

# **Supporting Information for**

## **Lead-halide Perovskites Quantum Dots Embedded in**

### **Mesoporous Silica as Heterogeneous Photocatalysts**

#### **Combined with Organocatalysts for Asymmetric Catalysis**

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## Section 1. Materials and Characterization Methods

**Materials.** Reactions requiring an inert atmosphere were conducted under nitrogen using standard Schlenk tube techniques. All reagents and solvents were purchased from commercially, and the solvents used for catalytic reactions were predried with molecular sieves. All photo-reactions were carried out directly in the atmosphere unless otherwise stated.

**Characterization methods** Power X-ray diffraction (XRD) was used to investigate the crystal structure of the samples using Cu K $\alpha$  radiation under 40 kV and 40 mA.

Transmission electron microscopy (TEM, Talos F200X) and energy dispersive X-ray spectrometer (EDS) system were employed to characterize the morphologies, microstructures and the chemical compositions of the products.

X-ray photoelectron spectroscopy (XPS) was carried out on ESCALAB MKII X-ray photoelectron spectrometer (ESCALAB 250XI, Thermo Kalpha) using Al K $\alpha$  radiation.

UV-vis diffuse reflectance spectra (DRS) of the samples were performed on a UV-2600 spectrophotometer.

Photoluminescence (PL) spectra were performed on Shimadzu RF-5301PC fluorescence spectrophotometer with an excitation wavelength of 365 nm.

N<sub>2</sub> adsorption-desorption (77K) isotherms were performed on a Micromeritics ASAP 2460 (Mike) to determine the BET surface, pore size distribution and pore volume.

The actual chemical compositions of the samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer NexION 2000/1000).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker 600 MHz spectrometer (AVANCE III HD 600MHz). Chiral high performance liquid chromatography (HPLC) analysis for *ee* value determinations was performed using a Shimadzu LC-20AT apparatus equipped with SPD-20a UV detector and Daicel columns IC or AD-H columns, using hexane/iso-propanol as the eluent.

The Mott-Schottky measurements of CsPbBr<sub>3</sub> and 20CPB@KIT-6 samples were performed on an electrochemical analyzer (CHI-760E, CH Instruments Ins.) in a standard three-electrode system, where 0.1 M 1-butyl-3-methylimidazolium hexafluorophosphate (TBAPF<sub>6</sub>) in CH<sub>2</sub>Cl<sub>2</sub> solution was used as the electrolyte and the as-prepared samples, a standard Ag/AgCl in saturated KCl and

a platinum wire were used as the working, reference and counter electrodes, respectively.

## Section 2. Sample synthesis and Catalytic procedures

### Synthesis of CsPbBr<sub>3</sub>@KIT-6 heterogeneous photocatalysts and organocatalysts.

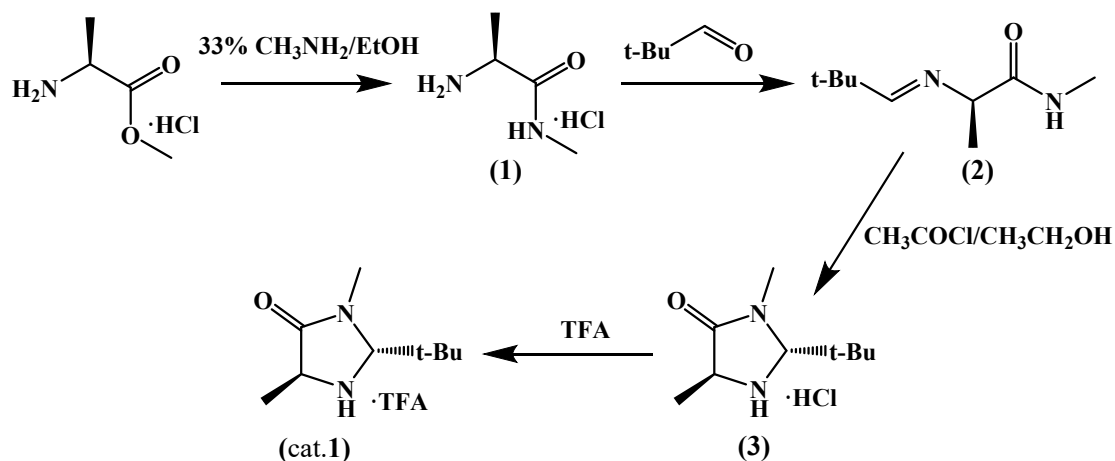
#### Synthesis of KIT-6, CsPbBr<sub>3</sub> and CsPbBr<sub>3</sub>@KIT-6 photocatalysts

The mesoporous silica (KIT-6) was synthesized based on previously reported literature<sup>1</sup>. 9 g of P123 (P123, poly(ethylene glycol)-poly-(propylene glycol)-poly(ethylene glycol)) was dissolved in the solution containing 325 g of distilled water and 17.40 g of HCl (37%). Continue stirring until the solution becomes clear. Then, 1-butanol (9.0 g) was added and the mixture was stirred at 35 °C for another 1h. 19.35 g of tetraethoxysilane was added into the uniform transparent solution, and the solution was continuously stirred at 35 °C for 24h, and then the solution was transferred to a Teflon bottle and heated to 100 °C for 24h. The obtained solid product was filtered, washed with deionized water and ethanol, and dried in a vacuum oven at 24h for 40 °C. The organic template in KIT-6 was removed by calcination treatment at 550 °C for 6h, and finally a white solid was obtained.

The CsPbBr<sub>3</sub>@KIT-6 composite photocatalysts were synthesized followed by a modified incipient wetness impregnation method<sup>2</sup>. To obtain different loading amounts of CsPbBr<sub>3</sub>, the amount of precursor CsBr and PbBr<sub>2</sub> (molar ratio 1:1) was changed, at the same time, KIT-6 (250 mg) and DMSO (0.33 mL) were added sequentially. The mixture was ground in an agate mortar and continuously ground for 30 min. The ground mixture was transferred to a vacuum drying oven at 150 °C for 30 min, and then the temperature was reduced to 80 °C for 6h. By varying the addition amounts, CsPbBr<sub>3</sub>@KIT-6 composites with loading amount of 5 wt%, 10 wt%, 20 wt% of CsPbBr<sub>3</sub> were prepared and denoted as 5CPB@KIT-6, 10CPB@KIT-6, 20CPB@KIT-6, respectively.

Large-scale synthesis of CsPbBr<sub>3</sub> nanoparticles. 255 mg CsBr and 441 mg PbBr<sub>2</sub> were dissolved in 30 mL DMF mixture solution (containing 3 mL oleic acid and 0.6 mL n-octylamine). The mixed solution was continuously at 60 °C until it became a clarified solution. Then, the precursor solution was quickly injected into 180 mL toluene (preheated to 60 °C) and vigorously stirred for 30s. The solution was washed several times with methyl acetate, and precipitated CsPbBr<sub>3</sub> nanoparticles were obtained by centrifugation and denoted as CPB.

### Synthesis of organocatalysts (cat.1 and cat.2).



### Synthesis of (*E*)-2-((2,2-dimethylpropylidene)amino)-*N*-methylpropanamide hydrochloride (2)

Under nitrogen, a solution of L-Alanine methyl ester hydrochloride (1.25 g, 8.95 mmol) was added in a 33 wt% solution of methylamine in ethanol (3.31 mL, 26.85 mmol) and stirred at room temperature for 48h. The mixture solution was concentrated under reduced pressure to afford a wet solid. Then, it was washed with toluene (10 mL  $\times$  3) to remove impurities and the solid was dried vacuum at 40 °C for 4h to afford a pasty solid. The pasty solid can be used directly for the next reaction without purification. MgSO<sub>4</sub> (0.85 g) and dry dichloromethane (4 mL) was added in the pasty solid. The mixture was stirred evenly at room temperature, then triethylamine (1.90 mL, 13.50 mmol) and pivaldehyde (1.08 mL, 9.63 mmol) were added, and the mixture was continued stirring at room temperature for 6h. Toluene (5.50 mL) was added to the above mixture solution and was continued stirring 15 min. Triethylamine and magnesium sulfate were removed by filtering and the solid was washed with toluene. The filtrate was evaporated under vacuum, and the emerging solid was washed with toluene again and filtered again. The filtrate was reconcentrated and dried at 45 °C for 4 h to obtain a pale oil **1** (0.55 g, yield: 57%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (s, 1H), 6.95 (s, 1H), 3.69 (d, *J* = 7.1, 1H), 2.85 (d, *J* = 5.0, 3H), 1.32 (d, *J* = 7.1, 3H), 1.08 (d, *J* = 2.8, 9H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  174.69, 173.05, 77.26, 77.05, 76.84, 67.49, 50.74, 36.39, 26.68, 25.85, 21.35.

### Synthesis of (2*R*,5*S*)-2-(*tert*-Butyl)-3,5-dimethylimidazolidin-4-one hydrochloride (3)

Under nitrogen, the bottle containing 12.48 mL of ethanol was placed in an ice water bath at 0 °C and acetyl chloride (1.79 mL, 24.64 mmol) was added dropwise to the solution of ethanol. **2**

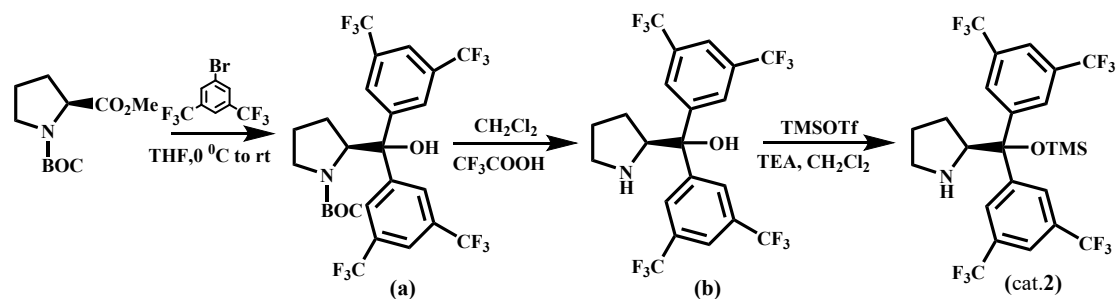
was added to the above solution, stirred for 20 min, then transferred to an oil bath at 70 °C and continued to react for 30 min. Finally, transfer to room temperature and continue stirring for 2 hours, then filter the crystals and wash it with ethanol (10 mL × 3) to obtain a white solid **3** (1.99 g, yield: 43%).

<sup>1</sup>H NMR (600 MHz, MeOD) δ 5.04 (s, 1H), 4.56 (q, J = 7.0, 1H), 3.35 (s, 3H), 1.85 (d, J = 7.1, 3H), 1.45 (s, 10H).

<sup>13</sup>C NMR (151 MHz, MeOD) δ 169.52, 80.37, 53.34, 36.13, 30.95, 23.85, 13.25.

*Synthesis of (2R,5S)-2-(tert-Butyl)-3,5-dimethylimidazolidin-4-one trifluoroacetate (cat.1)*

0.32 g of **3** was dissolved in 4 ml of saturated aqueous NaHCO<sub>3</sub>, and the organic layer was extracted with CHCl<sub>3</sub> (5 mL × 5) and collect it. The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The obtained oil was dissolved in anhydrous Et<sub>2</sub>O (5 mL) under ice water bath conditions, and TFA (141 μL, 1.9 mmol) was added dropwise while stirring, and a white solid was generated after stirring for 3 min. After continuing stirring for 10 min, it was filtered, washed with Et<sub>2</sub>O (25 mL × 2) and dried under vacuum to give a final white solid cat.1 (0.36 g, yield: 86%).



*Synthesis of tert-butyl (S)-2-(bis(3,5-bis(trifluoromethyl)phenyl)(hydroxy)methyl)pyrrolidine-1-carboxylate (a)*

Under nitrogen, a solution of 1-bromo-3,5-bis(trifluoromethyl)benzene (3.37 mL, 19.57 mmol) in 16 mL of anhydrous THF was cooled to 0 °C. A solution of isopropylmagnesium chloride lithium chloride (15.81 mL, 20.55 mmol) was added dropwise by an addition funnel. The reaction mixture was stirred at 0 °C for 1h and then a solution of N-BOC-L-proline methyl ester (1.121 mg, 4.89 mmol) in anhydrous THF (4.5 mL) was added to the reaction and stirred for another 3h. The reaction mixture was warmed up to room temperature and stirred overnight. Consumption conversion rate of the reactants was checked by TLC (Petroleum ether/EtOAc = 10:1). And it was

quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (40 mL) and extracted with ethylacetate (40 mL  $\times$  3). The organic layer dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel. The product was a white solid **a** (1.92 g, yield: 61%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (t,  $J = 11.0$  Hz, 4H), 7.81 (s, 2H), 4.82 (dd,  $J = 8.8, 5.7$  Hz, 1H), 3.47 (ddd,  $J = 11.2, 8.1, 6.1$  Hz, 1H), 2.84 (dt,  $J = 11.2, 7.2$  Hz, 1H), 2.08 (tt,  $J = 16.7, 8.3$  Hz, 1H), 1.77 (td,  $J = 13.5, 6.8$  Hz, 1H), 1.65 – 1.59 (m, 1H), 1.40 (s, 9H), 1.02 (dt,  $J = 20.6, 6.9$  Hz, 1H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  158.21 (s), 147.17 (s), 145.33 (s), 132.21 (s), 131.99 (s), 131.74 (d,  $J = 7.6$  Hz), 131.52 (d,  $J = 7.3$  Hz), 131.28 (s), 128.21 (d,  $J = 2.7$  Hz), 127.78 (d,  $J = 2.9$  Hz), 124.23 (d,  $J = 14.2$  Hz), 122.44 (dd,  $J = 13.8, 4.0$  Hz), 122.04 (ddt,  $J = 29.9, 7.6, 3.6$  Hz), 82.19 (s), 81.01 (s), 66.72 (s), 48.29 (s), 30.51 (s), 28.23 (s), 23.28 (s).

*Synthesis of (S)-bis(3,5-bis(trifluoromethyl)phenyl)(pyrrolidin-2-yl)methanol (b)*

A certain amount of **a** (1.956 g, 3.12 mmol) was added to a mixture of DCM (14 mL) and TFA (14 mL). The mixture was stirred at room temperature for 1h and then the volatile products were removed under vacuum. The residue was dissolved again in DCM and aqueous saturated  $\text{NaHCO}_3$  was added until pH = 7. The layers were separated and the aqueous phase was extracted with DCM (3  $\times$  6 mL). The combined organic layer dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel. The product was a white solid **b** (1.4 g, yield: 86%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (s, 2H), 7.96 (s, 2H), 7.76 (d,  $J = 6.6$  Hz, 2H), 5.07 (s, 1H), 4.35 (t,  $J = 7.7$  Hz, 1H), 3.10 – 3.02 (m, 2H), 1.82 – 1.76 (m, 2H), 1.64 – 1.46 (m, 3H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  149.54 (s), 146.61 (s), 132.55 (s), 132.31 (d,  $J = 4.8$  Hz), 132.09 (d,  $J = 4.8$  Hz), 131.87 (d,  $J = 4.8$  Hz), 126.13 (t,  $J = 9.0$  Hz), 125.79 (d,  $J = 3.1$  Hz), 124.24 (d,  $J = 1.7$  Hz), 122.43 (d,  $J = 1.9$  Hz), 121.87 – 121.32 (m), 120.62 (s), 76.76 (s), 64.35 (s), 47.10 (s), 26.85 (s), 25.70 (s).

*Synthesis of (s)-2-[Bis-(3-5-bistrifluoromethy-phenyl)-trimethyl-silanyloxy-methyl]-pyrrolidine (cat.2)*

Under nitrogen, a stirred solution of **b** (0.6 g, 1.14 mmol) and TEA (0.48 mL, 3.42 mmol) in  $\text{CH}_2\text{Cl}_2$  (4.5 mL) at 0 °C was added TMSOTf (1.71 mL, 9.45 mmol). Then, the reaction was stirred for 3 h and warmed to room temperature for another 3h. The solution was quenched by the



addition of water (6 mL). The layers were separated and the aqueous phase was extracted with EtOAc (3 x 4 mL). The composite layer was washed with saturated brine, the organic phase was dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel. The product was a white solid **cat.2** (0.55 g, yield: 81%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.00 (s, 1H), 7.84 (d, *J* = 5.6 Hz, 1H), 7.76 (s, 1H), 4.23 (s, 1H), 2.93 (dd, *J* = 16.7, 7.1 Hz, 1H), 2.57 (dd, *J* = 15.8, 6.5 Hz, 1H), 1.71 (s, 1H), 1.54 (s, 1H), 1.46 (s, 1H), 1.12 (s, 1H), -0.08 (s, 5H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 148.27 (s), 146.47 (s), 131.79 (s), 131.57 (s), 131.03 (s), 130.81 (s), 128.70 (s), 128.18 (s), 124.37 (s), 124.18 (s), 122.56 (s), 122.37 (s), 121.69 (d, *J* = 27.5 Hz), 82.42 (s), 64.36 (s), 47.35 (s), 27.65 (s), 25.37 (s), 2.00 (s).

### Section 3. Structure and morphology

Table S1. Summary of metal content in the samples.

Sample	Atomic ratio of Cs:Pb		CPB (wt.%)	
	In precursor	ICP	In precursor	ICP
CPB	1:1	1.07:0.93	--	--
5CPB@KIT-6	1:1	1.03:0.97	5.0	4.1
10CPB@KIT-6	1:1	1.06:0.94	10.0	8.9
20CPB@KIT-6	1:1	1.02:0.98	20.0	18.7

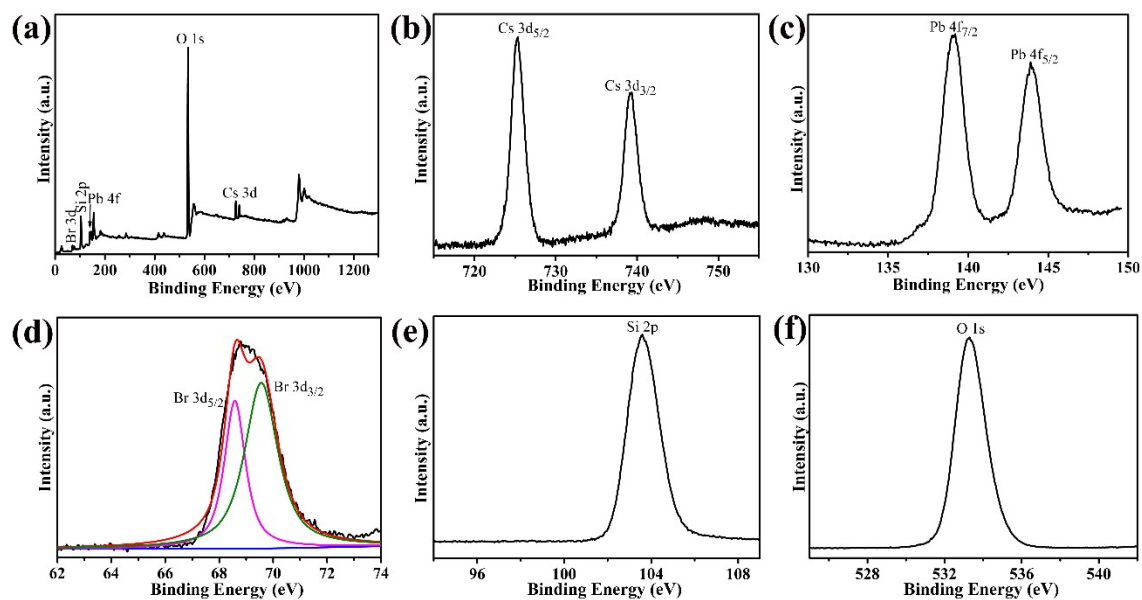


Fig. S1 X-ray photoelectron spectroscopy (XPS) analysis of 20CPB@KIT-6 photocatalysts.

## Section 4. Optical properties

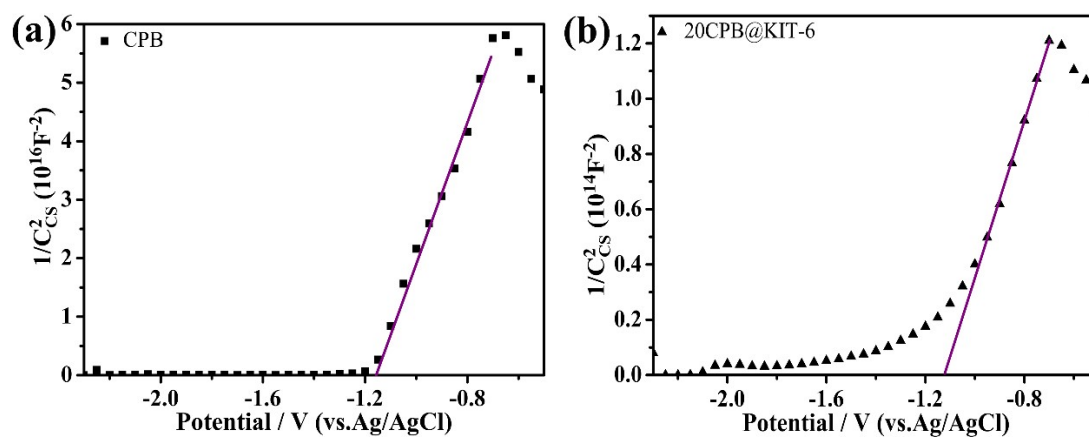


Fig. S2 The Mott-Schottky plots of CPB and 20CPB@KIT-6.

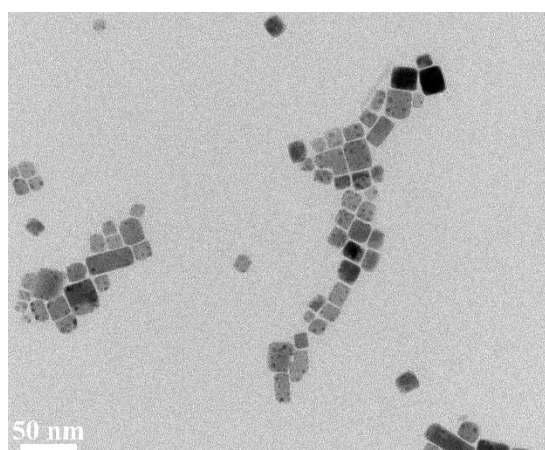


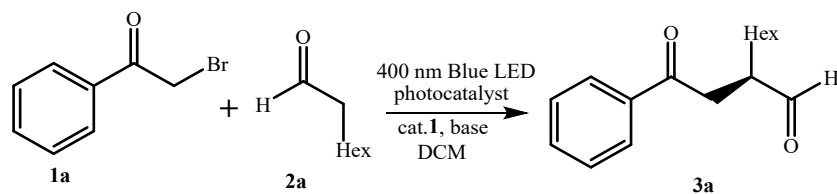
Fig. S3 HRTEM image of pure CPB quantum dots.

Table S2. The fitted time-resolved fluorescence decay parameters.

Photocatalyst	$\tau_1/\text{ns}$	$A_1/\%$	$\tau_2/\text{ns}$	$A_2/\%$	$\tau_{aver}/\text{ns}$
CPB	4.2711	31.46	22.2995	68.54	20.8426
20CPB@KIT-6	2.2677	42.84	8.3205	57.18	7.2945

## Section 5. Asymmetric photoredox reactions

### 5.1 General procedure for photocatalytic reaction of benzyl bromide with aldehydes (GP1):



Bromide **1a** (0.5 mmol, 1.0 eq), aldehyde **2a** (1.0 mmol, 2.0 eq), photocatalyst (based on CsPbBr<sub>3</sub>, 1 mg), cat.1 (20 mol%), additives (1.0 eq). solvent (1 mL) was added into a 5mL test tube, and stirred under the irradiated by 400 nm LEDs at room temperature for 14h without inert gas protection. After the reaction was complete, the mixture solution was quenched with water and the organic phases were extracted with Et<sub>2</sub>O (3 × 10 mL). The combined organic phases were dried over MgSO<sub>4</sub> and concentrated in vacuum to provide a crude mixture. The crude mixture was purified by column chromatography to afford the desired product. The *ee* value was determined by HPLC using chiral IC columns and hexane/iso-propanol as the eluent.

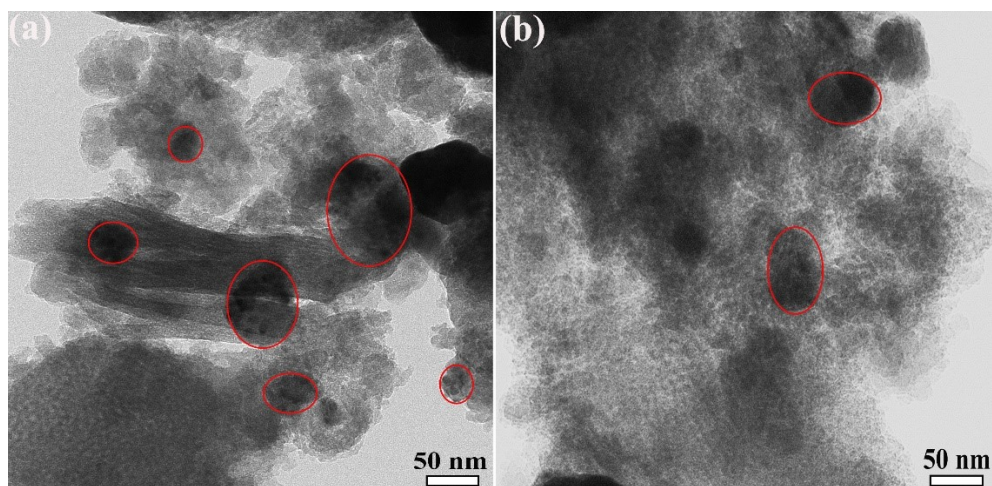


Fig. S4 TEM image of 20CPB/KIT-6 (a) before and (b) after the reaction.

Table S3. Selected the amount of base, cat.1 and substrate ratio for the reaction of benzyl bromide and aldehydes<sup>a</sup>

Entry	2,6-Lutidine (eq)	Substrate ratios 1a:2a	Cat.1 (mol %)	Yield <sup>d</sup> (%)	ee <sup>e</sup> (%)
1	2	1:2	20	68.4	90.2
2	0.5	1:2	20	50.3	89.9
3	1	1:2	20	54.3	89.7
4	3	1:2	20	61.9	83.6
5	2	1:0.5	20	59.2	70.2
6	2	1:1	20	61.7	79.3
7	2	1:3	20	63.9	82.5
8	2	1:2	10	56.2	82.1
9	2	1:2	15	64.1	87.4
10	2	1:2	25	58.2	90.2
11 <sup>b</sup>	2	1:2	20	82.4	89.0
12 <sup>c</sup>	2	1:2	20	40.2	41.6

<sup>a</sup> Reaction conditions: 1a (0.5 mmol), 2a (x eq), 20CPB@KIT-6(5 mg), cat.1 (x mol%), base (x eq) and solvent (1 mL) under 400 nm LED illumination at R.T.; <sup>b</sup> (0.5 mol%) Ru(bpy)<sub>3</sub>Cl<sub>2</sub> in N<sub>2</sub> atmosphere; <sup>c</sup> (0.5 mol%) Ru(bpy)<sub>3</sub>Cl<sub>2</sub> under normal atmospheric; <sup>d</sup> Yield of the isolated product after chromatography on silica gel; <sup>e</sup> Determined by HPLC analysis using a chiral IC column.

Table S4. Optimization of the control experiments<sup>a</sup>

Entry	Conditions	Yield (%)	ee (%)
1	standard conditions	68.4	90.2
2	dark	n.d.	--
3	No cat.1	58.2	--
4	No photocatalyst	n.d.	--

<sup>a</sup> Reaction conditions: 1a (0.5 mmol), 2a (1.0 mmol), 20CPB@KIT-6(5 mg), cat.1 (20 mol%), 2,6-lutidine (1.0 mmol) and DCM (1 mL) under 400 nm LED illumination at R.T.

**Recycle experiments.** According to **GPI**, the photocatalyst was filtered out after the reaction, washed and dried with dichloromethane, and can be directly used in the next reaction. Repeat this operation in the cyclic experiments.

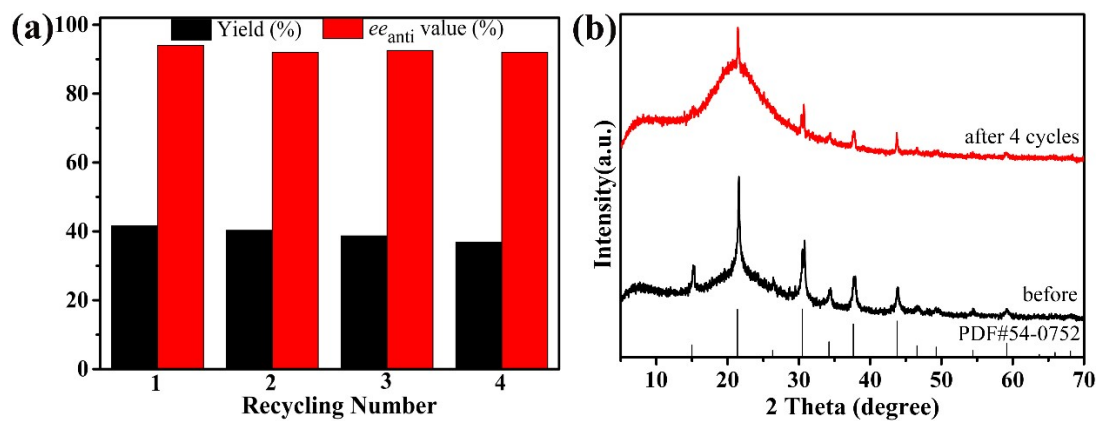


Fig. S5 (a) The recycle reactions for 20CPB@KIT-6. (b) XRD patterns of 20CPB@KIT-6 obtained before and after four cycles.

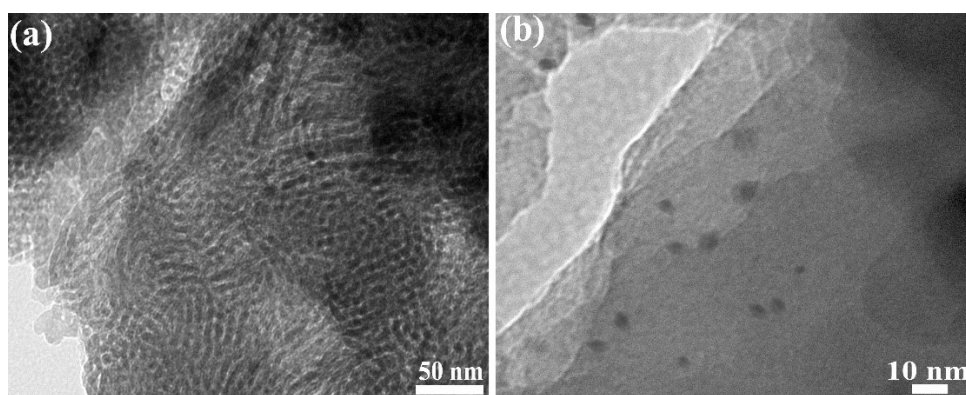


Fig. S6 TEM image of 20CPB@KIT-6 after 4 cycles.

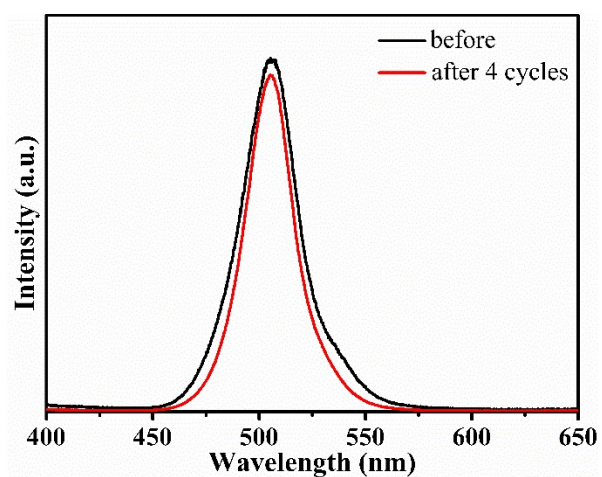


Fig. S7 PL intensity spectra of 20CPB@KIT-6 obtained before and after 4 cycles.

## 5.2 The turnover numbers and turnover frequency

Comparison of turnover numbers (TONs) between CPB, 20CPB@KIT-6 and noble-metal Ru(bpy)<sub>3</sub>Cl<sub>2</sub>. TON of CPB, 20CPB@KIT-6 or Ru(bpy)<sub>3</sub>Cl<sub>2</sub> photocatalyst are calculated in this way:

$$TON = \frac{\text{total mol of product}}{\text{total mol of photocatalyst}}$$

Here total mol of photocatalyst calculated based on Pb or Ru.

