Electronic Supplementary Material (ESI) for Green Chemistry.

Alkoxycarbonylation of olefins with carbon dioxide by reusable heterobimetallic ruthenium-cobalt catalytic system

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1. General information

1.1 Materials and apparatus

$RuCl_3 \cdot H_2O$ was purchased from Zhejiang Metallurgical Research Institute Co., Ltd. $Ru_3(CO)_{12}$ (99.5%) and $Co_2(CO)_8$ (98%) were purchased from Beijing HWRK Chem. Co., Ltd. and stored in a glove box. Cobalt(II) salts ($Co(NO_3)_2 \cdot 6H_2O$, $Co(OAc)_2 \cdot 4H_2O$, $CoSO_4 \cdot 7H_2O$ and $CoCl_2$) were purchased from Shanghai Titan Scientific Co., Ltd. concentrated hydrochloride, formic acid was purchased from Sinopharm Chemical Reagent Co., Ltd. Methanol (≥ 99.9%, HPLC grade solvent) was purchased from Sigma-Aldrich. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, Inc. CD_3OD was purchased from Meyer Chemical Technology Co., Ltd. Benzyl alcohol (≥99%) and isopropanol (≥99.5%) were purchased from Shanghai Mackling Biochemical Co., Ltd. Cyclohexene (99%, pure, stab.) was purchased from ACROS Organics. Cyclopentene was purchased from TCI (⩾98%). 1-Hexene (99%), styrene (99%), [Bmim]Cl (99%+), [Bmmim]Cl (99%+), [Bmim]Br (99%+), [Emim]Cl (99%+) [Hmim]Cl (99%+) and 2-phenyl-propene (99%) were purchased from Admas Reagent Co., Ltd. Cis-cyclooctene (95 %, stab.), norbornene (99%) and *p*-xylene (99%) were purchased from Alfa Aesar. LiCl (99%) and indene (95%) were purchased from EnergyChemical. [PPN]Cl, N_2 ((⩾99.95%)), carbon monoxide (⩾99.95%), CO_2 (⩾99.95%) and ethylene (⩾99.99%) cylinders were purchased from Wujiang Messer Industrial Gas Co Ltd. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. THF was purified using Pure Solv™ 7-SDS solvent drying system. All the alkoxycarbonylation reactions were conducted in 100 mL autoclave (Parr series 4792 pressure vessel system).

1.2 Analytic methods

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. range 60-90 °C). Gas chromatographic (GC) analyses were performed on Agilent 7890A instrument equipped with a flame ionization detector (FID) and a SE-54 capillary column. *p*-Xylene was employed as an internal standard. GC-MS spectra were recorded on a GCMS-QP2010 SE. The high resolution mass spectrum (HRMS) analyses were performed on Thermo Fisher Scientific LTQ FT Ultra with DART Positive Mode or Agilent 6530 Accurate-Mass Q-TOF LC/MS with ESI mode. NMR spectra were recorded on a 400 MHz for ^1H and 101 MHz for ^{13}C NMR, using tetramethylsilane as an internal reference and $CDCl_3$ as solvent. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton of $CDCl_3$ (δ 7.26). Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ = 77.0). Elemental analysis for carbon, hydrogen and nitrogen was performed on Elementar Vario EL/micro cube element analyzer. Inductively coupled plasma mass spectrometry (ICP-MS) analysis for ruthenium was performed on Thermo Fisher iCAP™ RQ ICP-MS. FT-IR spectrums were recorded on Thermo Scientific Nicolet 6700 FT-IR spectrometer.

2. The procedure of preparing $[Ru(CO)_3Cl_2]_2$ and investigating the evolution of $[Ru(CO)_3Cl_2]_2$ in the presence of [Bmim]Cl

The preparation of $[Ru(CO)_3Cl_2]_2$ from $RuCl_3 \cdot H_2O$, conc. HCl and formic acid followed the instruction of reported literature[1a]. A 250-mL round-bottom flask was charged with a magnetic stirring bar and $RuCl_3 \cdot H_2O$ (2.25 g, 10 mmol). Then the mixture of concentrated HCl (37 wt%, 40 mL) and formic acid (85 wt%, 40 mL) was poured into the flask and the flask was heated to reflux with the oil-bath heating for 17 hours. The initial brown-black color turned bright yellow over this period of time. After that, the mixture was allowed to cool down to room temperature. The solvent was evaporated in reduced pressure. The remaining yellow powder was further dried at 60 °C in vacuum oven for 24 hours to obtain $[Ru(CO)_3Cl_2]_2$.

The investigation of $[Ru(CO)_3Cl_2]_2$ evolution in the presence of [Bmim]Cl

A 100 mL flask was charged with $[Ru(CO)_3Cl_2]_2$ (26 mg, 0.05 mmol, 1 equiv.), [Bmim]Cl (17.5 mg, 0.1 mmol, 2 equiv.), MeOH (20 mL) and a magnetic stir bar. After stirring respectively for 20 minutes and 24 hours at room temperature, MeOH solution was sampled and analyzed on FT-IR. Then the solution was transferred into 100 mL autoclave. The autoclave was charged with N_2 (2 MPa) and heated at 140 °C for 4 h. After cooling to room temperature, N_2 gas was carefully released. The resulting solution was analyzed on FT-IR.

A 100 mL flask was charged with $[Ru(CO)_3Cl_2]_2$ (26 mg, 0.05 mmol, 0.5 mol%), [Bmim]Cl (1.5 equiv.), $Co_2(CO)_8$ (34.2 mg, 0.1 mmol, 1 mol%), [Bmim]Cl (2.61 g, 15 mmol, 1.5 equiv.), MeOH (20 mL) and a magnetic stir bar. After stirring respectively for 20 minutes at room temperature under N_2 atomspehere, MeOH solution was sampled and analyzed on FT-IR. Curve (a) in Figure S1 was recorded. Afterwards, the solution was transferred into 100-mL autoclave. The autoclave was charged with cyclohexene (821mg, 10 mmol) and CO_2 (4 MPa) and heated at 160 °C for 20 h. After cooling to room temperature, gas was carefully released. Methyl cyclohexanecarboxylate product and MeOH solvent were evaporated under reduced pressure. The resulted residue was diluted with MeOH and analyzed on FT-IR. Curve (b) in Figure S1 was then recorded.

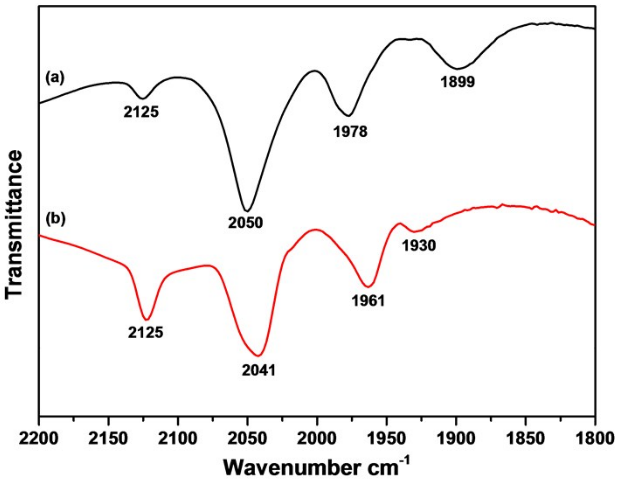


Figure S1 FT-IR of $[Ru(CO)_3Cl_2]$ (0.05 mmol), [Bmim]Cl (15 mmol), $Co_2(CO)_8$ (0.1 mmol) in MeOH (20 mL). (a) in the absence of cyclohexene (10 mmol) and CO_2 (4 MPa) before first run; (b) recycled catalyst after first run.

3. General procedure for the alkoxycarbonylation of olefins with CO_2 and alcohol

A 100-mL autoclave was charged with $[Ru(CO)_3Cl_2]_2$ (26 mg, 0.05 mmol, 1 mol% Ru) and [Bmim]Cl (2.61 g, 15 mmol, 1.5 equiv.). For liquid or solid alkene, MeOH solution (10 mL) dissolving alkene (10 mmol, 1.0 equiv.) and MeOH suspension (10 mL) containing $Co_2(CO)_8$ (34.2 mg, 0.1 mmol, 2 mol% Co) were successively injected into the autoclave by syringe under the protection of N_2 gas flushing. For ethylene, it was charged into autoclave after the addition of MeOH solution. Then CO_2 (4 MPa at room temperature) was introduced before the autoclave was heated to 160 ^{o}C. After 20 hours, the reaction was cooled down to room temperature and the pressure was carefully released. Then *p*-xylene (40 μL) was added into the reaction solution as internal standard. The mixture containing internal standard was analysed by gas chromatography with flame ionization detector. Except the alkoxycarbonylative products of ethylene, pure product could be isolated by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate).

4. General procedure for the reuse of ruthenium-cobalt bimetallic catalysts in the alkoxycarbonylation of cyclohexene with CO_2 and methanol

A 100 mL autoclave was charged with $[Ru(CO)_3Cl_2]_2$ (26 mg, 0.05 mmol) or $Ru_3(CO)_{12}$ (21 mg, 0.033 mmol) and [Bmim]Cl (2.61 g, 15 mmol, 1.5 equiv.). Under the protection of N_2 gas flushing, the MeOH solution (10 mL) of cyclohexene (821 mg, 10 mmol, 1.0 equiv.) and MeOH suspension (10 mL) containing $Co_2(CO)_8$ (34.2 mg, 0.1 mmol, 2 mol% Co) were successively injected into the autoclave by syringe. Then CO_2 (4 MPa at room temperature) was introduced before the autoclave was heated to 160 ^{o}C. After 20 hours, the reaction was cooled down to room temperature and the pressure was carefully released. Then *p*-xylene (40 μL) was added into the reaction solution as internal standard for GC analyse and 0.5 mL reaction solution containing internal standard was transferred into gas chromatography sample vial and diluted with acetone. Yields were determined by gas chromatography. The remaining solution containing volatile MeOH, cyclohexene and methyl cyclohexanoate were removed under reduced pressure. The oily residue containing ruthenium catalyst, cobalt catalyst and [Bmim]Cl was washed with *n*-hexane (40 mL) and then the hexane layer on top was separated off by seperatory funnel. The remaining hexane at the bottom layer was evaporated and recycled catalysts and [Bmim]Cl were obtained for the next run.

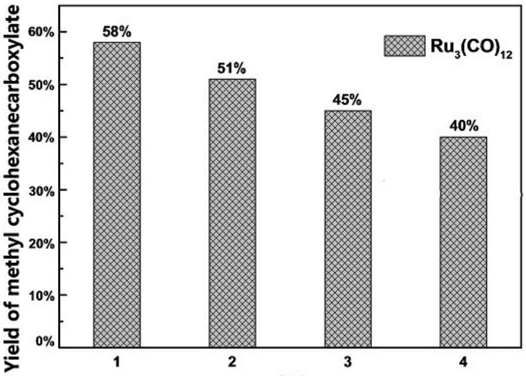


Figure S2 Reuse of single $Ru_3(CO)_{12}$ catalysts in the alkoxycarbonylation of cyclohexene with

CO_2. Reaction conditions: $Ru_3(CO)_{12}$ (0.33 mol%), [Bmim]Cl (1.5 equiv.), CO_2 (4 MPa), 160 ^{o}C, 20 h, cyclohexene (10 mmol, 1.0 equiv.), MeOH (20 mL). The yields were determined by GC-FID using *p*-xylene as an internal standard.

5. The effect of $Co_2(CO)_8$ and [Bmim]Cl on catalytic performance.

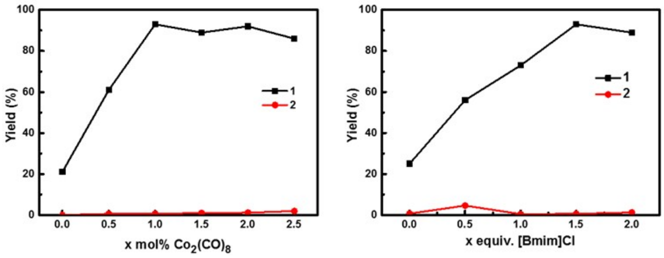


Figure S3 The effect of $Co_2(CO)_8$ and [Bmim]Cl on catalytic performance. Reaction conditions: cyclohexene (10 mmol, 1.0 equiv.), MeOH (20 mL), $[Ru(CO)_3Cl_2]_2$ (0.05 mmol), [Bmim]Cl (1.5 equiv.)-$Co_2(CO)_8$ (x mol%) or [Bmim]Cl (x equiv.)-$Co_2(CO)_8$ (1 mol%), 4 MPa CO_2, 160 ^{o}C, 20 h. Yields of carboxylic ester were determined by GC-FID using *p*-xylene as internal standard.

6. General procedure for the cyclohexene-absent control experiments

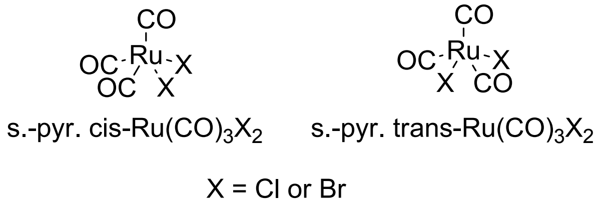
A 100 mL autoclave was charged with $[Ru(CO)_3Cl_2]_2$ (26 mg, 0.05 mmol, 1 mol% Ru), [Bmim]Cl (2.61 g, 15 mmol) and MeOH (20 mL). Then carbon dioxide (4 MPa at room temperature) was introduced before the autoclave was heated to 160 ^{o}C. After 20 hours, the reaction was cooled down to room temperature. Gas was collected by gas sampling bags after reaction at room temperature and then analysed by gas chromatography equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). TONs of gaseous products were determined by GC. Gas products were analyzed by TCD for the H_2 content and then studied by FID with a methanizer for CO. The concentration of gaseous products was quantified by the integral area ratio of the reduction products to standards. TON of methyl formate was determined by analyzing the liquid phase with GC-FID. The product in the liquid phase was analysed by GC-FID.

7. Computational methods and models

All calculations were performed with Gaussian09 program.[2] Geometries were optimized at 298.15 K and characterized by frequency calculations to be minima at the M06[3]/BS level in the gas phase, BS designating a mixed basis set of SDD[4] for Ru and Co atoms, and 6-311+g(d) for other atoms. The free energies (kcal mol^{-1}) at different temperature (respectively 298.15 K, 413.15 K and experiment temperature 433.15 K) were generally used in the following discussions.

7.1 The splitting of $[Ru(CO)_3Cl_2]_2$ dimer to $[Ru(CO)_3Cl_3]^-$

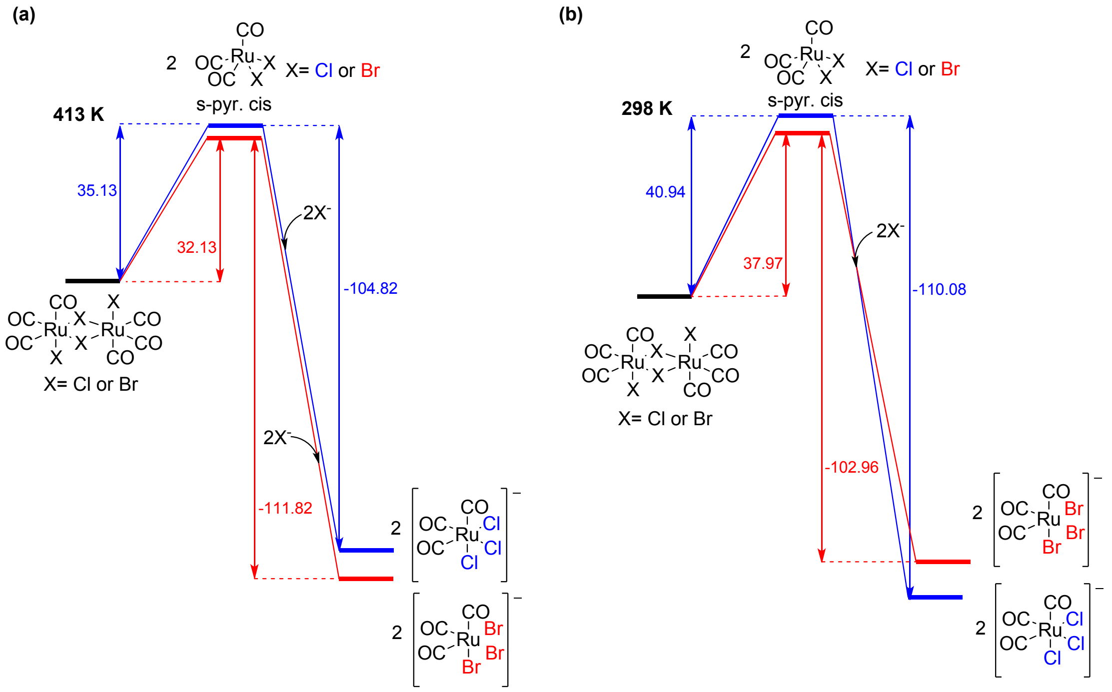
It is assumed that the halide-mediated $[Ru(CO)_3X_2]_2$ (X = Cl or Br) dimer splitting to $[Ru(CO)_3X_3]^-$ proceeds via the generation of mononuclear intermediate $[Ru(CO)_3X_2]$ and followed by the addition of halide anion (Cl^- or Br^-) onto $[Ru(CO)_3X_2]$. Three plausible pathways involving $[Ru(CO)_3X_2]$ with either single-pyramidal cis- or trans- configuration were considered.



Scheme S1. The configuration of mononuclear [$Ru(CO)_3Cl_2$].

