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{Bis[*N*,*N*<sup>2</sup>-(2-alkyl-6-*sec*-phenethylphenyl)imino]-1,2-dimethylethane}dibromonickel complexes bearing chiral *sec*-phenethyl groups: synthesis, characterization and their application in catalytic polymerization for ethylene and styrene

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# **Graphical abstract: synopsis**

A series of chiral and achiral nickel (II) complexes were synthesized. The molecular structures of ligand **2c**, complexes **3a**, **3b**, and **3d** were determined by X-ray crystallography. Chiral bulky complex **3c** shows highly catalytic activity for the polymerization of ethylene and styrene, and produced branched polyethylene and syndiotactic-rich polystyrene.



#### {Bis[N,N'-(2-alkyl-6-sec-phenethylphenyl)imino]-1,2-dimethylethane}dibromonickel

#### complexes bearing chiral sec-phenethyl groups: synthesis, characterization and their application

#### in catalytic polymerization for ethylene and styrene

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#### ABSTRACT

A series of new chiral and achiral nickel (II) complexes, {bis[*N*,*N*'-(2-methyl-6-*sec*-phenethylphenyl)imino]-1,2-dimethylethane}dibromonickel *rac-(RR/SS)*-**3a**, {bis[*N*,*N*'-(4-isopropyl-2-*sec*-phenethylphenyl)imino]-1,2-dimethylethane}dibromonickel *rac-(RSRS*)-**3b**,

{bis[*N*,*N*'-(2-methyl-4,6-di(*sec*-phenethyl)phenyl)imino]-1,2-dimethylethane}dibromonickel *rac-(RSRS*)-**3c**,

and

{bis[N,N'-(2,6-diisopropyl-4-(p-methylphenyl)phenyl)imino]-1,2-dimethylethane}dibromonickel **3d**, were synthesized and characterized. The molecular structures of the representative ligand *rac-(RSRS)*-**2c**, complex *rac-(RR/SS)*-**3a**, complex *rac-(RSRS)*-**3b**, and complex **3d** were determined by X-ray crystallography. Complex **3e** 

{bis[*N*,*N*'-(2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel was also synthesized for

comparison. These complexes, activated by diethylaluminum chloride (DEAC) were tested in the polymerization of ethylene and styrene under mild conditions. Complex *rac-(RSRS)-3c* bearing one *ortho-*methyl group and two chiral bulky *sec-*phenethyl groups in the *ortho-* and *para-*aryl position of the ligand, activated by diethylaluminum chloride (DEAC) shows highly catalytic activity for the

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polymerization of ethylene  $[5.56 \times 10^6 \text{ g PE/(mol Ni.h.bar)}]$  and produced branched polyethylene (75 methyl, 9 ethyl, 5 propyl and 19 butyl or longer branches/1000 C at 40°C). Interestingly, complex *rac-(RSRS)-***3c** also displays highly catalytic activity ( $3.62 \times 10^5$  g polystyrene/(mol Ni·h)) for styrene polymerization, and could produce syndiotactic-rich polystyrene (stereo-triad distributions: rr, 66.2%; mr, 18.8%; mm, 15.0%; stereo-diad distributions: r, 75.6%; m, 24.4% at 70 °C). The achiral catalyst **3d** gave nearly atactic polystyrene (stereo-triad distributions: rr, 37.0%; mr, 32.7%; mm, 30.3%; stereo-diad distributions: r, 53.4%; m, 46.6% at 70 °C).

*Key words*: Chiral α-diimine ligand; nickel (II) complex; crystal structure; branched polyethylene; syndiotactic polystyrene

#### 1. Introduction

The development of well-defined Ni(II)/Pd(II) catalysts containing a bulky  $\alpha$ -diimine ligand for the polymerization of ethylene and  $\alpha$ -olefins has been the subject of intense recent study [1–13]. In contrast to metallocene catalysts based on early transition metals [14–17], Ni(II) and Pd(II) catalysts discovered by Brookhart and coworkers could produce branched polyethylene with different concentration and individual length of branches, exclusively from the ethylene monomer and accommodated even polar monomers [1–13]. However, they generally produce amorphous, atactic polymers [11]. Recently, Geoffrey W. Coates and co-workers proposed a new Brookhart type catalyst for olefin polymerization, which bears a new class of chiral anilines and their incorporation in  $\alpha$ -diimine Ni(II) catalysts that exhibit stereoselectivity in  $\alpha$ -olefins polymerization [18,19]. However, the effects of *ortho* and *para* chiral substituents of the ligand on the catalytic behavior of  $\alpha$ -diimine-Ni(II) complexes and the

properties of the resulting polymers, especially on the stereoselectivity of the resulting polystyrenes has never been studied.

Recently, we have reported the "Chain Walking Polymerization" of ethylene using chiral [10–22] or achiral [23–25]  $\alpha$ -diimine Ni(II) complexes. In this work, we first report the synthesis and characterization of a series of new chiral nickel complexes of the type [NiBr<sub>2</sub>(Ar-DAB)] (Ar-DAB = *N*,*N*'-diaryl-1,4-diaza-1,3-butadiene) bearing bulky chiral *sec*-phenethyl groups in different aryl position of the ligand, in order to study the influence of chiral groups, steric effects and polymerization temperature on the catalyst activity, microstructure of polyethylene and, in particular, on the stereoregular structure of polystyrene.

#### 2. Results and discussion

2.1. Synthesis and characterization of ligands 2a-e and complexes 3a-e

#### Scheme 1

The general synthetic route to four nickel (II) complexes **3a-e** is shown in Scheme **1**. Reaction of the anilines with styrene at elevated temperature (160 °C) in the presence of CF<sub>3</sub>SO<sub>3</sub>H catalyst resulted in the corresponding *sec*-phenethylanilines *rac*-**1a-1c** (Scheme **1**). Reaction of the aniline with iodine at room temperature in the presence of NaHCO<sub>3</sub> in H<sub>2</sub>O resulted in 4-iodo-2,6-diisopropylaniline. The Suzuki coupling reaction of 4-iodo-2,6-diisopropylaniline and *p*-methylphenyboronic acid catalyzed by  $Pd(OAc)_2$  in PEG-400 led to the desired amine 2,6-diisopropyl-4-(*p*-methyl)aniline **1d** (Scheme **1**). The  $\alpha$ -diimine ligands (**2a-e**) were finally obtained by acid catalyzed condensation of the amines and

2,3-butanedione. The ligands (**2a-c**) were characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and were found elementally pure.

The reaction of equimolar amounts of NiBr<sub>2</sub>(DME) and the  $\alpha$ -diimine ligand **2a-e** in CH<sub>2</sub>Cl<sub>2</sub> led to the displacement of 1,2-dimethoxyethane and afforded the catalyst precursor **3a-e** as a moderately air-stable deep red microcrystalline solid in almost quantitative yields. Elemental analysis of ligand **2b**, complex **3a**, complex **3c**, and complex **3d** fits the molecular structure obtained by the X-ray structural studies (see below).

> Figure 1 Figure 2 Figure 3 Figure 4

2.2. X-ray crystallographic studies

Single crystals of ligand *rac-(RSRS)-2c*, complex *rac-(RR/SS)-3a*, complex *rac-(RSRS)-3b*, and complex **3d** for X-ray diffraction were obtained at -30 °C by double layering a  $CH_2Cl_2$  solution of the ligand and complexes with *n*-hexane.

The molecular structures of ligand *rac-(RSRS)-2c*, complex *rac-(RR/SS)-3a*, complex *rac-(RSRS)-3b*, and complex **3d** were determined, their corresponding diagrams are shown in Figures **1-4**, and selected bond distances and angles are summarized in Figures **1-4**. The X-ray structure of representative chiral ligand *rac-(RSRS)-2c* exhibits trans-conformation about the central C-C bond of the ligand backbone. Bond lengths and angles are within the expected range for  $\alpha$ -diimines; for example, the bond distances for the C24=N1 double bond and the central C24–C24a single bond are 1.262 (5) and 1.478 (8), which

are very close to the values for other structurally characterized free  $\alpha$ -diimines [26]. Both C24 and C11 possess essentially rather planar geometry (sp<sup>2</sup> character), as shown by the C24–N1–C11 angles 122.1 (4)°, which is very close to 120°.