TON of 20CPB@KIT-6:

As previously reported<sup>3</sup>, when the reaction was expanded by 50 times and 5 mg 20CPB@KIT-6 composite photocatalyst was still used, the yield of **3a** was 63.2% after 48 hours. The reaction mixture was separated by centrifugation to obtain 20CPB@KIT-6 and then reused in the next reaction of the same scale. After four cycles, the catalyst kept stable (yield 65.8%, 63.3%, 63.2%, 60.9%, average ~63.3%). TON of 20CPB@KIT-6 photocatalyst is calculated in this way: TON is equal to total mol of product **3a** in 4 cycles of reaction over mol of Pb. TON = (0.5 mmol×50×4×63.3%)/(1 mg/ 579.8 g mol<sup>-1</sup>) ≈ 36700

TON of CPB:

The TON of CPB was similar to that of 20CPB@KIT-6, except that 1 mg of CPB was added and the yield of **3a** was 58.4%, 56.7%, 56.2%, 54.3% (average ~56.4%). TON = (0.5 mmol×50×4×56.4%)/(1 mg/ 579.8 g mol<sup>-1</sup>) ≈ 32700.

TON of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> under N<sub>2</sub> atmosphere:

For 0.5 mmol scale reaction **1a**, 0.5 mol% Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was used, leading to **3a** in 82.4% yield after 14 hours. TON = (0.5 mmol×82.4%)/(0.5 mol%×0.5 mmol) ≈ 170.

TON of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> under normal atmospheric

For 0.5 mmol scale reaction **1a**, 0.5 mol% Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was used, leading to **3a** in 40.2% yield after 14 hours. TON = (0.5 mmol×40.2%)/(0.5 mol%×0.5 mmol) ≈ 80.

Comparison of turnover frequency (TOF) between CPB, 20CPB@KIT-6 and noble-metal Ru(bpy)<sub>3</sub>Cl<sub>2</sub>. TOF of CPB, 20CPB@KIT-6 or Ru(bpy)<sub>3</sub>Cl<sub>2</sub> photocatalyst are calculated in this way:

$$TOF = \frac{\text{total mol of product}}{\text{total mol of photocatalyst} \times \text{reaction time}}$$

Here total mol of photocatalyst calculated based on Pb or Ru.

TOF of 20CPB@KIT-6:

TOF of 20CPB@KIT-6 photocatalyst is calculated in this way: TOF is equal to total mol of product **3a** in 4 cycles of reaction over mol of Pb.  $\text{TOF} = (0.5 \text{ mmol} \times 50 \times 4 \times 63.3\%) / [(1 \text{ mg} / 579.8 \text{ g mol}^{-1}) \times 48 \text{ h}] \approx 764.6 \text{ h}^{-1}$ .

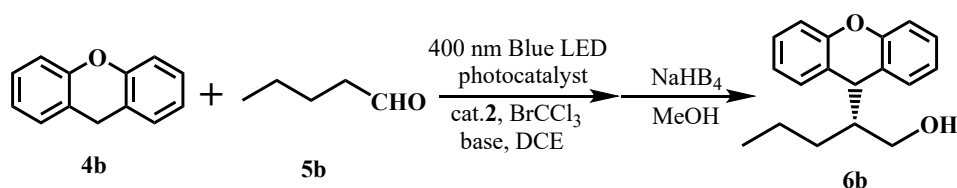
TOF of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> under N<sub>2</sub> atmosphere:

For 0.5 mmol scale reaction **1a**, 0.5 mol% Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was used, leading to **3a** in 82.4% yield after 14 hours.  $\text{TOF} = (0.5 \text{ mmol} \times 82.4\%) / [(0.5 \text{ mol}\% \times 0.5 \text{ mmol}) \times 14 \text{ h}] \approx 11.8 \text{ h}^{-1}$ .

TOF of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> under normal atmosphere:

For 0.5 mmol scale reaction **1a**, 0.5 mol% Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was used, leading to **3a** in 40.2% yield after 14 hours.  $\text{TOF} = (0.5 \text{ mmol} \times 40.2\%) / [(0.5 \text{ mol}\% \times 0.5 \text{ mmol}) \times 14 \text{ h}] \approx 5.7 \text{ h}^{-1}$ .

### 5.3 General procedure for photoredox cross-dehydrogenative coupling of aldehydes with xanthenes (GP2):



5 mL test tube was contained with xanthene **4b** (0.2 mmol, 1.0 eq), photocatalyst (based on CsPbBr<sub>3</sub>, 1 mg), cat.2 (11.9 mg, 0.02 mmol, 10 mol%), Na<sub>3</sub>PO<sub>4</sub> (49.2 mg, 0.3 mmol, 1.5 eq). DCE (2 mL) was added to the test tube, followed by aldehyde (0.6 mmol, 3.0 eq) and bromotrichloromethane (29.6  $\mu$ L, 0.3 mmol, 1.5 eq). The test tube was sealed and the reaction mixture was irradiated by 400 nm LEDs at 20 °C for 16 h without inert gas protection. After the reaction was complete, MeOH (1 mL) was added to the reaction mixture, and NaBH<sub>4</sub> (76 mg, 2 mmol) was cautiously added to the solution at 0 °C. The reaction mixture was stirred at room temperature for 0.5 h and subsequently quenched with water (1 mL) and HCl (1 M). The organic phase was separated and the aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  5 mL). The combined organic phases were dried over MgSO<sub>4</sub> and concentrated in vacuum to provide a crude mixture. The crude mixture was purified by column chromatography (Petroleum ether/EtOAc = 50:1 to 20:1) to afford the desired product. The *ee* value was determined by HPLC using chiral AD-H columns and hexane/iso-propanol as the eluent.



Table S5. The effect of temperature and time on the reaction <sup>a</sup>

Entry	Base	Solvent <sup>b</sup>	T (°C)	t (h)	Yield (%) <sup>c</sup>	ee (%) <sup>d</sup>
1	Na <sub>3</sub> PO <sub>4</sub>	DCE	35	14	44.8	89.2
2	Na <sub>3</sub> PO <sub>4</sub>	DCE	0	14	9.7	91.1
3	Na <sub>3</sub> PO <sub>4</sub>	DCE	R.T.	10	32.8	93.6
4	Na <sub>3</sub> PO <sub>4</sub>	DCE	R.T.	18	48.5	87.9

<sup>a</sup> Reaction conditions: 1b (0.2 mmol), 2b (0.6 mmol), 20CPB@KIT-6(5 mg), cat.2 (10 mol%), DCE (2 mL) and Na<sub>3</sub>PO<sub>4</sub> (0.3 mmol) under 400 nm LED illumination at R.T.; <sup>b</sup> molecule sieves predried solvent; <sup>c</sup> Yield of the isolated product after chromatography on silica gel; <sup>d</sup> Determined by HPLC analysis using a chiral AD-H column.

Table S6. Optimization of the control experiments <sup>a</sup>

Entry	Conditions	Yield (%)	ee (%)
1	standard conditions	41.6	94.2
2	dark	n.d.	--
3	No cat.2	43.2.	4.2
4	No photocatalyst	n.d.	--
5	No Na <sub>3</sub> PO <sub>4</sub>	6.4	10.9
6	No BrCCl <sub>3</sub>	n.d.	--

<sup>a</sup> Reaction conditions: 1b (0.2 mmol), 2b (0.6 mmol), 20CPB@KIT-6(5 mg), cat.2 (10 mol%), DCE (2 mL) and Na<sub>3</sub>PO<sub>4</sub> (0.3 mmol) under 400 nm LED illumination at R.T.

## Section 6. Asymmetric catalysis reaction mechanism

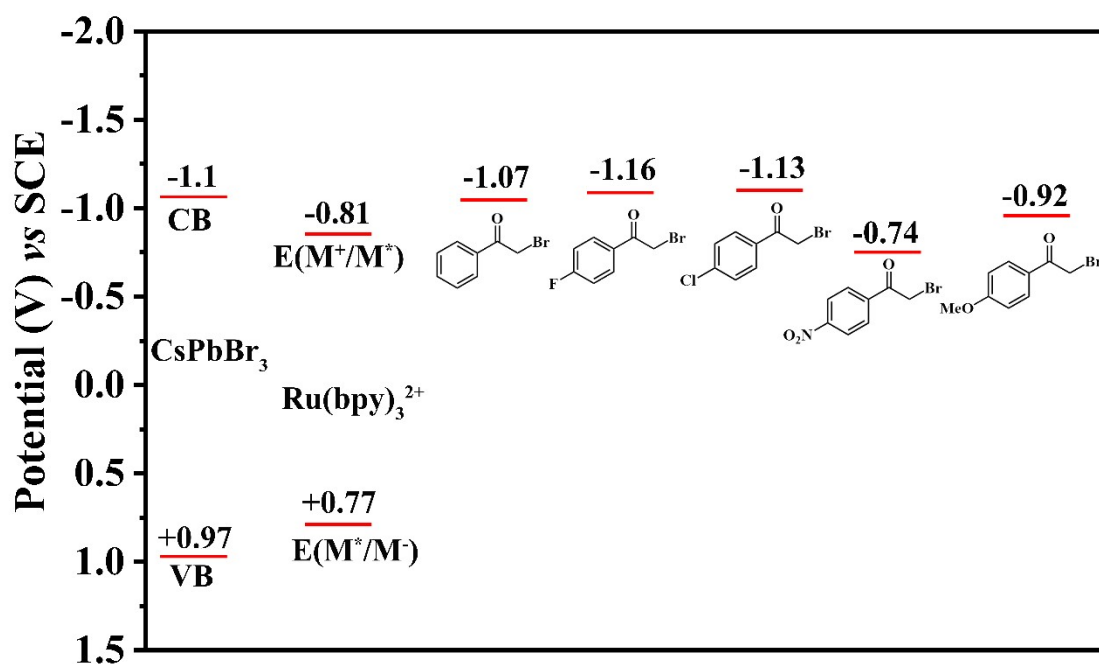
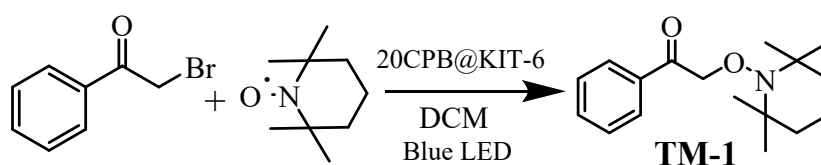


Fig. S8 Band energy of CsPbBr<sub>3</sub> vs the redox potentials of Ru(bpy)<sub>3</sub><sup>2+</sup> or substrates. The date of Ru(bpy)<sub>3</sub><sup>2+</sup> or substrates was obtained from the corresponding literature<sup>3-5</sup>.

### Radical Trapping Experiments



In a 5 mL vial, 2-bromoacetophenone (0.5 mmol), TEMPO (1 mmol), 20CPB@KIT-6 (5mg), and 1 mL DCM were added and then stirred under the irradiation with 400 nm LED lamp for 14h. The mixture was washed with water and the organic phases were extracted with Et<sub>2</sub>O (3 × 10 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum to provide a crude mixture. Purification of the crude product by column chromatography (silica gel) to afford the TEMPO trapped compound TM-1, which has been confirmed by <sup>1</sup>H-NMR.

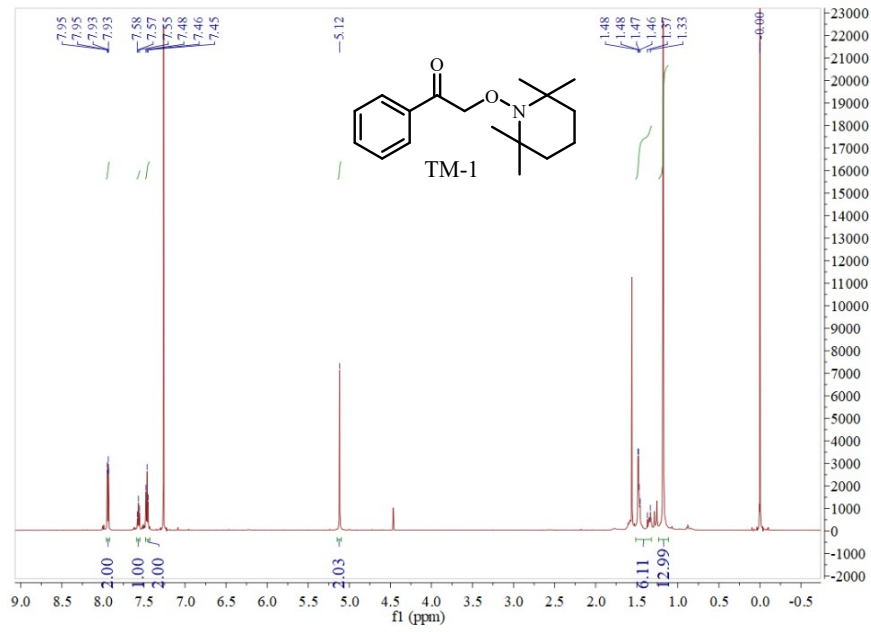


Figure S9. <sup>1</sup>H NMR for TM-1.

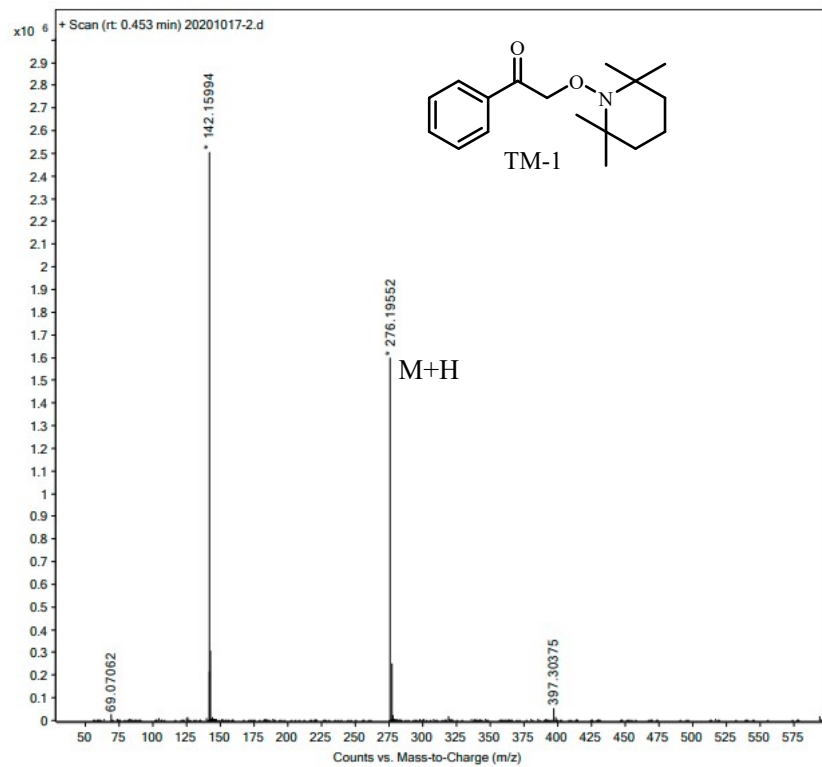
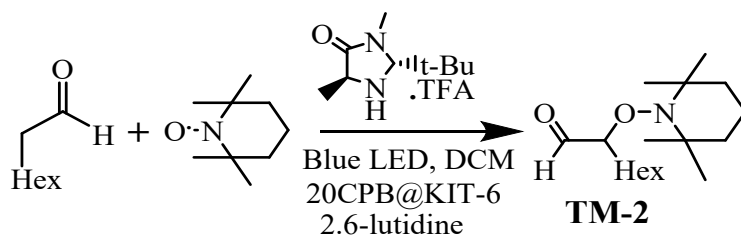


Figure S10 .HR-MS evidence for TM-1.



In a 5 mL vial, octanal (1 mmol), TEMPO (1 mmol), cocatalyst (0.2 mmol), 20CPB@KIT-6 (5mg), and 1 mL DCM were added and then stirred under the irradiation with 400 nm LED lamp for 14h. The mixture was washed with water and the organic phases were extracted with Et<sub>2</sub>O (3 × 10 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum to provide a crude mixture. Purification of the crude product by column chromatography (silica gel) to afford the TEMPO trapped compound TM-2, which has been confirmed by <sup>1</sup>H-NMR.

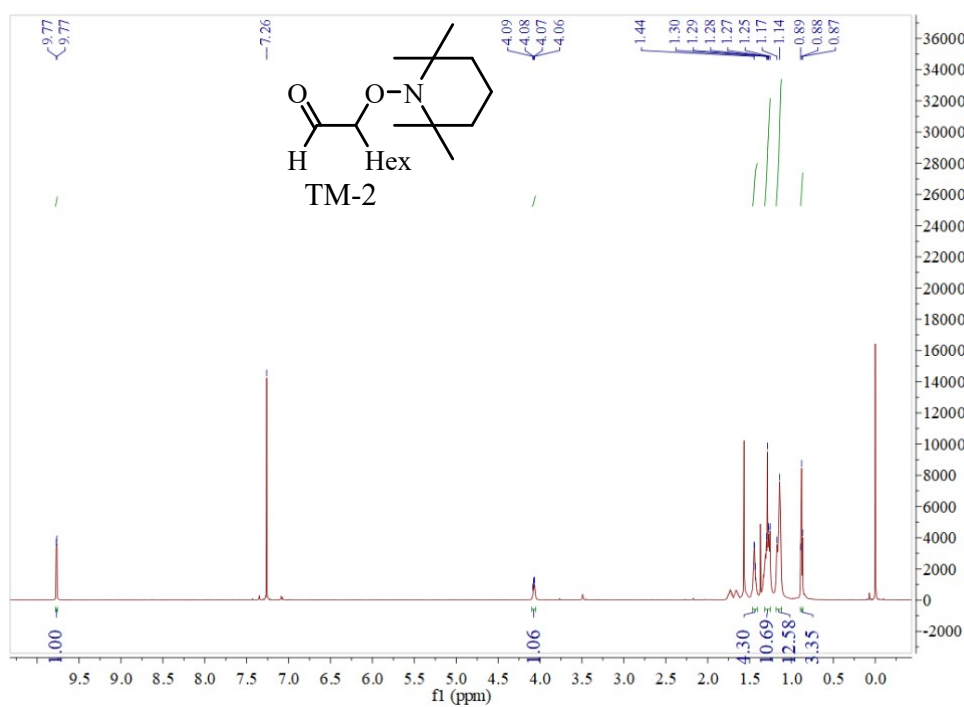


Figure S11. <sup>1</sup>H NMR for TM-2.

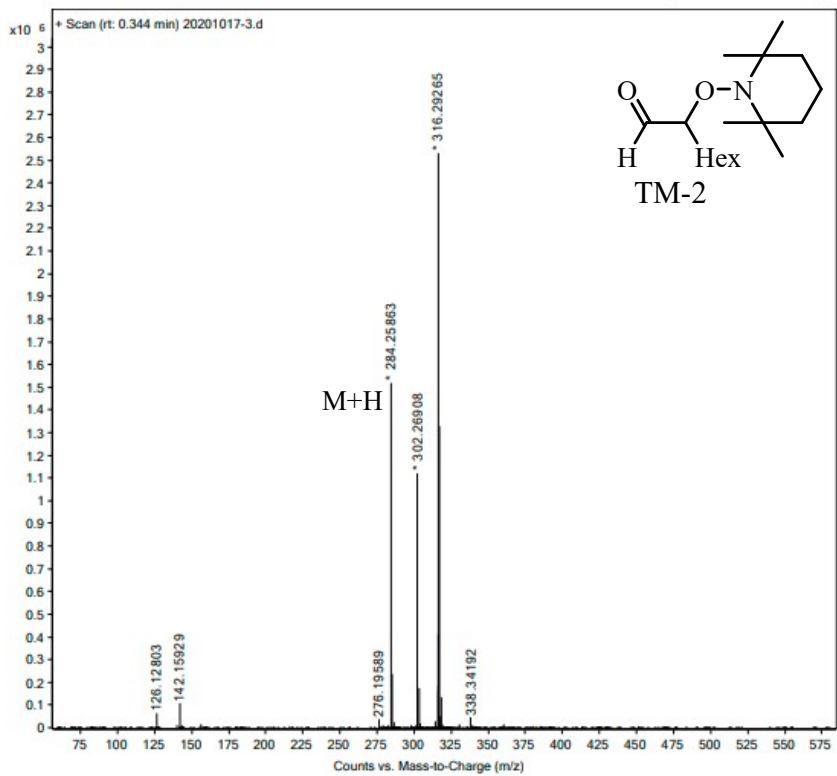
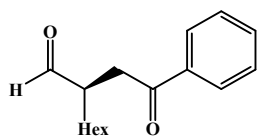


Figure S12. HR-MS evidence for TM-2.

## Section 7. Characterization data of products

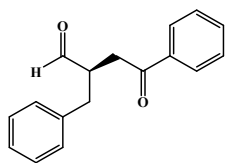


**(R)-2-(2-Oxo-2-phenylethyl)hexanal (3a):** The product was prepared

according to GP1 from octanal (1.0 mmol, 2.0 eq) and 2-bromoacetophenone (0.5 mmol, 1.0 eq) to afford colorless oil, yield: 68.4%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.83 (s, 1H), 7.98 (dd,  $J=8.3, 1.2$ , 2H), 7.58 (t,  $J=7.4$ , 1H), 7.47 (dd,  $J=11.0, 4.6$ , 2H), 3.48 (dd,  $J=17.8, 7.9$ , 1H), 3.10 (dt,  $J=12.5, 6.2$ , 1H), 3.02 (dd,  $J=17.8, 4.8$ , 1H), 1.79 (m, 1H), 1.54 (dd,  $J=13.6, 6.9$ , 1H), 1.31 (m, 9H), 0.88 (t,  $J=7.0$ , 3H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 203.66, 198.05, 136.61, 133.29, 128.64, 128.10, 77.23, 77.02, 76.81, 46.77, 37.67, 31.59, 29.34, 28.89, 27.07, 22.56, 14.04.

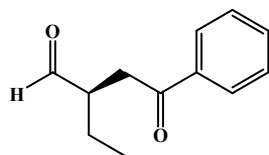


**R-2-Benzyl-4-oxo-4-phenylbutanal (3b):** The product was prepared

according to GP1 from 3-phenylpropionaldehyde (1.0 mmol, 2.0 eq) and 2-bromoacetophenone (0.5 mmol, 1.0 eq) to afford white solid, yield: 63.1%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.90 (s, 1H), 7.90 (dd,  $J=8.3, 1.2$ , 2H), 7.56 (t,  $J=7.4$ , 1H), 7.44 (t,  $J=7.8$ , 2H), 7.30 (t,  $J=7.5$ , 2H), 7.22 (m, 4H), 3.41 (m, 2H), 3.17 (dd,  $J=14.0, 6.2$ , 1H), 3.02 (m, 1H), 2.82 (m, 1H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 203.05, 197.88, 138.13, 136.45, 133.38, 129.06, 128.78, 128.64, 128.08, 126.76, 77.25, 77.04, 76.83, 48.38, 37.28, 34.75.



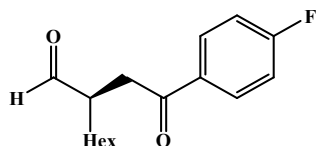
**(R)-2-ethyl-4-oxo-4-phenylbutanal (3c):** The product was prepared

according to GP1 from butyraldehyde (1.0 mmol, 2.0 eq) and 2-bromoacetophenone (0.5 mmol, 1.0 eq) to afford colorless oil, yield: 71.2%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.83 (s, 1H), 7.98 (d,  $J = 8.0$  Hz, 2H), 7.58 (t,  $J = 7.3$  Hz, 1H), 7.47

(t,  $J = 7.5$  Hz, 2H), 3.48 (dd,  $J = 17.5, 7.5$  Hz, 1H), 3.04 (m, 2H), 1.85 (dt,  $J = 14.3, 7.2$  Hz, 1H), 1.64 (m, 1H), 1.01 (t,  $J = 7.5$  Hz, 3H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  203.59, 198.03, 136.63, 133.30, 128.65, 128.10, 77.24, 77.03, 76.82, 48.07, 37.12, 21.89, 11.46.

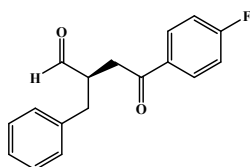


**(R)-2-(2-(4-fluorophenyl)-2-oxoethyl)-3-oxooctanal (3d):** The

product was prepared according to GP1 from octanal (1.0 mmol, 2.0 eq) and 2-bromo-4'-fluoroacetophenone (0.5 mmol, 1.0 eq) to afford colorless oil, yield: 60.6%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.82 (s, 1H), 8.01 (m, 2H), 7.14 (t,  $J=8.6$ , 2H), 3.45 (dd,  $J=17.8$ , 8.1, 1H), 3.11 (td,  $J=11.7, 6.9$ , 1H), 2.97 (dd,  $J=17.8, 4.6$ , 1H), 1.80 (dt,  $J=15.8, 6.6$ , 1H), 1.53 (m, 1H), 1.34 (m, 9H), 0.88 (t,  $J=7.0$ , 3H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 203.52, 196.47, 166.72, 165.03, 133.07, 130.75, 115.82, 115.68, 77.23, 77.02, 76.81, 46.80, 37.49, 31.59, 29.33, 28.87, 27.07, 22.56, 14.04. HRMS (ESI+) calculated for  $\text{C}_{16}\text{H}_{22}\text{FO}_2$  [M+H]: 265.16038 found 265.15813.

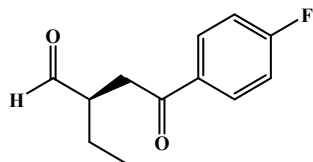


**(R)-2-benzyl-4-(4-fluorophenyl)-4-oxobutanal (3e):** The product was

prepared according to GP1 from 3-phenylpropionaldehyde (1.0 mmol, 2.0 eq) and 2-bromo-4'-fluoroacetophenone (0.5 mmol, 1.0 eq) to afford colorless oil, yield: 59.1%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.89 (s, 1H), 7.93 (m, 2H), 7.30 (t,  $J = 7.4$  Hz, 2H), 7.23 (t,  $J = 7.4$  Hz, 1H), 7.19 (d,  $J = 7.0$  Hz, 2H), 7.11 (t,  $J = 8.6$  Hz, 2H), 3.39 (m, 2H), 3.17 (dd,  $J = 14.0, 6.1$  Hz, 1H), 2.96 (m, 1H), 2.82 (dd,  $J = 14.0, 8.2$  Hz, 1H).

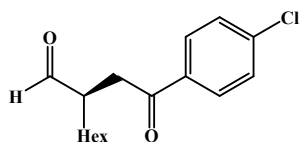
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  202.86, 196.27, 166.74, 165.05, 138.00, 132.92, 130.73, 129.02, 128.79, 126.81, 115.81, 115.66, 77.23, 77.02, 76.81, 48.40, 37.08, 34.71.



**(R)-2-ethyl-4-(4-fluorophenyl)-4-oxobutanal (3f):** The product was prepared according to GP1 from butyraldehyde (1.0 mmol, 2.0 eq) and 2-bromo-4'-fluoroacetophenone (0.5 mmol, 2.0 eq) to afford colorless oil, yield: 70.7%.

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.82 (s, 1H), 8.01 (dd,  $J = 8.9, 5.4$  Hz, 2H), 7.14 (dd,  $J = 12.0, 5.3$  Hz, 2H), 3.45 (dd,  $J = 17.7, 7.9$  Hz, 1H), 3.08 (dd,  $J = 11.6, 6.7$  Hz, 1H), 2.97 (m, 1H), 1.85 (m, 1H), 1.65 (dd,  $J = 14.2, 7.3$  Hz, 1H), 1.02 (t,  $J = 7.5$  Hz, 3H).

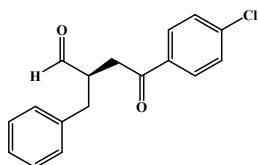
$^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  203.47, 196.45, 166.72, 165.03, 133.08, 130.75, 115.83, 115.68, 77.25, 77.04, 76.82, 48.08, 36.95, 21.87, 11.45.



**(R)-2-(2-(4-chlorophenyl)-2-oxoethyl)-3-oxooctanal (3g):** The product was prepared according to GP1 from octanal (1.0 mmol, 1.0 eq) and 2-bromo-4'-chloroacetophenone (0.5 mmol, 2.0 eq) to afford yellow oil, yield: 69.4%.

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.81 (s, 1H), 7.91 (d,  $J = 8.6$  Hz, 2H), 7.44 (d,  $J = 8.5$  Hz, 2H), 3.44 (dd,  $J = 17.8, 8.1$  Hz, 1H), 3.10 (dd,  $J = 13.0, 6.1$  Hz, 1H), 2.96 (dd,  $J = 17.8, 4.6$  Hz, 1H), 1.79 (m, 1H), 1.54 (m, 1H), 1.31 (m, 9H), 0.88 (t,  $J = 6.9$  Hz, 3H).

$^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  203.41, 196.86, 139.74, 134.95, 129.52, 128.95, 77.26, 77.05, 76.83, 46.79, 37.51, 31.58, 29.32, 28.84, 27.06, 22.55, 14.03.



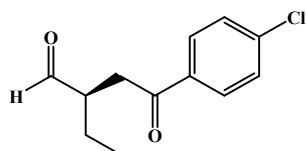
**(R)-2-benzyl-4-(4-chlorophenyl)-4-oxobutanal (3h):** The product was prepared according to GP1 from 3-phenylpropionaldehyde (1.0 mmol, 1.0 eq) and 2-bromo-4'-chloroacetophenone (0.5 mmol, 2.0 eq) to afford colorless oil, yield: 54.1%.

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.89 (s, 1H), 7.83 (m, 2H), 7.41 (m, 2H), 7.31 (dd,  $J=10.2, 4.6$ , 2H), 7.24 (m, 1H), 7.19 (m, 2H), 3.38 (m, 2H), 3.17 (m, 1H), 2.94 (dd,  $J=16.7, 3.4$ , 1H), 2.82 (m,



1H).

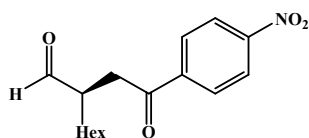
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 202.79, 196.68, 139.82, 137.93, 134.78, 129.48, 128.98, 128.81, 126.83, 77.23, 77.02, 76.80, 48.39, 37.07, 34.68. HRMS (ESI+) calculated for  $\text{C}_{17}\text{H}_{16}\text{ClO}_2$  [M+H]: 287.08388 found 287.08504.



**(R)-4-(4-chlorophenyl)-2-ethyl-4-oxobutanal (3i):** The product was prepared according to GP1 from butyraldehyde (1.0 mmol, 1.0 eq) and 2-bromo-4'-chloroacetophenone (0.5 mmol, 2.0 eq) to afford colorless oil, yield: 72.1%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.82 (s, 1H), 7.92 (d,  $J$  = 8.5 Hz, 2H), 7.45 (d,  $J$  = 6.8 Hz, 2H), 3.44 (dd,  $J$  = 17.8, 8.0 Hz, 1H), 3.07 (dd,  $J$  = 13.0, 6.0 Hz, 1H), 2.96 (dd,  $J$  = 17.8, 4.7 Hz, 1H), 1.85 (m, 1H), 1.64 (m, 1H), 1.02 (t,  $J$  = 7.5 Hz, 3H).

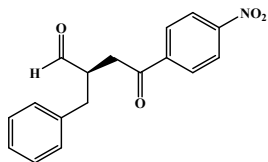
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  203.38, 196.86, 139.76, 134.96, 129.51, 128.97, 77.24, 77.03, 76.82, 48.06, 36.96, 21.85, 11.45.



**(R)-2-(2-(4-Nitrophenyl)-2-oxoethyl)octanal (3j):** The product was prepared according to GP1 from octanal (1.0 mmol, 1.0 eq) and 2-bromo-4'-nitroacetophenone (0.5 mmol, 2.0 eq) to afford yellow solid, yield: 52.8%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.81 (s, 1H), 8.32 (m, 2H), 8.13 (m, 2H), 3.52 (dd,  $J$ =17.9, 8.4, 1H), 3.18 (dd,  $J$ =13.4, 8.1, 1H), 2.97 (dd,  $J$ =17.9, 4.3, 1H), 1.83 (dt,  $J$ =15.8, 7.2, 1H), 1.56 (dd,  $J$ =14.5, 6.7, 1H), 1.33 (m, 8H), 0.89 (t,  $J$ =7.0, 3H).

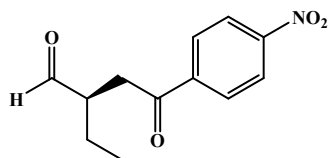
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 203.00, 196.76, 150.43, 141.11, 129.13, 123.89, 77.24, 77.03, 76.82, 46.93, 37.82, 31.57, 29.30, 28.72, 27.07, 22.55, 14.03.



