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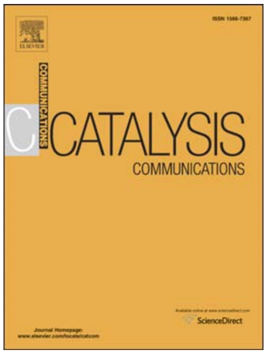

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Nickel-catalysed Suzuki-Miyaura cross-coupling reactions of aryl halides with arylboronic acids in ionic liquids

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Abstract

An efficient strategy for the nickel-catalysed synthesis of biaryls and terphenyls has been developed in environmentally-friendly reaction media. In the presence of β-diketone and PPh_3 ligands, $Ni(TFA)_2$ acted as an effective catalyst for the Suzuki-Miyaura cross-coupling of aryl halides and arylboronic acids in an ionic liquid solution. Biaryls and terphenyls were obtained in good yields under this catalytic system.

Keywords

Nickel-catalysed; ionic liquid; Suzuki-Miyaura cross-coupling; Biaryls

1. Introduction

The Suzuki-Miyaura cross-coupling reaction is a powerful synthetic tool for the synthesis of unsymmetric biaryls [1-3]. The major advantages of the Suzuki-Miyaura reactions are its low cost, relatively low toxicity, commercial availability of a large number of boronic acids, excellent functional group tolerance and good availability of diverse organoboron reagents that are stable in air [4-8]. Due to high sensitivity to air and moisture, the catalytically active Ni (0) complexes are often generated by Ni (II) complexes via in situ reactions [9]. Since Miyaura and co-workers reported the first nickel-catalysed Suzuki-Miyaura reactions of aryl halides and arylboronic acids [10], additional successful examples have been reported by Indolese [11], Genet [12], Miyaura and Inada [13], Percec [14-16], Hu [17], Shi [18], Garg [19], Yang [20-21], Han [22-24], Wang [25] and Valente [26].

In spite of the significant progress that has been obtained, it is still necessary to develop a more efficient catalytic system for transition metal catalysed Suzuki-Miyaura reactions under mild conditions. Recent efforts have been focused on green chemistry, sustainable development for academic and industrial research, the development of Suzuki-Miyaura reactions protocols based on atom economy and environmentally-friendly media. Therefore, Suzuki-Miyaura reactions have been developed in safe, economic and environmentally friendly media.

Imidazolium- and pyridinium-based ionic liquids that are appropriate solvents as well as mixed solvents consisting of water and an ionic liquid have attracted much interests in recent years, such as [bmim][BF_4][1]-H_2O [27-29], [bmim] [PF_6][2]-H_2O [30], [C2OC1mim][Tf_2N][3]-H_2O [31], nitrile-functionalized pyrrolidinium-based ILs-[emim] [Tf_2N][4]-H_2O [32], [C4MPy][BF_4][5]-H_2O [33] and [bmim][PF_6][2]-PEG[6]-H_2O [34]. Herein, we report an ionic liquid catalytic system for preparing biaryls, in which Suzuki-Miyaura cross-coupling reactions of aryl halides and arylboronic acids catalyzed by $Ni(TFA)_2$[7] under the presence of β-diketone and PPh_3 ligands. Terphenyls are also successfully synthesized by the same method. Importantly, the terphenyls can be separated from reaction mixture directly by precipitation, making this method attractive compared to existing methods.

2. Experimental

2.1. General

All of the chemicals were purchased from Aladdin, Alfa, Kermel Chemical Company and used without purification. The coupling reactions were monitored by TLC (silica gel). The NMR spectra of the products were recorded at room temperature with a Bruker Avance 300 spectrometer. $CDCl_3$ was used as solvent, and TMS was used as the internal standard. All of the products were isolated by short chromatography on a silica gel (200-300 mesh) column. The isolated yields that are reported in this paper were the average of two tests of the same reaction.

