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[View Article Online](#)
[View Journal](#) | [View Issue](#)Cite this: *RSC Sustainability*, 2024, 2, 2626Received 22nd May 2024
Accepted 19th July 2024

DOI: 10.1039/d4su00258j

rsc.li/rscsus

Facile synthesis of propargylamines by metal-free doubly decarboxylative coupling†

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Doubly decarboxylative coupling between two different carboxylic acids to form a new C–C bond is a powerful tool for the rapid assembly of complex compounds. Herein, we report a metal-free three-component decarboxylative strategy for the construction of diverse propargylamines in good yields with high chemoselectivity. This operationally simple method can be applied to various amino acids, α -keto acids, and terminal alkynes, providing a powerful new protocol for propargylamine synthesis. The reaction without the addition of metal catalysts has the advantages of broad scope and functional group compatibility, and environmental friendliness.

Sustainability spotlight

Sustainability in organic chemistry has been driving innovation for decades. Multicomponent reactions are a valuable tool in green chemistry, although they typically involve harsh solvents, additive reagents, and metal catalysts. The reduction of chemicals and waste in multicomponent reactions is an important development in sustainable chemistry and pharmacy, especially under metal-free conditions. Herein, we demonstrate a metal-free three-component decarboxylative coupling for the synthesis of propargylamines, which are highly versatile building blocks for accessing functional compounds in organic chemistry. Meanwhile, their utility in modulating the chemical and pharmaceutical properties of molecules makes propargylamines a desirable choice in pharmaceutical research. Our work emphasizes the importance of the following UN sustainable development goals: industry, innovation, and infrastructure (SDG 9), and climate action (SDG 13).

Introduction

Carboxylic acids represent one of the most ubiquitous and important chemical feedstocks, widely found in natural products, pharmaceuticals, agricultural chemicals, and functional materials.¹ Due to their abundance, stability and non-toxic nature, decarboxylative coupling—a potentially powerful C–C and C–X coupling method—serves as a fundamental and indispensable process in organic chemistry.^{2,3} These reactions have been shown to be an attractive pathway for the synthesis of various high-value-added products. Among them, transition metal-catalysis or metal-free decarboxylation strategies have been widely discussed for the modification of amino acids and peptide substrates.⁴ Recently, significant progress has been achieved in the photo-induced, photocatalytic and electrocatalytic decarboxylative coupling of amino acids and small peptides.^{5,6} With regard to decarboxylative alkynylation of amino acids, the use of transition metal catalysts is still

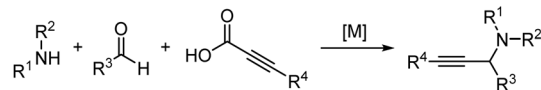
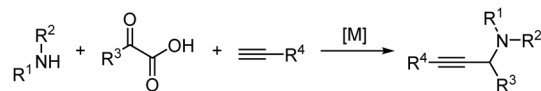
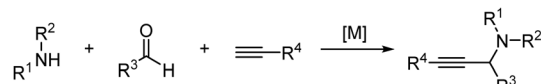
commonplace due to the activation of terminal alkynes usually requiring these catalysts.⁷

Propargylamine is one of the most important structural motifs in bioactive molecules,⁸ and is widely used in the preparation of heterocyclic compounds, natural products, and so on.^{9,10} In recent years, significant efforts have been made to develop efficient methods for the synthesis of propargylamines,¹¹ particularly through the use of A^3 -reactions and decarboxylative A^3 -couplings (Scheme 1A).¹² Among these methodologies, multi-component decarboxylative coupling of amino acids¹³ has attracted interest due to its readily available starting materials, synthetic efficiency, inherent atom economy, environmental friendliness, and simplicity of operation. For example, the Seidel¹⁴ and Lin¹⁵ groups independently reported a Cu or Zn-catalysed three-component decarboxylative coupling of secondary α -amino acids with aldehydes and terminal alkynes (Scheme 1B). It is noteworthy that a transition-metal catalyst was inevitably utilized in these decarboxylative couplings. More recently, our group also developed a highly efficient metal-free doubly decarboxylative coupling of amino acids with propiolic acids and ethyl glyoxylate to provide propargylamines (Scheme 1C).¹⁶ However, this strategy is limited to ethyl glyoxylate, and other aldehydes would stop the reaction. Therefore, the exploration of other metal-free synthetic methods for the construction of propargylamines is highly desirable. Inspired by carboxyl group-assisted transformations¹⁷

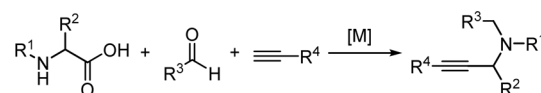
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† Electronic supplementary information (ESI) available: Experimental procedures, spectral data, and ¹H and ¹³C NMR spectra. See DOI: <https://doi.org/10.1039/d4su00258j>

