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# Photoredox-catalyzed dicarbofunctionalization of styrenes with amines and CO<sub>2</sub>: a convenient access to $\gamma$ -amino acids†

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**A visible-light-promoted carbocarboxylation of styrenes using CO<sub>2</sub> and amines is reported. The reaction is catalyzed by a photoredox catalyst and is compatible with a variety of amines and styrenes. This method affords highly functionalized  $\gamma$ -amino acids in good yields with high regioselectivity.**

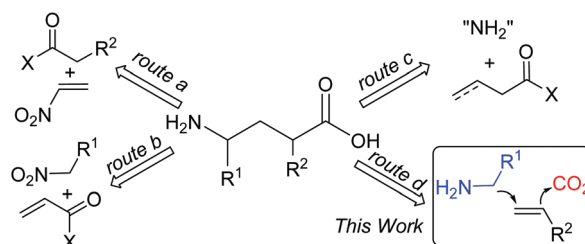
$\gamma$ -Amino acids are highly valuable compounds that exist widely in pharmaceuticals and exhibit a diverse range of biological activities as agonists and antagonists of receptors for mammalian neurotransmitters in the central nervous system.<sup>1</sup> Thus, considerable efforts have been devoted to the synthesis of  $\gamma$ -amino acids,<sup>2</sup> such as Michael addition of carbonyl compounds to nitroethylenes (Scheme 1, route a)<sup>3</sup> or conjugate addition of nitroalkanes to  $\alpha,\beta$ -unsaturated carbonyl compounds (Scheme 1, route b)<sup>4</sup> to afford  $\gamma$ -amino acids. Recently, Ye and coworkers reported  $\gamma$ -amination of  $\alpha,\beta$ -unsaturated acyl chlorides with azodicarboxylates followed by reductive ring opening of dihydropyridazinones to afford  $\gamma$ -amino acids (Scheme 1, route c).<sup>5</sup> Despite all these efforts, these synthetic methods suffer from limited substrate scope, multiple steps, and/or harsh reaction conditions. We envisioned that the simultaneous incorporation of both  $\alpha$ -aminoalkyl and carbon dioxide (CO<sub>2</sub>) to alkenes *via* dicarbofunctionalization of alkenes would serve as an ideal route to deliver  $\gamma$ -amino acids (Scheme 1, route d).

The evolving visible-light-mediated photoredox catalysis offers an operating strategy to access open shell radical species,<sup>6</sup> leading to novel methods for difunctionalization of alkenes.<sup>7</sup> Recently, photoredox-promoted single electron oxidation of amines and subsequent deprotonation to generate  $\alpha$ -aminoalkyl radicals **B** have been described (Scheme 2).<sup>8</sup> The

addition of the  $\alpha$ -aminoalkyl radical **B** to alkenes resulted in the formation of the alkyl radical species **C**, which undergoes a single electron reduction to capture an electrophile.<sup>9</sup> We anticipated that the incorporation of CO<sub>2</sub> as an electrophile in the reaction mixture might enable the formation of  $\gamma$ -amino acids.

CO<sub>2</sub> as a nontoxic, ubiquitous, and recyclable one-carbon source has attracted attention in organic synthesis.<sup>10</sup> The catalytic carboxylation of unsaturated compounds with CO<sub>2</sub> has attracted much attention from chemists.<sup>11</sup> Compared with the widely considered hydrocarboxylation of alkene with CO<sub>2</sub>,<sup>12</sup> photocatalytic functional carboxylation of alkenes with CO<sub>2</sub> is more challenging and rarely reported. Recently, the Martin, Yu, Wu, and Li groups demonstrated respectively the photoredox-catalyzed difunctionalization of alkenes under visible light to afford  $\beta$ -functionalized alkylcarboxylic acids with CO<sub>2</sub>.<sup>13</sup> Taking into account the potential of these transformations and our ongoing interest in the carboxylation of alkenes with CO<sub>2</sub> for the efficient dicarbofunctionalization reaction, herein, we report the photoredox-catalyzed  $\alpha$ -aminomethylcarboxylation of alkenes with amines and CO<sub>2</sub>. This strategy is sustainable, general, and practical, representing a rare example of redox-neutral dicarbofunctionalization of alkenes to generate important  $\gamma$ -amino acids with high efficiency and selectivity under mild reaction conditions.

