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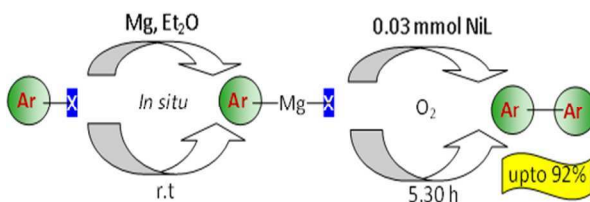
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Nickel Catalyzed One Pot Synthesis of Biaryls under Air at Room Temperature

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Present catalytic methodology of the homocoupling of *in situ* generated Grignard reagents using nickel(II) complex under atmospheric oxygen oxidant renders the system more simpler, economical and green.



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Abstract

A practical, room temperature catalytic system has been developed for the synthesis of biaryls in one step from the homocoupling of *in situ* generated Grignard reagents using the nickel(II) complex. Atmospheric oxygen used as an oxidant makes the system environment friendly. The reaction system is compatible with diverse functionality to afford biaryls in appreciable yields.

Key words: biaryls, homocoupling, Grignard reagent, atmospheric oxygen

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1. Introduction

The synthesis of biaryls is of particular interest to industry is easily shown by their broad applications in multidisciplinary fields.¹ These motifs increasingly turn up in materials important to society such as pharmaceuticals, biocides, and specialized engineering materials such as highstrength rigid-rod polymers, molecular wires, liquid crystals and nonlinear optical materials, all attracting enormous interest both within the chemical community and outside.² Transition metal catalyzed homocoupling of the Grignard reagents is one of the most efficient synthetic methods for the construction of a symmetrical biaryl backbone.³ To date, varieties of simple metal salts were used as catalyst for their synthesis.⁴⁻⁵ Though, many nickel-catalyzed coupling reactions were reported so far, the demand for stoichiometric amount of organic oxidant or an extra ligand limits their use for industrial scale applications.⁶⁻⁷ In demand for searching alternative protocol, environment benign molecular oxygen has found to be more attractive oxidant for the homocoupling reactions. Iron, manganese⁸ and palladium⁹ based catalysts are well-reported for such homocoupling reactions. But the problem encountered with these later methods is their two step synthetic route, where the organometallic compounds should be prepared first and then in a separate reaction converted into biaryl product. Recently reported cobalt catalyzed homocoupling of Grignard reagents in one step by Chen et al.¹⁰ did not discuss the catalytic mechanism and the system requires comparatively higher amount of catalyst loading than the present system.

Though a variety of metallic reagents can be applied in the coupling reaction, the development in the ligand framework which is susceptible for the changes during catalysis is highly appreciable. Because of their different coordination possibilities with metal ions and consequently their flexible complexing behavior, Schiff bases of 4-aminoantipyrine and its

complexes have been receiving increasing interest for their variety of applications.¹¹⁻¹² But these are less explored to the homocoupling reactions. Triphenylphosphine-based ligands have become increasingly important to systematically modify and tune the catalytic activity.¹³ The nickel complexes for c-c coupling represent an attractive area of endeavor mainly because of their wide applicable scope and excellent compatibility with many functional groups. Significantly, lower cost and excellent redox properties of nickel, in part, given the utility of its heavy metal congener, palladium, making this objective economically as well as synthetically alluring.¹⁴

In our previous work, we reported ruthenium(III) catalyst containing dmit (2-thioxo-1,3-dithiole-4,5-dithiolate) and triphenylphosphine ligands for the homocoupling reaction.¹⁵ In continuation with our interest to afford symmetrical biaryls, in this paper, the ligand and metal precursors are varied and their influence on the coupling reaction is being studied. Tridentate Schiff base is introduced in place of dmit ligand and nickel instead of ruthenium precursor. Herein we report one-pot synthesis of biaryls using octahedral nickel(II) complex, as a catalyst. The nickel(II) complex was synthesized from Schiff base, 4-{{(E)-(2,4-dihydroxyphenyl)methylidene]amino}-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one and triphenylphosphine ligands. The catalytic method adopted a much simple pathway of an *in situ* formation of the Grignard reagent. The reaction proceeded at room temperature using atmospheric oxygen as an oxidant.

2. Experimental

2.1 Materials and methods

All chemicals used were of analytical grade. The C, H and N contents of the compounds were determined by Thermoflash EA1112 series elemental analyzer. Magnetic susceptibility measurement was recorded on a Sherwood Scientific magnetic susceptibility balance (UK).

Thermal analysis was carried out (EXSTAR-6000) from room temperature to 700 °C at a heating rate of 10 °C/min. The electronic spectrum of the complex was measured on a GBC Cintra 101 UV – Vis double beam spectrophotometer using DMF in the 200-800 nm range. FT-IR spectrum was recorded on a Thermo Nicolet Avatar FT-IR spectrometer in the frequency range 400-4000 cm⁻¹. ¹H NMR (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded in Bruker AV 400 instrument using TMS as internal standards respectively. Coupling reactions were monitored by Gas Chromatography, Shimadzu 2014.

