Supporting Information

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1. General

New compounds were characterized by ^{1}H, ^{13}C, IR, MS, and HRMS. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz). ^{1}H NMR chemical shifts were determined relative to Me_4Si (0.0 ppm) as an internal standard. ^{13}C NMR chemical shifts were determined relative to $CDCl_3$ (77.0 ppm). Infrared spectra were recorded on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. Mass spectra were obtained on a SHIMADZU GCMS-QP2010 and a JEOL JMS-DX303HF mass spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. Chiral-phase high-performance liquid chromatography (HPLC) was performed on a SHIMADZU prominence series instruments equipped with chiral columns. Optical rotations were measured in a thermostated conventional 10 cm cell on a JASCO DIP-1000 polarimeter using the sodium-D line (589 nm). All reactions were carried out under nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.) or Chromatorex NH (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F_{254} and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

2. Materials

Dehydrated acetonitrile was used from a solvent purification system. Starting materials **1c**,[1] **1d**,[2] **1e**,[3] **1f**,[4] **1g**,[4] **1k**,[5] **1l**,[2] **1m**,[2] and **1n**[6] were prepared according to literature procedures. Analytical data for **1d**,[2] **1f**,[2] **1g**,[7] **1k**,[8] **1l**,[2] and **1m**,[2] were in excellent agreement with reported data. Iodic acid (HIO_3) and *N*–hydroxyphthalimide (NHPI) were purchased and used as obtained. All other solvents and reagents were purchased and used as obtained.

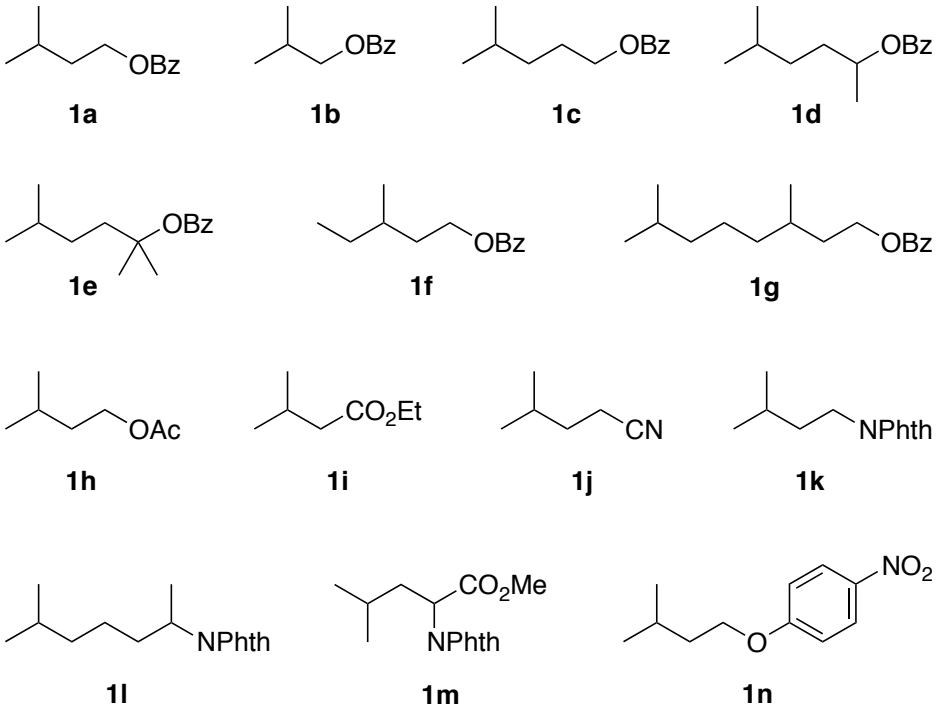
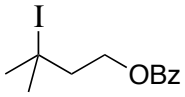


Figure S1. List of substrates

3. Preparation of 3-iodo-3-methylbutyl benzoate (6)



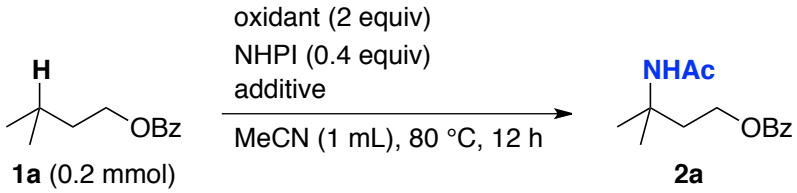
$MeSO_3H$ (0.95 mL, 14.5 mmol) was added dropwise to a solution of NaI (2.27 g, 15.1 mmol) and 3-hydroxy-3-methylbutyl benzoate (1.11 g, 5.3 mmol) in MeCN (25 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 4 h, then allowed to warm to room temperature and it was stirred for an additional 30 min. Next, the reaction mixture was diluted with Et_2O, washed (water, saturated $NaHCO_3$ aq., saturated $Na_2S_2O_3$ aq., and brine), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 95:5) to give the product as a yellow oil (1.00 g, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.57 (t, *J* = 6.8 Hz, 2H), 2.18 (t, *J* = 6.8 Hz, 2H), 2.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 133.0, 130.0, 129.5, 128.4, 65.1, 48.1, 46.3, 38.5; IR (ATR) 3063, 1717 cm^{-1}; MS (CI) *m*/*z* 319 ($[M+H]^+$, 42); HRMS: (CI) calcd for ($C_{12}H_{16}O_2I$) 319.0195 ($[M+H]^+$), found *m*/*z* 319.0189

4. Screening of oxidants

An oven dried 3 mL reaction vial containing a magnetic stir bar was charged with oxidant (0.40 mmol), NHPI (0.08 mmol), MeCN (1 mL), and isoamyl benzoate (**1a**) (0.20 mmol). The vial was purged with N_2 and sealed with a screw cap. The reaction mixture was stirred at 80 °C for 12 h. The reaction was then quenched by $Na_2S_2O_3$ aq. (1 M, 10 mL). The mixture was extracted with diethyl ether (3 x 10 mL), and the combined organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

The results are summarized in Table S1. The reaction using HIO_3 as well as I_2O_5 proceeded efficiently to provide **2a**, while $NaIO_3$ and NH_4IO_3 showed no reactivity (entries 1–4). Several common oxidants were not effective for this amination (entries 5–12). In the case of the reaction in the presence of I_2, CAN, Oxone, and *m*CPBA also effectively promoted the amination, while reactions using $PhI(OAc)_2$ and $K_2S_2O_8$ failed to give **2a** (entries 13–18).

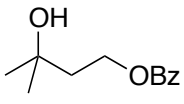
Table S1.



1a (0.2 mmol) **2a**

entry	oxidant	additive	yield (%)[a]	recovery (%)[a]
1[b,c]	HIO_3	-	72	<5
2[b,c,d]	I_2O_5	-	70	<5
3	$NaIO_3$	-	0	82
4	NH_4IO_3	-	0	85
5	CAN	-	19	44
6	Oxone	-	0	91
7	*m*CPBA	-	0	73
8	$PhI(OAc)_2$	-	<5	86
9	$K_2S_2O_8$	-	<5	56
10	Selectfluor	-	<5	24
11	DDQ	-	0	87
12	IBX	-	0	>95
13	CAN	I_2 (0.5 equiv)	53	13
14	Oxone	I_2 (0.5 equiv)	69	0
15	*m*CPBA	I_2 (0.5 equiv)	65	5
16	$PhI(OAc)_2$	I_2 (0.5 equiv)	<5	71
17	$K_2S_2O_8$	I_2 (0.5 equiv)	0	>95
18	-	I_2 (0.5 equiv)	0	>95

[a] Determined by ^1H NMR analysis. [b] Reactions were conducted on a 0.4 mmol scale. [c] Alcohol **2a'** was generated (entry 1: 5%, entry 2: 8%). [d] I_2O_5 (1 equiv) was used.



2a'

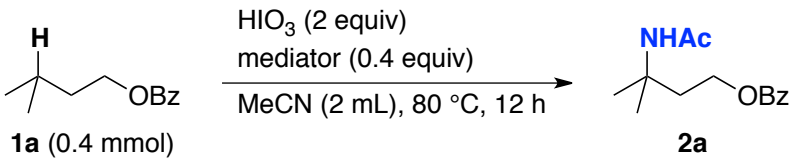
5. Screening of mediators

An oven dried 3 mL reaction vial containing a magnetic stir bar was charged with HIO_3 (0.80 mmol), mediator (0.16 mmol), MeCN (2 mL), and isoamyl benzoate (**1a**) (0.40 mmol). The vial was purged with N_2 and sealed with a screw cap. The reaction mixture

was stirred at 80 °C for 12 h. The solid precipitates were filtered off, and the filtrate was concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

The results are summarized in Table S2. Imide-based reagents, NHPI, NDHPI, and SuOH, were found to be suitable for this reaction (entries 1–3), and NHPI gave the best result. However, amide-based reagents, PBHA and NMBHA, were inactive (entries 4 and 5).

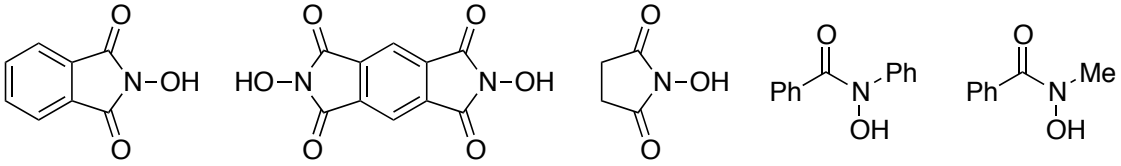
Table S2.



1a (0.4 mmol) **2a**

entry	mediator	yield (%)[a]	recovery (%)[a]
1	NHPI	77	<5
2	NDHPI	69	<5
3	SuOH	40	59
4	PBHA	0	>95
5	NMBHA	<5	>95

[a] Determined by ^{1}H NMR analysis.

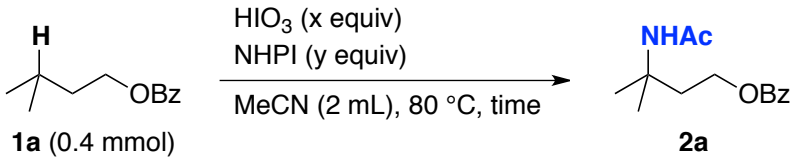


6. Optimization of reaction conditions

An oven dried 3 mL reaction vial containing a magnetic stir bar was charged with HIO_3, NHPI, MeCN (2 mL), and isoamyl benzoate (**1a**) (0.40 mmol). The vial was purged with N_2 and sealed with a screw cap. The reaction mixture was stirred at 80 °C for the indicated time. The reaction was quenched by passing the solution through a short column (NH silica gel) using EtOAc as the eluent. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Purification was performed by flash column chromatography on silica gel (hexane/EtOAc).

The results are summarized in Table S3. Examination of reactions by varying the amount of reagents (HIO_3 and NHPI) revealed that the use of HIO_3 (0.8 equiv) and NHPI (0.2 equiv) in conjunction with a longer reaction time of 24 h afforded **2a** in 74% yield (entries 1–4). Using lower amounts of reagents resulted in a decreased yield of the product (entries 5–8). The addition of I_2 had a negligible effect on the reaction (entry 9). Control experiments in the absence of either HIO_3 or NHPI revealed that both reagents were required for this transformation (entries 10 and 11). The reaction proceeded equally well, even in the dark (entry 12).

Table S3.



1a (0.4 mmol) **2a**

entry	HIO_3 (equiv)	NHPI (equiv)	time	yield (%)[a]	recovery (%)[a]
1	2.0	0.4	12	77 (70)	<5
2	1.0	0.4	12	78 (71)	<5
3	0.8	0.4	12	73	5
4	0.8	0.2	24	74 (71)	9
5	0.5	0.4	12	65	22
6	0.5	0.4	24	67	28
7	0.8	0.1	24	48	50
8	0.8	0.1	36	57	38
9[b]	0.8	0.2	24	76	5
10	0	0.2	24	0	92
11	0.8	0	24	0	94
12[c]	0.8	0.2	24	72	15

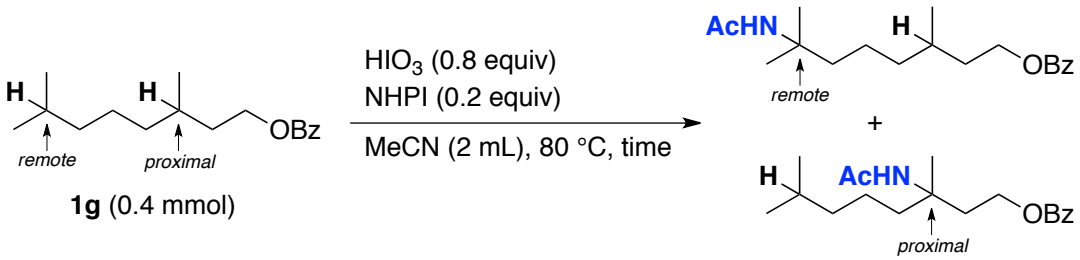
[a] Determined by ^1H NMR analysis. Values in parentheses are isolated yields.
[b] I_2 (0.5 equiv) was added. [c] The reaction was conducted under dark.

7. Regioselectivity in the reaction of 1g

An oven dried 3 mL reaction vial containing a magnetic stir bar was charged with HIO_3 (0.32 mmol), NHPI (0.08 mmol), MeCN (2 mL), and benzoate **1g** (0.40 mmol). The vial was purged with N_2 and sealed with a screw cap. The reaction mixture was stirred at 80 °C for the indicated time. The reaction was then quenched by passing the solution

through a short column (NH silica gel) using EtOAc as the eluent. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by GC analysis using dodecane as an internal standard. Purification was performed by flash column chromatography on silica gel (hexane/EtOAc).
The results are summarized in Table S4.

Table S4.



entry	time	yield (%)[a]		recovery (%)[a]
		remote	*proximal*	
1	3	16	5	72
2	6	27	7	59
3	12	41 (44)	9 (10)	28

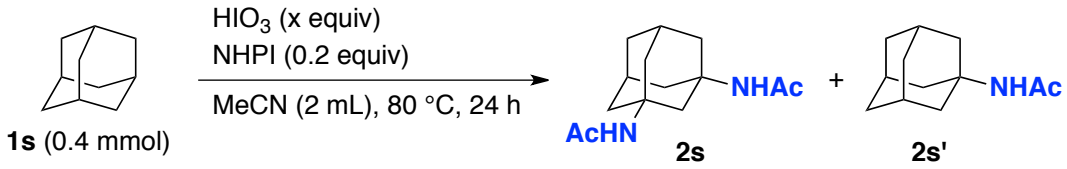
[a] Determined by GC analysis using dodecane as an internal standard. The response factor of minor isomer is not corrected. Values in parentheses are isolated yields.

8. Reaction of adamantane

An oven dried 3 mL reaction vial containing a magnetic stir bar was charged with HIO_3, NHPI (0.08 mmol), MeCN (2 mL), and adamantane (0.40 mmol). The vial was purged with N_2 and sealed with a screw cap. The reaction mixture was stirred at 80 °C for 24 h. The reaction was then quenched by passing the solution through a short column (NH silica gel) using EtOAc as the eluent. The solution was concentrated under reduced pressure to give the crude product. Purification was performed by flash column chromatography on silica gel (hexane/EtOAc then MeOH).
The results are summarized in Table S5. When the reaction was conducted using 0.4 equiv. of HIO_3, the monoaminated product **2s'** was obtained as the main product. Increasing the amount of HIO_3 provided the diaminated product **2s** efficiently, and the use of 1.2 equiv. of HIO_3 afforded **2s** in 61% yield. However, further increasing the amount of HIO_3 resulted in the formation of an complex mixture of products that could

not be separated.

Table S5.



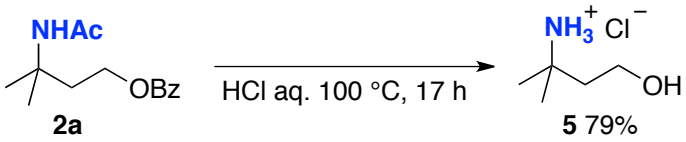
entry	HIO_3 (equiv)	yield (%)[a]	
		2s	**2s'**
1	0.4	13	49
2	0.8	43	26
3	1.2	61	13
4	1.6	n.d.	trace

[a] Isolated yields.

9. Hydrolysis of the acetamide product 2a

A reaction flask containing a magnetic stir bar was charged with 3-acetamido-3-methylbutyl benzoate (**2a**) (500.6 mg, 2.01 mmol) and HCl aq. (3 M, 10 mL). The reaction mixture was stirred at 100 °C for 17 h. Then, the reaction mixture was cooled to room temperature, and Et_2O (10 mL) and HCl aq. (2 M, 10 mL) was added. The separated aqueous solution was concentrated under reduced pressure to give the crude product as a solid, which was washed with acetone gave the pure product as a white solid (220.4 mg, 79% yield) (Scheme S1).

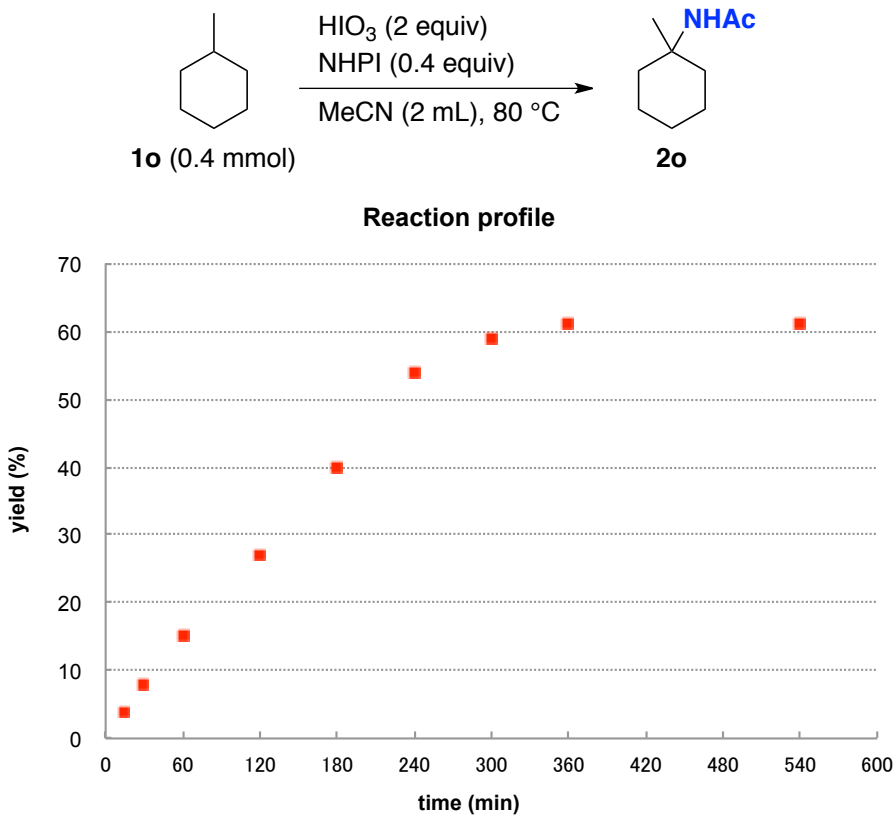
Schcme S1.



10. Reaction profile

Nine identical reaction mixtures were prepared as follows: an oven dried 3 mL reaction vial containing a magnetic stir bar was charged with HIO_3 (0.80 mmol), NHPI (0.16 mmol), MeCN (2 mL), and methylcyclohexane (0.40 mmol). The vial was purged with

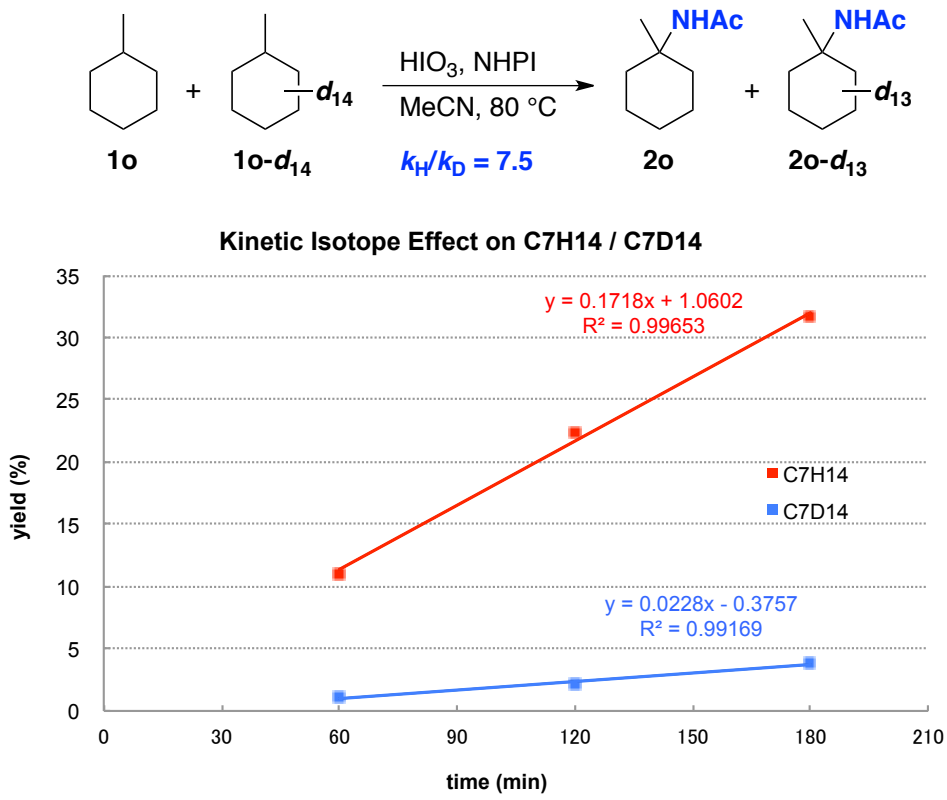
N_2 and sealed with a screw cap. Nine reaction mixtures were stirred in parallel at 80 °C for the indicated time. The reactions were quenched by passing the solution through a short column (NH silica gel) using EtOAc as the eluent. The solution was concentrated under reduced pressure to give the crude products, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Yields of **2o** were plotted versus time.



