

SUPPORTING INFORMATION

Ligand-Controlled Chemoselective Nickel-Catalyzed Cross-Electrophile Coupling of Cyclic Anhydrides with Alkyl Bromides

Tingzhi Lin,^a Junlong Jia,^{†,a} Yu Wu,^{†,b} Ziheng Li,^{†,a} Xueying Gao,^a Junyu Ma,^a Mengjiao Wei,^a Yifei Song,^a Zifan Wang,^a Xinrui Yuan,^a Patrick J. Walsh^{*,b} and Jianyou Mao^{*,a}

^aInstitute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, 30 South Puzhu Road, Nanjing 211816, China.

E-mail: ias_jymao@njtech.edu.cn

^bRoy and Diana Vagelos Laboratories, Penn/Merck Laboratory for High-Throughput Experimentation, University of Pennsylvania, Department of Chemistry, 231 South 34th Street, Philadelphia, Pennsylvania 19104, USA.

E-mail: pwalsh@sas.upenn.edu

[†]These authors contributed equally.

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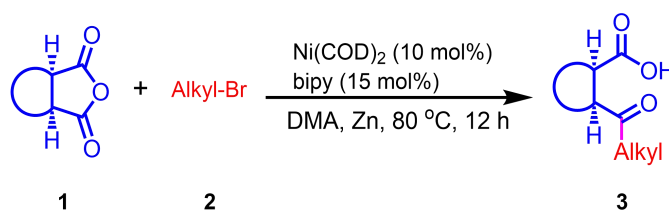
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1. General Information

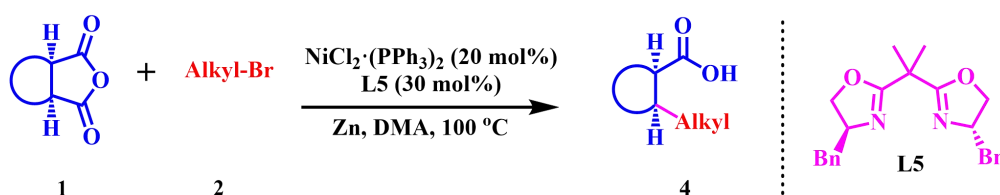
All reactions were carried out under an atmosphere of dry nitrogen. Anhydrous DMA was purchased from J&K and used without further purification. Unless otherwise stated, reagents were commercially available and used as purchased. Chemicals were obtained from Sigma-Aldrich, Acros, Innochem, Energy Chemical, TCI China or Alfa Aesar. The progress of the reactions was monitored by thin-layer chromatography using TLC plates and visualized by bromocresol green solution. Flash chromatography was performed with Qingdao Haiyang flash silica gel (200–300 mesh). The NMR spectra were obtained using a Bruker 400 MHz Fourier-transform NMR spectrometer. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz. The infrared spectra were obtained with KBr plates by using a IS10 FT-IR Spectrometer (ThermoFisher Corporation). High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QToF) using electrospray ionization (ESI) in positive or negative mode. Melting points were measured using a WRS-1C Melt-Temp apparatus and were uncorrected.

2. General Procedure A for the Synthesis of γ -Keto Acids



General Procedure A: To an oven-dried microwave vial (10 mL) equipped with a stir bar (10 × 5 mm) was added $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol) under nitrogen atmosphere inside a glove box at 25 °C. Next, 0.22 mL of dry DMA was added via syringe to give a purple solution. After the catalyst/ligand solution was stirred for 1 h at 25 °C inside the glove box, Zn powder (39.2 mg, 0.6 mmol, 2.0 equiv) was added to the reaction vial followed by the bicyclic anhydride (0.45 mmol, 1.5 equiv) and alkyl bromide (0.3 mmol, 1.0 equiv). The microwave vial was sealed with a cap containing a rubber septum and removed from the glove box. The reaction mixture was stirred (1000 rpm) at 80 °C for 12 h. The resulting dark brown solution was then quenched by addition of 5 drops water via syringe and then the vial opened to air. The reaction mixture was passed through a short pad of silica gel and rinsed with 5 mL of ethyl acetate to afford a dark brown solution. The solvent was removed by rotary evaporator. The crude residue was purified by flash column chromatography to yield the corresponding product.

3. General Procedure B for the Synthesis of β -Alkylated Acid Derivatives

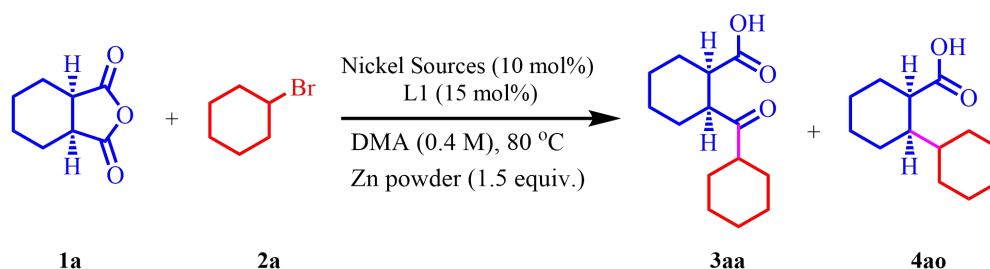


General Procedure B: To an oven-dried microwave vial (10 mL) equipped with a stir bar (10 × 5 mm)

was added NiCl₂·(PPh₃)₂ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol) under a nitrogen atmosphere inside a glove box at 25 °C. Next, 0.6 mL of dry DMA was added via syringe to give a purple solution. After the catalyst/ligand solution was stirred for 1 h at 25 °C inside the glove box, Zn powder (39.2 mg, 0.6 mmol, 2.0 equiv) was added to the reaction vial followed by the bicyclic anhydride (0.3 mmol, 1 equiv) and alkyl bromide (0.6 mmol, 2.0 equiv). The microwave vial was sealed with a cap containing a rubber septum and removed from the glove box. The reaction mixture was stirred (1000 rpm) at 100 °C for 24 h. The resulting dark brown solution was then quenched by addition of 5 drops water via syringe and then the vial opened to air. The reaction mixture was passed through a short pad of silica gel and rinsed with 5 mL of ethyl acetate to afford a dark brown solution. The solvent was removed by rotary evaporator. The crude residue was purified by flash column chromatography to yield the corresponding product.

4. Systematic Study of Reaction Conditions

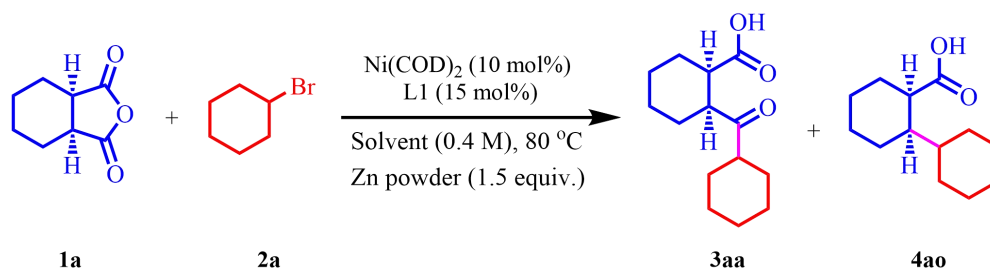
4.1 Table S1: Optimization of the nickel sources for the synthesis of γ -keto acids



Entry	Ni Sources	Yield (%) ^a (3aa : 4ao)
1	Ni(COD) ₂	22:0
2	NiBr ₂	7:0
3	NiI ₂	16:0
4	NiBr ₂ ·DME	18:0
5	Ni(acac) ₂	8:0
6	NiBr ₂ ·glyme	17:0
7	Ni(ClO ₄) ₂ ·6H ₂ O	0:0
8	NiF ₂	0:0
9	NiCl ₂	0:0
10	NiCl ₂ ·(PPh ₃) ₂	19:0

^aIsolated yields.

4.2 Table S2: Optimization of the solvent for the synthesis of γ -keto acids

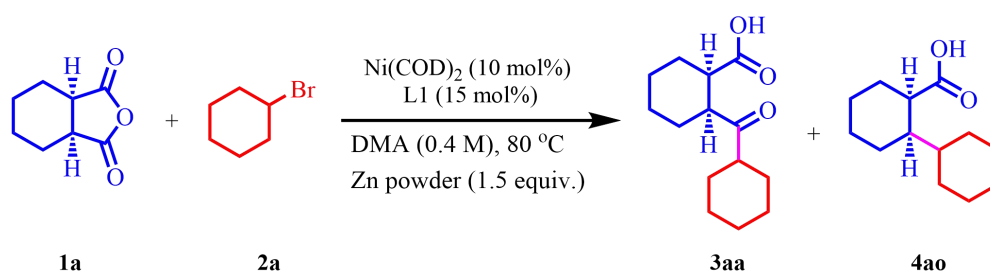


Entry	Solvents	Yield (%) ^a (3aa : 4ao)
-------	----------	--

1	DMA	22:0
2	DMF	trace
3	DMSO	trace
4	THF	trace
5	Dioxane	trace
6	CH ₃ CN	trace
7	Toluene	0
8	2-MeTHF	0
9	TBME	0
10	CPME	0

^aIsolated yields. Trace means the yield <5%.

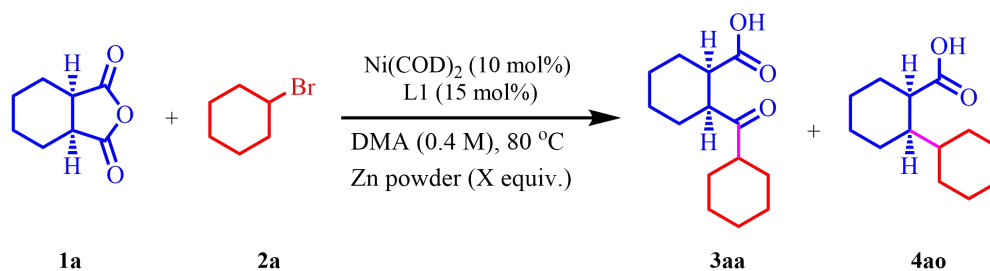
4.3 Table S3: Optimization of the ratio of 1a to 2a for the synthesis of γ -keto acids



Entry	1a:2a	Yield (%) ^a (3aa:4ao)
1	3:1	27:0
2	2:1	43:0
3	1.5:1	52:0
4	1:1	45:0
5	1:1.5	23:0
6	1:2	trace
7	1:3	trace

^aIsolated yields. Trace means the yield <5%.

4.4 Table S4: Optimization of the ratio of Zn powder for the synthesis of γ -keto acids

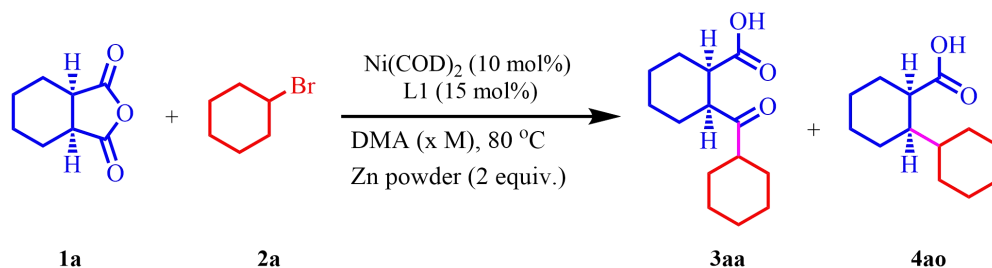


Entry	Zn powder (X equiv.)	Yield (%) ^a (3aa:4ao)
1	0.5	11:0
2	1	18:0
3	1.5	43:0
4	2	56:0

5	2.5	54:0
6	3	48:0
7	3.5	45:0

^aIsolated yields.

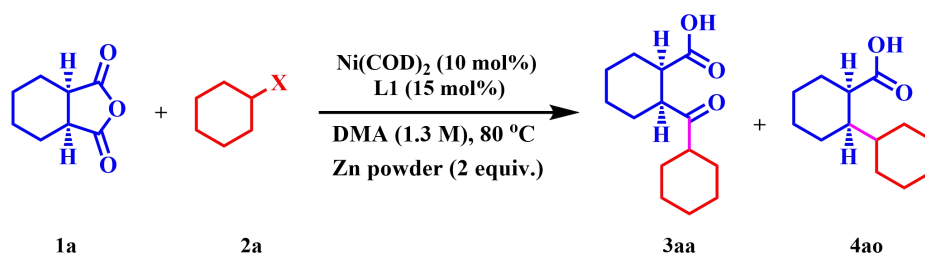
4.5 Table S5: Optimization of the reaction concentration for the synthesis of γ -keto acids



Entry	DMA (x M)	Yield (%) ^a (3aa:4ao)
1	0.2	47:0
2	0.4	56:0
3	0.5	58:0
4	1.0	72:0
5	1.3	78:0
6	2.0	66:0

^aIsolated yields.

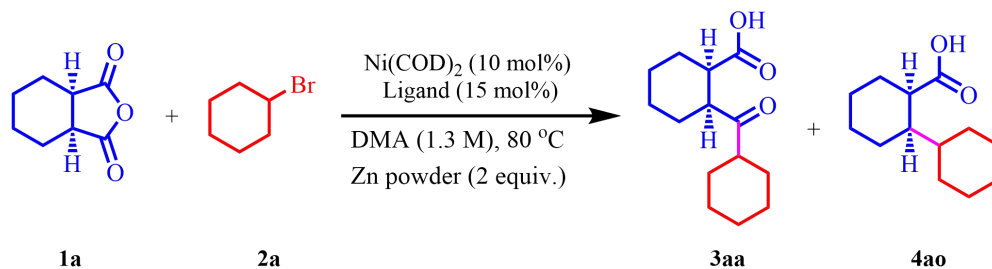
4.6 Table S6: Optimization of different electrophilic reagents



Entry	X	Yield ^a (%) (3aa:4ao)
1	Cl	46:0
2	Br	78:0
3	I	72:0

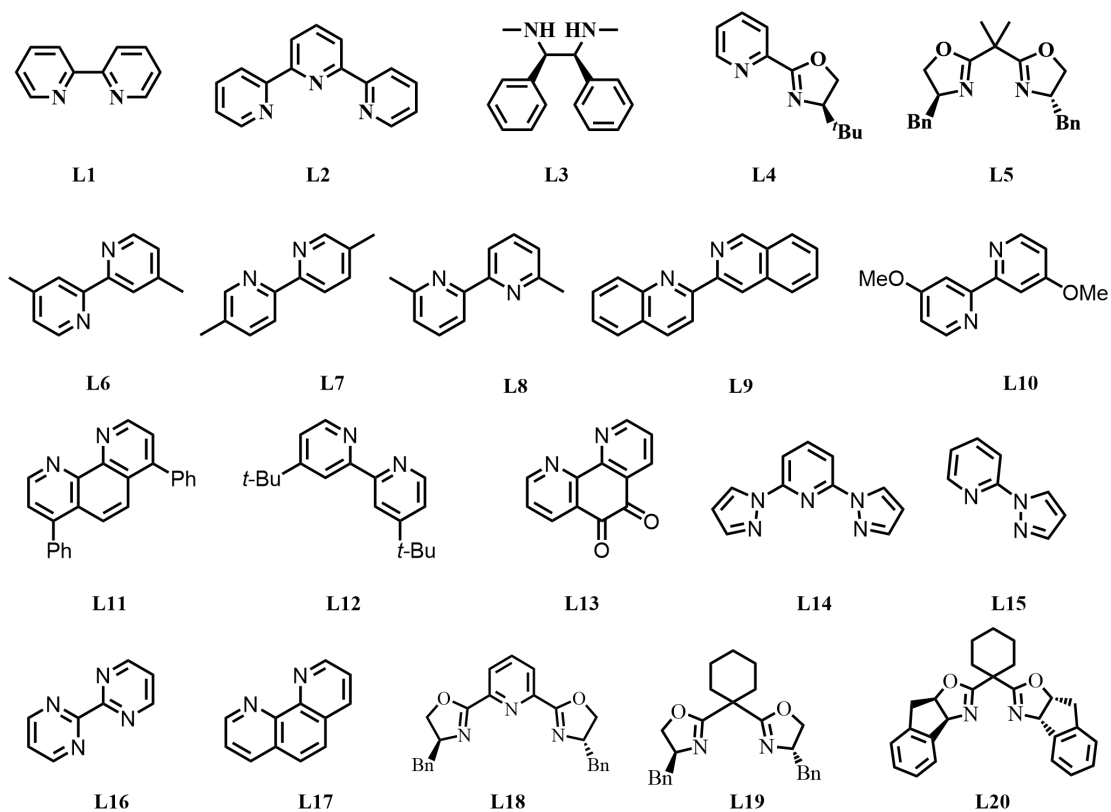
^aIsolated yields.

4.7 Table S7: Optimization of the ligand for the synthesis of γ -keto acids

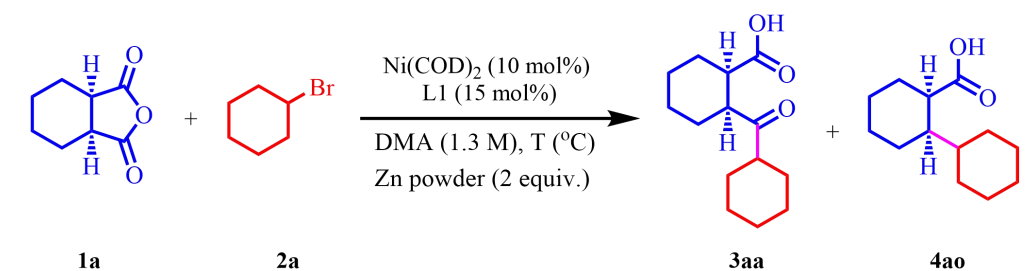


Entry	Ligand	Yield ^a (%) (3aa:4ao)
1	L1	78:0
2	L2	trace:0
3	L3	trace:0
4	L4	trace:0
5	L5	trace:12
6	L6	13:0
7	L7	11:0
8	L8	8:0
9	L9	trace
10	L10	0:0
11	L11	trace
12	L12	8:0
13	L13	trace
14	L14	12:0
15	L15	15:0
16	L16	9:0
17	L17	12:0
18	L18	trace
19	L19	trace
20	L20	trace

^aIsolated yields. Trace means the yield <5%.



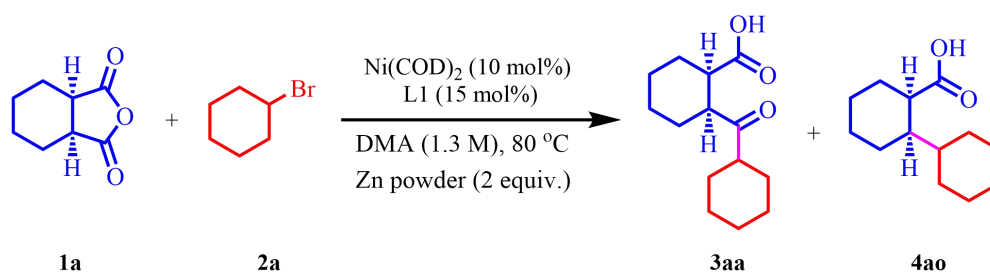
4.8 Table S8: Optimization of the reaction temperature for the synthesis of γ -keto acids



Entry	T/°C	Yield ^a (%) (3aa:4ao)
1	25	trace
2	40	33:0
3	60	57:0
4	80	78:0
5	100	74:0
6	120	66:0

^aIsolated yields. Trace means the yield <5%.

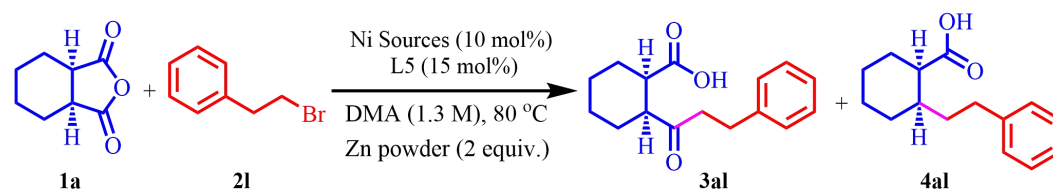
4.9 Table S9: Optimization of the reaction time for the synthesis of γ -keto acids



Entry	t/h	Yield ^a (%) (3aa:4ao)
1	3	17:0
2	6	36:0
3	9	63:0
4	12	78:0
5	15	77:0
6	18	78:0
7	21	74:0
8	24	72:0

^aIsolated yields.

4.10 Table S10: Optimization of the nickel sources for the synthesis of β -alkylated acid derivatives

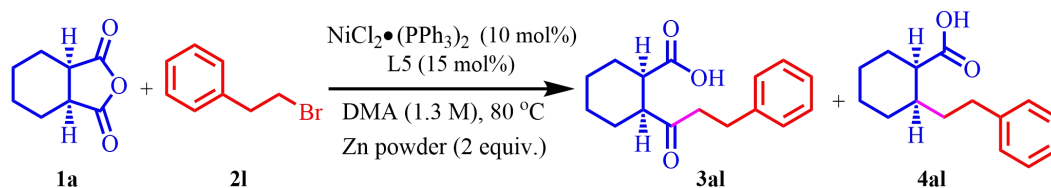


Entry	Ni Sources	Yield (%) ^a (3al:4al)
1	Ni(COD) ₂	trace:19

2	NiBr ₂	7:13
3	NiI ₂	6:28
4	NiBr ₂ ·DME	11:26
5	Ni(acac) ₂	trace
6	NiBr ₂ ·glyme	7:33
7	Ni(ClO ₄) ₂ ·6H ₂ O	trace
8	NiF ₂	trace
9	NiCl ₂	trace
10	NiCl ₂ ·(PPh ₃) ₂	trace:45

^aIsolated yields. Trace means the yield <5%.

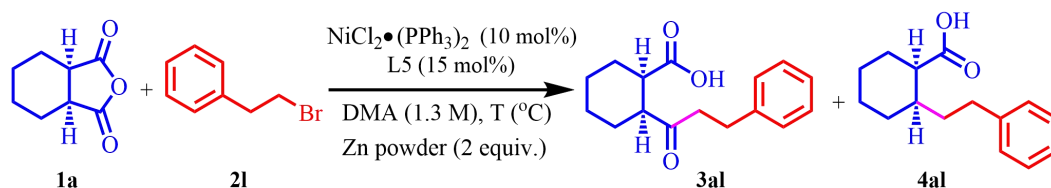
4.11 Table S11: Optimization of the ratio of 1a and 2l for the synthesis of β-alkylated acid derivatives



Entry	1a:2l	Yield (%) ^a (3al:4al)
1	3:1	trace:37
2	2:1	trace:42
3	1.5:1	trace:45
4	1:1	trace:46
5	1:1.5	trace:48
6	1:2	trace:57
7	1:3	trace:55

^aIsolated yields. Trace means the yield <5%.

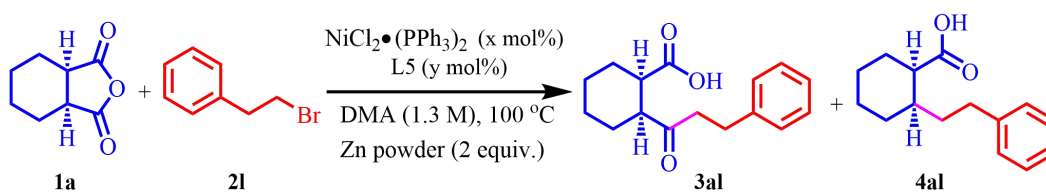
4.12 Table S12: Optimization of the temperature for the synthesis of β-alkylated acid derivatives



Entry	T/°C	Yield ^a (%) (3al:4al)
1	25	trace
2	40	trace
3	60	trace:35
4	80	trace:57
5	100	trace:64
6	120	Trace:60

^aIsolated yields. Trace means the yield <5%.

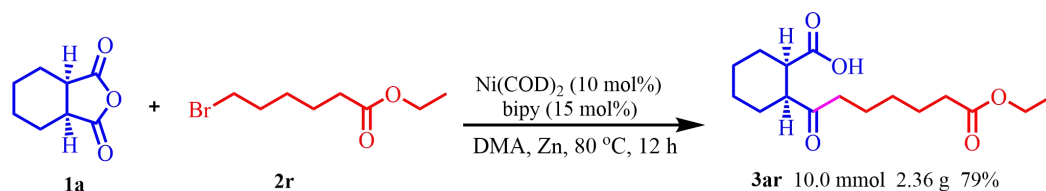
4.13 Table S13: Optimization of the catalyst mol% for the synthesis of β-alkylated acid derivatives



Entry	x (mol%)	y (mol%)	Yield ^a (%) (3al:4al)
1	5	7.5	trace
2	10	15	trace:64
3	15	22.5	trace:72
4	20	30	trace:80
5	30	45	trace:78

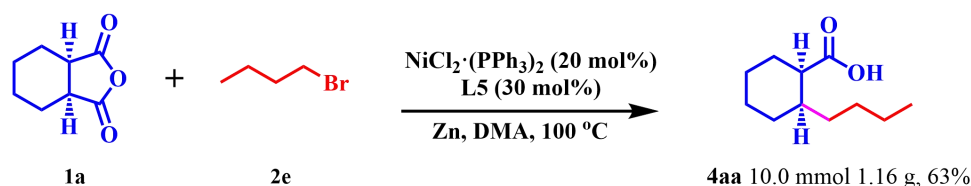
^aIsolated yields. Trace means the yield <5%.

5. Scale-up Transformation on 10.0 mmol Scale for the Synthesis of γ -Keto Acid 3ar



To an oven-dried microwave vial (25 mL) equipped with a stir bar (10 × 5 mm) was added Ni(COD)₂ (275 mg, 1.0 mmol), bipy (234 mg, 1.5 mmol) under a nitrogen atmosphere inside a glove box at 25 °C. Next, 7.5 mL of dry DMA was added via syringe to give a purple solution. After the catalyst/ligand solution was stirred for 1 h at 25 °C inside the glove box, Zn powder (1.3 g, 20 mmol, 2.0 equiv) was added to the reaction vial followed by the *cis*-1,2-cyclohexanedicarboxylic anhydride (2.31 g, 15 mmol, 1.5 equiv) and ethyl 6-bromohexanoate (1.78 mL, 10 mmol, 1.0 equiv). The microwave vial was sealed with a cap containing a rubber septum and removed from the glove box. The reaction mixture was stirred (1000 rpm) at 80 °C for 12 h. The resulting dark brown solution was then quenched by addition of 10 drops water via syringe and then the vial opened to air. The reaction mixture was passed through a short pad of silica gel and rinsed with 5 mL of ethyl acetate to afford a dark brown solution. The solvent was removed by rotary evaporator. The crude residue was purified by flash column chromatography to give **3ar** (2.36 g, 79%) as a colorless oil.

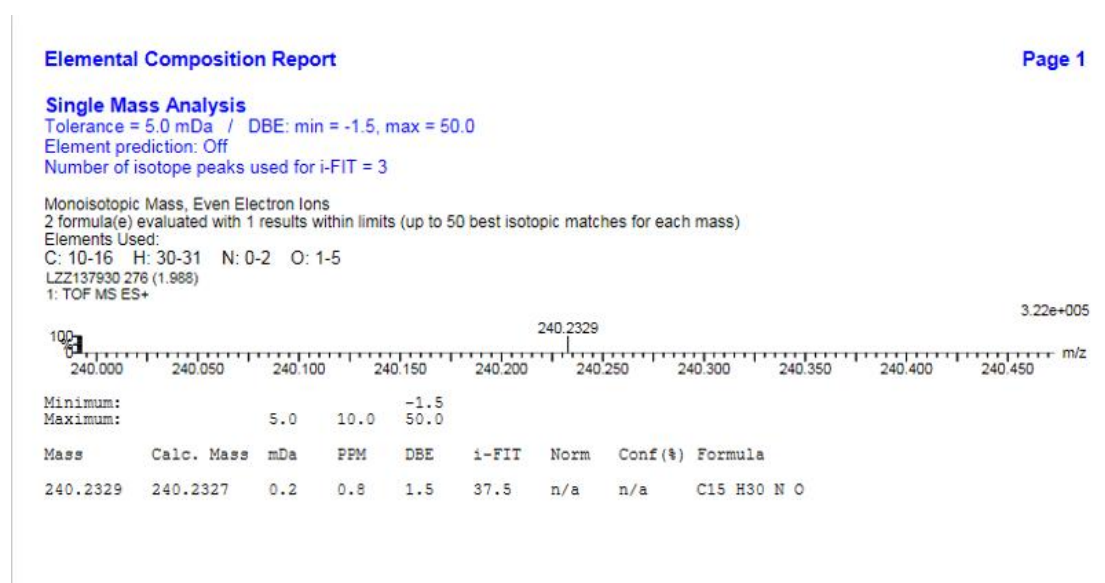
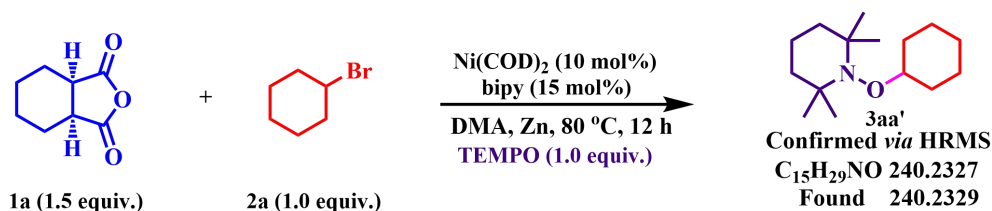
6. Scale-up Transformation on 10.0 mmol Scale for the Synthesis of β -Alkylated Acid 4aa



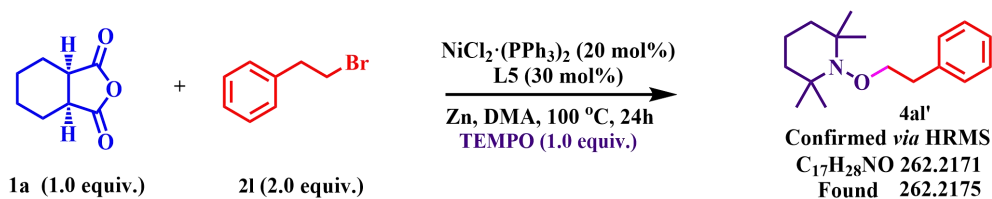
To an oven-dried microwave vial (50 mL) equipped with a stir bar (10 × 5 mm) was added NiCl₂·(PPh₃)₂ (1.31 g, 2 mmol), L5 (1.09 g, 3 mmol) under nitrogen atmosphere inside a glove box at 25 °C. Next, 20 mL of dry DMA was added via syringe to give a purple solution. After the catalyst/ligand solution was stirred for 1 h at 25 °C inside the glove box, Zn powder (1.31 g, 20 mmol, 2.0 equiv) was added to the reaction vial followed by the *cis*-1,2-cyclohexanedicarboxylic anhydride (1.54 g, 10 mmol, 1 equiv) and 1-bromobutane (2.74 g, 20 mmol, 2.0 equiv). The microwave vial was

sealed with a cap containing a rubber septum and removed from the glove box. The reaction mixture was stirred (1000 rpm) at 100 °C for 12 h. The resulting dark brown solution was then quenched by addition of 10 drops water via syringe and then the vial opened to air. The reaction mixture was passed through a short pad of silica gel and rinsed with 5 mL of ethyl acetate to afford a dark brown solution. The solvent was removed by rotary evaporator. The crude residue was purified by flash column chromatography to give **4aa** (1.16 g, 63%) as a colorless oil.

7. Mechanistic Studies



7.1 Figure S1. HRMS for **3aa'**



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

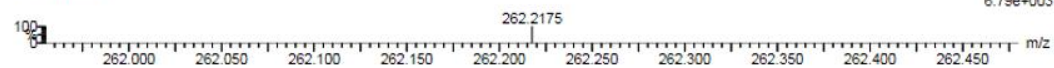
4 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 10-17 H: 28-31 N: 0-2 O: 1-5

LZZ137930 281 (2.024)

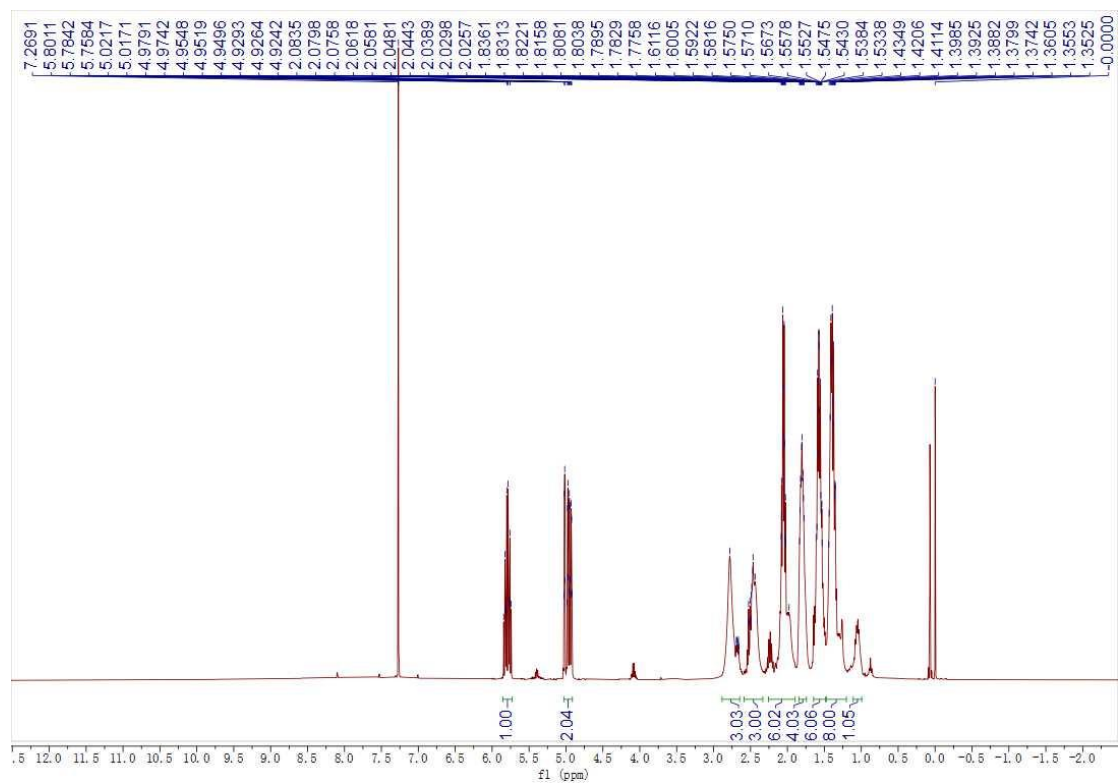
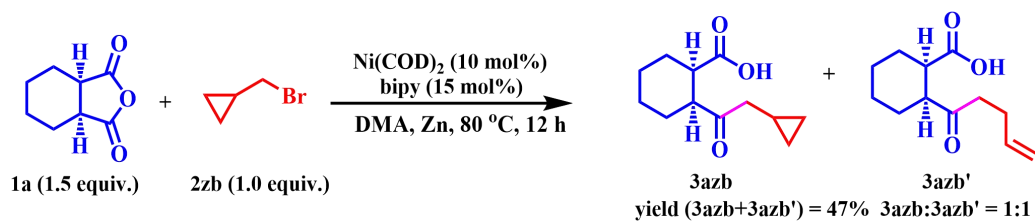
1: TOF MS ES+



Minimum: -1.5
Maximum: 5.0 10.0 50.0

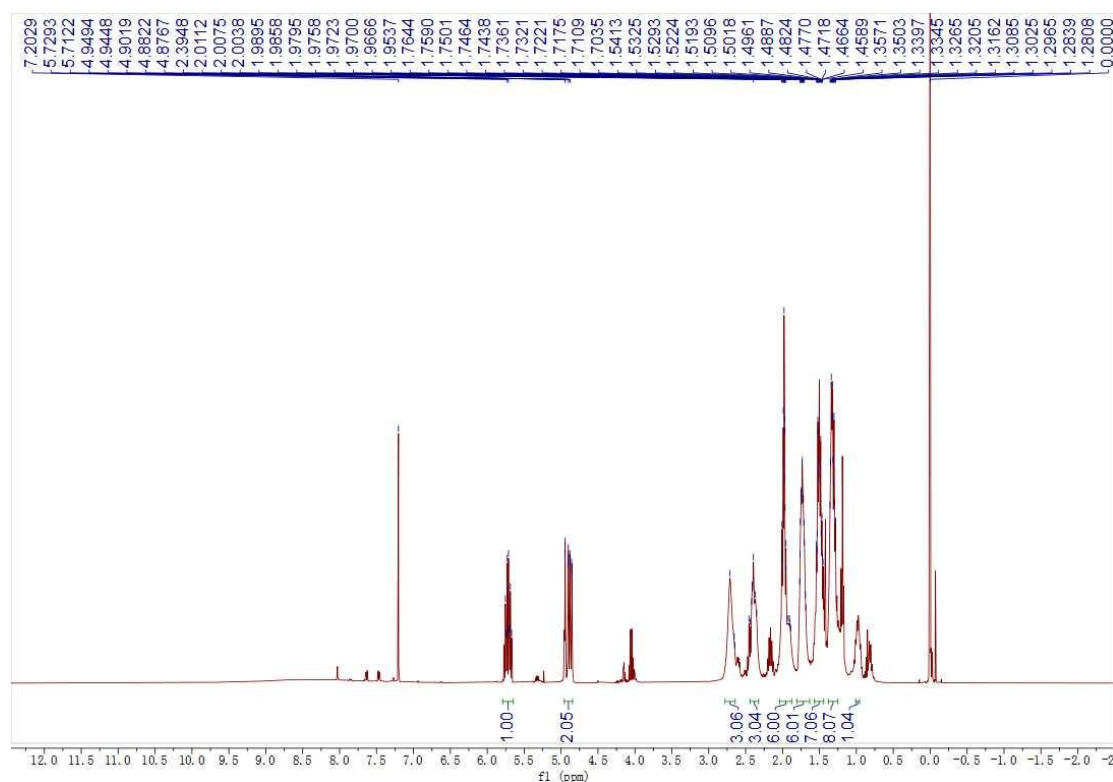
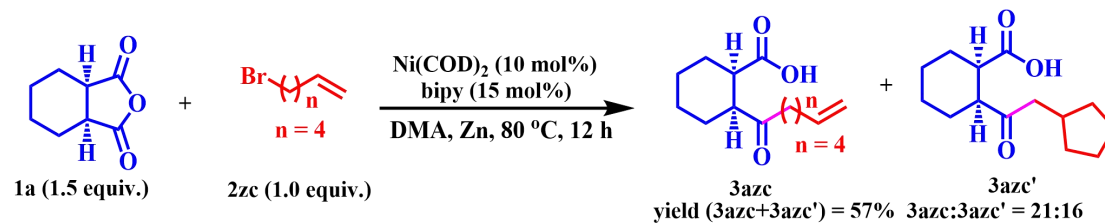
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
262.2175	262.2171	0.4	1.5	4.5	28.1	n/a	n/a	C17 H28 N O

7.2 Figure S2. HRMS for 4a1'

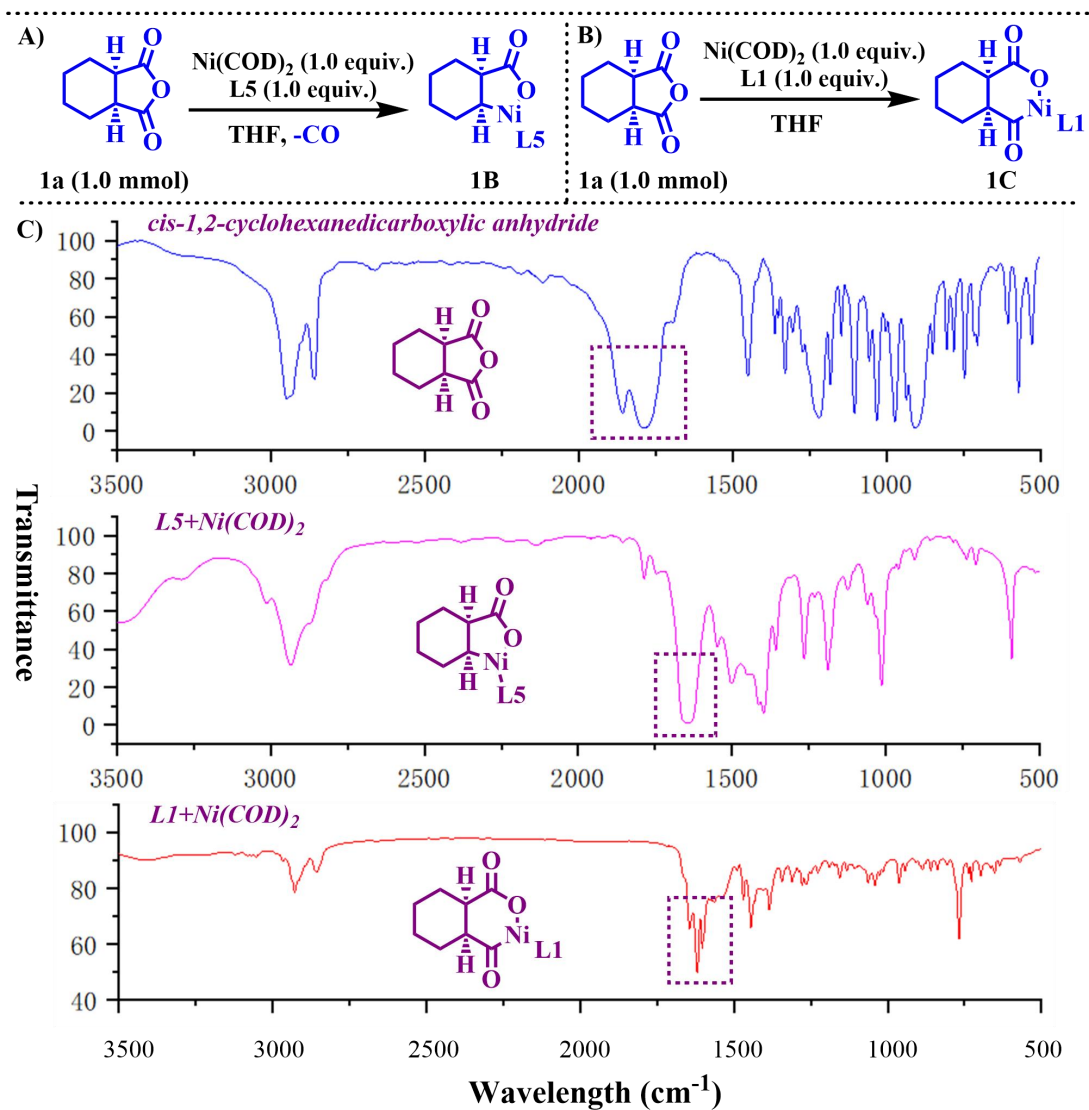


$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ : 7.26 – 5.01 (m, 1H, $-\text{C}=\text{CH}-$), 5.03 – 4.91 (m, 2H, $-\text{C}=\text{CH}_2$), 2.89 – 2.65 (m, 3H), 2.59 – 2.33 (m, 3H), 2.26 – 1.90 (m, 6H), 1.84 – 1.74 (m, 4H), 1.65 – 1.48 (m, 6H), 1.47 – 1.20 (m, 8H), 1.11 – 0.99 (m, 1H) ppm.

