Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPORTING IN FORMATION

FOR

Palladium Catalyzed Aliphatic C—H Acetoxylation of Aliphatic Primary Amines to *γ*-Amino Alcohol Derivatives

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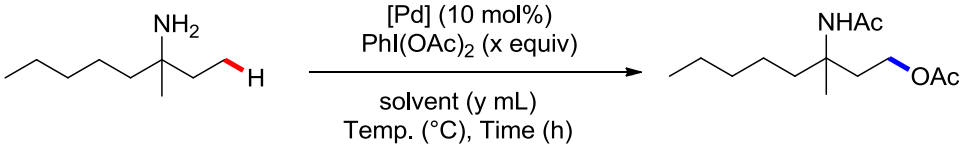
1. General Information

Chemical Reagents. Unless otherwise noted, materials and solvents were purchased from commercial suppliers and used without further purification. $Pd(OAc)_2$ was purchased from Sinocompound. Co., Ltd**.** $PhI(OAc)_2$ was obtained from Ouhe Co., Ltd. $CDCl_3$ and AcOH-d_4 were purchased from J&K Chemical and Cambridge Isotope Laboratories.

Instrumentation. ^1H NMR and ^{13}C NMR data were obtained on Bruker 400 MHz and 500 MHz nuclear resonance spectrometers unless otherwise specified. $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^1H NMR spectrum as 0.00 ppm. The data of ^1H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. Column chromatography was performed using 200 - 300 mesh silica gel with the indicated solvent system according to standard techniques. HRMS (ESI) analysis was performed by State Authorized Analytical Instrumentation Center, Peking University.

2. Optimization of Reaction Conditions

Table S1 Screening reaction parameters



Entry	Time (h)	Temp. (°C)	$PhI(OAc)_2$ (x equiv)	Pd cat.	AcOH (y mL)	Yield[a]
1	3	120	2.0	$Pd(OAc)_2$	1.0 mL	36%
2	6	120	2.0	$Pd(OAc)_2$	1.0 mL	45%
3	9	120	2.0	$Pd(OAc)_2$	1.0 mL	44%
4	12	120	2.0	$Pd(OAc)_2$	1.0 mL	38%
5	6	120	1.5	$Pd(OAc)_2$	1.0 mL	46% (50%)[b]
6	6	120	1.2	$Pd(OAc)_2$	1.0 mL	38%
7	6	100	1.5	$Pd(OAc)_2$	1.0 mL	36%
8	6	80	1.5	$Pd(OAc)_2$	1.0 mL	trace
9	6	120	1.5	$Pd(OPiv)_2$	1.0 mL	45%[b]
10	6	120	1.5	$Pd(MeCN)_4[BF_4]_2$	1.0 mL	42%[b]
11	6	120	1.5	$Pd(OBz)_2$	1.0 mL	50%[b]
12	6	120	1.5	$Pd(OAc)_2$	2.0 mL	56%[b]
13	6	120	1.5	$Pd(OAc)_2$	3.0 mL	60% (62%)[b]
14	6	120	1.5	$Pd(OAc)_2$	4.0 mL	53%[b]
15	6	120	1.5	$Pd(OAc)_2$	3.0 mL	59%[b, c]
16	6	120	1.5	$Pd(OAc)_2$	3.0 mL	58%[b, d]
17	6	120	1.5	$Pd(OAc)_2$	3.0 mL	63%[b, e]
18	**6**	**120**	**2.0**	**$Pd(OAc)_2$**	**3.0 mL**	**67%[b,e] (64%)[f]**
19	6	120	2.0	$Pd(OAc)_2$	9.0 mL	32%[b,e,g]

[a] NMR yield, with 1,3-benzodioxole as the internal standard. [b] Step 2: Ac_2O (2.0 equiv), NEt_3 (0.1 mL), DCM (3.0 mL). rt., 3 h. [c] in N_2 atmosphere. [d] in O_2 atmosphere. [e] The $Pd(OAc)_2$ and $PhI(OAc)_2$ were added in two batches. [f] Isolated yield of the combined parallel reactions (3 * 0.1 mmol scale) was obtained. [g] Isolated yield of 0.3 mmol scale reaction was obtained.

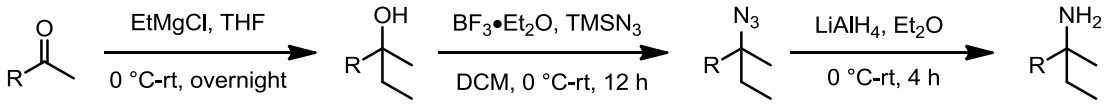
Solvents screening did not get the better results, such as the solvents of toluene, $PhCF_3$, C_6H_6, MeCN, DCE gave the trace yield of desired product, and the solvents of HFIP, 1,4-dioxone, THF, DMF, Ac_2O using in the reaction, no desired product was detected. Other Pd catalyst like $Pd(OTFA)_2$ and $Pd(PPh_3)Cl_2$ gave much worse results which could observe from TLC. Though $Pd(OBz)_2$ showed comparable catalytic activity with $Pd(OAc)_2$, we still chose $Pd(OAc)_2$ as the catalyst for it was more inexpensive and easily

available than $Pd(OBz)_2$. We also tried Ir, Rh and Cu complexes as the catalysts for C(sp^3)—H acetoxylation, but none of them could give the desired product.

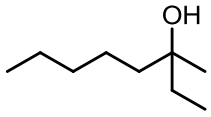
3. Preparation and Characterization of Reaction Substrates

Some of the intermediates' molecular ion peaks could not be capatured using HR-MS, e.g. all-carben azide compounds and small molecular compounds ([M] < 200). Thus, these intermediates were characterized by ^{1}H NMR, ^{13}C NMR, IR and GC-MS. IR spectra were recorded on Nicolet iS10 in wave numbers, cm^{-1}. GC-MS analysis was performed at Agilent 5977A series GC/MSD system.

3.1 General Procedure for the Synthesis of amines from ketones

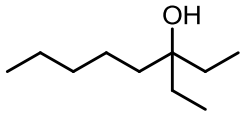


Step 1: To a solution of ketone (100.0 mmol, 1.0 equiv) in 30 mL of THF at 0 °C under N_2 atmosphere, EtMgCl (2.0 mol/L in THF, 50 mL) was injected by syringe. The mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with water and filtered through a celite pad. The filtrate was concentrated under reduced pressure until most of THF was evaporated. The residue was extracted with CH_2Cl_2 (3× 30 mL). The organic phase was dried over anhydrous Na_2SO_4 and then concentrated. The residue was purified by distillation under reduced pressure to get the tertiary alcohol.



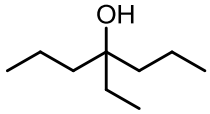
3-methyloctan-3-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 – 1.41 (m, 6H), 1.39 (s, 3H), 1.37 – 1.25 (m, 6H), 1.14 (s, 1H), 0.94 – 0.85 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.9, 41.3, 34.2, 32.5, 26.4, 23.5, 22.7, 14.0, 8.2. (Known compound: H. Leuser, S. Perrone, F. Liron, F. F. Kneisel, P. Knochel, *Angew. Chem. Int. Ed*. **2005**, *44*, 4627-4631)



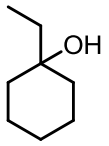
3-ethyloctan-3-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (q, *J* = 7.5 Hz, 4H), 1.43 – 1.37 (m, 2H), 1.37 – 1.20 (m, 6H), 1.08 (s, 1H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.64, 38.18, 32.53, 31.04, 23.09, 22.69, 14.09, 7.80. (Known compound: B. H. Lipshutz, R. S. Wilhelm, J. A. Kozlowski, D. Parker, *J. Org. Chem.* **1984**, *49*, 3928-3938)



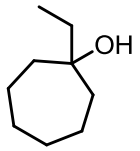
4-ethylheptan-4-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 – 1.36 (m, 6H), 1.35 – 1.26 (m, 4H), 1.09 (s, 1H), 0.92 (t, *J* = 7.1 Hz, 6H), 0.86 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.58, 41.17, 31.60, 16.72, 14.77, 7.85. (Known compound: B. Li, M. Driess, J. F. Hartwig, *J. Am. Chem. Soc*. **2014**, *136*, 6586-6589)



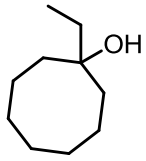
1-ethylcyclohexanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 – 1.34 (m, 11H), 1.33 – 1.16 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62, 1.60, 1.57, 1.54, 1.52, 1.49, 1.46, 1.45, 1.43, 1.39, 1.37, 1.27, 1.24, 0.91, 0.90, 0.88. ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.46, 36.91, 34.75, 25.90, 22.25, 7.24. (Known compound: D. Guijarro, G. Guillena, B. Mancheño, M. Yus, *Tetrahedron*. **1994**, *50*, 3427-3436)



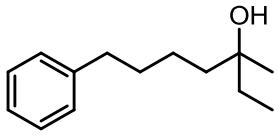
1-ethylcycloheptanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 – 1.56 (m, 8H), 1.55 – 1.45 (m, 4H), 1.45 – 1.33 (m, 2H), 1.15 (s, 1H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.53, 40.70, 35.82, 29.90, 22.49, 7.68. (Known compound: R. P. Kirchen, N. Okazawa, K. Ranganayakulu, A. Rauk, T. S. Sorensen, *J. Am. Chem. Soc*. **1981**, *103*, 597-604)



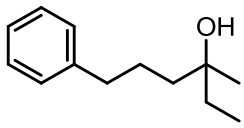
1-ethylcyclooctanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 – 1.31 (m, 16H), 1.13 (s, 1H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.87, 35.85, 33.77, 28.30, 25.04, 22.38, 7.43. IR (cm^{-1}): 2921, 959. GC-MS (EI): m/z: (127.2, $[M\text{-}Et]^+$, 100%), (138.2, $[M\text{-}H_2O]^+$, 6%).



3-methyl-7-phenylheptan-3-ol

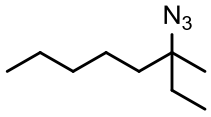
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 2.66 – 2.58 (m, 2H), 1.68 – 1.57 (m, 2H), 1.51 – 1.43 (m, 4H), 1.42 – 1.33 (m, 2H), 1.17 (s, 1H), 1.13 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.67, 128.40, 128.29, 125.66, 72.89, 41.20, 35.98, 34.27, 32.12, 26.40, 23.60, 8.22. HRMS (ESI): m/z: calculated for $C_{14}H_{26}NO$ $[M + NH_4]^+$ 224.20089, found 224.20087.



3-methyl-6-phenylhexan-3-ol

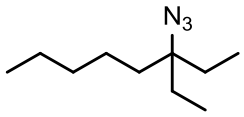
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.72 – 1.61 (m, 2H), 1.52 – 1.42 (m, 4H), 1.13 (s, 4H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.49, 128.41, 128.32, 125.76, 72.86, 40.92, 36.42, 34.25, 26.42, 25.85, 8.20. HRMS (ESI): m/z: calculated for $C_{13}H_{24}NO$ $[M + NH_4]^+$ 210.18524, found 210.18567.

Step 2: The azidation of tertiary alcohol was conducted according to a reported method with minor modification.[1] The tertiary alcohol (50 mmol, 1.0equiv) and $TMSN_3$ (6.9 g, 60 mmol, 1.2 equiv) were dissolved into 40 mL of CH_2Cl_2 and the solution was cooled down to 0°C. BF_3•Et_2O (8.5 g, 60 mmol, 1.2 equiv) was added dropwisely to this solution. The mixture was warmed up to room temperature and stirred for 12 h. Then the reaction was quenched with the addition of saturated $NaHCO_3$ (aq). The mixture was stirred vigorously for 15 min. The separated organic layer was washed by H_2O, brine and dried over anhydrous Na_2SO_4. The crude product of azide was obtained by removing the solvent under reduced pressure, which was used for the next step without further purification.



3-azido-3-methyloctane

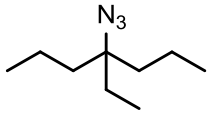
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 – 1.44 (m, 4H), 1.37 – 1.25 (m, 6H), 1.21 (s, 3H), 0.96 – 0.85 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.60, 38.83, 32.18, 31.95, 23.56, 22.85, 22.60, 14.03, 8.36. IR (cm^{-1}): 2095. GC-MS (EI): m/z: (112.2, $[M\text{-}N_3\text{-}Me]^+$).



3-azido-3-ethyloctane

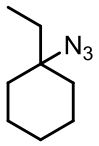
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (q, *J* = 7.5 Hz, 4H), 1.51 – 1.43 (m, 2H), 1.36 – 1.24 (m, 6H), 0.94 – 0.84 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.30, 35.41, 32.23, 28.56,

23.12, 22.59, 14.03, 7.98. IR (cm^{-1}): 2096. GC-MS (EI): m/z: (126.2, $[M-N_3-Me]^+$, 100%), (141.3, $[M-N_3]^+$, 91%).



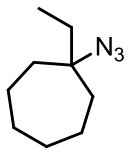
4-azido-4-ethylheptane

^1H NMR (400 MHz, $CDCl_3$) δ 1.54 (q, *J* = 7.5 Hz, 2H), 1.50 – 1.43 (m, 4H), 1.37 – 1.29 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.07, 38.34, 29.12, 16.85, 14.51, 8.05. IR (cm^{-1}): 2099. GC-MS (EI): m/z: (98.2, $[M-N_3-Et]^+$, 27%), (127.3, $[M-N_3]^+$, 100%).



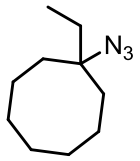
1-azido-1-ethylcyclohexane

^1H NMR (400 MHz, $CDCl_3$) δ 1.70 – 1.64 (m, 2H), 1.62 – 1.50 (m, 7H), 1.39 – 1.30 (m, 2H), 1.28 – 1.19 (m, 1H), 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.42, 34.13, 32.82, 25.55, 22.15, 7.74. IR (cm^{-1}): 2098. GC-MS (EI): m/z: (96.2, $[M-N_3-Me]^+$, 100%), (111.2, $[M-N_3]^+$, 98%), (124.2, $[M-Et]^+$, 10%).



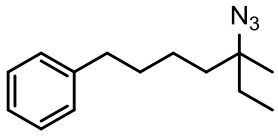
1-azido-1-ethylcycloheptane

^1H NMR (400 MHz, $CDCl_3$) δ 1.82 – 1.71 (m, 2H), 1.65 – 1.56 (m, 8H), 1.55 – 1.37 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.01, 37.69, 33.39, 29.54, 22.52, 8.25. IR (cm^{-1}): 2091. GC-MS (EI): m/z: (110.2, $[M-N_3-Me]^+$, 100%), (125.2, $[M-N_3]^+$, 86%), (138.2, $[M-Et]^+$, 7%).



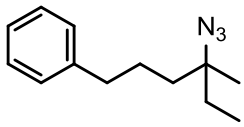
1-azido-1-ethylcyclooctane

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 – 1.78 (m, 2H), 1.69 – 1.51 (m, 11H), 1.45 (ddd, *J* = 10.7, 9.4, 4.8 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.98, 32.81, 31.66, 28.22, 24.88, 22.35, 8.14. IR (cm^{-1}): 2090. GC-MS (EI): m/z: (124.2, $[M\text{-}N_3\text{-}Me]^+$, 100%), (139.3, $[M\text{-}N_3]^+$, 48%), (152.2, $[M\text{-}Et]^+$, 6%).



(5-azido-5-methylheptyl)benzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 2.70 – 2.61 (m, 2H), 1.71 – 1.61 (m, 2H), 1.59 – 1.51 (m, 4H), 1.45 – 1.36 (m, 2H), 1.23 (s, 3H), 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.45, 128.39, 128.34, 125.75, 64.54, 38.78, 35.89, 32.01, 31.85, 23.63, 22.83, 8.39. IR (cm^{-1}): 2090, 698, 651. GC-MS (EI): m/z: (174.2, $[M\text{-}N_3\text{-}Me]^+$, 100%), (188.3, $[M\text{-}N_3\text{-}H]^+$, 37%), (189.3, $[M\text{-}N_3]^+$, 20%).



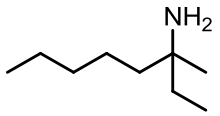
(4-azido-4-methylhexyl)benzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.62 (m, 2H), 1.56 – 1.48 (m, 4H), 1.20 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.07, 128.39, 125.90, 64.45, 38.49, 36.14, 32.00, 25.81, 22.84, 8.35. IR (cm^{-1}): 2093, 748, 698. GC-MS (EI): m/z: (160.2, $[M\text{-}N_3\text{-}Me]^+$, 100%), (174.2, $[M\text{-}N_3\text{-}H]^+$, 17%).

Step 3: To a solution of azide in 40 mL of Et_2O at 0 °C, $LiAlH_4$ (1.9 g, 50 mmol, 1.0

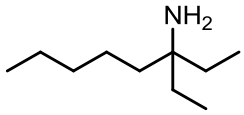
equiv) was added into small portions. The reaction was warmed up to room temperature and stirred for 4 h. Then the reaction was quenched with $Na_2SO_4 \cdot 10H_2O$ and filtered through a celite pad. The filtrate was concentrated to get the crude amine product, which was further purified by distillation to give the desired product.

Compound **1b-f**, **3a** and **3j** were prepared though the same procedure in smaller scales. The final amine products were purified by column chromatography (eluent: CH_2Cl_2 : MeOH = 50 : 1 to 20 : 1) instead of distillation. Substrate **1g** was purchased from TCI and used without purification.



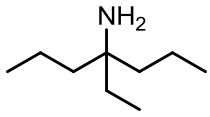
3-methyloctan-3-amine (1a)

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39-1.33 (m, 3H), 1.32-1.25 (m, 7H), 1.03 (br, 2H), 1.01 (s, 3H), 0.91-0.84 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.4, 42.2, 35.0, 32.6, 27.5, 23.6, 22.7, 14.0, 8.2. HRMS(EI): m/z: calculated for $C_9H_{21}N$ 143.1674, found $C_9H_{20}N$ 142.1590.



3-ethyloctan-3-amine (1b).

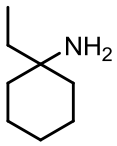
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36-1.25 (m, 12H), 1.01 (br, 2H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.1, 39.1, 32.6, 31.8, 23.0, 22.6, 14.0, 7.7. HRMS(EI): m/z: calculated for $C_{10}H_{23}N$ 157.1830, found $C_{10}H_{22}N$ 156.1749.



4-ethylheptan-4-amine (1c)

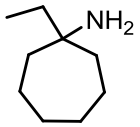
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (q, *J* = 7.5 Hz, 2H), 1.27-1.25 (m,

8H), 1.11 (br, 2H), 0.92-0.89 (m, 6H), 0.83 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.4, 42.1, 32.3, 16.6, 14.8, 7.8. HRMS(EI): m/z: calculated for $C_9H_{21}N$ 143.1674, found $C_9H_{20}N$ 142.1591.



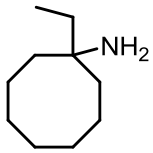
1-ethylcyclohexanamine (1d)

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53-1.46 (m, 5H), 1.41-1.29 (m, 7H), 1.07 (br, 2H), 0.87 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.3, 38.2, 34.8, 26.0, 22.2, 7.1. HRMS(EI): m/z: calculated for $C_8H_{17}N$ 127.1361, found $C_8H_{16}N$ 126.1278.



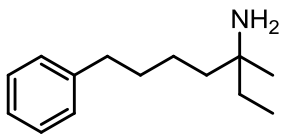
1-ethylcycloheptanamine (1e)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.57-1.53 (m, 10H), 1.46-1.37 (m, 6H), 0.88 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.4, 41.4, 36.2, 30.2, 22.7, 7.7. HRMS(EI): m/z: calculated for $C_9H_{19}N$ 141.1518, found $C_9H_{18}N$ 140.1434.



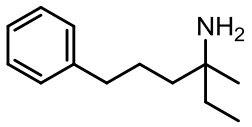
1-ethylcyclooctanamine (1f)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63-1.61 (m, 3H), 1.55-1.43 (m, 11H), 1.37 (q, J = 7.5 Hz, 2H), 1.13 (br, 2H), 0.86 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 36.4, 34.6, 28.5, 25.3, 22.7, 7.5. HRMS(EI): m/z: calculated for $C_{10}H_{21}N$ 155.1674, found $C_{10}H_{20}N$ 154.1591.



3-methyl-7-phenylheptan-3-amine (3a)

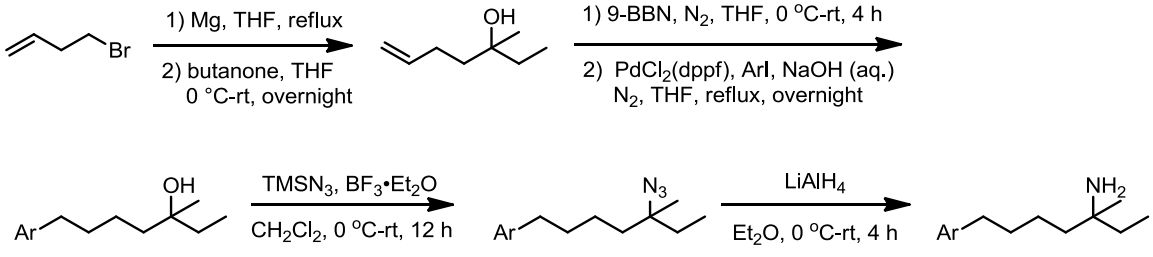
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.19-7.15 (m, 3H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.64-1.60 (m, 2H), 1.38-1.33 (m, 6H), 1.25 (br, 2H), 1.00 (s, 3H), 0.85 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 128.3, 128.2, 125.6, 51.3, 42.1, 35.9, 35.0, 32.2, 27.5, 23.6, 8.2. HRMS (ESI): m/z: calculated for $C_{14}H_{24}N$ $[M + H]^+$ 206.1903, found 206.1904.



3-methyl-6-phenylhexan-3-amine (3j)

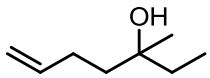
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.19-7.15 (m, 3H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.66-1.57 (m, 2H), 1.39-1.32 (m, 4H), 1.21 (br, 2H), 1.00 (s, 3H), 0.83 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 128.3, 128.2, 125.6, 51.3, 41.8, 36.5, 35.0, 27.5, 26.0, 8.2. HRMS(EI): m/z: calculated for $C_{13}H_{21}N$ 191.1674, found $C_{13}H_{18}N$ 188.1435.

3.2 General Procedure for the Synthesis of Aryl-Substituted amines



Step 1: To a oven-dried three-necked flask equipped with stirring bar, Mg chips (2.9 g, 120.0 mmol, 1.2 equiv) was added. Then the flask was purged with N_2 for three times and then 40 mL of THF was injected by syringe. 4-bromobut-1-ene (13.5 g, 100.0 mmol) in THF (60 mL) was slowly added to the reaction. After complete addition, the reaction was heated at reflux temperature for another 0.5 h. Then the solution was cooled down to 0 °C. A THF solution (20 mL) of butanone (7.2 g, 100.0 mmol, 1.0 equiv) was added dropwisely. The mixture was stirred at room temperature overnight. Then it was

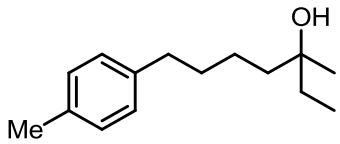
quenched with H_2O and filter through a celite pad. THF was removed under reduced pressure. The residue was dissolved into 100 mL of CH_2Cl_2 and washed by H_2O and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude product. Two batches of reactions were run parallel and then combined. The crude product was purified by distillation (b.p. 56-60 °C, 7 mmHg) and followed by column chromatography to afford 3-methylhept-6-en-3-ol (7.0 g, 54.7 mmol).



3-methylhept-6-en-3-ol

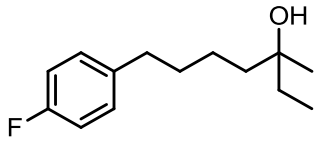
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.05 (dd, *J* = 17.1, 1.6 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 2.12 (dd, *J* = 16.3, 6.9 Hz, 2H), 1.58 – 1.47 (m, 4H), 1.24 (s, 1H), 1.16 (s, 3H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.12, 114.36, 72.85, 40.25, 34.36, 28.35, 26.31, 8.23. (Known compound: A. P. Pulis, D. J. Blair, E. Torres, V. K. Aggarwal, *J. Am. Chem. Soc.* **2013**, *135*, 16054-16057)

Step 2: Following a previously reported procedure[2], to the solution of 3-methylhept-6-en-3-ol (640 mg, 5.0 mmol, in 2.5 mL THF) was added a solution of 9-BBN (0.5 M in THF, 11.0 mmol, 22 mL) at 0 °C. The mixture was warmed up slowly to room temperature and then stirred for 4 h to give a solution of alkyl-9-BBN. To the above solution were added $PdCl_2$(dppf) (109.8 mg, 0.15 mmol, 3.0 mol%), ArI (5.0 mmol, 1.0 equiv), additional THF (10 mL), and aqueous NaOH (15.0 mmol, 5 mL of 3.0 M solution) at room temperature. The mixture was refluxed overnight. After the reaction was completed, the reaction was diluted with hexane (10 mL) and H_2O_2 (30 wt%, 2 mL) at 0 °C. The product was extracted with EtOAc (5 mL×3), washed with brine (10 mL), and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (eluent: PE : EA = 50 : 1) to give desired tertiary alcohol.



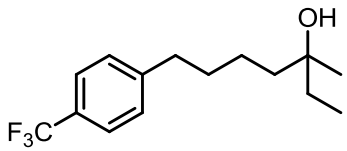
3-methyl-7-(p-tolyl)heptan-3-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.01 (m, 4H), 2.62 – 2.54 (m, 2H), 2.31 (s, 3H), 1.65 – 1.56 (m, 2H), 1.51 – 1.43 (m, 4H), 1.41 – 1.34 (m, 2H), 1.26 (s, 1H), 1.13 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.58, 135.05, 128.97, 128.26, 72.92, 41.20, 35.51, 34.25, 32.25, 26.39, 23.58, 21.00, 8.21. HRMS (ESI): m/z: calculated for $[M + Na]^+$ $C_{15}H_{24}NaO$: 243.17194, found 243.17173.



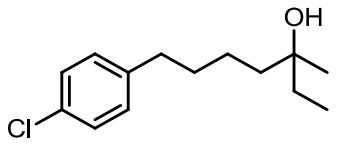
7-(4-fluorophenyl)-3-methylheptan-3-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 2H), 7.00 – 6.91 (m, 2H), 2.63 – 2.55 (m, 2H), 1.65 – 1.53 (m, 2H), 1.50 – 1.42 (m, 4H), 1.41 – 1.33 (m, 2H), 1.24 (s, 1H), 1.13 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -118.11. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.17 (d, *J* = 242.9 Hz), 138.20 (d, *J* = 3.1 Hz), 129.64 (d, *J* = 7.6 Hz), 114.97 (d, *J* = 21.1 Hz), 72.88, 41.13, 35.11, 34.27, 32.21, 26.39, 23.44, 8.21. HRMS (ESI): m/z: calculated for $[M + Na]^+$ $C_{14}H_{21}FNaO$: 247.14686, found 247.14671.



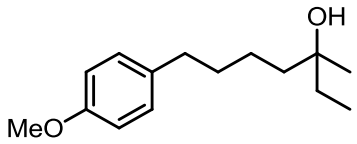
3-methyl-7-(4-(trifluoromethyl)phenyl)heptan-3-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.71 – 2.64 (m, 2H), 1.68 – 1.60 (m, 2H), 1.50 – 1.44 (m, 4H), 1.43 – 1.35 (m, 2H), 1.14 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.26. ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.75, 128.66, 128.06 (q, *J* = 32.3 Hz), 125.21 (q, *J* = 3.7 Hz), 124.41 (q, *J* = 271.7 Hz), 72.84, 41.08, 35.79, 34.31, 31.80, 26.38, 23.48, 8.20. HRMS (ESI): m/z: calculated for $[M + Na]^+$ $C_{15}H_{21}F_3NaO$: 297.14367, found 297.14332.



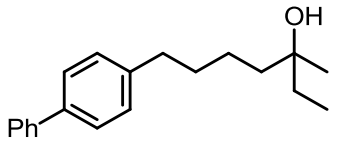
7-(4-chlorophenyl)-3-methylheptan-3-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 2.62 – 2.56 (m, 2H), 1.63 – 1.56 (m, 2H), 1.48 – 1.42 (m, 4H), 1.40 – 1.33 (m, 2H), 1.25 (s, 1H), 1.13 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.04, 131.34, 129.72, 128.36, 72.87, 41.11, 35.28, 34.29, 31.98, 26.39, 23.44, 8.21. HRMS (ESI): m/z: calculated for $[M + NH_4]^+$ $C_{14}H_{25}ClNO$: 258.16192, found 258.16204.



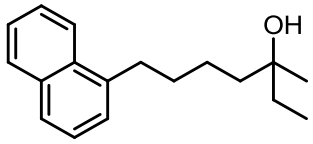
7-(4-methoxyphenyl)-3-methylheptan-3-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.60 – 2.52 (m, 2H), 1.63 – 1.55 (m, 2H), 1.50 – 1.42 (m, 4H), 1.40 – 1.32 (m, 2H), 1.24 (s, 1H), 1.13 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.65, 134.77, 129.24, 113.71, 72.90, 55.26, 41.19, 35.02, 34.25, 32.36, 26.40, 23.51, 8.22. HRMS (ESI): m/z: calculated for $[M + Na]^+$ $C_{15}H_{24}NaO_2$: 259.16685, found 259.16657.



7-([1,1'-biphenyl]-4-yl)-3-methylheptan-3-ol

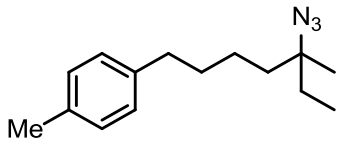
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.52 – 1.33 (m, 7H), 1.13 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.85, 141.19, 138.67, 128.86, 128.77, 127.08, 127.04, 72.94, 41.24, 35.65, 34.32, 32.15, 26.45, 23.68, 8.30. HRMS (ESI): m/z: calculated for $[M + Na]^+$ $C_{20}H_{26}NaO$: 305.18759, found 305.18744.



3-methyl-7-(naphthalen-1-yl)heptan-3-ol

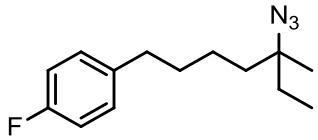
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.75 (m, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.37 (m, 2H), 7.37 – 7.29 (m, 1H), 7.26 (d, *J* = 6.8 Hz, 1H), 3.11 – 2.95 (m, 2H), 1.71 (dd, *J* = 9.8, 4.7 Hz, 2H), 1.53 – 1.36 (m, 7H), 1.09 (s, 3H), 0.85 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.86, 134.04, 132.01, 128.89, 126.61, 125.97, 125.79, 125.68, 125.51, 123.97, 72.92, 41.29, 34.39, 33.26, 31.54, 26.45, 24.18, 8.39. HRMS (ESI): m/z: calculated for $[M + Na]^+$ $C_{18}H_{24}NaO$: 279.17194, found 279.17177.

Step 3: A mixture of alcohol (3.8 mmol, 1.0 equiv) and trimethylsilyl azide (520.7 mg, 4.5 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) were cooled to 0 °C, and BF_3•Et_2O (641.5 mg, 4.5 mmol, 1.2 equiv) was added to the mixture. The reaction mixture was allowed to reach room temperature and stirred for 12 h. The mixture was diluted with saturated $NaHCO_3$ (10 mL), and the organic layer was washed with brine, and dried over anhydrous Na_2SO_4. The desired product was isolated and carried in to the next synthetic transformation without purification.



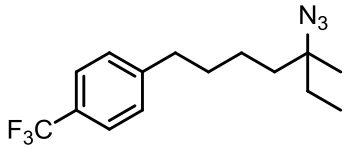
1-(5-azido-5-methylheptyl)-4-methylbenzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.04 (m, 4H), 2.65 – 2.55 (m, 2H), 2.34 (s, 3H), 1.67 – 1.58 (m, 2H), 1.58 – 1.49 (m, 4H), 1.44 – 1.35 (m, 2H), 1.22 (s, 3H), 0.93 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.36, 135.13, 129.01, 128.25, 64.54, 38.79, 35.41, 32.00, 31.97, 23.62, 22.82, 21.02, 8.37. IR (cm^{-1}): 2090, 1256, 807. GC-MS (EI): m/z: (188.3, $[M\text{-}N_3\text{-}Me]^+$, 100%), (203.3, $[M\text{-}N_3]^+$, 20%), (202.3, $[M\text{-}N_3\text{-}H]^+$, 27%).



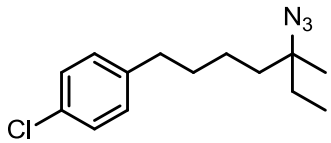
1-(5-azido-5-methylheptyl)-4-fluorobenzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 8.4, 5.6 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 2.63 – 2.55 (m, 2H), 1.64 – 1.55 (m, 2H), 1.55 – 1.46 (m, 4H), 1.41 – 1.32 (m, 2H), 1.20 (s, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -117.98. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.21 (d, *J* = 243.3 Hz), 137.98 (d, *J* = 3.1 Hz), 129.64 (d, *J* = 7.6 Hz), 115.02 (d, *J* = 21.1 Hz). 64.49, 38.73, 35.01, 31.99, 31.91, 23.47, 22.80, 8.36. IR (cm^{-1}): 2092, 824. GC-MS (EI): m/z: (192.3, $[M\text{-}N_3\text{-}Me]^+$, 100%), (206.3, $[M\text{-}N_3\text{-}H]^+$, 37%), (207.3, $[M\text{-}N_3]^+$, 21%).



1-(5-azido-5-methylheptyl)-4-(trifluoromethyl)benzene

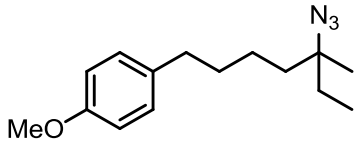
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.73 – 2.62 (m, 2H), 1.64 (dt, *J* = 15.4, 7.5 Hz, 2H), 1.56 – 1.47 (m, 4H), 1.44 – 1.34 (m, 2H), 1.20 (s, 3H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.29. ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.49, 128.64, 128.16 (q, *J* = 32.3 Hz), 125.25 (q, *J* = 3.8 Hz), 124.44 (q, *J* = 261.8 Hz), 64.42, 38.72, 35.68, 32.02, 31.48, 23.53, 22.78, 8.34. IR (cm^{-1}): 2091, 1162, 1122, 1067. GC-MS (EI): m/z: (242.2, $[M\text{-}N_3\text{-}Me]^+$, 100%), (256.3, $[M\text{-}N_3\text{-}H]^+$, 69%), (257.3, $[M\text{-}N_3]^+$, 29%).



1-(5-azido-5-methylheptyl)-4-chlorobenzene

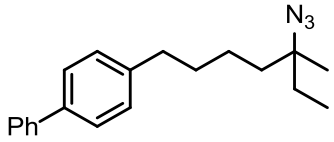
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.63 – 2.53 (m, 2H), 1.64 – 1.46 (m, 6H), 1.40 – 1.30 (m, 2H), 1.19 (s, 3H), 0.90 (t, *J* = 7.5 Hz,

3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.82, 131.43, 129.71, 128.41, 64.45, 38.73, 35.17, 32.01, 31.68, 23.48, 22.79, 8.36. IR (cm^{-1}): 2090, 1492, 1258, 1091. GC-MS (EI): m/z: (208.2, $[M\text{-}N_3\text{-}Me]^+$, 100%), (222.2, $[M\text{-}N_3\text{-}H]^+$, 39%).



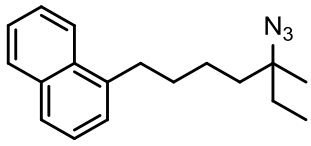
1-(5-azido-5-methylheptyl)-4-methoxybenzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.61 – 2.51 (m, 2H), 1.62 – 1.47 (m, 6H), 1.41 – 1.32 (m, 2H), 1.20 (s, 3H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.70, 134.53, 129.23, 113.73, 64.55, 55.27, 38.76, 34.91, 32.06, 31.98, 23.53, 22.82, 8.37. HRMS (ESI): m/z: calculated for $[M + H]^+$ $C_{15}H_{24}N_3O$: 262.19139, found 262.19179.



4-(5-azido-5-methylheptyl)-1,1'-biphenyl

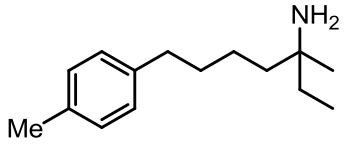
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 2.72 – 2.61 (m, 2H), 1.70 – 1.61 (m, 2H), 1.58 – 1.49 (m, 4H), 1.46 – 1.36 (m, 2H), 1.21 (s, 3H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.57, 141.13, 138.72, 128.79, 128.72, 127.07, 127.00, 64.53, 38.79, 35.48, 32.01, 31.79, 23.65, 22.83, 8.37. IR (cm^{-1}): 2090, 761, 697. GC-MS (EI): m/z: (250.2, $[M\text{-}N_3\text{-}Me]^+$, 100%), (264.3, $[M\text{-}N_3\text{-}H]^+$, 14%), (279.3, $[M\text{-}N_2]^+$, 73%).



1-(5-azido-5-methylheptyl)naphthalene

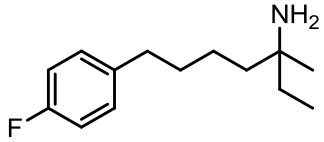
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.43 – 7.36 (m, 1H), 7.33 (d, *J* = 6.8 Hz, 1H), 3.15 – 3.03 (m, 2H), 1.82 – 1.71 (m, 2H), 1.59 – 1.48 (m, 6H), 1.23 (s, 3H), 0.93 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.51, 133.92, 131.84, 128.79, 126.57, 125.87, 125.72, 125.55, 125.42, 123.79, 64.53, 38.84, 33.05, 32.06, 31.12, 24.12, 22.81, 8.39. HRMS (m/z): calculated for $[M + Na]^+$ $C_{18}H_{23}N_3Na$: 304.17842, found 304.17804.

Step 4: The solution of azide in Et_2O (10 mL) was cooled to 0 °C, and the $LiAlH_4$ (170 mg, 1.2 equiv) was slowly added to the mixture. The reaction mixture was warmed up slowly to room temperature and stirred for 4 h. After the reaction was completed, the reaction was quenched with Na_2SO_4•$10H_2O$. The organic layer was filtered and concentrated. The crude product was purified by column chromatography (eluent : CH_2Cl_2 : MeOH = 50 : 1) to give the compound **3f** (333.0 mg, 1.4 mmol).



3-methyl-7-p-tolylheptan-3-amine (3b)

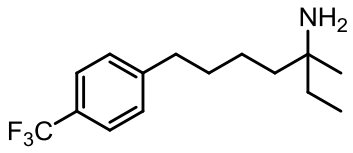
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.01 (m, 4H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.60 (m, 2H), 1.40-1.23 (m, 8H), 1.00 (s, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 135.0, 128.9, 128.2, 51.4, 42.1, 35.5, 35.0, 32.3, 27.5, 23.6, 20.9, 8.2. HRMS (ESI): m/z: calculated for $C_{15}H_{26}N$ $[M + H]^+$ 220.2060, found 220.2057.



7-(4-fluorophenyl)-3-methylheptan-3-amine (3c)

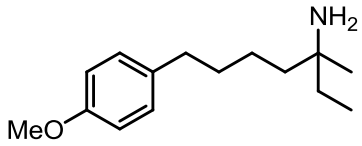
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 1.63-1.52 (m, 4H), 1.40-1.29 (m, 6H), 1.01 (s, 3H), 0.85 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -118.14. ^{13}C NMR (100 MHz,

$CDCl_3$) δ 161.1 (d, *J* = 242.9 Hz), 138.2 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 7.7 Hz), 114.9 (d, *J* = 21.0 Hz), 51.6, 41.8, 35.0, 34.8, 32.2, 27.3, 23.4, 8.2. HRMS (ESI): m/z: calculated for $C_{14}H_{23}FN$ $[M + H]^+$ 224.1809, found 224.1810.



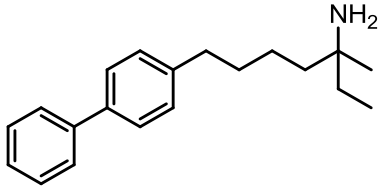
3-methyl-7-(4-(trifluoromethyl)phenyl)heptan-3-amine (3d)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.73-2.61 (m, 2H), 1.71 (br, 2H), 1.67-1.59 (m, 2H), 1.44-1.30 (m, 6H), 1.03 (s, 3H), 0.86 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.24. ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 128.6, 128.0 (q, *J* = 32.2 Hz), 125.1 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.7 Hz), 51.6, 41.8, 35.7, 34.9, 31.8, 27.4, 23.5, 8.2. HRMS (ESI): m/z: calculated for $C_{15}H_{23}F_3N$ $[M + H]^+$ 274.1777, found 274.1783.



7-(4-methoxyphenyl)-3-methylheptan-3-amine (3f)

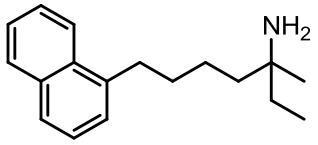
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 2.56 (t, *J* = 7.5 Hz, 2H), 1.62-1.53 (m, 2H), 1.51 (br, 2H), 1.39-1.28 (m, 6H), 1.00 (s, 3H), 0.85 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 134.6, 129.0, 113.5, 55.0, 51.4, 41.8, 34.8, 34.8, 32.3, 27.2, 23.4, 8.1. HRMS (ESI): m/z: calculated for $C_{15}H_{26}NO$ $[M + H]^+$ 236.2009, found 236.2011.



7-(biphenyl-4-yl)-3-methylheptan-3-amine (3h)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 7.8 Hz,

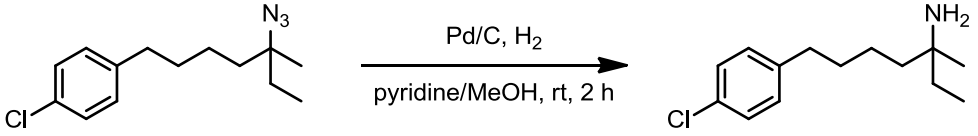
2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 2H), 2.71-2.62 (t, *J* = 7.6 Hz, 2H), 2.30 (br, 2H), 1.70-1.61 (m, 2H), 1.48-1.33 (m, 6H), 1.06 (s, 3H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 141.1, 138.5, 128.8, 128.7, 127.0 (2C), 126.9, 51.4, 42.1, 35.6, 35.1, 32.2, 27.6, 23.7, 8.3. HRMS (ESI): m/z: calculated for $C_{20}H_{28}N$ $[M + H]^+$ 282.2216, found 282.2219.



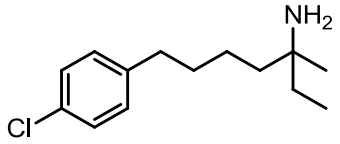
3-methyl-7-(naphthalen-1-yl)heptan-3-amine (3i)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.54-7.42 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 6.9 Hz, 1H), 3.13-3.05 (m, 2H), 1.80-1.68 (m, 2H), 1.48-1.36 (m, 6H), 1.21-1.26 (m, 2H), 1.02 (s, 3H), 0.86 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 133.8, 131.8, 128.7, 126.4, 125.8, 125.6, 125.5, 125.3, 123.8, 51.4, 42.1, 35.1, 33.1, 31.5, 27.5, 24.2, 8.3. HRMS (ESI): m/z: calculated for $C_{18}H_{26}N$ $[M + H]^+$ 256.2060, found 256.2061.

The preparation for compound **3e** followed the general steps except the reduction of the azide. The procedure for this reaction was described as follows:



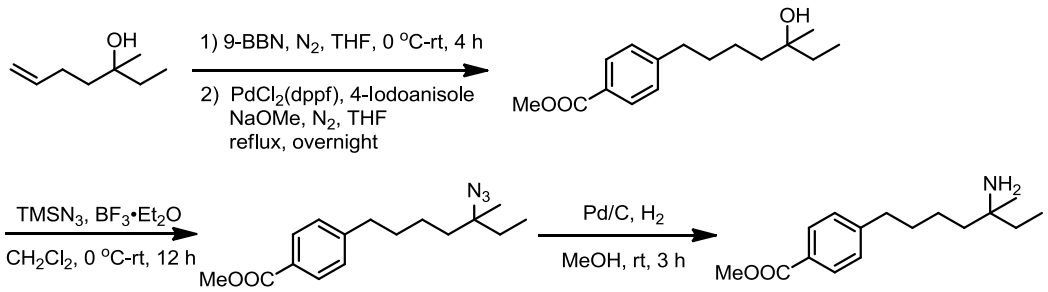
The azide (700.0 mg, 2.6 mmol) and 10% Pd/C (35 mg) were added into the mixed solvents of pyridine/MeOH (1 : 5, 15 mL). The mixture was stirred at room temperature under 1.0 atm of H_2 for 2 h. The reaction mixture was filtered through a short pad of celite pad, and then the celite pad was washed by MeOH (20 mL). The solvents were removed *in vacuo* to give the crude product, which was purified by column chromatography to afford Compound **3e** (373.7 mg, 1.6 mmol).



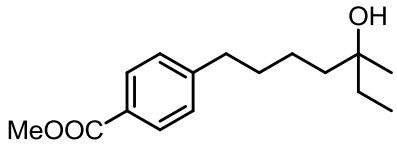
7-(4-chlorophenyl)-3-methylheptan-3-amine (3e)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.90 (br, 2H), 1.62-1.55 (m, 2H), 1.39-1.31 (m, 6H), 1.03 (s, 3H), 0.86 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 131.3, 129.7, 128.3, 51.9, 41.6, 35.2, 34.6, 32.0, 27.1, 23.4, 8.2. HRMS (ESI): m/z: calculated for $C_{14}H_{23}ClN$ $[M + H]^+$ 240.1514, found 240.1520.

The procedure for preparation of compound **3g** was the same as general procedure for cross-coupling except the powered NaOMe (1.5 equiv) as the base.



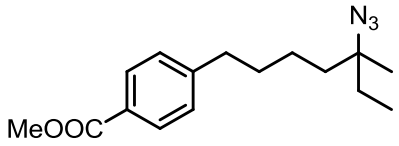
Following a previously reported procedure[2], to the solution of 3-methylhept-6-en-3-ol (640 mg, 5.0 mmol, in 2.5 mL THF) was added a solution of 9-BBN (0.5 M in THF, 11.0 mmol, 22 mL) at 0 °C. The mixture was warmed up slowly to room temperature and then stirred for 4 h to give a solution of alkyl-9-BBN. To the above solution were added $PdCl_2$(dppf) (109.8 mg, 0.15 mmol, 3.0 mol%), Methyl 4-iodobenzoate (1.31 g, 5.0 mmol, 1.0 equiv), additional THF (10 mL), and powered NaOMe (0.81 g, 15.0 mmol, 3.0 equiv) at room temperature. The mixture was refluxed overnight. After the reaction was completed, the reaction was diluted with hexane (10 mL) and H_2O_2 (30 wt%, 2 mL) at 0 °C. The product was extracted with EtOAc (5 mL×3), washed with brine (10 mL), and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography to give desired tertiary alcohol.



methyl 4-(5-hydroxy-5-methylheptyl)benzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 3.87 (s, 3H), 2.70 – 2.59 (m, 2H), 1.79 (s, 1H), 1.62 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.51 – 1.42 (m, 4H), 1.42 – 1.33 (m, 2H), 1.12 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.12, 148.23, 129.63, 128.36, 127.58, 72.59, 51.89, 41.05, 35.93, 34.19, 31.69, 26.27, 23.48, 8.21. HRMS (ESI): m/z: calculated for $[M + Na]^+$ $C_{16}H_{24}NaO_3$: 287.16177, found 287.16144.

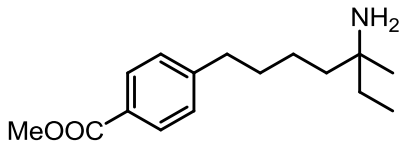
The azidation of tertiary aliphatic alcohols was prepared according to the reported procedure[3]. To a reaction tube containing the alcohol (2.1 g, 8.0 mmol) in nitromethane (4 mL) was added $TMSN_3$ (2.8 g, 24 mmol, 3.0 equiv), followed by $B(C_6H_5)_3$ (0.2 g, 0.4 mmol, 5.0 mol %). The mixture was stirred for 1 h at room temperature. After the reaction was completed, the volatiles of the reaction mixture were removed *in vacuo*. The crude product was purified by column chromatography (eluent: PE : EA = 50 : 1) to give the azide (1.4 g, 6.3 mmol).



methyl 4-(5-azido-5-methylheptyl)benzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.74 – 2.61 (m, 2H), 1.68 – 1.59 (m, 2H), 1.57 – 1.47 (m, 4H), 1.42 – 1.33 (m, 2H), 1.20 (s, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.18, 147.95, 129.71, 128.41, 127.79, 64.45, 51.99, 38.71, 35.87, 31.99, 31.41, 23.53, 22.80, 8.36. HRMS (ESI): m/z: calculated for $[M + H]^+$ $C_{16}H_{24}N_3O_2$: 290.18630, found 290.18660.

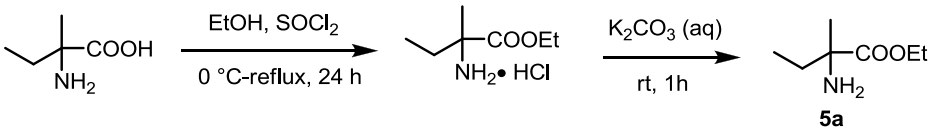
A mixture of alkyl azide (1.4 g, 6.3 mmol) and 10% Pd/C (100 mg) in MeOH (10 mL) was stirred under 1.0 atm of H_2 at room temperature for 3 h. Then, the solution was filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: CH_2Cl_2: MeOH = 50 : 1) to give Compound **3g** (780 mg, 3.0 mmol).



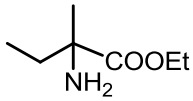
methyl 4-(5-amino-5-methylheptyl)benzoate (3g)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 3.90 (s, 3H), 2.67 (t, *J* = 7.7 Hz, 2H), 1.67-1.58 (m, 2H), 1.39-1.29 (m, 6H), 1.24 (br, 2H), 1.00 (s, 3H), 0.85 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 148.2, 129.6, 128.3, 127.6, 51.9, 51.3, 42.0, 35.9, 35.0, 31.8, 27.4, 23.5, 8.2. HRMS (ESI): m/z: calculated for $C_{16}H_{26}NO_2$ $[M + H]^+$ 264.1958, found 264.1962.

3.3 Procedure for the Synthesis of Compound 5a



2-amino-2-methylbutanoic acid (1.8 g, 15 mmol) was suspended in EtOH (30 mL) at 0 °C. $SOCl_2$ (2.1 g, 18.0 mmol, 1.2 equiv) was added into the mixture dropwisely. Then the reaction was heated to reflux for 24 h. The mixture was cooled down to room temperature and concentrated *in vacuo* to afford the titled hydrochloride salt. The salt was stirred at saturated K_2CO_3 (aq) (20 mL) at room temperature for 1 h. The aqueous phase was extracted with Et_2O (3 × 20 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: CH_2Cl_2: MeOH = 50 : 1 to 20 : 1) to get compound **5a** (785.2 mg, 5.4 mmol).

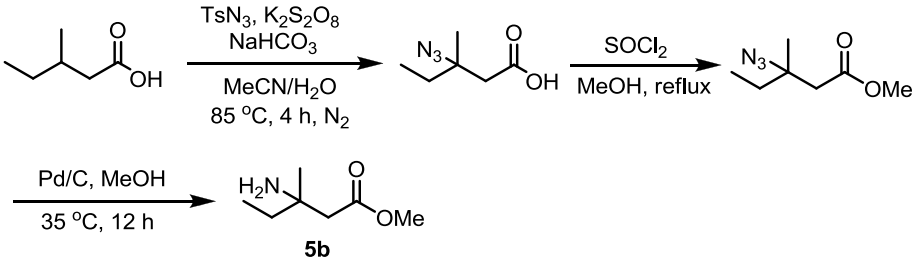


ethyl 2-amino-2-methylbutanoate (5a)

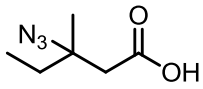
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 (q, *J* = 6.9 Hz, 2H), 1.80-1.71 (m, 1H), 1.63-1.56 (m, 3H), 1.31 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 60.8, 57.9, 33.8, 25.9, 14.2, 8.4. HRMS (EI): m/z: calculated for $C_7H_{16}NO_2$ $[M + H]^+$ 146.1181, found 146.1177.

3.4 Procedure for the Synthesis of Compound 5b



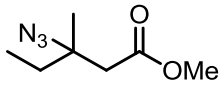
Step 1: Following a previously reported method of C—H azidation,[4] a 100 mL Schlenk tube was charged with 4-methylbenzenesulfonyl azide (3.5 g, 18.0 mmol, 1.5 equiv), $NaHCO_3$ (756.0 mg, 9.0 mmol, 1.0 equiv) and $K_2S_2O_8$ (9.7 g, 36.0 mmol, 3.0 equiv). The Schlenk tube was evacuated and filled with N_2 thrice, followed by addition of 57 mL of solvent ($MeCN/H_2O$ = 3 : 2) and 3-methylpentanoic acid (1.4 g, 12.0 mmol, 1.0 equiv). The system was stirred for 4 h at 85 °C. After cooling to room temperature, the reaction mixture was evaporated the MeCN under reduced pressure, and then diluted with EtOAc (50 mL) and H_2O (50 mL), then extracted with EtOAc (3×50 mL). The combined organic layer was dried over Na_2SO_4. The filtrate was concentrated *in vacuo* and the residue was used for next step without purification (The reaction was run for two times, and then treatment together).



3-azido-3-methylpentanoic acid

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 2.54 (d, *J* = 1.6 Hz, 2H), 1.72 (q, *J* = 7.4 Hz, 2H), 1.42 (s, 3H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.67, 62.23, 43.22, 32.45, 22.96, 8.32. IR (cm^{-1}): 2109, 1710, 1255. GC-MS (EI): m/z: (115.1, $[M-N_3]^+$, 100%), (128.1, $[M-Et]^+$, 32%).

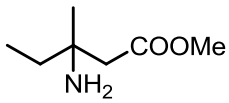
Step 2: Thionyl chloride (2 mL) was added to an ice-cooled stirred solution of 3-azido-3-methylpentanoic acid mixture in MeOH (80 mL) over a period of 10 min. The mixture was allowed to warm to reflux and was stirred for 12 h. The solvent was removed and the residual brown oil was distilled under reduced pressure to get the desired product as colorless liquid (613.0 mg, 3.6 mmol, b.p. 65 ^{o}C, 4 mmHg).



methyl 3-azido-3-methylpentanoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.47 (d, *J* = 2.4 Hz, 2H), 1.65 (q, *J* = 7.4 Hz, 2H), 1.35 (s, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.46, 62.36, 51.67, 43.21, 32.45, 22.91, 8.25. IR (cm^{-1}): 2107, 1740, 1262, 1213. GC-MS (EI): m/z: (129.2, $[M-N_3]^+$, 100%), (142.1, $[M-Et]^+$, 19%).

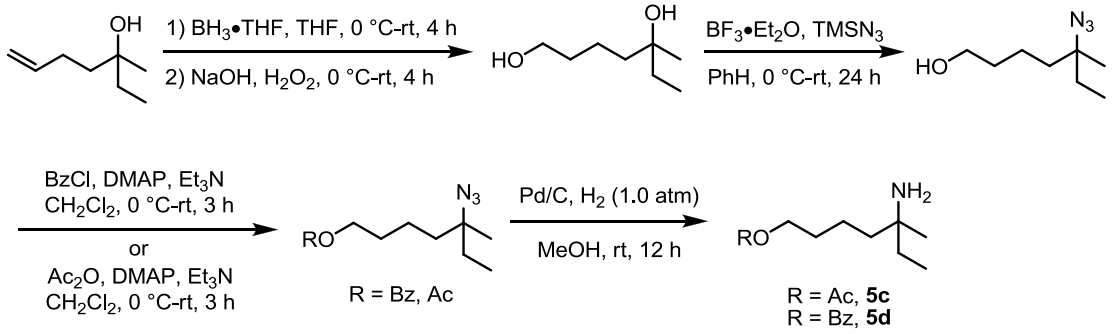
Step 3: To a solution of 5% Pd/C (100 mg) in MeOH (30 mL) was added the solution of methyl 3-azido-3-methylpentanoate (613 mg, 3.6 mmol) in MeOH (10 mL) at room temperature under 1.0 atm of H_2. After being stirred for 12 h at 35 ^{o}C, the reaction mixture was filtered through a short pad of celite and the celite was washed for 20 mL of MeOH. The reaction mixture was concentrated under reduced pressure. The crude residue was purified by flash column chromatography (eluent: CH_2Cl_2 : MeOH = 100 : 1 to 20 : 1) to get the desired product as colorless liquid (210.0 mg, 1.5 mmol).



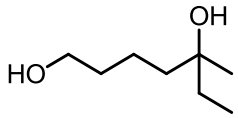
methyl 3-amino-3-methylpentanoate (5b)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (br, 2H), 3.70 (s, 3H), 2.53-2.49 (m, 2H), 1.58 (q, *J* = 7.5 Hz, 2H), 1.22 (s, 3H), 0.93 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 51.6, 51.4, 45.6, 35.4, 27.0, 8.3. HRMS (ESI): m/z: calculated for $C_7H_{16}NO_2$ $[M + H]^+$ 146.1176, found 146.1169.

3.5 Procedure for the Synthesis of Compound 5c and 5d



Step 1: To a solution of 3-methylhept-6-en-3-ol (3.9 g, 30.7 mmol) in 10 mL of dry THF under N_2 atmosphere, BH_3•THF complex (1.0 mol/L in THF, 37 mL, 1.2 equiv) was added slowly at 0 °C during 1 h. Then the mixture was warmed up to room temperature and stirred for another 3 h. The reaction was quenched with 5 M NaOH (aq) (36 mL) at 0 °C, and H_2O_2 (30 wt%, 30 mL) was added to the above solution. The mixture was stirred at room temperature for 4 h. Then the reaction was quenched with saturated Na_2SO_3 (aq). The aqueous phase was extracted by CH_2Cl_2 (4×50 mL). The organic phase was washed by saturated Na_2SO_3 (aq), H_2O_2 and brine, and then dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the residue was purified by column chromatography (eluent: PE : EtOAc = 1 : 1) to afford 5-methylheptane-1,5-diol (3.4 g, 23.0 mmol).

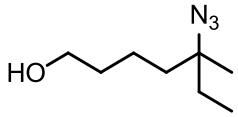


5-methylheptane-1,5-diol

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (t, *J* = 6.2 Hz, 2H), 1.66 – 1.33 (m, 10H), 1.15 (s, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.94, 62.74, 40.82, 34.31, 33.16, 26.36, 20.01, 8.26. HRMS (ESI): m/z: calculated for $[M + Na]^+$ $C_8H_{18}NaO_2$: 169.11990, found 169.11995.

Step 2: 5-methylheptane-1,5-diol (3.4 g, 23.0 mmol) and $TMSN_3$ (3.2 g, 27.6 mmol, 1.2 equiv) were dissolved into 30 mL of benzene and the solution was cooled down to 0 °C.

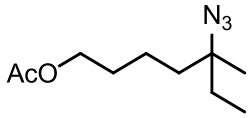
BF_3•Et_2O (3.9 g, 27.6 mmol, 1.2 equiv) was added dropwisely to the above solution. The mixture was warmed up to room temperature and stirred for 24 h. The reaction was quenched with the addition of saturated $NaHCO_3$ (aq). The mixture was stirred vigorously for 15 min. The mixture was diluted by 100 mL of CH_2Cl_2. The separated organic layer was washed by H_2O and brine, and then concentrated under reduced pressure. The residue was purified by column chromatography (eluent: PE : EtOAc = 10 : 1 to 5 : 1) to obtain the 5-azido-5-methylheptanol (2.0 g, 12 mmol). These two steps of reactions were conducted in multiple runs to accumulate enough amount of intermediate for substrate synthesis.



5-azido-5-methylheptan-1-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (t, *J* = 6.4 Hz, 2H), 1.62 – 1.49 (m, 7H), 1.46 – 1.38 (m, 2H), 1.22 (s, 3H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.50, 62.75, 38.65, 32.97, 31.98, 22.79, 20.22, 8.38. HRMS (ESI): m/z: calculated for $[M + H]^+$ $C_8H_{18}NO_3$: 172.14444, found 172.14450.

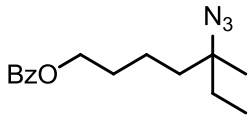
Step 3: To a solution of 5-azido-5-methylheptanol (1.0 g, 6.0 mmol), NEt_3 (910.7 mg, 9.0 mmol, 1.5 equiv) and 4-*N*,*N*-dimethylaminopyridine (146.6 mg, 1.2 mmol, 0.2 equiv) in 10 mL of CH_2Cl_2 at 0 °C, Acyl Chloride (7.2 mmol, 1.2 equiv) was added slowly. The mixture was warmed up to room temperature and stirred for 3 h. The reaction was diluted to 50 mL and quenched with H_2O. The organic layer was washed by H_2O and brine, dried over anhydrous Na_2SO_4. The solvent was removed and the resulting residue was purified by column chromatography (eluent: PE : EtOAc = 100 : 1) to obtain desired products.



5-azido-5-methylheptyl acetate

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (t, *J* = 6.6 Hz, 2H), 2.06 (s, 3H), 1.68 – 1.60 (m, 2H), 1.58 – 1.48 (m, 4H), 1.45 – 1.34 (m, 2H), 1.22 (s, 3H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 171.23, 64.36, 64.25, 38.50, 32.00, 28.88, 22.75, 21.03, 20.41, 8.36. HRMS (ESI): m/z: calculated for $[M + H]^+$ $C_{10}H_{20}N_3O_2$: 214.15500, found 214.15490.

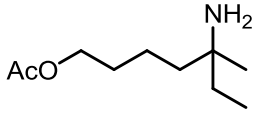


5-azido-5-methylheptyl benzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.34 (t, *J* = 6.6 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.62 – 1.44 (m, 6H), 1.23 (s, 3H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.63, 132.89, 130.40, 129.55, 128.37, 64.70, 64.34, 38.55, 32.02, 29.04, 22.75, 20.51, 8.35. HRMS (ESI): m/z: calculated for $[M + H]^+$ $C_{15}H_{22}N_3O_2$: 276.17065, found 276.17061.

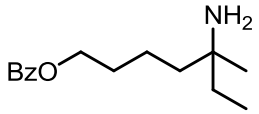
Step 4: To a solution of 10% Pd/C (77 mg) in MeOH (5 mL) was added the solution of 5-azido-5-methylheptyl benzoate (1.5 g, 5.6 mmol) in MeOH (5 mL) at room temperature under 1.0 atm of H_2. After being stirred for 12 h at the same temperature, the reaction mixture was filtered through a short pad of celite and the celite pad was washed for 20 mL of MeOH. The reaction mixture was concentrated under reduced pressure. The crude residue was purified by column chromatography (eluent: CH_2Cl_2 : MeOH = 50 : 1 to 20 : 1) to get the desired product **5d** as light yellow oil (779.5 mg, 3.1 mmol).

By using Ac_2O to protect 5-azido-5-methylheptanol, Compound **5c** could be obtained though the same synthetic route.



5-amino-5-methylheptyl acetate (5c)

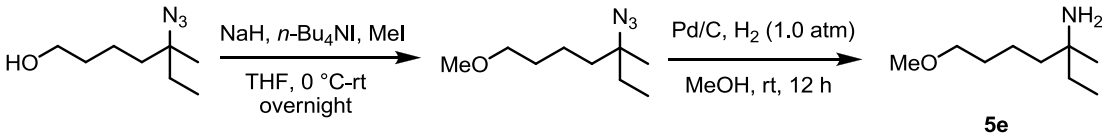
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 (t, *J* = 6.7 Hz, 2H), 2.05 (s, 3H), 1.64-1.61 (m, 2H), 1.40-1.32 (m, 6H), 1.27 (br, 2H), 1.02 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 64.4, 51.4, 41.8, 35.0, 29.2, 27.4, 21.0, 20.4, 8.2. HRMS (EI): m/z: calculated for $C_{10}H_{22}NO_2$ $[M + H]^+$ 188.1650, found 188.1646.



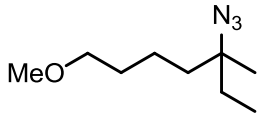
5-amino-5-methylheptyl benzoate (5d)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.03 (m, 2H), 7.58-7.53 (m, 1H), 7.46-7.42 (m, 2H), 4.34 (t, *J* = 6.6 Hz, 2H), 1.89 (br, 2H), 1.82-1.75 (m, 2H), 1.50-1.35 (m, 6H), 1.06 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 132.8, 130.4, 129.5, 128.3, 64.9, 51.8, 41.5, 34.7, 29.4, 27.2, 20.4, 8.2. HRMS (ESI): m/z: calculated for $C_{15}H_{24}NO_2$ $[M + H]^+$ 250.1802, found 250.1803.

3.6 Procedure for the Synthesis of Compound 5e



Step 1: To a stirring solution of 5-azido-5-methylheptanol (864.9 mg, 5.0 mol) in THF (5 mL) was added tetrabutylammonium iodide (184.7 mg, 0.5 mmol, 0.1 equiv) followed by methyl iodide (1.1g, 7.5 mmol, 1.5 equiv) and the reaction was cooled to 0 ℃. Sodium hydride (60% in mineral oil, 300.0 mg, 7.5 mmol, 1.5 equiv) was added in small portions and the reaction was stirred overnight with warming up to room temperature. The reaction was quenched with H_2O, filtered through a short celite pad, and washed with Et_2O. The organic solvent was removed under reduced pressure to give an oily residue, which was purified by column chromatography to afford 5-azido-1-methoxy-5-methylheptane (862.4 mg, 4.7 mmol).

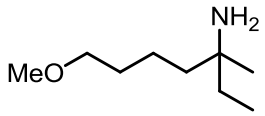


5-azido-1-methoxy-5-methylheptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (t, *J* = 6.4 Hz, 2H), 3.34 (s, 3H), 1.61 – 1.48 (m, 6H), 1.44 – 1.34 (m, 2H), 1.22 (s, 3H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.61, 64.52, 58.65, 38.72, 31.94, 29.97, 22.80, 20.67, 8.36. IR (cm^{-1}): 2092. GC-MS (EI):

m/z: (128.2, $[M\text{-}N_3\text{-}Me]^+$, 39%), (143.2, $[M\text{-}N_3]^+$, 100%).

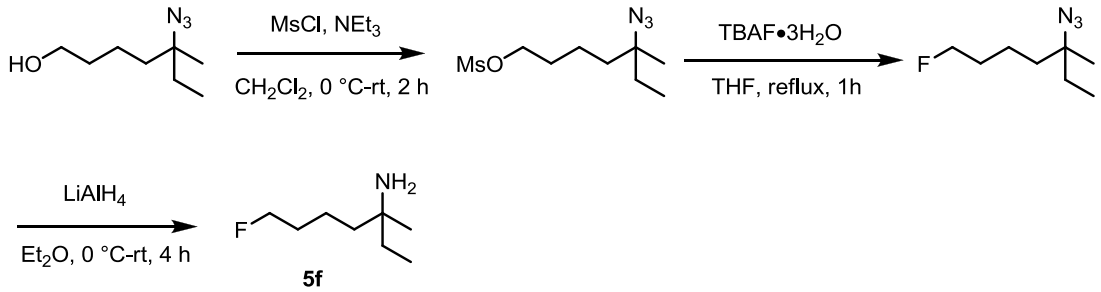
Step 2: The hydrogenation was carried out *via* the procedure described above to give the Compound **5e** (330.3 mg, 2.1 mmol).



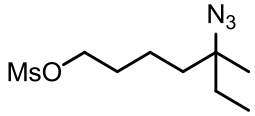
7-methoxy-3-methylheptan-3-amine (5e)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39 (t, *J* = 7.5 Hz, 2H), 3.33 (s, 3H), 1.88 (br, 2H), 1.59-1.55 (m, 2H), 1.43-1.35 (m, 6H), 1.04 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.7, 58.5, 51.8, 41.7, 34.6, 30.2, 27.2, 20.6, 8.2. HRMS (ESI): m/z: calculated for $C_9H_{22}NO$ $[M + H]^+$ 160.1701, found 160.1697.

3.7 Procedure for the Synthesis of Compound 5f



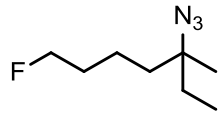
Step 1: To a stirring solution of 5-azido-5-methylheptanol (1.7 g, 10.0 mmol) and NEt_3 (1.5 g, 15.0 mmol, 1.5 equiv) in 10 mL of CH_2Cl_2, MsCl (1.4 g, 12.0 mmol, 1.2 equiv) was added dropwisely. The mixture was warmed up to room temperature and stirred for 2 h. The reaction was diluted by CH_2Cl_2 to 30 mL and quenched with saturated $NaHCO_3$ (aq). The organic layer was washed by H_2O, brine and dried over anhydrous Na_2SO_4. The crude product was obtained by removing the solvent under reduced pressure, which was used for the next step without further purification.



5-azido-5-methylheptyl methanesulfonate

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (t, *J* = 6.4 Hz, 2H), 3.02 (s, 3H), 1.81 – 1.72 (m, 2H), 1.60 – 1.44 (m, 6H), 1.23 (s, 3H), 0.93 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.72, 64.24, 38.26, 37.34, 31.98, 29.37, 22.67, 19.96, 8.33. HRMS (ESI): m/z: calculated for $[M + H]^+$ $C_9H_{20}N_3O_3S$: 250.12199, found 250.12160.

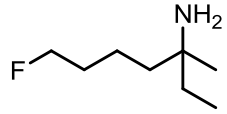
Step 2: The fluorination reaction followed a previous reported literature. The crude product of 5-azido-5-methylheptyl methylsulfonate was dissolved into 10 mL of THF and TBAF•$3H_2O$ (6.3 g, 20.0 mmol, 2.0 equiv) was added to this solution. The reaction was stirred at reflux temperature for 1 h and then cooled down to room temperature. The mixture was extracted by Et_2O (3×20 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: pentane : Et_2O = 100 : 1) to give the volatile compound 5-azido-1-fluoro-5-methylheptane (1.6 g, containing small amount of impurity).



5-azido-1-fluoro-5-methylheptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (t, *J* = 6.0 Hz, 1H), 4.40 (t, *J* = 6.0 Hz, 1H), 1.82 – 1.62 (m, 2H), 1.61 – 1.38 (m, 6H), 1.23 (s, 3H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.88 (d, *J* = 164.6 Hz), 64.37, 38.49, 31.96, 30.68 (d, *J* = 19.6 Hz), 22.75, 19.79, 8.35. IR (cm^{-1}): 2093. GC-MS (EI): m/z: (116.1, $[M\text{-}N_3\text{-}Me]^+$, 60%), (131.2, $[M\text{-}N_3]^+$, 100%).

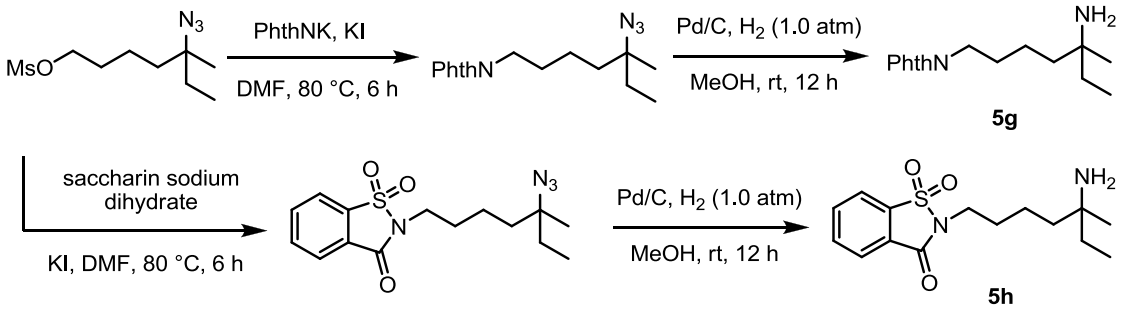
Step 3: The reduction of 5-azido-1-fluoro-5-methylheptane with $LiAlH_4$ *via* the procedure described above could finally afford the Compound **5f** (371.0 mg, 2.5 mmol).



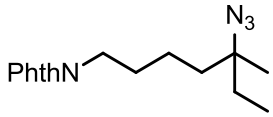
7-fluoro-3-methylheptan-3-amine (5f)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.52 (t, *J* = 6.1 Hz, 1H), 4.40 (t, *J* = 6.1 Hz, 1H), 1.69 (ddd, *J* = 25.4, 13.9, 6.2 Hz, 2H), 1.43-1.33 (m, 6H), 1.19 (br, 2H), 1.03 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -218.24. ^{13}C NMR (100 MHz, $CDCl_3$) δ 84.04 (d, *J* = 163.2 Hz), 51.4, 41.7, 35.0, 31.0 (d, *J* = 19.4 Hz), 27.4, 19.7 (d, *J* = 5.4 Hz), 8.2. HRMS(EI): m/z: calculated for $C_8H_{18}FN$ 147.1423, found $C_8H_{17}FN$ 146.1341.

3.8 Procedure for the Synthesis of Compound 5g and 5h



Step 1: 5-azido-5-methylheptyl methanesulfonate (623.3 mg, 2.5 mmol) was dissolved in 5 mL of DMF. Potassium phthalimide (463.1 mg, 2.5 mmol, 1.0 equiv) and potassium iodide (41.5 mg, 0.25 mmol, 0.1 equiv) were added in this solution. The mixture was heated at 80 °C for 6 h and then cooled down to room temperature. Then 20 mL of H_2O and 20 mL of CH_2Cl_2 were added to the mixture. The two phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3×15 mL). The combined organic layer was washed with H_2O and brine then dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and the residue was purified by column chromatography (eluent: PE : EtOAc = 10 : 1) to afford the product (521.1 mg, 1.7 mmol).

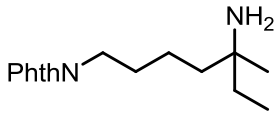


2-(5-azido-5-methylheptyl)isoindoline-1,3-dione

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.0 Hz,

2H), 3.70 (t, *J* = 7.3 Hz, 2H), 1.74 – 1.63 (m, 2H), 1.57 – 1.47 (m, 4H), 1.44 – 1.34 (m, 2H), 1.21 (s, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.42, 133.92, 132.15, 123.23, 64.32, 38.47, 37.79, 31.98, 28.90, 22.70, 21.24, 8.35. HRMS (ESI): m/z: calculated for $[M + H]^+$ $C_{16}H_{21}N_4O_2$: 301.16590, found 301.16601.

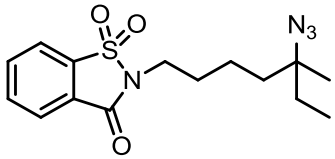
Step 2: The hydrogenation was carried out *via* the procedure described above to give the Compound **5g** (443.8 mg, 1.6 mmol).



***N*-2-(5-amino-5-methylheptyl)phthalimide (5g)**

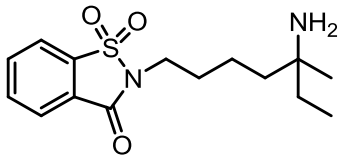
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 4.5, 3.4 Hz, 2H), 7.71 (dd, *J* = 4.6, 3.1 Hz, 2H), 3.70 (t, *J* = 7.3 Hz, 2H), 1.71-1.64 (m, 2H), 1.54 (br, 2H), 1.40-1.32 (m, 6H), 1.02 (s, 3H), 0.86 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 133.8, 132.1, 123.1, 51.6, 41.6, 37.9, 34.9, 29.2, 27.2, 21.2, 8.2. HRMS (ESI): m/z: calculated for $C_{16}H_{23}N_2O_2$ $[M + H]^+$ 275.1754, found 275.1758.

By using saccharin sodium dehydrate as the nucleophilic reagent, Compound **5h** could be obtained though the same synthetic route.



2-(5-azido-5-methylheptyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 1H), 7.96 – 7.90 (m, 1H), 7.90 – 7.80 (m, 2H), 3.79 (t, *J* = 7.5 Hz, 2H), 1.92 – 1.82 (m, 2H), 1.59 – 1.51 (m, 4H), 1.51 – 1.42 (m, 2H), 1.22 (s, 3H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.96, 137.69, 134.74, 134.33, 127.41, 125.17, 120.93, 64.29, 39.20, 38.35, 31.98, 28.70, 22.69, 21.23, 8.35. HRMS (ESI): m/z: calculated for $[M + H]^+$ $C_{15}H_{21}N_4O_3S$: 337.13289, found 337.13386.

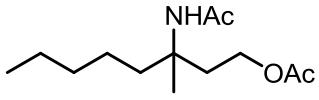


***N*-2-(5-amino-5-methylheptyl)saccharin (5h)**

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.1 Hz, 1H), 7.92 (d, *J* = 6.9 Hz, 1H), 7.89 – 7.79 (m, 2H), 3.79 (t, *J* = 7.5 Hz, 2H), 3.19 (br, 2H), 1.90-1.83 (m, 2H), 1.49-1.44 (m, 6H), 1.11 (s, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 137.6, 134.6, 134.2, 127.4, 125.1, 120.8, 52.8, 40.5, 39.2, 34.0, 28.9, 26.4, 21.1, 8.1. HRMS (ESI): m/z: calculated for $C_{15}H_{23}N_2O_3S$ $[M + H]^+$ 311.1424, found 311.1425.

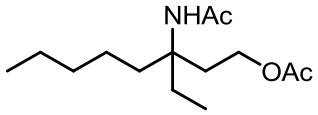
4. Pd-Catalyzed C(sp^3)—H Acetoxylation of Primary Amines

Three batches of C(sp^3)—H Acetoxylation reaction were conducted parallel in 0.1 mmol scale. For each reaction, primary amine (0.1 mmol, 1.0 equiv) and $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 5.0 mol%) were added into 25 mL reaction tube. AcOH (2 mL) was injected. Then, $PhI(OAc)_2$ (32.2 mg, 0.1 mmol, 1.0 equiv) was added into the above solution. The mixture was heated at 120 °C under air atmosphere for 3 h. And another batch of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 5.0 mol%) and $PhI(OAc)_2$ (32.2 mg, 0.1 mmol, 1.0 equiv) dissolved in 1 mL AcOH was injected into the above mixture. The reaction was stirred at 120 °C for another 3 h. After cooled down to room temperature, the reaction mixture was collected together and filtered through a short celite pad, which was washed by 5 mL CH_2Cl_2 for 3 times. The solvents were removed *in vacuo*. The residue was dissolved in 9 mL CH_2Cl_2 (3×3 mL). NEt_3 (3×0.1 mL) and Ac_2O (61.2 mg, 0.6 mmol, 3×2.0 equiv) were added sequentially. The mixture was stirred at room temperature for 3 h and then concentrated. The crude product was purified by column chromatography to obtain the corresponding product.



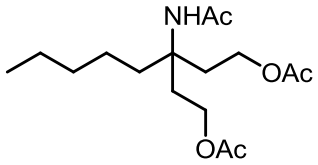
3-acetamido-3-methyloctyl acetate (2a)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 (s, 1H), 4.11 (t, *J* = 6.9 Hz, 2H), 2.20 (dt, *J* = 14.0, 7.0 Hz, 1H), 2.04 (s, 3H), 1.99 (dd, *J* = 14.2, 7.0 Hz, 1H), 1.93 (s, 3H), 1.82-1.76 (m, 1H), 1.61-1.55 (m, 1H), 1.32-1.23 (m, 9H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.5, 61.2, 55.3, 38.9, 36.1, 32.0, 24.5, 24.3, 23.2, 22.6, 21.0, 13.9. HRMS (ESI): m/z: calculated for $C_{13}H_{26}NO_3$ $[M + H]^+$ 244.1907, found 244.1909.



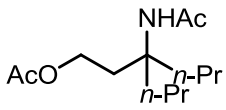
3-acetamido-3-ethyloctyl acetate (2b)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13 (s, 1H), 4.09 (t, *J* = 7.1 Hz, 2H), 2.12 (dt, *J* = 14.1, 7.2 Hz, 2H), 2.04 (s, 3H), 1.94 (s, 3H), 1.81 (dt, *J* = 14.8, 7.4 Hz, 1H), 1.75-1.67 (m, 1H), 1.64-1.49 (m, 2H), 1.34-1.28 (m, 3H), 1.26-1.20 (m, 3H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 169.4, 61.0, 58.2, 34.8, 32.8, 32.0, 27.7, 24.4, 22.6, 22.6, 21.0, 14.0, 7.4. HRMS (ESI): m/z: calculated for $C_{14}H_{28}NO_3$ $[M + H]^+$ 258.2064, found 258.2067.



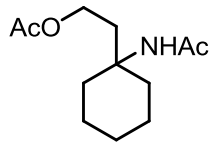
3-acetamido-3-pentylpentane-1,5-diyl diacetate (2b')

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42 (s, 1H), 4.11 (t, *J* = 6.9 Hz, 4H), 2.25 (dt, *J* = 13.9, 6.8 Hz, 2H), 2.07-1.98 (m, 2H), 2.04 (s, 6H), 1.95 (s, 3H), 1.66-1.62 (m, 2H), 1.34-1.29 (m, 2H), 1.28-1.26 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 169.6, 60.6, 57.1, 36.0, 33.5, 32.0, 24.3, 22.8, 22.6, 21.0, 14.0. HRMS (ESI): m/z: calculated for $C_{16}H_{30}NO_5$ $[M + H]^+$ 316.2118, found 316.2120.



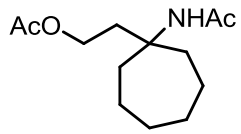
3-acetamido-3-propylhexyl acetate (2c)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13 (s, 1H), 4.09 (t, *J* = 7.0 Hz, 2H), 2.12 (t, *J* = 7.1 Hz, 2H), 2.04 (s, 3H), 1.93 (s, 3H), 1.76-1.68 (m, 2H), 1.56-1.49 (m, 2H), 1.29-1.25 (m, 2H), 1.24-1.19 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 169.3, 61.0, 58.0, 37.7, 33.2, 24.4, 21.0, 16.3, 14.3. HRMS (ESI): m/z: calculated for $C_{13}H_{26}NO_3$ $[M + H]^+$ 244.1907, found 244.1907.



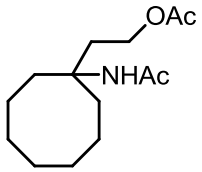
2-(1-acetamidocyclohexyl)ethyl acetate (2d)

Light yellow wax. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19 (s, 1H), 4.11 (t, *J* = 7.0 Hz, 2H), 2.17 (t, *J* = 7.0 Hz, 2H), 2.09-2.04 (m, 2H), 2.03 (s, 3H), 1.97 (s, 3H), 1.55-1.52 (m, 3H), 1.44-1.39 (m, 4H), 1.31-1.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 169.6, 61.0, 54.9, 35.8, 35.0, 25.5, 24.4, 21.6, 21.0. HRMS (ESI): m/z: calculated for $C_{12}H_{22}NO_3$ $[M + H]^+$ 228.1594, found 228.1598.



2-(1-acetamidocycloheptyl)ethyl acetate (2e)

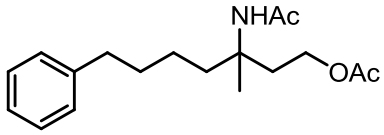
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.16 (s, 1H), 4.08 (t, *J* = 7.1 Hz, 2H), 2.20 (t, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.95 (s, 3H), 1.95-1.90 (m, 2H), 1.76-1.70 (m, 2H), 1.57-1.55 (m, 4H), 1.49-1.47 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 169.6, 61.3, 58.7, 38.6, 36.0, 29.4, 24.5, 22.2, 21.1. HRMS (ESI): m/z: calculated for $C_{13}H_{24}NO_3$ $[M + H]^+$ 242.1751, found 242.1751.



2-(1-acetamidocyclooctyl)ethyl acetate (2f)

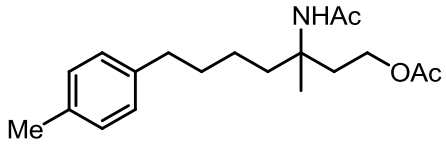
This compound could not be isolated from unknown impurities. 1,3-benzodioxale (12.2 mg, 0.1 mmol) was added as the internal standard for NMR analysis. HRMS (ESI): m/z:

calculated for $C_{14}H_{26}NO_3$ $[M + H]^+$ 256.1907, found 256.1908.



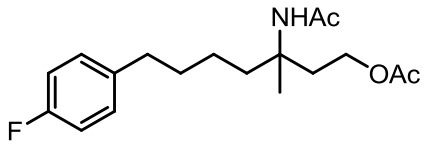
3-acetamido-3-methyl-7-phenylheptyl acetate (4a)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.19-7.15 (m, 3H), 5.34 (s, 1H), 4.11 (td, *J* = 7.0, 1.7 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.21 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.03 (s, 3H), 1.97 (dd, *J* = 14.2, 7.1 Hz, 1H), 1.91 (s, 3H), 1.88-1.82 (m, 1H), 1.66-1.58 (m, 3H), 1.34-1.27 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.5, 142.3, 128.3, 128.2, 125.6, 61.1, 55.2, 38.6, 36.2, 35.7, 31.5, 24.5, 24.3, 23.1, 21.0. HRMS (ESI): m/z: calculated for $C_{18}H_{28}NO_3$ $[M + H]^+$ 306.2064, found 306.2061.



3-acetamido-3-methyl-7-p-tolylheptyl acetate (4b)

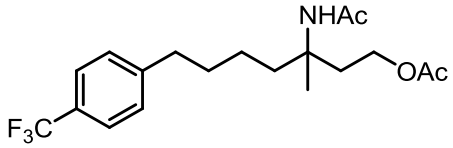
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (q, *J* = 8.1 Hz, 4H), 5.27 (s, 1H), 4.11 (t, *J* = 7.0 Hz, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 2.31 (s, 3H), 2.21 (dt, *J* = 14.1, 6.9 Hz, 1H), 2.03 (s, 3H), 1.97 (dt, *J* = 14.2, 7.0 Hz, 1H), 1.92 (s, 3H), 1.88-1.81 (m, 1H), 1.65-1.56 (m, 3H), 1.36-1.28 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.5, 139.3, 135.1, 128.9, 128.2, 61.2, 55.3, 38.7, 36.2, 35.3, 31.7, 24.6, 24.4, 23.1, 21.0 (2C). HRMS (ESI): m/z: calculated for $C_{19}H_{30}NO_3$ $[M + H]^+$ 320.2220, found 320.2222.



3-acetamido-7-(4-fluorophenyl)-3-methylheptyl acetate (4c)

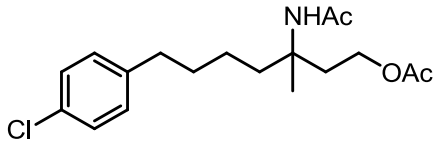
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.59 (t, *J* = 8.7 Hz, 2H), 5.40 (s, 1H), 4.11 (td, *J* = 7.0, 2.5 Hz, 2H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.22 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.03 (s, 3H), 1.95 (dd, *J* = 14.3, 7.2 Hz, 1H), 1.92 (s, 3H), 1.88-1.84

(m, 1H), 1.66-1.55 (m, 3H), 1.33-1.27 (m, 2H), 1.25 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -117.99. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.5, 161.1 (d, *J* = 241.5 Hz), 137.9 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 7.7 Hz), 114.9 (d, *J* = 20.9 Hz), 61.1, 55.2, 38.5, 36.2, 34.8, 31.6, 24.5, 24.3, 23.0, 21.0. HRMS (ESI): m/z: calculated for $C_{18}H_{27}FNO_3$ $[M + H]^+$ 324.1969, found 324.1967.



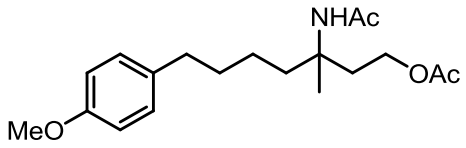
3-acetamido-3-methyl-7-(4-(trifluoromethyl)phenyl)heptyl acetate (4d)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 5.36 (s, 1H), 4.11 (td, *J* = 6.9, 2.5 Hz, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 2.23 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.03 (s, 3H), 1.97-1.87 (m, 2H), 1.92 (s, 3H), 1.68-1.59 (m, 3H), 1.35-1.29 (m, 2H), 1.25 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.26. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.6, 146.5, 128.6, 128.0 (q, *J* = 32.0 Hz), 125.1 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 270.0 Hz), 61.1, 55.2, 38.4, 36.3, 35.5, 31.2, 24.5, 24.3, 23.0, 21.0. HRMS (ESI): m/z: calculated for $C_{19}H_{27}F_3NO_3$ $[M + H]^+$ 374.1938, found 374.1934.



