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Synthesis of δ- and α-Carbolines via Nickel-Catalyzed [2 + 2 + 2] Cycloaddition of Functionalized Alkyne-Nitriles with Alkynes

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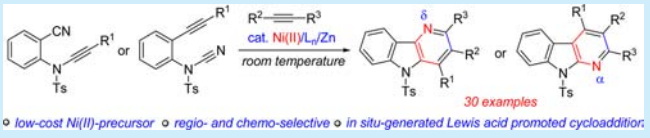
Supporting Information

ABSTRACT: A new method for the synthesis of δ- and α-carbolines through Ni-catalyzed [2 + 2 + 2] cycloaddition of ynamide-nitriles or alkyne-cyanamides with alkynes has been developed. The catalytic system of $NiCl_2(DME)$/dppp/Zn with a low-cost Ni(II)-precursor was first utilized in Ni-catalyzed [2 + 2 + 2] cycloaddition reactions, and the in situ generated Lewis acid may play an important role for the successful transformation. Not only internal alkynes but also terminal alkynes undergo the desired cycloaddition reactions efficiently to furnish the carboline derivatives with wide diversity and functional group tolerance.



δ- and α-Carbolines (pyridine-fused indoles) have received increasing interest in recent years since they serve as key structural units in a diverse array of natural products and pharmaceuticals (Figure 1).[1] Many of the synthetic and natural δ- and α-carbolines have displayed important and wide ranging biological activities such as antiviral, antitumor, anti-inflammatory, and central nervous system stimulating activities, etc.[2] Although the analogues of β-carbolines that are prevalent in natural products and biologically active substances have been investigated intensively, the synthetic approaches to δ- and α-carbolines are considerably less developed. The reported methods mainly involve Fischer synthesis, azide-mediated cyclizations, Pd-catalyzed amination and arylation reactions, derivatization of indoles for δ-carbolines,[3] and Graebe−Ullmann reactions, Diels−Alder reactions, cyclization of azaindoles, etc. for α-carbolines.[4] These methods usually suffer from multistep processes, harsh reaction conditions, low yields, etc. Therefore, the development of their synthesis from easily available starting materials with high efficiency and a wide substrate scope under mild reaction conditions is highly attractive.

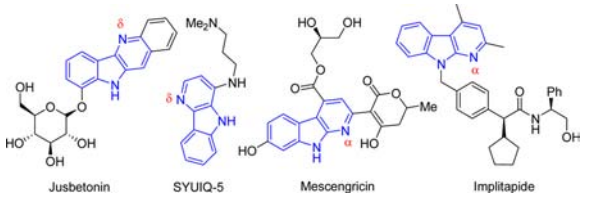
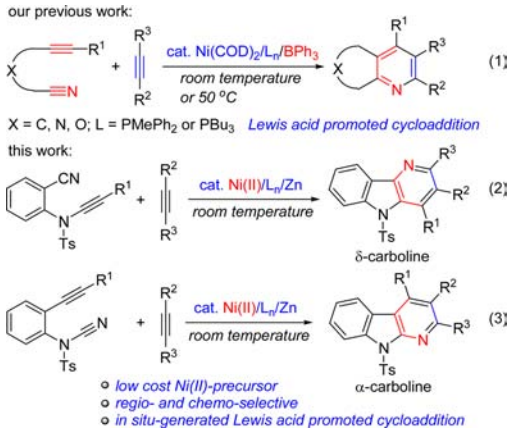


Figure 1. Representative bioactive δ- and α-carbolines.

Yet, transition-metal-catalyzed [2 + 2 + 2] cycloaddition of two alkynes with a nitrile represents a powerful route for the construction of pyridine derivatives.[5] Although much progress has been achieved in this area, the cycloaddition of the preassembled alkyne-nitriles with alkynes are far less investigated, which is mainly based on Co-catalyzed transformations.[6] However, these reactions usually require elevated temperatures, irradiation conditions, and inconvenient manipulations. More recently, Fe-catalyzed cycloaddition has been developed in this field.[7] However, the method is limited to internal alkynes as the alkyne component. We have recently developed a first example of Ni-catalyzed [2 + 2 + 2] cycloaddition of linear alkyne-nitriles or *o*-(cyano)phenyl propargyl ethers with alkynes through Ni-$(COD)_2/L_n$ and Lewis acid (BPh_3) cocatalysis, which provides an efficient route to fused pyridines (Scheme 1, eq 1).[8,9] The reaction likely proceeds via heterocoupling of an alkyne with a nitrile moiety leading to an azanickelacycle as a key reaction intermediate. The Lewis acid cocatalyst is crucial for these transformations, which is suggested to promote the oxidative

