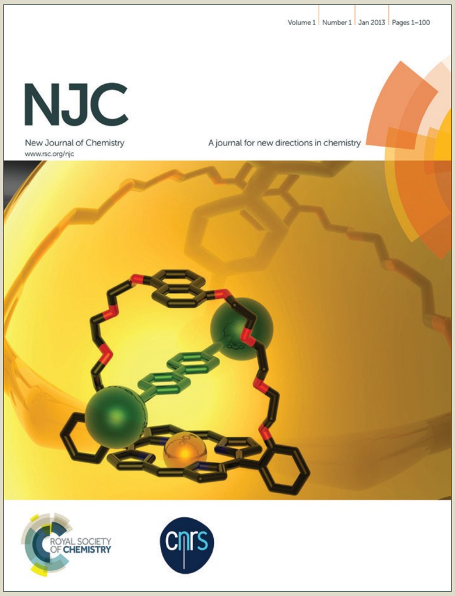

Journal Name

ARTICLE

Nickel-glycerol: An efficient, recyclable catalysis system for Suzuki cross coupling reaction using aryl diazonium salt

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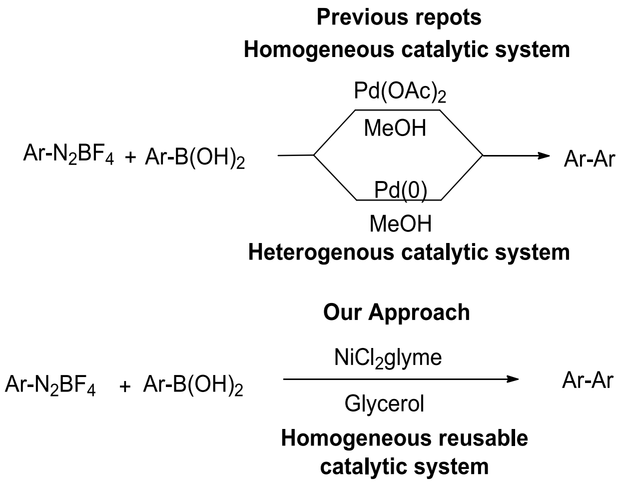
Nickel catalysed Suzuki reaction of phenyl boronic acid with aryl diazonium salt in glycerol as a reaction medium has been reported. Various aryl diazonium salts were efficiently reacts with aryl boronic acids under optimized conditions to give respective diaryl compounds in good to excellent yield. The base free conditions, use of glycerol as a solvent which can be recycled successfully upto five consecutive cycles have made the present protocol environmentally benign in nature.

Keywords: Aryl diazonium salt, Aryl boronic acid, $NiCl_2$-glyme,Glycerol, Suzuki reaction

Introduction

Transition metal catalysed cross coupling reactions play an important role in organic synthesis. Particularly, Suzuki reaction is a powerful tool for the construction of C-C bond using palladium catalyst.[1-7] Its major applications are in the pharmaceuticals, fine chemicals and agro industries.[8] The cross coupling reactions are commonly catalysed by palladium. However the first row transition elements such as Ni, Co, Fe and Cu are also used as alternative to palladium in cross coupling reactions.[9-14] Use of Nickel as catalyst in many cross coupling reactions namely Suzuki Miyaura reaction,[15-17] Sonogashira reaction,[18-20] Negishi reaction[21-23] is well known. Its use as a catalyst serves two purposes viz. it is inexpensive than palladium and produces low residual metal content in the reaction mass.[24] The Suzuki reaction catalysed by using nickel as a catalyst follow similar mechanism as that of palladium.[25-26]

