

SYNTHESIS, SPECTROSCOPIC INVESTIGATION AND CATALYTIC STUDIES OF NICKEL(II) AROMATIC AZOMETHINE COMPLEXES

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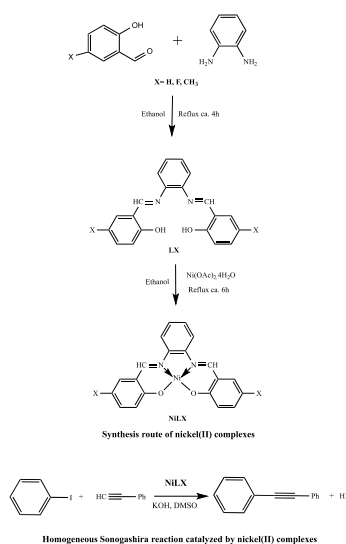
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Graphical abstract



Abstract

Coupling reaction between aryl halide and terminal alkyne in Sonogashira coupling reaction is important due to its extensive application in the resynthesis of natural products, production of drugs, dyes, and polymers. Efforts to increase rate of reaction has involved exploration of new catalysts. The current catalysts such as phosphine-based complexes are costly, air-sensitive and environmentally harmful. Nickel(II) Schiff base complexes were synthesized by reacting aromatic Schiff base ligands 2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))diphenol (L1H), 2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(4-fluorophenol) (L1F), and 2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(4-methylphenol) (L1M) with nickel(II) acetate tetrahydrate to form NiL1H, NiL1F and NiL1M. The chemical structures were elucidated through physicochemical and spectral techniques namely elemental analysis, melting point, FTIR, ¹H and ¹³C NMR, magnetic susceptibility and molar conductivity. All nickel(II) complexes were tested as catalysts in homogenous Sonogashira reaction between iodobenzene and phenylacetylene in DMSO for 12 hours at 140 °C. NiLF, a new nickel(II) complex, converted the highest percentage of iodobenzene (91%) while NiLH and NiLC converted 78% and 83% of iodobenzene, respectively.

Keywords: Schiff bases, substituent, nickel(II) complexes, Sonogashira, catalysis

Abstrak

Tindak balas gandingan antara aril halida dan terminal alkina dalam tindak balas Sonogashira adalah penting kerana aplikasinya yang meluas dalam penghasilan semula produk semulajadi, penghasilan ubatan, perwarna dan juga polimer. Usaha untuk meningkatkan kadar tindak balas telah melibatkan penerokaan pemangkin baru. Pemangkin sedia ada seperti kompleks berasaskan fosfin adalah mahal, sensitif terhadap udara dan berbahaya bagi alam sekitar. Kompleks Schiff bes nikel(II) telah disintesis dengan menindak balas ligan aromatik Schiff bes iaitu 2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene)) bis(methanylylidene))diphenol (L1H), 2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(4-fluorophenol) (L1F), and 2,2'-((1E,1'E)-

(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(4methylphenol),(L1M) dengan nikel(II) asetat tetrahidrat menghasilkan NiL1H, NiL1F dan NiL1M. Struktur kimia telah dijelaskan melalui teknik fizikokimia dan spektrum iaitu analisis unsur, takat didih, FTIR, ^1H dan ^{13}C NMR, kerentanan magnetik dan kekonduksian molar. Semua kompleks nikel(II) telah diuji sebagai pemangkin bagi tindak balas homogen Sonogashira antara iodobenzena dan fenilasetilena dalam DMSO selama 12 jam pada 140 °C. NiLF, sebuah kompleks nikel(II) baru menunjukkan peratusan penukaran iodobenzena yang paling tinggi (91%) manakala NiLH dan NiLC masing-masing menukarkan 78% dan 83% iodobenzena.

Kata kunci: Schiff bes, pengganti, nikel(II) kompleks, Sonogashira, pemangkinan

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1.0 INTRODUCTION

Schiff base metal complexes containing oxygen and nitrogen donor ligands have attracted interest for many years because of the versatility of their steric and electronic properties, which can be fine-tuned by selecting the right amine precursors and ring substituents [1, 2]. The properties of these tetradentate N_2O_2 ligands and their transition-metal complexes, as catalysts in Sonogashira coupling reaction, have attracted substantial attention as the main products from this reaction have been widely used as dyes, polymers, organic building blocks, fluorescent probes in medical imaging, as well as pharmaceutical drugs [3, 4].

