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Journal of Organometallic Chemistry 693 (2008) 1683–1695
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis, characterization and catalytic behaviors of neutral nickel complexes: Arylnickel *N*-alkyl-6-(1-(arylimino)ethyl)picolinamide

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Received 20 December 2007; received in revised form 3 January 2008; accepted 3 January 2008
Available online 15 January 2008

In memorial of the late Professor Dr. F. Albert Cotton, Texas A&M University.

Abstract

A series of novel neutral nickel complexes, aryl (phenyl or naphthyl) nickel *N*-alkyl-6-(1-(arylimino)ethyl)picolinamides, were synthesized and characterized by NMR and IR spectroscopy and elemental analysis. Single-crystal X-ray diffraction analyses of the complexes **C2, C3** and **C7** reveal distorted square-planar geometry along with the molecular structure of one free ligand **L1**. On activation with diethylaluminum chloride (Et_2AlCl), the nickel complexes exhibited moderate catalytic activities for ethylene oligomerization, and the catalytic activity was up to 2.45×10^5 g mol^{-1}(Ni) h^{-1} in the presence of 1 equiv. PPh_3. Moreover, these complexes also exhibit moderate activities for Kumada–Corriu reaction and polymerization of methyl methacrylate.

Keywords: *N*-Alkyl-6-(1-(arylimino)ethyl)picolinamide; Neutral nickel complex; Ethylene oligomerization; Kumada–Corriu reaction; Polymerization of methyl methacrylate

1. Introduction

In the past decade, late-transition metal complexes including nickel complexes have attracted great attention in both academic and industrial researches of catalytic chemistry [1]. Two main kinds of nickel complexes: neutral and cationic complexes have been recognized according to the nature of ligands and their bonding around the nickel atom. The cationic nickel complexes are commonly four-coordinated nickel halides containing bidentate ligands such as P^O [2], P^P [3], and N^N [4], and also some of the five-coordinated nickel halides incorporating tridentate ligands of N^N^O [5], N^P^N [6], P^N^P [7], P^N^N [7], and N^N^N [8]. The neutral nickel complexes are nickel coordinated with anionic ligands and alkyl or aryl groups such as SHOP precursor of bis(P–O) nickel complexes [9] or neutral nickel catalysts designed by Grubbs and coworkers [10]. Neutral nickel catalysts are less electrophilic than those of the cationic family, and this property has been used to produce copolymerization of olefins containing polar functional groups [10].

A series of nickel halide complexes containing tridentate N^N^N ligands have been the focus of our group [8a,8d,11]. These complexes exhibit good to high activities towards ethylene reactivity. Inspired by the unique properties of neutral nickel complexes, we have prepared some new anionic organic compounds for use as ligands in the preparation some neutral nickel complexes. Some ligands developed by our group, for example, the 2-(ethylcarboxylato)-6-imino pyridines were used in forming cationic complexes of iron [12], cobalt [12], nickel [5b] and palladium [13]. These could also be used to construct tridentate anionic ligands through facile transformations of the *N*-alkyl-6-(1-(arylimino)ethyl)picolinamides. Further reactions with *trans*-[NiCl(Ph)(PPh_3)$_2$] or *trans*-[NiCl(Naph)(PPh_3)$_2$]

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doi:10.1016/j.jorganchem.2008.01.004

yielded their neutral nickel complexes. In the presence of diethylaluminum chloride (Et_2AlCl), all the nickel complexes performed moderate activities toward ethylene oligomerization, and such activity was up to 2.45×10^5 g mol^{-1}(Ni) h^{-1} in the presence of 1 equiv. PPh_3. Under proper conditions, these complexes also exhibit moderate activities toward the Kumada–Corriu reaction and polymerization of methyl methacrylate. Herein, the synthesis and characterization of these new neutral nickel complexes are reported along with their catalytic behaviors towards ethylene oligomerization, the Kumada–Corriu reaction and polymerization of methyl methacrylate.

2. Results and discussion

2.1. Synthesis and characterization of ligands *L1–L8*

The ester-substituted pyridylimine compounds used in the following were prepared according to the previously reported procedures [12,13b]. The direct reactions of ethyl-6-(1-(arylimino)ethyl)picolinate with butylamine or octylamine or phenylmethanamine gave the (*E*)-*N*-akyl-6-(1-(arylimino)ethyl)picolinamide derivatives in good yields (Scheme 1). Solvents such as MeOH, EtOH, pyridine and toluene, MeOH was found to be the most efficient one. The organic compounds **L1–L8** were routinely characterized with elemental analysis, IR spectroscopic and NMR analysis. **L1** was further characterized by the single-crystal X-ray diffraction analysis (Fig. 1).

Single crystals of **L1** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from solutions in diethyl ether. The molecular structure revealed its *E* conformation at the C=N bonds of pyridyl group with aryl or alkyl groups, which minimizes steric constraints in the free molecule. In addition, the dihedral angle between phenyl ring and pyridyl ring is 93.4°. The imino group with a bond length of 1.274(3) Å is in typical range of the C=N length. Selected bond lengths and angles are listed below, see Fig. 1.

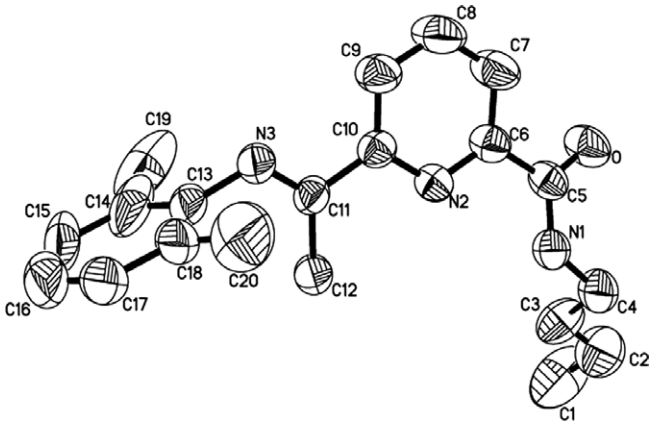
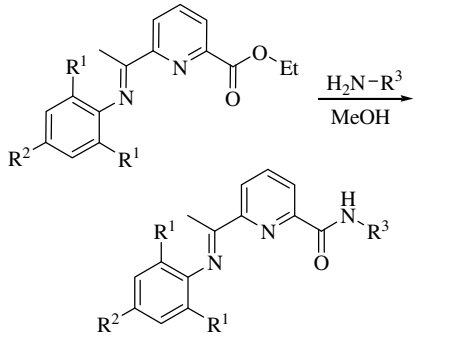


Fig. 1. Molecular structure of **L1**. Thermal ellipsoids are shown at 30% probability.

Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: N(2)–C(10), 1.351(3); N(3)–C(11), 1.274(3); N(3)–C(13), 1.425(4); O–C(5), 1.224(3); N(1)–C(5), 1.315(4); N(1)–C(4), 1.443(4); C(11)–N(3)–C(13), 121.2(3); C(5)–N(1)–C(4), 124.0(3); O–C(5)–N(1), 123.7(3); N(1)–C(5)–C(6), 116.5(3).

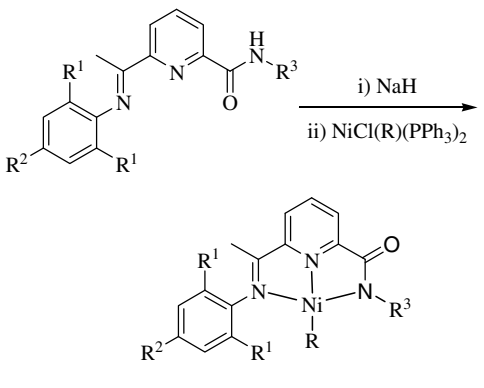
2.2. Synthesis and characterization of neutral nickel complexes *C1–C10*

The nickel complexes **C1–C10** were prepared according to a modified procedure (Scheme 2) [10a,14,15]. The 3 equiv. NaH was added into the THF solution of the corresponding ligands. Gas evolved and the solution color changed to orange in 1 h. Then the resultant solution was filtered, and the filtrate was dried under vacuum to yield the sodium salt, which was combined with *trans*-[NiCl(Naph)$(PPh_3)_2$] or *trans*-[NiCl(Ph)$(PPh_3)_2$] in toluene. The mixture was then stirred at room temperature for 12 h to yield a deep brown solution. After filtration, concentration and then precipitation by layering with pentane, the crude product was obtained in satisfactory yields (43–61%).



	L1	L2	L3	L4	L5	L6	L7	L8
R^1	Me	Et	*i*-Pr	Me	Me	Me	*i*-Pr	Me
R^2	H	H	H	H	H	H	H	Me
R^3	*n*-Bu	*n*-Bu	*n*-Bu	*n*-C_8H_{15}	*n*-C_8H_{15}	Bn	Bn	*n*-Bu

Scheme 1. Synthesis of **L1–L8**.



R = Naph Ln Cn
R = Ph L1 C9
R = Ph L3 C10

Scheme 2. Synthesis of nickel complexes **C1–C10**.