Aryl halide is the most common reagent used for such cross coupling reactions. However, the high cost and low reactivity of these substrates limits their application and the use of C-O or C-N electrophiles such as carbamates, sulfamates and tosylates have been gained much attention in various organic transformations.[27-28] Recently the most interesting research is carried out with popular electrophilic partner such as aryl diazonium salts. Diazonium salts have several advantages over aryl halides. They can be easily prepared from inexpensive aniline, which is more reactive than aryl halides.[29-32] Diazonium salts were used for various cross coupling reactions such as C-N, C-S, and C-O bond formation reactions.[33-37] The Suzuki reaction is studied using diazonium salt at lower temperature without bases.[38-42] The reagent used for this cross coupling reaction is organoboronic reagent which is stable in air and easily available.[43] It possesses low toxicity, and high moisture resistance. Due to growing awareness about environmental issues, researchers have diverted their attention to develop environment friendly route as an alternative to conventional processes. Recently various researchers have reported different cross coupling reactions in aqueous medium as they are environmentally benign and inexpensive.[44-48] However, aqueous medium imposes some limitations such as low solubility of starting material and lower heating temperature as compared to other organic solvents. Hence new greener routes for cross coupling reactions are developed which are environmentally benign. Cross coupling reactions are well



Scheme1 General scheme for Suzuki cross coupling reaction

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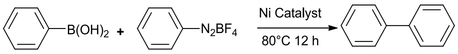
reported using greener and recyclable solvents like ionic liquid, PEG and Glycerol.[49-53] Glycerol is economical and environmentally safer solvent due to its physico-chemical properties such as high boiling point, high polarity, biodegradability, low flammability and high solubility for organic and inorganic compounds.[54-60] All above facts and observations prompted us to explore catalytic activity of nickel for Suzuki reaction by using glycerol as solvent and diazonium salt as starting material.

Result and Discussion

We initially chose phenyl boronic acid and diazonium salt of aniline as starting material for optimization of Suzuki reaction using nickel chloride as precatalyst and glycerol as solvent. The reaction mixture stirred at 80°C for 12h afforded 42 % yield of the desired product. Various nickel precatalysts were screened for the optimization of reaction conditions. First we carried out reaction in the absence of precatalyst and obtained trace amount of desired product (Table 1, entry 1).It was found that, reaction carried out using $NiCl_2$.glyme gave maximum yield as compared to other nickel precatalysts (Table 1, entries 2-8). This catalyst is easily available, and also air and moisture stable. The yield of desired product was found to increase with catalyst loading from 5 to 10 mol%. Further rise in catalyst loading from 10 to 15 mol% gave marginal increase in the yield (Table 1, entries 6, 9and 10).

Table1 Screening and optimization of catalyst



Entry	Catalyst	Yield[b]
1	-	Trace
2	$NiCl_2$	42
3	$NiSO_4$	31
4	$NiCl_2(PPh_3)_2$	18
5	$Ni(OAc)_2$	46
6	$NiCl_2$. Glyme	61
7	$Ni(acac)_2$	25
8	$Ni(COD)_2$	54
9	$NiCl_2$. Glyme	52[c]
10	$NiCl_2$. Glyme	69[d]

[a]Reaction Conditions: Aryl diazonium salt (1.2 mmol), aryl boronic acid (1 mmol), Catalyst 10mol%, glycerol (2 mL), Temperature 80 °C for 12 h, [b]Isolated yield%, [c]catalyst 5mol%, [d]catalyst 15mol%.

Different solvents such as DMSO, DMF, Methanol and MeCN were screened to select suitable co-solvent (Table 2, entries 1-4). Homocoupling of diazonium salt was observed in methanol as co solvent, whereas presence of MeCN gave acetanilide as major product. Amongst studied solvents DMSO was found to the be most favourable solvent as yield of desired product was increased from 69% to 86% after addition of DMSO (Table 2, entry 1). Some the reaction DMSO used as oxidant.[61] We carried out the reaction in the absence of glycerol more or less same yield of cross coupling product as well as homo coupling product of diazonium salt were obtained (Table 2, entry 5). The reaction carried out nitrogen atmosphere and afforded 84% yield of desired product was obtained (Table 2, entry 6).

