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Report

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Copper-Catalyzed Modular Access to N-Fused Polycyclic Indoles and 5-Aroyl-pyrrol-2-ones via Intramolecular N–H/C–H Annulation with Alkynes: Scope and Mechanism Probes

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Summary of main observation and conclusion Copper-catalyzed intramolecular N–H/C–H annulation with alkynes has been developed. A variety of densely functionalized heterocycles, such as pyrrolo[1,2-a]indoles, indolo[1,2-c]quinazolin-2-ones, oxazolo[3,4-a]indoles, and imidazo[1,5-a]indoles, were synthesized in an atom- and step-economical manner, owing to the high modularized feature of aniline moiety, the linker moiety, as well as the alkyne moiety. By simply changing the oxidant from DTBP to TEMPO, the reaction could readily be transformed to the aminooxygenation pathway, which grabs one oxygen atom from the TEMPO to generate 5-aroyl-pyrrol-2-ones. Mechanistic experiments indicate that vinyl radical is involved in this reaction and an amidyl-radical-initiated radical cascade might be responsible for this transformation.

Background and Originality Content

Fused heterocyclic compounds constitute one of the most significant structural motifs in natural products and pharmaceuticals, among which polycyclic indoles are important subtypes.[1] For example, the melatonin analogues featuring a tricyclic indole cores show stronger anti-inflammatory and anti-nociceptive activity compared to melatonin itself.[1b] The artificial nucleotide pairs dCPPI has been used to stablize the DNA triplexes.[1c] Flinderole C, a tricyclic indole alkaloid isolated from the plant genus Flindersia, shows significant antimalarial activity.[1d] MK-7246 was disclosed by Merck researchers as a potent and selective CRTH2 antagonist for the potential treatment of respiratory disease.[1e]

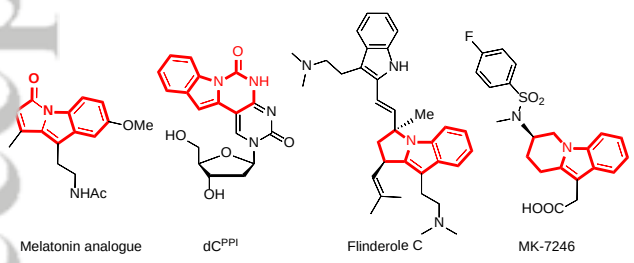


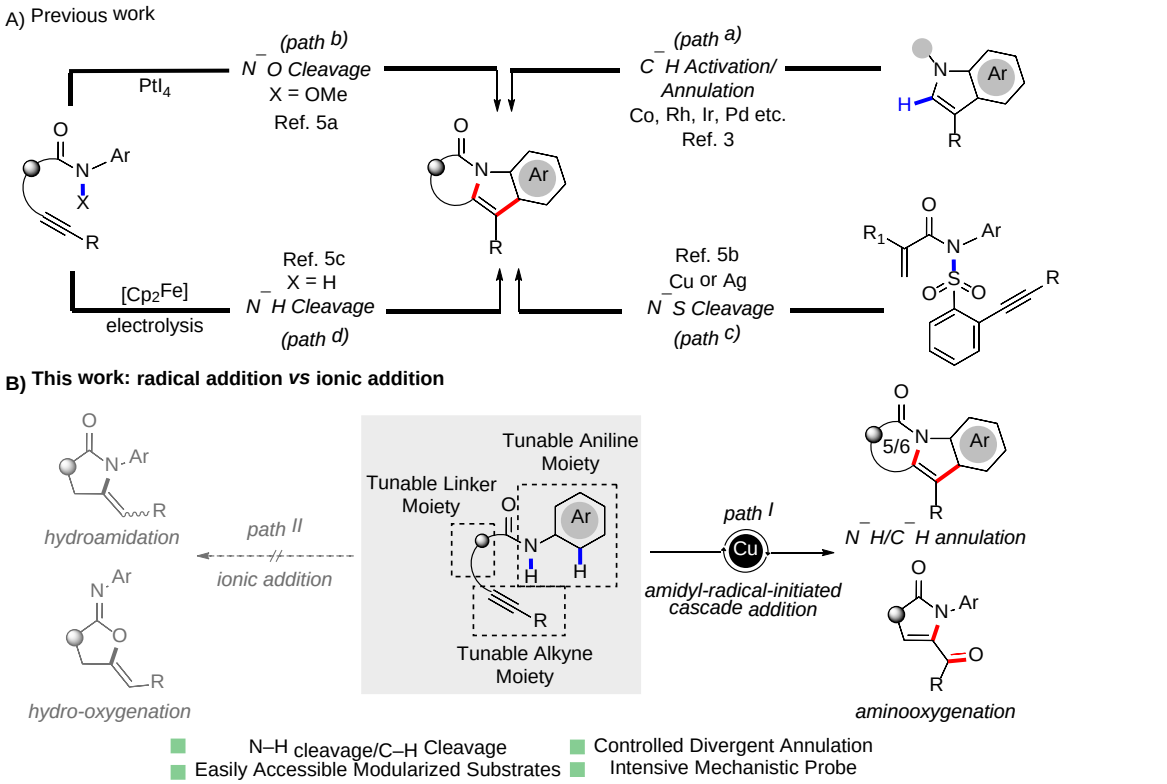
Figure 1 Biologically Active Compounds Bearing Tricyclic Indole Cores.

Therefore, novel synthesis of these compounds is of significance.[2] In this context, annulation of indole derivatives with alkenes, alkynes or diazo compounds has been extensively studied (Scheme 1 A, path a).[3] In contrast, the direct indolization would be a more appealing strategy since it employs more accessible anilines as building blocks, thus conferring the products with more diversity and tunability.[4] Nakamura[5] and Nevado[6a] reported the transition-metal-catalyzed synthesis of tricyclic indoles based on the cleavage of N–O/C–H bond or N–S/C–H (Scheme 1 A, path b, c) via Pt-carbenoid insertion into C(sp^2)–H bond or carbon-centered-radical initiated cascade reaction[6b,6c,6d] separately. Recently, without pre-activation of the N–H bond, Xu and coworkers reported an electrochemical oxidative annulation to access these scaffolds (Scheme 1 A, path d).[7] The generation of a N-centered radical and a subsequent addition across the alkyne units was involved in this process. Various highly functionalized (Aza) indoles was synthesized via the 6-membered-ring closure pattern from urea type substrates. However, 5-membered-ring closure pattern as well as carboxylic amide substrates was not reported due to the high energy barrier for cyclization of the former or the higher oxidation potential of the latter.

Herein, as part of our interest in constructing heterocycles in an atom- and step-economic manner,[8] we developed a copper-catalyzed intramolecular oxidative annulation of alkynes with N–H/C–H bonds (Scheme 1 B, *path I*). This reaction features its obviation of prefunctionalization of N–H & C–H bond, excellent functional group tolerance (including highly electron-withdrawing group) and high structure flexibility (amides, ureas, carbamates etc.). Various densely functionalized heterocyclic scaffolds such as pyrrolo[1,2-a] indoles, indolo[1,2-c]quinazolin-2-ones, oxazolo[3,4-a]indoles and imidazo[1,5-a]indoles could be obtained in an atom- and step-economical manner. Besides, by changing the oxidant from DTBP to TEMPO the reaction could be channeled towards aminooxygenation pathway efficiently (Scheme 1 B, *path II*). Notably, further tuning of reaction

parameters significantly accelerated or suppressed the incidental hydroamidation and/or hydro-oxygenation products through an ionic addition pathway (Scheme 1 B, *path II*), highlighting the divergent nature of this reaction. Extensive mechanistic probes were conducted via judicious reaction design and trapping of key intermediates. The results suggest the reaction cascade might be initiated by oxidatively generated amidyl radical, a *N*-centered radical species which gained resurgent and increasing interest in recent years.[9]

Scheme 1 A) Strategies for the synthesis of polycyclic indoles; B) This work: Cu-catalyzed highly modular N–H/C–H annulations for the synthesis of polycyclic indoles: radical addition vs ionic addition.