2.2 Synthesis

2.2.1 Synthesis of 4-*[(E)-(2,4-dihydroxyphenyl)methylidene]amino*}-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (**L**₁)

The Schiff base **L**₁ was synthesized according to the reported procedure.¹⁶ Solution of 4-Aminoantipyrine (2.03 g, 10mmol) in ethanol was added drop wise to a solution of 2,4-dihydroxybenzaldehyde (2,4-DHB) (1.38 g, 10mmol) in ethanol. The mixture was stirred at room temperature for 15 minutes and then refluxed for 2 hours. The yellow colored solid product was filtered, washed, recrystallized with ethanol and dried in *vacuo*.

Ligand L₁: Yield: (2.32 g, 72%); **mp:** 234 °C; **Elemental analysis** calcd. for C₁₈H₁₇N₃O₃(%): C, 66.86; H: 5.30, N: 13.00. found: C, 66.85; H, 5.27; N, 12.98; **FT-IR** (cm⁻¹): 1605 (C=O), 1576 (-CH=N-), 1314 (C-O); **¹H NMR** δ_H (400 MHz; DMSO; Me₄Si): 13.32 (br s, -OH), 9.56 (s, -CH=N-), 6.2-7.6 (m, Ar-H), 3.26 (s, N-CH₃), 2.38 (s, =C-CH₃); **MS (ESI)** (m/z) calcd. for C₁₈H₁₇N₃O₃ [M+1]: 323.34. found: 324.3; **UV-Vis** λ_{max} (nm): 278, 315, 340, 390.

2.2.2 Synthesis of Ni(II) complex (**NiL**)

The metal precursor NiCl₂(PPh₃)₂ was synthesized according to the earlier reported procedure.¹⁷ The nickel(II) complex, **NiL**, was obtained by refluxing the solution of **L**₁ (1

mmol) and $[\text{NiCl}_2(\text{PPh}_3)_2]$ (1 mmol) in methanol for 3 hours with constant stirring (**Figure 1**).

The yellowish green coloured product obtained was filtered, washed with methanol, petroleum ether (60-80 °C) and dried *in vacuo*.

NiL: Yield: (1.22 g, 65%); **Elemental Analysis** found (calc.) for $\text{C}_{54}\text{H}_{46}\text{ClNi}_3\text{O}_3\text{P}_2$, C: 68.84 (68.92), H: 4.89 (4.93), N: 4.42 (4.47); IR (KBr, cm^{-1}): 1618 (C=O), 1538 (-CH=N-), 1337 (C-O), 1071, 749, 693, 488 (M-O), 441(M-N); $^1\text{H NMR}$ δ_{H} (400 MHz; DMSO; Me_4Si): 9.69(s, -CH=N-), 7.18-8.83 (m, Ar-H), 3.24 (s, N- CH_3), 2.50 (s, =C- CH_3); $^{31}\text{P NMR}$ δ_{P} (H_3PO_4): 26.52; **MS (ESI)** (m/z) calcd. for $\text{C}_{54}\text{H}_{46}\text{ClNi}_3\text{O}_3\text{P}_2$ [M^+]: 941.1. found: 941.4; **UV-Vis** λ_{max} (nm): 288, 334, 411, 511, 563, 658. μ_{eff} : 3.266.

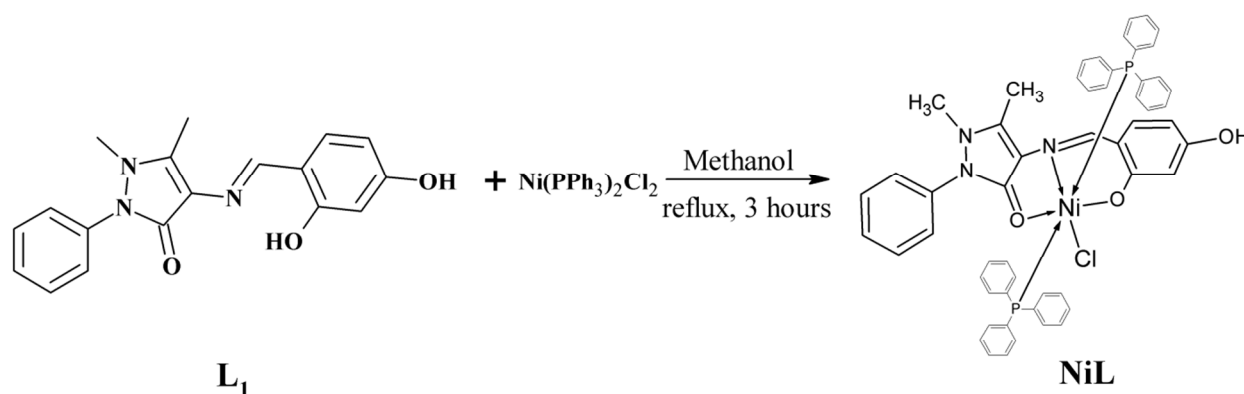


Figure1: Reaction scheme for the synthesis of **NiL**.