The structures of complexes rac-(RR/SS)-3a and 3d have pseudo-tetrahedral geometry about the nickel center, showing a pseudo- $C_2$  molecular symmetry for rac-(RR/SS)-3a, and a pseudo- $C_{2y}$ molecular symmetry for 3d. The X-ray structures of ligands rac-(RR/SS)-2a and 2d (similar as representative ligand rac-(RSRS)-2c) and their complexes rac-(RR/SS)-3a and 3d exhibit trans- and cis-conformation about the central C-C bond of the backbone, respectively. In the solid state, the most interesting feature of ligands rac-(RR/SS)-2a and 2d are the conformation of the substituents attached to N1 and N1a (or N2). These groups are rotated about 180° from the position they must occupy to chelate metal Ni. The rotation has been confirmed by the crystal structure of their complexes rac-(RR/SS)-3a and 3d. Their imino C=N bonds have typical double bond character with C=N bond lengths of 1.279 (3) and 1.279 (12) Å for rac-(RR/SS)-3a and 3d, respectively. Both aryl rings bonded to the iminic nitrogens of the  $\alpha$ -diimine lie nearly perpendicular to the plane formed by the nickel and coordinated nitrogen atoms (torsion angles for rac-(RR/SS)-3a: C2-C1-N1-Ni1, 93.9 (3)°; C6-C1-N1-Ni1, -84.1 (3)°; torsion angles for 3d: C2-C1-N1-Ni1, -76.9 (13)°; C6-C1-N1-Ni1, 99.5 (11)°). The chiral phenethyl, methyl or isopropyl groups in the 2,6-position of the aniline fragments in rac-(RR/SS)-3a and 3d point toward each other above and below the plane, thus shielding the apical positions of the Ni(II) center. The axial sites for the metal center are almost blocked by the ortho-sec-phenethyl methyl or isopropyl substituents, which will play a critical role in maintaining high activity and obtaining high-molecular-weight polymers at elevated temperatures. Their structures are similar to those reported in the literature for other similar [NiBr<sub>2</sub>( $\alpha$ -diimine)] compounds characterized

by X-ray diffraction, {bis[*N*,*N*'-4-bromo-2,6-dimethylphenyl]imino]acenaphthene}dibromonickel [27] and {bis[*N*,*N*'-(2,4,6-trimethylphenyl)imino]acenaphthene}dibromonickel [28]. In fact, the Ni-N bond distances in complexes *rac*-(*RR/SS*)-**3a** and **3d** (Ni1–N1, 2.0090 Å for *rac*-(*RR/SS*)-**3a**; Ni1–N1, 2.012 Å for **3d**) are similar to those determined for these compounds (2.026 and 2.021 Å, respectively), as well as the Ni-Br bond distances (2.3569 Å for complex *rac*-(*RR/SS*)-**3a**, 2.329 Å for complex **3d** vs. 2.3229 and 2.323 Å, respectively) and the N–Ni–Br angles (116.13° for complex *rac*-(*RR/SS*)-**3a**, 113.2° for complex **3d** vs. 113.32 and 114.4°, respectively).

Interestingly, the structure of complex *rac-(RSRS)-3b* has pseudo-hexahedral geometry about each nickel center, showing pseudo- $C_{2v}$  molecular symmetry. Complex *rac-(RSRS)-3b* contains two normal  $\alpha$ -diimine nickel complexes, its two nickel atoms are connected via two bromine bridges, and each nickel atom is surrounded by a *N,N'-(4-isopropyl-2-sec-phenethylphenyl)imino]-1,2-dimethylethane* ligand and three bromides, showing pseudo-hexahedral geometry about each nickel center. The geometry of the five-coordinate complex can be described as two distorted hexahedron, with the plane composed by the three atoms N1, N2 and Br1a (or N1a, N2a and Br1) as the basal plane and the Br1, Br2 (or Br1a, Br2a) atoms occupying the apical positions.

# 2.3. Polymerization of ethylene with nickel complexes 3a-e

The five  $\alpha$ -diimine nickel (II) complexes **3a-e**, activated by DEAC, were tested as catalyst precursors for the polymerization of ethylene, under the same reaction conditions. The results of the polymerization experiments are shown in Table **1**. Noteworthy is the fact that blank experiments carried out with DEAC alone, under similar conditions, showed its inability to polymerize ethylene on its own.

#### Table 1

At 20 °C, the activity of complex *rac*-(*RR/SS*)-**3a** increases slightly with the increase of [Al]/[Ni] ratio (runs 1-3), the maximum around [Al]/[Ni] ratio 600 (run 3), and then the activity decreases slightly with the increase of [Al]/[Ni] ratio (runs 3-5). For a ratio [Al]/[Ni] 600, an increase in the polymerization temperature in the range 0-60 °C decreases slightly the activity of the precatalyst *rac*-(*RR/SS*)-**3a** (runs 6, 7, 3, 8 and 9). The performances of the nickel precatalysts are significantly affected by the *ortho*- and *para*-position substituents on the aryl rings of the *α*-diimine Ni(II) complexes (Table 1). Complex *rac*-(*RSRS*)-**3c**, bearing one *ortho*-methyl group and two bulky chiral *sec*-phenethyl groups in the *ortho*- and *para*-aryl positions of the ligand, displays the highest catalytic activity,  $5.56 \times 10^6$  g PE/(mol Ni·h·bar), and produces one of higher molecular weights (run 15, Mw =  $22.1 \times 10^4$  g/mol, 0 °C, [Al]/[Ni] = 600) among our five complexes. Complex **3d**, bearing two *ortho*-isopropyl groups and one bulky methylphenyl group in the *para*-aryl positions of the ligand, also displays high catalytic activity (the highest activity: run 21,  $3.53 \times 10^6$  g PE/(mol Ni·h·bar), Mw =  $19.7 \times 10^4$  g/mol).

Complex *rac*-(*RR/SS*)-**3a** (bearing a *ortho*-position methyl group and one bulky chiral *sec*-phenethyl group in the *ortho*-aryl positions of the ligand), exhibits slightly lower catalytic activity [the highest activity: run 3,  $2.91 \times 10^6$  g PE/(mol Ni·h·bar)] due to the absence of *para*-position bulky group. Complex **3e** (bearing two *ortho*-position methyl groups), shows the lowest catalytic activity [the highest activity: run 26,  $1.36 \times 10^6$  g PE/(mol Ni·h·bar)] among our five complexes due to the absence of both *ortho*-position and *para*-position bulky groups.

Interesting, new chiral hexahedral bis[a-diimine Ni(II)] complex rac-(RSRS)-3b also exhibits high

activity toward ethylene polymerization [run 10, the highest activity:  $1.89 \times 10^6$  g PE/(mol Ni·h·bar); M<sub>w</sub>:  $12.4 \times 10^4$  g/mol] under low ethylene pressure, which is comparable to that of catalyst precursor **3e** under the same experimental conditions. These high activities may indicate that the active species operating in the case of our precatalyst *rac-(RSRS)-3b* ([NiBr<sub>2</sub>(Ar-DAB)]<sub>2</sub>) is the same as that admitted for the corresponding species [NiBr<sub>2</sub>(Ar-DAB)] [10]. The bis[*a*-diimine nickel(II)] used in the present work may be involved in an equilibrium where two bromine bridges of [NiBr<sub>2</sub>(Ar-DAB)]<sub>2</sub> dissociate, giving rise to two complexes [NiBr<sub>2</sub>(Ar-DAB)] (Scheme **2**). The [NiBr<sub>2</sub>(Ar-DAB)] precatalyst can then follow the classical polymerization mechanism put forward by Brookhart and co-workers [10].

## Scheme 2

These results indicate that the rate of chain propagation is greatly promoted by the bulky *ortho-sec*-phenethyl groups of the ligand's aryl rings and significantly affected by the bulky *para-sec*-phenethyl groups of the ligand's aryl rings [*rac-(RR/SS)-3a*]. As a result, the following activity trend can be summarized for our substituted precatalysts under low ethylene pressure (0.2 bar), in the range 0-60 °C: 3c>3d>3a>3b-3e.

#### Figure 5

#### Figure 6

The type and amount of branches formed in the polymerization of ethylene promoted by typical  $\alpha$ -diimine nickel precatalysts depend on reaction parameters such as the reaction temperature, ethylene pressure and ligand structure [10]. Generally, low ethylene pressure and high polymerization temperature favor the Chain-Walking, and afford high branched polyethylenes [10]. However, the effect of ligand structure on polyethylene branching is much more complicated.

