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Morita-Baylis-Hillman 加合物和 *N*-羟基邻苯二甲酰亚胺的电化学烯丙基烷基化形成 C(sp^3)—C(sp^3)键

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摘要 报道了一种无外加氧化还原剂、电还原方法, 使 Morita-Baylis-Hillman (MBH)加合物实现烯丙基烷基化. 这种转变的一个关键特征是, 既不需要外部化学还原剂也不需要金属催化剂. *N*-烷酰氧基邻苯二甲酰亚胺(NHP)酯通过电子还原产生烷基自由基, 在烷基化过程中以高立体选择性和区域选择性展示出对烯烃取代的广泛官能团耐受性.

关键词 烯丙基烷基化; Morita-Baylis-Hillman (MBH)加合物; 电化学还原路径

Electrochemical Allylic Alkylation of Morita-Baylis-Hillman Adducts and *N*-Hydroxyphthalimide Esters towards C(sp^3)—C(sp^3) Bond Formation

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Abstract A redox-free, electroreductive approach to achieve allylic alkylation by employing Morita-Baylis-Hillman (MBH) adducts is reported. A critical feature of this transformation is that neither external chemical oxidants nor metal catalysts are required. Alkyl radical produced by electron reduction with *N*-hydroxyphthalimide (NHP) esters, displaying broad tolerance of functional groups and alkene substitution patterns in high stereoselectivity and regioselectivity.

Keywords allylic alkylation; Morita-Baylis-Hillman (MBH) adducts; electroreductive approach

1 Introduction

Allylic alkylation is a powerful protocol for streamline organic synthesis that may find wide compound applications for further transformations.[1] Previous work in this area has focused on the utilization of allylic alcohol derivatives as the electrophilic materials catalyzed by transition-metal complexes, and an array of interesting results has been presented over the past few decades. Recently, the reaction of Morita-Baylis-Hillman (MBH) adducts with various O-,[2] N-,[3] P-,[4] S-[5] and C-[6]based nucleophiles could proceed allylic substitution to afford either *α*- or *γ*-substituted products via transition metal catalysis and with phosphine or tertiary amine-involved organocatalysis, which has emerged as a very versatile approach to deliver multifunctional allylic-substituted compounds (Scheme 1a). Moreover, MBH adducts were also successfully applied in photoredox S_N2'-type radical addition at the terminal site to build trisubstituted alkenes[7] and metal- or photocatalytic radical S_N2-type alkylation to afford *α*-sub-

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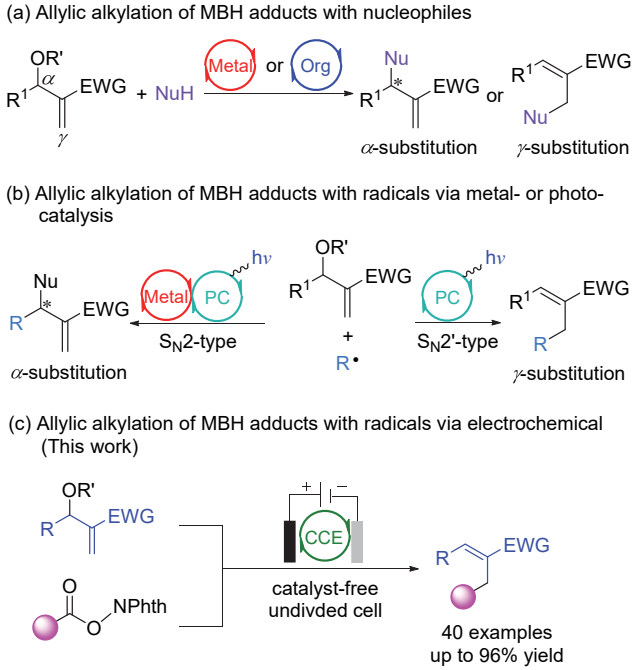
stituted products with stereogenic centers[8] (Scheme 1b). High efficacy and excellent regioselectivities have been noted for a number of allylic alkylation reactions of MBH adducts. Notwithstanding the progress, these methods still require noble-metal catalysts and stoichiometric chemical oxidants. Therefore, the development of effective catalytic systems and new allylic alkylation reactions for MBH adducts is in high demand.

Electrochemistry represents an environmentally benign strategies in organic synthesis.[9] Recently, alkylation reactions based on radical mechanism have attracted considerable attentions.[10] The acid-base neutral *N*-hydroxyphthalimide (NHP) ester can undergo a reductive decarboxylative protocol to generate the corresponding carbon radical at the cathode.[11] We envisioned that Morita-Baylis-Hillman (MBH) adducts could undergo radical alkylation under electrochemical conditions. Herein, we communicate the allylic alkylation of MBH adducts with NHP esters to afford C(sp^3)—C(sp^3) bond using electrochemical strategies without any catalysts (Scheme 1).

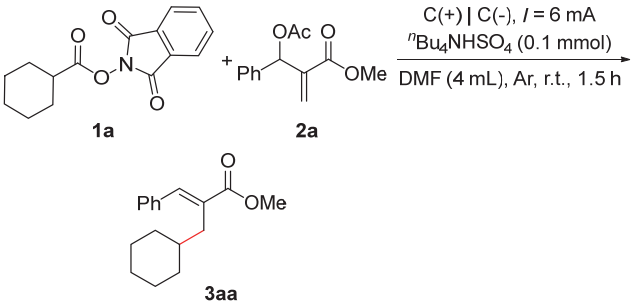


Scheme 1 Protocol for allylic alkylation of Morita-Baylis-Hillman (MBH) adducts

2 Results and discussion

Our investigation by using the NHP ester (**1a**) and MBH adduct (**2a**) under electricity system in undivided cell was started. By using ^{n}Bu$_4$NHSO$_4$ as the electrolyte and *N*,*N*-dimethylformamide (DMF) as the solvent, the desired product **3a** could be obtained in 90% isolated yield under 6 mA constant current for 90 min (Table 1, Entry 1). For the solvent, polar solvents such as MeCN and dimethyl sulfoxide (DMSO) seemed to be worse (Table 1, Entries 2 and 3). Tetrabutylamine tetrafluoride (TBABF$_4$) was not as effective as ^{n}Bu$_4$NHSO$_4$ where the yield was about 67% (Table 1, Entry 4). The variation of electrodes had the biggest influence on this reaction. The yields were greatly reduced using platinum or iron as the cathode or anode by the unique absorption capacity of carbon graphite cloth (Table 1, Entries 5～7). When the current decreased, the yield decreased (Table 1, Entries 8 and 9). The yield of the reaction was slightly reduced when **1a** was 1.5 equiv., while the raw material of **2a** was fixed (Table 1, Entry 10). The Boc-protected MBH adduct demonstrated similar reactivity to the Ac-protected MBH adduct (Table 1, Entry 11). Furthermore, changing operating reaction in air was proved to be lower efficiency (Table 1, Entry 12). Finally, the product cannot be detected without electric current (Table 1, Entry 13).

