Supplementary Information

Nitrogen-doped carbon supported cobalt catalyst for highly selective catalysis of cyclohexane amino carbonylation

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1. General Information and Experimental Section

General Information

Unless otherwise noted, all commercially available reagents were used with extra-dry solvents.

The contents of Pd in the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using Iris advantage Thermo Jarrel Ash device.

Fourier transform infrared (FT-IR) spectrum were recorded with a Bruker VERTEX 70FTIR spectrometer.

The liquid nuclear magnetic resonance spectra (NMR) were recorded on a Bruker AvanceTM III 400 MHz in deuterated chloroform unless otherwise noted.

Powder X-ray diffraction (PXRD) measurements were conducted by a STADIP automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator selecting CuKα1 radiation and a 6° position sensitive detector (PSD) (step size: 0.014°, step time: 25.05 s). The XRD patterns were scanned in the 2θ range of 5–80°.

Nitrogen adsorption-desorption isotherms were measured at 77 K using an American Quantachrome iQ_2 automated gas sorption analyzer. The samples were outgassed at 120 °C for 12 h before the measurements. Surface areas were calculated from the adsorption data using Langmuir and Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using the Barrett, Joyner, and Halenda (BJH) method.

X-ray photoelectron spectroscopy (XPS) measurements were carried out by a VG ESCALAB 210 instrument equipped with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyzer, and a 5 keV Ar^+ ion gun. All spectra were recorded by using AlKa (1361 eV) radiation. The electron binding energy was referenced to the C1s peak at 284.8 eV.

Raman spectra were recorded on a micro-Raman spectrometer (Renishaw) equipped with a CCD detector using a He/Ne laser with a wavelength of 532 nm.

Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 5.0 kV.

High-resolution transmission electron microscope (HR-TEM) analysis was carried out on a Talos F200S operating at 200 kV.

GC-MS analyses were performed with on an Agilent 5977 A MSD GC-MS.

Experimental Section

All solvents and chemicals were obtained commercially and used as received.

Synthetic procedure of Co/NC-2D

Typically, $Zn(NO_3)_2 \cdot 6H_2O$ (1.68 g) was dissolved in 50 mL of deionized water. Then 50 mL deionized water solution of 3.70 g 2-methylimidazole (2-MI) was rapidly added to it with vigorous stirring for 45 min. The resulting white precipitate was left undisturbed for 12 hours. Then the white product was separated by centrifugation and washed with deionized water three times. Finally, the white powder was dried overnight at 80 °C and denoted as ZIF-8-p (p: plane). Then the ZIF-8-p was annealed in N_2 flow at 1000 °C for 1 h at a rate of 5 °C·min^{-1}, the obtained powder was denoted as NC-2D. Then 200 mg NC-2D was dispersed in 50 mL ethanol, and then 5 mL $Co(acac)_2$ ethanol solution with a concentration of 0.4 mg Co mL^{-1} was added dropwise. To thoroughly mix the metal solution and the supports, the mixture was stirred for 12 h, and dried by rotary evaporation. Finally, the precursor was treated with N_2 at 800 °C for 2 h at a rate of 5 °C·min^{-1}, which was designed as Co/NC-2D.

Synthetic procedure of Co/NC-3D

$Zn(NO_3)_2 \cdot 6H_2O$ (1.28 g) was dissolved in 50 mL methanol, and the mixture of 2.92 g 2-MI in 50 mL methanol was rapidly added to the above solution with vigorous stirring for 45 min. The resulting precipitate was standing for 12 hours. The white product was separated by centrifugation and washed with methanol. Finally, the white powder was dried overnight at 80 °C and designed as ZIF-8-s (s: space). Then the ZIF-8-s was annealed in N_2 flow at 1000 °C for 1 h at a rate of 5 °C·min^{-1}, the obtained powder was denoted as NC-3D. Then 200 mg NC-3D was dispersed in 50 mL ethanol, and then 5 mL $Co(acac)_2$ ethanol solution with a concentration of 0.4 mg Co mL^{-1} was added dropwise, the mixture was stirred for 12 h, and dried by rotary evaporation. Finally, the precursor was treated with N_2 at 800 °C for 2 h at a rate of 5 °C·min^{-1}, which was designed as Co/NC-3D.

Synthetic procedure of Co/AC

Active carbon (200 mg) was dispersed in 50 mL ethanol, and then 5 mL $Co(acac)_2$ ethanol solution with a concentration of 0.4 mg Co mL^{-1} was added dropwise, the mixture was stirred for 12 h, and dried by rotary evaporation. Finally, the precursor was treated with N_2 at 800 °C for 2 h at a rate of 5 °C·min^{-1}, which was designed as Co/AC.

Synthetic procedure of Co/EC

Ethyl Cellulose was calcined at 800 °C for 2 h with a heating rate of 5 °C·min^{-1} in a tube furnace under flowing N_2 gas and the obtained powder was denoted as EC. The Carboxymethyl Cellulose (CMC), Cellulose Acetate (CA), Sucrose (SUC) and Sodium Lignosulfonate (SL) were treated by the same method.

EC (200 mg) was dispersed in 50 mL ethanol, and then 5 mL $Co(acac)_2$ ethanol solution with a concentration of 0.4 mg Co mL^{-1} was added dropwise, the mixture was stirred for 12 h, and dried by rotary evaporation. Finally, the precursor was treated with N_2 at 800 °C for 2 h at a rate of 5 °C·min^{-1}, which was designed as Co/EC. The Co/CMC, Co/CA, Co/SUC and Co/SL were prepared

by the same method.

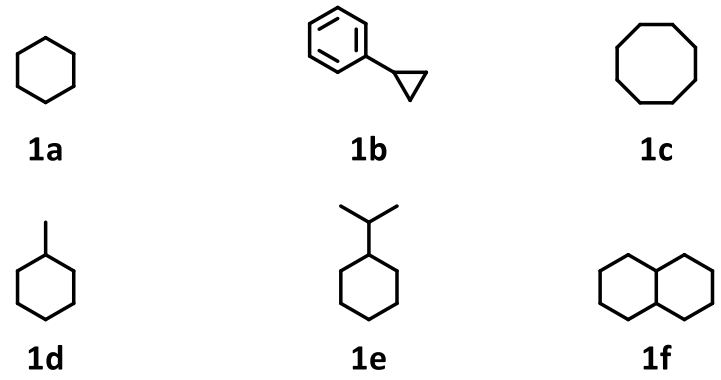
Synthetic procedure of Co/g-C_3N_4

Melamine was calcined in muffle furnace at 500 °C for 2 h with a heating rate of 5 °C·min^{-1} and the obtained powder was denoted as g-C_3N_4. Then g-C_3N_4 (200 mg) was dispersed in 50 mL ethanol, and then 5 mL $Co(acac)_2$ ethanol solution with a concentration of 0.4 mg Co mL^{-1} was added dropwise, the mixture was stirred for 12 h, and dried by rotary evaporation. Finally, the precursor was treated with N_2 at 500 °C for 2 h at a rate of 5 °C·min^{-1}.

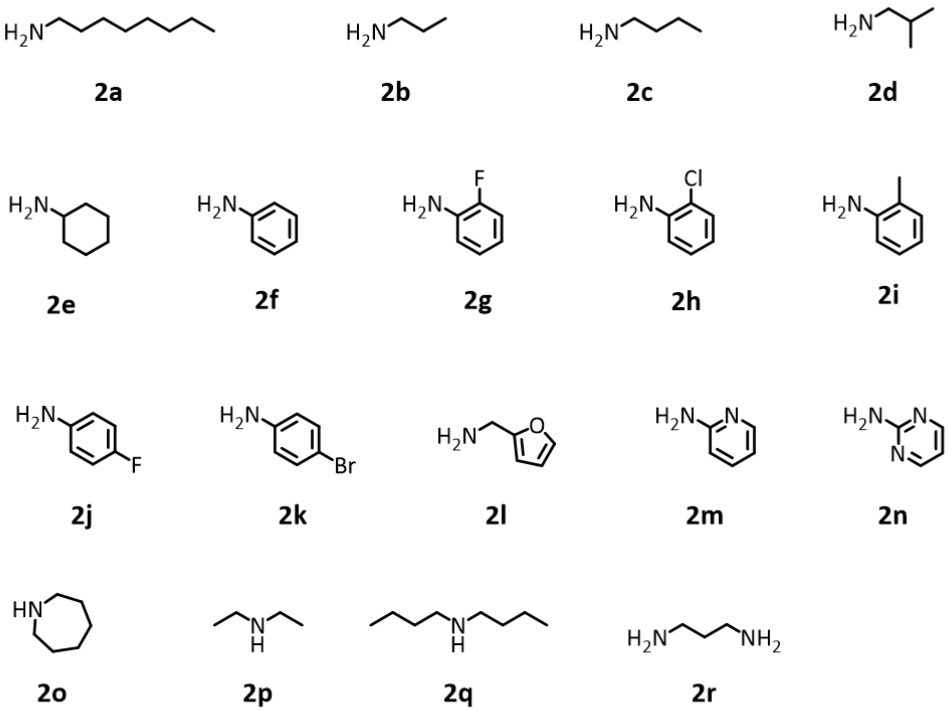
Detailed procedure for cyclohexane carbonylation amino carbonylation

As a typical carbonylation procedure, the freshly prepared Co/NC-2D (25 mg), octylamine (64 mg, 0.5 mmol), di-tert-butyl peroxide (109 mg, 0.75 mmol), cyclohexane (1.5 mL), and 1,2-dichloroethane (1.0 mL) were added into an 80 mL stainless-steel autoclave equipped with a glass liner. After sealing the autoclave and purging with CO four times, the pressure of CO was adjusted to 4 MPa. The autoclave was then placed in a preheated reactor and stirred at 110 °C for 12 hours. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with anhydrous ethanol (9.0 mL), and the catalyst was removed from the system by centrifugation. The resulting mixture was analyzed by ^1H NMR, and the yield product were determined by NMR analysis using triphenylmethane as the internal standard. For recycling, the Co/NC-2D was separated by centrifugation, washed with anhydrous ethanol (10.0 mL × 3), dried under vacuum at 80 °C for 12 hours, and then used directly for the next run.

2. Structure of Substrates



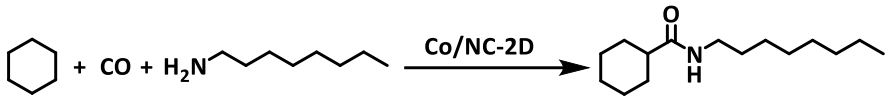
Scheme S1. Structure of alkanes.



Scheme S2. Structure of amines.

3. Optimization of the reaction conditions

Table S1. Screening of Carbon Supports for the Carbonylation of Cyclohexane[a]



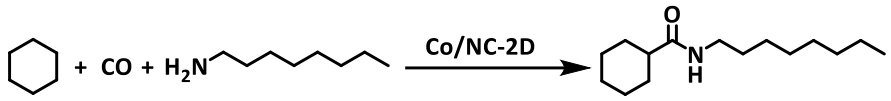
1a **2a** **3aa**

Entry	Carbon Support	Yield (%)
1	Co/AC	36
2	Co/NC-2D	83
3	Co/NC-3D	67
4	Co/g-C_3N_4	49
5	Co/EC	48
6	Co/CMC	45
7	Co/CA	50
8	Co/SUC	41
9	Co/SL	27

[a] Reaction conditions: cyclohexane (1.5 mL), octylamine (0.5 mmol), DTBP (1.5 equiv), Catalysts 25 mg (The loading amount of Co in each catalyst is 1 wt%), DCE (1 mL), CO (4 MPa), 110 °C for 12 h. AC=Active Carbon, EC=Ethyl Cellulose, CMC=Carboxymethyl Cellulose, CA=Cellulose Acetate, SUC=Sucrose, SL=Sodium Lignosulfonate.

[b] Determined by NMR analysis using triphenylmethane as the internal standard for yield.

Table S2. Screening of Reaction Temperature for the Carbonylation of Cyclohexane[a]



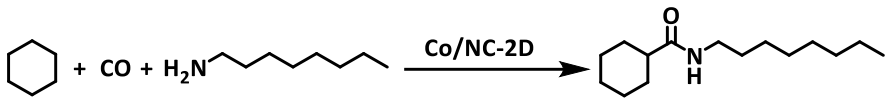
1a **2a** **3aa**

Entry	Reaction Temperature (°C)	Yield (%)
1	90	17
2	100	54
3	110	83
4	120	65
5	130	44
6	140	30

[a] Reaction conditions: cyclohexane (1.5 mL), octylamine (0.5 mmol), DTBP (1.5 equiv), Co/NC-2D 25 mg, CO (4 MPa), DCE (1 mL), 12 h.

[b] Determined by NMR analysis using triphenylmethane as the internal standard for yield.

