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N Heterocycles

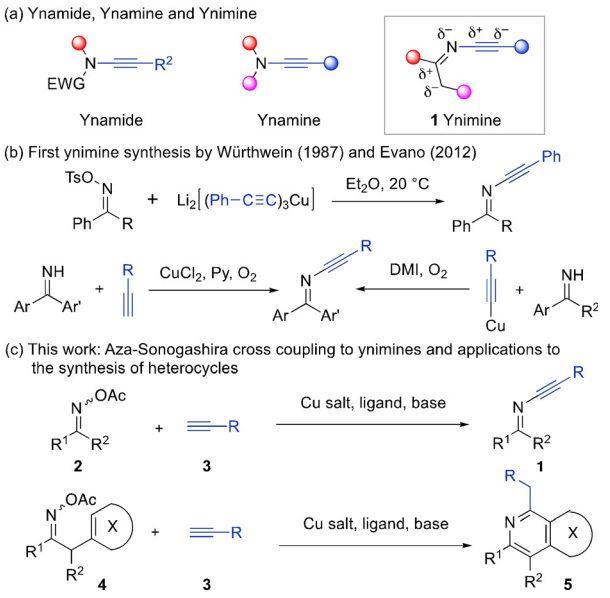
Copper-Catalyzed Aza-Sonogashira Cross-Coupling To Form Ynimines: Development and Application to the Synthesis of Heterocycles

*Rémi Lavernhe, Rubén O. Torres-Ochoa, Qian Wang, and Jieping Zhu**

Abstract: *Nitrogen-substituted alkynes, such as ynamines and ynamides, are versatile synthetic building blocks. Ynimines bearing additional nucleophilic and electrophilic centers relative to ynamines and ynamides are expected to have high synthetic potential. However, their chemical reactivity remains unexplored owing mainly to the lack of synthetic accessibility. We report herein a versatile copper-catalyzed synthesis of ynimines from readily available O-acetyl ketoximes and terminal alkynes. A wide range of O-acetyl ketoximes derived from diaryl ketones, aryl alkyl ketones and dialkyl ketones underwent cross-coupling with a diverse set of terminal alkynes to afford the ynimines in good to excellent yields. An unprecedented [5+1] heteroannulation reaction exploiting the reactivity of the ynimine generated in situ was subsequently developed for the synthesis of medicinally important heterocycles, including isoquinolines, azaindoles, azabenzofurans, azabenzothiophenes and carbolines.*

Stimulated by the development of efficient and practical methods to prepare ynamides (Scheme 1 a),[1] stabilized form of ynamines,[2] at the turn of this century, the synthetic potential of this multifunctional building block has been exploited extensively and many powerful transformations have been developed over the last two decades.[3] Ynimine **1** is yet another variant of ynamine possessing additional electrophilic and nucleophilic carbon centers. However, its chemistry remains essentially unexplored. Würthwein reported in 1987 the first synthesis of ynimines by reaction of ketoxime tosylates with higher order organocuprates (Scheme 1 b) and found that the two ynimines prepared (R = Ph and R = Me) were stable in air for only a few hours.[4] Twenty-five years later, Evano and co-workers described two complementary syntheses via oxidative cross-coupling of imines with alkynes or alkynyl copper species.[5] In view of the multifunctionalities of ynimines, many powerful transformations could in principle be envisaged. However, investigation on their chemical reactivities remains scarce due presumably to the limited synthetic accessibility.[6]

The elegant copper-catalyzed oxidative cross-coupling between imines and terminal alkynes developed by Evano is without doubt the most atom economic way to access ynimines. However, terminal alkynes in the presence of Cu salt[7] and copper acetylides[8] are readily dimerized under oxygen atmosphere. In addition, most of the primary imines, especially those derived from aryl alkyl and dialkyl ketones, are difficult to prepare and are extremely unstable. They also have the propensity to undergo copper-catalyzed dimerization to diazines.[5] Therefore, an excess of difficultly accessible primary imines is generally employed to favour the desired cross-coupling reactions. All these considerations prompted us to investigate the iminyl N-alkynylation using readily available and bench stable oxime esters as donors of iminyl moiety.[9] Herein, we report an operationally simple, general and scalable synthesis of ynimines **1** by way of copper-catalyzed aza-Sonogashira cross-coupling between *O*-acetyl



Scheme 1. Ynimines: structure and synthesis.

