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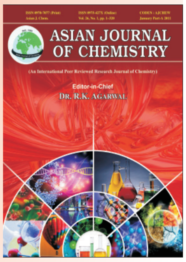

Synthesis of 4-Vinylbiphenyl Derivatives by Pd(II)-1,2-Diamino-cyclohexane Complex Catalyzed Suzuki-Miyaura Reaction

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A series of 4-vinylbiphenyl derivatives were synthesized by Pd(II)-1,2-diaminocyclohexane complex catalyzed Suzuki-Miyaura reactions in the presence of $K_3PO_4·3H_2O$ as base in toluene at 80 °C and the corresponding products achieved 39-95 % yields. According to this efficient C-C bond-forming method, the obtained yields of 4-vinylbiphenyl liquid crystal compounds were up to 89 %.

Keywords: 4-Vinylbiphenyl derivatives, Synthesis, Suzuki-Miyaura reaction, Palladium, Catalyzed.

INTRODUCTION

4-Vinylbiphenyl derivatives as important functional monomers are frequently found in the polymer materials and organic chemical reactions[1-5]. Thus, the development of simple and efficient methods for the synthesis of such compounds has attracted considerable attention. In general, Pd-catalyzed Suzuki-Miyaura reaction due to the broad functional group tolerance and the low toxicity associated with boron compounds is one of the most powerful methods for selective carbon-carbon bond formation in the synthesis of biaryl molecules[6,7]. But its application in the synthesis of 4-vinylbiphenyl derivatives is very limited. McCluskey *et al.*[8] reported the synthesis of substituted 4-vinylbiphenyl monomers by 1 mol % $Pd(DIPHOS)_2$-catalyzed Suzuki-Miyaura reactions, but this catalysis reaction was carried out under the microwave-assisted condition at 100 °C, and 4-vinylphenylboronic acid as a bifunctional substrate is prone to give the undesired homo-coupling product at high temperature. Based on our previous research works[9-14], herein we report a simple and efficient approach for the synthesis of 4-vinylbiphenyl derivatives by Pd(II)-1,2-diaminocyclohexane complex catalyzed Suzuki-Miyaura reactions.

EXPERIMENTAL

All reactions were carried out under air using magnetic stirring unless otherwise noted. Column chromatography was performed with silica gel (300-400 mesh) purchased from Qingdao Haiyang Chemical Co., Ltd. All the other reagents were of analytical grade quality, purchased commercially and used as received.

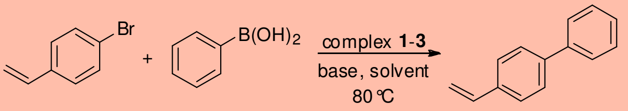
Detection method: ^1H NMR spectral data were recorded on a Bruker DPX-400 spectrometers using TMS as internal standard and $CDCl_3$ as solvent. Mass spectra were recorded on GC-MS (Agilent 7890A/5975C) instrument under EI model.

The Schlenk tube (20 mL) equipped with a stir bar was charged with complex **2** (1 mol %), $K_3PO_4·3H_2O$ (3 equiv.) *p*-bromostyrene (0.5 mmol), phenylboronic acid (0.75 mmol) and toluene (2 mL) were added and the mixture was stirred at 80 ºC until the substrate was completely consumed. After cooling to room temperature, the solution was quenched with water and extracted with EtOAc (3 × 10 mL). The combined EtOAc extracts were dried over anhydrous Na_2SO_4 and filtrated, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with petroleum ether as eluent to obtain the desired products. All products reported herein are known products and were characterized by ^1H NMR and GC-MS.

RESULTS AND DISCUSSION

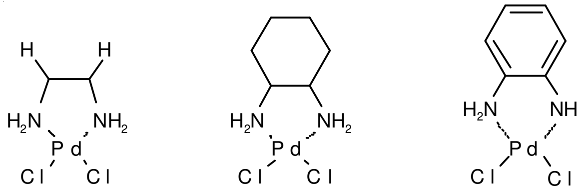
Complexes **1-3** were synthesized by the literature methods (Fig. 1)[15,16]. Initially, the catalytic activity of the complexes **1-3** was evaluated to obtain an optimum catalytic system by the coupling of *p*-bromostyrene with phenylboronic acid in the presence of $K_3PO_4·3H_2O$ at 80 °C for 6 h in toluene (Table-1). Although complexes **1-3** examined the desired product, the coupling reaction catalyzed by complex **2** produced the desired product in excellent yield (95 %, Table-1, entries 1-3). When the reaction was conducted at 50 °C or 100 °C, the low yield not was obtained (Table-1, entries 4 and 5). Similarly, the yield was increased with extending the reaction time to 10 h (Table-1, entry 6). Subsequently, we select the complex **2** as the precatalyst to further investigate the effect of bases on the coupling reaction. When the NaF, Na_2CO_3 were used as base, the desired product was not obtained (Table-1, entries 7 and 8). K_2CO_3 also promoted the occurrence of the coupling reaction, but the corresponding product was obtained only in 78 % yield (Table-1, entry 9). So $K_3PO_4·3H_2O$ was used in the subsequent studies. Solvent is another important factor affecting catalysis. It was found that toluene performed well as the prime solvent. EtOH and DMF were not the good reaction solvents (Table-1, entries 10 and 11). Finally, the combination of complex **2** (1 %), $K_3PO_4·3H_2O$ (3 equiv.) at 80 °C in toluene was chosen as the optimal conditions for the coupling reaction of *p*-bromostyrene with phenylboronic acid.