Table 1 Effects of reaction parameters

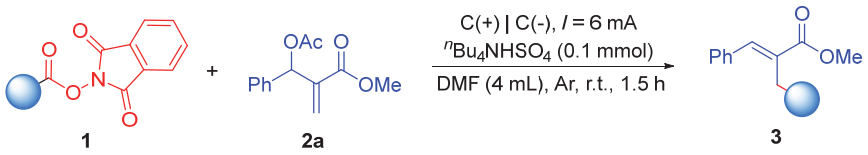


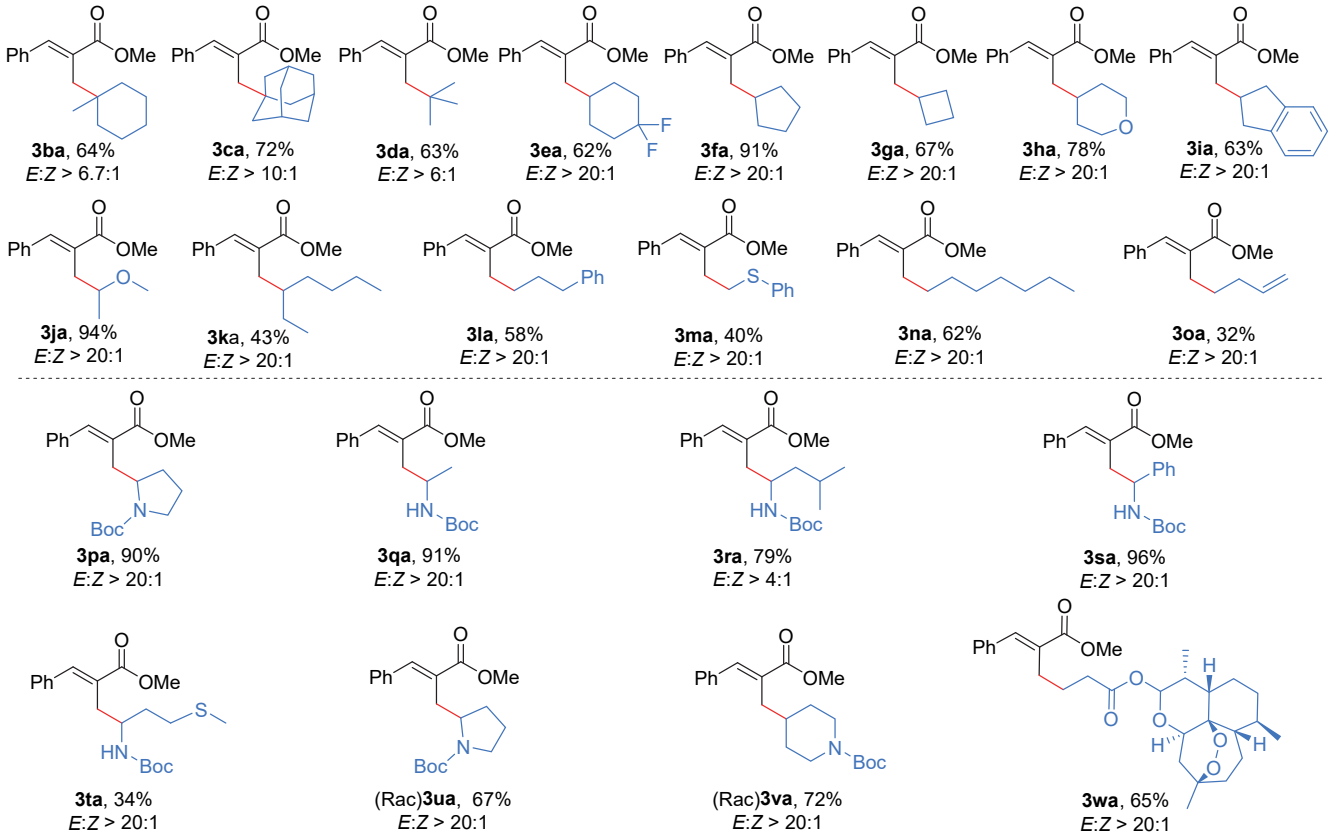
Entry	Variation from condition[a]	Yield[b]/%
1	None	90
2	CH_3CN instead of DMF	77
3	DMSO instead of DMF	48
4	^{n}Bu$_4$NBF$_4$ instead of ^{n}Bu$_4$NHSO$_4$	67
5	Pt (−) instead of C (−)	41
6	Fe (−) instead of C (−)	43
7	Pt (+) instead of C (+)	58
8	*I*=4 mA, 135 min	88
9	*I*=8 mA, 68 min	72
10	**1a** 0.15 mmol	72
11	Boc instead of Ac	89
12	Air instead of Ar	67
13	No electric current	N.D.

[a] Standard reaction conditions: carbon graphite cloth (10 mm×7.5 mm) cathode, carbon graphite cloth (10 mm×7.5 mm) anode, constant current=6 mA, **1a** (0.2 mmol), **2a** (0.1 mmol), ^{n}Bu$_4$NHSO$_4$ (0.1 mmol), DMF (4.0 mL), r.t., 1.5 h, undivided cell. [b] Yield of isolated product, *E* ∶ *Z*>20 ∶ 1; N.D. implies that no product could be detected by GC-MS and GC.

With the best optimized reaction conditions in hand, we focused on exploring the substrate scope (Table 2). Firstly, both cyclic tertiary and chain carboxylic esters could afford the corresponding products in moderate to good yield (**3ba**～**3da**). For secondary aliphatic carboxylic esters, the products were obtained with good yield (**3ea**～**3ka**) except for the isooctanoate (**3ka**). With regard to primary acids, high site selectivity was shown and a moderated yield could be generated, without rearrangement (**3la**～**3oa**). Meanwhile, the alkenyl group can be retained under this system (**3oa**). Pleasingly, amino acid derived NHP esters

Table 2 Substrate scope of the reaction[a]





[a] Standard reaction conditions: carbon graphite cloth (10 mm×7.5 mm) cathode, carbon graphite cloth (10 mm×7.5 mm) anode, constant current=6 mA, **1** (0.2 mmol), **2a** (0.1 mmol), $^{n}Bu_4NHSO_4$ (0.1 mmol), DMF (4.0 mL), r.t., 1.5 h, undivided cell.

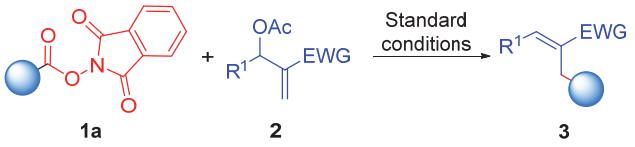
1pa～**1wa** as well as artesunate derived **1wa** generated competent alkyl radicals for the alkylation of **2a** (**3pa**～**3wa**, 34%～96% yields). This demonstrates the possibility to employ naturally occurring acids as precursors of functionalized radicals.