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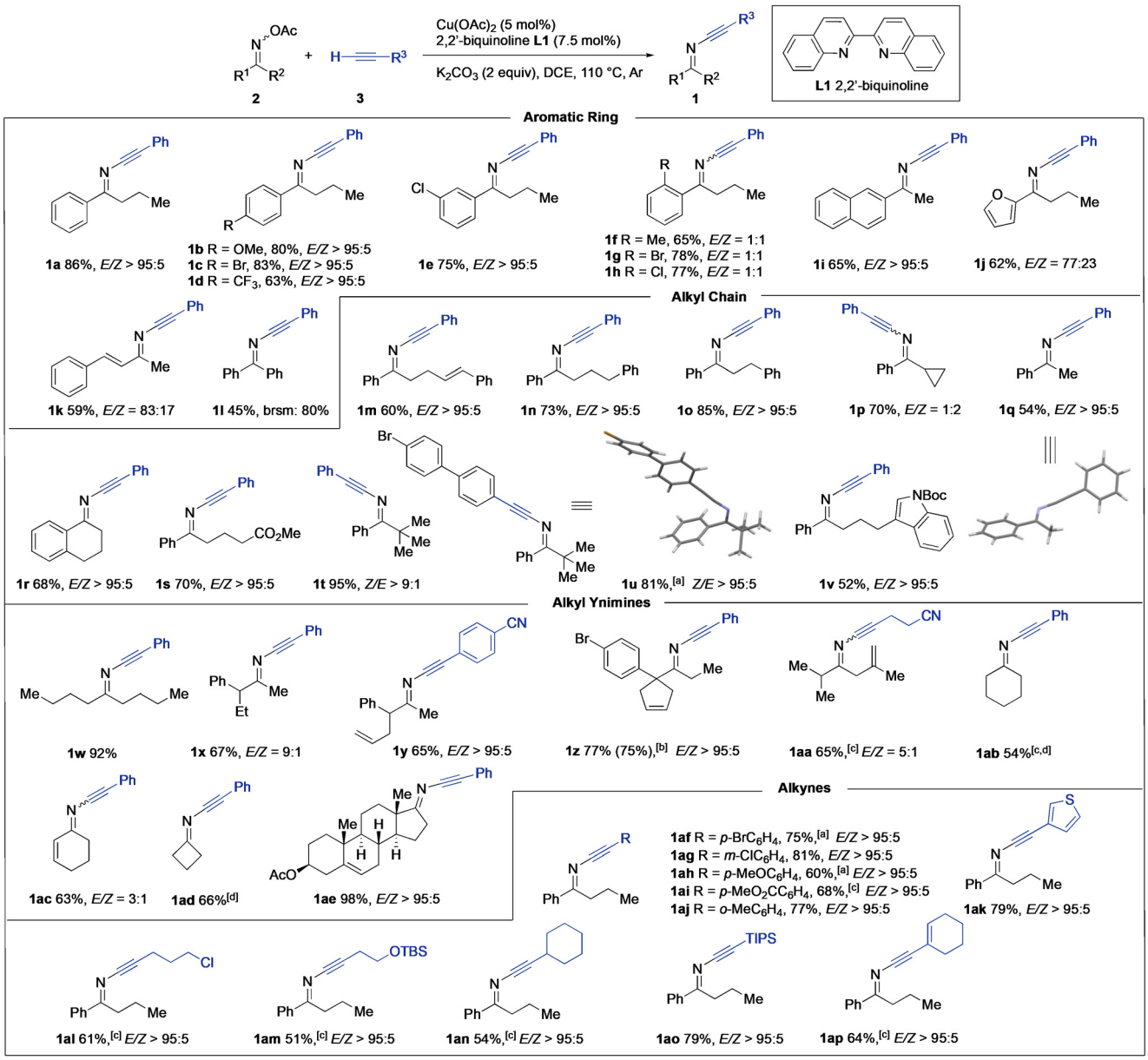
oximes **2** and terminal alkynes **3**. Taking advantage of the multifunctionalities of the resulting ynimines, a one-pot synthesis of medicinally important heterocycles **5**, such as isoquinolines, azaindoles, azabenzofuranes, azabenzothiophenes, β- and γ-carbolines, was subsequently developed through an unusual formal [5+1] heteroannulation reaction between oxime esters **4** and terminal alkynes **3** (Scheme 1c).