Table S3. Screening of the pressure of CO for the Carbonylation of Cyclohexane[a]



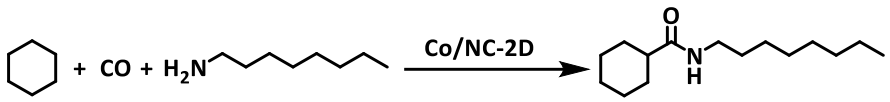
1a **2a** **3aa**

Entry	CO (MPa)	Yield (%)
1	1	19
2	2	35
3	3	62
4	4	83
5	5	78
6	6	70

[a] Reaction conditions: cyclohexane (1.5 mL), octylamine (0.5 mmol), DTBP (1.5 equiv), Co/NC-2D 25 mg, DCE (1 mL), 110 °C for 12 h.

[b] Determined by NMR analysis using triphenylmethane as the internal standard for yield.

Table S4. Screening of Solvent for the Carbonylation of Cyclohexane[a]



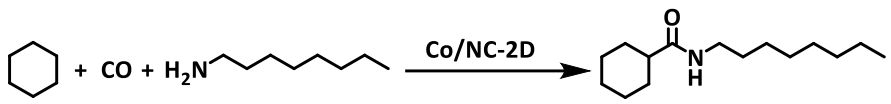
1a 2a 3aa

Entry	Solvent	Yield (%)
1	DCE	83
2	DCM	61
3	1,4-Dioxane	23
4	MeCN	15
5	THF	18
6	—	26

[a] Reaction conditions: cyclohexane (1.5 mL), octylamine (0.5 mmol), DTBP (1.5 equiv), Co/NC-2D 25 mg, Solvent (1 mL), CO (4 MPa), 110 °C for 12 h.

[b] Determined by NMR analysis using triphenylmethane as the internal standard for yield.

Table S5. Screening of the amount of DTBP for the Carbonylation of Cyclohexane[a]



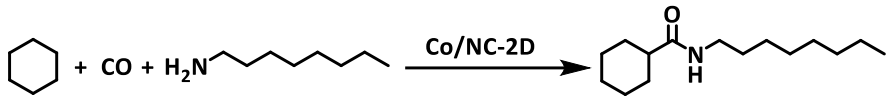
1a 2a 3aa

Entry	DTBP (equiv)	Yield (%)
1	0.5	28
2	1.0	59
3	1.5	83
4	2	67
5	2.5	45
6	3	21

[a] Reaction conditions: cyclohexane (1.5 mL), octylamine (0.5 mmol), Co/NC-2D 25 mg, DCE (1 mL), CO (4 MPa), 110 °C for 12 h.

[b] Determined by NMR analysis using triphenylmethane as the internal standard for yield.

Table S6. Screening of the Time for the Carbonylation of Cyclohexane[a]



1a 2a 3aa

Entry	Time (h)	Yield (%)
1	2	38
2	4	56
3	6	71
4	8	78
5	10	81
6	12	83

[a] Reaction conditions: cyclohexane (1.5 mL), octylamine (0.5 mmol), DTBP (1.5 equiv), Co/NC-2D 25 mg, DCE (1 mL),CO (4 MPa), 110 °C for 12 h.

[b] Determined by NMR analysis using triphenylmethane as the internal standard for yield.

4. Characterization

Table S7. The Raman test analysis content of two peak areas in NC-2D and Co/NC-2D

Sample	D-band (1360 cm^{-1})	G-band (1580 cm^{-1})	I_D/I_G
NC-2D	97428.8	52503.2	1.86
Co/NC-2D	70131	35370.82	1.98

Table S8. The information of BET of Catalysts

Sample	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore Radius (nm)
ZIF-8-p	193.040	0.122	1.485
NC-2D	794.982	1.390	0.456
Co/NC-2D	857.521	1.701	0.441
used-Co/NC-2D	534.582	1.037	0.447

Table S9. Co Contents in the Fresh and Used Catalysts.

Sample	Co contents (wt.%)
The fresh Co/NC-2D	1.02
The used Co/NC-2D	0.97

[a] Co contents were determined by ICP-AES.

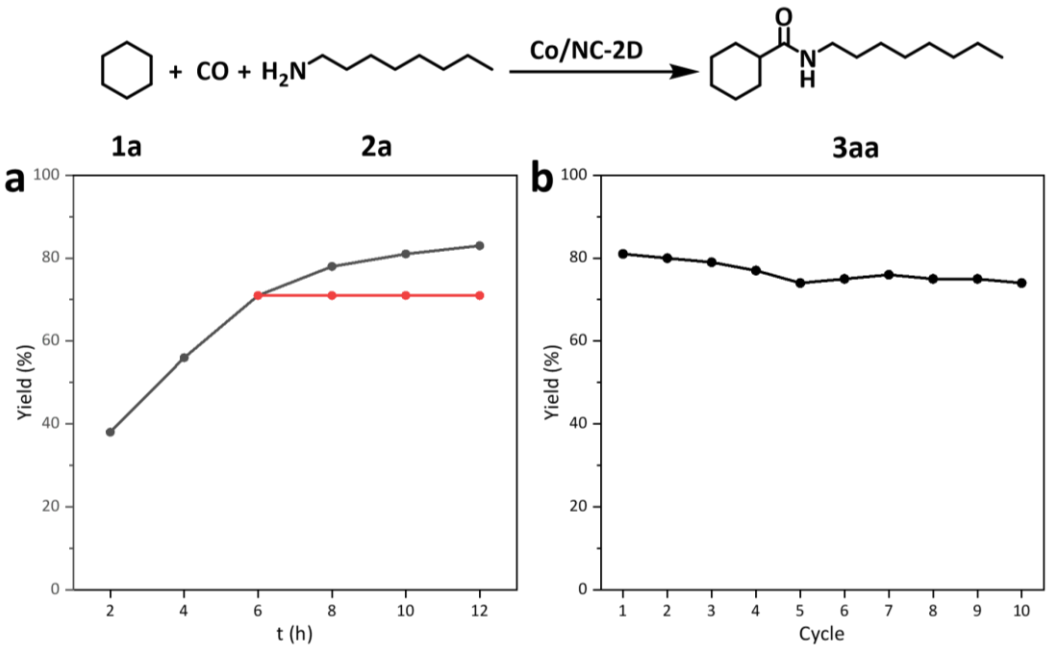


Fig. S1. Control experiments: (a) Influence of reaction time and hot filtration experiment of cyclohexane carbonylation reaction over Co/NC-2D catalyst. Black line: yield with the presence of catalyst; Red line: yield with the catalyst filtered out. (b) Stability test of cyclohexane carbonylation reaction over Co/NC-2D catalyst. Reaction conditions: cyclohexane (1.5 mL), octylamine (0.5 mmol), DTBP (1.5 equiv), catalyst 25 mg, CO (4 MPa), DCE (1 mL), 110 °C for 12 h. Determined by NMR analysis using triphenylmethane as the internal standard.

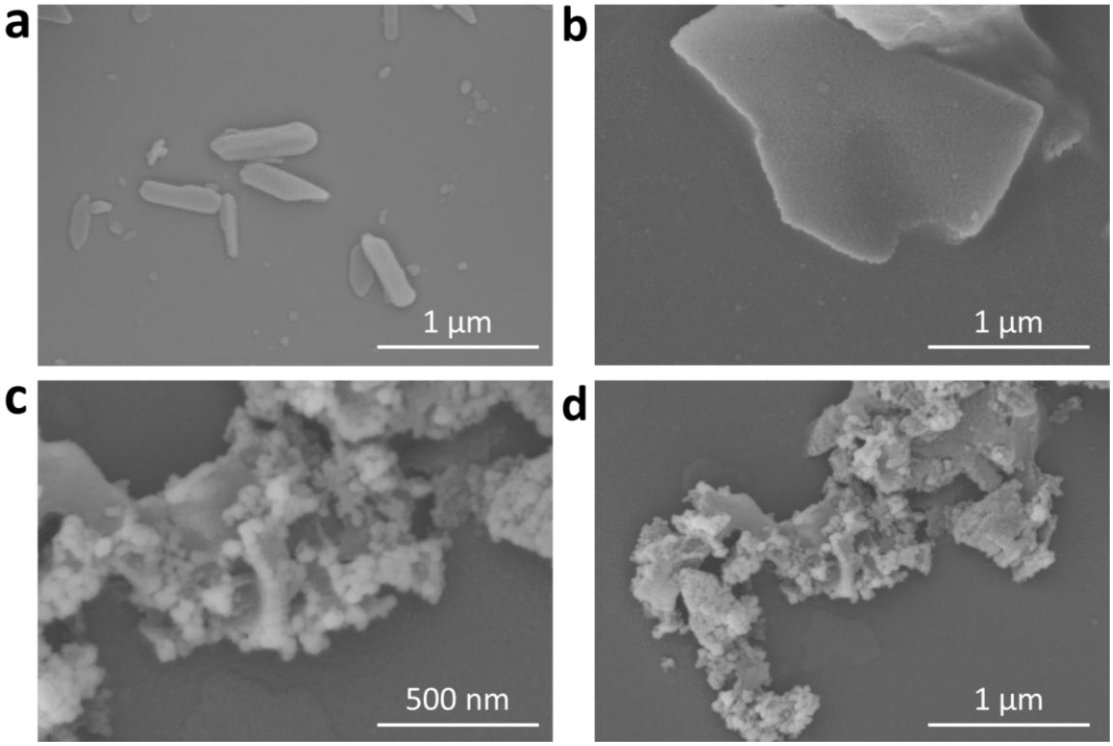


Fig. S2. SEM images: (a) ZIF-8-p; (b) NC-2D; (c) Co/NC-2D; (d) used-Co/NC-2D.

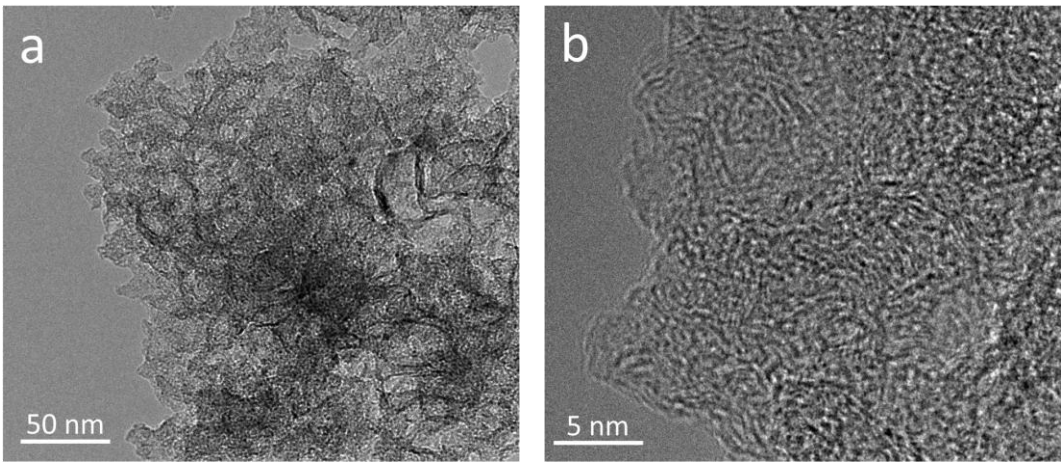


Fig. S3. (a) TEM image of used-Co/NC-2D; (c) HR-TEM image of used-Co/NC-2D.

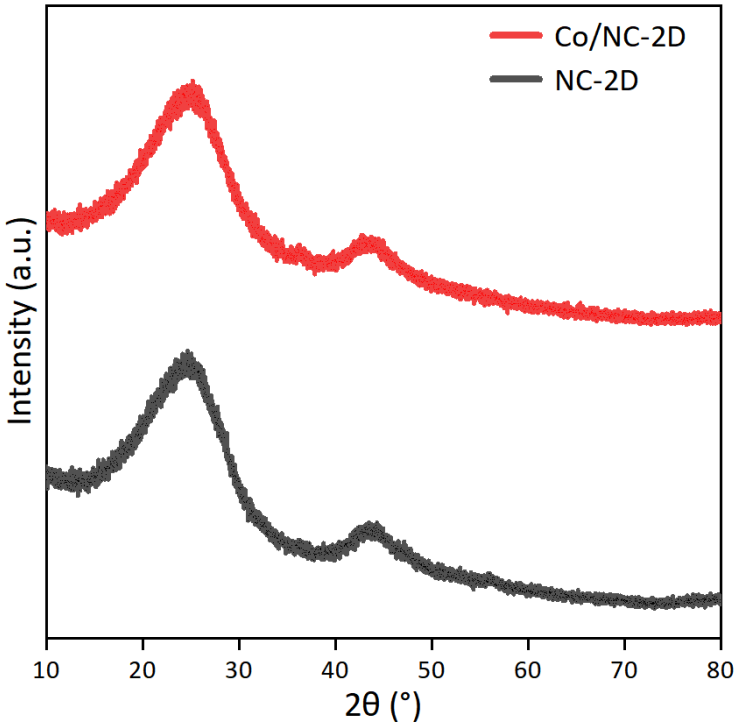


Fig. S4. XRD patterns of NC-2D and Co/NC-2D.

