Iron(II)-Catalyzed Intermolecular Amino-Oxygenation of Olefins through the N−O Bond Cleavage of Functionalized Hydroxylamines

Deng-Fu Lu, Cheng-Liang Zhu, Zhen-Xin Jia, and Hao Xu*

Department of Chemistry, Georgia State University, 100 Piedmont Avenue SE, Atlanta, Georgia 30303, United States

Ⓢ *Supporting Information*

ABSTRACT: An iron-catalyzed diastereoselective *inter-molecular* olefin amino-oxygenation reaction is reported, which proceeds via an iron-nitrenoid generated by the N−O bond cleavage of a functionalized hydroxylamine. In this reaction, a bench-stable hydroxylamine derivative is used as the amination reagent and oxidant. This method tolerates a range of synthetically valuable substrates that have been all incompatible with existing amino-oxygenation methods. It can also provide amino alcohol derivatives with regio- and stereochemical arrays complementary to known amino-oxygenation methods.

Scheme 1. Iron-Catalyzed Olefin Amino-Oxygenation with Functionalized Hydroxylamines

Selective olefin difunctionalization with an amino- and an oxygen-based group is an important transformation for organic synthesis because vicinal amino alcohol derivatives are widely present in synthetically valuable molecules. The osmium-based Sharpless aminohydroxylation continues to be a prevalent stereospecific method for olefin amino-oxygenation.[1] This pioneering method has also inspired extensive efforts for the development of alternative approaches for a broader substrate scope and better regioselectivity.[2,3] Among these approaches, nonprecious metal-catalyzed processes emerge with increasing interest: Chemler developed Cu-catalyzed methods for olefin amino-oxygenation and other difunctionalizations;[2a−d] Yoon developed Cu- and Fe-catalyzed sulfonyl oxaziridine based methods.[2e−h] Despite these and other excellent discoveries, new nonprecious metal-catalyzed olefin amino-oxygenation methods which achieve a broader substrate scope and regio- and stereoselectivity complementary to known methods are greatly desirable. In particular, the *intermolecular* olefin amino-oxygenation mediated by an iron nitrenoid has not been reported.

Unlike the N-atom transfer mediated by a rhodium nitrenoid,[3,4] the iron nitrenoid mediated process is more prone to proceed through radical pathways.[5] Therefore, new strategies are required to control an iron nitrenoid's reactivity in an olefin amino-oxygenation reaction. We have previously discovered iron-catalyzed *intramolecular* olefin amino-oxygenation and amino-fluorination reactions (Scheme 1A).[6] Our studies suggested that an iron nitrenoid is a possible intermediate in these stereoconvergent transformations and that the stereoselectivity can be modulated by N-based bidentate ligands.[7]
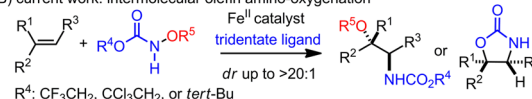
Our initial attempts to develop an *intermolecular* olefin amino-oxygenation with the catalyst previously identified to be effective for *intramolecular* amino-oxygenation failed due to the lack of reactivity. To modulate the reactivity of the iron nitrenoid to achieve a fine balance between reactivity, stability, and selectivity,

we explored a variety of new amination reagents, iron catalysts, and ligands. Herein, we disclose an iron-catalyzed intermolecular olefin amino-oxygenation that proceeds through the N−O bond cleavage of a functionalized hydroxylamine. In this transformation, a bench-stable hydroxylamine derivative is applied as the amination reagent and oxidant (Scheme 1B).

This method has a few unique features that complement the existing iron-catalyzed olefin amino-oxygenation method with sulfonyl oxaziridines.[2g,h] First, this method allows significant asymmetric induction with internal olefinic substrates, while the oxaziridine-based asymmetric approach is only effective for terminal olefins. Second, this method tolerates a broad range of synthetically valuable substrates, including allyl silanes, cyclopentadienes, enol ethers, glycals, indene, and silyl dienols, which are all incompatible with the iron-catalyzed olefin amino-oxygenation method with sulfonyl oxaziridines. Furthermore, this method can effectively afford amino alcohol derivatives with regio- and stereochemical arrays complementary to existing amino-oxygenation methods, especially osmium-based approaches. Therefore, we envision that this discovery will be a valuable tool for selective olefin amino-oxygenation.