As shown in Table 1 and Figure 5, complex rac-(RSRS)-3c bearing one ortho-methyl group and two

bulky chiral sec-phenethyl groups in the ortho- and para-aryl positions of the ligand, generated polyethylene with the highest degrees of branching. The total branching degrees of the polymer samples prepared with rac-(RSRS)-3c/DEAC (runs 16, 18 and 19, branching degree: 90.6, 110.0 and 126.7 branches/1000 C at 20, 40 and 60 °C, respectively) are significantly higher than those observed for rac-(RR/SS)-3a/DEAC (runs 3, 8 and 9, branching degree: 83.5, 97.6 and 108.2 branches/1000 C at 20, 40 and 60 °C, respectively), rac-(RSRS)-3b/DEAC (runs 11, 13 and 14, branching degree: 71.8, 81.3 and 95.4 branches/1000 C at 20, 40 and 60 °C, respectively), 3d/DEAC (runs 21, 23 and 24, branching degree: 82.3, 94.5 and 103.5 branches/1000 C at 20, 40 and 60 °C, respectively), and 3e/DEAC systems (runs 26, 28 and 29, branching degree: 69.7, 80.6 and 91.2 branches/1000 C at 20, 40 and 60 °C, respectively). Also the total branching degrees of the polymer samples prepared with rac-(RSRS)-3c/DEAC are higher than those observed for similar precatalyst/DEAC systems such as {bis[N,N'-(4-tert-butyl-diphenylsilyl-2,6-diisopropylphenyl)imino]acenaphthene}dibromonickel (45 branches/1000 C, at 20 °C) [10] or precatalyst/MAO systems such as {bis[N,N'-(2,6-diisopropylphenyl)imino]-1,2-dimethylethane}dibromonickel (30, 67, 80 and 90 branches/1000 C. 25. 50. 80 °C, respectively) 65 and [10], and at {bis[N,N'-(2,6-diisopropylphenyl)imino]acenaphthene}dibromonickel (65 branches/1000 C, at 25 °C) [10], although the reaction conditions are not exactly the same as in the present work. The total branching degree of the polymer sample obtained with 3e bearing two ortho-methyl groups is the lowest among our five nickel complexes.

The <sup>13</sup>C NMR spectrum of the polyethylene prepared with the catalyst *rac-(RSRS)*-**3c**/DEAC at 40 °C is shown in Figure **6**. The number of branches was calculated according to the literature [30], and it was found that the polyethylene with 107 branches/1000 carbons (73 methyl, 9 ethyl, 4 propyl and 21

butyl or longer branches/1000 C) was obtained at 40 °C (run 16 in Table 1). This result was consistent with that calculated from <sup>1</sup>H NMR.

2.4. Polymerization of styrene with nickel complexes 3a-d

#### Table 2

Polymerizations of styrene with complexes *rac-(RR/SS)-3a*, *rac-(RSRS)-3b rac-(RSRS)-3c* and 3d in combination with DEAC were carried out at 30-90 °C, and the results are summarized in Table 2. For a ratio [Al]/[Ni] 600, the activity of the complexes increases slightly with the increase of temperature (30-70), the maximum around 70 °C, and then the activity decreases slightly with the increase of temperature (70-90). The molecular weight decreases significantly with the increase of polymerization temperature (70-90). The rate of chain propagation is significantly promoted by the bulky *ortho* and *para-sec*-phenethyl of the ligand's aryl rings (the highest activity: *rac-(RR/SS)-3a* run 3: 2.14 ×10<sup>5</sup> g PSt/(mol Ni·h); *rac-(RSRS)-3b* run 7:  $0.96 \times 10^5$  g PSt/(mol Ni·h); *rac-(RSRS)-3c* run 11: 3.62 ×10<sup>5</sup> g PSt/(mol Ni·h); 3d run 16:  $3.04 \times 10^5$  g PSt/(mol Ni·h)).

The aromatic *ipso* carbon spectra of the polystyrenes obtained with catalysts *rac-(RSRS)-3c* and 3d/DEAC were analyzed in term of triads (Table 2 and Figure 7). The three main peaks, at 144.7-145.4, 145.5-145.9 and 146.0-146.4 ppm, are assigned to syndiotactic (rr), heterotactic (mr) and isotactic triads (mm), respectively [31–34]. As in Table 2, and Figure 7, chiral catalyst *rac-(RSRS)-3c* bearing one *ortho*-methyl group and two bulky chiral *sec*-phenethyl groups in the *ortho-* and *para-aryl* positions of the ligand, generated polystyrene with the highest degrees of stereoregularity. The stereoregularity degrees of the polymer sample prepared with *rac-(RSRS)-3c/DEAC* (stereo-triad

distributions run 11: rr, 66.2%; mr, 18.8%; mm, 15.0%; stereo-diad distributions: r, 75.6%; m, 24.4% at 70 °C) are significantly higher than those observed for *rac-(RR/SS)-3a/DEAC* (stereo-triad distributions run 3: rr, 49.9%; mr, 25.3%; mm, 24.8%; stereo-diad distributions: r, 62.6%; m, 37.4% at 70 °C), *rac-(RSRS)-3b/DEAC* (stereo-triad distributions run 7: rr, 46.2%; mr, 26.8%; mm, 27.0%; stereo-diad distributions: r, 59.6%; m, 40.4% at 70 °C), and 3d/DEAC (stereo-triad distributions run 15: rr, 37.0%; mr, 32.7%; mm, 30.3%; stereo-diad distributions: r, 53.4%; m, 46.6% at 70 °C). The achiral catalyst 3d gave nearly atactic polystyrene at 70 °C. An aryl ligand bearing chiral bulky *sec*-phenethyl groups in the *ortho* and/or *para-*aryl position may better control the stereoselective of monomer insertion, which should afford a highly syndiotactic polystyrene.

An decrease of the reaction temperature has a minor influence on the sequence distribution (Table 2: runs 1 and 3, performed with *rac-(RR/SS)-3a/DEAC* at 30 and 70 °C, respectively) as a slight increase of the syndiotactic content is observed (at 30 °C run 1, stereo-triad distributions: rr, 51.2%; mr, 24.6%; mm, 24.2%; stereo-diad distributions: r, 63.5%; m, 36.5%).

#### Figure 7

#### 3. Conclusions

A series of new  $\alpha$ -diimine ligands containing *sec*-phenethyl or naphthyl groups and their Ni(II) complexes have been prepared and characterized. Ligands **2a-e** were modified in an attempt to change chiral environment, steric effects and the electronic density of the metal center, eventually to improve the activity in the polymerization of ethylene/styrene and control the microstructure of polyethylene, in particular, the stereoregularity structure of polystyrene. The results obtained show that the chiral

complex *rac-(RSRS)-***3c** produces highly active catalyst system for the polymerization of ethylene and highly branched polyethylene due to its bulky *ortho* and *para-sec*-phenethyl groups of the ligand's aryl rings. Interestingly, *rac-(RSRS)-***3c**/DEAC catalyst system could produce high stereoregularity of syndiotactic polystyrene at 70 °C due to its chiral bulky *sec*-phenethyl groups in the *ortho-* and *para-*aryl position.

#### 4. Experimental

#### 4.1. General Considerations

All operations were carried out under N<sub>2</sub> atmosphere using standard Schlenk techniques unless otherwise noted. Methylene chloride and *o*-dichlorobenzene were predried with 4 Å molecular sieves and distilled from CaH<sub>2</sub> under dry nitrogen. Toluene, diethyl ether, and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone under N<sub>2</sub> atmosphere. Anhydrous NiBr<sub>2</sub> (99%), 4-methylphenylboronic acid (97%), trifluoromethanesulfonic acid (99%), Pd(OAc)<sub>2</sub> and diethylaluminum chloride (DEAC, 0.9 M solution in toluene) were obtained from Acros. 2,3-Butanedione (98%), 2-methylaniline (98%), 4-isopropylaniline (98%), 2,6-diisopropylaniline (98%) and styrene (98%) were purchased from Alfa Aesar, used without further purification. NiBr<sub>2</sub>(DME) was synthesized according to the literature [35].

NMR spectra were recorded at 400 (<sup>1</sup>H) and 100 (<sup>13</sup>C) MHz, respectively, on a Varian Mercury plus-400 instrument TMS as internal standard. FT-IR spectra were recorded on a Digilab Merlin FTS 3000 FTIR Spectrophotometer in KBr pellets. The molecular weights and molecular weight

distributions (Mw/Mn) of the polymers were determined by Gel Permeation Chromatography/Size-Exclusion Chromatography (GPC/SEC) via a Waters Alliance GPCV2000 chromatograph, using 1,2,4-trichlorobenzene as eluent, at a flow rate of 1.0 ml/min and operated at 140 °C. The elemental content of samples was determined by elemental analyzer (Vaiio-EL106, Germany). The single-crystal structure was determined on a Bruker APEX-II CCD diffractometer with MoKa radiation ( $\lambda = 0.71073$  Å) a  $\omega$  scan mode.