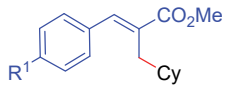
This protocol was further expanded to different activated MBH acetate **2** (Table 3). Benzene rings bearing fluorine, chlorine, bromine, methyl, cyano, trifluoromethyl, and methyl ester at the *para* position were all compatible with moderate to high yields (**3ab**～**3ah**). 3-Fluorine benzene on the MBH acceptor was well tolerated in 95% yield. Also, 3-chloro, 3-methyl or 3-methoxy-substituted benzene were reacted with NHP ester with lower yields (**3aj**～**3al**). The study also investigated the steric effect by using *ortho*-substituted benzene, such as 2-chloro, 2-bromo and 2-methoxy, where good yields were obtained (**3am**～**3ao**). When it came to 2-bromo-4-fluorobenze, the desired product **3ap** in 66% yield was obtained. Moreover, the electrochemical alkylation product of 2-bromo-4-chlorobenzene was afforded in 79% yield (**3aq**). In addition to MBH adducts with R=Ph, hydrogen was also investigated with NHP ester. Fortunately, 30% isolated yield of **3xr** was obtained under the standard conditions. When CO_2Me was replaced by CN, no desired product was observed.

The scalability of this electrochemical electrochemical alkylation of MBH acetate was further evaluated by performing the gram-scale reaction. The 5 mmol scale reaction afforded the corresponding **3aa** (1.10 g) in a high reaction efficiency with 86% yield (Scheme 2a). To get brief insights into the mechanism, radical trapping experiments were conducted (Scheme 2b). The reactions under electrochemical conditions in the presence of a radical scavenger 1,1-diphenylethylene or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) gave trace yield of **3aa**. Meanwhile, a radical coupling adduct was observed, indicating that this reaction possibly proceeded via a radical pathway.

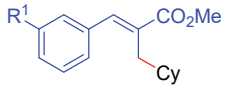
To further investigate the electrochemical properties of each substrate, cyclic voltammetry (CV) tests were performed. A reduction peak at −1.48 V (vs. AgCl/Ag, the same below) was observed, which belonged to the ester (Figure 1). And, for the MBH acetate, an obvious reduction peak could be observed at −2.64 V for **2a** relative to

Table 3 Substrate scope of the reaction[a]

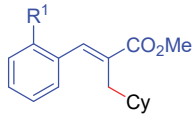




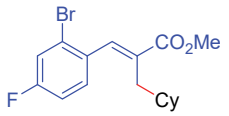
R^1 = F, **3ab**, 57%, *E*:*Z* > 20:1
R^1 = Cl, **3ac**, 82%, *E*:*Z* > 20:1
R^1 = Br, **3ad**, 65%, *E*:*Z* > 20:1
R^1 = Me, **3ae**, 95%, *E*:*Z* > 20:1
R^1 = CN, **3af**, 70%, *E*:*Z* > 20:1
R^1 = CF_3, **3ag**, 62%, *E*:*Z* > 20:1
R^1 = CO_2Me, **3ah**, 75%, *E*:*Z* > 20:1



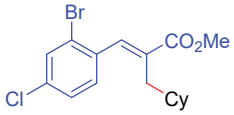
R^1 = F, **3ai**, 95%, *E*:*Z* > 20:1
R^1 = Cl, **3aj**, 44%, *E*:*Z* > 20:1
R^1 = Me, **3ak**, 27%, *E*:*Z* > 20:1
R^1 = OMe, **3al**, 50%, *E*:*Z* > 20:1



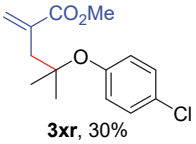
R^1 = Cl, **3am**, 75%, *E*:*Z* > 20:1
R^1 = Br, **3an**, 94%, *E*:*Z* > 20:1
R^1 = OMe, **3ao**, 39%, *E*:*Z* > 20:1



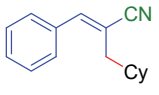
3ap, 66%, *E*:*Z* > 10:1



3aq, 79%, *E*:*Z* > 20:1

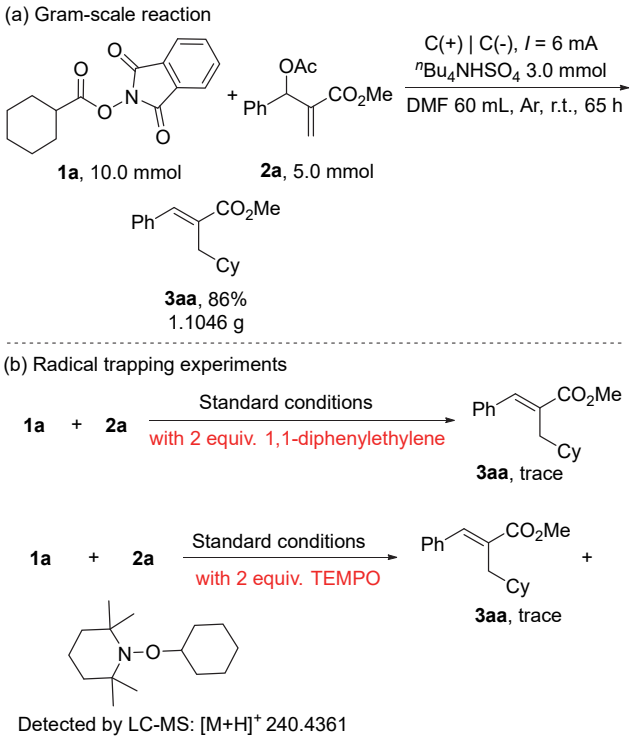


3xr, 30%



3as, N.D

[a] Standard reaction conditions: carbon graphite cloth (10 mm×7.5 mm) cathode, carbon graphite cloth (10 mm×7.5 mm) anode, constant current=6 mA, **1a** (0.2 mmol), **2** (0.1 mmol), ^{n}Bu$_4$NHSO$_4$ (0.1 mmol), DMF (4.0 mL), Ar, r.t., 1.5 h, undivided cell.