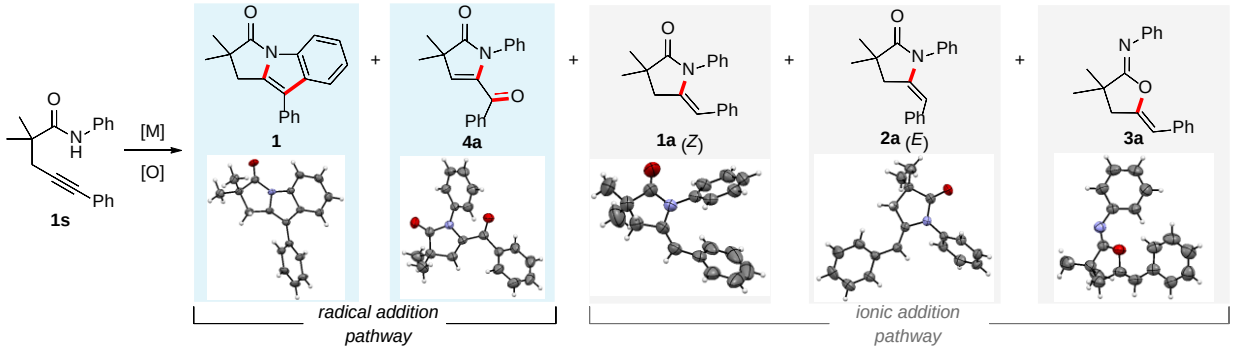


Results and Discussion

Reaction Design and Optimization

We commenced our study using easily procured 2,2-dimethyl-*N*,5-diphenylpent-4-ynamide **1s** as a model substrate (Table 1). Predictably, one of the major hurdles for this substrate is the liable intramolecular hydroamidation or hydro-oxygenation pathway (Scheme 1 B, *path II*).[10] Indeed, when **1s** was subjected to the reaction using 2.0 equivalents of $Cu(OAc)_2$ as oxidant in pivalonitrile, the hydroamidation (**1a**, 26%, CCDC 1870711) and hydro-oxygenation (**3a**, 32%, CCDC 1870710) pathway proved competitive. However, to our delight the desired product **1** (CCDC 1870709) could be obtained in 33% yield (Entry 1). Ag_2CO_3 also mediated the reaction, acting as oxidants, although in relatively low efficiency (Entries 2, 3). To override the side reactions, a thorough screening of solvents, oxidants, temperature and other factors were conducted (see SI for detailed optimizations). When O_2 was used as sole oxidant, **1** was only obtained in 15% yield with the concomitant formation of (*E*)-**2a** (CCDC 1870712). An unexpected product with one oxygenation atom integration was observed (entry 4, **4a**, 10%, CCDC 1870713). The use of $K_2S_2O_8$ as oxidant proved in vain (entry 5), while the use of BaO_2 or catalytic amount of Li_2O_2 delivered the hydroamidation product **1a** in almost quantitative yield (entries 6 and 7). When using silver salt (such as $AgNO_3$) as catalyst, in combination with 2.0 equiv HOAc, the hydro-oxygenation product **3a** was obtained in 75% yield while the desired product **1** was not obtained either (See SI).[11] Intriguingly, the annulation product **1** could be obtained in 83% yield when using 1.3 equiv DTBP as oxidant and 5 mol % loading of CuI as catalyst (entry 8, **CONDITIONS I**, for details See the Supporting Information). Surprisingly, when using TEMPO as oxidant the aminooxygenation product **4a** could be obtained in 84% yield (entry 9, **CONDITIONS II**), reflecting the decisive effect of oxidants and divergent nature of this reaction. Other copper catalyst did not show higher efficiency (entries 10–13). Solvents optimization indicated the crucial role of *t*-BuCN as solvent both for the high yield and good chemical selectivity of the divergent synthesis (See SI). Finally, control experiment revealed the indispensability of oxidant (entry 14).

Table 1 Optimization of reaction parameters to control the reaction pathway[a]



entry	[M] (mol %)	oxidant (equiv)	Solvent (mL)	T (°C)	T (h)	yield (%) 1	1a	2a	3a	4a	CONDITIONS
1	$Cu(OAc)_2$ (200)	\	*t*-BuCN (1.0)	140	8	33	26		**32**		
2	Ag_2CO_3 (200)	\	*t*-BuCN (0.5)		3	10	20	14			
3	Ag_2CO_3 (200)	\	DMSO (0.5)		3	31	48	18			
4	CuI (5)	O_2	Ph-CF_3	140	12	15		29		10	
5	CuI (5)	$K_2S_2O_8$ (2.0)	*t*-BuCN (1.0)	140	12	trace					
6	CuI (5)	BaO_2 (1.0)	*t*-BuCN (1.0)	140	3		88	5			
7	CuI (5)	Li_2O_2 (0.2)	*t*-BuCN (1.0)	120	3		89[b]	5			
8	**CuI (5)**	**DTBP (1.3)**	***t*-BuCN (1.0)**	**140**	**12**	**83[b]**	**4**	**8**			**CONDITIONS I**
9	**CuI (5)**	**TEMPO (2.0)**	***t*-BuCN (1.0)**	**140**	**12**					**84[b]**	**CONDITIONS II**
10	CuOAc (5)	DTBP (1.3)	*t*-BuCN (1.0)	140	12	57		22			
11	CuBr (5)	DTBP (1.3)	*t*-BuCN (1.0)	140	12	62	3	6			
12	Cu powder (10)	DTBP (1.3)	*t*-BuCN (1.0)	140	12	41	3	4			
13	$Cu(MeCN)_4PF_6$ (5)	DTBP (1.3)	*t*-BuCN (1.0)	140	12	70		12			
14	CuI (5)	\	*t*-BuCN (1.0)	140	12	ND	ND	ND	ND	ND	

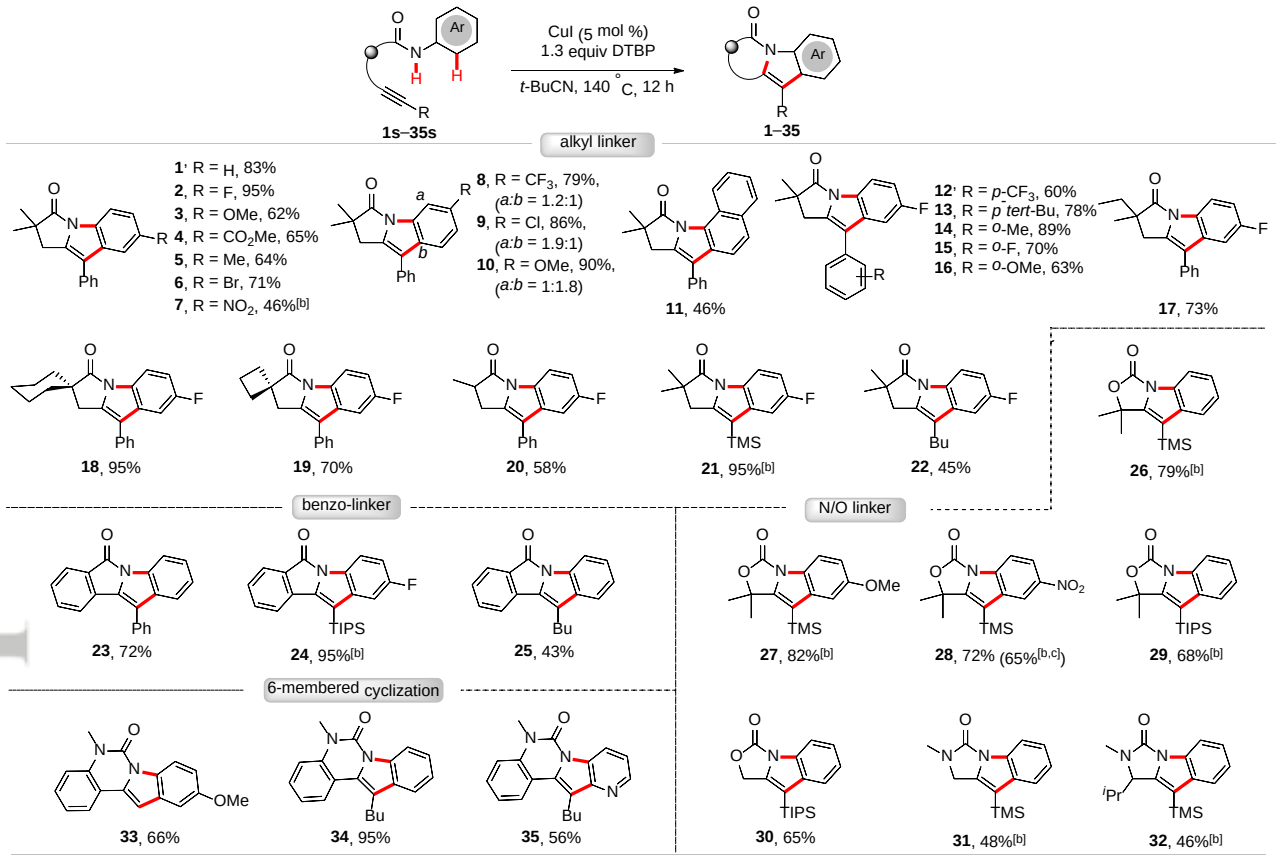
[a] Reactions were performed on a 0.1 mmol scale in 1 mL *t*-BuCN under N_2 atmosphere unless otherwise noted. Yield was determined by ^1H NMR analysis using CH_2Br_2 as internal standard. [b] Isolated yield. *t*-BuCN = pivalonitrile. DTBP = di-*tert*-butyl peroxide. ND = not detected.