2.3 Catalytic study

2.3.1 General procedure for Homocoupling of aryl Grignard reagents

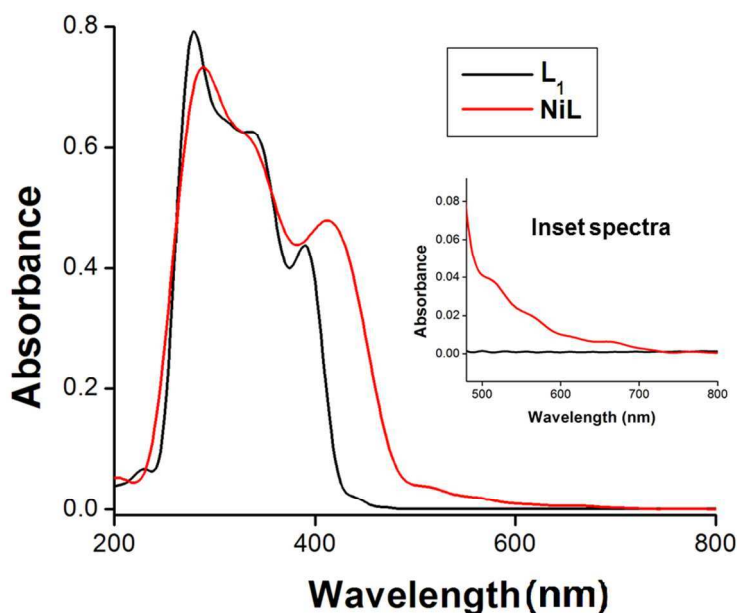
In this procedure, magnesium turnings (13 mmol, 0.320 g atom) were placed in a two necked round bottom flask with a calcium chloride guard tube and a crystal of iodine was added. Aryl bromide (2 mmol of total 10 mmol) in 5 ml of anhydrous diethyl ether was added with constant stirring at room temperature. Initially, increase in the temperature of the reaction mixture was observed and the appearance of turbidity after few minutes indicated the initiation

of the reaction. The remaining aryl bromide (8 mmol) in 5 ml of ether was added drop wise and the reaction mixture was stirred for 40 minutes. Then, to the reaction mixture, catalyst NiL (0.03 mmol) was added. The reaction mixture darkened immediately upon addition of the catalyst. The stirring was continued. After 5 hours the reaction mixture was cooled and hydrolyzed with a saturated solution of 10% aqueous ammonium chloride. After extraction with ether (3x50 mL), the combined organic layers were dried over anhydrous magnesium sulfate. All volatiles were removed under reduced pressure and the residue was chromatographed on silica gel to afford respective biphenyl. The products obtained compared well with authentic samples using gas chromatography.

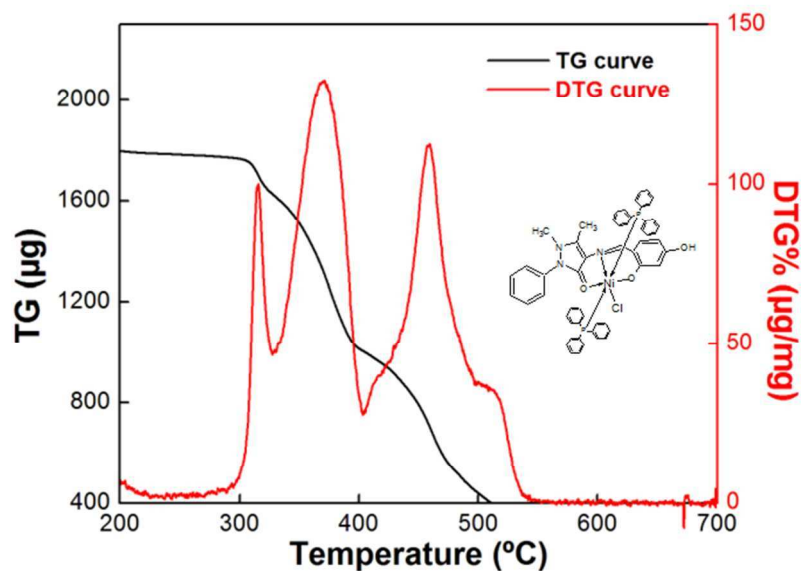
3. Results and Discussion

The elemental analyses (C, H, N) were in good agreement with the molecular formula proposed for L_1 and NiL. The FT-IR spectra of the ligand exhibit intense bands at 1605 cm^{-1} and 1576 cm^{-1} corresponding to antipyrine exocyclic ketone $\nu(\text{C}=\text{O})$ and azomethine $\nu(\text{CH}=\text{N})$, respectively. Their coordination to the metal ion was confirmed by the frequency shift to 1618 and 1538 cm^{-1} , respectively.¹⁸ The band in the region 1314 cm^{-1} which is assigned to the phenolic $\nu(\text{C}-\text{O})$ in the free ligand shifts to a higher wave number 1337 cm^{-1} in the complex suggesting its involvement in the coordination. Thus L_1 acts as tridentate ligand with O,N,O coordination sites. The peaks at 1071 , 749 and 693 cm^{-1} can be attributed to the presence of triphenylphosphine in the complex. Appearance of the medium bands at 441 and 488 cm^{-1} could be attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$, respectively. In the ^1H NMR spectra of the complex,¹⁹ absence of a sharp singlet at 13.32 ppm shows that the phenolic oxygen coordinates after deprotonation. The presence of peak at 9.67 ppm in the complex confirms the coordination of azomethine nitrogen to the metal ion. The complex shows multiplets at 7.18 - 8.83 ppm due to the

aromatic proton of the coordinated ligand. $^{31}\text{P}\{1\text{H}\}$ NMR spectrum exhibits a sharp singlet at 26.52 ppm supporting the presence of the triphenylphosphine groups in trans position.²⁰ The mass analysis further confirms the structure of L_1 and NiL . As shown in the **Figure 2a**, the electronic spectrum of the complex shows an intense absorption band in the region 292-409 nm, due to intra ligand charge transitions (ILCT) and a band in the region 411 nm can be attributed to the ligand to metal charge transfer transitions (LMCT). The characteristic d-d transition observed in the region 511-658 nm. The room temperature magnetic moment of 3.26 BM shows that the complex is octahedral in nature.²¹ From the TG analysis (**Figure 2b**), the weight loss was observed at temperature range around 310-318, 335-393 and 450-524 °C which corresponds to the loss of one chloride molecule, one ligand moiety and two molecules of triphenylphosphine respectively further confirms the assumed structure.