Sonogashira coupling reactions are commonly catalysed by palladium complexes with copper salts as co-catalysts. The use of copper salt in the reaction, however, has caused Glaser-type homocoupling [5, 6] that reduces product yields. Thus, research on copper-free Sonogashira coupling reaction is very pertinent. The application of palladium complexes as main catalyst in the reaction has been reported to give a good to excellent conversion of reactants. However, the cost of palladium salts is 500 times higher than that of nickel salts and nickel salts are more earth-abundant [8]. Thus, economically, there is a need for the research on nickel(II) complexes to be employed as catalyst in Sonogashira as they are more cost-effective.

Nickel(II) complexes have been applied as catalyst in other coupling reactions but these complexes are mostly phosphine-based [9] which are costly and prone to being structurally kinked when exposed to air, high temperature and moisture [10, 11]. These issues can cause handling difficulties in synthesis.

The catalytic activities of nickel(II) Schiff base complexes have been reported [12, 13, 14] but their application as catalysts in Sonogashira reaction is still limited. Schiff bases have been reported to possess stability towards air and moisture leading to facile synthesis and applications [15].

Hence, this paper aims at reporting the synthesis and characterization of three (3) aromatic tetradentate Schiff base ligands and their nickel(II)

complexes derived from *ortho*-phenylenediamine and salicylaldehyde derivatives having hydrogen, fluorine, and methyl substituents. The catalytic activities of these tetradentate nickel(II) complexes were evaluated in homogeneous copper-free Sonogashira coupling reaction between aryl iodide and phenylacetylene.

2.0 METHODOLOGY

All chemicals and solvents purchased from commercial suppliers were used without further purification. The micro-analytical data (C, H, and N) of all ligands and complexes were obtained from Thermo Scientific Flash 2000 Elemental Analyser. Melting points were determined using Stuart SMP10 and were uncorrected. Perkin-Elmer Spectrum One FTIR spectrometer using KBr pellets were employed to record Infrared (IR) spectra of ligands and complexes between 4000 – 450 cm^{-1} . ^1H and ^{13}C NMR spectra were recorded on a Bruker Varian-600MHz spectrometer using deuterated CDCl_3 and expressed in a unit of parts per million (δ , ppm). The magnetic moment of the complexes was measured using Sherwood Auto Magnetic Susceptibility Balance. The molar conductivity was measured using Mettler Toledo Inlab 730 conductivity meter in DMSO. The percent conversion of iodobenzene was monitored using Gas Chromatography-Flame Ionization Detection (GC-FID) model Agilent 6890N.

2.1 Synthesis of Schiff Base Ligands

A hot solution of *ortho*-phenylenediamine $\text{C}_6\text{H}_8\text{N}_2$ (1 mmol) in absolute ethanol (10 mL) was added to a stirred solution of salicylaldehyde derivatives (2 mmol) in absolute ethanol (5 mL). The solution was refluxed for 4 hours, then cooled to room temperature and chilled. The obtained yellow solid was filtered off, washed with cold ethanol and air-dried. The general synthesis of Schiff bases is shown in Figure 1.

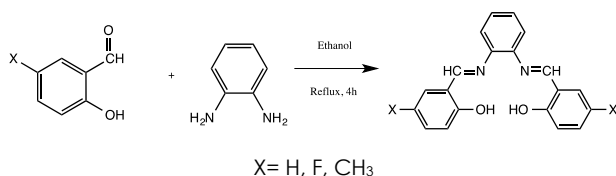


Figure 1 General synthesis of Schiff bases

2.1.1 L1H

M.p. (°C) 168-170; Yield: 56.0%; IR (KBr Pellets) cm⁻¹ 1612 (C=N), 1237 (C-OH); ¹H NMR (CDCl₃) δ: 6.93-7.41 (6H, m, ArH), 13.24 (1H, s, OH); Anal. Found (Calc.) for C₂₀H₁₄N₂O₂; C: 73.85 (75.93), H: 4.87 (5.10), N: 8.54 (8.86).