#### 4.2. Synthesis of 2-methyl-6-sec-phenethylphenylaniline 1a

CF<sub>3</sub>SO<sub>3</sub>H (0.06 g, 0.40 mmol), 2-methylaniline (0.21 g, 2.00 mmol), styrene (0.31 g, 3.00 mmol) and xylene (1 ml) were placed in a 10 ml Schlenk flask and allowed to stir at 160 °C for 5 h. Volatile materials were removed and the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 50:1) to give 2-methyl-6-*sec*-phenethylaniline (0.30 g, 71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.21-7.39 (m, 6H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub> and aniline ring), 7.07 (d, *J* = 7.0 Hz, 1H, aniline ring), 6.86 (d, *J* = 7.5 Hz, 1H, aniline ring), 4.18 (q, *J* = 7.0 Hz, 1H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 3.71 (br, s, 2H,  $-NH_2$ ), 2.20 (s, 3H,  $-CH_3$  of aniline), 1.68 (d, *J* = 7.1 Hz, 3H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  145.56 (aniline carbon connected with NH<sub>2</sub>), 141.71 (phenethyl ring carbon connected with ethyl), 129.40 (aniline carbon connected with methyl), 128.67 (phenyl carbon), 122.80 (aniline carbon), 127.41 (phenyl carbon), 126.29 (phenyl carbon), 125.14 (aniline carbon), 122.80 (aniline carbon), 128.30 (aniline carbon connected with phenethyl), 40.06 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 21.97 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 17.38 (-CH<sub>3</sub> of aniline).

4.3. Synthesis of 4-isopropyl-2-sec-phenethylaniline 1b

Using the same procedure as for the synthesis of **1a**, **1b** was obtained as light yellow oil (0.38 g, 79% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.17-7.32 (m, 6H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub> and aniline ring), 6.98 (d, *J* = 7.2 Hz, 1H, aniline ring), 6.60 (d, *J* = 7.4 Hz, 1H, aniline ring), 4.10 (q, *J* = 7.2 Hz, 1H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 3.23 (br, s, 2H, –NH<sub>2</sub>), 2.89 (m, 1H, –CH(CH<sub>3</sub>)<sub>2</sub>), 1.65 (d, *J* = 7.2 Hz, 3H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 1.28 (d, *J* = 6.9 Hz, 6H, –CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  146.08 (aniline carbon connected with NH<sub>2</sub>), 142.34 (phenethyl ring carbon connected with ethyl), 139.44 (aniline carbon connected with isopropyl), 130.04 (aniline carbon), 128.99 (phenyl carbon), 127.65 (phenyl carbon), 126.46 (phenyl carbon), 125.60 (aniline carbon), 124.93 (aniline carbon connected with phenethyl), 116.60 (aniline carbon), 40.69 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 33.72 (–CH(CH<sub>3</sub>)<sub>2</sub> of aniline), 24.57 (–CH(CH<sub>3</sub>)<sub>2</sub> of aniline), 22.09 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>).

#### 4.4. Synthesis of 2-methyl-4,6-di-sec-phenethylphenylaniline 1c

CF<sub>3</sub>SO<sub>3</sub>H (0.06 g, 0.40 mmol), 2-methylaniline (0.21 g, 2.00 mmol), styrene (0.62 g, 6.00 mmol) and xylene (1 ml) were placed in a 10 ml Schlenk flask and allowed to stir at 160 °C for 12 h. Volatile materials were removed and the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 50:1) to give 2-methyl-4,6-di-*sec*-phenethylaniline (0.46 g, 73% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.29-7.57 (m, 11H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub> and aniline ring), 7.11 (s, 1H, aniline ring), 4.25-4.41 (m, 2H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 3.65 (br, s, 2H, -NH<sub>2</sub>), 2.29 (s, 3H, -CH<sub>3</sub> of aniline), 1.78-1.96 (m, 6H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  147.18 (*para*-phenethyl ring carbon connected with ethyl), 145.61(*ortho*-phenethyl ring carbon connected with ethyl), 140.17 (aniline carbon

connected with NH<sub>2</sub>), 135.63 (aniline *para*-carbon connected with methyl), 130.35 (aniline carbon connected with methyl), 128.56 (*para*-phenethyl ring carbon), 128.12 (*ortho*-phenethyl ring carbon), 127.64 (aniline carbon), 127.39 (*para*-phenethyl ring carbon), 127.28 (*ortho*-phenethyl ring carbon), 126.15 (*para*-phenethyl ring carbon), 125.60 (*ortho*-phenethyl ring carbon), 124.29 (aniline carbon), 122.44 (aniline *ortho*-carbon connected with methyl), 44.13 ( $C_6H_5CHCH_3$ ), 40.38 ( $C_6H_5CHCH_3$ ), 22.20 ( $C_6H_5CHCH_3$ ), 21.95 ( $C_6H_5CHCH_3$ ), 17.74 (-*C*H<sub>3</sub> of aniline).

#### 4.5. Synthesis of 4-iodo-2,6-diisopropylaniline

NaHCO<sub>3</sub> (0.43 g, 4.30 mmol), 2,6-diisopropylaniline (0.50 g, 2.82 mmol) and I<sub>2</sub> (0.72 g, 2.84 mmol) were placed in a 10 ml flask and allowed to stir for 24 h, in the presence of 2.56 g H<sub>2</sub>O. The mixture was extracted three times with 15 ml diethyl ether. The combined organic phase was dried over MgSO<sub>4</sub>, filtered, and the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 10:1) to give 4-iodo-2,6-diisopropylaniline (0.51g, 60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.15 (s, 2H, aniline ring), 3.57 (br, s, 2H, -NH<sub>2</sub>), 2.87-3.09 (m, 2H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d, *J* = 7.1 Hz, 12H, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  138.45 (aniline carbon connected with NH<sub>2</sub>), 135.21 (aniline carbon connected with isopropyl), 132.79 (aniline carbon near I), 112.17 (aniline carbon connected with I), 28.25 (-CH(CH<sub>3</sub>)<sub>2</sub>), 21.91 (-CH(CH<sub>3</sub>)<sub>2</sub>).

#### 4.6. Synthesis of 2,6-diisopropyl-4-(4-methyl)phenylaniline 1d

Pd(OAc)<sub>2</sub> (0.01 g, 0.04 mmol), 2,6-diisopropylamine (0.91 g, 3.00 mmol), K<sub>2</sub>CO<sub>3</sub> (0.55 g, 4.00

mmol) and 4-methylphenyboronic acid (0.45 g, 3.31 mmol) were placed in a 50 ml flask and allowed to stir at 25 °C for 24 h, in the presence of 10 ml PEG-400. The mixture was extracted three times with 15 ml diethyl ether. The combined organic phase was dried over MgSO<sub>4</sub>, filtered, and the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 20:1) to give 2,6-diisopropyl-4-(4-methyl)phenyaniline (0.42 g, 52% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.44 (d, *J* = 7.5 Hz, 2H, -C<sub>6</sub>*H*<sub>2</sub>H<sub>2</sub>CH<sub>3</sub>), 7.24 (s, 2H, aniline ring), 7.20 (d, *J* = 8.4 Hz, 2H, -C<sub>6</sub>H<sub>2</sub>*H*<sub>2</sub>CH<sub>3</sub>), 3.70 (br, s, 1H, -NH<sub>2</sub>), 2.91-3.01 (m, 2H, -C*H*(CH<sub>3</sub>)<sub>2</sub>), 2.36 (s, 3H, -C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.31 (d, *J* = 6.8 Hz, 12H, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  139.65 (aniline ring carbon connected with NH<sub>2</sub>), 139.59 (methylphenyl ring carbon connected with CH<sub>3</sub>), 135.76 (methylphenyl ring carbon connected with aniline), 132.83 (aniline ring carbon connected with isopropyl), 131.58 (aniline ring carbon connected with methylphenyl), 129.37 (methylphenyl ring carbon), 126.67 (methylphenyl ring carbon), 121.76 (aniline ring carbon), 28.20 (-CH(CH<sub>3</sub>)<sub>2</sub>), 22.61 (-CH(CH<sub>3</sub>)<sub>2</sub>), 21.13 (-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>).