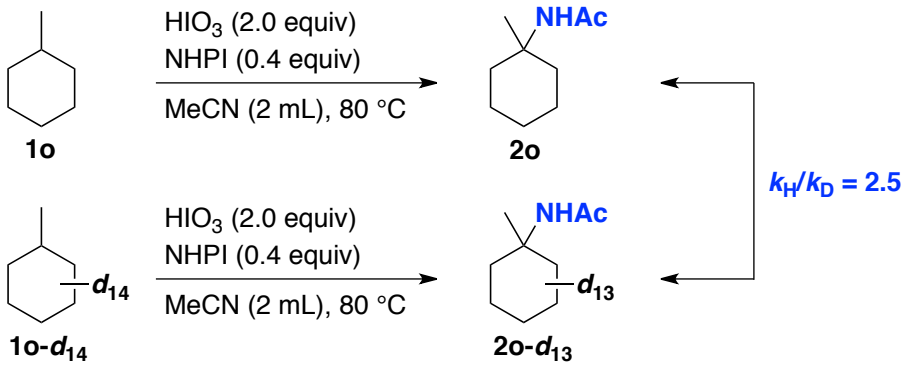
11. Investigation of KIE

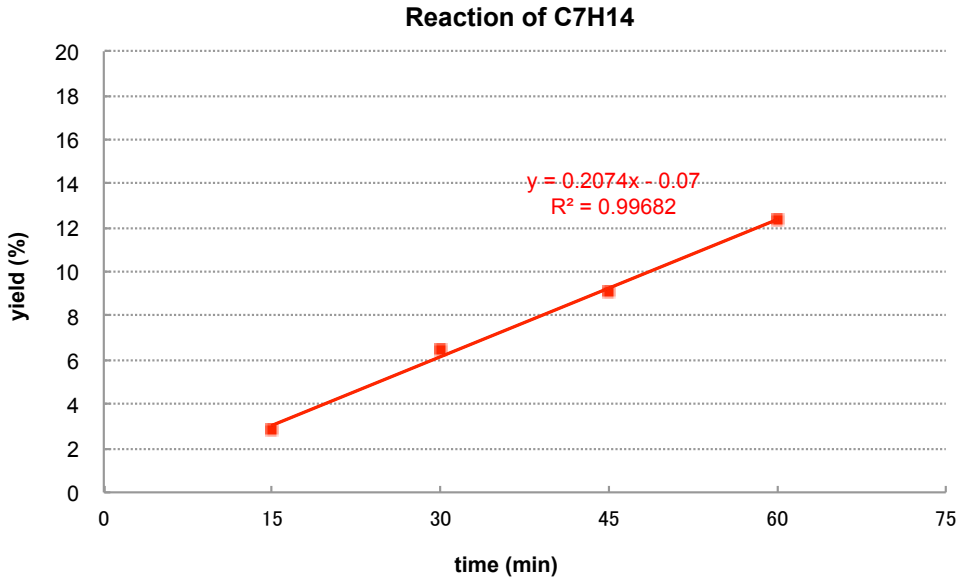
Reaction in the same vessel: Three identical reaction mixtures were prepared as follows: an oven dried 3 mL reaction vial containing a magnetic stirring bar was charged with HIO_3 (0.20 mmol), NHPI (0.04 mmol), MeCN (0.5 mL), methylcyclohexane (0.50 mmol), and methylcyclohexane-d_{14} (0.50 mmol). The vial was purged with N_2 and sealed with a screw cap. Three reaction mixtures were stirred in parallel at 80 °C for 60, 120, and 180 min, respectively. The reactions were quenched by passing the solution through a short column (NH silica gel) using EtOAc as the eluent. The solution was concentrated under reduced pressure to give the crude products, which

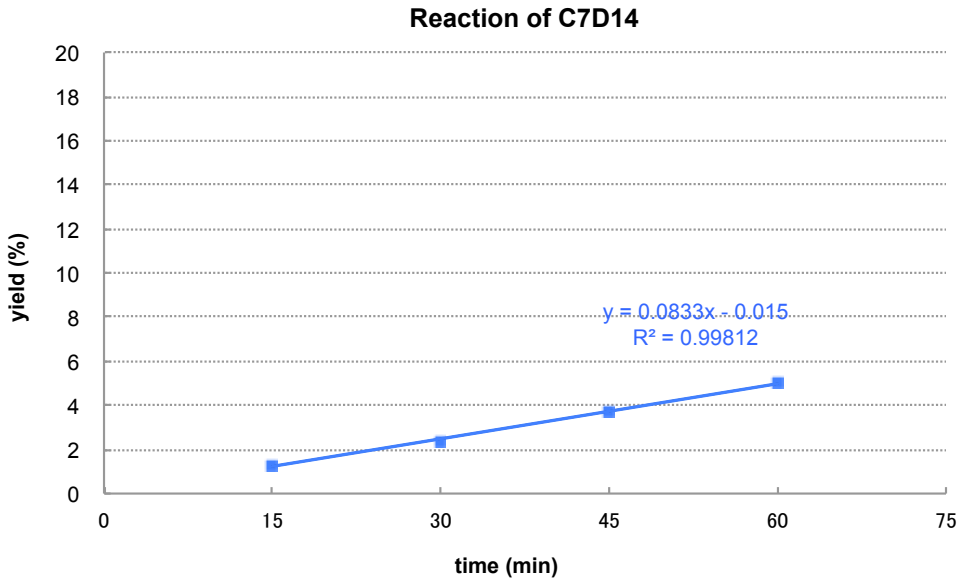
were analyzed by GC using dodecane as an internal standard. Yields of **2o** and **2o-d_{13}** were plotted versus time, and the KIE value was calculated to be k_H/k_D = 0.1718/0.0228 = 7.5.



Reactions in separate vessels: Four identical reaction mixtures were prepared as follows: an oven dried 3 mL reaction vial containing a magnetic stir bar was charged with HIO_3 (0.80 mmol), NHPI (0.16 mmol), MeCN (2 mL), and methylcyclohexane (0.40 mmol). Four reaction mixtures were stirred in parallel at 80 °C for 15, 30, 45, and 60 min, respectively. The reactions were quenched by passing the solution through a short column (NH silica gel) using EtOAc as the eluent. The solution was concentrated under reduced pressure to give the crude products, which were analyzed by GC using dodecane as an internal standard. Yields of **2o** were plotted versus time. Experiments using methylcyclohexane-d_{14} instead of methylcyclohexane were conducted in the same way. The KIE value was calculated to be k_H/k_D = 0.2074/0.0833 = 2.5.


HIO3 (2.0 equiv)
NHPI (0.4 equiv)
MeCN (2 mL), 80 °C
NHAc
1o
2o
kH/kD = 2.5
d14
d13
1o-d14
2o-d13

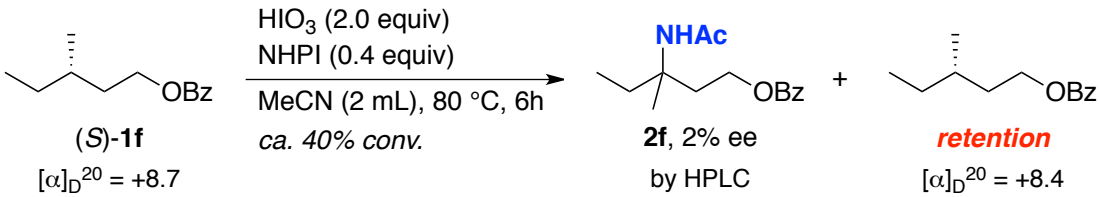

Reaction of C7H14
yield (%)
time (min)
y = 0.2074x - 0.07
R² = 0.99682


Reaction of C7D14
yield (%)
time (min)
y = 0.0833x - 0.015
R² = 0.99812

12. Stereochemical course of the reaction using (*S*)-1f

An oven dried 3 mL reaction vial containing a magnetic stir bar was charged with HIO_3 (0.80 mmol), NHPI (0.16 mmol), MeCN (2 mL), and (*S*)-**1f** (0.40 mmol). The vial was purged with N_2 and sealed with a screw cap. The reaction mixture was stirred at 80 °C for 6 h. The reaction was then quenched by passing the solution through a short column (NH silica gel) using EtOAc as the eluent. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Purification by flash column chromatography on silica gel (hexane/EtOAc) gave **2f** (33.1 mg, 32% yield, 2% ee, HPLC analysis (Chiralpak IC-3; 1.0 mL/min; *i*-PrOH/*n*-hexane 5:95; λ = 254 nm). The stereochemical information of the recovered **1f** (44.7 mg, 56% yield) was determined by a value of specific rotation (Specific rotation $[\alpha]_D^{20}$ = +8.4 (c = 0.99, $CHCl_3$)). The value was in excellent agreement with that of the starting material (*S*)-**1f** (Specific rotation $[\alpha]_D^{20}$ = +8.7 (c = 1.06, $CHCl_3$)).

Schcme S2.



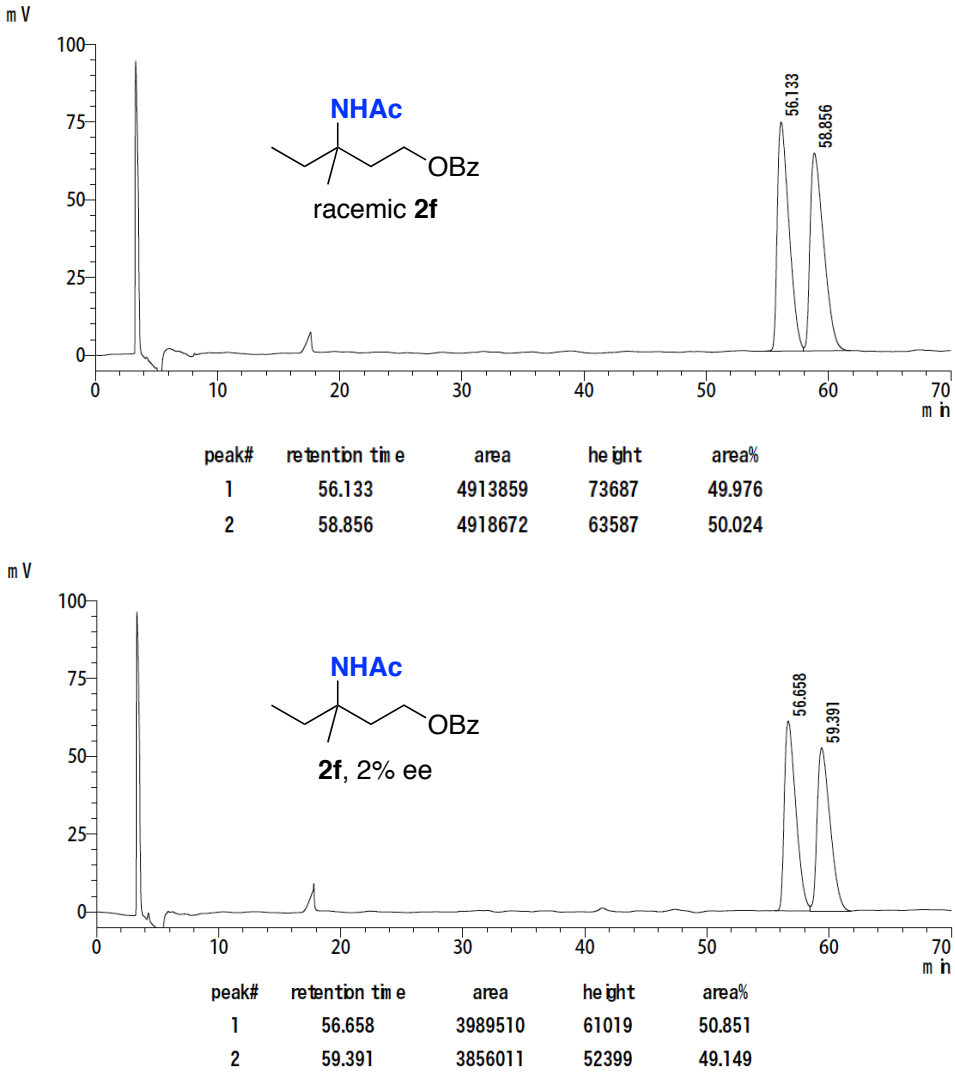


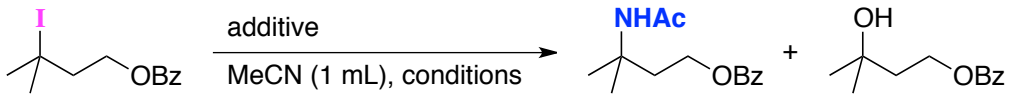
Figure S2. HPLC charts of racemic 2f and 2f generated from (*S*)-1f

13. Reaction of alkyl iodide 6 leading to amide 2a

An oven dried reaction flask containing a magnetic stir bar was charged with iodide **6** (0.20 mmol), MeCN (1 mL), and an additive. The flask was purged with N_2. The reaction mixture was stirred under the indicated reaction conditions. The reaction was then quenched by $Na_2S_2O_3$ aq. (1 M, 10 mL). The mixture was extracted with diethyl ether (3 x 10 mL), and the combined organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

The results are summarized in Table S6. Stirring a solution of **6** in MeCN at 80 °C failed to give **2a**, while the aminaton proceeded in the presence of HIO_3, affording **2a** in low yield (entries 1–3). In the reaction under the standard conditions, an alkyl iodide could be catalytically generated in situ , thus the slow addition of **6** to a suspension of HIO_3 in MeCN at 80 °C was examined, and the yield of **2a** was then increased to 56% yield (entry 4). In the reaction at room temperature, **2a** was obtained in the presence of HIO_3 while no reaction was observed in the absence of HIO_3 (entries 6 and 7). An acid-promoted mechanism can be ruled out, since **2a** was not obtained in the presence of CF_3CO_2H (entries 8 and 9).

Table S6.



6 (0.2 mmol) **2a** **2a'**

entry	additive	conditions	yield (%)[a]		recovery (%)[a]
			2a	**2a'**	
1	-	80 °C, 1.5 h	0	0	0 (>95)[b]
2	HIO_3 (0.8 equiv)	80 °C, 30 min	9	37	0
3[c]	HIO_3 (0.8 equiv)	80 °C, 30 min	9	44	0
4[d]	HIO_3 (0.8 equiv)	80 °C, 1 h	56	7	0
5[c,d]	HIO_3 (0.8 equiv)	80 °C, 1 h	48	9	0
6	-	rt, 3 h	0	0	>95
7	HIO_3 (0.8 equiv)	rt, 1 h	46	n.d.	0
8	CF_3CO_2H (1 equiv)	rt, 3 h	0	0	>95
9	CF_3CO_2H (1 equiv)	80 °C, 1.5 h	0	0	0 (84)[b]

[a] Determined by ^{1}H NMR analysis. [b] Yield of benzoic acid. [c] NHPI (0.2 equiv) was added. [d] Iodide **6** in MeCN (0.5 mL) was added dropwise for 1 h.

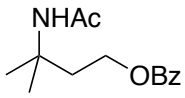
14. The Ritter-type C–H amination: typical procedure and product data

Typical procedure: An oven dried 3 mL reaction vial containing a magnetic stir bar was charged with HIO_3 (0.32 mmol), NHPI (0.08 mmol), MeCN (2 mL), and substrates (0.40 mmol). The vial was purged with N_2 and sealed with a screw cap. The reaction mixture was stirred at 80 °C for the indicated time. The reaction was then quenched by passing the solution through a short column (NH silica gel) using EtOAc as the eluent. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Purification by flash column chromatography on silica gel (hexane/EtOAc) gave the pure product.

Experimental procedure of gram-scale reaction of 1a: An oven dried reaction flask equipped with a magnetic stir bar and reflux condenser was charged with HIO_3 (1.41 g, 8.01 mmol), NHPI (0.326 g, 2.00 mmol), MeCN (50 mL), and isoamyl benzoate (1.97 g, 10.2 mmol). The vial was purged with N_2, and the reaction mixture was stirred under reflux (thermostated at 120 °C) for 24 h. The reaction was then quenched by $Na_2S_2O_3$ aq. (1 M, 50 mL). The mixture was extracted with EtOAc (100 mL), and the organic layer was washed with NaOH aq. (2 M, 2 x 50 mL) and dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel (hexane/EtOAc) to give the pure product as a pale yellow solid (1.81 g, 71% yield).

Product data

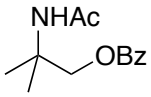
3-acetamido-3-methylbutyl benzoate (2a)



According to the typical procedure, the reaction using HIO_3 (56.4 mg, 0.32 mmol), NHPI (13.3 mg, 0.08 mmol), MeCN (2 mL), and isoamyl benzoate (76.4 mg, 0.40 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a pale yellow solid (69.7 mg, 71% yield). mp: 38.5–40.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 5.59 (brs, 1H), 4.39 (t, J = 6.6 Hz, 2H), 2.27 (t, J = 6.6 Hz, 2H), 1.90 (s, 3H), 1.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 166.6, 132.9, 130.1, 129.4, 128.3, 61.8, 52.7, 37.8, 27.5, 24.3; IR (ATR) 3300, 3069, 1717, 1651, 1549 cm^{-1}; MS (CI) *m/z* 250 ([M+H]$^+$, 21); HRMS: (EI) calcd for

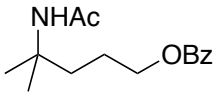
($C_{14}H_{19}NO_3$) 249.1365 (M^+), found *m*/*z* 249.1365

2-acetamido-2-methylpentyl benzoate (2b)



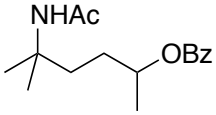
According to the typical procedure, the reaction using HIO_3 (141.1 mg, 0.80 mmol), NHPI (51.8 mg, 0.32 mmol), MeCN (2 mL), and isobutyl benzoate (71.8 mg, 0.40 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a white solid (44.1 mg, 47% yield). mp: 92.2–93.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 5.77 (brs, 1H), 4.45 (s, 2H), 1.95 (s, 3H), 1.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 166.5, 133.1, 129.9, 129.6, 128.4, 69.5, 53.6, 24.4, 24.1; IR (ATR) 3269, 3078, 1717, 1643, 1557 cm^{-1}; MS (CI) *m*/*z* 236 ($[M+H]^+$, 100); HRMS: (CI) calcd for ($C_{13}H_{18}NO_3$) 236.1287 ($[M+H]^+$), found *m*/*z* 236.1287

4-acetamido-4-methylpentyl benzoate (2c)



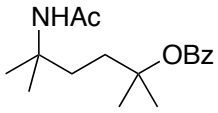
According to the typical procedure, the reaction using HIO_3 (56.0 mg, 0.32 mmol), NHPI (13.0 mg, 0.08 mmol), MeCN (2 mL), and 4-methylpentyl benzoate (79.1 mg, 0.38 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a white solid (79.5 mg, 79% yield). mp: 74.9–76.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.28 (brs, 1H), 4.31 (t, *J* = 7.0 Hz, 2H), 1.98–1.82 (m, 5H), 1.80–1.68 (m, 2H), 1.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.6, 132.8, 130.3, 129.5, 128.3, 65.1, 53.4, 35.9, 27.1, 24.4, 23.8; IR (ATR) 3285, 3078, 1719, 1638, 1558 cm^{-1}; MS (CI) *m*/*z* 264 ($[M+H]^+$, 100); HRMS: (CI) calcd for ($C_{15}H_{22}NO_3$) 264.1600 ($[M+H]^+$), found *m*/*z* 264.1601

5-acetamido-5-methylhexan-2-yl benzoate (2d)



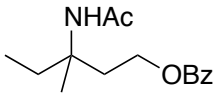
According to the typical procedure, the reaction using HIO_3 (56.4 mg, 0.32 mmol), NHPI (13.2 mg, 0.08 mmol), MeCN (2 mL), and 5-methylhexan-2-yl benzoate (85.4 mg, 0.39 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a yellow viscous liquid (86.0 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 5.49 (brs, 1H), 5.12 (sext, J = 6.0 Hz, 1H), 1.92 (s, 3H), 1.89–1.52 (m, 4H), 1.35 (d, J = 6.0 Hz, 3H), 1.314 (s, 3H), 1.309 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.1, 132.7, 130.6, 129.4, 128.2, 71.7, 53.2, 35.2, 30.5, 26.9, 26.8, 24.3, 19.9; IR (ATR) 3306, 3071, 1715, 1651, 1547 cm^{-1}; MS (CI) *m*/*z* 278 ([M+H]$^+$, 100); HRMS: (CI) calcd for ($C_{16}H_{24}NO_3$) 278.1756 ([M+H]$^+$), found *m*/*z* 278.1752

5-acetamido-2,5-dimethylhexan-2-yl benzoate (2e)



According to the typical procedure, the reaction using HIO_3 (141.6 mg, 0.80 mmol), NHPI (26.3 mg, 0.16 mmol), MeCN (2 mL), and 2,5-dimethylhexan-2-yl benzoate (91.5 mg, 0.39 mmol) was conducted at 80 °C for 12 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a white solid (95.4 mg, 84% yield). mp: 82.4–82.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 5.32 (brs, 1H), 2.01–1.88 (m, 5H), 1.86–1.73 (m, 2H), 1.56 (s, 6H), 1.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 165.9, 132.6, 131.7, 129.4, 128.2, 83.1, 53.3, 34.8, 34.0, 26.9, 26.4, 24.5; IR (ATR) 3285, 3086, 1711, 1639, 1558 cm^{-1}; HRMS: (CI) calcd for ($C_{17}H_{26}NO_3$) 292.1913 ([M+H]$^+$), found *m*/*z* 292.1912

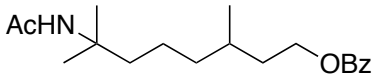
3-acetamido-3-methylpentyl benzoate (2f)



According to the typical procedure, the reaction using HIO_3 (140.5 mg, 0.80 mmol), NHPI (25.7 mg, 0.16 mmol), MeCN (2 mL), and 3-methylpentyl benzoate (81.9 mg, 0.40 mmol) was conducted at 80 °C for 12 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a yellow viscous liquid (62.9 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz,

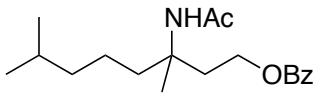
2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 5.43 (brs, 1H), 4.39 (t, *J* = 6.8 Hz, 2H), 2.38 (dt, *J* = 14.0, 6.8 Hz, 1H), 2.14 (dt, *J* = 14.4, 6.8 Hz, 1H), 2.00–1.82 (m, 4H), 1.67 (dt, *J* = 21.2, 7.2 Hz, 1H), 1.32 (s, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 166.7, 132.9, 130.1, 129.4, 128.3, 61.7, 55.6, 35.9, 31.4, 24.3, 24.1, 7.9; IR (ATR) 3304, 3071, 1721, 1641, 1549 cm^{-1}; MS (CI) *m*/*z* 264 ([M+H]$^+$, 24); HRMS: (CI) calcd for ($C_{15}H_{22}NO_3$) 264.1600 (M^+), found *m*/*z* 264.1598

7-acetamido-3,7-dimethyloctyl benzoate (2g)



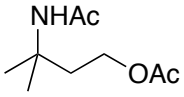
According to the typical procedure, the reaction using HIO_3 (56.4 mg, 0.32 mmol), NHPI (13.1 mg, 0.08 mmol), MeCN (2 mL), and 3,7-dimethyloctyl benzoate (106.0 mg, 0.40 mmol) was conducted at 80 °C for 12 h. The crude product was analyzed by gas chromatography using dodecane as an internal standard. Purification by flash column chromatography on silica gel (hexane/EtOAc = 8:2) gave the product as a yellow viscous liquid (56.5 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.30 (brs, 1H), 4.42–4.29 (m, 2H), 1.91 (s, 3H), 1.89–1.74 (m, 1H), 1.72–1.50 (m, 4H), 1.43–1.09 (m, 10H), 0.96 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.6, 132.8, 130.4, 129.5, 128.3, 63.4, 53.6, 40.3, 37.1, 35.5, 29.9, 26.9, 24.4, 21.4, 19.5; IR (ATR) 3298, 3071, 1717, 1651, 1545 cm^{-1}; MS (CI) *m*/*z* 320 ([M+H]$^+$, 100); HRMS: (CI) calcd for ($C_{19}H_{30}NO_3$) 320.2226 ([M+H]$^+$), found *m*/*z* 320.2224

3-acetamido-3,7-dimethyloctyl benzoate



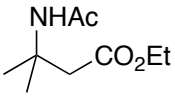
The title compound was also isolated by flash column chromatography on silica gel (hexane/EtOAc = 8:2) gave the product as a yellow viscous liquid (13.0 mg, 10% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 5.33 (brs, 1H), 4.34 (dd, *J* = 6.8, 6.8 Hz, 2H), 2.37 (dt, *J* = 14.0, 6.8 Hz, 1H), 2.16 (dt, *J* = 14.0, 6.8 Hz, 1H), 1.91 (s, 3H), 1.91–1.76 (m, 1H), 1.74–1.46 (m, 2H), 1.42–1.05 (m, 7H), 0.86 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 166.7, 133.0, 130.2, 129.5, 128.4, 61.7, 55.5, 39.3, 39.1, 36.2, 27.9, 24.7, 24.4, 22.5, 21.3; IR (ATR) 3298, 3073, 1717, 1651, 1541 cm^{-1}; MS (CI) *m*/*z* 320 ([M+H]$^+$, 30); HRMS: (CI) calcd for ($C_{19}H_{30}NO_3$) 320.2226 ([M+H]$^+$), found *m*/*z* 320.2230

