$NaBAr^F_4$-Catalyzed Oxidative Cyclization of 1,5- and 1,6-Diynes: Efficient and Divergent Synthesis of Functionalized γ- and δ-Lactams

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An efficient $NaBAr^F_4$-catalyzed oxidative cyclization of readily available 1,5- and 1,6-diynes has been developed. Importantly, this transition metal-free oxidative catalysis proceeds via a presumable Lewis acid-catalyzed S_N2' pathway, which is distinct from the relevant oxidative rhodium and gold catalysis. This method leads to the facile and practical construction of a diverse range of synthetically useful γ- and δ-lactams in mostly good to excellent yields with broad substrate scope.

Keywords oxidation • cyclization • homogeneous catalysis • alkynes • heterocycles

Introduction

The conjugated γ- and δ-lactam structural motifs are common in many pharmaceuticals and natural products (Figure 1).[1-3] Many of them demonstrate a broad spectrum of biological activities (e.g., anticancer, antitumoral, anti-inflammatory and antitubercular). Consequently, the development of new synthetic methods for their preparation are highly desired, especially those with high flexibility, efficiency, enantioselectivity, and good modularity.

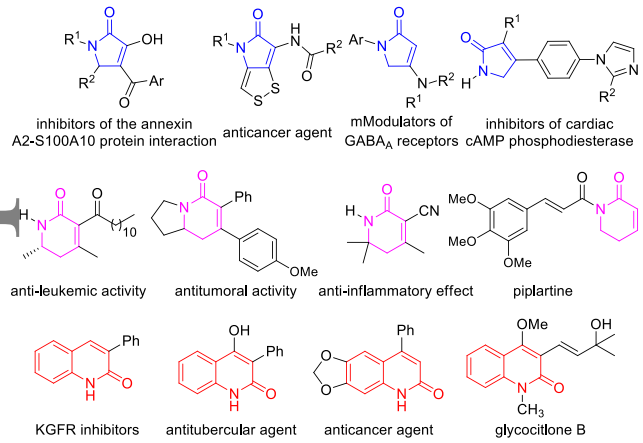

Figure 1 Selected examples bearing the conjugated γ- and δ-lactam core structure.

In recent years, catalytic intermolecular diyne oxidation by an N–O bond oxidant[4] has attracted considerable interest as this chemistry offers great potential to build structurally complex cyclic molecules from readily available diynes.[5-9] For instance, Hashmi et al. reported an elegant protocol for the gold-catalyzed oxidative diyne cyclization involving diyne oxidation, 1,6-carbene transfer, followed by Wagner−Meerwein chemistry, CH insertions or double oxidation.[5] Such a gold-catalyzed oxidative cyclization of diynes has been significantly advanced by Zhang, Ji, Ohno and Liu.[6] Moreover, Tang et al. disclosed that rhodium could also catalyze this diyne oxidation, thus leading to the facile construction of a variety of 2-oxopyrrolidines (Scheme 1a).[7] Of note, gold-catalyzed such a direct diyne cyclization could lead to the efficient formation of indeno[1,2-*c*]pyrroles (Scheme 1b).[8] Very recently, our group realized the relevant copper- and $NaBAr^F_4$-catalyzed oxidative cyclization of 1,5-diynes, allowing the divergent and practical synthesis of various valuable tricyclic *N*-heterocycles.[9]

Inspired by these results and our recent study on the catalytic alkyne oxidations,[9,10] we envisioned that the preparation of synthetically useful γ- and δ-lactams might be achieved via catalytic oxidative cyclization of readily available 1,5- and 1,6-diynes. Herein, we report an efficient $NaBAr^F_4$-catalyzed such an oxidative diyne cyclization, and importantly, this transition metal-free oxidative catalysis proceeds via a presumable Lewis acid-catalyzed S_N2' pathway, which is distinct from the relevant oxidative rhodium and gold catalysis (Scheme 1c). This method leads to the facile and practical construction of a diverse range of valuable γ- and δ-lactams in mostly good to excellent yields with broad substrate scope.

