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PII:	S0277-5387(18)30664-8
DOI:	https://doi.org/10.1016/j.poly.2018.10.028
Reference:	POLY 13502
Τ	
To appear in:	Polynearon

Received Date:4 September 2018Revised Date:7 October 2018Accepted Date:9 October 2018



Please cite this article as: N. Muthukumaran, A. Sathyanarayana, M. Vaddamanu, K. Ramesh, M. Maruthupandi, M. Adinarayana, G. Prabusankar, Highly Active Homoleptic Nickel(II) Bis-N-heterocyclic Carbene Catalyst for Suzuki–Miyaura and Heck Cross-coupling Reactions, *Polyhedron* (2018), doi: https://doi.org/10.1016/j.poly. 2018.10.028

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# Highly Active Homoleptic Nickel(II) Bis-N-heterocyclic Carbene Catalyst for Suzuki–Miyaura and Heck Cross-coupling Reactions<sup>§</sup>

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#### **§-Equal Contribution**

Keywords: Nickel(II), bis-N-heterocyclic carbene, Suzuki-Miyaura cross-coupling, Heck coupling

#### Abstract

New homoleptic nickel(II) biscarbene complex was synthesized and structurally characterized. The complex depicted the excellent catalytic activities with only 3 mol% catalyst loading along with wide substrate scope for the Suzuki–Miyaura cross-coupling reactions (twenty six examples) and Heck coupling reactions (eighteen examples).

#### 1. Introduction

The application of Ni(II)-NHC's (NHC's = N-heterocyclic carbenes) in Suzuki-Miyaura and Heck cross coupling reactions have attracted much of attentions towards basic research to industrial applications [1]. Several Ni(II)-NHC systems have been demonstrated with superior catalytic activity over their expensive Pd(II) analogues [2-6]. Thus, a great success of Ni-NHC complexes in Suzuki-Miyaura and Heck cross-coupling chemistry has been accomplished mostly through ligand manipulation. For example, the sterically and electronically controlled mono, bis, tris and tetra NHC ligands have been employed to isolate the Ni(II)-NHC catalysts [1].

In particular, the application of mono-NHC supported nickel complexes have been extensively investigated for the Suzuki-Miyaura and Heck cross coupling reactions. For example, the SciFinder search for "nickel carbene" (945 references) followed by refine search on "Suzuki-Miyaura" resulted forty references, while "nickel carbene" followed by refine search on "Heck" gave twenty eight references (as on 04<sup>th</sup> September 2018). Though, the catalytic applications of nickel NHC have been extensively investigated, only sixteen plus homoleptic nickel NHC derivatives have been reported as of now. Surprisingly, only one reference has been described for

the homoleptic  $[{(PhCH_2N(CH)_2N(C:))CH_2}_2Ni(II)]^{2+2}Br^-(I)$  precatalyst mediated Suzuki-Miyaura and Heck coupling reactions [7]. Heck reaction of aryl bromides catalyzed by 5mol% of I with poor yield (4-56%). However, the quantitative yield was obtained in the Heck coupling reaction between iodobenzene and butyl acrylate in the presence of Na<sub>2</sub>CO<sub>3</sub> or NEt<sub>3</sub>. Suzuki-Miyaura cross-coupling of aryl halides with phenylboronic acid using 5mol% precatalyst catalyst I gave quantitative yield only for phenyl bromide, while substituted bromo or chloro or fluro aryl derivatives gave very poor yield (3-42% yield). Thus, the following challenges remain unexplored with homoleptic Ni(II)NHC's: (i) catalytic activities of well defined homoleptic nickel(II)NHC catalyst mediated Suzuki-Miyaura and Heck reactions; (ii) optimization of catalyst loading and scope of the well defined homoleptic nickel(II)NHC catalysts in Suzuki–Miyaura and Heck reactions. Continuing our interest in NHC-metal based catalytic reactions [8], in this paper we reported the new sterically less hindered homoleptic nickel(II) complex  $[{(CH_2CHN(CH)_2N(C:))CH_2CH_2}_2Ni(II)]^{2+}.2Br.2H_2O]$  (2) from the reaction between [{(CH<sub>2</sub>CHN(CH)<sub>2</sub>N(CH))CH<sub>2</sub>CH<sub>2</sub>}<sup>2+</sup>.2Br<sup>-</sup>] (1) and Ni(OAc)<sub>2</sub>. Subsequently, catalyst 2 depicted the superior activity towards Suzuki-Miyaura and Heck coupling with less catalyst loading.



