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# **Supporting Information**

## Visible Light/Copper Catalysis Enabled Heck-Like Coupling between Alkenes and Cyclic Sulfonium Salts via Selective C-S Bond Cleavage

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## **Table of Contents**

I. General Considerations	2
II. Optimization of Reaction Conditions	4
III. Experimental Procedures	7
IV. Experiments of Investigations on The Mechanism	17
V. Characterization of Products	20
VI. References	43
VII. NMR Spectrum and HRMS of The Products	45

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#### I. General considerations

All reagents and solvents were obtained from commercial suppliers and used without further purification. The starting materials were synthesized according to literature procedures. Flash chromatography was performed on silica gel (200~300 mesh).  $^{1}$ H,  $^{13}$ C NMR data were recorded on a BRUKER 400 MHz or 500 MHz spectrometer. Proton and carbon magnetic resonance spectra ( $^{1}$ H NMR,  $^{13}$ C NMR) were recorded using tetramethylsilane (TMS) as the internal standard in CDCl<sub>3</sub>. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: CHCl<sub>3</sub> ( $\delta$  = 7.26 for  $^{1}$ H NMR and  $\delta$  = 77.0 for  $^{13}$ C NMR). Data are reported as follows: chemical shift  $\delta$ /ppm, integration ( $^{1}$ H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof;  $^{13}$ C and  $^{19}$ F signals are singlets unless otherwise stated), coupling constants J in Hz, assignment.

**UV-visible spectroscopy** of reaction solution was recorded on a UV-2600 UV-Vis spectrophotometer.

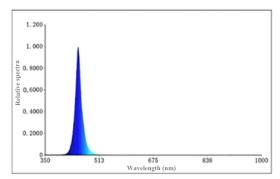
**The power density** of the incident light was recorded on CEL-FZ-A radiometer. The reactor was 3.0 cm from a 20W blue LED.

#### The spectrum of our lamp and the visible-light irradiation instrument

All reactions have been studied in borosilicate glass vessels irradiated by a blue light LED manufactured by Xuzhou Ai Jia Electronic Technology Co., Ltd. without using filters.



Figure S1. The blue light LED.



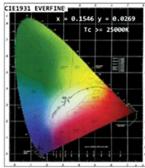


Figure S2. The spectrum of our lamp (blue LED).

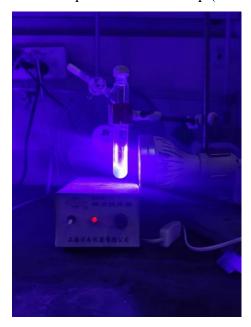
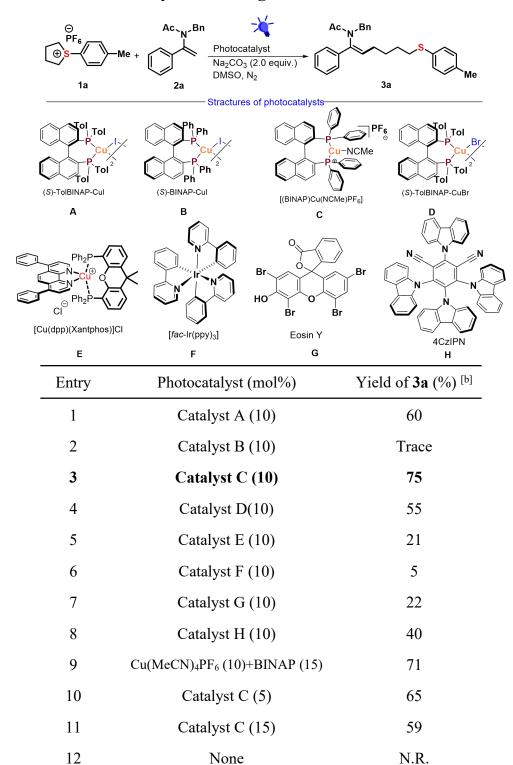


Figure S3. Photograph of the reaction setup.

## **II. Optimization of Reaction Conditions**

## 1. Table S1. Photocatalyst Screening [a]



<sup>[</sup>a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), photocatalyst (10 mol%), base (2.0 equiv.) and degassed anhydrous solvent (2.0 mL) at room temperature under irradiation with 20 W blue LED (455 nm) for 24 h under a nitrogen atmosphere. [b] Isolated yield. [c] N.R. = no reaction.

## 2. Table S2. Base Screening [a]

Entry	Base	Yield of <b>3a</b> (%) [b]
1	$K_2CO_3$	67
2	$Cs_2CO_3$	Trace
3	$Et_3N$	11
4	Pyridine	21
5	DIPEA	Trace
6	DBU	Trace
7	None	N.R.

<sup>[</sup>a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), photocatalyst C (10 mol%), base (2.0 equiv.) and DMSO (2.0 mL) at room temperature under irradiation with 20 W blue LED (455 nm) for 24 h under a nitrogen atmosphere. [b] Isolated yield. [c] N.R. = no reaction.

## 2. Table S3. Solvent Screening [a]

<sup>[</sup>a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), photocatalyst C (10 mol%), Na<sub>2</sub>CO<sub>3</sub> (2.0 equiv.) and degassed anhydrous solvent (2.0 mL) at room temperature under irradiation with 20 W

blue LED (455 nm) for 24 h under a nitrogen atmosphere.  $^{[b]}$  Isolated yield.  $^{[c]}$  No LED irradiation.  $^{[d]}$  Under 40  $^{\circ}$ C instead of light.  $^{[e]}$  Under 60  $^{\circ}$ C instead of light.  $^{[f]}$  N.R. = no reaction.

#### III. Experimental procedures

## 1. General method for sulfonium salt synthesis 1, 2, 3, 4, 5:

SH 
$$\xrightarrow{R^1}$$
  $\xrightarrow{n=1,2}$   $\xrightarrow{Br}$   $\xrightarrow{1. Et_3N, Et_2O, r.t.}$   $\xrightarrow{Ar}$   $\xrightarrow{Ar}$   $\xrightarrow{PF_6}$   $\xrightarrow{PF_6}$ 

General procedure: Triethylamine (3.9 mL, 27.23 mmol, 1.5 equiv.) was slowly added to a 50 mL round-bottom flask containing thiophenol (2.25 g, 18.15 mmol, 1.0 equiv.), dibromide (4.3 mL, 36.3 mmol, 2.0 equiv.) and Et<sub>2</sub>O (20 mL). The reaction mixture was stirred until the substrate was completely consumed which monitored by TLC. Then use 1.2 M HCl (15 mL) and EA (3 × 15 mL) to treat the reaction solution, and wash with saturated NaHCO<sub>3</sub> solution. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), later the crude material was dissolved in acetone (20 mL) after the solvents were evaporated, and add NH<sub>4</sub>PF<sub>6</sub> (4.44 g, 27.23 mmol) to the solution. Reflux and stir until the substrate was completely consumed which monitored by TLC, then the reaction mixture was filtered through glass bush funnel and the filtrate was concentrated to 10 mL under reduced pressure. After that add Et<sub>2</sub>O (20 mL) to precipitate white or beige solid, the resulting solid was filtered and washed with water (30 mL) and ethanol (30 mL). Finally, the product was dried under vacuum and obtained in 10-70% yield.

General procedure: Triethylamine (3.9 mL, 27.23 mmol, 1.5 equiv.) was slowly added to a 50 mL round-bottom flask containing thiophenol (2.25 g, 18.15 mmol, 1.0 equiv.), dibromide (4.3 mL, 36.3 mmol, 2.0 equiv.) and Et<sub>2</sub>O (20 mL). The reaction mixture was stirred until the substrate was completely consumed which monitored by TLC. Then use 1.2 M HCl (15 mL) and EA (3 × 15 mL) to treat the reaction solution, and wash with saturated NaHCO<sub>3</sub> solution. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), later the crude material was dissolved in acetone (20 mL) after the solvents were

evaporated, and addAgOTf (27.23 mmol) to the solution. Reflux and stir until the substrate was completely consumed which monitored by TLC, then the reaction mixture was filtered through glass bush funnel and the filtrate was concentrated under reduced pressure. Purification by column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub>:1:20) afforded the desired product.

General procedure: A 100 mL two-necked flask was charged with magnesium turnings (11 mmol). After successive additions of THF (10 mL) and 1,2-dibromoethane (2 drops) at room temperature, aryl bromide (10 mmol in 10 mL of THF) was added slowly. The resulting mixture was stirred for 3 h at room temperature. Dimethyl disulfide (2.0 mL, 22 mmol) was then added at 0 °C, and the resulting solution was stirred for an additional 2 h at room temperature before addition of hexane (30 mL). The resulting mixture was diluted with water and the solution was extracted with EtOAc, washed with brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvents were removed under reduced pressure and the crude product was purified by silica gel column chromatography.

To a solution of the obtained aryl sulfide (10 mmol) in DCM (10 mL) was dropwise added methyl trifluoromethanesulfonate (11 mmol), and the resulting solution was stirred at room temperature for 12 h. Then, Et2O (20 mL) was added slowly. The precipitated solids were filtered off and washed with Et2O (3  $\times$  20 mL) to afford sulfonium salt as a solid.

General procedure: Sodium tetrafluoroborate (5 equiv.) was added to a rapidly stirred solution of the sulfide (5 equiv.) and alkylbromide (1 equiv.) in acetone (0.5 M) at rt. Stirring was then continued for 48 h after which time the resulting NaBr was filtered off and the filtrate was concentrated under reduced pressure. Purification by column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub>:1:20) afforded the desired product.

General procedure: Tf<sub>2</sub>O (5.5 mmol, 1.1 equiv.) and styrene (5 mmol, 1.0 equiv.) were slowly added sequentially to a stirred solution of the corresponding tetramethylene sulfoxide (10 mmol, 1.1 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at -30 °C under a nitrogen atmosphere. The resulting solution was stirred at this temperature for 15 minutes before warming to 0 °C. After stirring for 1 h, TLC analysis showed complete consumption of the styrene starting material, at which point the solvent was removed in vacuo. The product was then precipitated by the addition of Et<sub>2</sub>O. The Et<sub>2</sub>O was then decanted and the crude product was washed with further portions of Et<sub>2</sub>O. The pure product was obtained as a yellow solid by recrystallisation (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O); yield 55%.

General procedure: A flame-dried 100 mL flask was placed under an atmosphere of nitrogen and charged with a stir bar and alcohol (5.0 mmol, 1.0 equiv). The alcohol was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20.0 mL) and cooled to -30 °C before adding pyridine (6.0 mmol, 1.2 equiv). While stirring, triflic anhydride (29.3 mmol, 1.2 equiv.) was added dropwise, and then the reaction mixture stirred for 3 h while remaining at -5 °C. While the flask was still in a -5 °C bath, 0.5 M H<sub>2</sub>SO<sub>4</sub> (30 mL) was added. The flask was removed from the cold bath, and the mixture was transferred to a separatory funnel and extracted with 3×20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were combined and washed 1×50mL of distilled water. The collected organic layers were then dried over MgSO<sub>4</sub>, then filtered and concentrated to a 10 mL liquid under vacuum (without heating), which was used directly in the next step. Flame-dried 25 mL Schlenk tube was added phenyl sulfide (5.0 mmol, 1.0 equiv.), then the above liquid was added. The mixture was stired at 55 °C for 24 h. The mixture was carefully condensed under reduced pressure at 25 °C and purified by precipitation with Et<sub>2</sub>O/DCM. Most of the unreacted dibenzothiophene was removed by repeating the precipitation procedure 2

or 3 times. If the salt still did not precipitate, it was subjected to silica gel chromatography with acetone/DCM.

### 2. Procedure for the synthesis of starting materials enamides<sup>6</sup>:

#### (A) General method for starting N-acyl enamides:

**Synthetic procedure:** (a) A mixture of ketone (10.0 mmol, 1.0 equiv.), NaOAc (1.2 equiv.), hydroxylamine hydrochloride (1.2 equiv.), EtOH (7.5 mL) and H<sub>2</sub>O (22.5 mL) was stirred for 2 h at 95 °C. Then the mixture was evaporated under vacuum and extracted with ethyl acetate. The organic layer was collected, dried over Na<sub>2</sub>SO<sub>4</sub> and vacuo to afford the ketoxime which was used without further purification for the next step.

(b) To an oven-dried 250 mL round-bottom flask assembled with condenser was added the above ketoxime, then acetic anhydride (2.0 equiv.), sodium bisulfite (3.0 equiv.), cuprous iodide (0.1 equiv.) and DCE (100 mL) were added. The flask was vacuumed and back filled with nitrogen for three times. The reaction flask was put into a 120 °C oil bath for 12 h. After the reaction completed and cooled to room temperature, the organic layer was extracted with ethyl acetate. The organic layer was collected, dried over Na<sub>2</sub>SO<sub>4</sub> and vacuo to afford the *N*-acyl enamides, which was directly purified by column chromatography.

#### (B) Synthesis of benzylated enamides:

**Synthetic procedure:** (3.0 mmol, 1.0 equiv.) of the *N*-acyl enamide was dissolved in 9.0 mL of dry DMF taken in a dry two-necked flask under nitrogen. The solution was cooled to 0 °C and (4.5 mmol, 1.5 equiv.) of sodium hydride was added in portions. The resulting suspension was stirred at the same temperature for 10 min. (6.0 mmol,

2.0 equiv.) of BnBr was then added dropwise and the mixture was warmed to room temperature overnight. The completion of the reaction was confirmed by checking TLC and the excess of sodium hydride was quenched by adding 3 mL of water at 0 °C. The organic layer was extracted with ethyl acetate through stages of extraction with water. The combined organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel to give the benzylated enamides.

## 3. General procedures for the alkenes<sup>7</sup>:

**Synthetic procedure:** Alkenes were prepared according a reported procedure.2 To a stirred suspension of alkyltriphenylphoshonium bromide (9.6 mmol) in dry THF (25 mL) was added 'BuOK (9.6 mmol) under Argon atmosphere. After 30 min, ketone (4.8 mmol) was added into the flask and the mixture was stirred for 12 h at room temperature (the progress can be monitored via TLC). After the reaction, the resulting reaction mixture was poured into water and subsequently extracted with ethyl ether for three times. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. Afterwards, products were obtained via silica gel chromatography.

## 4. Synthesis of Copper-Based Photocatalyst<sup>8,9,10</sup>:

[(BINAP)Cu(NCMe)PF<sub>6</sub>]: A solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>) (0.3723 g, 1 mmol) in 10 mL of THF was added to a THF solution of 35 mL with BINAP (0. 623 g, 1 mmol). The solution was allowed to stir for 3 hours and the solvent was reduced in vacuo to 15 mL. Approximately 20 mL of hexanes was added to precipitate a white solid. The resulting solid was collected by vacuum filtration and dried under reduced pressure.

(S)-TolBINAP-CuI: A solution of CuI (0.191 g, 1 mmol) in 10 mL of DCM was added to a DCM solution of 35 mL with (S)-TolBINAP (0.679 g, 1 mmol). The solution was allowed to stir for 3 hours and the solvent was reduced in vacuo to 15

mL. Approximately 20 mL of hexanes was added to precipitate a white solid. The resulting solid was collected by vacuum filtration and dried under reduced pressure.

(S)-BINAP- CuI: A solution of CuI (0.191 g, 1 mmol) in 10 mL of DCM was added to a DCM solution of 35 mL with (S)-TolBINAP (0.623 g, 1 mmol). The solution was allowed to stir for 3 hours and the solvent was reduced in vacuo to 15 mL. Approximately 20 mL of hexanes was added to precipitate a white solid. The resulting solid was collected by vacuum filtration and dried under reduced pressure.

(S)-TolBINAP-CuBr: A solution of CuBr (0.143 g, 1 mmol) in 10 mL of DCM was added to a DCM solution of 35 mL with (S)-TolBINAP (0.679 g, 1 mmol). The solution was allowed to stir for 3 hours and the solvent was reduced in vacuo to 15 mL. Approximately 20 mL of hexanes was added to precipitate a white solid. The resulting solid was collected by vacuum filtration and dried under reduced pressure.

[Cu(dpp)(Xantphos)]CI: To a solution of CuCl (0.099 g, 1 mmol) in dry dichloromethane (80 mL) was added Xantphos (0.58 g, 0.5 mmol) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 5 hours. A solution of dpp (0.1728 g, 0.52 mmol) in dry dichloromethane (3 mL) was then added dropwise under a nitrogen atmosphere and the resulting reaction mixture was heated to reflux for another 12 hours (oil bath). The reaction mixture was then allowed to cool to room temperature. Then the resulting filtrate was concentrated under reduced pressure to one tenth of the original volume and n-hexane was added to precipitate the product. It was filtered and washed with n-hexane. The resulting solid was further purified by recrystallization in a DCM/n-Hexane mixture at 4 °C. The yellow precipitate was collected by filtration and dried under vacuum to give the desired copper complex Cu[(dpp)(Xantphos)]Cl as a yellow solid.

## 5. General procedure for the synthesis of 3:

General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt (0.3)mmol), followed by the addition [(BINAP)Cu(NCMe)PF<sub>6</sub>] (10 mol%)and Na<sub>2</sub>CO<sub>3</sub> (2.0 equiv.). Then the tube was evacuated and backfilled with nitrogen (five times). 2 (0.2 mmol) in degassed anhydrous DMSO (2.0 mL) was added and the mixture was irradiated under 20 W blue LED at room temperature for 24 h. The residue was added brine (10 mL) and extracted with ethyl acetate (5 × 4 mL). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products 3 in 50-75% yield.

#### 6. Gram scale experiment

To an oven-dried 50 mL Schlenk Tube with a stirring bar was added sulfonium salt 1a (5.85 mmol), followed by the addition of [(BINAP)Cu(NCMe)PF<sub>6</sub>] (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (2.0 equiv.). Then, air was withdrawn and backfilled with N<sub>2</sub> (five times). 2a (3.9 mmol) in degassed anhydrous DMSO (30 mL) was added and the mixture was irradiated under two 20 W blue LEDs at room temperature for 48 h. When the reaction is completed, the reaction mixture was added water and extracted with ethyl acetate, washed with brine, dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (petroleum ether/EtOAc, v/v = 5:1) to afford the product 3a (1.08 g, 64.1%).

#### 7. Product derivatization<sup>6, 11,12</sup>

To a stirred solution of the sulfide 3a (0.2 mmol, 1 equiv.) in 2 mL methanol was added H<sub>2</sub>O<sub>2</sub> (30% in water, 0.06 mL, 0.8 mmol, 4.0 equiv.) at room temperature. The reaction was stirred for 48 h and then concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (petroleum ether/EtOAc, v/v = 3:1) to give 6 in 61% yield.

The **3a** (0.2 mmol, 1 equiv.), m-CPBA (0.4 mmol, 2 equiv.), and CH<sub>2</sub>Cl<sub>2</sub> (2 mL) were added to an oven-dried test tube equipped with a magnetic stirring bar. Then, the reaction tube was sealed with an air balloon (atmospheric pressure) and stirred at the desired temperature overnight. After the reaction was completed, the reaction solution was extracted by EtOAc (3 × 2 mL). The organic solvent was removed in vacuo, and the residue was purified by flash column chromatography (petroleum ether/EtOAc, v/v = 5:1) on silica gel to give **7** in 74% yield

The 3a (0.2 mmol, 1 equiv.), HCl (12 mol/L,0.4 mmol, 2 equiv.) and THF (2 mL) were added to an oven-dried test tube equipped with a magnetic stirring bar. Then, the reaction tube was sealed with an air balloon (atmospheric pressure) and stirred at the desired temperature overnight. After the reaction was completed, the reaction solution was extracted by EtOAc (3 × 2 mL). The organic solvent was removed in vacuo, and the residue was purified by flash column chromatography (petroleum ether/EtOAc, v/v = 50:1) on silica gel to give 8 in 79% yield.

The **3a** (0.2 mmol, 1 equiv.), PIDA (0.5 mmol, 2.5 equiv.) and CH<sub>3</sub>COONH<sub>4</sub> (0.5 mmol, 2.5 equiv.) were added to a flask containing a stirrer bar. MeOH was used as solvent and the reaction was stirred at 25 °C for 3 h. After the indicated reaction time, solvent was removed under reduced pressure and purified by column chromatography (petroleum ether/EtOAc, v/v = 1:1) which afforded 9 in 65% yield.

#### 8. Investigation of other aliphatic olefins

$$+ \bigvee_{\bigoplus_{P \in G}} \bigvee_{Na_2 \in O_3} (2.0 \text{ equiv.}), \text{ DMSO}$$

$$+ \bigvee_{\bigoplus_{P \in G}} \bigvee_{Na_2 \in O_3} (2.0 \text{ equiv.}), \text{ DMSO}$$

$$+ \bigvee_{\bigoplus_{P \in G}} \bigvee_{Na_2 \in O_3} (2.0 \text{ equiv.}), \text{ DMSO}$$

$$+ \bigvee_{\bigoplus_{P \in G}} \bigvee_{Na_2 \in O_3} (2.0 \text{ equiv.}), \text{ DMSO}$$

$$+ \bigvee_{\bigoplus_{P \in G}} \bigvee_{Na_2 \in O_3} (2.0 \text{ equiv.}), \text{ DMSO}$$

$$+ \bigvee_{\bigoplus_{P \in G}} \bigvee_{Na_2 \in O_3} (2.0 \text{ equiv.}), \text{ DMSO}$$

$$+ \bigvee_{\bigoplus_{P \in G}} \bigvee_{Na_2 \in O_3} (2.0 \text{ equiv.}), \text{ DMSO}$$

$$+ \bigvee_{\bigoplus_{P \in G}} \bigvee_{Na_2 \in O_3} (2.0 \text{ equiv.}), \text{ DMSO}$$

General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt 1 (0.3 mmol), followed by the addition of [(BINAP)Cu(NCMe)PF<sub>6</sub>] (10 mol%)and Na<sub>2</sub>CO<sub>3</sub> (2.0 equiv.). Then the tube was evacuated and backfilled with nitrogen (five times). 2 (0.2 mmol) in degassed anhydrous DMSO (2.0 mL) was added and the mixture was irradiated under 20 W blue LED at room temperature for 24 h. The residue was added brine (10 mL) and extracted with ethyl acetate (5 × 4 mL). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. It is a pity that the above four aliphatic olefins cannot obtain ideal products under current conditions.

#### 8. Investigation of non-functionalized sulfonium salt of styrene, the

#### ring size of the cyclic sulfonium salts and open chain sulfonium salts

General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt (0.3)mmol), followed by the addition [(BINAP)Cu(NCMe)PF<sub>6</sub>] (10 mol%)and Na<sub>2</sub>CO<sub>3</sub> (2.0 equiv.). Then the tube was evacuated and backfilled with nitrogen (five times). 2 (0.2 mmol) in degassed anhydrous DMSO (2.0 mL) was added and the mixture was irradiated under 20 W blue LED at room temperature for 24 h. The residue was added brine (10 mL) and extracted with ethyl acetate (5 × 4 mL). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. It is a pity that the above four aliphatic olefins cannot obtain ideal products under current conditions.

## IV. Experiments of investigations on the mechanism

General procedure: A mixture 1a (0.3 mmol), 2a (0.2 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.0 equiv.), [(BINAP)Cu(NCMe)PF<sub>6</sub>] (10 mol%) and 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO, 3.0 equiv.) in degassed anhydrous DMSO (2 mL) at room temperature under irradiation with 20 W blue LED (455 nm) for 24 h in N<sub>2</sub>. The radical trapping experiments were conducted with 1a and 2a under the standard conditions with a trapping agent 2, 2, 6, 6-tetramethyl-1-piperidinyloxy to capture the radical intermediate expected in our system, and to afford the product 10 in 55% yield.

#### 2. Sunlight-driven experiment

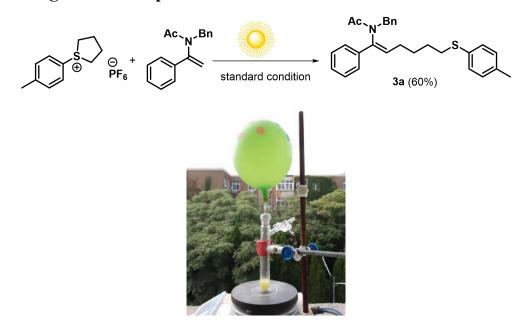


Figure S4. Sunlight-Driven experiment.

General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt **1a** (0.3 mmol), followed by the addition of [(BINAP)Cu(NCMe)PF<sub>6</sub>] (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (2.0 equiv.). Then the tube was evacuated and backfilled with nitrogen (five times). **2a** (0.2 mmol) in degassed anhydrous DMSO (2.0 mL) was added and the mixture was stirred under solar light

for four days (a total of 24 hours of sunlight irradiation, location: 36°8′54″ N, 120°23′3″ E). Afterward, the residue was added water (10 mL) and extracted with ethyl acetate (5 mL × 4). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, and the resulting crude residue was purified via column chromatography on silica gel to afford 3a in 60% yield.

#### 3. UV-Vis absorption experiment

UV-visible spectroscopy of reaction solution was recorded on a UV-2600 UV-Vis spectrophotometer. The sample was prepared by **1a** (10<sup>-4</sup> M), **2a** (10<sup>-4</sup> M), BINAP (10<sup>-4</sup> M), Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (10<sup>-4</sup> M), [(BINAP)Cu(NCMe)PF<sub>6</sub>] (10<sup>-4</sup> M) in DMSO. The absorption was collected and the result was listed in Figure S5.

