



Aerobic ligand-free domino Suzuki coupling–Michael addition reaction catalyzed by in situ generated palladium nanoparticles in water: a general method for the synthesis of benzo[*c*]chromene derivatives

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ABSTRACT

A general method has been developed for the synthesis of benzo[*c*]chromene derivatives via aerobic ligand-free domino Suzuki coupling and Michael addition reaction catalyzed by in situ generated palladium nanoparticles in water leading to C–C and C–O bond formations simultaneously.

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Benzo[*c*]chromenes are very important oxygen containing heterocycles because of their presence in a large number of bioactive molecules as a key structural subunits.¹ Figure 1 represents some important bioactive molecules containing these moieties.² Utility of benzo[*c*]chromenes in photochemical reactions as photoswitches is important.³ For example, 5*H*-dibenzo[*c,g*]chromen-3-ol shows biological activity as an estrogen receptor agonist.⁴ So development of a general route for the synthesis of benzo[*c*]chromene skeletons by using readily available starting materials has attracted researchers over past decades.

Palladium catalyst has proven its novelty and versatility toward the synthesis of fused-heterocycles via C–C bond formation.⁵ In continuation of our work on palladium chemistry, we have developed a methodology for the synthesis of benzo[*c*]chromene deriv-

atives via domino Suzuki coupling⁶ followed by intramolecular Michael addition reaction in water catalysis by metal nanoparticles that has proven its novelty toward cross coupling since last few years.⁷ Recently Liang and his co-workers synthesized these by palladium-catalyzed annulations of arynes with 2-(2-iodophenoxy)-1-arylethanones⁸ and Ferraccioli and co-workers by palladium- and nobornene-catalyzed reaction of aryl halides, *o*-substituted with electron releasing substituents, *o*-bromophenols, and activated alkenes,⁹ Satyanarayana and co-workers by a domino palladium-catalyzed C–C and C–O bonds formation via dual O–H bond activation¹⁰ and very recently Xu and co-workers by palladium-catalyzed tandem reactions of β-(2-bromophenyl)-α,β-unsaturated carbonyl compounds with 2-hydroxyphenylboronic acid.⁴

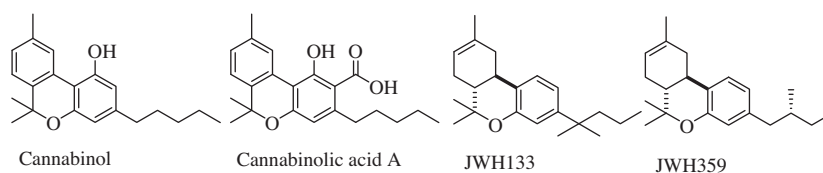
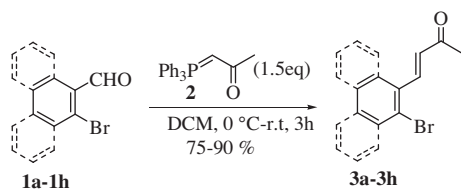


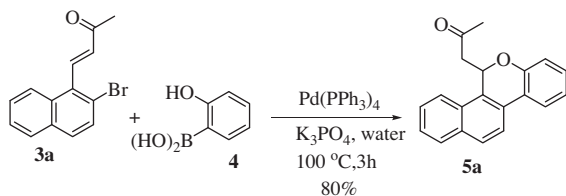
Figure 1. Bioactive molecules containing benzo[*c*]chromene moieties.

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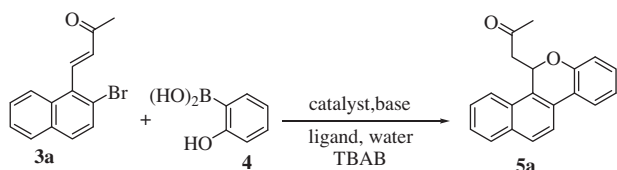


Scheme 1. Wittig reaction with 2-bromocarboxaldehydes.



Scheme 2. Synthesis of benzo[c]chromene derivative.

Table 1
Optimal condition determination^{a,b}



Entry	Catalyst	Ligand	Base	Temp (°C)	Yield ^c (%)
1	Pd(PPh ₃) ₄	—	K ₃ PO ₄	100	80
2	Pd(OAc) ₂	PPh ₃	K ₃ PO ₄	100	82
3	Pd(OAc)₂	—	K₃PO₄	100	90
4	Pd(OAc) ₂	—	K ₃ PO ₄	90	88
5	Pd(OAc) ₂	—	Cs ₂ CO ₃	100	75
6	Pd(OAc) ₂	—	Na ₂ CO ₃	100	55
7	Pd(OAc) ₂	—	K ₂ CO ₃	100	52
8	PdCl ₂	—	K ₃ PO ₄	90	82

^a Reagents and conditions: **3a** (1 mmol), 2-hydroxyphenylboronic acid (1.6 mmol), catalyst (10 mol %), base (4 mmol), TBAB (0.5 mmol), and water (6 mL) heated at 100 °C for 3 h.

^b Reaction was done in a two-necked round-bottomed flask fitted with condenser.

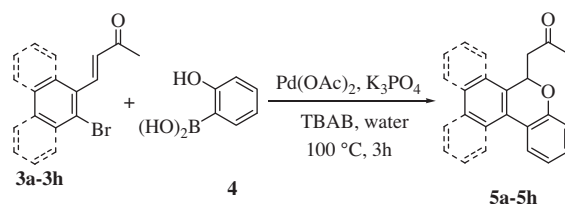
^c Yields refer to the isolated yields after purification through column chromatography.

Herein, we report aerobic ligand-free in situ generated palladium nanoparticles catalyzed a general methodology for the synthesis of substituted benzo[c]chromenes by the treatment of 2-hydroxyphenylboronic acid with β-(2-bromoaryl)-α,β-unsaturated carbonyl compounds where C–C followed by C–O bonds are formed simultaneously in a domino Suzuki coupling followed by Michael addition fashion in water.

The starting materials for the domino reactions were prepared by the Wittig reaction. Wittig products **3a–3h** were synthesized in 75–90% by the treatment of 1-(triphenylphosphoranylidene)-2-propanone **2** with 2-bromocarboxaldehydes **1a–1h** in dry DCM at 0 °C to rt for 3 h (Scheme 1).¹¹

Initially precursor **3a** on domino reaction with 2-hydroxyphenylboronic acid **4** in the presence of Pd(PPh₃)₄ catalyst, K₃PO₄ as base, and TBAB in water at 100 °C for 3 h yielded

Table 2
Synthesis of various benzo[c]chromene derivatives^a



Entry	Substrate	Product	Yield ^b (%)
1	3a	5a	90
2	3b	5b	87
3	3c	5c	72
4	3d	5d	78
5	3e	5e	74
6	3f	5f	82
7	3g	5g	76
8	3h	5h	78

^a Reagents and conditions: all the reactions were carried out under the following conditions: substrates **3a–3h** (1 mmol), 2-hydroxyphenylboronic acid (1.6 mmol), Pd(OAc)₂ (10 mol %), TBAB (0.5 mmol), K₃PO₄ (4 mmol), water (6 mL) at 100 °C, reaction time 3 h.

^b Yields were determined after purification through column chromatography.

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