Table S1. Energy profile for the splitting of [$Ru(CO)_3X_2$]$_2$ dimer to [$Ru(CO)_3X_2$] intermediate. (X = Cl or Br)

Temperature (K)	ΔG (kcal/mol)		
	two s.-pyr. cis-$Ru(CO)_3X_2$	two s.-pyr. trans-$Ru(CO)_3X_2$	one s.-pyr. cis- $Ru(CO)_3X_2$ and one s.-pyr. trans-$Ru(CO)_3X_2$
298.15	40.94 (Cl) 37.97 (Br)	50.93 (Cl) 44.10 (Br)	45.94 (Cl) 41.04 (Br)
413.15	35.13 (Cl) 32.13 (Br)	44.95 (Cl) 38.32 (Br)	40.04 (Cl) 35.22 (Br)
433.15	34.13 (Cl) 31.13 (Br)	43.92 (Cl) 37.32 (Br)	39.02 (Cl) 34.23 (Br)



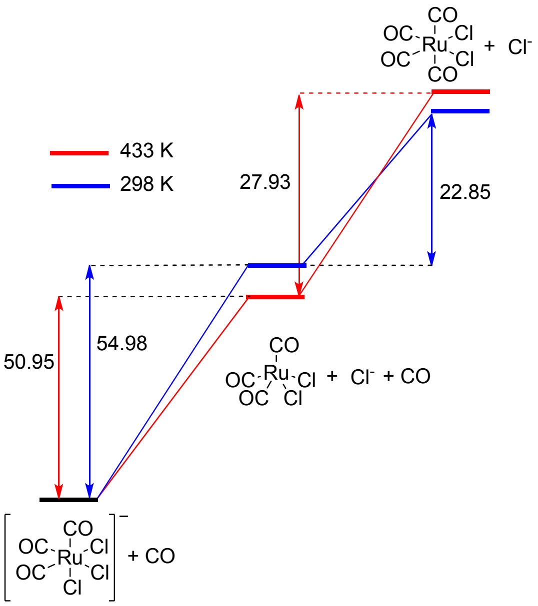
Scheme S2. The DFT-computed overall energy profile of chloride-mediated [$Ru(CO)_3X_2$]$_2$ (X = Cl or Br) dimer splitting process via two single-pyramidal cis-[$Ru(CO)_3X_2$] intermediates at 413 K **(a)** and 298 K **(b)**. The values of free energy are given in kcal/mol.

The calculated energy profile indicated that the splitting of dimer [$Ru(CO)_3Cl_2$]$_2$ to [$Ru(CO)_3Cl_2$] was highly endothermic (> 40 kcal/mol at 298 K; > 35 kcal/mol at 413 K) and the generation of two single-pyramidal cis-[$Ru(CO)_3Cl_2$] intermediates is much more energetically favored than other two pathways (Table S1). Thus only the reaction channel of adding chloride anion onto single-pyramid cis-[$Ru(CO)_3Cl_2$] was further considered. The result indicated that the addition of chloride onto single-pyramid cis-[$Ru(CO)_3Cl_2$] is exothermic (ΔG = -55.04 kcal/mol at 298 K; ΔG = -52.41 kcal/mol at 413 K). Based on these results, the splitting of 1 equiv. [$Ru(CO)_3Cl_2$]$_2$ to 2 equiv. [$Ru(CO)_3Cl_3$]$^-$ via [$Ru(CO)_3Cl_2$] intermediates is thermodynamically favored but requires relatively high energy for the intermediate generation at room temperature. Therotically, the conversion of [$Ru(CO)_3Cl_2$]$_2$ should also be sluggish at room temperature The experimental results are consistent with the DFT calculation results of chloride-mediated [$Ru(CO)_3Cl_2$]$_2$ splitting process.

Similarly, for the bromide-mediated splitting of dimer [$Ru(CO)_3Br_2$]$_2$ to [$Ru(CO)_3Br_2$], generating two single-pyramidal cis-[$Ru(CO)_3Br_2$] (**Path D**) is far more energetically favored than other two pathways. The addition of bromide anion onto single-pyramidal cis-[$Ru(CO)_3Br_2$] is exothermic (ΔG = -51.48 kcal/mol at 298 K; ΔG = -55.91 kcal/mol at 413 K) as well. Therefore theoretically the bromide-mediated splitting of dimer [$Ru(CO)_3Br_2$]$_2$ to [$Ru(CO)_3Br_3$]$^-$ should also be sluggish at room temperature and high temperature is required to promote the splitting process.

7.2 The conversion of s.-pyr cis-$Ru(CO)_3Cl_2$ to cis-[$Ru(CO)_4Cl_2$]

The IR spectral comparison of bimetallic Ru-Co catalyst system before and after reaction showed that the characteristic carbonyl absorption band at 2125 cm^{-1} was still present in the recycled catalysts after reaction. Considering the fact that the total conversion of [$Ru(CO)_3Cl_2$]$_2$ dimer splitting to fac-[$Ru(CO)_3Cl_3$]$^-$ in the presence of [Bmim]Cl additive at 140 ^{o}C under nitrogen atmosphere after 4 hours as well as the high wavenumbers of peak and also based on the reported IR spectral data, we suspected that it was probably contributed from CO-abundant ruthenium complexes such as cis-[$Ru(CO)_4Cl_2$] or coordinatively unsaturated single-pyramid cis-$Ru(CO)_3Cl_2$. Then in order to verify the feasibility of generating cis-[$Ru(CO)_4Cl_2$], the free energy for the conversion of fac-[$Ru(CO)_3Cl_3$]$^-$ to cis-[$Ru(CO)_4Cl_2$] via s-pyr. cis-$Ru(CO)_3Cl_2$ under 1 atm CO was calculated. The results indicated that the formation of cis-[$Ru(CO)_4Cl_2$] from fac-[$Ru(CO)_3Cl_3$]$^-$ or s-pyr. cis-$Ru(CO)_3Cl_2$ was energetically disfavoured under low CO pressure and required elevated temperature, so they might be transiently formed during the reaction conditions and were infeasible to be present in the recycled catalysts.



Scheme S3 The DFT-computed energy profile of fac-$[Ru(CO)_3Cl_3]^-$ to cis-$[Ru(CO)_4Cl_2]$ via s-pyr. cis-$[Ru(CO)_3X_2]_2$ under 1 atm CO atmosphere at 433 K (red) and 298 K (blue). The values of free energy are given in kcal/mol.

7.3 The addition of ruthenium and cobalt hydride onto cyclohexene

Based on the previous literatures, $[RuCl_2(CO)_2H(cyclohexene)]^-$ and $[HCo(CO)_3(cyclohexene)]$ were proposed as the plausible ruthenium and cobalt hydride complexes intermediate. The energy profile for adding the Ru-H and Co-H onto the double bond of cyclohexene was computed.

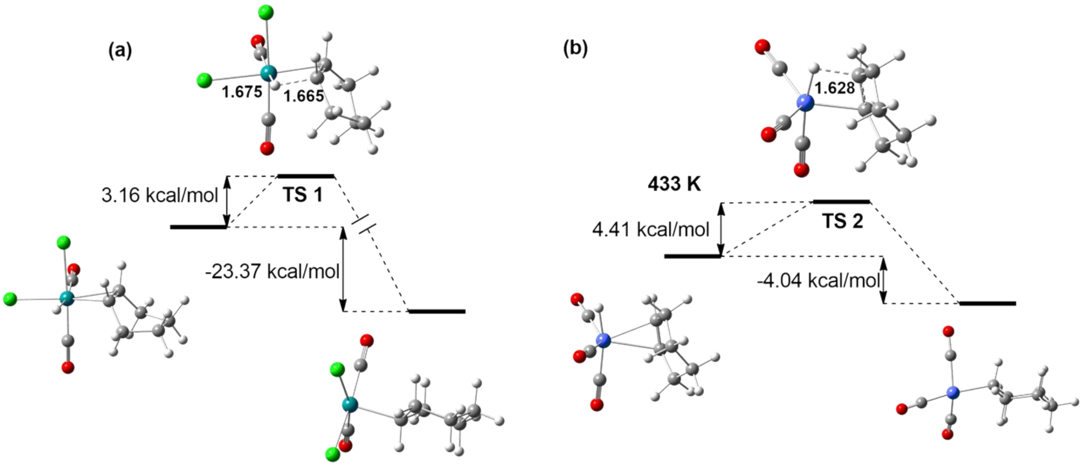


Figure S4 Energy profiles for the addition of Ru-H (**a**) and Co-H (**b**) onto cyclohexene. The values of bond lengths are given in angstroms. Grey balls for C atoms, red balls for O atoms, white balls for H atoms, green balls for Cl atoms, cyan-blue balls for Ru atoms and blue balls for Co atoms.

Table S2-16. The Cartesian coordinates (xyz) for all optimized structures at 298.15 K.

$[Ru(CO)_3Cl_2]_2$			
Ru	-1.17818600	0.09017100	-1.37463800

Ru	1.17818600	-0.09017100	1.37463800
C	-1.07017000	2.03794600	-1.28899100
C	-1.00271500	-0.00135400	-3.26644100
C	-3.07622800	0.03612600	-1.47130300
C	1.07017000	-2.03794600	1.28899100
C	1.00271500	0.00135400	3.26644100
C	3.07622800	-0.03612600	1.47130300
Cl	1.21617000	2.30793600	1.37352300
Cl	-1.21617000	-2.30793600	-1.37352300
O	1.02383600	-3.16654900	1.25815100
O	0.88772600	0.08979600	4.38918800
O	4.20588300	0.02746300	1.51091100
O	-4.20588300	-0.02746300	-1.51091100
O	-0.88772600	-0.08979600	-4.38918800
O	-1.02383600	3.16654900	-1.25815100
Cl	1.28930900	-0.01749500	-1.10398900
Cl	-1.28930900	0.01749500	1.10398900

s-pyr. trans-$Ru(CO)_3Cl_2$			
Ru	0.00000000	0.00000000	-0.16168700
Cl	2.32376800	0.00000000	-0.58549500
Cl	-2.32376800	0.00000000	-0.58549500
C	0.00000000	1.99493100	-0.18668600
C	0.00000000	0.00000000	1.65680900
C	0.00000000	-1.99493100	-0.18668600
O	0.00000000	-3.12117700	-0.19098000
O	0.00000000	0.00000000	2.79701100
O	0.00000000	3.12117700	-0.19098000

s-pyr. cis-$Ru(CO)_3Cl_2$			
Ru	-0.00047200	-0.02862100	-0.16895400
Cl	1.64393500	1.63785600	-0.20357300
Cl	-1.64258800	1.63986600	-0.20362300
C	-1.45944900	-1.26781200	-0.49851600
C	0.00104000	-0.44826000	1.62284000
C	1.45788100	-1.26819600	-0.50024700
O	-2.33097100	-1.95931200	-0.70551900
O	2.32924100	-1.95958800	-0.70823100
O	0.00186300	-0.65064300	2.74023200

fac-$[Ru(CO)_3Cl_3]^-$			
Ru	0.00000000	0.00000000	0.11851500
C	0.00000000	1.64144600	1.08233100

C	-1.42153400	-0.82072300	1.08233100
C	1.42153400	-0.82072300	1.08233100
O	0.00000000	2.63499900	1.63930700
O	-2.28197600	-1.31749900	1.63930700
O	2.28197600	-1.31749900	1.63930700
Cl	-1.75340600	1.01232900	-1.25568600
Cl	1.75340600	1.01232900	-1.25568600
Cl	0.00000000	-2.02465900	-1.25568600

$[Ru(CO)_3Br_2]_2$			
Ru	-1.23556200	0.08735800	-1.44516400
Ru	1.23556200	-0.08735800	1.44516400
C	-1.11585700	2.03104700	-1.33519900
C	-1.05022600	-0.00785400	-3.34037500
C	-3.13764000	0.02367000	-1.54271600
C	1.11585700	-2.03104700	1.33519900
C	1.05022600	0.00785400	3.34037500
C	3.13764000	-0.02367000	1.54271600
O	1.05649700	-3.15910200	1.27984300
O	0.93098500	0.09015500	4.46385100
O	4.26791600	0.03841200	1.58726600
O	-4.26791600	-0.03841200	-1.58726600
O	-0.93098500	-0.09015500	-4.46385100
O	-1.05649700	3.15910200	-1.27984300
Br	1.36327600	-0.01894700	-1.16436000
Br	-1.36327600	0.01894700	1.16436000
Br	1.32737700	2.45772900	1.50920100
Br	-1.32737700	-2.45772900	-1.50920100

s-pyr. trans-$Ru(CO)_3Br_2$			
Ru	0.00000000	0.00000000	-0.00045100
C	0.00000000	1.98957200	-0.03506100
C	0.00000000	0.00000000	1.82160500
C	0.00000000	-1.98957200	-0.03506100
O	0.00000000	-3.11686500	-0.04802800
O	0.00000000	0.00000000	2.96231400
O	0.00000000	3.11686500	-0.04802800
Br	2.44574500	0.00000000	-0.47741600
Br	-2.44574500	0.00000000	-0.47741600

s-pyr. cis-$Ru(CO)_3Br_2$			
Ru	0.00007400	0.43920300	-0.14555800
C	1.46546000	1.65234200	-0.54743700

C	0.00069700	0.93630600	1.62807800
C	-1.46569400	1.65234100	-0.54682300
O	2.33478300	2.33586100	-0.79065800
O	-2.33530500	2.33566900	-0.78951300
O	0.00113800	1.19479900	2.73458400
Br	-1.75562200	-1.30984100	-0.08611800
Br	1.75530900	-1.31020100	-0.08627200

cis-Ru(CO)$_4$Cl$_2$			
Ru	0.00000000	0.00000000	0.15728400
C	0.00000000	1.45012100	1.44015800
C	0.00000000	-1.45012100	1.44015800
C	1.98108400	0.00000000	-0.09170000
O	0.00000000	2.31767400	2.16778900
O	0.00000000	-2.31767400	2.16778900
O	3.08237200	0.00000000	-0.32128600
Cl	0.00000000	1.71592400	-1.54841300
Cl	0.00000000	-1.71592400	-1.54841300
C	-1.98108400	0.00000000	-0.09170000
O	-3.08237200	0.00000000	-0.32128600

fac-[Ru(CO)$_3$Br$_3$]$^-$			
Ru	0.00000000	0.00000000	0.51008700
C	1.42992000	0.82556500	1.46273800
C	0.00000000	-1.65112900	1.46273800
C	-1.42992000	0.82556500	1.46273800
O	2.29116000	1.32280200	2.01920100
O	-2.29116000	1.32280200	2.01920100
O	0.00000000	-2.64560300	2.01920100
Br	0.00000000	2.15802100	-0.92603700
Br	1.86890100	-1.07901100	-0.92603700
Br	-1.86890100	-1.07901100	-0.92603700

[Ru(CO)$_2$Cl$_2$H-(*c*-C$_6$H$_{10}$)]$^-$			
Ru	-0.60776000	0.09410300	-0.20252100
H	-0.48732100	0.35743400	-1.80422700
C	-0.10571300	1.85301100	0.00888700
C	-1.13683400	-0.29262000	1.72225200
O	-1.46889700	-0.51985400	2.78608200
O	0.20071600	2.96157200	0.11475600
Cl	-1.32212900	-2.24345600	-0.70434500
C	2.26168800	-0.07122400	1.35434700
C	1.29235400	-0.83182900	0.48722500

C	1.36309100	-0.57875800	-0.89139200
C	2.42561100	0.39617000	-1.32931500
C	3.76384300	-0.05034800	-0.72568600
C	3.68402200	-0.26172500	0.80204300
H	2.02692300	1.00043400	1.36708900
H	0.99967100	-1.83058800	0.81050700
H	1.12550300	-1.39097900	-1.57639300
H	2.48909300	0.44383800	-2.42307200
H	4.06186000	-0.98990300	-1.21174700
H	4.36997300	0.41943700	1.32448400
H	2.20948700	-0.40102700	2.39983800
H	4.02244300	-1.27685300	1.05127300
H	4.54716000	0.67851200	-0.97513000
H	2.20280500	1.41744100	-0.99854500
Cl	-2.91134500	0.88592200	-0.52094900

$[Ru(CO)_2Cl_2(c\text{-}C_6H_{11})]^-$			
Ru	0.98699100	0.15947800	-0.08468400
C	0.96160700	1.87210400	0.60184300
C	0.64658100	0.73923200	-1.81600500
O	0.97650900	2.94648400	1.02327700
O	0.44939100	1.10398400	-2.89202900
Cl	1.58309800	-0.65071500	2.12948200
C	-1.07041600	0.07487200	0.38638000
C	-1.98858400	1.09922800	-0.25299700
C	-1.54492400	-1.33638200	0.08949900
C	-3.42891600	0.91340100	0.22285500
H	-1.65246300	2.12231000	-0.03660100
C	-2.98682700	-1.52862500	0.56348900
H	-1.48702800	-1.52775700	-0.99392800
C	-3.91967200	-0.49946300	-0.05615900
H	-3.47971100	1.10721100	1.30676700
H	-3.02057600	-1.43498600	1.66109700
H	-4.94767900	-0.63248000	0.31228400
H	-0.88547900	-2.06951100	0.56634600
H	-1.06594900	0.22515800	1.47814700
H	-1.96526100	0.98890000	-1.34932200
H	-4.08632100	1.65459700	-0.25530100
H	-3.95878900	-0.65795200	-1.14678400
H	-3.32520500	-2.54854300	0.33042500
Cl	1.65375900	-1.97598600	-1.04892000

Transition state from $[Ru(CO)_2Cl_2H\text{-}(c\text{-}C_6H_{10})]^-$ to $[Ru(CO)_2Cl_2(c\text{-}C_6H_{11})]^-$

Ru	-0.54740900	0.04228200	-0.09173000
H	0.03819300	-0.14913800	-1.64963900
C	0.18987400	1.72939800	0.03375700
C	-1.33028000	0.07727300	1.70187700
O	-1.74371100	0.04980300	2.76616300
O	0.61369700	2.80273400	0.08500600
Cl	-1.61405300	-2.17703700	-0.40342600
C	2.25617400	-0.52367000	1.42150400
C	1.20399300	-1.09945600	0.50113200
C	1.29179700	-0.96484600	-0.91853300
C	2.44087200	-0.18197900	-1.54358600
C	3.64282200	-0.10466200	-0.61175700
C	3.22017600	0.44134200	0.74221700
H	1.79713200	-0.05502100	2.30294100
H	0.77888600	-2.04306600	0.84403200
H	0.96419600	-1.83915800	-1.48196600
H	2.71719800	-0.65275400	-2.49658400
H	4.08087400	-1.10804700	-0.47883800
H	2.75454600	1.42724100	0.60655300
H	2.84860000	-1.36984500	1.81350500
H	4.09436400	0.60340200	1.38815100
H	4.42607500	0.52093100	-1.06206600
H	2.12972700	0.83849700	-1.79699600
Cl	-2.56219800	1.17150000	-1.05080900

