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PII: S0040-4039(16)30966-2
DOI: http://dx.doi.org/10.1016/j.tetlet.2016.07.098
Reference: TETL 47960

To appear in: *Tetrahedron Letters*

Received Date: 6 June 2016
Revised Date: 16 July 2016
Accepted Date: 30 July 2016

Please cite this article as: Zhu, F., Lu, B., Sun, H., Shen, Q., A facile sp^3 C-H bonds amidation of *N,N*-dimethylanilines by a novel ionic iron(III) complex containing an imino-functionalized imidazolium cation, *Tetrahedron Letters* (2016), doi: http://dx.doi.org/10.1016/j.tetlet.2016.07.098

Tetrahedron Letters
journal homepage: www.elsevier.com

A facile sp^3 C-H bonds amidation of *N*,*N*-dimethylanilines by a novel ionic iron(III) complex containing an imino-functionalized imidazolium cation

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Iron(III) complex
Imidazolium salts
Amidation of C-H bond
N,*N*-Dimethylanilines

ABSTRACT

A new imino-functionalized imidazolium salt, 1-[1-(2,6-diisopropylphenylimino)ethyl]-3-benzylimidazolium chloride ([HL]Cl,), was designed and used to prepare a novel ionic iron(III) complex [HL][$FeCl_4$] (**2**). Complex **2** was an efficient and easy-to-use catalyst for the direct sp^3 C-H bonds amidation of *N*,*N*-dimethylanilines, affording a wide variety of *N*-substitued aromatic or aliphatic amides in moderate to good yields. This reaction is the first example of iron-catalyzed intermolecular amidation of unactivated sp^3 C-H bonds of tertiary amines by aromatic or aliphatic amides under mild reaction conditions.

1. Introduction

The development of novel methods for the construction of C–N bonds is an important and long-standing research topic in organic synthesis because nitrogen-containing functional groups are ubiquitous in natural products, bioactive molecules and functional materials.[1] In the past two decades, transition-metal-catalyzed direct amidation of sp^3 C–H bonds has emerged as an attractive strategy for the C–N bond formation in terms of sustainablity.[2] In this context, good progress has recently made in copper[3-7]- or cobalt[8]-catalyzed intermolecular amidation of sp^3 C–H bonds, including allylic and/or benzylic sp^3 C–H bonds,[3-5,8] sp^3 C–H bonds adjacent to a nitrogen atom[3b,6] and even unactivated sp^3 C–H bonds in alkanes,[5,7] using simple amide reagents via oxidative cross-coupling of C–H and N–H bonds.[3-8] These amidation reactions open up new opportunities that complement metal–nitrene amidation protocols in that both primary and secondary amides can be used as coupling partners.[2a] In addition, transition-metal-free intermolecular amidation of allylic and benzylic sp^3 C–H bonds have also been developed.[9]

Significant effort has been devoted to the development of iron-catalyzed C–H bond functionalization because iron is abundant inexpensive, nontoxic, and environmentally benign, and therefore, provides "greener" strategies for organic synthesis.[10] Until now only two papers describing the iron-catalyzed intermolecular amidation of sp^3 C–H bonds have been published. In 2008, Fu and co-workers reported the first example of the direct amidation of benzylic sp^3 C–H bonds using an $FeCl_2$/NBS catalyst/oxidant system.[11] Recently, Zhu et al. developed an $FeCl_2{\cdot}4H_2O$/bipyridine/TBHP system for the direct amidation of the sp^3 C–H bonds adjacent to nitrogen atoms of tertiary amides.[12] To the best of our knowledge, there has been no systematic study of iron-catalyzed oxidative cross-coupling of tertiary amines with amides, that proceed by amidation of unactivated sp^3 C–H bonds adjacent to nitrogen atoms in tertiary amines.[6]

As a continuation of our studies on the development of iron-based catalysis for C–C bond formation,[13-15] we now report the use of an imino-functionalized imidazolium salt **1** in the facile synthesis of a novel ionic iron(III) complex **2**, and the use of **2** as an efficient catalyst for the sp^3 C–H bond amidation of *N*,*N*-dimethylanilines. A series of readily available imino-functionalized imidazolim salts have shown great potential in several catalytic systems, including rhodium-based systems for cyclopropanation reactions,[16] palladium-based systems for Suzuki–Miyaura cross-coupling reactions,[17] direct arylation of electron-deficient fluoroarenes[18] and norbornene polymerization.[19] However, their potential use in iron-based catalytic systems remains poorly explored.[20]

2. Results and discussion

*2.1 Synthesis and characterization of **1** and **2***

A novel imino-functionalized imidazolium chloride, 1-[1-(2,6-diisopropylphenylimino)ethyl]-3-benzylimidazolium chloride ([HL]Cl, **1**), was readily synthesized using a published procedure.[16] As shown in Scheme 1 (Eq. 1), **1** was obtained in 90% yield as a white solids with considerable air and moisture

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