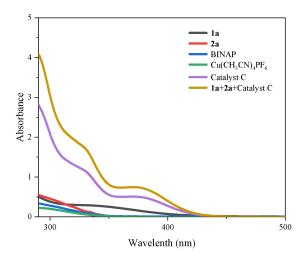


Figure S5. UV-Vis absorption spectra

#### 4. Calculation of apparent quantum efficiency (A. Q. E)

The energy of one photon  $(E_{photon})$  with wavelength of  $\lambda_{inc}$  (nm) is calculated using the following equation:

$$E_{photon} = \frac{hc}{\lambda_{inc}(455 \ nm)} = \frac{6.63 \times 10^{-34} \ j. \ s \times 3 \times 10^8 \ m. \ s^{-1}}{455 \times 10^{-9} \ m} = 4.37 \times 10^{-19} \ j$$

And the total energy of the incident monochromatic light (E<sub>total</sub>) is calculated using the following equation:

$$E_{total} = PSt = 186.3 \times 10^{-3} W.\, cm^{-2} \times 2.99 \, cm^2 \times 24 \times 3600 s = 4.80 \times 10^4 j$$

The total number of incident photons can be obtained through the following equation:

$${\rm Number\ of\ incident\ photons} = \frac{E_{total}}{E_{photon(455\ nm)}} = \frac{4.80\times 10^4\ j}{4.37\times 10^{-19}\ j} = 1.1\times 10^{23} = 182.4\ mmol$$

As a result, the apparent quantum yield (A.Q.Y) is defined as follows:

$$\text{A.Q.Y. (\%)} = \frac{\textit{Number of product}}{\textit{Number of incident photons}} = \frac{0.15 \, \textit{mmol}}{182.4 \, \textit{mmol}} = 0.082\% < 1$$

Where  $\mathbf{h}$  (J·s) is Planck's constant,  $\mathbf{c}$  (m·s<sup>-1</sup>) is the speed of light and  $\lambda_{inc}$  (m) is the wavelength of the incident light.  $\mathbf{P}$  (W·cm<sup>-2</sup>) is the power density of the incident light,  $\mathbf{S}$  (cm<sup>2</sup>) is the irradiation area and  $\mathbf{t}$  (s) is the photoreaction time. The  $\mathbf{A}.\mathbf{Q}.\mathbf{Y}$  (%) result indicated that our reaction not involved radical chain pathway.

#### 5. Effect of visible light irradiation

The reaction between **1a** and **2a** was conducted under the standard conditions on a 0.2 mmol scale. The mixture was subjected to sequential periods of stirring under visible light irradiation (20 W blue LED) followed by stirring in the absence of light, and so on. At each time point, one reaction system was suspended. The yield of **3a** was determined by <sup>1</sup>H NMR spectroscopy using 1, 3, 5-trimethoxybenzene as the internal standard.

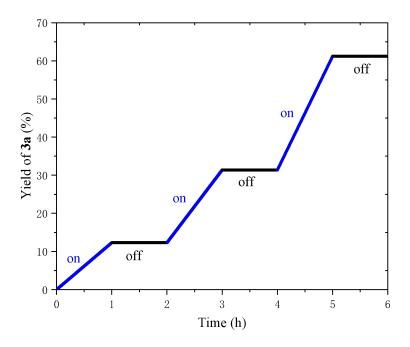


Figure S6. Visible light irradiation On/Off experiment

#### V. Characterization of products

#### Characterization data of compounds 3a-10

(*Z*)-*N*-Benzyl-*N*-(1-phenyl-7-(*p*-tolyl)hept-1-en-1-yl)acetamide (3a). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 63 mg, 75% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.38 (m, 3H), 7.31 – 7.28 (m, 2H), 7.28 – 7.25 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.29 (t, *J* = 7.6 Hz, 1H), 4.50 (s, 2H), 2.80 (t, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 2.22 – 2.18 (m, 5H), 1.52 (q, *J* = 7.4, 6.9 Hz, 2H), 1.45 (q, *J* = 7.5 Hz, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  169.67, 137.80, 136.61, 134.10, 133.95, 131.01, 130.89, 129.44, 127.98, 127.62, 127.58, 127.21, 126.18, 48.03, 32.61, 28.67, 27.52, 27.37, 26.97, 21.24. HRMS calcd for C<sub>28</sub>H<sub>32</sub>NOS<sup>+</sup> [M+H]<sup>+</sup>: 430.2199; found 430.2198.

#### (Z)-N-Benzyl-N-(6-((4-chlorophenyl)thio)-1-phenylhex-1-en-1-yl)acetamide (3b).

Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 60 mg, 68% yield. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.32 – 7.29 (m, 2H), 7.23 – 7.09 (m, 12H), 5.19 (t, J = 7.6 Hz, 1H), 4.40 (s, 2H), 2.71 (t, J = 7.1 Hz, 2H), 2.16 – 2.03 (m, 5H), 1.49 – 1.40 (m, 2H), 1.39 – 1.29 (m, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-d)  $\delta$  169.67, 137.80, 136.61, 134.10, 133.95, 131.01, 130.89, 129.44, 127.98, 127.62, 127.58, 127.21, 126.18, 48.03, 32.61, 28.67, 27.52, 27.37, 26.97, 21.24. HRMS calcd for  $C_{27}H_{29}CINOS^+$  [M+H]<sup>+</sup>: 450.1653; found 450.1651.

#### (Z)-N-Benzyl-N-(6-((4-(tert-butyl)phenyl)thio)-1-phenylhex-1-en-1-yl)acetamide

(3c). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 66 mg, 77% yield.  $^{1}$ H NMR (400 MHz, Chloroform-d)  $\delta$  7.33 – 7.28 (m, 3H), 7.23 – 7.22 (m, 1H), 7.21 – 7.20 (m, 1H), 7.19 – 7.13 (m, 7H), 7.12 – 7.09 (m, 2H), 5.20 (t, J = 7.7 Hz, 1H), 4.40 (s, 2H), 2.71 (t, J = 7.1 Hz, 2H), 2.14 – 2.06 (m, 5H), 1.47 – 1.40 (m, 2H), 1.39 – 1.32 (m, 2H), 1.22 (s, 9H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  169.71, 148.28, 137.67, 136.62, 133.99, 131.87, 131.24, 128.37, 127.99, 127.63, 127.58, 127.52, 127.21, 126.17, 124.91, 48.04, 33.41, 32.77, 30.26, 27.77, 27.43, 27.02, 21.25. HRMS calcd for  $C_{31}H_{38}NOS^{+}$  [M+H] $^{+}$ : 472.2669; found 472.2663.

#### (Z)-N-Benzyl-N-(1-(4-methoxyphenyl)-6-(p-tolylthio)hex-1-en-1-yl)acetamide

(3d). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 58 mg, 60% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.28 – 7.13 (m, 9H), 7.07 (d, J = 7.9 Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H), 5.17 (t, J = 7.6 Hz, 1H), 4.47 (s, 2H), 3.83 (s, 3H), 2.77 (t, J = 7.1 Hz, 2H), 2.31 (s, 3H), 2.21 – 2.10 (m, 5H), 1.53 – 1.45 (m, 2H), 1.45 – 1.35 (m, 2H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  171.14, 159.69, 138.19, 137.54, 136.14, 132.65, 131.16, 130.02, 129.94, 129.67, 129.04, 127.22, 114.00, 55.35, 49.07, 34.07, 28.77, 28.44, 28.04, 27.78, 27.46, 22.19, 21.02.HRMS calcd for  $C_{29}H_{34}NO_{2}S^{+}$  [M+H] $^{+}$ : 460.2305; found 460.2306.

(*Z*)-*N*-Benzyl-*N*-(6-((4-chlorophenyl)thio)-1-(4-methoxyphenyl)hex-1-en-1-yl)acet amide (3e). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 65 mg, 67% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.31 – 7.25 (m, 5H), 7.23 – 7.16 (m, 6H), 6.93 (d, *J* = 8.5 Hz, 2H), 5.21 (t, *J* = 7.5 Hz, 1H), 4.50 (s, 2H), 3.87 (s, 3H), 2.81 (t, *J* = 7.1 Hz, 2H), 2.24 – 2.13 (m, 5H), 1.57 – 1.50 (m, 2H), 1.48 – 1.40 (m, 2H). <sup>13</sup>C NMR

(151 MHz, Chloroform-d)  $\delta$  170.83, 159.78, 138.52, 137.75, 135.21, 131.94, 130.88, 130.49, 130.01, 129.07, 128.29, 127.24, 114.07, 55.42, 49.06, 33.66, 29.78, 28.61, 28.50, 28.06, 22.34. HRMS calcd for  $C_{28}H_{31}CINO_2S^+$  [M+H]+: 480.1759; found 480.1757.

#### (Z)-N-Benzyl-N-(1-(2-chlorophenyl)-6-((4-fluorophenyl)thio)hex-1-en-1-yl)aceta

mide (3f). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 65 mg, 68% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 7.41 (d, J = 7.9 Hz, 1H), 7.29 – 7.17 (m, 9H), 7.08 (d, J = 7.6 Hz, 1H), 6.96 (t, J = 8.7 Hz, 2H), 5.48 (t, J = 7.6 Hz, 1H), 4.43 (s, 2H), 2.73 (t, J = 7.0 Hz, 2H), 2.33 (s, 3H), 1.94 (q, J = 7.4 Hz, 2H), 1.52 – 1.40 (m, 4H). <sup>13</sup>C NMR (126 MHz, Chloroform-d) δ 170.99, 161.71 (d, J = 246.96 Hz)137.65, 136.79, 133.99, 133.61, 132.62, 132.19(d, J = 7.56 Hz) 131.92, 130.35, 130.01, 128.44, 128.17, 127.00, 126.76,115.98(d, J = 21.42 Hz) 48.62, 34.65, 28.72, 28.21, 27.81, 22.59. <sup>19</sup>F NMR (470 MHz, Chloroform-d) δ -115.65. HRMS calcd for C<sub>27</sub>H<sub>28</sub>ClFNOS<sup>+</sup> [M+H]<sup>+</sup>: 468.1559; found 468.1560.

#### (Z)-N-Benzyl-N-(1-(2-chlorophenyl)-6-((4-chlorophenyl)thio)hex-1-en-1-yl)aceta

**mide (3g).** Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 60 mg, 65% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 7.44 (d, J = 7.9 Hz, 1H), 7.33 – 7.23 (m, 8H), 7.22 – 7.19 (m, 3H), 7.11 (d, 1H), 5.51 (t, J = 7.7 Hz, 1H), 4.46 (s, 2H), 2.79 (t, J = 6.9 Hz, 2H), 2.36 (s, 3H), 1.98 (q, J = 7.6 Hz, 2H), 1.53 (q, J = 7.3 Hz, 2H), 1.47 (q, J = 7.5 Hz, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-d) δ 171.02, 137.74, 136.94, 135.18, 132.60, 131.99, 130.51, 130.43, 130.09, 129.05, 128.51, 128.24, 127.07, 126.84, 60.47, 48.69, 33.61, 28.63, 28.25, 27.92, 22.65, 21.12, 14.28. HRMS calcd for  $C_{27}H_{28}Cl_2NOS^+$  [M+H]\*: 484.1263; found 484.1260.

#### (Z)-N-Benzyl-N-(6-((4-bromophenyl)thio)-1-(2-chlorophenyl)hex-1-en-1-yl)aceta

**mide (3h).** Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 60 mg, 58% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.41 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.30 (t, J = 7.7 Hz, 1H), 7.26 – 7.16 (m, 6H), 7.10 (dd, J = 12.9, 7.5 Hz, 3H), 5.49 (t, J = 7.7 Hz, 1H), 4.43 (s, 2H), 2.76 (t, J = 7.1 Hz, 2H), 2.34 (s, 3H), 1.95 (q, J = 7.4 Hz, 2H), 1.52 (p, J = 7.1 Hz, 2H), 1.44 (p, J = 7.4 Hz, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 170.92, 137.68, 136.89, 135.83, 133.98, 133.64, 132.48, 131.88, 130.59, 130.35, 130.00, 128.43, 128.16, 126.99, 126.76, 119.65, 48.62, 33.35, 29.70, 28.52, 28.16, 27.84, 22.56. HRMS calcd for C<sub>27</sub>H<sub>28</sub>BrClNOS<sup>+</sup> [M+H]<sup>+</sup>: 528.0758; found 528.0749.

#### (Z)-N-Benzyl-N-(6-((4-(tert-butyl)phenyl)thio)-1-(p-tolyl)hex-1-en-1-yl)acetamide

(3i). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 65 mg, 67% yield.  $^{1}$ H NMR (400 MHz, Chloroform-d)  $\delta$  7.30 – 7.16 (m, 11H), 7.12 (d, J = 7.9 Hz, 2H), 5.22 (t, J = 7.6 Hz, 1H), 4.47 (s, 2H), 2.78 (t, J = 7.1 Hz, 2H), 2.38 (s, 3H), 2.21 – 2.02 (m, 5H), 1.55 – 1.48 (m, 2H), 1.45 – 1.37 (m, 2H), 1.30 (s, 9H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  171.17, 149.26, 138.56, 138.54, 137.66, 132.90, 131.99, 131.76, 129.35, 129.31, 129.01, 128.56, 128.22, 127.17, 125.93, 49.00, 34.45, 33.76, 31.30, 28.80, 28.49, 28.07, 22.28, 21.28. HRMS calcd for  $C_{32}H_{40}NOS^{+}$  [M+H]<sup>+</sup>: 486.2825; found 486.2826.

(Z)-N-Benzyl-N-(6-((4-fluorophenyl)thio)-1-(p-tolyl)hex-1-en-1-yl)acetamide (3j).

Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 61 mg, 62% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.32 – 7.27 (m, 5H), 7.24 – 7.20 (m, 4H), 7.15 (d, J = 7.8 Hz, 2H), 7.00 (t, J = 8.6 Hz, 2H), 5.24 (t, J = 7.6 Hz, 1H), 4.50 (s, 2H), 2.78 (t, J = 7.2 Hz, 2H), 2.42 (s, 3H), 2.24 – 2.17 (m, 5H), 1.54 – 1.48 (m, 2H), 1.46 – 1.40 (m, 2H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  169.93, 160.72 (d, J =245 Hz), 137.62 (d, J =21.25 Hz),137.59, 136.60, 131.21, 131.15, 130.93, 130.61, 130.32, 128.31, 128.00, 127.53, 127.20, 126.17, 114.96 (d, J =7.5 Hz), 48.04, 33.71, 27.69, 27.35, 27.00, 21.24, 20.23. 19F NMR (470 MHz, Chloroform-d)  $\delta$  -115.84. HRMS calcd for C28H31FNOS+ [M+H]+: 448.2105; found 448.2108.

#### (Z)-N-Benzyl-N-(6-((4-methoxyphenyl)thio)-1-(p-tolyl)hex-1-en-1-yl)acetamide

(3k). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 64 mg, 65% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.33 – 7.26 (m, 5H), 7.24 – 7.19 (m, 4H), 7.15 (d, J = 7.8 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 5.24 (t, J = 7.6 Hz, 1H), 4.50 (s, 2H), 3.82 (s, 3H), 2.74 (t, J = 7.1 Hz, 2H), 2.42 (s, 3H), 2.26 – 2.15 (m, 5H), 1.51 – 1.45 (m, 2H), 1.45 – 1.39 (m, 2H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  169.74, 157.90, 137.61, 137.48, 136.70, 132.10, 131.04, 130.70, 128.27, 127.98, 127.54, 127.18, 126.12, 125.53, 113.54, 54.31, 48.00, 34.50, 27.85, 27.33, 27.03, 21.23, 20.23. HRMS calcd for  $C_{29}H_{34}NO_2S^+$  [M+H]+: 460.2305; found 460.2306.

#### (Z)-N-Benzyl-N-(6-((2,4-dimethylphenyl)thio)-1-(p-tolyl)hex-1-en-1-yl)acetamide

(31). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 63 mg, 65% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.28 – 7.22 (m, 3H), 7.20 – 7.16 (m, 4H), 7.12 (d, J = 7.9 Hz, 3H), 6.99 (d, J = 2.0 Hz, 1H), 6.93 (dd, J = 7.9, 2.0 Hz, 1H), 5.21 (t, J = 7.6 Hz, 1H), 4.47 (s, 2H), 2.73 (t, J = 7.1 Hz, 2H), 2.38 (s, 3H), 2.32 (s, 3H), 2.28 (s,

3H), 2.20 - 2.14 (m, 5H), 1.54 - 1.46 (m, 2H), 1.46 - 1.38 (m, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  170.83, 138.59, 138.53, 138.07, 137.70, 135.85, 132.01, 131.98, 131.74, 131.08, 129.31, 129.21, 129.01, 128.56, 128.22, 127.17, 127.10, 48.98, 33.28, 28.65, 28.58, 28.08, 22.30, 21.29, 20.89, 20.38. HRMS calcd for  $C_{30}H_{36}NOS^{+}$  [M+H]<sup>+</sup>: 458.2512; found 458.2513.

#### (Z)-N-Benzyl-N-(6-((4-isopropylphenyl)thio)-1-(p-tolyl)hex-1-en-1-yl)acetamide

(3m). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 69 mg, 75% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.30 – 7.28 (m, 2H), 7.27 – 7.24 (m, 3H), 7.24 – 7.20 (m, 4H), 7.18 – 7.14 (m, 4H), 5.25 (t, J = 7.6 Hz, 1H), 4.50 (s, 2H), 2.90 (p, J = 6.9 Hz, 1H), 2.81 (t, J = 7.2 Hz, 2H), 2.42 (s, 3H), 2.28 – 2.17 (m, 5H), 1.61 – 1.51 (m, 2H), 1.50 – 1.40 (m, 2H), 1.27 (d, J = 6.9 Hz, 6H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  170.74, 147.07, 138.67, 138.50, 137.73, 133.16, 132.08, 131.68, 129.85, 129.29, 129.01, 128.56, 128.20, 127.14, 127.03, 49.01, 33.97, 33.67, 28.80, 28.46, 28.04, 23.91, 22.25, 21.24. HRMS calcd for  $C_{31}H_{38}NOS^{+}$  [M+H]+: 472.2669; found 472.2666.

#### (Z)-N-Benzyl-N-(1-(3-bromophenyl)-6-(p-tolylthio)hex-1-en-1-yl)acetamide (3n).

Eluent petroleum ether/ethyl acetate (5:1). Colorless oil, 54 mg, 65% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.48 (d, J = 8.1 Hz, 1H), 7.32 (t, J = 1.8 Hz, 1H), 7.26 (dd, J = 6.6, 4.6 Hz, 3H), 7.20 (d, J = 8.2 Hz, 2H), 7.18 – 7.12 (m, 3H), 7.08 (d, J = 8.0 Hz, 2H), 5.30 (t, J = 7.7 Hz, 1H), 4.48 (s, 2H), 2.77 (t, J = 7.1 Hz, 2H), 2.31 (s, 3H), 2.19 – 2.11 (m, 5H), 1.54 – 1.47 (m, 2H), 1.44 – 1.38 (m, 2H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  170.70, 137.44, 137.33, 137.21, 136.22, 133.45, 132.54,

131.64, 131.41, 130.13, 130.08, 129.70, 128.98, 128.33, 127.36, 127.32, 122.79, 49.23, 34.07, 29.72, 28.74, 28.30, 28.04, 22.29, 21.03 HRMS calcd for C<sub>31</sub>H<sub>38</sub>NOS<sup>+</sup> [M+H]<sup>+</sup>: 508.1304; found 508.1310.

#### (Z)-N-Benzyl-N-(6-((3,5-dimethylphenyl)thio)-1-phenylhex-1-en-1-yl)acetamide

(3n). Eluent petroleum ether/ethyl acetate (5:1). Colorless, 51 mg, 60% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.36 (dd, J = 11.7, 7.0 Hz, 3H), 7.24 (dd, J = 15.0, 6.2 Hz, 5H), 7.18 (d, J = 6.5 Hz, 2H), 6.90 (s, 2H), 6.79 (s, 1H), 5.27 (t, J = 7.6 Hz, 1H), 4.47 (s, 2H), 2.79 (t, J = 7.1 Hz, 2H), 2.26 (s, 6H), 2.21 – 2.14 (m, 5H), 1.55 – 1.47 (m, 2H), 1.47 – 1.38 (m, 2H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  170.78, 138.68, 138.49, 137.63, 136.05, 135.00, 132.28, 129.03, 128.67, 128.63, 128.57, 128.26, 127.84, 127.22, 126.75, 49.04, 33.29, 28.73, 28.50, 28.07, 22.29, 21.26. HRMS calcd for  $C_{31}H_{38}NOS^{+}$  [M+H] $^{+}$ : 444.2356; found 444.2361.

#### (Z)-N-Benzyl-N-(1-(naphthalen-2-yl)-6-(p-tolylthio)hex-1-en-1-yl)acetamide (3p).

Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 64 mg, 65% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.89 – 7.79 (m, 3H), 7.67 (s, 1H), 7.56 – 7.49 (m, 2H), 7.33 (d, J = 8.5 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.22 – 7.16 (m, 4H), 7.06 (d, J = 7.8 Hz, 2H), 5.37 (t, J = 7.7 Hz, 1H), 4.53 (s, 2H), 2.78 (t, J = 6.9 Hz, 2H), 2.31 (s, 3H), 2.28 – 2.21 (m, 5H), 1.55 – 1.44 (m, 4H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  170.74, 147.07, 138.67, 138.50, 137.73, 133.16, 132.08, 131.68, 129.85, 129.29, 129.01, 128.56, 128.20, 127.14, 127.03, 49.01, 33.97, 33.67, 28.80, 28.46, 28.04, 23.91, 22.25, 21.24. HRMS calcd for  $C_{32}H_{34}NOS^{+}$  [M+H]+: 480.2356; found 480.2352.

#### (Z)-N-Benzyl-N-(1-(4-methoxyphenyl)-7-(p-tolylthio)hept-1-en-1-yl)acetamide

(3q). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 61 mg, 65% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.32 – 7.27 (m, 3H), 7.27 – 7.22 (m, 4H), 7.21 – 7.19 (m, 2H), 7.12 (d, J = 7.7 Hz, 2H), 6.94 (d, J = 8.1 Hz, 2H), 5.22 (t, J = 7.5 Hz, 1H), 4.51 (s, 2H), 3.88 (s, 3H), 2.83 (t, J = 7.3 Hz, 2H), 2.35 (s, 3H), 2.23 (s, 3H), 2.20 – 2.14 (m, 2H), 1.59 – 1.50 (m, 2H), 1.34 – 1.29 (m, 4H).  $^{13}$ C NMR (151 MHz, Chloroform-d)  $\delta$  138.21, 137.84, 136.09, 131.49, 130.03, 129.95, 129.74, 129.11, 128.71, 128.43, 128.28, 127.22, 126.52, 114.07, 55.43, 49.08, 34.32, 29.06, 28.45, 28.38, 22.37, 21.08. HRMS calcd for  $C_{30}H_{36}NO_{2}S^{+}$  [M+H]\*: 474.2461; found 474.2461.

(*Z*)-*N*-Benzyl-*N*-(1-phenyl-7-(*p*-tolylthio)hept-1-en-1-yl)acetamide (3r). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 61 mg, 67% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.45 – 7.38 (m, 3H), 7.31 – 7.25 (m, 6H), 7.25 – 7.22 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.31 (t, *J* = 7.7 Hz, 1H), 4.52 (s, 2H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.35 (s, 3H), 2.25 (s, 3H), 2.21 – 2.16 (m, 2H), 1.56 (t, *J* = 7.2 Hz, 2H), 1.35 – 1.30 (m, 4H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  170.77, 138.46, 137.68, 136.00, 135.06, 132.89, 132.64, 129.87, 129.64, 129.03, 128.64, 128.59, 128.50, 128.21, 127.16, 49.01, 34.20, 28.95, 28.34, 28.26, 22.28, 20.99. HRMS calcd for C<sub>29</sub>H<sub>34</sub>NOS<sup>+</sup> [M+H]<sup>+</sup>: 444.2356; found 444.2355.

#### (Z)-N-Benzyl-N-(1-(naphthalen-2-yl)-7-(p-tolylthio)hept-1-en-1-yl)acetamide (3s).

Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 65 mg, 64% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.90 – 7.79 (m, 3H), 7.66 (s, 1H), 7.55 – 7.50 (m, 2H), 7.34 – 7.24 (m, 4H), 7.23 – 7.15 (m, 4H), 7.05 (d, J = 7.9 Hz, 2H), 5.36 (t, J = 7.7 Hz, 1H), 4.52 (s, 2H), 2.77 (t, J = 6.9 Hz, 2H), 2.30 (s, 3H), 2.28 – 2.15 (m, 5H), 1.54 – 1.40 (m, 4H).  $^{13}$ C NMR (151 MHz, Chloroform-d)  $\delta$  170.96, 138.85, 137.71, 136.22, 133.22, 133.18, 132.68, 132.64, 132.49, 130.12, 129.74, 129.09, 128.43, 128.35, 128.30, 128.28, 127.78, 127.32, 126.83, 126.68, 126.05, 49.30, 34.15, 28.83, 28.48, 28.21, 22.49, 21.07. HRMS calcd for  $C_{33}H_{36}NOS^{+}$  [M+H] $^{+}$ : 494.2512; found 494.2509.

