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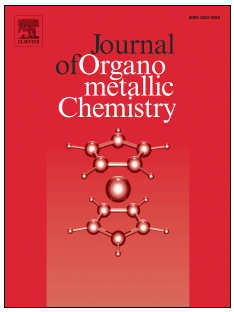

Synthesis and catalytic activity of nickel(II) complexes of CNC pincer-type *N*-heterocyclic carbene ligands

Shuchao Wang, Fang Ren, Yuping Qiu, Meiming Luo

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Graphical abstract: synopsis

A new type of nickel(II) complexes containing CNC pincer-type bis-NHC ligands with an anionic diarylamindo backbone has been synthesized and characterized.

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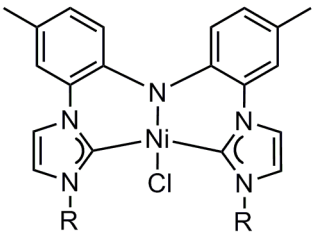

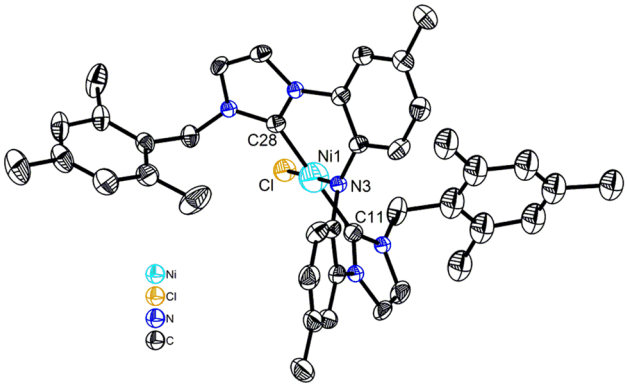

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Synthesis and catalytic activity of nickel(II) complexes of CNC pincer-type *N*-heterocyclic carbene ligands

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Abstract

Air- and moisture-stable nickel(II) complexes **2a-c** of CNC pincer-type *N*-heterocyclic carbene ligands have been prepared from the corresponding imidazolium salts by carbene-transfer reaction of a silver-NHC complex with $Ni(DME)Cl_2$ (DME = dimethoxylethane). Pincer complexes **2a-c** are characterized by mass and NMR spectroscopy. The structure of **2a** is also identified by X-ray diffraction analysis. Pincer complex **2a** has been shown to be active catalyst for the Suzuki coupling reactions.

Keywords

Nickel complex; pincer-type ligand; *N*-heterocyclic carbene; Ni(II)-*N*-heterocyclic carbene complex; Suzuki reaction

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1. Introduction

Transition metal-catalyzed Suzuki coupling reactions represent a powerful synthetic method for the synthesis of biaryl compounds [1] which are important components in materials science, natural products, and medicines [2]. The easy availability of boron reagents, broad functional group tolerance, and general applicability of the reaction contributed to its increasing importance in both academic research and industrial production [3]. In this field, the catalysts are largely dominated by palladium and nickel complexes due to their high catalytic activity for a wide range of substrates and high functional group tolerance [4]. However, in the majority of cases, these common catalysts are hampered by (1) the high cost of palladium and related ligands; (2) most of the so far reported nickel catalysts use nickel(0) such as $Ni(COD)_2$, $Ni(PPh_3)_4$, etc. as catalysts, and such nickel sources would be difficult to handle because of their toxicity and thermal instability [5]; (3) nickel (II) complexes with expensive and air-sensitive phosphine ligands [6,7] or $AgBF_4$ for the necessary ion-exchange [8]; (4) a high loading of the nickel complex (usually 3-10 mol% is required) [9], which limits their use in industrial applications. Therefore, development of inexpensive, efficient and practical Ni-based catalysts for Suzuki coupling reactions is desirable.

During the past decades, nickel-pincer complexes based on CNC [8,10], NNN [11], PNP [12], and PCP [13] ligands have attracted considerable attention, and been widely employed as versatile active catalysts in organic synthesis. In addition, a pincer ligand with one or two *N*-heterocyclic carbene (NHC) donors would combine the unique properties of the NHC ligand and amplify the high thermal stability of pincer catalysts. For these reasons, much effort has been devoted to the synthesis and structural characterization of nickel-pincer complexes containing NHC ligands. However, nickel complexes of CNC pincer-type bis-NHC ligands have rarely been studied. So far, only a few CNC-type pincer complexes of

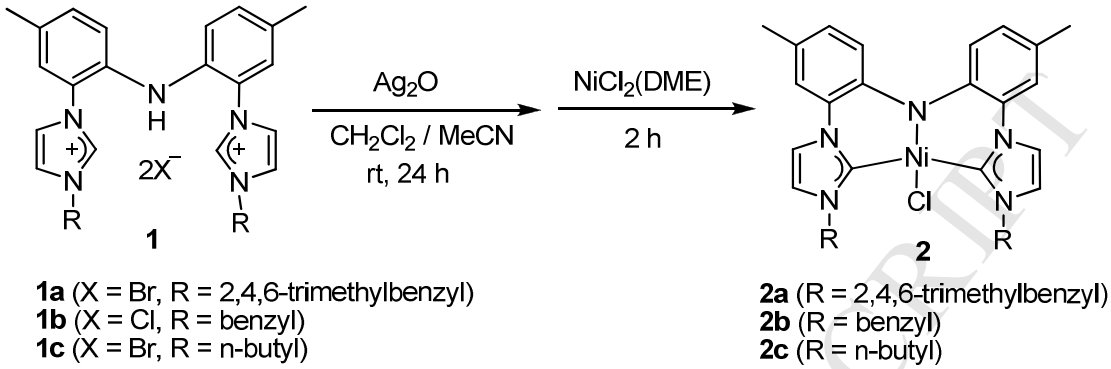
nickel with pyridine backbone have been reported recently [8,10]. Although palladium and rhodium complexes of CNC pincer-type bis-NHC ligands with an anionic amido backbone have been reported exhibiting unique structural feature and excellent catalytic activity [14], nickel complex of CNC pincer-type bis-NHC ligands with an anionic amido backbone is still unprecedented. We previously reported palladium(II) complexes of CNC pincer-type bis-NHC ligands with an anionic diarylamido backbone and their high catalytic activity in Suzuki coupling reactions [14c]. As a continuation, here in this paper we describe the synthesis and structural characterization of nickel(II) complexes containing CNC pincer-type bis-NHC ligands with an anionic amido backbone. These pincer nickel complexes have been found to be highly efficient catalysts for the Suzuki coupling reactions.

2. Results and discussion

2.1. Preparation of bis-NHC-Ni(II) complexes

Imidazolium salts **1a-c** were prepared by our previously reported procedures [14c]. Like the synthesis of palladium(II) complexes [14c], complexes **2a-c** were successfully obtained by the carbene-transfer reaction of the corresponding silver-NHC complex with $Ni(DME)Cl_2$ (DME = dimethoxylethane) (Scheme 1). These complexes were isolated as air- and moisture-stable purple crystalline solids. The formation of **2a-c** is confirmed by comparing their ^{1}H and ^{13}CNMR spectra with those of imidazolium salt precursors **1a-c**. The absence of the NH and the NC(H)N proton resonances in the ^{1}H NMR spectra demonstrates that the ligand is coordinated to nickel in a monoanionic bis-NHC form. Notably, the signals for the carbene carbon atoms of **2a-c** in the ^{13}C NMR spectra appear at 161.9-160.9 ppm, which are characteristic peaks for nickel-carbene complexes. Usually the ^{13}C chemical shifts of known

Ni-NHC complexes appear in the range of 149-171 ppm depending on the ancillary ligands [15].



Scheme 1. Synthesis of complexes 2a-c.

Purple single crystals of complex **2a** suitable for an X-ray diffraction study were grown from a solution of CH_2Cl_2 and ethyl acetate.[16] The molecular structure of complex **2a** is depicted in Figure 1. The central Ni(II) ion is coordinated by the amido nitrogen, two carbene atoms and one chloride ion, forming two six-membered chelate rings. The geometry about Ni is approximately square planar, with the C28-Ni1-C11 angle of 172.8(2)° being a consequence of the chelate constraint. N3, Ni1, and Cl lie on a crystallographic axis of symmetry. The two aromatic rings in **2a** are distinctly nonparallel, with an angle of ca. 67.04°. The twist in the chelate backbone presumably arises from repulsion between the two *ortho* hydrogens on the aromatic rings. ^{1}H NMR spectra showed that the benzylic CH_2 protons are diastereotopic in solution, indicating that the two *ortho* hydrogens prevent ligand twisting in solution at room temperature. In addition, the NHC rings are not coplanar with the aryl backbone (two aromatic rings) and are all tilted by 25°. The nickel-carbene distances (Ni1−C11 = 1.899(5) Å and (Ni1−C28 = 1.902(5) Å) are very similar to the Ni−$C_{carbene}$ bond distances found for pincer complexes with two *trans*-positioned imidazolin-2-ylidene donor groups [8a,10a]. The

Ni1−N3 bond distance is 1.891(4) Å which is similar to the distance observed in NNN and PNP pincer-type nickel (II) complexes based on a diarylamido backbone [11a,12a].