The weak N−O bond of oxime (e.g. BDE of MeCH=N−OH, 49.7 kcal mol^{-1}) and its *O*-acyl derivatives renders the reductive single electron transfer (SET) process facile. Indeed, most of Cu^{I} salts catalyzed reactions of *O*-acyl oxime **2** proceed through a SET process.[10] Notwithstanding this established fact, we reasoned that by fine tuning the ligand structure and the nature of the acyl group, it might be possible to switch the SET to two electron process achieving therefore the desired cross-coupling reaction.[11] We began our studies using ketoxime acetate **2a** (R^1 = Ph, R^2 = *n*Pr) and phenylacetylene (R = Ph, **3a**) as test substrates for conditions optimization (SI, Tables S1–S7). The key observations are summarized as follows: a) the *O*-acetyl oxime was superior than other *O*-acyl derivatives; b) $Cu(OAc)_2$ (5 mol%) was the catalyst of choice and 2,2′-biquinoline (**L1**) was the optimum ligand; c) solvents and bases other than DCE and K_2CO_3 led to low yields of ynimine **1a**; d) water was tolerated but the reaction setup had to be oxygen free; e) the reaction was hardly initiated at temperature below 80 °C. Overall, the optimum conditions consisted of performing the reaction of **2a** (0.1 mmol) with **3a** (0.2 mmol) in DCE in the presence of a catalytic amount of $Cu(OAc)_2$ (5.0 mol%), 2,2′-biquinoline (7.5 mol%) and potassium carbonate (2.0 equiv) under argon at 110 °C. Under these conditions, *E*-ynimine **1a** was isolated in 86% yield with an excellent *E*/*Z* selectivity (Scheme 2).

The reaction displays broad substrate scope across a wide range of both coupling partners (Scheme 2). Oxime acetates derived from aryl alkyl ketones irrespective of the electronic nature (donating or withdrawing) and positions (*ortho*, *meta* and *para*) of the substituents on the aromatic ring participated in the reaction to afford the corresponding ynimines (**1a**–**1h**) in good yields. Ynimines bearing a naphthyl (**1i**), a furanyl (**1j**) and a styryl (**1k**) group were equally accessible. Of mechanistic importance, oxime acetates with alkyl chains susceptible to undergo other known competitive reactions such as cyclization (**1m**),[12] remote C(sp^3)−H alkynylation (**1n**, **1v**)[13] or β-scission (**1u**, **1ad**, **1ae**)[14] were converted to the products with similar synthetic efficiency. Acyclic aliphatic oxime esters (**1w**–**1aa**) and cyclic ketone oxime esters including those derived from cyclohexanone (**1ab**), cyclohexenone (**1ac**), cyclobutanone (**1ad**) and dehydroepiandrosterone acetate (**1ae**) were successfully converted to the corresponding ynimines. Aryl acetylenes bearing electron withdrawing and electron donating groups (**1af**–**1aj**) on the aromatic ring underwent the N-alkynylation reaction to afford the desired products in good yields. Notably, alkyl substituted terminal alkynes (**1al**–**1an**), ethynyltriisopropylsilane (**1ao**) and 1,3-enyne (**1ap**) were effective reaction partners for this coupling reaction. The presence of functional groups (alkenes, methoxycarbonyl, aryl halide, alkyl chloride, silyl ether, acetate, nitrile) and heterocycles such as furan (**1j**), indole (**1v**) and thiophene (**1ak**) was well tolerated. A similar yield of **1z** was obtained when the reaction was performed at 1.0 mmol scale indicating the robustness of the protocol. All these ynimines are purified by conventional flash column chromatography on deactivated silica gel. The stereochemistry of the ynimines **1q** and **1u** was determined by single crystal X-ray diffraction analysis.[19] Ynimine **1q** derived from acetophenone was isolated as single *E* isomer whereas in the case of ynimine **1u** bearing a bulky *tert*-butyl group, the *Z* isomer was isolated as a major product. It is important to note that in (*E*)-**1q**, the phenyl ring is coplanar to the C=N double bond, whereas in (*Z*)-**1u**, the phenyl ring is almost perpendicular to the imine function to avoid the steric clash between the *ortho*-CH and the triple bond. The *E*/*Z* selectivity appeared therefore to be governed by both the steric and the stereoelectronic factors and the nonselective formation of **1f**–**1h** is the result of the counterbalance of these two factors. The stereochemistry of all other ynimines was assigned by comparison of the chemical shifts of the β-sp carbon, which is more shielded in the *Z* isomers (typically δ = 88–91 ppm) than the *E* isomers (δ = 93–100 ppm). We note that the stereochemistry of the oxime esters has no impact on that of the ynimines.

