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(54) **Title**: STERICALLY EMCUMBERED BIDENTATE AND TRIDENTATE NAPHTHOXY-IMINE METALLIC COMPLEXES

(57) **Abstract**: The present invention discloses post-metallocene complexes based on sterically encumbered bi- and tri-dentate naphthoxy-imine ligands. It also relates to the use of such post-metallocene complexes in the oligomerisation of ethylene to selectively prepare vinyl-end capped linear alpha-olefins.

STERICALLY EMCUMBERED BIDENTATE AND TRIDENTATE NAPHTHOXY-IMINE METALLIC COMPLEXES.

The present invention relates to the field of post-metallocene complexes based on sterically encumbered bi- and tri-dentate naphthoxy-imine ligands. It also relates to the use of such post-metallocene complexes in the oligomerisation of ethylene to selectively prepare vinyl-end capped linear alpha-olefins.

There is a need for new highly active alkene polymerisation catalyst systems based on post-metallocenes and a lot of research has been carried out in that field, such as reviewed for example in Gibson and Sptizmesser (Gibson, V. C.; Spitzmesser, S. K. in Chem. Rev. 2003, 103, 283) or in Ittel et al. (Ittel, S. D.; Johnson, L. K.; Brookhart, M. in Chem. Rev. 2000, 100, 1169 or in Britovsek et al. (Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. in Angew. Chem., Int. Ed. 1999, 38, 429).

Among the plethora of newly disclosed catalytic systems, discrete group 3-6 metal complexes bearing various chelating aryloxide-based ligands have demonstrated astonishing performances in the polymerisation of ethylene and α-olefins. In particular, industry-relevant highly effective Cr(III) based phenoxy-imine systems were scrutinized by Gibson et al., such as disclosed for example in Jones et al. (Jones, D.J.; Gibson, V.C.; Green, S.M.; Maddox, P.J.; White, A.J.P.; Williams, D.J. in J. Am. Chem. Soc. 2005, 127, 11037) or in Meurs et al. (van Meurs, M.; Britovsek, G.J.P.; Gibson, V.C.; Cohen, S.A. in J. Am. Chem. Soc. 2005, 127, 9913) or in Gibson and O'Reilly (Gibson, V.C.; O'Reilly, R.K. US 20060258867A1) or in Gibson et al. (Gibson, V.C.; Mastroianni, S.; Newton, C.; Redshaw, C.; Solan, G.A.; White, A.J.P.; Williams, D.J. Dalton Trans. 2000, 1969). Typical metallic complexes of this family are represented in Figure 1.

List of Figures.

Figure 1 represents various Cr(III) phenoxy-imino compounds disclosed in literature that are suitable for the oligomerisation or polymerisation of ethylene.

Figure 2 represents the scheme used for the preparation of {ONN}H and {ON}H pro-ligands.

Figure 3 represents the ^{1}H NMR spectrum of pro-ligand **2a**.

Figure 4 represents the molecular structure of pro-ligand **2a**.

Figure 5 represents the ^{1}H NMR spectrum of pro-ligand **2b**.

Figure 6 represents the ^{1}H NMR spectrum of pro-ligand **2c**.

Figure 7 represents the molecular structure of chromium complex **3a**.

Figure 8 represents the molecular structure of chromium complex **3b**.

Figure 9 represents a typical ^{1}H NMR spectrum of vinyl end-capped oligoethylenes produced with the system **3a**/MAO.

Figure 10 represents a typical ^{13}C NMR (high field region) spectrum of vinyl end-capped oligoethylenes produced with the system **3a**/MAO.

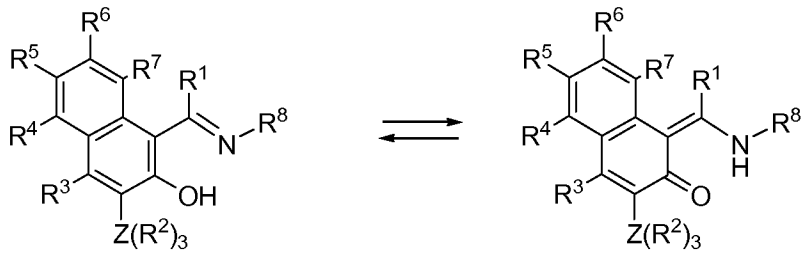
There is however still a need to develop new, very active catalyst systems having specific functionalities in order to tailor polymers with desired properties.

It is an aim of the present invention to prepare sterically encumbered ligands based on naphthoxy groups.

It is also an aim of the present invention to prepare very active catalyst systems for the oligomerisation and polymerisation of ethylene and alpha-olefins.

Any one of these aims is, at least partially, fulfilled by the present invention.

Accordingly, the present invention discloses a pro-ligand of formula **I** or its tautomeric form of formula **I'**



I I'

Wherein R^1, R^3, R^4, R^5, R^6 and R^7 are each independently selected from hydrogen, unsubstituted or substituted hydrocarbyl, or inert functional group, wherein two or more of said groups can be linked together to form one or more rings,
wherein Z is an atom selected from group 14 of the Periodic Table,
wherein each R^2 is independently selected from a substituted or unsubstituted aryl group having at most 8 carbon atoms, and/or an alkyl group, with the restriction that $Z(R^2)_3$ is a bulky group, at least as bulky as *tertio*-butyl,
wherein R^8 is a unsubstituted or substituted, aliphatic or aromatic hydrocarbyl group, possibly containing donor atoms such as halogens, or atoms selected from groups 15 and 16 of the periodic Table such as N, P, O, S.

Alternatively, $Z(R^2)_3$ can be a substituted aryl group.

Preferably R^1, R^3, R^4, R^5, R^6 and R^7 are each independently selected from hydrogen or alkyl groups having at most 6 carbon atoms, more preferably they all are hydrogen.

Preferably R^8 is CH_2-(2-pyridyl), alpha-quinoleine or C_6F_5.

Preferably, Z is C or Si, more preferably, it is Si.

Preferably all R^2 are the same and are substituted or unsubstituted phenyl group, or higher aromatic group (e.g. naphtyl), or alkyl. More preferably, each R^2 is unsubstituted phenyl group or a *tertio*-butyl group.

By inert functional group, is meant a group, other than hydrocarbyl or substituted hydrocarbyl, that is inert under the complexation conditions to which the compound containing said group is subjected. They can be selected for example from halo, ester,

ether, amino, imino, nitro, cyano, carboxyl, phosphate, phosphonite, phosphine, phosphinite, thioether and amide. Preferably, they are selected from halo, such as chloro, bromo, fluoro and iodo, or ether of formula – OR* wherein R* is unsubstituted or substituted hydrocarbyl. After metallation of the ligand, an inert functional group must not coordinate to the metal centre.

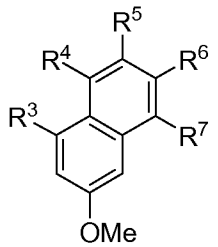
The present ligand includes a naphtoxy group whereas most ligands disclosed in the prior art include a phenoxy group. The catalyst systems based on the present ligand that includes a naphtoxy group are more tolerant thanks to a combination of steric and/or electronic effects.

In addition, in the preferred ligands according to the present invention, Z is Si. Replacing C by Si also results in improving the tolerance of the catalyst system. For example, a catalyst system wherein Z is C sees its activity destroyed by the addition of acetonitrile, whereas there is no observed change either in activity or in oligomer/polymer properties for an equivalent catalyst system wherein Z is Si.

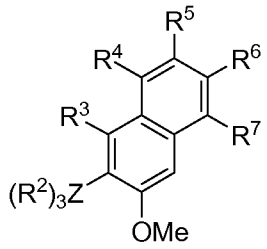
Several procedures have been tested in order to prepare the ligands of the present invention, most of them without success.

They can be prepared in good yield starting from 2-methoxynapthalene by a process that comprises the steps of:

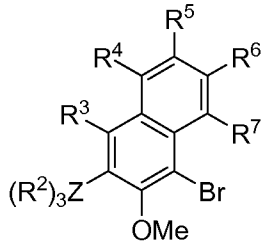
a) providing 2-methoxynaphthalene of formula



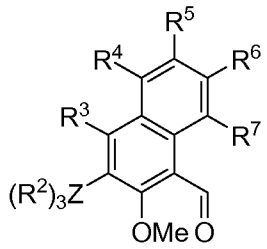
b) reacting with $(R^2)_3ZX'$, wherein X' is an halogen, in the presence of *sec*-BuLi in a solvent to obtain a compound of formula



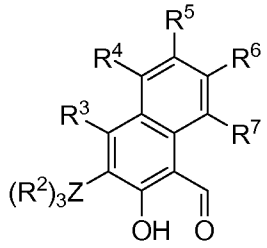
c) reacting with *N*-bromosuccinimide to obtained a compound of formula



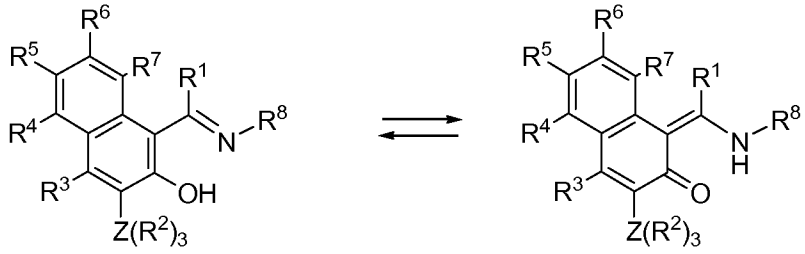
d) reacting with DMF in the presence of 2 equivalents of *tert*-BuLi in a solvent to obtain a compound of formula



e) deprotecting the compound obtained in step d) in order to obtain a compound of formula



f) condensation of the compound obtained in step e) with amine R^8-NH_2 in the presence of catalytic amounts of about 1 mol-% of formic acid, to obtain a compound of formula **I** and its tautomeric form **I'**.