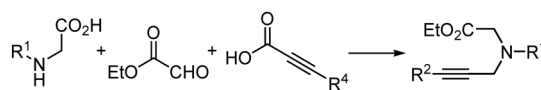
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A. Metal catalysed A³-coupling or decarboxylative A³-coupling

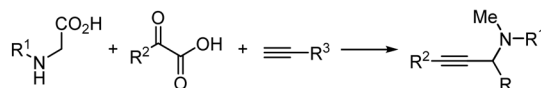
B. Cu or Zn catalysed decarboxylative coupling of amino acid



C. Our previous work: metal-free decarboxylative coupling



D. This work: metal-free doubly decarboxylative coupling

Scheme 1 A³-coupling/decarboxylative A³-type coupling.

and our continuous efforts on multi-component decarboxylative reactions,¹⁸ herein we describe a facile method for the synthesis of propargylamines by metal-free doubly decarboxylative coupling of amino acids with α -keto acids and alkynes (Scheme 1D).

Results and discussion

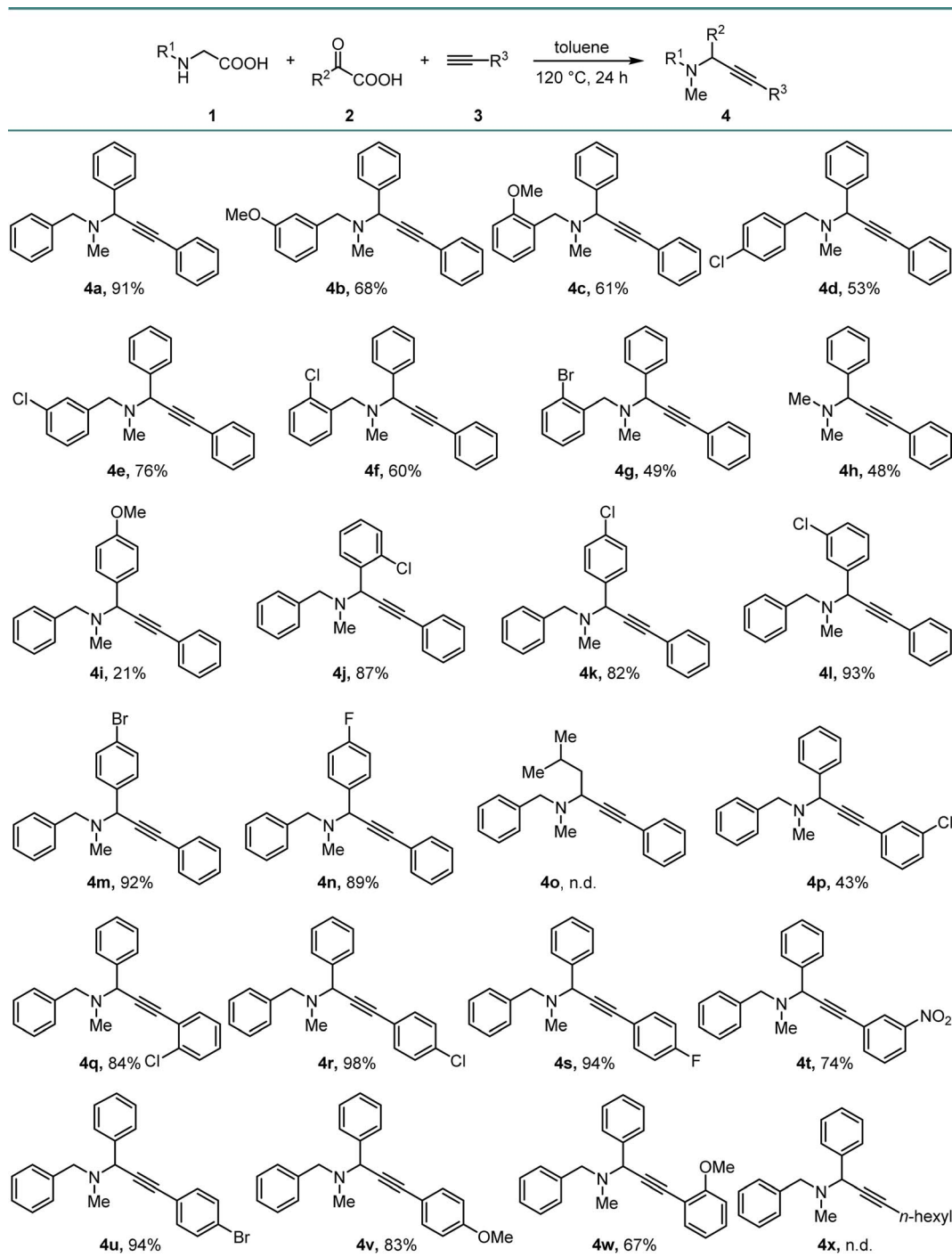
First, *N*-benzylglycine **1a**, phenylglyoxylic acid **2a**, and phenylacetylene **3a** were chosen as model substrates to optimize the metal-free reaction conditions (Table 1). We initiated our investigation by evaluating the solvents at 110 °C for 20 h (entries 1–6). Among the solvents tested, toluene seemed to be the most effective for this decarboxylative coupling, giving the target product **4a** in 40% yield (entry 1). Lower yields were obtained when acetonitrile, 1,2-dichloroethane (DCE) and isopropanol (IPA) were used as solvents (entries 2–4). However, no reaction was observed when tetrahydrofuran and 1,4-dioxane were used (entries 5 and 6). The decarboxylative coupling was then optimized by varying the reaction parameters in the presence of toluene (entries 7–13). Decreasing the reaction temperature to 100 °C would significantly reduce the yield of product **4a** to 10% (entry 7), whereas increasing the temperature to 120 °C could lead to higher yield (entry 8). Interestingly, changing the amount of the starting materials was significantly beneficial in improving the yield of the target product (entries 9–12). The best molar ratio of **1a** : **2a** : **3a** was found to be 1.5 : 1.5 : 1.0, resulting in the formation of **4a** in 86% yield (entry 11). A slightly lower yield was obtained when the amount of *N*-benzylglycine **1a** was reduced to 1.2 equiv. (entry 12). Further optimization showed that the best reaction conditions were toluene as solvent for 24 h, improving the yield to 91% (entry 13). Notably, when benzaldehyde was used instead of phenylglyoxylic acid **2a**, only 24% yield of **4a** was isolated (entry 14). This result indicates that phenylglyoxylic acid plays a very important role in promoting this doubly decarboxylative coupling reaction. As the reaction temperature is higher than the boiling point of the solvent, we carried out the reaction