7.3 Figure S3. $^1\text{H NMR}$ (400 MHz, CDCl_3) for $3\text{azc}+3\text{azc}'$



7.4 Figure S4. $^1\text{H NMR}$ (400 MHz, CDCl_3) for $3\text{azc}+3\text{azc}'$



7.5 **Figure S5.** (A) Preparation of the Ni homoenolate **1B**; (B) Preparation of the alkyl nickel species **1C**; (C) Infrared spectroscopy of anhydride **1a**, **1B** and **1C** (The infrared spectra were obtained with KBr plates by using a IS10 FT-IR Spectrometer).

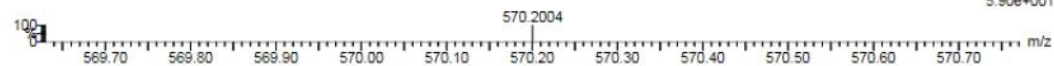
Elemental Composition Report

Page 1

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
 38 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 30-30 H: 35-37 N: 1-3 O: 3-5 Ni: 0-2 Na: 1-3

20250512030 493 (3.535)
 1: TOF MS ES+



Minimum: -1.5
 Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
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7.6 Figure S6. HRMS for 1B

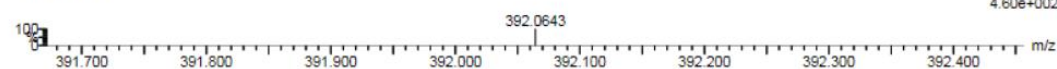
Elemental Composition Report

Page 1

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
 54 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 18-18 H: 17-19 N: 1-3 O: 2-4 Na: 1-3 Ni: 0-2

20250512030 245 (1.767)
 1: TOF MS ES+

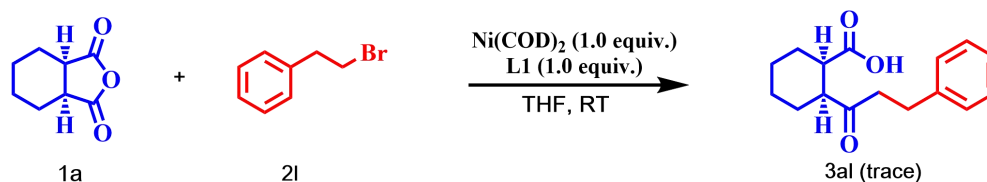


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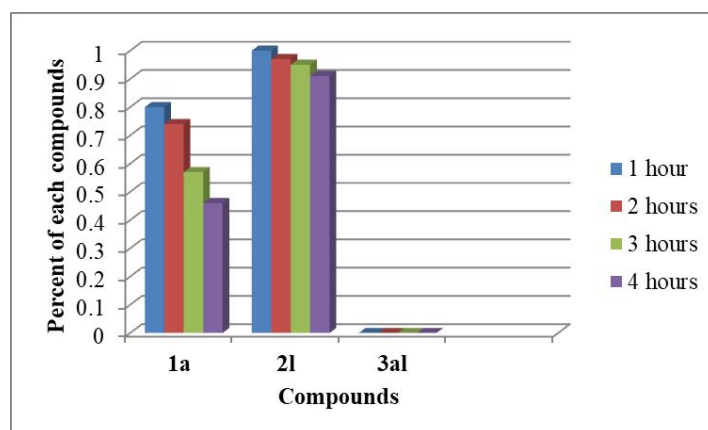
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
392.0643	392.0647	-0.4	-1.0	10.5	22.4	n/a	n/a	C18 H19 N2 O3 Na Ni

7.7 Figure S7. HRMS for 1C

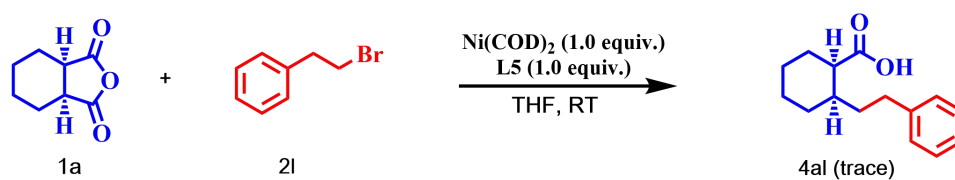
7.8 Table S13: Selectivity in oxidative addition to (L)Ni⁰. Percent of remaining 1a and 2l with yield of 3al



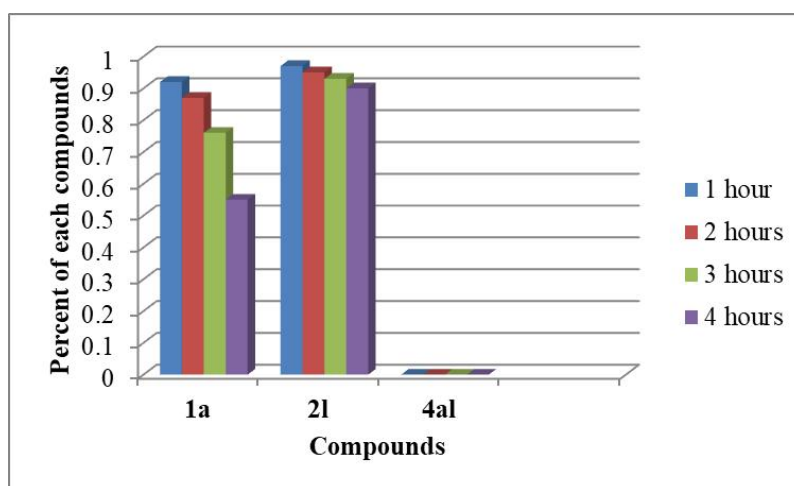
entry	t (h)	1a	2l	3al
1	1	0.8	1	0
2	2	0.74	0.97	0
3	3	0.57	0.95	0
4	4	0.46	0.91	0



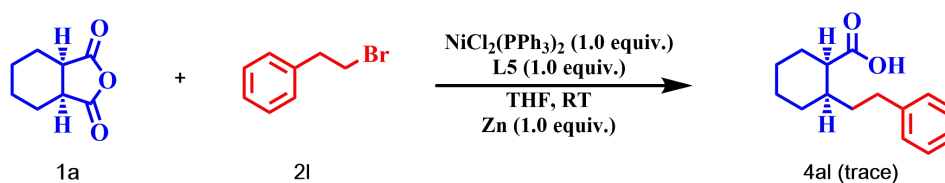
7.9 Table S14: Selectivity in oxidative addition to $(L)Ni^0$. Percent of remaining 1a and 2l with yield of 4al



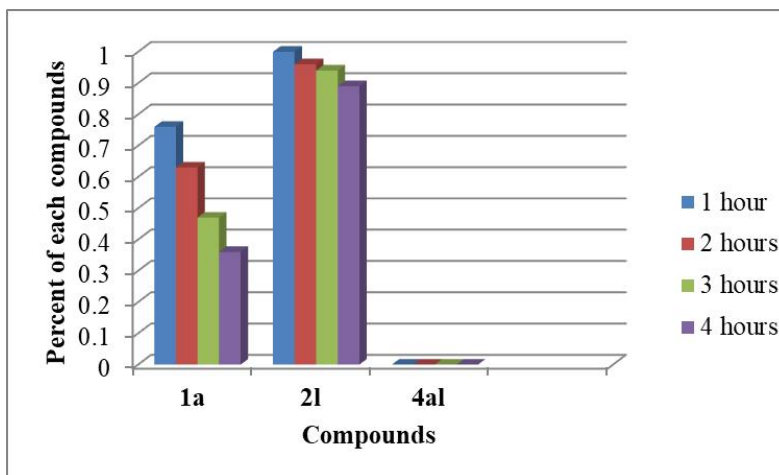
entry	t (h)	1a	2l	4al
1	1	0.92	0.97	0
2	2	0.87	0.95	0
3	3	0.76	0.93	0
4	4	0.55	0.9	0



7.10 Table S15: Selectivity in oxidative addition to $(L)Ni^{II}$. Percent of remaining 1a and 2l with yield of 4al



entry	t (h)	1a	2l	4al
1	1	0.76	1	0
2	2	0.63	0.96	0
3	3	0.47	0.94	0
4	4	0.36	0.89	0



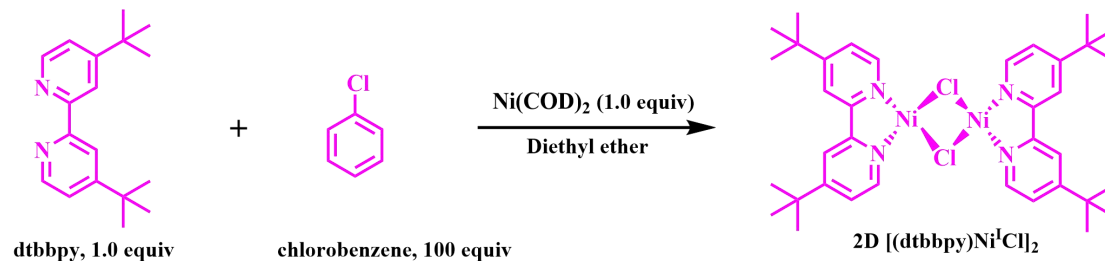
7.11 Procedures for the synthesis of $[(dtbbpy)Ni^I Cl]_2$

To a 20 mL vial with septum cap containing a stir bar was added $Ni(COD)_2$ (100 mg, 0.36 mmol) and dtbbpy ligand (98 mg, 0.36 mmol, 1 equiv) in a nitrogen-filled glovebox. 10 mL of diethyl ether was added via syringe transfer. The contents were stirred for 10 minutes and the solution turned to a dark purple color. Chlorobenzene (3.7 mL, 36.4 mmol, 100 equiv) was added via syringe. The vial was then capped and stirred at room temperature for 16 hours.

After 16 hours, the now deep red solution was evaporated to dryness under reduced pressure in the glovebox. Approximately 10 mL of pentane was then added, and the suspension was stirred for 10 minutes. The brick-red solids were isolated through filtration, and the crude was used without further purification.

The spectroscopic data for the complex matches the report from the literature, with the leftover of chlorobenzene as the major impurity.

1H NMR (500 MHz, CD_3CN) δ : 140.41 (brs, 1H), 58.79 (brs, 2H), 41.60 (brs, 1H), 3.65 (brs, 4H), 1.80 (brs, 4H, possibly overlapped with the CD_3CN peak), 1.42 (brs, 36H).



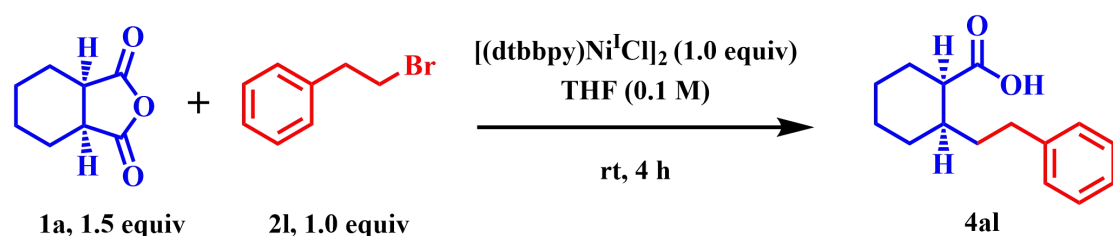
7.12 Procedures for the reactivity test of cyclic anhydrides and alkyl bromides using the $[(dtbbpy)Ni^I Cl]_2$ complex.

Note: the mass of $[(dtbbpy)Ni^I Cl]_2$ complex added was adjusted based on the chlorobenzene leftover as detected by 1H NMR.

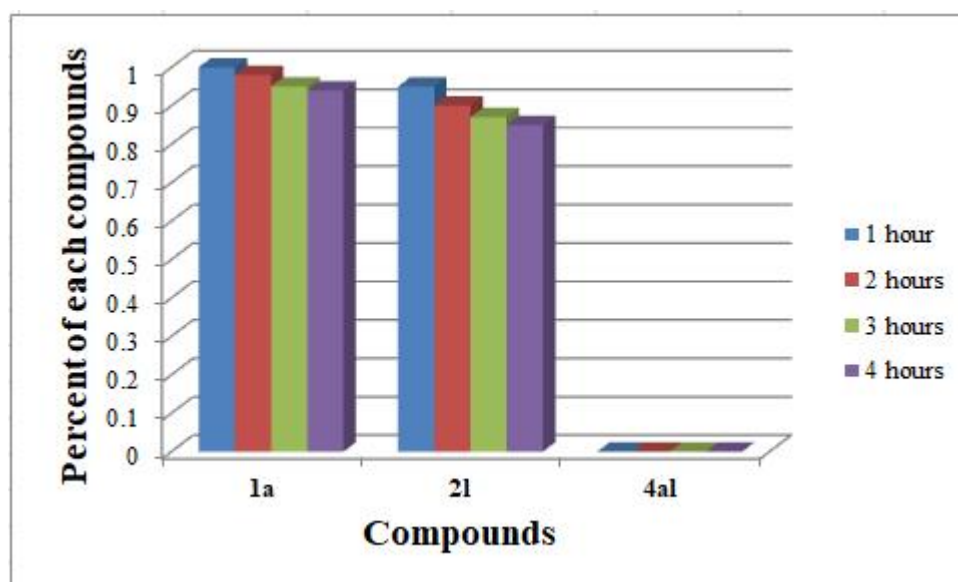
To an 8 mL vial with septum cap containing a stir bar was added [(dtbbpy)Ni^ICl]₂ (36.2 mg, 0.1 mmol, 1 equiv of Ni^I), cyclic anhydride **1a** (23.12 mg, 0.15 mmol, 1.5 equiv) and alkyl bromide **2l** (13.6 μL, 0.1 mmol, 1 equiv) in a nitrogen-filled glovebox. 1 mL of anhydrous THF was added via syringe transfer. The resulting content was stirred for 5 minutes and showed as a red mixture. 200 μL of the content was transferred to a 4 mL vial with septum cap containing a stir bar via a micro pipette, and 4 reaction vials were prepared in the same way. The reaction vials were then capped and brought out of the glovebox.

The vials were stirred at room temperature, and each vial was stopped at the target time points in a four-hour time period. The vial was opened to expose to air and filtered through a pad of silica gel with an extra 2 mL of rinse of ethyl acetate. The resulting solution was analyzed through GC-MS with 4,4'-di-tert-butylbiphenyl as an internal standard.

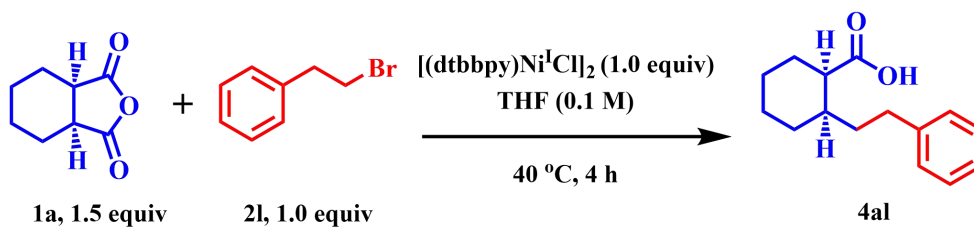
7.13 Table S16: Selectivity in oxidative addition to (L)Ni^I at room temperature. Percent of remaining 1a and 2l with yield of 4al



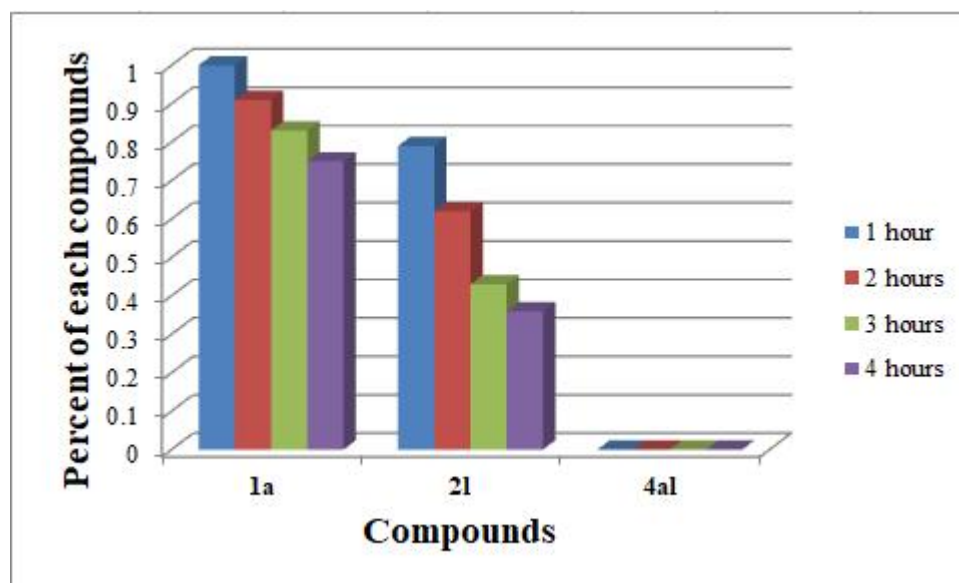
entry	t (h)	1a	2l	4al
1	1	1	0.95	0
2	2	0.98	0.90	0
3	3	0.95	0.87	0
4	4	0.94	0.85	0



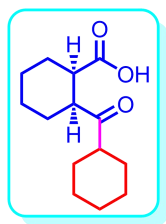
7.14 Table S17: Selectivity in oxidative addition to (L)Ni^I at 40 °C heating. Percent of remaining 1a and 2l with yield of 4al



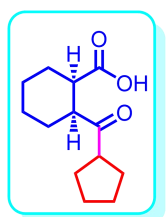
entry	t (h)	1a	2l	4al
1	1	1.0	0.79	0
2	2	0.91	0.62	0
3	3	0.83	0.43	0
4	4	0.75	0.36	0



8. Characterization Data for All Products



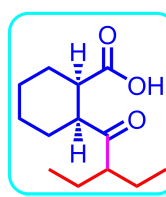
Cis-2-(cyclohexanecarbonyl)cyclohexane-1-carboxylic acid (3aa). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and bromocyclohexane (**2a**) (36.9 μ L, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (54.3 mg, 76% yield) as a white solid. Mp 31.9 – 32.6 °C. R_f = 0.50 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ : 10.63 (s, 1H), 3.03 – 3.00 (m, 1H), 2.64 – 2.56 (m, 2H), 2.06 – 2.03 (m, 2H), 1.81 – 1.65 (m, 5H), 1.65 – 1.64 (m, 3H), 1.43 – 1.23 (m, 8H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ : 214.9, 180.5, 47.6, 47.3, 42.4, 29.3, 28.1, 26.3, 25.9, 25.8, 25.4, 25.3, 24.2, 23.2 ppm. IR(neat): 3385, 2930, 2857, 1725, 1697, 1683, 1450, 1311, 1294, 1264, 1143, 995, 950, 923, 738, 540. HRMS: calcd for C₁₄H₂₃O₃ [M+H]⁺ 239.1647, found 239.1644.



Cis-2-(cyclopentanecarbonyl)cyclohexane-1-carboxylic acid (3ab). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and bromocyclopentane (**2b**) (32.2 μ L, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (51.8 mg, 77% yield) as a white solid. Mp 31.1 – 31.8 °C. R_f = 0.47 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ : 3.07 – 3.03 (m, 1H), 2.97 – 2.96 (m, 1H), 2.68 – 2.66 (m, 1H), 2.07 – 2.03 (m, 2H), 1.82 – 1.78 (m, 3H), 1.68 – 1.63 (m, 6H), 1.56 – 1.52 (m, 2H), 1.42 – 1.34 (m, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ : 214.8, 180.4, 48.7, 48.2, 42.4, 30.4, 28.9, 26.2, 26.0, 25.5, 24.1, 23.4 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 3380, 2943, 2868, 2718, 2610, 1721, 1684, 1454, 1416, 1311, 1265, 1084, 1015, 950, 862, 737, 533. HRMS: calcd for C₁₃H₂₁O₃ [M+H]⁺ 225.1491, found 225.1487.

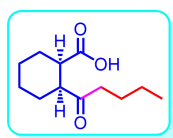


Cis-2-isobutyrylcyclohexane-1-carboxylic acid (3ac). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 2-bromopropane (**2c**) (28.2 μ L, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (48.2 mg, 81% yield) as a white solid. Mp 31.6 – 31.9 °C. R_f = 0.48 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ : 3.03 – 2.84 (m, 1H), 2.84 – 2.81 (m, 1H), 2.67 – 2.64 (m, 1H), 2.07 – 2.00 (m, 2H), 1.81 – 1.78 (m, 2H), 1.63 – 1.61 (m, 1H), 1.44 – 1.31 (m, 3H), 1.07 – 1.01 (m, 6H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ : 216.0, 180.4, 47.3, 42.4, 37.4, 26.2, 25.3, 24.1, 23.2, 19.1, 18.1 ppm. IR(neat): 3385, 2930, 2613, 1722, 1685, 1450, 1311, 1264, 1143, 1078, 995, 923, 871, 738, 540. HRMS: calcd for C₁₁H₁₉O₃ [M+H]⁺ 199.1334, found 199.1332.

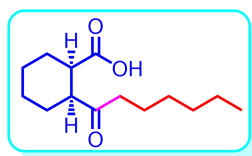


Cis-2-(2-ethylbutanoyl)cyclohexane-1-carboxylic acid (3ad). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 3-bromopentane (**2d**) (37.3 μ L, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (61.1 mg, 90% yield) as a white solid. Mp 30.4 – 31.0 °C. R_f = 0.56 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ : 3.00 – 2.98 (m, 1H), 2.59 –

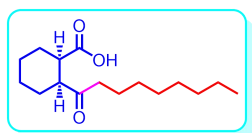
2.54 (m, 2H), 2.09 – 2.04 (m, 2H), 1.84 – 1.75 (m, 2H), 1.66 – 1.60 (m, 3H), 1.43 – 1.32 (m, 5H), 0.85 – 0.79 (m, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 215.0, 180.5, 51.3, 48.8, 42.2, 26.1, 25.3, 24.7, 24.3, 23.3, 22.8, 12.0, 11.2 ppm. IR(neat): 3382, 2964, 2874, 2673, 1722, 1682, 1457, 1423, 1312, 1265, 1166, 1014, 962, 924, 846, 742, 543. HRMS: calcd for $\text{C}_{13}\text{H}_{23}\text{O}_3$ $[\text{M}+\text{H}]^+$ 227.1647, found 227.1644.



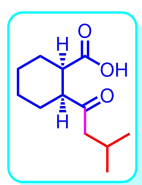
Cis-2-pentanoylcyclohexane-1-carboxylic acid (3ae). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromobutane (**2e**) (32.2 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (51.6 mg, 81% yield) as a colorless oil. R_f = 0.61 (Petroleum ether:EtOAc = 2:1). The spectroscopic data for this product match the literature data¹.



Cis-2-heptanoylcyclohexane-1-carboxylic acid (3af). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromohexane (**2f**) (42.1 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (50.5 mg, 70% yield) as a colorless oil. R_f = 0.60 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 2.79 – 2.72 (m, 2H), 2.45 – 2.41 (m, 2H), 2.06 – 1.99 (m, 2H), 1.80 – 1.77 (m, 2H), 1.55 – 1.51 (m, 3H), 1.40 – 1.39 (m, 3H), 1.28 – 1.24 (m, 6H), 0.87 (t, J = 6.9 Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 211.9, 180.4, 49.2, 42.3, 40.0, 31.6, 28.8, 26.1, 25.7, 23.9, 23.5, 23.4, 22.5, 14.0 ppm. IR(neat): 3600, 2962, 2581, 1722, 1683, 1466, 1249, 1127, 933, 888, 725, 612, 573. HRMS: calcd for $\text{C}_{14}\text{H}_{25}\text{O}_3$ $[\text{M}+\text{H}]^+$ 241.1804, found 241.1802.

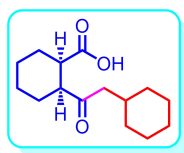


Cis-2-nonanoylcyclohexane-1-carboxylic acid (3ag). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromooctane (**2g**) (51.8 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (67.6 mg, 84% yield) as a white solid. Mp 29.7 – 30.1 $^\circ\text{C}$. R_f = 0.73 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 2.81 – 2.74 (m, 2H), 2.45 – 2.41 (m, 2H), 2.07 – 1.98 (m, 2H), 1.81 – 1.73 (m, 2H), 1.55 – 1.51 (m, 3H), 1.41 – 1.38 (m, 3H), 1.29 – 1.24 (m, 10H), 0.85 (t, J = 6.5 Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 212.0, 180.3, 49.2, 42.3, 40.0, 31.8, 29.4, 29.2, 29.1, 26.1, 25.7, 24.0, 23.6, 23.5, 22.6, 14.1 ppm. IR(neat): 3445, 2929, 2804, 1723, 1684, 1645, 1635, 1452, 1306, 1125, 750, 642, 523, 466, 434, 423, 415, 411. HRMS: calcd for $\text{C}_{16}\text{H}_{29}\text{O}_3$ $[\text{M}+\text{H}]^+$ 269.2117, found 269.2114.

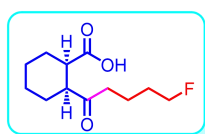


Cis-2-(3-methylbutanoyl)cyclohexane-1-carboxylic acid (3ah). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromo-2-methyl-propan (**2h**) (32.6 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (46.5 mg, 73% yield) as a white solid. Mp 31.3 – 31.8 $^\circ\text{C}$. R_f = 0.56 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 2.80 – 2.77 (m, 1H), 2.71 – 2.70 (m, 1H), 2.33 –

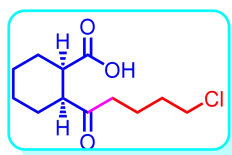
2.30 (m, 2H), 2.16 – 2.12 (m, 1H), 2.04 – 2.01 (m, 2H), 1.81 – 1.77 (m, 2H), 1.60 – 1.58 (m, 1H), 1.38 – 1.35 (m, 3H), 0.89 (d, $J = 2.9$ Hz, 3H), 0.87 (d, $J = 2.9$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 211.5, 180.5, 49.5, 49.1, 42.4, 26.2, 25.7, 24.2, 24.1, 23.4, 22.6, 22.5 ppm. IR(neat): 3455, 1728, 1680, 1636, 1450, 1366, 1170, 870, 433, 425, 417, 410. HRMS: calcd for $\text{C}_{12}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$ 213.1491, found 213.1486.



Cis-2-(2-cyclohexylacetyl)cyclohexane-1-carboxylic acid (3ai). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and cyclohexylmethyl bromide (**2i**) (41.9 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (68.9 mg, 91% yield) as a white solid. Mp 31.4 – 31.9 $^\circ\text{C}$. $R_f = 0.52$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 2.79 – 2.78 (m, 1H), 2.69 – 2.62 (m, 1H), 2.37 – 2.22 (m, 2H), 2.07 – 2.03 (m, 2H), 1.79 – 1.77 (m, 3H), 1.66 – 1.64 (m, 6H), 1.41 – 1.30 (m, 3H), 1.27 – 1.21 (m, 2H), 1.16 – 1.09 (m, 1H), 0.93 – 0.83 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 211.5, 180.3, 49.6, 47.7, 42.3, 33.4, 33.2, 33.1, 26.3, 26.12, 26.09, 25.6, 24.1, 23.4 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 3389, 2854, 2559, 1725, 1685, 1448, 1262, 1149, 1018, 964, 895, 848, 768, 728, 637, 524, 411. HRMS: calcd for $\text{C}_{15}\text{H}_{25}\text{O}_3$ $[\text{M}+\text{H}]^+$ 253.1804, found 253.1799.

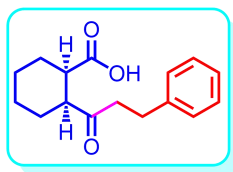


Cis-2-(5-fluoropentanoyl)cyclohexane-1-carboxylic acid (3aj). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromo-4-fluorobutane (**2j**) (32.2 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (42.8 mg, 62% yield) as a colorless oil. $R_f = 0.52$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 4.49 (t, $J = 5.6$ Hz, 1H), 4.37 (t, $J = 5.7$ Hz, 1H), 2.78 – 2.70 (m, 2H), 2.58 – 2.51 (m, 2H), 2.09 – 1.98 (m, 2H), 1.81 – 1.76 (m, 2H), 1.69 – 1.66 (m, 4H), 1.62 – 1.57 (m, 1H), 1.41 – 1.40 (m, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 211.3, 180.3, 83.9 (d, $J_{\text{C-F}} = 165.2$ Hz), 49.2, 42.4, 39.3, 29.7 (d, $J_{\text{C-F}} = 19.7$ Hz), 26.0, 25.8, 23.9, 23.4, 19.3 (d, $J_{\text{C-F}} = 5.1$ Hz) ppm. ^{19}F NMR (376 MHz, Chloroform- d) δ : -218.3 (s, 1F). IR(neat): 3648, 3154, 2827, 1722, 1683, 1668, 1615, 1452, 1307, 996, 749, 627, 518, 492, 448, 441, 424, 417. HRMS: calcd for $\text{C}_{12}\text{H}_{20}\text{FO}_3$ $[\text{M}+\text{H}]^+$ 231.1396, found 231.1398.



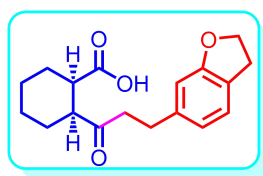
Cis-2-(5-chloropentanoyl)cyclohexane-1-carboxylic acid (3ak). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromo-4-chlorobutane (**2k**) (34.6 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (52.6 mg, 71% yield) as a colorless oil. $R_f = 0.53$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 3.51 (t, $J = 6.2$ Hz, 2H), 2.77 – 2.66 (m, 2H), 2.51 – 2.47 (m, 2H), 2.08 – 1.95 (m, 2H), 1.81 – 1.66 (m, 6H), 1.65 – 1.56 (m, 1H), 1.40 – 1.39 (m, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 211.2, 180.4, 49.1, 44.7, 42.4, 38.9, 31.8, 26.0, 25.8, 23.9, 23.4, 20.8 ppm. IR(neat): 3646, 3158, 2064, 1720, 1686, 1667, 1447, 1307, 1127, 722, 648, 514, 482, 448, 425, 410. HRMS: calcd for $\text{C}_{12}\text{H}_{20}\text{ClO}_3$ $[\text{M}+\text{H}]^+$ 247.1101, found 247.1103.

Cis-2-(3-phenylpropanoyl)cyclohexane-1-carboxylic acid (3al). The reaction was performed



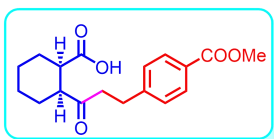
following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and (2-bromoethyl)benzene (**2l**) (41.0 μL, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (62.5 mg, 80% yield) as a colorless oil. *R_f* = 0.61 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 7.29 – 7.25 (m, 2H), 7.19 – 7.17 (m, 3H), 2.91 – 2.87 (m, 2H), 2.79 – 2.77 (m, 4H), 2.09 – 2.05 (m, 1H), 1.96 – 1.94 (m, 1H), 1.81 – 1.79 (m, 2H), 1.58 – 1.56 (m, 1H), 1.38 – 1.36 (m, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 210.8, 180.1, 141.3, 128.4, 128.3, 126.0, 49.4, 42.3, 41.8, 29.6, 25.9, 23.9, 23.5 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 3385, 2964, 2843, 1727, 1684, 1495, 1423, 1313, 1200, 1092, 986, 916, 860, 743, 603, 552, 493, 420. HRMS: calcd for C₁₆H₂₁O₃ [M+H]⁺ 261.1491, found 261.1489.

Cis-2-(3-(2,3-dihydrobenzofuran-6-yl)propanoyl)cyclohexane-1-carboxylic acid (3am). The

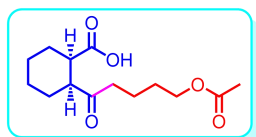


reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 6-(2-bromoethyl)-2,3-dihydrobenzofuran (**2m**) (68.1 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (73.5 mg, 81% yield) as a colorless oil. *R_f* = 0.48 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 7.01 (s, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 4.53 (t, *J* = 8.6 Hz, 2H), 3.16 (t, *J* = 8.7 Hz, 2H), 2.85 – 2.76 (m, 6H), 2.09 – 2.04 (m, 1H), 1.96 – 1.95 (m, 1H), 1.81 – 1.70 (m, 2H), 1.57 – 1.56 (m, 1H), 1.38 – 1.25 (m, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 210.9, 180.1, 158.3, 133.2, 128.3, 127.6, 127.0, 124.9, 109.0, 71.1, 49.4, 42.3, 34.3, 29.7, 29.0, 25.9, 23.9, 23.5 ppm. IR(neat): 3689, 2935, 2857, 1724, 1680, 1540, 1492, 1361, 1243, 1197, 1028, 982, 942, 886, 814, 736, 419. HRMS: calcd for C₁₈H₂₃O₄ [M+H]⁺ 303.1596, found 303.1598.

Cis-2-(3-(4-(methoxycarbonyl)phenyl)propanoyl)cyclohexane-1-carboxylic acid (3an). The

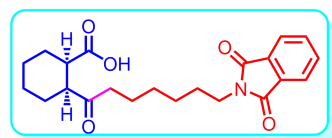


reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and methyl 4-(2-bromoethyl)benzoate (**2n**) (72.9 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (59.2 mg, 62% yield) as a colorless oil. *R_f* = 0.42 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 7.94 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.90 (s, 3H), 2.76 – 2.70 (m, 1H), 2.68 – 2.59 (m, 2H), 1.87 – 1.84 (m, 1H), 1.80 – 1.50 (m, 8H), 1.39 – 1.37 (m, 2H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 210.3, 179.8, 167.1, 146.9, 129.7, 128.4, 127.9, 52.0, 49.3, 42.4, 41.2, 29.5, 25.9, 23.9, 23.4 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 3726, 2935, 2858, 1723, 1717, 1712, 1683, 1607, 1541, 1436, 1281, 1180, 994, 766, 636, 508, 447, 426. HRMS: calcd for C₁₈H₂₃O₅ [M+H]⁺ 319.1545, found 319.1548.

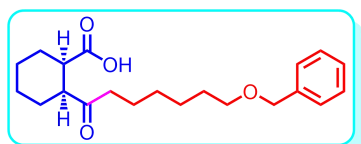


Cis-2-(5-acetoxypentanoyl)cyclohexane-1-carboxylic acid (3ao). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 4-bromobutyl acetate (**2o**) (43.4 μL, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (52.7 mg, 65% yield) as a colorless oil. $R_f = 0.49$ (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 4.05 – 4.02 (m, 2H), 2.76 – 2.67 (m, 2H), 2.53 – 2.48 (m, 2H), 2.07 – 2.06 (m, 1H), 2.02 (s, 3H), 1.96 – 1.90 (m, 1H), 1.81 – 1.77 (m, 2H), 1.61 – 1.60 (m, 5H), 1.40 – 1.38 (m, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 211.3, 179.8, 171.3, 64.2, 49.1, 42.3, 39.3, 27.9, 26.0, 25.8, 23.9, 23.4, 20.9, 19.9 ppm. IR(neat): 3568, 2940, 2860, 1744, 1727, 1720, 1683, 1451, 1367, 1247, 1039, 902, 808, 736, 608, 514, 441. HRMS: calcd for C₁₄H₂₃O₅ [M+H]⁺ 271.1545, found 271.1543.

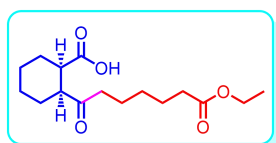
Cis-2-(7-(1,3-dioxisoindolin-2-yl)heptanoyl)cyclohexane-1-carboxylic acid (3ap). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and *N*-(6-bromohexyl)phthalimide (**2p**) (93.1 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (75.2 mg, 65% yield) as a colorless oil. $R_f = 0.45$ (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 7.83 – 7.80 (m, 2H), 7.70 – 7.68 (m, 2H), 3.66 – 3.63 (m, 2H), 2.75 – 2.65 (m, 2H), 2.49 – 2.41 (m, 2H), 2.03 – 1.96 (m, 2H), 1.78 – 1.75 (m, 2H), 1.68 – 1.62 (m, 2H), 1.54 – 1.51 (m, 3H), 1.38 – 1.35 (m, 3H), 1.31 – 1.29 (m, 4H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 211.7, 179.7, 168.4, 133.8, 132.0, 123.1, 49.2, 42.2, 39.8, 37.8, 28.6, 28.3, 26.5, 26.1, 25.7, 23.9, 23.4, 23.3 ppm. IR(neat): 3654, 3165, 2064, 1767, 1726, 1684, 1667, 1652, 1635, 1616, 1435, 1386, 1185, 1043, 792, 622, 529, 464, 433, 414. HRMS: calcd for C₂₂H₂₈NO₅ [M+H]⁺ 386.1967, found 386.1972.



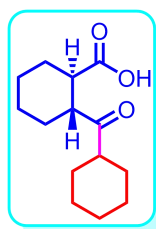
Cis-2-(7-(benzyloxy)heptanoyl)cyclohexane-1-carboxylic acid (3aq). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 6-benzyloxyhexyl bromide (**2q**) (81.4 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (85.3 mg, 82% yield) as a colorless oil. $R_f = 0.45$ (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 7.36 – 7.33 (m, 4H), 7.29 – 7.26 (m, 1H), 4.50 (s, 2H), 3.46 (t, $J = 6.6$ Hz, 2H), 2.79 – 2.74 (m, 2H), 2.50 – 2.43 (m, 2H), 2.05 – 1.99 (m, 2H), 1.80 – 1.79 (m, 2H), 1.62 – 1.54 (m, 5H), 1.40 – 1.34 (m, 5H), 1.31 – 1.26 (m, 2H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 211.8, 180.0, 138.5, 128.3, 127.6, 127.4, 72.7, 70.3, 49.2, 42.3, 40.0, 29.5, 28.9, 26.1, 25.9, 25.8, 25.7, 23.9, 23.4 ppm. IR(neat): 3632, 2939, 2858, 1725, 1687, 1555, 1453, 1408, 1362, 1256, 1187, 1098, 992, 735, 698, 610, 548, 491, 441, 410. HRMS: calcd for C₂₁H₃₁O₄ [M+H]⁺ 347.2222, found 347.2222.