Scheme 2 Gram-scale reaction and radical trapping experiments

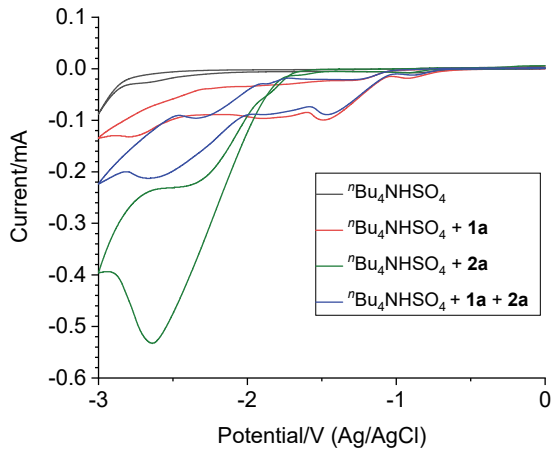


Figure 1 Cyclic voltammograms of substrates **1a**, **2a**

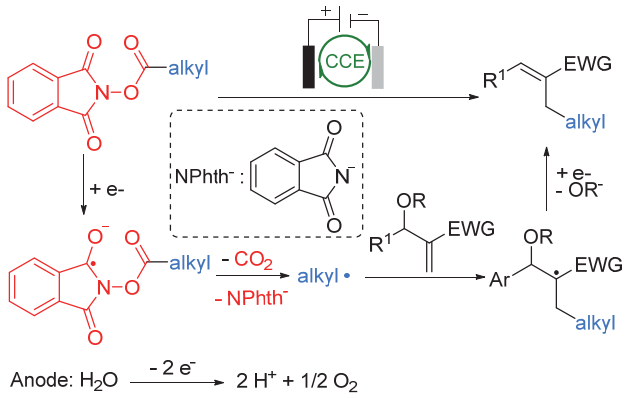
(A) Black line: DMF (10 mL), ^{n}Bu$_4$NHSO$_4$ (0.1 mmol), N_2, glassy carbon electrode as the working electrode, platinum electrode as the counter electrode, Ag/AgCl as the reference electrode; (B) Red line: DMF (10 mL), ^{n}Bu$_4$NHSO$_4$ (0.1 mmol), **1a** (0.1 mmol), N_2, glassy carbon electrode as the working electrode, platinum electrode as the counter electrode, Ag/AgCl as the reference electrode (−1.48 V); (C) Green line: DMF (10 mL), ^{n}Bu$_4$NHSO$_4$ (0.1 mmol), **2a** (0.1 mmol), N_2, glassy carbon electrode as the working electrode, platinum electrode as the counter electrode, Ag/AgCl as the reference electrode (−2.64 V); (D) Blue line: DMF (10 mL), ^{n}Bu$_4$NHSO$_4$ (0.1 mmol), **1a** (0.1 mmol), **2a** (0.1 mmol), N_2, glassy carbon electrode as the working electrode, platinum electrode as the counter electrode, Ag/AgCl as the reference electrode (−1.40, −2.74 V). The scan rate is 0.1 V/s, ranging from 0 V to −3 V

the blank control. These results indicated that NHP ester was likely to be firstly reduced under electrochemical conditions.

Based on previous reports and the above experimental results,[10,12] a possible mechanism for electrochemcial allylic alkylation was shown in Scheme 3. This reaction was initiated by the formation of a radical anion through cathode reduction, which further releasing CO_2 and phthalimide anion to form the corresponding alkyl radical (Scheme 3). Then the alkyl radical could attack electrophilic double bond of **2** to form a new C—C bond. Finally, the generated alkyl radical could be reduced and then the target product was given through elimination. However, it is difficult to rule out the way that alkyl radical would directly render the observed product and the acetoxy radical, undergoing reduction to the acetate anion. That might be H_2O was oxidized at anode.[13]

3 Conclusions

In summary, electrochemical allylic alkylation of Morita-Baylis-Hillman (MBH) adducts with *N*-hydroxyphthalimide (NHP) ester has been demonstrated. By employing the developed protocol, the prompt synthesis of C(sp^3)—C(sp^3) bond formation could be achieved from stable and easily available alkyl carboxylic acids under mild conditions. Further applications of functionalization of Morita-Baylis-Hillman (MBH) adducts are currently underway in our laboratory.



Scheme 3 Proposed reaction mechanism

4 Experimental section

4.1 Instruments and reagents

The instrument for electrolysis was dual display potentiostat (DJS-292B) (made in China). The anode electrode and cathode electrode were both carbon graphite cloth (10 mm×7.5 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200～300 mesh silica gel in petroleum (boiling point is between 60～90 ℃). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR). Tetramethylsilane was used as an internal standard. All ^{1}H NMR spectra were reported in delta (δ) units, downfield from the internal standard. High resolution mass spectra (HRMS) were measured with a SCIEX X500R, ESI. All glasswares were oven dried at 110 ℃ for hours and cooled down under vacuum. All materials were obtained from commercial suppliers and used without further purification.

4.2 Experimental procedure

In an oven-dried undivided flask (10 mL) equipped with a stir bar, NHP ester (0.20 mmol), MBH adduct (0.10 mmol), ^{n}Bu$_4$NHSO$_4$ (33.3 mg, 0.1 mmol) and DMF (4 mL) were combined and added. The flask was equipped with the carbon graphite cloth (10 mm×7.5 mm) as the anode and cathode, and was then charged with Argon. The reaction mixture was stirred and electrolyzed at a constant current of 6 mA under room temperature for 90 min. When the reaction was completed, the mixture was diluted with brine and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

Methyl-2-(cyclohexylmethyl)-3-phenylacrylate (**3aa**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 90% isolated yield (23.3 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (s, 1H), 7.39～7.35 (m, 4H), 7.32～7.27 (m, 1H), 3.80 (s, 3H), 2.48 (d, *J*=6.8 Hz, 2H), 1.67～1.61 (m, 5H), 1.56～1.48 (m, 1H), 1.18～1.06 (m, 3H), 0.91～0.81 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.42, 139.46, 136.05, 132.74, 129.30, 128.42, 128.14, 51.96, 37.86, 34.46, 33.25, 26.41, 26.33; HRMS (ESI) calcd for $C_{17}H_{23}O_2$ $[M+H]^+$ 259.1698, found 259.1780.

Methyl 2-((1-methylcyclohexyl)methyl)-3-phenylacrylate (**3ba**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 64% isolated yield (17.5 mg), *E*/*Z* ratio: >6.7∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (s, 1H), 7.37～7.25 (m, 5H), 3.80 (s, 3H), 2.65 (s, 2H), 1.38～1.25 (m, 6H), 1.15～1.10 (m, 4H), 0.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.54, 139.86, 136.75, 132.52, 128.93, 128.36, 127.69, 51.94, 37.78, 35.91, 26.21, 21.95; HRMS (ESI) calcd for $C_{18}H_{25}O_2$ $[M+H]^+$ 273.1855, found 273.1945.

Methyl-2-(((3*R*,5*R*,7*R*)-adamantan-1-yl)methyl)-3-phenylacrylate (**3ca**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 72% isolated yield (22.4 mg), *E*/*Z* ratio: >10∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (s, 1H), 7.30～7.20 (m, 5H), 3.73 (s, 3H), 2.45 (s, 2H), 1.76 (s, 3H), 1.53～1.42 (m, 6H), 1.25 (d, *J*=2.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.43, 140.05, 136.65, 131.34, 129.05, 128.35, 127.77, 52.03, 42.31, 39.44, 36.81, 35.45, 28.66; HRMS (ESI) calcd for $C_{21}H_{27}O_2$ $[M+H]^+$ 311.2011, found 311.2126.

Methyl-2-benzylidene-4,4-dimethylpentanoate (**3da**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 63% isolated yield (14.7 mg), *E*/*Z* ratio: >6∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (s, 1H), 7.29～7.18 (m, 5H), 3.74 (s, 3H), 2.58 (s, 2H), 0.68 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.37, 139.93, 136.60, 132.63, 128.96, 128.38, 127.80, 52.01, 38.23, 33.42, 29.56.

Methyl-2-((4,4-difluorocyclohexyl)methyl)-3-phenylacrylate (**3ea**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 62% isolated yield (18.3 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 7.43～7.33 (m, 5H), 3.85 (s, 3H), 2.57 (d, *J*=6.8 Hz, 2H), 2.05～1.98 (m, 2H), 1.74～1.62 (m, 5H), 1.28～1.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.96, 140.40, 135.69, 131.84, 129.05, 128.58, 128.40, 52.08, 35.65, 33.62, 33.40, 33.14, 32.69, 28.83, 28.74; HRMS (ESI) calcd for $C_{20}H_{19}FNaSSe$ $[M+Na]^+$ 413.0254, found 413.0262.