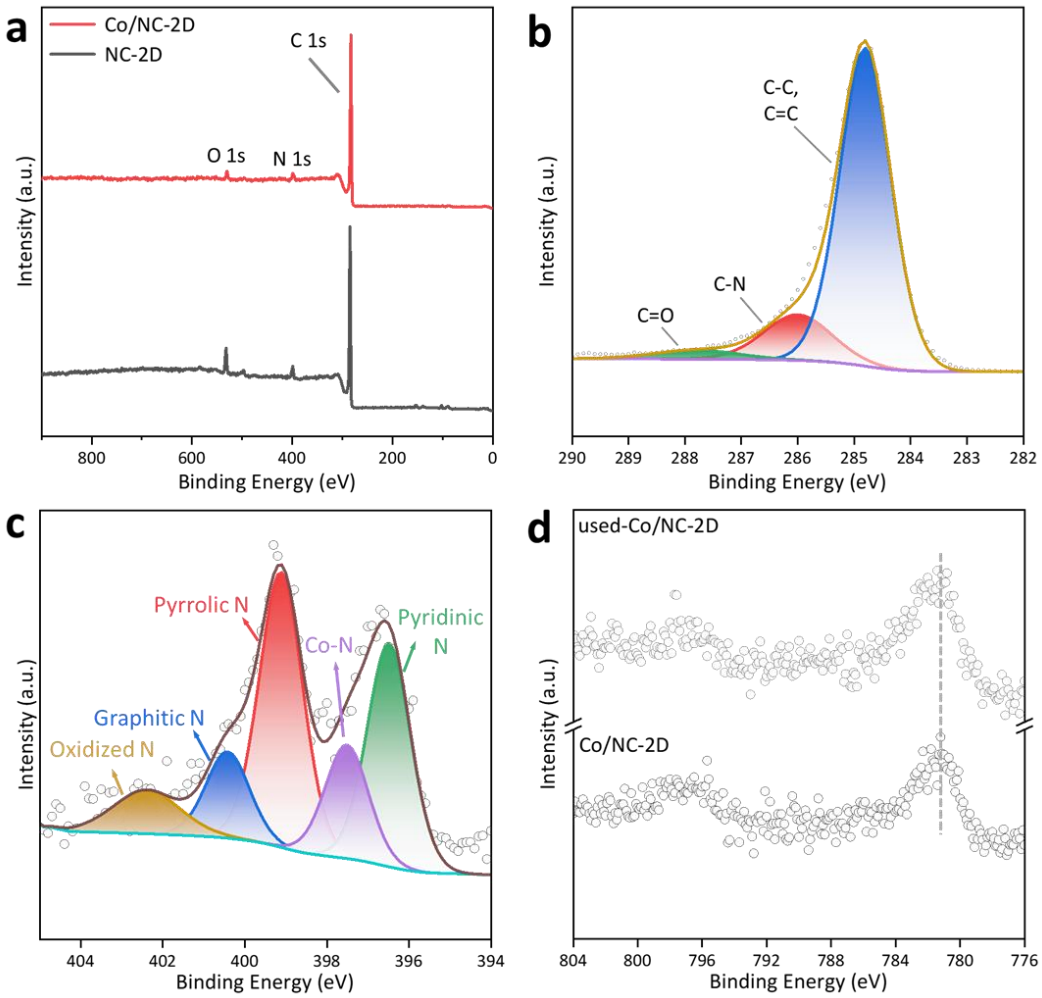


Fig. S5. (a) XPS wide-scan spectra of NC-2D and Co/NC-2D; (b) C 1s core level XPS spectrum of Co/NC-2D; (c) N 1s core level XPS spectrum of distinguishes N in Co/NC-2D; (d) Co 2p XPS spectra of Co/NC-2D and used-Co/NC-2D.

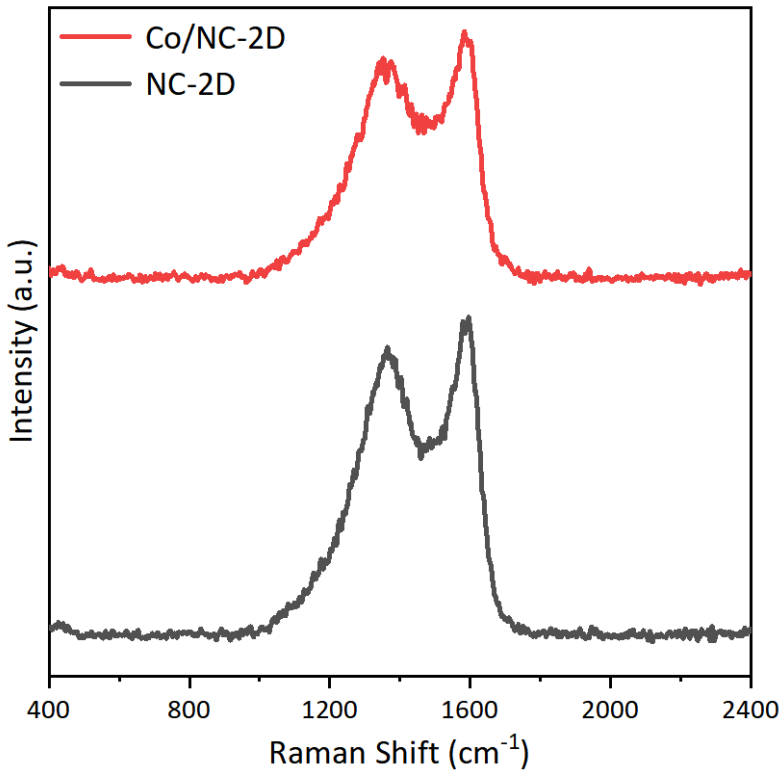
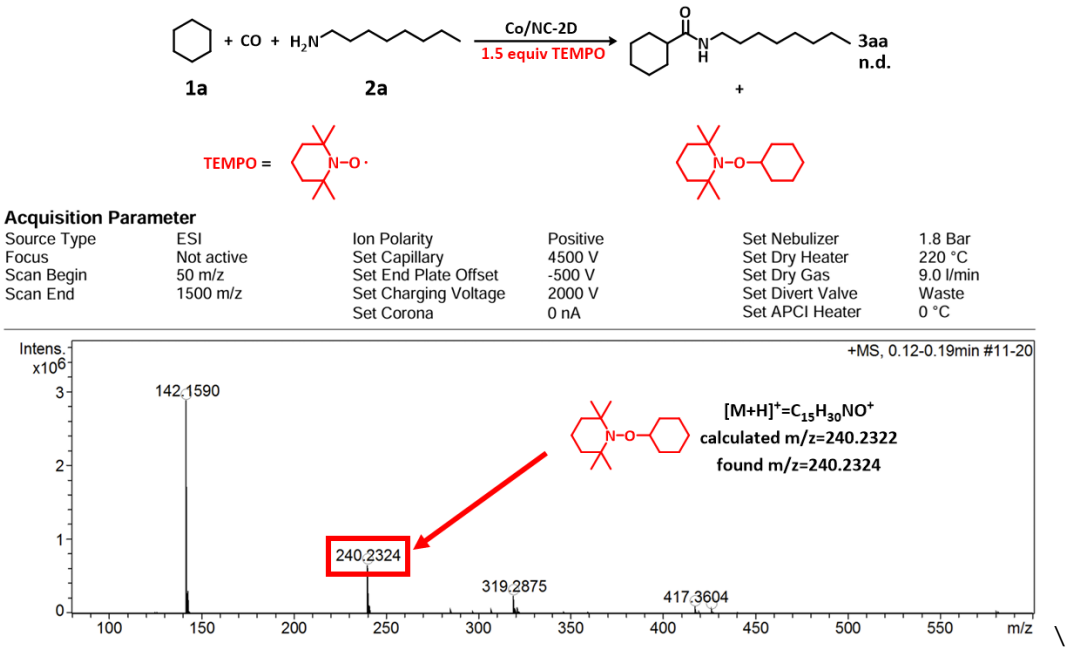
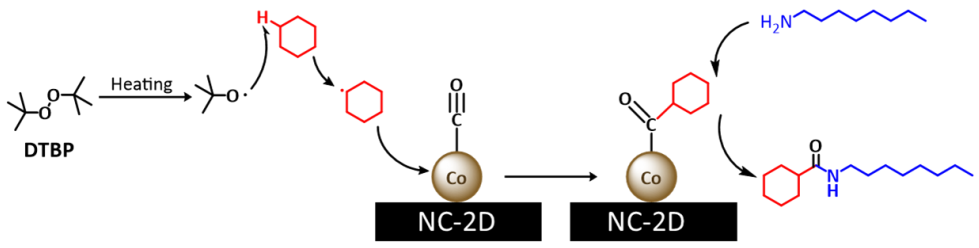


Fig. S6. Raman spectra of NC-2D and Co/NC-2D.



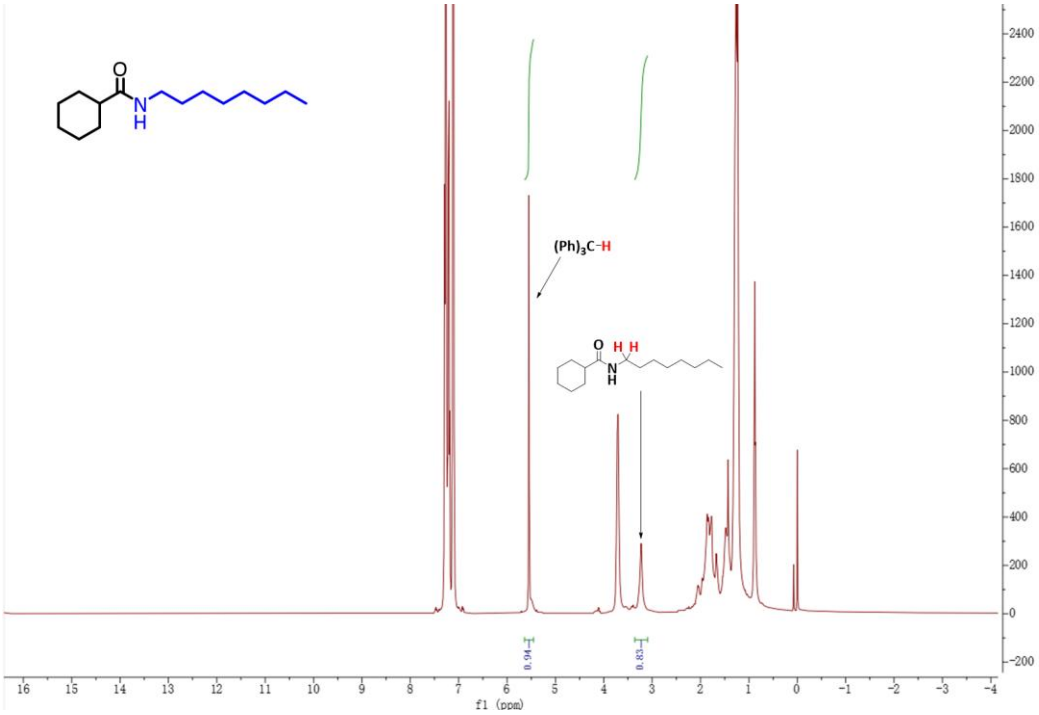
Scheme S3. High-Resolution Mass Spectrometry of radical trapping experiment with TEMPO. Reaction conditions: cyclohexane (1.5 mL), octylamine (0.5 mmol), DTBP (1.5 equiv), catalyst 25 mg, CO (4 MPa), DCE (1 mL), 110 °C for 12 h. Determined by NMR analysis using triphenylmethane as the internal standard.



Scheme S4. Plausible reaction mechanism.