Table 1 Optimization of the reaction conditions^a

$Bn-NH-CH_2-COOH + Ph-C(=O)COOH + \equiv Ph \longrightarrow Bn-N(Me)-CH_2-C\equiv Ph$					
Entry	Ratio (1a : 2a : 3a)	Solvent	Time (h)	Temp. ^c (°C)	Yield (%)
1	2.0 : 1.0 : 1.0	Toluene	20	110	40
2	2.0 : 1.0 : 1.0	MeCN	20	110	23
3	2.0 : 1.0 : 1.0	DCE	20	110	20
4	2.0 : 1.0 : 1.0	IPA	20	110	18
5	2.0 : 1.0 : 1.0	THF	20	110	n.d.
6	2.0 : 1.0 : 1.0	1,4-Dioxane	20	110	n.d.
7	2.0 : 1.0 : 1.0	Toluene	20	100	10
8	2.0 : 1.0 : 1.0	Toluene	20	120	60
9	1.0 : 1.0 : 1.0	Toluene	20	120	66
10	1.0 : 1.5 : 1.0	Toluene	20	120	57
11	1.5 : 1.5 : 1.0	Toluene	20	120	86
12	1.2 : 1.5 : 1.0	Toluene	20	120	84
13	1.2 : 1.5 : 1.0	Toluene	24	120	91
14 ^b	1.2 : 1.5 : 1.0	Toluene	24	120	24
15	1.2 : 1.5 : 1.0	DMF	24	120	Trace
16	1.2 : 1.5 : 1.0	DMSO	24	120	n.d.

^a Reaction conditions: **1a** (0.5–1.0 mmol), **2a** (0.5–0.75 mmol), and **3a** (0.5 mmol) were added to solvent (2.0 mL), and the solution was kept at 100–120 °C for 20–24 h under atmospheric conditions; isolated yield; n.d. = not detected. ^b Benzaldehyde was used instead of phenylglyoxylic acid. ^c Oil bath temperature.





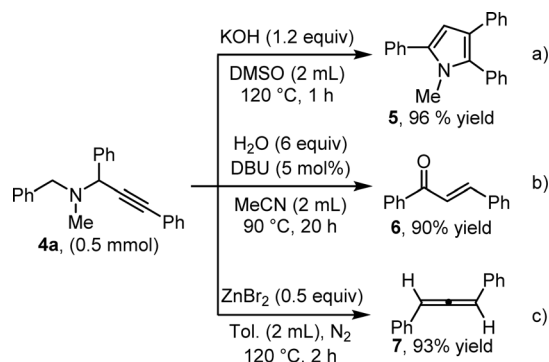
Scheme 2 Scope of doubly decarboxylative coupling. ^aReaction conditions: amino acids **1** (0.60 mmol), α -keto acids **2** (0.75 mmol), and alkynes **3** (0.50 mmol) were added to toluene (2.0 mL), and the solution was kept at 120 °C for 24 h under atmospheric conditions; n.d. = not detected.

using higher boiling solvents such as DMF and DMSO as solvents. However, both gave a negative result with the formation of the decarboxylation product benzaldehyde (entries 15 and 16).