Chart 1. Known homoleptic nickel(II) biscarbene complex for Suzuki–Miyaura cross-coupling and Heck coupling reactions 2. Results and discussion

### 2.1. Synthesis and characterization of 2

The 1,1'-divinyl-3,3-ethylenediimidazolium dibromide salt **1** was obtained by reacting vinylimidazole with 1,2-dibromoethane [8]. The neat reaction of **1** with anhydrous nickel(II) acetate and tetra butyl ammonium bromide (TBAB) at 128 °C yielded bis(1,1]-ethylene-3,3]-divinylimidazole-2,2'-diylidene)nickel(II) dibromide dihydrate (**2**) as a light yellow solid in very good yield (Scheme 1). **2** is soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>CN, DMSO and insoluble in diethyl ether. The formation of **2** was confirmed by FT-IR, multinuclear NMR and elemental analysis, and

the structure was confirmed by single crystal X-ray crystallography. Upon complex **2** formation, the absence of imidazolium (NC*H*N) proton was observed in <sup>1</sup>H NMR spectrum of **2**. The signature <sup>1</sup>H NMR peaks for the backbone of NHC ring was observed at about 7.61-7.72 ppm.



Scheme 1. Synthesis of 2.

The presence of downfield <sup>13</sup>C NMR signal of N*C*N carbene carbon at 169.71 ppm in **2** confirms the Ni-C<sub>carbene</sub> bond formation [7]. The peaks appeared between 124.22 and 120.52 ppm were attributed to NHC carbon. In <sup>13</sup>C NMR, the vinyl carbon appeared at 106.94 ppm and -NC $H_2$ - carbon appeared at 47.34 ppm.

The structure of **2** was confirmed through single-crystal X-ray diffraction technique. The structural parameters are listed in table 1. 2 was crystallized in the triclinic space group,  $P\bar{i}$  with bis(1,1 -ethylene-3,3 -divinylimidazole-2,2'-divlidene)nickel(II), one bromide ion along along with couple of water molecules in the asymmetric unit. Figure 1 depicts the solid state structure of 2. The selected bond lengths and angles are tabulated in table 2. As shown in figure 1, the nickel atom in 2 displays a square-planar geometry with four C-donor atoms lying on the same plan. The distances of the Ni-C<sub>carbene</sub> bonds (1.892(4) and 1.916(4) Å) in 2 are comparable to those of the (1.896(2))Å Å) square-planar I and 1.906(2)and  $[{(p-^tBu C_{6}H_{4}CH_{2}N(CH)_{2}N(C:)CH_{2}_{2}Ni(II)^{2+}2Br^{-}(1.894(3) \text{ Å and } 1.899(3) \text{ Å})$  [7]. The C(8)–Ni–C(3) and C(8)-Ni-C(3)' bond angles (90.30° and 89.70°) show negligible deviation from 90°. These comparable with of  $(93.90(10)^{\circ})$  $86.10(10)^{\circ}$ are that Ι and and  $[{(p-^tBu C_{6}H_{4}CH_{2}N(CH)_{2}N(C:)CH_{2}_{2}Ni(II)^{2+}2Br (93.75(11)^{\circ} and 86.25(11)^{\circ})$  [7]. The C(8)–Ni–C(8)' and C(3)-Ni-C(3)' angles are 180°. The coordination environment around nickel is satisfied by four carbons, C(3), C(8), C(3)' and C(8)' forming the basal plane. One of -CH<sub>2</sub>-CH<sub>2</sub>, proton shows a weak C–H…Ni hydrogen bonding interaction at the apical position of NiC<sub>4</sub> plan. The C–H…Ni angle is 100.9° with H…Ni distance of 2.866 Å, which is much stronger than C– H…Ni hydrogen bonding interaction fond in the earlier reports [9-11].

