Available online at www.sciencedirect.com
ScienceDirect
C. R. Chimie 10 (2007) 1200–1208
COMPTES RENDUS CHIMIE
http://france.elsevier.com/direct/CRAS2C/

Full paper / Mémoire

Nickel complexes bearing 2-(1*H*-benzimidazol-2-yl)-phenoxy ligands: Synthesis, characterization and ethylene oligomerization

Qisong Shi [a,b], Shu Zhang [a], Fei Chang [a], Peng Hao [a], Wen-Hua Sun [a,*]

[a] *Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

[b] *Department of Materials Science and Engineering, Beijing Institute of Petrochemical Technology, Beijing 102600, China*

Received 9 March 2007; accepted after revision 3 July 2007
Available online 27 August 2007

Abstract

A series of 2-(1*H*-benzimidazol-2-yl)-phenols and their nickel complexes have been synthesized and characterized by elemental and spectroscopic analysis. The molecular structures of ligand **L4** and complex **C5** were confirmed by X-ray diffraction analysis. X-ray crystallographic analysis revealed that complex **C5** has a six-coordinated distorted octahedral geometry. Upon activation with Et_2AlCl, these nickel(II) complexes showed good activity for ethylene oligomerization. When PPh_3 was added as an auxiliary ligand to the catalytic system, an increased activity as high as 1.60×10^7 g mol^{-1} (Ni) h^{-1} was observed. The ligand environment and reaction conditions remarkably affected the catalytic behavior of these nickel complexes. ***To cite this article: Q. Shi et al., C. R. Chimie 10 (2007).***

Keywords: 2-(1*H*-Benzimidazol-2-yl)-phenol; Nickel complex; Ethylene oligomerization

1. Introduction

The oligomerization of ethylene as a major industrial process provides linear α-olefins, which are extensively used in the preparation of detergents, plasticizers, and fine chemicals and as comonomers in the production of linear low-density polyethylene (LLDPE). Linear α-olefins were originally manufactured by the Ziegler (Alfen) process [1] and the well-known Shell Higher Olefin Process (SHOP), which was developed with nickel complexes as catalysts [2]. Over the past decades, increasing interest has been focused on both modification of original ligands and exploration of new ligands for nickel catalysts. The recent review articles have covered the progress of nickel complexes as catalysts for ethylene reactivity [3]; in general, the nickel complexes perform catalytic activities in the assistance of combined multi-chelating ligands, such as N–N [4,5], P–N [6], N–O [7], N–N–O [8], N–P–N, P–N–P, P–O–P [9], P–N–N [9b,10] and N–N–N [11]. Approximately simultaneously with the above cationic catalysts, a class of neutral nickel catalysts based on salicylaldimine ligands [12] was reported independently by Johnson et al. [13] and Grubbs and coworkers [7a,7b]. Like SHOP-type catalyst containing P–O-based ligands, the monoanionic bidentate N–O-ligands and their nickel complexes deserve further

* Corresponding author.
E-mail address: whsun@iccas.ac.cn (W.-H. Sun).

1631-0748/$ - see front matter © 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.crci.2007.07.001

investigation. In addition to designing catalysts for ethylene oligomerization and polymerization, it remains important to synthesize new compounds and find their application potential.

In this work, a series of 2-(1*H*-benzimidazol-2-yl)-phenols and their nickel complexes have been synthesized and characterized. These nickel complexes have been evaluated in the oligomerization of ethylene upon treatment with Et_2AlCl. We report the synthesis and characterization of bis(2-(1*H*-benzimidazol-2-yl)-phenoxy) nickel and the investigation of their catalytic behavior for ethylene oligomerization. The influence of the ligand environment and of various reaction conditions, such as different cocatalysts, Al/Ni molar ratio, reaction temperature, reaction time as well the addition of auxiliary ligand PPh_3, on the catalytic properties of the title nickel complexes will be discussed.

2. Results and discussion

2.1. Synthesis and characterization

The 2-(1*H*-benzimidazol-2-yl)-phenol derivatives (**L1–3**) were synthesized according to the previous reports [14], while the derivatives (**L4–6**) were prepared by the literature methods [15]. All these compounds were readily purified by recrystallization from their ethanol solutions and characterized by FT-IR, NMR and elemental analysis. Their nickel complexes were obtained by mixing the methanol solution of $Ni(Ac)_2{\cdot}4H_2O$ ($Ac = MeCO_2$) and the corresponding ligands with KOH at room temperature (Scheme 1). The solution color was immediately changed from green to yellow with formation of a precipitate, which indicated that the coordination of 2-(1*H*-benzimidazol-2-yl)-phenol to nickel is fast. The resulting nickel complexes

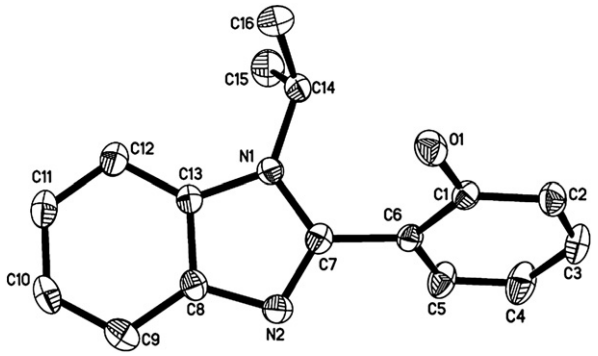
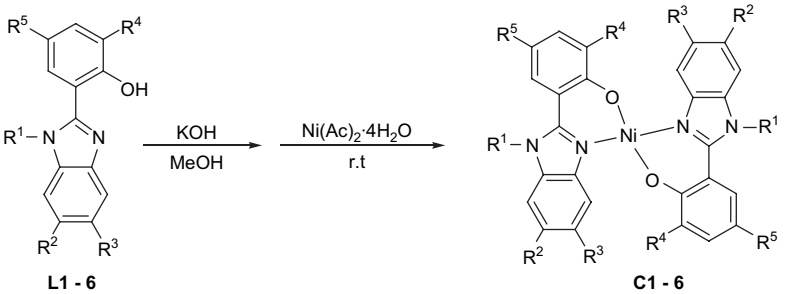


