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可见光诱导甲酸盐参与的烯烃氢羧化反应

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摘要 发展了一种温和条件下以甲酸盐作为还原剂和羰基来源的 β-选择性烯烃氢羧化反应. 利用该方法, 一系列的烯烃能够被有效地转化为高价值的羧酸产品. 该方法具备催化剂用量小、官能团耐受性好、易于放大等特点.
关键词 烯烃; 氢羧化; 光催化; 二氧化碳自由基负离子; 甲酸盐

Hydrocarboxylation of Alkenes with Formate Salts via Photocatalysis

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Abstract A transition-metal-free β-selective hydrocarboxylation of alkenes under mild conditions has been developed using a formate salt as the reductant, carbonyl source. A broad range of alkenes were compatible with this method and can be efficiently converted into value-added carboxylic acid products. This method also features low catalyst loading, good functional group tolerance, and easy scalability.
Keywords alkenes; hydrocarboxylation; photocatalysis; carbon dioxide radical anion; formate salt

1 Introduction

Catalytic hydrocarboxylation of alkenes has been widely employed to synthesize valuable carboxylic acids.[1-2] A classic carbonyl source for such transformations is the toxic and flammable carbon monoxide (CO) gas. In recent years, with the growing demand for green chemistry and carbon neutrality, the utilization of new green carbonyl sources, such as carbon dioxide (CO_2) and formic acid or formate salts which can be generated from the degradation of biomass[3] and hydrogenation of CO_2,[4] has become extremely attractive in this transformation.[5-6] Compared with CO_2, liquid formic acid and solid formate salts are much easier to handle, store and transport. Therefore, formic acid and formate salts are ideal green carbonyl sources. Recently, photocatalysis induced hydrocarboxylation of alkenes using formate salts has attracted much attention.[7-9] The carbon dioxide anion radical ($CO_2^{\bullet-}$) which is an efficient reductant ($E_{1/2}$ = −2.2 V vs. SCE)[10] has been proven to be the key intermediate of such transformations. In our previous work,[11] we disclosed a visible-light-promoted additive-free hydrocarboxylation using a formate salt as the reductant, carbonyl source and hydrogen atom transfer (HAT) reagent. Nevertheless, the transition metal catalyst or high temperature is required in the system (Scheme 1a). Wickens and Jui groups[7-9] demonstrated that using thiols as HAT catalysts, the hydrocarboxylation could be accomplished via a radical chain mechanism, respectively (Scheme 1b). However, the use of expensive catalysts, such as 1,3-dicyano-2,4,5,6-tetrakis(diphenylamino)benzene (4-DPAIPN), limits the wide application of these systems. Thus, more promising approaches are still necessary.

Herein, an alkene hydrocarboxylation system using Rose Bengal was reported, which was a cheap and readily available organic dye,[12] as the catalyst and the formate salt as the carbonyl source (Scheme 1c). A range of alkenes, including biologically active molecules, could be efficiently converted into value-added carboxylic acid products via $CO_2^{\bullet-}$ participated radical chain mechanism.

2 Results and discussion

We began our investigations using styrene **1a** as model substrates and cesium formate as the $CO_2^{\bullet-}$ source. To our delight, desire acid product (**2a**, 3-phenylpropionic acid) was observed in good yield (81%) (Table 1, Entry 1), when

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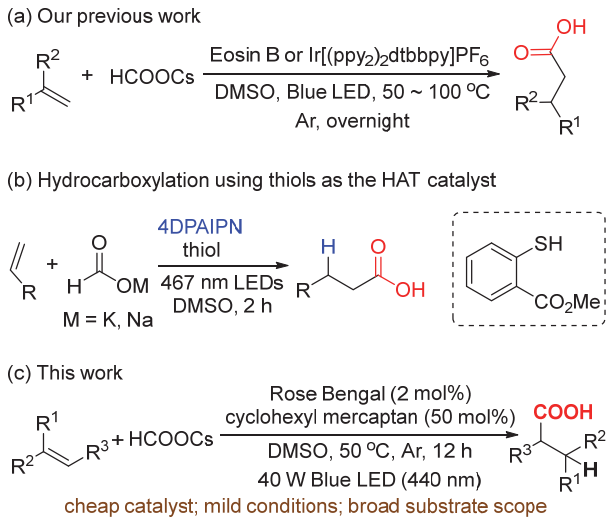