#### Figure 1.

#### 2.2 Catalysis

2.2.1. Suzuki-Miyaura cross coupling

The 2 was investigated for the Suzuki-Miyaura cross coupling. In order to optimize the catalytic systems, the coupling of iodobenzene and phenylboronic acid in the presence of 2 and K<sub>2</sub>CO<sub>3</sub>was fixed as the prototype reaction (Table 3). The catalytic reactions were carried out in different mid-polar and polar solvents (Table 3, Entries 1-9). Among different solvents (toluene, acetonitrile, 1,4-dioxane, EtOH, DMF, DMF/H<sub>2</sub>O, *p*-xylene, DMSO, and water), the mixture of DMF/H<sub>2</sub>O seems to be the ideal choice (Table 3, Entry 6). To explore the choices of base, various bases (such as K<sub>2</sub>CO<sub>3</sub> NaHCO<sub>3</sub> KHCO<sub>3</sub> NaOH, KOH, KOtBu and NaOtBu) (Table 3, Entries 10-15) were screened. Among various bases, a mild, inexpensive yet effective base K<sub>2</sub>CO<sub>3</sub> was found to be the best (Table 3, Entry 6). To understand the role of catalyst, the catalytic experiment was carried-out without the base (Table 3, Entry 16) or the catalyst (Table 3, Entry 17). As expected, there was no reaction even after an extended reaction time (12 h) (Table 3, Entry 18). Subsequently, we have further investigated the capacity of catalyst loading (Figure 2). The reactions were performed by changing the quantity of the catalysts ranging from 0.5 to 4 mol%. The catalytic loading of 3 mol% was found to be the optimized amount to get better out-come. No significant increase in the efficiency of the reaction was observed on further raise of catalyst loading to 4 mol% (Figure 2). Compared to the known protocols documented in in the literature [1, 7], the catalyst **2** was active enough to promote the Suzuki-Miyaura cross coupling reactions under milder conditions in DMF/H<sub>2</sub>O mixture under aerobic conditions [7, 9, 10].

#### Figure 2.

Besides, the scope of the catalytic reactions was explored between a wide range of aryl boronic acid derivatives and substituted/unsubstituted aryl halides (Table 4). The reactions take place gently and furnished the corresponding biphenyls in good to high yield (Table 4, entries 1-26). The reaction of 4-formylphenylboronic acid with iodobenzene or 4-bromo-nitrobenzene reacted gently to offer the corresponding biphenyl compounds in 99 % yield (Table 4, Entries 4 and 17). Both the electron rich and electron poor aryl bromides were fruitfully transformed to the corresponding products in excellent yields (Table 4, Entries 6,7,9,16-19,21,22,24,25). The electron poor phenyl boronicacids afforded the desired biphenyls in good yields (Table 4, Entries 4,17,21,23,24). The coupling of 1-bromonaphthalene with phenylboronic acid and 4-methoxy phenylboronic acids gives the coupled products in excellent yield (Table 4, Entries 8 and 20).

Furthermore, aryl iodides were excellent substrates for the coupling reaction could be converted effectively (Table 4, Entries 1-5 and 10-15). Subsequently, the reaction scope of **2** was examined with few aryl chlorides comprising electron withdrawing and donating substituents underwent coupling reactions with arylboronic acids to provide the expected biaryls in moderate to good yields (Table 4, Entries 21 and 26). Notably, our present catalytic system 2, shows greater activity towards Suzuki-Miyaura cross-coupling reactions compared to [Ni(diNHC)<sub>2</sub>].2Br<sup>-</sup> [7, 9, 10]. Notably, all these reactions were performed under phosphine free condition [11-13].

