Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

A CO_2-Mediated Base Catalysis Approach for Hydration of Triple Bonds in Ionic Liquids

Minhao Tang,[a,b] Fengtao Zhang,[a,b] Yanfei Zhao,*[a,b] Yuepeng Wang,[a,b] Zhengang Ke,[a] Ruipeng Li,[a,b] Wei Zeng,[a,b] Buxing Han,[a,b] and Zhimin Liu*[a,b]

Abstract: Herein, we report a CO_2-mediated base catalysis approach for the activation of triple bonds in ionic liquids (ILs) with anions that can chemically capture CO_2 (*e.g.*, azolate, phenolate, acetate), which can achieve hydration of triple bonds to carbonyl chemicals. It is discovered that the anion-complexed CO_2 could abstract one proton from proton resources (*e.g.*, IL cation) and transfer it to the C≡N or C≡C bonds *via* a six-membered ring transition state, thus realizing their hydration. In particular, tetrabutylphosphonium 2-hydroxypyridine shows high efficiency for hydration of nitriles and C≡C bond-containing compounds under a CO_2 atmosphere, affording a series of carbonyl compounds in excellent yields. This catalytic protocol is simple, green, and highly efficient and opens a new way to access carbonyl compounds *via* triple bond hydration under mild and metal-free conditions.

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1. Experimental Section

1.1 Materials

CO_2 was supplied by Beijing Analytical Instrument Factory with a purity of 99.999%. Various nitrile substrates and deuterated solvents (D_2O, DMSO-d_6) were purchased from Beijing Innochem Science & Technology Co., Ltd. Tetrabutylphosphonium hydroxide ([P_{4444}][OH], 40% wt.% aqueous solution), tetrabutylammonium hydroxide ([N_{4444}][OH], 40 wt.% aqueous solution), tetraethylammonium hydroxide ([N_{2222}][OH], 25 wt.% aqueous solution), tetramethylammonium hydroxide ([N_{1111}][OH], 25 wt.% aqueous solution), [N_{2222}][Cl], imidazole, 2-methylimidazole, 2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine were obtained commercially from Tokyo chemical industry Co., Ltd. and J&K Scientific Ltd, respectively. The ILs [BMIm][NTf_2], [BMIm][PF_6], [BMIm][Ac] were provided by Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences (CAS). All chemicals were of analytical grade and used as received.

The ILs [P_{4444}][Im], [P_{4444}][2-MIm], [P_{4444}][2-OP], [P_{4444}][3-OP], [P_{4444}][4-OP], [N_{4444}][2-OP], [N_{2222}][2-OP], [N_{1111}][2-OP] were synthesized by neutralizing corresponding bases (including [P_{4444}][OH], [N_{4444}][OH], [N_{2222}][OH], [N_{1111}][OH]) with proton donors (including imidazole, 2-methylimidazole, 2-hydroxypyridine, 3-hydroxypyridine and 4-hydroxypyridine), respectively, based on the reported procedures [1]

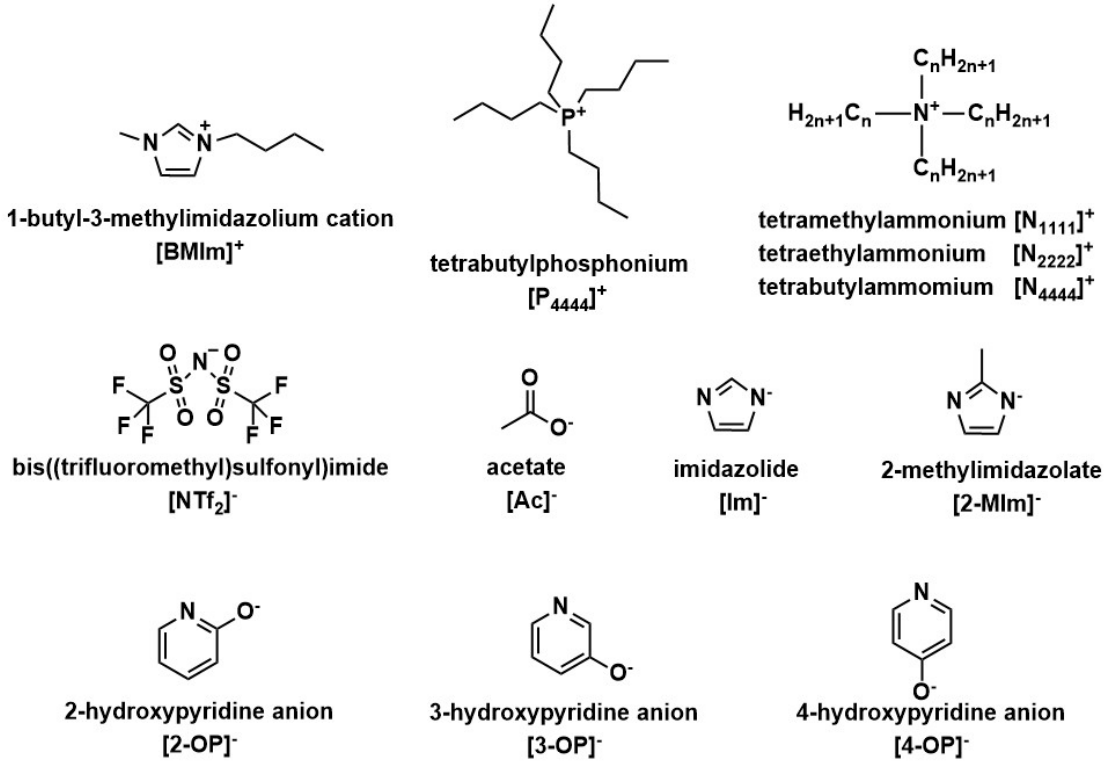


Figure S1. The cation and anion structures of ILs used in this work.

1.2 Instrumentation

NMR spectra were recorded on Bruker Avance III 400 HD or 500 WB spectrometer equipped with 5 mm pulsed-field-gradient probes, and on a Bruker Neo 700 NMR spectrometer equipped with a cryo BBO probe. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). To eliminate the effects of solvents, wilmad coaxial insert NMR tube was used for ^{1}H NMR, ^{13}C NMR, ^{15}N NMR and ^{31}P NMR analysis at 70 °C or 90 °C. DMSO-d_6 was added into the inner tube, and the sample was added into the outer tube.

GC-MS analysis was performed using gas chromatography-mass spectrometry (GC-MS, SHIMADZU-QP2010) with a packed column DB-5 MS.

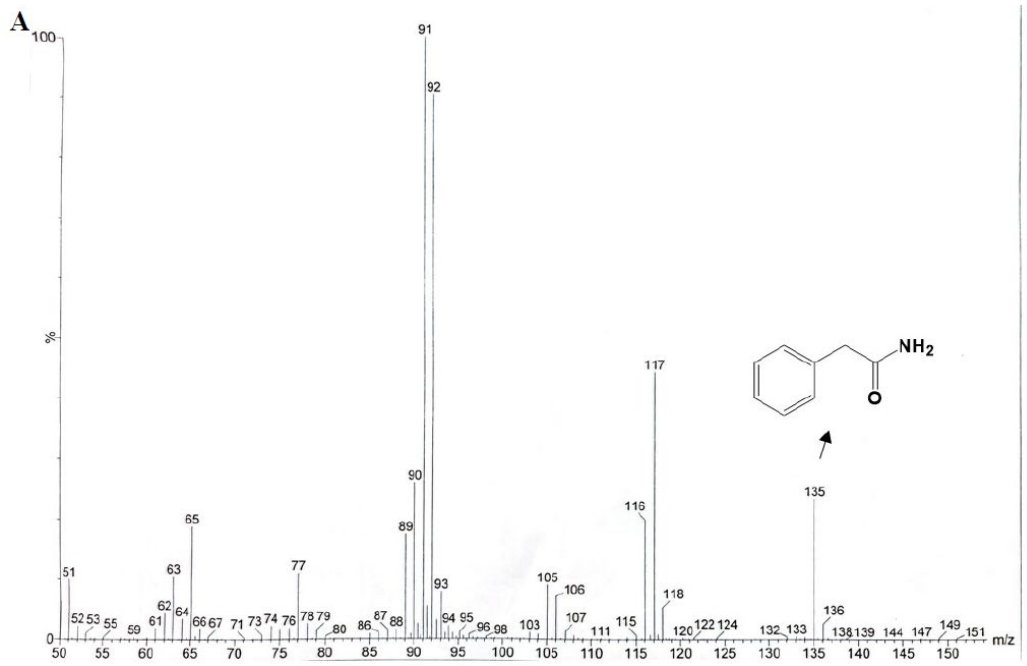
1.3 General procedure for hydration

All reactions were conducted in a sealed tube (2 mL of inner volume) equipped with a magnetic stirrer. In a typical experiment, phenylacetonitrile (1 mmol, 0.1172 g), [P_{4444}][2-OP] (1 mmol, 0.3536 g) and H_2O (1 mmol, 0.0180 g) were sequentially added into the reactor and sealed under CO_2 atmosphere. Subsequently, the reactor was moved to an oil-bath of 100°C and stirred for 12 h. After reaction, the reactor was cooled down in ice water. The quantitative analysis of the reaction solution was conducted by ^{1}H NMR spectroscopy using mesitylene as an internal standard. To isolate the product, water was added to the reaction solution, resulting in precipitation of the target product. The products were isolated by recrystallization from ethyl ether/water, and their isolated yields were calculated based on the masses determined by mass balance.

1.4 Computational methods

All DFT calculations in this study were performed using Gaussian 16 package.[2] The M06-2X functional with 6-31+g** basis set was employed, coupled with Grimme's D3 dispersion correction to perform geometry optimization.[3] All calculated structures were verified with no imaginary frequency (IF). The transition state (TS) structures were verified with intrinsic reaction coordinate (IRC) path. Besides, an ultrafine integration grid (99,590) was used for numerical integrations. Thermal corrections were carried out with harmonic frequency analysis using Shermo code on optimized structures under T=298.15 K and 1 atm pressure.[4] The binding energies were evaluated at M06-2X functional with 6-311++g** basis set according to the previous optimized structures. The VMD molecular visualizing program was employed to draw 3D molecular structures and Multiwfn program was employed to perform analysis of electrostatic potential (ESP) energy and draw pictures.[5]

2. GC-MS and ^{1}H NMR analysis of some products



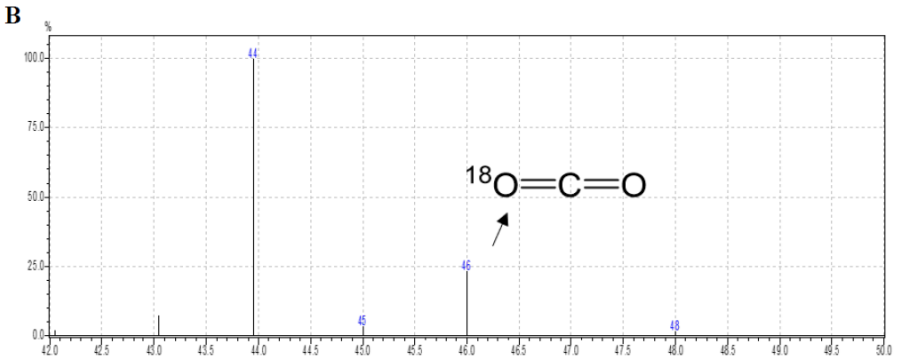


Figure S2. GC-MS spectra of the product from phenylacetonitrile hydration in the presence of CO_2. (A) Phenylacetamide (2a). (B) CO_2. Reaction conditions: phenylacetonitrile (**1a**, 1 mmol), [P_{4444}][2-OP] (1 mmol), $H_2{}^{18}O$ (1 mmol), 100°C, 12 h, CO_2 atmosphere.

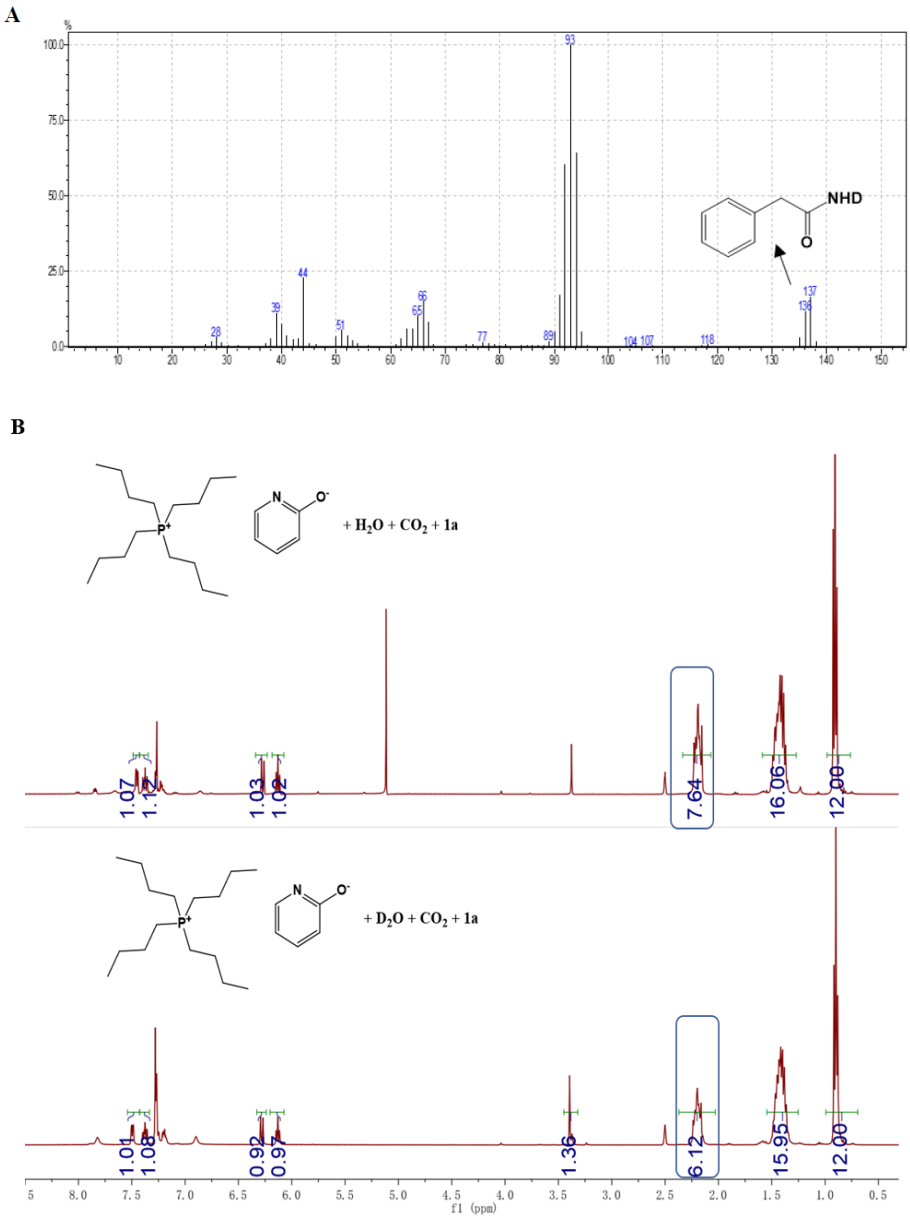
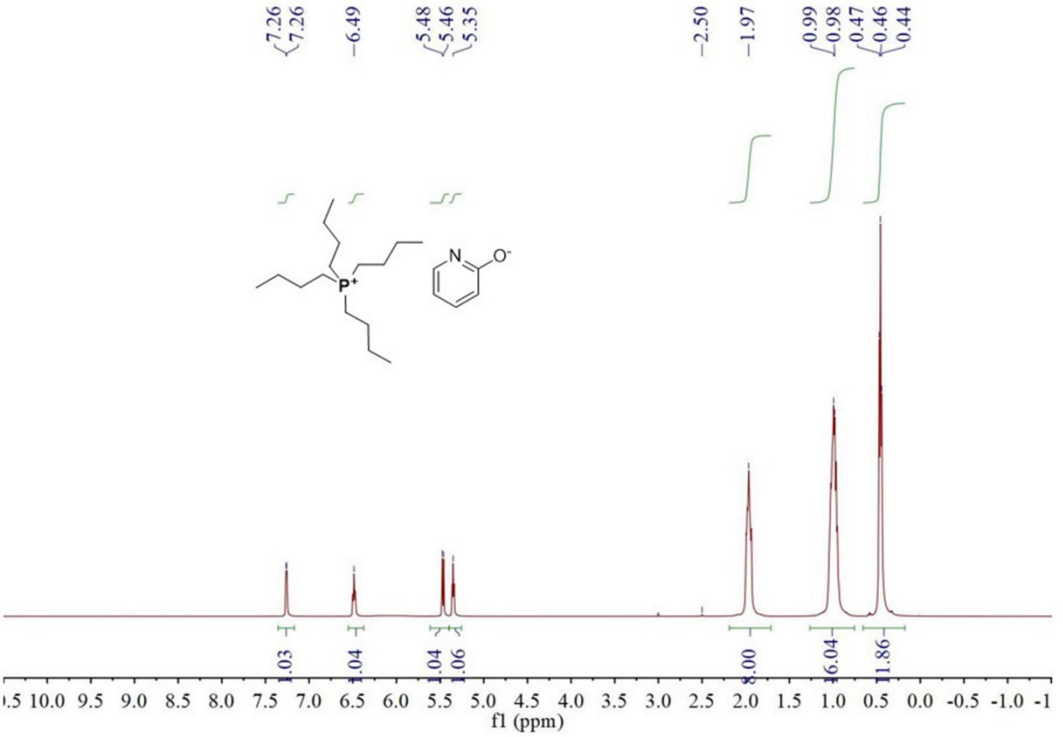
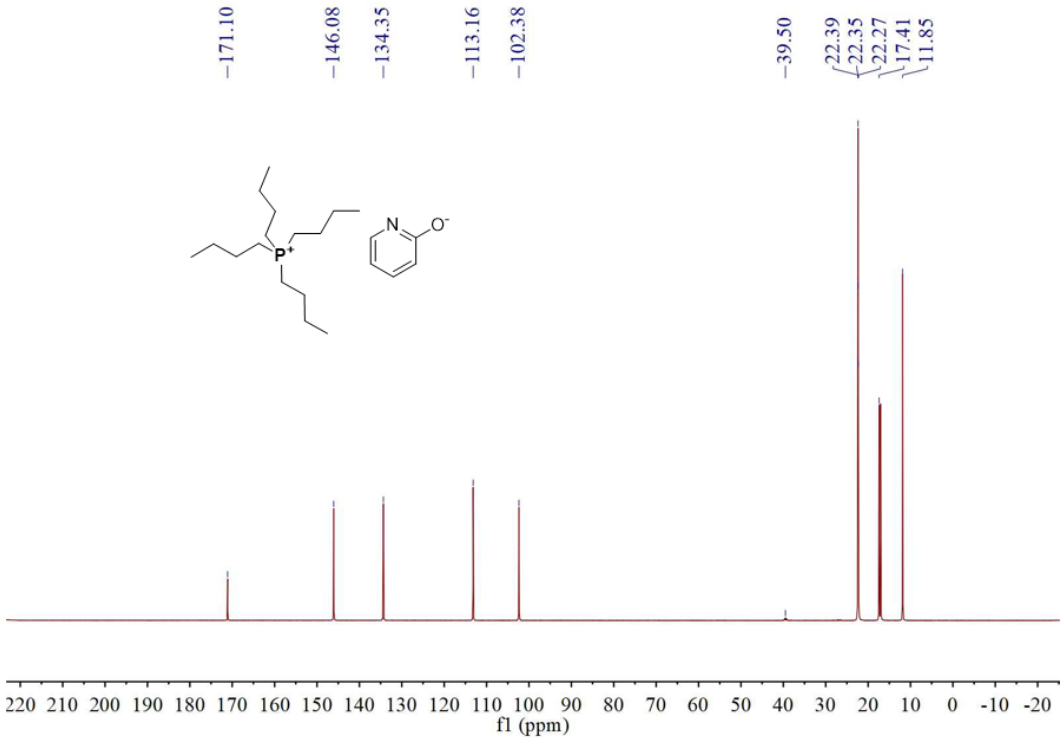
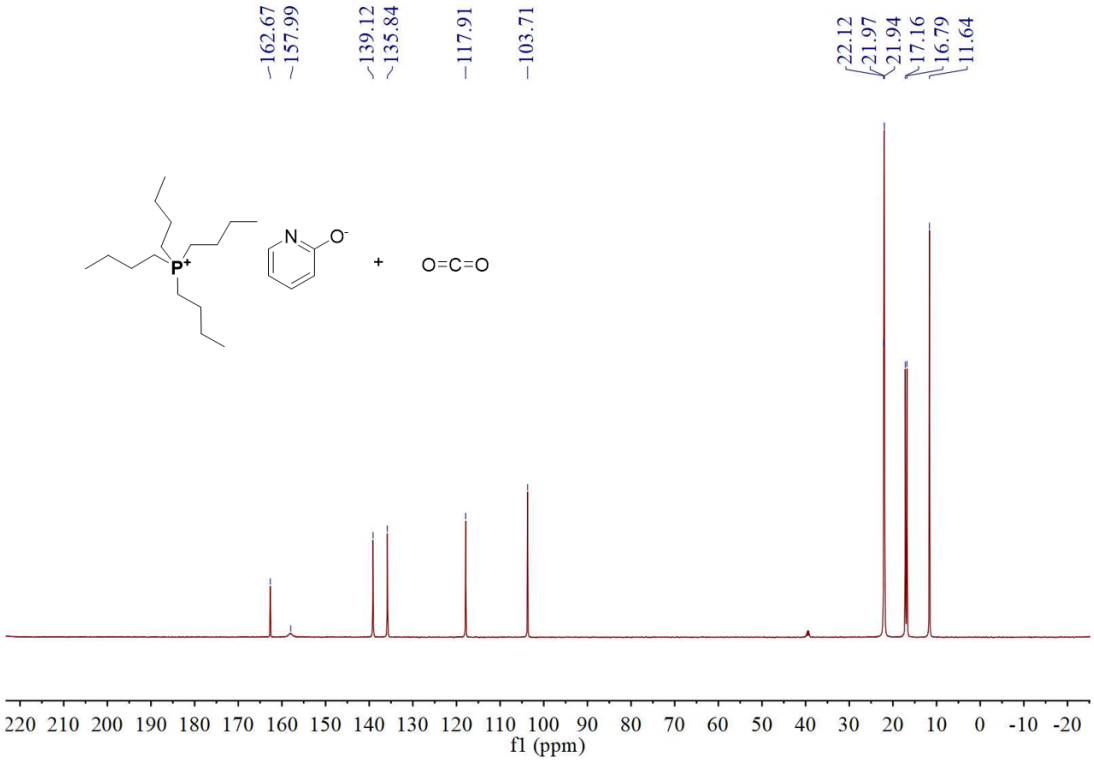