3-acetamido-3-methylbutyl acetate (2h)



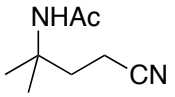
According to the typical procedure, the reaction using HIO_3 (55.9 mg, 0.32 mmol), NHPI (13.1 mg, 0.08 mmol), MeCN (2 mL), and isoamyl acetate (52.9 mg, 0.41 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 6:4) gave the product as a white solid (37.4 mg, 49% yield). mp: 58.9–59.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (brs, 1H), 4.12 (t, J = 6.8 Hz, 2H), 2.11 (t, J = 6.8 Hz, 2H), 2.05 (s, 3H), 1.93 (s, 3H), 1.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.6, 61.3, 52.6, 37.7, 27.3, 24.3, 21.0; IR (ATR) 3296, 3086, 1732, 1643, 1553 cm^{-1}; MS (CI) m/z 188 ([M+H]$^+$, 44); HRMS: (EI) calcd for ($C_9H_{17}NO_3$) 187.1208 (M^+), found m/z 187.1209

ethyl 3-acetamido-3-methylbutanoate (2i)



According to the typical procedure, the reaction using HIO_3 (140.9 mg, 0.80 mmol), NHPI (26.1 mg, 0.16 mmol), MeCN (2 mL), and ethyl isovalerate (50.1 mg, 0.38 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a yellow viscous liquid (42.2 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (brs, 1H), 4.14 (q, J = 7.2 Hz, 2H), 2.71 (s, 2H), 1.93 (s, 3H), 1.43 (s, 6H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 169.9, 60.3, 52.0, 44.0, 27.0, 24.3, 14.1; IR (ATR) 3289, 3076, 1730, 1651, 1549 cm^{-1}; MS (CI) m/z 188 ([M+H]$^+$, 100); HRMS: (EI) calcd for ($C_9H_{17}NO_3$) 187.1208 (M^+), found m/z 187.1210

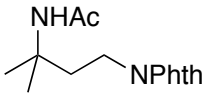
4-acetamido-4-methylpentanonitrile (2j)



According to the typical procedure, the reaction using HIO_3 (140.2 mg, 0.80 mmol), NHPI (25.8 mg, 0.16 mmol), MeCN (2 mL), and isocapronitrile (37.4 mg, 0.38 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a white solid (45.3 mg, 76% yield). mp:

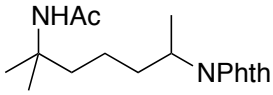
84.9–85.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (brs, 1H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.20 (t, *J* = 7.2 Hz, 2H), 1.95 (s, 3H), 1.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 120.0, 52.9, 34.0, 27.2, 24.2, 12.5; IR (ATR) 3271, 3076, 2247, 1643, 1555 cm^{-1}; MS (CI) *m*/*z* 155 ($[M+H]^+$, 100); HRMS: (EI) calcd for ($C_8H_{14}N_2O$) 154.1106 (M^+), found *m*/*z* 154.1105

_N_-phthaloyl-3-acetamido-3-methylbutylamine (2k)



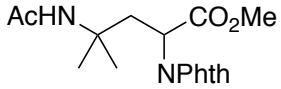
According to the typical procedure, the reaction using HIO_3 (56.3 mg, 0.32 mmol), NHPI (13.1 mg, 0.08 mmol), MeCN (2 mL), and *N*-isopentylphthalimide (97.3 mg, 0.45 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 6:4) gave the product as a white solid (59.2 mg, 48% yield). mp: 136.1–137.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.78 (m, 2H), 7.77–7.66 (m, 2H), 5.59 (brs, 1H), 3.74 (t, *J* = 7.2 Hz, 2H), 2.10 (t, *J* = 7.2 Hz, 2H), 1.89 (s, 3H), 1.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 168.2, 133.9, 132.0, 123.1, 52.7, 38.0, 33.7, 26.9, 24.2; IR (ATR) 3277, 3086, 1715, 1643, 1557 cm^{-1}; MS (CI) *m*/*z* 275 ($[M+H]^+$, 100); HRMS: (CI) calcd for ($C_{15}H_{19}N_2O_3$) 275.1396 ($[M+H]^+$), found *m*/*z* 275.1399

_N_-phthaloyl-6-acetamido-6-methylheptan-2-amine (2l)



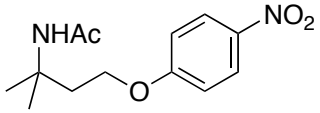
According to the typical procedure, the reaction using HIO_3 (56.3 mg, 0.32 mmol), NHPI (13.1 mg, 0.08 mmol), MeCN (2 mL), and *N*-phthaloyl-6-methylheptan-2-amine (102.4 mg, 0.39 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a pale yellow viscous liquid (95.2 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.78 (m 2H), 7.77–7.62 (m 2H), 5.34 (brs, 1H), 4.42–4.28 (m 1H), 2.16–2.02 (m, 1H), 1.88 (s, 3H), 1.82–1.55 (m, 3H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.35–1.12 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.5, 133.8, 131.8, 123.0, 53.4, 47.0, 39.6, 33.7, 26.9, 26.5, 24.3, 21.0, 18.6; IR (ATR) 3302, 3078, 1703, 1657, 1541 cm^{-1}; MS (EI) *m*/*z* 316 (M^+, 1), 259 (20), 174 (58), 130 (32), 110 (21), 101 (21), 100 (100), 99 (21), 60 (23), 58 (100); HRMS: (CI) calcd for ($C_{18}H_{25}N_2O_3$) 317.1865 ($[M+H]^+$), found *m*/*z* 317.1862

_N_-phthaloyl-4-acetamido-_L_-leucine methyl ester (2m)



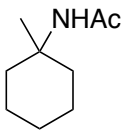
According to the typical procedure, the reaction using HIO_3 (139.1 mg, 0.79 mmol), NHPI (26.1 mg, 0.16 mmol), MeCN (2 mL), and *N*-phthaloyl-*L*-leucine methyl ester (102.4 mg, 0.37 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 4:6) gave the product as a white solid (66.6 mg, 54% yield). mp: 114.2–115.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.82 (m, 2H), 7.81–7.64 (m, 2H), 5.50 (brs, 1H), 4.92 (dd, *J* = 8.0, 4.4 Hz, 1H), 3.73 (s, 3H), 2.82–2.60 (m, 2H), 1.71 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.7, 167.4, 134.2, 131.8, 123.5, 53.1, 52.7, 48.6, 38.2, 27.6, 27.0, 24.1; IR (ATR) 3279, 3078, 1749, 1715, 1645, 1557 cm^{-1}; MS (CI) *m*/*z* 333 ([M+H]$^+$, 100); HRMS: (EI) calcd for ($C_{17}H_{20}N_2O_5$) 332.1372 (M^+), found *m*/*z* 332.1370

4-nitrophenyl 2-acetamido-2-methylbutan-2-yl ether (2n)



According to the typical procedure, the reaction using HIO_3 (140.5 mg, 0.80 mmol), NHPI (52.4 mg, 0.32 mmol), MeCN (2 mL), and isoamyl 4-nitrophenyl ether (78.2 mg, 0.37 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a white solid (43.1 mg, 43% yield). mp: 129.8–130.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.6 Hz, 2H), 6.94 (d, *J* = 9.6 Hz, 2H), 5.66 (brs, 1H), 4.15 (t, *J* = 6.4 Hz, 2H), 2.32 (t, *J* = 6.4 Hz, 2H), 1.95 (s, 3H), 1.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 163.7, 141.3, 125.9, 114.3, 65.8, 52.8, 38.0, 27.6, 24.4; IR (ATR) 3117, 3080, 1668, 1589, 1528, 1337 cm^{-1}; MS (CI) *m*/*z* 267 ([M+H]$^+$, 100); HRMS: (CI) calcd for ($C_{13}H_{19}N_2O_4$) 267.1345 ([M+H]$^+$), found *m*/*z* 267.1346

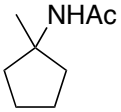
***N*-(1-methylcyclohexyl)acetamide (2o)**



According to the typical procedure, the reaction using HIO_3 (140.7 mg, 0.80 mmol), NHPI (26.4 mg, 0.16 mmol), MeCN (2 mL), and methylcyclohexane (38.5 mg, 0.39 mmol) was conducted at 80 °C for 12 h. Then, volatiles were removed under reduced

pressure to give the crude product, which was purified by flash column chromatography on silica gel (hexane/EtOAc = 7:3) to give the pure product as a pale yellow solid (38.8 mg, 63% yield). mp: 82.7–83.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (brs, 1H), 2.05–1.84 (m, 5H), 1.60–1.16 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 53.3, 36.7, 26.1, 25.5, 24.6, 22.0; IR (ATR) 3297, 3087, 1641, 1555 cm^{-1}; MS (CI) *m*/*z* 156 ($[M+H]^+$, 100); HRMS: (EI) calcd for ($C_9H_{17}NO$) 155.1310 (M^+), found *m*/*z* 155.1308

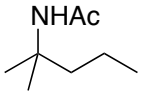
_N_-(1-methylcyclopentyl)acetamide (2p)



According to the typical procedure, the reaction using HIO_3 (140.2 mg, 0.80 mmol), NHPI (26.2 mg, 0.16 mmol), MeCN (2 mL), and methylcyclopentane (33.1 mg, 0.39 mmol) was conducted at 80 °C for 12 h. Then, volatiles were removed under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:5) to give the pure product as a pale yellow solid (28.1 mg, 51% yield).

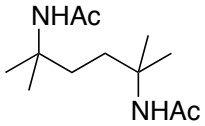
The analytical data for this compounds were in excellent agreement with the reported data.[9]

_N_-(2-methylpentan-2-yl)acetamide (2q)



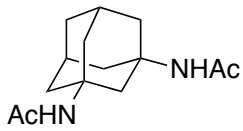
According to the typical procedure, the reaction using HIO_3 (56.5 mg, 0.32 mmol), NHPI (13.2 mg, 0.08 mmol), MeCN (2 mL), and 2-methylpentane (35.2 mg, 0.41 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a pale yellow solid (27.6 mg, 47% yield). mp: 46.8–48.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (brs, 1H), 1.91 (s, 3H), 1.74–1.56 (m, 2H), 1.40–1.18 (m, 8H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 53.6, 42.5, 26.8, 24.3, 17.2, 14.3; IR (ATR) 3290, 3085, 1643, 1559 cm^{-1}; MS (CI) *m*/*z* 144 ($[M+H]^+$, 100); HRMS: (EI) calcd for ($C_8H_{17}NO$) 143.1310 (M^+), found *m*/*z* 143.1311

2,5-diacetamido-2,5-dimethylhexane (2r)



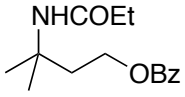
According to the typical procedure, the reaction using HIO_3 (140.7 mg, 0.80 mmol), NHPI (52.0 mg, 0.32 mmol), MeCN (2 mL), and 2,5-dimethylhexane (45.1 mg, 0.39 mmol) was conducted at 80 °C for 24 h. Flash column chromatography on silica gel (hexane/EtOAc = 7:3 then MeOH) gave the product as a solid, which was washed by cold acetone (-40 °C) to give the pure product as a white solid (40.5 mg, 45% yield). mp: 224.8–225.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.19 (brs, 2H), 1.73 (s, 6H), 1.54 (s, 4H), 1.14 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 52.2, 33.4, 26.8, 23.6; IR (ATR) 3285, 3082, 1641, 1562, 1557 cm^{-1}; MS (CI) *m*/*z* 229 ([M+H]$^+$, 100); HRMS: (EI) calcd for ($C_{12}H_{24}N_2O_2$) 228.1838 (M^+), found *m*/*z* 228.1839

1,3-diacetamidoadamantane (2s)



According to the typical procedure, the reaction using HIO_3 (83.2 mg, 0.47 mmol), NHPI (13.3 mg, 0.08 mmol), MeCN (2 mL), and adamantane (55.0 mg, 0.40 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 6:4 then MeOH) gave the product as a white solid (62.0 mg, 61% yield). mp: 222.3–223.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (brs, 2H), 2.29 (s, 2H), 2.27–2.18 (m, 2H), 2.08–1.80 (m, 14H), 1.65–1.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 53.0, 44.9, 40.4, 35.1, 29.8, 24.6; IR (ATR) 3287, 3073, 1636, 1549 cm^{-1}; MS (CI) *m*/*z* 251 ([M+H]$^+$, 100); HRMS: (CI) calcd for ($C_{14}H_{23}N_2O_2$) 251.1760 ([M+H]$^+$), found *m*/*z* 251.1756

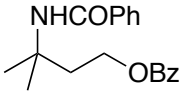
3-methyl-3-propionylaminobutyl benzoate (3)



According to the typical procedure, the reaction using HIO_3 (139.7 mg, 0.79 mmol), NHPI (26.4 mg, 0.16 mmol), EtCN (2 mL), and isoamyl benzoate (77.3 mg, 0.40 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a yellow viscous liquid (47.5 mg, 46%

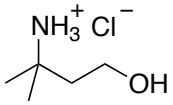
yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.55 (brs, 1H), 4.38 (t, *J* = 6.8 Hz, 2H), 2.28 (t, *J* = 6.8 Hz, 2H), 2.13 (q, *J* = 7.6 Hz, 2H), 1.41 (s, 6H), 1.10 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 166.6, 132.9, 130.1, 129.4, 128.3, 61.8, 52.5, 37.8, 30.3, 27.5, 9.7; IR (ATR) 3306, 3067, 1717, 1647, 1541 cm^{-1}; MS (CI) *m*/*z* 264 ([M+H]$^+$, 30); HRMS: (CI) calcd for ($C_{15}H_{22}NO_3$) 264.1600 ([M+H]$^+$), found *m*/*z* 264.1597

3-benzamido-3-methylbutyl benzoate (4)



According to the typical procedure, the reaction using HIO_3 (140.5 mg, 0.80 mmol), NHPI (26.4 mg, 0.16 mmol), PhCN (2 mL), and isoamyl benzoate (76.7 mg, 0.40 mmol) was conducted at 80 °C for 24 h. Purification by flash column chromatography on silica gel (hexane/EtOAc = 7:3) gave the product as a white solid (64.0 mg, 52% yield). mp: 99.8–100.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.41–7.30 (m, 4H), 6.27 (brs, 1H), 4.46 (t, *J* = 6.4 Hz, 2H), 2.37 (t, *J* = 6.4 Hz, 2H), 1.54 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.6, 135.4, 132.9, 131.2, 130.0, 129.5, 128.4, 128.3, 126.7, 61.9, 53.2, 38.3, 27.4; IR (ATR) 3358, 3063, 1719, 1639, 1539 cm^{-1}; MS (CI) *m*/*z* 312 ([M+H]$^+$, 65); HRMS: (CI) calcd for ($C_{19}H_{22}NO_3$) 312.1600 ([M+H]$^+$), found *m*/*z* 312.1596

3-hydroxy-1,1-dimethyl-propylamine hydrochloride (5)



^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (brs, 3H), 4.83 (brs, 1H), 3.53 (t, *J* = 6.8 Hz, 2H), 1.72 (t, *J* = 6.8 Hz, 2H), 1,24 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 56.4, 53.0, 41.5, 25.3

15. References

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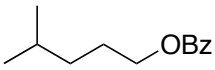
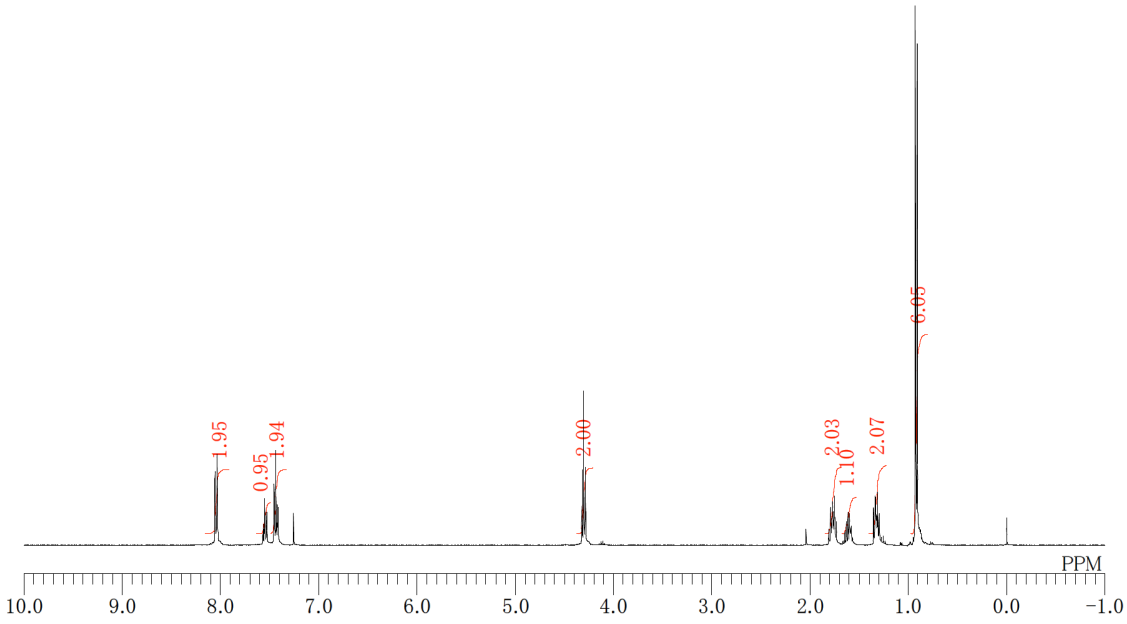
(9) Kalkhambkar, R. G.; Waters, S. N.; Laali, K. K. *Tetrahedron Lett*. **2011**, *52*, 867.

16. NMR spectra

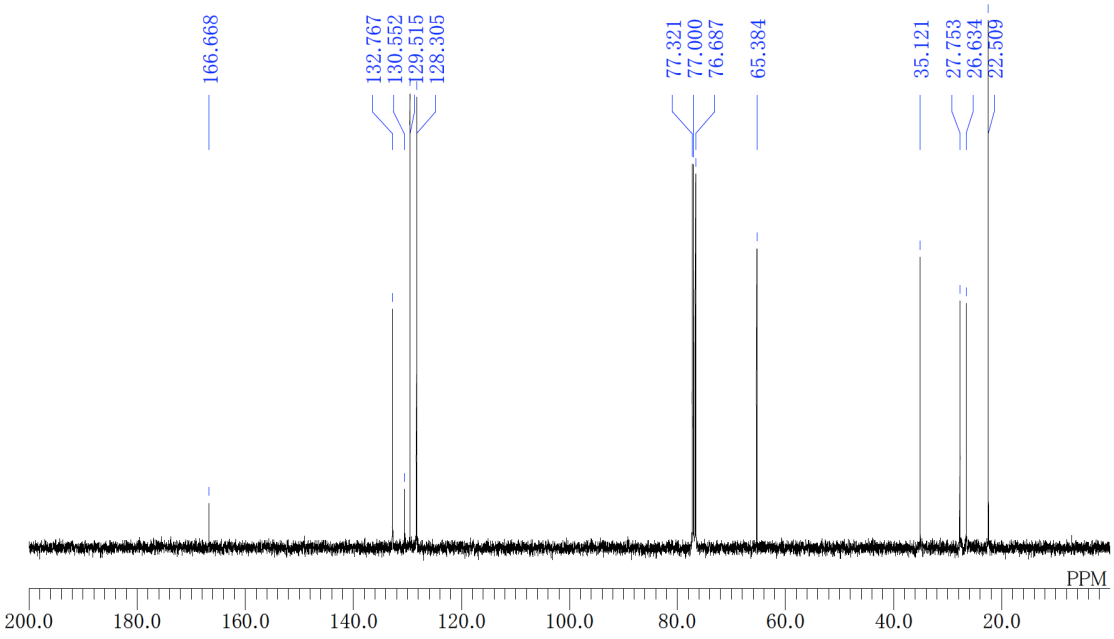
4-methylpentyl benzoate (1c)



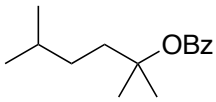
^{1}H NMR: (400 MHz, $CDCl_3$)



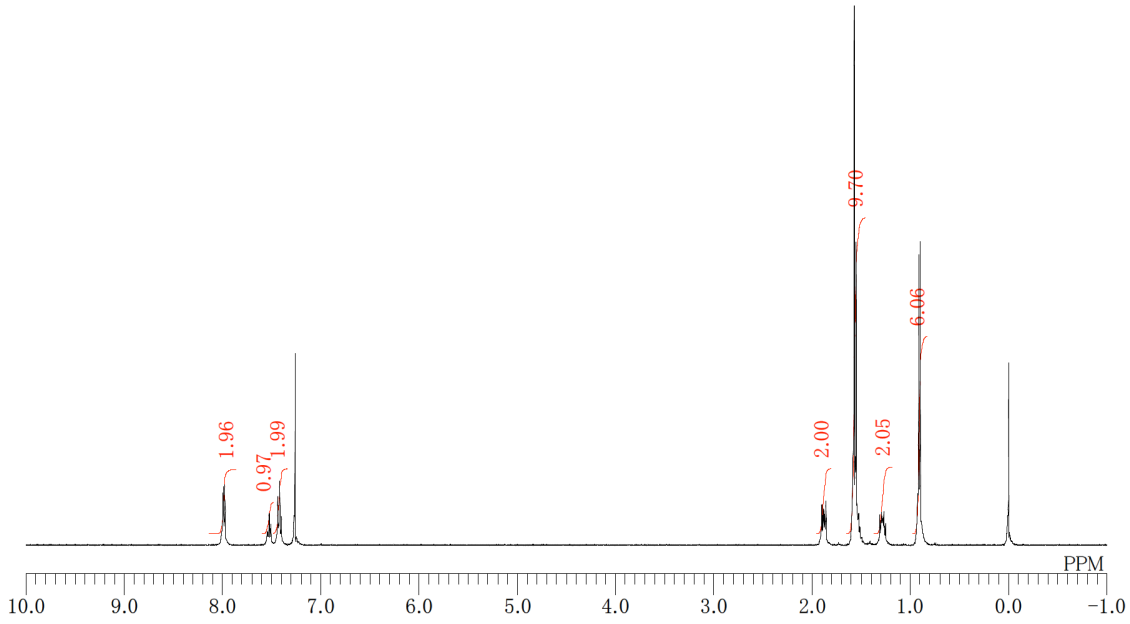
^{13}C NMR: (100 MHz, $CDCl_3$)



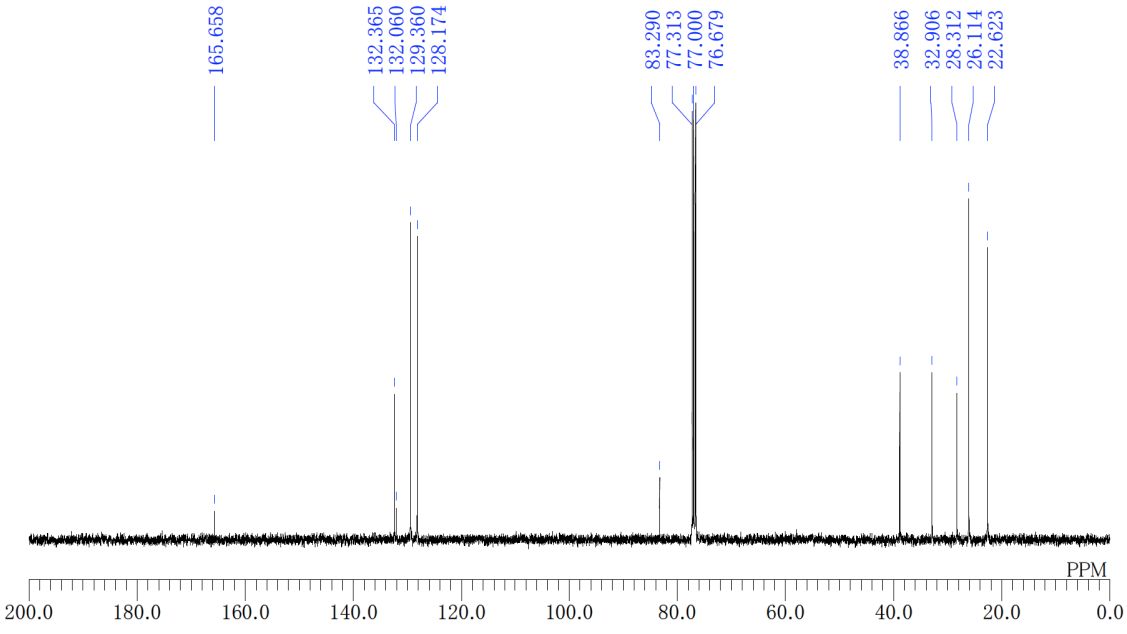
2,5-dimethylhexan-2-yl benzoate (1e)



