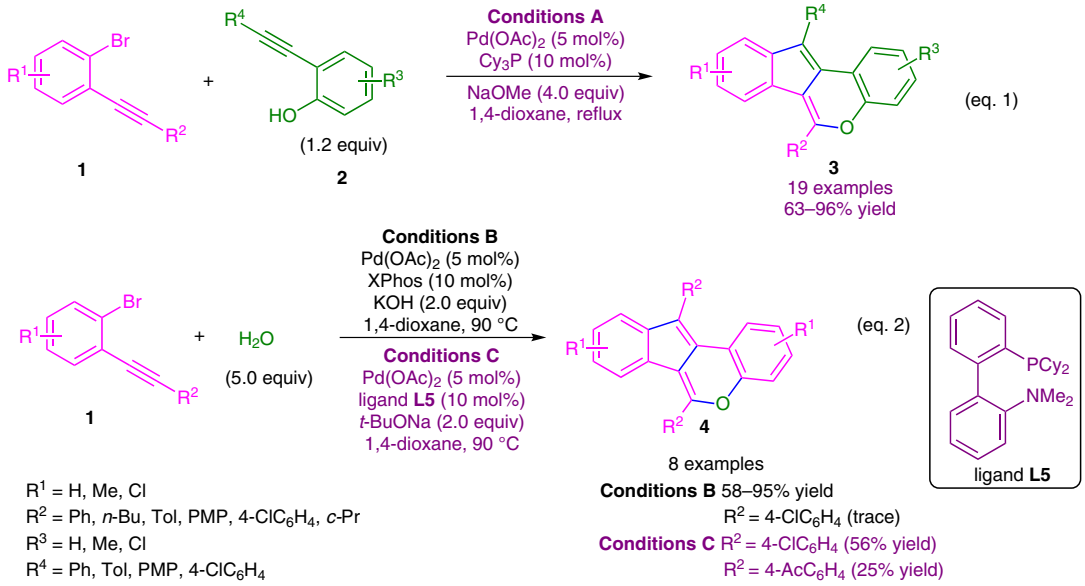
X. PAN, H. NIE, Y. LUO, Y. GAO,* J. WU* (FUDAN UNIVERSITY, SHANGHAI, SHANGHAI UNIVERSITY OF T.C.M. AND SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY, P. R. OF CHINA)

Facile Assembly of Indeno[1,2-*c*]chromenes via a Palladium-Catalyzed Reaction of 2-Alkynylhalobenzene
Org. Biomol. Chem. **2012**, *10*, 8244–8250.

Pd-Catalyzed Synthesis of Indeno[1,2-*c*]-chromenes from 2-Alkynylhalobenzenes



Significance: Reported is the synthesis of indeno[1,2-*c*]chromenes **3** and **4** via a palladium-catalyzed reaction of 2-alkynylbromobenzenes **1** with either 2-(2-arylethynyl)phenols **2** or with water. A range of ligands was used during the optimization study to reveal that the reaction proceeds only with Cy_3P as ligand (eq. 1). Sodium methoxide in toluene or 1,4-dioxane was better than other combinations. The substrate scope of this transformation was modestly demonstrated. The reaction also proceeded to give **3** in 78% yield by treatment of 1-chloro-2-(2-phenylethynyl)benzene with **2** (R^3 = H, R^4 = Ph). Surprisingly, re-optimization was required in the reaction of **1** with water (eq. 2). Both alkyl- and aryl-substituted alkynes were tolerated under the optimized conditions. However, the reaction parameters had to be re-screened to give a satisfactory yield of compounds with electron-withdrawing groups (R^2 = 4-ClC_6H_4, 4-AcC_6H_4).

Comment: The [6.5.6.6]-tetracyclic core of indenochromenes **3** and **4** is present in several bioactive compounds (B. S. Min et al. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 7436). Very few synthetic methods such as iron-mediated [3+2]-annulation reactions are available to provide access to this tetracyclic system (Z.-Q. Wang et al. *Org. Lett*. **2011**, *13*, 14). The present method provides a rapid construction of various substituted indenochromenes from easily accessible starting materials. One drawback of this method is the lower yield for electron-poor substrates. Although, this work provides a facile synthesis of indeno[1,2-*c*]-chromenes, it is strikingly similar to the authors' previous work (Y. Luo, L. Hong, J. Wu *Chem. Commun*. **2011**, *47*, 5298) .

SYNFACTS Contributors: Victor Snieckus, Suneel P. Singh
Synfacts 2013, 9(1), 0031 Published online: 17.12.2012
DOI: 10.1055/s-0032-1317868; **Reg-No.:** V15212SF

Category
Synthesis of Heterocycles

Key words
indeno[1,2-*c*]-chromenes
2-alkynyl-bromobenzenes
2-(2-phenylethynyl)-phenols
palladium catalysis