Journal of Organometallic Chemistry 694 (2009) 389–396

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Pincer-type bis(carbene)-derived complexes of nickel(II): Synthesis, structure, and catalytic activity

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ARTICLE INFO

Article history:
Received 26 September 2008
Received in revised form 29 October 2008
Accepted 4 November 2008
Available online 7 November 2008

Keywords:
Pincer complex
Nickel
N-heterocyclic carbene
Suzuki–Miyaura coupling

ABSTRACT

Air- and moisture-stable NHC (N-heterocyclic carbene)-derived CNC-type pincer complexes of nickel(II) **4a–d** were successfully synthesized, and their structures were fully characterized using X-ray crystallography and analytical and spectroscopic methods. These complexes exhibit a high catalytic activity for the Suzuki–Miyaura coupling reaction of aryl bromides and chlorides with aryl- and alkenylboronic acids, providing an array of biphenyls and stilbenes generally in high yields.

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1. Introduction

The longstanding search for efficient catalytic systems in transition metal-catalyzed coupling reactions remains an active subject in organic synthesis. Metallacycles possessing the pincer ligand framework could be an efficient system because of their considerable thermal and oxidative stabilities [1–9]. Various types (e.g., PCP–, NCN–, CNC–) of pincer complexes of transition metals have been reported to date; among them, palladium–pincer complexes have been widely investigated and employed as catalysts for cross-coupling reactions [10–15]. Much less attention has been paid to the nickel–pincer complexes [16–22], although the use of nickel catalysts instead of palladium catalysts sometimes offers advantages, such as cost effectiveness and distinct catalytic abilities [23–33]. In this regard, we recently reported the synthesis of a CNC-type pincer complex of nickel **1** (Fig. 1) and showed its high catalytic activities in Heck reaction, Suzuki–Miyaura coupling, and Kumada–Tamao–Corriu coupling [34,35]. Herein, we report the synthesis and characterization of a series of new NHC-derived nickel–pincer complexes **4a–d** and provide a preliminary account of their catalytic activities.

2. Results and discussion

2.1. Synthesis and characterization of NHC-derived nickel–pincer complexes *4a–d*

Scheme 1 shows the synthetic route for novel NHC-derived nickel–pincer complexes **4a–d**. Bis-imidazolium salts **2a–d** were readily prepared from the reactions of 2,6-dibromopyridine or 2,6-dibromomethylpyridine with the corresponding imidazoles [36]. Unlike the synthesis of nickel complex **1** we previously reported, the direct cyclometallation of **2** with several nickel sources was not successful. Instead, nickel–pincer complexes were obtained via the transmetallation of silver salts **3a–d**, which were easily synthesized from the reactions of the corresponding imidazolium salts **2** with Ag_2O [36]. Counter anion exchange using $AgBF_4$ finally gave the desired nickel–pincer complexes **4a–d**, which were all yellow crystals and quite stable in air [37]. They were soluble in $CHCl_3$, CH_2Cl_2, MeOH, DMSO, and MeCN and could be recrystallized from CH_2Cl_2 and light petroleum. The complexes **4a–d** were characterized by analytical and spectroscopic methods. In the ^1H NMR spectra of **4c** and **4d**, the signals corresponding to the methyl groups of the *ortho*-methyls of mesityl groups and the DIPP (2,6-diisopropylphenyl) appear as one singlet (12H) and two doublets (12H + 12H), respectively, indicating that these two complexes have a symmetrical plane. On the other hand, the ^1H NMR spectra of **4a** and **4b** show that signals corresponding to the same methyl groups appear as two singlets (6H + 6H) and four doublets (6H + 6H + 6H + 6H), respectively, resulting from the

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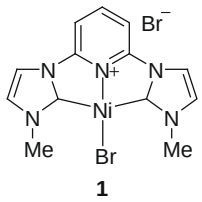
doi:10.1016/j.jorganchem.2008.11.003



1

Fig. 1. Previously reported nickel–pincer complex.

unsymmetrical structures of these complexes. These observations were previously reported for the palladium analogues [36].

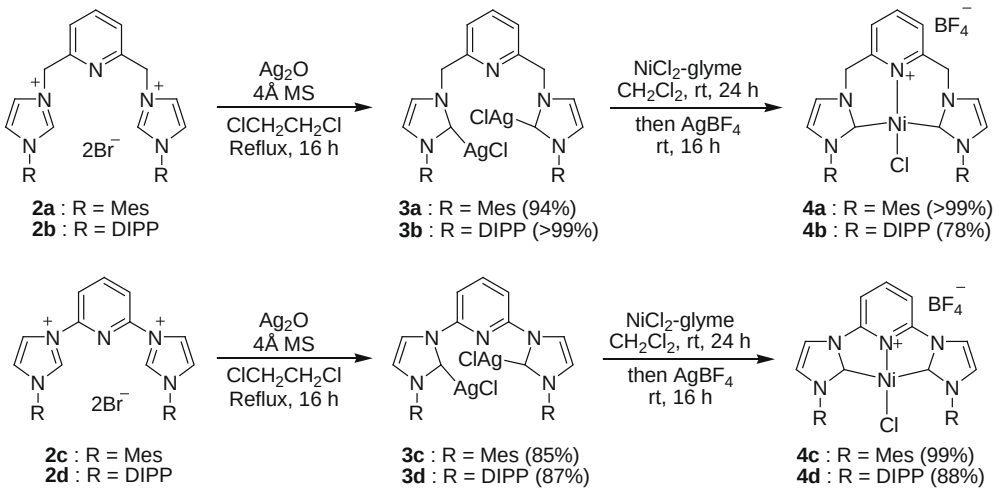
2.2. Crystal structures of complexes *4a–d*

We determined the structures of all complexes in the solid-state using X-ray crystallographic analysis. Table 1 summarizes selected crystallographic data. The molecular structures are depicted in Fig. 2 and Table 2 lists selected bond lengths and bond angles.