**(R)-2-Benzyl-4-(4-nitrophenyl)-4-oxobutanal (3k):** The product was prepared according to GP1 from 3-phenylpropionaldehyde (1.0 mmol, 1.0 eq) and 2-bromo-4'-nitroacetophenone (0.5 mmol, 2.0 eq) to afford yellow oil, yield: 41.4%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.89 (s, 1H), 8.30 (s, 2H), 8.04 (d,  $J = 8.8$  Hz, 2H), 7.32 (t,  $J = 7.5$  Hz, 2H), 7.24 (d,  $J = 7.4$  Hz, 1H), 7.20 (s, 2H), 3.45 (m, 2H), 3.21 (dd,  $J = 14.0, 6.0$  Hz, 1H), 2.94 (dd,  $J = 17.2, 3.6$  Hz, 1H), 2.84 (dd,  $J = 13.9, 8.4$  Hz, 1H).

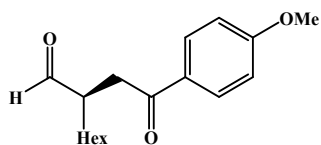
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  202.32, 196.57, 150.45, 140.96, 137.61, 129.00, 127.00, 123.86, 77.23, 77.02, 76.81, 48.59, 37.39, 34.60.



**(R)-2-ethyl-4-(4-nitrophenyl)-4-oxobutanal (3l):** The product was prepared according to GP1 from butyraldehyde (1.0 mmol, 2.0 eq) and 2-bromo-4'-nitroacetophenone (0.5 mmol, 2.0 eq) to afford yellow oil, yield: 47.1%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.82 (s, 1H), 8.32 (d,  $J = 8.6$  Hz, 2H), 8.14 (d,  $J = 8.7$  Hz, 2H), 3.52 (dd,  $J = 17.9, 8.3$  Hz, 1H), 3.14 (m, 1H), 2.97 (dd,  $J = 17.9, 4.4$  Hz, 1H), 1.89 (m, 1H), 1.68 (m, 1H), 1.05 (t,  $J = 7.5$  Hz, 3H).

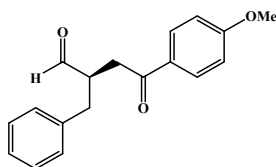
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  202.98, 196.74, 150.45, 141.12, 129.13, 123.90, 77.24, 77.03, 76.82, 48.18, 37.30, 21.76, 11.45.



**(R)-2-(2-(4-Methoxyphenyl)-2-oxoethyl)octanal (3m):** The product was prepared according to GP1 from octanal (1.0 mmol, 1.0 eq) and 2-bromo-4'-methoxyacetophenone (0.5 mmol, 2.0 eq) to afford colorless oil, yield: 52.6%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta =$  9.82 (s, 1H), 7.96 (d,  $J=8.9$ , 2H), 6.94 (d,  $J=8.9$ , 2H), 3.87 (s, 3H), 3.42 (dd,  $J=17.5, 7.8$ , 1H), 3.08 (m, 1H), 2.99 (dd,  $J=17.5, 4.9$ , 1H), 1.79 (m, 1H), 1.53 (m, 1H), 1.31 (ddd,  $J=20.0, 13.7, 5.1$ , 8H), 0.88 (t,  $J=7.0$ , 3H).

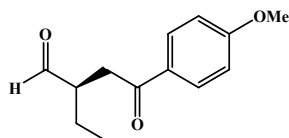
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  = 203.89, 196.53, 163.65, 130.39, 129.71, 113.78, 77.24, 77.03, 76.81, 55.50, 46.85, 37.41, 31.60, 29.35, 28.95, 27.08, 22.56, 14.04. HRMS (ESI+) calculated for  $\text{C}_{17}\text{H}_{25}\text{O}_3$   $[\text{M}+\text{H}]$ : 277.18037 found 277.18218.



**R-2-Benzyl-4-(4-methoxyphenyl)-4-oxobutanal (3n):** The product was prepared according to GP1 from 3-phenylpropionaldehyde (1.0 mmol, 1.0 eq) and 2-bromo-4'-methoxyacetophenone (0.5 mmol, 2.0 eq) to afford yellow solid, yield: 58.8%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.89 (s, 1H), 7.88 (m, 2H), 7.29 (t,  $J$  = 7.4 Hz, 2H), 7.21 (dd,  $J$  = 22.0, 7.2 Hz, 3H), 6.91 (m, 2H), 3.86 (s, 3H), 3.36 (m, 2H), 3.15 (dd,  $J$  = 14.0, 5.9 Hz, 1H), 2.98 (dd,  $J$  = 20.4, 7.5 Hz, 1H), 2.82 (dd,  $J$  = 14.1, 7.6 Hz, 1H).

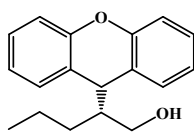
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  203.22, 196.29, 163.70, 138.26, 130.37, 129.55, 129.06, 128.72, 126.68, 113.76, 77.24, 77.03, 76.82, 55.48, 48.41, 37.00, 34.77, 31.51, 30.14.



**(R)-2-ethyl-4-(4-methoxyphenyl)-4-oxobutanal (3o):** The product was prepared according to GP1 from butyraldehyde (1.0 mmol, 1.0 eq) and 2-bromo-4'-methoxyacetophenone (0.5 mmol, 2.0 eq) to afford colorless oil, yield: 60.1%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.83 (d,  $J$  = 0.9 Hz, 1H), 7.96 (d,  $J$  = 8.9 Hz, 2H), 6.94 (d,  $J$  = 8.9 Hz, 2H), 3.87 (s, 3H), 3.42 (dd,  $J$  = 17.3, 7.5 Hz, 1H), 3.05 (dd,  $J$  = 12.7, 6.4 Hz, 1H), 2.99 (dd,  $J$  = 17.3, 5.0 Hz, 1H), 1.83 (m, 1H), 1.63 (m, 1H), 1.00 (t,  $J$  = 7.5 Hz, 3H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  203.82, 196.51, 163.66, 130.39, 129.72, 113.79, 77.24, 77.03, 76.82, 55.50, 48.16, 36.86, 21.94, 11.48.

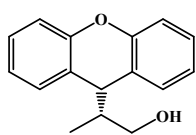


**(R)-2-(9H-xanthen-9-yl)pentan-1-ol (6b):** The product was prepared according to GP2 from xanthene (36.4 mg, 1.0 eq) and valeraldehyde (63.8  $\mu\text{L}$ , 3.0 eq) to afford colorless oil,

yield:41.6%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (dd,  $J = 15.5, 8.1$  Hz, 4H), 7.11 – 7.03 (m, 4H), 4.26 (t,  $J = 9.2$  Hz, 1H), 3.56 – 3.45 (m, 2H), 1.83 (qd,  $J = 9.2, 4.8$  Hz, 1H), 1.35 – 1.20 (m, 3H), 1.18 – 1.11 (m, 1H), 1.07 – 0.98 (m, 1H), 0.79 – 0.71 (m, 3H).

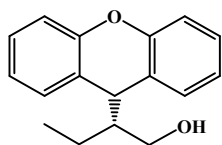
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  153.17 (d,  $J = 6.6$  Hz), 129.50 (s), 128.91 (s), 127.56 (d,  $J = 5.3$  Hz), 124.75 (s), 123.66 (s), 123.19 (s), 122.98 (s), 116.26 (d,  $J = 4.5$  Hz), 77.21 (s), 77.00 (s), 76.79 (s), 62.46 (s), 50.00 (s), 39.29 (s), 29.04 (s), 20.55 (s), 14.16 (s).



**(R)-2-(9H-xanthen-9-yl)propan-1-ol (6c):** The product was prepared according to GP2 from xanthene (36.4 mg, 1.0 eq) and propionaldehyde (43.2  $\mu\text{L}$ , 3.0 eq) to afford colorless oil, yield:48.8%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 – 7.17 (m, 4H), 7.13 – 7.03 (m, 4H), 4.21 (t,  $J = 9.9$  Hz, 1H), 3.52 (dt,  $J = 16.8, 8.4$  Hz, 1H), 3.46 – 3.42 (m, 1H), 2.03 – 1.95 (m, 1H), 1.53 (s, 1H), 0.62 (dd,  $J = 17.5, 4.6$  Hz, 3H).

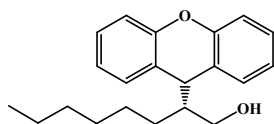
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  153.35 (s), 153.10 (s), 129.66 (s), 128.76 (s), 127.71 (s), 127.53 (s), 125.14 (s), 123.26 (s), 122.89 (s), 122.51 (s), 116.24 (d,  $J = 14.1$  Hz), 64.90 (s), 45.09 (s), 40.25 (s), 12.00 (s).



**(R)-2-(9H-xanthen-9-yl)butan-1-ol (6d):** The product was prepared according to GP2 from xanthene (36.4 mg, 1.0 eq) and butyraldehyde (53.9  $\mu\text{L}$ , 3.0 eq) to afford colorless oil, yield:42.3%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 – 7.17 (m, 4H), 7.13 – 7.04 (m, 4H), 4.28 (d,  $J = 4.3$  Hz, 1H), 3.59 – 3.54 (m, 1H), 3.53 – 3.48 (m, 1H), 1.77 – 1.70 (m, 1H), 1.40 (t,  $J = 13.7$  Hz, 1H), 1.36 – 1.31 (m, 1H), 1.11 – 1.03 (m, 1H), 0.81 (t,  $J = 7.5$  Hz, 3H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  153.21 (d,  $J = 7.5$  Hz), 129.51 (s), 128.93 (s), 127.59 (d,  $J = 3.9$  Hz), 124.87 (s), 123.74 (s), 123.23 (s), 123.02 (s), 116.29 (d,  $J = 2.0$  Hz), 62.05 (s), 52.02 (s), 39.29 (s), 19.73 (s), 12.06 (s).

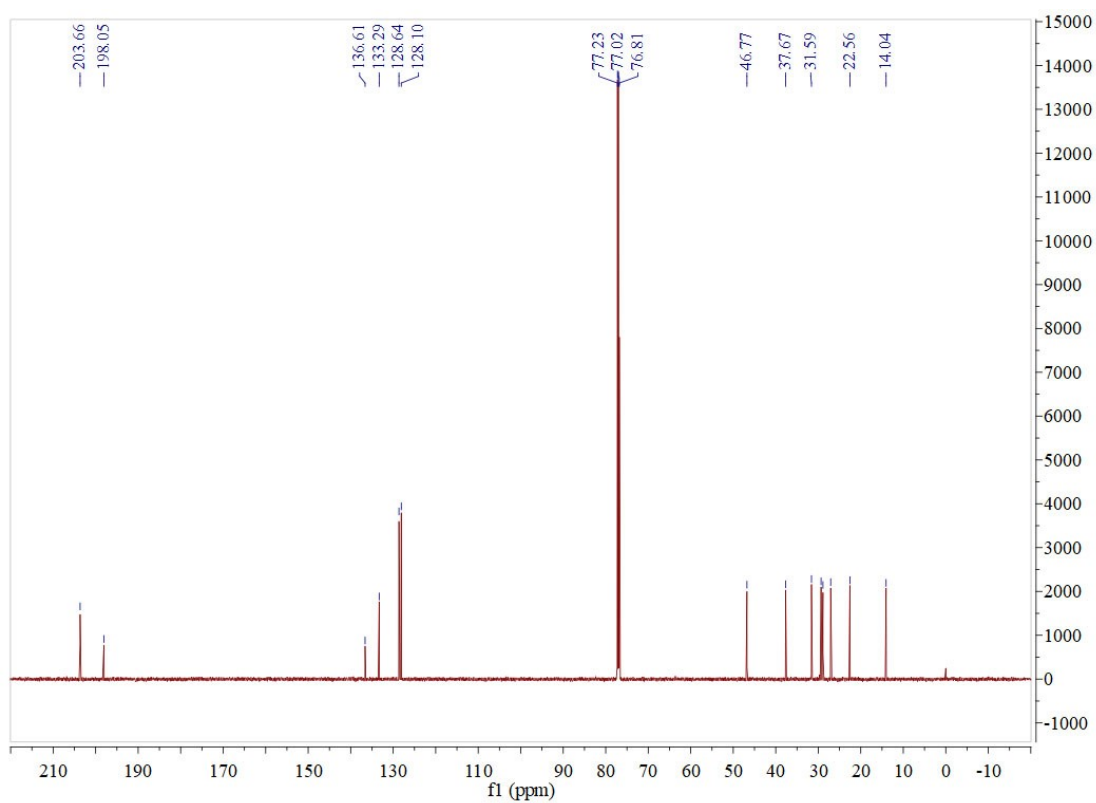
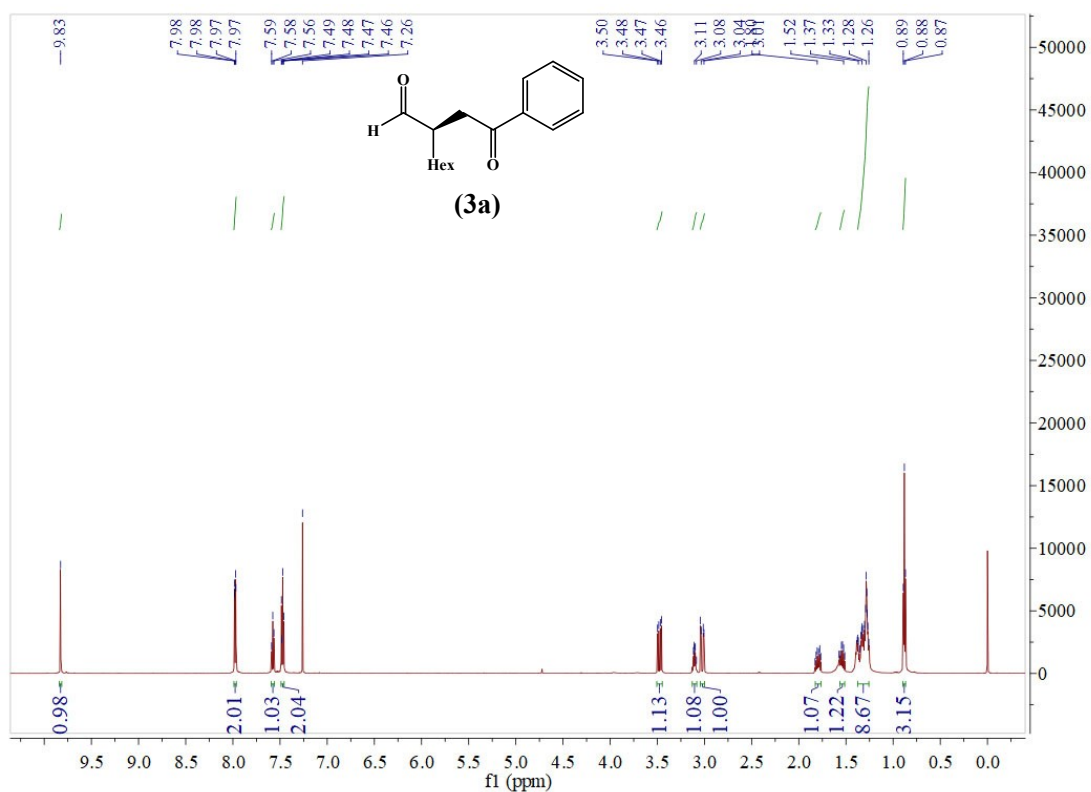


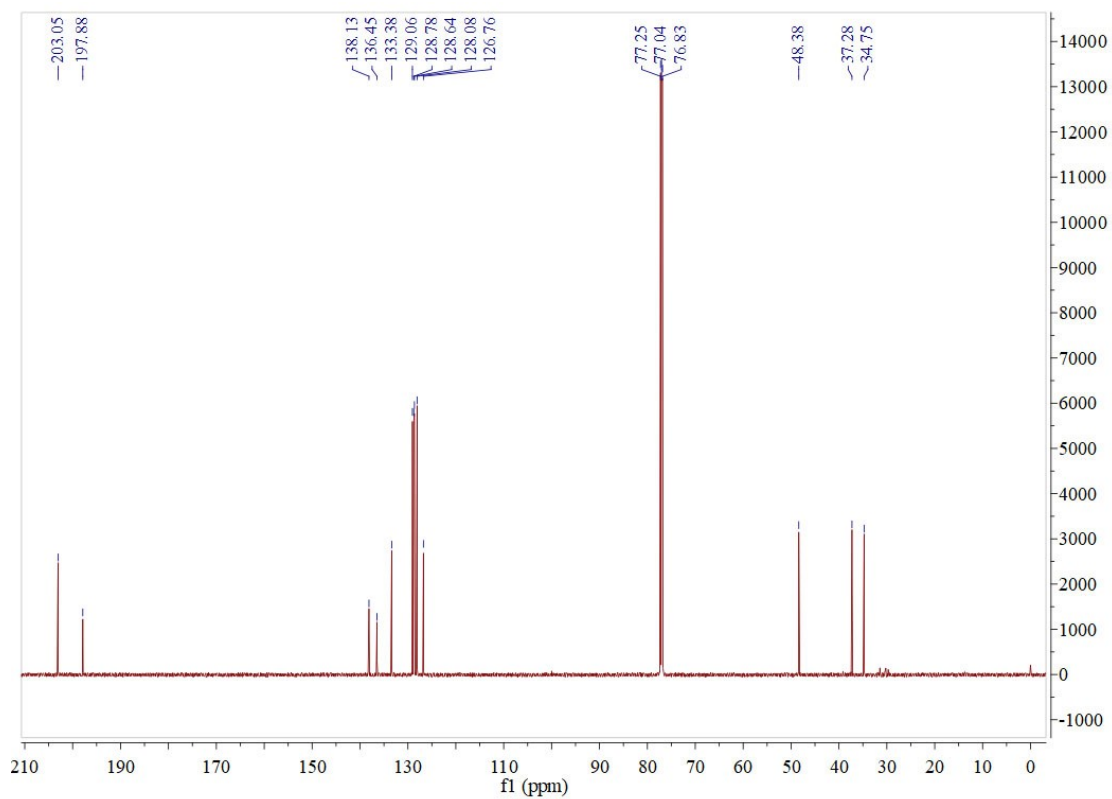
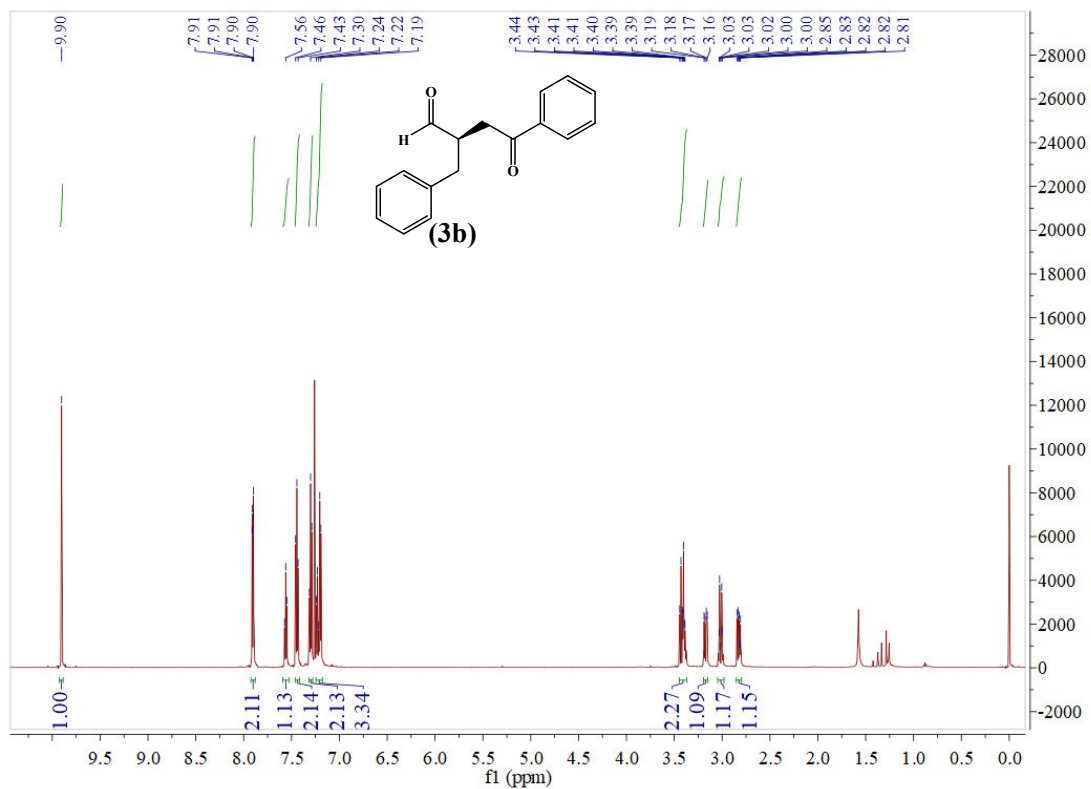
**(R)-2-(9H-xanthen-9-yl)octan-1-ol (6e):** The product was prepared according to GP2 from xanthene (36.4 mg, 1.0 eq) and n-octanaldehyde (94  $\mu\text{L}$ , 3.0 eq) to afford colorless oil, yield:30.3%.

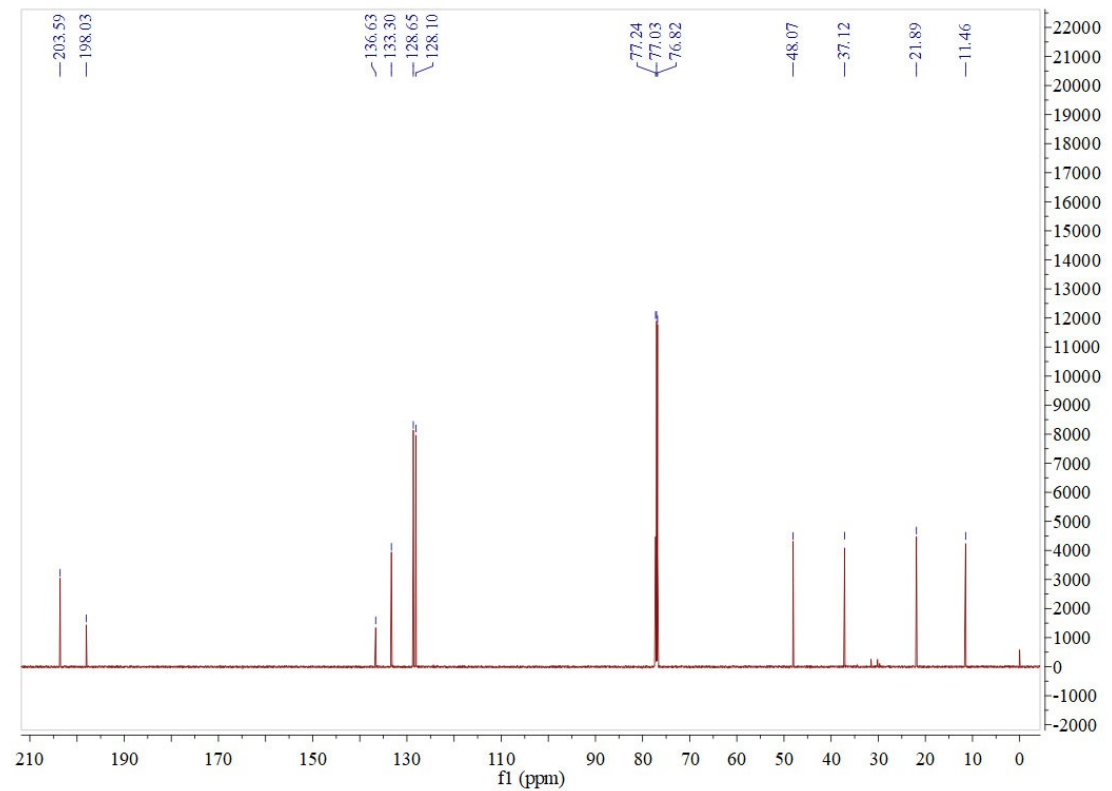
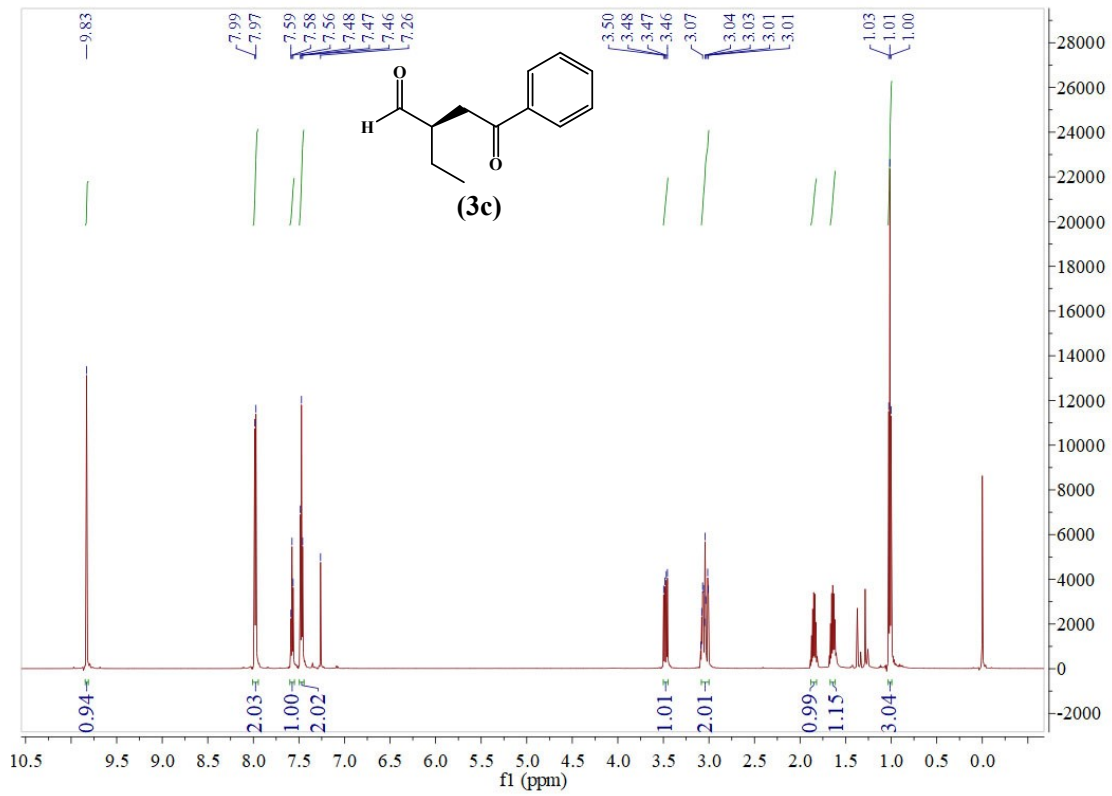
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (ddd,  $J = 13.9, 9.5, 4.1$  Hz, 4H), 7.13 – 7.02 (m, 4H), 4.27 (d,  $J = 4.2$  Hz, 1H), 3.52 (qd,  $J = 11.0, 6.4$  Hz, 2H), 1.82 (qd,  $J = 9.2, 4.9$  Hz, 1H), 1.62 (s, 1H), 1.25 – 0.96 (m, 11H), 0.82 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  153.19 (d,  $J = 5.4$  Hz), 129.52 (s), 128.93 (s), 127.59 (d,  $J = 3.7$  Hz), 124.77 (s), 123.72 (s), 123.21 (s), 123.01 (s), 116.29 (d,  $J = 4.2$  Hz), 77.23 (s), 77.02 (s), 76.81 (s), 62.52 (s), 50.20 (s), 39.34 (s), 31.64 (s), 29.34 (s), 27.40 (s), 26.77 (s), 22.57 (s), 14.05 (s).

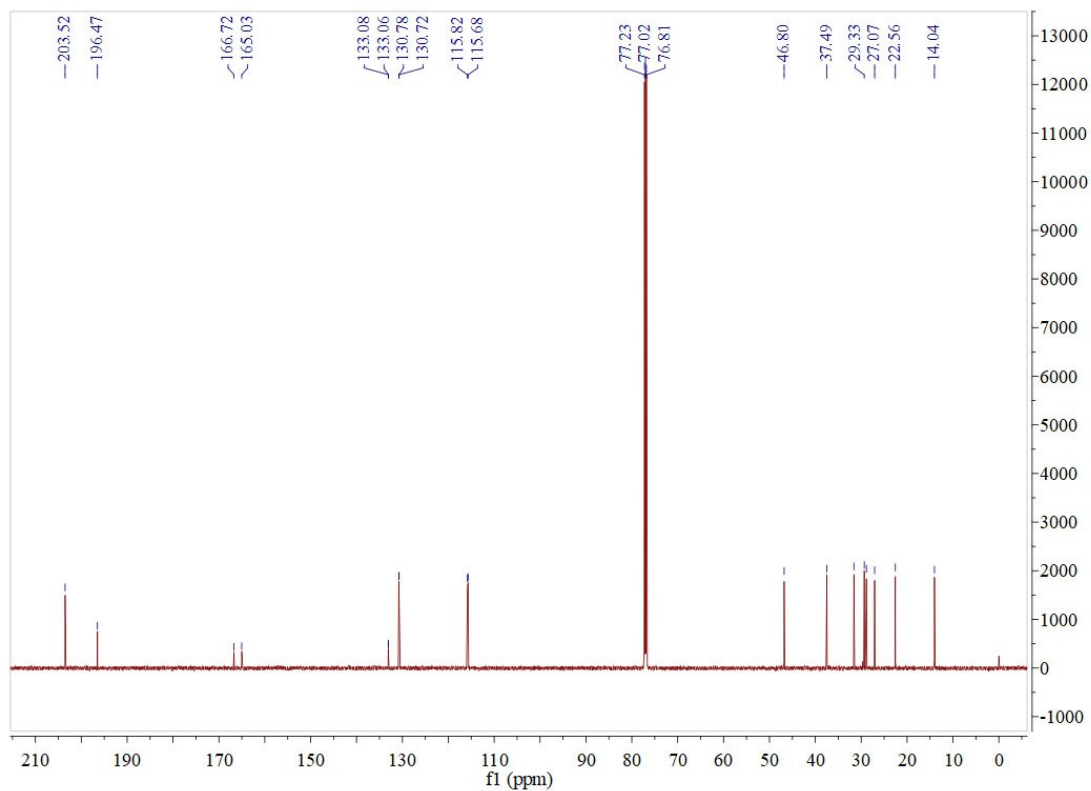
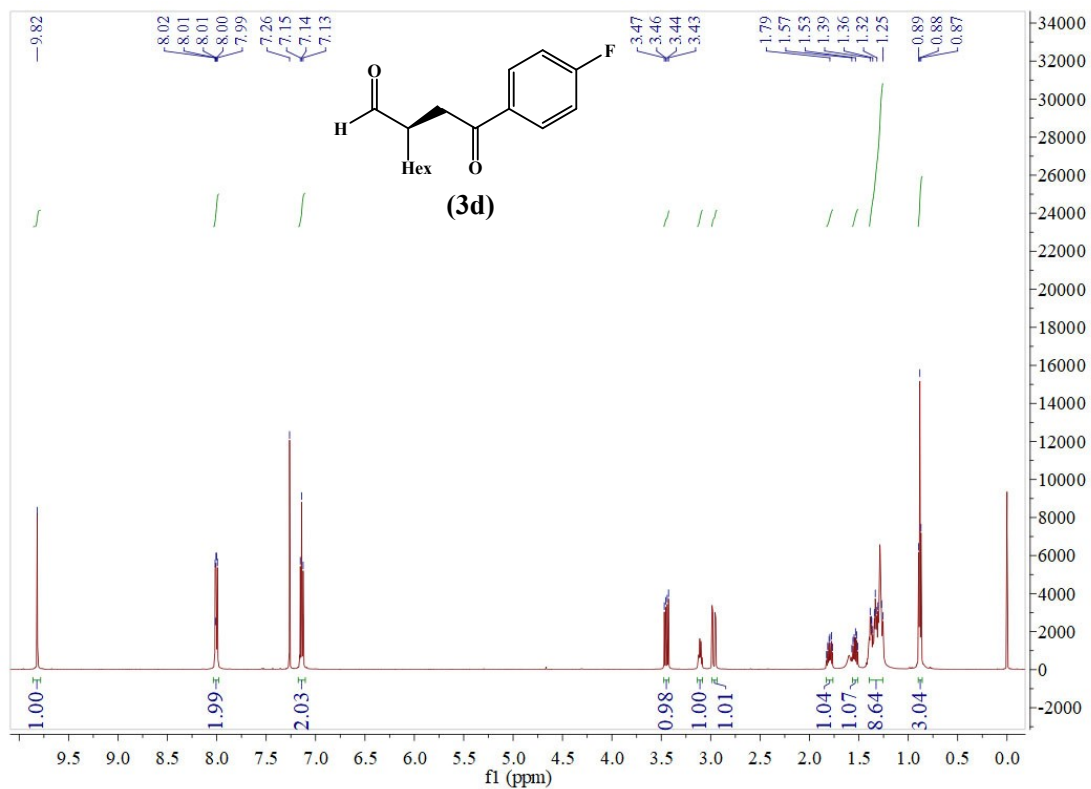
## Section 8. NMR spectra of all compounds