Scope of the N–H/C–H Annulation Reaction (Aminoarylation, CONDITIONS I)

With the optimized conditions in hand we explored the reaction scopes of polycyclic indoles first (Scheme 2). For the aniline moiety, both electron-withdrawing (**2**, F; **6**, Br; **8**, CF_3) and -donating (**3**, OMe; **5**, Me) substituents *para* to the amide N moiety were compatible, affording the diversely functionalized indole-cores in good yields. Notably, substrates bearing strong electron-withdrawing groups, such as ester and especially the nitro group which contains highly polarized N–H bond could also gave the aminoarylation product **4** and **7** in moderate yield (65%, 46%), mainly due to the competitive ion-type hydroamination reaction. Substrates bearing substitutes *meta* to the amide N moiety afforded a mixture of regio-isomers (**8**, **9**, **10**). The *N*-naphthylpropynamide **11s** also reacted smoothly to give **11** in 46% yield. Various substituents, such as *p*-trifluoromethyl, *p*-*tert*-butyl, *o*-methyl, *o*-fluoro and *o*-methoxyl at the phenyl group of the alkyne moiety could be tolerated, affording the

desired products in good yields (**12**–**16**). The scope of alkyl-linker was also investigated, and spiro-compounds **18** and **19** could be obtained in good yields (**18**, 95%; **19**, 70%) while *tertiary*-carbon at the α-position was less compatible and resulted in decreased yield (**20**, 58%) due to the Thorpe-Ingold effect.[12] For the terminal group of the pendant alkyne, TMS group was well tolerated giving the desired product **21** in 95% yield and the alkyl group was also reactive delivering **22** in 45% yield. This method was found to accommodate benzo-fused linker affording the tetracyclic indoles in moderate to good yields (**23**–**25**). Similarly, the silyl group showed superior reactivity than the phenyl or alkyl group terminus (**24** *vs* **23** and **25**). Notably, substrates bearing substituents *ortho* to the amide N moiety failed to give the desired products, a similar phenomenon was never observed by Nevado[6a] and Xu[13]. Nevertheless, this reaction anomaly offered us opportunites for mechanism elucidation (*vide infra*, Scheme 6, **40s**→**42**). The heteroatom-fused substrates such as carbamates and ureas could smoothly underwent the N–H/C–H annulation reaction delivering the oxazolo[3,4-*a*]indoles (**26**–**30**) and imidazo[1,5-*a*]indoles (**31**, **32**) with modest yield. Finally, we were pleased to find the 6-membered-ring cyclization pattern was also tolerated and various indolo[1,2-c]quinazolinone cores could be obtained. As exemplified, **33** was successfully obtained in 66% yield, which was desilylated during the silica gel column purification. Contrary to the low reactivity of alkyl terminated alkynes in the 5-membered-ring closure pattern (**22** and **25**), in the 6-membered-ring closure pattern, **34** could be obtained in almost quantitative yield (95%). Furthermore, the electron deficient pyridine as the *N*-aryl moiety could also be tolerated (**35**, 56%), which further expanded the structural complexity.

Scheme 2 Scope of N–H/C–H annulation reaction[a]



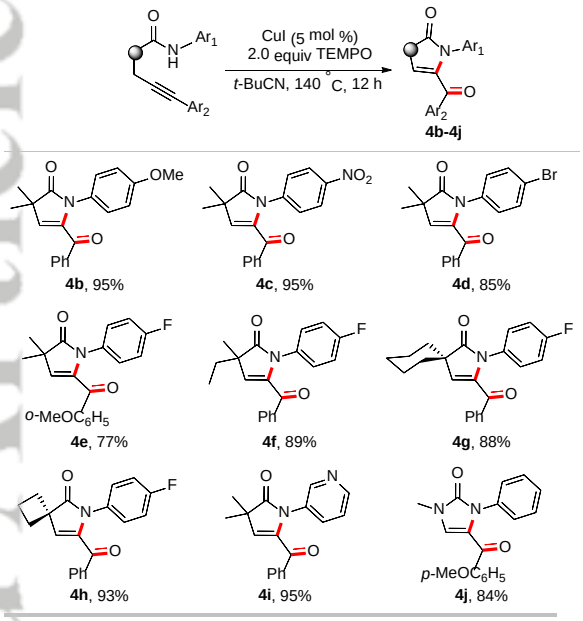
[a] Reactions were performed on 0.1 mmol scale. Isolated yields for the average for three runs. [b] 120 °C. [c] With the formation of 18% hydroamidation product **1h**, see Scheme 4 A.

Scope of the Aminooxygenation Reaction (CONDITIONS II)

Cu-catalyzed aminooxygenation of alkynes using O_2 as oxygen source has been reported.[14] TEMPO as a persistent radical species has been used in broad range of laboratory and industrial processes, for example acting as alkyl radical scavenger, however, it has rarely been used to trap a vinyl group[15] or as the source of an oxygen atom as disclosed in this aminooxygenation reaction.

Accordingly, we explored the reaction scope using *N*-arylpropynamides as substrates. A series of 5-aroyl-pyrrol-2-one cores could be synthesized in high to excellent yields (77%–95%) regardless of the electronic nature of the N-aryl groups (Scheme 3, **4b**, **4c**). And ureas could also be tolerated (**4j**). Slightly frustrated, the aryl substituents at the terminal of alkyne moiety proved requisite and when **22s** was subjected to this condition, a complex mixture was obtained.[16]

Scheme 3 Scope for the aminooxygenation[a]



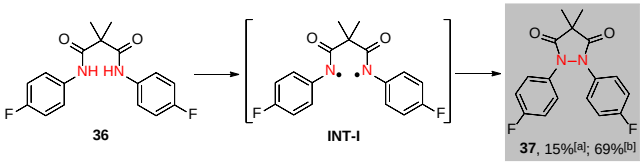
[a] Substrate (0.1 mmol), CuI (5 mol %), TEMPO (2.0 equiv) in 1 mL *t*-BuCN at 140 °C for 12 h. Isolated yields of the average for two runs.

Mechanistic Probes

We speculate that a radical pathway involving the transient vinyl radical species[17] might be involved and the subsequent attack of this species to the N-aryl group or TEMPO yielded the different products. This highly reactive species might be generated by the amidyl radical (which is formed by the chemical oxidation of the amide N–H bond[18]) addition onto the pendant alkyne group, or by the *cis*-aminocupration of alkyne and a subsequent homolysis of the vinylcuprate species. Whereas the actual mechanism might be complex, a series of control experiments supported our speculation.