Styrene **1** was selected as a model substrate for catalyst discovery (Table 1). Our initial attempts with Fe(OTf)₂−*N,N′*-bidentate ligands failed due to the lack of reactivity. Inspection of a range of ligands revealed that the N-based tridentate ligands are necessary for the proposed reactivity and that an achiral bisoxazoline PyBOX ligand **L1** is uniquely effective:[8] the Fe(OTf)₂−**L1** complex catalyzes the styrene amino-oxygenation with a range of functionalized hydroxyl amines (**2a−2d**, entries 1−4), affording both an alkoxyl oxazoline **3** and a protected amino alcohol **4** with good to excellent combined yields and regioselectivity complementary to the osmium-based methods.[1a]

Table 1. Catalyst Discovery for the Iron-Catalyzed Intermolecular Olefin Amino-Oxygenation

entry[b]	Fe(X)$_2$	ligand	2	conversion[c]	yield (3)[d]	yield (4)[d]	yield (5)[d]
1	Fe(OTf)$_2$	L1	2a	76%	51%	8%	57%
2	Fe(OTf)$_2$	L1	2b	69%	<5%[e]	6%	48%[e]
3	Fe(OTf)$_2$	L1	2c	>95%	71%	12%	82%
4	Fe(OTf)$_2$	L1	2d	>95%	63%	10%	72%
5	Fe(OTf)$_2$	L2	2c	67%	44%	14%	57%
6	Fe(OTf)$_2$	L3	2c	<5%	<5%	<5%	<5%
7	Fe(NTf$_2$)$_2$	L1	2c	>95%	62%	15%	76%
8	FeCl$_2$	L1	2c	<5%	<5%	<5%	<5%

[a]Molecular sieves were used to remove deleterious moisture. [b]Reactions were carried out under N$_2$ in 1 h and then quenched with saturated NaHCO$_3$ solution, unless stated otherwise. The crude mixture was first subjected to acidic conditions with TsOH (1.0 equiv) and then to basic conditions with LiOH (2.0 equiv) to afford **5**. [c]Conversion was measured by GC. [d]Isolated yield. [e]An oxazolidinone was isolated directly without the additional step (41% yield); see Supporting Information.

We also discovered that both **3** and **4** can be easily converted to oxazolidinone **5** with high yield through a same hydrolytic procedure. Furthermore, we noted that more electrophilic reagents lead to higher reactivity (entries 3−4 vs 1−2). Additionally, ligand screening revealed that an Fe(OTf)$_2$−**L2** complex[8] is less reactive and an Fe(OTf)$_2$−**L3** complex is inactive (entries 5−6). Since we have observed a strong counterion effect in the intramolecular olefin amino-oxygenation,[6] we also examined various iron salts and concluded that Fe(NTf$_2$)$_2$ is equally reactive compared to Fe(OTf)$_2$ and FeCl$_2$ is inactive (entries 7−8).

To explore the scope and limitations of this method, a variety of olefins and dienes were evaluated under the optimized conditions (Table 2). We observed that α-methylstyrene is an excellent substrate (entry 2, 75% yield). Subsequently, we examined olefins that have been problematic for the existing amino-oxygenation methods (entries 3−8). First, an allyl silane, a substrate that is incompatible with other iron-based methods, can be efficiently amino-oxygenated with **2d** (entry 3, 78% yield). Further exploration revealed that cyclopentadiene with a labile C−H bond can smoothly participate in the iron-catalyzed reaction with **2b**, directly affording an oxazolidinone with a decent yield and excellent dr (entry 4, dr > 20:1). We further observed that cyclohexadiene can be converted to an oxazolidinone with a complementary regioselectivity compared with the osmium-based method (entry 5).[1a] Although enol ethers have been challenging substrates for existing amino-oxygenation methods, they are excellent substrates for the iron-catalyzed syn-amino-oxygenation which delivers protected amino alcohols with a good yield and dr (entries 6−7, yield up to 77% and dr up to >20:1).[9] Importantly, a protected glycal can also participate in the amino-oxygenation with **2b**, affording a 2-amino-α-sugar with a decent yield and excellent dr (entry 8, 63% yield, dr > 20:1 at both C1 and C2 positions).[9,10] Additionally, indene can be efficiently amino-oxygenated and this reaction

Table 2. Substrate Scope for the Iron-Catalyzed Olefin Amino-Oxygenation

| entry[a]	olefin	X	ligand	2	product	yield[b]
1[c,d]	Ph	OTf	L1	2c		82%
2[d,e]		OTf	L1	2c		75%
3	TIPS	OTf	L1	2d		78%
4[f,g]		OTf	L2	2b	dr > 20:1	61%
5[f,g]		OTf	L2	2b	dr > 20:1	62%
6[e]		OTf	L1	2d	dr > 20:1	72%
7[h]		OTf	L1	2d	dr = 10:1	77%
8[h,i]		NTf$_2$	L2	2b	dr > 20:1	63%
9[c,i]		NTf$_2$	L1	2c	dr > 20:1	71%
10[d,j]	Ph	OTf	L1	2c		62%
11[c,k]	Ph	Cl+OTf	L1	2c		84%
12[f,g]	C$_6$H$_{13}$	OTf	L2	2b		61%
13[f,g]		OTf	L2	2b		76%
14[f,g]	OTBS	OTf	L1	2b		63%
15[f,g]	CO$_2$Me	OTf	L1	2b		54%
16[f,g]	C$_6$H$_{13}$	ClO$_4$	L1	2b		51%
17[d,l]	C$_5$H$_{11}$	OTf	L1	2c		48%