(a)



(b)

Figure 2: (a) UV-Vis spectra of L_1 and NiL (b) TG analysis of NiL .

The present catalytic methodology involves an *in situ* formation of aryl Grignard reagent. Iodine was used as a surface activator for commercially available magnesium turnings. Addition of aryl bromide during the formation of the Grignard reagent takes a very important role. Various side products were observed on their fast addition, mainly ROH. When bromobenzene was added at faster rate, we obtained phenol as main side product.²² Controlled addition of the aryl bromides yielded respective Grignard reagents with negligible amount of side product. Thus formed Grignard reagent on reaction with catalytic amount of nickel(II) complex afforded biaryl in moderate to good yield. The coupling reaction was successfully carried out in open air at room temperature. The atmospheric oxygen was used as an oxidant, making the system energy efficient and environment friendly. No external oxidants were used.

Optimization studies with respect to various parameters such as solvent, catalyst concentration and reaction time were done for the coupling of phenyl magnesium bromide (**1e**). The solvent effect on coupling activity using NiL was analyzed in various solvents like

tetrahydrofuran, diethyl ether, benzene, etc., in presence of atmospheric oxygen. The best yield was obtained in diethyl ether which can be attributed to its ability to coordinate with the Grignard reagent and thus stabilize the intermediate complex.²³ It was observed that the yield increases with the reaction time (**Figure 3**) and total reaction time of 5.30 hours at room temperature gave a constant conversion of 83%.

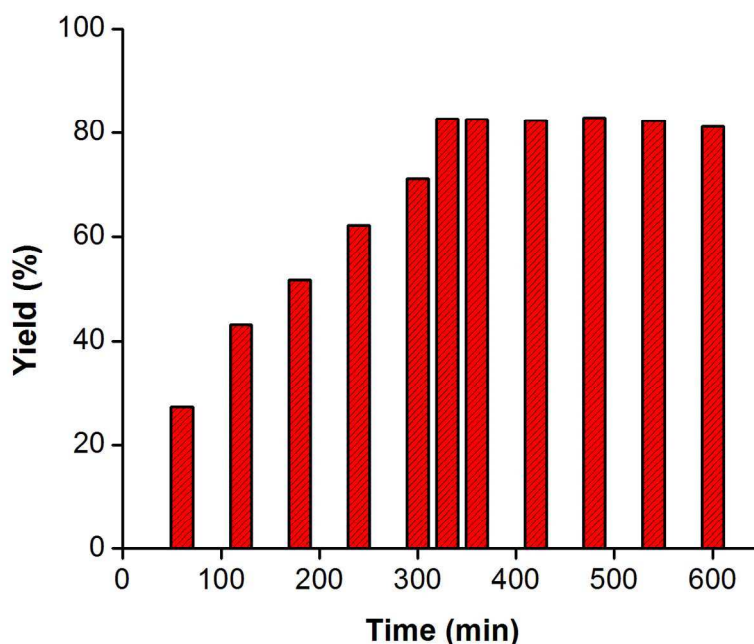
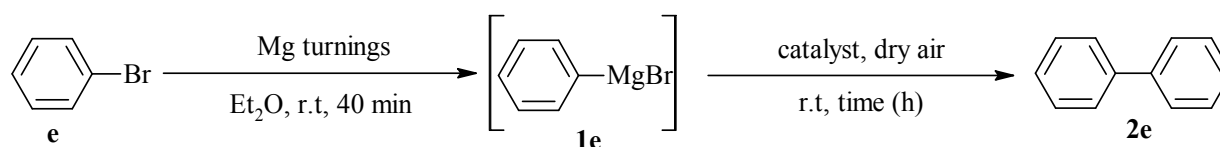


Figure 3: Dependence of biaryl yield on the reaction time in presence of NiL.

The effect of catalyst concentration on the yield of coupling product (**Figure 4**) was examined by varying substrate to catalyst ratio from total amount 0.01 mmol to 0.05 mmol. Initially for comparison study, we carried out the catalytic activities using simple nickel metal precursors, NiCl₂ and [Ni(PPh₃)₂Cl₂]. The result in the **Table 1** indicates that better yield could be achieved by increasing the amount of NiCl₂ and [Ni(PPh₃)₂Cl₂] (**entries 2-9**). Next, we turned our attention to the NiL. The yield increased with NiL loading and reached the highest value of 83% with 0.03 mmol of NiL at 5.30 hours (**entry 6**). Influence of air is the key factor in the present catalytic system. A good yield was observed in presence of atmospheric oxygen. In the

absence of air, the reaction was carried out in an inert atmosphere (argon), resulting lower yield, which may be attributed to the lack of formation of peroxo-nickel(III) active species (**entry 10**). In the absence of **NiL**, only traces of coupling products were obtained (**entry 1**) that showed the effective catalytic role of **NiL**. The efficiency of the complex is so prominent, that the present coupling can be readily scaled up to the reaction of 50.0 mmol of the aryl halide using 0.150 mmol of the catalyst, which yields 80% of biaryl in 8 hours with negligible amount of byproducts (**entry 11**). To exclude the effect of magnesium, the reaction was carried out using commercial phenylmagnesium bromide as a starting material in the presence of air (**entry 12**). To our surprise the yield was less (37%). This may be due to the difficulty in handling the commercial phenylmagnesium bromide.¹⁰ Most of the reported Grignard reagent based catalytic system^{5,8} requires sophisticated set-up to handle the reagents in moisture free environment compared to the present work.

