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Electrochemical selective hydrocarboxylation of acrylamides with carbon dioxide for precise control of α - and β -carboxylation



Xiuli Zhao^{1,2}, Ziren Chen¹, Fei Xue¹, Haomin Chen¹, Lin Zhang¹, Bin Wang¹, Shaofeng Wu¹, Yu Xia¹, Shoucai Wang¹, Weiwei Jin³, Yonghong Zhang¹ & Chenjiang Liu^{1,4}

The hydrocarboxylation of acrylate with carbon dioxide (CO₂) have been achieved through metal-catalysis, photochemistry catalysis or electrochemistry catalysis in recent years. The hydrocarboxylation of acrylamide has rarely been studied so far, because of the electron cloud density of the carbon-carbon double bond in acrylamide molecules is lower than that of acrylates. Herein, we report an electrochemical selective hydrocarboxylation method of acrylamides with CO₂. The α -carboxylation and β -carboxylation products can be obtained by adjusting the reaction conditions. The present protocol features mild conditions, good regioselectivity, broad substrate scope and high atom economy. Furthermore, detailed control experiments and DFT calculations results showed that the carboxylation at the α - and β - sites undergo different reaction processes.

CO₂ is the main component of greenhouse gases and has an important impact on climate change¹. However, CO₂ is also an abundant, sustainable, and non-toxic one-carbon (C1) building block that could react with olefins^{2–14}, alkynes^{15–18}, imines^{19,20}, cyclic ethers^{21–23}, halides^{24–31}, arenes^{32–34}, etc. to synthesize many types of compounds^{35,36}. Electron-deficient alkenes do not react easily with CO₂ due to the descend electron cloud density of carbon-carbon double bond³⁷. To date, despite some hydrocarboxylation methods of electron-deficient alkenes with CO₂ have been reported, the reaction substrates were mainly focus on acrylates. Mikami's group used expensive [RhCl(cod)]₂ as catalyst and highly flammable ZnEt₂ as reducing agent to achieve the hydrocarboxylation of acrylate with CO₂ (Fig. 1a i)³⁸. In recent years, with the rise of green organic synthesis, organic photochemistry has developed rapidly. Yu's lab achieved β -carboxylation of acrylates with CO₂ through an electron donor-acceptor (EDA) photochemical strategy (Fig. 1a ii)³⁹.

Electrochemistry, as another synthesis strategy of green chemistry, has attracted the attention of organic chemists because it avoids the need for chemical oxidation-reduction agents^{40–48}. Buckley's group successfully accomplished the hydrocarboxylation of acrylate with

CO₂ through electrochemistry, yielding β -carboxylation products (Fig. 1a iii)⁴⁹. Unlike acrylate, the conjugation of the nitrogen atom and the carbonyl group in acrylamide molecule results in a more dispersed electron cloud around the carbon-carbon double bond, which weakens the nucleophilicity of acrylamide⁵⁰. Consequently, the hydrocarboxylation of acrylamide with CO₂ presents a significant challenge. Despite relevant research reports, these reactions could only be achieved through photocatalytic methods, and were limited to the β -carboxylation of acrylamide (Fig. 1b)^{51,52}.

Based on our research foundations in electrochemical organic synthesis^{53–59}, and our research interest in CO₂ conversion. Herein, we report an electrochemical approach that enables the selective hydrocarboxylation of acrylamide to obtain α - and β -carboxylation products by adjusting solvents and electrolytes under mild reaction conditions (Fig. 1c).

Results and Discussion

We commenced our study using *N*-methyl-*N*-phenylmethacrylamide (**1a**) as the model substrate in an undivided cell under 1 atm of CO₂ atmosphere (Table 1). Pleasantly, the β -carboxylation product **2a** was

¹State Key Laboratory of Chemistry and Utilization of Carbon Based Energy Resources, Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education & Xinjiang Uygur Autonomous Region, Urumqi Key Laboratory of Green Catalysis and Synthesis Technology, College of Chemistry, Xinjiang University, Urumqi, China. ²Medical College, Hexi University, Zhangye, China. ³Key Laboratory of Specialty Agri-Product Quality and Hazard Controlling Technology of Zhejiang Province, College of Life Sciences, China Jiliang University, Hangzhou, China. ⁴School of Chemistry and Chemical Engineering, Xinjiang Normal University, Urumqi, China. ✉e-mail: pxylcj@126.com

