

## PAPER

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## Use of unprotected amino acids in metal-free tandem radical cyclization reactions: divergent synthesis of 6-alkyl/acyl phenanthridines†

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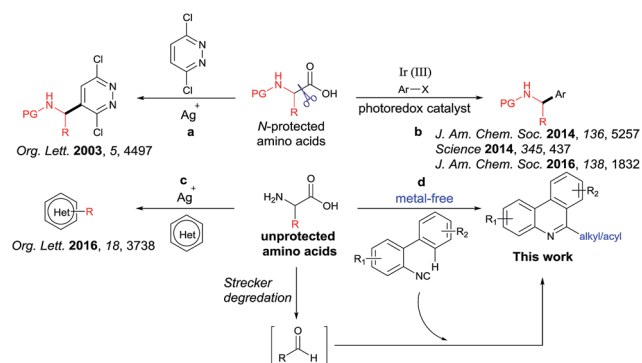
We reported the first example of the construction of C–C bonds using unprotected amino acids as stable alkyl/acyl radical precursors under metal-free conditions. This novel, environmentally friendly, and one-pot procedure was successfully applied to the radical alkylation or acylation/cyclization of isocyanides, which selectively affords 6-alkyl or acyl phenanthridines, depending on the substituent pattern of amino acid side chain groups.

## Introduction

As an important building block, amino acids present the advantages of high stability, abundant natural resources, structural diversity and low cost, which make them ideal synthons for chemical synthesis.<sup>1</sup> Although numerous methods for the introduction of amino acids into diverse organic structures *via* peptide coupling have been described,<sup>2</sup> the application of amino acids in C–C bond-forming reactions is far less studied. In this context, synthetic utilization of  $\alpha$ -aminoalkyl radicals generated by metal- or photo-catalyzed radical decarboxylation of N-protected amino acids has been achieved for the construction of C–C bonds (Scheme 1a and b). These reactions involved cross-coupling,<sup>3</sup> conjugate additions,<sup>4</sup> and Minisci reactions with electron-deficient heteroarenes.<sup>5</sup> However, the strategy for the generation of the alkyl radicals from unprotected amino acids was seldom applied to molecular transformations due to their tendency for rapid oxidation of unprotected  $\alpha$ -aminoalkyl radicals. Very recently, Baxter successfully realized a silver-catalyzed heterocycle C–H alkylation reaction using unprotected amino acids as stable radical precursors (Scheme 1c).<sup>6</sup> This transformation was believed to undergo *in situ* aldehyde formation, namely Strecker degradation,<sup>7</sup> followed by a Minisci-type radical decarbonylation/alkylation process. While radical alkylation reactions *via* aldehyde decarbonylation are known,<sup>8</sup> aliphatic aldehydes are

redox-sensitive liquids and usually require cold storage and special operations. In contrast, the resulting alkyl radicals *via* the multistep oxidative degradation of amino acids showed better selectivity and reactivity.<sup>6</sup> However, all of the reactions involving the use of amine acids as radical precursors reported so far require a toxic transition metal catalytic system. In view of this, the development of a green reaction system for the construction of C–C bonds using amino acids as stable radical precursors is highly desirable and challenging.

Recently, the radical oxidative addition/cyclization of 2-isocyanobiphenyls with different radical precursors to synthesize functionalized phenanthridines, which are widely found in various natural products and possess a wide range of biological activities,<sup>9</sup> have been extensively investigated.<sup>10</sup> Our group has recently also reported a radical cascade decarboxylation/cyclization of 2-isocyanobiphenyls with carboxylic acids to afford 6-alkyl/aryl phenanthridines.<sup>10d</sup> Although these methods have their own specific applications, they still suffer from one or more limitations, such as a limited reaction scope, harsh



Scheme 1 Amino acids as a source of alkyl radicals for C–C bond-forming reactions.