2.2. Typical procedure for the nickel-catalysed Suzuki-Miyaura reaction

A 50mL round-bottomed flask was charged with aryl halides (0.5 mmol), arylboronic acid (0.6 mmol), K_2CO_3 (1.25 mmol), $Ni(TFA)_2$ (0.025 mmol), β-diketone ligand (0.05 mmol), PPh_3 (0.05 mmol), 1.5 g of the ionic liquid (IL) and 0.5 g of H_2O. Then, the mixture was stirred at 80 ℃ open to the atmosphere. The reaction was monitored by TLC and then stopped after the starting material was completely consumed. Next, the mixture was diluted with water (10 mL) and extracted with ether (3×10 mL). The combined organic layers were washed with brine (3×10 mL), dried over $MgSO_4$, and concentrated in vacuum. The cross coupling products were not the only product of the reaction. A small amount of homo-coupled products and removal boron product from boric acids were observed. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 10:1).

3. Result and Discussion

In the first set of experiments, the reaction of 4-bromotoluene (1.0 equiv) and phenylboronic acid (1.2 equiv) was carried out as a model reaction in ionic liquid and

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[1] 1-butyl-3-methylimidazolium tetrafluoroborate
[2] 1-butyl-3-methylimidazolium hexafluorophosphate
[3] 1-(1-methoxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)amide
[4] 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[5] N-alkyl-4-methyl pyridinium tetrafluoroborate
[6] Polyethylene glycols
[7] Nickel(II) trifluoroacetate

water. The effect of the Ni(TFA)$_2$ catalyst and ligand on the Suzuki-Miyaura reaction is discussed.

As shown in Table 1, no product was obtained when only ligand was added in the absence of the catalyst (entry 1). An increase in the amount of the Ni(TFA)$_2$ catalyst from 2.5 mol% to 5.0 mol% led the formation of the desired product with an isolated yield as high as 82.1% (entries 2 and 3). No significant improvement in the yield was observed when 10.0 mol % of the catalyst was added (entry 4). These results indicated that at least 5.0 mol% of the Ni(TFA)$_2$ catalyst should be used to maintain the efficiency of the catalyst. Only the catalyst with no ligand produced less product (entry 5). The β-diketone ligand exhibited showed good yield in Suzuki-Miyaura reaction (entries 3). When 10.0 mol% of the ligands was added, the yield was better than that obtained with 5.0 mol% and 15.0 mol% of the ligands (entries 3 and 6-7). In general, N,N ligands are compared to O,O ligands. β-diketones (L1 and L2) exhibited efficient yields, but N,N ligands (L3 and L4) had no effect (entries 3 and 7-9). According to the report by Miyaura and Inada [13], the more affordable Ni-catalyst could affect the Suzuki-Miyaura reactions of aryl halides and boronic acids using PPh$_3$ as external supporting ligands. When 10.0 mol% of PPh$_3$, which were used as external supporting ligands, was added, the yield was as high as 96.7%. No significant improvement in the yield was observed when 15.0mol% PPh$_3$ was added (entries 10-13). Because the cheap and readily available PPh$_3$ exhibited efficiency during the initial screening, no further screening was performed for phosphine ligands.

Various reaction parameters including the solvent, temperature and base were screened, and the results are shown in Table 2. Initially, single solvents, such as 1,4-dioxane, toluene and DMF, were compared to [bmim][Tf$_2$N] (entries 1,2,3 and 4). Water exerted a significant accelerating effect on the Suzuki coupling with the good yields at an [bmim][Tf$_2$N]-H$_2$O mass ratio of 3:1 (entries 4, 5 and 6). Shreeve [35] confirmed that using water with ionic liquids increase the solubility of the inorganic salt that forms. When the temperature decreased to 70℃ for 24 h, the yield decreased from 96.7% to 60.2% (entries 5, 7). Cations and anions have a substantial effect on the ionic liquid, and the results reveal that [bmim][Tf$_2$N] is the best choice among the solvents for this catalytic system (entries 5, 8-10).

The nature of the base was also an important factor that determined the efficiency of the Suzuki cross-coupling reaction. Organic and inorganic bases, such as K_2CO_3, K_3PO_4, Na_2CO_3, KOH, Cs_2CO_3 and Et_3N, were tested with the optimized conditions. When K_3PO_4 was used, the yield of the Suzuki-Miyaura reaction decreased (entry 11). The weaker base Na_2CO_3 resulted in a low yield (entry 12) and strongly basic KOH was substantially inferior to K_2CO_3 (entry 13). The yield of Cs_2CO_3 is similar to K_2CO_3 (entry 14). Unfortunately, Et_3N yielded a disappointing result (entry 15). Based on the economic and environmental advantages, K_2CO_3 was chosen as the base.