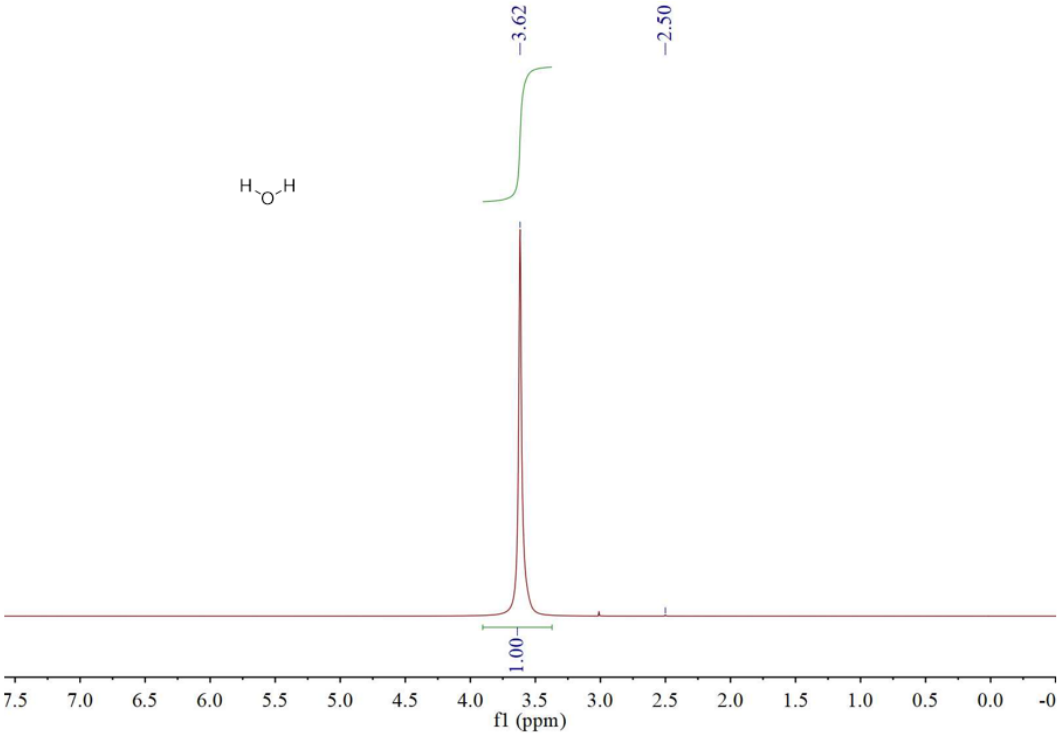
Figure S3. Spectra of the **1a** hydration with D_2O. (A) GC-MS spectrum for **2a**. (B) ^1H NMR spectra after the reaction. Reaction conditions: **1a** (1 mmol), [P_{4444}][2-OP] (1 mmol), H_2O/D_2O (1 mmol), 100 °C, 12 h, CO_2 atmosphere.

3. *In-situ* NMR analysis at high temperature






162.67
157.99
139.12
135.84
117.91
103.71
22.12
21.97
21.94
17.16
16.79
11.64
N
O-
P+
+
O=C=O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


3.62
2.50
H
O
H
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

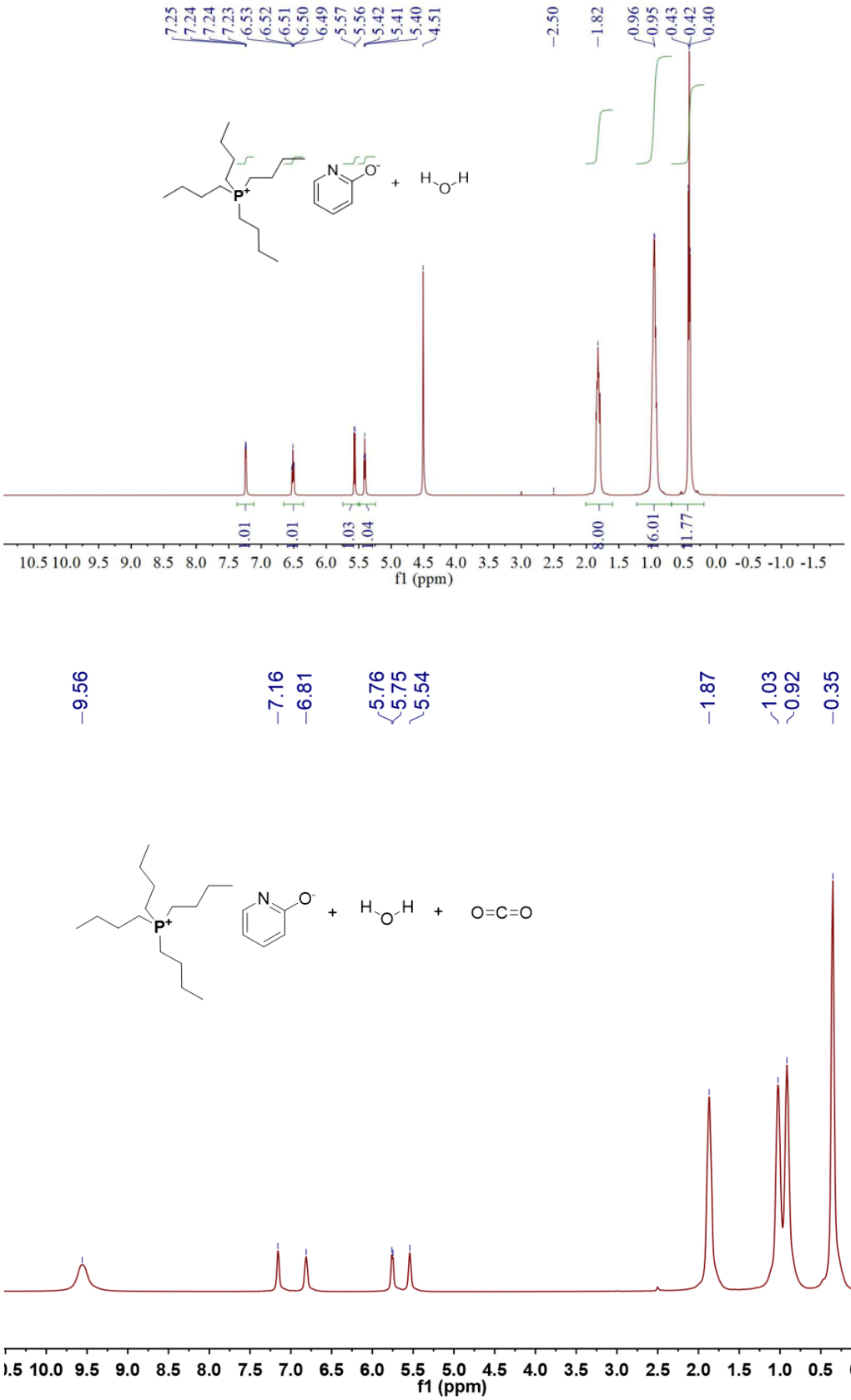


Figure S4. ^{1}H and ^{13}C NMR spectra of $[P_{4444}][2\text{-OP}]$, $[P_{4444}][2\text{-OP}]+CO_2$, H_2O, $[P_{4444}][2\text{-OP}]+H_2O$ and $[P_{4444}][2\text{-OP}]+CO_2+H_2O$ at 90 °C.

Table S1. NMR chemical shifts of C1, C2 and N of 1a in the mixture of **1a** and [P_{4444}][2-OP] with different molar ratios of **1a** to IL at 70°C.

Molar ration of 1a to [P_{4444}][2-OP]	C1 Chemical shift (ppm)	C2 Chemical shift (ppm)	N Chemical shift (ppm)
Neat	117.10	21.67	250.12
10:1	117.26	21.60	249.66
5:1	117.36	21.59	249.27
2:1	117.49	21.56	248.89
1:1	117.59	21.55	248.73

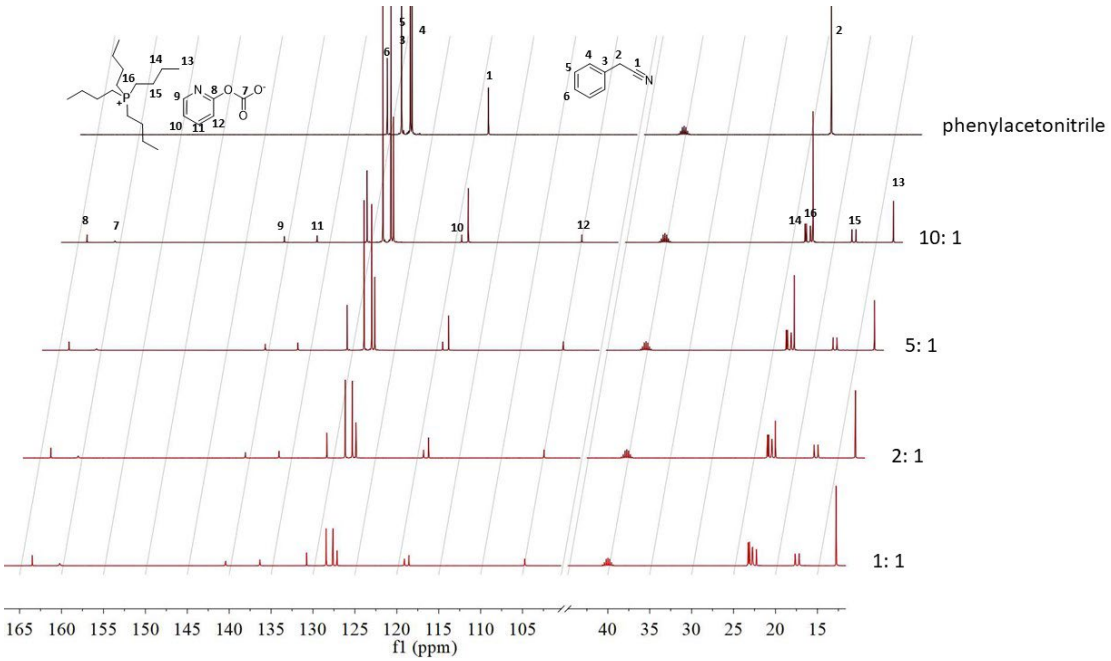


Figure S5. ^{13}C NMR spectra of **1a** and the mixtures of **1a**+[P_{4444}][2-OP] with different **1a**: IL ratios under CO_2 atmosphere at 70 °C.

Note: The ^{13}C NMR spectra of the mixtures of IL-CO_2+**1a** (with different **1a**: IL ratios) were recorded at 70°C. The peaks assigning to C1 gradually shifted from 117.10 ppm for pure **1a** to 117.59 ppm for the mixture with the **1a**: IL=1: 1, meaning that the electron density of C1 decreases.

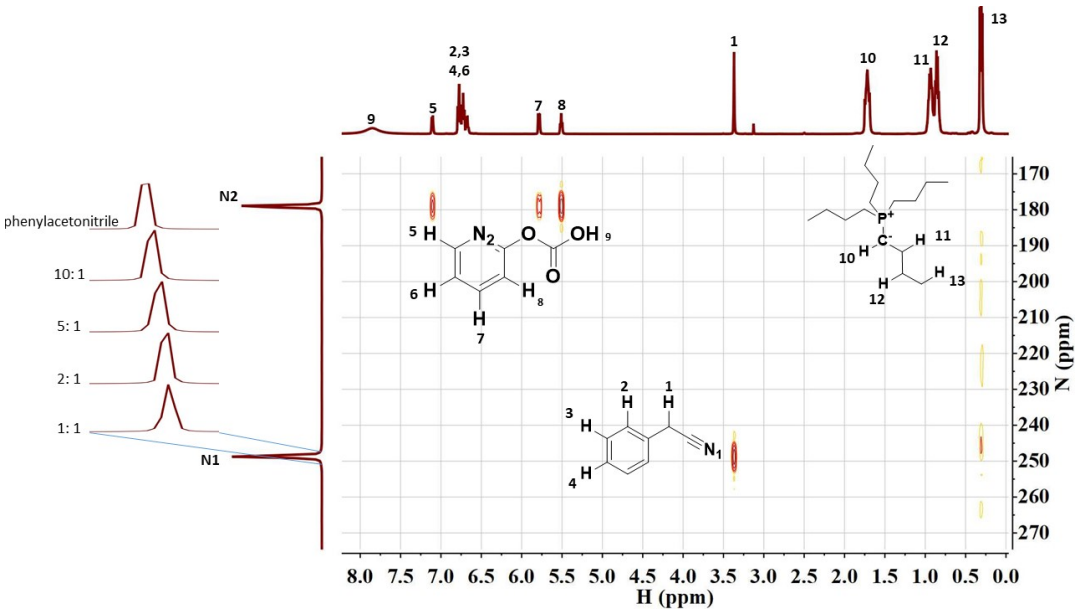


Figure S6. ^{1}H-^{15}N HMBC spectra of **1a** and the mixtures of **1a**+[P_{4444}][2-OP] with different ratios under CO_2 atmosphere at 70 °C.

Note: The ^{1}H-^{15}N HMBC spectra of the mixtures of IL-CO_2 +**1a** (with different **1a**: IL ratios) were recorded at 70°C. The peaks assigning to N1 gradually shifted from 250.12 ppm for pure **1a** to 248.73 ppm for the mixture with the **1a**: IL=1: 1, meaning that the electron density of N1 increases.

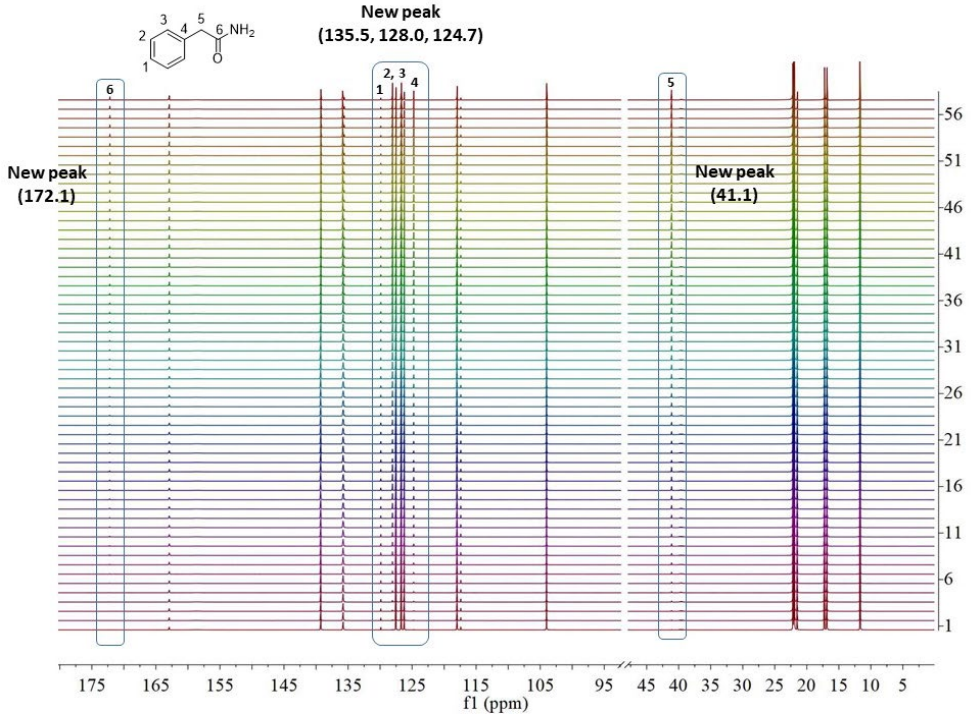


Figure S7. *In-situ* ^{13}C NMR spectra of the reaction solutions of **1a** hydration over [P_{4444}][2-OP] at 90 °C.