Based on the literature [11-14], we assume that in C-C cross-coupled bond formation reaction, the bis-carbene Ni(II)-NHC systems are supposed to be reduced *in-situ* to active zero-valent nickel, which catalyzes the coupling reaction *via* a Ni(0) $\leftrightarrow$ Ni(II) cycle. Our current homoleptic Ni(NHC<sub>2</sub>)<sub>2</sub>X<sub>2</sub> catalytic system gives a different tactic to revamp the coordination sphere of the metal by contemplating both the electronic and steric atmosphere of the nickel center for incoming catalytic substrates.

#### 3.2. Heck coupling reaction

Heck coupling is a straightforward and excellent method to synthesis  $C_{sp2}$ - $C_{sp2}$  single bonds through base-promoted cross-coupling strategy within aryl halides and olefins [15-20]. For the better optimizing condition, a screening was done for a prototype reaction of iodobenzene with butyl acrylate. Figure 3 summarizes the influence of base and catalyst loading on heck reaction, while figure 4 depicts the choice of solvent in catalyst **2** mediated Heck coupling reaction. In order to determine the essential role of base, various bases such as TBAE, NaOAc, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub> were screened. Among the bases employed, an excellent yield of desired product was isolated in the presence of K<sub>2</sub>CO<sub>3</sub> or Cs<sub>2</sub>CO<sub>3</sub>. However, Cs<sub>2</sub>CO<sub>3</sub> is not economical compared to K<sub>2</sub>CO<sub>3</sub>. Out of different solvents tested, DMF was identified as the best solvent towards the Heck cross-coupling reaction (with 96 % yield, Figure 4). Water was found to be ineffective for this system.

#### Figure 3. Figure 4.

Thus, the reactions of different arylchlorides with olefins were carried out under the optimized condition (3 mol% catalyst, 2 eq. K<sub>2</sub>CO<sub>3</sub>, DMF, 100°C, 4 h). Table 5, summarizes the obtained product yield. The observation revealed that the coupling between aryl iodides and ethyl/butyl acrylates proceeded in excellent yield (Table 5, Entries 1-7). Similarly, the styrene was

successfully coupled with various aryl halides produced the appropriate products with the yield ranging from 83 to 99 % (Table 5, Entries 11-18). The electron-rich as well as the electron-deficient aryl bromides showed a high activity when electron-deficient olefins are used (Table 5, entries 7-10). By adopting the identical reaction condition, the aryl chloride was successfully converted to the desired product in 83-98 % yield (Table 5, Entry 17). Even, bromonaphthalene reacted nicely with electron poor butyl acrylate (Table 5, Entry 10).

On the basis of earlier literature report [21], we believe that Ni(II) in 2 is reduced *in-situ* to active zero-valent nickel, and the activation of aryl halides was further achieved by the oxidative addition. In the second step, an olefin substrate coordinates to the nickel metal with the subsequent insertion of the alkene at the C-Ni. Final step is an intramolecular  $\beta$ -hydride elimination, which led to the formation of desired product by removal of HX.

#### 4. Conclusions

In conclusion, the first sterically less crowded well defined homoleptic nickel(II) biscarbene **2** mediated Suzuki–Miyaura cross coupling reactions and Heck coupling reactions were demonstrated. **2** was isolated and characterized by elemental analysis, FT-IR and NMR (<sup>1</sup>H and <sup>13</sup>C) spectrometry. The structure of **2** was confirmed by single-crystal X-ray diffraction technique. The nickel center in **2** adopts a square planar geometry with chelating di-NHC ligands along with two non-coordinating bromide counter ions and two water molecules. **2** was found to be highly active catalyst in Suzuki–Miyaura cross coupling reactions (eighteen different examples) and Heck coupling reactions (twenty four different examples). Catalyst **2** depicted the excellent functional group tolerance towards wide range of reactants in Suzuki–Miyaura and Heck cross-coupling reactions with only **3** mol% catalyst loading.