5. Data of the Products

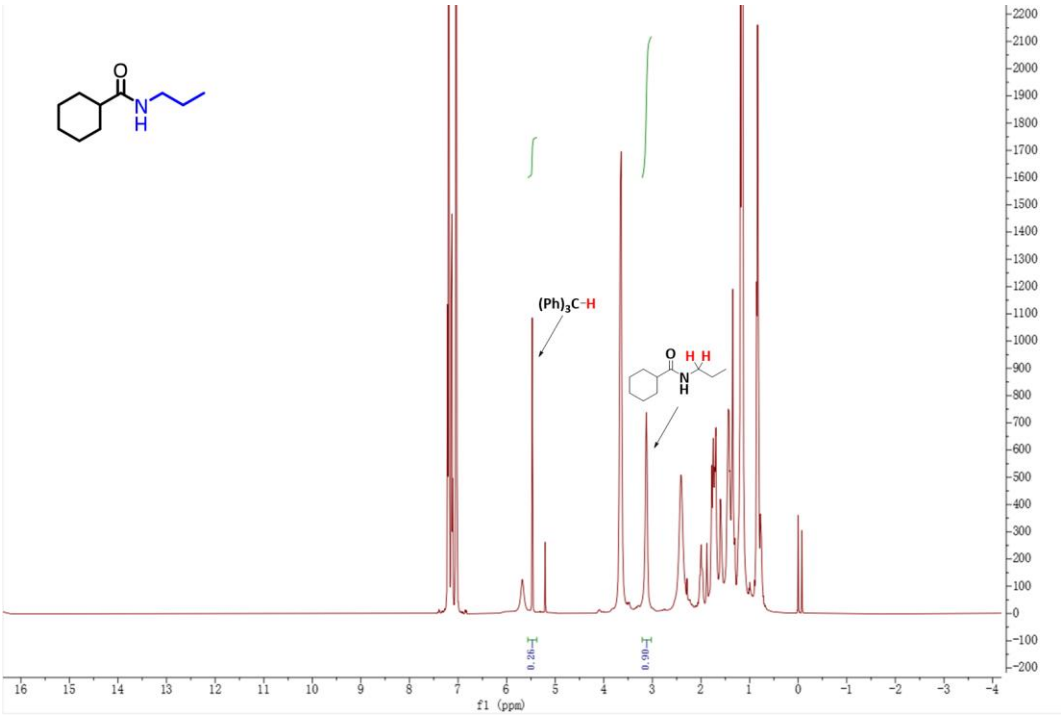
N-octyl cyclohexane carboxamide **(3aa)**



n(triphenylmethane)=0.94 mmol, n(**2a**)=0.5 mmol

∴ Yield(**3aa**)=$\frac{\mathrm{n}(\mathbf{3aa})}{\mathrm{n}'(\mathbf{3aa})}=\frac{\frac{0.83}{2}\mathrm{mmol}}{0.5\mathrm{mmol}}\times 100\%=83\%$

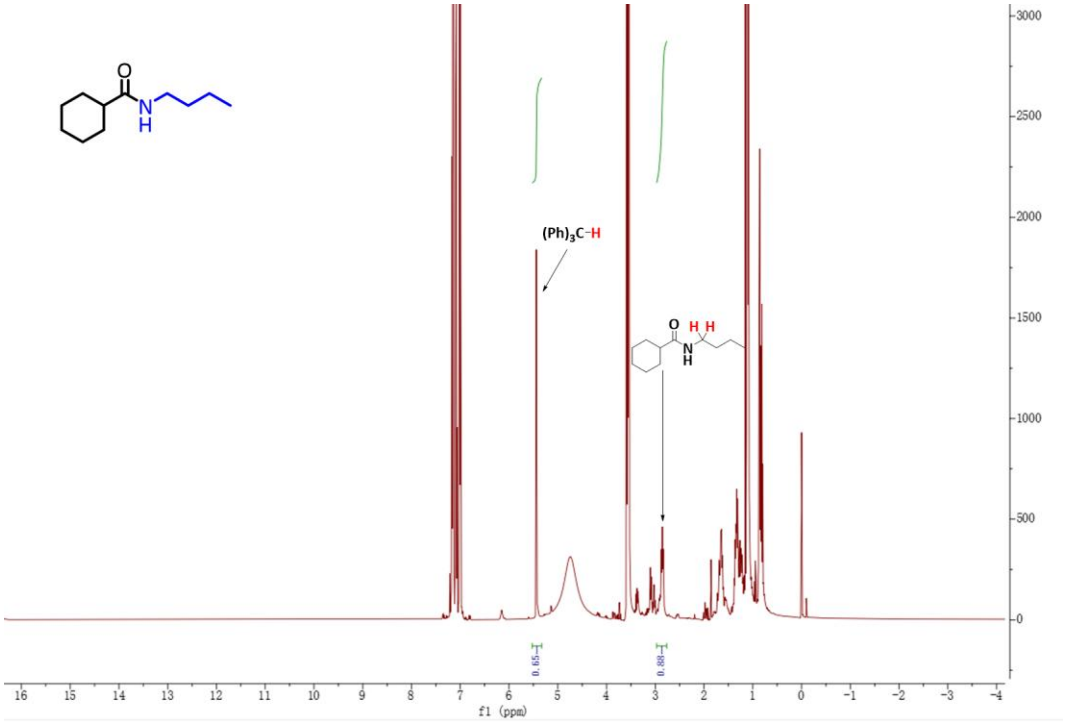
N-propyl cyclohexane carboxamide (**3ab**)



n(triphenylmethane)=0.26 mmol, n(**2b**)=0.5 mmol

∴ Yield(**3ab**)=$\frac{\mathrm{n}(\mathbf{3ab})}{\mathrm{n}'(\mathbf{3ab})}=\frac{\frac{0.90}{2}\mathrm{mmol}}{0.5\mathrm{mmol}}\times 100\%=90\%$

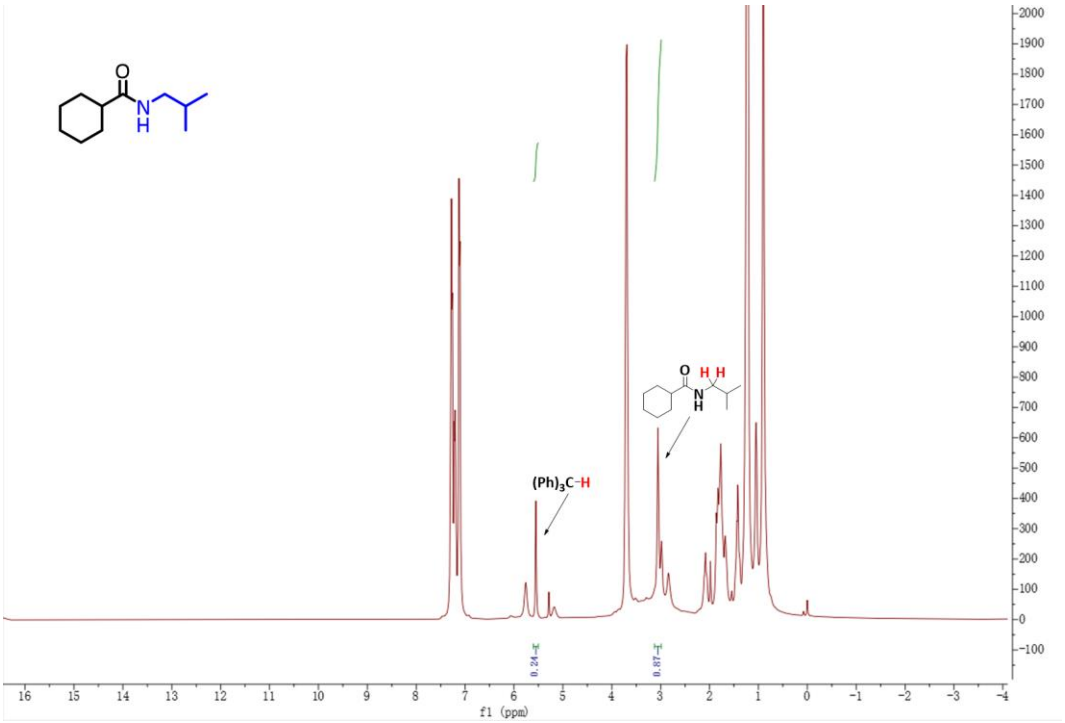
N-butyl cyclohexane carboxamide (**3ac**)



n(triphenylmethane)=0.65 mmol, n(**2c**)=0.5 mmol

∴ Yield(**3ac**)=$\frac{\mathrm{n}(\mathbf{3ac})}{\mathrm{n}'(\mathbf{3ac})}=\frac{\frac{0.88}{2}\mathrm{mmol}}{0.5\mathrm{mmol}}\times 100\%=88\%$

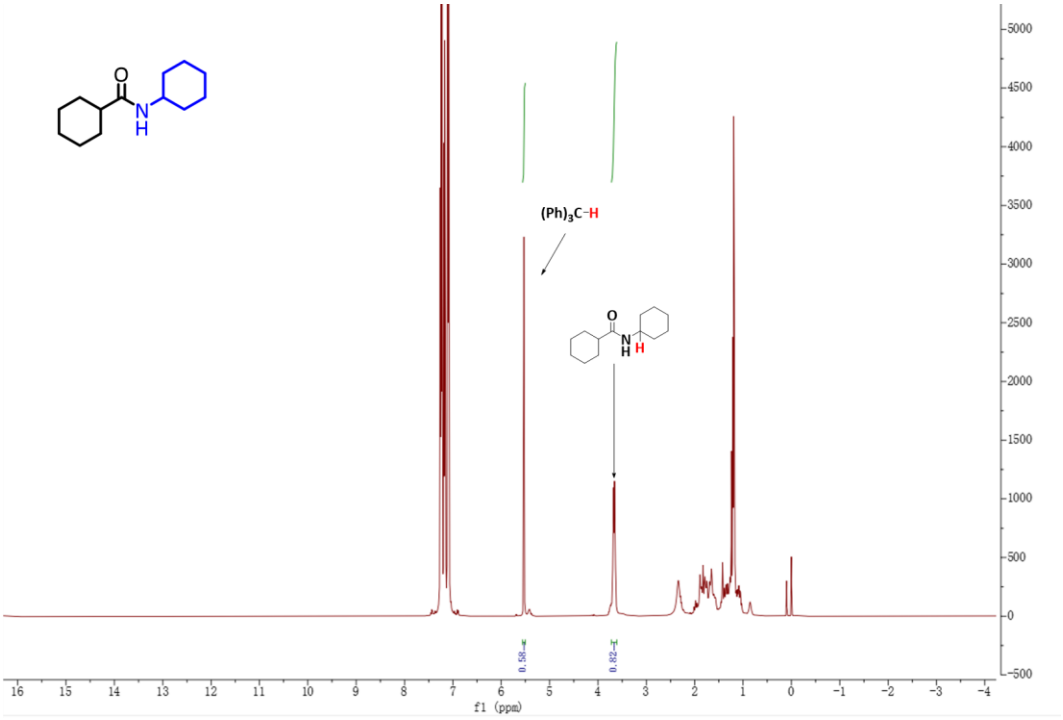
N-isobutyl cyclohexane carboxamide (**3ad**)



n(triphenylmethane)=0.24 mmol, n(**2d**)=0.5 mmol

∴ Yield(**3ad**)=$\frac{\mathrm{n}(\mathbf{3ad})}{\mathrm{n}'(\mathbf{3ad})}=\frac{\frac{0.87}{2}\mathrm{mmol}}{0.5\mathrm{mmol}}\times 100\%=87\%$

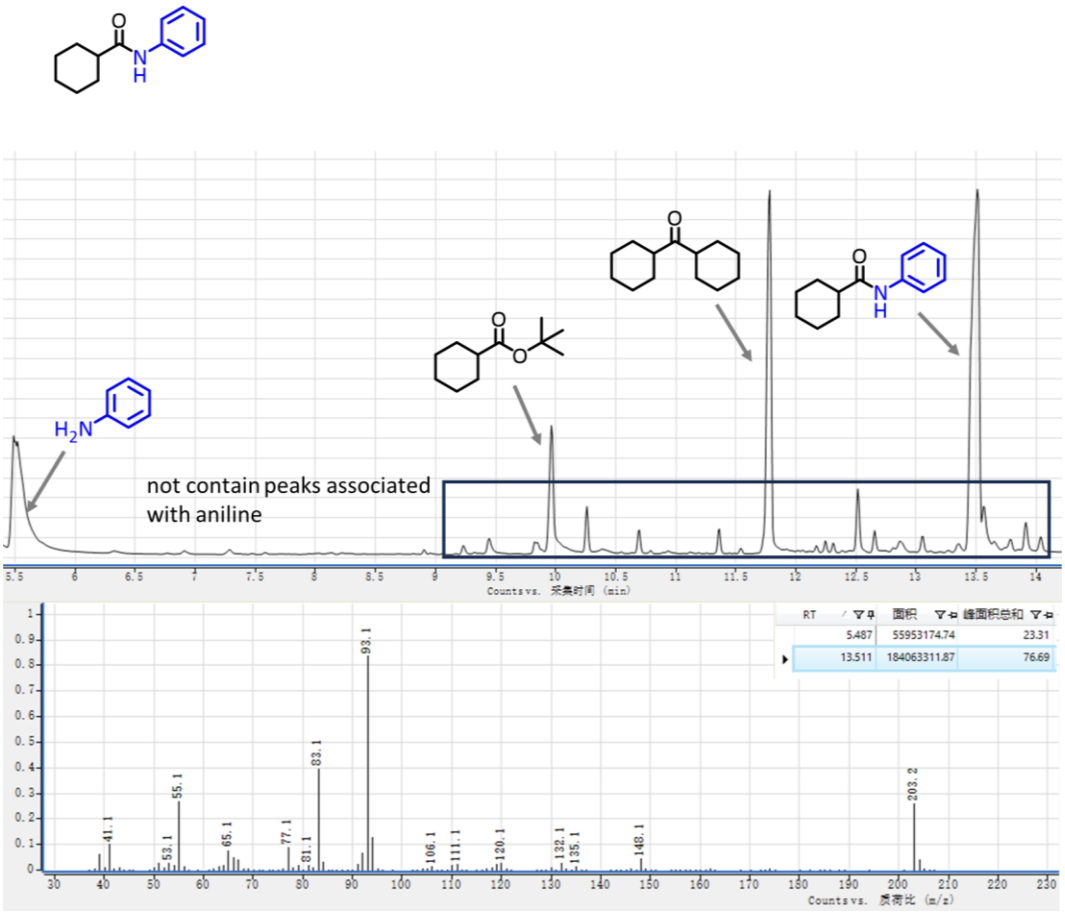
N-cyclohexyl cyclohexane carboxamide (**3ae**)