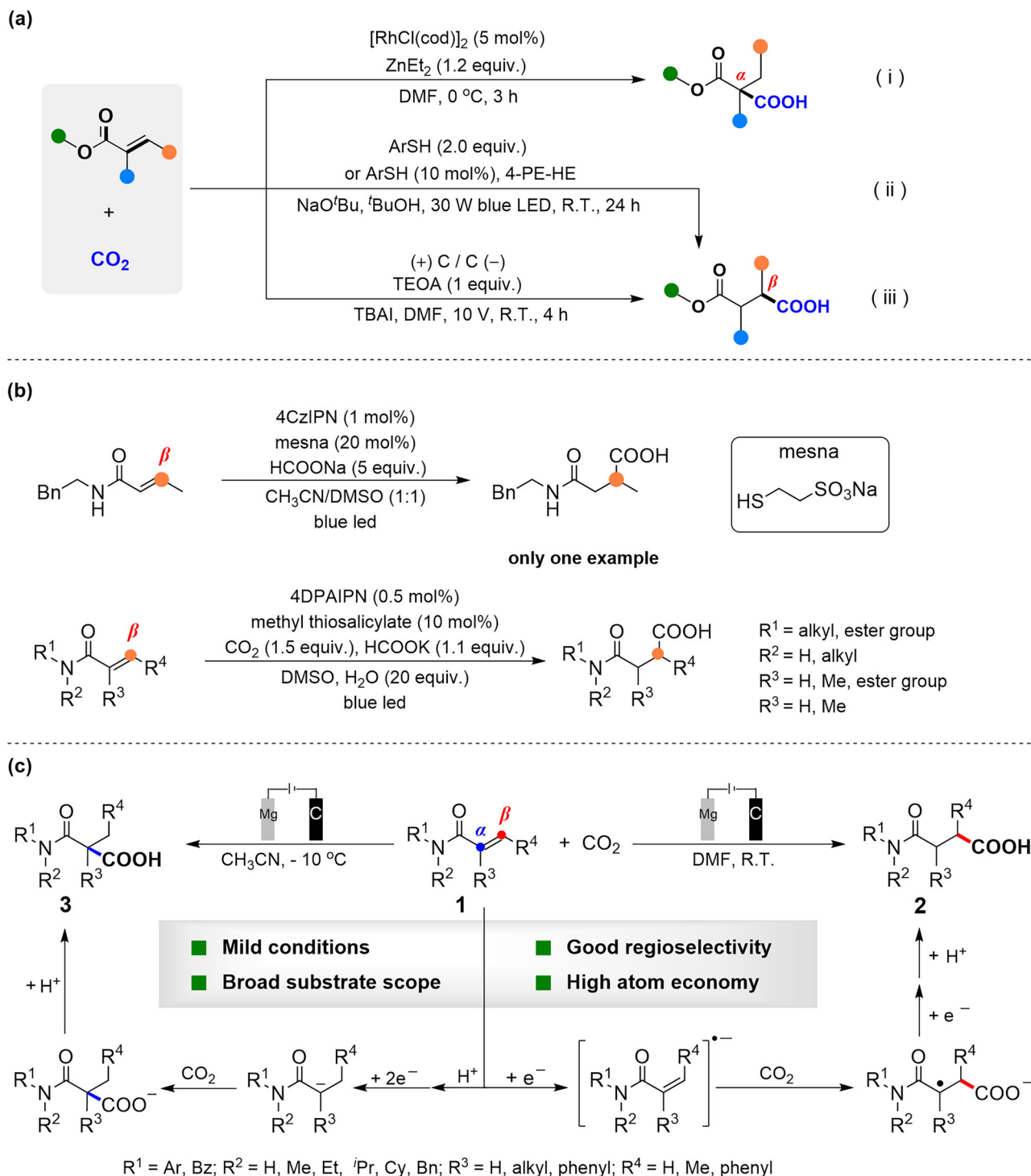
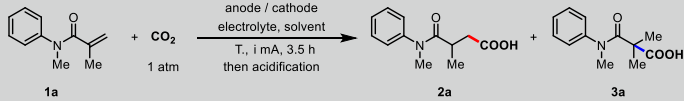


Fig. 1 | Hydrocarboxylation of electron-deficient alkenes with CO₂. **a** Hydrocarboxylation reactions of acrylates with CO₂. **b** Previous hydrocarboxylation of acrylamides with CO₂. **c** This work: Electrochemical selective hydrocarboxylation of acrylamides with CO₂.

obtained in a 70% isolated yield when a magnesium sheet was used as the anode, and TBAC was used as a supporting electrolyte in DMF at room temperature (entry 1). By substituting Mg with Al or Zn as the anode (entries 2, 3), the reaction efficiency was significantly decreased. Surprisingly, the reaction still occurred when graphite carbon was used as the anode (entry 4). This might be due to the oxidation of chloride ions at the anode. When TBAI (entry 5), TBABF₄ (entry 6), TBAPF₆ (entry 7), and TBAClO₄ (entry 8) were employed as the supporting electrolyte, the yield of **2a** was low. Several other solvents, including DMAc, NMP, DMSO, and CH₃CN, were evaluated; the results were

not satisfactory (entries 9–12). However, interestingly, α -carboxylation product **3a** was obtained when using DMSO and CH₃CN as solvents. This indicates that the solvent was crucial in determining the reaction site. Subsequently, using CH₃CN as the solvent, we examined the electrochemical conditions of the α -carboxylation reaction. After replacing TBAC with other electrolytes, the yield of **3a** did not increase significantly, whereas the formation of **2a** was markedly reduced (entries 13–16). Notably, the use of TBAClO₄ as the electrolyte led to the exclusive formation of the α -carboxylation product **3a** (entry 17). The synergistic effect of TBAClO₄ and CH₃CN enables the selective

Table 1 | Optimization of the reaction conditions^[a]