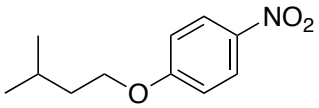
^{1}H NMR: (400 MHz, $CDCl_3$)



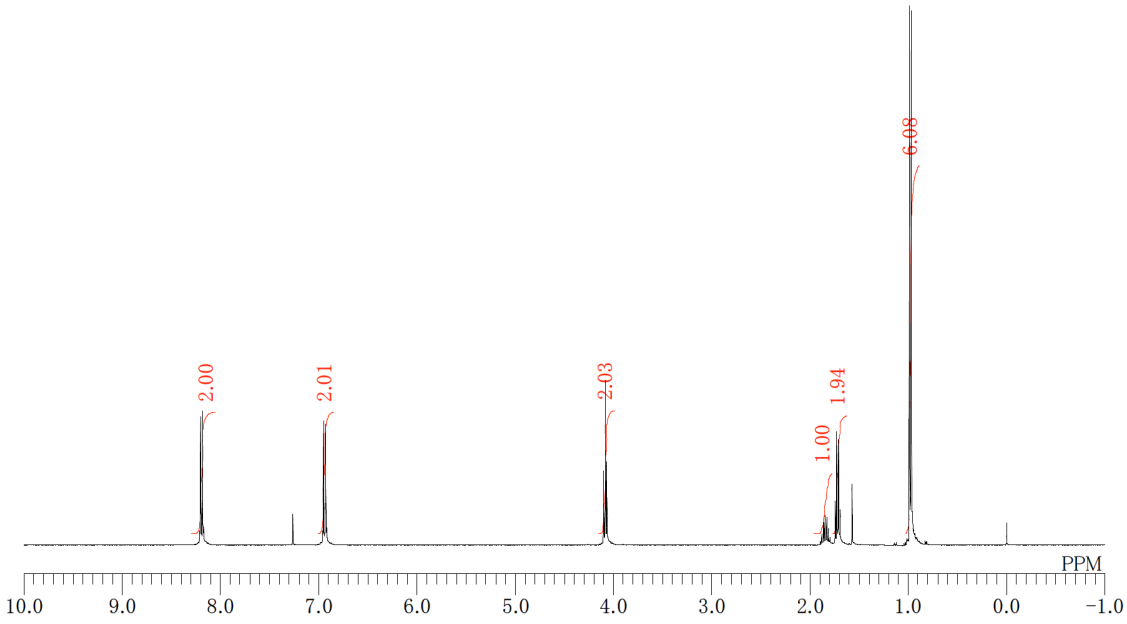
^{13}C NMR: (100 MHz, $CDCl_3$)



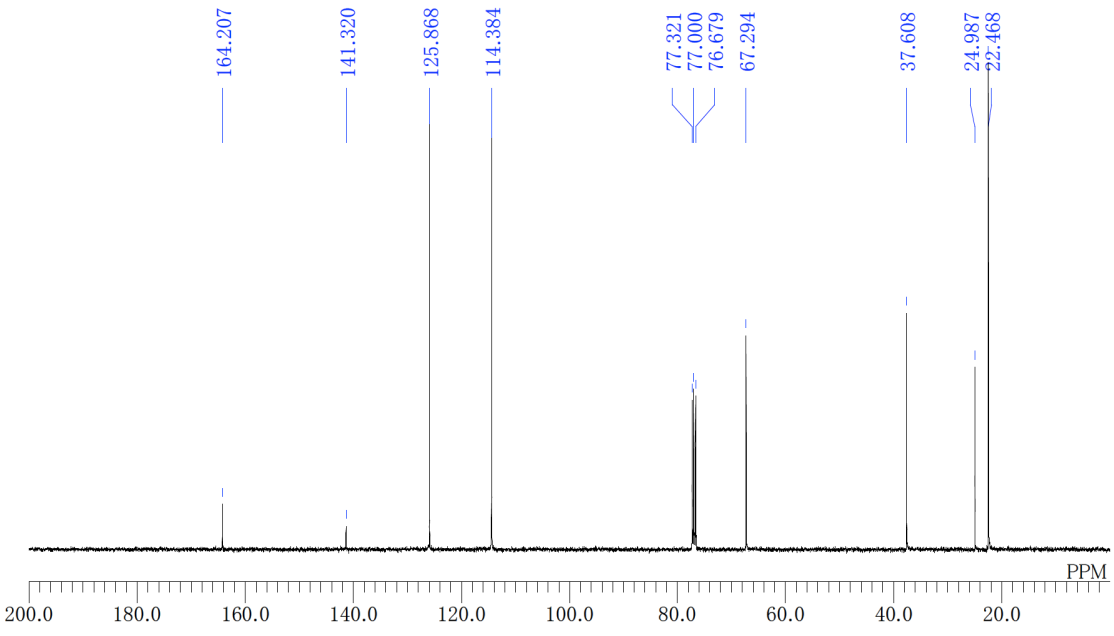
isoamyl 4-nitrophenyl ether (1n)



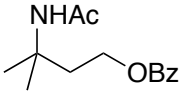
^{1}H NMR: (400 MHz, $CDCl_3$)



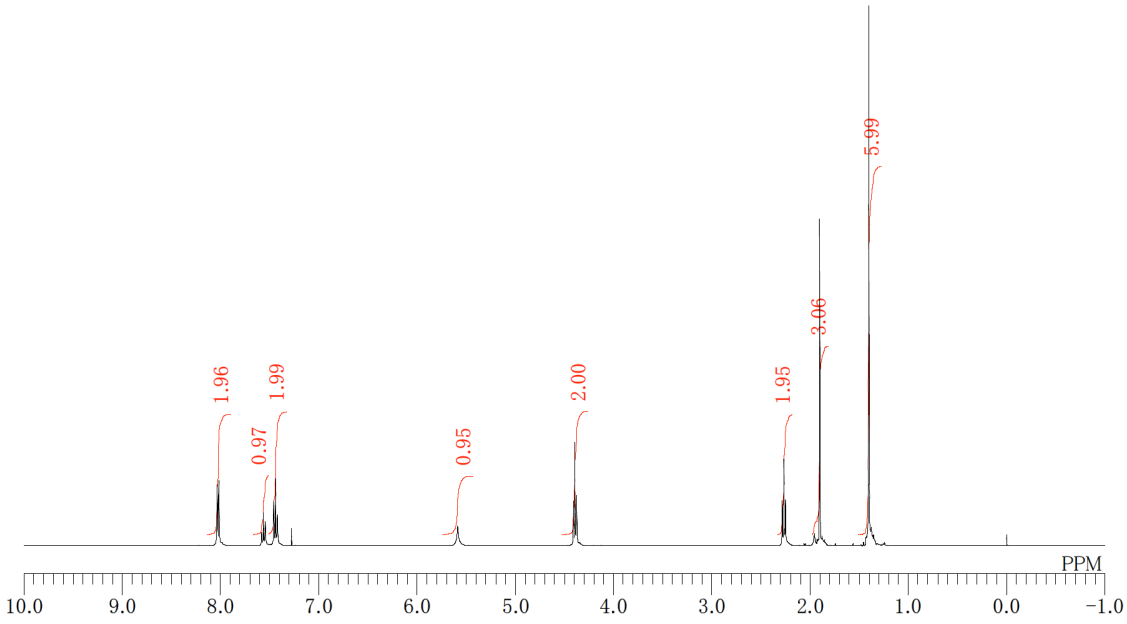
^{13}C NMR: (100 MHz, $CDCl_3$)



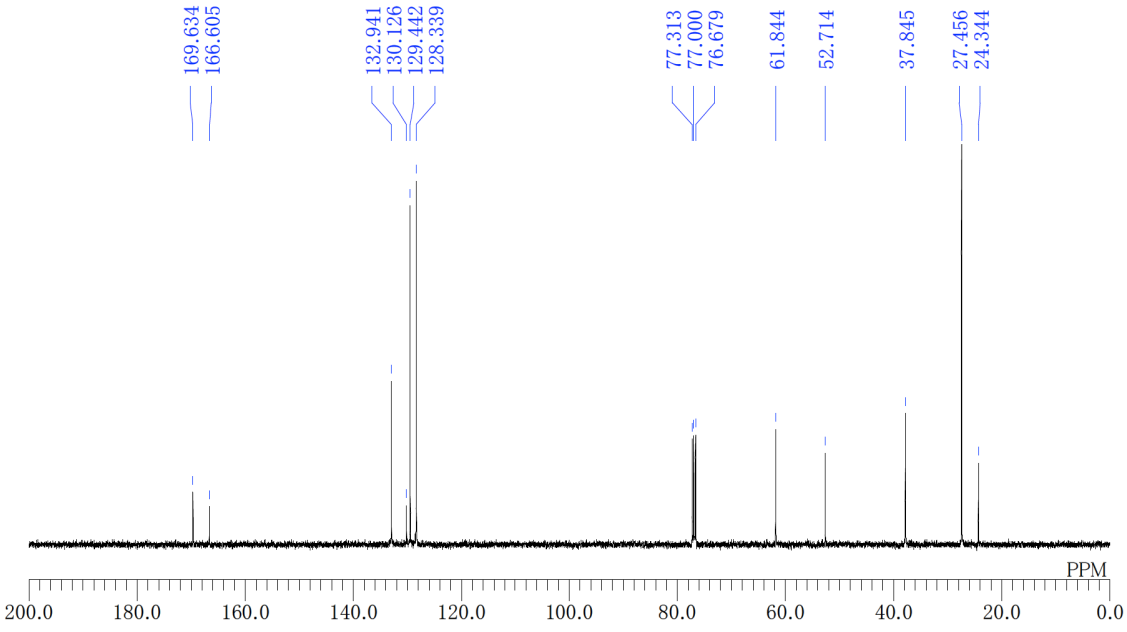
3-acetamido-3-methylbutyl benzoate (2a)



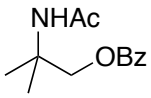
^{1}H NMR: (400 MHz, $CDCl_3$)



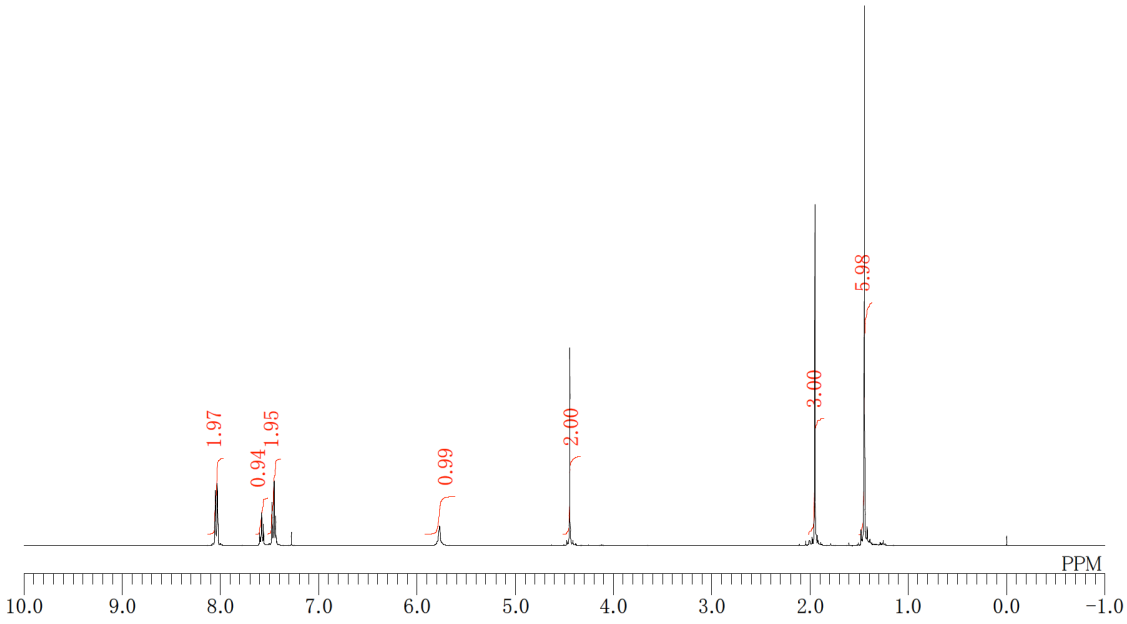
^{13}C NMR: (100 MHz, $CDCl_3$)



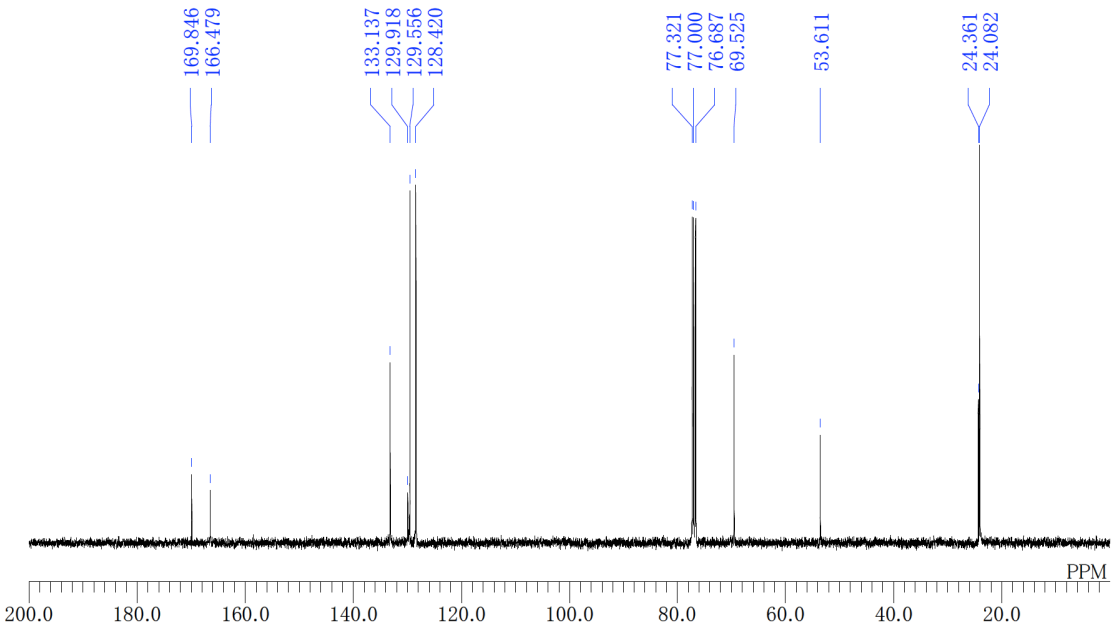
2-acetamido-2-methylpentyl benzoate (2b)



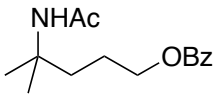
^{1}H NMR: (400 MHz, $CDCl_3$)



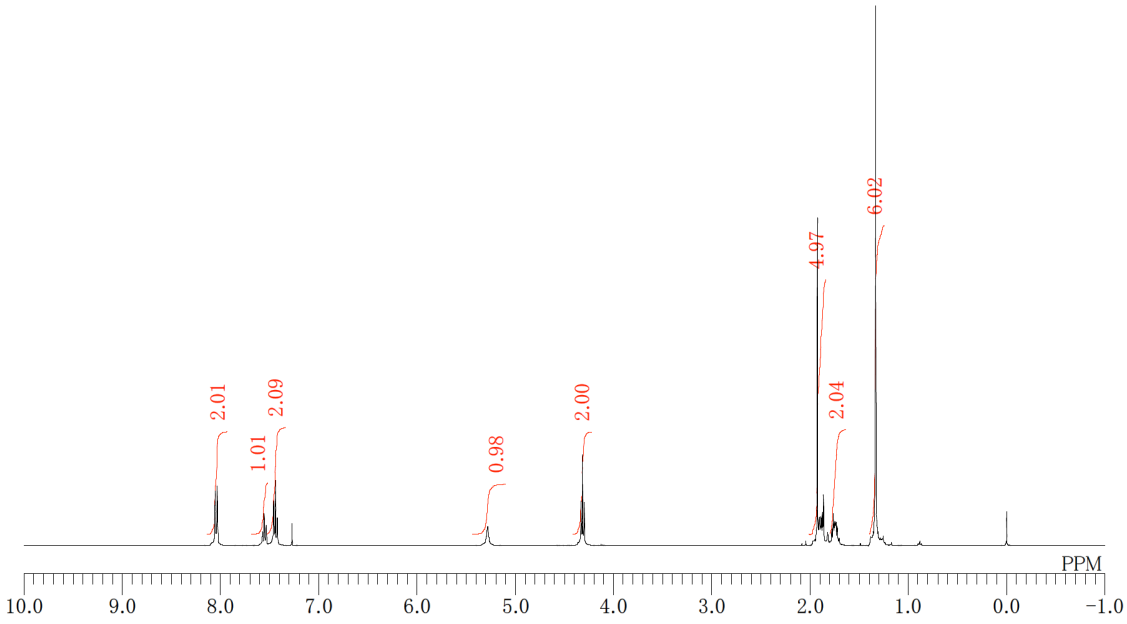
^{13}C NMR: (100 MHz, $CDCl_3$)



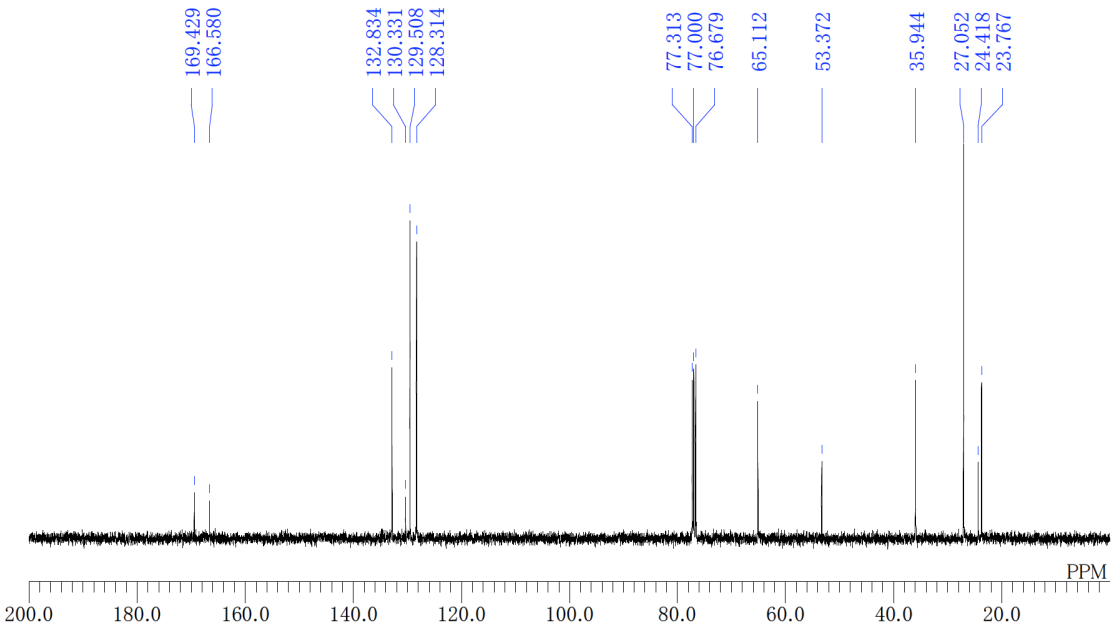
4-acetamido-4-methylpentyl benzoate (2c)



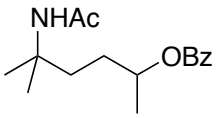
^{1}H NMR: (400 MHz, $CDCl_3$)



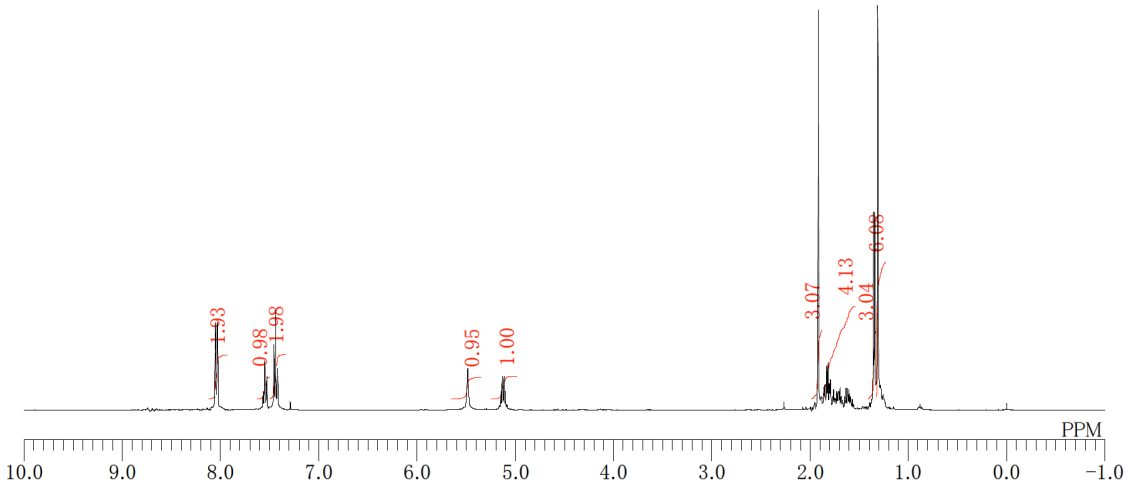
^{13}C NMR: (100 MHz, $CDCl_3$)



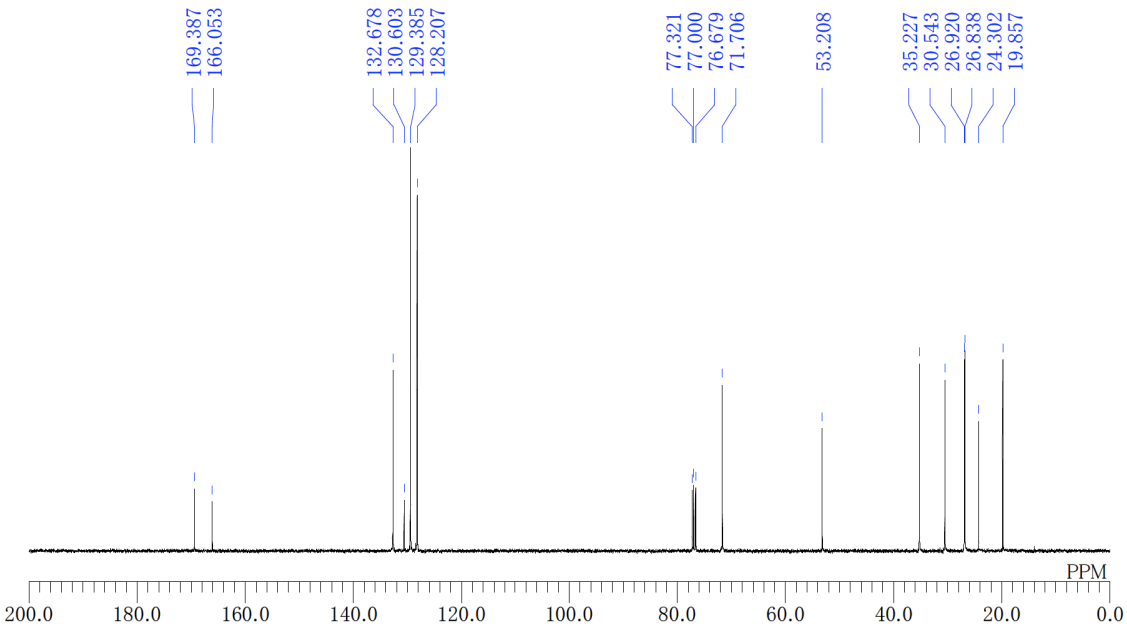
5-acetamido-5-methylhexan-2-yl benzoate (2d)