The nickel center of all complexes exhibited an only slightly distorted square-planar coordination geometry, similar to that of the previously reported nickel complex **1**. A least-squares plane fitted to the nickel and surrounding ligand atoms (i.e., the chlorine atom, the nitrogen atom of pyridine, and the two carbenes) showed a small deviation within 0.048 Å for all four complexes.

Although the pyridine ring plane was nearly coplanar with the least-square planes (i.e., the Cl(1)–C(1)–N(3)–C(11)) for both **4c** (3.80°) and **4d** (2.63°), the pyridine plane of **4a** and **4b** rotated (i.e., the pyridine ring and Cl(1)–C(1)–N(3)–C(13) planes) through an angle of 46.60° and 46.73°, respectively. These structural differences could be correlated with the catalytic activity of **4a**,**b** and **4c**,**d**, as described later.

The structural feature of the complexes that is related to the stability toward air and moisture is also found in a crystal structure.



Scheme 1. Synthesis of **4a–d**.

Table 1
Summary of crystallographic data for **4a–d**.

Compound	4a	4b	4c	4d
Empirical formula	$C_{31}H_{33}BClF_4N_5Ni \cdot CH_3COCH_3$	$C_{37}H_{45}BClF_4N_5Ni \cdot CH_2Cl_2$	$C_{29}H_{29}BClF_4N_5Ni \cdot CH_2Cl_2$	$C_{35}H_{41}BClF_4N_5Ni$
Formula weight	714.67	825.69	713.47	712.70
Temperature (K)	173(1)	173(1)	173(1)	173(1)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$
a (Å)	8.969(3)	9.297(4)	10.631(6)	35.07(6)
b (Å)	21.811(8)	12.077(4)	19.059(11)	8.559(20)
c (Å)	17.727(7)	17.791(7)	16.230(9)	23.06(4)
α (°)	90	85.993(9)	90	90
β (°)	96.947(5)	88.314(7)	99.646(9)	100.399(19)
γ (°)	90	85.993(8)	90	90
V (Å^3)	3442(2)	1987.1(13)	3242(3)	6809(23)
Z	4	2	4	8
$D_{calcd.}$ (g/m^3)	1.379	1.380	1.462	1.390
μ (mm^{-1})	1.432	1.346	1.114	1.421
$F(000)$	1488	860	1464	2976
Reflections collected/unique [$R_{(int)}$]	49991/7812 (0.142)	29797/9033 (0.064)	45833/7272 (0.079)	48592/7745 (0.084)
Completeness to θ	27.47 (99.0%)	27.47 (99.3%)	27.35 (99.1%)	27.50 (99.2%)
Absorption correction	Numerical	Numerical	Numerical	Numerical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on (GOF) F^2	0.796	1.010	1.005	1.002
Final R indices [$I > 2\sigma I$)]	R_1 = 0.0543, wR_2 = 0.1087	R_1 = 0.0536, wR_2 = 0.1262	R_1 = 0.0594 wR_2 = 0.1600	R_1 = 0.0518, wR_2 = 0.0899
Maximum peak/hole (e Å^{-3})	2.67/−1.46	0.98/−0.84	1.11/−0.99	1.03/−0.92

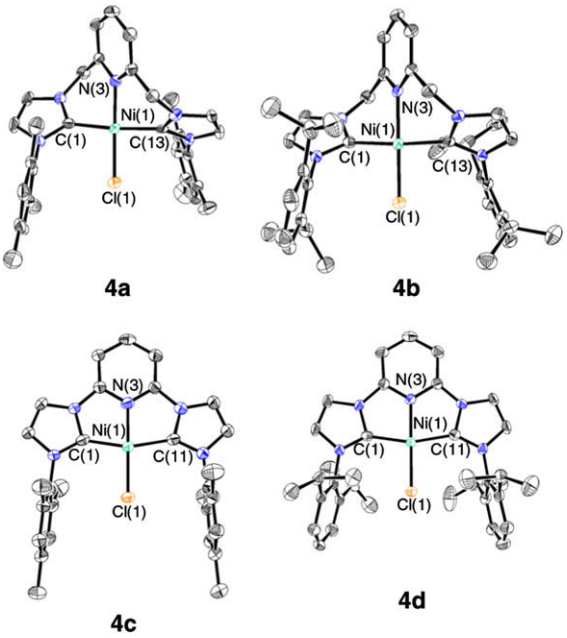


Fig. 2. Molecular structures of the complexes of **4a–d** showing 30% probability ellipsoids. Hydrogen atoms, $(BF_4)^-$ anion, and the solvent molecular have been omitted for clarity.

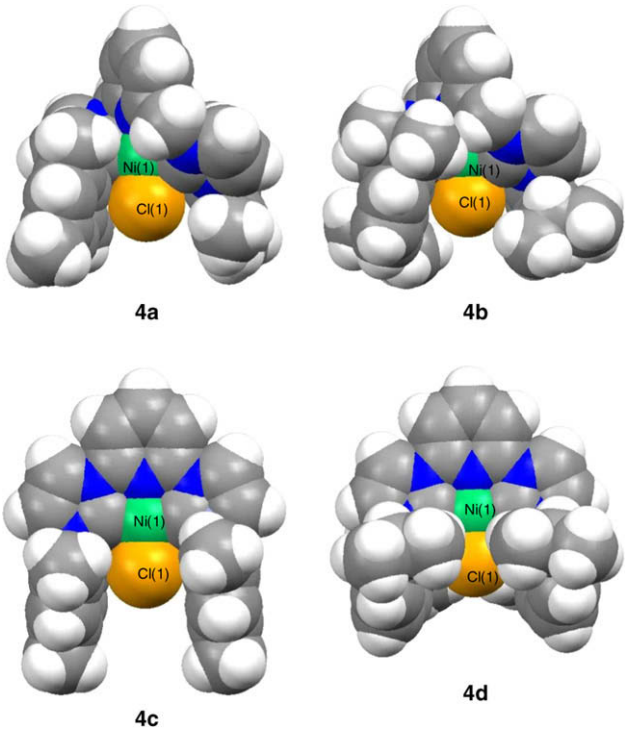


Fig. 3. Space-filling representation of the solid-state molecular structure of the complexes of **4a–d**. Hydrogen atoms, $(BF_4)^-$ anion, and the solvent molecular have been omitted for clarity.