Table 1: Optimization of homocoupling of **1e** w.r.to catalyst concentration^a



Entry	Catalyst (mmol)	time (h)	Yield(%) ^b
1	No catalyst	10	01
	NiCl ₂ (0.01)	6	8
2	[Ni(PPh ₃) ₂ Cl ₂] (0.01)	6	11
	NiL (0.01)	5.30	32
	NiCl ₂ (0.015)	6	11
3	[Ni(PPh ₃) ₂ Cl ₂] (0.015)	6	15
	NiL (0.015)	5.30	43
	NiCl ₂ (0.02)	6	17
4	[Ni(PPh ₃) ₂ Cl ₂] (0.02)	6	16
	NiL (0.02)	5.30	59
	NiCl ₂ (0.025)	6	21
5	[Ni(PPh ₃) ₂ Cl ₂] (0.025)	6	19
	NiL (0.025)	5.30	67
6	NiCl ₂ (0.03)	6	23

	[Ni(PPh ₃) ₂ Cl ₂] (0.03)	6	21
	NiL (0.03)	5.30	83
	NiCl ₂ (0.035)	6	26
7	[Ni(PPh ₃) ₂ Cl ₂] (0.035)	6	24
	NiL (0.035)	5.30	82
	NiCl ₂ (0.04)	6	30
8	[Ni(PPh ₃) ₂ Cl ₂] (0.04)	6	26
	NiL (0.04)	5.30	81
	NiCl ₂ (0.05)	6	37
9	[Ni(PPh ₃) ₂ Cl ₂] (0.05)	6	35
	NiL (0.05)	5.30	81
10^c	NiL (0.03)	5.30	5
11^d	NiL (0.15)	8	80
12^e	NiL (0.03)	5.30	37

^a Reactions were carried out with 10 mmol of bromobenzene in presence of atmospheric oxygen. ^b Isolated yield. ^c Inert atmosphere (argon). ^d With 50.0 mmol of bromobenzene in the presence of 0.150 mmol catalyst for 8 hours. ^e Reactions were carried out with 10 mmol of commercial phenylmagnesium bromide in presence of atmospheric oxygen.

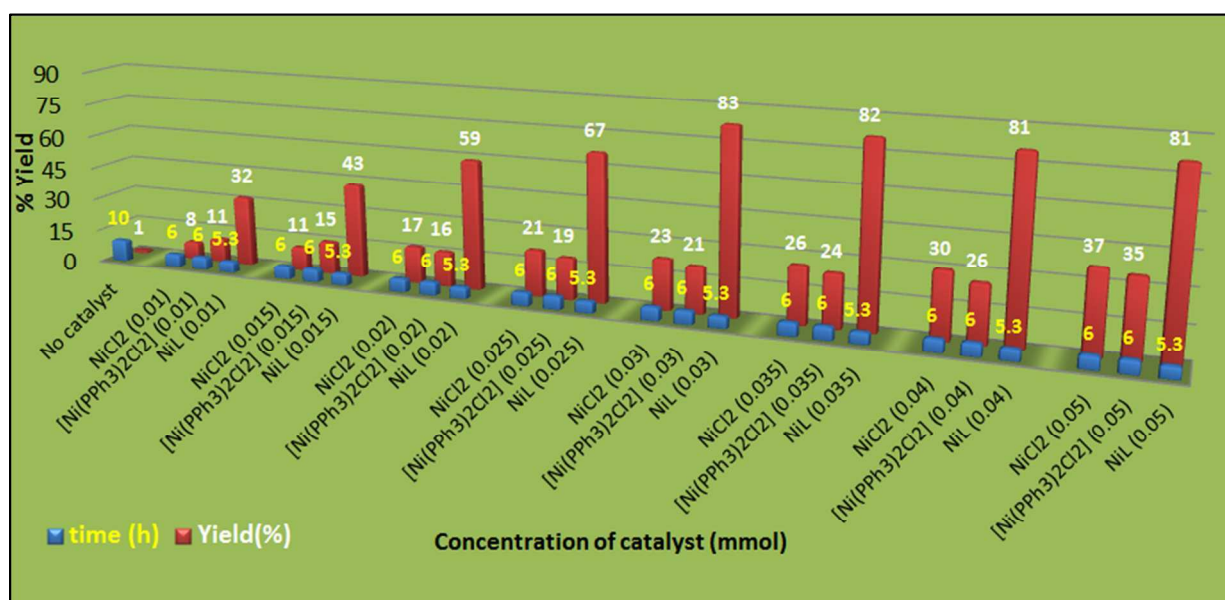
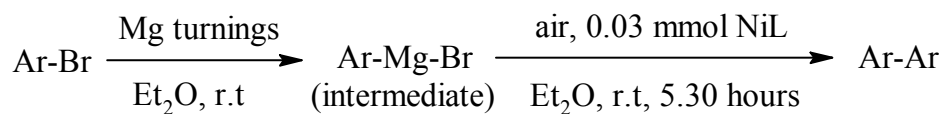


Figure 4: Histogram of optimization of homocoupling of **1e** w.r.to catalyst concentration.