4.7. Synthesis of bis[N,N'-(2-methyl-6-sec-phenethylphenyl)imino]-1,2-dimethylethane 2a

4-Methylbenzenesulfonic acid (17 mg, 0.10 mmol) was added to a stirred solution of 2,3-butanedione (0.09 g, 1.00 mmol) and 2-methyl-6-*sec*-phenethylphenylaniline (0.44g, 2.10 mmol) in toluene (20 ml). The mixture was refluxed for 16 h, and then the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl ester (v/v = 20:1) to give a light yellow powder. Yield: 0.35 g (74 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.18-7.35 (m, 12H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub> and aniline ring), 7.04 (d, *J* = 7.5 Hz, 2H, aniline ring), 6.67 (d, *J* = 7.0 Hz, 2H, aniline ring), 4.11 (q, *J* = 7.0 Hz, 2H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 2.21 (s, 6H, -CH<sub>3</sub> of aniline), 1.53 (d, *J* = 7.1 Hz, 6H,

C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 1.19 (s, 6H,  $-N=C(CH_3)C(CH_3)=N-$ ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.65 (*C*=N), 148.02 (aniline carbon connected with N), 146.99 (phenylethyl ring carbon connected with ethyl), 133.05 (aniline carbon connected with phenylethyl), 128.97 (aniline carbon connected with methyl), 128.52 (phenylethyl ring carbon), 127.54 (phenylethyl ring carbon), 126.74 (aniline carbon), 125.67 (aniline carbon), 124.28 (aniline carbon), 123.26 (phenylethyl ring carbon), 40.93 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 22.87 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 17.98 (-*C*H<sub>3</sub> of aniline), 15.55 (-N=C(*C*H<sub>3</sub>)C(*C*H<sub>3</sub>)=N-). Anal. Calc. for C<sub>34</sub>H<sub>36</sub>N<sub>2</sub>: C, 86.40; H, 7.68; N, 5.93. Found: C, 86.52; H, 7.54; N, 5.72.

4.8. Synthesis of bis[N,N'-(2-sec-phenethylphenyl-4-isopropyl)imino]-1,2-dimethylethane 2b

Using the same procedure as for the synthesis of **2a**, **2b** was obtained as light yellow powder (0.44 g, 83% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.16-7.34 (m, 12H, C<sub>6</sub>H<sub>3</sub>CHCH<sub>3</sub> and aniline ring), 7.04 (d, *J* = 6.1 Hz, 2H, aniline ring), 6.92 (d, *J* = 7.1 Hz, 2H, aniline ring), 4.20 (q, *J* = 7.1 Hz, 2H, C<sub>6</sub>H<sub>3</sub>CHCH<sub>3</sub>), 3.89 (m, 2H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.70 (d, *J* = 7.2 Hz, 6H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 1.47 (d, *J* = 7.2 Hz, 12H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.15 (s, 6H, -N=C(CH<sub>3</sub>)C(CH<sub>3</sub>)=N-). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.25 (*C*=N), 146.00 (aniline carbon connected with NH<sub>2</sub>), 144.82 (phenethyl ring carbon connected with ethyl), 143.41 (aniline carbon connected with isopropyl), 132.43 (aniline carbon connected with phenethyl), 128.38 (aniline carbon), 128.31 (phenyl carbon), 127.79 (phenyl carbon), 127.38 (phenyl carbon), 125.82 (aniline carbon), 123.25 (aniline carbon), 40.06 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 33.73 (-CH(CH<sub>3</sub>)<sub>2</sub> of aniline), 24.23 (-CH(CH<sub>3</sub>)<sub>2</sub> of aniline), 22.22 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 16.65 (-N=C(CH<sub>3</sub>)C(CH<sub>3</sub>)=N-). Anal. Calc. for C<sub>38</sub>H<sub>44</sub>N<sub>2</sub>: C, 86.31; H, 8.39; N, 5.30. Found: C, 86.40; H, 8.21; N, 5.12. 4.9. Synthesis of bis[N,N'-(2-(2-methyl-4,6-di-sec-phenethylphenyl)imino]-1,2-dimethylethane 2c

Using the same procedure as for the synthesis of 2a, 2c was obtained as yellow powder (0.52 g, 76% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.09-7.34 (m, 20H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 6.98 (s, 2H, aniline ring), 6.92 (s, 2H, aniline ring), 4.20 (q, J = 7.1 Hz, 2H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 3.87 (q, J = 7.1 Hz, 2H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 1.96 (s, 6H, -CH<sub>3</sub> of aniline), 1.70 (d, J = 7.2 Hz, 6H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 1.47 (d, J = 7.2 Hz, 6H, C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 1.15 (s, 6H, -N=C(CH<sub>3</sub>)C(CH<sub>3</sub>)=N-). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.64 (C=N), 147.04 (phenylethyl ring carbon connected with ethyl), 146.88 (phenylethyl ring carbon connected with ethyl), 145.86 (aniline carbon connected with N), 140.77 (aniline carbon connected with phenylethyl), 132.64 (aniline carbon connected with phenylethyl), 128.34 (phenylethyl ring carbon), 128.24 (phenylethyl ring carbon), 127.58 (phenylethyl ring carbon), 127.54 (phenylethyl ring carbon), 127.41 (aniline carbon connected with methyl), 125.83 (aniline carbon near methyl), 125.60 (aniline carbon near phenethyl), 123.94 (phenylethyl ring carbon), 123.70 (phenylethyl ring carbon), 44.42 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 40.85 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 22.65 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 22.00 (C<sub>6</sub>H<sub>5</sub>CHCH<sub>3</sub>), 18.01 (-CH<sub>3</sub> of aniline), 15.57 (-N=C(CH<sub>3</sub>)C(CH<sub>3</sub>)=N-). Anal. Calc. for C<sub>50</sub>H<sub>52</sub>N<sub>2</sub>: C,88.19; H, 7.70; N, 4.11. Found: C, 88.23; H, 7.61; N, 4.35. Single crystals of ligand 2c suitable for X-ray analysis were obtained at -30 °C by dissolving the ligand in  $CH_2Cl_2$ , following by slow layering of the resulting solution with *n*-hexane.

4.10. Synthesis of bis[N,N'-(2,6-diisopropyl-4-(4-methyl)phenylphenyl)imino]-1,2-dimethylethane 2d

Using the same procedure as for the synthesis of **2a**, **2d** was obtained as orange powder (0.49 g, 84% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 (m, 4H,  $-C_6H_2H_2CH_3$ ), 7.36 (s, 4H, aniline ring), 7.25 (m,

4H,  $-C_6H_2H_2CH_3$ ), 2.74-2.76 (m, 4H,  $-CH(CH_3)_2$ ), 2.40 (s, 6H,  $-C_6H_4CH_3$ ), 2.12 (s, 6H,  $-N=C(CH_3)C(CH_3)=N-$ ), 1.23 (m, 24H,  $-CH(CH_3)_2$ ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.51 (*C*=N), 145.52 (aniline ring carbon connected with NH<sub>2</sub>), 139.21 (methylphenyl ring carbon connected with CH<sub>3</sub>), 136.67 (methylphenyl ring carbon connected with aniline), 136.48 (aniline ring carbon connected with methylphenyl), 135.55 (aniline ring carbon connected with isopropyl), 129.50 (methylphenyl ring carbon), 126.91 (methylphenyl ring carbon), 121.97 (aniline ring carbon), 28.81 ( $-CH(CH_3)_2$ ), 23.19 ( $-CH(CH_3)_2$ ), 22.86 ( $-CH(CH_3)_2$ ), 21.21 ( $-C_6H_4CH_3$ ), 16.86 ( $-N=C(CH_3)C(CH_3)=N-$ ). Anal. Calc. for  $C_{42}H_{52}N_2$ : C, 86.25; H, 8.96; N, 4.79. Found: C, 86.37; H, 8.76; N, 4.61.

4.11. Synthesis of bis[N,N'-(2,6-dimethylphenyl)imino]-1,2-dimethylethane 2e

Bis[*N*,*N*'-(2,6-dimethylphenyl)imino]-1,2-dimethylethane **2e** was synthesized according to the literature [36].

4.12.

#### Synthesis

of

 $\{bis [N,N'-(2-methyl-6-sec-phenethylphenyl) imino]-1,2-dimethylethane\} dibromonickel \ \textbf{3a} (n,N'-(2-methyl-6-sec-phenethylphenyl))$ 

[NiBr<sub>2</sub>(DME)] (0.31 g, 1.00 mmol), the ligand **2a** (0.47 g, 1.00 mmol) and dichloromethane (30 ml) were mixed in a Schlenk flask and stirred at room temperature for 16 h. The resulting suspension was filtered. The solvent was removed under vacuum and the residue was washed with diethyl ether ( $3 \times 16$  ml), and then dried under vacuum at room temperature to give catalyst **3a** as light brown micro-crystals. Yield: 0.63 g (91%). Anal. Calc. for C<sub>34</sub>H<sub>36</sub>Br<sub>2</sub>NiN<sub>2</sub>: C, 59.08; H, 5.25; N, 4.05. Found: C, 58.86; H,

5.37; N, 28. FT-IR (KBr): 1628 cm<sup>-1</sup> ( $v_{C=N}$ ). Single crystals of complex **3a** suitable for X-ray analysis were obtained at -30 °C by dissolving the complex in CH<sub>2</sub>Cl<sub>2</sub>, following by slow layering of the resulting solution with *n*-hexane.