We first devoted to gain insight into whether an amidyl radical might be generated in this reaction. N-centered radicals (NCRs) are traditionally highly reactive short-lived species, and the process for proving their existence would be tedious. However, these species could be stabilized by resonance with an electron-donating group (such as a phenyl group) or by transition-metal coordination.[9] Experimentally, the oxidative dimerization of *N*-alkoxyl amides by strong metal oxidants has been recognized as a solid evidence for the formation of *N*-alkyoxylamidyl radical.[18i,19] However, attempts to isolate the intermolecular dimerization product using *N*-phenylacetamide under the aminoarylation condition resulted in the clean recovery of starting materials (See SI). This turned our attention to the intramolecular pattern. As shown in Scheme 2, **36** was successfully converted to **37** in the presence of 20 mol% CuI, 1.3 equiv DTBP and 20 mol% 1,2-diphenylacetylene (might act as ligand). When 50 mol% CuCl was used the yield could be improved to 69% without the addition of 1,2-diphenylacetylene. Though not conclusive, this result reminiscent of the recent reports by Waldvogel,[20] suggests that **37** might be formed by an intramolecular recombination of (copper-coordinated) diamidylradical species **INT-I**.

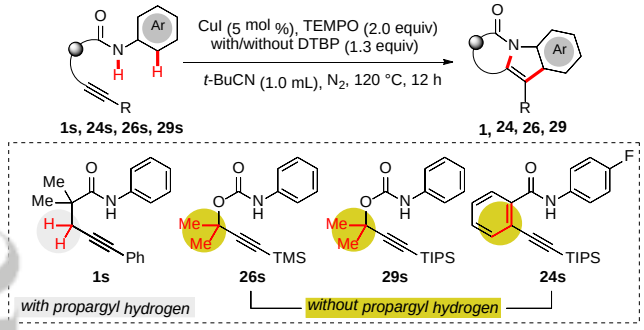
Scheme 4 Proposal for the generation of amidyl radical.



[a] Conditions A: CuI (20 mol %), 1.3 equiv DTBP, diphenylacetylene (20 mol %), t-BuCN (1.0 mL), 140 °C, 20 h, N_2. [b] Conditions B: CuCl (50 mol %), 1.3 equiv DTBP, t-BuCN (1.0 mL), 120 °C, 12 h, N_2.

The generation of **4a** when using O_2 (Table 1, entry 4) or TEMPO (Table 1, entry 9) as oxidant offers a mechanistic clue that vinyl radical species might be involved. Accordingly, attempt was made to isolate the TEMPO-trapped species (Scheme 5).[14,15] To avoid the aminooxygenation reaction, **24s**, **26s**, and **29s** possessing no propargylic hydrogen atom were subjected to the TEMPO inhibition reaction. While **26s** suffered a significant decrease in yield (entry 2, 30% *vs* 79%), the yield of **29s** and **24s** kept unaffected (entries 3 and 4). We attribute this result to the steric bulk of the triisopropylsilyl (TIPS) terminus, which would inhibit the intermolecular capture of the resulting vinyl radical species by TEMPO and therefore lead to the intramolecular cyclization. Of particular significance is that when **26s** and **24s** were subjected to the aminooxygenation condition (replacing DTBP with TEMPO), the annulation products **26** and **24** could be obtained in comparable yields (entries 5 and 6). These results reveal that: 1) TEMPO indeed interrupted the current reaction; 2) both TEMPO and DTBP could act as oxidant for the N–H/C–H annulation reactions and they might share the same vinyl radical species if this species was involved. This promoted us to further design/choose substrates to retard the following vinyl radical addition to the aryl moiety to ensure a prolonged lifetime for the TEMPO trapping.

Scheme 5 TEMPO inhibition experiments.

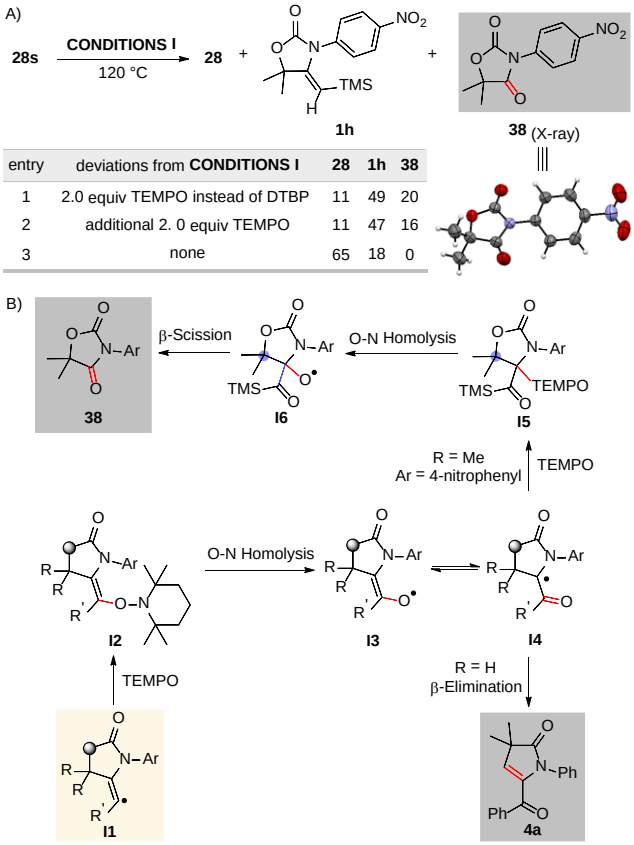


entry	s.m.	TEMPO (equiv)	DTBP	yield (%)	yield (%) under **CONDITIONS I**
1	**1s**	2.0	w	0[a]	83
2	**26s**	2.0	w	30	79
3	**29s**	2.0	w	70	68
4	**24s**	2.0	w	>95	95
5	**26s**	2.0	w/o	34	79
6	**24s**	2.0	w/o	65 (95[b])	95

[a] **4a** was isolated in 91% yield. [b]140 °C. s.m. = starting material.

When evaluating the substrate scope of the aminoarylation reaction, we observed that electron-deficient substrate **28s** reacted sluggishly to give **28** and yielded significant amount of hydroamidation product **1h** (Scheme 2). We speculated that the lower electron density may hampered the addition of vinyl radical to the aryl moiety, and prolonged the life time of the potential radical species and thus more prone to be captured. In addition, the absence of propargylic hydrogen atom renders **28s** a perfect model substrate for TEMPO trapping experiment. As shown in Scheme 6 A, the addition of TEMPO significantly impeded the aminoarylation pathway and gave increased yield of the hydroamidation product **1h** (entries 1 and 2). Careful isolation of the reaction mixture showed the generation of an unexpected product **38** (entry 1, 20%; entry 2, 16%) which was unambiguously confirmed by X-ray crystallography analysis (CCDC 1870708). The standard **CONDITIONS I** gave no formation of **38**, indicating the oxygen atom source was from TEMPO (entry 3). The generation of **4a** and **38** could be well explained by the involvement of vinyl radical, as delineated in Scheme 4 B. The vinyl radical **I1** is captured by TEMPO to yield **I2**. **I2** undergoes homolytic cleavage of the weak N–O bond, either by thermal cleavage or Fenton type cleavage,[21] generating the O-centered radical **I3**, which keeps equilibrium with the C-centered radical **I4**. When no H atom exists at the β-position (R = Me), the C-centered radical of **I4** is captured by TEMPO to form **I5**,[22] followed by N–O homolysis and β-scission to give **38**.[14c,23] In contrast, the oxidative β-hydrogen elimination of **I4** would be a preferred pathway when adjacent hydrogen atom exists, which finally generates **4a**.