To extend the scope of this methodology, we investigated the scope and limitations of this catalytic system using different aryl halides and various arylboronic acids. The experimental results are shown in Table 3.

As shown in Table 3, Suzuki-Miyaura reactions of the aryl halides (X=I,Br,Cl) with phenylboronic acid exhibited a high efficiency (entry 1). Both electron-rich and electron-poor aryl bromides proceeded smoothly with phenylboronic acid to afford the corresponding cross coupling products in high yields (entries 2-5). In addition, various 4-substituted aryl bromides bearing either electron-rich and electron-poor groups, such as cyano, formyl, methyl, methoxy, provided the corresponding products in excellent yields, except for the nitro-substituted aryl bromides (entry 6), which were unreactive. This result may be related to the loss of catalytic activity due to the formation of a stable (nitroso) nickel (II) species, as proposed by Miyaura and Saito [10].

The cross-coupling reaction using electron-donating arylboronic acid proceeded quite efficiently relative to unsubstituted phenylboronic acids (Entries 7-11). Noticeably, 3, 4-dimethoxyphenylboronic acid underwent the Suzuki-Miyaura cross-coupling with 4-bromonitrobenzene to afford the desired product in 86.9% yield in 18 h (entry 9). To the best of our knowledge, arylboronic acid bearing electron-withdrawing groups typically exhibits lower reactivity in the Suzuki reaction. In this catalytic system, 4-(trifluoromethyl) phenylboronic acid coupled with various aryl bromides also gave high yields (entries 12-16). For example, 4-(trifluoromethyl) phenylboronic acid reacted with 4-bromotoluene to afford the desired product in 83.7% yield in 18 h (entry 14). The Suzuki reaction was sensitive to the electronic nature of the substituent on the arylboronic acid. For example, the coupling of the same arylboronic acids bearing electron-withdrawing groups exhibited higher reactivity than those bearing electron-donating groups.

The effect of steric hindrance was investigated, and the results are shown in Table 3 (entries 17-20). The steric crowding around the reaction sites was acceptable because it does not hinder the synthesis. For example, the coupling reaction between 4-bromobenzonitrile and 2, 5-dimethylphenyl boronic acid occurred, and the expected biaryl derivatives were produced in 75.1% yield (entry 17). In contrast, 70.8% yield was achieved when 1-bromo-4-methoxy benzene was coupled with 2, 5-dimethyl phenylboronic acid (entry 18). In addition, the coupling of 4-bromotoluene and 2-chlorophenyl boronic acid yielded a moderate result (entry 20).

Suzuki-Miyaura cross-coupling reactions were also employed for the synthesis of terphenyls. Terphenyls and their derivatives may have promising roles in the fields of high performance engineering and optical materials as well as spacers in catenane and porphyrin chemistry. We focused our attention on synthesising terphenyls, which are shown in Table 3. A moderate yield was obtained in the coupling reaction of 4-biphenyl boronic acid and 2-naphthyl boronic acid (entries 21 and 22). However, the amount of boric acid increased to 2 eq during these reactions. Naphthalene and biphenyl were observed in the reactions due to the boron removal of boric acids. In addition, the coupling of 1, 4-dibromobenzene with phenylboronic acid, 2-chlorophenyl boronic acid and 3-thiophenyl boronic acid afforded the corresponding products in moderate yields by increasing the amounts of boric acids to 3 eq (entries 23-25). The experimental results indicated that this catalytic system was efficient for the formation of polyaryls.

4. Conclusions

From the perspective of green chemistry, we have developed a nickel-catalysed Suzuki-Miyaura cross-coupling reaction for the preparation of biaryl derivatives using ionic liquids as the solvent in good yields. Reaction conditions for this method were optimized by quantity of catalyst, ligands, solvents, temperature, etc. Biaryls and terphenyls were synthesised using Suzuki-Miyaura cross-coupling reactions of aryl bromides and arylboronic acids with the optimised method.

