

Original article

Tetrazole-1-acetic acid as a ligand for copper-catalyzed *N*-arylation of imidazoles with aryl iodides under mild conditions

Feng-Tian Wu, Ping Liu, Xiao-Wei Ma, Jian-Wei Xie*, Bin Dai

School of Chemistry and Chemical Engineering/the Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, China

ARTICLE INFO

Article history:

Received 3 May 2013

Received in revised form 20 May 2013

Accepted 22 May 2013

Available online 2 July 2013

Keywords:

Tetrazole-1-acetic acid

N-Arylation

Imidazoles

Copper

Aryl iodides

ABSTRACT

Tetrazole-1-acetic acid was found to serve as a superior ligand for CuI-catalyzed *N*-arylation of imidazoles with aryl iodides under a low catalyst loading (5 mol% of CuI). A variety of aryl iodides could be aminated to provide the *N*-arylated products in good to excellent yields without the need of an inert atmosphere.

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1. Introduction

Copper-catalyzed carbon–nitrogen cross-coupling reactions have been established as a powerful strategy for the preparation of *N*-arylation of nitrogen nucleophiles, which play a vital role as intermediates for agrochemicals, pharmaceuticals, energetic materials and fine chemical industries [1]. Traditionally, these reactions were often suffered from harsh reaction conditions involving elevated temperatures and highly polar solvents, and stoichiometric amounts of copper reagents [2]. Recently, pioneered by the Buchwald's and Taillefer's works [3], the process of Cu-based C–N coupling reactions have reinvigorated by the implementation of several classes of mono- and bidentate chelating ligands [4]. However, more work still needs to be done to identify new ligands to widen the scope of substrate tolerance, lower copper loading, milder reaction conditions, enhanced chemoselectivity and enantioselectivity of copper-catalyzed C–N coupling reactions.

On the other hand, it is well-known that carboxylate O atoms and tetrazolyl ring N atoms have good coordination capacities [5], and tetrazole-1-acetic acid (TZA), with both a carboxylate and tetrazolyl ring, is a multifunctional ligand. Therefore, it could bind to several metals *via* N and/or O atoms to form multi-dimensional coordination polymers with various coordination modes [6–9].

However, TZA, to our knowledge, has seldom been used as ligand in copper-mediated cross-coupling reactions. In continuation of our endeavors to develop copper-catalyzed cross couplings [10–12], we report herein TZA as an accelerating ligand for copper-catalyzed *N*-arylation of imidazoles with aryl iodides under mild reaction conditions.

2. Experimental

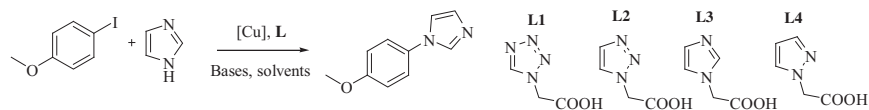
All reagents were purchased from commercial suppliers and used without further purification. All known products were characterized by GC–MS, and ¹H NMR, which were compared with the previously reported dates. ¹H NMR spectra were recorded at room temperature on a Varian Inova-400 instrument at 400 MHz, and the chemical shifts were recorded in ppm (δ) with TMS as internal standard. Mass spectra were recorded on GC–MS (Agilent 7890A/5975C) instrument under EI model.

General procedure for the *N*-arylation of imidazoles with aryl halides: CuI (0.05 mmol), **L1** (0.1 mmol), aryl halides (1.0 mmol), imidazoles (1.5 mmol), NaOH (2 mmol), and DMSO (2 mL) were added to a 10 mL of sealed tube. The reaction mixture was reacted at 110 °C in a preheated oil bath for 12 h. The reaction mixture was cooled to r.t., diluted with 10 mL H₂O, and then the mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic phases was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether, 2:1 to pure ethyl acetate) to afford the target products.

* Corresponding author.

E-mail address: cesxjw@gmail.com (J.-W. Xie).

Table 1
Screening of the reaction conditions on the coupling reaction of 4-iodoanisole with imidazole.^a



Entry	[Cu]	Ligand	Solvent	Base	T (°C)	Yield (%) ^b
1	CuI	L1	DMSO	NaOH	110	93
2	CuI	L2	DMSO	NaOH	110	84
3	CuI	L3	DMSO	NaOH	110	77
4	CuI	L4	DMSO	NaOH	110	88
5	CuI	–	DMSO	NaOH	110	75
6	CuO	L1	DMSO	NaOH	110	81
7	CuSO ₄	L1	DMSO	NaOH	110	71
8	Cu(OAc) ₂	L1	DMSO	NaOH	110	83
9	CuCl	L1	DMSO	NaOH	110	87
10	CuBr	L1	DMSO	NaOH	110	89
11	–	L1	DMSO	NaOH	110	0
12	CuI	L1	DMF	NaOH	110	48
13	CuI	L1	DMAC	NaOH	110	80
14	CuI	L1	1,4-Dioxane	NaOH	110	40
15	CuI	L1	H ₂ O	NaOH	110	Trace
16	CuI	L1	DMSO	KOH	110	79
17	CuI	L1	DMSO	K ₃ PO ₄	110	88
18	CuI	L1	DMSO	Cs ₂ CO ₃	110	81
19	CuI	L1	DMSO	K ₂ CO ₃	110	11
20	CuI	L1	DMSO	NaOH	100	88
21	CuI	L1	DMSO	NaOH	80	16
22	CuI	L1	DMSO	NaOH	110	92 ^c (70 ^d)
23	CuI	L1	DMSO	NaOH	110	80 ^e

^a Reaction conditions: 4-iodoanisole (0.5 mmol), imidazole (0.75 mmol), [Cu] (10 mmol%), **L** (20 mmol%), base (1.0 mmol), solvent (1 mL), 12 h.

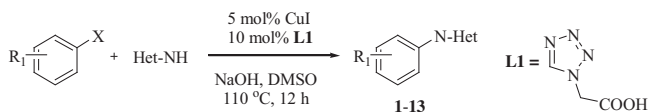
^b Isolated yield.

^c 5 mol% CuI, 10 mol% **L1**.

^d 5 mol% CuI, ligand-free.

^e 2.5 mol% CuI, 5 mol% **L1**.

Table 2
CuI-catalyzed N-arylation of imidazoles with aryl iodides using tetrazole-1-acetic acid as ligand under mild conditions.^a



Entry	ArX	Het-NH	Product	Yield (%) ^b
1				92 (70 ^c)
2				90
3				85
4				84 (71 ^c)
5				91 (81 ^c)

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