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Iron-Catalyzed Direct Diazidation for a Broad Range of Olefins

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Abstract

Reported herein is a new iron-catalyzed diastereo-selective olefin diazidation reaction which occurs at room temperature (1–5 mol % of catalysts and d.r. values of up to > 20:1). This method tolerates a broad range of both unfunctionalized and highly functionalized olefins, including those that are incompatible with existing methods. It also provides a convenient approach to vicinal primary diamines as well as other synthetically valuable nitrogen-containing building blocks which are difficult to obtain with alternative methods. Preliminary mechanistic studies suggest that the reaction may proceed through a new mechanistic pathway in which both Lewis acid activation and iron-enabled redox-catalysis are crucial for selective azido-group transfer.

Keywords

alkenes; amination; homogeneous catalysis; iron; synthetic methods

Selective nitrogen-atom-transfer for olefin functionalization is a powerful transformation which generates high-value chemicals from hydrocarbons. Among a range of olefin functionalization processes by azido-group transfer, catalytic olefin diazidation has emerged with unique value for a few reasons.[1] First, this reaction provides a convenient approach to producing synthetically important vicinal primary diamines which are difficult to obtain with the existing olefin diamination methods.[2] Next, it can also rapidly convert olefins into a variety of probes for the robust azide–alkyne click chemistry, which becomes increasingly important for biological and material sciences.[1h] Therefore, searching for a general, yet selective olefin diazidation method has been an important research topic and a range of methods for certain limited types of olefins have been developed.[3]

Among these methods, Minisci developed an Fe^{II}–Fe^{III}-mediated stoichiometric approach, with peroxydisulfate and NaN_3, specifically for styrenyl olefins. However, this method is incompatible with nonstyrenyl olefins.[3a] Fristad and coworkers reported a Mn^{III}-mediated stoichiometric method only for nonfunctionalized aliphatic olefins with a large excess of NaN_3 in acetic acid at 110°C. Snider later reported a key improvement using TFA at −20°C.[3b,c] This modified procedure is effective for glycal diazidation, however, it is

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unsuitable for acyclic aliphatic olefins. The groups of Armimoto and Magnus independently reported $(PhIO)_n$/$TMSN_3$-mediated methods specifically for electron-rich allyl silanes and cyclic silyl enol ethers, respectively, at −78°C.[3e,f]

These methods have been valuable for synthetic chemistry, however, significant gaps still exist for this important transformation. First, a general and selective catalytic method that is compatible with a broad range of both unfunctionalized and highly functionalized olefins has yet to be developed. Second, a diastereoselective method for internal olefins has not yet been reported. Furthermore, a new diazidation reaction which proceeds through a new selective pathway under mild reaction conditions (thus avoiding both heating and cryogenic cooling) has yet to be discovered.

Herein, we describe an iron-catalyzed diastereoselective olefin diazidation at room temperature with low catalyst loading (Scheme 1).[4] This new method tolerates a broad range of olefins, including those that are incompatible with existing methods. Notably, the *anti*-selectivity can be modulated by iron catalysts (d.r. up to > 20:1). This method also provides a convenient approach to a variety of nitrogen-containing molecules, including vicinal primary diamines and 2-azido glycosyl azides, which are valuable for N-linked glycoprotein synthesis. Furthermore, preliminary mechanistic studies suggest that this reaction may proceed through a new selective pathway, which has a promise to become a general strategy for selective olefin difunctionalization.