Isoquinolines **4** are important heterocycles found widely in bioactive natural products, pharmaceuticals and functional materials.[15] One recently developed approach involves transition metal catalyzed [4+2] heteroannulation between aryl ketone *O*-acyl oximes with alkynes.[16] However, one intrinsic drawback associated with this approach was the lack of regioselectivity when unsymmetrical alkynes or terminal alkynes were utilized as reaction partners,[17] except for the one developed by Kanai and Matsunaga.[18] As a prelude to explore the intrinsic reactivities of ynimines, a synthesis of these heterocycles through a formal [5+1] heteroannulation reaction was devised. We expected that the reaction of benzyl ketone *O*-acetyl oximes **5** with terminal alkynes **3** could afford directly the desired isoquinolines via ynimine intermediates. Gratefully, reaction of oxime ester **5a** (R^1 = Me, R^2 = Ph, R^3 = H) derived from 1,1-diphenylpropan-2-one with phenylacetylene (**3a**, R = Ph) under standard conditions afforded isoquinoline **4a** in 30% yield. Fine-tuning of the reaction conditions indicated that the tridentate pybox ligand **L2** was optimum leading to **4a** in 65% yield (SI, Table S8). The loading of $Cu(OAc)_2$ was reduced to 2.5 mol% in this case. This novel isoquinoline synthesis turned out to be generally applicable to a wide range of oxime acetates and terminal alkynes allowing a ready access to diversely substituted isoquinolines (Scheme 3). Arylacetylenes bearing a strong electron donating (OMe, **4d**) or withdrawing groups [CN (**4e**, **4ac**), COOMe (**4ad**)] participated in the reaction, so were alkylacetylenes (**4s**–**4u**). Electron-deficient alkynes, such as propiolate, are in general poor substrates for the Sonogashira-type cross-coupling reaction,[20] it is therefore interesting to note that *tert*-butyl propiolate took part in the reaction to afford isoquinoline **4v** in 60% yield. With 4-PinB-substituted phenylacetylene, formation of ynimine occurred at the expense of the alternative Chan–Lam C−N bond coupling process.[21] The presence of both electron-donating or withdrawing (**4af**/**4af′**) group on the phenyl ring of **4** is also well tolerated. Finally, moxaverine (**4ag**), a marketed vasodilator,