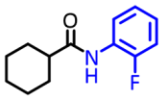
n(triphenylmethane)=0.29 mmol, n(**2e**)=0.5 mmol

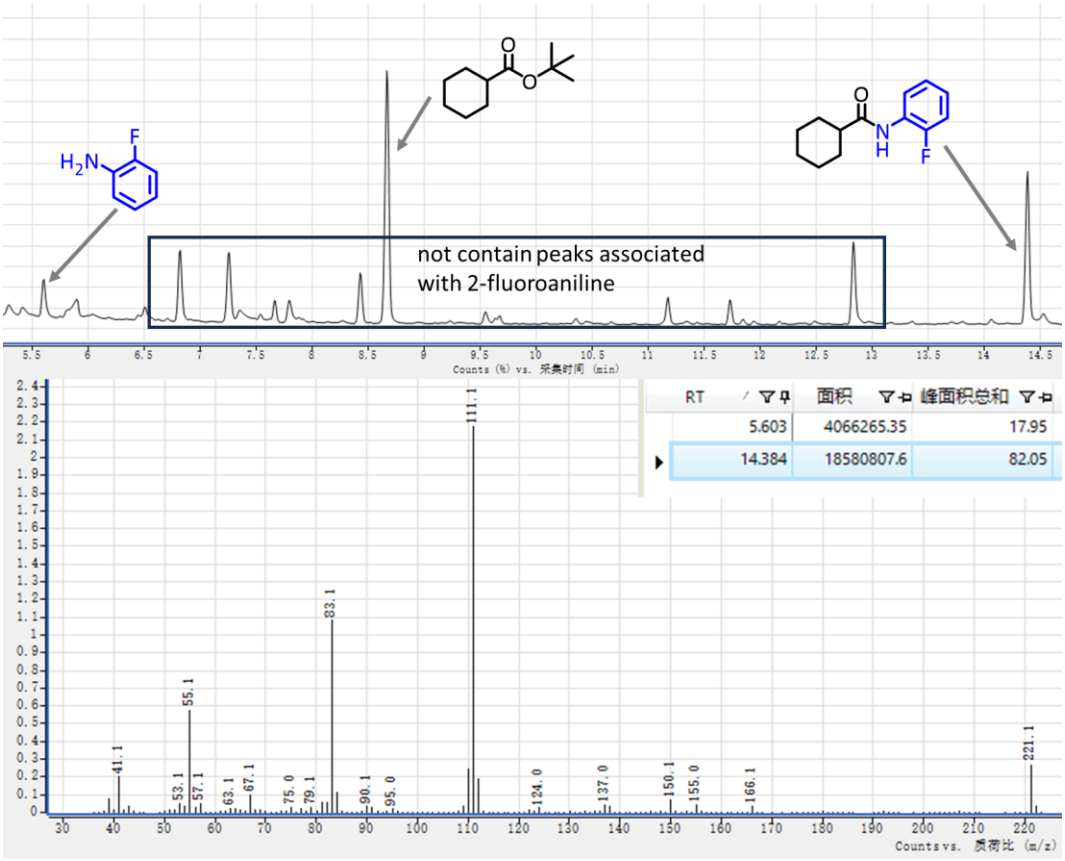
∴ Yield(**3ae**)=$\frac{n(\mathbf{3ae})}{n'(\mathbf{3ae})}=\frac{\frac{0.82}{2}\text{mmol}}{0.5\text{mmol}}\times 100\%=82\%$

N-phenyl cyclohexane carboxamide (**3af**)

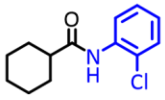


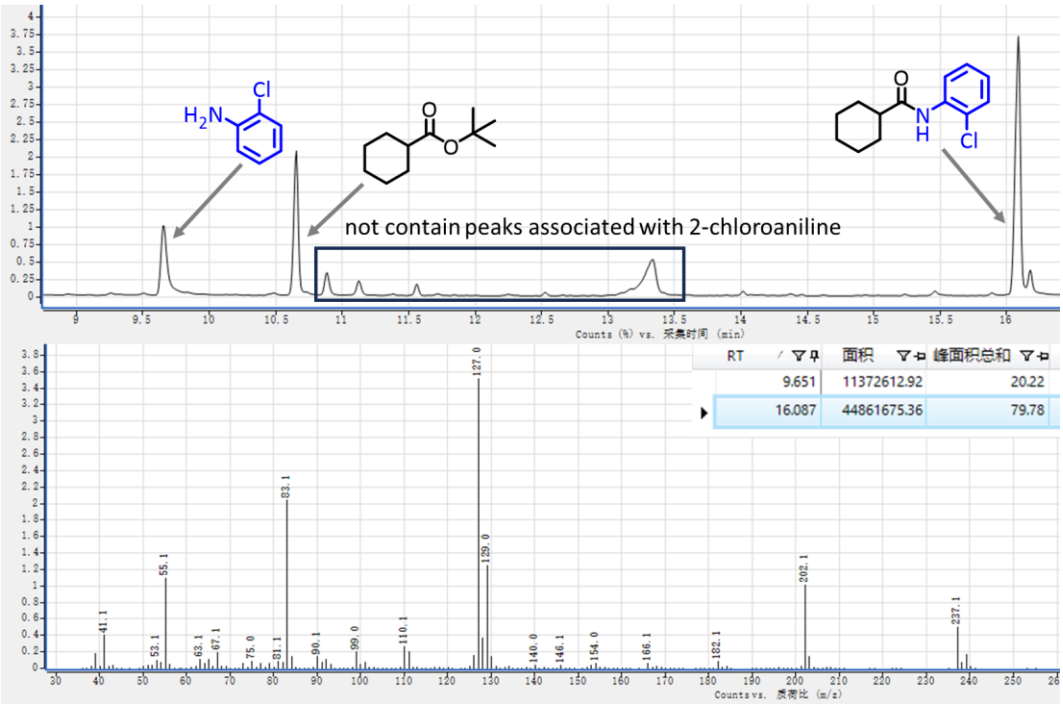
N-(2-fluorophenyl) cyclohexane carboxamide (**3ag**)



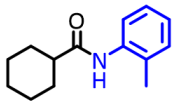


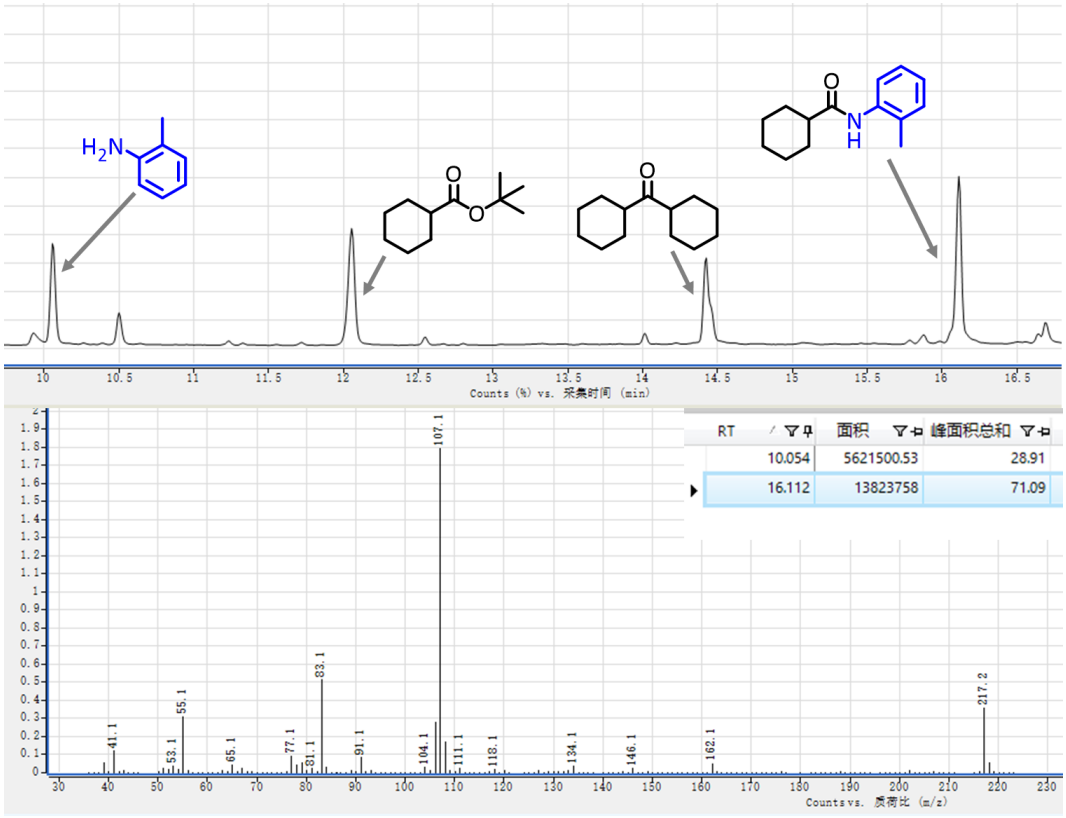
N-(2-chlorophenyl) cyclohexane carboxamide (**3ah**)





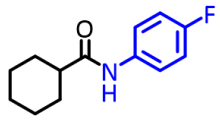
N-(o-tolyl) cyclohexane carboxamide (**3ai**)

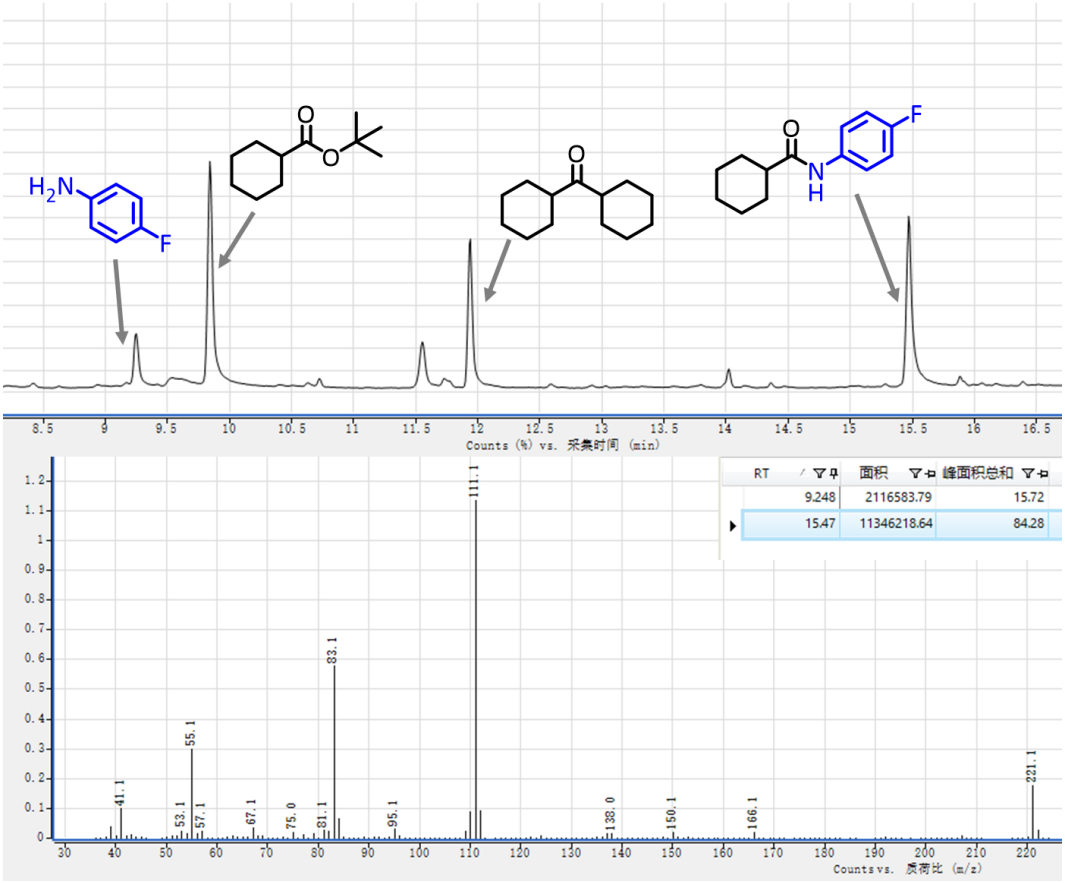




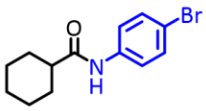
RT	面积	峰面积总和
10.054	5621500.53	28.91
16.112	13823758	71.09

