Tetrahedron Letters 59 (2018) 1605–1613

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Digest paper

Photoredox-catalyzed C(sp^2)–N coupling reactions

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ARTICLE INFO

Article history:
Received 25 January 2018
Revised 9 March 2018
Accepted 19 March 2018
Available online 20 March 2018

Keywords:
Photoredox catalysis
Photochemistry
C(sp^2)–N coupling reactions
Radical reactions
Aryl amines

ABSTRACT

Photoredox-catalyzed radical reactions have attracted intense interest from synthetic chemists over the past several years. The photoredox-catalyzed C(sp^2)–N coupling reactions, including Ullmann type C–N coupling (C–X/N–H type coupling), redox neutral C–N coupling (C–H/N–X type coupling) and oxidative C–N coupling (C–H/N–H type coupling), have been summarized in this digest.

Contents

Introduction

Nitrogen-containing compounds exist in many biologically active molecules and natural products,[1] and also act as functional groups in material science.[2] Therefore, the development of efficient methods for the synthesis of nitrogen-containing compounds has been extensively investigated by synthetic chemists.[3]

Classic methods for construct carbon–nitrogen (C(sp^2)–N) bonds involve: 1) Ullmann type C(sp^2)–N coupling;[4] 2) Buchwald-Hartwig cross coupling.[5] Recent years, the development of visible-light-promoted reactions offer a new approach toward C(sp^2)–N bond construction via radical-triggered process. There is no doubt that novel photoredox catalyzed C(sp^2)–N coupling reactions characterized with mild conditions and good functional group tolerance attract extensive interest from synthetic community. In this digest, we highlight recent progresses in the photoredox-catalyzed C(sp^2)–N coupling reactions: 1) Ullmann type C(sp^2)–N coupling reactions (C–X/N–H type coupling); 2) redox neutral C(sp^2)–N coupling reactions (C–H/N–X type coupling); 3) oxidative C(sp^2)–N coupling reactions (C–H/N–H type coupling) (Scheme 1).

Ullmann type C(sp^2)–N coupling reactions

One of major drawbacks of classic Ullmann reactions is that the reactions have to be carried out at elevated temperature. In 2012,

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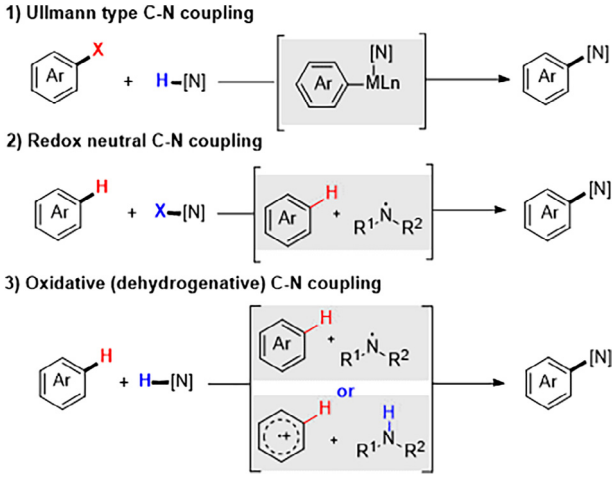
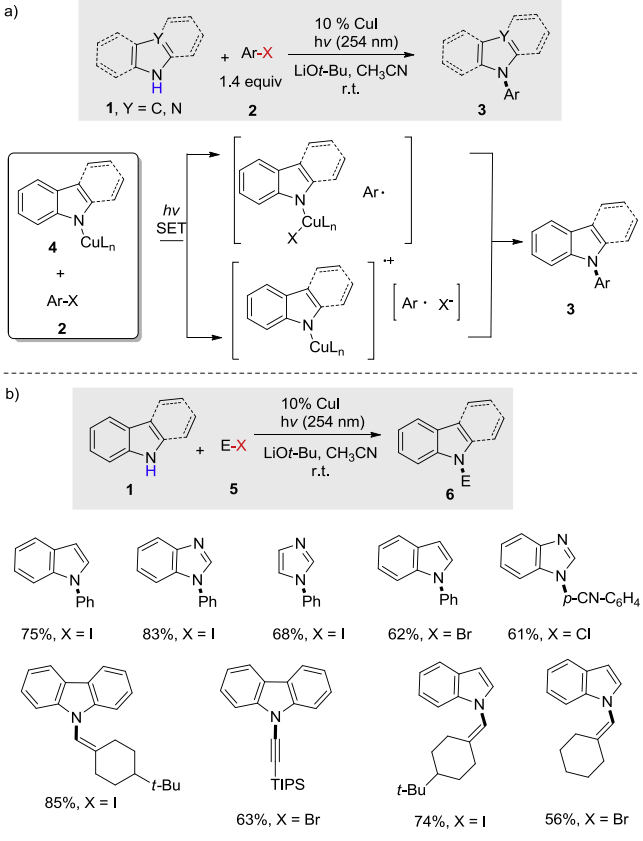
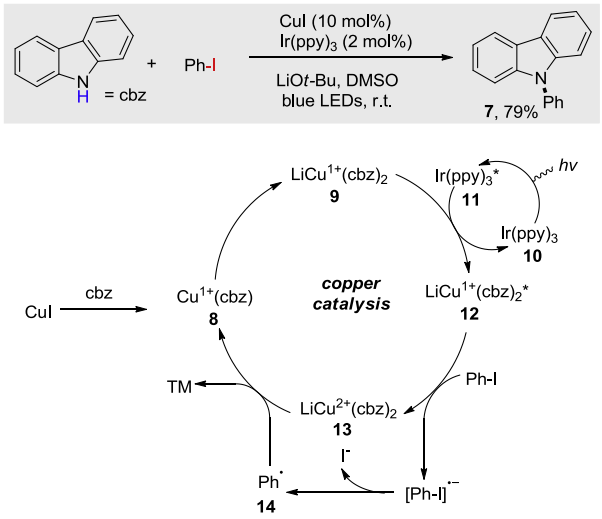
https://doi.org/10.1016/j.tetlet.2018.03.050
0040-4039/



