

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue of Photocatalysis for Solar Fuels)

Photo-induced reductive cross-coupling of aldehydes, ketones and imines with electron-deficient arenes to construct aryl substituted alcohols and amines



Zan Liu ^{a,b}, Xiaolei Nan ^{a,b}, Tao Lei ^{a,b}, Chao Zhou ^{a,b}, Yang Wang ^{a,b}, Wenqiang Liu ^{a,b}, Bin Chen ^{a,b}, Chenho Tung ^{a,b}, Lizhu Wu ^{a,b,*}

^a Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 17 September 2017

Accepted 26 October 2017

Published 5 March 2018

Keywords:

Aryl substituted alcohols and amines

Radical-radical cross coupling

Polarity reversal

Photocatalysis

Arylation

ABSTRACT

Umpolung reactions of C=X bonds (X = O, N) are valuable ways of constructing new C–C bonds, which are sometimes difficult to be constructed using traditional synthetic pathways. Classical polarity inversion of C=X bonds (X = O, N) usually requires air or moisture-sensitive and strong reducing agents, which limit the feasibility of substrate scope. Herein we describe a photo-induced reductive cross-coupling reaction of aldehydes, ketones and imines with electron-deficient arenes (aromatic nitriles) using *fac*-Ir(ppy)₃ as a photocatalyst and diisopropylethylamine (DIPEA) as a terminal reductant under visible light irradiation. Mild conditions and high yields mean that this new polarity inversion strategy can be used with aryl-substituted alcohols and amines. Spectroscopic studies and control experiments have demonstrated the oxidative quenching of Ir(ppy)₃^{*} by electron-deficient arenes involved in the key step for the C–C bond formation.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Substantial development in visible-light catalysis has been witnessed over recent years [1–3]. Due to the unique ability of visible-light harvesting, Ru(II) [4–11] and Ir(III) [12–17] complexes, organic dyes [18–21] and semiconductors [22,23] have been successfully used in single electron transfer (SET) to activate a variety of functional groups. In this regard, the umpolung conversion of C=X double bonds (X = O, N) is highly attractive. Classical polarity inversion of aldehydes, ketones and imines usually requires excess metals or unstable strong reducing agents under harsh conditions, meaning that only a narrow

range of substrates are compatible [24,25], greatly limiting their subsequent transformation. In contrast to using traditional methods, these C=X double bonds (X = O, N) can easily obtain one electron via visible-light catalysis to be converted into a practical nucleophilic intermediate. In 2013, Knowles *et al.* [26,27] reported an intramolecular reductive coupling between ketones and hydrazones or electron-deficient olefins under visible-light catalysis via proton coupled electron transfer. In the same year, MacMillan *et al.* [28,29] demonstrated the coupling of ketones and amines with activated C–H bonds, including benzylic ethers with the β -position of enamines generated *in situ*. More recently, Rueping *et al.* [30,31] realized the dimer-

* Corresponding author. Tel/Fax: +86-10-82543580; E-mail: lzhu@mail.ipc.ac.cn

This work was supported by the Ministry of Science and Technology of China (2013CB834804, 2014CB239402), the National Natural Science Foundation of China (21390404, 91427303), and the Strategic Priority Research Program of the Chinese Academy of Science (XDB17030400).

DOI: 10.1016/S1872-2067(17)62896-1 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 39, No. 3, March 2018

ization of C=X double bonds (X = O, N) and the cross coupling of tertiary amines and ketones assisted by photo-induced two-center/three-electron intermediates. Xiao *et al.* [32] expanded this cross coupling reaction to include secondary amines. Chen *et al.* [33] demonstrated the visible-light-induced polarity-reversed allylation of aldehydes, ketones and imines with electron-withdrawing allyl sulfones. Furthermore, Ngai *et al.* [34] described reductive coupling of these polar C=X double bonds (X = O, N) with weak electrophilic alkenylpyridines through chelation with a lanthanide. Visible-light-induced polarity inversion of C=X bonds (X = O, N) has demonstrated the potential to synthesize alkyl alcohols and amines. We were keen to investigate if a visible-light strategy could be applied to the construction of aryl-substituted products, which are generally synthesized using air- or water-sensitive Grignard reagents under thermal conditions (Scheme 1). This would provide a simple and mild way to generate aryl alcohols and amines, with no need for harsh conditions and sensitive reagents.

2. Experimental

2.1. General methods

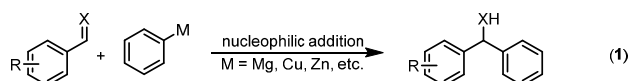
^1H NMR spectra were recorded using a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals. Mass spectra were recorded using a Trio-2000 GC-MS spectrometer. Commercially available reagents and solvents were used without further purification. Blue LEDs (3 W, $\lambda = 450 \pm 10$ nm, 145 lm @ 700 mA) were used as the irradiation light.