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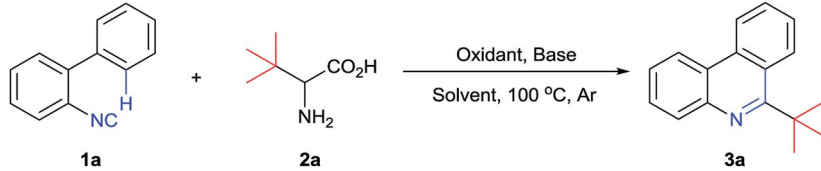
reaction conditions, long reaction times, and the use of transition-metal catalysts. Therefore, it is still necessary to develop more radical precursors for practical, general, and environmentally benign methods to realize the addition/cyclization of 2-isocyanobiphenyls. To the best of our knowledge, amino acids have not been used as a source of radicals for construction of heterocycles. Herein, we develop a novel strategy that utilizes unprotected amino acids as inexpensive alkyl/acyl radical precursors for the addition/cyclization of 2-isocyanobiphenyls under metal-free conditions in aqueous solution, which provides a simple and general protocol for the divergent synthesis of 6-alkyl/acyl phenanthridines (Scheme 1d).

## Results and discussion

In our initial studies, we selected 2-isocyno-1,1'-biphenyl (**1a**) and *L*-tert-leucine (**2a**) as model substrates to investigate the reaction conditions. Inspired by our previous research on decarboxylative cross-coupling reactions, the model reaction was carried out in CH<sub>3</sub>CN/H<sub>2</sub>O (1 : 1) at 80 °C in the presence of 3.0 equiv. of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 1.5 equiv. of K<sub>2</sub>CO<sub>3</sub>. To our delight, the desired product **3a** was obtained in a 36% yield. In view of the fact that the addition of 20 mol% of AgNO<sub>3</sub> cannot improve the yield (Table 1, entry 1), we decided to explore the metal-free

oxidative radical cyclization for the construction of 6-alkyl phenanthridines. A survey of the reaction parameters, such as the oxidants, bases, solvents and temperature, were conducted. Increasing the temperature to 100 °C gave good conversion to the expected product (Table 1, entry 2). Further investigation on the bases, such as Na<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, Cs<sub>2</sub>CO<sub>3</sub>, and NaOAc, revealed that K<sub>2</sub>CO<sub>3</sub> was the best choice (Table 1, entries 3–6). Subsequently, we attempted to examine the effect of different solvent systems on the model reaction. Among the solvents screened, water-miscible solvents (Table 1, entries 7–10) as well as water (Table 1, entry 11) were not effective for this transformation. In addition, the reaction was also not carried out in biphasic mixtures (DCE/H<sub>2</sub>O) (Table 1, entry 12). It was observed that increasing the ratio of CH<sub>3</sub>CN to H<sub>2</sub>O had a positive effect on the yield of **3a** (Table 1, entries 13 and 14). When the ratio was 5 : 1, the reaction can be achieved in a 78% yield. However, 98% of the reactant **1a** was recovered while using CH<sub>3</sub>CN as the sole solvent (Table 1, entry 15). Similarly, other anhydrous organic solvents such as DMF, DMSO, or THF were not effective for this conversion. Further investigation showed that both Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> negatively affected the reaction (Table 1, entries 16 and 17). Meanwhile, the decreasing the amount of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> led to a low yield (Table 1, entry 18). The control experiment indicated that K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was necessary for the transformation (Table 1, entry 19). The optimal conditions were finally determined to be