Methyl-2-(cyclopentylmethyl)-3-phenylacrylate (**3fa**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 91% isolated yield (22.3 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (s, 1H), 7.31～7.22 (m, 5H), 3.74 (s, 3H), 2.53 (d, *J*=7.2 Hz, 2H), 2.00～1.89 (m, 1H), 1.64～1.57 (m, 2H), 1.48～1.36 (m,

4H), 1.06～0.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.44, 138.95, 136.02, 133.60, 129.30, 128.45, 128.15, 52.01, 40.16, 32.37, 32.34, 24.71; HRMS (ESI) calcd for $C_{16}H_{21}O_2$ $[M+H]^+$ 245.1542, found 245.1625.

Methyl-2-(cyclobutylmethyl)-3-phenylacrylate (**3ga**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 67% isolated yield (15.5 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (s, 1H), 7.34～7.23 (m, 5H), 3.74 (s, 3H), 2.59 (d, *J*=7.2 Hz, 2H), 2.46～2.39 (m, 1H), 1.93～1.86 (m, 2H), 1.72～1.51 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.30, 139.14, 135.96, 132.45, 129.28, 128.45, 128.21, 52.00, 35.97, 33.52, 28.44, 18.47; HRMS (ESI) calcd for $C_{20}H_{19}FNaSSe$ $[M+Na]^+$ 413.0254, found 413.0262.

Methyl-3-phenyl-2-((tetrahydro-2*H*-pyran-4-yl)methyl)-acrylate (**3ha**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 78% isolated yield (20.3 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (s, 1H), 7.41～7.30 (m, 5H), 3.90～3.86 (m, 2H), 3.82 (s, 3H), 3.30 (td, *J*=11.6, 2.0 Hz, 2H), 2.55 (d, *J*=7.2 Hz, 2H), 1.82～1.73 (m, 1H), 1.55～1.52 (m, 2H), 1.28～1.17 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.06, 140.38, 135.79, 131.53, 129.11, 128.53, 128.34, 67.97, 52.06, 34.92, 33.81, 32.91; HRMS (ESI) calcd for $C_{16}H_{20}NaO_3$ $[M+Na]^+$ 283.1310, found 283.1403.

Methyl-2-((2,3-dihydro-1*H*-inden-2-yl)methyl)-3-phenylacrylate (**3ia**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 63% isolated yield (18.4 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (s, 1H), 7.33～7.25 (m, 5H), 7.12～7.07 (m, 4H), 3.83 (s, 3H), 2.98～2.94 (m, 2H), 2.78～2.71 (m, 3H), 2.59～2.56 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 169.08, 143.14, 139.96, 135.78, 132.64, 129.22, 128.45, 128.27, 126.07, 124.39, 51.96, 39.74, 38.81, 32.06; HRMS (ESI) calcd for $C_{20}H_{20}NaO_2$ $[M+Na]^+$ 315.1361, found 315.1469.

Methyl-2-benzylidene-4-methoxypentanoate (**3ja**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 94% isolated yield (21.9 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (s, 1H), 7.44 (d, *J*=7.6 Hz, 2H), 7.33～7.23 (m, 3H), 3.76 (s, 3H), 3.58～3.50 (m, 1H), 3.23 (s, 3H), 2.78 (dd, *J*=13.6, 7.6 Hz, 1H), 2.55 (dd, *J*=13.6, 5.6 Hz, 1H), 1.05 (t, *J*=6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.01, 140.93, 135.60, 130.33, 129.42, 128.44, 76.17, 56.65, 52.08, 34.51, 19.57; HRMS (ESI) calcd for $C_{14}H_{18}NaO_3$ $[M+Na]^+$ 257.1154, found 257.1230.

Methyl-2-benzylidene-3-ethylheptanoate (**3ka**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 43% isolated yield (11.9 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (s, 1H), 7.30～7.21 (m, 5H), 3.74 (s, 3H), 2.45 (d, *J*=7.2 Hz, 2H), 1.20～1.08 (m, 9H), 0.77～0.73 (m, 3H), 0.68 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.41, 139.52, 136.09, 133.47, 129.17, 128.39, 128.06, 51.98, 38.73, 32.49, 31.15, 28.51, 25.78, 23.04, 14.13, 10.72; HRMS (ESI) calcd for $C_{18}H_{26}NaO_2$ $[M+Na]^+$ 297.1830, found 297.1801.

Methyl-2-benzylidene-6-phenylhexanoate (**3la**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 58% isolated yield (16.9 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (s, 1H), 7.32～7.18 (m, 7H), 7.12～7.08 (m, 3H), 3.73 (s, 3H), 2.57～2.46 (m, 4H), 1.66～1.48 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.97, 142.50, 139.01, 135.77, 133.38, 129.22, 128.53, 128.43, 128.38, 128.29, 125.70, 52.05, 35.54, 31.43, 28.84, 27.41; HRMS (ESI) calcd for $C_{20}H_{22}NaO_2$ $[M+Na]^+$ 317.1517, found 317.1486.

Methyl-2-benzylidene-4-(phenylthio)butanoate (**3ma**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 40% isolated yield (11.9 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (s, 1H), 7.25～7.15 (m, 10H), 7.11～7.08 (m, 1H), 3.73 (s, 3H), 3.03～2.99 (m, 2H), 2.88～2.75 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.37, 152.27, 140.96, 130.76, 129.63, 129.15, 128.92, 128.64, 126.14, 52.18, 32.48, 28.01; HRMS (ESI) calcd for $C_{18}H_{18}NaO_2S$ $[M+Na]^+$ 321.0925, found 321.0902.

Methyl-2-benzylidenedecanoate (**3na**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 62% isolated yield (27.4 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (s, 1H), 7.34～7.23 (m, 5H), 3.74 (s, 3H), 2.43 (t, *J*=8.0 Hz, 2H), 1.50～1.42 (m, 2H), 1.29～1.19 (m, 10H), 0.81 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.06, 138.74, 135.85, 133.70, 129.25, 128.48, 128.31, 52.01, 31.91, 29.75, 29.28, 27.58, 22.71, 14.18; HRMS (ESI) calcd for $C_{18}H_{27}O_2$ $[M+H]^+$ 275.2011, found 275.2763.

Methyl-2-benzylidenehept-6-enoate (**3oa**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 32% isolated yield (7.4 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (s, 1H), 7.35～7.24 (m, 5H), 5.80～5.70 (m, 3H), 4.96～4.88 (m, 2H), 3.75 (s, 3H), 2.48～2.44 (m, 2H), 2.05 (dd, *J*=7.2, 14.0 Hz, 2H), 1.61～1.53 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.96, 139.12, 138.30, 135.72, 133.26, 129.25, 128.51, 128.40, 114.92, 52.06, 33.80, 28.45, 27.11; HRMS (ESI) calcd for $C_{15}H_{19}O_2$ $[M+H]^+$ 231.1385, found 231.1360.

tert-Butyl-2-(2-(methoxycarbonyl)-3-phenylallyl)pyrolidine-1-carboxylate (**3pa**): White solid was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=10∶1] in 90% isolated yield (29.8 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (s, 1H), 7.41～7.29 (m, 5H), 4.18 (s, 1H), 3.83 (s, 3H), 3.31～2.29 (m, 1H), 3.07～2.85 (m, 2H), 2.62～2.51 (m, 1H), 1.80～1.54 (m, 4H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.86, 154.61, 141.33,

130.80, 128.76, 128.51, 128.23, 56.09, 52.01, 45.77, 31.85, 30.76, 28.45, 22.50; HRMS (ESI) calcd for $C_{20}H_{27}NNaO_4$ $[M+Na]^+$ 368.1838, found 368.1788.