Fig. 1. Crystal structure of ligand **L4**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity.

precipitated and were separated by filtration, washed with diethyl ether and dried in vacuum. All compositions of nickel complexes were consistent with their elemental analyses. Considering their IR spectra, the typical stretching frequencies of N–H (3058 cm^{-1}) and C=N (1622–1635 cm^{-1}) bonds in **C1–3** shifted to lower wave numbers, in comparison with their corresponding free ligands **L1–3** (ν(N–H): 3236–3326 cm^{-1}; ν(C=N): 1632–1638 cm^{-1}). In contrast, the stretching frequencies of C=N bonds in **C4–6** *experienced* little change; however, the peak intensity was greatly reduced. To clarify their molecular structures, ligand **L4** and complex **C5** were further analyzed by single-crystal X-ray diffraction.

Single crystals of the organic compound (**L4**) suitable for X-ray diffraction analysis were obtained by slow evaporation of its methanol solution, while single crystals of complex **C5** were obtained by slow diffusion of diethyl ether into its methanol solution. Their molecular structures are shown in Figs. 1 and 3 and selected bond lengths and angles are listed in Table 1.



1: $R^1 = R^2 = R^3 = R^4 = R^5 = H$;

2: $R^1 = R^3 = R^4 = R^5 = H$; $R^2 = CH_3$

3: $R^1 = R^4 = R^5 = H$, $R^2 = R^3 = CH_3$;

4: $R^1 = i\text{-Pr}$, $R^2 = R^3 = R^4 = R^5 = H$

5: $R^1 = i\text{-Pr}$, $R^2 = R^3 = H$, $R^4 = R^5 = Cl$;

6: $R^1 = i\text{-Pr}$, $R^2 = R^3 = R^4 = H$, $R^5 = CH_3O$

Scheme 1. Synthesis of nickel complexes **C1–6**.

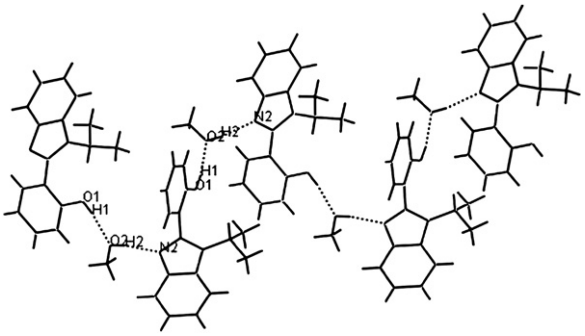


Fig. 2. The 1-D chain formed by intermolecular hydrogen bond interactions in **L4**.

In the solid state of **L4**, the benzimidazole plane and the phenol plane make a dihedral angle of 61.8°. Furthermore, hydrogen bonding interactions exist between ligand molecules and methanol molecules and form a 1-D infinite zigzag chain (Fig. 2). The O-atom O(2) from methanol forms hydrogen bond with H(1) (H(1)⋯O(2) = 1.834 Å) and the N atom N(2) from benzimidazole forms hydrogen bond to H(2) (H(2)⋯N(2) = 1.881 Å). The data of these hydrogen bond interactions are listed in Table 2.

Complex **C5** shows a six-coordinated nickel core due to the coordination of two solvent molecules, in which the nickel center is surrounded by two ligands in a greatly distorted octahedral environment. The two oxygen atoms from two ligands lie in *trans*-positions, whereas the two nitrogen atoms are in *cis*-positions. The Ni–O bond (Ni(1)–O(2) = 2.126 Å) formed by methanol molecule is about 0.09 Å longer than that formed with the ligand (Ni(1)–O(1) = 2.031 Å). The length of the C=N double bond (N(1)–C(7) = 1.331 Å) is slightly longer than that in ligand **L4** (N(2)–C(7) = 1.322 Å). The bond angles around the nickel center are in the range of 88.05(1)° (O(1)–Ni(1)–N(1))–98.89(7)° (O(2)–Ni(1)–O(2A)).

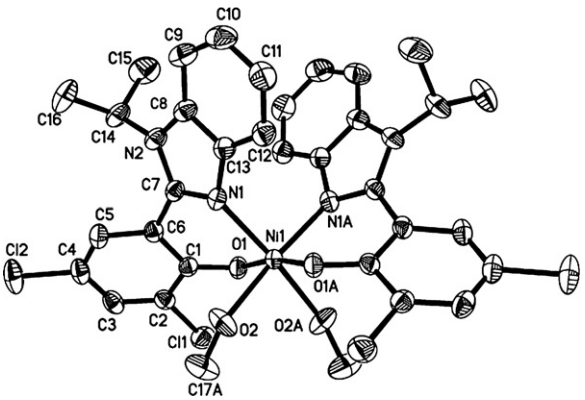


Fig. 3. Molecular structure of **C5**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity.

2.2. Ethylene oligomerization

The catalytic activities of **C1–6** for ethylene oligomerization have been carried out in the presence of diethylaluminum chloride (Et_2AlCl). In all cases, these catalysts generate butenes and hexenes as main oligomeric products.

2.2.1. Ethylene oligomerization at ambient pressure

These nickel complexes were initially studied for their catalytic activities in ethylene oligomerization at ambient pressure. The effects of various cocatalysts, such as MAO, MMAO and Et_2AlCl were studied in detail with **C5** for the ethylene reactivity. The results indicated that different organoaluminums greatly influenced their catalytic behavior. The active Ni species was initially formed with alkylation by cocatalyst, and different cocatalysts showed characteristic features in activating nickel catalyst. The catalytic system with Et_2AlCl showed the highest activity; therefore, our further studies were carried out with Et_2AlCl as cocatalyst. The results at ambient pressure are collected in Table 3.