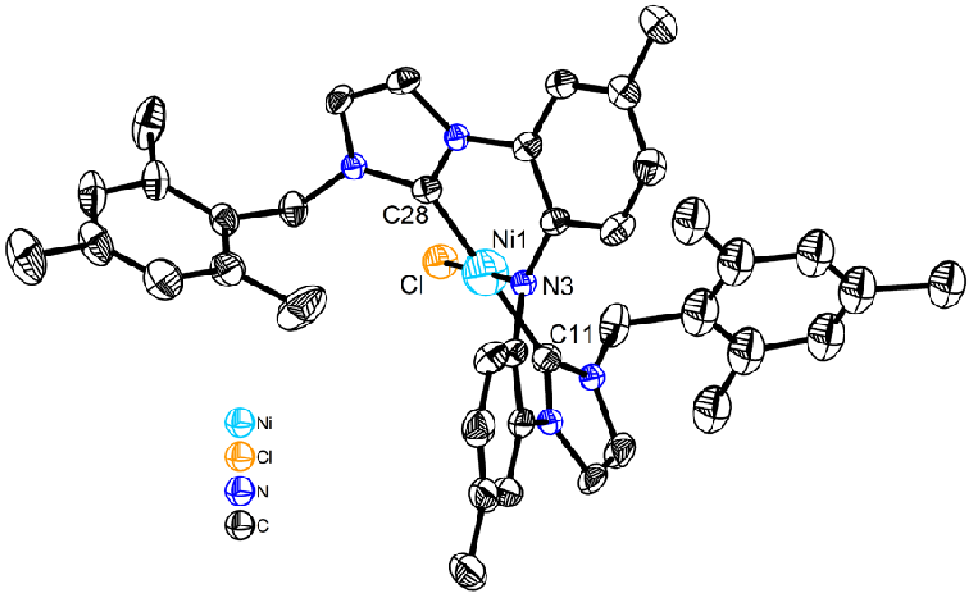


Figure1. Molecular structure of complex **2a**, showing 30% probability displacement ellipsoids. Selected interatomic distances (Å) and angles (deg): Ni1−N3 = 1.891(4), Ni1−C11 = 1.899(5), Ni1−C28 = 1.902(5), Ni1−Cl = 2.2178(14), N3−Ni1−Cl = 179.43(13), C11−Ni1−C28 = 172.8(2).

2.2. Catalytic Suzuki coupling reactions

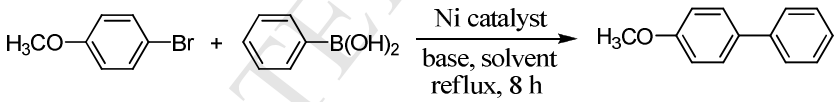
To evaluate the catalytic activity of complexes **2a-c** in the Suzuki coupling reactions, the reaction of 4-bromoanisole with phenylboronic acid was initially chosen to optimize the reaction conditions. The results listed in Table 1 showed that the use of Ni(DME)Cl_2 alone gave essentially no coupling product (entry 1). The combination of Ni(DME)Cl_2 and pincer-type imidazolium salt **1a** did not exhibit any catalytic activity (entry 2). Fortunately, 4-bromoanisole was successfully reacted with phenylboronic acid in dioxane in the presence of 2 mol% complex **2a** together with potassium phosphate at reflux to afford the desired product in 95% yield (entry 3). When the amount of catalyst loading was reduced to 1 mol%, the yield was not significantly changed (entry 4). However, further decrease of the catalyst

loading to 0.5 mol% led to 78% coupling product yield (entry 5). These data illustrated that 1 mol% of catalyst **2a** is sufficient for the coupling of 4-bromoanisole with phenylboronic acid.

At this catalyst loading, complexes **2b** and **2c** catalyzed the couplings to afford the biphenyls in 77% and 63%, respectively (entries 6 and 7). We next examined the effect of the solvent, and found that the choice of solvent was very critical, as the reaction in dioxane was much more efficient than those in toluene, DMSO and THF (entries 8-10). Subsequently, the reaction was investigated in the presence of different bases. The results showed that among the bases explored, K_3PO_4 is the most effective, and others such as Na_2CO_3, K_2CO_3, Cs_2CO_3 and KO^{t}Bu led to lower yields (entries 11-14). Thus, the optimized reaction conditions for the present corss-coupling of 4-bromoanisole with phenylboronic acid involve the use of 1.0 mol% of **2a** as the catalyst, K_3PO_4 as the base, dioxane as the solvent and at reflux.

Table 1.

Optimization of reaction conditions in Suzuki coupling reactions catalyzed by complexes **2a-c**[a]



Entry	Catalyst (mol%)	Solvent	Base	Yield (%)[b]
1	$Ni(DME)Cl_2$ (2)	dioxane	K_3PO_4	0
2	**1a** (2) + $Ni(DME)Cl_2$ (2)	dioxane	K_3PO_4	trace
3	**2a** (2)	dioxane	K_3PO_4	95
4	**2a** (1)	dioxane	K_3PO_4	95
5	**2a** (0.5)	dioxane	K_3PO_4	78
6	**2b** (1)	dioxane	K_3PO_4	77
7	**2c** (1)	dioxane	K_3PO_4	63
8	**2a** (1)	toluene	K_3PO_4	64
9	**2a** (1)	DMSO	K_3PO_4	trace
10	**2a** (1)	THF	K_3PO_4	0

11	**2a** (1)	dioxane	Na_2CO_3	59
12	**2a** (1)	dioxane	K_2CO_3	49
13	**2a** (1)	dioxane	Cs_2CO_3	0
14	**2a** (1)	dioxane	KO^tBu	44

[a] Reaction conditions: 0.5 mmol of 4-bromoanisole, 0.75 mmol of phenylboronic acid, 2.0 mmol of base, 4.0 mL of solvent, reflux, under N_2.

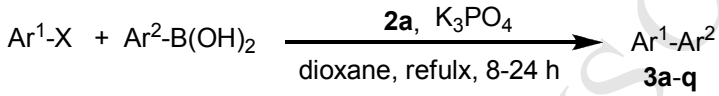
[b] Isolated by silica gel column chromatography and based on 4-bromoanisole.

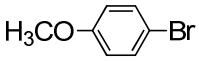
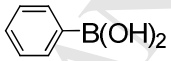
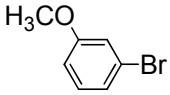
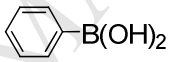
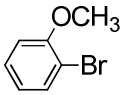
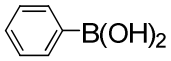
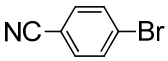
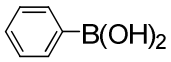
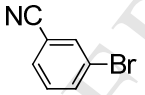
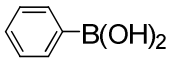
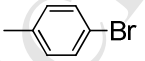
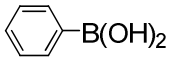
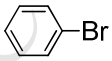
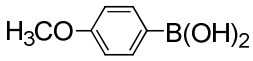
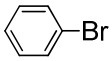
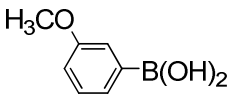
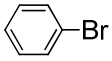
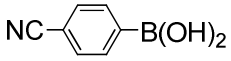
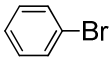
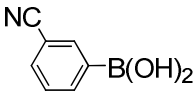
Having defined the optimized reaction conditions, we then attempted the cross-coupling reactions of various aryl bromides with arylboronic acids under the optimal reaction conditions. As shown in Table 2, most of the substrates with a variety of substituents afforded the products in good to excellent yields. Bromobenzenes bearing electron-donating groups such as methoxy (entries 1-3 and 13), methyl (entries 6 and 14) and amino (entry 15) reacted with arylboronic acids smoothly giving the corresponding cross-coupling products in 86-95% yields. *Ortho* methoxy-substituted aryl bromides (entry 3) gave lower yields as compared to *para*- and *meta*-substituted analogues (entries 1 and 2, respectively), probably due to the steric hindrance. Aryl bromides with electron-withdrawing cyano (entries 4 and 5), fluoro (entry 16) and acetyl (entry 17) could be transformed to biaryl products in 85-91% yields. Coupling reactions of phenylboronic acid (entries 1-6) and arylboronic acids containing electron-donating groups (entries 7, 8 and 13-19) with aryl bromides gave products in high yields. Arylboronic acids with electron-withdrawing *para*- and *meta*-cynao group gave products in slightly lower yields of 78% and 80%, respectively (entries 9 and 10). The reactions involving 1-naphthylboronic acid and its analogue, 2-naphthylboronic acid, performed well to give products in 92% and 89% yields, respectively (entries 11 and 12).