Methyl-2-benzylidene-4-((*tert*-butoxycarbonyl)amino)-pentanoate (**3qa**): White solid was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=10∶1] in 91% isolated yield (28.9 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.71 (s, 1H), 7.35～7.26 (m, 5H), 4.47 (d, *J*=6.8 Hz, 1H), 3.88 (s, 1H), 3.77 (s, 3H), 2.65～2.53 (m, 2H), 1.33 (s, 9H), 1.05 (d, J=6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 169.18, 155.27, 141.28, 135.58, 130.35, 129.20, 128.61, 128.50, 78.85, 52.24, 46.81, 34.36, 28.40, 21.63; HRMS (ESI) calcd for $C_{18}H_{25}NNaO_4$ $[M+Na]^+$ 342.1681, found 342.1634.

Methyl-2-benzylidene-4-((*tert*-butoxycarbonyl)amino)-6-methylheptanoate (**3ra**): White solid was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=10∶1] in 79% isolated yield (28.6 mg), *E*/*Z* ratio: >4∶1; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.70 (s, 1H), 7.34～7.23 (m, 5H), 3.76 (s, 3H), 2.60～2.48 (m, 2H), 1.58～1.53 (m, 1H), 1.32 (s, 9H), 1.22～1.12 (m, 2H), 0.84～0.79 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 169.48, 169.04, 165.44, 155.44, 141.11, 139.62, 137.76, 135.82, 130.70, 129.01, 128.53, 128.30, 127.71, 125.83, 78.68, 73.13, 52.14, 48.94, 45.55, 33.46, 28.40, 24.93, 22.82, 22.41, 21.15; HRMS (ESI) calcd for $C_{21}H_{32}NO_4$ $[M+H]^+$ 362.2331, found 362.1349.

Methyl-2-benzylidene-4-((*tert*-butoxycarbonyl)amino)-4-phenylbutanoate (**3sa**): White solid was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=10∶1] in 96% isolated yield (36.6 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.62 (s, 1H), 7.26～7.11 (m, 8H), 7.04 (d, *J*=7.2 Hz, 2H), 4.77 (d, *J*=8.0 Hz, 1H), 3.96 (s, 1H), 3.74 (s, 3H), 2.94 (q, *J*=4.4 Hz, 1H), 2.67～2.52 (m, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 169.60, 155.41, 141.25, 138.14, 135.07, 129.81, 129.59, 129.38, 128.55, 128.54, 128.44, 126.45, 78.93, 52.63, 52.29, 42.55, 31.09, 28.43; HRMS (ESI) calcd for $C_{23}H_{27}NKO_4$ $[M+K]^+$ 420.1577, found 420.2039.

Methyl-2-benzylidene-4-((*tert*-butoxycarbonyl)amino)-6-(methylthio)hexanoate (**3ta**): White solid was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=10∶1] in 34% isolated yield (13.0 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.79 (s, 1H), 7.42～7.33 (m, 5H), 3.84 (s, 3H), 3.70～3.64 (m, 1H), 2.69～2.67 (m, 1H), 2.51～2.45 (m, 1H), 2.11～2.04 (m, 4H), 1.58 (s, 9H), 1.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 155.50, 135.56, 130.09, 129.05, 128.63, 52.22, 35.70, 30.58, 29.71, 28.36, 27.75, 15.56; HRMS (ESI) calcd for $C_{20}H_{29}NNaO_4S$ $[M+Na]^+$ 402.1715, found 402.1678.

tert-Butyl (*E*)-2-(2-(methoxycarbonyl)-3-phenylallyl)-pyrolidine-1-carboxylate (**3ua**): White solid was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=10∶1] in 67% isolated yield (23.2 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.80 (s, 1H), 7.41～7.29 (m, 5H), 4.19～4.17 (m, 1H), 3.83 (s, 3H), 3.33～2.29 (m, 1H), 3.04～2.84 (m, 2H), 2.62～2.51 (m, 1H), 1.80～1.46 (m, 4H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 168.71, 154.61, 141.33, 135.82, 130.78, 128.76, 128.50, 128.22, 56.08, 52.00, 45.74, 31.84, 30.76, 29.70, 28.44, 22.50; HRMS (ESI) calcd for $C_{20}H_{27}NNaO_4$ $[M+Na]^+$ 368.1838, found 368.1793.

tert-Butyl-4-(2-(methoxycarbonyl)-3-phenylallyl)piperidine-1-carboxylate (**3va**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=50∶1] in 72% isolated yield (25.8 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.76 (s, 1H), 7.34～7.24 (m, 5H), 3.75 (s, 3H), 2.57～2.51 (m, 2H), 2.46 (d, *J*=7.2 Hz, 2H), 1.63～1.56 (m, 1H), 1.54～1.50 (m, 2H), 1.36 (s, 9H), 1.01～0.91 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 169.06, 154.80, 140.40, 135.73, 131.60, 129.12, 128.57, 128.38, 79.27, 52.14, 36.00, 33.49, 31.99, 28.47; HRMS (ESI) calcd for $C_{21}H_{29}NNaO_4$ $[M+Na]^+$ 382.1994, found 382.1947.

1-Methyl 6-((3*R*,5a*S*,6*R*,8a*S*,9*R*,12*R*,12a*R*)-3,6,9-trimethyldecahydro-12*H*-3,12-methano[1,2]dioxepino[4,3-*i*]isochromen-10-yl) 2-(-benzylidene)hexanedioate (**3wa**): White solid was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=10∶1] in 65% isolated yield (33.3 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.71 (s, 1H), 7.43～7.31 (m, 5H), 5.79 (d, *J*=10.0 Hz, 1H), 5.44 (s, 1H), 3.82 (s, 3H), 2.59～2.53 (m, 3H), 2.49～2.37 (m, 3H), 2.06～2.00 (m, 1H), 1.93～1.87 (m, 3H), 1.79～1.59 (m, 5H), 1.53～1.35 (m, 5H), 1.31～1.25 (m, 4H), 0.97 (d, *J*=6.4 Hz, 3H), 0.81 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 172.05, 168.68, 139.92, 135.46, 134.33, 132.24, 129.22, 128.61, 128.51, 104.46, 91.80, 91.51, 80.15, 77.35, 77.03, 76.71, 52.09, 51.59, 45.27, 37.28, 36.24, 34.10, 31.80, 26.93, 25.97, 24.59, 24.11, 22.01, 20.23, 12.13; HRMS (ESI) calcd for $C_{30}H_{40}NaO_7$ $[M+Na]^+$ 535.2672, found 535.2488.