Scheme 1. Nickel-Catalyzed [2 + 2 + 2] Cycloaddition of Alkyne-Nitriles with Alkynes



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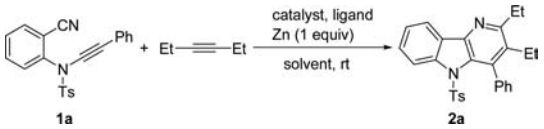
coupling process. Inspired by this work, we envisioned that δ- and α-carbolines might be assembled by [2 + 2 + 2] cycloaddition using designed alkyne-nitriles bearing an ynamide[10] or a cyanamide functionality as the building blocks[11,12] (Scheme 1, eqs 2 and 3). In addition, it was noted that a Ni(0) catalyst prepared through reduction of a Ni(II)Cl_2L_2 (L = phosphine ligands) complex by zinc metal would be accomplished with the formation of $ZnCl_2$, which may act as a Lewis acid to facilitate the cycloaddition process. We are therefore prompted to explore the possibility of using a low-cost and less sensitive Ni(II) phosphine complex as the catalyst for cycloaddition reactions. Herein, we report the partially intermolecular [2 + 2 + 2] cycloaddition of functionalized alkyne-nitriles with alkynes to δ- and α-carbolines catalyzed by a Ni(II) phosphine complex under extremely mild reaction conditions.

To test the feasibility, we first investigated the Ni-catalyzed cycloaddition of ynamide-derived alkyne-nitrile **1a** with 3-hexyne using $NiCl_2$(DME) as a precatalyst along with various ligands in the presence of 1.0 equiv of Zn metal. It was found that $PMePh_2$ and PBu_3, which were quite effective in our previous study,[8] led to either the desired δ-carboline **2a** in moderate yield (61%, Table 1, entry 1) or no formation of **2a** in DCM (entry 2). The use of triarylphosphine ligands such as PPh_3 or P(p-$CF_3C_6H_4$)$_3$ showed similar results to that obtained from $PMePh_2$ (entries 3–4). Further optimizations revealed that bidentate ligands such as dppp and dppb were highly promising for this reaction, furnishing **2a** in 81–83% yields within 4–6 h at rt (entries 6–7). $NiBr_2$(DME) also catalyzed the desired transformation