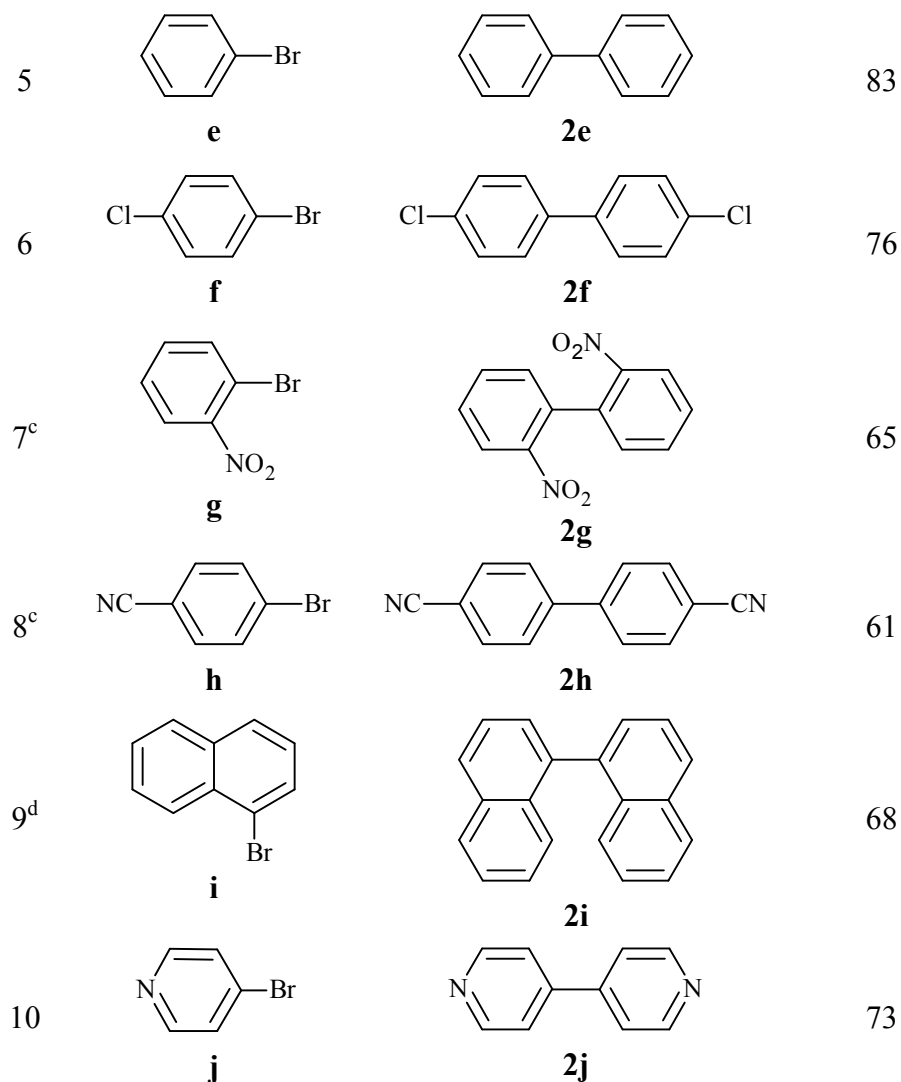
This encouraging result led us to the extension of the scope of the reaction to various aryl Grignard reagents to synthesize simple and functionalized biaryls in good yield (**Table 2**). It was observed that under similar reaction conditions high yields of **2a** and **2b** were obtained upon efficient coupling of 4-Methoxy- and 2-methoxyphenylmagnesium bromide, respectively (**entries 1 and 2**). The presence of methyl group at the ortho-position of the aryl Grignard

reagent resulted in somewhat lower yield of the homocoupling product (**entry 4**). It is noteworthy that the present reaction system is tolerant of aryl chloride functionality (**entry 6**). The nitro and nitrile groups were tolerated (**entries 7 and 8**), hence the reaction is chemoselective. Although, sterically demanding substrate **1i** required higher reaction temperature and longer reaction time, it gave the corresponding biaryl **2i** in moderate to good yield (**entry 9**). Also, it allows the coupling of heteroaryl Grignard reagent **1j** successfully (**entry 10**). It was observed that the Grignard reagent containing electron donating group enhances the yield of coupling product compared to that of electron withdrawing group. Formations of cross-coupling products found very less in all said experiments.

Table 2: Nickel-catalyzed homocoupling of Grignard reagents using atmospheric oxygen as an oxidant^a



Entry	Ar-Br	Product	Yield (%) ^b
1			92
2			79
3			86
4			75



^a Reaction conditions: Mg turnings (0.320 g), aryl bromide (10 mmol), catalyst (0.03 mmol), Et₂O (10 ml). ^b Isolated yield. ^c Reactions at -5 °C to rt. ^d In THF, 60 °C, 9 hours.