Indene (**1**) was selected as a model substrate for catalyst discovery since it is incompatible with existing diastereoselective olefin diazidation methods. Azidoiodinane (**2a**) and $Fe(OTf)_2$ were initially selected as the azido-transfer reagent and the catalyst, respectively. We observed that $Fe(OTf)_2$ was ineffective for the azido-group transfer in the absence of $TMSN_3$ and both **1** and **2a** were fully recovered (Table 1, entry 1). However, in the presence of $TMSN_3$, a catalytic amount of $Fe(OTf)_2$ was sufficient to turn over the catalytic cycle, thus affording the indene diazide **3** in high yields (entries 2, 4, and 5). Notably, in the absence of iron catalysts, no desired product was observed and **1** was fully recovered (entry 3). These observations suggest that $TMSN_3$ is necessary to activate **2a** for the azido-group transfer and that iron catalysts are also necessary for the olefin diazidation. Although the $Fe(OTf)_2$/**L1** complex catalyzed a moderately diastereoselective reaction (entry 2), the d.r. value was significantly improved when the ligand **L2** was used (entry 4). Notably, a bulkier ligand (**L3**) induced a higher d.r. value (entry 5). Since **2a** is prepared from bench-stable benziodoxole (**2b**) with an excess amount of $TMSN_3$, and **2b** is barely soluble under the olefin diazidation conditions,[5] we explored using **2b** as the terminal oxidant under heterogeneous conditions (entry 6). To our pleasure, **3** was obtained with essentially the same yield and d.r. value under these new reaction conditions. This observation suggests that **2a** may be rapidly derived from **2b** in situ. Note that precautions with regard to handling $TMSN_3$ should be taken during the reaction workup.[6]

We thereby evaluated the counterion effect and discovered that $Fe(NTf_2)_2$ was equally effective (Table 1, entry 7). Surprisingly, the $Fe(OAc)_2$/**L3** complex catalyzed highly diastereoselective *anti*-diazidation of **1** with an excellent yield (entry 8).[7] Since **3** is a convenient precursor for the indene diamine, it is further converted into the *anti*-indene

diaminium salt **4** in a high yield by a mild reduction/protonation sequence. Furthermore, standard resolution with tartaric acid readily provided the indene diamine essentially in its enantiopure form (97% *ee*).[8]

To examine the scope of this new iron-catalyzed olefin diazidation, we explored the reactivity with a broad range of olefins (Table 2). Since the C/N ratios for these diazides generally vary from 1 to 3, careful isolation were executed strictly under small-scale (< 100 mg) conditions.[6] Additionally, direct diazide reduction without solvent concentration conveniently affords a variety of vicinal primary diamines. First, olefins with labile C–H bonds, including allyl benzene and an allyl silane, were evaluated because they have been challenging substrates for the existing diazidation methods.[10] For synthetic convenience, **L2**, with a lower molecular weight, was selected as the ligand for terminal olefins, and we discovered that the $Fe(OTf)_2$/**L2** complex catalyzed the efficient diazidation: the amount of competing direct C–H azidation product is less than 5% (entries 1 and 2).[10] Mild derivatization converted the diazides into functionalized diaminium salts with excellent yields. Styrenyl and aliphatic terminal olefins are also excellent substrates: the corresponding diazides were isolated with good yields (entries 3–6). Next, we evaluated a range of cyclic olefins and discovered that the $Fe(OAc)_2$/**L3** complex is effective for highly diastereoselective diazidation of indene, dihydronaphthalene, dihydroquinoline, and indole (entries 7–10).[11] Standard derivatization afforded a range of valuable *anti*-vicinal diamines, which are challenging to synthesize with existing diazidation or diamination methods.[11] Further evaluation of acyclic internal olefins revealed that *trans*-2-octene is an excellent substrate for the diazidation yet with a low d.r. value (entry 11).[12] Fortunately, the diastereomers were separable and the straightforward derivatization converted them into vicinal primary diamines, which are difficult to obtain with the existing olefin diamination methods. We also observed that an electron-deficient cinnamate ester is an excellent substrate, and an electron-rich enamide is also compatible with this method (entries 12 and 13). We further evaluated geranyl acetate and observed that the diazidation occurred regioselectively at the distal position with a more electron-rich olefin (entry 14).

Furthermore, we explored this new method with densely functionalized olefins (Scheme 2). The acetyl quinine **5** smoothly participates in the diazidation to afford the diazide **6**, which provides a new structural motif for organocatalysis. Additionally, the glycal **7** is also a reasonable substrate, which affords the 2-azido glycosyl azides **8**.[13] Interestingly, both diastereomers were elaborated into the 2-azido N-linked glycopeptide **9** as a single diastereomer by a reduction/ligation procedure.[13] Notably, **9** is also a valuable building block for N-linked glycoprotein synthesis.[13]

