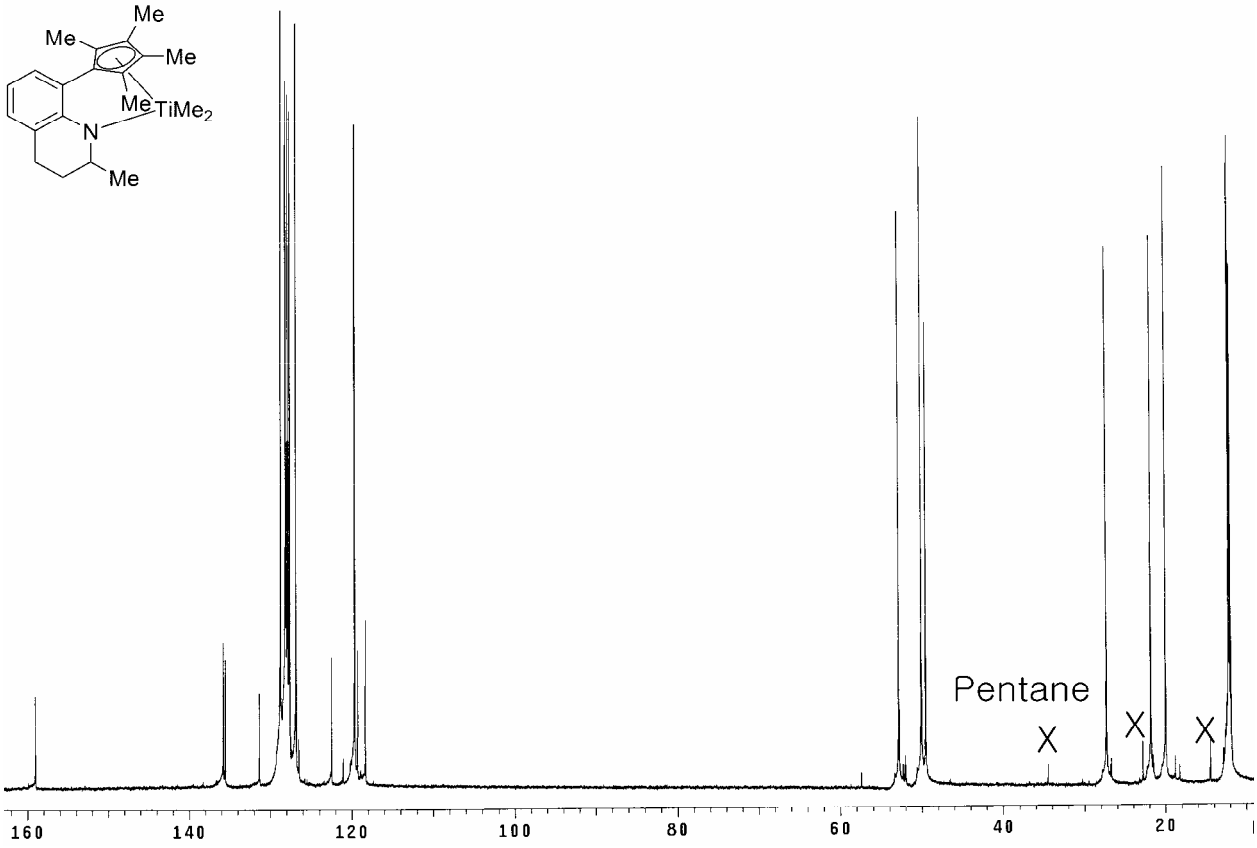
<The ^{1}H and ^{13}C NMR spectra of 6 (crude product)>



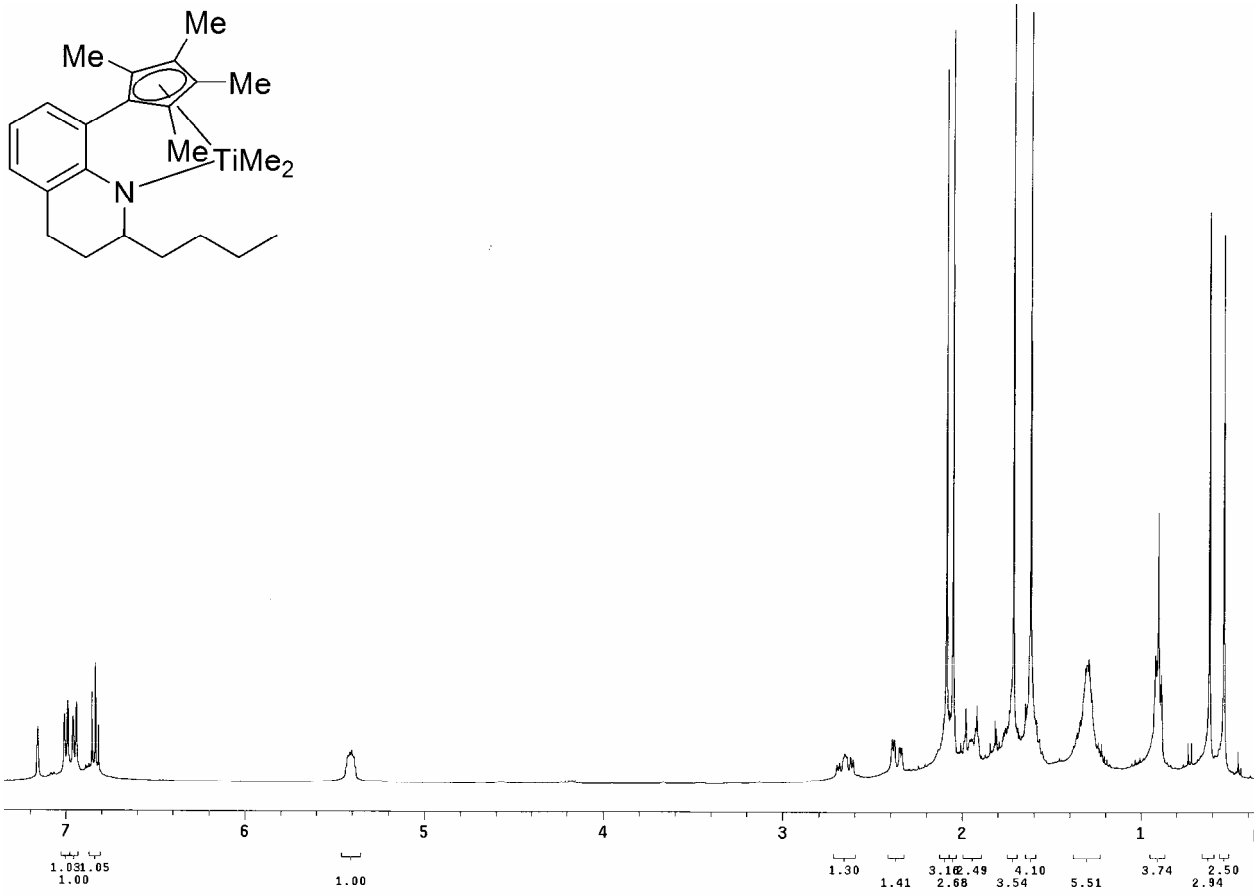


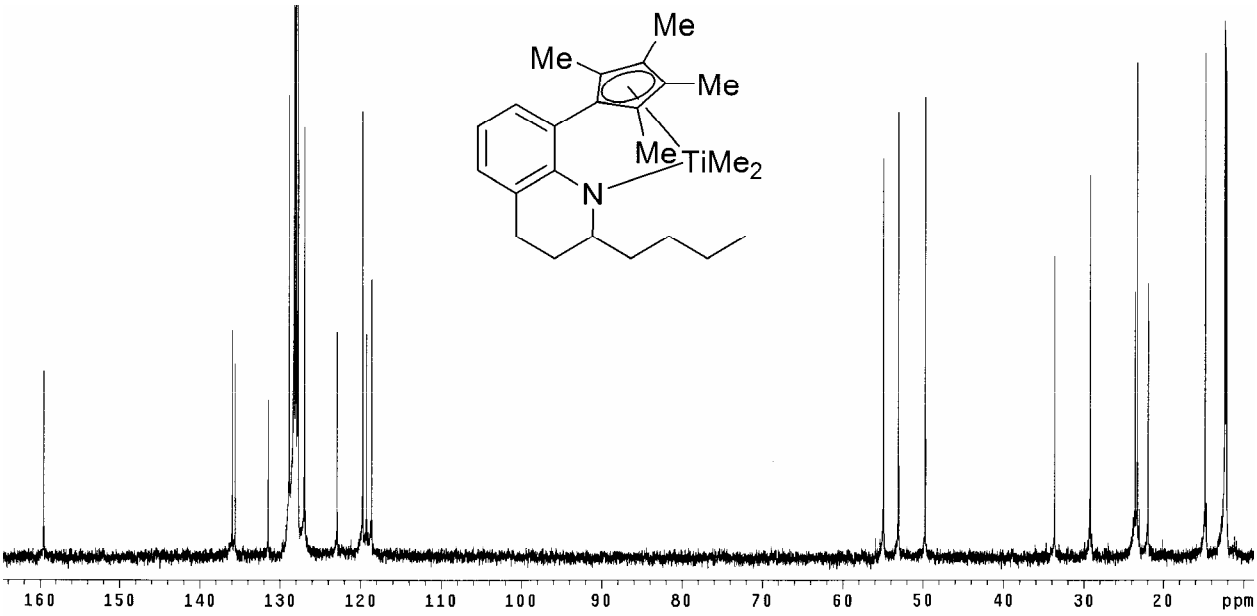
<The ^{1}H and ^{13}C NMR spectra of 7 (crude product)>