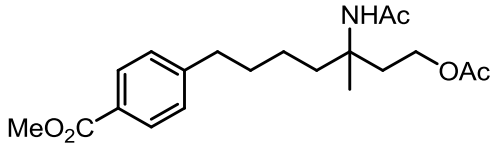
3-acetamido-7-(4-chlorophenyl)-3-methylheptyl acetate (4e)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 5.35 (s, 1H), 4.11 (td, *J* = 6.9, 2.2 Hz, 2H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.25-2.17 (m, 1H), 2.03 (s, 3H), 1.97-1.94 (m, 1H), 1.92 (s, 3H), 1.90-1.84 (m, 1H), 1.66-1.55 (m, 3H), 1.31-1.28 (m, 2H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.5, 140.8, 131.3, 129.6, 128.3, 61.1, 55.2, 38.5, 36.2, 35.0, 31.4, 24.5, 24.3, 23.0, 21.0. HRMS (ESI): m/z: calculated for $C_{18}H_{27}ClNO_3$ $[M + H]^+$ 340.1674, found 340.1677.



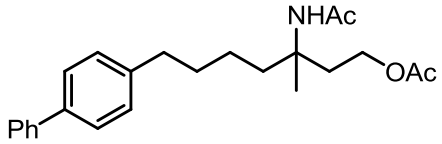
3-acetamido-7-(4-methoxyphenyl)-3-methylheptyl acetate (4f)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 5.34 (s, 1H), 4.11 (t, *J* = 6.3 Hz, 2H), 3.78 (s, 3H), 2.55 (t, *J* = 7.7Hz, 2H), 2.21 (dt, *J* = 14.0, 6.8 Hz, 1H), 2.03 (s, 3H), 1.97 (dd, *J* = 14.3, 7.2 Hz, 1H), 1.92 (s, 3H), 1.89-1.81 (m, 1H), 1.65-1.54 (m, 3H), 1.32-1.29 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.5, 157.6, 134.4, 129.2, 113.6, 61.1, 55.2 (2C), 38.6, 36.2, 34.8, 31.8, 24.5, 24.3, 23.0, 21.0. HRMS (ESI): m/z: calculated for $C_{19}H_{30}NO_4$ $[M + H]^+$ 336.2169, found 336.2165.



methyl 4-(5-acetamido-7-acetoxy-5-methylheptyl)benzoate (4g)

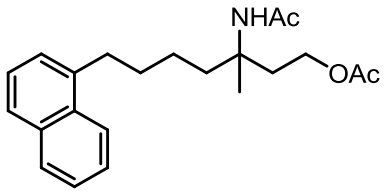
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 5.41 (s, 1H), 4.11 (td, *J* = 7.0, 2.5 Hz, 2H), 3.90 (s, 3H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.23 (dt, *J* = 13.9, 6.8 Hz, 1H), 2.03 (s, 3H), 1.97-1.86 (m, 2H), 1.92 (s, 3H), 1.67-1.60 (m, 3H), 1.34-1.26 (m, 2H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.5, 167.1, 147.9, 129.6, 128.3, 127.6, 61.1, 55.2, 51.9, 38.5, 36.2, 35.7, 31.1, 24.5, 24.3, 23.0, 21.0. HRMS (ESI): m/z: calculated for $C_{20}H_{30}NO_5$ $[M + H]^+$ 364.2118, found 364.2121.



3-acetamido-7-(biphenyl-4-yl)-3-methylheptyl acetate (4h)

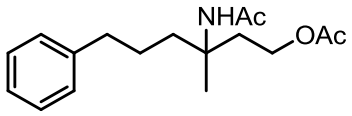
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.27 (s, 1H), 4.12 (td, *J* = 7.0, 1.3 Hz, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 2.22 (dt, *J* = 13.9, 6.9 Hz, 1H), 2.03 (s, 3H), 1.97 (dt, *J* = 14.3, 7.1 Hz, 1H), 1.92 (s, 3H), 1.87-1.85 (m, 1H),

1.70-1.61 (m, 3H), 1.35-1.29 (m, 2H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.5, 141.5, 141.1, 138.6, 128.8, 128.7, 127.0, 127.0, 126.9, 61.2, 55.3, 38.7, 36.3, 35.4, 31.5, 24.6, 24.4, 23.2, 21.0. HRMS (ESI): m/z: calculated for $C_{24}H_{32}NO_3$ $[M + H]^+$ 382.2377, found 382.2372.



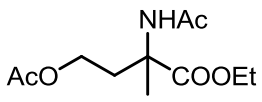
3-acetamido-3-methyl-7-(naphthalen-1-yl)heptyl acetate (4i)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.52-7.44 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30-7.29 (m, 1H), 5.41 (s, 1H), 4.11 (t, *J* = 6.9 Hz, 2H), 3.06 (t, *J* = 7.8 Hz, 2H), 2.23 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.01 (s, 3H), 1.99-1.85 (m, 2H), 1.91 (s, 3H), 1.78-1.61 (m, 3H), 1.43-1.34 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.6, 138.4, 133.8, 131.7, 128.7, 126.4, 125.8, 125.6, 125.4, 125.3, 123.7, 61.1, 55.2, 38.7, 36.1, 32.9, 30.8, 24.5, 24.3, 23.6, 21.0. HRMS (ESI): m/z: calculated for $C_{22}H_{30}NO_3$ $[M + H]^+$ 356.2220, found 356.2215.



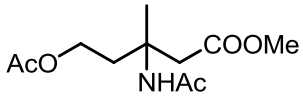
3-acetamido-3-methyl-6-phenylhexyl acetate (4j)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.20-7.16 (m, 3H), 5.32 (s, 1H), 4.09 (t, *J* = 6.9 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 2.21 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.02 (s, 3H), 1.97 (dd, *J* = 14.2, 7.1 Hz, 1H), 1.91 (s, 3H), 1.89-1.85 (m, 1H), 1.70-1.55 (m, 3H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.5, 142.2, 128.3, 128.3, 125.8, 61.1, 55.2, 38.6, 36.2, 36.0, 25.7, 24.5, 24.3, 21.0. HRMS (ESI): m/z: calculated for $C_{17}H_{26}NO_3$ $[M + H]^+$ 292.1907, found 292.1911.



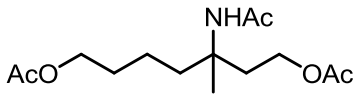
ethyl 2-acetamido-4-acetoxy-2-methylbutanoate (6a)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.50 (s, 1H), 4.31-4.15 (m, 2H), 4.05 (dd, *J* = 7.6, 4.8 Hz, 2H), 2.70 (dt, *J* = 14.6, 4.8 Hz, 1H), 2.29 (dt, *J* = 14.9, 7.6 Hz, 1H), 2.01 (s, 3H), 1.98 (s, 3H), 1.62 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 170.6, 169.4, 61.9, 60.6, 58.5, 34.2, 24.0, 23.6, 20.7, 14.0. HRMS (ESI): m/z: calculated for $C_{11}H_{20}NO_5$ $[M + H]^+$ 246.1336, found 246.1337.



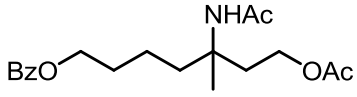
methyl 3-acetamido-5-acetoxy-3-methylpentanoate (6b)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (s, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 3.68 (s, 3H), 2.95 (d, *J* = 15.0 Hz, 1H), 2.63 (d, *J* = 15.0 Hz, 1H), 2.35-2.28 (m, 1H), 2.16-2.09 (m, 1H), 2.05 (s, 3H), 1.96 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 171.0, 170.1, 60.7, 53.6, 51.6, 42.4, 36.6, 24.7, 24.3, 21.0. HRMS (ESI): m/z: calculated for $C_{11}H_{19}NNaO_5$ $[M + Na]^+$ 268.1155, found 268.1150.



3-acetamido-3-methylheptane-1,7-diyl diacetate (6c)

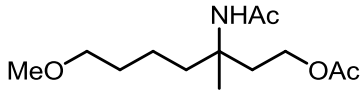
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.47 (s, 1H), 4.12 (t, *J* = 7.0, 1.8 Hz, 2H), 4.07 (t, *J* = 6.5 Hz, 2H), 2.23 (dt, *J* = 13.9, 6.8 Hz, 1H), 2.05 (s, 3H), 2.04 (s, 3H), 1.99-1.96 (m, 1H), 1.94 (s, 3H), 1.92-1.84 (m, 1H), 1.67-1.59 (m, 3H), 1.36-1.29 (m, 2H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 171.1, 169.6, 64.2, 61.0, 55.1, 38.4, 36.2, 28.8, 24.4, 24.2, 21.0, 20.9, 20.0. HRMS (ESI): m/z: calculated for $C_{14}H_{26}NO_5$ $[M + H]^+$ 288.1805, found 288.1806.



5-acetamido-7-acetoxy-5-methylheptyl benzoate (6d)

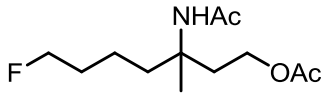
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.45 (s, 1H), 4.34 (td, *J* = 6.4, 2.1 Hz, 2H), 4.13 (td, *J* = 6.9,

1.5 Hz, 2H), 2.25 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.04 (s, 3H), 2.00-1.90 (m, 2H), 1.93 (s, 3H), 1.81-1.74 (m, 2H), 1.72-1.64 (m, 1H), 1.46-1.35 (m, 2H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.6, 166.6, 132.9, 130.3, 129.5, 128.3, 64.6, 61.1, 55.1, 38.4, 36.3, 28.9, 24.5, 24.3, 21.0, 20.0. HRMS (ESI): m/z: calculated for $C_{19}H_{28}NO_5$ $[M + H]^+$ 350.1962, found 350.1958.



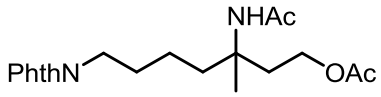
3-acetamido-7-methoxy-3-methylheptyl acetate (6e)

This compound could not be isolated from unknown impurities. 1,3-benzodioxale (12.2 mg, 0.1 mmol) was added as the internal standard for NMR analysis. HRMS (ESI): m/z: calculated for $C_{13}H_{26}NO_4$ $[M + H]^+$ 260.1856, found 260.1855.



3-acetamido-7-fluoro-3-methylheptyl acetate (6f)

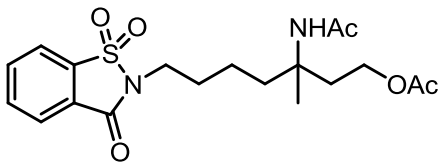
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42 (s, 1H), 4.51 (t, *J* = 5.9 Hz, 1H), 4.39 (t, *J* = 5.9 Hz, 1H), 4.13 (td, *J* = 6.9, 2.4 Hz, 2H), 2.25 (dt, *J* = 13.9, 6.8 Hz, 1H), 2.04 (s, 3H), 1.98-1.87 (m, 2H), 1.94 (s, 3H), 1.75-1.62 (m, 3H), 1.44-1.33 (m, 2H), 1.28 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -218.75. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.6, 83.9 (d, *J* = 163.2 Hz), 61.0, 55.2, 38.2, 36.3, 30.5 (d, *J* = 19.6 Hz), 24.5, 24.3, 21.0, 19.4 (d, *J* = 5.0 Hz). HRMS (ESI): m/z: calculated for $C_{12}H_{23}FNO_3$ $[M + H]^+$ 248.1656, found 248.1655.



3-acetamido-7-(1,3-dioxoisoindolin-2-yl)-3-methylheptyl acetate (6g)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.73 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.57 (s, 1H), 4.12 (t, *J* = 7.0 Hz, 2H), 3.70 (t, *J* = 6.8 Hz, 2H), 2.21 (dt, *J* = 13.9, 6.9 Hz, 1H), 2.06-2.01 (m, 1H), 2.04 (s, 3H), 1.95 (s, 3H), 1.88 (td, *J* = 13.1, 4.6 Hz, 1H), 1.73-1.57 (m, 3H), 1.38-1.32 (m, 2H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ 171.1, 169.7, 168.5, 133.9, 132.0, 123.2, 61.1, 55.0, 38.3, 37.3, 36.3, 28.6, 24.3, 24.2, 21.0, 20.5. HRMS (ESI): m/z: calculated for $C_{20}H_{27}N_2O_5$ $[M + H]^+$ 375.1914, found 375.1908.



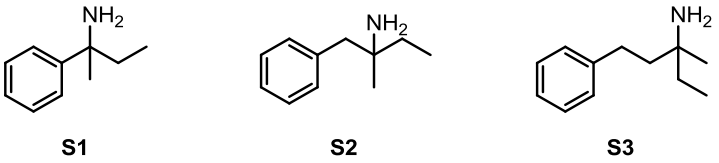
3-acetamido-7-saccharinyl-3-methylheptyl acetate (6h)

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.05 (m, 1H), 7.94-7.83 (m, 3H), 5.49 (s, 1H), 4.12 (t, *J* = 6.9 Hz, 2H), 3.79 (t, *J* = 7.1 Hz, 2H), 2.23 (dt, *J* = 13.9, 6.9 Hz, 1H), 2.04 (s, 3H), 2.00 (dd, *J* = 14.2, 7.1 Hz, 1H), 1.94 (s, 3H), 1.91-1.78 (m, 3H), 1.68-1.60 (m, 1H), 1.46-1.35 (m, 2H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 169.7, 159.1, 137.6, 134.8, 134.3, 127.3, 125.1, 120.9, 61.1, 55.1, 39.0, 38.2, 36.3, 28.4, 24.4, 24.3, 21.0, 20.6. HRMS (ESI): m/z: calculated for $C_{19}H_{27}N_2O_6S$ $[M + H]^+$ 411.1584, found 411.1576.

Inferior Results in the Substrate Investigation

Substrates which gave negative results were listed in the following figure.

Figure S1



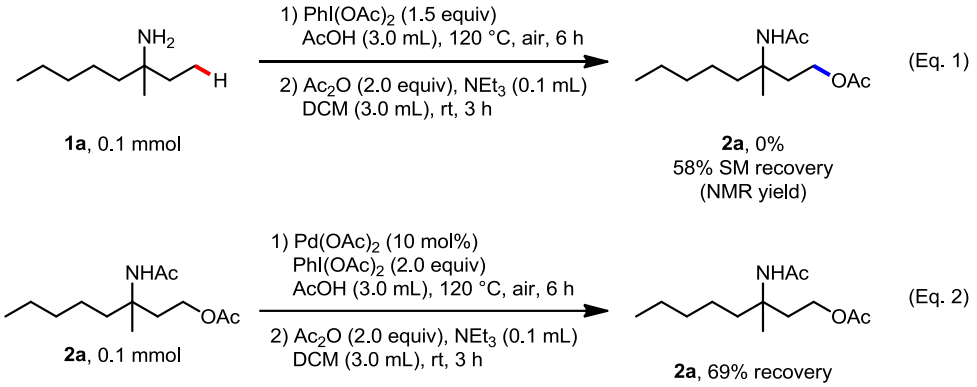
S1 **S2** **S3**

We investigated the substrates with aryl group at *α, β* or *γ* position to the amino group. When the aromatic ring was close to the amino group, the substrates became easily decomposed. And the C(sp^2)—H bond on the aromatic ring was susceptible to Pd catalysts and oxidants. For **S1**, no desired C(sp^3)—H acetoxylation product was found and 24% of C(sp^2)—H di-acetoxylation product was tested. For **S2**, 18% *N*-Ac protected starting material was recovered, and less than 10% of C(sp^2)—H di-acetoxylation product was isolated. However, no desired C(sp^3)—H acetoxylation product was found. For **S3**,

21% *N*-Ac protected starting material was recovered. Both C(sp^3)—H and C(sp^2)—H acetoxylation product were generated in a total yield of ca. 30%, which could be hardly separated from each other.

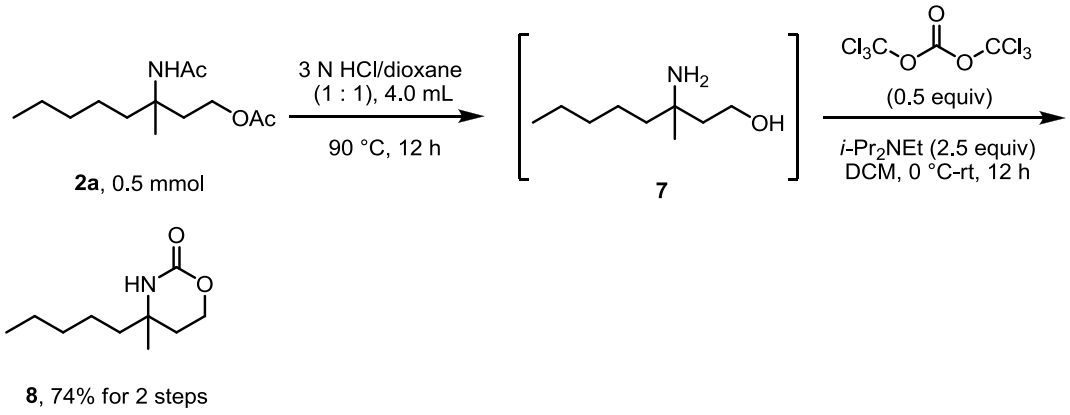
Control experiments

According to control experiments, the limited yield of C—H acetoxylation product was mainly attributed to the decomposition of both primary amines and desired products in this reaction system.



5. Transformations of the γ-Amino Alcohol Derivatives

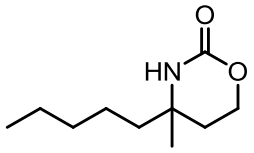
Procedure for the Synthesis of Compound 8



Compound **2a** (121.7 mg, 0.5 mmol) was dissolved in 3 N HCl (aq) and 1,4-dioxane (1 : 1 mixture, 4 mL) and the solution was heated at 120 °C for 12 h. The reaction mixture

was then cooled down to room temperature and basified with excess saturated K_2CO_3 (aq). The aqueous phase was extracted with CH_2Cl_2 (3×20 mL). The organic layer was combined and dried over anhydrous Na_2SO_4. The solvent was then removed to get the crude product of amino alcohol **7**, which was used without purification for the next step.

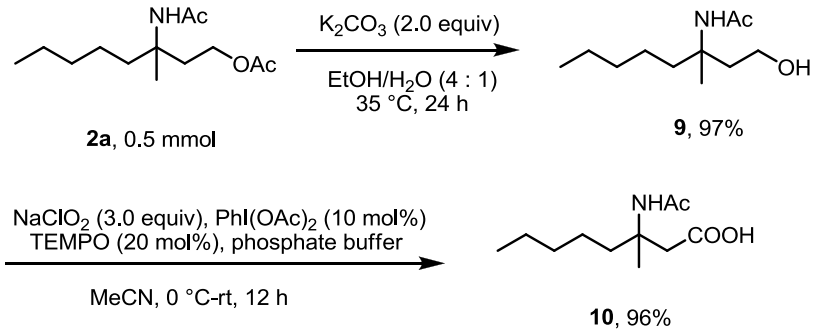
Amino alcohol **7** and diisopropylethylamine (161.6 mg, 1.25 mmol, 2.5 equiv) were dissolved in 10 mL of CH_2Cl_2. The solution was cooled down to 0 °C in ice bath. The triphosgene (74.2 mg, 0.25 mmol, 0.5 equiv) was added slowly. The mixture was then warmed up to room temperature and stirred for 12 h. Then the reaction was diluted to 30 mL and quenched with H_2O. The organic layer was separated and washed with H_2O, 0.1 N HCl (aq) and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (eluent: PE: EtOAc = 3 : 2 to 1 : 1) to obtain the desired product **8** (68.3 mg, 74% for 2 steps) as light yellow oil.



4-methyl-4-pentyl-1,3-oxazinan-2-one (8)

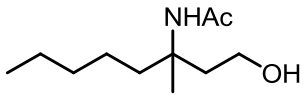
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (s, 1H), 4.28 (dd, *J* = 6.6, 4.6 Hz, 2H), 1.87 (dt, *J* = 6.7, 5.8 Hz, 1H), 1.72 (dt, *J* = 14.0, 5.0 Hz, 1H), 1.59-1.45 (m, 2H), 1.34-1.29 (m, 6H), 1.26 (s, 3H), 0.89 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 63.4, 53.0, 42.4, 32.3, 31.9, 27.4, 23.1, 22.4, 13.9. HRMS (ESI): m/z: calculated for $C_{10}H_{20}NO_2$ $[M + H]^+$ 186.1489, found 186.1484.

Procedure for the Synthesis of Compound 9 and 10



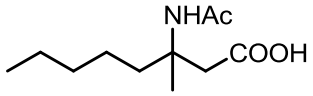
According to a reported literature,[5] Compound **2a** (121.7 mg, 0.5 mmol) was dissolved in EtOH/H_2O (4 : 1, 5 mL), K_2CO_3 (138.2 mg, 1.0 mmol, 2.0 equiv) was added into the above solution. The mixture was stirred at 35 °C for 24 h. The reaction mixture was diluted with H_2O and then extracted with CH_2Cl_2 (3×20 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (eluent: CH_2Cl_2: MeOH = 50 : 1) to get **9** (97.8 mg, 97%) as white wax.

The oxidation of *N*-Ac amino alcohol **9** to corresponding amino acid **10** was referred to literature procedure.[6] To a solution of **9** (88.0 mg, 0.44 mmol) in MeCN (2 mL) / phosphate buffer (pH = 6.4) (2.4 mL) were added $PhI(OAc)_2$ (14.2 mg, 0.044 mmol, 0.1 equiv) and TEMPO (13.8 mg, 0.088 mmol, 0.2 equiv) at room temperature, then the mixture was cooled down to 0 ℃. To the stirring mixture was added $NaClO_2$ (75 wt%, 159.2 mg, 1.32 mmol, 3.3 equiv) at the same temperature and the resulting solution was warmed up to room temperature. After stirring at same temperature for 12 h, the mixture was quenched with saturated aqueous NH_4Cl, and extracted with ethyl acetate (5×15 mL). The organic layer was washed with 1 N HCl (aq), brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography (eluent: CH_2Cl_2 : MeOH = 25 : 1) to afford **10** (90.8 mg, 96%) as white wax.



***N*-(1-hydroxy-3-methyloctan-3-yl)acetamide (9)**

White wax. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (s, 1H), 3.78 (d, *J* = 4.3 Hz, 2H), 2.26 (s, 1H), 2.01 (dt, *J* = 12.7, 6.3 Hz, 1H), 1.92 (s, 3H), 1.80-1.70 (m, 3H), 1.34 (s, 3H), 1.32-1.28 (m, 2H), 1.27-1.24 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 59.2, 55.9, 41.0, 39.0, 32.1, 24.6, 24.5, 23.4, 22.6, 14.0. HRMS (ESI): m/z: calculated for $C_{11}H_{23}NNaO_2$ $[M + Na]^+$ 224.1621, found 224.1615.

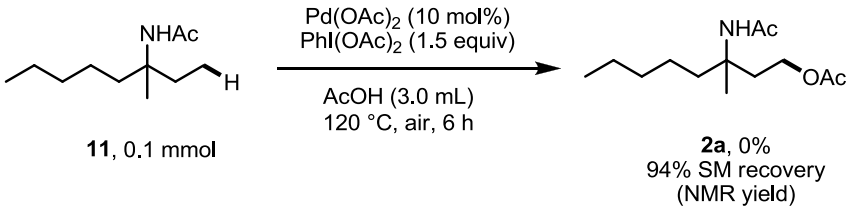


3-acetamido-3-methyloctanoic acid (10)

White wax. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.43 (br, 1H), 6.22 (s, 1H), 2.86 (d, *J* = 14.8 Hz, 1H), 2.62 (d, *J* = 14.8 Hz, 1H), 1.97 (s, 3H), 1.87-1.81 (m, 1H), 1.76-1.71 (m, 1H), 1.40 (s, 3H), 1.31-1.27 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 171.0, 54.8, 42.4, 38.8, 31.9, 24.4, 24.0, 23.2, 22.5, 13.9. HRMS (ESI): m/z: calculated for $C_{11}H_{22}NO_3$ $[M + H]^+$ 216.1594, found 216.1591.

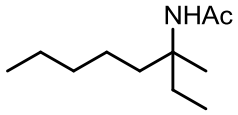
6. Mechanistic Studies

Pd-Catalyzed C(sp^3)—H Acetoxylation of Acetamide 11



Acetamide **11** (18.5 mg, 0.1 mmol, 1.0 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 10 mol%) were added into 25 mL reaction tube. AcOH (3 mL) was injected. Then, $PhI(OAc)_2$ (48.3 mg, 0.15 mmol, 1.5 equiv) was added into the above solution. The mixture was heated at 120 °C under air atmosphere for 6 h. After cooled down to room temperature, the reaction mixture was filtered through a short celite pad, which was washed by 5 mL of CH_2Cl_2 for 3 times. The solvents were removed *in vacuo*. The residue was dissolved into 20 mL of CH_2Cl_2 and the organic phase was washed by saturated

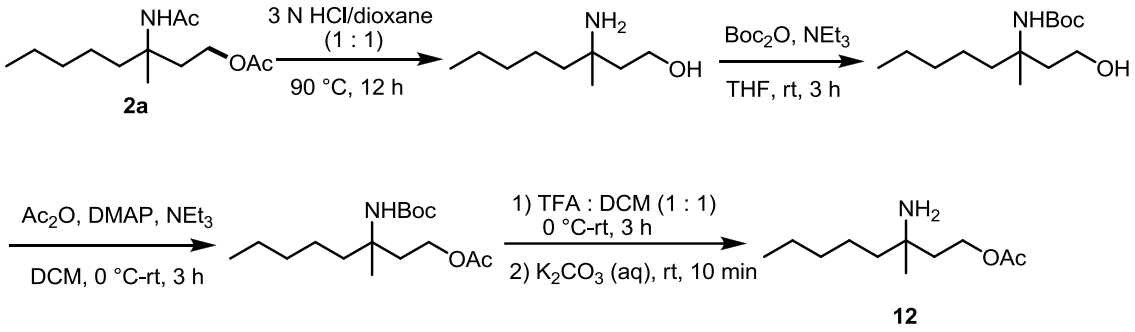
$NaHCO_3$ (aq). The solution was dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure. To the resulting residue, 1,3-benzodioxale (12.2 mg, 0.1 mmol) was added as the internal standard for NMR analysis. No C(sp^3)—H acetoxylation product **2a** was detected. However, 94% (NMR yield) of starting material was recovered, which indicated that the amide group could not function as the directing group for this reaction.



***N*-(3-methyloctan-3-yl)acetamide (11)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (s, 1H), 1.93 (s, 3H), 1.81-1.56 (m, 4H), 1.33 -1.22 (m, 9H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.82 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 56.5, 37.9, 32.2, 30.6, 24.4, 23.8, 23.3, 22.6, 14.0, 8.0. HRMS (ESI): m/z: calculated for $C_{11}H_{24}NO$ $[M + H]^+$ 186.1852, found 186.1848.

Procedure for the Synthesis of Compound 12

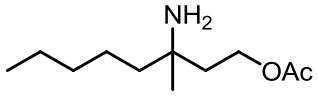


Step 1: Compound **2a** (860.3 mg, 3.5 mmol) was dissolved in 3 N HCl (aq) and 1,4-dioxane (1 : 1 mixture, 20 mL) and the solution was heated at 120 °C for 12 h. The reaction mixture was then cooled down to room temperature and basified with excess saturated K_2CO_3 (aq). The aqueous phase was extracted with CH_2Cl_2 (5×20 mL). The organic layer was combined and dried over anhydrous Na_2SO_4. The solvent was then removed to get the crude product of amino alcohol, which was used without purification for the next step.

Step 2: To a solution of crude amino alcohol and NEt_3 (430.0 mg, 4.2 mmol, 1.2 equiv) in 10 mL of THF, Boc_2O (849.0 mg, 3.9 mmol, 1.1 equiv) was added dropwisely. The mixture was stirred at room temperature for 3 h. Then it was quenched with the addition of water. Then the solution was concentrated under reduced pressure to remove most of THF. The aqueous phase was extracted by CH_2Cl_2 (3×20 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated to afford the crude product, which was used directly in the next step.

Step 3: To a solution of crude *N*-Boc-protected amino alcohol, NEt_3 (537.3 mg, 5.3 mmol, 1.5 equiv) and 4-*N*,*N*-dimethylaminopyridine (86.7 mg, 0.7 mmol, 0.2 equiv) in 10 mL of CH_2Cl_2 at 0 °C, Ac_2O (397.5 mg, 3.9 mmol, 1.1 equiv) was added dropwisely. Then the mixture was warmed up to room temperature and stirred for 3 h. The reaction was quenched with water and diluted with 50 mL of CH_2Cl_2. The organic phase was washed with H_2O and brine. Then the solution was dried over anhydrous Na_2SO_4 and concentrated to afford the crude product, which was used directly in the next step.

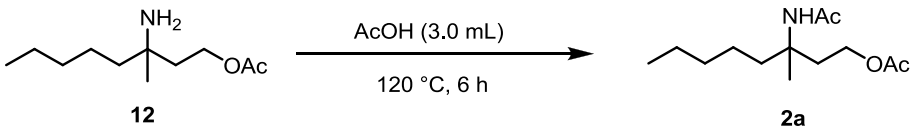
Step 4: The protected amino alcohol was dissolved in 4 mL of CH_2Cl_2. The solution was cooled down to 0 °C and TFA (4 mL) was added dropwisely. The mixture was warmed up to room temperature and stirred for 3 h. Then the solvents were removed under reduced pressure. The residue was dissolved in 5 mL saturated K_2CO_3 (aq) and stirred for about 10 min. The solution was diluted by H_2O and extracted with CH_2Cl_2 (3×20 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (eluent: CH_2Cl_2 : MeOH = 50 : 1 to 20 : 1) to afford the desire product **12** as yellow oil (268.9 mg, 1.3 mmol).



3-amino-3-methyloctyl acetate (12)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.18 (t, *J* = 7.3 Hz, 2H), 2.05 (s, 3H), 1.70 (t, *J* = 7.3 Hz, 2H), 1.37-1.26 (m, 10H), 1.08 (s, 3H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 61.6, 50.8, 43.4, 40.4, 32.4, 28.3, 23.6, 22.6, 21.1, 14.0. HRMS (ESI): m/z: calculated for $C_{11}H_{24}NO_2$ $[M + H]^+$ 202.1802, found 202.1795.

***In-Situ* Acylation of 12 to form 2a**



12 **2a**

Compound **12** (40.2 mg, 0.2 mmol) was dissolved into 3 mL of AcOH. The solution was stirred at 120 °C for 6 h. Then AcOH was removed *in vacuo* and the residue was dissolved in 20 mL CH_2Cl_2. The organic phase was washed by saturated $NaHCO_3$ (aq). The solution was dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure. The residue was purified by column chromatography (eluent: CH_2Cl_2 : MeOH = 50 : 1) to get product **2a** (38.5 mg, 79%).

7. References

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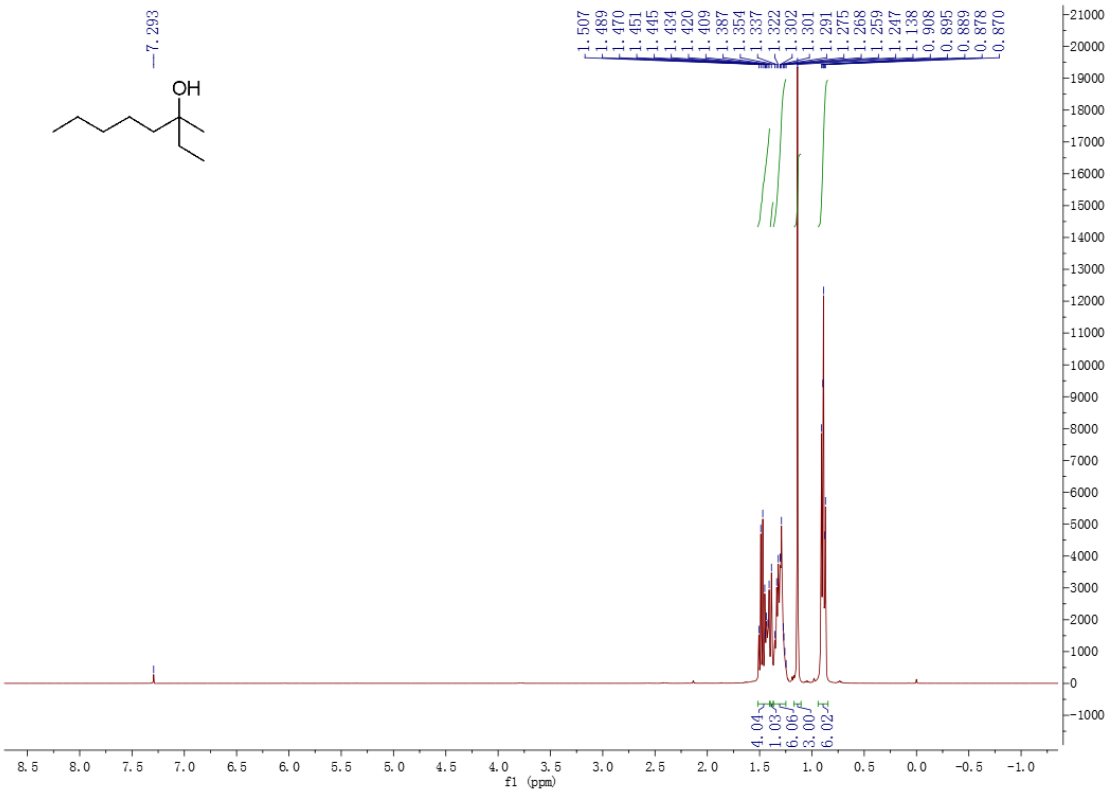
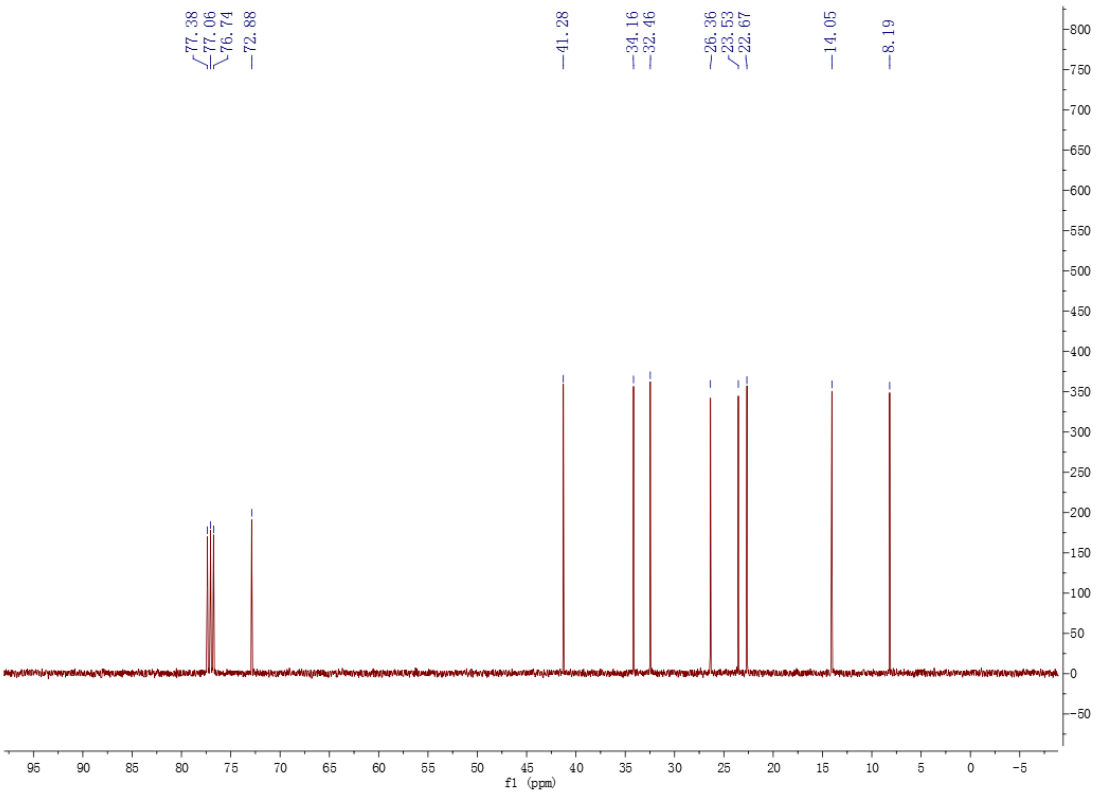
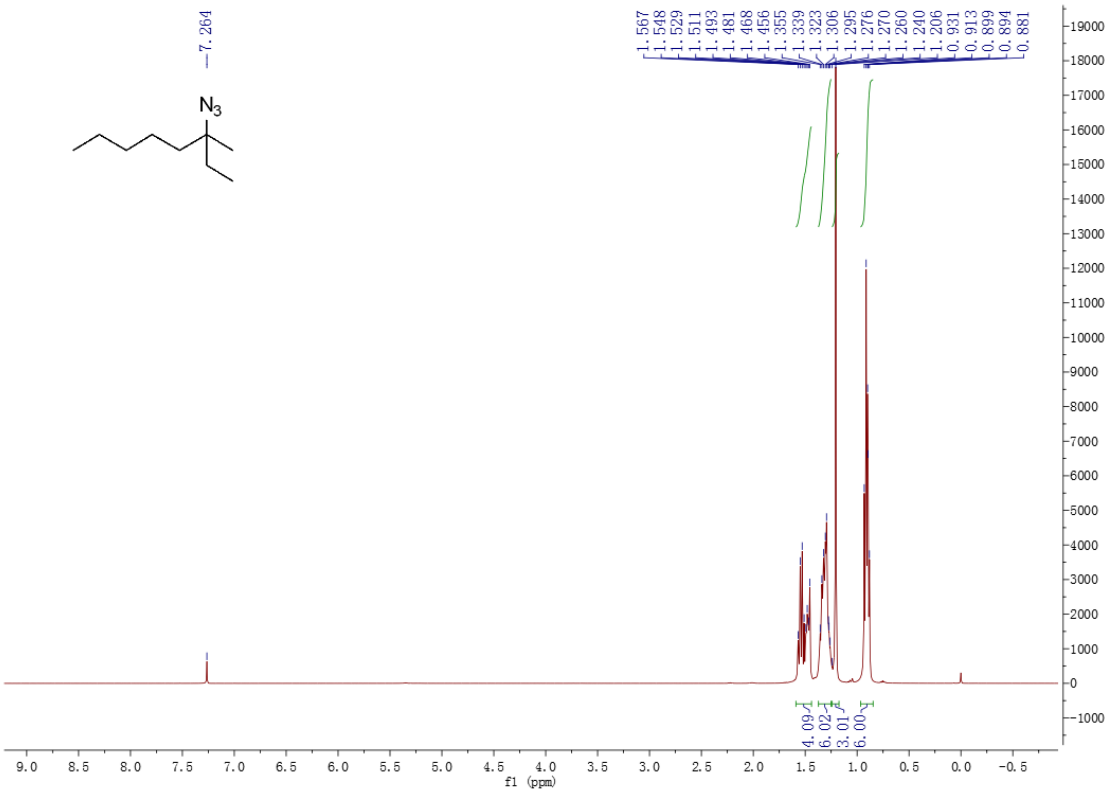
8. NMR Spectra