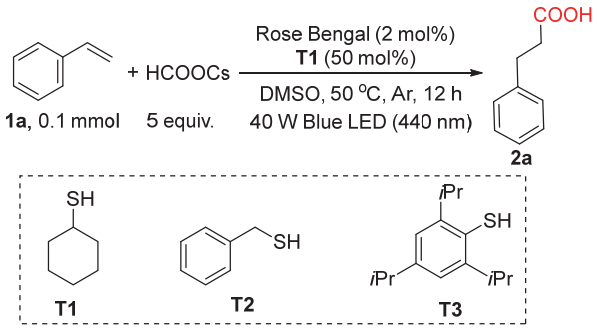
Scheme 1 Hydrocarboxylation of alkenes with formate salts via photocatalysis

Rose Bengal (2 mol%) was used as photocatalyst and **T1** (cyclohexyl mercaptan, 50 mol%) was used as additive. Other organic catalysts (Table 1, Entries 2 and 3) and thiols (Table 1, Entries 4 and 5) gave lower yields. Increasing the amount of **T1** could not improve the yield of desire product (Entry 6). The yields decreased while reducing the amount of Rose Bengal and the thiol (Entries 7 and 8). When other formates, such as $HCOONH_4$, HCOONa, and HCOOK, were employed as the carbonyl source, the yields of the product were lower (Entries 9～11). The transformation was suppressed by using other solvents (Entries 12～14). Then, control experiments proved that the catalyst, **T1** and light were required in the transformation (Entries 15～17).

The scope of the alkene hydrocarboxylation reaction was then examined. As shown in the Scheme 2, a variety of styrenes bearing both electron-donating groups (**2b**～**2f**) and electron-withdraw groups (**2g**～**2m**) gave the corresponding products in moderate to good yields. *α*-Alkyl and aryl substituted styrenes were compatible with the reaction conditions, delivering the expected products in good yields (**2n**～**2r**). Notably, when internal alkenes were used as substrates, acid products were obtained in moderate yields (**2s**～**2t**). Acrylates (**2u**～**2y**) were well suitable substrates, which gave products in good yields. Furthermore, the approach could be applied to the late-stage functionalization of biologically relevant complex molecules, giving corresponding products in good yields (**2z**～**2ac**). In addition, a gram-scale experiment was performed using 1,1-bis(4-methylphenyl)ethylene (**1q**) (5 mmol, 1.04 g) under standard conditions with irradiation of 40 W blue LEDs (440 nm), and 0.65 g of **2q** was obtained in 51% isolated yield (Scheme 2b).