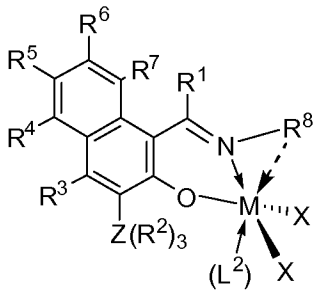
I **I'**

The method of preparation can be summarised in the scheme presented in Figure 2.

Deprotection step e) can be carried out for example by treatment with BBr_3.

The acid of step f) can be selected for example from HCOOH or PTSA.

The invention also discloses metallic complexes of general formula **II**



(II)

Metallic complexes **II** result from the complexation of pro-ligand **I** (**I'**) with metallic salts MX_n in a solvent, wherein M is a metal Group 6 of the periodic Table, wherein each X is the same or different and is an alkyl, benzyl substituted or not, aryl substituted or not, amido, alkoxide, and/or halide such as Cl, Br or I, and wherein L^2 is a solvent such as for example acetonitrile, THF or pyridine, preferably acetonitrile.

Preferably X are either all the same and are Br, or one X is *para*-tolyl and the other X is Br.

Preferably M is chromium.

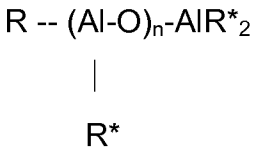
Preferably one equivalent of metallic salt is used per naphthoxy-imine complex.

The metallation reaction is carried out at a temperature of from -80 °C to a temperature of +25 °C and for a period of time of 1 to 18 hours.

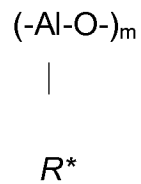
The present invention also discloses a catalyst system comprising the Group 6 metal single-site catalyst component of formula **II** and an activating agent having an alkylating/ionising action.

Suitable activating agents are well known in the art. The activating agent can be an aluminium alkyl represented by formula $AlR^{+}_{n}X_{3-n}$ wherein R^{+} is an alkyl having from 1 to 20 carbon atoms and X is a halogen, in combination with $[Ph_3C][B(C_6F_5)_4]$. The preferred aluminium alkyls are triisobutylaluminium (TIBAL) or triethylaluminium (TEAL). Aluminium alkyls are used in combination with trityl.

Alternatively, it can be aluminoxane and comprise oligomeric linear and/or cyclic alkyl aluminoxanes represented by formula



for oligomeric, linear aluminoxanes and by formula



for oligomeric, cyclic aluminoxane,

wherein *n* is 1-40, preferably 1-20, *m* is 3-40, preferably 3-20 and R* is a C_1-C_8 alkyl group and preferably methyl or isobutyl.

Preferably, the activating agent is methylaluminoxane (MAO).

The amount of activating agent is selected to give an Al/M ratio of from 500 to 10000, preferably of from to 1000 to 5000. The amount of activating agent depends upon its nature.

Suitable boron-containing agents may also be used for activating Group 6 metal single-site catalyst component of formula **II** where $R^{\$}$ is an alkyl or benzyl group. These include for example a triphenylcarbenium boronate such as tetrakis(pentafluorophenyl)borato-triphenylcarbenium as described in EP-A-0427696, or those of the general formula $[L'\text{-}H]^+$ $[B\ Ar_1\ Ar_2\ X_3\ X_4]^-$ as described in EP-A-0277004 (page 6, line 30 to page 7, line 7).

The amount of boron-containing activating agent is selected to give a B/M ratio of from 0.5 to 5, preferably of about 1.

In another embodiment, according to the present invention, the single-site catalyst component of formula **II** may be deposited on a conventional support. Preferably, the conventional support is silica impregnated with MAO. Alternatively the support may also be an activating support such as fluorinated alumina silica.

The catalyst system may comprise an optional scavenger that may be selected from triethylaluminium, triisobutylaluminum, tris-*n*-octylaluminium, tetraisobutyldialuminoxane or diethylzinc.

The present invention discloses a method for the oligomerisation or the homo- or co-polymerisation of ethylene and alpha-olefins that comprises the steps of:

a) injecting the active catalyst system into the reactor;
b) injecting the monomer and optional comonomer either before or after or simultaneously with step a);
c) maintaining under polymerisation conditions;
d) retrieving the oligomers and/or polymer.

The pressure in the reactor can vary from 0.5 to 50 bars, preferably from 5 to 25 bars.

The polymerisation temperature can range from 10 to 100 °C, preferably from 25 to 85 °C.

The preferred monomer and optional comonomer can be selected from ethylene, propylene, 1-hexene. The preferred monomer is ethylene.

Examples.

All experiments were performed under a purified argon atmosphere using standard Schlenk techniques, or in a glovebox. Solvents were distilled under nitrogen, from Na/benzophenone for THF and Et_2O, from CaH_2 for acetonitrile and from Na/K alloy for toluene and pentane. They were degassed thoroughly and stored under nitrogen prior to use. Deuterated solvents (benzene-d_6, toluene-d_8, THF-d_8; >99.5% D, Eurisotop) were vacuum-transferred from Na/K alloy into storage tubes. Starting materials were purchased from Acros, Strem and Aldrich. NMR spectra of complexes were recorded on Bruker AC-200, AC-300 and AM-500 spectrometers in Teflon-valved NMR tubes at 25 ºC unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported in ppm vs. $SiMe_4$ and were determined by reference to the residual solvent peaks. Assignment of resonances for organometallic complexes was made from ^1H–^{13}C HMQC and HMBC NMR experiments. Coupling constants are given in Hertz. Elemental analyses were performed by the Microanalytical Laboratory at the Institute of Chemistry of Rennes and are the average of two independent determinations.

I. Preparation of {ONN}H and {ON}H ligands.

A. Preparation of 3-methoxy-2naphthyl-triphenylsilane.

A solution of 15.3 mL of *sec*-BuLi 1.3 M in hexane/cyclohexane (19.91 mmol) was added dropwise to a stirred solution of 3.0 g of 2-methoxynaphthalene (18.96 mmol) in 70 mL of tetrahydrofuran (THF) at a temperature of -30 °C and for a period of time of 15 min. After stirring overnight at room temperature, to the resultant tinted solution was

added a solution of 5.87 g of Ph_3SiCl (19.91 mmol) and 3.46 mL of hexamethylphosphoramide (HMPA) (19.88 mmol) in 50 mL of THF. The reaction mixture was heated at reflux for a period of time of 20 h, cooled and diluted with 500 mL of water. The organic part was extracted with 3 times 50 mL of Et_2O. The combined organic extracts were dried over $MgSO_4$, and evaporated. The crude residue was recrystallised from heptane and dried under vacuum to give 7.11 g of (3-methoxy-2-naphthyl)(triphenyl)silane (17.07 mmol) with a yield of 90 %.

The NMR spectrum was as follows:

^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ 7.80 (m, 2H), 7.67 (m, 7H), 7.55-7.23 (m, 12 H), 3.69 (s, 3H, OCH_3).

Anal. calcd. for $C_{29}H_{24}OSi$: C, 83.61; H, 5.81. Found: C, 82.15; H, 5.23.

B. Preparation of (4-bromo-3-methoxy-2-naphtyl)-triphenylsilane.

A 150 mL Schlenk flask was charged with 4.68 g of (3-methoxy-2-naphthyl)(triphenyl)silane (11.23 mmol) and 2.20g of N-bromosuccinimide (NBS) (12.36 mmol) under argon followed by addition of 10 mL of dimethylformamide (DMF). The resultant mixture was stirred overnight at room temperature, then diluted with 500 mL of water and extracted with 3 times 50 mL of CH_2Cl_2. The combined organic extracts were washed with 200 mL of water, brine and dried over Na_2SO_4. The product was purified by passing through short column (silica) using a mixture heptane:EtOAc in a ratio of 15:1 as eluent to afford 5.28 g of product as off-white solid (10.66 mmol) with a yield of 96 %.

The NMR spectrum was as follows:

^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ 8.29 (d, J = 8.4 Hz, 1H), 7.80 (s, 1H), 7.66 (m, 8H), 7.52-7.27 (m, 10 H), 3.18 (s, 3H, OCH_3).

Anal. calcd. for $C_{29}H_{23}BrOSi$: C, 70.30; H, 4.68. Found: C, 68.99; H, 4.56.

C. Preparation of 2-hydroxy-3-(triphenylsilyl)-1-naphthaldehyde (**1**).

A solution of 16.1 mL of *tert*-BuLi 1.5 M in pentane (24.10 mmol) was added dropwise to a stirred solution of 6.02 g of (4-bromo-3-methoxy-2naphtyl)-triphenylsilane (12.05 mmol) in 50 mL of Et_2O at -78°C. The reaction mixture was stirred during 1.5 h at a given temperature and 30 min at 0°C followed by addition of 0.94 mL of DMF. The resultant mixture was stirred overnight at room temperature and diluted with 200 mL of

water. The organic part was extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were dried over $MgSO_4$. The resultant solution was transferred to a Schlenk flask under argon and a solution of 24.1 mL of BBr_3 1M in CH_2Cl_2 (24.1 mmol) was added dropwise at -78 °C. The reaction mixture was stirred overnight at room temperature, then carefully hydrolysed with 500 mL of water. The organic part was extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were dried over $MgSO_4$, and evaporated. The crude residue was recrystallised from methanol and dried under vacuum to give 5.44 g of **1** (12.63 mmol) with a yield of 95 %.