Scheme 1 Catalytic cascade cyclization of alkyne-ynamides

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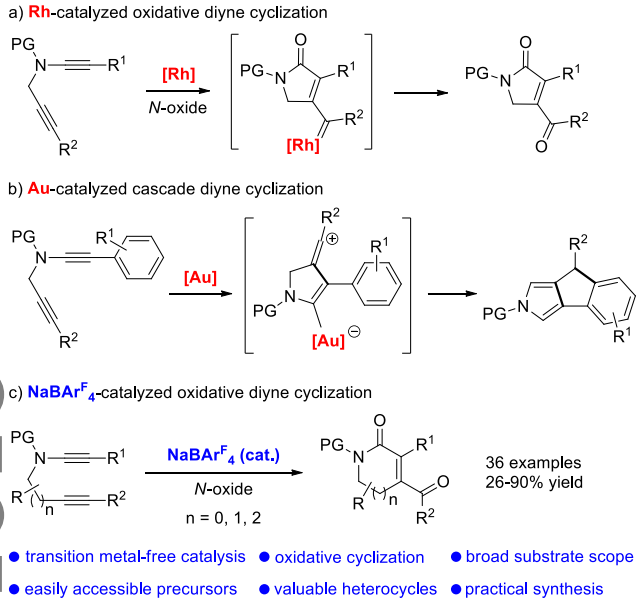


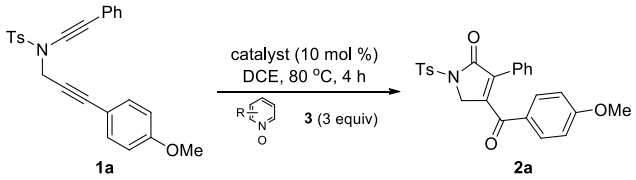
Experimental

NaBAr$^F_4$ (0.02 mmol, 17.8 mg) was added to a mixture of the *N*-propargyl ynamide **1** (0.20 mmol) and 2,6-dichloropyridine *N*-oxide **3a** (98.4 mg, 0.60 mmol) in DCE (4.0 mL) at room temperature. Then, the reaction mixture was stirred at 80 °C and the progress of the reaction was monitored by TLC. The reaction typically took 4 h. Upon completion, the mixture was concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired γ-lactam **2**.

Results and Discussion

We set out to screen different conditions for this reaction by using alkyne-ynamide **1a** as the model substrate,[11,12] and the representative data are summarized in Table 1. When the reaction was performed under the previously optimized reaction conditions (10 mol % of NaBAr$^F_4$, 3 equiv of pyridine *N*-oxide **3a**, DCE, 80°C, 4 h),[9b] we were delighted to find that the envisioned oxidative cyclization product **2a** was formed in 81% yield (Table 1, entry 1). The reactions were also catalyzed by many other Lewis acids including Zn(OTf)$_2$, In(OTf)$_3$, Yb(OTf)$_2$, etc., but these gave decreased yields (Table 1, entries 2-8). Attempts with other pyridine *N*-oxides such as **3b** and **3c** could not further improve the reaction (Table 1, entries 9-10). The use of chlorobenzene as solvent gave comparable yield (Table 1, entry 11) while other solvents such as toluene and CH_3CN led to a significantly decreased yield. Finally, it was found that the reaction also proceeded smoothly in the presence of 5 mol % of NaBAr$^F_4$ albeit with a slightly decreased yield and a longer reaction time (Table 1, entry 12). It is notable that Brønsted acids such as CF_3CO_2H and MsOH could also be used to catalyze this reaction but with low efficiency (<50% yield), and no background tricyclic *N*-heterocycle formation was observed in all these cases.[8]

Table 1 Optimization of reaction conditions[a]

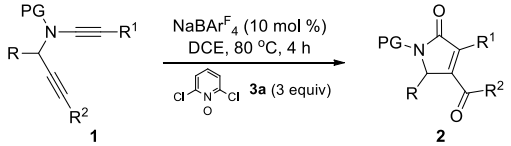


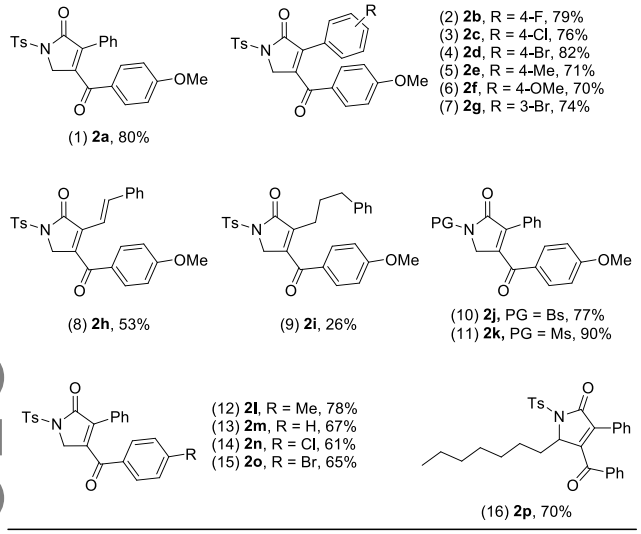
Entry	Catalyst	Oxidant (R)	Yield[b]/%
1	NaBAr$^F_4$	**3a** (R = 2,6-Cl$_2$)	81
2	Zn(OTf)$_2$	**3a** (R = 2,6-Cl$_2$)	70
3	Cu(OTf)$_2$	**3a** (R = 2,6-Cl$_2$)	60
4	CuOTf	**3a** (R = 2,6-Cl$_2$)	69
5	In(OTf)$_3$	**3a** (R = 2,6-Cl$_2$)	75
6	Yb(OTf)$_3$	**3a** (R = 2,6-Cl$_2$)	73
7	Y(OTf)$_3$	**3a** (R = 2,6-Cl$_2$)	71
8	Dy(OTf)$_3$	**3a** (R = 2,6-Cl$_2$)	53
9	NaBAr$^F_4$	**3b** (R = 2,6-Br$_2$)	63
10	NaBAr$^F_4$	**3c** (R = 2-Br)	58
11[c]	NaBAr$^F_4$	**3a** (R = 2,6-Cl$_2$)	80
12[d]	NaBAr$^F_4$	**3a** (R = 2,6-Cl$_2$)	76