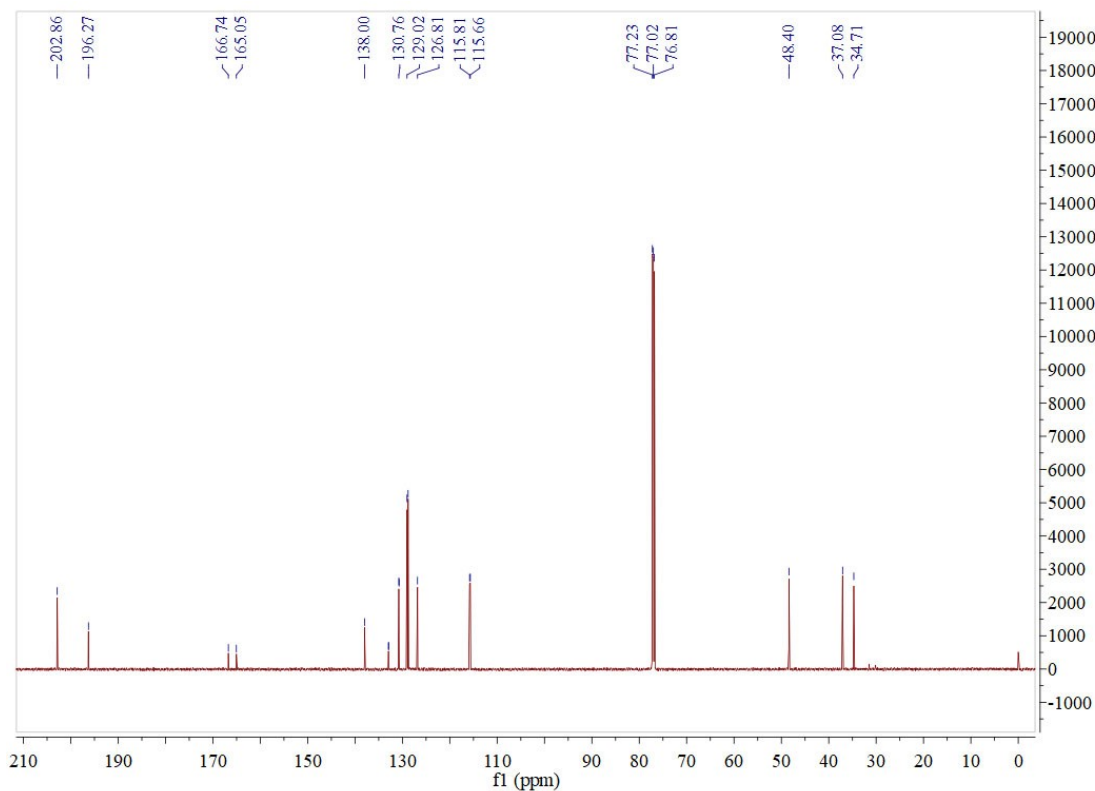
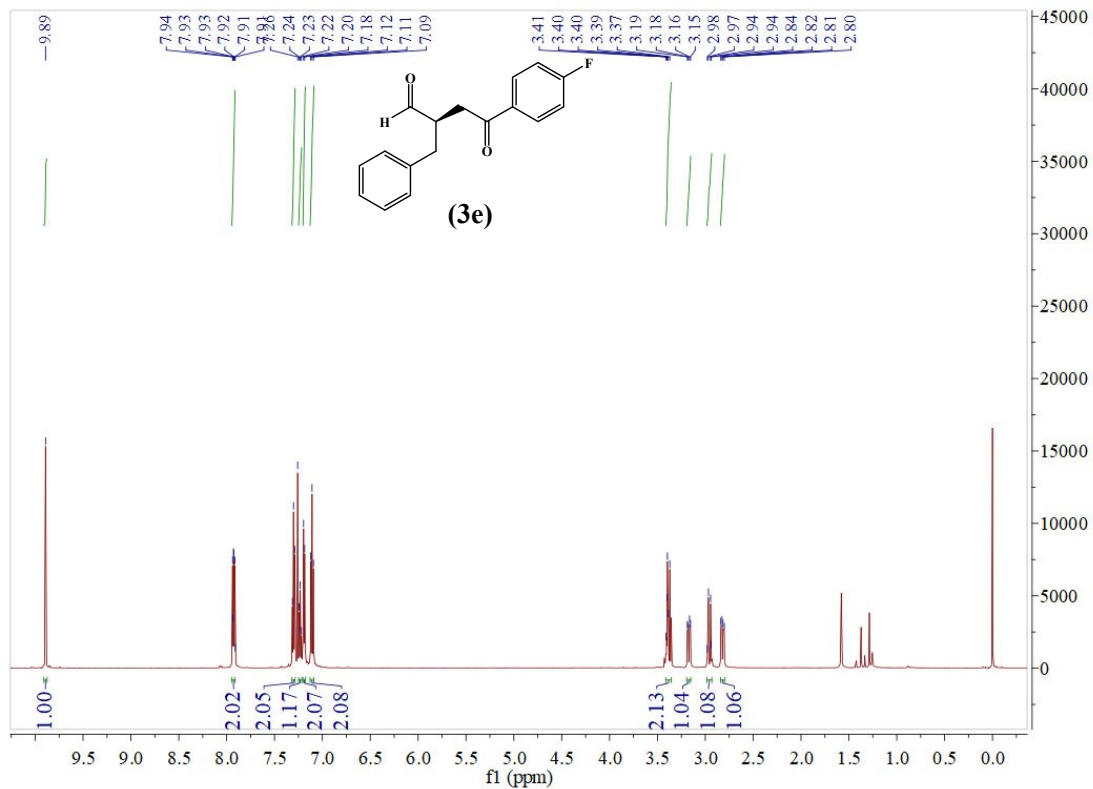


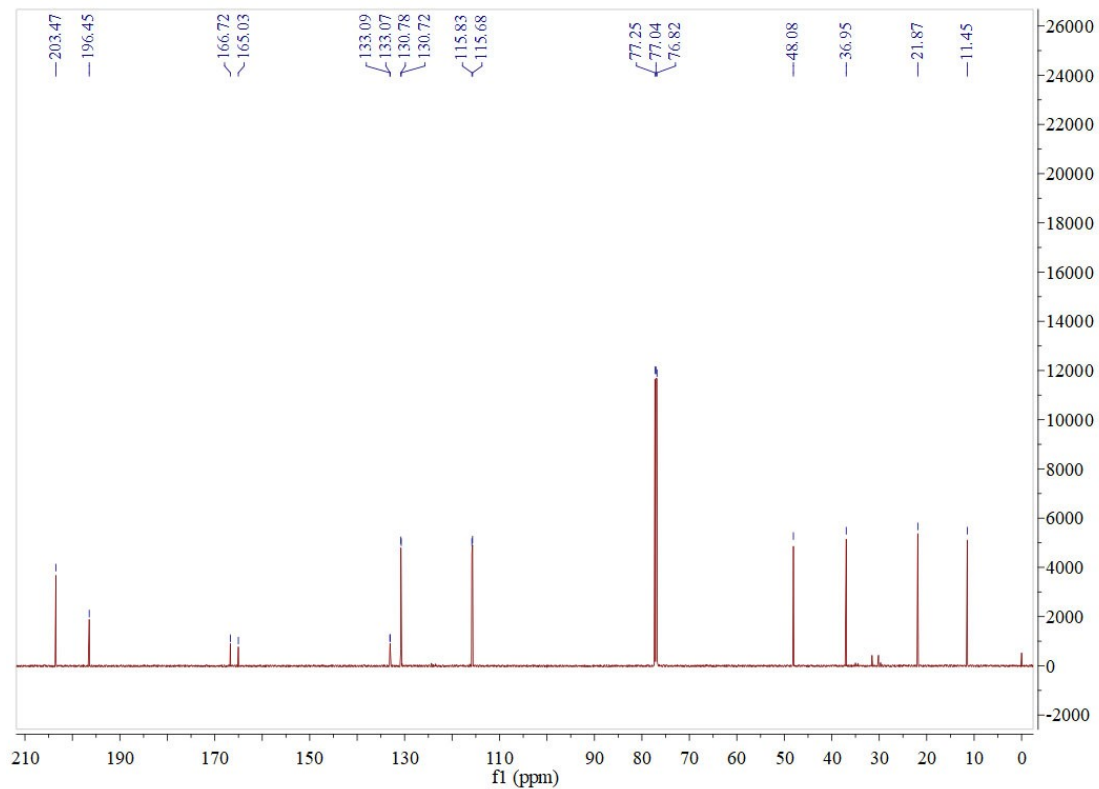
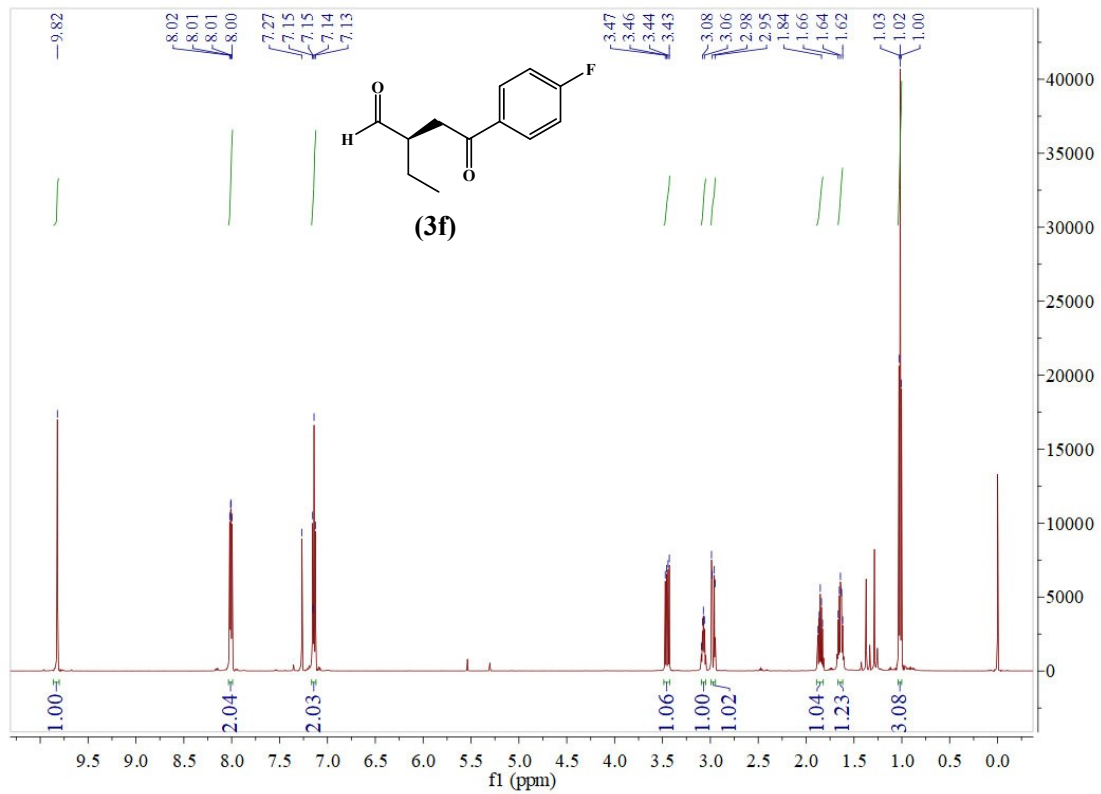


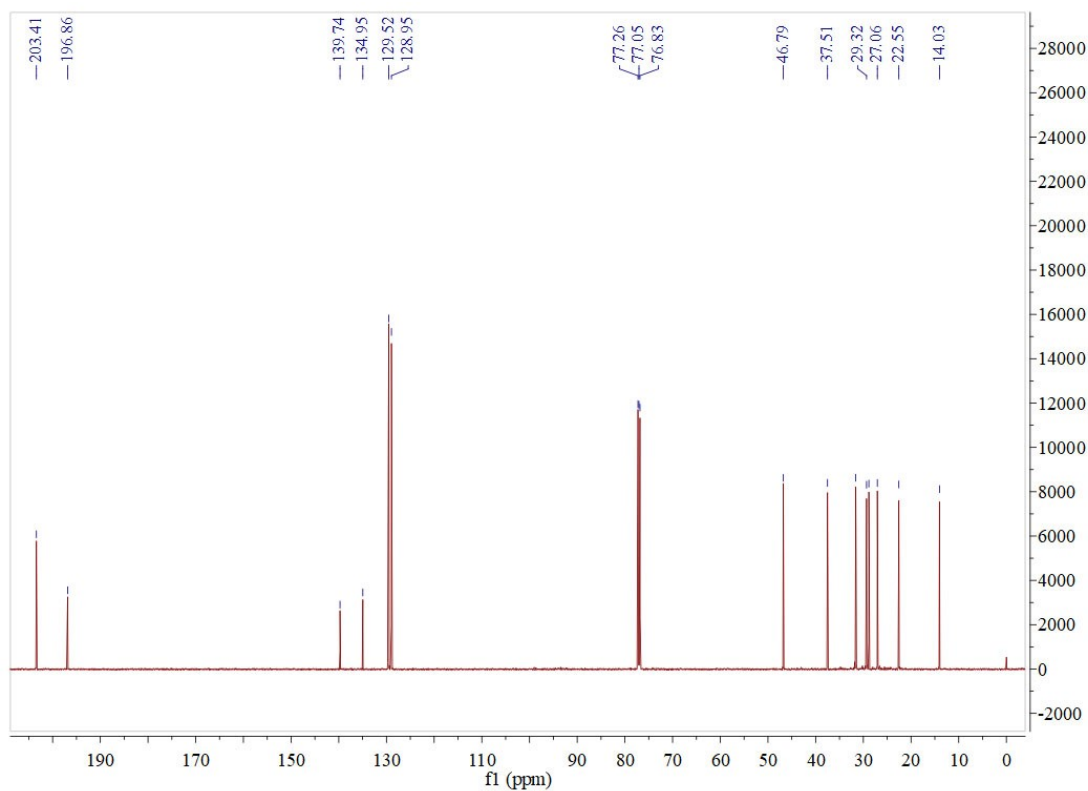
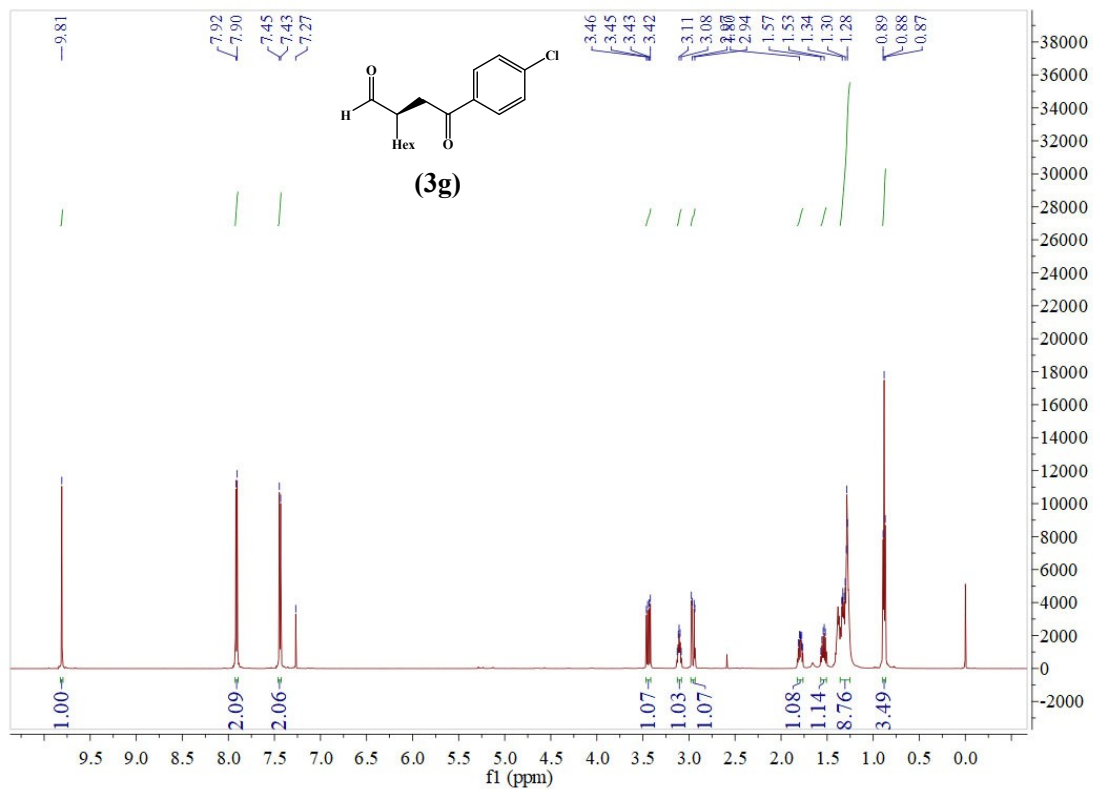


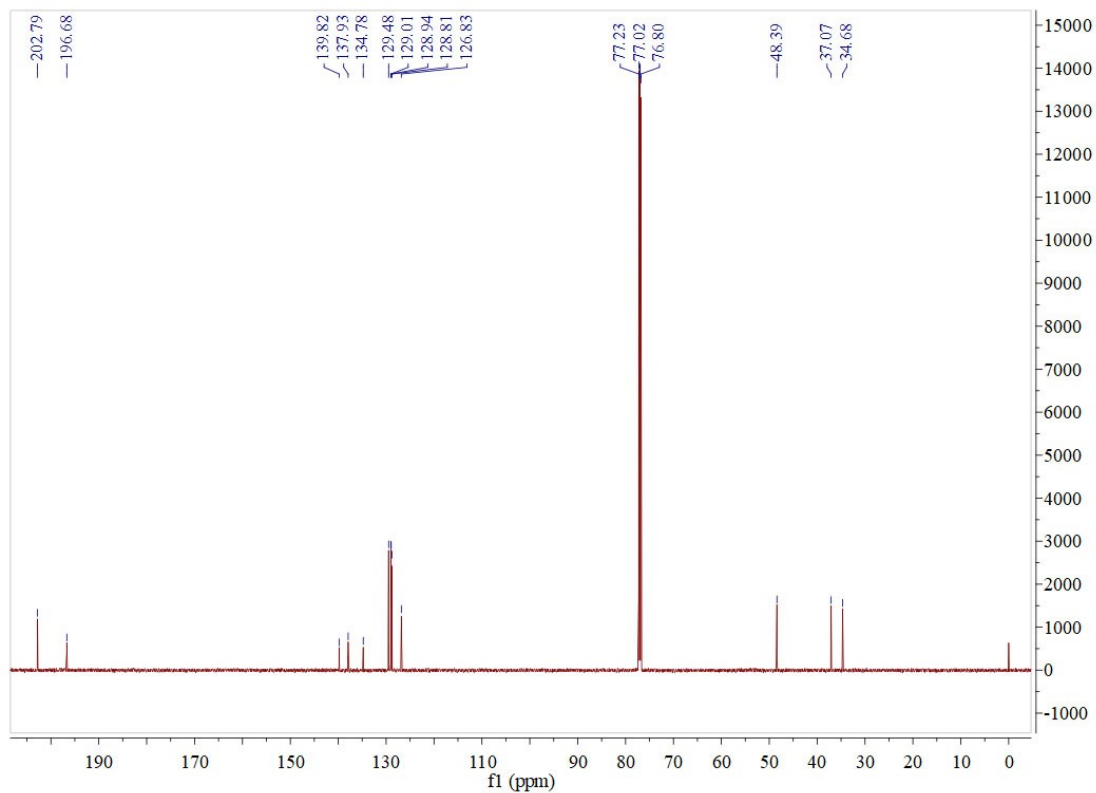
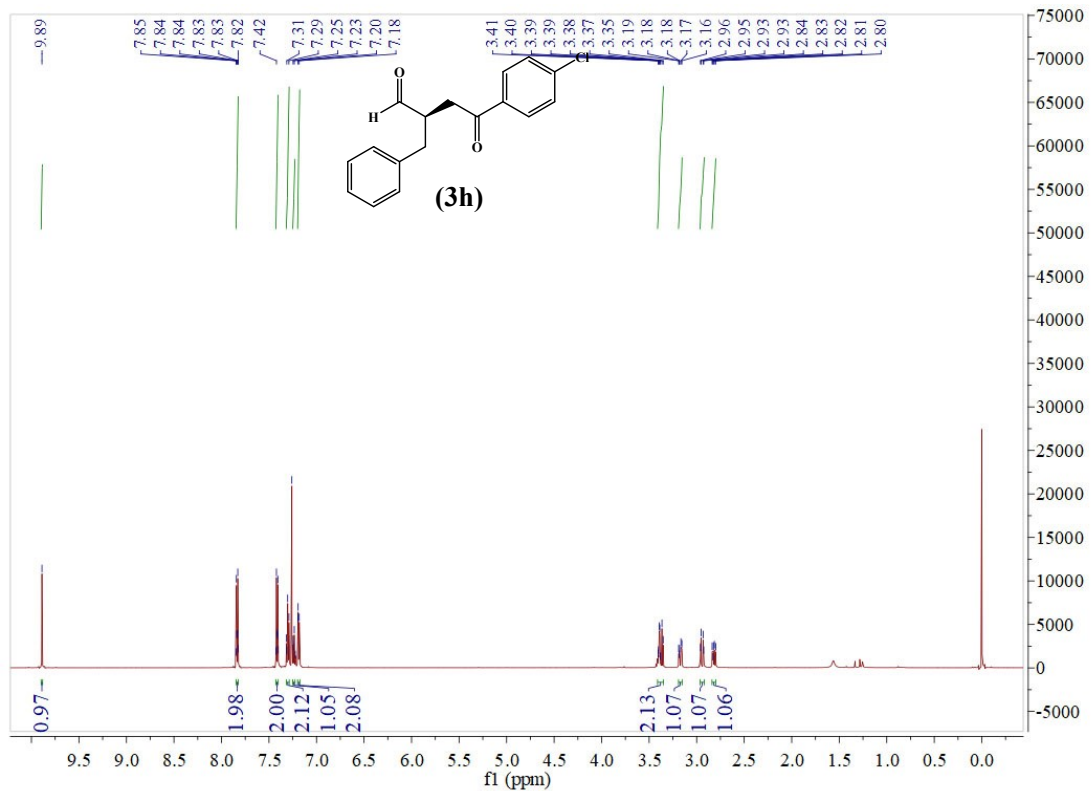


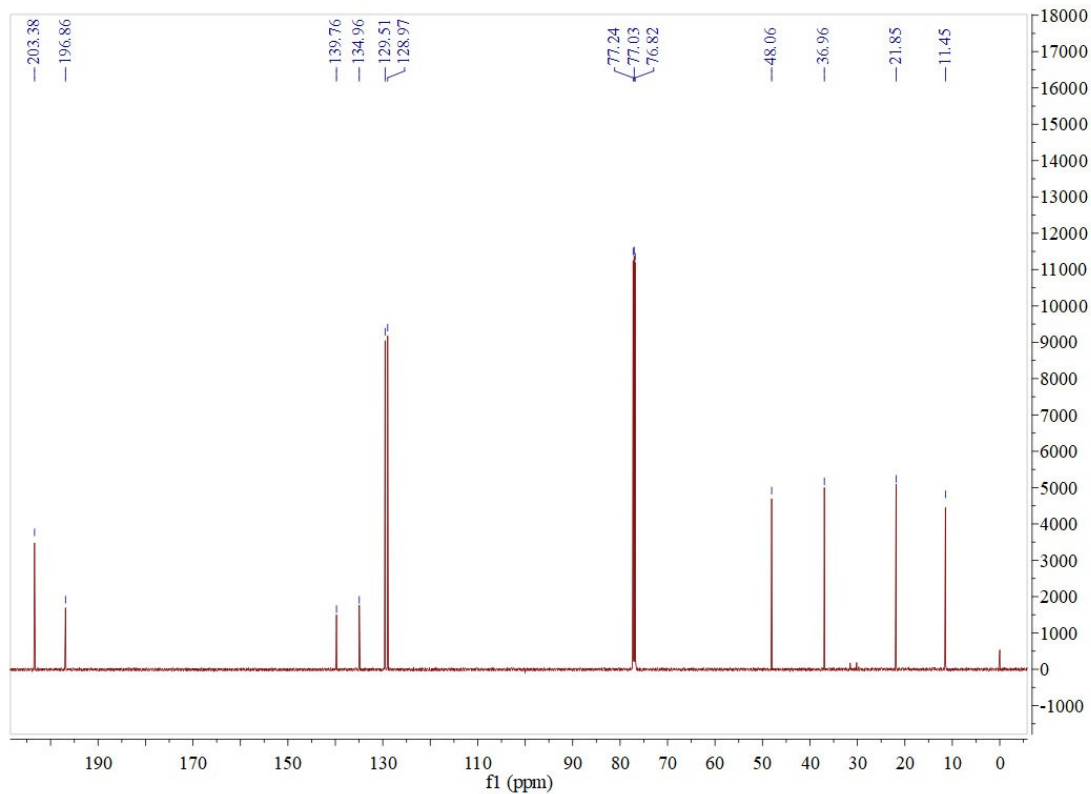
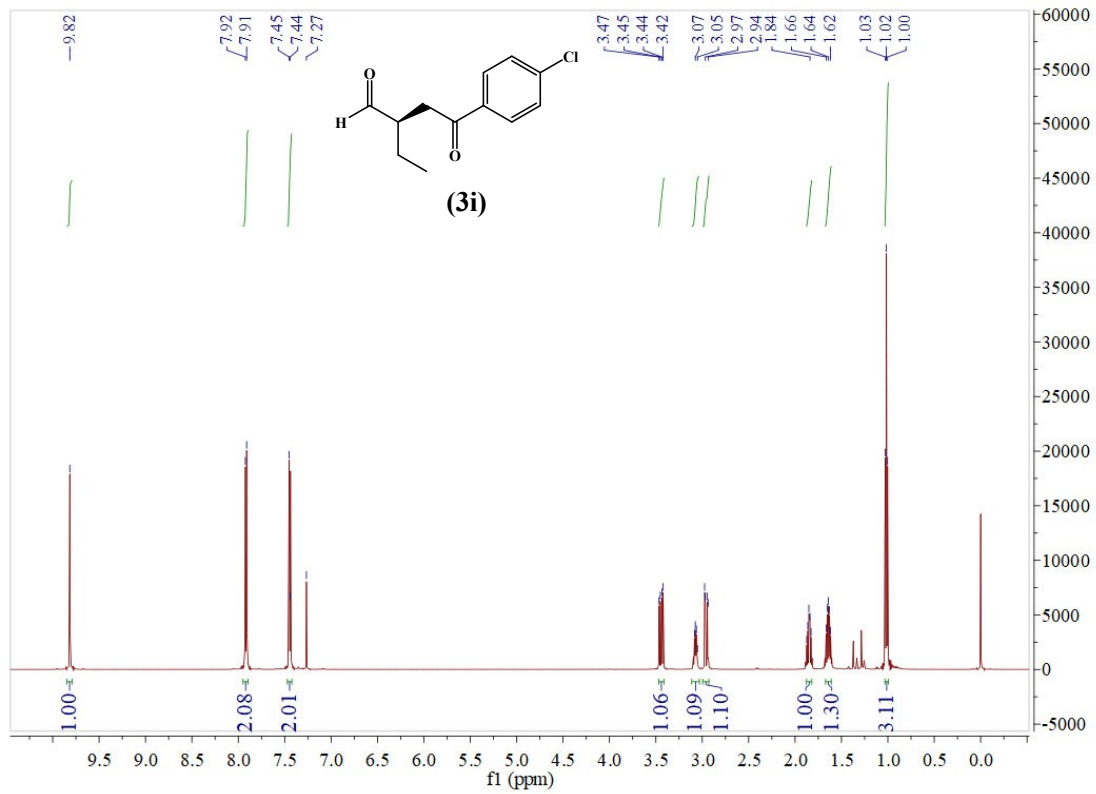


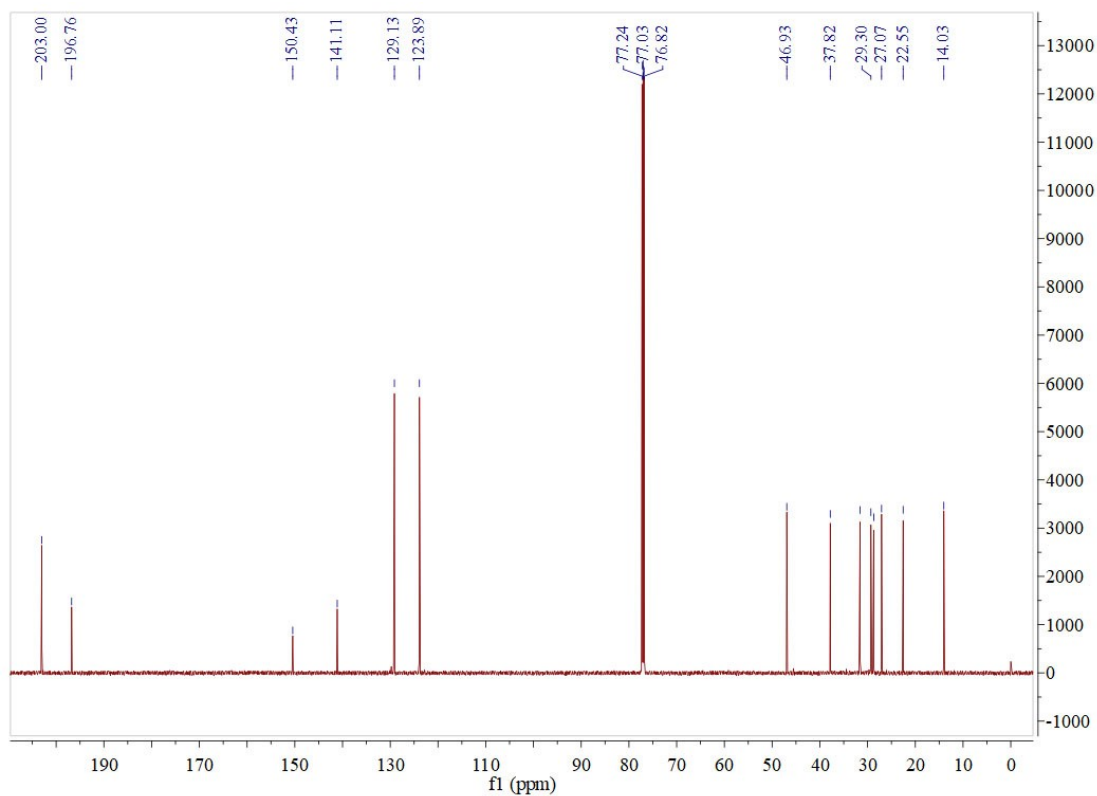
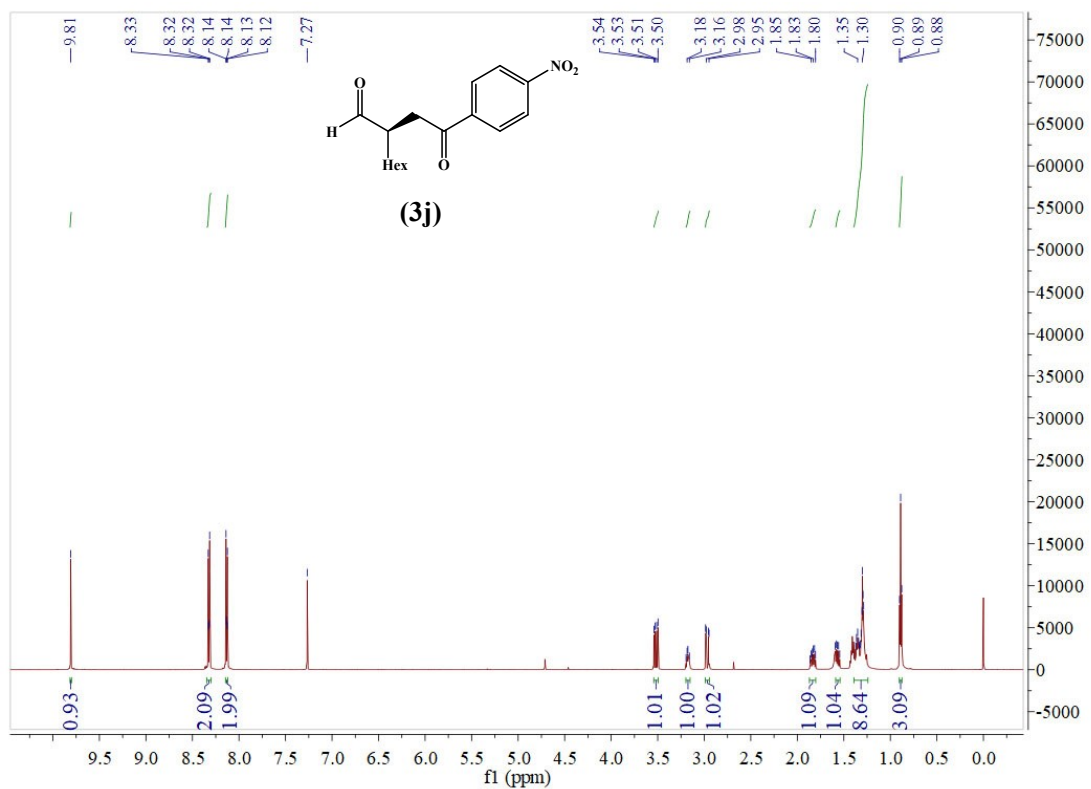