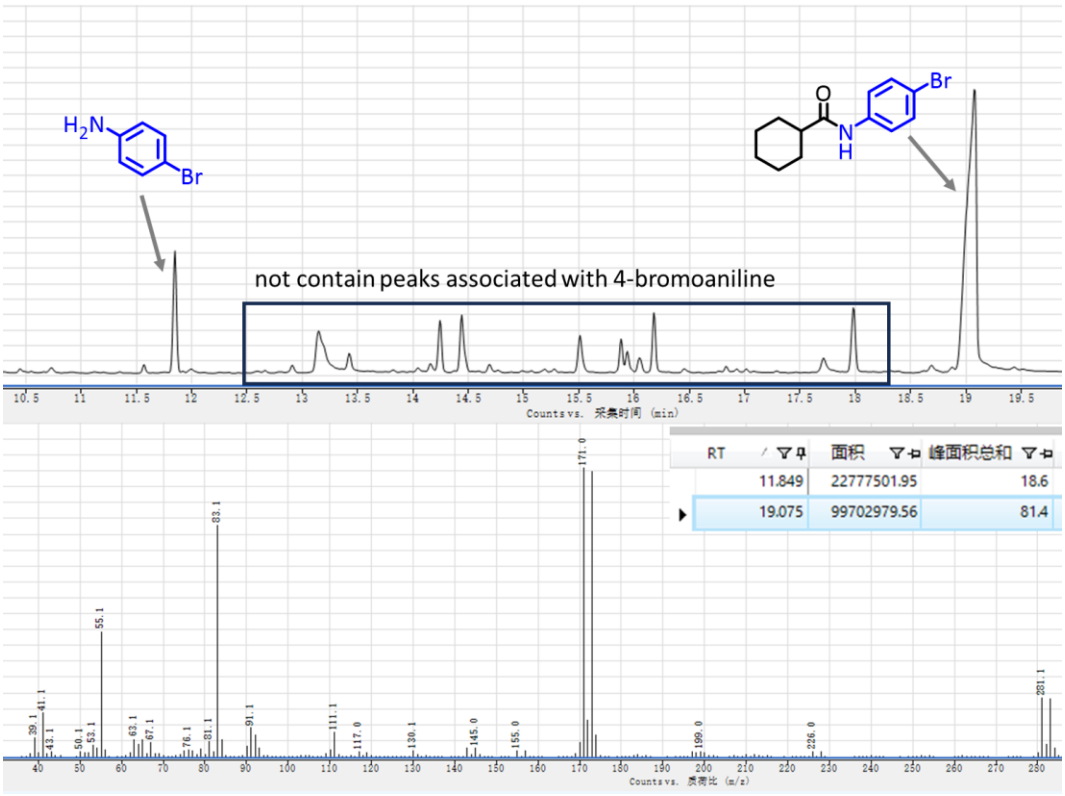
N-(4-fluorophenyl) cyclohexane carboxamide (**3aj**)



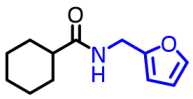


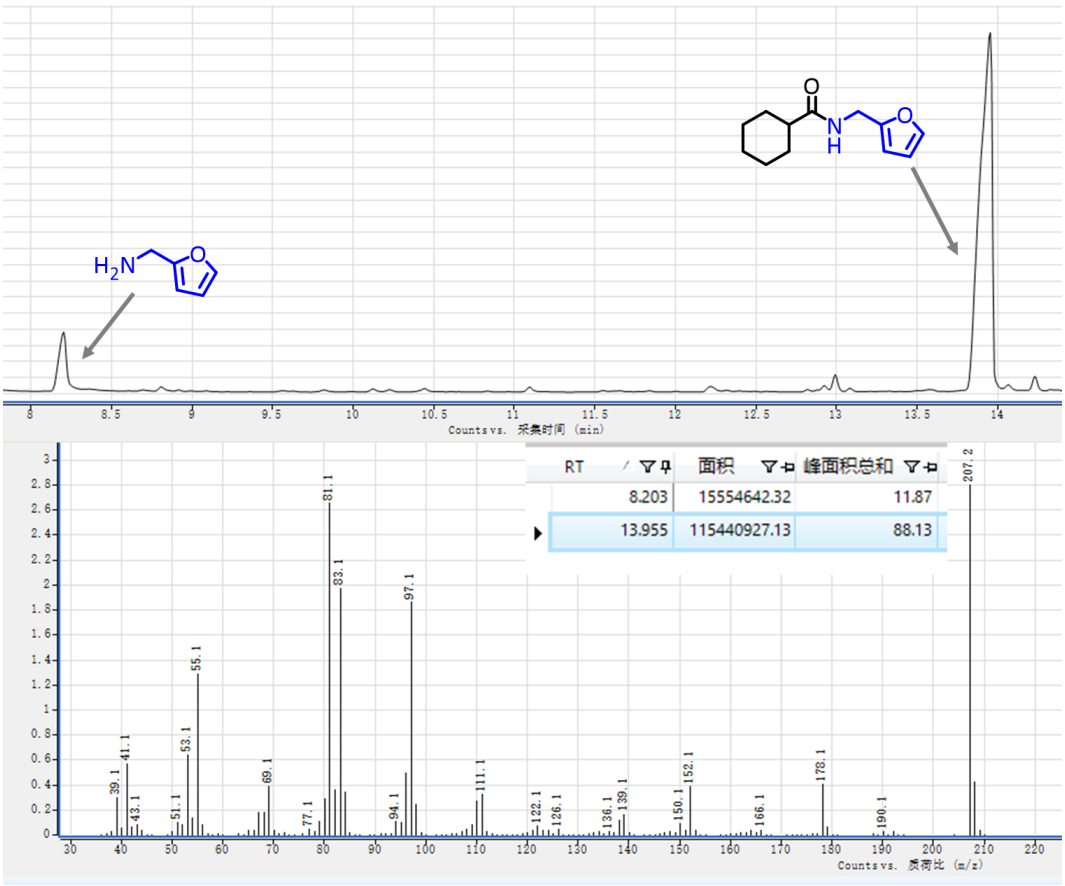
N-(4-bromophenyl) cyclohexane carboxamide (**3ak**)



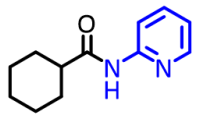


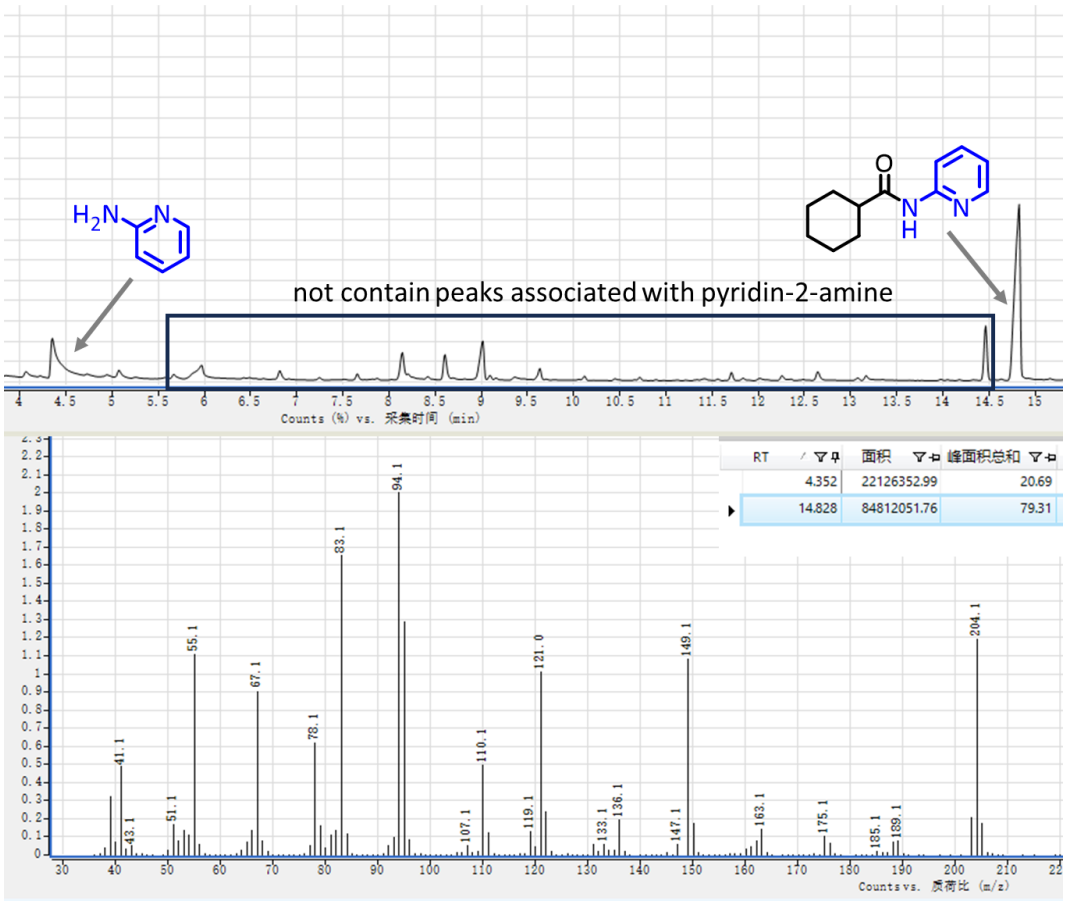
N-(furan-2-ylmethyl) cyclohexane carboxamide (**3al**)



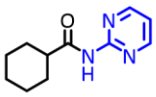


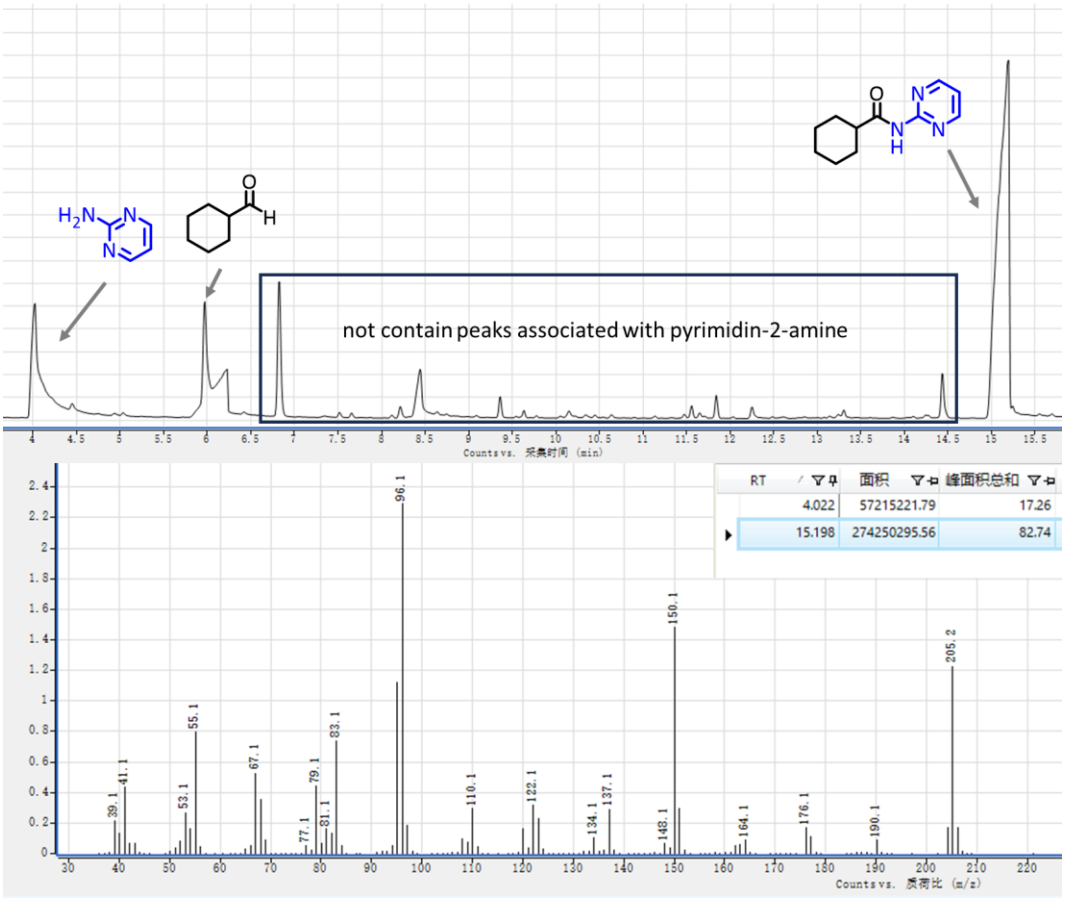
N-(pyridin-2-yl) cyclohexane carboxamide (**3am**)



