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Digest Paper

Stoichiometric copper or silver salt-mediated oxidative C–H/C–H cross-coupling reactions

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ABSTRACT

Over the past few years, transition metal-mediated oxidative cross-coupling reactions have emerged as a versatile method to construct C–C bonds. However, most of the precedents require high-priced precious metal catalysts such as Rh, Pd, and Ru in combination with a stoichiometric amount of metal oxidant including copper and silver salt. Recently, stoichiometric copper or silver salt-mediated oxidative C–H/C–H cross-coupling reactions in the absence of high-priced metal catalyst have shown up prominently. This short review covers the latest progress in the applications of this emerging strategy, highlights their advantages and limitations, and provides a comprehensive overview on existing procedures and employed methodologies.

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Introduction

Carbon–carbon (C–C) bonds are the fundamental linkages ubiquitous in biologically active compounds, natural products, pharmaceuticals, ligands, and various materials. As a consequence, seeking more efficient ways to construct C–C bonds is always the central topic in organic synthesis.¹ Over the past 10 years, the strategy for the construction of a C–C bond directly from two simple C–H bonds with the assistance of transition metal catalysts and additional oxidants has captured growing attention in the synthetic organic chemistry community. Compared with the traditional transition metal-catalyzed cross-coupling reactions such as Suzuki–Miyaura, Negishi, Kumada, Hiyama, and Stille coupling

(Scheme 1, route A), the oxidative C–H/C–H cross-coupling reactions could bypass the lengthy and troublesome preactivation of two substrates and allow the utilization of easily available, environmentally benign starting materials (Scheme 1, route B). To date, a great deal of impressive achievements in transition-metal-catalyzed oxidative cross-coupling reactions have been made.² However, most of the precedents required high-priced precious metal catalysts such as Rh, Pd, and Ru in combination with a stoichiometric amount of metal oxidant including copper and silver salt. Undoubtedly, the expensive and complex reaction systems would limit their application scope to some extent, and spur the invention of more efficient, inexpensive and simple alternatives.

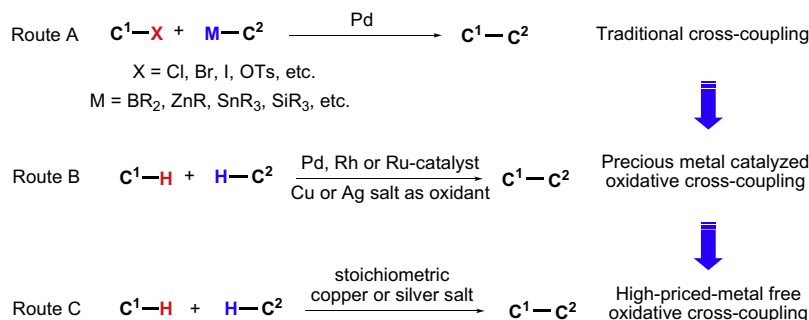
Recently, we have noticed that some elegant examples about copper or silver salt-mediated oxidative C–H/C–H cross-coupling reactions in the absence of precious metal catalysts have been reported. In these pioneer works, stoichiometric copper or silver

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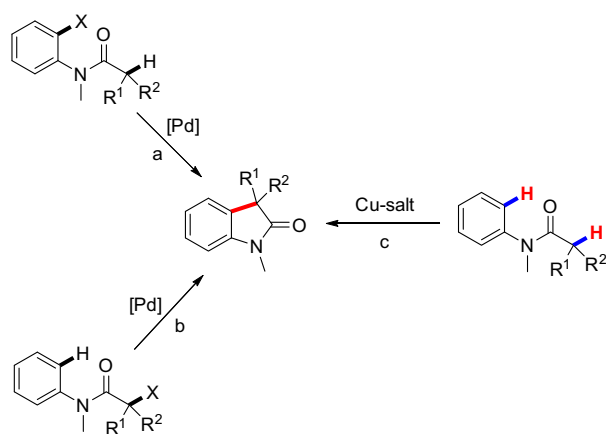
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Scheme 1.

salts could serve as both the promoter and terminal oxidant, which largely reduce the cost and simplify the reaction systems (Scheme 1, route C). In this paper, we summarize the recent progresses in stoichiometric copper or silver salt-mediated oxidative

C–H/C–H cross-coupling reactions, and also hope this review would highlight the scope and limitations of this new strategy and serve as a handy reference for the chemists who are interested in this research area.

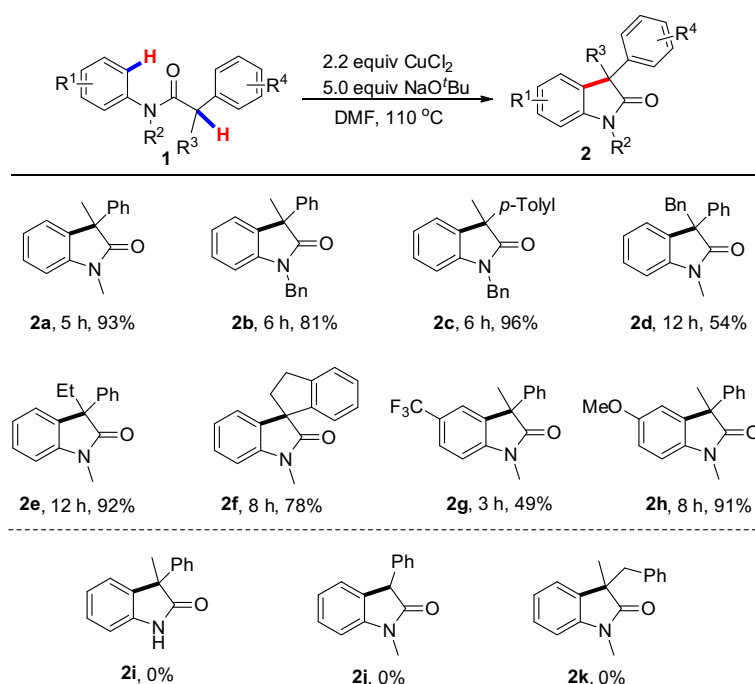


Scheme 2.

Intramolecular oxidative $C(sp^2)$ –H/ $C(sp^3)$ –H cross-coupling reactions

Oxindoles are a kind of important and common structural units in natural compounds and pharmaceuticals. Previous reports on the synthesis of oxindoles in the presence of transition metal catalysts mainly rely on Pd-catalyzed intramolecular $C(sp^3)$ –H arylation with aryl halide (Scheme 2, a)^{3a} or intramolecular $C(sp^2)$ –H alkylation with alkyl halide (Scheme 2, b).^{3b} Obviously, these two kinds of reactants need to be prefunctionalized. In 2009, Kündig and co-workers reported a simple and efficient reaction system for the intramolecular $C(sp^2)$ –H/ $C(sp^3)$ –H cross-coupling reactions, providing a straightforward access to oxindole skeleton (Scheme 2, c).⁴

The reaction protocol is compatible with a variety of acetanilide derivatives, delivering a series of 3,3-disubstituted oxindoles in moderate to good yields (Scheme 3). However, some limitations still remain with respect to the substrate scope. For example, no



Scheme 3.

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