We started the investigation by employing *N,N*-dimethylaniline **1a** and methyl 4-vinylbenzoate **2a** as model substrates

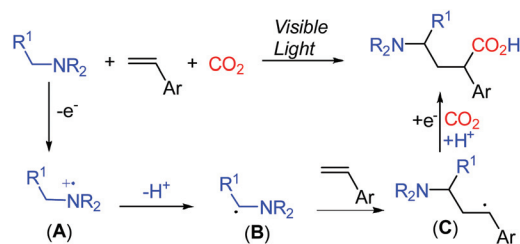


**Scheme 1** Typical approaches to  $\gamma$ -amino acid derivatives.

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Scheme 2 Photocatalytic preparation of  $\gamma$ -amino acids from  $\text{CO}_2$ .

under the irradiation of 5 W blue light emitting diodes (LEDs) with atmospheric pressure  $\text{CO}_2$ . Yields were determined after methyl esterification with  $\text{TMSCHN}_2$  (Table 1). After numerous extensions of the reaction parameters, the desired product **3'aa** was obtained in 95% yield when 4 mol% of 1,2,3,5-tetrakis-

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

| Entry           | Deviation from standard conditions  | Yield of <b>3'aa</b> <sup>b</sup> [%] | Yield of <b>4aa</b> <sup>b</sup> [%] |
|-----------------|-------------------------------------|---------------------------------------|--------------------------------------|
| 1               | None                                | 95 (89)                               | 4                                    |
| 2               | Ir-1 instead of 4CzIPN              | 84                                    | 4                                    |
| 3               | Ir-2 instead of 4CzIPN              | 76                                    | 4                                    |
| 4               | Ir-3 instead of 4CzIPN              | 12                                    | 1                                    |
| 5               | Ru-1 instead of 4CzIPN              | 83                                    | 2                                    |
| 6               | Without 4CzIPN                      | —                                     | —                                    |
| 7               | LiF instead of LiCl                 | 44                                    | 3                                    |
| 8               | $\text{LiBF}_4$ instead of LiCl     | 39                                    | 5                                    |
| 9               | $\text{LiOAc}$ instead of LiCl      | 43                                    | 7                                    |
| 10              | NaCl instead of LiCl                | 20                                    | 2                                    |
| 11              | KCl instead of LiCl                 | 26                                    | 3                                    |
| 12              | Without LiCl                        | 62                                    | 3                                    |
| 13              | 2 eq. instead of 4 eq. of LiCl      | 82                                    | 5                                    |
| 14              | Add 20 mol% Q-1                     | 46                                    | 24                                   |
| 15              | Add 20 mol% Q-2                     | 48                                    | 15                                   |
| 16              | DMF instead of DMSO                 | 80                                    | 15                                   |
| 17              | MeCN instead of DMSO                | 8                                     | 44                                   |
| 18              | THF instead of DMSO                 | 8                                     | 28                                   |
| 19 <sup>c</sup> | 0.025 M instead of 0.1 M            | 56                                    | 19                                   |
| 20              | 2 eq. instead of 6 eq. of <b>1a</b> | 79                                    | 9                                    |
| 21              | 4 eq. instead of 6 eq. of <b>1a</b> | 73                                    | 11                                   |
| 22              | 7 eq. instead of 6 eq. of <b>1a</b> | 94                                    | 3                                    |

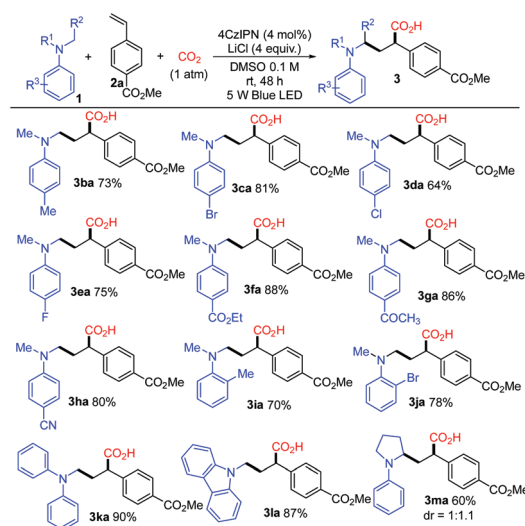
Ir-1 R<sup>1</sup>=R<sup>2</sup>=H  
Ir-2 R<sup>1</sup>=CF<sub>3</sub>, R<sup>2</sup>=F