#### 5. Experimental

#### 5.1. General procedures and methods

All manipulations were carried out under argon using Schlenk-vaccum line techniques and argon filled glove box. The solvents were puchased from commercial sources and purified according to standard procedures [22]. Unless otherwise stated, the chemicals were purchased from commercial sources. 1 was synthesiszed as reported [8]. FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. NMR spectra were recorded on Bruker Ultrashield-400 spectrometers at 25 °C unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. The crystal

structure of **2** was measured on an Oxford Xcalibur 2 diffractometer. Data were collected at 150 K. The structure of **2** was solved by direct methods using the Olexprogram [23] and refined with a full matrix least-squares method on F2 using the SHELXL-97 program [24, 25]. **2** depicts three "B level" alerts. The U(eq) value of an C(7) atom is compared with the average U(eq) for to non-hydrogen atoms bonded to it. Large differences may indicate that the high thermal parameter of terminal carbon atom. The short non-bonding inter H(2B)..H((12A) contact could be due to the strong bite angle of NHC ligand. Potential hydrogen bond donors are checked for the presence of suitable acceptors using commonly used (Jeffrey) H-bond criteria. As a general rule there should be an acceptor for each donor. In **2**, this could be due to the absence of acceptor for O(2)-H(2B)as the hydrogen atoms have been fixed by calculated position. CCDC 1832286 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

#### 5.2. Synthesis of 2

A mixture of bisvinyl imidazolium dibromide salt **1** (0.100 g, 0.26 mmol), anhydrous nickel(II) acetate (0.047 g, 0.26 mmol) and tetra butyl ammonium bromide (0.400 g, 1.24 mmol) were mixed and heated under vacuum in Schlenk tube at 60 °C for 1 h, followed by at 128 °C for 5 h. The molten reaction mixture was allowed to attain at room temperature, water (10 mL) was added to the reaction mixture. The resulting mixture was extracted with dichloromethane (40 mL). The organic layer was collected, dried on sodium sulphate and concentrated then stored at room temperature to get the desired product as light yellow crystals. Yield: 65% (Based on nickel(II) acetate) M.p.: 260-262 °C (decomp.). Anal. Calcd (%) for C<sub>24</sub>H<sub>32</sub>Br<sub>2</sub>N<sub>8</sub>Ni (648.0481): C, 44.27; H, 4.95; N, 17.21; found: C, 44.2; H, 5.0; N, 17.21. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  4.79-4.84 (4H, m, NC*H*<sub>2</sub>), 3.66-3.70, 4.99-5.01 (4H, d, <sup>3</sup>*J*<sub>HH</sub>=7.6 Hz, NCH=CH*H*<sub>cis</sub>), 5.28-5.31 (4H, d, <sup>3</sup>*J*<sub>HH</sub>=15.3 Hz,NCH=CH*H*<sub>trans</sub>), 5.57-5.62 (4H, m, NC*H*<sub>2</sub>), 7.16-7.22 (4H, dd, vinylC*H*), 7.61(4H, s, Im*H*), 7.72 (4H, s, Im*H*). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.71 (*Ni*-C), 131.61(NCN), 124.22 (ImC), 120.52 (ImC), 106.94 (vinyl-C), 47.34 (NCH<sub>2</sub>). FT–IR (neat,  $\bar{v}$ , cm<sup>-1</sup>): 3419 (w), 3371 (w), 3082 (w), 3055 (w), 2970 (w), 1632 (s), 1444 (m), 1398 (s), 1329 (m), 1246 (s), 1188 (m), 1080 (w) 1040 (m), 960 (m), 913 (s), 730 (m) 680 (s).