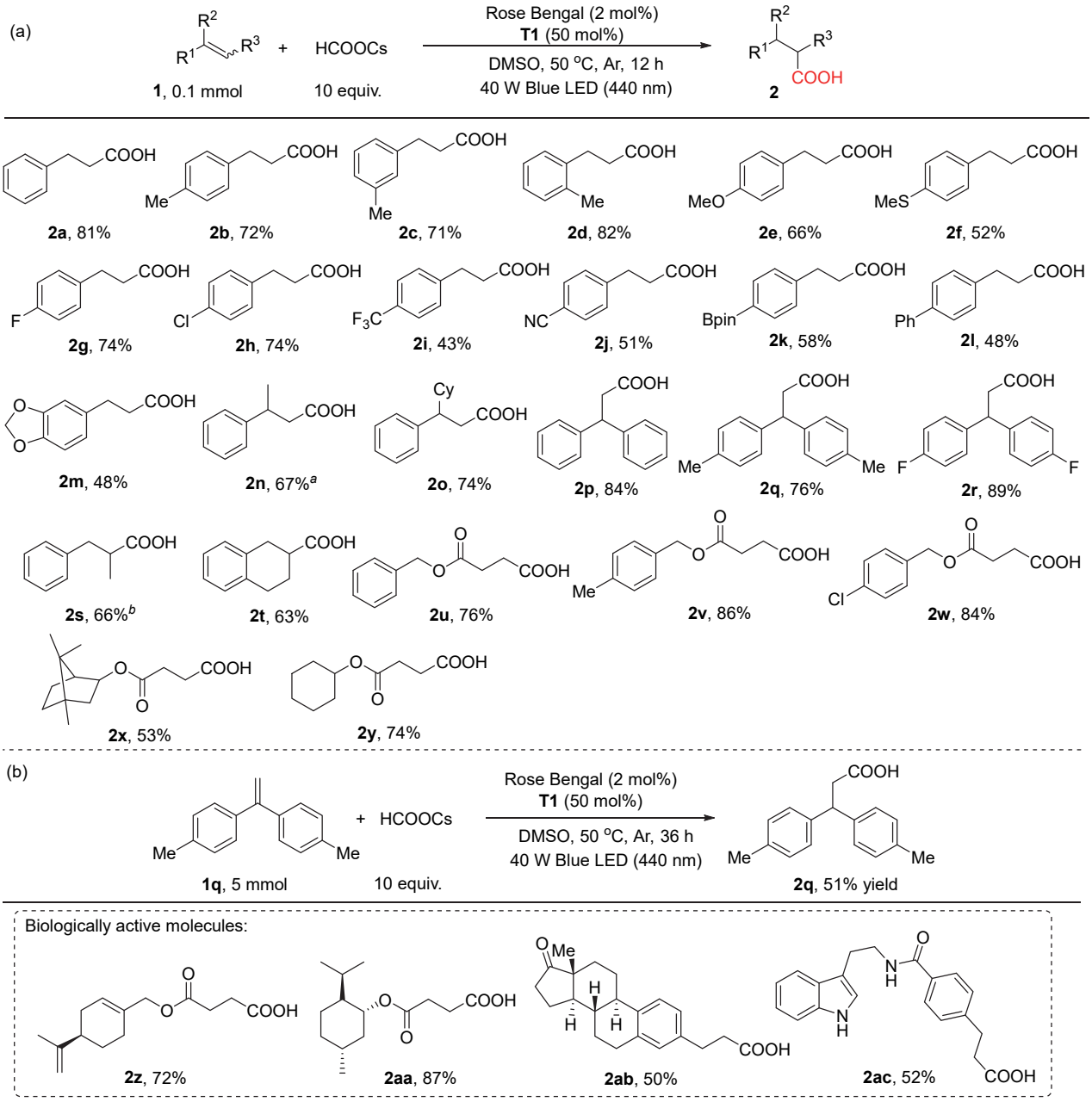
To gain more insights into the reaction mechanism, the following experiments were carried out: (a) radical-trapping regent 2,2,6,6-tetramethylpiperidinooxy (TEMPO) was added to the reaction mixture, no desired product **2a** was detected (Scheme 3a). (b) A radical-clock experiment was performed using *α*-cyclopropylstyrene (**1ad**) as the substrate under standard conditions, and the ring-opening products (**2ad**) was obtained in 24% isolated yield. The results of radical-trapping and radical-clock experiments suggested the formation of radical intermediates. (c) Deuterium labeling experiments were carried out to explore the source of *α*-position H-atom. Only 23% of *α*-H was labeled using DCOOCs instead of HCOOCs (Scheme 3c), while 49%～80% of *α*-H was labeled by adding D_2O to the system (Scheme 3d). The incomplete deuteration of the product indicates that **T1** may be the potential H-donor. Furthermore, the photochemical quantum yield (φ = 1.9) was determined, suggesting that the transformation should be a racial chain process.

Table 1 Optimization of hydrocarboxylation of styrene[a]



Entry	Deviation	Yield[b]/%
1	None	81
2	Eosin B instead of Rose Bengal	63
3	Fluorescein instead of Rose Bengal	36
4	**T2** instead of **T1**	18
5	**T3** instead of **T1**	47
6	1 equiv. **T1**	54
7	25 mol% **T1**	37
8	1 mol% Rose Bengal	76
9	$HCOONH_4$ instead of HCOOCs	55
10	HCOONa instead of HCOOCs	56
11	HCOOK instead of HCOOCs	78
12	DMF instead of DMSO	N.D.
13	NMP instead of DMSO	N.D.
14	EA instead of DMSO	32
15	Without Rose Bengal	N.D.
16	Without **T1**	N.D.
17	In the dark	N.D.

