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Iron(II) Halide Promoted Cyclization of Cyclic 2-Enynamides: Stereoselective Synthesis of Halogenated Bicyclic γ-Lactams

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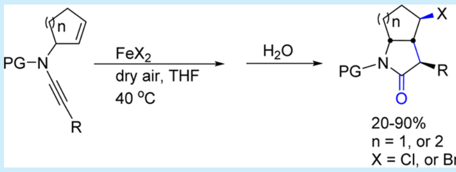
Supporting Information

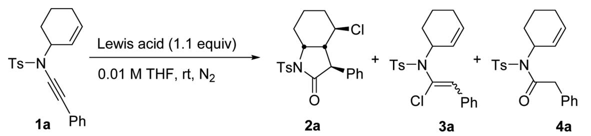
ABSTRACT: A simple and mild process was developed for the highly stereoselective synthesis of halogenated bicyclic [4.3.0] and [3.3.0] γ-lactams, possessing four stereocenters, from easily available cyclic 2-enynamides. The reaction required only an inexpensive iron(II) halide under dry air and was tolerant of aryl, heteroaryl, and alkyl groups at the alkyne terminus.



Lactams are common core structures that can be found in various biologically important natural products and pharmaceuticals.[1] Recently developed methods for the synthesis of lactams involved the transition-metal-catalyzed insertion of an external CO into C(sp^3)–H of alkylamines,[2] the intramolecular Ugi multicomponent reaction of γ-ketoacids with an amine and an isocyanide,[3] the $Al(OTf)_3$-catalyzed cascade cyclization and ionic hydrogenation reaction of nitrogen substituted ketoamides,[4] the gold-catalyzed tandem cycloisomerization/oxidation of homopropargyl amides,[5] the $Sc(OTf)_3$-catalyzed Mukaiyama–aldol-type reaction of 2,5-bis(trimethylsilyloxy)furan with imines,[6] the Pd-catalyzed oxidative intramolecular cyclization of amides with an alkene,[7] the cobalt-catalyzed intramolecular reductive coupling reaction of nitriles and acrylamides,[8] the gold(I)-catalyzed cyclization of *N*-alkenyl β-ketoamides,[9] the Pd-catalyzed oxidation cyclization of *N*-allylpropiolamides,[10] and the $FeCl_2$-catalyzed intramolecular chloroamination of cyclohexene-tethered acyl azides.[11] Here, we report our results on a simple and unprecedented synthesis of halogenated bicyclic [4.3.0] and [3.3.0] γ-lactams in stereoselective manners by reaction of six- and five-membered ring 2-enynamides with inexpensive and environmentally friendly iron(II) halides and green oxidant air.[12]

The readily prepared six-membered ring *N*-tosyl-2-enynamide **1a** was chosen as a model substrate for screening Lewis acids and optimizing the reaction conditions. Compound **1a** was prepared from cyclohex-2-enol using the known literature protocols[13] via a Mitsunobu reaction of cyclohex-2-enol with NHTsBoc,[14] deprotection of the Boc group, and a copper-catalyzed amidation[15] of phenylethynyl bromide with the amide to afford **1a** in 70% yield over three steps. First, several chlorine-containing Lewis acids at 0.01 M concentration in THF were tested for the cyclization of **1a** at room temperature under nitrogen (see the SI for details). While employing CuCl, $ZnCl_2$, and $InCl_3$ resulted in the quantitative recovery of the enynamide **1a** (see the SI), the use of $TiCl_4$, TMSCl, and $AlCl_3$ led to predominantly the hydrochlorination product **3a** and a trace amount of the hydrolysis product **4a** (Scheme 1). Only **3a** was obtained in 30% yield when **1a** was treated with $CuCl_2$. To

Scheme 1. Reaction of Lewis Acids with 1a



our delight, when **1a** was subjected to $FeCl_2$ or $FeCl_3$ (0.01 M in THF) at room temperature under nitrogen for 52–60 h, a major product, identified as the bicyclic γ-lactam **2a**, was obtained as a single diastereomer and in 49 and 46% yield, respectively. The relative stereochemistry of **2a**, derived from *anti*-addition of a chloride ion and the ynamide tether across the pendant double bond, was determined with NOESY (nuclear Overhauser effect spectroscopy) measurements and was further confirmed by X-ray crystallography.[16]