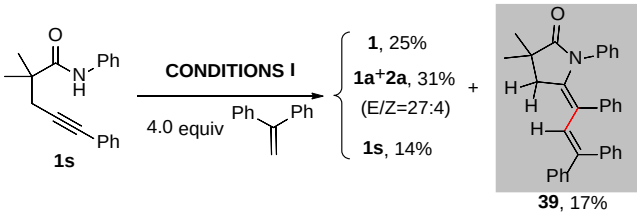
Scheme 6 Mechanistic Probe of Vinyl Radical by TEMPO Trapping Experiments; B) Rational Explanation for the Generation of **4a** and **38**.



entry	deviations from **CONDITIONS I**	**28**	**1h**	**38**
1	2.0 equiv TEMPO instead of DTBP	11	49	20
2	additional 2. 0 equiv TEMPO	11	47	16
3	none	65	18	0

As 1,1-diphenylethylene (DPE) was commonly used as a radical trapping agent,[24] the DPE trapping experiment was also conducted to further corroborate this scenario. Far beyond our expectation, **39** was successfully obtained in 17% yield along with the normal products of **1** in 25% yield (Scheme 7). This result clearly supported the existence of vinyl radical.

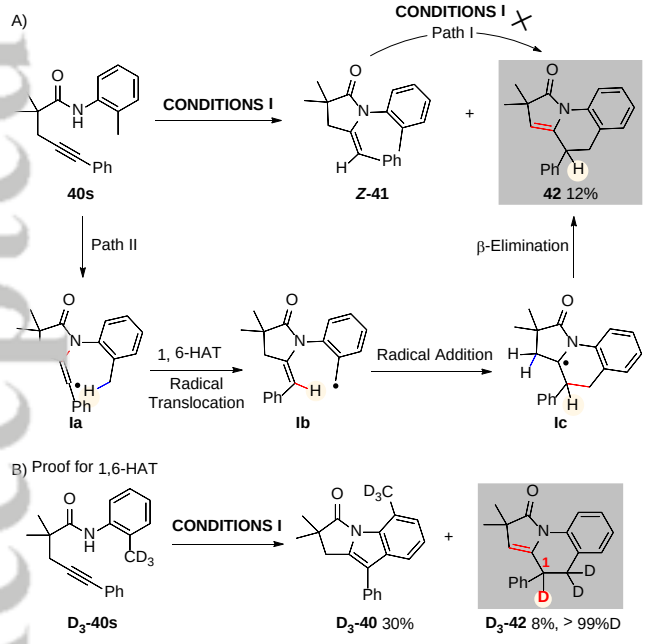
Scheme 7 DPE Trapping Experiments



Nevado[6] has ever reported a novel vinyl radical initiated, 4-aryl migration or *ortho*-methyl substitution reaction pathway of the *ortho*-methylated aniline moiety. Considering the incompatibility of the substrate containing an *ortho*-methylated

aniline moiety (**40s**), we wondered whether the reported reaction pathways was responsible for the complexity of the reaction mixtures. Thus, a careful isolation and analysis of the reaction mixture of **40s** under **CONDITIONS I** was conducted (Scheme 8). In addition to the hydroamidation product *Z*-**41**, an unexpected product **42** was isolated in 12% yield. The desired aminoarylation product as well as the methyl group-substituted product (predicted by Nevado's pathway) could not be isolated. This is a distinct result from what was reported by Nevado. Control experiment excluded the possibility of generation of **42** from *Z*-**41** (Scheme 8 A, path I, See the Supporting Information), and a vinyl radical initiated 1, 6-hydrogen atom transfer pathway (path II) was proposed to rationalize the generation of **42**. The *in situ* generated vinyl radical **Ia** is converted to benzyl radical **Ib** via a novel 1, 6-HAT pathway.[25] Subsequent radical addition to the alkene staff gives an *N*-fused tertiary radical **Ic**, which undergoes oxidative β-H elimination to deliver **42**. Subsequently, the proposed reaction path II was further confirmed by the deuterium-labelled experiment (Scheme 8 B). When **D_3-40s** was subjected to **CONDITIONS I**, quantitative deuterium incorporation at C1 position was observed form the isolated **D_3-42**, unambiguously indicating the involvement of 1, 6-HAT pathway, and the involvement of vinyl radical species **Ia**. Interestingly, the aminoarylation product **D_3-40** could be isolated in 30% yield, in sharp contrast to the reaction of **40s**.

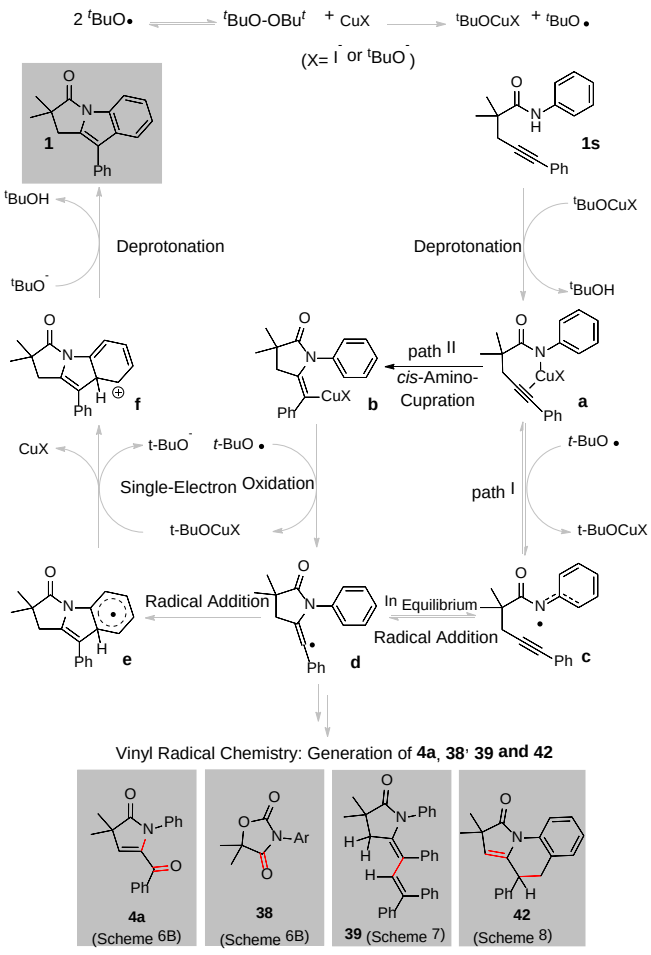
Scheme 8 A) Generation of **42** and A Rational Explanation; B) Proof of 1, 6-HAT.



Finally, a kinetic isotope effect experiment was conducted and a KIE value of about 0.96 and 1.32 was observed for the intramolecular and intermolecular competition experiment (See the Supporting Information)). This indicates that the putative C–H cleavage step of aniline moiety is not involved in the rate-determining step and this KIE value is consist with the proposed radical addition type pathway.[26]

Taken together, a reaction mechanism was proposed in Scheme 9. Coordination and deprotonation of N–H bond in **1s** generates the N–Cu(II) amidate **a**. In path I, **a** undergoes a reversible disassociation with CuX forming the electrophilic N-phenyl amidyl radical **c**. Radical type addition onto alkyne gives vinyl radical species **d**. Electrophilic addition of vinyl radical to the aryl group yields the Wheland intermediate **e**. Subsequent single-electron oxidation by Cu(II) and re-aromatization of **f** delivers the final product **1**. The interception of vinyl radical by different trappers would yield **4a**, **38**, **39** and **42** as demonstrated in Scheme 4–6. However, an alternative pathway II cannot be excluded at this point. In this pathway, vinyl radical **d** is generated via a successive *cis*-aminocupration of alkyne and homolytic cleavage of C(sp^2)-Cu bond, the valent of the copper center is not clear for the moment in this process.

Scheme 9 Proposed mechanism for aminoarylation reaction.



Conclusions

In conclusion, using alkynes tethered to the anilines as precursors we have identified a Cu-catalyzed highly controllable radical cascade providing access to versatile densely functionalized heterocyclic compounds from a wide array of carbamates, amides, and ureas. Via judicious choice of oxidant, the transition-metal-catalyzed ion-type hydroamination or hydrooxygenation could be suppressed significantly. The structure of these products could be easily designed via modularized modification of the arylamine moieties, the linker moieties and the alkyne moieties conferring the product structures with high flexibility. Extensive control experiments were designed implying that the reaction might by initiated by the Cu-catalyzed amidyl radical-triggered radical cascade, which to some extent facilitates the formation of the active amidyl radical species and offers strategic bond disconnections for the synthesis of complex molecules.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.
X-ray crystallographic data for compound **1** (CIF)
X-ray crystallographic data for compound **1a** (CIF)
X-ray crystallographic data for compound **2a** (CIF)
X-ray crystallographic data for compound **3a** (CIF)
X-ray crystallographic data for compound **4a** (CIF)
X-ray crystallographic data for compound **38** (CIF)
Experimental procedures and spectral data (PDF).