Note: Each *in-situ* ^{13}C NMR spectrum was recorded every 13.5 min from 0 to 12 h. The new signals with chemical shifts at δ=41.1, 124.7, 128.0, 135.5, 172.1 ppm, respectively, refer to C atoms of the final product. These peaks appeared within the first 13.5 min, which indicates that the reaction took place fast. The absence of extra peaks indicates that no by-product formed and the transformation of intermediates into product occurred quickly.

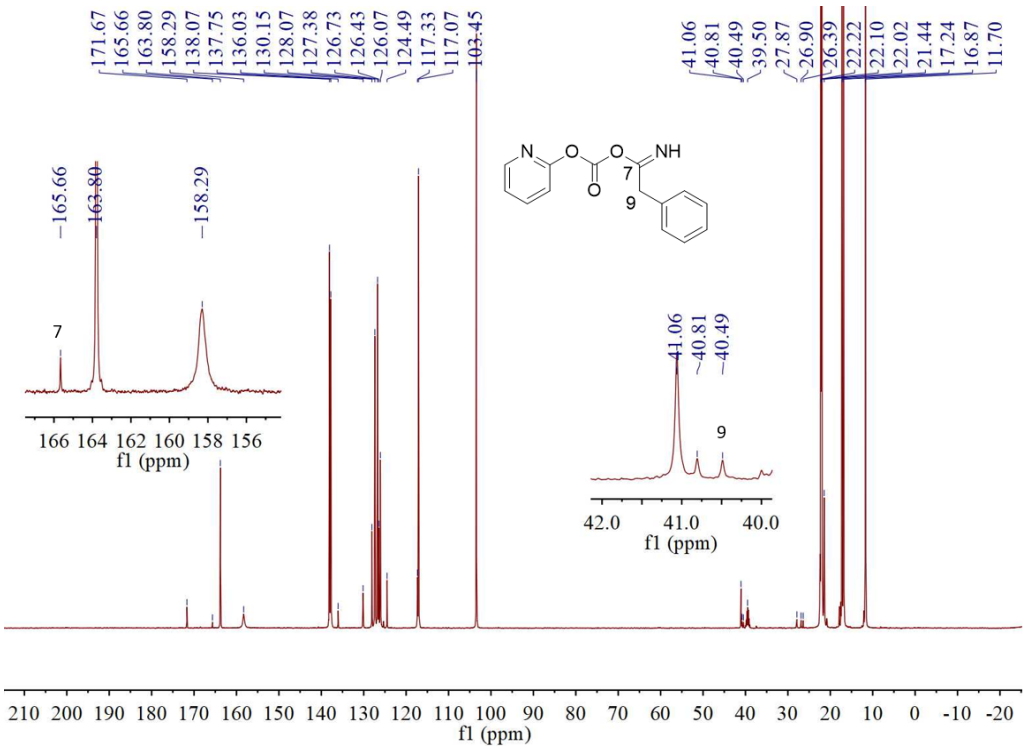


Figure S8. *In-situ* ^{13}C NMR spectrum of the reaction system of 1a hydration over $[P_{4444}][2\text{-OP}]$ performed at 90 °C for 4 h.

Chemical shifts with low intensity at δ = 165.66, 158.29 and 40.49 ppm were observed, which are ascribed to the intermediate as shown in the figure.

4. ESP map of IL-CO_2

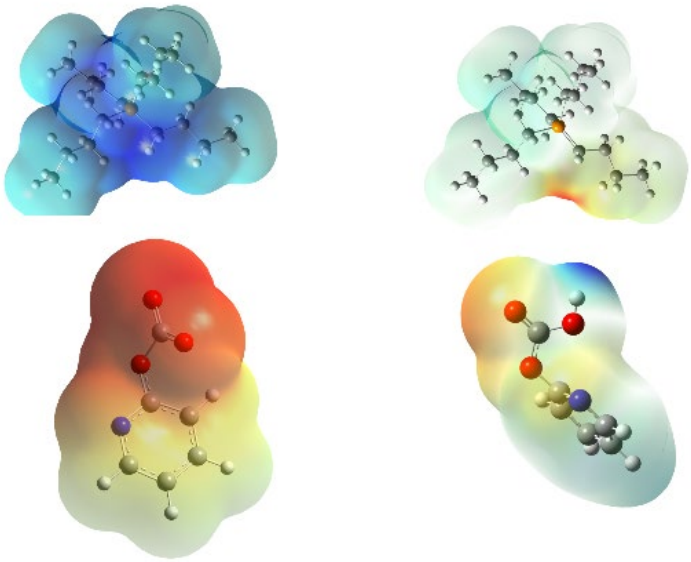


Figure S9. ESP map before and after the formation of 2-pyridyl carbonic acid intermediate.

5. NMR analysis over other ILs

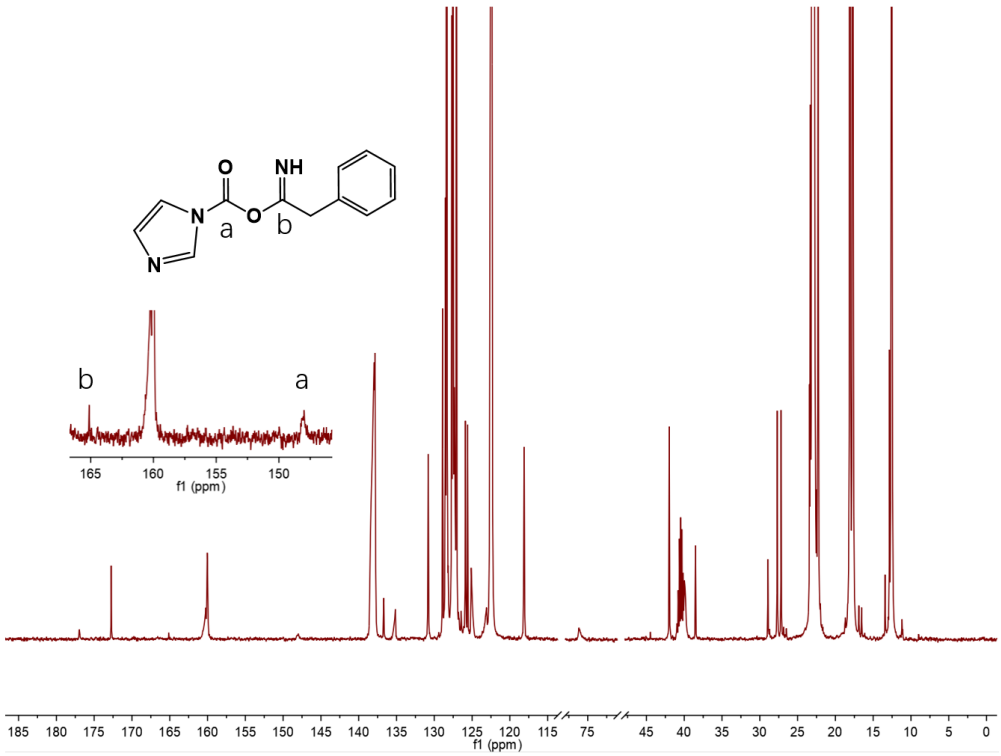
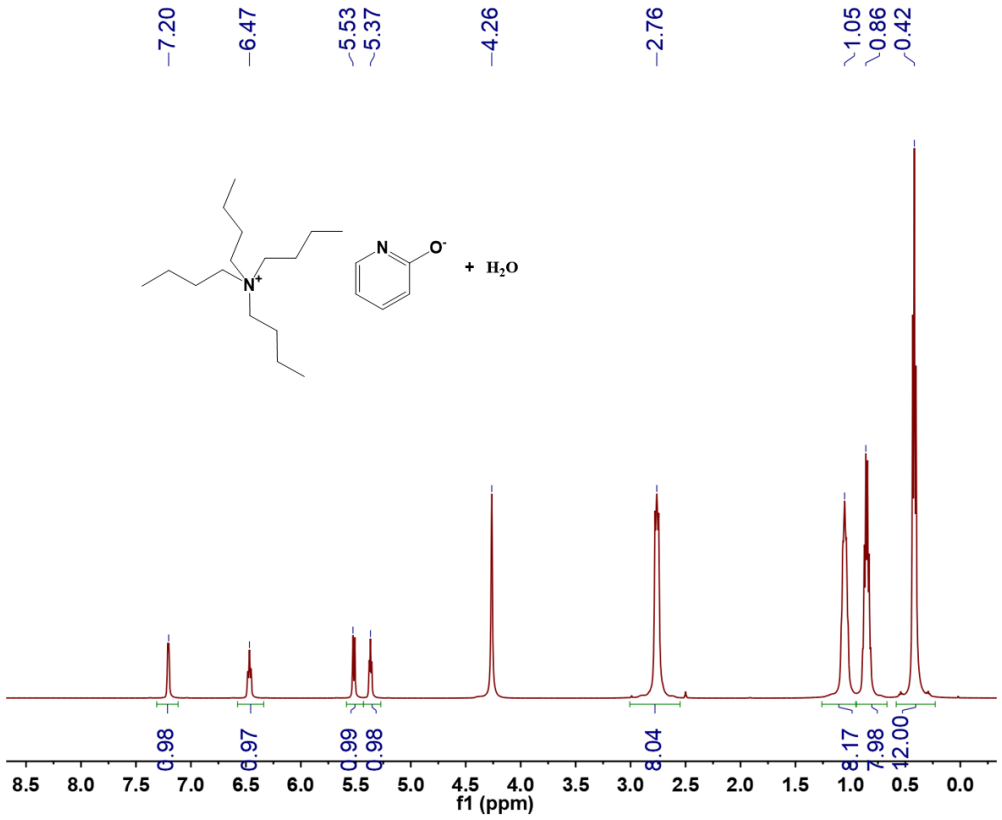
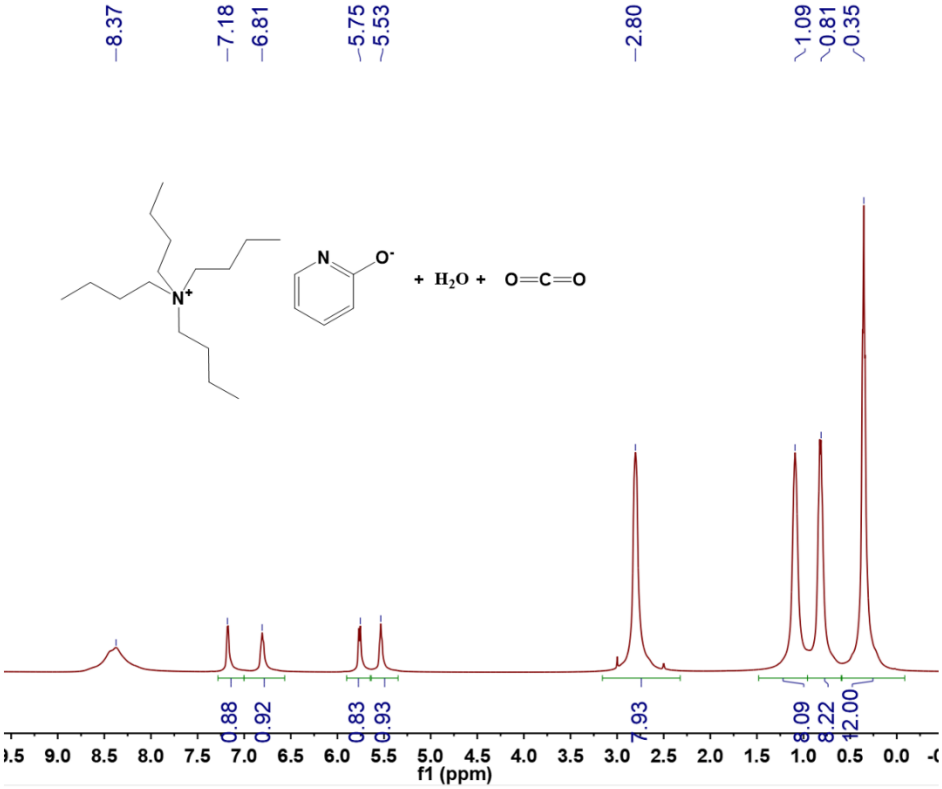
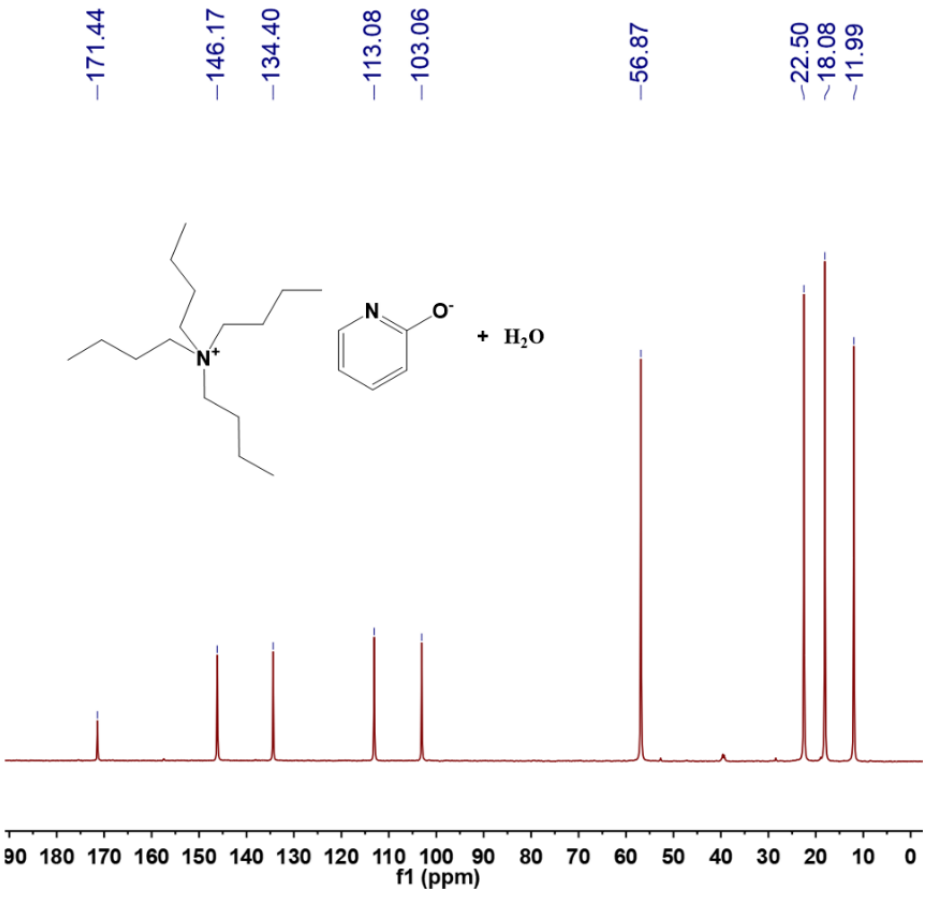


Figure S10. *In-situ* ^{13}C NMR spectrum for the reaction solution of **1a** hydration over $[P_{4444}][Im]$ performed at 90 °C for 4 h.

Note: Chemical shifts with low intensity at δ = 164.15, 147.01 ppm were observed, which are ascribed to the intermediate as shown in the figure.




8.37
7.18
6.81
5.75
5.53
2.80
1.09
0.81
0.35
+ H2O + O=C=O
0.88
0.92
0.83
0.93
7.93
8.09
8.22
12.00
f1 (ppm)


171.44
146.17
134.40
113.08
103.06
56.87
22.50
18.08
11.99
+ H2O
f1 (ppm)

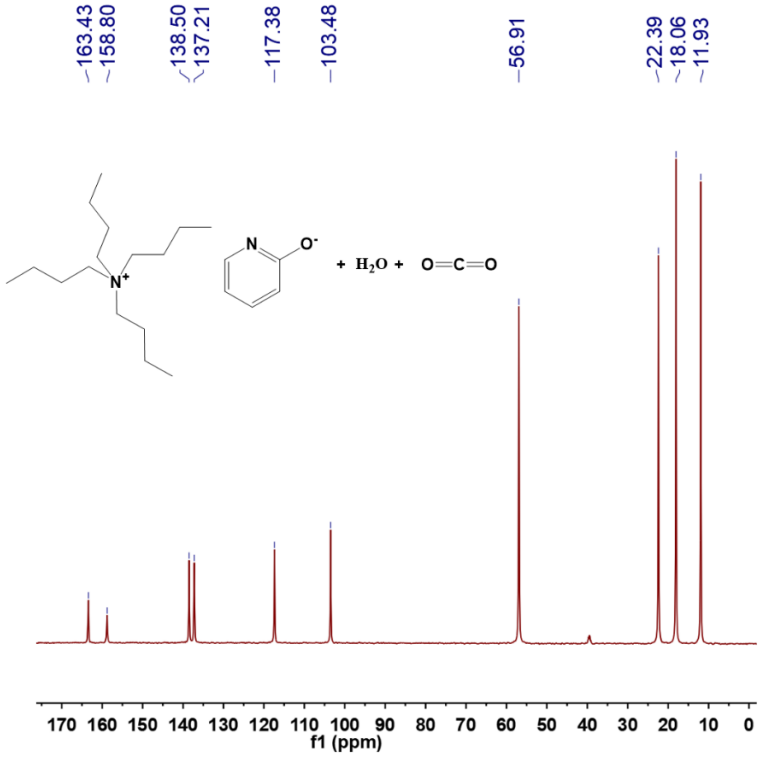


Figure S11. ^{1}H and ^{13}C NMR spectra of $[N_{4444}][2\text{-OP}]+ H_2O$ and $[N_{4444}][2\text{-OP}]+ H_2O+ CO_2$ at 90 °C.

Note: A wide peak at 8.37 ppm was observed in the ^{1}H NMR spectrum and a new peak appeared at 158.80 ppm in the ^{13}C NMR spectrum of the $[N_{4444}][2\text{-OP}]\text{-}CO_2$ system at 90 °C, which indicate the formation of anion-based carbonic acid, meanwhile both ^{1}H and ^{13}C NMR spectra of cation have little changed. These results demonstrate that the anion-complexed CO_2 (i.e., $[2\text{-OP-COO}]^-$) may attract H from H_2O to form anion-based carbonic acid.