$Co(CO)_3H$-(c-C_6H_{10})			
Co	0.94133700	-0.21655100	0.12651500
C	0.36559500	-0.66855300	1.73696000
C	2.35483000	-0.60739100	-0.87381800
C	1.31497800	1.50460800	0.45111000
O	1.56198700	2.59507500	0.67521000
O	3.27812900	-0.93096900	-1.46266700
O	0.05427600	-1.03645900	2.77317300
C	-0.78840300	0.66693700	-1.23491000
H	-0.26685600	-1.21934900	-2.02501100
C	-1.81589400	1.51294200	-0.52484600
C	-1.97979200	-1.46388200	-0.64326900
C	-0.87075800	-0.68794000	-1.29153100
C	-3.10494900	0.73844400	-0.28288300
H	-1.42918900	1.89423200	0.43077100
C	-2.80902700	-0.62541200	0.31881000
H	-2.62887100	-1.83924900	-1.45209500
H	-3.63330800	0.60381200	-1.23959100

H	-3.73794100	-1.15406800	0.56450900
H	-3.77650100	1.31593500	0.36367100
H	-2.27339100	-0.49523400	1.26980200
H	-1.58682900	-2.36093200	-0.14864500
H	0.88180300	-1.71766400	0.04660400
H	-2.01542500	2.40602500	-1.13154500
H	-0.10420300	1.17367400	-1.91383600

$Co(CO)_3(c\text{-}C_6H_{11})$			
Co	1.08495800	0.00441300	-0.00340400
C	0.87387600	-1.73928800	0.28082000
C	2.70876600	-0.10387700	-0.76151100
C	1.32058800	1.55336300	0.84192300
O	1.47447000	2.48086200	1.48629900
O	3.72488600	-0.16328600	-1.27254100
O	0.81074900	-2.83387400	0.59361400
C	-0.86825000	0.28940300	0.35922200
H	-0.51899800	1.33838900	-1.53280200
C	-1.79317600	-0.77691900	0.91455000
C	-2.63852600	0.99994400	-1.27140800
C	-1.17652400	0.56297500	-1.10775200
C	-3.24684000	-0.32842500	0.77946800
H	-1.67286100	-1.72044600	0.35882400
C	-3.58658800	-0.02887800	-0.67383500
H	-2.77784600	1.96817400	-0.76673100
H	-3.40935600	0.57442000	1.38933700
H	-4.62509500	0.31568200	-0.76494300
H	-3.92117100	-1.09665500	1.18079500
H	-3.52160700	-0.96133500	-1.25781100
H	-2.86376700	1.16609300	-2.33331100
H	-1.02014800	-0.35057800	-1.70592500
H	-1.55308500	-1.00192200	1.96195800
H	-1.05072000	1.20963900	0.93469900

Transition state from $Co(CO)_3H\text{-}(c\text{-}C_6H_{10})$ to $Co(CO)_3(c\text{-}C_6H_{11})$			
Co	0.84627600	-0.13278000	0.05476200
C	0.45920400	-0.25610600	1.80916600
C	2.32708500	-0.91181700	-0.60884800
C	1.36951300	1.56005800	-0.01721200
O	1.67531200	2.65844600	-0.07381500
O	3.27387300	-1.42327300	-0.99103000
O	0.26216100	-0.35928300	2.92969900
C	-0.75266400	0.47929100	-1.19887600

H	-0.39314800	-1.49039100	-1.90555300
C	-1.78878800	1.39640500	-0.57587100
C	-2.03006500	-1.57829800	-0.43462500
C	-0.83435300	-0.91784900	-1.08879800
C	-3.09220900	0.66815600	-0.27157300
H	-1.41481800	1.85055400	0.35133600
C	-2.81924700	-0.63584100	0.45880400
H	-2.68332700	-1.91799200	-1.25437700
H	-3.62399400	0.44949900	-1.21099800
H	-3.75568900	-1.11940400	0.76247100
H	-3.75422500	1.31665000	0.31500300
H	-2.26515400	-0.43121900	1.38647500
H	-1.73715500	-2.48585700	0.10687500
H	0.26389400	-1.51975900	-0.04814400
H	-1.97269300	2.23629100	-1.25805500
H	-0.23476200	0.86557000	-2.07544500

8. Characterization of catalyst and product compounds

$[Ru(CO)_3Cl_2]_2$

IR (KBr pellet): ν (CO) = 2145, 2072, 2027 cm^{-1}. The IR spectra is in accordance with the reported data in the literature.[1a,1b]

The mixture of dissolved $[Ru(CO)_3Cl_2]_2$ and [Bmim]Cl (molar ratio of 1:2) in MeOH solvent after stirring at room temperature for 24 hours[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.44 (s, 1H), 7.32 (d, *J* = 23.9 Hz, 2H), 4.27 (t, *J* = 7.0 Hz, 2H), 3.99 (s, 3H), 1.87-1.71 (m, 2H), 1.31 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).

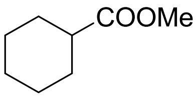
^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.13, 137.11, 123.37, 121.70, 49.74, 37.08, 32.15, 19.34.

Element analysis calculated for: C, 30.68; H, 3.51; N, 6.50. Found: C, 31.26; H, 3.82; N, 6.77. 13.38.

Calculated ruthenium content for the mixture of $[Ru(CO)_3Cl_2]_2$ and [Bmim]Cl with 1:2 mole ratio: 23.47%; ICP-measured Ru content for the 1:2 mixture of $[Ru(CO)_3Cl_2]_2$ and [Bmim]Cl: 25.03%

IR (MeOH): ν(CO) = 2129 (s), 2055 (s, br), 1995 (s) cm^{-1}. Compared with the characteristic absorptions of $[Ru(CO)_3Cl_2]_2$ in KBr pellet, the characteristic carbonyl absorptions of $[Ru(CO)_3Cl_2]_2$ in MeOH solution has obvious red shift. This trait is similar to the report in the supplementary data of previous literature[1a].

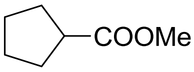
Methyl cyclohexanecarboxylate (**1**)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 (s, 1H), 2.29 (tt, *J* = 11.3, 3.6 Hz, 1H), 1.88 (d, J = 13.3 Hz, 2H), 1.79-1.66 (m, 2H), 1.65-1.57 (m, 1H), 1.47-1.35 (m, 1H), 1.32-1.15 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.63, 51.47, 43.10, 29.01, 25.73, 25.44.

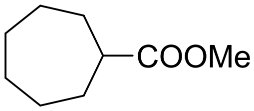
Methyl cyclopentanecarboxylate (**3a**)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 3H), 2.69 (p, *J* = 8.0 Hz, 1H), 1.91-1.44 (m, 8H)

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.22, 51.51, 43.63, 29.96, 25.75.

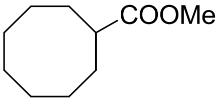
Methyl cycloheptanecarboxylate (**3b**)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 3H), 2.48-2.43 (m, 1H), 1.95-1.82 (m, 2H), 1.72-1.38 (m, 10H).

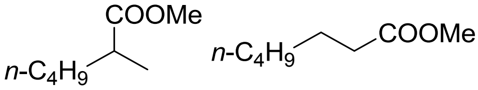
^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.58, 51.52, 44.87, 30.78, 28.26, 26.29.

Methyl cyclooctanecarboxylate (**3c** and **3m**)



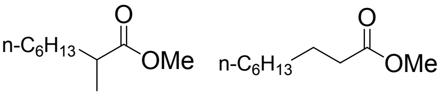
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 3H), 2.58-2.44 (m, 1H), 1.92-1.79 (m, 2H), 1.74-1.61 (m, 4H), 1.59-1.42 (m, 8H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.79, 51.49, 43.44, 28.70, 26.73, 26.09, 25.20.

Mixture of methyl 2-methylhexanoate and methyl heptanoate (The alkoxycarbonylative products of 1-hexene, calculated molar ratio of 2-methylhexanoate to methyl heptanoate determined by ^{1}H NMR of product mixture is 0.38 : 1) (**3d**)



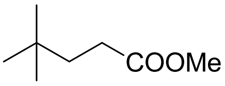
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 3H for $-COOCH_3$ of both methyl 2-methylhexanoate and methyl heptanoate) 2.40 (m, 1H for methyl 2-methylhexanoate), 2.27 (t, *J* = 7.5 Hz, 2H for methyl heptanoate), 1.61-1.55 (m), 1.30-1.26 (m), 1.11 (d, *J* = 7.0 Hz, 3H for methyl 2-methylhexanoate), 0.86-0.80 (m).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.39, 51.48, 39.52, 34.18, 33.63, 31.55, 29.53, 28.92, 25.01, 22.68, 22.57, 17.15, 14.08, 14.02.

Mixture of methyl 2-methyloctanoate and methyl nonanoate (The alkoxycarbonylative products of 1-octene, molar ratio of 2-methyloctanoate to methyl nonanoate is 0.28 : 1, determined by ^{1}H NMR of product mixture,) (**3e**)



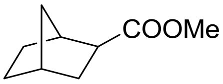
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3H belong to $-COOCH_3$ of both methyl 2-methyloctanoate and methyl nonanoate), 2.47-2.38 (m, 1H for methyl 2-methyloctanoate), 2.29 (t, *J* = 7.5 Hz, 2H for methyl nonanoate), 1.62 (dd, *J* = 20.5, 13.8 Hz, 1H), 1.39 (s, 1H), 1.25 (s, 3H), 1.13 (d, *J* = 7.0 Hz, 1H), 0.86 (t, *J* = 6.2 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.48, 174.40, 51.48, 39.47, 34.13, 33.85, 31.82, 31.71, 29.24, 29.17, 29.14, 27.22, 24.97, 22.67, 22.62, 17.10, 14.12.

Methyl 4,4-dimethylpentanoate (**3f**)



1H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3H), 2.33-2.24 (t, *J* = 8.4 Hz, 2H), 1.62-1.50 (t, *J* = 8.4 Hz, 2H), 0.90 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.83, 51.47, 38.60, 30.02, 29.88, 28.95.

Methyl bicyclo[2.2.1]heptane-2-carboxylate (**3e**). (*exo* : *endo* = 1:0.12, determined by ^{1}H NMR) (**3g**)

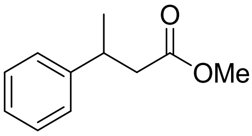


^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.64 (s, 3H), 2.46 (s, 1H), 2.32-2.19 (m, 2H), 1.86-1.74 (m, 1H), 1.54-1.39 (m, 4H), 1.26-1.09 (m, 3H).
^{13}C NMR (101 MHz, CDCl$_3$): δ = 176.54, 51.56, 46.31, 40.88, 36.44, 35.98, 34.12, 29.44, 28.60.

Mixture of methyl 4-phenylbutanoate and methyl 2-methyl-3-phenylpropanoate (The alkoxycarbonylative products of allyl benzene, molar ratio of 4-phenylbutanoate to 2-methyl-3-phenylpropanoate is 1:0.22, determined by ^{1}H NMR of product) (**3h**)

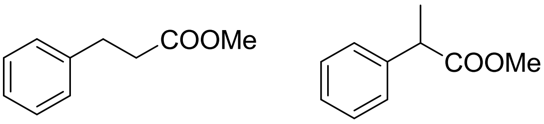
^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.66 (s, 3H for 4-phenylbutanoate), 3.63 (s, 3H for methyl 2-methyl-3-phenylpropanoate), 3.03 (dd, *J* = 13.1, 6.5 Hz, 2H for 2-methyl-3-phenylpropanoate), 2.74 (dd, *J* = 14.2, 7.0 Hz, 1H for 2-methyl-3-phenylpropanoate), 2.65 (t, *J* = 7.6 Hz, 2H for 4-phenylbutanoate), 2.33 (t, *J* = 7.5 Hz, 2H), 1.96 (p, *J* = 7.6 Hz, 2H for 4-phenylbutanoate), 1.15 (d, *J* = 6.8 Hz, 3 H for methyl 2-methyl-3-phenylpropanoate)
^{13}C NMR (100 MHz, CDCl$_3$) : δ = 173.90, 141.37, 128.95, 128.48, 128.38, 126.31, 125.98, 51.46, 41.41, 39.72, 35.13, 33.39, 26.48, 16.73.

Methyl 3-phenylbutanoate (**3i**)



^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.33-7.16 (m, 5H), 3.61 (s, 3H), 3.28 (dd, *J* = 14.6, 7.2 Hz, 1H), 2.58 (qd, *J* = 15.2, 7.6 Hz, 2H), 1.29 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, CDCl$_3$): δ = 172.87, 145.72, 128.54, 126.74, 126.45, 51.53, 42.75, 36.45, 21.81.

Mixture of methyl 3-phenylpropanoate and methyl 2-phenylpropanoate (The alkoxycarbonylative products of styrene substrate, calculated molar ratio of methyl 3-phenylpropanoate to methyl 2-phenylpropanoate determined by ^{1}H NMR of product mixture is 1:0.5) (**3j**)



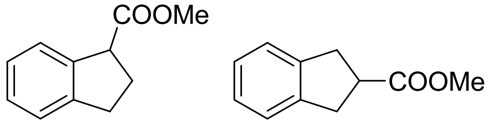
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.35-7.22 (m, 5H, belongs to methyl 3-phenylpropanoate), 7.22-7.15 (m, 5H, belongs to methyl 2-phenylpropanoate), 3.71 (q, *J* = 7.2 Hz, 1H belongs to methyl 2-phenylpropanoate), 3.64 (s, 3H, belongs to methyl 3-

phenylpropanoate), 3.63 (s, 3H, belongs to methyl 2-phenylpropanoate), 2.94 (t, *J* = 7.8 Hz, 2H, belongs to methyl 3-phenylpropanoate), 2.62 (t, *J* = 7.8 Hz, 2H, belongs to belongs to methyl 3-phenylpropanoate), 1.49 (d, *J* = 7.2 Hz, 3H, belongs to methyl 2-phenylpropanoate)

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.01, 173.35, 140.60, 140.55, 128.69, 128.55, 128.32, 127.51, 127.18, 126.31, 52.04, 51.63, 45.44, 35.74, 30.98, 18.65.

Mixture of methyl 2,3-dihydro-1*H*-indene-2-carboxylate and methyl 2,3-dihydro-1*H*-indene-1-carboxylate

(The alkoxycarbonylative products of 1*H*-indene, molar ratio of methyl 2,3-dihydro-1*H*-indene-1-carboxylate to product 2,3-dihydro-1*H*-indene-2-carboxylate determined by ^{1}H NMR of product mixture is 1 : 1.7) (**3k**)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.14 (t, J = 7.3 Hz, 1H for 2,3-dihydro-1*H*-indene-1-carboxylate), 3.81 (s, 3H for 2,3-dihydro-1*H*-indene-2-carboxylate), 3.80 (s, 3H for 2,3-dihydro-1*H*-indene-1-carboxylate), 3.00 (dt, *J* = 15.6, 7.6 Hz, 1H), 2.59-2.47 (m, 1H), 2.47-2.35 (m, 1H).

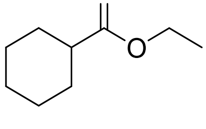
^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.78, 174.42, 144.14, 141.58, 140.72, 127.59, 126.66, 126.48, 124.83, 124.73, 124.37, 52.06, 51.96, 50.12, 43.52, 36.22, 31.80, 28.79.

Mixture of methyl 2-methyloctanoate and methyl nonanoate from 1,7-octadiene (**3m**)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3H for both methyl nonanoate and methyl 2-methyloctanoate), 2.50-2.38 (m, 1H for 2-methyloctanoate), 2.30 (t, *J* = 7.5 Hz, 2H for methyl nonanoate), 1.68-1.60 (m, 2H for methyl nonanoate), 1.28-1.27 (m, -$(CH_2)_5$- for methyl nonanoate and -$(CH_2)_5$- for methyl 2-methyloctanoate), 1.14 (d, *J* = 6.9 Hz, 3H for 2-methyloctanoate), 0.89-0.86 (t, *J* = 6.8 Hz, 3H for methyl nonanoate and methyl 2-methyloctanoate)

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.47, 174.38, 51.47, 39.57, 34.21, 33.94, 31.91, 31.80, 29.32, 29.27, 29.22, 27.30, 25.07, 22.73, 17.14, 14.14.

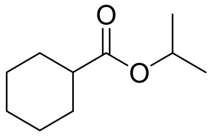
Ethyl cyclohexanecarboxylate (**3n**)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.07 (q, *J* = 7.1 Hz, 2H), 2.30-2.17 (m, 1H), 1.90-1.81 (m, 2H), 1.77-1.66 (m, 2H), 1.64-1.55 (m, 1H), 1.39 (q, *J* = 11.8 Hz, 2H), 1.30-1.14 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.14, 60.00, 43.19, 28.99, 25.74, 25.43, 14.20.