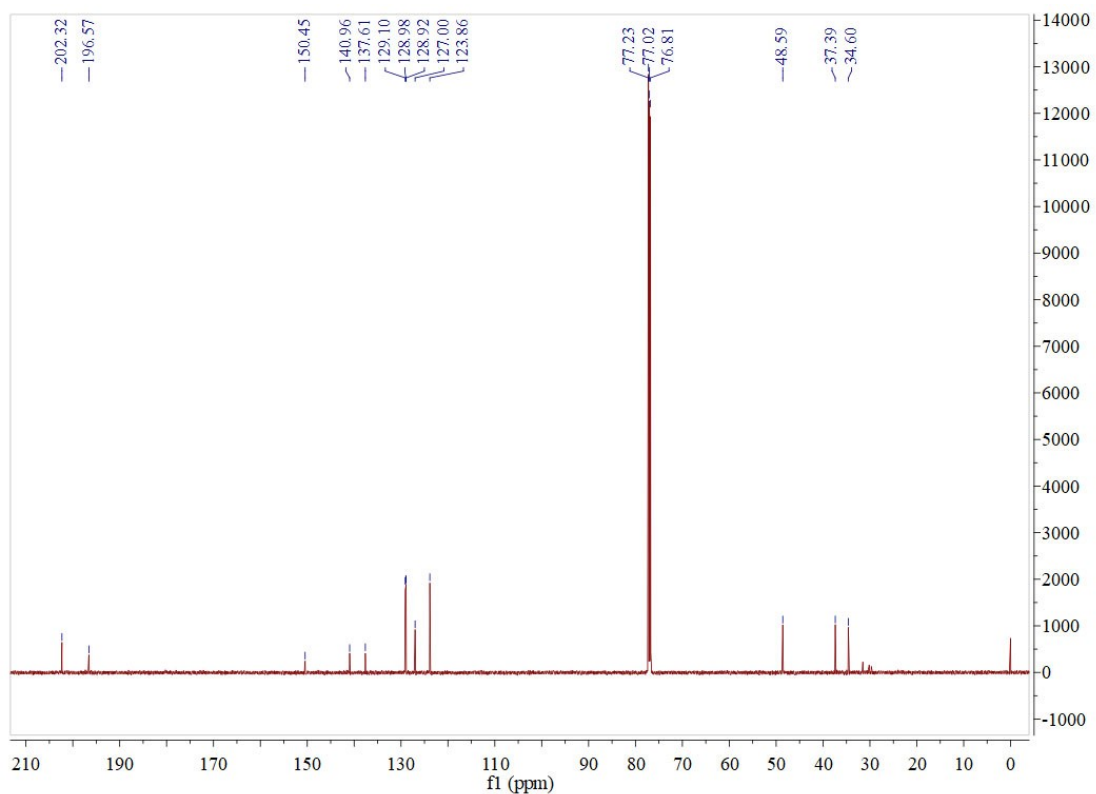
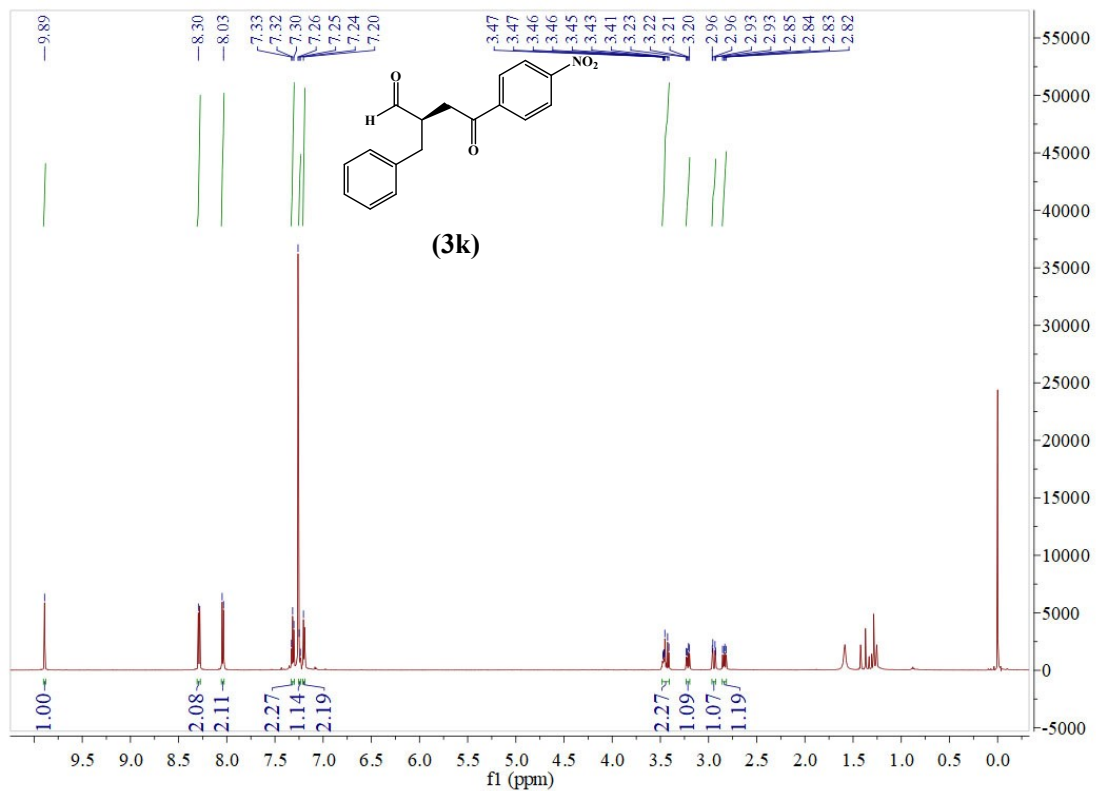




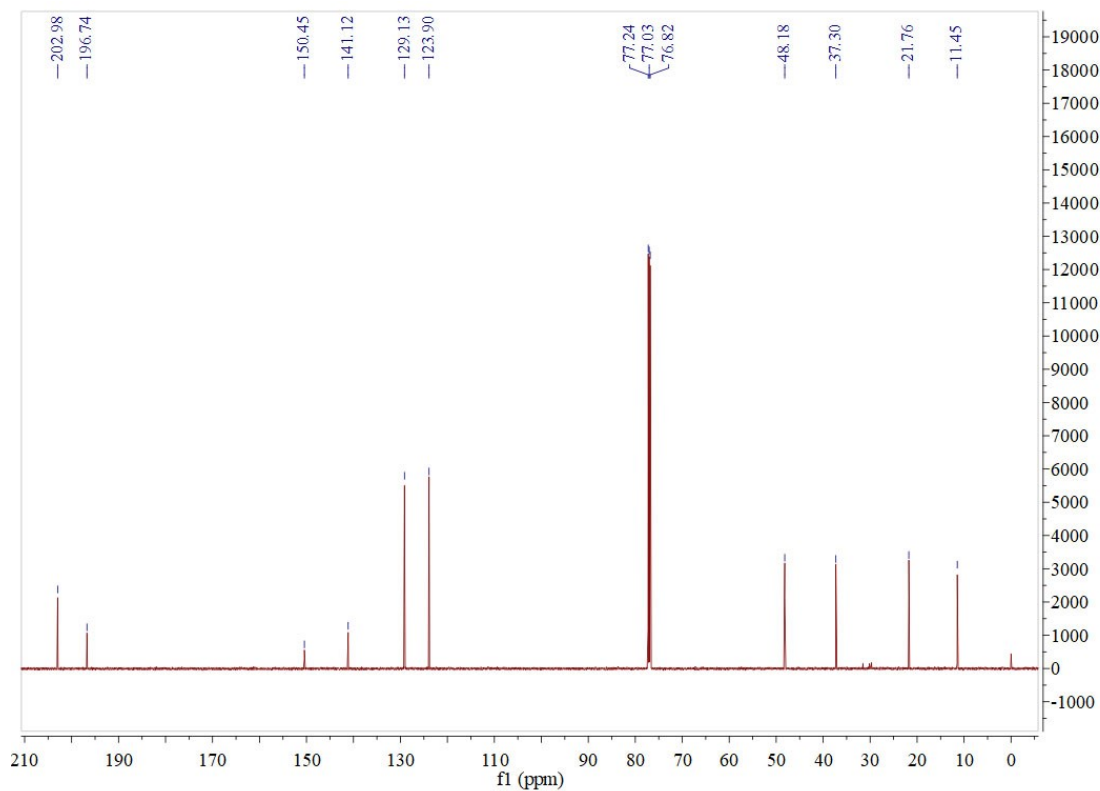
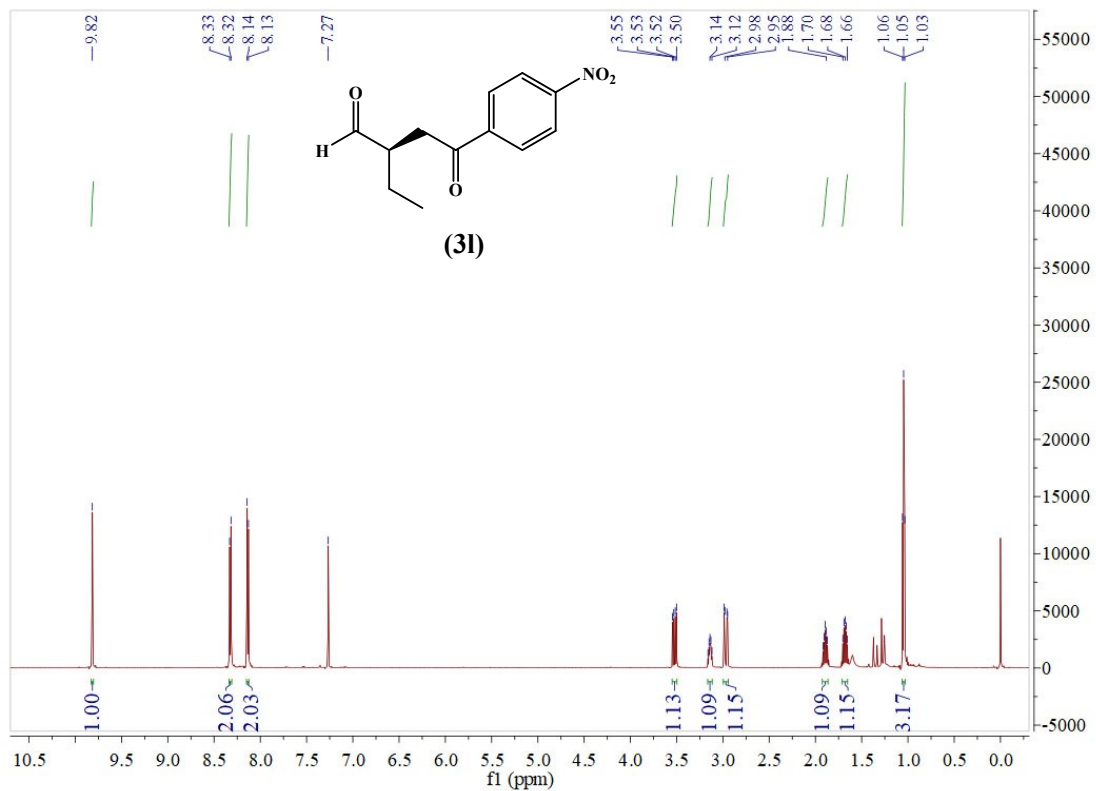


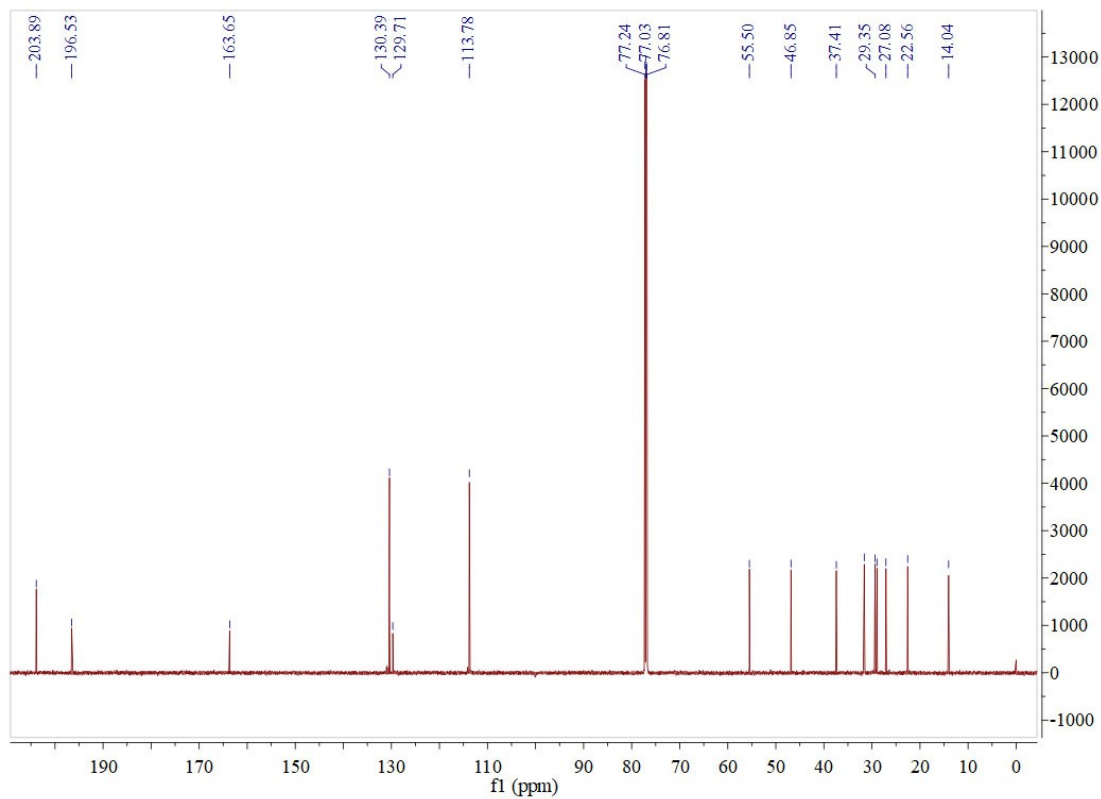
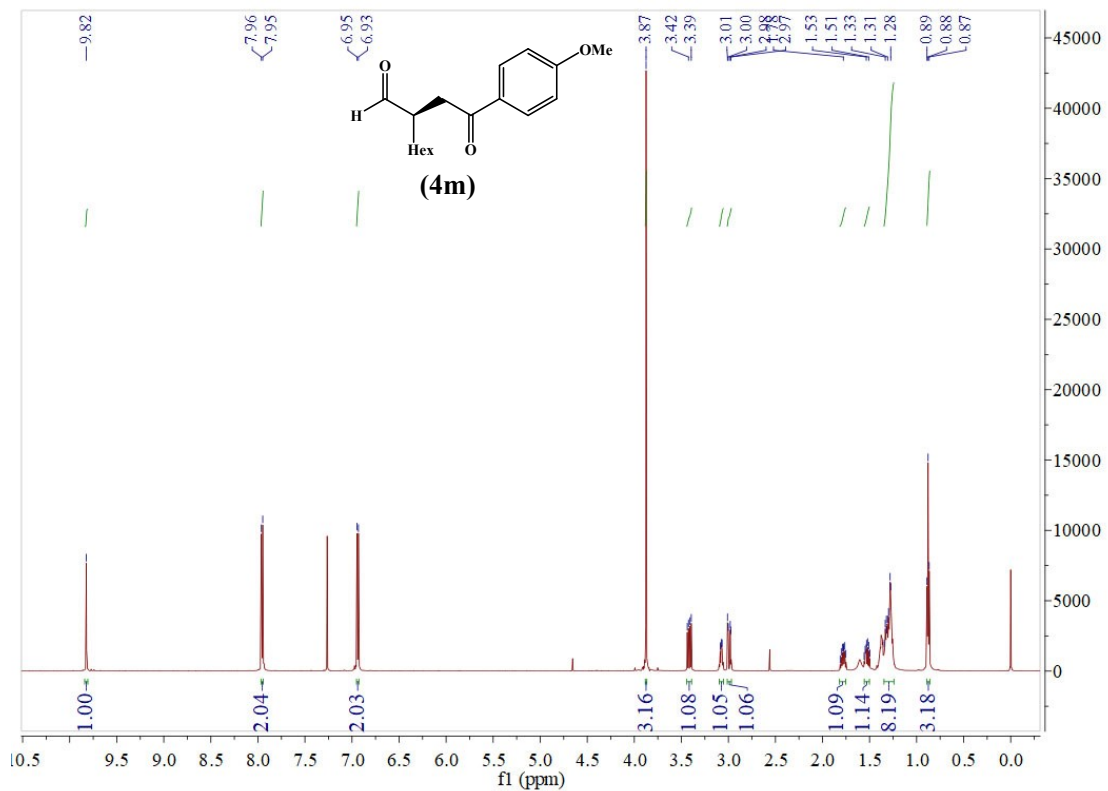


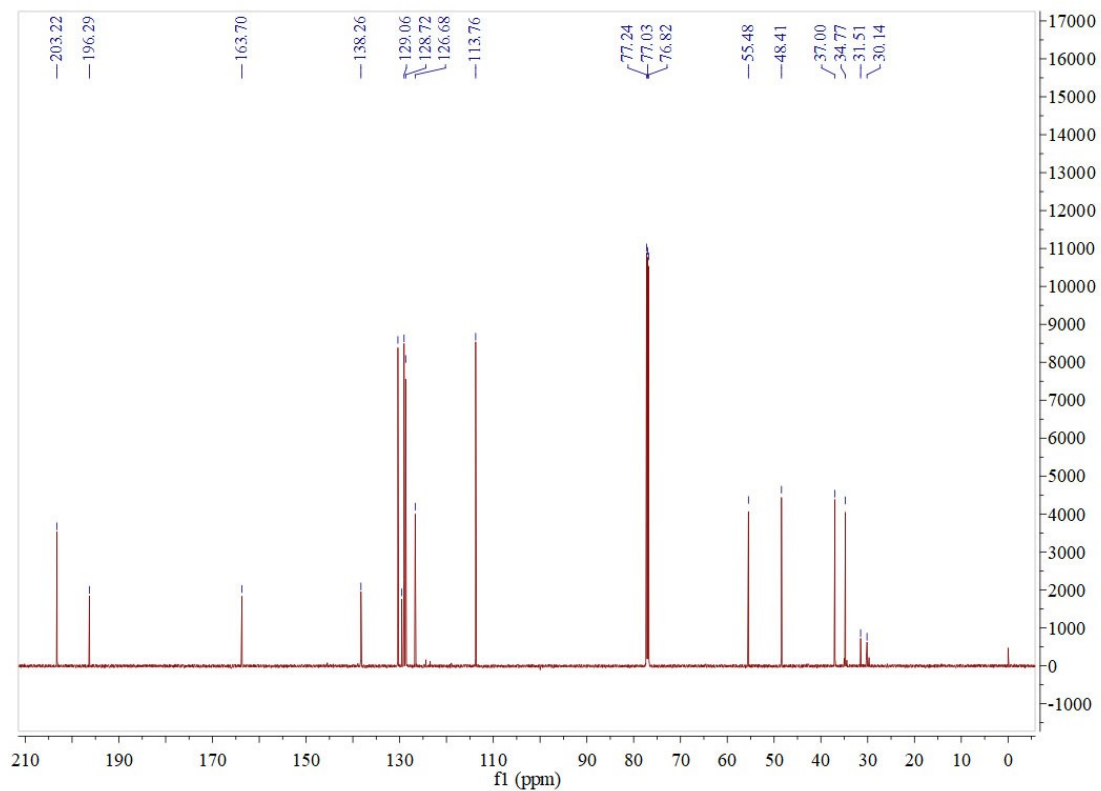
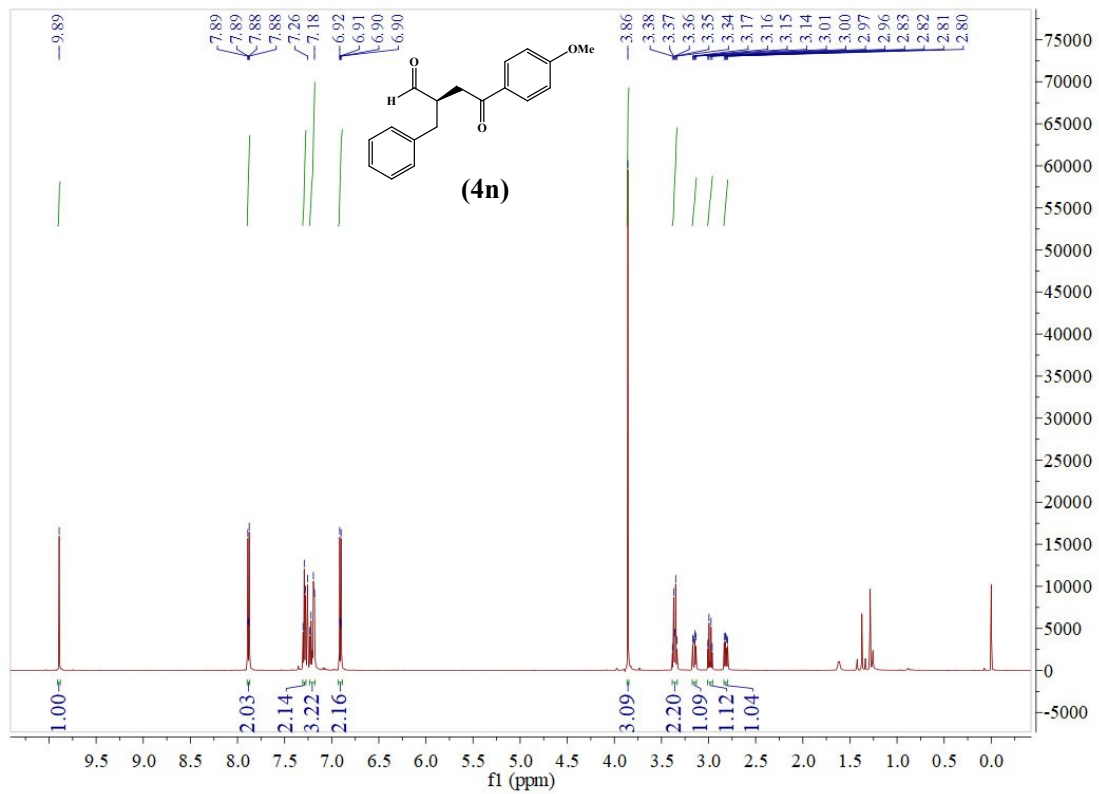


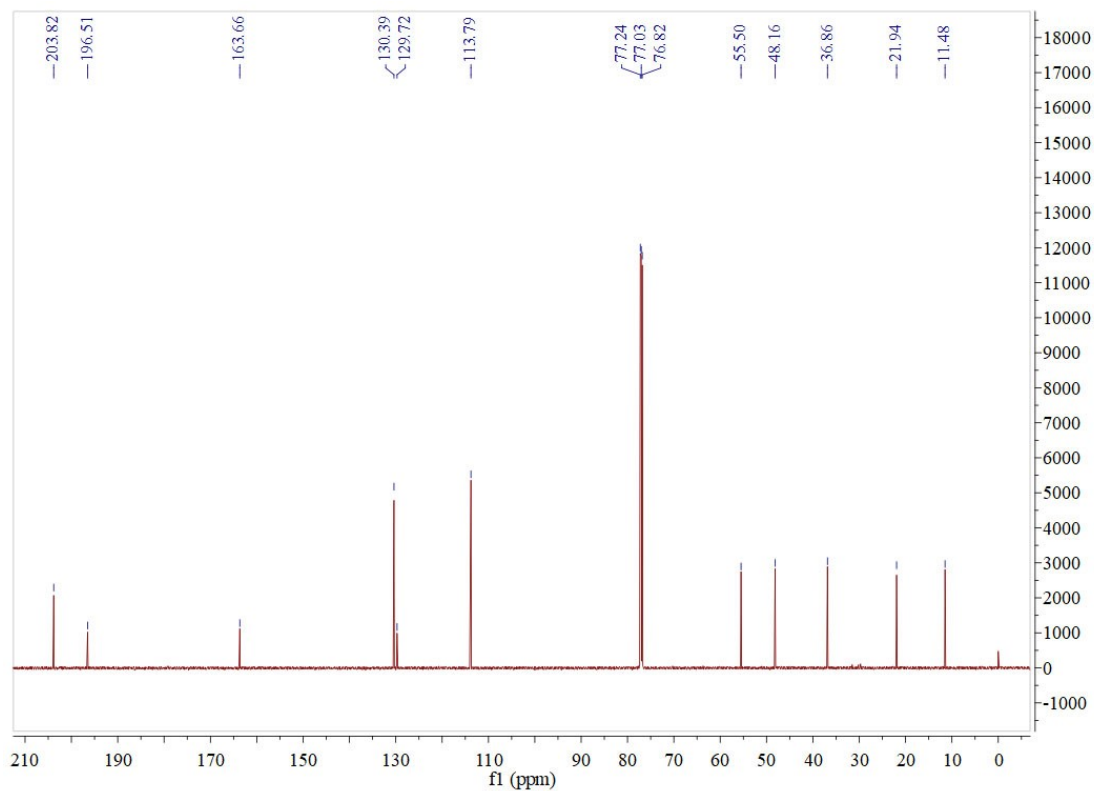
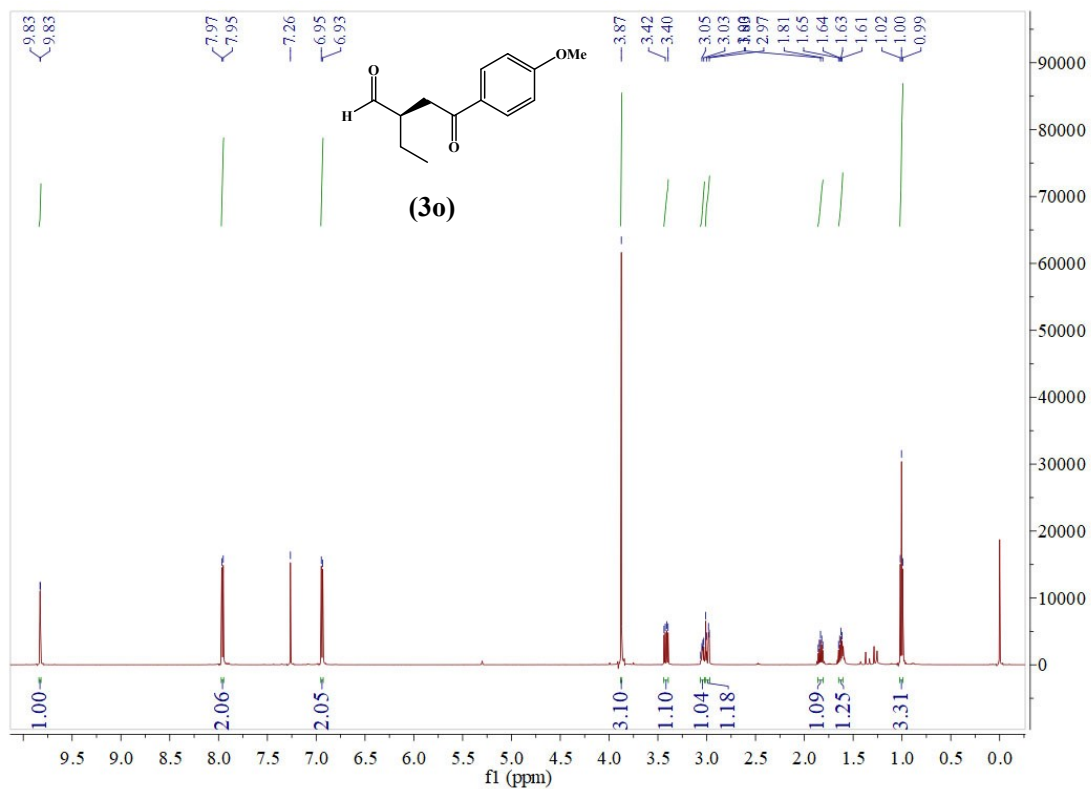


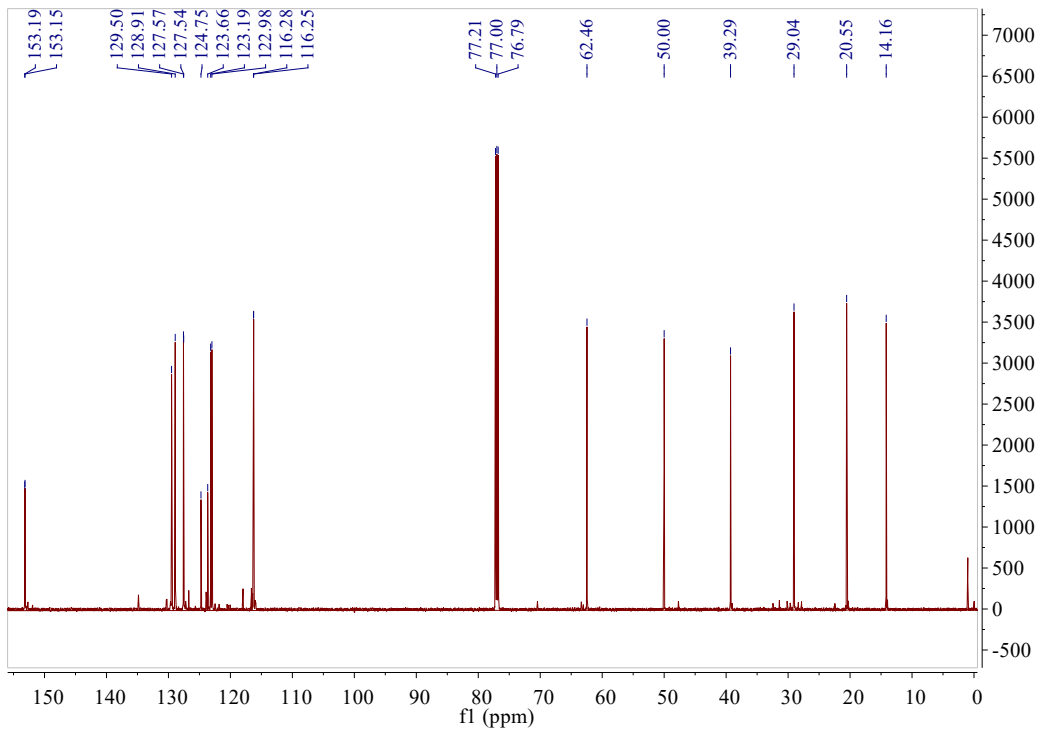
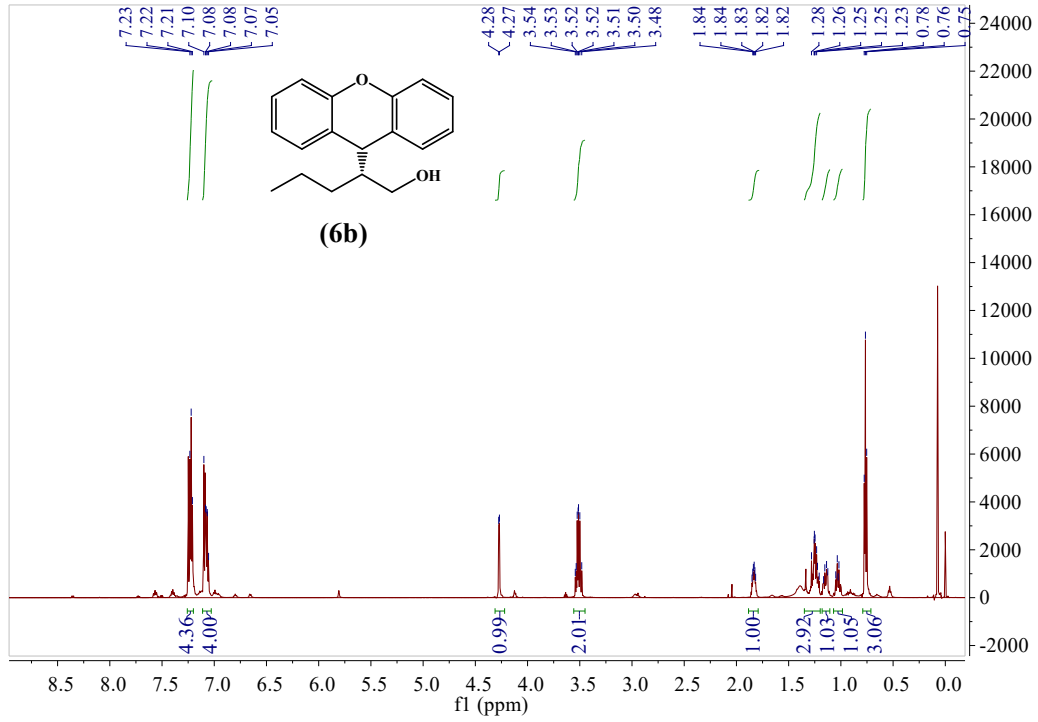