Complexes **C1**–**C10** are all air-stable deep brown powders and highly soluble in toluene, diethyl ether, CH_2Cl_2 and $CHCl_3$, but insoluble in alkanes. The naphthyl-containing complexes **C1**–**C8** are stable in solution and in the solid state, however, the phenyl-containing complexes **C9** and **C10** slowly decompose in solution after several days. All the complexes were carefully characterized by elemental analysis, IR spectroscopic and NMR analysis. According to the NMR spectra, the diamagnetic Ni(II) complexes adopt square-planar geometry. In addition, complexes **C2**, **C3** and **C7** were further characterized by single-crystal X-ray diffraction analysis. These complexes show new molecular structures of the nickel complexes.

Crystals of **C2** suitable for single-crystal X-ray analysis were obtained by slow evaporation of its diethyl ether solution. The molecular structure of **C2** is shown in Fig. 2, and selected bond lengths and angles are listed in Table 1. In the solid state, the molecule adopts distorted square-planar geometry around the central nickel atom. The nickel center slightly deviates by 0.021 Å from the coplanar plane formed by N(1), N(2), N(3) and C(19). The N(1)–Ni(1)–N(3) angle is 163.21(2)°, and the corresponding N(2)–Ni(1)–C(19) angle is even much closer to linear at 176.93(2)°. The "intra-chelate angles" at Ni are 80.58(2)° (N(2)–Ni(1)–N(3)) and 82.63(2)° (N(2)–Ni(1)–N(1)) respectively, whereas the remaining pair of ligand angles at nickel are 99.5(2)° (N(1)–Ni(1)–C(19)) and 97.27(2)° (C(19)–Ni(1)–N(3)). The plane of the naphthyl ring is rotated from the coordination plane by 77.6°. The imino-N phenyl ring is nearly perpendicular to the coordination plane with the dihedral angle of 86.1°. The Ni–N and Ni(1)–C19 bonds are around 1.9 Å which are similar to those known for nickel complexes [10]. However, the Ni(1)–N(2) distance (1.862(4) Å) is about 0.10 Å shorter than the bond length of Ni(1)–N(3) (1.933(3) Å) and only slightly shorter than that of Ni(1)–N(1) (1.887(4) Å).

Table 1
Selected bond lengths (Å) and angles (°) for complexes **C2** and **C3**

	C2	**C3**
Bond lengths		
Ni(1)–N(1)	1.887(4)	1.891(3)
Ni(1)–N(2)	1.863(4)	1.851(3)
Ni(1)–N(3)	1.932(3)	1.947(3)
Ni(1)–C(19)	1.914(5)	1.896(4)
N(1)–C(4)	1.458(9)	1.506(5)
N(1)–C(5)	1.330(7)	1.338(5)
N(3)–C(11)	1.302(5)	1.297(4)
N(3)–C(13)	1.444(6)	1.461(4)
O(1)–C(5)	1.255(6)	1.247(4)
Bond angles		
N(2)–Ni(1)–N(1)	82.63(2)	82.13(1)
N(2)–Ni(1)–C(19)	176.93(2)	175.83(2)
N(1)–Ni(1)–C(19)	99.5(2)	96.26(1)
N(2)–Ni(1)–N(3)	80.58(2)	80.87(1)
N(1)–Ni(1)–N(3)	163.21(2)	162.89(1)
C(19)–Ni(1)–N(3)	97.27(2)	100.83(1)

Crystals of complex **C3** were grown from a mixed solution of diethyl ether and hexane. The molecular structure of **C3** is shown in Fig. 3. In complex **C3**, the nickel center deviates by 0.020 Å from the plane formed by N(1), N(2), N(3) and C(19), the four chelate angles are 80.87(1)° (N(2)–Ni(1)–N(3)), 82.13(1)° (N(2)–Ni(1)–N(1)), 96.26(1)° (N(1)–Ni(1)–C(19)) and 100.83(1)° (C(19)–Ni(1)–N(3)), respectively. The structure is similar to that of **C2**. The similarities include the shortest Ni(1)–N(2) (pyridyl) (1.851(3) Å) compared with Ni–N(1) (1.891(3) Å) bond and Ni–N(3) (imino) (1.947(3) Å) bond. The most noticeable differences are the dihedral angles (75.9°) between the coordination plane and the naphthyl plane and (86.9°) between phenyl ring at the imino-N and coordination plane. The differences are probably due to the more bulky groups at the *ortho*-positions of the imino-N aryl ring.

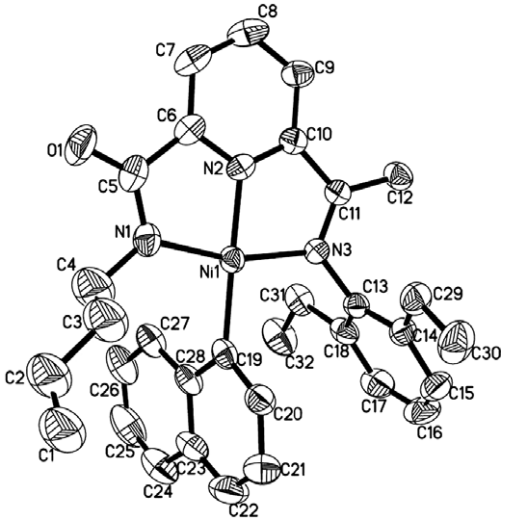


Fig. 2. Molecular structure of complex **C2**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

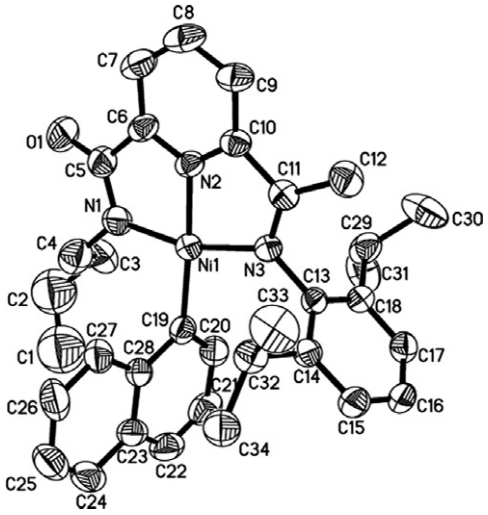


Fig. 3. Molecular structure of complex **C3**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

In the structure of complex **C7**, there are two independent molecules that have slightly different bond lengths and bond angles (Table 2). In molecule (a), the average deviation from the plane of Ni(1), N(1), N(2), N(3), C(19) is 0.1001 Å while this deviation is 0.0989 Å in molecule (b). Furthermore, differences are observed for the dihedral angles between the naphthyl plane and the coordination plane, and between the phenyl ring attached to the imino-N and the coordination plane (110.2° and 100.2° in (a), 108.4° and 82.0° in (b), respectively). Similarly, in both of the molecules, the Ni–N distances and the imino C=N distance are nearly identical and the Ni–N (pyridyl) bond is shorter than that of the other two Ni–N bonds in each molecule, which is also similar to the case in the complexes **C2** and **C3**. All the Ni–N bonds of these three complexes (**C2**, **C3**, **C7**) are obviously shorter than the Ni–N bond of the cationic nickel complexes bearing 2-(ethylcarboxylato)-6-iminopyridyl ligand [14] (see Fig. 4).

2.3. Ethylene oligomerization

The titled nickel complexes were initially investigated toward ethylene reactivity with promotion by various cocatalysts including MAO, MMAO, Et_2AlCl and $AlEt_3$. Basically all systems are active for ethylene oligomerization according to the data observed with **C1** (entries 1–4 in Table 3). The best cocatalyst is Et_2AlCl. Therefore, further studies of all the nickel complexes for ethylene oligomerization were carried out with Et_2AlCl as cocatalyst, and various reaction parameters were investigated for their catalytic performances (Table 3).

2.3.1. Effects of reaction parameters

The catalytic system of **C1**/Et_2AlCl was typically investigated with various reaction conditions, such as the molar ratio of Al/Ni, reaction temperature and ethylene pressure. 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 100–500 (entries 4–8 in Table 3), the highest activity was observed at the Al/Ni ratio of 200 with 7.86×10^4 g mol^{-1}(Ni) h^{-1} (entry 5 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 activate the catalytic precursor efficiently; however, too much of Et_2AlCl might over-reduce the nickel species and cause their deactivation. This behavior is commonly observed in catalytic systems using late-transition metal catalysts [8d]. The reaction temperature also affected the activity, because the ethylene oligomerization is a highly exothermic reaction, and the solubility of ethylene in toluene and the stability of active species are also affected by temperature. The optimum activity was observed at the temperature of 20 °C (entry 5 in Table 3). Increasing the reaction temperature from 20 °C to 80 °C led to shut down the catalytic activities (entries 5 and 9–11 in Table 3), which might be ascribed to decomposition of the active species and lower ethylene solubility at higher temperature.