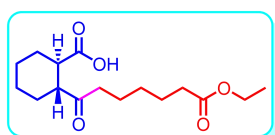
Cis-2-(7-ethoxy-7-oxoheptanoyl)cyclohexane-1-carboxylic acid (3ar). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1a** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and ethyl 6-bromohexanoate (**2r**) (53.4 μL, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted



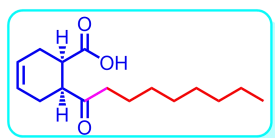
with Petroleum ether:EtOAc = 5:1) to give the product (68.0 mg, 76% yield) as a colorless oil. R_f = 0.60 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 4.10 (t, J = 7.1 Hz, 2H), 2.76 – 2.75 (m, 2H), 2.44 – 2.43 (m, 2H), 2.27 (t, J = 7.5 Hz, 2H), 2.06 – 1.96 (m, 2H), 1.79 – 1.76 (m, 2H), 1.63 – 1.52 (m, 5H), 1.39 – 1.38 (m, 3H), 1.32 – 1.27 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 211.7, 179.7, 173.8, 60.2, 49.2, 42.3, 39.7, 34.1, 28.6, 26.0, 25.7, 24.7, 23.9, 23.4, 23.1, 14.2 ppm. IR(neat): 3627, 3193, 2983, 1726, 1684, 1671, 1651, 1636, 1450, 1373, 1162, 672, 629, 498, 456, 448, 429, 421, 410. HRMS: calcd for $\text{C}_{16}\text{H}_{27}\text{O}_5$ $[\text{M}+\text{H}]^+$ 299.1858, found 299.1856.



Trans-2-(cyclohexanecarbonyl)cyclohexane-1-carboxylic acid (3ba). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1b** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and bromocyclohexane (**2a**) (36.9 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (58.6 mg, 82% yield) as a white solid. Mp 32.0 – 32.4 $^\circ\text{C}$. R_f = 0.71 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 3.13 – 3.02 (m, 1H), 2.65 – 2.56 (m, 2H), 2.09 – 2.03 (m, 2H), 1.81 – 1.74 (m, 5H), 1.72 – 1.65 (m, 3H), 1.43 – 1.22 (m, 8H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 215.0, 180.3, 47.7, 47.4, 42.4, 29.4, 28.2, 26.3, 25.9, 25.8, 25.5, 25.4, 24.2, 23.3 ppm. IR(neat): 3628, 3270, 2634, 1724, 1685, 1652, 1644, 626, 522, 470, 448, 433, 429, 421, 412. HRMS: calcd for $\text{C}_{14}\text{H}_{23}\text{O}_3$ $[\text{M}+\text{H}]^+$ 239.1647, found 239.1648.

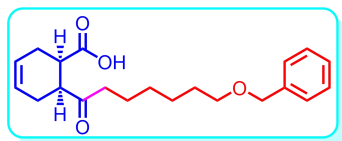


Trans-2-(7-ethoxy-7-oxoheptanoyl)cyclohexane-1-carboxylic acid (3br). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1b** (69.4 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and ethyl 6-bromohexanoate (**2r**) (53.4 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (71.6 mg, 80% yield) as a colorless oil. R_f = 0.52 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 4.10 (q, J = 7.2 Hz, 2H), 2.78 – 2.74 (m, 2H), 2.49 – 2.43 (m, 2H), 2.27 (t, J = 7.5 Hz, 2H), 2.05 – 1.98 (m, 2H), 1.80 – 1.75 (m, 2H), 1.62 – 1.54 (m, 5H), 1.39 – 1.37 (m, 3H), 1.30 – 1.28 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 211.7, 179.9, 173.8, 60.2, 49.2, 42.3, 39.7, 34.1, 28.5, 26.1, 25.8, 24.7, 23.9, 23.4, 23.1, 14.2 ppm. IR(neat): 3651, 2941, 2860, 1722, 1716, 1702, 1698, 1688, 1451, 1373, 1185, 896, 857, 737, 704, 579, 514, 478, 426. HRMS: calcd for $\text{C}_{16}\text{H}_{27}\text{O}_5$ $[\text{M}+\text{H}]^+$ 299.1858, found 299.1856.



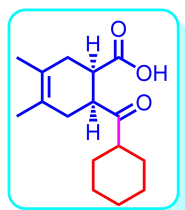
Cis-6-nonanoylcyclohex-3-ene-1-carboxylic acid (3cg). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1c** (68.5 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromooctane (**2g**) (51.8 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (67.9 mg, 85% yield) as a colorless oil. R_f = 0.64 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 5.71 – 5.64 (m, 2H), 3.04 – 3.00 (m, 1H), 2.93 – 2.91 (m, 1H), 2.63 – 2.58 (m, 1H), 2.49 – 2.45 (m, 3H), 2.38 – 2.32 (m, 1H), 1.57 – 1.53 (m, 2H), 1.30 – 1.25 (m, 11H), 0.87 (t, J = 6.6 Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 211.2, 179.5, 125.9, 124.5, 46.4, 39.9, 39.2, 31.8, 29.4, 29.2, 29.1, 25.9, 25.4, 23.6, 22.6, 14.1 ppm. IR(neat): 3675, 2927,

2855, 1728, 1704, 1683, 1454, 1257, 1196, 1011, 933, 878, 812, 757, 723, 620, 524, 430, 419. HRMS: calcd for C₁₆H₂₇O₃ [M+H]⁺ 267.1960, found 267.1957.



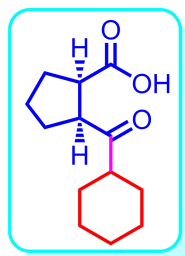
Cis-6-(7-(benzyloxy)heptanoyl)cyclohex-3-ene-1-carboxylic acid (3cq).

The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1c** (68.5 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 6-benzyloxyhexyl bromide (**2q**) (81.4 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (86.8 mg, 84% yield) as a colorless oil. R_f = 0.54 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 7.34 – 7.32 (m, 4H), 7.28 – 7.25 (m, 1H), 5.69 – 5.64 (m, 2H), 4.49 (s, 2H), 3.45 (t, J = 6.6 Hz, 2H), 3.02 – 2.90 (m, 2H), 2.63 – 2.58 (m, 1H), 2.48 – 2.45 (m, 3H), 2.37 – 2.32 (m, 1H), 1.64 – 1.53 (m, 4H), 1.40 – 1.25 (m, 5H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 210.9, 179.3, 138.5, 128.3, 127.6, 127.4, 125.8, 124.4, 72.7, 70.2, 46.4, 39.7, 39.2, 29.5, 28.9, 25.92, 25.87, 25.4, 23.4 ppm. IR(neat): 3443, 3031, 2937, 2858, 1723, 1701, 1684, 1655, 1495, 1454, 1437, 1365, 1298, 1200, 1099, 943, 907, 736, 699, 664, 610, 460. HRMS: calcd for C₂₁H₂₉O₄ [M+H]⁺ 345.2066, found 345.2063.



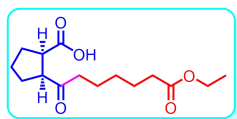
Cis-6-(cyclohexanecarbonyl)-3,4-dimethylcyclohex-3-ene-1-carboxylic acid (3da).

The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1d** (81.1 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and bromocyclohexane (**2a**) (36.9 μL, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (61.8 mg, 78% yield) as a white solid. Mp 31.0 – 31.2 °C. R_f = 0.62 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 3.08 – 3.04 (m, 1H), 2.94 – 2.91 (m, 1H), 2.59 – 2.50 (m, 2H), 2.35 – 2.34 (m, 2H), 2.26 – 2.21 (m, 1H), 1.84 – 1.81 (m, 1H), 1.78 – 1.75 (m, 2H), 1.67 – 1.62 (m, 8H), 1.33 – 1.20 (m, 5H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 214.5, 179.5, 124.7, 123.1, 47.6, 45.4, 40.0, 31.9, 31.7, 29.2, 28.4, 25.83, 25.81, 25.5, 19.0, 18.8 ppm. IR(neat): 3476, 2906, 2646, 1736, 1722, 1682, 1677, 1432, 1368, 1287, 1052, 983, 893, 784, 752, 686, 571, 453, 412. HRMS: calcd for C₁₆H₂₅O₃ [M+H]⁺ 265.1804, found 265.1799.

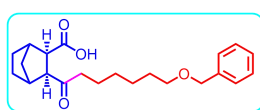


Cis-2-(cyclohexanecarbonyl)cyclopentane-1-carboxylic acid (3ea).

The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1e** (63.1 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and bromocyclohexane (**2a**) (36.9 μL, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (48.5 mg, 72% yield) as a white solid. Mp 29.2 – 29.6 °C. R_f = 0.61 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 3.39 – 3.33 (m, 1H), 3.28 – 3.21 (m, 1H), 2.49 – 2.44 (m, 1H), 2.06 – 2.00 (m, 2H), 1.90 – 1.87 (m, 2H), 1.79 – 1.77 (m, 3H), 1.72 – 1.64 (m, 4H), 1.42 – 1.37 (m, 1H), 1.29 – 1.20 (m, 4H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 214.7, 181.0, 52.2, 50.3, 45.5, 30.7, 29.9, 28.7, 28.1, 25.8, 25.7, 25.6, 25.5 ppm. IR(neat): 3610, 2929, 2852, 1723, 1701, 1687, 1450, 1379, 1208, 1145, 934, 896, 788, 759, 689, 514, 435. HRMS: calcd for C₁₃H₂₁O₃ [M+H]⁺ 225.1491, found 225.1487.



Cis-2-(7-ethoxy-7-oxoheptanoyl)cyclopentane-1-carboxylic acid (3er). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1e** (63.1 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and ethyl 6-bromohexanoate (**2r**) (53.4 μL, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (71.7 mg, 84% yield) as a colorless oil. $R_f = 0.58$ (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 4.11 (q, $J = 7.1$ Hz, 2H), 3.25 – 3.18 (m, 2H), 2.52 – 2.48 (m, 2H), 2.28 (t, $J = 7.5$ Hz, 2H), 2.06 – 2.00 (m, 2H), 1.91 – 1.86 (m, 1H), 1.72 – 1.60 (m, 7H), 1.34 – 1.29 (m, 2H), 1.24 (t, $J = 7.1$ Hz, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 211.3, 180.4, 173.8, 60.3, 54.0, 45.2, 41.8, 34.1, 30.2, 29.9, 28.6, 25.5, 24.7, 23.2, 14.2 ppm. IR(neat): 3654, 3138, 2064, 1722, 1716, 1683, 1667, 1613, 1452, 1373, 1189, 795, 525, 487, 476, 448, 426, 418. HRMS: calcd for C₁₅H₂₅O₅ [M+H]⁺ 285.1702, found 285.1701.

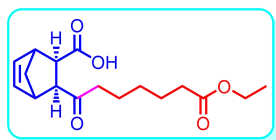


Cis-3-(7-(benzyloxy)heptanoyl)bicyclo[2.2.1]heptane-2-carboxylic acid (3fq). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1f** (74.8 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 6-benzyloxyhexyl bromide (**2q**) (81.4 mg, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (97.9 mg, 91% yield) as a colorless oil. $R_f = 0.71$ (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 7.36 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 4.50 (s, 2H), 3.46 (t, $J = 6.6$ Hz, 2H), 3.37 – 3.35 (m, 1H), 2.85 – 2.84 (m, 1H), 2.66 – 2.64 (m, 1H), 2.56 – 2.50 (m, 1H), 2.47 – 2.40 (m, 2H), 1.64 – 1.56 (m, 5H), 1.43 – 1.35 (m, 6H), 1.30 – 1.26 (m, 2H), 1.22 – 1.20 (m, 1H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 210.4, 179.4, 138.5, 128.3, 127.6, 127.4, 72.8, 70.2, 55.7, 47.0, 41.6, 41.2, 39.8, 37.3, 29.5, 29.4, 29.0, 25.9, 24.4, 23.8 ppm. IR(neat): 3655, 3130, 2065, 1720, 1682, 1608, 1496, 1453, 1362, 1260, 1233, 1181, 814, 748, 697, 548, 510, 491, 461, 425, 412. HRMS: calcd for C₂₂H₃₁O₄ [M+H]⁺ 359.2222, found 359.2224.

Cis-3-(7-ethoxy-7-oxoheptanoyl)bicyclo[2.2.1]heptane-2-carboxylic acid (3fr). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1f** (74.8 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and ethyl 6-bromohexanoate (**2r**) (53.4 μL, 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (86.6 mg, 93% yield) as a colorless oil. $R_f = 0.57$ (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 4.11 (q, $J = 7.1$ Hz, 2H), 3.37 – 3.34 (m, 1H), 2.84 – 2.83 (m, 1H), 2.67 – 2.65 (m, 1H), 2.57 – 2.53 (m, 1H), 2.47 – 2.42 (m, 2H), 2.28 (t, $J = 7.5$ Hz, 2H), 1.64 – 1.56 (m, 5H), 1.49 – 1.45 (m, 1H), 1.43 – 1.36 (m, 3H), 1.36 – 1.30 (m, 2H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.21 – 1.20 (m, 1H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 210.2, 179.3, 173.7, 60.3, 55.7, 47.0, 41.5, 41.3, 39.8, 37.3, 34.1, 29.4, 28.6, 24.7, 24.5, 23.5, 14.2 ppm. IR(neat): 3655, 3130, 2827, 1723, 1715, 1682, 1652, 1608, 1260, 814, 748, 697, 634, 556, 510, 448, 425, 412. HRMS: calcd for C₁₇H₂₇O₅ [M+H]⁺ 311.1858, found 311.1860.

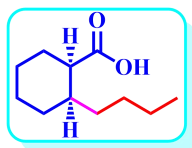
Cis-3-(7-(benzyloxy)heptanoyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (3gq). The reaction was performed following the General Procedure A with Ni(COD)₂ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1g** (73.9 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and 6-benzyloxyhexyl bromide (**2q**) (81.4 mg, 0.3 mmol). The crude product was purified by flash chromatography

on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (77.0 mg, 72% yield) as a colorless oil. R_f = 0.49 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 7.35 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 6.31 – 6.29 (m, 1H), 6.17 – 6.15 (m, 1H), 4.50 (s, 2H), 3.48 – 3.45 (m, 3H), 3.26 – 3.25 (m, 1H), 2.99 – 2.98 (m, 1H), 2.77 – 2.76 (m, 1H), 2.64 – 2.47 (m, 2H), 1.63 – 1.57 (m, 4H), 1.53 – 1.51 (m, 1H), 1.40 – 1.26 (m, 5H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 210.5, 179.1, 138.5, 137.6, 135.7, 128.3, 127.6, 127.5, 72.8, 70.3, 54.4, 46.9, 46.6, 46.4, 45.2, 42.3, 29.5, 29.0, 26.0, 23.8 ppm. IR(neat): 3646, 3184, 1723, 1680, 1660, 1651, 1496, 1453, 1362, 1332, 1265, 1204, 1074, 737, 698, 610, 522, 472, 441, 410. HRMS: calcd for $\text{C}_{22}\text{H}_{29}\text{O}_4$ $[\text{M}+\text{H}]^+$ 357.2066, found 357.2068.

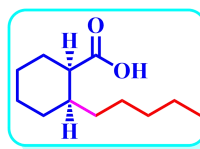


Cis-3-(7-ethoxy-7-oxoheptanoyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (3gr). The reaction was performed following the General Procedure A with $\text{Ni}(\text{COD})_2$ (8.3 mg, 0.03 mmol), bipy (7.0 mg, 0.045 mmol), **1g** (73.9 mg, 0.45 mmol), Zn powder (39.2 mg, 0.6 mmol), and ethyl

6-bromohexanoate (**2r**) (53.4 μL , 0.3 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (70.3 mg, 76% yield) as a colorless oil. R_f = 0.48 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 6.29 – 6.28 (m, 1H), 6.17 – 6.15 (m, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.45 – 3.43 (m, 1H), 3.30 – 3.25 (m, 1H), 2.99 – 2.98 (m, 1H), 2.76 – 2.75 (m, 1H), 2.63 – 2.48 (m, 2H), 2.29 (t, J = 7.5 Hz, 2H), 1.65 – 1.57 (m, 3H), 1.52 – 1.50 (m, 1H), 1.40 – 1.38 (m, 1H), 1.36 – 1.30 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.23 – 1.19 (m, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 210.3, 179.3, 173.7, 137.6, 135.7, 60.3, 54.4, 46.9, 46.5, 46.4, 45.2, 42.1, 34.1, 28.6, 24.6, 23.4, 14.2 ppm. IR(neat): 3734, 2978, 2871, 1732, 1725, 1716, 1683, 1634, 1540, 1454, 1373, 1185, 1033, 948, 866, 744, 558, 499, 410. HRMS: calcd for $\text{C}_{17}\text{H}_{25}\text{O}_5$ $[\text{M}+\text{H}]^+$ 309.1702, found 309.1704.

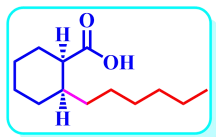


Cis-2-butylcyclohexane-1-carboxylic acid (4aa). The reaction was performed following the General Procedure B with $\text{NiCl}_2\cdot(\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), **L5** (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromobutane (**2e**) (82.8 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (44.8 mg, 81% yield) as a colorless oil. R_f = 0.82 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 2.61 (dt, J = 8.2, 4.2 Hz, 1H), 1.93 – 1.82 (m, 1H), 1.80 – 1.59 (m, 4H), 1.58 – 1.49 (m, 1H), 1.48 – 1.40 (m, 2H), 1.38 – 1.21 (m, 7H), 0.88 (t, J = 6.9 Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 181.4, 45.3, 37.0, 29.8, 29.6, 28.1, 25.3, 23.9, 22.8, 22.5, 14.1 ppm. IR(neat): 3627, 2923, 2876, 1706, 1688, 1523, 1387, 1210, 1110, 927, 899, 743, 710, 692, 520, 444. HRMS: calcd for $\text{C}_{11}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$ 185.1542, found 185.1547.

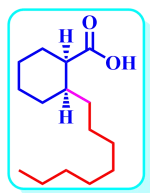


Cis-2-pentylcyclohexane-1-carboxylic acid (4ab). The reaction was performed following the General Procedure B with $\text{NiCl}_2\cdot(\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), **L5** (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromopentane (**2s**) (90.6 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (47.6 mg, 80% yield) as a colorless oil. R_f = 0.83 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 2.54 (dt, J = 8.2, 4.1 Hz, 1H), 1.84 – 1.74 (m, 1H), 1.72 – 1.53 (m, 4H), 1.49 – 1.41 (m, 1H), 1.40 – 1.31 (m, 2H), 1.30 – 1.14 (m, 9H), 0.80 (t, J = 6.9 Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 181.6, 45.3, 37.0, 31.9, 29.8, 28.1, 27.2, 25.3, 23.9, 22.6, 22.5, 14.0 ppm.

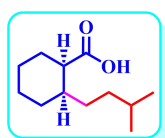
IR(neat): 3620, 2933, 2850, 1704, 1690, 1577, 1397, 1253, 1189, 932, 865, 740, 692, 567, 421. HRMS: calcd for C₁₂H₂₃O₂ [M+H]⁺ 199.1698, found 199.1703.



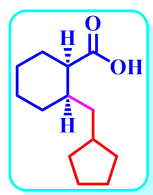
Cis-2-hexylcyclohexane-1-carboxylic acid (4ac). The reaction was performed following the General Procedure B with NiCl₂·(PPh₃)₂ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromohexane (**2f**) (99 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (52.9 mg, 83% yield) as a colorless oil. R_f = 0.87 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 2.61 (dt, *J* = 8.3, 4.3 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.79 – 1.59 (m, 4H), 1.52 (q, *J* = 5.1 Hz, 1H), 1.47 – 1.38 (m, 2H), 1.36 – 1.21 (m, 11H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 181.4, 45.3, 37.1, 31.8, 29.9, 29.4, 28.1, 27.5, 25.3, 23.9, 22.6, 22.5, 14.1 ppm. IR(neat): 3673, 2935, 2857, 1706, 1682, 1453, 1266, 1120, 935, 843, 749, 642, 553, 445. HRMS: calcd for C₁₃H₂₅O₂ [M+H]⁺ 213.1855, found 213.1853.



Cis-2-octylcyclohexane-1-carboxylic acid (4ad). The reaction was performed following the General Procedure B with NiCl₂·(PPh₃)₂ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromooctane (**2g**) (115.9 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (62 mg, 86% yield) as a colorless oil. R_f = 0.86 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 2.61 (dt, *J* = 8.1, 4.2 Hz, 1H), 1.85 (q, *J* = 8.8, 8.0 Hz, 1H), 1.79 – 1.60 (m, 4H), 1.57 – 1.48 (m, 1H), 1.47 – 1.38 (m, 2H), 1.26 (s, 15H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 181.5, 45.3, 37.0, 31.9, 29.9, 29.8, 29.6, 29.3, 28.1, 27.5, 25.3, 23.8, 22.7, 22.5, 14.1 ppm. IR(neat): 3653, 2920, 2854, 1707, 1690, 1422, 1250, 1167, 935, 878, 723, 628, 521, 435. HRMS: calcd for C₁₅H₂₉O₂ [M+H]⁺ 241.2168, found 241.2173.

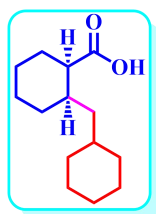


Cis-2-isopentylcyclohexane-1-carboxylic acid (4ae). The reaction was performed following the General Procedure B with NiCl₂·(PPh₃)₂ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromo-3-methylbutane (**2t**) (90.6 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (41.1 mg, 69% yield) as a colorless oil. R_f = 0.85 (Petroleum ether:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ: 2.62 (dt, *J* = 8.2, 4.2 Hz, 1H), 1.80 (s, 1H), 1.79 – 1.62 (m, 4H), 1.56 – 1.43 (m, 3H), 1.41 – 1.30 (m, 3H), 1.26 – 1.10 (m, 3H), 0.87 (d, *J* = 2.1 Hz, 3H), 0.85 (d, *J* = 2.1 Hz, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 180.8, 45.2, 37.3, 36.8, 28.1, 28.1, 27.6, 25.3, 23.8, 22.8, 22.5, 22.4 ppm. IR(neat): 3643, 2927, 2856, 1706, 1688, 1372, 1266, 1178, 945, 864, 746, 630, 527, 422. HRMS: calcd for C₁₂H₂₃O₂ [M+H]⁺ 199.1698, found 199.1697.

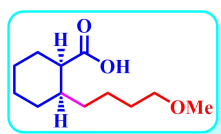


Cis-2-(cyclopentylmethyl)cyclohexane-1-carboxylic acid (4af). The reaction was performed following the General Procedure B with NiCl₂·(PPh₃)₂ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and cyclohexylmethyl bromide (**2u**) (97.8 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (51.1 mg, 81% yield) as a colorless oil. R_f =

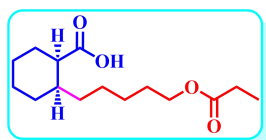
0.86 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 2.59 (dt, $J = 8.1, 4.2$ Hz, 1H), 1.96 – 1.88 (m, 1H), 1.85 – 1.65 (m, 6H), 1.64 – 1.46 (m, 7H), 1.42 (dd, $J = 8.8, 4.1$ Hz, 1H), 1.37 – 1.25 (m, 2H), 1.16 (td, $J = 8.6, 4.3$ Hz, 1H), 1.08 – 0.99 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 180.8, 45.3, 37.5, 36.2, 35.9, 33.2, 32.1, 28.2, 25.3, 25.0, 24.9, 23.9, 22.8 ppm. IR(neat): 3423, 2925, 2851, 2092, 1688, 1637, 1448, 1247, 1212, 570. HRMS: calcd for $\text{C}_{13}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$ 211.1698, found 211.1693.



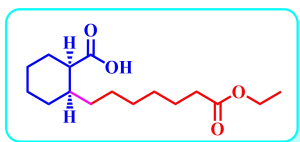
Cis-2-(cyclohexylmethyl)cyclohexane-1-carboxylic acid (4ag). The reaction was performed following the General Procedure B with $\text{NiCl}_2\cdot(\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and cyclohexylmethyl bromide (**2i**) (106.2 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (59.2 mg, 88% yield) as a colorless oil. $R_f = 0.85$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 2.58 (dt, $J = 8.2, 4.3$ Hz, 1H), 2.04 – 1.90 (m, 1H), 1.69 (dt, $J = 23.2, 8.2$ Hz, 9H), 1.56 – 1.44 (m, 2H), 1.39 – 1.25 (m, 4H), 1.25 – 1.12 (m, 3H), 1.11 – 1.05 (m, 1H), 1.03 – 0.72 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 181.2, 45.4, 37.5, 34.8, 34.3, 33.7, 32.7, 28.4, 26.8, 26.5, 26.3, 25.2, 23.9, 22.5 ppm. IR(neat): 3628, 2928, 2824, 1702, 1688, 1552, 1370, 1223, 1130, 974, 892, 798, 673, 515, 472. HRMS: calcd for $\text{C}_{14}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$ 225.1855, found 225.1858.



Cis-2-(4-methoxybutyl)cyclohexane-1-carboxylic acid (4ah). The reaction was performed following the General Procedure B with $\text{NiCl}_2\cdot(\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and 1-bromo-4-methoxybutane (**2v**) (100.2 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (34.1 mg, 53% yield) as a colorless oil. $R_f = 0.43$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 3.37 (t, $J = 6.5$ Hz, 2H), 3.33 (s, 3H), 2.63 (d, $J = 6.6$ Hz, 1H), 1.88 (d, $J = 15.0$ Hz, 1H), 1.82 – 1.63 (m, 4H), 1.61 – 1.52 (m, 3H), 1.49 – 1.40 (m, 3H), 1.37 – 1.26 (m, 4H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 185.1, 72.8, 58.5, 37.1, 29.8, 29.7, 28.0, 25.6, 25.5, 24.1, 23.8, 22.6 ppm. IR(neat): 3630, 3180, 1703, 1685, 1662, 1499, 1432, 1302, 1267, 1154, 1074, 757, 610, 536, 477, 418. HRMS: calcd for $\text{C}_{12}\text{H}_{23}\text{O}_3$ $[\text{M}+\text{H}]^+$ 199.1698, found 199.1703.

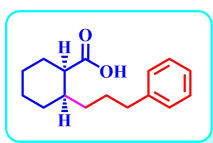


Cis-2-(5-(propionyloxy)pentyl)cyclohexane-1-carboxylic acid (4ai). The reaction was performed following the General Procedure B with $\text{NiCl}_2\cdot(\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and 5-bromopentyl propionate (**2w**) (133.7 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (48.7 mg, 60% yield) as a colorless oil. $R_f = 0.32$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 4.08 – 4.03 (m, 2H), 2.55 – 2.43 (m, 1H), 2.23 – 2.19 (m, 2H), 1.78 – 1.74 (m, 1H), 1.66 – 1.49 (m, 7H), 1.42 – 1.22 (m, 9H), 1.18 (d, $J = 1.8$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 180.8, 173.9, 60.2, 45.1, 37.0, 34.3, 29.8, 29.2, 28.1, 27.1, 25.4, 24.9, 23.7, 22.6, 14.2 ppm. IR(neat): 3701, 2998, 2851, 1730, 1703, 1688, 1647, 1542, 1423, 1344, 1176, 1032, 955, 846, 702, 504, 493. HRMS: calcd for $\text{C}_{15}\text{H}_{27}\text{O}_4$ $[\text{M}+\text{H}]^+$ 271.1909, found 271.1911.



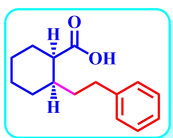
Cis-2-(7-ethoxy-7-oxoheptyl)cyclohexane-1-carboxylic acid (4aj).

The reaction was performed following the General Procedure B with $\text{NiCl}_2 \cdot (\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and ethyl 7-bromoheptanoate (**2x**) (142.2 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (52.9 mg, 62% yield) as a colorless oil. $R_f = 0.37$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 4.13 (q, $J = 7.1$ Hz, 2H), 2.61 (dt, $J = 8.1, 4.1$ Hz, 1H), 2.28 (t, $J = 7.5$ Hz, 2H), 1.85 (p, $J = 9.0, 7.1$ Hz, 1H), 1.79 – 1.59 (m, 6H), 1.56 – 1.39 (m, 3H), 1.39 – 1.26 (m, 9H), 1.26 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 180.6, 174.0, 60.2, 45.1, 36.9, 34.3, 29.8, 29.3, 29.1, 28.1, 27.3, 25.3, 24.9, 23.8, 22.5, 14.2 ppm. IR(neat): 3857, 3443, 2075, 1715, 1689, 1635, 1374, 1246, 581, 419. HRMS: calcd for $\text{C}_{16}\text{H}_{29}\text{O}_4$ $[\text{M}+\text{H}]^+$ 285.3991, found 285.3997.



Cis-2-(3-phenylpropyl)cyclohexane-1-carboxylic acid (4ak). The reaction was performed following the General Procedure B with $\text{NiCl}_2 \cdot (\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and (3-bromopropyl)benzene (**2y**) (119.4 mg, 0.6 mmol).

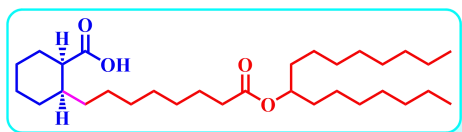
The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (52.5 mg, 71% yield) as a colorless oil. $R_f = 0.37$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 4.13 (q, $J = 7.1$ Hz, 2H), 2.61 (dt, $J = 8.1, 4.1$ Hz, 1H), 2.28 (t, $J = 7.5$ Hz, 2H), 1.85 (p, $J = 9.0, 7.1$ Hz, 1H), 1.79 – 1.59 (m, 6H), 1.56 – 1.39 (m, 3H), 1.39 – 1.26 (m, 9H), 1.26 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 181.2, 142.6, 128.3, 128.2, 125.6, 45.1, 36.9, 35.9, 29.7, 29.5, 28.1, 25.3, 23.8, 22.5 ppm. IR(neat): 3449, 2936, 2858, 2077, 1687, 1638, 1496, 1453, 1417, 745, 698, 427. HRMS: calcd for $\text{C}_{16}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$ 247.3526, found 247.3523.



Cis-2-phenethylcyclohexane-1-carboxylic acid (4al). The reaction was performed following the General Procedure B with $\text{NiCl}_2 \cdot (\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and (2-bromoethyl)benzene (**2i**) (111 mg, 0.6 mmol). The crude product was

purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (59.2 mg, 88% yield) as a colorless oil. $R_f = 0.80$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 7.28 – 7.23 (m, 2H), 7.23 – 7.05 (m, 3H), 2.73 – 2.60 (m, 2H), 2.62 – 2.52 (m, 1H), 1.97 – 1.84 (m, 1H), 1.83 – 1.66 (m, 4H), 1.66 – 1.55 (m, 3H), 1.52 (q, $J = 8.2, 7.1$ Hz, 1H), 1.35 (q, $J = 8.2$ Hz, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 180.9, 142.4, 128.3, 128.2, 125.7, 44.9, 36.8, 33.8, 32.3, 28.1, 25.6, 23.6, 22.8 ppm. IR(neat): 3633, 2930, 2827, 1709, 1689, 1545, 1377, 1230, 1132, 990, 854, 722, 653, 556, 470. HRMS: calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$ 233.1542, found 233.1546.

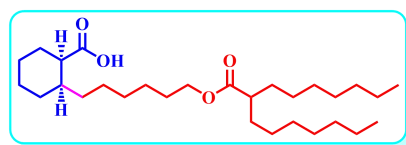
Cis-2-(8-(hexadecan-8-yloxy)-8-oxooctyl)cyclohexane-1-carboxylic acid (4am). The reaction was performed following the General Procedure B with $\text{NiCl}_2 \cdot (\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and hexadecan-8-yl-8-bromooctanoate (**2z**)



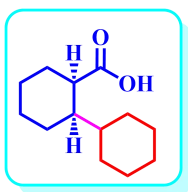
(268.5 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (108.3 mg, 73% yield) as a colorless oil. $R_f =$

0.81 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 4.87 (p, J = 6.3 Hz, 1H), 2.60 (dt, J = 8.1, 4.2 Hz, 1H), 2.28 (t, J = 7.5 Hz, 2H), 1.87 – 1.80 (m, 1H), 1.76 – 1.58 (m, 6H), 1.49 (p, J = 6.8, 6.1 Hz, 5H), 1.27 (d, J = 10.3 Hz, 35H), 0.88 (t, J = 6.7 Hz, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 180.7, 173.8, 74.1, 45.1, 36.9, 34.7, 34.1, 31.8, 29.9, 29.52, 29.49, 29.2, 29.1, 28.1, 27.4, 25.3, 25.1, 23.8, 22.7, 22.5, 14.1 ppm. IR(neat): 3449, 2927, 2855, 2074, 1731, 1716, 1686, 1637, 1464, 1376, 1252, 1175, 1123, 551, 428. HRMS: calcd for $\text{C}_{31}\text{H}_{59}\text{O}_4$ $[\text{M}+\text{H}]^+$ 495.7978, found 495.7972.

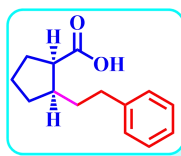
Cis-2-(6-((2-heptylnonanoyl)oxy)hexyl)cyclohexane-1-carboxylic acid (4an). The reaction was performed following the General Procedure B with $\text{NiCl}_2\cdot(\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and 6-bromoethyl 2-heptylnonanoate (**2a**) (251.4 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (107.8 mg, 77% yield) as a colorless oil. R_f = 0.84 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 4.06 (t, J = 6.7 Hz, 2H), 2.63 – 2.59 (m, 1H), 2.34 – 2.27 (m, 1H), 1.86 – 1.83 (m, 1H), 1.80 – 1.73 (m, 1H), 1.73 – 1.65 (m, 2H), 1.62 – 1.55 (m, 5H), 1.54 – 1.39 (m, 5H), 1.36 – 1.30 (m, 6H), 1.28 – 1.23 (m, 23H), 0.89 – 0.85 (m, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 180.4, 176.8, 64.1, 45.8, 45.1, 37.0, 32.5, 31.8, 31.7, 29.5, 29.4, 29.33, 29.25, 29.2, 28.6, 28.0, 27.5, 27.4, 25.9, 25.3, 23.7, 22.7, 22.6, 14.11, 14.07 ppm. IR(neat): 3453, 2928, 2856, 2076, 1731, 1717, 1689, 1635, 1464, 1376, 1259, 1163, 617, 443. HRMS: calcd for $\text{C}_{29}\text{H}_{55}\text{O}_4$ $[\text{M}+\text{H}]^+$ 467.7446, found 467.7443.



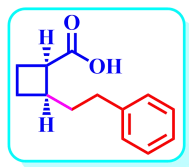
Cis-[1,1'-bi(cyclohexane)]-2-carboxylic acid (4ao). The reaction was performed following the General Procedure B with $\text{NiCl}_2\cdot(\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1a** (46.2 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and bromocyclohexane (**2a**) (97.8 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (35.9 mg, 57% yield) as a colorless oil. R_f = 0.76 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 2.90 – 2.87 (m, 1H), 2.09 – 2.01 (m, 1H), 1.93 – 1.83 (m, 2H), 1.81 – 1.67 (m, 4H), 1.66 – 1.49 (m, 5H), 1.39 – 1.34 (m, 1H), 1.27 – 1.10 (m, 5H), 0.93 – 0.72 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 181.3, 44.8, 41.1, 39.5, 31.2, 30.9, 29.4, 26.5, 26.4, 26.3, 26.1, 25.0, 22.1 ppm. IR(neat): 3817, 3423, 2925, 2851, 2092, 1687, 1637, 1448, 1247, 1212, 570. HRMS: calcd for $\text{C}_{13}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$ 211.3205, found 211.3201.



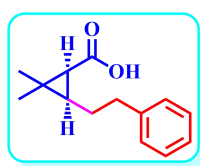
Cis-2-phenethylcyclopentane-1-carboxylic acid (4bl). The reaction was performed following the General Procedure B with $\text{NiCl}_2\cdot(\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1e** (42.0 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and (2-bromoethyl)benzene (**2l**) (111.0 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (48.5 mg, 74% yield) as a colorless oil. R_f = 0.62 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 7.25 (d, J = 7.3 Hz, 2H), 7.19 – 7.13 (m, 3H), 2.88 (s, 1H), 2.70 – 2.60 (m, 2H), 2.15 – 2.05 (m, 1H), 1.98 – 1.91 (m, 1H), 1.89 – 1.70 (m, 4H), 1.65 – 1.48 (m, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 175.3, 142.3, 128.4, 128.3, 125.7, 43.2, 34.8, 32.8, 30.9, 28.6, 23.7 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 3350, 2963, 2874, 2732, 1705, 1683, 1663, 1450, 1319, 1188, 1065, 988, 843, 753, 502, 426. HRMS: calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$ 219.1385, found 219.1383.



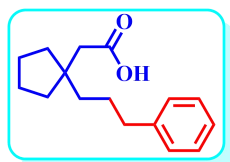
Cis-2-phenethylcyclopentane-1-carboxylic acid (4bl). The reaction was performed following the General Procedure B with $\text{NiCl}_2\cdot(\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), L5 (32.6 mg, 0.09 mmol), **1e** (42.0 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and (2-bromoethyl)benzene (**2l**) (111.0 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (48.5 mg, 74% yield) as a colorless oil. R_f = 0.62 (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 7.25 (d, J = 7.3 Hz, 2H), 7.19 – 7.13 (m, 3H), 2.88 (s, 1H), 2.70 – 2.60 (m, 2H), 2.15 – 2.05 (m, 1H), 1.98 – 1.91 (m, 1H), 1.89 – 1.70 (m, 4H), 1.65 – 1.48 (m, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 175.3, 142.3, 128.4, 128.3, 125.7, 43.2, 34.8, 32.8, 30.9, 28.6, 23.7 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 3350, 2963, 2874, 2732, 1705, 1683, 1663, 1450, 1319, 1188, 1065, 988, 843, 753, 502, 426. HRMS: calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$ 219.1385, found 219.1383.



Cis-2-phenethylcyclobutane-1-carboxylic acid (4cl). The reaction was performed following the General Procedure B with $\text{NiCl}_2 \cdot (\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), **L5** (32.6 mg, 0.09 mmol), **1h** (37.8 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and (2-bromoethyl)benzene (**2I**) (111.0 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (44.7 mg, 73% yield) as a colorless oil. $R_f = 0.62$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 9.14 (s, 1H), 7.17 (t, $J = 6.5$ Hz, 2H), 7.11 – 7.05 (m, 3H), 3.19 (s, 1H), 2.65 – 2.57 (m, 1H), 2.47 (dd, $J = 21.3, 12.1$ Hz, 2H), 2.24 – 2.16 (m, 1H), 2.06 – 1.94 (m, 2H), 1.89 – 1.75 (m, 2H), 1.70 – 1.60 (m, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 175.3, 141.9, 128.4, 128.3, 125.7, 37.2, 33.4, 32.9, 24.9, 20.4 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 3402, 2927, 2804, 2723, 1704, 1683, 1497, 1343, 1209, 1004, 986, 832, 702, 656, 586, 372. HRMS: calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$ 205.1229, found 205.1228.



Cis-2-phenethylcyclobutane-1-carboxylic acid (4dl). The reaction was performed following the General Procedure B with $\text{NiCl}_2 \cdot (\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), **L5** (32.6 mg, 0.09 mmol), **1i** (40.0 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and (2-bromoethyl)benzene (**2I**) (111.0 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (65.4 mg, 82% yield) as a colorless oil. $R_f = 0.65$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 7.19 (dt, $J = 6.3, 1.8$ Hz, 2H), 7.12 – 7.08 (m, 3H), 2.63 – 2.51 (m, 2H), 1.94 – 1.87 (m, 2H), 1.36 (d, $J = 8.8$ Hz, 1H), 1.17 – 1.11 (m, 1H), 1.07 (d, $J = 5.7$ Hz, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 178.3, 142.0, 128.6, 128.2, 125.7, 35.9, 34.5, 29.0, 28.5, 27.0, 25.5, 14.2 ppm. IR(neat): 3402, 2927, 2853, 2798, 1705, 1682, 1662, 1475, 1372, 1227, 1163, 952, 847, 753, 664, 562, 482, 417. HRMS: calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$ 219.1385, found 219.1383.