#### (Z)-N-Benzyl-N-(1-phenyl-6-(thiophen-2-ylthio)hex-1-en-1-yl)acetamide (3t).

Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 65 mg, 64% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  7.41 – 7.34 (m, 3H), 7.31 (d, J = 5.3 Hz, 1H), 7.28 – 7.22 (m, 5H), 7.20 – 7.15 (m, 2H), 7.05 (d, J = 2.2 Hz, 1H), 6.95 (dd, J = 5.4, 3.5 Hz, 1H), 5.26 (t, J = 7.7 Hz, 1H), 4.47 (s, 2H), 2.68 (t, J = 7.1 Hz, 2H), 2.22 – 2.11 (m, 5H), 1.52 – 1.45 (m, 2H), 1.43 – 1.36 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-d)  $\delta$  170.78, 138.70, 137.62, 134.97, 134.49, 133.48, 132.23, 129.15, 129.01, 128.66, 128.63, 128.58, 128.25, 127.53, 127.21, 49.04, 38.50, 28.89, 28.09, 28.01, 22.30. HRMS calcd for C<sub>25</sub>H<sub>28</sub>NOS<sub>2</sub>+ [M+H]+: 422.1607; found 477.1608.

(6,6-Bis(4-methoxyphenyl)hex-5-en-1-yl)(p-tolyl)sulfane (5a). Eluent petroleum ether. Yellow oil, 70 mg, 88% yield.  $^1$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.24 – 7.20 (m, 2H), 7.14 – 7.11 (m, 2H), 7.09 – 7.05 (m, 4H), 6.90 – 6.87 (m, 2H), 6.81 – 6.78 (m, 2H), 5.90 (t, J = 7.4 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.82 (t, J = 7.1 Hz, 2H), 2.31 (s, 3H), 2.12 (q, J = 7.2 Hz, 2H), 1.65 – 1.59 (m, 2H), 1.58 – 1.54 (m, 2H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  158.68, 158.47, 140.95, 135.91, 135.88, 132.95, 132.71, 131.00, 129.96, 129.62, 128.36, 127.57, 113.51, 113.43, 55.28, 55.21, 29.13, 29.05, 28.67, 21.00. HRMS calcd for  $C_{27}H_{31}O_{2}S^{+}$  [M+H]+: 419.2039; found 419.2037.

(6,6-Bis(4-methoxyphenyl)hex-5-en-1-yl)(4-methoxyphenyl)sulfane (5b). Eluent petroleum ether. Yellow oil, 55 mg, 65% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.37 – 7.32 (m, 2H), 7.18 – 7.14 (m, 2H), 7.12 – 7.08 (m, 2H), 6.95 – 6.90 (m, 2H), 6.88 – 6.81 (m, 4H), 5.93 (t, J = 7.4 Hz, 1H), 3.87 (s, 3H), 3.84 – 3.81 (m, 6H), 2.80 (t, J = 6.9 Hz, 2H), 2.15 (q, J = 7.0 Hz, 2H), 1.65 – 1.55 (m,4H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  158.79, 158.67, 158.46, 140.91, 135.88, 133.10, 132.71, 131.01, 128.36, 127.62, 126.73, 114.51, 113.51, 113.43, 55.32, 55.28, 55.22, 35.60, 29.15, 28.95, 28.75. HRMS calcd for  $C_{27}H_{31}O_{3}S^{+}$  [M+H] $^{+}$ : 435.1988; found 435.1984.

(6,6-Bis(4-methoxyphenyl)hex-5-en-1-yl)(4-(*tert*-butyl)phenyl)sulfane (5c). Eluent petroleum ether. Colorless oil, 62 mg, 76% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.34 – 7.28 (m, 4H), 7.20 – 7.17 (m, 2H), 7.13 – 7.10 (m, 2H), 6.95 – 6.92 (m, 2H), 6.85 – 6.83 (m, 2H), 5.96 (t, J = 7.4 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.88 (t, J = 7.2 Hz, 2H), 2.18 (q, J = 7.2 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.62 (q, J = 7.1 Hz, 2H), 1.34 (s, 9H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  158.70, 158.49, 149.07, 140.99, 135.87, 133.21, 132.72, 132.25, 131.01, 129.29, 128.36, 127.56, 125.88, 113.53, 113.45, 55.27, 55.21, 33.85, 31.30, 29.13, 29.10, 28.73. HRMS calcd for  $C_{30}H_{37}O_{2}S^{+}$  [M+H] $^{+}$ : 461.2509; found 461.2505.

(6,6-Bis(4-methoxyphenyl)hex-5-en-1-yl)(4-isopropylphenyl)sulfane (5d). Eluent petroleum ether. Colorless oil, 64 mg, 78% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.30 – 7.27 (m, 2H), 7.20 – 7.15 (m, 4H), 7.12 – 7.08 (m, 2H), 6.95 – 6.91 (m, 2H), 6.85 – 6.82 (m, 2H), 5.95 (t, J = 7.4 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.94 – 2.84 (m, 3H), 2.17 (q, J = 7.3 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.64 – 1.58 (m, 2H), 1.28 (s, 3H), 1.26 (s, 3H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  158.68, 158.47, 146.86, 140.95, 135.87, 133.40, 132.71, 131.01, 129.74, 128.35, 127.57, 127.00, 113.51, 113.43, 55.27, 55.21, 34.01, 33.67, 29.13, 29.08, 28.71, 23.93. HRMS calcd for  $C_{29}H_{35}O_{2}S^{+}$  [M+H]+: 447.2352; found 447.2347.

(6,6-Bis(4-methoxyphenyl)hex-5-en-1-yl)(2,4-dimethylphenyl)sulfane (5e). Eluent petroleum ether. Yellow oil, 59 mg, 70% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  7.1 (d, J = 8.7 Hz, 2H), 7.1 (d, J = 8.6 Hz, 1H), 7.0 – 7.0 (m, 2H), 7.0 – 6.9 (m, 2H), 6.9 (d, J = 8.5 Hz, 2H), 6.8 (d, J = 8.6 Hz, 2H), 5.9 (t, J = 7.4 Hz, 1H), 3.8 (s, 3H), 3.8

(s, 3H), 2.8 (t, J = 7.1 Hz, 2H), 2.4 (s, 3H), 2.3 (s, 3H), 2.1 (q, J = 7.2 Hz, 2H), 1.7 – 1.6 (m, 2H), 1.6 – 1.6 (m, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-d)  $\delta$  162.88, 158.69, 158.48, 140.97, 137.98, 135.88, 135.63, 132.72, 132.25, 131.00, 129.15, 128.36, 127.57, 127.08, 113.53, 113.49, 113.44, 55.27, 55.20, 33.39, 29.19, 28.58, 20.86, 20.38. HRMS calcd for  $C_{28}H_{33}O_{2}S^{+}$  [M+H]<sup>+</sup>: 433.2196; found 433.2190.

(6,6-Bis(4-methoxyphenyl)hex-5-en-1-yl)(4-chlorophenyl)sulfane (5f). Eluent petroleum ether. Colorless oil, 57 mg, 68% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.25 (d, J = 2.4 Hz, 4H), 7.15 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.92 (t, J = 7.4 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.85 (t, J = 7.1 Hz, 2H), 2.16 (q, J = 7.2 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.62 – 1.57 (m, 2H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  158.71, 158.49, 141.10, 135.78, 135.38, 132.64, 130.98, 130.36, 128.94, 128.34, 127.34, 113.51, 113.44, 58.49, 55.29, 55.21, 33.62, 29.01, 28.96, 28.35, 18.44. HRMS calcd for  $C_{26}H_{28}ClO_{2}S^{+}$  [M+H] $^{+}$ : 439.1493; found 439.1491.

(6,6-Bis(4-methoxyphenyl)hex-5-en-1-yl)(4-bromophenyl)sulfane (5g). Eluent petroleum ether. Yellow oil, 52 mg, 61% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.36 (d, J = 8.5 Hz, 2H), 7.13 (dd, J = 11.8, 8.7 Hz, 4H), 7.06 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 5.88 (t, J = 7.4 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.81 (t, J = 7.2 Hz, 2H), 2.13 (q, J = 7.3 Hz, 2H), 1.64 – 1.59 (m, 2H), 1.58 – 1.54 (m, 2H).  $^{13}$ C NMR (101 MHz, Chloroform-d)  $\delta$  158.73, 158.50, 141.13, 136.13, 132.65, 132.26, 131.86, 130.99, 130.51, 128.36, 127.33, 119.46,

113.53, 113.46, 55.30, 55.23, 33.43, 29.01, 28.96, 28.32. HRMS calcd for  $C_{26}H_{28}BrO_2S^+$  [M+H]<sup>+</sup>: 483.0988; found 483.0977.

(6,6-Bis(4-methoxyphenyl)hex-5-en-1-yl)(3,5-dimethylphenyl)sulfane (5h). Eluent petroleum ether. Yellow oil, 57 mg, 67% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.14 – 7.10 (m, 2H), 7.08 – 7.05 (m, 2H), 6.92 (s, 2H), 6.89 – 6.86 (m, 2H), 6.81 – 6.77 (m, 3H), 5.90 (t, J = 7.4 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 2.84 (t, J = 7.2 Hz, 2H), 2.26 (s, 7H), 2.13 (q, J = 7.3 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.60 – 1.54 (m, 2H).  $^{13}$ C NMR (101 MHz, Chloroform-d)  $\delta$  158.68, 158.48, 140.96, 138.42, 136.37, 135.89, 132.72, 131.01, 128.36, 127.66, 127.58, 126.67, 113.52, 113.43, 55.29, 55.21, 33.39, 29.18, 29.16, 28.65, 21.24. HRMS calcd for  $C_{28}H_{33}O_{2}S^{+}$  [M+H]+: 433.2196; found433.2198.

(7,7-Bis(4-methoxyphenyl)hept-6-en-1-yl)(4-(*tert*-butyl)phenyl)sulfane (5i). Eluent petroleum ether. Yellow oil, 56 mg, 65% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.33 (d, J = 8.3 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.18 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.95 (t, J = 7.4 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 2.90 (t, J = 7.4 Hz, 2H), 2.14 (q, J = 6.8 Hz, 2H), 1.64 (q, J = 7.2 Hz, 2H), 1.51 – 1.44 (m, 4H), 1.34 (s, 9H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  157.65, 157.45, 148.01, 139.70, 134.96, 132.34, 131.79, 129.99, 128.15, 127.32, 126.92, 124.85, 112.50, 112.43, 54.26, 54.20, 33.40, 32.98, 30.27, 28.61, 28.57, 28.15, 27.44. HRMS calcd for  $C_{31}H_{39}O_{2}S^{+}$  [M+H] $^{+}$ : 475.2665; found 475.2657.

(6,6-Bis(4-chlorophenyl)hex-5-en-1-yl)(p-tolyl)sulfane (5j). Eluent petroleum ether. Colorless oil, 66 mg, 78% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.38 – 7.34 (m, 2H), 7.27 – 7.23 (m, 4H), 7.14 – 7.07 (m, 6H), 6.06 (t, J = 7.5 Hz, 1H), 2.85 (t, J = 6.8 Hz, 2H), 2.36 (s, 3H), 2.13 (q, J = 7.1 Hz, 2H), 1.66 – 1.57 (m, 5H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  140.75, 139.86, 138.08, 136.09, 133.10, 132.93, 132.74, 131.21, 130.56, 130.08, 129.67, 128.59, 128.45, 128.31, 34.17, 29.19, 28.68, 28.61, 21.01. HRMS calcd for  $C_{25}H_{25}Cl_2S^+$  [M+H]+: 427.1049; found 427.1044.

(6,6-Bis(4-chlorophenyl)hex-5-en-1-yl)(4-methoxyphenyl)sulfane (5k). Eluent petroleum ether. Yellow oil, 60 mg, 68% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  9.90 – 9.83 (m, 4H), 9.78 – 9.73 (m, 2H), 9.64 – 9.57 (m, 4H), 9.40 – 9.35 (m, 2H), 8.56 (t, J = 7.5 Hz, 1H), 6.33 (s, 3H), 5.35 – 5.23 (m, 2H), 4.67 – 4.58 (m, 2H), 4.13 – 4.06 (m, 4H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  158.90, 140.76, 139.84, 138.09, 133.21, 133.09, 132.92, 131.21, 130.60, 128.58, 128.44, 128.32, 126.54, 114.55, 55.32, 35.58, 29.18, 28.68, 28.57. HRMS calcd for  $C_{25}H_{25}Cl_{2}OS^{+}$  [M+H]<sup>+</sup>: 443.0998; found 443.0998.

(6,6-Bis(4-chlorophenyl)hex-5-en-1-yl)(4-(*tert*-butyl)phenyl)sulfane (5l) . Eluent petroleum ether. Colorless oil, 64 mg, 74% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  7.38 – 7.32 (m, 4H), 7.30 – 7.25 (m, 4H), 7.15 – 7.08 (m, 4H), 6.08 (t, J = 7.5 Hz,

1H), 2.87 (t, J = 6.9 Hz, 2H), 2.15 (q, J = 7.2 Hz, 2H), 1.70 – 1.59 (m, 4H), 1.34 (s, 9H). <sup>13</sup>C NMR (126 MHz, Chloroform-d)  $\delta$  149.26, 140.74, 139.88, 138.09, 133.11, 133.00, 132.94, 131.21, 130.55, 129.43, 128.59, 128.44, 128.32, 125.92, 34.44, 33.86, 31.29, 29.19, 28.72, 28.66. HRMS calcd for  $C_{28}H_{31}C_{12}S^{+}$  [M+H]<sup>+</sup>: 469.1518; found 469.1519.

(6,6-Bis(4-chlorophenyl)hex-5-en-1-yl)(4-isopropylphenyl)sulfane (5m). Eluent petroleum ether. Colorless oil, 60 mg, 68% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.36 (d, J = 7.9 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.17 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 6.07 (t, J = 7.4 Hz, 1H), 2.95 – 2.89 (m, 1H), 2.86 (t, J = 6.9 Hz, 2H), 2.14 (q, J = 7.1 Hz, 2H), 1.66 – 1.58 (m, 4H), 1.27 (d, J = 7.2 Hz, 6H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  147.05, 140.75, 139.86, 138.08, 133.18, 133.10, 132.93, 131.21, 130.55, 129.88, 128.58, 128.44, 128.32, 127.04, 34.02, 33.68, 29.19, 28.71, 28.65, 23.93. HRMS calcd for  $C_{27}H_{29}Cl_2S^+$  [M+H] $^+$ : 455.1362; found 455.1363.

(6,6-Bis(4-chlorophenyl)hex-5-en-1-yl)(2,4-dimethylphenyl)sulfane (5n). Eluent petroleum ether. Yellow oil, 63 mg, 72% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.38 – 7.33 (m, 2H), 7.27 – 7.22 (m, 2H), 7.18 (d, J = 7.9 Hz, 1H), 7.13 – 7.07 (m, 4H), 7.04 – 7.02 (m, 1H), 6.98 (dd, J = 7.9, 2.0 Hz, 1H), 6.06 (t, J = 7.4 Hz, 1H), 2.81 (t, J = 6.8 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 2.14 (q, J = 7.1 Hz, 2H), 1.65 – 1.59 (m, 4H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  140.75, 139.87, 138.11, 138.08, 135.83, 133.10, 132.93, 132.06, 131.19, 131.06, 130.55, 129.32, 128.59, 128.44, 128.31, 127.11, 33.39, 29.23, 28.82, 28.53, 20.87, 20.38. HRMS calcd for  $C_{26}$ H<sub>27</sub>Cl<sub>2</sub>S<sup>+</sup>

[M+H]+: 441.1205; found 441.1205.

(6,6-Bis(4-chlorophenyl)hex-5-en-1-yl)(4-chlorophenyl)sulfane (50). Eluent petroleum ether. Colorless oil, 62 mg, 71% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.36 – 7.31 (m, 2H), 7.26 – 7.18 (m, 6H), 7.11 – 7.03 (m, 4H), 6.02 (t, J = 7.5 Hz, 1H), 2.83 (t, J = 7.0 Hz, 2H), 2.11 (q, J = 7.2 Hz, 2H), 1.63 – 1.54 (m, 4H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  141.73, 140.84, 139.06, 137.07, 134.08, 133.72, 132.19, 131.54, 131.06, 130.65, 129.57, 129.43, 129.30, 35.15, 30.17, 29.66, 29.59, 22.00. HRMS calcd for  $C_{24}H_{22}Cl_{3}S^{+}$  [M+H] $^{+}$ : 447.0502; found 447.0502.

(6,6-Bis(4-chlorophenyl)hex-5-en-1-yl)(naphthalen-2-yl)sulfane (5p). Eluent petroleum ether. Yellow oil, 63 mg, 70% yield.  $^{1}$ H NMR (500 MHz, Chloroform-d)  $\delta$  7.8 (d, J = 7.8 Hz, 1H), 7.8 – 7.7 (m, 3H), 7.6 – 7.4 (m, 3H), 7.4 – 7.3 (m, 2H), 7.2 (d, J = 8.5 Hz, 2H), 7.1 – 7.1 (m, 4H), 6.1 (t, J = 7.5 Hz, 1H), 3.0 (t, J = 7.1 Hz, 2H), 2.2 (q, J = 7.3 Hz, 2H), 1.8 – 1.7 (m, 2H), 1.7 (q, J = 7.4 Hz, 2H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  140.72, 139.98, 138.08, 134.19, 133.83, 133.14, 132.96, 131.76, 131.20, 130.45, 128.61, 128.43, 128.38, 128.33, 127.76, 127.46, 127.04, 126.92, 126.59, 125.64, 33.39, 29.20, 28.76, 28.51. HRMS calcd for  $C_{28}H_{25}C_{12}S^{+}$  [M+H] $^{+}$ : 463.1049; found 463.1043.

(7,7-Bis(4-chlorophenyl)hept-6-en-1-yl)(p-tolyl)sulfane (5q). Eluent petroleum

ether. Yellow oil, 58 mg, 65% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  7.4 – 7.3 (m, 2H), 7.3 – 7.2 (m, 4H), 7.2 – 7.1 (m, 3H), 7.1 – 7.1 (m, 3H), 6.1 (t, J = 7.4 Hz, 1H), 2.9 (t, J = 7.3 Hz, 2H), 2.3 (s, 3H), 2.2 – 2.1 (m, 2H), 1.6 – 1.6 (m, 2H), 1.5 – 1.4 (m, 4H). <sup>13</sup>C NMR (126 MHz, Chloroform-d)  $\delta$  140.83, 139.61, 138.16, 135.95, 132.88, 131.21, 130.90, 129.87, 129.64, 129.20, 128.64, 128.56, 128.43, 128.30, 34.27, 29.61, 29.31, 29.05, 28.32, 20.98. HRMS calcd for C<sub>26</sub>H<sub>27</sub>Cl<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 441.1205; found 441.1204.

#### (S)-(6,6-Bis(4-chlorophenyl)-4-methylhex-5-en-1-yl)(4-(tert-butyl)phenyl)sulfane

(5r). Eluent petroleum ether. Colorless oil, 62 mg, 74% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  7.3 (d, J = 8.2 Hz, 2H), 7.3 (d, J = 8.3 Hz, 2H), 7.2 (d, J = 7.0 Hz, 4H), 7.1 (d, J = 8.5 Hz, 2H), 7.1 (d, J = 8.5 Hz, 2H), 5.9 (d, J = 10.3 Hz, 1H), 2.8 – 2.8 (m, 2H), 2.3 – 2.2 (m, 1H), 1.7 – 1.6 (m, 2H), 1.5 – 1.5 (m, 2H), 1.3 (s, 9H), 1.0 (d, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-d)  $\delta$  149.84, 141.08, 139.18, 138.91, 137.16, 133.63, 133.54, 133.52, 132.87, 131.62, 130.06, 129.23, 128.89, 126.49, 36.97, 35.01, 34.64, 34.04, 31.86, 27.71, 21.90. HRMS calcd for C<sub>29</sub>H<sub>33</sub>Cl<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 483.1675; found 483.1685.

(*S*)-(6,6-Bis(4-methoxyphenyl)-4-methylhex-5-en-1-yl)(p-tolyl)sulfane (5s). Eluent petroleum ether. Colorless oil, 65 mg, 68% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  7.2 (d, J = 8.1 Hz, 2H), 7.2 – 7.1 (m, 2H), 7.1 (dd, J = 8.4, 6.6 Hz, 4H), 6.9 – 6.9 (m, 2H), 6.8 (d, J = 8.7 Hz, 2H), 5.7 (d, J = 10.2 Hz, 1H), 3.9 (s, 3H), 3.8 (s, 3H), 2.8 –

2.7 (m, 2H), 2.3 (s, 3H), 1.7 – 1.5 (m, 3H), 1.5 – 1.4 (m, 2H), 1.1 (d, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-d)  $\delta$  158.71, 158.45, 139.71, 135.83, 135.68, 133.84, 133.06, 133.01, 130.79, 129.95, 129.58, 128.22, 113.58, 113.54, 113.44, 55.29, 55.18, 36.66, 34.37, 33.23, 27.07, 21.59, 20.99. HRMS calcd for  $C_{28}H_{33}O_{2}S^{+}$  [M+H]<sup>+</sup>: 433.2196; found 433.2198.

(*S*)-(6,6-Bis(4-methoxyphenyl)-4-methylhex-5-en-1-yl)(4-(*tert*-butyl)phenyl)sulfan e (5t). Eluent petroleum ether. Colorless oil, 66 mg, 71% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  7.3 (d, J = 5.4 Hz, 2H), 7.2 (d, J = 8.7 Hz, 2H), 7.1 (d, J = 8.7 Hz, 2H), 7.0 (d, J = 8.7 Hz, 2H), 6.9 (d, J = 8.6 Hz, 2H), 6.8 (d, J = 8.8 Hz, 2H), 5.7 (d, J = 10.1 Hz, 1H), 3.8 (s, 3H), 3.8 (s, 3H), 2.8 – 2.7 (m, 2H), 2.4 – 2.3 (m, 1H), 1.7 – 1.6 (m, 2H), 1.5 – 1.4 (m, 2H), 1.3 (s, 9H), 1.0 (d, J = 6.5 Hz, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-d)  $\delta$  149.34, 140.58, 138.67, 138.41, 136.66, 133.13, 133.04, 133.01, 132.37, 131.33, 131.12, 130.78, 129.56, 128.72, 128.39, 125.98, 36.47, 34.51, 34.13, 33.53, 31.36, 27.21, 21.40. HRMS calcd for C<sub>31</sub>H<sub>39</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 475.2665; found 475.2669.

(*S*)-(4-(*tert*-Butyl)phenyl)(4-methyl-6,6-diphenylhex-5-en-1-yl)sulfane (5u). Eluent petroleum ether. Colorless oil, 64 mg, 68% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.4 – 7.4 (m, 2H), 7.4 – 7.3 (m, 2H), 7.3 – 7.2 (m, 8H), 7.2 – 7.2 (m, 2H), 5.9 (d, J = 10.1 Hz, 1H), 2.9 – 2.7 (m, 2H), 2.4 – 2.3 (m, 1H), 1.7 – 1.6 (m, 2H), 1.5 – 1.5 (m, 2H), 1.3 (s, 9H), 1.1 (d, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  142.75, 142.02, 140.20, 138.06, 135.70, 132.24, 131.05, 129.93, 129.48, 128.20, 128.10, 127.24, 127.11, 126.93, 126.87, 33.44, 29.22, 29.07, 28.61, 20.89, 20.41.

HRMS calcd for  $C_{29}H_{35}S^{+}$  [M+H]<sup>+</sup>: 415.2454; found 415.2449.

(*E*)-(4-Methoxyphenyl)(6-phenylnon-5-en-1-yl)sulfane (5v). Eluent petroleum ether. Colorless oil, 66 mg, 69% yield.  $^{1}$ H NMR (600 MHz, Chloroform-*d*) δ 7.3 – 7.3 (m, 4H), 7.2 – 7.2 (m, 1H), 7.1 – 7.1 (m, 2H), 6.8 – 6.8 (m, 2H), 5.5 – 5.3 (m, 1H), 3.8 (s, 3H), 2.7 (dt, J = 28.1, 7.4 Hz, 2H), 2.3 – 2.3 (m, 2H), 2.0 – 1.9 (m, 2H), 1.6 – 1.5 (m, 2H), 1.5 – 1.3 (m, 2H), 1.3 – 1.3 (m, 2H), 0.9 (dt, J = 37.1, 7.4 Hz, 3H).  $^{13}$ C NMR (151 MHz, Chloroform-*d*) δ 158.81, 141.39, 140.19, 133.54, 132.64, 129.63, 128.96, 128.78, 128.42, 128.01, 127.67, 126.87, 126.44, 115.00, 114.97, 114.12, 55.11, 35.83, 28.80, 28.33, 27.68, 22.30, 21.25, 14.82. HRMS calcd for  $C_{22}H_{28}NaOS^{+}$  [M+Na]<sup>+</sup>: 363.1753; found 363.1755.