5.3. General procedure for the Suzuki-Miyaura reactions

The typical procedure is as follows. Oven dried Schlenk tube was charged with aryl halides (1 mmol), aryl phenylboronic acid (1.2 mmol),  $K_2CO_3$  (2 mmol) and catalyst **2** (3 mol %) in1:1 mixture of DMF/H<sub>2</sub>O medium. The reaction mixture was stirred in an oil bath at 100 °C in the presence of air. After completion of the reaction, the reaction mixture was then cooled to room temperature and diluted with Et<sub>2</sub>O/H<sub>2</sub>O (1:1, 20 mL). The organic layer was separated and dried with anhydrous MgSO<sub>4</sub>. The product was filtered and dried under vacuum. The resulting crude compound was purified by column chromatography on silica gel to afford the corresponding products.

#### 5.4. General procedure for the Heck reactions

The typical procedure is as follows. Oven dried Schlenk tube was equipped with stirrer bar, was charged with aryl halides (1 mmol), acrylates (1.2 mmol),  $K_2CO_3$  (2 mmol) and catalyst **2** (3 mol %) in DMF medium. The reaction mixture was stirred in an oil bath at 100 °C under argon atmosphere for an appropriate period of time. After completion of the reaction, the reaction mixture was then cooled to room temperature and diluted with  $Et_2O/H_2O$  (1:1, 20 mL). The organic layer was separated and dried with anhydrous MgSO<sub>4</sub>. The product was filtered and dried under vacuum. The resulting crude compound was purified by column chromatography on silica gel to afford the corresponding products.

#### Appendix A. Supplementary data

Supplementary data: (<sup>1</sup>H and <sup>13</sup>C NMR spectra of the synthesized complex. Catalysis protocols and characterization data of coupling products) related to this article can be found. CCDC. CCDC 1832286 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

#### Acknowledgment

GP gratefully acknowledge the Council of Scientific and Industrial Research (No: 01(2884)/17/EMR-II) for financial support. NM thank DST-NPDF (PDF/2016/001834) for fellowship.

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Fig. 1. Top: The solid state structure of 2. Two water molecules and two bromide ions have been omitted for clarity. Bottom: The geometrical representation of nickel center in 2. Two water molecules, two bromide ions and hydrogen atoms on carbons have been omitted for clarity. Fig. 2. Effect of catalyst (mol%) with respect to time.

Fig. 3. Effect of catalyst (mol%) and base on Heck coupling of iodobenzene with butyl acrylate.

Fig. 4. Effect of solvent on Heck coupling of iodobenzene with butyl acrylate.

Parameters	2
Empirical formula	$C_{24}H_{36}Br_2N_8NiO_4$
Formula weight	719.14
Temperature (K)	150
Crystal system	Triclinic
Space group	$P\overline{\iota}$
a/Å	7.6367(5)
b/Å	10.7808(7)
$c/{ m \AA}$	11.0785(7)
avo	114.455(6)
<i>β/</i> °	96.028(5)
$\gamma/^{\circ}$	107.167(6)
Volume (Å <sup>3</sup> )	765.73(9)
Ζ	1

 Table 1. Crystal data and structure refinement parameters of 2.