Isopropyl cyclohexanecarboxylate (**3o**)

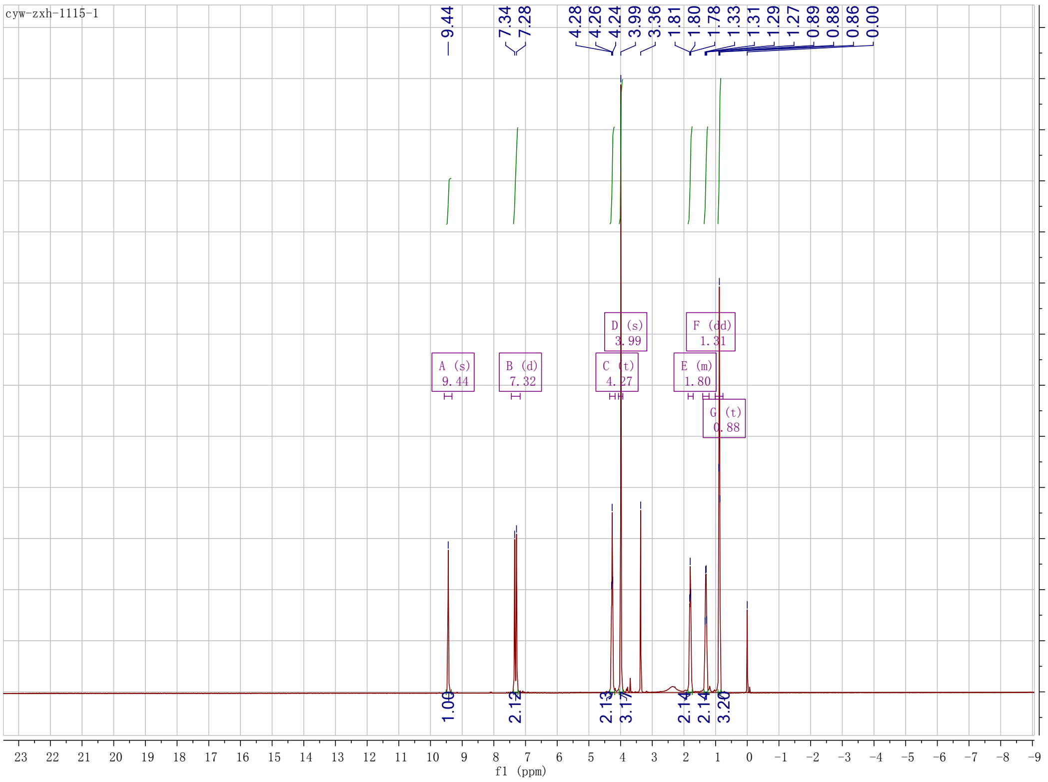


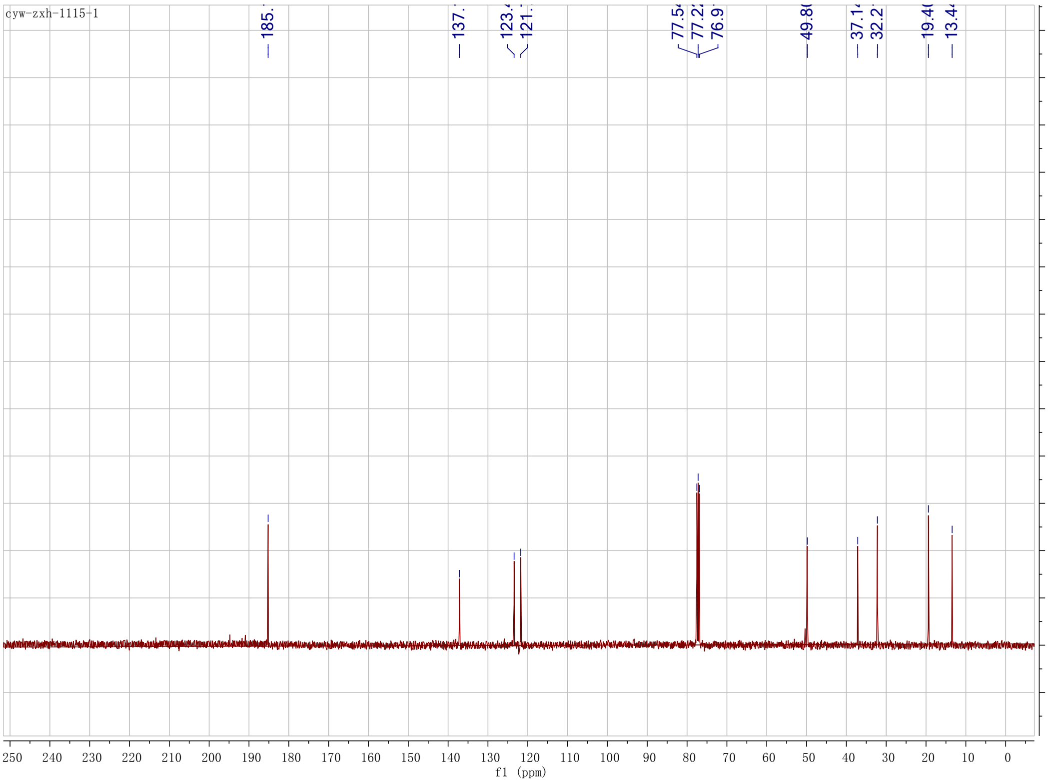
^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.97 (dt, *J* = 12.5, 6.2 Hz, 1H), 2.22 (tt, *J* = 11.0, 3.3 Hz, 1H), 1.80-1.54 (m, 5H), 1.46-1.34 (m, 3H), 1.31-1.14 (m, 13H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 175.69, 66.99, 43.37, 28.97, 25.78, 25.44, 21.78.

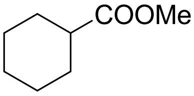
10. NMR spectrum copies of catalyst and carboxylic ester products.

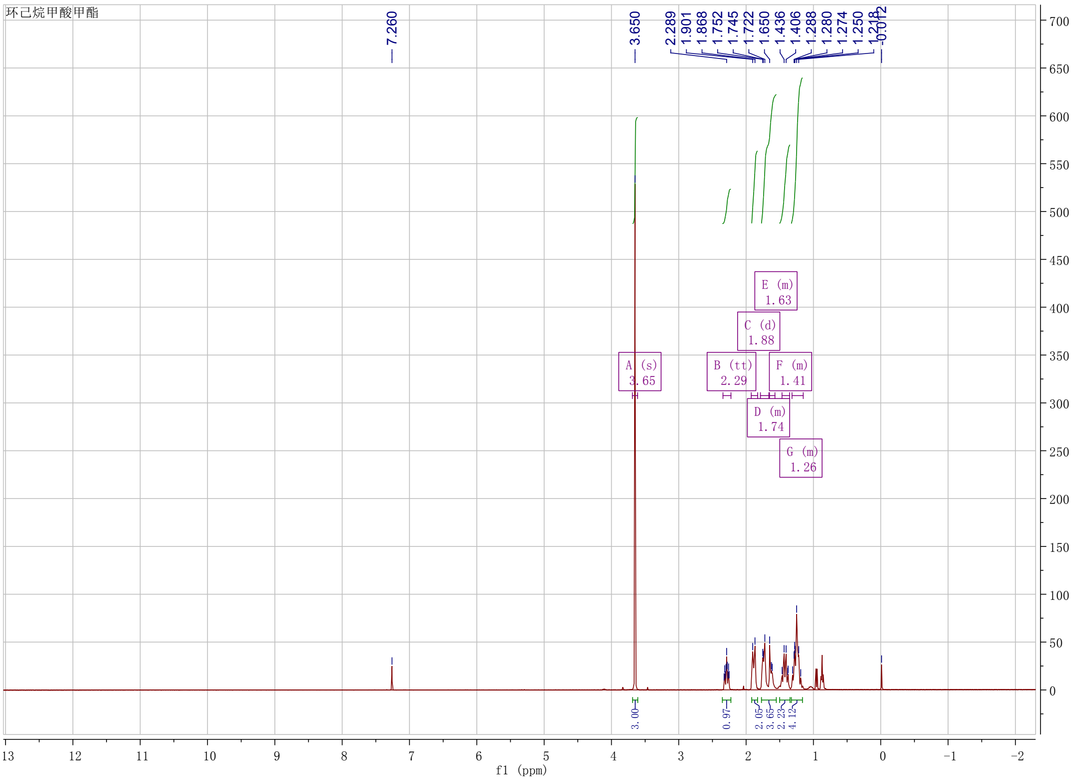
The mixture of $[Ru(CO)_3Cl_2]_2$ and [Bmim]Cl with 1:2 molar ratio after stirring at room temperature

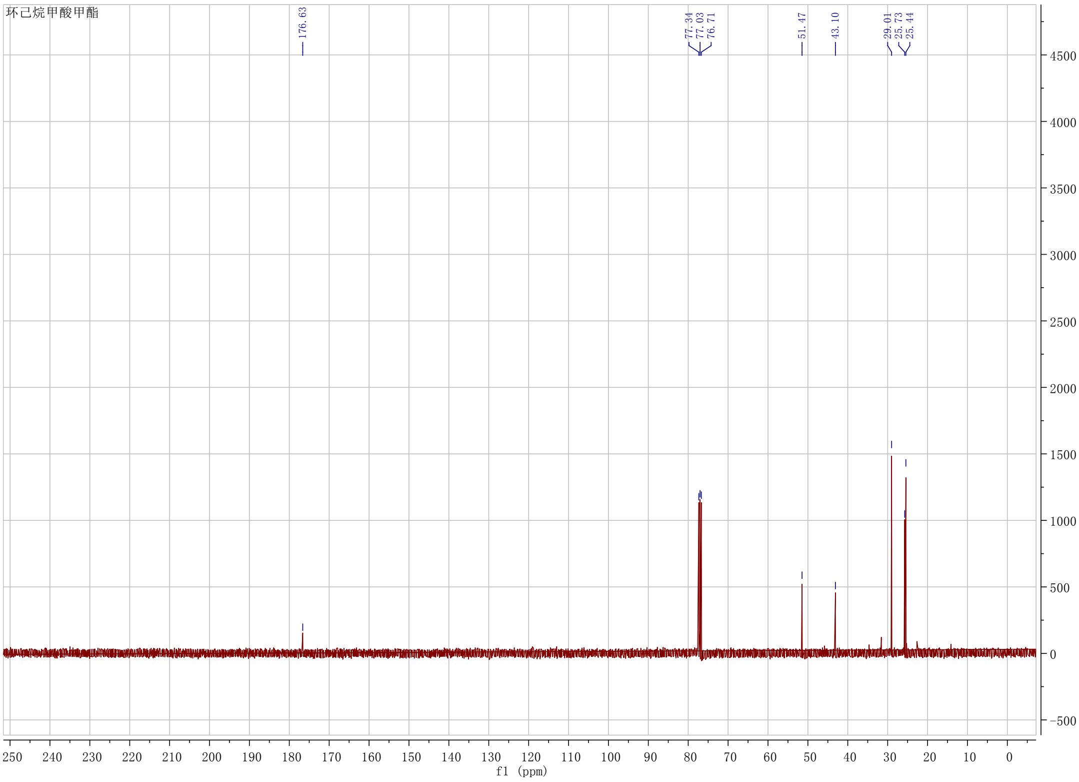




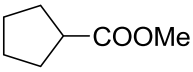
Methyl cyclohexanecarboxylate (**1**)

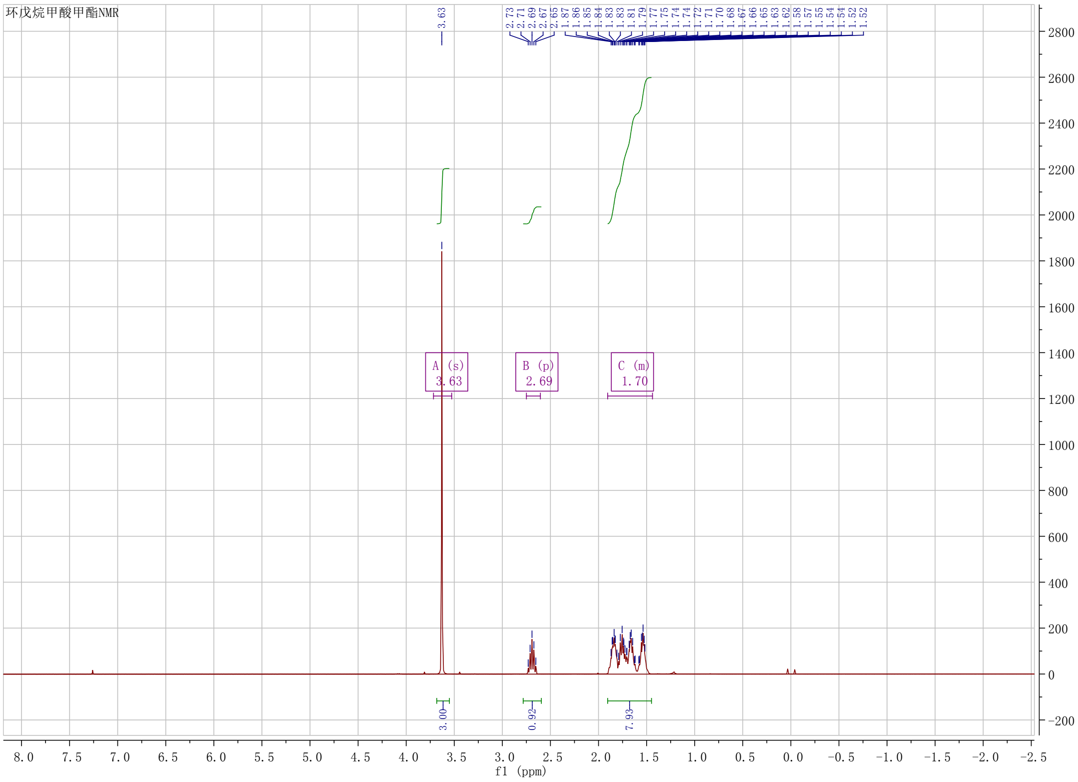


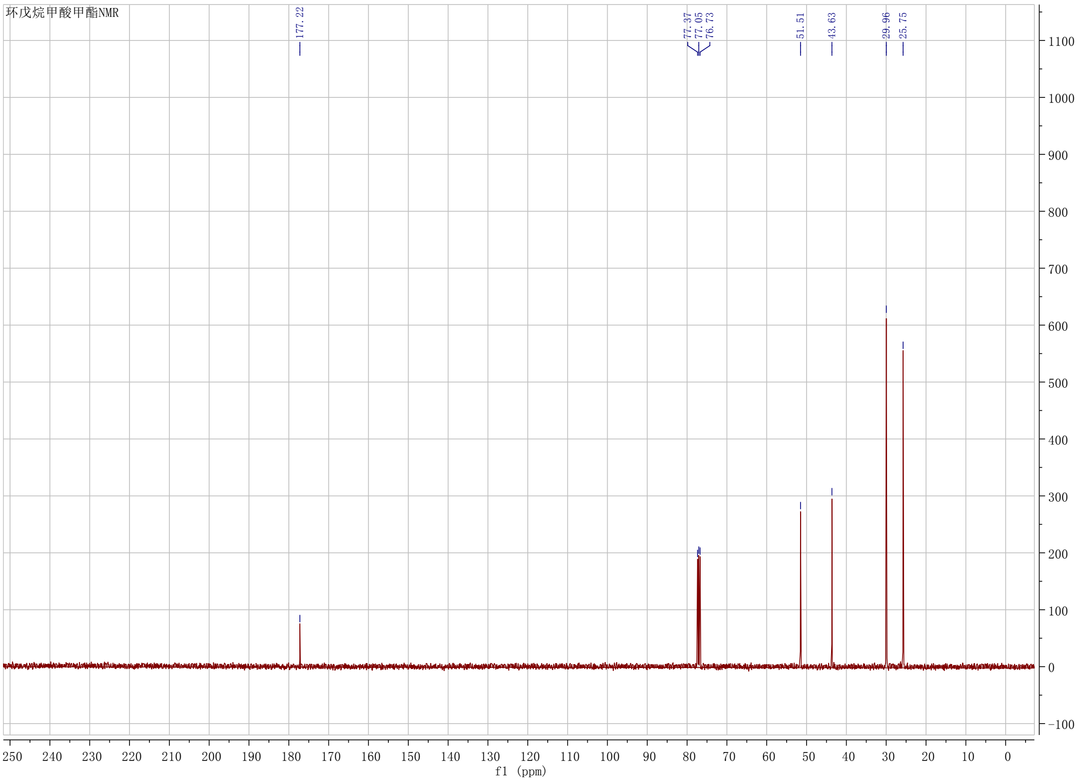




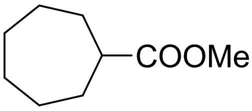
Methyl cyclopentanecarboxylate (**3a**)

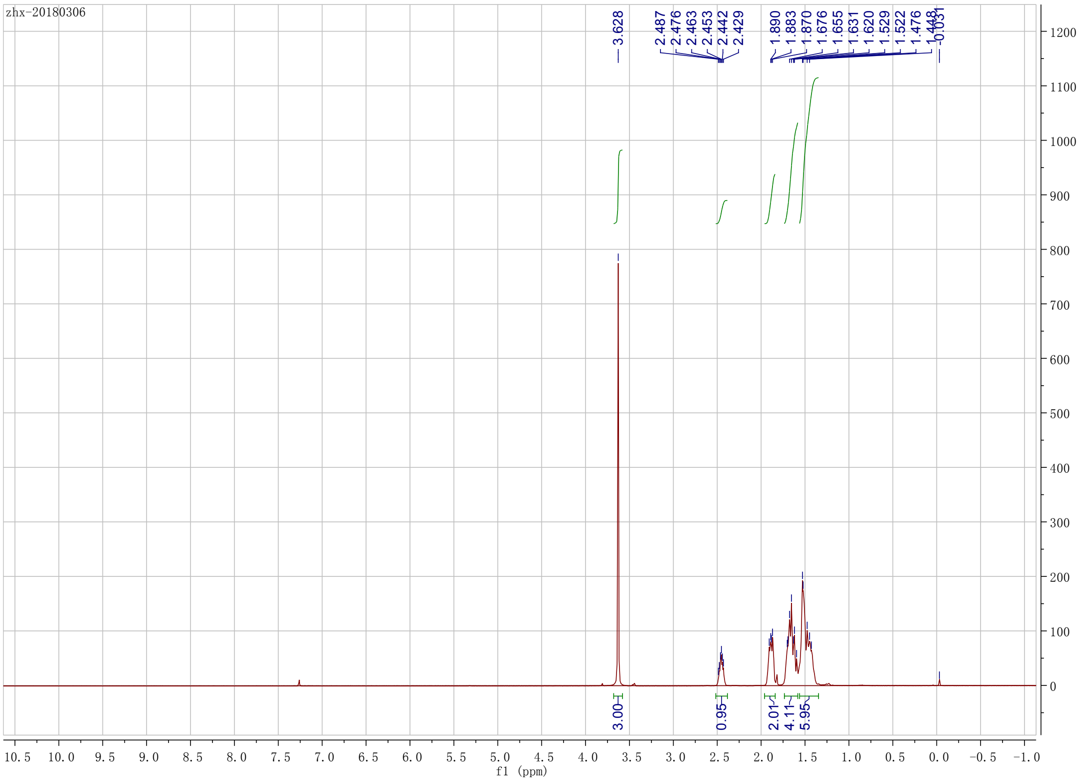


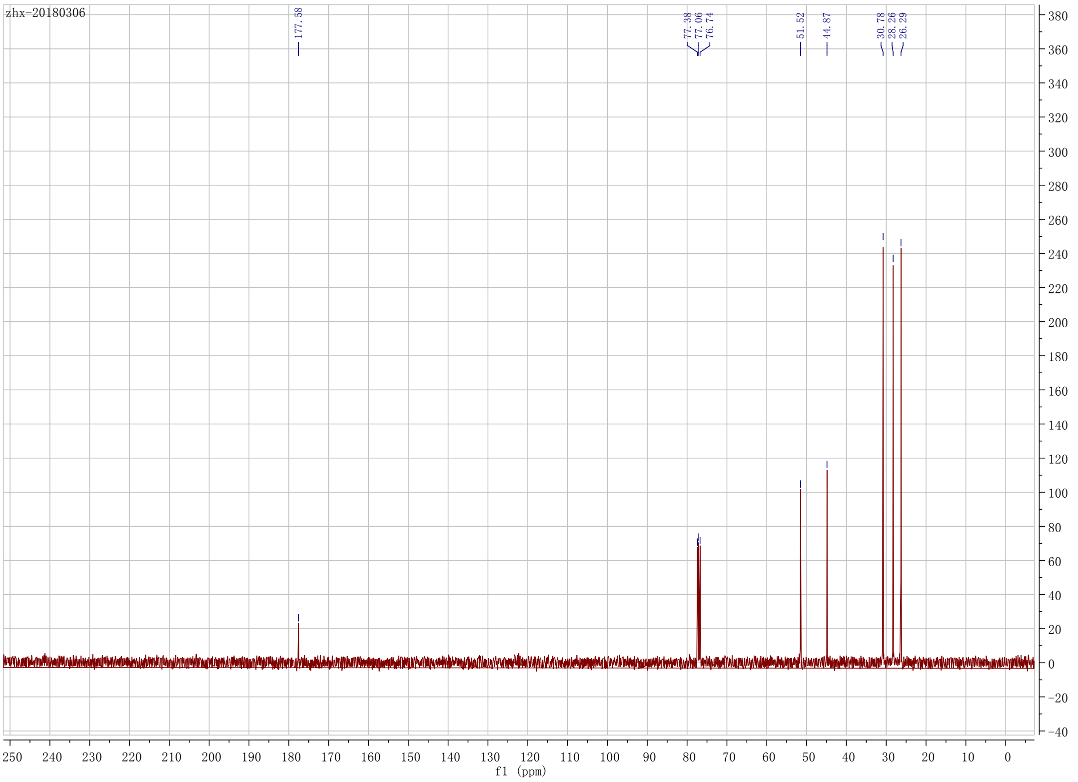




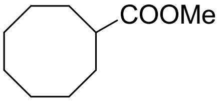
Methyl cycloheptanecarboxylate (**3b**)

