Dalton Transactions



View Article Online

PAPER

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Cite this: Dalton Trans., 2020, 49, 15238

Received 19th August 2020, Accepted 6th October 2020 DOI: 10.1039/d0dt02918a

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Introduction

Benzofused five or six membered O- and N-heterocyclic compounds like benzofuran, indole, isocoumarin and isoquinolone have ubiquitous presence in natural products¹ and pharmaceuticals.² Over the years, extensive efforts have been directed to develop synthetic methodologies for this class of compounds.³⁻⁵ Compared to multi-step traditional methods, the transition-metal-catalyzed protocol that involves Sonogashira coupling reaction between 2-haloaryl heteroatom derivatives and terminal alkynes, followed by intramolecular cyclization is an attractive option because of its atomeconomy, operational simplicity and environmental benefits.⁶⁻¹⁰ Several catalysts based on Pd,^{6c-j,7} Cu,⁸ Pd/ Cu,^{6a,k-n,9a-f} Ni,^{9g,h} Zn,⁹ⁱ Ni/Zn^{9j} and other metals^{9k-o} have been

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Palladium complexes with an annellated mesoionic carbene (MIC) ligand: catalytic sequential Sonogashira coupling/cyclization reaction for one-pot synthesis of benzofuran, indole, isocoumarin and isoquinolone derivatives†

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Two Pd(II) complexes (**1** and **2**) featuring a fused π -conjugated imidazo[1,2-a][1,8]naphthyridine-based mesoionic carbene ligand have been synthesized and structurally characterized. Both complexes effectively catalyze the one-pot synthesis of benzofuran starting from phenylacetylene and 2-iodophenol under mild conditions. Complex **1** is found to be an excellent catalyst for the straightforward access to a library of benzofuran, indole, isocoumarin and isoquinolone derivatives by the reaction of terminal alkynes with 2-iodo derivates of phenol, *N*-methyl aniline, benzoic acid and *N*-methyl benzamide, respectively. The general utility of the catalytic method is demonstrated using a variety of diversely substituted terminal alkynes and the corresponding desired products are obtained in good to excellent yields. On the basis of control experiments, a two-cycle mechanism is proposed which involves the Sonogashira coupling of 2-iodo derivatives with alkynes and the subsequent cyclization of the corresponding 2-alkynyl compounds.

employed for this tandem process. In particular, Pd complexes bearing a variety of ligands including phosphines^{6c-e,k,7a,b,g-k} and N-heterocyclic carbenes (NHCs)^{7c-f} have shown promising results for the synthesis of 2-substituted benzofuran derivatives.

Bosiak reported $[Pd(dppf)Cl_2]/CuI (dppf = 1,1'-bis(diphenyl$ phosphino)ferrocene] catalyzed one-pot, four-step synthesis of 2-arylbenzofurans starting from aryl halides, trimethylsilylacetylene and 2-halophenols.^{6a} Wang and Manabe employed an in situ generated Pd catalytic system derived from PdCl₂(CH₃CN)₂/HTP (hydroxyterphenylphosphine) to access 2-substituted benzofurans via coupling/cyclization pathway.6c Latter, the same group used DHTP (dihydroxyterphenylphosphine) which improved the catalytic efficiency as compared to the HTP ligand.^{6d,7g} A $[Pd(\eta^3-C_3H_5)Cl]_2$ /tetraphosphine based system was reported by Li and coworkers for the synthesis of benzofuran from 2-halophenols and alkynes.7b A handful of Pd-based catalysts have also been utilized under heterogeneous conditions for this tandem process.^{6f-j} Bäckvall's group employed Pd nanoparticles immobilized on siliceous mesocellular foam to access benzofuran and indole derivatives.^{6f} Recently, Yang and coworkers used supported Pd nanoparticles for the synthesis of biologically active benzofurans.⁶

NHC ligands offer several advantages over phosphines in many organometallic transformations.¹¹ Mata and coworkers

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[†]Electronic supplementary information (ESI) available: Experimental details, supporting figures, spectroscopic and crystallographic data. CCDC 2014440 and 2014441. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt02918a

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