Q-1 R=H  
Q-2 R=OAc

<sup>a</sup> Reaction conditions: **1a** (0.6 mmol), **2a** (0.1 mmol), 4CzIPN (0.004 mmol), LiCl (0.4 mmol), DMSO (1 mL), 1 atm  $\text{CO}_2$ , 5 W blue LED, room temperature, 48 h, quenched with HCl (2 M) solution, after extraction with ethyl acetate, MeOH:ether = 1:1 (0.5 mL) and  $\text{TMSCHN}_2$  (3 equiv.) were added. <sup>b</sup> Yields determined by GC using *n*-dodecane as an internal standard; isolated yield in parentheses. <sup>c</sup> 4 mL of DMSO was used instead of 1 mL.

(carbazole-9-yl)-4,6-dicyanobenzene (4CzIPN) was used as a photoredox catalyst and LiCl as an additive in DMSO (0.1 M) at room temperature after 48 h irradiation (entry 1). The hydro-aminoalkylation product **4aa** was also detected by GC as a by-product.  $\text{Ir}(\text{ppy})_2(\text{dtbbpy})(\text{PF}_6)$ ,  $\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})(\text{PF}_6)$ , and  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  were employed as photoredox catalysts which performed less effectively than 4CzIPN (entries 2, 3 and 5). A trace amount of **3'aa** was obtained using  $\text{Ir}(\text{ppy})_3$  instead of 4CzIPN (entry 4). The reaction could not proceed without the photoredox catalyst (entry 6). The choice of the additive was pivotal; LiF,  $\text{LiBF}_4$ ,  $\text{LiOAc}$ , NaCl, and KCl were used as additives to afford lower yields of **3'aa** (entries 7–11). Notably, the reaction proceeded to give the desired product **3'aa** in 62% yield in the absence of LiCl (entry 12). When two equivalents of LiCl were employed, the desired product **3'aa** was obtained in 82% yield (entry 13). Hydrogen atom transfer (HAT) is frequently involved in photocatalysis, which offers enormous opportunities for C–H activation.<sup>14</sup> The combination of the photoredox catalyst 4CzIPN (4 mol%) with HAT catalysts such as quinuclidin-3-yl acetate and quinuclidine (20 mol%) provided the desired product **3'aa** in 46% and 48% yields, respectively (entries 14 and 15). Among the solvents examined, DMSO resulted in the best reactivity and selectivity (entries 1 and 16–18). Both reactivity and selectivity significantly decreased with the dilution of **1a** as expected (entry 19). The utilization of 6 equivalents of amine was proved to be necessary to obtain the desired product in a good yield (entries 1, 20–22).

With the optimized conditions, a study on the substrate scope was carried out. Firstly, a variety of tertiary amines **1** were used in the reaction with methyl 4-vinylbenzoate **2a** to synthesize  $\gamma$ -amino acids with a range of substituents on anilines. The representative results are shown in Scheme 3. The



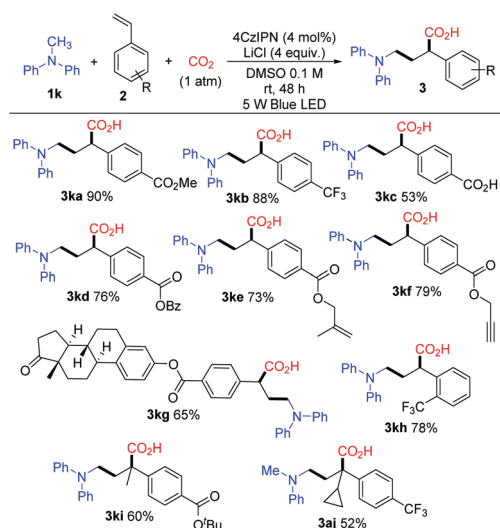
Scheme 3 Photocatalytic reactions of methyl 4-vinylbenzoate **2a** with amines. Reaction conditions: **1** (1.2 mmol), **2a** (0.2 mmol), 4CzIPN (0.008 mmol), LiCl (0.8 mmol), DMSO (2 mL), 1 atm  $\text{CO}_2$ , 5 W blue LED, room temperature, 48 h, quenched with HCl (2 M) solution. Yields of isolated carboxylic acid **3** without esterification with  $\text{TMSCHN}_2$ .

