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ARTICLE TYPE

Eco-friendly synthesis of pyridines *via* rhodium-catalyzed cyclization of diyne with oxime

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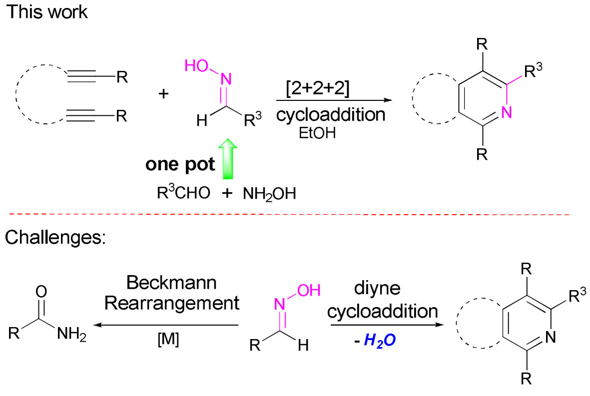
We described a new route for the synthesis of pyridines *via* [2+2+2] cycloaddition of diynes and oximes catalyzed by $Rh(NBD)_2BF_4$/MeO-Biphep using ethanol as an alternative green reaction medium, affording the desired pyridine derivatives with the yield up to 93%. This environmentally friendly method meets the requirement for green chemistry in minimizing pollution from solvent and is tolerant of a range of functional groups.

High functionalized pyridines have attracted considerable attention in organic chemistry because they could contribute to widespread application in academic science and industrial filed, such as pharmaceuticals, surfactants, dyestuffs, agrochemical [1]. Transition-metal-catalyzed [2+2+2] cycloaddition of diynes and nitriles is a well established synthetic tool for the preparation of pyridine derivatives[2-8]. The past decades, numerous catalyst systems have been reported. However, these synthetic approaches either suffer from harsh conditions or use of volatile, toxic and flammable organic solvents. Therefore, chemists endeavored to develop elegant and clean technologies to improve traditional method with relatively environment-friendly benign solvent. In this context, we reported ruthenium-catalyzed cycloaddition of diynes and nitriles in pure water under mild conditions[9]. However, limited scope of nitriles suppress the development of this method and bestir us to design a new strategy–to afford pyridines. Based on that we demonstrated novel annulations of diynes and oximes, delivering pyridines in satisfactory result[10], figuring out the following challenges: 1) insufficient reactivity of the C=N double bond of oxime remains a challenging problem towards cycloaddition [11], 2) the metal-catalyzed rearrangement[12] or Beckmann rearrangement[13] of oximes into corresponding amides should be suppressed or abbreviated, and 3) unneglectable amount of water generated in situ from dehydration of cycloadduct has an directly effect on the efficiency of metal catalyst. However, volatile and toxic organic solvent CF_3CH_2OH was used. Considering the growing environmental and economical concerns, industrial availability and general applicability, it is essential for synthetic community to develop a friendly protocol for formation of pyridines using green reaction media. Be similar with water, ethanol was validated as a green solvent for organic reactions, providing a prospective field of green chemistry[14]. In continuation with our ongoing research into the development of green chemistry method, this paper we reported an eco-friendly, simple and efficient synthesis of high substituted pyridines from diynes and aldoximes catalyzed by the combination of rhodium catalyst and MeO-Biphep with a focus on benign solvent such as EtOH with up to high yield (Scheme 1).

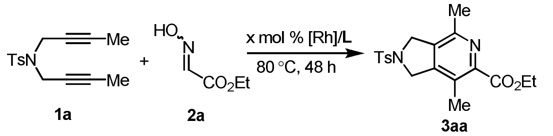


Scheme 1 Synthesis of pyridines *via* cycloaddition.

Reactions of NTs-diyne **1a** with ethyl 2-(hydroxyimino) acetate **2a** catalyzed by complexes generated from $Rh(NBD)_2BF_4$ and a series of bidentate phosphine ligands (**L1**-**L6**) in ethanol media are summarized in Table 1. The initial use of BINAP as ligand showed low reactivity, providing pyridine **3aa** in 38% yield (entry 1). Several bidentate phosohines containing biaryl backbones received in moderate yields while the best result was formed when MeO-Biphep was employed (entry 2-5). Interestingly, no product was observed when an obviously different bidentate phposphine such as dppf and dppe was used (entry 4 and entry 5). The reaction was further optimized by increasing the loading of metal source and ligand from 5 mol% to 10 mol%, furnishing an obvious improvement (entry 6). To our delight, the efficiency of this cycloaddtion of **1a** and **2a** could be substantially enhanced by raising the loading of **2a** from 3.8 equiv to 16 equiv, achieving an efficient and fast cyclization to afford the highest yield (96%, entry 8). Moreover, lowering the reaction time caused an slight decrease in yield (entry 9). Overall, the optimal reaction conditions were: $Rh(NBD)_2BF_4$ (10 mol%), MeO-biphep (10 mol%) in EtOH at 80 °C in the presence of 4Å MS (400 mg).