2-(1-(3-phenylpropyl)cyclopentyl)acetic acid (4el). The reaction was performed following the General Procedure B with $\text{NiCl}_2 \cdot (\text{PPh}_3)_2$ (39.3 mg, 0.06 mmol), **L5** (32.6 mg, 0.09 mmol), **1j** (50.4 mg, 0.3 mmol), Zn powder (39.2 mg, 0.6 mmol), and (2-bromoethyl)benzene (**2I**) (111.0 mg, 0.6 mmol). The crude product was purified by flash chromatography on silica gel (eluted with Petroleum ether:EtOAc = 5:1) to give the product (41.8 mg, 83% yield) as a colorless oil. $R_f = 0.72$ (Petroleum ether:EtOAc = 2:1). ^1H NMR (400 MHz, CDCl_3) δ : 7.26 (dd, $J = 5.1, 3.1$ Hz, 2H), 7.20 – 7.14 (m, 3H), 2.59 (t, $J = 7.6$ Hz, 2H), 2.33 (s, 2H), 1.68 – 1.55 (m, 8H), 1.48 (q, $J = 8.2, 6.5$ Hz, 4H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ : 182.6, 142.6, 128.3, 128.2, 125.6, 44.6, 42.3, 38.8, 37.6, 36.6, 32.8, 26.9, 24.3 ppm. One resonance was not observed due to overlapping resonances. IR(neat): 3313, 2934, 2855, 2763, 1705, 1682, 1490, 1313, 1207, 1173, 932, 982, 857, 777, 672, 517, 493. HRMS: calcd for $\text{C}_{16}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$ 247.1698, found 247.1700.

9. References

1. Bercot, E. A.; Rovis, T. *J. Am. Chem. Soc.* **2005**, *127*, 247.

10. NMR Spectra

Cis-2-(cyclohexanecarbonyl)cyclohexane-1-carboxylic acid (**3aa**)

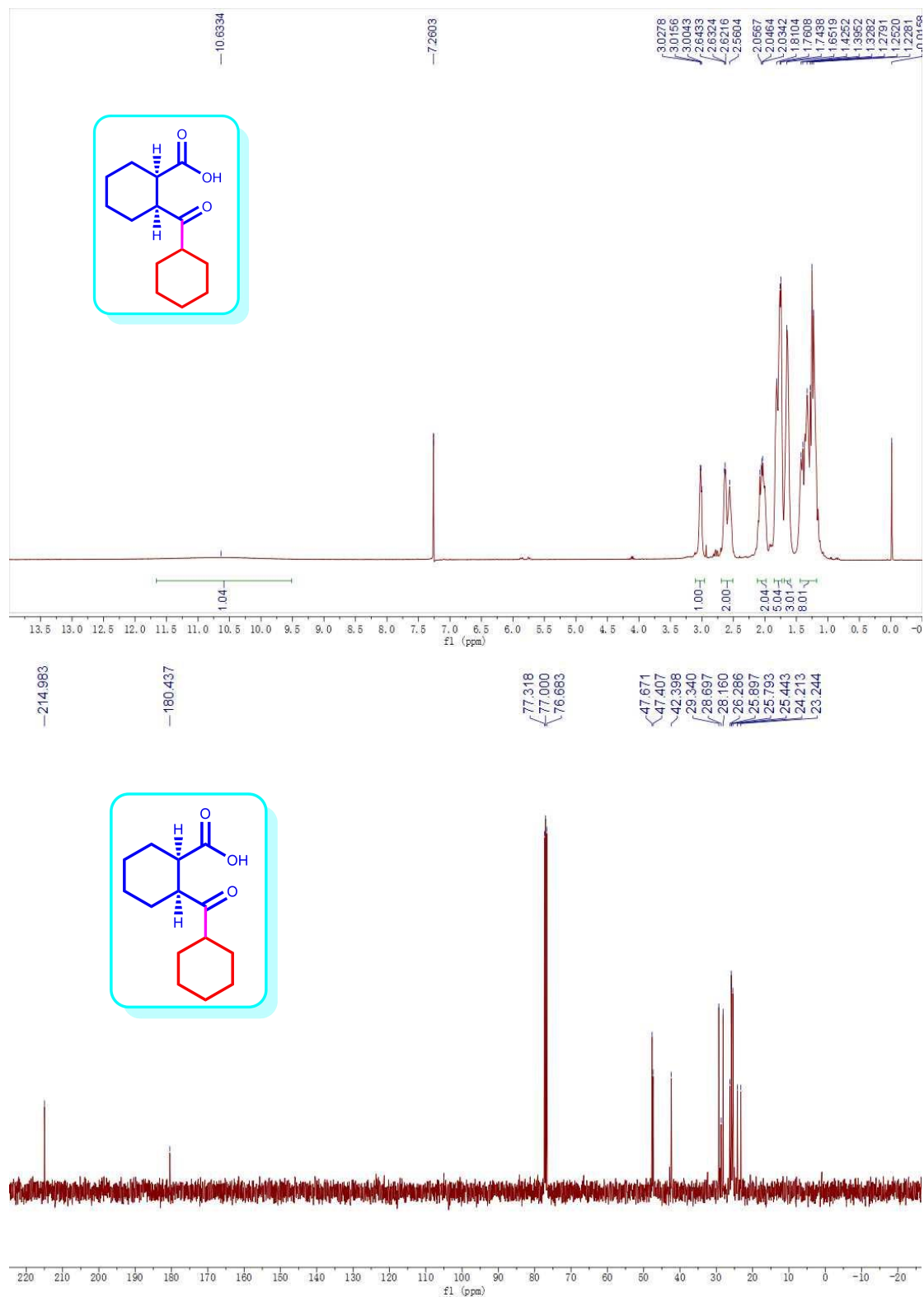


Figure S8. ^1H (400 MHz) and ^{13}C { ^1H } (101 MHz) NMR spectra of **3aa** in CDCl_3

***Cis*-2-(cyclopentanecarbonyl)cyclohexane-1-carboxylic acid (3ab)**

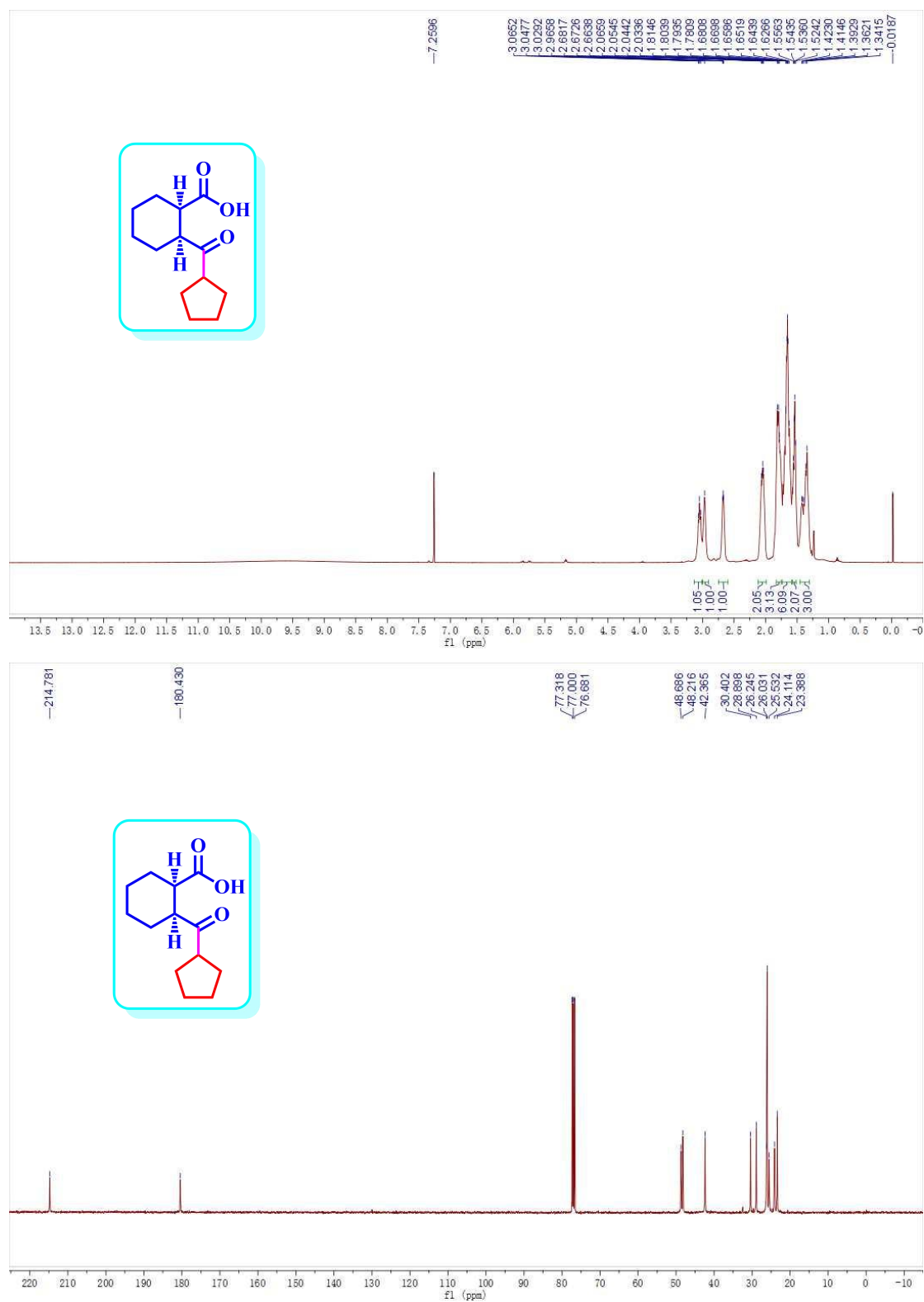


Figure S9. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3ab in CDCl₃

Cis-2-isobutyrylcyclohexane-1-carboxylic acid (**3ac**)

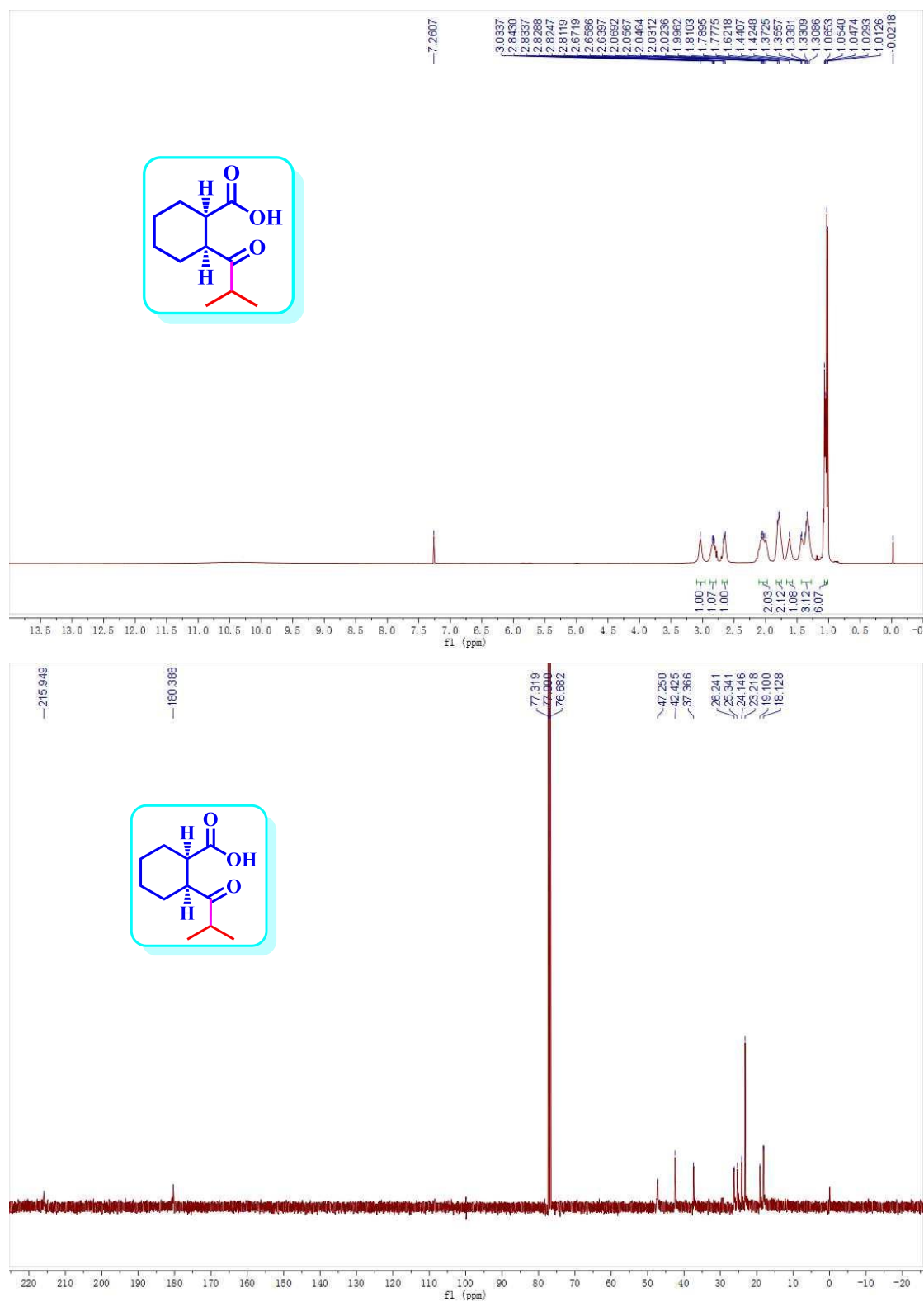


Figure S10. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of **3ac** in CDCl₃

***Cis*-2-(2-ethylbutanoyl)cyclohexane-1-carboxylic acid (3ad).**

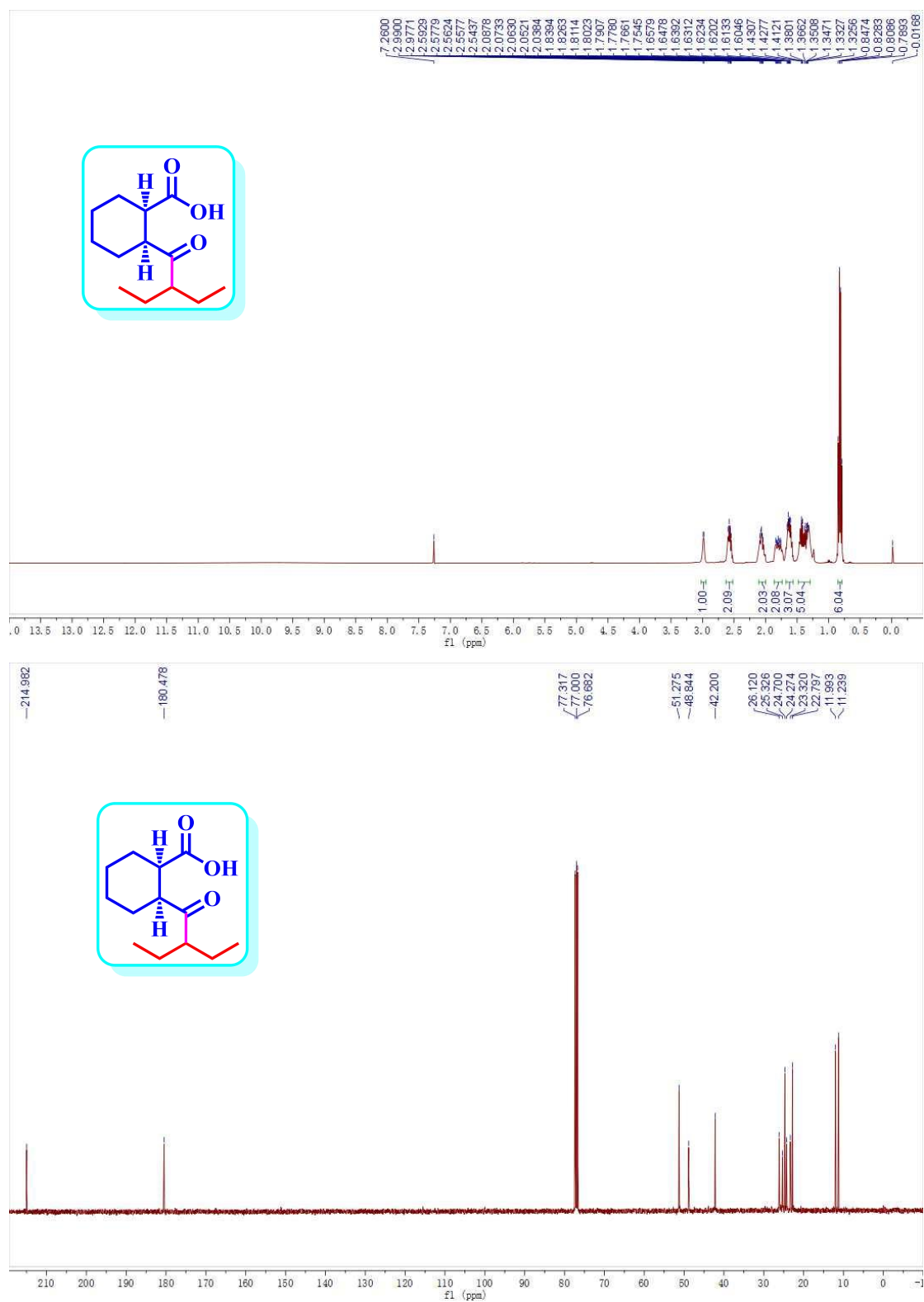


Figure S11. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3ad in CDCl₃

Cis-2-pentanoylcyclohexane-1-carboxylic acid (**3ae**)

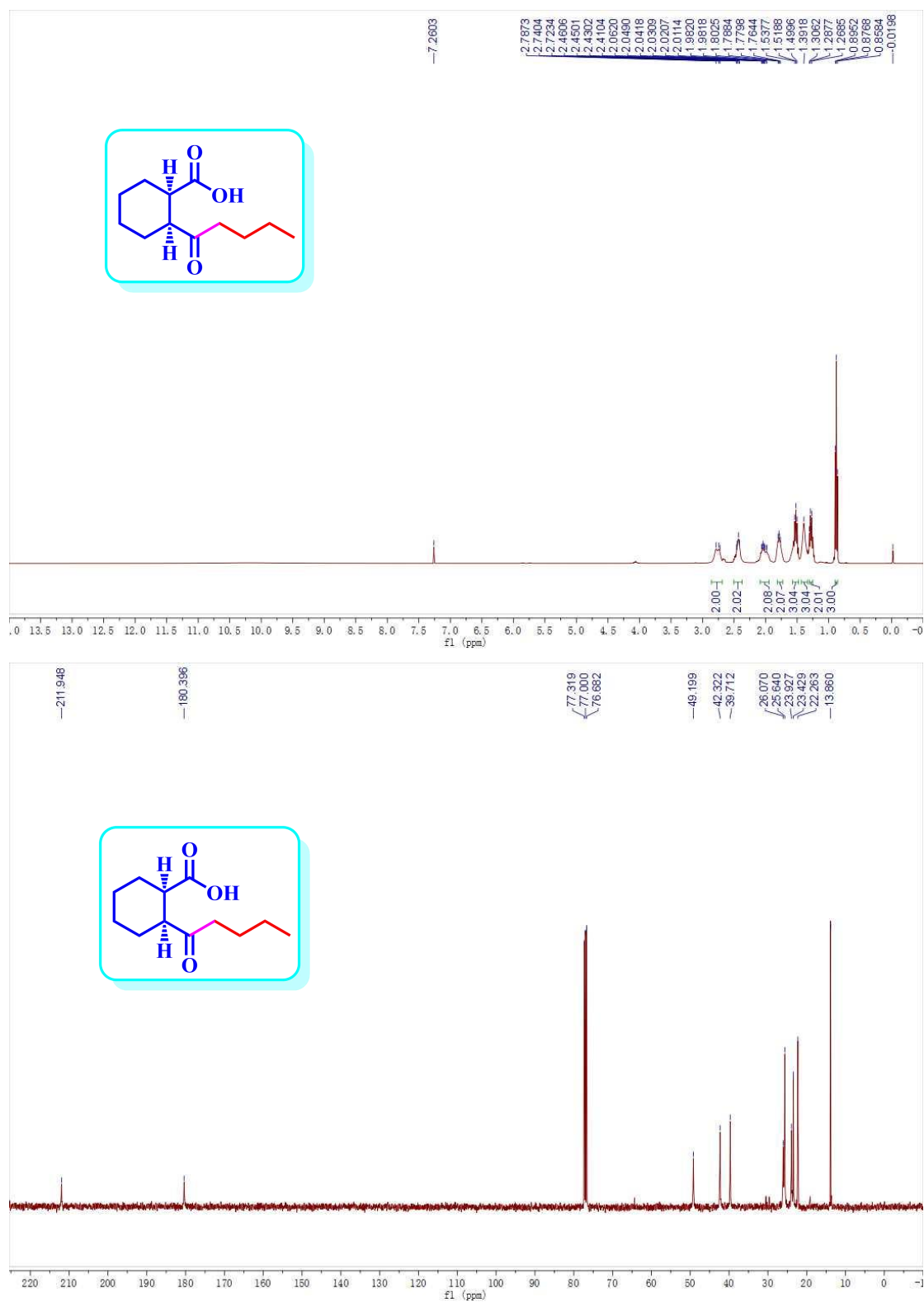


Figure S12. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of **3ae** in CDCl₃

Cis-2-heptanoylcyclohexane-1-carboxylic acid (3af)

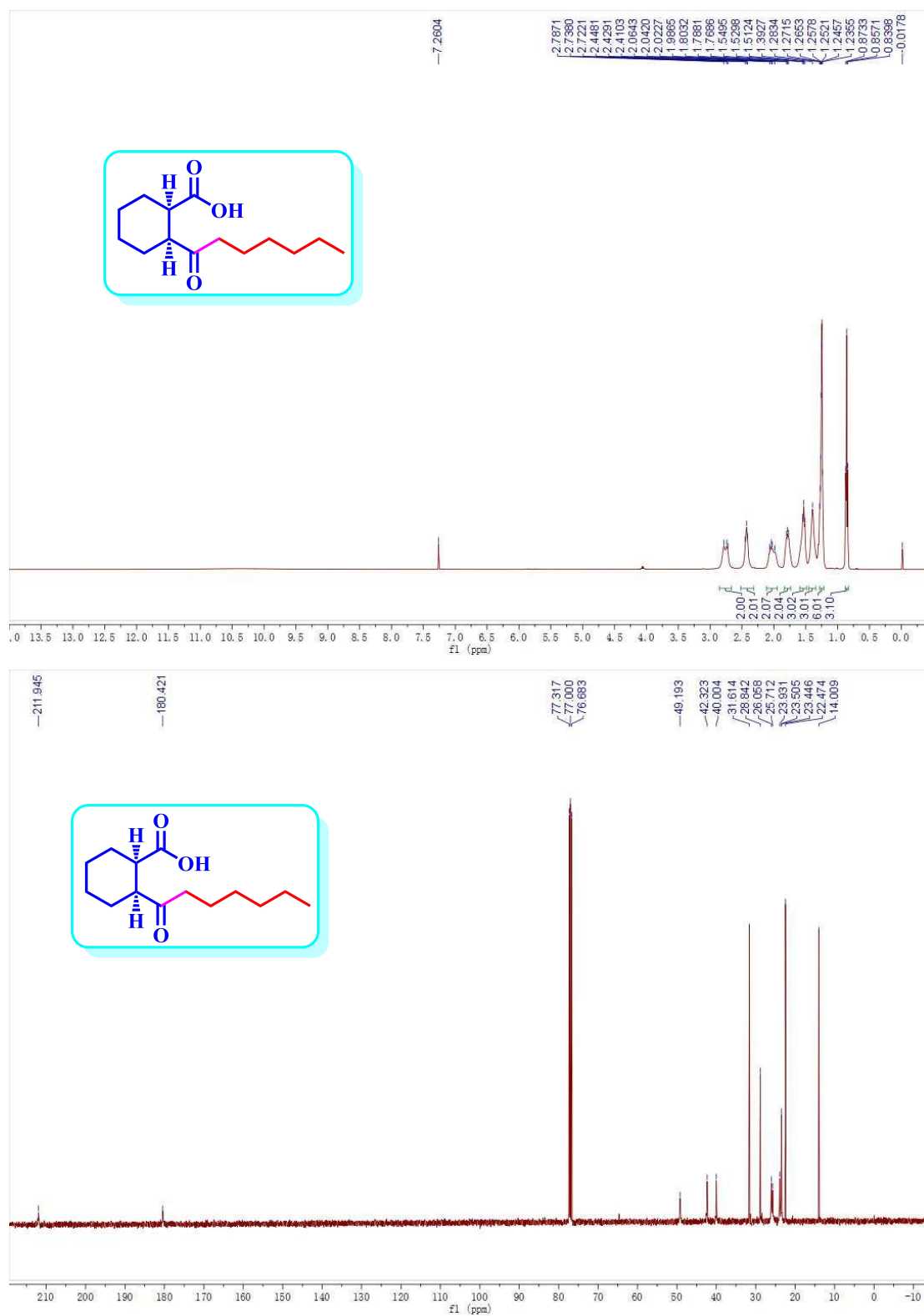


Figure S13. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3af in CDCl₃

***Cis*-2-nonanoylcyclohexane-1-carboxylic acid (3ag)**

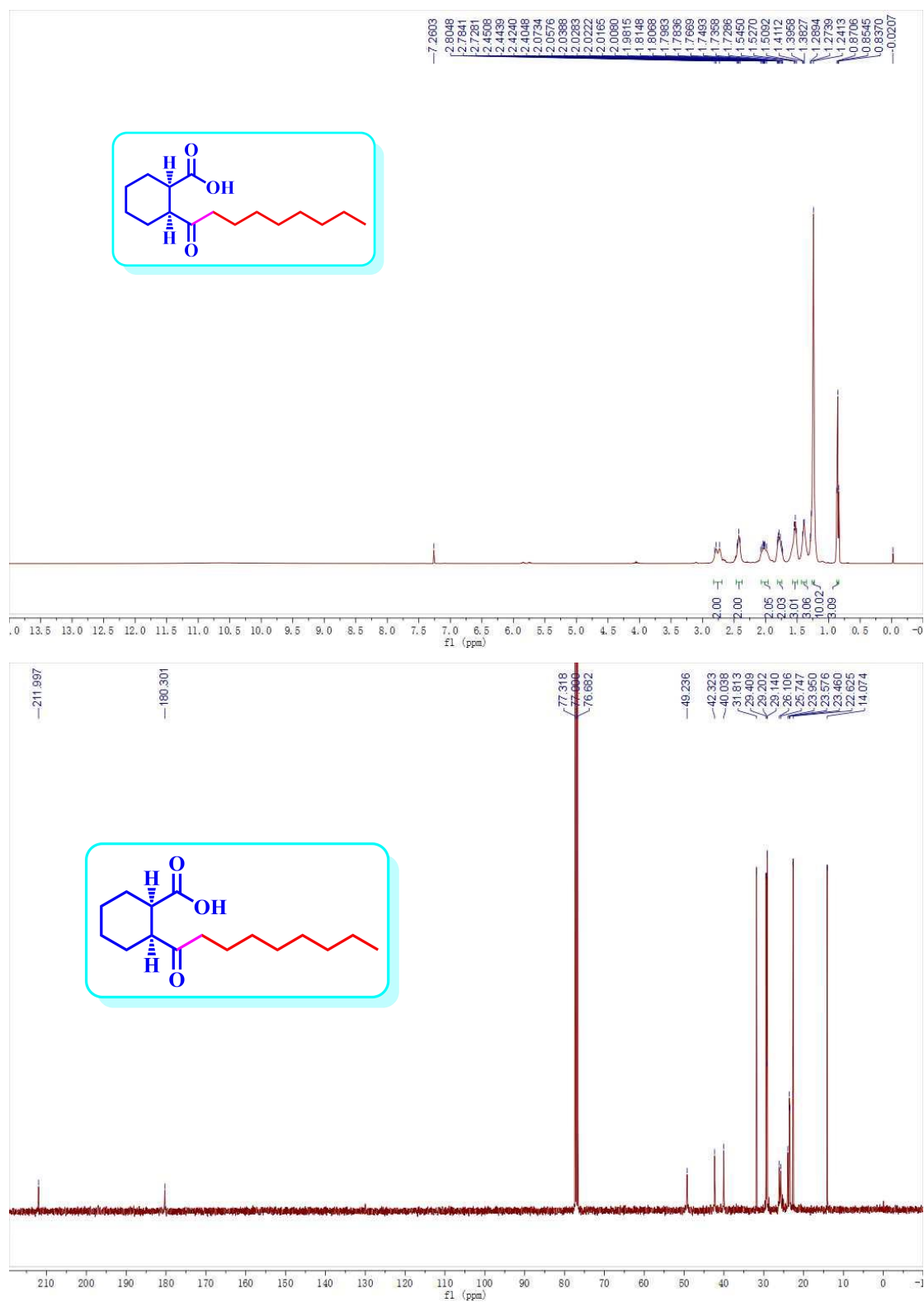


Figure S14. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3ag in CDCl₃

***Cis*-2-(3-methylbutanoyl)cyclohexane-1-carboxylic acid (3ah)**

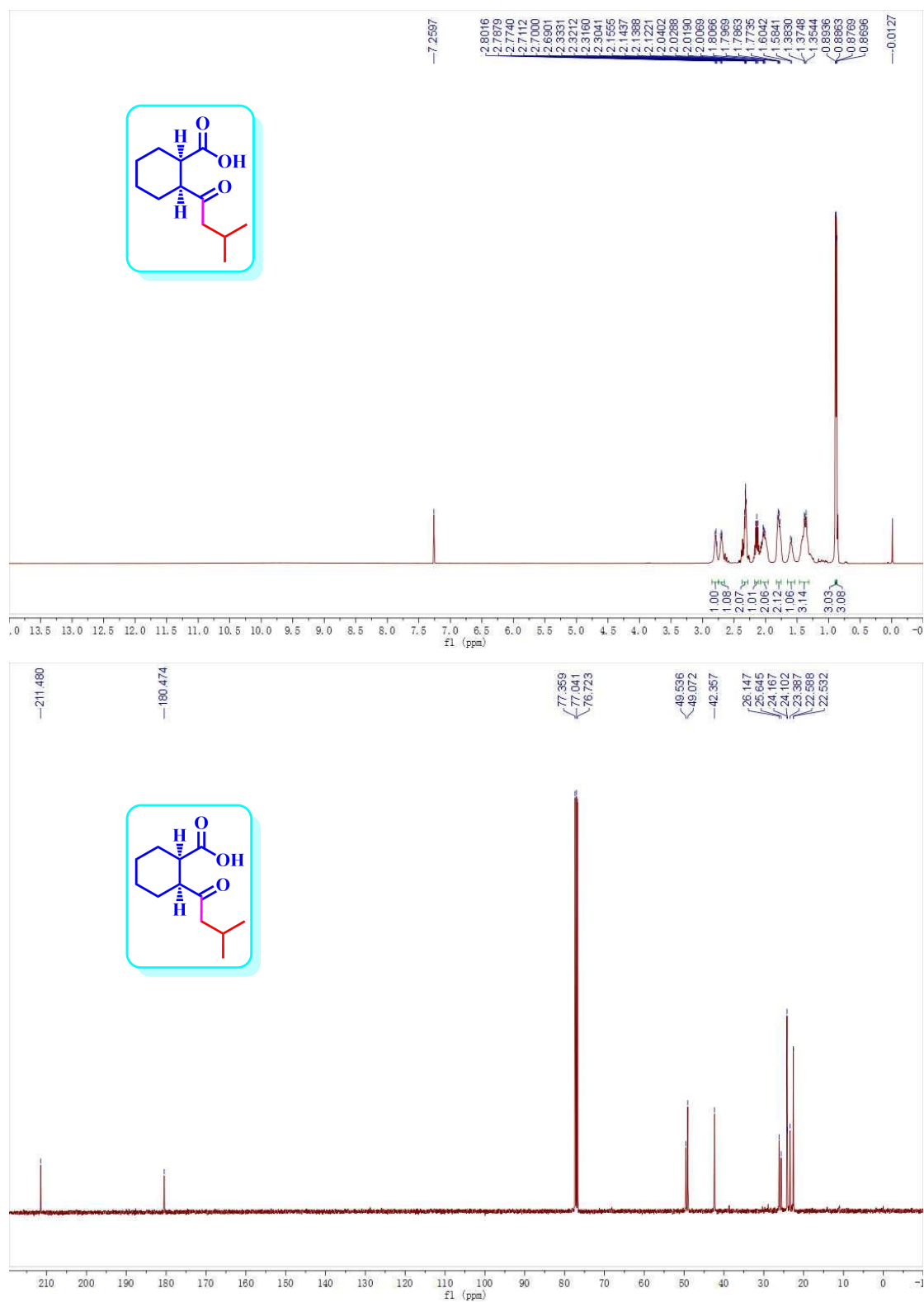


Figure S15. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3ah in CDCl₃

Cis-2-(2-cyclohexylacetyl)cyclohexane-1-carboxylic acid (3ai)

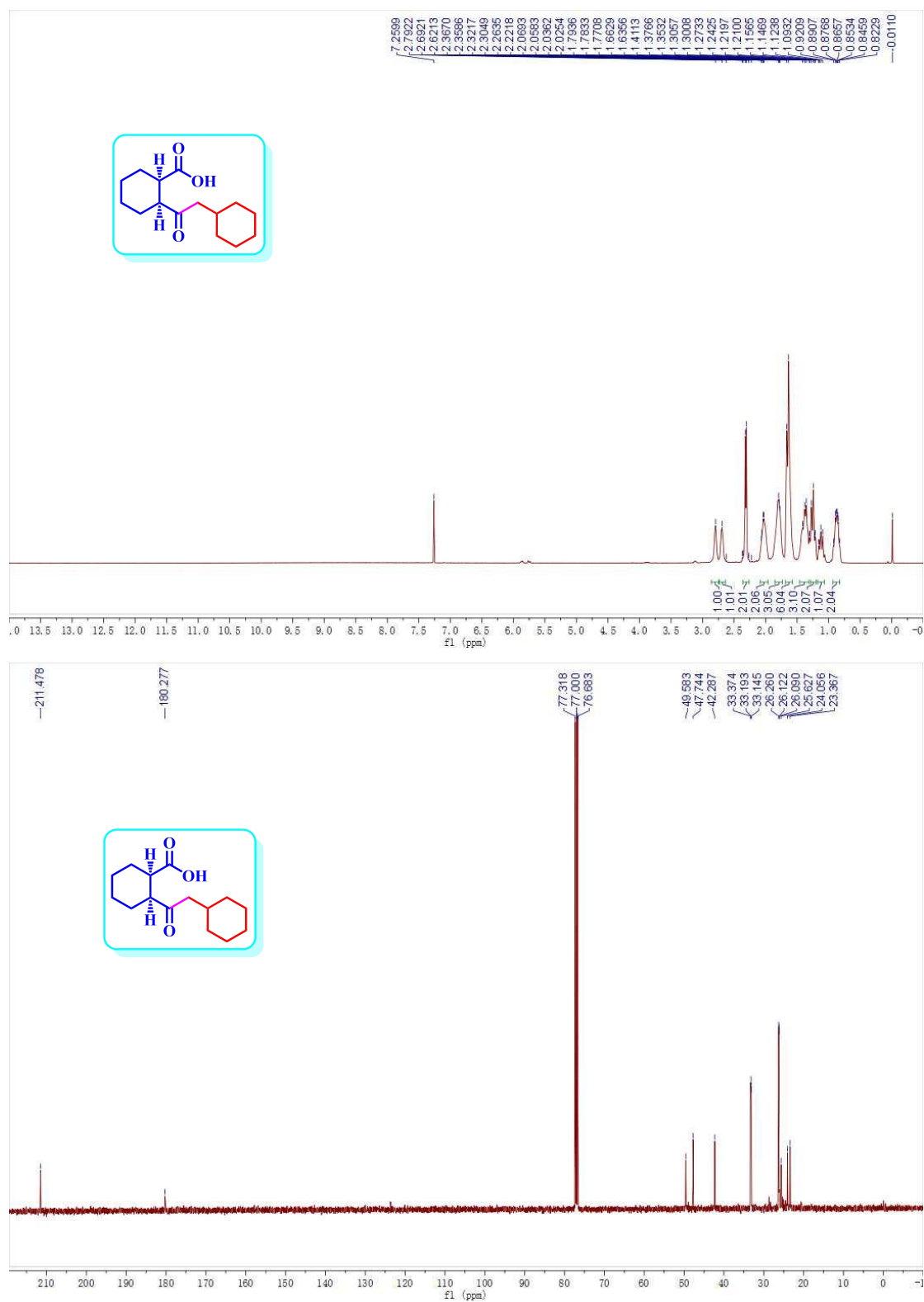
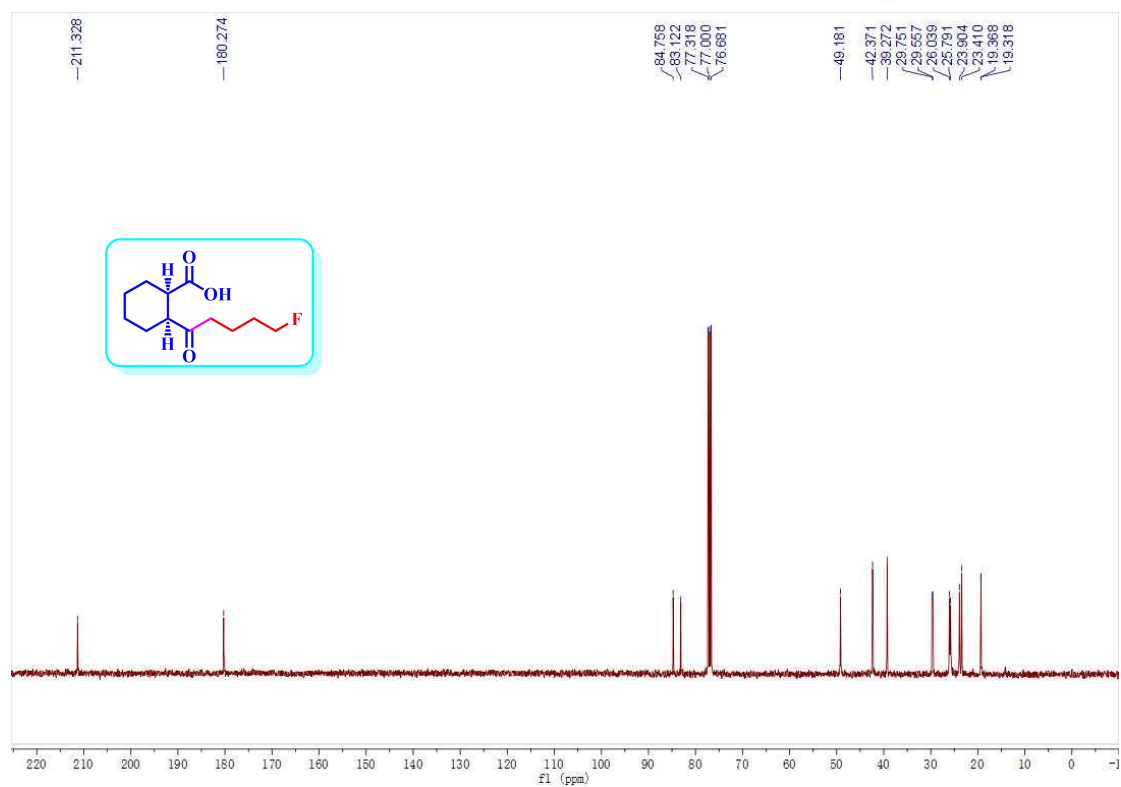
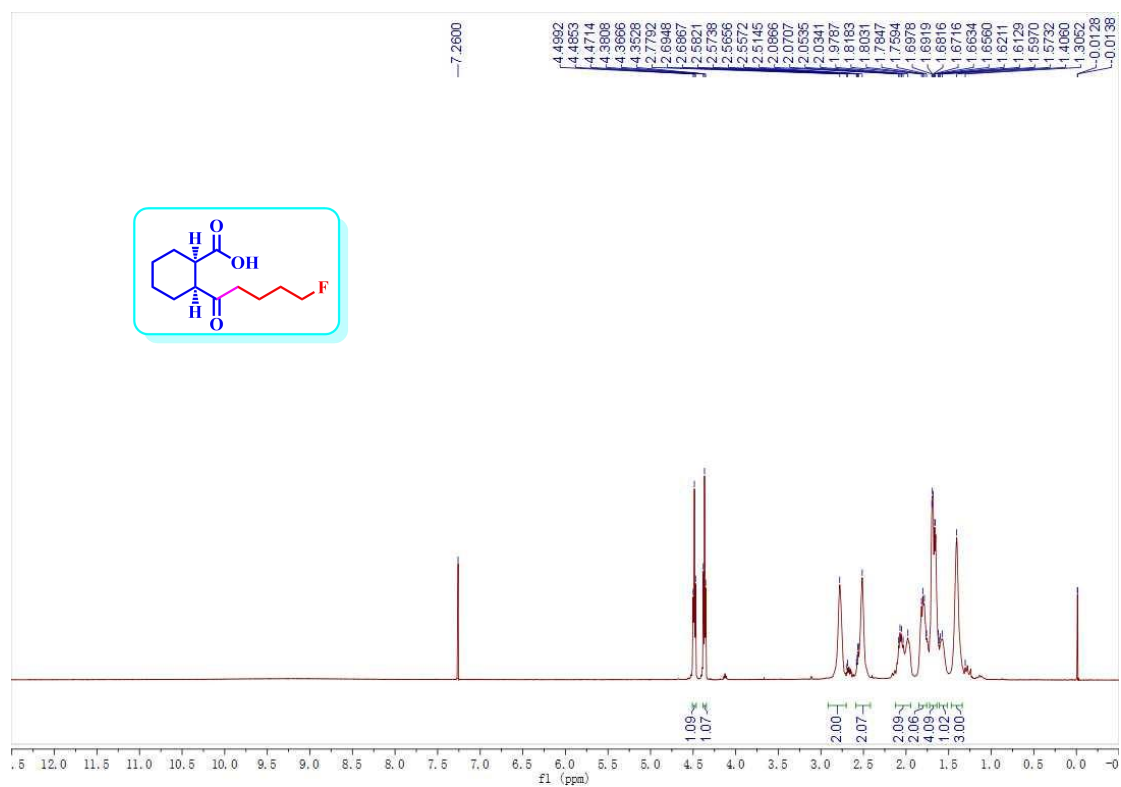