Encouraged by the successful transformation of **1a** into **2a** using inexpensive iron chlorides, we next screened the effect of solvent, concentration, temperature, and atmosphere to improve the yield of **2a** (Table 1). The most relevant results of evaluating proper solvents revealed that THF was the best among the solvents (THF, ether, toluene, and DCM) screened at rt (Table 1, entries 1–4) for the cyclization of **1a** with $FeCl_2$ (1.1 equiv). Pleasingly, the yield of **2a** could be substantially raised to 77% when the concentration of **1a** was increased to 0.25 M in THF (Table 1, entry 5). The effect of the reaction temperature was also significant, as when **1a** was treated with 1.1 equiv of $FeCl_2$ in THF (0.25 M) under nitrogen at 40 °C for 40 h, the desired γ-lactam **2a** was isolated in 88% yield (Table 1, entry 6). To our surprise, the reaction time could be significantly reduced to 6 h when the reaction was conducted in open air at 40 °C and delivered **2a** in 75% yield (Table 1, entry 7), together with a trace amount of the hydrolysis product **4a**. We envisioned that the undesired hydrolysis product **4a** could be avoided by attaching a calcium chloride drying tube to the reaction flask. Indeed, treatment of **1a** with 1.1 equiv of $FeCl_2$ in THF at 0.25 M concentration under dry air gave an 84%

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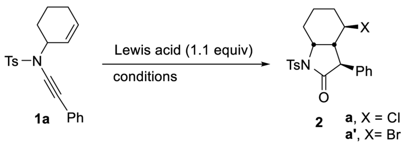
Table 1. Optimization of Reaction Conditions



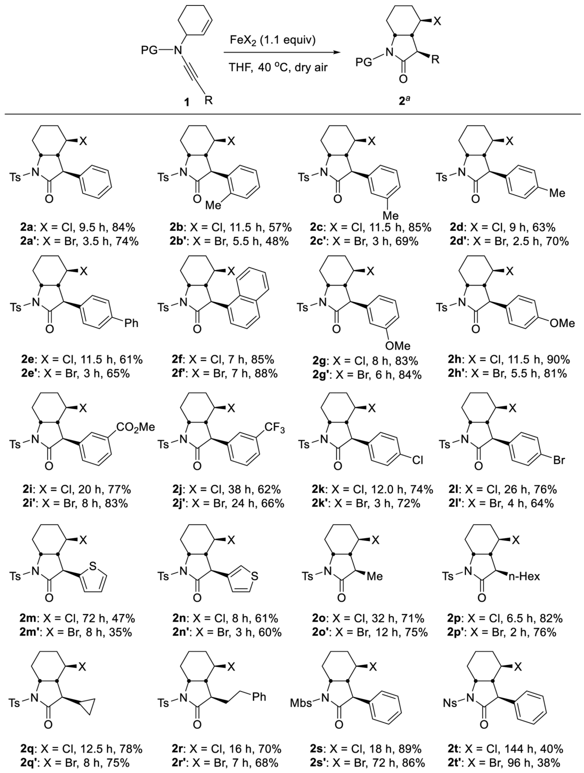
entry	FeX_n	solvent	[M]	T (°C)	atmos	time (h)	yield[a] (%)
1	$FeCl_2$	THF	0.01	rt	N_2[b]	60	49
2	$FeCl_2$	ether	0.01	rt	N_2[b]	24	4
3	$FeCl_2$	toluene	0.01	rt	N_2[b]	24	9
4	$FeCl_2$	DCM	0.01	rt	N_2[b]	24	
5	$FeCl_2$	THF	0.25	rt	N_2[b]	48	77
6	$FeCl_2$	THF	0.25	40	N_2[b]	40	88[c]
7[d]	$FeCl_2$	THF	0.25	40	air	6.0	75
8	$FeCl_2$	THF	0.25	40	dry air	9.5	84[c]
9[e]	$FeCl_2$	THF	0.25	40		9.5	-
10	$FeCl_2$	THF	0.25	40	O_2	4.0	18
11	$FeCl_3$	THF	0.25	40	dry air	1.0	69
12	$FeBr_2$	THF	0.25	40	dry air	3.5	74
13	$FeBr_3$	THF	0.25	40	dry air	2.5	68
14[f]	$FeCl_2$	THF	0.25	40	dry air	6.5	69

[a]NMR yields. [b]N_2 is contaminated with a small amount of O_2. [c]Isolated yield. [d]A small amount of **4a** was isolated. [e]The reaction mixture in a reaction vessel was first evacuated to remove all air and the vessel was then sealed and heated to 40 °C. [f]1.1 equiv of hydroquinone was added.