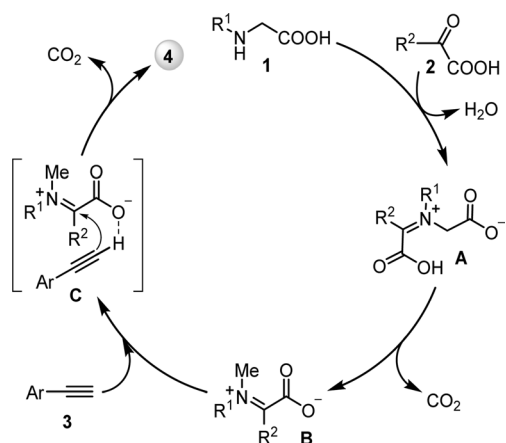
With the optimized conditions in hand (Table 1, entry 13), we next evaluated the scope of the doubly decarboxylative coupling method using different amino acids **1**, α -keto acids **2** and alkynes **3** (Scheme 2). First, a diverse range of α -amino acids

were tested. The results showed that the reaction tolerated various electron-donating and electron-withdrawing groups on the benzene ring of *N*-benzylglycines, affording the corresponding products **4a–4g** in 49–91% yields. We were pleased to find that methylglycine also underwent doubly decarboxylative coupling to give product **4h** in 48% yield. When we chose to use cyclic amino acids, such as proline, a mixture of isomers was observed (see ESI†). We then turned our attention to the scope





Scheme 3 Divergent transformations of products **4a**. (a) Cyclization of **4a**. (b) Deamination of **4a** with water. (c) Allene synthesis from **4a**.



Scheme 4 Proposed reaction pathway.

of α -keto acids. In the case of the aromatic α -keto acids with an electron-withdrawing substituent, excellent yields (82–93%) of the corresponding products **4j–4n** were obtained. However, the introduction of an electron-donating group on the aromatic α -keto acid resulted in a low reaction yield of **4i** of 21%. When an alkyl α -keto acid such as 4-methyl-2-oxovaleric acid was used in the reaction, the target product **4o** was not observed. In addition, the target product was not observed when glyoxylic acid was used (see ESI†). Finally, a wide range of alkynes was investigated. Both electron-withdrawing and electron-donating aryl-substituted alkynes worked well to produce the corresponding products **4p–4w** in 43–98% yields. However, an alkyl alkyne such as octyne was found to be inert and failed to yield the product **4x**.

Importantly, the wide range of substrates encouraged further testing of product transformations (Scheme 3). For example, compound **4a** was converted to the pyrrole **5** in 96% yield by intramolecular cyclization under basic conditions (Scheme 3a).¹⁹ Meanwhile, the DBU-catalysed deaminative hydrolysis of **4a** was also successful in affording the chalcone **6** in 90% yield (Scheme 3b).^{10b} Finally, the allene compound **7** was obtained by Zn-catalysed domino 1,5-H transfer and β -elimination of **4a** under anhydrous and oxygen-free conditions (Scheme 3c).

These results showed that the obtained products were amenable to valuable downstream synthetic manipulations.²⁰

Based on the experimental observations and previous literature reports,^{14,15,17d} a plausible reaction pathway for the synthesis of propargylamines is proposed in Scheme 4. Initially, the species **A**, generated from the α -amino acids **1** and α -keto acids **2**, underwent heat-induced decarboxylation to form iminium salts **B**.^{21a} Subsequently, the carboxyl group-induced activation of alkynes **3** was achieved^{21b,c} using intermediate **B** to access unstable transitional species **C**, which smoothly underwent a domino nucleophilic addition process and decarboxylation process to produce propargylamines **4**.

Conclusion

In summary, we have developed an efficient and mild metal-free doubly decarboxylative coupling of amino acids, α -keto acids, and terminal alkynes to provide a direct construction of propargylamines in moderate to excellent yields. The nucleophilic addition of alkynes to the intermediate iminium salts is induced by the carboxyl group introduced from the α -keto acids. This sustainable reaction tolerates a wide range of starting materials and represents a significant improvement in decarboxylation strategies for constructing synthetically useful propargylamines.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There is no conflict of interest to report.

Acknowledgements

We gratefully acknowledge the National Natural Science Foundation of China (No. 22078192) and National Key Research and Development Program of China (No. 2023YFC2412400, 2023YFC2412403) for financial support.

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