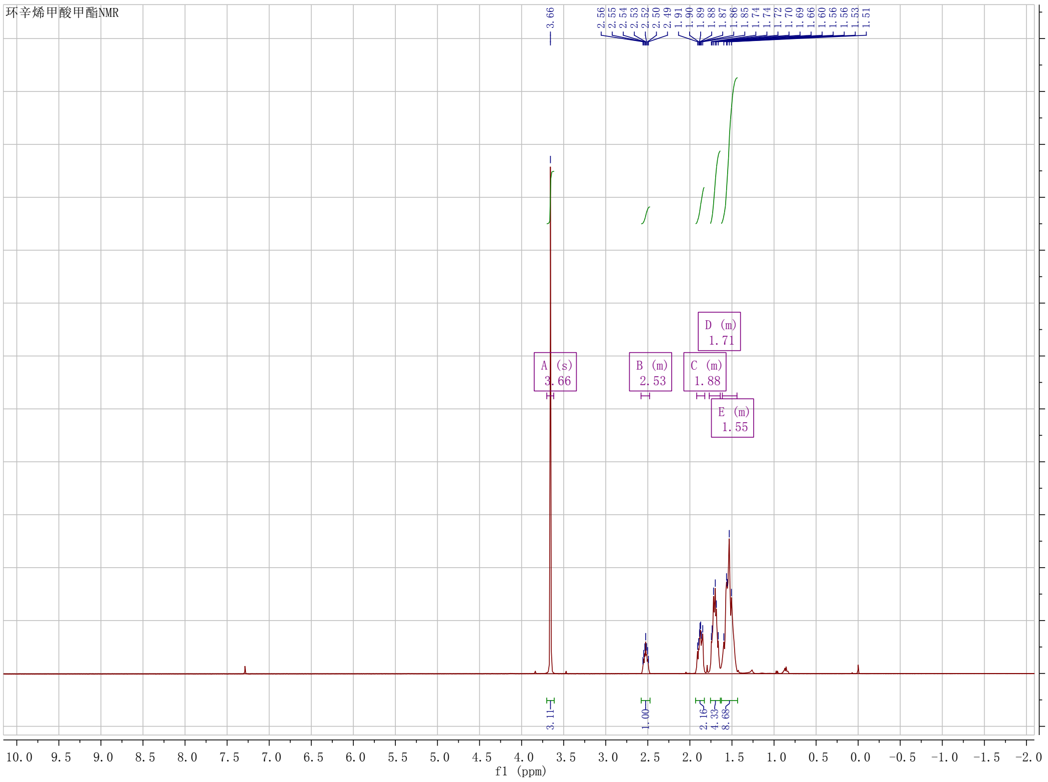


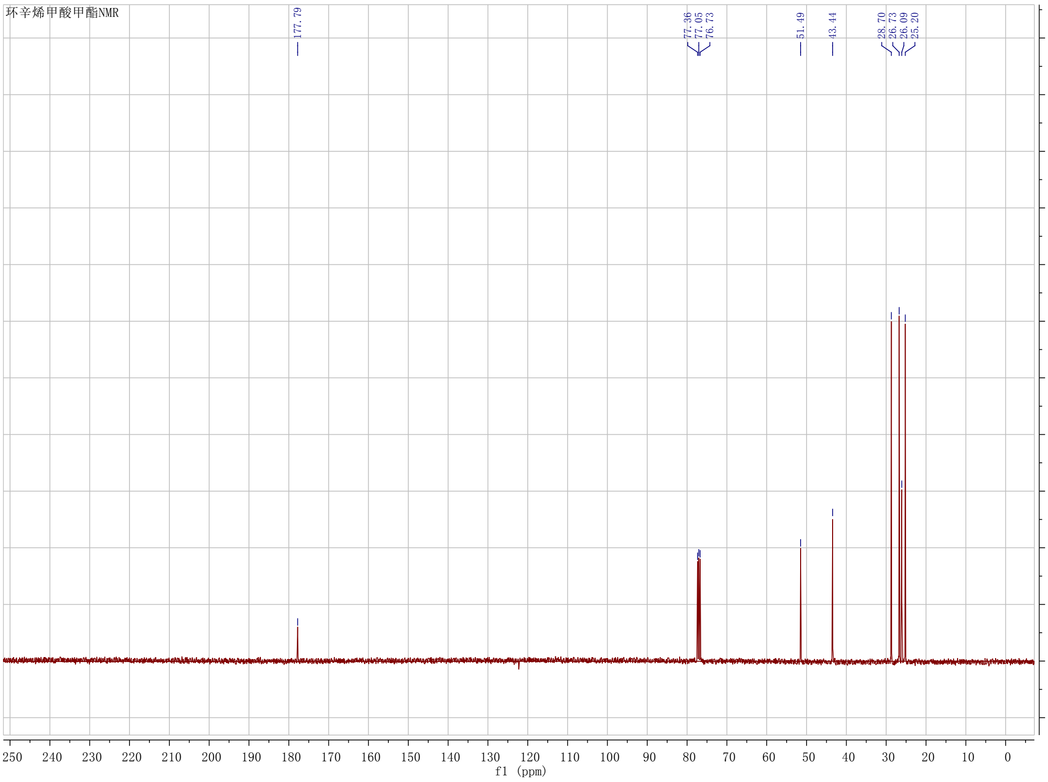




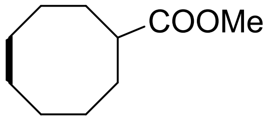
Methyl cyclooctanecarboxylate from cyclooctene (**3c**)

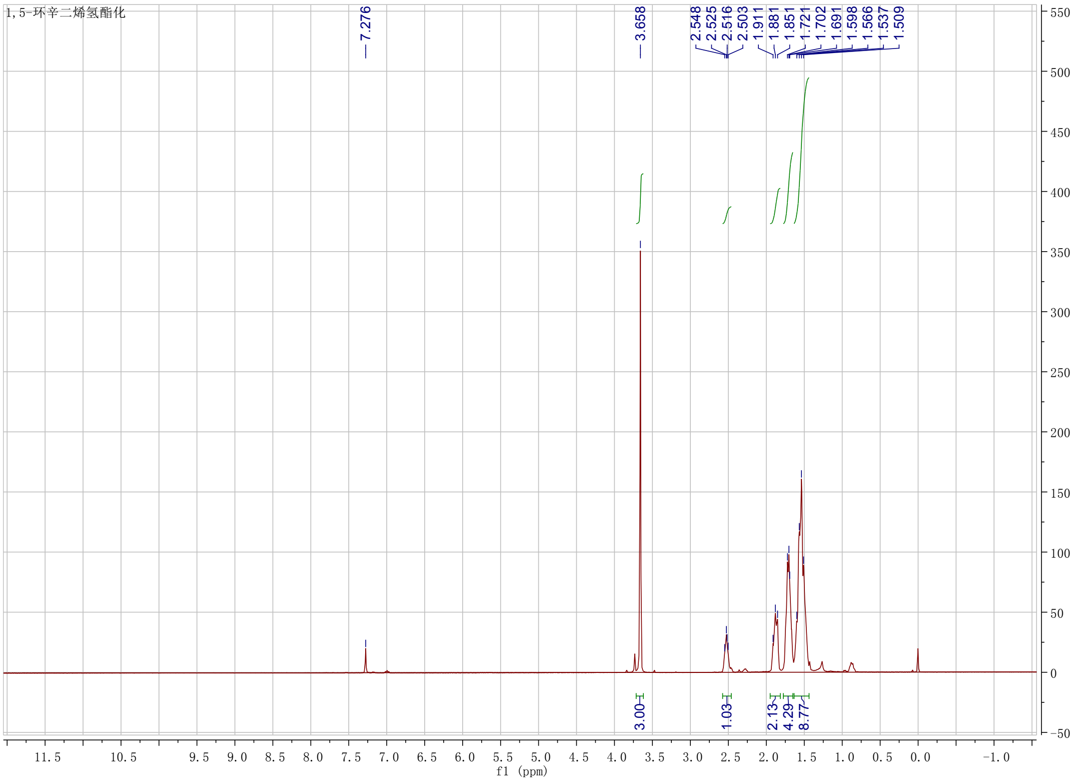


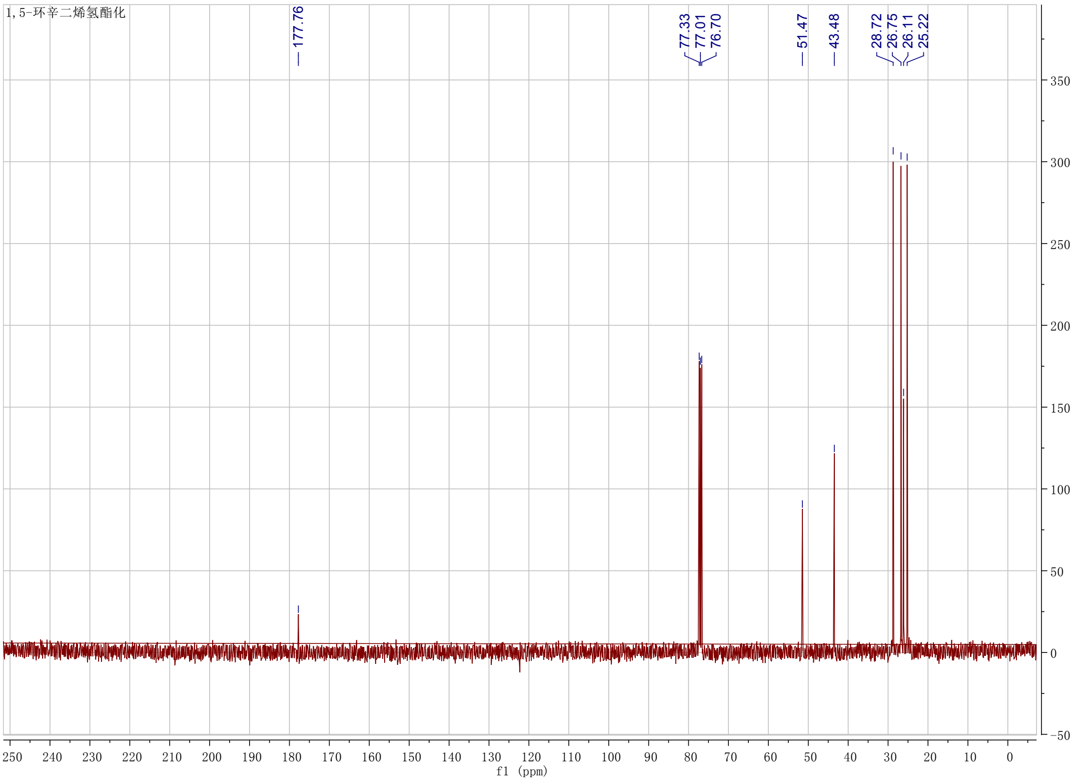




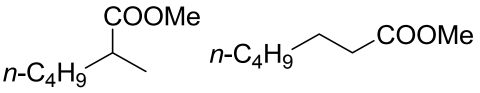
Methyl cyclooctanecarboxylate from 1,5-cyclooctdiene (**3m**)

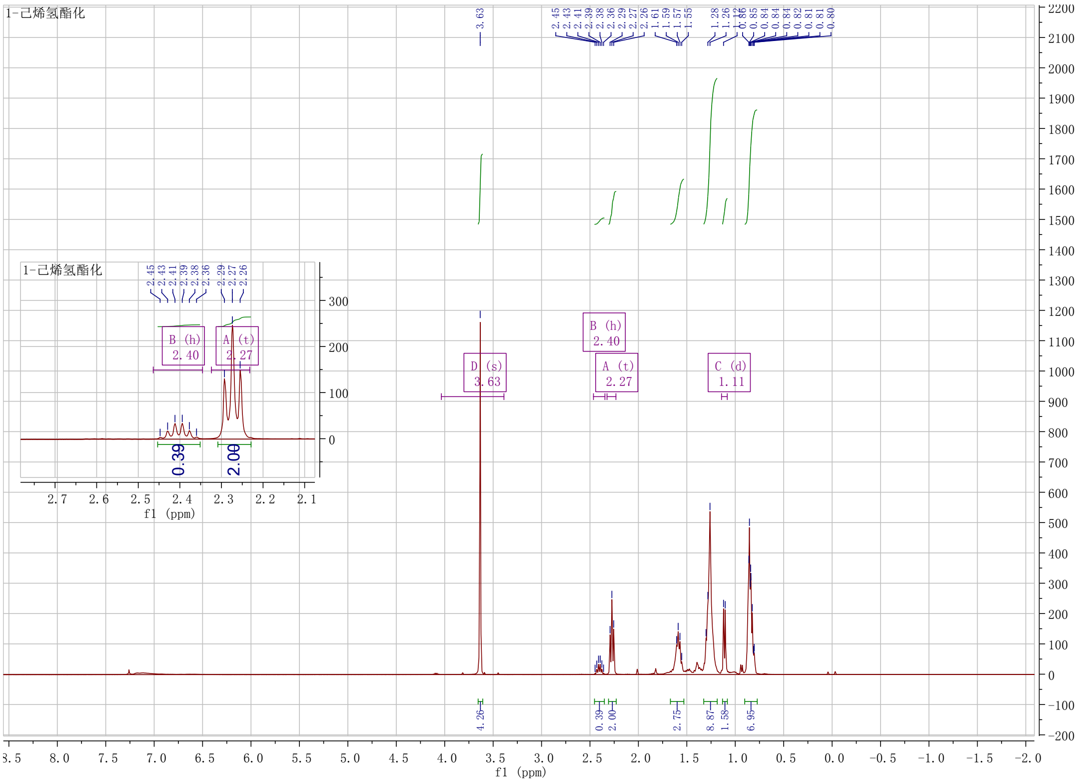


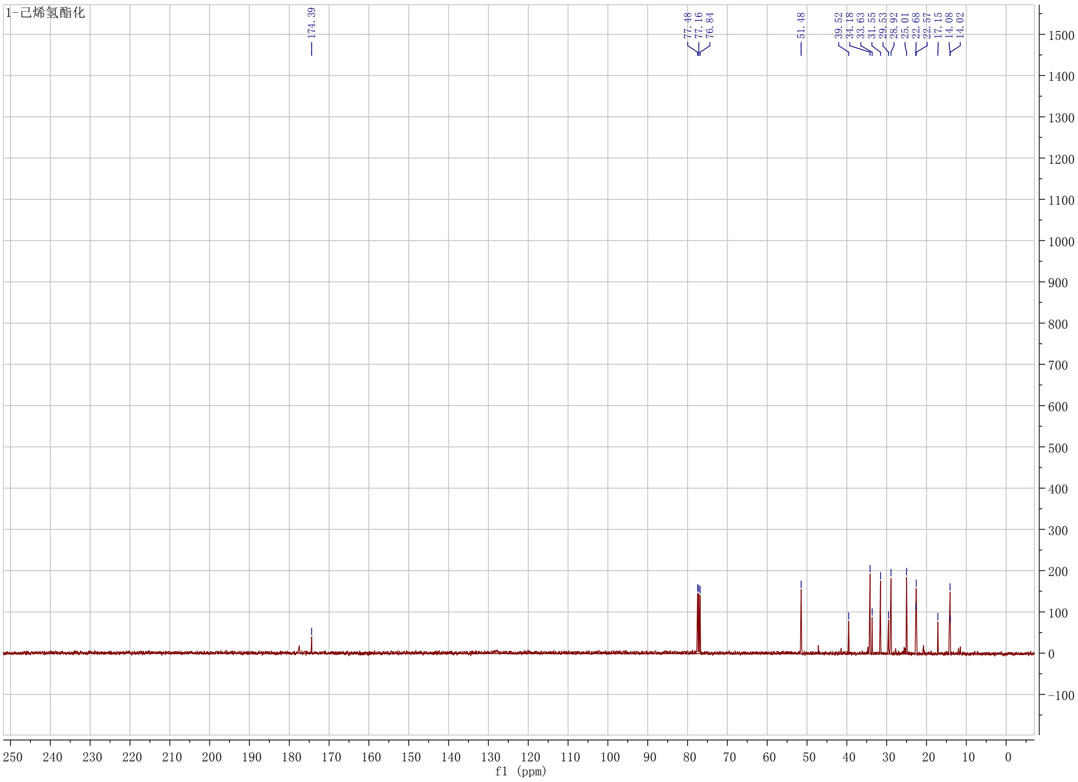




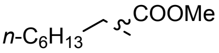
Mixture of methyl 2-methylhexanoate and methyl heptanoate (**3d**)