Finally, we also investigated the Suzuki reactions between heteroaryl bromides and boronic acids using **2a** as the catalyst. Bromopyridine and 2,6-dibromopyridine were used as the heteroaromatic component in these reactions, and the high yields of 86-94% (entries 18-21) indicated that complex **2a** also exhibited excellent catalytic activity for the coupling of heteroaryl-halides with different arylboronic acids.

Table 2.

Catalytic Suzuki coupling reactions of aryl bromides with arylboronic acids[a]



Entry	Arylbromide	Arylboronic acid	Product	Yield(%)[b]
1			**3a**	95
2			**3b**	91
3			**3c**	86
4			**3d**	91
5			**3e**	88
6[c]			**3f**	89 (5)
7			**3a**	95
8			**3b**	85
9[d]			**3d**	78
10[d]			**3e**	80

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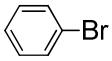
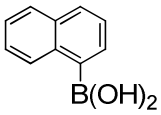
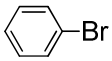
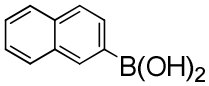
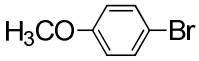
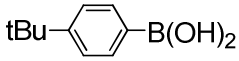
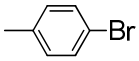
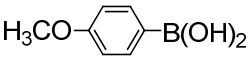
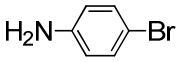
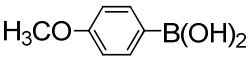
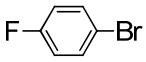
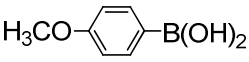
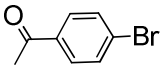
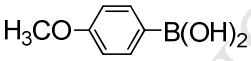
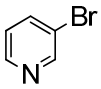
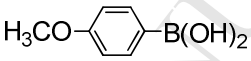
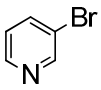
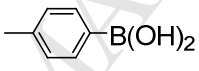
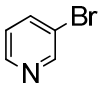
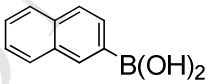
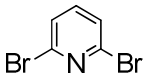
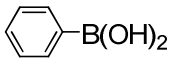
11			**3g**	92
12			**3h**	89
13			**3i**	87
14			**3j**	95
15			**3k**	92
16			**3l**	85
17			**3m**	87
18			**3n**	91
19			**3o**	89
20			**3p**	94
21[e]			**3q**	86

[a] Reaction conditions: 0.5 mmol of aryl bromide, 0.75 mmol of arylboronic acid, 1.0 mol% of **2a**, 2.0 mmol of K_3PO_4, 4.0 mL of dioxane, reflux, under N_2.

[b] Isolated by silica gel column chromatography and based on aryl bromides.

[c] Self-coupling byproduct of phenylboronic acid in parentheses was detected by GC-MS. In this case the self-coupling byproduct could not be separated from the cross-coupling product by silica gel column chromatography.

[d] 2.0 mol% of **2a**.

[e] 1.5 mmol of phenylboronic acid, 2.0 mol% of catalyst; 4.0 mmol of K_3PO_4. The product is 2,6-diphenylpyridine.

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3. Conclusion

In summary, we have successfully prepared a new type of nickel(II) complexes containing CNC pincer-type bis-NHC ligands with an anionic diarylamindo backbone. Complexes **2a-c** are stable toward moisture and air and tolerate high temperatures. The structure of complex **2a** has been revealed by X-ray structural analysis. The complexes have been shown to be effective in the Suzuki cross-coupling reactions of a variety of aryl bromides, even with less active aryl bromides and heteroaryl halides. The potential of these nickel complexes in other organic transformation is under investigation.

4. Experimental Section

4.1. General

Unless otherwise noted, all manipulations were performed under an argon atmosphere using standard Schlenk techniques. All solvents were dried according to standard procedures. $Ni(DME)Cl_2$ was prepared according to known procedures [17]. All other reagents are commercially available and were used without further purification. ^{1}H (400 MHz, 600 MHz) and ^{13}C NMR (100 MHz, 125 MHz) spectra were recorded using Bruker instruments. ^{1}H and ^{13}C chemical shifts are reported in ppm and calibrated to TMS on the basis of the solvent as an internal standard (2.49 ppm, DMSO-d_6; 7.27 ppm, $CDCl_3$). All NMR spectra were acquired at room temperature. Melting points were determined with an XRC-1 melting point apparatus and were uncorrected. Mass spectra were obtained by using Bruker Autoflex III instrument. Elemental analyses were performed on a CARLO ERBA-1106 instrument.

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4.2. X-ray crystal structure determination and refinement

X-ray single-crystal diffraction data for complex **2a** were collected on an Enraf−Nonius CAD-4 diffractometer at 294(2) K with Mo Kα radiation (λ = 0.71073 Å) by $\omega/2\theta$ scan mode. The structures were solved with direct methods using SHELXS-97 and refined by full-matrix least-squares refinement on F^2 with SHELXL-97 [18]. All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model.

Crystal/refinement data for **2a**·CH_2Cl_2: formula $C_{41}H_{44}Cl_3N_5Ni$, M = 771.87, size 0.42 × 0.38 × 0.30 mm, monoclinic, space group P21/c, a = 14.187(9)Å, b = 28.721(15) Å, c = 10.1289(6) Å, α = 90°, β = 102.06 (6)°, γ = 90°, F(000) = 1616, V = 4036.1(4) $Å^3$, T = 294(2) K, Z = 4, D(calcd) = 1.270 Mg/m^3, μ = 0.714 mm^{-1}, range of h, k, l = -17/11, -35/35, -12/12, reflns collected 16072, unique reflns 8193, refinement method full-matrix least-squares on F^2, parameters 411, R1 = 0.0891 (observed data with I > 2σ(I)), wR2 = 0.2076, GOF = 1.210.

*4.3. General procedure for the synthesis of [bis(2-(3-alkylimidazolin-2-yliden-1-yl)-4-methylphenyl)amido]chloronickel(II) (**2a-c**)*

A mixture of one of the bis(imidazolium) salts **1a-c** (0.100 mmol) and silver(I) oxide (27.6 mg, 0.120 mmol) in 5 mL of solvent (CH_2Cl_2/MeCN, v/v = 1:1) was stirred at room temperature for 24 h. The reaction mixture was filtered and washed with CH_2Cl_2 (5 mL × 2). The combined filtrate was reduced to 5 mL under vacuum. Ni(DME)Cl_2 (22.0 mg, 0.100 mmol) in CH_2Cl_2 (3 mL) was added to the resulting solution and stirred at room temperature for 2 h. The reaction mixture was filtered and washed with CH_2Cl_2 (5 mL × 2). The combined solution was evaporated under reduced pressure to leave a raw product which was purified by

flash chromatography on silica gel (dichloromethane) to give a purple solid.

*4.3.1.[Bis{2-(3-(2,4,6-trimethylbenzyl)imidazolin-2-yliden-1-yl)-4-methylphenyl}amido]chloronickel(II) (**2a**)*

Yield: 38.0 %. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.80 (d, J = 2 Hz, 2H, imi-*H*), 7.51 (s, 2H, Ar-*H*), 6.83 (s, 4H, Ar-*H*), 6.77 (d, J = 1.6 Hz, 2H, imi-*H*), 6.72 (d, J = 8.4 Hz, 2H, Ar-*H*), 6.70 (d, J = 8.4 Hz, 2H, Ar-*H*), 5.95 (d, J = 15.2 Hz, 2H, NCH_2), 5.52 (d, J = 15.2 Hz, 2H, NCH_2), 2.30 (s, 18H, ArCH_3), 2.19 (s, 6H, ArCH_3). ^{13}C NMR (150 MHz, DMSO-d_6): δ 161.9 ($C_{carbene}$), 140.4, 137.9, 137.6, 132.2, 130.7, 129.6, 127.6, 126.5, 123.7, 122.7, 120.3, 118.4 (Ar-*C*, imi-*C*), 48.4 (N*C*H$_2$), 21.0 (*C*H$_3$), 20.8 (*C*H$_3$), 20.2 (*C*H$_3$). Mp: > 280 °C. Anal. Calcd for $C_{40}H_{42}N_5NiCl$: C, 69.94; H, 6.16; N, 10.19. Found: C, 69.87; H, 6.10; N, 10.22. MS (MALDI-TOF, *m/z*) calcd for $C_{40}H_{42}N_5NiCl$: 685.25, found 650.28 $[M - Cl]^+$.