(*E*)-(4-Chlorophenyl)(6-phenylnon-5-en-1-yl)sulfane (5w). Eluent petroleum ether. Colorless oil, 67 mg, 71% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.3 – 7.3 (m, 2H), 7.3 – 7.2 (m, 5H), 7.1 – 7.1 (m, 2H), 5.4 (dt, J = 14.6, 7.4 Hz, 1H), 2.8 (dt, J = 27.7, 7.5 Hz, 2H), 2.3 – 2.2 (m, 2H), 1.9 (q, J = 8.0 Hz, 2H), 1.6 – 1.5 (m, 2H), 1.4 (dt, J = 26.0, 7.6 Hz, 2H), 1.3 – 1.3 (m, 2H), 0.9 – 0.8 (m, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 141.62, 141.45, 141.33, 140.10, 135.60, 135.53, 131.70, 131.67, 130.39, 130.28, 129.32, 129.01, 128.48, 128.07, 126.64, 126.45, 41.49, 39.03, 33.85, 33.71, 29.09, 28.87, 28.41, 28.27, 28.22, 27.65, 22.31, 21.25, 14.82, 13.70, 1.12. HRMS calcd for C<sub>21</sub>H<sub>26</sub>ClS<sup>+</sup>[M+H]<sup>+</sup>: 345.1438; found 345.1436.

(8*R*,9*S*,14*S*)-2-((6,6-Diphenylhex-5-en-1-yl)thio)-3-methoxy-8,9,13,14-tetramethyl -6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (5*x*). Eluent petroleum ether/ethyl acetate (10:1). Yellow oil, 64 mg, 54% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.4 (t, J = 7.3 Hz, 2H), 7.3 (d, J = 6.9 Hz, 1H), 7.3 – 7.3 (m, 2H), 7.3 – 7.2 (m, 4H), 7.2 (d, J = 7.0 Hz, 2H), 6.6 (s, 1H), 6.1 (t, J = 7.4 Hz, 1H), 3.9 (s, 3H), 2.9 – 2.9 (m, 2H), 2.8 (q, J = 6.5 Hz, 2H), 2.5 (dd, J = 19.1, 8.6 Hz, 1H), 2.4 – 2.4 (m, 1H), 2.2 (dd, J = 8.3, 5.4 Hz, 2H), 2.1 – 2.0 (m, 2H), 2.0 – 2.0 (m, 1H), 1.7 – 1.6 (m, 6H), 1.6 – 1.5 (m, 4H), 1.3 – 1.3 (m, 2H), 0.9 (s, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 220.92, 156.06, 142.80, 141.97, 140.27, 136.12, 132.27, 129.98, 129.61, 128.28, 128.23, 128.16, 127.27, 126.95, 126.91, 121.38, 111.13, 55.90, 50.44, 48.07, 44.03, 38.38, 35.94, 32.83, 31.64, 29.63, 29.34, 29.14, 28.74, 26.59, 26.05, 21.66, 13.94. HRMS calcd for C<sub>40</sub>H<sub>49</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 593.3448; found 593.3447.

*N*-Benzyl-*N*-((*Z*)-6-(((8*R*,9*S*,14*S*)-3-Methoxy-8,9,13,14-tetramethyl-17-oxo-7,8,9,1 1,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)thio)-1-phenyl hex-1-en-1-yl)acetamide (5y). Eluent petroleum ether/ethyl acetate (3:1). Yellow oil, 59 mg, 44% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.4 – 7.4 (m, 3H), 7.3 – 7.2 (m, 6H), 7.2 (d, J = 6.5 Hz, 2H), 6.6 (s, 1H), 5.3 (t, J = 7.6 Hz, 1H), 4.5 (s, 2H), 3.8 (s, 3H), 2.9 – 2.9 (m, 2H), 2.8 – 2.7 (m, 2H), 2.5 (dd, J = 19.0, 8.7 Hz, 1H), 2.4 – 2.3 (m, 1H), 2.2 – 2.2 (m, 5H), 2.1 – 2.0 (m, 2H), 2.0 – 1.9 (m, 1H), 1.6 – 1.5 (m, 8H), 1.3 – 1.2 (m, 4H), 0.9 (s, 3H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 220.97, 170.91, 156.09, 138.65, 137.65, 136.39, 135.03, 132.46, 132.28, 129.07, 128.73, 128.68, 128.63, 128.42, 128.32, 127.28, 121.02, 111.17, 55.89, 50.41, 49.13, 48.06, 44.01, 38.35, 35.95, 32.70, 31.64, 29.79, 29.64, 28.75, 28.61, 28.21, 26.56, 26.06, 22.35, 21.65, 13.95. HRMS calcd for C<sub>43</sub>H<sub>54</sub>NO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 664.3819; found 664.3817.

(*Z*)-*N*-Benzyl-*N*-(1-phenyl-6-(*p*-tolylsulfinyl)hex-1-en-1-yl)acetamide (6). Eluent petroleum ether/ethyl acetate (2:1). Colorless oil, 54 mg, 61% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.5 (d, J = 8.0 Hz, 2H), 7.4 – 7.4 (m, 3H), 7.3 (d, J = 8.0 Hz, 2H), 7.3 – 7.2 (m, 5H), 7.2 (d, J = 7.3 Hz, 2H), 5.3 (t, J = 7.6 Hz, 1H), 4.5 (s, 2H), 2.7 (tt, J = 10.6, 4.8 Hz, 2H), 2.4 (s, 3H), 2.2 – 2.1 (m, 5H), 1.6 – 1.3 (m, 4H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*)  $\delta$  170.75, 141.60, 140.55, 139.05, 137.66, 134.90, 131.68, 130.02, 129.06, 128.75, 128.70, 128.33, 127.29, 124.09, 56.82, 49.09, 29.78, 28.52, 28.16, 22.35, 21.75, 21.50. HRMS calcd for C<sub>28</sub>H<sub>32</sub>NO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 446.2148; found 446.2150.

(*Z*)-*N*-Benzyl-*N*-(1-phenyl-6-tosylhex-1-en-1-yl)acetamide (7). Eluent petroleum ether/ethyl acetate (3:1). Colorless oil, 62 mg, 74% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.7 (d, J = 7.7 Hz, 2H), 7.4 (p, J = 6.8 Hz, 3H), 7.4 (d, J = 8.0 Hz, 2H), 7.3 – 7.2 (m, 5H), 7.2 (d, J = 7.2 Hz, 2H), 5.2 (t, J = 7.6 Hz, 1H), 4.5 (s, 2H), 3.0 (t, 2H), 2.5 (s, 3H), 2.2 – 2.1 (m, 5H), 1.7 – 1.6 (m, 2H), 1.4 – 1.3 (m, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*)  $\delta$  170.86, 144.84, 139.20, 137.57, 136.19, 134.81, 131.40, 130.01, 129.05, 128.84, 128.79, 128.69, 128.34, 128.11, 127.33, 56.03, 49.17, 28.11, 28.02, 22.48, 22.33, 21.72. HRMS calcd for C<sub>28</sub>H<sub>32</sub>NO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 462.2097; found 462.2097.

**1-Phenyl-6-(***p***-tolylthio)hexan-1-one (8)**. Eluent petroleum ether. Colorless oil, 61 mg, 79% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  8.0 (d, J = 7.2 Hz, 2H), 7.6 (t, J

= 7.4 Hz, 1H), 7.5 (t, J = 7.7 Hz, 2H), 7.3 (d, J = 8.4 Hz, 2H), 7.1 (d, J = 7.9 Hz, 2H), 3.0 (t, J = 7.3 Hz, 2H), 2.9 (t, J = 7.3 Hz, 2H), 2.3 (s, 3H), 1.8 (p, J = 7.4 Hz, 2H), 1.7 – 1.7 (m, 2H), 1.5 (tt, J = 10.1, 6.1 Hz, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-d)  $\delta$  200.31, 137.09, 136.08, 133.06, 132.93, 130.06, 129.75, 128.68, 128.13, 38.44, 34.29, 29.15, 28.48, 23.84, 21.10. HRMS calcd for C<sub>19</sub>H<sub>23</sub>OS<sup>+</sup> [M+H]<sup>+</sup>: 299.1464; found 299.1463.

(*Z*)-*N*-Benzyl-*N*-(6-(4-methylphenylsulfonimidoyl)-1-phenylhex-1-en-1-yl)acetami de (9). Eluent petroleum ether/ethyl acetate (1:1). Colorless oil, 56 mg, 65% yield.  $^{1}$ H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.8 – 7.8 (m, 2H), 7.4 – 7.3 (m, 3H), 7.3 (d, *J* = 7.9 Hz, 2H), 7.3 – 7.2 (m, 3H), 7.2 – 7.2 (m, 2H), 7.2 – 7.1 (m, 2H), 5.2 (t, *J* = 7.6 Hz, 1H), 4.4 (s, 2H), 3.1 – 2.9 (m, 2H), 2.4 (s, 3H), 2.2 – 2.1 (m, 5H), 1.6 – 1.5 (m, 2H), 1.3 – 1.3 (m, 2H), 1.2 (s, 1H).  $^{113}$ C NMR (151 MHz, Chloroform-*d*)  $\delta$  170.74, 144.14, 139.13, 138.93, 137.61, 134.84, 131.44, 129.93, 129.03, 128.78, 128.75, 128.68, 128.48, 128.31, 127.28, 57.21, 49.12, 28.10, 28.07, 22.94, 22.33, 21.61. HRMS calcd

for C<sub>28</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 461.2257; found 461.2256.

**2,2,6,6-Tetramethyl-1-(4-(***p***-tolylthio)butoxy)piperidine** (10). Eluent petroleum ether. Colorless oil, 51 mg, 55% yield. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.25 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 3.73 (t, J = 6.2 Hz, 2H), 2.90 (t, J = 7.2 Hz, 2H), 2.30 (s, 3H), 1.75 – 1.68 (m, 2H), 1.67 – 1.60 (m, 2H), 1.58 – 1.48 (m, 1H), 1.46 – 1.38 (m, 4H), 1.33 – 1.26 (m, 1H), 1.12 (s, 6H), 1.07 (s, 6H). HRMS calcd for  $C_{20}H_{34}NOS^{+}$  [M+H]<sup>+</sup>: 336.2356; found 336.2359.

#### (Z)-N-Benzyl-N-(4-(naphthalen-1-yl)-1-phenylbut-1-en-1-yl)acetamide (12).

Eluent petroleum ether/ethyl acetate (5:1). Colorless oil, 33 mg, 41% yield.  $^{1}$ H NMR (600 MHz, Chloroform-d)  $\delta$  7.87 – 7.81 (m, 2H), 7.71 (d, J = 8.2 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.31 (dt, J = 8.1, 4.6 Hz, 7H), 7.22 – 7.17 (m, 2H), 7.12 – 7.08 (m, 2H), 7.04 (d, J = 7.0 Hz, 1H), 5.44 (t, J = 7.7 Hz, 1H), 4.48 (s, 2H), 3.07 (t, J = 7.4 Hz, 2H), 2.68 – 2.60 (m, 2H), 2.12 (s, 3H).  $^{13}$ C NMR (126 MHz, Chloroform-d)  $\delta$  170.92, 139.30, 137.71, 136.69, 134.92, 133.91, 131.67, 131.50, 128.98, 128.89, 128.59, 128.33, 127.23, 127.02, 126.18, 125.96, 125.58, 125.52, 123.41, 63.07, 49.18, 36.27, 32.52, 29.35, 22.22. HRMS calcd for Chemical Formula:  $C_{29}H_{26}NNaO^{+}$  [M+Na] $^{+}$ : 428.1985; found 428.1985.

#### VI. References

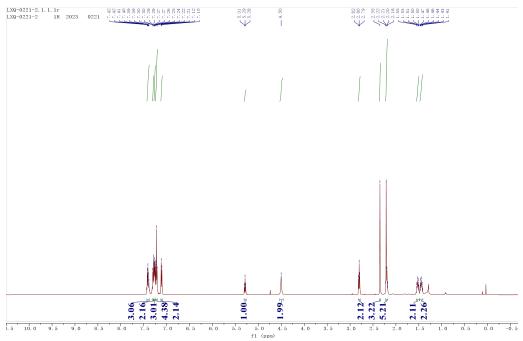
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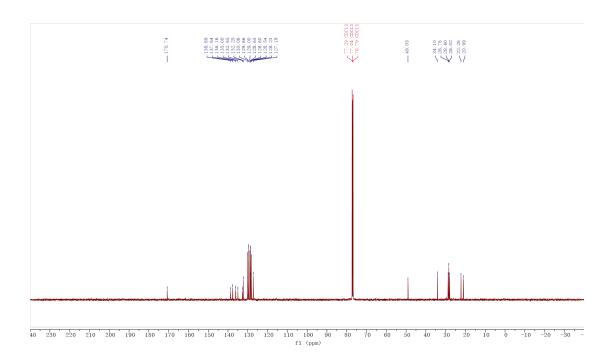
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# **VII. NMR Spectrum and HRMS of The Products**

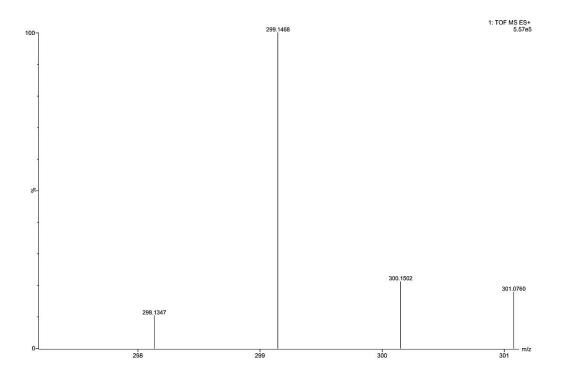
#### <sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3a**



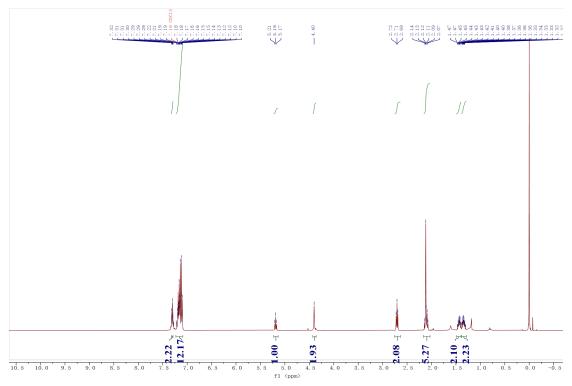
<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **3a** 



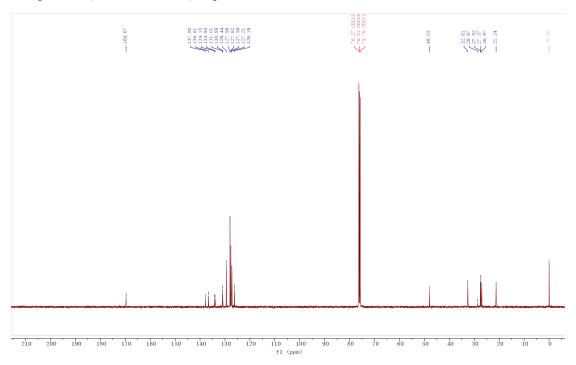
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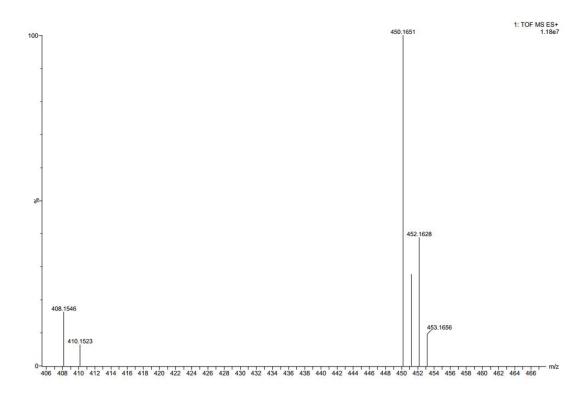


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3b** 

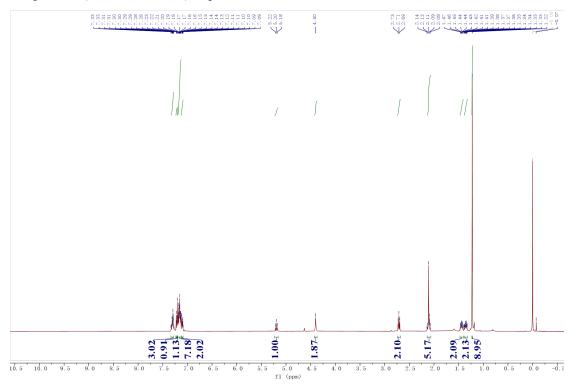


<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **3b** 

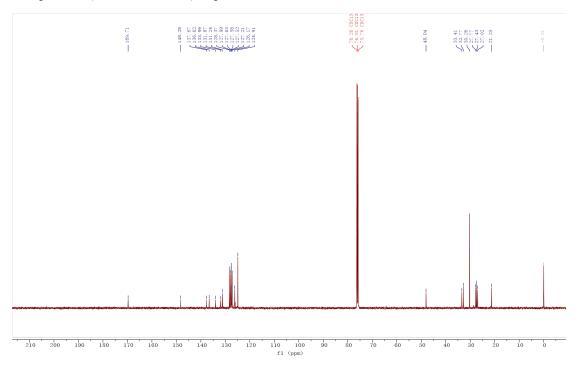




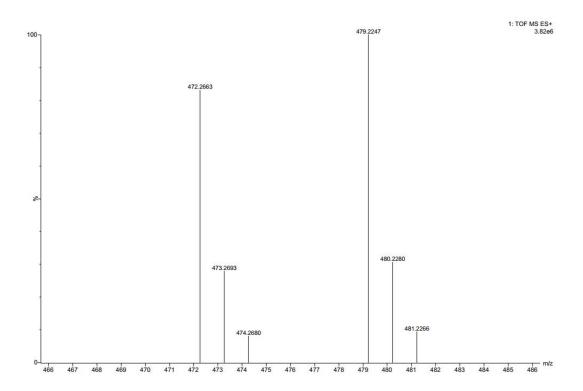
### <sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3c**

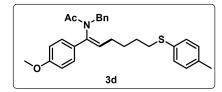


### $^{13}$ C spectrum (126 MHz, CDCl<sub>3</sub>) of product 3c

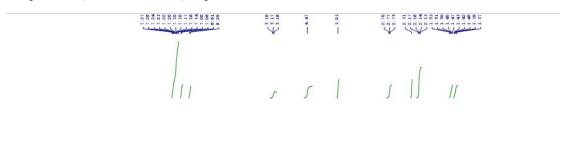


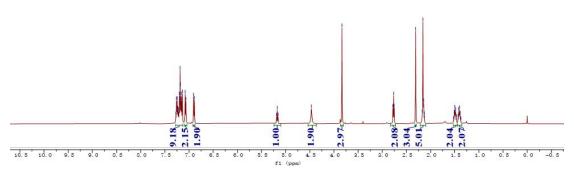
# HRMS of product 3c



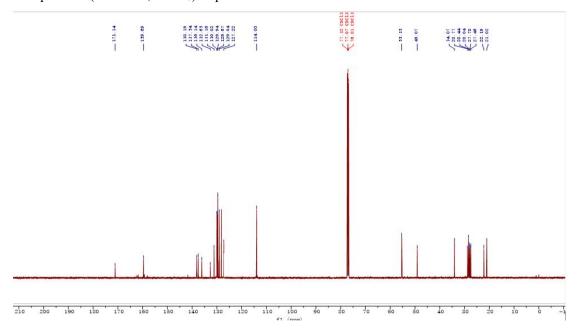


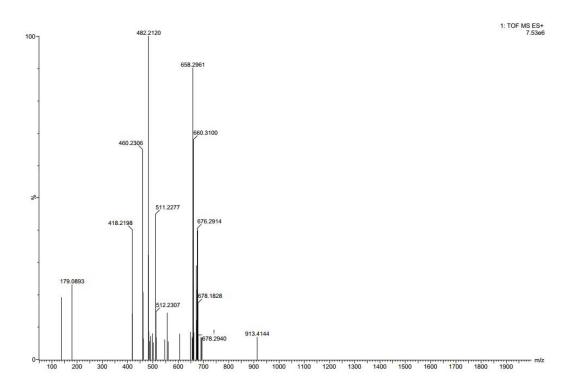
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3d** 



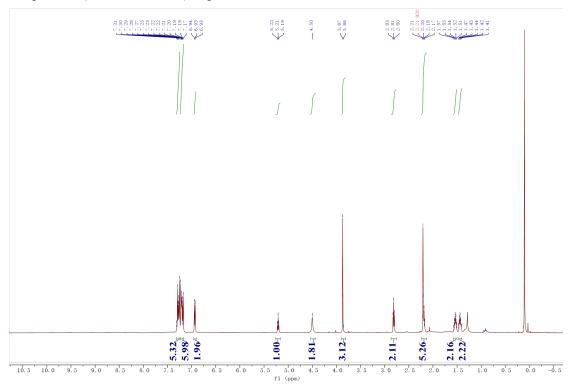


<sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product **3d** 

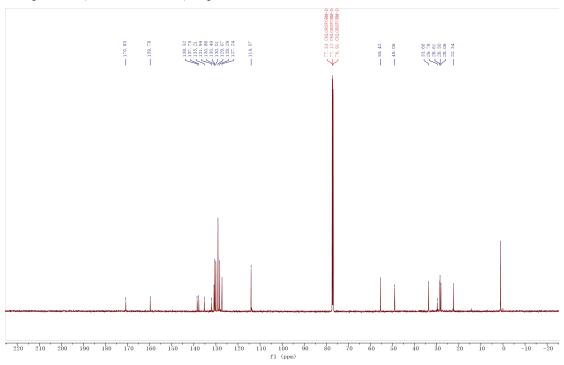


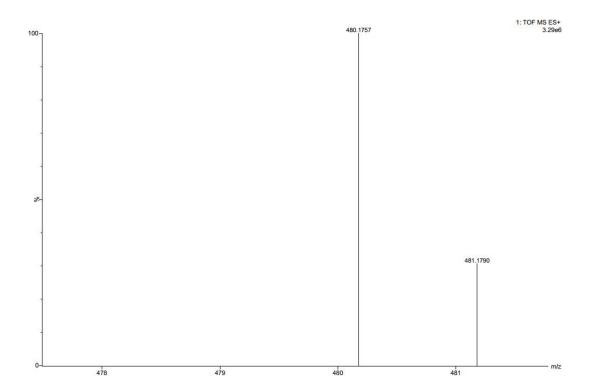


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3e** 

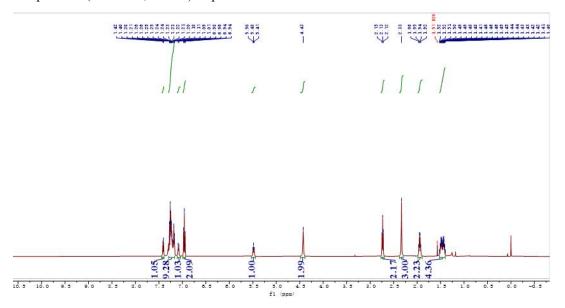


<sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product **3e** 

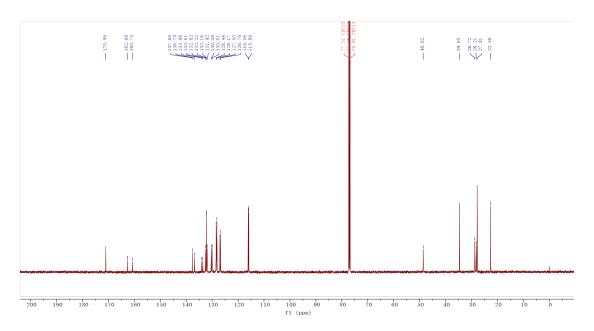




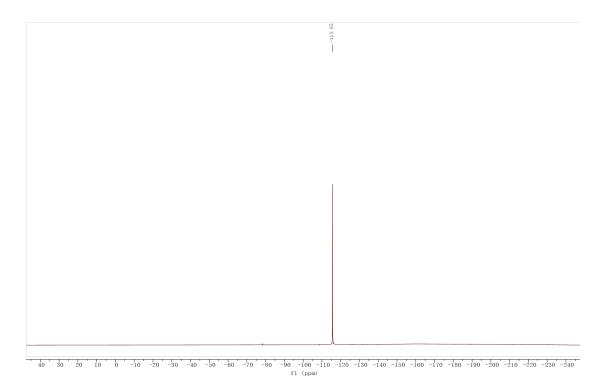
 $^{1}\text{H}$  spectrum (500 MHz, CDCl<sub>3</sub>) of product 3f



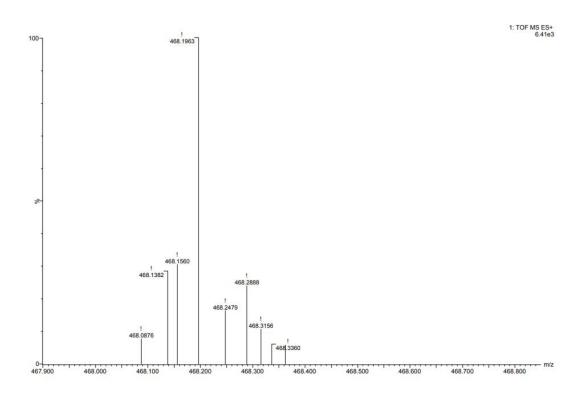
<sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product **3f** 