Generally, the catalytic activity is increased at high ethylene pressures; the same phenomenon was also observed in this system. At 10 atm, in the presence of 200 equiv. of

Table 2
Selected bond lengths (Å) and angles (°) for complex **C7**

Bond lengths			
Ni(1)–N(1)	1.895(3)	Ni(2)–N(4)	1.891(4)
Ni(1)–N(2)	1.851(3)	Ni(2)–N(5)	1.851(4)
Ni(1)–N(3)	1.928(3)	Ni(2)–N(6)	1.941(4)
Ni(1)–C(28)	1.907(4)	Ni(2)–C(65)	1.897(4)
N(1)–C(7)	1.470(5)	N(4)–C(44)	1.476(5)
N(1)–C(8)	1.355(5)	N(4)–C(45)	1.362(5)
N(3)–C(14)	1.320(5)	N(6)–C(51)	1.310(6)
N(3)–C(16)	1.470(5)	N(6)–C(53)	1.442(6)
O(1)–C(8)	1.237(5)	O(2)–C(45)	1.237(4)
Bond angles			
N(2)–Ni(1)–N(1)	82.71(2)	N(5)–Ni(2)–N(4)	83.06(2)
N(2)–Ni(1)–C(28)	170.23(2)	N(5)–Ni(2)–C(65)	170.20(2)
N(1)–Ni(1)–C(28)	97.38(2)	N(4)–Ni(2)–C(65)	96.08(2)
N(2)–Ni(1)–N(3)	80.94(2)	N(5)–Ni(2)–N(6)	80.95(2)
N(1)–Ni(1)–N(3)	162.57(2)	N(4)–Ni(2)–N(6)	162.98(2)
C(28)–Ni(1)–N(3)	99.76(2)	C(65)–Ni(2)–N(6)	100.67(2)

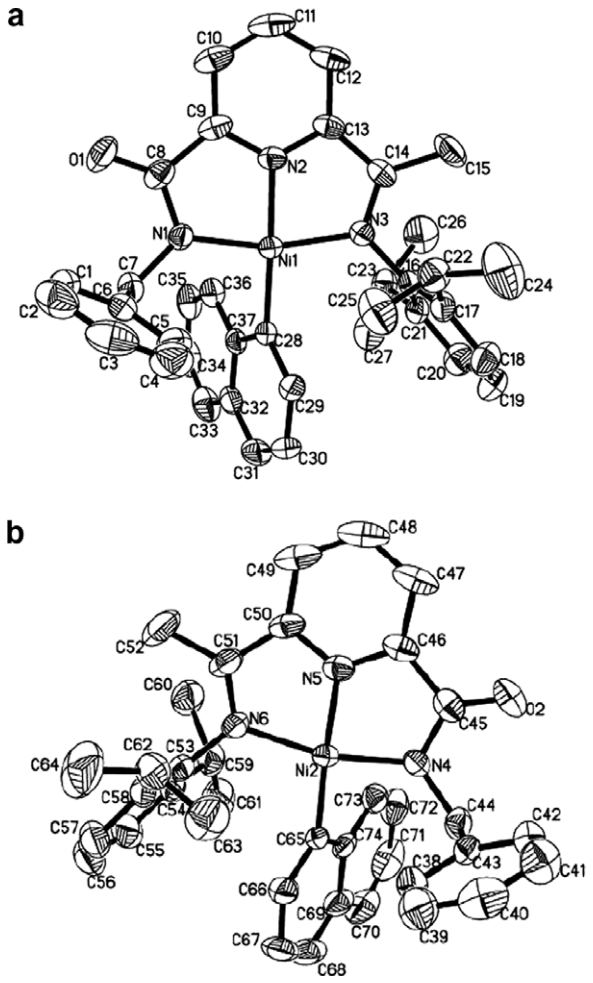


Fig. 4. Molecular structure of complex **C7**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

Table 3
Results of ethylene oligomerization with catalysts **C1**–**C10**[a]

Entry	Catalyst	Cocatalyst	T (°C)	Al/Ni	Activity[b]	Oligomer distribution[c]	
						$C_4/\sum C$	$C_6/\sum C$
1	**C1**	MAO	20	1000	0.46	97.1	2.9
2	**C1**	MMAO	20	1000	0.71	100	0
3	**C1**	Et_3Al	20	1000	1.95	98.7	1.3
4	**C1**	Et_2AlCl	20	100	4.83	93.4	6.6
5	**C1**	Et_2AlCl	20	200	7.86	95.5	4.5
6	**C1**	Et_2AlCl	20	250	7.47	89.2	10.8
7	**C1**	Et_2AlCl	20	300	5.72	95.1	4.9
8	**C1**	Et_2AlCl	20	500	4.07	96.4	4.6
9	**C1**	Et_2AlCl	40	200	7.22	94.2	5.8
10	**C1**	Et_2AlCl	60	200	6.94	93.6	6.4
11	**C1**	Et_2AlCl	80	200	5.21	93.2	6.8
12[d]	**C1**	Et_2AlCl	20	200	62.5	91.4	8.6
13	**C2**	Et_2AlCl	20	200	0.36	86.1	13.9
14	**C3**	Et_2AlCl	20	200	0.33	89.2	10.8
15	**C4**	Et_2AlCl	20	200	4.36	88.5	11.5
16	**C5**	Et_2AlCl	20	200	0.41	87.4	12.6
17	**C6**	Et_2AlCl	20	200	0.39	92.1	8.9
18	**C7**	Et_2AlCl	20	200	3.26	93.5	6.5
19	**C8**	Et_2AlCl	20	200	4.05	94.1	5.9
20	**C9**	Et_2AlCl	20	200	7.82	92.5	7.5
21	**C10**	Et_2AlCl	20	200	0.65	96.2	3.8

[a] Conditions: 5 μmol of precatalyst; 30 min; 30 ml of toluene.
[b] In units of 10^4 g (mol of Ni)$^{-1}$ h^{-1}.
[c] Determined by GC.
[d] 10 atm, 100 ml toluene.

Et_2AlCl, complex **C1** showed an activity of 6.25×10^5 g mol^{-1}(Ni) h^{-1} for ethylene oligomerization (entry 12 in Table 3) which was almost 10 times higher than that at ambient pressure.

2.3.2. Effects of ligand environment

Changes in the ligand environments of these systems led to different catalytic behaviors. The R^1 substituents on the imino-N aryl ring performed significant influence on their activities. It was clearly observed that their catalytic activities decreased with increasing the steric hindrance of their ligands, the regulation was easily confirmed in the catalytic systems of the complexes **C3** (2,6-diisopropyl), **C2** (2,6-diethyl) and **C1** (2,6-dimethyl). Their activities decreased in the order **C3** < **C2** < **C1** (entries 5, 13 and 14 in Table 3). This could be attributed to the more bulky groups at the *ortho*-positions of the imino-N aryl ring which may prevent the addition of ethylene to the catalytic sites. However, the oligomerization activities decreased in the order of **C7** < **C4** < **C1** (entries 5, 15 and 18 in Table 3) with the increasing size of R^3, and this case could be caused by electronic influences of ligands. In contrast to the results observed with **C1** and **C9** or **C3** and **C10** (entries 5 and 20, 14 and 21 in Table 3), there was little influence in the catalytic activities upon changing R (phenyl or naphthyl) groups.

2.3.3. Effects of the 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 lifetimes [8,10]. Therefore, the oligomerization with **C1**/Et_2AlCl was carried out with different amount of PPh_3. The results are summarized in Table 4. In the presence of 1 equiv. PPh_3 at ambient pressure, the catalytic activity of complex **C1** was clearly improved (entry 2 in Table 4); however, larger amounts of PPh_3 obviously showed a decreased activity. The most plausible effect of auxiliary ligand PPh_3 is to associate and dissociate from the nickel center, and this affects the subsequent activation and protection of the active sites. Besides, it was readily observed that the catalytic activities increased under higher pressure with 1 equiv. PPh_3 (entry 6 in Table 4).

2.4. Kumada–Corriu reaction

Beyond the structural novelty of these nickel complexes, their moderate catalytic activities toward ethylene oligomerization have made sense in understanding of their academic interests, but there are other interesting applications of these catalysts. For example, C–C coupling is always an important topic in organic synthesis, and more attention has been paid to C–C bond formation between Grignard reagents and aryl halides by Group 10 metal complexes [15,16] since the pioneering work of Kumada and Corriu [17]. In addition, those coupling reactions provide substances as building blocks for the synthesis of natural products, liquid crystals, polymers, and ligands in transition metal complexes [18]. Recently, some square-planar coor-

Table 4
Ethylene reactivity with **C1**/Et_2AlCl/PPh_3[a]

Entry	*P* (atm)	PPh_3 (equiv)	Activity[b]	Oligomer distribution[c]	
				$C_4/\sum C$	$C_6/\sum C$
1	1	0.5	8.0	93.4	6.6
2	1	1	23.9	97.2	2.8
3	1	2	14.3	98.8	1.2
4	1	5	7.76	97.6	2.4
5	1	10	5.74	98.6	1.4
6[d]	10	1	245	89.7	10.3

[a] Conditions: 5 μmol of precatalyst; Al/Ni = 200; 30 min; 20 °C; 30 ml of toluene.
[b] In units of 10^4 g (mol of Ni)$^{-1}$ h^{-1}.
[c] Determined by GC.
[d] 100 ml toluene.