[a] Reaction conditions: [**1a**] = 0.05 M. [b] Measured by ^{1}H NMR using diethyl phthalate as the internal standard. [c] In chlorobenzene. [d] 5 mol % of NaBAr$^F_4$ was used, 8 h.

The substrate scope of this oxidative cyclization reaction was then investigated using the optimal conditions (Table 1, entry 1). A variety of aryl-substituted 1,5-diynes (R^1 = Ar) were first screened, and the corresponding γ-lactams **2a**–**2g** were obtained in 70–82% yields (Table 2, entries 1-7). The reaction could also be extended to styryl- and alkyl-substituted ynamides to produce the desired **2h** and **2i** in 53% and 26% yields, respectively, and similar low yield in the case of alkyl-substituted ynamide was also observed in our previous protocols (Table 2, entries 8-9).[9a,13] Further investigation of *N*-protecting groups demonstrated that both the Bs- and Ms-protected 1,5-diynes were suitable substrates, affording products **2j** and **2k** in 77% and 90% yields, respectively (Table 2, entries 10-11). Moreover, ynamides with electron-donating group (EDG such as methyl) and electron-withdrawing groups (EWGs such as Cl and Br) are applicable to the present reaction, thus delivering the desired γ-lactams **2l**–**2o** in moderate to good yields (Table 2, entries 12-15). Finally, it was found that alkyl-substituted ynamide **1p** could be readily converted into the desired product **2p** in 70% yield (Table 2, entry 16).

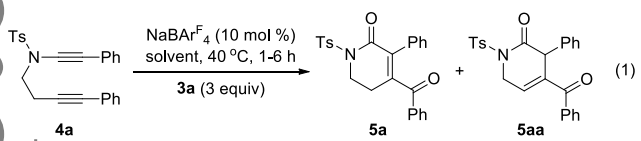
Table 2 Synthesis of γ-lactams **2**[a]





[a] Reactions run in vials; [**1**] = 0.05 M; isolated yields.

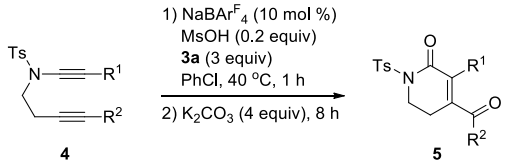
We then turned our attention to an evaluation of 1,6-diyne substrates. As shown in Eq. 1, the oxidative cyclization of 1,6-diyne **4a** resulted in the formation of the desired δ-lactam **5a** together with the isomerized δ-lactam **5aa** in the above optimized reaction conditions. The use of chlorobenzene as solvent led to a slightly improved yield while the use of MsOH (0.2 equiv) as additive substantially accelerate the reaction (1 h *vs* 6 h). To our delight, it was found that **5aa** could be readily isomerized into **5a** by the treatment with K_2CO_3 (4 equiv) for another 8 h in one pot.

