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Editor's choice paper

Pd catalyzed couplings of "superactive esters" and terminal alkynes: Application to flavones and γ-benzopyranones construction

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ABSTRACT

Lewis base, *N*-methylmorpholine (NMM) accelerated Pd-catalyzed Sonogashira coupling of steric hindered super active esters, 1a–1e, and terminal alkynes. This approach provided an efficient synthetic protocol for a broad array of acylated *o*-alkynoylphenols compounds, 3a–3e, under moderate conditions. The mechanistic study clearly demonstrated that NNM stabilized the catalytic palladium species, and accelerated the leaving of triazine moiety during the catalytic cycle of the cross-coupling reactions. In addition, piperazine was found to efficiently catalyze the 6-endo cyclization of acylated *o*-alkynoylphenols, which achieved the diversity oriented synthesis of γ-benzopyranones, 4aa–4eg, with 93–99% yields.

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1. Introduction

The γ-benzopyranones represent one of the most prevalent structural heterocycles in natural products, plant physiology and pharmaceuticals [1]. The importance of γ-benzopyranones derivatives has led to the development of a variety of general approaches for synthesizing their varied derivatives, such as Allan-Robinson method [2], Baker-Venkataraman rearrangement [3], Algar-Flynn-Oymanda method [4], the cyclization of chalcones [5]. Despite these advances, the most of these methods are of limited use as they suffer from low yields and often afford a mixture of products containing flavones, flavanones and aurones [6]. These procedures, generally require prolonged reaction times, multiple-step manipulation and use of harsh reaction condition of high temperatures or strong bases. Consequently, the efficient approaches towards the diversity oriented synthesis of γ-benzopyranones have received considerable attention.

The palladium catalyzed cross-coupling offers one of the most convergent approaches for the construction of complex molecular frameworks. Ynones are important structural motifs in natural products [7], they are often employed as key intermediates in the rapid construction of sophisticated γ-benzopyranones [8]. Yang et al. developed $PdCl_2(PPh_3)_2$-Thiourea-dppp catalyst system for the carbonylative annulation of *o*-acetoxyiodobenzenes with arylacetylenes using DBU as base and diethylamine as solvent (Scheme 1a) [9]. Wu et al. adopted a step by step approach towards γ-benzopyranones in which Pd/Cu catalyzed the cross-coupling of *o*-acetylsalicyloyl chlorides and terminal alkynes whilst KO^tBu prompted the annulation of 1,3-ynones (Scheme 1b) [10]. The inevitable employment of dangerous toxic and odorless CO as well as the requirement of strong bases limited these reactions from development. At these points, developing a facile CO- free synthesis of γ-benzopyranones under mild condition is of vital importance. Herein, we wish to report Lewis bases accelerated Pd-catalyzed alkynylation of 2-acetoxybenzoic acid ester, and the piperazine-mediated annulation for the diversity oriented synthesis of γ-benzopyranones (Scheme 1c). The new catalyst system of $Pd(OAc)_2$ and NMM were applied for the cross-coupling of steric hindered 2-acetoxybenzoic acid esters and terminal alkynes of 24 examples with satisfactory yields. The mechanistic experiments found that NMM stabilized the catalytic species, and promoted the deprotonation of terminal alkynes. To best our knowledge, the