Table2 Effect of co solvent

Entry	Catalyst	Co solvent	Yield[b]
1	$NiCl_2$. glyme	DMSO	86
2	$NiCl_2$. glyme	DMF	64
3	$NiCl_2$. glyme	Methanol	32
4	$NiCl_2$. glyme	MeCN	43
5	$NiCl_2$. glyme	DMSO	44[c]
6	$NiCl_2$. glyme	DMSO	84[d]

[a]Reaction Conditions: Aryl diazonium salt (1.2 mmol), aryl boronic acid (1 mmol), $NiCl_2$.glyme 10 mol%, glycerol (2mL), co solvent (0.5mL), Temperature: 80 °C for 12h, [b]Isolated yield. [C] absence of glycerol, [d] N_2 atmosphere.

The effect of temperature was studied from room temperature to 80 °C (Table 3, entries 1- 4). The reaction not initiated at room temperature however, increasing the reaction temperature from room temperature to 40 °C gives 45% yield of desired product. Further rise in temperature from 40 to 80 °C, increases yield from 45% to 90% in 12 h (Table 3, entries 2-4).To optimize reaction time, we performed reactions at different time intervals (Table 3, entries 5,6). It was observed that reaction after 8 h under optimized conditions gave only 59% yield (table 3, entry 5) whereas increasing the reaction time to 16 h did not show much improvement in the yield (table 3, entry 6).

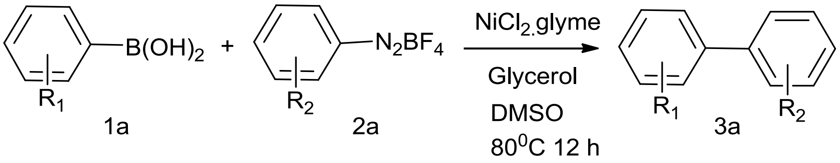
Table3 Effect of temperature and time for nickel catalysed Suzuki reaction

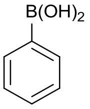
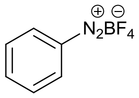
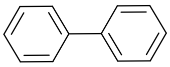
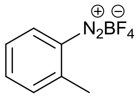
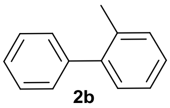
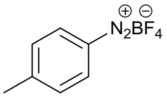
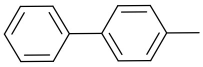
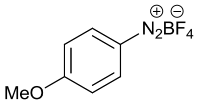
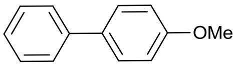
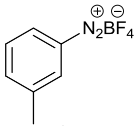
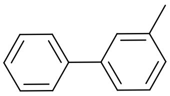
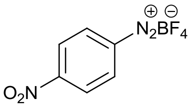
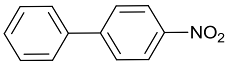
Entry	Catalyst	Temp.	Yield[b]
1	$NiCl_2$. glyme	RT	15
2	$NiCl_2$. glyme	40	45
3	$NiCl_2$. glyme	60	63
4	$NiCl_2$. glyme	80	90
5	$NiCl_2$. glyme	80	59[c]
6	$NiCl_2$. glyme	80	90[d]

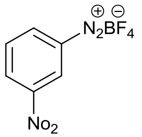
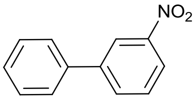
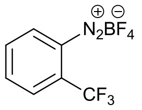
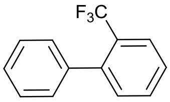
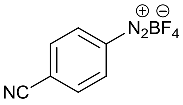
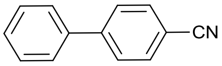
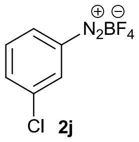
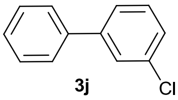
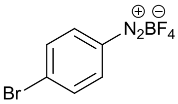
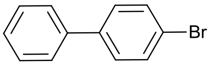
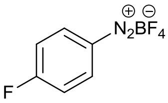
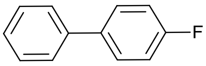
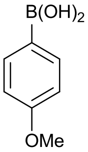
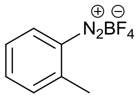
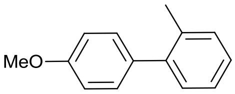
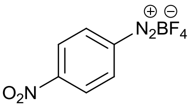
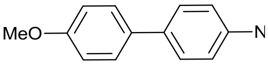
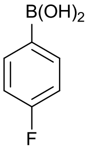
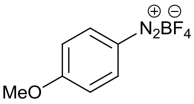
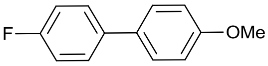
[a] Reaction Conditions: Aryl diazonium salt (1.2 mmol), aryl boronic acid (1 mmol), $NiCl_2$.glyme (10 mol%), glycerol (2), DMSO (0.5mL); [b] Isolated yield, reaction time 12 h; [c] reaction time: 8 h; [d] reaction time: 16 h.