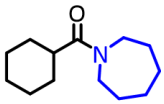


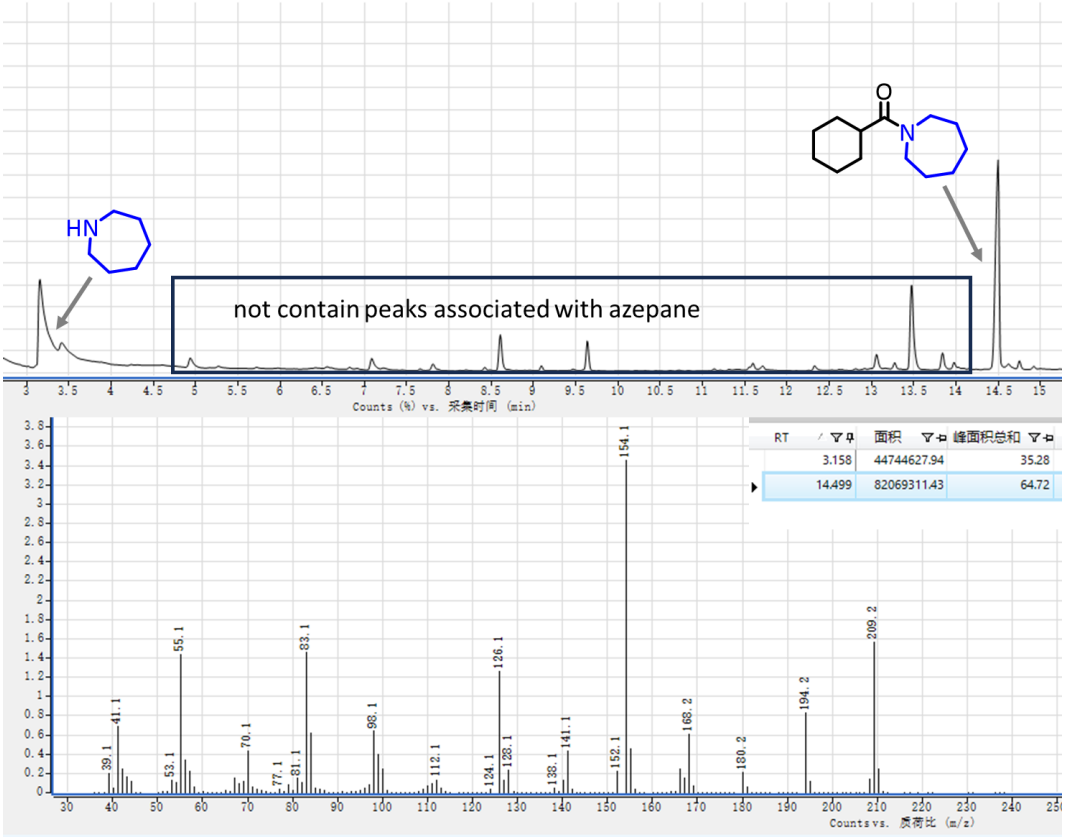
N-(pyrimidin-2-yl) cyclohexane carboxamide (**3an**)



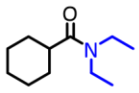


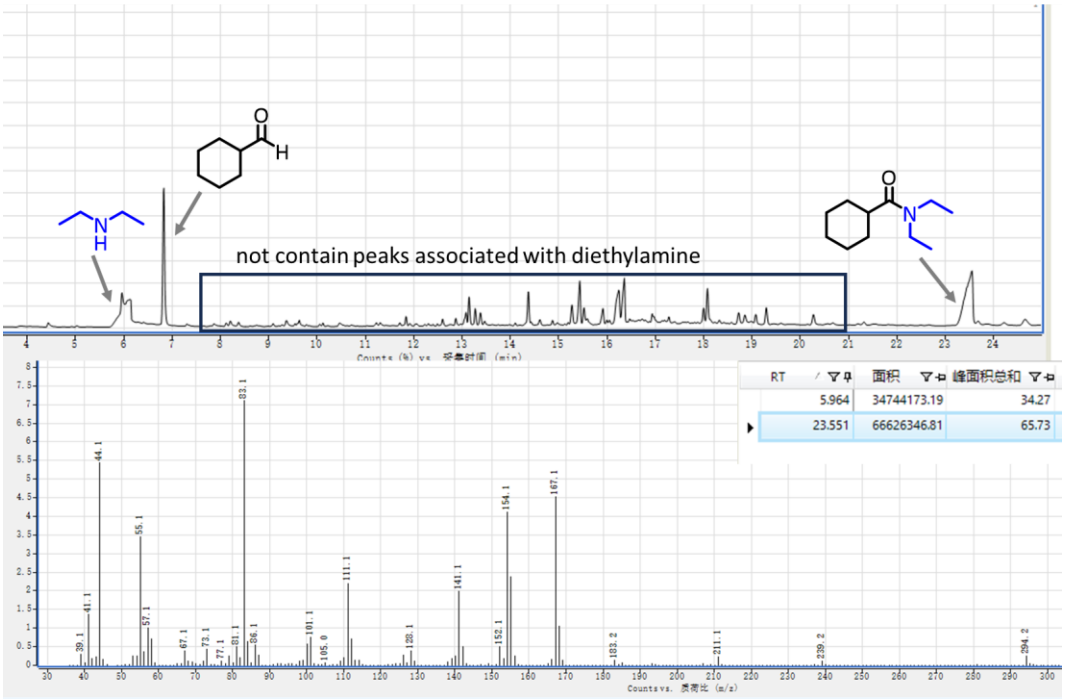
azepan-1-yl(cyclohexyl) methanone (**3ao**)



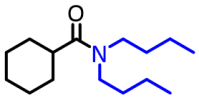


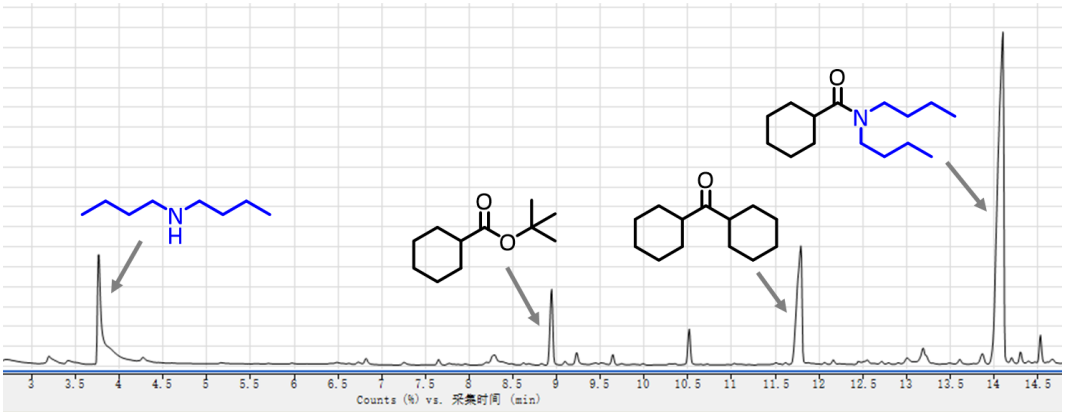
N,N-diethyl cyclohexane carboxamide (**3ap**)



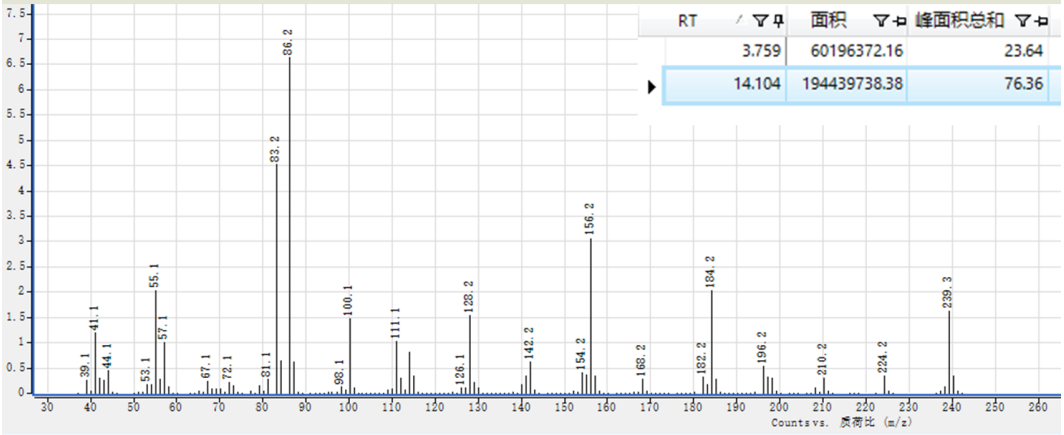


N,N-dibutyl cyclohexane carboxamide (**3aq**)

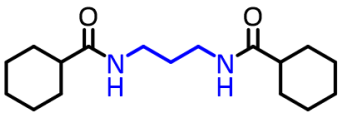


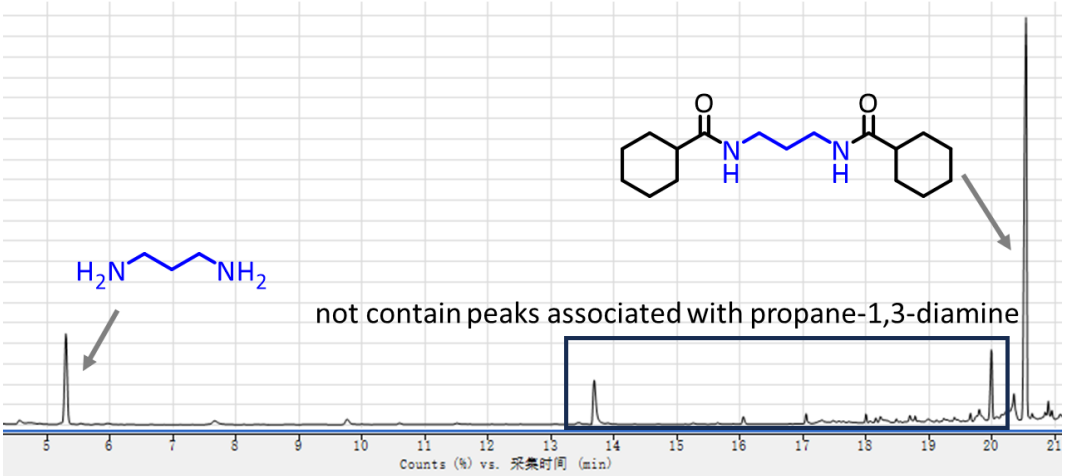


RT	面积	峰面积总和
3.759	60196372.16	23.64
14.104	194439738.38	76.36

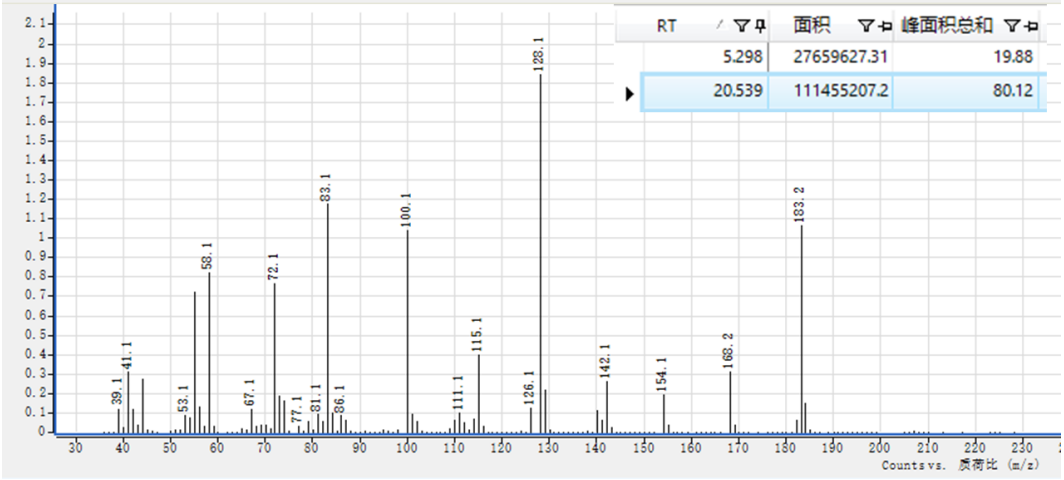


N-(3-((2-cyclohexyl-2-oxoethyl)amino)propyl) cyclohexane carboxamide (**3ar**)

