



# FeCl<sub>3</sub>·6H<sub>2</sub>O-mediated reaction of [60]fullerene with amidoximes



Fang Fang<sup>a</sup>, Jianmin Zhang<sup>a,b,\*</sup>, Lei Cao<sup>a</sup>, Subo Shen<sup>a</sup>, Yuwei Guo<sup>a</sup>, Zhiqing He<sup>a</sup>, Han Hu<sup>a</sup>

<sup>a</sup> Department of Chemistry, College of Sciences, Shanghai University, Shanghai 200444, PR China

<sup>b</sup> Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China

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## ABSTRACT

A FeCl<sub>3</sub>·6H<sub>2</sub>O-mediated reaction of [60]fullerene with amidoximes for the preparation of fulleroimidazolines has been presented. This reaction shows a wide substrate scope, and the products obtained from alkyl-substituted amidoximes are first disclosed. In addition, a possible mechanism is proposed.

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## 1. Introduction

Amidoximes possess good coordination with metal, which can be used for synthesis of various complexes,<sup>1</sup> or as selective extracting reagents for toxic metal cations.<sup>2</sup> It is well known that amidoximes are favorable building blocks for the preparation of all kinds of organic heteroatom compounds, such as imidazoles,<sup>3</sup> benzimidazoles,<sup>4</sup> oxadiazoles,<sup>5</sup> and triazoles.<sup>6</sup> However, there are few reports about the synthesis of imidazolines through the reaction of amidoximes with electron-deficient alkenes or alkynes. Based on our experience in the synthesis of fullerene heterocyclic derivatives,<sup>7</sup> we reckon that fullerene who possess special electron-deficient olefins may react with amidoximes to construct [60] fullerene-fused imidazolines, which by the way would also be in favor of the search for new reaction of electron deficient alkenes or alkynes to imidazolines.

On account of the potential applications of C<sub>60</sub> derivatives in material science and biological chemistry,<sup>8</sup> the efficient methodologies for their synthesis have strongly attracted lots of researchers' attention. Recently, an interesting topic is the synthesis of the [60]fullerene-fused imidazolines, when Wang's group firstly reported the synthesis of the [60]fullerene-fused imidazolines via silver carbonate promoted reaction of C<sub>60</sub> with *N*-

arylbenzamidines,<sup>9</sup> coincidentally, Yang's group reported the reaction using CuI/Phen (1,10-phenanthroline) instead of Ag<sub>2</sub>CO<sub>3</sub>.<sup>10a</sup> Currently, they also described 4-dimethylaminopyridine (DMAP)-catalyzed reaction of *N*-tosylaziridinofullerenes with amidines for the preparation of fulleroimidazole derivatives.<sup>10b</sup> However, amidines bearing alkyl group cannot afford the corresponding products with these methods.<sup>10</sup> By now, the reported fulleroimidazolines are synthesized using amidines as starting materials. Therefore, it is still significant and challenging to achieve various fulleroimidazole derivatives.

On the other hand, transition-metal-catalyzed or -mediated approaches become increasingly popular in the field of organic synthesis, including iron which is the second highest metal element in the crust. It is prevalent with the feature of cheap, easily available, nontoxic and effective catalyst for numerous organic reactions in catalytic area.<sup>11</sup> Bearing these in mind, we set out to explore the possibilities and fortunately we found that FeCl<sub>3</sub>·6H<sub>2</sub>O could successfully promote the reaction of amidoximes with C<sub>60</sub>.

Herein, we report a FeCl<sub>3</sub>·6H<sub>2</sub>O-mediated cycloaddition reaction of C<sub>60</sub> with amidoximes to provide fulleroimidazole derivatives with a broad substrate scope.

## 2. Results and discussion

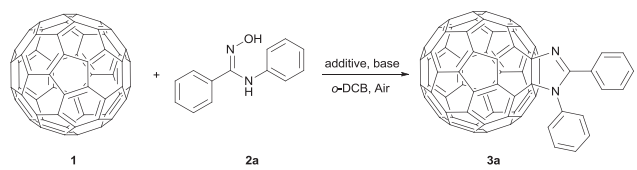
When we found that the reaction of C<sub>60</sub> with *N*-phenylbenzamidoxime **2a** in the presence of FeCl<sub>3</sub>·6H<sub>2</sub>O in a molar ratio of

\* Corresponding author. Tel./fax: +86 21 66133801; e-mail address: [jmzhang@shu.edu.cn](mailto:jmzhang@shu.edu.cn) (J. Zhang).