2.2.2. Effects of reaction parameters

The catalytic system of **C5**/Et_2AlCl was typically investigated with varying reaction conditions, such as the molar ratio of Al/Ni and reaction temperature. The amount of Et_2AlCl played an important role on the catalytic properties of the system. When the Al/Ni molar ratio was changed in the range of 100–700 (entries 3–6 in Table 3), the highest activity was observed at the Al/Ni ratio of 200 (2.51×10^5 g mol^{-1} (Ni) h^{-1}, entry 4 in Table 3), while a higher molar ratio led to lower activity. A possible reason could be that a threshold amount of Et_2AlCl as cocatalyst was necessary to efficiently activate the catalytic precursor; however, larger amounts of Et_2AlCl might over-reduce the nickel species and cause their deactivation. This phenomenon was commonly observed in catalytic systems using late-transition metals; the direct evidence (intermediate) might be difficult to obtain due to excessive amounts of cocatalyst and the sensitivity of the intermediate formed.

The reaction temperature also had an important effect on the catalytic properties of the system, which remarkably affected the oligomerization activity, and the optimum activity was observed at the temperature

Table 1
Selected bond lengths (Å) and angles (°) for **L4** and **C5**

L4		**C5**	
Bond lengths			
O(1)–C(1)	1.353(3)	Ni(1)–O(1)	2.0309(2)
O(1)–H(1)	0.8200	Ni(1)–O(1A)	2.0310(2)
N(1)–C(7)	1.359(3)	Ni(1)–N(1A)	2.0569(2)
N(1)–C(13)	1.388(3)	Ni(1)–N(1)	2.0569(2)
N(1)–C(14)	1.475(3)	Ni(1)–O(2)	2.126(2)
N(2)–C(7)	1.322(3)	Ni(1)–O(2A)	2.126(2)
N(2)–C(8)	1.397(3)	N(1)–C(7)	1.331(3)
Bond angles			
C(1)–O(1)–H(1)	109.5	N(1)–Ni(1)–O(2A)	169.46(8)
C(7)–N(1)–C(13)	106.47(2)	O(1)–Ni(1)–N(1A)	98.89(7)
C(7)–N(1)–C(14)	126.2(2)	O(1)–Ni(1)–N(1)	88.27(7)
C(13)–N(1)–C(14)	127.2(2)	N(1A)–Ni(1)–N(1)	90.76(1)
C(7)–N(2)–C(8)	104.58(2)	O(1)–Ni(1)–O(2)	91.47(8)
N(2)–C(7)–N(1)	113.4(2)	O(2)–Ni(1)–O(2A)	88.05(1)
O(1)–Ni(1)–O(1A)	169.85(1)		

of 20 °C (entry 4 in Table 3). The catalyst **C5** showed higher oligomerization activity at lower temperature, and a further increase of the reaction temperature to 40 °C and 60 °C led to the sharp decrease of oligomerization activities (entries 8 and 9 in Table 3), which might be ascribed to the decomposition of the active catalytic sites and lower ethylene solubility at higher temperature.

The catalyst lifetime is one significant factor in industrial considerations. The effect of reaction time on catalytic activity was also studied using the **C5**/Et_2AlCl system with Al/Ni molar ratio of 200 at 20 °C (entries 4 and 10–13 in Table 3). The oligomerization activity progressively decreased when the reaction was prolonged from 5 to 60 min, which indicated that the catalyst lifetime was relatively short. At the same time, the amount of higher carbon-number oligomers slightly increased with prolonged reaction time.

2.2.3. Effects of ligand environment

It can be observed that the ligand environment has considerable effects on the catalyst behavior, such as activity and distribution of products. Under similar conditions, the activity decreased in the order **C3** < **C2** < **C1**, which indicated that the more substituted the phenyl group, the lower the ethylene reactivity (entries 14–16 in Table 3). This can probably be attributed to the increasing nucleophilicity of the metal center with the higher number of methyl groups on the phenyl ring, which weakens the interaction between the nickel atom and the π-electrons of ethylene monomer and decreases the rate of ethylene insertion in the chain-growth steps.

Table 2
Hydrogen-bond interactions in **L4**

D–H···A	D···H/Å	H···A/Å	D···A/Å	∠DHA/°
C(1)–H(1)···O(2)	0.820	1.834	2.642	168.71
O(2)–H(2)···N(2)	0.820	1.881	2.693	170.24

On the other hand, the incorporation of an isopropyl group on the N atom of imidazole into the complexes led to a decrease in ethylene reactivity. As shown in Table 3, complex **C4** showed lower activity than **C1**. Complexes **C1**–**C3**, containing N–H groups, showed relatively higher catalytic activities compared with other analogues. This could be possibly caused by their deprotonation to give anionic amide ligands when activated by Et_2AlCl. The anionic amide ligands could be free or form N–Al species to increase their catalytic activity [14a].

It should be pointed out that the selectivity for linear α-olefins of oligomers was varied with the reaction parameters and ligand environments. However, no unambiguous trend could be identified. In general, the selectivity for α-olefins was relatively low. The low selectivity for linear α-olefins with the nickel complexes can be attributed to their ability to reversibly eliminate β-H after ethylene insertion and reinsert butene after chain transfer or to lead to isomerization of 1-butene by a re-uptake mechanism [6e]. Moreover, the ability of Ni(II) complexes to isomerize α-olefins was also observed in previous studies [5i,6b].

