Synthesis of 2-{2-[5(4)-aryl-2*H*-[1,2,3]-triazol-4(5)-yl]vinyl}chromen-4-ones

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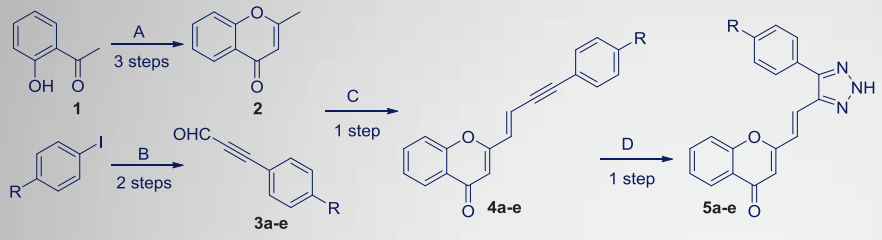
Introduction

Chromones are a family of oxygen-containing heterocyclic compounds that have been shown particular relevant biological activity [1]. In what concerns to 2-methylchromones, their reactivity is well-known and allow to exploit many different kinds of chemical reactions. The acidic character of the 2-methyl group, due to the low electron density at C-2 caused by carbonyl group enable this class of compounds to undergo oxidation, photolysis, cycloaddition and condensation reactions [2].

In this communication we will highlight the condensation reaction of 2-methylchromone **2** [3] with propargyl aldehydes **3** [4] in order to obtain (*E*)-2-(4-arylbut-1-en-3-ynyl)-4*H*-chromen-4-ones **4**. The internal alkyne of these molecules allow us to explore the azide-alkyne Huisgen cycloaddition, that is a very straightforward way to functionalize these kind of chromone derivatives. In this work we studied the reactivity of the alkyne moiety with sodium azide in order to obtain 2-{2-[5(4)-aryl-2*H*-[1,2,3]-triazol-4(5)-yl]vinyl}chromen-4-ones **5**.

Experimental and Results



Compound	R	Yield (%)
4a	H	52
4b	Br	59
4c	OCH_3	80
4d	CH_3	80
4e	NO_2	30

Compound	R	Yield (%)
5a	H	90
5b	Br	97
5c	OCH_3	98
5d	CH_3	98
5e	NO_2	91

Reaction Conditions:

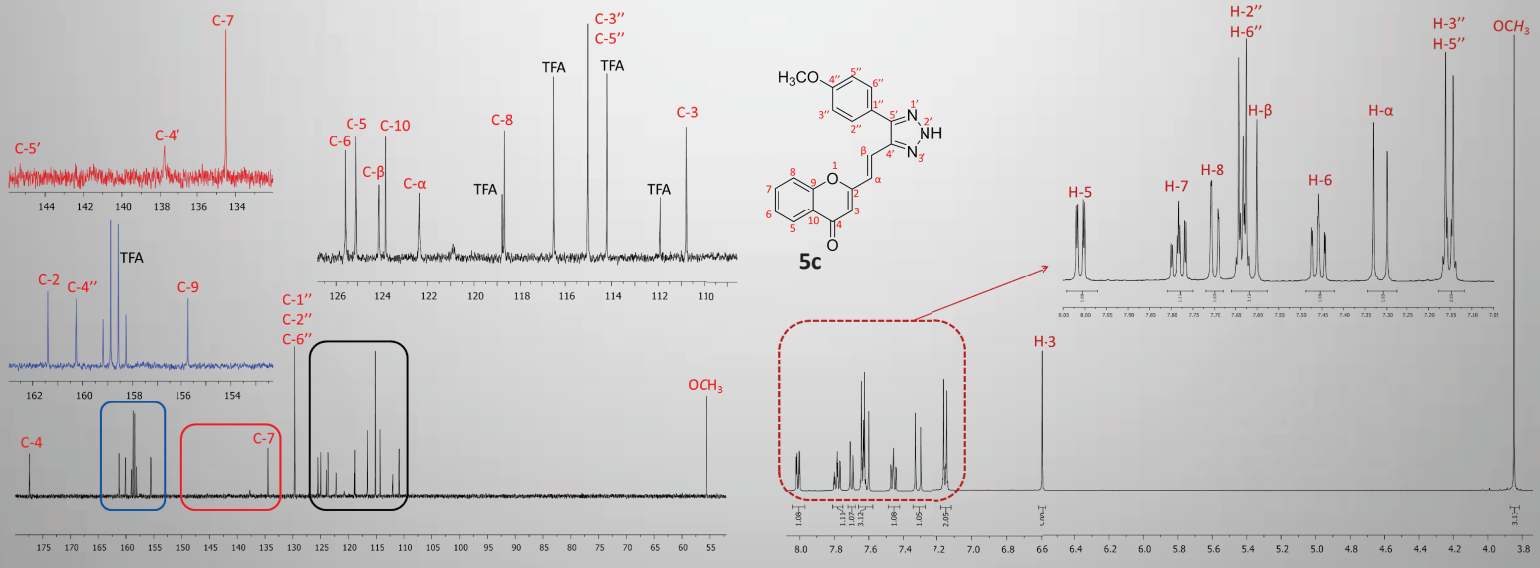
A: (i) MeCOCl, dry pyridine, r.t., 12 h; (ii) NaH, dry THF, reflux, 2 h; (iii) *p*-TSA, DMSO, 100°C, 2 h.

B: (i) $Pd(PPh_3)Cl_2$, PPy, CuI, propargyl alcohol, toluene, 60 °C, 2h; (ii) activated MnO_2, ethyl acetate, reflux, 2h.

C: Sodium, dry EtOH, r.t., 4 h.

D: NaN_3, DMF, reflux, 2h.

Structural Analysis



Conclusions

(*E*)-2-(4-arylbut-1-en-3-ynyl)-4*H*-chromen-4-ones were synthesized via aldol condensation of 2-methylchromone with propargyl aldehydes in fair to good yields. 2-{2-[5(4)-aryl-2*H*-[1,2,3]-triazol-4(5)-yl]vinyl}chromen-4-ones were obtained in excellent yields by the 1,3-dipolar cycloaddition reaction between the alkyne moiety of (*E*)-2-(4-arylbut-1-en-3-ynyl)-4*H*-chromen-4-ones and sodium azide. The assignment of C-4' and C-5' resonances of the 1,2,3-triazole ring of all compounds was only possible by the addition of a few drops of trifluoracetic acid (TFA) to the DMSO-d6 solution and further ^{13}C NMR acquisition.

References:

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