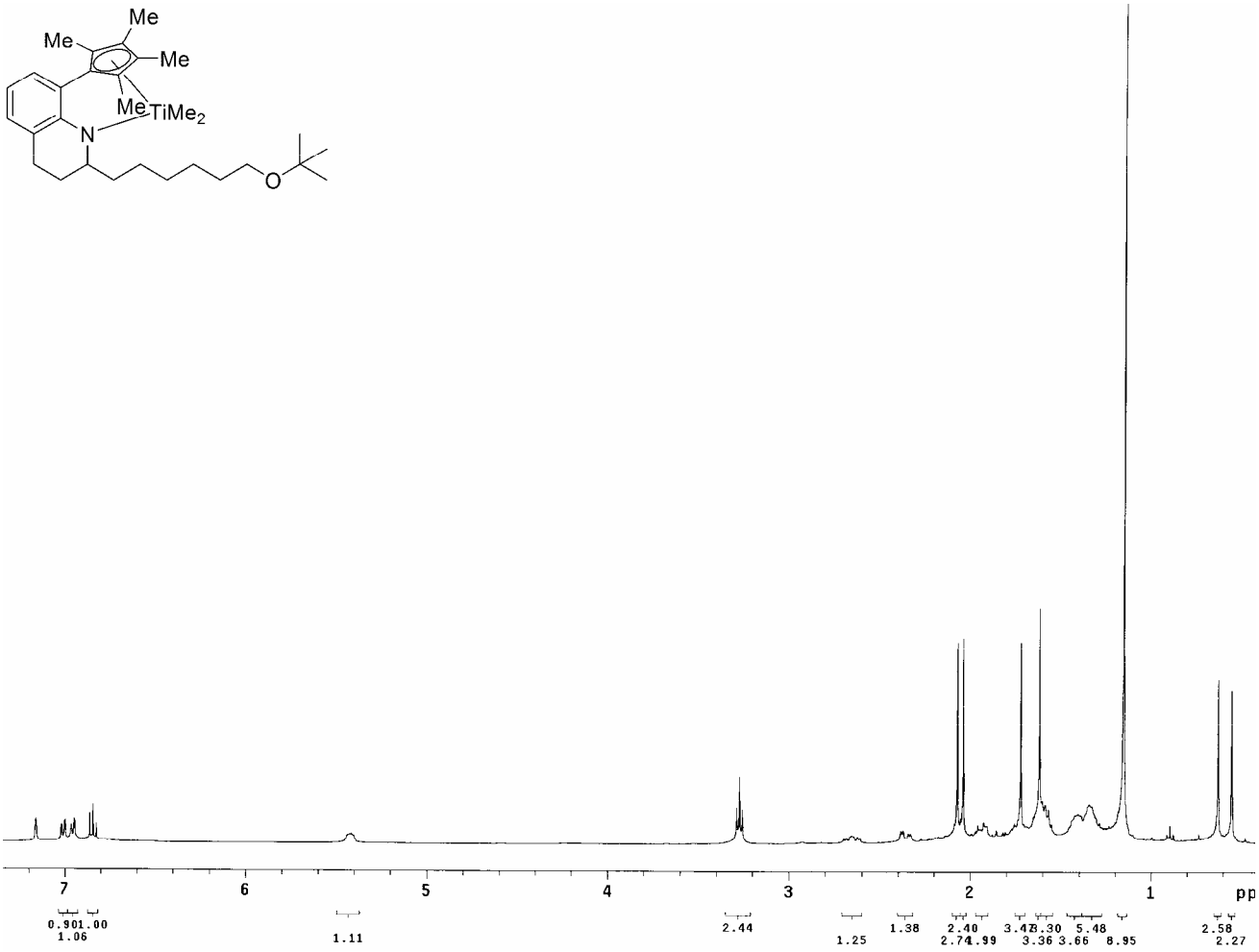


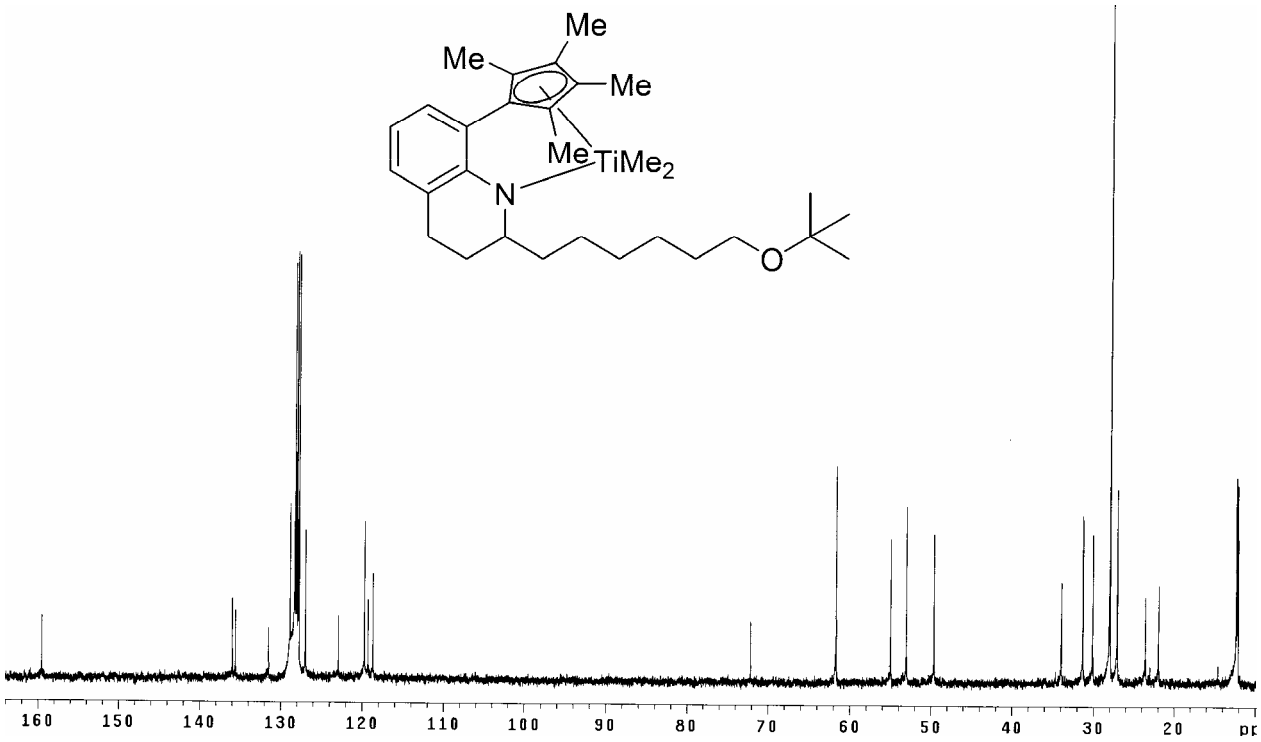
<The ^{1}H and ^{13}C NMR spectra of 8 (crude product)>