The NMR spectrum was as follows:

^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 13.58 (s, 1H, O*H*), 10.88 (s, 1H, =C*H*O), 8.40 (d, *J* = 8.4 Hz, 1H), 8.03 (s, 1H), 7.67 (m, 6H), 7.43 (m, 12H).

Anal. calcd. for $C_{29}H_{22}O_2Si$: C, 80.90; H, 5.15. Found: C, 80.17; H, 4.67.

D. Preparation of 1-[(quinolin-8-ylamino)methylene]-3-(triphenylsilyl)naphthalen-2-one (**2a**) as a stable tautomeric form of 1-[(quinolin-8-ylimino)methyl]-3-(triphenylsilyl)-2-naphthol.

To a stirred mixture of 1.09 g (2.53 mmol) of **1** and 0.37 g (2.53 mmol) of 8-aminoquinoline in 40 mL of methanol, was added formic acid (ca. 10 mg) at room temperature. The resultant mixture was stirred at reflux for 25 hours and the product precipitated as microcrystalline powder. The reaction mixture was transferred onto a Schott filter and filtered. The obtained orange solid was washed with cold methanol and dried under vacuum to give 0.77 g (1.38 mmol) of **2a** with a yield of 55%.

The NMR spectra were as follows:

^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 15.31 (d, *J* = 11.1 Hz, 1H, N*H*), 9.31 (d, *J* = 11.1 Hz, 1H, =C*H*N), 9.02 (dd, 1H), 8.26 (dd, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.81 (m, 2H), 7.73 (m, 7H), 7.66 (m, 1H), 7.57-7.40 (m, 12H), 7.27 (m, 1H).

^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): δ 185.2, 151.7, 150.1, 146.4, 139.8, 137.4, 136.4, 136.1, 135.8, 135.0, 133.2, 130.0, 129.3, 129.2, 129.0, 127.7, 126.6, 126.5, 124.4, 123.5, 122.3, 118.3, 113.9, 108.2.

The ^{1}H NMR of the pro-ligand is represented in Figure 3.

Anal. calcd. for $C_{38}H_{28}N_2OSi$: C, 81.98; H, 5.07. Found: C, 81.04; H, 4.98.

The molecular structure of this ligand can be seen in Figure 4.

E. Preparation of 1-{[(pyridin-2-ylmethyl)amino]methylene}-3-(triphenylsilyl)naphthalen-2-one (**2b**) as a stable tautomeric form of 1-[(pyridin-2-ylmethyl)imino]methyl}-3-(triphenylsilyl)-2-naphthol.

Using the same protocol as described above, pro-ligand **2b** was prepared in 0.78 g yield (1.50 mmol, 60 %) from 1.08 g of **1** (2.51 mmol) and 0.29 g of 2-aminomethylpyridine (1.50 mmol).

The NMR spectra were as follows:

^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 14.44 (br m, 1H, N*H*), 8.96 (d, *J* = 8.8 Hz, 1H), 8.63 (dd, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.79 (s, 1H), 7.70 (m, 1H), 7.67 (m, 6H), 7.60-7.35 (m, 11H), 7.32 (d, 1H), 7.25 (m, 1H), 7.23 (m, 1H), 4.88 (m, 2H, C*H*$_2$Py).

^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): δ 180.6, 158.6, 156.4, 149.8, 149.3, 136.9, 136.3, 135.6, 135.1, 131.5, 129.8, 129.2, 128.9, 127.7, 126.1, 122.8, 122.6, 121.9, 117.8, 106.1, 57.7.

The ^{1}H NMR of the pro-ligand is represented in Figure 5.

Anal. calcd. for $C_{35}H_{28}N_2OSi$: C, 80.73; H, 5.42. Found: C, 79.94; H, 5.00.

F. Preparation of 1-[(pentafluorophenyl)imino]methyl}-3-(triphenylsilyl)-2-naphthol (**2c**).

Pro-ligand **2c** was synthesised by condensation of 1.04 g of **1** (2.42 mmol) and 0.44 g of pentafluoro-aniline (2.42 mmol) in toluene at reflux for 40 hours in the presence of PTSA (ca. 5 %w), using Dean-Stark apparatus. The reaction mixture was evaporated and the residue was recrystallized from methanol to give **2c** in 0.93 g yield (1.57 mmol, 65 %).

The NMR spectra were as follows:

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 14.49 (s, 1H, O*H*), 9.76 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.96 (s, 1H), 7.71 (d, J = 6.7 Hz, 6H), 7.69 (d, *J* = 10.2 Hz, 1H), 7.62 (t, *J* = 10.2 Hz, 1H), 7.52-7.30 (m, 10H).

^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 168.5, 165.9, 148.1, 136.4, 134.2, 134.0, 130.2, 129.6, 129.4, 127.9, 127.7, 126.3, 123.9, 118.9, 108.8 (signals from the Ph group were hardly observed).

^{19}F NMR (188 MHz, $CDCl_3$, 25 °C): δ -152 .4 (m, 2F), -159.1 (t, 1F), -162.8 (m, 2F).

The ^{1}H NMR of the pro-ligand is represented in Figure 6.

Anal. calcd. for $C_{35}H_{22}F_5NOSi$: C, 70.58; H, 3.72. Found: C, 69.89; H, 3.14.

II. Preparation of complexes.

A. Synthesis of complex (*p*-Tol)$CrBr_2(THF)_3$.

Synthesis of complex (*p*-Tol)$CrBr_2(THF)_3$ was performed using modified procedure published in (Daly, J.J.; Sneeden, R.P.A.; Zeiss, H.H. J. Am. Chem. Soc. 1966, 88, 4287-4288) from $CrCl_3$ and (*p*-Tol)MgBr in THF.
Anal. calcd. for $C_{19}H_{31}Br_2CrO_3$: C, 43.95; H, 6.02. Found: C, 43.81; H, 5.78.

B. Synthesis of complex (ONN^{Quin})$CrBr_2$(MeCN) (**3a**).

A Schlenk tube was charged with 0.150 g of **2a** (0.269 mmol) and 0.140 g of (*p*-Tol)$CrBr_2(THF)_3$ (0.269 mmol), and 5 mL of toluene were vacuum transferred therein. The reaction mixture was stirred overnight at room temperature, evaporated and dried in vacuum. The deep-pink residue was recrystallised from 20-25 mL of dried acetonitrile to give 0.187 g (0.232 mmol) of **3a** with a yield of 86%.
UV-vis (CH_2Cl_2, 298 K, $mol^{-1}\cdot dm^3\cdot cm^{-1}$): ε_{527} 5660, ε_{500} 5296, ε_{371} 6455.
FAB-MS (m/z): $CHCl_3$: 1163.7 ($[L_2Cr]^{+\cdot}$).
μ(B.M.) = 3.87.
Anal. calcd. for $C_{40}H_{30}Br_2CrN_3OSi$: C, 59.42; H, 3.74. Found: C, 58.65; H, 3.08.
The molecular structure of the chromium complex is represented in Figure 7.

C. Synthesis of complex (ONN^{Py})$CrBr_2$(MeCN) (**3b**).

Following the same procedure as that used to prepare complex **3a,** complex **3b** was obtained from 0.100 g of **2b** (0.192 mmol) and 0.100 g of (*p*-Tol)$CrBr_2(THF)_3$ (0.192 mmol) and isolated in an amount of 0.135 g (0.175 mmol) with a yield of 91 %.
UV-vis (CH_2Cl_2, 298 K, $mol^{-1}\cdot dm^3\cdot cm^{-1}$): ε_{456} 2865, ε_{319} 7384.
FAB-MS (m/z): $CHCl_3$: 1090.7 ($[ML_2]^{+\cdot}$); acetonitrile: 1090.6 ($[L_2Cr]^{+\cdot}$).
Anal. calcd. for $C_{37}H_{30}Br_2CrN_3OSi$: C, 57.52; H, 3.91. Found: C, 57.11; H, 3.13.
The molecular structure of the chromium complex is represented in Figure 8.

D. Synthesis of complex (ON-Ph^F)$CrBr_2(MeCN)_2$ (**3c**).

Similarly complex **3c** was prepared from 0.100 g of **2c** (0.168 mmol) and 0.087 g of (*p*-Tol)$CrBr_2(THF)_3$ (0.168 mmol) and isolated in an amount of 0.101 g (0.114 mmol) with a yield of 68 %.

UV-vis (CH_2Cl_2, 298 K, $mol^{-1}\cdot dm^3\cdot cm^{-1}$): ε_{438} 6500, ε_{337} 10035, ε_{303} 9626.

FAB-MS (m/z): $C_2H_4Cl_2$: 1240.2 ($[L_2Cr]^{+\cdot}$).

μ(B.M.) = 3.87.

Anal. calcd. for $C_{39}H_{27}Br_2CrF_5N_3OSi$: C, 52.72; H, 3.06. Found: C, 51.89; H, 2.78.

Homopolymerisation of ethylene.

The polymerisation was carried out as follows.