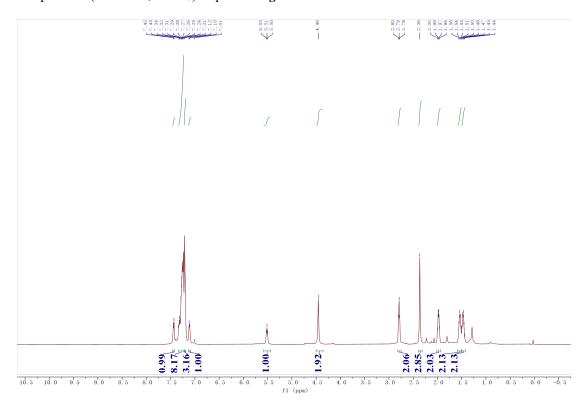
 $^{19}F$  spectrum (470 MHz, CDCl<sub>3</sub>) of product  $\boldsymbol{3f}$ 



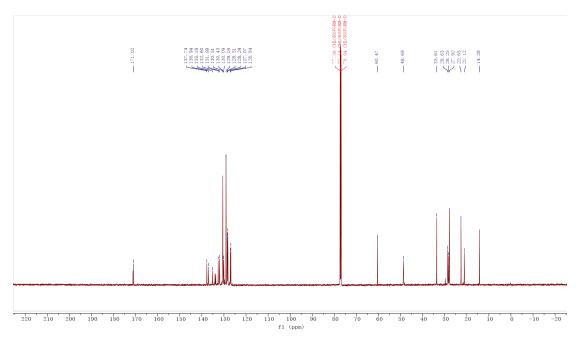
### HRMS of product **3f**



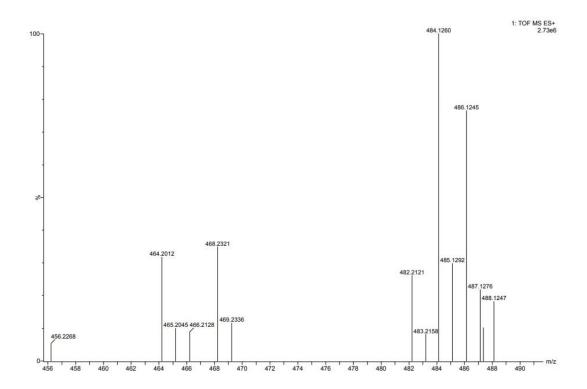
### $^{1}\text{H}$ spectrum (500 MHz, CDCl<sub>3</sub>) of product 3g



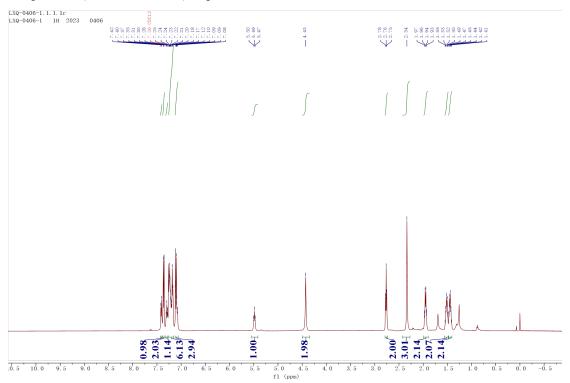
### $^{13}\text{C}$ spectrum (151 MHz, CDCl<sub>3</sub>) of product 3g



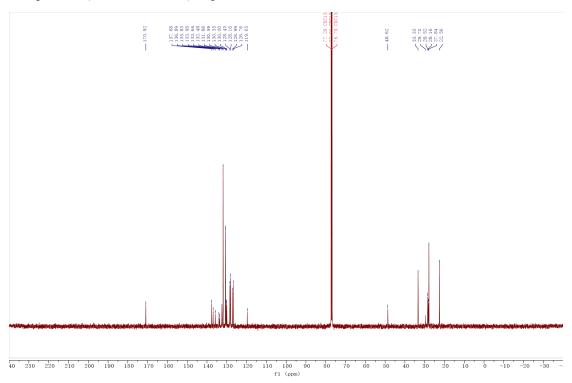
# HRMS of product 3g

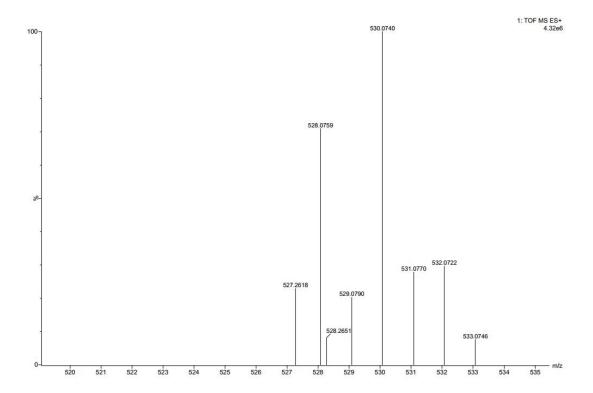


### <sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3h**

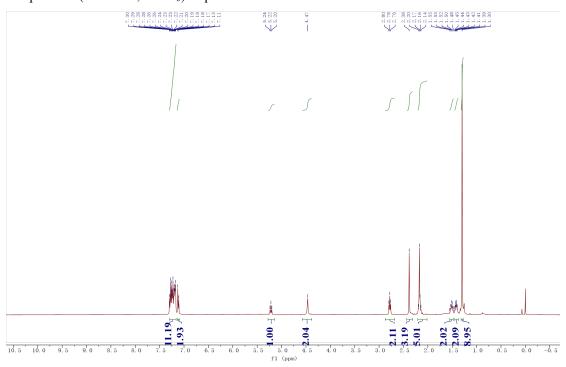


### <sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **3h**

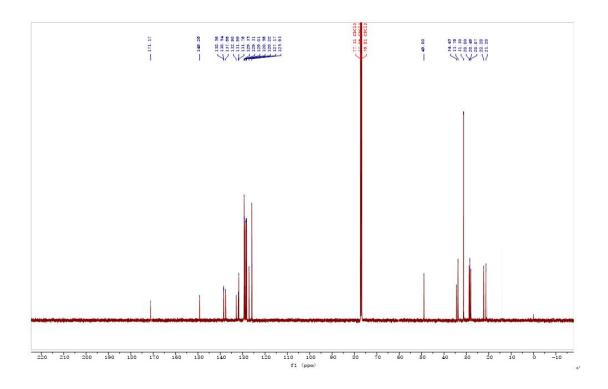




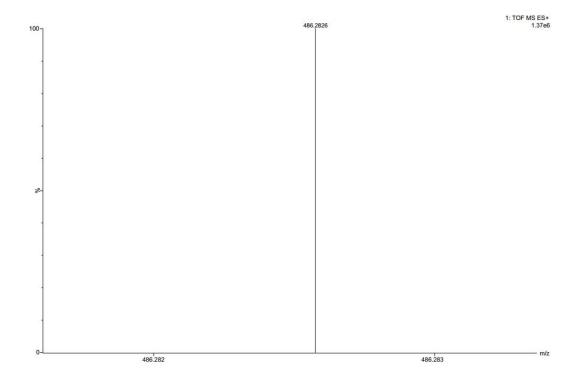
<sup>1</sup>H spectrum (400 MHz, CDCl<sub>3</sub>) of product **3i** 



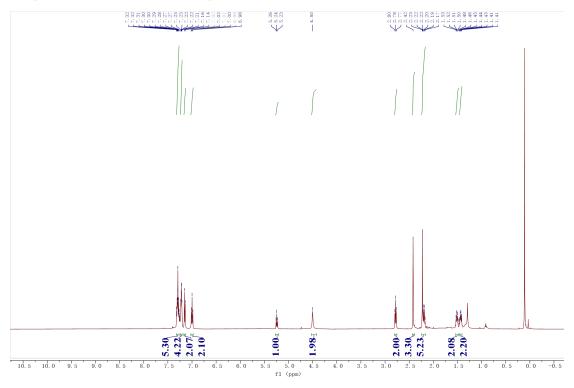
<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **3i** 



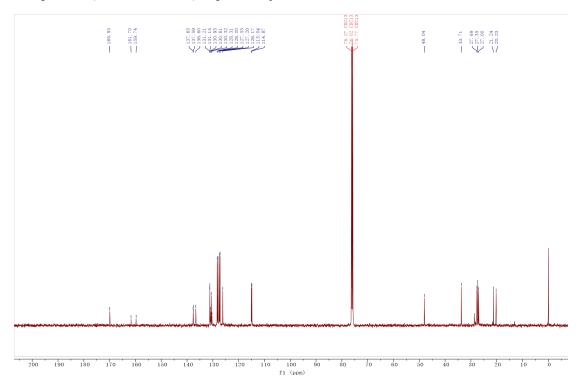
# HRMS of product 3i



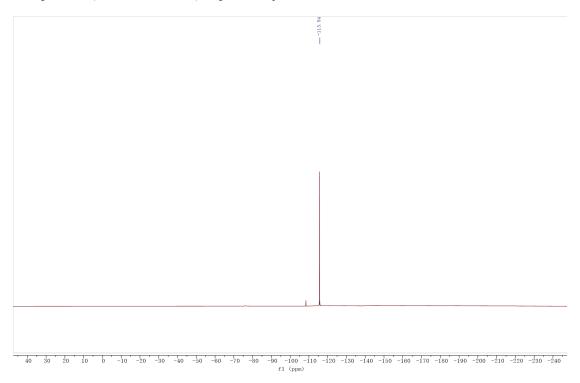
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3j** 



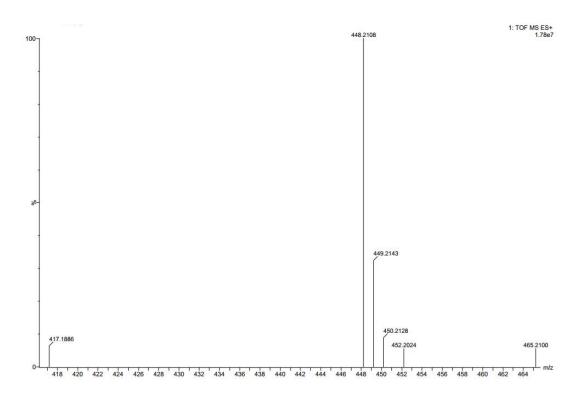
<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **3j** 



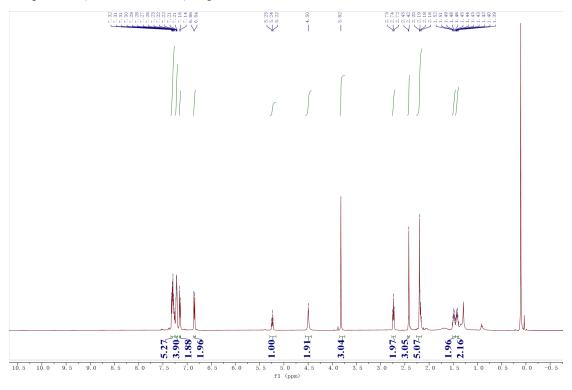
 $^{19}F$  spectrum (470 MHz, CDCl<sub>3</sub>) of product 3j



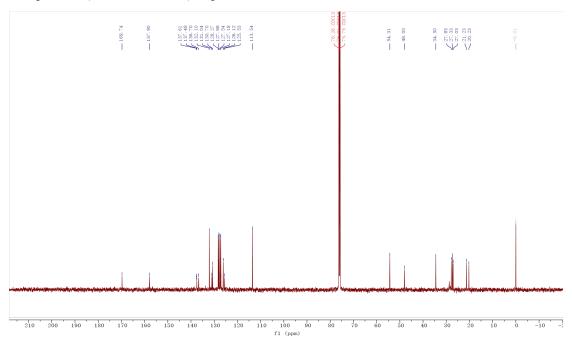
#### HRMS of product 3j



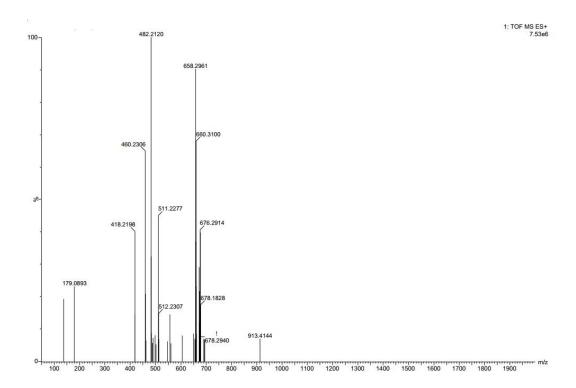
### <sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3k**



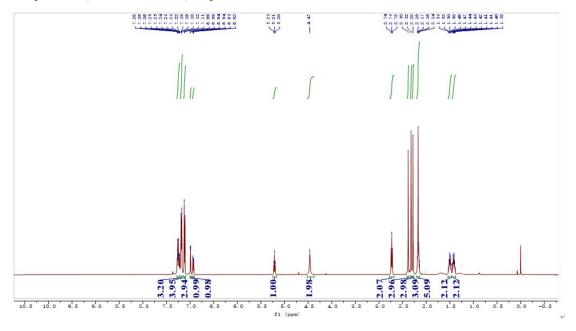
### <sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **3k**



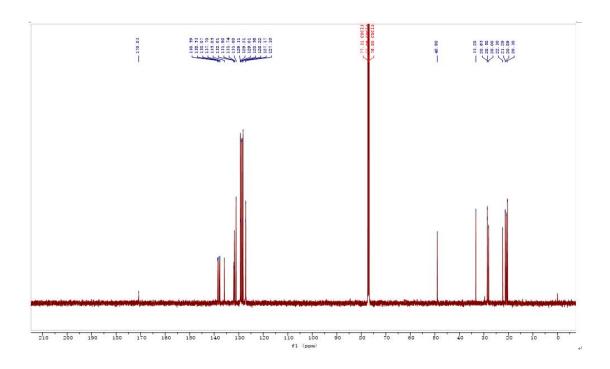
### HRMS of product 3k

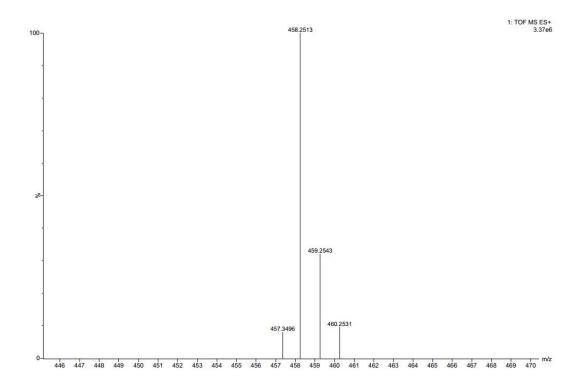


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **31** 

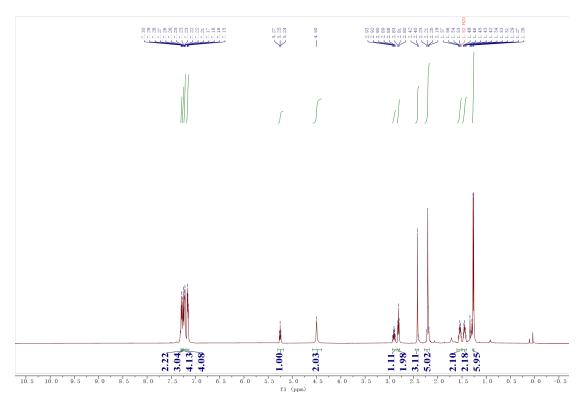


<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **31** 

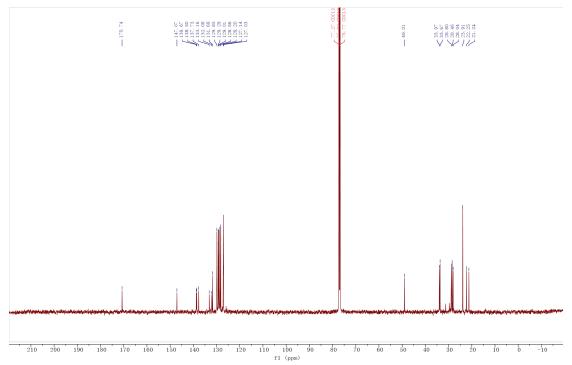




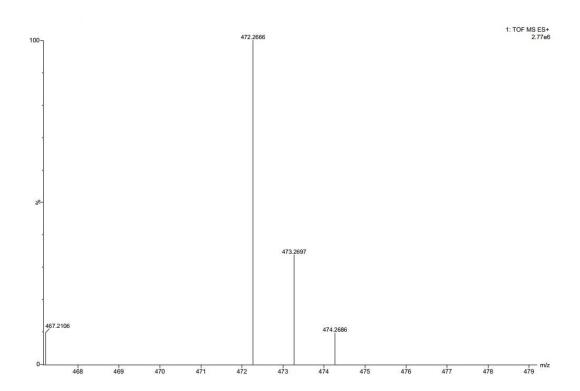
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3m** 



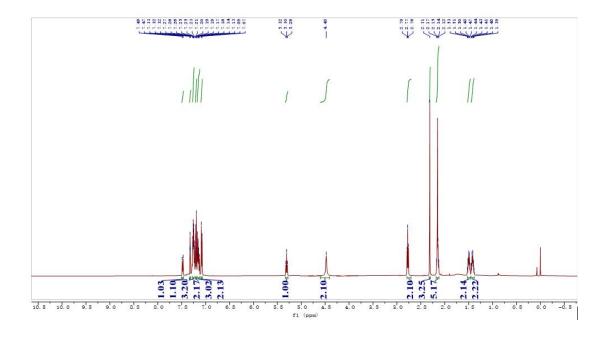
 $^{13}$ C spectrum (126 MHz, CDCl<sub>3</sub>) of product 3m



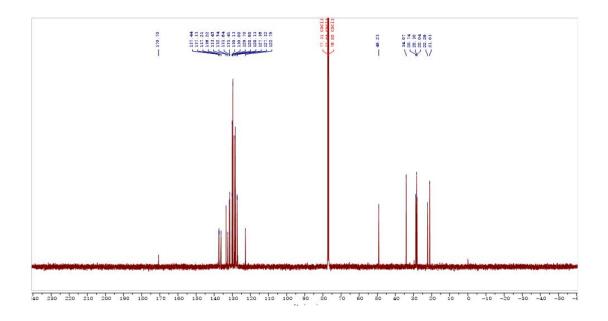
# HRMS of product 3m



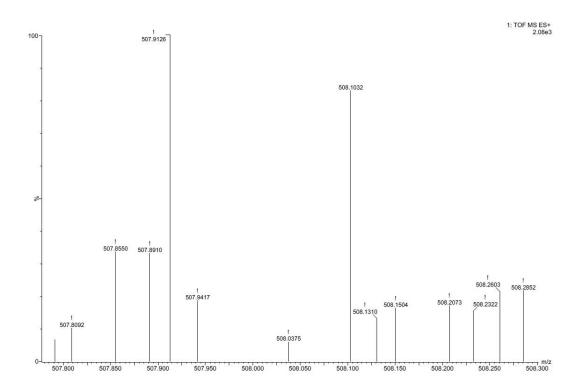
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3n** 



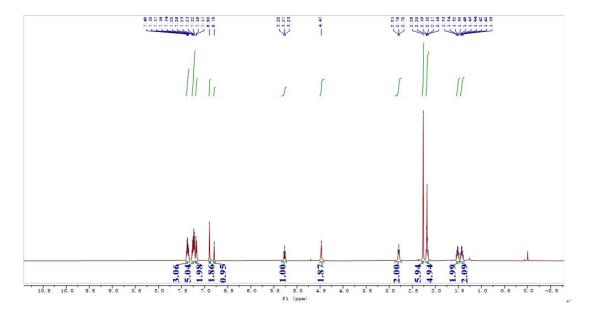
<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **3n** 



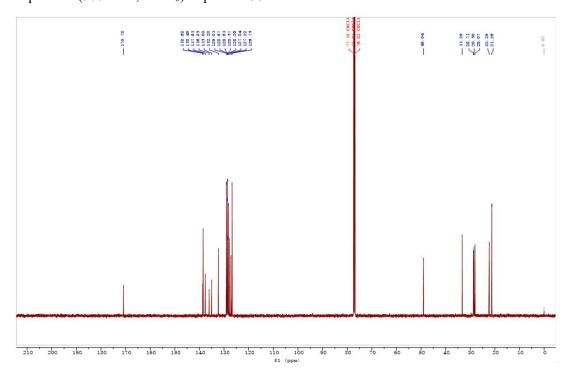
### HRMS of product 3n



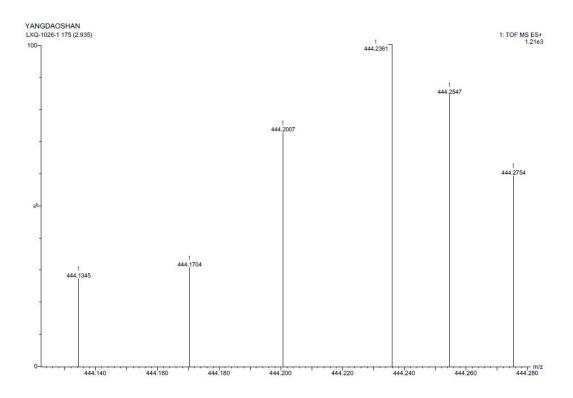
 $^1\mbox{H}$  spectrum (500 MHz, CDCl3) of product 3o



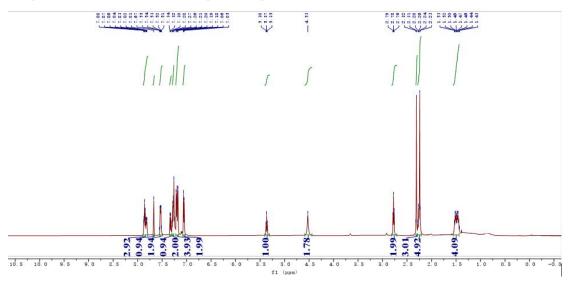
 $^{1}\text{H}$  spectrum (500 MHz, CDCl<sub>3</sub>) of product 3o



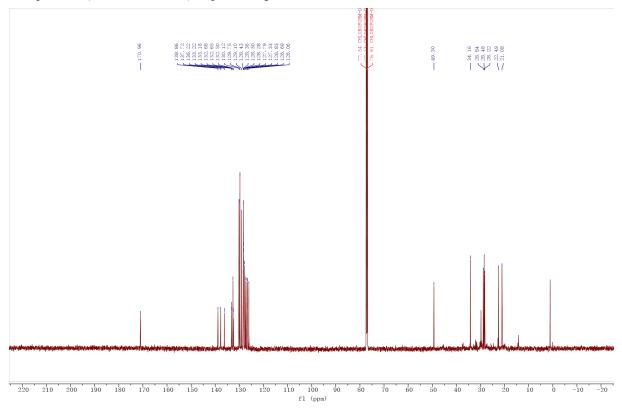
#### HRMS of product 30



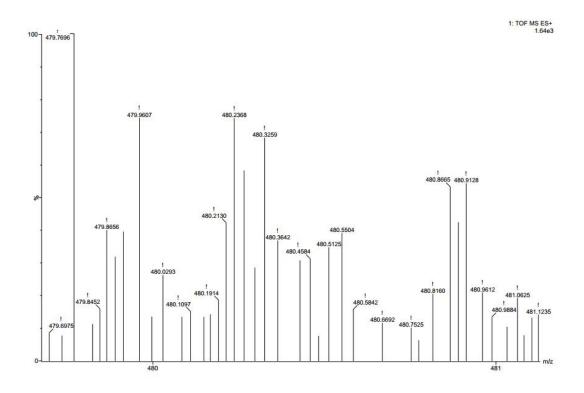
 $^1\mbox{H}$  spectrum (500 MHz, CDCl3) of product 3p



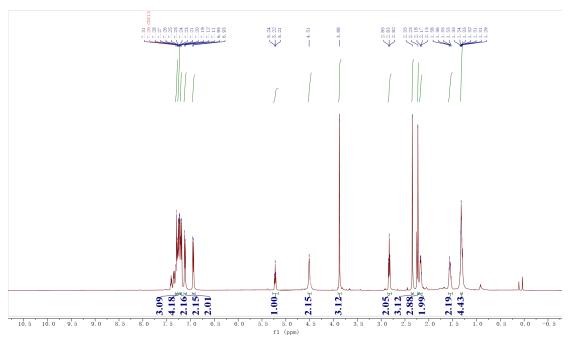
 $^{13}\text{C}$  spectrum (151 MHz, CDCl<sub>3</sub>) of product 3p



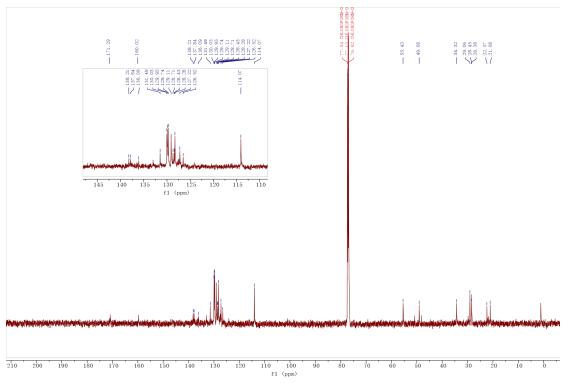
# HRMS of product 3p



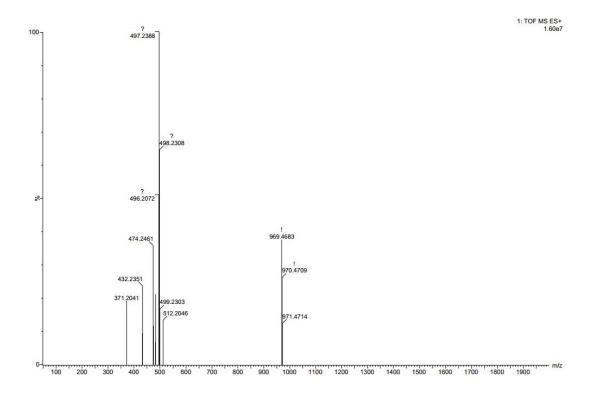
 $^{1}\text{H}$  spectrum (500 MHz, CDCl<sub>3</sub>) of product 3q