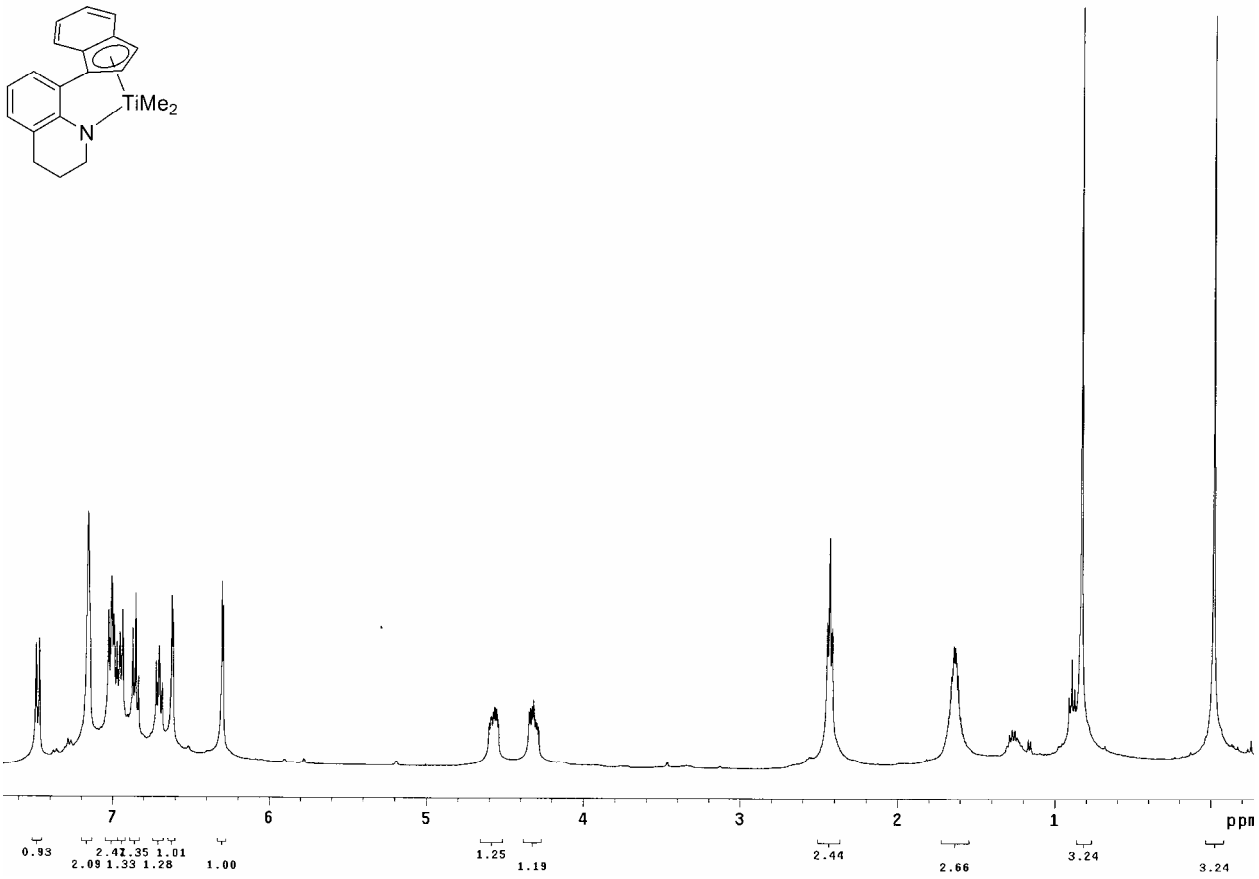


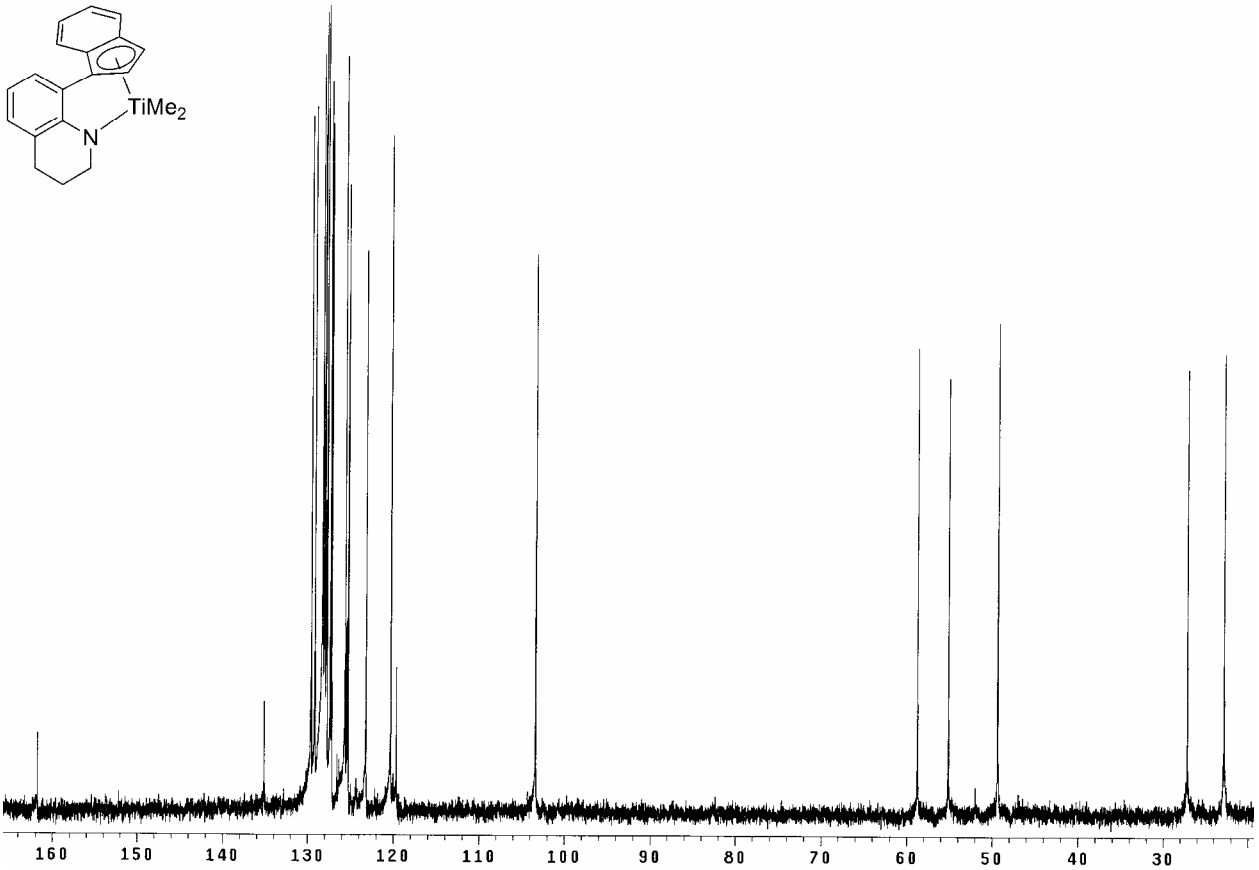
<The ^{1}H and ^{13}C NMR spectra of 9 (crude product)>