1:5:1 at 130 °C under air atmosphere for 10 h afforded the desired product **3a** in 13% yield (Table 1, entry 1), we used this as model reaction and moved ahead to pursue optimized reaction conditions by varying the use of additives, bases, their molar ratio and reaction temperatures (Table 1). And finally, a molar ratio of C<sub>60</sub>, **2a**, FeCl<sub>3</sub>·6H<sub>2</sub>O, and DMAP as 1:5:1:2 and a temperature of 130 °C in 1,2-dichlorobenzene (*o*-DCB) turned out as the best optimized reaction conditions (Table 1, entry 11). It is worth noting that there is no reaction in the absence of FeCl<sub>3</sub>·6H<sub>2</sub>O (Table 1, entry 14).

Armed with the above optimized reaction conditions, we step forward to investigate the scope of the FeCl<sub>3</sub>·6H<sub>2</sub>O-mediated cycloaddition reaction of C<sub>60</sub> with various amidoximes, and the results are presented in Table 2. Both electron-donating and electron-withdrawing groups were applied to test the applicability of this methodology, and it was found that the vast majority of the amidoximes could successfully complete the transformation and give the desired [60]fullereimidazolines with 15–40% isolated yields. When the substituent group on the *para* position of R<sup>2</sup> phenyl ring is methyl or fluorine, the substituent group on the R<sup>1</sup> phenyl ring has little or no significant influence on the reaction (Table 2, entries 3, 7, 13, entries 9, 14), except **2k** bearing a nitro group afforded **3k** with somewhat lower isolated yield (Table 2, entry 11). An electron-donating group on the R<sup>2</sup> aromatic ring gave a slightly higher yield than electron-withdrawing group when amidoximes carrying the same R<sup>1</sup> aromatic ring (Table 2, entries 7, 9–14). Additionally, with the increasing of the steric hindrance on substituted group R<sup>2</sup>, the yields tended to decline such as **3c** and **3b** dropping from 35% to 20%, **3g** and **3e** from 33% to 0 (Table 2, entries 2, 3, 5–7). Here unfortunately the *ortho*-substitute on R<sup>2</sup> phenyl ring inhibited the cycloaddition reaction. Luckily, the present method was also

**Table 1**  
Optimization of the reaction conditions<sup>a</sup>



Entry	Additive	Base	Molar ratio <sup>b</sup>	Yield (%) <sup>c</sup>
1	FeCl <sub>3</sub> ·6H <sub>2</sub> O	—	1:5:1:0	13 (75)
2	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	—	1:5:1:0	4 (60)
3	Ag <sub>2</sub> CO <sub>3</sub>	—	1:5:1:0	0
4	CuI	—	1:5:1:0	Trace
5	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	—	1:5:1:0	0
6	Mn(OAc) <sub>2</sub> ·4H <sub>2</sub> O	—	1:5:1:0	0
7	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	—	1:5:1:0	0
8	PhI(OAc) <sub>2</sub>	—	1:5:1	Trace
9	FeCl <sub>3</sub> ·6H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub>	1:5:1:2	7 (42)
10	FeCl <sub>3</sub> ·6H <sub>2</sub> O	CS <sub>2</sub> CO <sub>3</sub>	1:5:1:2	18 (70)
11	<b>FeCl<sub>3</sub>·6H<sub>2</sub>O</b>	<b>DMAP</b>	<b>1:5:1:2</b>	<b>40 (96)</b>
12	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DABCO	1:5:1:2	Trace
13	FeCl <sub>3</sub>	DMAP	1:5:1:2	41 (89)
14	—	DMAP	1:5:0:2	0
15 <sup>d</sup>	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DMAP	1:5:1:2	17 (65)
16 <sup>e</sup>	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DMAP	1:5:1:2	39 (83)
17 <sup>f</sup>	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DMAP	1:5:1:2	35 (82)
18	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DMAP	1:5:0.5:2	21 (76)
19	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DMAP	1:5:2:2	38 (84)
20	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DMAP	1:3:1:2	23 (94)
21	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DMAP	1:8:1:2	35 (81)
22	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DMAP	1:5:1:1	29 (91)
23	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DMAP	1:5:1:3	40 (94)

<sup>a</sup> Unless specified, all reactions were performed in 7 mL *o*-DCB at 130 °C for 10 h under air.

<sup>b</sup> Molar ratio refers to C<sub>60</sub>/2a/additive/base.

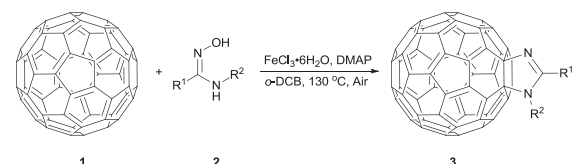
<sup>c</sup> Isolated yield; the values in parentheses were based on consumed C<sub>60</sub>.