reaction of **2a** with dimethyldiphenylamine (**1a**) proceeded smoothly to give  $\gamma$ -amino acid **3aa** in 88% isolated yield without esterification with TMSCHN<sub>2</sub>. Introduction of a substituent such as methyl, bromo, chloro, or fluoro at the *para*-position of the benzene ring did not affect much the yield of  $\gamma$ -amino acids **3** (**3ba** in 73%, **3ca** in 81%, **3da** in 64%, **3ea** in 75%). The amines bearing highly electron-withdrawing groups such as an ester, keto carbonyl, or cyano group at the *para*-position in the benzene ring yielded the expected products **3** in high yields (**3fa** in 88%, **3ga** in 86%, **3ha** in 80%). The substituents such as methyl or bromo located at the *ortho*-position in the benzene ring also afforded the target products **3** in good yields (**3ia** in 70%, **3ja** in 78%). To our delight, methyl-diphenylamine **1k** was well applicable and delivered the corresponding  $\gamma$ -amino acid **3ka** in 90% yield.  $\gamma$ -Amino acids with a carbazolyl group have potential in materials science; in this reaction, 9-methyl-9H-carbazole **1l** was also applicable and delivered the corresponding  $\gamma$ -amino acid **3la** in 87% yield. The cyclic amine 1-phenylpyrrolidine **1m** was transformed into **3ma** in 60% yield. It is noteworthy that the utilization of primary and secondary amines such as octan-1-amine and *N*-methylaniline as well as other aromatic amines such as 4-methoxy-*N,N*-dimethylaniline and *N*-dimethylnaphthalen-1-amine did not lead to the corresponding products.

Next, we examined the photocatalytic reactions with a variety of alkenes **2**; the typical results are shown in Scheme 4. A series of substituted styrenes with electron-withdrawing substituents at the *para*-position such as trifluoromethyl (**2b**), carboxyl (**2c**) and esters (**2a**, **2d**, **2e**, **2f**, **2g**, and **2i**) could be accommodated and afforded the corresponding products **3** in good yields. Remarkably,  $\gamma$ -amino acid **3kc** was prepared smoothly when 4-vinylbenzoic acid (**2c**) was employed. When

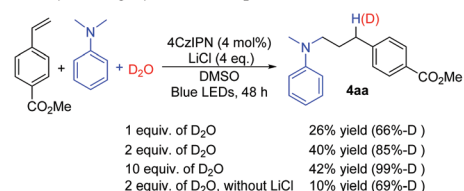
benzyl-, alkenyl-, and alkynyl-derived ester styrenes such as **2d**, **2e**, and **2f** were employed, the corresponding products **3kd**, **3ke**, and **3kf** were formed in good yields, respectively. Moreover, estrone-derived ester styrene **2g** was also tested, and the corresponding  $\alpha$ -aminomethylcarboxylation product **3kg** was obtained in 65% yield. It is noteworthy that estrone linked with  $\gamma$ -amino-acid moiety could be well soluble in organic solutions while estrone cannot. Notably, the styrene with a substituent at the *ortho*-position of the benzene ring also gave the corresponding product **3kh** in 78% yield. Vinylpyridine was employed as the styrene in this reaction and a trace amount of the desired product was detected. Furthermore,  $\alpha$ -substituted styrenes could be used resulting in the target compounds **3ki** and **3aj** with quaternary carbon centers. Unfortunately,  $\beta$ -substituted styrenes such as methyl (*E*)-4-(prop-1-en-1-yl)benzoate could not undergo the reaction. In addition, we did not detect the desired products when butyl acrylate and acrylonitrile were used in this reaction. In general, an electron-withdrawing group at the benzene ring of the styrene is essential to obtain the corresponding  $\gamma$ -amino acid in this reaction.