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References

[1] (a) Gribble, G. W. Indole ring synthesis: From natural products to drug discovery; John Wiley & Sons, Ltd.: West Sussex, UK, 2016; (b) Elmegeed, G. A.; Baiuomy, A. R.; Abdel-Salam, O. M. E., Evaluation of the Anti-inflammatory and Anti-nociceptive Activities of Novel Synthesized Melatonin Analogues. *Eur. J. Med. Chem.* **2007**, *42*, 1285–1292; (c) Mizuta, M.; Banba, J.; Kanamori, T.; Tawarada, R.; Ohkubo, A.; Sekine, M.; Seio, K., New Nucleotide Pairs for Stable DNA Triplexes Stabilized by Stacking Interaction. *J. Am. Chem. Soc.* **2008**, *130*, 9622–9623; (d) Vallakati, R.; May, J. A., Biomimetic Synthesis of the Antimalarial Flindersial Alkaloids. *J. Am. Chem. Soc.* **2012**, *134*, 6936–6939; (e) Molinaro, C.; Bulger, P. G.; Lee, E. E.; Kosjek, B.; Lau, S.; Gauvreau, D.; Howard, M. E.; Wallace, D. J.; O'Shea, P. D., CRTH2 Antagonist MK-7246: A Synthetic Evolution from Discovery through Development. *J. Org. Chem.* **2012**, *77*, 2299–2309.

[2] (a) de Sá Alves, F. R.; Barreiro, E. J.; Fraga, C. A. M. From Nature to Drug Discovery: The Indole Scaffold as a 'Privileged Structure'. *Mini-Rev. Med. Chem.* **2009**, *9*, 782–793; (b) Zhang, B.; Studer, A. Recent advances in the synthesis of nitrogen heterocycles via radical cascade reactions using isonitriles as radical acceptors. Chem. Soc. Rev. **2015**, *44*, 3505-3521; (c) Yuan, K.; Jia, Y. Recent Progress in the Synthesis of 3,4-Fused Indole Alkaloids. *Chin. J. Org. Chem.* **2018**, *38*, 2386-2399; (d) Wang, Z.; He, W.-M. Radical Cyclization Strategy towards Indolo[1,2-a]quinolones. *Chin. J. Org. Chem.* **2019**, *39*, 3594-3595.

[3] (a) Monakhova, N.; Ryabova, S.; Makarov, V. Synthesis and Some Biological Properties of Pyrrolo[1,2-a]indoles. *J. Heterocyclic Chem*., **2016**, *53*, 685–709; (b) Wilson, R. M.; Thalji, R. K.; Bergman, R. G.; Ellman, J. A. Enantioselective Synthesis of a PKC Inhibitor via Catalytic C−H Bond Activation. *Org. Lett.* **2006**, *8*, 1745–1747; (c) Ding, Z.-H.; Yoshikai, N. Cobalt-Catalyzed Intramolecular Olefin Hydroarylation Leading to Dihydropyrroloindoles and Tetrahydropyridoindoles. *Angew. Chem. Int. Ed.* **2013**, *52*, 8574–8578; (d) Ikemoto, H.; Yoshino, T.; Sakata, K.; Matsunaga, S.; Kanai, M. Pyrroloindolone Synthesis via a Cp*CoIII-Catalyzed Redox-Neutral Directed C−H Alkenylation/Annulation Sequence. *J. Am. Chem. Soc.* **2014**, *136*, 5424–5431; (e) Zheng, J.; Zhang, Y.; Cui, S. Rh(III)-Catalyzed Selective Coupling of N Methoxy 1H indole-1-carboxamides and Aryl Boronic Acids. *Org. Lett.* **2014**, *16*, 3560–3563; (f) Chen, X.; Hu, X.-W.; Bai, S.; Deng, Y.-F.; Jiang, H.-F.; Zeng, W. Rh(III)-Catalyzed [4+2] Annulation of Indoles with Diazo Compounds: Access to Pyrimido[1,6 a]indole-1(2H) ones. *Org. Lett.* **2016**, *18*, 192–195; (g) Kandukuri, S. R.; Schiffner, J. A.; Oestreich, M. Aerobic Palladium(II)-Catalyzed 5-endo-trig Cyclization: An Entry into the Diastereoselective C2 Alkenylation of Indoles with Tri- and Tetrasubstituted Double Bonds. *Angew. Chem. Int. Ed.* **2012**, *51*, 1265–1269.

[4] (a) Larock, R. C.; Yum, E. K. *J. Am. Chem. Soc.* **1991**, *113*, 6689–6690; (b) Larock, R. C.; Yum, E. K.; Refvik, M. D. *J. Org. Chem.* **1998**, *63*, 7652–7662; (c) Chen, Y.; Markina, N. A.; Yao, T.; Larock, R. C. *Org. Synth.* **2011**, *88*, 377–387; (d) Dong, Z.; Zhang, X.-W.; Li, W.; Li, Z.-M.; Wang, W.-Y.; Zhang, Y.; Liu, W.; Liu, W.-B. Synthesis of N-Fused Polycyclic Indoles via Ligand-Free PalladiumCatalyzed Annulation/Acyl Migration Reaction. *Org. Lett.* **2019**, *21*, 1082−1086; (e) Tao, L.; Shi, M. $(CH_3)_2CuLi/Cu(OTf)_2$ Mediated N- or O-Cyclization of Urea-Tethered Cyclobuta[b]indolines. *Org. Lett.* **2019**, *21*, 129−133.

[5] Sato, Y.; Terada, M.; Nakamura, I. Platinum-Catalyzed Dehydroalkoxylation-Cyclization Cascade via N−O Bond Cleavage. *J. Am. Chem. Soc.* **2009**, *131*, 4198−4199.

[6] (a) Fuentes, N.; Kong, W.-Q.; Fernández-Sánchez, L.; Merino, E.; Nevado, C. Cyclization Cascades via N-Amidyl Radicals toward Highly Functionalized Heterocyclic Scaffolds. *J. Am. Chem. Soc.* **2015**, *137*, 964−973. For some recent reviews on the radical cascade cyclization, see: (b) Zhang, Y.; Sun, K.; Lv, Q.; Chen, X.; Qu, L.; Yu, B. Recent applications of radical cascade reaction in the synthesis of functionalized 1-indenones. *Chin. Chem. Lett.* **2019**, *30,* 1361−1368; (c) Liu, X.-Y.; Qin, Y. Indole Alkaloid Synthesis Facilitated by Photoredox Catalytic Radical Cascade Reactions. *Acc. Chem. Res.* **2019**, *52*, 1877–1891; (d) Huang, M.-H.; Hao, W.-J.; Li, G.; Tu, S.-J.; Jiang, B. Recent advances in radical transformations of internal alkynes. *Chem. Commun.* **2018**, *54,* 10791−10811.

[7] Hou, Z.-W.; Mao, Z.-Y.; Zhao, H.-B.; Melcamu, Y. Y.; Lu, X.; Song, J.-S.; Xu, H.-C. Electrochemical C−H/N−H Functionalization for the

Synthesis of Highly Functionalized (Aza)indoles. *Angew. Chem. Int. Ed.* **2016**, *55*, 9168−9172.