4.13.

# Synthesis

of

{bis[N,N'-(4-isopropyl-2-sec-phenethylphenyl)imino]-1,2-dimethylethane}dibromonickel 3b

Using the same procedure as for the synthesis of **3a**, **3b** was obtained as brown micro-crystals. Yield: 0.69 g (92%). Anal. Calc. for  $C_{38}H_{44}Br_2NiN_2$ : C, 61.08; H, 5.93; N, 3.75. Found: C, 61.14; H, 5.76; N, 3.62. FT-IR (KBr): 1624 cm<sup>-1</sup> ( $\nu_{C=N}$ ). Single crystals of complex **3b** suitable for X-ray analysis were obtained at -30 °C by dissolving the complex in CH<sub>2</sub>Cl<sub>2</sub>, following by slow layering of the resulting solution with *n*-hexane.

4.14.

#### Synthesis

of

{bis[N,N'-(2-methyl-4,6-di-sec-phenethylphenyl)imino]-1,2-dimethylethane}dibromonickel 3c

Using the same procedure as for the synthesis of **3a**, **3c** was obtained as brown micro-crystals. Yield: 0.79 g (88%). Anal. Calc. for  $C_{50}H_{52}Br_2NiN_2$ : C, 66.77; H, 5.83; N, 3.11. Found: C, 66.91; H, 5.69; N, 2.97. FT-IR (KBr): 1625 cm<sup>-1</sup> ( $v_{C=N}$ ).

4.15.

#### Synthesis

of

{bis[N,N'-(2,6-diisopropyl-4-(4-methyl)phenylphenyl)imino]-1,2-dimethylethane}dibromonickel 3d

Using the same procedure as for the synthesis of **3a**, **3d** was obtained as dark brown micro-crystals. Yield: 0.69 g (86%). Anal. Calc. for  $C_{42}H_{52}Br_2NiN_2$ : C, 62.79; H, 6.52; N, 3.49. Found: C, 62.97; H, 6.38; N, 3.66. FT-IR (KBr): 1629 cm<sup>-1</sup> ( $v_{C=N}$ ). Single crystals of complex **3d** suitable for X-ray analysis were obtained at -30 °C by dissolving the complex in CH<sub>2</sub>Cl<sub>2</sub>, following by slow layering of the resulting solution with *n*-hexane.

4.16. Synthesis of {bis[N,N'-(2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel 3e

{Bis[N,N'-(2,6-dimethylphenyl)imino]-1,2-dimethylethane}dibromonickel **3e** was synthesized according to the literature [36].

4.17. X-ray Structure Determinations

Single crystals of ligand 2c, complex 3a, complex 3b and complex 3d suitable for X-ray analysis were obtained at -30 °C by dissolving the ligand and nickel complexes in CH<sub>2</sub>Cl<sub>2</sub>, following by slow layering of the resulting solution with *n*-hexane. Data collections were performed at 296(2) K on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo*K* $\alpha$ radiation ( $\lambda$ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on *F*<sup>2</sup> anisotropically for all non-hydrogen atoms by the full-matrix least-squares method.

The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection, and refinement parameters are listed in Table **3**.

Table 3

4.18. Ethylene polymerization

The polymerization of ethylene was carried out in a flame dried 250 ml crown capped pressure bottle sealed with neoprene septa. After drying the polymerization bottle under  $N_2$  atmosphere, 50 ml of dry toluene was added to the polymerization bottle. The resulting solvent was then saturated with a prescribed ethylene pressure. The co-catalyst (DEAC) was then added in Al/Ni or Al/Pd molar ratios in the range of 200-1000 to the polymerization bottle via a syringe. At this time, the solutions were thermostated to the desired temperature and allowed to equilibrate for 15 min. Subsequently, an *o*-dichlorobenzene solution of Ni or Pd catalyst was added to the polymerization reactor. The polymerization, conducted under a dynamic pressure of ethylene (0.2 bar), was terminated by quenching the reaction mixtures with 100 ml of a 2% HCI-MeOH solution. The precipitated polymer was filtered, washed with methanol and dried under vacuum at 60 °C to a constant weight.

4.19. Polymerization of styrene

The homopolymerization of styrene was carried out in a flame dried 250 ml Schlenk flask under dry nitrogen in toluene at 30-90 °C. Dry toluene (25 ml) and dry styrene (5 ml) were added to the

polymerization reactor, the co-catalyst (DEAC) was then added in Al/Ni molar ratios 600 to the polymerization bottle via a syringe. Subsequently, an *o*-dichlorobenzene solution of Ni catalyst was added to the polymerization reactor. After a given reaction time, the polymerization mixture was terminated by quenching the reaction mixtures with 100 ml of a 2% HCl-MeOH solution. The precipitated polymer was filtered, washed with methanol and dried under vacuum at 50 °C to a constant weight.

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#### Appendix A. Supplementary material

CCDC 979396, 979404, 979419 and 979406 contain the supplementary crystallographic data for ligand **2c** and complexes **3a**, **3b**, **3d**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk, or from the Cambridge Crystallographic Data Centre, 12 Union Road,

Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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# Tables

 Table 1 Ethylene polymerizations using nickel precatalysts 3a-e activated by DEAC.

Table 2 Polymerization results for styrene using **3a-d**/DEAC<sup>a</sup> catalytic systems.

Table 3 Crystal data and structure refinements of ligand 2c, complex 3a, complex 3b and complex 3d.

Run	Complex	[Al]/[Ni]	Т	t	Yield	Activity <sup>b</sup>	TOF <sup>c</sup>	$\mathbf{M}\mathbf{w}^{\mathrm{d}}$	Mw/Mn <sup>d</sup>	Branches
			(°C)	(min)	(g)	5				/1000C <sup>e</sup>
1	3a	200	20	10	0.47	0.79	0.28	11.2	1.66	-
2	3a	400	20	10	0.88	1.49	0.53	14.8	1.64	-
3	3a	600	20	10	1.72	2.91	1.04	20.2	1.73	83.5
4	3a	800	20	10	1.1	1.86	0.66	15.5	1.82	-
5	3a	1000	20	10	0.95	1.60	0.57	13.2	1.87	-
6	3a	600	0	10	1.77	2.99	1.07	23.6	1.79	- /
7	3a	600	10	10	1.76	2.97	1.06	21.9	1.83	
8	3a	600	40	10	0.87	1.47	0.52	9.6	1.98	97.6
9	3a	600	60	10	0.44	0.74	0.27	6.9	1.74	108.2
10	3b	600	0	10	1.49	1.89	0.67	12.4	2.03	
11	3b	600	20	10	1.32	1.67	0.60	10.2	1.63	71.8
12	3b	600	30	10	1.27	1.61	0.57	8.5	1.64	-
13	3b	600	40	10	0.92	1.16	0.42	4.6	2.03	81.3
14	3b	600	60	10	0.87	1.10	0.39	2.4	1.84	95.4
15	3c	600	0	10	2.49	5.56	1.99	22.1	1.78	-
16	3c	600	20	10	1.89	4.22	1.51	20.8	1.71	90.6
17	3c	600	30	10	1.51	3.37	1.20	18.7	1.87	-
18	3c	600	40	10	1.37	3.06	1.09	15.5	1.93	110.0
19	3c	600	60	10	1.5	3.35	1.20	12.3	1.85	126.7
20	3d	600	0	10	1.07	2.15	0.77	20.3	1.74	-
21	3d	600	20	10	1.76	3.53	1.26	19.7	1.92	82.3
22	3d	600	30	10	1.57	3.15	1.13	12.5	2.05	-
23	3d	600	40	10	1.47	2.95	1.05	8.9	1.87	94.8
24	3d	600	60	10	0.93	1.87	0.67	7.4	1.84	103.5
25	3e	600	0	10	1.12	1.13	0.40	10.6	1.74	-
26	3e	600	20	10	1.35	1.36	0.49	17.8	1.83	69.7
27	3e	600	30	10	1.02	1.03	0.37	8.6	1.92	-
28	3e	600	40	10	0.52	0.53	0.19	4.2	1.87	80.6
29	3e	600	60	10	0.34	0.34	0.12	3.1	1.79	91.2

 Table 1

 Ethylene polymerizations using nickel precatalysts 3a-e activated by DEAC.<sup>a</sup>

<sup>a</sup>Polymerization conditions and definitions:  $n(3a) = 2.96 \mu mol$ ,  $n(3b) = 3.95 \mu mol$ ,  $n(3c) = 2.24 \mu mol$ ,  $n(3d) = 2.24 \mu mol$ ,  $n(3e) = 4.95 \mu mol$ ; ethylene relative pressure = 0.2 bar, ethylene absolute pressure=1.2 bar; t = polymerization time; solvent = toluene (50ml); T = polymerization temperature. <sup>b</sup>Activity in 10<sup>6</sup> g PE/(mol Ni·h·bar). <sup>c</sup>Turnover frequency in 10<sup>5</sup> mol Ethylene/(mol Ni·h·bar). <sup>d</sup>Mw in 10<sup>4</sup> g/mol, determined by GPC. <sup>e</sup>Estimated by <sup>1</sup>H NMR [29].