Methyl-2-(cyclohexylmethyl)-3-(4-fluorophenyl)acrylate (**3ab**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 57% isolated yield (15.6 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.56 (s, 1H), 7.27 (dd, *J*=5.6, 2.4 Hz, 2H), 7.02～6.98 (m, 2H), 3.74 (s, 3H), 2.38 (d, *J*=7.2 Hz, 2H), 1.59～1.56 (m, 5H), 1.45～1.38 (m, 1H), 1.14～1.00 (m, 3H), 0.83～0.75 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 169.35, 162.39 (d, *J*=249.6 Hz), 138.30, 132.59, 132.04(d, *J*=3.4 Hz), 131.13 (d, *J*=8.2 Hz), 115.52 (d, *J*=21.5 Hz), 52.08, 37.82, 34.37, 33.25, 26.36, 26.30; ^{19}F NMR (377 MHz, $CDCl_3$) *δ*: −112.85; HRMS (ESI) calcd for $C_{17}H_{21}FNaO_2$ $[M+H]^+$ 277.1604, found 277.1574.

Methyl-3-(4-chlorophenyl)-2-(cyclohexylmethyl)acrylate (**3ac**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 82% isolated yield (23.8 mg), *E*/*Z*

ratio: >20∶1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (s, 1H), 7.29～7.19 (m, 4H), 3.73 (s, 3H), 2.37 (d, J=7.2 Hz, 2H), 1.58～1.55 (m, 4H), 1.44～1.39 (m, 1H), 1.18～0.99 (m, 4H), 0.81～0.73 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.16, 138.09, 134.46, 134.02, 133.35, 130.57, 128.69, 52.08, 37.81, 34.46, 33.24, 26.29; HRMS (ESI) calcd for $C_{17}H_{22}ClO_2$ $[M+H]^+$ 293.1308, found 293.1283.

Methyl-3-(4-bromophenyl)-2-(cyclohexylmethyl)acrylate (**3ad**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 65% isolated yield (21.9 mg), *E*/*Z* ratio: >20∶1; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (s, 1H), 7.44 (d, J=8.4 Hz, 2H), 7.15 (d, J=8.4 Hz, 2H), 3.74 (s, 3H), 2.37 (d, J=7.2 Hz, 2H), 1.58～1.54 (m, 5H), 1.45～1.38 (m, 1H), 1.14～0.99 (m, 3H), 0.81～0.72 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.16, 138.12, 134.92, 133.46, 131.65, 130.83, 122.27, 52.10, 37.80, 34.48, 33.24, 26.34, 26.29; HRMS (ESI) calcd for $C_{17}H_{22}BrO_2$ $[M+H]^+$ 337.0803, found 337.0787.

Methyl-2-(cyclohexylmethyl)-3-(*p*-tolyl)acrylate (**3ae**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 95% isolated yield (25.8 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (s, 1H), 7.23～7.19 (m, 2H), 7.11 (d, J=8.0 Hz, 2H), 3.73 (s, 3H), 2.42 (d, J=7.2 Hz, 2H), 2.30 (s, 3H), 1.60～1.56 (m, 5H), 1.49～1.40 (m, 1H), 1.12～1.00 (m, 3H), 0.87～0.77 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.64, 139.48, 138.29, 133.08, 131.82, 129.45, 129.19, 51.97, 37.89, 34.49, 33.27, 26.42, 26.35, 21.36; HRMS (ESI) calcd for $C_{18}H_{24}NaO_2$ $[M+Na]^+$ 295.1674, found 295.1255.

Methyl-3-(4-cyanophenyl)-2-(cyclohexylmethyl)acrylate (**3af**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 70% isolated yield (19.9 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62～7.57 (m, 3H), 7.36 (d, J=8.4 Hz, 2H), 3.76 (s, 3H), 2.35 (d, J=7.2 Hz, 2H), 1.57～1.54 (m, 5H), 1.45～1.36 (m, 1H), 1.10～0.98 (m, 3H), 0.77～0.68 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.65, 140.82, 137.18, 135.58, 132.23, 129.68, 118.67, 111.54, 52.28, 37.77, 34.59, 33.21, 26.25; HRMS (ESI) calcd for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1651, found 284.1612.

Methyl-2-(cyclohexylmethyl)-3-(4-(trifluoromethyl)-phenyl)acrylate (**3ag**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 62% isolated yield (20.1 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60～7.56 (m, 3H), 7.37 (d, J=8.4 Hz, 2H), 3.76 (s, 3H), 2.36 (d, J=7.2 Hz, 2H), 1.58～1.54 (m, 5H), 1.46～1.39 (m, 1H), 1.14～0.98 (m, 3H), 0.79～0.71 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.91, 139.70, 137.73, 134.79, 129.35, 125.36, 52.18, 37.79, 34.55, 33.21, 26.26; HRMS (ESI) calcd for $C_{18}H_{22}F_3O_2$ $[M+H]^+$ 327.1572, found 327.1548.

Methyl-4-(2-(cyclohexylmethyl)-3-methoxy-3-oxoprop-1-en-1-yl)benzoate (**3ah**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=50∶1] in 75% isolated yield (23.7 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J=8.4 Hz, 2H), 7.61 (s, 1H), 7.34 (d, J=8.0 Hz, 2H), 3.85 (s, 3H), 3.75 (s, 3H), 2.38 (d, J=7.2 Hz, 2H), 1.56～1.49 (m, 5H), 1.45～1.38 (m, 1H), 1.13～0.97 (m, 3H), 0.78～0.70 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.97, 166.72, 140.74, 138.24, 134.56, 129.66, 129.46, 129.11, 52.23, 52.14, 37.80, 34.55, 33.20, 26.31, 26.24; HRMS (ESI) calcd for $C_{19}H_{25}O_4$ $[M+H]^+$ 317.1753, found 317.1714.

Methyl-2-(cyclohexylmethyl)-3-(3-fluorophenyl)acrylate (**3ai**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 95% isolated yield (26.2 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (s, 1H), 7.37～7.31 (m, 1H), 7.13～6.99 (m, 3H), 3.81 (s, 3H), 2.45 (d, J=7.2 Hz, 2H), 1.66～1.60 (m, 5H), 1.54～1.46 (m, 1H), 1.22～1.07 (m, 3H), 0.90～0.81 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.09, 162.65 (d, J=246.8 Hz), 138.24, 137.98, 133.95, 129.93 (d, J=8.5 Hz), 125.04 (d, J=2.8 Hz), 115.89 (d, J=22.0 Hz), 115.10, 114.89, 77.35, 77.03, 76.71, 52.07, 37.79, 34.47, 33.22, 26.34, 26.27; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −112.85; HRMS (ESI) calcd for $C_{17}H_{22}FO_2$ $[M+H]^+$ 277.1604, found 277.1575.

Methyl-3-(3-chlorophenyl)-2-(cyclohexylmethyl)acrylate (**3aj**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 44% isolated yield (12.9 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (s, 1H), 7.34～7.27 (m, 3H), 7.24～7.21 (m, 1H), 3.81 (s, 3H), 2.44 (d, J=7.2 Hz, 2H), 1.66～1.63 (m, 5H), 1.52～1.45 (m, 1H), 1.19～1.06 (m, 3H), 0.89～0.81 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.03, 137.84, 137.80, 134.31, 134.11, 129.68, 129.14, 128.11, 127.29, 77.35, 77.03, 76.72, 52.10, 37.82, 34.49, 33.22, 26.33, 26.27; HRMS (ESI) calcd for $C_{17}H_{22}ClO_2$ $[M+H]^+$ 293.1308, found 293.1282.