2.2.4. Effects of ethylene pressure

Ethylene oligomerization with complex **C5** was also conducted under different ethylene pressures. The results are shown in Table 4. And at 30 atm, in the

Table 3
Results of ethylene oligomerization with **C1–6** at ambient pressure[a]

Entry	Cat.	Cocat.	Al/Ni	T[b] (°C)	t[c] (min)	Oligomer distribution[d] (%)			Activity[e]
						$C_4/\sum C$	$C_6/\sum C$	α-olefin (%)	
1	**C5**	MAO	1000	20	30	87.3	12.7	>21	0.2
2	**C5**	MMAO	1000	20	30	97.0	3.0	>25	1.19
3	**C5**	Et_2AlCl	100	20	30	91.6	8.4	>24	2.19
4	**C5**	Et_2AlCl	200	20	30	92.2	7.8	>26	2.51
5	**C5**	Et_2AlCl	500	20	30	93.7	6.3	>28	1.42
6	**C5**	Et_2AlCl	700	20	30	95.1	4.9	>31	1.03
7	**C5**	Et_2AlCl	200	0	30	95.3	4.7	>25	1.96
8	**C5**	Et_2AlCl	200	40	30	96.8	3.2	>58	0.058
9	**C5**	Et_2AlCl	200	60	30	100	—	>62	0.056
10	**C5**	Et_2AlCl	200	20	5	95.4	4.6	>39	3.36
11	**C5**	Et_2AlCl	200	20	15	93.6	6.4	>33	2.87
12	**C5**	Et_2AlCl	200	20	45	90.5	9.5	>31	1.64
13	**C5**	Et_2AlCl	200	20	60	90.4	9.6	>31	1.55
14	**C1**	Et_2AlCl	200	20	30	92.4	7.6	>15	3.01
15	**C2**	Et_2AlCl	200	20	30	93.4	6.6	>23	2.28
16	**C3**	Et_2AlCl	200	20	30	92.8	7.2	>22	2.00
17	**C4**	Et_2AlCl	200	20	30	93.1	6.9	>17	2.37
18	**C6**	Et_2AlCl	200	20	30	91.6	8.4	>17	3.39

[a] Conditions: 5 μmol of catalysts; solvent: toluene (30 ml).
[b] Reaction temperature.
[c] Reaction time.
[d] Determined by GC.
[e] Oligomerization activity: 10^5 g mol^{-1} (Ni) h^{-1}.

presence of 200 equiv of Et_2AlCl, complex **C5** showed an activity of 8.9×10^6 g mol^{-1}(Ni) h^{-1} for ethylene oligomerization. It could be seen that the catalytic activities apparently increased under higher pressure, which could be attributed to the higher monomer concentration.

2.2.5. *Effects of auxiliary ligand (PPh_3)*

Our previous studies on nickel catalysts have demonstrated that the incorporation of PPh_3 into the catalytic system can lead to higher activity and longer lifetime of the catalyst [5i,7g,11d]. Accordingly, complexes **C1** and **C5** were selectively studied with the effect of PPh_3, and their results are summarized in Table 5. In the presence of 10 equiv PPh_3 at ambient pressure, the catalytic activities of complexes **C1** and **C5** were clearly improved; while increasing ethylene pressure to 30 atm, their catalytic activities were greatly improved, with activities of 6.52×10^6 g mol^{-1} (Ni) h^{-1} (for **C1**) and 1.6×10^7 g mol^{-1} (Ni) h^{-1} (for **C5**), respectively (entries 3 and 4 in Table 5). Previously, an active species containing PPh_3 was isolated [7g]; however, different catalytic systems involve different active species. The plausible effect of auxiliary ligand PPh_3 is to associate and dissociate from the nickel center, and this influences the subsequent activation and protection of the active sites.

Table 4
Results of ethylene oligomerization with **C5** at different ethylene pressure[a]

Entry	Cat.	P (atm)	Oligomer distribution[b] (%)		Activity[c]
			$C_4/\sum C$	$C_6/\sum C$	
1	**C5**	10	95.3	4.7	0.72
2	**C5**	20	91.8	8.2	3.70
3	**C5**	30	93.6	6.4	8.90

[a] Conditions: 5 μmol of catalysts; cocat: Et_2AlCl, Al/Ni = 200; solvent: toluene (100 ml); reaction time: 30 min; reaction temperature: 20 °C.
[b] Determined by GC.
[c] Oligomerization activity: 10^6 g mol^{-1} (Ni) h^{-1}.

Table 5
Oligomerization of ethylene with **C1**, **C5**/Et_2AlCl/PPh_3 system[a]

Entry	Cat.	P (atm)	Oligomer distribution[b] (%)		Activity[c]
			$C_4/\sum C$	$C_6/\sum C$	
1	**C1**	1	93.3	6.7	1.10
2	**C5**	1	93.0	7.0	1.44
3	**C1**	30	91.1	9.1	6.52
4	**C5**	30	93.0	7.0	16.0

[a] General conditions: 5 μmol complex; 30 ml toluene (1 atm), 100 ml toluene (30 atm); reaction time: 30 min; reaction temperature: 20 °C; cocat: Et_2AlCl, Al/Ni = 200; 10 equiv of PPh_3.
[b] Determined by GC.
[c] Oligomerization activity: 10^6 g mol^{-1} (Ni) h^{-1}.

3. Conclusion

A series of nickel complexes containing 2-(1*H*-benzimidazol-2-yl)-phenoxy ligands were synthesized. X-ray determination revealed that the complexes adopt a six-coordinated distorted octahedral geometry. Activated by Et_2AlCl, all nickel complexes exhibited considerably high catalytic activities for ethylene oligomerization with C_4–C_6 olefins as the main products. The ethylene oligomerization activity was found to be affected by the substituents in the ligand's framework and reaction parameters. The addition of PPh_3 as an auxiliary ligand led to increased catalytic activity.

4. Experimental

4.1. General procedures

All manipulations of air- or moisture-sensitive compounds were carried out under atmosphere of argon using standard Schlenk techniques. IR spectra were recorded on PerkinElmer FT-IR 2000 spectrometer by using KBr disc in the range 4000–400 cm^{-1}; ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX-300 instrument with TMS as the internal standard. Elemental analysis was performed on a Flash EA1112 microanalyzer. GC analysis was performed with a VARIAN CP-3800 gas chromatograph equipped with a flame ionization detector and a 30-m (0.2-mm i.d., 0.25-μm film thickness) CP-Sil 5 CB column.