						
Entry	Anode/ Cathode	Electrolyte	Solvent	T.	Yield (%) ^[d]	
					2a	3a
1	Mg/C	TBAC	DMF	R.T.	80 (70) ^[e]	-
2	Al/C	TBAC	DMF	R.T.	51	-
3	Zn/C	TBAC	DMF	R.T.	26	-
4	C/C	TBAC	DMF	R.T.	39	-
5	Mg/C	TBAI	DMF	R.T.	45	-
6	Mg/C	TBABF ₄	DMF	R.T.	63	-
7	Mg/C	TBAPF ₆	DMF	R.T.	33	-
8	Mg/C	TBAClO ₄	DMF	R.T.	55	-
9	Mg/C	TBAC	DMA _C	R.T.	72	-
10	Mg/C	TBAC	NMP	R.T.	52	-
11	Mg/C	TBAC	DMSO	R.T.	47	6
12	Mg/C	TBAC	CH ₃ CN	R.T.	62	14
13 ^[b]	Mg/C	TBAB	CH ₃ CN	R.T.	20	13
14 ^[b]	Mg/C	TBAI	CH ₃ CN	R.T.	11	7
15 ^[b]	Mg/C	TBABF ₄	CH ₃ CN	R.T.	13	16
16 ^[b]	Mg/C	TBAPF ₆	CH ₃ CN	R.T.	16	14
17 ^[b]	Mg/C	TBAClO ₄	CH ₃ CN	R.T.	-	18
18 ^[b]	Mg/C	TEAClO ₄	CH ₃ CN	R.T.	-	37
19 ^{[b][c]}	Mg/C	TEAClO ₄	CH ₃ CN	R.T.	-	46
20 ^{[b][c]}	Mg/C	TEAClO ₄	CH ₃ CN	0 °C	-	64
21 ^{[b][c]}	Mg/C	TEAClO ₄	CH ₃ CN	-10 °C	-	77 (70) ^[e]
22 ^{[b][c]}	Mg/C	TEAClO ₄	CH ₃ CN	-20 °C	-	73
23	Mg/C	TBAC	DMF	-10 °C	76	-

[a] Reaction conditions: undivided cell, Mg plate anode (10 mm × 20 mm × 0.5 mm), C plate cathode (10 mm × 20 mm × 1.0 mm), **1a** (0.2 mmol), electrolyte (0.2 mmol), CO₂ (1 atm), solvent (3.0 mL), 8 mA, 3.5 h, room temperature (R.T.). [b] 6 mA. [c] **1a** (0.1 mmol). [d] The yield was determined by ¹H NMR using maleic acid as the internal standard. [e] Isolated yield. DMF = *N,N*-dimethylformamide, DMSO dimethyl sulfoxide, CH₃CN acetonitrile, NMP *N*-methyl-2-pyrrolidone, DMA_C = *N,N*-dimethylacetamide, TBAC tetrabutylammonium chloride, TBAI tetrabutylammonium iodide, TBAB tetrabutylammonium bromide, TBAClO₄ tetrabutylammonium perchlorate, TBABF₄ tetrabutylammonium tetrafluoroborate, TBAPF₆ tetrabutylammonium hexafluorophosphate.

control of the carboxylation reaction at the α position. Employing TEAClO₄ as the electrolyte further improved the yield of **3a** (entry 18). This might be because, during the initial stage of the reaction, the tetraethylammonium cation with lower steric hindrance is more conducive to stabilizing the carboxylate formed at the α position⁶⁰. After reducing the concentration of **1a**, the reaction efficiency has improved (entry 19). We speculate that the structure of compound **3a** may be thermodynamically unstable compared to compound **2a**. Therefore, the reaction for generating **3a** might be a kinetic-controlled process, and low temperatures may be beneficial for the reaction. Based on this, we attempted to lower the reaction temperature (entries 20–22). The experimental results were in line with expectations, and the target product **3a** was obtained with a yield of 70% at -10 °C (entry 21). In contrast, reducing the temperature will not increase the yield of **2a** (entry 23).

With the optimal reaction conditions for the selective hydrocarboxylation of acrylamide in hand, the substrate scope was further investigated under these conditions. We first tested the range of substrates for the β -carboxylation reaction (Fig. 2). *N*-methyl-*N*-phenylmethacrylamide bearing either electron-donating or electron-

withdrawing groups on the benzene ring all reacted smoothly to afford the desired products **2a–2m** in 32 to 90% yields. The substrate containing naphthalene ring or tetrahydroquinoline ring was gained products **2n** and **2o** with the yield of 75% and 53%, respectively. *N*-phenylmethacrylamide with different *N*-substituents showed very high reactivity to afford the corresponding products **2p–2s** in good to excellent yields. The acrylamide substrates containing different substituents in the olefin could also undergo the reaction smoothly and yield the corresponding target products (**2t–2w**). When the benzoyl group was substituted for the phenyl group, the β -carboxylation products **2x–2z** were still obtained with moderate yields. The structures of products **2r** and **2x** were determined by X-ray crystallographic analysis.

Later, a diverse range of aryl-substituted substrates have been examined in the α -carboxylation reaction of acrylamide with CO₂, and the results were summarized in Fig. 3. The substrates containing various electron-donating groups on the phenyl group of compounds **1** were more suitable for this method (**3a–3g**). The yields decreased modestly when the 4-position of the phenyl group was substituted with electron-withdrawing groups (**3h–3l**). Substrates containing