2.1.2 L1F

M.p. (°C) 193-195; Yield – 79.3%; IR (KBr Pellets) cm⁻¹ 1618 (C=N), 1270 (C-OH); ¹H NMR (CDCl₃) δ: 7.01-7.41 (5H, m, ArH), 12.82 (1H, s, OH); Anal. Found (Calc.) for C₂₀H₁₄F₂N₂O₂; C: 69.69 (68.18), H: 3.93 (4.01), N: 8.03 (7.95)

2.1.3 L1M

M.p. (°C) 129-135; Yield – 79.2%; IR (KBr Pellets) cm⁻¹ 1616 (C=N), 1251 (C-OH); ¹H NMR (CDCl₃) δ: 6.86-7.47(5H, m, ArH), 12.67 (1H, s, OH); Anal. Found (Calc.) for C₂₂H₂₀N₂O₂; C: 75.85 (76.72), H: 5.77 (5.85), N: 8.05 (8.13)

2.2 Synthesis of Nickel(II) Schiff Base Complexes

The nickel(II) acetate tetrahydrate (1 mmol) was dissolved in 10 mL of ethanol in a round bottom flask. 1 mmol of salicylaldehyde/derivatives was dissolved separately in 10 mL of ethanol (Figure 2). The ligand solution was added dropwise into the flask containing the metal solution. The mixture was refluxed for 6 hours. The mixture was cooled to room temperature and chilled. Then, the solid was filtered off, washed with a small amount of cold ethanol and air-dried.

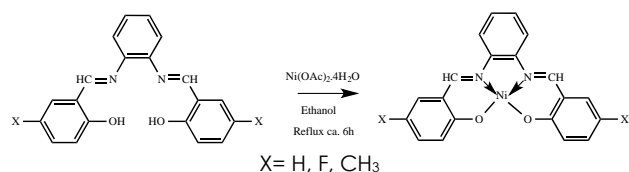


Figure 2 General synthesis of Ni(II) Schiff base complexes

2.2.1 Ni L1H

M.p. (°C) >300; Yield – 74.7%; IR (KBr Pellets) cm⁻¹ 1607 (C=N), 1248 (C-O); ¹H NMR (CDCl₃) δ: 6.63-8.22 (6H, m, ArH); Anal. Found (Calc.) for C₂₀H₁₄N₂O₂Ni; C: 64.31 (64.40), H: 3.76 (3.78), N: 7.62 (7.58); Magnetic

Susceptibility: 0 μ_{eff}; Molar conductivity: 0 λ_m/Ω⁻¹cm² mol⁻¹

2.2.2 Ni L1F

M.p. (°C) >300; Yield – 93.8%; IR (KBr Pellets) cm⁻¹ 1603 (C=N), 1286 (C-O); Anal. Found (Calc.) for C₂₀H₁₂F₂N₂O₂Ni; C: 59.07 (58.73), H: 3.06 (2.96), N: 6.97 (6.85); Magnetic Susceptibility: 0 μ_{eff}; Molar conductivity: 0 λ_m/Ω⁻¹cm² mol⁻¹

2.2.3 Ni L1M

M.p. (°C) >300; Yield – 76.3%; IR (KBr Pellets) cm⁻¹ 1605 (C=N), 1266 (C-O); Anal. Found (Calc.) for C₂₀H₁₈N₂O₂Ni; C: 65.41 (65.88), H: 4.53 (4.52), N: 7.02 (6.98); Magnetic Susceptibility: 0 μ_{eff}; Molar conductivity: 0 λ_m/Ω⁻¹cm² mol⁻¹

2.3 Catalytic Activity of Nickel(II) Schiff Base Complexes for Sonogashira Reaction

A Radley tube was charged with iodobenzene (1.0 mmol), phenylacetylene (1.5 mmol), nickel(II) Schiff base complex (2 mmol%) and KOH (2.0 mmol), with stirring under aerobic condition in 7 mL of DMSO (Figure 3). The different reaction mixtures were run simultaneously on a 12-slot Radley carousel. The mixture was heated at 140 °C for 12 hours and monitored at every 3 hours by GC-FID to determine the percentage conversion of iodobenzene, calculated as follows:

$$\% \text{ Conversion} = (A_{\text{int}} - A_{\text{final}}) / A_{\text{int}} \quad (1)$$