[a]Reactions were carried out under N$_2$ in 2 h, unless stated otherwise. [b]Isolated yield. [c]Reaction time: 1 h. [d]The crude mixture was treated with TsOH and then LiOH. [e]Reaction temp: −40 °C. [f]Catalyst loading: 20 mol %; reaction temp: 0 °C. [g]Reaction time: 12 h. [h]Reaction temp: −30 °C. [i]Fe(NTf$_2$)$_2$ (15 mol %), **L1** (15 mol %). [j]Catalyst loading: 15 mol %. [k]Fe(OTf)$_2$ (2.5 mol %) and FeCl$_2$ (2.5 mol %) were used. [l]Catalyst loading: 30 mol %; reaction temp: 0 °C; reaction time: 24 h.

affords a protected cis-2-amino indanol, a valuable building block that is difficult to obtain directly with existing amino-oxygenation methods (entry 9, 71% yield, dr > 20:1).[11]

We also explored conjugated ene-ynes and dienes (entries 10− 15). An ene-yne is an excellent substrate for the amino-oxygenation (entry 10, 62% overall yield). Conjugated dienes

Scheme 2. Iron-Catalyzed Asymmetric Olefin Amino-Oxygenation and Control Experiments To Probe Reaction Mechanisms

Scheme 3. Mechanistic Working Hypothesis for the Iron-Catalyzed Olefin Amino-Oxygenation
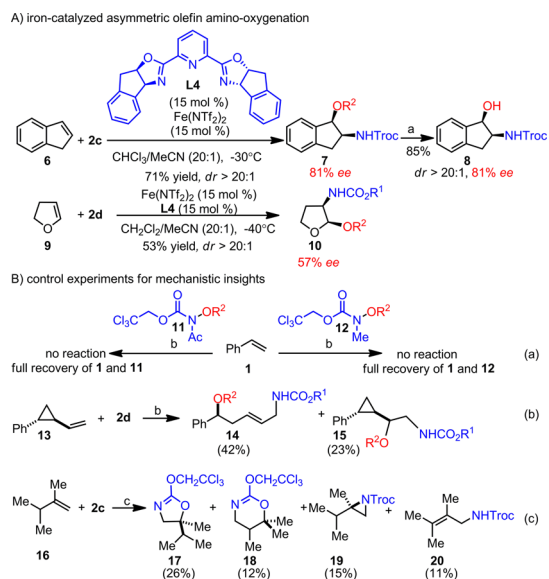
[a]LAH, THF, −20 °C, 85%. [b] Fe(OTf)$_2$ (10 mol %), **L1** (10 mol %), CH$_2$Cl$_2$/MeCN (15:1), −15 °C, 1 h. [c] Fe(ClO$_4$)$_2$ (20 mol %), **L1** (20 mol %), CH$_2$Cl$_2$/MeCN (15:1), −15 °C, 2 h. [d] R^1: CF$_3$CH$_2$; R^2: 2,4-Cl$_2$-benzoyl.

with either aliphatic or aromatic substituents can also be efficiently transformed into protected 1,2-amino alcohols with excellent regioselectivity (entries 11−13).[12] To our delight, this method is also compatible with a silyl dienol with a labile C−H bond (entry 14, 63% yield). Also, a dienoate proves to be an acceptable substrate for this transformation (entry 15, 54% yield).

Additionally, we applied this method to isolated olefins. The Fe(ClO$_4$)$_2$−**L1** complex can catalyze the amino-oxygenation of a 1,1-disubstituted olefin with **2b**, affording an oxazolidinone (entry 16, 51% yield).[13] We further observed that the Fe(OTf)$_2$−**L1** complex catalyzes the reaction of a monosubstituted olefin with **2c** to afford the oxazolidinone with a fair yield (entry 17, 48% yield).

The catalytic asymmetric amino-oxygenation of indene **6** has been a challenge in synthetic chemistry, and osmium-based protocols deliver a mixture of racemic 1- and 2-amino indanols.[11] In order to fill this gap, we have explored the asymmetric induction for the indene amino-oxygenation and discovered that an iron−chiral ligand **L4**[14] complex is uniquely effective to deliver a 2-amino indanol derivative **7** with a significant *ee* (Scheme 2A, 81% *ee*, *dr* > 20:1). Facile transformation converts **7** to **8** without erosion of its *ee* and *dr*. The asymmetric enol ether amino-oxygenation has also been unprecedented, and we observed that **L4** is effective for asymmetric induction with dihydrofuran **9** as well (57% *ee*, *dr* > 20:1).

