



A simple and novel amide ligand based on quinoline derivative used for palladium-catalyzed Suzuki coupling reaction



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ABSTRACT

This paper discusses the synthesis of the amide ligand N,N-diisopropyl quinoline-2-carboxamide from quinoline-2-carboxylic acid and diisopropylamine. The prepared ligand was utilized in the palladium catalyzed Suzuki cross-coupling reaction in ethanol-water 1:1 (v/v). The reaction exhibited high catalytic efficiency with low Pd loading (0.05 mol %) under mild reaction conditions (at 60–90 °C under air atmosphere). In this study, the catalyst was successfully used in coupling reactions between various aryl halides with phenylboronic acid to obtain desired products in excellent yields. Spectrometric methods of ¹H NMR, ¹³C NMR, and HR-MS were used to characterize this amide ligand, and its binding properties toward the Pd center were also investigated in detail via HR-MS measurements.

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1. Introduction

Palladium-catalyzed coupling reactions have played an important role in organic synthesis in recent decades [1–5]. Among these reactions, the Suzuki reaction stands out as one of the most powerful, convenient, and versatile methods for cross-coupling aryl halides with arylboronic acids [6–13]. This method has been identified as a reliable platform for carbon–carbon bond formation and has extensive use in the synthesis of natural products, pharmaceuticals, and advanced materials [14–19]. Usually, the most common ligands used for the Suzuki cross-coupling reaction are phosphines [20–26]. However, most of them are sensitive to air and moisture and are expensive and toxic, which significantly limits their industrial applications [27–30]. Recently, significant progress has been made toward the Suzuki coupling reaction through the use of phosphine-free ligands, such as N-heterocyclic carbene, N,N,O-tridentate, N,N,N-tridentate, N,O-bidentate, N,S-bidentate, and N,N-bidentate ligands (including diimine and

diamino) [2,31–47]. The latter-mentioned heteroatoms act as chelating sites toward a center metal in a proper chemical environment. Few studies practiced the use of amide ligands for Suzuki cross-coupling reaction, even though it has been verified that heteroatoms of the amide carbonyl can act as chelating sites for transition metal [48–51].

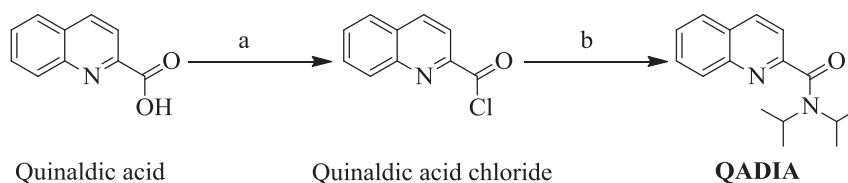
In 1993, Minisci's group obtained N,N-diisopropyl quinoline-2-carboxamide in order to study the introduction of a carbamoyl group into heteroaromatic bases via the homolytic carbamoylation of monoamides of oxalic acid [52]. It should be noted that Minisci et al. did not report the application of this amide compound. Herein, we report a palladium-based catalytic system for the Suzuki reaction using this novel, simple, and efficient amide ligand (the product of quinoline-2-carboxylic acid chloride reacting with diisopropylamine, QADIA) in aqueous media (H₂O–EtOH, 1:1) to obtain the desired coupling products in good yields under mild reaction conditions. The synthetic route of this amide ligand is illustrated in Scheme 1. The new ligand was characterized via ¹H NMR (Fig. S1), ¹³C NMR (Fig. S2), and HR-MS (Fig. S3) spectrometry.

2. Results and discussion

We initially tested the reaction of phenylboronic acid with 4-

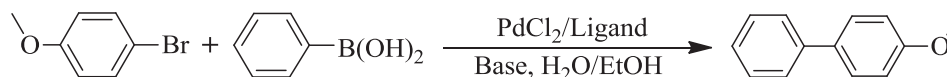
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Scheme 1. The synthetic route of QADIA. (a) CH_2Cl_2 , oxalyl chloride, reflux, 4 h; (b) CH_2Cl_2 , diisopropylamine, RT, 2 h.

Table 1
Effect of water in the palladium-catalyzed Suzuki–Miyaura reaction^a.



Entry	Ligand	[Pd] source	Solvent, V/V	Temp. (°C)/time (h)	Yield ^b (%)
1	QADIA	PdCl ₂	Only EtOH	80/2	78
2	QADIA	PdCl ₂	EtOH/H ₂ O, 9/1	80/2	83
3	QADIA	PdCl ₂	EtOH/H ₂ O, 4/1	80/2	89
4	QADIA	PdCl ₂	EtOH/H ₂ O, 2/1	80/2	94
5	QADIA	PdCl ₂	EtOH/H ₂ O, 1/1	80/2	99
6	QADIA	PdCl ₂	EtOH/H ₂ O, 1/1	60/4	98
7	QADIA	PdCl ₂	EtOH/H ₂ O, 1/1	25/24	19
8	QADIA	PdCl ₂	EtOH/H ₂ O, 1/2	80/2	95
9	QADIA	PdCl ₂	EtOH/H ₂ O, 1/4	80/2	76
10	QADIA	PdCl ₂	EtOH/H ₂ O, 1/9	80/2	46
11	QADIA	PdCl ₂	Only H ₂ O	80/2	23

^a Reaction conditions: n (ligand)/n (Pd) = 2,4-bromo anisole (1 mmol), phenylboronic acid (1.25 mmol), K₃PO₄ (2.0 mmol).