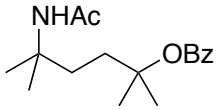
^{1}H NMR: (400 MHz, $CDCl_3$)



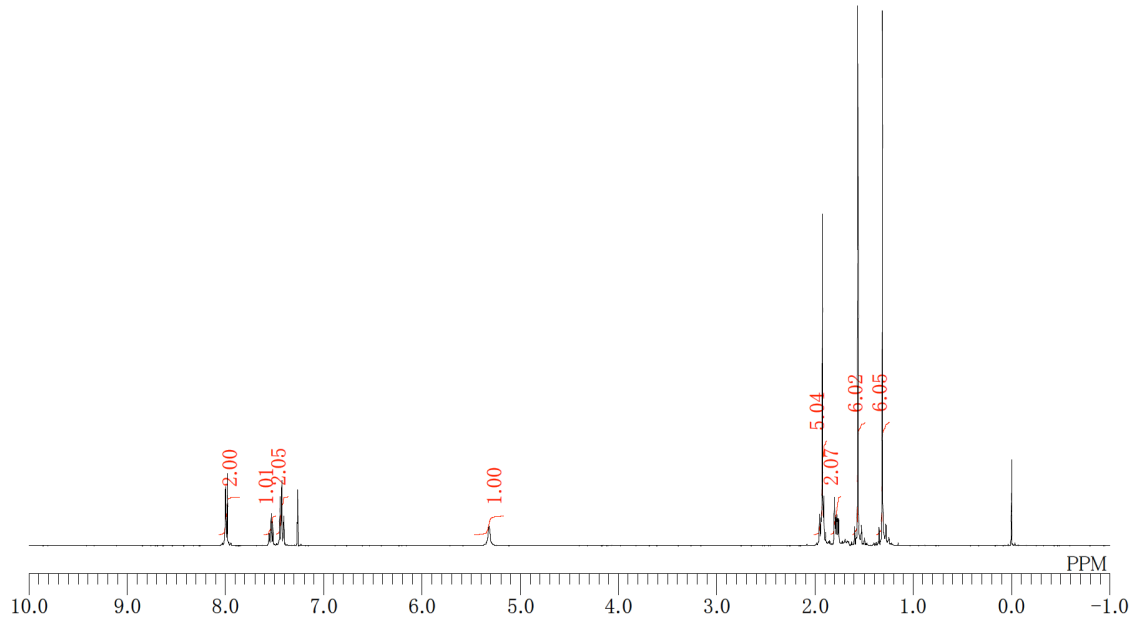
^{13}C NMR: (100 MHz, $CDCl_3$)



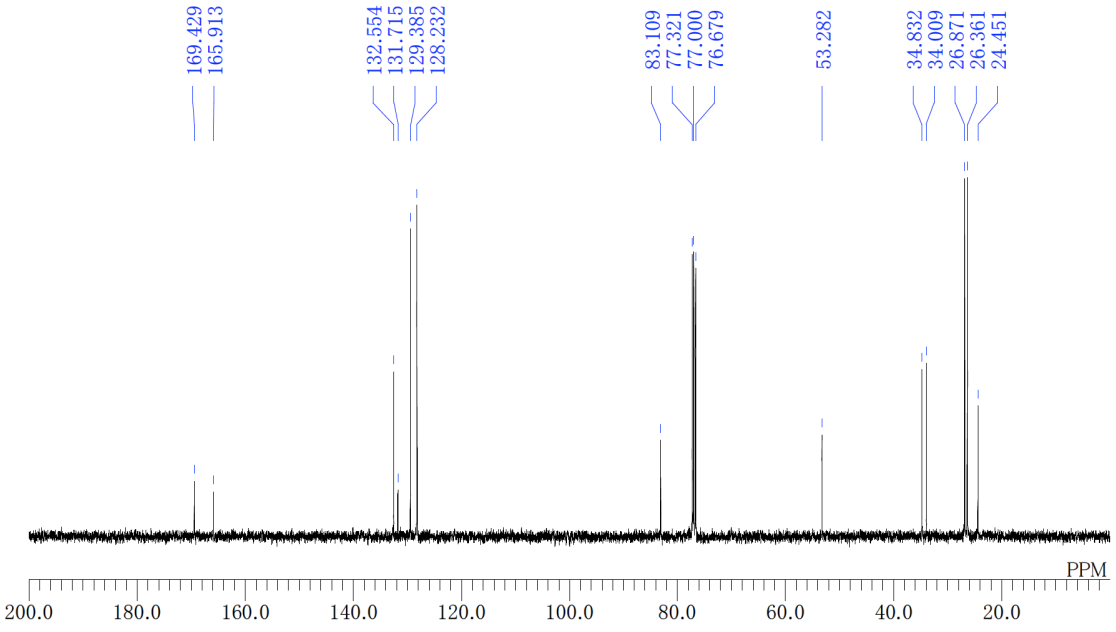
5-acetamido-2,5-dimethylhexan-2-yl benzoate (2e)



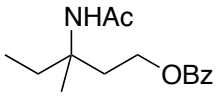
^{1}H NMR: (400 MHz, $CDCl_3$)



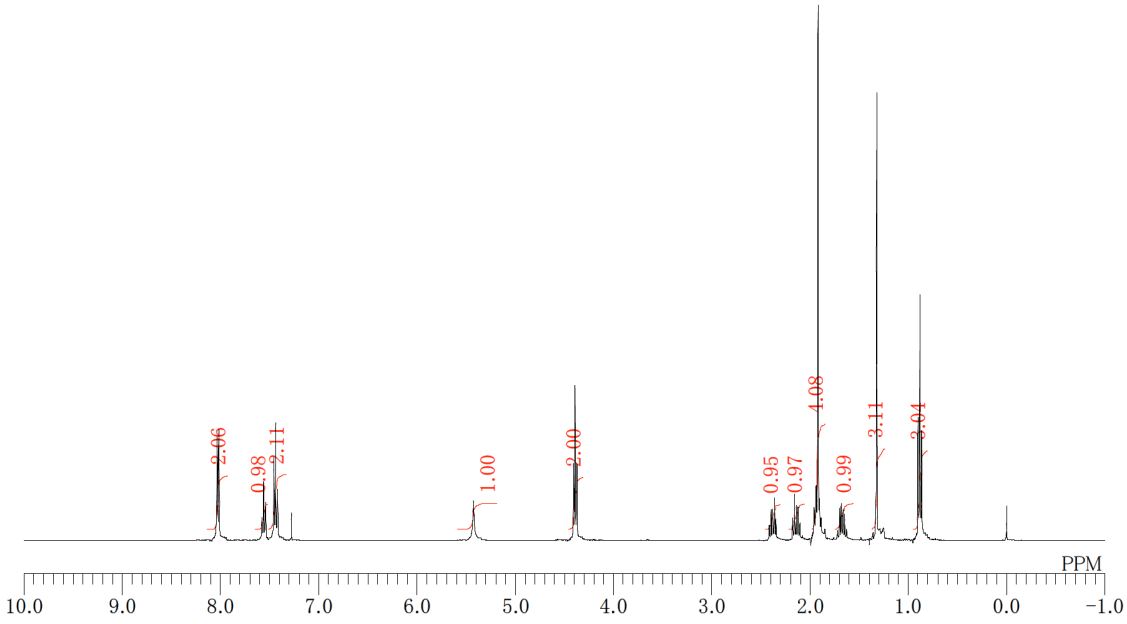
^{13}C NMR: (100 MHz, $CDCl_3$)



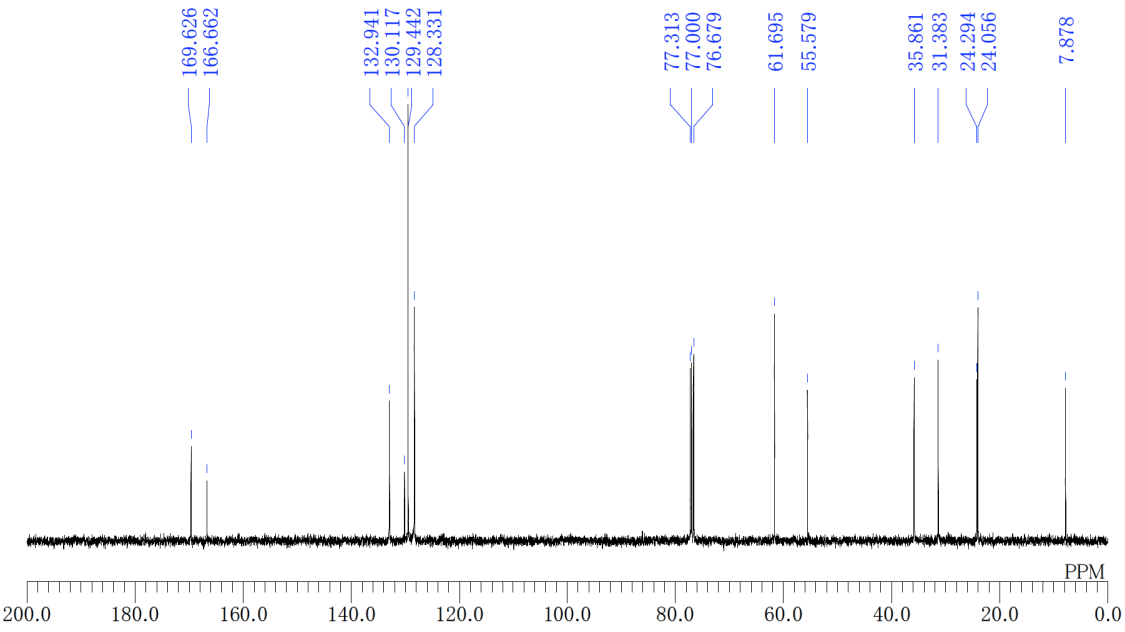
3-acetamido-3-methylpentyl benzoate (2f)



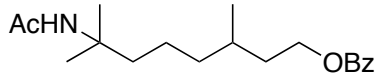
^{1}H NMR: (400 MHz, $CDCl_3$)



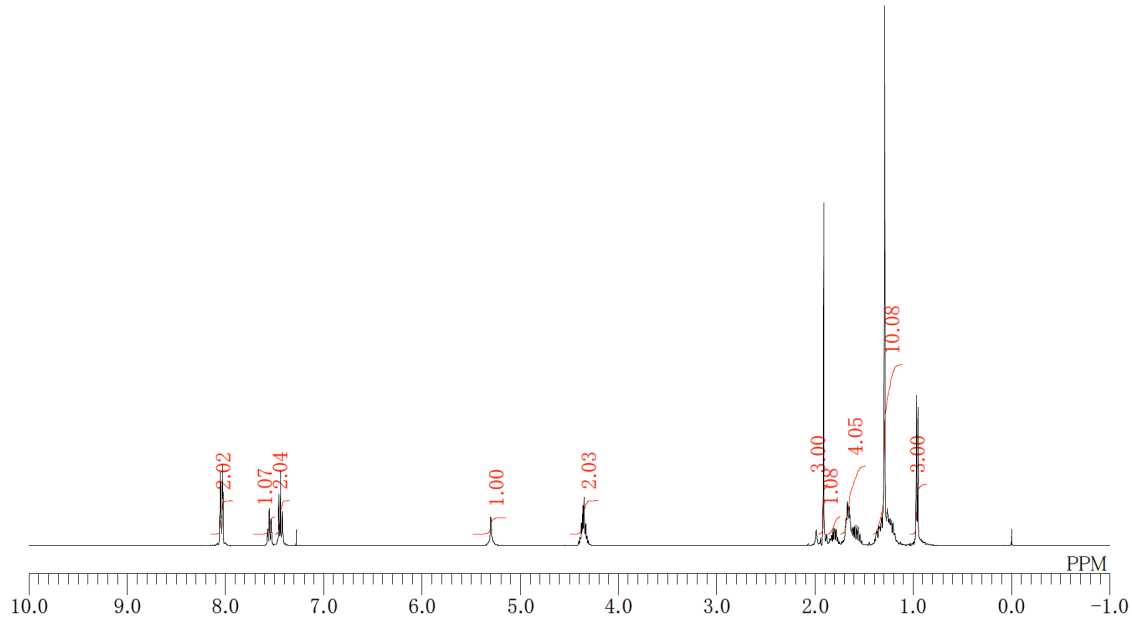
^{13}C NMR: (100 MHz, $CDCl_3$)



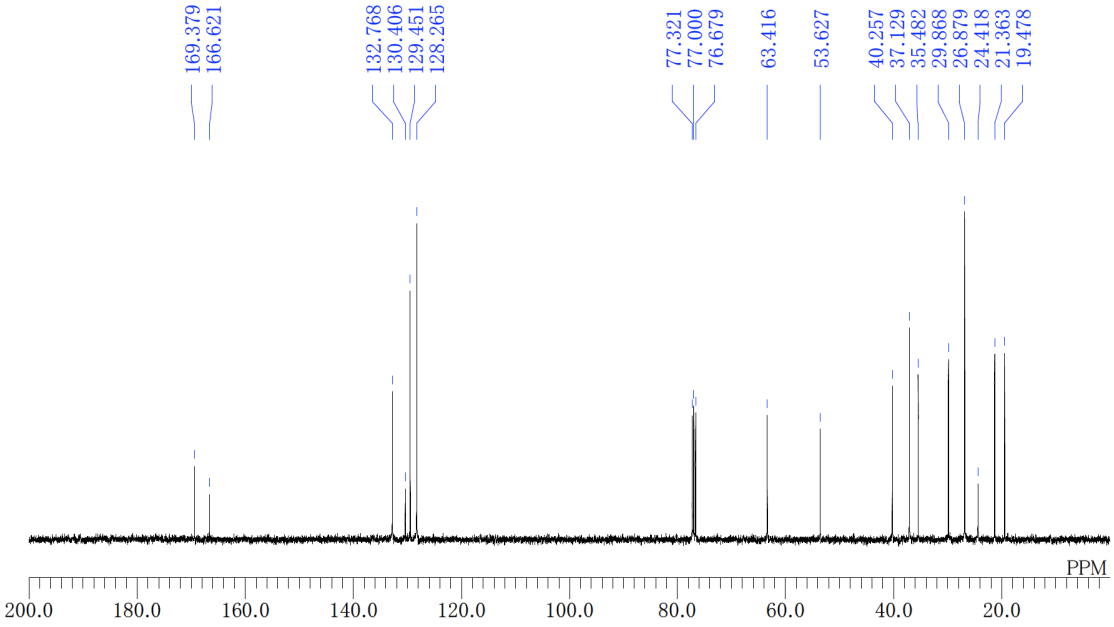
7-acetamido-3,7-dimethyloctyl benzoate (2g)



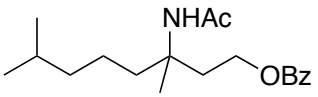
^{1}H NMR: (400 MHz, $CDCl_3$)



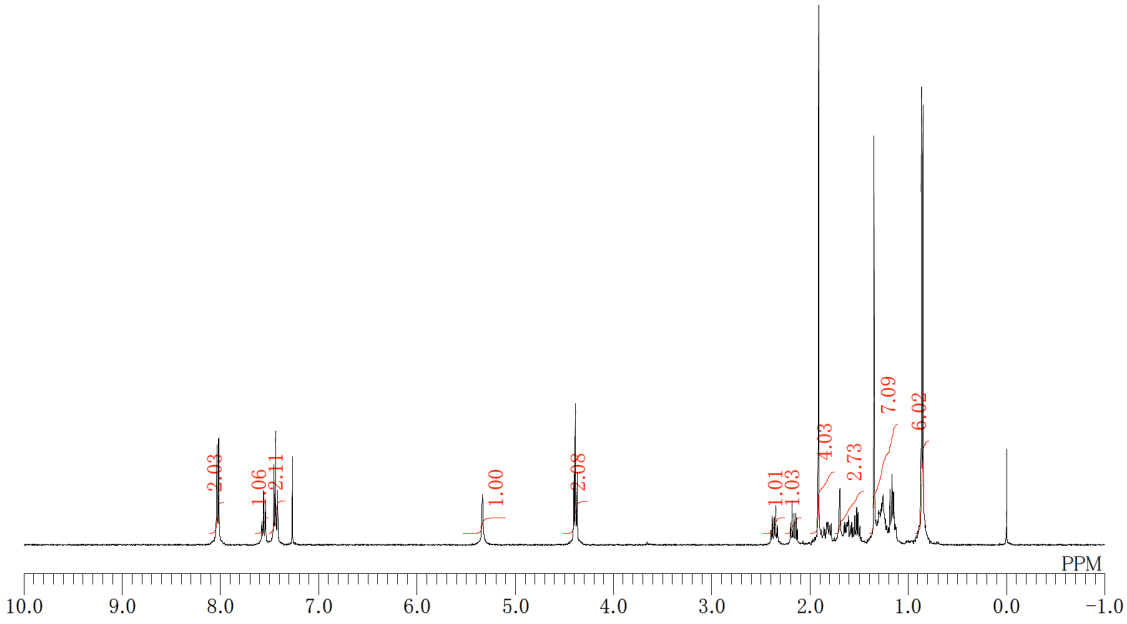
^{13}C NMR: (100 MHz, $CDCl_3$)



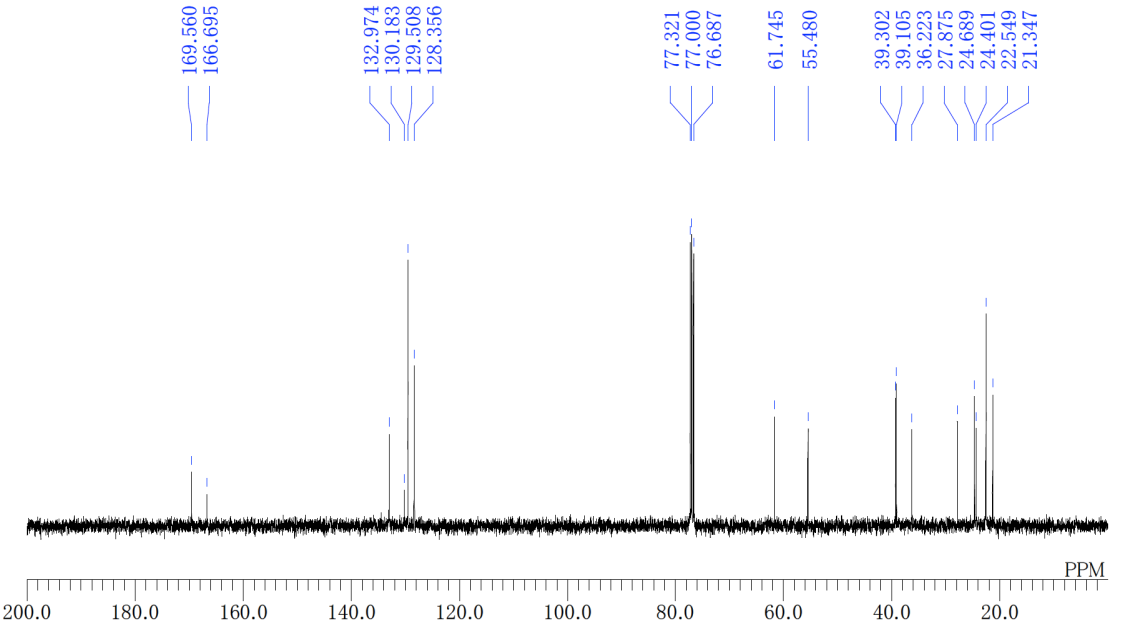
3-acetamido-3,7-dimethyloctyl benzoate



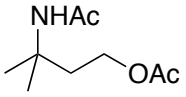
^{1}H NMR: (400 MHz, $CDCl_3$)



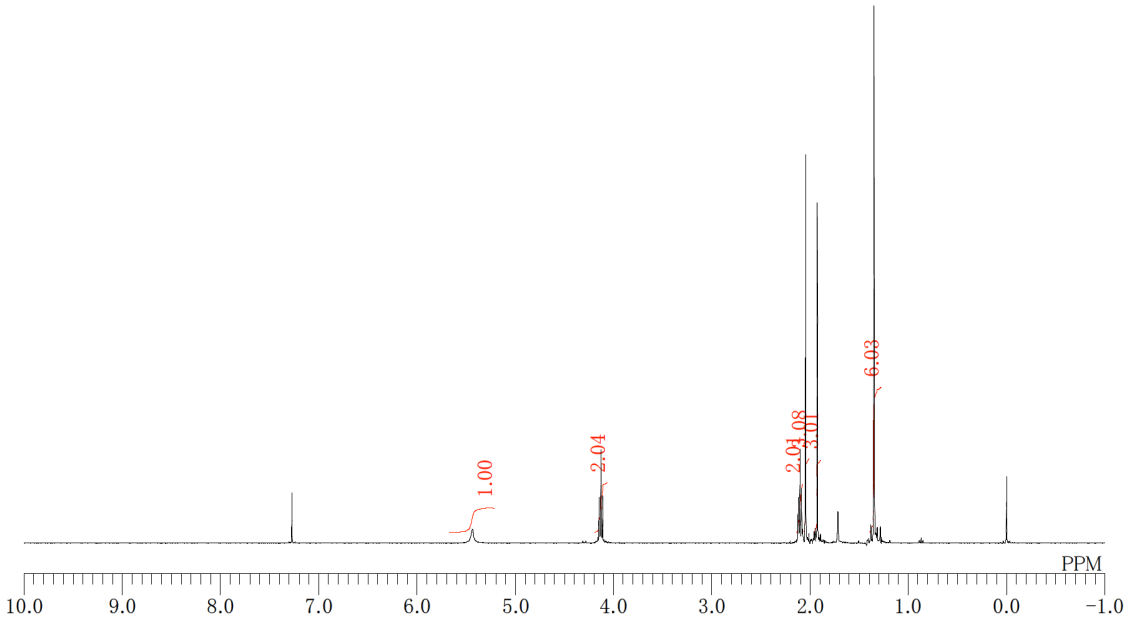
^{13}C NMR: (100 MHz, $CDCl_3$)