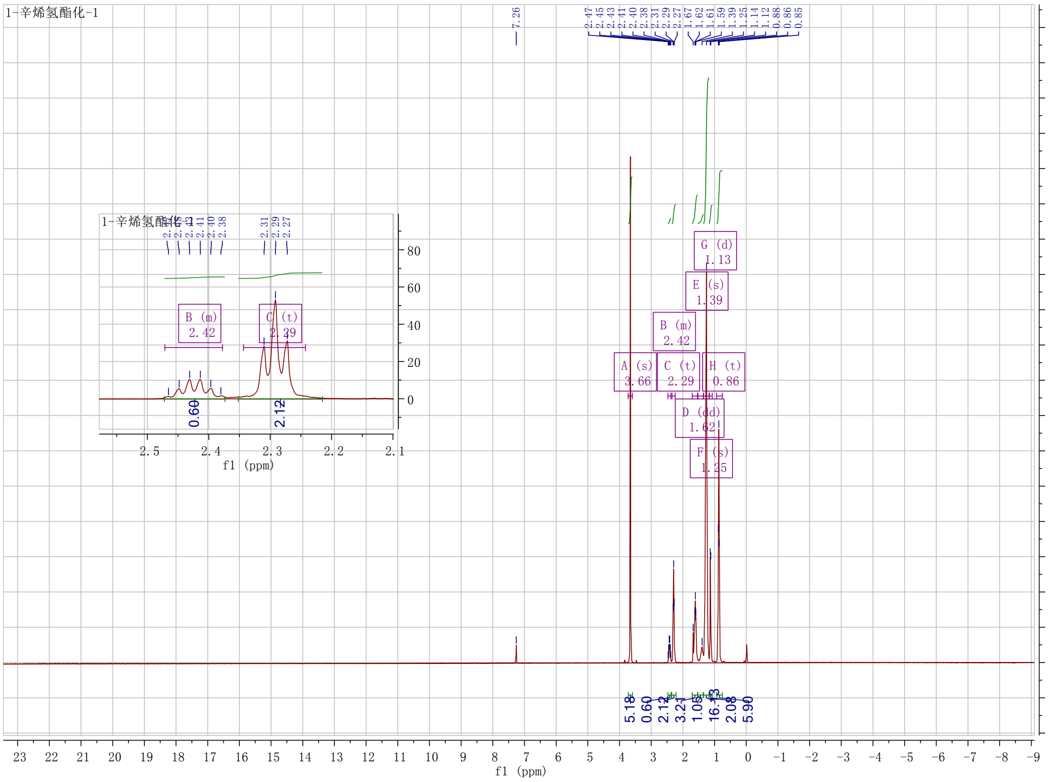


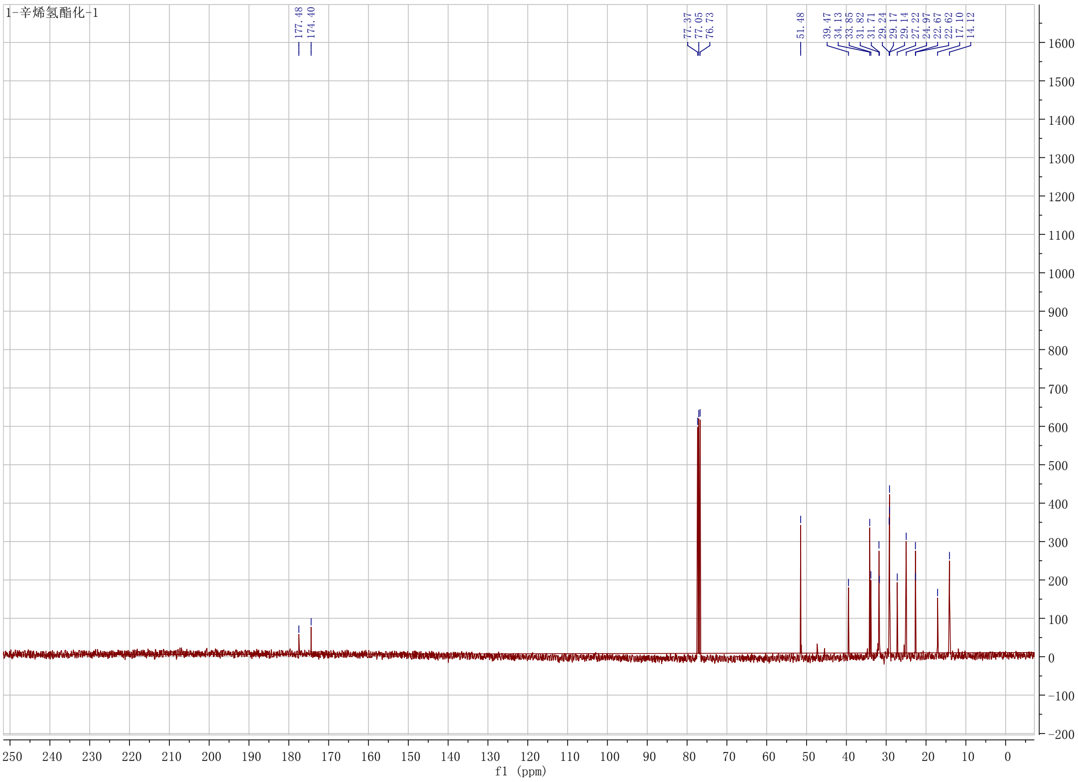




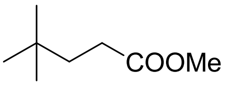
Mixture of methyl 2-methyloctanoate and methyl nonanoate from 1-ocatene (**3e**)

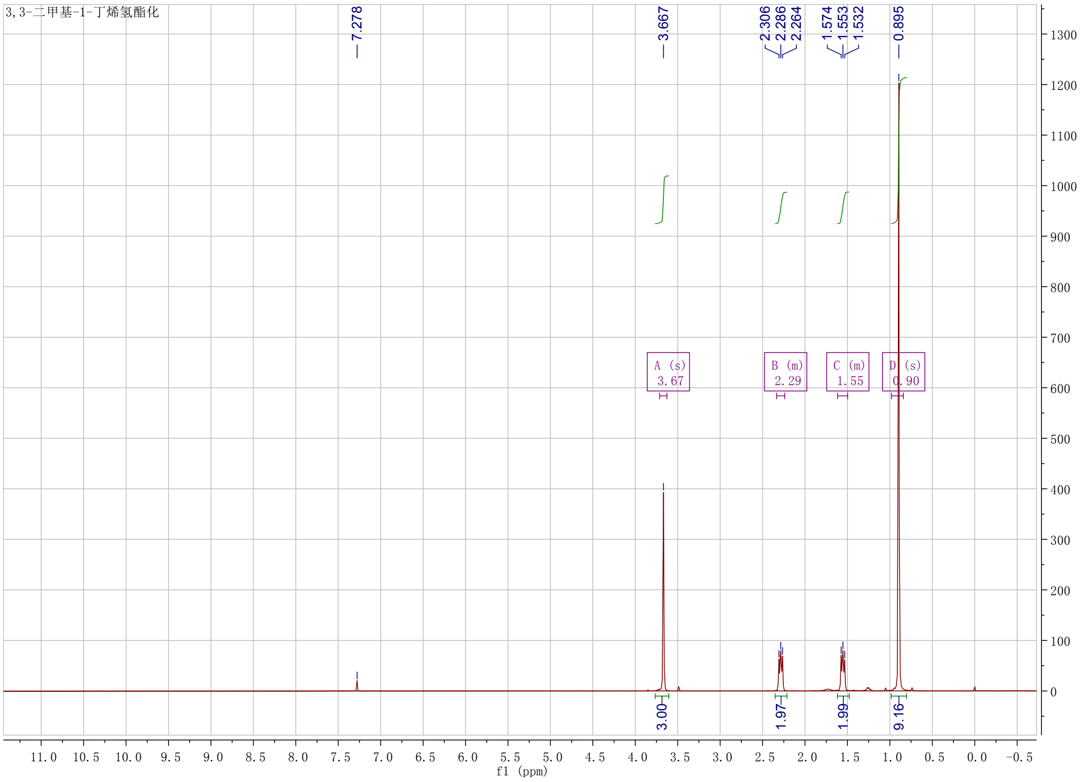


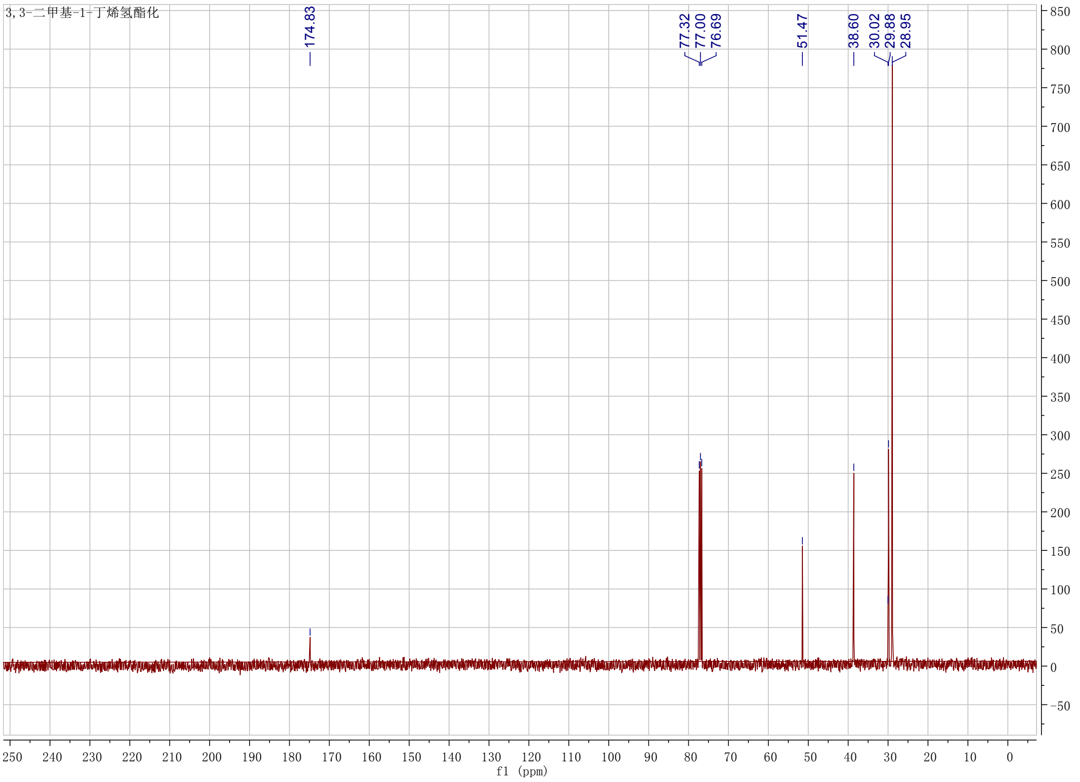




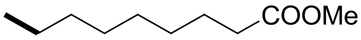
Methyl 4,4-dimethylpentanoate (**3f**)

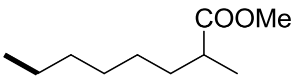


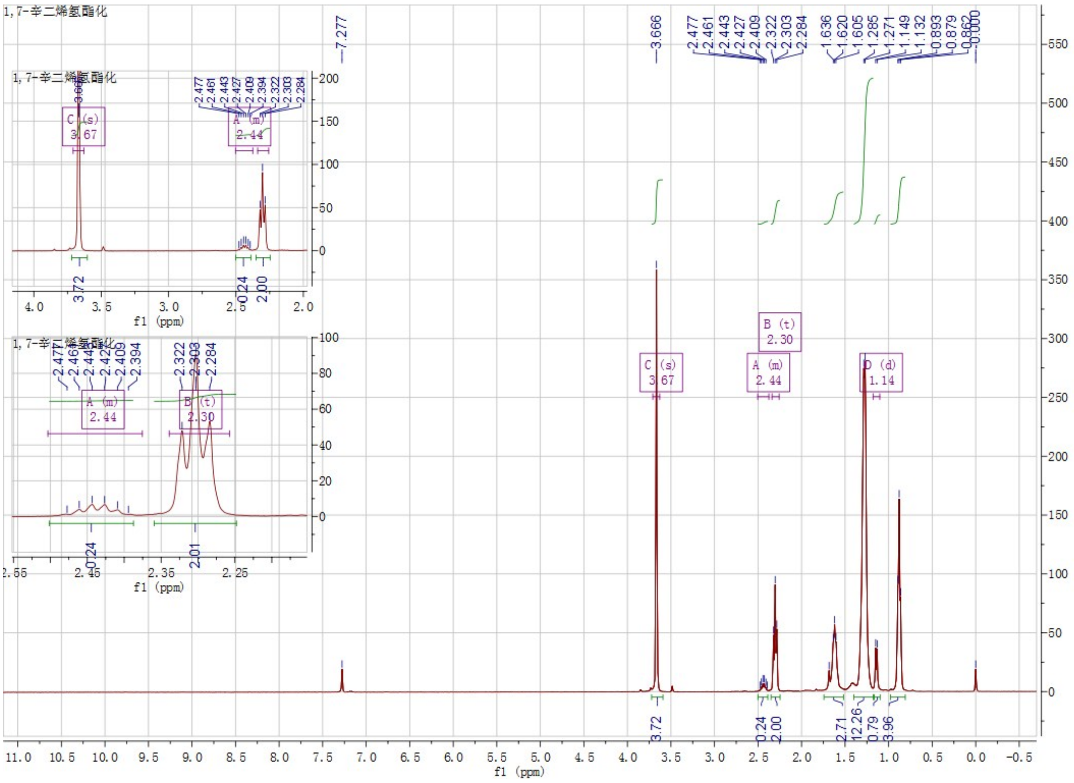


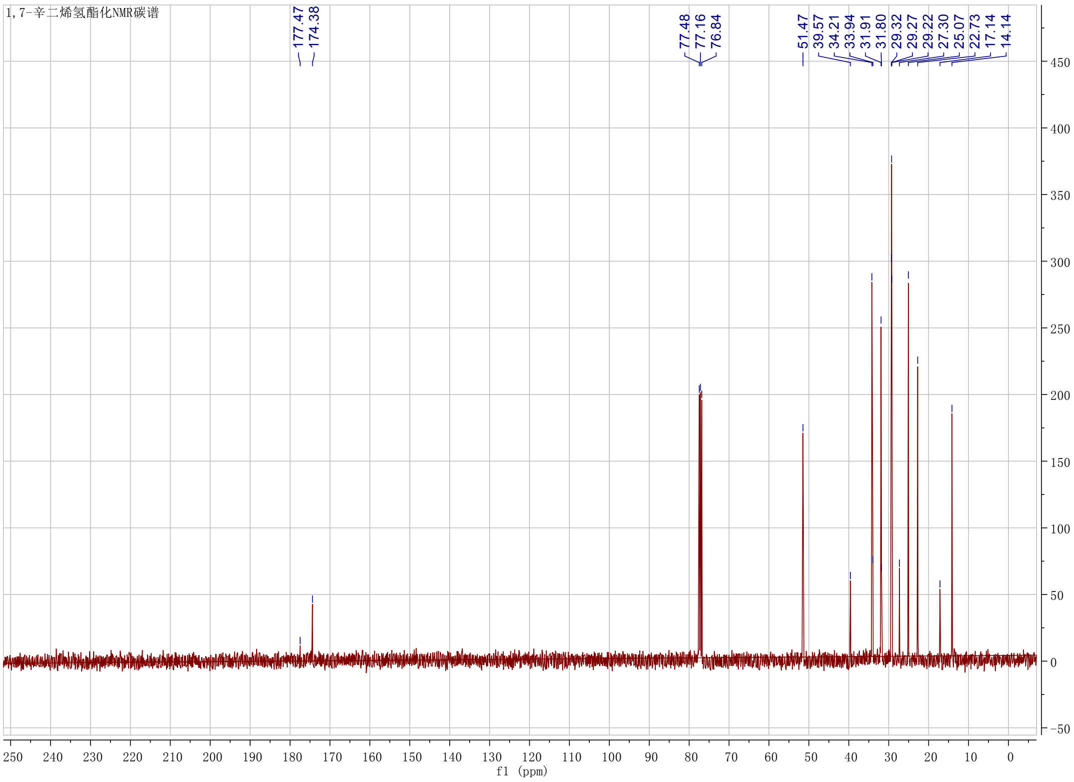


Mixture of methyl 2-methyloctanoate and methyl nonanoate from 1,7-octadiene (**3m**)