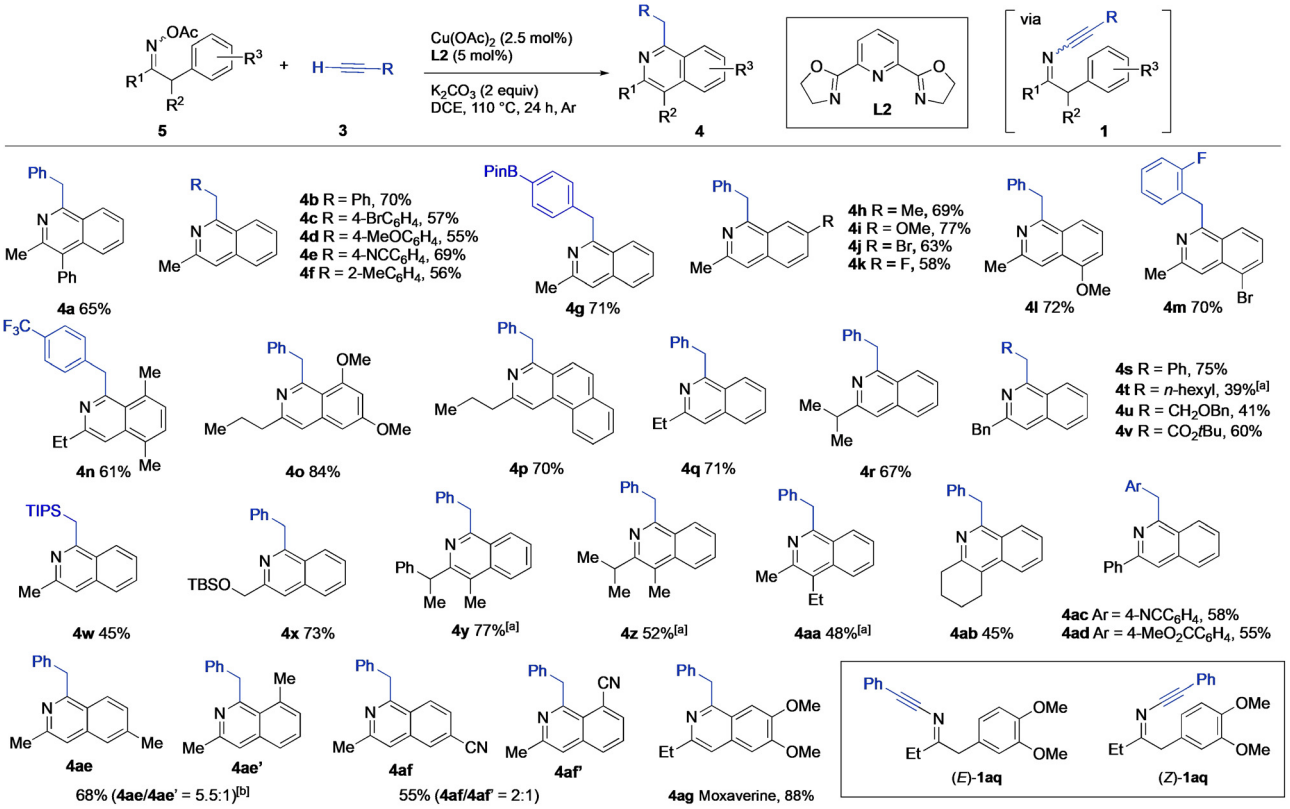


Scheme 2. Synthesis of ynimines. All reactions were performed with 0.1 mmol of **2** and 0.2 mmol of **3**. [a] The reaction was carried out at 120 °C. [b] The value in parenthesis refers to the reaction performed on a 1.0 mmol scale. [c] The reaction was carried out with 2.5 mol% $Cu(OAc)_2$ and 5 mol% 2,2′-biquinoline. [d] The reaction was carried out at 90 °C. Boc = *tert*-butoxycarbonyl, DCE = 1,2-dichloroethane, TBS = *tert*-butyldimethylsilyl, TIPS = triisopropylsilyl.

has been synthesized in 88% yield from simple oxime ester **5v** (R^1 = Et, R^2 = H, R^3 = 3,4-dimethoxy) and phenylacetylene **3a** (R = Ph). Many functional groups such as halides, cyano, alkoxycarbonyl, ether, silyl and boronate groups are tolerated under these heteroannulation conditions. Monitoring the reaction progress indicated clearly that ynimines were the intermediates on the way to these heterocycles and in case the cyclization was slow, addition of triflic acid (TfOH, 5 equiv) to the reaction mixture accelerated effectively the cyclization step (**4t**, **4x**–**4aa, 5c**–**5i**). Of mechanistic importance, when an isolated mixture of ynimine (*E*)-**1aq** and (*Z*)-**1aq** (1.9:1) was resubmitted to the reaction conditions, compound **4ag** was isolated in 83% yield. Monitoring the reaction progress indicated that no significant change of the *E*/*Z* ratio during the reaction. Therefore, we speculate that the *E*/*Z* isomerization might not be the rate-limiting step.