Solvents were dried by the appropriate drying reagents and distilled under nitrogen prior to use. Methylaluminoxane (MAO) was purchased from Albemarle as a 1.46 M solution in toluene. Modified methylaluminoxane (MMAO, 1.9 M in heptane, 3A) was purchased from Akzo Corp. Diethylaluminum chloride (Et_2AlCl, 2 M in hexane) was purchased from Acros Chemicals. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

4.2. Synthesis of ligands

4.2.1. 2-(1H-Benzimidazol-2-yl)-phenol (*L1*)

Typical procedure is as follows: to a solution of salicylaldehyde (1.83 g, 15.0 mmol) in EtOH (50 ml), sodium metabisulfite (1.60 g, 8.5 mmol) in water was added in portions. The reaction mixture was stirred vigorously and more EtOH was added. The mixture was kept in a refrigerator for several hours. The precipitate was filtered and dried. The mixture of these salts and 1,2-phenylenediamine (0.43 g, 4.0 mmol) in DMF (10 ml) were heated at 130 °C for 4 h. The reaction mixture was cooled, poured into water, and the solid was filtered. After recrystallization from EtOH, the ligand was obtained. Yield: 80.9%. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.96 (t, 1H, $J = 7.08$ Hz), 7.13 (d, 1H, $J = 7.96$ Hz), 7.31–7.39 (m, 2H), 7.58 (d, 2H, $J = 7.32$ Hz), 7.75 (s, 1H), 9.41 (s, 1H, N–H), 13.09 (s, 1H, O–H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 111.7, 116.1, 117.8, 121.6, 124.7, 130.3, 150.8, 157.3. IR (KBr disc, cm^{-1}): 3326, 3057, 1632, 1590, 1492, 1419,1395, 1261, 1133, 840, 754, 727. Anal. Calc. for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.42; H, 4.99; N, 13.14.

4.2.2. 2-(6-Methyl-1H-benzimidazol-2-yl)-phenol (*L2*)

L2 was prepared by using the same procedure as the synthesis of **L1** except that 4-methyl-*o*-phenylenediamine was used instead of 1,2-phenylenediamine. Yield: 75.0%. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.50 (s, 3H, CH_3), 6.96 (t, 1H, $J = 7.56$ Hz), 7.08–7.14 (m, 2H), 7.32–7.46 (m, 2H), 7.51–7.60 (m, 2H), 9.21 (s, 1H, N–H), 12.98 (s, 1H, O–H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.0, 111.7, 113.2, 116.0, 117.7, 123.0, 124.4, 128.2, 130.0, 131.1, 150.4, 157.1. IR (KBr disc, cm^{-1}): 3236, 3082, 3058, 2913, 2858, 1732, 1697, 1638, 1599, 1487, 1420, 1390, 1322, 1235, 1161, 847, 819, 802. Anal. Calc. for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.74; H, 5.45; N, 12.23.

4.2.3. 2-(5,6-Dimethyl-1H-benzimidazol-2-yl)-phenol (*L3*)

L3 was prepared by using the same procedure as the synthesis of **L1** except that 4,5-dimethylbenzene-1,2-diamine was used instead of 1,2-phenylenediamine. Yield: 60.2%. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.38 (d, 6H, CH_3), 6.95 (t, 1H, $J = 6.85$ Hz), 7.15 (t, 1H, $J = 8.60$ Hz), 7.33–7.41 (m, 3H), 7.58 (t, 1H, $J = 7.24$ Hz), 9.75 (s, 1H, N–H), 13.98 (s, 1H, O–H). IR (KBr disc, cm^{-1}): 3259, 3051, 2977, 2923, 1638, 1583, 1531, 1490, 1466, 1438, 1416, 1386, 1287, 1240, 1167, 1038, 852. Anal. Calc. for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.90; N, 11.76. Found: C, 75.38; H, 6.01; N, 11.36.

4.2.4. 2-(1-Isopropyl-1H-benzimidazole-2-yl)-phenol (*L4*)

L4 was prepared by using the same procedure as the synthesis of **L1** except that *N*-isopropyl-benzene-1,2-diamine was used instead of 1.2-phenylenediamine. Yield: 77.3%. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.74 (d, 6H, $J = 6.88$ Hz, CH_3), 5.16–5.23 (m, 1H, C–H), 7.00 (t, 1H, $J = 7.55$ Hz), 7.17 (d, 1H, $J = 8.26$ Hz), 7.27–7.34 (m, 2H), 7.38 (t, 1H, $J = 7.78$ Hz), 7.46 (d, 1H, $J = 7.83$ Hz), 7.67 (d, 1H, $J = 7.81$ Hz), 7.78 (t, 1H,

$J = 5.68$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.3, 49.32, 112.7, 113.7, 117.9, 118.8, 119.3, 122.4, 122.5, 141.8, 151.0, 158.0. IR (KBr disc, cm^{-1}): 2979, 2935, 1544. 1934, 1894, 1778, 1608, 1523, 1457, 1389, 1288, 1230, 1180, 1132, 1102, 1043, 971, 914, 849, 747, 694, 667, 630. Anal. Calc. for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.35; H, 6.35; N, 10.89.

4.2.5. 2,4-Dichloro-6-(1-isopropyl-1H-benzimidazol-2-yl)-phenol (*L5*)

L5 was prepared by using the same procedure as the synthesis of **L4** except that 3,5-dichloro-salicylaldehyde was used instead of salicylaldehyde. Yield: 87.4%, ^{1}H NMR ($CDCl_3$, 300 MHz): 1.69 (d, 6H, $J = 6.93$ Hz, CH_3), 4.88–4.97 (m, 1H, C–H), 7.20 (t, 2H, $J = 6.06$ Hz), 7.25 (d, 1H, $J = 2.20$ Hz), 7.40 (d, 1H, $J = 2.39$ Hz), 7.56–7.60 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.3, 49.6, 112.6, 116.8, 119.1, 122.8, 123.1, 123.6, 124.5, 126.2, 131.1, 132.4, 141.0, 149.2, 152.6. IR (KBr disc, cm^{-1}): 2046, 2987, 2939, 2389, 1755, 1611, 1588, 1500, 1455, 1423, 1369, 1291, 1269, 1198, 1134, 1057, 1014, 866, 747, 692, 640, 572. Anal. Calc. for $C_{16}H_{14}Cl_2N_2O$: C, 59.83; H, 4.39; N, 8.72. Found: C, 59.52; H, 4.40; N, 8.38.