^b Isolated yield.

bromo anisole in 6 mL water as a model reaction to establish the best conditions for cross-coupling in the presence of 0.1 mol% of PdCl₂ and 0.2 mol% of ligand. The effect of various bases (LiOH, NaOH, NaHCO₃, Na₂CO₃, KOH, KHCO₃, K₂CO₃, K₃PO₄, Cs₂CO₃, and Et₃N) on the Suzuki reaction was investigated in the experiment. It was discovered that reactions with KOH, K₃PO₄, and Cs₂CO₃ produced the desired product in good yields (Table S1). With the consideration of practical application, K₃PO₄ was chosen as the optimal base for enhancing the efficiency of this protocol.

Simultaneously, commonly used solvents (H₂O, DMF, THF, Dioxane, MeOH, EtOH, *i*-PrOH and *t*-BuOH) were also tested in the reaction. It was determined that EtOH performed best; the reaction in EtOH afforded the desired product in 78% yield after 2 h at 80 °C oil bath in the presence of 0.1 mol% PdCl₂ and 0.2 mol% ligand (Table S2). The addition of appropriate amounts water to EtOH promoted activity of the catalysis system and resulted in the desired products in better yields [53] (Table 1, entries 2–10), may be). Reasoning for this occurrence may be attributed to the possibility that the proper polarity of the media is conducive to the Suzuki coupling reaction [5,43,53]. These results suggest that the proper ratio of water and ethanol plays a key role in the model reaction with good solubility of two substrates (aryl halides and phenylboronic acid) in these mixed solvents. Ultimately, the mixture of EtOH and H₂O (1:1, v/v) was chosen as the best medium for this catalyst system.

In this study, two different catalytic precursors (PdCl₂ and Pd(OAc)₂) were tested. From Fig. 1, it can be seen that PdCl₂ performed better than Pd(OAc)₂ in the model reaction. In order to compare the catalytic effect of the system (QADIA/PdCl₂ in EtOH and H₂O), diisopropylamine (DIPA), quinoline-2-carboxylic acid (QLCA), and a simple combination of QLCA and DIPA were also tested in the model reaction. It was found that QADIA performed best and could stabilize the Pd(0) species more efficiently than quinoline-2-carboxylic acid and diisopropylamin (Fig. 1). It is

pertinent to note that DIPA, as a ligand, can also coordinate the metal center and promote the model reaction with the same Pd-loading to some extent, which was similar to Qiu's research [54].

Thorough understanding of the binding mechanism between the center metal and the ligand is critical in the Pd-catalyzed Suzuki coupling system. Eseola and Plass et al. confirmed that their 2-(oxazol-2-yl) pyridine compounds (N,N-bidentate ligands) coordinated with the Pd center in a 1:1 bonding model [43]. Amadio and Scriveri et al. verified that their thioether-triazole compound (N,S-bidentate ligand) coordinated with the Pd center in a 1:1 bonding model [39]. Li et al. confirmed that their β-oxo amide ligand coordinated with Pd center in a 2:1 bonding model [48]. In order to have more insight into the binding properties of QADIA toward center

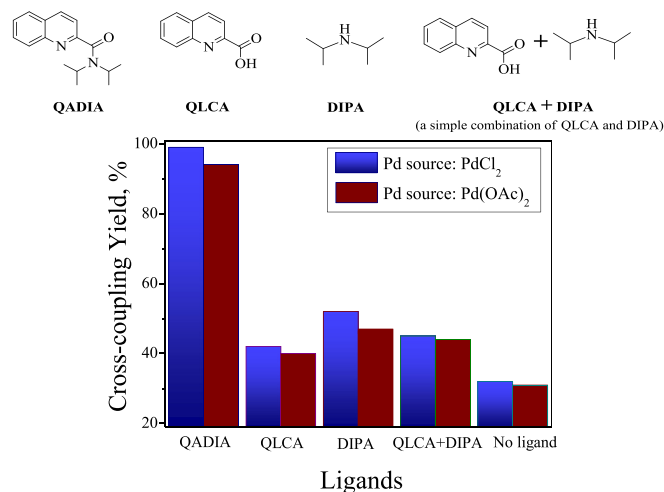


Fig. 1. Effect of different ligands and Pd sources in the model reaction (Above: QLCA, DIPA and “QLCA + DIPA” are the potential ligands comparing to QADIA).

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