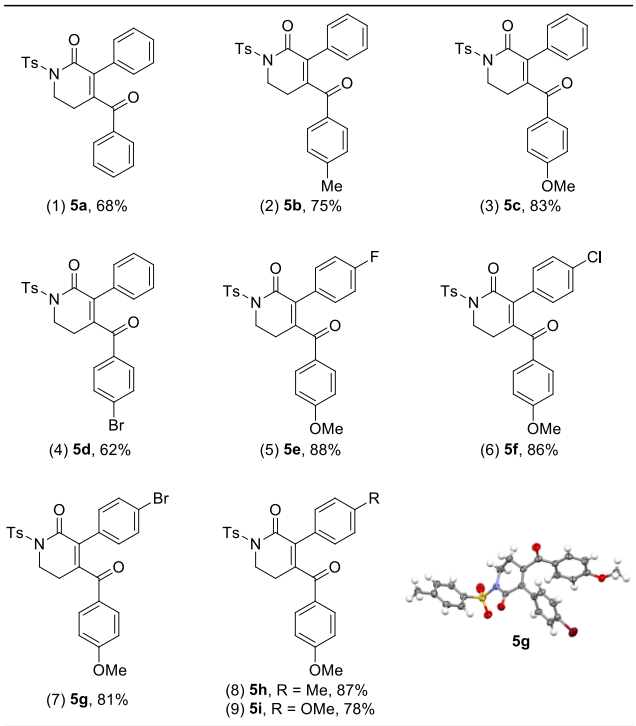


DCE, 6 h: **5a**, 13%; **5aa**, 45%
PhCl, 6 h: **5a**, 16%; **5aa**, 53%
PhCl, MsOH (0.2 equiv), 1 h: **5a**, 18%; **5aa**, 52%
PhCl, MsOH (0.2 equiv), 1 h; K_2CO_3 (4 equiv), 8 h: **5a**, 68%; **5aa**, <1%

With the optimal reaction conditions in hand, the reaction scope was also studied. As depicted in Table 3, 1,6-diynes **4** were successfully engaged in this oxidative cyclization to give the desired δ-lactams **5a**–**5i** in mostly good to excellent yields. Ynamides bearing different R^2 groups were compatible with this cyclization (Table 3, entries 1-4), and the substrate with electron-donating OMe group gave the best yield (Table 3, entry 3). In addition, the reaction also proceeded well with various aryl-substituted 1,6-diynes (R^1 = Ar), affording the desired **5e**–**5i** in 78–88% yields (Table 3, entries 5–9). The molecular structure of **5g** was unambiguously assigned by X-ray analysis.[14]

Table 3 Synthesis of δ-lactams **5**[a]

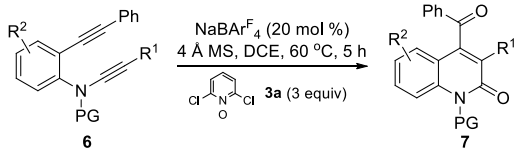


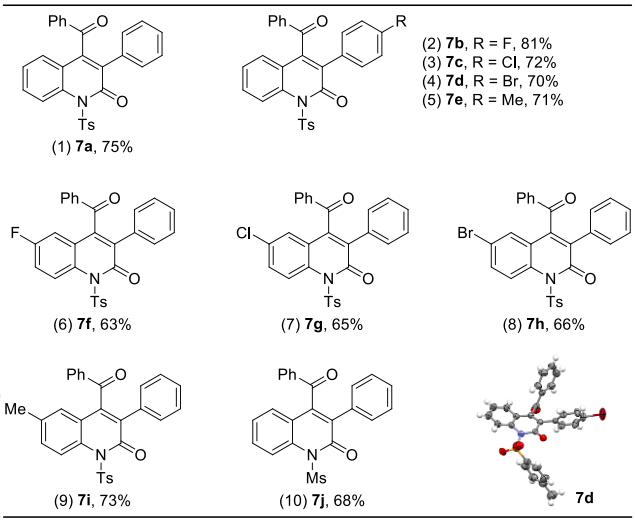


[a] Reactions run in vials; [**4**] = 0.2 M; K_2CO_3 was added in one pot after the oxidative cyclization was completed; isolated yields.

Besides aliphatic alkyl-linked 1,6-diynes, this oxidative cyclization also occurred efficiently with aryl-linked 1,6-diynes **6**, delivering the desired 2-quinolinones **7** in 63–81% yields under the optimized reaction conditions (Table 4). The reaction tolerated substrates with different aryl groups (R^1 = Ar), leading to the desired **7a**–**7e** in good yields (Table 4, entries 1–5). Moreover, aryl-linked 1,6-diynes with electron-withdrawing (EWGs such as F, Cl and Br) and -donating substituents (EDG such as methyl) on the aromatic backbone were suitable substrates for this tandem reaction to produce the corresponding **7f**–**7i** in moderate to good yields (Table 4, entries 6–9). Finally, it was found that Ms protected ynamide also underwent this oxidative cyclization smoothly (Table 4, entry 10). The molecular structure of **7d** was further confirmed by X-ray crystallography.[14]

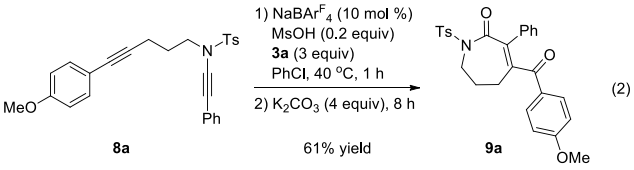
Table 4 Synthesis of γ-lactams **7**[a]





[a] Reactions run in vials; [**6**] = 0.05 M; isolated yields.