yield of **2a** after the reaction mixture was heated at 40 °C for 9.5 h (entry 8). To further understand the effect of atmosphere, the following experiments were performed. The reaction mixture (**1a**, 1.1 equiv of $FeCl_2$, in 0.25 M THF) in a reaction vessel was evacuated to remove all air, and the vessel was then sealed. No trace of **2a**, **3a**, and **4a** was detected by TLC analysis (entry 9), and **1a** was recovered in 82% yield after the reaction mixture was heated at 40 °C for 9.5 h. Therefore, oxidation of $FeCl_2$ with oxygen in the air or in the oxygen-contaminated nitrogen gas (entries 1, 5, and 6) was essential for the cyclization. However, treatment of **1a** with $FeCl_2$ (1.1 equiv) under an atmosphere of oxygen at 40 °C for 4 h led to a small amount of **2a** (18%, entry 10). The result may indicate that a great portion of **1a** was decomposed under oxygen. Although the more reactive iron(III) chloride (1.1 equiv) reduced the reaction time to 1 h, it could cause the decomposition of **1a** and afforded **2a** in only 69% yield (entry 11). Switching iron chlorides to iron bromides revealed that $FeBr_2$ was also capable of transforming **1a** to **2a′** (entry 12, X = Br) in 3.5 h and in 74% yield. Due to the slow decomposition of **1a** with $FeBr_3$, **1a** was consumed in 2.5 h, and the reaction provided **2a′** in 68% yield (entry 13, X = Br). Therefore, it was concluded that the use of 1.1 equiv of $FeCl_2$ (entry 8) and $FeBr_2$ (entry 12) in dry THF under dry air, to avoid the formation of hydrolysis product **4a**, at 40 °C were the best conditions for the cyclization. To further understand the reaction mechanism, the standard cyclization was conducted in the presence of 1.1 equiv of hydroquinone (a radical scavenger). The reaction produced bicyclic γ-lactam **2a** in 69% yield (entry 14). Since the radical scavenger did not impede the cyclization, it was suggested that the reaction may not proceed through a radical process. It must be mentioned that a few transition metals have been employed for the synthesis of bicyclic lactams from ynamides tethering an unsaturated C−C bond; however, these methods required various oxides (*N*-oxides, sulfoxides, or epoxides) as oxidant for the formation of α-oxo metal carbene intermediates, which were then trapped with an alkene or alkyne to form bicyclic lactams.[17] Furthermore, halogenated bicyclic γ-lactams had been synthesized via metal-catalyzed radical additions of cycloalkene-tethered acid derivatives, such as acyl azides or trichloroacetamides,[11,18] and our synthesis of halogenated bicyclic γ-lactams using the simple cyclic NTs-tethered enynes, nontoxic and inexpensive iron(II) halides, and dry air.

With the optimal reaction conditions in hand, we examined the substrate scope of the cyclization using various six-membered ring 2-enynamides (Scheme 2). Good to excellent

Scheme 2. Scope of the Cyclization of Cyclohexene-Tethered 2-Enynamides



[a]Isolated yields from column chromatography over silica gel.

yields were observed when the cyclic enynamides bearing an aryl group were at the alkyne terminus. In general, electron-neutral substituents on the phenyl ring, **1a,c−f**, afforded the corresponding bicyclic γ-lactams in good yields (61−88%), though the sterically hindered *o*-tolyl enynamide **1b** gave the chlorinated bicyclic lactam **2b** (57%) and brominated bicyclic lactam **2b′** (48%) in lower yields and required longer reaction times. Substrates **1g** and **1h** bearing the electron-rich methoxy group on the phenyl ring reacted efficiently and provided the corresponding lactams in high yields (81−90%), whereas electron-deficient aryl enynamides **1i** and **1j** led to the desired products in lower yields (62−83%). Substrates that were substituted with a chlorine or bromine atom on the phenyl ring, for example, **1k** and **1l**, performed with equal levels of efficiency with $FeCl_2$ and $FeBr_2$, resulting in good yields (64−76%) of the desired products **2k**, **2k′**, **2l**, and **2l′**. Thienyl-substituted enynamides **1m** and **1n** were also effective, however, affording the corresponding lactams in diminished yields (35-61%). Next,