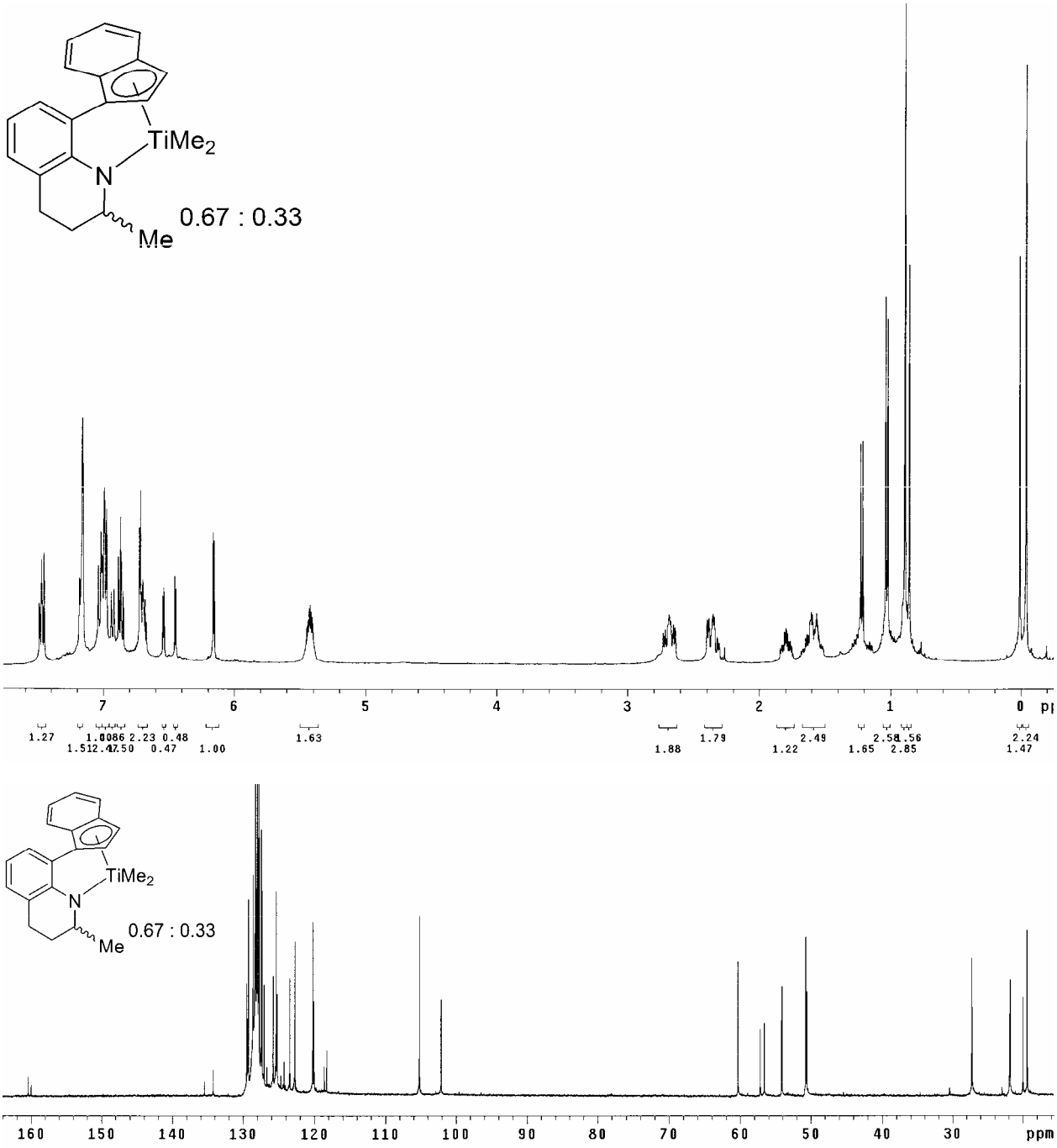


<The ^{1}H and ^{13}C NMR spectra of 10 (crude product)>

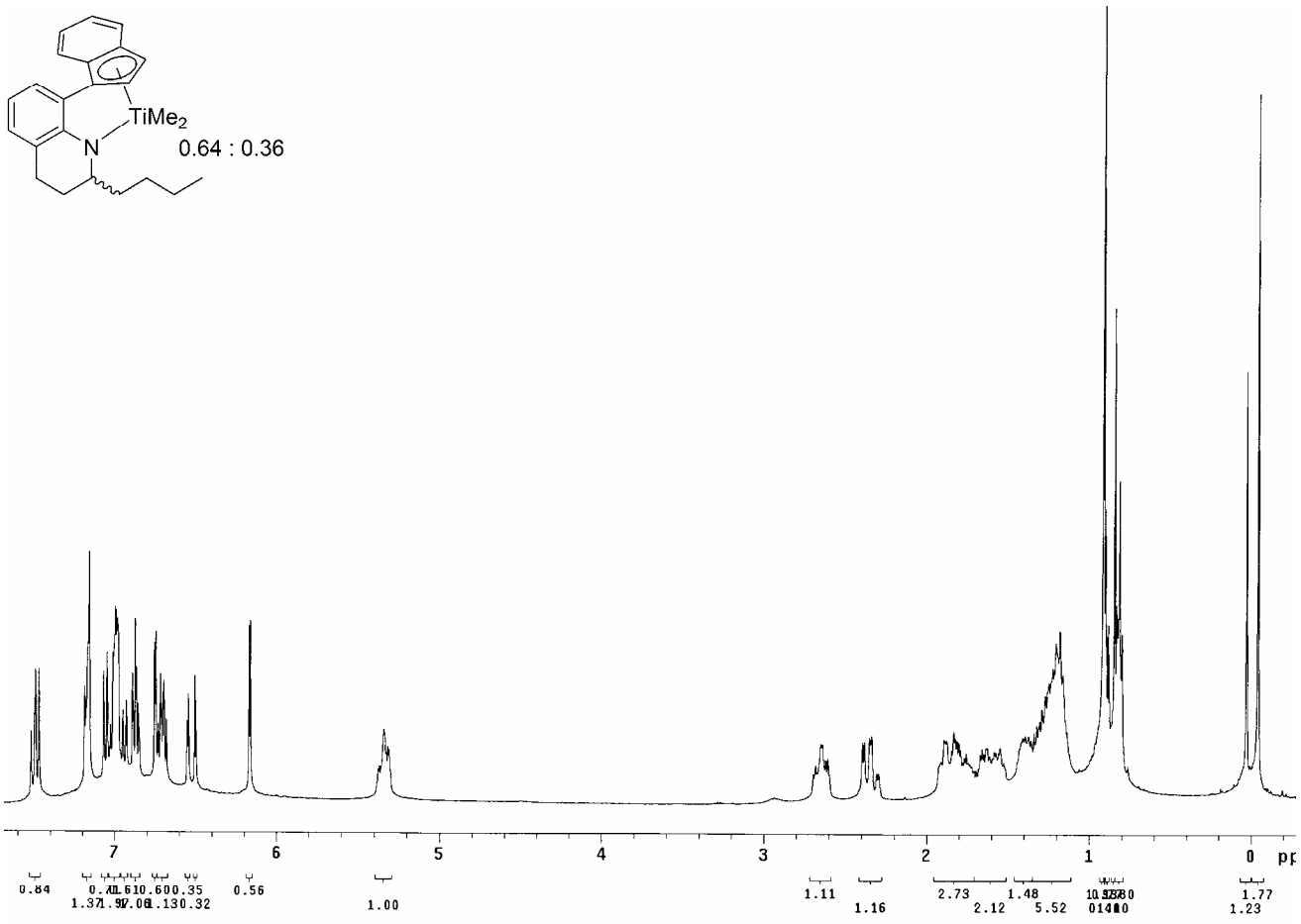


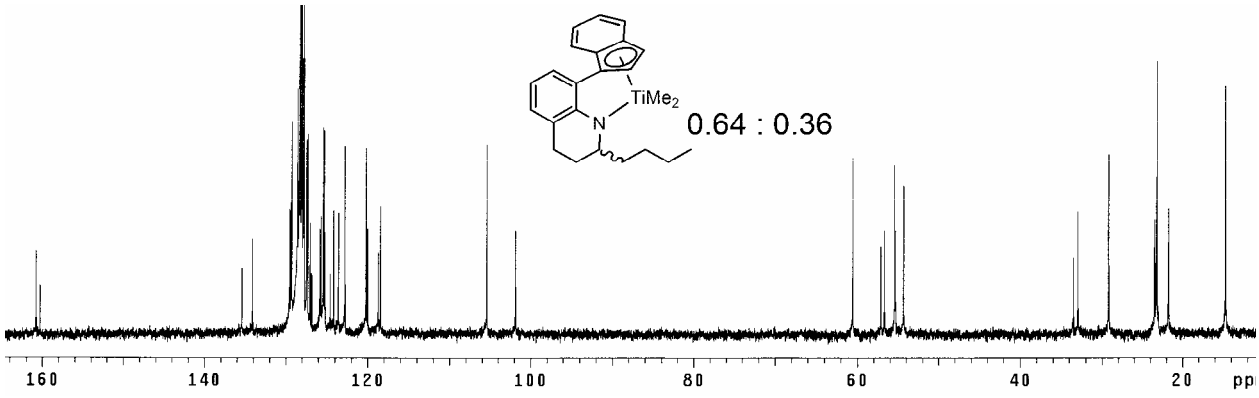