Acknowledgements

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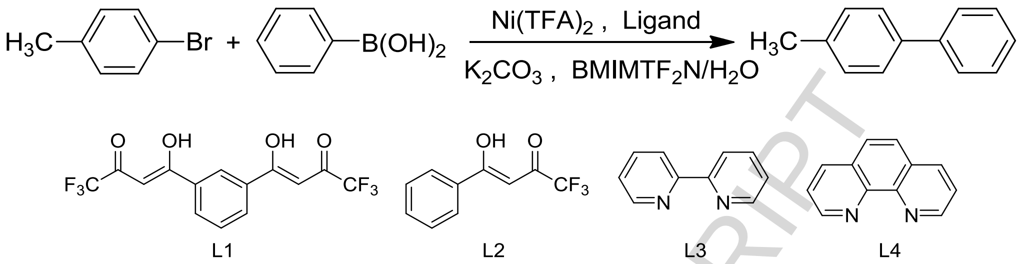
Table 1. Screening reaction ligands for nickel-catalysed cross-coupling reaction of 4-bromotoluene with phenylboronic acid[a].

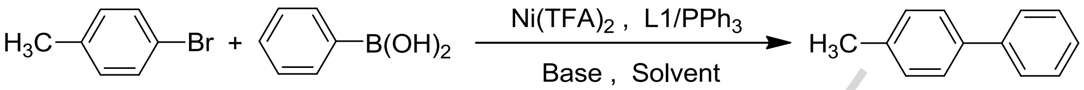


Entry	$[Ni(TFA)_2]$(quatity[mol%])	Ligand(quatity[mol%])	Yield(%)[b]
1	0	L1 (10.0)	-
2	2.5	L1 (10.0)	57.2
3	5.0	L1 (10.0)	82.1
4	10.0	L1 (10.0)	81.5
5	5.0	-	10.3
6	5.0	L1 (5.0)	51.0
7	5.0	L1 (15.0)	80.8
8	5.0	L2 (10.0)	58.6
9	5.0	L3 (10.0)	-
10	5.0	L4 (10.0)	10.0
11	5.0	L1 (10.0) PPh_3 (10.0)	96.7
12	5.0	L1 (10.0) PPh_3 (5.0)	85.9
13	5.0	L1 (10.0) PPh_3 (15.0)	96.9
14	5.0	PPh_3 (10.0)	55.7

a Conditions: aryl bromides (0.5 mmol), phenylboronic acid (0.6 mmol), K_2CO_3 (1.25 mmol), [bmim]TF_2N 1.5 g, H_2O 0.5 g, 80 ℃, 18 h. The reaction was monitored by TLC.

b Isolated yield.

Table 2. Screening reaction conditions for nickel-catalysed cross-coupling of 4-bromotoluene with phenylboronic acid[a].



Entry	Base	Solvent [g] (m/m)	T/℃	Yield(%)[b]
1	K_2CO_3	1,4-dioxane [c]	80	65.2
2	K_2CO_3	toluene [c]	80	59.1
3	K_2CO_3	DMF [c]	80	43.8
4	K_2CO_3	[bmim][Tf_2N][8]	80	80.0
5	K_2CO_3	[bmim][Tf_2N]/H_2O=3:1	80	96.7
6	K_2CO_3	[bmim][Tf_2N]/H_2O=3:2	80	89.7
7[d]	K_2CO_3	[bmim][Tf_2N]/H_2O=3:1	70	60.2
8	K_2CO_3	[emim][Tf_2N][9]/H_2O=3:1	80	78.2
9	K_2CO_3	[omim][Tf_2N][10]/H_2O=3:1	80	76.2
10	K_2CO_3	[bmim][PF_6][2]/H_2O=3:1	80	77.5
11	K_3PO_4	[bmim][Tf_2N]/H_2O=3:1	80	65.5
12	Na_2CO_3	[bmim][Tf_2N]/H_2O=3:1	80	70.0
13	KOH	[bmim][Tf_2N]/H_2O=3:1	80	49.5
14	Cs_2CO_3	[bmim][Tf_2N]/H_2O=3:1	80	90.2
15	Et_3N	[bmim][Tf_2N]/H_2O=3:1	80	16.5

a Conditions: aryl bromides (0.5 mmol), phenylboronic acid (0.6 mmol), $Ni(TFA)_2$ (0.025 mmol), L1 ligand (0.05 mmol), PPh_3 (0.05 mmol), K_2CO_3 (1.25 mmol), IL 1.5 g, 18 h. The reaction was monitored by TLC.

b Isolated yield.

c 4mL.

d 24 h.