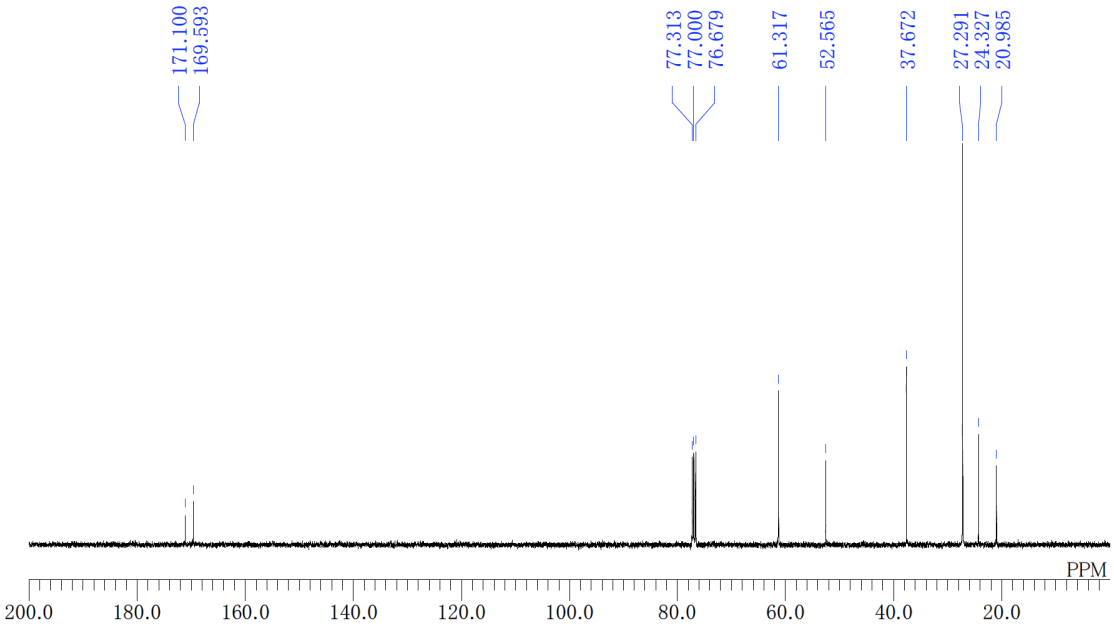
3-acetamido-3-methylbutyl acetate (2h)



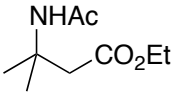
^{1}H NMR: (400 MHz, $CDCl_3$)



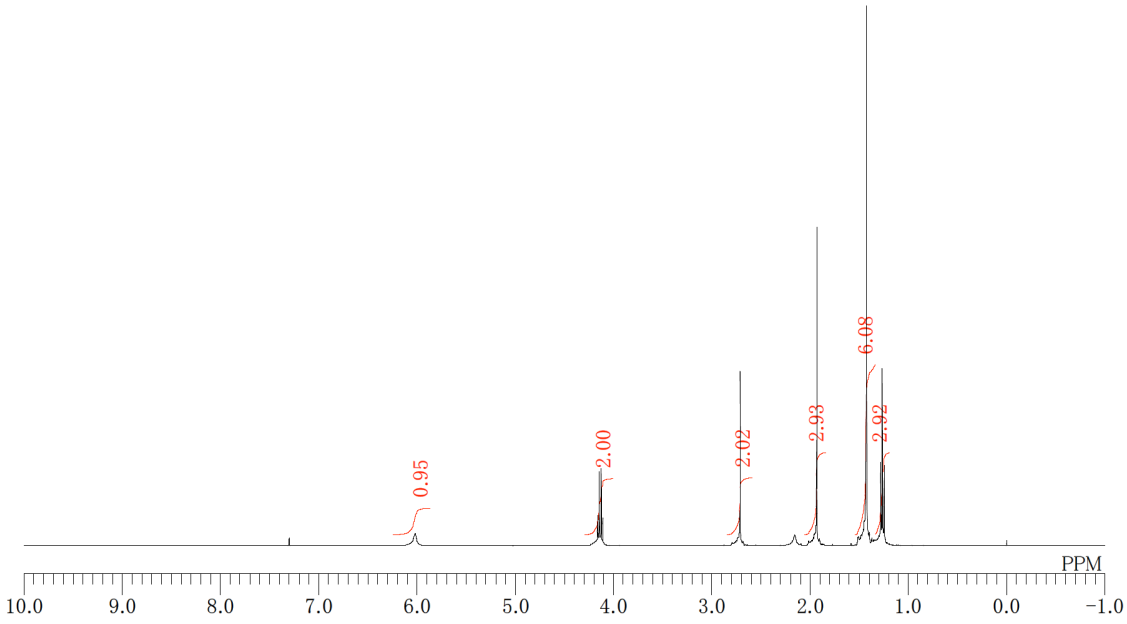
^{13}C NMR: (100 MHz, $CDCl_3$)



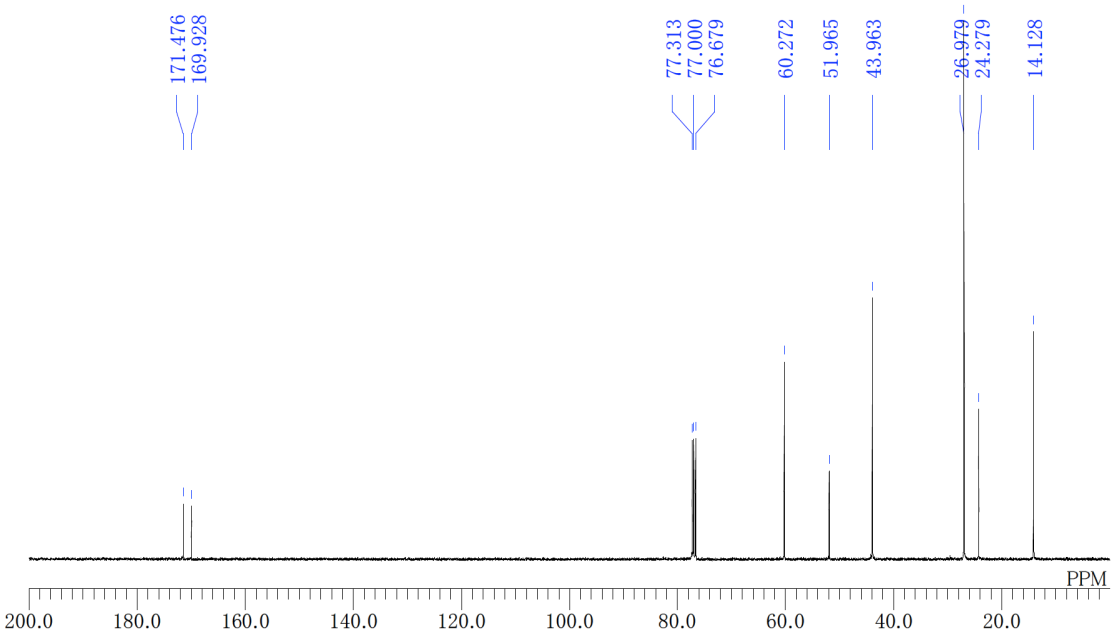
ethyl 3-acetamido-3-methylbutanoate (2i)



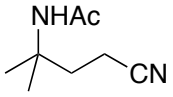
^{1}H NMR: (400 MHz, $CDCl_3$)



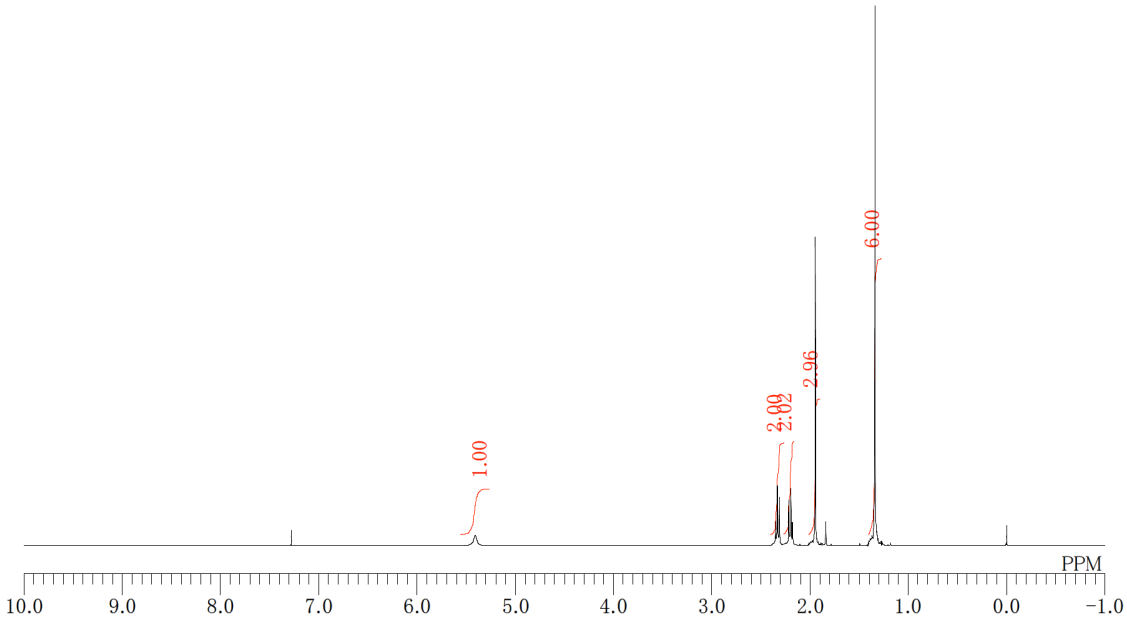
^{13}C NMR: (100 MHz, $CDCl_3$)



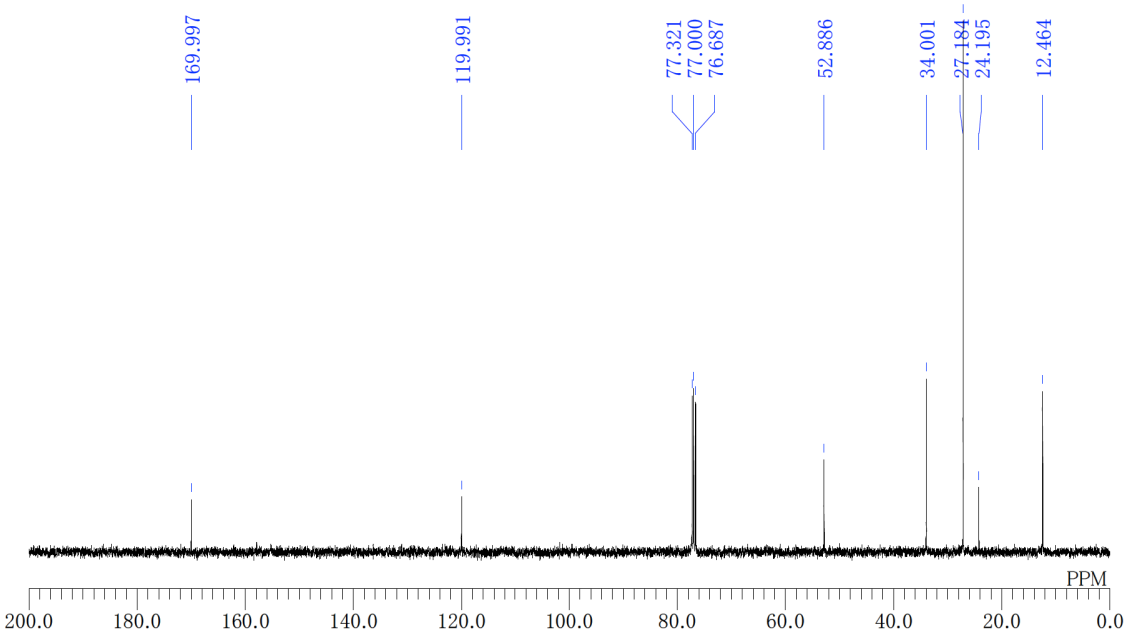
4-acetamido-4-methylpentanonitrile (2j)



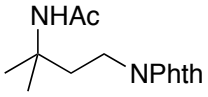
^{1}H NMR: (400 MHz, $CDCl_3$)



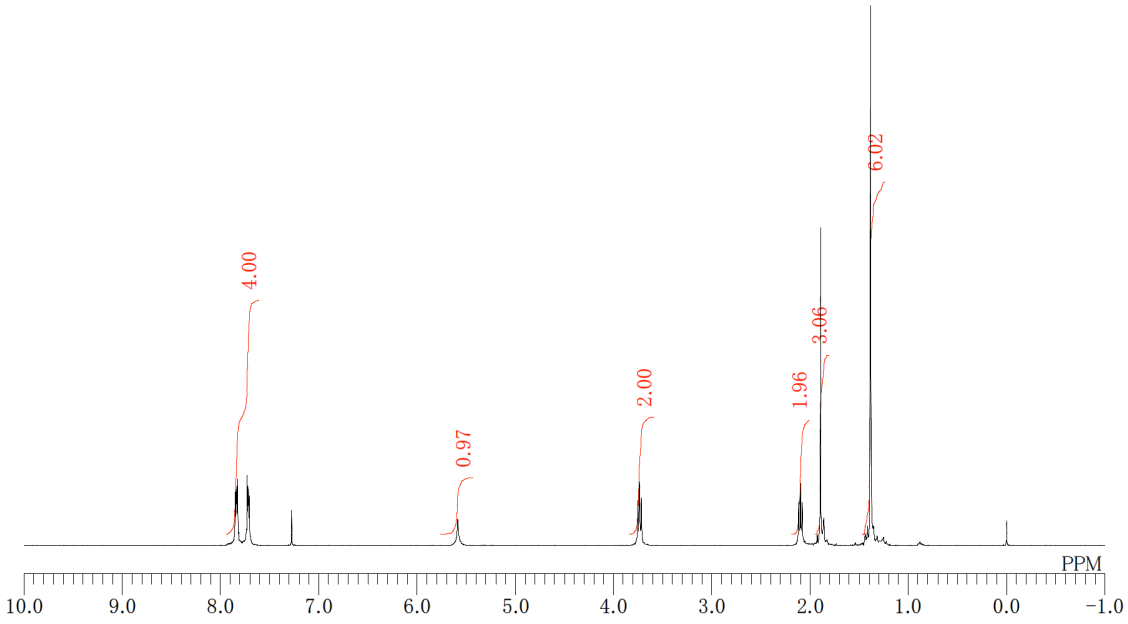
^{13}C NMR: (100 MHz, $CDCl_3$)



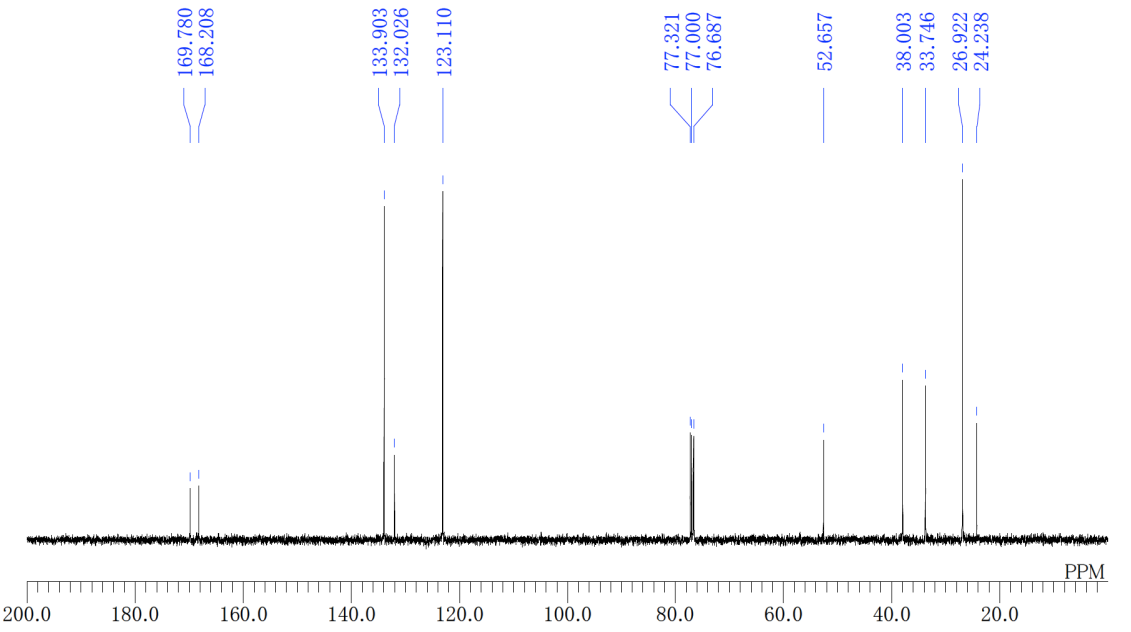
_N_-phthaloyl-3-acetamido-3-methylbutylamine (2k)



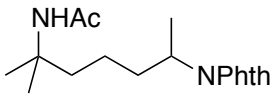
^{1}H NMR: (400 MHz, $CDCl_3$)



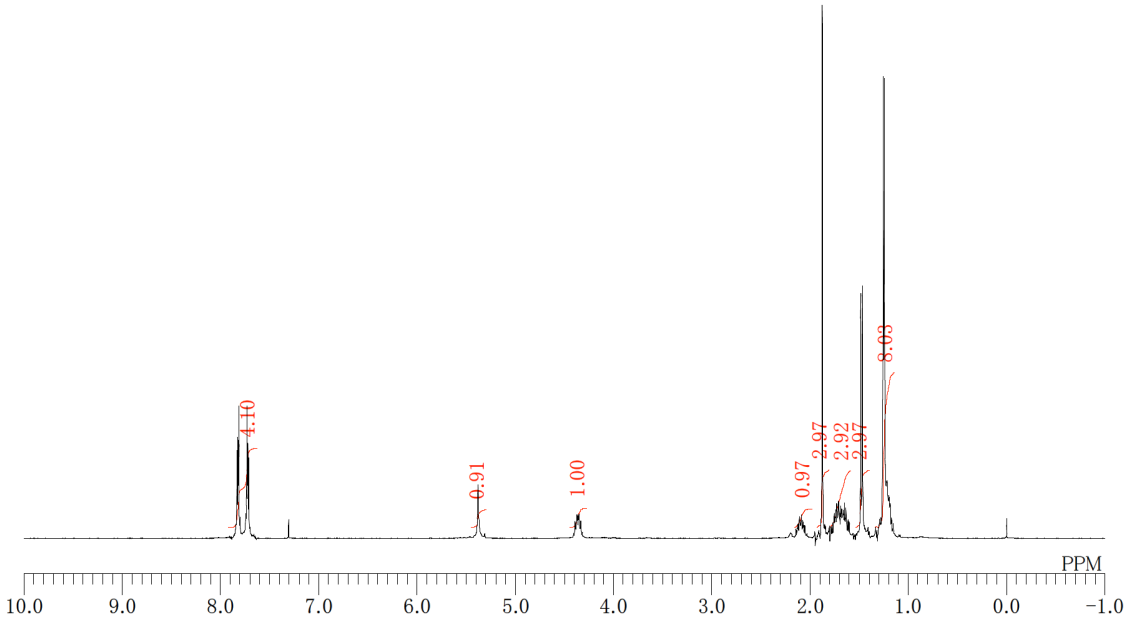
^{13}C NMR: (100 MHz, $CDCl_3$)



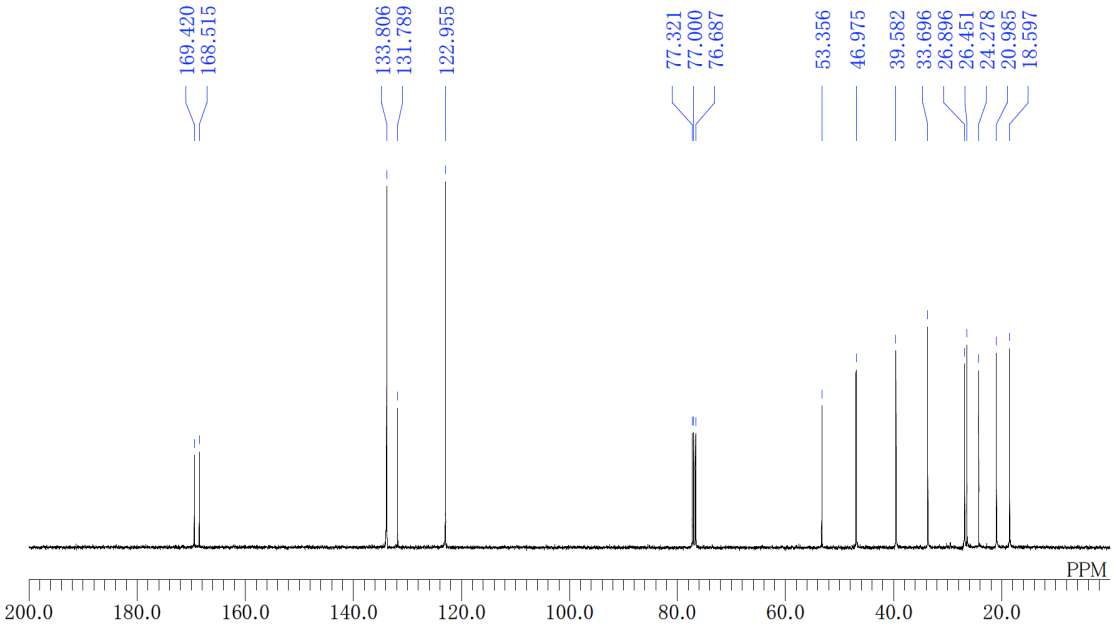
***N*-phthaloyl-6-acetamido-6-methylheptan-2-amine (2l)**



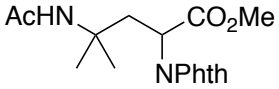
^{1}H NMR: (400 MHz, $CDCl_3$)



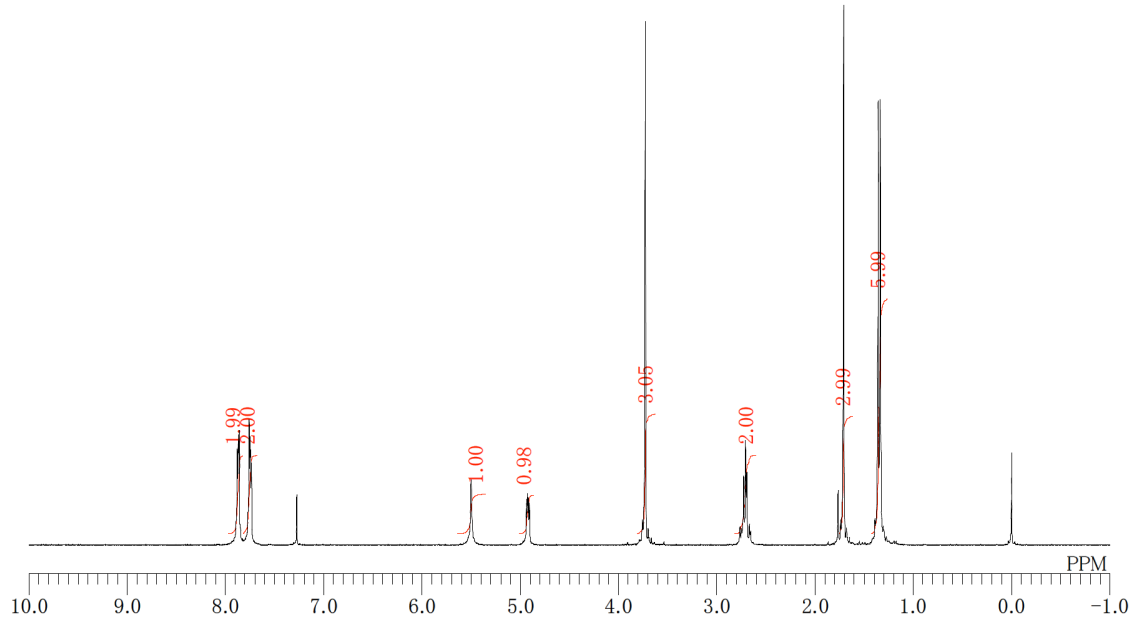
^{13}C NMR: (100 MHz, $CDCl_3$)