<The ^{1}H and ^{13}C NMR spectra of 11 (crude product)>

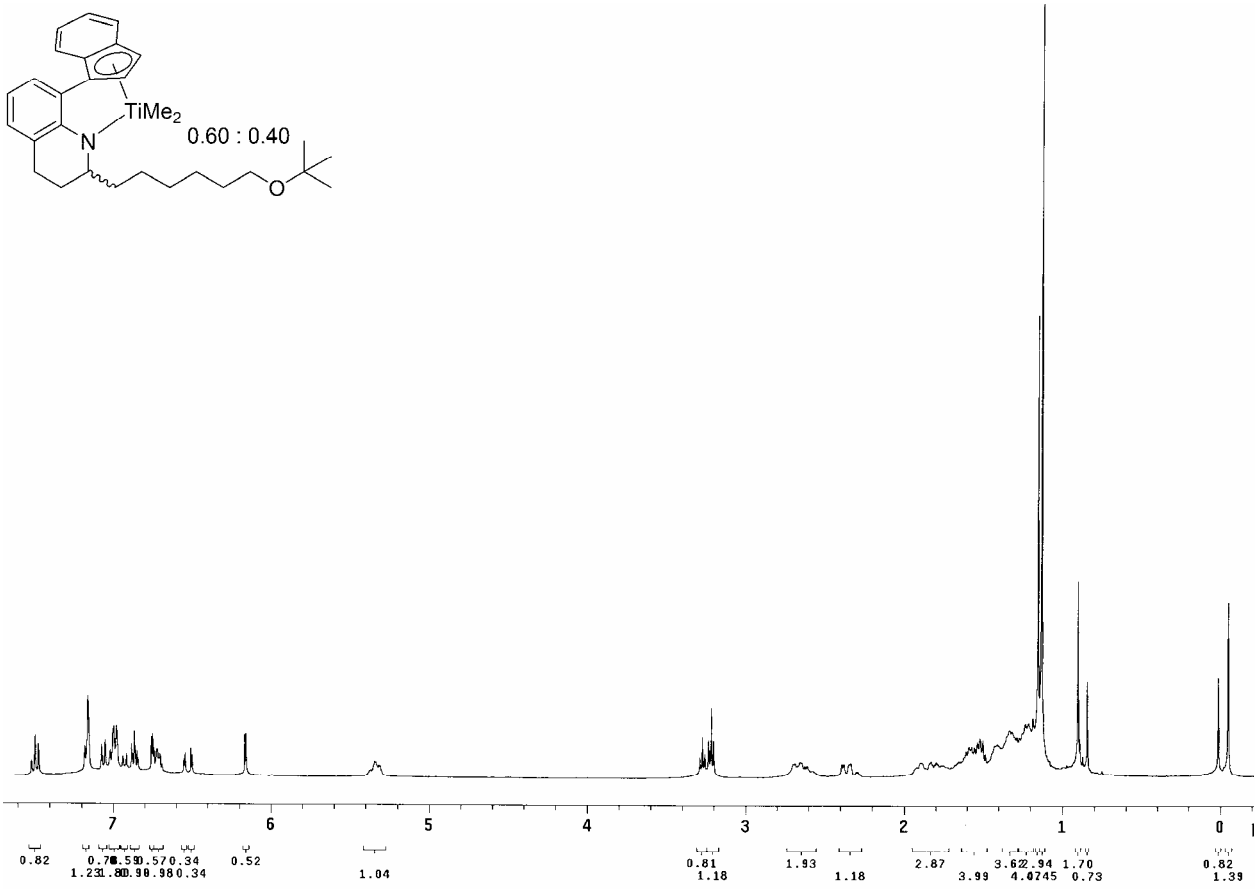


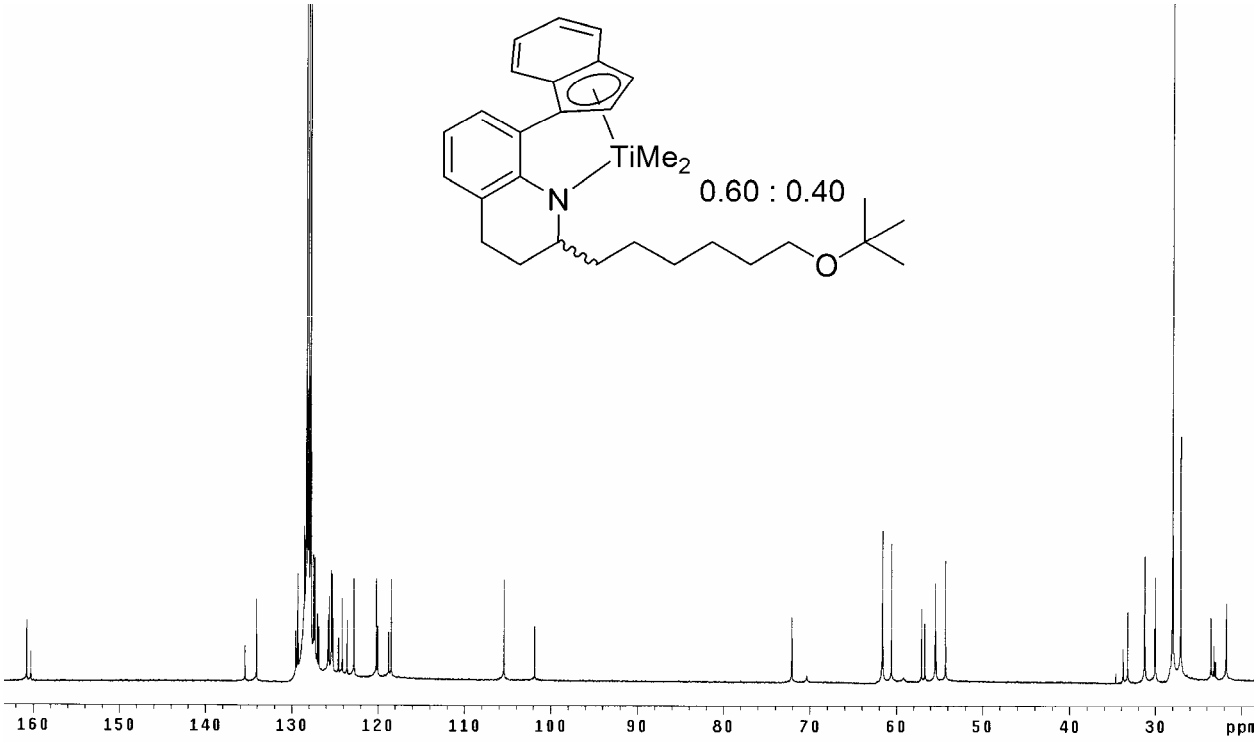
<The ^{1}H and ^{13}C NMR spectra of 12 (crude product)>