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1.306
1.295
1.276
1.270
1.260
1.240
1.206
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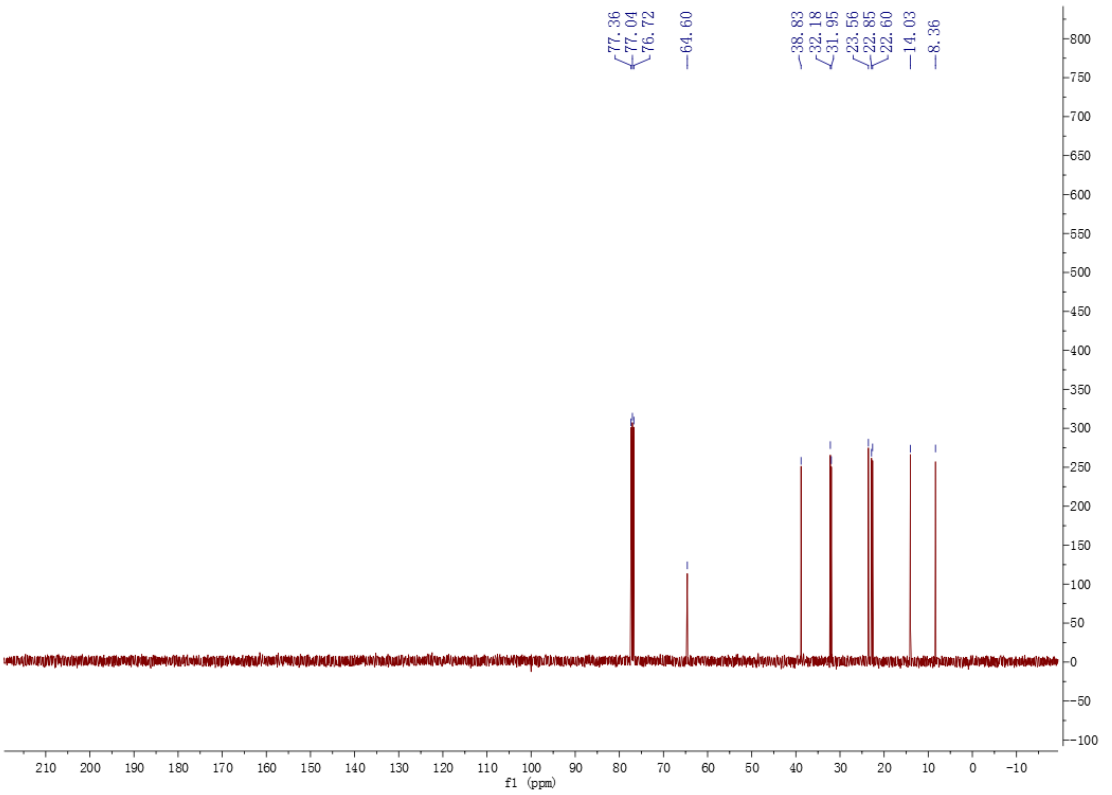
6.02
3.01
6.00
f1 (ppm)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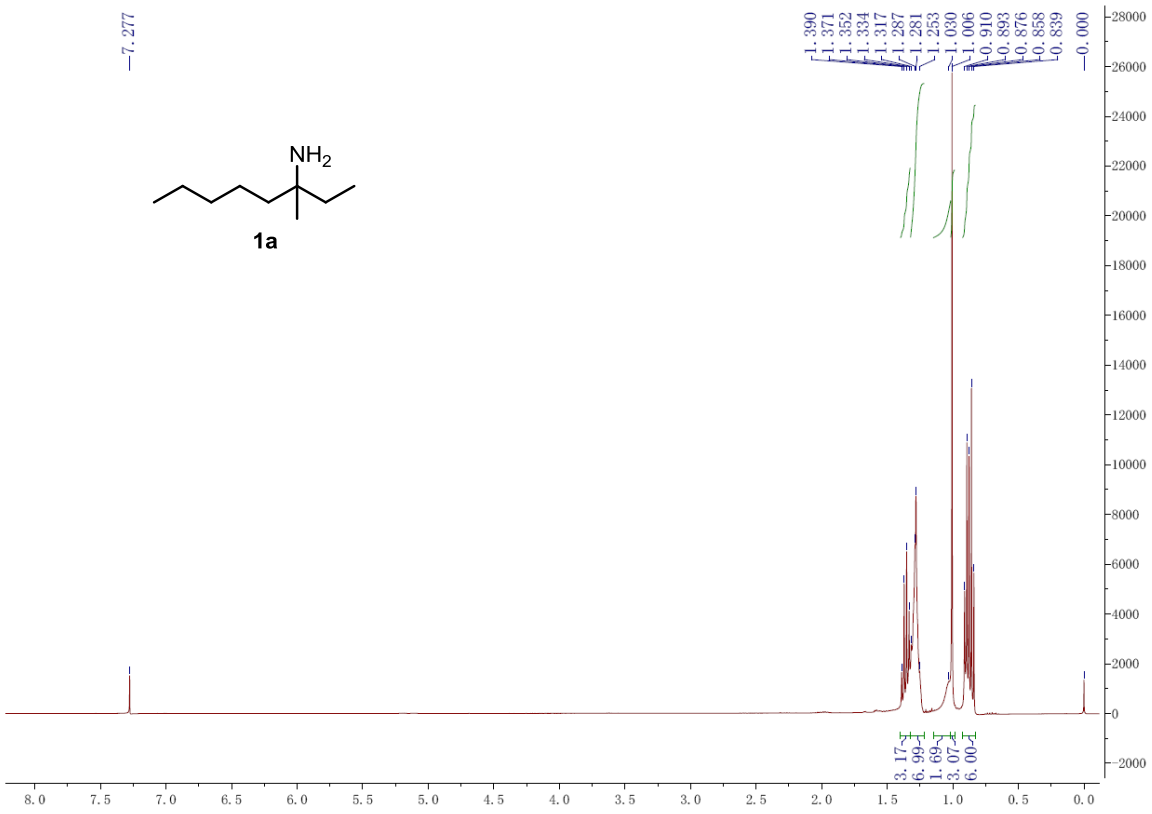
f1 (ppm)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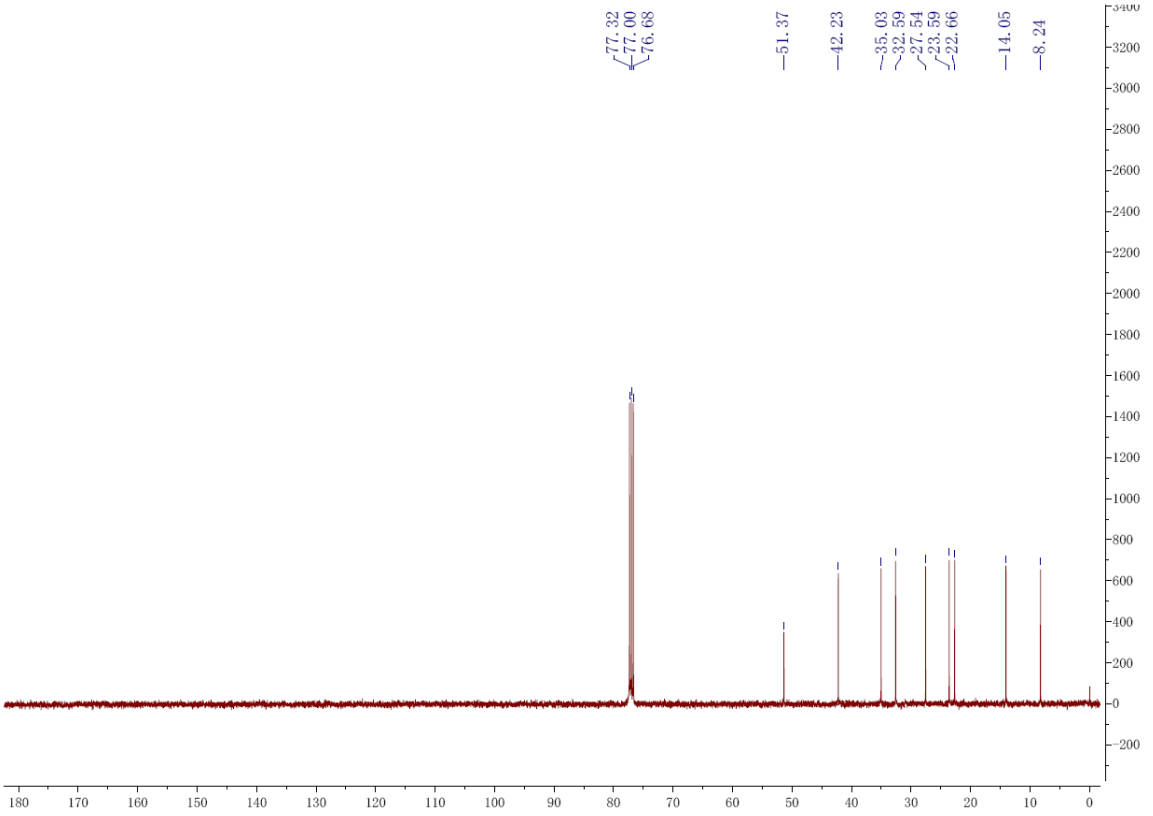
6.00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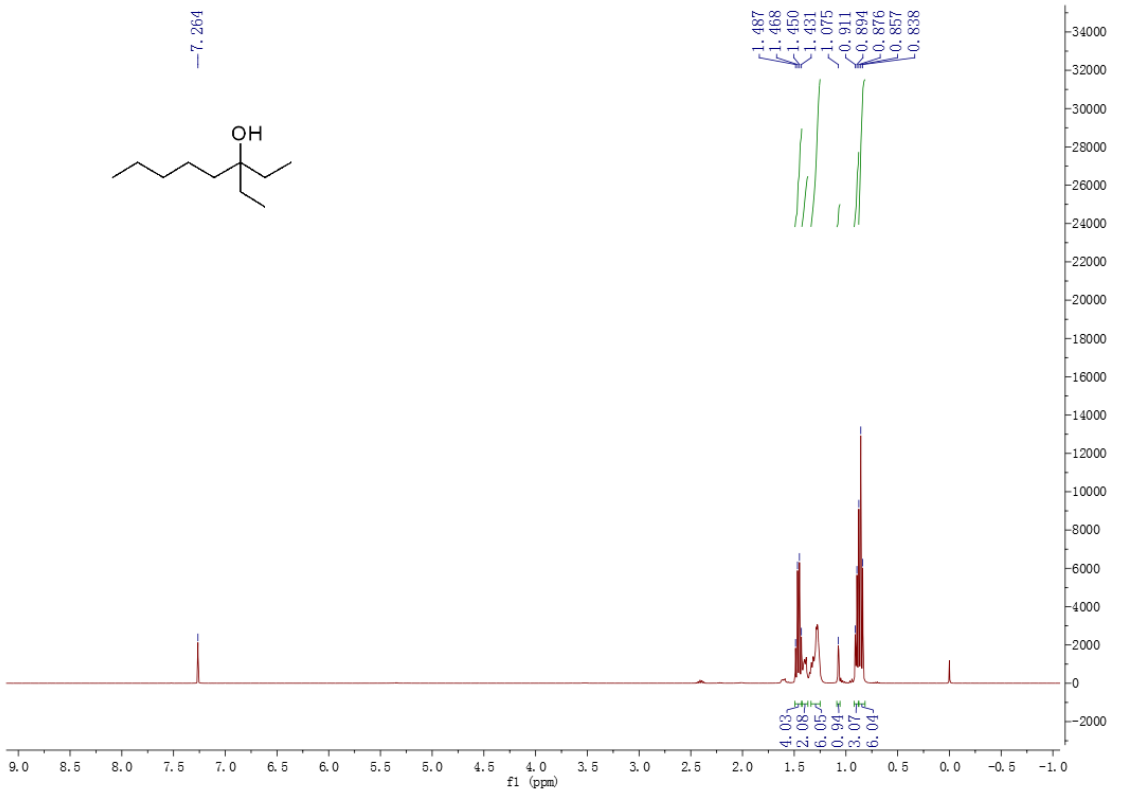
8.24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2.08
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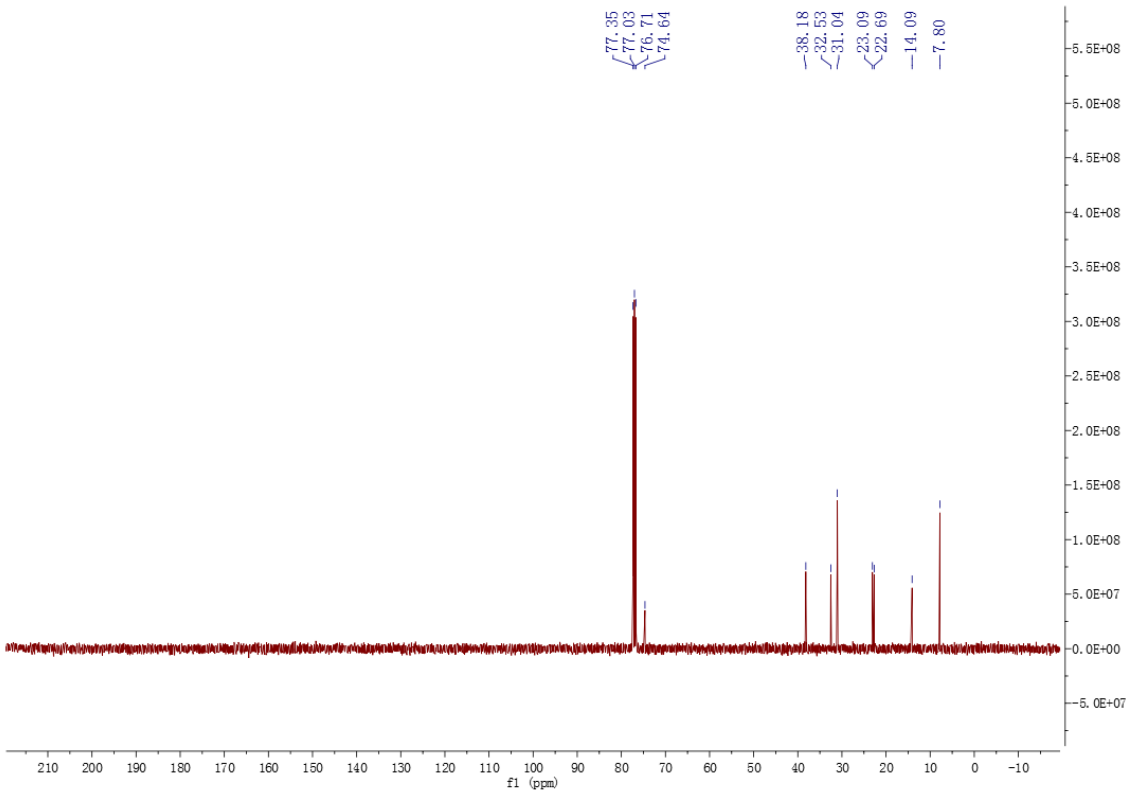
0.94
3.07
6.04
f1 (ppm)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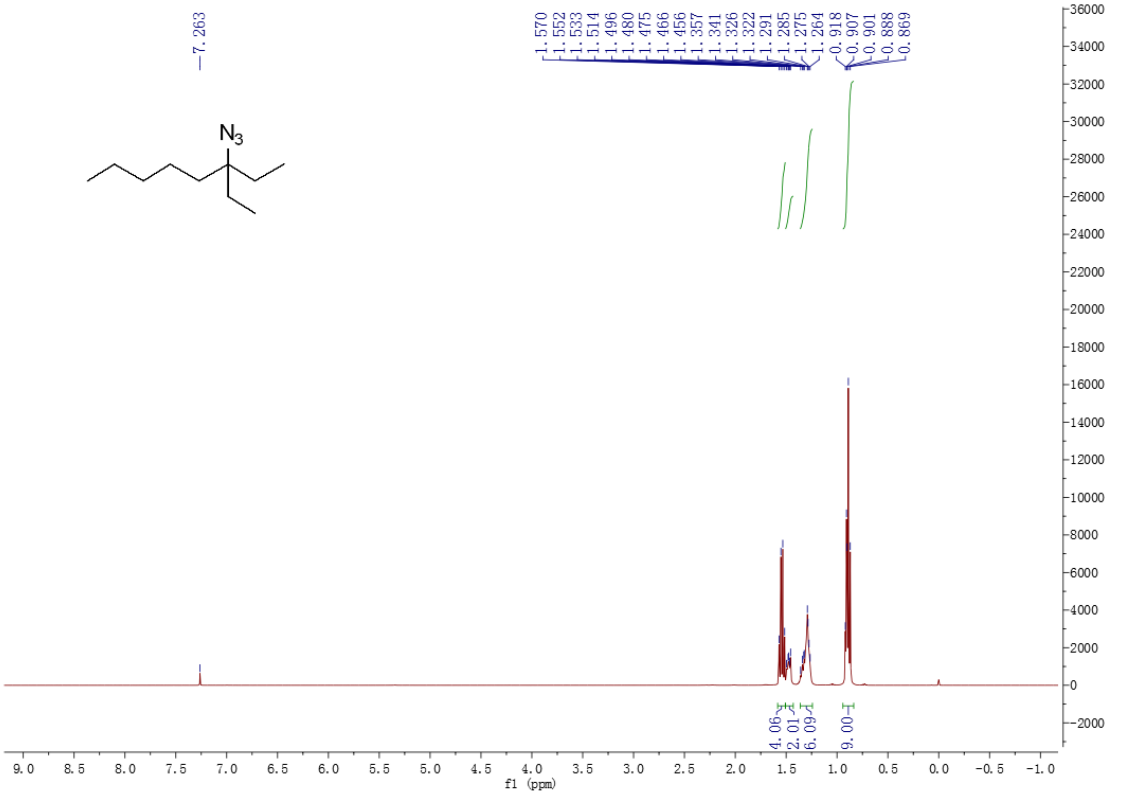
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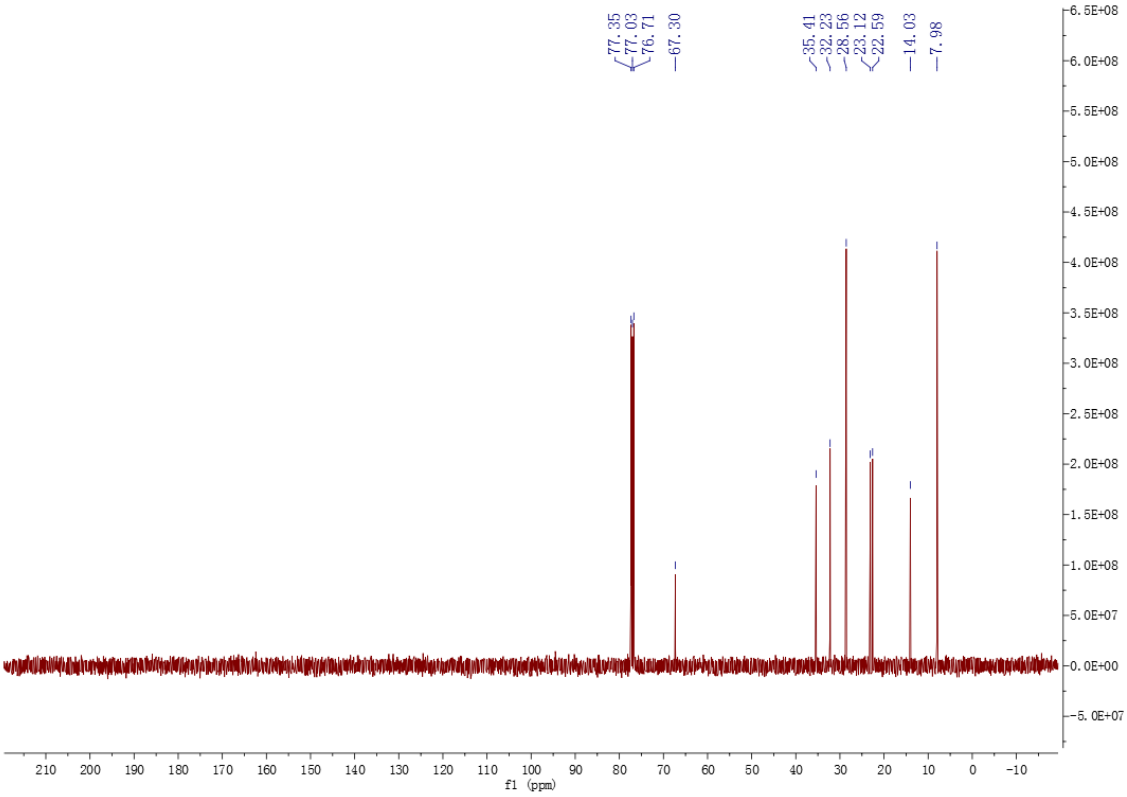
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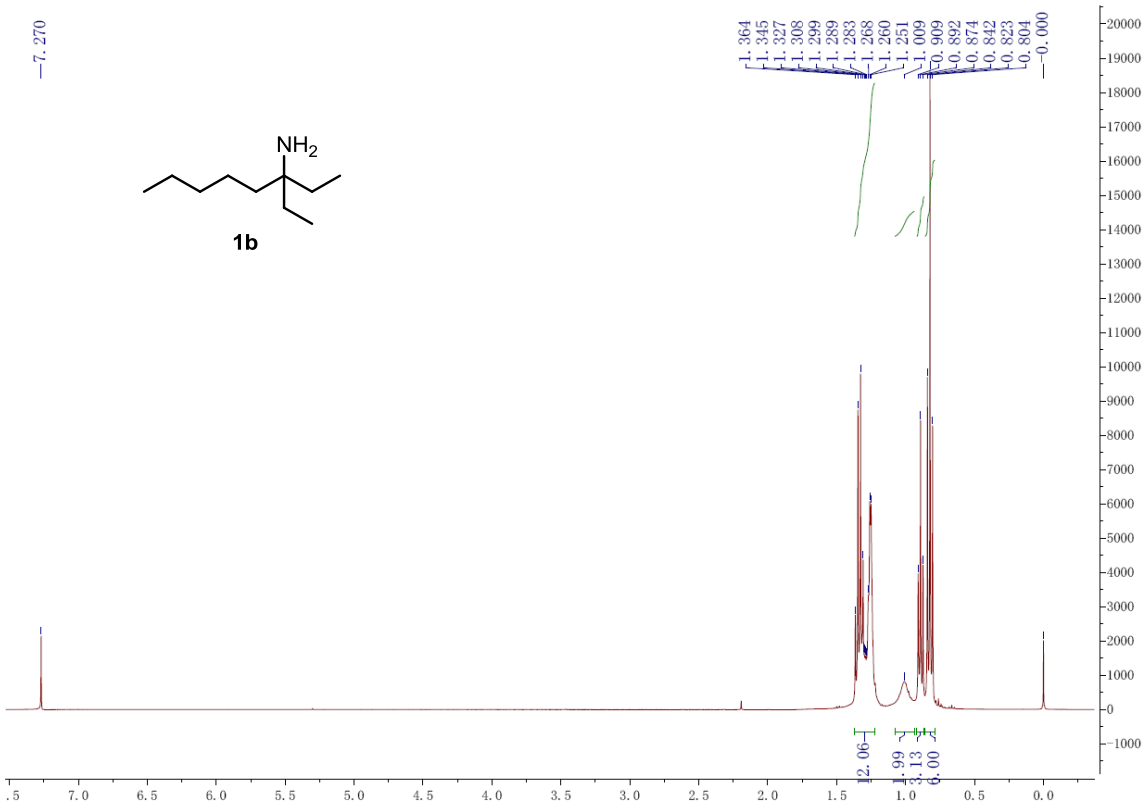
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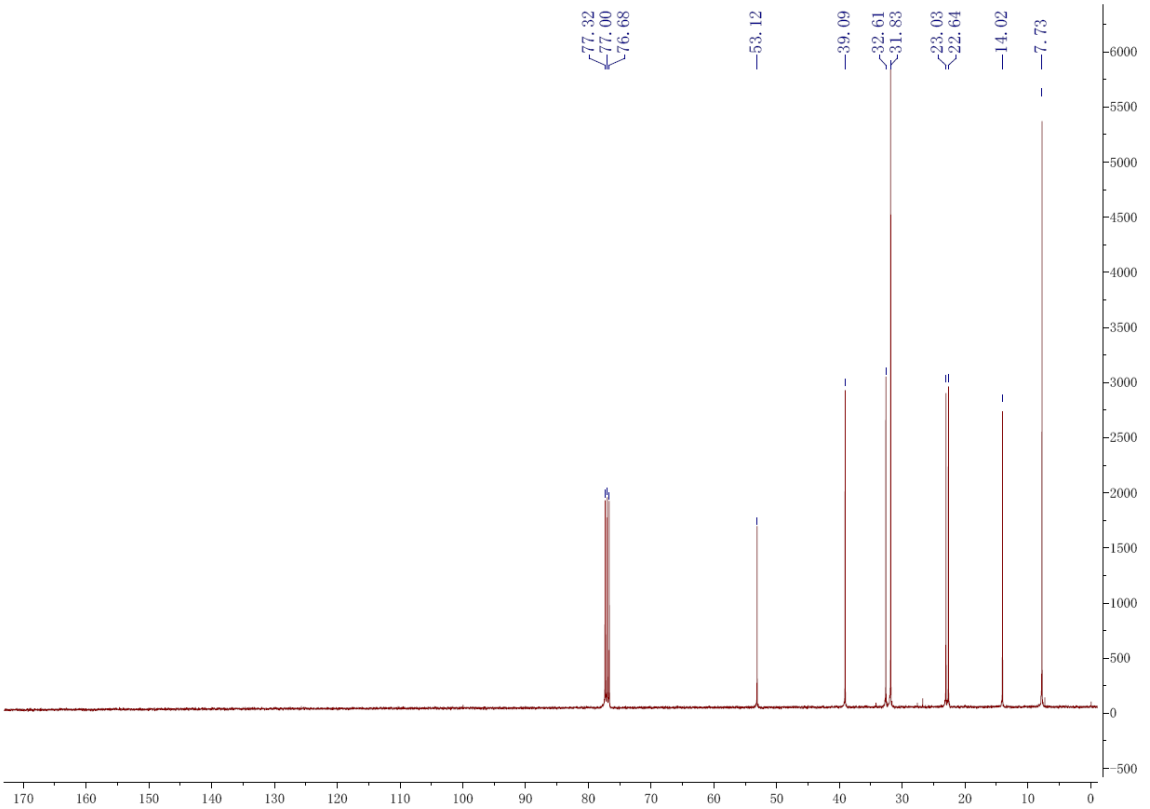
6.00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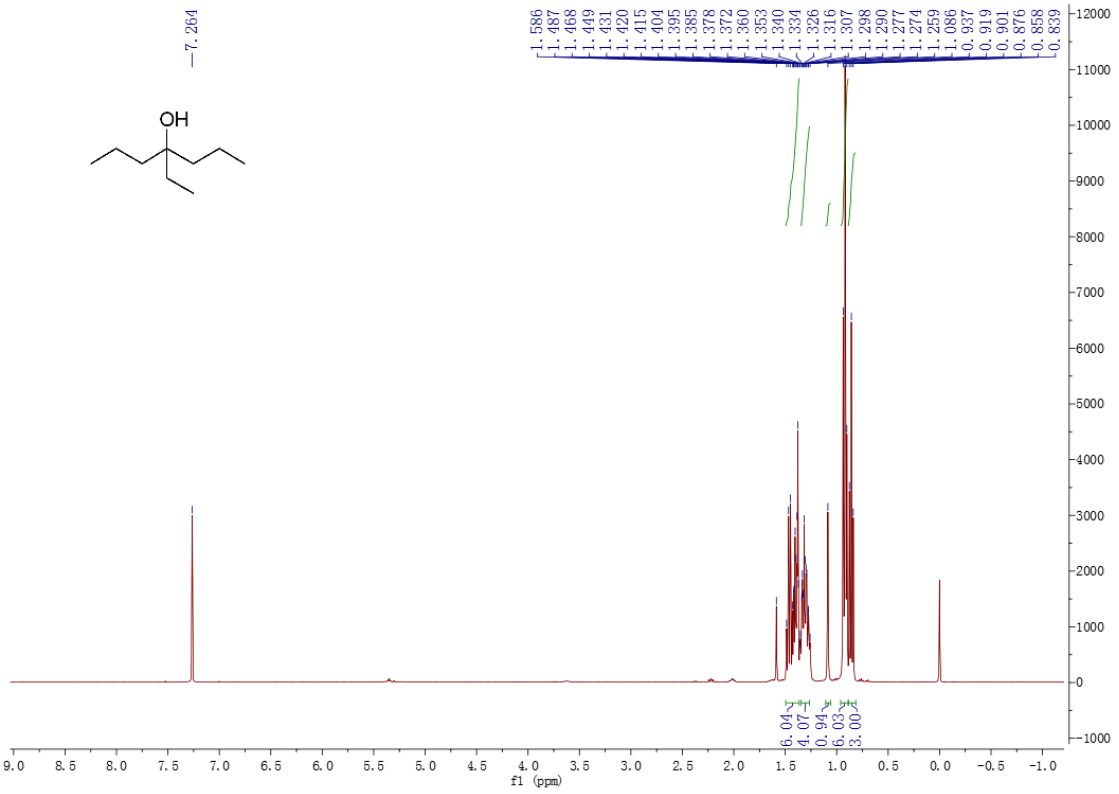
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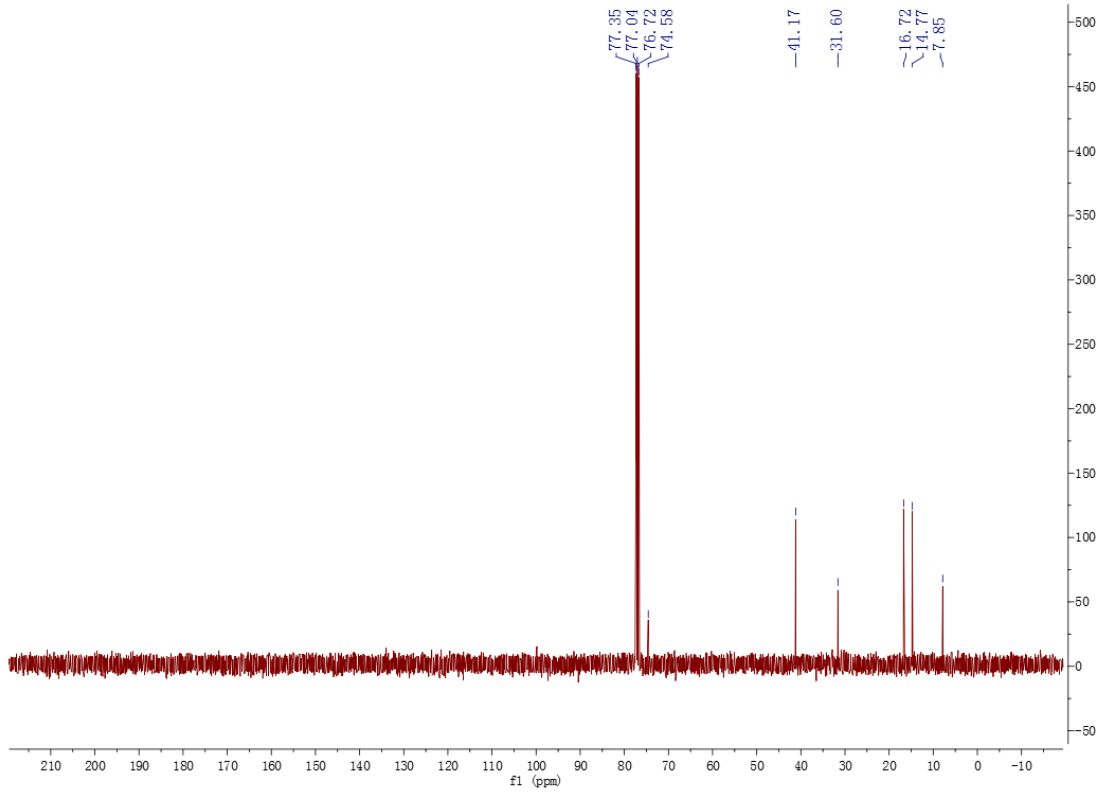
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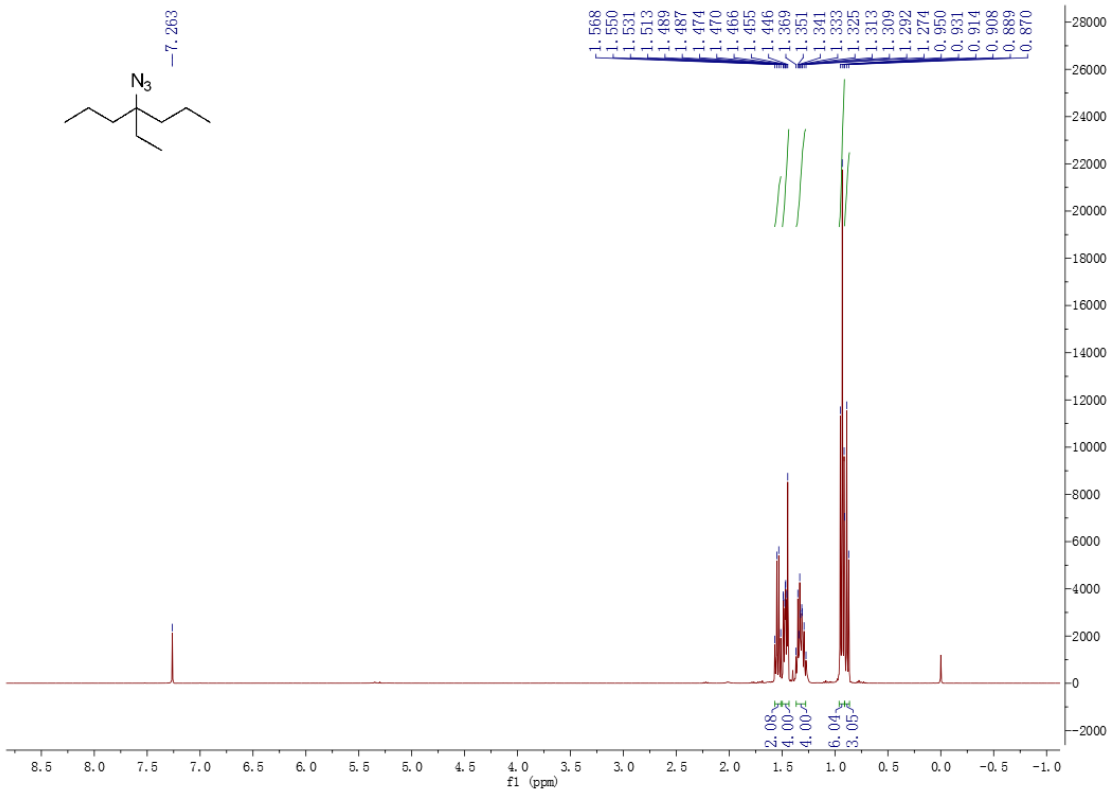
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4.00
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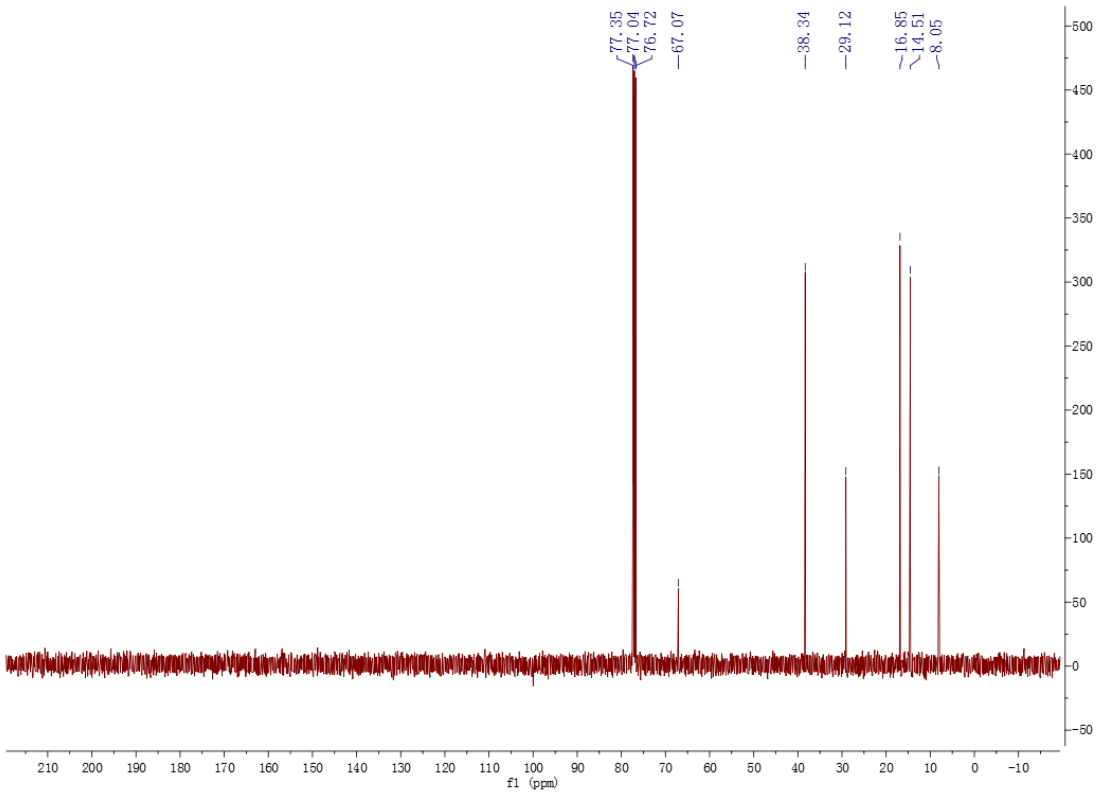
3.05
f1 (ppm)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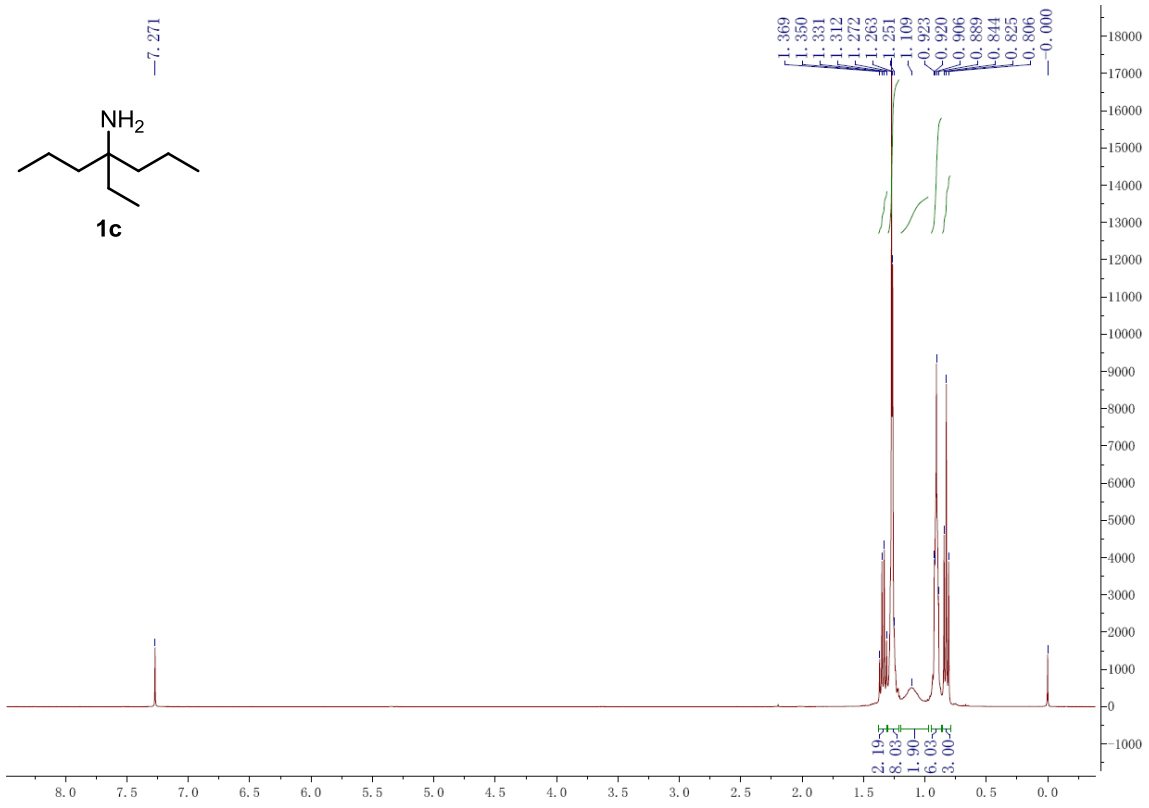
14.51
8.05
f1 (ppm)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1.251
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0.906
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0.000
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1c
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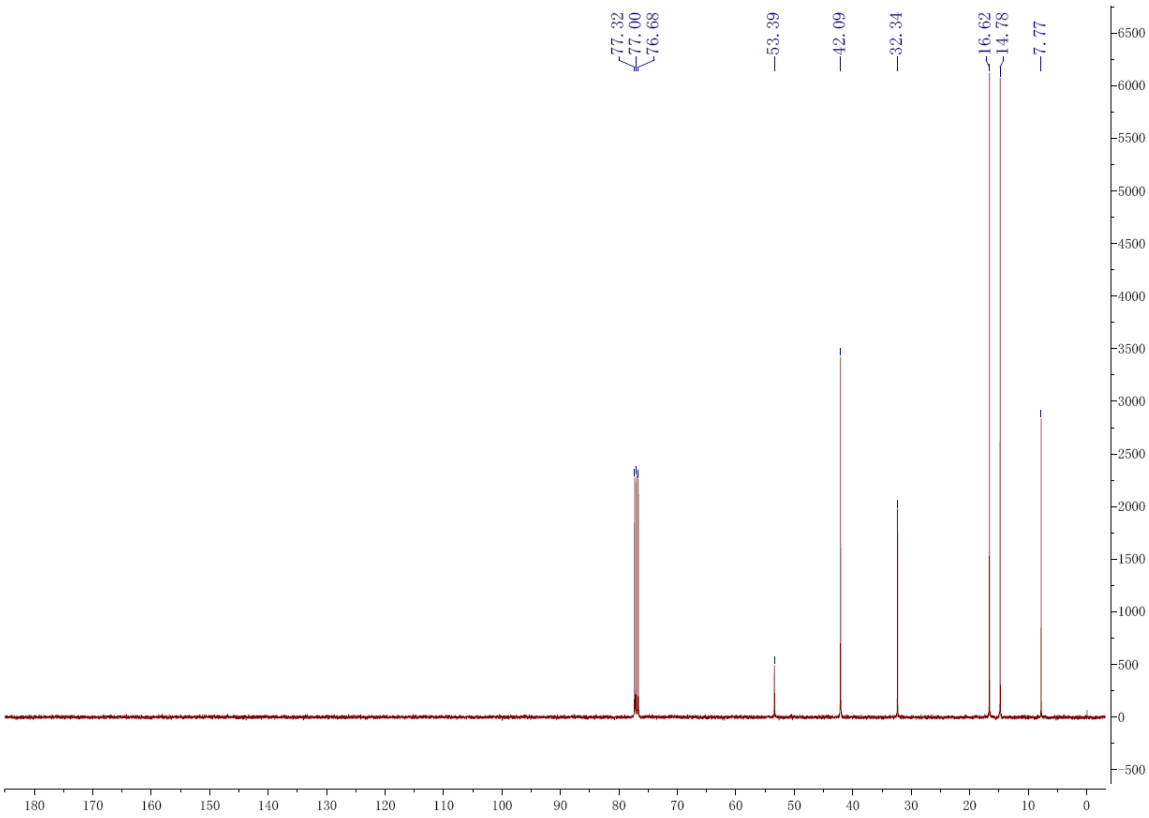
6.03
3.00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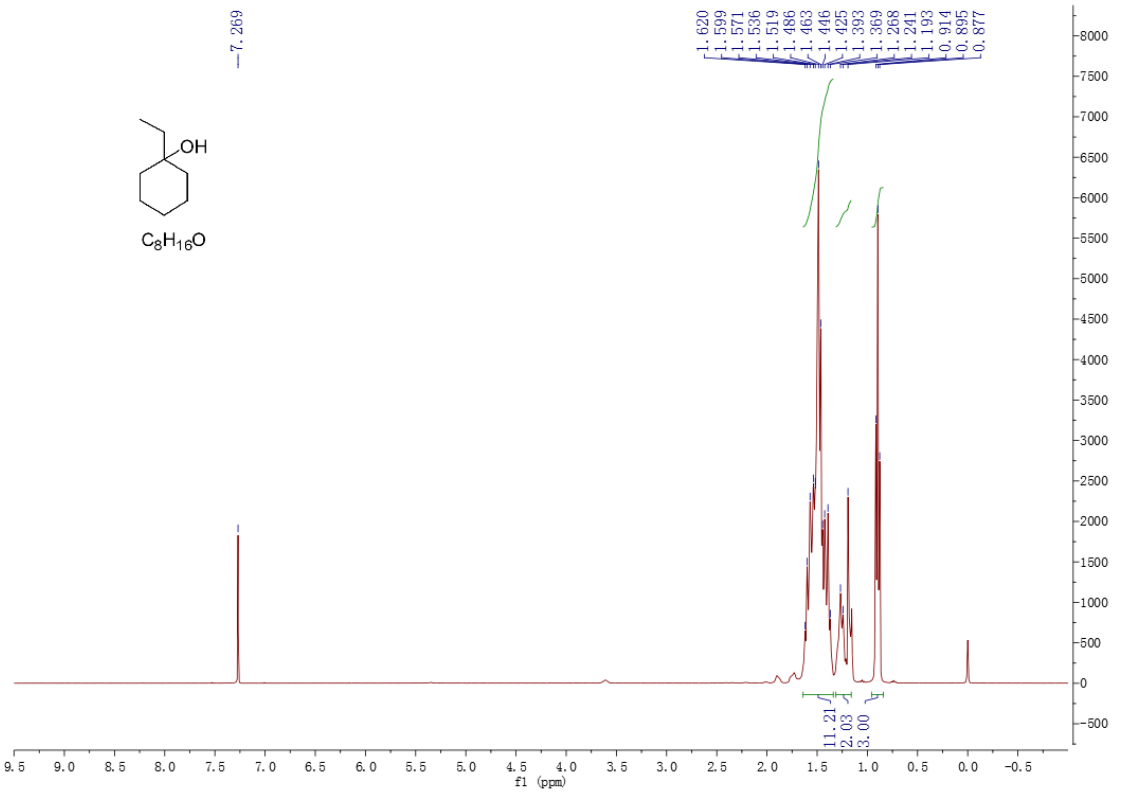
7.77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1.268
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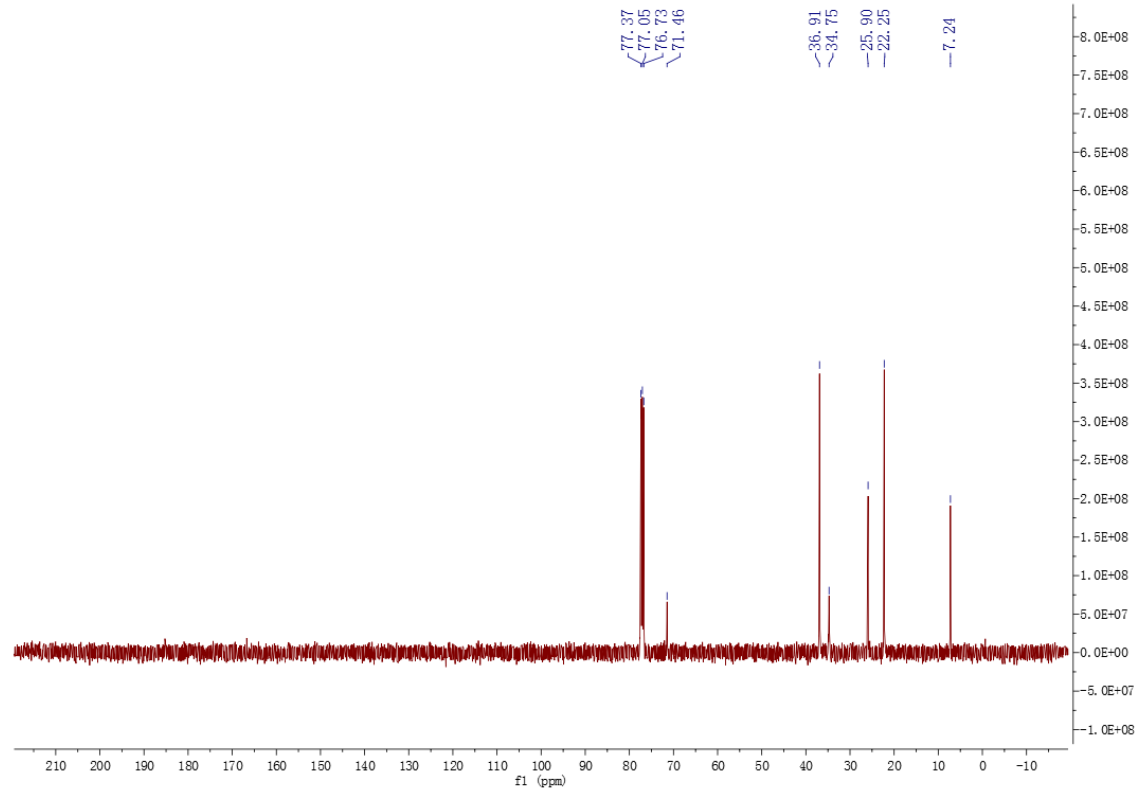
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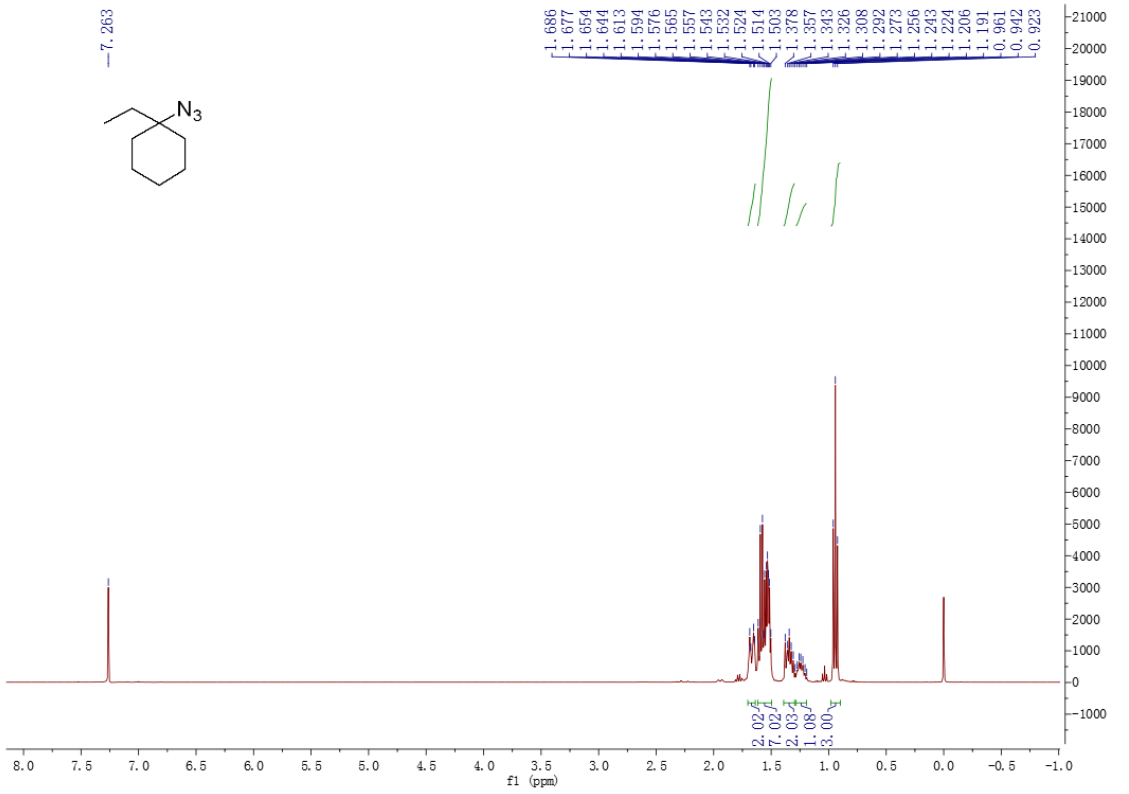
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1.503
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1.326
1.308
1.292
1.273
1.256
1.243
1.224
1.206
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2.02
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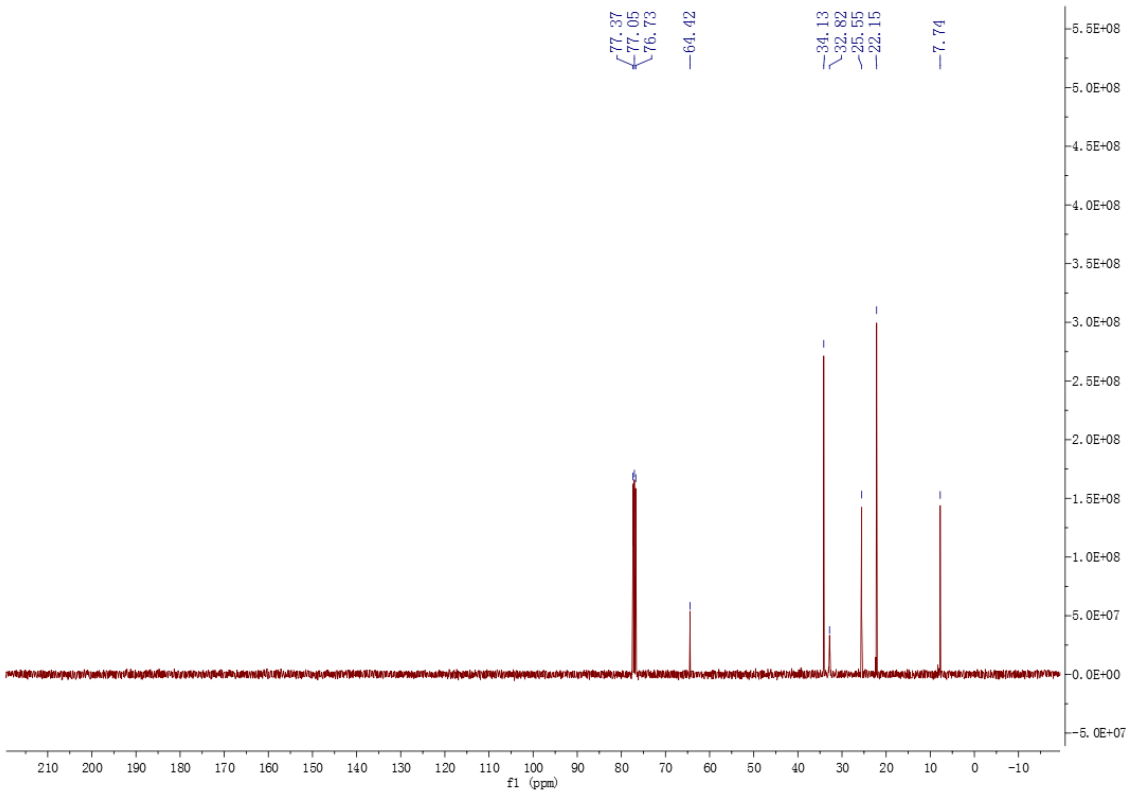
3.00
f1 (ppm)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7.74
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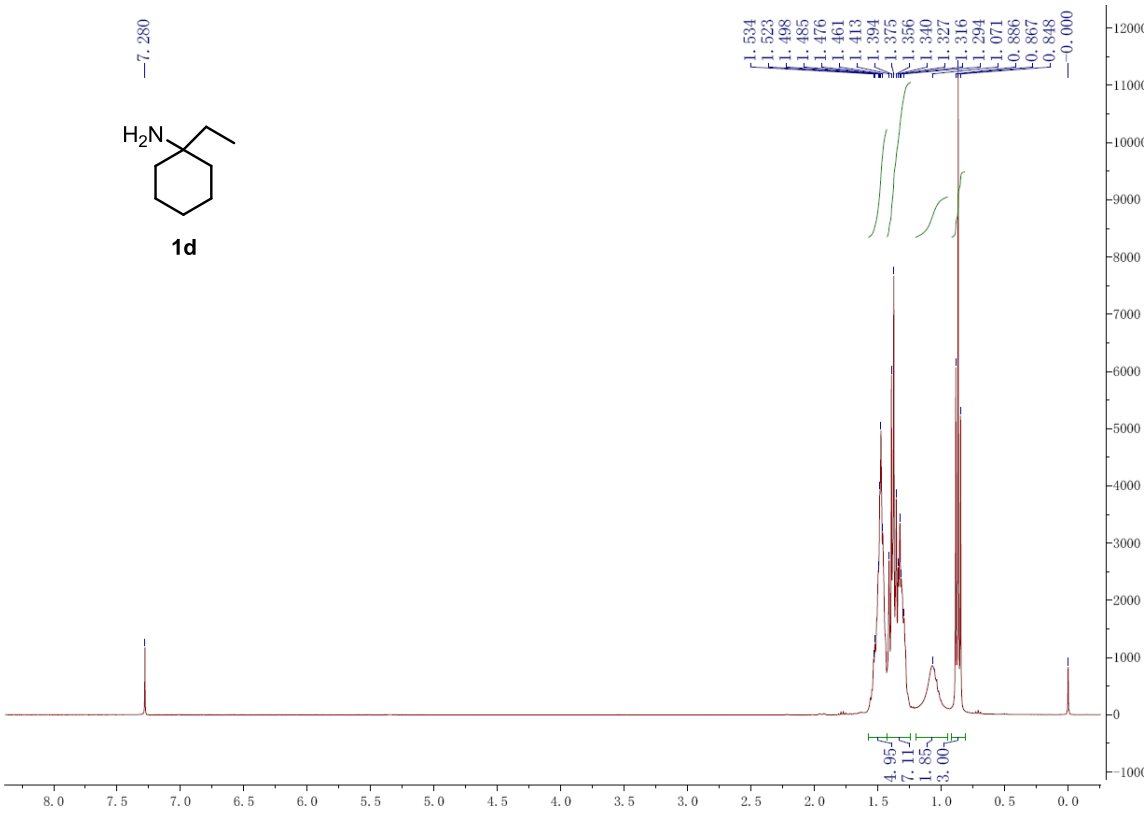
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1.327
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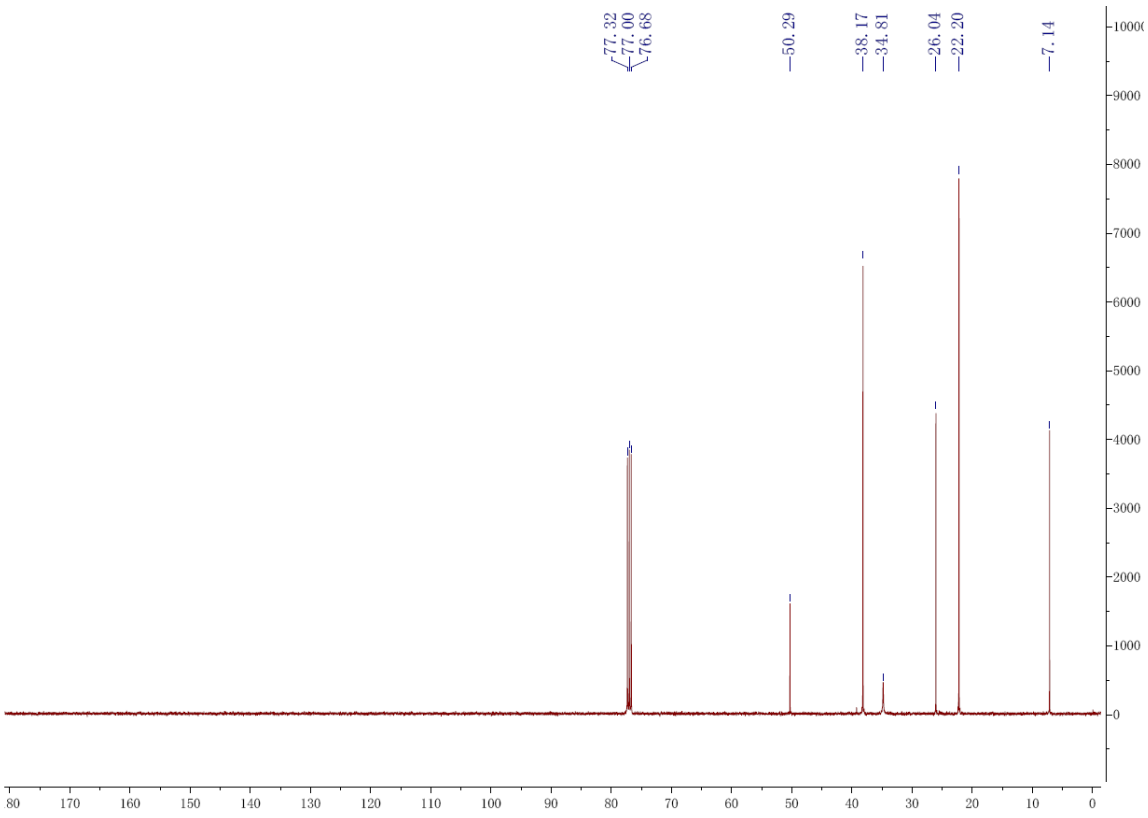
1d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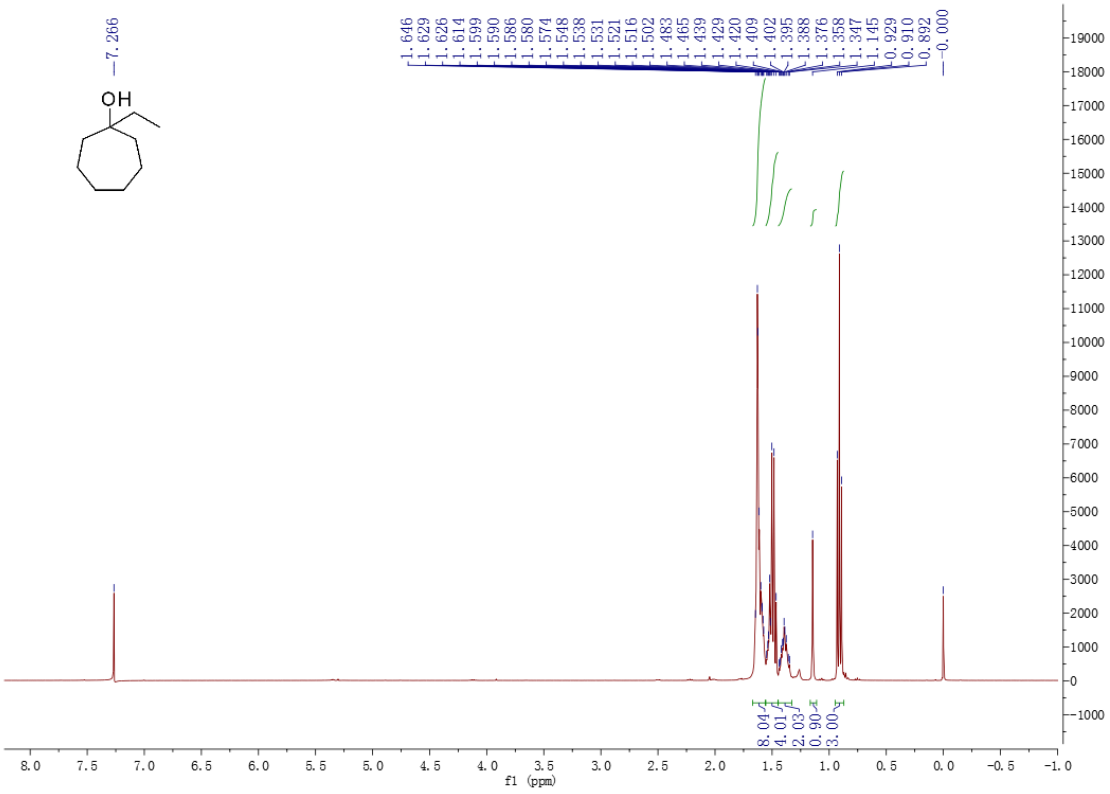
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1.599
1.590
1.586
1.580
1.574
1.548
1.538
1.531
1.521
1.516
1.502
1.483
1.465
1.439
1.429
1.420
1.409
1.402
1.395
1.388
1.376
1.358
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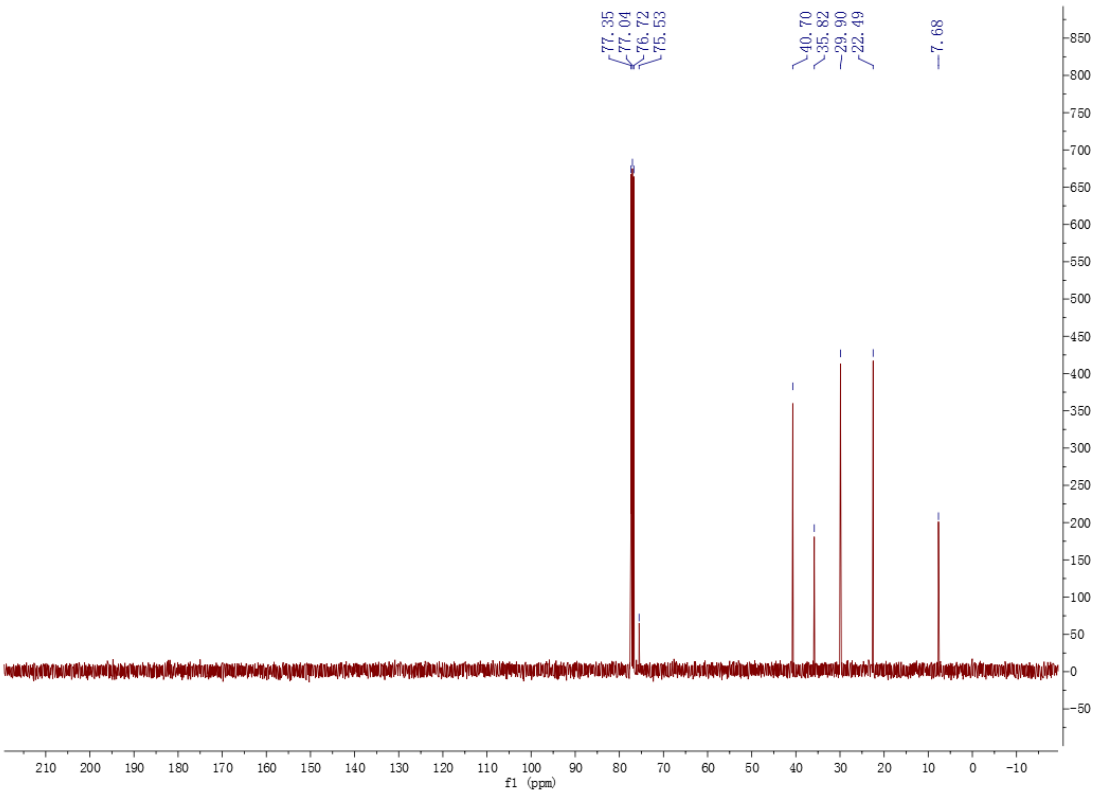
3.00
f1 (ppm)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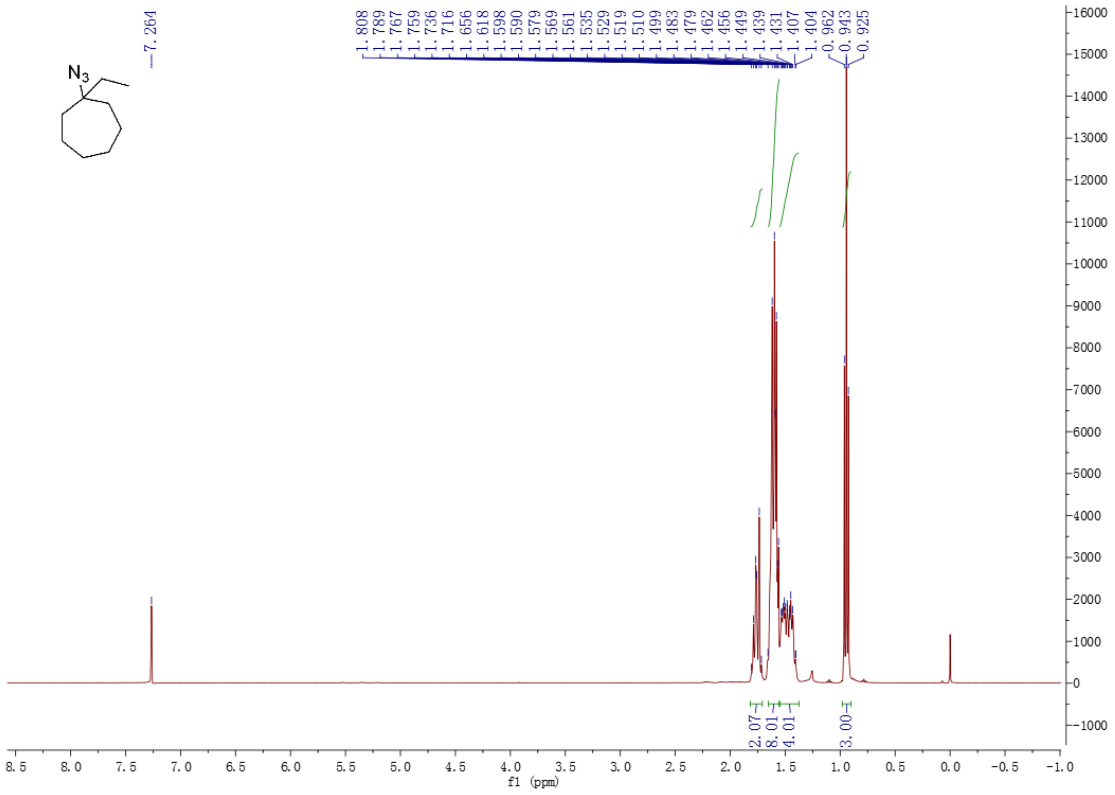
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1.598
1.590
1.579
1.569
1.561
1.535
1.529
1.519
1.510
1.499
1.483
1.479
1.462
1.456
1.449
1.439
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0.962
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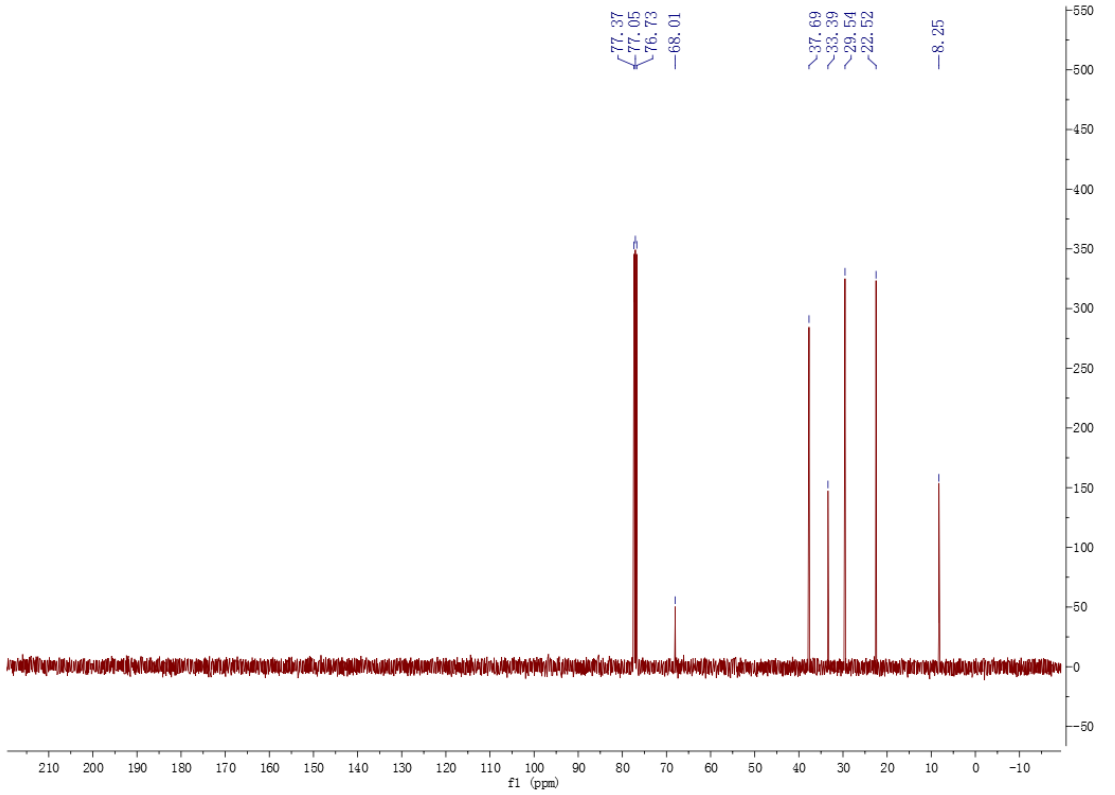
4.01
3.00
f1 (ppm)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33.39
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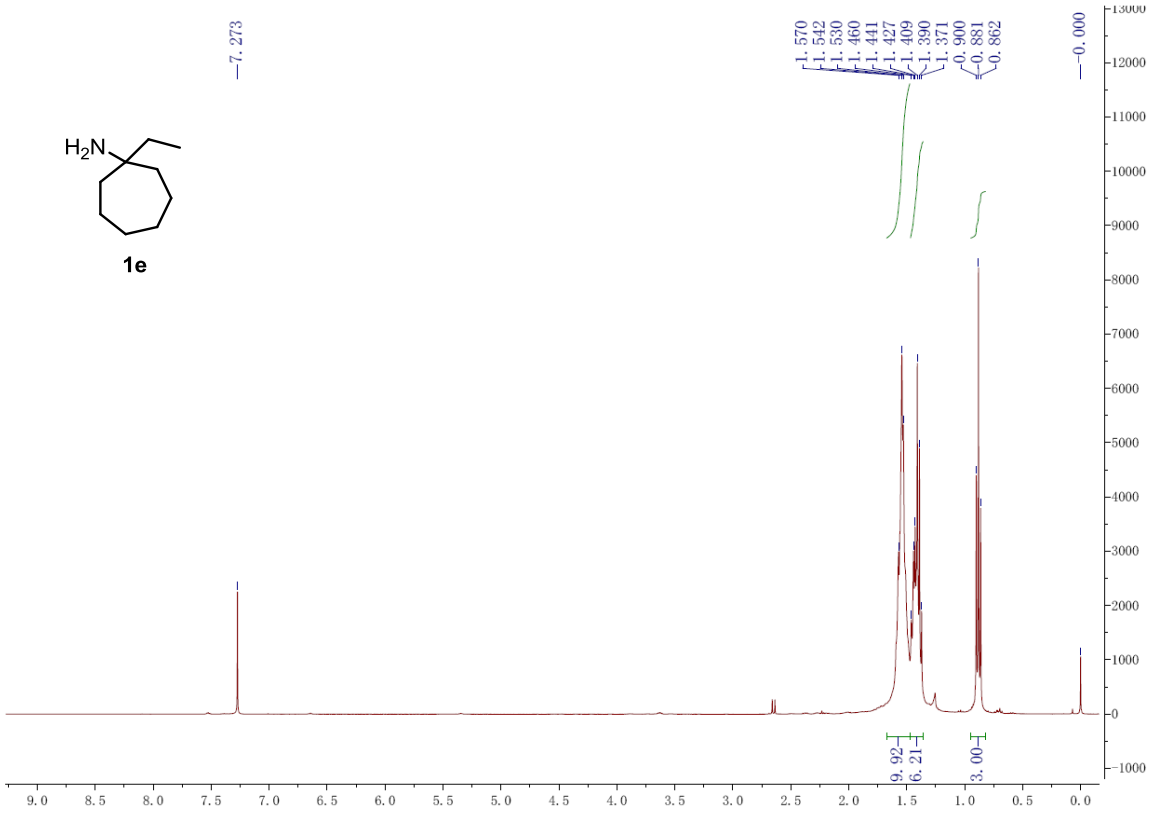
22.52
8.25
f1 (ppm)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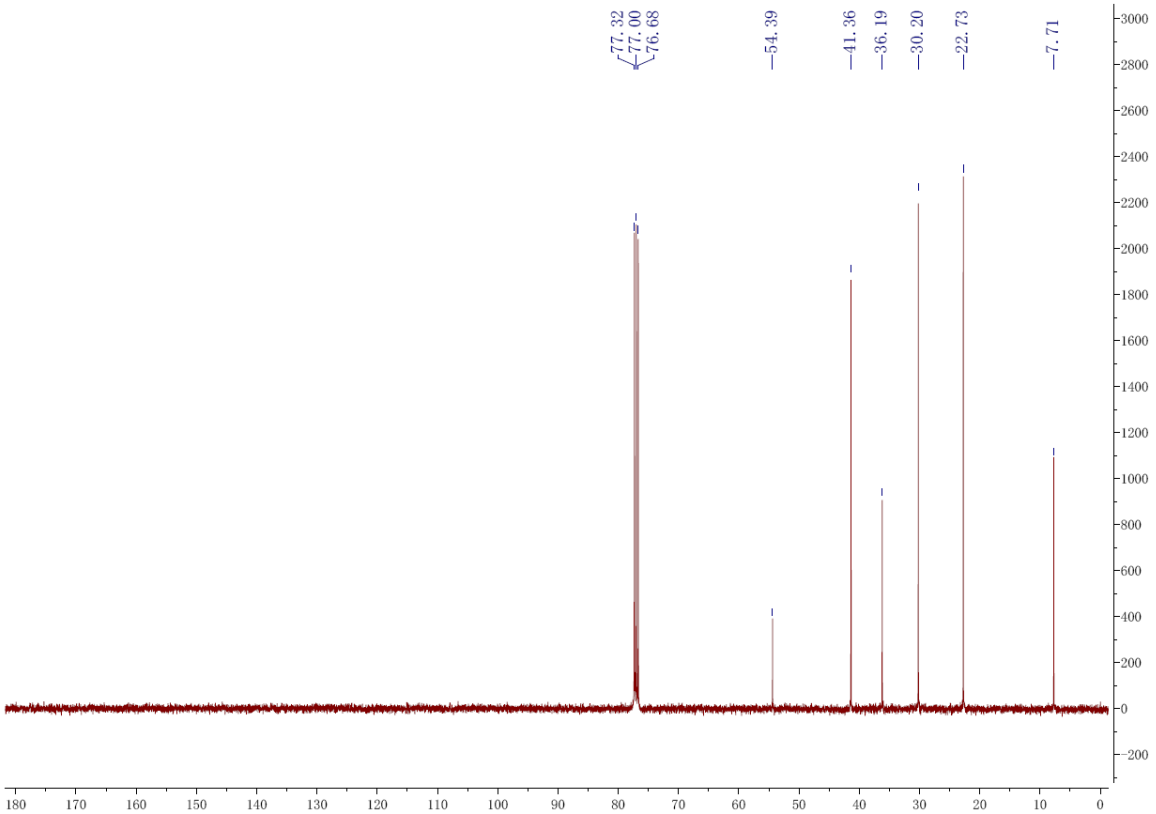
1e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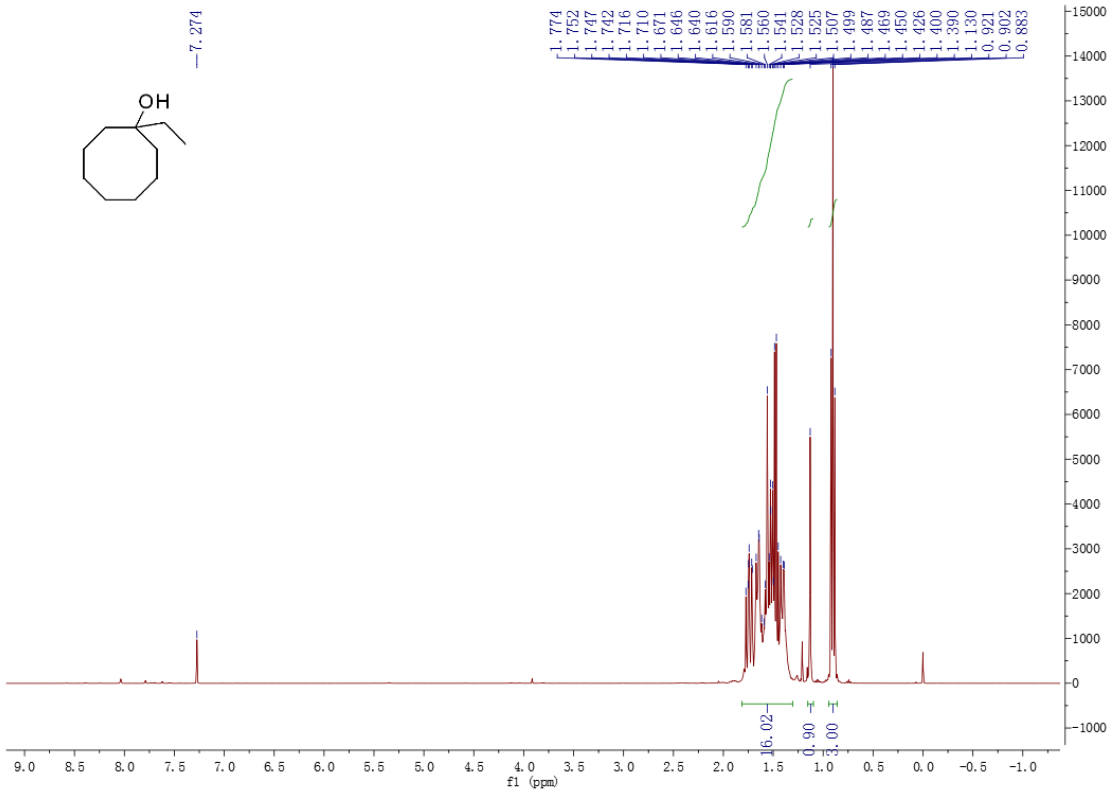
7.71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1.581
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1.541
1.528
1.525
1.507
1.499
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1.469
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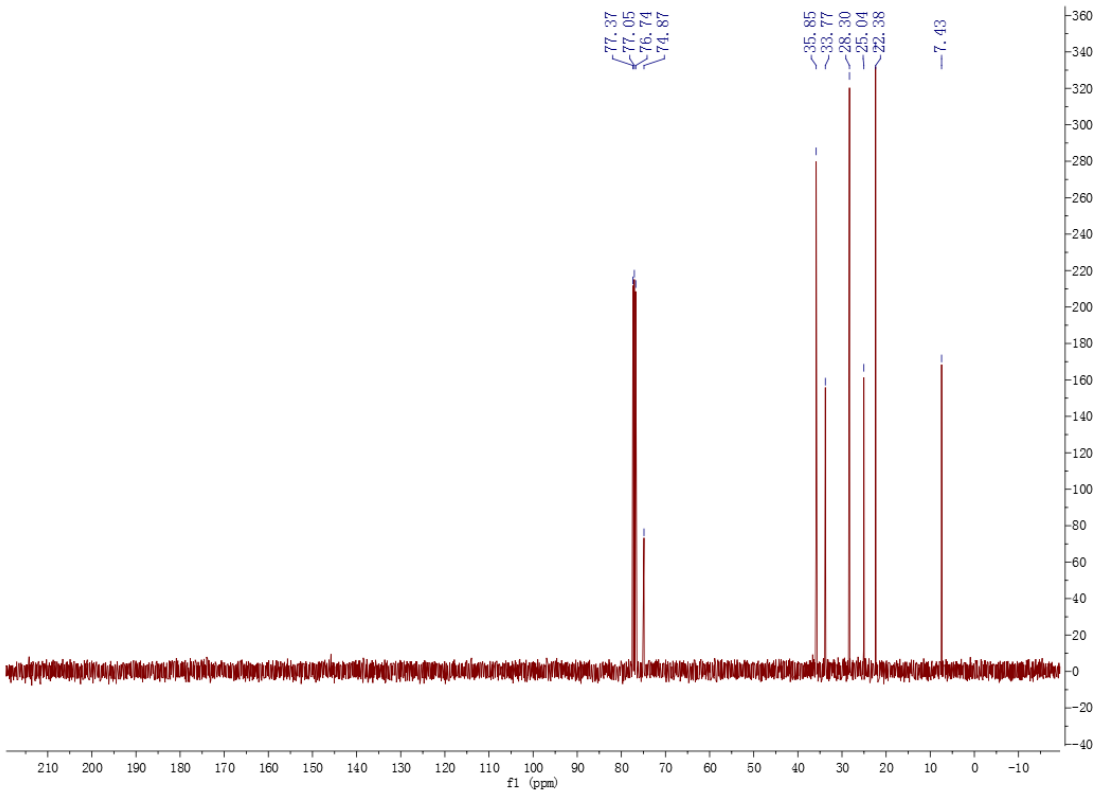
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7.43
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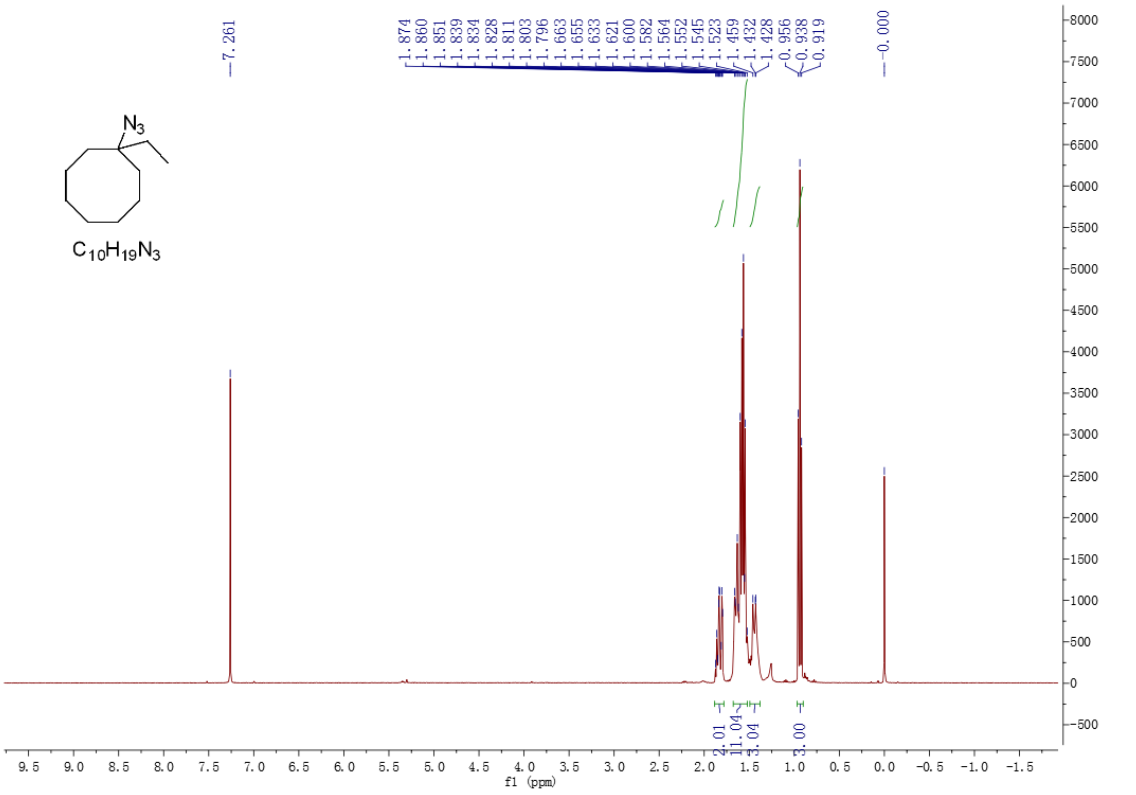
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1.655
1.633
1.621
1.600
1.582
1.564
1.552
1.545
1.523
1.459
1.432
1.428
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C10H19N3
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3.00
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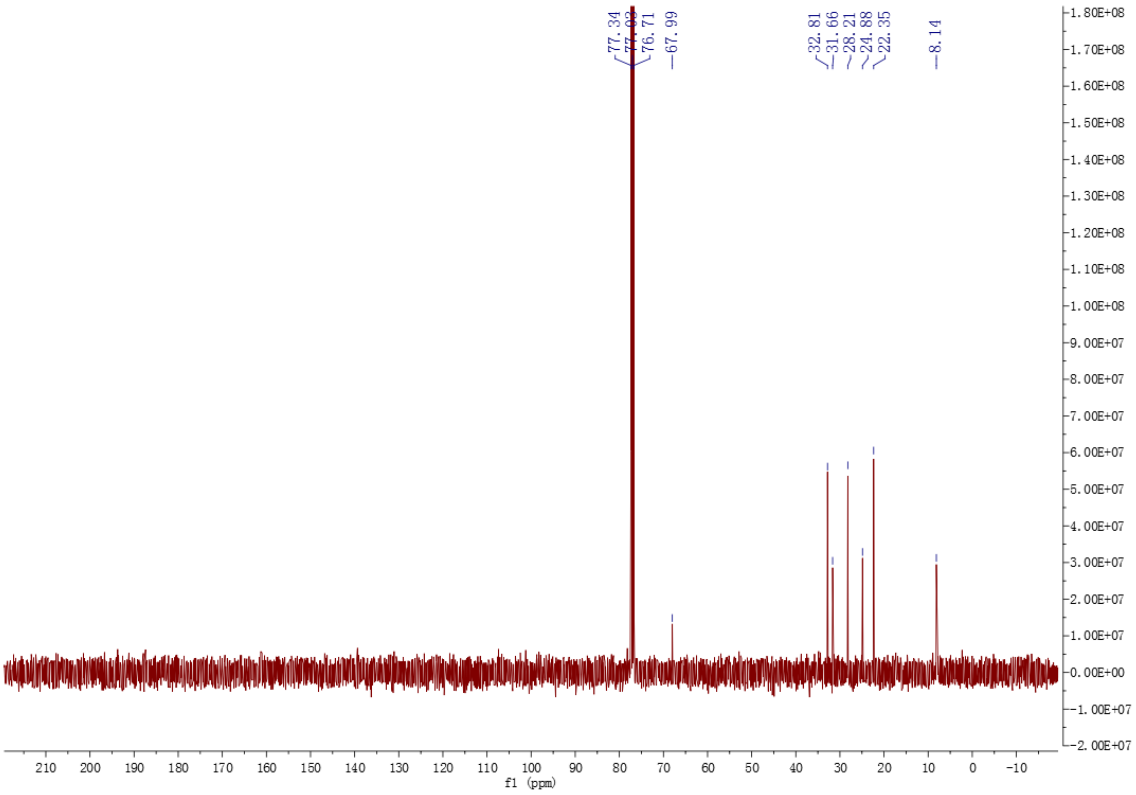
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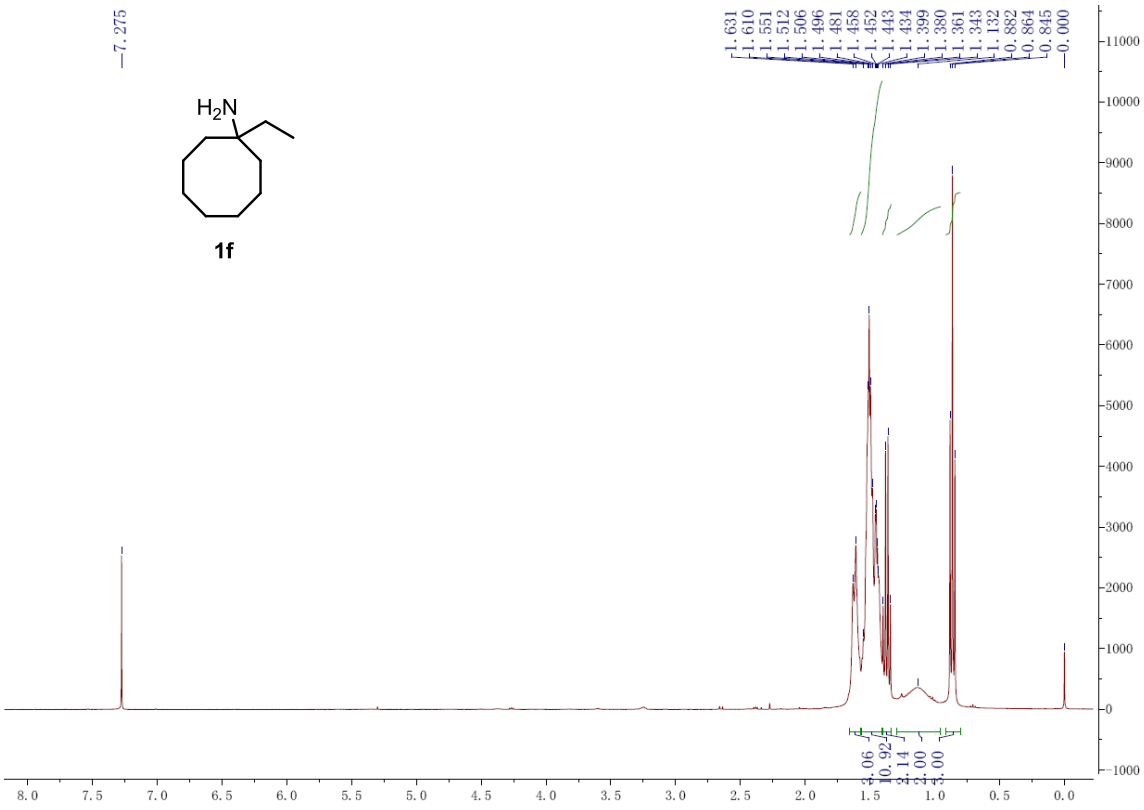
f1 (ppm)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1.380
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2.00
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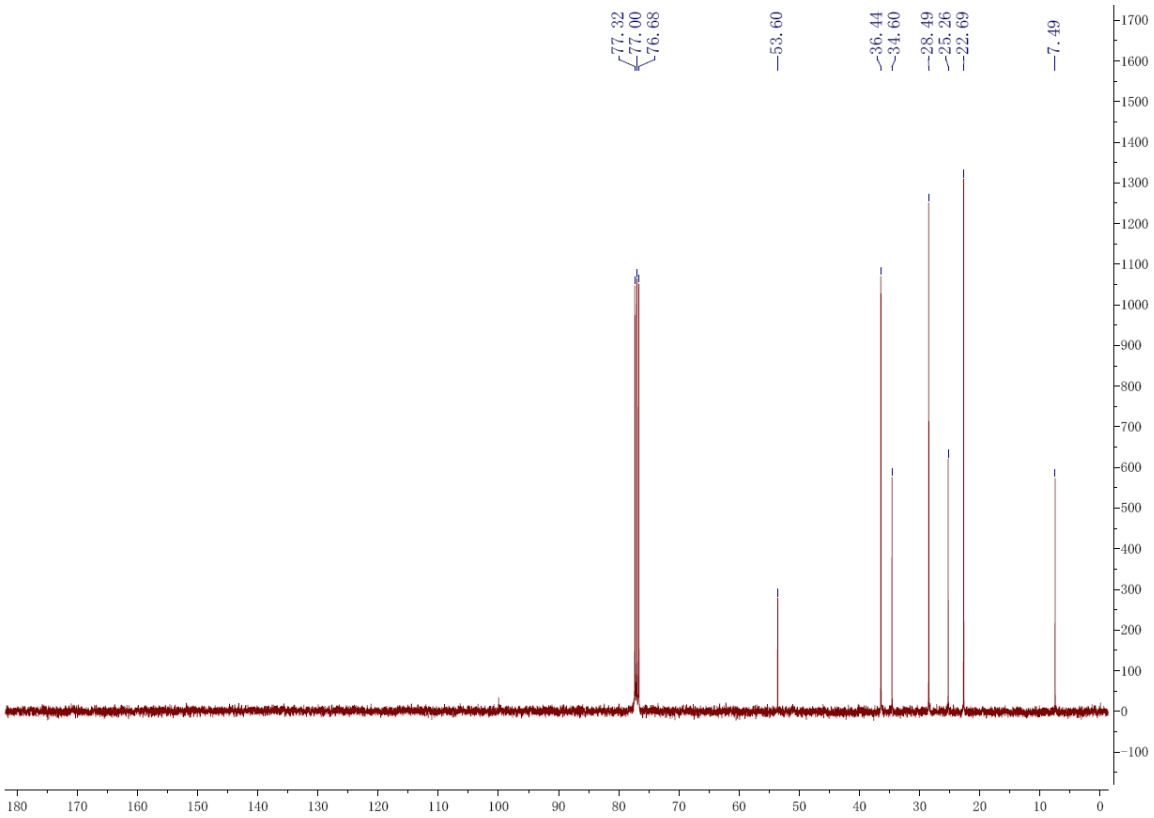
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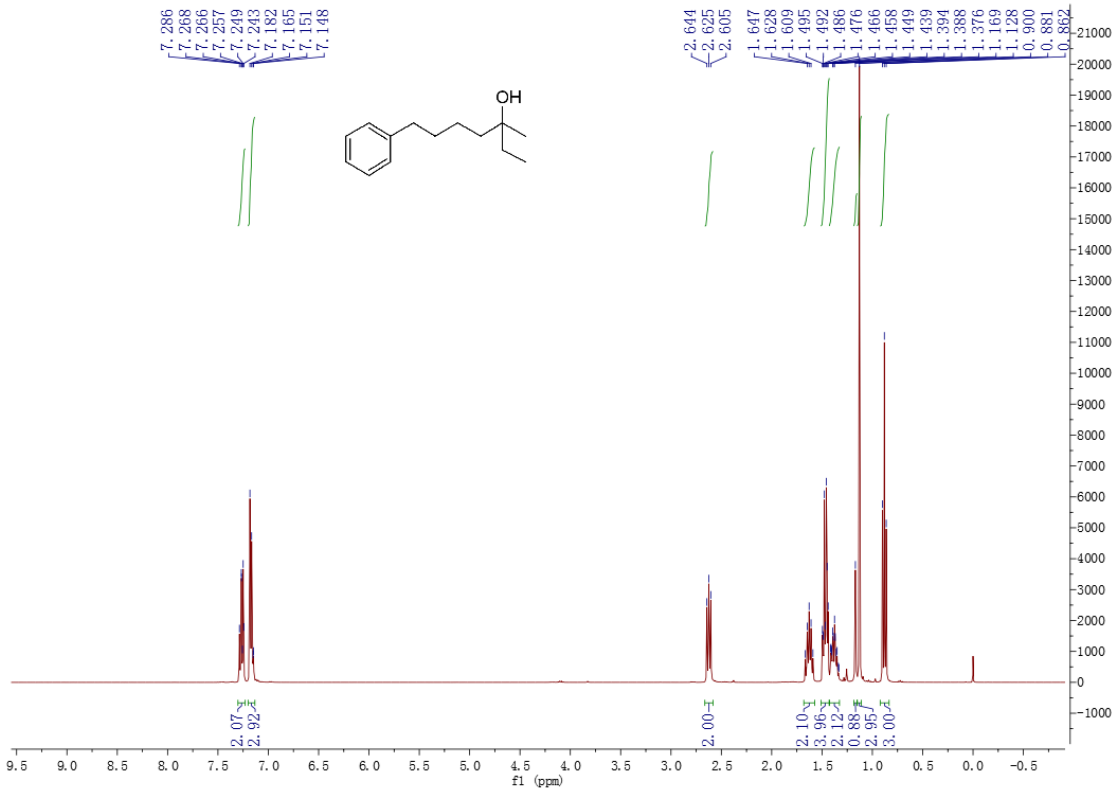
1f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1.476
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1.439
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1.376
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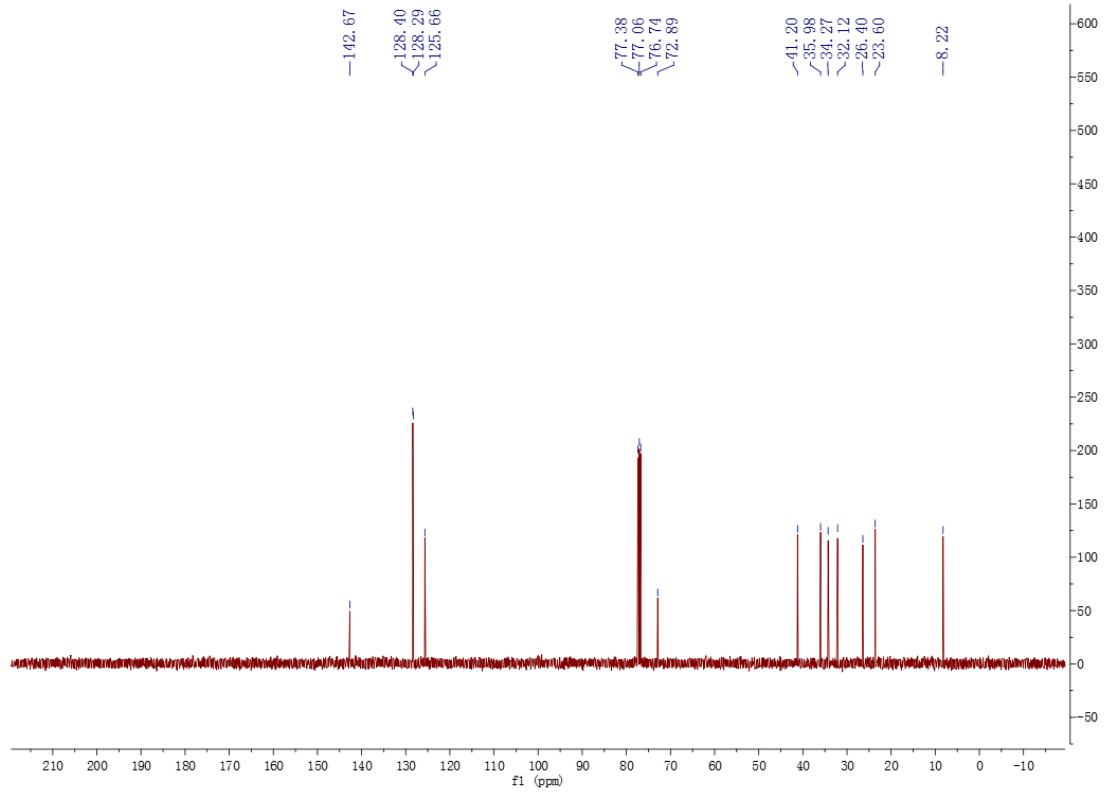
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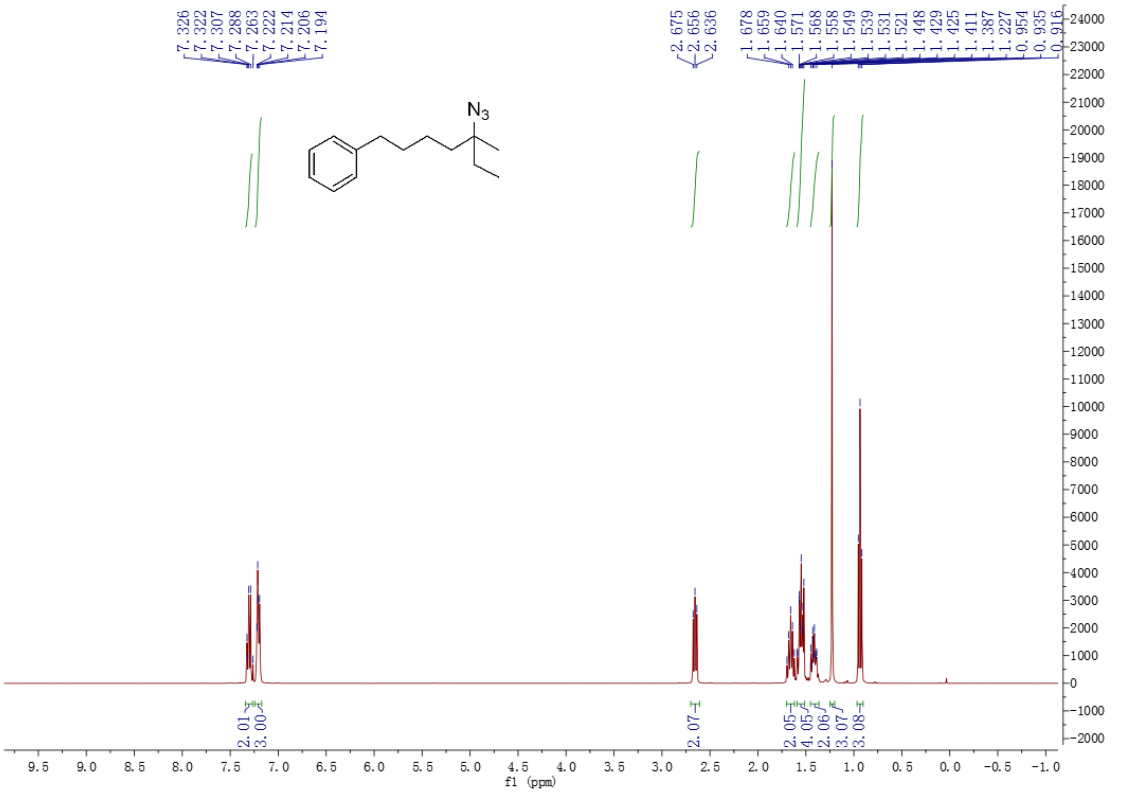
f1 (ppm)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1.640
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1.568
1.558
1.549
1.539
1.531
1.521
1.448
1.429
1.425
1.411
1.387
1.227
0.954
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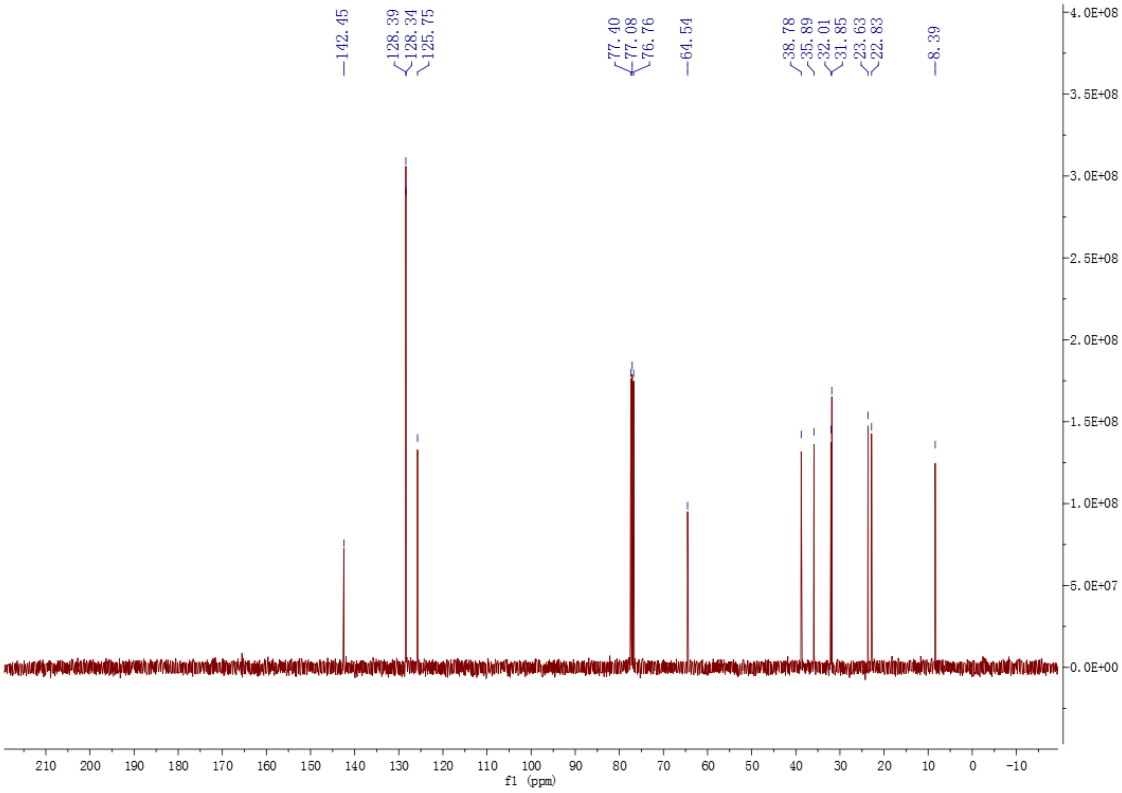
2.07
2.05
4.05
2.06
3.07
3.08
f1 (ppm)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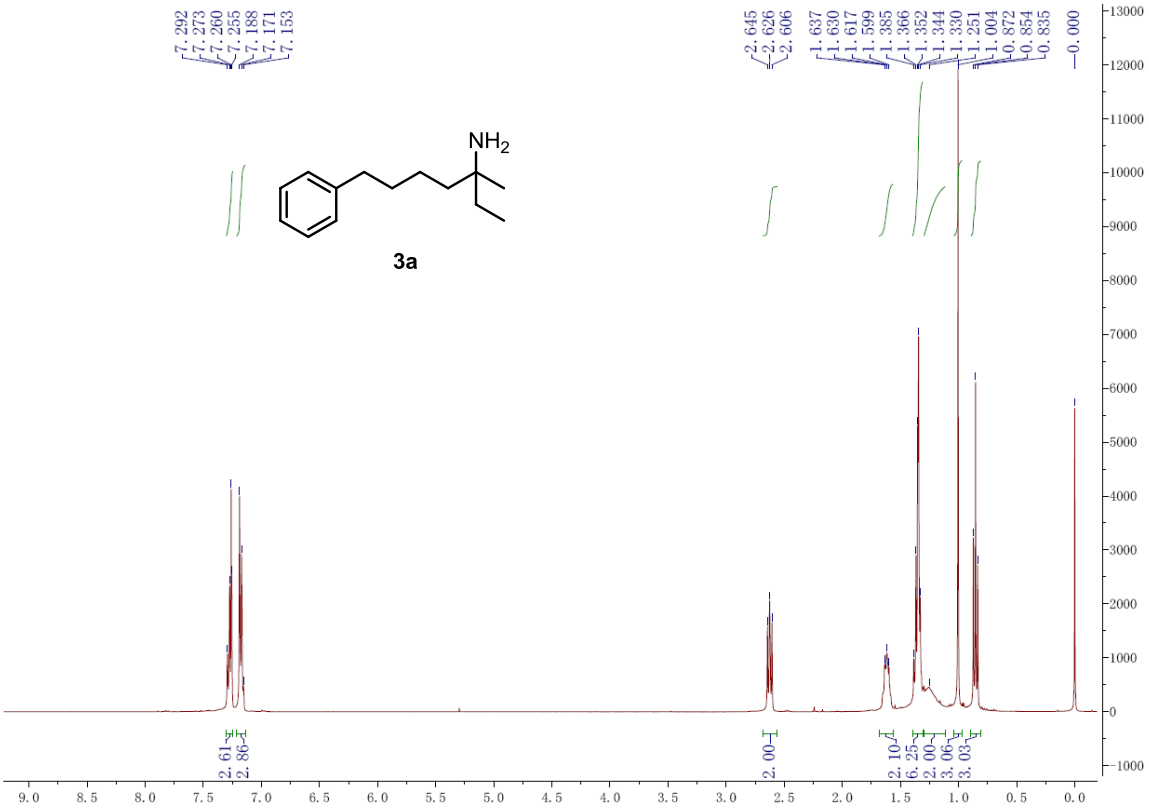
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1.385
1.366
1.352
1.344
1.330
1.251
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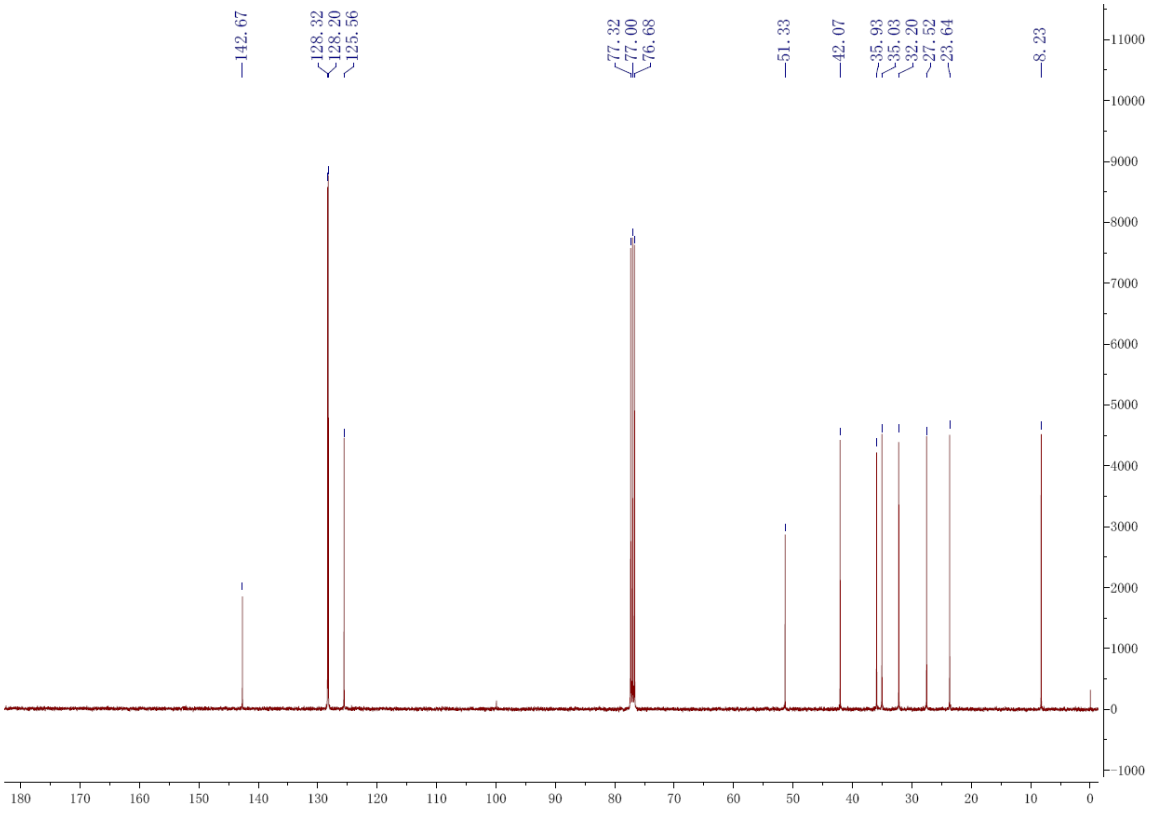
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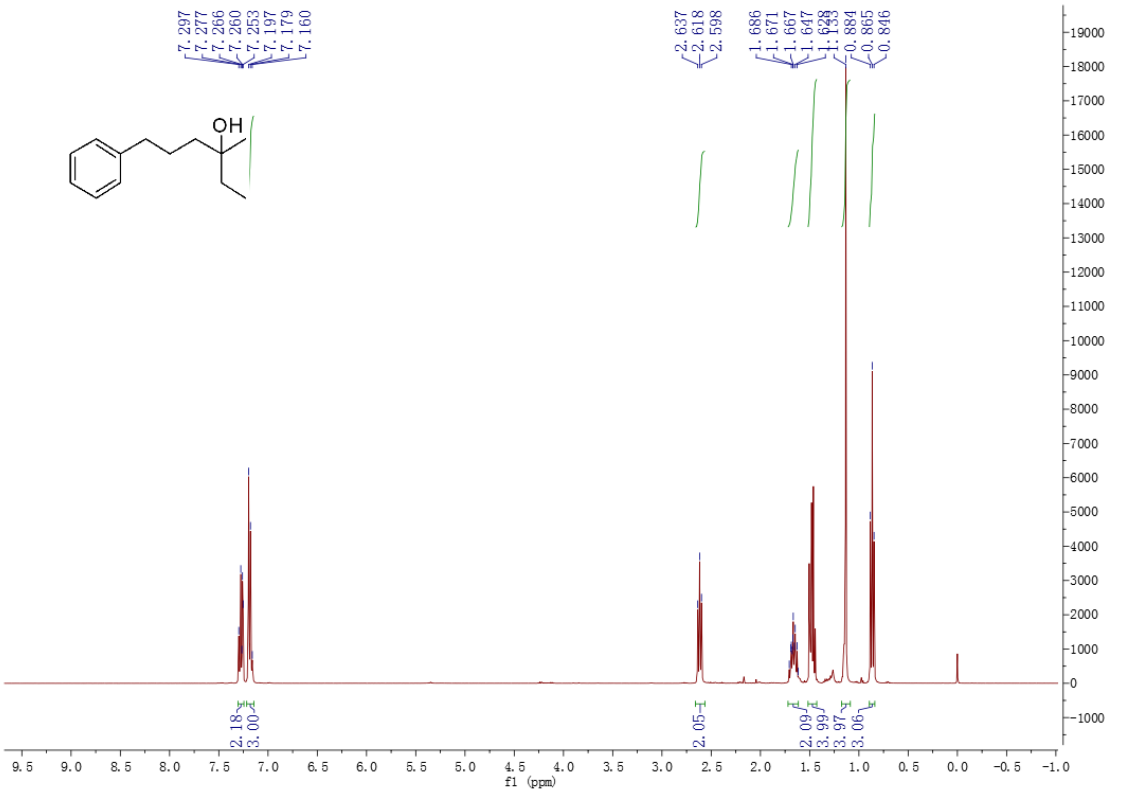
8.23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1.647
1.628
1.133
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OH
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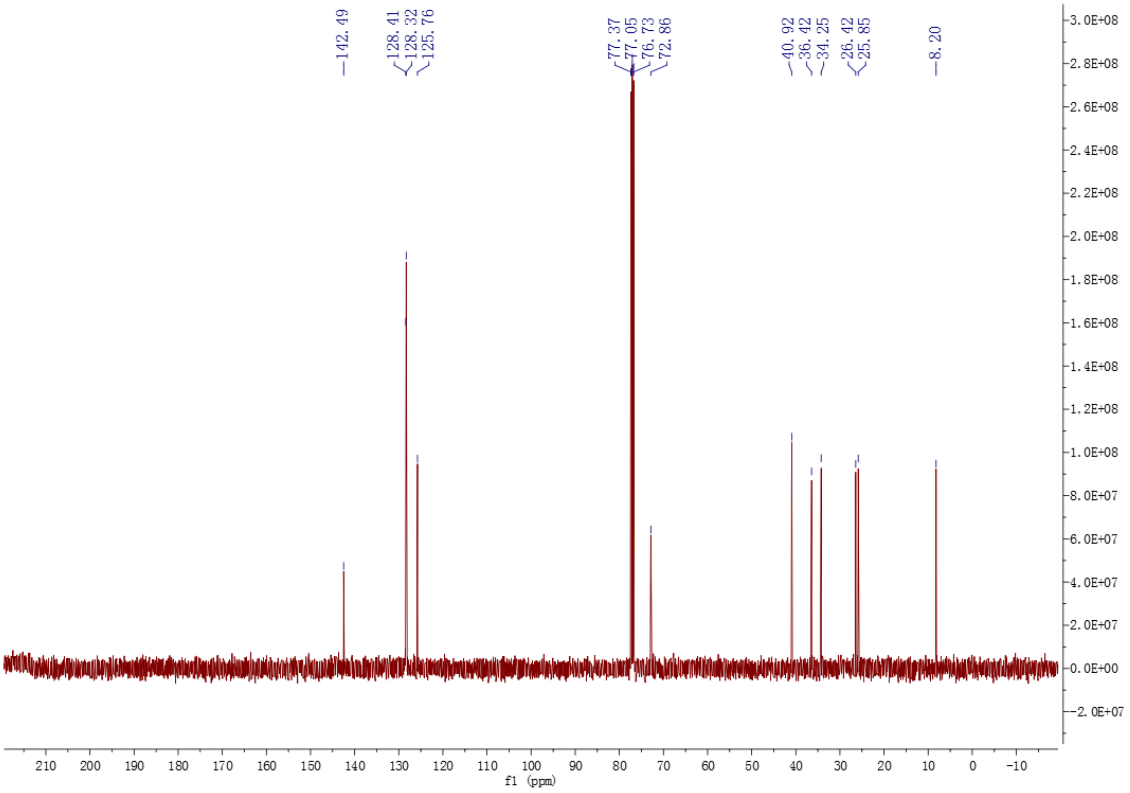
f1 (ppm)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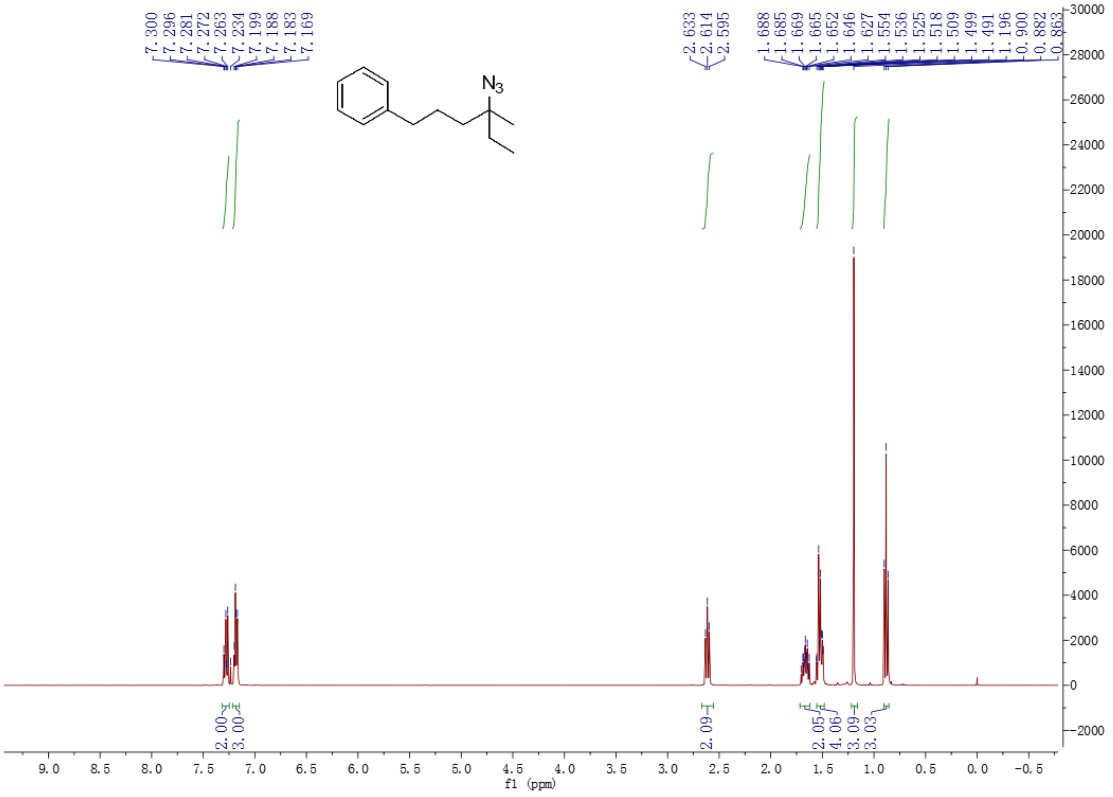
f1 (ppm)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1.685
1.669
1.665
1.652
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1.554
1.536
1.525
1.518
1.509
1.499
1.491
1.196
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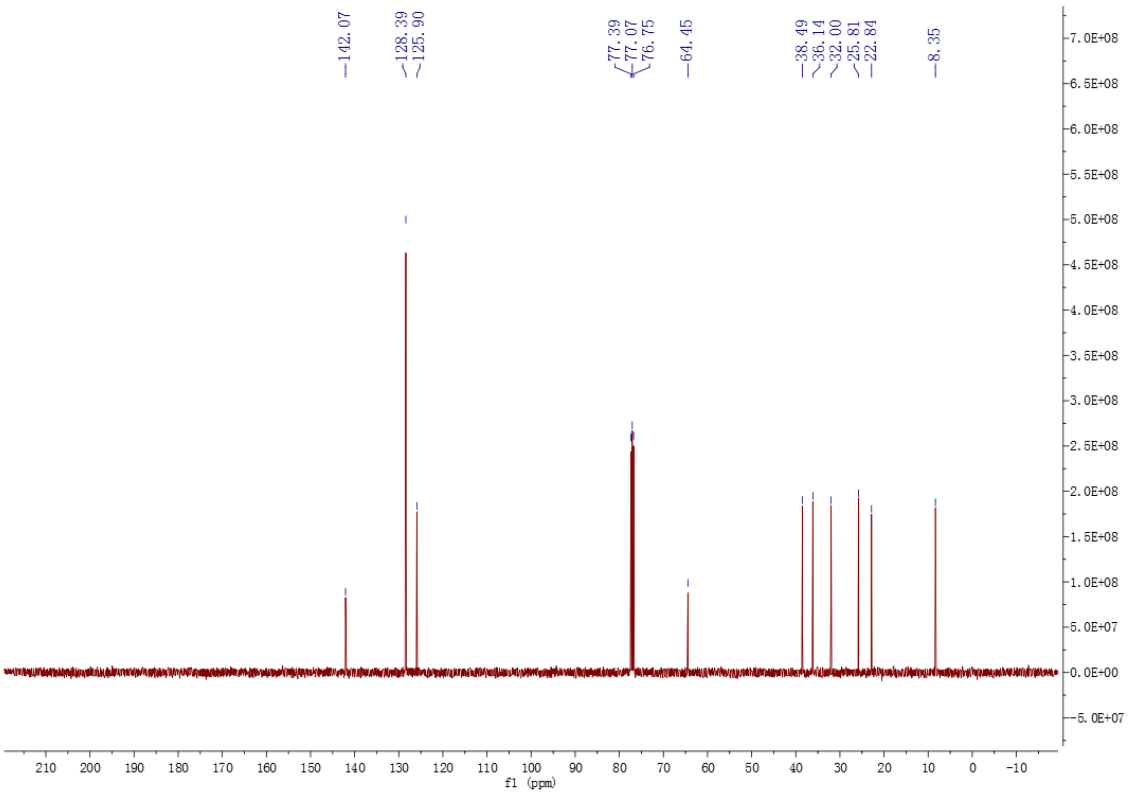
3.03
f1 (ppm)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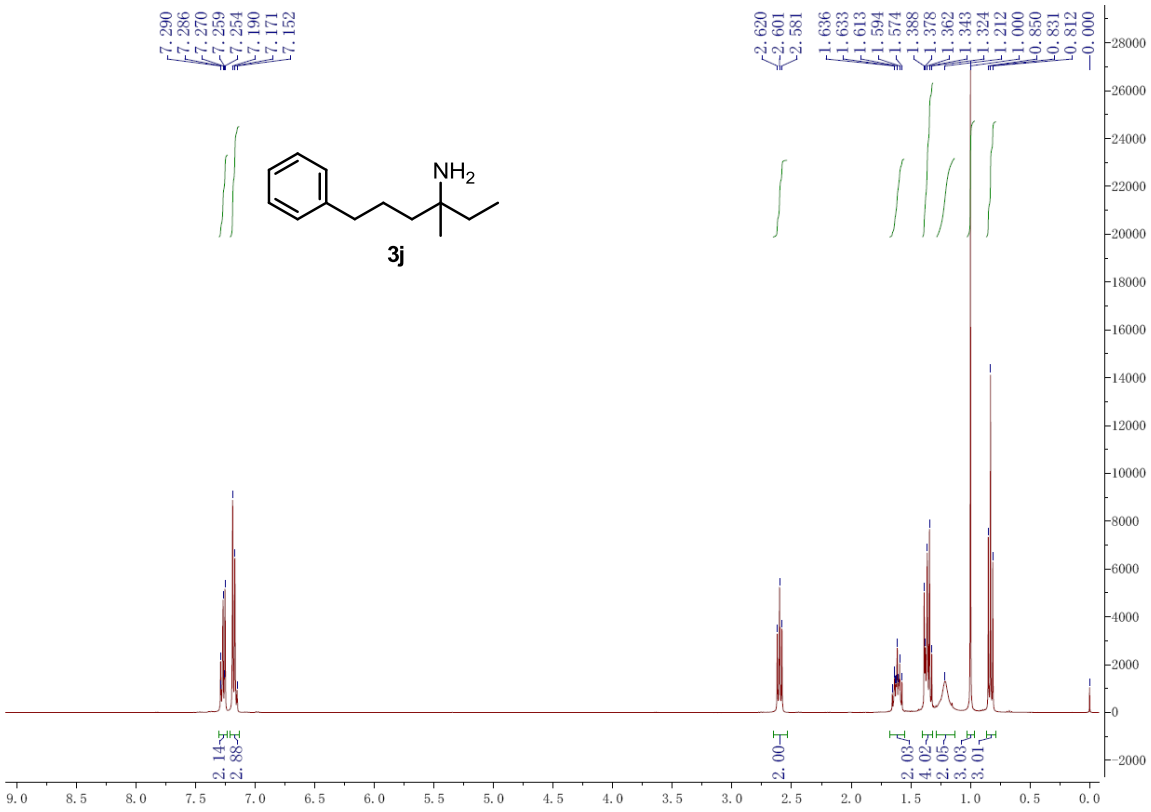
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1.388
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1.362
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0.831
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2.03
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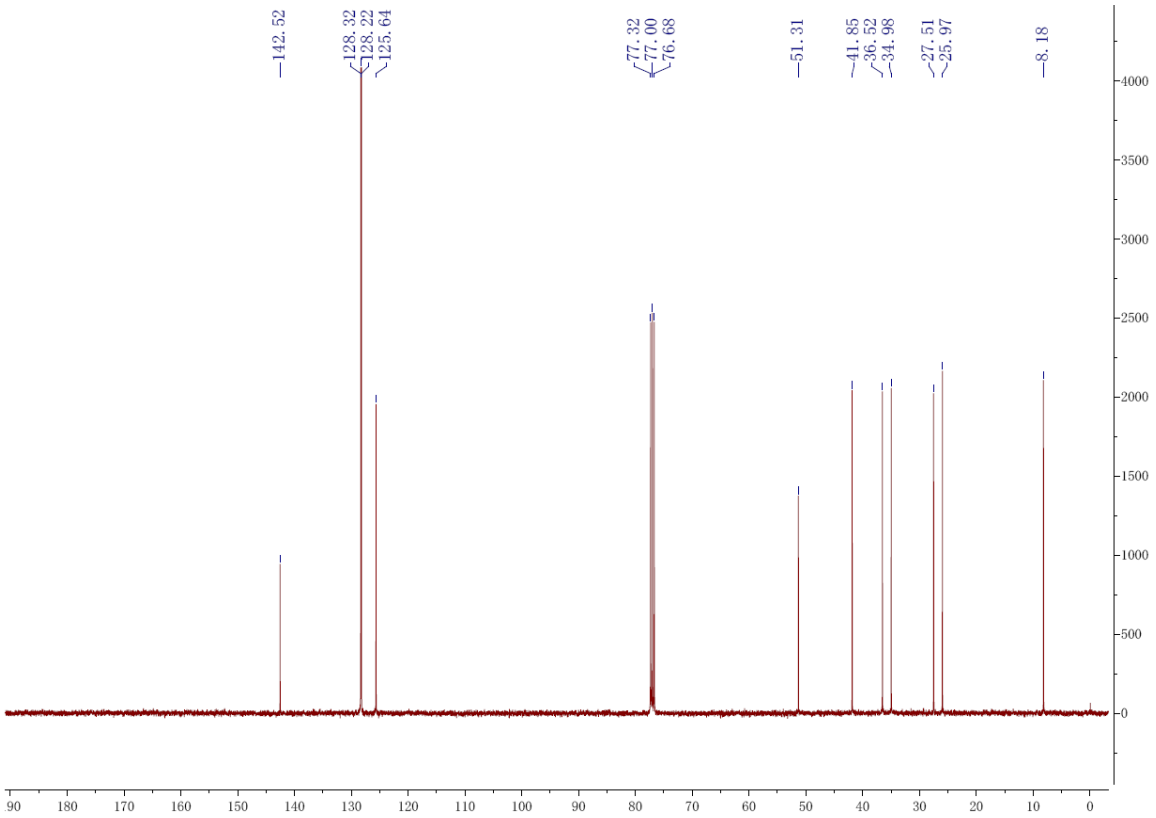
3.03
3.01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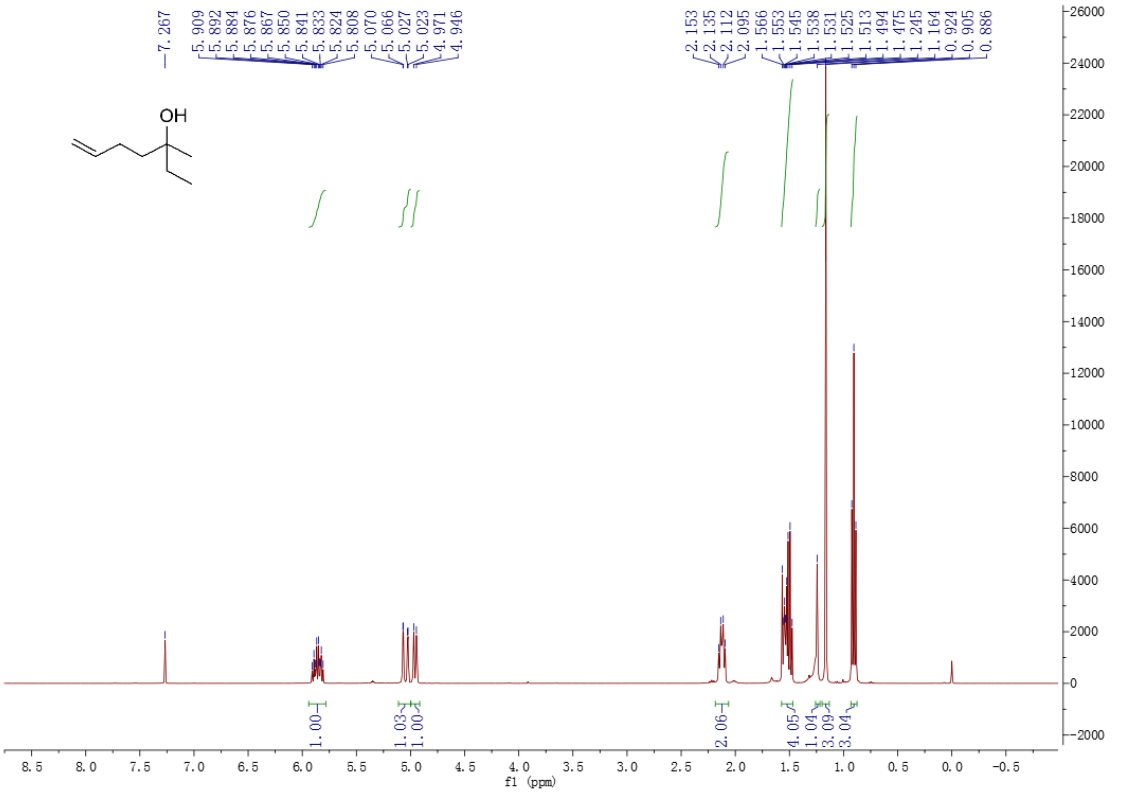
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5.892
5.884
5.876
5.867
5.850
5.841
5.833
5.824
5.808
5.070
5.066
5.027
5.023
4.971
4.946
2.153
2.135
2.112
2.095
1.566
1.553
1.545
1.538
1.531
1.525
1.513
1.494
1.475
1.245
1.164
0.924
0.905
0.886
OH
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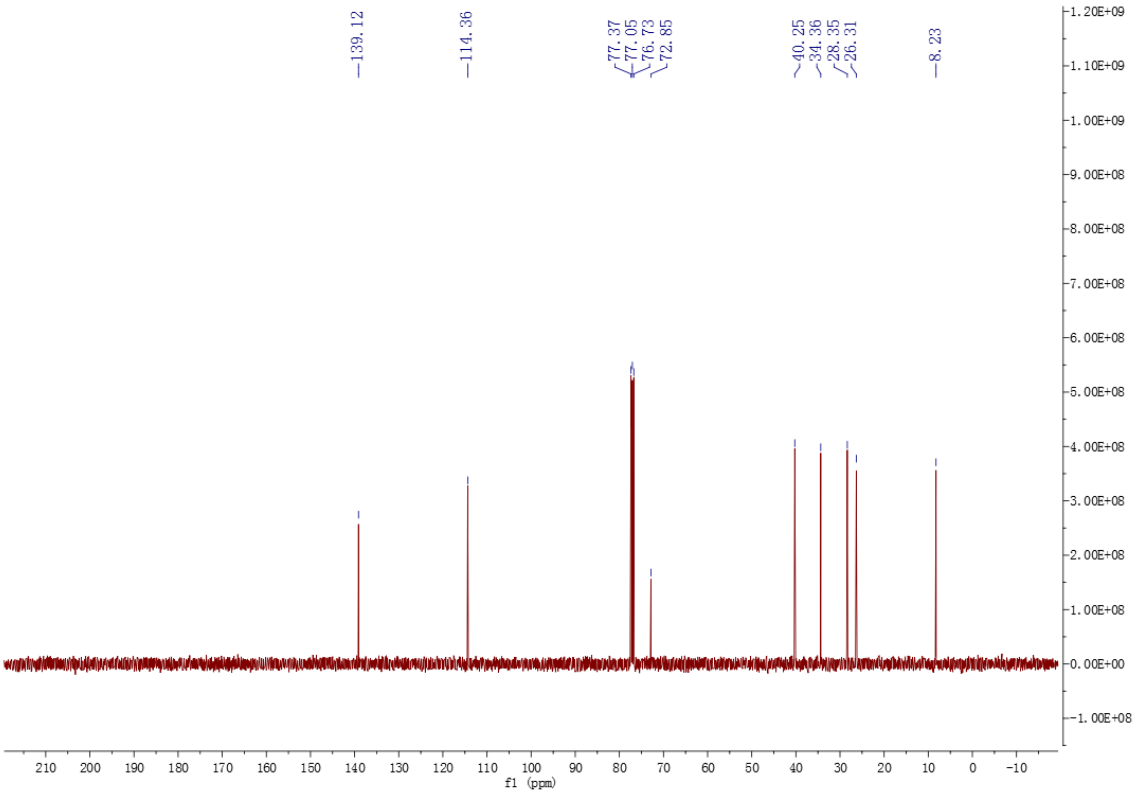
1.03
1.00
2.06
4.05
1.04
3.09
3.04
f1 (ppm)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34.36
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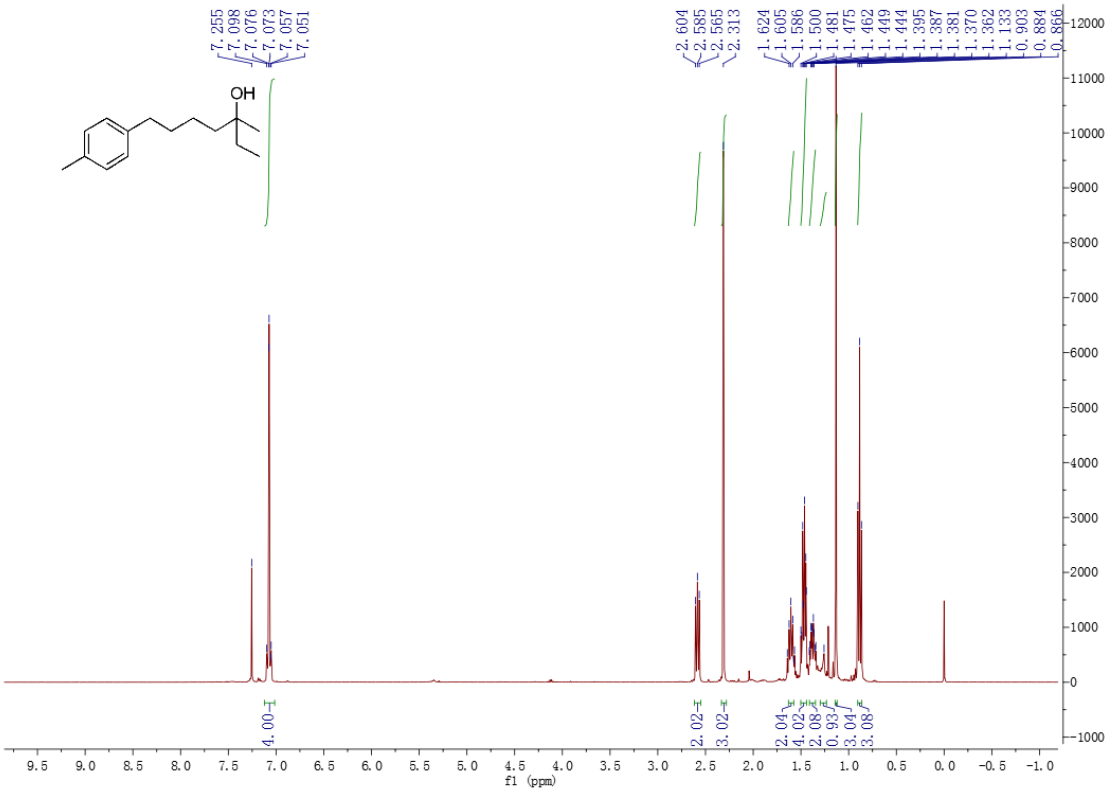
26.31
8.23
f1 (ppm)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1.605
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1.500
1.481
1.475
1.462
1.449
1.444
1.395
1.387
1.381
1.370
1.362
1.133
0.903
0.884
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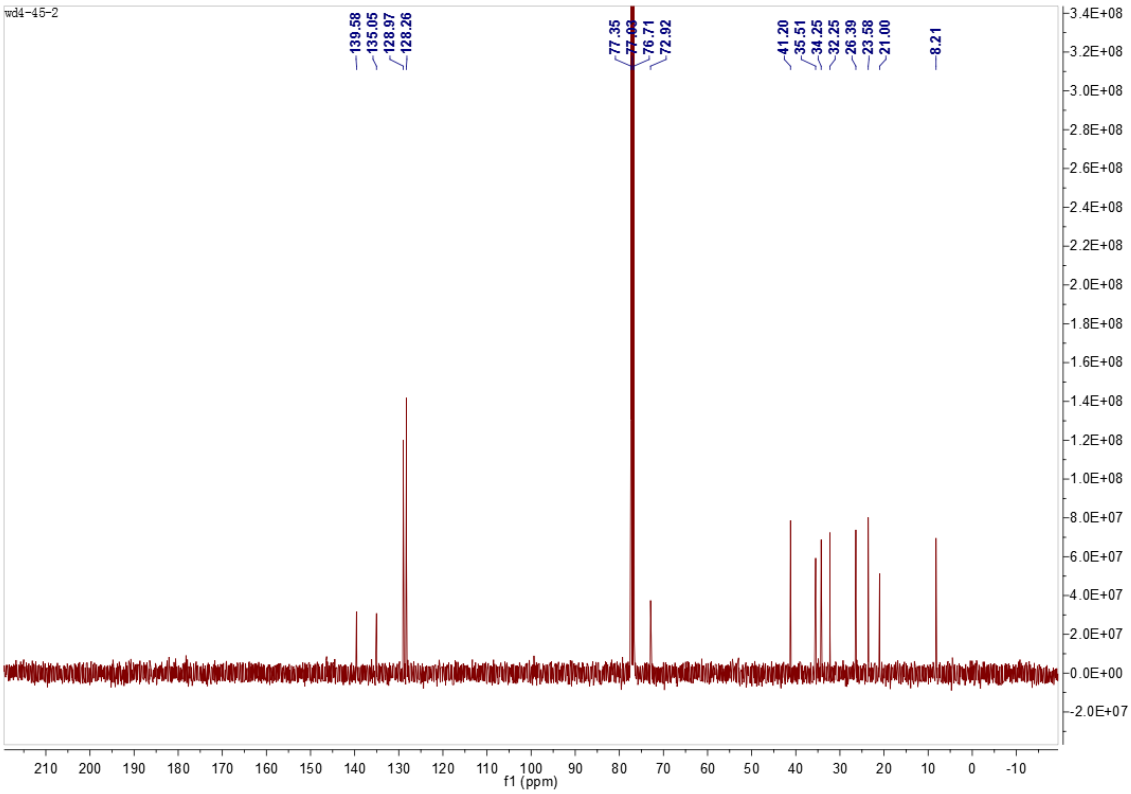
0.93
3.04
3.08
f1 (ppm)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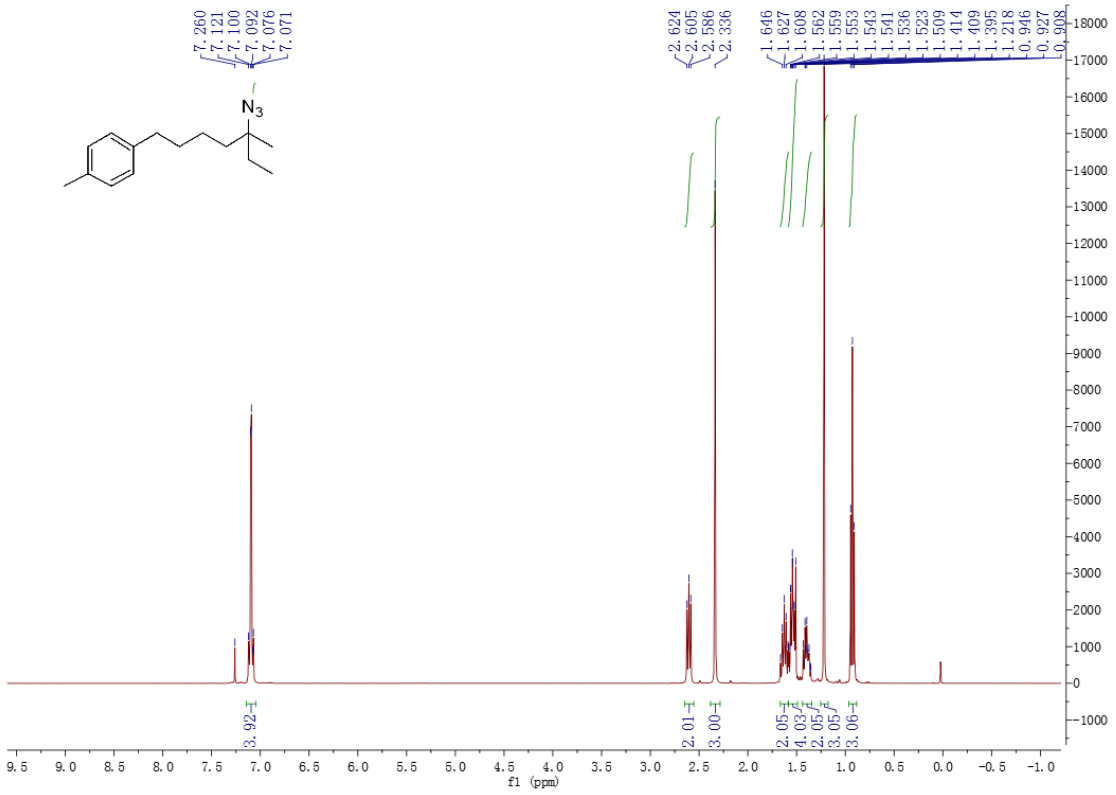
26.39
23.58
21.00
8.21
f1 (ppm)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7.071
N3
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2.586
2.336
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1.627
1.608
1.562
1.559
1.553
1.543
1.541
1.536
1.523
1.509
1.414
1.409
1.395
1.218
0.946
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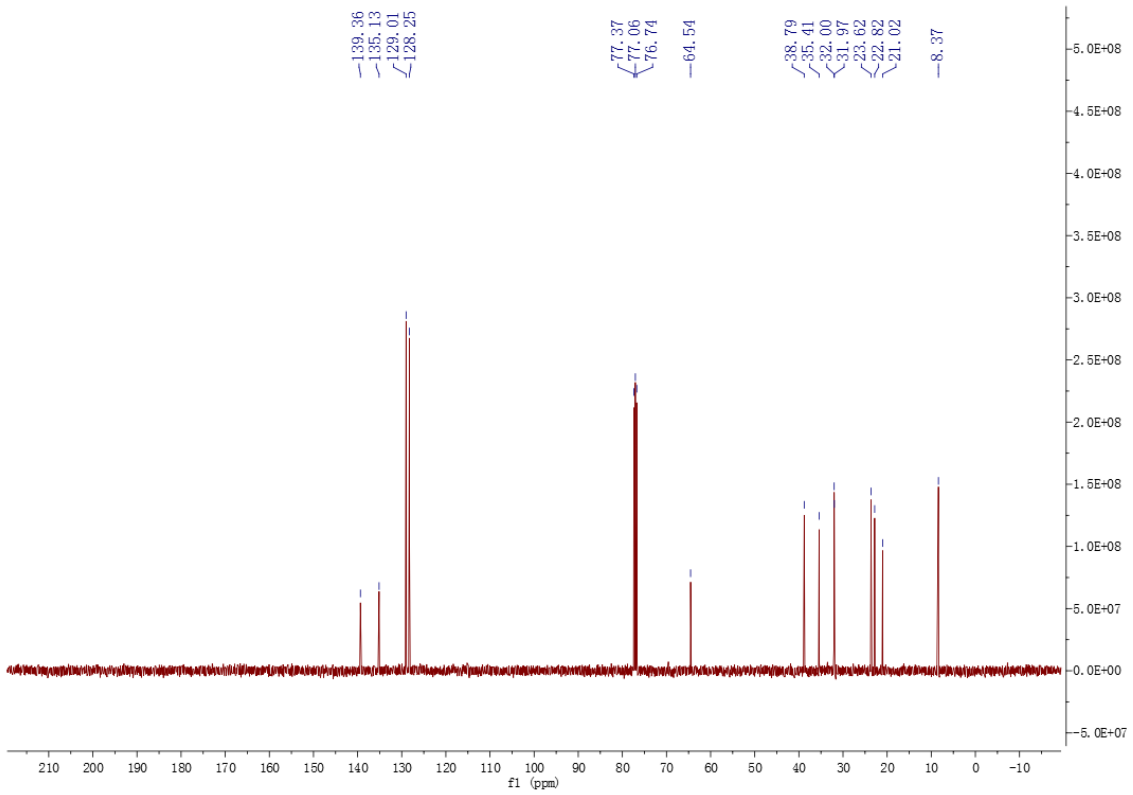
3.00
2.05
4.03
2.05
3.05
3.06
f1 (ppm)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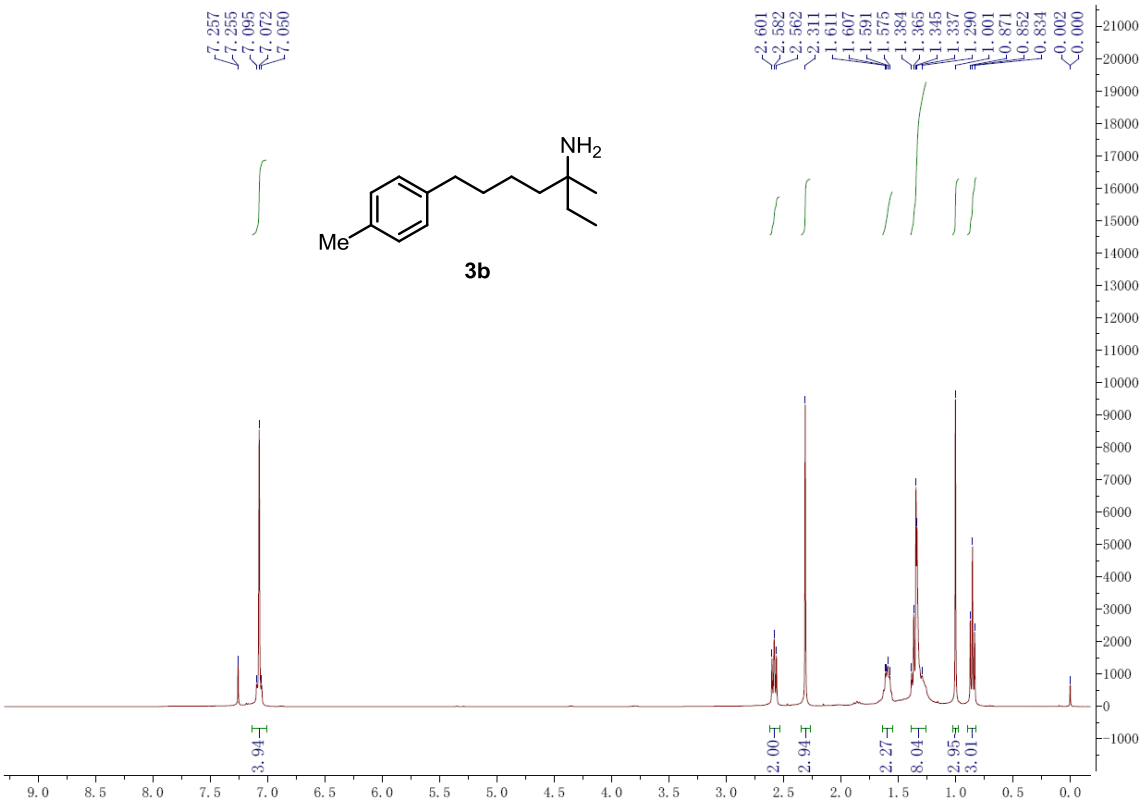
22.82
21.02
8.37
f1 (ppm)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1.384
1.365
1.345
1.337
1.290
1.001
0.871
0.852
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NH2
Me
3b
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2.94
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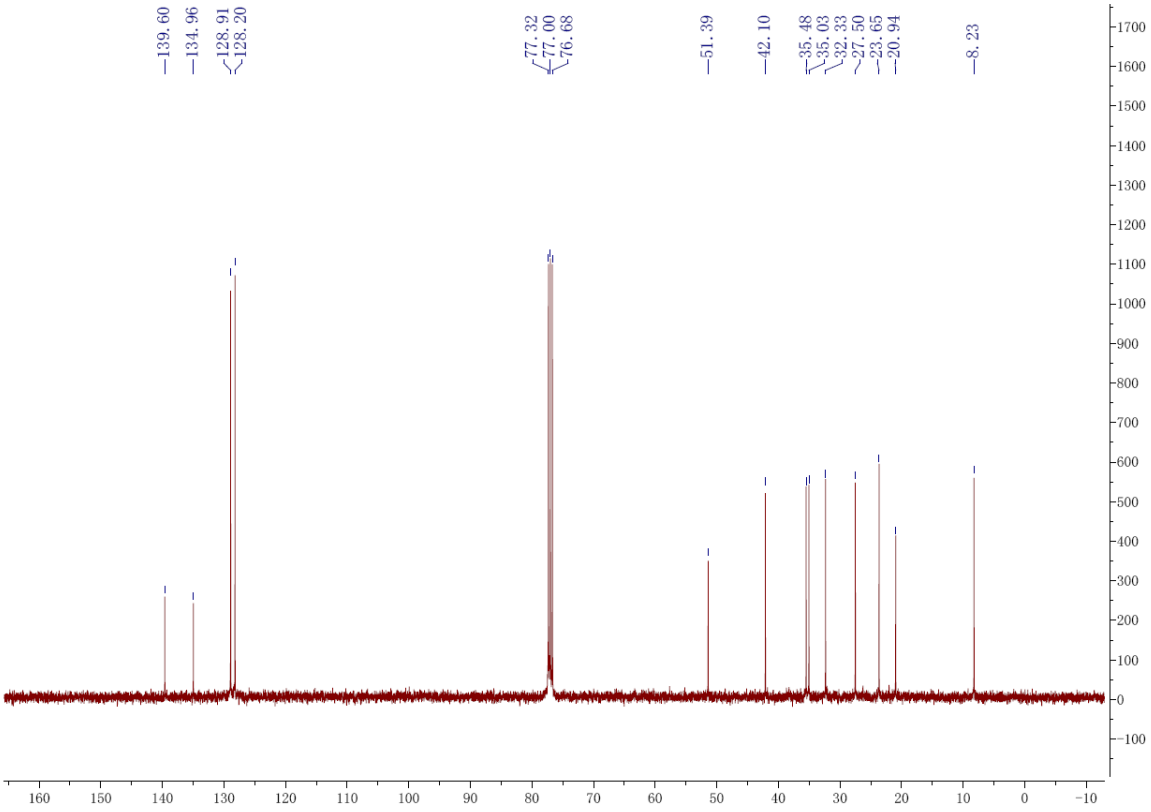
8.04
2.95
3.01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32.33
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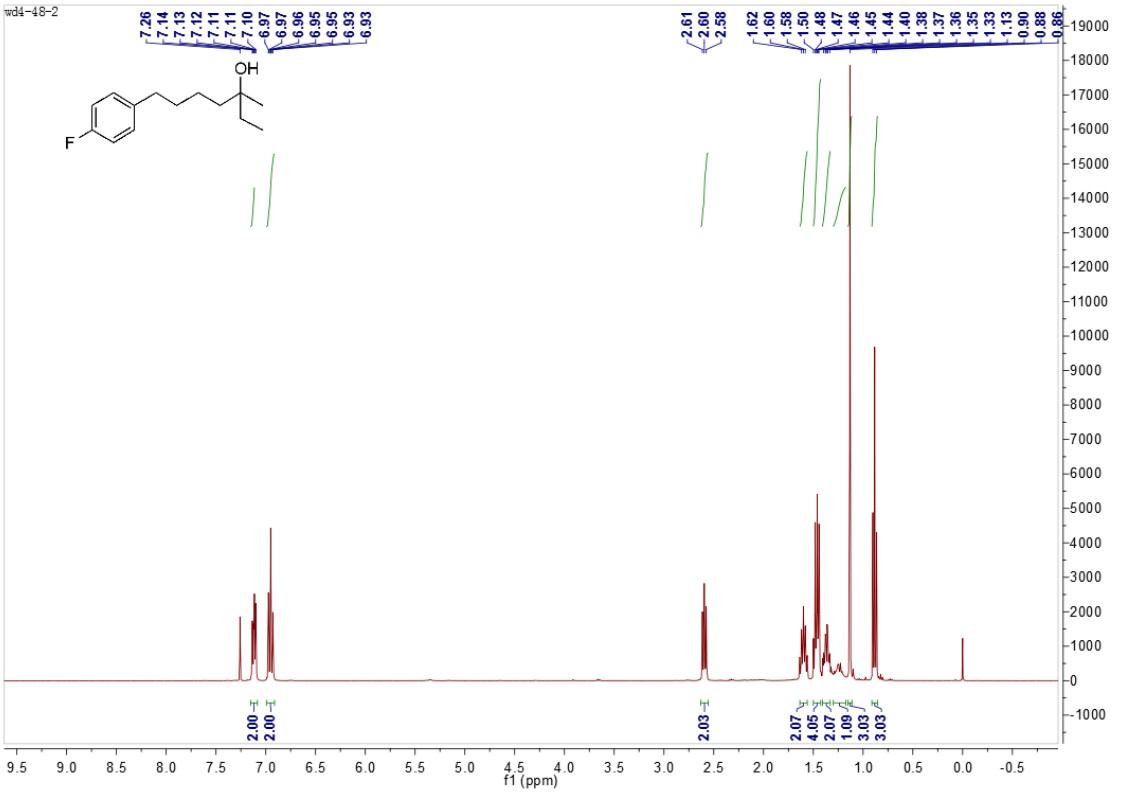
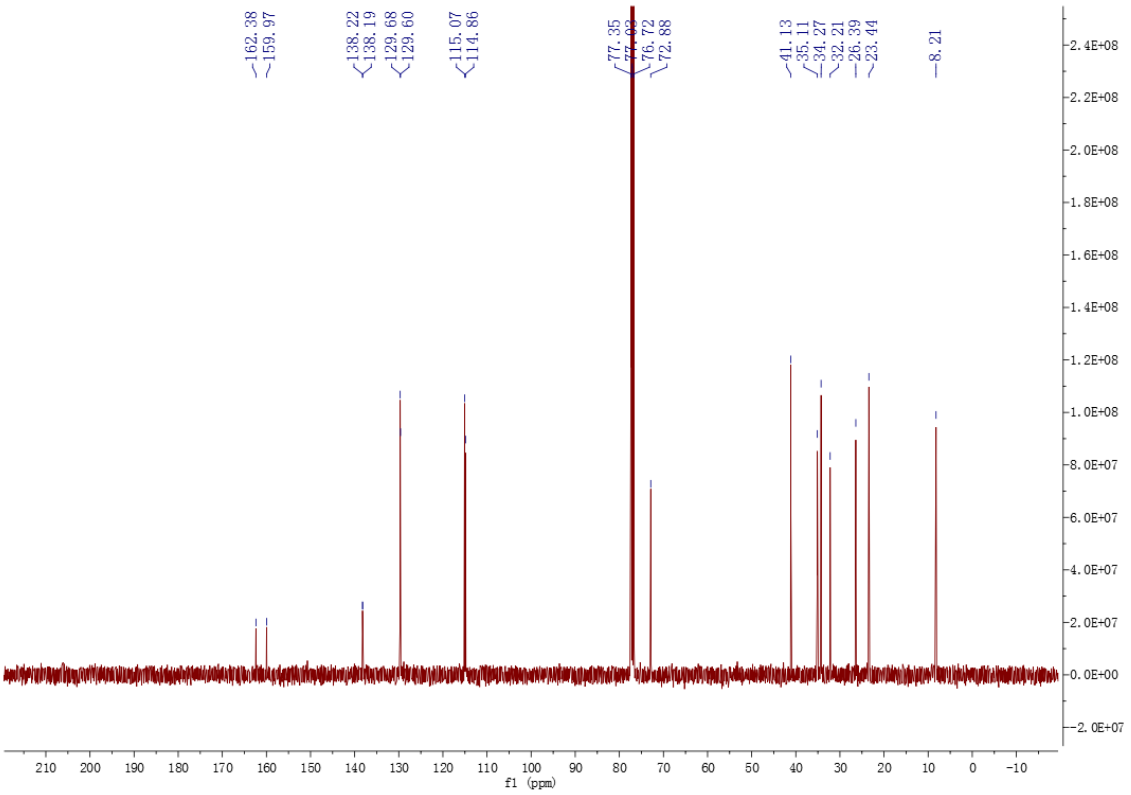
20.94
8.23