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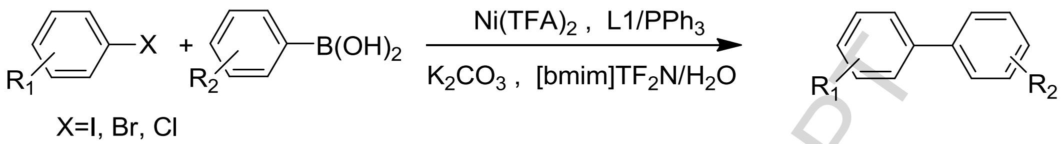
[8] 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

[9] 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

[10] 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

Table 3. Nickel-catalysed Suzuki-Miyaura reactions of aryl halides with arylboronic acid[a].



Entry	X	R_1	R_2	No.	Yield(%)[b]
	I	4-CHO	H		97.8
1	Br	4-CHO	H	A1	98.4
	Cl	4-CHO	H		81.3[c]
2	Br	4-CN	H	A2	97.8
3	Br	4-Me	H	A3	96.7
4	Br	4-OMe	H	A4	95.5
5	Br	3,4-OMe	H	A5	94.8
6	Br	4-NO_2	H	A6	-
7	Br	4-CHO	3,4-OMe	A7	90.2
8	Br	4-CN	3,4-OMe	A8	88.7
9	Br	4-Me	3,4-OMe	A9	86.9
10	Br	4-OMe	3,4-OMe	A10	85.0
11	Br	3,4-OMe	3,4-OMe	A11	83.6
12	Br	4-CHO	4-CF_3	A12	82.7
13	Br	4-CN	4-CF_3	A13	81.9
14	Br	4-Me	4-CF_3	A14	83.7
15	Br	4-OMe	4-CF_3	A15	84.3
16	Br	3,4-OMe	4-CF_3	A16	86.0
17	Br	4-CN	2,5-Me	A17	75.1
18	Br	4-OMe	2,5-Me	A18	70.8
19	Br	3,4-OMe	2,5-Me	A19	67.5
20	Br	4-Me	2-Cl	A20	71.7
21	Br	4-Me	4-Ph	A21	76.9[d]
22	Br	4-Me	2-naphthyl-$B(OH)_2$	A22	72.7[d]
23	Br	4-Br	H	A23	68.3[e]
24	Br	4-Br	2-Cl	A24	65.8[e]
25	Br	4-Br	3-thiophene-$B(OH)_2$	A25	62.1[e]

a Conditions: aryl bromides (0.5 mmol), arylboronic acid (0.6 mmol), $Ni(TFA)_2$ (0.025 mmol), L1 (0.05 mmol), PPh_3 (0.05 mmol), K_2CO_3 (1.25 mmol), IL 1.5 g, H_2O 0.5 g 18 h. The reaction was monitored by TLC.

b Isolated yield.

c Lasted for 24 h.

d 2 eq of boric acid.

e 3 eq of boric acid.

Nickel-catalysed Suzuki-Miyaura cross-coupling reactions of aryl halides with arylboronic acids in ionic liquids

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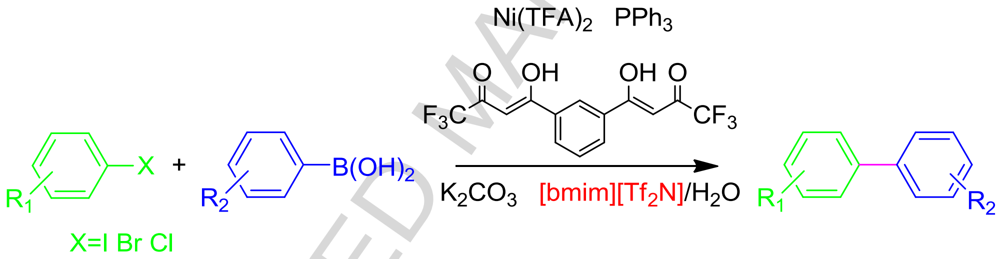

Nickel-catalysed Suzuki-Miyaura cross-coupling reactions of aryl halides with arylboronic acids in ionic liquids

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Highlights

- ✧ Excellent green catalytic system for the nickel-catalysed Suzuki reaction.
- ✧ Efficient yield for aryl halides with arylboronic acids in ionic liquids.
- ✧ Large amount of synthesis using a simple and economical process.