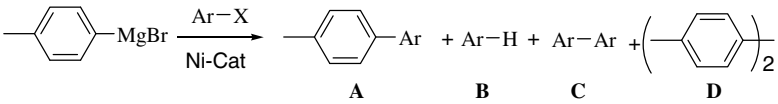
dination nickel complexes were reported to be effective in this reaction [16,18,19]. In order to explore the scope of using the titled nickel complexes, their catalytic behaviors in Kumada–Corriu reaction were investigated. These results are collected in Table 5.

According to the data in Table 5, both of the aryl bromides and chlorides react smoothly with the Grignard reagent in the presence of a catalytic amount of the titled nickel complexes. It was found that the mixture solvent (1:1) of THF and toluene was superior to the pure solvent of toluene or THF (entries 1–3 in Table 5), in the conversion yields and the selectivity for product **A**. Higher temperatures give higher conversion yields (entries 3 and 4 in Table 5). Increasing the amount of Grignard reagent gave higher conversions based on bromobenzene, but more byproduct **D** was obtained (entries 5–7 in Table 5). In most cases, there was no byproduct **C** detected by GC, and no exchange reactions between Grignard reagent and aryl halides. These results obviously indicated that the titled nickel complexes are effective catalysts for Kumada–Corriu reaction at ambient temperature.

2.5. Polymerization of methyl methacrylate (MMA)

Recently, great progress has been made in using late-transition metal-based complexes as catalysts in atom transfer radical polymerization (ATRP) [20], and a series of Ni(II) catalysts such as $NiBr_2(PPh_3)_2$ [20e,20f] and $NiBr_2(PBu^n_3)_2$ [20g] can induce ATRP of methyl methacrylate (MMA) in the presence of organic halides as an initiator (such as CCl_4, CCl_3Br or ethyl-2-bromoisobutyrate). Extensive studies revealed the formation of the carbon radical from R–X via a series of consecutive reversible redox reactions between Ni(II) and Ni(III) species. Inspired by these findings, the titled complexes were investigated for polymerization of methyl methacrylate. The preliminary results are summarized in Table 6.

Table 5
Kumada–Corriu reactions of Grignard reagent with aryl halide[a]



Entry	Catalyst (mol%)	Ar	X	Reaction conditions	Conversion of Ar–X(%)	Yield (%)[b]		
						A	B	D
1[c]	**C9** (1%)	Ph	Br	RT, 24 h	79	51	18	11
2[d]	**C9** (1%)	Ph	Br	RT, 24 h	82	60	14	27
3	**C9** (1%)	Ph	Br	RT, 24 h	86	62	20	24
4	**C9** (1%)	Ph	Br	80 °C, 24 h	91	70	19	26
5[e]	**C9** (1%)	Ph	Br	RT, 24 h	64	45	16	8
6[f]	**C9** (1%)	Ph	Br	RT, 24 h	100	74	25	31
7	**C1** (1%)	Ph	Br	RT, 24 h	84	57	30	24
8	**C3** (1%)	Ph	Br	RT, 24 h	91	63	22	18
9	**C10** (1%)	Ph	Br	RT, 24 h	96	68	21	21
10	**C3** (1%)	Naph	Br	RT, 24 h	90	65	22	19
11	**C9** (1%)	Naph	Br	RT, 24 h	87	62	15	21
12	**C3** (4%)	Ph	Cl	RT, 24 h	94	61	17	20
13	**C9** (4%)	Ph	Cl	RT, 24 h	96	71	12	24
14	**C3** (1%)	*o*-MePh	Br	RT, 24 h	56	42	8	16
15	**C9** (1%)	*p*-MeOPh	Br	80 °C, 24 h	75	54	16	18
16	**C3** (4%)	Naph	Cl	80 °C, 24 h	80	66	9	14

[a] Conditions: 1.5 equiv. Grignard reagent; a mixed solvents of THF and toluene (1:1).
[b] GC yield.
[c] THF as solvent.
[d] Toluene as solvent.
[e] 1.0 equiv. Grignard reagent.
[f] 2.0 equiv. Grignard reagent.

Table 6
The MMA polymerization with nickel complex/ethyl-2-bromoisobutyrate system[a]

Entry	Catalyst	MMA: Cat:initiator	T (°C)	Yield (%)	M_n^b	M_w/M_n^b
1	**C9**	250:1:1	80	26.4	14173	1.85
2	**C10**	250:1:1	80	21.2	14032	1.89
3	**C9**	250:1:0.5	80	23.8	12931	1.86
4	**C9**	250:1:2	80	73.2	34302	3.13
5	**C9**	250:1:1	90	93.2	45632	2.00
6	**C10**	250:1:1	90	66.3	41201	2.01
7	**C1**	250:1:1	90	0	–	–
8	**C3**	250:1:1	90	0	–	–

[a] Conditions: 2 ml of MMA; 5 ml of toluene; 24 h.
[b] After precipitation in MeOH, calculated from GPC, using PMMA standard samples.

In proper conditions, the phenyl nickel complex showed considerable activity as observed in Entry 5 in Table 6 for the polymerization of MMA. However, the naphthenyl nickel analogues appear to have no activity (entries 7 and 8 in Table 6). This maybe due to the fact that naphthenyl nickel complexes are more difficult to transform to the Ni(III) species. The preliminary results show that these neutral Ni(II) complexes with metal–carbon bonds are potentially effective catalysts for the ATRP of MMA. Unfortunately, the ability of this system for inducing ATRP of MMA is relatively low compared to reported systems [20e,20d,20f], the polydispersity was relatively broad. Further investigations are progressing on controlling the resultant polyMMAs with desiring molecular weights and distributions.

3. Conclusion

A series of novel NˆNˆN tridentate neutral nickel complexes, arylnickel *N*-alkyl-6-(1-(arylimino)ethyl)picolinamides, were synthesized and characterized. X-ray structural determinations revealed that the complexes adopt a distorted square-planar coordination around the central metal atom. Activated by Et_2AlCl, all nickel complexes exhibited moderate catalytic activities for ethylene oligomerization. Their catalytic activities decreased with increasing steric hindrance of their ligands. The addition of PPh_3 as an auxiliary ligand led to increase the catalytic activity. These complexes also performed moderate catalytic activities in Kumada–Corriu reaction and considerable conversion yields for polymerization of methyl methacrylate.

4. Experimental

4.1. General considerations

All manipulations for air- or/and moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Melting points (Mp) were determined with a digital electrothermal apparatus without calibration. The IR spectra were recorded on a Perkin–Elmer FT-IR 2000 spectrophotometer using KBr disc in the range of 4000–400 cm^{-1}. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DMX-300 MHz instrument at ambient temperature using TMS as an internal standard. Splitting patterns are designated as follows: s, singlet; bs, broad singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet. The elemental analyses were performed on a Flash EA 1112 microanalyser. Distribution of oligomers obtained was measured on a Varian VISTA 6000 GC spectrometer and a HP 5971A GC–MS detector.

THF and toluene were refluxed over sodium-benzophenone until purple color appeared and were distilled under nitrogen atmosphere prior to use. CH_2Cl_2 and pentane were distilled under nitrogen from CaH_2. NaH was washed with *n*-hexane (4 × 20 ml) and dried before use. *Trans*-[NiCl(Naph)$(PPh_3)_2$] [21] and *trans*-[NiCl(Ph)$(PPh_3)_2$] [22] were prepared according to literature procedure. Methylaluminoxane (MAO, 1.46 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. Diethylaluminum chloride (Et_2AlCl, 1.9 M in hexane) was purchased from Acros Chemicals. All other chemicals were obtained commercially and were used without further purification unless stated otherwise.

4.2. Synthesis of N-alkyl-6-(1-(arylimino)ethyl)-picolinamide

*Synthesis of (E)-N-butyl-6-(1-(2,6-dimethylphenylimino)ethyl)picolinamide (***L1***)*: (*E*)-Ethyl 6-(1-(2,6-dimethylphenylimino)ethyl)picolinate (0.593 g, 2 mmol) and 1-butylamine (0.228 g, 3 mmol) were dissolved in 30 ml methanol and further stirred for 12 h. The compound, (*E*)-*N*-butyl-6-(1-(2,6-dimethylphenylimino)ethyl)picolinamide, was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7/1) and obtained as yellow solid in 94% yield (0.61 g). Mp: 101–103 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, 1H, $J = 7.9$ Hz, Py *Hm*), 8.31 (d, 1H, $J = 7.9$ Hz, Py *Hm*), 8.04 (br s, 1H), 7.97 (t, 1H, $J = 7.9$ Hz, Py *Hp*), 7.08 (d, 2H, $J = 7.5$ Hz), 6.95 (t, 1H, $J = 7.5$ Hz), 3.52 (m, 2H), 2.20 (s, 3H), 2.03 (s, 6H), 1.65 (m, 2H), 1.47 (m, 2H), 0.98 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 164.2, 153.9, 148.7, 147.4, 137.5, 127.1, 124.6, 123.2, 122.8, 122.6, 38.6, 30.9, 19.3, 16.4, 15.2, 12.4. FT-IR (KBr disc, cm^{-1}): 3331, 3070, 2936, 2863, 1653 ($\nu_{C=O}$), 1643 ($\nu_{C=N}$), 1531, 1467, 1208, 768, 691. Anal. Calc. for $C_{20}H_{25}N_3O$: C, 74.27; H, 7.79; N, 12.99. Found: C, 74.57; H, 7.95; N, 12.86%.