Table 1 Optimization of the reaction conditions<sup>a</sup>



Entry	Oxidant (equiv.)	Base (equiv.)	Solvent (v/v)	Yield <sup>b</sup>
1 <sup>c</sup>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (3.0)	K <sub>2</sub> CO <sub>3</sub> (1.5)	CH <sub>3</sub> CN/H <sub>2</sub> O (1 : 1)	36 (38) <sup>d</sup>
2	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (1 : 1)	62 (54) <sup>e</sup> (60) <sup>f</sup>
3	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	Na <sub>2</sub> CO <sub>3</sub> (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (1 : 1)	53
4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>3</sub> PO <sub>4</sub> (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (1 : 1)	42
5	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	Cs <sub>2</sub> CO <sub>3</sub> (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (1 : 1)	46
6	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	NaOAc (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (1 : 1)	27
7	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	DMF/H <sub>2</sub> O (1 : 1)	0
8	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	Dioxane/H <sub>2</sub> O (1 : 1)	0
9	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	DMSO/H <sub>2</sub> O (1 : 1)	12
10	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	Acetone/H <sub>2</sub> O (1 : 1)	0
11	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	H <sub>2</sub> O	0
12	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	DCE/H <sub>2</sub> O (1 : 1)	0
13	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (3 : 1)	72
14	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (5 : 1)	78
15	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	CH <sub>3</sub> CN	0
16	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (5 : 1)	42
17	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (4.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (5 : 1)	30
18	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (2.0)	K <sub>2</sub> CO <sub>3</sub> (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (5 : 1)	28
19	—	K <sub>2</sub> CO <sub>3</sub> (2.0)	CH <sub>3</sub> CN/H <sub>2</sub> O (5 : 1)	0

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.8 mmol), K<sub>2</sub>CO<sub>3</sub> (0.4 mmol), in 6.0 mL of solvent at 100 °C for 60 min under Ar.

<sup>b</sup> Isolated yield. <sup>c</sup> At 80 °C. <sup>d</sup> 20 mol% of AgNO<sub>3</sub> was used as a catalyst. <sup>e</sup> At 90 °C. <sup>f</sup> At 110 °C.