Table 1. Optimization Studies for the Formation of δ-Carboline 2a



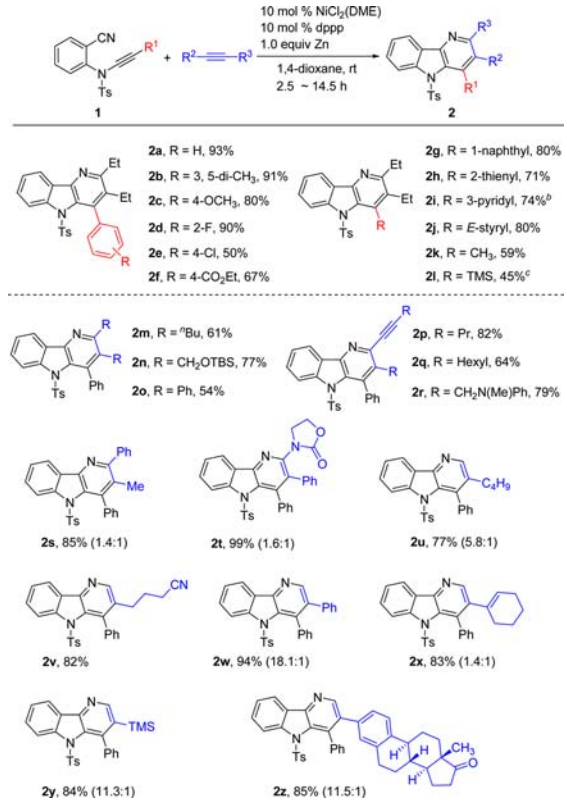
entry	catalyst	ligand (mol %)	solvent	time (h)	yield (%)[a]
1	$NiCl_2$(DME) (10)	$PMePh_2$ (20)	DCM	4	61
2	$NiCl_2$(DME) (10)	PBu_3 (20)	DCM	4	-(94)
3	$NiCl_2$(DME) (10)	PPh_3 (20)	DCM	8	59
4	$NiCl_2$(DME) (10)	P(p-$CF_3C_6H_4$)$_3$ (20)	DCM	4	62
5	$NiCl_2$(DME) (10)	dppe (10)	DCM	12	70
6	$NiCl_2$(DME) (10)	dppp (10)	DCM	6	83
7	$NiCl_2$(DME) (10)	dppb (10)	DCM	4	81
8	$NiCl_2$(DME) (10)	dppf (10)	DCM	12	6
9	$NiCl_2$(DME) (10)	2, 2′-bipy (10)	DCM	4	-(82)
10	$NiBr_2$(DME) (10)	dppp (10)	DCM	6	83
11	$Ni(acac)_2$ (10)	dppp (10)	DCM	6	20
12	$NiCl_2$(DME) (10)	dppp (10)	DCE	6	57
13	$NiCl_2$(DME) (10)	dppp (10)	1,4-dioxane	2.5	89
14	$NiCl_2$(DME) (10)	dppp (10)	THF	4	80
15[b]	$NiCl_2$(DME) (10)	dppp (10)	1,4-dioxane	2.5	93
16[b,c]	$NiCl_2$(DME) (10)	dppp (10)	1,4-dioxane	2.5	89
17[b]	$NiCl_2$(DME) (5)	dppp (5)	1,4-dioxane	12	68
18[b]	$NiCl_2$(dppp) (10)	-	1,4-dioxane	5	67
19[b]	$NiCl_2$(DME) (10)	-	1,4-dioxane	2.5	-(94)
20[b]	-	dppp (10)	1,4-dioxane	2.5	-(97)

[a]Isolated yields. Unless noted, all the reactions were carried out using **1a** (1 equiv) and 3-hexyne (1 equiv). The yields of the recovered **1a** are shown in parentheses. [b]**1a** (1.05 equiv) and **2a** (1.0 equiv) were used. [c]0.2 equiv of Zn was used.

efficiently (entry 10). However, $Ni(acac)_2$ was ineffective (entry 11). The reaction also proceeded smoothly in 1,4-dioxane and THF, in which **2a** was obtained in 89% and 80% yields, respectively (entries 13–14). The best result was achieved by using a slight excess amount of ynamide **1a** (1.05 equiv, 93% yield of **2a**, entry 15). Lowering the Ni catalyst loading to 5 mol % led to a marked decrease in the yield of **2a** (entry 17). The use of a preassembled nickel phosphine complex $NiCl_2$(dppp) also afforded a lower yield of **2a** (entry 18). As expected, **2a** was not observed in the absence of a ligand or a Ni catalyst (entries 19–20).

With optimized reaction conditions established (Table 1, entry 15), the substrate scope was next evaluated. The scope of ynamide-nitriles was first investigated using 3-hexyne as the reaction partner. As shown in Scheme 2, a wide range of

Scheme 2. Scope of Ynamide-Nitriles and Alkynes[a,b,c]



[a]Isolated yield. Only the structure of the major regioisomer is shown. The ratio of two regioisomers is shown in the paretheses. [b]60 °C, 24 h. [c]50 °C, 48 h.

functional groups including aryl, heteroaryl, vinyl, alkyl, and TMS groups on the alkyne terminus were compatible for this reaction, leading to the desired δ-carbolines in moderate to excellent yields. The reactions of ynamides bearing an electron-donating group such as 3,5-dimethyl or p-MeO on aryl rings resulted in high yields of δ-carbolines **2b** and **2c**. Substrates with an electron-withdrawing substituent on the aryl ring such as o-F, p-Cl, and p-CO_2Et proved to be also suitable, furnishing **2d–2f** in 50–90% yields. Notably, a chlorine substituent, which is not well-tolerated in Ni-catalyzed reactions, remained intact and the desired **2e** was obtained in moderate yield. A sterically demanding 1-naphthyl substituted ynamide gave the corresponding **2g** in 80% yield. Heteroaryl-substituted ynamides (e.g., 2-thienyl- or 3-pyridyl-substituted) transformed to **2h** and **2i** successfully in 71–74%