*Synthesis of (E)-N-butyl-6-(1-(2,6-diethylphenylimino)ethyl)picolinamide (***L2***)*: The reaction of (*E*)-ethyl-6-(1-(2,6-diethylphenylimino)ethyl)picolinate (0.649 g, 2 mmol) and 1-butylamine (0.228 g, 3 mmol) in methanol gave (*E*)-*N*-butyl-6-(1-(2,6-diethylphenylimino)ethyl)picolinamide as yellow solid in 92% yield (0.65 g). Mp: 122–124 °C. ^1H

NMR (300 MHz, $CDCl_3$): δ 8.51 (d, 1H, $J = 7.9$ Hz, Py *Hm*), 8.31 (d, 1H, $J = 7.9$ Hz, Py *Hm*), 8.04 (br s, 1H), 7.97 (t, 1H, $J = 7.9$ Hz, Py *Hp*), 7.12 (d, 2H, $J = 5.6$ Hz), 7.05 (t, 1H, $J = 7.5$ Hz), 3.52 (m, 2H), 2.36 (m, 4H), 2.21 (s, 3H), 1.66 (m, 2H), 1.45 (m, 2H), 1.13 (t, 6H), 0.98 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.7, 162.5, 153.7, 148.1, 146.4, 136.7, 129.9, 124.8, 122.2, 121.9, 37.9, 30.7, 23.4, 19.0, 15.4, 12.4. FT-IR (KBr disc, cm^{-1}): 3352, 3053, 2964, 2932, 2871, 1657 ($\nu_{C=O}$), 1640 ($\nu_{C=N}$), 1527, 1452, 1111, 773, 684. Anal. Calc. for $C_{22}H_{29}N_3O$: C, 75.18; H, 8.32; N, 11.96. Found: C, 75.08; H, 8.30; N, 11.74%.

*Synthesis of (E)-N-butyl-6-(1-(2,6-diisopropylphenylimino)ethyl)picolinamide (***L3***)*: The reaction of (*E*)-ethyl 6-(1-(2,6-diisopropylphenylimino)ethyl)picolinate (0.702 g, 2 mmol) and 1-butylamine (0.228 g, 3 mmol) in methanol gave (*E*)-*N*-butyl-6-(1-(2,6-diisopropyylphenylimino)ethyl)-picolinamide as yellow solid in 96% yield (0.73 g). Mp.: 142–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (d, 1H, $J = 7.9$ Hz, Py *Hm*), 8.32 (d, 1H, $J = 7.9$ Hz, Py *Hm*), 8.06 (br s, 1H), 7.98 (t, 1H, $J = 7.9$ Hz, Py *Hp*), 7.11–7.19 (m, 3H), 3.52 (m, 2H), 2.71 (m, 2H), 2.24 (s, 3H), 1.66 (m, 2H), 1.45 (m, 2H), 1.15 (d, 12H), 0.98 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 162.5, 153.6, 148.1, 145.1, 136.7, 134.5, 122.6, 122.3, 121.9, 121.8, 37.9, 30.7, 27.1, 21.8, 21.4, 19.0, 15.7, 12.4. FT-IR (KBr disc, cm^{-1}): 3385, 3062, 2959, 2868, 1677 ($\nu_{C=O}$), 1645 ($\nu_{C=N}$), 1525, 1451, 777, 636. Anal. Calc. for $C_{24}H_{33}N_3O \cdot 0.5H_2O$: C, 74.19; H, 8.82; N, 10.81. Found: C, 74.67; H, 8.45; N, 10.16%.

*Synthesis of (E)-6-(1-(2,6-dimethylphenylimino)ethyl)-N-octylpicolinamide (***L4***)*: The reaction of (*E*)-ethyl 6-(1-(2,6-dimethylphenylimino)ethyl)picolinate (0.593 g, 2 mmol) and 1-octylamine (0.388 g, 3 mmol) in methanol gave (*E*)-6-(1-(2,6-dimethyl phenylimino)ethyl)-*N*-octylpicolinamide as yellow oil in 85% yield (0.64 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (d, 1H, $J = 7.9$ Hz, Py *Hm*), 8.31 (d, 1H, $J = 7.9$ Hz, Py *Hm*), 8.04 (m, 1H), 7.97 (t, 1H, $J = 7.9$ Hz, Py *Hp*), 7.08 (d, 2H), 6.95 (t, 1H), 3.51 (m, 2H), 2.21 (s, 3H), 2.03 (s, 6H), 0.85 (t, 3H), 1.20–1.45 (m, 12H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9, 163.7, 154.7, 149.2, 148.5, 137.7, 128.0, 127.8, 124.9, 123.4, 123.3, 39.5, 31.8, 29.8, 29.3, 29.2, 27.0, 22.6, 20.7, 17.8, 17.5, 16.2, 14.0. FT-IR (KBr disc, cm^{-1}): 3400, 3019, 2926, 2856, 1677 ($\nu_{C=O}$), 1643 ($\nu_{C=N}$), 1524, 1450, 1206, 836, 764. Anal. Calc. for $C_{24}H_{33}N_3O$: C, 75.95; H, 8.76; N, 10.07. Found: C, 75.62; H, 8.73; N, 10.12%.

*Synthesis of (E)-6-(1-(2,6-diisopropylphenylimino)ethyl)-N-octylpicolinamide (***L5***)*: The reaction of (*E*)-ethyl 6-(1-(2,6-diisopropylphenylimino)ethyl)picolinate (0.702 g, 2 mmol) and 1-octylamine (0.388 g, 3 mmol) in methanol gave (*E*)-6-(1-(2,6-diisopropyl phenylimino)ethyl)- *N*-octyl-picolinamide as yellow solid in 86% yield (0.75 g). Mp: 80–82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (d, 1H, $J = 7.9$ Hz, Py *Hm*), 8.32 (d, 1H, $J = 7.9$ Hz, Py *Hm*), 8.06 (br s, 1H), 7.98 (t, 1H, $J = 7.9$ Hz, Py *Hp*), 7.11–7.19 (m, 3H), 3.51 (m, 2H), 2.71(m, 2H), 2.23 (s, 3H), 1.67 (m, 2H), 1.26–1.45 (m, 12H), 0.85 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9, 163.8, 154.6, 148.9, 146.1, 137.8, 135.5, 123.7, 13.3, 122.9, 39.4, 31.7, 29.7, 29.1, 28.2, 26.9, 23.0, 22.7, 22.5, 16.9, 14.0. FT-IR (KBr disc, cm^{-1}): 3332, 3069, 2956, 2937, 2864, 1650 ($\nu_{C=O}$), 1645 ($\nu_{C=N}$), 1529, 1207, 768. Anal. Calc. for $C_{28}H_{41}N_3O$: C, 77.20; H, 9.49; N, 9.65. Found: C, 77.42; H, 9.13; N, 9.72%.

*Synthesis of (E)-N-benzyl-6-(1-(2,6-dimethylphenylimino)ethyl)picolinamide (***L6***)*: The reaction of (*E*)-ethyl-6-(1-(2,6-dimethylphenylimino)ethyl)picolinate (0.593 g, 2 mmol) and phenylmethanamine (0.321 g, 3 mmol) in methanol gave (*E*)-*N*-benzyl-6-(1-(2,6-dimethylphenylimino)ethyl)picolinamide as yellow solid in 93% yield (0.67 g). Mp.: 127–129 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (d, 1H, $J = 7.9$ Hz, *Py Hm*), 8.36 (m, 3H), 7.99 (m, 1H), 7.33–7.40 (m, 5H), 7.07 (d, 2H), 6.94 (t, 1H), 4.74 (d, 2H), 2.15 (s, 3H), 2.02 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.8, 162.9, 153.6, 147.5, 147.2, 137.1, 136.7, 127.5, 127.0, 126.7, 126.3, 126.2, 124.0, 122.6, 122.5, 122.0, 42.2, 16.7, 13.3, 15.2. FT-IR (KBr disc, cm^{-1}): 3335, 3066, 2939, 2854, 1671 ($\nu_{C=O}$), 1650 ($\nu_{C=N}$), 1524, 1455, 1436, 1208, 768, 702. Anal. Calc. for $C_{23}H_{23}N_3O$: C, 77.28; H, 6.49; N, 11.76. Found: C, 77.42; H, 6.13; N, 11.72%.