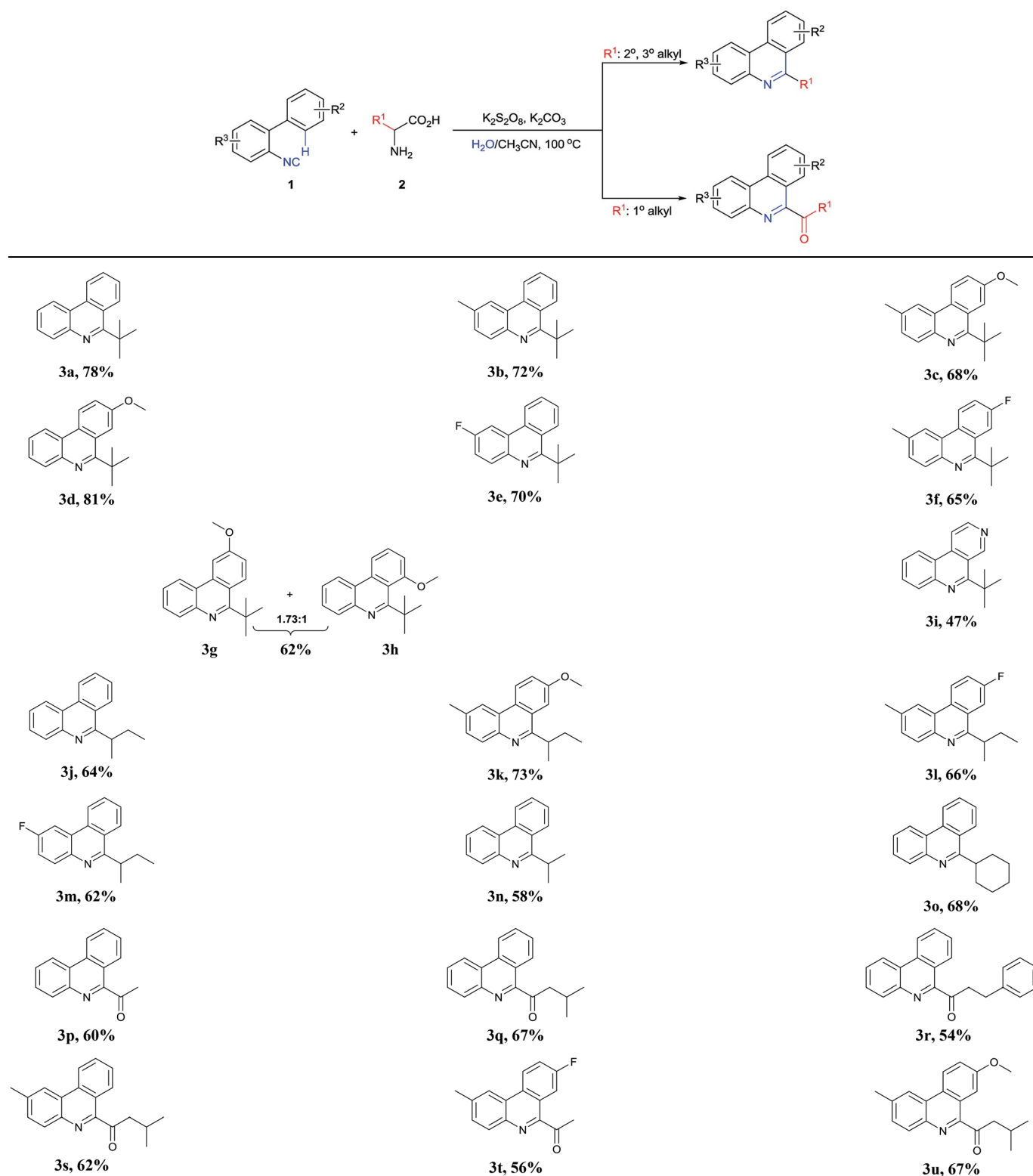
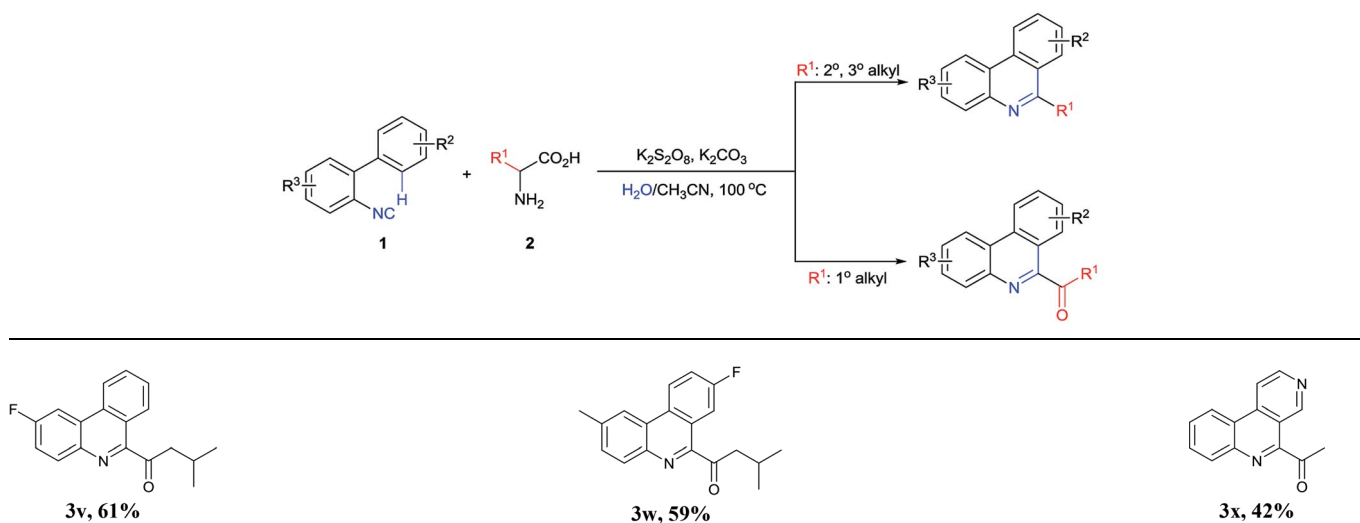
Table 2 Scope of the oxidative cyclization of isocyanobiphenyls **1** and amino acids **2**<sup>a,b</sup>

Table 2 (Contd.)