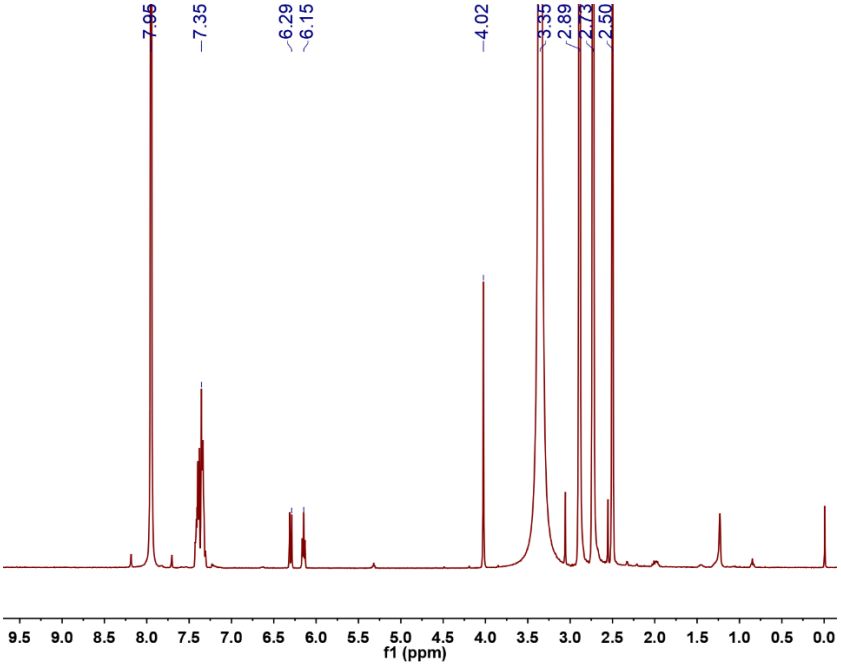


Figure S12. ^{1}H NMR spectrum of the reaction solution of **1a** hydration over [Na][2-OP].

Note: No signals ascribing to the target product were observed, indicating that no reaction occurred.

6. Influences of the reaction conditions on the hydration of phenylacetonitrile (1a)

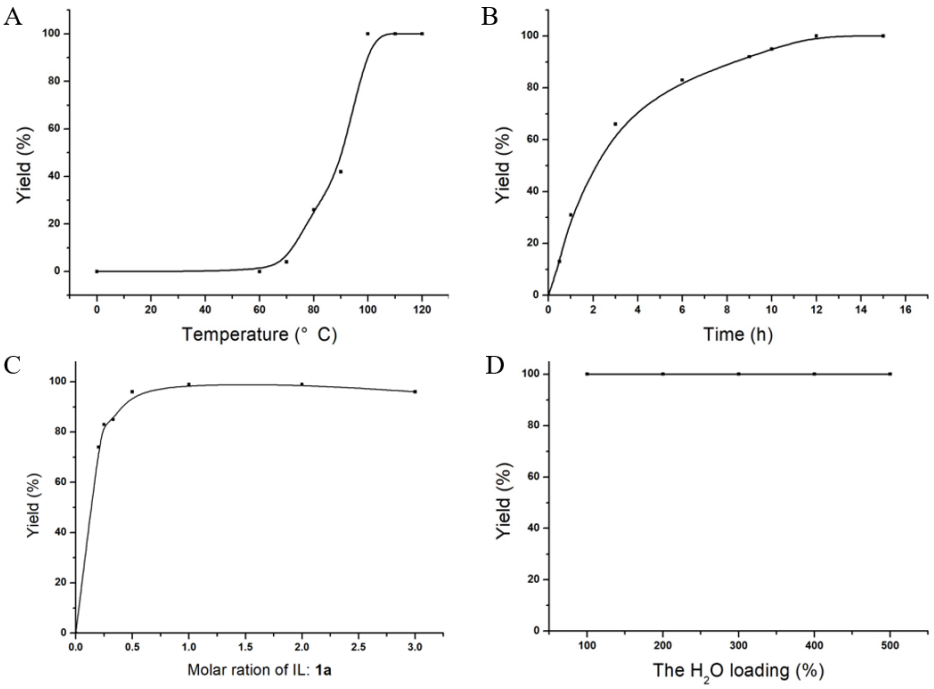


Figure S13. Effects of reaction factors on the product yields. Reaction conditions: **1a** (1 mmol) and CO_2 atmosphere; (a) $[P_{4444}][2\text{-OP}]$ (1 mmol), H_2O (1 mmol), 12 h; (b) $[P_{4444}][2\text{-OP}]$ (1 mmol), H_2O (1 mmol), 100 °C; (c) H_2O (1 mmol), 100 °C, 12 h; (d) $[P_{4444}][2\text{-OP}]$ (1 mmol), 100 °C, 12 h.

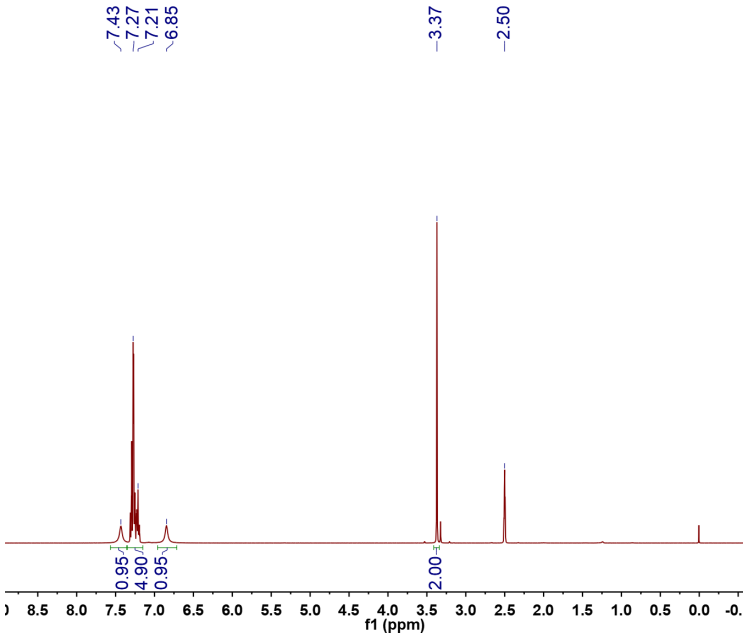


Figure S14. ^1H NMR spectrum of the product for **1a** Gram-scale reaction. Reaction conditions: **1a** (10 mmol), $[P_{4444}][2\text{-OP}]$ (10 mmol), H_2O (10 mmol), 100 °C, 12 h, CO_2 atmosphere.

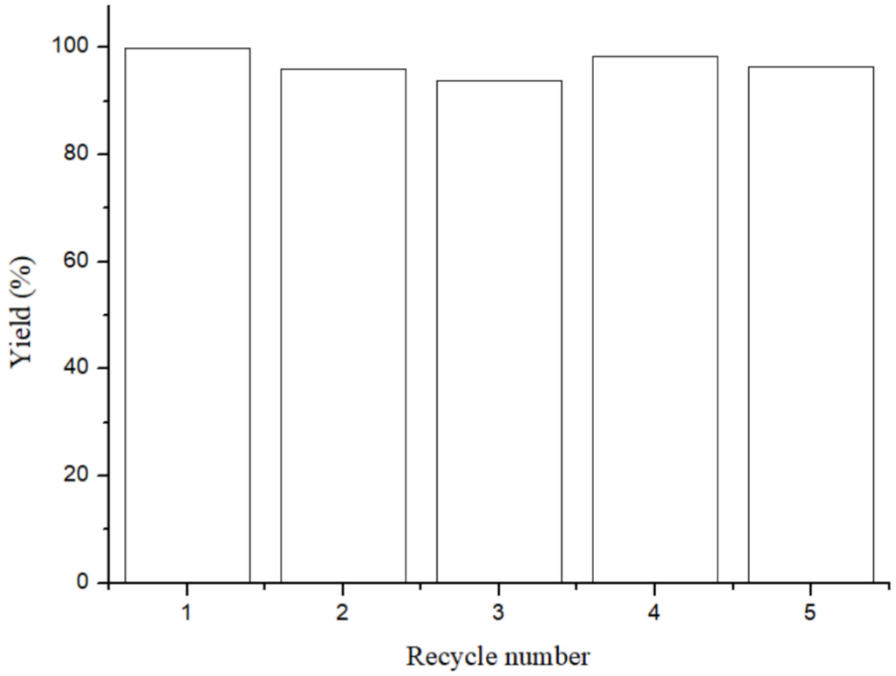


Figure S15. Recycling tests. Reaction conditions: **1a** (1 mmol), [P_{4444}][2-OP] (1 mmol), H_2O (1 mmol), 100°C, 12 h, CO_2 atmosphere.

7. *In-situ* NMR analysis and proposed mechanism of propargylic amine hydration

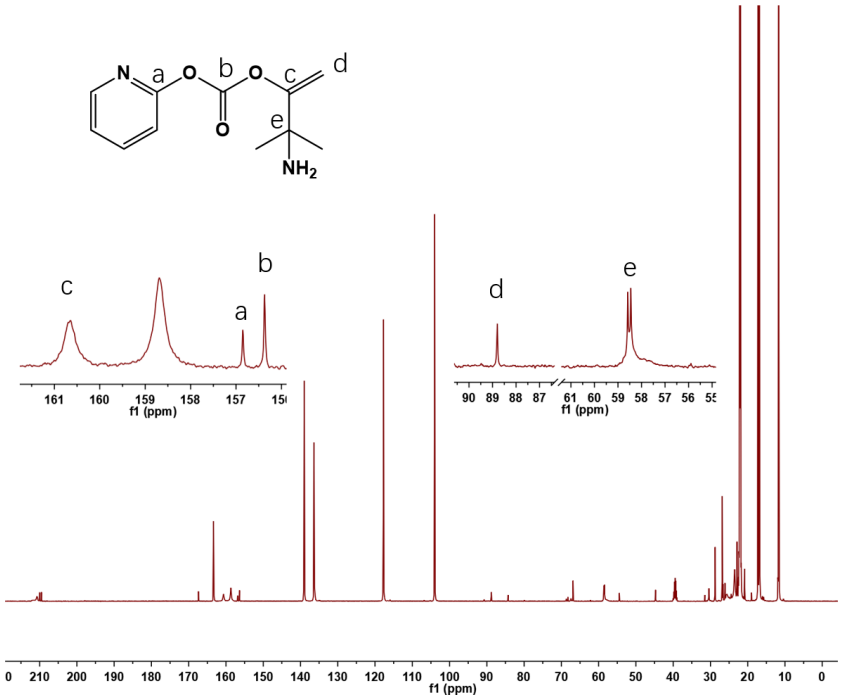


Figure S16. *In-situ* ^{13}C NMR spectrum of the reaction solution of propargylic amine hydration over $[P_{4444}][2\text{-OP}]$ performed at 90°C for 4 h.

Note: Chemical shifts with low intensity at δ = 160.65, 156.85, 156.37, 88.80, 58.45 ppm were observed, which are ascribed to the intermediate as shown in the figure.

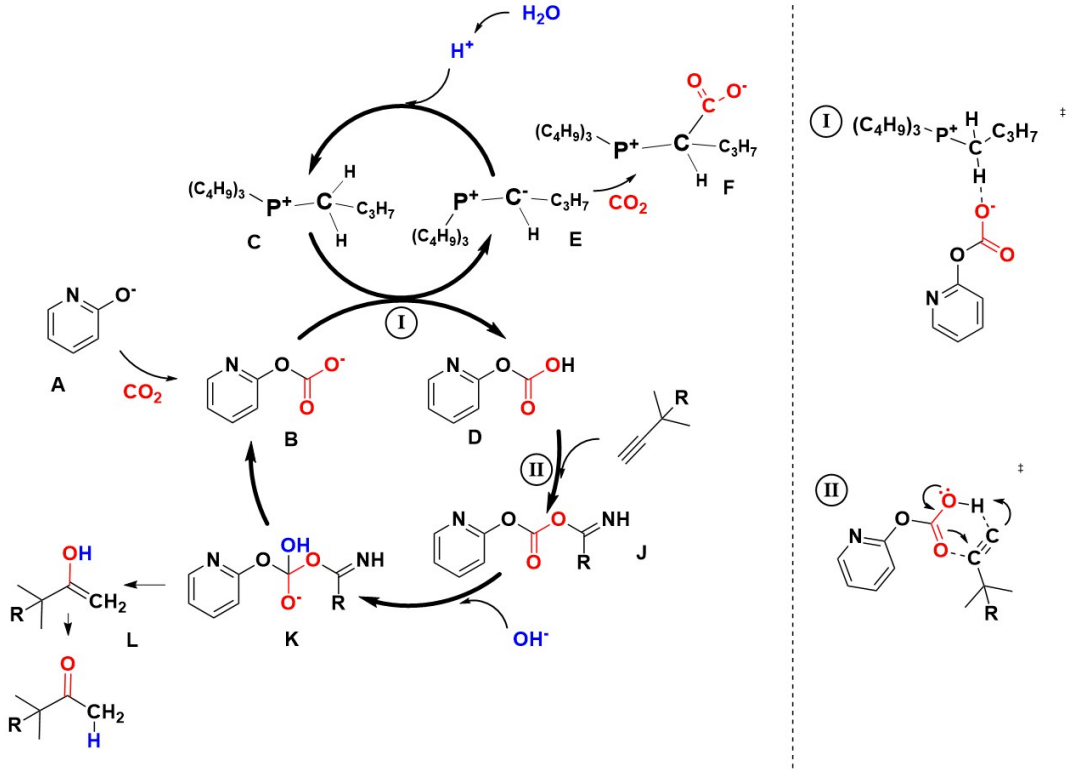
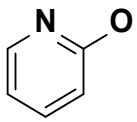
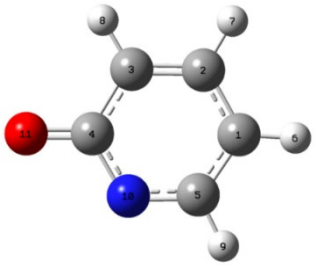


Figure S17. Proposed catalytic cycle for alkyne hydration.

8. DFT Details

Color Scheme: carbon (grey), oxygen (red), nitrogen (blue), hydrogen (white)





A

Coordinates

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C	1.00150900	-1.19192300	0.00002200
H	2.86793500	-0.10814900	0.00004600
H	1.65938100	2.12131200	0.00006800
H	-0.82599200	2.13766400	0.00003000
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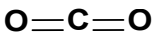

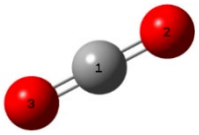

Coordinates

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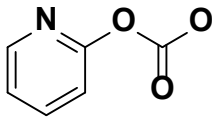
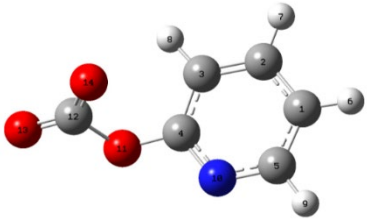
O	0.00000000	0.00000000	-1.16262600

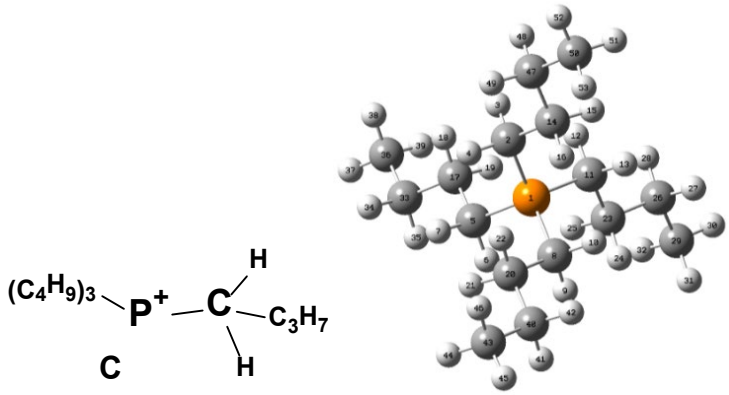


B



Coordinates

C	2.81920100	0.22730900	0.14262700
C	1.97181400	1.26620500	-0.25477100
C	0.62903500	1.00006300	-0.46574700
C	0.17743000	-0.31042300	-0.26008500
C	2.26773600	-1.03506300	0.30736500
H	3.87668600	0.39192600	0.31704500
H	2.35810100	2.27041500	-0.40177800
H	-0.06899000	1.76846700	-0.77704300
H	2.88821100	-1.87453100	0.61063400
N	0.96720000	-1.30780300	0.11505200
O	-1.11313800	-0.65361000	-0.51894800
C	-2.17849900	0.05736000	0.14335000
O	-3.28407400	-0.23828100	-0.32663000
O	-1.84587700	0.81259500	1.06674600



Coordinates

P	0.00000000	0.00000000	0.00000000
C	-1.48928500	0.00000000	1.04021900
H	-2.34261600	0.04312300	0.35750300
H	-1.52050900	-0.97240800	1.54026000
C	0.00000000	-1.48928500	-1.04021900
H	0.97240800	-1.52050900	-1.54026000
H	-0.04312300	-2.34261600	-0.35750300
C	1.48928500	0.00000000	1.04021900
H	2.34261600	-0.04312300	0.35750300
H	1.52050900	0.97240800	1.54026000
C	0.00000000	1.48928500	-1.04021900
H	-0.97240800	1.52050900	-1.54026000
H	0.04312300	2.34261600	-0.35750300
C	-1.54085800	1.14523900	2.05758900
H	-1.49259200	2.10660000	1.53637300
H	-0.66774800	1.09597300	2.71585400
C	-1.14523900	-1.54085800	-2.05758900
H	-2.10660000	-1.49259200	-1.53637300
H	-1.09597300	-0.66774800	-2.71585400
C	1.54085800	-1.14523900	2.05758900
H	1.49259200	-2.10660000	1.53637300
H	0.66774800	-1.09597300	2.71585400
C	1.14523900	1.54085800	-2.05758900
H	2.10660000	1.49259200	-1.53637300
H	1.09597300	0.66774800	-2.71585400
C	1.09106100	2.81500700	-2.90391900
H	1.13444100	3.68757500	-2.24208500
H	0.12464700	2.86203100	-3.41889300
C	2.22443700	2.88531600	-3.92631100
H	2.16745500	3.80286200	-4.51899300
H	3.20179400	2.86666300	-3.43327400
H	2.18434400	2.03788300	-4.61836300
C	-1.09106100	-2.81500700	-2.90391900
H	-1.13444100	-3.68757500	-2.24208500
H	-0.12464700	-2.86203100	-3.41889300
C	-2.22443700	-2.88531600	-3.92631100
H	-2.16745500	-3.80286200	-4.51899300
H	-3.20179400	-2.86666300	-3.43327400
H	-2.18434400	-2.03788300	-4.61836300
C	2.81500700	-1.09106100	2.90391900
H	3.68757500	-1.13444100	2.24208500
H	2.86203100	-0.12464700	3.41889300
C	2.88531600	-2.22443700	3.92631100
H	2.86666300	-3.20179400	3.43327400
H	3.80286200	-2.16745500	4.51899300
H	2.03788300	-2.18434400	4.61836300

C	-2.81500700	1.09106100	2.90391900
H	-3.68757500	1.13444100	2.24208500
H	-2.86203100	0.12464700	3.41889300
C	-2.88531600	2.22443700	3.92631100
H	-2.86666300	3.20179400	3.43327400
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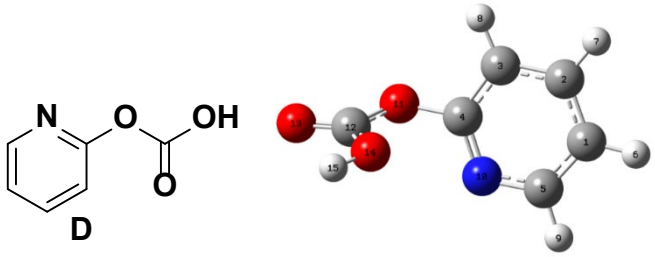
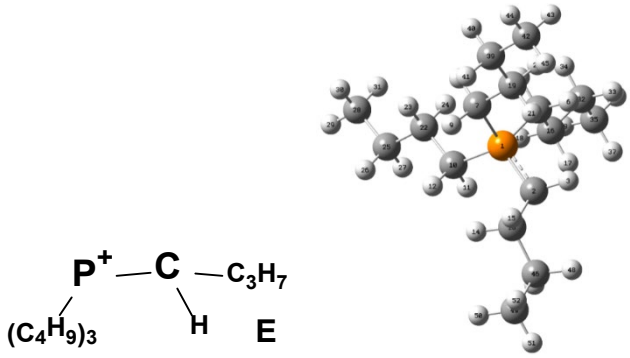