*4.3.2. [Bis(2-(3-benzylimidazolin-2-yliden-1-yl)-4-methylphenyl)amido]chloronickel(II) (**2b**)*

Yield: 35.0 %. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.86 (s, 2H, imi-*H*), 7.48–7.55(m, 6H, Ar-*H*, imi-*H*), 7.34 (s, 2H, Ar-*H*), 7.17–7.21 (m, 2H, Ar-*H*), 7.10–7.12 (m, 4H, Ar-*H*), 6.75 (d, J = 8.4 Hz, 2H, Ar-*H*), 6.50 (d, J = 8.4 Hz, 2H, Ar-*H*), 6.02 (d, J = 14.8 Hz, 2H, NCH_2), 5.34 (d, J = 15.2 Hz, 2H, NCH_2), 2.32 (s, 6H, ArCH_3). ^{13}CNMR (100 MHz, DMSO-d_6): δ 161.5 ($C_{carbene}$), 140.4, 138.6, 132.4, 128.7, 127.8, 127.7, 126.7, 124.9, 123.6, 120.5, 118.5 (Ar-*C*, imi-*C*), 52.1 (N*C*H$_2$), 20.8 (Ar*C*H$_3$). Mp： 272–274 °C. Anal. Calcd for $C_{34}H_{30}N_5NiCl$: C, 67.75; H, 5.02; N, 11.62. Found: C, 67.68; H, 5.05; N, 11.66. MS (MALDI-TOF, *m/z*) calcd for $C_{34}H_{30}N_5NiCl$: 601.15, found 566.19 $[M - Cl]^+$.

*4.3.3. [Bis(2-(3-butylimidazolin-2-yliden-1-yl)-4-methylphenyl)amido]chloronickel(II) (**2c**)*

Yield: 36.5 %. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85 (d, J = 1.2 Hz, 2H, imi-*H*), 7.47 (s, 2H, imi-*H*), 6.66 (d, J = 8Hz, 2H, Ar-*H*), 6.45 (d, J = 8Hz, 2H, Ar-*H*), 4.52–4.59 (m, 2H, NCH_2), 4.06–4.15 (m, 2H, NCH_2), 2.27 (s, 6H, ArCH_3), 1.86–1.91 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.73–1.78 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.17–1.22 (m, 4H, $NCH_2CH_2CH_2CH_3$), 0.82 (d, J = 7.2 Hz, 6 H, $NCH_2CH_2CH_2CH_3$). ^{13}CNMR (100 MHz, DMSO-d_6): δ 160.9 ($C_{carbene}$), 140.4, 132.3, 127.4, 126.3, 124.6, 123.6, 120.3, 117.8 (Ar-*C*, imi-*C*), 48.9 ($NCH_2CH_2CH_2CH_3$), 33.3 ($NCH_2CH_2CH_2CH_3$), 20.8 (ArCH_3), 19.5 ($NCH_2CH_2CH_2CH_3$), 13.8 ($NCH_2CH_2CH_2CH_3$). Mp: 144–146 °C. Anal. Calcd for $C_{28}H_{34}N_5NiCl$: C, 62.89; H, 6.41; N, 13.10. Found: C, 62.78; H, 6.52; N, 13.09. MS (MALDI-TOF, *m/z*) calcd for $C_{28}H_{34}N_5NiCl$: 533.19, found 498.21 $[M - Cl]^+$.

4.4. General procedure for the bis-NHC-Ni(II) complex-catalyzed Suzuki coupling reactions

In a typical reaction, to a 25-mL Schlenk tube equipped with a magnetic stirring bar were added nickel(II) catalyst **2a** (0.005 mmol, 1.0 mol %), aryl halides (0.5 mmol), phenylboronic acids (0.75 mmol), and anhydrous K_3PO_4 (2.0 mmol). The tube was then evacuated (3 × 5 min) under vacuum and backfilled with N_2. Dried dioxane (4.0 mL) was injected via a syringe, and the reaction mixture was stirred at reflux until the aryl halides had disappeared as monitored by TLC. The reaction mixture was treated with H_2O (20 mL), then extracted with Et_2O (3 × 15 mL). The combined organic extracts were washed with sat. aq NaCl (10 mL) and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by silica gel column chromatography to give the corresponding biaryl. All the coupling products are known and their structures were identified by comparing their ^{1}H NMR and ^{13}C NMR spectral data with those reported in literature.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://

References

[1] (a) N. Miyaura, K. Yamada, A. Suzuki, Tetrahedron Lett. 20 (1979) 3437;

(b) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457;

(c) A. Suzuki, J. Organomet. Chem. 576 (1999) 147;

(d) N. Miyaura, J. Organomet. Chem. 653 (2002) 54;

(e) A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4176;

(f) A. Suzuki, Chem. Commun. (2005) 4759;

(g) F. Alonso, I.P. Beletskaya, M. Yus, Tetrahedron 64 (2008) 3047;

(h) G.A. Molander, B. Canturk, Angew. Chem. Int. Ed. 48 (2009), 9240;

(i) A. Suzuki, Angew. Chem. Int. Ed. 50 (2011) 6722.

[2] For examples, see: (a) U. Mitschke, P. Bauerle, J. Mater. Chem. 10 (2000) 1471;

(b) T. Yamamoto, J. Organomet. Chem. 653 (2002) 195;

(c) S. Lightowler, M. Hird, Chem. Mater. 17 (2005) 5538;

(d) E. Holder, B.M.W. Langeveld, U.S. Schubert, Adv. Mater. 17 (2005) 1109;

(e) A.V. Ambade, E.N. Savariar, S. Thayumanavan, Mol. Pharm. 2 (2005) 264;

(f) K.C. Nicolaou, P.G. Bulger, D. Sarlah, Angew. Chem. Int. Ed. 44 (2005) 4442;

(g) C. Torborg, M. Beller, Adv. Synth. Catal. 351 (2009) 3027;

(h) G. Bringmann, T. Gulder, T.A.M. Gulder, M. Breuning, Chem. Rev. 111 (2011) 563;

(i) J. Magano, J.R. Dunetz, Chem. Rev. 111 (2011) 2177.

[3] (a) S.L. Buchwald, R. Martin, Acc. Chem. Res. 41 (2008) 1461;

(b) S. Wurtz, F. Glorius, Acc. Chem. Res. 41 (2008) 1523;

(c) G.A. Molander, N. Ellis, Acc. Chem. Res. 40 (2007) 275;

(d) G.A. Molander, B. Canturk, Angew. Chem. Int. Ed. 48 (2009) 9240;

(e) N. Miyaura, Top. Curr. Chem. 219 (2002) 11;

(f) M. Tobisu, N. Chatani, Angew. Chem. Int. Ed. 48 (2009) 3565.

[4] (a) *Handbook of Organopalladium Chemistry for Organic Synthesis;* Wiley-Interscience: New York, 2002.

(b) F.S. Han, Chem. Soc. Rev. 42 (2013) 5270;

(c) C.C.C. Johanson Seechurn, M.O. Kitching, T.J. Colacot, V. Snieckus, Angew. Chem. Int. Ed. 51 (2012) 5062.

[5] For examples, see: (a) J.P. Wolfe, S.L. Buchwald, J. Am. Chem. Soc. 119 (1997) 6054;

(b) B.H. Lipshutz, H. Ueda, Angew. Chem. Int. Ed. 39 (2000) 4492;

(c) B.H. Lipshutz, S. Tasler, W. Chrisman, B. Spliethoff, B. Tesche, J. Org. Chem. 68 (2003) 1177;

(d) S. Tasler, B.H. Lipshutz, J. Org. Chem. 68 (2003) 1190;

(e) B. Gradel, E. Brenner, R. Schneider, Y. Fort, Tetrahedron Lett. 42 (2001) 5689;

(f) C. Desmarets, R. Schneider, Y. Fort, J. Org. Chem. 67 (2002) 3029.

[6] (a) Z.-Y. Tang, Q.-S. Hu, J. Am. Chem. Soc. 126 (2004) 3058;

(b) P. Leowanawat, N. Zhang, M. Safi, D.J. Hoffman, M.C. Fryberger, A. George, V. Percec, J. Org. Chem. 77 (2012) 2885.

[7] (a) V. Percec, G.M. Golding, J. Smidrkal, O. Weichold, J. Org. Chem. 69 (2004) 3447;

(b) Y. Zhou, Z. Xi, W. Chen, D. Wang, Organometallics 27 (2008) 5911;

(c) X.J. Li, J.L. Zhang, Y. Geng, Z. Jin, J. Org. Chem. 78 (2013) 5078.

[8] (a) K. Inamoto, J.-I. Kuroda, E. Kwon, K. Hiroya, T. Doi, J. Organomet. Chem. 694 (2009) 389;

(b) J.-I. Kuroda, K. Inamoto, K. Hiroya, T. Doi, Eur. J. Org. Chem. (2009) 2251.