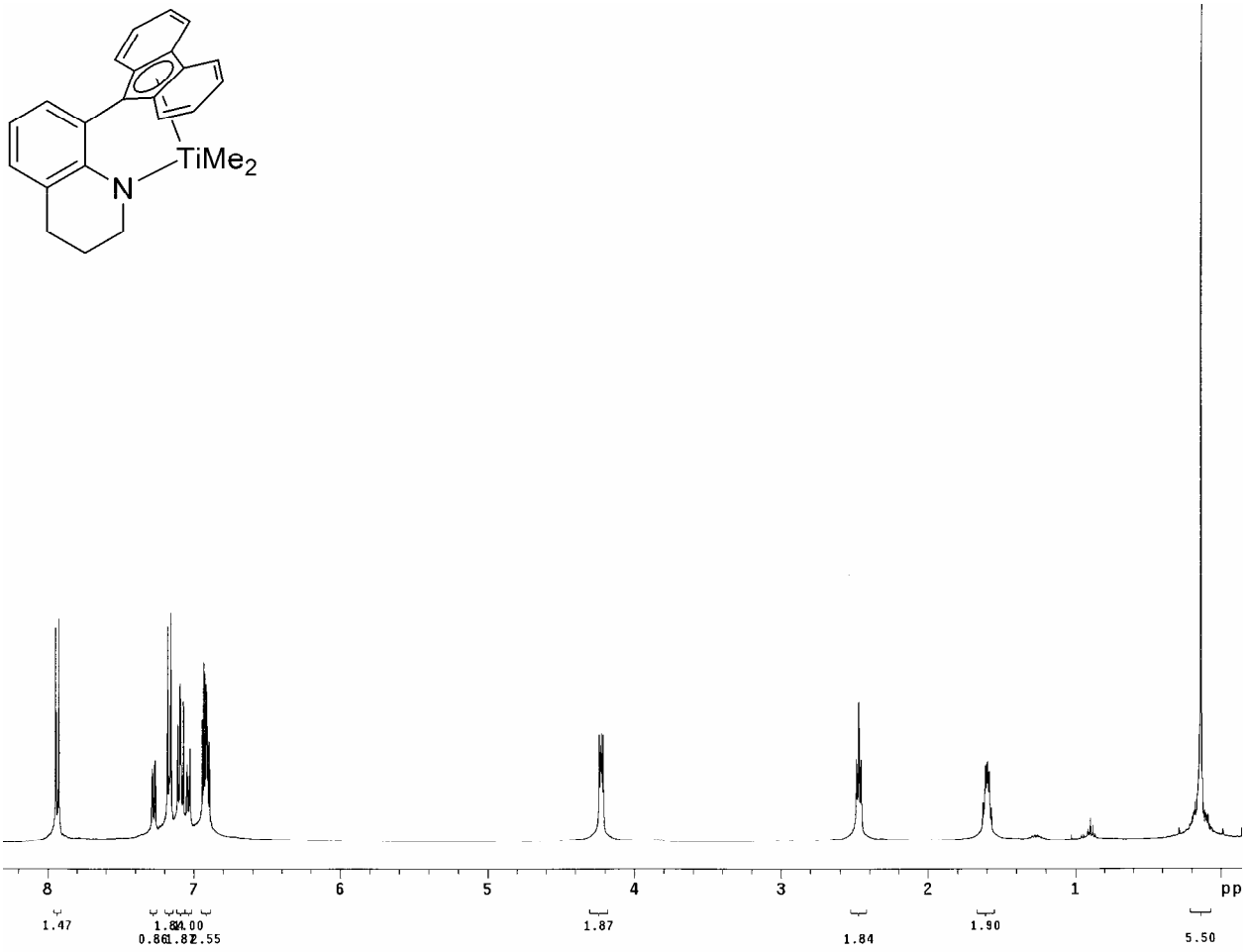


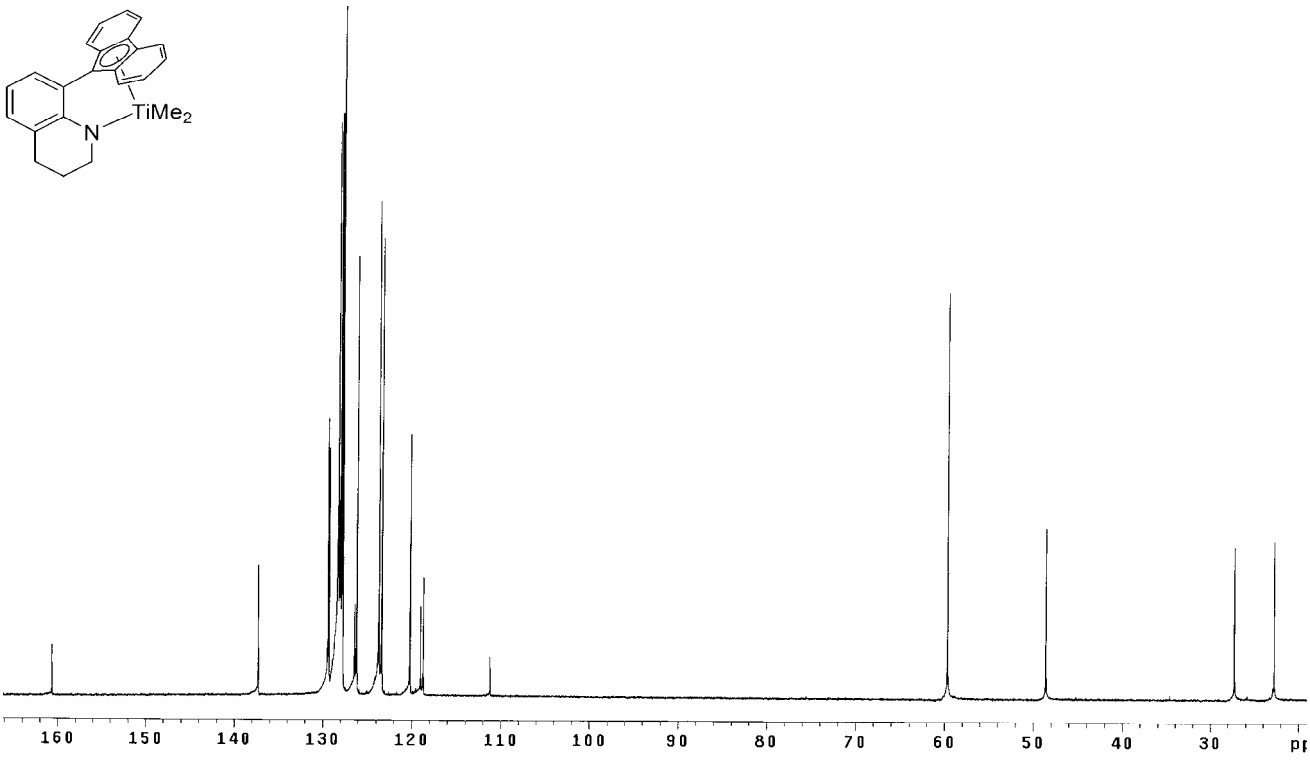
<The ^{1}H and ^{13}C NMR spectra of 13 (crude product)>



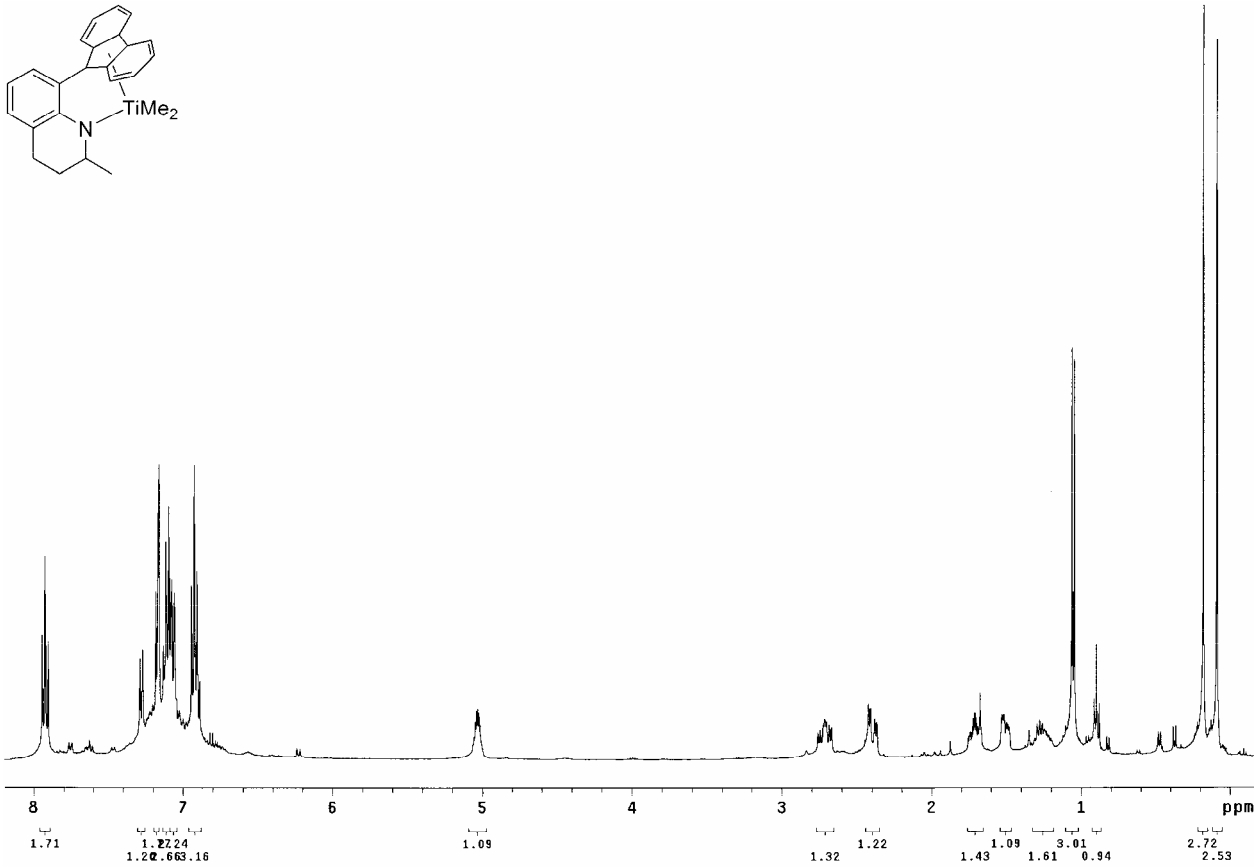


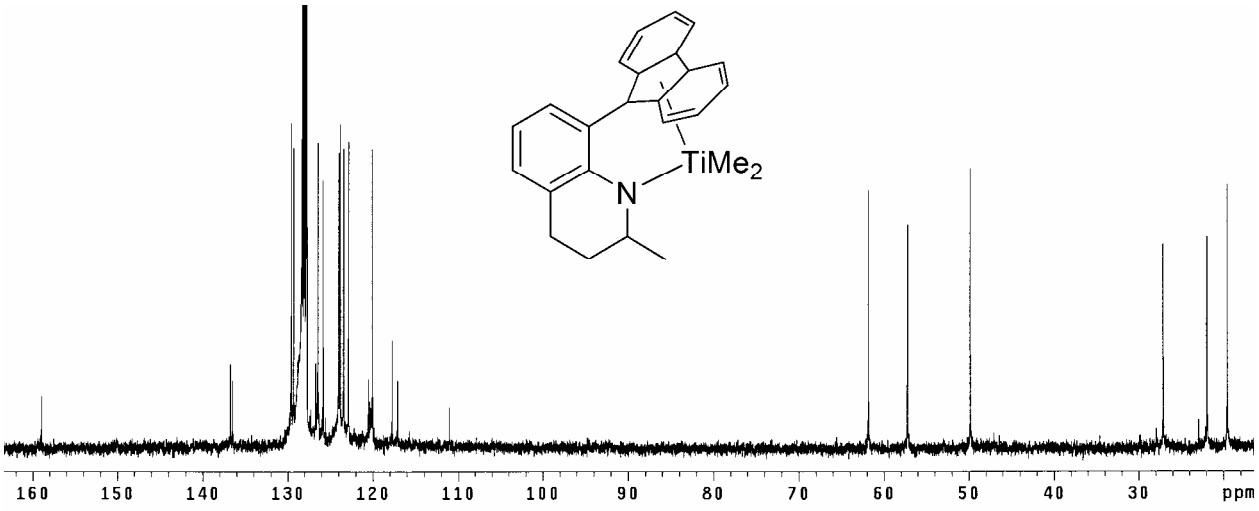
<The ^{1}H and ^{13}C NMR spectra of 14 (crude product)>