With the optimized catalytic system in hand, We then investigated the scope of diynes and the results are highlighted in Table 2. In general, nitrogen-based diynes[15] derived from various sulfamide derivatives participated in cycloaddition

Table 1 Optimization of reaction conditions for pyridine formation in environmentally friendly media[a]



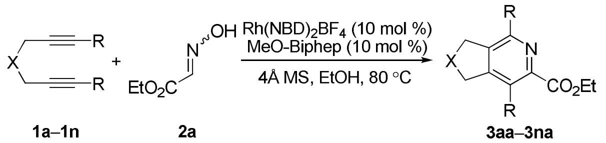
entry	x(mol %)	ligand	yield (%)[b]
1	5	BINAP	38
2	5	Segphos	54
3	5	MeO-Biphep	75
4	5	dppf	trace
5	5	dppe	trace
6	10	MeO-Biphep	80
7[c]	10	MeO-Biphep	87
8[d]	10	MeO-Biphep	96
9[e]	10	MeO-Biphep	91

[a] Reaction conditions: diyne **1a** (0.25 mmol), oxime **2a** (3.8 equiv), $Rh(NBD)_2BF_4$ (x mol %), ligand (x mol %), 4Å MS (400 mg), EtOH (6 mL) at 80 °C for 48 h. [b] Determined by HPLC with 1-methylnaphthalene as internal standard. [c] **2a** (8 equiv). [d] **2a** (16 equiv). [e] **2a** (16 equiv), 36 h.

with**2a** to afford the corresponding pyridines in moderate to high yields (entries 1-12). Diyne containing electron-withdrawing at the ortho position reacted more smoothly than the para-substituted compounds, delivering higher yields respectively (entries 1, 2 and entries 3, 4). In contrast, when diynes bearing an electron-donating group, such as **1a** and **1f**, were subjected to the standard reaction conditions, the expected products **3aa** were obtained in better yield (entries 5, 6). Electron-rich (i.e., -MeO), electron-neutral (i.e., -H) substrates underwent [2+2+2] cyclization with **2a** smoothly in 80% and 81% yield (entries 7, 8). However, diyne derived from 4-bromobenzene-sulfonamide afforded **3ha** and **3ia** in a 5 : 3 ratio with an overall yield of 81% because of reduction of the bromine group (entry 9). In accordance with these observations, the reaction with N,N-di(but-2-ynyl)methanesulfonamide **1j** or N,N-di(but-2-ynyl)naphthaene-2-sulfonamide **1k** gave the desired products in respective yields of 72% and 79% (entries 10, 11). With this satisfactory result in hand, we decided to use terminal diyne **1l** in this cyclization. To our satisfaction, terminal diyne **1l** was successfully applied to the synthesis of pyridine, providing the target product **3la** in 73% yield under slow dropwise addition condition at the effort of minimizing the dimerization product (entry 12). Encouraged by aboved promising results, we disclosed that the reaction of **1m** derived from benzamide with **2a** proceeded favorably at 80 °C for 48 h, delivering **3ma** in 75% yield (entry 13). Extremely noteworthy is that the cycloaddition of ether-based diyne **1n** with **2a** also resulted in good yield (entry 14).

We next focused on the cyclization of **1a** with a variety of aryloximes using the optimized conditions and the results are listed in Table 3. Comparing to the previous catalyst system, a serial of aryloximes cyclized with **1a** successfully to achieve pyridines but with less reactivity and different regulation. **2b** and **2c** reacted smoothly with **1a** to deliver pyridines **4ab** and **4ac** in acceptable yield while only trace amount of pyridine was detected when sterically hindered substrate **2o** was applied to this reaction (entries 1, 2, 14). Aryloximes with electron-withdrawing groups such as 3-Br, 4-Br or electron-neutral group on the benzene ring afforded pyridine derivatives in moderate yield (entries 3-5). If the substituent on the aryloximes was strong electron-withdrawing groups, the annulations just gave the product in relatively lower yield (entries 6-8). Aryloximes with strong electron-donating groups were proved to be less active substrates (entries 9-11). Notely, both 2-naphthaldehyde oxime **2m** and heterocyclic oxime **2n** reacted favorably with **1a** in respective yields of 26% and 15%. To our disappointment, no reaction occurred for alkyloximes such as acetaldehyde oxime **2p** and 3-phenylpropanal oxime **2q** (entries 15-16).

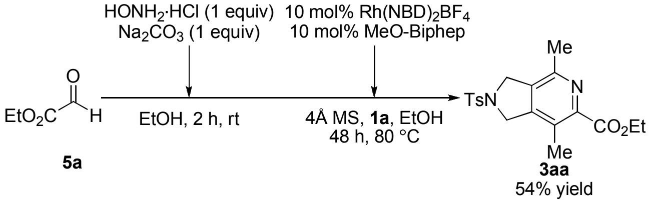
Table 2 Synthesis of Pyridines from Diynes (**1a**–**1n**) and Ethyl 2-(hydroxyimino)acetate **2a**[a]