[a] Reaction conditions: **1a** (0.1 mmol), HCOOCs (1.0 mmol), Rose Bengal (2 mol%), **T1** (50 mol%), DMSO (3 mL), 50 ℃, 40 W blue LED (440 nm), Ar, 12 h. DMSO: dimethyl sulfoxide, DMF: *N*,*N*-dimethylformamide, NMP: *N*-methyl-2-pyrrolidone, EA: ethyl acetate, N.D.: not detected. [b] Isolated yield.



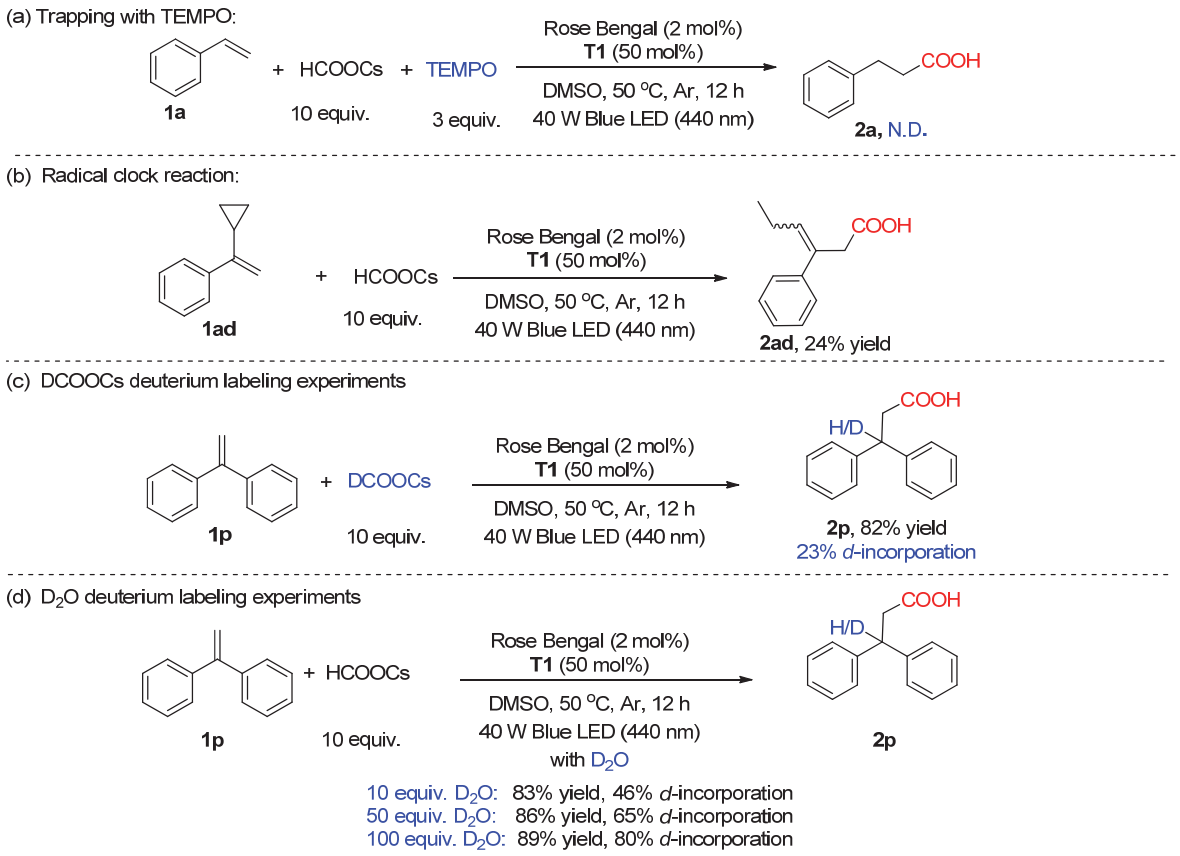
Reaction condition: **1a** (0.1 mmol), HCOOCs (1.0 mmol), Rose Bengal (2 mol%), **T1** (50 mol%), DMSO (3 mL), 50 ℃, 40 W blue LED (440 nm), Ar, 12 h. [a] 100 ℃. [b] Isolated yield.