Reactions of various substituted aryl diazonium salts with phenyl boronic acid compounds were carried out under optimized reaction conditions. It was observed that, aryl diazonium salt with electron donating substituents at para position gave comparatively higher yields(Table 4,entries3-4)than that present at ortho or meta position (Table 4,entries 2,5).The electron withdrawing substituents such as NO_2, CN and CF_3 gave good yield of desired products (Table 4, entries 6-9). Diazonium salt substituted with halogens such as –F, –Cl and –Br showed chemo-selective coupling reaction (Table 4, entries 10-12).We also examined synthesis of unsymmetrical diaryls using phenyl boronic acid containing electron donating substituent at para position with phenyl diazonium salt containing electron donating substituent at ortho position and electron withdrawing substituent at para position (Table 4, entries 13,14). Reaction of 4-methoxy phenyl boronic acid with diazonium salt of 2-methyl aniline gives moderate yield (Table 4, entry 13), on the other hand it gives comparatively higher yield with diazonium salt of 4-nitro aniline (table 4, entry 14). Reaction of 4-fluro phenyl boronic acid with diazonium salt of 4-methoxy aniline was found to give higher yield of respective unsymmetrical diaryl product (Table 4, entry 15).

Table 4 Substrate study[a]



Entry	Aryl boronic acid	Aryl diazonium salt	Product	Yield[b]
1	 1a	 2a	 3a	90
2	**1a**	 2b	 2b	73
3	**1a**	 2c	 3c	84
4	**1a**	 2d	 3d	87
5	**1a**	 2e	 3e	75
6	**1a**	 2f	 3f	76

7	**1a**	 **2g**	 **3g**	74
8	**1a**	 **2h**	 **3h**	71
9	**1a**	 **2i**	 **3i**	77
10	**1a**	 **2j**	 **3j**	79
11	**1a**	 **2k**	 **3k**	82
12	**1a**	 **2l**	 **3l**	80
13	 **1b**	 **2m**	 **3m**	70
14	**1b**	 **2n**	 **3n**	76
15	 **1c**	 **2o**	 **3o**	77

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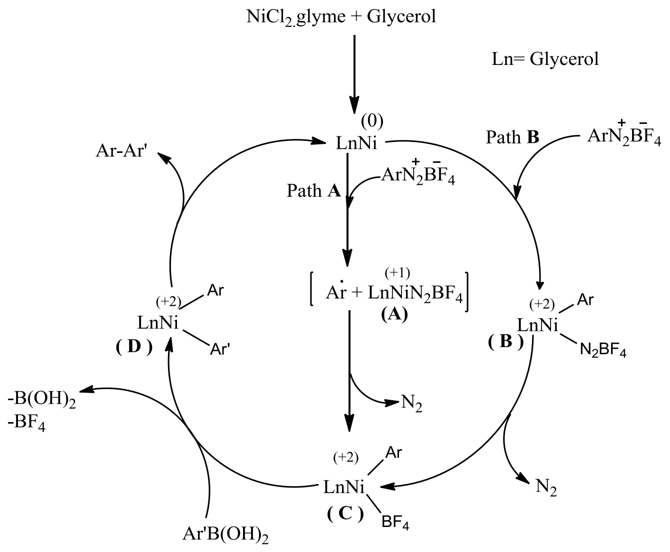
[a] Reaction Conditions: Aryl diazonium salt (1.2 mmol), Aryl boronic acid (1 mmol), $NiCl_2$.glyme (10 mol %), DMSO(0.5mL), glycerol (2 mL), temperature: 80°C for 12 h, [b] Isolated yield.