4.2.6. 2-(1-Isopropyl-1H-benzimidazol-2-yl)-6-methoxy-phenol (*L6*)

L6 was prepared by using the same procedure as the synthesis of **L4** except that 5-methoxy-salicylaldehyde was used instead of salicylaldehyde. Yield: 82.0%. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.64 (d, 6H, $J = 6.93$ Hz, CH_3), 3.76 (s, 1H, CH_3O), 4.87–4.96 (m, 1H, C–H), 6.76–6.80 (m, 1H), 6.90 (d, 1H, $J = 2.97$ Hz), 7.08 (d, 1H, $J = 9.00$ Hz), 7.29–7.36 (m, 2H), 7.61–7.66 (m, 1H), 7.82–7.85 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.3, 49.3, 55.8, 112.6, 113.1, 114.0, 116.9, 118.5, 119.4, 122.4, 122.6, 132.9, 135.1, 142.0, IR (KBr disc, cm^{-1}): 2941, 2541, 1613, 1512, 1494, 1431, 1371, 1270, 1220, 1107, 1040, 821, 751. Anal. Calc. for $C_{17}H_{18}N_2O_2$ C, 72.32; H, 6.43; N, 9.92. Found: C, 72.38; H, 6.23; N, 9.72.

4.3. Synthesis of complexes *C1–6*

4.3.1. Bis[2-(1H-Benzimidazol-2-yl)-phenoxy] nickel (*C1*)

To a solution of **L1** (0.106 g, 0.5 mmol) and KOH (0.028 g, 0.5 mmol) in methanol was added a solution of $Ni(Ac)_2 \cdot 4H_2O$ (0.062 g, 0.25 mmol) in methanol. The color changed immediately. And the reaction mixture was stirred for 10 h at room temperature. The resulting precipitate was filtered and dried in vacuum to yield **C1** as a yellow powder in 81% yield. IR (KBr disc, cm^{-1}): 3098, 3054, 2919, 2866, 2769, 1622, 1605, 1565, 1541, 1480, 1448, 1387, 1262, 913, 865, 765, 755, 728, 702, 550. Anal. Calc. for $C_{26}H_{18}N_4NiO_2 \cdot CH_3OH$: C, 63.69; H, 4.35; N, 11.00. Found: C, 63.66; H, 3.95; N, 11.31.

4.3.2. Bis[2-(6-Methyl-1H-benzimidazol-2-yl)-phenoxy] nickel (*C2*)

In a manner similar to that described for **C1**, **C2** was prepared as a yellow solid in 75% yield. IR (KBr disc, cm^{-1}): 3058, 2972, 2919, 1622, 1606, 1565, 1540, 1481, 1458, 1448, 1328, 1309, 1263, 1141, 865, 765, 756, 727, 703, 549. Anal. Calc. for $C_{28}H_{22}NiN_4O_2 \cdot CH_3OH$: C, 64.83; H, 4.88; N, 10.43. Found: C, 64.59; H, 4.48; N, 10.48.

4.3.3. Bis[2-(5,6-Dimethyl-1H-benzimidazol-2-yl)-phenoxy] nickel (*C3*)

In a manner similar to that described for **C1**, **C3** was prepared as a yellow solid in 82% yield. IR (KBr disc, cm^{-1}): 3062, 2966, 2933, 2357, 1635, 1606, 1556, 1535, 1481, 1448, 1378, 1320, 1263, 1138, 1038, 1017, 880, 843, 753, 697, 569. Anal. Calc. for $C_{30}H_{26}N_4NiO_2 \cdot CH_3OH$: C, 65.87; H, 5.35; N, 9.91. Found: C, 65.64; H, 5.12; N, 10.17.

4.3.4. Bis[2-(1-Isopropyl-1H-benzimidazole-2-yl)-phenoxy] nickel (*C4*)

In a manner similar to that described for **C1**, **C4** was prepared as a yellow solid in 75% yield. IR (KBr disc, cm^{-1}): 2981, 2935, 1609, 1599, 1506, 1551, 1473, 1426, 1384, 1329, 1284, 1265, 1145, 1105, 1045, 1022, 861, 812, 741, 697, 647. Anal. Calc. for $C_{32}H_{30}N_4NiO_2 \cdot 2CH_3OH$: C, 65.30; H, 6.12; N, 8.96. Found: C, 65.03; H, 5.89; N, 8.67.

4.3.5. Bis[2,4-Dichloro-6-(1-isopropyl-1H-benzimidazol-2-yl)-phenoxy] nickel (*C5*)

In a manner similar to that described for **C1**, **C5** was prepared as a yellow solid in 75% yield. IR (KBr disc, cm^{-1}): 3080, 2977, 2880, 2938, 1612, 1588, 1498, 1459, 1448, 1385, 1300, 1248, 1155, 1135, 1107, 1052, 1017, 858. Anal. Calc. for $C_{32}H_{26}Cl_4N_4NiO_2 \cdot 2CH_3OH$: C, 53.51; H, 4.49; N, 7.34. Found: C, 53.91; H, 4.42; N, 7.44.

4.3.6. Bis[2-(1-Isopropyl-1H-benzimidazol-2-yl)-6-methoxy-phenoxy] nickel (*C6*)

In a manner similar to that described for **C1**, **C6** was prepared as a yellow solid in 77% yield. IR

(KBr disc, cm^{-1}): 3056, 2974, 2937, 2830, 1615, 1549, 1505, 1484, 1390, 1306, 1267, 1215, 1173, 1137, 1112, 1044, 931, 869, 822. Anal. Calc. for $C_{34}H_{34}N_4NiO_4 \cdot 2CH_3OH$: C, 63.08; H, 6.18; N, 8.17. Found: C, 62.78; H, 6.39; N, 7.90.