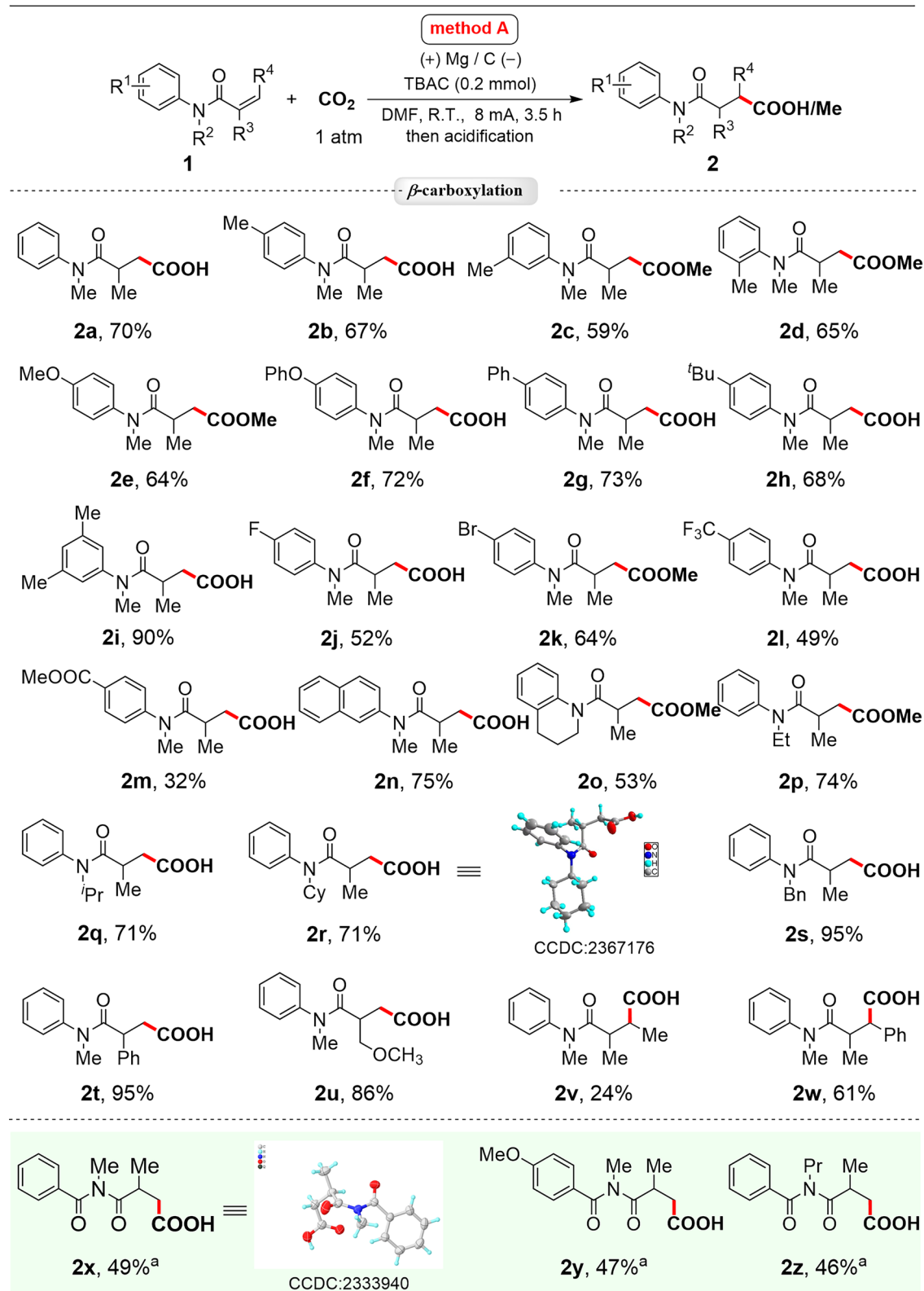


Fig. 2 | Scope of the β -carboxylation reaction. Reaction conditions: undivided cell, Mg plate anode (10 mm \times 20 mm \times 0.5 mm), C plate cathode (10 mm \times 20 mm \times 1.0 mm), **1** (0.2 mmol), TBAC (0.2 mmol), CO₂ (1 atm), DMF (3.0 mL), 8 mA, 3.5–5 h. ^a 4 mA, 6 h.

3,4-dimethyl-substituted benzene ring, naphthalene ring, or tetrahydroquinoline ring also exhibited moderate reactivity (**3m–3o**). Altering the nitrogen protecting group to isopropyl, cyclohexyl, or benzyl would also lead to the desired products in medium to high yields

(**3p–3r**). To our surprise, the unprotected NH substrates were also able to produce α -carboxylation products (**3s–3t**), which may be used for further functionalization to synthesize other kinds of important complex molecules. When there are other substituents at the α - or β -position