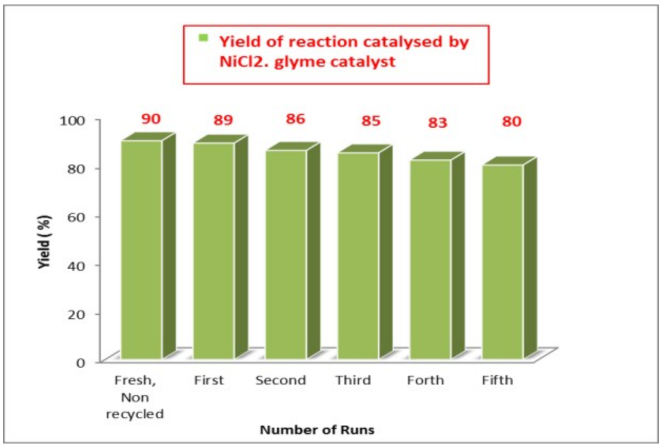


Scheme2 Plausible mechanism for Suzuki cross coupling reaction

On the basis of previous reports we propose a plausible mechanism for the Nickel catalysed Suzuki reaction (**Scheme 2)**. Initially there is in situ generation of Ni (0) species due to glycerol[62]. The reaction may proceed either via single electron transfer (SET) or oxidative addition mechanism.[63] **Path A,** followed SET mechanism where Ni (0) is converted into Ni (I) intermediate **A** by the oxidative addition of aryldiazonium salt which immediately gets converted into intermediate **C.** In path B oxidative addition of aryl diazonium salt converts Ni(0) to Ni(II) which immediately gets transformed into Intermediate **C**. Aryl boronic acid gets complex with intermediate **C** which facilitates the subsequent transfer of the phenyl group to nickel complex (transmetalation) intermediate **D.** In the final step there is formation of C-C bond by reductive elimination which generates Ni (0) catalyst. We are still working on this mechanism.

The catalyst and solvent recyclability study was performed using diazonium salt of aniline with phenyl boronic acid. After completion of reaction, the product was extracted in ethyl acetate and the glycerol layer containing Nickel catalyst was used for next run. The results obtained were summarized in Table 5. It was found that, the catalyst and solvent can be efficiently recycled over five runs without any significant loss in the product yield.

Table 5 Recyclability study



Conclusion:

In conclusion, we have developed an efficient, economical, base free protocol for Suzuki cross coupling reaction. The protocol is cost effective as diazonium salts is a cheaper arylating source than aryl halides and also $NiCl_2$ glyme is a cheaper catalyst than palladium complexes. DMSO used as a co solvent increases the yield of the desired product. The protocol is applicable to a variety of diazonium salts and boronic acid giving good to excellent yields of desired product. Recyclability of the homogeneous catalyst upto five cycles and used of glycerol as the green solvent are merits of this protocol.

Experimental section

General: All chemicals were purchased from Sigma Aldrich, S.D Fine Chemical, Avra, Spectrochem Ltd, Loba Chemmie and commercial suppliers and used without further purifications. The reaction was monitored by TLC and GC analysis performed on PerkinElmer Clarus 480. GC equipped with flame ionized detector with capillary column (Elite- 1701, 30m X 0.32 X 0.25). The product mass conformed by GC–MS-QP 2010 instrument (Rtx-17, 30 m_25 mm ID, film thickness 0.25 µm, column flow: 2 mLmin–1, 80 to 240 °C at 10 °C/ min rise). The products were purified by column chromatography using (60-120 mesh) silica gel with pet ether as eluent. The pure product ^{1}H NMR Spectroscopic data of compounds was recorded on a Varian Mercury plus- 300 spectrometer using DMSO and $CDCl_3$ as a solvent and TMS as internal standard. $NiCl_2$.glyme has been synthesized by known literature method. Aryl diazonium tetraboroflourate are synthesis by known method.