[9] Selected references: (a) V. Perces, J.-Y. Bae, D.H. Hill, J. Org. Chem. 60 (1995) 1060;

(b) B.H. Lipshutz, T. Butler, E. Swift, Org. Lett. 10 (2008) 697;

(c) D.A. Wilson, C.J. Wilson, B.M. Rosen, V. Percec, Org. Lett. 10 (2008) 4879;

(d) X.-H. Fan, L.-M. Yang, Eur. J. Org. Chem. (2010) 2457;

(e) C.-H. Xing, J.-R. Lee, Z.-Y. Tang, J.R. Zheng, Q.-S. Hu, Adv. Synth. Catal. 353 (2011) 2051;

(f) P. Leowanawat, N. Zhang, A.-M. Resmerita, V. Percec, J. Org. Chem. 76 (2011) 9946.

[10] (a) K. Inamoto, J.-I. Kuroda, K. Hiroya, Y. Noda, M. Watanabe, T. Sakamoto, Organometallics 25 (2006) 3095;

(b) T. Tu, H. Mao, C.M. Herbert, K.H. Dötz, Chem. Commun. 46 (2010) 7796.

[11] (a) Z. Csok, O. Vechorkin, S.B. Harkins, R. Scopelliti, X.L. Hu, J. Am. Chem. Soc. 130 (2008) 8156;

(b) O. Vechorkin, Z. Csok, R. Scopelliti, X.L. Hu, Chem. Eur. J. 15 (2009) 3889;

(c) O. Vechorkin, X.L. Hu, Angew. Chem. Int. Ed. 48 (2009) 2937.

[12] (a) L.C. Liang, P.S. Chien, J.M. Lin, M.H. Huang, Y.L. Huang, J.H. Liao, Organometallics 25 (2006) 1399;

(b) D. Benito-Garagorri, E. Becker, J. Wiedermann, W. Lackner, M. Pollak, K. Mereiter, J. Kisala, K. Kirchner, Organometallics 25 (2006) 1900.

[13] A. Castonguay, A.L. Beauchamp, D. Zargarian, Organometallics 27 (2008) 5723.

[14] (a) R.E. Douthwaite, J. Houghton, B.M. Kariuki, Chem. Commun. (2004) 698;

(b) M. Moser, B. Wucher, D. Kunz, F. Rominger, Organometallics 26 (2007) 1024;

(c) W. Wei, Y. Qin, M. Luo, P. Xia, M.S. Wong, Organometallics 27 (2008) 2268.

[15] (a) W.A. Herrmann, J. Schwarz, M.G. Gardiner, M. Spiegler, J. Organomet. Chem. 575 (1999) 80;

(b) Q.X. Liu, F.B. Xu, Q.S. Li, H.B. Song, Z.Z. Zhang, Organometallics 23 (2004) 610;

(c) C.Y. Liao, K.T. Chan, Y.C. Chang, C.Y. Chen, C.Y. Tu, C.H. Hu, H.M. Lee, Organometallics 26 (2007) 5826;

(d) P.L. Chiu, C.L. Lai, C.F. Chang, C.H. Hu, H.M. Lee, Organometallics 24 (2005) 6169;

(e) D. Pugh, A. Boyle, A.A. Danopoulos, Dalton Trans. (2008) 1087.

[16] CCDC: 1037269.

[17] S.Y. Tyree, J. Inorg. Synth. 4 (1953) 104.

[18] G.M. Scheldrick, SHELXS -97 and SHELXL -97, Program for Solution and Refinement of Crystal Structures; University of Göttingen: Germany, 1997.

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Highlights

- ►A new type of nickel(II) complexes containing CNC pincer-type bis-NHC ligands was synthesized.
- ►One of the complexes was characterized by X-ray diffraction.
- ►The complexes showed high efficiency in catalyzing Suzuki cross-coupling reactions.

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Supporting Information for

Synthesis and catalytic activity of nickel(II) complexes of CNC pincer-type *N*-heterocyclic carbene ligands

Shuchao Wang, Fang Ren, Yuping Qiu, Meiming Luo*

Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China

Contents

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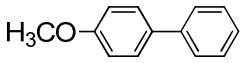
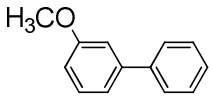
I. Analytical data for cross-coupling products

4-Methoxybiphenyl[1](**3a**) (Table 2, entry 1)



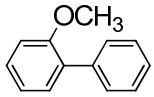
White solid, MP: 89-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.51 (m, 4H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.15-6.96 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 140.8, 133.8, 128.7, 128.2, 126.8, 126.7, 114.2, 55.4.

3-Methoxybiphenyl[2](**3b**) (Table 2, entry 2)



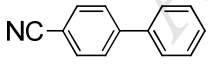
Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.57 (m, 2H), 7.45-7.41 (m, 2H), 7.37-7.32(m, 2H), 7.20-7.17(m, 1H), 7.13-7.12 (m, 1H), 6.91-6.88 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 142.8, 141.1, 129.7, 128.7, 127.4, 127.2, 119.7, 112.9, 112.7, 55.3.

2-Methoxybiphenyl[2](**3c**) (Table 2, entry 3)



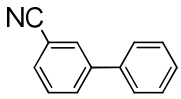
Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.33-7.30 (m, 3H), 7.06-6.96 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)： δ 156.4, 138.5, 130.9, 130.7, 129.5, 128.6, 128.0, 126.9, 120.8, 111.2, 55.5.

biphenyl-4-carbonitrile[3](**3d**) (Table 2, entry 4)



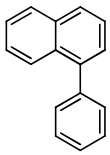
White solid, Mp: 84-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.67 (m, 4H), 7.61-7.58 (m, 2H), 7.51-7.47(m, 2H), 7.45-7.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 139.1, 132.6, 129.1 128.6, 127.7, 127.2, 118.9, 110.9.

Biphenyl-3-carbonitrile[3](**3e**) (Table 2, entry 5)



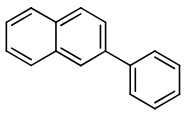
White solid, Mp: 36-37 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.85-7.83 (m, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.60-7.57(m, 3H), 7.53-7.49 (m, 2H), 7.46-7.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 138.8, 131.6, 130.6, 129.6, 129.1, 128.4, 127.0, 118.8, 112.9.

1-Phenylnaphthalene[4](**3g**) (Table 2, entry 11)



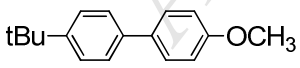
Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.52-7.46 (m, 6H), 7.45-7.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 140.2, 133.8, 131.6, 130.1, 128.2, 127.6, 127.2, 126.9, 126.0, 125.8, 125.4.

2-Phenylnaphthalene[2](**3h**) (Table 2, entry 12)



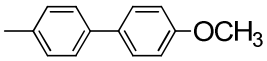
White solid, Mp:101-102 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.92-7.85 (m, 3H), 7.76-7.71 (m, 3H), 7.52-7.47 (m, 4H), 7.39-7.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 138.5, 133.7, 132.6, 128.9, 128.4, 128.2, 127.6, 127.4, 127.3, 126.3, 125.9, 125.8, 125.6.

4-(tert-Butyl)-4'-methoxy-1,1'-biphenyl[5](**3i**) (Table 2, entry 13)



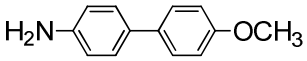
White solid, Mp: 125-126 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.43 (m, 6H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 149.6, 137.9, 133.6, 128.0, 126.3, 125.6, 114.1, 55.3, 34.4, 31.4.

4-Methoxy-4'-methylbiphenyl[6](**3j**) (Table 2, entry 14)



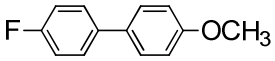
White solid, MP: 107-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.40 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.91-6.87 (m, 2H), 3.77 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 137.9, 136.3, 133.7, 129.4, 127.9, 126.6, 114.1, 55.3, 21.0.

4-Methoxy-4'-[(1,1'-biphenyl)-amine][7](**3k**) (Table 2， entry 15)



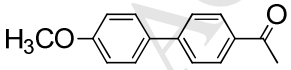
White solid, Mp: 144-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 7.5Hz, 2H), 3.87 (s, 3H), 3.71 (brs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 145.5, 133.8, 131.4, 127.6, 127.4, 115.4, 114.1, 55.3.

4-methoxyl-4'-fluorobiphenyl[8](**3l**) (Table 2，entry 16)



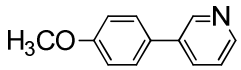
White solid, Mp: 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.45 (m, 4H), 7.10 (t, *J* = 8.8, 2H), 6.97 (d, *J* = 8.8, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1(d, *J* = 244 Hz), 159.13, 136.98 (d, *J* = 3.4 Hz), 132.85, 128.22 (d, *J* = 7.9 Hz), 128.04, 115.53 (d, *J* = 21.2 Hz), 114.26, 55.36.

4(4'-Methoxyphenyl)acetophenone[9](**3m**) (Table 2，entry 17)



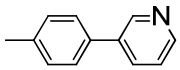
White solid, Mp: 152-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 159.9, 145.3, 135.2, 132.2, 128.9, 128.3, 126.6, 114.4, 55.3, 26.6.