Additional experiments were performed to gain insight into the reaction mechanism. Light on-off experiments indicated that continuous light irradiation was essential to perform the reaction, and during the process, hydroaminoalkylation was restrained all the way. The quantum yield of the reaction of **1a** with **2a** under the optimized conditions was 0.0414 (see the ESI†). The isotope labelling experiments with D<sub>2</sub>O implied that  $\gamma$ -amino benzylic anionic species could be the intermediates (Scheme 5a). It is noteworthy that the yield of **4aa** increased with increasing amount of D<sub>2</sub>O, and LiCl also played



**Scheme 4** Photocatalytic reactions of methyl-diphenylamine **1k** and **1a** with alkenes. Reaction conditions: **1k** or **1a** (1.2 mmol), **2** (0.2 mmol), 4CzIPN (0.008 mmol), LiCl (0.8 mmol), DMSO (2 mL), 1 atm CO<sub>2</sub>, 5 W blue LED, RT, 48 h, quenched with HCl (2 M) solution. Yields of isolated products.

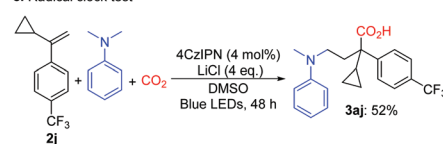
**a. Isotope labelling experiments with D<sub>2</sub>O**



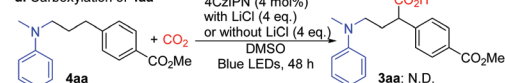
**b. Trapping with radical scavengers**



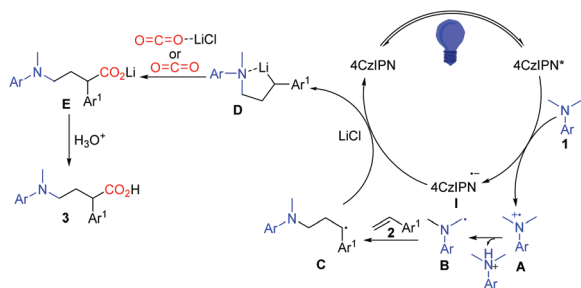
**c. Radical clock test**



**d. Carboxylation of 4aa**



**Scheme 5** Control experiments for elucidation of the mechanism.



**Scheme 6** The proposed reaction mechanism.

a vital role in this reaction. When the radical scavengers 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) were used in the reaction, the desired product **3aa** was not obtained (Scheme 5b) respectively; these results indicated that this transformation might rely on a radical process. Furthermore, the radical clock substrate **2j** was used under the optimal reaction conditions; however, no ring-opening product was detected (Scheme 5c), which suggested that the single electron reduction step from the benzyl radical to the benzyl anion is quite quick. Compound **4aa** was treated with standard conditions, and **3aa** was not observed and **4aa** was retained (Scheme 5d), which rules out the direct C–H carboxylation pathway.<sup>15</sup>

Based on the aforementioned results, a plausible mechanism was proposed and is shown in Scheme 6. Photo-excited 4CzIPN is reductively quenched with aniline leading to **I** and the radical cation intermediate **A**, which then deprotonates and gives  $\alpha$ -aminoalkyl radical **B** in the presence of a base. The carbon radical **B** undergoes addition to the C=C bond of styrene **2** to selectively generate the  $\gamma$ -amino benzylic radical **C**. A subsequent single-electron transfer (SET) between **C** and the reduced photocatalyst 4CzIPN gives the  $\gamma$ -amino benzylic carbanion **D**, which is proposed as a lithium chelated species to stabilize the carbanion and accelerate the SET process. The nucleophilic addition to CO<sub>2</sub> or activated CO<sub>2</sub> by LiCl and protonation complete this reaction and yield the expected  $\gamma$ -amino acids.

## Conclusions

In summary, we have developed a catalytic intermolecular dicarbofunctionalization of styrenes with CO<sub>2</sub> and amines through photoredox catalysis. The carbocarboxylation has the advantages of superior step and atom economy, broad substrate scope, and mild conditions. This study represents a rare example of the catalytic carbocarboxylation of alkenes with CO<sub>2</sub> in a redox-neutral fashion, which could lead to a new general alkene dicarbofunctionalization strategy using abundant and inexpensive chemical feedstock.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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