Thus, the metal center is effectively protected by the ligand, as shown in the space-filling model of the complexes (Fig. 3).

2.3. Catalytic activity of complexes *4a–d*

To evaluate the catalytic activity of the nickel–pincer complexes **4a–d**, we first examined the Suzuki–Miyaura coupling reaction of 4-bromobenzonitrile with phenylboronic acid in the presence of 1 mol% of **4a** (Table 3). After several screenings, **4a** turned out to be an efficient catalyst for this process. Thus, using K_3PO_4 as a base, the coupling reaction proceeded efficiently at 120 °C in various solvents such as MeCN (entry 2), dioxane (entry 4), and toluene (entry 6). Decreasing the reaction temperature to 100 °C, however, led to poorer results in those solvents (entries 3, 5, and 7). Among the reaction media tested, only ^{s}BuOH produced a relatively high yield even at 100 °C, although a longer reaction time was necessary for the completion of the reaction (entries 12 and 13) [38]. Complexes **4b**, **4c**, and **4d** also showed a catalytic activity for this process. Interestingly, the reaction proceeds faster with **4c** and **4d**, which both have the five-membered metallacycle backbone, compared to **4a** and **4b**, which possess two fused six-membered rings [39]. A possible explanation for this result is that **4c** and **4d** possess a more sterically hindered environment around nickel compared to **4a** and **4b**, which could enhance the reductive elimination step during the catalytic cycle. However, the precise reaction mechanism remains to be elucidated.

Under the optimal conditions identified, several aryl bromides and chlorides with both electron-withdrawing and electron-donating groups were smoothly reacted with phenylboronic acid in the presence of 1 mol% of nickel–pincer complexes **4a–d**, producing biphenyl compounds **5–9** generally in high yields (Table 4).

Various aryl- and alkenylboronic acids also were suitable substrates for this coupling process (Table 5). Thus, an array of biphenyl or stilbene compounds were successfully obtained from this reaction in the presence of **4d**.

3. Conclusion

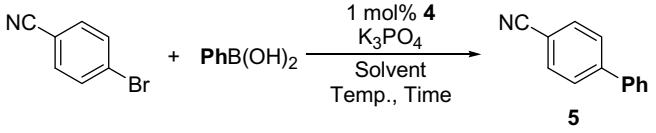
In summary, a series of novel NHC-derived nickel–pincer complexes were successfully synthesized, fully characterized by analytical and spectroscopic methods, and further identified by X-ray crystallography. These complexes were all four-coordinated cationic complexes with a slightly distorted square-planar coordination geometry, and they were successfully used as catalysts for the Suzuki–Miyaura coupling reaction of aryl bromides and chlorides with aryl- or alkenylboronic acids, producing biphenyls and stilbenes in good to high yields. It is worth noting that nickel catalysts **4a–d** we developed, which are easily prepared from inexpensive, commercially available materials, are considerably stable to both air and moisture, which makes our system highly applicable. Ongoing work is directed at elucidating the precise reaction mechanism, further evaluating the catalytic activities of these

Table 2
Selected bond length and angles of **4a–d**.

	Ni–C(carbene_1)	Ni–N	Ni–C(carbene_2)	Ni–X	angle N–Ni–Cl	angle C–Ni–C
4a	1.910(4)	1.921(3)	1.891(3)	2.1581(11)	170.31(10)	173.42(16)
4b	1.918(2)	1.950(2)	1.911(2)	2.1466(8)	178.29(7)	174.73(11)
4c	1.913(3)	1.867(2)	1.921(3)	2.1521(9)	177.05(10)	162.37(14)
4d	1.910(3)	1.858(2)	1.912(2)	2.1348(8)	178.56(8)	162.31(12)
1[a]	1.932(4)	1.862(3)	1.920(5)	2.2783(7)	176.36(11)	163.02(19)

[a] Data from Ref. [34].

Table 3
Optimization of reaction parameters.[a]



Entry	4	Solvent	Temperature (°C)/time (h)	Yield (%)[b,c]
1	**4a**	DMSO	120/1	0
2		MeCN	120/1	82
3		MeCN	100/1	31 (53)
4		1,4-Dioxane	120/1	83
5		1,4-Dioxane	100/1	31 (53)
6		Toluene	120/1	77
7		Toluene	100/1	64 (24)
8		EtOH	120/1	53 (38)
9		EtOH	100/1	26 (56)
10		BuOH	100/1	Trace (84)
11		^{s}BuOH	120/1	85
12		^{s}BuOH	100/1	70 (20)
13		^{s}BuOH	100/3	77
14	**4b**	^{s}BuOH	100/3	86
15	**4c**	^{s}BuOH	100/45 (min)	80
16	**4d**	^{s}BuOH	100/20 (min)	87
17	**1**	^{s}BuOH	100/1	88

[a] *Reagents*: 4-bromobenzonitrile (0.20 mmol), $PhB(OH)_2$ (0.60 mmol), **4** (0.0020 mmol), K_3PO_4 (0.40 mmol), and a solvent (1 mL) in a sealed tube.
[b] Isolated yield.
[c] Yield of recovered starting material in parentheses.

complexes in various coupling processes, and preparing a series of nickel–pincer complexes with various substitution patterns to disclose the correlation between the structure of nickel complexes and their catalytic activities.