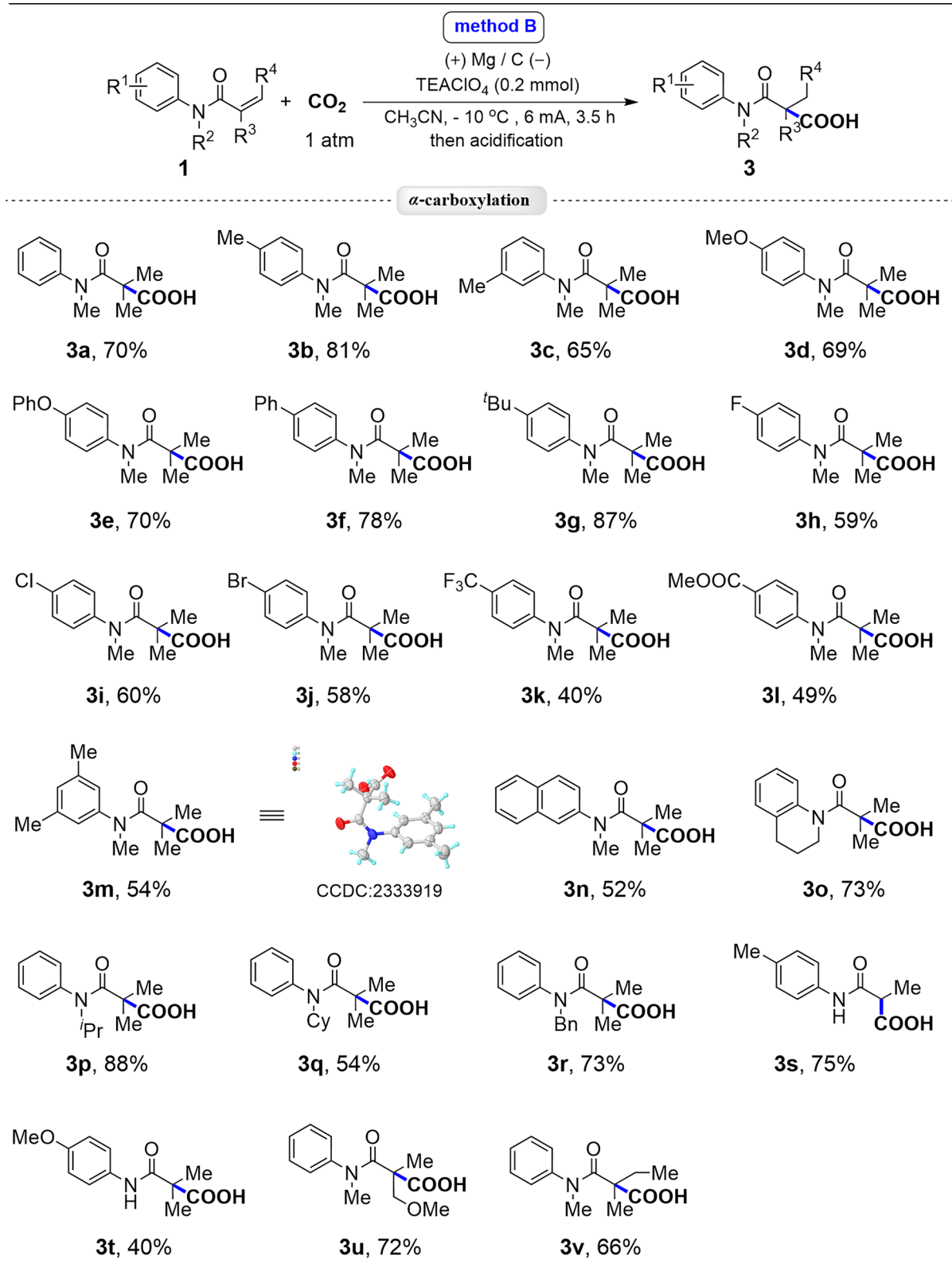


Fig. 3 | Scope of the α -carboxylation reaction. Reaction conditions: undivided cell, Mg plate anode (10 mm \times 20 mm \times 0.5 mm), C plate cathode (10 mm \times 20 mm \times 1.0 mm), **1** (0.1 mmol), TEAClO₄ (0.2 mmol), CO₂ 1 atm, CH₃CN (3.0 mL), 6 mA, 3.5–5 h.

of the double bond, the target products could be obtained with a moderate yield (**3 u**, **3 v**). Unfortunately, the α -phenyl and β -phenyl substituted acrylamides have not yielded the target compounds due to the influence of electronic effects. Unexpectedly, replacing benzene ring

with indole ring, the β -carboxylation products (**5a–5f**) were detected under the conditions of method B (Fig. 4).

To demonstrate the practicability of this electrocarboxylation reaction, large-scale reactions between **1a** and CO₂ were conducted

Fig. 4 | The other scope of the β -carboxylation reaction. Reaction conditions: undivided cell, Mg plate anode (10 mm \times 20 mm \times 0.5 mm), C plate cathode (10 mm \times 20 mm \times 1.0 mm), **4** (0.1 mmol), TEAClO₄ (0.2 mmol), CO₂ (1 atm), CH₃CN (3.0 mL), 4 mA, 6 h.