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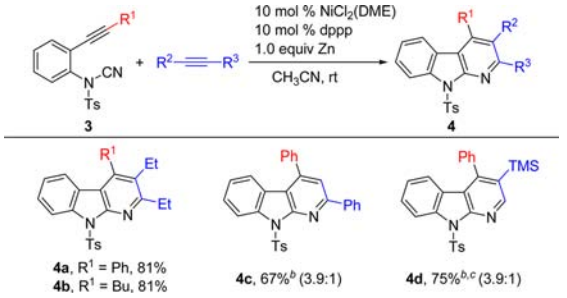
yields. In the latter case, higher a reaction temperature (60 °C) and longer reaction time (24 h) were required to complete the reaction. Ynamide with an alkenyl group was well accommodated, leading to the product **2j** in 80% yield. Alkyl-substituted ynamides, as exemplified by one that was methyl-substituted, was converted into **2k** smoothly. A TMS substituent could also be incorporated into the product **2l** which might be further functionalized.

Next, the scope of alkynes was investigated. It was observed that, for symmetrical internal alkynes, those bearing alkyl or aryl groups underwent cycloaddition efficiently to provide **2m**−**2o** in 54−77% yields, and functional groups such as OTBS on the alkyl side chain was well tolerated. The reactivity of a series of unsymmetrical alkynes was also evaluated. Cycloadditions of 1,3-butadiynes bearing *n*-propyl, *n*-hexyl, or $-CH_2N(Me)Ph$ groups with **1a** proceeded regioselectively to afford **2p**−**2r** in 64−82% yields, in which the alkynyl moiety was located closer to the pyridine nitrogen in the major regioisomers. The regioselectivity is consistent with those observed in Ni(0)/BPh_3 catalyzed reactions.[8] The reaction of 1-phenylpropyne with **1a** gave carboline **2s** as a mixture of two regioisomers with a ratio of 1.4:1. The ratio of regioisomers was much lower than that observed using *o*-(cyano)phenyl propargyl ether as the substrate.[8] Interestingly, ynamides such as 3-(phenylethynyl)oxazolidin-2-one cyclized readily with **1a** to afford amino-functionalized *δ*-carboline **2t** in quantitative yield. Importantly, terminal alkynes, which usually resulted in low product yields in metal-catalyzed [2 + 2 + 2] cycloaddition reactions due to the rapid trimerization or oligomerization reactions,[6a,b,e] cyclized quite well with **1a** under the current reaction conditions. For example, the reactions of **1a** with 1-hexyne, hex-5-ynenitrile, phenylacetylene, 1-ethynylcyclohex-1-ene, or ethynyltrimethylsilane afforded the corresponding **2u**−**2y** in 77−94% yields. In most cases, two regioisomers were observed with the ratio ranging from 1.4:1 to 18.1:1, where the larger substituent is distal to the pyridine nitrogen in the major regioisomers. Especially, high regioselectivities were observed in the cases of cyanoalkyl-, phenyl-, and TMS-substituted alkynes. Notably, the regioselectivity is the reverse of that observed in our previous study using *o*-(cyano)phenyl propargyl ether as the substrate.[8] To demonstrate the synthetic utility of this reaction, a terminal alkyne with an 1,3,5(10)-estratrien-3-ol-17-one derivative was prepared, which reacted efficiently with **1a** to produce the carboline **2z** in 85% yield. It is worth mentioning that all the regioisomers obtained in the above reactions could be easily separated through column chromatography. The structure of *δ*-carboline products was confirmed by X-ray crystallographic analyses of **2p**, **2s**′ (minor isomer), **2t**′ (minor isomer), and **2u** (major isomer).[13] In addition, the tosyl-protection group could be easily removed by TBAF in refluxing THF. For example, under these conditions, carboline **2a** transformed to detosylated product **2a**′ in 82% yield.[13]

The above results prompted us to extend the method for the synthesis of *α*-carbolines using alkyne-cyanamides as the substrates. Although cyanamides have been used in partially or fully intermolecular [2 + 2 + 2] cycloaddition reactions,[14] there is no report of [2 + 2 + 2] cycloadditions involving alkyne-tethered cyanamides with alkynes. To our delight, the desired *α*-carbolines were formed in good to high yields by switching the solvent from 1,4-dioxane to CH_3CN (Scheme 3). Both aryl- and alkyl-substituted alkynes successfully provided the *α*-carbolines **4a** or **4b** in high yields. Internal alkynes and terminal alkynes were all compatible for this reaction. Interestingly, the opposite