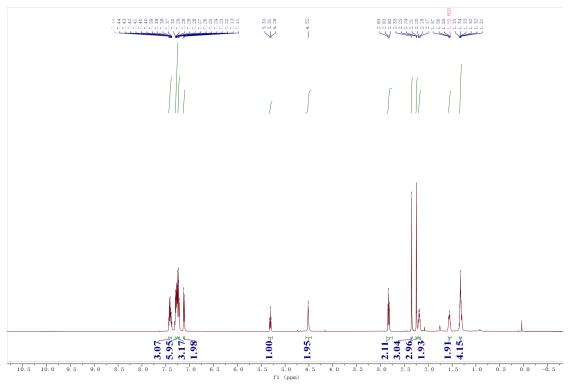
#### $^{13}$ C spectrum (151MHz, CDCl<sub>3</sub>) of product 3q



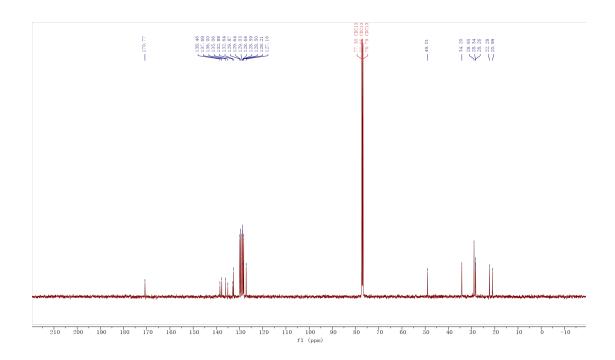
## HRMS of product 3q



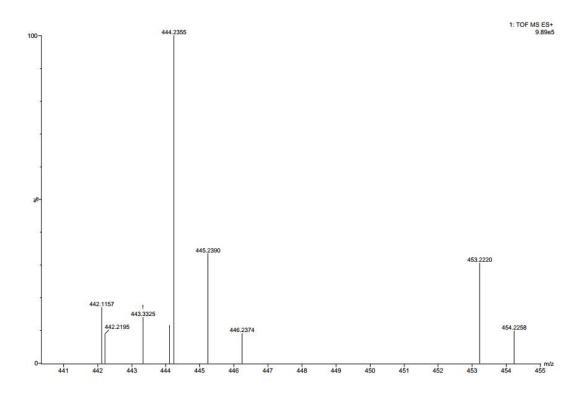
 $^{1}\mbox{H}$  spectrum (500 MHz, CDCl3) of product 3r



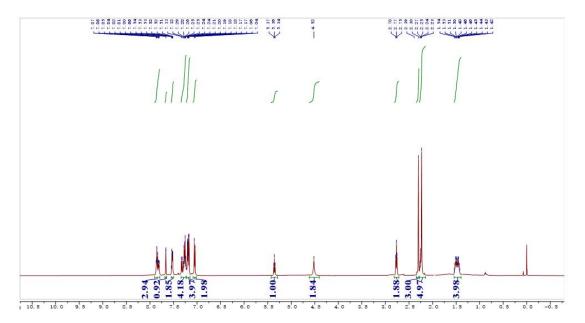
 $^{13}\text{C}$  spectrum (126 MHz, CDCl3) of product  $\boldsymbol{3r}$ 



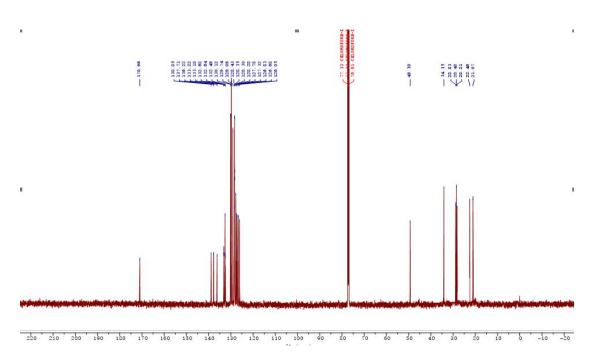
#### HRMS of product 3r

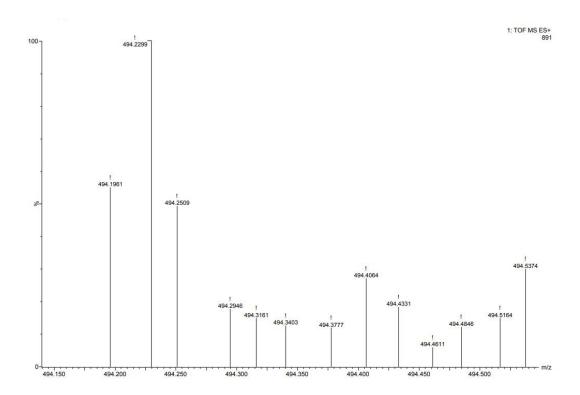


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3s** 

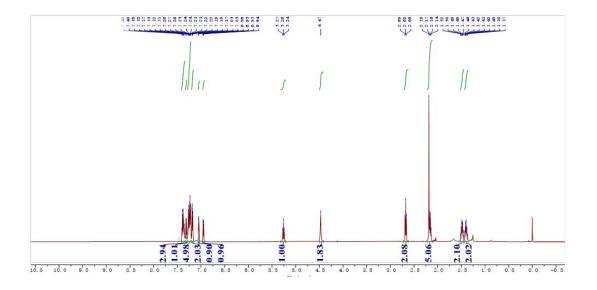


 $^{13}\mathrm{C}$  spectrum (151 MHz, CDCl<sub>3</sub>) of product 3s

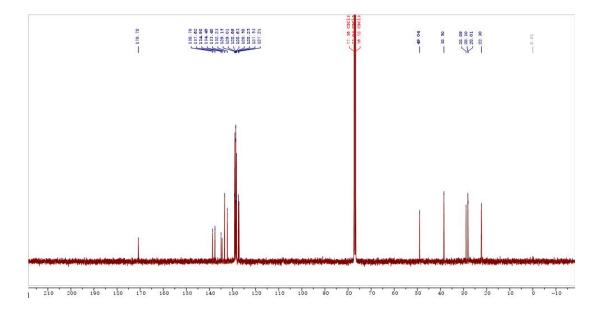


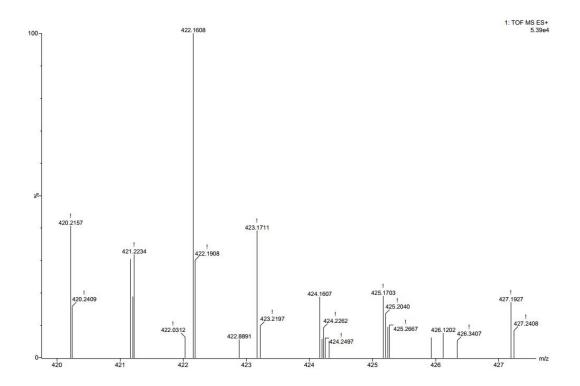


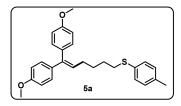
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **3t** 



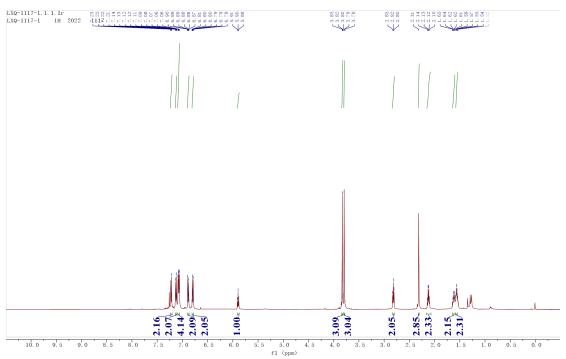
<sup>13</sup>C spectrum (100 MHz, CDCl<sub>3</sub>) of product **3t** 



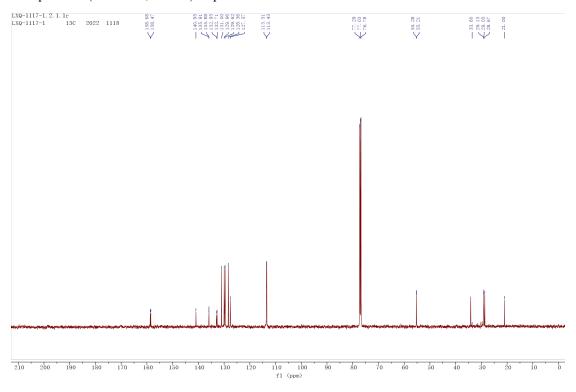




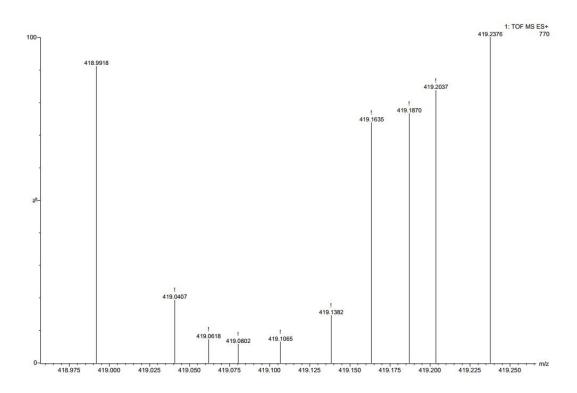
#### <sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5a**



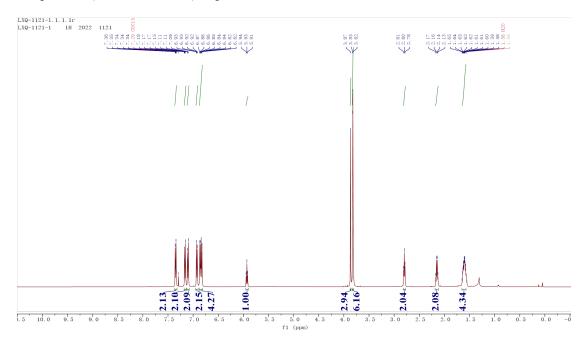
#### <sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5a**



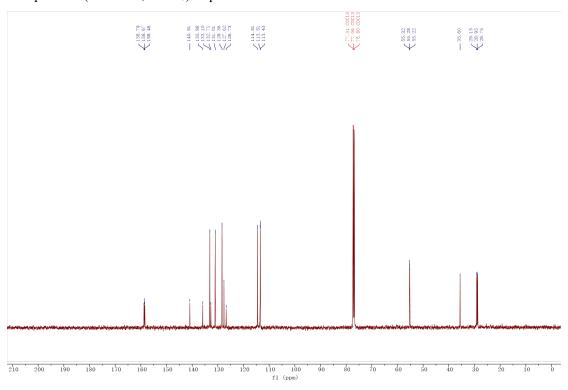
#### HRMS of product 5a

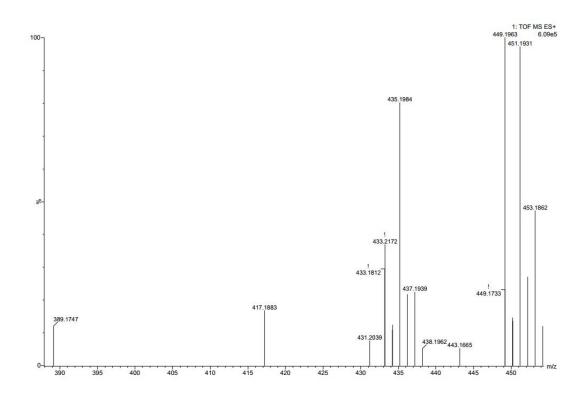


## $^{1}\mbox{H}$ spectrum (500 MHz, CDCl3) of product $\boldsymbol{5b}$

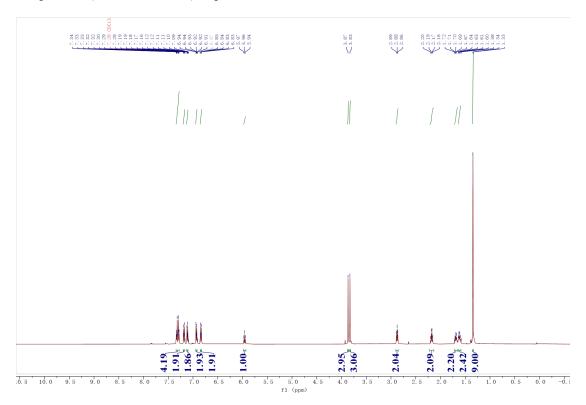


#### <sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5b**

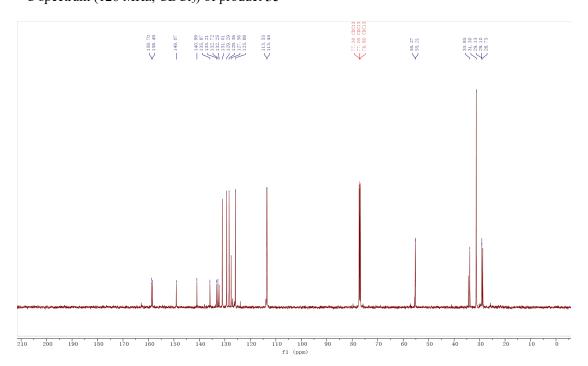




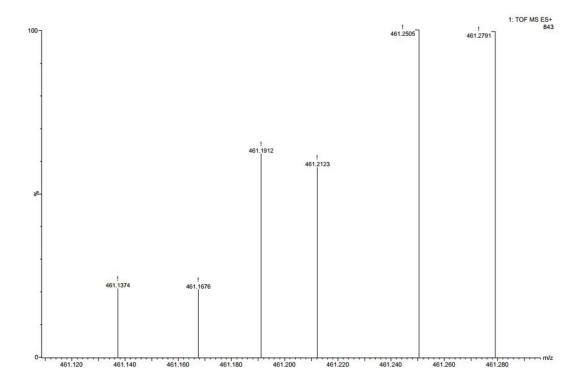
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5c** 



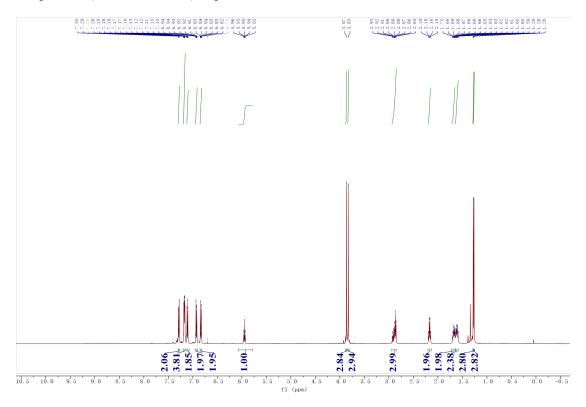
<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5c** 



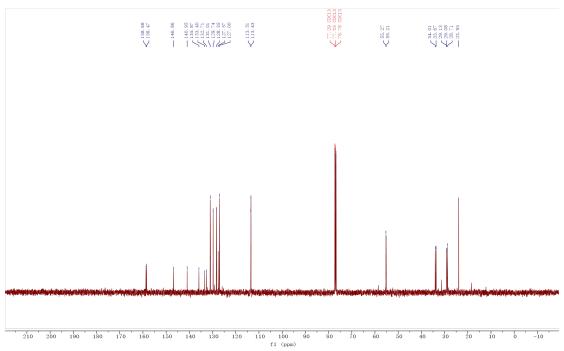
## HRMS of product **5c**



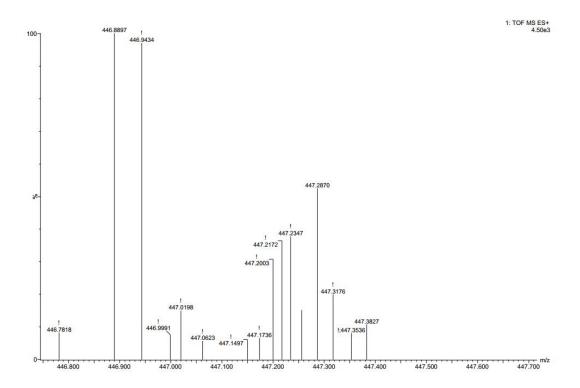
 $^{1}\text{H}$  spectrum (500 MHz, CDCl<sub>3</sub>) of product **5d** 



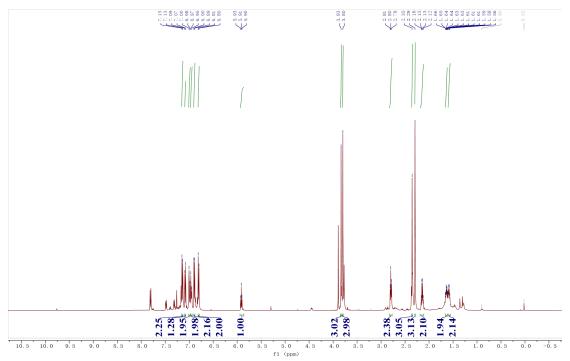
<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5d** 



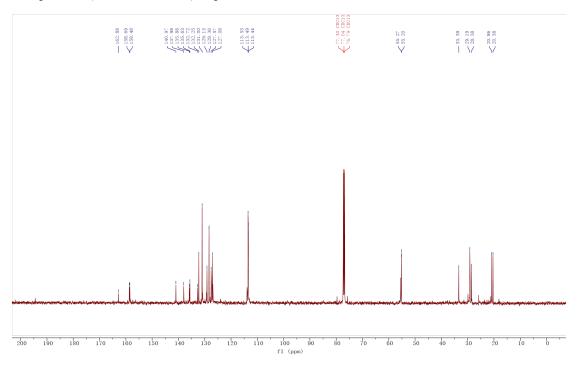
## HRMS of product **5d**



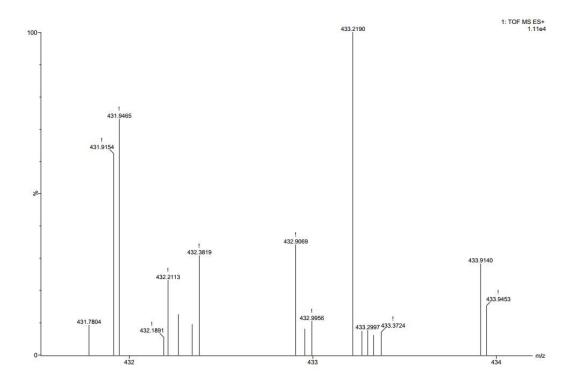
 $^1\mbox{H}$  spectrum (500 MHz, CDCl3) of product 5e



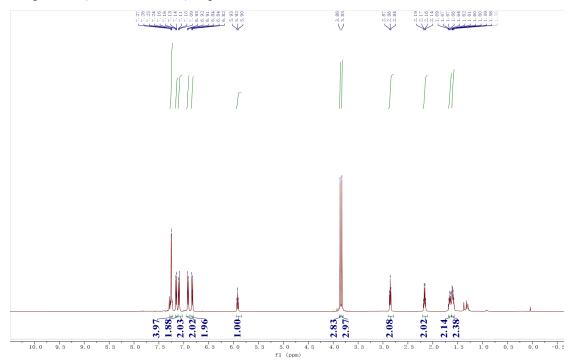
<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5e** 



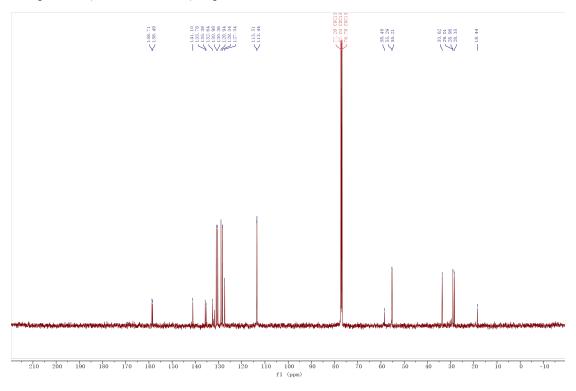
## HRMS of product **5e**



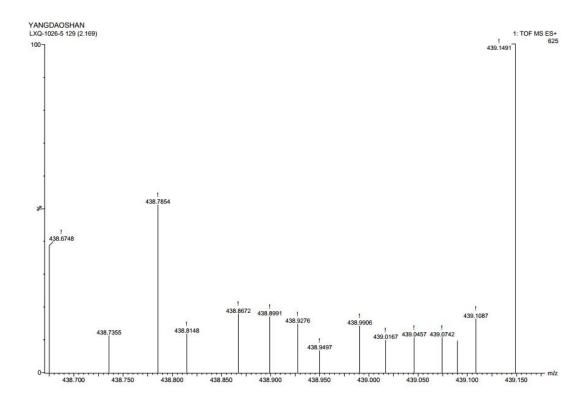
 $^1H$  spectrum (500 MHz, CDCl $_3)$  of product  $\boldsymbol{5f}$ 



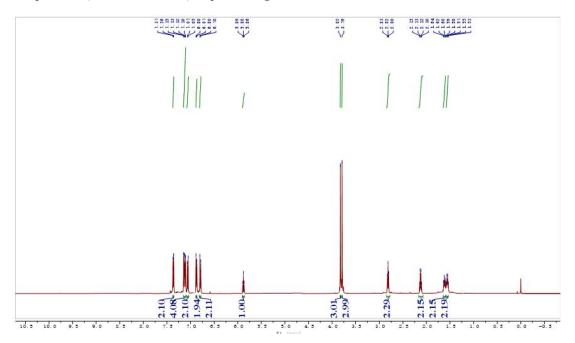
<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5f** 



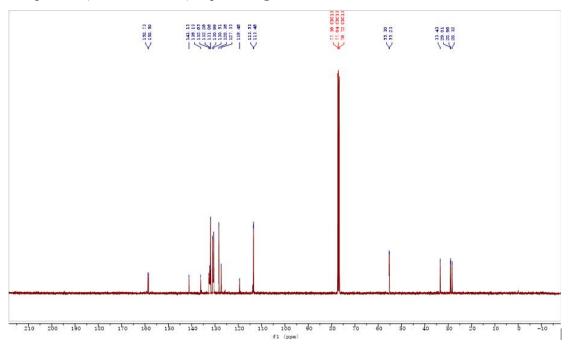
## HRMS of product **5f**



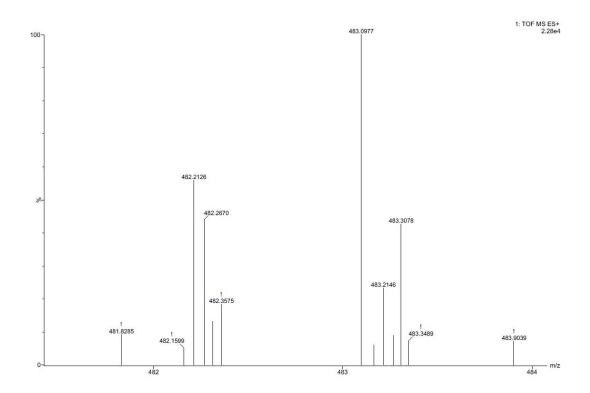
 $^1H$  spectrum (500 MHz, CDCl $_3)$  of product  ${\bf 5g}$ 



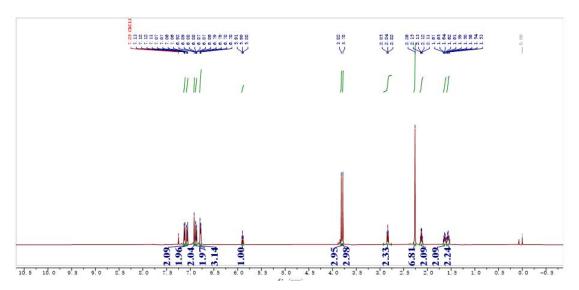
<sup>13</sup>C spectrum (101 MHz, CDCl<sub>3</sub>) of product **5g** 



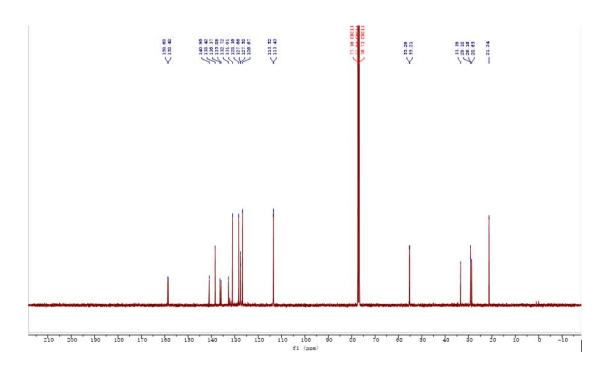
## HRMS of product **5g**



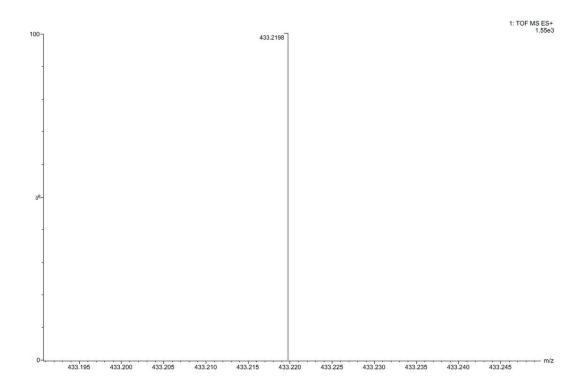
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5h** 