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substrates with an alkyl group (methyl-, hexyl-, cyclopropyl-, or 2-phenylethyl) at the alkyne terminus were also tolerated, delivering the target bicyclic γ-lactams **2o−r**[16] and **2o′−r′** in the range of 68−82% yields. Furthermore, the replacement of the *N*-tosyl group with easily deprotected *N*-4-methoxybenzenesulfonyl (*N*-Mbs) or *N*-4-nitrobenzenesulfonyl (*N*-Ns) groups, for example, **1s** and **1t**, required much longer reaction times. While the electron-rich *N*-Mbs-protected enynamide **1s** afforded higher yields of lactams **2s** (89%) and **2s′** (86%), the electron-poor *N*-Ns-protected enynamide **1t** gave lactams **2t** and **2t′** in only 40 and 38% yield, respectively. Furthermore, the tosyl group of **2a** could be removed by treatment of **2a** with magnesium powder and ammonium chloride in MeOH under sonication for 1 h, providing the deprotected bicyclic γ-lactam quantitatively (see the SI for details).[19]

To gain further insight into the reaction path, substrate **5** with an additional *trans*-acetoxy substituent at the 4-position of the ring was subjected to the optimal reaction conditions (Figure 1). The transformation provided exclusively the desired

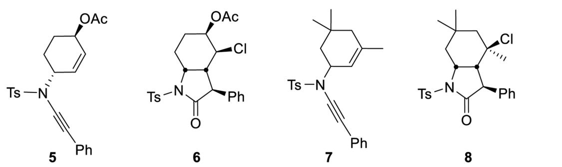
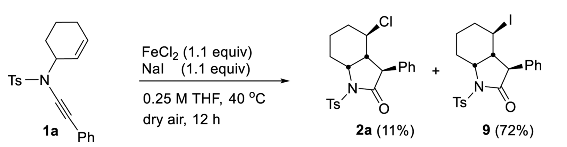


Figure 1. Compounds **5**−**8**.

bicyclic γ-lactam **6** (7 h, 54% yield). Moreover, the 3,5,5-trimethyl-substituted cyclohex-2-ene-tethered ynamide **7** was also reactive, yielding the corresponding bicyclic γ-lactam **8** in 57% yield (Figure 1). Both lactams **6** and **8**[16] were obtained as a single diastereomer with the same stereochemistry as those of **2**. Therefore, the additional acetoxy or methyl groups on the six-membered ring did not alter the stereo preference (*anti*-addition) for the cyclization.

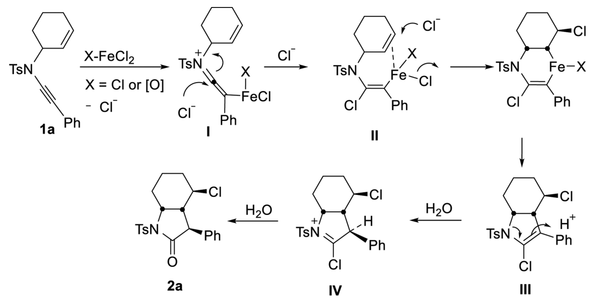
Finally, **1a** was subjected to 1.1 equiv of $FeCl_2$ and NaI under the optimal reaction conditions. The reaction was performed with the expectation that the more nucleophilic iodide would lead to an iodinated γ-lactam. Indeed, addition of 1.1 equiv of NaI to the reaction mixture provided the corresponding iodinated bicyclic γ-lactam **9** in 72% yield and **2a** in 11% yield under the standard reaction conditions (Scheme 3).

Scheme 3. Synthesis of Iodinated Bicyclic γ-Lactam 9



Since hydroquinone (a radical scavenger) did not impede the cyclization (Table 1, entry 14) and the formation of lactams **2q** and **2q′** with the cyclopropyl ring intact (Scheme 2), it may indicate that the cyclization does not proceed through a radical process. Scheme 4 shows a plausible path for the cyclization of **1a** with $FeCl_2$ or $FeCl_3$. First, $FeCl_2$ was oxidized to [O]-$FeCl_2$. Metalation of the cyclic 2-enynamide **1a** with [O]-$FeCl_2$ afforded the keteniminium ion **I** (X = [O]). In the case of $FeCl_3$, **1a** may react faster with more reactive $FeCl_3$ to afford intermediate **I** (X = Cl). Trapping intermediate **I** by a chloride ion followed by coordination of the iron center to the pendant