<sup>d</sup> The reaction was operated at 110 °C.

<sup>e</sup> The reaction was operated at 150 °C.

<sup>f</sup> The reaction was carried out under a N<sub>2</sub> atmosphere.

**Table 2**  
Substrate scope of FeCl<sub>3</sub>·6H<sub>2</sub>O-mediated reaction of C<sub>60</sub> with amidoximes<sup>a</sup>



Entry	R <sup>1</sup>	R <sup>2</sup>	Product	Yield (%) <sup>b</sup>
1	Ph	Ph	<b>3a</b>	40 (96)
2	Ph	<i>m</i> -MePh	<b>3b</b>	20 (72)
3	Ph	<i>p</i> -MePh	<b>3c</b>	35 (82)
4	<i>p</i> -MePh	Ph	<b>3d</b>	33 (79)
5	<i>p</i> -MePh	<i>o</i> -MePh	<b>3e</b>	0
6	<i>p</i> -MePh	<i>m</i> -MePh	<b>3f</b>	27 (84)
7	<i>p</i> -MePh	<i>p</i> -MePh	<b>3g</b>	33 (80)
8	<i>p</i> -MePh	<i>m</i> -FPh	<b>3h</b>	19 (76)
9	<i>p</i> -MePh	<i>p</i> -FPh	<b>3i</b>	29 (74)
10	<i>p</i> -MePh	<i>p</i> -ClPh	<b>3j</b>	32 (76)
11	<i>p</i> -NO <sub>2</sub> Ph	<i>p</i> -MePh	<b>3k</b>	20 (58)
12	<i>p</i> -NO <sub>2</sub> Ph	<i>p</i> -OMePh	<b>3l</b>	30 (79)
13	<i>p</i> -FPh	<i>p</i> -MePh	<b>3m</b>	33 (70)
14	<i>p</i> -FPh	<i>p</i> -FPh	<b>3n</b>	29 (80)
15	2-phenylethyl	<i>p</i> -MePh	<b>3o</b>	15 (37)
16	<i>p</i> -MePh	Bn	<b>3p</b>	25 (60)

<sup>a</sup> Unless otherwise noted, all reactions were carried out with a molar ratio of C<sub>60</sub>/2/FeCl<sub>3</sub>·6H<sub>2</sub>O/DMAP=1:5:1:2 in 7 mL *o*-DCB at 130 °C for 8–12 h under air.

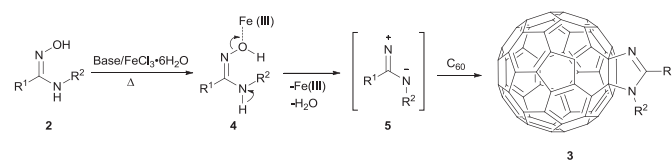
<sup>b</sup> Isolated yield; the values in parentheses were based on consumed C<sub>60</sub>.

successfully expanded to the preparation of [60]fullereimidazolines **3o** and **3p**, which derived from amidoximes containing an alkyl group (Table 2, entries 15 and 16).

All of the known compounds were confirmed through interpretation of their spectral data in accordance with those reported in the literatures.<sup>9,10</sup> The structures of new C<sub>60</sub>-fused imidazole derivatives **3b**, **3f**, **3h**, **3i**, **3l**–**3p** were fully characterized by their MALDI-FTICR-MS, <sup>1</sup>H NMR, <sup>19</sup>F NMR, <sup>13</sup>C NMR, FTIR, and UV–vis spectra.

In order to get a deeper understanding of the reaction mechanism, a free radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 5 equiv) was added to the reaction mixture (see Supplementary data). The cycloaddition reaction was not hindered, which indicates that the reaction may not relate to the formation of an iminyl or nitrogen radical.<sup>12</sup>

Based on the above results and previous literatures on iron-catalyzed or -mediated reactions,<sup>12,13</sup> a plausible mechanism for the reaction of C<sub>60</sub> with amidoximes is proposed and described in Scheme 1. First, in the presence of FeCl<sub>3</sub>·6H<sub>2</sub>O and base, the amidoxime **2** gives the intermediate **4** under heating condition, followed by the elimination of H<sub>2</sub>O and Fe(III) to afford dipole **5**, which then partakes in a 1,3-dipolar cycloaddition reaction with C<sub>60</sub> to generate fullereimidazoline **3**.



**Scheme 1.** Plausible mechanism for the formation of **3**.

### 3. Conclusion

In conclusion, a novel and efficient method has been successfully developed to establish C<sub>60</sub>-fused imidazolines via a FeCl<sub>3</sub>·6H<sub>2</sub>O-mediated 1,3-dipolar cycloaddition reaction of [60]

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