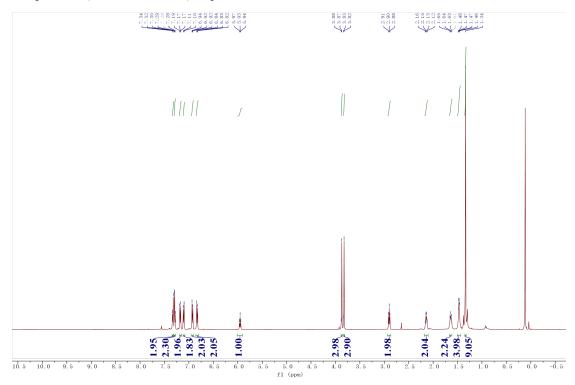
<sup>13</sup>C spectrum (101 MHz, CDCl<sub>3</sub>) of product **5h** 



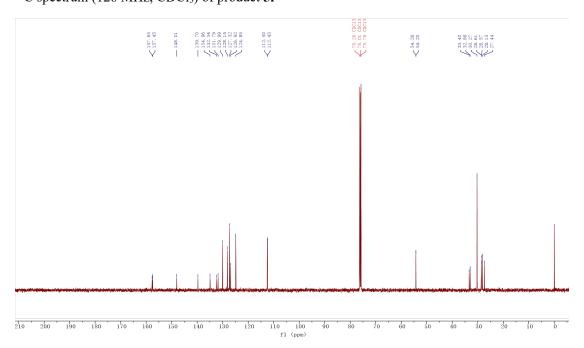
## HRMS of product **5h**



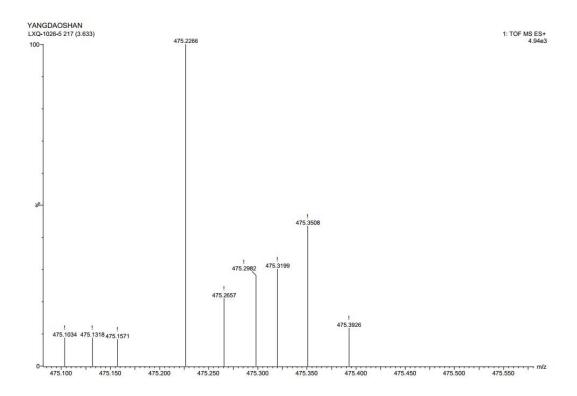
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5i** 



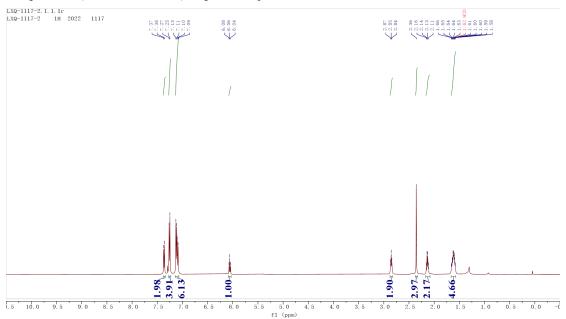
 $^{13}\text{C}$  spectrum (126 MHz, CDCl<sub>3</sub>) of product 5i



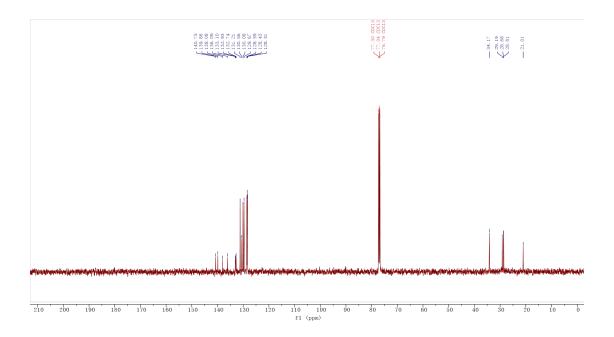
## HRMS of product 5i

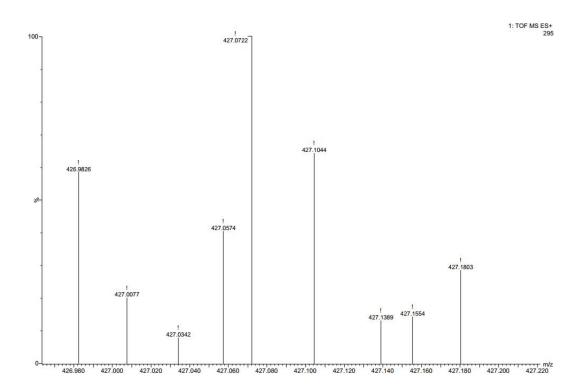


#### $^{1}\text{H}$ spectrum (500 MHz, CDCl<sub>3</sub>) of product 5j

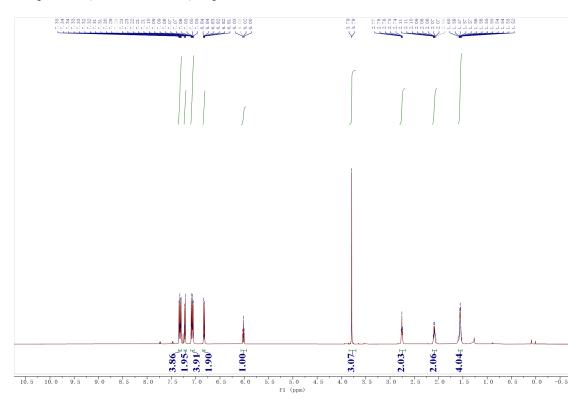


#### <sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5j**

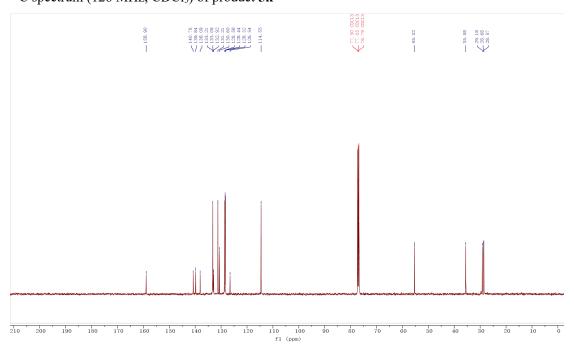




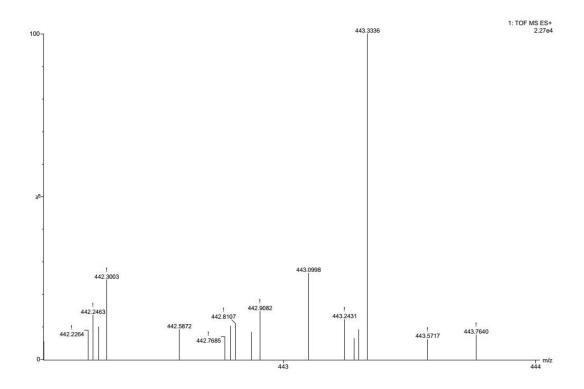
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5k** 



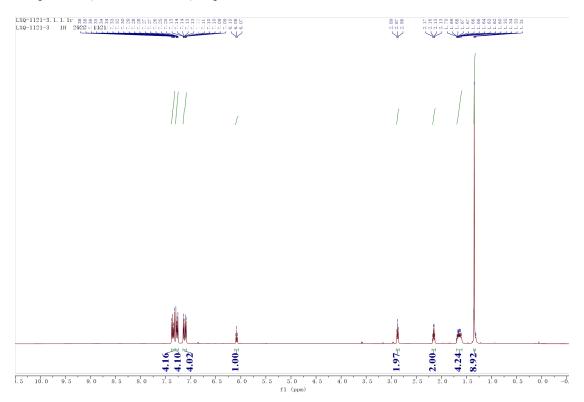
#### $^{13}\text{C}$ spectrum (126 MHz, CDCl<sub>3</sub>) of product 5k



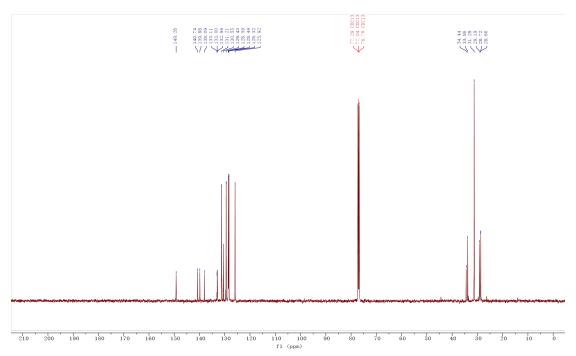
## HRMS of product **5k**



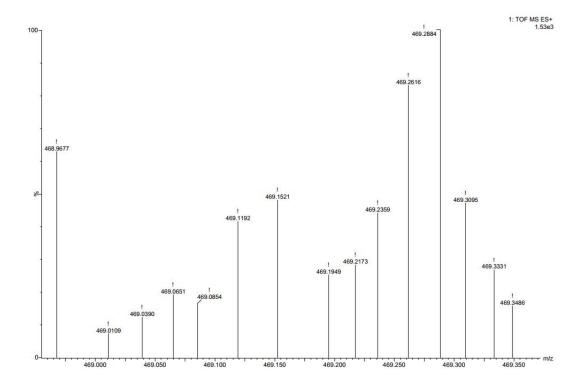
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5l** 



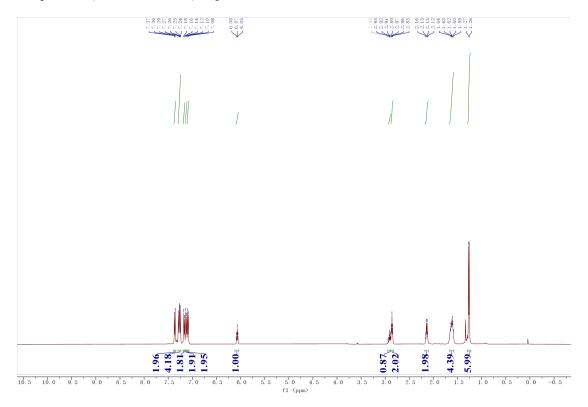
<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **51** 