Figure S16. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3ai in CDCl₃

***Cis*-2-(5-fluoropentanoyl)cyclohexane-1-carboxylic acid (3aj)**



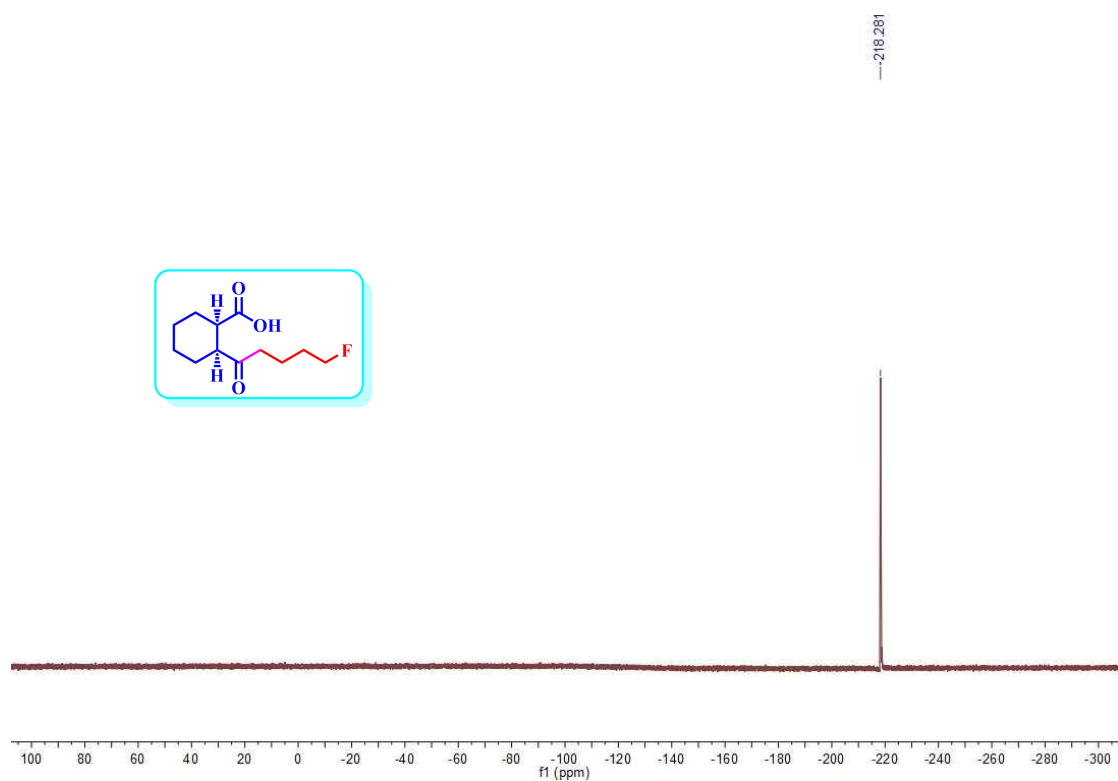


Figure S17. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR and ^{19}F NMR spectra of 3aj in CDCl_3

Cis-2-(5-chloropentanoyl)cyclohexane-1-carboxylic acid (3ak)

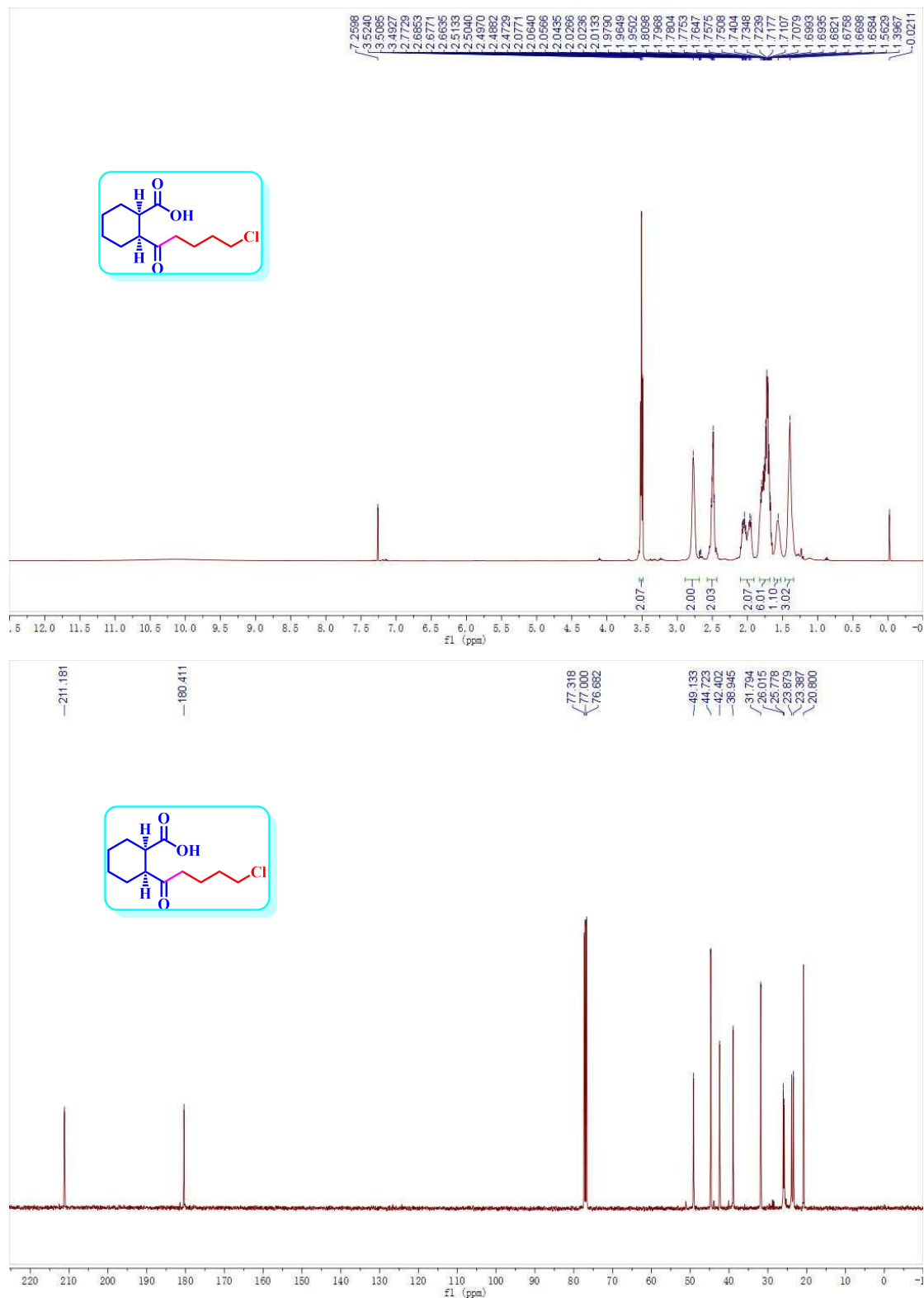


Figure S18. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 3ak in CDCl_3

Cis -2-(3-phenylpropanoyl)cyclohexane-1-carboxylic acid (3a)

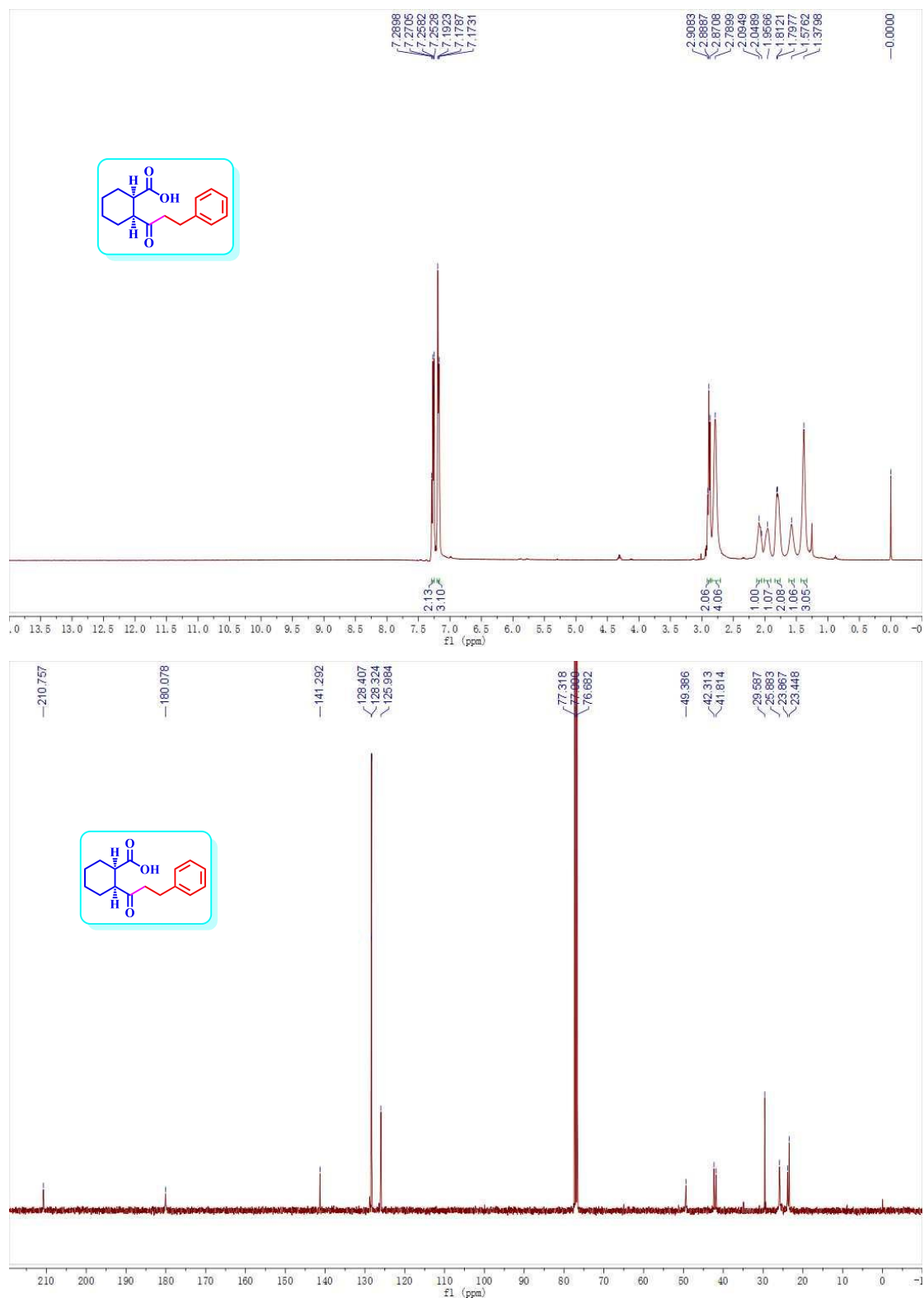


Figure S19. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3a in CDCl₃

***Cis*-2-(3-(2,3-dihydrobenzofuran-6-yl)propanoyl)cyclohexane-1-carboxylic acid (3am)**

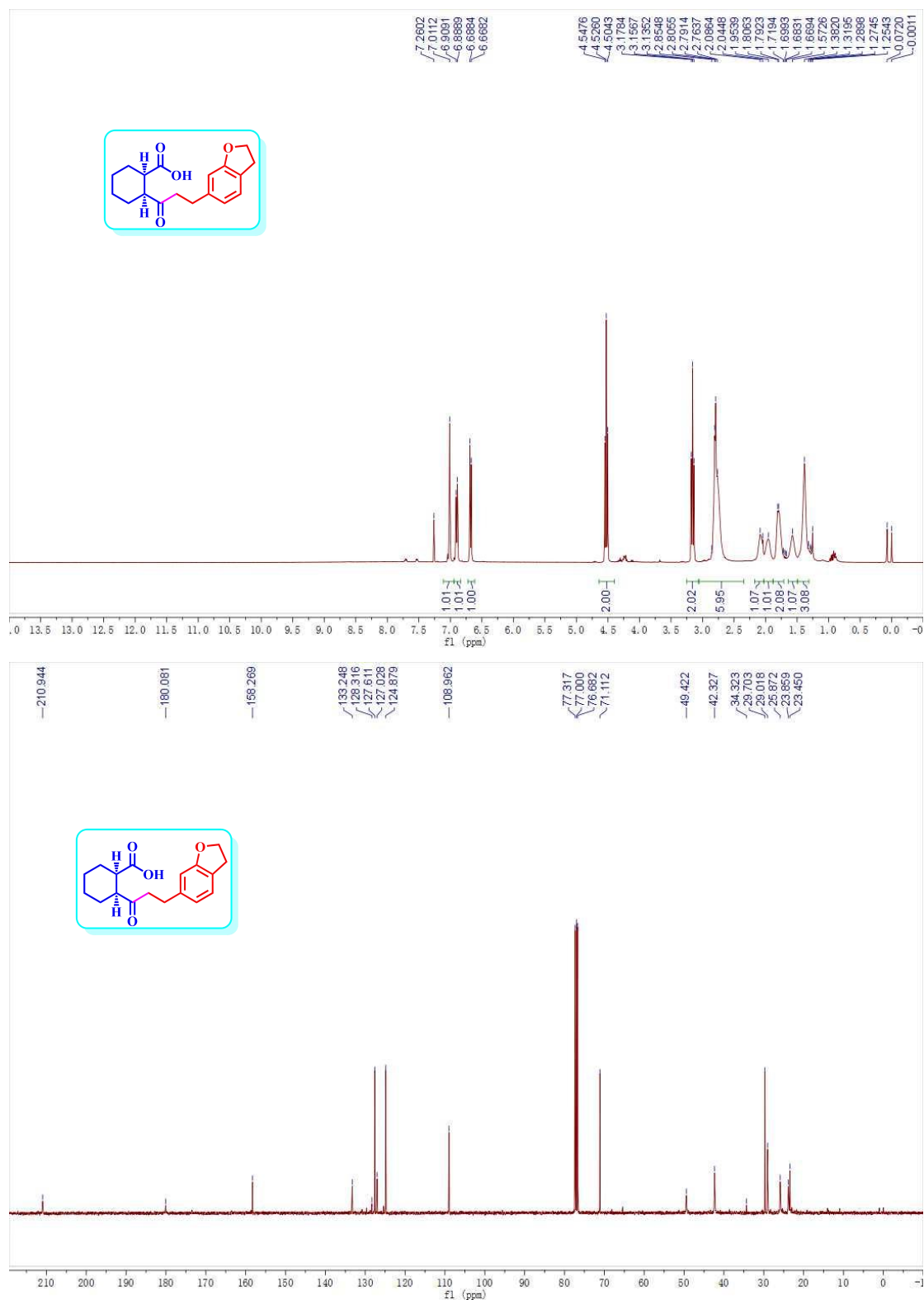


Figure S20. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 3am in CDCl_3

***Cis*-2-(3-(4-(methoxycarbonyl)phenyl)propanoyl)cyclohexane-1-carboxylic acid (3an)**

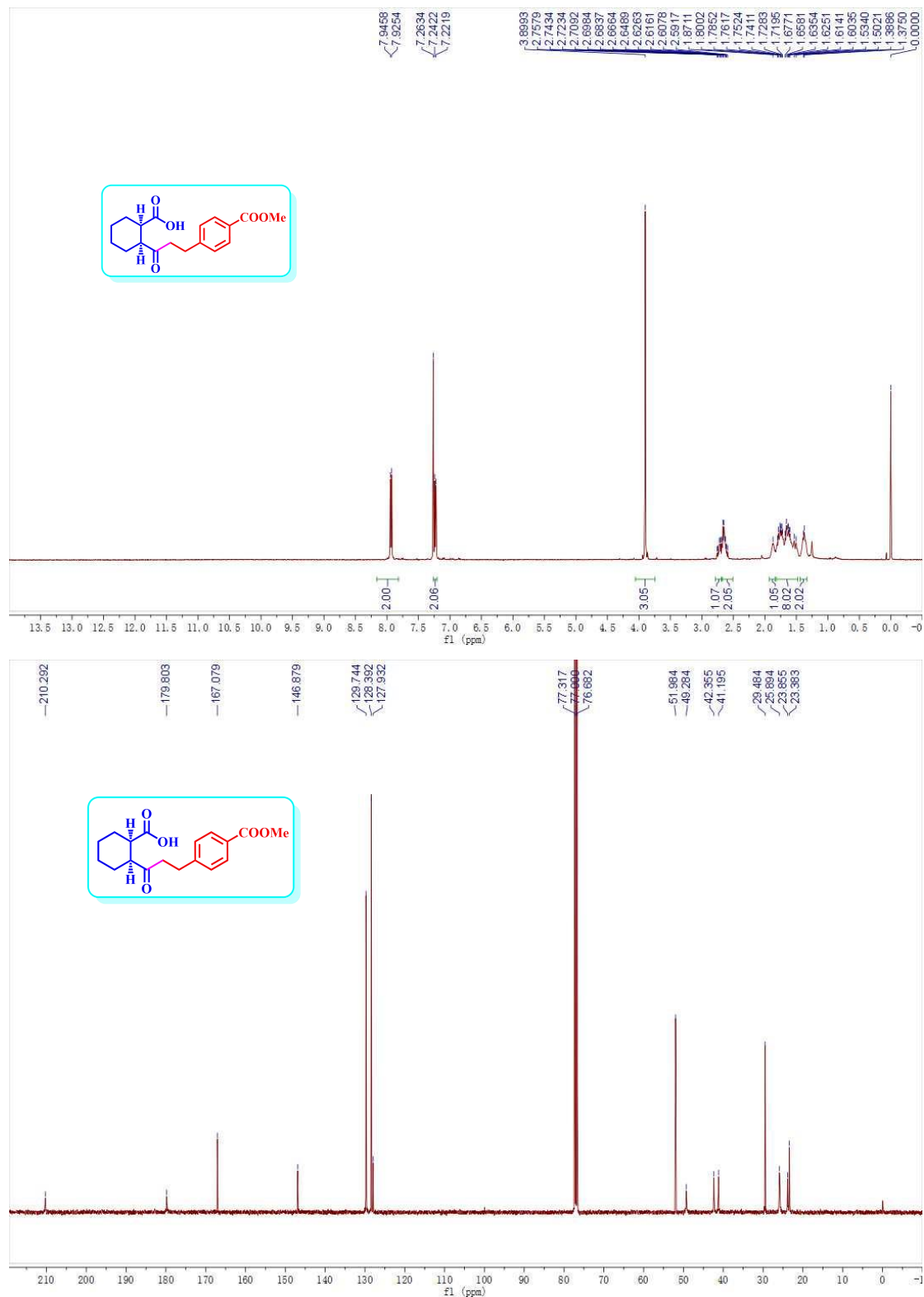


Figure S21. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 3an in CDCl_3

Cis-2-(5-acetoxypentanyl)cyclohexane-1-carboxylic acid (3ao)

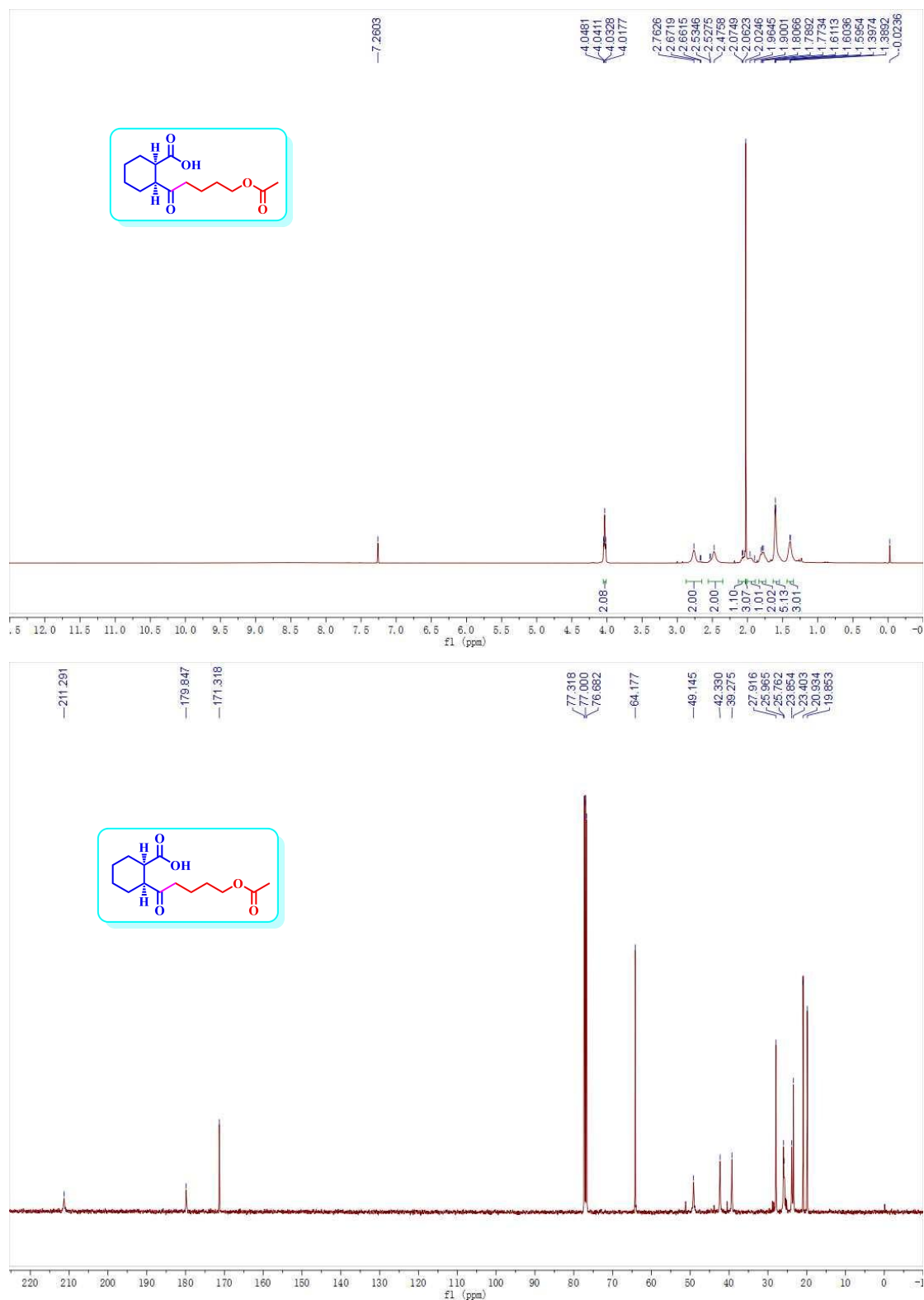


Figure S22. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 3ao in CDCl_3

***Cis*-2-(7-ethoxy-7-oxoheptanoyl)cyclohexane-1-carboxylic acid (3ap)**

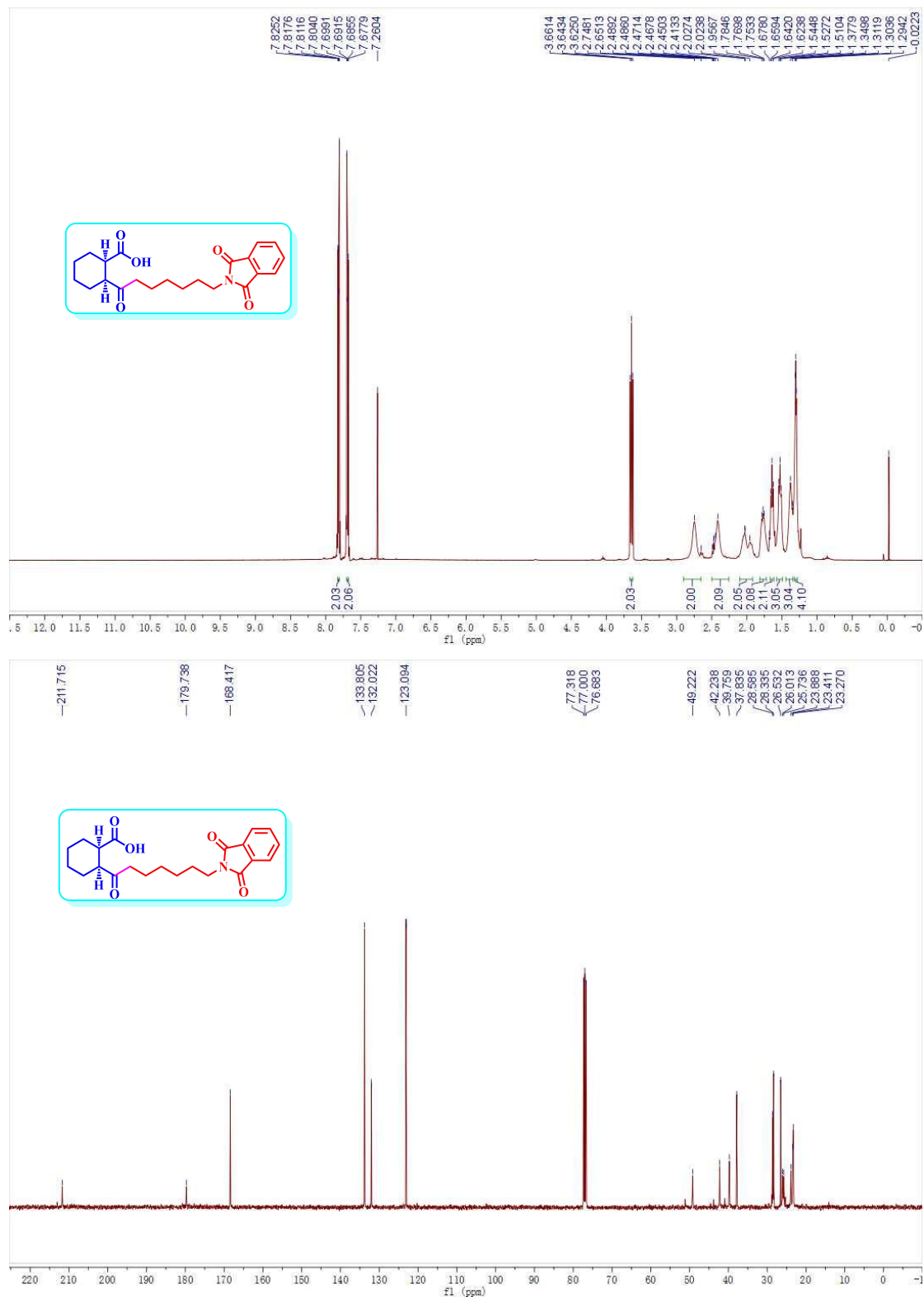


Figure S23. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3ap in CDCl₃

***Cis*-2-(7-(benzyloxy)heptanoyl)cyclohexane-1-carboxylic acid (3aq)**

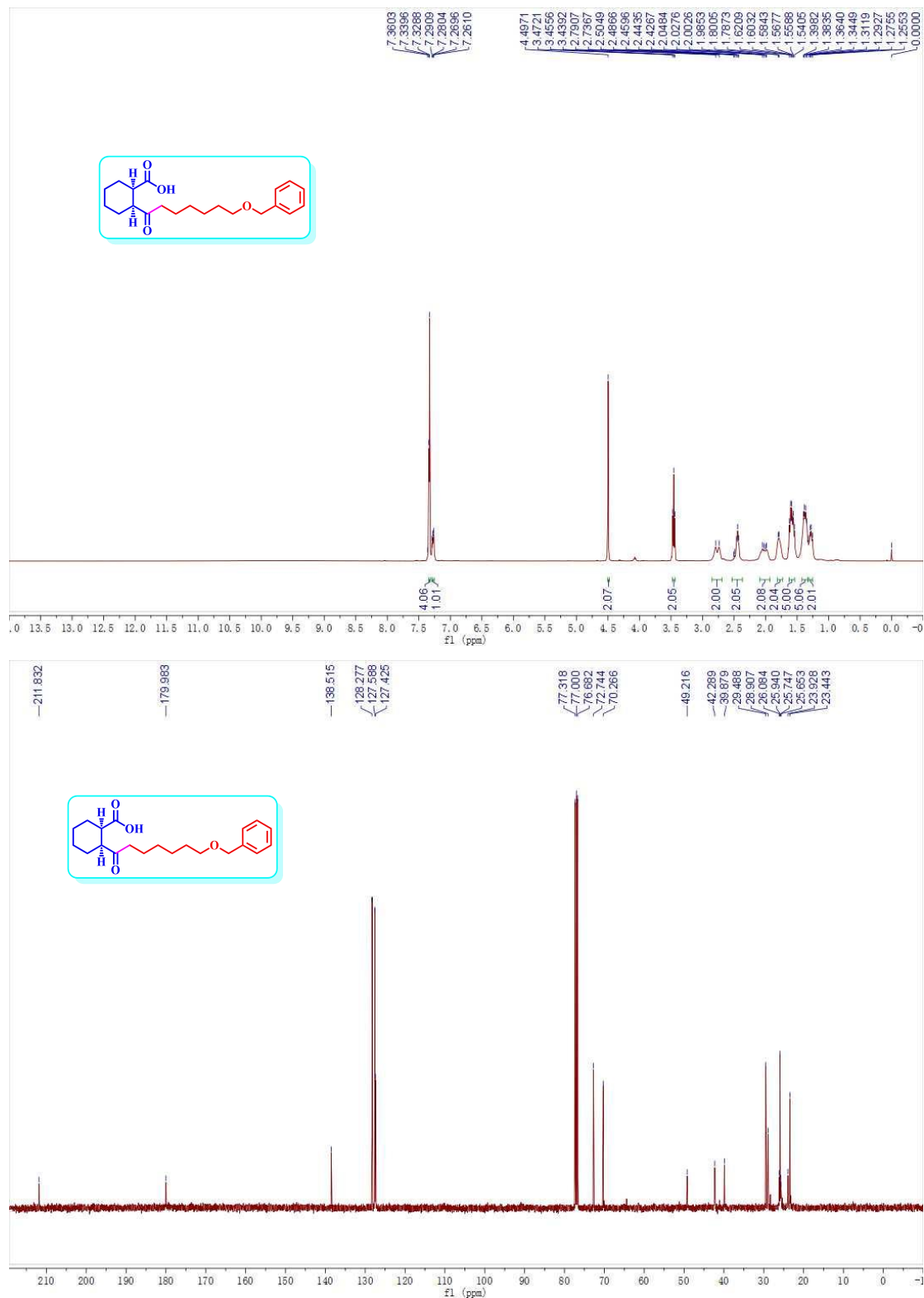


Figure S24. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3aq in CDCl₃

Cis-2-(7-ethoxy-7-oxoheptanoyl)cyclohexane-1-carboxylic acid (3ar)

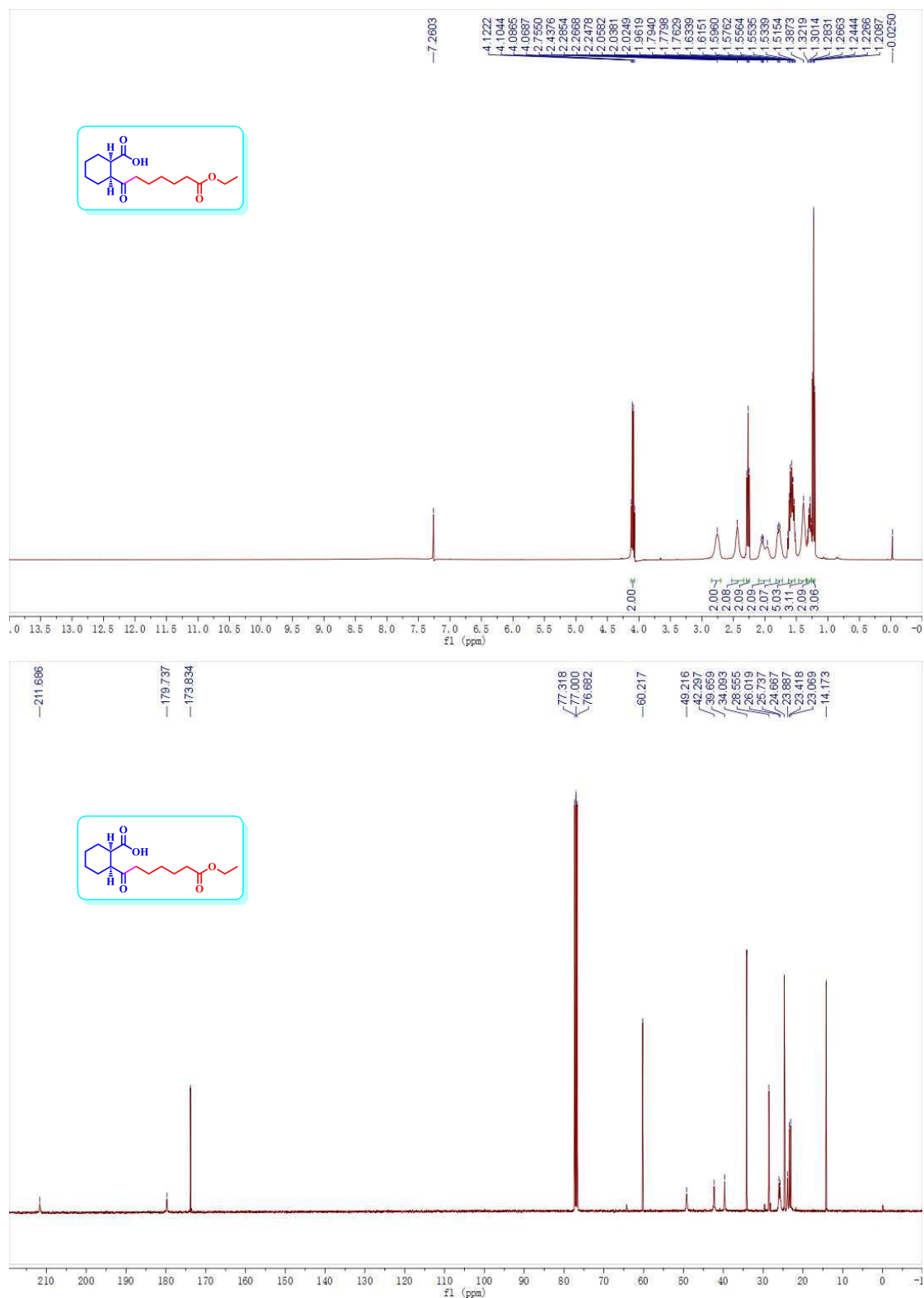


Figure S25. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 3ar in CDCl_3

Trans-2-(cyclohexanecarbonyl)cyclohexane-1-carboxylic acid (3ba)