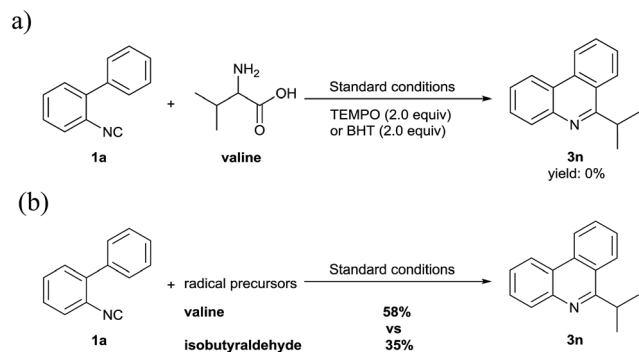
<sup>a</sup> Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol),  $K_2S_2O_8$  (0.8 mmol),  $K_2CO_3$  (0.4 mmol),  $CH_3CN/H_2O$  (6 mL, v/v = 5/1), 100 °C, under Ar for 1 h.  
<sup>b</sup> Isolated yield.

2.0 equiv. of amino acid, 2.0 equiv. of  $K_2CO_3$  and 4.0 equiv. of  $K_2S_2O_8$  in  $CH_3CN/H_2O$  (v/v = 5/1) under Ar at 100 °C for 1 h (Table 1, entry 14).

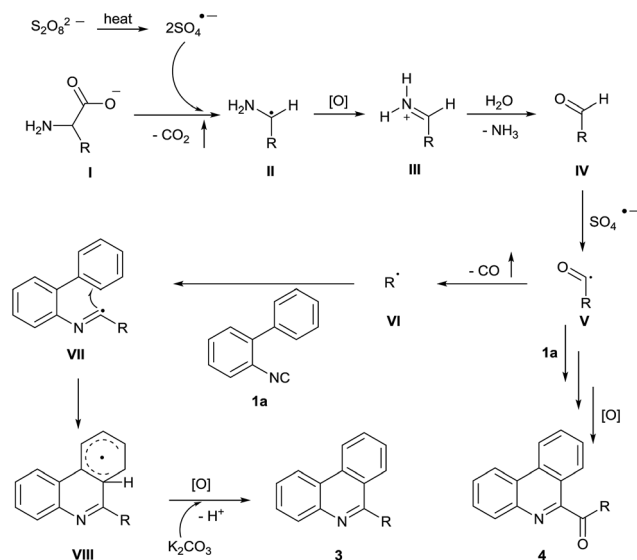
With the optimized conditions in hand, the scope and limitations of this tandem reaction were then investigated (Table 2). A variety of 2-isocyanobiphenyls containing an electron-withdrawing or electron-donating substituent were reacted with *L*-tert-leucine **2a** efficiently to afford the corresponding 6-alkyl phenanthridines in moderate to good yields (**3a–h**). Among them, the cyclization of the meta-substituted substrate preferably took place at the less sterically hindered position (**3g** and **3h**). In addition, heterocyclic 2-isocyanobiphenyl was also favored in this system and afforded the corresponding product in a 42% yield (**3i**). On the other hand, the oxidative cyclization of other unprotected amino acids bearing secondary alkyl substituents (such as valine, isoleucine, and cyclohexylglycine) performed well with a series of 2-isocyanobiphenyls (**3j–o**). It should be noted that this process was

limited to simple alkyl-bearing amino acids, while other amino acids with polar side chains, such as asparagine, glutamine, and lysine, failed to afford the corresponding products under the optimized conditions.