D

Coordinates

C	2.80262800	-0.29373300	0.18529200
C	2.34255400	1.01395900	0.33256900
C	1.00874100	1.29655700	0.05685700
C	0.21850200	0.23240000	-0.35559100
C	1.90639800	-1.26982800	-0.23942900
H	3.83459500	-0.55507200	0.39044700
H	3.01071500	1.80430600	0.65927000
H	0.58736700	2.29060900	0.15245800
H	2.22566600	-2.29952900	-0.37128600
N	0.62066800	-1.01191200	-0.51469200
O	-1.10375300	0.50227400	-0.70806900
C	-2.11323100	0.01345800	0.03088900
O	-3.25467900	0.09408300	-0.34540100
O	-1.70588900	-0.50613400	1.18339200
H	-2.48200800	-0.83560200	1.66906400

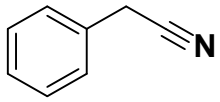


E

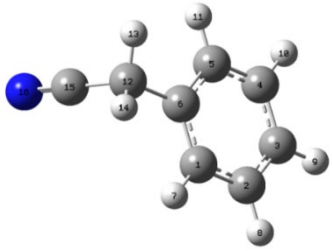
Coordinates

P	-0.20686600	-0.04994600	0.06124800
C	-1.14739300	-1.33484800	0.67647300
H	-1.52552700	-1.11401100	1.67653000
C	0.87837900	0.61371800	1.37876100
H	1.28182400	1.56605600	1.02268800
H	0.22562700	0.84148700	2.22699400
C	-1.03885900	1.46190600	-0.63062700
H	-0.28076600	2.18323400	-0.95066100
H	-1.57340400	1.12956900	-1.52811500
C	0.85519400	-0.61306700	-1.32550400
H	1.41086800	-1.47309600	-0.94317600
H	0.18312100	-0.99212600	-2.10174700
C	-2.10563300	-2.09161500	-0.22940800
H	-1.70344400	-2.13695300	-1.25020200
H	-3.08875100	-1.59729200	-0.32943000

C	2.00804200	-0.32283900	1.81468200
H	1.58438300	-1.27907200	2.13547100
H	2.65857900	-0.54008400	0.96078500
C	-2.01473400	2.10264900	0.35778900
H	-1.46688600	2.46686600	1.23456200
H	-2.71241700	1.34099800	0.72476100
C	1.81153500	0.43043000	-1.91026800
H	1.24390600	1.24885300	-2.36327600
H	2.41523400	0.87369700	-1.11058700
C	2.74614500	-0.17182400	-2.96318700
H	2.14488000	-0.62295300	-3.76115100
H	3.31857900	-0.98840600	-2.50820600
C	3.70461600	0.85816500	-3.55993700
H	4.36372900	0.40504600	-4.30605600
H	3.15660200	1.67016400	-4.04879300
H	4.33623400	1.30393400	-2.78460000
C	2.84853900	0.27268400	2.94702300
H	2.19751700	0.48587800	3.80294800
H	3.25912100	1.23659200	2.62335400
C	3.98659200	-0.64930600	3.38373000
H	4.57151400	-0.20557200	4.19463200
H	3.60025100	-1.61034500	3.73797900
H	4.66968900	-0.85284500	2.55265100
C	-2.80740300	3.26101300	-0.25362200
H	-2.10916600	4.02181000	-0.62206700
H	-3.35553300	2.89519600	-1.12984300
C	-3.78462700	3.89664000	0.73510300
H	-3.25801000	4.29728800	1.60742600
H	-4.34071000	4.71889300	0.27535500
H	-4.51233500	3.16258400	1.09598000
C	-2.36293500	-3.53193900	0.23832100
H	-1.40547900	-4.06398800	0.27762500
H	-2.74068300	-3.50726400	1.26817800
C	-3.34899100	-4.29113800	-0.65045800
H	-2.98058800	-4.35751900	-1.68002700
H	-3.51366100	-5.31169400	-0.29124000
H	-4.32211700	-3.78949700	-0.68069900



1a

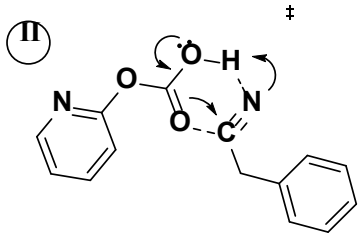


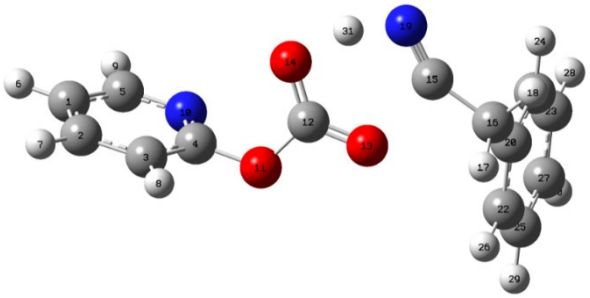
Coordinates

C	-0.52173800	1.20552100	0.24981900
C	-1.84498700	1.20902900	-0.19025500
C	-2.51031500	0.00361300	-0.41497700
C	-1.84883000	-1.20516900	-0.19679700
C	-0.52562700	-1.20832000	0.24326200
C	0.14312200	-0.00304500	0.46770700
H	-0.00261000	2.14431900	0.42619200
H	-2.35568600	2.15292700	-0.35528600
H	-3.54096700	0.00606900	-0.75638300
H	-2.36267200	-2.14644900	-0.36699200
H	-0.00929200	-2.14955800	0.41465400
C	1.58851400	-0.00681200	0.93209100
H	1.80666800	-0.89603000	1.53106000
H	1.80751600	0.87403300	1.54298000

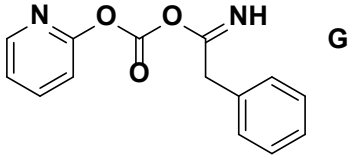
C	2.51637200	0.00047600	-0.20475400
N	3.23971000	0.00613500	-1.10754200

II ‡

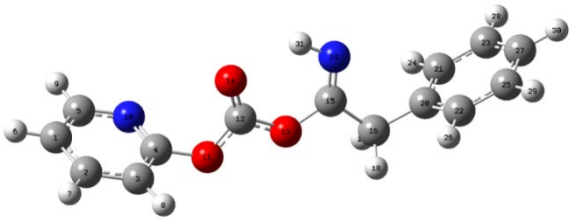




C	-5.34393300	0.90553200	0.58380100
C	-5.23336300	0.07296700	-0.52895700
C	-3.97059200	-0.20504800	-1.04119000
C	-2.88835100	0.37976000	-0.39616300
C	-4.18085300	1.43207100	1.13695900
H	-6.30905800	1.14611400	1.01521600
H	-6.11644900	-0.35646600	-0.99126400
H	-3.81514100	-0.84578400	-1.90162600
H	-4.22360200	2.08809300	2.00165400
N	-2.95817400	1.17683200	0.65167200
O	-1.61665900	0.17099800	-0.92251900
C	-0.79725100	-0.67695900	-0.25884800
O	0.37154000	-0.73351900	-0.72106800
O	-1.25399500	-1.33060600	0.71490000
C	1.48578400	-1.95878100	0.24783300
C	2.73120400	-1.74089200	-0.50564400
H	2.52064100	-1.89344500	-1.56657700
H	3.41545100	-2.52602900	-0.16587000
N	0.87641500	-2.48037600	1.12658300
C	3.30892500	-0.36217700	-0.25082800
C	3.83730400	-0.04774400	1.00413200
C	3.31553300	0.59878200	-1.26212700
C	4.36844300	1.21801100	1.24453900
H	3.83120000	-0.79605900	1.79358700
C	3.85070800	1.86476500	-1.02312700
H	2.89650500	0.35717300	-2.23522600
C	4.37668300	2.17661500	0.23005700
H	4.77710300	1.45480300	2.22223100
H	3.85280000	2.60675400	-1.81588900
H	4.79166300	3.16254000	0.41641500
H	-0.21733000	-2.06927700	1.12643300



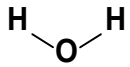
G

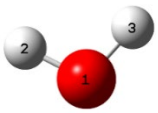


Coordinates

C	-6.10547500	-0.23425500	-0.36967600
C	-5.63182100	1.06851300	-0.22407700
C	-4.31068200	1.26800200	0.16430300
C	-3.55071500	0.12883500	0.38513300
C	-5.23664500	-1.29132200	-0.11563000
H	-7.12776500	-0.43166200	-0.67177400
H	-6.27899700	1.91910800	-0.41208100
H	-3.87850400	2.25351800	0.29409000

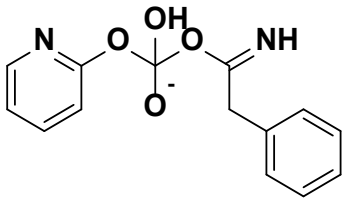
H	-5.56737700	-2.32092500	-0.21490900
N	-3.96366900	-1.11493600	0.26397700
O	-2.23733700	0.29370900	0.83500300
C	-1.27027300	0.02051900	-0.05065400
O	-0.10768800	0.13480100	0.60460700
O	-1.43631800	-0.25217700	-1.21063600
C	1.14478900	-0.05402800	-0.01120900
C	2.18909500	0.28703000	1.01626000
H	2.02070400	-0.36695300	1.87974700
H	1.99251100	1.31112100	1.35330800
N	1.36489500	-0.44103800	-1.18415500
C	3.59764900	0.15070800	0.50154000
C	4.26887700	-1.07195000	0.58745900
C	4.24537400	1.24129500	-0.08479200
C	5.56637400	-1.20421900	0.09418700
H	3.77042000	-1.92439400	1.04311700
C	5.54319700	1.11306100	-0.57891200
H	3.72866700	2.19563400	-0.15432600
C	6.20677000	-0.11102900	-0.49059600
H	6.07758300	-2.15949100	0.16842800
H	6.03601700	1.96881400	-1.03085700
H	7.21815400	-0.21199100	-0.87280800
H	0.51167000	-0.61857700	-1.71250000

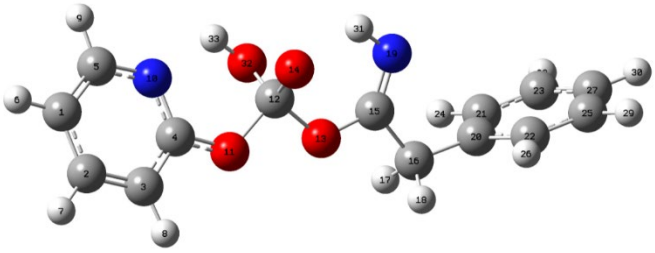




Coordinates

O	0.00000000	0.00000000	0.11736200
H	0.00000000	0.76690300	-0.46944700
H	0.00000000	-0.76690300	-0.46944700

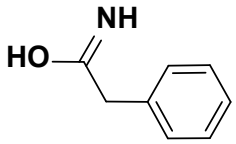




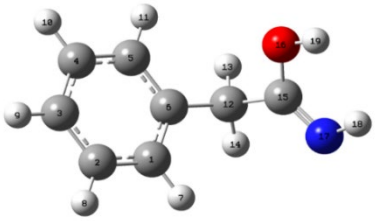
Coordinates

C	-6.14859100	0.17083600	0.07719400
C	-5.74396900	-1.14417000	-0.18621000
C	-4.39698700	-1.42723600	-0.31104600
C	-3.47530400	-0.37059200	-0.17649000
C	-5.16267300	1.13717000	0.19464100
H	-7.19434300	0.43421500	0.18722500
H	-6.47792900	-1.93867700	-0.28543100
H	-4.02977500	-2.42896100	-0.50479900
H	-5.42477400	2.17276600	0.39742900
N	-3.84966500	0.88519900	0.06681900
O	-2.18086700	-0.67575100	-0.33951000
C	-1.15901400	0.26618000	0.22423300
O	0.01262800	-0.45257800	-0.29522200
O	-1.22503500	0.40335400	1.47588200
C	1.24224400	0.00695000	0.01884700
C	2.27813000	-0.87378300	-0.64841500
H	2.08965900	-0.83668800	-1.72727900
H	2.07916000	-1.90342100	-0.33001700
N	1.54906400	1.00712300	0.74243900

C	3.70158600	-0.49129200	-0.34558000
C	4.40023300	0.38150100	-1.18462800
C	4.34502800	-0.99242800	0.79030000
C	5.71395900	0.75037700	-0.89452900
H	3.90787600	0.77735700	-2.06991300
C	5.65787800	-0.62663800	1.08496600
H	3.80902800	-1.67107300	1.44993700
C	6.34696900	0.24663500	0.24205600
H	6.24259700	1.43031900	-1.55644100
H	6.14315700	-1.02414400	1.97174000
H	7.37008100	0.53141600	0.46920700
H	0.70258900	1.44197200	1.11326500
O	-1.19527300	1.43430700	-0.56789400
H	-2.00167000	1.89294300	-0.27781900

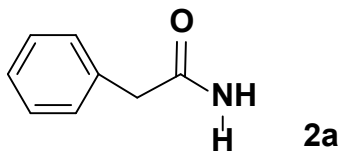


I

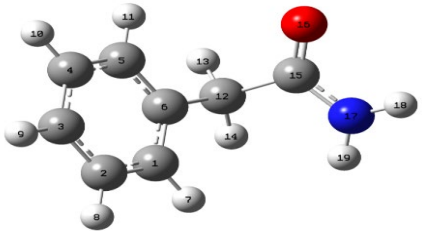


Coordinates

C	-0.80870200	-1.22575100	-0.17556900
C	-2.10508100	-1.28871100	0.33346800
C	-2.86216600	-0.12354200	0.46596900
C	-2.31540800	1.10216800	0.08654000
C	-1.01770800	1.16207700	-0.42262700
C	-0.25383000	-0.00002900	-0.55875400
H	-0.21951700	-2.13420400	-0.27970600
H	-2.52523100	-2.24719000	0.62384100
H	-3.87294600	-0.17165100	0.85987500
H	-2.89861600	2.01309300	0.18490800
H	-0.59239800	2.11824800	-0.71749500
C	1.16631700	0.05527100	-1.08339200
H	1.32311700	0.98723900	-1.63631800
H	1.36596800	-0.78690200	-1.74823100
C	2.16526000	-0.00008600	0.04148800
O	2.07362900	1.09653300	0.82919600
N	2.96451600	-0.97641100	0.19635000
H	3.56497500	-0.84619700	1.01484900
H	2.70190900	1.04180300	1.56751800