A 300 mL glass high-pressure reactor was charged with 80 mL of freshly distilled toluene under argon flash. Mechanical stirring (Pelton turbine, 1000 rpm) was started, the reactor was then purged with ethylene and loaded with a solution of scavenger selected from MAO or DEAC, at atmospheric pressure, and then kept at the desired temperature by circulating water in a double wall. A solution of pre-catalyst in 2 mL of toluene was injected in by syringe. The gas pressure in the reactor was maintained immediately and kept constant with a back regulator throughout the experiment. The ethylene consumption was monitored via an Aalborg flowmeter. After a given time period, the reactor was depressurised and the reaction was quenched by adding about 5 mL of a 10% solution of HCl in methanol. The polymer was further precipitated by adding 500 mL of methanol, washed and dried in vacuum overnight at room temperature. The polymerisation conditions are summarised in Table I and the polymerisation results are presented in Table II.

Cat 1 was generated *in situ* from **2a** and (*p*-Tol)$CrBr_2(THF)_3$

Cat 2 is generated *in situ* from **2b** and (*p*-Tol)$CrBr_2(THF)_3$

Cat 3 is isolated complex **3a**

Cat 4 is isolated complex **3b**

Cat 5 is isolated complex **3c**

The monomer was ethylene.

TABLE I.

Run	Cat	Amount cat (µmol)	Activator	Activator/M	P_{C2H4} (bar)	T (°C)	t (min)

1	cat 1	23	MAO	800	1	50	60
2	cat 2	23	MAO	800	1	50	60
3	cat1	5	MAO	500	6	50 (93)[a]	10
4 [b]	cat1	21	MAO	800	1	50 (93)[a]	60
5	cat 3	5	DEAC	500	6	50	60
6	cat 3	5	MAO	500	6	50 (90)[a]	10
7	cat 3	5	MAO	500	1	50	20
8	cat 3	5	MAO	500	6	25 (107)[a]	5
9 [c]	cat 3	5	MAO	500	6	50 (94)[a]	10
10 [d]	cat 3	5	MAO	500	6	50 (93)[a]	10
11	cat 4	5	MAO	500	6	50 (83)[a]	10
12	cat 5	5	MAO	500	6	50	60
13	cat 5	5	DEAC	500	6	50	60

[a] The polymerisation reaction proceeded exothermally; the maximal temperature reached is given into brackets.

[b] MeCN (4 equiv. vs Cr) was added.

[c] THF (4 equiv. vs Cr) was added.

[d] Pyridine (4 equiv. vs Cr) was added.

TABLE II.

Run	Mass PE (g)	Productivity (g_{polym}/g_{cata})	Activity (kgPE/mol/h)	M_n [e] (Da)	M_n [f] (Da)	M_w/M_n [f]	Vinyl [e] (mol%)	T_m [g] (°C)
1	3.50	270	151	nd	630	1.99	< 40	114
2	0.62	52	27	1430	800	2.10	67	119
3	9.22	2305	11060	1070	nd	nd	85	118
4	1.15	58	55	1130	nd	nd	90	116
5	0.11	27	22	-	-	-	-	-
6	11.80	2950	14160	1140	800	2.23	90	118
7	4.29	1072	2574	1450	nd	nd	90	119
8	9.89	2470	23730	1100	nd	nd	87	119
9	8.75	2190	10500	1320	nd	nd	88	118
10	12.43	3110	14900	1210	nd	nd	88	118
11	10.50	2760	12600	1340	850	2.22	91	122
12	0.20	45	40	-	-	-	-	-
13	traces	-	-	-	-	-	-	-

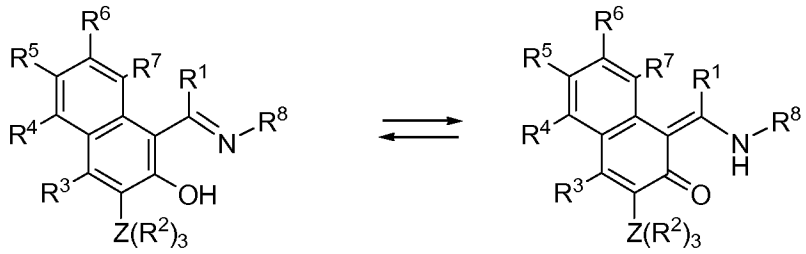
[e] Determined from the ^1H NMR spectrum in $C_2D_2Cl_4$ at 100 °C.

[f] Determined by GPC at 150 °C in trichlorobenzene *vs* polystyrene standards.

[g] Determined by DSC.

CLAIMS.

1. A pro-ligand of formula **I** or its tautomeric form of formula **I'**



I **I'**

Wherein R^1, R^3, R^4, R^5, R^6 and R^7 are each independently selected from hydrogen, unsubstituted or substituted hydrocarbyl, or inert functional group, wherein two or more of said groups can be linked together to form one or more rings,
wherein Z is an atom selected from group 14 of the Periodic Table.
wherein each R^2 is independently selected from a substituted or unsubstituted aryl group having at most 8 carbon atoms, and/or an alkyl group, with the restriction that $Z(R^2)_3$ is a bulky group, at least as bulky as *tertio*-butyl,
wherein R^8 is a unsubstituted or substituted, aliphatic or aromatic hydrocarbyl group, possibly containing donor atoms such as halogens, or atoms selected from groups 15 and 16 of the periodic Table.

2. The pro-ligand of claim 1 wherein R^1, R^3, R^4, R^5, R^6 and R^7 are each independently selected from hydrogen or alkyl group having at most 6 carbon atoms, and preferably are the same and are hydrogen.

3. The pro-ligand of claim 1 or claim 2 wherein Z is C or Si, preferably Si.

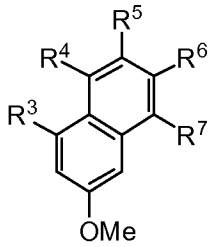
4. The pro-ligand of any one of the preceding claims wherein R^8 is CH_2-(2-pyridyl), alpha-quinoleine or C_6F_5.

5. The pro-ligand of any one of the preceding claims wherein all R^2 are the same substituted or unsubstituted phenyl group, higher aromatic group or alkyl having at most 10 carbon atoms.

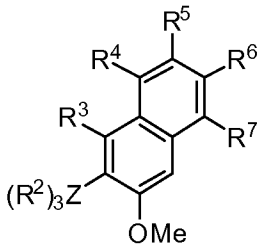
6. The pro-ligand of claim 5 wherein R^2 is unsubstituted phenyl group or *tertio*-butyl group.

7. A process for preparing the pro-ligand of any one of the preceding claims that comprises the steps of:

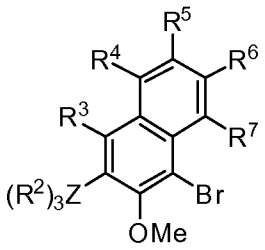
a) providing 2-methoxynaphthalene of formula



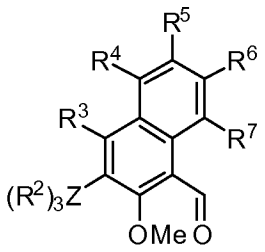
b) reacting with $(R^2)_3ZX'$, wherein X' is an halogen, in the presence of *sec*-BuLi in a solvent to obtain a compound of formula



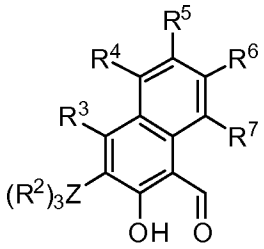
c) reacting with *N*-bromosuccinimide to obtained a compound of formula



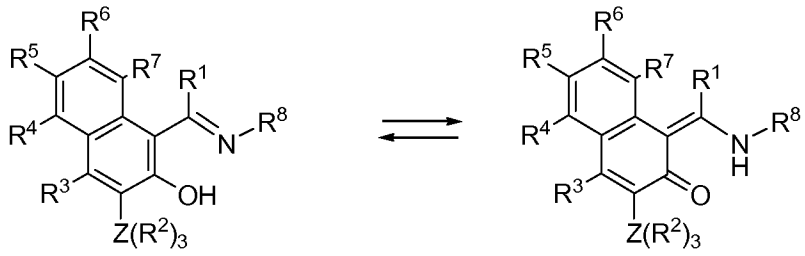
d) reacting with DMF in the presence of *tert*-BuLi (two equivalents) in a solvent to obtain a compound of formula



e) deprotecting the compound obtained in step d), e.g. by treatment with BBr_3 in order to obtain a compound of formula

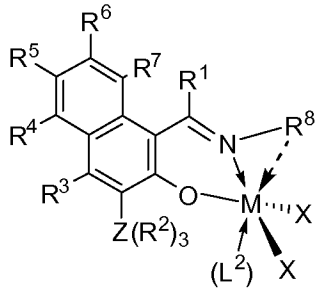


f) condensation of the compound obtained in step e) with the appropriate amine R^8-NH_2 in the presence of catalytic amounts of an acid, such as HCOOH or PTSA, to obtain compounds of formula **I** and its tautomeric form **I'**.



I **I'**

8. A metallic complex of formula **II**



(II)

wherein M is a metal Group 6 of the periodic Table, preferably chromium, wherein each X is the same or different and is an alkyl, benzyl substituted or not, aryl substituted or not, amido, alkoxide, and/or halide, wherein L^2 is a solvent and wherein all other parameters are as described previously.

9. The metallic complex of claim 8 wherein either X are all the same and are Br, or one X is *para*-tolyl and the two other X are Br.