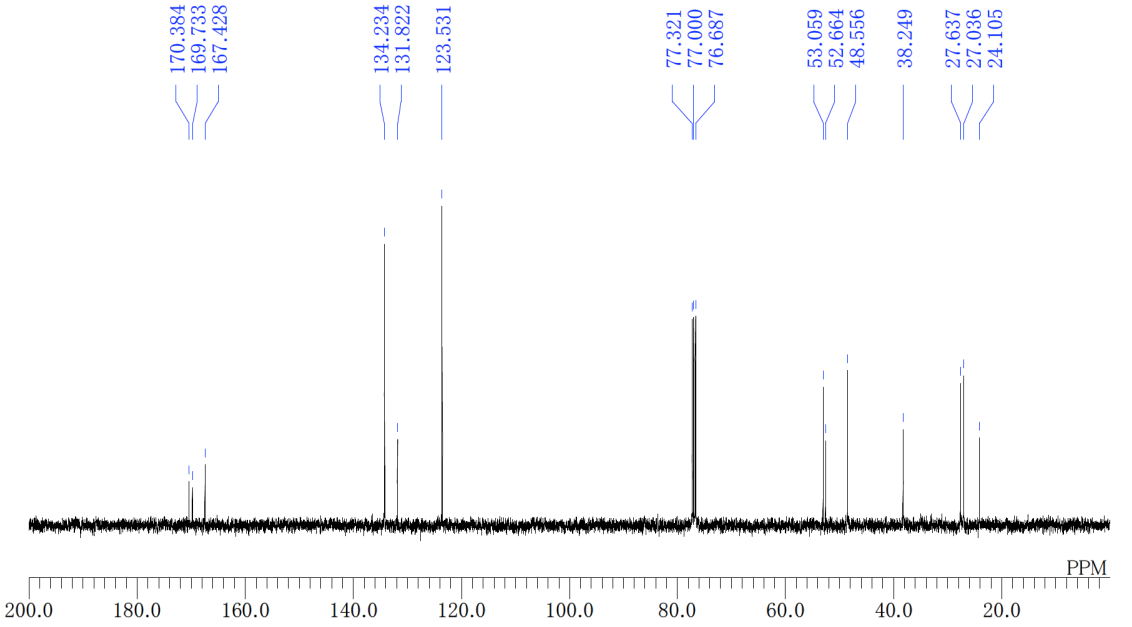
_N_-phthaloyl-4-acetamido-_L_-leucine methyl ester (2m)



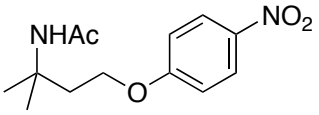
^{1}H NMR: (400 MHz, $CDCl_3$)



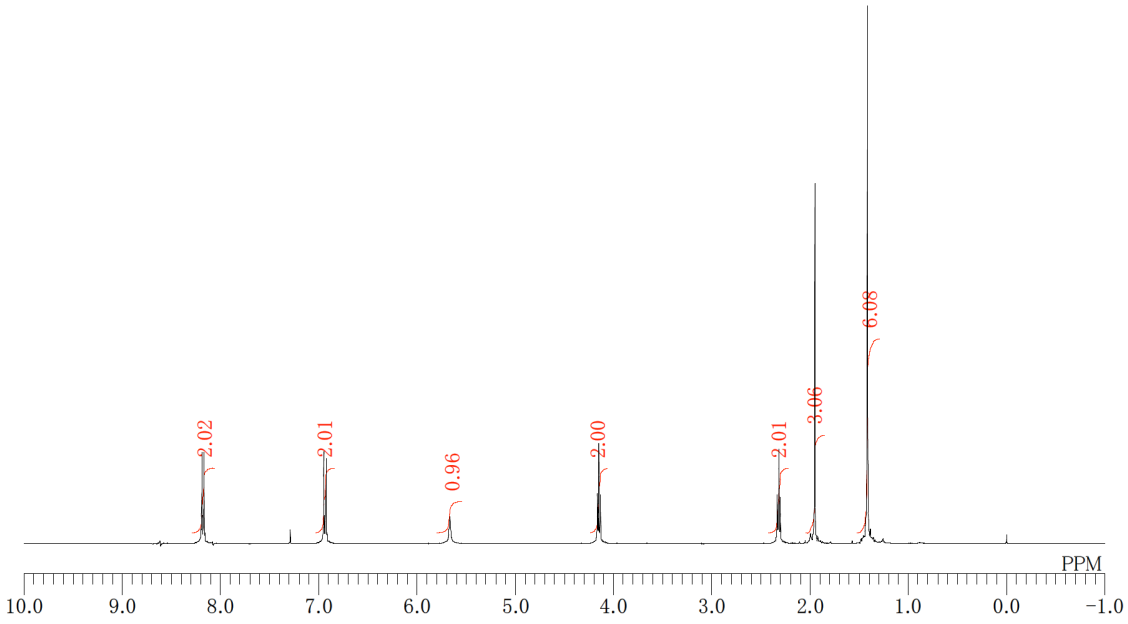
^{13}C NMR: (100 MHz, $CDCl_3$)



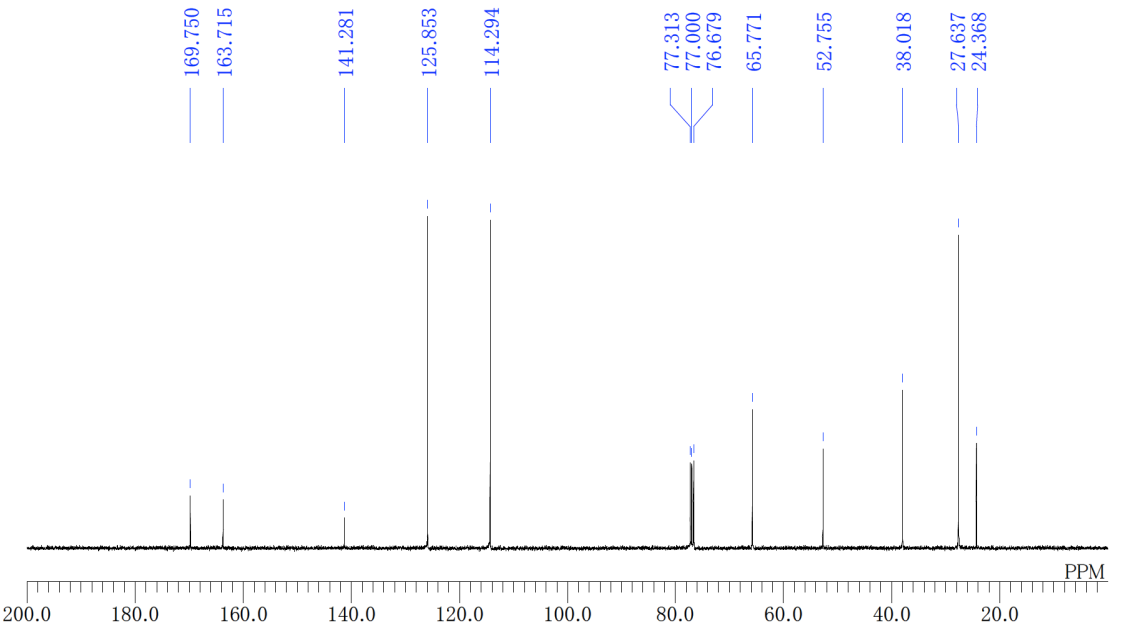
4-nitrophenyl 2-acetamido-2-methylbutan-2-yl ether (2n)



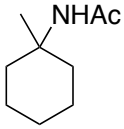
^{1}H NMR: (400 MHz, $CDCl_3$)



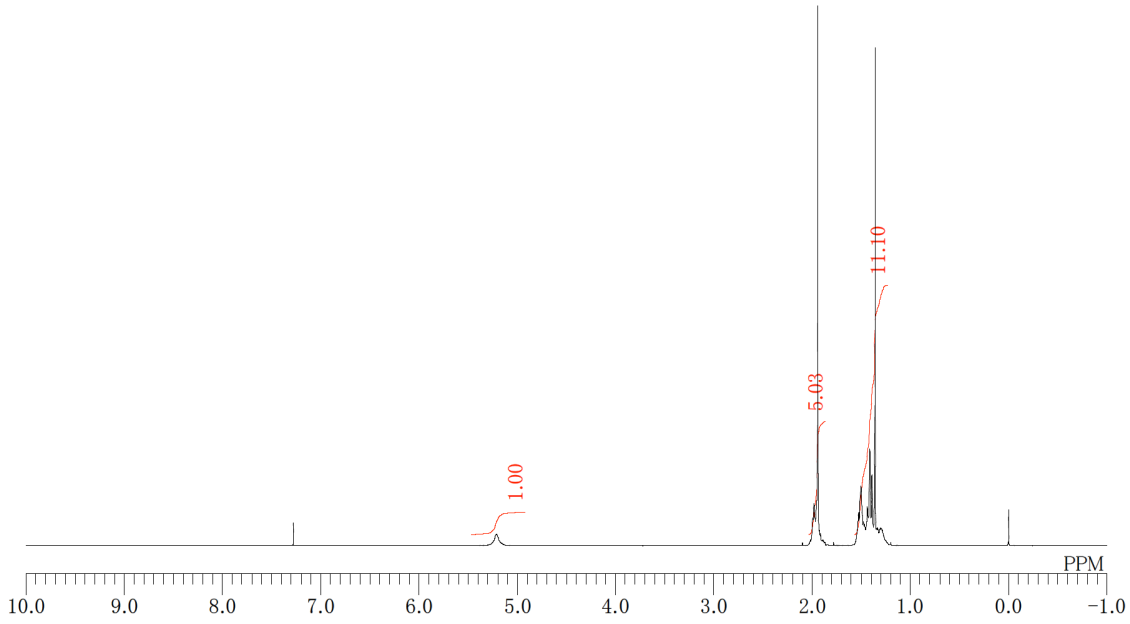
^{13}C NMR: (100 MHz, $CDCl_3$)



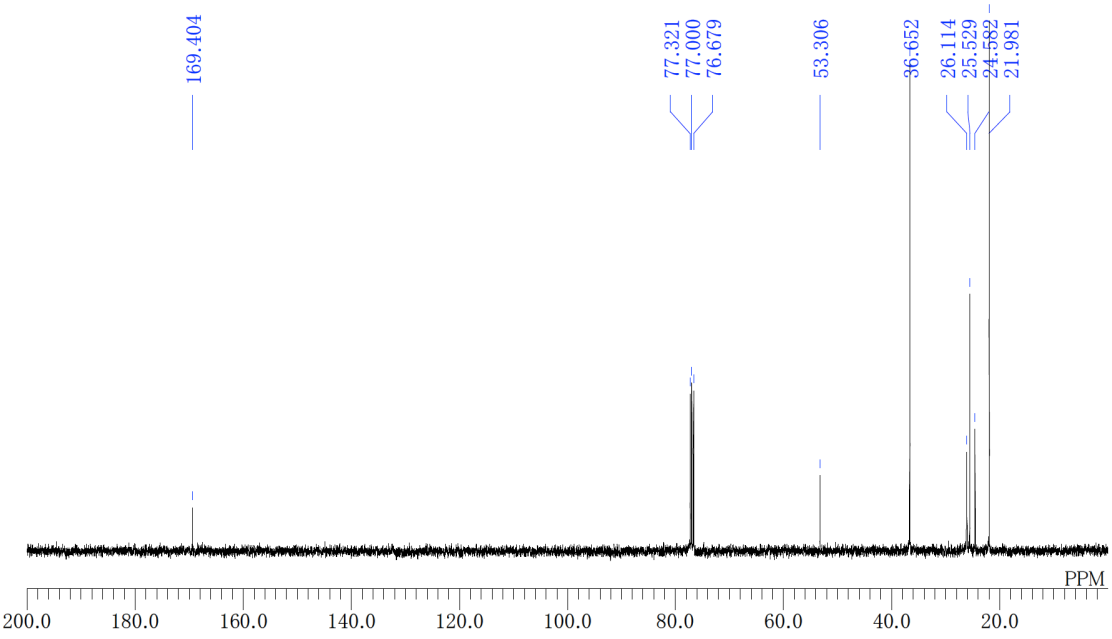
_N_-(1-methylcyclohexyl)acetamide (2o)



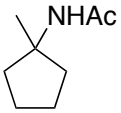
^{1}H NMR: (400 MHz, $CDCl_3$)



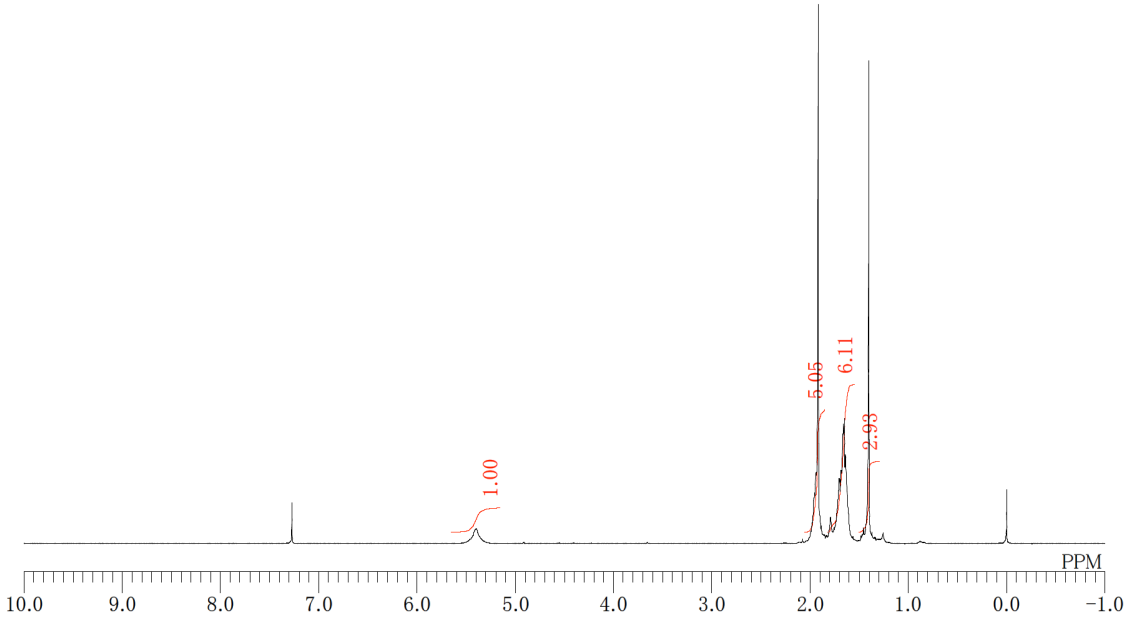
^{13}C NMR: (100 MHz, $CDCl_3$)



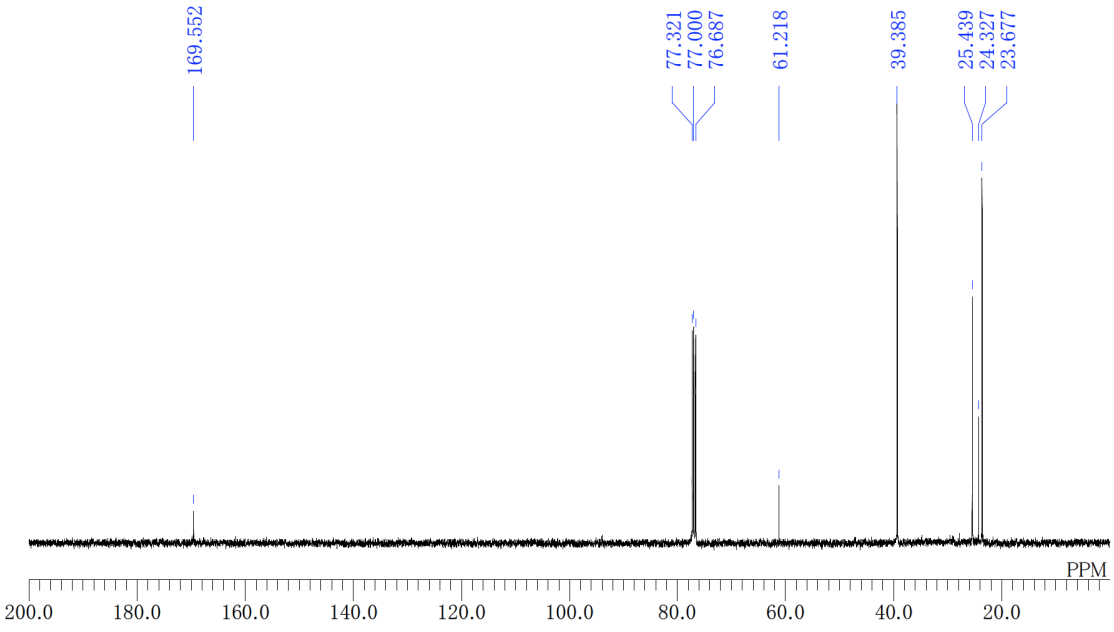
_N_-(1-methylcyclopentyl)acetamide (2p)



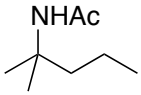
^{1}H NMR: (400 MHz, $CDCl_3$)



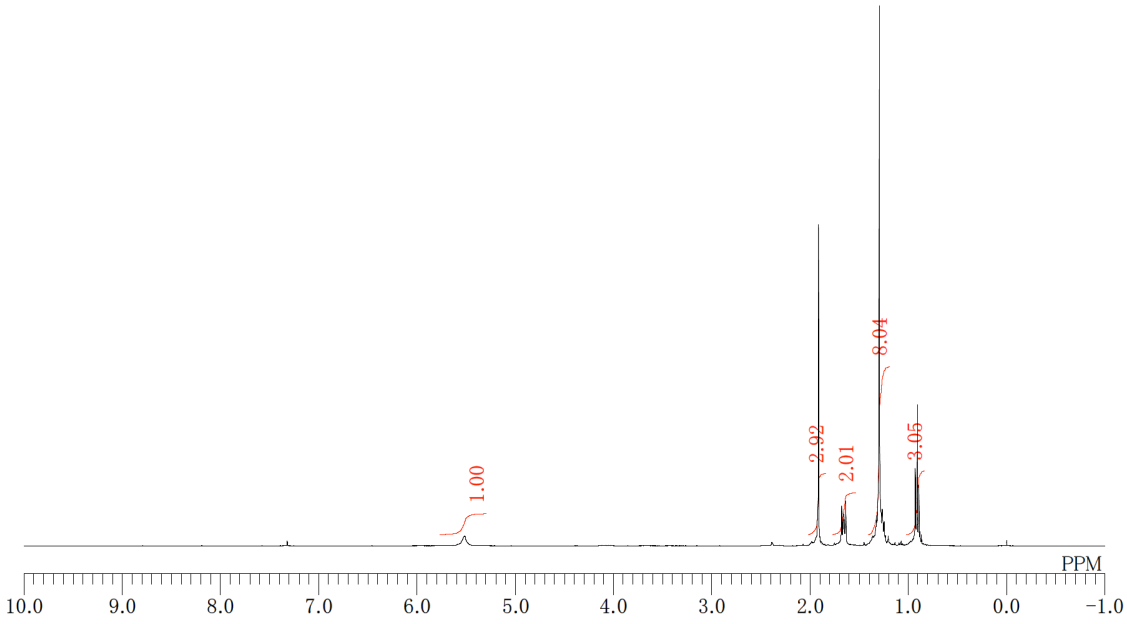
^{13}C NMR: (100 MHz, $CDCl_3$)



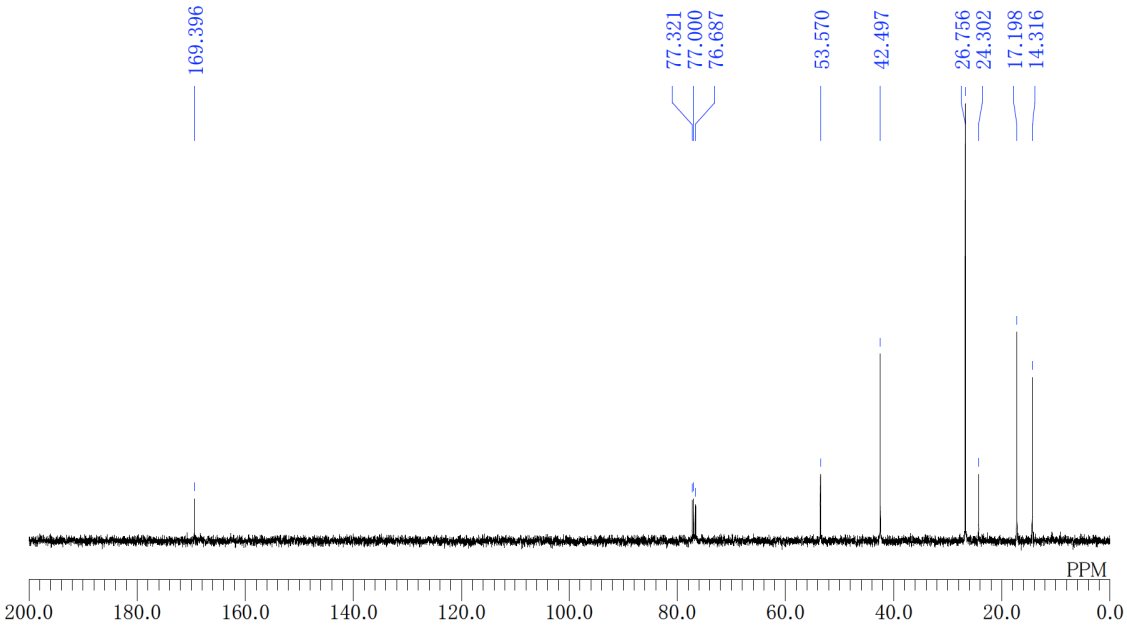
_N_-(2-methylpentan-2-yl)acetamide (2q)



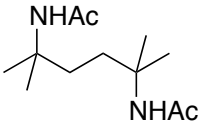
^{1}H NMR: (400 MHz, $CDCl_3$)



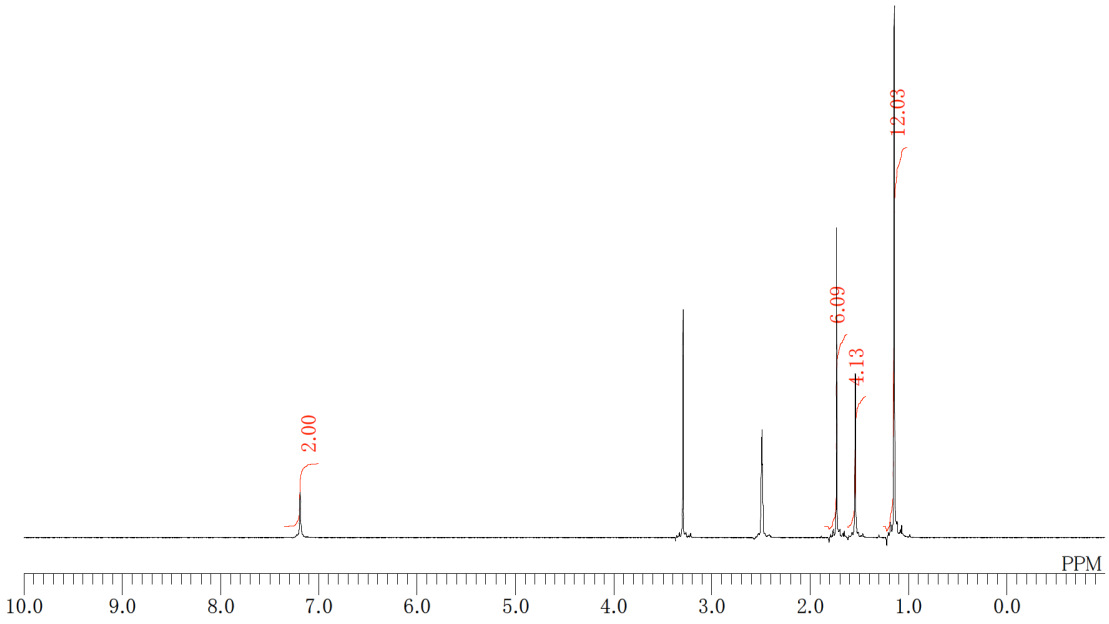
^{13}C NMR: (100 MHz, $CDCl_3$)