4. Experimental

4.1. General procedure

^{1}H NMR spectra were recorded on JEOL JNM-AL400 (400 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are given from TMS (0 ppm) and coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, dd = double doublet, dt = double triplet, m = multiplet, and br = broad signal. ^{13}C NMR spectra were recorded on JEOL JNM-AL400 (100 MHz) spectrometer and chemical shifts (δ) are given from $^{13}CDCl_3$ (77.0 ppm) and $(^{13}CD_3)_2SO$ (39.7 ppm). Mass spectra and high resolution mass spectra were measured on JEOL JMS-DX303 and MS-AX500 instruments, respectively. Elemental analyses were performed by Yanaco CHN CORDER MT-6. IR spectra were recorded on a SHIMADZU FTIR-8400. Melting points were measured with a Yazawa micro melting point apparatus and uncorrected. Compounds **2a**–**d** were prepared according to the literature [36].

4.2. Synthesis of 2,6-bis(3-mesitylimidazolin-2-ylidene)lutidine disilver dichloride (*3a*)

A mixture of **2a** (0.50 g, 0.79 mmol), Ag_2O (0.91 g, 3.9 mmol), and powderous 4 Å molecular sieves in $ClCH_2CH_2Cl$ (8 mL) was heated to reflux for 16 h. The reaction mixture was filtered through a pad of Celite® and the filtrate was evaporated. The residue was crystallized from acetone/light petroleum to obtain a light brown solid (0.56 g, 94%). 400 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm): 1.99 (12H, s), 2.34 (6H, s), 5.52 (4H, s), 6.96 (4H, s), 6.99 (2H, d, J = 1.6 Hz), 7.18 (2H, d, J = 7.7 Hz), 7.47 (2H, d, J = 1.6 Hz), 7.75 (1H, t, J = 7.7 Hz). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 17.8, 21.1, 56.8, 121.4, 122.3, 123.0, 129.3, 134.4, 135.2, 138.0, 138.7, 139.5, 155.6.

4.3. Synthesis of 2,6-bis[3-(2,6-diisopropylphenyl)imidazolin-2-ylidene]lutidine disilver dichloride (*3b*)

A mixture of **2b** (0.20 g, 0.28 mmol), Ag_2O (0.13 g, 0.56 mmol), and powderous 4 Å molecular sieves in $ClCH_2CH_2Cl$ (10 mL) was heated to reflux for 16 h. The reaction mixture was filtered through a pad of Celite® and the filtrate was evaporated. The residue was crystallized from acetone/light petroleum to obtain a light brown solid (0.23 g, quant.). 400 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm): 1.14 (12H, d, J = 6.8 Hz), 1.23 (12H, d, J = 6.8 Hz), 2.36–2.43 (4H, m), 5.56 (4H, s), 7.05 (2H, s), 7.21–7.27 (6H, m), 7.47 (2H, t, J = 7.8 Hz), 7.52 (2H, s), 7.78 (1H, t, J = 7.6 Hz). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 24.3, 24.7, 28.3, 56.7, 121.4, 122.08, 122.13, 124.2, 130.5, 134.6, 138.6, 145.51, 145.43, 155.5.

4.4. Synthesis of 2,6-bis(3-mesitylimidazolin-2-ylidene)pyridine disilver dichloride (*3c*)

A mixture of **2c** (1.2 g, 2.0 mmol), Ag_2O (0.93 g, 4.0 mmol), and powderous 4 Å molecular sieves in $ClCH_2CH_2Cl$ (15 mL) was heated to reflux for 16 h. The reaction mixture was filtered through a pad of Celite® and the filtrate was evaporated. The residue was crystallized from acetone/light petroleum to obtain an off-white solid (1.2 g, 85%). 400 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm): 2.01 (12H, s), 2.36 (6H, s), 7.00 (4H, s), 7.16 (2H, s), 8.12–8.31 (5H, br). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 17.6, 20.8, 115.2, 121.0, 123.6, 129.0, 134.0, 135.0, 139.1, 142.5, 149.2.

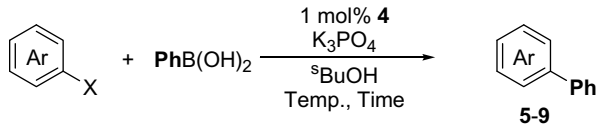
4.5. Synthesis of 2,6-bis[3-(2,6-diisopropylphenyl)imidazolin-2-ylidene]pyridine disilver dichloride (*3d*)

A mixture of **2d** (1.4 g, 2.0 mmol), Ag_2O (0.93 g, 4.0 mmol), and powderous 4 Å molecular sieves in $ClCH_2CH_2Cl$ (15 mL) was heated to reflux for 16 h. The reaction mixture was filtered through a pad of Celite® and the filtrate was evaporated. The residue was crystallized from acetone/light petroleum to obtain a light brown solid (1.4 g, 87%). 400 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm): 1.17 (12H, d, J = 6.8 Hz), 1.29 (12H, d, J = 6.8 Hz), 2.50 (4H, sept, J = 6.8 Hz), 7.23 (2H, d, J = 1.6 Hz), 7.31 (4H, d, J = 7.8 Hz), 7.52 (2H, t, J = 7.8 Hz), 8.17–8.23 (3H, m), 8.33 (2H, br). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 24.2, 24.4, 28.1, 115.5, 120.8, 124.1, 124.9, 130.5, 134.4, 142.6, 145.2, 149.7, 172.5.