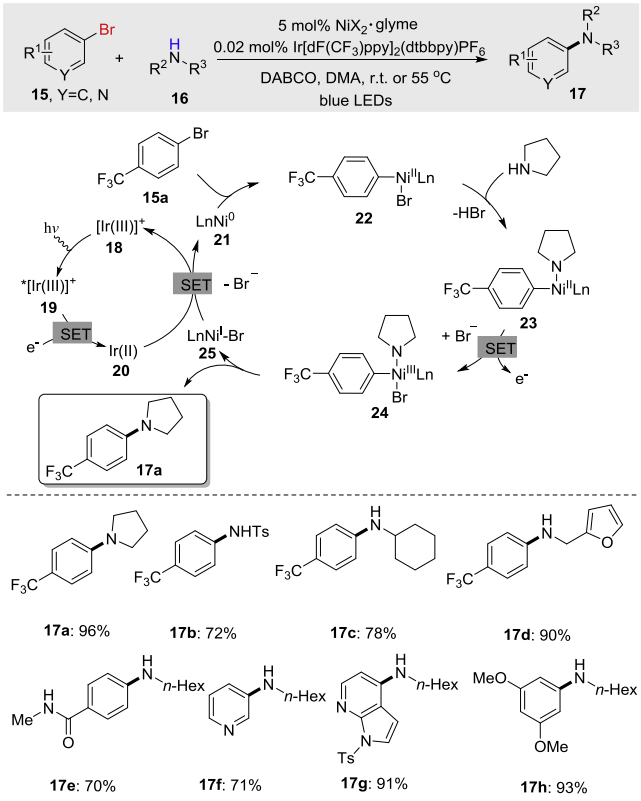
Scheme 1. Photoredox-catalyzed C(sp^2)–N coupling reactions.



Scheme 2. Photoinduced Ullmann C(sp^2)–N bond formation *via* a copper–carbazolide complex.



Scheme 3. Visible-light induced coupling reaction of carbazole derivatives and aryl iodides.



Scheme 4. Ni-catalyzed C(sp^2)–N coupling promoted by visible light.

Fu and Peters groups had reported an Ullmann type C(sp^2)–N coupling reaction promoted by ultraviolet irradiation (Scheme 2a).[6] Their coupling reactions were promoted by a stoichiometric or a catalytic amount of copper, which enabled the coupling of carbazolide and aryl iodides under unusually mild conditions (room temperature or even − 40 °C). An array of mechanistic studies revealed that the photo-induced C(sp^2)–N bond formation proceed *via* a single-electron transfer (SET) process mediated by copper–carbazolide complex. When a carbon-centered radical is generated, copper-mediated C(sp^2)–N bond formation can ensue.

Later on, they expanded the scope with respect to both the nucleophiles and the electrophiles of the photo-induced copper-catalyzed process (Scheme 2b).[7] Nitrogen-based nucleophiles (such as indoles, benzimidazoles, and imidazoles) and diverse electrophiles (e.g., hindered/deactivated/heterocyclic aryl iodides, an aryl bromide, an activated aryl chloride, alkenyl halides, and an alkynyl bromide) could serve as suitable partners and give C–N coupling products in moderate to good yields.

Kobayashi and co-workers also explored the Ullmann type C–N coupling reactions and reported a visible-light induced coupling