A_{int} = peak area of iodobenzene before reaction

A_{final} = peak area of iodobenzene after reaction



Figure 3 General procedure of Sonogashira reaction

3.0 RESULTS AND DISCUSSION

3.1 Infrared Spectroscopy

The important bands for ligands and Ni(II) complexes are listed in Table 1. The hydroxyl ν(O-H) band appears in the range of 3225-3226 cm⁻¹ in the free ligands but the band is absent in all spectra of nickel(II) complexes. This indicates that the coordination between metal centre and phenolic oxygen has taken place through the deprotonation of hydroxyl group [17]. The strong peaks assignable to C=N of all ligands appeared in the range of 1612-1618 cm⁻¹. As detailed in Table 1 and Figure 4, these peaks shifted by about 10 cm⁻¹ to lower frequencies of 1603-1607

cm^{-1} in all Ni(II) complexes indicating a decrease in the C=N bond order due to the coordinate bond of the metal with the imine nitrogen lone pair [18, 19]. The C-O bands also experienced a shift from 1237-1270 cm^{-1} to 1248-1286 cm^{-1} , indicating a weakening C-O bond upon coordination of metal with phenolic oxygen [1]. C-N band has shifted from 1317-1357 cm^{-1} in free ligands to 1331-1360 in nickel(II) complexes suggesting the coordination between metal centre with imine nitrogen [20].

The shifting of C=N, C-O, and C-N bands and the absence of hydroxyl peak in nickel(II) complexes are indicators that coordination between metal centers with phenolic oxygen and imine nitrogen has been achieved.

The Ni-O and Ni-N, new weak bands were observed in the spectra of nickel(II) complexes in the vicinity of 461-494 cm^{-1} and 521-526 cm^{-1} , respectively. These bands were absent in the spectra of free ligands. This is another useful evidence that the coordination between ligands and metal centres through the phenolic oxygen and azomethine nitrogen. The appearance of metal-nitrogen and metal-oxygen sometimes can be very difficult to be seen in the spectra of metal complexes [21].

Table 1 Infrared spectra of Schiff bases/ligands and their Nickel(II) complexes

Comp	Frequency, cm^{-1}					
	OH	C=N	C-N	C-O	Ni-N	Ni-O
L1H	3225	1612	1317	1237	-	-
NiL1H	-	1607	1342	1248	526	494
L1F	3232	1618	1320	1270	-	-
NiL1F	-	1603	1331	1286	521	474
L1M	3306	1616	1357	1251	-	-
NiL1M	-	1605	1360	1266	521	461

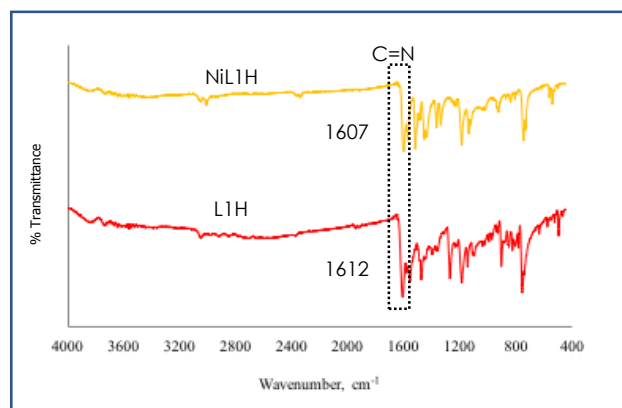


Figure 4 Representative spectra showing the shifting of $\nu(\text{C}=\text{N})$ bands in NiL1H

3.2 ^1H and ^{13}C NMR Spectroscopy

^1H NMR data show that OH appears as singlet at 12.67-13.09 ppm in free ligands. Its protons are deshielded downfield due to the formation of hydrogen bonding [22]. The absence of OH peak in all spectra of

complexes supported the IR evidence that the coordination to metal centres was established through deprotonation of the hydroxyl groups [23].