2a

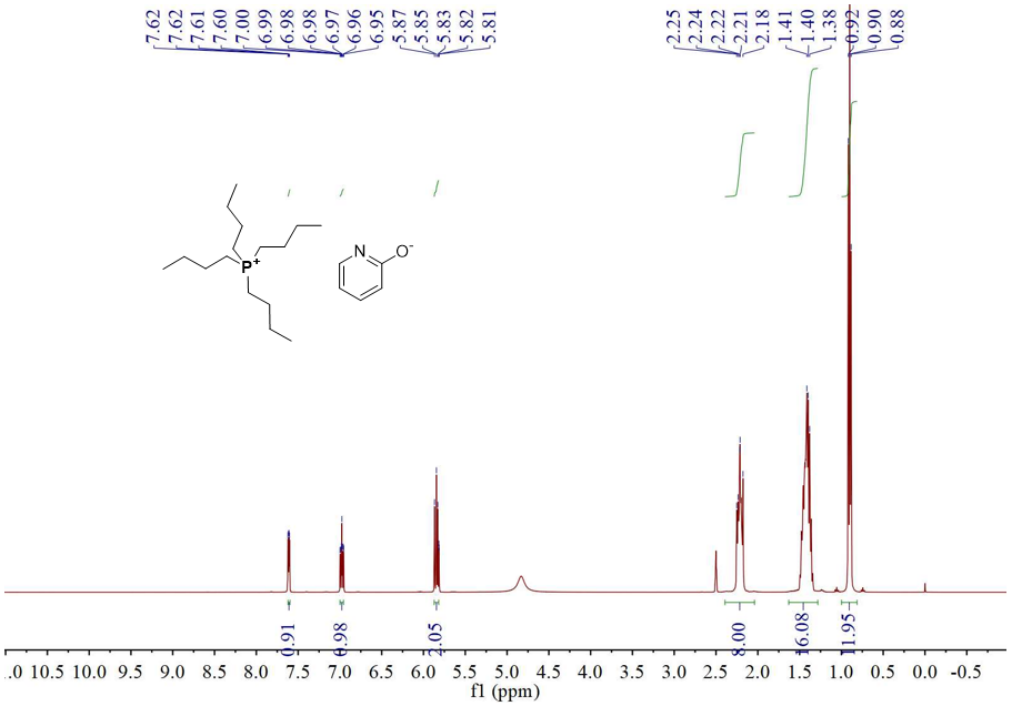


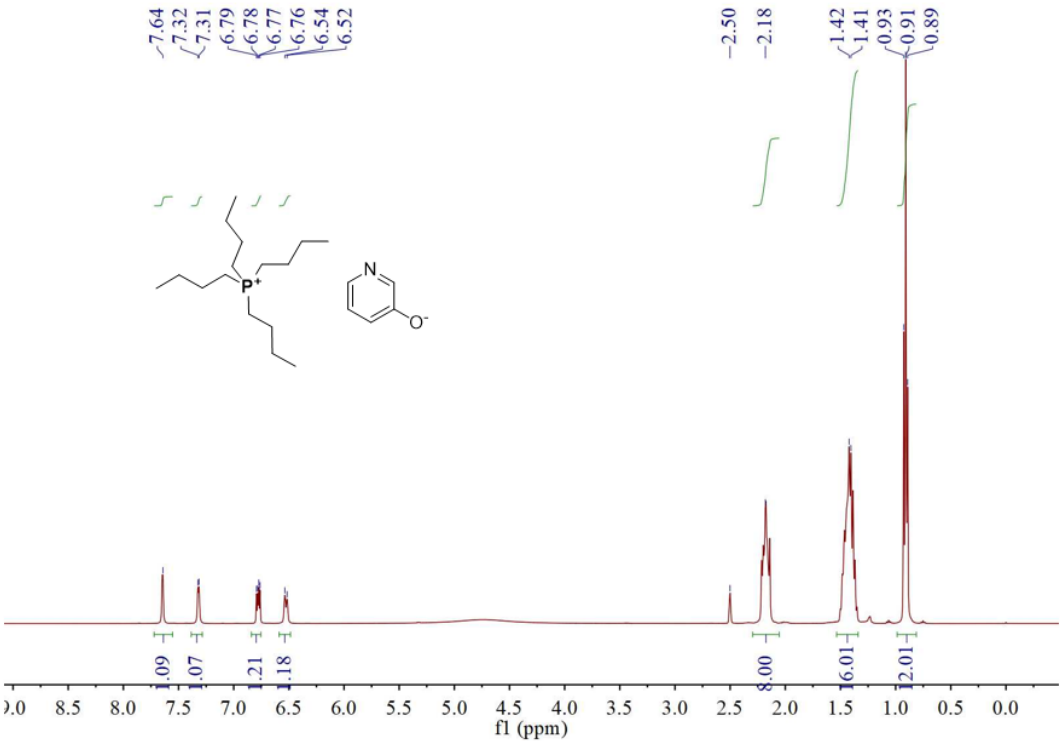
Coordinates

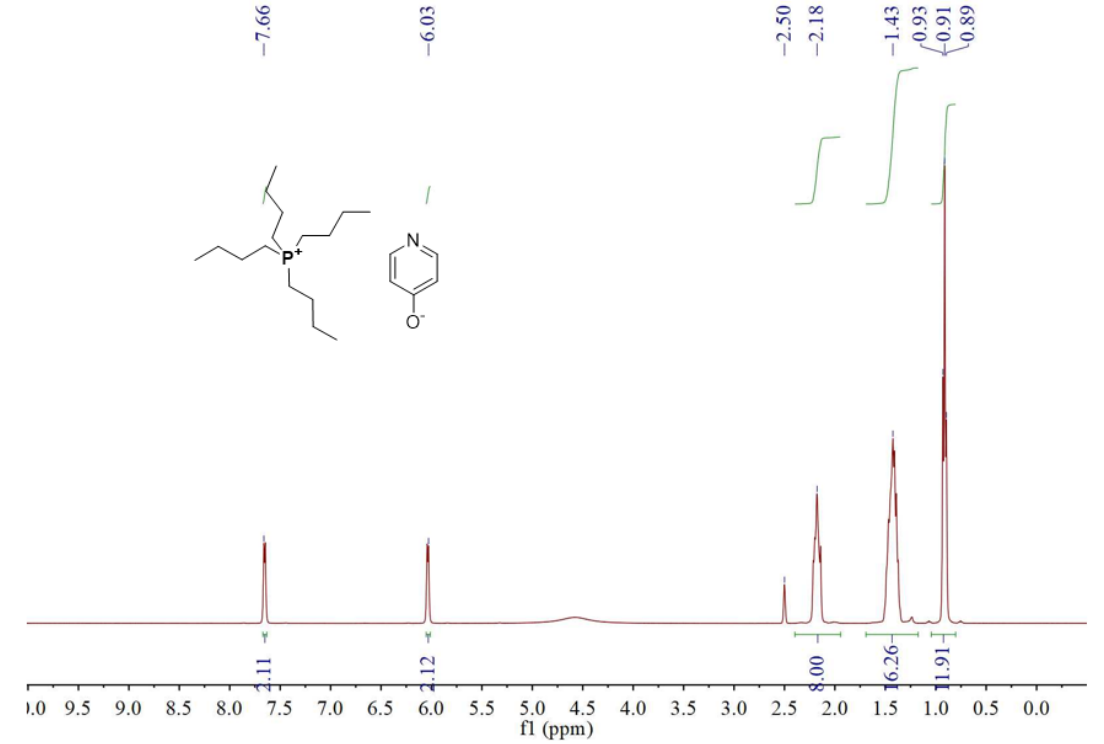
C	0.89645500	-1.23294100	0.25489000
C	2.19456400	-1.23953700	-0.25563800
C	2.86517300	-0.03638200	-0.47577100
C	2.23173600	1.17147100	-0.18038800
C	0.93469500	1.17562300	0.33155300
C	0.25462300	-0.02667400	0.55239700
H	0.37698500	-2.17269200	0.42809200
H	2.68209600	-2.18412000	-0.47839100
H	3.87652800	-0.03977300	-0.87102000
H	2.74882100	2.11216800	-0.34543000

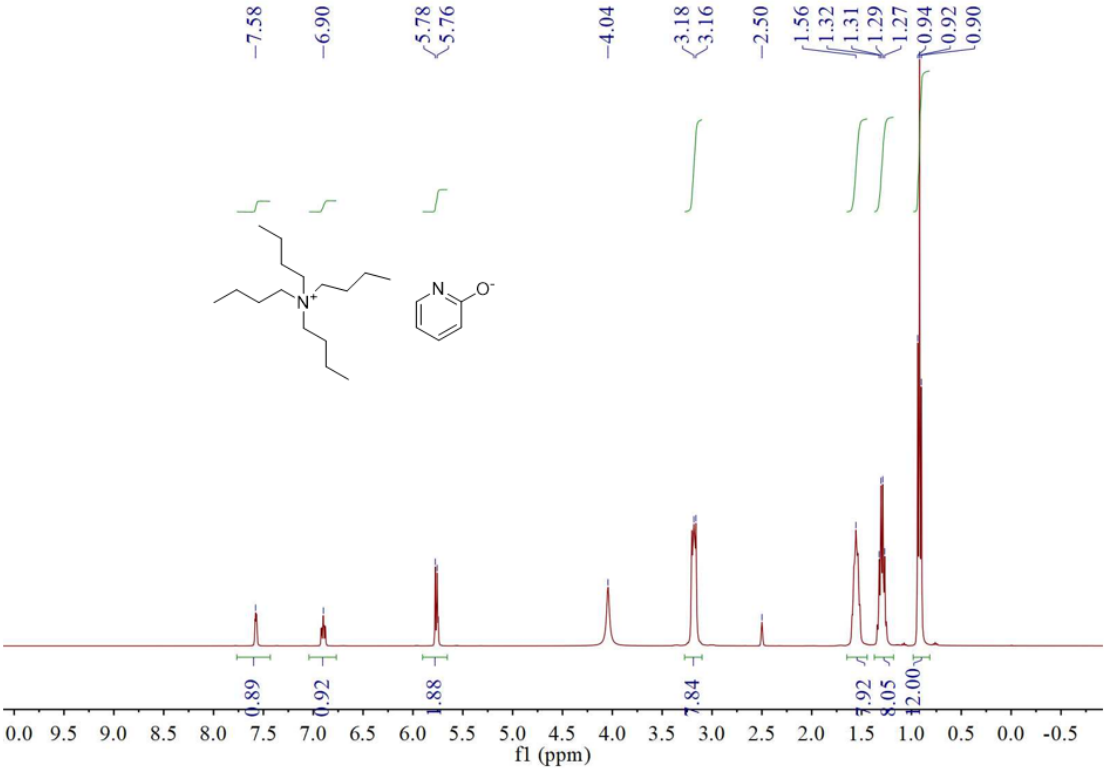
H	0.44391300	2.11731200	0.56355200
C	-1.16782800	-0.02295200	1.06983200
H	-1.32115400	0.81808900	1.75099000
H	-1.37825700	-0.95275000	1.60507900
C	-2.13905400	0.15892500	-0.08812300
O	-2.31538300	1.25863800	-0.61300700
N	-2.76241700	-0.95643100	-0.51578900
H	-3.38470600	-0.90430600	-1.31200900
H	-2.60643300	-1.85321500	-0.07879300

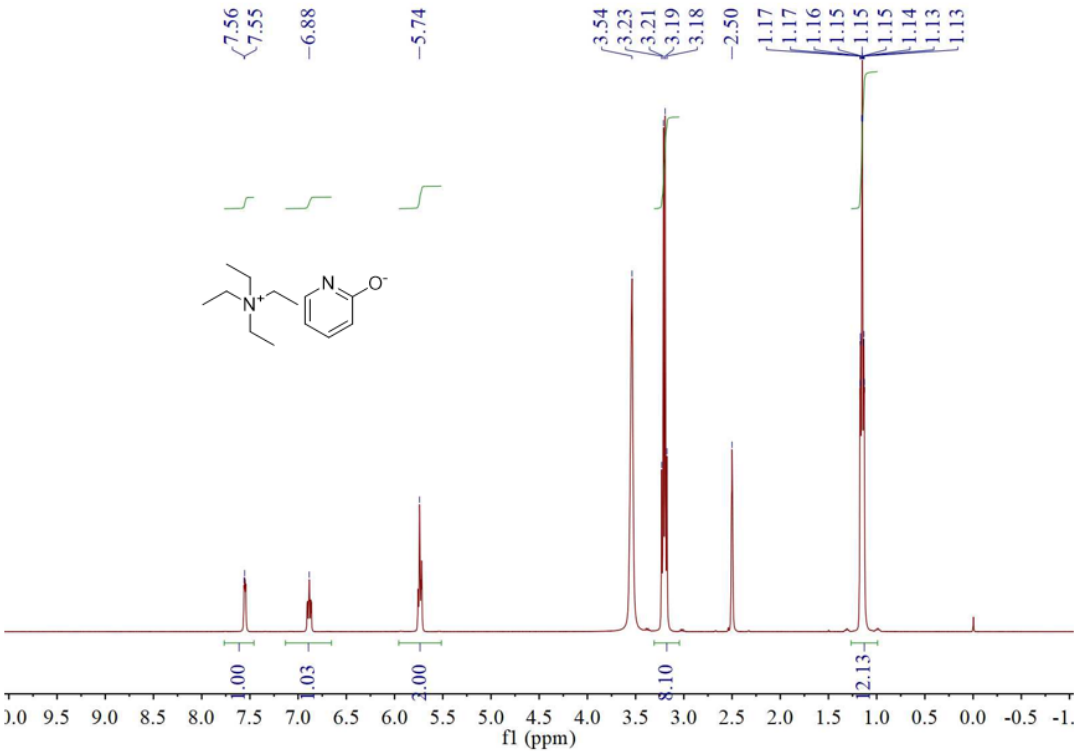
9. ^{1}H NMR spectra of the ILs used

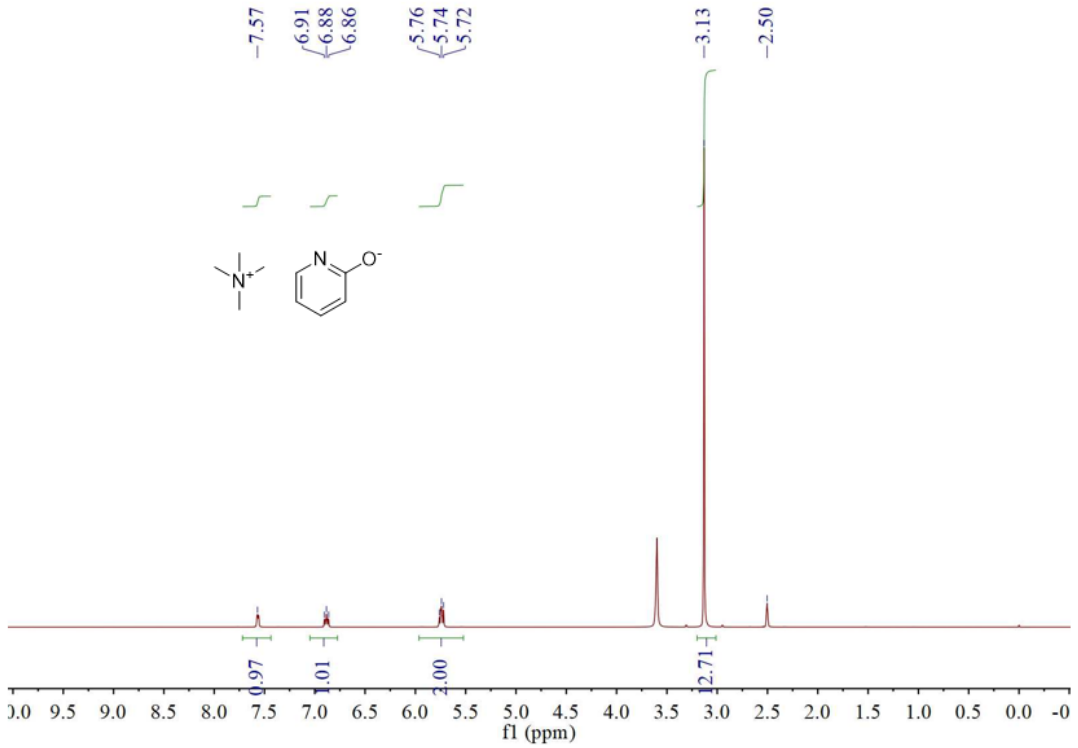


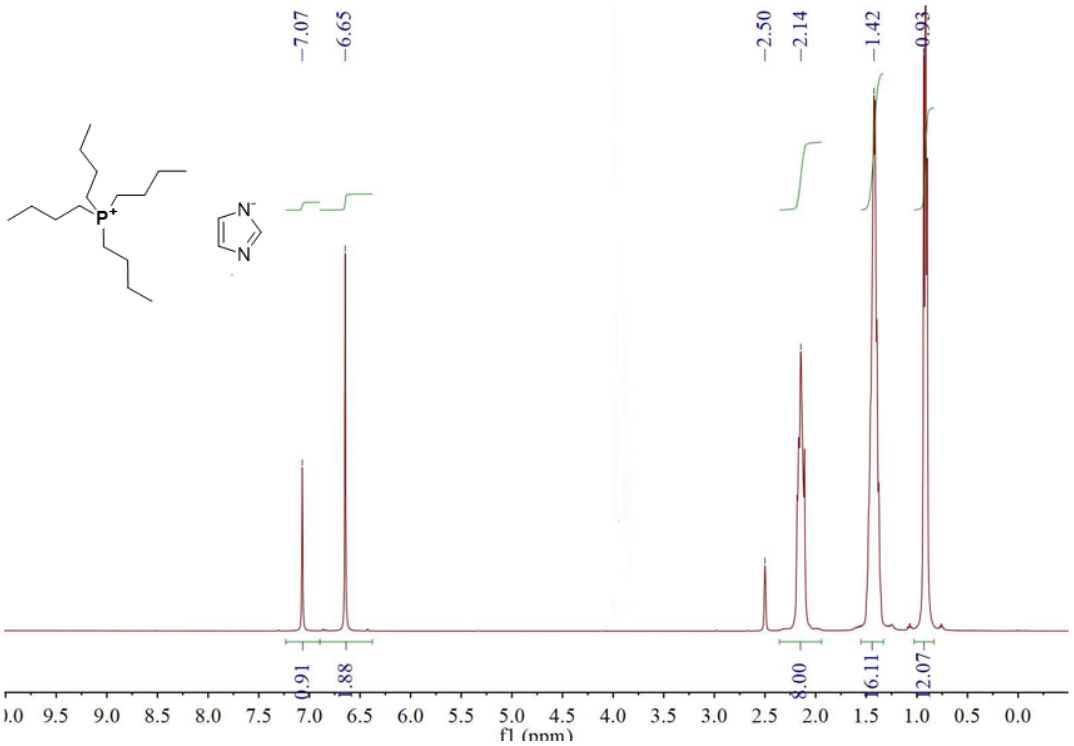


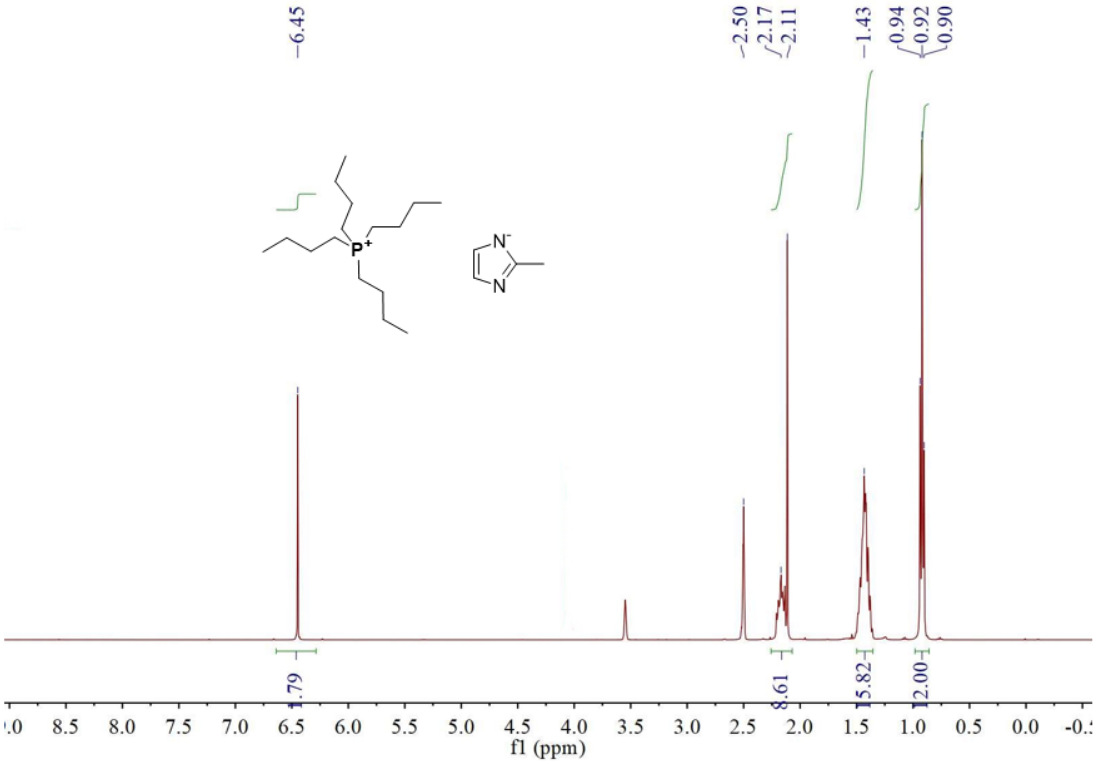

7.66
6.03
2.50
2.18
1.43
0.93
0.91
0.89
P+
N
O-
2.11
2.12
8.00
16.26
11.91
fl (ppm)

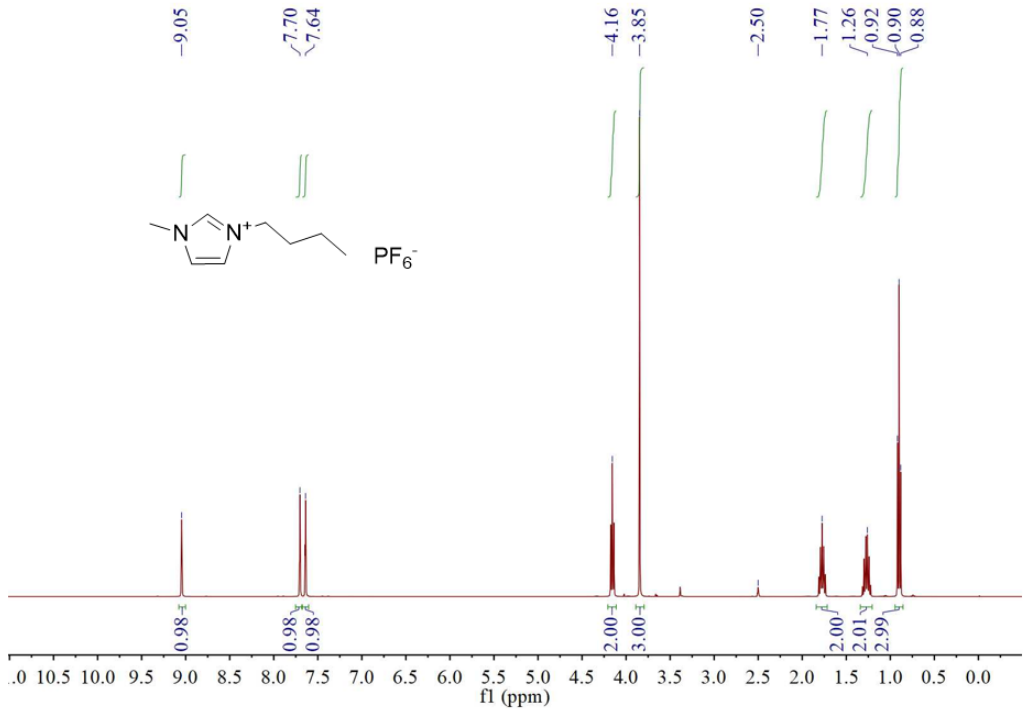

7.58
6.90
5.78
5.76
4.04
3.18
3.16
2.50
1.56
1.32
1.31
1.29
1.27
0.94
0.92
0.90
N+
N
O-
0.89
0.92
1.88
7.84
7.92
8.05
12.00
fl (ppm)