10. A process for preparing the metallic complex of claim 8 or claim 9 by complexation reaction of the ligand of any one of claims 1 to 7 with metallic salt MX_n in a solvent.

11. A catalyst system comprising the metallic complex of claim 8 or claim 9 and an activating agent having an ionising action selected from aluminium alkyl, aluminoxane or boron containing agents.

12. A process for oligo-, homo- or co-polymerising ethylene and alpha-olefins that comprises the steps of:

a) injecting the catalyst system of claim 11 into the reactor;

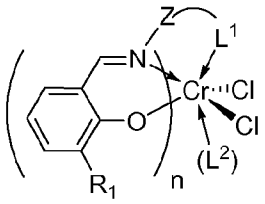
b) injecting the monomer and optional comonomer either before or after or simultaneously with step a);

c) maintaining under polymerisation conditions;

d) retrieving the oligomers and/or polymer.

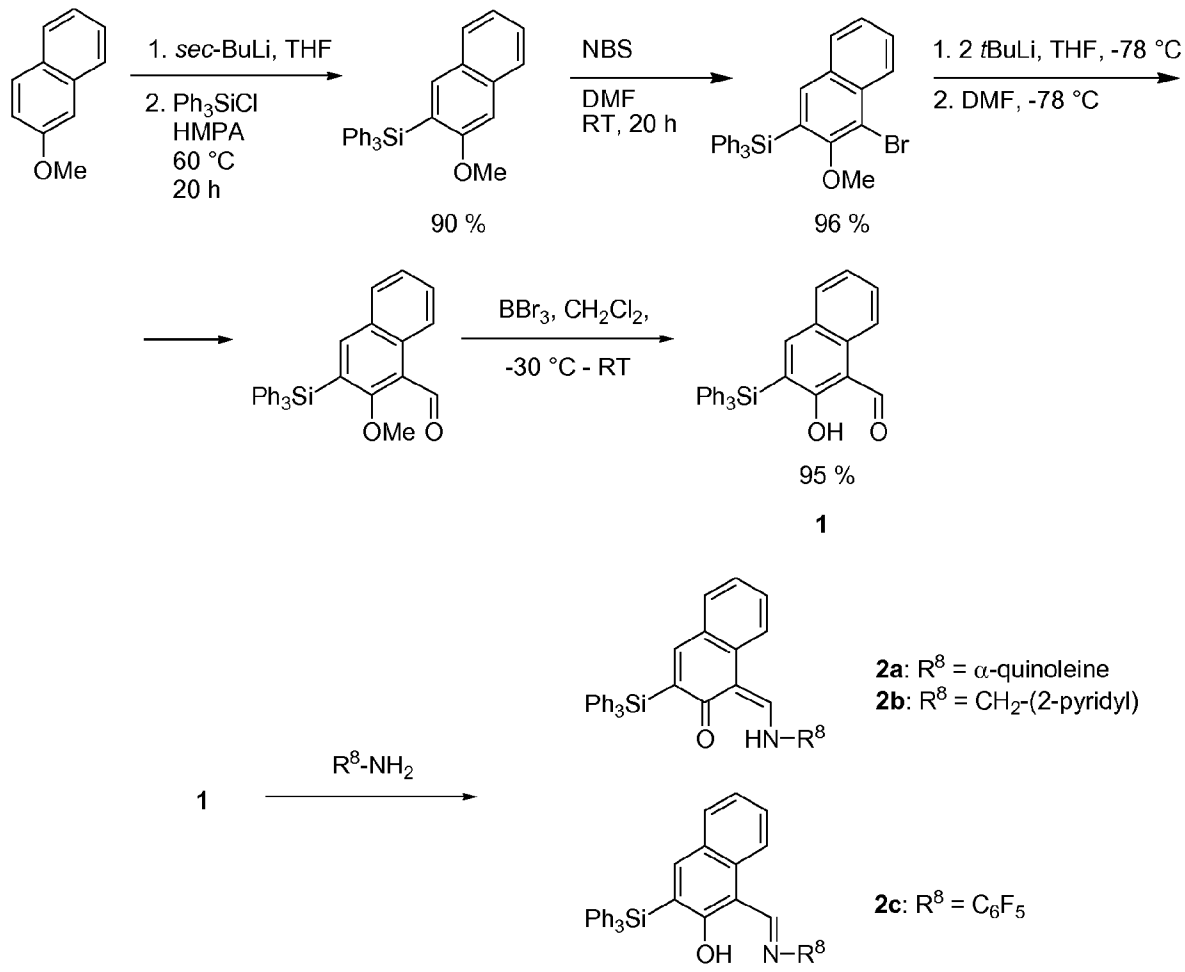
13. The process of claim 12 wherein the monomer is ethylene or propylene, preferably ethylene, and the optional comonomer is propylene or 1-hexene.

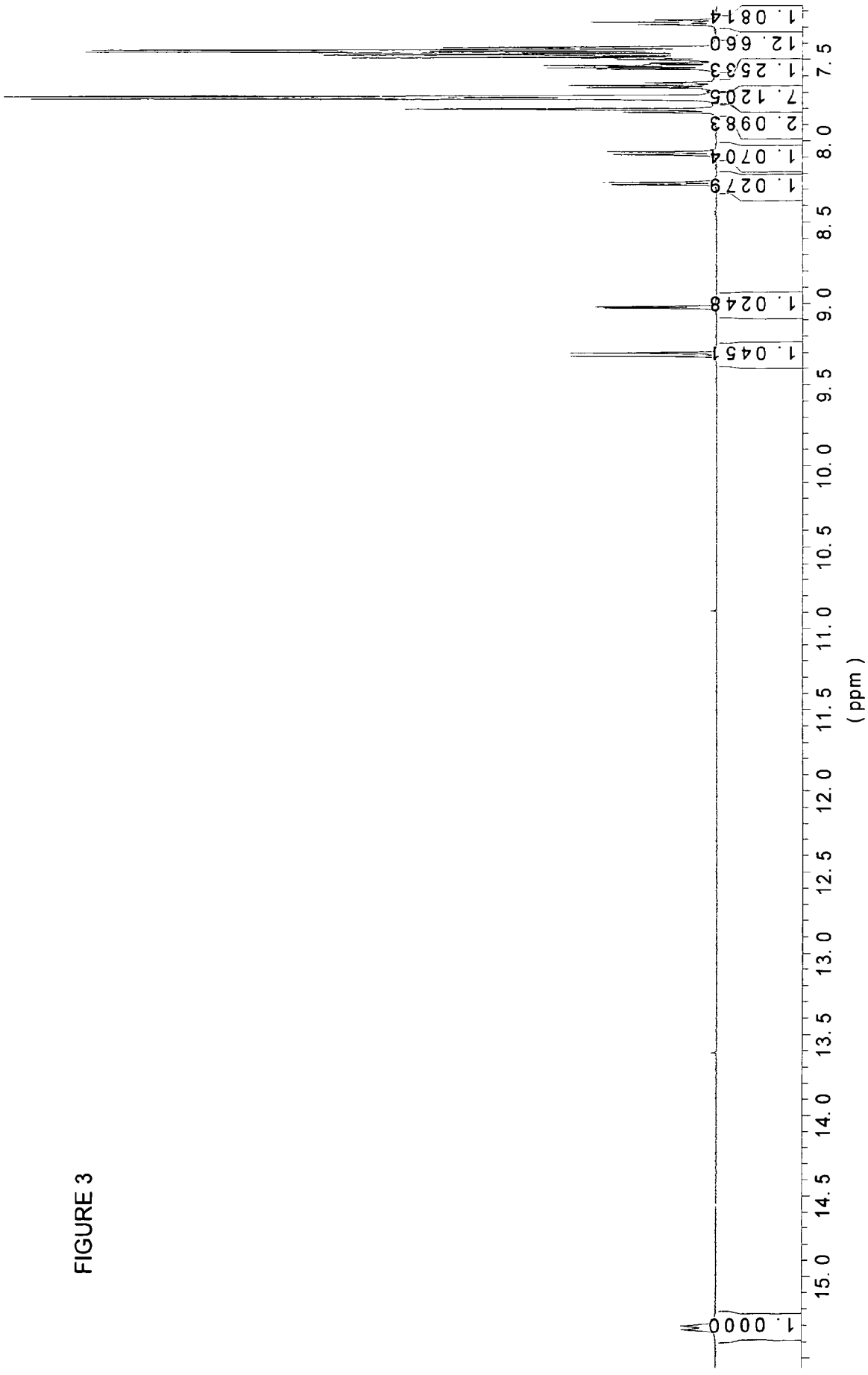
FIGURE 1



n = 1 or 2
R_1 = tBu, adamanthyl, anthracenyl, triptycenyl
Z = linker or non-coordinating R group (alkyl, aryl)
L^1 = pendant donor group (amino, pyridine, quinoline)
L^2 = donor molecule (acetonitrile, THF, pyridine)