wd4-48-2
OH
F
f1 (ppm)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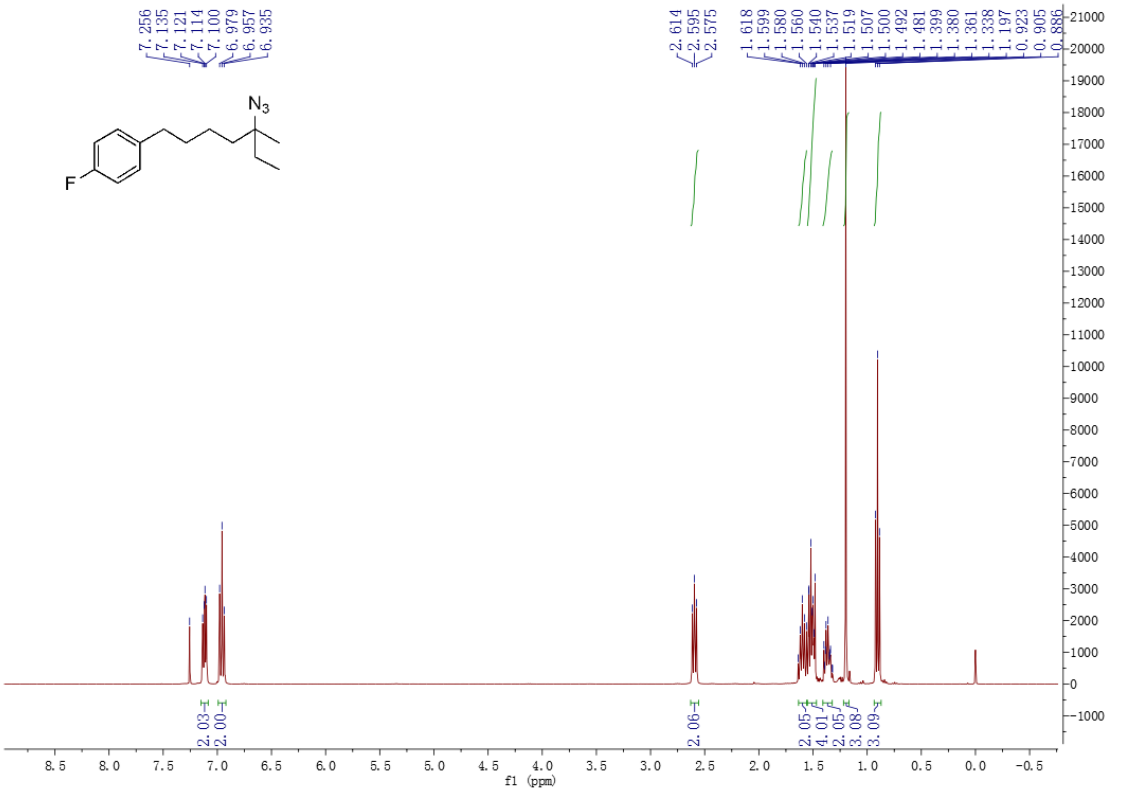
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1.580
1.560
1.540
1.537
1.519
1.507
1.500
1.492
1.481
1.399
1.380
1.361
1.338
1.197
0.923
0.905
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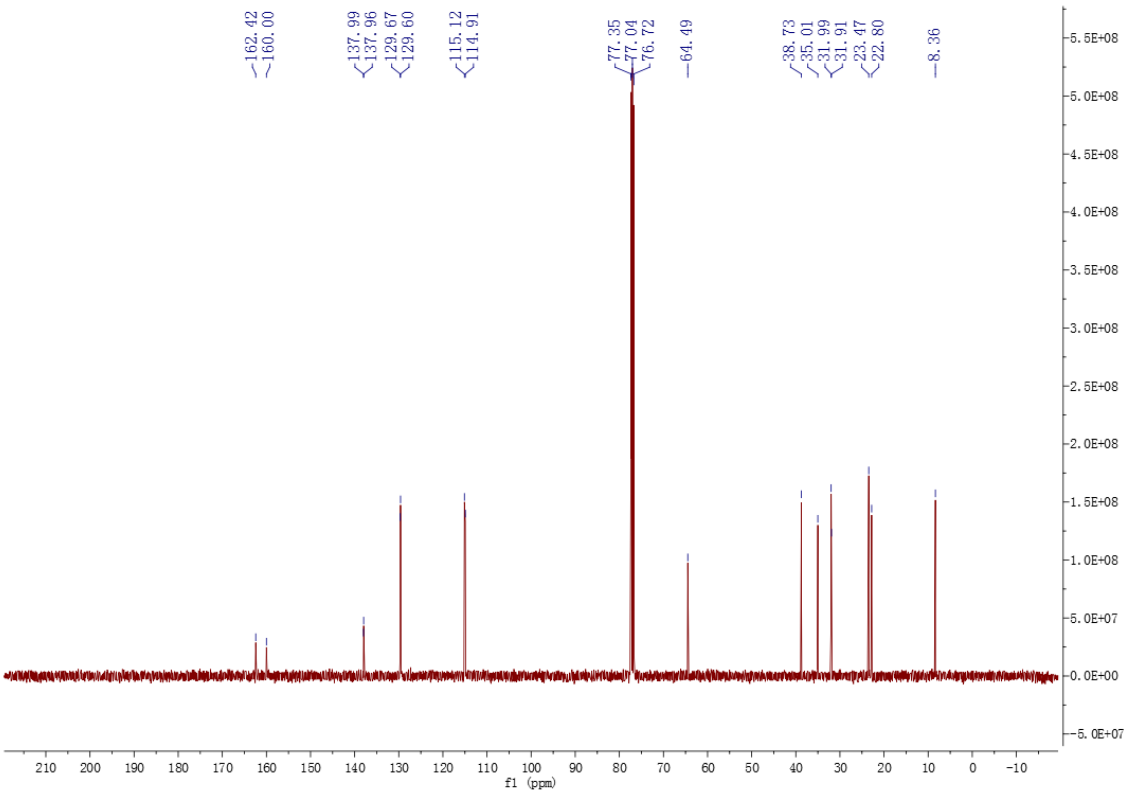
N3
F
2.03
2.00
2.06
2.05
4.01
2.05
3.08
3.09
f1 (ppm)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137.96
129.67
129.60
115.12
114.91
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77.04
76.72
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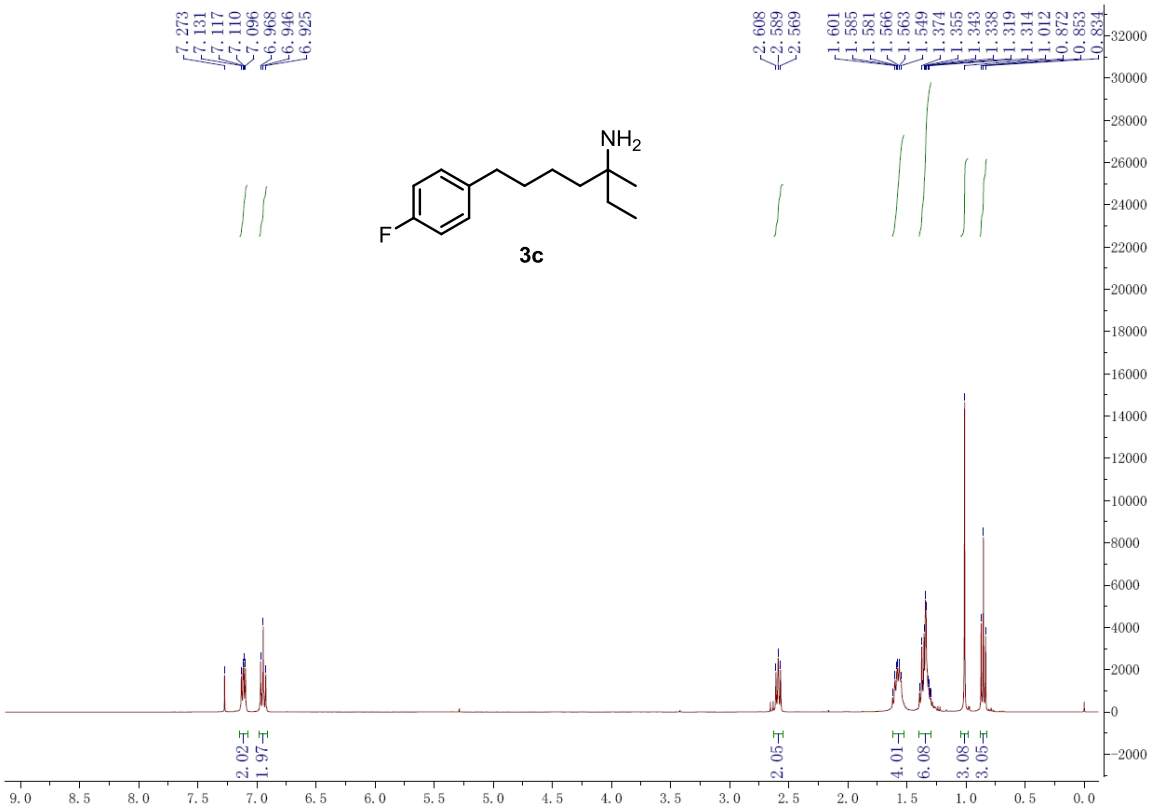
35.01
31.99
31.91
23.47
22.80
8.36
f1 (ppm)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6.946
6.925
2.608
2.589
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1.601
1.585
1.581
1.566
1.563
1.549
1.374
1.355
1.343
1.338
1.319
1.314
1.012
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NH2
F
3c
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1.97
2.05
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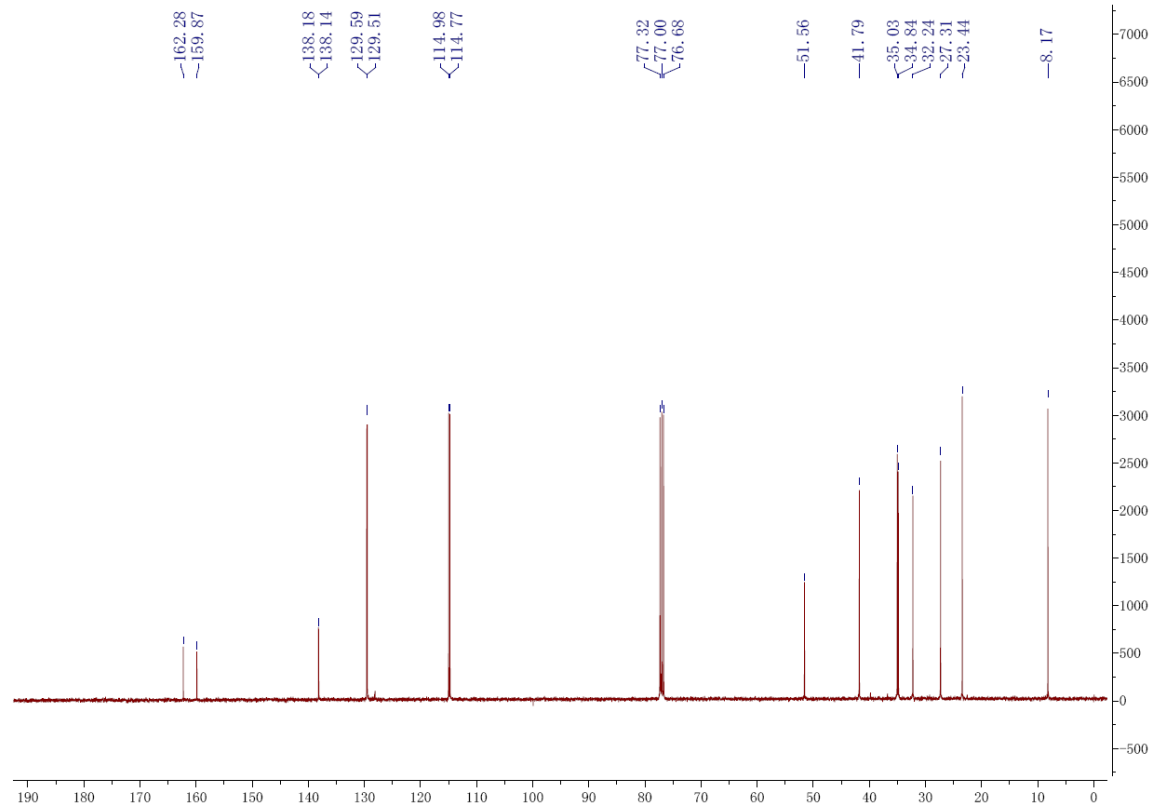
6.08
3.08
3.05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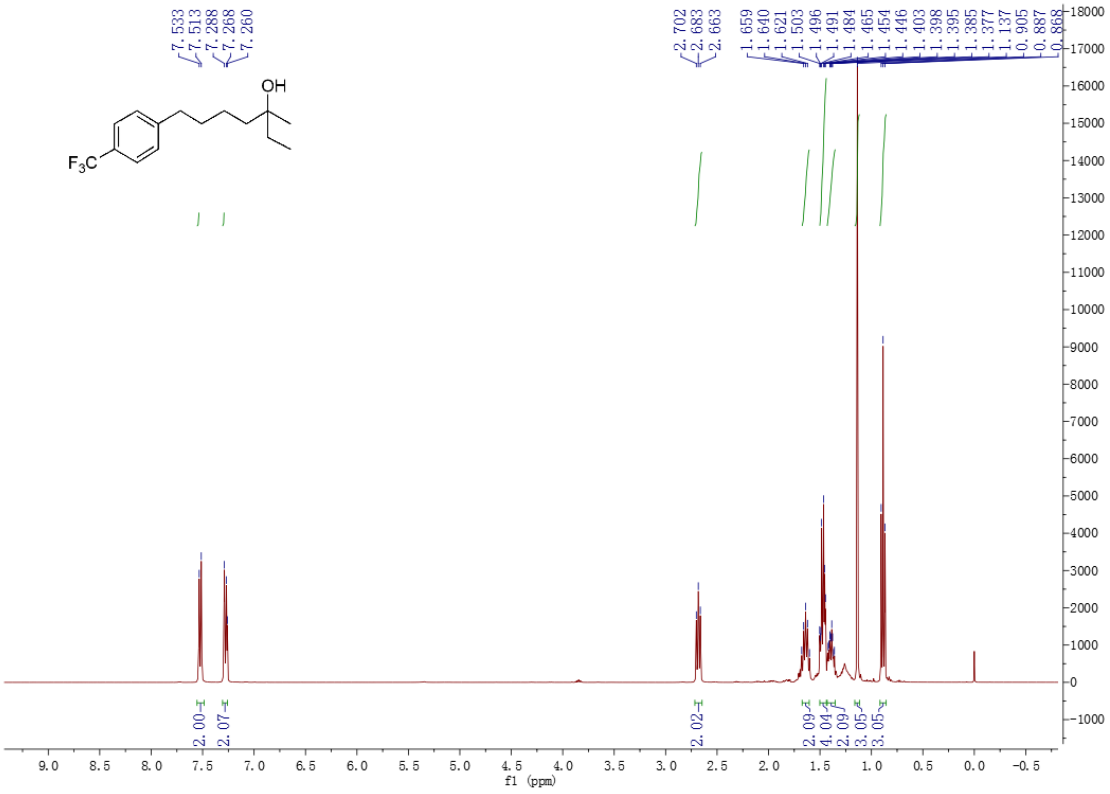
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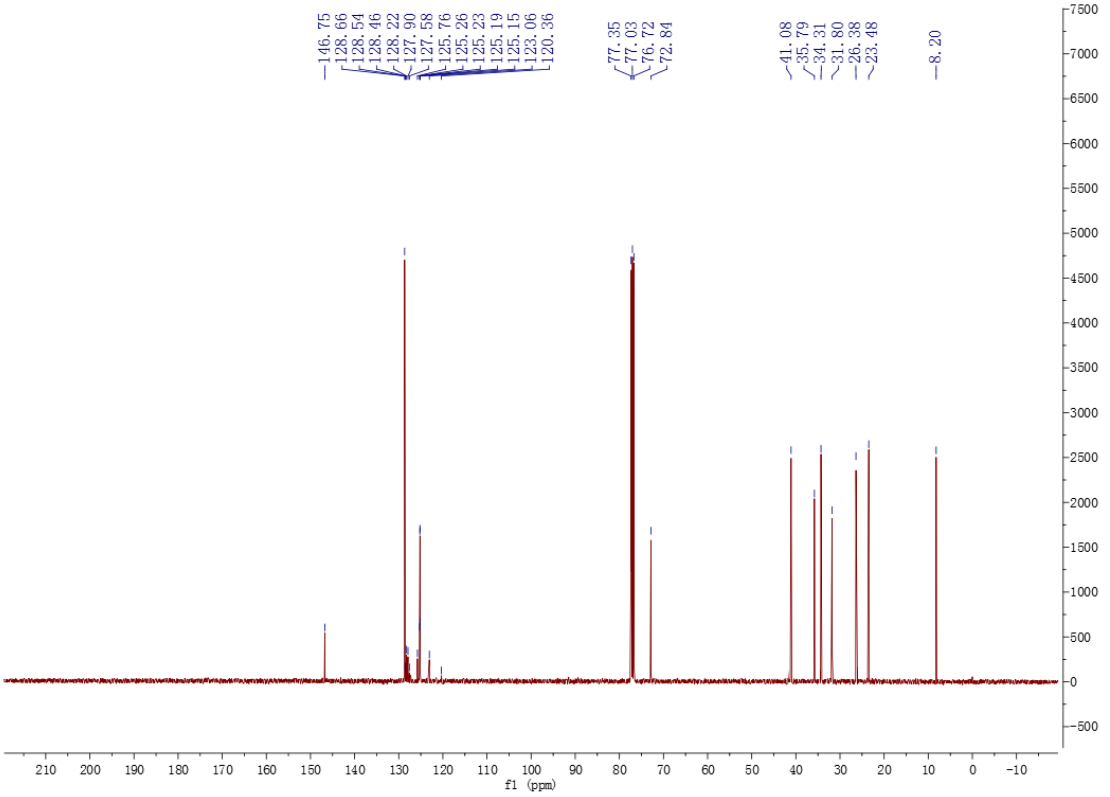
1.621
1.503
1.496
1.491
1.484
1.465
1.454
1.446
1.403
1.398
1.395
1.385
1.377
1.137
0.905
0.887
0.868
OH
F3C
2.00
2.07
2.02
2.09
4.04
2.09
3.05
3.05
f1 (ppm)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125.76
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123.06
120.36
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77.03
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72.84
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35.79
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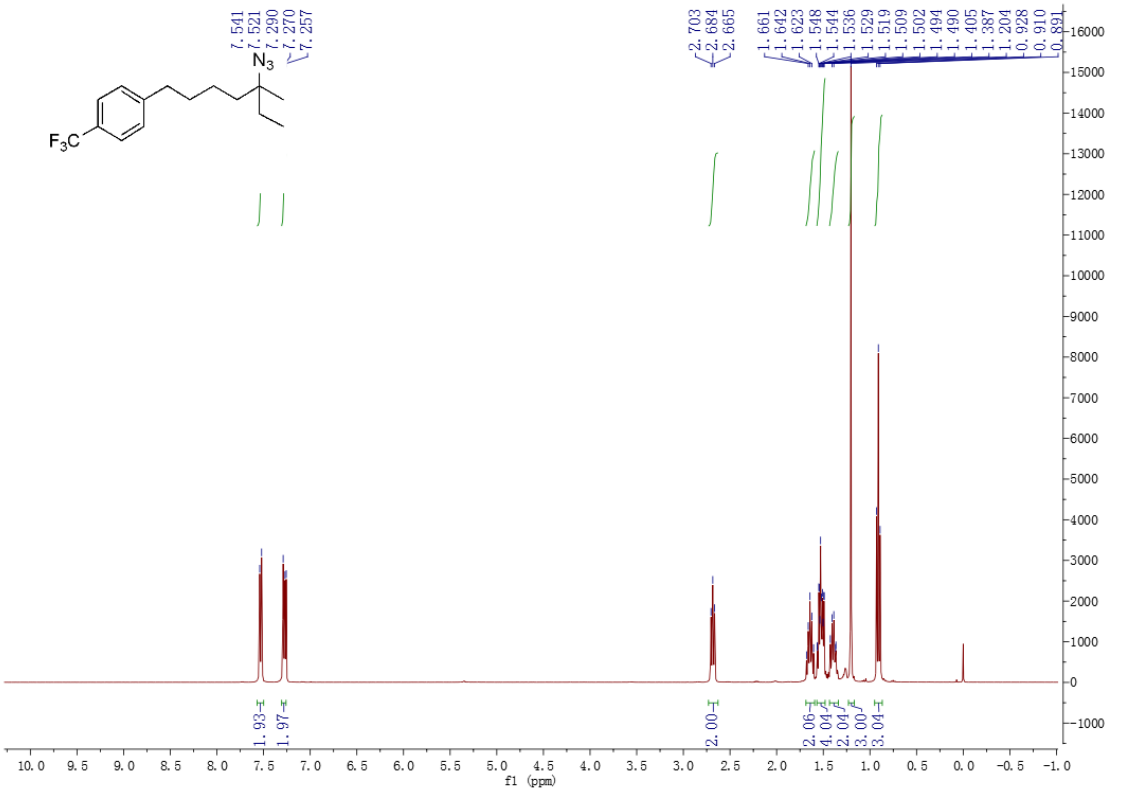
31.80
26.38
23.48
8.20
f1 (ppm)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F3C
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1.642
1.623
1.548
1.544
1.536
1.529
1.519
1.509
1.502
1.494
1.490
1.405
1.387
1.204
0.928
0.910
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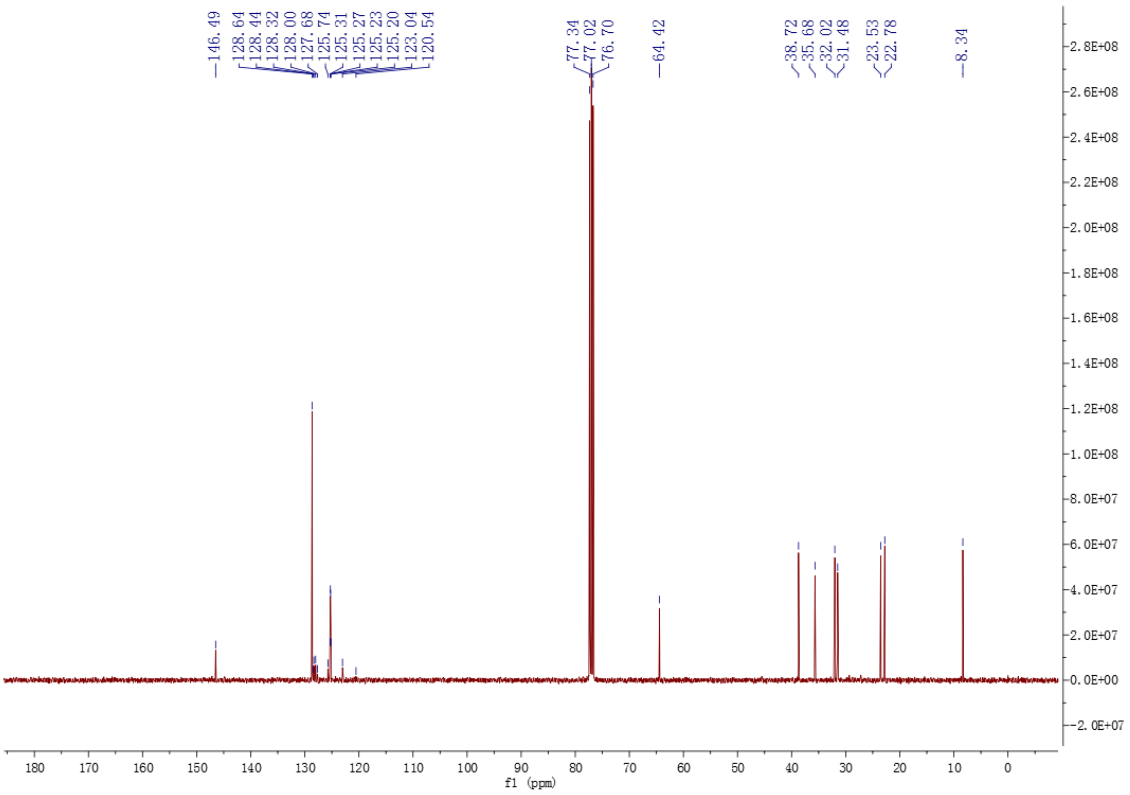
1.97
2.00
2.06
4.04
2.04
3.00
3.04
f1 (ppm)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125.23
125.20
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120.54
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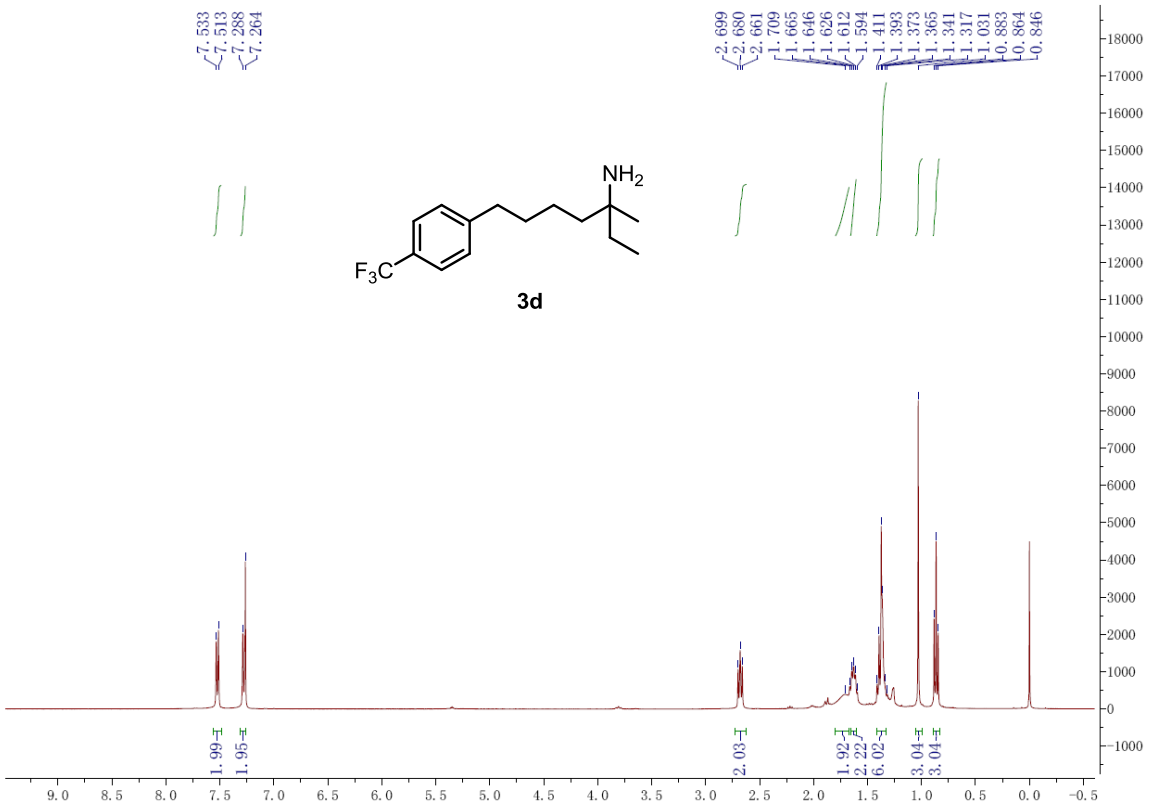
f1 (ppm)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1.373
1.365
1.341
1.317
1.031
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F3C
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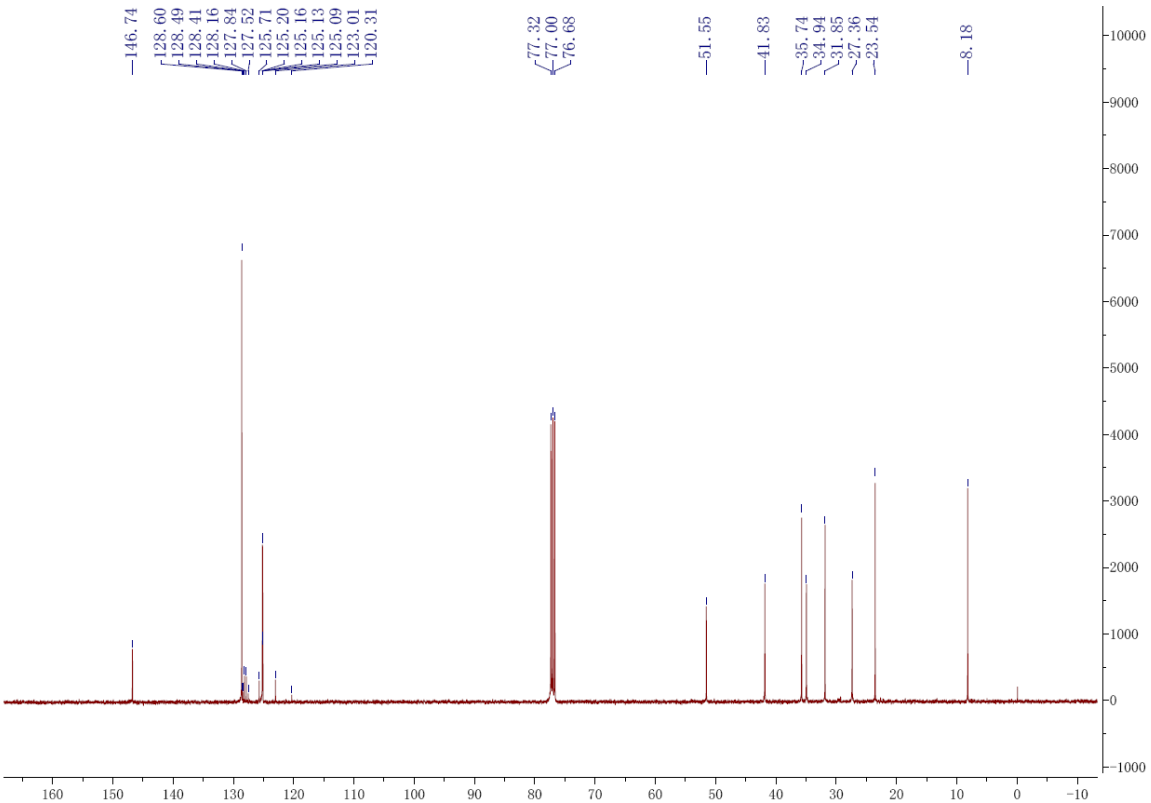
3d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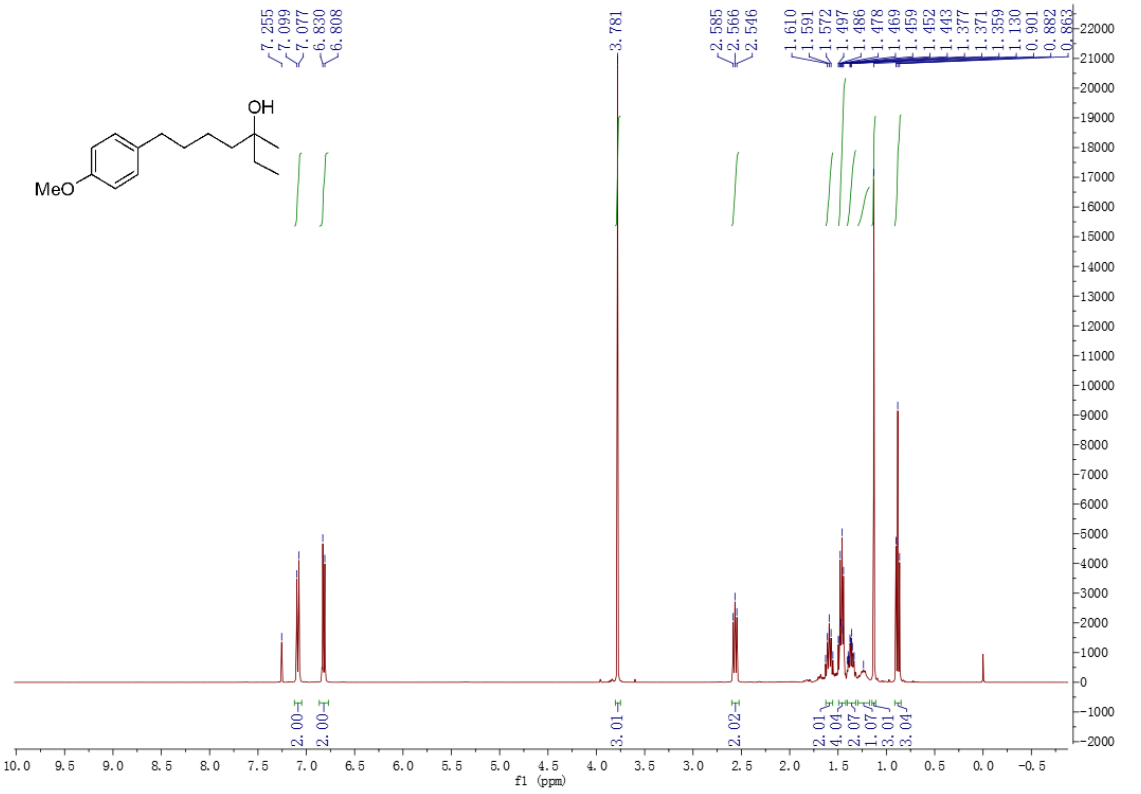
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1.486
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1.443
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0.882
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OH
MeO
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2.01
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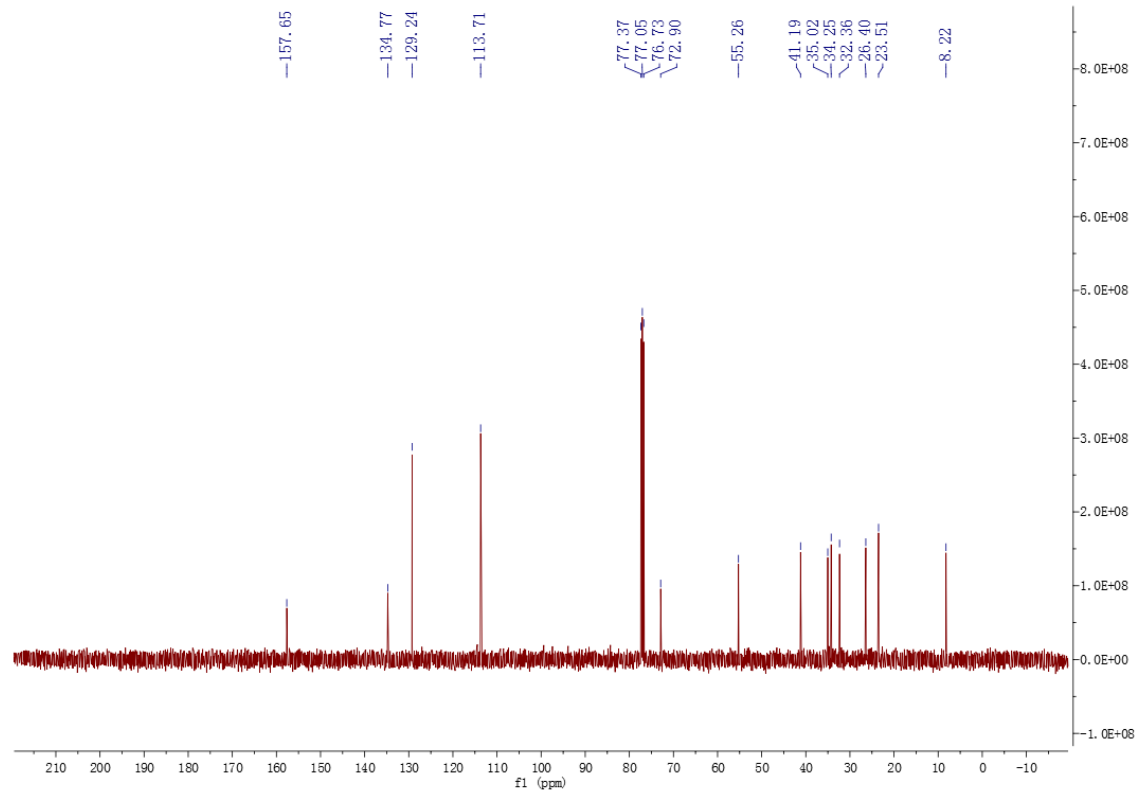
1.07
3.01
3.04
f1 (ppm)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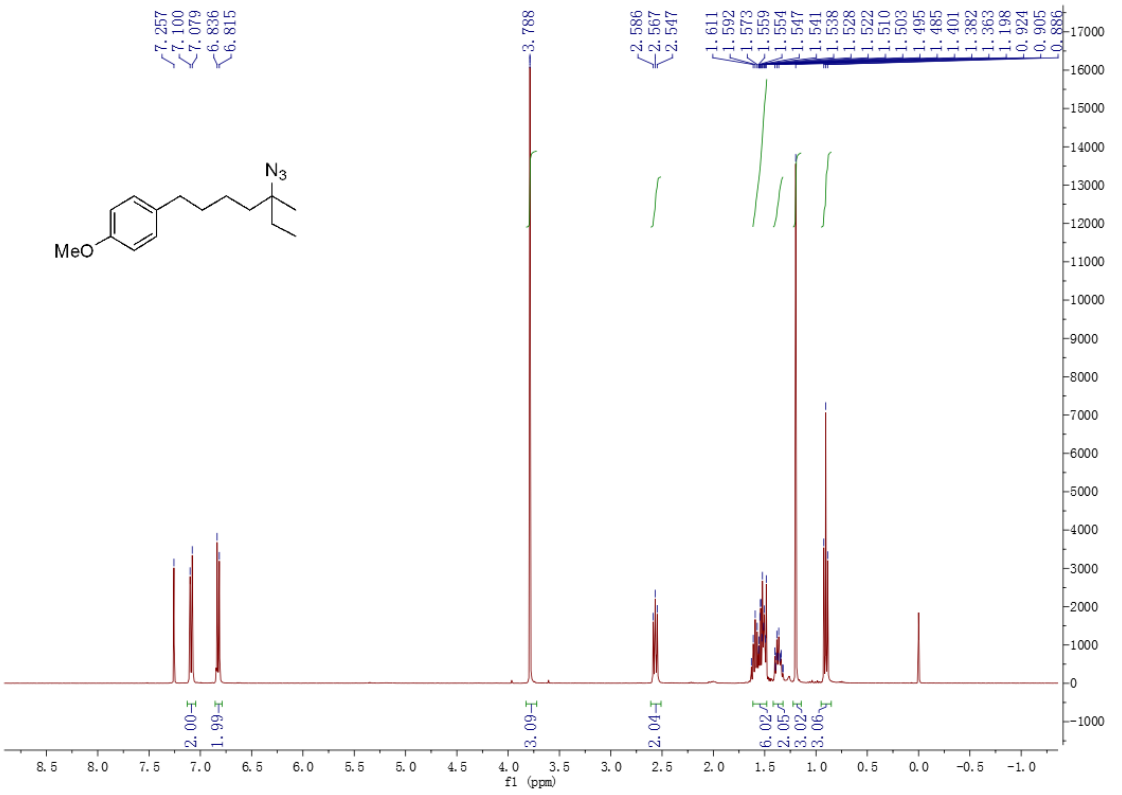
8.22
f1 (ppm)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1.554
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1.528
1.522
1.510
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1.495
1.485
1.401
1.382
1.363
1.198
0.924
0.905
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MeO
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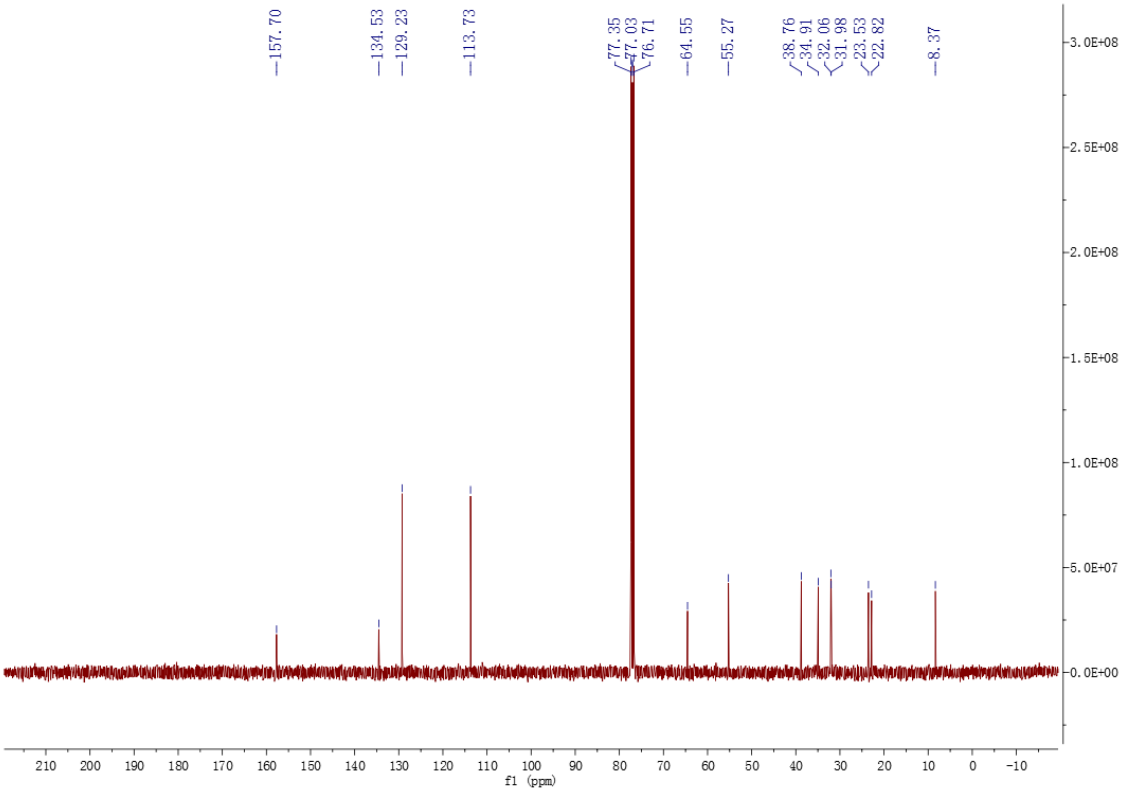
1.99
3.09
2.04
6.02
2.05
3.02
3.06
f1 (ppm)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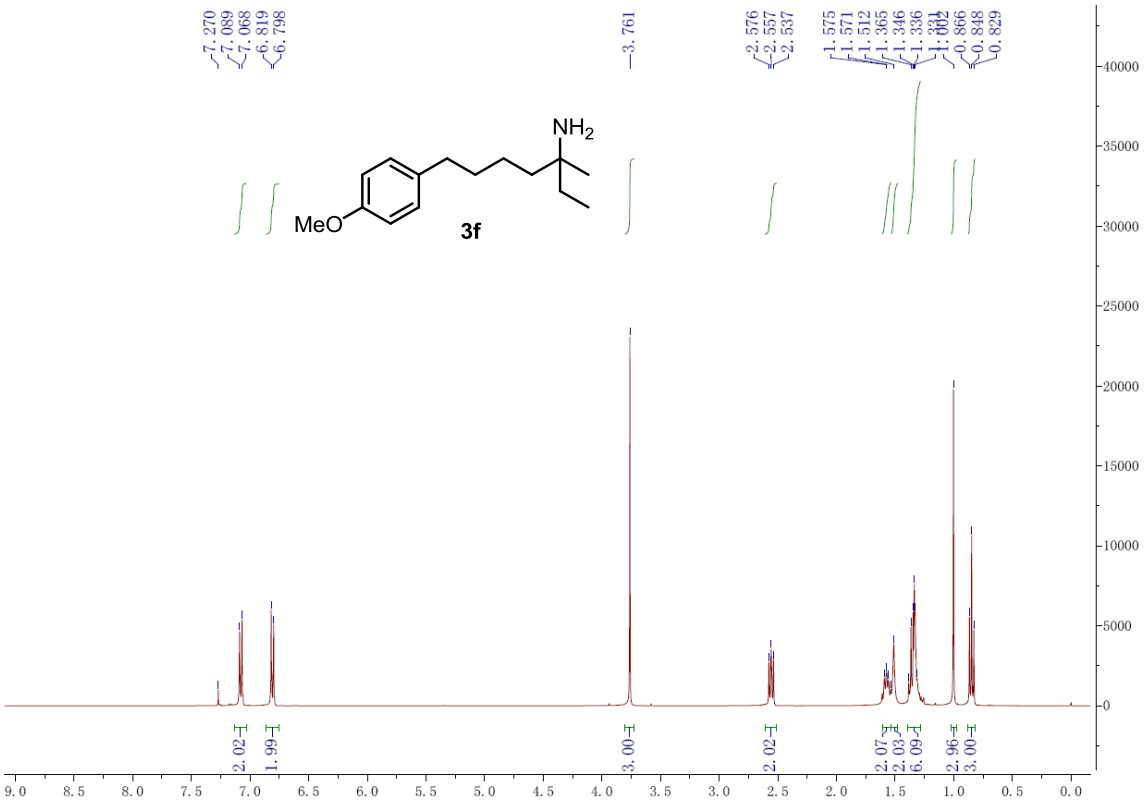
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1.365
1.346
1.336
1.002
0.866
0.848
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MeO
3f
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2.07
2.03
6.09
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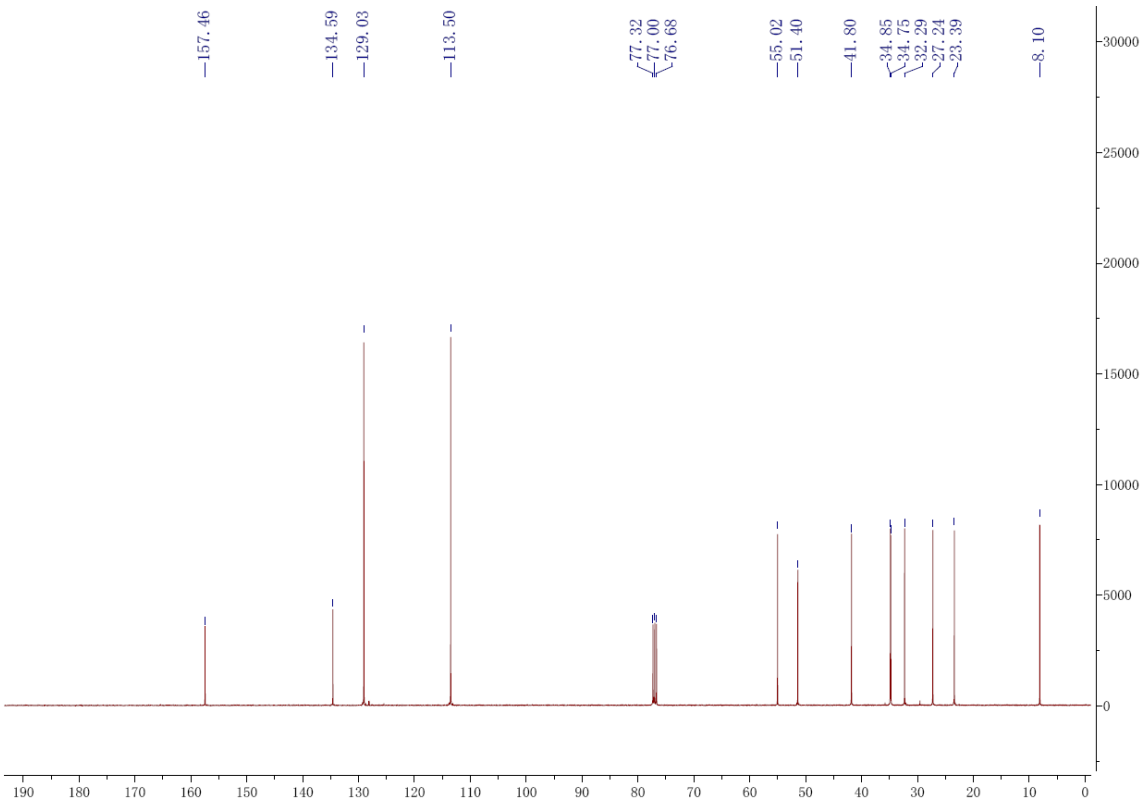
3.00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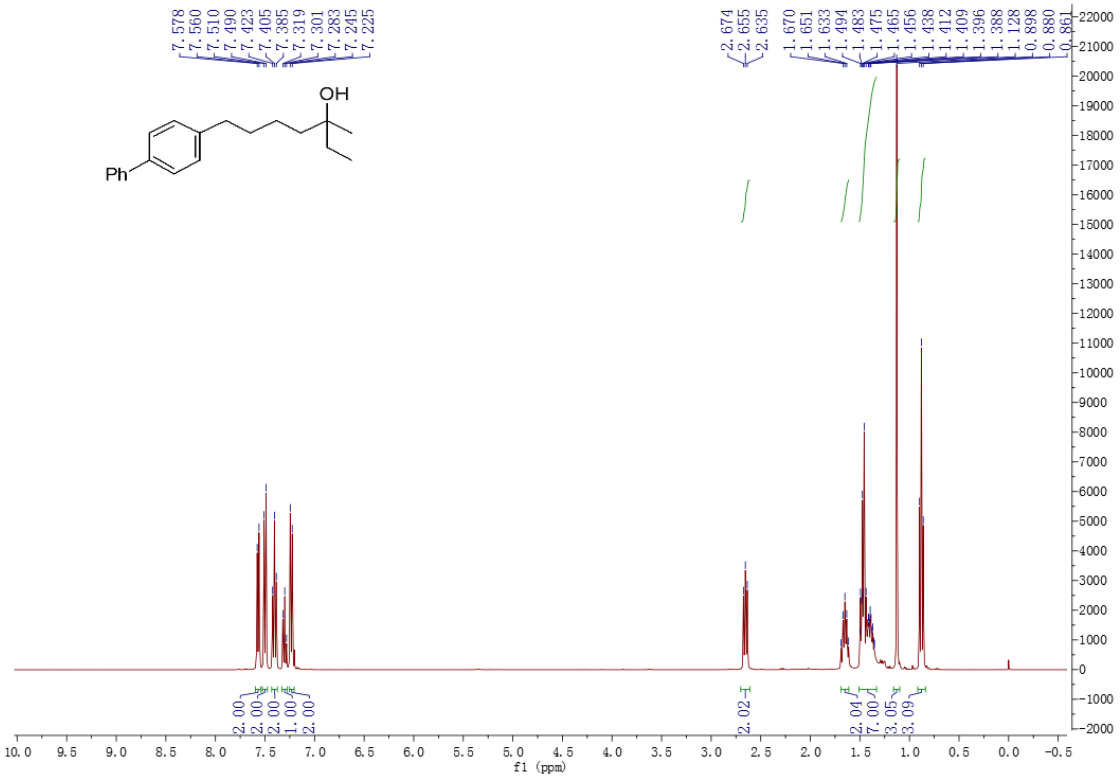
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OH
Ph
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1.475
1.465
1.456
1.438
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1.388
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7.00
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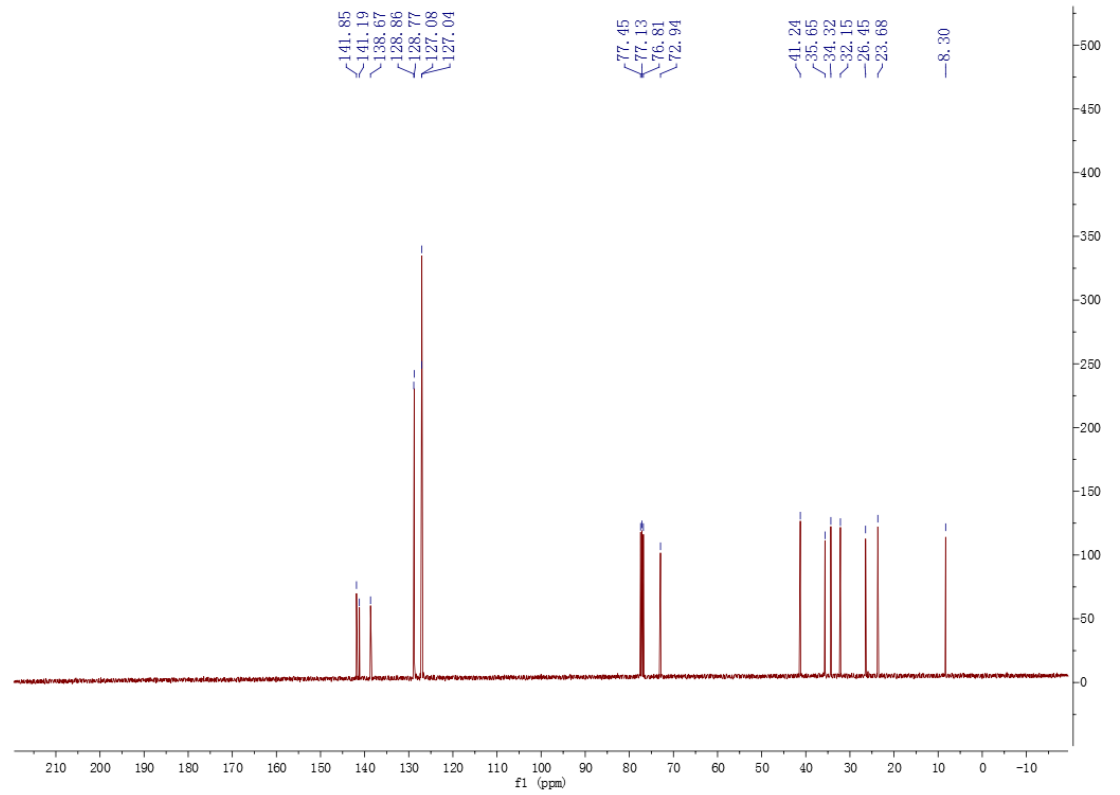
3.09
f1 (ppm)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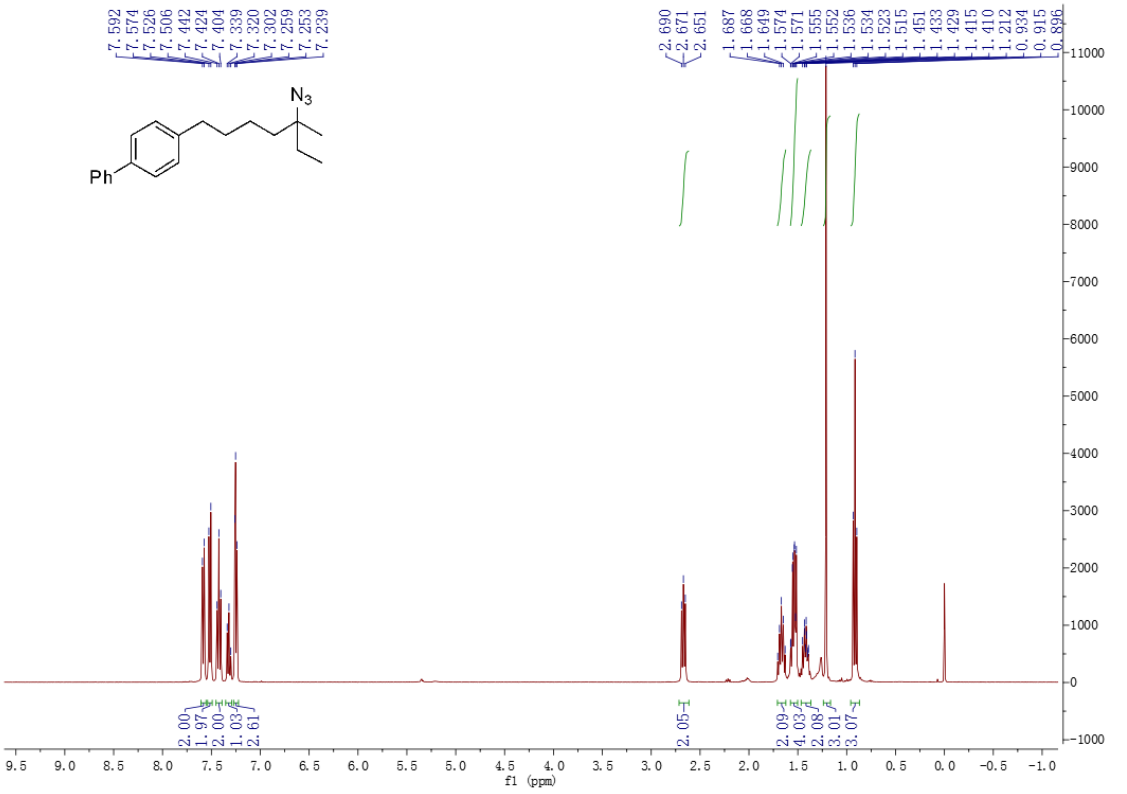
f1 (ppm)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N3
Ph
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1.410
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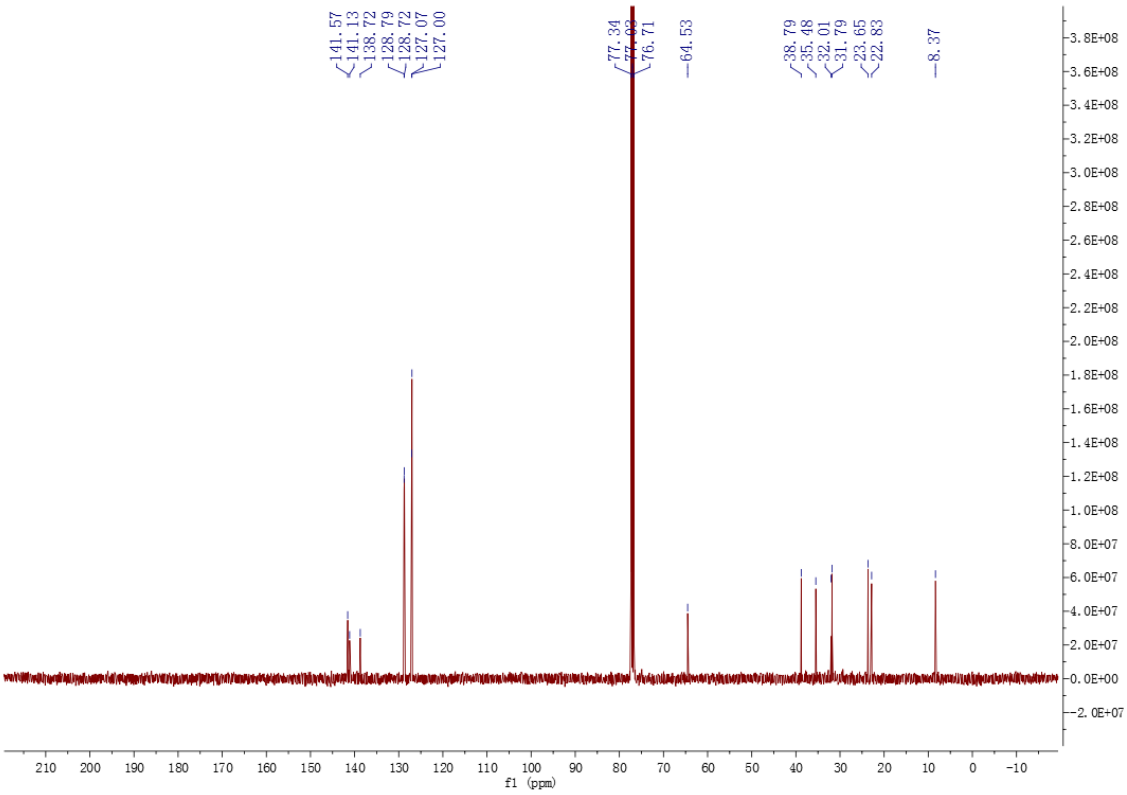
3.07
f1 (ppm)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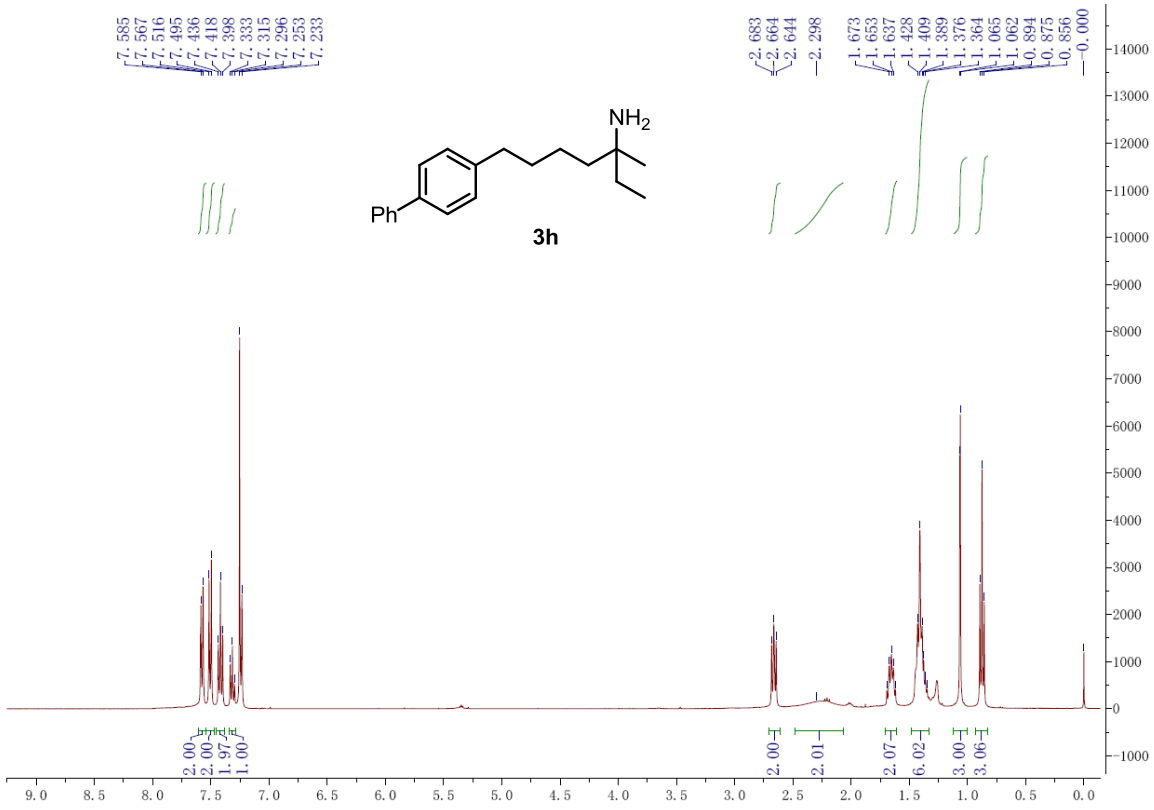
f1 (ppm)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1.376
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0.856
0.000
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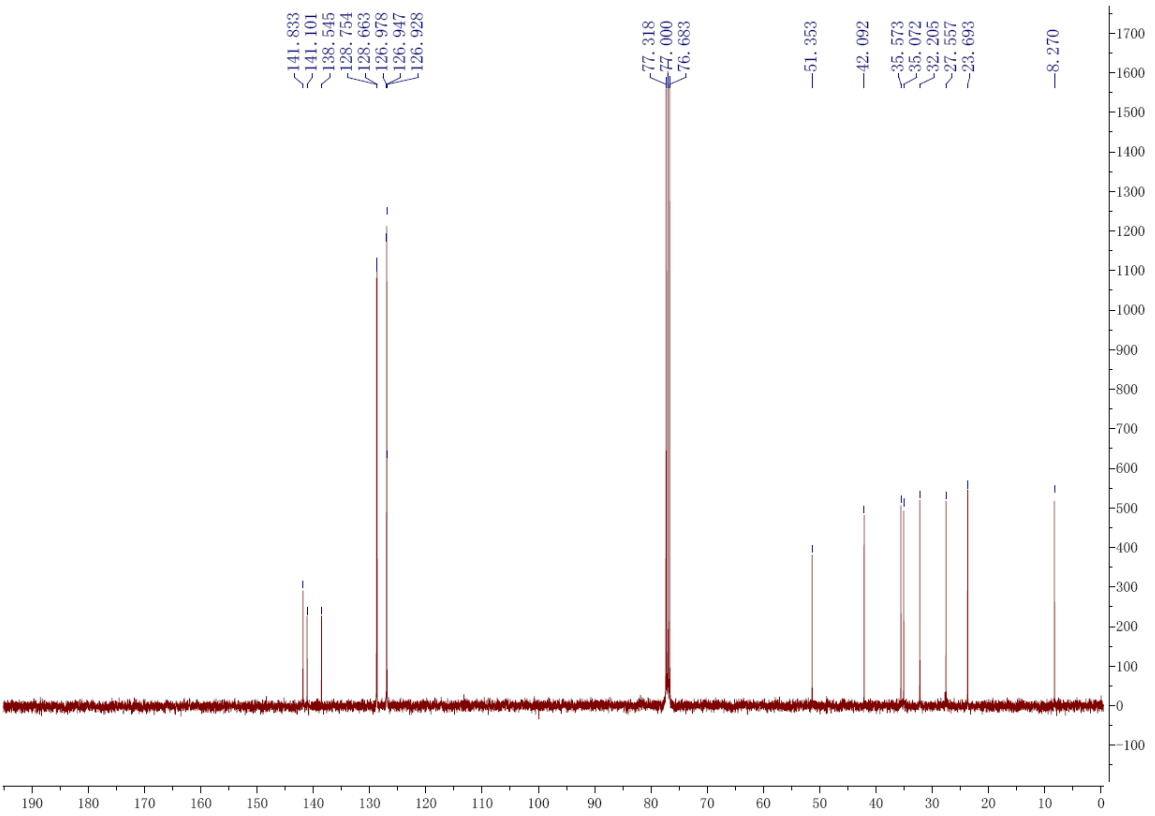
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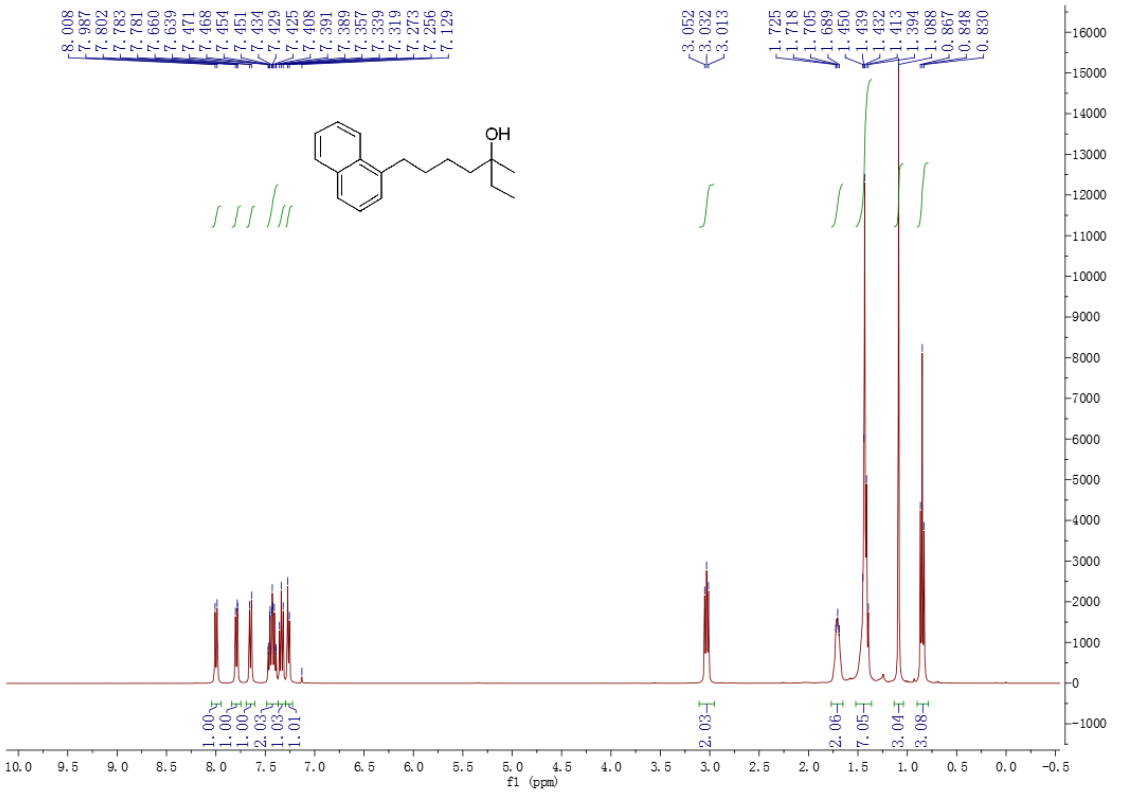
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2.06
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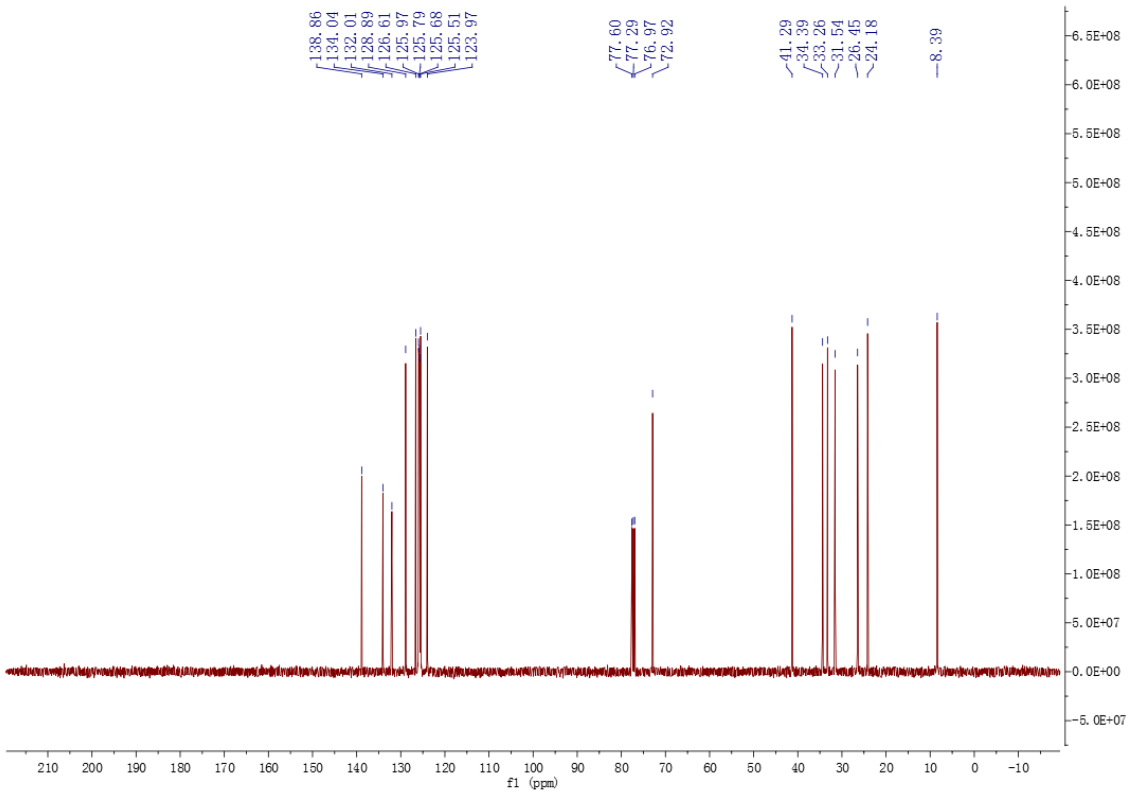
3.08
f1 (ppm)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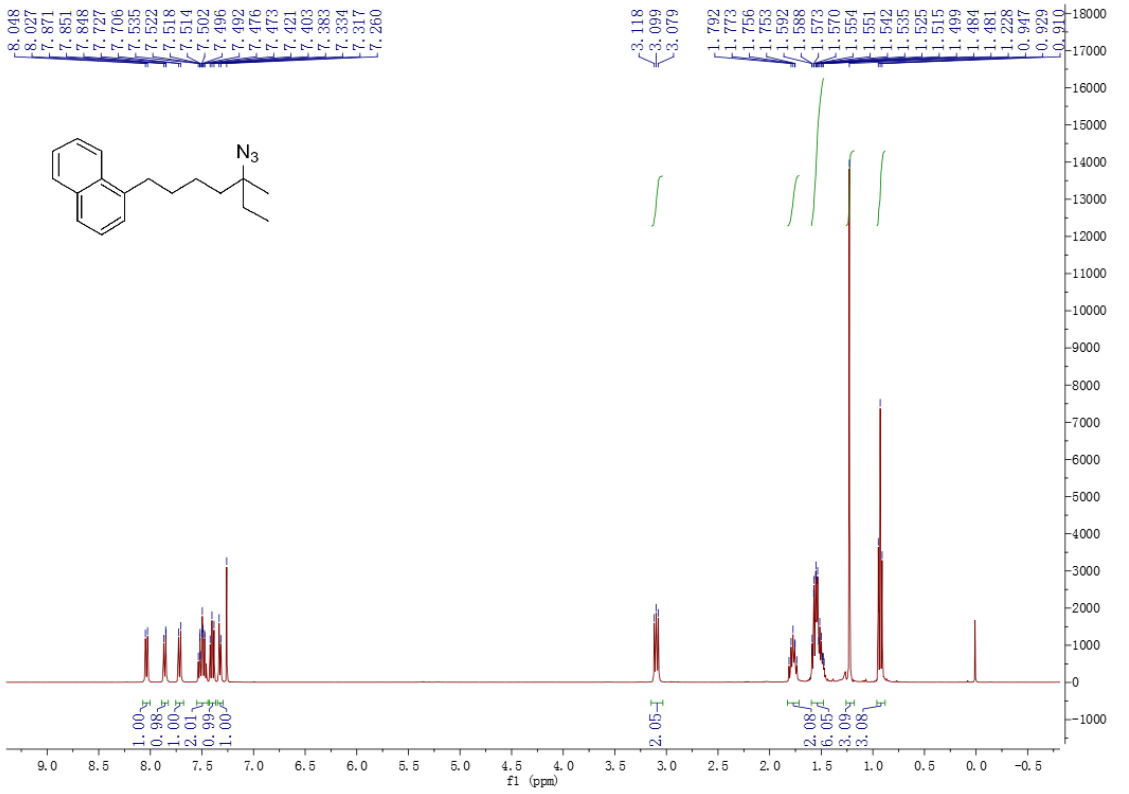
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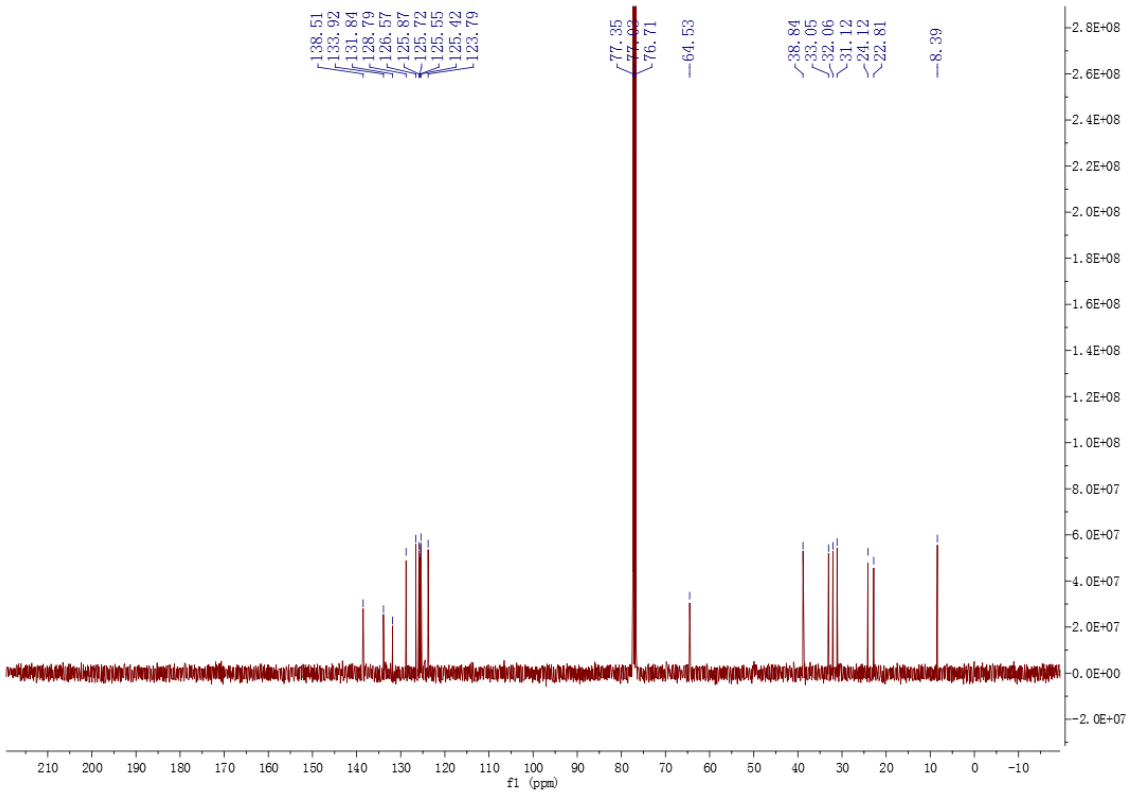
3.08
f1 (ppm)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24.12
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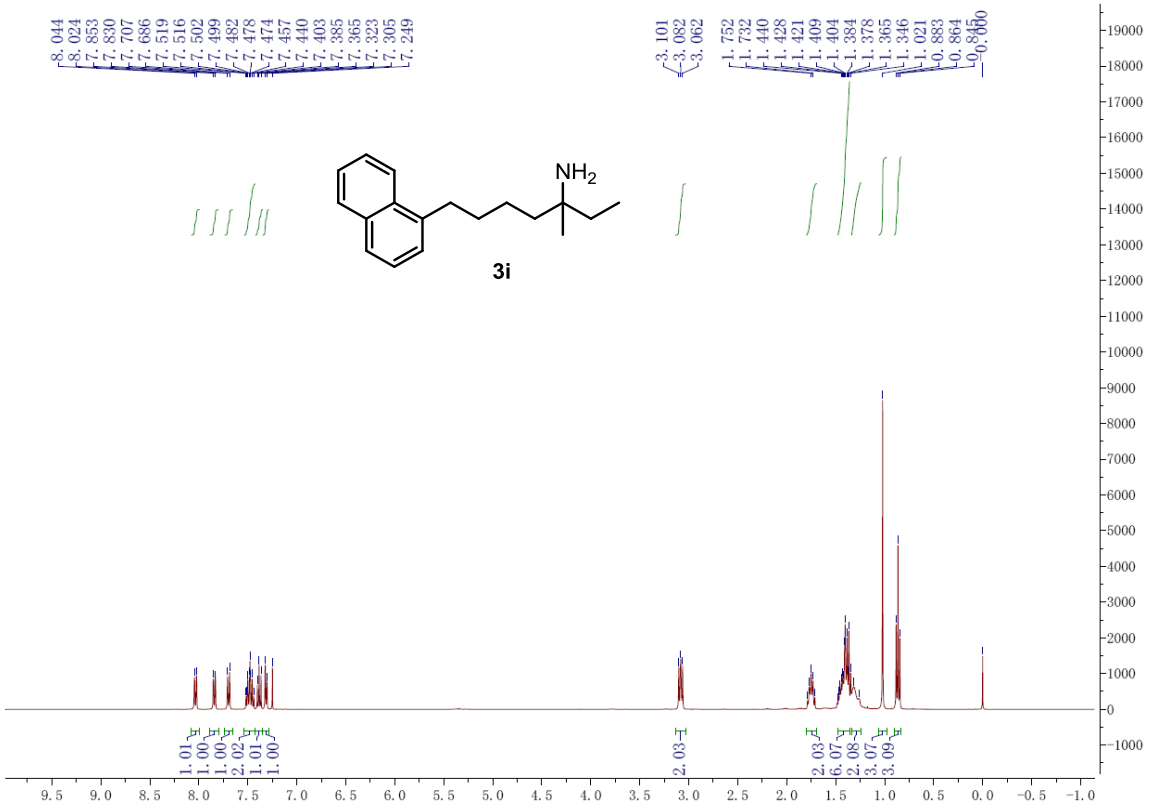
8.39
f1 (ppm)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7.457
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3i
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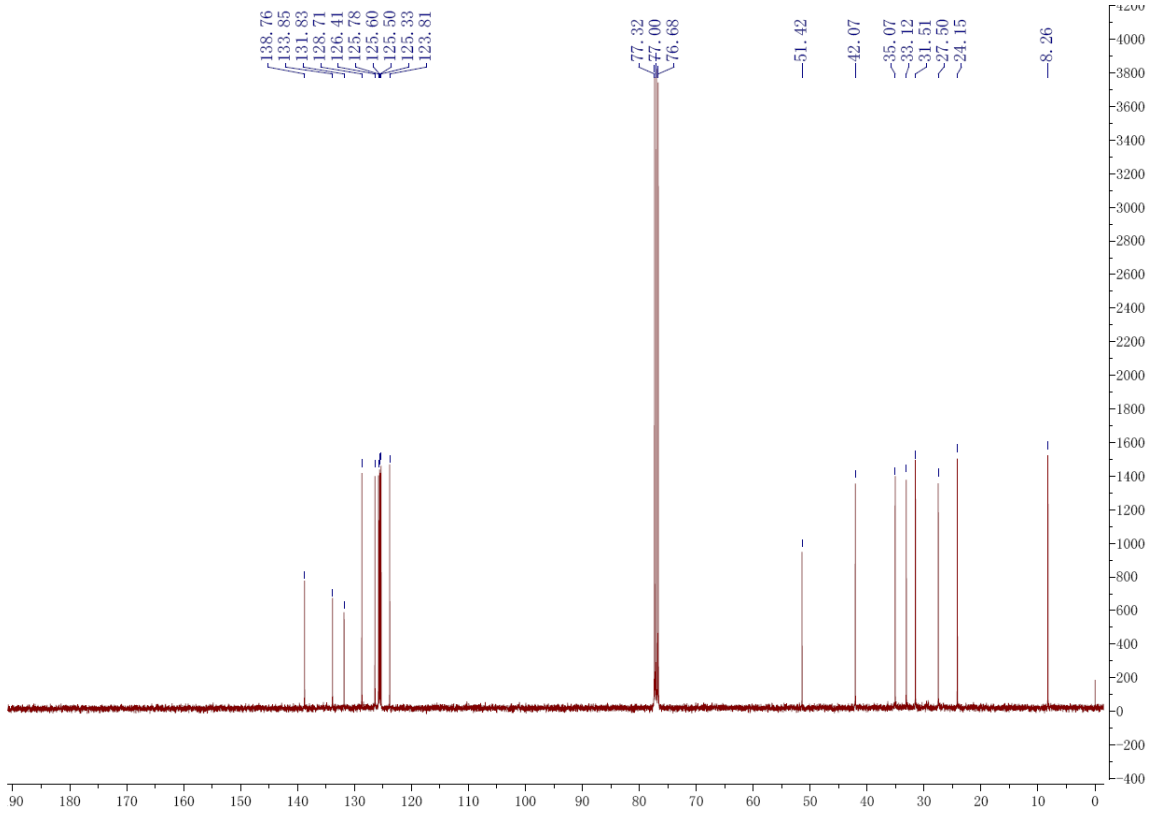
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33.12
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27.50
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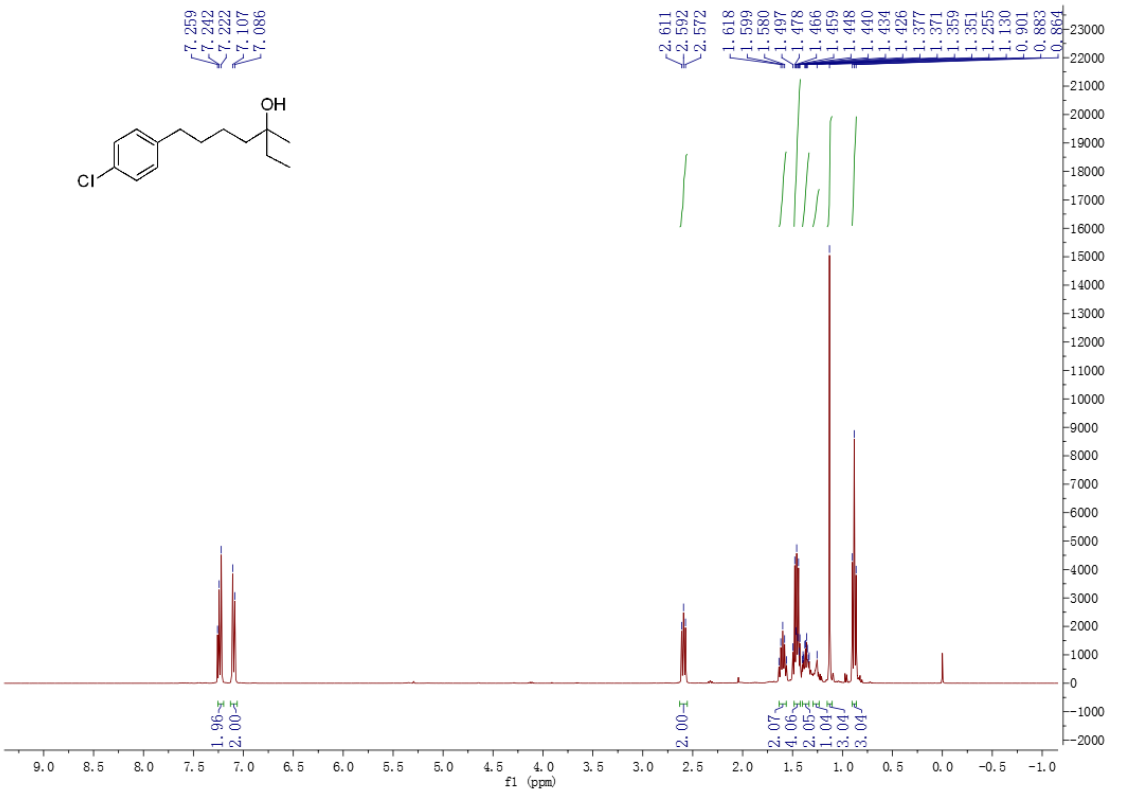
8.26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7.222
7.107
7.086
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Cl
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1.580
1.497
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1.466
1.459
1.448
1.440
1.434
1.426
1.377
1.371
1.359
1.351
1.255
1.130
0.901
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2.00
2.07
4.06
2.05
1.04
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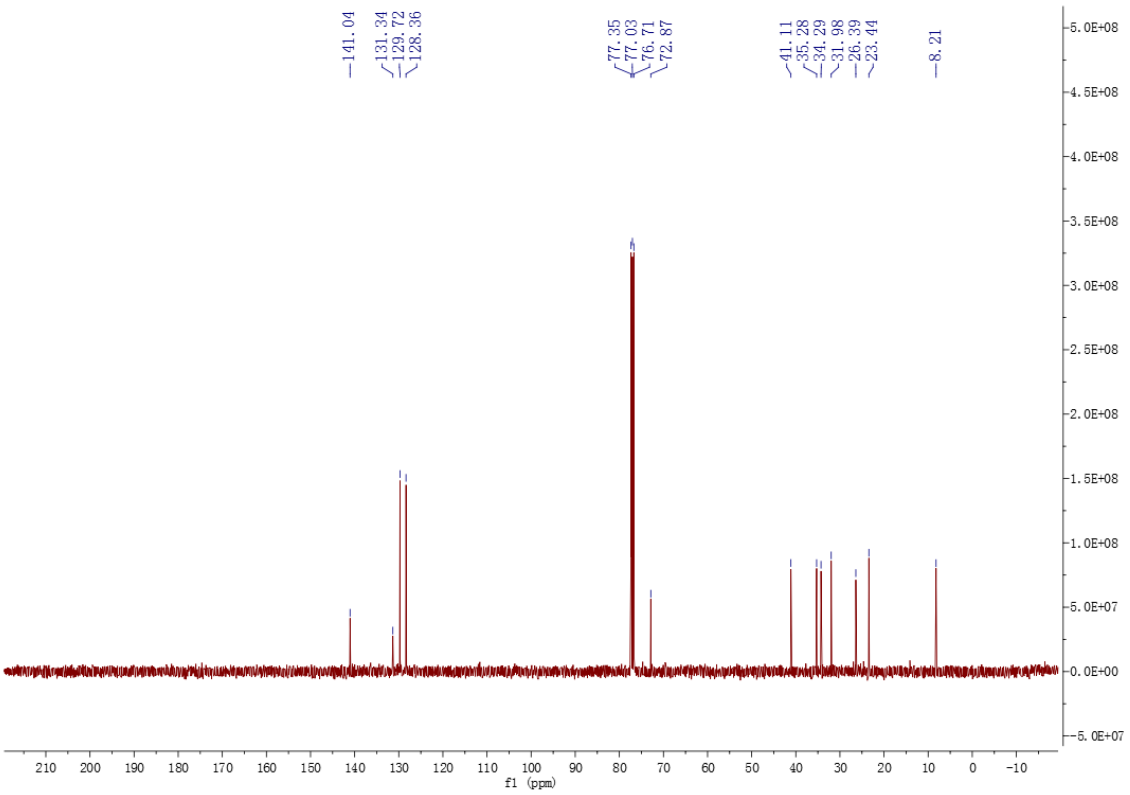
3.04
f1 (ppm)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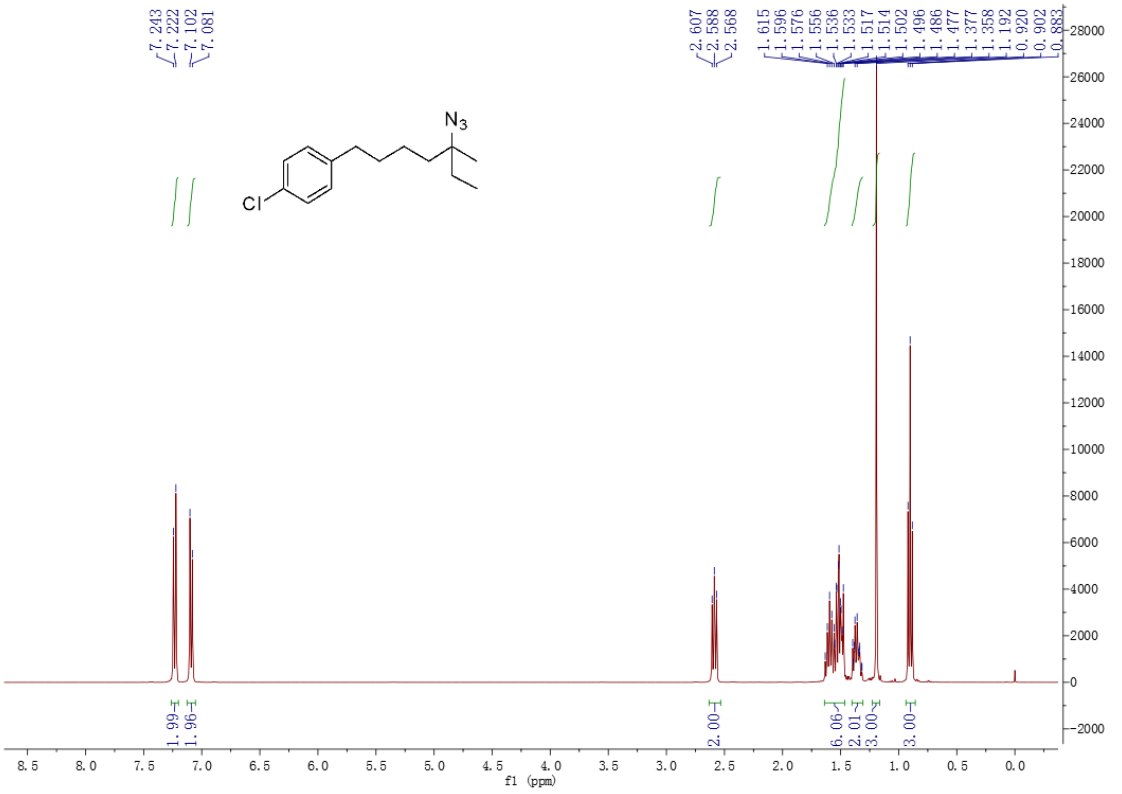
f1 (ppm)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1.533
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1.514
1.502
1.496
1.486
1.477
1.377
1.358
1.192
0.920
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Cl
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2.00
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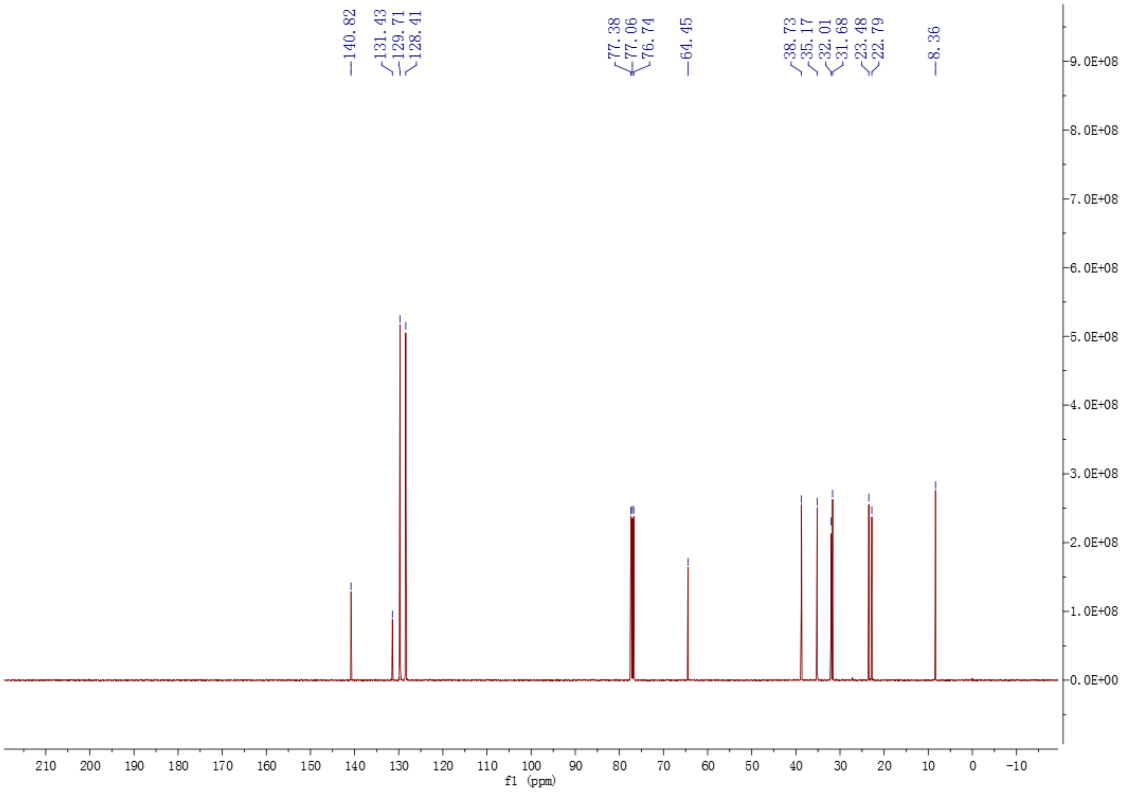
2.01
3.00
3.00
f1 (ppm)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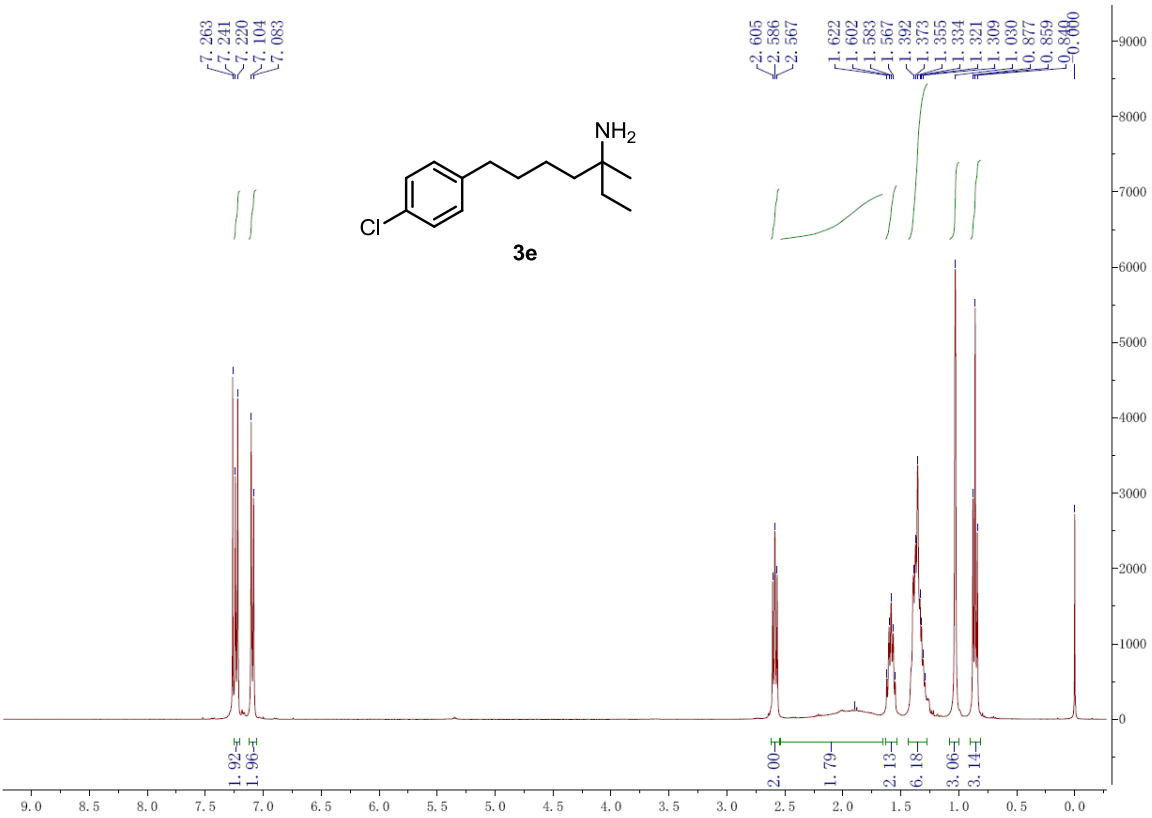
f1 (ppm)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1.373
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1.334
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Cl
3e
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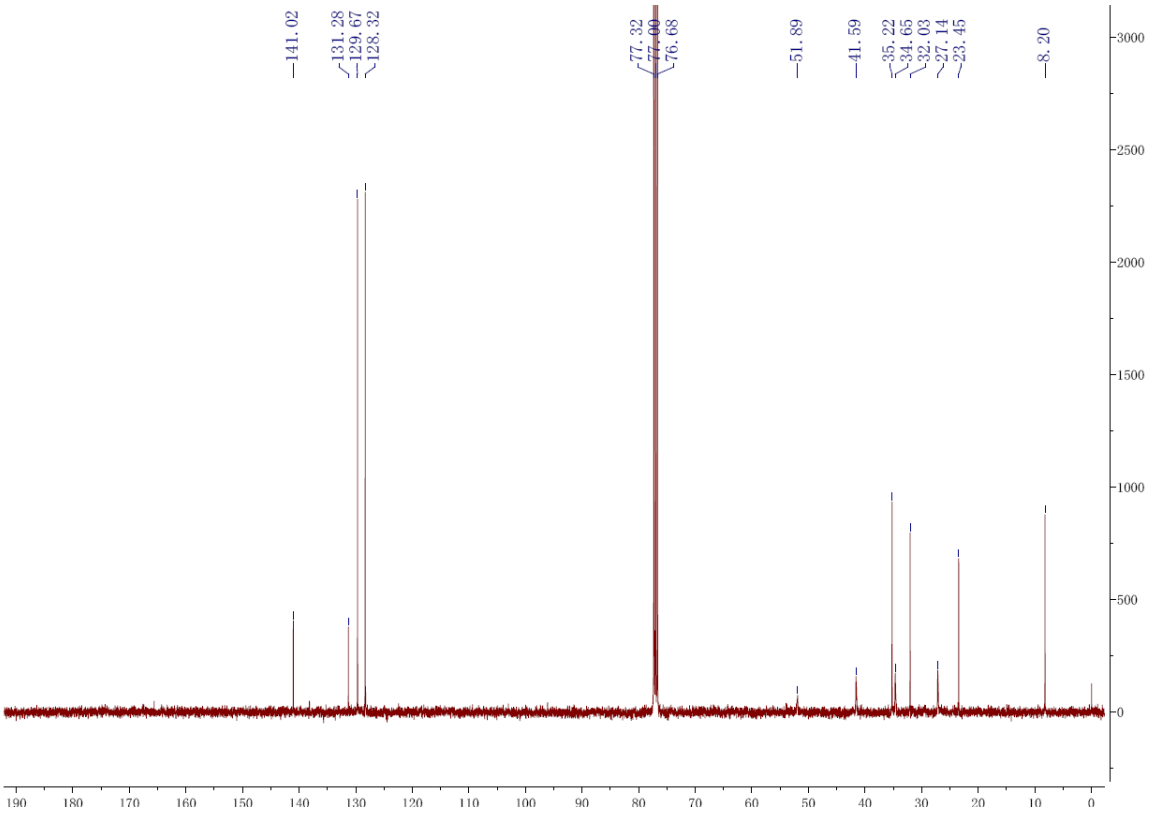
6.18
3.06
3.14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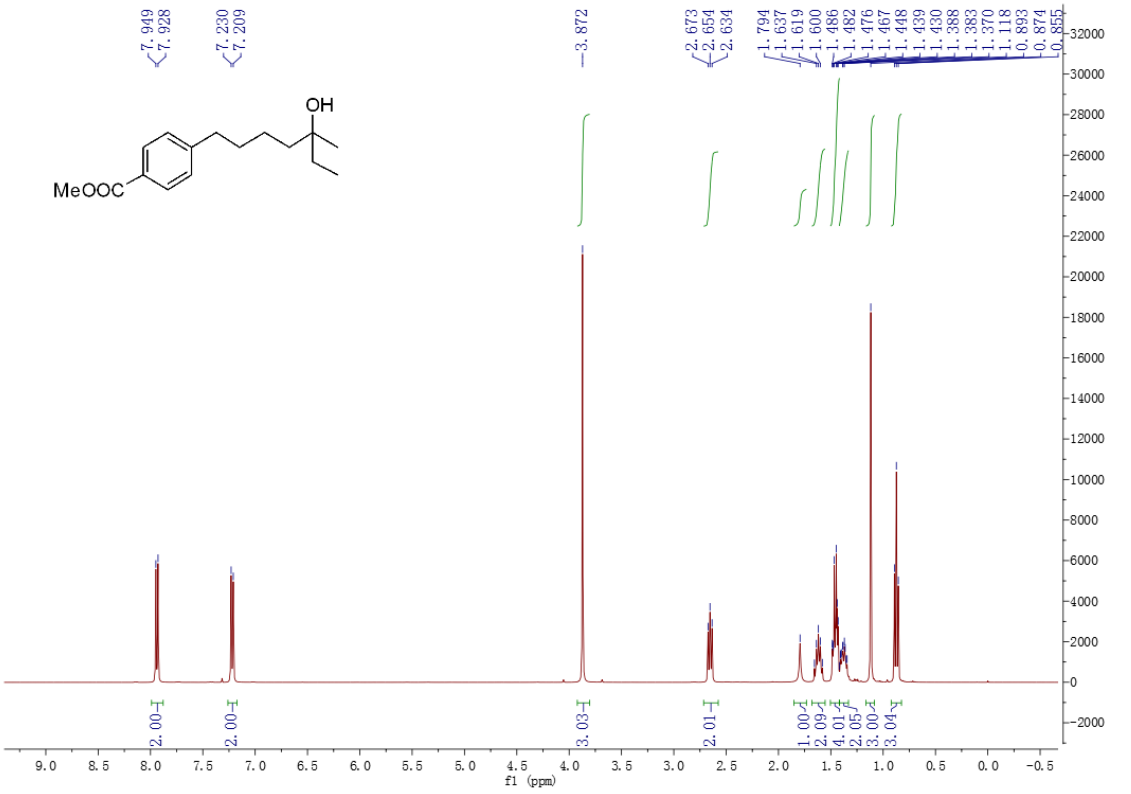
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1.467
1.448
1.439
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1.388
1.383
1.370
1.118
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0.874
0.855
OH
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1.00
2.09
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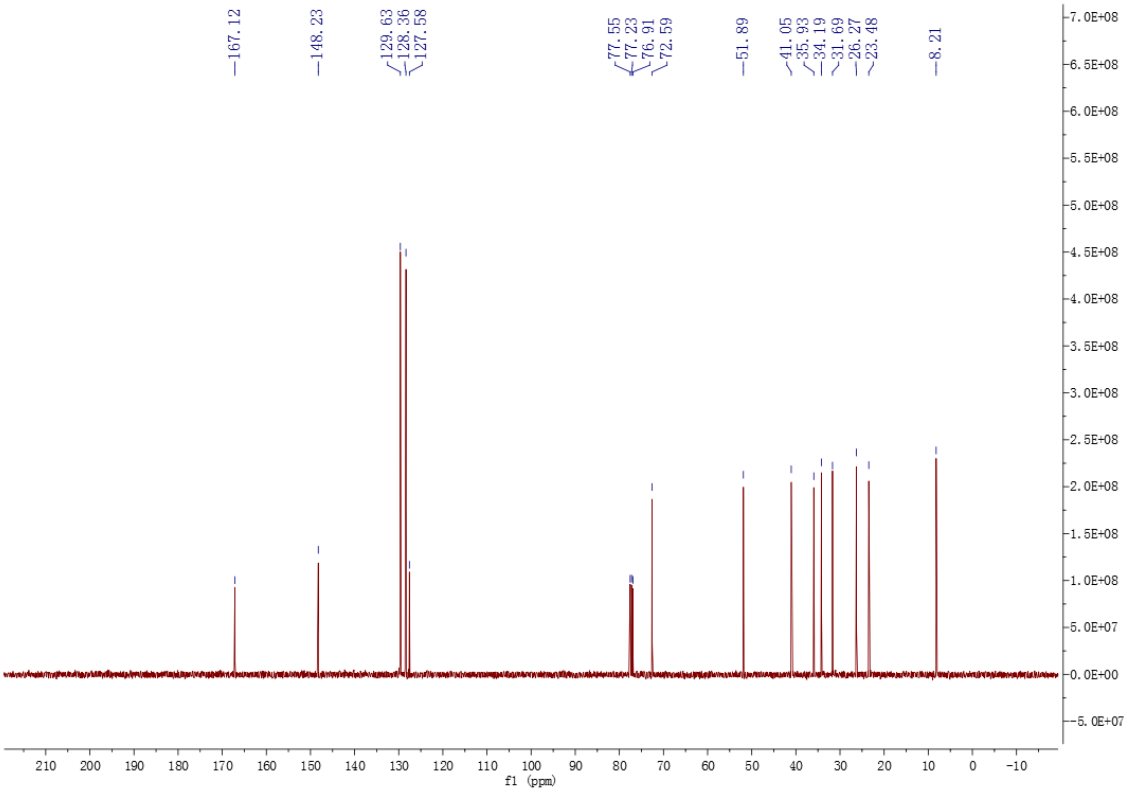
2.05
3.00
3.04
f1 (ppm)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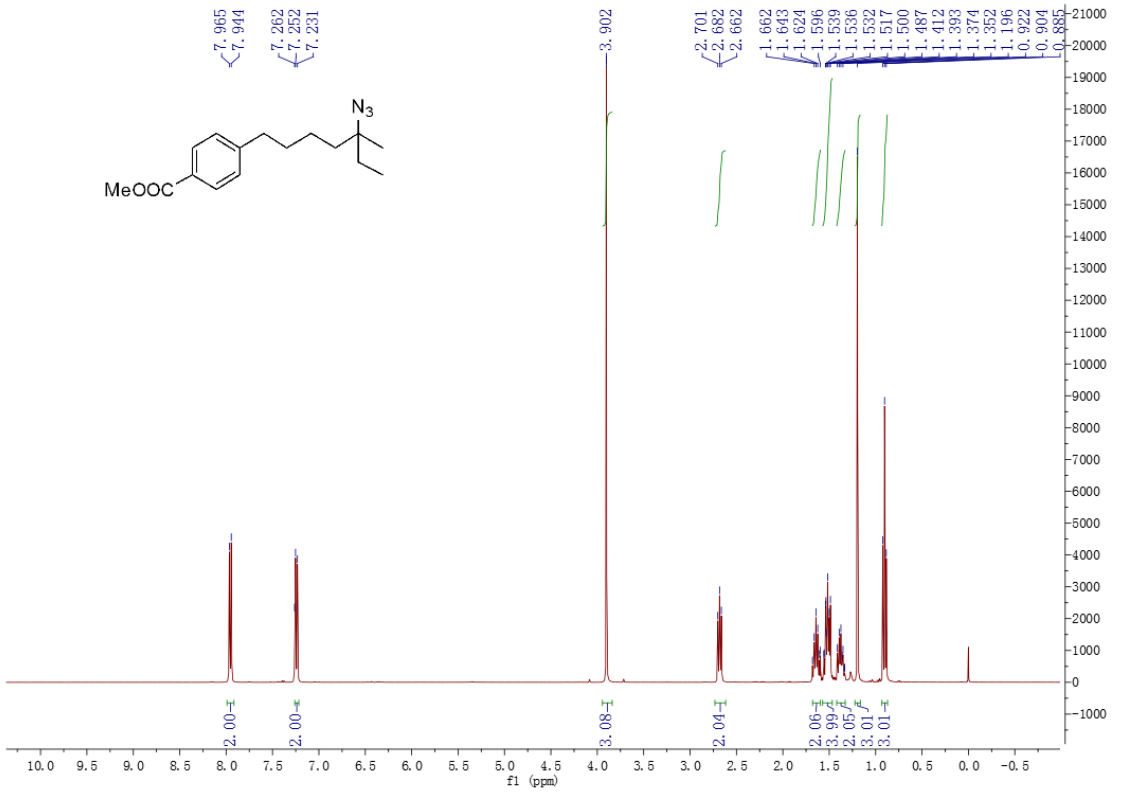
8.21
f1 (ppm)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1.539
1.536
1.532
1.517
1.500
1.487
1.412
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1.374
1.352
1.196
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0.904
0.885
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3.01
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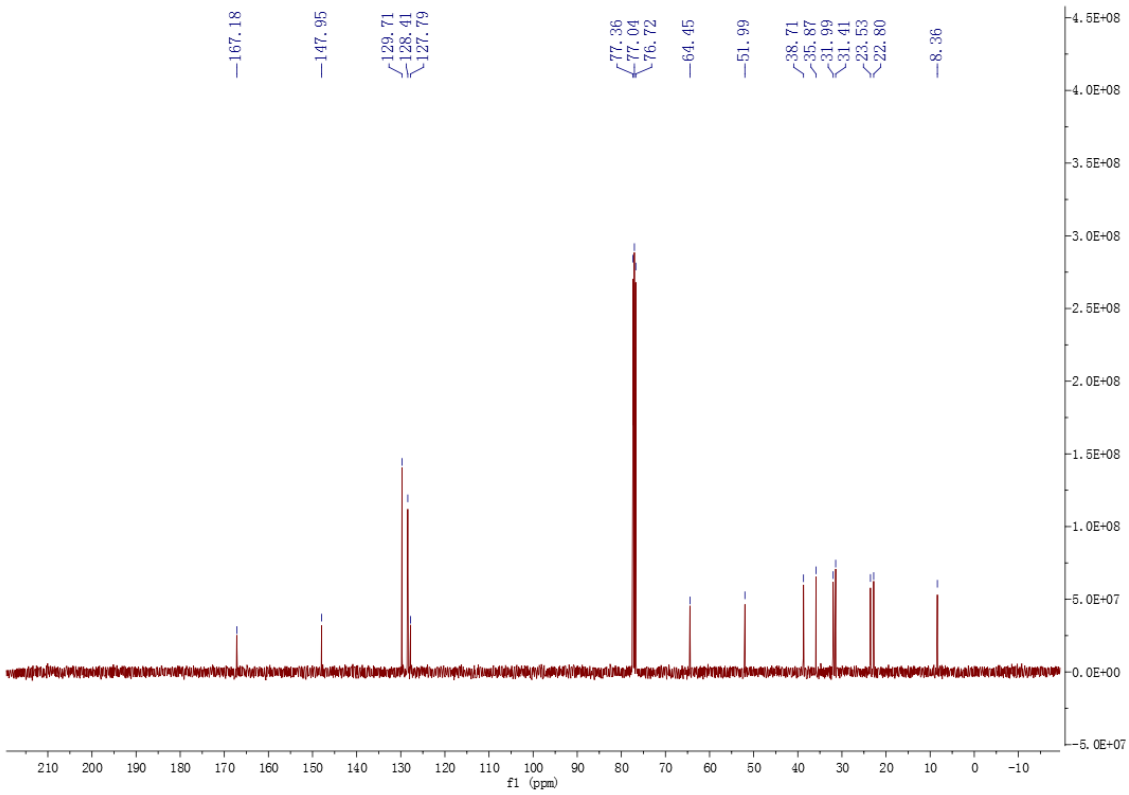
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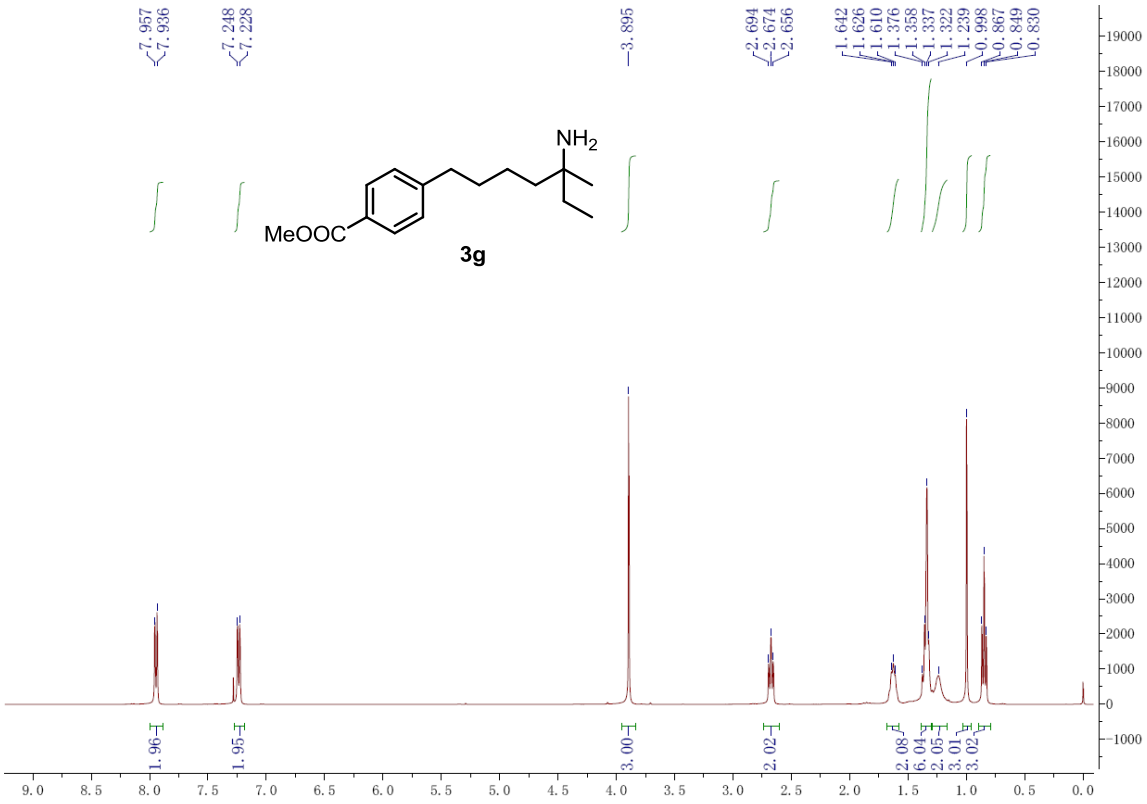
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1.358
1.337
1.322
1.239
0.998
0.867
0.849
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1.95
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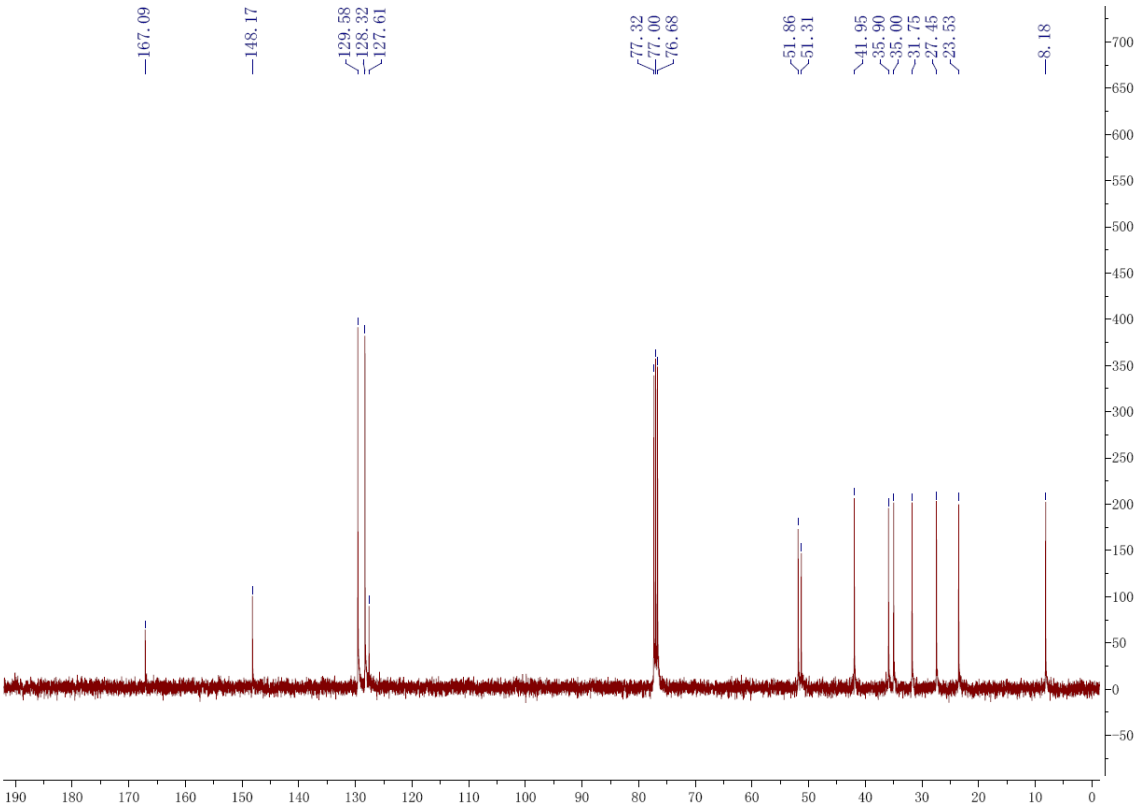
6.04
2.05
3.01
3.02