A proposed mechanism is depicted in **Figure 5** for NiL catalyzed reaction. A low valent nickel species is generated by the Grignard reagent, which is a strong reducing agent, involved in catalytic cycle.²⁴⁻²⁶ The oxidative addition of atmospheric oxygen to a low valent nickel complex (**a**) forms peroxo-nickel(III) intermediate (**b**) which is the key step of this catalytic cycle.²⁷ It then reacts with two equivalents of RMgX to give biarylnickel(III) intermediate (**c**) and XMgOOMgX.^{28,8} Thus formed biarylnickel(III) intermediate (**c**) undergoes rapid reductive elimination which eventually yields homocoupling product Ar-Ar and nickel(I) is regenerated. It

is very reasonable to think that the formation of the unstable nickel(III) species (**c**) is required to achieve a very quick reductive elimination that gives (**d**) as the best way to favor the reductive elimination is to increase the oxidation state of the metal. The formation of peroxo-nickel(III) intermediate was confirmed by the UV-Vis spectrophotometer analysis (**Figure 6**). The absorption peak of the catalytic reaction mixture that appeared at 419 nm can be attributed to peroxo-nickel(III) intermediate²⁷ and its absence in the reaction mixture carried out under inert condition further confirms the necessity of atmospheric oxygen for the present catalytic system. Various iron,²⁹ copper³⁰ and palladium³¹ - catalyzed reactions are well established with such peroxo complex as catalytic intermediate.

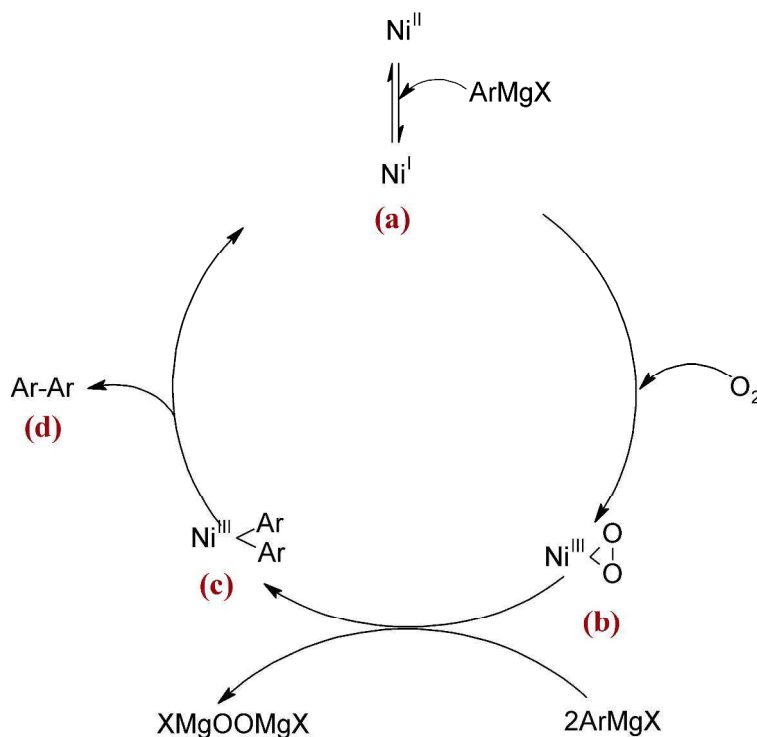


Figure 5: Proposed mechanism.

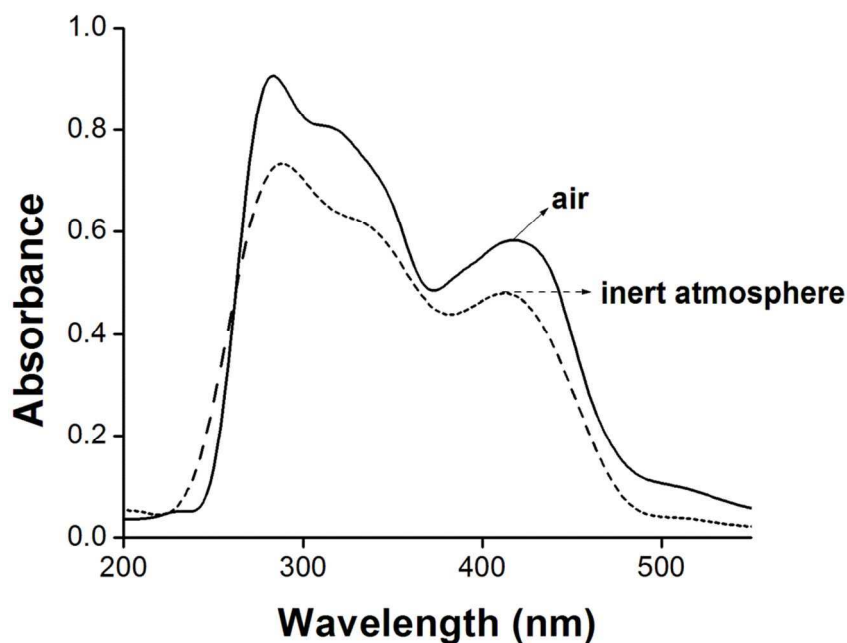


Figure 6: UV-Vis spectra for the confirmation of peroxo-nickel(III) intermediate.