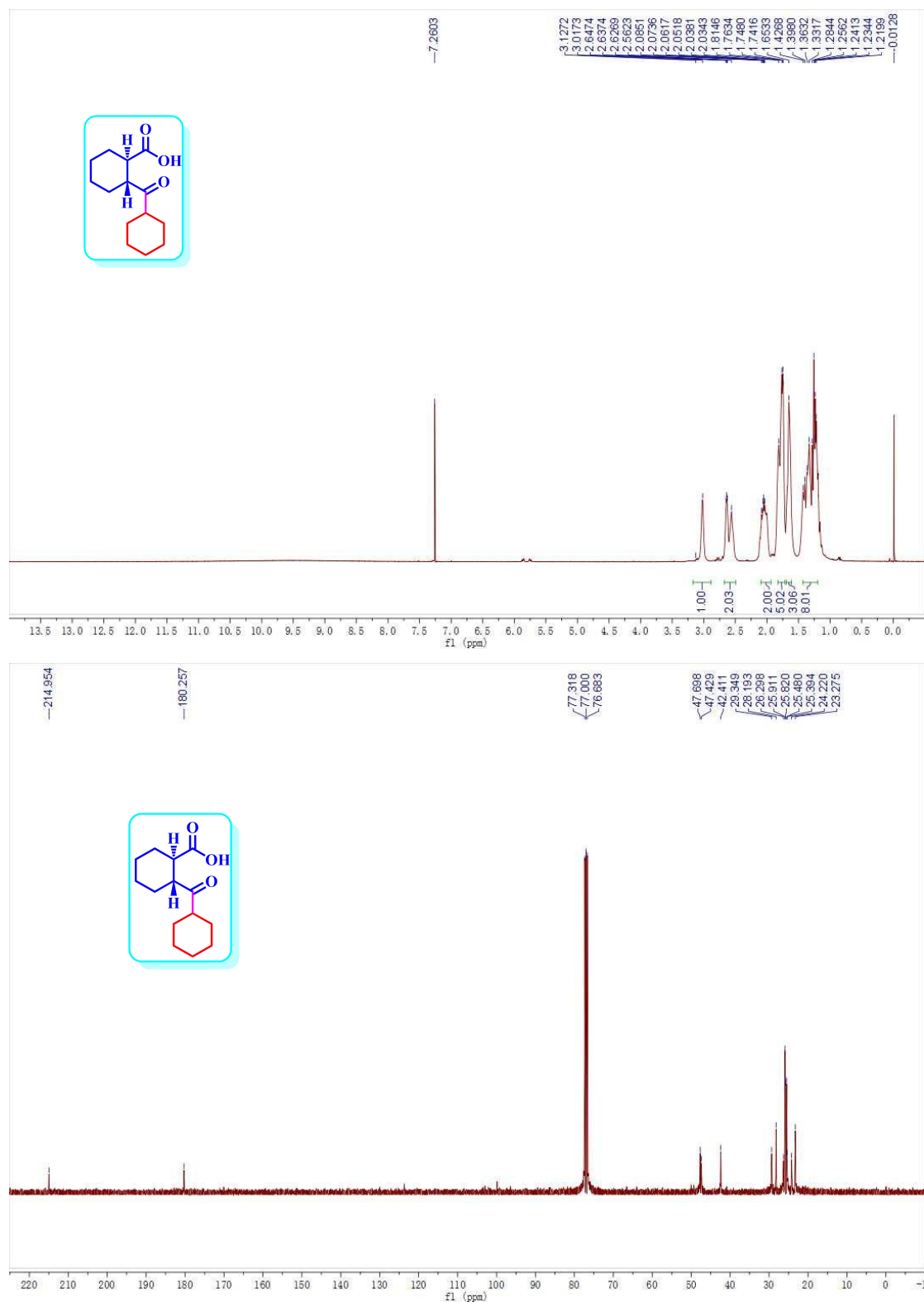


Figure S26. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 3ba in CDCl_3

**Trans-2-(7-ethoxy-7-oxoheptanoyl)cyclohexane-1-carboxylic acid
(3br)**

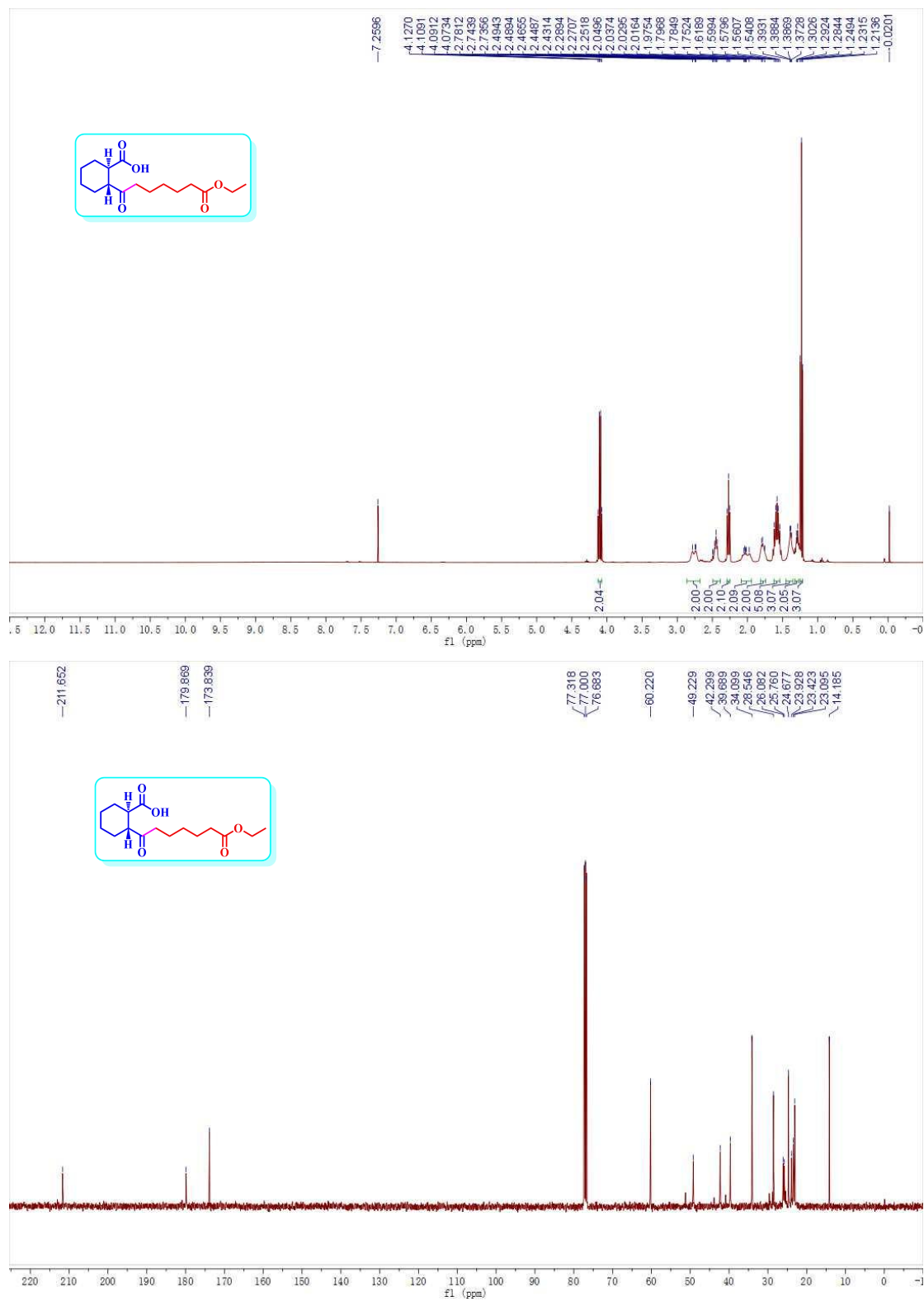


Figure S27. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 3br in CDCl_3

***Cis*-6-nonanoylcyclohex-3-ene-1-carboxylic acid (3cg)**

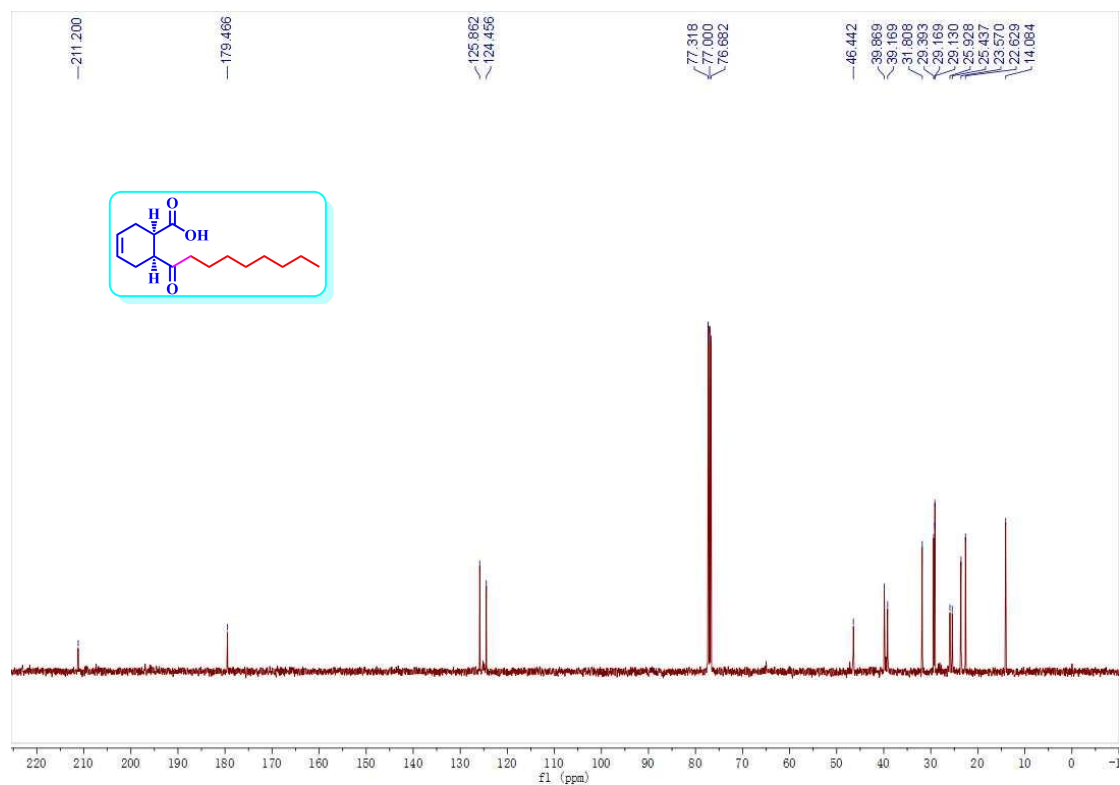
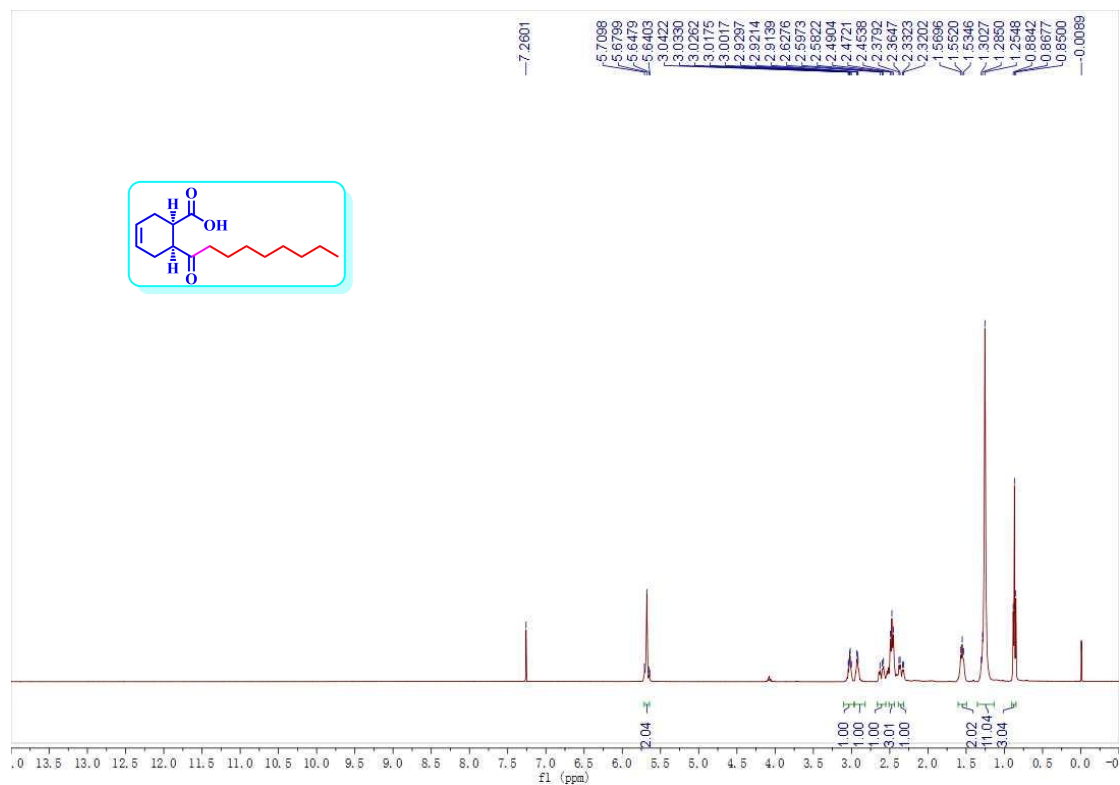


Figure S28. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3cg in CDCl₃

***Cis*-6-(7-(benzyloxy)heptanoyl)cyclohex-3-ene-1-carboxylic acid (3cq)**

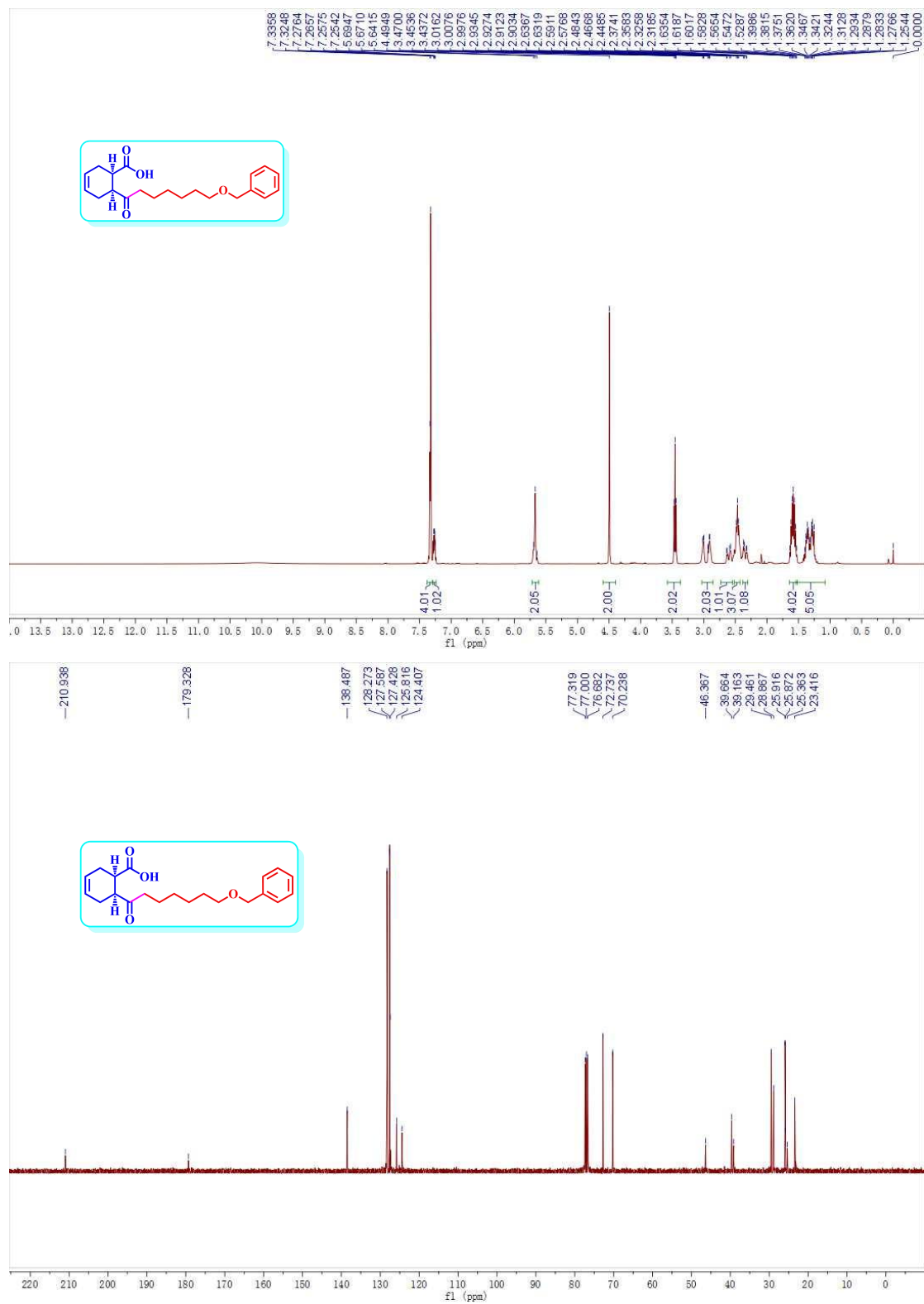


Figure S29. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3cq in CDCl₃

***Cis*-6-(cyclohexanecarbonyl)-3,4-dimethylcyclohex-3-ene-1-carboxylic acid (3da)**

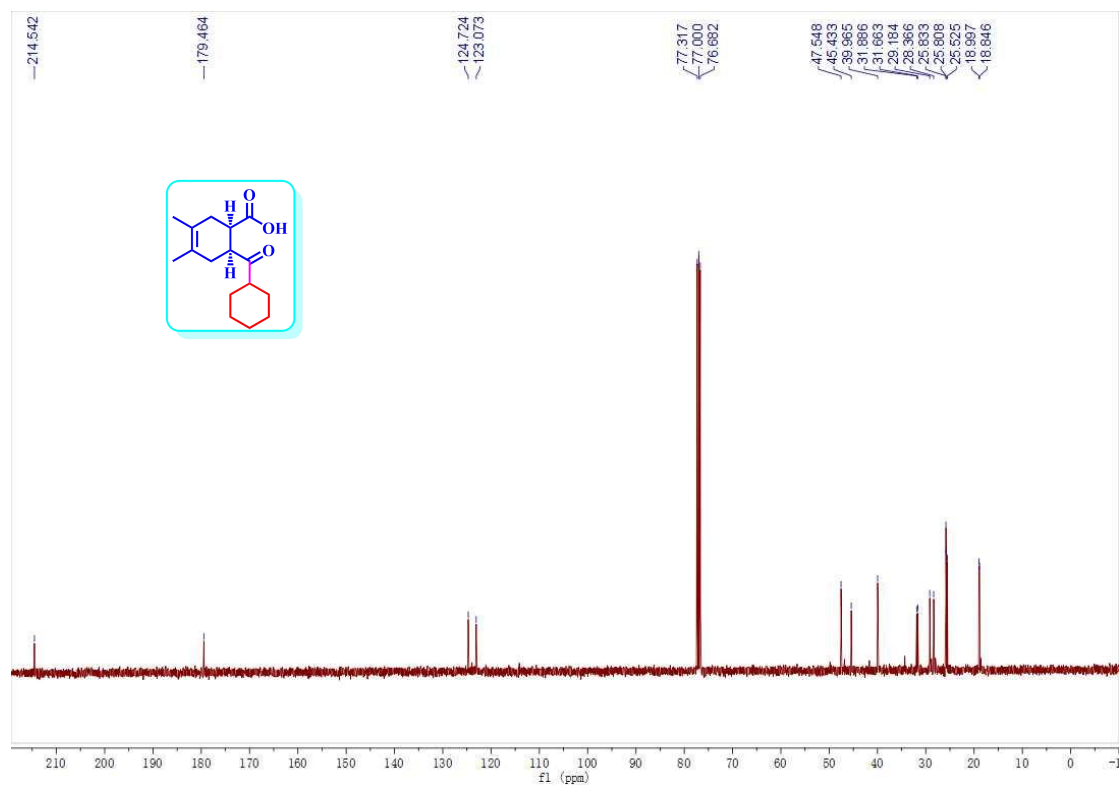
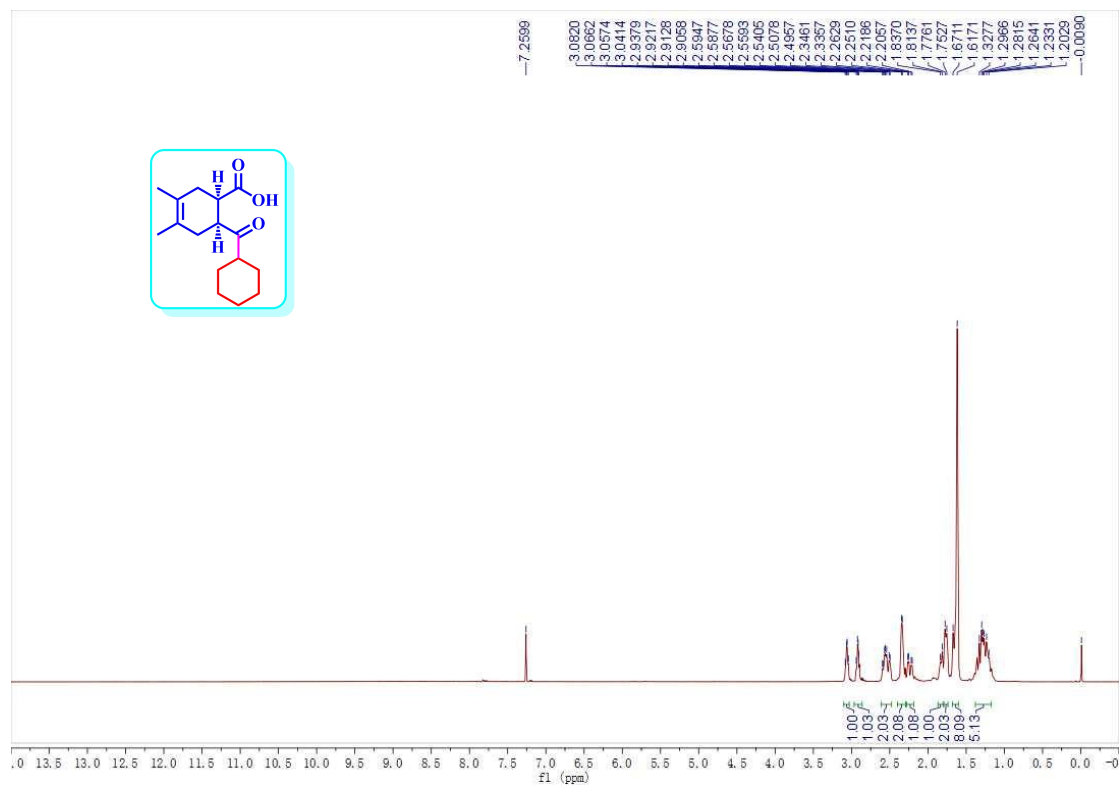


Figure S30. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 3da in CDCl_3

Cis-2-(cyclohexanecarbonyl)cyclopentane-1-carboxylic acid (3ea)

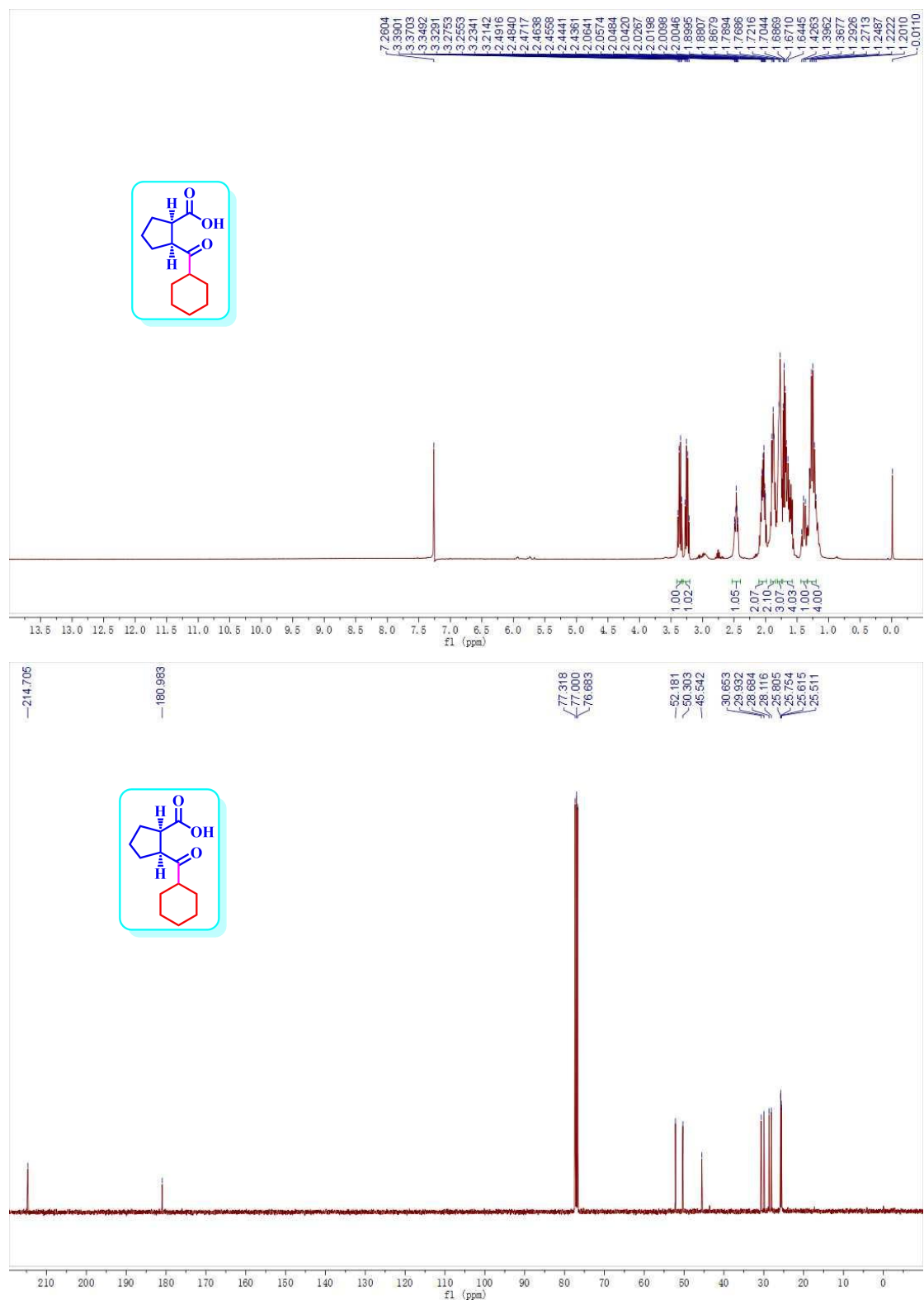


Figure S31. ^1H (400 MHz) and ^{13}C { ^1H } (101 MHz) NMR spectra of 3ea in CDCl_3

***Cis*-2-(7-ethoxy-7-oxoheptanoyl)cyclopentane-1-carboxylic acid (3er)**

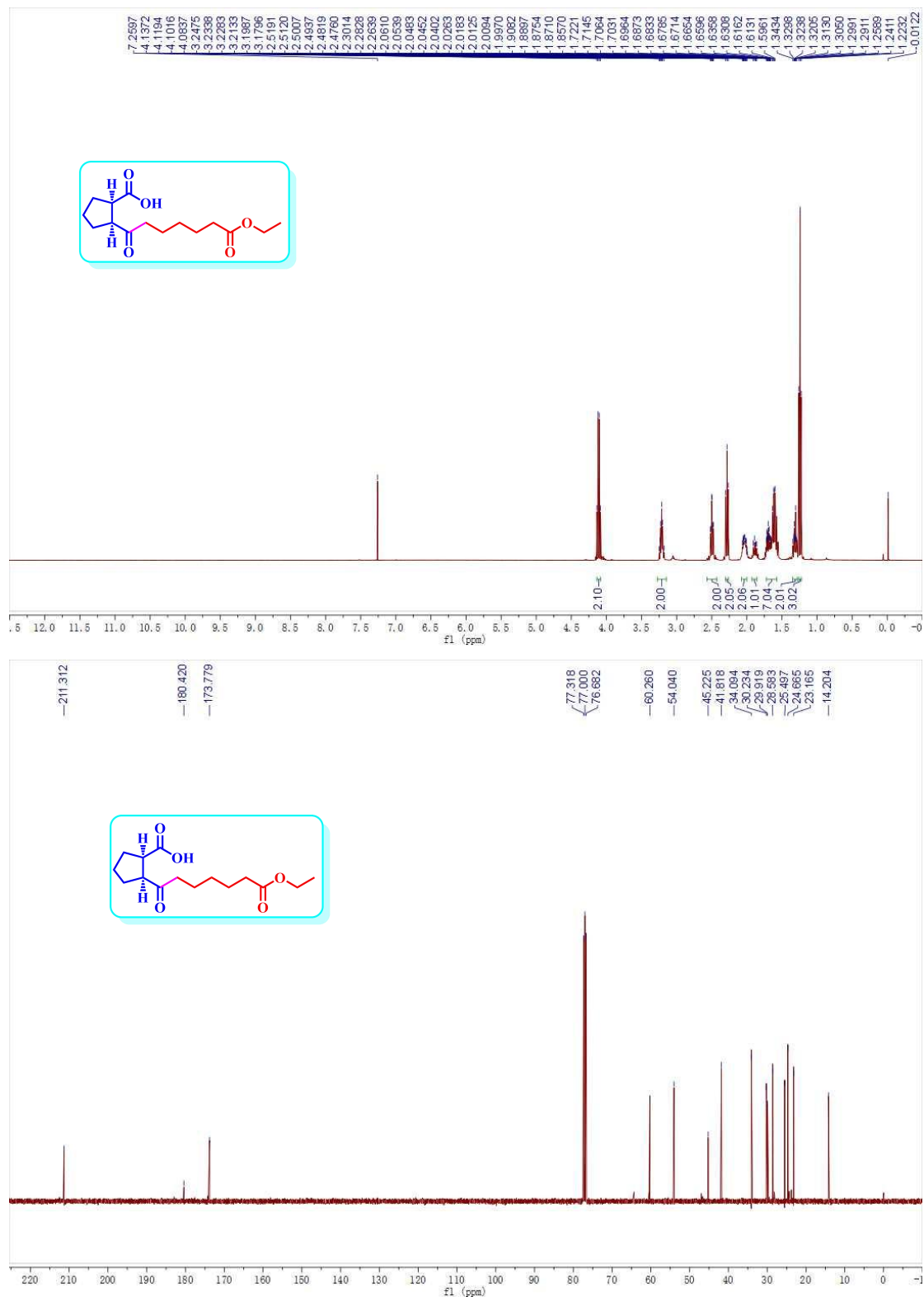


Figure S32. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3er in CDCl₃

***Cis*-3-(7-(benzyloxy)heptanoyl)bicyclo[2.2.1]heptane-2-carboxylic acid (3fq)**

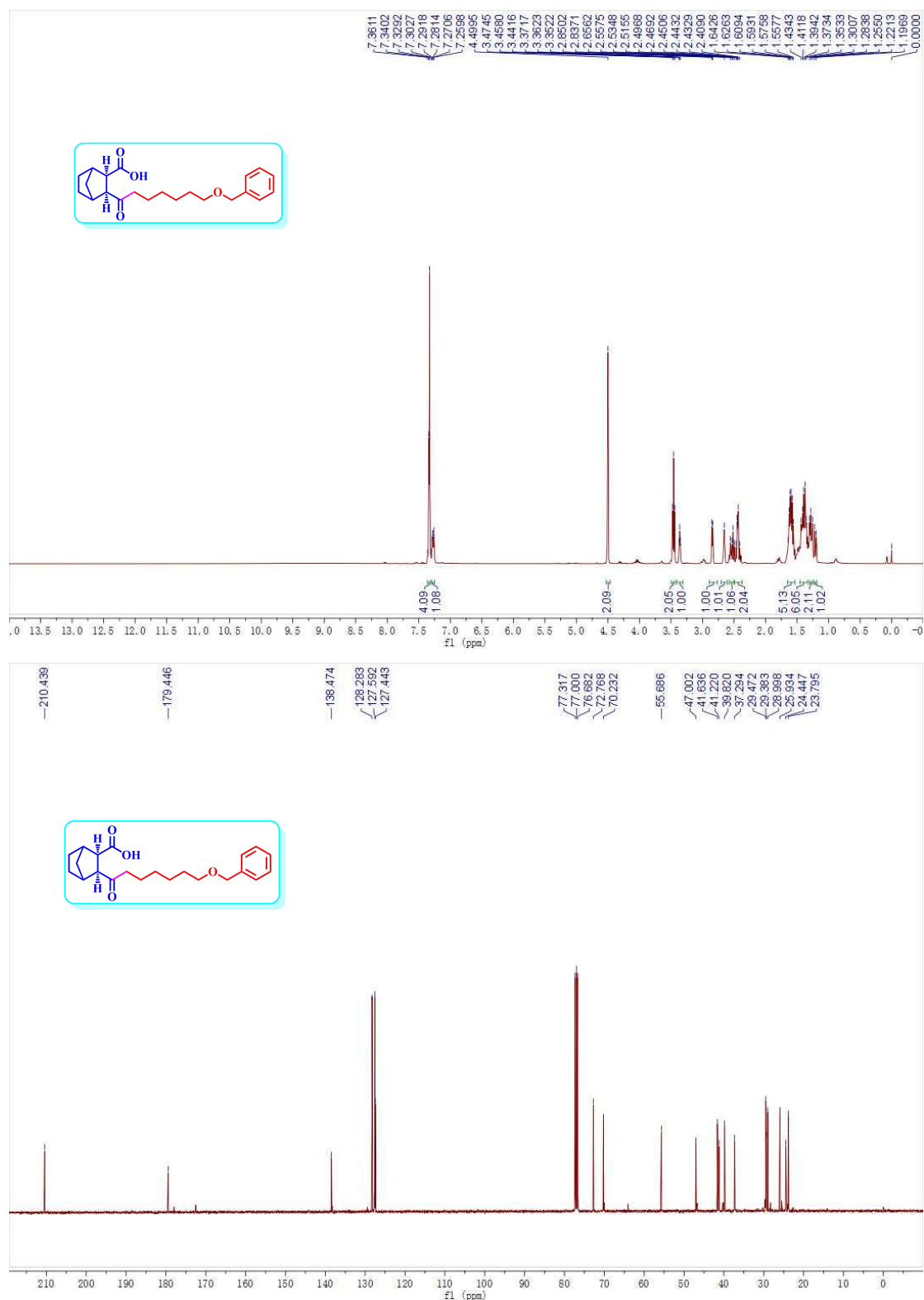


Figure S33. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3fq in CDCl₃

***Cis*-3-(7-ethoxy-7-oxoheptanoyl)bicyclo[2.2.1]heptane-2-carboxylic acid (3fr)**

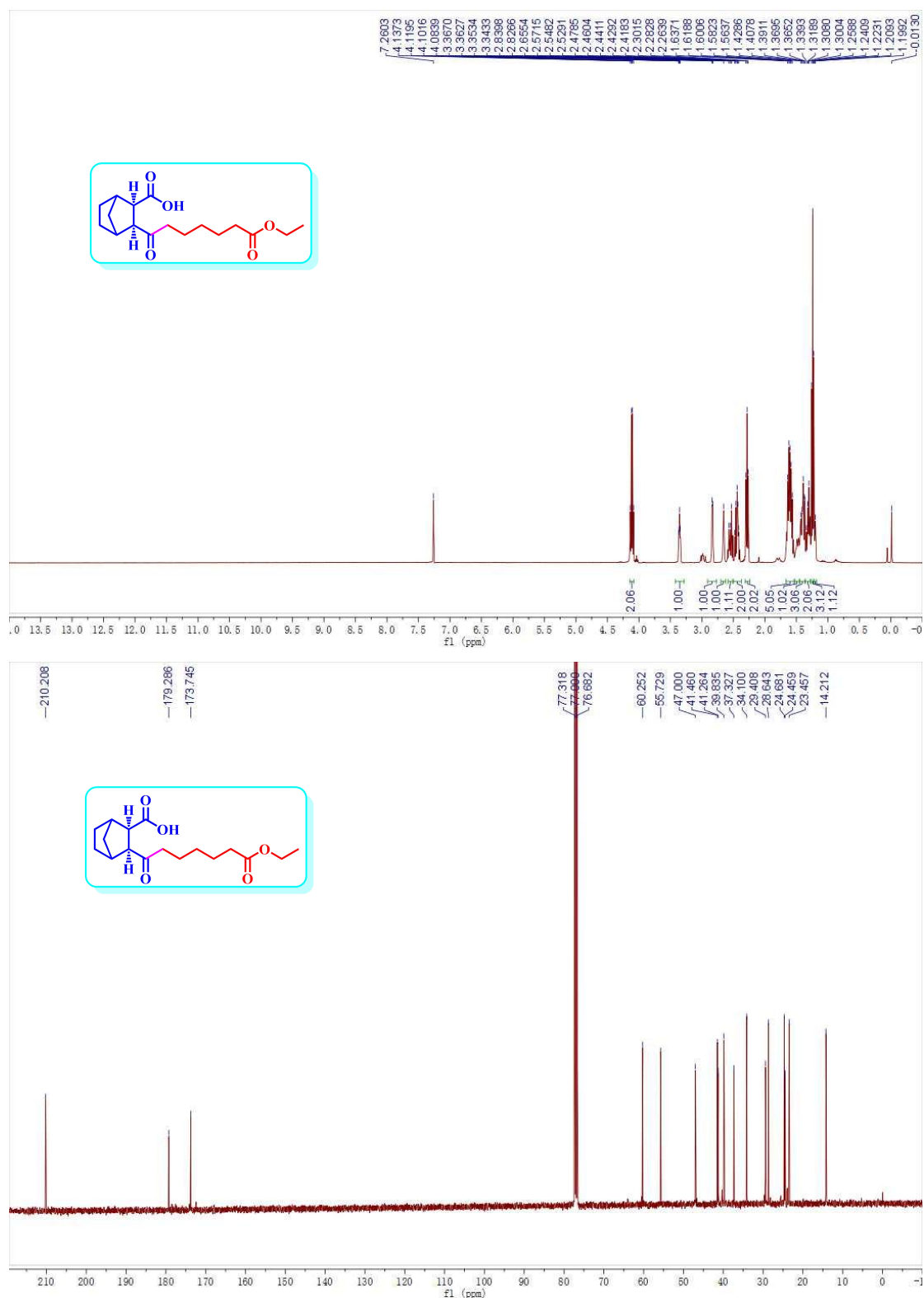


Figure S34. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3fr in CDCl₃

***Cis*-3-(7-(benzyloxy)heptanoyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (3gq)**

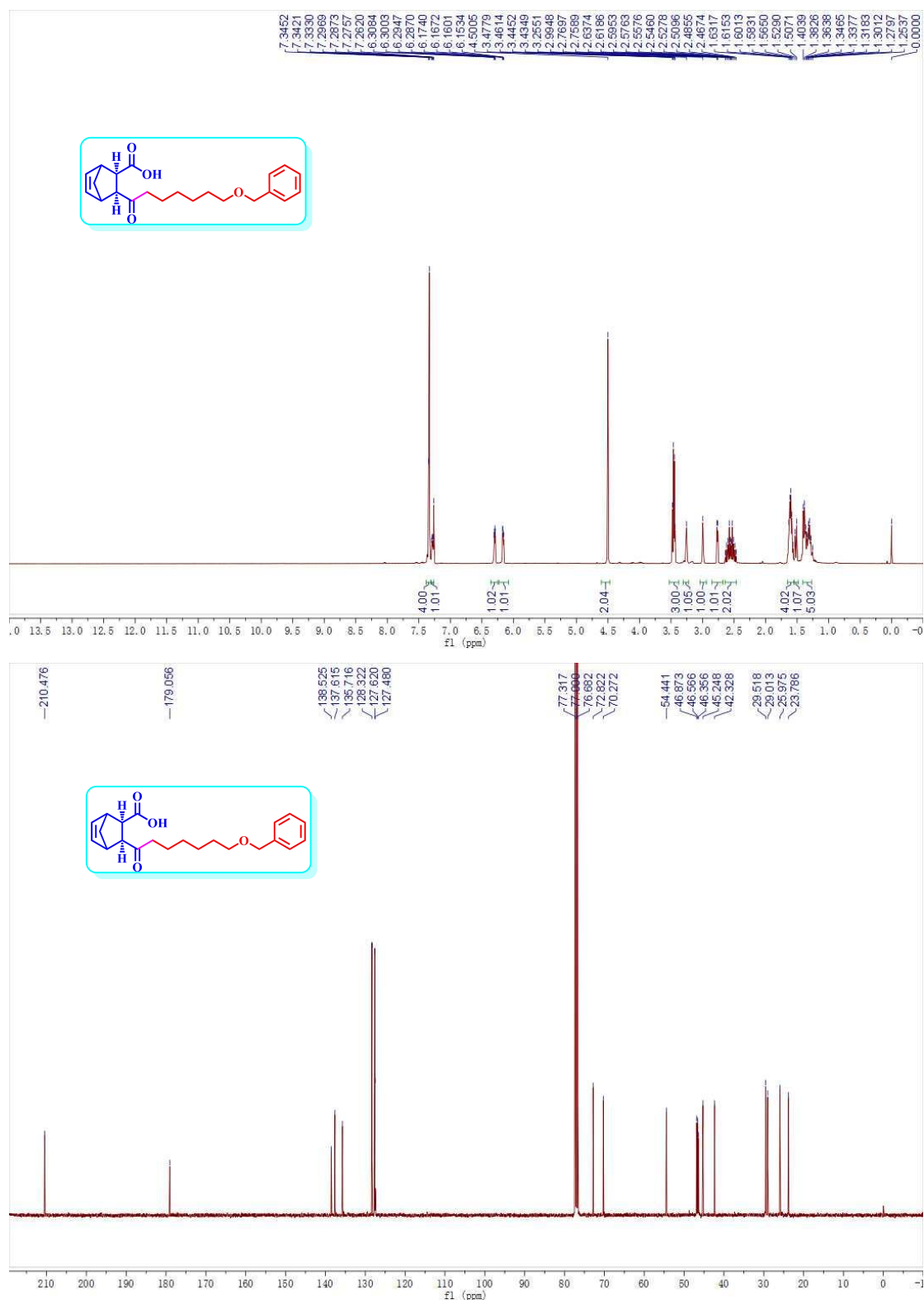


Figure S35. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3gq in CDCl₃

***Cis*-3-(7-ethoxy-7-oxoheptanoyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (3gr)**

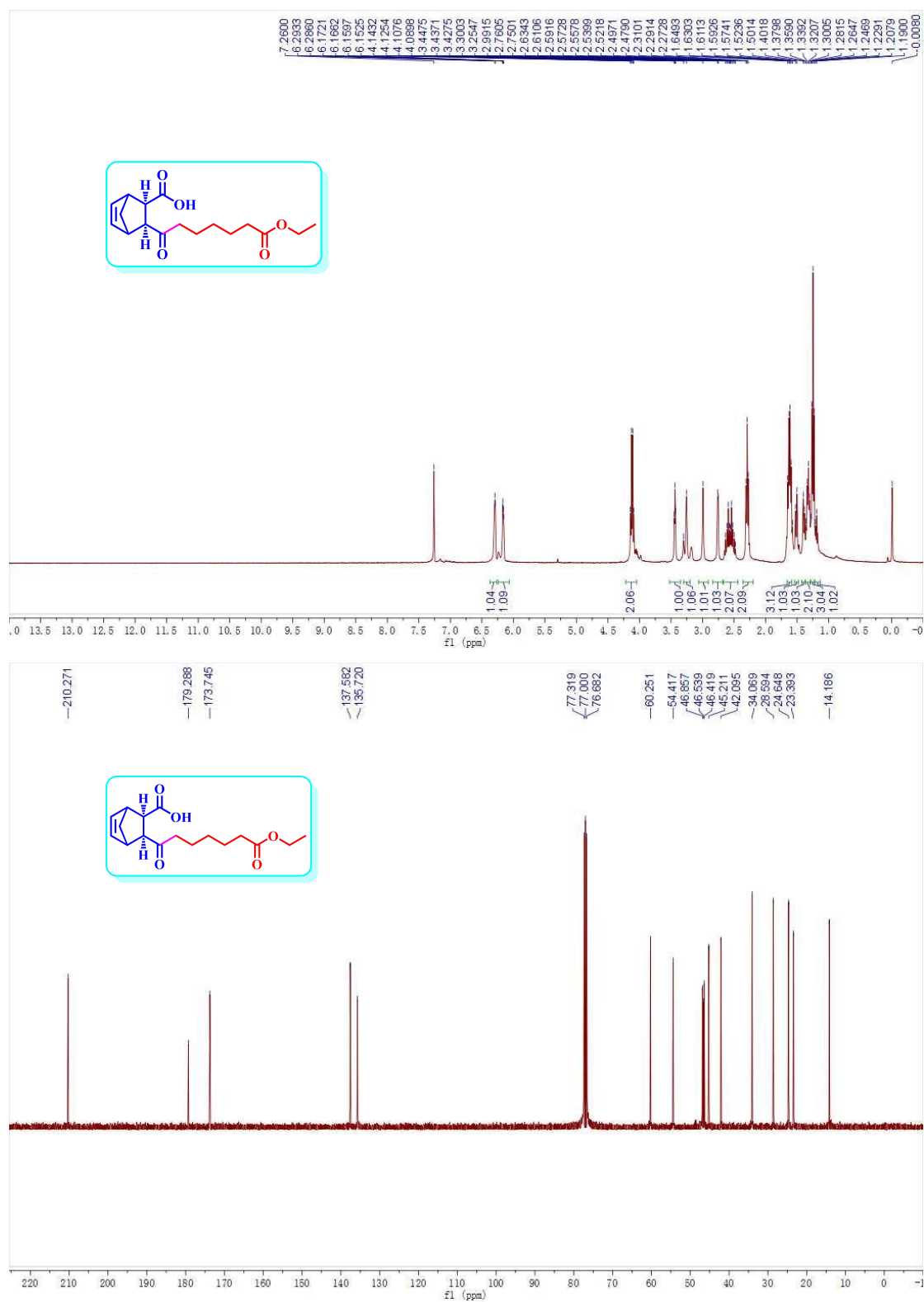


Figure S36. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 3gr in CDCl₃

Cis-2-butylcyclohexane-1-carboxylic acid (4aa)