3-(4-Methoxyphenyl)pyridine[10](**3n**) (Table 2, entry 18)



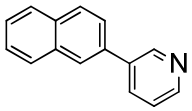
White solid, Mp: 60-61 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.55 (s, 1H), 7.84 (s, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.34 (s, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 148.0, 147.8**,** 136.6, 133.8, 130.2, 128.2, 123.6, 114.5, 55.3.

3-(p-Tolyl)pyridine[10](**3o**) (Table 2, entry 19)



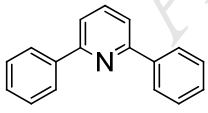
Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, *J* = 2.1 Hz, 1H), 8.57 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.87-7.84 (m, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.35 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 138.0, 136.5, 134.9, 134.1, 129.7, 126.9, 123.4, 21.1.

3-(Naphthalen-2-yl)pyridine[11](**3p**) (Table 2, entry 20)



White solid, Mp: 99-100 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (s, 1H), 8.66 (s, 1H), 8.07 (s, 1H), 8.03-7.89 (m, 4H), 7.74 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.56-7.52 (m, 2H), 7.44 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 136.6, 135.1, 134.5, 133.6, 132.9, 128.9, 128.2, 127.7, 126.6, 126.4, 126.1, 125.0, 123.6.

2,6-Diphenylprydine[12](**3q**) (Table 2, entry 21)



White solid, Mp: 78-79 ^{o}C. ^{1}H NMR(400MHz, $CDCl_3$); δ 8.16 (d, *J* = 7.2, 4H), 7.82 (t, *J* = 7.2, 1H) , 7.7 (d, *J* = 7.7, 2H) , 7.50(d, *J* = 7.7, 4H) , 7.46-7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ156.9, 139.5, 137.6, 129.1, 128.8, 127.1, 118.5

References

(1) Denmark, S. E.; Ober, M. H. *Org. Lett*. **2003**, *5*, 1357

(2) Liu, W.; Cao, H.; Lei, A. *Angew. Chem. Int. Ed*. **2010**, *49*, 2004.

(3) Tao, B.; Boykin, D. W. *J. Org. Chem*. **2004**, *69*, 4330

(4) Stevens, P. D.; Fan, J.; Gardimalla, H. M. R.; Yen, M.; Gao, Y. *Org. Lett*. **2005**, *7*, 2085.

(5) Li, X. J.; Zhang, J. L.; Geng, Y.; Jin, Z. *J. Org. Chem.* **2013**, *78*, 5078.

(6) Liu, L.; Zhang, Y.; Wang, Y. *J. Org. Chem*. **2005**, *70*, 6122.

(7) Hoshi, T. S.; Honma, T. B.; Mori, A.; Konishi, M.; Sato, T. *J. Org. Chem*. **2013**, *78*, 11513.

(8) Wang, Z. Y.; Chen, G. Q.; Shao, L. X. *J. Org. Chem*. **2012**, *77*, 6608.

(9) Chen, X. F.; Ke, H. H.; Chen, Y.; Guan, C.W.; Zou, G. *J. Org. Chem*., **2012**, *77*, 7572.

(10) Fu, X. L.; Wu, L. L.; Fu, H. Y.; Chen, H.; Li, R. X. *Eur. J. Org. Chem*. **2009**, 2051.

(11) Gooßen, L. J.; Rodríguez, N.; Lange, P. P.; Linder, C. *Angew. Chem. Int. Ed*. **2010**, *49*, 1111.

(12) Xi, Z. X.; Zhou, Y. B.; Chen, W. Z. *J. Org. Chem*. **2008**, *73*, 8497.

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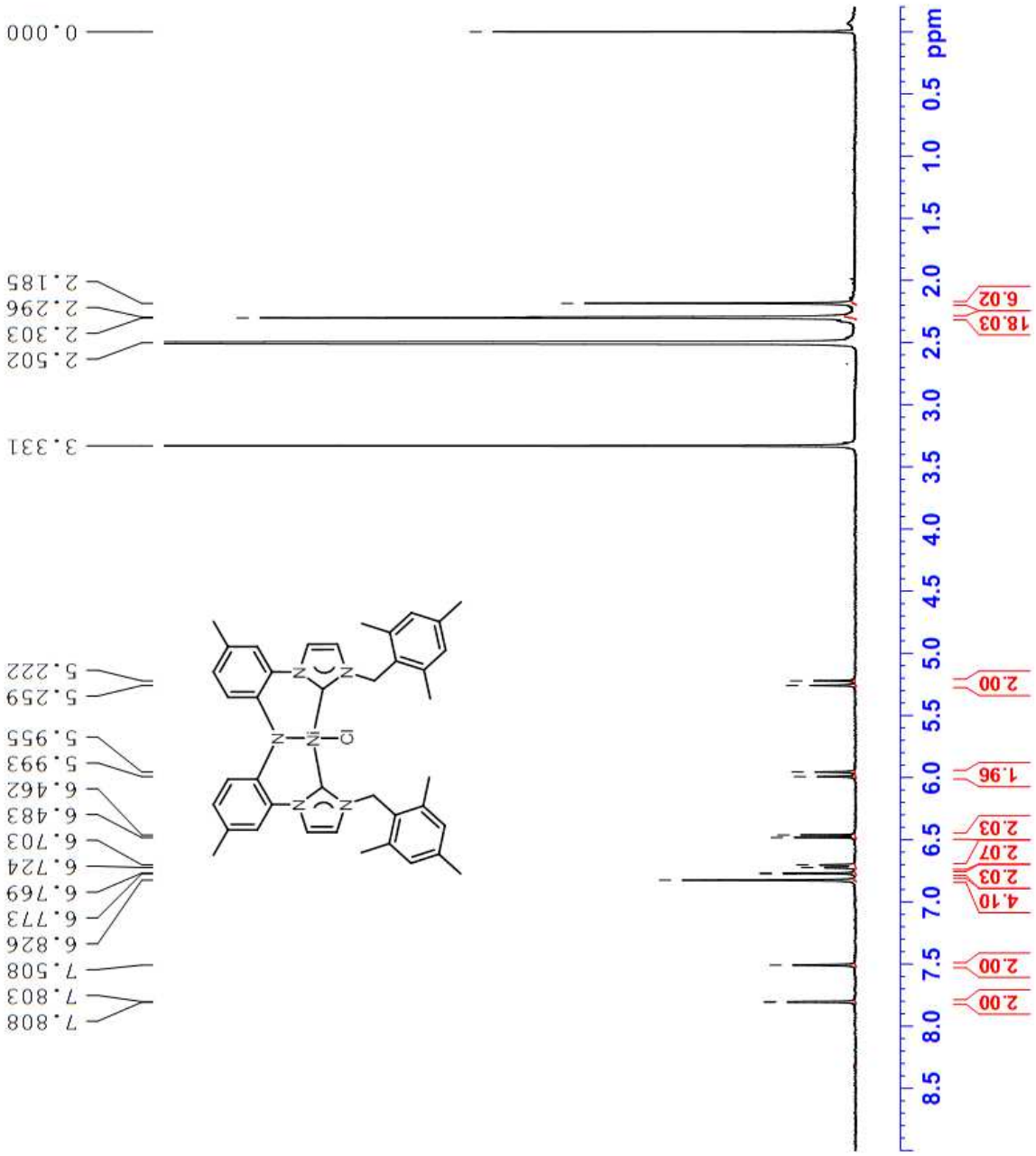
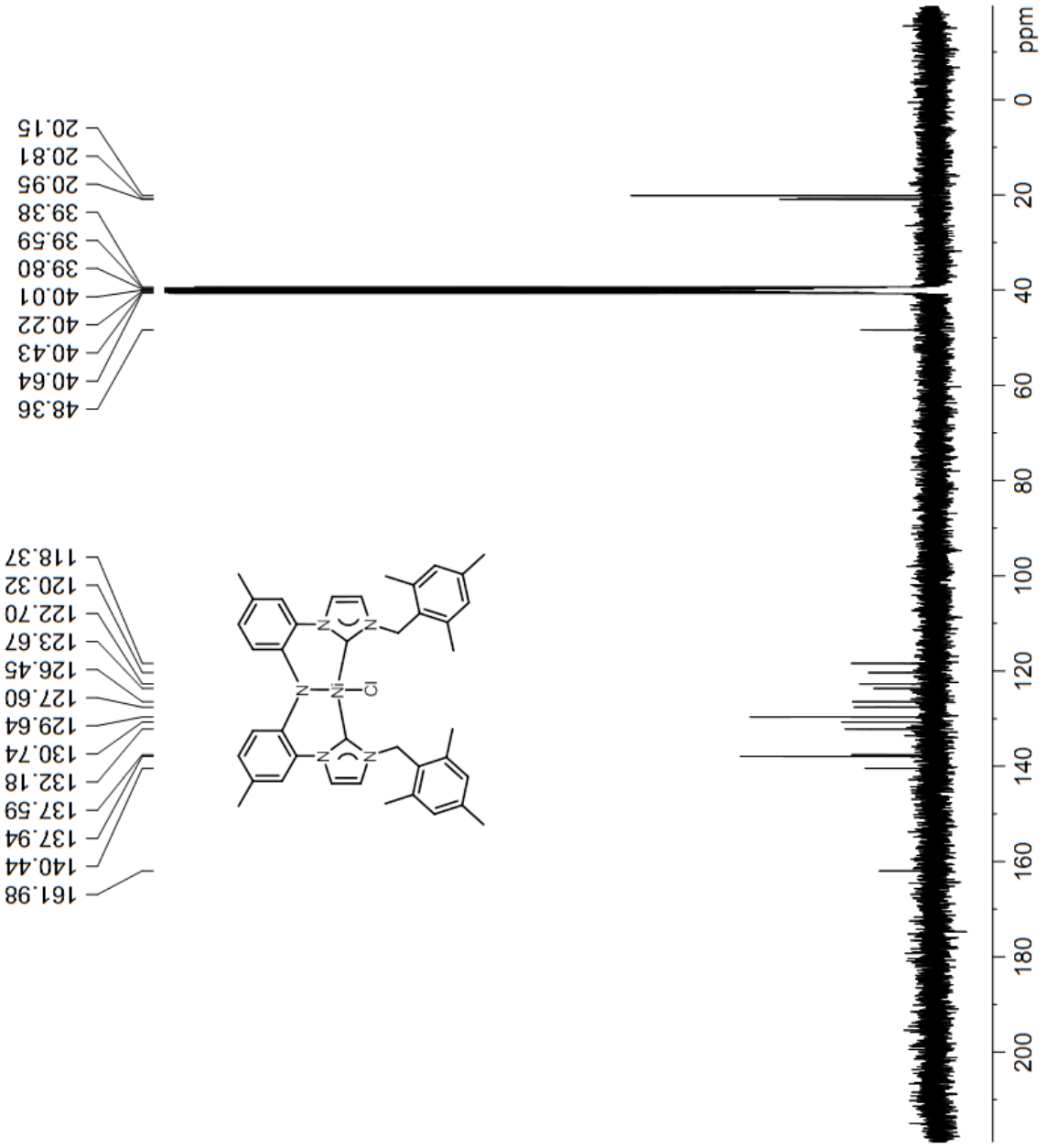
II. Copies of NMR spectra for 2a−c.