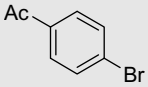
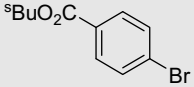
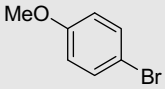
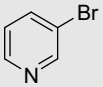
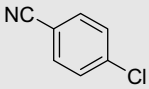
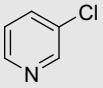
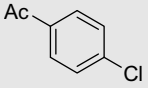
4.6. Synthesis of [2,6-bis(3-mesitylimidazolin-2-ylidene)lutidine]chloronickel tetrafluoroborate (*4a*)

To a suspension of $NiCl_2$(DME) (0.091 g, 0.41 mmol) in CH_2Cl_2 (120 mL) was added slowly a solution of **3a** (0.30 g, 0.39 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred at room temperature for 24 h. To the mixture was added a solution of $AgBF_4$ (0.080 g, 0.41 mmol) in CH_2Cl_2 (30 mL) and stirred at room temperature for 16 h. The reaction mixture was filtered through a pad of Celite® and the filtrate was evaporated. The resulting solid was crystallized from CH_2Cl_2/light petroleum to obtain an yellow solid (0.26 g, quant.). The product was purified by recrystallization from CH_2Cl_2/light petroleum to give yellow needles. M.p.: > 250 °C. 400 MHz ^{1}H NMR (DMSO-d_6) δ (ppm): 1.85 (6H, s), 2.05 (6H, s), 2.25 (6H, s), 5.82 (2H, d, J = 15.8 Hz), 6.15 (2 H, d, J = 15.8 Hz), 6.84 (2H, s), 6.84 (2H, s), 7.01 (2H, s), 7.20 (2H, s), 7.81 (2H, d, J = 7.1 Hz), 8.14 (1H, t, J = 7.1 Hz). 100 MHz ^{13}C NMR (DMSO-d_6) δ (ppm): 17.7, 18.1, 20.5, 53.6, 121.8, 124.6, 125.2, 128.5, 128.7,

Table 4
Suzuki–Miyaura coupling of aryl halides with phenylboronic acid.[a]



5-9

Entry	Ar–X	4	Temperature (°C)/time (h)	Product	Yield (%)[b,c]
1		**4a**	120/2	**6**	83
2		**4b**			75
3		**4c**	120/2		76
4		**4d**	100/3 100/2		75
5		**4a**	120/3	**7**	64 (27)
6		**4b**	120/4		63
7		**4c**	100/2		50
8		**4d**	100/2		73 (16)
9		**4a**	120/2	**8**	67
10		**4b**	120/2		61
11		**4c**	120/2		57
12		**4d**	120/1		38
13		**4a**	100/5	**9**	85
14		**4b**	100/5		85
15		**4c**	100/2		97
16		**4d**	100/1		94
17		**4a**	100/3	**5**	71
18		**4b**	100/3		77
19		**4c**	100/2		74
20		**4d**	100/2		67
21		**4a**	100/5	**9**	79
22		**4b**	100/5		76
23		**4c**	100/3		79
24		**4d**	100/3		77
25		**4a**	120/4	**6**	86
26		**4b**	120/4		51
27		**4c**	120/4		76
28		**4d**	120/3		48

[a] *Reagents*: an aryl halide (0.20 mmol), $PhB(OH)_2$ (0.60 mmol), **4** (0.0020 mmol), K_3PO_4 (0.40 mmol), and ^sBuOH (1 mL) in a sealed tube.
[b] Isolated yield.
[c] Yield of recovered starting material in parentheses.

133.3, 134.6, 135.3, 137.4, 141.0, 156.0, 164.6. Anal. Calc. for $C_{31}H_{33}BClF_4N_5Ni$: C, 56.70; H, 5.07; N, 10.67. Found: C, 56.60; H, 5.09; N, 10.63%.

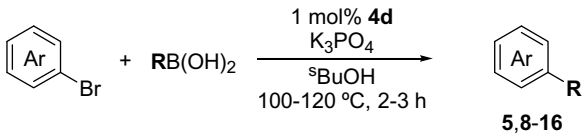
*4.7. Synthesis of {2,6-bis[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]lutidine}chloronickel tetrafluoroborate (**4b**)*

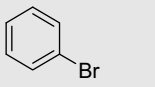
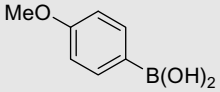
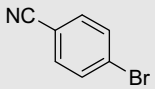
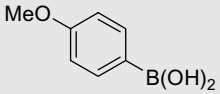
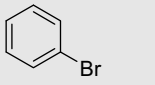
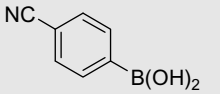
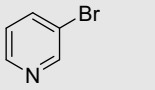
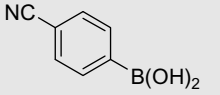
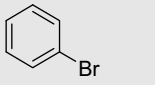
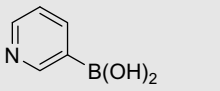
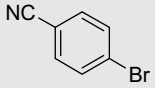
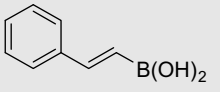
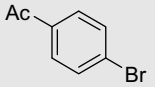
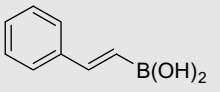
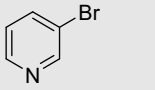
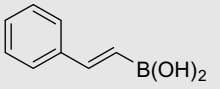
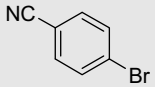
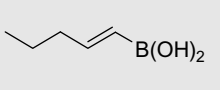
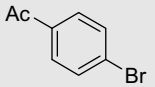
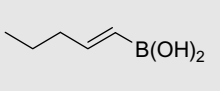
To a suspension of $NiCl_2$(DME) (0.079 g, 0.36 mmol) in CH_2Cl_2 (120 mL) was added slowly a solution of **3b** (0.29 g, 0.34 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred at room temperature for 24 h. To the mixture was added $AgBF_4$ (0.070 g, 0.36 mmol) and stirred at room temperature for 16 h. The reaction mixture was filtered through a pad of Celite® and the filtrate was evaporated. The resulting solid was crystallized from CH_2Cl_2/light petroleum to obtain an yellow solid (0.20 g, 78%). The product was purified by recrystallization from CH_2Cl_2/light petroleum to give yellow needles. M.p.: > 250 °C. 400 MHz ^{1}H NMR (DMSO-d_6) δ (ppm): 0.71 (6H, d, J = 6.9 Hz), 0.99 (6H, d, J = 6.9 Hz), 1.02 (6H, d, J = 6.9 Hz), 1.55 (6H, d, J = 6.9 Hz), 2.08 (2H, sept, J = 6.9 Hz), 2.32 (2H, sept, J = 6.9 Hz), 5.85 (2H, d, J = 15.6 Hz), 6.04 (2H, d, J = 15.6 Hz), 7.16 (2H, d, J = 7.9 Hz), 7.28–7.30 (4H, m), 7.38 (2H, t, J = 7.9 Hz), 7.68 (2H, d, J = 1.6 Hz), 7.85 (2H, d, J = 7.7 Hz), 8.20 (1H, t, J = 7.7 Hz). 100 MHz ^{13}C NMR (DMSO-d_6) δ (ppm): 22.2, 23.7, 24.1, 25.3, 28.1, 28.2, 53.5, 121.5, 123.0, 123.5, 125.1, 126.4, 129.3, 134.9, 141.1, 144.1, 145.6, 155.7, 164.3. Anal. Calc. for $C_{37}H_{45}BClF_4N_5Ni$: C, 59.99; H, 6.12; N, 9.46. Found: C, 59.74; H, 6.24; N, 9.40%.