General procedure for Suzuki coupling with aryl diazonium salt

To an oven-dried 25 mL schlenk tube equipped with a magnetic stirring bar was charged with arene diazonium salt (1.2mmol), phenyl boronic acid (1 mmol), NiCl$_2$.glyme (10 mol %), followed by anhydrous DMSO (0.5mL), glycerol (2 mL). Reaction mixture was stirred at 80°C for 12 h. The reaction was monitored by GC and TLC. After completion of the reaction, the reaction mixture was diluted with ethyl acetate. The resulting ethyl acetate layer was washed with water and 20% brine solutions. The organic layer was dried over anhydrous sodium sulphate. The solvent was removed under vacuum to get the crude product, which was purified by column chromatography on silica gel eluting with the pet ether (100%) to afford the pure product. The purity and identity of known products are conformed by ^{1}H NMR and GC-MS Spectroscopic techniques. The glycerol layer contained catalyst was used for further reactions.

Spectral data for the representative compounds

Biphenyl (3a)[36]**:** White solid; yield: 0.137 g (90%); mp 68-70°C. **GC-MS m/z** (% relative intensity): 154(M+, 30), 105 (100), 77(60), 51(17)

2-methyl-1, 1'-biphenyl (3b) [35]**:** Colourless liquid; yield: 0.121 g (73%). **GC-MS m/z** (% relative intensity): 168(M+, 100), 167 (73), 152(27), 128(6), 115(14),102(4), 91(8), 82(10)

4-methyl-1, 1'-biphenyl (3c) [35]**:** Off white solid; yield: 0.142 g (84%); mp 46-47°C. **GC-MS m/z** (% relative intensity): 168(M+, 100), 153 (43), 12(7), 115(13), 102(3), 91(6),89(8), 83(15).

4-methoxy-1, 1'-biphenyl (3d) [35]**:** White solid; yield: 0.161 g (87%); mp 87-89°C.^{1}**H NMR :** (300 MHZ,d- DMSO, TMS): δ 7.61(d, 2H,Ar-H), 7.59(d, 2H,Ar-H),7.45(d, 1H, Ar-H),7.32(d,2H,Ar-H), 7.02(d, 2H,Ar-H), 3.81(s,3H,CH$_3$),,**GC-MS m/z** (% relative intensity): 184(M+, 100), 169(56.39), 141(57.10),139(14),115(43), 92(5), 76(8)

3-methyl-1, 1'-biphenyl (3e) [27]**:** Colourless liquid; yield: 0.125 g (75%).**GC-MS m/z** (% relative intensity): 168(M+, 100), 167(62), 152 (25), 128(4), 115(8), 102(2), 91(6), 89(5), 83(10).

4-nitro-1, 1'-biphenyl (3f) [36]**:** Yellowish solid; yield: 0.150 g (76%); mp 110-112°C.^{1}**H NMR**: (300 MHZ, d- DMSO, TMS): δ 8.32(d,2H,Ar-H), 7.98(dd, 2H,Ar-H), 7.81(d, 2H,Ar-H), 7.58(d, 2H,Ar-H),7.45(m, 1H,Ar-H) **GC-MS m/z** (% relative intensity): 199(M+, 97), 152 (100), 127(9), 115(9), 102(5), 87(4), 76(20).