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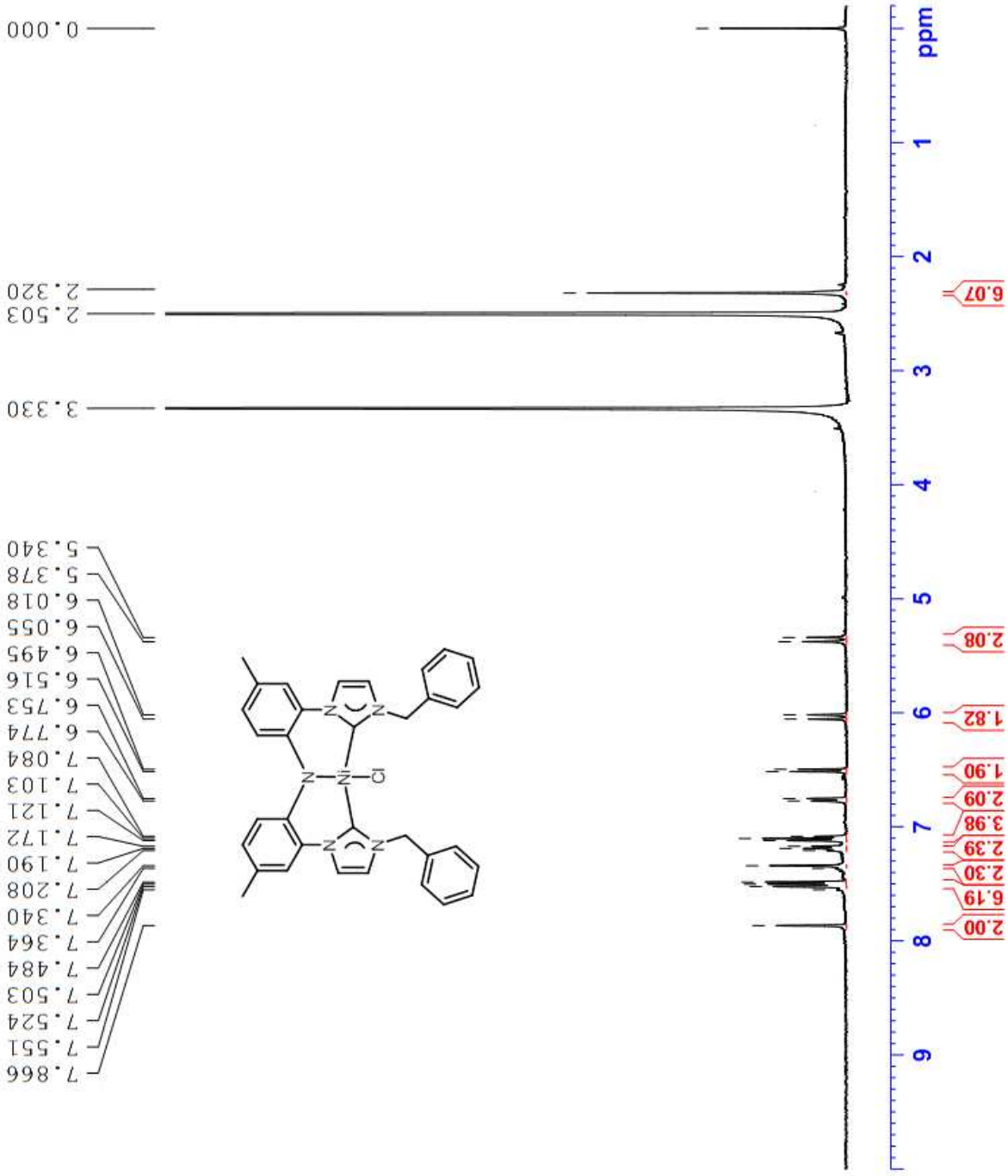
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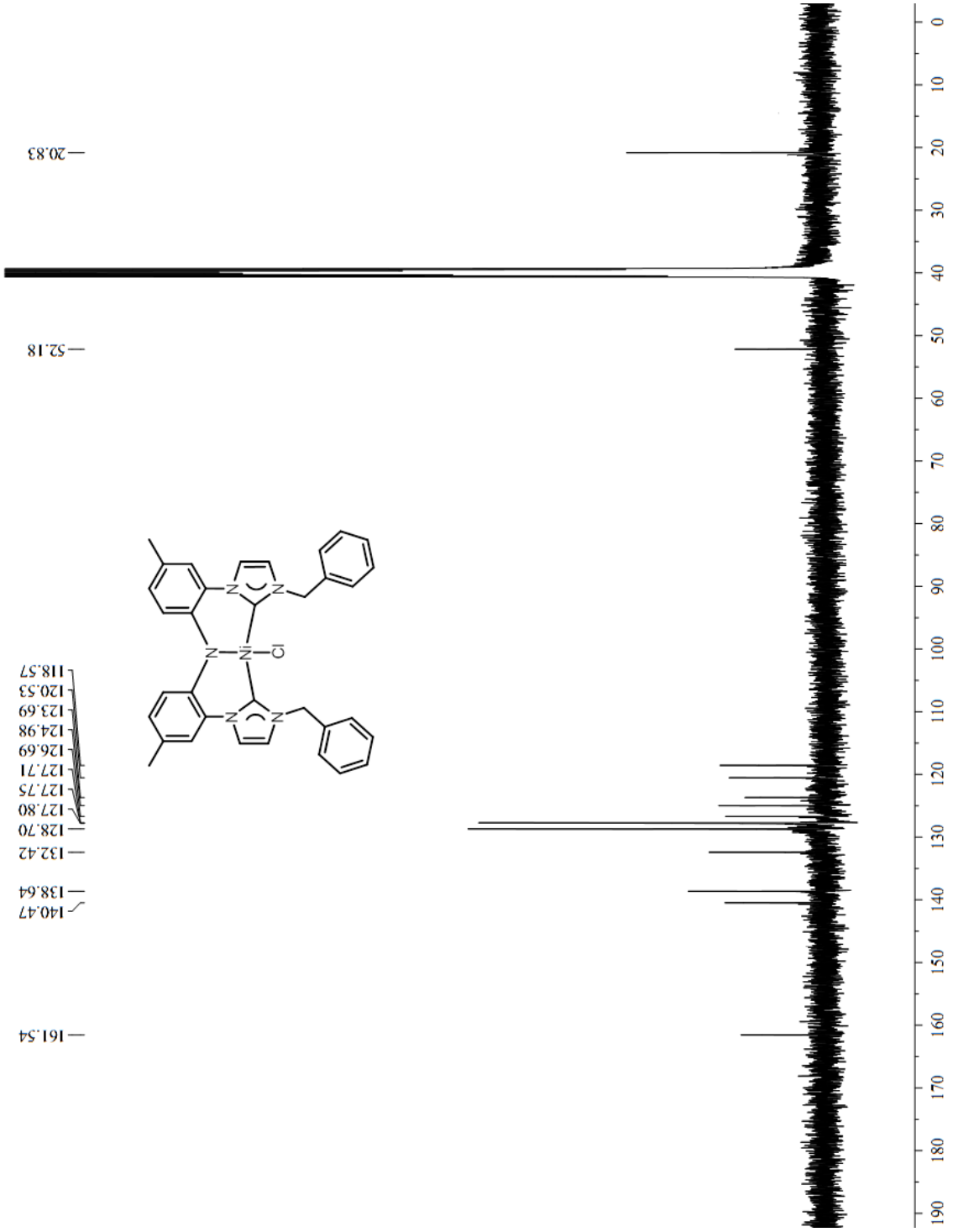