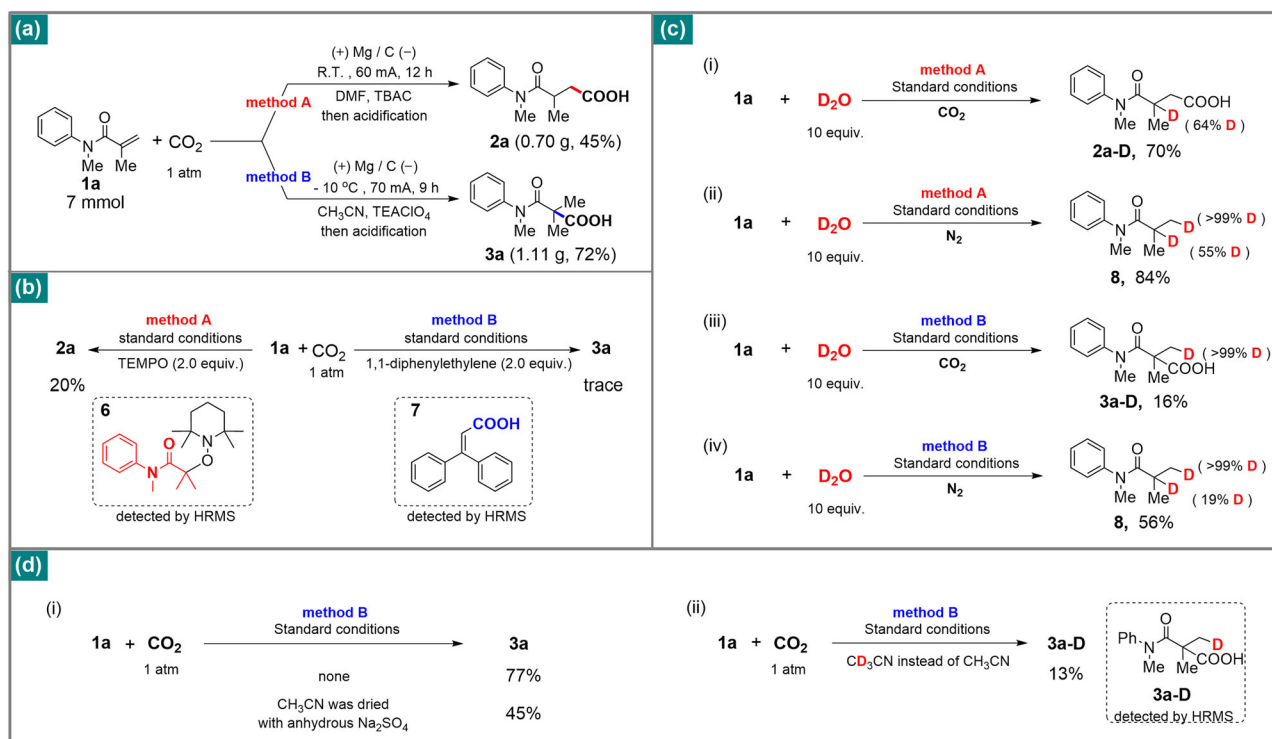
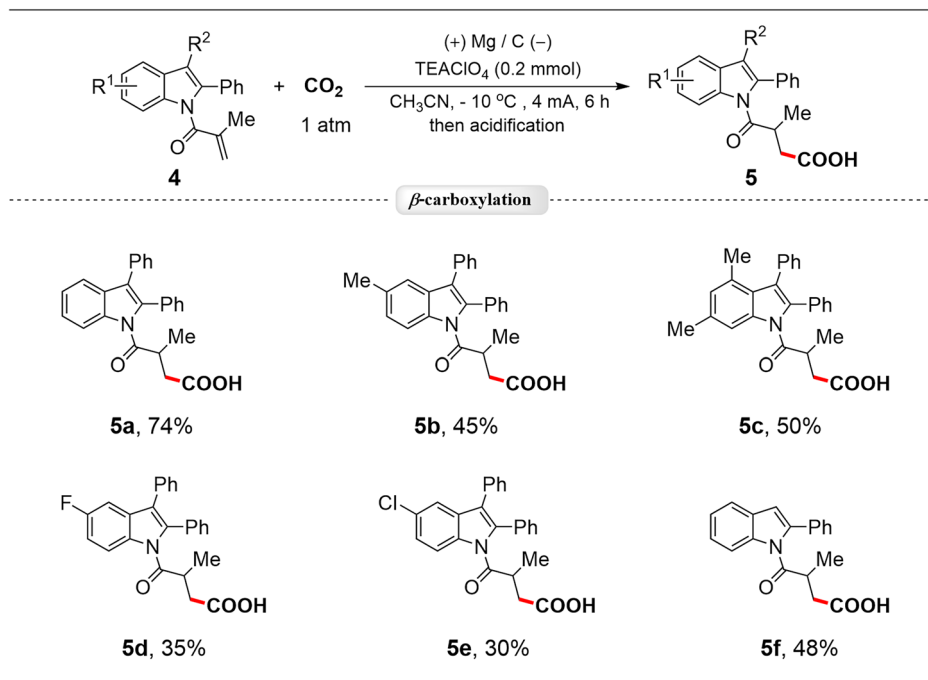


Fig. 5 | Control experiments. **a** Large-scale reactions. **b** Radical trap experiments. **c** Deuterium labeling experiments. **d** Proton source exploration experiments.

under the conditions of methods A and B, respectively, the results were shown in Fig. 5a. Next, various control experiments were tested in order to gain more insights into the reaction mechanism. The free radical scavengers were added into the reaction systems of the conditions A and B respectively, the hydrocarboxylation reactions were almost inhibited, which suggested that the reactions presumably adopted a radical pathway (Fig. 5b). Meanwhile, compounds **6** and **7** were observed by HRMS, which indicated the existence of α -carbon radical intermediate in method A and CO₂ radical anion

intermediate in method B. In addition, sodium formate was discovered in the absence of **1a** through ¹H NMR and ¹³C NMR under the reaction conditions of method A and method B respectively, the experiment results showed that CO₂ could also be reduced in both method A and B (see Supporting Information S5 for more details)³⁹.