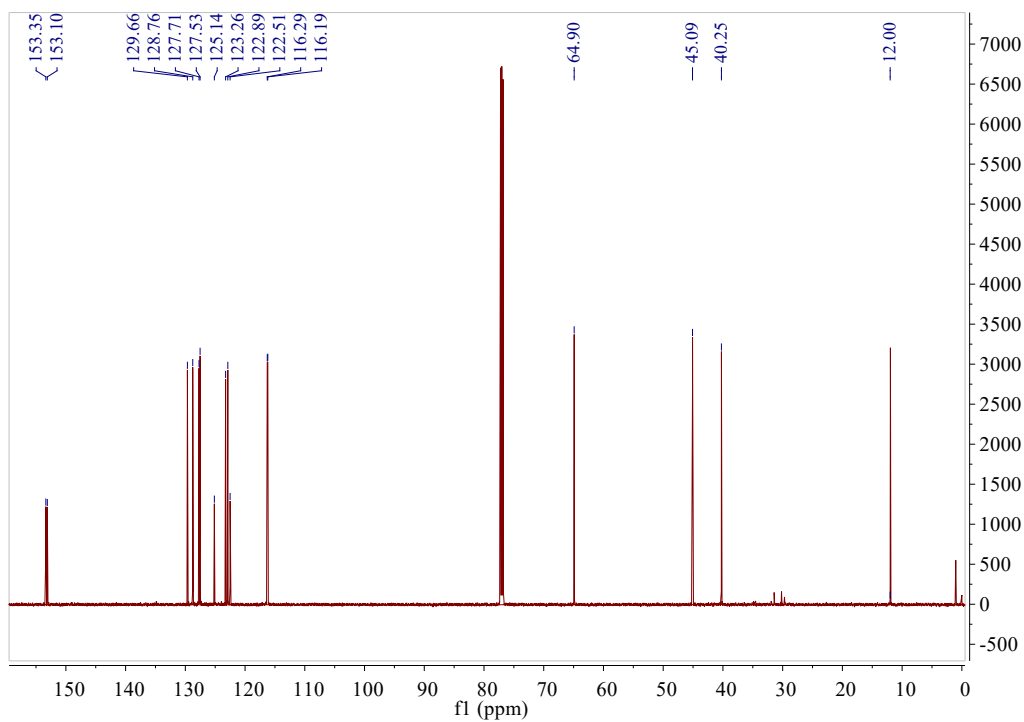
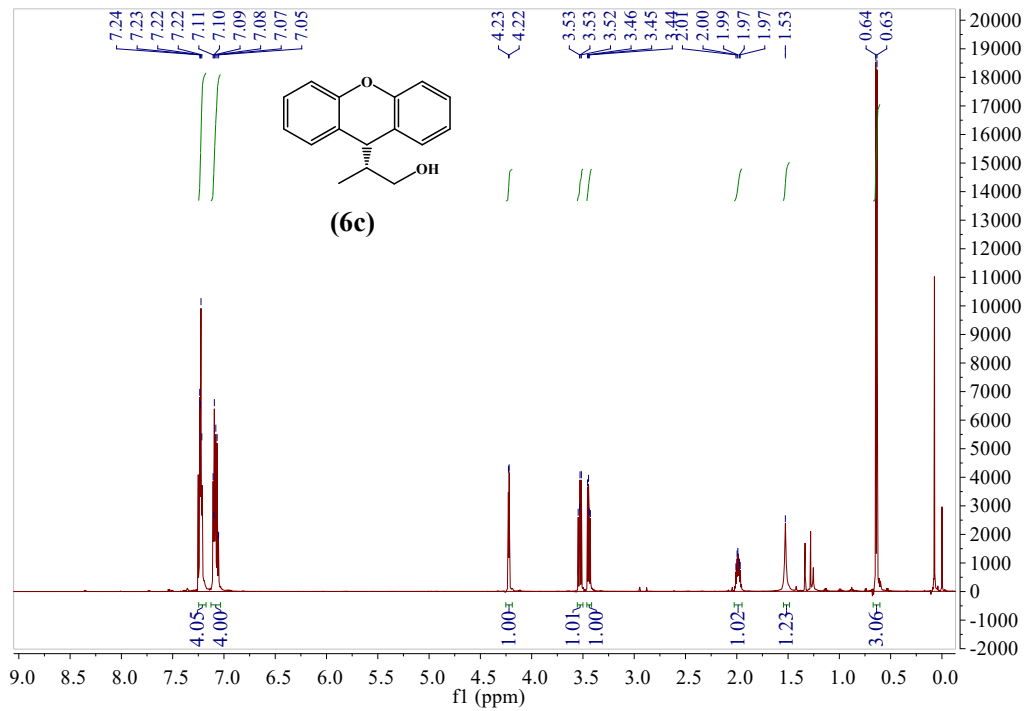


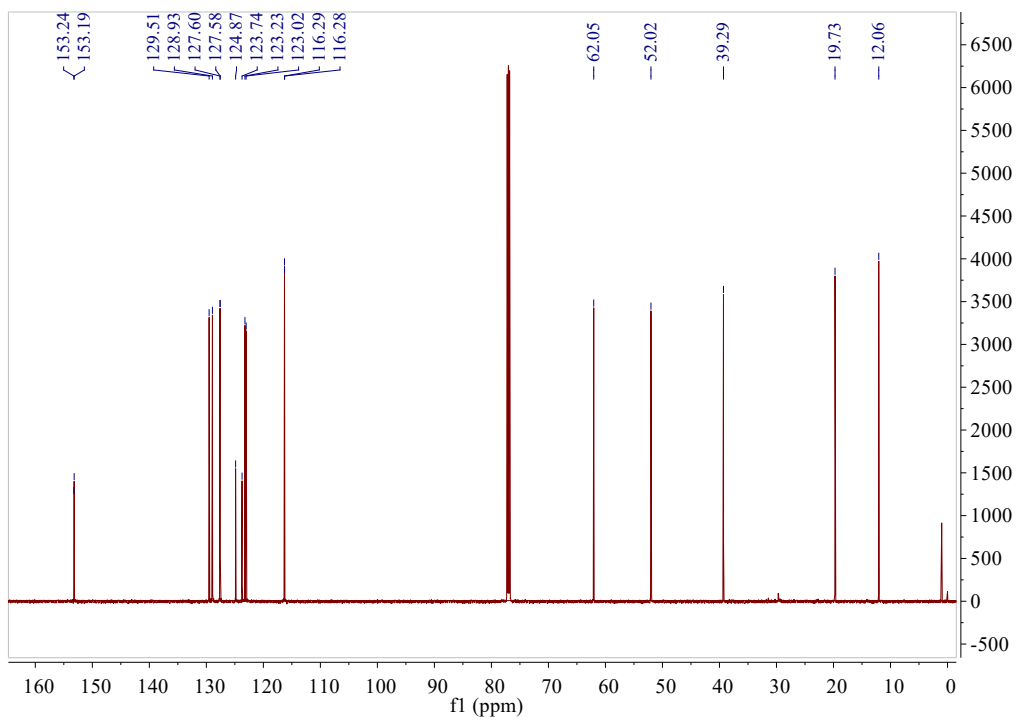
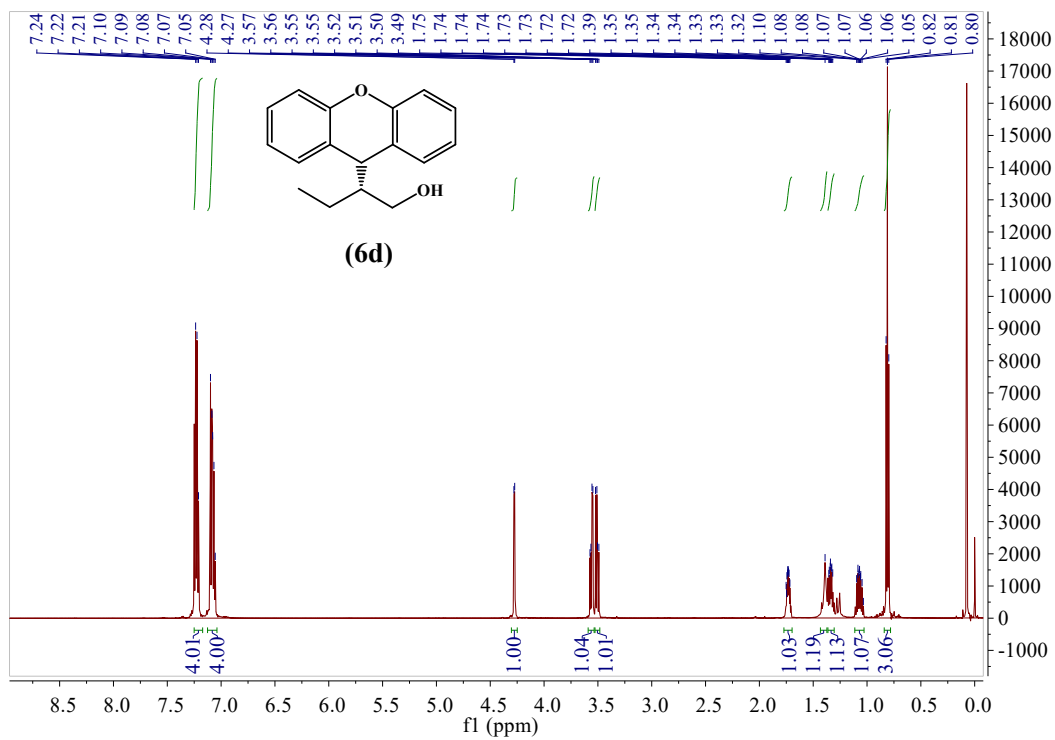


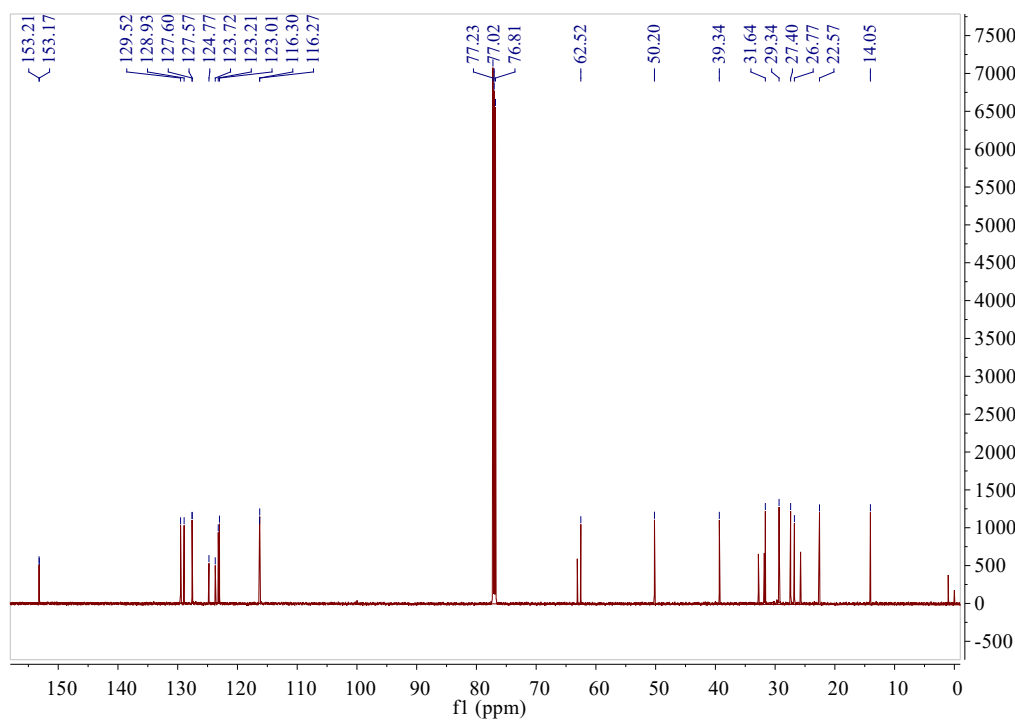
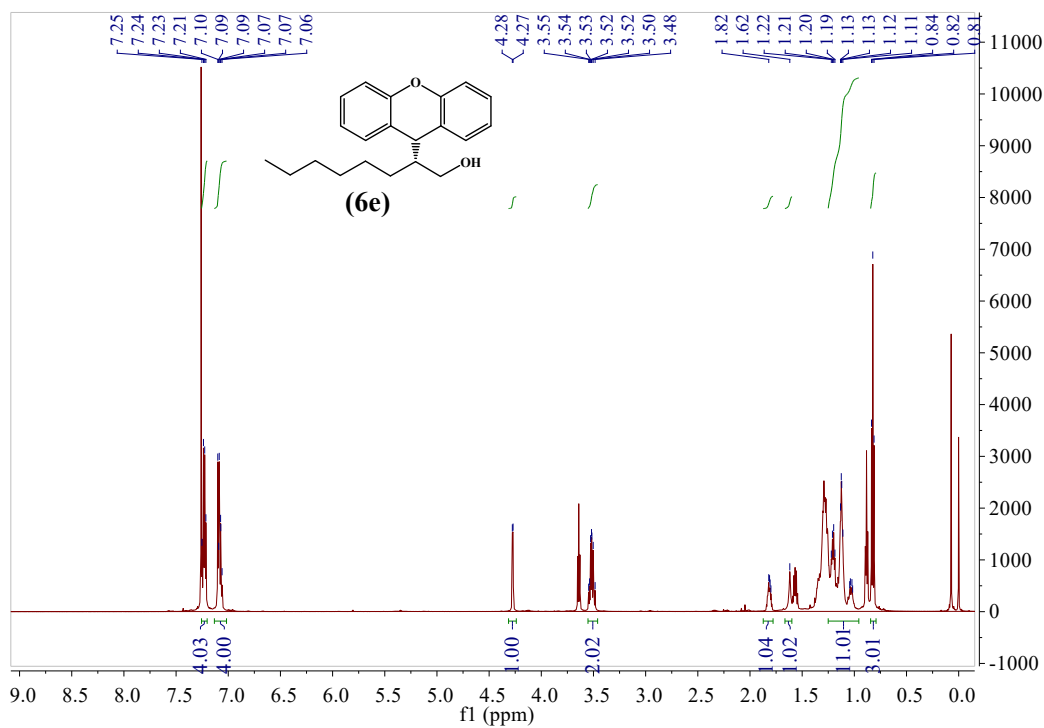






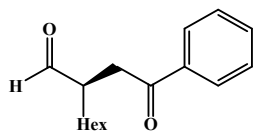






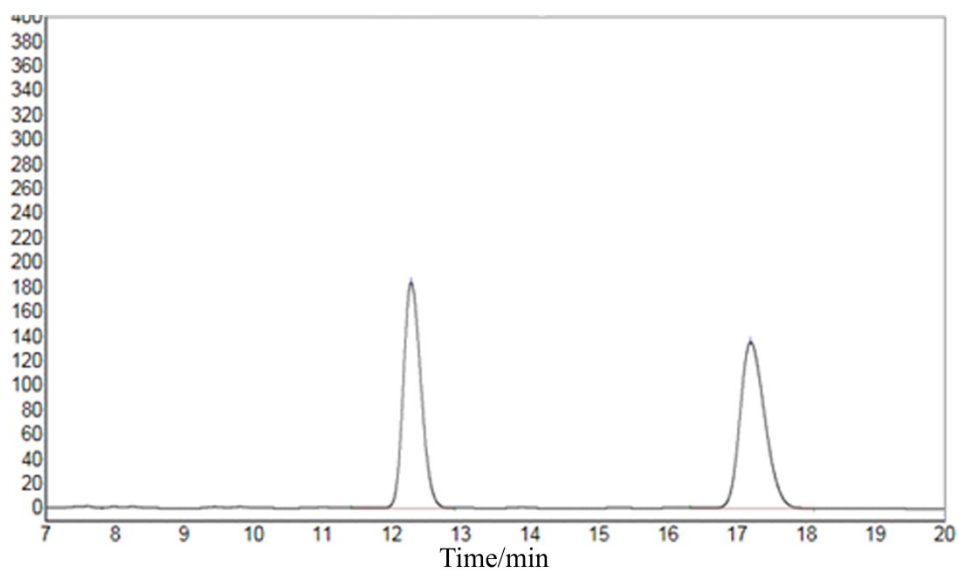


## Section 9. HPLC traces



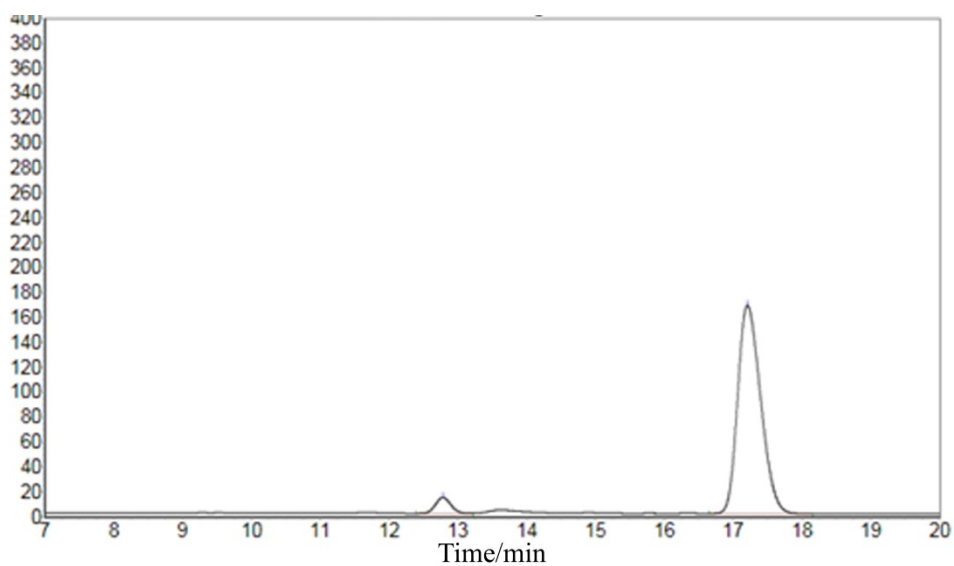
**(R)-2-(2-Oxo-2-phenylethyl)hexanal (3a):** The enantiomeric excess was determined by HPLC with Chiralpack IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 12.288$  min,  $t_{\text{major}} = 17.198$  min.

Racemic:



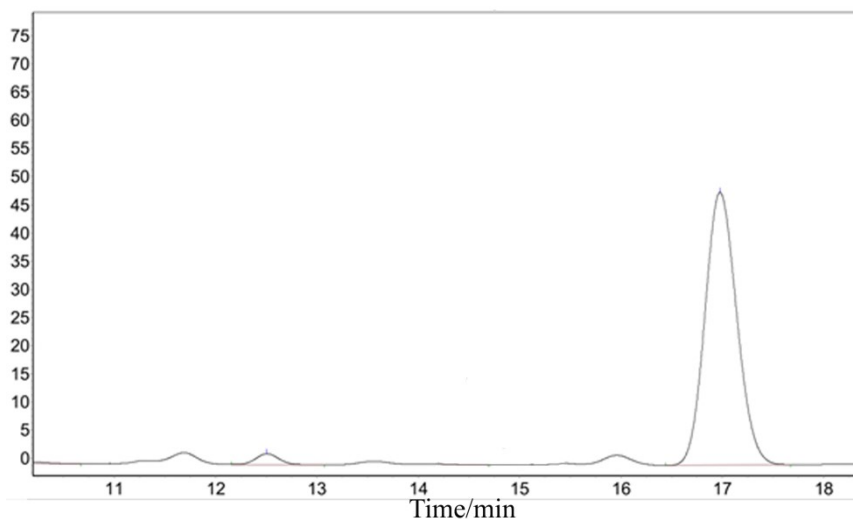
No.	Retention Time	Area	Height	Concentration
1	12.288	3271376.750	183983.891	49.1406
2	17.198	3385796.000	135443.125	50.8594

20CPB@KIT-6 enantioenriched (*ee*: 90.2%):



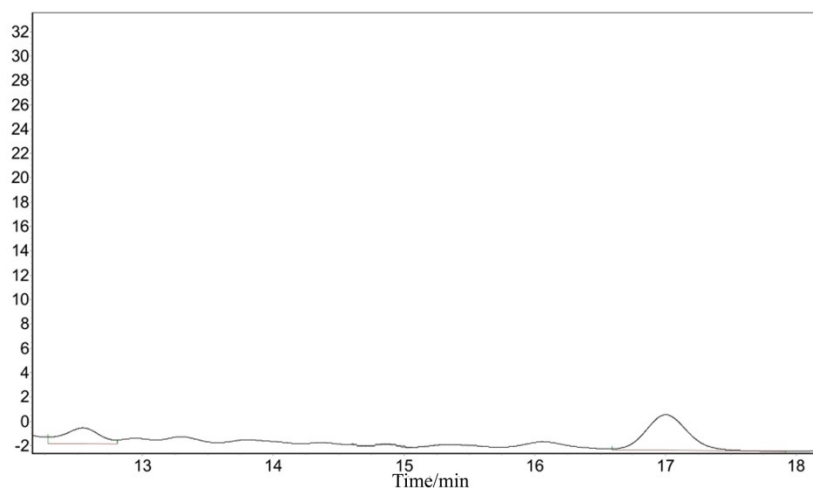
No.	Retention Time	Area	Height	Concentration
1	12.782	200163.672	12787.520	4.8917
2	17.208	3891722.000	167230.375	95.1083

Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (N<sub>2</sub> atmosphere) enantioenriched (*ee*: 89.0%):

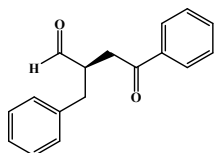


No.	Retention Time	Area	Height	Concentration
1	12.505	139707.422	8552.136	5.4872
2	16.977	2406437.500	106123.805	94.5128

Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (under normal atmospheric) enantioenriched (*ee*: 41.6%):

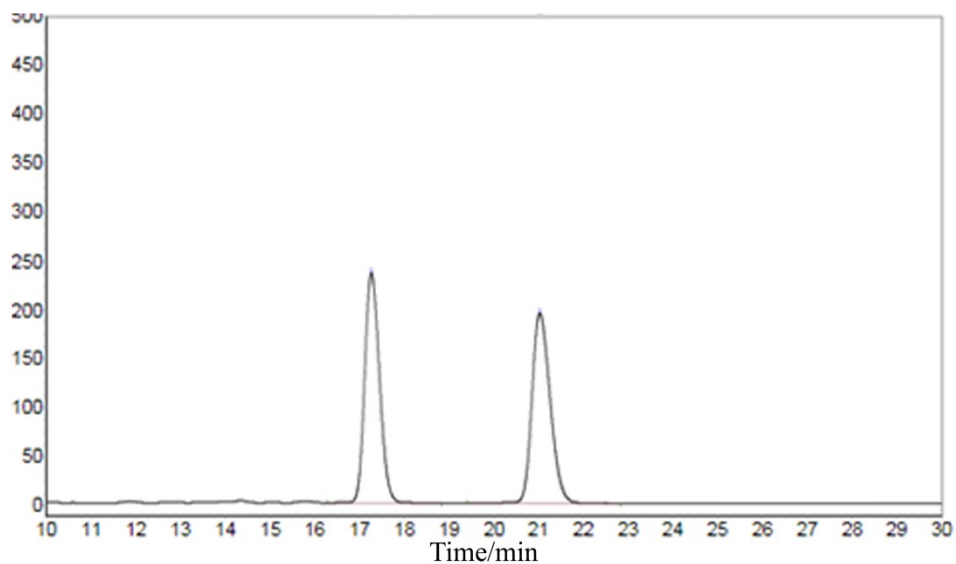


No.	Retention Time	Area	Height	Concentration
1	12.542	26392.980	1322.819	29.1818
2	17.005	64044.313	2905.177	70.8182



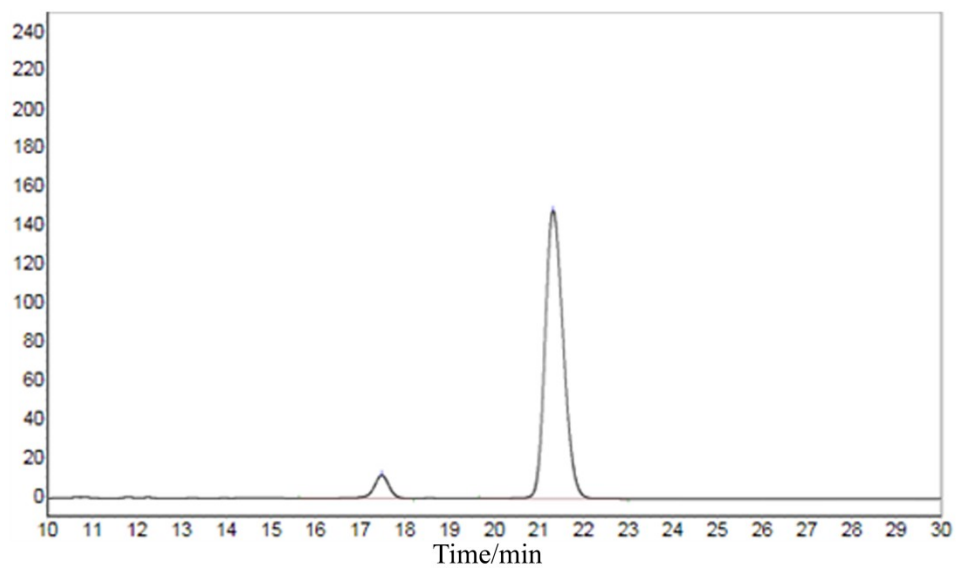
**R-2-Benzyl-4-oxo-4-phenylbutanal (3b):** The enantiomeric excess was determined by HPLC with Chiralpack IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 17.265$  min,  $t_{\text{major}} = 21.028$  min.

Racemic:

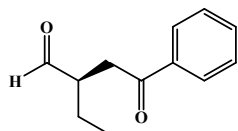


No.	Retention Time	Area	Height	Concentration
1	17.265	5403438.000	235423.938	49.5888
2	21.028	5493054.000	194166.188	50.4112

Enantioenriched (*ee*: 86.7%):



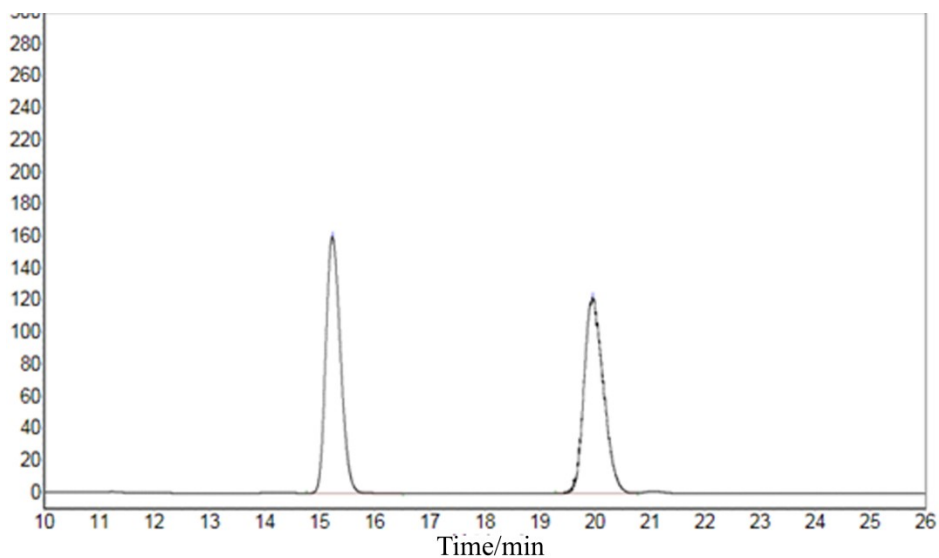
No.	Retention Time	Area	Height	Concentration
1	17.482	301465.156	12060.616	6.6822
2	21.320	4209998.000	148457.438	93.3178



**(R)-2-ethyl-4-oxo-4-phenylbutanal (3c):** The enantiomeric excess was

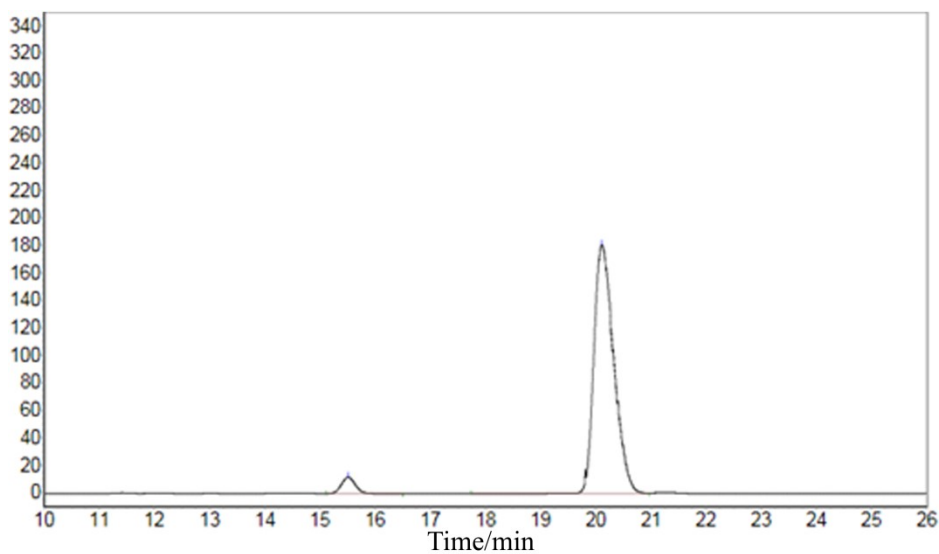
determined by HPLC with Chiralpack IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 15.233$  min,  $t_{\text{major}} = 19.957$  min.

Racemic:

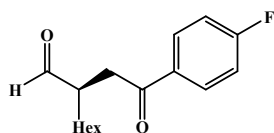


No.	Retention Time	Area	Height	Concentration
1	15.233	2967648.500	160399.141	49.6581
2	19.957	3008517.000	122642.656	50.3419

Enantioenriched (*ee*: 91.3%):



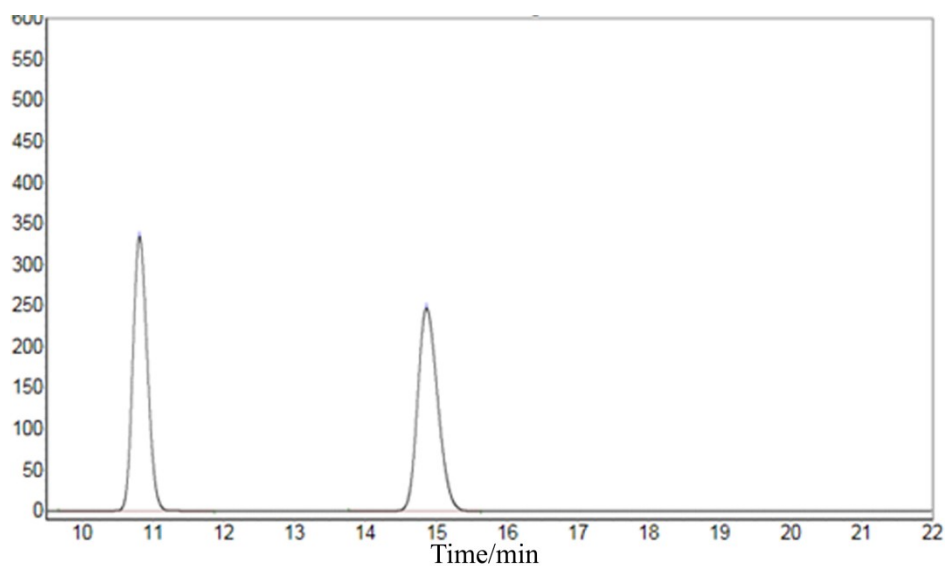
No.	Retention Time	Area	Height	Concentration
1	15.512	208711.625	11963.169	4.3938
2	20.110	4541465.000	180981.641	95.6062



**(R)-2-(2-(4-fluorophenyl)-2-oxoethyl)-3-oxooctanal (3d):** The

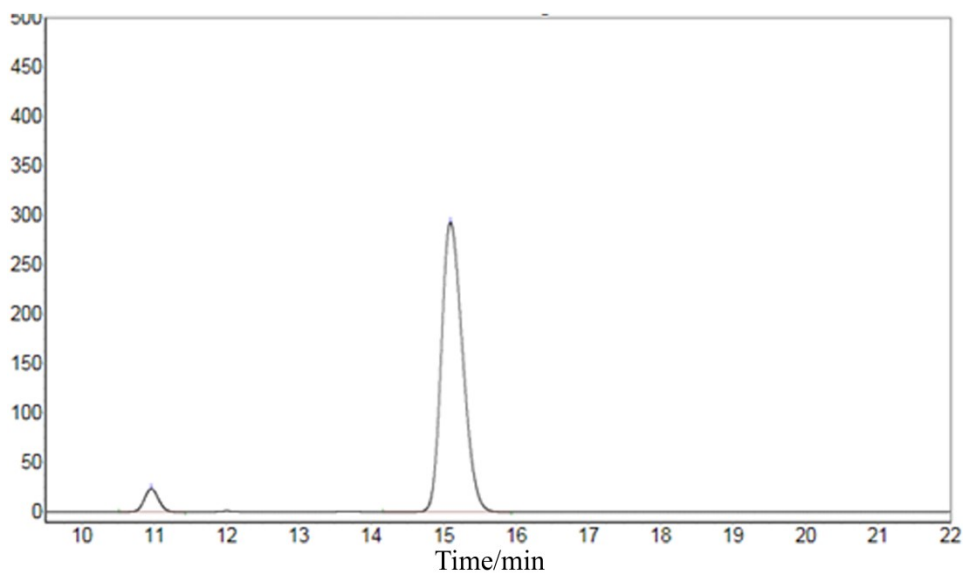
enantiomeric excess was determined by HPLC with Chiralpack IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 10.813$  min,  $t_{\text{major}} = 14.860$  min.