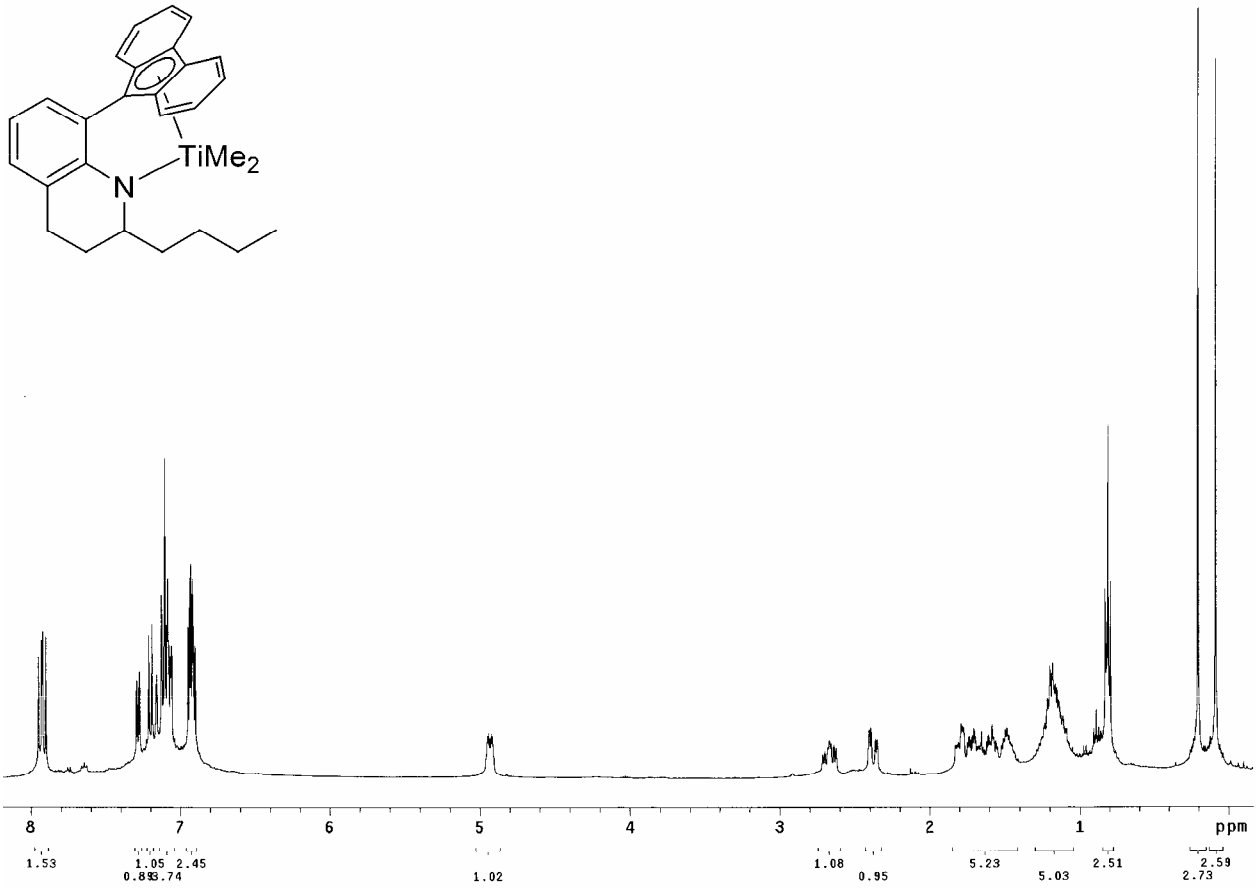


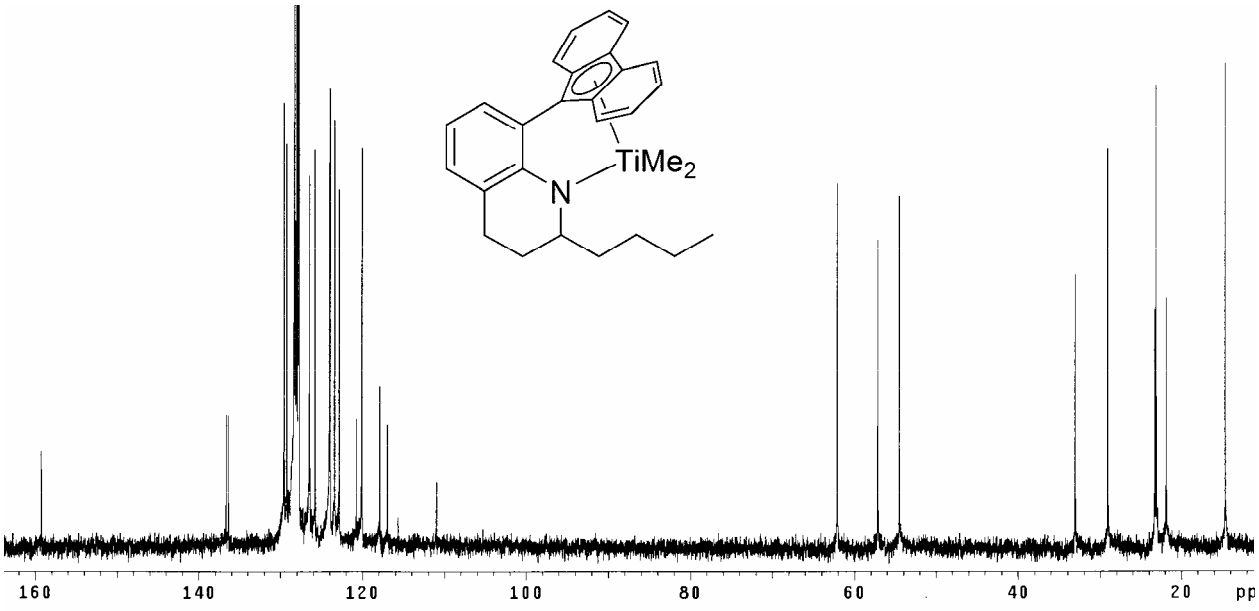
<The ^{1}H and ^{13}C NMR spectra of 15 (crude product)>