FIGURE 2


1. sec-BuLi, THF
2. Ph3SiCl
HMPA
60 °C
20 h
90 %
NBS
DMF
RT, 20 h
96 %
1. 2 tBuLi, THF, -78 °C
2. DMF, -78 °C
BBr3, CH2Cl2,
-30 °C - RT
95 %
1
R8-NH2
2a: R8 = α-quinoleine
2b: R8 = CH2-(2-pyridyl)
2c: R8 = C6F5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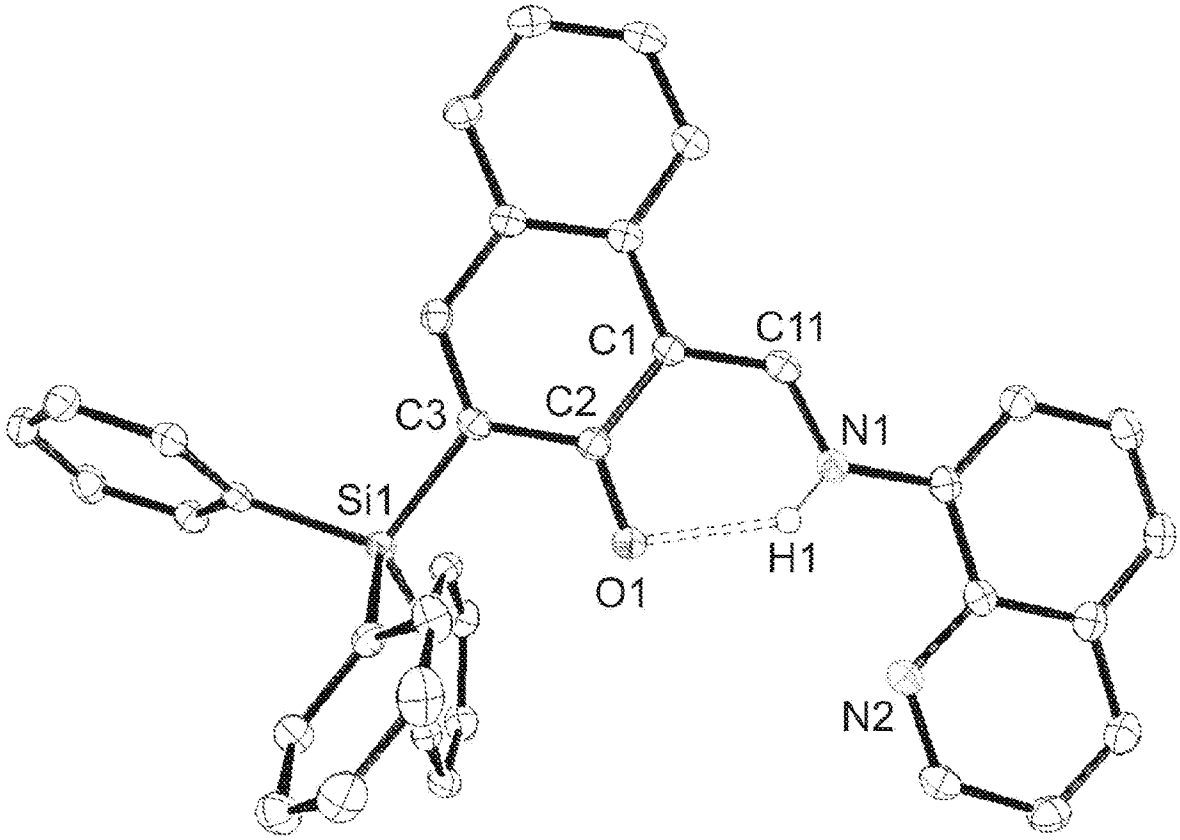
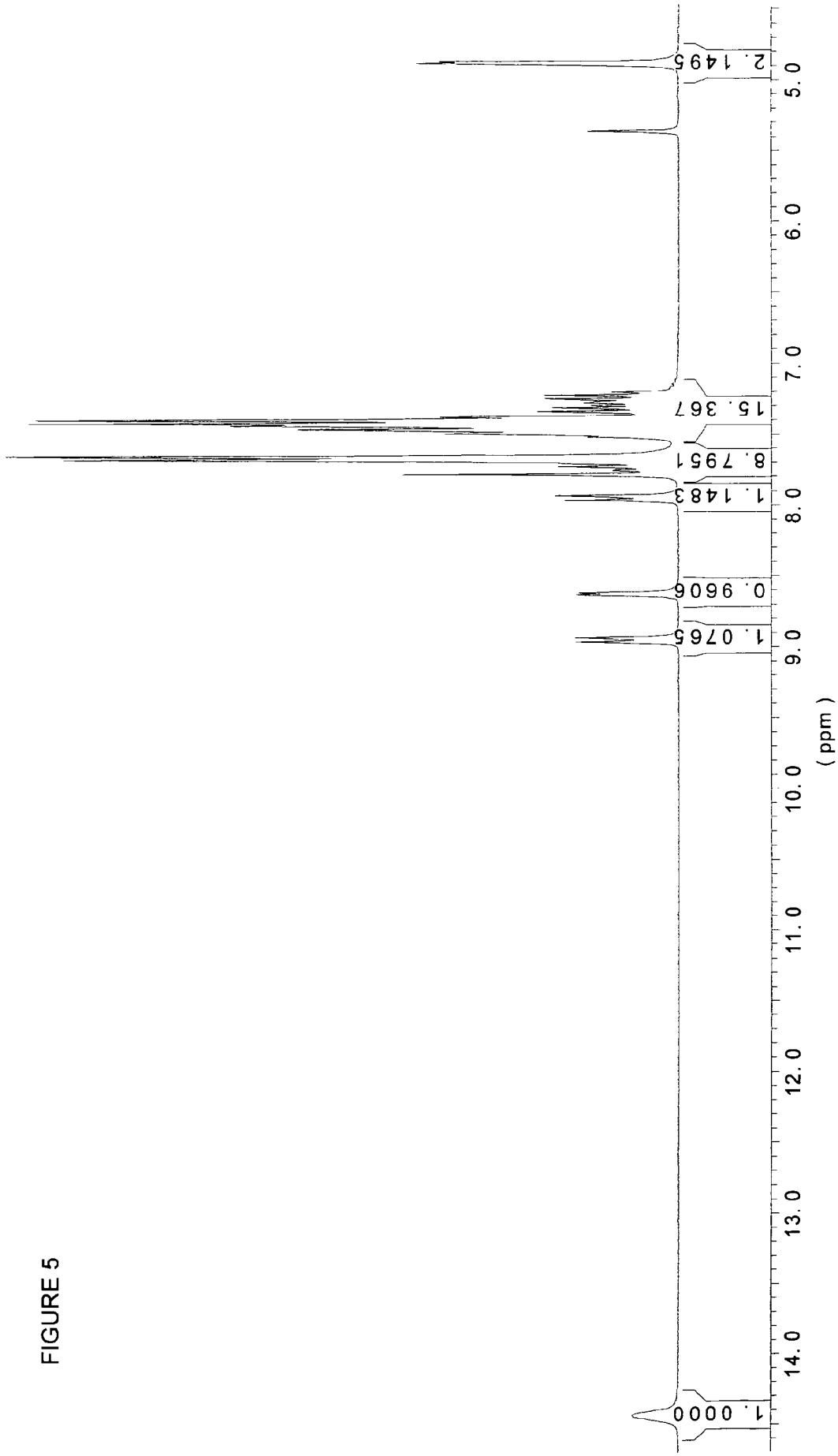
12.6600
1.2533
7.1205
2.0983
1.0704
1.0279
1.0248
1.0451
1.0000
15.0
14.5
14.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
(ppm)

FIGURE 3

FIGURE 4

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15.367
8.7951
1.1483
0.9606
1.0765
1.0000
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
(ppm)