The catalytic system reported herein shows appreciable improvement for the yield of biaryl in comparison with our previous work.¹⁵ This can be attributed to the efficiency of the NiL, which facilitates the faster reductive elimination reaction in catalytic cycle. Hypothetically, it may be due to the presence of more hindered ancillary ligands. The effect presumably arises from a relief in steric congestion upon generation of the free organic product and a resulting metal center with a reduced coordination number.³²

4. Conclusions

In conclusion, we have developed an energy efficient nickel-catalyzed coupling methodology to couple aryl Grignard reagents at room temperature, using atmospheric oxygen as an oxidant. The reaction system is compatible with diverse functionality to afford biaryls in good to excellent yields. It is noteworthy that the reaction is chemoselective. An *in situ* preparation of the Grignard reagent, a small amount of catalyst loading, mild reaction conditions, make the catalytic methodology practicable to large scale synthesis of symmetrical biaryls.

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Supplementary material

The online version of this article contains spectroscopic and analytical data of the products.

References

- 1 J. Magano and J. R. Dunetz, *Chem. Rev.*, 2011, **111**, 2177.
- 2 G. Bringmann, T. Gulder, T. A. M. Gulder and M. Breuning, *Chem. Rev.*, 2011, **111**, 563.
- 3 C. F. Nising, U. K. Schmid, M. Nieger and S. Brase, *J. Org. Chem.*, 2004, **69**, 6830.
- 4 N. Iranpoor and M. Shekarriz, *J. Chem. Research (S)*, 1999, 442.
- 5 Z. Zhou and W. Xue, *J. Organomet. Chem.*, 2009, **694**, 599.
- 6 S. Y. W. Lau, G. Hughes, P. D. O'Shea and I. W. Davies, *Org. Lett.*, 2007, **9**, 2239.
- 7 N. Yoshikai, H. Matsuda and E. Nakamura, *J. Am. Chem. Soc.*, 2009, **131**, 9590.
- 8 G. Cahiez, A. Moyeux, J. Buendia and C. Duplais, *J. Am. Chem. Soc.*, 2007, **129**, 13788.
- 9 D. D. Hennings, T. Iwama and V. H. Rawal, *Org. Lett.*, 1999, **1**, 1205.
- 10 S.-J. Chen, J. Zhang, Y.-H. Li, J. Wen, S.-Q. Bian and X.-Q. Yu, *Tetrahedron Lett.*, 2009, **50**, 6795.
- 11 K. Z. Ismail, A. El-Dissouky and A. Z. Shehadab, *Polyhedron*, 1997, **16**, 2909.
- 12 X. W. Wang and Y. Q. Zheng, *Inorg. Chem. Commun.*, 2007, **10**, 709.
- 13 A. V. Rooy, J. N. H. de Bruijn, K. F. Roobeek, P. C. J. Kamer and P. W. N. M. Van Leeuwen, *J. Organomet. Chem.*, 1996, **507**, 69.
- 14 A. Jutand and A. Mosleh, *J. Org. Chem.*, 1997, **62**, 261.

- 15 P. I. Aparna and B. R. Bhat, *J. Mol. Cata. A: Chemical*, 2012, **358**, 73.
- 16 P. M. Selvakumar, E. Suresh and P. S. Subramanian, *Polyhedron*, 2007, **26**, 749.
- 17 M. L. Venanzi, *J. Chem. Soc.*, 1958, 719.
- 18 R. M. Issa, A. M. Khedr and H. F. Rizk, *Spectrochim. Acta Part A.*, 2005, **62**, 621.
- 19 N. Raman, C. Thangaraja and S. Johnsonraja, *Cent. Eur. J. Chem.*, 2005, **3(3)**, 537.
- 20 M. Kettunen, A. S. Abu-Surrah, H. M. Abdel-Halim, T. Repo, M. Leskela, M. Laine, I. Mutikainen and M. Ahlgren, *Polyhedron*, 2004, **23**, 1649.
- 21 R. N. Patel, N. Singh and V. L. N. Gundla, *Polyhedron*, 2007, **26**, 757.
- 22 G. Kiefer, L. Jeanbourquin and K. Severin, *Angew. Chem.*, 2013, **125**, 6422.
- 23 M. A. Fox, and J. K. Whitesell, In *Organic Chemistry*, Jones & Bartlett: US, 2004, Third Edn., pp. 615-618.
- 24 X. Xu, D. Cheng and W. Pei, *J. Org. Chem.*, 2006, **71**, 6637.
- 25 C. Chen and L.-M. Yang, *J. Org. Chem.*, 2007, **72**, 6324.
- 26 T. Ramnial, S. A. Taylor, J. A. C. Clyburne and C. J. Walsby, *Chem. Commun.*, 2007, **(20)**, 2066.
- 27 J. Cho, R. Sarangi, J. Annaraj, S. Y. Kim, M. Kubo, T. Ogura, E. I. Solomon and W. Nam, *Nat. Chem.*, 2009, **1**, 568.
- 28 T. T. Tsou, J. K. Kochi and J. Am. Chem. Soc., 1979, **101(25)**, 7547.
- 29 J. Cho, S. Jeon, S. A. Wilson, L.V. Liu, E. A. Kang, J. J. Braymer, M. H. Lim, B. Hedman, K. O. Hodgson, J. S. Valentine, E. Solomon and W. Nam, *Nature*, 2011, **478**, 502.
- 30 J. Zapata-R, R. Caballol and C. J. Calzado, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20241.

31 C. Adamo, C. Amatore, I. Ciofini, A. Jutand and H. Lakmini, *J. Am. Chem. Soc.*, 2006, **128**, 6829.

32 J. F. Hartwig, *Inorg. Chem.*, 2007, **46**, 1936.