In order to gather evidence for a mechanistic working hypothesis, we have carried out several control experiments (Scheme 2B). First, two analogues (**11** and **12**) of reagent **2c** were prepared, such that the N−H group was masked by either an acetyl or a methyl group. Both were evaluated for the model reaction and neither was found to be reactive (eq a). These experiments suggest that the N−H group in **2c** is critical for its activation. Next, we evaluated a cyclopropyl-substituted olefin **13**
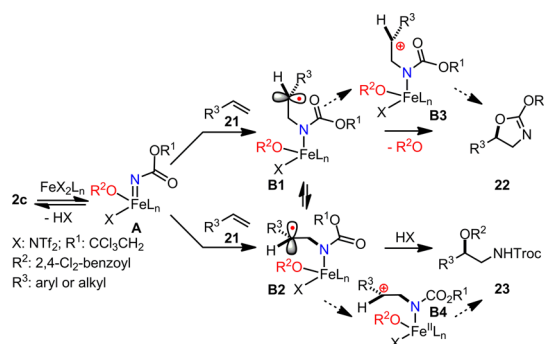
as a radical clock probe under the reaction conditions and observed the presence of both the ring-opening product **14** and the 1,2-amino-oxygenation product **15** (eq b). This result suggests that the reaction proceeds through a stepwise process that includes a radical amination step.

To probe the mechanism beyond the radical amination step, we further evaluated an isopropyl-substituted terminal olefin **16** (eq c). If a carbocation is generated after the radical amination, 1,2-hydride shift products may be observed. The amino-oxygenation with **16** afforded four products: in addition to the standard 1,2-amino-oxygenation product **17**, an 1,3-amino-oxygenation product **18**, aziridine **19**, and allylic amine **20** were isolated (eq c). Importantly, *19 cannot be converted to any of the three other products under the reaction conditions*. These results suggest that a carbocation may be involved in the olefin amino-oxygenation and that the corresponding aziridine is unlikely an intermediate along this pathway.

Furthermore, we studied *cis/trans* β-methyl styrenes as mechanistic probes and the experimental results corroborate that the amino-oxygenation occurs in a stepwise fashion and they also suggest that the C−N bond formation is likely the rate-determining step.[15] Finally, we evaluated the electronic effect on styrene amino-oxygenation and concluded that amino alcohol formation is favored with substrates that can stabilize electrophilic radical species.[15]

Based upon the collective evidence, a mechanistic working hypothesis of olefin amino-oxygenation that best corroborates the experimental data is presented in Scheme 3. First, the iron−ligand complex may reductively cleave the N−O bond in **2c**, possibly converting it to an iron-nitrenoid **A**. **A** may then initiate radical amination with olefin **21** to afford radical species **B1** together with its conformer **B2** in equilibrium. Presumably, **B1** can be oxidized by the iron center to a carbocation **B3**,[16,17] which will be rapidly captured by the neighboring carbamate group, thereby affording **22**. Alternatively, oxidative carboxylate ligand transfer[16] may directly occur with **B2** to afford the protected amino alcohol **31**. We still cannot completely rule out the possibility that electron transfer from **B2** to the iron center occurs first and that the oxidation product **B4** will then be captured by a carboxylate to deliver **23**. When the substituent (R^3) has a less significant radical-stabilizing effect, **B1** and **B2** are relatively short-lived high energy species; therefore, the oxidative neighboring group participation through **B1** may be favored to afford **22**. However, when the substituent has a strong radical-stabilizing effect and both species are relatively long-lived, the ligand transfer from the iron center through **B2** may become dominant to deliver **23**.

In conclusion, we have discovered a new iron-catalyzed stereoselective olefin amino-oxygenation method. This method tolerates a broad range of synthetically valuable olefins including those that are incompatible with existing amino-oxygenation methods. Our preliminary mechanistic studies revealed that an iron nitrenoid is a possible intermediate and its enantioselectivity can be controlled by chiral ligands. This discovery demonstrates the feasibility of developing a unique approach for iron-catalyzed selective olefin difunctionalization. Our ongoing efforts focus on understanding the mechanism of this new reaction and its applications in organic synthesis.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental procedure, characterization data for all new compounds, selected NMR spectra, and HPLC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
hxu@gsu.edu
Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(8) For details of ligand synthesis, see Supporting Information (SI).

(9) For stereochemistry determination, see SI.

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(12) Fe(OTf)$_2$/FeCl$_2$ mixed salts were applied as the catalyst in entry 11. Fe(OTf)$_2$ led to rapid decomposition of the diene; FeCl$_2$ was inactive. See SI for details.

(13) Other Fe salts led to rapid allylic amination products. See SI for details.

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