*Synthesis of (E)-N-benzyl-6-(1-(2,6-diisopropylphenylimino)ethyl)picolinamide (***L7***):* The reaction of (*E*)-ethyl-6-(1-(2,6-diisopropylphenylimino)ethyl)picolinate (0.702 g, 2 mmol) and phenylmethanamine (0.321 g, 3 mmol) in methanol gave (*E*)-*N*-benzyl-6-(1-(2,6-diisopropylphenylimino)ethyl)picolinamide as yellow solid in 93% yield (0.77 g). Mp.: 182–184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (d, 1H, $J = 7.9$ Hz, P*y Hm*), 8.36 (m, 3H), 8.00 (m, 1H), 7.29–7.41 (m, 5H); 7.16 (d, 2H), 7.08 (t, 1H), 4.74 (d, 2H), 4.74 (d, 2H), 2.70 (m, 2H), 2.18 (s, 3H), 1.13 (d, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 162.8, 153.7, 147.7, 145.0, 137.7, 136.8, 134.5, 127.4, 126.2, 126.1, 122.6, 122.2, 121.8, 42.0, 27.1, 21.8, 214, 15.8. FT-IR (KBr disc, cm^{-1}): 3387, 3068, 2960, 2866, 1674, 1649, 1517, 1451, 1255, 773, 698. Anal. Calc. for $C_{27}H_{31}N_3O$: C, 78.42; H, 7.56; N, 10.16; O, 4.48. Found: C, 78.62; H, 7.23; N, 10.02%.

*Synthesis of (E)-N-butyl-6-(1-(mesitylimino)ethyl)picolinamide (***L8***)*: The reaction of (*E*)-ethyl 6-(1-(mesitylimino)ethyl)picolinate (0.620 g, 2 mmol) and 1-butylamine (0.228 g, 3 mmol) in methanol gave (*E*)-*N*-butyl-6-(1-(mesitylimino)ethyl)picolinamide as yellow solid in 86% yield (0.58 g). Mp.: 97–99 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (d, 1H, $J = 7.9$ Hz, *Py Hm*), 8.30 (d, 1H, $J = 7.9$ Hz, *Py Hm*), 8.03 (br s, 1H), 7.98 (t, 1H, $J = 7.9$ Hz, *Py Hp*), 6.90 (s, 2H), 3.51 (m, 2H), 2.29 (s, 3H), 2.19 (s, 3H), 2.00 (s, 6H), 1.64 (m, 2H), 1.44 (m, 2H), 0.98 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 165.2, 156.4, 147.6, 147.4, 137.3, 131.0, 126.1, 125.9, 124.3, 123.5, 61.9, 24.5, 16.8, 14.3, 13.7. IR (KBr, cm^{-1}): 1722, 1640, 1580, 1540, 1454, 1394. FT-IR (KBr disc, cm^{-1}): 3386, 3083, 2933, 2872, 1678 ($\nu_{C=O}$), 1645 ($\nu_{C=N}$), 1526, 1481, 1363, 1217,

771, 667. Anal. Calc. for $C_{21}H_{27}N_3O$: C, 74.74; H, 8.06; N, 12.45. Found: C, 74.42; H, 8.36; N, 12.69%.

4.3. Synthesis of complexes

*1-Naphthylnickel N-butyl-6-(1-(2,6-dimethylphenylimino)ethyl)picolinamide (**C1**)*: A flame-dried Schlenk tube was charged with **L1** (323 mg, 1 mmol) and sodium hydride (72 mg, 3 mmol) under nitrogen. THF (10 ml) was added to the mixture at 0 °C. Many bubbles were immediately produced. The resulting mixture was stirred at room temperature for 1 h, filtered, and evaporated. The Na salt was immediately used in the next step without further purification. Solid *trans*-[NiCl(Naph)(PPh_3)$_2$] (746 mg, 1 mmol) was added to the Schlenk tube under positive nitrogen flow. The mixture was charged with toluene (30 ml) and stirred at 20 °C for 12 h. Then, the reaction mixture was filtered and the filtrate was concentrated in vacuo to ca. 5 ml. Hexane (50 ml) was added to this solution. A solid was precipitated and isolated by cannula filtration to get a brown powder in 59% yield (345 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.23 (d, 1H, $J = 7.38$ Hz), 8.08 (t, 1H, $J = 7.62$ Hz), 8.03 (d, 1H); 7.66 (d, 1H, $J = 7.59$), 7.47 (d, 1H, $J = 7.5$ Hz), 7.07 (d, 1H, $J = 7.98$), 6.84 (d, 1H, $J = 7.77$ Hz), 6.73 (m, 2H), 6.37 (d, 1H), 7.26–7.29 (m, 3H), 2.94 (m, 1H, $J = 12.06$, NCH_2), 2.38 (s, 3H), 1.85 (s, 3H), 1.83 (m, 1H, NCH_2), 1.64 (s, 3H), 1.11 (m, 2H), 0.76 (m, 2H), 0.39 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.4, 170.8, 159.5, 154.0, 149.8, 144.7, 139.6, 140.2, 139.6, 132.7, 132.5, 132.2, 132.1, 128.7, 128.5, 128.4, 128.0, 127.6, 126.1, 123.9, 123.2, 123.1, 122.8, 122.1, 46.5, 32.9, 20.2, 18.9, 17.8, 16.5, 13.7. FT-IR (KBr disc, cm^{-1}): 3040, 2956, 1613, 1602, 1546, 1432, 1371, 1199, 766. Anal. Calc. for $C_{30}H_{31}N_3NiO \cdot 0.5H_2O$: C, 69.66; H, 6.24; N,8.12. Found: C, 69.57; H, 6.27; N, 8.02%.

*1-Naphthylnickel N-butyl-6-(1-(2,6-diethylphenylimino)ethyl)picolinamide (**C2**)*: In a similar manner described for **C1**, the complex **C2** was obtained from the reaction of *trans*-[NiCl(Naph)(PPh_3)$_2$] and **L2** as a brown powder in 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.20 (d, 1H, $J = 7.89$ Hz), 8.08 (m, 2H), 7.66 (d, 1H, $J = 7.38$), 7.45 (d, 1H), 7.18–7.27 (m, 1H, $J = 7.23$), 7.16 (d, 1H, $J = 6.54$), 7.03 (d, 1H, $J = 7.89$), 6.92 (d, 1H, $J = 7.53$), 6.82 (t, 1H, $J = 7.56$), 6.68 (t, 1H, $J = 7.38$), 6.41 (d, 1H, $J = 7.56$), 3.05 (m, 1H), 2.98 (m, 1H), 2.58 (m, 1H), 2.18 (m, 1H), 1.96 (m, 1H), 1.89 (s, 3H), 1.83 (m, 1H), 1.34 (t, 3H), 1.11 (m, 2H), 0.72 (m, 2H), 0.50 (t, 3H). 0.37 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.7, 170.8, 159.7, 153.8, 149.8, 143.5, 140.0, 139.8, 133.6, 133.3, 132.9, 132.7, 132.4, 127.6, 126.4, 124.7, 124.6, 123.8, 123.2, 123.0, 122.4, 122.1, 32.9, 24.6, 23.5, 20.2, 16.6, 17.0, 13.7, 13.5, 12.3. FT-IR (KBr disc, cm^{-1}): 3038, 2959, 2928, 1613, 1590, 1546, 1435, 1371, 787, 760. Anal. Calc. for $C_{32}H_{35}N_3NiO \cdot 0.5EtOH$: C, 70.86; H, 6.85; N, 7.51. Found: C, 71.10; H, 6.92; N, 7.47%.

*1-Naphthylnickel N-butyl-6-(1-(2,6-diisopropylphenylimino)ethyl)picolinamide (**C3**)*: In a similar manner described for **C1**, the complex **C3** was obtained from the reaction of *trans*-[NiCl(Naph)(PPh_3)$_2$] and **L3** as a brown powder in 53% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.21 (d, 1H, $J = 7.89$ Hz), 8.05 (m, 2H), 7.63 (d, 1H, $J = 7.23$), 7.48 (m, 5H), 7.18–7.27 (m, 1H), 7.17 (d, 1H), 7.04 (m, 3H),6.92 (d, 1H, $J = 7.53$), 6.67 (t, 1H, $J = 7.38$), 6.57 (d, 1H, $J = 7.56$), 3.24 (m, 1H), 3.05 (m, 1H), 2.03 (s, 3H), 1.80 (d, 4H), 1.39 (m, 1H), 1.16 (d, 4H), 1.06 (m, 2H), 0.78 (m, 2H), 0.71 (d, 4H), 0.41 (t, 3H), −0.34 (d, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.7, 170.5, 157.5, 154.1, 149.7, 140.9, 140.5, 139.5, 138.7, 133.4, 133.3, 132.1, 127.7, 127.3, 123.9, 123.7, 123.5, 123.4, 123.3, 122.3, 122.2, 45.7, 33.0, 28.7, 24.5, 24.3, 21.0, 20.2, 18.9, 13.8. FT-IR (KBr disc, cm^{-1}): 3032, 2955, 2866, 1609, 1597, 1545, 1432, 1370, 1193, 786, 759. Anal. Calc. for $C_{34}H_{39}N_3NiO$: C, 72.36; H, 6.97; N, 7.45. Found: C, 71.10; H, 6.92; N, 7.47%.