Moreover, this chemistry could also be extended to the preparation of medium-sized lactams. As depicted in Eq. 2, the oxidative cyclization of 1,7-diyne **8a** under the above optimal reaction conditions delivered the anticipated seven-membered lactam **9a** in 61% yield.



According to the above experimental observations and previous studies,[9b] a plausible reaction mechanism for the formation of γ-lactam **2** is proposed (Scheme 2). First, the *N*-oxide **3a** attacks the BAr^F_3-activated ynamide **1** to generate the vinyl borate intermediate **B**, which is further converted into the vinyl cation **C** with the release of pyridine via an intramolecular S_N2' pathway.[15] Intermediate **C** can undergo the subsequent trapping by another oxidant to produce intermediate **D**. Finally, pyridine release leads to the product **2** and regenerates the catalyst to initiate a new catalytic cycle. It should be mentioned that BAr^F_3 is probably dissociated from $NaBAr^F_4$ with the assistance of *N*-oxide, and serves as a Lewis acid to activate the C-C triple bond.[9b]

Scheme 2 Plausible reaction mechanism

Conclusions

In conclusion, we have developed an efficient $NaBAr^F_4$-catalyzed oxidative cyclization of readily available 1,5- and 1,6-diynes, and importantly, this transition metal-free oxidative catalysis proceeds via a presumable Lewis acid-catalyzed S_N2' pathway, which is distinct from the relevant oxidative rhodium and gold catalysis where the metal carbene[16] intermediate is presumably proposed. This method allows the facile and practical synthesis of a diverse range of valuable γ- and δ-lactams in mostly good to excellent yields with broad substrate scope. The use of readily available substrates, and a simple procedure and, in particular, no need to exclude moisture or air ("open flask") render this method highly interesting for use in organic synthesis. Further synthetic applications of this oxidative cascade cyclization are currently under investigation in our laboratory.

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[16] For recent selected reviews on the generation of metal carbenes from alkynes, see: (a) Zi, W.; Toste, F. D. *Chem. Soc. Rev.* **2016**, 45, 4567. (b) Harris, R. J.; Widenhoefer, R. A. *Chem. Soc. Rev.* **2016**, *45*, 4533. (c) Jia, M.; Ma, S. *Angew. Chem. Int. Ed.* **2016**, *55*, 9134. (d) Dorel, R.; Echavarren, A. M. *Chem. Rev.* **2015**, *115*, 9028. (e) Wang, Y.; Muratore, M. E.; Echavarren, A. M. *Chem. - Eur. J.* **2015**, *21*, 7332. (f) Qian, D.; Zhang, J. *Chem. Soc. Rev.* **2015**, *44*, 677. (g) Fensterbank, L.; Malacria, M. *Acc. Chem. Res.* **2014**, *47*, 953. (h) Obradors, C.; Echavarren, A. M. *Acc. Chem. Res.* **2014**, *47*, 902. (i) Hashmi, A. S. K. *Acc. Chem. Res.* **2014**, *47*, 864.

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NaBAr$^F_4$-Catalyzed Oxidative Cyclization of 1,5- and 1,6-Diynes: Efficient and Divergent Synthesis of Functionalized γ- and δ-Lactams

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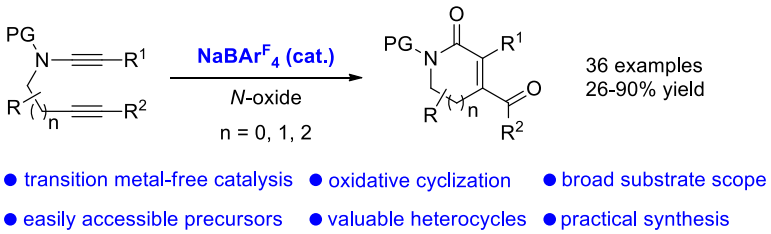

Text for Table of Contents: We report a NaBAr$^F_4$-catalyzed oxidative cyclization of 1,5- and 1,6-diynes via a presumable Lewis acid-catalyzed S_N2' pathway. This method leads to the efficient and practical construction of a diverse range of synthetically useful γ- and δ-lactams in mostly good to excellent yields with broad substrate scope.