[8] (a) Chen, F.-J.; Liao, G.; Li, X.; Wu, J.; Shi, B.-F. Copper-Mediated C−S/N−S Bond Formation via C−H Activation: Access to Benzoisothiazolones Using Elemental Sulfur. *Org. Lett.* **2014**, *16*, 5644−5647; (b) Li, B.; Wang, S.-Q.; Liu, B.; Shi, B.-F. Synthesis of Oxazolines from Amides via Palladium-Catalyzed Functionalization of Unactivated C(sp^3)−H Bond. *Org. Lett.* **2015**, *17*, 1200−1203; (c) Zhang, Z.-Z.; Liu, B.; Wang, C.-Y.; Shi, B.-F. Cobalt(III)-Catalyzed C2-Selective C-H Alkynylation of Indoles. *Org. Lett.* **2015**, *17*, 4094-4097; (d) Liu, B.; Hu, F.; Shi, B.-F. Recent Advances on Ester Synthesis via Transition-Metal-Catalyzed C-H Activation. *ACS Catal.* **2015**, *5*, 1863-1881; (e) Rao, W.-H.; Shi, B.-F. Recent Advances in Copper-Mediated Chelation-Assisted Functionalization of Unactivated C-H Bonds. *Org. Chem. Front.* **2016**, *3*, 1028-1047; (f) Zhang, Z.-Z.; Liu, B.; Xu, J.-W.; Yan, S.-Y.; Shi, B.-F. Indole Synthesis via Cobalt(III)-Catalyzed Oxidative Coupling of N-Arylureas and Internal Alkynes. *Org. Lett.* **2016**, *18*, 1776-1779; (g) Zhang, Q.; Shi, B.-F. From Reactivity and Regioselectivity to Stereoselectivity: An Odyssey of Designing PIP Amine and Related Directing Groups for C-H Activation. *Chin. J. Chem.* **2019**, *37*, 647-656; (h) Zhang, S.; Liao, G.; Shi, B.-F. Enantioselective Synthesis of Atropoisomers Featuring Pentatomic Heteroaromatics. *Chin. J. Org. Chem.* **2019**, *39*, 1522-1528; (i) Zhang, S.; Yao, Q.-J.; Liao, G.; Li, X.; Li, H.; Chen, H.-M.; Hong, X.; Shi, B.-F. Enantioselective Synthesis of Atropisomers Featuring Pentatomic Heteroaromatics by Pd-Catalyzed C–H Alkynylation. *ACS Catal.* **2019**, *9*, 1956-1961; (j) Liu, Y.-H.; Xia, Y.-N.; Shi, B.-F. Ni-Catalyzed Chelation-Assisted Direct Functionalization of Inert C-H Bonds. *Chin. J. Chem.* **2020**, *38*, 635-662; (k) Zhou,, T.; Jiang, M.-X.; Yang, X.; Yue, Q.; Han, Y.-Q.; Ding, Y.; Shi, B.-F. Synthesis of Chiral β-Lactams by Pd-Catalyzed Enantioselective Amidation of Methylene C(sp^3)–H Bonds. *Chin. J. Chem.* **2020**, *38*, 242-246; (l) Liao, G.; Wu, Y.-J.; Shi, B.-F. Noncovalent Interaction in Transition Metal-Catalyzed Selective C-H Activation. *Acta Chim. Sinica*, **2020**, *78*, 289-298.

[9] (a) Yu, X.-Y.; Zhao, Q.-Q.; Chen, J.; Xiao, W.-J.; Chen, J.-R. When Light Meets Nitrogen-Centered Radicals: From Reagents to Catalysts. *Acc. Chem. Res.* **2020**, *53*, 1066-1083; (b) Xiong, P.; Xu, H.-C. Chemistry with Electrochemically Generated N-Centered Radicals. *Acc. Chem. Res.* **2019**, *52,* 3339–3350; (c) Zhao, Y.; Xia, W. Recent Advances in Radical-based C–N bond Formation via Photo-/electrochemistry. *Chem. Soc. Rev.*, **2018**, *47*, 2591−608; (d) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J., Visible Light Photoredox-controlled Reactions of N-radicals and Radical Ions. *Chem. Soc. Rev.* **2016**, *45*, 2044−2056; (e) Xiong, T.; Zhang, Q. New Amination Strategies Based on Nitrogen-centered Radical Chemistry. *Chem. Soc. Rev.* **2016**, *45*, 3069−3087; (f) Chen, J.-R. Hu, X.-Q. Lu, L.-Q. Xiao, W.-J., Exploration of Visible-Light Photocatalysis in Heterocycle Synthesis and Functionalization: Reaction Design and Beyond. *Acc. Chem. Res.*, **2016**, *49*, 1911−1923; (g) Gentry, E. C.; Knowles, R. R. Synthetic Applications of Proton-Coupled Electron Transfer. *Acc. Chem. Res*. **2016**, *49*, 1546−1556. (h) Kärkäs, M. D. Photochemical Generation of Nitrogen-Centered Amidyl, Hydrazonyl, and Imidyl Radicals: Methodology Developments and Catalytic Applications. *ACS Catal.* **2017**, *7*, 4999−5022; (i) Song, H.; Liu, X.; Qin, Y. Advances on Nitrogen-centered Radical Chemistry: A Photocatalytic N-H Bond Activation Approach. *Acta Chim. Sinica*, **2017**, *75*, 1137-1149. (j) Xuan, J.; Studer, A. Radical cascade cyclization of 1, n-enynes and diynes for the synthesis of carbocycles and heterocycles. *Chem. Soc. Rev.* **2017**, *46*, 4329-4346. (k) Zard, S. Z. Recent Progress in the Generation and Use of Nitrogen-centred Radicals. *Chem. Soc. Rev.* **2008**, *37*, 1603−1618.

[10] (a) Huang, L.-B.; Arndt, M.; Gooßen, K.; Heydt, H.; Gooßen, L. J. Late Transition Metal-Catalyzed Hydroamination and Hydroamidation. Chem. *Rev.* **2015**, *115*, 2596−2697; (b) Godoi, B.; Schumacher, R. F.; Zeni, G. Synthesis of Heterocycles via Electrophilic Cyclization of Alkynes Containing Heteroatom. *Chem. Rev.* **2011**, *111*, 2937–2980.

[11] Rao, W.-H.; Yin, X.-S.; Shi, B.-F. Catalyst-Controlled Amino- versus Oxy-Acetoxylation of Urea-Tethered Alkenes: Efficient Synthesis of Cyclic Ureas and Isoureas. *Org. Lett.* **2015**, *17*, 3758−3761.

[12] Jung, M. E.; Piizzi, G. gem-Disubstituent Effect: Theoretical Basis and Synthetic Applications. *Chem. Rev.* **2005**, *105*, 1735−1766.

[13] (a) Xu Z.; H.-B.; Hou, Z.-W.; Liu, Z.-J.; Zhou, Z.-F.; Song, J.; Xu, H.-C. Amidinyl Radical Formation through Anodic N−H Bond Cleavage and Its Application in Aromatic C−H Bond Functionalization. *Angew. Chem. Int. Ed.* **2017**, *56*, 587–590. (b) Hou, Z.-W.; Yan, H.; Song, J.-S.; Xu, H.-C. Electrochemical Synthesis of (Aza)indolines via Dehydrogenative [3+2] Annulation: Application to Total Synthesis of (±)-Hinckdentine A. *Chin. J. Chem.* **2018**, *36*, 909-915; (c) Qian, X.; Xiong, P.; Xu, H.-C. Modular Synthesis of Functionalized 4-Quinolones via a Radical Cyclization Cascade Reaction. *Acta Chimica Sinica.* **2019**, *77*, 879-883.

[14] (a) Zhang, C.; Jiao, N. Dioxygen Activation under Ambient Conditions: Cu-Catalyzed Oxidative Amidation-Diketonization of Terminal Alkynes Leading to α-Ketoamides. *J. Am. Chem. Soc.* **2010**, *132*, 28–29; (b) Lu, Q.; Zhang, J.; Zhao, G.; Qi, Y.; Wang, H.; Lei, A. Dioxygen-Triggered Oxidative Radical Reaction: Direct Aerobic Difunctionalization of Terminal Alkynes toward β-Keto Sulfones. *J. Am. Chem. Soc.* **2013**, *135*, 11481−11484; (c) Peng, X.-X.; Wei, D.; Han, W.-J.; Chen, F.; Yu, W.; Han, B. Dioxygen Activation via Cu-Catalyzed Cascade Radical Reaction: An Approach to Isoxazoline/Cyclic Nitrone-Featured α-Ketols. *ACS Catal.* **2017**, *7*, 7830−7834.