Scheme 2 Scope of hydrocarboxylation of alkenes

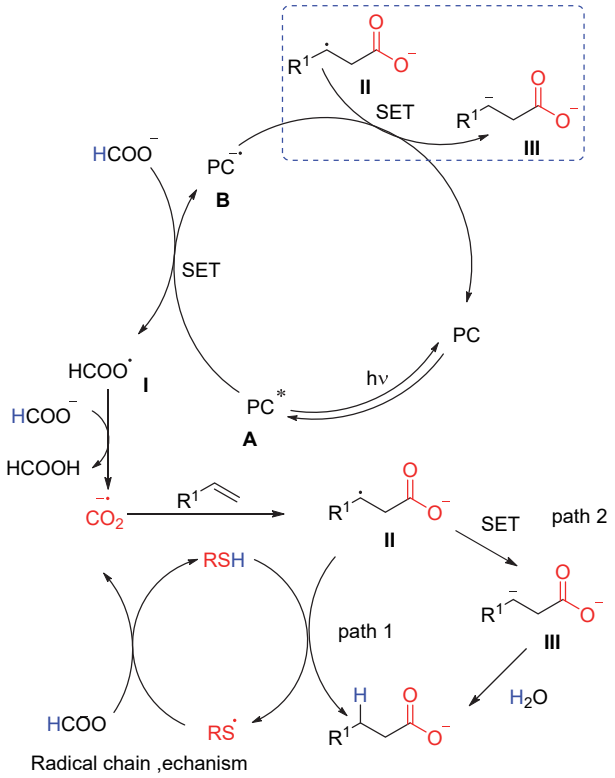
Based on results of control experiments, a tentative mechanism was proposed (Scheme 4). The excited photocatalyst could be quenched by formate salt to give radical intermediate (**I**) and the reduced catalyst (**B**). Then, **I** can trap the hydrogen of formate salts providing $CO_2^{\bullet-}$ which can react with alkenes to give adduct **II**. There may be two pathways for generation of the acid product from the addition product **II**. In path 1, hydrogen atom transfer from the thiol to **II** can occur directly, delivering the product. The thiol radical can abstract hydrogen from the formate salt to give the thiol. Another possible way is the single electron transfer process (path 2). The adduct **II** may be reduced by **B** or $CO_2^{\bullet-}$ to give carbon anion species **III**. After the subsequent protonation, the product could be obtained. Although $CO_2^{\bullet-}$ from formate salts is still the key intermediate in the new system, the addition of the thiol catalyst promoted the radical chain process that enables the hydrocarboxylation occur under milder conditions comparing with our previous work.

3 Conclusions

In summary, a transition-metal-free hydrocarboxylation of alkenes with formate salts via photocatalysis has been developed in this work. Using Rose Bengal as the catalyst,



Scheme 3 Control experiments: (a) radical-trapping experiment with TEMPO, (b) radical clock experiment, (c) DCOOCs deuterium labeling experiments and (d) D_2O deuterium labeling experiments



Scheme 4 Proposed mechanism of hydrocarboxylation of alkenes with formate salts via photocatalysis

formate salts as carbonyl source, a wide range of alkenes including a series of biologically active molecules, could be converted into valuable acid products under blue light irradiation. This method shows great potential for application in organic synthesis.

4 Experimental section

4.1 General method

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 500MHz spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: δ 7.26 for ^{1}H NMR, δ 77.16 for ^{13}C NMR; DMSO-d_6: δ 2.50 for ^{1}H NMR, δ 39.52 for ^{13}C NMR). All high-resolution mass spectra (HRMS) were obtained on an AB Sciex TripleTOF 4600 spectrometer. Cyclic voltammetry experiments were performed on a CH Instruments Electrochemical Analyzer. Blue LED (40 W, λ_{max}=440 nm) purchased from Kessil was used for blue light irradiation. Reactions were monitored using thin layer chromatography (TLC) on aluminium backed plates and visualized by UV radiation at a wavelength of 254 nm. Visualization was accomplished with UV light (254 nm) and exposure to phosphomolybdic acid (PMA) or potassium perm anganate solution followed by heating.