Deuterium labeling experiments confirmed the presence of β -carbon anion intermediates in the reaction pathway of method A (Fig. 5c, i and ii)^{8,19}. And in method B, the β -site was easily deuterated in both CO₂ and N₂ atmospheres (Fig. 5c, iii and iv), indicating that the proton may

have undergone an addition reaction with **1a** prior to CO₂, and water provided protons in the reaction. After that, we conducted the following experiments to investigate the source of water. We conducted experiments using a solvent dried with anhydrous sodium sulfate and found a significant decrease in the yield of **3a** (Fig. 5d, i). And **3a-D** was detected when using CD₃CN as a solvent (Fig. 5d, ii). The above experimental results indicate that protons mainly originate from the trace water present in acetonitrile and acetonitrile itself⁶¹. Perchlorate may have facilitated the proton dissociation process of acetonitrile (Fig. S9). At the same time, the results of DFT calculations (Fig. 6) showed that the β -carboxylation product **2a** would be gained whether it is **1a** reduction or CO₂ reduction³², and the carboxylation of α -site was not initiated by single electron reduction⁶², which is consistent with the results of deuterium labeling experiments.

Cyclic voltammetry experiments were conducted to observe the changes of redox profile (Fig. 7). Compared with CO₂⁶², **1a** is more difficult to reduce (Fig. 7a, red), and the reduction potential of **1a** did not

change significantly in different solvents (see Supporting Information Fig. S6 for more details). When the solution was saturated with CO₂, the profile of the reduction wave changed significantly (Fig. 7a, green), because of the reaction between the radical anion and CO₂⁶. The cyclic voltammetry test results indicate that **4a** could not only be reduced (-1.73 V) but also easily oxidized (0.07 V) (Fig. 7b, blue). Therefore, indole-type compounds were detected in the reaction solution^{47,63}. However, under the reaction conditions of Method A, no carboxylation products were observed, which might be related to the presence of multiple reduction peaks in this condition (see Supporting Information S15 and Fig. S8 for more details).

On the basis of the above mechanistic studies, the plausible reaction pathways have been proposed (Fig. 8). In method A, **1a** was reduced to a radical anion (**I**), which underwent nucleophilic attack to CO₂ to give the carboxylic radical anion (**II**), the radical intermediate (**II**) was reduced through another one-electron reduction process to give the carboxylation product **2a** after work-up⁶⁴. The α -carboxylation process proceeded as follows: **1a** and proton undergo Markovnikov's addition, then two single electron reductions occurred, resulting in the formation of a carbon anion intermediate (**V**). Subsequently, the intermediate **V** was attacked by CO₂ to form **VI**, which was then protonated to yield **3a**^{3,65}.

Conclusion

Although there have been reports on the hydrocarboxylation reaction of acrylamide with CO₂, effective control over the reaction site has not yet been achieved. This study presents an effective electrochemical selective hydrocarboxylation method of acrylamide with CO₂ under mild conditions. By selecting electrochemical conditions such as electrolytes and solvents, the selective carboxylation of the α - and β -positions can be easily achieved. Control experiments and DFT calculations results show that the carboxylation of the α - and β -sites follows different reaction processes. Specifically, β -carboxylation is initiated by the reduction of **1a** or CO₂, while α -carboxylation is initiated by the hydrogenation reduction of **1a**.

Methods

Synthesis of compounds 2a-2z (general procedure)

Acrylamide (**1**) (0.2 mmol) and TBAC (0.2 mmol, 1.0 equiv.) were added to a 10 mL reaction tube containing a stir bar. The reaction tube is then installed with a graphite carbon cathode and Mg plate

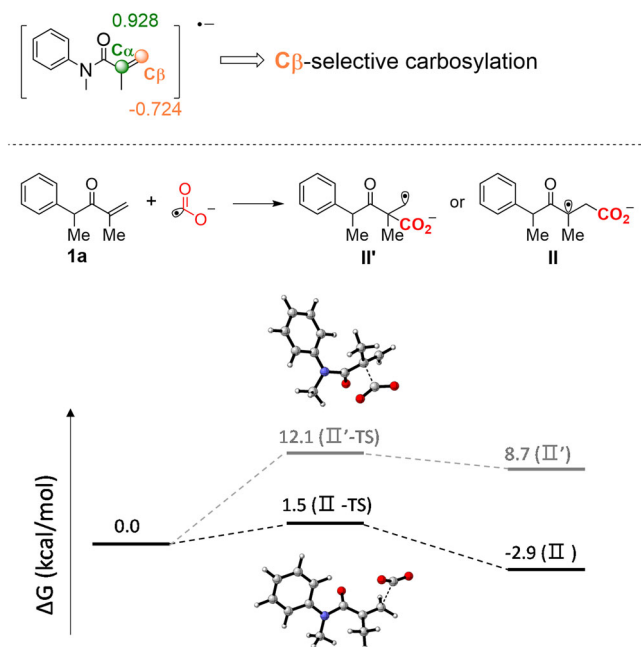


Fig. 6 | Calculated reduction potentials and reaction diagrams for the carboxylation of **1a**. **1a** is reduced (top) and CO₂ is reduced (bottom).