Racemic:

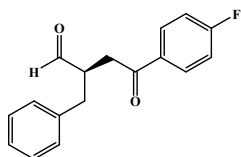


No.	Retention Time	Area	Height	Concentration
1	10.813	4730568.000	334422.406	49.2514
2	14.860	4874377.000	247260.297	50.7486

Enantioenriched (*ee*: 89.7%):

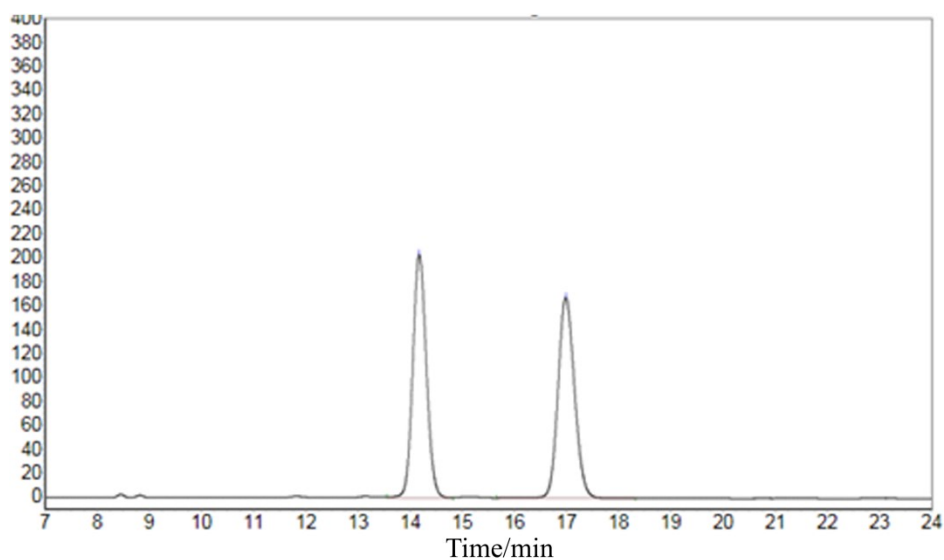


No.	Retention Time	Area	Height	Concentration
1	10.962	323815.531	23563.344	5.1378
2	15.097	5978756.000	292894.781	94.8622



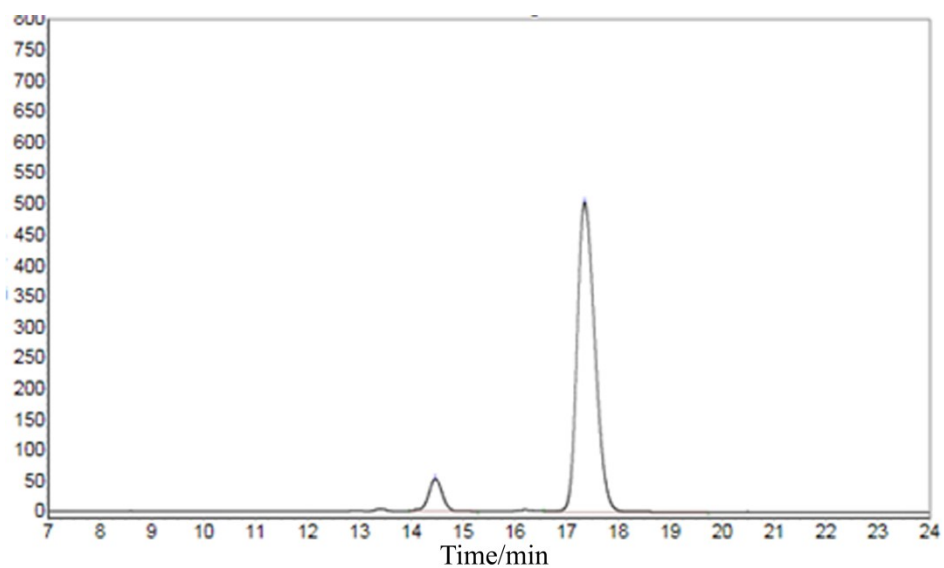
**(R)-2-benzyl-4-(4-fluorophenyl)-4-oxobutanal (3e):** The enantiomeric excess was determined by HPLC with Chiralpak IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 14.172$  min,  $t_{\text{major}} = 16.983$  min.

Racemic:

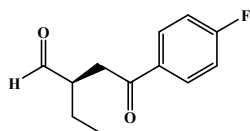


No.	Retention Time	Area	Height	Concentration
1	14.172	3693680.250	203535.328	50.0985
2	16.983	3679150.750	167740.016	49.9015

Enantioenriched ( $ee$ : 84.7%):

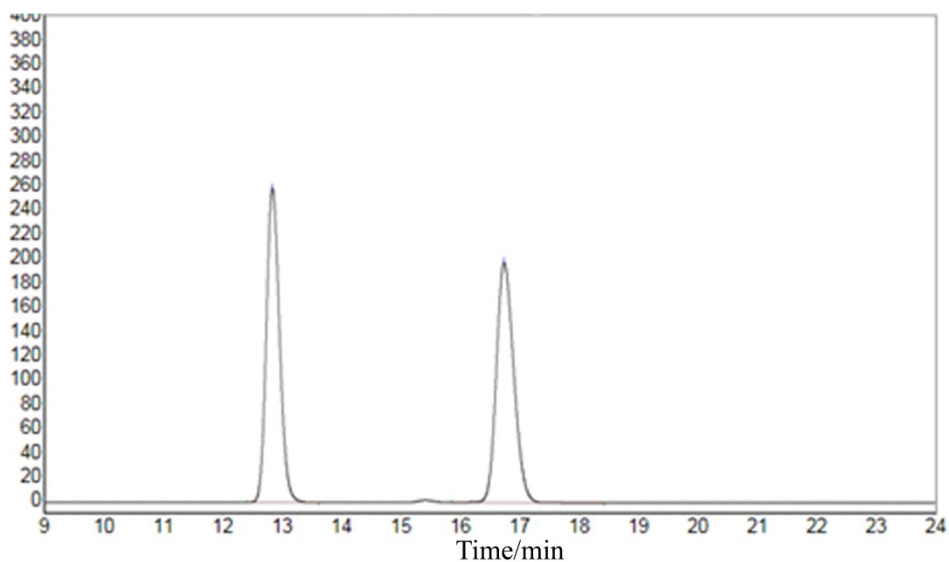


No.	Retention Time	Area	Height	Concentration
1	14.465	995829.625	52917.609	7.6483
2	17.350	12024391.000	503387.219	92.3517



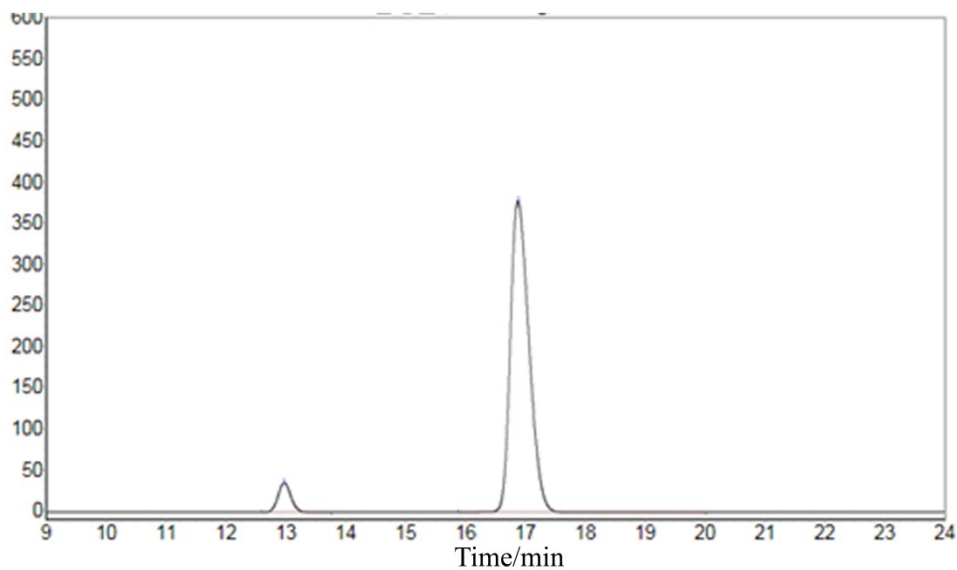
**(R)-2-ethyl-4-(4-fluorophenyl)-4-oxobutanal (3f):** The enantiomeric excess was determined by HPLC with Chiralpak IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 12.833$  min,  $t_{\text{major}} = 16.733$  min.

Racemic:

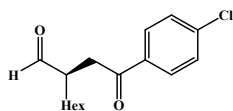


No.	Retention Time	Area	Height	Concentration
1	12.833	4005363.750	258910.641	49.7311
2	16.733	4048684.000	197903.969	50.2689

Enantioenriched (*ee*: 87.6%):



No.	Retention Time	Area	Height	Concentration
1	12.967	540480.875	35893.922	6.2000
2	16.878	8176901.500	378506.688	93.8000

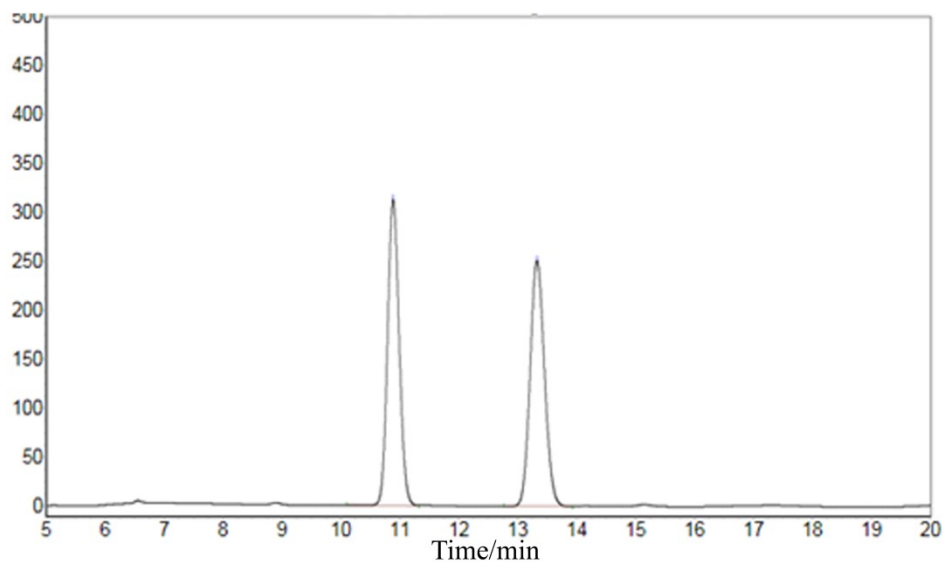


**(R)-2-(2-(4-chlorophenyl)-2-oxoethyl)-3-oxooctanal (3g):** The enantiomeric

excess was determined by HPLC with Chiralpack IC column at 254 nm; eluent: hexane:i-PrOH

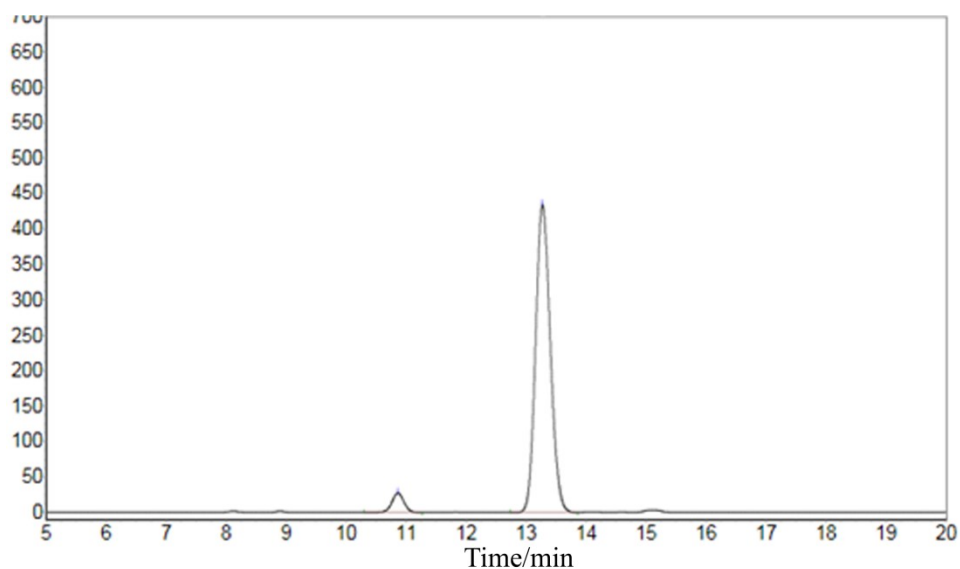
(90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 10.882$  min,  $t_{\text{major}} = 13.328$  min.

Racemic:



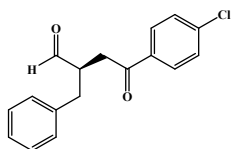
No.	Retention Time	Area	Height	Concentration
1	10.882	4277746.000	312771.906	50.0564
2	13.328	4268104.500	250727.063	49.9436

Enantioenriched (*ee*: 89.9%):



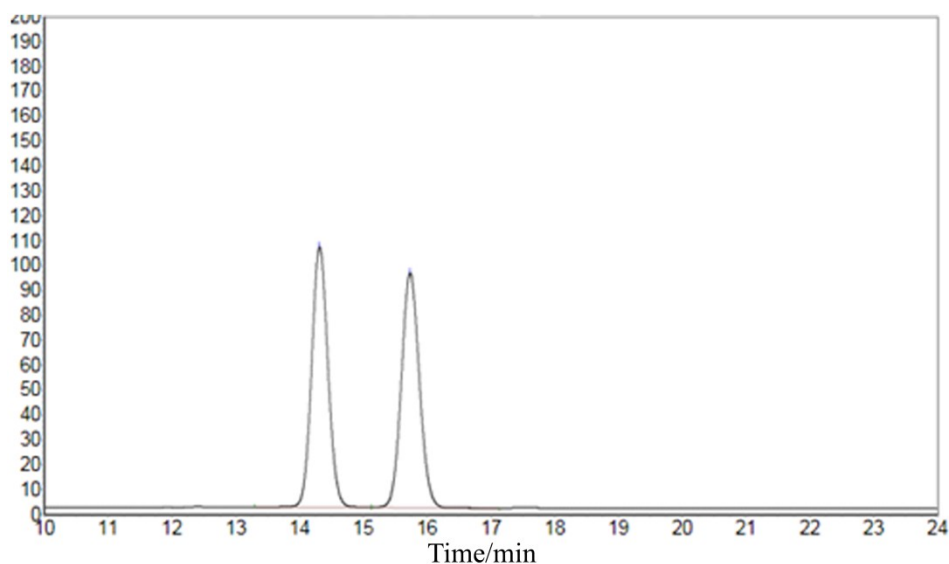
No.	Retention Time	Area	Height	Concentration
1	10.860	391780.031	27536.564	5.0040
2	13.272	7437556.000	434836.938	94.9960





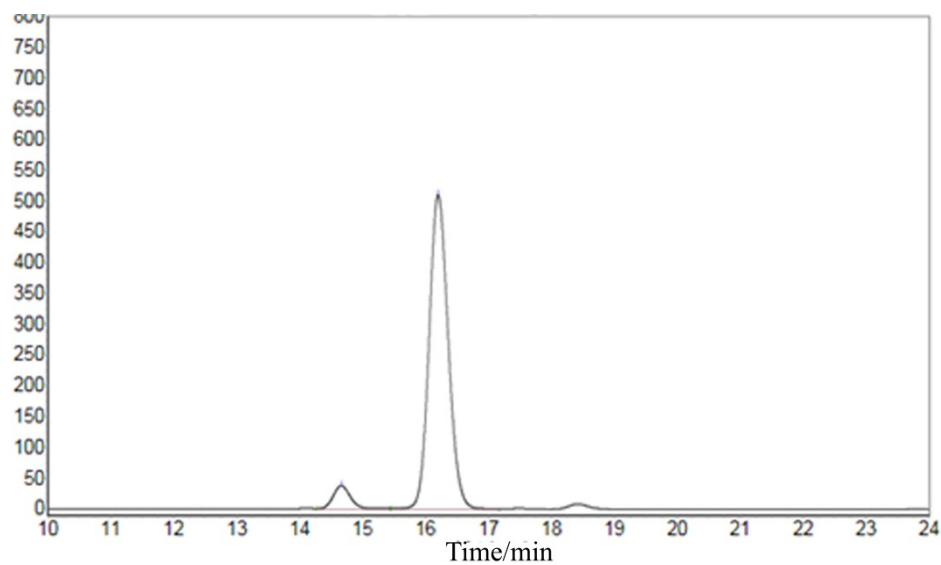
**(R)-2-benzyl-4-(4-chlorophenyl)-4-oxobutanal (3h):** The enantiomeric excess was determined by HPLC with Chiralpak IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 14.310$  min,  $t_{\text{major}} = 15.733$  min.

Racemic:

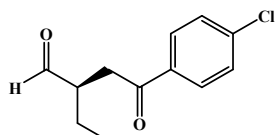


No.	Retention Time	Area	Height	Concentration
1	14.310	1889923.250	105035.938	50.3675
2	15.733	1862340.875	94594.922	49.6325

Enantioenriched (*ee*: 86.7%):

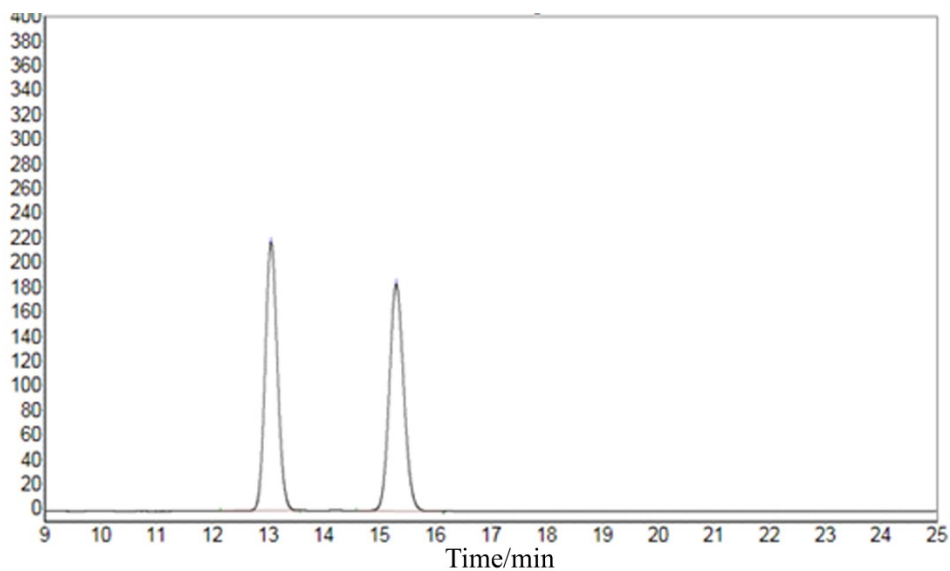


No.	Retention Time	Area	Height	Concentration
1	14.663	776043.313	38387.324	6.6896
2	16.198	10824678.000	510943.344	93.3104



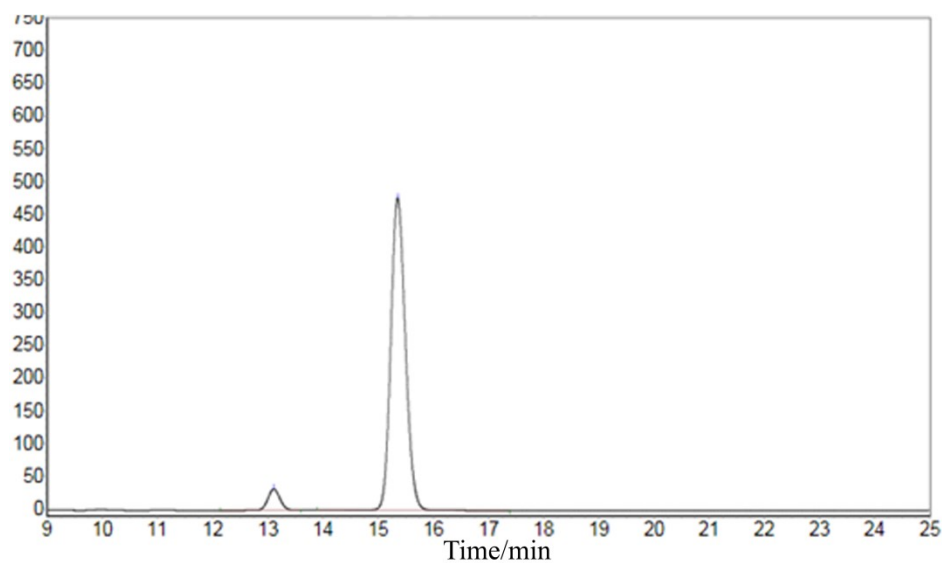
**(R)-4-(4-chlorophenyl)-2-ethyl-4-oxobutanal (3i):** The enantiomeric excess was determined by HPLC with Chiralpack IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 13.058$  min,  $t_{\text{major}} = 15.303$  min.

Racemic:

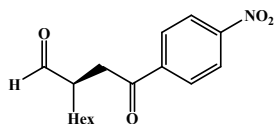


No.	Retention Time	Area	Height	Concentration
1	13.058	3319069.500	217902.609	50.0306
2	15.303	3315004.500	184384.734	49.9694

Enantioenriched (*ee*: 89.3%):



No.	Retention Time	Area	Height	Concentration
1	13.107	491827.844	32318.121	5.3208
2	15.355	8751634.000	476544.375	94.6792

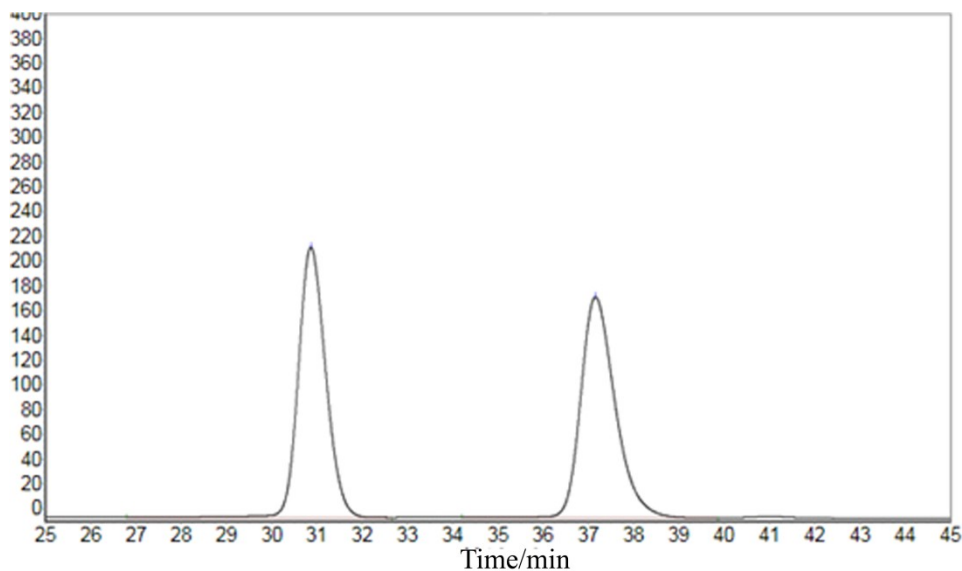


**(R)-2-(2-(4-Nitrophenyl)-2-oxoethyl)octanal (3j):** The enantiomeric

excess was determined by HPLC with Chiralpack IC column at 254 nm; eluent: hexane:i-PrOH

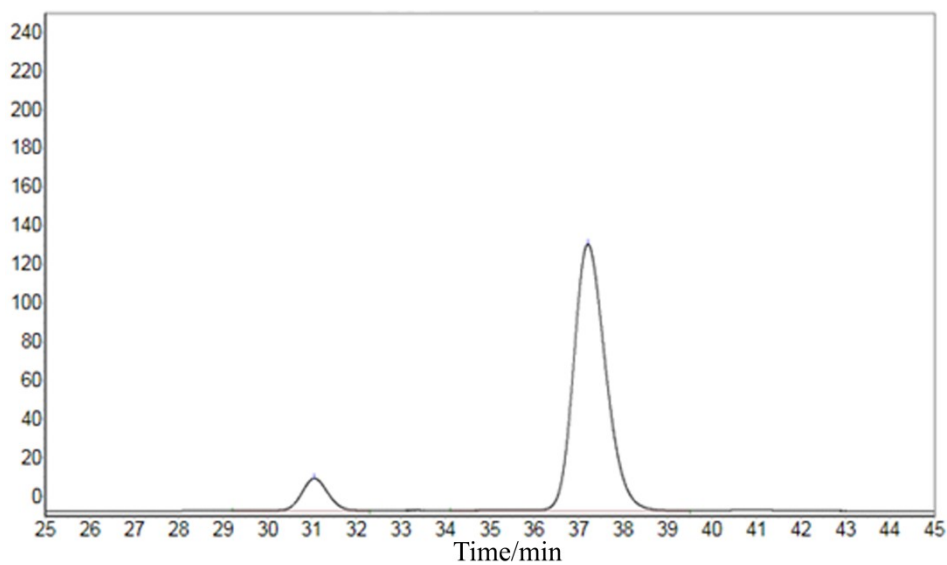
(90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 30.870$  min,  $t_{\text{major}} = 37.153$  min.

Racemic:

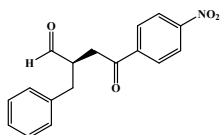


No.	Retention Time	Area	Height	Concentration
1	30.870	9302498.000	218656.969	49.4816
2	37.153	9497432.000	178538.063	50.5184

Enantioenriched (*ee*: 80.7%):

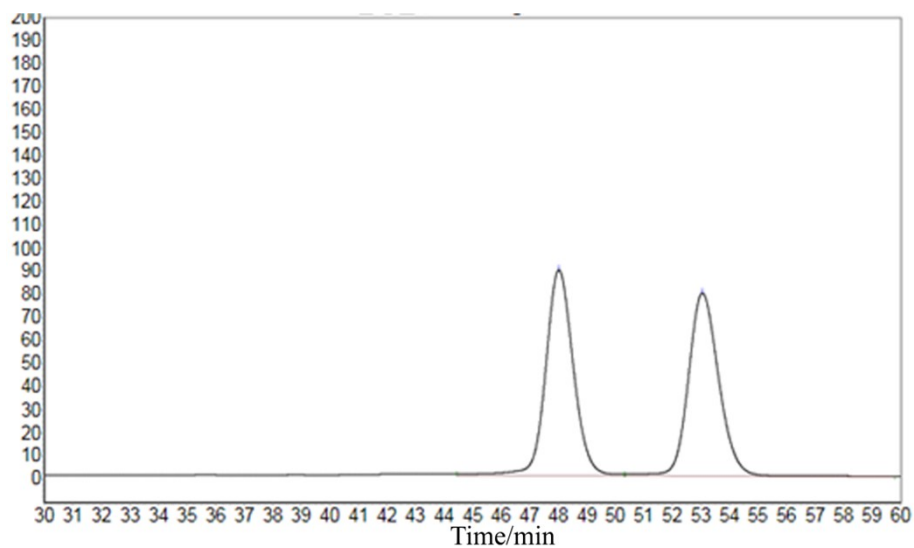


No.	Retention Time	Area	Height	Concentration
1	31.052	745310.625	17020.127	9.6004
2	37.208	7018037.500	138170.875	90.3996



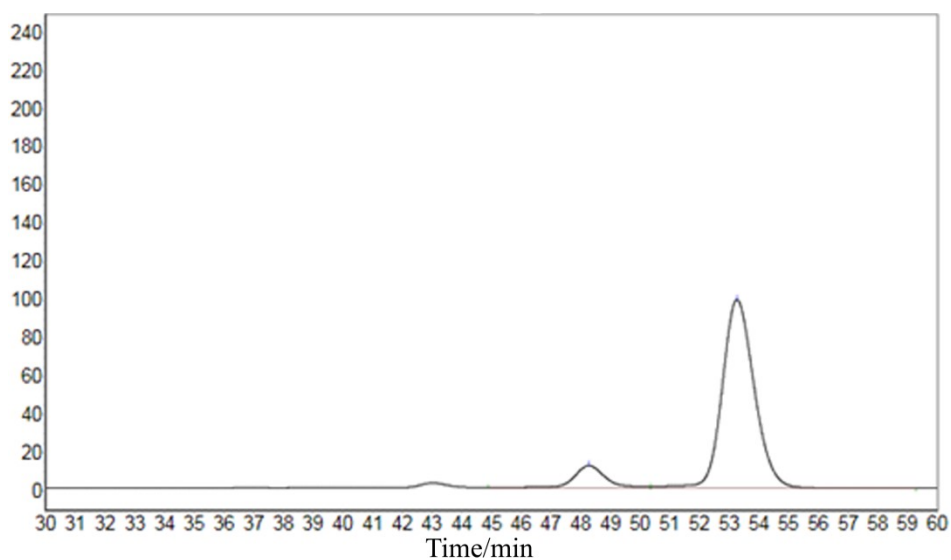
**R-2-Benzyl-4-(4-nitrophenyl)-4-oxobutanal (3k):** The enantiomeric excess was determined by HPLC with Chiralpack IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 48.027$  min,  $t_{\text{major}} = 53.055$  min.