The observed catalyst-modulated diastereoselectivity is mechanistically important because it suggests that iron catalysts are involved in the d.r.-determining step. Therefore, we selected *cis*-stilbene [(*Z*)-**10**] as a probe for several control experiments (Scheme 3). First, when $TMSN_3$ is absent, no reaction was observed and both (*Z*)-**10** and **2a** were fully recovered. Next, under iron-free conditions, but in the presence of $TMSN_3$, (*Z*)-**10** was isomerized into *trans*-stilbene [(*E*)-**10**] and no diazidation product was observed. We further observed that (*Z*)-**10**, as well as (*E*)-**10**, were converted into **11** with essentially the same d.r. value.[14] Furthermore, **12** was obtained in the presence of TEMPO. These experiments provide

several mechanistic insights. First, $TMSN_3$ is crucial to activate **2a**. Next, an azido radical species is possibly involved in the olefin diazidation and a reversible radical addition may convert (*Z*)-**10** into a carbo radical species under both standard and iron-free conditions. Additionally, this radical can be captured by TEMPO. Moreover, stereo-convergent diazidation of *cis*/*trans* stilbenes suggest that the second azido-group transfer may be rate-limiting.

To probe the role of $TMSN_3$, it was further replaced by $n Bu_4NN_3$ (Scheme 3). Surprisingly, no diazidation was observed and (*Z*)-**10** was fully recovered. However, in the presence of both $TMSN_3$ and $n Bu_4NN_3$, (*Z*)-**10** was isomerized to (*E*)-**10** and no diazidation was observed. These observations suggest that the Lewis-acidic TMS group is crucial for the activation of **2a** and that an excess amount of azide anion may deactivate iron catalysts.

Based on the collective evidence from the aforementioned control experiments and key observations in catalyst discovery (Table 1), we propose a mechanism which is supported by the experimental data (Scheme 4). First, $TMSN_3$ reacts with **2b** and possibly converts **2b** into **2a** in situ. Next, **2a** may be further activated by $TMSN_3$ to reversibly generate the intermediate **A**. In the absence of iron catalysts, **A** may react with (*Z*)-**10**, presumably through reversible azido radical addition, thus affording the carbo radical species **B** and azidoiodobenzene **C**. Nevertheless, **B** may not be further oxidized in the absence of iron and the elimination from **B** will afford more stable (*E*)-**10** and regenerate **A**. However, in the presence of an iron catalyst, it may reductively cleave the $I–N_3$ bond of **A**, and presumably generates a high-valent iron species and an azido radical. The azido radical may thereby react with (*Z*)-**10** to afford another carbo radical species (**E**), which is associated with the iron catalyst. Since the d.r. value of olefin diazidation can be modulated both by the ligand and counterion of the catalyst, it is likely that the high-valent iron species may further oxidize **E** through inner-sphere azido ligand transfer to afford the diazide **11**.[15]

In conclusion, we have discovered a new iron-catalyzed diastereoselective olefin diazidation method which tolerates a broad range of olefins, including those which are incompatible with the existing methods. It can also afford a variety of synthetically valuable building blocks which are difficult to prepare with alternative methods. Our mechanistic studies suggest that the reaction may proceed through a new selective pathway in which Lewis-acid activation is indispensable for the first azido-group transfer and that iron catalysts are crucially involved with the second azido-group transfer. Our current efforts focus on mechanistic understanding of this new reaction and achieving effective asymmetric induction through new catalyst discovery.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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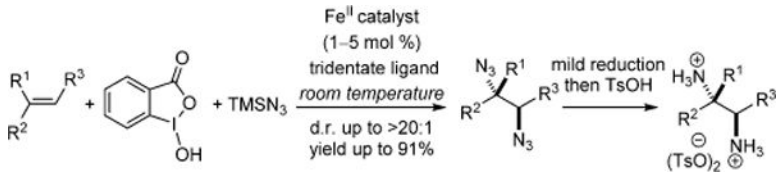
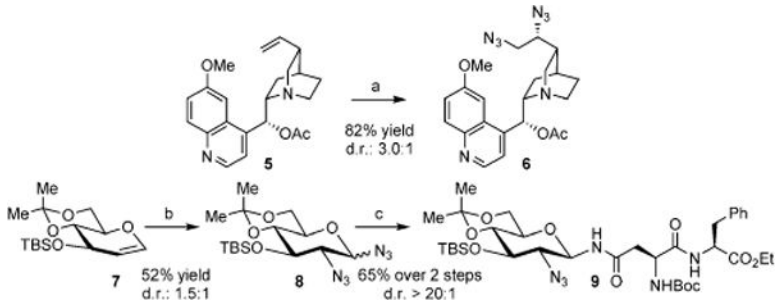
5. For preparation of 2a from 2b, see:Zhdankin VV, Krasutsky AP, Kuehl CJ, Simonsen AJ, Woodward JK, Mismash B, Bolz JT. J Am Chem Soc. 1996; 118:5192.Both 2a and 2b have limited solubility in the reaction mixture (ca. 10 μM in CH_2Cl_2/MeCN (20:1). They can be removed through filtration during the workup.
6. For safely handling $TMSN_3$ and organic azides, see the Supporting Information.
7. Exploration with a variety of ligands suggests that the observed counter ion effect is consistent across a range of ligands. See the Supporting Information.
8. For the detailed procedure of indene diamine optical resolution, see the Supporting Information.