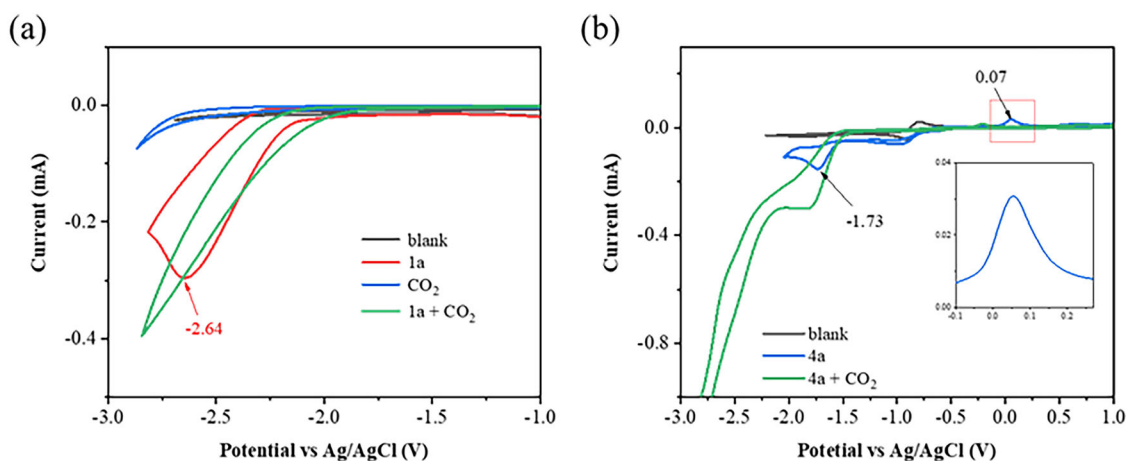
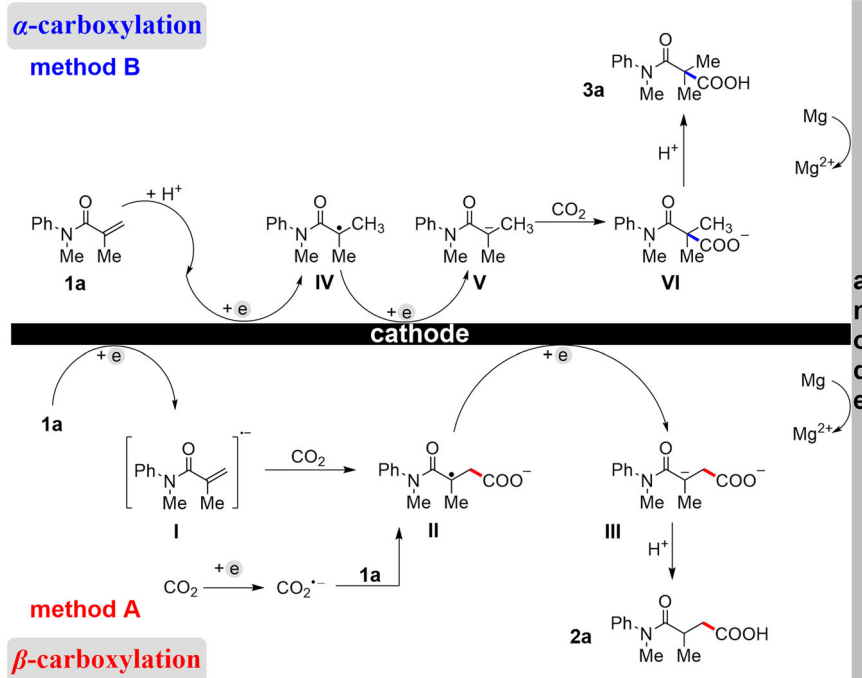


Fig. 7 | Cyclic voltammetry studies. a Cyclic voltammograms of method A. b Cyclic voltammograms of **4a** in CH₃CN.

Fig. 8 | Plausible mechanism. The reaction pathways of α -carboxylation (top) and β -carboxylation (bottom).



anode and evacuated and backfilled with CO₂ for at least 3 times. Then dry DMF (3.0 mL) was added to the reaction mixture by syringe. The reaction mixture was electrolyzed under a constant current of 8 mA for 3.5 h at room temperature. After the electrolytic reaction, the mixture was carefully quenched with HCl (2 N, 2 mL) and extracted three times with ethyl acetate (3 × 20 mL). The combined extracts were washed with brine, and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure, and the crude residue was purified by flash column chromatography to give the desired products **2a-2z**.

Synthesis of compounds 3a-3v and 5a-5f (general procedure)

Acrylamide (**1**) (0.1 mmol) and TEAClO₄ (0.2 mmol, 2.0 equiv.) were added to a 10 mL reaction tube containing a stir bar. The reaction tube is then installed with a graphite carbon cathode and Mg plate anode and evacuated and backfilled with CO₂ for at least 3 times. Then dry CH₃CN (3.0 mL) was added to the reaction mixture by syringe. The reaction mixture was electrolyzed under a constant current of 6 mA for 3.5 h at -10 °C. After the electrolytic reaction, the mixture was carefully quenched with HCl (2 N, 2 mL) and extracted three times with ethyl acetate (3 × 20 mL). The combined extracts were washed with brine and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure, and the crude residue was purified by flash column chromatography to give the desired products **3a-3v** and **5a-5f**.

Data availability

The data generated in this study are provided in the Supplementary Information file. For the experimental procedures, data of NMR and HRMS analysis, and computational details, see Supplementary Information file. The X-ray crystallographic coordinates for structures reported in this study are provided Supplementary Data 1 and have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 2333919, 2333940, and 2367176. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Author contributions

X.L. Zhao, H.M. Chen, L. Zhang, S. C. Wang, and Y. H. Zhang designed and performed synthetic experiments, analyzed experimental data. F. Xue and B. Wang carried out the NMR analysis. Y. Xia, S. F. Wu, and W. W. Jin analyzed Cyclic voltammetry test results. X.L. Zhao, Y. H. Zhang, Z. R. Chen, and C. J. Liu drafted the manuscript with contributions from all authors. All authors participated in the discussions.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Chenjiang Liu.

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