As detailed in Table 2, azomethine proton, $\text{HC}=\text{N}$ appears as singlet at region of 8.61-8.87 ppm for all free ligands. However, this peak was found at the upfield region of 8.22 ppm in NiL1H complexes. This indicates that in complexes, the protons are being less shielded due to reduction in electron density of the imine bond caused by sharing of electrons with metal centres [23].

Table 2 ^1H NMR chemical shifts (δ /ppm) of compounds

Comp.	Chemical shifts, δ (ppm)			
	δ (O-H)	δ (HC=N)	δ (Ar-H)	δ (CH_3)
L1H	13.09(s)	8.65(s)	6.93-7.41(m)	-
NiL1H	-	8.22(s)	6.63-7.31(m)	-
L1F	12.82(s)	8.61(s)	7.01-7.41(m)	-
L1M	12.67(s)	8.87(s)	6.86-7.47(m)	2.28(s)

Note: (s) = singlet; (m) = multiplet; Ar = aromatic

Table 3 ^1H NMR chemical shifts δ (ppm) of aromatic protons of L1H

δ (Ar-H)	Multiplicity	Coupling constants, J (Hz)	Number of H
6.95	t	7.50	1
7.08	d	8.29	1
7.25	dd	3.46, 5.80	1
7.36	dd	3.43, 5.90	1
7.40	d	7.58	2

Note: (td) = triplet of doublet; (dd) = doublet of doublet; Ar = aromatic

The chemical shifts of aromatic hydrogen appear as multiplets in the range of 6.63-7.47 ppm. This is in agreement with the chemical shifts reported by Mohd. Tajuddin *et al.* [22]. These hydrogens experience the shielding effect of diamagnetic anisotropy caused by circulating π electrons in the aromatic rings. The values of coupling constants as shown in Table 3 suggest the presence of *ortho* and *meta* hydrogens. The number of hydrogens obtained from the integration is in conformance with the proposed chemical structures.

^{13}C NMR data (Table 4) show that azomethine carbon, C=N was found at 163.74 ppm in L1H and it appears in lower field regions for complexes at 166.45 ppm in NiL1H. The shifting corroborated ^1H NMR and IR data that coordination of metal centres to the ligands was successfully established.

Complexation can also be noticed from the shifting of aromatic carbons [1] from 117.56-133.39 ppm in free ligands to the region of 114.86-135.34 ppm in complexes. The displacement of C-OH peak by about 6-9 ppm in the complex is also another evidence of the metal-phenolic oxygen coordination.

Table 4 ^{13}C NMR chemical shifts (δ /ppm) of ligands and some complexes

Comp.	Chemical shifts, δ (ppm)		
	C-OH/C-O	HC=N	Ar-H
L1H	161.37	163.74	117.56-133.39
NiL1H	154.20	166.45	114.86-135.34
L1F	157.51	162.63	117.00-128.15
L1M	158.69	164.41	116.98-134.65

Due to solubility limitations, NMR data of NiL1F and NiL1M could not be obtained.

3.3 Magnetic Susceptibility and Molar Conductivity

All complexes gave 0 effective magnetic moment values (μ_{eff}) indicating the absence of lone pair of electrons, corresponding to the diamagnetic square planar d^8 nickel(II) system, similar to the behaviour reported by Antony and co-workers [24].

The complexes also showed $0 \lambda_{\text{m}}/\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$ for molar conductivity suggesting the non-electrolytic nature of the compounds. The anionic ligands are indicated to be in the coordination sphere [24].

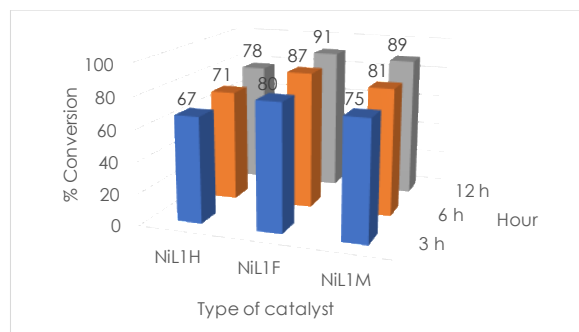
3.4 Catalytic Activity of Nickel(II) Schiff Base Complexes for Sonogashira Reaction

All nickel(II) complexes were screened as a catalyst in Sonogashira cross-coupling reaction of iodobenzene with phenylacetylene in the presence of potassium hydroxide (KOH) in Dimethylsulfoxide (DMSO) at 140°C and 2 mmol% catalyst loading.