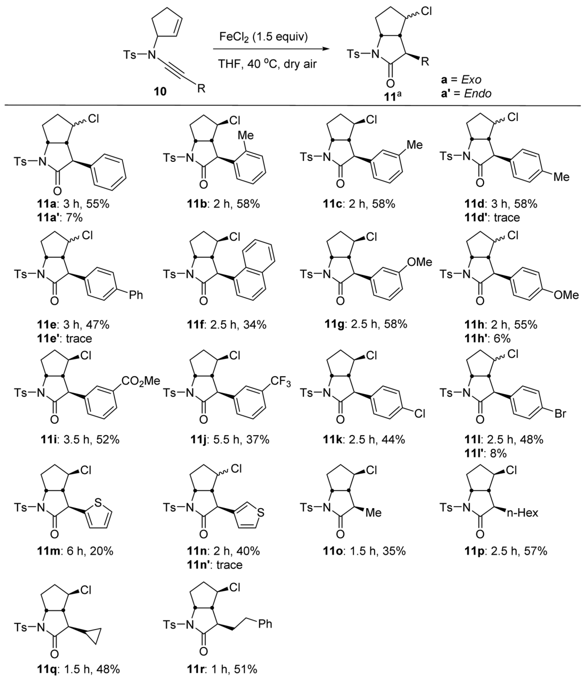
Scheme 4. Proposed Mechanism for the Formation of 2a from 1a



C−C double bond gave intermediate **II**.[20] *Anti*-addition of a chloride ion to the activated double bond followed by reductive elimination afforded intermediate **III**. Protonolysis of **III** upon workup generated the iminium ion **IV** with the phenyl group at the more stable convex face. Hydrolysis of the resulting iminium ion delivered the bicyclic lactam **2a**. For the system of $FeCl_2$/NaI (Scheme 3), *anti*-addition of an iodide ion onto the olefin of **II** would lead to the iodinated bicyclic lactam **9**.

Next, five-membered ring starting substrates **10a−r** were subjected to $FeCl_2$ (1.5 equiv, THF, 40 °C, dry air), and results are summarized in Scheme 5. Although shorter reaction times

Scheme 5. Scope of the Cyclization of Cyclopentene-Tethered 2-Enynamides



[a]Isolated yields from column chromatography over silica gel.

(1.0−6.0 h) were observed, the reactions gave lower yields of the desired chlorinated bicyclic [3.3.0] γ-lactams **11a**[16]**−r** (20−58%). The shorter reaction times and lower yields resulting from **10a−r** may be partly due to the fact that the five-membered ring substrates were less stable and decomposed under the reaction conditions. In some cases, a small amount of the isomers resulting from *syn*-addition of a chloride ion and the iron moiety to the olefin (Figure 2, intermediate **VI**) were observed (**11a′**,[16] **11d′**, **11e′**, **11h′**, **11l′**, and **11n′**). Compared

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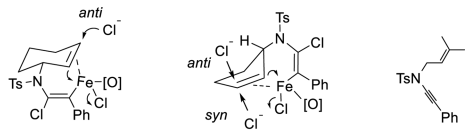

V VI 12

Figure 2. Intermediates **V** and **VI** and compound **12**.

to intermediate **V**, the α-face of the five-membered ring intermediate **VI** is less sterically congested (Figure 2). Therefore, a *syn*-addition of a chloride ion and the iron moiety to the olefin would lead to *syn* products in some cases. Unfortunately, acyclic NTs-tethered enyne **12** (Figure 2) failed to give lactams under the standard reaction conditions (THF, dry air, 40 °C, 20 h).

In conclusion, we have developed a simple and reliable method for the synthesis of halogenated bicyclic [4.3.0] and [3.3.0] γ-lactams from readily available cyclic NTs-tethered enynes. The reaction only required inexpensive iron halides and green oxidant air as promoters, providing direct access to the bicyclic γ-lactams with four stereocenters in a single step. The key feature of this reaction is an *anti*-addition of a halide ion and the postulated vinyl iron species across the pendant olefin. Further mechanistic studies on the reaction and applications on the use of the present method to the synthesis of other heterocycles are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00916.

Experimental procedures, characterizations, and NMR spectra of all new compounds (PDF)
X-ray crystallographic data for **2a** (CIF)
X-ray crystallographic data for **2a′** (CIF)
X-ray crystallographic data for **2n** (CIF)
X-ray crystallographic data for **2o** (CIF)
X-ray crystallographic data for **2r** (CIF)
X-ray crystallographic data for **8** (CIF)
X-ray crystallographic data for **11a** (CIF)
X-ray crystallographic data for **11a′** (CIF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Professor Masahiro Murakami (Kyoto University) on the occasion of his 60th birthday.

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