Using heteroarene derived oxime ester **6** as reaction partners of alkynes **3**, 5-azaindoles **7a** and **7b**, 5-azabenzofuran **8**, 5-azabenzothiophene **9** and 6-azabenzothiophene **10** were readily prepared (Scheme 4a).[22] Finally, β-carboline **11** and γ-azacarbazole **12** were synthesized in good yields by reaction of **3a** with C3- and C2-substituted indoles **13** and **14**, respectively (Scheme 4b).

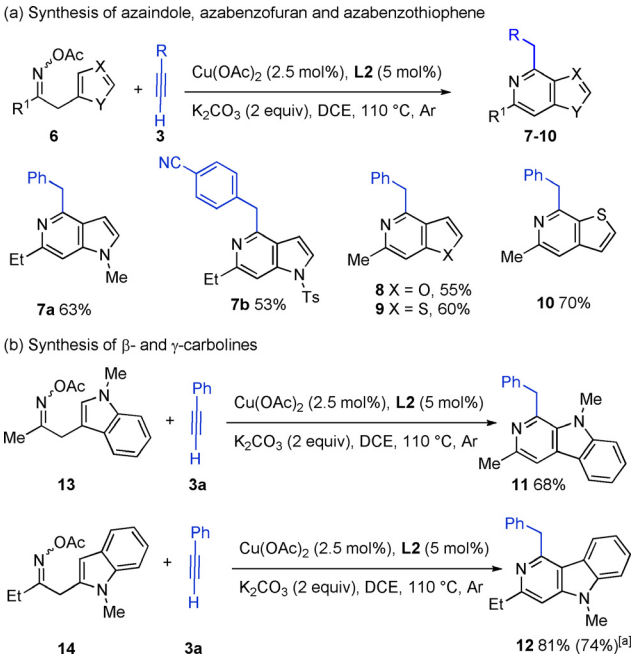
Copper-catalyzed cyclization of γ,δ-unsaturated *O*-acyl oximes[9a] and β,γ-unsaturated *O*-acyl oximes[23] to dihydropyrroles and pyrroles via iminyl radical intermediates is



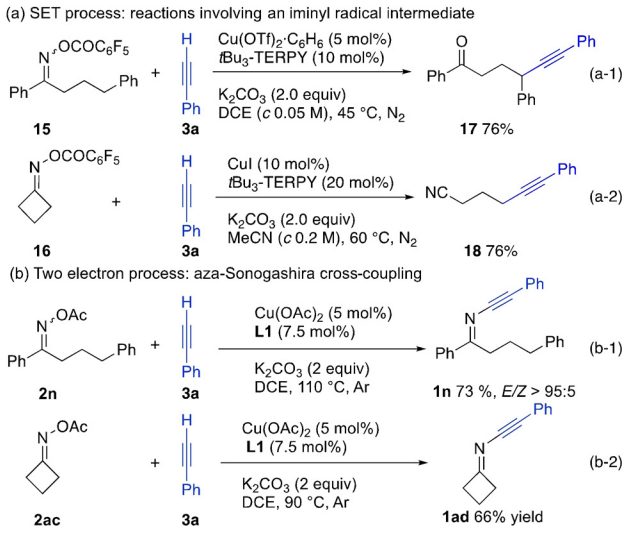
Scheme 3. A [5+1] heteroannulation approach to isoquinolines via ynimine intermediates. All reactions were performed with 0.1 mmol of **5** and 0.2 mmol of **3**. [a] TfOH (5 equiv) was added after 12 h. [b] The reaction was carried out at 100 °C. Bn = benzyl, Pin = pinacolato.

known. However, these competitive reactions were not observed under our present reaction conditions in the preparation of compounds **1m**, **1y** and **1aa**. Even more relevantly, copper-catalyzed reactions of phenylacetylene (**3a**) with oximes **15** or **16** affording C(sp^3)–H alkynylated ketone **17** (Scheme 5a-1) or nitrile **18** (Scheme 5a-2), respectively, by 1,5-HAT and β-scission of the in situ generated iminyl radicals, have recently been reported.[24] Notwithstanding these precedents, the same reactions of **3a** with **2n** or **2ac** under present conditions afforded **1n** (Scheme 5b-1) and **1ad** (Scheme 5b-2) without competitive formation of **17** and **18**. Furthermore, addition of TEMPO, a radical scavenger, to the reaction of **2a** with **3a** did not inhibit the formation of **1a**. All these experimental observations indicate that iminyl radicals might not be involved in the formation of ynimines.