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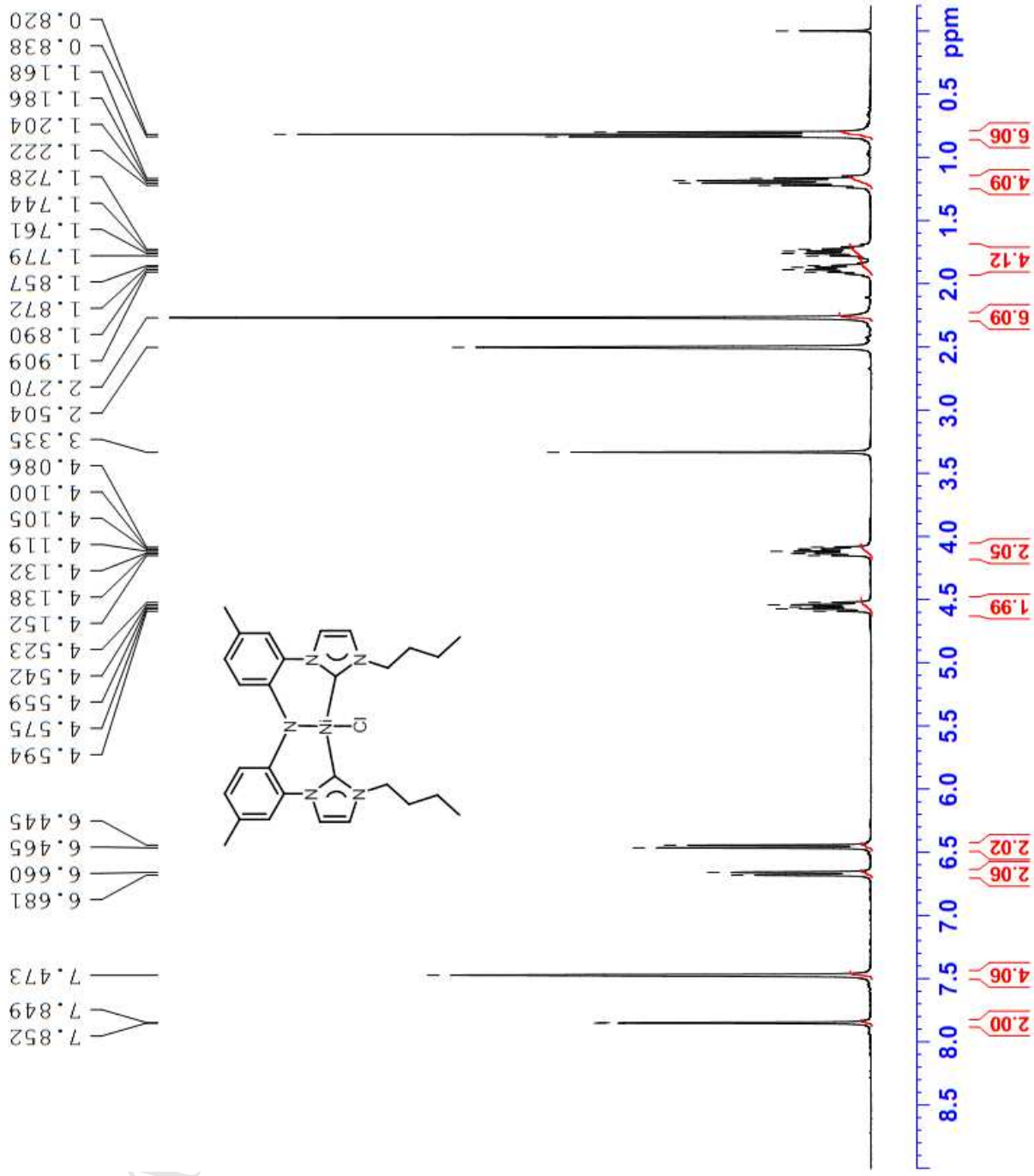
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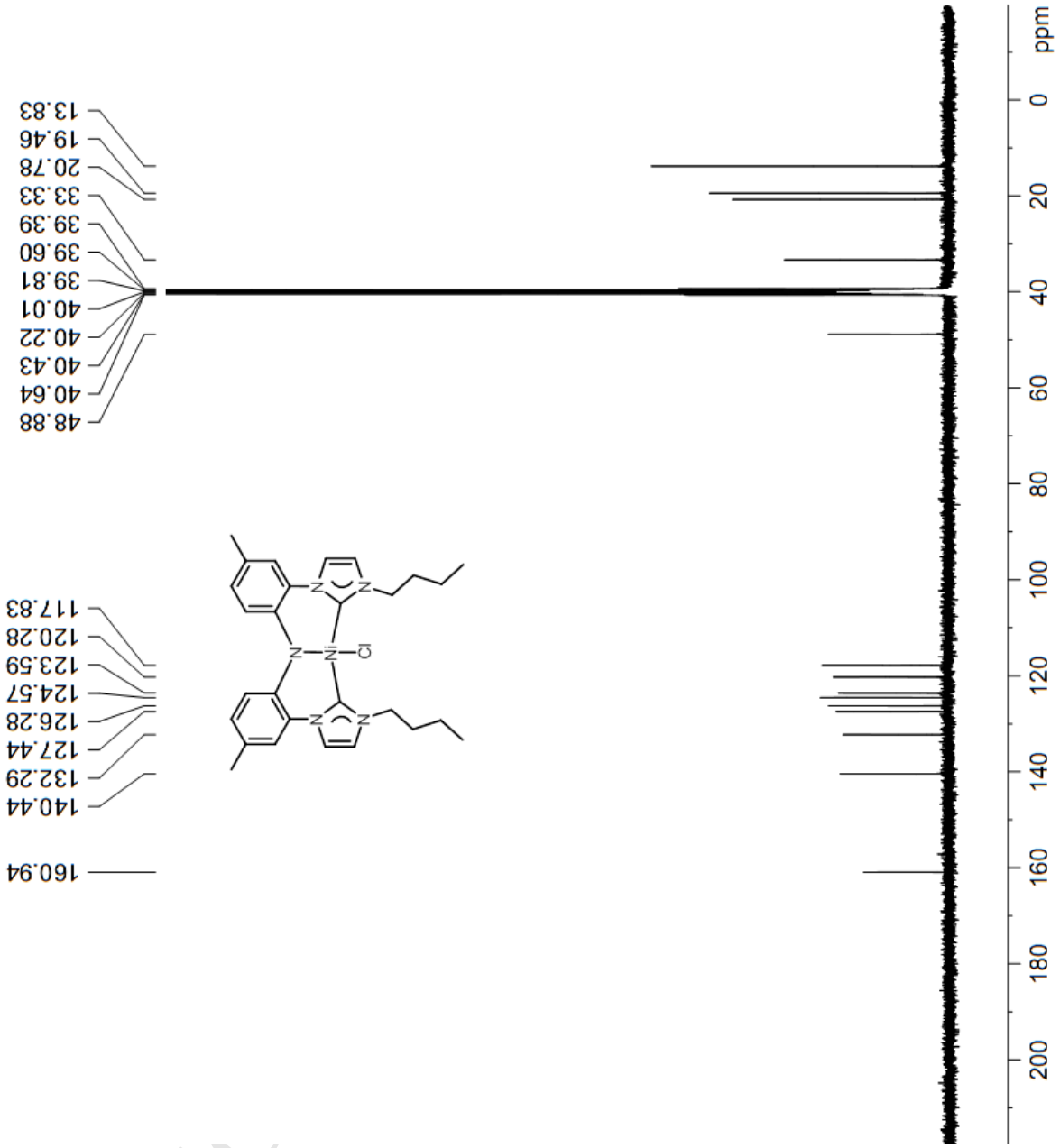
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