entry	X	R	yield (%)[b]
1	4-$ClC_6H_4SO_2N$ (**1b**)	R = Me	83 (**3ba**)
2	2-$ClC_6H_4SO_2N$ (**1c**)	R = Me	92 (**3ca**)
3	4-$NO_2C_6H_4SO_2N$ (**1d**)	R = Me	60 (**3da**)
4	2-$NO_2C_6H_4SO_2N$ (**1e**)	R = Me	66 (**3ea**)
5	4-$CH_3C_6H_4SO_2N$ (**1a**)	R = Me	93 (**3aa**)
6	2-$CH_3C_6H_4SO_2N$ (**1f**)	R = Me	81 (**3fa**)
7	4-$MeOC_6H_4SO_2N$ (**1g**)	R = Me	80 (**3ga**)
8	$C_6H_4SO_2N$ (**1h**)	R = Me	81 (**3ha**)
9	4-$BrC_6H_4SO_2N$ (**1i**)	R = Me	30[c] (**3ia**)
10	CH_3SO_2N (**1j**)	R = Me	72 (**3ja**)
11	2-naphthylSO_2N (**1k**)	R = Me	79 (**3ka**)
12	4-$CH_3C_6H_4SO_2N$ (**1l**)	R = H	73[d] (**3la**)
13	C_6H_5CON (**1m**)	R = Me	75 (**3ma**)
14	O (**1n**)	R = Me	69 (**3na**)

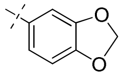
[a] **1a**–**1n** (0.25 mmol) was added to a solution of $Rh(NBD)_2BF_4$ (10 mol %), MeO-Biphep (10 mol %) and **2a** (16 equiv, 0.4 ml) in EtOH, in the presence of 4Å MS (400 mg), then reacted for 48 h. [b] Isolated yield. [c] Debromide product **3ha** was formed in 51% yield. [d] **1l** was added slowly by syringe.

With the aim of expanding further application of the catalyst system, target product **3aa** was obtained when aldehyde **5a** and hydroxylamine were treated with diyne **1a** in one pot, abbreviating the operation process even with a lower yield (54% yield, vs 93% yield, Table 2, entry 5) (Scheme 2).



Scheme 2 One-pot formation of pyridines from aldehyde **5a**, hydroxylamine and diyne **1a**.

Table 3 Formation of pyridines from diynes **1a** and oximes **2b-2q** in EtOH[a]

entry	R	yield (%)[b]
1	4-MeC$_6$H$_4$ (**2b**)	31(**4ab**)
2	3-MeC$_6$H$_4$ (**2c**)	37(**4ac**)
3	C$_6$H$_5$ (**2d**)	60(**4ad**)
4	3-BrC$_6$H$_4$ (**2e**)	64(**4ae**)
5	4-BrC$_6$H$_4$ (**2f**)	50(**4af**)
6	3-FC$_6$H$_4$ (**2g**)	31(**4ag**)
7	3-CF$_3$C$_6$H$_4$ (**2h**)	38(**4ah**)
8	4-CF$_3$C$_6$H$_4$ (**2i**)	44(**4ai**)
9	4-MeOC$_6$H$_4$ (**2j**)	25(**4aj**)
10	3,4-MeOC$_6$H$_4$ (**2k**)	26(**4ak**)
11	 (**2l**)	29(**4al**)[c]
12	2-naphthyl (**2m**)	26(**4am**)[d]
13	2-furyl (**2n**)	15(**4an**)[e]
14	2-MeC$_6$H$_4$ (**2o**)	trace
15	CH$_3$ (**2p**)	N.D.
16	PhCH$_2$CH$_2$ (**2q**)	N.D.

[a] **1a** (0.25 mmol) was added to a solution of Rh(NBD)$_2$BF$_4$ (10 mol %), MeO-Biphep (10 mol %) and oximes (16 equiv) in EtOH, in the presence of 4Å MS (400 mg), then reacted for 48 h. [b] Isolated yield. [c] **2l** (14.0 equiv). [d] **2m** (5.3 equiv). [e] **2n** (4 equiv).

Conclusions

In conclusion, pyridines derivatives were successfully synthesized with up to high yields *via* the cationic rhodium(I)/MeO-biphep complex-catalyzed [2+2+2] cycloaddition of oximes with diynes using ethanol as a alternative green reaction medium. A range of functional groups and substitution patterns are compatible with this sequence. In addition, this catalyst system is expedient and practical to operate without preactivation of catalyst and it could tolerate moisture. From an environmental and industrial point of view, this simple, effective, economical, and eco-friendly tactic is run under mild conditions with emphasis on benign solvent: EtOH, progressive replacing the toxic solvent in the described literature. Besides the above developed feature, we also demonstrate one-pot reaction of aldehyde, hydroxylamine and diynes in terms of convenient operation, rendering pyridine in reasonable yield. Due to easy to handle and storage of oximes, further reactivity studies with oximes are currently underway.

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† Electronic supplementary information (ESI) available: [^{1}H, ^{13}C and ^{19}F and NMR analysis for all products]. See DOI: 10.1039/b000000x/

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Eco-friendly synthesis of pyridines *via* rhodium-catalyzed cyclization of diyne with oxime

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