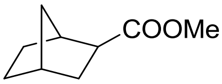


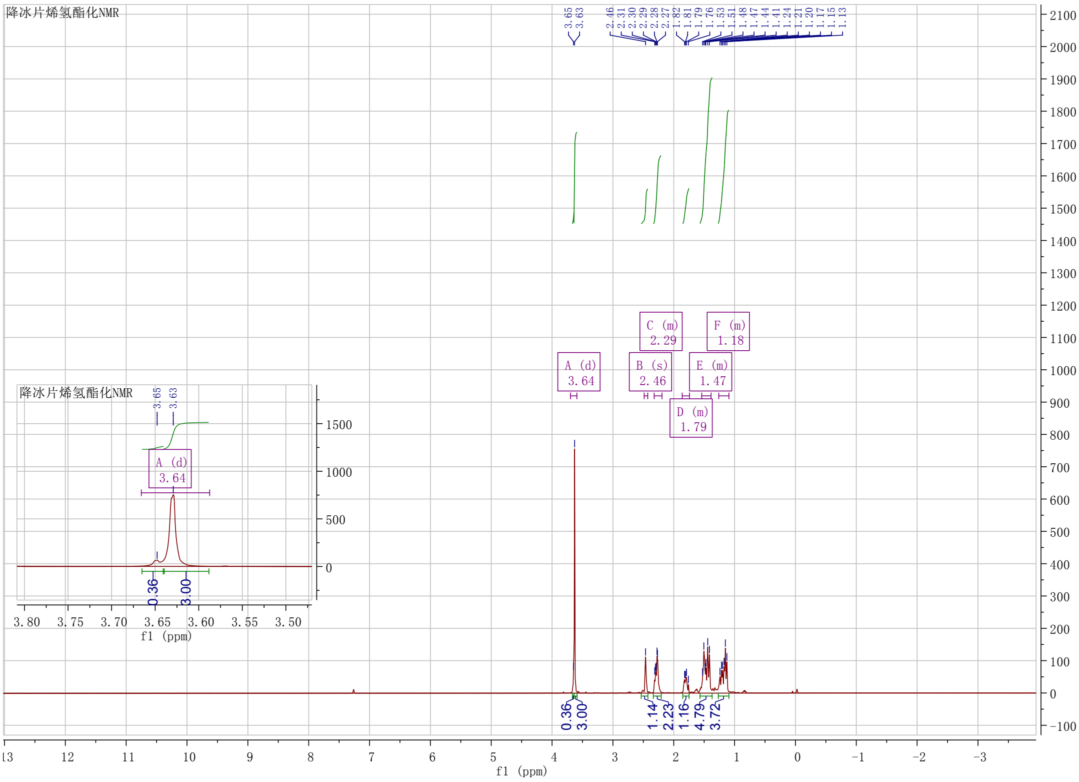


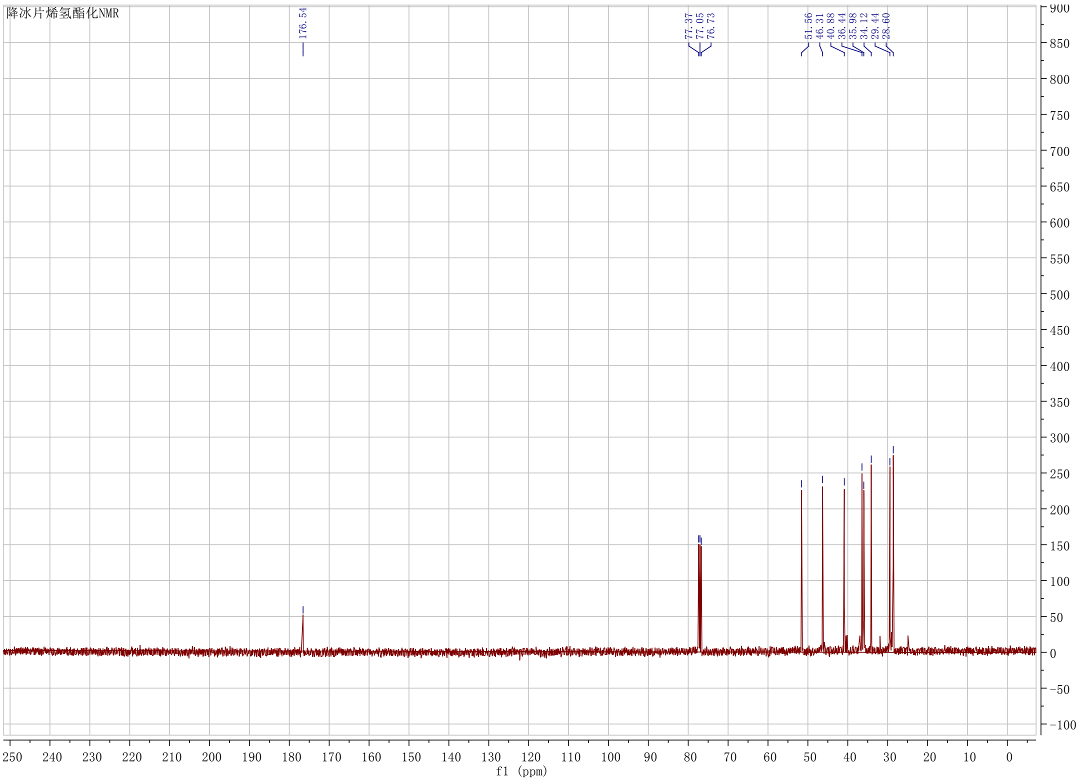




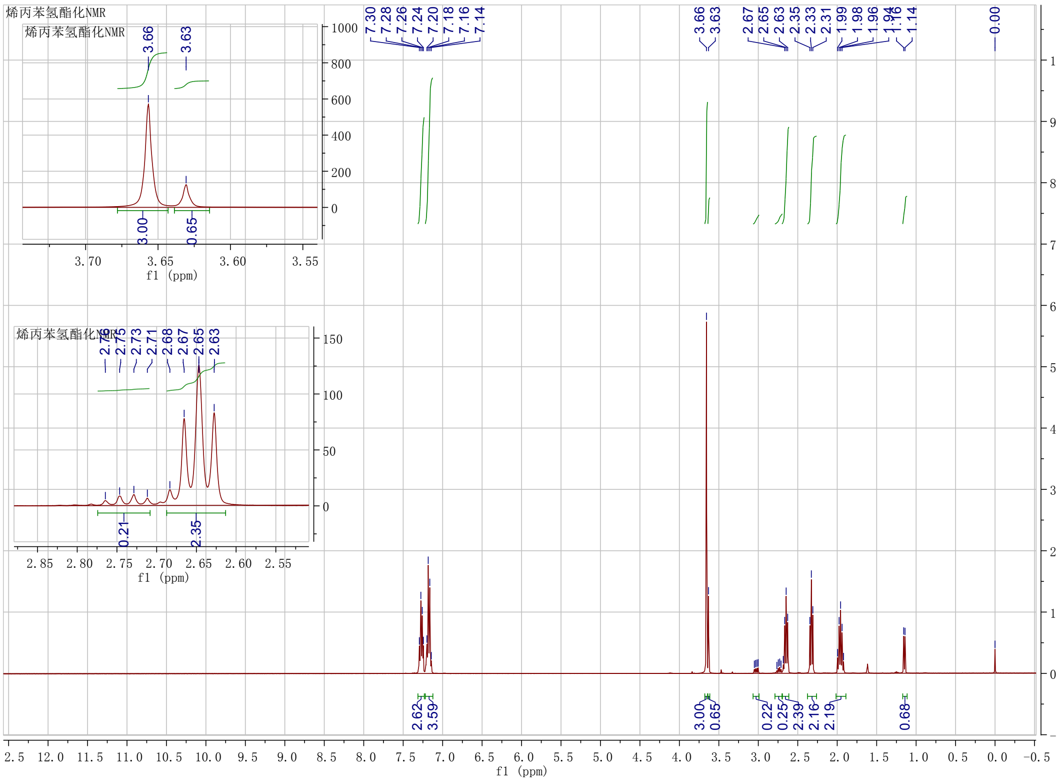
Methyl bicyclo[2.2.1]heptane-2-carboxylate (**3g**)

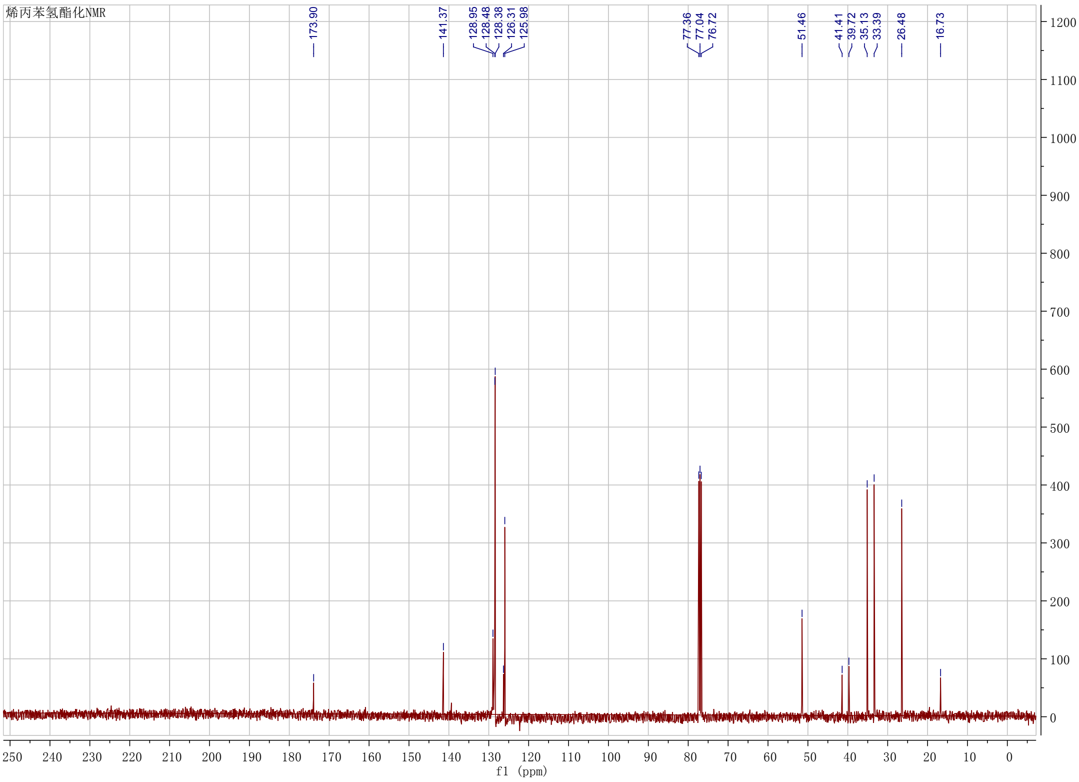




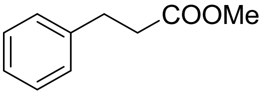


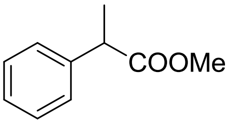
The mixture of methyl 4-phenylbutanoate and methyl 2-methyl-3-phenylpropanoate from allyl benzene (**3h**)

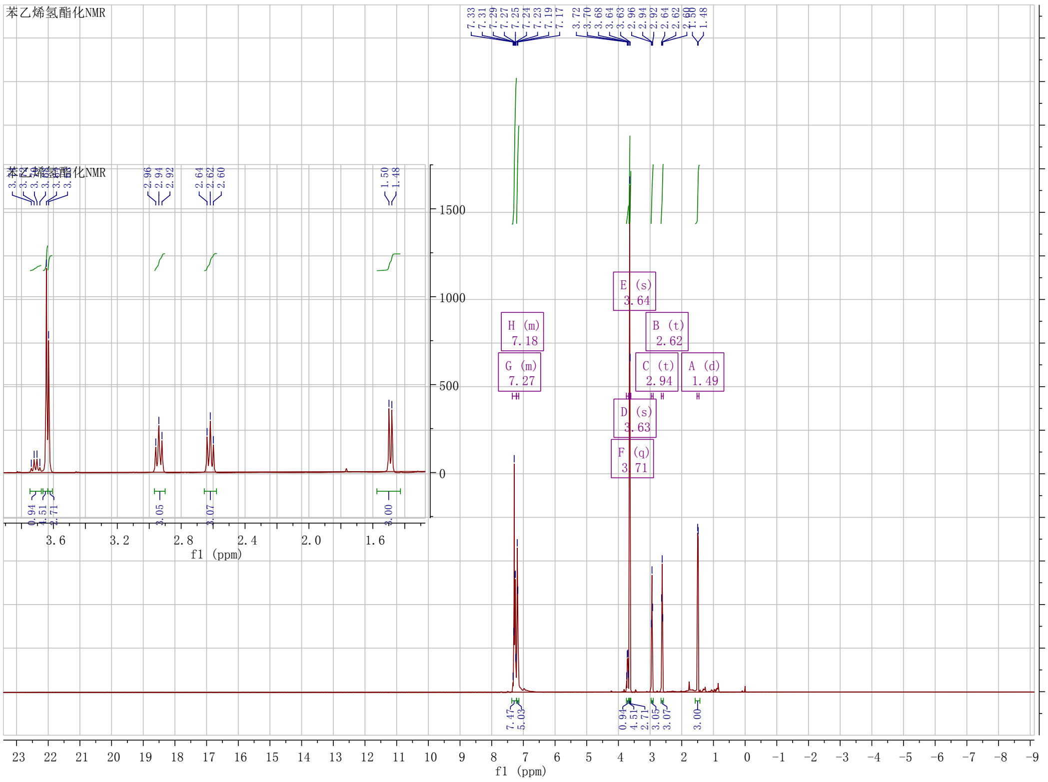




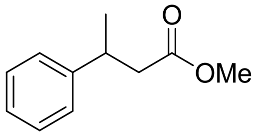
The mixture of linear product methyl 3-phenylpropanoate and branch product methyl 2-phenylpropanoate from styrene substrate (**3j**)

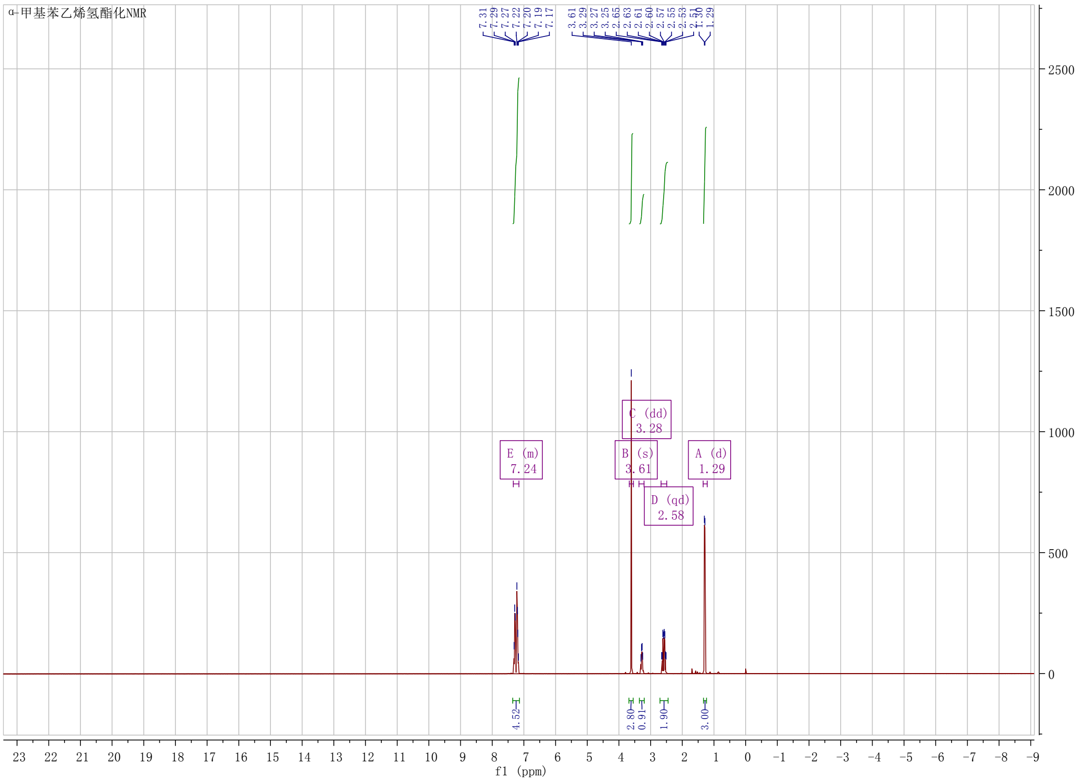


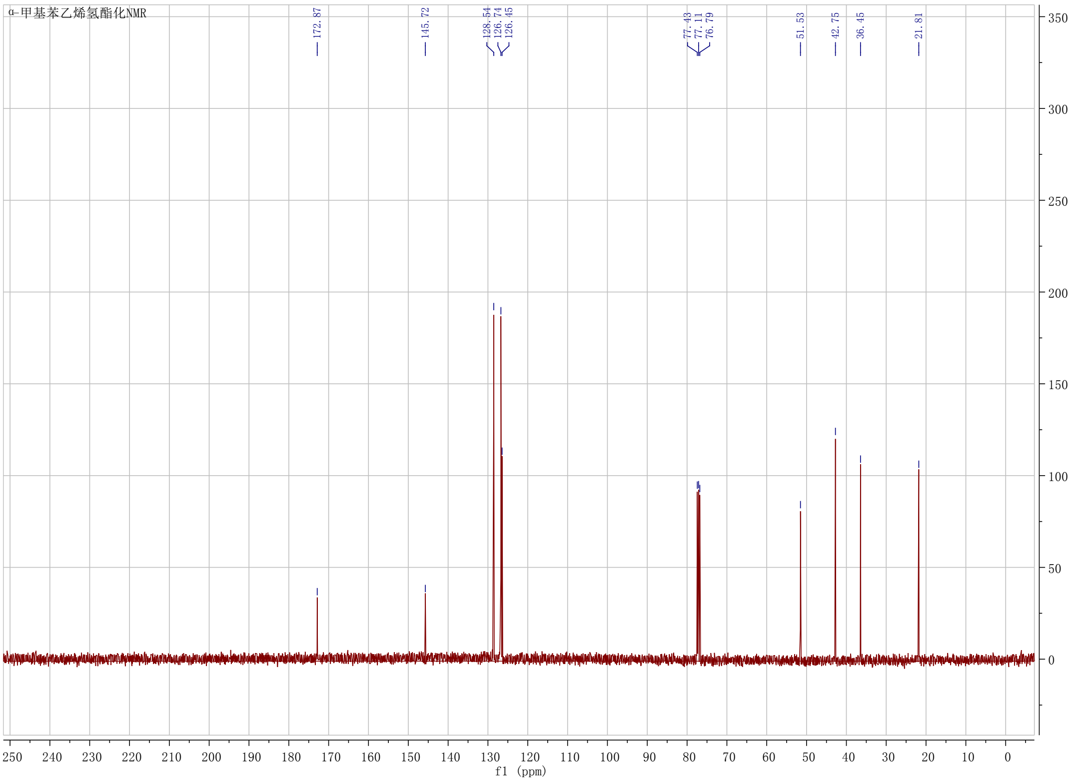




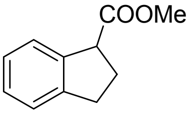
Methyl 3-phenylbutanoate (**3i**)