*4.8. Synthesis of [2,6-bis(3-mesitylimidazolin-2-ylidene)pyridine]chloronickel tetrafluoroborate (**4c**)*

To a solution of $NiCl_2$(DME) (0.095 g, 0.43 mmol) in CH_2Cl_2 (120 mL) was added slowly a solution of **3c** (0.30 g, 0.41 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred at room temperature for 24 h. To the mixture was added $AgBF_4$ (0.083 g, 0.43 mmol) and stirred at room temperature for 16 h. The reaction mixture was filtered through a pad of Celite® and the filtrate was evaporated. The resulting solid was crystallized from CH_2Cl_2/light petroleum to obtain an yellow solid (0.26 g, 99%). The product was purified by recrystallization from CH_2Cl_2/light petroleum to give yellow needles. M.p.: > 250 °C. 400 MHz ^{1}H NMR (DMSO-d_6) δ (ppm): 1.99 (12H, s), 2.21 (6H, s), 6.87 (4H, s), 7.53 (2H, s), 7.99 (2H, d, J = 7.8 Hz), 8.54 (1H, t, J = 7.8 Hz), 8.67 (2H, s). 100 MHz ^{13}C NMR (DMSO-d_6) δ (ppm): 17.3, 20.5, 108.2, 117.5, 127.0, 128.2, 129.0,

Table 5
Suzuki–Miyaura coupling of aryl halides with various boronic acids.[a]



Entry	Ar–X	RB(OH)$_2$	Product	Yield (%)[b]
1			**8**	69
2			**10**	77
3			**5**	49
4			**11**	42
5			**9**	29
6			**12**	82[d]
7			**13**	65[d]
8			**14**	48[d]
9[c]			**15**	76[d]
10			**16**	80[d]

[a] *Reagents*: an aryl bromide (0.10 mmol), **R**B(OH)$_2$ (0.30 mmol), **4d** (0.0010 mmol), K_3PO_4 (0.20 mmol), and ^{s}BuOH (0.5 mL) in a sealed tube.
[b] Isolated yield.
[c] 1,4-Dioxane was used instead of ^{s}BuOH.
[d] *E*-Isomer exclusively formed.

133.5, 133.7, 137.9, 146.1, 150.3. Anal. Calc. for $C_{29}H_{29}BClF_4N_5Ni \cdot H_2O$: C, 53.87; H, 4.83; N, 10.83, Found: C, 54.11; H, 4.80; N, 10.89%.

4.9. Synthesis of {2,6-bis[3-(2,6-diisopropylphenyl)imidazol-2-ylidene]pyridine}chloronickel tetrafluoroborate (*4d*)

To a suspension of $NiCl_2$(DME) (0.085 g, 0.39 mmol) in CH_2Cl_2 (120 mL) was added slowly a solution of **3d** (0.30 g, 0.37 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred at room temperature for 24 h. To the mixture was added $AgBF_4$ (0.075 g, 0.39 mmol) and stirred at room temperature for 16 h. The reaction mixture was filtered through a pad of Celite® and the filtrate was evaporated. The resulting solid was crystallized from CH_2Cl_2/light petroleum to obtain an yellow solid (0.23 g, 88%). The product was purified by recrystallization from CH_2Cl_2/light petroleum to give yellow needles. M.p.: > 250 °C. 400 MHz ^{1}H NMR (DMSO-d_6) δ (ppm): 1.04 (12H, d, J = 6.8 Hz), 1.13 (12H, d, J = 6.8 Hz), 2.42–2.49 (4H, m), 7.14 (4H, d, J = 7.7 Hz), 7.32 (2H, t, J = 7.7 Hz), 7.69 (2H, d, J = 1.6 Hz), 7.93 (2H, d, J = 8.4 Hz), 8.53–8.56 (3H, m). 100 MHz ^{13}C NMR (DMSO-d_6) δ (ppm): 22.9, 24.1, 27.9, 108.5, 117.1, 123.1, 128.2, 129.7, 133.2, 144.0, 146.2, 150.6, 162.4. Anal. Calc. for $C_{35}H_{41}BClF_4N_5Ni$: C, 58.98; H, 5.80; N, 9.83, Found: C, 58.63; H, 6.00; N, 9.55%.

4.10. X-ray diffraction studies

X-ray diffraction data of the crystal were collected with a Rigaku Saturn CCD diffractometer using a graphite monochromated Mo Kα (λ = 0.71070 Å) at −100 °C. The data were corrected for Lorentz and polarization effects, and a numerical absorption correction was applied using a refined crystal shape. The structure was solved by direct methods (SIR 2004) [40] and expanded using Fourier techniques. All data were refined by full-matrix least-squares minimizations of $\sum(F_o - F_c)^2$ with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were assigned based on expected geometry and a riding model was used during the refinement process. A summary of the crystallographic data is given in Table 1.