4.4. General procedure for ethylene oligomerization

4.4.1. Ethylene oligomerization at 1 atm of ethylene pressure

The catalytic precursor was dissolved in toluene in a Schlenk tube and the reaction solution was stirred under 1 atm ethylene at the controlled reaction temperature. The reaction was initiated by adding the desired amount of cocatalysts such as diethylaluminum chloride (Et_2AlCl), methylaluminoxane (MAO) or MMAO. After the desired period of time, a small amount of the resulting solution was collected with syringe and quenched with 5% aqueous hydrogen chloride. An analysis by gas chromatography (GC) was carried out to determine the distribution of oligomers obtained.

4.4.2. Ethylene oligomerization at higher ethylene pressure

Ethylene oligomerization at elevated ethylene pressure was carried out in a 250-ml autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. Briefly, toluene, the desired amount of cocatalyst and toluene solution of catalytic precursor (the total volume was 100 ml) was added to the reactor in this order under an ethylene atmosphere. Reaching the desired reaction temperature, ethylene with the desired pressure was introduced to start the reaction, and the ethylene pressure was kept by constant feeding of ethylene. After 30 min, the reaction was stopped. A small amount of the reaction solution was collected, terminated by the addition of 5% aqueous hydrogen chloride and then analyzed by gas chromatography (GC) for determining the distribution of oligomers obtained.

4.5. X-ray crystal structure determination of *L4* and *C5*

Single-crystal X-ray diffraction studies for ligand **L4** and complex **C5** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least-squares refinements. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods, and refined by full-matrix least-square on F^2. Each hydrogen atom was placed in a calculated position, and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Structure solution and refinement were performed using SHELXL-97 package [16]. Crystal date and processing parameters are summarized in Table 6. The data of **L4** and **C5** have been deposited with the Cambridge Crystallographic Data Center under CCDC 639668 and 639669, respectively.

Table 6
Crystallographic data and refinement for **L4** and **C5**

	L4	**C5**
Formula	$C_{17}H_{20}N_2O_2$	$C_{35}H_{38}Cl_4N_4NiO_5$
Formula weight	284.35	795.20
Crystal system	Orthorhombic	Orthorhombic
Space group	*P*2(1)2(1)2(1)	*Pccn*
a (Å)	10.430(2)	20.579(4)
b (Å)	12.033(2)	8.8868(2)
c (Å)	12.468(3)	20.278(4)
V (Å^3)	1564.8(5)	3708.5(1)
Z	4	4
D_{calc} (g/cm^{-3})	1.207	1.424
F(000)	608	1648
θ range (°)	2.35–27.40	2.69–27.35
Reflections collected	2036	31735
Parameters	192	238
Goodness-of-fit	0.764	0.860
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0376$	$R_1 = 0.0439$
	$wR_2 = 0.0628$	$wR_2 = 0.0996$
R indices (all data)	$R_1 = 0.0753$	$R_1 = 0.0812$
	$wR_2 = 0.0683$	$wR_2 = 0.1079$

Acknowledgements

This project was supported by NSFC no 20473099.

References

[1] D. Vogt, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, VCH, Weinheim, 2002, p. 240.
[2] (a) W. Keim, F.H. Kowaldt, R. Goddard, C. Krüger, Angew. Chem. Int. Ed. Engl. 17 (1978) 466;
(b) W. Keim, A. Behr, B. Limbäcker, C. Krüger, Angew. Chem. Int. Ed. Engl. 22 (1983) 503.
[3] (a) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169;
(b) S. Mecking, Angew. Chem. Int. Ed. 40 (2001) 534;
(c) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283;
(d) F. Speiser, P. Braunstein, L. Saussine, Acc. Chem. Res. 38 (2005) 784;
(e) W. Zhang, W. Zhang, W.-H. Sun, Prog. Chem. 17 (2005) 310;
(f) S. Jie, S. Zhang, W.-H. Sun, Petrochem. Tech. (Shiyou Huagong) 35 (2006) 295;

(g) W.-H. Sun, D. Zhang, S. Zhang, S. Jie, J. Hou, Kinet. Catal. 47 (2006) 278.

[4] (a) L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414;
(b) L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267;
(c) C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664.

[5] (a) C.M. Killian, L.K. Johnson, M. Brookhart, Organometallics 16 (1997) 2005;
(b) S.A. Svejda, M. Brookhart, Organometallics 18 (1999) 65;
(c) S.P. Meneghetti, P.J. Lutz, J. Kress, Organometallics 18 (1999) 2734;
(d) T.V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Löfgren, M. Leskelä, Macromol. Rapid Commun. 20 (1999) 487;
(e) T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskelä, J. Organomet. Chem. 606 (2000) 112;
(f) Z. Li, W.-H. Sun, Z. Ma, Y. Hu, C. Shao, Chin. Chem. Lett 12 (2001) 691;
(g) B.Y. Lee, X. Bu, G.C. Bazan, Organometallics 20 (2001) 5425;
(h) C. Shao, W.-H. Sun, Z. Li, Y. Hu, L. Han, Catal. Commun 3 (2002) 405;
(i) X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen, W. Chen, J. Organomet. Chem. 690 (2005) 1570;
(j) S. Jie, D. Zhang, T. Zhang, W.-H. Sun, J. Chen, Q. Ren, D. Liu, G. Zheng, W. Chen, J. Organomet. Chem. 690 (2005) 1739;
(k) E. Nelkenbaum, M. Kapon, M.S. Eisen, J. Organomet. Chem. 690 (2005) 2297;
(l) J.M. Benito, E. de Jesús, F.J. de la Mata, J.C. Flores, F. Gómez, P. Gómez-Sal, Organometallics 25 (2006) 3876;
(m)Y. Song, S. Zhang, Y. Deng, S. Jie, L. Li, X. Lu, W.-H. Sun, Kinet. Catal., in press.
(n) C. Zhang, W.-H. Sun, Z.-X. Wang, Eur. J. Inorg. Chem. 23 (2006) 4895.