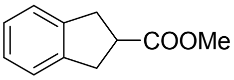


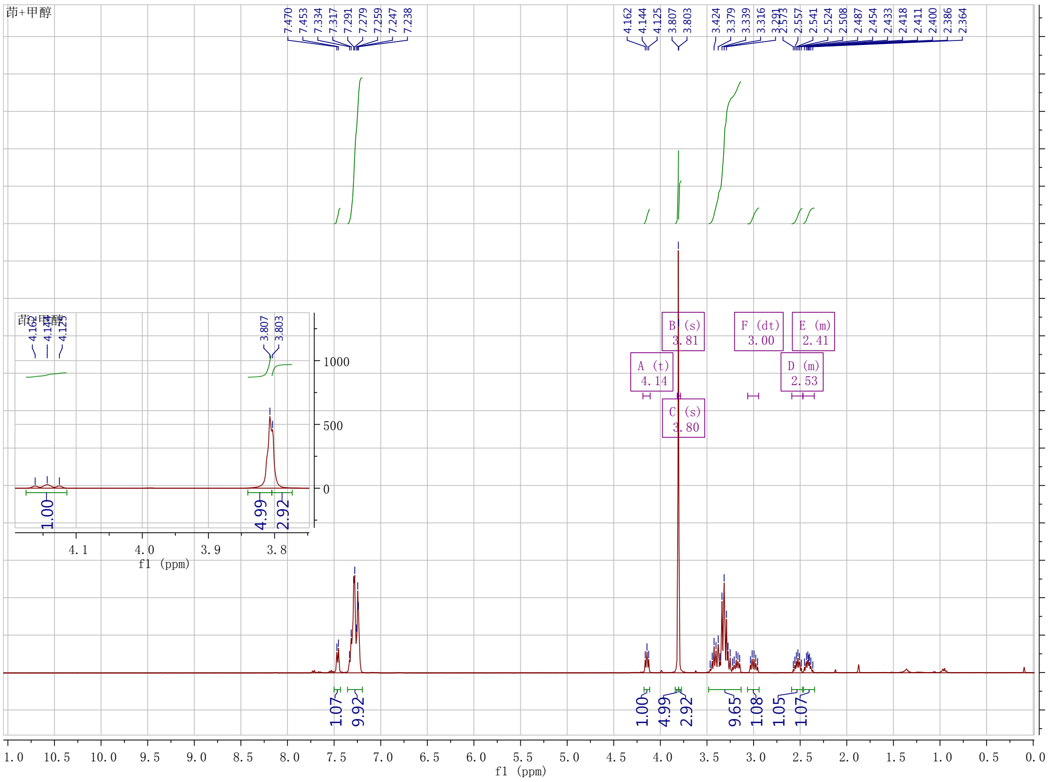


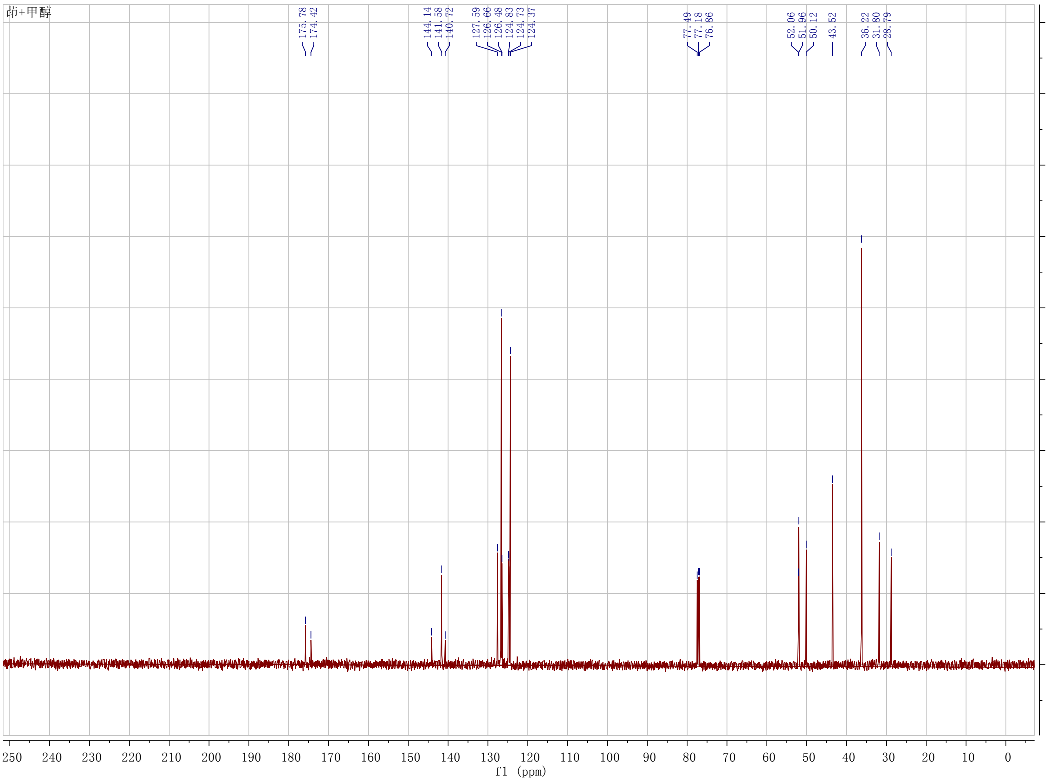


The mixture of methyl 2,3-dihydro-1*H*-indene-2-carboxylate and methyl 2,3-dihydro-1*H*-indene-1-carboxylate from 1*H*-indene substrate (**3k**)

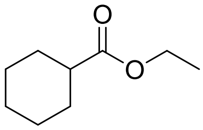


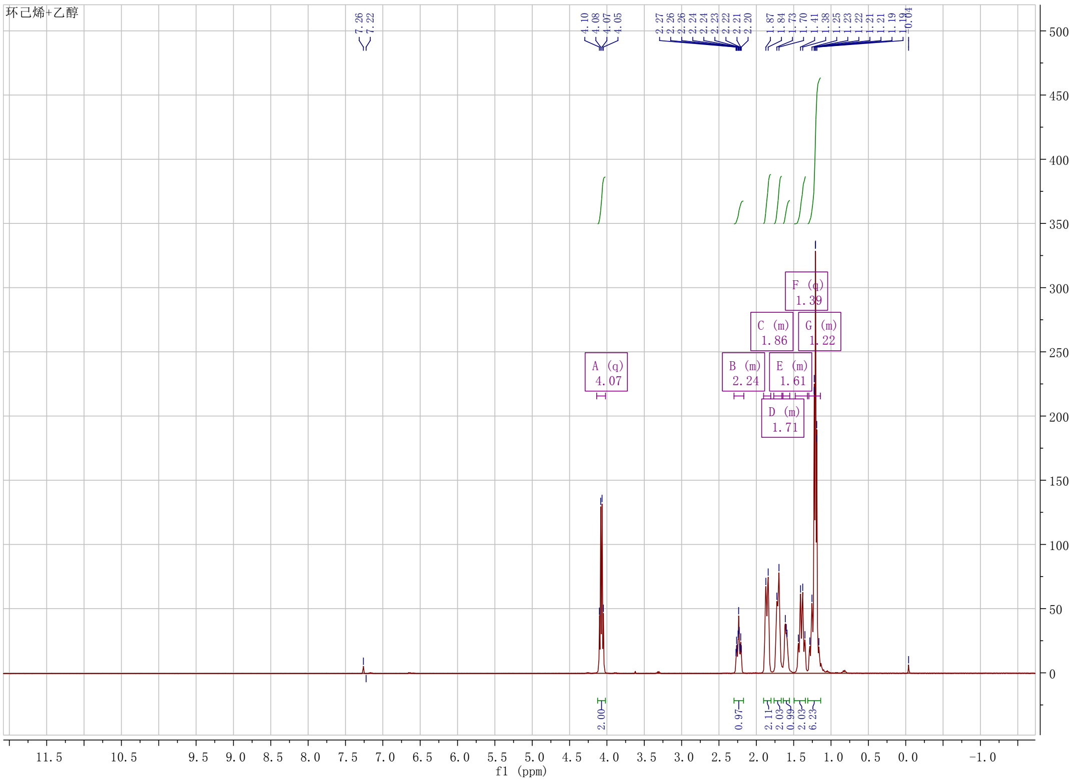


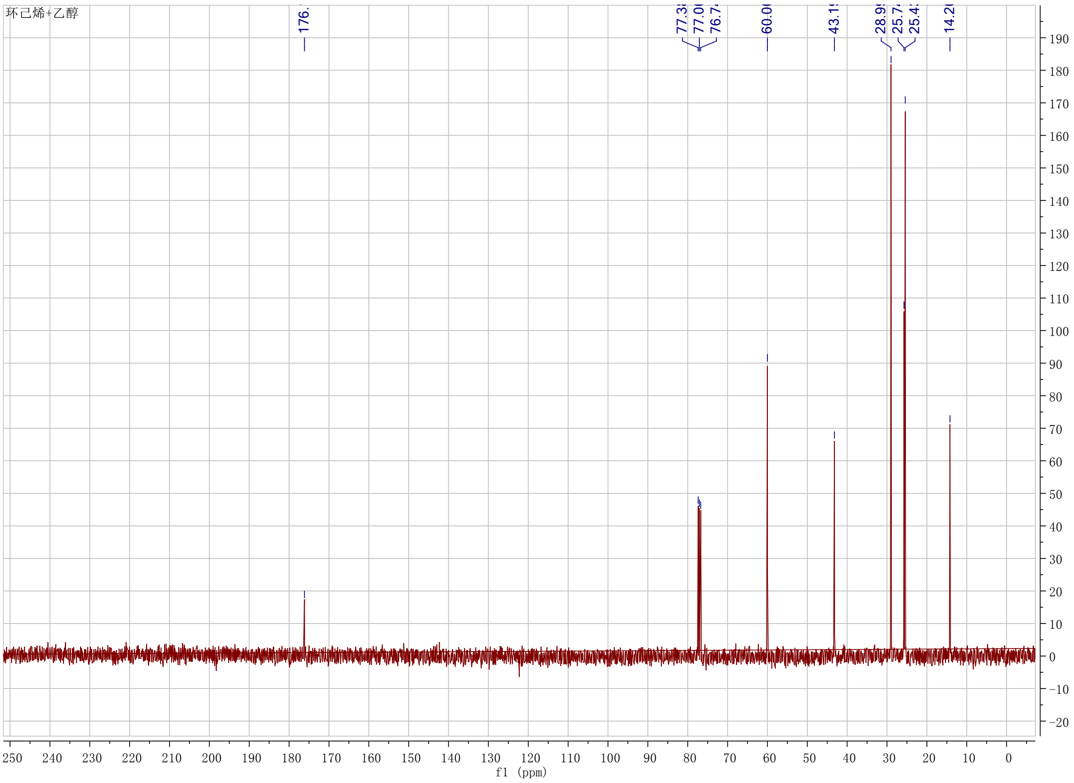




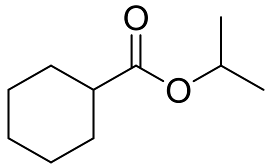
Ethyl cyclohexanecarboxylate (**3n**)

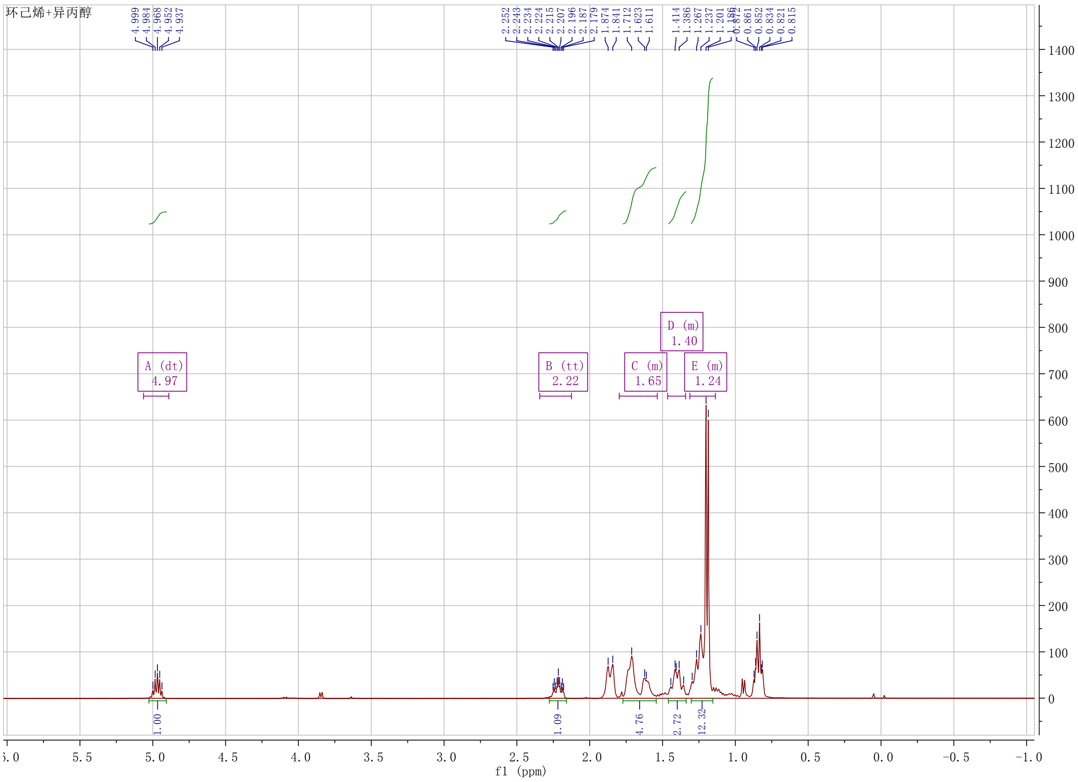






Isopropyl cyclohexanecarboxylate (**3o**)





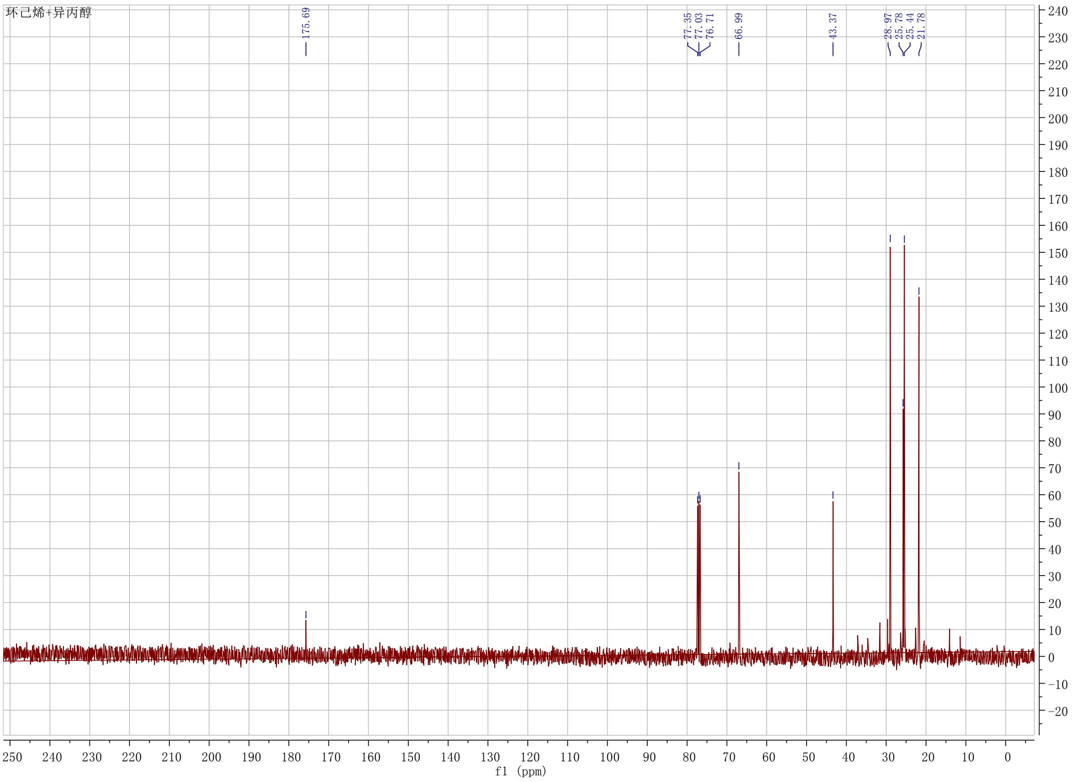
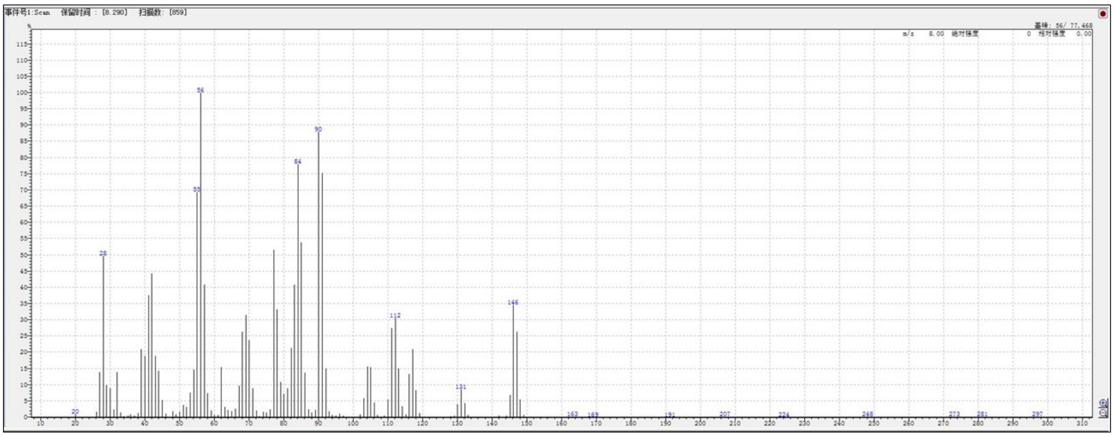


Figure S5 MS (EI) of deuterium-sbustituted cyclohexanecarboxylate produced from cyclohexene and CD_3O_D.



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[1] (a) S. Werner, N. Szesni, A. Bittermann, M. J. Schneider, P Härter, M Haumann, P Wasserscheid, *Appl. Catal. A Gen.* **2010**, *377*, 70-75; (b) M. J. Cleare, W. P. Griffith, *J. Chem. Soc. A* **1969**, 372-380; (b) J. R. Zoeller, *Inorg. Chem.* **1986**, *25*, 3933-3937; (c) N. Lugan, G. Lavigne, J. M. Soulié, S. Fabre, P. Kalck, J. Y. Saillard, J. F. Halet, *Organometallics* **1995**, *14*, 1712-1731.

[2] M. J. Frisch *et al.* Gaussian 09, revision A.01; Gaussian, Inc., Wallingford, CT, 2009.

[3] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241.

[4] (a) D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123-141. (b) L. E. Roy, P. J. Hay, R. L. Martin, *J. Chem. Theory Comput.* **2008**, *4*, 1029-1031.