Percentage conversion of iodobenzene was monitored using GC-FID where sampling was done at 3, 6 and 12 hours. Table 5 and Figure 5 show that the NiL1F catalyzed the highest conversion of iodobenzene (91%) followed by NiL1M (89%) and NiL1H (78%). Control reaction with the absence of catalyst was carried out where no conversion of iodobenzene after 12 hours of reaction was detected.

Table 5 Percentage of iodobenzene conversion

Catalyst	% Conversion of Iodobenzene		
	3 h	6 h	12 h
NiL1H	67	71	78
NiL1F	80	87	91
NiL1M	75	81	89

**Figure 5** Percent conversion of iodobenzene after 12 hour of reaction

The results show that the highest conversion of iodobenzene was attained at 12 hours, the maximum investigated reaction time. It appears that the catalytic property of these compounds is mainly affected by electronic factor where the electron-withdrawing substituent, fluoro, in NiL1F most effectively facilitated the coupling activity with 91% conversion. NiL1M that contains electron donating $-\text{CH}_3$ exhibited a lower performance of 89% conversion and unsubstituted NiL1H was the least reactive with 78% conversion.

4.0 CONCLUSION

In this study, three aromatic azomethine ligands and their nickel(II) complexes were successfully synthesized and characterized. NiL1F showed the highest conversion of iodobenzene with 91% followed by NiL1M (89%) and NiL1H (78%) after 12 hour of reaction.

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References

- [1] Gupta, K. C., & Sutar, A. K. 2008. Catalytic Activities of Schiff Base Transition Metal Complexes. *Coordination Chemistry Reviews*. 252: 1420-1450. <http://doi.org/10.1016/j.ccr.2007.09.005>.
- [2] Pawanoji, A. A., & Mehta, B. H. 2016. Transition Metal Complexes of Schiff Base Ligands as Efficient Catalysts for Epoxidation of Alkenes. *Imperial Journal of Interdisciplinary Research (IJIR)*. 2(12): 448-473.
- [3] Chinchilla, R., & Nájera, C. 2011. Recent Advances in Sonogashira Reactions. *Chemical Society Reviews*. 40(10): 5084. <http://doi.org/10.1039/c1cs15071e>.
- [4] Djakovitch, L., & Rollet, P. 2004. Sonogashira Cross-coupling Reactions Catalysed by Heterogeneous Copper-free Pd-