Racemic:

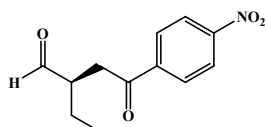


No.	Retention Time	Area	Height	Concentration
1	48.027	6069701.000	89256.102	50.9138
2	53.055	5851815.500	79273.852	49.0862

Enantioenriched (*ee*: 77.7%):



No.	Retention Time	Area	Height	Concentration
1	48.277	933283.125	11817.975	11.1187
2	53.265	7460556.500	98891.047	88.8813

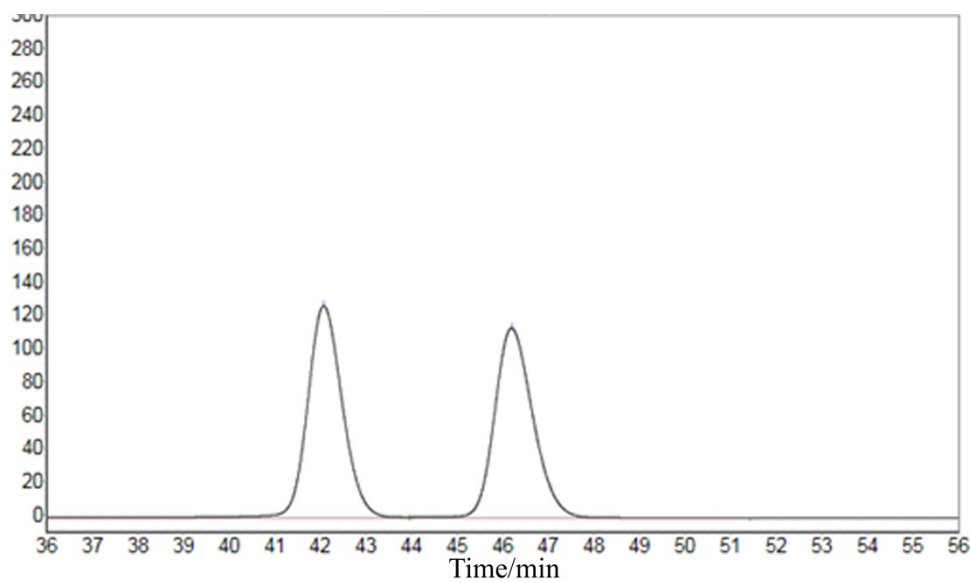


**(R)-2-ethyl-4-(4-nitrophenyl)-4-oxobutanal (3l):** The enantiomeric

excess was determined by HPLC with Chiralpak IC column at 254 nm; eluent: hexane:i-PrOH

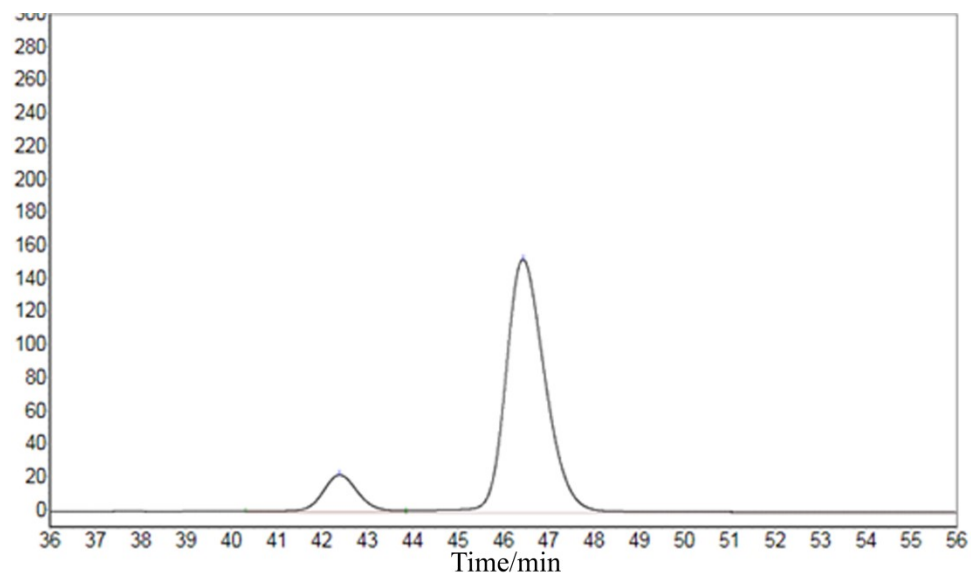
(90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 42.078$  min,  $t_{\text{major}} = 46.198$  min.

Racemic:

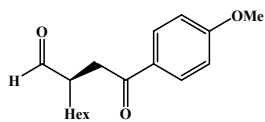


No.	Retention Time	Area	Height	Concentration
1	42.078	6863038.500	127327.930	50.6770
2	46.198	6679660.500	114053.555	49.3230

Enantioenriched (*ee*: 75.3%):

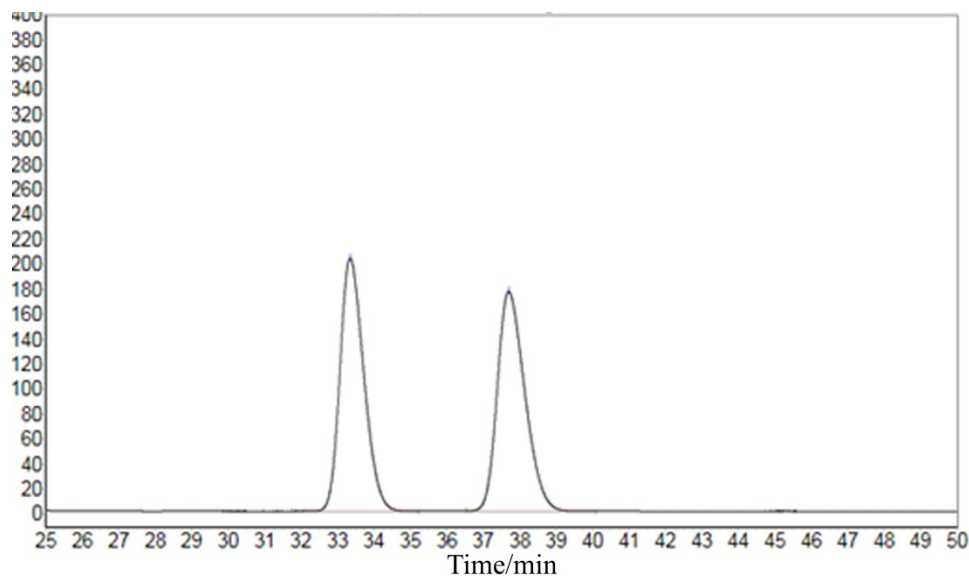


No.	Retention Time	Area	Height	Concentration
1	42.387	1312254.750	22587.395	12.3420
2	46.438	9320195.000	153062.344	87.6580



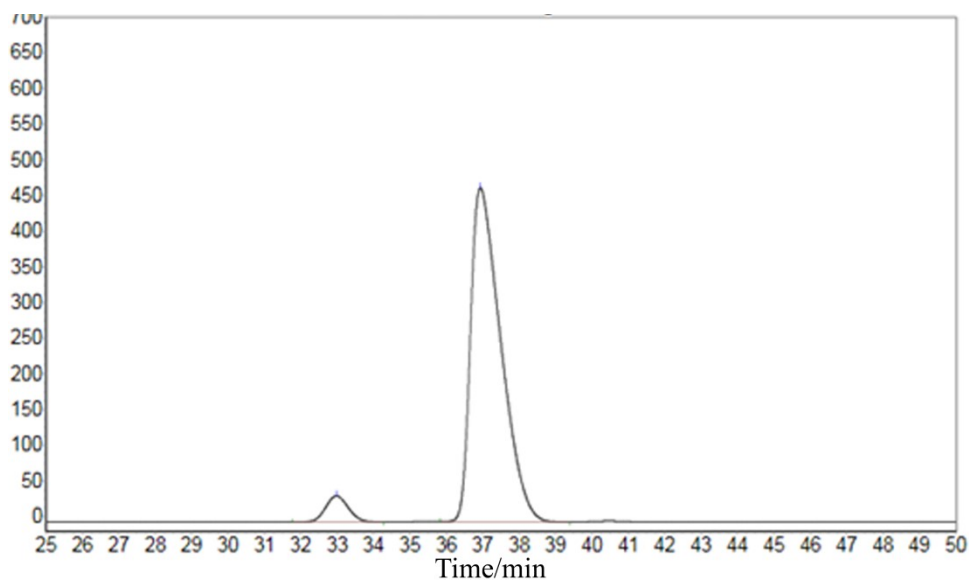
**(R)-2-(2-(4-Methoxyphenyl)-2-oxoethyl)octanal (3m):** The enantiomeric excess was determined by HPLC with Chiralpack IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 33.350$  min,  $t_{\text{major}} = 37.702$  min.

Racemic:

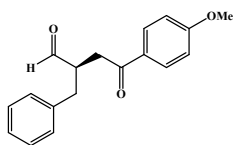


No.	Retention Time	Area	Height	Concentration
1	33.350	9219743.000	202581.781	49.9261
2	37.702	9247034.000	175868.625	50.0739a

Enantioenriched (*ee*: 89.1%):

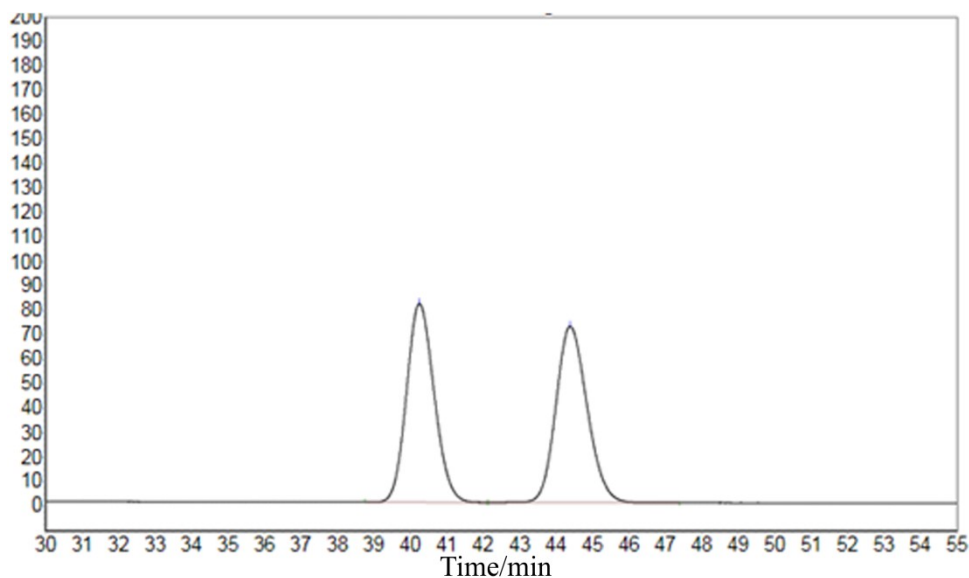


No.	Retention Time	Area	Height	Concentration
1	32.982	1595017.500	36650.984	5.5808
2	36.937	26985396.000	468144.813	94.4192



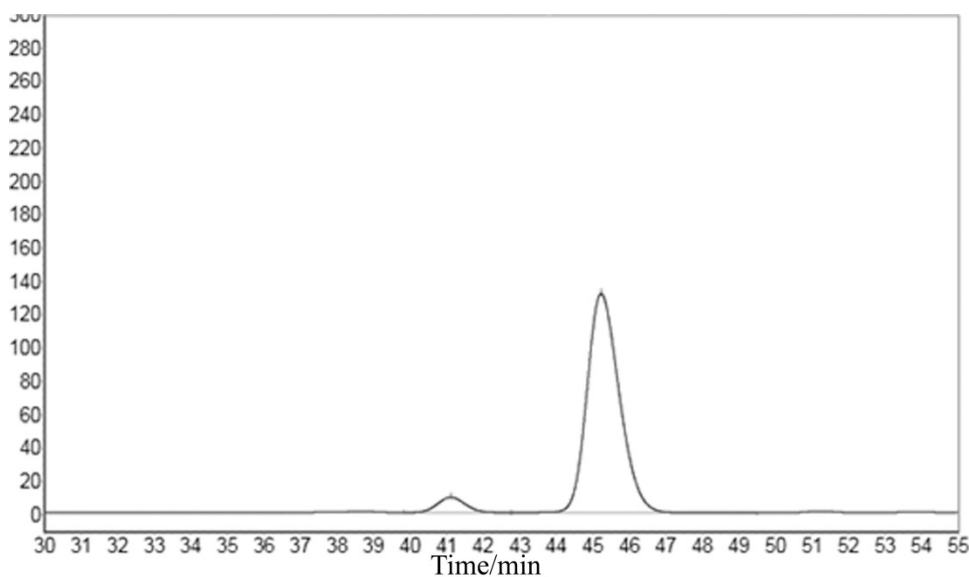
**R-2-Benzyl-4-(4-methoxyphenyl)-4-oxobutanal (3n):** The enantiomeric excess was determined by HPLC with Chiralpak IC column at 254 nm; eluent: hexane:i-PrOH (90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 40.255$  min,  $t_{\text{major}} = 44.392$  min.

Racemic:

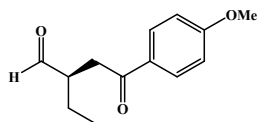


No.	Retention Time	Area	Height	Concentration
1	40.255	4289478.000	81299.047	49.9369
2	44.392	4300312.500	72108.039	50.0631

Enantioenriched ( $ee$ : 88.3%):



No.	Retention Time	Area	Height	Concentration
1	41.117	506268.313	9207.026	5.8704
2	45.233	8117877.000	131518.016	94.1296

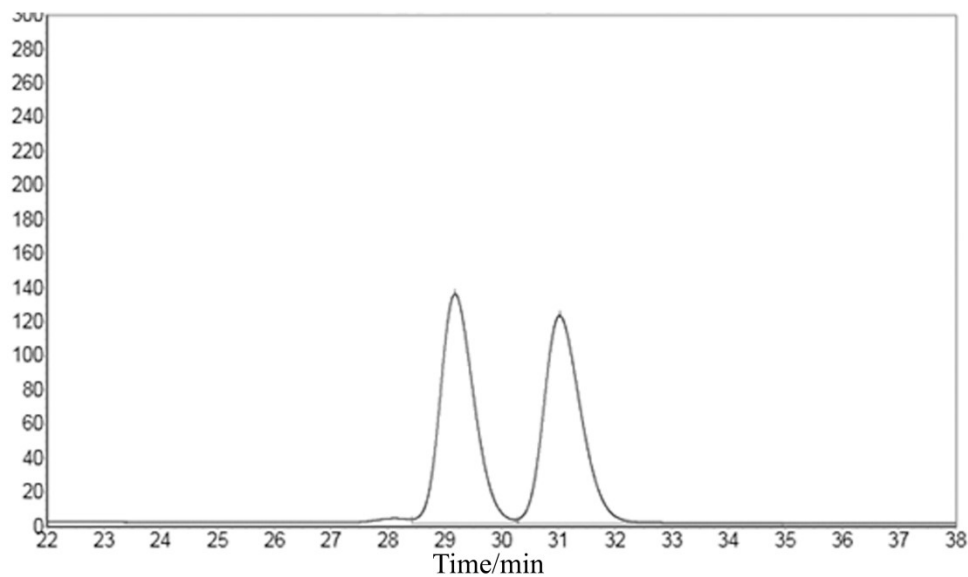


**(R)-2-ethyl-4-(4-methoxyphenyl)-4-oxobutanal (30):** The enantiomeric

excess was determined by HPLC with Chiralpak IC column at 254 nm; eluent: hexane:i-PrOH

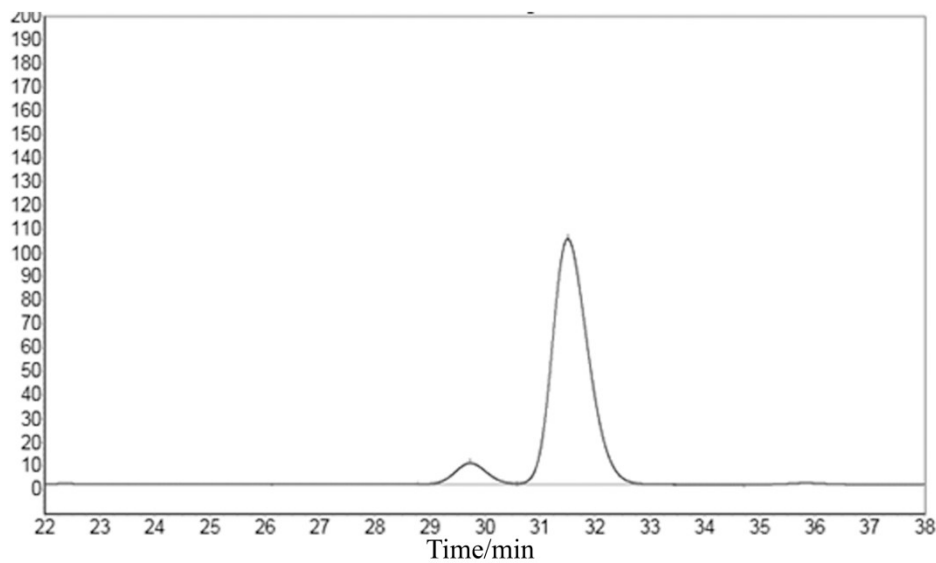
(90: 10), flow rate = 1 mL/min,  $t_{\text{minor}} = 29.185$  min,  $t_{\text{major}} = 31.028$  min.

Racemic:



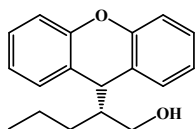
No.	Retention Time	Area	Height	Concentration
1	29.185	5518262.000	134197.984	50.1380
2	31.028	5487889.000	121491.289	49.8620

Enantioenriched (*ee*: 85.1%):



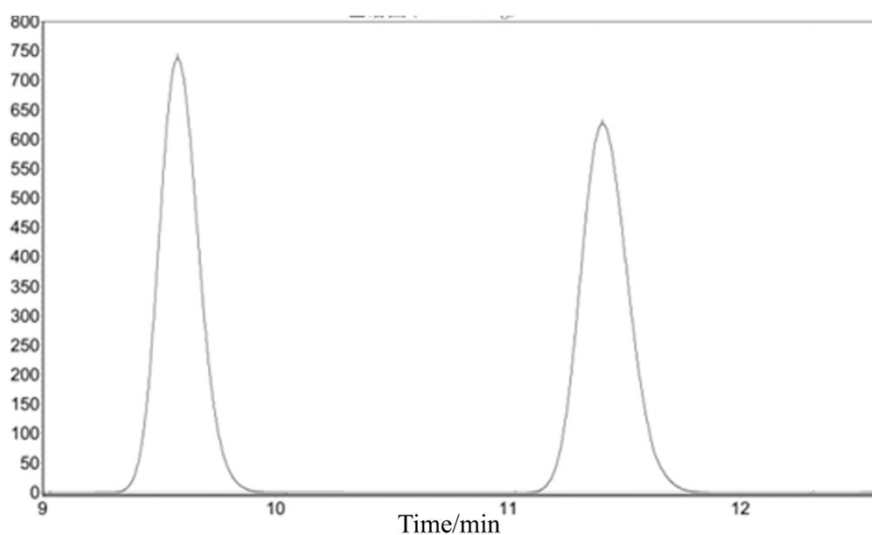
No.	Retention Time	Area	Height	Concentration
1	29.733	380006.875	9034.960	7.4514
2	31.513	4719825.000	103769.508	92.5486





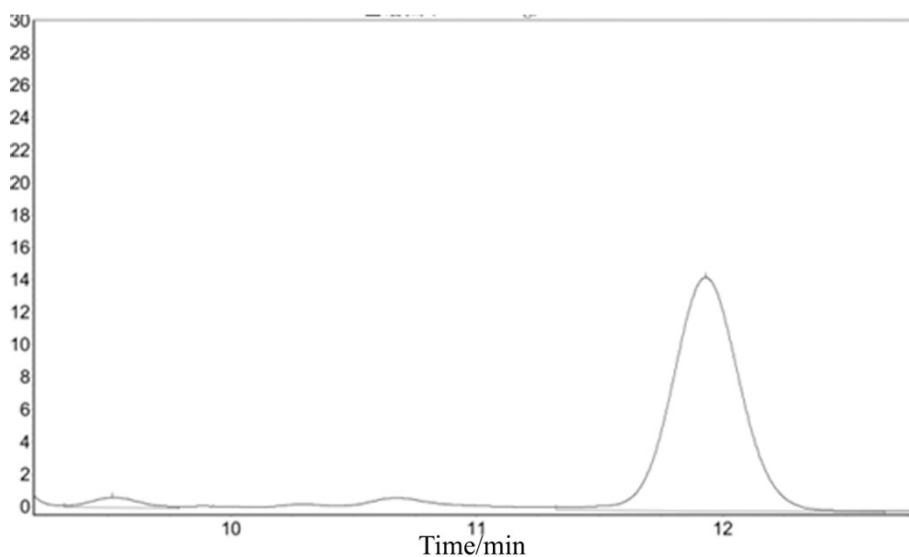
**(R)-2-(9H-xanthen-9-yl)pentan-1-ol (6b):** The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 240 nm; eluent: hexane:i-PrOH (95: 5), flow rate = 1 mL/min,  $t_{\text{minor}} = 9.580$  min,  $t_{\text{major}} = 11.405$  min.

Racemic:

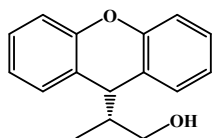


No.	Retention Time	Area	Height	Concentration
1	9.580	9052384.000	739010.875	49.4828
2	11.405	9241627.000	627690.250	50.5172

Enantioenriched (*ee*: 94.0%):

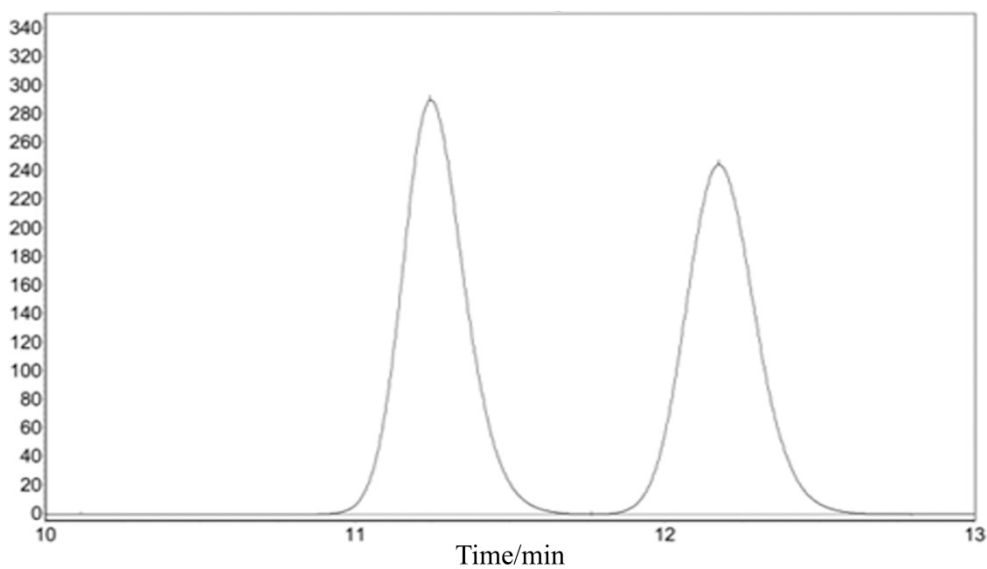


No.	Retention Time	Area	Height	Concentration
1	9.518	8548.613	613.130	2.9880
2	11.930	277553.094	14409.948	97.0120



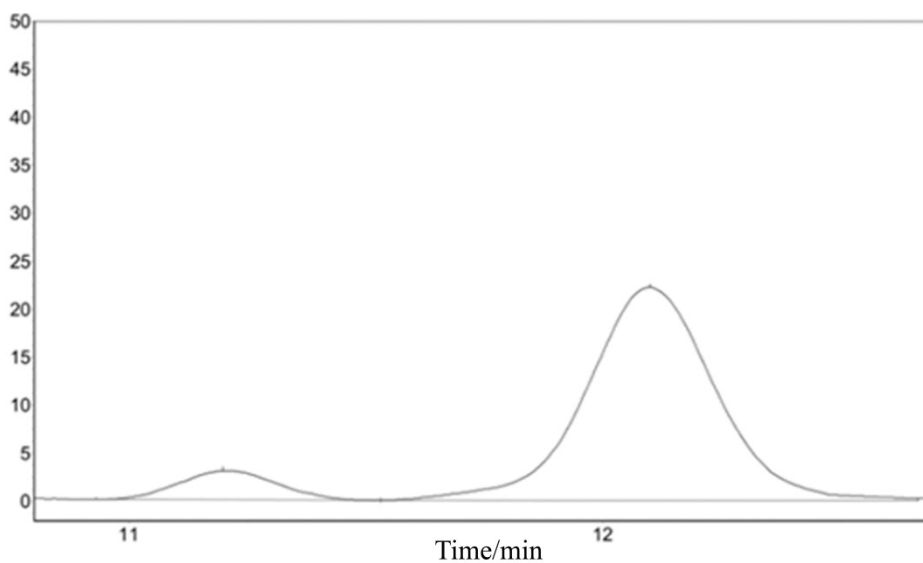
**(R)-2-(9H-xanthen-9-yl)propan-1-ol (6c):** The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 240 nm; eluent: hexane:i-PrOH (95: 5), flow rate = 1 mL/min,  $t_{\text{minor}} = 11.242$  min,  $t_{\text{major}} = 12.173$  min.

Racemic:

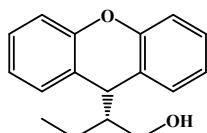


No.	Retention Time	Area	Height	Concentration
1	11.242	4237338.500	290310.063	51.5745
2	12.173	3978613.000	245027.656	48.4255

Enantioenriched (*ee*: 81.1%):

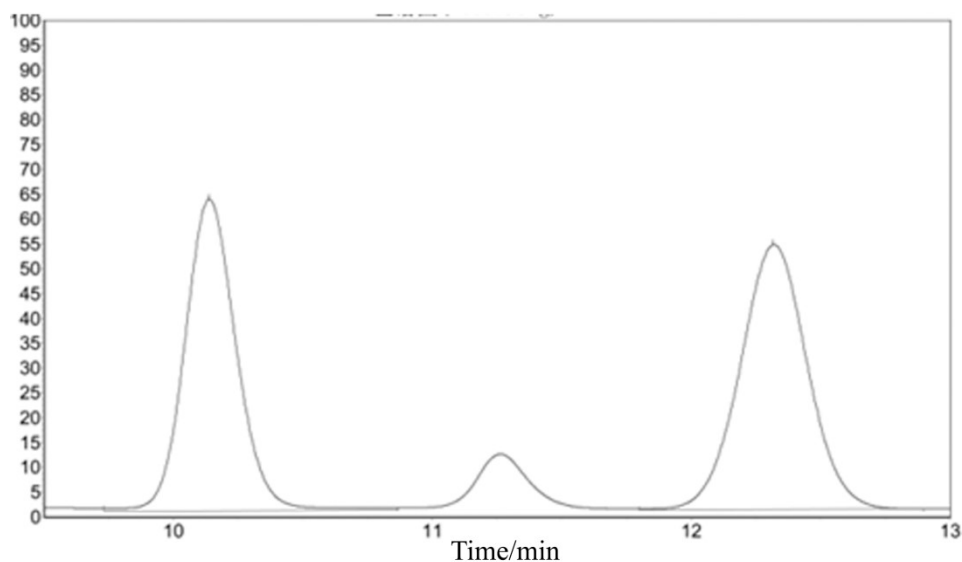


No.	Retention Time	Area	Height	Concentration
1	11.198	44031.902	3028.571	9.4506
2	12.100	421884.875	22224.035	90.5494



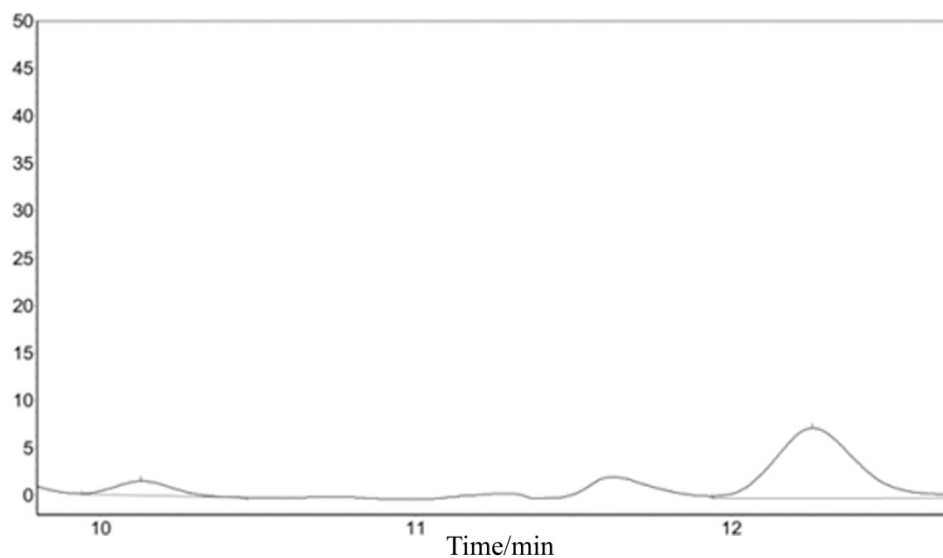
**(R)-2-(9H-xanthen-9-yl)butan-1-ol (6d):** The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 240 nm; eluent: hexane:i-PrOH (95: 5), flow rate = 1 mL/min,  $t_{\text{minor}} = 10.135$  min,  $t_{\text{major}} = 12.317$  min.

Racemic:

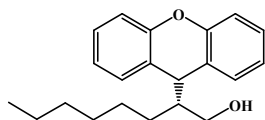


No.	Retention Time	Area	Height	Concentration
1	10.135	871345.000	62702.672	47.4539
2	12.317	964849.625	53338.953	52.5461

Enantioenriched (*ee*: 74.9%):

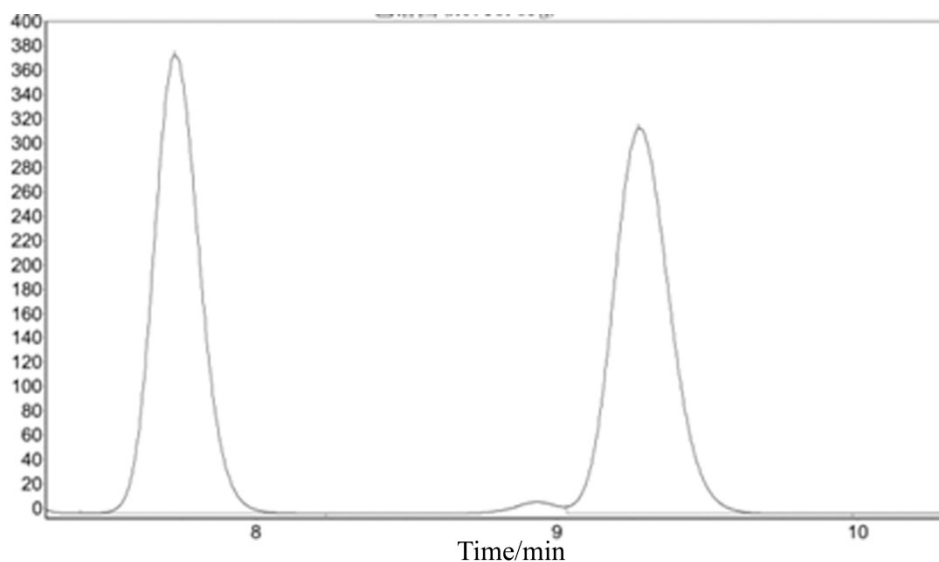


No.	Retention Time	Area	Height	Concentration
1	10.130	19434.209	1535.336	12.5260
2	12.257	135715.391	7387.268	87.4740



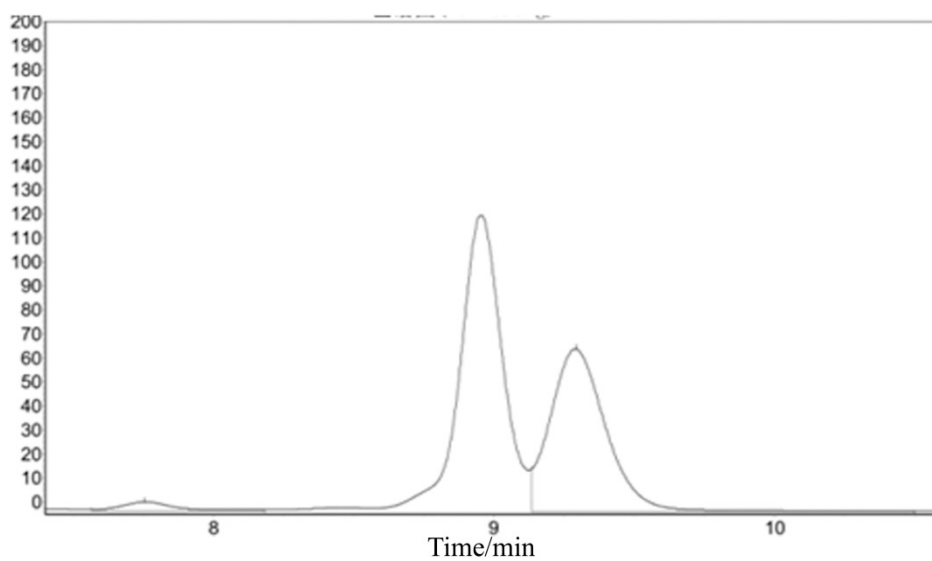
**(R)-2-(9H-xanthen-9-yl)octan-1-ol (6e):** The enantiomeric excess was determined by HPLC with Chiralpack AD-H column at 240 nm; eluent: hexane:i-PrOH (95:5), flow rate = 1 mL/min,  $t_{\text{minor}} = 7.727$  min,  $t_{\text{major}} = 9.270$  min.

Racemic:



No.	Retention Time	Area	Height	Concentration
1	7.727	4054709.750	375757.313	49.4211
2	9.270	4149699.00	316169.375	50.5789

Enantioenriched (*ee*: 92.6%):



No.	Retention Time	Area	Height	Concentration
1	7.755	34040.418	1822.691	3.7175
2	9.292	881649.250	47165.6441	96.2825



## Section 10. References

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- (3) X. Zhu, Y. Lin, Y. Sun, M. C. Beard and Y. Yan, *J. Am. Chem. Soc.*, 2019, **141**, 733–738.
- (4) X. Zhu, Y. Lin, J. San Martin, Y. Sun, D. Zhu and Y. Yan, *Nat. Commun.*, 2019, **10**, 2843.
- (5) Y. Guo, Y. Lou, J. Chen and Y. Zhao, *ChemSusChem*, 2021, **15**, e202102334.