4.2 Representative produce for the conversion of alkenes to carboxylic acid (**2a**)

An oven-dried Schlenk tube (10 mL) with a magnetic stir bar was added HCOOCs (Cesium formate, 1.0 mmol, 10 equiv.) and Rose Bengal (2 mol%). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfilled with argon for three times. Subsequently, **1a** (0.1 mmol), cyclohexyl mercaptan (50 mol%) and anhydrous DMSO (3 mL) were added through injection port under argon atmosphere. Then the reaction was placed under a blue LED (wavelength 440 nm, 40 W) with an argon balloon and irradiated for 12 h at 50 ℃. The mixture was acidified with 1 mL of dilute HCl (2 N) and quenched with H_2O. Extracted with EtOAc three times, the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography isolation on silica gel (eluent: petroleum ether/EA, V∶V=100∶1 to 2∶1) to give the pure desired product 3-phenylpropanoic acid (**2a**)[11] as white solid (12.2 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.3～7.2 (m, 5H), 3.1 (t, J=7.8 Hz, 2H), 2.8 (t, J=7.8 Hz, 2H).

3-(*p*-Tolyl)propanoic acid (**2b**):[11] 11.9 mg, 72% yield. Yellow solid, m.p. 105.3～107.1 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.2～7.1 (m, 4 H), 2.9 (t, J=7.8 Hz, 2H), 2.7 (t, J=7.8 Hz, 2H), 2.32 (s, 3H).

3-(3-Methylphenyl)propionic acid (**2c**):[11] 11.7 mg, 71% yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.2 (t, J=7.7 Hz, 1H), 7.1～7.0 (m, 3H), 2.9 (t, J=7.8 Hz, 2H), 2.7 (t, J=7.9 Hz, 2H), 2.3 (s, 3H).

3-(2-Methylphenyl)propanoic acid (**2d**):[11] 13.5 mg, 82% yield. White solid, m.p. 100.2～103.5 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.2～7.1 (m, 4H), 3.0 (t, J=7.8 Hz, 2H), 2.7 (t, J=7.9 Hz, 2H), 2.3 (s, 3H).

3-(4-Methoxyphenyl)-propanoic acid (**2e**):[11] 11.8 mg, 66% yield. White solid, m.p. 97.2～102.3 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.1 (d, J=8.5 Hz, 2H), 6.8 (d, J=8.6 Hz, 2H), 3.8 (s, 3H), 2.9 (t, J=7.7 Hz, 2H), 2.7 (t, J=7.7 Hz, 2H).

3-(4-Methylthio)propanoic acid (**2f**):[11] 10.2 mg, 52% yield. White solid, m.p. 101.3～105.1 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.2 (d, J=8.3 Hz, 2H), 7.1 (d, J=8.2 Hz, 2H), 2.9 (t, J=7.7 Hz, 2H), 2.7 (t, J=7.7 Hz, 2H), 2.5 (s, 3H).

3-(4-Fluorophenyl)propanoic acid (**2g**):[11] 12.5 mg, 74% yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.2 (dd, J=8.3,5.5 Hz, 2H), 7.0 (t, J=8.7 Hz, 2H), 2.9 (t, J=7.7 Hz, 2H), 2.7 (t, J=7.7 Hz, 2H).

3-(4-Chlorophenyl)propanoic acid (**2h**):[11] 13.7 mg, 74% yield. White solid, m.p. 109.6～116.3 ℃; ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 7.7 (d, J=7.9 Hz, 2H), 7.5 (d, J=7.8 Hz, 2H), 3.0 (t, J=7.5 Hz, 2H), 2.7 (t, J=7.5 Hz, 2H).

3-[4-(Trifluoromethyl)phenyl]propanoic acid (**2i**):[11] 9.4 mg, 43% yield. Colorless solid, m.p. 78.3～80.1 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.6 (d, J=8.0 Hz, 2H), 7.3 (d, J=7.8 Hz, 2H), 3.0 (t, J=7.6 Hz, 2H), 2.7 (t, J=7.6 Hz).

3-(4-Cyanophenyl)propionic acid (**2j**):[11] 8.9 mg, 51% yield. White solid, m.p. 117.7～120.1 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.6 (d, J=8.2 Hz, 2H), 7.3 (d, J=8.1 Hz, 2H), 3.0 (t, J=7.6 Hz, 2H), 2.7 (t, J=7.6 Hz, 2H).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene propanoic acid (**2k**):[11] 16.0 mg, 58% yield. Light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.7 (d, J=8.0 Hz, 2H), 7.2 (d, J=7.9 Hz, 2H), 3.0 (t, J=7.8 Hz, 2H), 2.7 (t, J=7.8 Hz, 2H), 1.3 (s, 12H).