3g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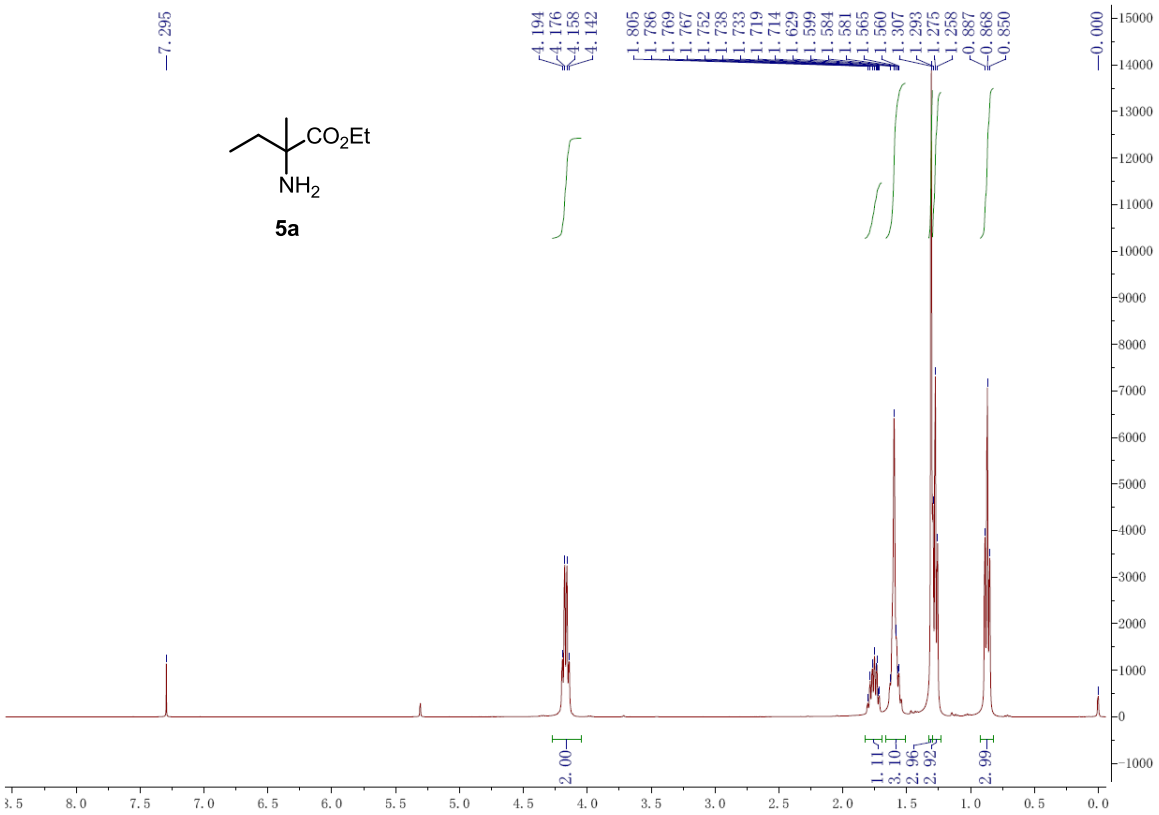
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1.581
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1.307
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1.275
1.258
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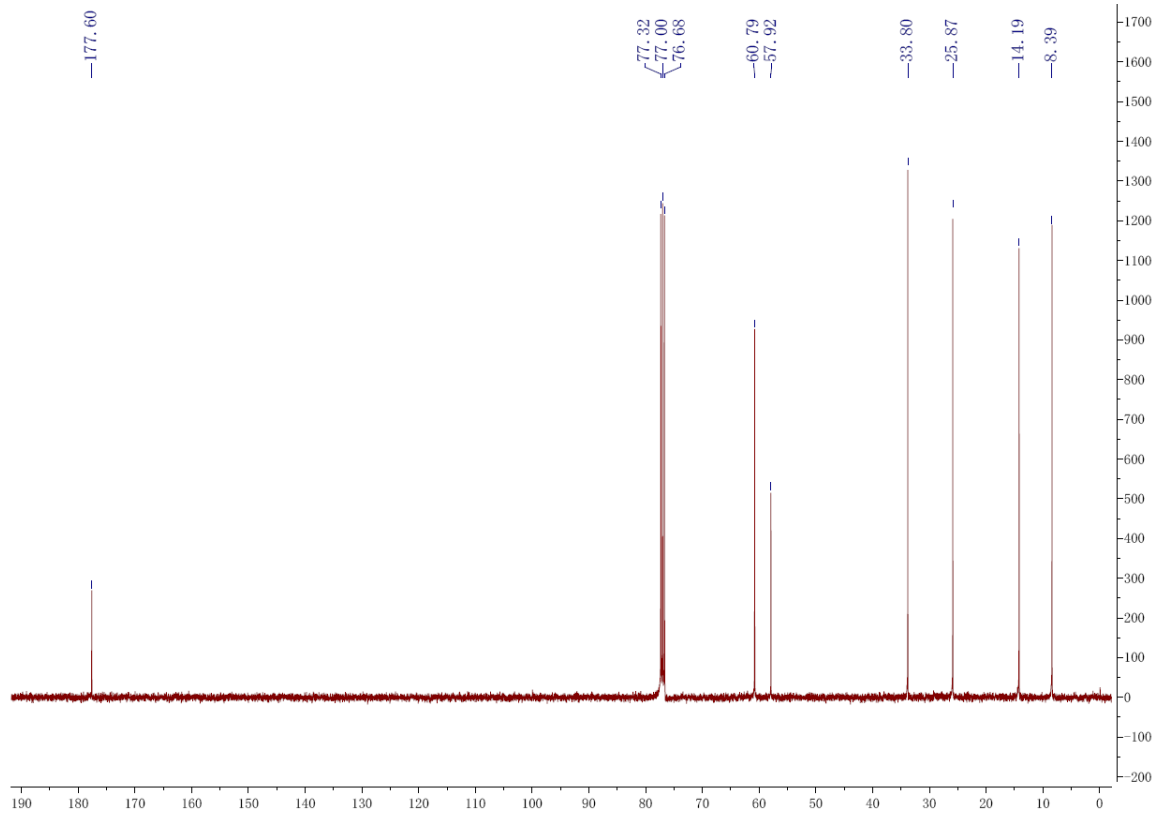
2.99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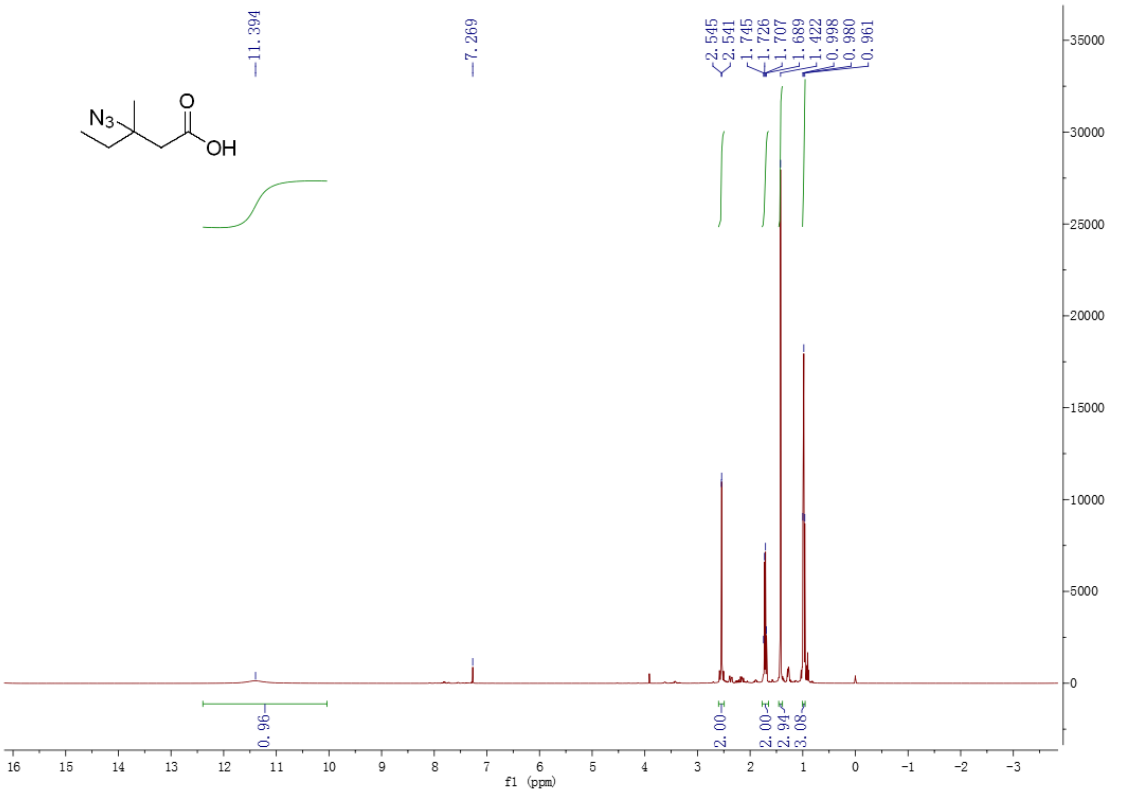
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OH
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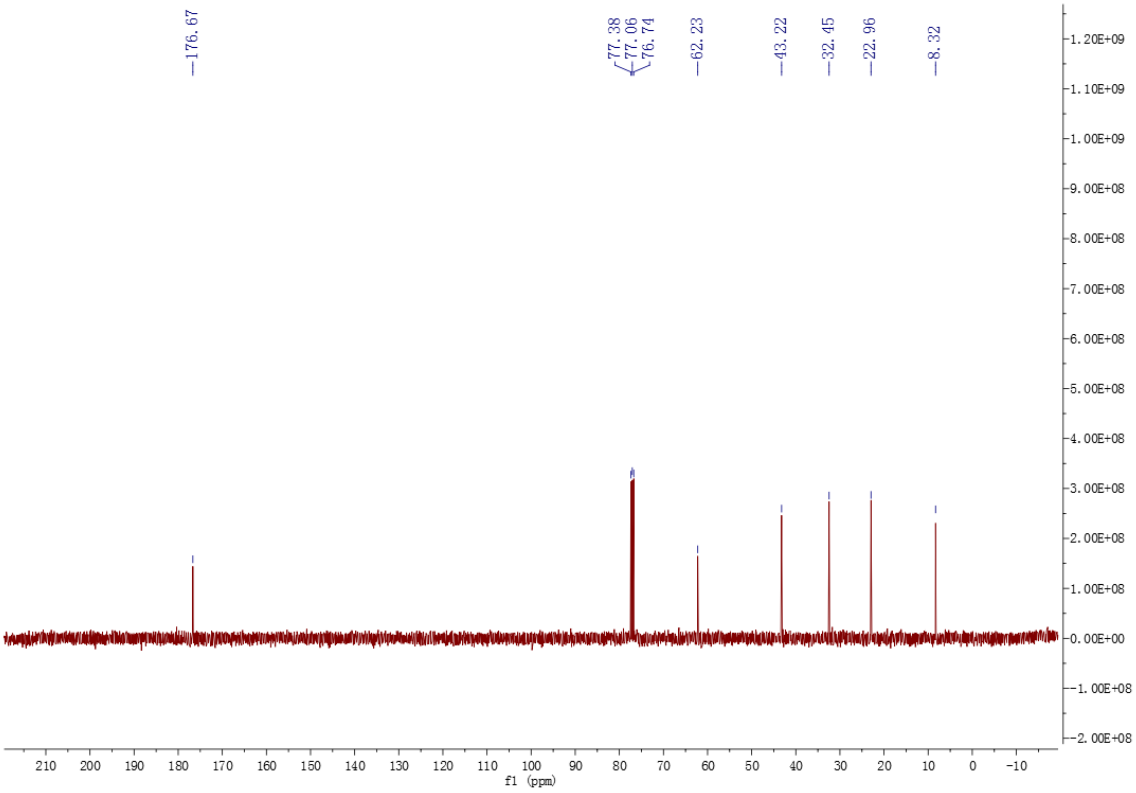
f1 (ppm)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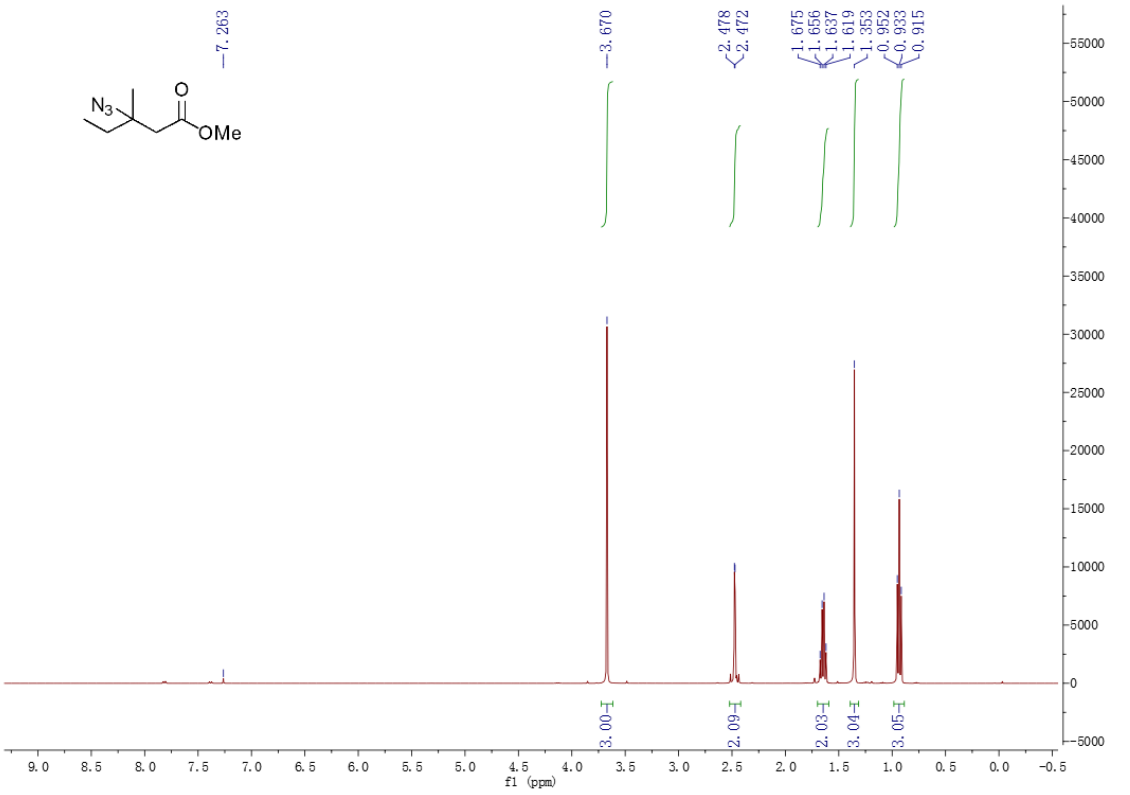
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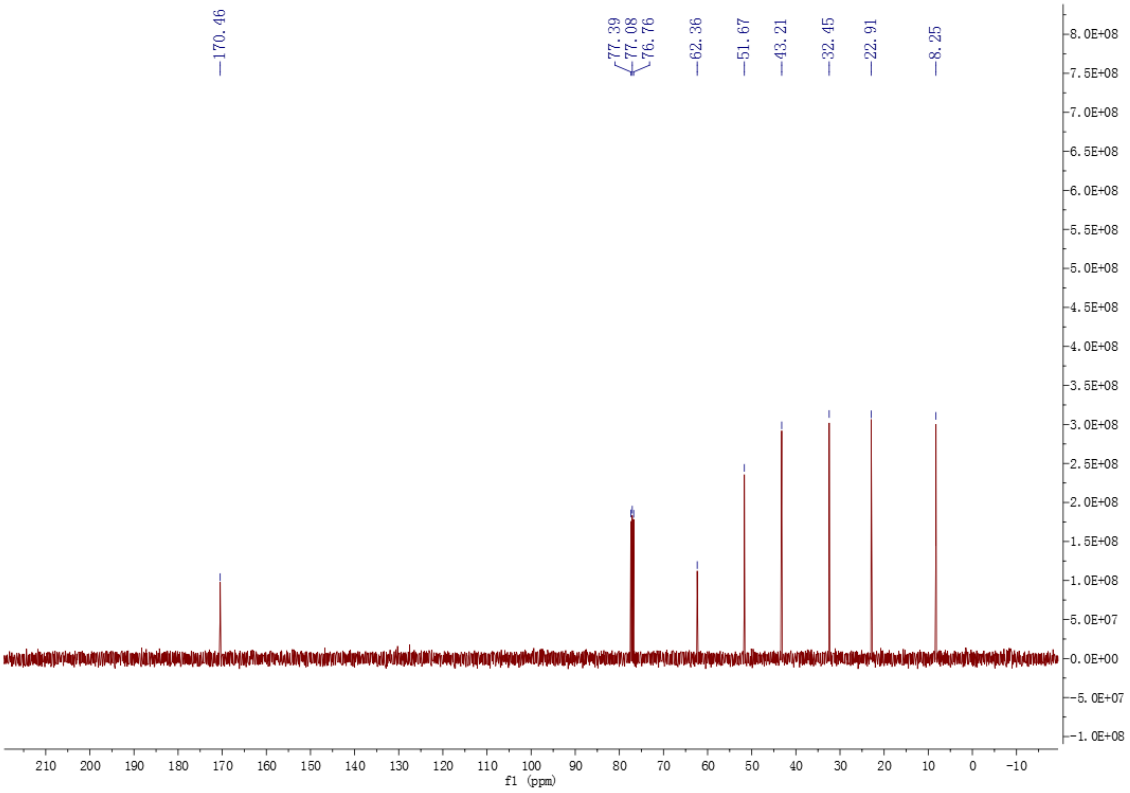
2.03
3.04
3.05
f1 (ppm)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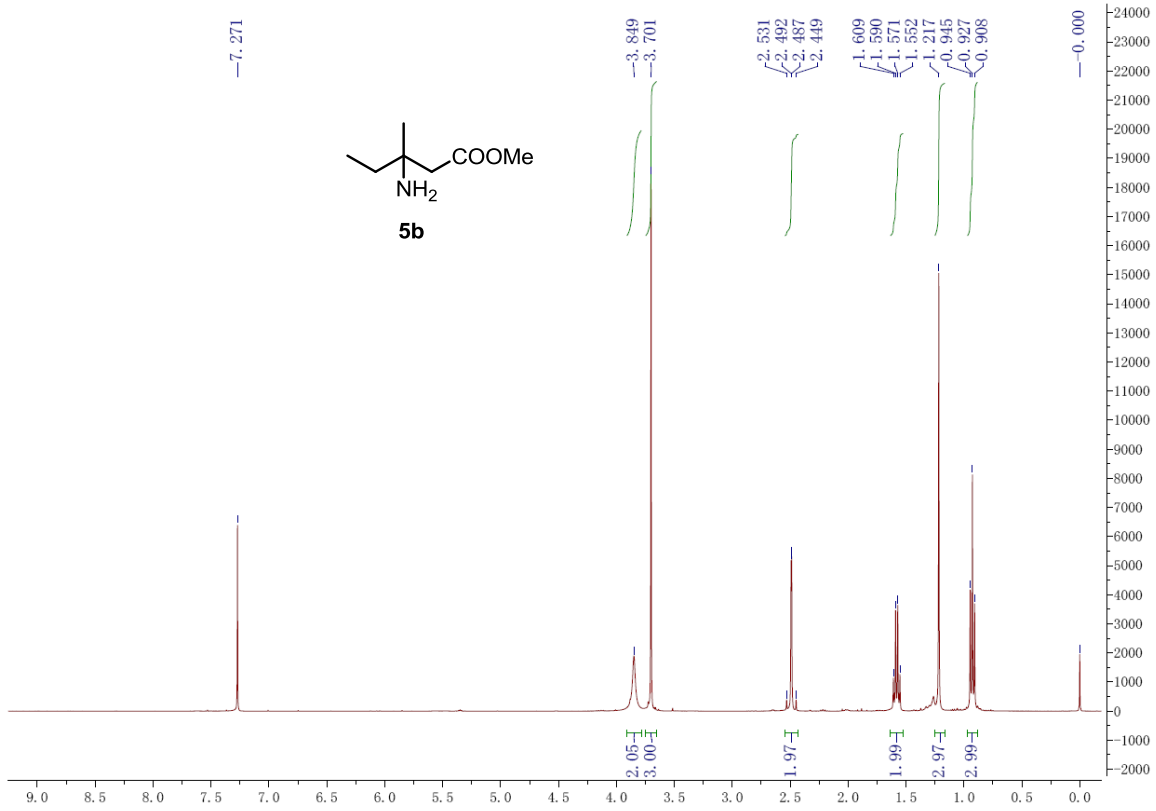
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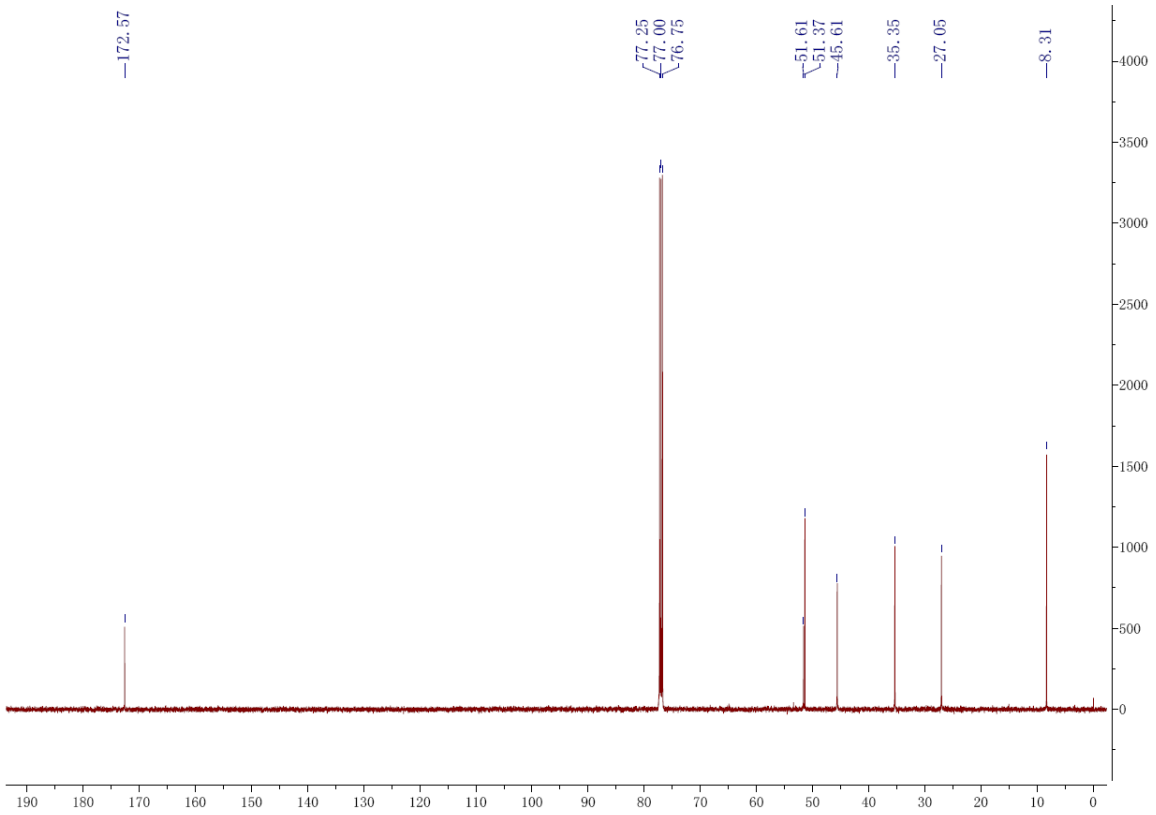
2.99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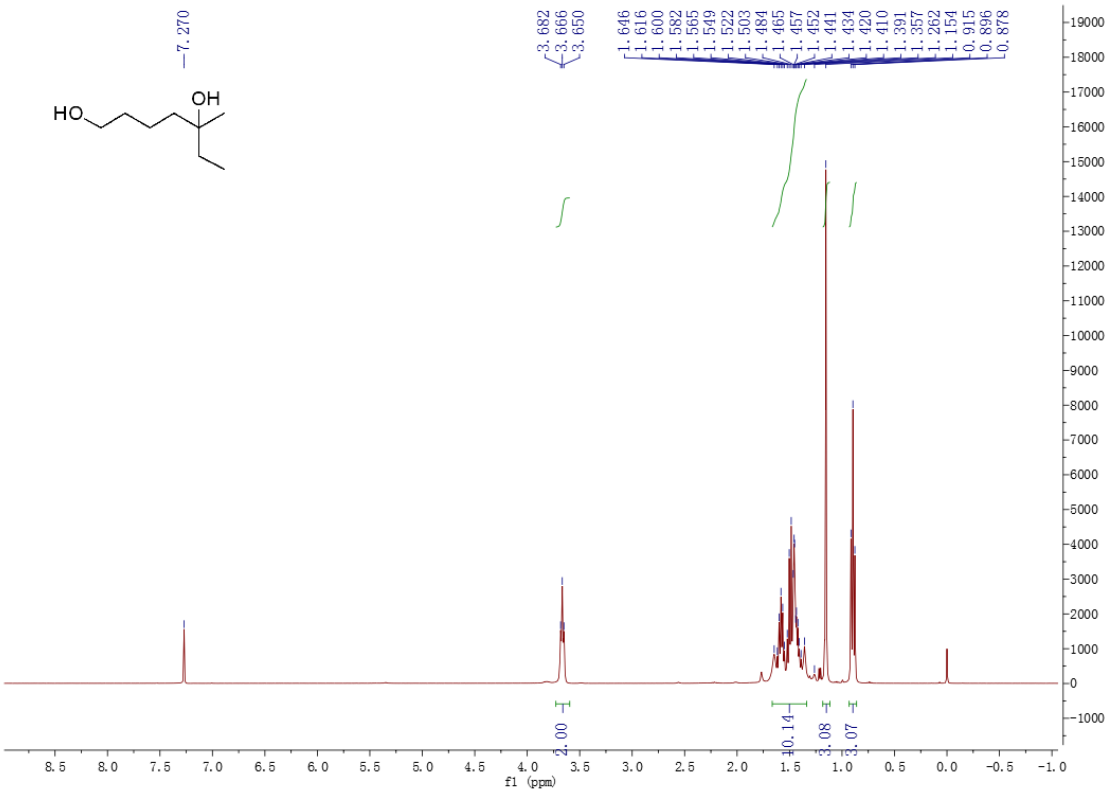
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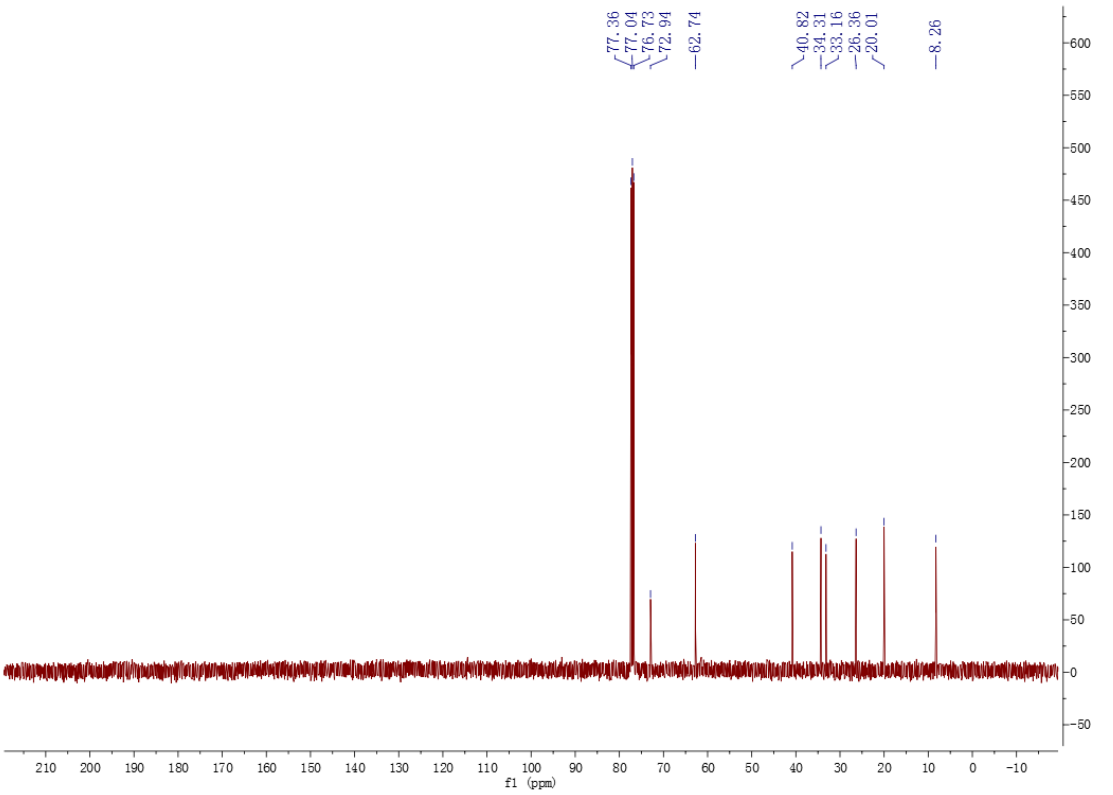
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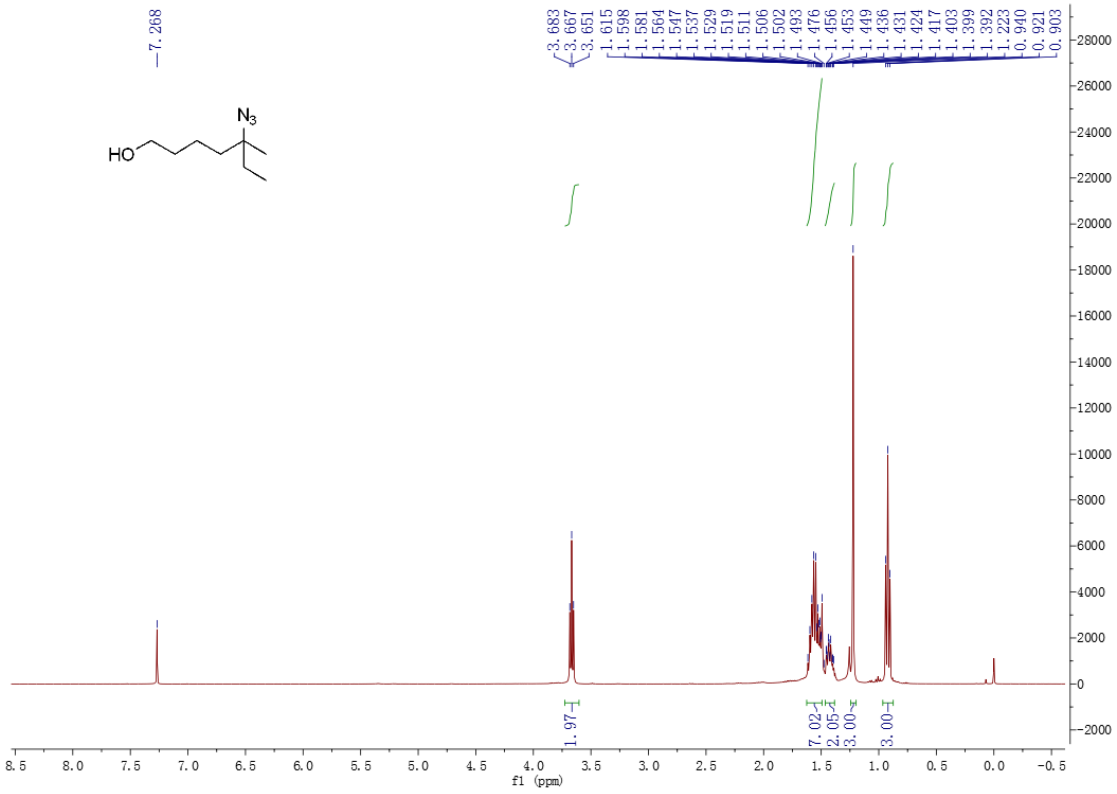
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0.940
0.921
0.903
HO
N3
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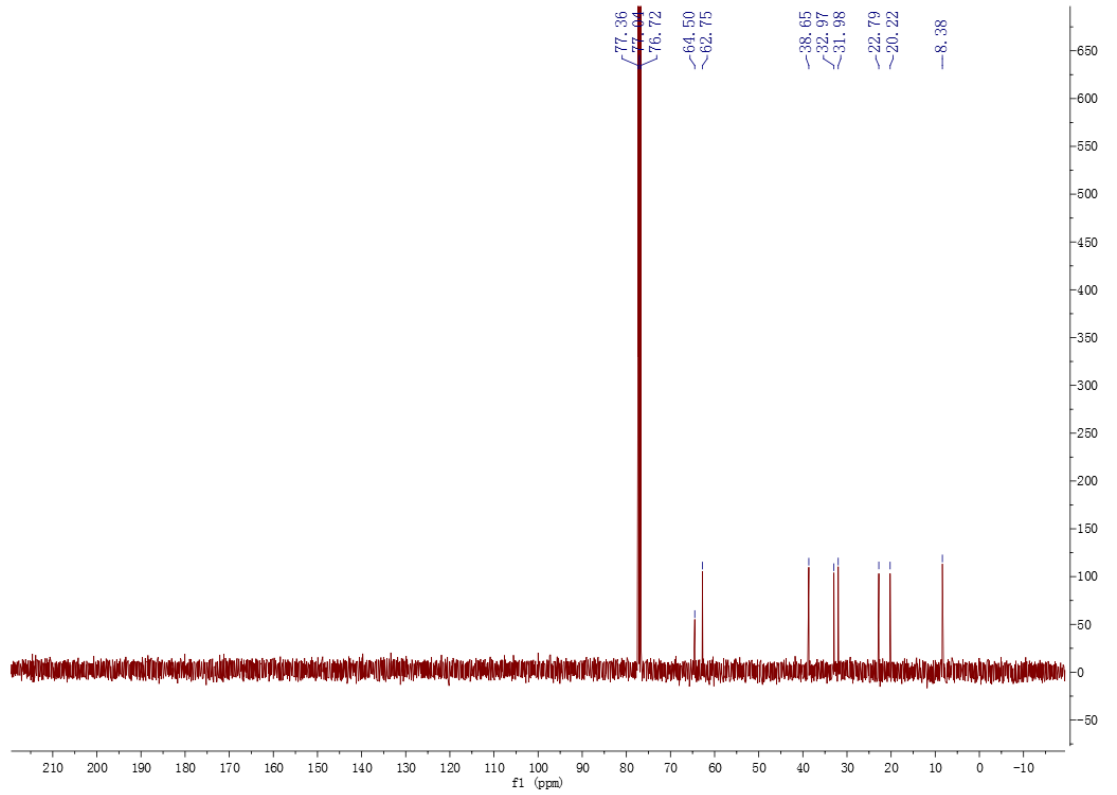
7.02
2.05
3.00
3.00
f1 (ppm)


