

# Selective coupling reaction between 2,6-diiodoanisoles and terminal alkynes catalyzed by palladium complex.

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## INTRODUCTION

The cross-coupling reaction between aryl halides and terminal alkynes catalyzed by palladium complexes and copper (I) salts can be considered an useful synthetic tool in the C(sp<sup>2</sup>)-C(sp) bond formation leading to disubstituted acetylenic compounds.<sup>1</sup> Accordingly, in this work we present our preliminary results involving the selective coupling reaction between 2,6-diiodoanisoles and terminal alkynes catalyzed by palladium and copper, in order to produce disubstituted alkynes bearing a functionalized aromatic ring.

## RESULTS AND DISCUSSION

Initially, we treated 2,6-diiodoanisole (**1a**) with phenylacetylene (**2a**) employing a palladium salt or complex and CuI as catalysts under varied reaction conditions, in the attempt to obtain selectively the mono-coupling product **3a** (Table 1).

Table 1. Synthesis of the compound **3a**.

entry	Pd salt or complex (mol%)	CuI (mol%)	<b>2a</b> (equiv)	base (equiv)	solvent	temp. (°C)	isolated yield (%)
1	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (10)	10	1.5	NEt <sub>3</sub> (2)	MeCN	50	41
2	Pd(OAc) <sub>2</sub> (5)	5	1.5	NEt <sub>3</sub> (2)	MeCN	50	43
3	Pd(PPh <sub>3</sub> ) <sub>4</sub> (10)	10	1.5	NEt <sub>3</sub> (2)	THF	60	37
4	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5)	15	2	(1)	toluene	r.t.	68

Aiming to obtain the mono-coupling product **3a** in a better yield (Table 1, entry 4), subsequent work focused on optimization of the conditions for the reaction (Table 2).

Table 2. Optimization of the synthesis for the compound **3a**.

entry	<b>2a</b> (equiv)	diisopropylamine (equiv)	temp. (°C)	time (h)	isolated yield (%)
1	1	1	r.t.	12	42
2	1.5	1	r.t.	12	57

3	2	1	r.t.	12	68
4	2	2	r.t.	12	82
5	2	2	50	12	71
6	2	2	r.t.	24	81

Employing the optimized reaction conditions for the selective cross-coupling reaction between 2,6-diiodoanisole (**1a**) and phenylacetylene (**2a**) (Table 2, entry 4), we synthesized disubstituted alkynes bearing a functionalized aromatic ring (**3**) (Table 3).

Table 3. Synthesis of disubstituted alkynes bearing a functionalized aromatic ring (**3**).<sup>a</sup>

entry	2,6-diiodoanisole (1)	terminal alkyne (2)	mono-coupling product (3)	isolated yield (%)
1				82
2				89
3				95
4				93

<sup>a</sup>Reaction conditions: 1 mmol of **1**, 2 mmol of **2**, 2 mmol of diisopropylamine, 5 mol% of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and 15 mol% of CuI were stirred at room temperature under nitrogen atmosphere for 12 h.

## CONCLUSION

We optimized the reaction conditions for the selective coupling between 2,6-diiodoanisoles (**1**) and terminal alkynes (**2**) catalyzed by Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and CuI, which produced disubstituted alkynes bearing a functionalized aromatic ring (**3**) in good yields.

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## REFERENCES

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