3-(*p*-Biphenyl)propionic acid (**2l**):[13] 10.9 mg, 48% yield. White solid, m.p. 142.1～147.5 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.6 (d, J=7.1 Hz, 2H), 7.5 (d, J=8.2 Hz, 2H), 7.4 (t, J=7.7 Hz, 2H), 7.3 (t, J=7.4 Hz, 1H), 7.2 (d, J=8.2 Hz, 2H), 3.0 (t, J=7.8 Hz, 2H), 2.7 (t, J=7.8 Hz, 2H).

1,3-Benzodioxole-5-propanoic acid (**2m**):[14] 9.3 mg, 48% yield. White powder, m.p. 79.2～81.9 ℃; ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 6.8 (s, 1H), 6.7 (q, J=7.9 Hz, 2H), 5.9 (s, 2H), 2.8 (t, J=7.6 Hz, 2H), 2.6 (t, J=7.7 Hz, 2H).

3-Phenylbutanoic acid (**2n**):[11] 11.0 mg, 67% yield. Amber oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.3 (t, J=7.6 Hz, 2H), 7.3～7.2 (m, 3H), 3.3～3.2 (m, 1H), 2.7 (dd, J=15.6, 6.9 Hz, 1H), 2.6 (dd, J=15.5, 8.2 Hz, 1H), 1.3 (d, J=7.0 Hz, 3H).

β-Cyclohexylbenzenepropanoic acid (**2o**):[8] 17.2 mg, 74% yield. White solid, m.p. 98.4～105.3 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.3 (t, J=7.4 Hz, 2H), 7.2 (t, J=7.3 Hz, 1H), 7.1 (d, J=7.2 Hz, 2H), 2.9～2.8 (m, 1H), 2.8 (dd, J =15.5, 5.6 Hz, 1H), 2.6 (dd, J=15.5, 9.4 Hz, 1H), 1.8 (dd, J=33.3, 12.8 Hz, 2H), 1.6 (t, J=11.0 Hz, 2H), 1.5～1.4 (m, 2H), 1.2～1.0 (m, 3H), 0.9～0.8 (m, 1H), 0.8～0.7 (m, 1H).

3,3-Diphenylpropanoic acid (**2p**):[11] 19.0 mg, 84% yield. White solid, m.p. 143.6～148.3 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.3～7.2 (m, 4H), 7.2～7.1 (m, 6H), 4.5 (t, J=7.9 Hz, 1H), 3.1 (d, J=7.9 Hz, 2H).

3,3-Di(4-methylphenyl)-propanoic acid (**2q**):[11] 19.3 mg, 76% yield. Colorless solid, m.p. 190.2～192.0 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.2- 7.0 (m, 8H), 4.5 (t, J=7.9 Hz, 1H), 3.1 (d, J=7.9 Hz, 2H), 2.3 (s, 6H).

3,3-Di(4-fluorophenyl)propanoic acid (**2r**):[11] 23.2 mg, 89% yield. Colorless crystalline solid, m.p. 100.2～101.4 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.2～7.1 (dd, J=8.6, 5.3 Hz, 4H), 7.0～6.9 (t, J=8.6 Hz, 4H), 4.5 (t, J=7.9 Hz, 1H), 3.0 (d, J=7.9 Hz, 2H).

2-Methyl-3-phenylpropanoic acid (**2s**):[11] 10.8 mg, 66% yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.3 (t, J=7.4 Hz, 2H), 7.2 (dd, J=18.1, 7.3 Hz, 3H), 3.1 (dd, J=13.4, 6.4 Hz, 1H), 2.8～2.7 (m, 1H), 2.6 (dd, J=13.5, 8.1 Hz, 1H), 1.2 (d, J=6.9 Hz, 3H).

1,2,3,4-Tetrahydro-2-naphthoic acid (**2t**):[11] 11.2 mg, 63% yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.2～7.0 (m, 4H), 3.1～2.9 (m, 2H), 2.9～2.7 (m, 3H), 2.3～2.2 (m, 1H), 2.0～1.8 (m, 1H).

4-(Benzyloxy)-4-oxobutanoic acid (**2u**):[11] 15.8 mg, 76% yield. White solid, m.p. 52.2～58.3 ℃; ^{1}H NMR

(500 MHz, $CDCl_3$) δ: 7.4～7.2 (m, 5H), 5.2 (s, 2H), 2.7～2.6 (m, 4H).