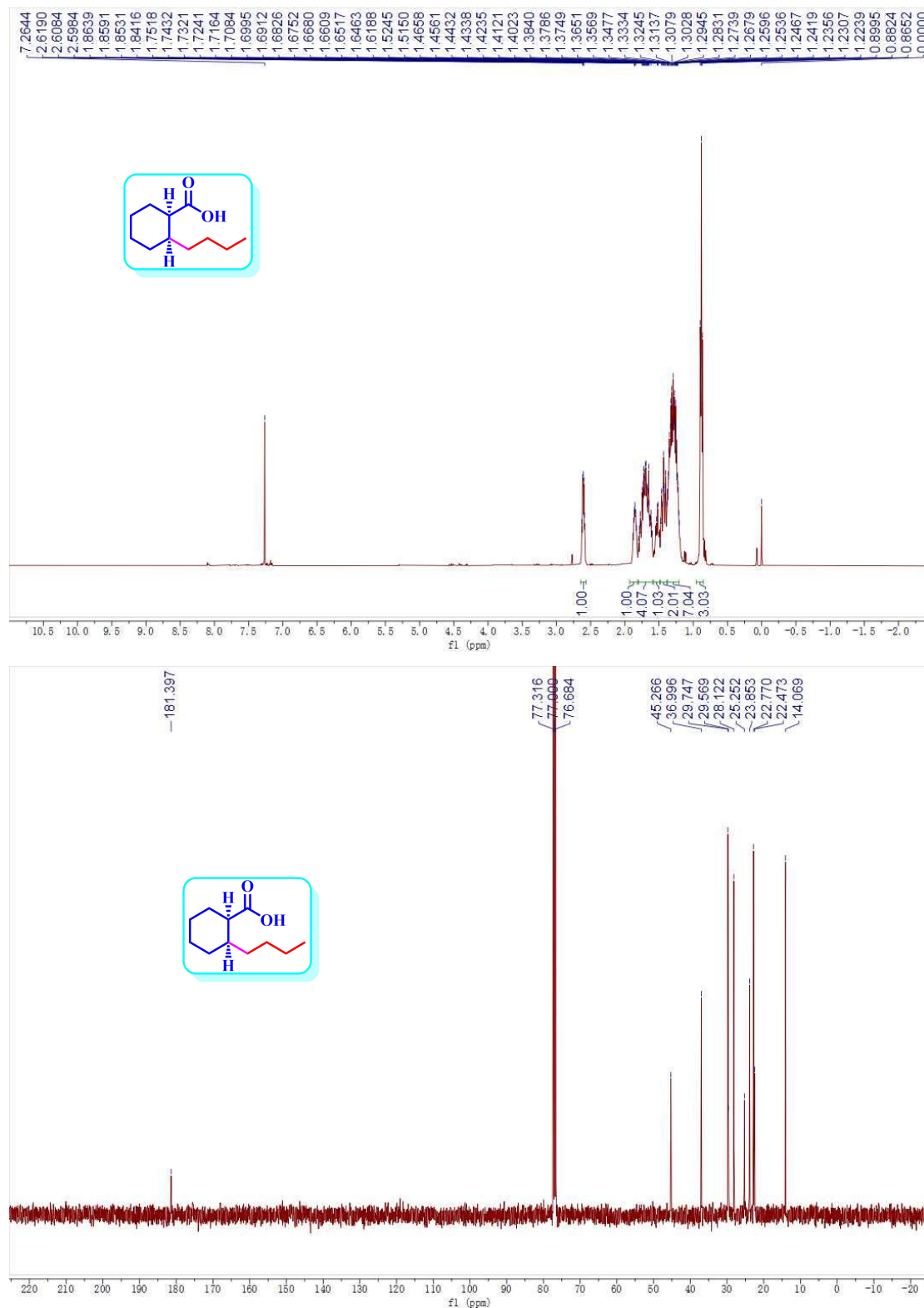


Figure S37. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4aa in CDCl₃

Cis-2-pentylcyclohexane-1-carboxylic acid (4ab)

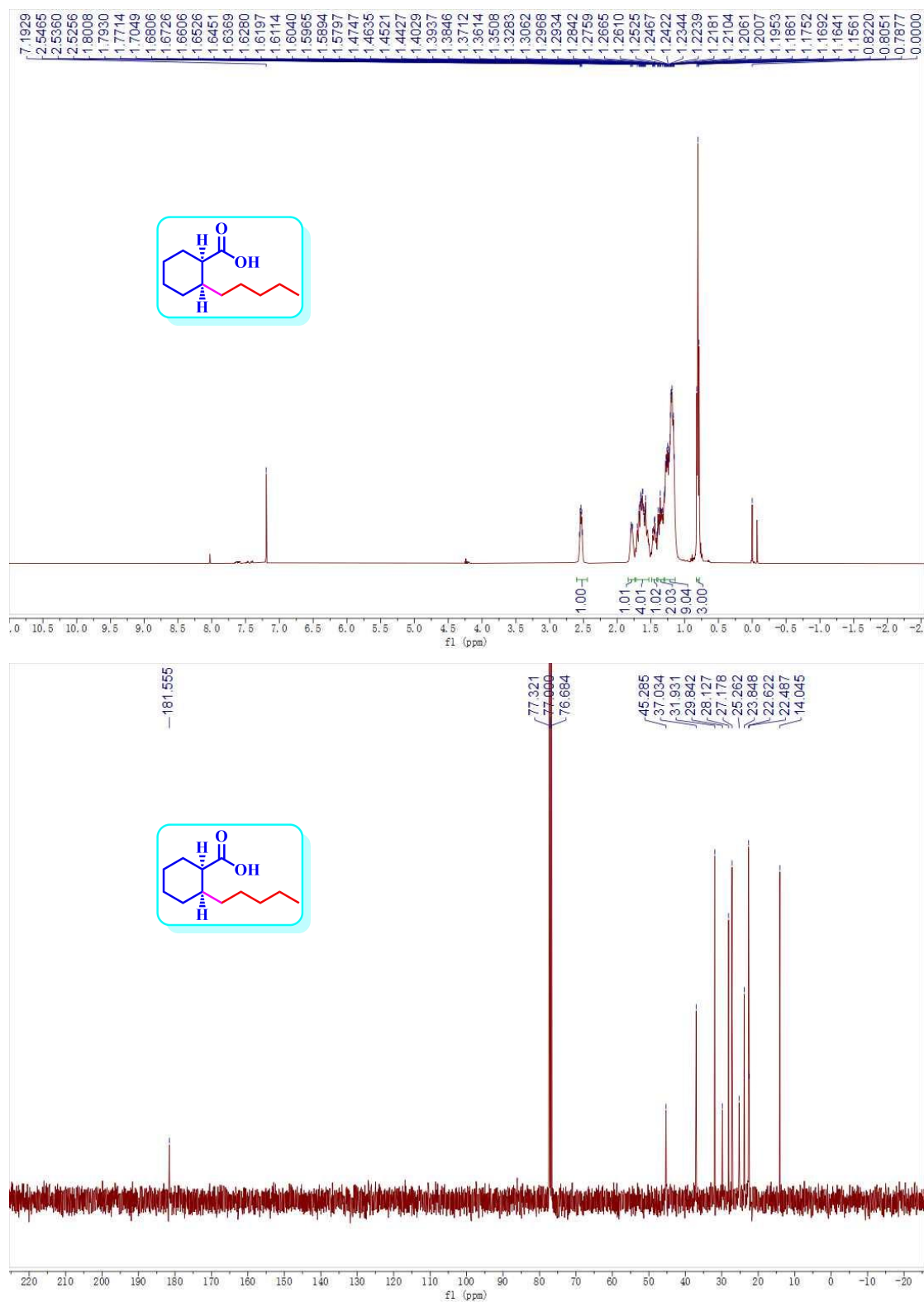


Figure S38. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4ab in CDCl₃

Cis-2-hexylcyclohexane-1-carboxylic acid (4ac)

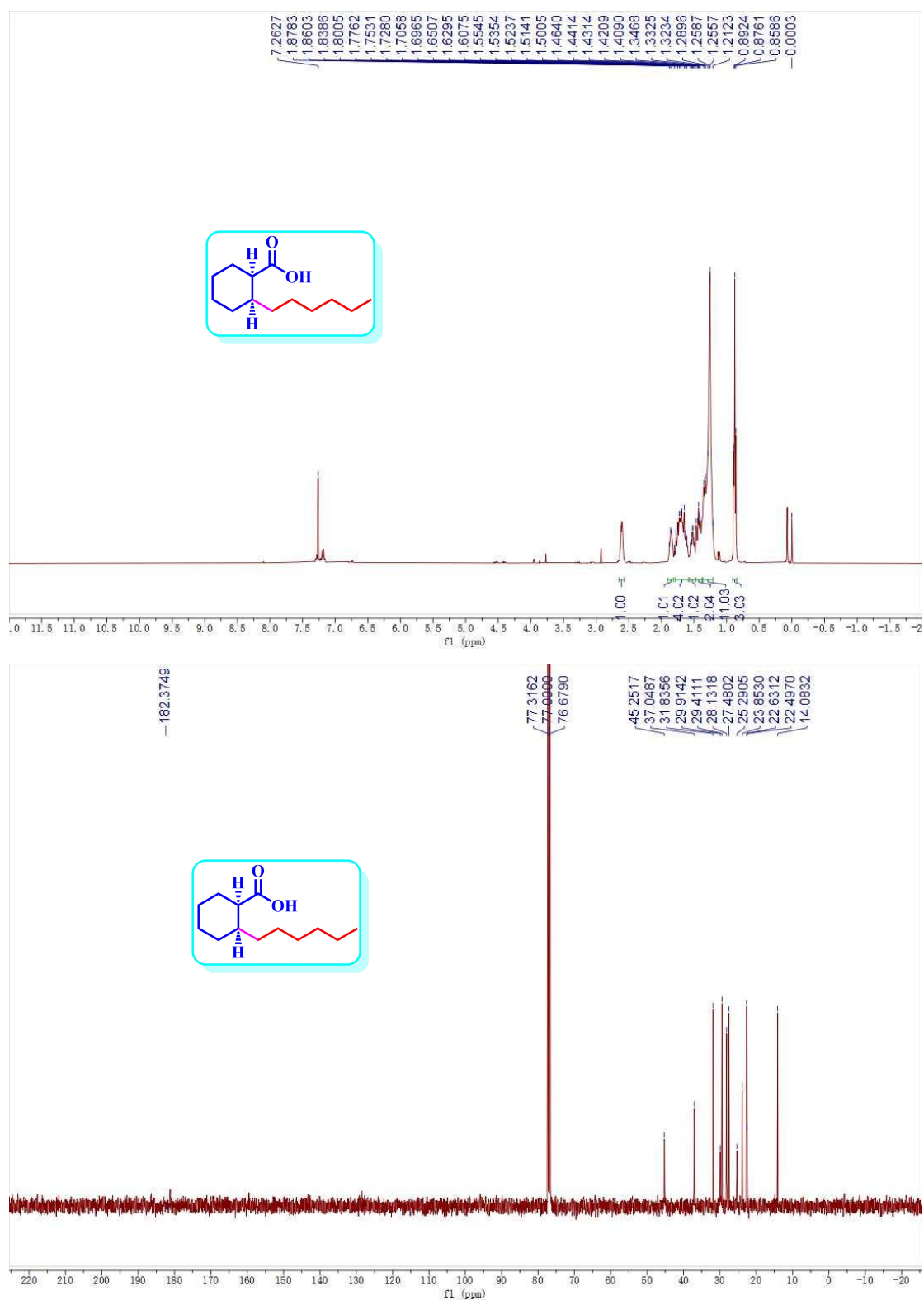


Figure S39. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 4ac in CDCl_3

Cis-2-octylcyclohexane-1-carboxylic acid (4ad)

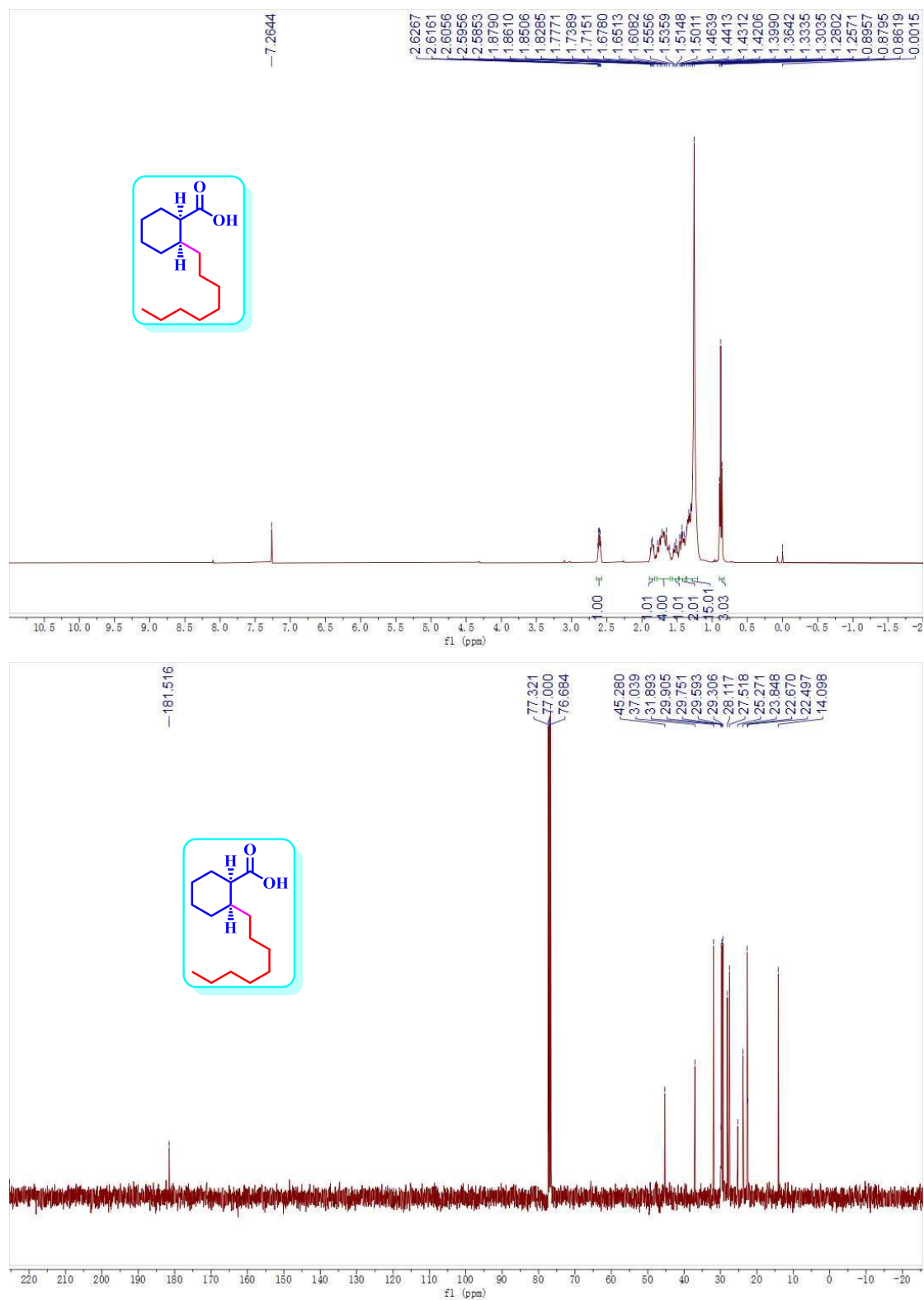


Figure S40. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 4ad in CDCl_3

Cis-2-isopentylcyclohexane-1-carboxylic acid (4ae)

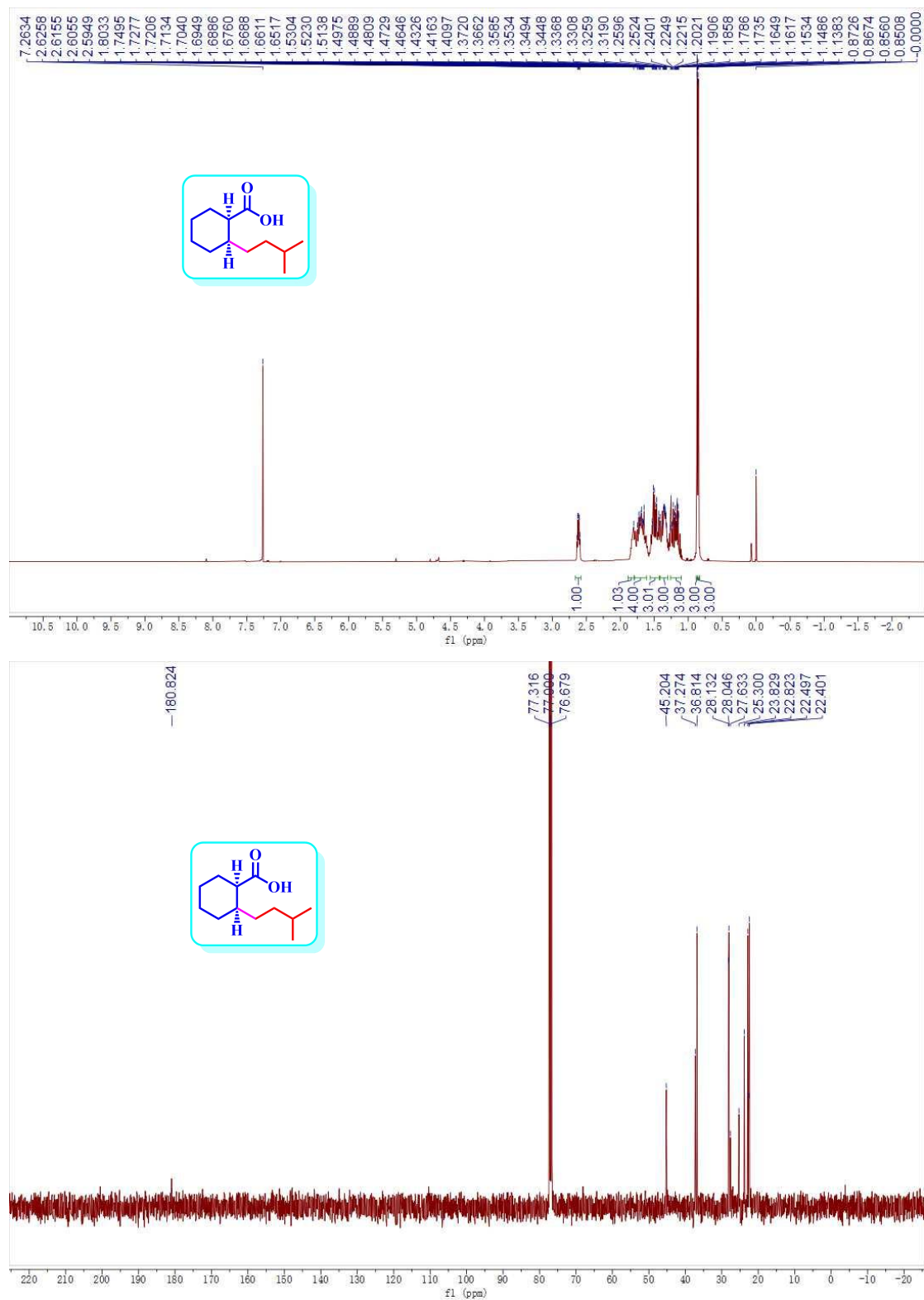


Figure S41. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4ae in CDCl₃

Cis-2-(cyclopentylmethyl)cyclohexane-1-carboxylic acid (4af)

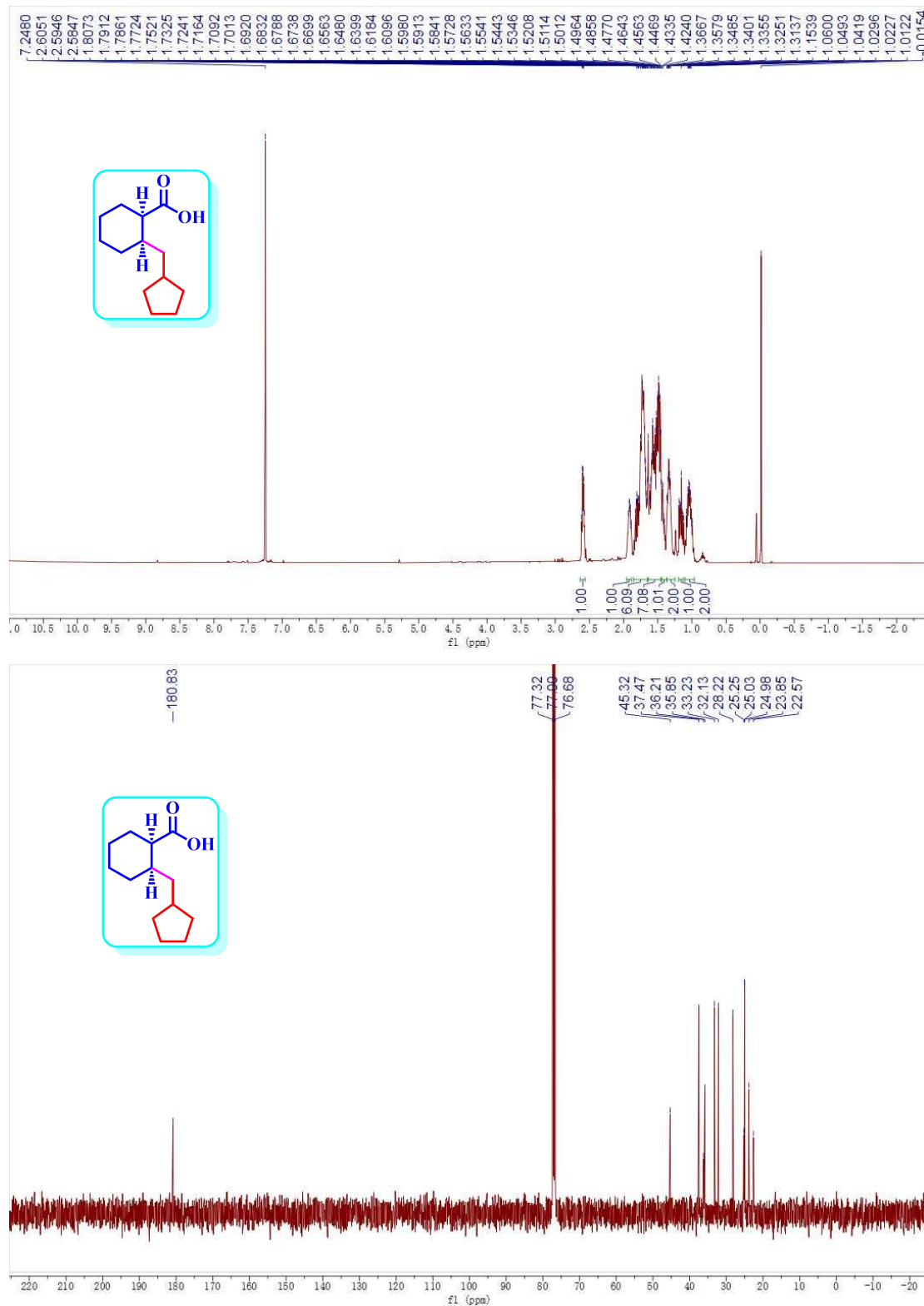


Figure S42. ^1H (400 MHz) and ^{13}C { ^1H } (101 MHz) NMR spectra of 4af in CDCl_3

Cis-2-(cyclohexylmethyl)cyclohexane-1-carboxylic acid (4ag)

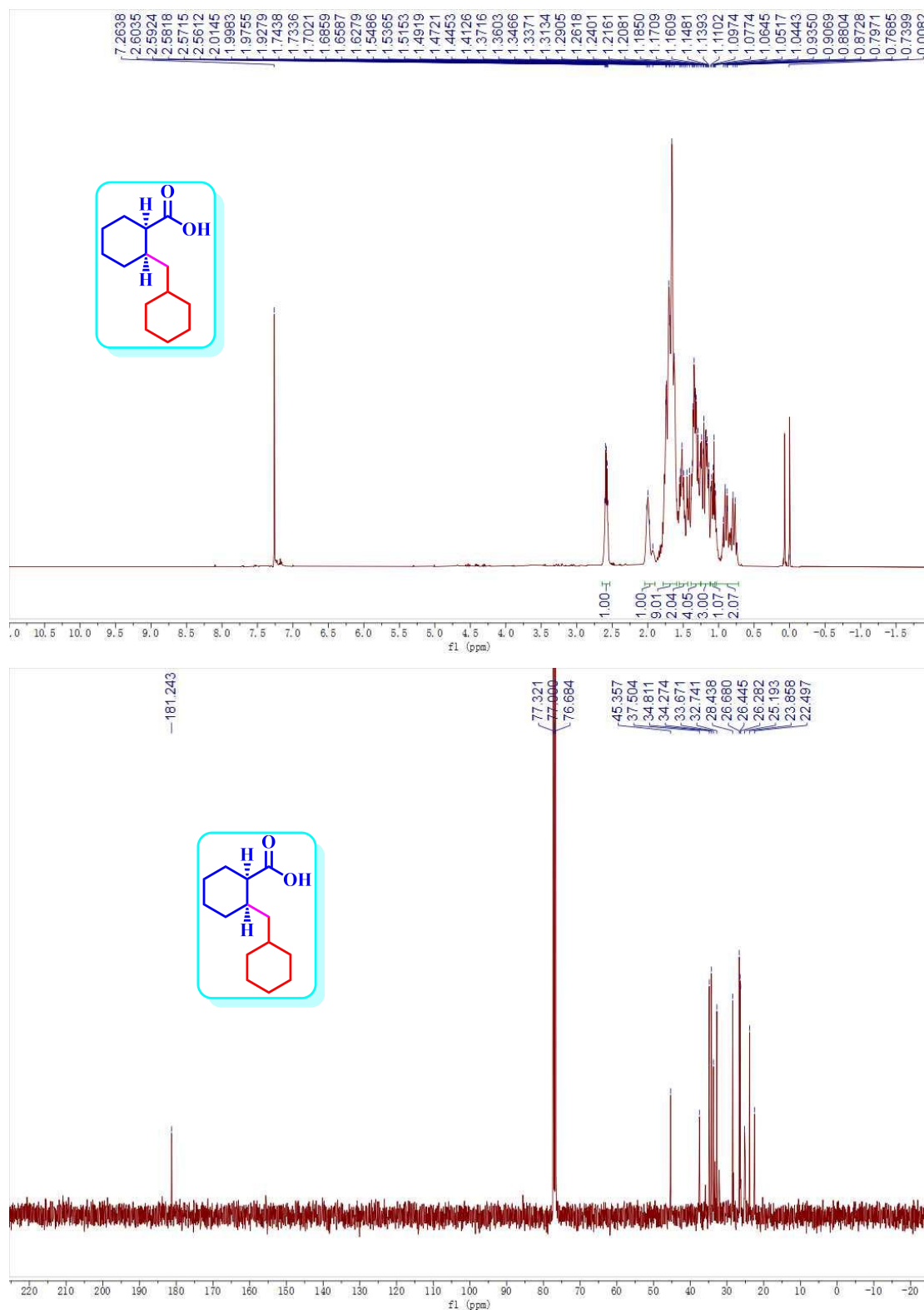


Figure S43. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4ag in CDCl₃

Cis-2-(4-methoxybutyl)cyclohexane-1-carboxylic acid (4ah)

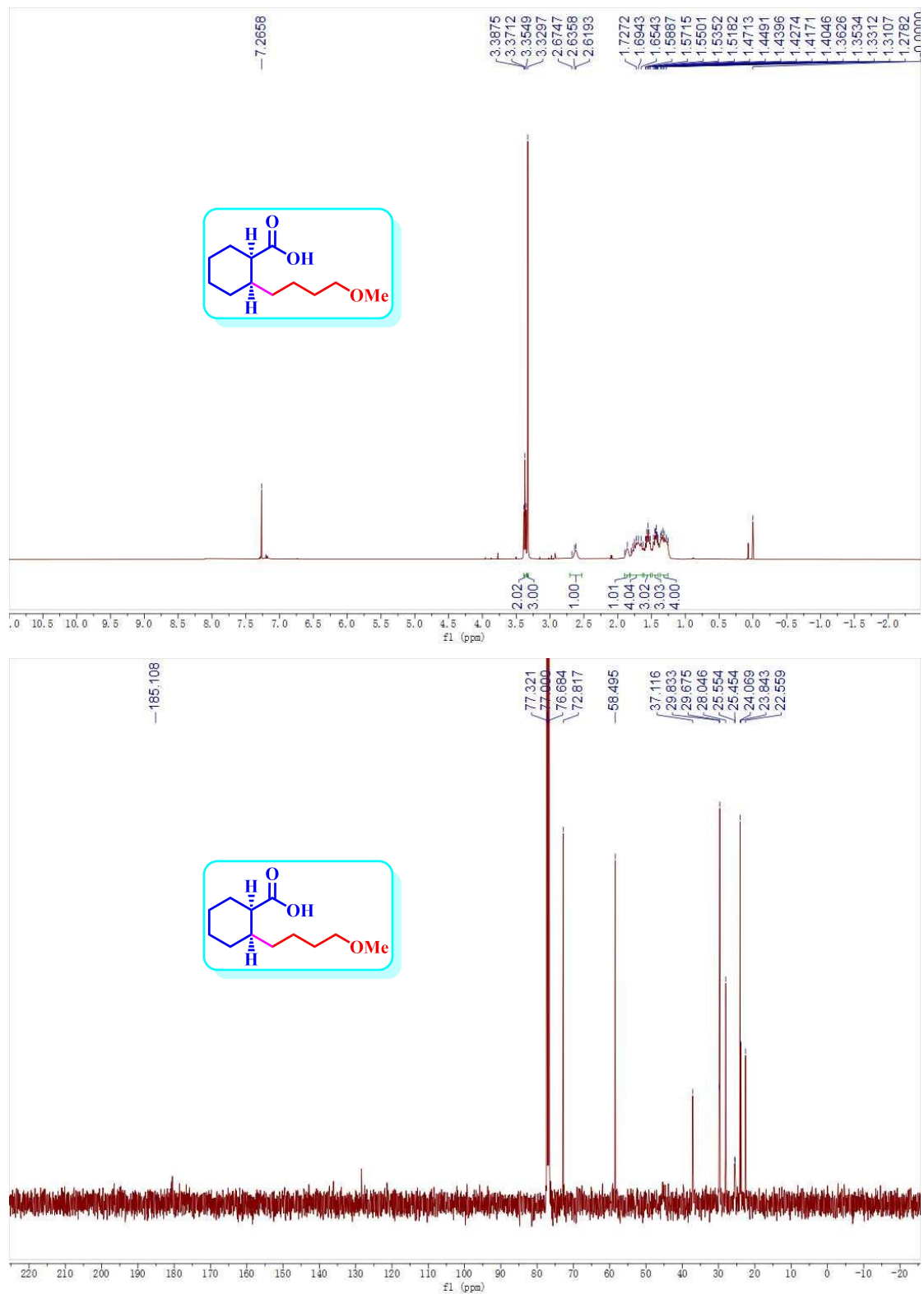


Figure S44. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4ah in CDCl₃

***Cis*-2-(5-(propionyloxy)pentyl)cyclohexane-1-carboxylic acid (4ai)**

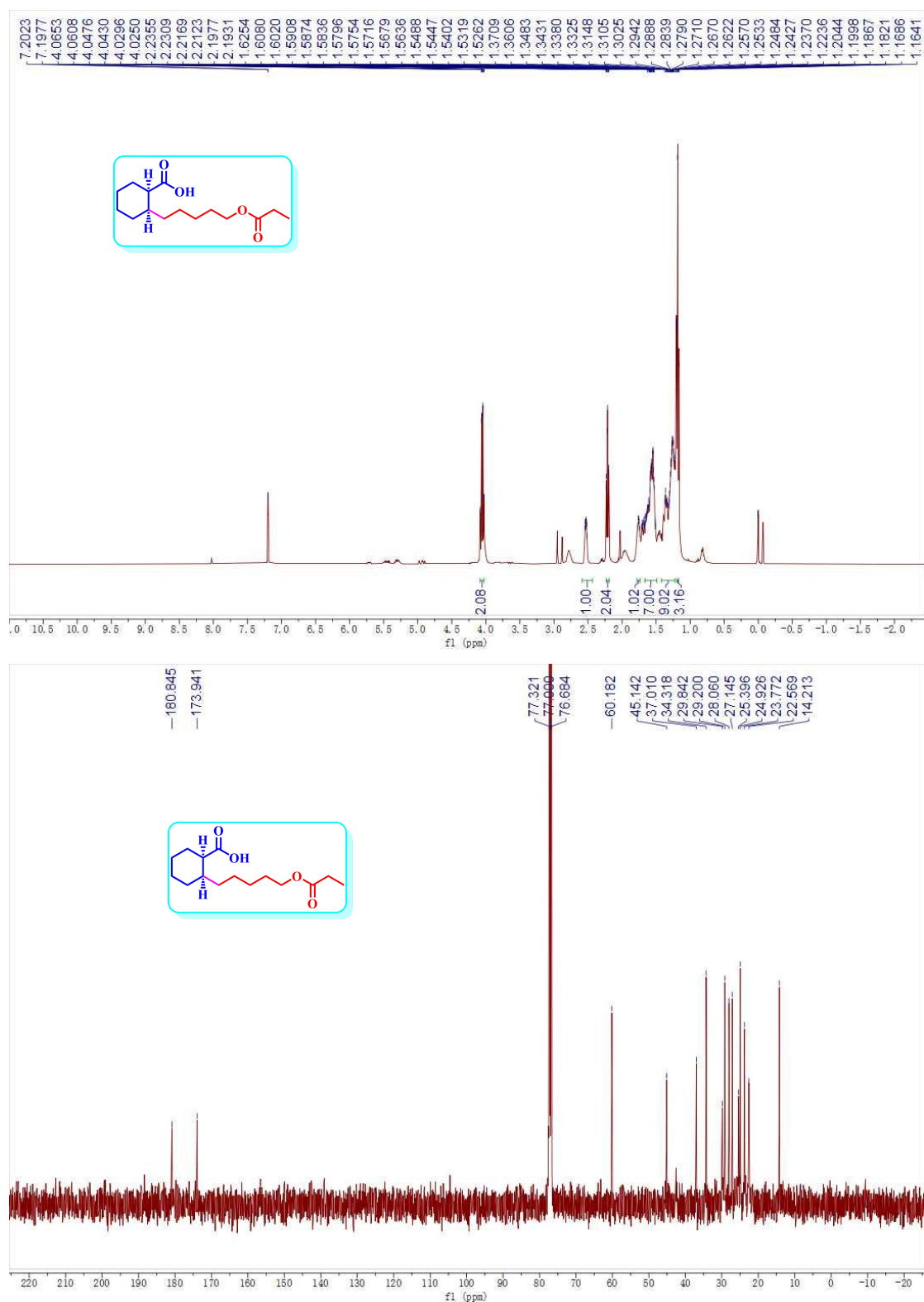


Figure S45. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 4ai in CDCl_3

Cis-2-(7-ethoxy-7-oxoheptyl)cyclohexane-1-carboxylic acid (4aj)

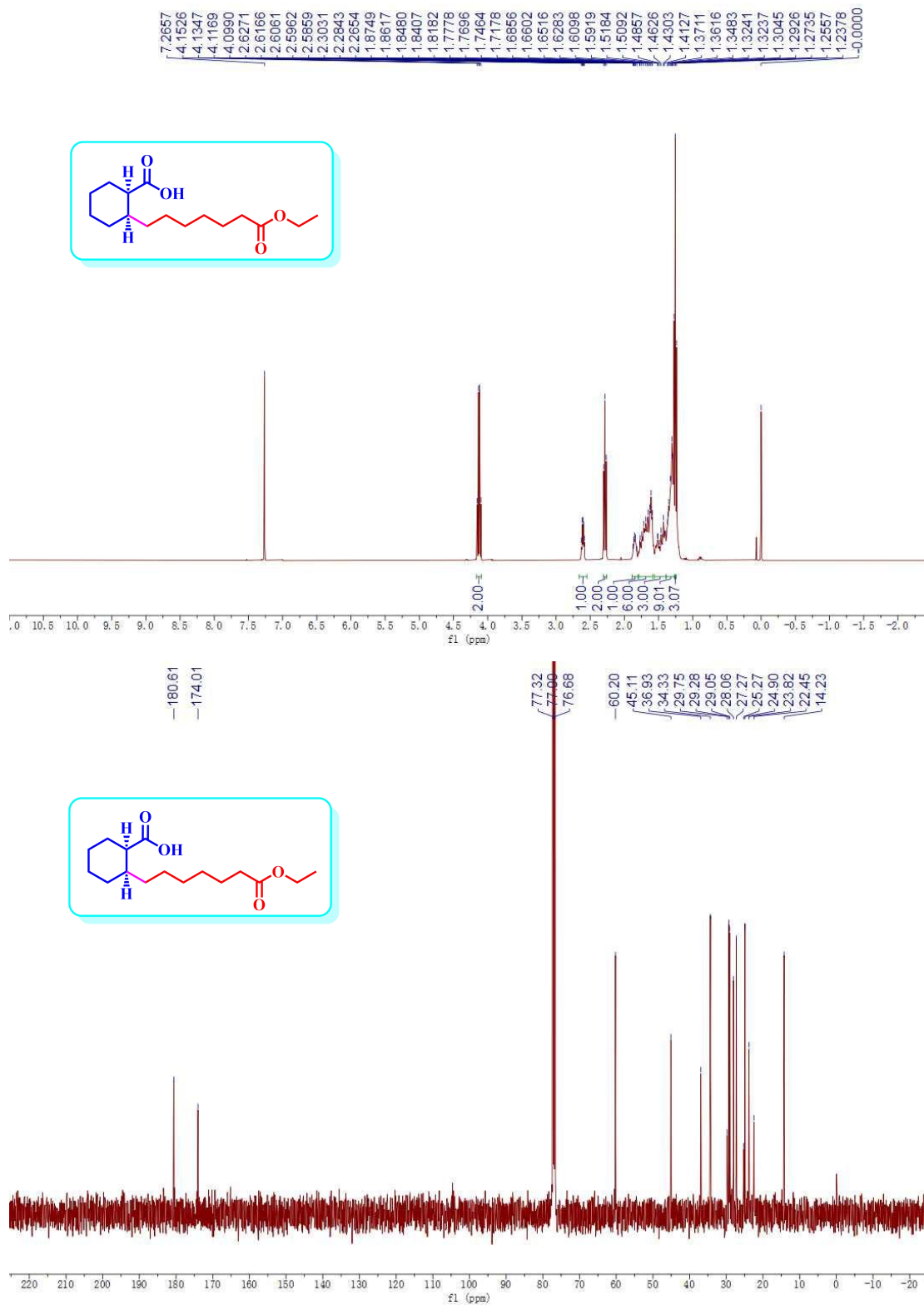


Figure S46. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4aj in CDCl₃

Cis-2-(3-phenylpropyl)cyclohexane-1-carboxylic acid (4ak)