FIGURE 5

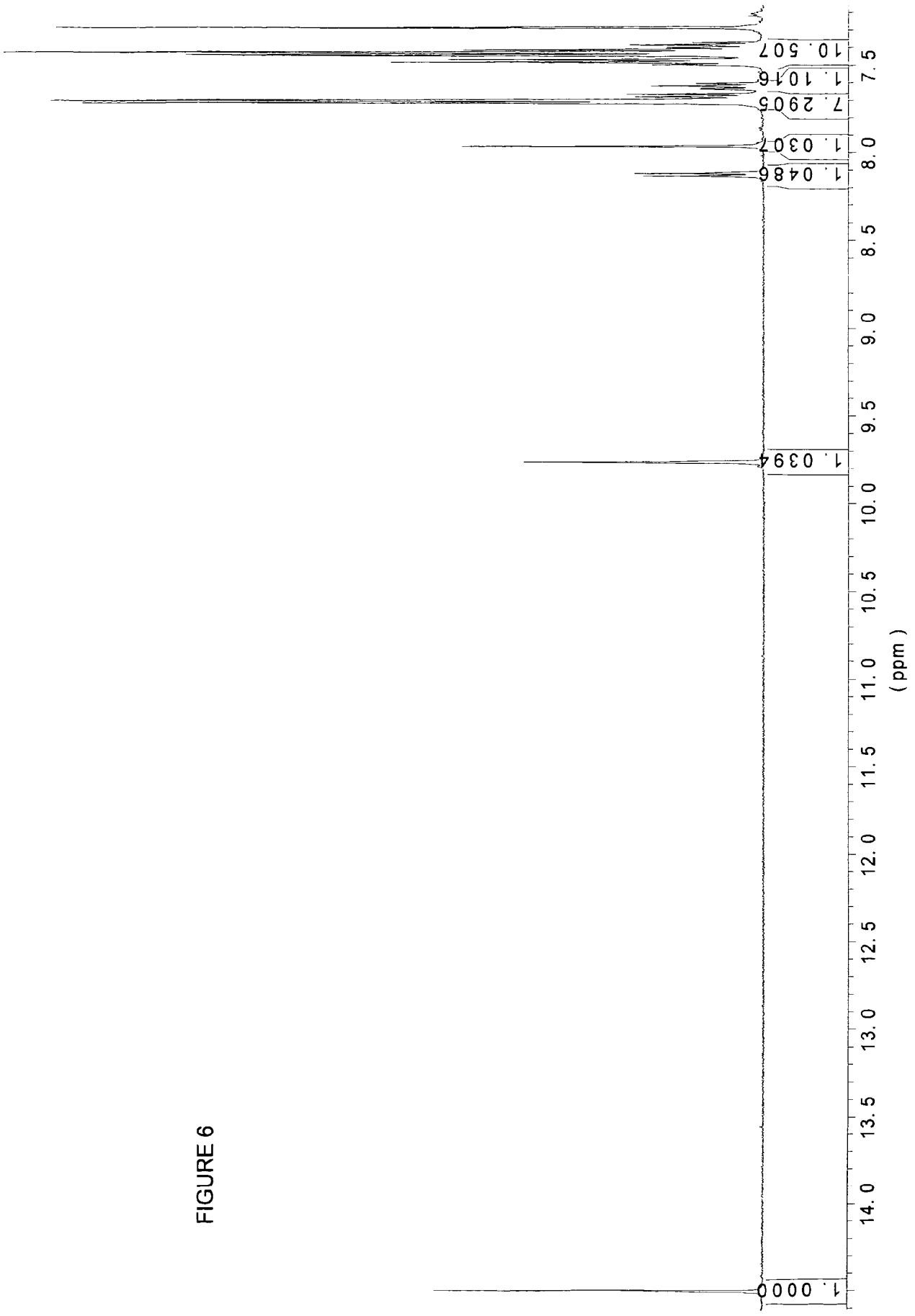

10.507
1.1016
7.2905
1.0307
1.0486
1.0394
1.0000
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
13.5
14.0
(ppm)

FIGURE 6

FIGURE 7

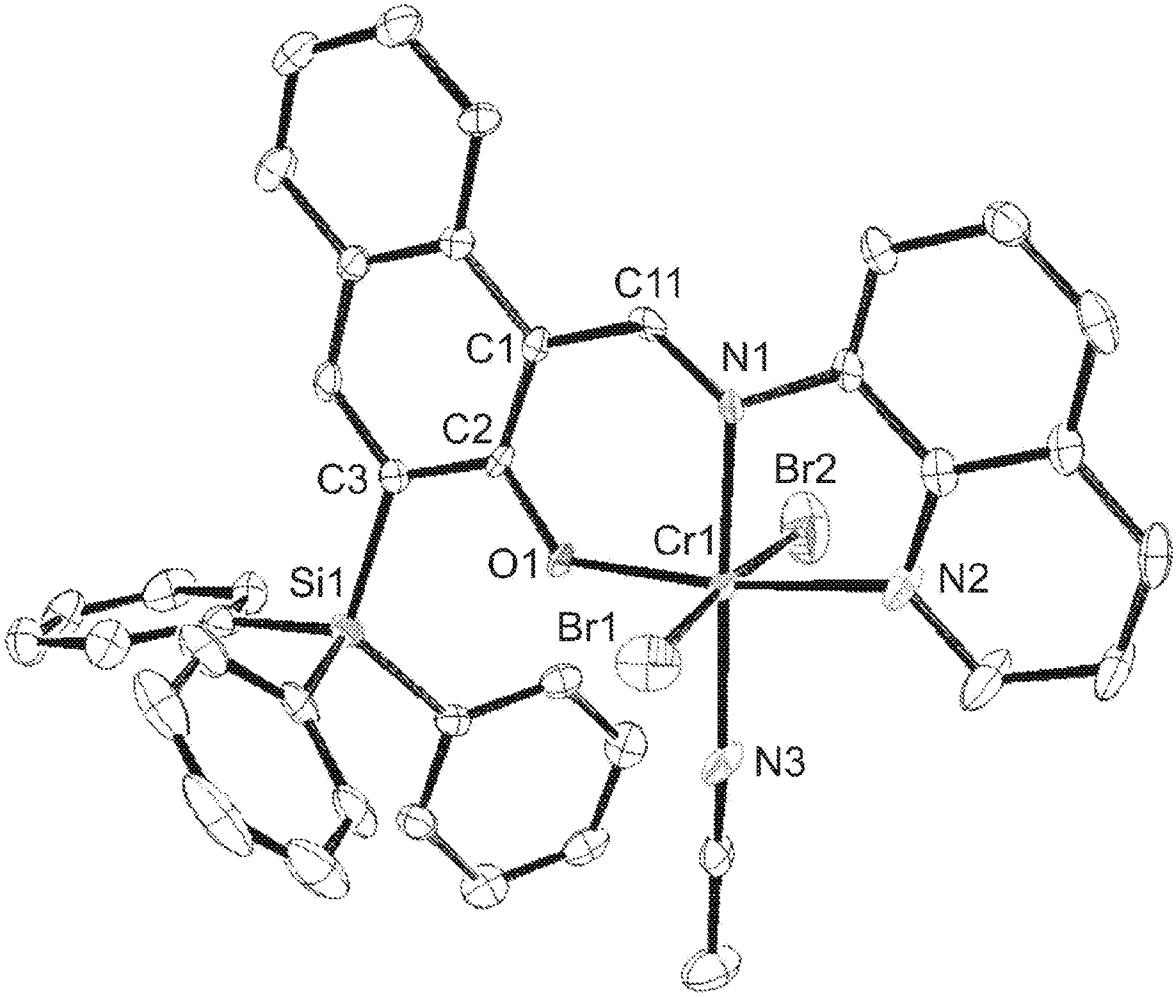
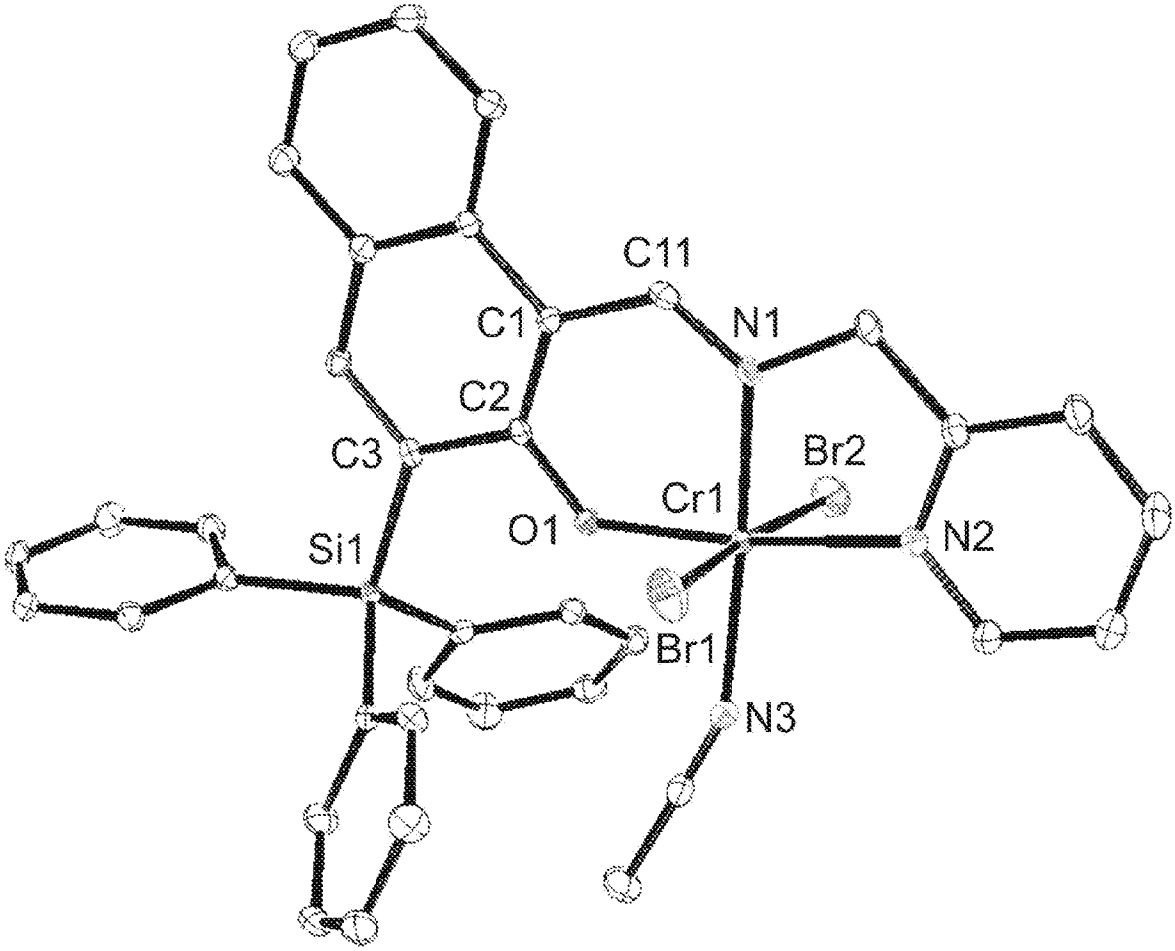