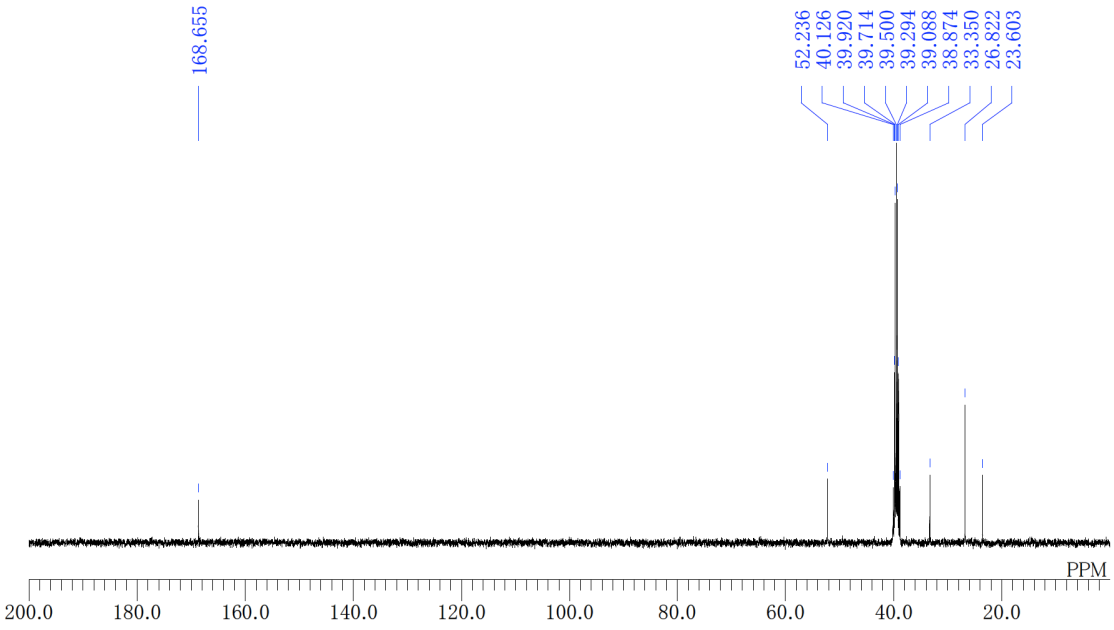
2,5-diacetamido-2,5-dimethylhexane (2r)



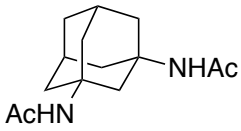
^{1}H NMR: (400 MHz, DMSO-d_6)



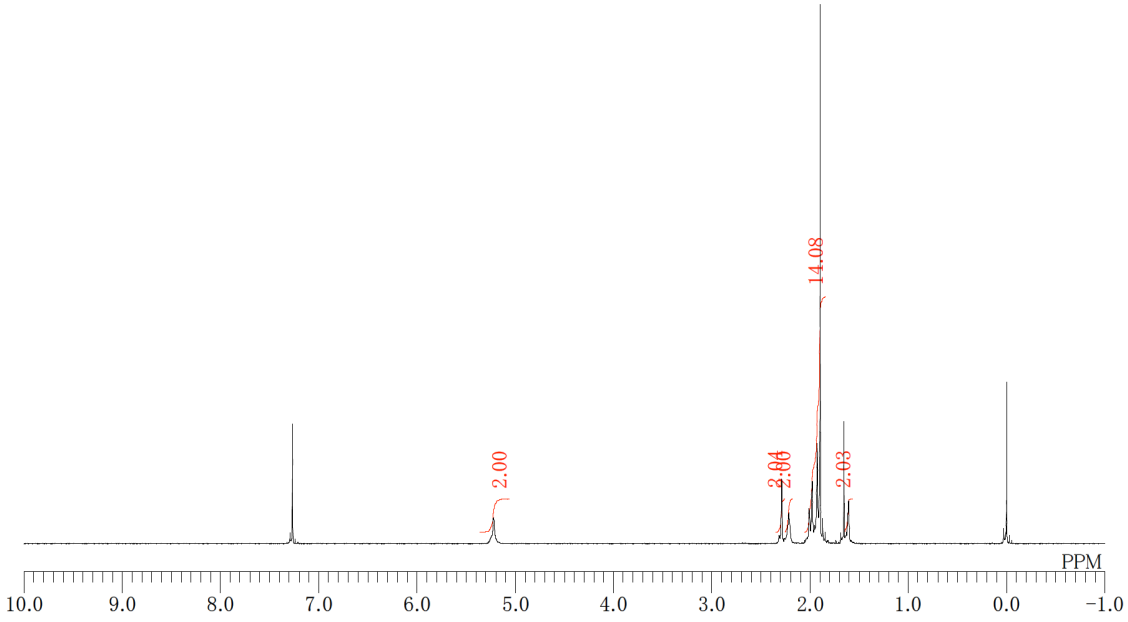
^{13}C NMR: (100 MHz, DMSO-d_6)



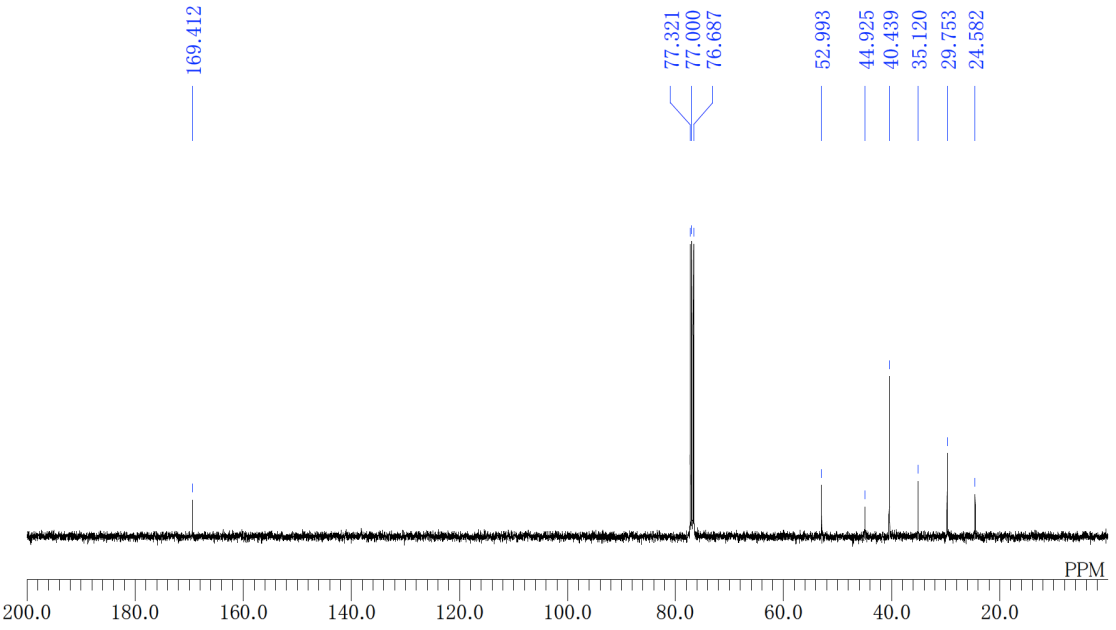
1,3-diacetamidoadamantane (2s)



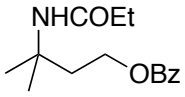
^{1}H NMR: (400 MHz, $CDCl_3$)



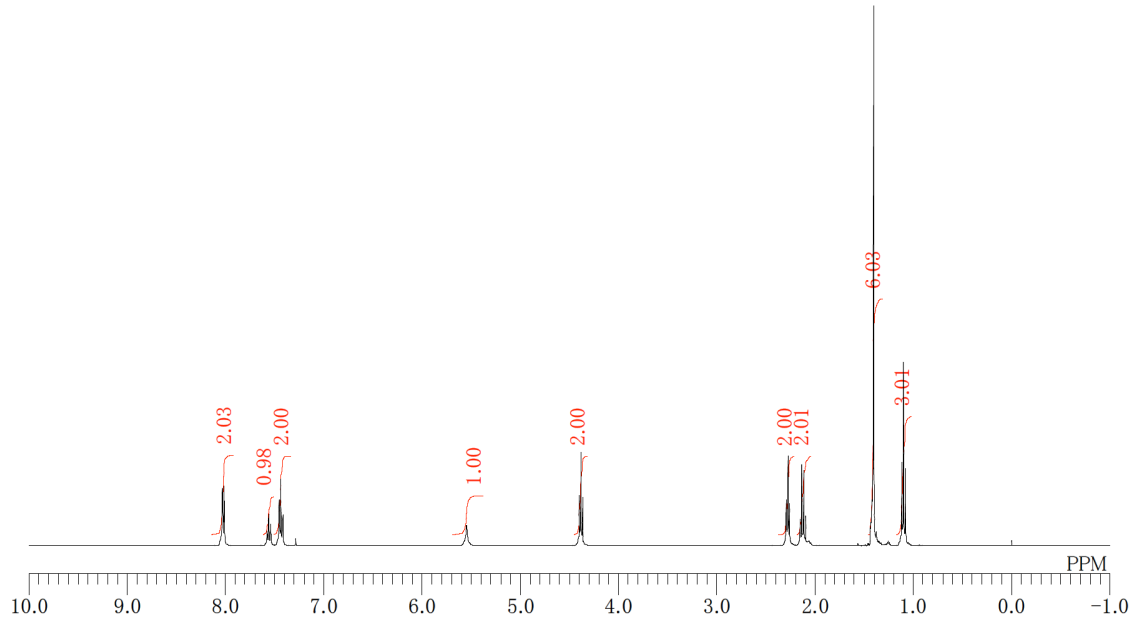
^{13}C NMR: (100 MHz, $CDCl_3$)



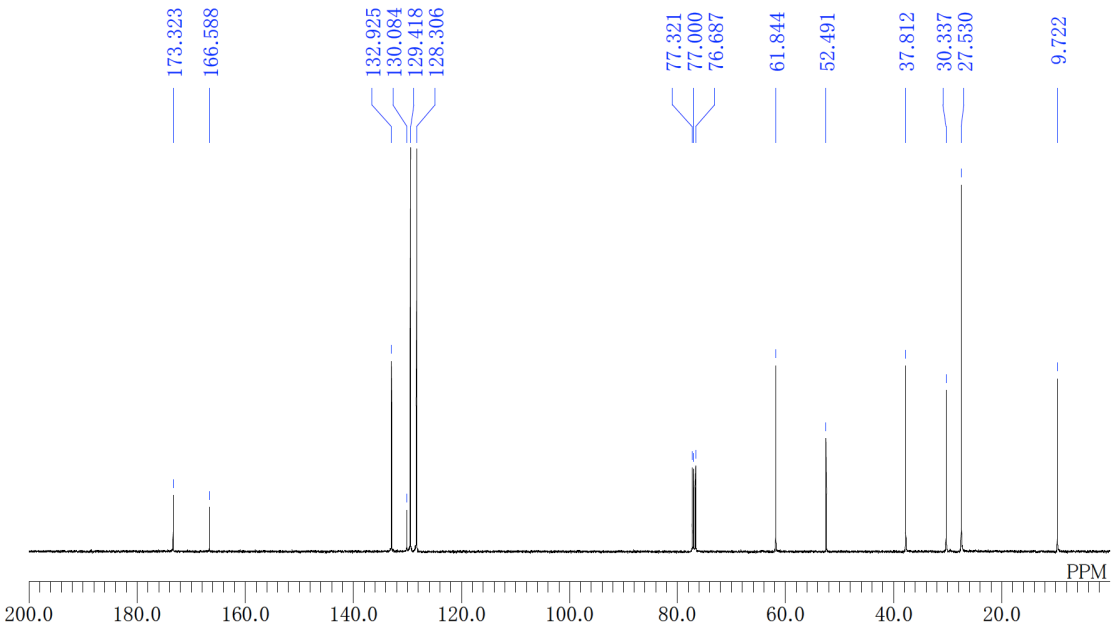
3-methyl-3-propionylaminobutyl benzoate (3)



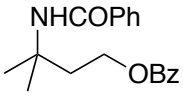
^{1}H NMR: (400 MHz, $CDCl_3$)



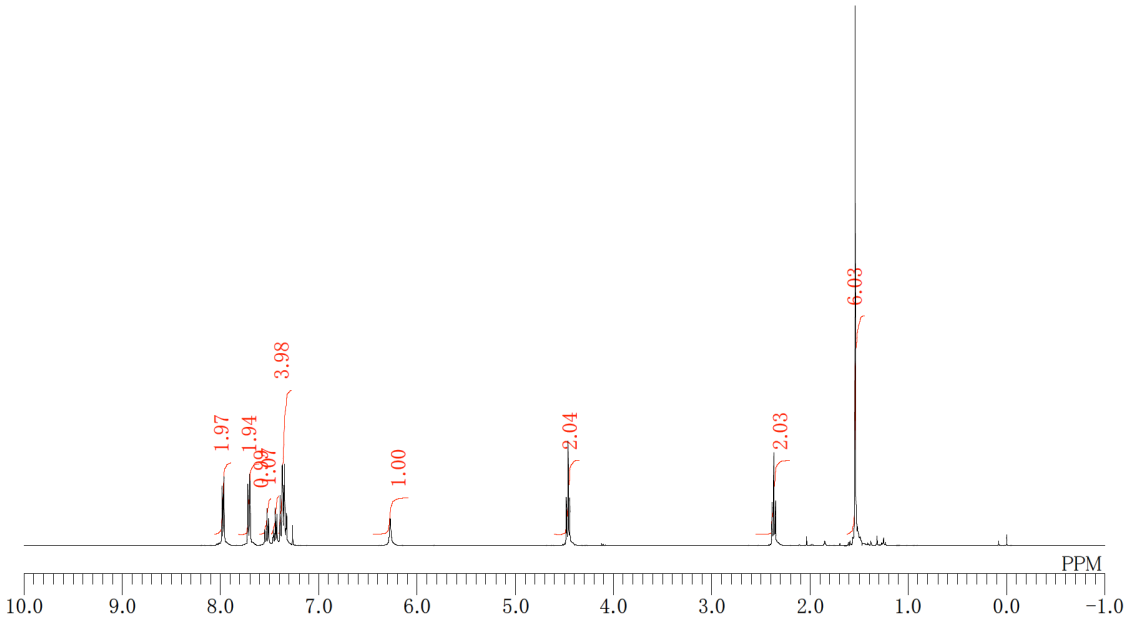
^{13}C NMR: (100 MHz, $CDCl_3$)



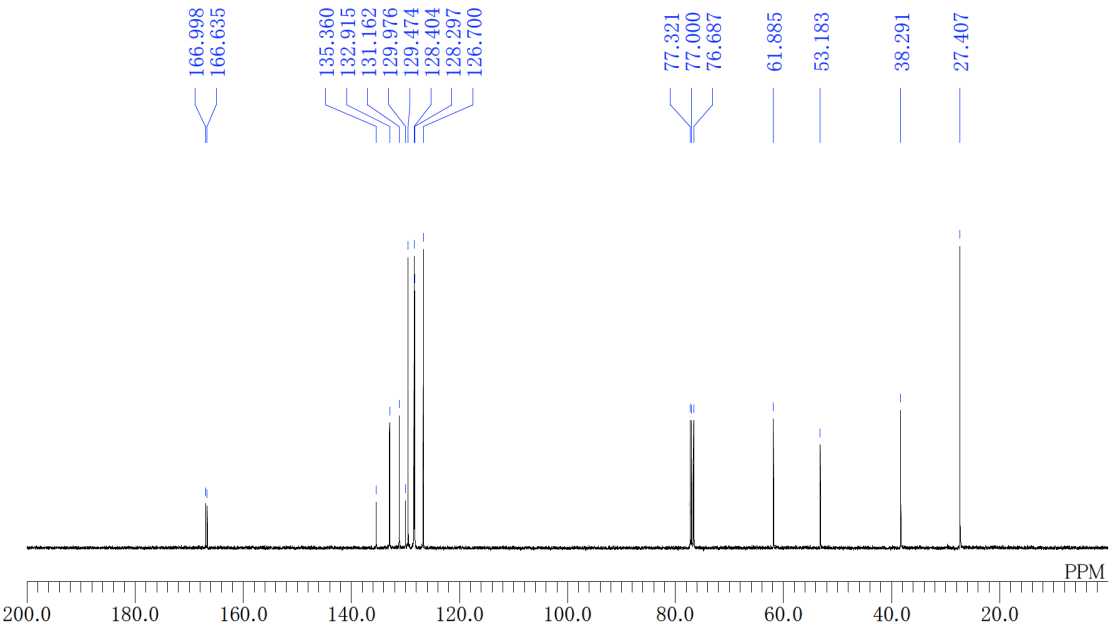
3-benzamido-3-methylbutyl benzoate (4)



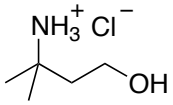
^{1}H NMR: (400 MHz, $CDCl_3$)



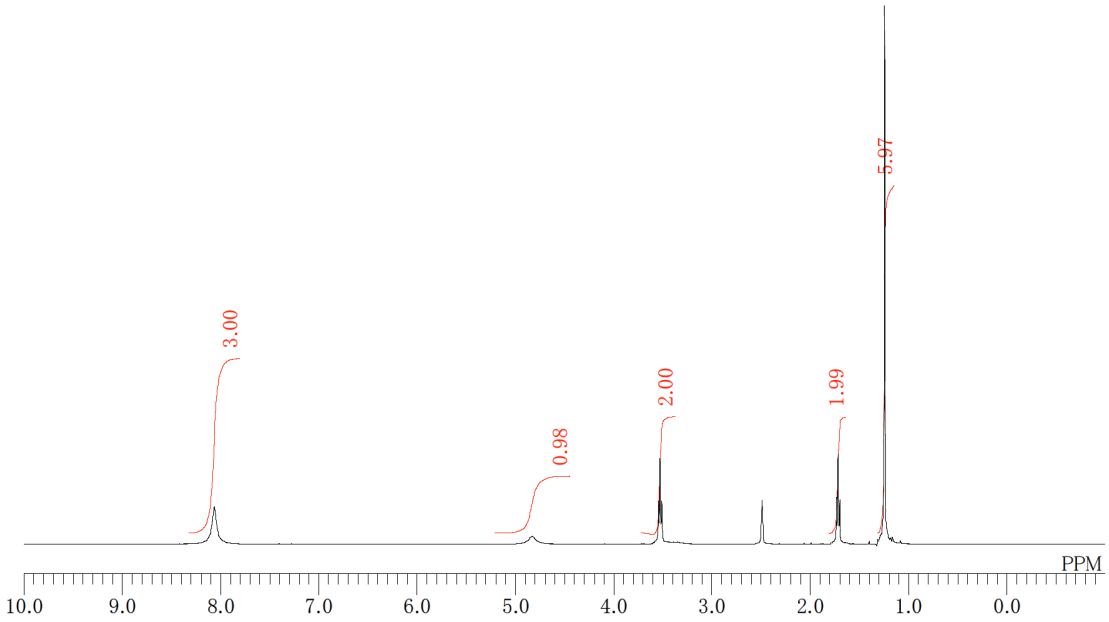
^{13}C NMR: (100 MHz, $CDCl_3$)



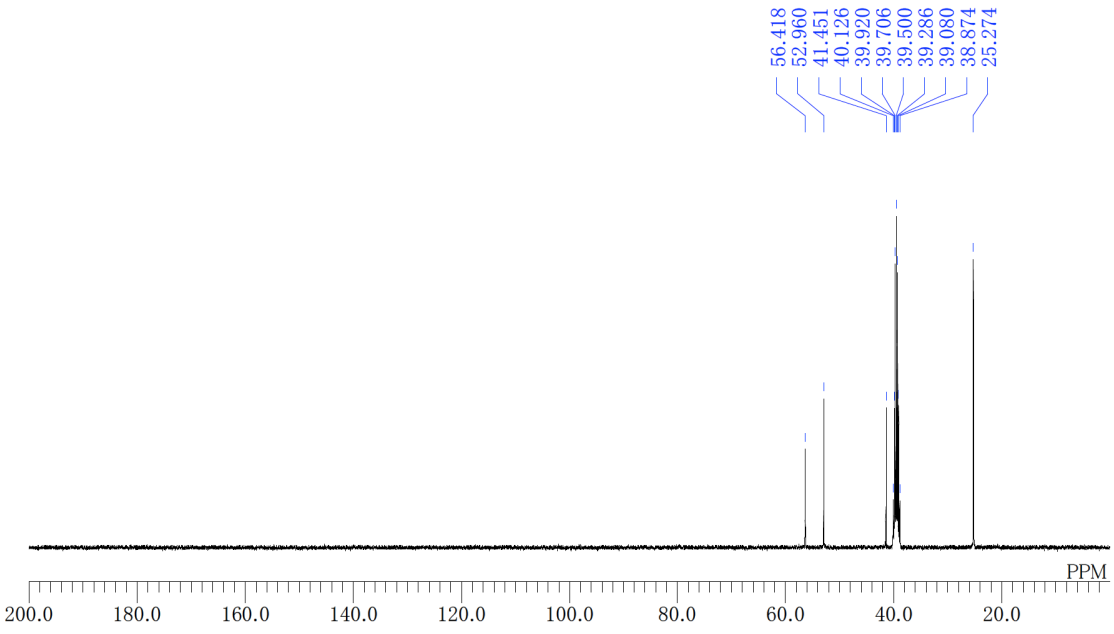
3-hydroxy-1,1-dimethyl-propylamine hydrochloride (5)



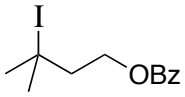
^{1}H NMR: (400 MHz, DMSO-d_6)



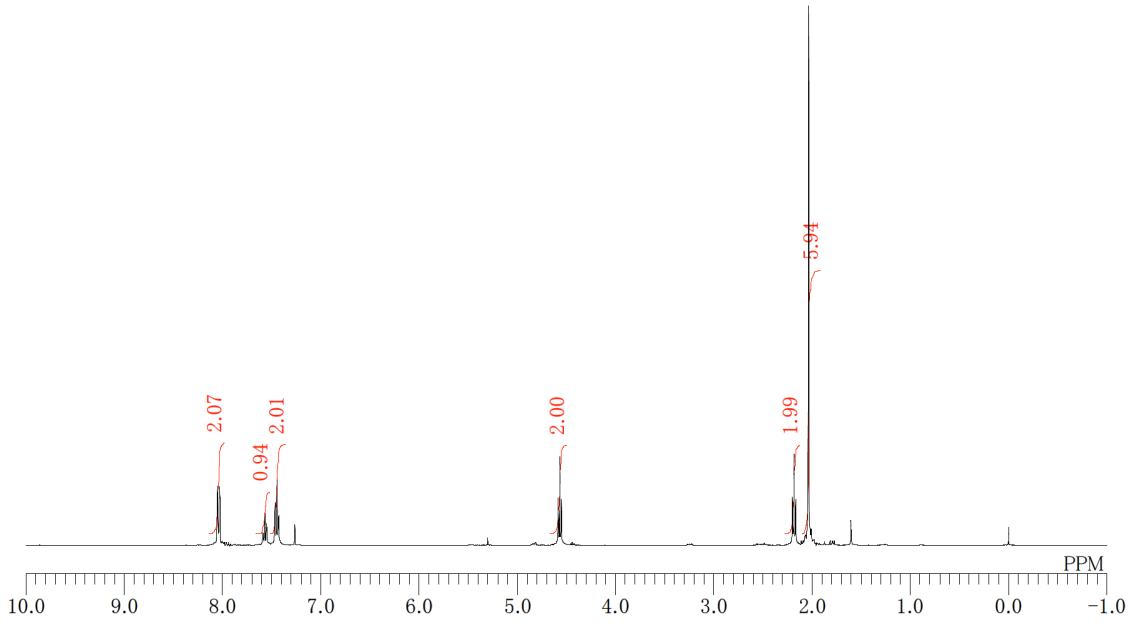
^{13}C NMR: (100 MHz, DMSO-d_6)



3-iodo-3-methylbutyl benzoate (6)



^{1}H NMR: (400 MHz, $CDCl_3$)



^{13}C NMR: (100 MHz, $CDCl_3$)