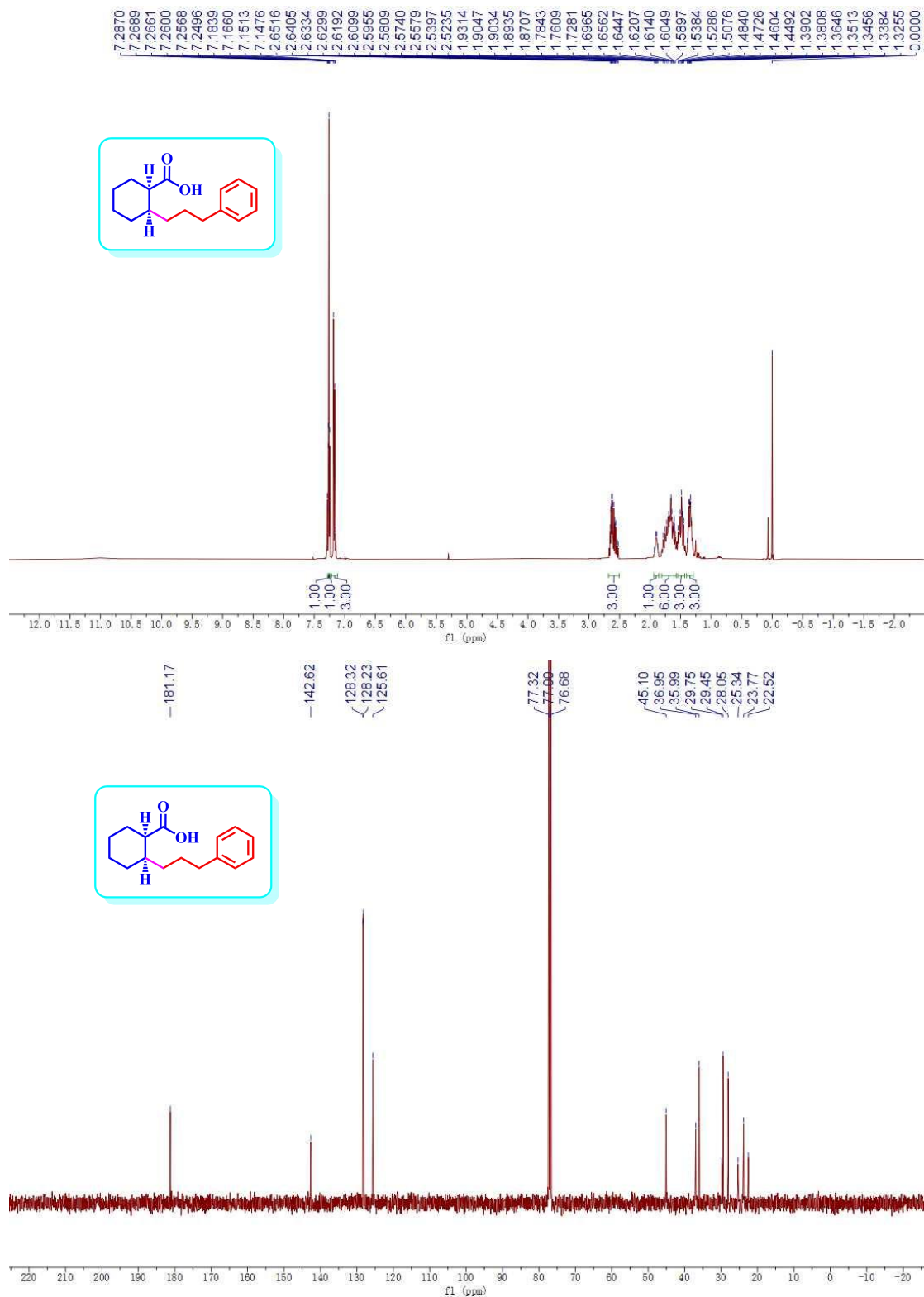


Figure S47. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4ak in CDCl₃

Cis-2-phenethylcyclohexane-1-carboxylic acid (4a)

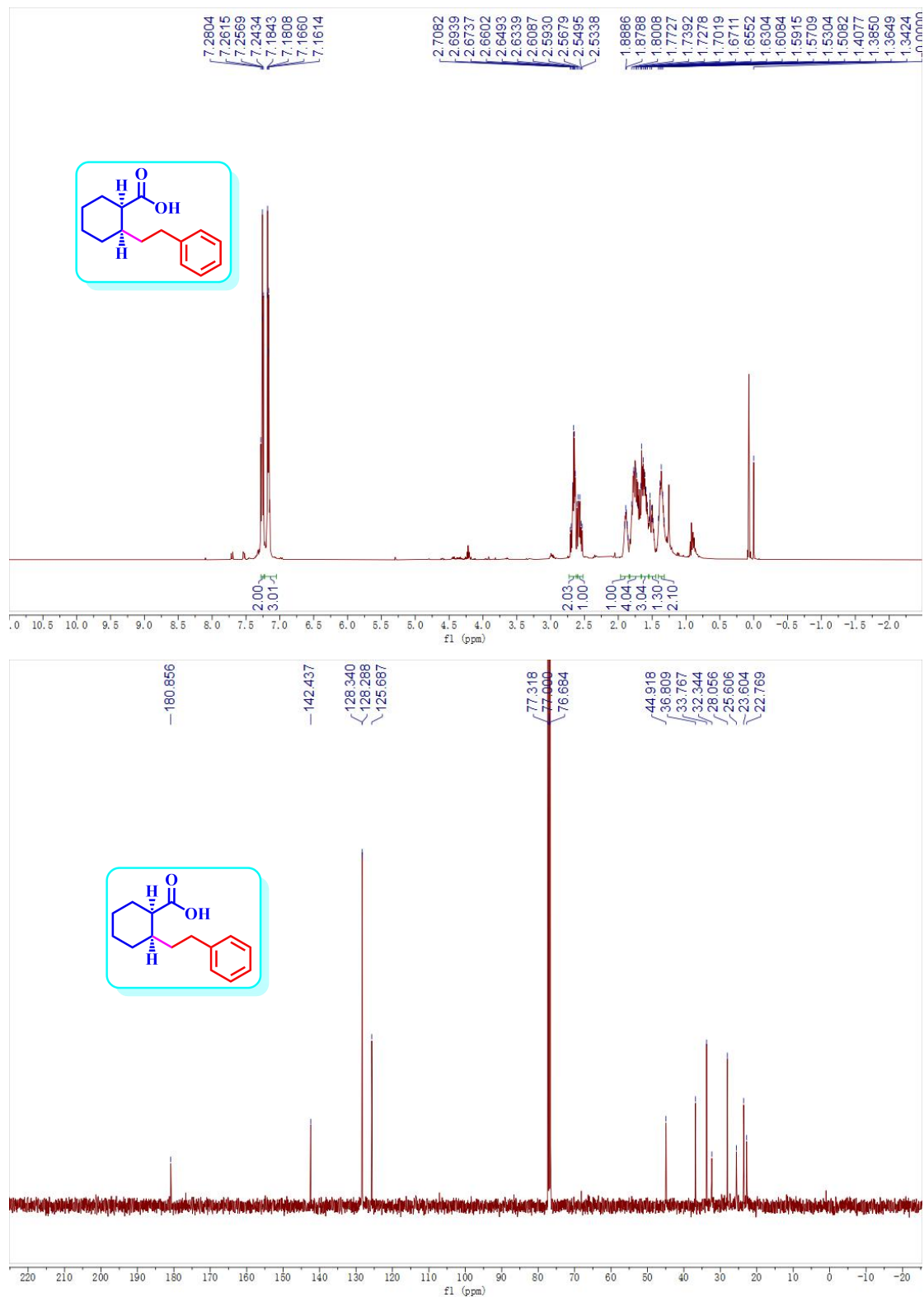


Figure S48. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 4a in CDCl_3

***Cis*-2-(8-(hexadecan-8-yloxy)-8-oxooctyl)cyclohexane-1-carboxylic acid (4am)**

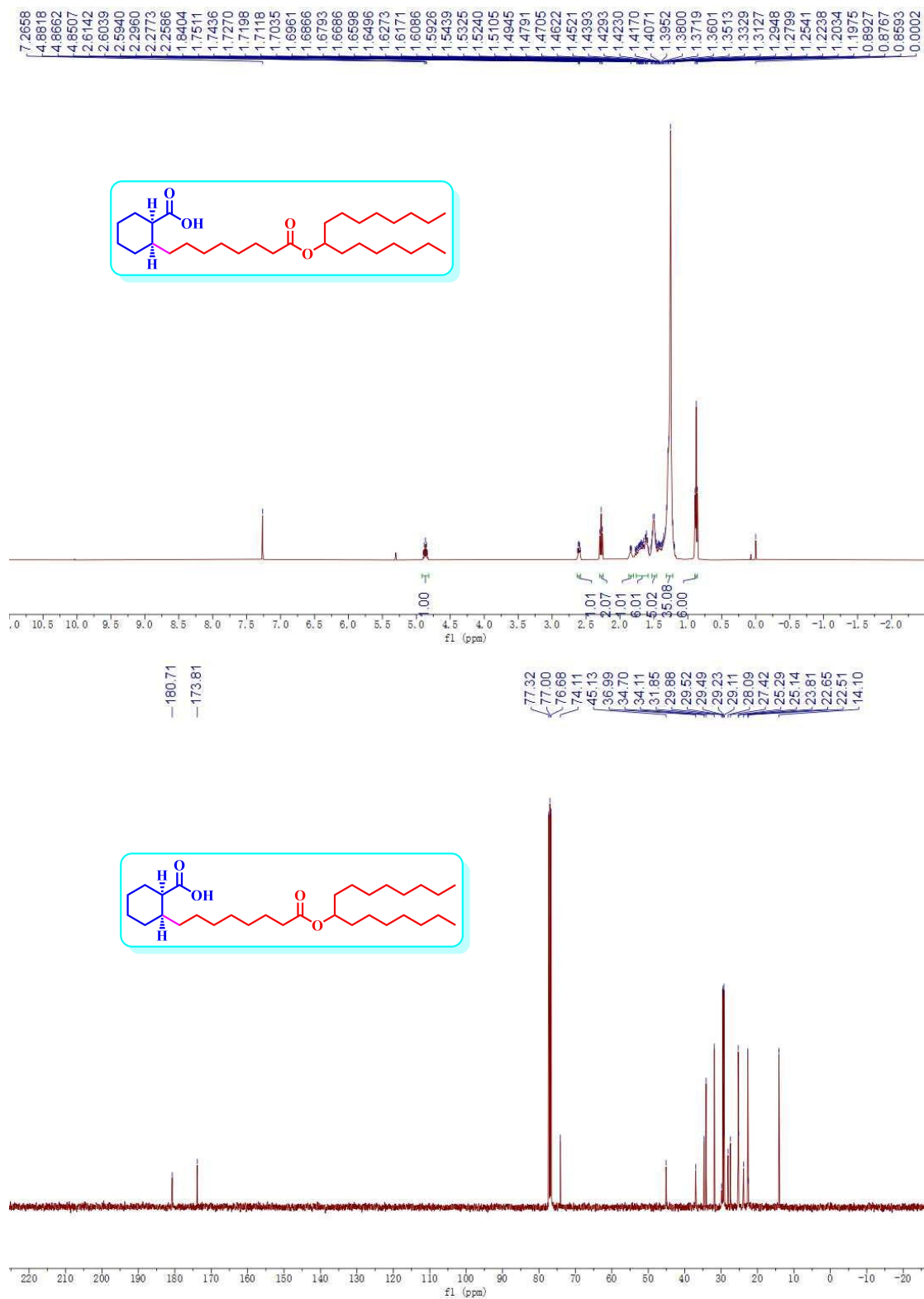


Figure S49. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4am in CDCl₃

Cis-2-(6-((2-heptylnonanoyl)oxy)hexyl)cyclohexane-1-carboxylic acid (4an)

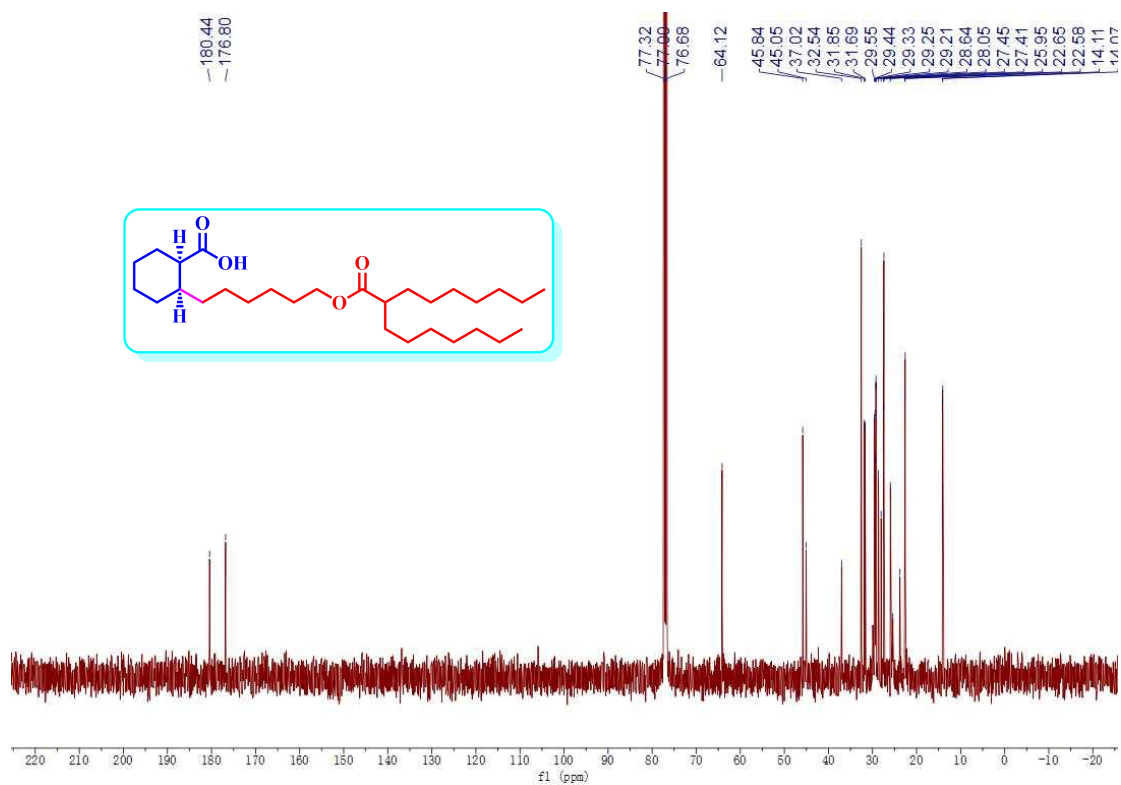
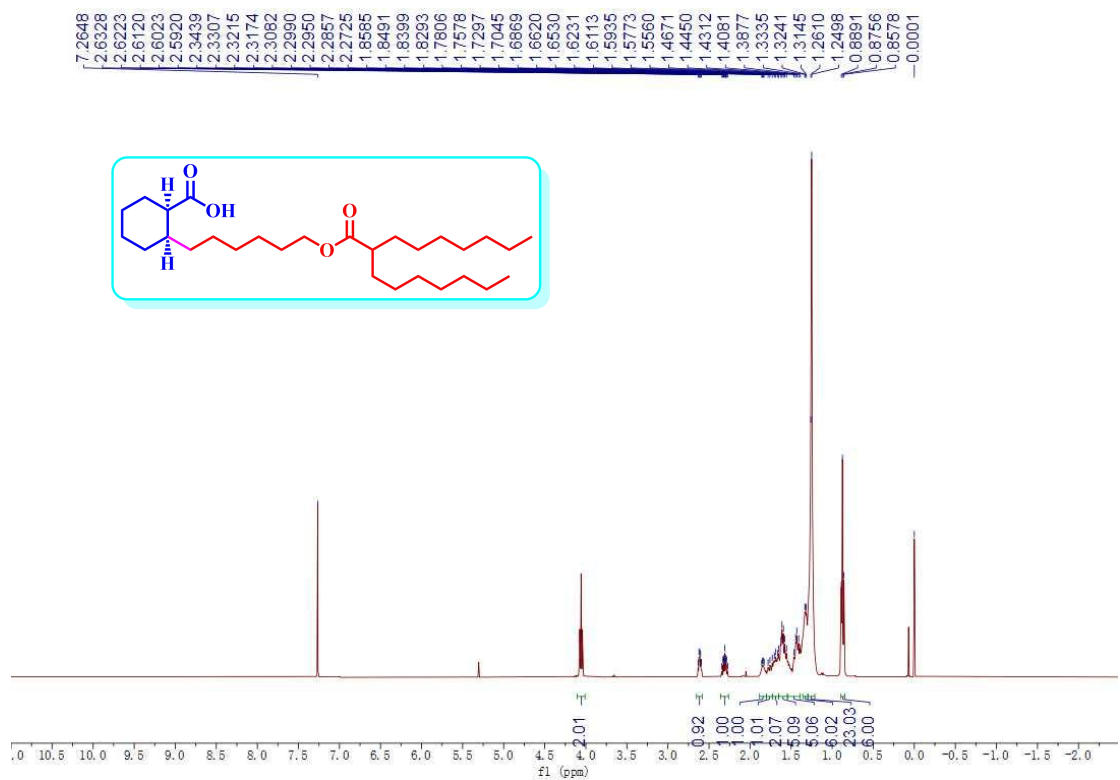


Figure S50. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of **4an** in CDCl₃

Cis-[1,1'-bi(cyclohexane)]-2-carboxylic acid (4ao)

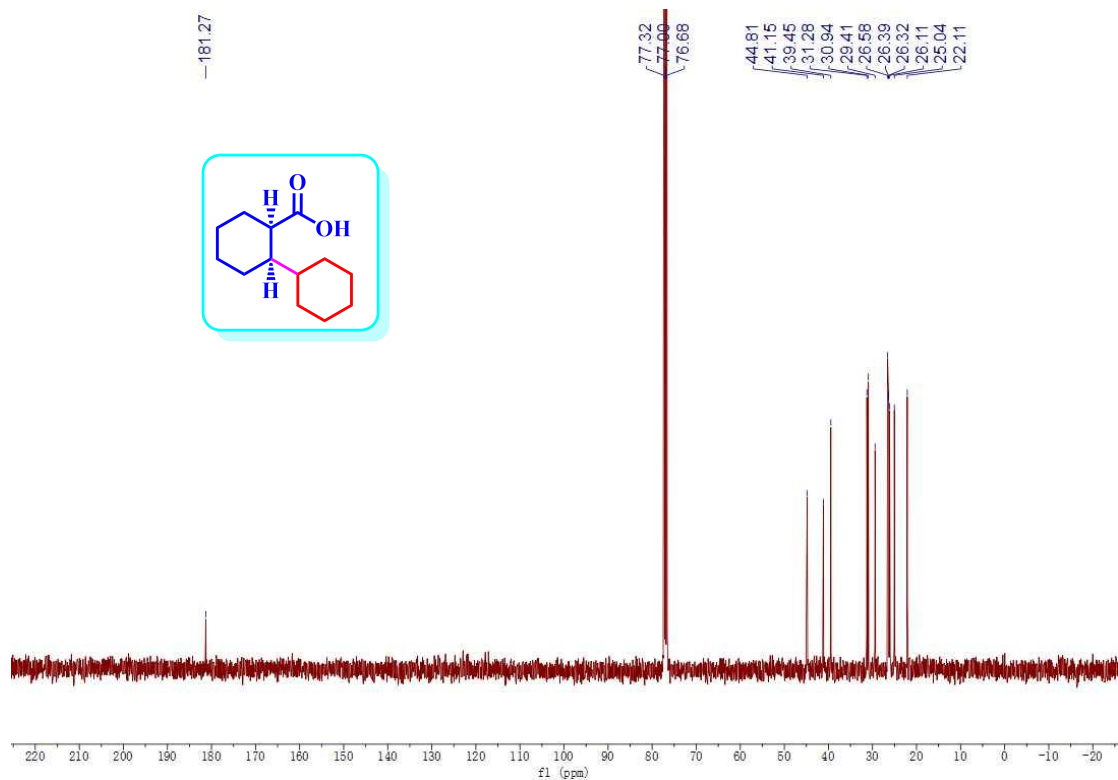
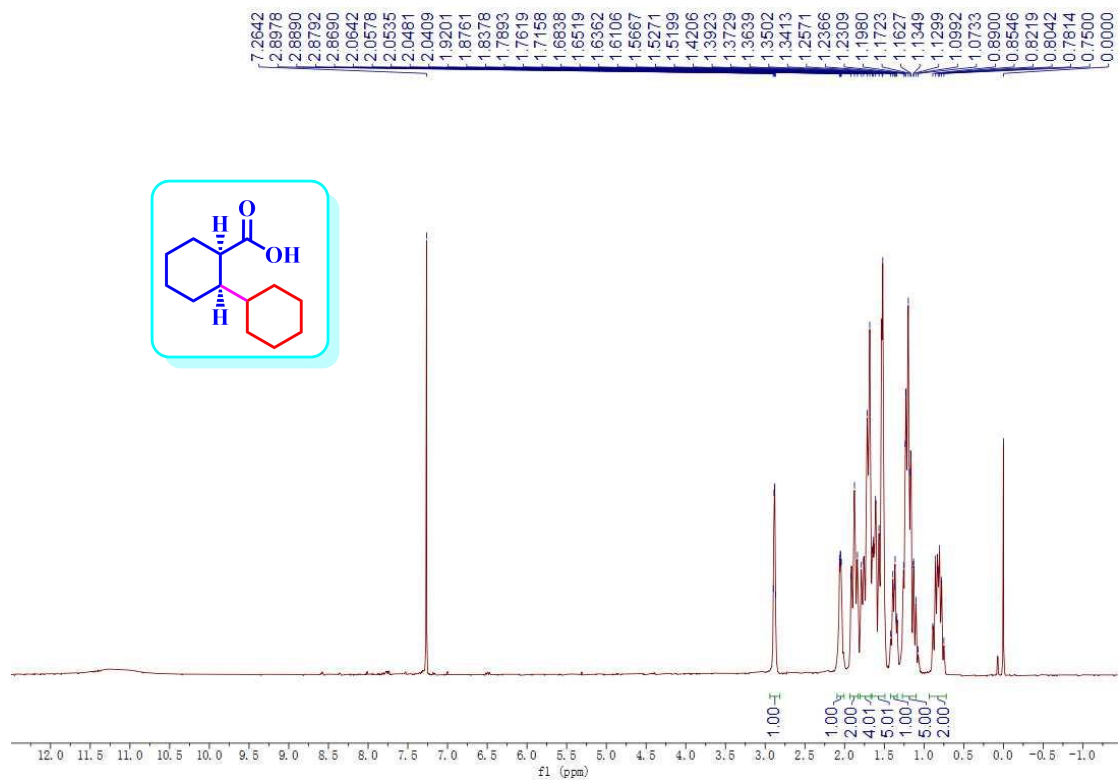


Figure S51. ^1H (400 MHz) and ^{13}C $\{^1\text{H}\}$ (101 MHz) NMR spectra of 4ao in CDCl_3

Cis-2-phenethylcyclopentane-1-carboxylic acid (4bl)

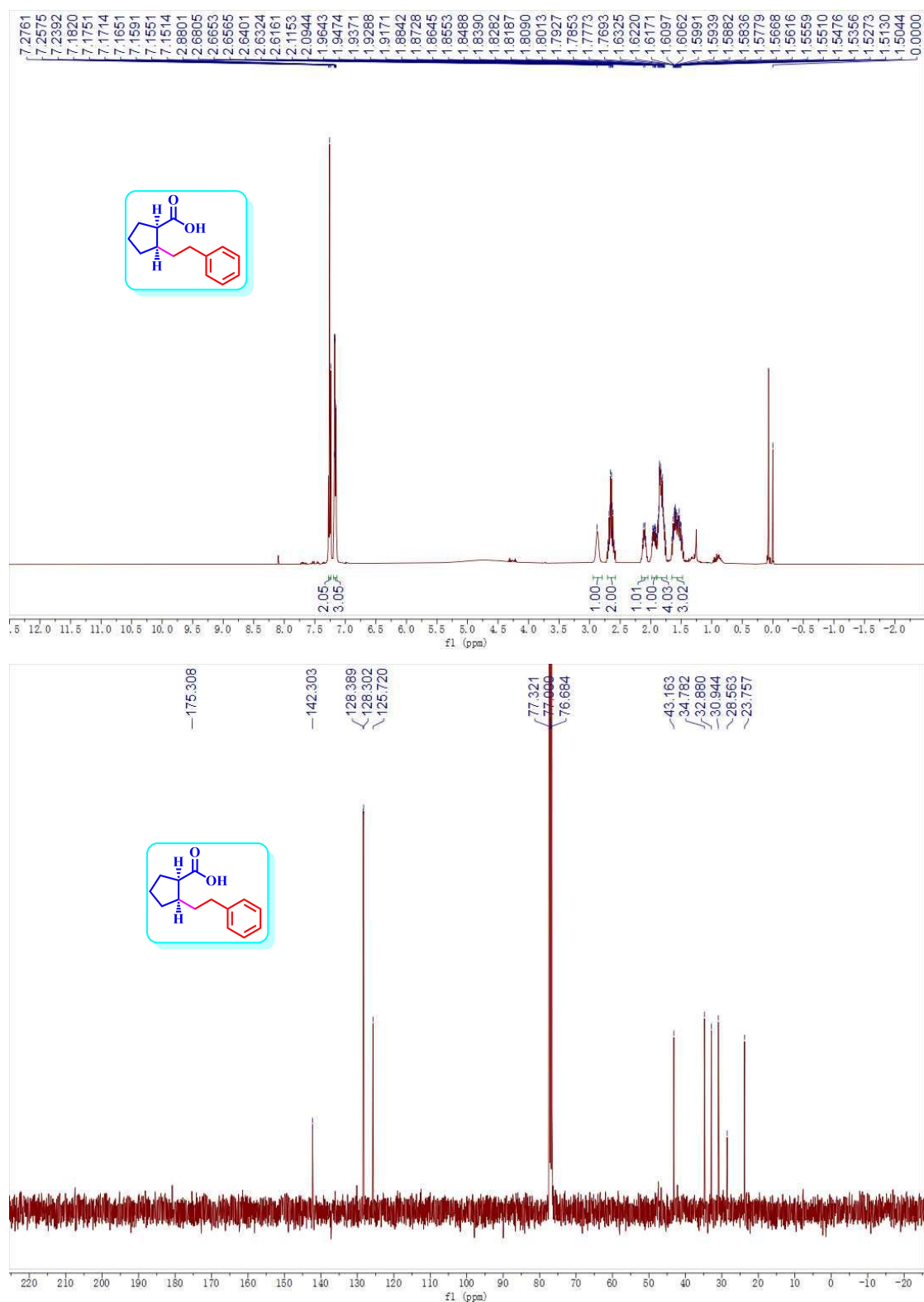


Figure S52. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4bl in CDCl₃

Cis-2-phenethylcyclobutane-1-carboxylic acid (4cl)

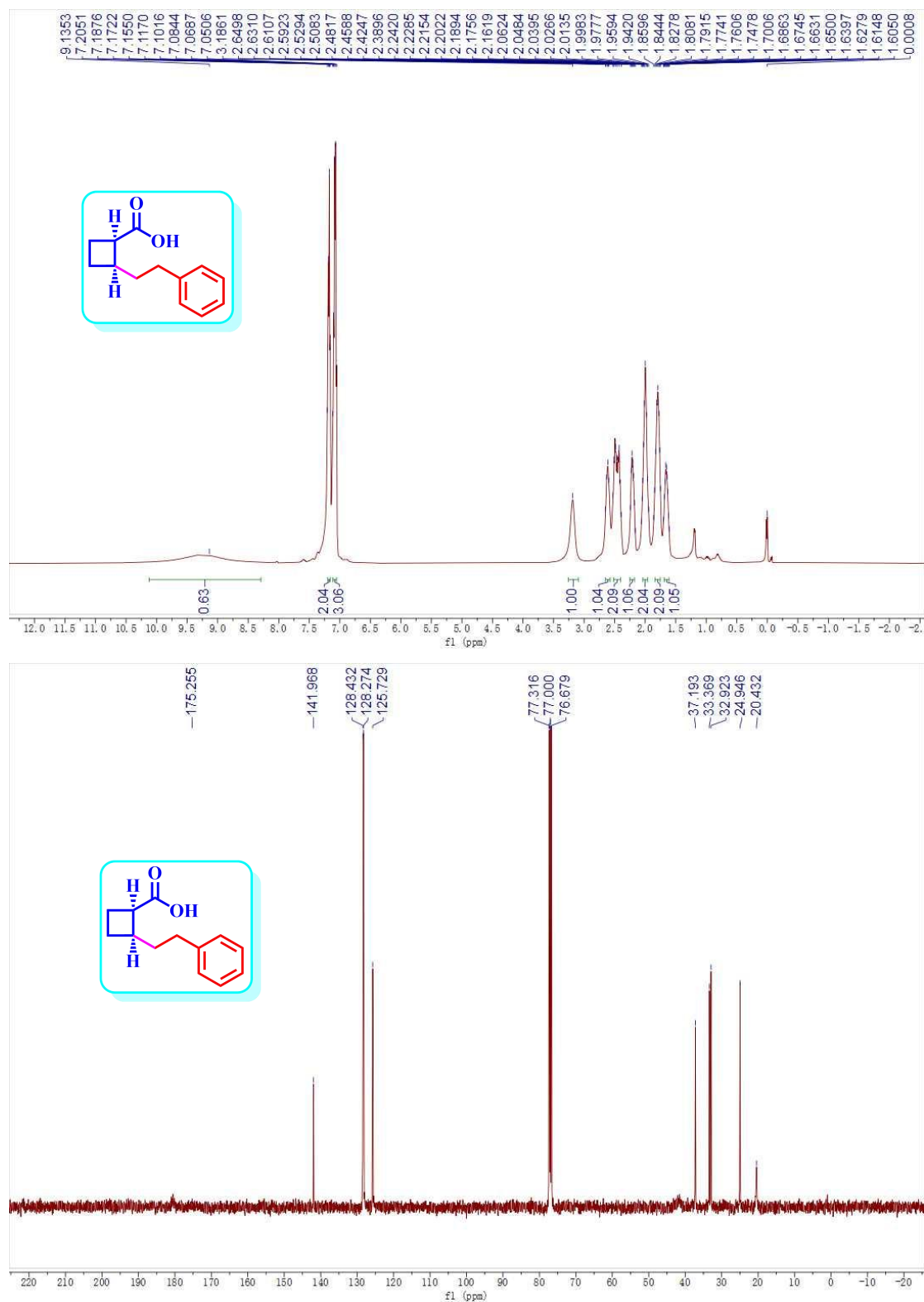


Figure S53. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4cl in CDCl₃

Cis-2-phenethylcyclobutane-1-carboxylic acid (4dl)

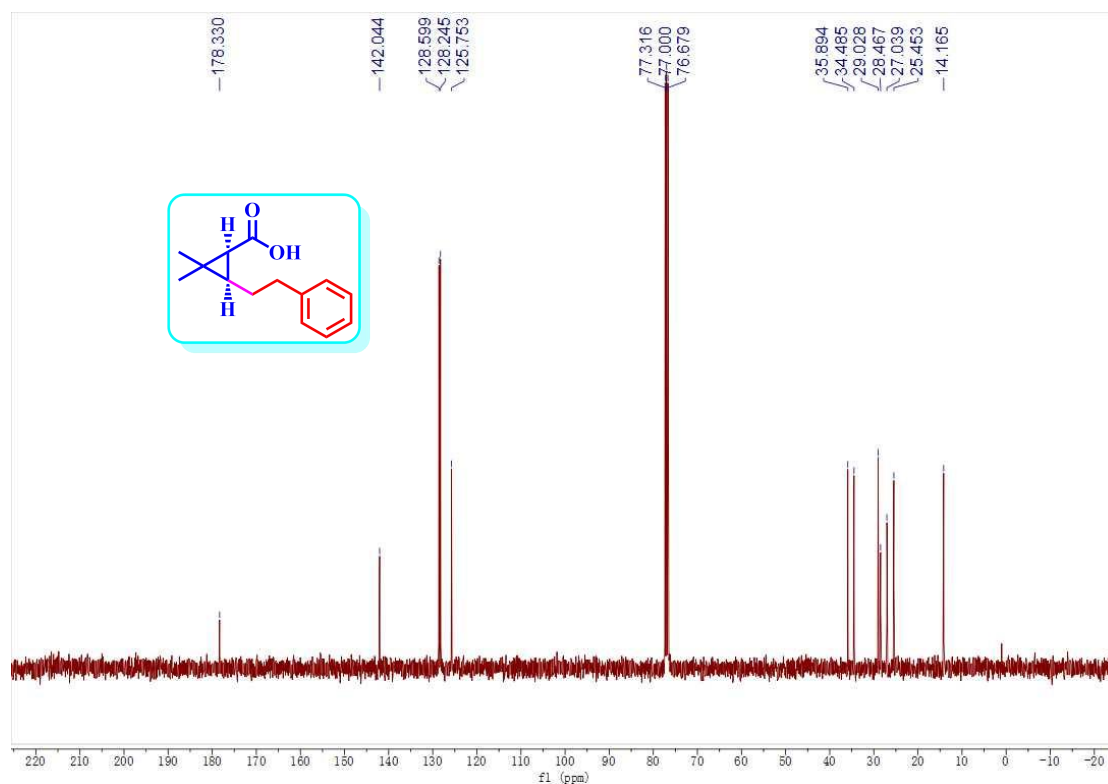
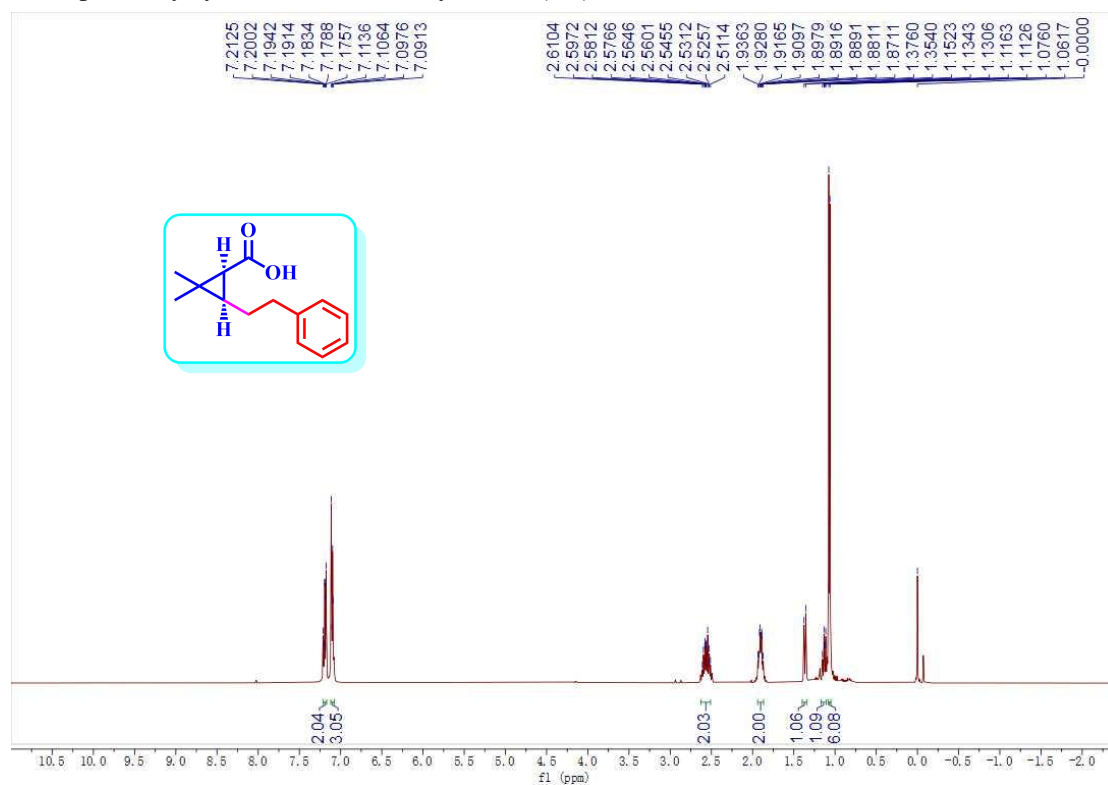


Figure S54. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4dl in CDCl₃

2-(1-(3-phenylpropyl)cyclopentyl)acetic acid (4el)

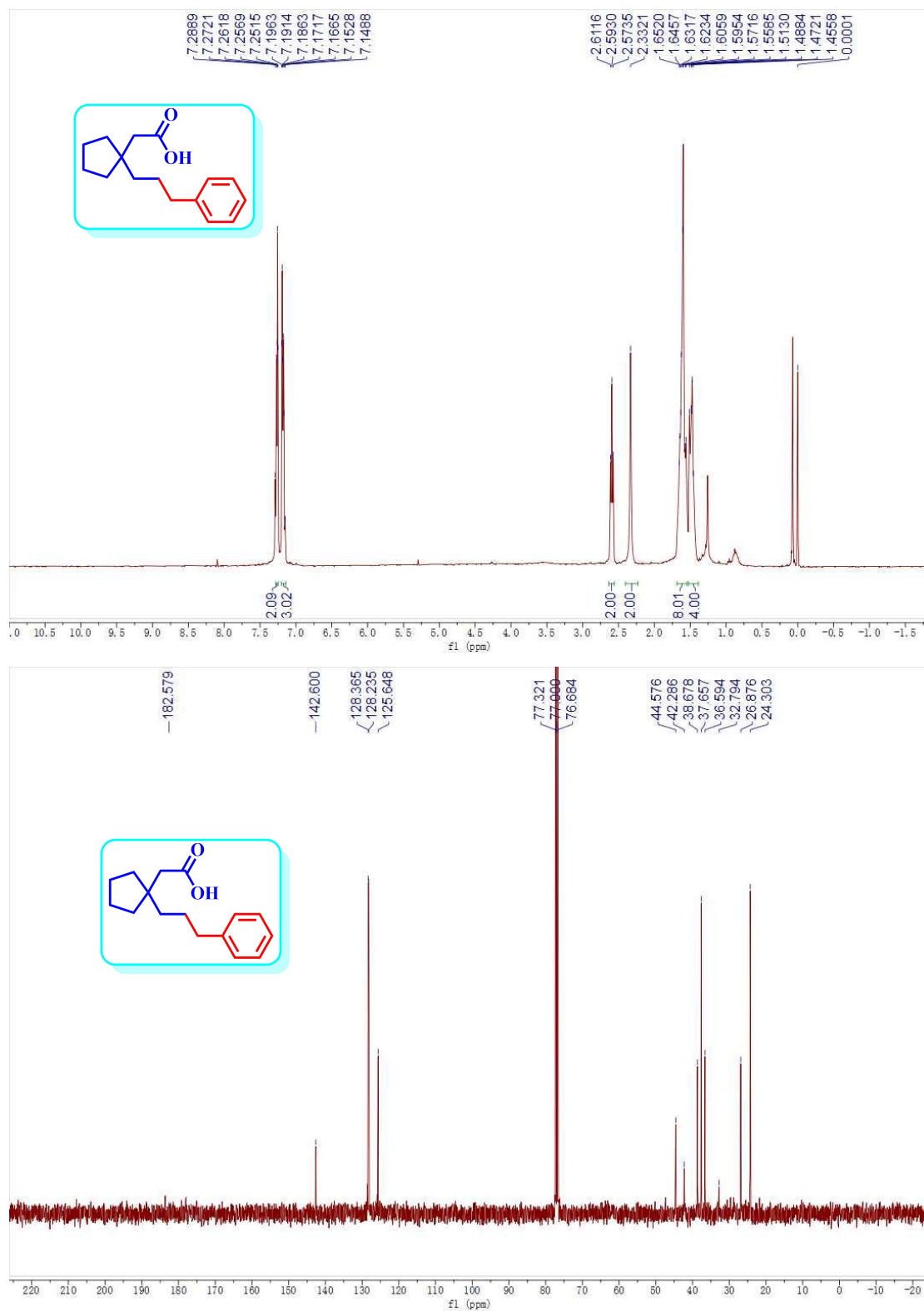


Figure S55. ¹H (400 MHz) and ¹³C {¹H} (101 MHz) NMR spectra of 4el in CDCl₃