FIGURE 8



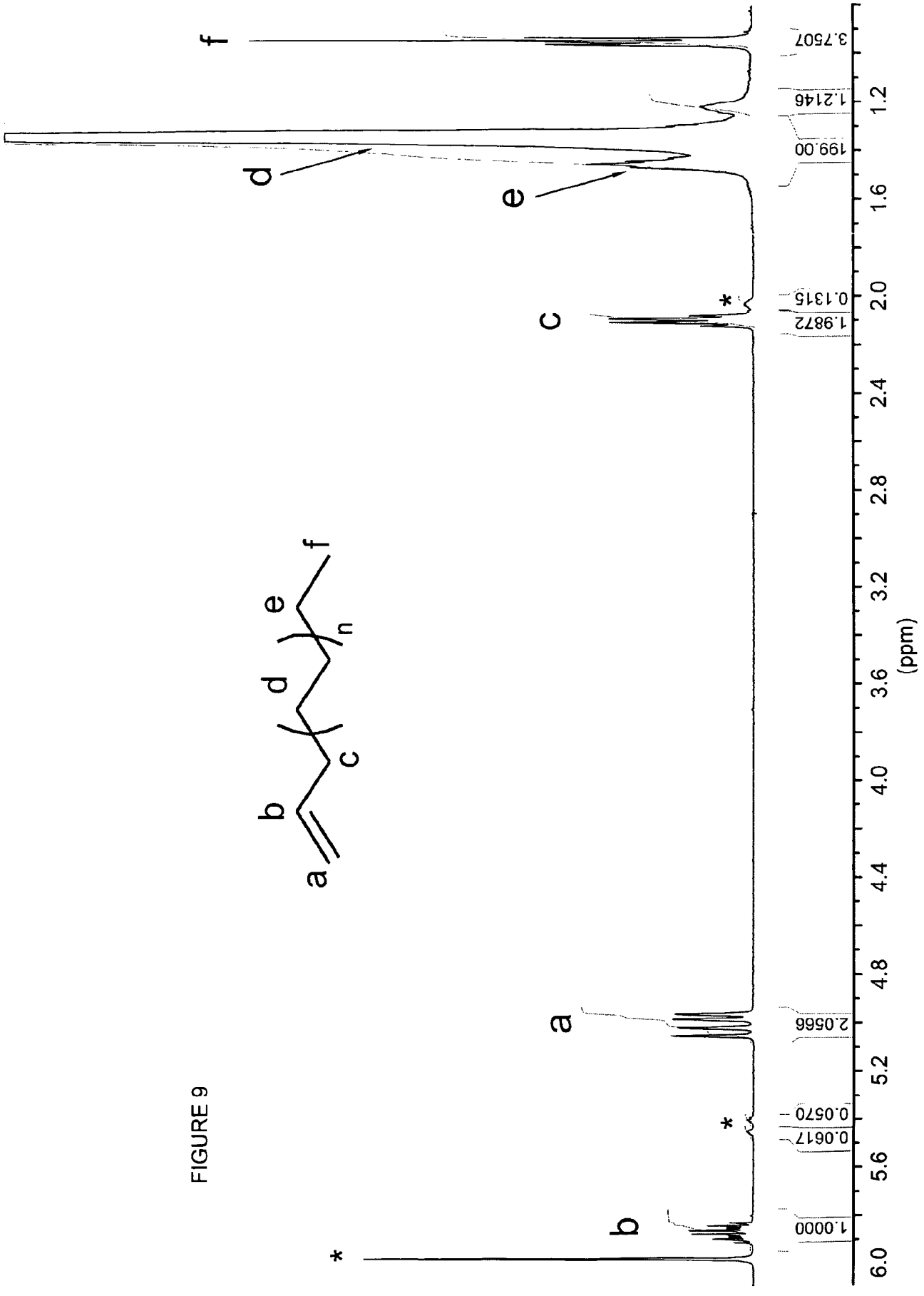

f
d
e
c
a
b
*
*
*
3.7507
1.2146
199.00
0.1315
1.9872
2.0566
0.0570
0.0617
1.0000
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
(ppm)
a
b
c
d
e
f
n

FIGURE 9

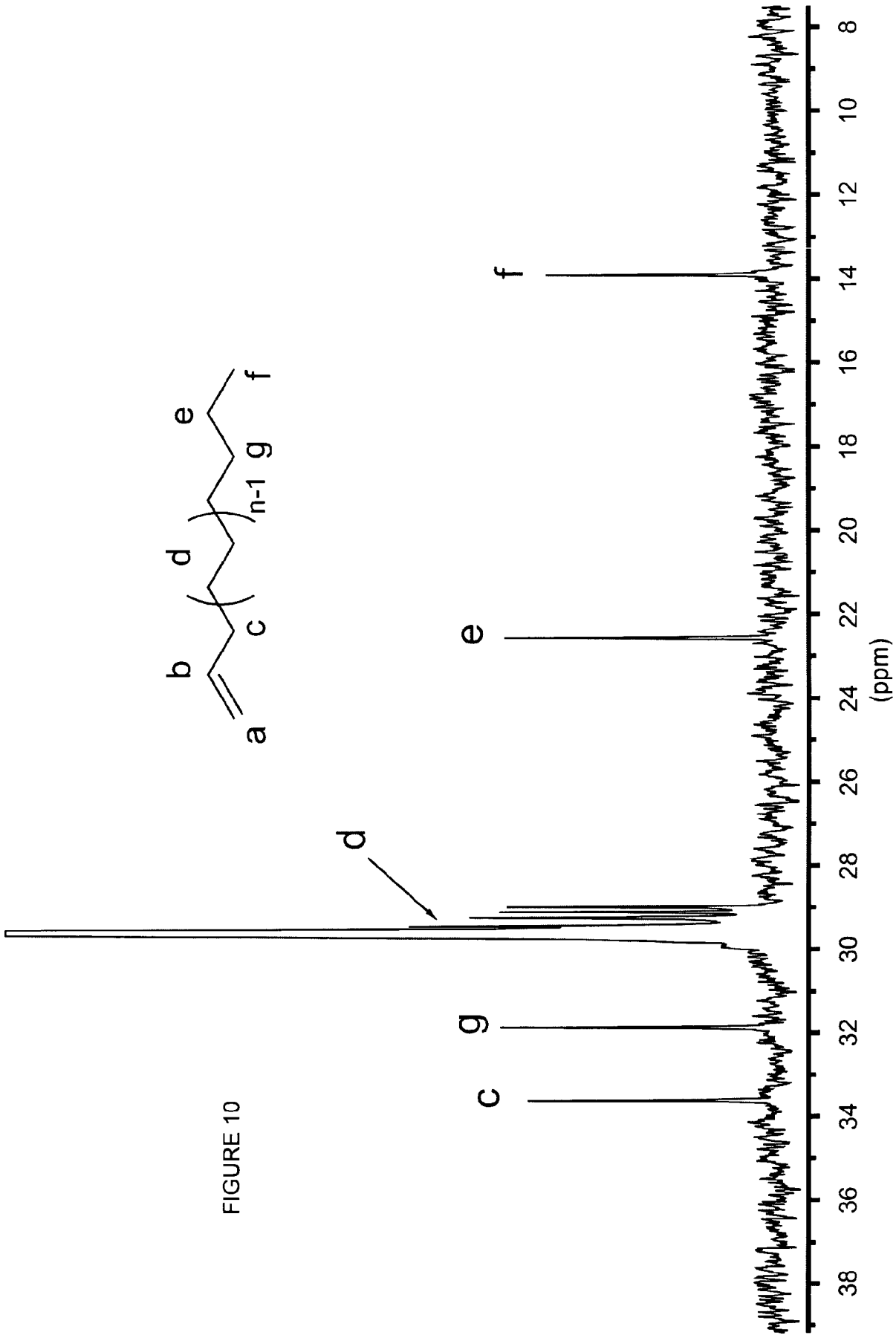


FIGURE 10

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/054947

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F11/00 B01J31/16 C08F4/69

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07F B01J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JONES D J ET AL: "Discovery of anew family of chromium ethylene polymerization catalysts using high throughput screening methodology" CHEMICAL COMMUNICATIONS - CHEMCOM, ROYAL SOCIETY OF CHEMISTRY, GB, vol. 2002, 16 April 2002 (2002-04-16), pages 1038-1039, XP002330206 ISSN: 1359-7345 figures 1,4 ----- -/--	1-13

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 June 2009	23/06/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Bareyt, Sébastian

2

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	BLUHM M E ET AL: "Chromium imine and amine complexes as homogeneous catalysts for the trimerisation and polymerisation of ethylene" JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 690, no. 3, 28 January 2005 (2005-01-28), pages 713-721, XP004720238 ISSN: 0022-328X figure 1; table 1; compounds 1A-K	1-13
Y	MITANI MAKOTO ET AL: "Fluorine- and trimethylsilyl-containing phenoxy--imine Ti complex for highly syndiotactic living polypropylenes with extremely high melting temperatures." JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 10 JUL 2002, vol. 124, no. 27, 10 July 2002 (2002-07-10), pages 7888-7889, XP002495982 ISSN: 0002-7863 figure 1; table 1; compounds 1-4	1-13
Y	EP 1 426 385 A (SHANGHAI INST ORGANIC CHEM [CN]) 9 June 2004 (2004-06-09) paragraphs [0062], [0077]; compounds A-32, F-1, G-1, H-1, L32	1-13
Y	JIANG ET AL: "Titanium (IV) as an essential promoter in the asymmetric addition of diethylzinc to aldehydes catalyzed by aminonaphthol and imine ligands based on 3-substituted binaphthol" JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 692, no. 20, 23 August 2007 (2007-08-23), pages 4377-4380, XP022211795 ISSN: 0022-328X figure 1; table 1; compound 4	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/054947

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1426385 A	09-06-2004	WO 03010207 A1	06-02-2003
		US 2005004331 A1	06-01-2005