4.11. Typical procedure for the nickel-catalyzed Suzuki–Miyaura coupling reactions (Table 3, entry 13)

A mixture of 4-bromobenzonitrile (36.4 mg, 0.20 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), **4a** (1.3 mg, 0.0020 mmol), K_3PO_4 (86.0 mg, 0.40 mmol), and ^{s}BuOH (1 mL) was heated to 100 °C for 3 h. After cooling to room temperature, the reaction mixture was treated with H_2O (15 mL) and extracted with AcOEt (15 mL × 3). The combined extracts were washed with saturated aqueous NaCl (15 mL × 3) and the organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane/AcOEt (19:1) as an eluent to obtain **5** as a colorless solid (27.6 mg, 77%).

4-Cyanobiphenyl (***5***): M.p. 85–86 °C (colorless prisms from hexane/AcOEt, lit. [41] m.p. 84–86 °C. IR ν (film) cm^{-1}: 2228. 400 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm): 7.40–7.50 (3H, m), 7.58 (2H, dd, J = 7.2, 1.2 Hz), 7.66–7.73 (4H, m). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 110.8, 118.9, 127.1, 127.6, 128.6, 129.0, 132.5, 139.0, 145.5. EI-MS m/z (relative intensity): 179 (M^+, 100%). HRMS Calcd. for $C_{13}H_9N$: 179.0735; found: 179.0739.

4-Acetylbiphenyl (***6***): M.p. 121–122 °C (colorless needles from hexane/AcOEt, lit. [41] m.p. 117–119 °C). IR ν (film) cm^{-1}: 1680. 400 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm): 2.64 (3H, s), 7.40 (1H, t, J = 7.8 Hz), 7.47 (2H, t, J = 7.8 Hz), 7.62 (2H, d, J = 7.8 Hz), 7.68 (2H, d, J = 8.4 Hz), 8.03 (2H, d, J = 8.4 Hz). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 26.9, 127.26, 127.31, 128.3, 128.96, 129.00, 135.9, 139.9, 145.8, 197.7. EI-MS m/z (relative intensity): 196 (M^+, 64%), 181 (M^+−15, 100%). HRMS Calcd. for $C_{14}H_{12}O$: 196.0888; found: 196.0884.

4-sec-Butoxycarbonylbiphenyl (***7***): IR ν (film) cm^{-1}: 1279, 1713. 400 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm): 0.99 (3H, t, J = 6.3 Hz), 1.35 (3H, d, J = 6.3 Hz), 1.63–1.82 (2H, m), 5.12 (1H, sext, J = 6.3 Hz), 7.38 (1H, tt, J = 7.4, 1.6 Hz), 7.46 (2H, t, J = 7.4 Hz), 7.60–7.66 (4H, m), 8.11 (2H, dt, J = 8.4, 1.8 Hz). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 9.8, 19.7, 29.0, 72.9, 126.9, 127.2, 128.0, 128.8, 129.6, 129.9, 140.0, 145.3, 166.0. EI-MS m/z (relative intensity): 254 (M^+, 37%), 225 (M^+−29, 2%), 198 (M^+−56, 100%),

181 (M^+−73, 61%). HRMS Calcd. for $C_{17}H_{18}O_2$: 254.1307; found: 254.1306.

4-Methoxybiphenyl (***8***): M.p. 86–87 °C (colorless prisms from hexane/AcOEt, lit. [41] m.p. 85–87 °C). IR ν (film) cm^{-1}: 1609, 1036. 400 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm): 3.83 (3H, s), 6.96 (2H, d, J = 8.8 Hz), 7.29 (1H, t, J = 7.5 Hz), 7.40 (2H, t, J = 7.5 Hz), 7.51–7.55 (4H, m). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 55.3, 114.1, 126.56, 126.64, 128.0, 128.6, 133.7, 140.7, 159.0. EI-MS *m/z* (relative intensity): 184 (M^+, 100%), 169 (M^+−15, 43%), 141 (M^+−43, 26%). HRMS Calcd. for $C_{13}H_{12}O$: 184.0888; found: 184.0886.

3-Phenylpyridine (***9***): IR ν (neat) cm^{-1}: 3396. 400 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm): 7.35–7.43 (2H, m), 7.48 (2H, t, J = 7.4 Hz), 7.58 (2H, d, J = 7.4 Hz), 7.87 (1H, dt, J = 7.8, 1.9 Hz), 8.59 (1H, d, J = 4.0 Hz), 8.85 (1H, s). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 123.4, 127.1, 128.0, 129.0, 134.2, 136.5, 137.7, 148.2, 148.3. EI-MS *m/z* (relative intensity): 155 (M^+, 100%). HRMS Calcd. for $C_{11}H_9N$: 155.0735; found: 155.0738.

4-Cyano-4′-methoxybiphenyl (***10***): M.p. 101–102 °C (colorless plates from hexane/AcOEt, lit. [42] m.p. 103–104 °C). IR ν (film) cm^{-1}: 1038, 1607, 2224. 400 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm): 3.86 (3H, s), 7.00 (2H, d, J = 8.8 Hz), 7.53 (2H, d, J = 8.8 Hz), 7.63 (2H, d, J = 8.0 Hz), 7.69 (2H, d, J = 8.0 Hz). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 55.4, 110.1, 114.6, 119.1, 127.1, 128.3, 131.5, 132.6, 145.2, 160.2. EI-MS *m/z* (relative intensity): 209 (M^+, 100%), 194 (M^+−15, 29%), 166 (M^+−43, 20%). HRMS Calcd. for $C_{14}H_{11}NO$: 209.0841; found: 209.0826.