Branches /1000C = 
$$\frac{\frac{1}{3}I_{CH_3}}{\frac{I_{CH_2} + I_{CH_3} + I_{CH}}{2}} \times 1000$$

Polyme	erization result	s for styre	ne using <b>3a</b> -	d/DEAC cat	alytic sy	/stems. <sup>a</sup>					
Entry	Precatalyst	T (°C)	Yield (g)	Activity <sup>b</sup>	М	Mw/Mn <sup>c</sup>	Triad	fraction	s (%) <sup>d</sup>	Diad frac	tions (%) <sup>e</sup>
					n <sup>c</sup>		rr	mr	mm	r	m
1	3a	30	0.55	1.10	22.5	2.04	51.2	24.6	24.2	63.5	36.5
2	3a	50	0.92	1.84	19.8	1.89	-	-	-	-	-
3	3a	70	1.07	2.14	13.7	1.96	49.9	25.3	24.8	62.6	37.4
4	3a	90	1.02	2.04	11.7	1.83	-	-	-	-	
5	3b	30	0.21	0.42	13.6	1.97					
6	3b	50	0.35	0.70	11.4	2.25					
7	3b	70	0.48	0.96	9.7	1.88	46.2	26.8	27.0	59.6	40.4
8	3b	90	0.33	0.66	7.2	1.76					1
9	3c	30	1.32	2.64	23.9	1.98	-	-	-7	/	-
10	3c	50	1.75	3.50	20.2	2.07	-	-	-	)	-
11	3c	70	1.81	3.62	17.4	2.03	66.2	18.8	15.0	75.6	24.4
12	3c	90	1.72	3.44	14.3	1.87	-		•	-	-
13	3d	30	0.75	1.50	21.7	2.11	- /	-	) -	-	-
14	3d	50	1.48	2.96	17.6	1.95	-	-	-	-	-
15	3d	70	1.52	3.04	12.2	1.94	37.0	32.7	30.3	53.4	46.6
16	3d	90	1.5	3.00	10.4	1.88		-	-	-	-

Polymerization	results for styre	ene using 39-d	DEAC catalytic	

Table 2

<sup>a</sup> Polymerization conditions:  $n(3a) = n(3c) = n(3d) = 5 \mu mol$ , Al/Ni = 600 mol/mol; 5 ml styrene; solvent = toluene (25 ml); T = 100 mol/mol; 5 ml styrene; solvent = toluene (25 ml); T = polymerization temperature; polymerization time, 1 h. <sup>b</sup> Activity in 10<sup>5</sup> g PSt/(mol Ni·h). <sup>c</sup>Mn in 10<sup>3</sup> g/mol, determined by GPC. <sup>d</sup> Observed in <sup>13</sup>C NMR spectra of quaternary carbon resonance, from low to high field in the spectra (δ 147–144 ppm) [31–34]. <sup>e</sup> Calculated from: (m) = (mm) + 0.5 (mr).

.5 (m)

# Table 3

Crystal data and structure refinements of ligand 2c, complex 3a, complex 3b and complex 3d.

Complex	2c	3a	3b	3d
Empirical Formula	$C_{50}H_{52}N_2$	C34H36Br2N2Ni	C38H44Br2N2Ni	$C_{42}H_{52}Br_2N_2Ni$
Formula mass	680.94	691.18	747.27	803.39
Temperature (K)	296	293	297	293
Wavelength (Å)	0.71073	1.54180	0.71070	1.54180
Crystal size (mm <sup>3</sup> )	0.25×0.23×0.21	0.37×0.36×0.28	0.31×0.28×0.14	0.28×0.27×0.06
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	P1	P21/n	P21/n
a (Å)	27.51 (2)	8.8596 (5)	10.8184 (7)	14.769 (2)
b (Å)	6.599 (5)	13.0208 (10)	30.893 (3)	15.1418 (17)
c (Å)	25.42 (3)	14.7853 (10)	11.035 (1)	18.075 (3)
V (Å <sup>3</sup> )	3962 (6)	1651.3 (2)	3643.9 (5)	3952.3 (10)
Z	4	2	4	4
Density (calcd.) (mg/cm <sup>3</sup> )	1.142	1.390	1.360	1.350
Absorption coefficient (mm <sup>-1</sup> )	0.07	3.85	2.75	3.29
F(000)	1464	704	1532	1664
Theta range for data collec. (°)	$\theta = 3.0 - 19.8$	$\theta = 4.2 - 70.6$	$\theta = 3.5 - 21.4$	$\theta = 4.254.8$
Limiting indices	h = −32→33	$h = -10 \rightarrow 7$	$h = -13 \rightarrow 7$	$h = -18 \rightarrow 14$
	k = −7→7	k = −15→15	k = −38→34	$k = -18 {\rightarrow} 18$
	$1 = -30 \rightarrow 20$	1=−18→18	1=−12→13	1=-22→21
Reflections collected	1771	5497	3566	2910
Independent reflections	3664	6271	7181	7527
Rint	0.064	0.030	0.074	0.102
Final R indices $[I > 2\theta(I)]$	$R_1 = 0.0950$	$R_1 = 0.0406$	$R_1 = 0.0760$	$R_1 = 0.1142$
	$wR_2 = 0.2106$	$wR_2 = 0.1307$	$wR_2 = 0.1018$	$wR_2 = 0.3226$
R indices (all data)	$R_1 = 0.1819$	$R_1 = 0.0446$	$R_1 = 0.1677$	$R_1 = 0.1933$
	$wR_2 = 0.2487$	$wR_2 = 0.1375$	$wR_2 = 0.1352$	$wR_2 = 0.4295$
Goodness of fit on F <sup>2</sup>	1.03	1.00	1.06	1.10
Max. and min. transmission	0.986 and 0.984	1.000 and 0.631	1.000 and 0.865	1.000 and 0.163
Largest diff. peak and hole (e.Å-3)	0.43 and -0.25	0.65 and -0.83	0.64 and -0.47	1.44 and -1.34

# Figures

**Scheme 1.** Syntheses of  $\alpha$ -diimine ligands **2a-e** (\*: chiral carbon) and their corresponding  $\alpha$ -diimine nickel (II) dibromide complexes **3a-e**.

**Fig. 1.** Molecular structure of ligand *rac-(RSRS)*-**2c**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for ligand *rac-(RSRS)*-**2c**: C24–C24a, 1.478 (8); C24–C25, 1.500 (6); N1–C11, 1.422 (5); N1–C24, 1.262 (5); N1–C11–C12, 119.2 (4); N1–C11–C10, 119.5 (4); C11–N1–C24, 122.1 (4). **Fig. 2.** Molecular structure of complex *rac-(RR/SS)*-**3a**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for complex *rac-(RR/SS)*-**3a**. Ni1–N1, 2.0090 (18); Ni1–N2, 2.0052 (19); Ni1–Br2, 2.3569 (5); Ni1–Br3, 2.3273 (6); N1–C1, 1.451 (3); N1–C16, 1.279 (3); N1–Ni1–N2, 80.74 (8); N1–Ni1–Br2, 116.13 (6); N2–Ni1–Br2, 116.13 (6); N1–N11–Br3, 107.84 (6); N2–Ni1–Br3, 117.35 (6); Br2–Ni1–Br3, 122.81 (2). Selected torsion angles (deg): C2–C1–N1–Ni1, 93.9 (3); C6–C1–N1–Ni1, -84.1 (3). **Fig. 3.** Molecular structure of complex *rac-(RSRS)*-**3b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for complex *rac-(RSRS)*-**3b**. Ni1–N1, 2.001 (5); Ni1–N2, 2.073 (5); Ni1–Br1, 2.4831 (11); Ni1–Br2, 2.4313 (11); Ni1–Br1a, 2.5316 (11); Ni1–Br1, 2.5316 (11); N1–C6, 1.441 (8); N1–C18, 1.281 (7); N1–Ni1–N2, 79.2 (2); N1–Ni1–Br1, 110.88 (15); N2–Ni1–Br1, 90.00 (15); N1–Ni1–Br2, 95.62 (15); N2–Ni1–Br2, 92.11 (15); Br1–Ni1–Br2, 153.33 (5); N1–Ni1–Br1a, 102.30 (17); N2–Ni1–Br1a, 174.53 (15); Br2–Ni1–Br1a, 92.96 (4); Br1–Ni1–Br1a, 84.54 (4). Selected torsion angles (deg): C1–C6–N1–Ni1, 90.7 (7); C5–C6–N1–Ni1, –84.0 (7).