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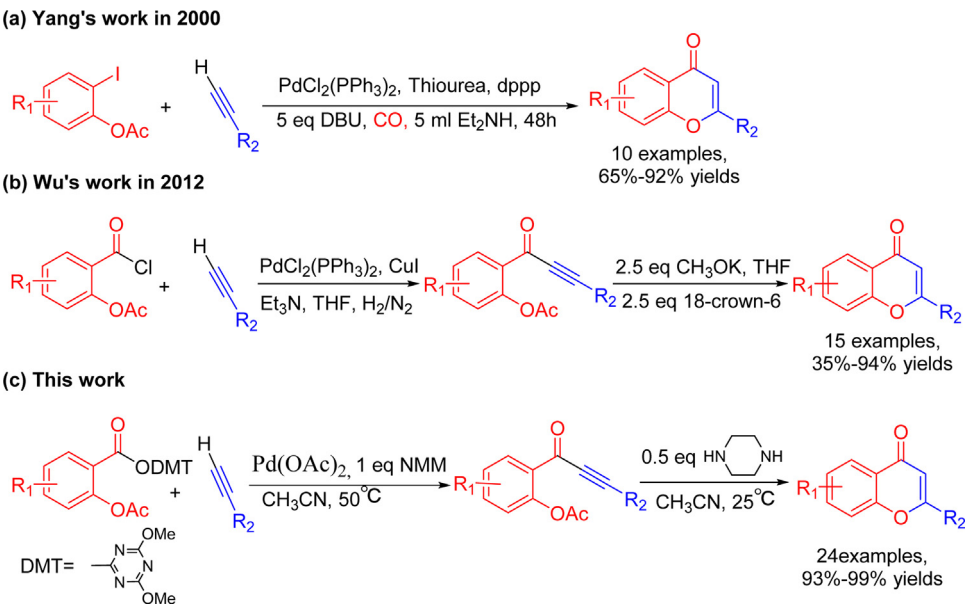
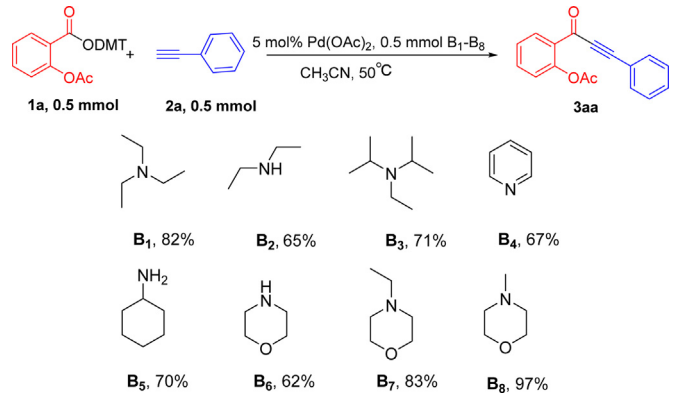


Scheme 1. Pd catalyzed diversity-oriented synthesis of γ-benzopyranones.



Scheme 2. Amines accelerated Pd catalyzed cross-coupling of "Superactive Ester" with phenylacetylene.

piperazine is the most active base, which efficiently mediated the annulation at room temperature with 93%-99% yields.

2. Experimental

2.1. General materials and methods

Solvents for reactions were used without distillation (CH_3CN, Alfa, purity). All reagents were purchased from the suppliers (TCI, Alfa, Acros, Aldrich) and used without further purification unless specified otherwise. Triazine ester reagents were prepared according to the general procedure. Unless otherwise stated, all manipulations were performed in a sealed Schlenk tubes under nitrogen atmosphere. Flash chromatography was performed using 200–300 mesh silica gel with the indicated solvent system according to standard techniques and analytical thin layer chromatography was carried out using 250 μm commercial silica gel plates. ^1H and ^{13}C NMR spectra were recorded on a Bruker EQUINX55 (400 MHz for ^1H; 101 MHz for ^{13}C) spectrometer in $CDCl_3$. For ^1H NMR, tetramethylsilane (TMS) served as internal standard ($\delta = 0$) and ^1H NMR chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CDCl_3$ at 7.26 ppm) unless otherwise noted. The data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), and coupling constant in Hz. For ^{13}C NMR, $CDCl_3$ was used as internal standard ($\delta = 77.16$) and spectra were obtained with complete proton decoupling. LRMS (ESI) analysis was performed and (LRMS) data were reported with sodium mass/charge (m/z) ratios as values in atomic mass units.

2.2. General procedure for the synthesis of products *3aa-3eg*

Under the protection of N_2, 3 mL CH_3CN was transferred into Schlenk tubes containing $Pd(OAc)_2$ (0.025 mmol) and triazine esters **1a–1e** (0.5 mmol). Alkynyl reagent **2a–2k** (0.75 mmol) was added by syringe. The reaction mixture was stirred at 50 °C for 10 h. Then added 1.0eq NMM for 8 h. After the reaction cooled down to room temperature, the crude products were extracted with ethyl acetate and water, the water layer got white precipitate by using rotary evaporator ($C_{10}H_{18}N_4O_4$ (258.11): calcd. C, 46.50; H, 7.02; N, 21.69; O, 24.78; found C 46.48, H 7.06, N 21.57 O 24.72). And then organic layer were filtered off and purified by column chromatography on silica gel using ethyl acetate/petroleum ether as eluent. All products **3aa–3eg** were identified by comparing their spectral data with those of authentic samples.

2.3. General procedure for the synthesis of products *4aa–4eg*:

Under atmospheric conditions, 3 mL CH_3CN without water was transferred into Schlenk tubes containing 1,3-yones **3aa–3eg** (0.5 mmol), then piperazine (0.25 mmol) was added. The reaction mixture was stirred at 25 °C for 1.5 h–3 h. After the reaction proceed completely, and the organic layer was purified by column chromatography on silica gel using dichloromethane or ethyl acetate/petroleum ether as eluent. All products **4aa-4eg** were identified by comparing their spectral data with those of authentic samples.

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