





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(sp²)-C(sp) bond formation leading to disubstituted acetylenic compounds.¹ 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

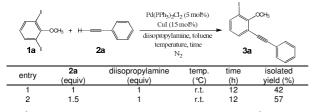
Initially, we treated 2,6-diiodoanisole (1a) with phenylacetylene (2a) employing a palladium salt or complex and Cul as catalysts under varied reaction conditions, in the attempt to obtain selectively the mono-coupling product 3a (Table 1).

Table 1. Synthesis of the compound 3a.

	-ocH ₆ +	н——— 2а	-	Pd salt or con CuI ca base, sol temperatur N ₂	vent >	- 🔾	OCH3	\mathbf{i}
entry	Pd salt or complex (mol%)	Cul (mol%)	2a (equiv)	base (equiv)	solv.	temp. (℃)	time (h)	isolated yield (%)
1	Pd(PPh ₃) ₂ Cl ₂ (10)	10	1.5	NEt ₃ (2)	MeCN	50	24	41
2	Pd(OAc) ₂ (5)	5	1.5	NEt ₃ (2)	MeCN	50	24	43
3	Pd(PPh ₃) ₄ (10)	10	1.5	NEt ₃ (2)	THF	60	24	37
4	Pd(PPh ₃) ₂ Cl ₂ (5)	15	2		toluene	r.t.	12	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).

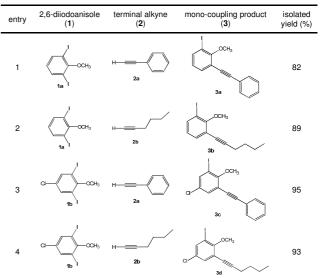
Table 2. Optimization of the synthesis for the compound 3a.



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	
0	2	2	1.1.	24	01	-

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).^{*a*}



^aReaction conditions: 1 mmol of 1, 2 mmol of 2, 2 mmol of diisopropylamine, 5 mol% of Pd(PPh₃)₂Cl₂ 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 $Pd(PPh_3)_2Cl_2$ and Cul, which produced disubstituted alkynes bearing a functionalized aromatic ring (3) in good yields.

ACKNOWLEDGEMENTS

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REFERENCES

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