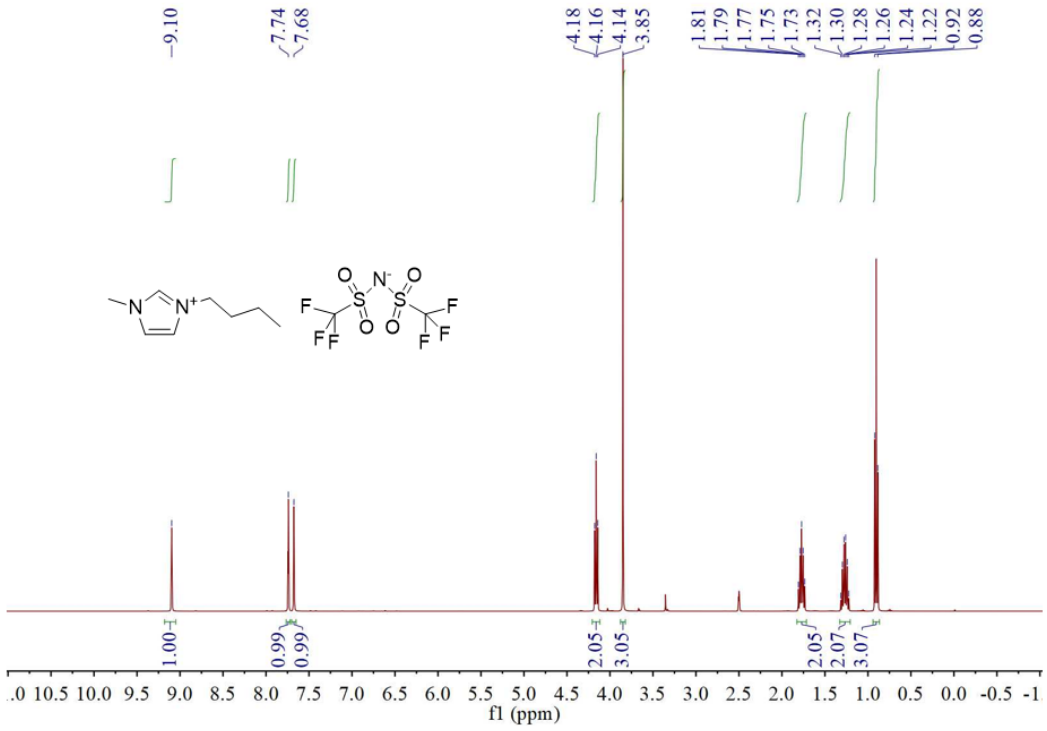

7.56
7.55
6.88
5.74
3.54
3.23
3.21
3.19
3.18
2.50
1.17
1.17
1.16
1.15
1.15
1.15
1.14
1.13
1.13
1.00
1.03
2.00
8.10
12.13
f1 (ppm)

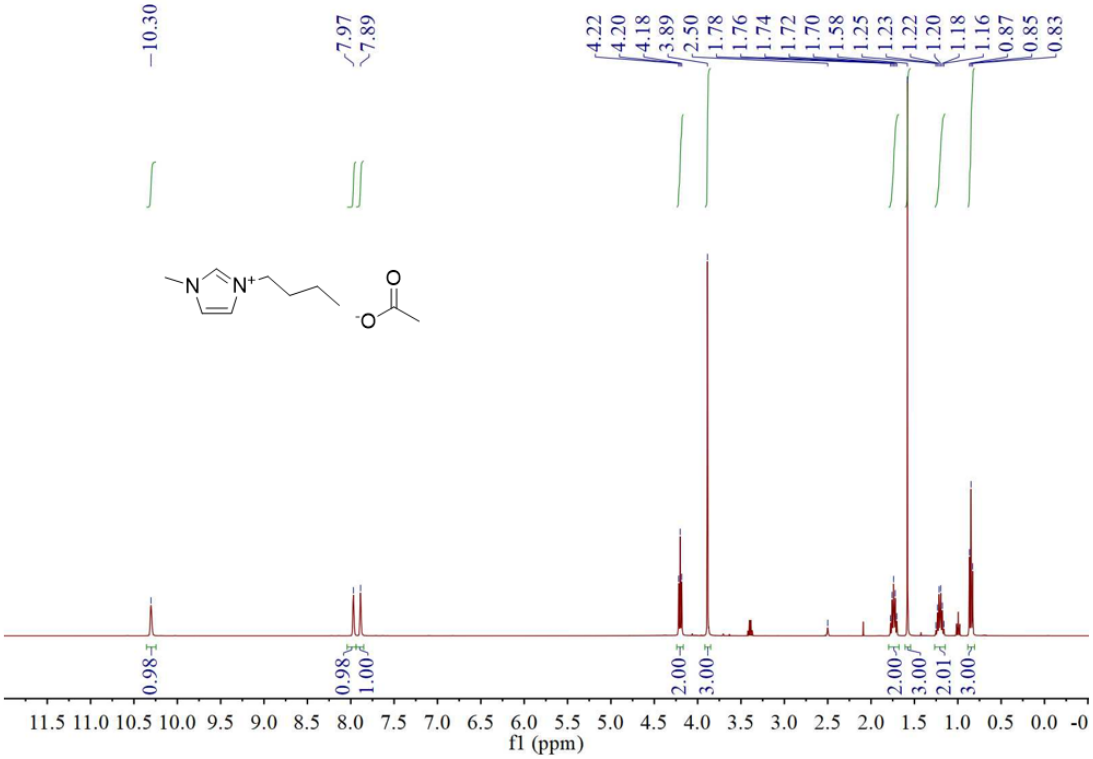

7.57
6.91
6.88
6.86
5.76
5.74
5.72
3.13
2.50
0.97
1.01
2.00
12.71
f1 (ppm)

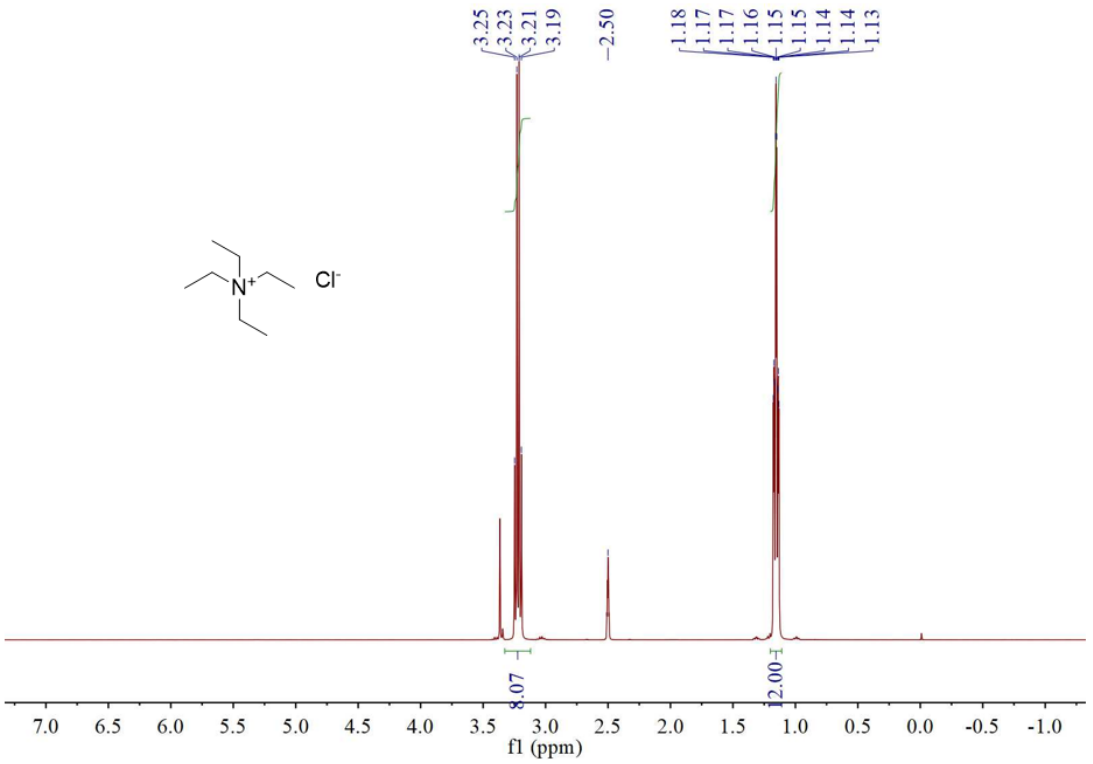

7.07
6.65
2.50
2.14
1.42
0.93
0.91
1.88
8.00
16.11
12.07
fl (ppm)

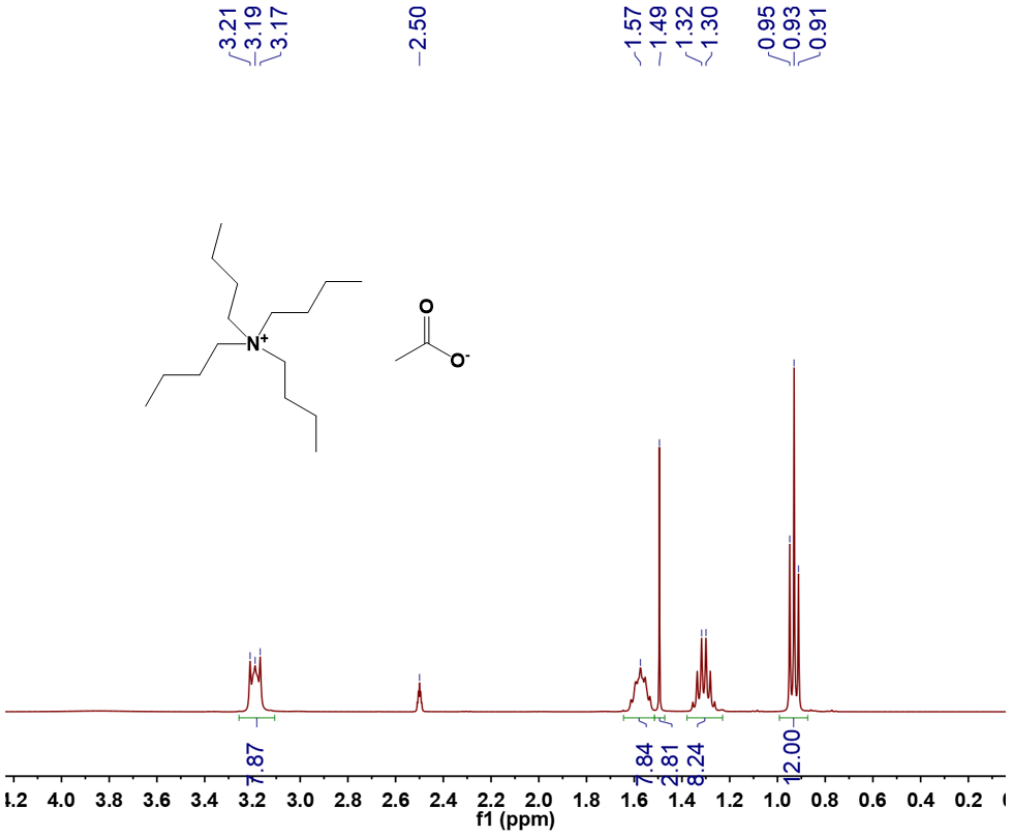

6.45
2.50
2.17
2.11
1.43
0.94
0.92
0.90
1.79
8.61
15.82
12.00
fl (ppm)

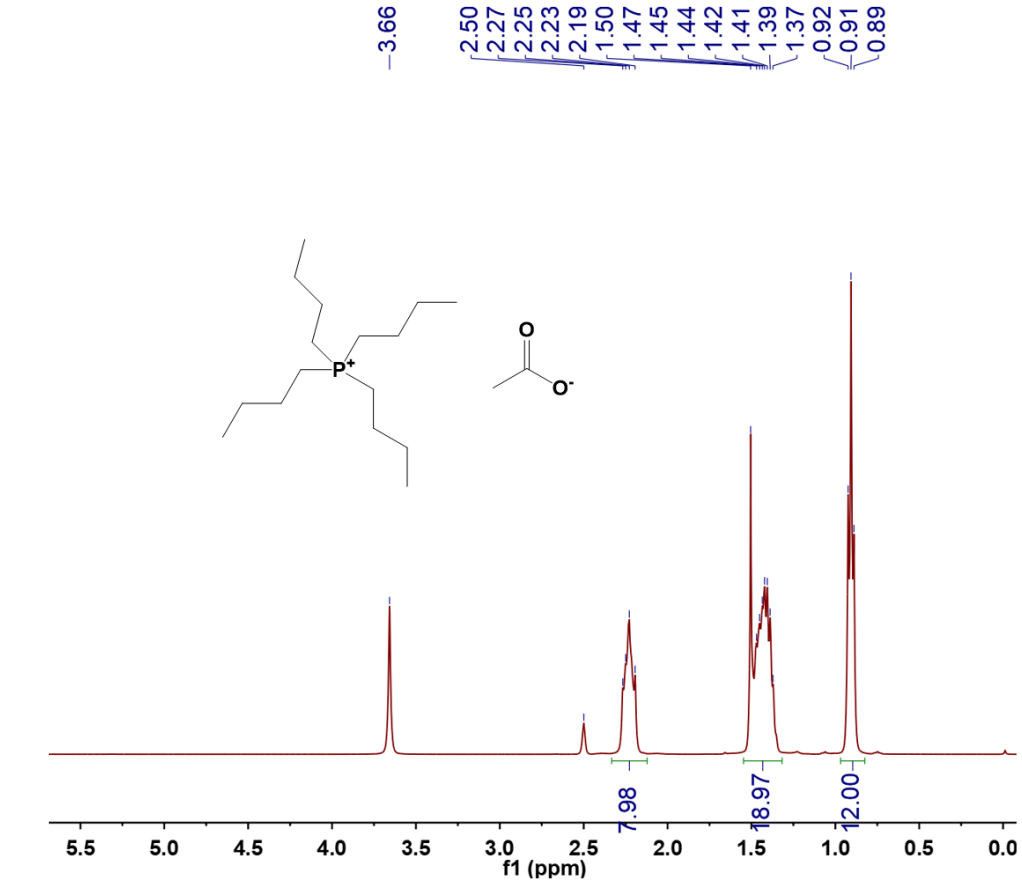

9.05
7.70
7.64
4.16
3.85
2.50
1.77
1.26
0.92
0.90
0.88
PF6-
0.98
0.98
0.98
2.00
3.00
2.00
2.01
2.99
f1 (ppm)

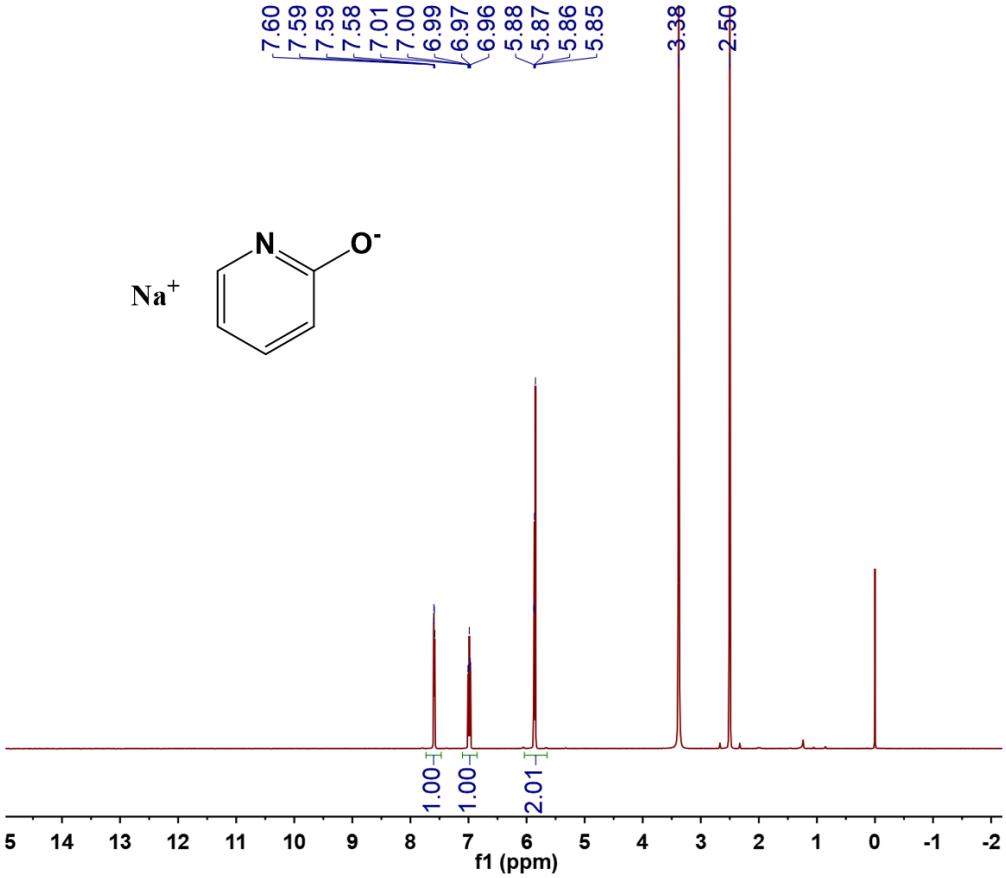

9.10
7.74
7.68
4.18
4.16
4.14
3.85
1.81
1.79
1.77
1.75
1.73
1.32
1.30
1.28
1.26
1.24
1.22
0.92
0.88
1.00
0.99
0.99
2.05
3.05
2.05
2.07
3.07
f1 (ppm)


10.30
7.97
7.89
4.22
4.20
4.18
3.89
2.50
1.78
1.76
1.74
1.72
1.70
1.58
1.25
1.23
1.22
1.20
1.18
1.16
0.87
0.85
0.83
0.98
0.98
1.00
2.00
3.00
2.00
3.00
2.01
3.00
f1 (ppm)