Scheme 3. Synthesis of *α*-Carbolines[a,b,c]

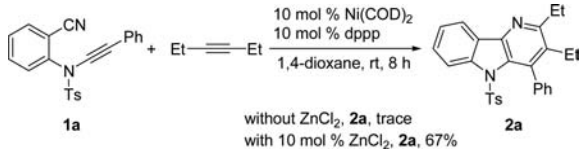


[a]Isolated yields. Only the structure of the major regioisomer was shown. [b]50 °C. [c]1,4-Dioxane was used as the solvent.

regioselectivity was observed when phenyl and TMS substituted acetylenes were employed as the alkyne substrates.

To understand the possible role of the in situ generated Lewis acid, the following control experiments were performed (Scheme 4). Reaction of ynamide **1a** with 3-hexyne catalyzed by 10 mol %

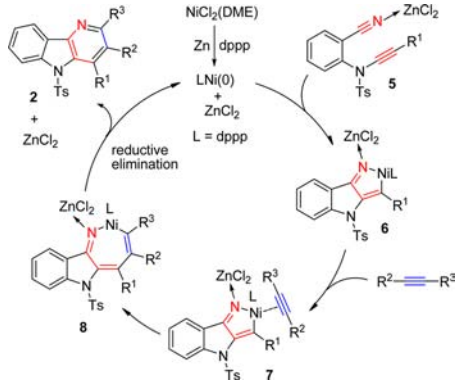
Scheme 4. Control Experiments



of $Ni(COD)_2$/dppp afforded only a trace of **2a**. However, addition of 10 mol % of $ZnCl_2$ to the reaction mixture led to the formation of **2a** in 67% yield. The results suggest that the Lewis acid may also be crucial for successful transformation in our catalytic system using Ni(II) as precursor.

On the basis of the above experimental results and our previous work,[8] we propose the following reaction mechanism for this reaction (Scheme 5). The observed effects of Lewis acid

Scheme 5. Possible Reaction Mechanism



led us to consider a mechanism involving the activation of the nitrile moiety through coordination with a Lewis acid,[15] thereby increasing the electrophilicity of the nitrile. Subsequent oxidative coupling of the alkyne with the nitrile moiety at the Ni(0) center is then facilitated leading to the formation of an azanickelacycle **6**. Insertion of the alkyne to intermediate **6** followed by reductive elimination delivers the *δ*-carboline products **2**. The high regioselectivity observed in most cases of terminal alkynes in the synthesis of *δ*-carbolines appears to be dominated by

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electronic effects rather than steric factors. The Ni−C bond is highly nucleophilic in azanickelacycle intermediate **7** due to the presence of an enamine moiety, causing a clear and distinct preference for insertion of terminal alkynes through electronic control. Thus, the C−C bond formation selectively occurs at the more positive inner site of the terminal alkyne. It should be noted that, in the presence of a Lewis acid such as BPh_3 or $AlMe_3$, the carbocyanation of nitrile with alkynes catalyzed by nickel might occur under appropriate reaction conditions;[16] however, such a reaction was not observed in our reaction system.

In summary, we have developed a new method for the synthesis of δ- and α-carbolines through nickel-catalyzed [2 + 2 + 2] cycloaddition of ynamide-nitriles or alkyne-cyanamides with alkynes. The catalytic system of $NiCl_2$(DME)/dppp/Zn with a low-cost Ni(II)-precursor was first utilized in nickel-catalyzed [2 + 2 + 2] cycloaddition reactions. Not only internal alkynes but also terminal alkynes undergo the desired cycloaddition reactions efficiently to furnish the carboline derivatives with wide diversity and functional group tolerance. Further applications of this new catalytic system to the synthesis of diverse nitrogen heterocycles are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03385.

Experimental details, spectroscopic characterization of all new compounds (PDF)
X-ray crystallography of **2p** (CIF)
X-ray crystallography of **2s′** (minor isomer) (CIF)
X-ray crystallography of **2t′** (minor isomer) (CIF)
X-ray crystallography of **2u** (major isomer) (CIF)
X-ray crystallography of **4c** (major isomer) (CIF)

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Notes

The authors declare no competing financial interest.

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