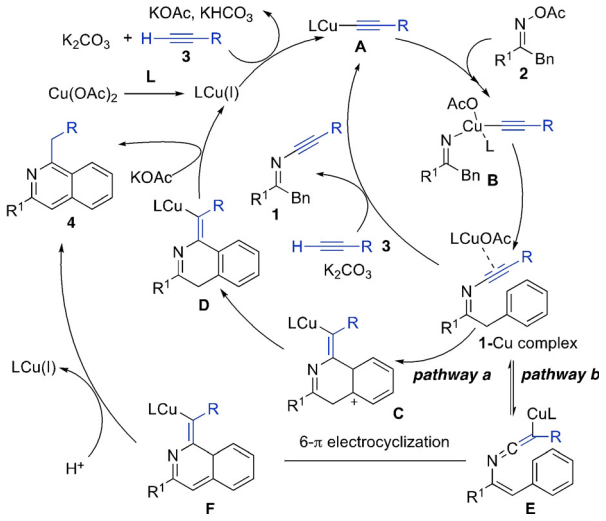
On the basis of these results, a possible reaction pathway is proposed for the formation of ynimines **1** and isoquinolines **4** (Scheme 6). Potassium carbonate promoted reaction of in situ generated CuOAc species with terminal alkyne would afford the copper acetylide **A** which upon oxidative addition to the N–O bond of *O*-acetyl oxime **2** would furnish the Cu^{III} complex **B**.[25] Reductive elimination of the latter would provide ynimine **1**–Cu^{I} complex which, upon ligand exchange with terminal alkyne **3**, would afford ynimine **1** with concurrent regeneration of the Cu^{I} acetylide **A**, completing therefore the catalytic cycle. For the conversion of ynimine **1** to isoquinoline **4**, two possible reaction manifolds could be



Scheme 4. A [5+1] heteroannulation approach to bi- and tricyclic heteroarenes via ynimine intermediates. All reactions were performed with 0.1 mmol of the oxime ester and 0.2 mmol of alkyne **3**. [a] The value in parenthesis refers to the reaction performed on a 1.0 mmol scale.



Scheme 5. Reaction divergency depending on the conditions. tBu$_3$-TERPY = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine.



Scheme 6. Possible reaction pathways.

envisaged. Friedel–Crafts-type cyclization of the **1**–Cu complex would afford intermediate **C** which upon deprotonation would be converted to **D** (pathway a). Protonation of **D** followed by aromatization would provide isoquinoline **4**. Alternatively, the **1**–Cu complex could be in equilibrium with enamino-ketenimine **E** (pathway b). The 6-π electrocyclization of the latter would then afford **F** which, after protonation and aromatization, would be converted to product **4** with concurrent regeneration of Cu^{I} species. While both pathways might be occurring concurrently, the fact that both *E* and *Z* ynimines cyclized to isoquinolines and that the electron-poor arene participated in the cyclization (see Scheme 3, **4af**/**4af′**) indicated that the latter mechanistic manifold might be operational.

In summary, we have developed an operationally simple Cu(OAc)$_2$-catalyzed synthesis of elusive ynimines from readily available *O*-acetyl oximes and terminal alkynes with a broad substrate scope. The ready accessibility of these multifunctional building blocks allowed us to develop a one-pot synthesis of medicinally important isoquinolines, pyridines, azabenzofurans, azabenzothiophenes and carbolines. This [5+1] heteroannulation reaction between oximes and terminal alkynes involves a 1,1-difunctionalization of terminal alkynes which is conceptually different from the previous approaches. We believe that the present work could stimulate the development of hitherto underexploited ynimine chemistry and impact the field of heterocyclic chemistry, natural product synthesis as well as medicinal chemistry.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: cross-coupling · domino reactions · heterocycles · homogeneous catalysis · ynimines

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