9. 3.6 equiv of $TMSN_3$ is sufficient to obtain high yields with anhydrous **2b** which is stored in a glove-box. 4.0 equiv of $TMSN_3$ is used to achieve the same yield with **2b** stored outside of a glove-box.
10. Allyl benzene is incompatible with the existing olefin diazidation methods. A small amount (14%) of triazidation product was isolated, presumably through the azido radical addition followed by elimination and the further addition reaction. See the Supporting Information.
11. $Fe(NTf_2)_2$/**L3** and $Fe(OTf)_2$/**L3** complexes catalyzed rapid indole and dihydroquinoline diazidation with excellent d.r. values. Indene, dihydronaphthalene, dihydroquinoline, and indoles are incompatible with the existing olefin diamination reactions. Dihydroquinoline is incompatible with existing diazidation methods. The d.r. values for existing indene and indole diazidation (via an iodo azide) are 1:1 and 3.5:1, respectively.
12. The $Fe(OAc)_2$/**L3** complex catalyzed a slower diazidation with a modest improvement of the d.r. value.
13. The aza-ylides generated from 8 rapidly epimerize under the reduction conditions. See the Supporting Information. For selected references of N-linked glycoprotein synthesis, see:a) Wang P, Dong S, Shieh JH, Peguero E, Hendrickson R, Moore MAS, Danishefsky SJ. Science. 2013; 342:1357. [PubMed: 24337294] b) Doores KJ, Mimura Y, Dwek RA, Rudd PM, Elliott T, Davis BG. Chem Commun. 2006:1401.
14. For stereoconvergent stilbene diazidation, see the Supporting Information.
15. For the oxidation of a radical species by a high-valent metal through ligand transfer, see:a) Kharasch MS, Sosnovsky G. J Am Chem Soc. 1958; 80:756.b) Kochi JK. Science. 1967; 155:415. [PubMed: 17737550]



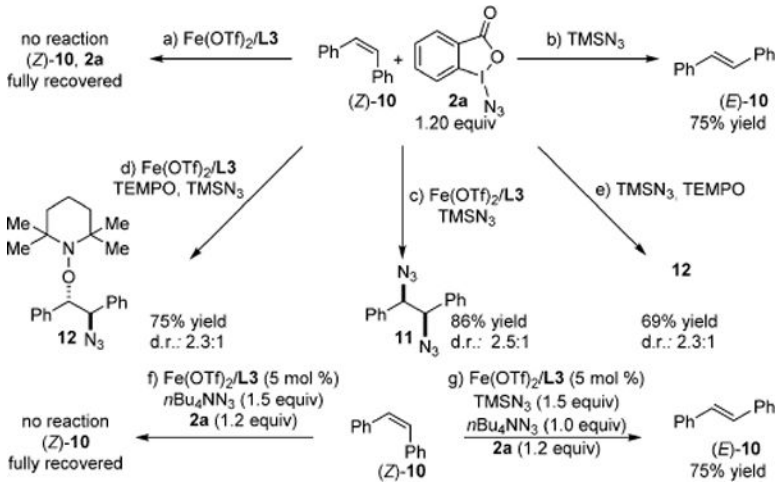
Scheme 1.

Iron-catalyzed diastereoselective olefin diazidation. TMS = trimethylsilyl, Ts = 4-toluenesulfonyl.