$ ho_{ m calc}/ m mg~mm^{-3}$		1.560	Table 2. Selected structural
Absorption coef	fficient (mm <sup>-1</sup> )	4.328	parameters of 2
F(000)		366	<b>Table 3.</b> Evaluation of
Data collected		5016	conditions for the Suzuki-
Unique data		2863	conditions for the Suzuki-
$R_{ m int}$		0.0410	Miyaura cross-coupling
GOF on $F^2$		1.075	reaction using <b>2</b> <sup>a,b</sup>
$R_1 (I \ge 2 \sigma(I))$	HO	0.0711	reaction using 2
$WR_2(I > 2\sigma(I))$		0.2026	
$R_1$ values (all da	.ta) 🗸 + 🚺	0.0748	
w $R_2$ values (all	data)	0.2062	
Interatomic distances (Å	()		
C(3) - Ni(1)	1.892(4)		
C(8) - Ni(1)	1.916(4)		
C(3) - N(1)	1.361(6)		
C(3)-N(2)	1.347(6)		
C(8)-N(3)	1.353(6)		
C(8)-N(4)	1.373(6)		
Bond angles(°)			
N(2)-C(3)-N(1)	104.1(4)		
N(2)-C(3)-Ni(1)	124.8(3)		
N(1)-C(3)-Ni(1)	130.9(4)		
N(3)-C(8)-N(4)	104.1(4)		
N(3)-C(8)-Ni(1)	129.6(4)		
N(4)-C(8)-Ni(1)	126.1(3)		
C(3) - Ni(1) - C(3)	180.000(1)		
C(8) - Ni(1) - C(8)	180.000(1)		
C(8)–Ni– $C(3)$	89.70 (19)		
C(8) - Ni - C(3)	90.30(19)		
C			
P			

Entry	Base	Solvent	Temp (°C)	Time (h)	Yield (%) <sup>b</sup>	Table 4.
1	$K_2CO_3$	Toluene	110	8	69	Complay
2	$K_2CO_3$	Acetonitrile	82	8	56	Complex
3	$K_2CO_3$	1,4-dioxane	101	8	62	2
4	$K_2CO_3$	C <sub>2</sub> H <sub>5</sub> OH	78	8	24	antalwood
5	$K_2CO_3$	DMF	150	8	79	catalyzeu
6 <sup>e</sup>	$K_2CO_3$	DMF/H <sub>2</sub> O	100	8	97	Suzuki-
7	$K_2CO_3$	<i>p</i> -xylene	138	12	32	Mirronro
8	$K_2CO_3$	DMSO	140	12	61	wiiyaura
9	$K_2CO_3$	H <sub>2</sub> O	100	12	n.r	coupling
10	NaHCO <sub>3</sub>	DMF/H <sub>2</sub> O	100	12	22	of anyl
11	KHCO <sub>3</sub>	DMF/H <sub>2</sub> O	100	12	17	of aly
12	NaOH	DMF/H <sub>2</sub> O	100	12	59	halides
13	КОН	DMF/H <sub>2</sub> O	100	12	61	and
14	KO <i>t</i> Bu	DMF/H <sub>2</sub> O	100	12	53	anu
15	NaOtBu	DMF/H <sub>2</sub> O	100	12	47	
16°	-	DMF/H <sub>2</sub> O	100	12	n.r	
17 <sup>d</sup>	$K_2CO_3$	DMF/H <sub>2</sub> O	100	8	n.r	
18 <sup>d</sup>	$K_2CO_3$	DMF/H <sub>2</sub> O	100	24	n.r	

<sup>a</sup>Reaction conditions: iodo benzene (1 mmol), phenylboronic acid (1.2 mmol), base (2 mmol) and catalyst (3 mol %) in solvent (4 mL).

<sup>b</sup>Isolated yield based on column chromatography.

<sup>c</sup>The reaction was carried out using iodo benzene (1 mmol), phenylboronic acid (1.2 mmol), without base, catalyst (3 mol %).

<sup>d</sup>The reaction was carried out using iodo benzene (1 mmol), phenylboronic acid (1.2 mmol), base (2 mmol), without catalyst.

<sup>e</sup>Better optimization condition.



arylboronicacids.<sup>a,b</sup> X = Br, Cl, I

Entry	Aryl halide	Aryl boronic acid	Product	Yield (%) <sup>b</sup>
1		но, вон		96
2		HO, B, OH	✓—✓—	99







<sup>b</sup> Isolated yield based on column chromatography.





<sup>a</sup> Reaction conditions: aryl halide (1 mmol), acrylate(1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol) and catalyst (3 mol %) in DMF (4 mL). <sup>b</sup> Isolated yield based on column chromatography.