[15] Dutta, U.; Maity, S.; Kancherla, R.; Maiti, D. Aerobic Oxynitration of Alkynes with tBuONO and TEMPO. *Org. Lett.* **2014**, *16*, 6302−6305.

[16] Hou, Z.-W.; Xu, H.-C. Electrochemically Enabled Intramolecular Aminooxygenation of Alkynes via Amidyl Radical Cyclization. *Chin. J. Chem.* **2020**, *38*, 394–398.

[17] Wille, U. Radical Cascades Initiated by Intermolecular Radical Addition to Alkynes and Related Triple Bond Systems. *Chem. Rev.* **2013**, *113*, 813−853.

[18] (a) Liwosz, T. W.; Chemler, S. R. Copper-Catalyzed Oxidative Amination and Allylic Amination of Alkenes. *Chem.-Eur. J.* **2013**, *19*, 12771−12777 ; (b) Wang, Y.-F.; Chen, H.; Zhu, X.; Chiba, S. Copper-Catalyzed Aerobic Aliphatic C-H Oxygenation Directed by an Amidine Moiety. *J. Am. Chem. Soc.* **2012**, *134*, 11980−11983; (c) Li, Z.; Song, L.; Li, C. Silver-Catalyzed Radical Aminofluorination of Unactivated Alkenes in Aqueous Media. *J. Am. Chem. Soc.* **2013**, *135*, 4640−4643; (d) Zhou, L.; Tang, S.; Qi, X.; Lin, C.; Liu, K.; Liu, C.; Lan, Y.; Lei, A. Transition-Metal-Assisted Radical/Radical Cross-Coupling: A New Strategy to the Oxidative C(sp^3)-H/N-H Cross-Coupling. *Org. Lett.* **2014**, *16*, 3404−3407; (e) Liu, T.; Myers, M. C.; Yu, J.-Q. Copper-Catalyzed Bromination of C(sp^3)-H Bonds Distal to Functional

Groups. *Angew. Chem. Int. Ed.* **2017**, *56*, 306−309; (f) Zhou, T.; Luo, F.-X.; Yang, M.-Y.; Shi, Z.-J. Silver-Catalyzed Long-Distance Aryl Migration from Carbon Center to Nitrogen Center. *J. Am. Chem. Soc.*, **2015**, *137*, 14586-14589; (g) Wang, N.; Gu, Q.-S.; Li, Z.-L.; Li, Z.; Guo, Y.-L.; Guo, Z.; Liu, X.-Y. Direct Photocatalytic Synthesis of Medium-Sized Lactams through C–C Bond Cleavage. A*ngew. Chem. Int. Ed.* **2018**, *57*, 14225−14229; (h) Duan, X.-Y.; Zhou, N.-N.; Fang, R.; Yang, X.-L.; Yu, W.; Han, B. Transition from p Radicals to s Radicals: Substituent-Tuned Cyclization of Hydrazonyl Radicals. *Angew. Chem. Int. Ed.* **2014**, *53*, 3158 –3162; (i) Chen, F.; Lai, S.-Q.; Zhu, F.-F.; Meng, Q.; Jiang, Y.; Yu, W.; Han, B. Cu-Catalyzed Radical Cascade Annulations of AlkyneTethered N-alkoxyamides with Air: Facile Access to Isoxazolidine/1,2-Oxazinane-Fused Isoquinolin-1(2H)-ones. *ACS Catal.,* **2018**, *8*, 8925–8931; (j) Zhang, Q.-Q.; Hu, X.-Q.; Yang, M.-N.; Chen, J.-R.; Xiao, W.-J. A visible-light photocatalytic N-radical cascade of hydrazones for the synthesis of dihydropyrazole-fused benzosultams. *Chem. Commun.*, **2016**, 52, 12749−12752.

[19] (a) Crawford, R. J.; Raap, R. The Synthesis and Reactions of N, N'-Dicarbalkoxy-N, N'-dialkoxyhydrazines and Some Observations on Carbalkoxylium Ions. *J. Org. Chem*., **1963**, *28*, 2419−2424; (b) Cooley, J. H.; Mosher. M. W.; Khan, M. A. Preparation and Reactions of N, N'-Diacyl-N, N-dialkoxyhydrazines. *J. Am. Chem. Soc.*, **1968**, *90*, 1867−1871; (c) Zhou, L.; Yi, H.; Zhu, L.; Qi, X.; Jiang, H.; Liu, C.; Feng, Y.; Lan, Y.; Lei. A. Tuning the Reactivity of Radical through a Triplet Diradical Cu(II) Intermediate in Radical Oxidative Cross-Coupling. *Sci. Rep.* **2015**, *5*, 15934. (d) Shao, A.; Li, N.; Gao, Y.; Zhan, J.; Chiang, C.-W.; Lei, A. Electrochemical Intramolecular C—H/O—H Cross-Coupling of 2-Arylbenzoic Acids. *Chin. J. Chem.* **2018**, *36*, 619-624; (e) Yu, X.; Zhou, F.; Chen, J.; Xiao, W. Visible Light Photocatalytic N-Radicalbased Intramolecular Hydroamination of Benzamides. *Acta Chim. Sinica,* **2017**, *75*, 86-91.

[20] (a) Gieshoff, T.; Schollmeyer, D.; Waldvogel, S. R. Access to Pyrazolidin-3,5-diones through Anodic N–N Bond Formation. *Angew. Chem. Int. Ed.* **2016**, *55*, 9437−9440; (b) Gieshoff, T.; Kehl, A.; Schollmeyer, D.; Moeller, K. D.; Waldvogel, S. R. Insights into the Mechanism of Anodic N−N Bond Formation by Dehydrogenative Coupling. *J. Am. Chem. Soc.* **2017**, *139*, 12317−12324.

[21] Rachmilovich-Calis, S.; Masarwa, A.; Meyerstein, N.; Meyerstein, D.; van Eldik, R. New Mechanistic Aspects of the Fenton Reaction. *Chem.-Eur. J.* **2009**, *15*, 8303−8309.

[22] A similar capture of tertiary C-centered by TEMPO has been reported, see Ling, F.; Li, Z.; Zheng, C.; Liu, X.; Ma, C. Palladium/Copper-Catalyzed Aerobic Intermolecular Cyclization of Enediyne Compounds and Alkynes: Interrupting Cycloaromatization for (4 +2) Cross-Benzannulation. *J. Am. Chem. Soc.* **2014**, *136*, 10914−10917.

[23] Though the detail mechanism was not clear, a similar β-scission pathway to release small molecules was ever reported, see 24c, and another example: Huang, X.; Li, X.; Zou, M.; Song, S.; Tang, C.; Yuan, Y.; Jiao, N. From Ketones to Esters by a Cu-Catalyzed Highly Selective C(CO)−C(alkyl) Bond Cleavage: Aerobic Oxidation and Oxygenation with Air. *J. Am. Chem. Soc.* **2014**, *136*, 14858–14865.

[24] Liwosz, T. W.; Chemler, S. R. Copper-Catalyzed Enantioselective Intramolecular Alkene Amination/Intermolecular Heck-Type Coupling Cascade. *J. Am. Chem. Soc.* **2012**, *134*, 2020−2023.

[25] Nechab, M.; Mondal, S.; Bertrand, M. P. 1, n-Hydrogen-Atom Transfer (HAT) Reactions in Which n≠5: An Updated Inventory. *Chem.-Eur. J.* **2014**, *20*, 16034–16059.

[26] Simmons, E. M.; Hartwig, J. F. On the Interpretation of Deuterium Kinetic Isotope Effects in C–H Bond Functionalizations by Transition Metal Complexes. *Angew. Chem., Int. Ed.* **2012**, *51*, 3066−3072.

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Title Copper-Catalyzed Modular Access to N-Fused Polycyclic Indoles and 5-Aroyl-pyrrol-2-ones via Intramolecular N–H/C–H Annulation with Alkynes: Scope and Mechanism Probes

Yan-Hua Liu, Hong Song, Chi Zhang, Yue-Jin Liu, Bing-Feng Shi*

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