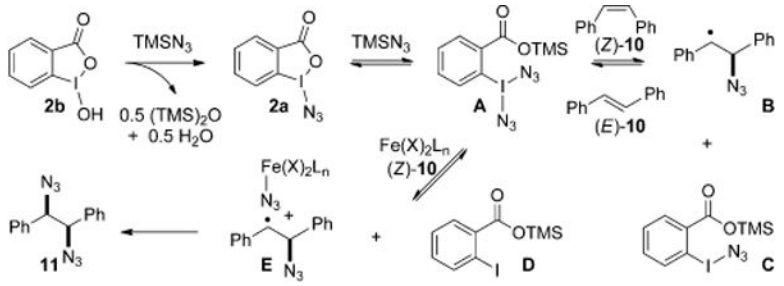
Scheme 2.

Iron-catalyzed diazidation of acetyl quinine and glycals for N-linked glycopeptide synthesis. a) $Fe(OTf)_2$/**L2** (10 mol%), **2b**, $TMSN_3$, 22°C; 82% yield, d.r.: 3:1. b) $Fe(OTf)_2$/**L2** (5 mol %), **2b**, $TMSN_3$, 0°C; 52% yield, d.r.: 1.5:1. c) PMe_3 in THF, −60−22°C; then H_2O in THF, 40°C; 76% yield, d.r. > 20:1; then HATU, DIPEA, the corresponding peptide acid, DMF, 22°C, 86% yield for the ligation step. DIPEA = diisopropylethylamine, DMF= *N*,*N*-dimethylformamide, HATU = 1-[bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-*b*]pyridinium 3-oxid hexafluorophosphate.



Scheme 3.

Control experiments for mechanistic insights of the ironcatalyzed olefin diazidation. a) $Fe(OTf)_2$/**L3** (5 mol%). b) $TMSN_3$. c) $Fe(OTf)_2$/**L3** (5 mol%), $TMSN_3$. d) $Fe(OTf)_2$/**L3** (5 mol%), $TMSN_3$, TEMPO. e) $TMSN_3$, TEMPO. f) $Fe(OTf)_2$/**L3** (5 mol%), $n$$Bu_4NN_3$, **2a**, −15−22°C. g) $Fe(OTf)_2$/**L3** (5 mol%), $n$$Bu_4NN_3$, $TMSN_3$, 2a, −15−22°C. Other reactions were carried out at 22°C.



Scheme 4.

Proposed mechanism for the iron-catalyzed olefin diazidation using benziodoxole and $TMSN_3$.

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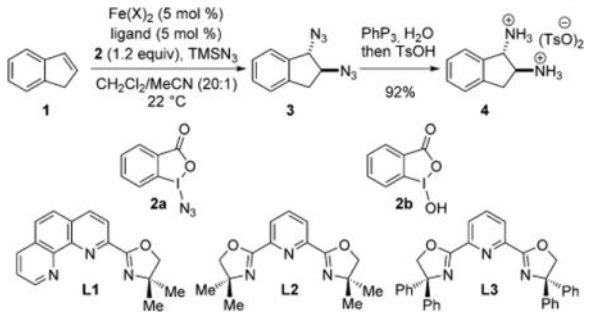
Table 1

Catalyst discovery for the diastereoselective indene diazidation.[a]



Entry	$Fe(X)_2$	Ligand	2	$TMSN_3$ [equiv]	*t* [h]	Yield[b] [%]	d.r.[b]
1[c]	$Fe(OTf)_2$	**L1**	**2a**	0	24.0	< 5	–
2	$Fe(OTf)_2$	**L1**	**2a**	1.5	1.0	81	3.7:1
3	none	**none**	**2a**	1.5	1.0	< 5	–
4	$Fe(OTf)_2$	**L2**	**2a**	1.5	1.0	82	7.1:1
5	$Fe(OTf)_2$	**L3**	**2a**	1.5	1.0	85	8.5:1
6	$Fe(OTf)_2$	**L3**	**2b**	3.6	1.0	82	8.6:1
7	$Fe(NTf_2)_2$	**L3**	**2b**	3.6	1.0	78	8.0:1
8	$Fe(OAc)_2$	**L3**	**2b**	3.6	3.5	87	> 20:1

[a] Reactions were carried out under N_2 and then quenched with saturated $NaHCO_3$ solution. Reduction conditions: PPh_3, H_2O, THF, 50°C, 2 h, then TsOH. Reactions in the absence of ligands [$FeCl_2$ or $Fe(NTf_2)_2$ only] afford the product with a low d.r. value.