*1-Naphthylnickel N-octyl-6-(1-(2,6-dimethylphenylimino)ethyl)picolinamide (**C4**)*: In a similar manner described for **C1**, the complex **C4** was obtained from the reaction of *trans*-[NiCl(Naph)(PPh_3)$_2$] and **L4** as a brown powder in 43% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.22 (d, $J = 7.56$, 1H), 8.07 (m, 3H), 7.67 (m, 2H), 7.46 (m, 2H), 7.05 (m, 2H), 6.83 (d, $J = 7.56$, 1H), 6.70 (m, 3H), 6.36 (d, $J = 7.53$, 1H), 2.91 (m, 1H), 2.37 (s, 3H), 2.32 (m, 1H), 1.89 (s, 3H), 1.63 (s, 3H), 0.90–1.40 (m, 12H), 0.77 (t,3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 170.7, 159.4, 154.0, 149.8, 144.7, 140.2, 139.7, 133.3, 132.8, 132.7, 132.5, 128.4, 128.2, 128.1, 128.0, 127.6, 126.1, 123.9, 123.3, 123.1, 122.9, 122.2, 46.9, 31.8, 30.7, 29.1, 27.1, 22.7, 18.9, 17.8, 16.5, 14.2. FT-IR (KBr disc, cm^{-1}): 3042, 2955, 2946, 1618, 1596, 1463, 1371, 1117, 779, 758. Anal. Calc. for $C_{34}H_{39}N_3NiO$: C, 72.36; H, 6.97; N, 7.45. Found: C, 72.71; H, 6.90; N, 7.67%.

*1-Naphthylnickel N-octyl-6-(1-(2,6-diisopropylphenylimino)ethyl)picolinamide (**C5**)*: In a similar manner described for **C1**, the complex **C5** was obtained from the reaction of *trans*-[NiCl(Naph)(PPh_3)$_2$] and **L5** as a brown powder in 51% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.31 (d, 1H, $J = 7.56$ Hz), 8.08 (m, 3H), 7.66 (m, 2H), 7.45 (m, 2H), 7.00–7.27 (m, 2H),6.92 (d, 1H, $J = 7.53$), 6.67 (t, 1H, $J = 7.38$), 6.57 (d, 1H, $J = 7.2$), 3.24 (m, 1H), 3.00 (m, 1H), 2.65 (m, 1H), 2.01 (s, 3H), 1.93 (m, 1H), 1.80 (d, 3H), 0.72–1.82 (m, 21H), −0.34 (d, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 170.5, 157.6, 154.2, 149.8, 142.5, 140.9, 140.6, 139.6,138.7, 134.7, 134.6, 133.5, 132.2, 127.7, 127.3, 126.4, 124.0, 123.6, 123.2, 123.0, 122.3, 122.2, 31.9, 30.9, 30.6, 29.4, 29.3, 29.0, 28.8, 27.1, 24.9, 24.5, 24.4, 22.7, 21.0, 18.9, 14.2 FT-IR (KBr disc, cm^{-1}): 3051, 2958, 2925, 2854, 1613, 1591, 1462, 1436, 1371, 1119, 786, 761. Anal. Calc. for $C_{38}H_{47}N_3NiO \cdot 0.5H_2O$: C, 72.50; H, 7.69; N, 6.68. Found: C, 72.57; H, 6.37; N, 7.02%.

*1-Naphthylnickel N-benzyl-6-(1-(2,6-dimethylphenylimino)ethyl)picolinamide (**C6**)*: In a similar manner described

for **C1**, the complex **C6** was obtained from the reaction of *trans*-[NiCl(Naph)(PPh_3)$_2$] and **L6** as a brown powder in 48% yield (298 mg). ^{1}H NMR (300 MHz): δ 9.16 (d, 1H), 8.06 (m, 2H), 7.65 (d, 1H, $J = 6.87$), 7.46 (m, 1H), 6.80–7.25 (m, 10H),6.63 (m, 2H), 6.33 (d, 1H, $J = 7.53$), 4.31 (d, 1H, $J = 13.74$), 3.01 (d, 1H, $J = 13.38$), 2.31 (s, 3H), 1.86 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.7, 154.3, 150.7, 140.1, 133.3, 129.6, 128.5, 128.3, 128.2, 127.9, 127.6, 126.4, 125.7, 124.1, 123.7, 123.4, 123.3, 122.7, 122.5, 50.3, 19.1, 18.1, 16.8. FT-IR (KBr disc, cm^{-1}): 3032, 2908, 1615, 1597, 1436, 1190, 1118, 696, 541. Anal. Calc. for $C_{33}H_{29}N_3NiO$: C, 73.09; H, 5.39; N, 7.75. Found: C, 73.10; H, 5.22; N, 7.47%.

*1-Naphthylnickel N-benzyl-6-(1-(2,6-diisopropylphenylimino)ethyl)picolinamide (***C7***):* In a similar manner described for **C1**, the complex **C7** was obtained from the reaction of *trans*-[NiCl(Naph)(PPh_3)$_2$] and **L7** as a brown powder in 57% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.22 (d, 1H, $J = 6.87$ Hz), 8.06 (m, 2H), 7.82 (m, 1H), 7.7–7.2 (m, 4H), 7.07 (d, 1H), 6.74 (t, $J = 7.38$, 1H), 6.63 (s, 1H), 6.15 (s, 1H), 2.95 (m, 1H), 2.31 (s, 3H), 2.01 (s, 3H), 1.57 (s, 3H), 1.12 (m, 2H), 0.75 (m, 2H), 0.39 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.7, 156.6, 153.7, 149.8, 142.6, 142.3, 140.7, 140.6, 139.6, 138.7, 134.0, 133.3, 131.8, 128.2, 127.8, 127.4, 125.4, 124.0, 123.8, 123.6, 123.5, 123.2, 122.5, 122.4, 73.4, 49.3, 28.8, 24.9, 24.4, 24.2, 18.8. FT-IR (KBr disc, cm^{-1}): 3055, 2961, 1615, 1593, 1547, 1437, 1371, 786, 760. Anal. Calc. for $C_{37}H_{37}N_3NiO \cdot 0.5H_2O \cdot 0.5Et_2O$: C, 72.68; H, 6.73; N, 6.52; Ni, 9.11. Found: C, 72.72; H, 6.31; N, 6.86%.

*1-Naphthylnickel N-butyl-6-(1-(mesitylimino)ethyl)picolinamide (***C8***)*: In a similar manner described for **C1**, the complex **C8** was obtained from the reaction of *trans*-[NiCl(Naph)(PPh_3)$_2$] and **L8** as a brown powder in 61% yield (298 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.31 (d, 1H, $J = 7.89$ Hz), 8.08 (m, 2H), 7.66 (m, 3H), 7.45 (d, 1H), 7.18–7.27 (m, 1H, $J = 7.23$), 7.16 (d, 1H, $J = 6.54$), 7.03 (d, 1H, $J = 7.89$), 6.92 (d, 1H, $J = 7.53$), 6.82 (t, 1H, $J = 7.56$), 6.68 (t, 1H, $J = 7.38$), 6.41(d, 1H, $J = 7.56$), 3.05 (m, 1H), 2.98 (m, 1H), 2.58 (m, 1H), 2.18 (m, 1H), 1.96 (m, 1H), 1.89 (s, 3H), 1.83 (m, 1H), 1.34 (t, 3H), 1.11 (m, 2H), 0.72 (m, 2H), 0.50 (t, 3H), 0.37 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.7, 170.5, 157.5, 154.1, 149.7, 140.9, 140.5, 139.5, 138.7, 133.4, 133.3, 132.1, 127.7, 127.3, 123.9, 123.7, 123.5, 123.4, 123.3, 122.3, 122.2, 45.7, 33.0, 28.7, 24.5, 24.3, 21.0, 20.2, 18.9, 13.8. FT-IR (KBr disc, cm^{-1}): 3032, 2955, 2866, 1609, 1597, 1545, 1432, 1370, 1193, 786, 759. Anal. Calc. for $C_{31}H_{33}N_3NiO$: C, 71.29; H, 6.37; N, 8.05. Found: C, 71.10; H, 6.82; N, 7.87%.