2.2. General procedure for the preparation of imines

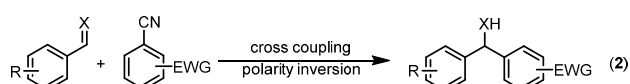
The aldehyde (1.0 mmol) was added to a solution of aryl amine (1.0 mmol) in anhydrous Et_2O (20 mL) in the presence of molecular sieves (4 Å 1.6 mm pellets, 7 g). The reaction was performed at room temperature (RT) under magnetic stirring and monitored by TLC. When the reaction was complete, the molecular sieves were removed by filtration, and the solvent was removed under vacuum. The residue was recrystallized from $\text{Et}_2\text{O}/n$ -hexane to afford the imines directly as pure (*E*) products.

2.3. General procedure for radical trapping experiments

Previous work: Grignard reagent, sensitive to air and water



This work: Visible light catalysis, mild conditions



Scheme 1. Visible light catalyzed umpolung reactions of C=X (X = O, N) with electron-deficient arenes.

A 10-mL Pyrex tube equipped with a magnetic stir bar was charged with 1,4-dicyanobenzene (1,4-DCB) (25.6 mg, 0.2 mmol), *fac*-Ir(ppy)₃ (2.6 mg, 2 mol%), TEMPO (0.4 mmol, 2 equiv.) and DMSO (2 mL). The Pyrex tube was sealed with rubber plug and then deaerated by bubbling Ar for 15 min. benzaldehyde (30.5 μL , 0.3 mmol) and DIPEA (52.4 μL , 0.3 mmol) were added. The reaction system was irradiated with blue LEDs ($\lambda = 450 \pm 10$ nm) for 12 h at RT. When the reaction was complete, the aqueous solution was extracted with ethyl acetate (5 mL \times 3). The organic extracts were combined, washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, then diphenylacetonitrile (23.2 mg) was added as an internal standard and the yield (19%) was detected by ^1H NMR.

2.4. General procedure for the polarity inversion/arylation process

A 10-mL Pyrex tube equipped with a magnetic stir bar was charged with 1,4-DCB (25.6 mg, 0.2 mmol), *fac*-Ir(ppy)₃ (2.6 mg, 2 mol%) and DMSO (2 mL). The Pyrex tube was sealed with rubber plug and then deaerated by bubbling Ar for 15 min, then benzaldehyde (30.5 μL , 0.3 mmol) and DIPEA (52.4 μL , 0.3 mmol) were added. The reaction system was irradiated with blue LEDs ($\lambda = 450 \pm 10$ nm) for 12 h at RT. When the reaction was complete, the aqueous solution was extracted with ethyl acetate (5 mL \times 3). The organic extracts were combined, washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the residue was purified by chromatography on silica gel (petroleum ether: ethyl acetate = 3:1) to afford the desired product.

4-(Hydroxy(phenyl)methyl)benzotrile (**3**): colorless oil, isolated yield: 83%. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.38–7.26 (m, 5H), 5.83 (s, 1H), 2.65 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) 149.01, 142.93, 132.34, 128.96, 128.36, 127.12, 126.78, 118.91, 111.18, 75.69. HRMS (EI) calculated for $\text{C}_{14}\text{H}_{11}\text{NO}$ [$\text{M}-\text{H}$]⁺: 208.0762, found: 208.0761.

4-(Hydroxy(phenyl)methyl)-2-methylbenzotrile and 4-(hydroxyl(phenyl)methyl)-3-methylbenzotrile (**4**): colorless oil, isolated yield: 82%, the ratio of regioselectivity = 1.47. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.0$ Hz, 0.40 H), 7.58–7.50 (m, 1.00 H), 7.41–7.21 (m, 6.60 H), 5.95/5.80 (s, 1.00H), 2.53 (d, $J = 2.7$ Hz, 0.60 H), 2.50 (s, 1.80H), 2.45 (d, $J = 3.1$ Hz, 0.40H), 2.20 (s, 1.20H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.80, 146.78, 143.04, 142.28, 141.65, 136.64, 133.87, 132.74, 130.04, 128.94, 128.93, 128.40, 128.30, 128.11, 127.40, 126.92, 126.75, 124.36, 119.06, 118.22, 111.68, 111.22, 75.75, 73.22, 20.66, 19.33. HRMS (EI) calculated for $\text{C}_{15}\text{H}_{13}\text{NO}$ [M]⁺: 223.0997, found: 223.0999.

Phenyl(4-(phenylsulfonyl)phenyl)methanol (**5**): white solid, isolated yield: 52%. ^1H NMR (400 MHz, CDCl_3) δ 7.97–7.79 (m, 4H), 7.54–7.45 (m, 5H), 7.37–7.22 (m, 5H), 5.83 (s, 1H), 2.59 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.46, 142.96, 141.68, 140.52, 133.30, 129.39, 128.92, 128.29, 127.94, 127.76, 127.33, 126.77, 75.69. HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{16}\text{O}_3\text{S}$ [$\text{M}+\text{Na}$]⁺: 347.0712, found: 347.0709.

Download English Version:

<https://daneshyari.com/en/article/6505720>

Download Persian Version:

<https://daneshyari.com/article/6505720>

[Daneshyari.com](https://daneshyari.com)