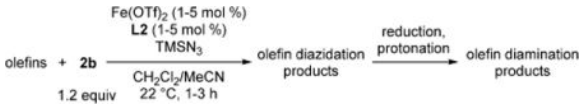
[b] Yield of isolated product. The d.r. value was measured by ^1H NMR analysis.

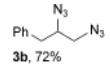
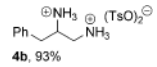
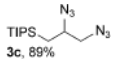
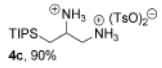
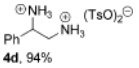
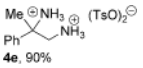
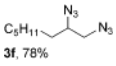
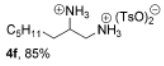
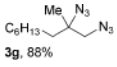
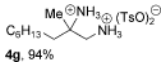
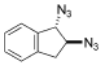
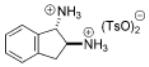
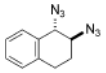
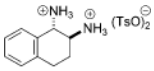
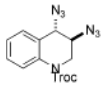
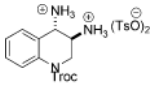
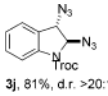
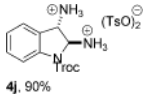
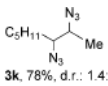
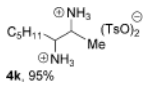
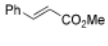
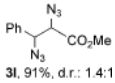
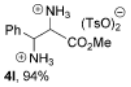
[c] Conversion is < 5% in the absence of $TMSN_3$.

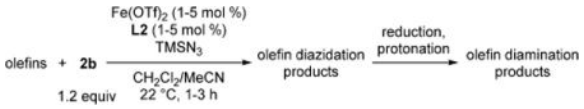
Tf = trifluoromethanesulfonyl.

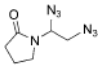
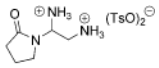
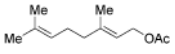
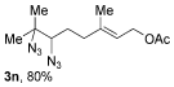
Table 2

Substrate scope for the iron-catalyzed olefin diazidation.[a]



Entry	Olefin	Diazide[b]	Diaminium salt[b]
1[c,d]		 **3b**, 72%	 **4b**, 93%
2[d]		 **3c**, 89%	 **4c**, 90%
3[d]		 **3d**, 85%	 **4d**, 94%
4[e]		 **3e**, 83%	 **4e**, 90%
5[d]		 **3f**, 78%	 **4f**, 85%
6[e]		 **3g**, 88%	 **4g**, 94%
7[d,f]		 **3a**, 87%, d.r. >20:1	 **4a**, 92%
8[d,f]		 **3h**, 79%, d.r.: 12:1	 **4h**, 90%
9[e,g]		 **3i**, 66%, d.r. >20:1	 **4i**, 89%
10[e,h]		 **3j**, 81%, d.r. >20:1	 **4j**, 90%
11[d,h]		 **3k**, 78%, d.r.: 1.4:1	 **4k**, 95%
12[d,h]		 **3l**, 91%, d.r.: 1.4:1	 **4l**, 94%



Entry	Olefin	Diazide[b]	Diaminium salt[b]
13[d,i]		 **3m**, 80%	 **4m**, 72%
14[j,k]		 **3n**, 80%	

[a] $TMSN_3$ (3.6–4.0 equiv)[9] was used.

[b] Yield of isolated product is given.

[c] $Fe(OTf)_2$/**L2** (1 mol%), 2 h.

[d] PPh_3, H_2O, 50°C, then TsOH.

[e] Pd/C, H_2 22°C, then TsOH.

[f] $Fe(OAc)_2$/**L3** (5 mol%), 4 h.

[g] $Fe(NTf_2)_2$/**L3** (10 mol%), 4 h.

[h] $Fe(OTf)_2$/**L3** (5 mol%).

[i] PMe_3, H_2O, 50°C, then TsOH.

[j] 0°C, 10 h.

[k] 92% yield for reduction. HRMS analysis was performed on diamimium salts.

TIPS=triisopropylsilyl, Troc=2,2,2-trichlorethoxycarbonyl.