[6] (a) W. Keim, S. Killat, C.F. Nobile, G.P. Suranna, U. Englert, R. Wang, S. Mecking, D.L. Schröder, J. Organomet. Chem. 662 (2002) 150;
(b) W.-H. Sun, Z. Li, H. Hu, B. Wu, H. Yang, N. Zhu, X. Leng, H. Wang, New J. Chem. 26 (2002) 1474;
(c) F. Speiser, P. Braunstein, L. Saussine, R. Welter, Organometallics 23 (2004) 2613;
(d) F. Speiser, P. Braunstein, L. Saussine, Organometallics 23 (2004) 2625;
(e) F. Speiser, P. Braunstein, L. Saussine, Organometallics 23 (2004) 2633;
(f) F. Speiser, P. Braunstein, L. Saussine, R. Welter, Inorg. Chem. 43 (2004) 1649;
(g) Z. Weng, S. Teo, T.S.A. Hor, Organometallics 25 (2006) 4878.

[7] (a) C. Wang, S. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149;
(b) T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Bansleben, Science 287 (2000) 460;
(c) C. Carlini, M. Isola, V. Liuzzo, A.M.R. Galletti, G. Sbrana, Appl. Catal. A: Gen. 231 (2002) 307;
(d) L. Wang, W.-H. Sun, L. Han, Z. Li, Y. Hu, C. He, C. Yan, J. Organomet. Chem. 650 (2002) 59;
(e) S. Wu, S. Lu, Appl. Catal. A: Gen. 246 (2003) 295;
(f) D. Zhang, S. Jie, T. Zhang, J. Hou, W. Li, D. Zhao, W.-H. Sun, Acta Polym. Sinica 5 (2004) 758;
(g) W.-H. Sun, W. Zhang, T. Gao, X. Tang, L. Chen, Y. Li, X. Jin, J. Organomet. Chem. 698 (2004) 917;
(h) T. Hu, L.-M. Tang, X.-F. Li, Y.-S. Li, N.-H. Hu, Organometallics 24 (2005) 2628.

[8] Q.-Z. Yang, A. Kermagoret, M. Agostinho, O. Siri, P. Braunstein, Organometallics 25 (2006) 5518.

[9] (a) F. Speiser, P. Braunstein, L. Saussine, J. Chem. Soc., Dalton Trans. (2004) 1539;
(b) P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, C.R. Chim. 8 (2005) 31;
(c) P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A.D. Cian, J. Fischer, J. Chem. Soc., Chem. Commun. (1994) 2203.

[10] J. Hou, W.-H. Sun, S. Zhang, H. Ma, Y. Deng, X. Lu, Organometallics 25 (2006) 236.

[11] (a) L. Wang, W.-H. Sun, L. Han, H. Yang, Y. Hu, X. Jin, J. Organomet. Chem. 658 (2002) 62;
(b) F.A. Kunrath, R.F. De Souza, O.L. Casagrande Jr., N.R. Brooks, V.G. Young Jr., Organometallics 22 (2003) 4739;
(c) N. Ajellal, M.C.A. Kuhn, A.D.G. Boff, M. Hörner, C.M. Thomas, J.-F. Carpentier, O.L. Casagrande Jr., Organometallics 25 (2006) 1213;
(d) W.-H. Sun, S. Zhang, S. Jie, W. Zhang, Y. Li, H. Ma, J. Chen, K. Wedeking, R. Fröhlich, J. Organomet. Chem. 691 (2006) 4196;
(e) S. Al-Benna, M.J. Sarsfield, M. Thornton-Pett, D.L. Ormsby, P.J. Maddox, P. Brès, M. Bochmann, J. Chem. Soc., Dalton Trans. (2000) 4247;
(f) P. Hao, S. Zhang, W.-H. Sun, Q. Shi, W. Zuo, X. Tang, Organometallics 26 (2007) 2439;
(g) W.-H. Sun, P. Hao, S. Zhang, Q. Shi, W. Zuo, X. Tang, Organometallics 26 (2007) 2720;
(h) S. Adewuyi, G. Li, S. Zhang, W. Wang, P. Hao, W.-H. Sun, N. Tang, J. Yi, J. Organomet. Chem. 692 (2007) 3532;
(i)M. Zhang, S. Zhang, P. Hao, S. Jie, W.-H. Sun, P. Li, X. Lu, Eur. J. Inorg. Chem. (2007) 3816.

[12] S.Y. Desjardins, K.J. Cavell, J.L. Hoare, B.W. Skelton, A.N. Sobolev, A.H. White, W. Keim, J. Organomet. Chem. 544 (1997) 163.

[13] L.K. Johnson, A.M.A. Bennett, S.D. Ittel, L. Wang, A. Parthasarathy, E. Hauptman, R.D. Simpson, J. Feldman, E.B. Coughlin (DuPont), WO 98/30609, 1998.[Chem. Abstr. 129 (1998) 149362j].

[14] (a) W. Zhang, W.-H. Sun, S. Zhang, J. Hou, K. Wedeking, S. Schultz, R. Fröhlich, H. Song, Organometallics 25 (2006) 1961;
(b) A.W. Addison, P.J. Burke, J. Heterocycl. Chem. 18 (1981) 803;
(c) G. Muller, J.-C.G. Bünzli, K.J. Schenk, C. Piguet, G. Hopfgartner, Inorg. Chem. 40 (2001) 2642.

[15] (a) A. Figge, H.J. Altenbach, D.J. Brauer, P. Tielmann, Tetrahedron, Asymmetry 13 (2002) 137;
(b) I. Tapia, L. Alonso-Cires, P.L. López-Tudanca, R. Mosquera, L. Labeaga, A. Innerárity, A. Orjales, J. Med. Chem. 42 (1999) 2870.

[16] G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.