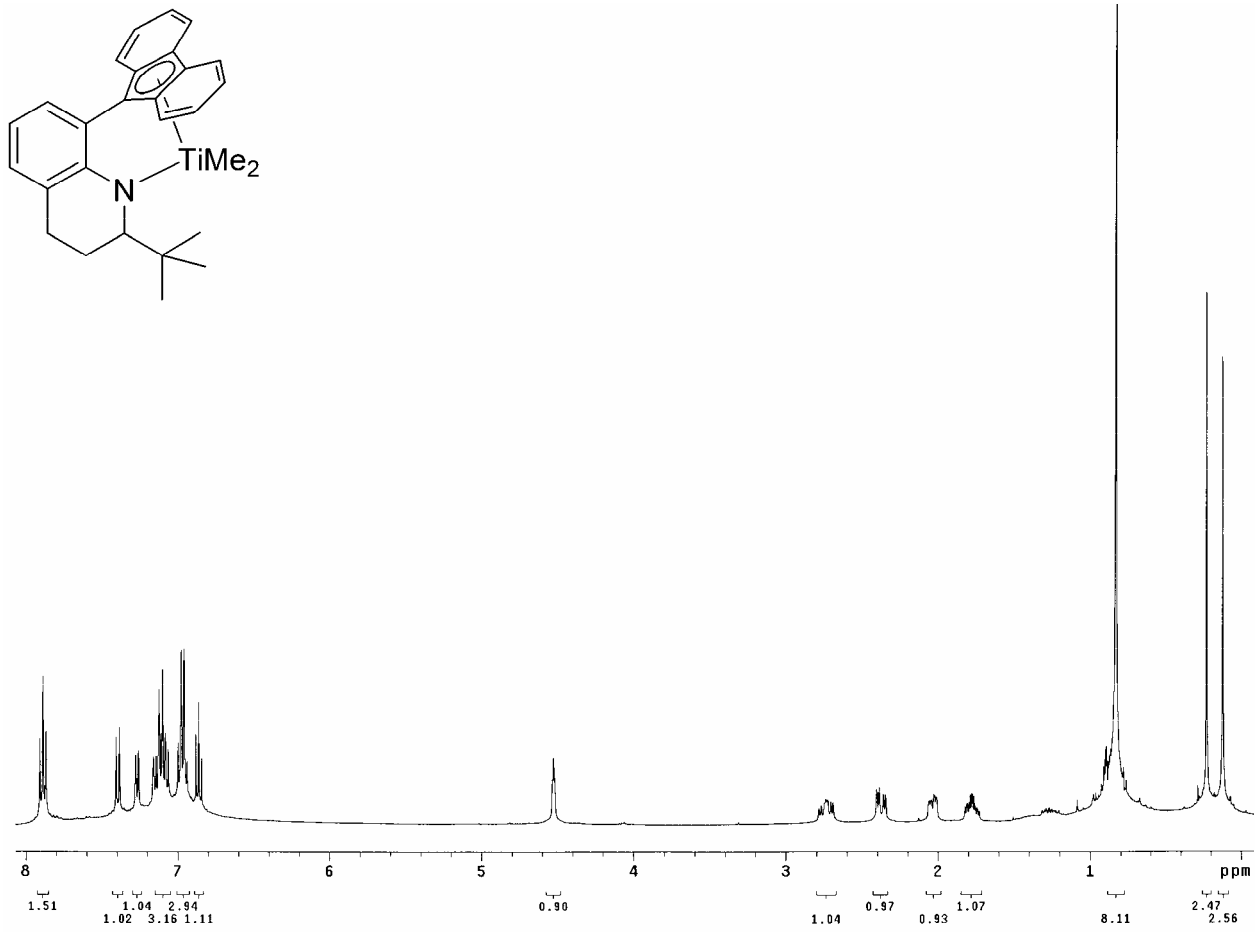


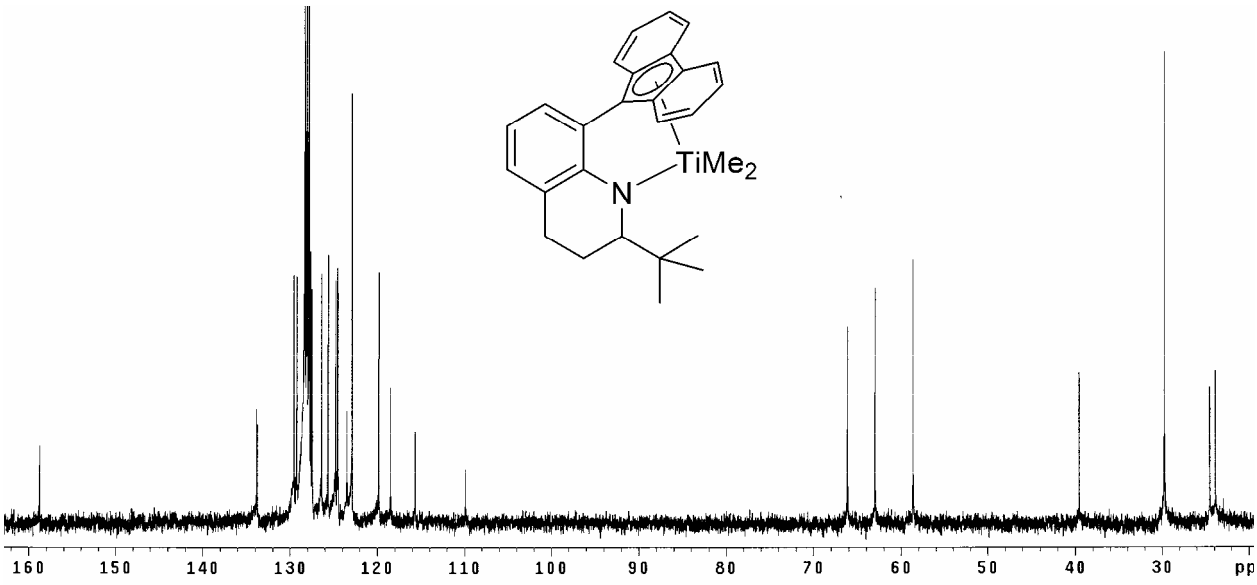
<The ^{1}H and ^{13}C NMR spectra of 16 (crude product)>





<The ^{1}H and ^{13}C NMR spectra of 17 (crude product)>

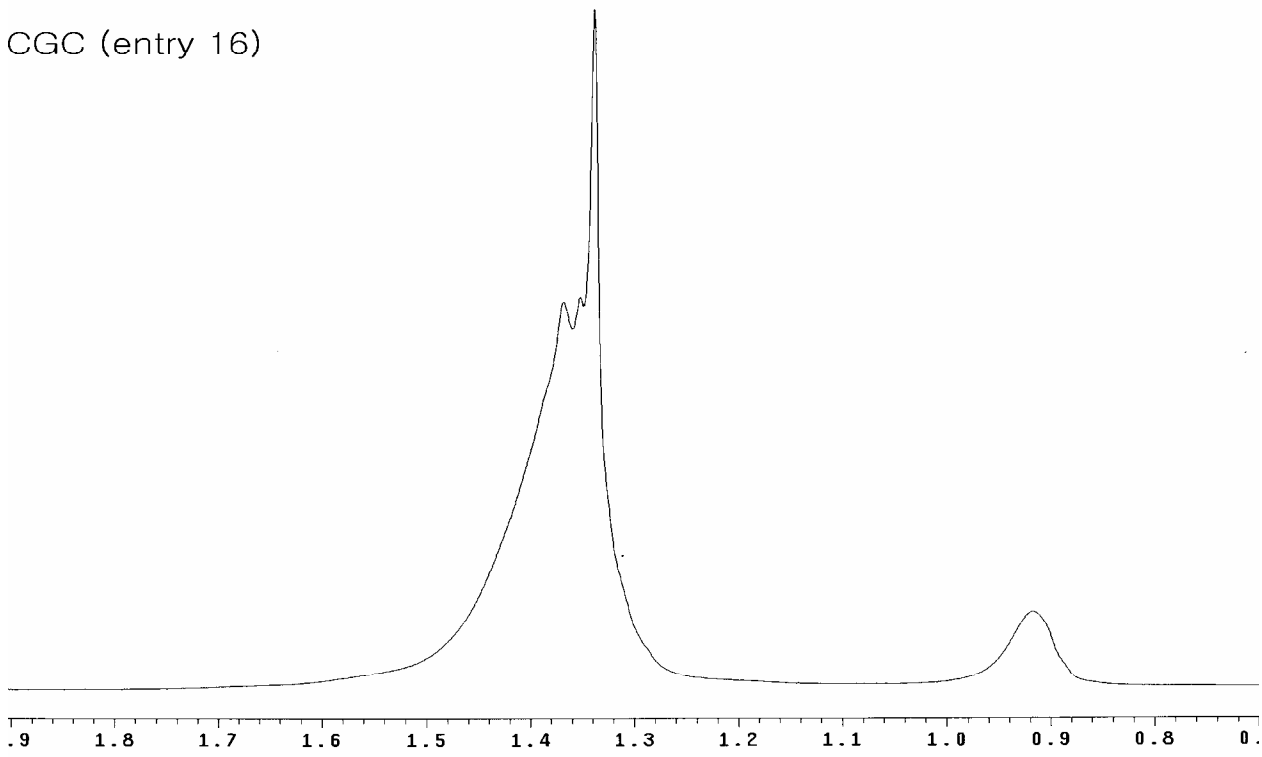


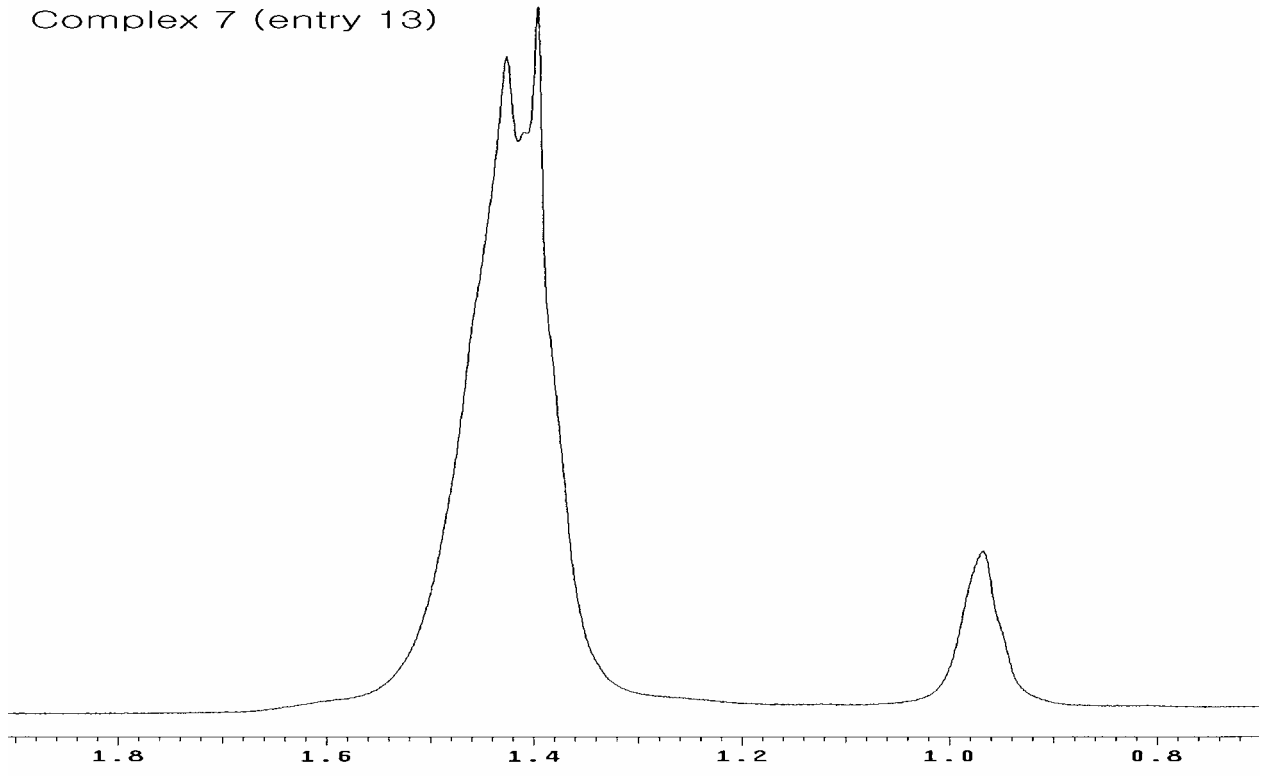


<The ^{1}H spectra of the polymers obtained by CGC and 7 (entries, 16 and 13 in Table 1)>

If "Integration value of 1.6-1.2 ppm region" = A; " Integration value of 1.0-0.85 ppm region" = B

Then, [1-Octene] (mol%) = [(B/3)]/{(B/3) + [A-(B/3)×13]/4}






Polymer
Prepared by 7
Polymer
Prepared by CGC