3-(4-Cyanophenyl)pyridine (***11***): M.p. 94–96 °C (colorless prisms from hexane/AcOEt, lit. [43] m.p. 95–96 °C). IR ν (film) cm^{-1}: 2226, 3358. 400 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm): 7.42 (1H, t, J = 6.7 Hz), 7.69 (2H, d, J = 8.2 Hz), 7.78 (2H, d, J = 8.2 Hz), 7.89 (1H, d, J = 6.7 Hz), 8.67 (1H, s), 8.86 (1H, s). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 111.9, 118.5, 123.7, 127.7, 132.8, 134.4, 134.7, 142.2, 148.1, 149.6. EI-MS *m/z* (relative intensity): 180 (M^+, 100%). HRMS Calcd. for $C_{12}H_8N_2$: 180.0688; found: 180.0670.

(E)-4-Cyanostilbene (***12***): M.p. 111–113 °C (colorless plates from hexane/AcOEt, lit. [44] m.p. 114–116 °C). IR ν (film) cm^{-1}: 1601, 2226. 400 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm): 7.07 (1H, d, J = 16.4 Hz), 7.20 (1H, d, J = 16.4 Hz), 7.31 (1H, t, J = 7.5 Hz), 7.38 (2H, t, J = 7.5 Hz), 7.52 (2H, d, J = 7.5 Hz), 7.56 (2H, d, J = 8.4 Hz), 7.62 (2H, d, J = 8.4 Hz). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 110.5, 118.9, 126.6, 126.7, 126.8, 128.5, 128.7, 132.3, 132.4, 136.1, 141.7. EI-MS *m/z* (relative intensity): 205 (M^+, 100%). HRMS Calcd. for $C_{15}H_{11}N$: 205.0892; found: 205.0903.

(E)-4-Acetylstilbene (***13***): M.p. 139–142 °C (colorless prisms from hexane/AcOEt, lit. [44] m.p. 141–144 °C). IR ν (film) cm^{-1}: 1601, 1678. 400 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm): 2.60 (3H, s), 7.12 (1H, d, J = 16.4 Hz), 7.22 (1H, d, J = 16.4 Hz), 7.29 (1H, t, J = 7.1 Hz), 7.37 (2H, t, J = 7.1 Hz), 7.53 (2H, dd, J = 7.1, 1.2 Hz), 7.58 (2H, d, J = 8.2 Hz), 7.94 (2H, d, J 8 8.2 Hz). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 26.6, 126.4, 126.7, 127.3, 128.2, 128.7, 128.8, 131.4, 135.8, 136.6, 141.9, 197.3. EI-MS *m/z* (relative intensity): 222 (M^+, 99%), 207 (M^+−15, 100%). HRMS Calcd. for $C_{16}H_{14}O$: 222.1045; found: 222.1060.

(E)-1-Phenyl-2-(3-pyridyl)ethylene (***14***): IR ν (film) cm^{-1}: 3393. 400 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm): 7.06 (1H, d, J = 16.4 Hz), 7.16 (1H, d, J = 16.4 Hz), 7.25–7.31 (2H, m), 7.37 (2H, t, J 8 7.2 Hz), 7.52 (2H, d, J = 7.2 Hz), 7.82 (1H, d, J = 8.0 Hz), 8.48 (1H, d, J = 4.0 Hz), 8.72 (1H, s). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 123.4, 124.8, 126.6, 128.1, 128.7 (2 carbons), 130.7, 132.6, 132.9, 136.5, 148.4. EI-MS *m/z* (relative intensity): 181 (M^+, 59%), 180 (M^+−1, 100%). HRMS Calcd. for $C_{13}H_{11}N$: 181.0892; found: 181.0881.

1-(E)-Pentenyl-4-benzonitrile (***15***): IR ν (film) cm^{-1}: 1651, 2224. 400 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm): 0.96 (3H, t, J = 7.2 Hz), 1.51 (2H, sext, J = 7.2 Hz), 2.20–2.25 (2H, m), 6.33–6.42 (2H, m), 7.40 (2H, d, J = 8.4 Hz), 7.56 (2H, d, J = 8.4 Hz). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 13.8, 22.3, 35.2, 109.8, 119.1, 126.3, 128.5, 132.2, 135.2, 142.3. EI-MS *m/z* (relative intensity): 171 (M^+−15, 60%), 142 (M^+−29, 74%), 129 (M^+−42, 100%), 115 (M^+−56, 19%). HRMS Calcd. for $C_{12}H_{13}N$: 171.1048; found: 171.1029.

1-(E)-Pentenyl-4-acetophenone (***16***): IR ν (film) cm^{-1}: 1603, 1682. 400 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm): 0.96 (3H, t, J = 7.2 Hz), 1.52 (2H, sext, J = 7.2 Hz), 2.22 (2H, q, J = 7.2 Hz), 2.58 (3H, s), 6.35–6.44 (2H, m), 7.41 (2H, d, J 8 8.4 Hz), 7.88 (2H, d, J = 8.4 Hz). 100 MHz ^{13}C NMR ($CDCl_3$/TMS) δ (ppm): 13.8, 22.4, 26.6, 35.3, 125.8, 128.7, 129.0, 134.2, 135.3, 142.6, 197.5. EI-MS *m/z* (relative intensity): 188 (M^+, 100%), 173 (M^+−15, 88%), 146 (M^+−42, 19%), 131 (M^+−57, 19%), 43 (M^+−145, 36%). HRMS Calcd. for $C_{13}H_{16}O$: 188.1201; found: 188.1208.

Acknowledgement

This work was supported in part by a Grant-in-Aid for JSPS Fellows from the Japan Society for the Promotion of Science (JSPS).

Appendix A. Supplementary material

CCDC 701129, 701130, 701131 and 701132 contains the supplementary crystallographic data for **4a**, **4b**, **4c** and **4d**. 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.2008.11.003.

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