Methyl-2-(cyclohexylmethyl)-3-(*m*-tolyl)acrylate (**3ak**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 27% isolated yield (7.3 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (s, 1H), 7.34～7.25 (m, 2H), 7.19～7.08 (m, 2H), 3.81(s, 1H), 2.48 (d, J=7.2 Hz, 2H), 2.37 (s, 3H), 1.67～1.59 (m, 5H), 1.53～1.45 (m, 1H), 1.26～1.10 (m, 3H), 0.93～0.74 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.52, 140.59, 139.59, 137.97, 135.96, 132.53, 130.17, 128.92, 128.28, 126.30, 77.34, 77.02, 76.71, 51.94, 37.88, 34.49, 33.25, 33.10, 26.33, 21.48; HRMS (ESI) calcd for $C_{18}H_{25}O_2$ $[M+H]^+$ 273.1855, found 273.1830.

Methyl-2-(cyclohexylmethyl)-3-(3-methoxyphenyl)acrylate (**3al**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 50% isolated yield (14.3 mg), *E*/*Z*

ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (s, 1H), 7.24～7.19 (m, 1H), 6.88 (d, J=7.6 Hz, 1H), 6.83～6.78 (m, 2H), 3.74 (d, J=4.4 Hz, 6H), 2.41 (d, J=7.2 Hz, 2H), 1.60～1.56 (m, 5H), 1.49～1.40 (m, 1H), 1.14～0.99 (m, 3H), 0.85～0.75 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.43, 159.46, 139.33, 137.34, 132.94, 129.43, 121.82, 114.57, 113.86, 55.26, 52.03, 37.90, 34.56, 33.28, 26.40, 26.34; HRMS (ESI) calcd for $C_{18}H_{25}O_3$ $[M+H]^+$ 289.1804, found 289.1766.

Methyl-3-(2-chlorophenyl)-2-(cyclohexylmethyl)acrylate (**3am**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 75% isolated yield (21.9 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (s, 1H), 7.35～7.33 (m, 1H), 7.20 (d, J=3.2 Hz, 3H), 3.76 (s, 3H), 2.25 (d, J=7.2 Hz, 2H), 1.56～1.50 (m, 5H), 1.43～1.34 (m, 1H), 1.09～0.93 (m, 3H), 0.68～0.58 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.68, 137.02, 134.86, 134.25, 133.83, 130.18, 129.51, 129.19, 126.46, 52.10, 37.33, 34.66, 33.03, 26.34, 26.22; HRMS (ESI) calcd for $C_{17}H_{22}ClO_2$ $[M+H]^+$ 293.1308, found 293.1277.

Methyl-3-(2-bromophenyl)-2-(cyclohexylmethyl)acrylate (**3an**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 94% isolated yield (31.6 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57～7.53 (m, 2H), 7.25 (t, J=7.2 Hz, 1H), 7.19～7.17 (m, 1H), 7.13～7.09 (m, 1H), 3.76 (s, 3H), 2.23 (d, J=7.2 Hz, 2H), 1.56～1.50 (m, 5H), 1.42～1.34 (m, 1H), 1.08～0.93 (m, 3H), 0.67～0.57 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.66, 139.09, 136.72, 133.90, 132.65, 130.26, 129.33, 127.08, 123.89, 52.12, 37.30, 34.59, 33.05, 26.34, 26.21; HRMS (ESI) calcd for $C_{17}H_{22}BrO_2$ $[M+H]^+$ 337.0803, found 337.0766.

Methyl-2-(cyclohexylmethyl)-3-(2-methoxyphenyl)acrylate (**3ao**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 39% isolated yield (11.2 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (s, 1H), 7.32～7.26 (m, 2H), 6.97～6.88 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 2.39 (d, J=7.2 Hz, 2H), 1.65～1.58 (m, 5H), 1.53～1.44 (m, 1H), 1.18～1.04 (m, 3H), 0.83～0.74 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.31, 157.47, 135.84, 132.54, 129.69, 129.52, 125.20, 120.14, 110.54, 77.35, 77.04, 76.72, 55.49, 51.86, 37.67, 34.67, 33.14, 26.42, 26.31; HRMS (ESI) calcd for $C_{18}H_{24}NaO_3$ $[M+Na]^+$ 311.1623, found 311.1589.

Methyl-3-(2-bromo-4-fluorophenyl)-2-(cyclohexylmethyl)acrylate (**3ap**): White solid was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 66% isolated yield (23.4 mg), *E*/*Z* ratio: >10∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57～7.53 (m, 2H), 7.01～6.90 (m, 2H), 3.83 (s, 3H), 2.30 (d, J=7.2 Hz, 2H), 1.63～1.56 (m, 5H), 1.49～1.41 (m, 1H), 1.20～1.02 (m, 3H), 0.77～0.67 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.33, 161.45 (d, J=248.2 Hz), 138.44, 138.36, 137.80, 134.86, 133.91 (d, J=8.3 Hz), 118.11(d, J=3.2 Hz), 117.24 (d, J=23.4 Hz), 116.63, 116.40, 52.16, 37.31, 34.61, 33.07, 26.29, 26.18. ^{19}F NMR (377 MHz, $CDCl_3$) δ: −114.61; HRMS (ESI) calcd for $C_{17}H_{21}BrFO_2$ $[M+H]^+$ 355.0709, found 355.0687.

Methyl-3-(2-bromo-4-chlorophenyl)-2-(cyclohexylmethyl)acrylate (**3aq**): White solid was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 79% isolated yield (29.2 mg), *E*/*Z* ratio: >20∶1. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, J=2.0 Hz, 1H), 7.49 (s, 1H), 7.24 (dd, J=8.4, 1.6 Hz, 1H), 7.12 (d, J=8.4 Hz, 1H), 3.76 (s, 3H), 2.21 (d, J=7.2 Hz, 2H), 1.54～1.52 (m, 5H), 1.42～1.32 (m, 1H), 1.12～0.94 (m, 3H), 0.67～0.57 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.39, 137.89, 135.26, 134.54, 134.30, 132.39, 130.94, 127.47, 124.28, 52.19, 37.30, 34.66, 33.06, 26.30, 26.20; HRMS (ESI) calcd for $C_{17}H_{21}BrClO_2$ $[M+H]^+$ 371.0413, found 371.1002.

Methyl 4-(4-chlorophenoxy)-4-methyl-2-methylenepentanoate (**3xr**): Colorless oil was obtained by column chromatography on silica gel [eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=100∶1] in 30% isolated yield (7.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22～7.19 (m, 2H), 6.90～6.88 (m, 2H), 6.28 (d, J=1.2 Hz, 1H), 3.75 (s, 3H), 2.75 (s, 2H), 1.24 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 168.36, 153.86, 137.19, 128.92, 128.53, 128.30, 125.04, 80.53, 51.89, 43.38, 26.09.

Supporting Information The detailed procedure for the synthesis and cyclic voltammetry (CV) experiment, copies of ^{1}H NMR, ^{13}C NMR of the products **3**, and ^{19}F NMR of products **3ab**, **3ai**, **3ap**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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