TABLE-1
OPTIMIZATION OF THE REACTION CONDITIONS[a]



Entry	Complex	Solvent	Base	Temp. (°C)	Time (h)	Yield (%)[b]
1	**1**	Toluene	$K_3PO_4·3H_2O$	80	6	76
2	**2**	Toluene	$K_3PO_4·3H_2O$	80	6	95
3	**3**	Toluene	$K_3PO_4·3H_2O$	80	6	30
4	**2**	Toluene	$K_3PO_4·3H_2O$	50	6	10
5	**2**	Toluene	$K_3PO_4·3H_2O$	100	6	68
6	**2**	Toluene	$K_3PO_4·3H_2O$	80	10	86
7	**2**	Toluene	NaF	80	6	0
8	**2**	Toluene	Na_2CO_3	80	6	Trace
9	**2**	Toluene	K_2CO_3	80	6	78
10	**2**	EtOH	$K_3PO_4·3H_2O$	80	6	Trace
11	**2**	DMF	$K_3PO_4·3H_2O$	80	6	Trace

[a]Reaction conditions: 0.50 mmol 4-bromostyrene, 0.75 mmol phenylboronic acid, 1.50 mmol base, 0.5% mmol complex **1-3**, 2.0 mL solvent; [b]Isolated yields

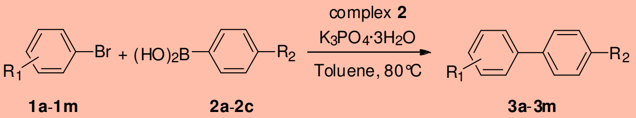


1 **2** **3**

Fig. 1. List of complexes **1-3**

Under the optimized reaction conditions, a number of aryl bromides were successfully employed in this transformation (Table-2). 1-Bromo-4-vinylbenzene reacted with phenylboronic acid smoothly to afford the desired product **3a** in 86 % yield (Table-2, entry 1) and arylboronic acid with electron-donating groups such as (4-methoxyphenyl)boronic acid could also be coupled with the 1-bromo-4-vinylbenzene to give the product **3b** in 95 % yield (Table-2, entry 2). The substrate (4-vinylphenyl)boronic acid resulted in a decreased the yield of **3c** (Table-2, entry 3), whereas the reaction worked well with **1b-1d**, furnishing the expected products **3d-3f** in good yields (Table-2, entries 4-6). Aryl bromides with electron-withdrawing groups, such as 4-COMe, 4-F and 3,4-difluoro also afforded the corresponding coupling products in 39-81 % yields (Table-2, entries 7-9). But a steric effect was observed in this reaction when aryl bromide **1j** has a substituent in the ortho position, the reaction gave a lower yield in comparison with **1i** (**3k** *vs*. **3j**) (Table-2, entries 10 and 11). In order to expand the scope of the methodology, this new catalytic system was applied to the synthesis of 4-vinyl biphenyl liquid crystal compounds. The liquid crystal products could be obtained successfully in 84-89 % yields (Table-2, entries 12-14).

TABLE-2
SUZUKI-MIYAURA REACTIONS
CATALYZED BY COMPLEX 2[a]



Entry	R_1	R_2	Product	Yield (%)[b]
1	4-Ethenyl (**1a**)	4-H (**2a**)	**3a**	86
2	**1a**	4-OMe (**2b**)	**3b**	95
3	**1a**	4-Ethenyl (**2c**)	**3c**	48
4	4-CHO (**1b**)	**2c**	**3d**	80
5	4-OMe (**1c**)	**2c**	**3b**	70
6	4-Me (**1d**)	**2c**	**3e**	75
7	4-COMe (**1f**)	**2c**	**3f**	64
8	4-F (**1g**)	**2c**	**3g**	39
9	3,4-Difluoro (**1h**)	**2c**	**3h**	61
10	3,4,5-Trifluoro (**1i**)	**2c**	**3i**	81
11	2,4,5-Trifluoro (**1j**)	**2c**	**3j**	46
12	4,4'-Propyl-cyclohexyl (**1l**)	**2c**	**3k**	89
13	4,4'-Pentyl-cyclohexyl (**1k**)	**2c**	**3l**	84
14	4,4'-Pentyl-bicyclohexyl (**1m**)	**2c**	**3m**	88

[a]Reaction conditions: aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), complex **2** (0.5 mol%), $K_3PO_4.3H_2O$ (3.0 equiv), toluene (2.0 mL), 80 °C, 6 h; [b]Isolated yields

Conclusion

In summary, we have developed a simple and efficient catalyst system for the synthesis of 4-vinylbiphenyl derivatives by Pd(II)-1,2-diaminocyclohexane complex catalyzed Suzuki-Miyaura reactions in moderate to excellent yields under mild conditions. With simple reaction procedure and broad available substrate range, this method was particularly useful for the efficient synthesis of 4-vinylbiphenyl functional monomers and liquid crystal compounds.

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