77.36
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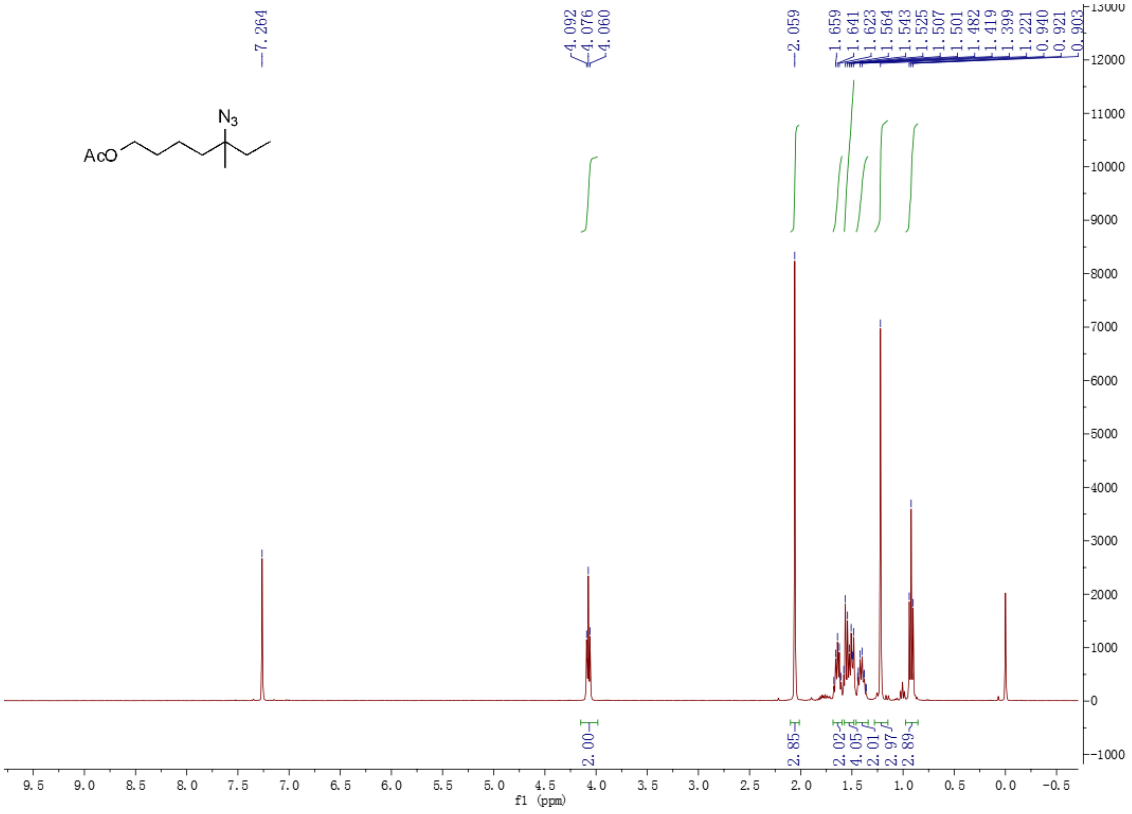
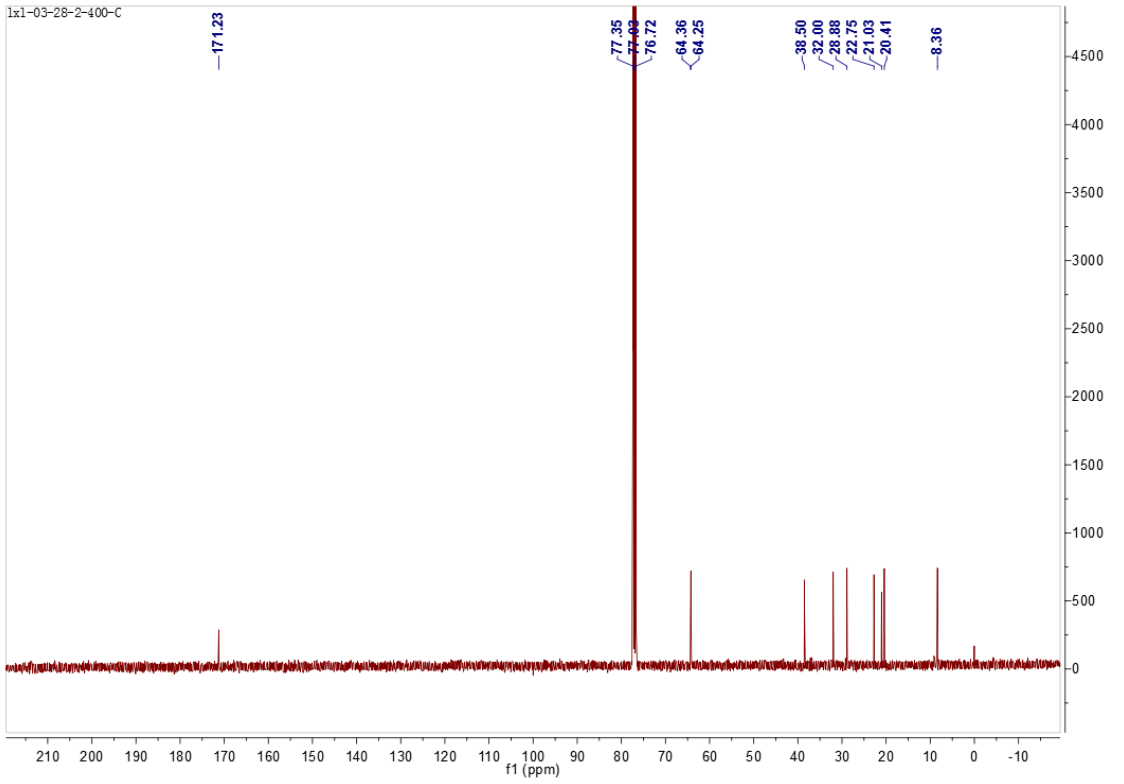
64.50
62.75
38.65
32.97
31.98
22.79
20.22
8.38
f1 (ppm)


7.264
4.092
4.076
4.060
2.059
1.659
1.641
1.623
1.564
1.543
1.525
1.507
1.501
1.482
1.419
1.399
1.221
0.940
0.921
0.903
N3
AcO
2.00
2.85
2.02
4.05
2.01
2.97
2.89
f1 (ppm)


lxl-03-28-2-400-C
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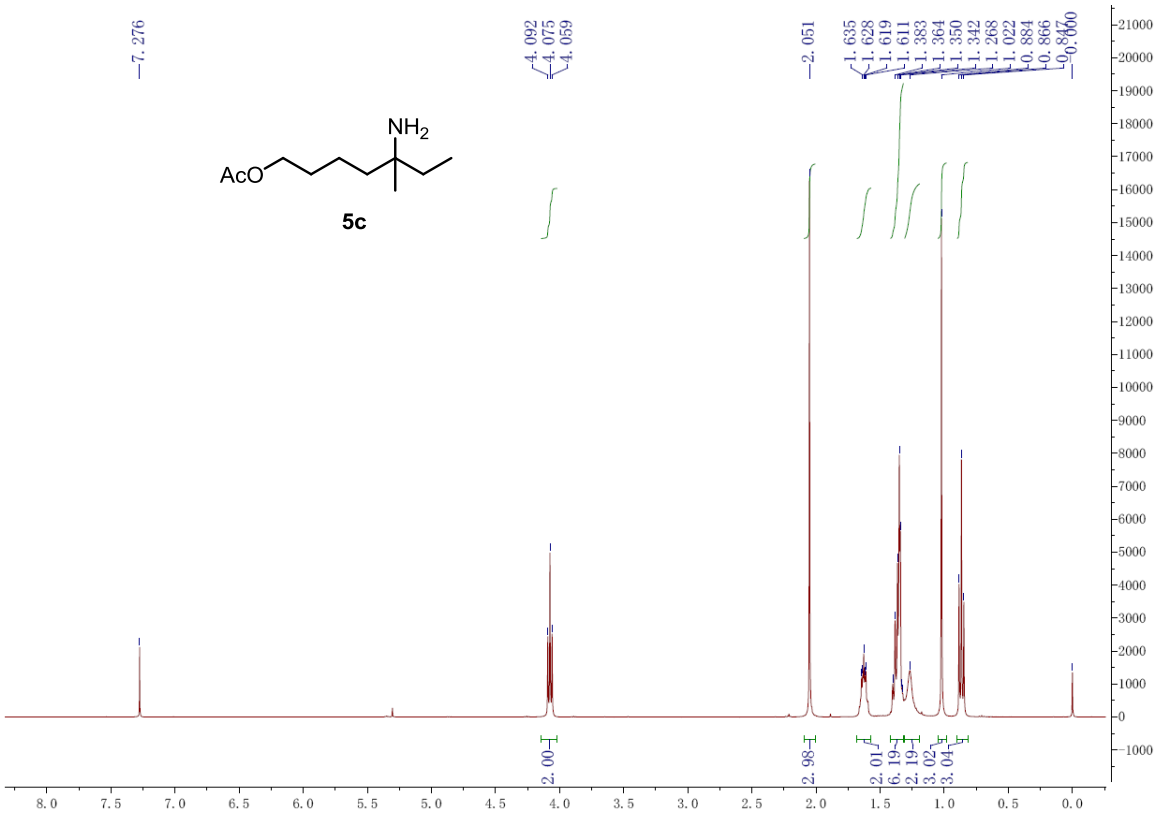
77.35
77.03
76.72
64.36
64.25
38.50
32.00
28.88
22.75
21.03
20.41
8.36
f1 (ppm)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2.051
1.635
1.628
1.619
1.611
1.383
1.364
1.350
1.342
1.268
1.022
0.884
0.866
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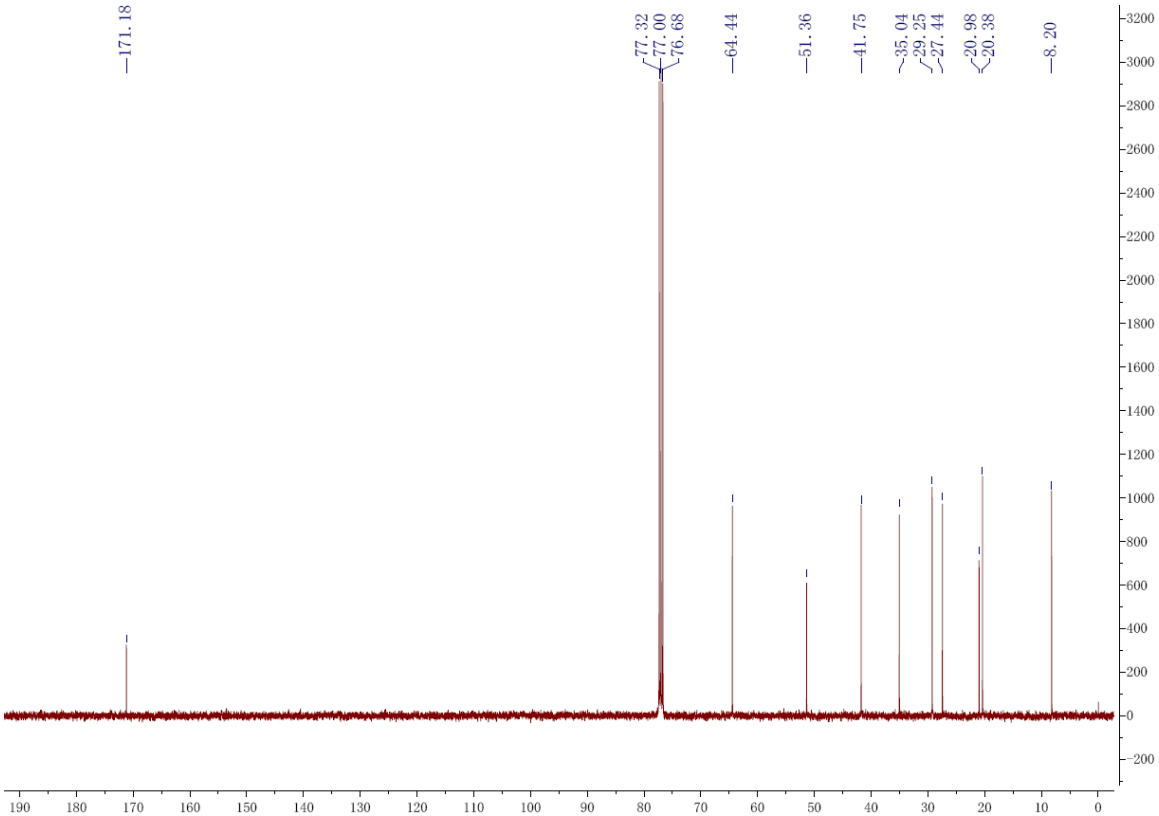
NH2
AcO
5c
2.00
2.98
2.01
6.19
2.19
3.02
3.04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41.75
35.04
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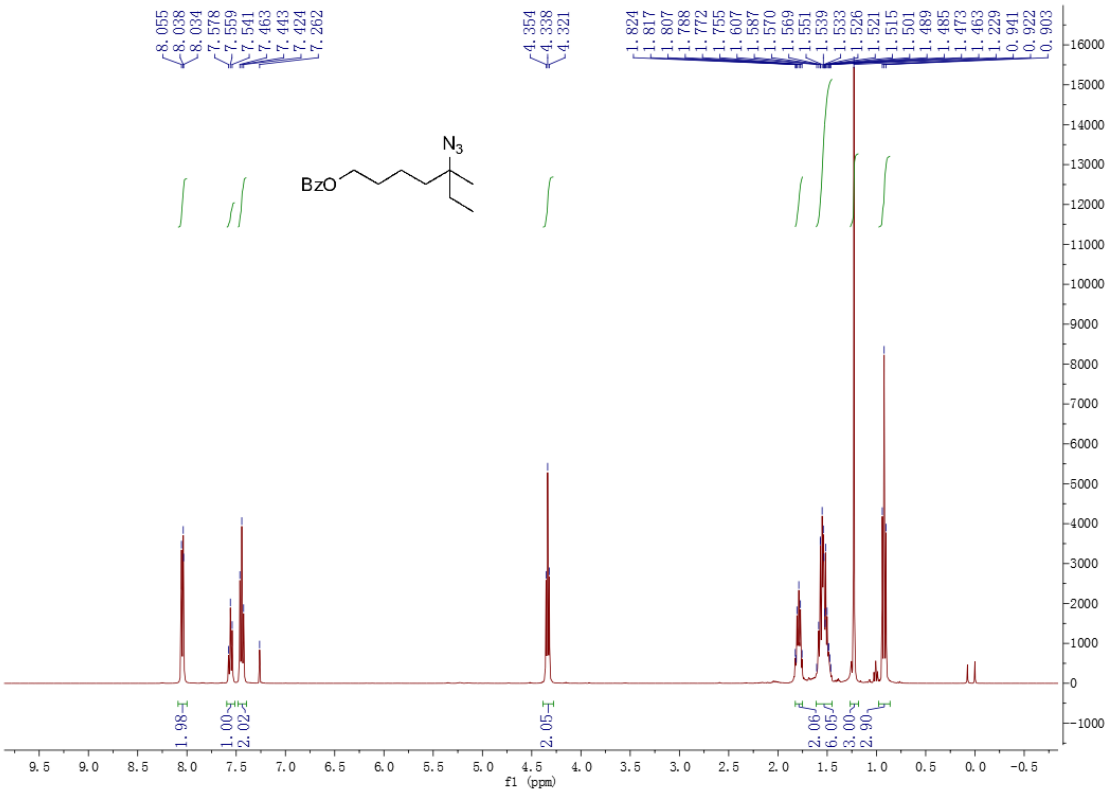
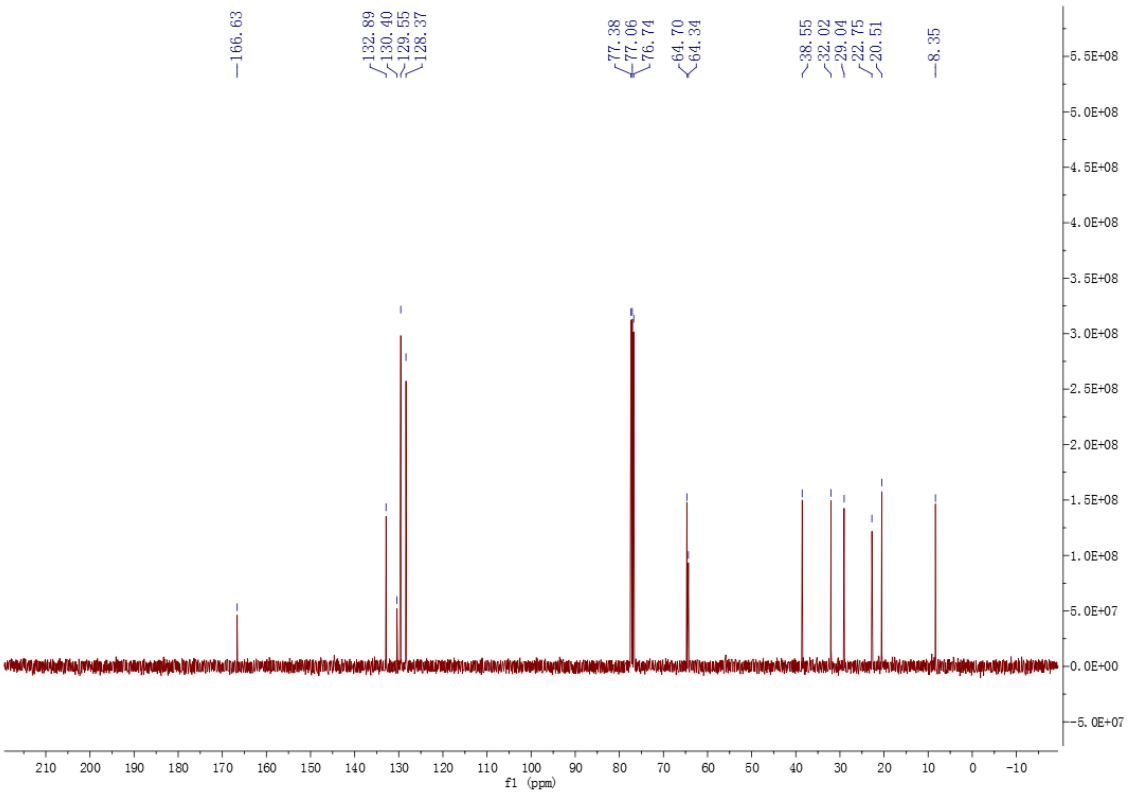
27.44
20.98
20.38
8.20


8.055
8.038
8.034
7.578
7.559
7.541
7.463
7.443
7.424
7.262
4.354
4.338
4.321
1.824
1.817
1.807
1.788
1.772
1.755
1.607
1.587
1.570
1.569
1.551
1.539
1.533
1.526
1.521
1.515
1.501
1.489
1.485
1.473
1.463
1.229
0.941
0.922
0.903
N3
BzO
1.98
1.00
2.02
2.05
2.06
6.05
3.00
2.90
f1 (ppm)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130.40
129.55
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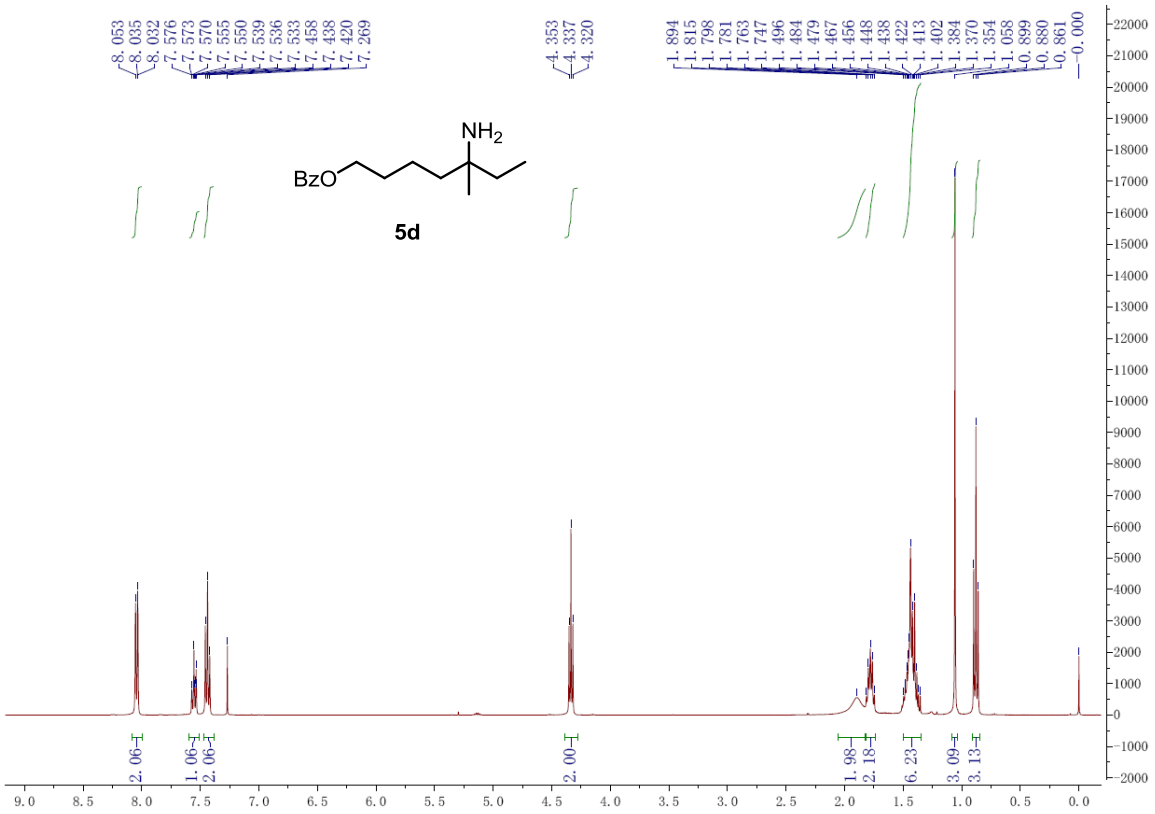
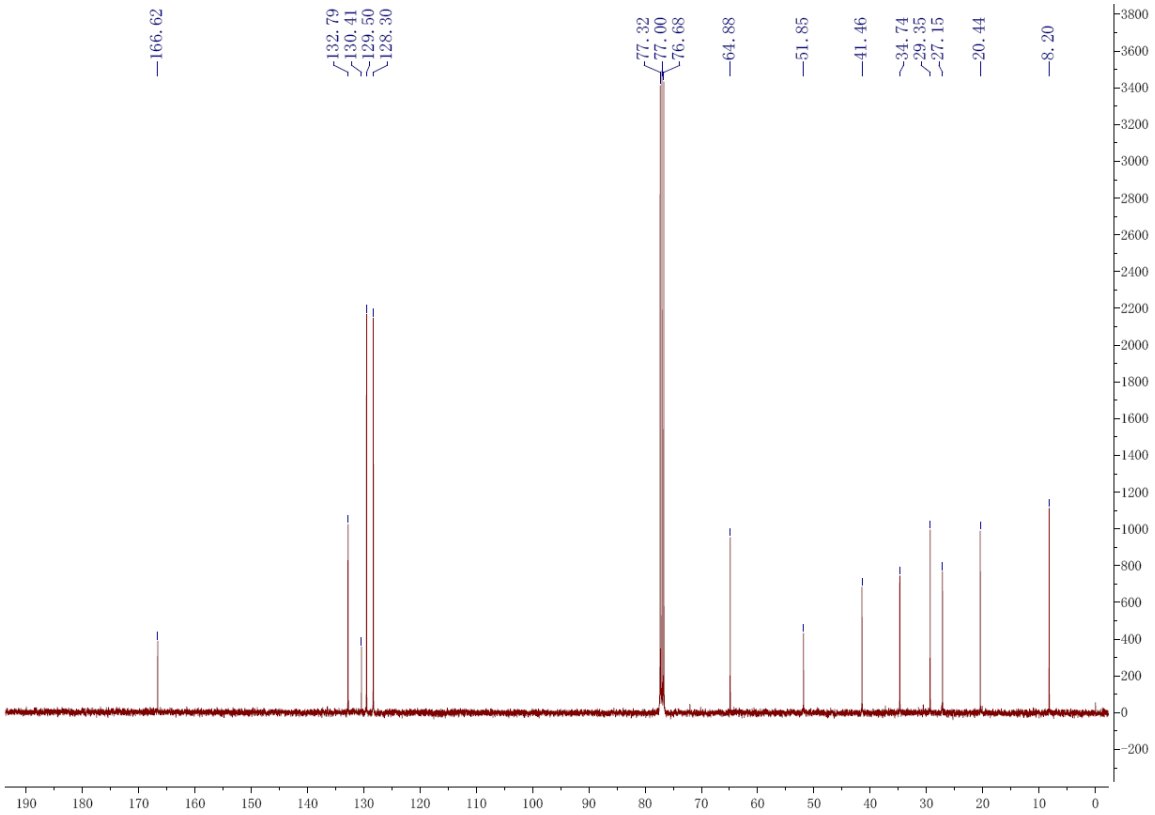
77.38
77.06
76.74
64.70
64.34
38.55
32.02
29.04
22.75
20.51
8.35
f1 (ppm)


8.053
8.035
8.032
7.576
7.573
7.570
7.555
7.550
7.539
7.536
7.533
7.458
7.438
7.420
7.269
4.353
4.337
4.320
1.894
1.815
1.798
1.781
1.763
1.747
1.496
1.484
1.479
1.467
1.456
1.448
1.438
1.422
1.413
1.402
1.384
1.370
1.354
1.058
0.899
0.880
0.861
0.000
NH2
BzO
5d
2.06
1.06
2.06
2.00
1.98
2.18
6.23
3.09
3.13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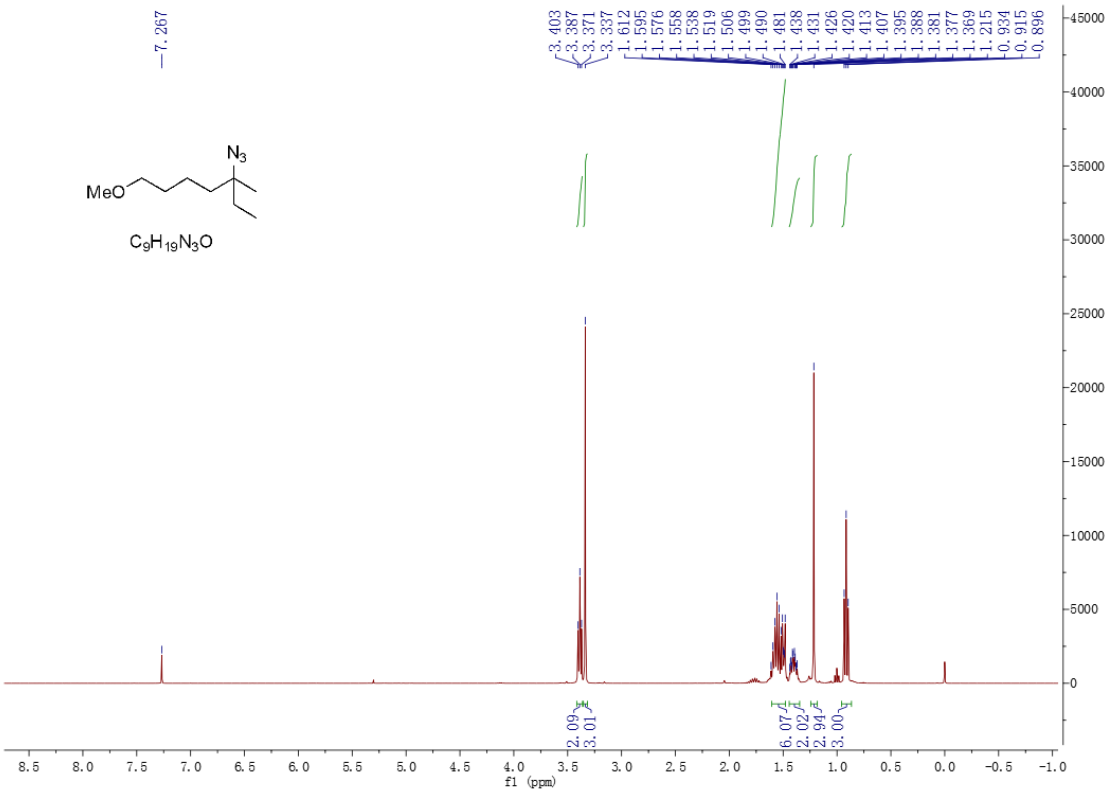
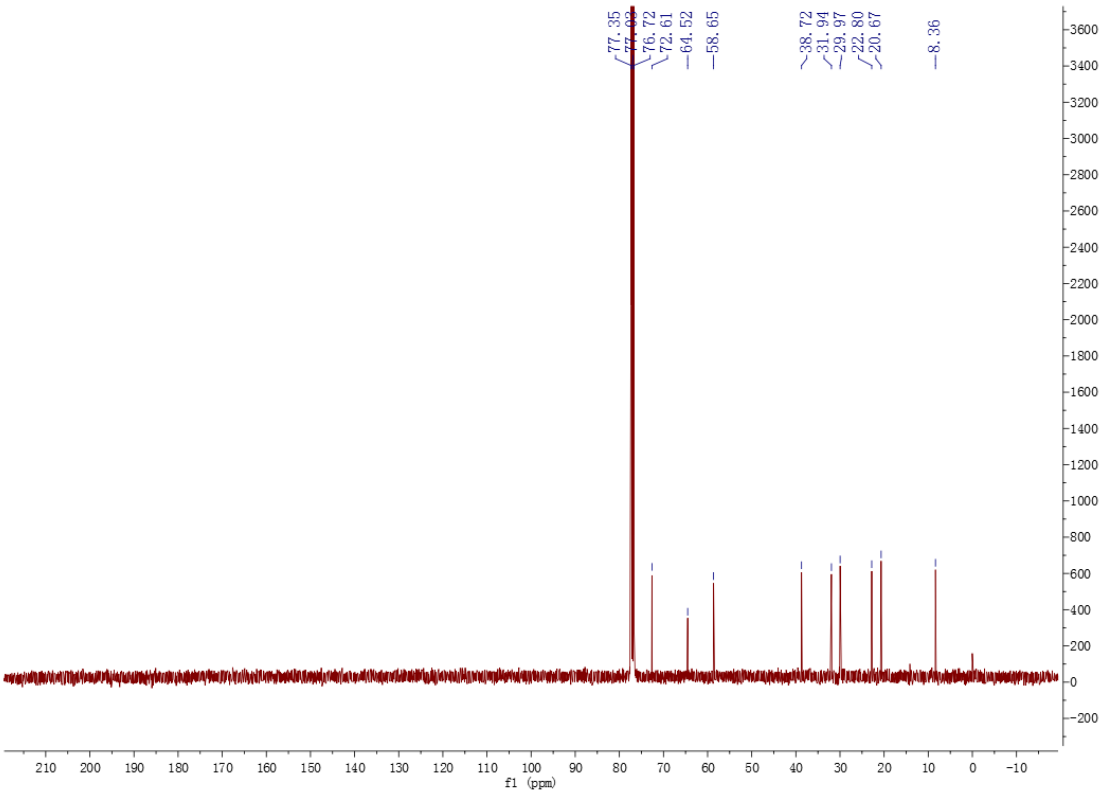
132.79
130.41
129.50
128.30
77.32
77.00
76.68
64.88
51.85
41.46
34.74
29.35
27.15
20.44
8.20


7.267
3.403
3.387
3.371
3.337
1.612
1.595
1.576
1.558
1.538
1.519
1.506
1.499
1.490
1.481
1.438
1.431
1.426
1.420
1.413
1.407
1.395
1.388
1.381
1.377
1.369
1.215
0.934
0.915
0.896
N3
MeO
C9H19N3O
2.09
3.01
6.07
2.02
2.94
3.00
f1 (ppm)


77.35
77.03
76.72
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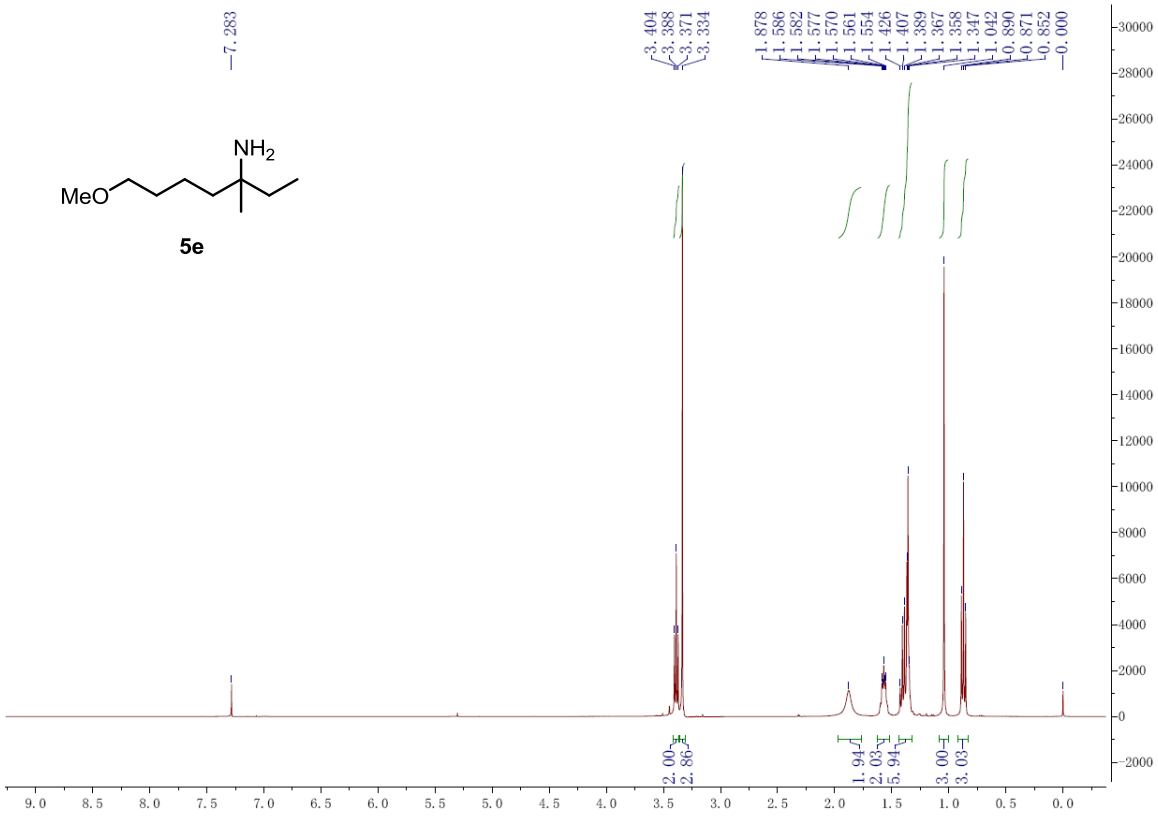
64.52
58.65
38.72
31.94
29.97
22.80
20.67
8.36
f1 (ppm)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3.404
3.388
3.371
3.334
1.878
1.586
1.582
1.577
1.570
1.561
1.554
1.426
1.407
1.389
1.367
1.358
1.347
1.042
0.890
0.871
0.852
0.000
NH2
MeO
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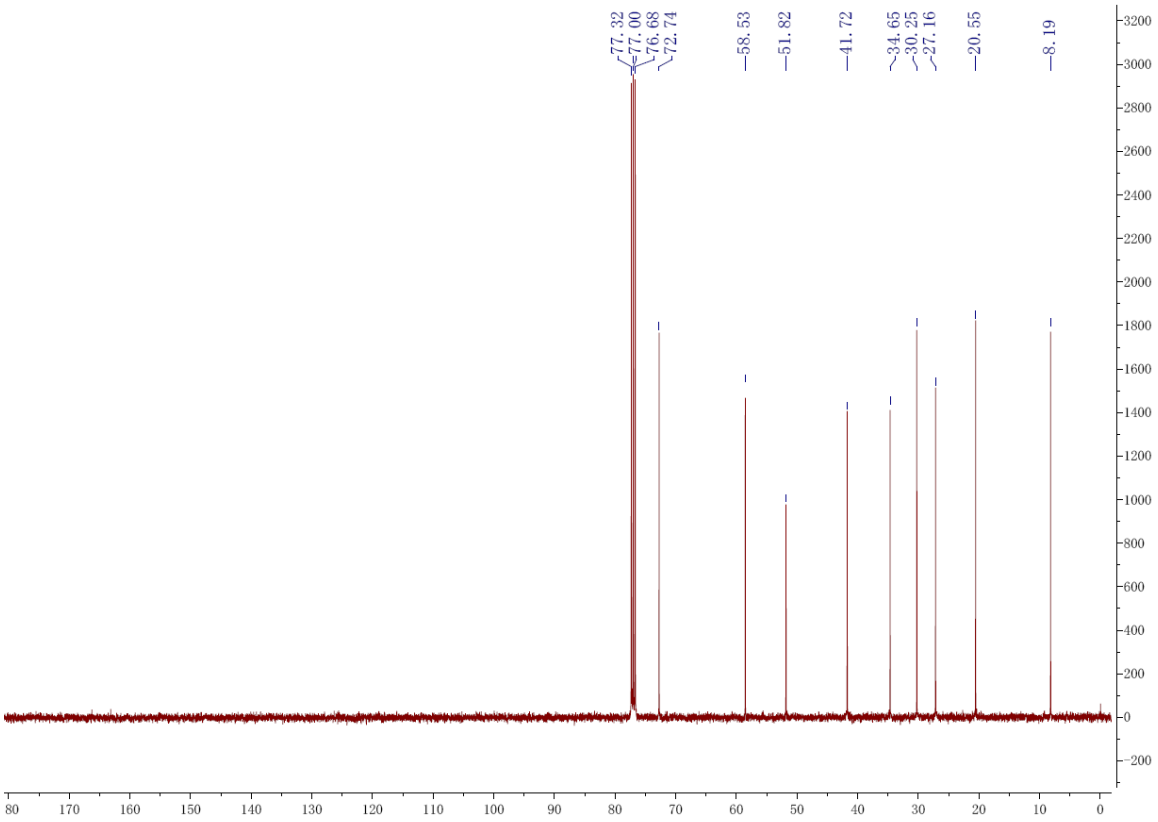
2.86
1.94
2.03
5.94
3.00
3.03

5e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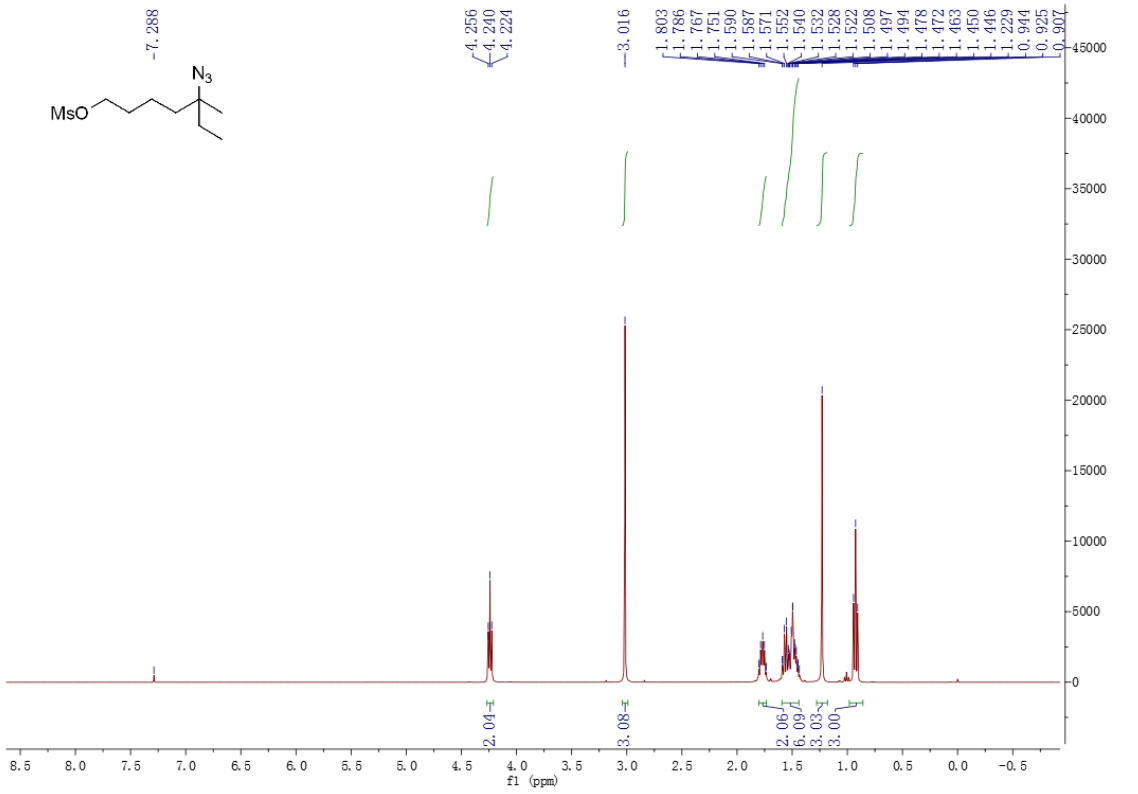
72.74
58.53
51.82
41.72
34.65
30.25
27.16
20.55
8.19


MsO
N3
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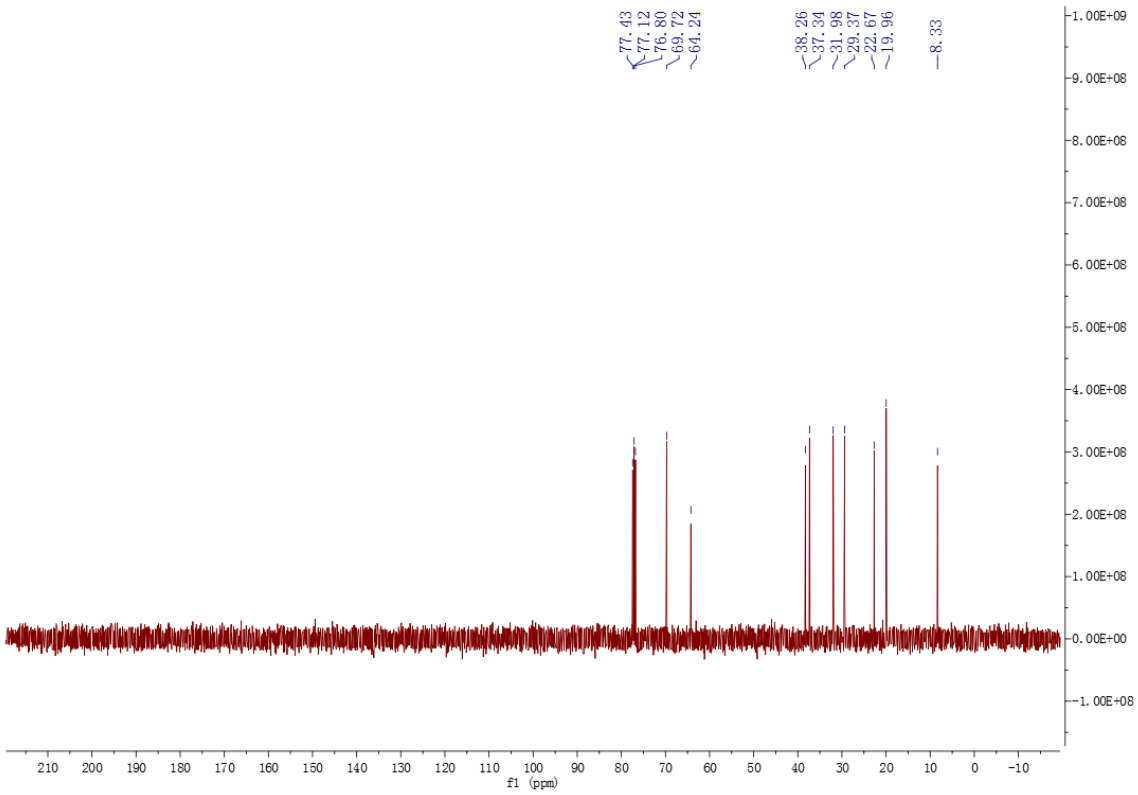
4.256
4.240
4.224
3.016
1.803
1.786
1.767
1.751
1.590
1.587
1.571
1.552
1.540
1.532
1.528
1.522
1.508
1.497
1.494
1.478
1.472
1.463
1.450
1.446
1.229
0.944
0.925
0.907
2.04
3.08
2.06
6.09
3.03
3.00
f1 (ppm)


77.43
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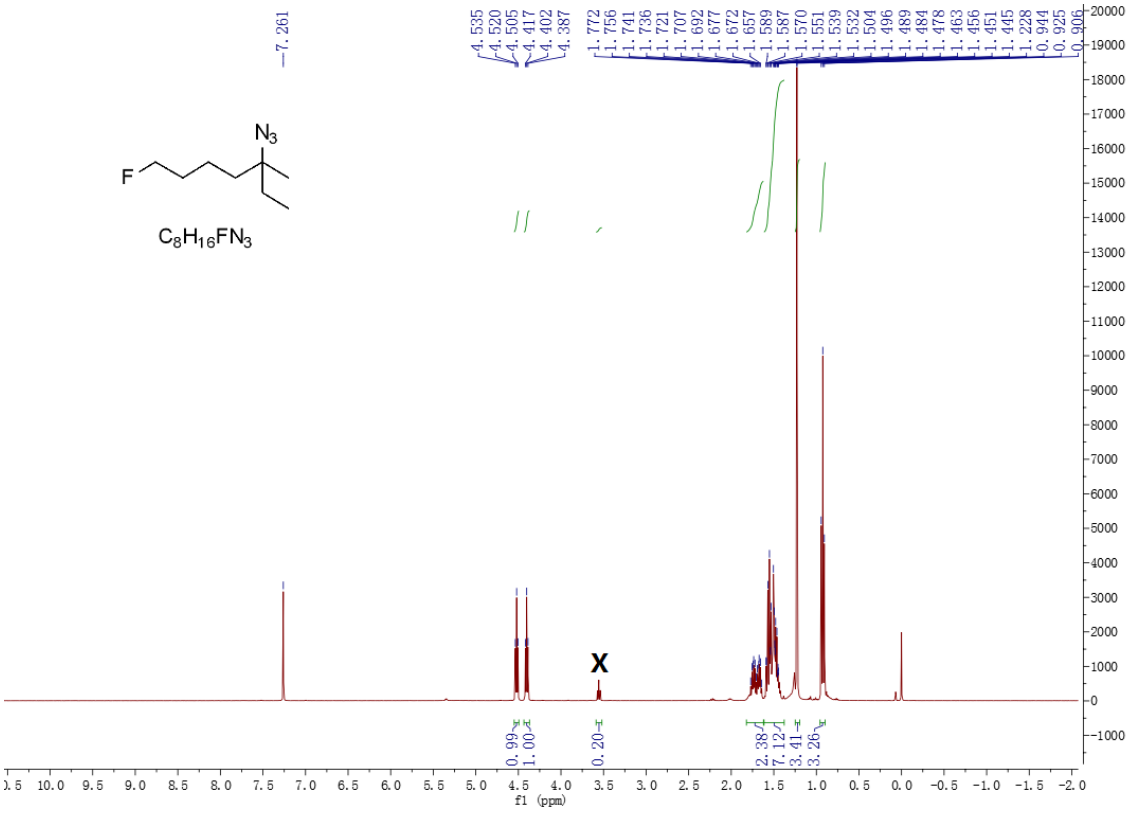
76.80
69.72
64.24
38.26
37.34
31.98
29.37
22.67
19.96
8.33
f1 (ppm)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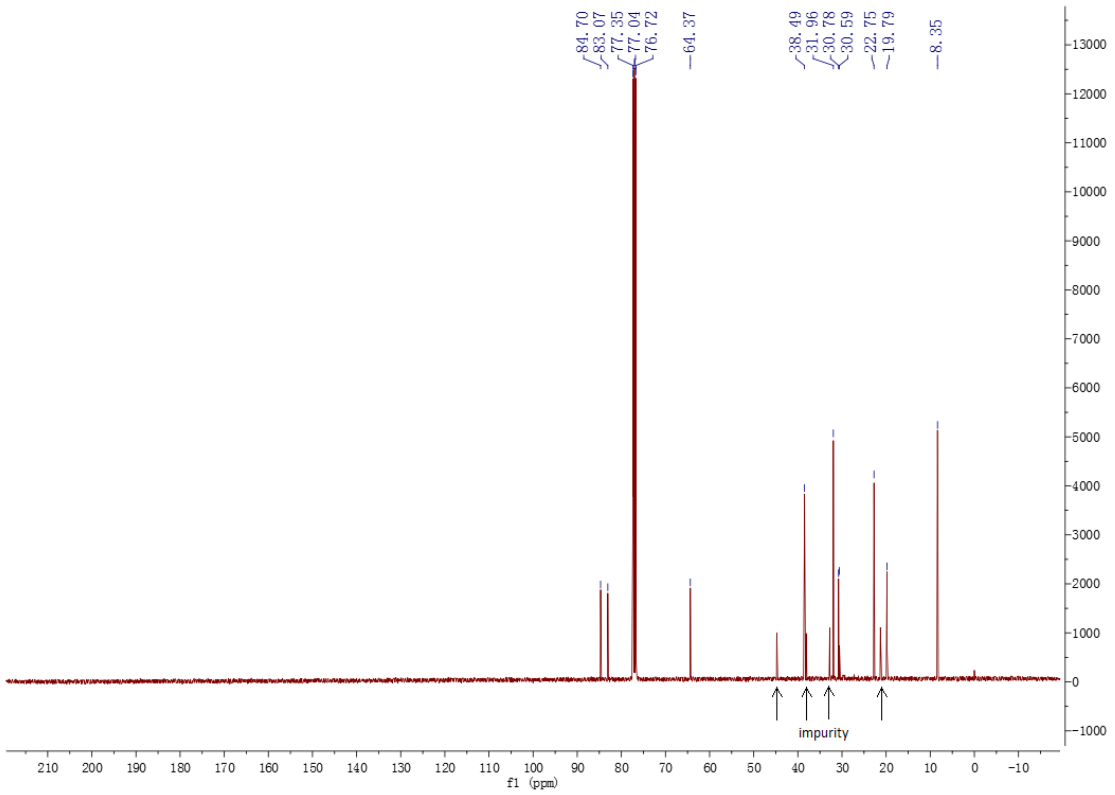
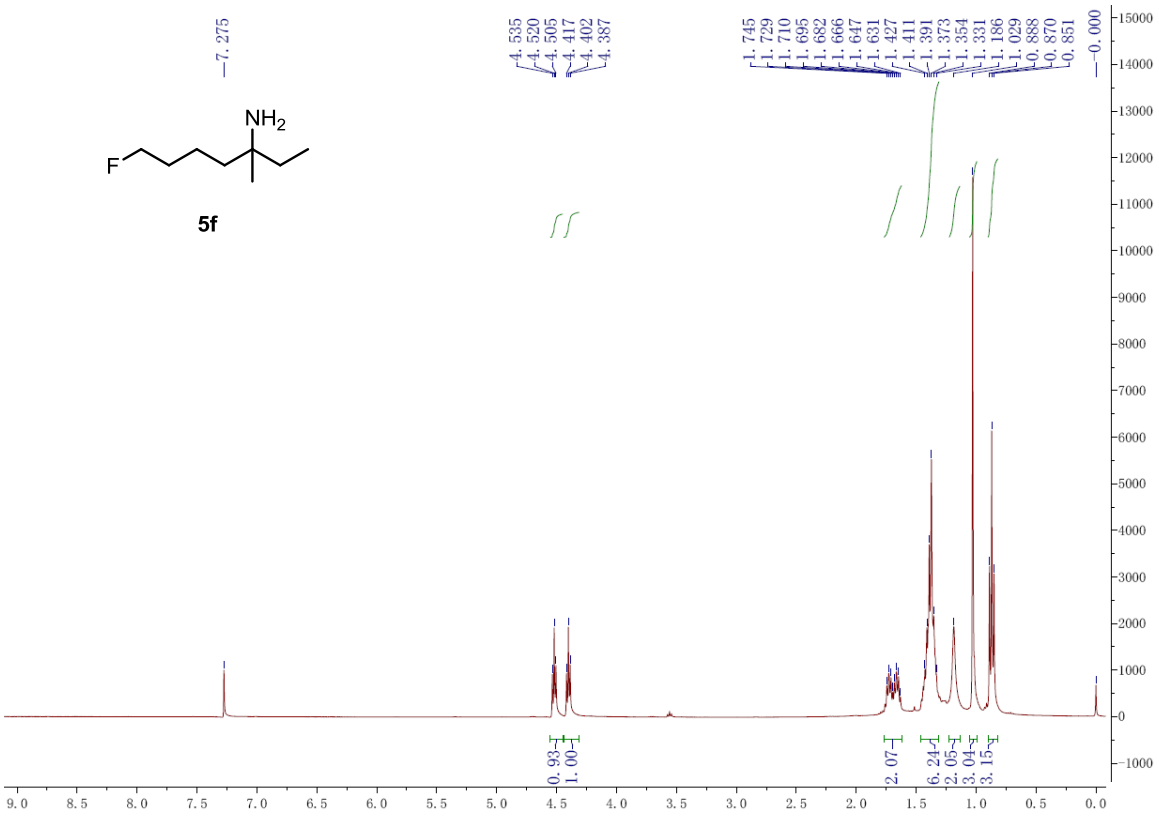
4.505
4.417
4.402
4.387
1.772
1.756
1.741
1.736
1.721
1.707
1.692
1.677
1.672
1.657
1.589
1.587
1.570
1.551
1.539
1.532
1.504
1.496
1.489
1.484
1.478
1.463
1.456
1.451
1.445
1.228
0.944
0.925
0.906
N3
F
C8H16FN3
X
0.99
1.00
0.20
2.38
7.12
3.41
3.26
f1 (ppm)


84.70
83.07
77.35
77.04
76.72
64.37
38.49
31.96
30.78
30.59
22.75
19.79
8.35
impurity
f1 (ppm)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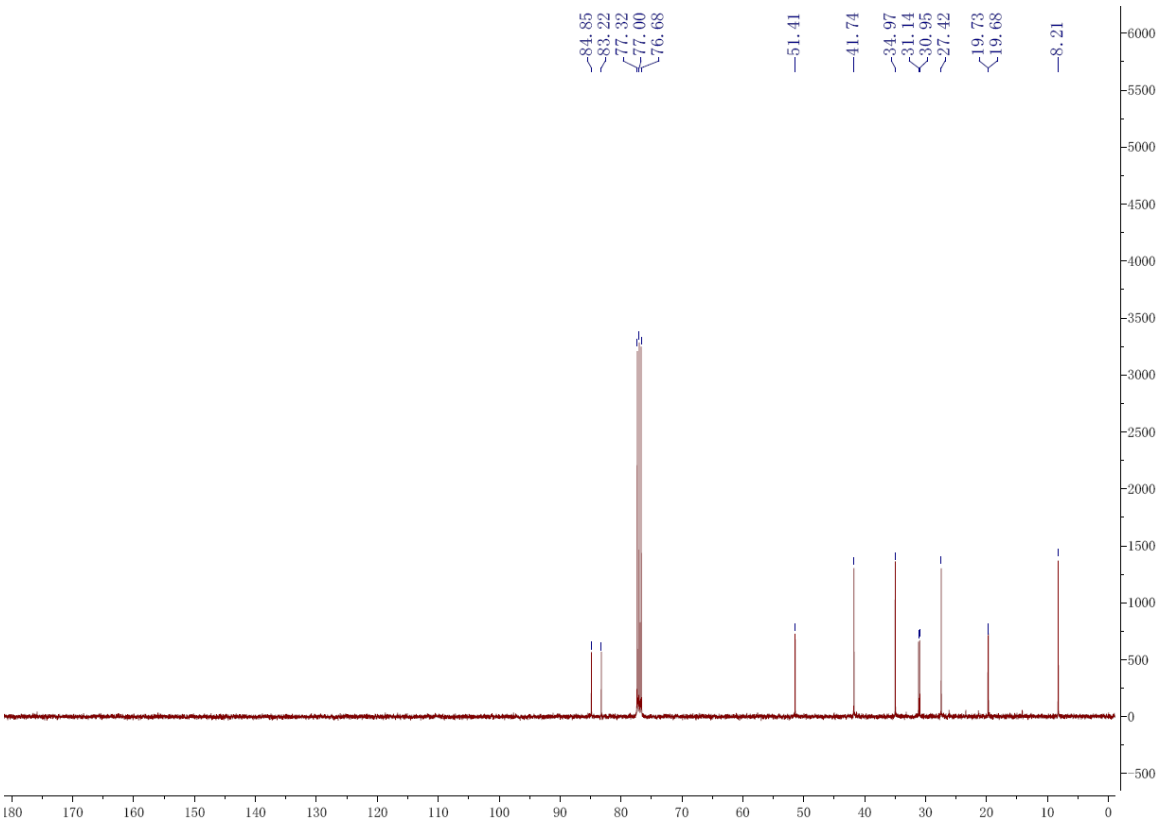
4.535
4.520
4.505
4.417
4.402
4.387
1.745
1.729
1.710
1.695
1.682
1.666
1.647
1.631
1.427
1.411
1.391
1.373
1.354
1.331
1.186
1.029
0.888
0.870
0.851
0.000
NH2
F
5f
0.93
1.00
2.07
6.24
2.05
3.04
3.15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83.22
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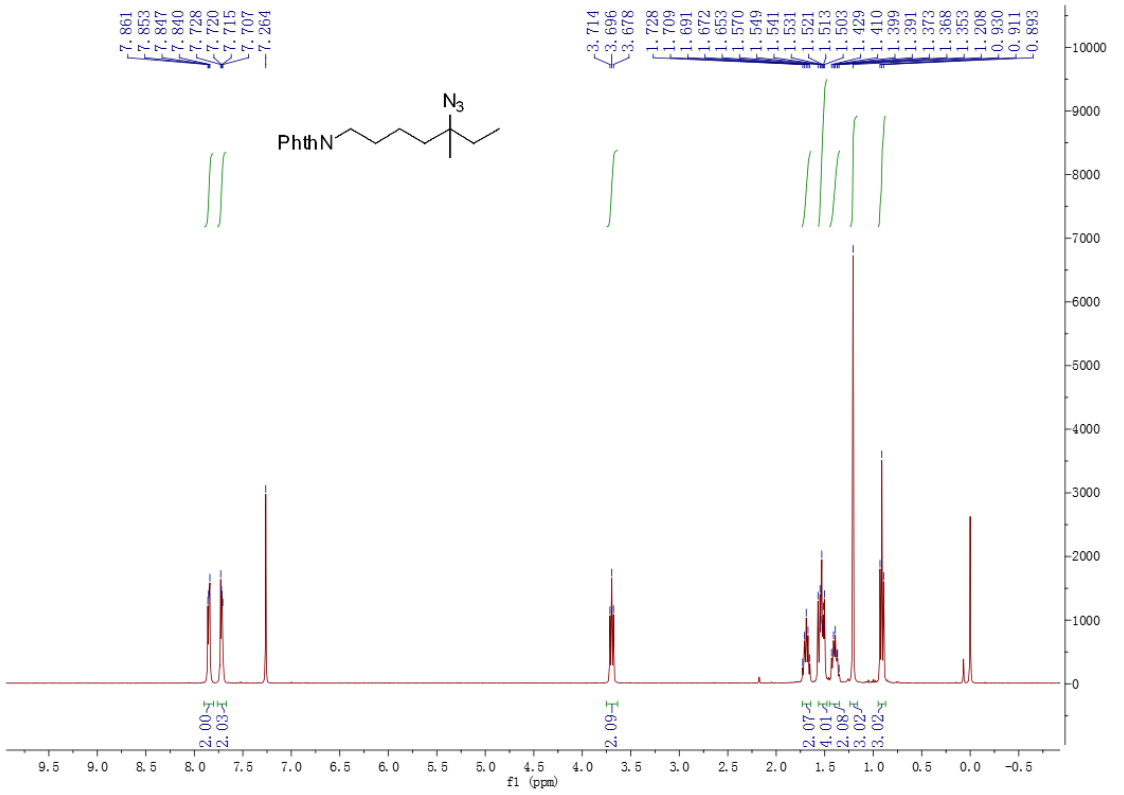
51.41
41.74
34.97
31.14
30.95
27.42
19.73
19.68
8.21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7.720
7.715
7.707
7.264
3.714
3.696
3.678
1.728
1.709
1.691
1.672
1.653
1.570
1.549
1.541
1.531
1.521
1.513
1.503
1.429
1.410
1.399
1.391
1.373
1.368
1.353
1.208
0.930
0.911
0.893
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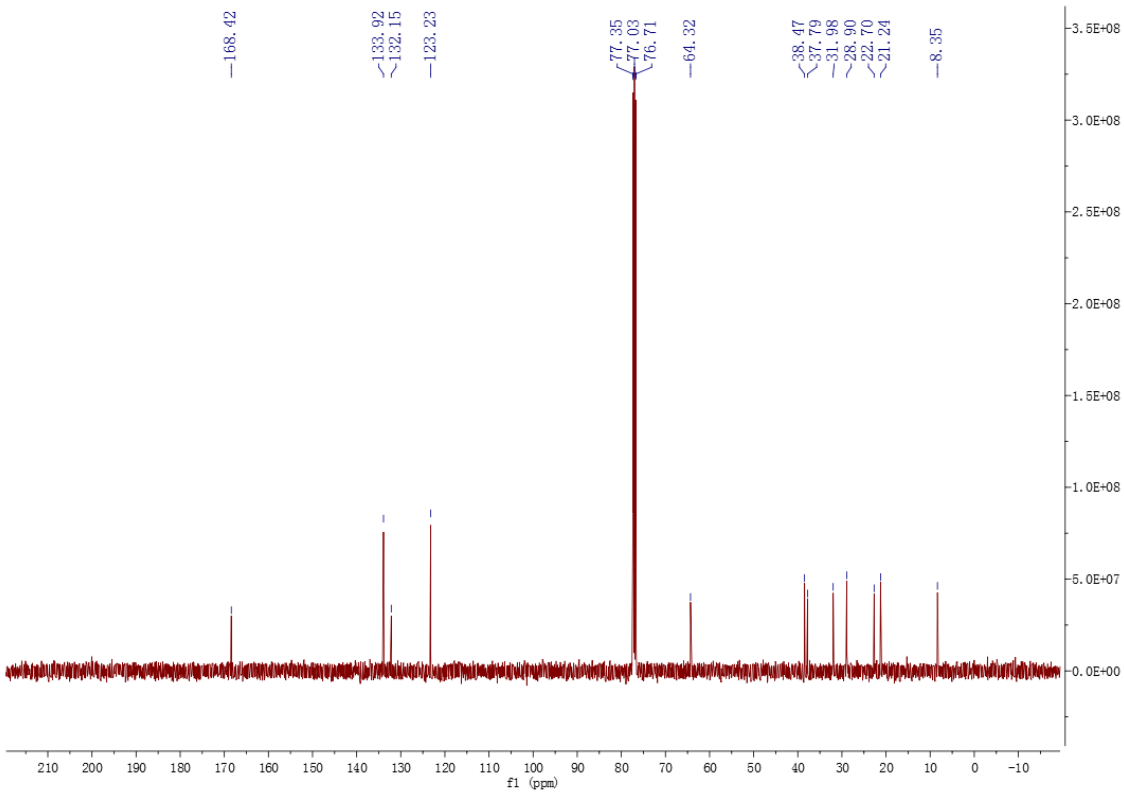
PhthN
2.00
2.03
2.09
2.07
4.01
2.08
3.02
3.02
f1 (ppm)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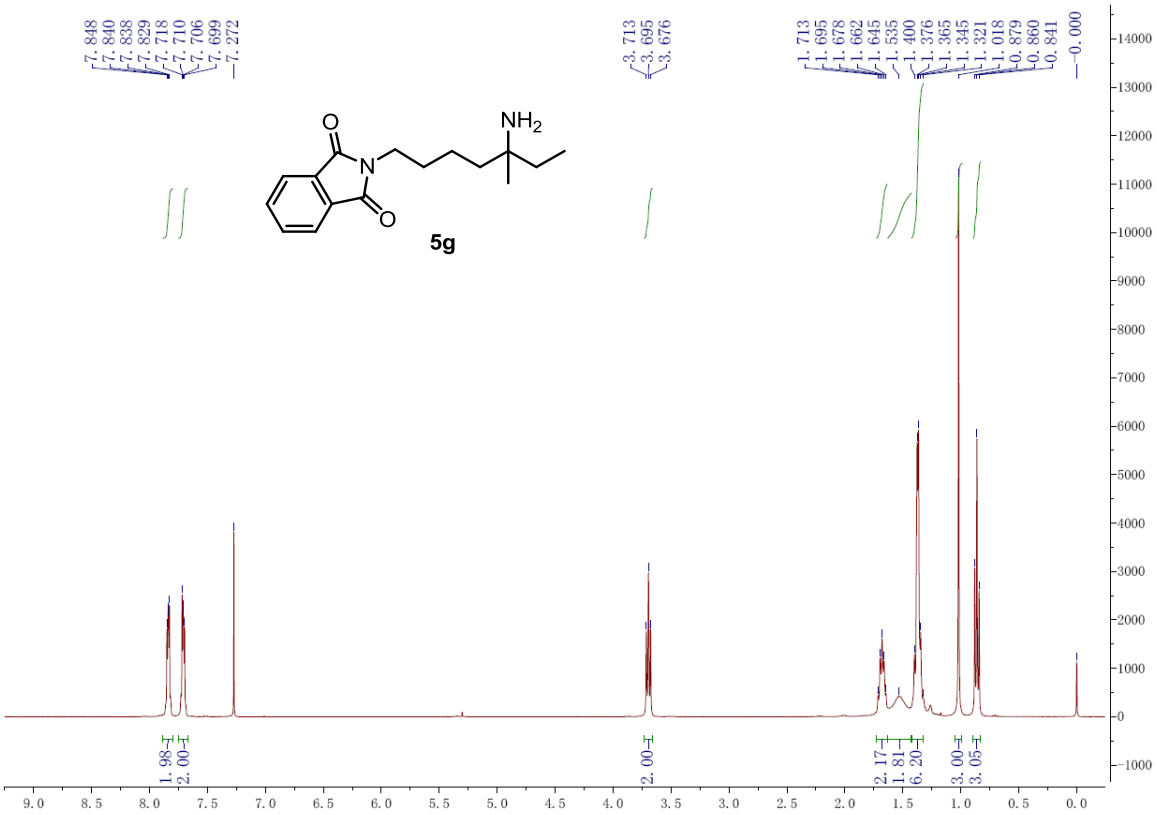
133.92
132.15
123.23
77.35
77.03
76.71
64.32
38.47
37.79
31.98
28.90
22.70
21.24
8.35
f1 (ppm)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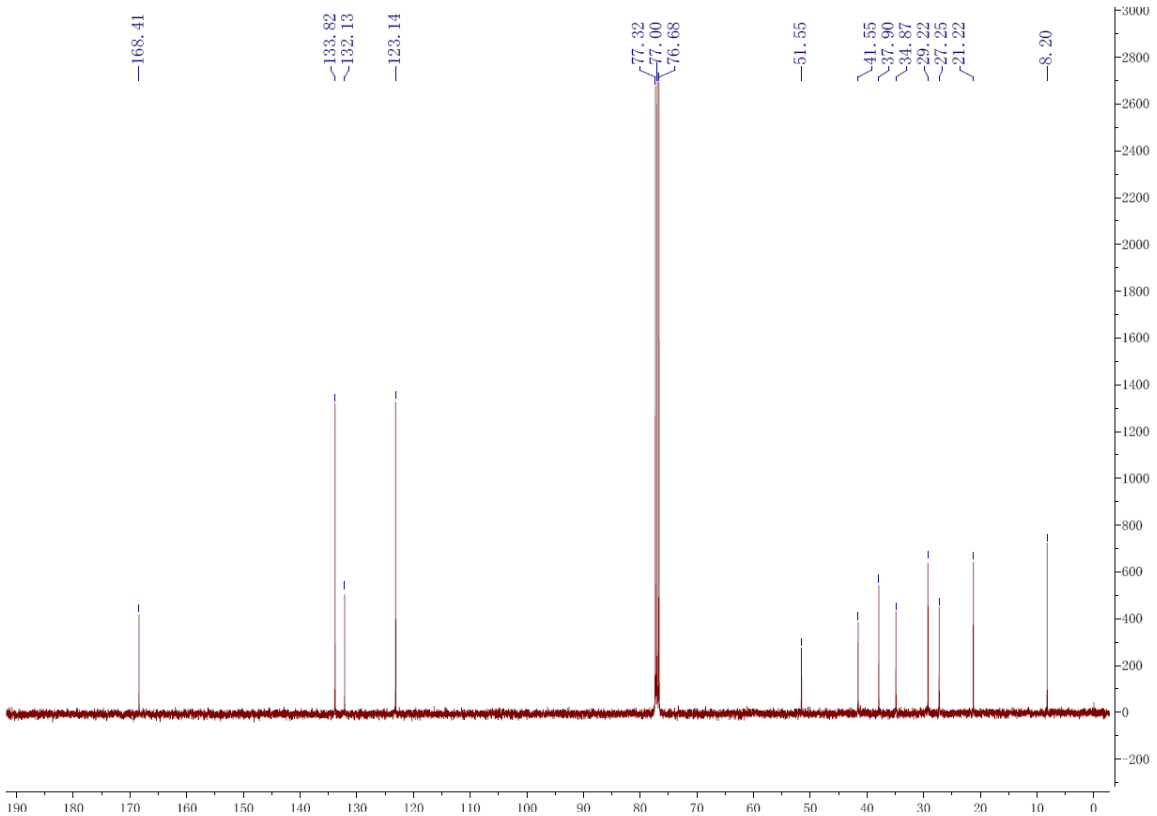
7.838
7.829
7.718
7.710
7.706
7.699
7.272
3.713
3.695
3.676
1.713
1.695
1.678
1.662
1.645
1.535
1.400
1.376
1.365
1.345
1.321
1.018
0.879
0.860
0.841
0.000
O
N
O
NH2
5g
1.98
2.00
2.00
2.17
1.81
6.20
3.00
3.05


168.41
133.82
132.13
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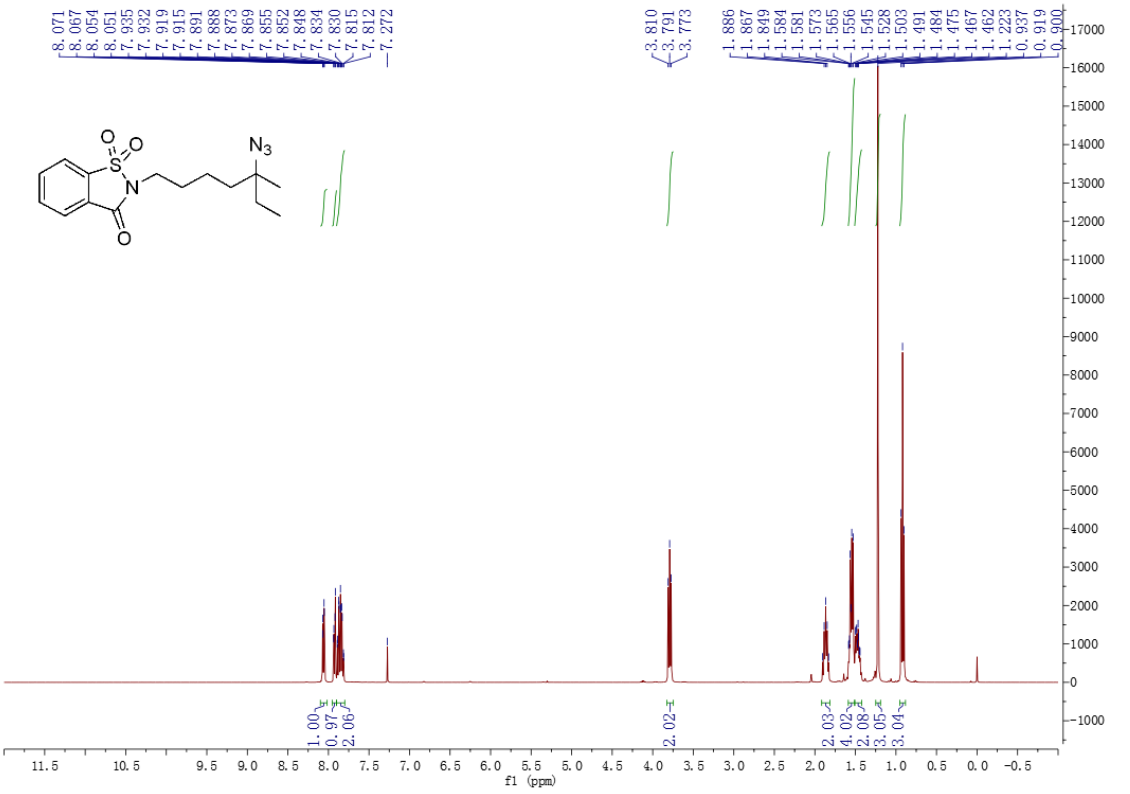
77.00
76.68
51.55
41.55
37.90
34.87
29.22
27.25
21.22
8.20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7.915
7.891
7.888
7.873
7.869
7.855
7.852
7.848
7.834
7.830
7.815
7.812
7.272
3.810
3.791
3.773
1.886
1.867
1.849
1.584
1.581
1.573
1.565
1.556
1.545
1.528
1.503
1.491
1.484
1.475
1.467
1.462
1.223
0.937
0.919
0.900
O
S
O
N
N3
O
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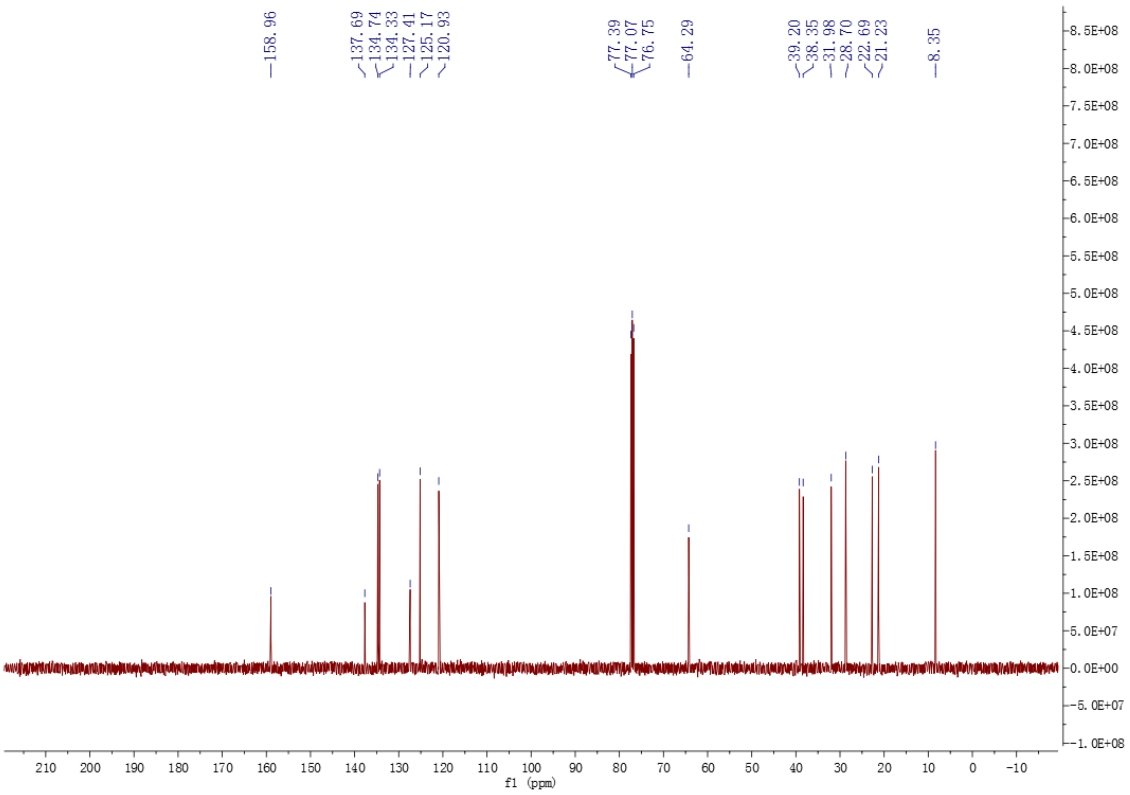
0.97
2.06
2.02
2.03
4.02
2.08
3.05
3.04
f1 (ppm)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127.41
125.17
120.93
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77.07
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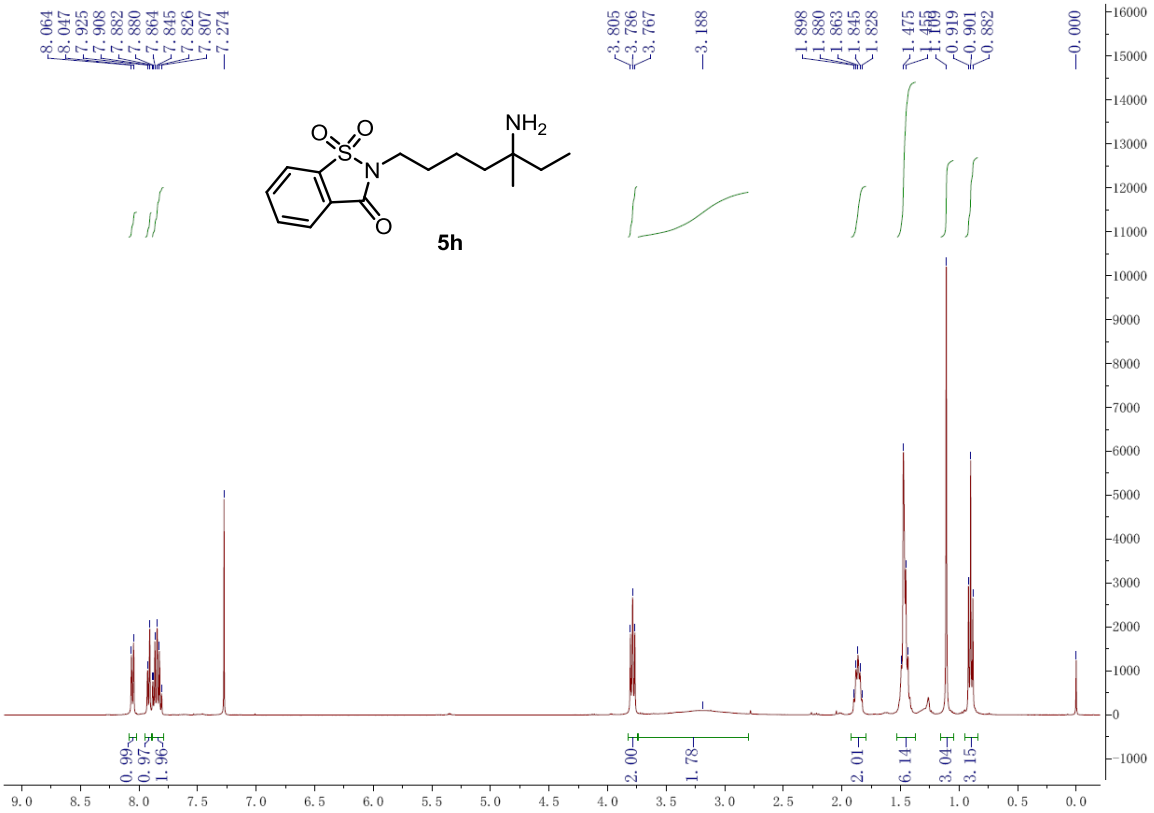
64.29
39.20
38.35
31.98
28.70
22.69
21.23
8.35
f1 (ppm)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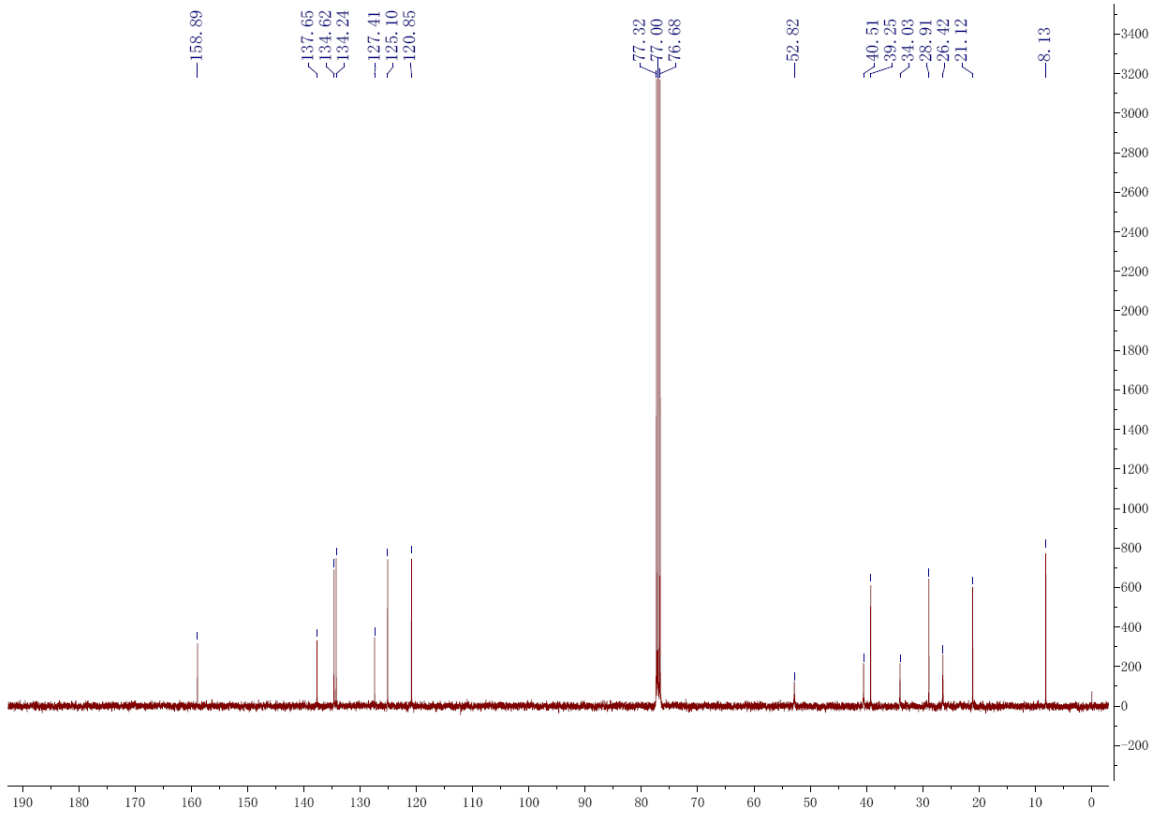
7.880
7.864
7.845
7.826
7.807
7.274
3.805
3.786
3.767
3.188
1.898
1.880
1.863
1.845
1.828
1.475
1.109
0.919
0.901
0.882
0.000
NH2
O
O
S
N
O
5h
0.99
0.97
1.96
2.00
1.78
2.01
6.14
3.04
3.15


158.89
137.65
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134.24
127.41
125.10
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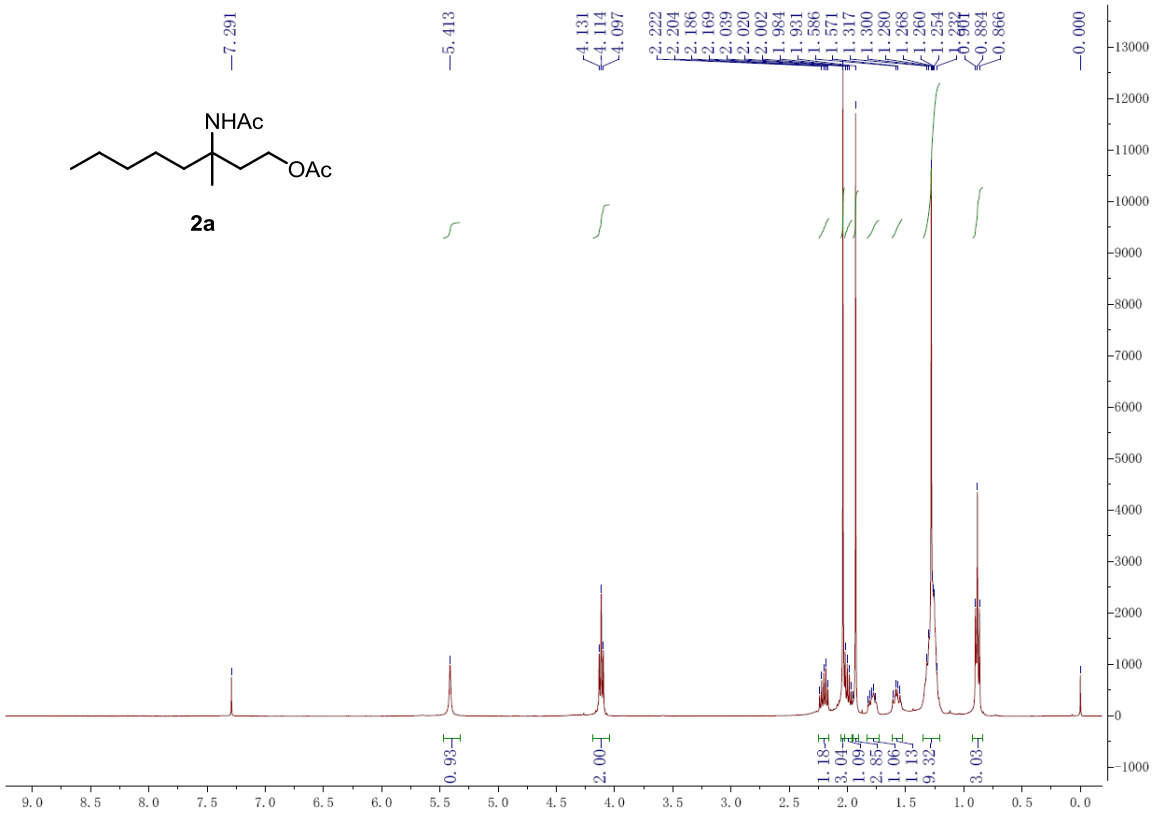
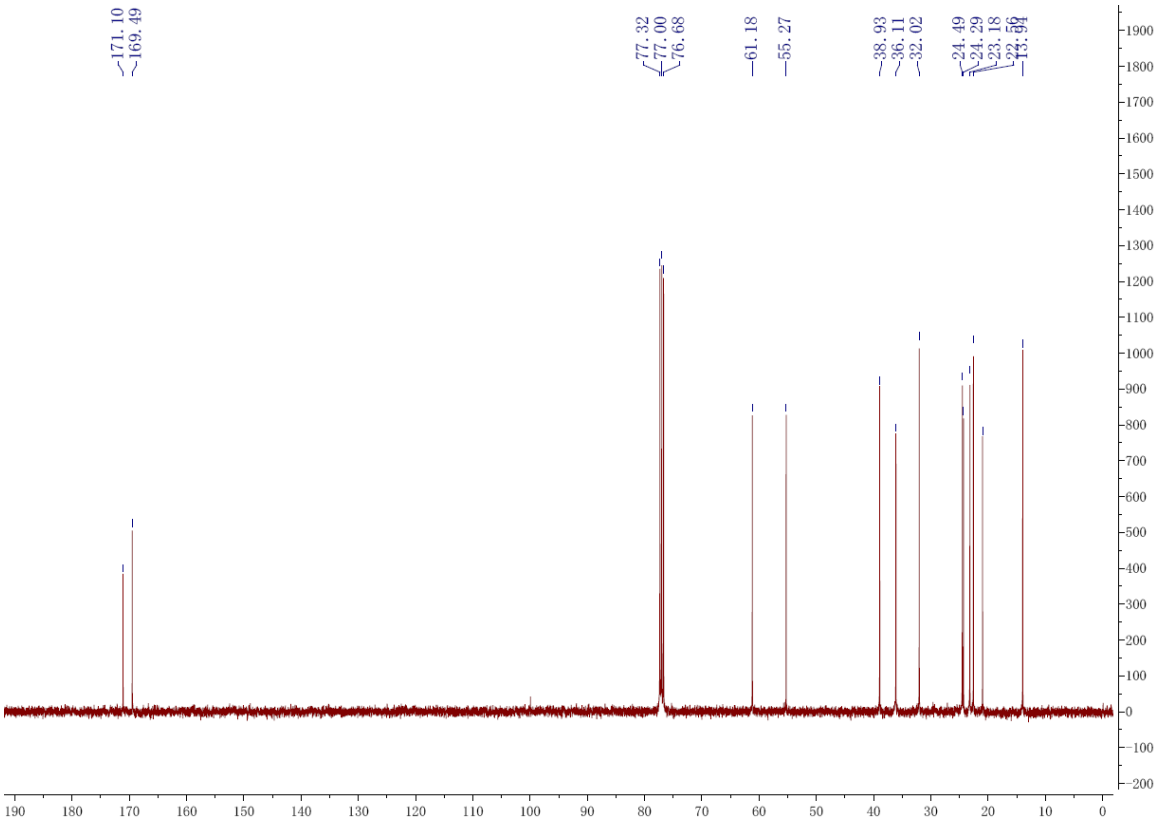
77.32
77.00
76.68
52.82
40.51
39.25
34.03
28.91
26.42
21.12
8.13