- Zeolites. *Tetrahedron Letters*. 45: 1367-1370. <http://doi.org/10.1016/j.tetlet.2003.12.077>.
- [5] Panda, B., & Sarkar, T. K. 2010. Gold and Palladium Combined for the Sonogashira-type Cross-coupling of Arenediazonium Salts. *Chem. Commun.* 46: 3131-3133. <http://doi.org/10.1039/c001277g>.
- [6] Bakherad, M., Keivanloo, A., Bahramian, B., & Hashemi, M. 2009. Copper-free Sonogashira Coupling Reactions Catalyzed by a Water-soluble Pd – Salen Complex Under Aerobic Conditions. *Tetrahedron Letters*. 50(14): 1557-1559. <http://doi.org/10.1016/j.tetlet.2009.01.053>.
- [7] Han, F.-S. 2013. Transition-metal-catalyzed Suzuki-Miyaura Cross-coupling Reactions: A Remarkable Advance from Palladium to Nickel Catalysts. *Chemical Society Reviews*. 42(12): 5270-98. <http://doi.org/10.1039/c3cs35521a>.
- [8] Beletskaya, I. P., Latyshev, G. V., Tsvefkov, A. V., & Lukashev, N. V. 2003. The Nickel-catalyzed Sonogashira–Hagihara Reaction. *Tetrahedron Letters*. 44(27): 5011-5013.
- [9] Suzuka, T., Okada, Y., Ooshiro, K., & Uozumi, Y. 2010. Copper-free Sonogashira Coupling in Water with an Amphiphilic Resin-supported Palladium Complex. *Tetrahedron*. 66(5): 1064-1069. <http://doi.org/10.1016/j.tet.2009.11.011>.
- [10] Nowrouzi, N., & Zarei, M. 2015. NiCl₂.6H₂O: An Efficient Catalyst Precursor for Phosphine-free Heck and Sonogashira Cross-coupling Reactions. *Tetrahedron*. 71: 7847-7852. <http://doi.org/10.1016/j.tet.2015.08.023>.
- [11] Yang, S., Xu, Y., & Li, J. 2016. Theoretical Study of Nickel-Catalyzed Proximal C–C Cleavage in Benzocyclobutenones with Insertion of 1, 3-Diene: Origin of Selectivity and Role of Ligand. *Org. Lett.* 18(24): 6244-6247.
- [12] Gniewek, A. 2016. Suzuki-Miyaura Cross-coupling of Phenylboronic Acid with Aryl Halides Catalyzed by Palladium and Nickel Species Supported on Alumina-based Oxides. *Journal of Organometallic Chemistry*. 823: 90-96.
- [13] Iwasaki, T., & Kambe, N. 2016. Ni-Catalyzed C–C Couplings Using Alkyl Electrophiles. *Topics in Current Chemistry*. 374(5): 66.
- [14] Cozzi, P. G., Ciamician, C. G., & Selmi, V. 2004. Metal–Salen Schiff Base Complexes in Catalysis: Practical Aspects. *Chemical Society Reviews*. 33: 410-421.
- [15] Gupta, K. C., & Sutar, A. K. 2008. Catalytic Activities of Schiff Base Transition Metal Complexes. *Coordination Chemistry Reviews*. 252: 1420-1450. <http://doi.org/10.1016/j.ccr.2007.09.005>.
- [16] Mani Saravana Veerappan, S., Ramaswamy, N., & Kartha, B. 2015. Synthesis of Mononuclear Schiff Base Cu (II), Ni (II), Co (II) and Mn (II) Complexes and their Application for DNA Cleavage and Antibacterial Agent. *Chemical Science Review and Letters*. 4(13): 121-128.
- [17] Mohd Tajuddin, A., Bahron, H., Kassim, K., Wan Ibrahim, W. N., & M.Yamin, B. 2012. Synthesis and Characterisation of Palladium (II) Schiff Base Complexes and Their Catalytic Activities for Suzuki Coupling Reaction. *Malaysian Journal of Analytical Sciences*. 16(1): 79-87.
- [18] Philip, V., Suni, V., & Kurup, M. R. P. 2004. Structural and Spectral Studies of Nickel (II) Complexes of di-2-pyridyl. 23: 1225-1233. <http://doi.org/10.1016/j.poly.2004.02.004>.
- [19] Percy, G. C. 1972. Infrared Spectra of N-Aryl Salicylaldimine Complexes Substituted in Both Aryl Rings. *Journal of Inorganic and Nuclear Chemistry*. 35: 2319-2327.
- [20] Tajuddin, A. M., Bahron, H., & Ahmad, S. N. 2015. Synthesis and Characterization of Pd (II) and Ni (II) Complexes of Schiff Bases and Catalytic Activity of Pd (II) Complexes. *Scientific Research Journal*. 12(2): 1-7.
- [21] Aranha, P. E., Santos, M. P., Romera, S., & Dockal, E. R. 2006. Synthesis, Characterization, and Spectroscopic Studies of Tetradentate Schiff Base Chromium (III) Complexes. *Polyhedron*. 26(7): 1373-1382. <http://doi.org/10.1016/j.poly.2006.11.005>.
- [22] Antony, R., Theodore David Manickam, S., Saravanan, K., Karuppasamy, K., & Balakumar, S. 2013. Synthesis, Spectroscopic and Catalytic Studies of Cu(II), Co(II) and Ni(II) Complexes Immobilized on Schiff Base Modified Chitosan. *Journal of Molecular Structure*. 1050: 53-60. <http://doi.org/10.1016/j.molstruc.2013.07.006>.