*Phenylnickel N-butyl-6-(1-(2,6-diisopropylphenylimino)ethyl)picolinamide (***C9***)*: In a similar manner described for **C1**, the complex **C9** was obtained from the reaction of *trans*-[NiCl(phenyl)(PPh_3)$_2$] and **L1** as a brown powder in 43% yield (298 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (m, 2H); 7.61 (d, 2H, $J = 7.2$); 7.21 (m, 2H), 6.82 (m, 3H) 6.59 (m, 3H), 2.64 (t, 2H); 2.20 (s, 6H); 1.88 (s, 3H); 1.17 (m, 2H); 0.90 (m, 2H); 0.58 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ170.8,170.4, 156.8, 153.9, 149.5, 144.8, 139.3, 135.0, 128.2, 127.7, 126.2, 124.8, 122.7, 122.0, 121.7, 45.8, 32.3, 20.2, 18.4, 16.3, 13.7. FT-IR (KBr disc, cm^{-1}): 3048, 3955, 2927, 1612, 1590, 1560, 1416, 761, 733, 699. Anal. Calc. for $C_{26}H_{29}N_3NiO$: C, 68.15; H, 6.38; N, 9.17. Found: C, 68.10; H, 6.72; N, 9.47%.

*Phenylnickel N-butyl-6-(1-(2,6-diisopropylphenylimino)ethyl)picolinamide (***C10***)*: In a similar manner described for **C1**, the complex **C10** was obtained from the reaction of *trans*-[NiCl(phenyl)(PPh_3)$_2$] and **L3** as a brown powder in 49% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (m, 2H), 7.63 (d, 1H, $J = 7.2$), 7.11 (m, 2H), 6.98 (d, 2H) 6.60 (m, 3H), 3.10 (m, 2H), 2.62 (t, 2H), 1.98 (s, 3H), 1.21 (d, 6H), 1.15 (m, 2H), 1.02 (d, 2H), 0.95 (m, 2H), 0.58 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 170.4, 155.0, 154.1, 149.7, 142.5, 139.5, 136.3, 127.7, 125.0, 123.6, 123.1, 122.4, 122.1, 45.4, 32.6, 28.8, 24.5, 23.4, 20.3, 18.7, 14.0. FT-IR (KBr disc, cm^{-1}): 3045, 2957, 2924, 2868, 1610, 1593, 1560, 1421, 757, 733, 698. Anal. Calc. for $C_{30}H_{37}N_3NiO$: C, 70.06; H, 7.25; N, 8.17. Found: C, 71.10; H, 7.42; N, 8.47%.

4.4. Procedure for ethylene oligomerization

Ethylene oligomerization at 1 atm of ethylene pressure was carried out as follows: the catalyst precursor was dissolved in toluene in a Schlenk tube, and the reaction solution was stirred with a magnetic stir under ethylene atmosphere (1 atm) with the reaction temperature being controlled by a water bath. The required amount of cocatalyst (MAO, MMAO, or Et_2AlCl) and the solution of PPh_3 were added by a syringe. After the reaction was carried out of the required period, the reactor was cold to lower temperature in ice-bath. Then a small amount of the reaction solution was collected and terminated by the addition of cold 10% aqueous hydrogen chloride. The organic layer was analyzed quickly by gas chromatography (GC) for determining the composition and mass distribution of oligomers.

High-pressure ethylene oligomerization was performed in a stainless steel autoclave (0.5 L capacity) equipped with gas ballast through a solenoid clave for continuous feeding of ethylene at constant pressure. A 100 ml amount of toluene containing the catalyst precursor was transferred into the fully dried reactor under a nitrogen atmosphere. The required amount of cocatalyst (Et_2AlCl) was then injected into the reactor using a syringe. Then the reactor was pressurized to the desired pressure (10 atm). After the reaction mixture was stirred for the desired period of time, the reaction was stopped without ethylene inputting. Then the autoclave was cold in ice-bath for an hour, the pressure was released. A small amount of the reaction solution was collected and terminated by the addition of cold 10% aqueous hydrogen chloride. C_4 and C_6 were dissolved in organic layer which was analyzed quickly by gas chromatography (GC) for determining the composition and mass distribution of oligomers obtained.

4.5. Procedure for Kumada–Corriu reaction

A typical procedure (entry 4 in Table 5): A Schlenk tube was charged with **C9** (4.6 mg, 0.01 mmol), toluene (1.5 ml) and bromobenzene (106 μl, 1.0 mmol) in an N_2 atmosphere. A solution of *p*-MeC_6H_4MgBr in THF (1.5 mmol, ca. 1 M in THF) was dropwise added to the above stirring solution at room temperature. Stirring was continued at room temperature for 24 h. The reaction was quenched by addition of water (6 ml). The mixture was extracted with Et_2O (3 × 5 ml) and examined by GC/FID.

4.6. Procedure for methyl methacrylate polymerization

All procedures for polymerization were carried out under purified N_2 atmosphere. Ethyl-2-bromoisobutyrate was added to a mixture of complex and degassed MMA (2.0 ml, 19 mmol) in toluene (5 ml). After the mixture stood at a definite reaction temperature for 24 h, HCl/methanol (10%, 0.5 ml) was added to decompose the catalyst, and THF (5 ml) was added to dissolve the resulting polymers, which were precipitated as a white wadding by the addition of large excess of ethanol. Poly(methyl methacrylate) (PMMA) was washed with Methanol and dried in vacuum at room temperature for 24 h. MMA conversion was approximately determined from the amount of PMMA obtained.

4.7. X-ray crystallographic studies

Single-crystal X-ray diffraction measurements on **L1**, **C2**, **C3** and **C7** were performed by using a Rigaku R-AXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 296(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [23]. Crystal data and processing parameters for **L1**, **C2**, **C3** and **C7** are summarized in Table 7.

Table 7
Crystal data and refinement details for **L1**, **C2**, **C3** and **C7**

	L1	**C2**	**C3**	**C7**
Empirical formula	$C_{20}H_{25}N_3O$	$C_{32}H_{35}N_3NiO$	$C_{34}H_{39}N_3NiO$	$C_{74}H_{74}N_6Ni_2O_2$
Formula weight	323.43	536.34	564.39	1196.81
Crystal color	Yellow	Brown	Brown	Brown
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	11.9976(4)	8.8717(5)	10.8309(3)	19.2307(6)
b (Å)	19.0143(7)	21.4616(1)	18.1594(5)	19.2721(6)
c (Å)	9.2871(4)	15.2609(9)	16.2467(5)	19.0119(6)
β (°)	109.265(3)	104.993(2)	108.488(2)	117.854(2)
Volume (Å^3)	1999.99(2)	2806.8(3)	3030.53(2)	6229.8(3)
Z	4	4	4	4
D_{calc} (Mg m^{-3})	1.074	1.269	1.237	1.276
μ (mm^{-1})	0.067	0.720	0.670	0.656
$F(000)$	696	1136	1200	2528
Crystal size (mm)	0.29 × 0.08 × 0.07	0.35 × 0.2 × 0.15	0.32 × 0.23 × 0.13	0.35 × 0.25 × 0.18
θ Range (°)	1.80–28.34	1.68–28.34	1.73–28.32	2.11–28.28
Limiting indices	$-15 \leqslant h \leqslant 15$ $-22 \leqslant k \leqslant 25$ $-12 \leqslant k \leqslant 12$	$-9 \leqslant h \leqslant 11$ $-28 \leqslant k \leqslant 28$ $-20 \leqslant l \leqslant 19$	$-14 \leqslant h \leqslant 14$ $-24 \leqslant k \leqslant 24$ $-21 \leqslant l \leqslant 21$	$-25 \leqslant h \leqslant 23$ $-25 \leqslant k \leqslant 22$ $-18 \leqslant l \leqslant 25$
Number of reflections collected	18423	21039	32453	50181
Number of unique reflections [R_{int}]	4950 [0.0573]	6907 [0.0468]	7528 [0.0695]	15383 [0.1097]
Completeness to θ (%)	99.2 ($\theta = 28.34°$)	98.7 ($\theta = 28.34°$)	99.7 ($\theta = 28.32°$)	99.4 ($\theta = 28.28°$)
Absorption correction	Empirical	Empirical	Empirical	Empirical
Data/restraints/parameters	4950/0/210	6907/0/316	7528/1/342	15383/0/757
Goodness-of-fit on F^2	0.875	1.040	0.825	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0770$ $wR_2 = 0.2648$	$R_1 = 0.0850$ $wR_2 = 0.2234$	$R_1 = 0.0532$ $wR_2 = 0.1373$	$R_1 = 0.0821$ $wR_2 = 0.1223$
R indices (all data)	$R_1 = 0.1935$ $wR_2 = 0.3300$	$R_1 = 0.1338$ $wR_2 = 0.2507$	$R_1 = 0.1646$ $wR_2 = 0.1610$	$R_1 = 0.1964$ $wR_2 = 0.1575$
Largest difference in peak and hole (e Å^{-3})	0.311, −0.216	1.224, −1.424	0.494, −0.390	0.246, −0.276

Acknowledgements

This work was supported by NSFC No. 20674089 and MOST No. 2006AA03Z553. We are grateful to Prof. Richard D. Adams and Mr. Saliu Alao Amolegbe for the English corrections.

Appendix A. Supplementary material

CCDC 671289, 671290, 671291, 671292 contain the supplementary crystallographic data for compounds **L1**, **C2**, **C3**, **C7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.01.004.

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