NHAc
OAc
2a
7.291
5.413
4.131
4.114
4.097
2.222
2.204
2.186
2.169
2.039
2.020
2.002
1.984
1.931
1.586
1.571
1.317
1.300
1.280
1.268
1.260
1.254
0.901
0.884
0.866
0.000
0.93
2.00
1.18
3.04
1.09
2.85
1.06
1.13
9.32
3.03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61.18
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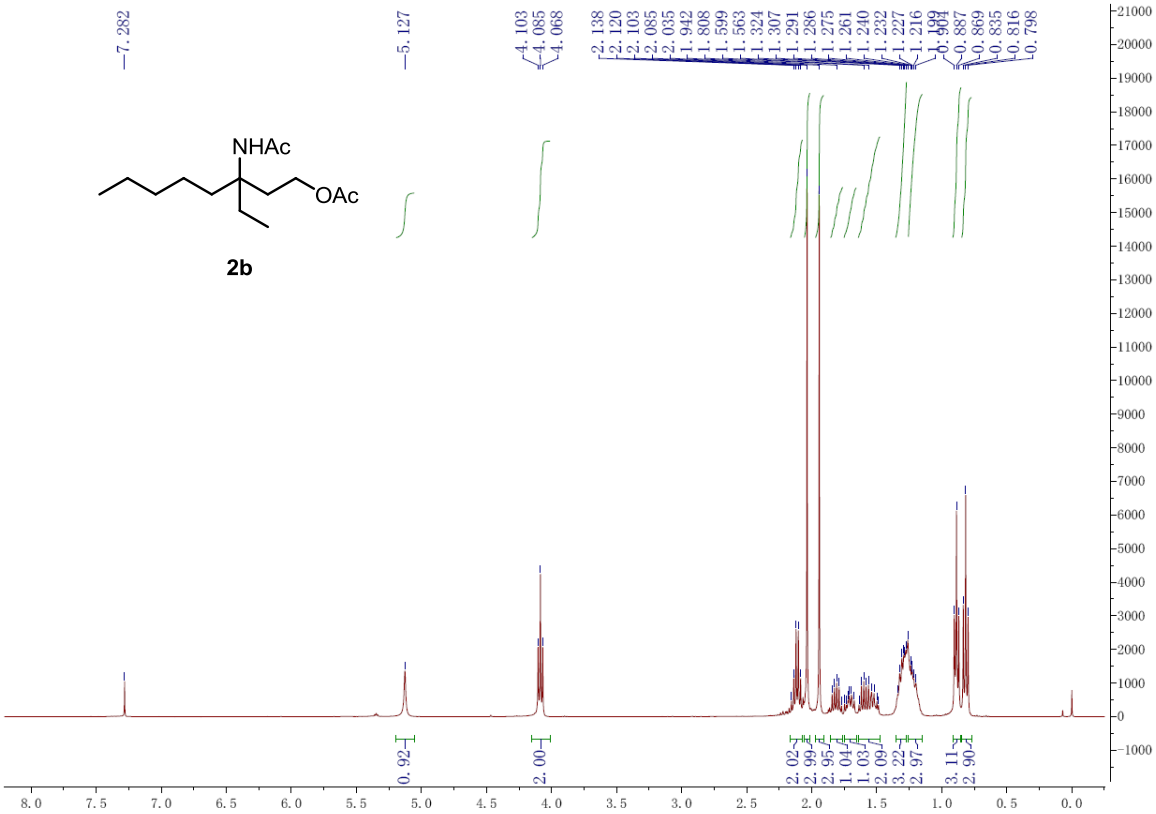
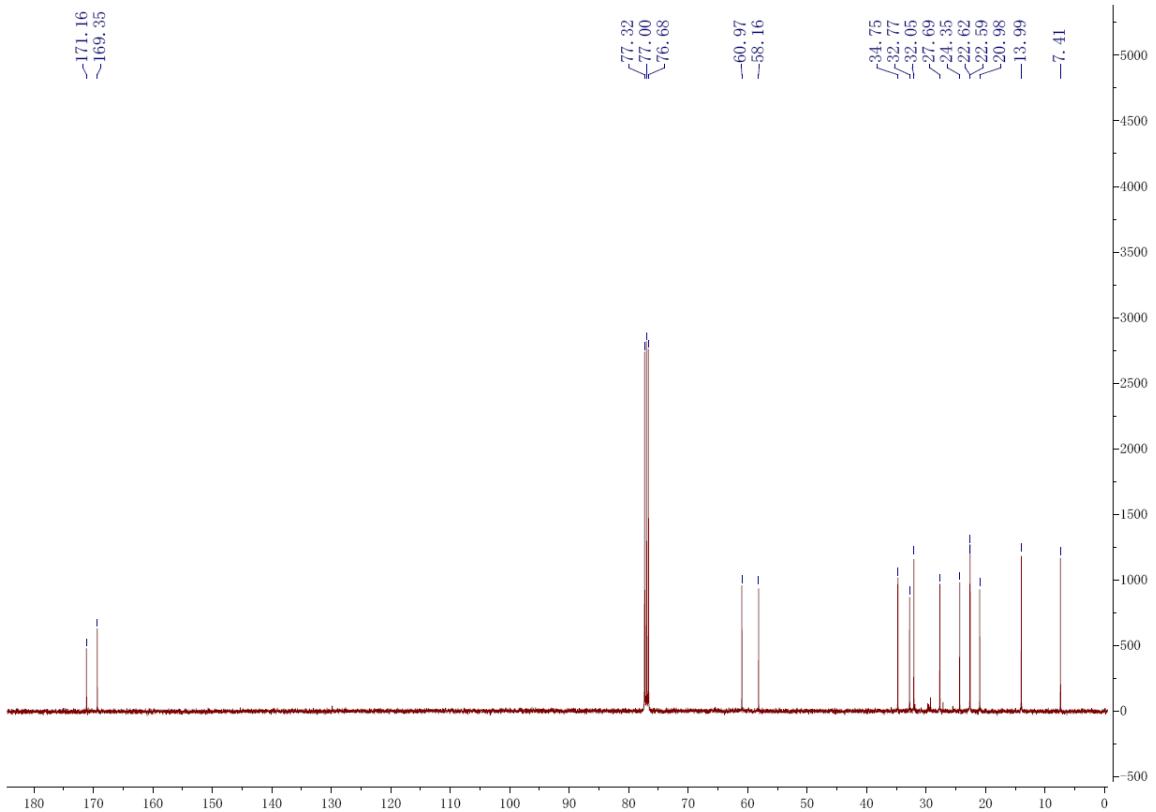
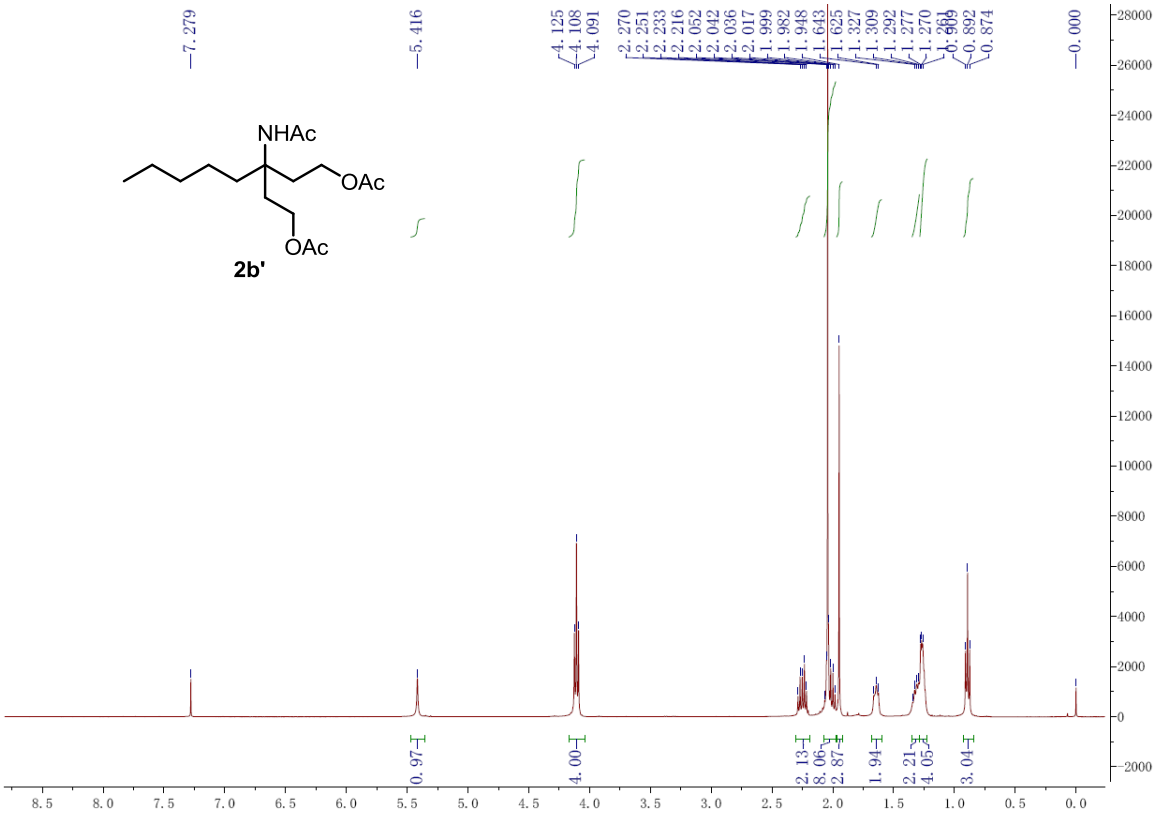
38.93
36.11
32.02
24.49
24.29
23.18


NHAc
OAc
2b

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OAc
OAc
2b'
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4.091
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2.042
2.036
2.017
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1.948
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1.625
1.327
1.309
1.292
1.277
1.270
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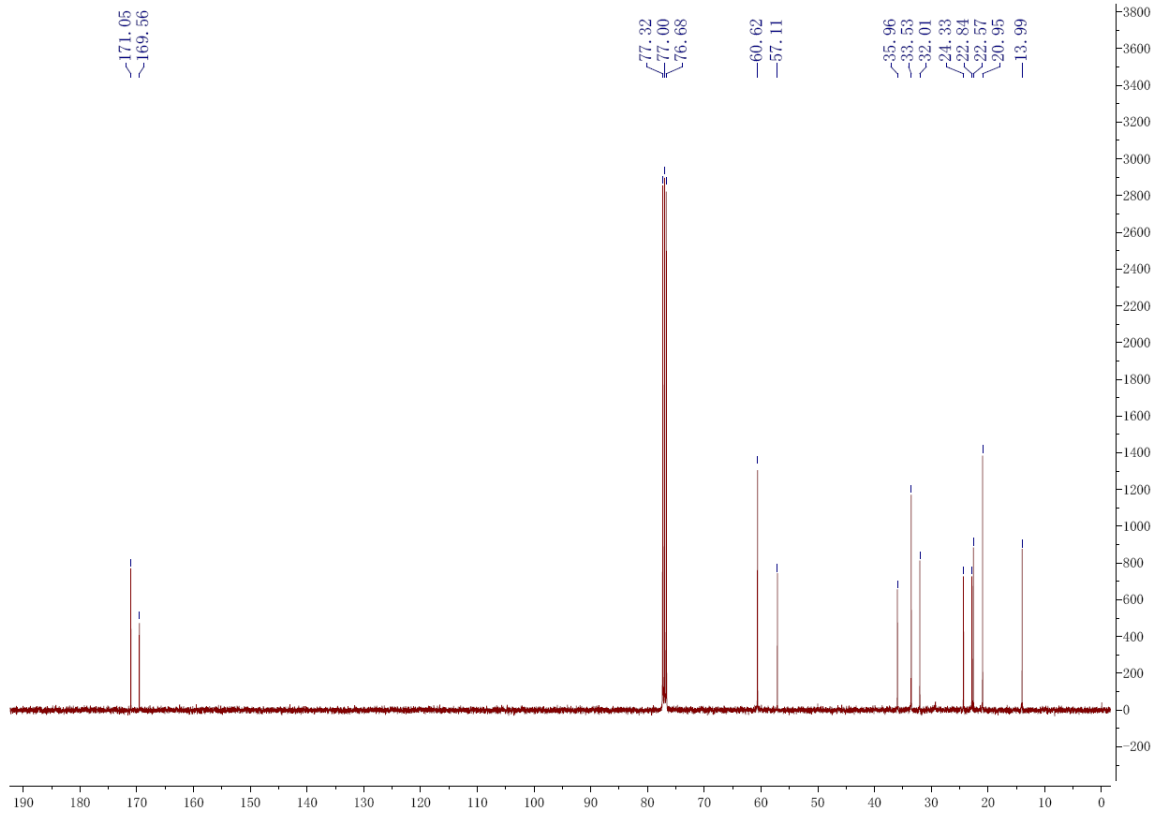
3.04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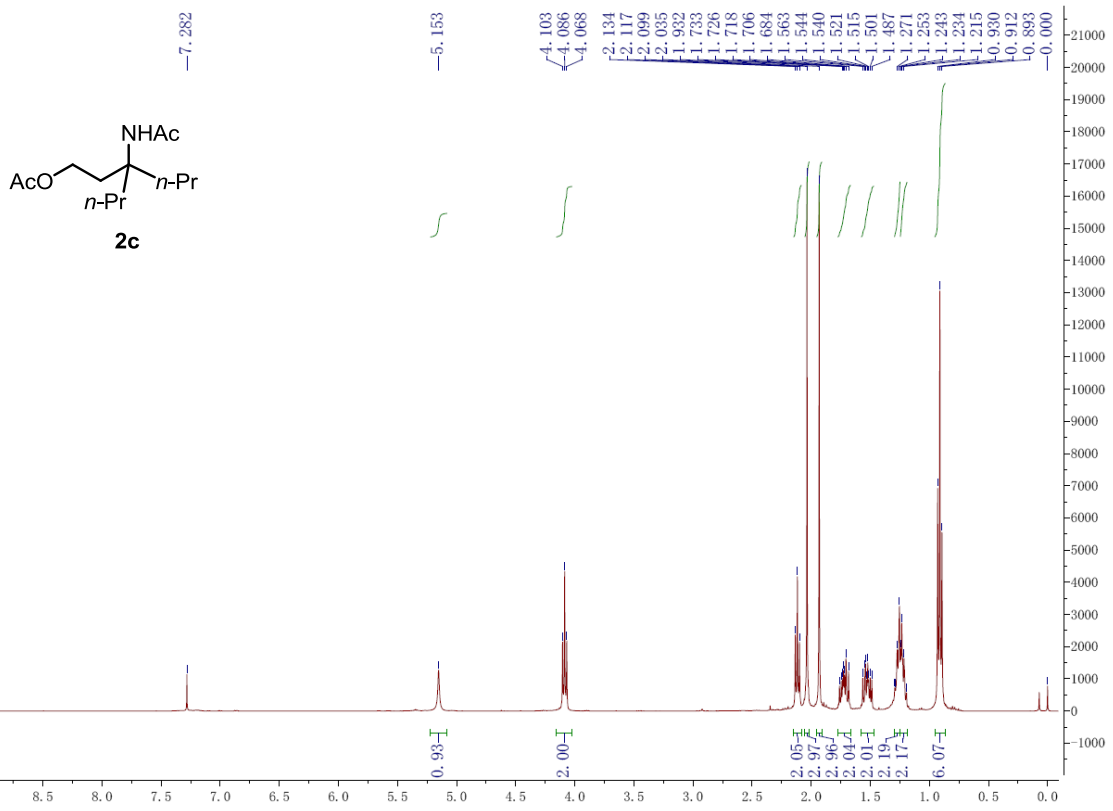
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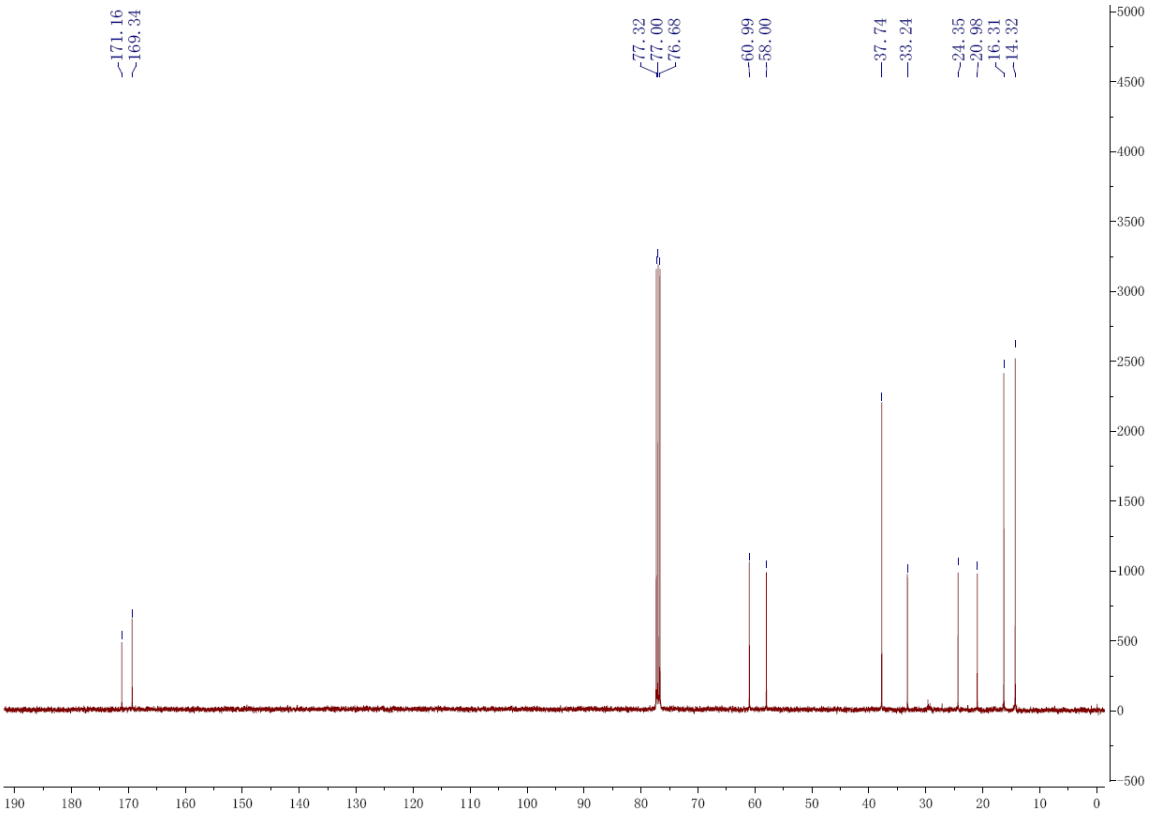
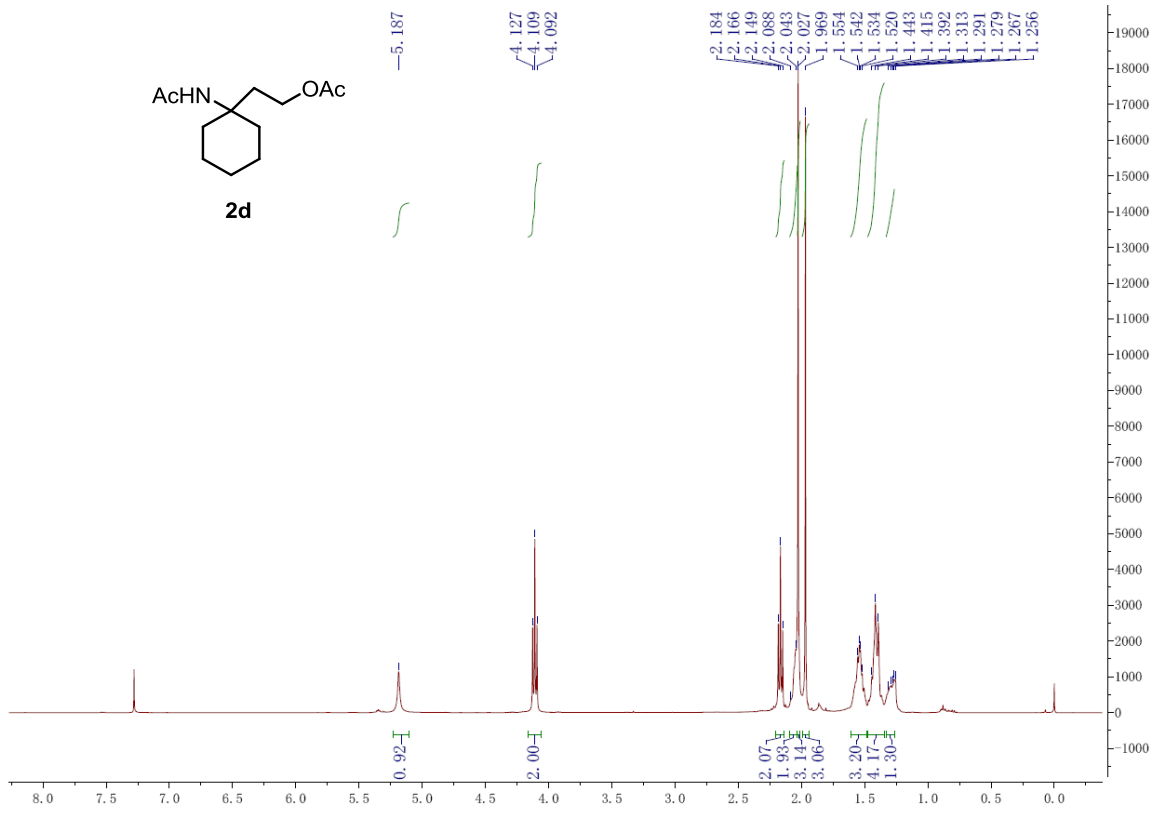
n-Pr
2c

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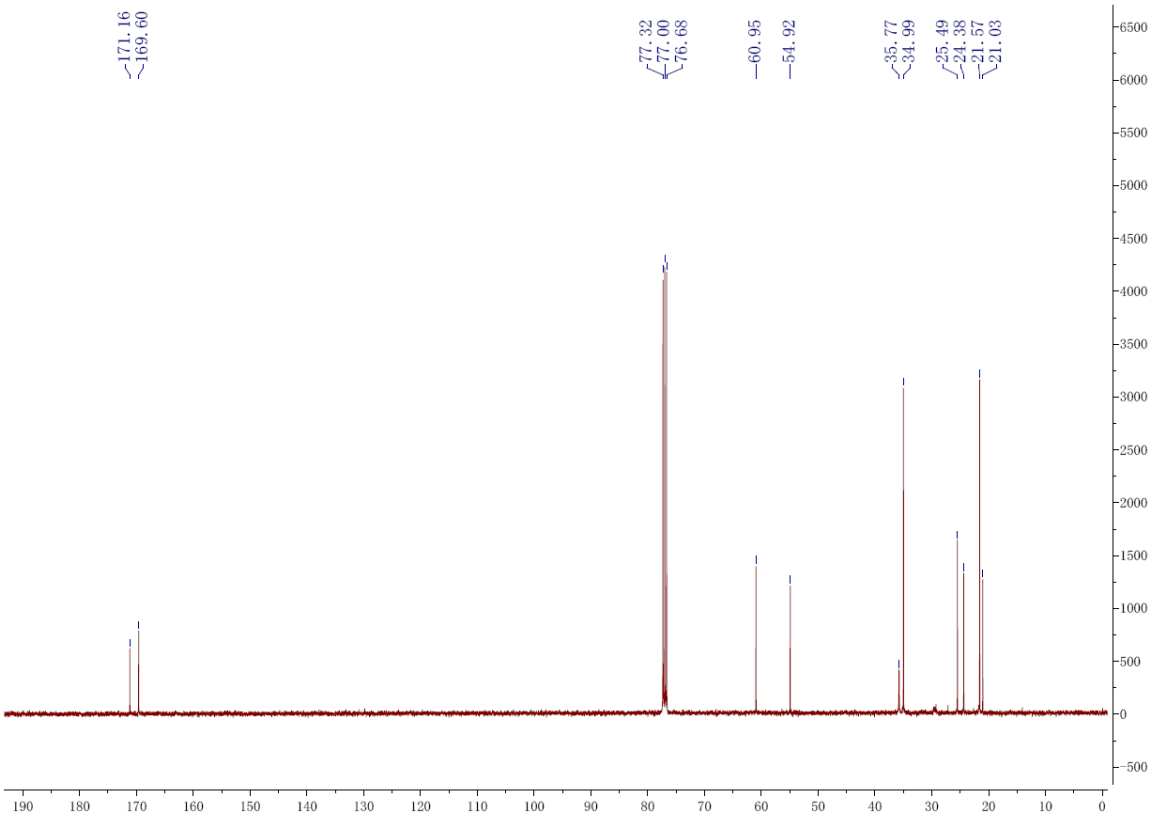
1.30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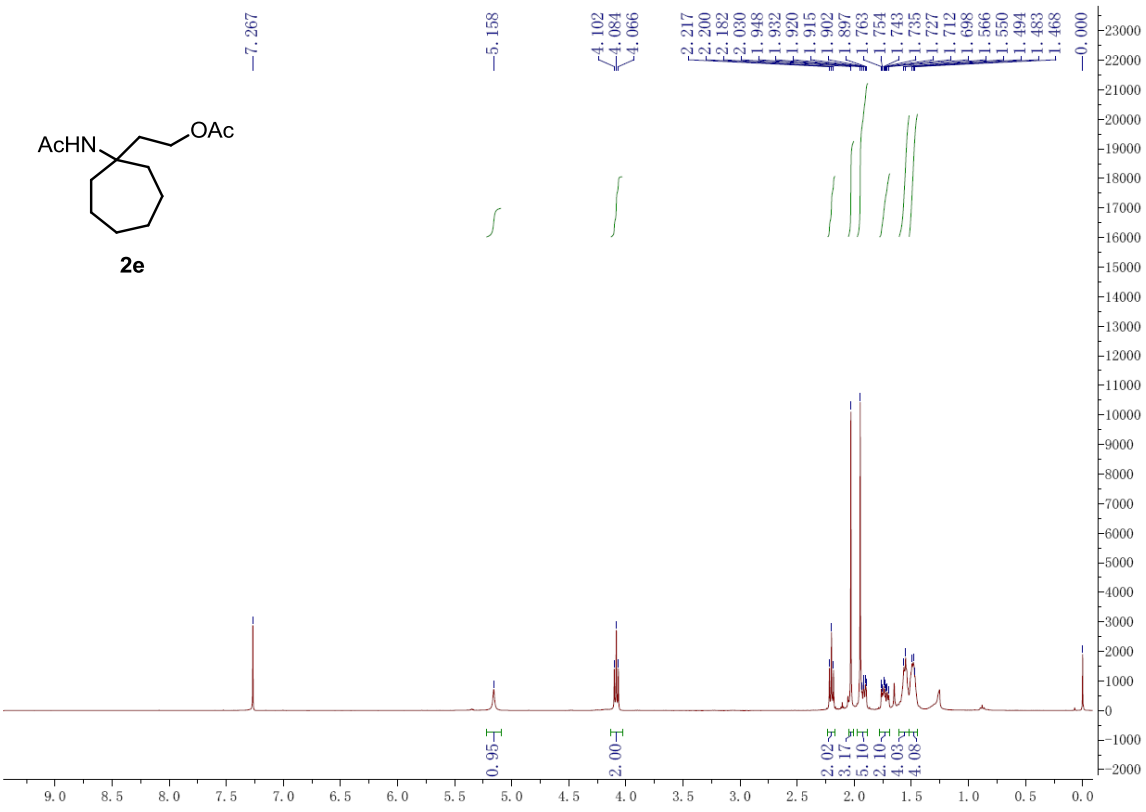
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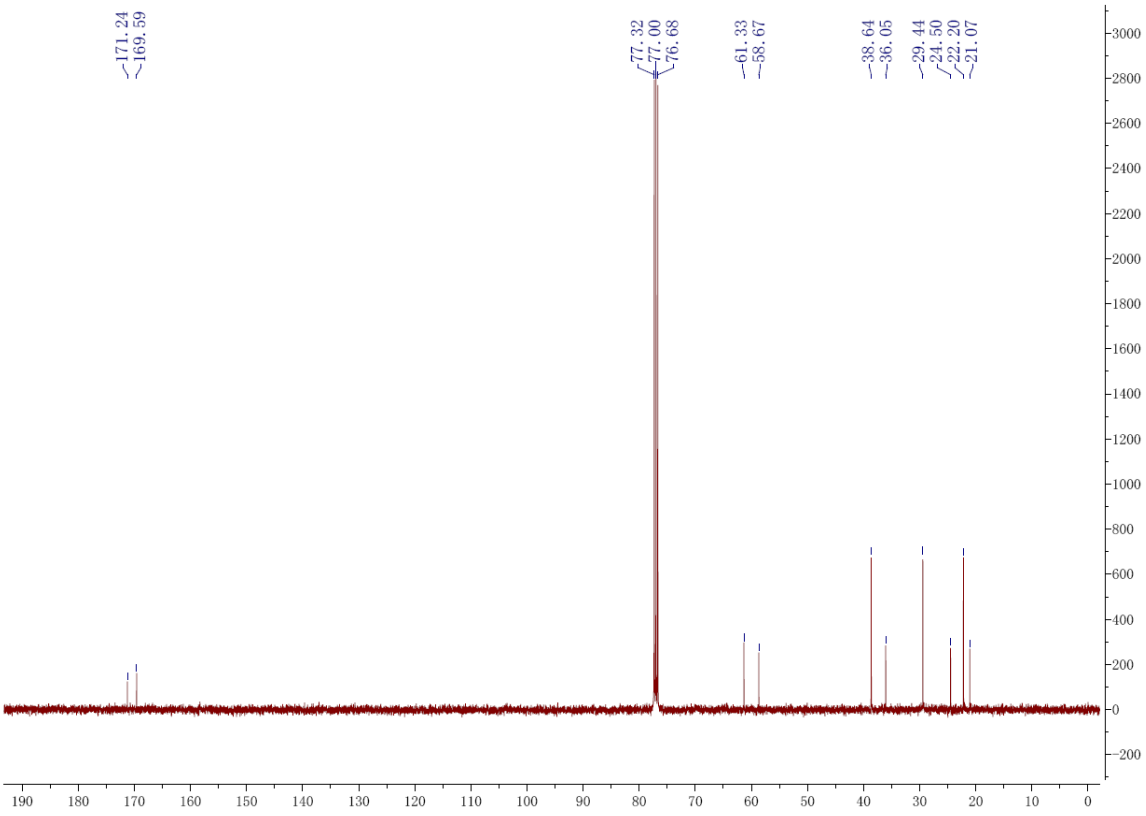
4.08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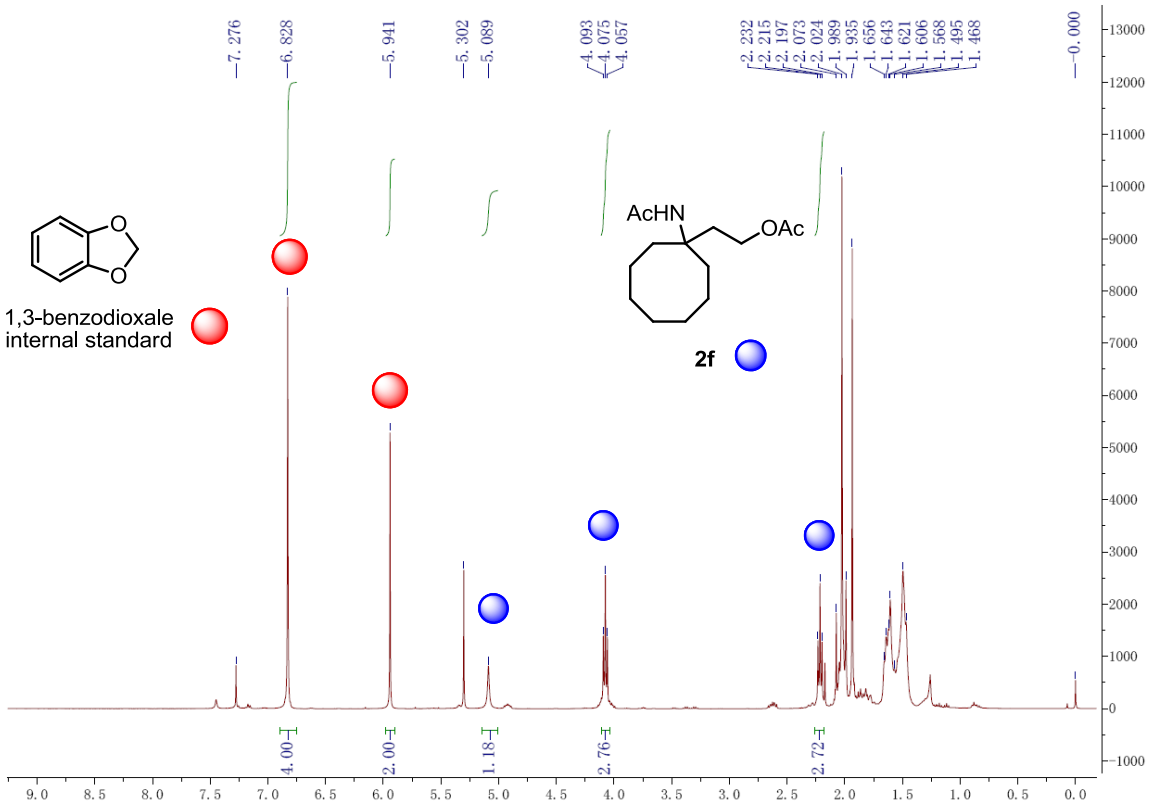
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4.057
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1.935
1.656
1.643
1.621
1.606
1.568
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OAc
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internal standard
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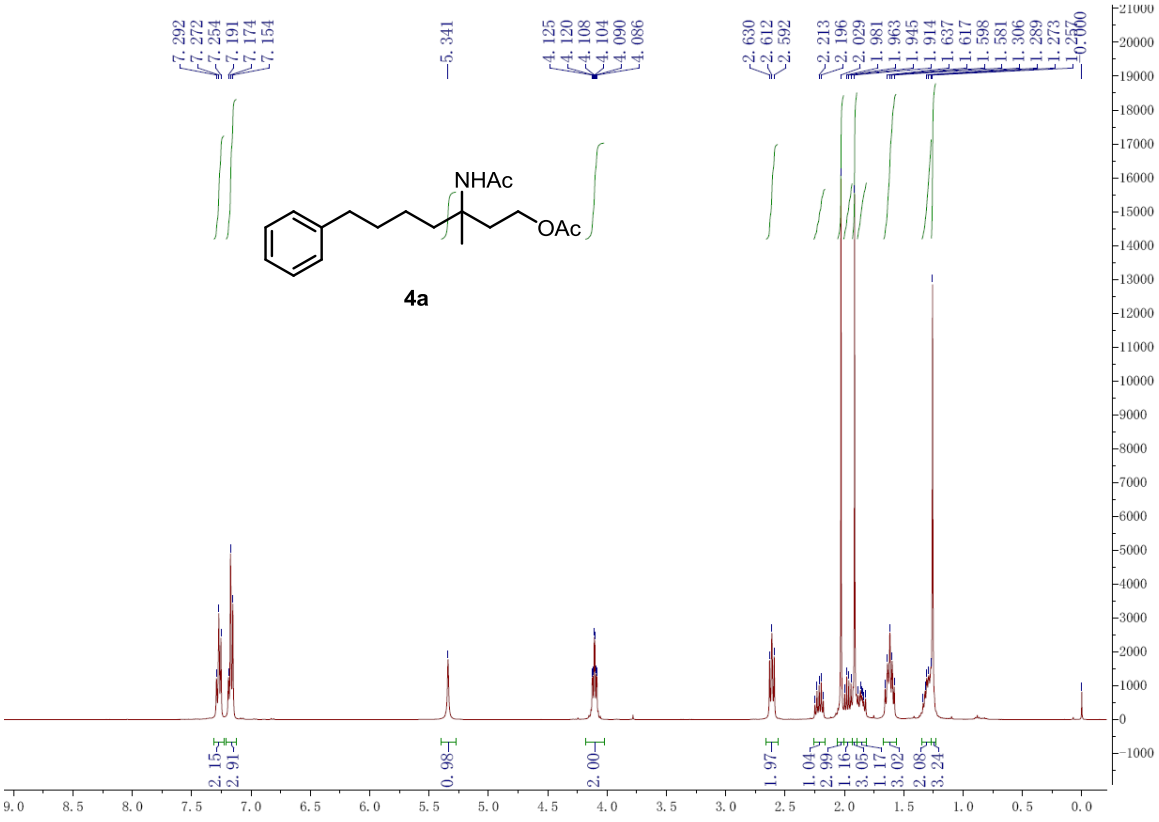
2.72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4.086
2.630
2.612
2.592
2.213
2.196
2.029
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1.963
1.945
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1.637
1.617
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1.306
1.289
1.273
0.000
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OAc
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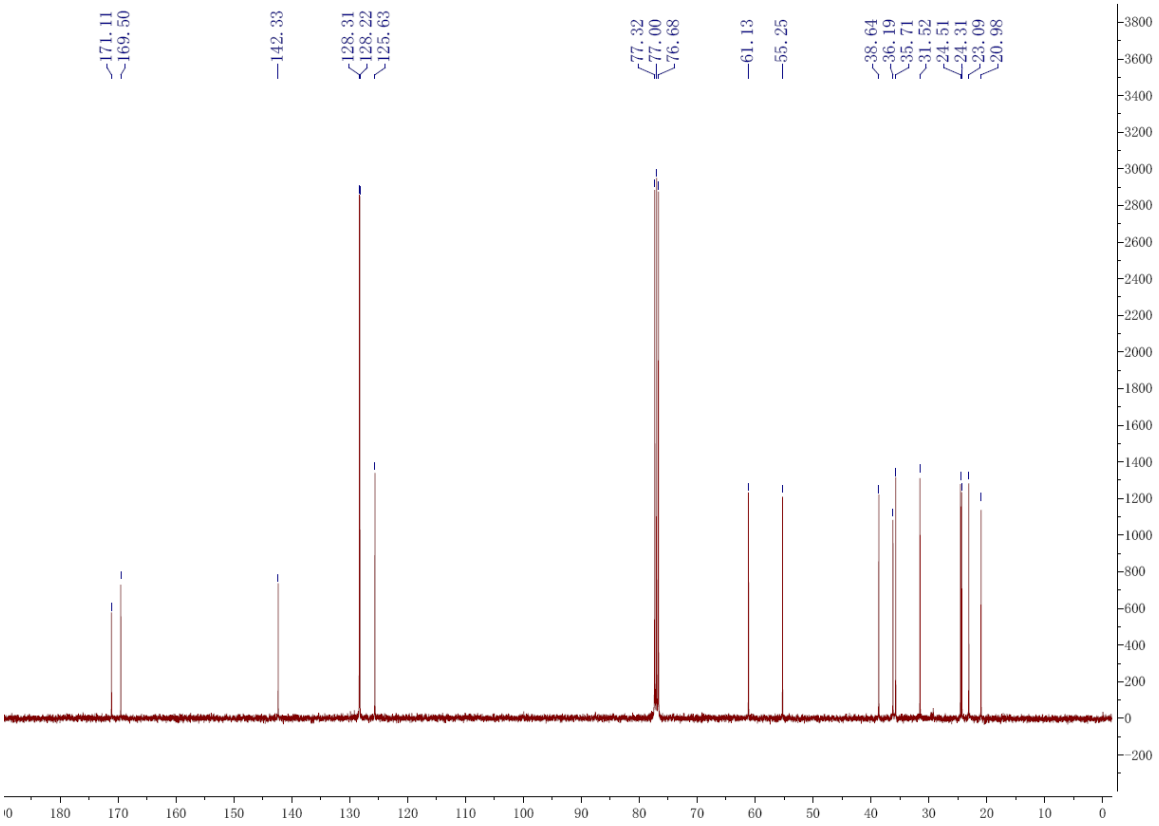
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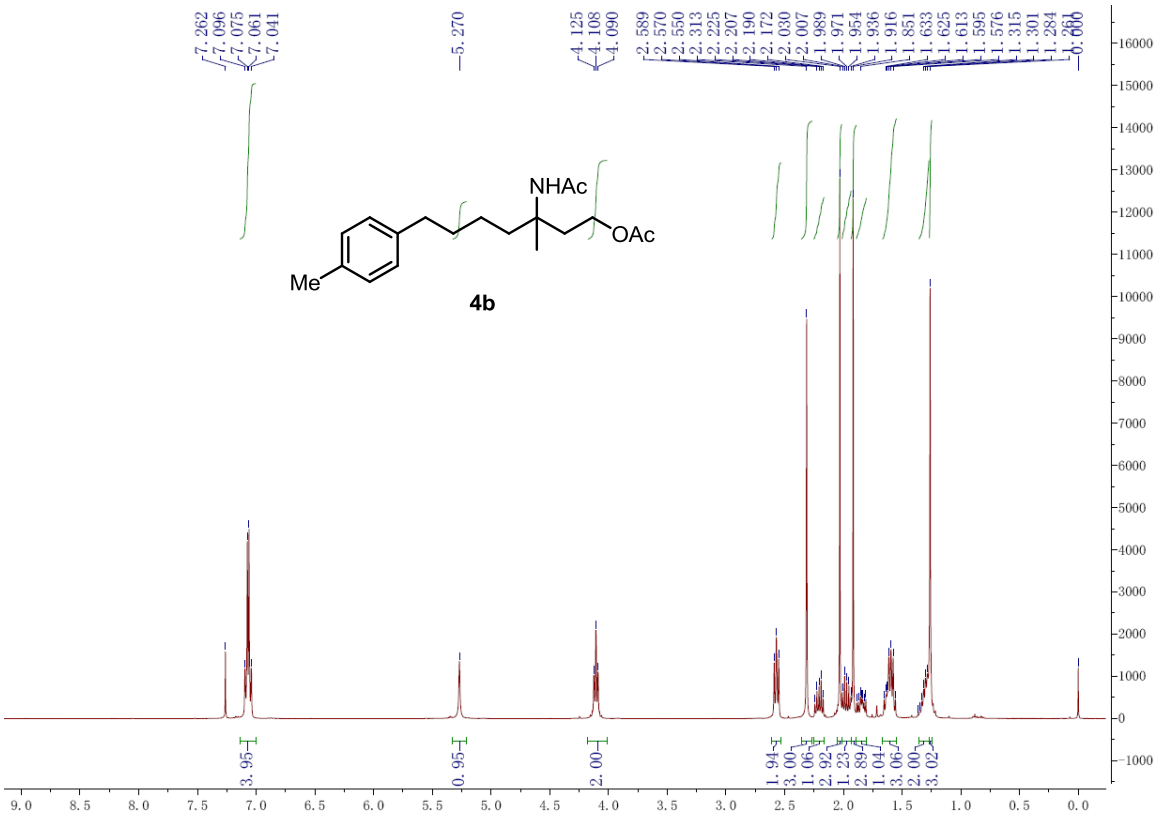
24.31
23.09
20.98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1.613
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1.315
1.301
1.284
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OAc
Me
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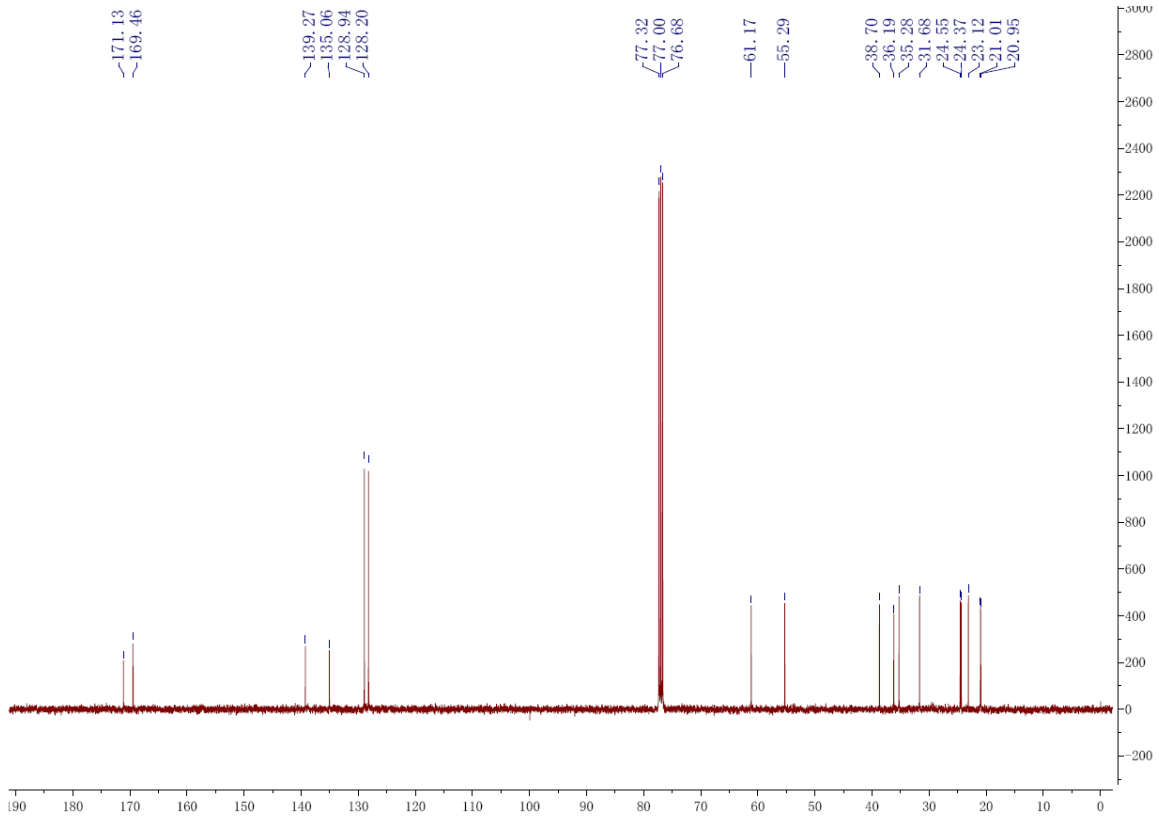
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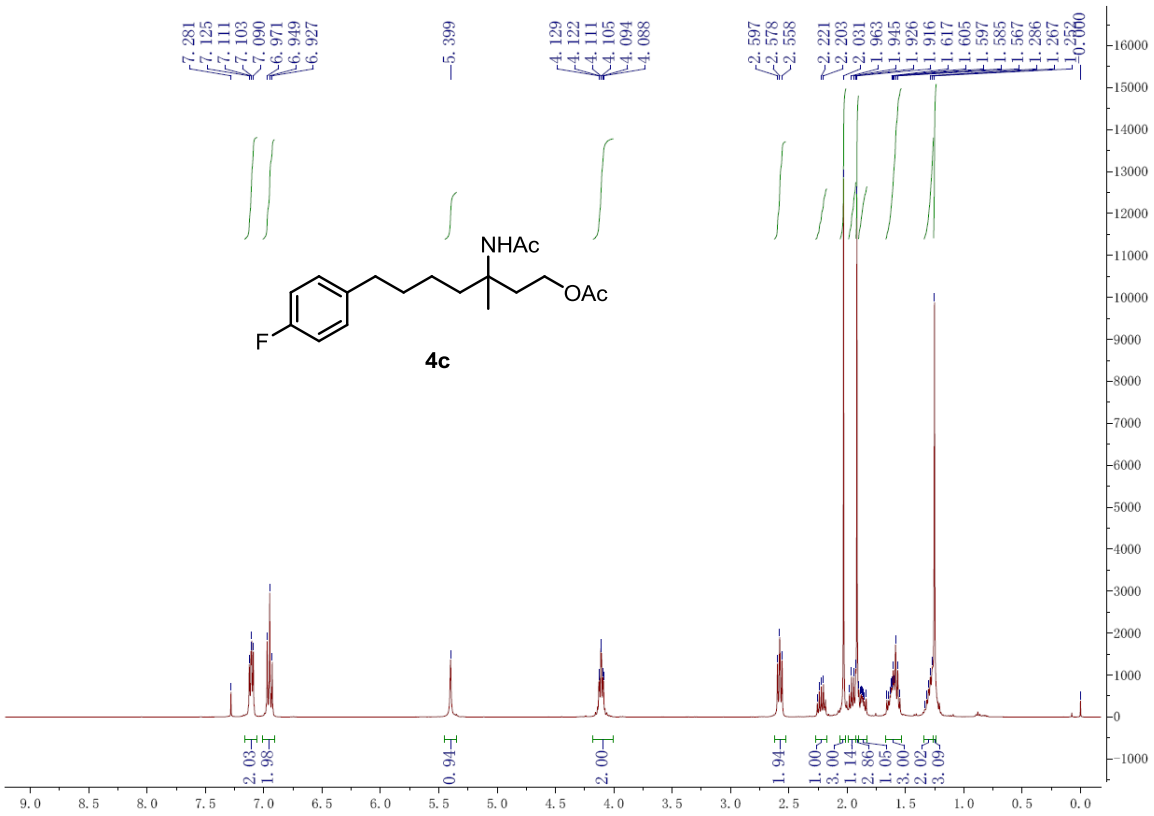
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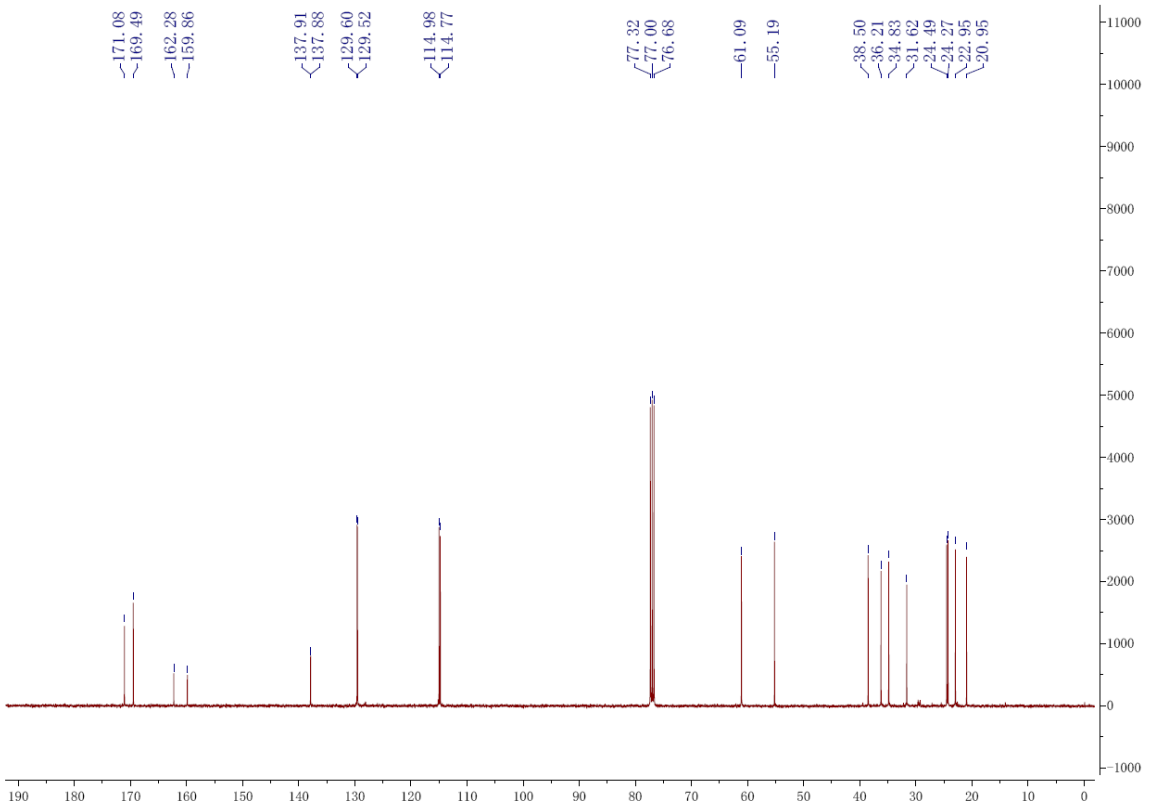

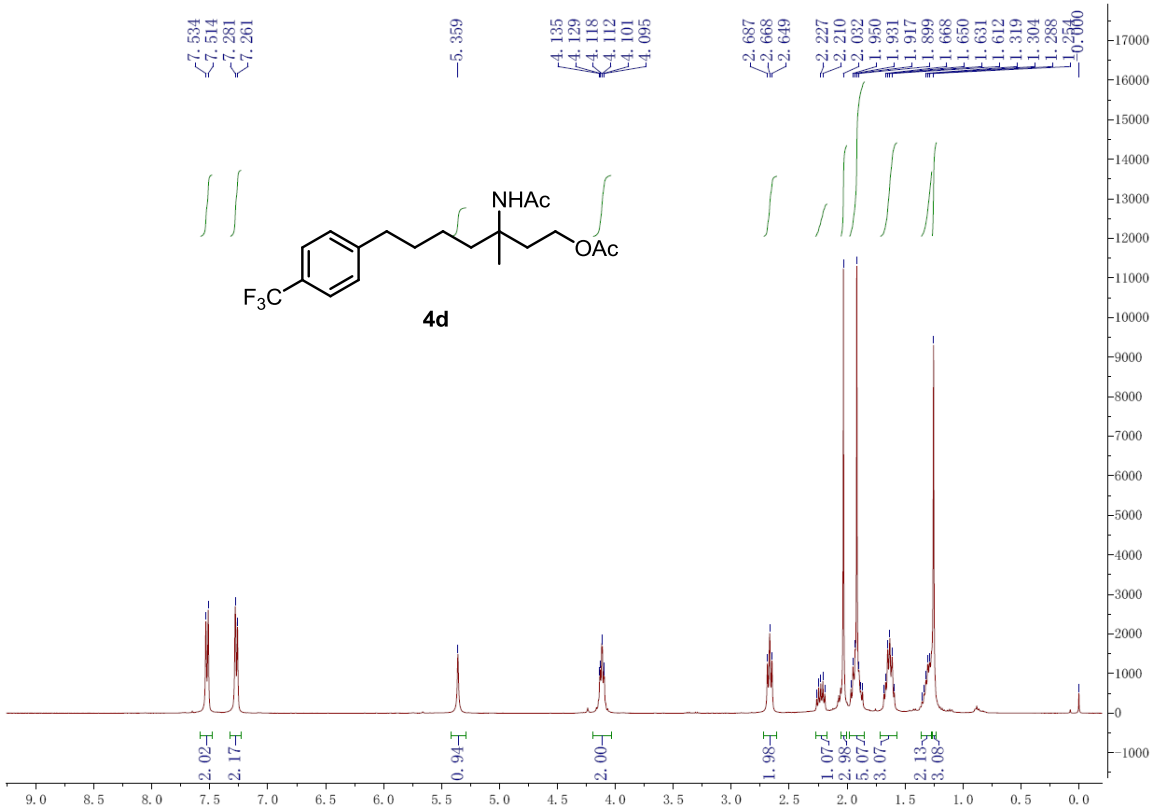
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OAc
F3C
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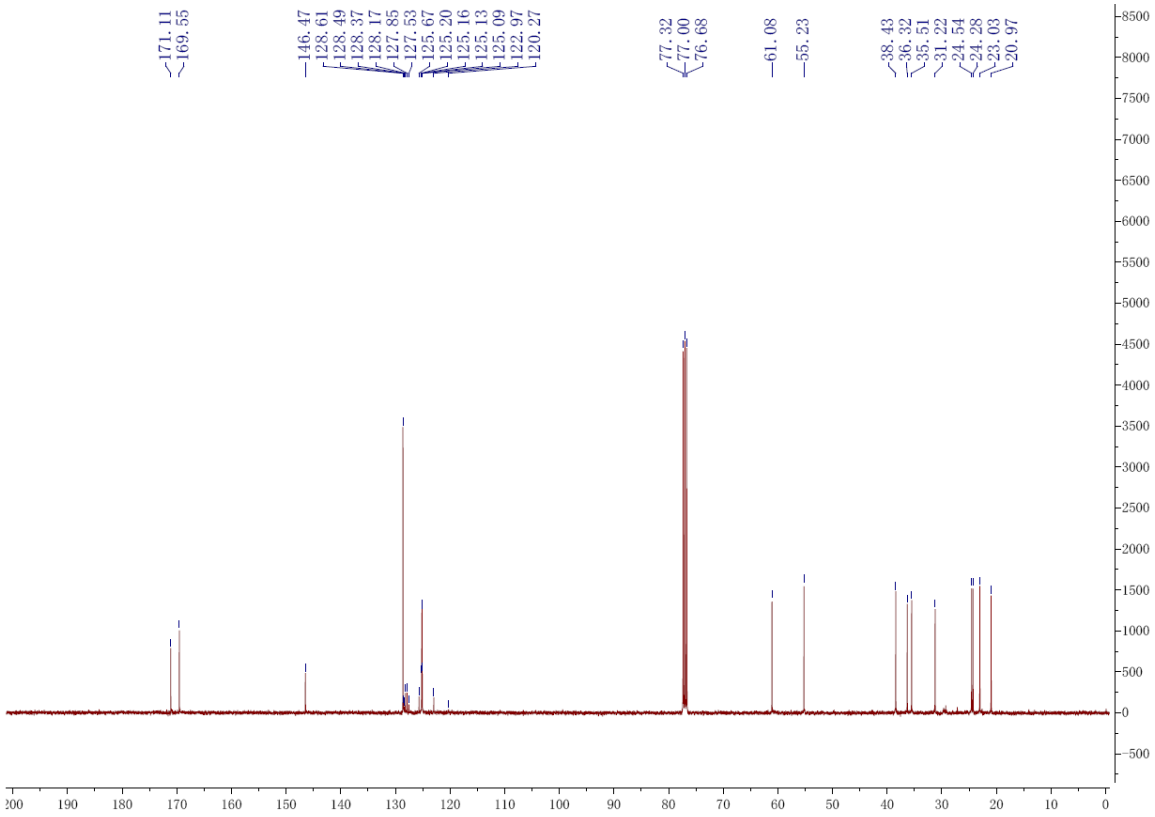
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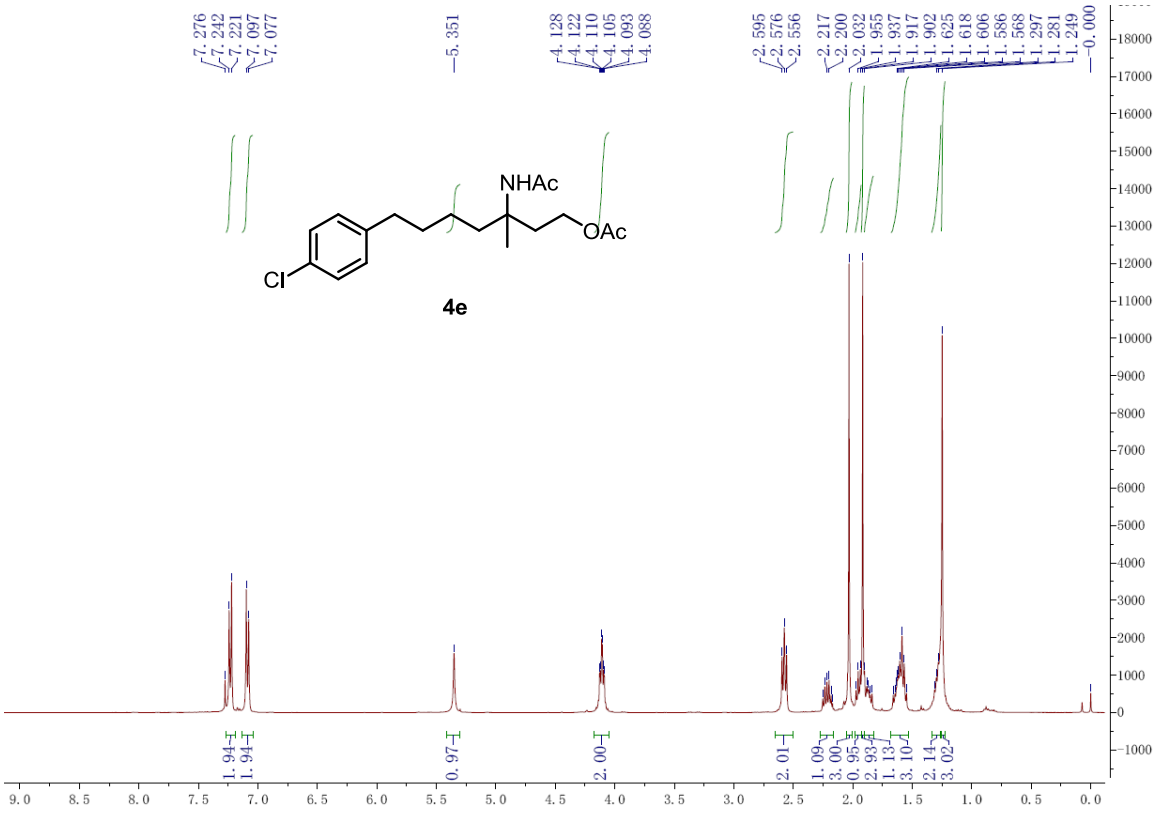
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OAc
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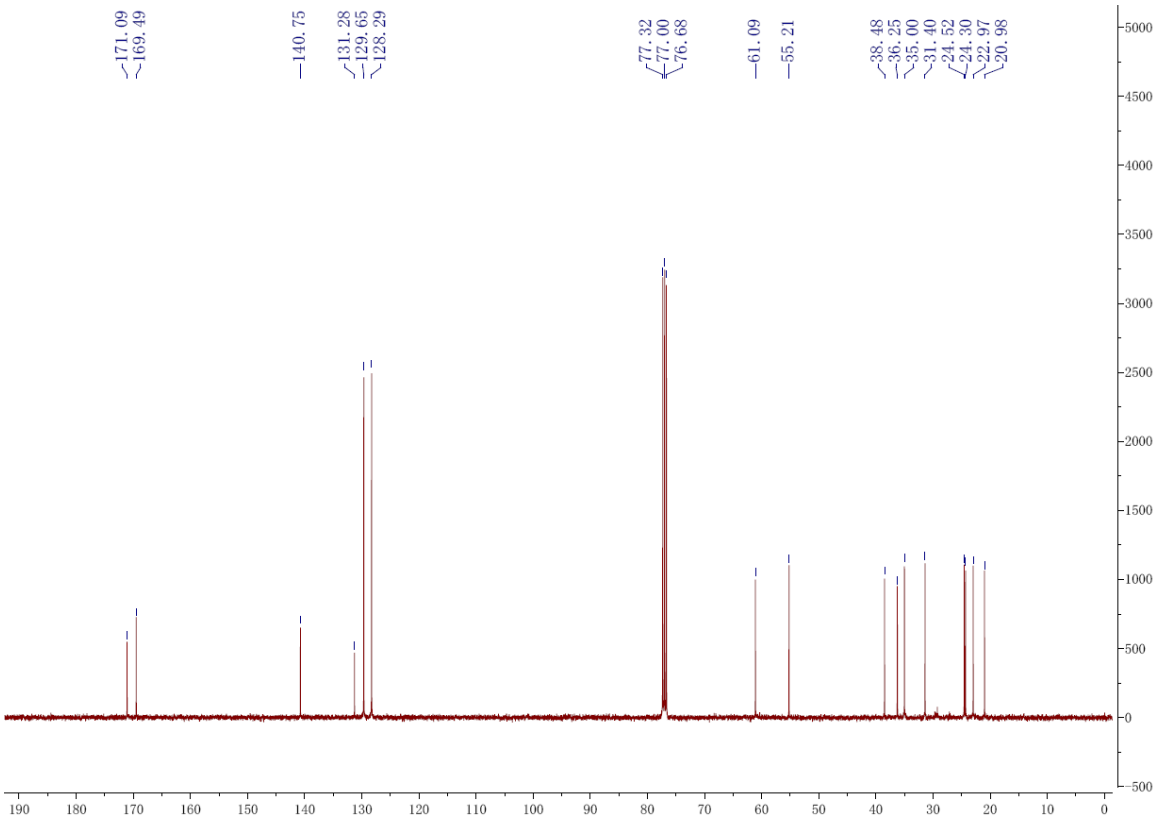
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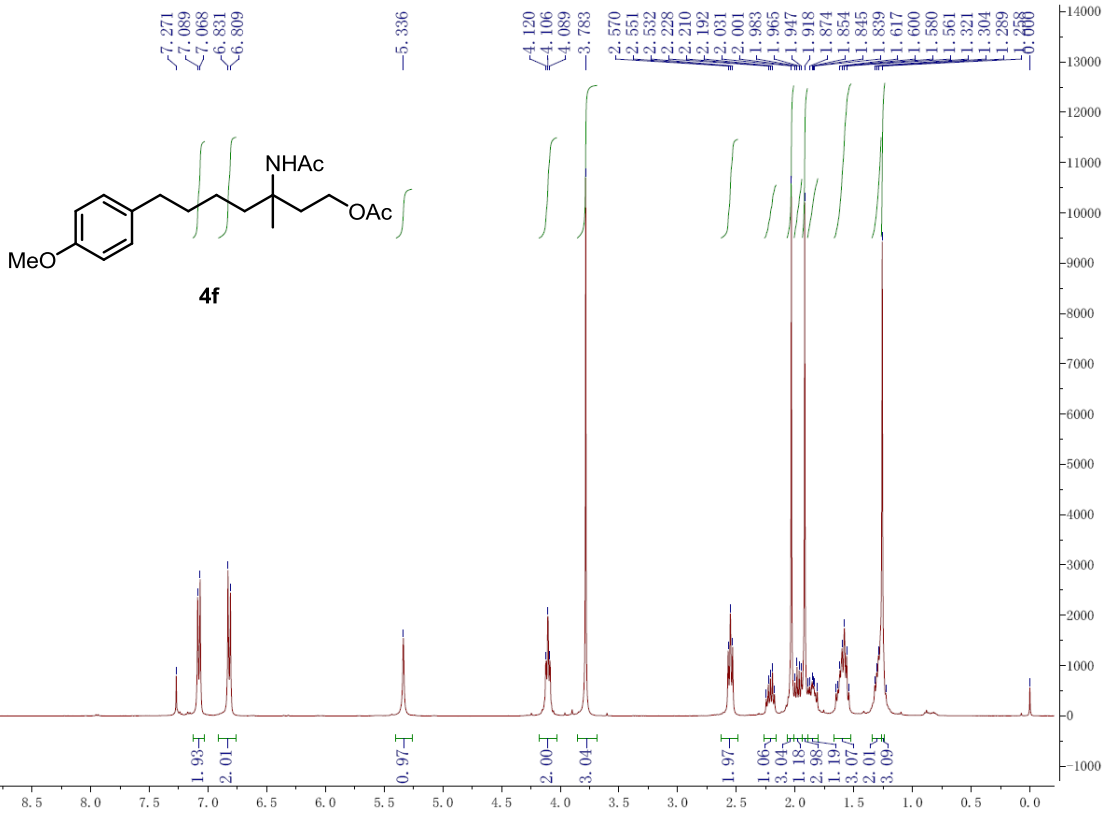
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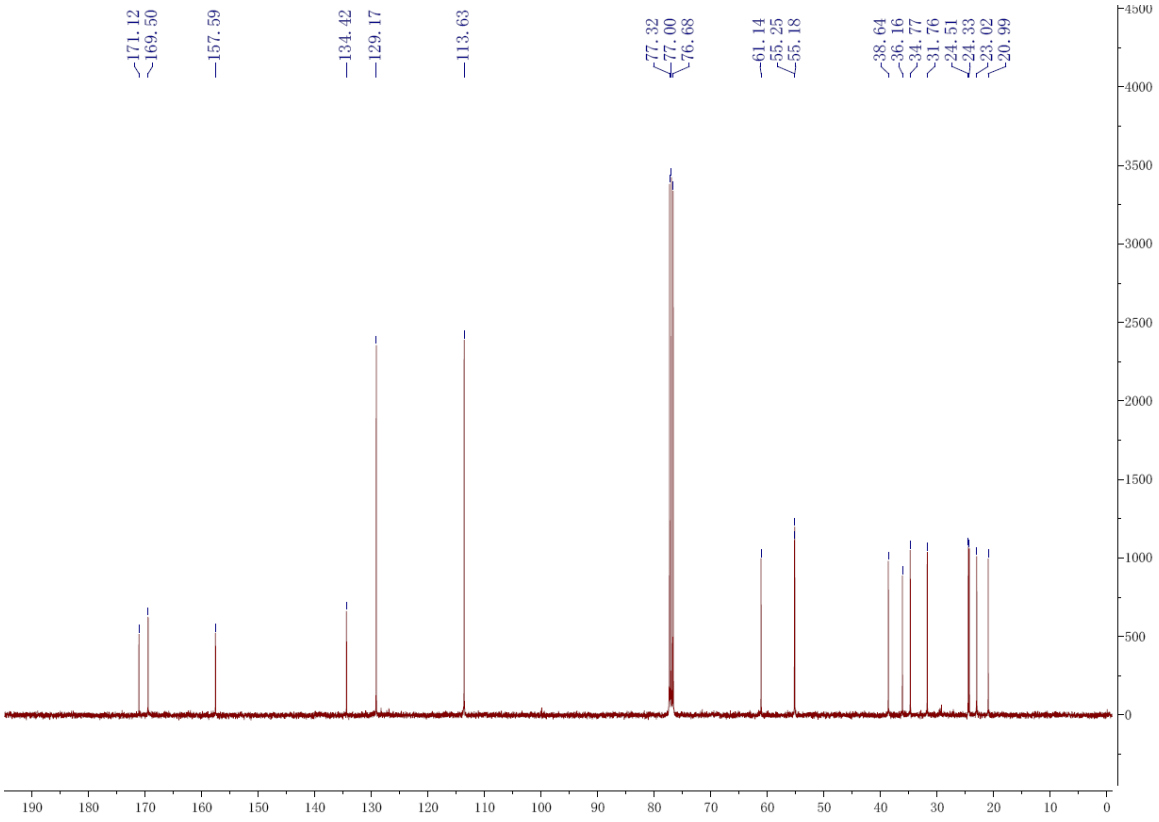

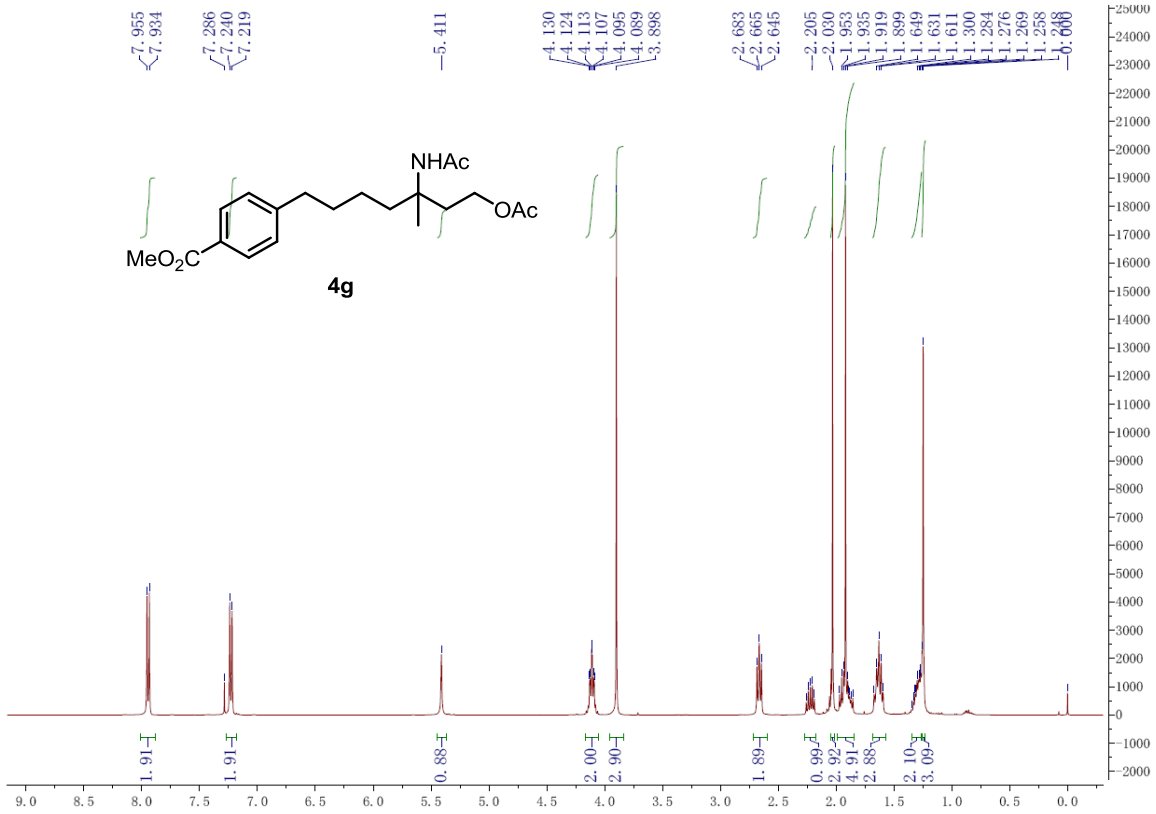
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OAc
MeO2C
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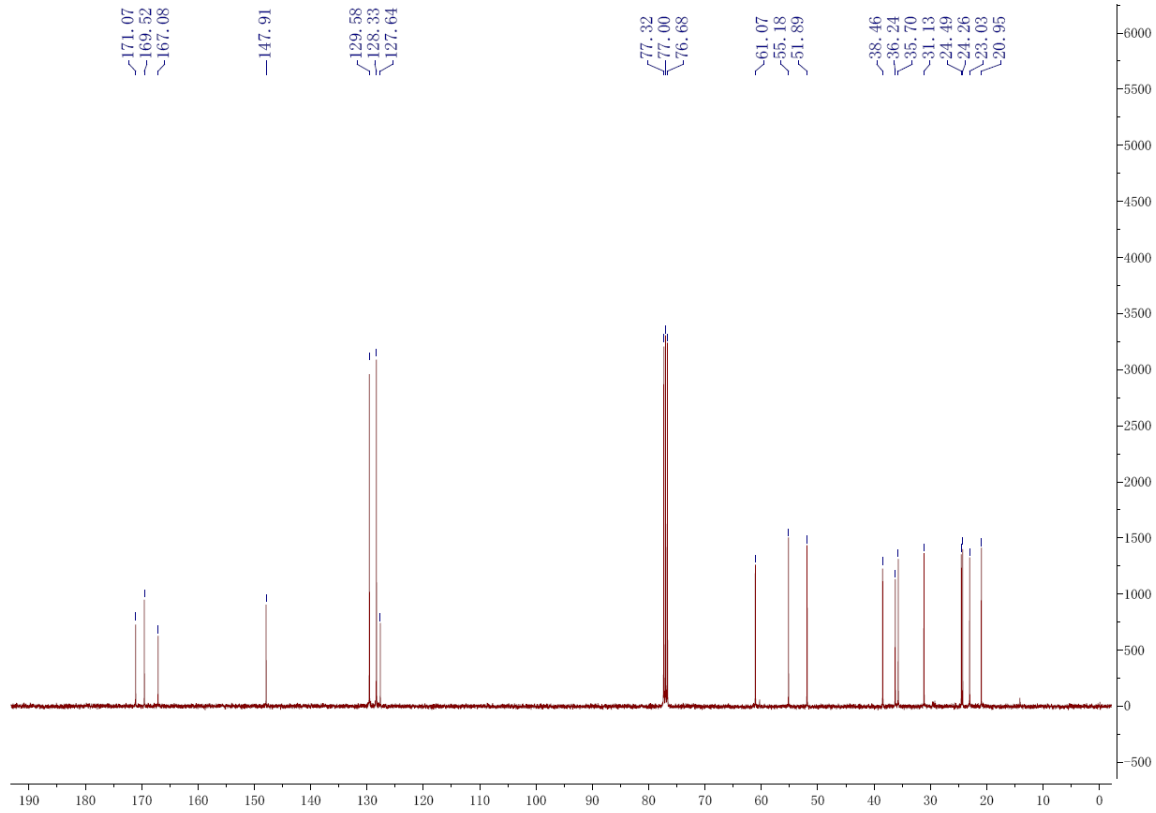
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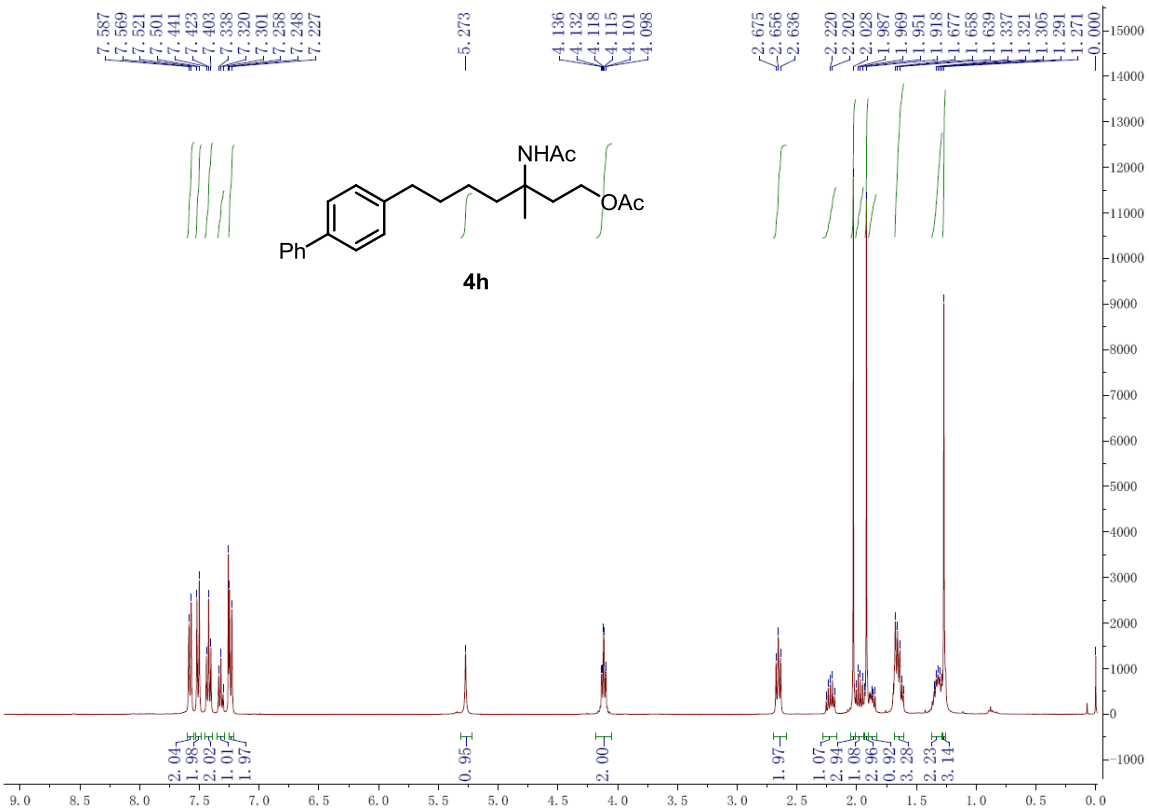

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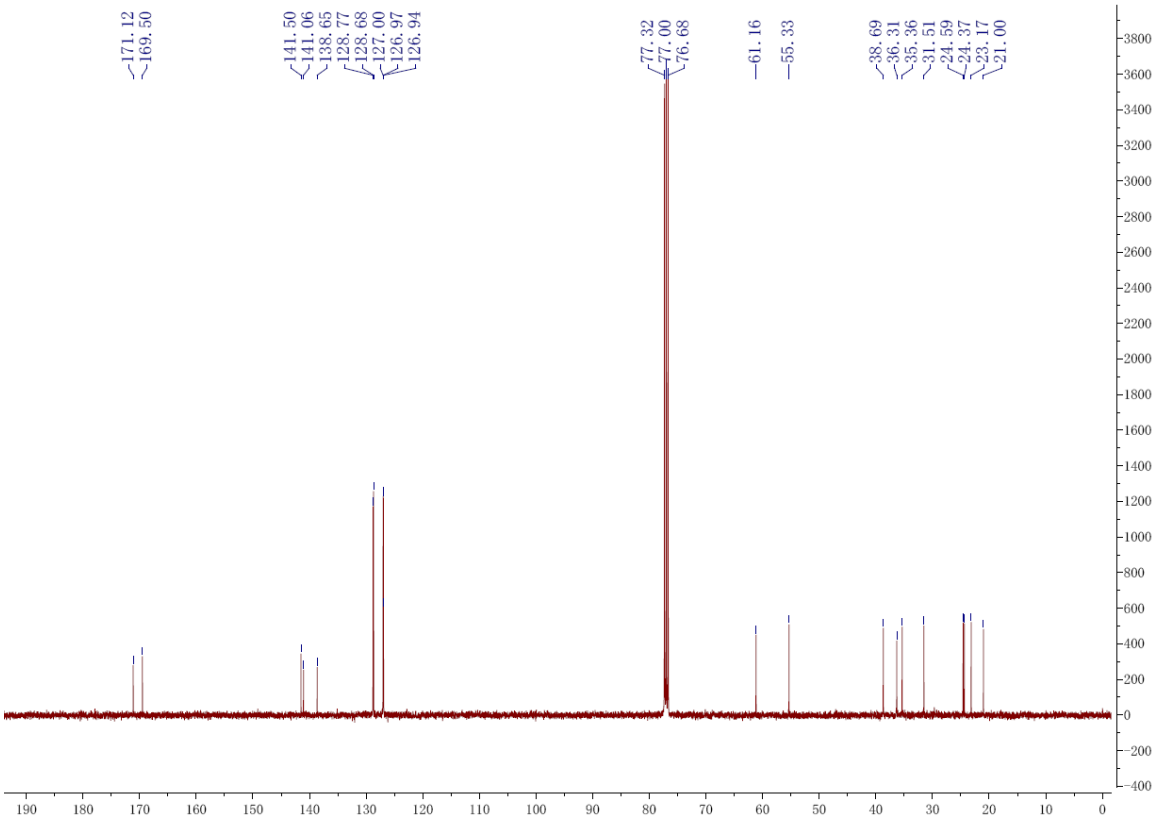

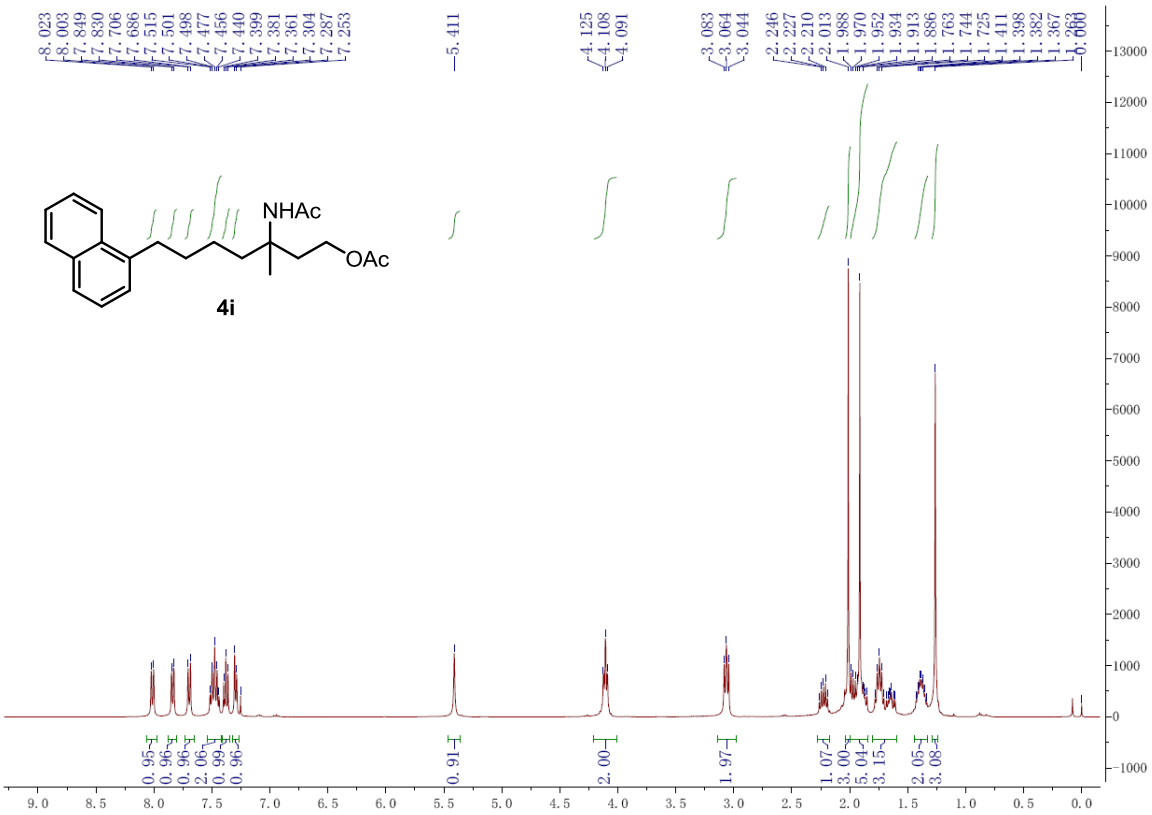
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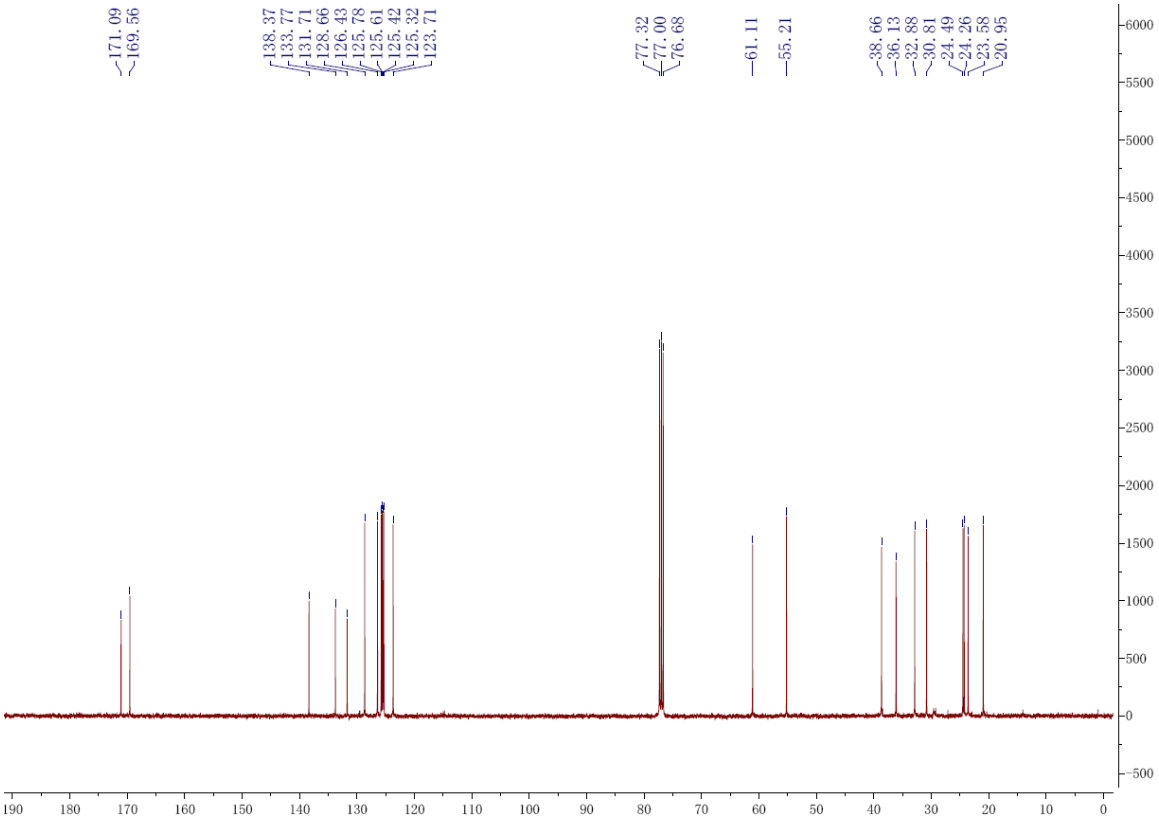