3-nitro-1, 1'-biphenyl (3g) [27]**:** Pale yellow solid; yield: 0.146 g (74%); mp 57-59°C. ^{1}**H NMR**: (300 MHZ, d- DMSO, TMS): δ 8.42(s, 1H, Ar-H),8.25 (d, 1H, Ar-H),7.79(t,2H, Ar- H), 7.54(dd,4H,Ar-H), 7.42(s,1H,Ar-H). **GC-MS m/z** (% relative intensity): 199(M+, 100), 169(43), 152(96), 127(9), 115(15), 102(6),87(3), 76(15)

2-(trifluoromethyl)-1, 1'-biphenyl (3h)[7]**:** colourless liquid; yield: 0.156 g (71%); **GC-MS m/z** (% relative intensity): 222(M+, 100), 201(13), 183(3), 172(3), 154(24), 152(27), 125(3), 111(6.36), 85(4)

[1, 1'-biphenyl]- 4- carbonitrile (3i) [36]: White solid; yield: 0.136 g (77%); mp 84-86°C. **GC-MS m/z** (% relative intensity): 179(M+, 100), 151 (13), 126(5), 113(2), 100(3),89(18), 73(10).

4-chloro -1, 1'-biphenyl (3j) [37]**:** White solid; yield: 0.147 g (79%); mp 70-72°C. **GC-MS m/z** (% relative intensity): 188(M+, 100), 153(33), 152(58), 76(27).

4-bromo -1, 1'-biphenyl (3k) [35]**:** Off white solid; yield: 0.190 g (82%); mp 89-90°C. ^{1}**H NMR**: (300 MHZ, d- DMSO, TMS): δ 7.64(m, 2H, Ar-H), 7.51(d, 2H, Ar -H), 7.55(m, 4H,Ar-H), 7.41(d,1H,Ar-H). **GC-MS m/z** (% relative intensity): 232(M+, 77), 152 (100), 126(9), 116(5), 102(4), 87(3), 76(35).

4-fluoro -1, 1'-biphenyl (3l) [12]**:** White solid; yield: 0.137 g (80%); mp 71-73°C. ^{1}**H NMR**: (300 MHZ, d- DMSO, TMS): δ 7.91(m, 4H,Ar-H),7.75(d,2H,Ar-H), 7.49(m,3H,Ar-H).**GC-MS m/z** (% relative intensity): 172(M+, 100), 146 (3), 133(3), 120(2), 85(9), 83(15).

4'- methoxy-2- methyl-1, 1'- biphenyl (3m) [12]: Pale yellow solid; yield: 0.137 g (70%); mp 120-122°C. **GC-MS m/z** (% relative intensity): 198(M+, 100), 183 (16), 167(34), 153(11), 128(4), 115(6), 99(3), 89(3), 77(6).

4- methoxy-4'- nitro-1, 1'- biphenyl (3n) [36]**:** Pale yellow solid: 0.174 g (76%); mp 108-110°C. ^{1}**H NMR:** (300 MHZ, d- DMSO, TMS): δ8.28(d, 2H,Ar-H),7.91(d, 2H,Ar-H), 7.79(d, 2H,Ar-H), 7.10(d,2H,Ar-H), 3.82(s,3H, CH$_3$), **GC-MS m/z** (% relative intensity): 229(M+, 100), 214 (2), 199(2), 183(7), 168(45), 156(3), 140(26), 139(64), 113(4), 102(6), 89(5), 75(3).

4- fluoro- 4'- methoxy-1, 1'- biphenyl (3o) [10]**:** White solid; yield: 0.155 g (77%); mp 85-86°C. ^{1}**H NMR:** (300 MHZ, d- DMSO, TMS): δ7.63(d, 2H,Ar-H),7.58(m,2H, Ar-H), 7.26(d,2H, Ar-H), 7.02(d, 2H,Ar-H), 3.79(s,3H –OCH$_3$). **GC-MS m/z** (% relative intensity): 202(M+, 100), 187 (68), 170(6), 159(64), 144(2) 133(47), 120(3), 101(7), 83(5)

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Nickel-glycerol: An efficient, recyclable catalysis system for Suzuki cross coupling reaction using aryl diazonium salt

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Palladium free, chemo selective, environmental benign protocol for C-C bond formation reaction