1-[(4-Methylphenyl)methyl]butanedioate (**2v**):[11] 19.2 mg, 86% yield. Colorless solid, m.p. 78.4～82.1 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.2 (s, 2H), 7.2 (t, J=4.0 Hz, 2H), 5.1 (s, 2H), 2.7～2.6 (m, 4H), 2.4 (s, 3H).

1-((4-Chlorophenyl)methyl)butanedioate (**2w**):[11] 20.4 mg, 84% yield. Colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.4～7.3 (4H), 5.1 (s, 2H), 2.7～2.6 (m, 4H).

1-((1*R*,2*R*,4*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl]-butanedioate (**2x**):[11] 13.4 mg, 53% yield. Light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.7 (m, 1H), 2.7～2.6 (m, 2H), 2.6～2.5 (m, 2H), 1.9～1.6 (m, 4 H), 1.6～1.5 (m, 1H), 1.2～1.0 (m, 2H), 0.9 (s, 3H), 0.8 (s, 6H).

1-(Cyclohexylmethyl) butanedioate (**2y**):[11] 14.7 mg, 74% yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.6 (s, 1H), 4.8～4.7 (m, 1H), 2.7～2.5 (m, 4H), 1.8～1.6 (m, 4H), 1.5～1.2 (m, 6H).

(*S*)-4-Oxo-4-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)-methoxy)butanoic acid (**2z**):[11] 18.2 mg, 72% yield. Light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.7 (s, 1H), 4.7 (d, J=9.4 Hz, 2H), 4.5 (s, 2H), 2.7 (dd, J=7.4, 4.7 Hz, 2H), 2.6 (dd, J=7.2, 4.4 Hz, 2H), 2.2～1.8 (m, 6H), 1.73 (s, 3H), 1.5～1.4 (m, 1H).

4-(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)-4-oxobutanoic acid (**2aa**):[11] 22.3 mg, 87% yield. Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.7～4.5 (m, 1H), 2.6～2.5 (m, 4H), 1.9 (d, J = 12.2 Hz, 1H), 1.9 ~ 1.8 (m, 1H), 1.7 (d, J=10.3 Hz, 2H), 1.5～1.4 (m, 1H), 1.3 (d, J= 11.4 Hz, 1H), 1.1～1.0 (m, 3H), 0.9 (t, J = 6.6 Hz, 6H), 0.7 (d, J=6.9 Hz, 3H).

3-((8*S*,9*R*,13*R*,14*R*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)propanoic acid (**2ab**):[11] 16.3 mg, 50% yield. White solid, m.p. 178.1～180.3 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.2 (d, J=8.0 Hz, 1H), 7.0 (d, J=8.0 Hz, 1H), 6.9 (s ,1H), 2.9 (t, J=7.7 Hz, 4H), 2.7 (t, J=7.9 Hz, 2H), 2.5 (dd, J=19.0, 8.7 Hz, 1H), 2.5～2.4 (m, 1H), 2.4～2.3 (m, 1H), 2.3～2.2 (m, 1H), 2.2～2.1 (m, 1H), 2.0～1.8 (m, 2H), 1.7～1.4 (m, 6H), 0.9 (s, 3H).

(3-(4-((2-(1*H*-Indol-3-yl)ethyl)carbamoyl)phenyl)-propanoic acid (**2ac**):[11] 17.5 mg, 52% yield. Dark-brown oil. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 12.2 (s, 1H), 10.80 (s, 1H), 8.5 (t, J=5.6 Hz, 1H), 7.8 (d, J=8.1 Hz, 2H), 7.6 (d, J=7.9 Hz, 1H), 7.3 (dd, J=14.2, 8.1 Hz, 3H), 7.2 (d, J=1.8 Hz, 1H), 7.1 (t, J=7.4 Hz, 1H), 7.0 (t, J=7.4 Hz, 1H), 3.6～3.5 (m, 2H), 2.9 (t, J=7.5 Hz, 2H), 2.8 (t, J= 7.5 Hz, 2H), 2.6 (t, J=7.7 Hz, 2H).

Supporting Information Procedure for control experiment and the characterization data for carboxylic acid. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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