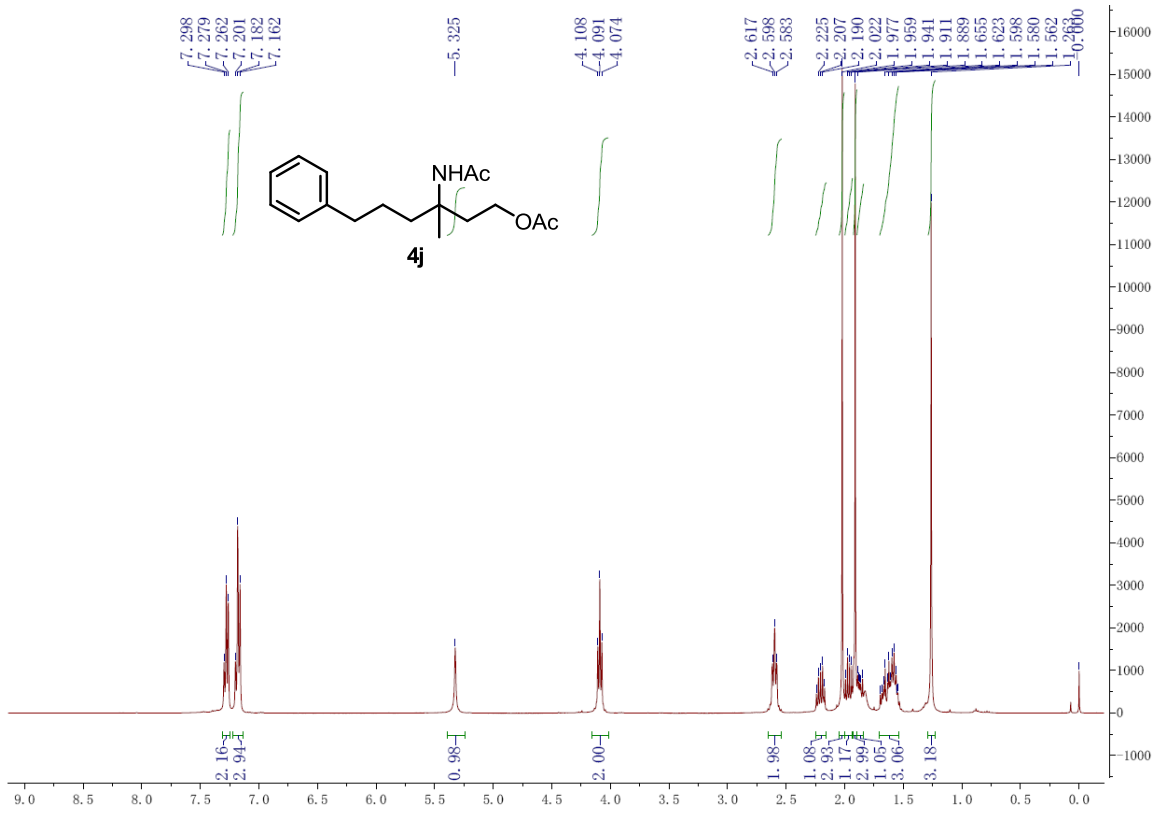
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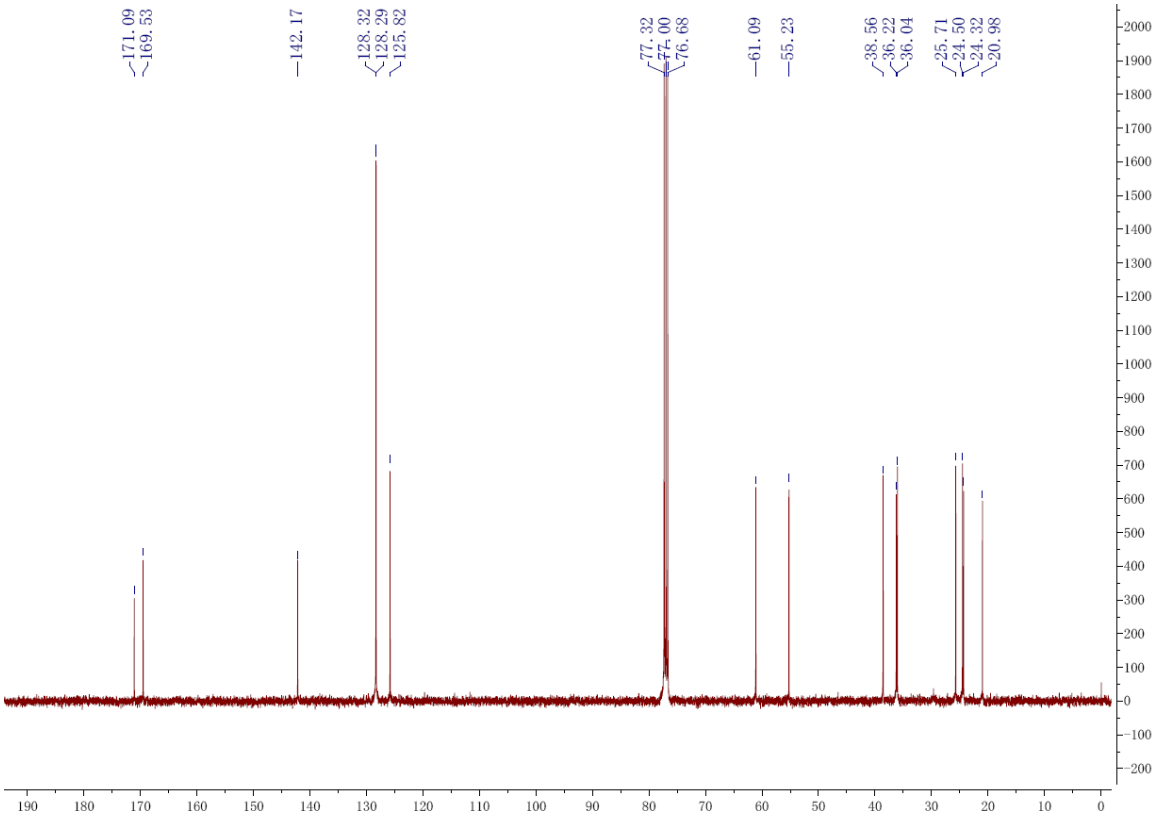
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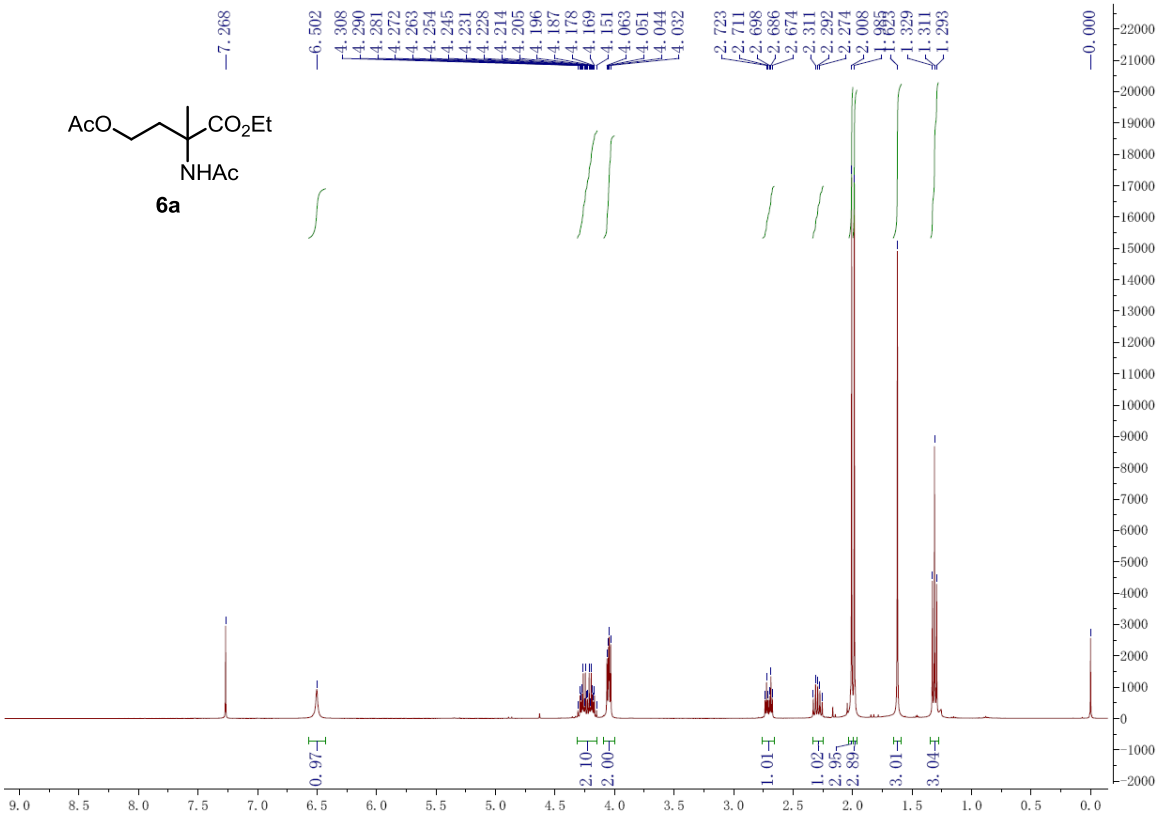
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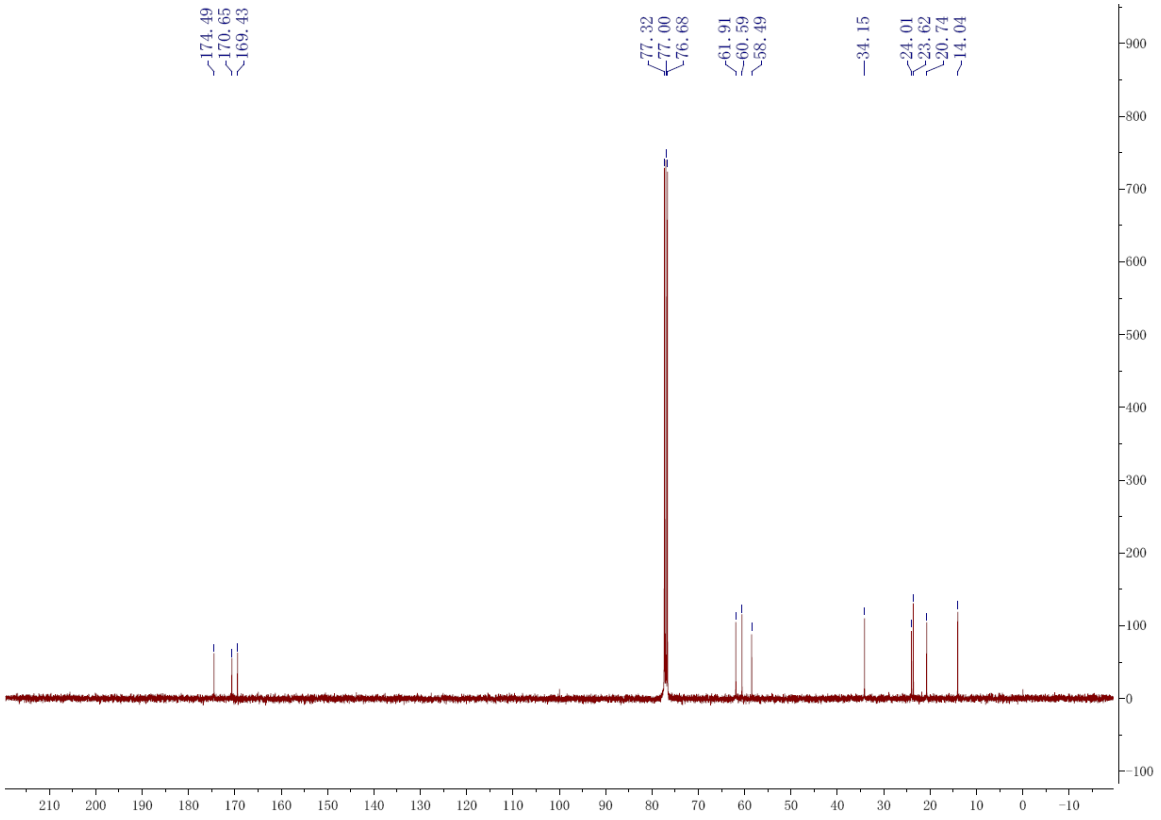

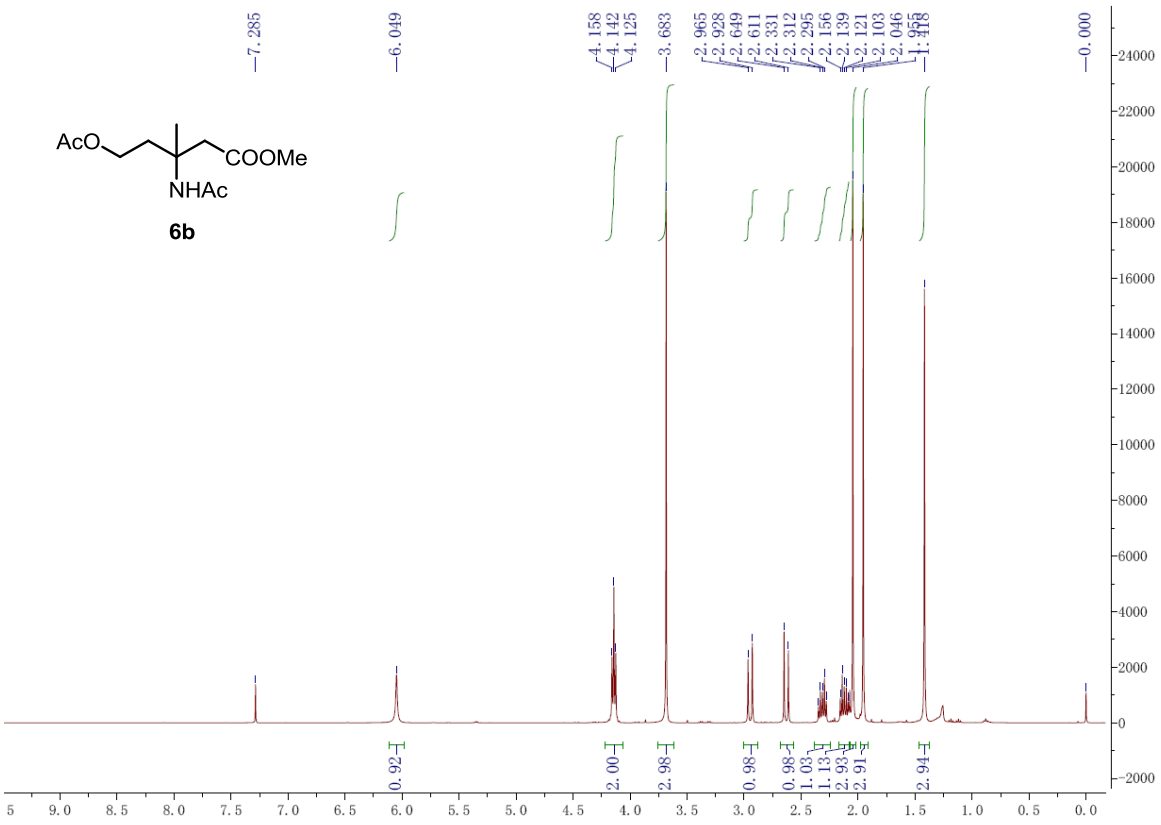
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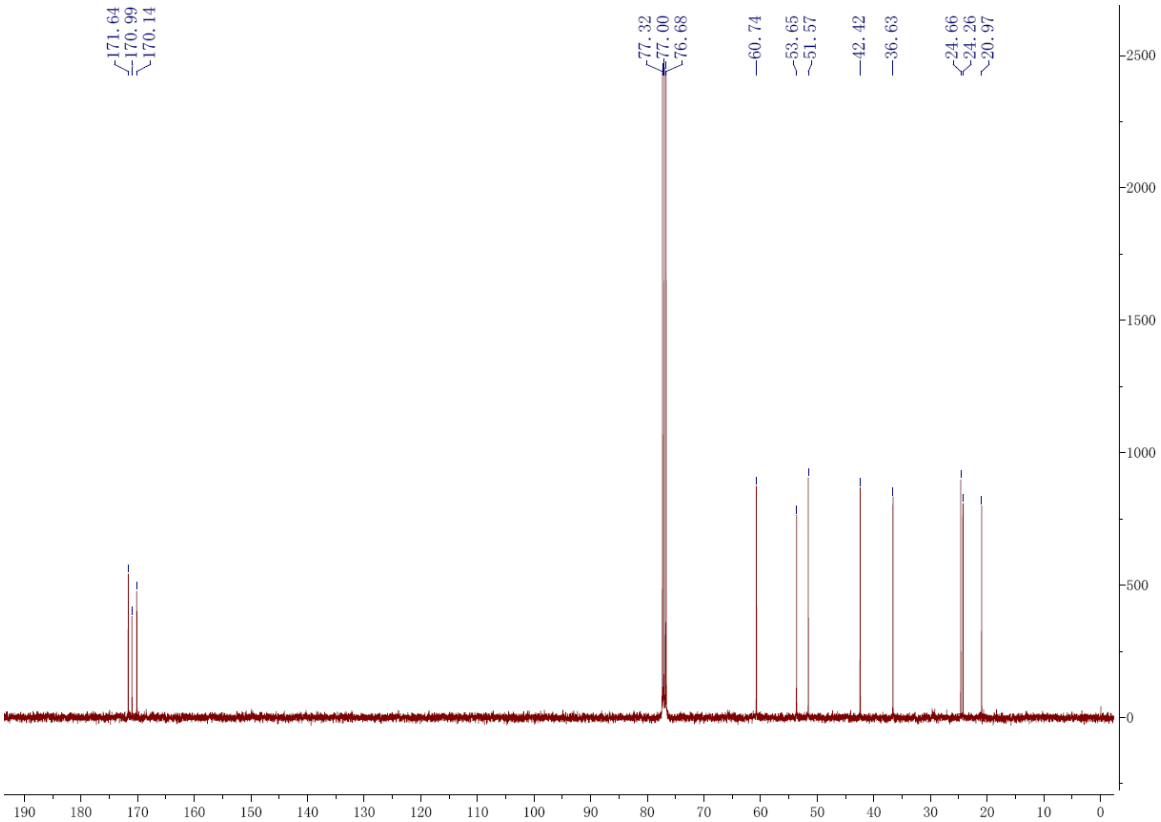
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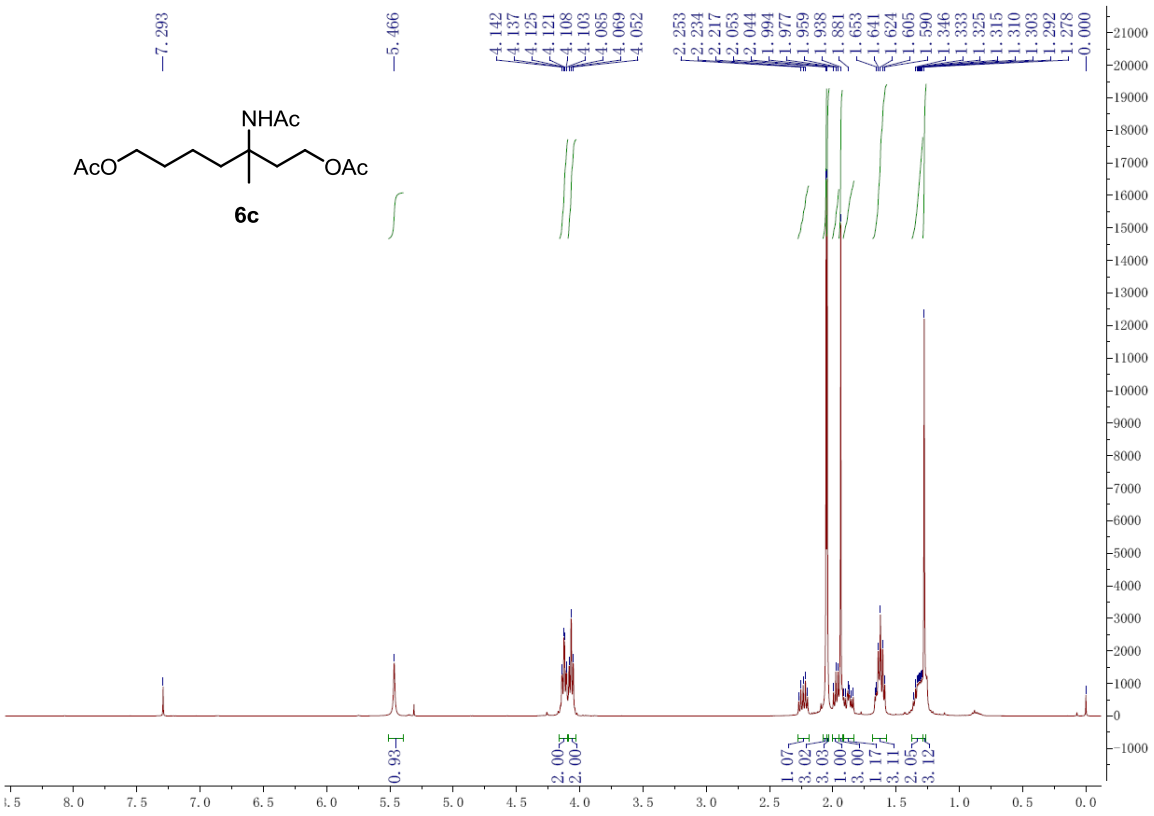
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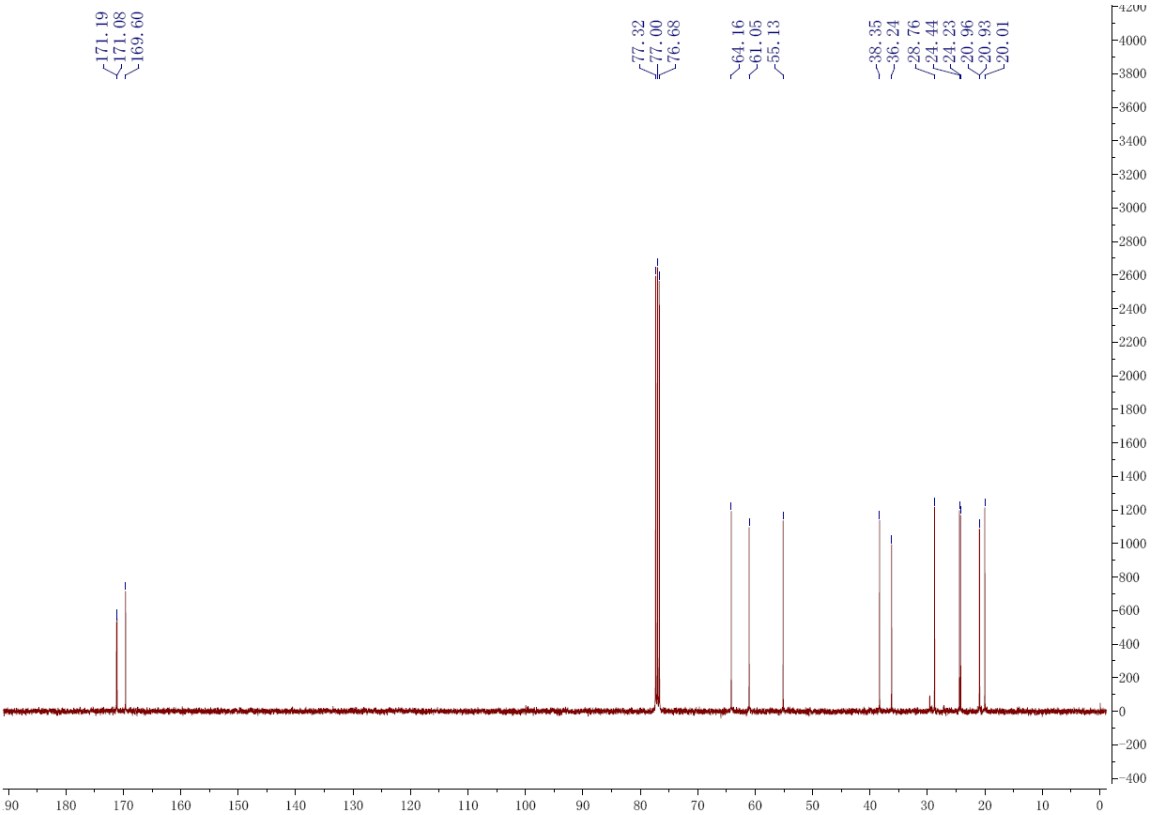
3.12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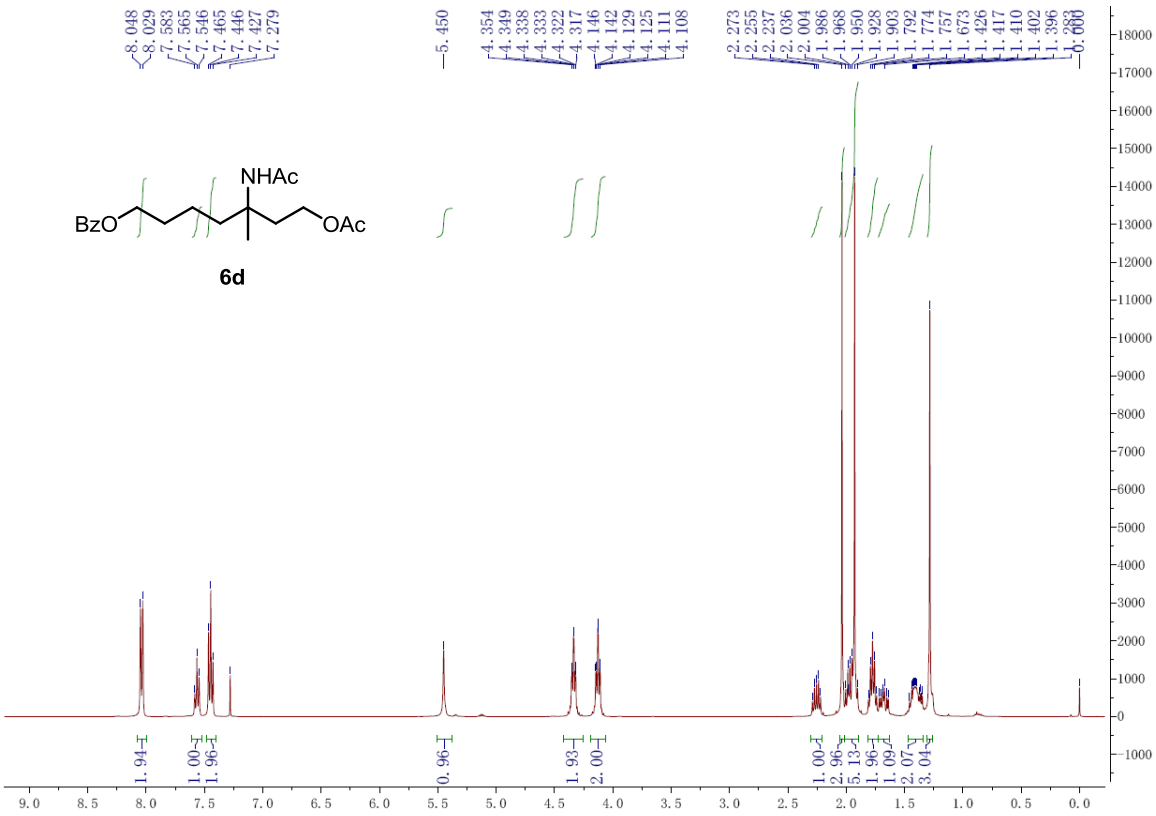
171.08
169.60
77.32
77.00
76.68
64.16
61.05
55.13
38.35
36.24
28.76
24.44
24.23
20.96
20.93
20.01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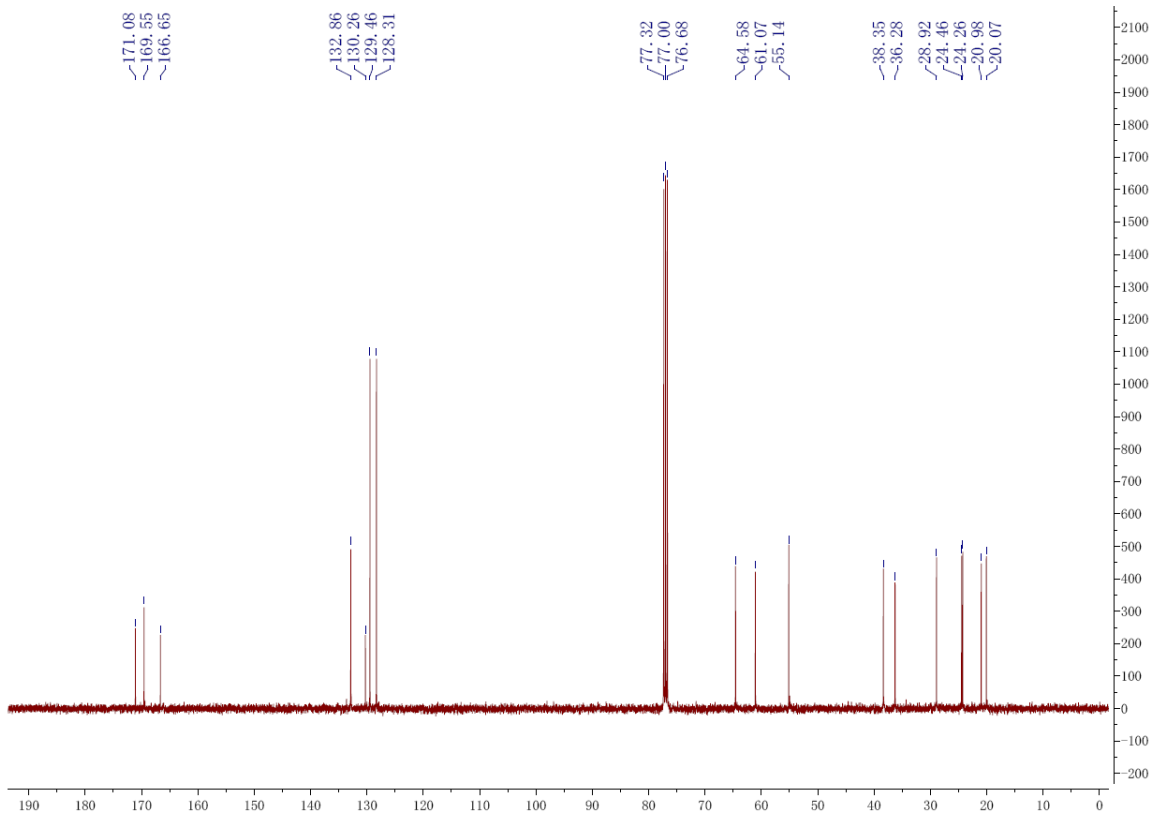
8.029
7.583
7.565
7.546
7.465
7.446
7.427
7.279
5.450
4.354
4.349
4.338
4.333
4.322
4.317
4.146
4.142
4.129
4.125
4.111
4.108
2.273
2.255
2.237
2.036
2.004
1.986
1.968
1.950
1.928
1.903
1.792
1.774
1.757
1.673
1.426
1.417
1.410
1.402
1.396
0.000
NHAc
BzO
OAc
6d
1.94
1.00
1.96
0.96
1.93
2.00
1.00
2.96
5.13
1.96
1.09
2.07
3.04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166.65
132.86
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129.46
128.31
77.32
77.00
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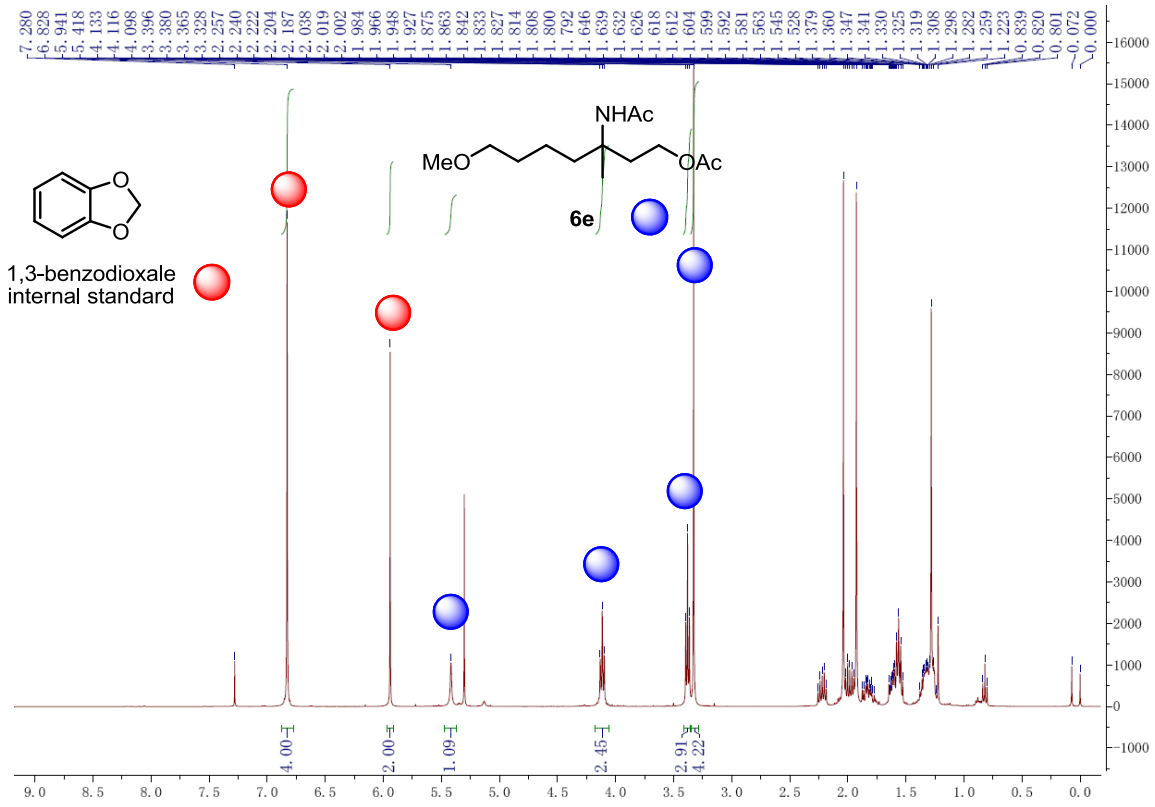
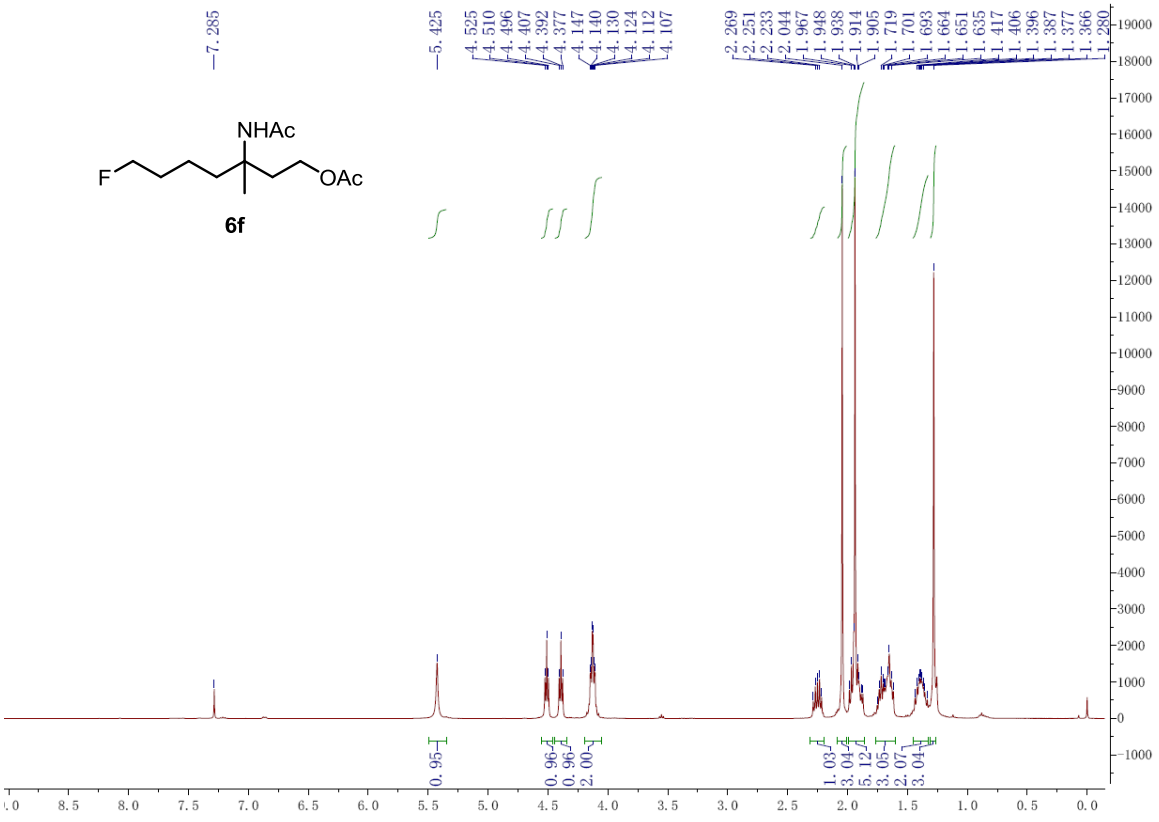
64.58
61.07
55.14
38.35
36.28
28.92
24.46
24.26
20.98
20.07


NHAc
MeO
OAc
6e
1,3-benzodioxale
internal standard
4.00
2.00
1.09
2.45
2.91
4.22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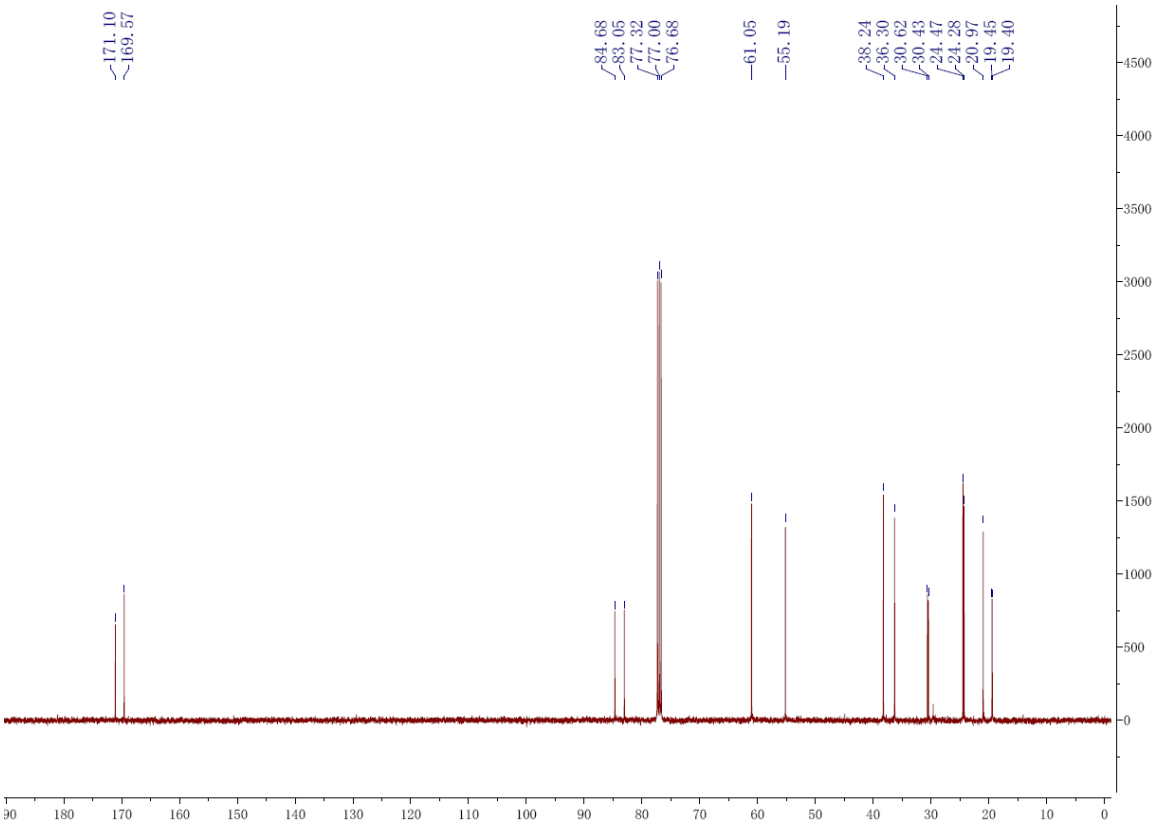
5.425
4.525
4.510
4.496
4.407
4.392
4.377
4.147
4.140
4.130
4.124
4.112
4.107
2.269
2.251
2.233
2.044
1.967
1.948
1.938
1.914
1.905
1.719
1.701
1.693
1.664
1.651
1.635
1.417
1.406
1.396
1.387
1.377
1.366
1.280
NHAc
F
OAc
6f
0.95
0.96
0.96
2.00
1.03
3.04
5.12
3.05
2.07
3.04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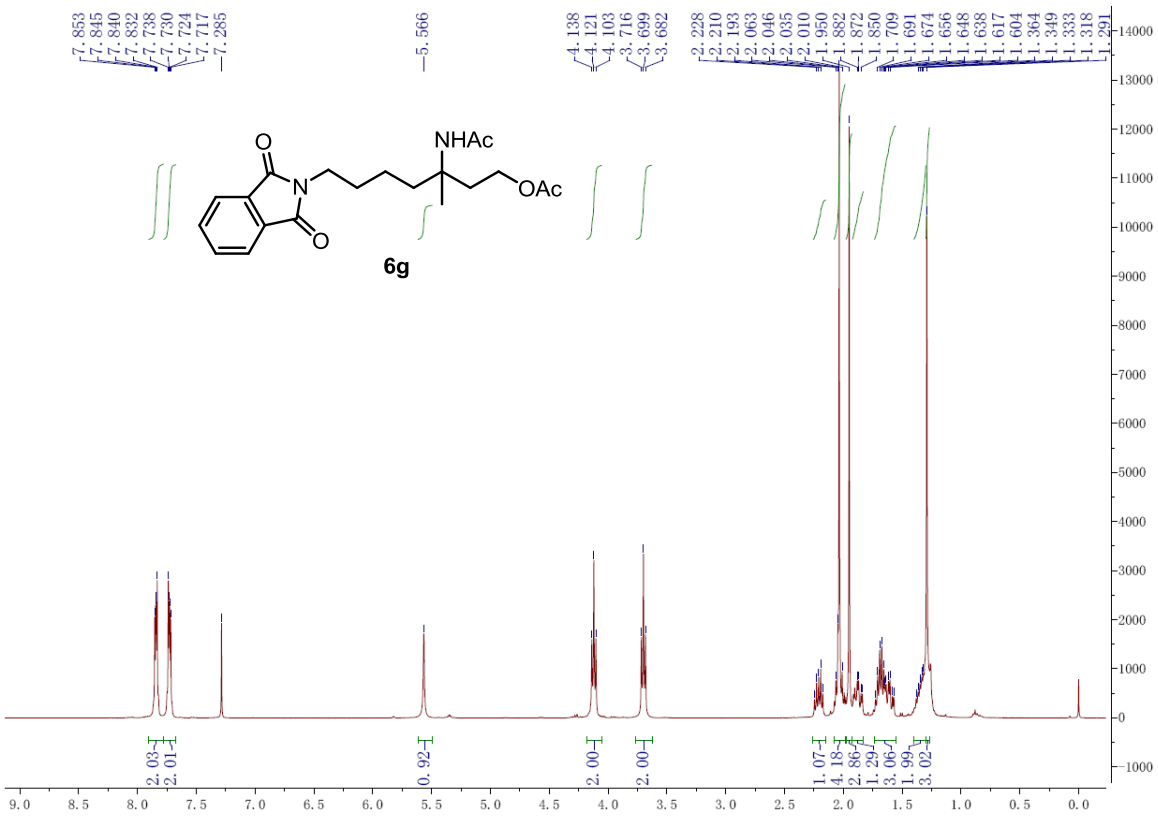
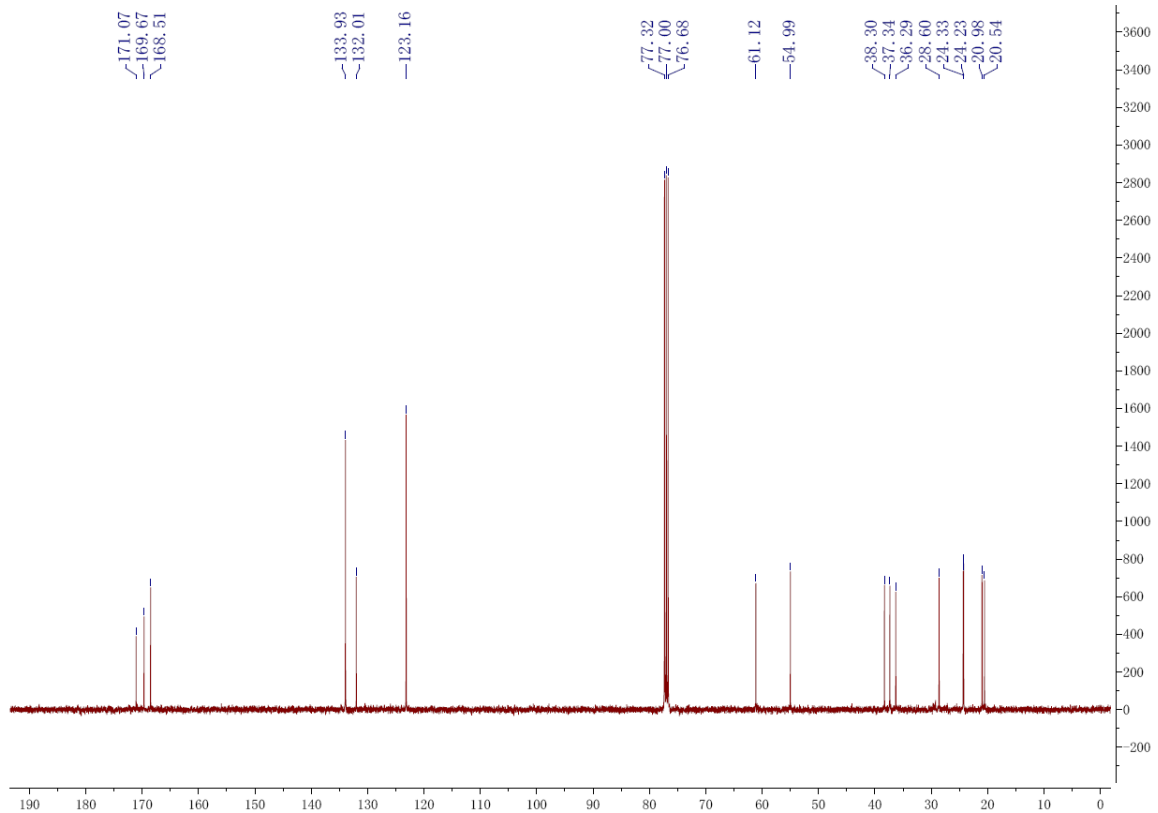
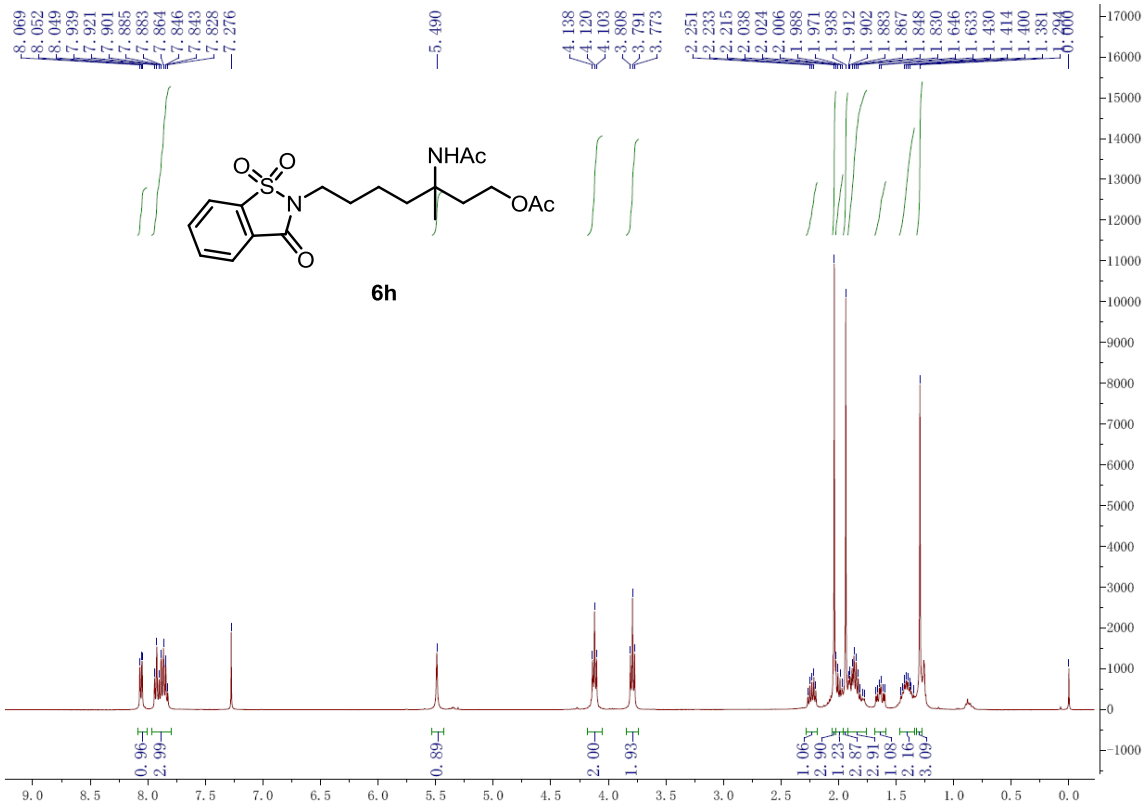
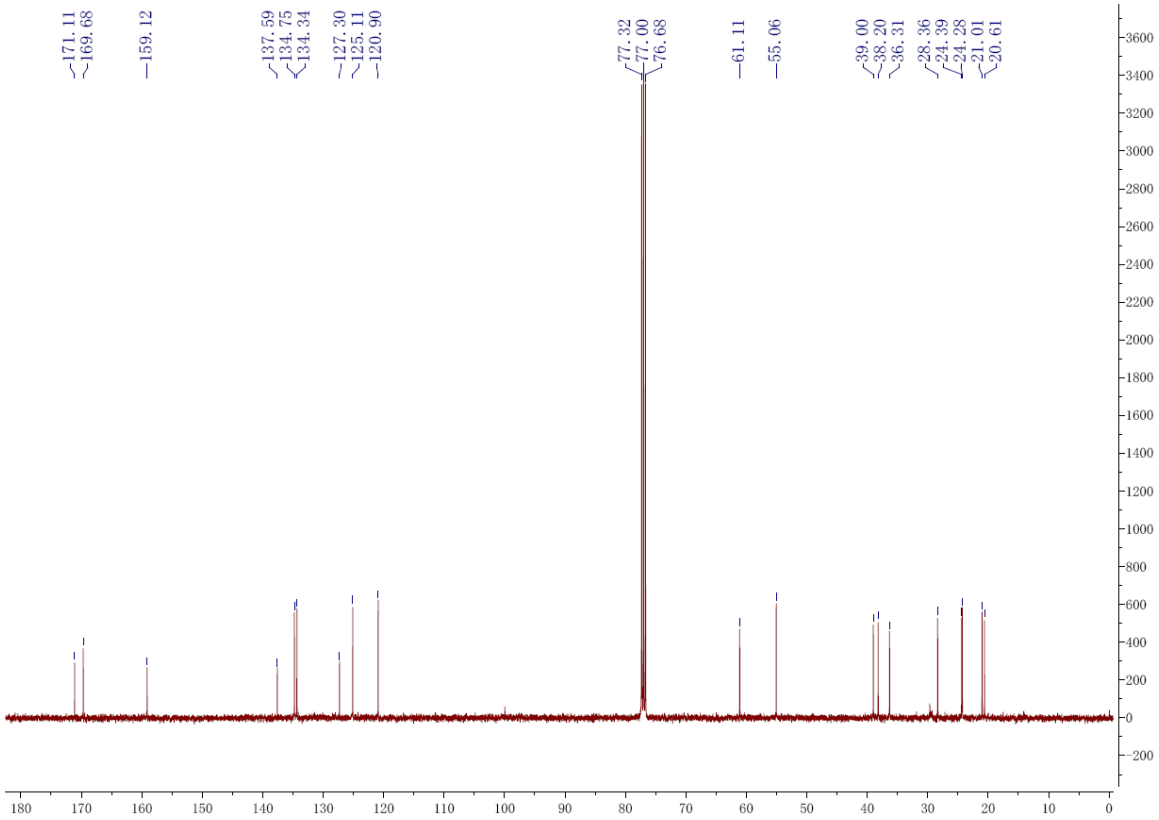
169.57
84.68
83.05
77.32
77.00
76.68
61.05
55.19
38.24
36.30
30.62
30.43
24.47
24.28
20.97
19.45
19.40


7.853
7.845
7.840
7.832
7.738
7.730
7.724
7.717
7.285
5.566
4.138
4.121
4.103
3.716
3.699
3.682
2.228
2.210
2.193
2.063
2.046
2.035
2.010
1.950
1.882
1.872
1.850
1.709
1.691
1.674
1.656
1.648
1.638
1.617
1.604
1.364
1.349
1.333
1.318
1.291
NHAc
OAc
O
N
O
6g
2.03
2.01
0.92
2.00
2.00
1.07
4.18
2.86
1.29
3.06
1.99
3.02


171.07
169.67
168.51
133.93
132.01
123.16
77.32
77.00
76.68
61.12
54.99
38.30
37.34
36.29
28.60
24.33
24.23
20.98
20.54


8.069
8.052
8.049
7.939
7.921
7.901
7.885
7.883
7.864
7.846
7.843
7.828
7.276
5.490
4.138
4.120
4.103
3.808
3.791
3.773
2.251
2.233
2.215
2.038
2.024
2.006
1.988
1.971
1.938
1.912
1.902
1.883
1.867
1.848
1.830
1.646
1.633
1.430
1.414
1.400
1.381
0.000
NHAc
OAc
O
O
S
N
O
6h
0.96
2.99
0.89
2.00
1.93
1.06
2.90
1.23
2.87
2.91
1.08
2.16
3.09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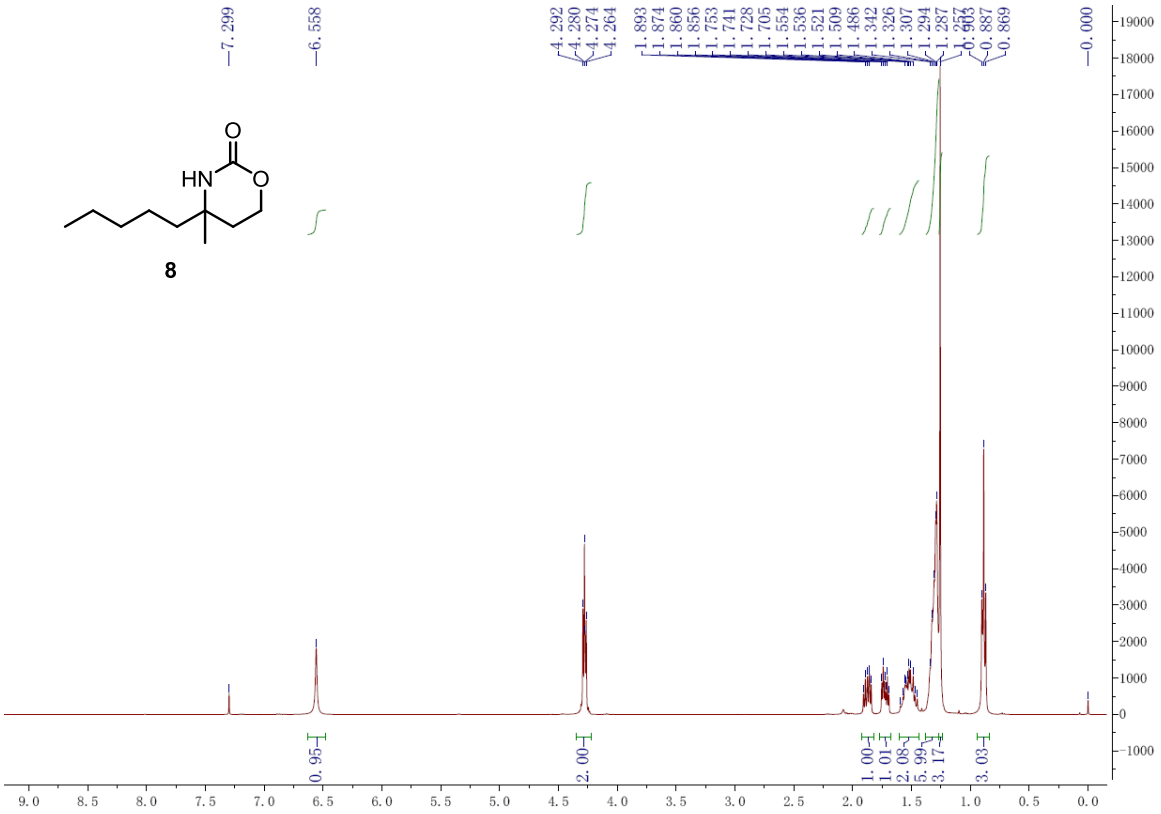
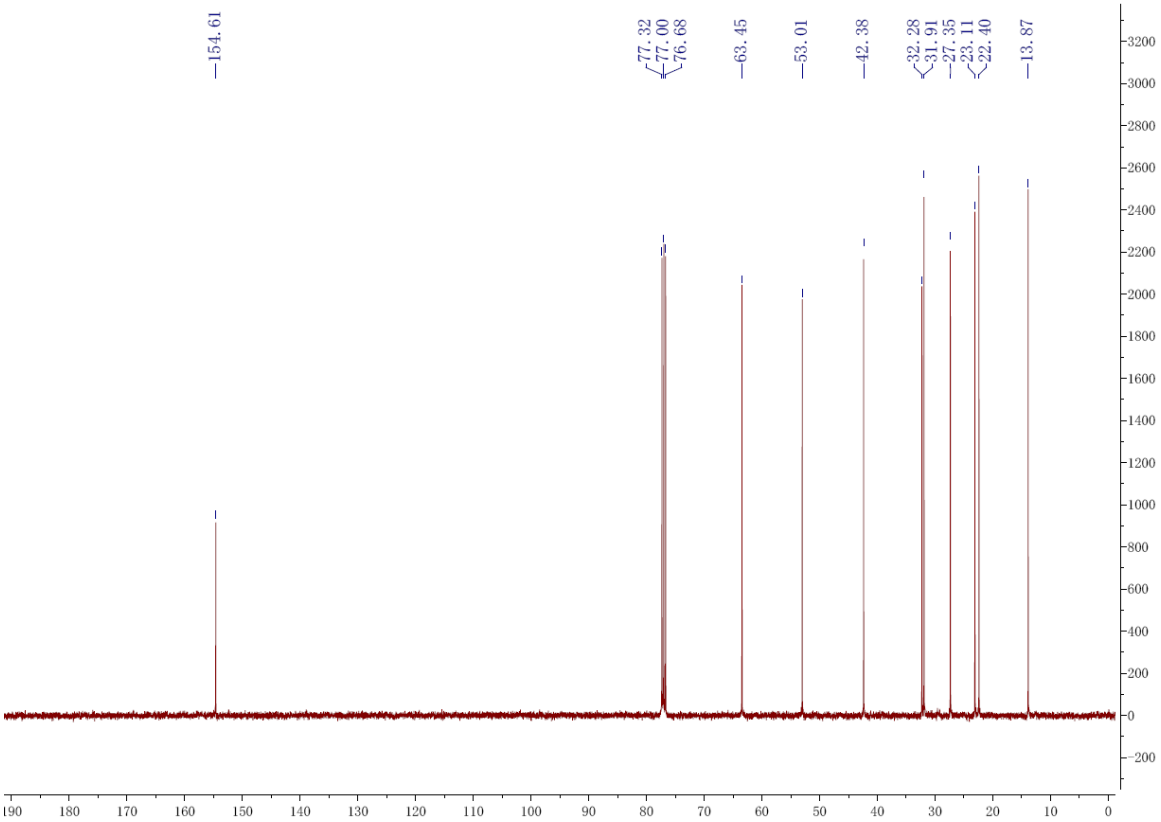
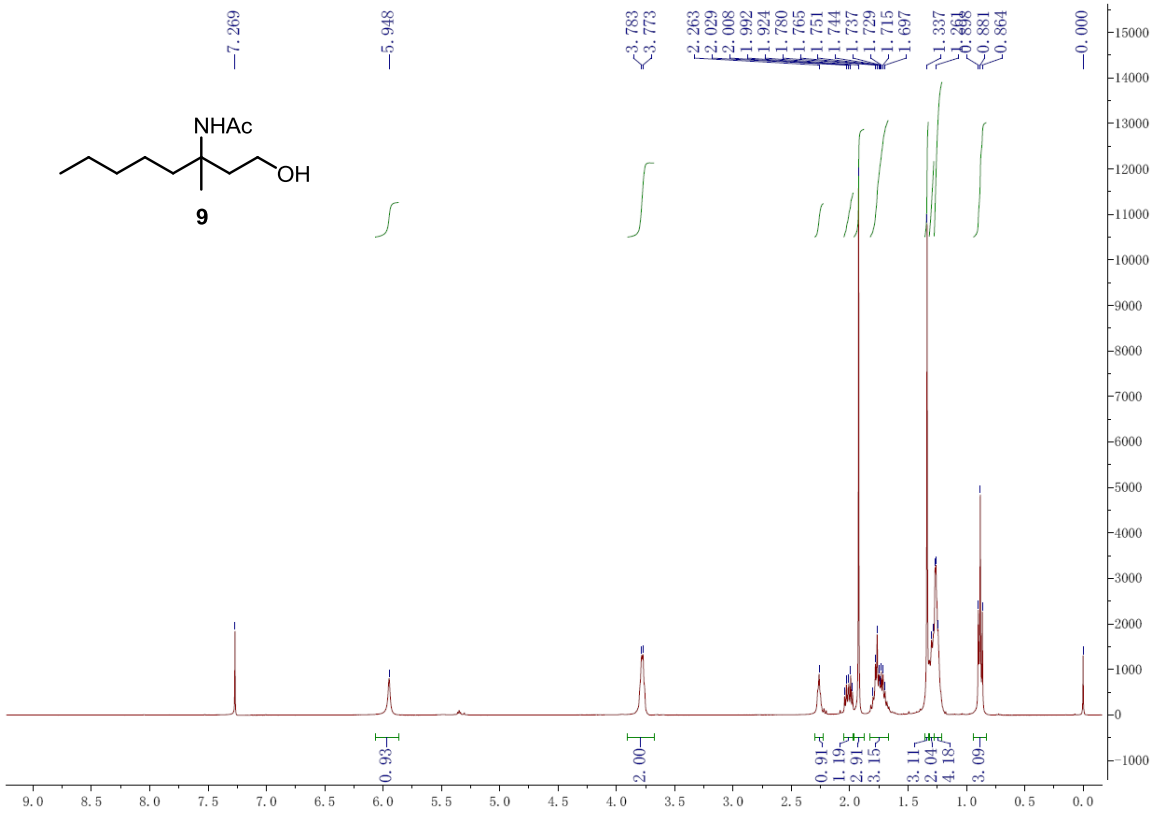
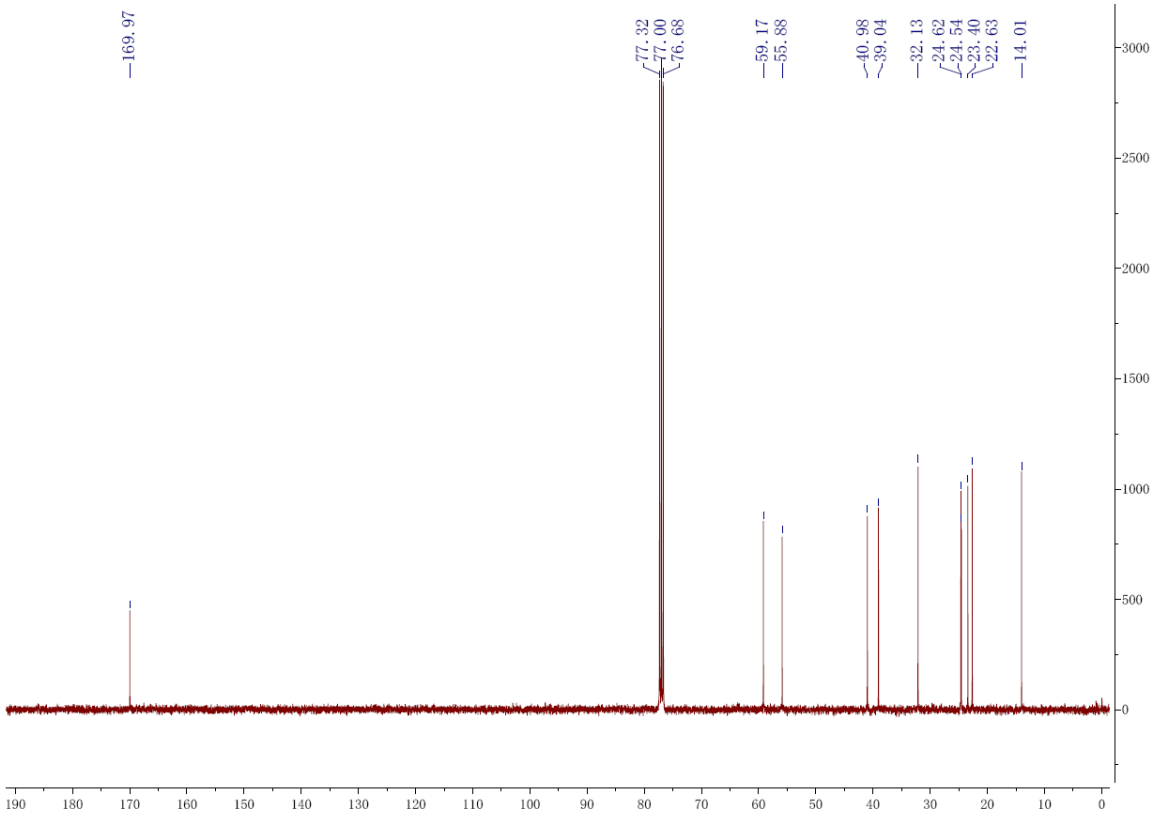
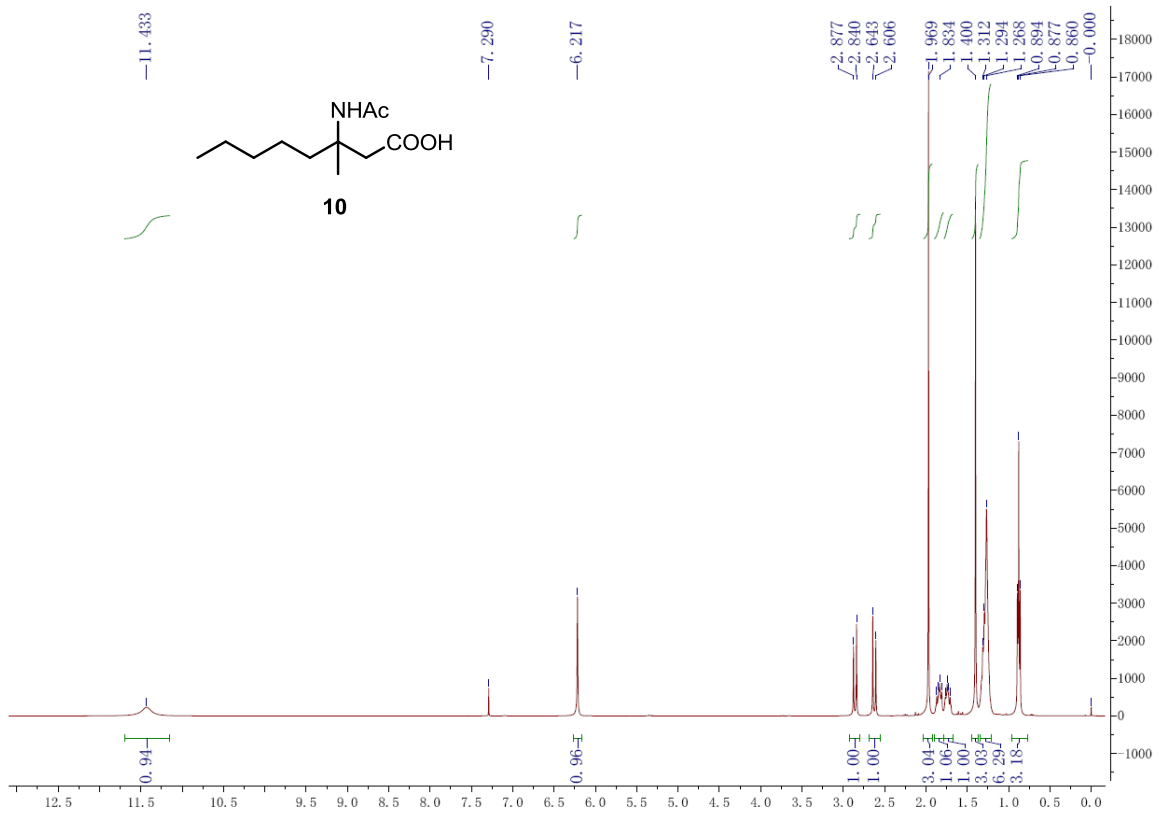
169.68
159.12
137.59
134.75
134.34
127.30
125.11
120.90
77.32
77.00
76.68
61.11
55.06
39.00
38.20
36.31
28.36
24.39
24.28
21.01
20.61


7.299
6.558
4.292
4.280
4.274
4.264
1.893
1.874
1.860
1.856
1.753
1.741
1.728
1.705
1.554
1.536
1.521
1.509
1.486
1.342
1.326
1.307
1.294
1.287
0.903
0.887
0.869
0.000
HN
O
O
8
0.95
2.00
1.00
1.01
2.08
5.99
3.17
3.03


154.61
77.32
77.00
76.68
63.45
53.01
42.38
32.28
31.91
27.35
23.11
22.40
13.87


NHAc
OH
9
7.269
5.948
3.783
3.773
2.263
2.029
2.008
1.992
1.924
1.780
1.765
1.751
1.744
1.737
1.729
1.715
1.697
1.337
0.898
0.881
0.864
0.000
0.93
2.00
0.91
1.19
2.91
3.15
3.11
2.04
4.18
3.09


169.97
77.32
77.00
76.68
59.17
55.88
40.98
39.04
32.13
24.62
24.54
23.40
22.63
14.01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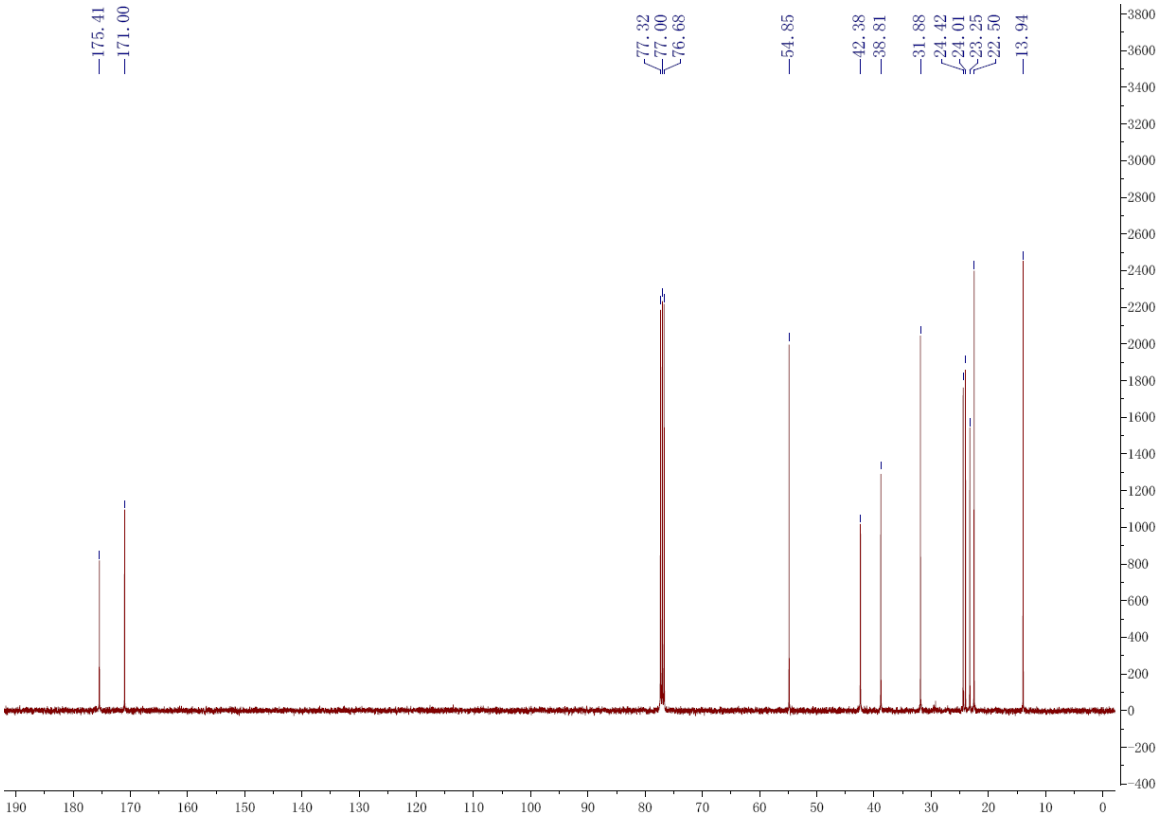
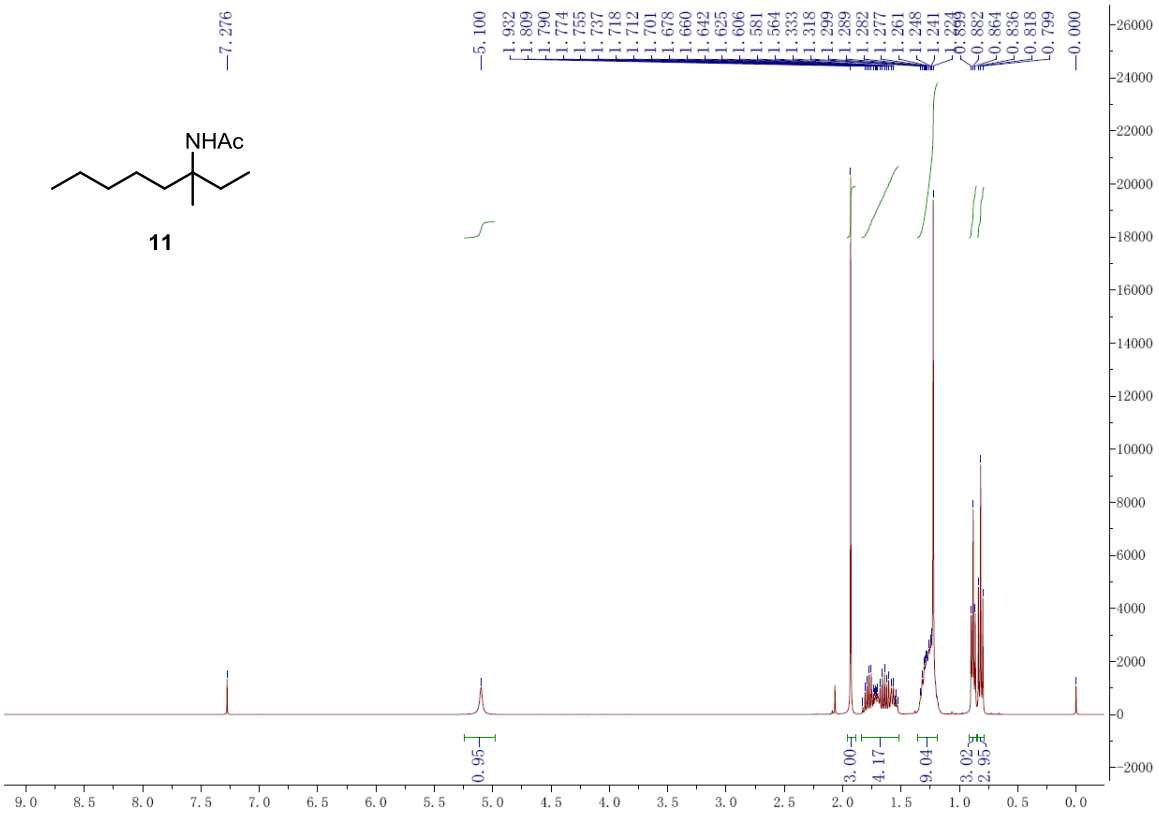
7.290
6.217
2.877
2.840
2.643
2.606
1.969
1.834
1.400
1.312
1.294
1.268
0.894
0.877
0.860
0.000
NHAc
COOH
10
0.94
0.96
1.00
1.00
3.04
1.06
1.00
3.03
6.29
3.18


175.41
171.00
77.32
77.00
76.68
54.85
42.38
38.81
31.88
24.42
24.01
23.25
22.50
13.94


NHAc
11
7.276
5.100
1.932
1.809
1.790
1.774
1.755
1.737
1.718
1.712
1.701
1.678
1.660
1.642
1.625
1.606
1.581
1.564
1.333
1.318
1.299
1.289
1.282
1.277
1.261
1.248
1.241
1.224
0.899
0.882
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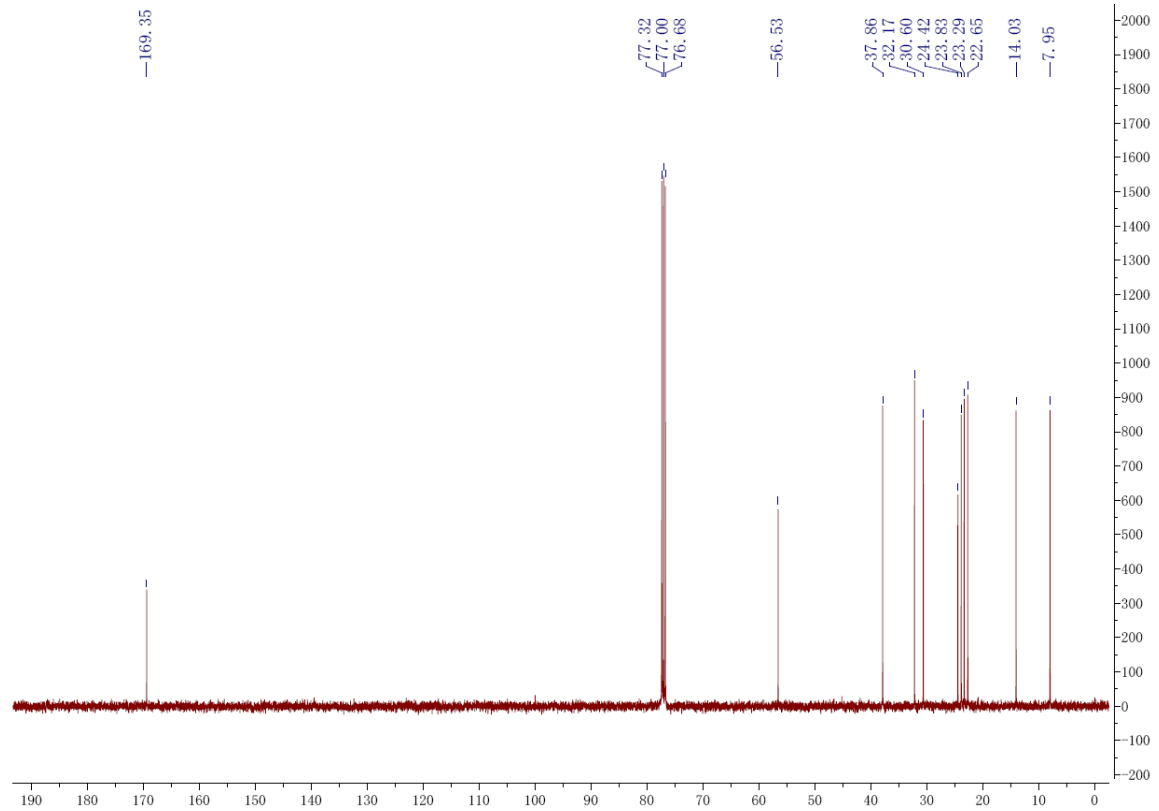
0.836
0.818
0.799
0.000
0.95
3.00
4.17
9.04
3.02
2.95


169.35
77.32
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37.86
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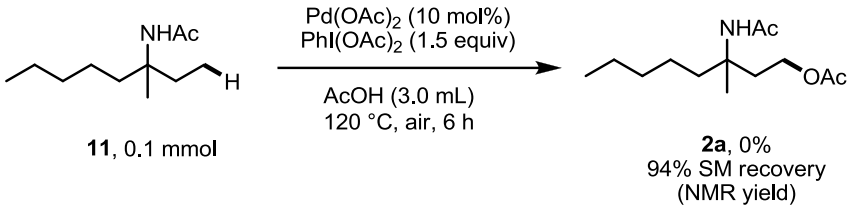
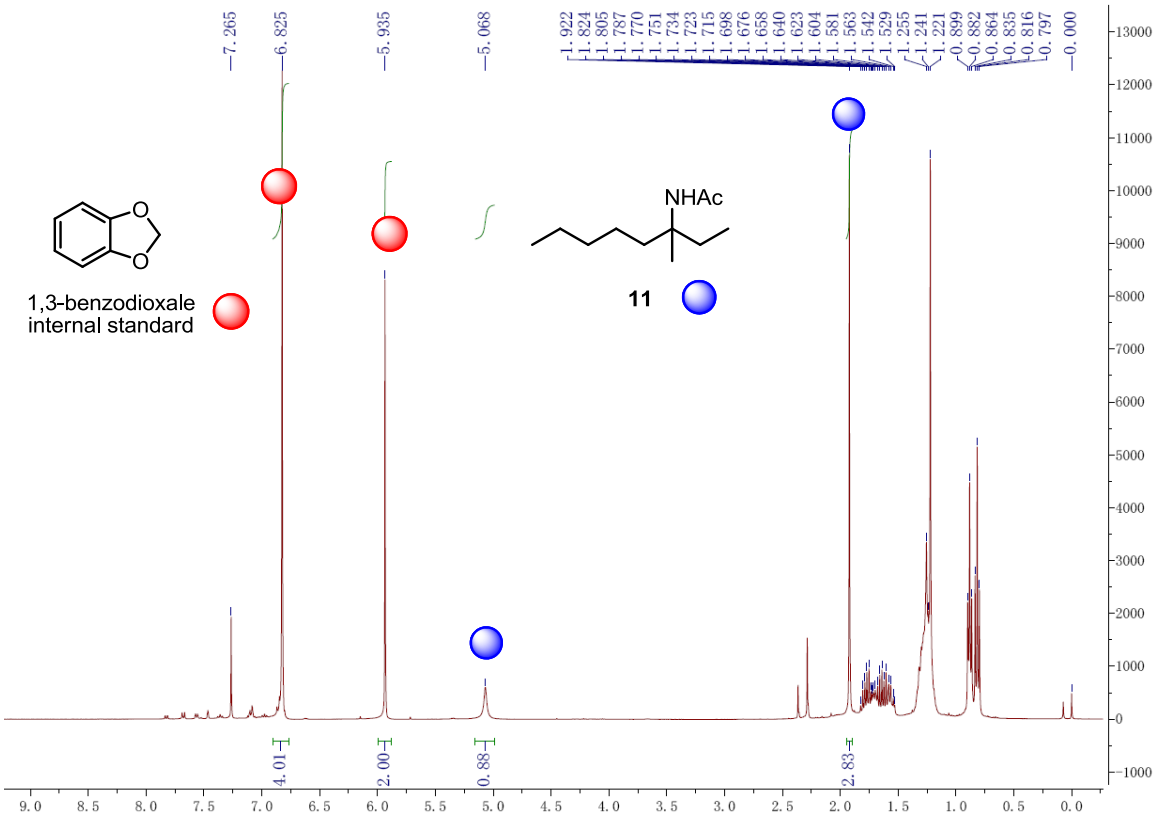
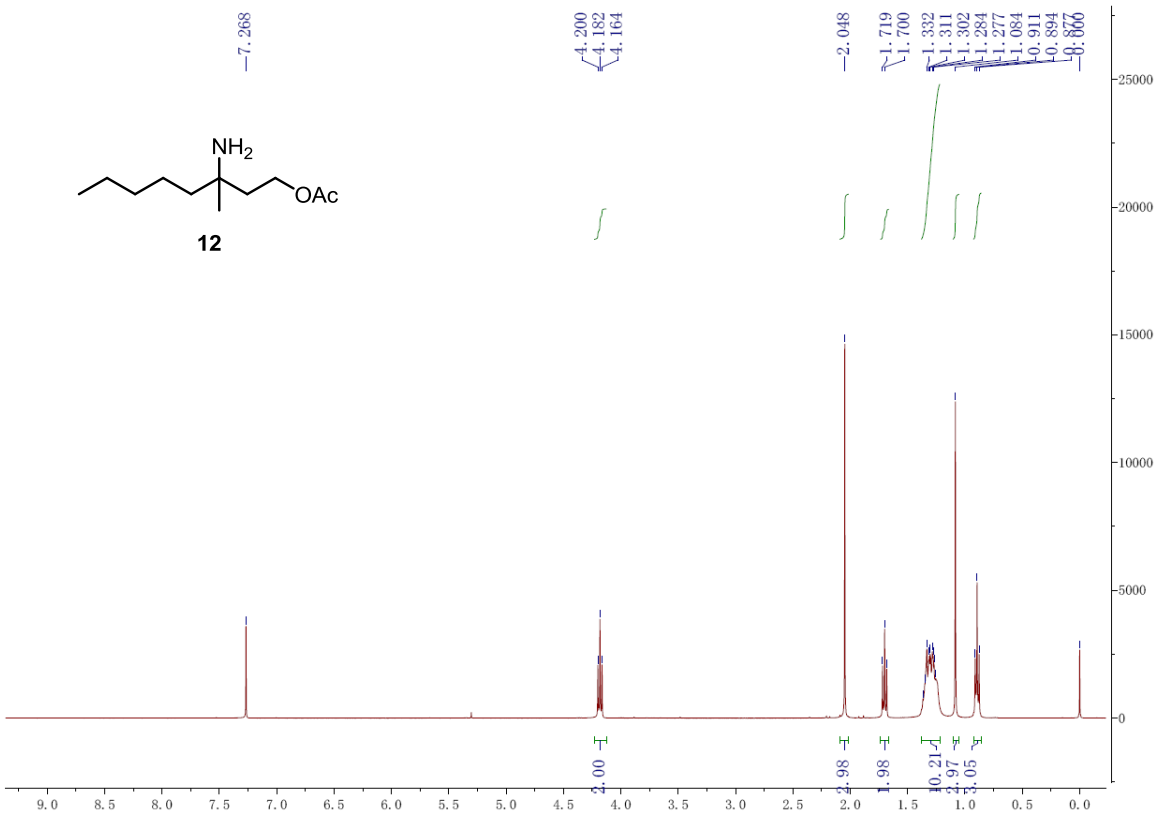
30.60
24.42
23.83
23.29
22.65
14.03
7.95



11, 0.1 mmol

2a, 0%
94% SM recovery
(NMR yield)




7.268
4.200
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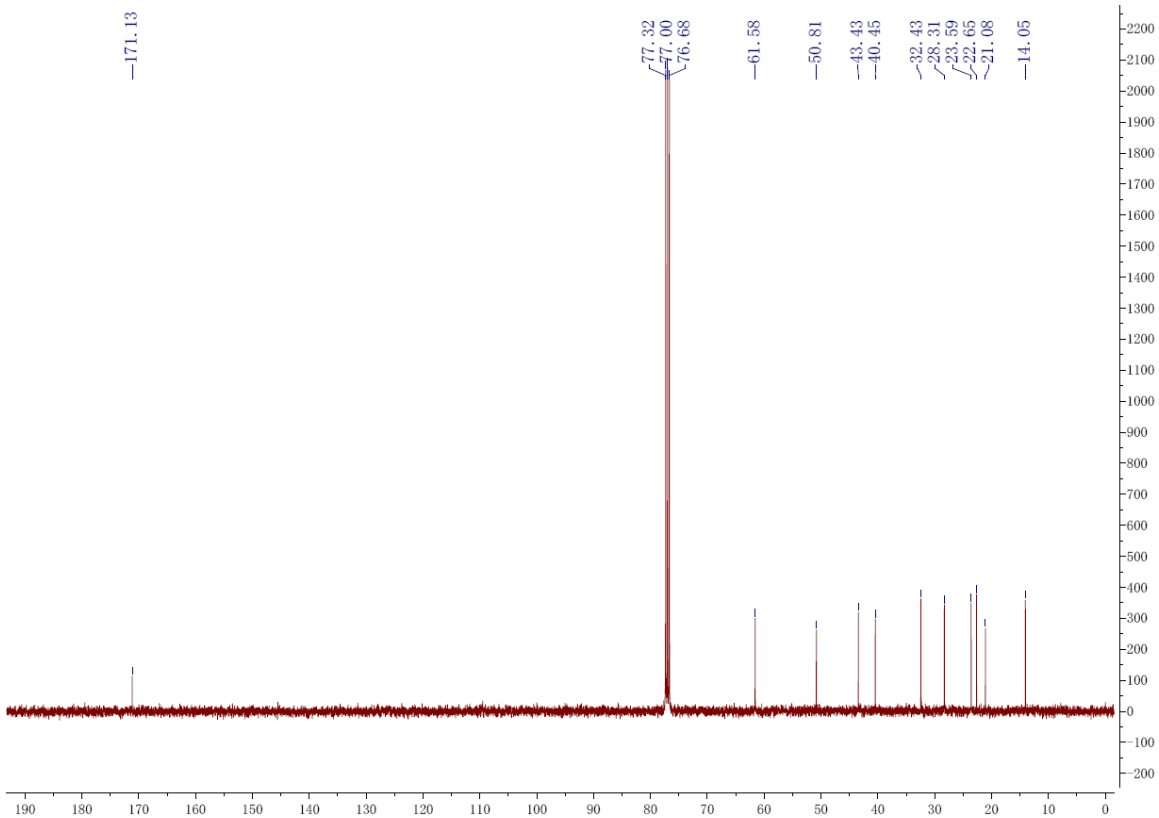
4.164
2.048
1.719
1.700
1.332
1.311
1.302
1.284
1.277
1.084
0.911
0.894
0.877
0.860
NH2
OAc
12
2.00
2.98
1.98
10.21
2.97
3.05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40.45
32.43
28.31
23.59
22.65
21.08
14.05