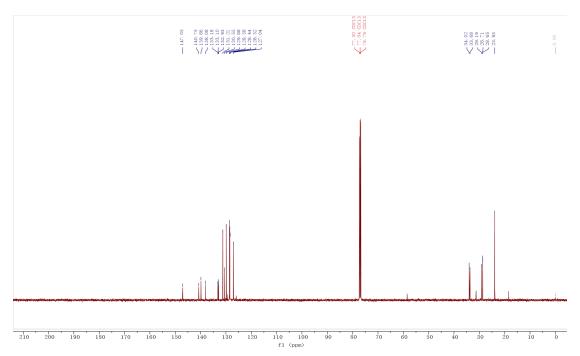
## HRMS of product 51

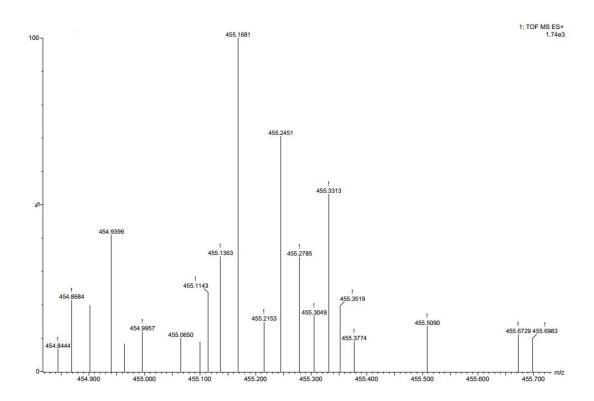


 $^1H$  spectrum (500 MHz, CDCl<sub>3</sub>) of product  $\boldsymbol{5m}$ 

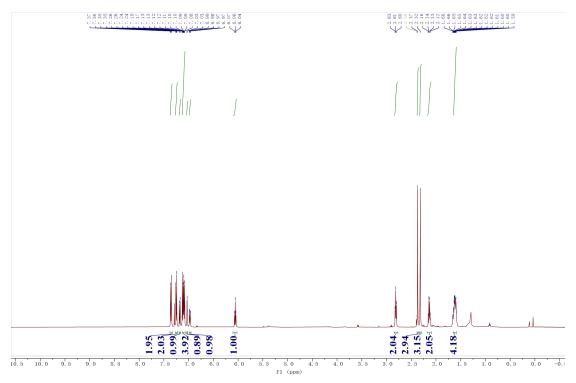


<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5m** 

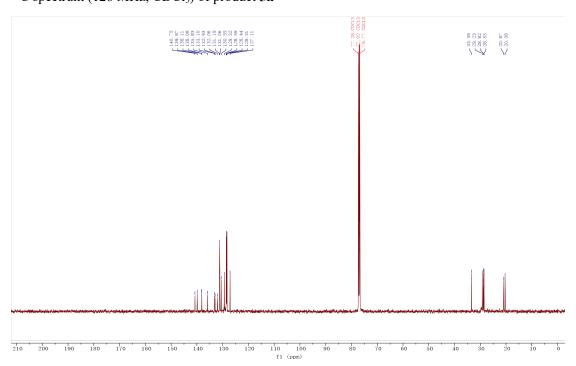


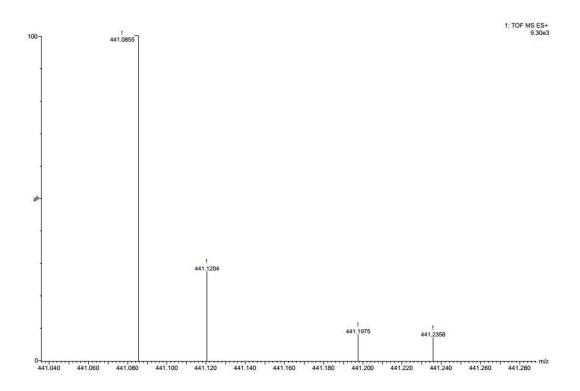


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5n** 

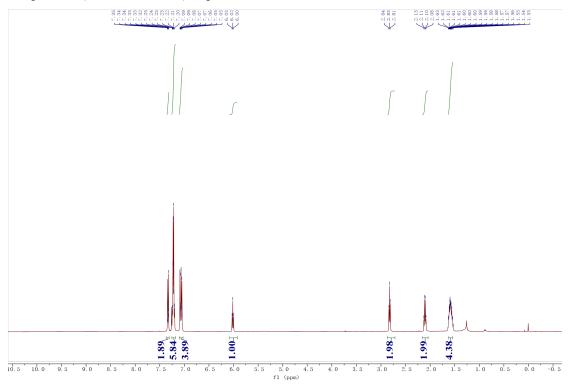


<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5n** 

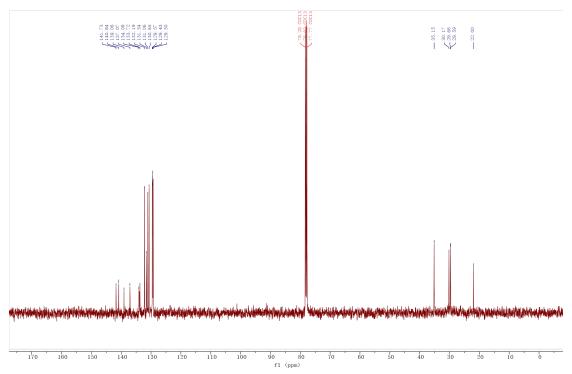


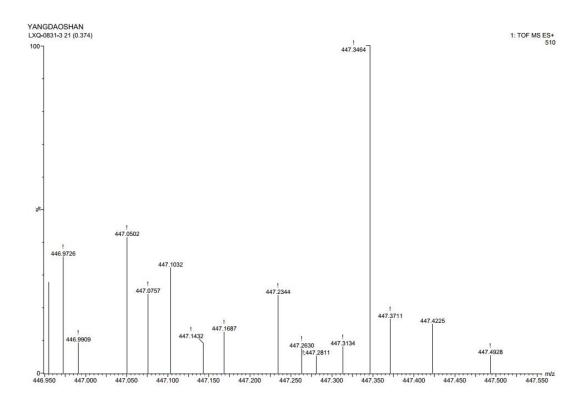


 $^{1}\text{H}$  spectrum (500 MHz, CDCl<sub>3</sub>) of product **50** 

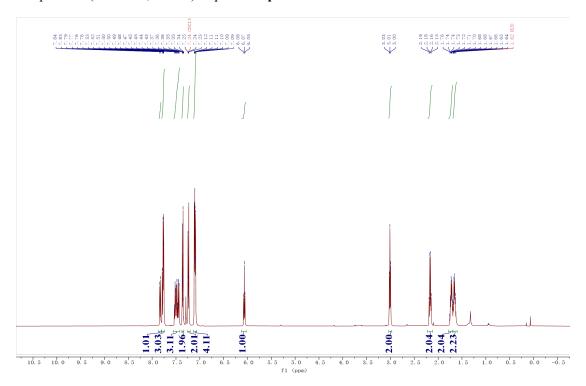


 $^{13}\text{C}$  spectrum (126 MHz, CDCl3) of product 50

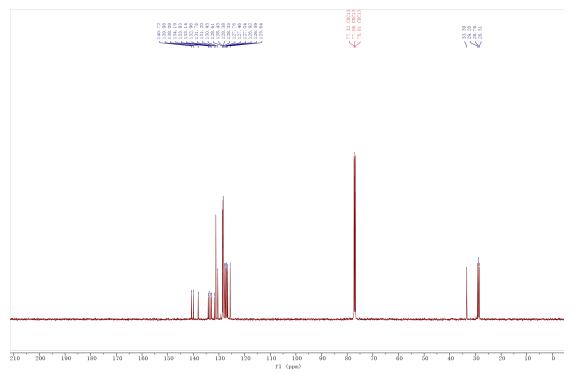


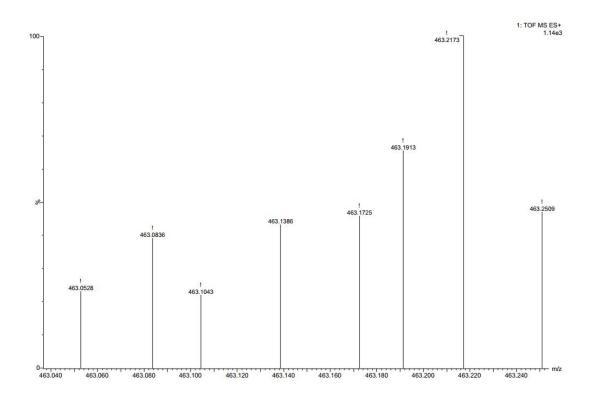


 $^{1}\text{H}$  spectrum (500 MHz, CDCl<sub>3</sub>) of product 5p

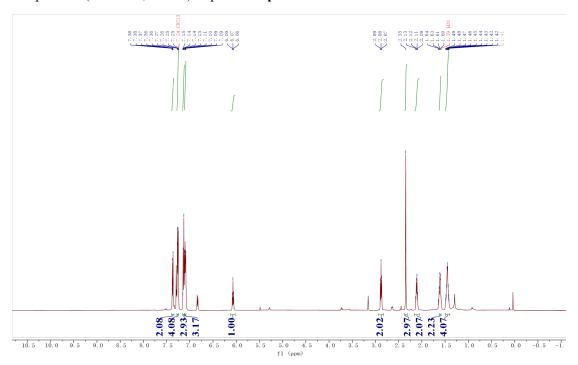


<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5p** 

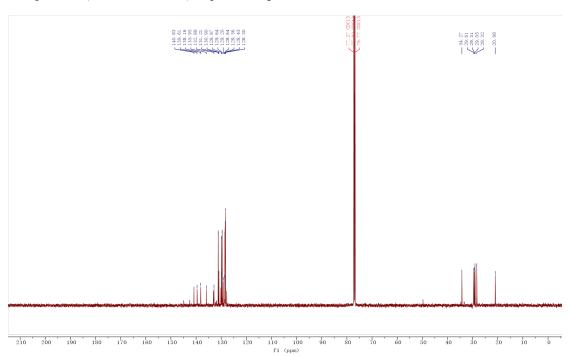


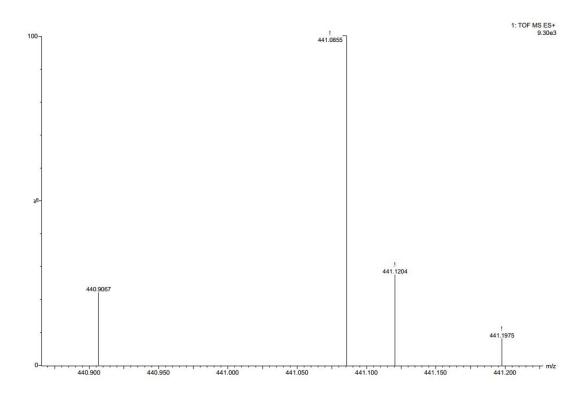


 $^{1}\text{H}$  spectrum (500 MHz, CDCl<sub>3</sub>) of product  $\mathbf{5q}$ 

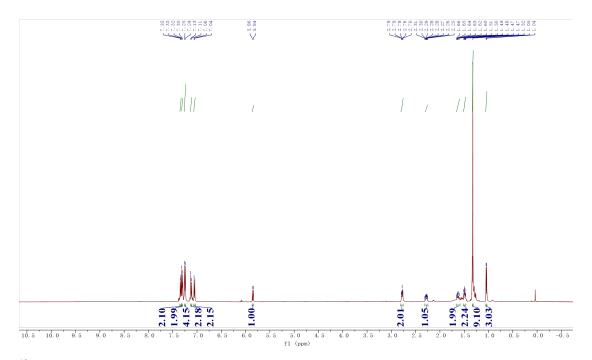


### <sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5q**

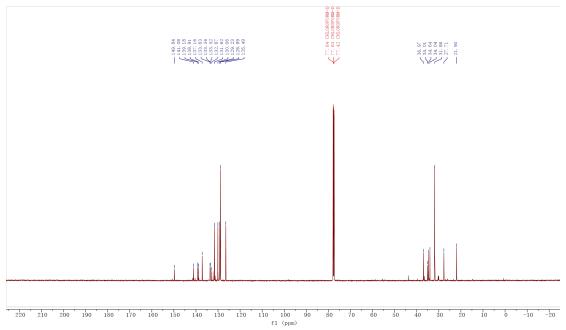


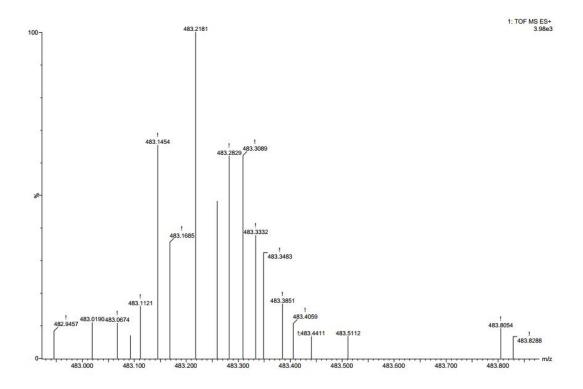


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5r** 

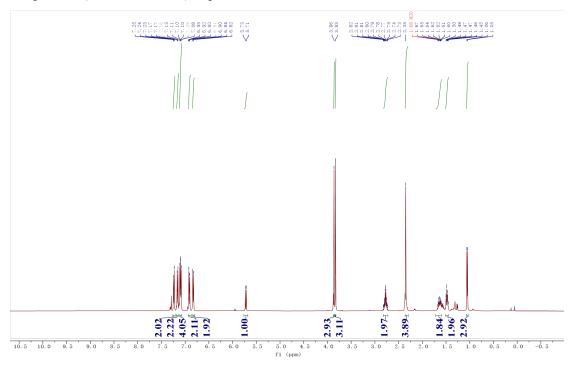


<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5r** 

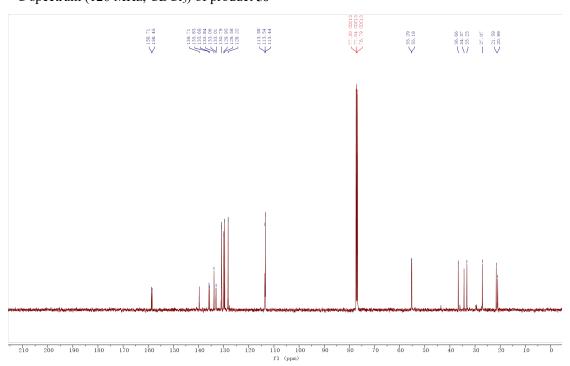


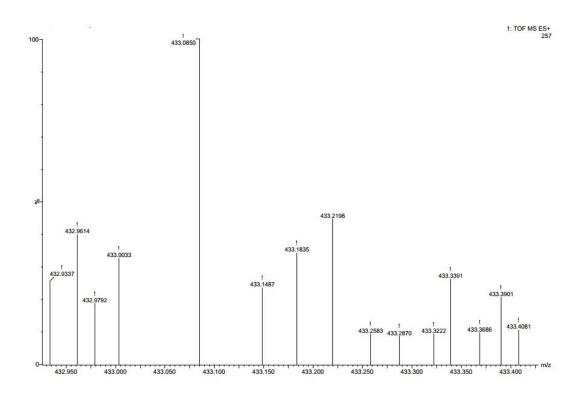


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5s** 

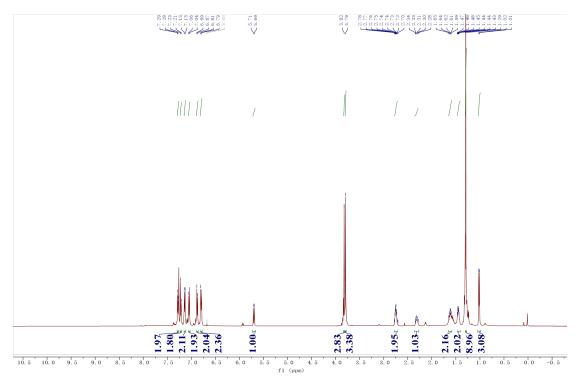


<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5s** 

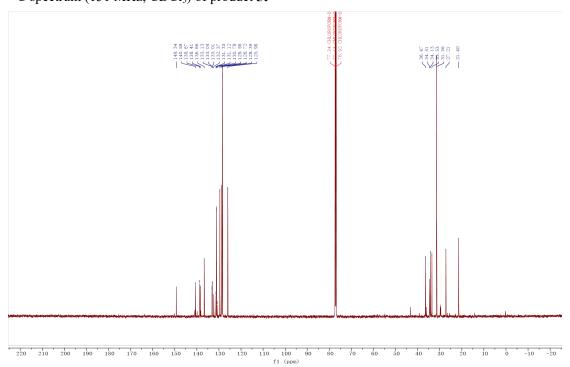


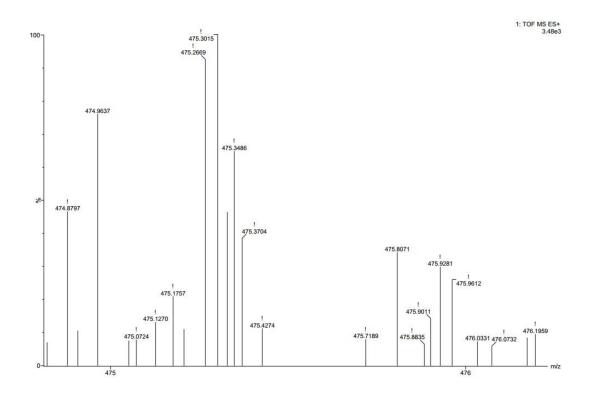


 $^{1}\text{H}$  spectrum (500 MHz, CDCl<sub>3</sub>) of product 5t

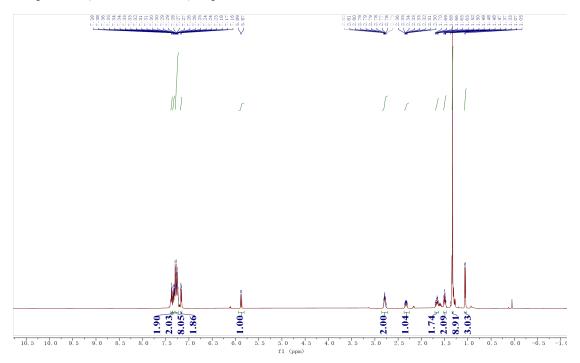


<sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product **5t** 

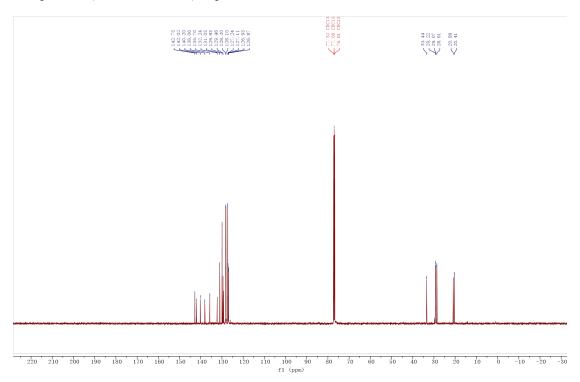


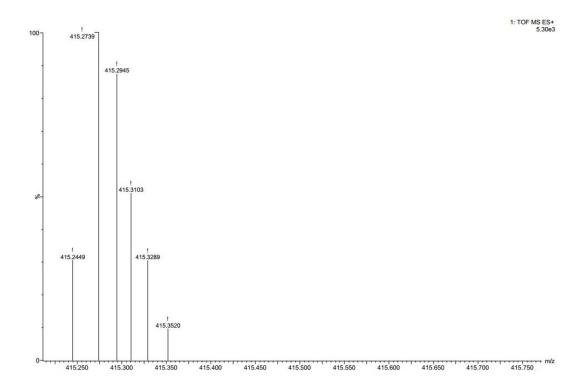


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5u** 

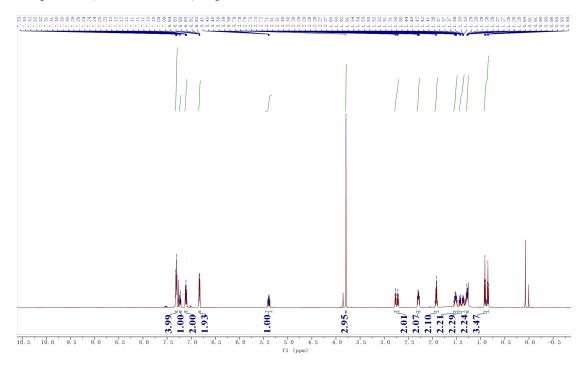


<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **5u** 

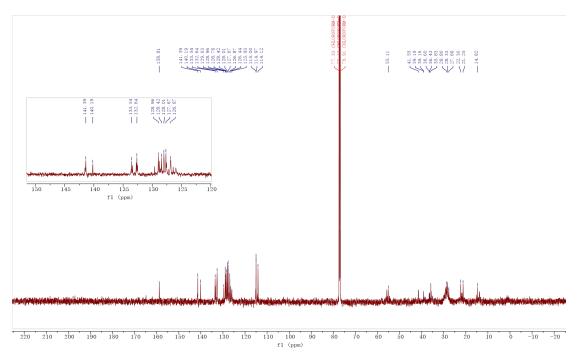


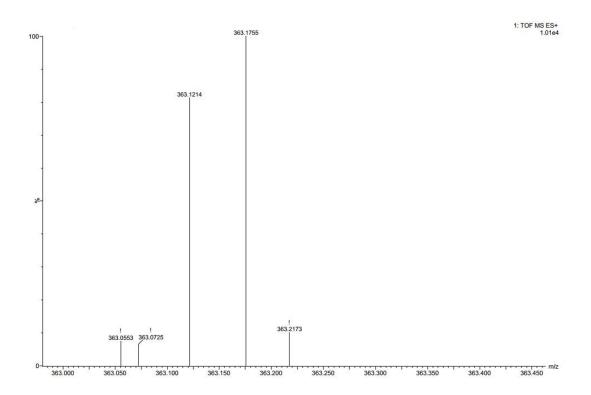


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5v** 

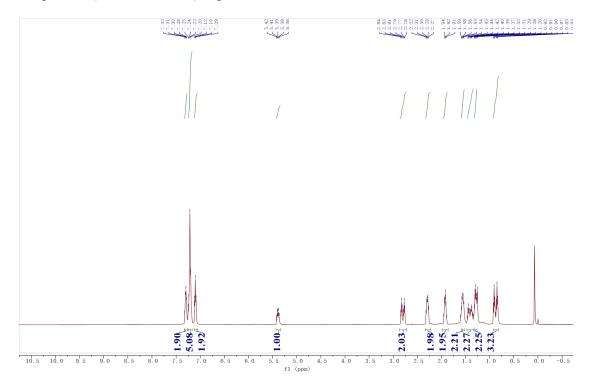


 $^{13}\text{C}$  spectrum (151 MHz, CDCl<sub>3</sub>) of product 5v

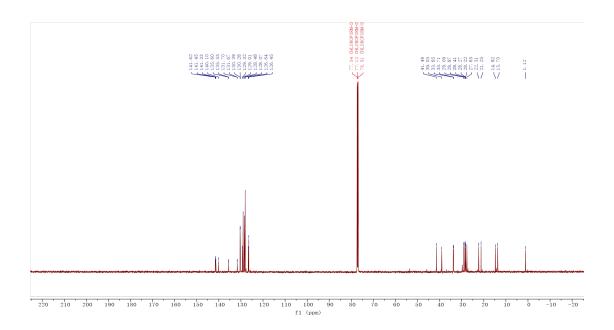


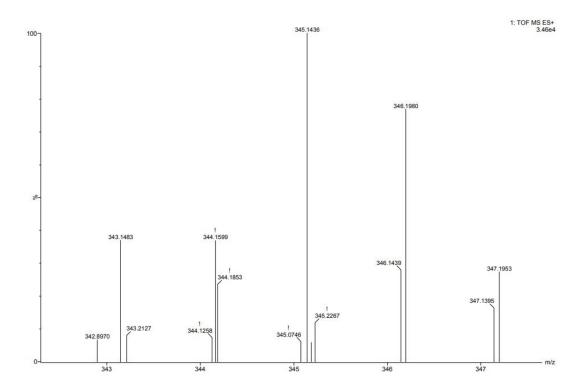


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product 5w

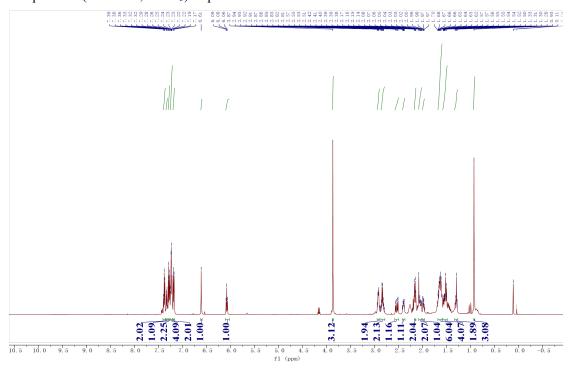


<sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product **5w** 

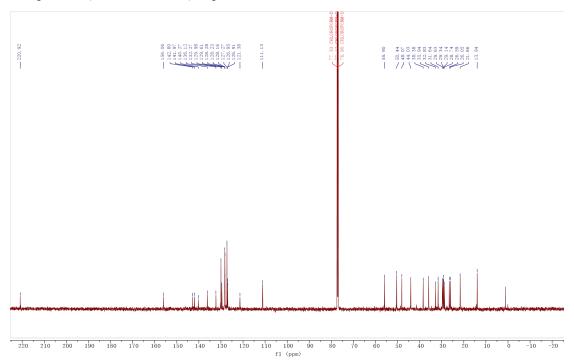


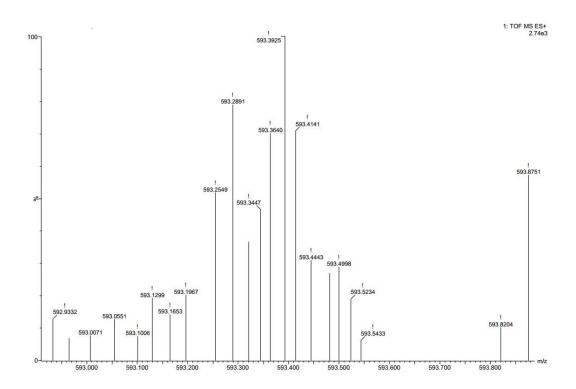


 $^{1}\text{H}$  spectrum (500 MHz, CDCl<sub>3</sub>) of product 5x

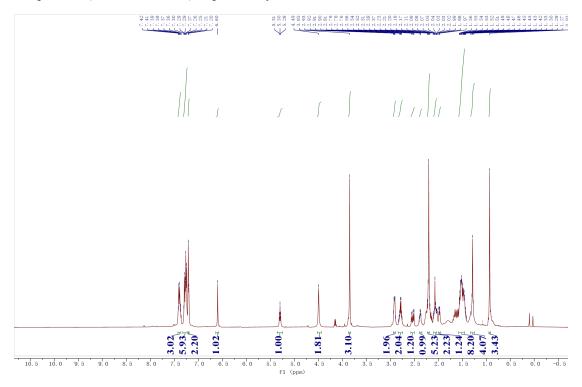


### <sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product **5x**

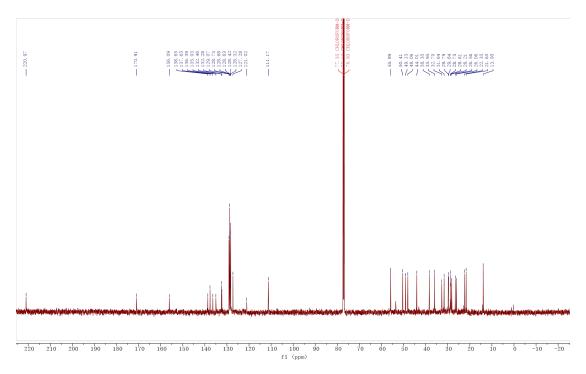


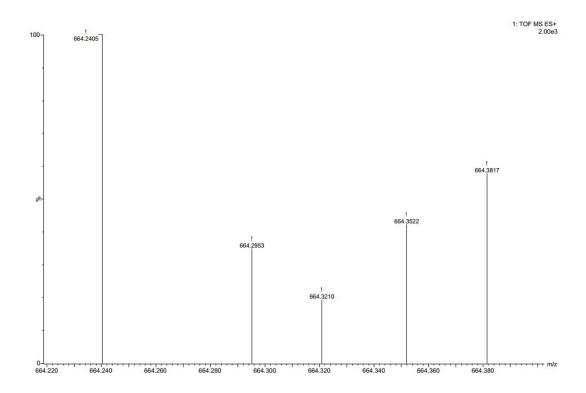


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product **5y** 

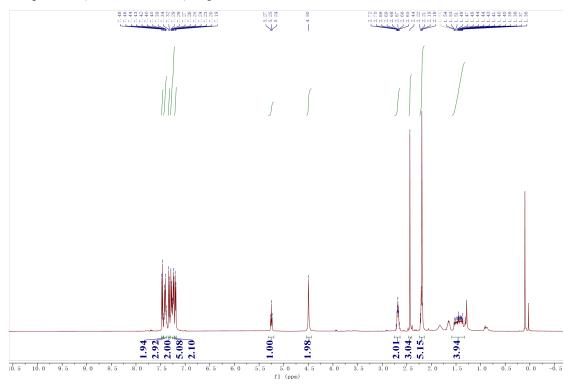


<sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product **5y** 

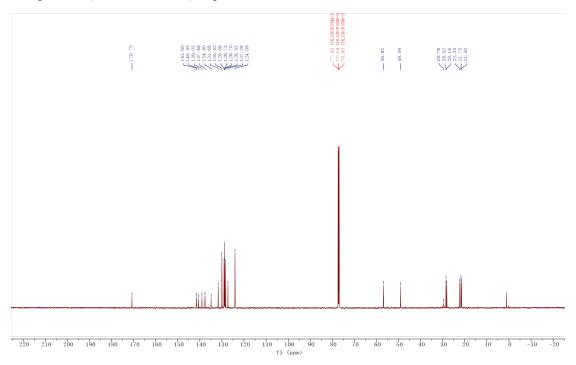


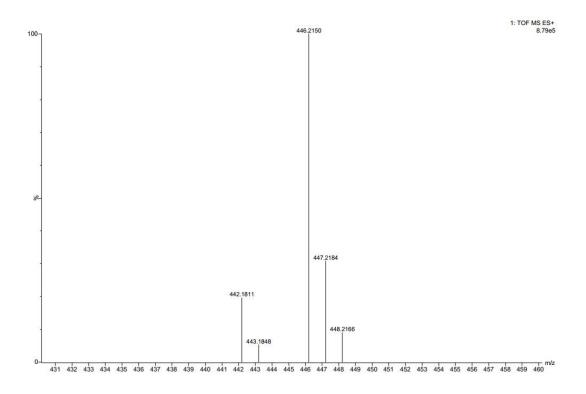


#### <sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product 6

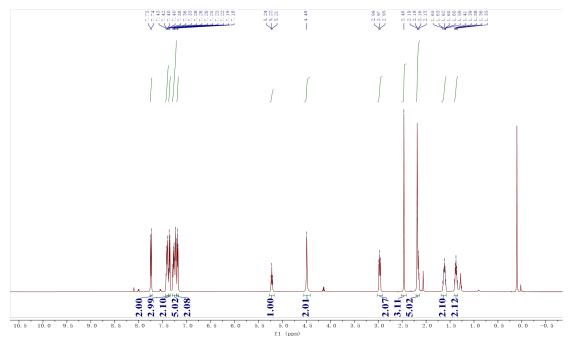


### <sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product 6

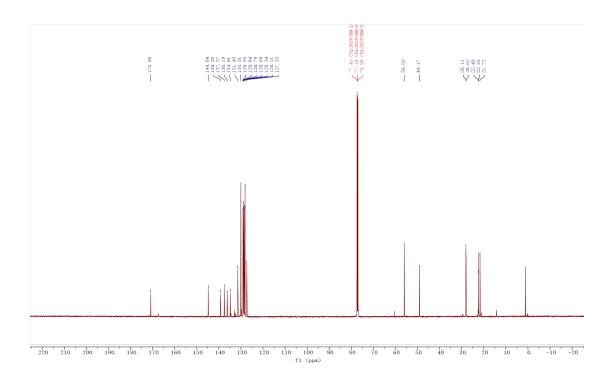


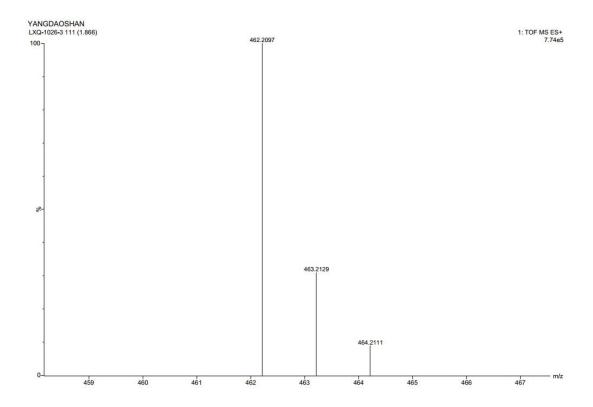


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product 7

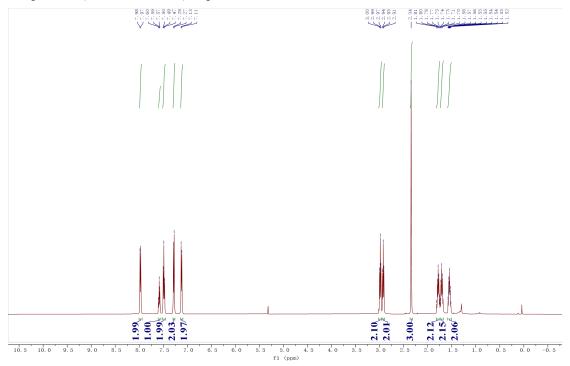


#### <sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product 7

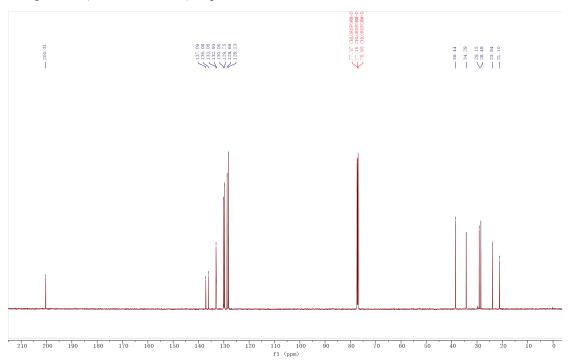




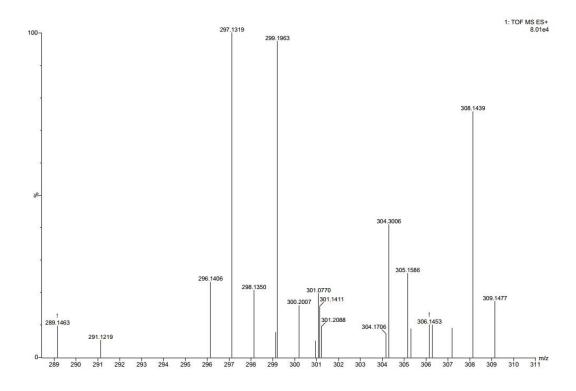
<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product 8



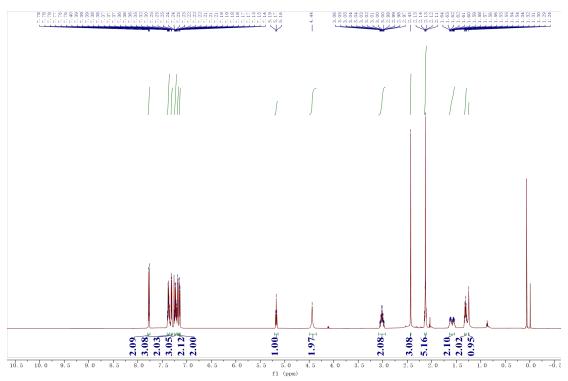
<sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product 8



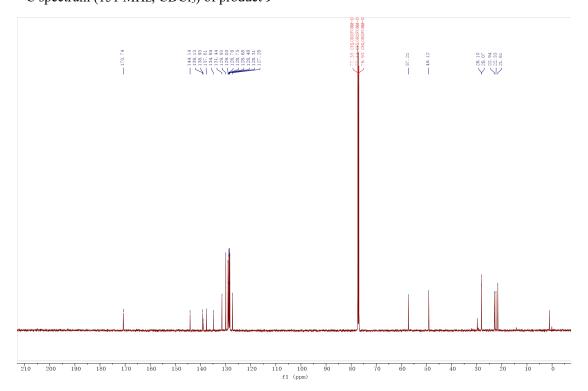
HRMS of product 8

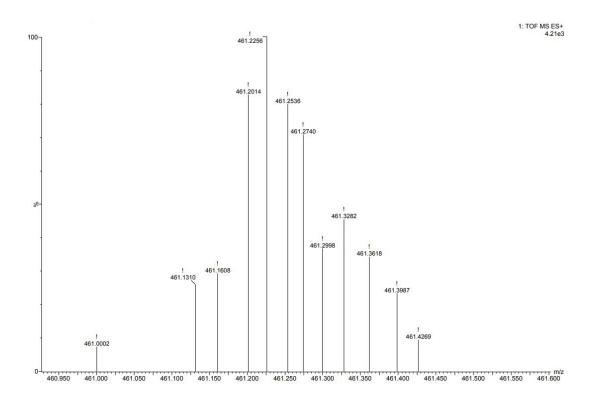


<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of product 9

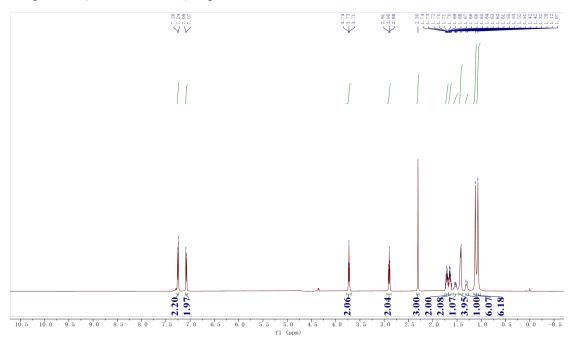


<sup>13</sup>C spectrum (151 MHz, CDCl<sub>3</sub>) of product 9

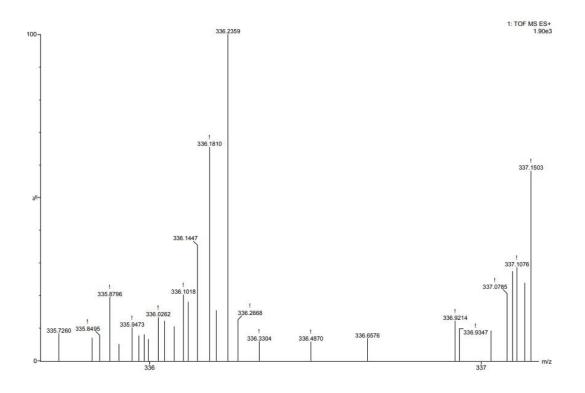




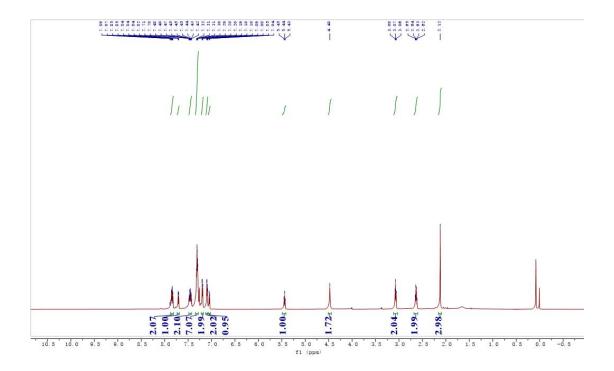
 $^{1}\mbox{H}$  spectrum (500 MHz, CDCl3) of product  $\boldsymbol{10}$ 



HRMS of product 10



<sup>1</sup>H spectrum (600 MHz, CDCl<sub>3</sub>) of product 12



<sup>13</sup>C spectrum (126 MHz, CDCl<sub>3</sub>) of product **12** 