**Fig. 4.** Molecular structure of complex **3d**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for complex **3d**: Ni1–N1, 2.012 (8); Ni1–N2, 2.007 (8); Ni1–Br1, 2.329 (3); Ni1–Br2, 2.337 (3); N1–C1, 1.469 (12); N1–C38, 1.279 (12); N1–Ni1–N2, 80.4 (3); N1–Ni1–Br1, 113.2 (3); N2–Ni1–Br1, 125.8 (3); N1–Ni1–Br2, 109.6 (3); N2–Ni1–Br2, 99.1 (3); Br1–Ni1–Br2, 121.23 (9). Selected torsion angles (deg): C2–C1–N1–Ni1, -76.9 (13); C6–C1–N1–Ni1, 99.5 (11).

Scheme 2. Possible dissociative equilibrium involving *rac-(RSRS)-*3b and initiation of the polymerization of ethylene.

**Fig. 5.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/1,2,4-trichlorobenzene, v/v=1:3) spectra of the polyethylenes catalyzed by **3a-e** /DEAC at 40 °C (Table 1: run 8, run 13, run 18, run 23, and run 28). I<sub>CH3</sub>: integrated intensity between 0.8-1.0 ppm; I<sub>CH2</sub> + I<sub>CH</sub>: integrated intensity between 1.0-1.5 ppm.

**Fig. 6.** <sup>13</sup>C NMR (CDCl<sub>3</sub>/*o*-dichlorobenzene, v/v=1:3) spectrum of polyethylene catalyzed by *rac*-(*RSRS*)-**3c**/DEAC at 40 °C (Table 1, Run 16). Note on labels *xBy*: By is a branch of length y carbons; x is the carbon being discussed, and the methyl at the end of the branch is numbered 1. Thus, the second carbon from the end of a butyl branch is  $2B_4$ .  $xBy_+$  refers to branches of length y and longer. The methylenes in the backbone are labeled with Greek letters which determine how far from a branch point methine each methylene is;  $\alpha$  denotes the first methylene next to the methine. Thus,  $\gamma B_{1+}$  refers to methylenes  $\gamma$  from a branch of length 1 or longer. **Fig. 7.** <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectra of the polystyrenes catalyzed by **3a-d**/DEAC at 70 °C.



Scheme 1. Syntheses of α-diimine ligands 2a-e (\*: chiral carbon) and their corresponding α-diimine nickel (II) dibromide complexes 3a-e.



**Fig. 1.** Molecular structure of ligand *rac-(RSRS)-2c*. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for ligand *rac-(RSRS)-2c*: C24–C24a, 1.478 (8); C24–C25, 1.500 (6); N1–C11, 1.422 (5); N1–C24, 1.262 (5); N1–C11–C12, 119.2 (4); N1–C11–C10, 119.5 (4); C11–N1–C24, 122.1 (4).



Fig. 2. Molecular structure of complex rac-(RR/SS)-3a. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles

(deg) for complex *rac-(RR/SS)*-**3a**: Ni1–N1, 2.0090 (18); Ni1–N2, 2.0052 (19); Ni1–Br2, 2.3569 (5); Ni1–Br3, 2.3273 (6); N1–C1, 1.451 (3); N1–C16, 1.279 (3); N1–Ni1–N2, 80.74 (8); N1–Ni1–Br2, 116.13 (6); N2–Ni1–Br2, 116.13 (6); N1–Ni1–Br3, 107.84 (6); N2–Ni1–Br3, 117.35 (6); Br2–Ni1–Br3, 122.81 (2). Selected torsion angles (deg): C2–C1–N1–Ni1, 93.9 (3); C6–C1–N1–Ni1, -84.1 (3).



**Fig. 3.** Molecular structure of complex *rac-(RSRS)-***3b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for complex *rac-(RSRS)-***3b**: Ni1–N1, 2.001 (5); Ni1–N2, 2.073 (5); Ni1–Br1, 2.4831 (11); Ni1–Br2, 2.4313 (11); Ni1–Br1a, 2.5316 (11); Ni1–Br1a, 2.5316 (11); N1–C6, 1.441 (8); N1–C18, 1.281 (7); N1–Ni1–N2, 79.2 (2); N1–Ni1–Br1, 110.88 (15); N2–Ni1–Br1, 90.00 (15); N1–Ni1–Br2, 95.62 (15); N2–Ni1–Br2, 92.11 (15); Br1–Ni1–Br2, 153.33 (5); N1–Ni1–Br1a, 102.30 (17); N2–Ni1–Br1a, 174.53 (15); Br2–Ni1–Br1a, 92.96 (4); Br1–Ni1–Br1a, 84.54 (4). Selected torsion angles (deg): C1–C6–N1–Ni1, 90.7 (7); C5–C6–N1–Ni1, -84.0 (7).



Fig. 4. Molecular structure of complex 3d. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for complex 3d: Ni1–N1, 2.012 (8); Ni1–N2, 2.007 (8); Ni1–Br1, 2.329 (3); Ni1–Br2, 2.337 (3); N1–C1, 1.469 (12); N1–C38, 1.279 (12); N1–Ni1–N2, 80.4 (3); N1–Ni1–Br1, 113.2 (3); N2–Ni1–Br1, 125.8 (3); N1–Ni1–Br2, 109.6 (3); N2–Ni1–Br2, 99.1 (3); Br1–Ni1–Br2, 121.23 (9). Selected torsion angles (deg): C2–C1–N1–Ni1, –76.9 (13); C6–C1–N1–Ni1, 99.5 (11).



Scheme 2. Possible dissociative equilibrium involving *rac-(RSRS)-3b* and initiation of the polymerization of ethylene.



**Fig. 5.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/1,2,4-trichlorobenzene, v/v=1:3) spectra of the polyethylenes catalyzed by **3a-e** /DEAC at 40 °C (Table 1: run 8, run 13, run 18, run 23, and run 28). I<sub>CH3</sub>: integrated intensity between 0.8-1.0 ppm; I<sub>CH2</sub> + I<sub>CH</sub>: integrated intensity between 1.0-1.5 ppm.



**Fig. 6.** <sup>13</sup>C NMR (CDCl<sub>3</sub>/*o*-dichlorobenzene, v/v=1:3) spectrum of polyethylene catalyzed by *rac*-(*RSRS*)-**3c**/DEAC at 40 °C (Table 1, Run 16). Note on labels *xBy*: By is a branch of length y carbons; x is the carbon being discussed, and the methyl at the end of the branch is numbered 1. Thus, the second carbon from the end of a butyl branch is  $2B_4$ .  $xBy_+$  refers to branches of length y and longer. The methylenes in the backbone are labeled with Greek letters which determine how far from a branch point methine each methylene is;  $\alpha$  denotes the first methylene next to the methine. Thus,  $\gamma B_{1+}$  refers to methylenes  $\gamma$  from a branch of length 1 or longer.



Fig. 7. <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectra of the polystyrenes catalyzed by **3a-d**/DEAC at 70 °C.

# Highlights

- Chiral nickel complexes are active in the ethylene and styrene polymerization
- High catalytic activities are obtained when diethylaluminum chloride is a cocatalyst
- The chiral bulky sec-phenethyl group at the ligand's aryl ring influences the activity and M<sub>n</sub>
- The chiral group has a great impact on stereoregular structure of polystyrene

# **Supporting Information**

- Fig. S1. <sup>1</sup>H spectrum of ligand 2a.
- Fig. S2. <sup>1</sup>H spectrum of ligand 2b.
- **Fig. S3.** <sup>1</sup>H spectrum of ligand **2c**.
- **Fig. S4.** <sup>1</sup>H spectrum of ligand **2d**.





**Fig. S3.** <sup>1</sup>H spectrum of ligand **2c**.