Encouraged by the above results, we then investigated the reactivity of amino acids bearing primary side chains (such as alanine, leucine, and homophenyl alanine) toward 2-isocyanobiphenyls. Interestingly, the green system afforded 6-acyl phenanthridines as main products instead of 6-alkyl phenanthridines with moderate to good yields (**3p–x**). These results could be attributed to the stability of the alkyl radical species by



Scheme 2 Control experiments for preliminary mechanism study.



Scheme 3 Postulated reaction pathway.



decarbonylation of the corresponding acyl radicals.<sup>8g</sup> Although some groups have reported their efforts for the synthesis of 6-acyl phenanthridines through the reactions of 2-isocyanobiphenyls with corresponding radical precursors including aromatic aldehydes,<sup>11</sup> potassium oxophenylacetate,<sup>12</sup> and benzylic alcohols<sup>13</sup> under iron- or silver-catalyzed radical conditions, the construction of 6-aliphatic acyl phenanthridines remains elusive. In view of this, this strategy afforded a novel, environmentally friendly and complementary approach to produce 6-acyl phenanthridines.

To gather some insights into the mechanism of this reaction, (2,2,6,6-tetramethylpiperdin-1-yl)oxyl (TEMPO, 2.0 equiv.) and 2,6-di-*tert*-butyl-*p*-cresol (BHT) as radical scavengers were exposed separately to the standard reaction condition (Scheme 2a). As a consequence, the reaction was completely inhibited, which could indicate that this transformation involves radical intermediates. Then, we chose isobutyraldehyde as a radical precursor to test the radical mechanism (Scheme 2b). The results showed the expected **3n** could be obtained in a 35% yield under the same reaction conditions. By contrast, the multistep degradation of amino acids to generate alkyl radicals offer better reactivity.

On the basis of this observation and the literature evidence,<sup>6,10</sup> a proposed mechanism is shown in Scheme 3. First, the single-electron oxidative decarboxylation of amino acid anion **I** affords a radical **II** in the presence of sulfate anion radicals generated through homolytic cleavage of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Second, **II** is rapidly oxidized to the corresponding iminium species **III** and is converted to aldehyde **IV** in the presence of water. A sulfate anion radical abstracts the aldehyde hydrogen atom to provide the acyl radical **V**, which undergoes radical decarbonylation to yield the alkyl radical **VI**. Subsequently, the radical **VI** adds to the isocyanide **1a** to provide the imidoyl radical **VII**, which undergoes an intramolecular radical cyclization to form the intermediate **VIII**. Finally, the intermediate **VIII** is then further oxidized to form the corresponding carbocation, which can be converted to the desired product **3** by losing a proton. In the case of 1° substituted amino acids, acyl radical **V** may be trapped by the isocyanide **1a** to form the acylated product **4** in a similar manner.

## Experimental section

### General procedure for synthesis of 6-alkyl/acyl phenanthridines

A 25 mL oven-dried sealed tube was charged with 2-isocyanobiphenyls (**1**, 0.20 mmol, 1.0 equiv.), amine acids (**2**, 0.40 mmol, 2.0 equiv.), K<sub>2</sub>CO<sub>3</sub> (55 mg, 0.40 mmol, 2.0 equiv.) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (216 mg, 0.80 mmol, 4.0 equiv.) in CH<sub>3</sub>CN/H<sub>2</sub>O (6.0 mL, v/v = 5 : 1). The tube was sealed and heated at 100 °C for 1 h under an Ar atmosphere. After completion of the reaction, the reaction mixture was added water (5 mL), and then extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100 : 1) to afford **3**.

## Conclusions

In conclusion, we have demonstrated a novel protocol utilizing unprotected amino acids as stable radical sources under metal-free conditions. The method is able to efficiently functionalize 2-isocyanobiphenyls by virtue of the corresponding amino acids, which presents the major advantages of environmentally benign character, a broad substrate scope, and readily available starting materials. Further studies of the reaction mechanism and the extension of the substrate scope are currently underway in our laboratory.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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