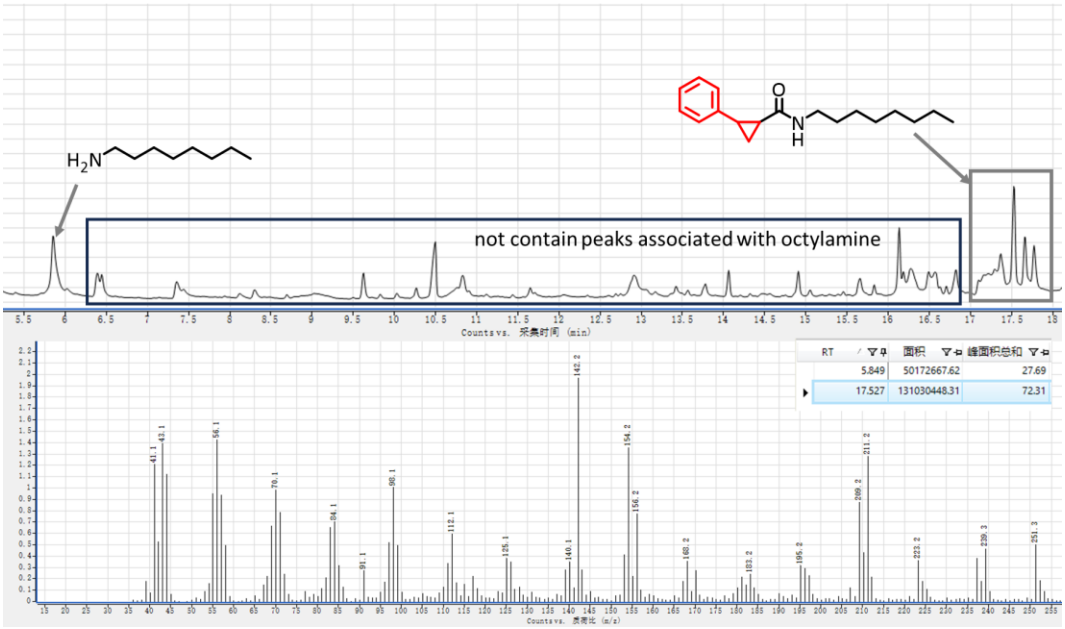




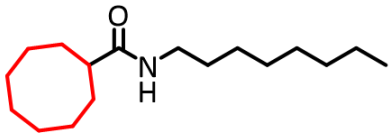
RT	面积	峰面积总和
5.298	27659627.31	19.88
20.539	111455207.2	80.12

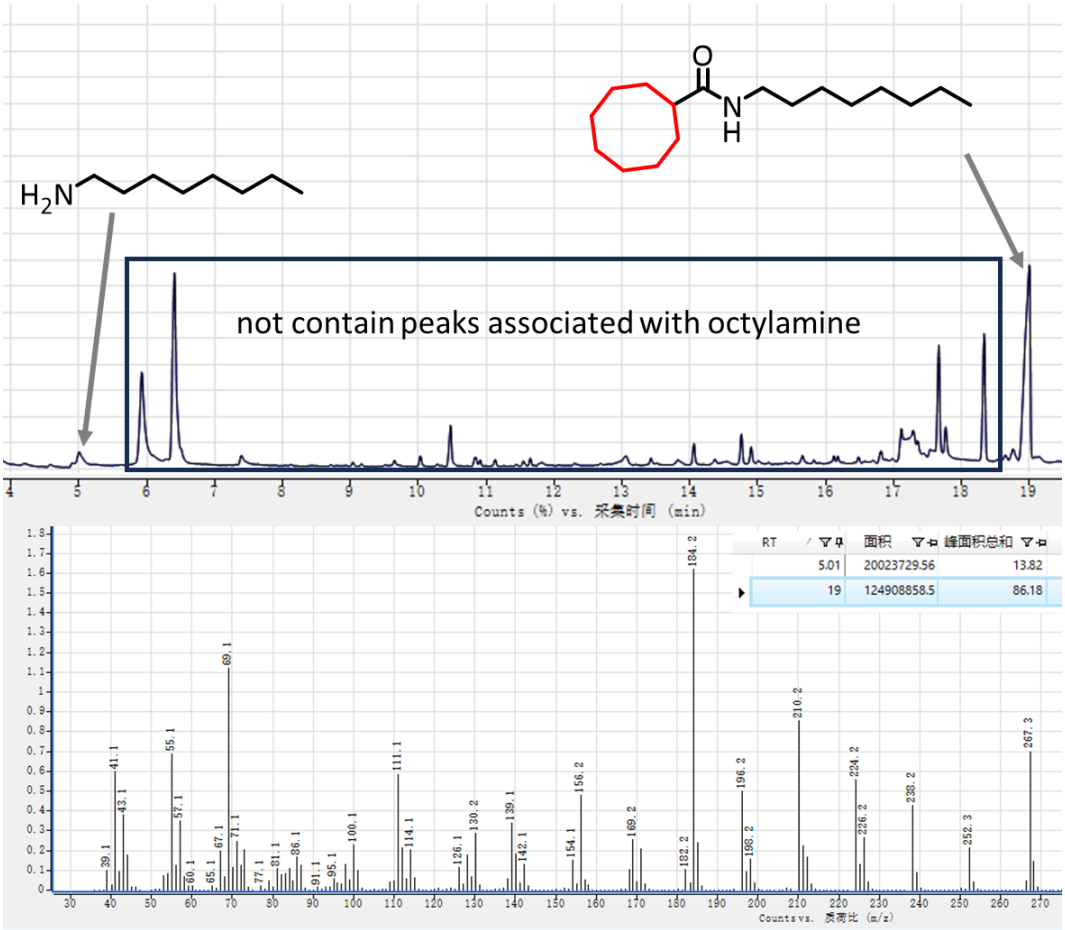


N-octyl-2-phenylcyclopropane-1-carboxamide (**3ba**)



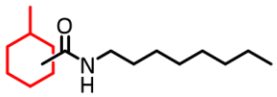
N-octyl cyclooctane carboxamide (**3ca**)

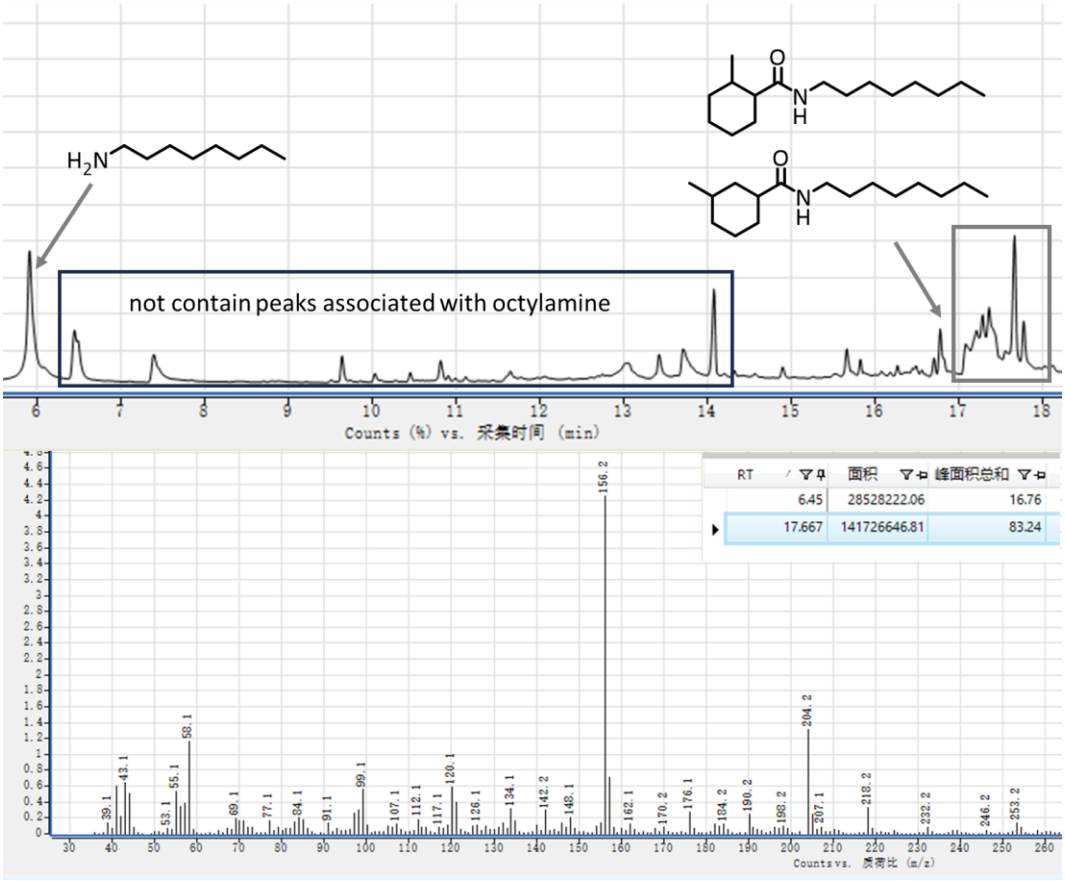




2-methyl-N-octylcyclohexane-1-carboxamide (**3da$_1$**)

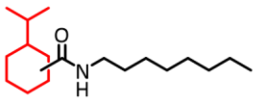
3-methyl-N-octylcyclohexane-1-carboxamide (**3da$_2$**)

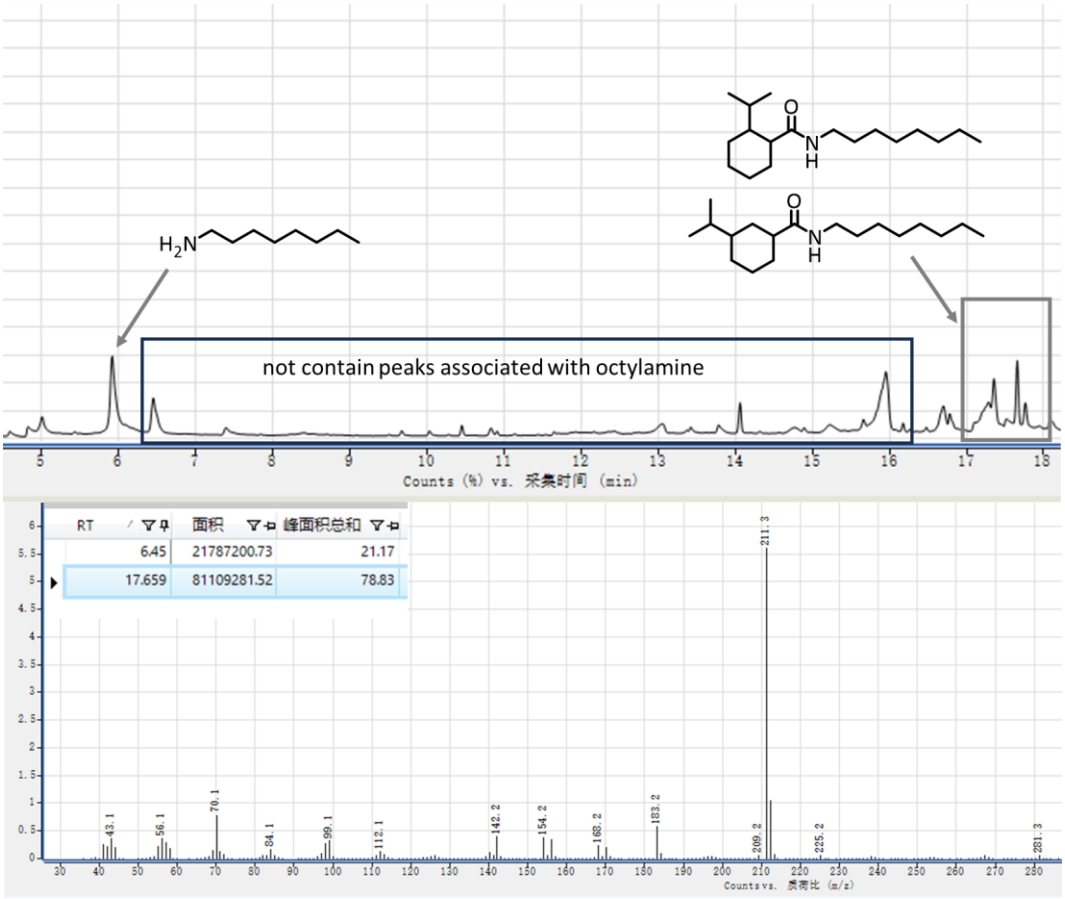




2-isopropyl-N-octylcyclohexane-1-carboxamide (**3ea$_1$**)

3-isopropyl-N-octylcyclohexane-1-carboxamide (**3ea$_2$**)





N-octyldecahydronaphthalene-2-carboxamide (**3fa$_1$**)

N-octyldecahydronaphthalene-1-carboxamide (**3fa$_2$**)