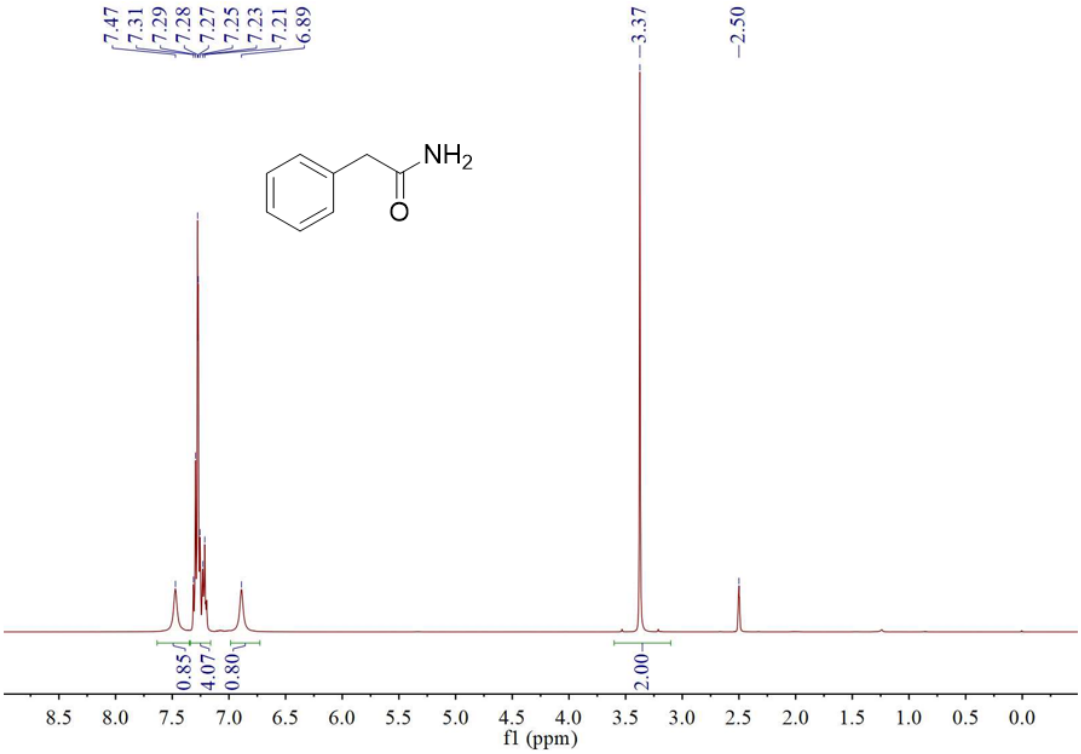

3.25
3.23
3.21
3.19
2.50
1.18
1.17
1.17
1.16
1.15
1.15
1.14
1.14
1.13
Cl-
8.07
12.00
f1 (ppm)

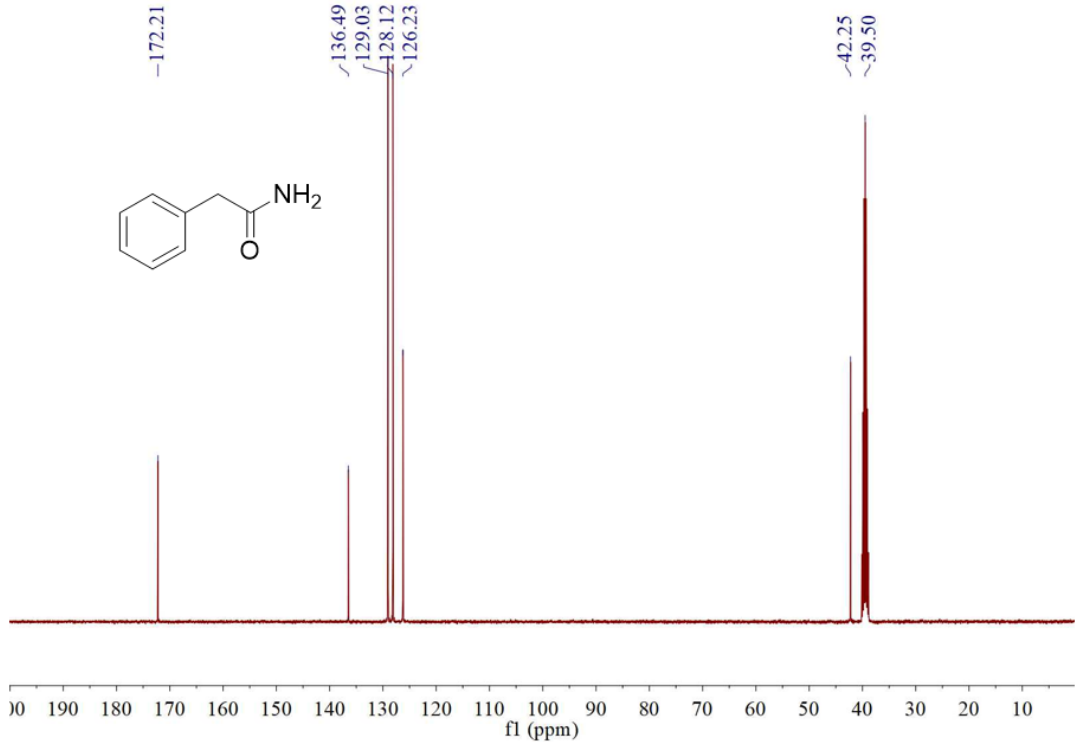

3.21
3.19
3.17
2.50
1.57
1.49
1.32
1.30
0.95
0.93
0.91
O
N+
O-
7.87
7.84
2.81
8.24
12.00
f1 (ppm)

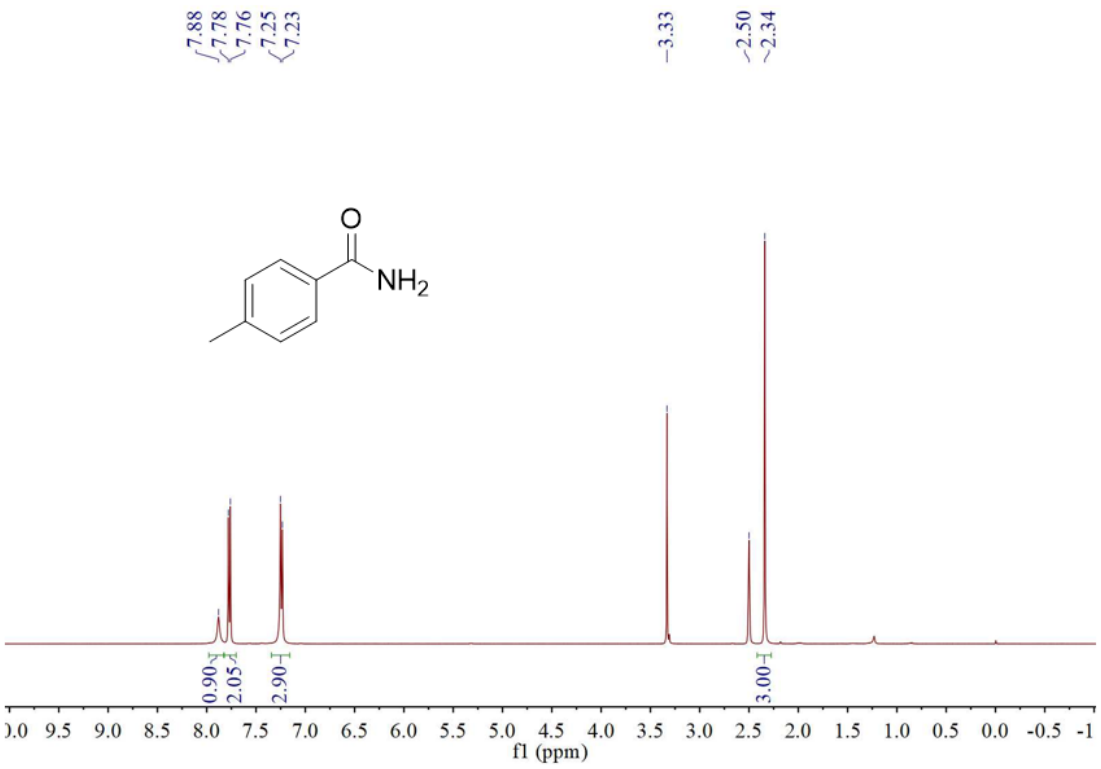

3.66
2.50
2.27
2.25
2.23
2.19
1.50
1.47
1.45
1.44
1.42
1.41
1.39
1.37
0.92
0.91
0.89
O
P+
O-
7.98
18.97
12.00
f1 (ppm)

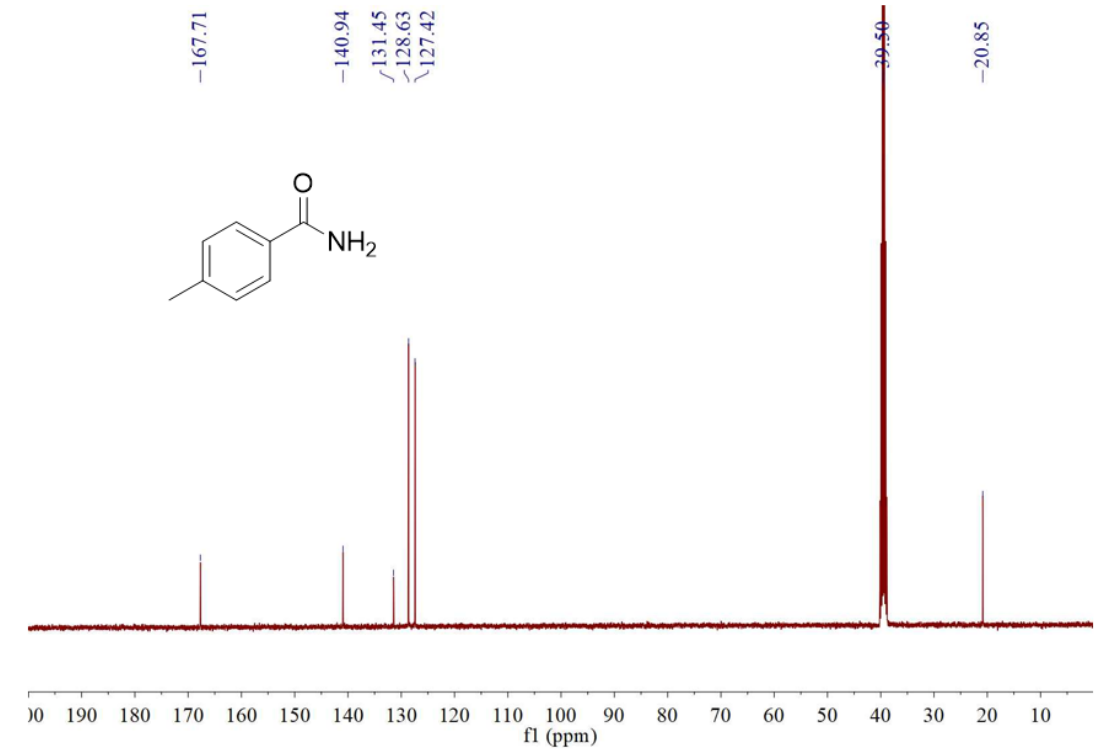

7.60
7.59
7.59
7.58
7.01
7.00
6.99
6.97
6.96
5.88
5.87
5.86
5.85
3.38
2.50
N
O-
Na+
1.00
1.00
2.01
5 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

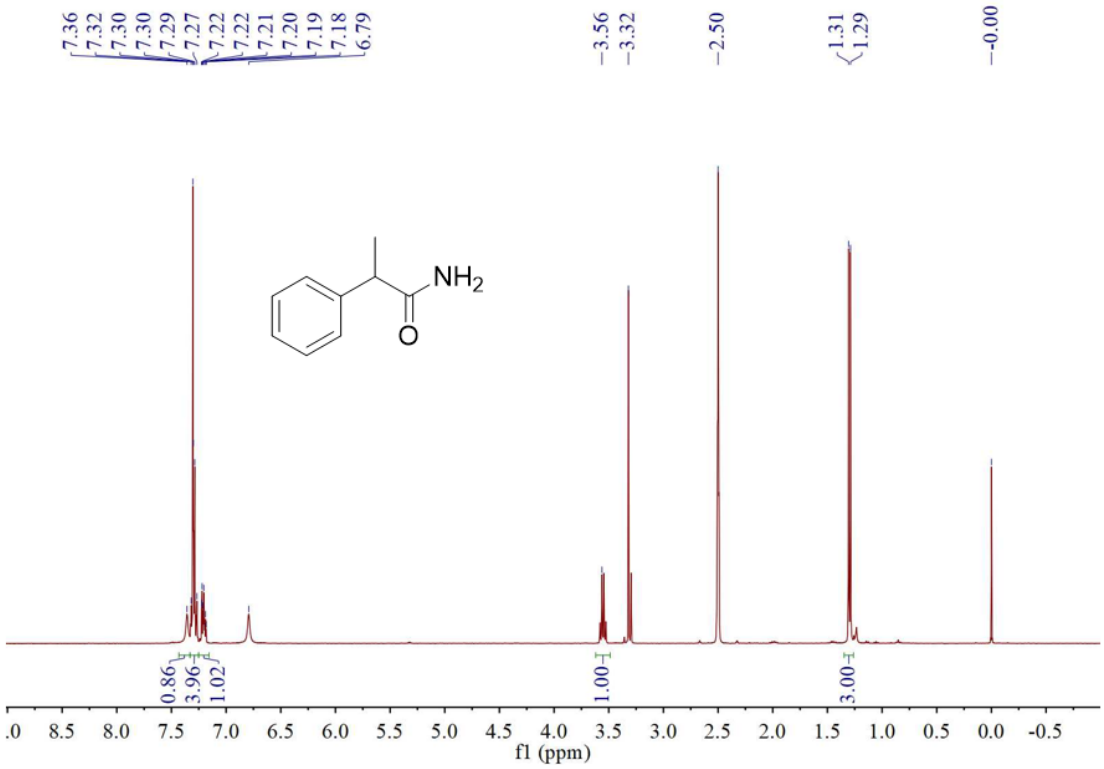
10. ^{1}H and ^{13}C NMR spectra of the products

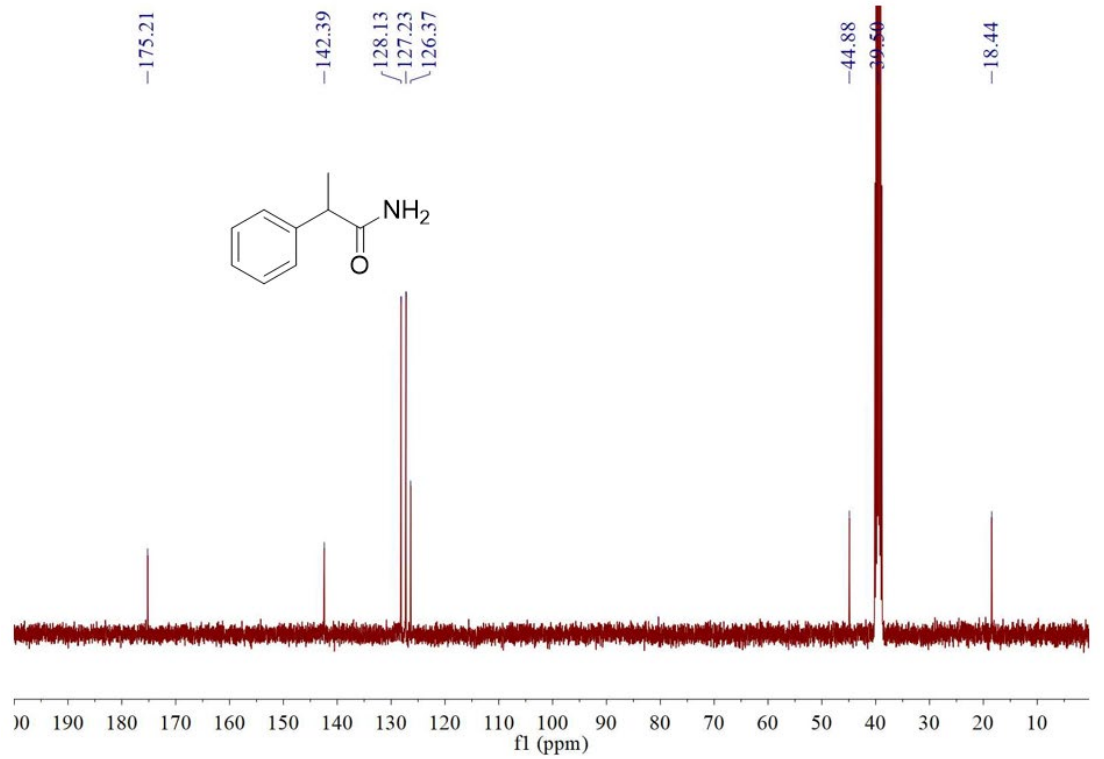


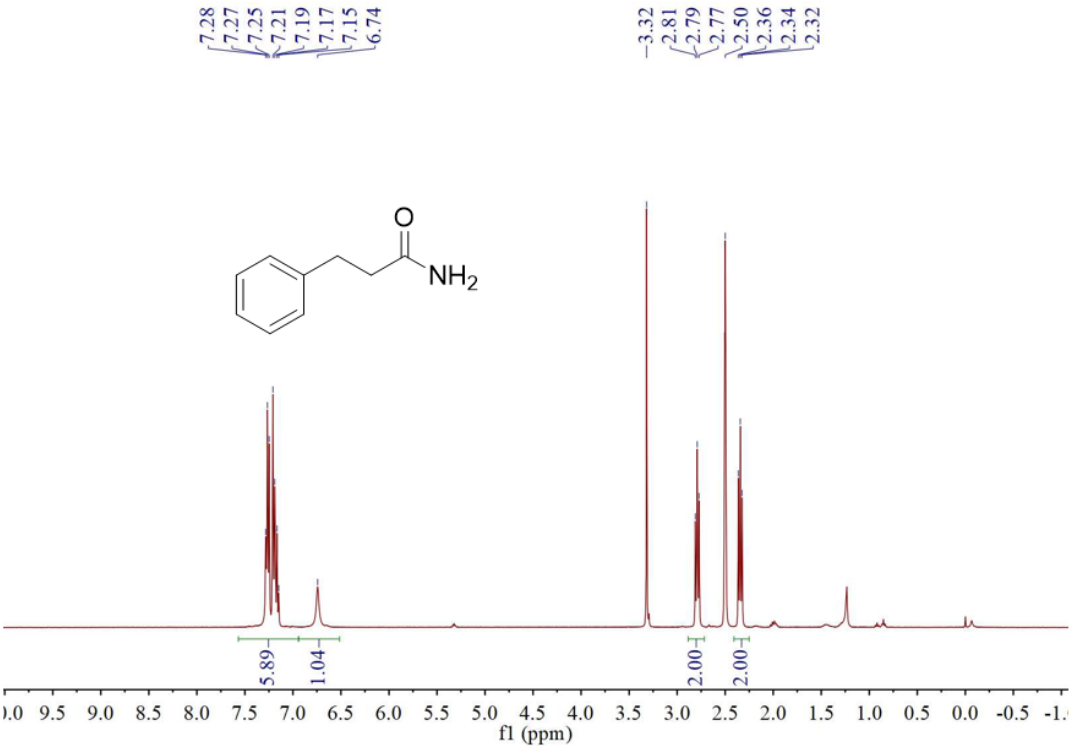


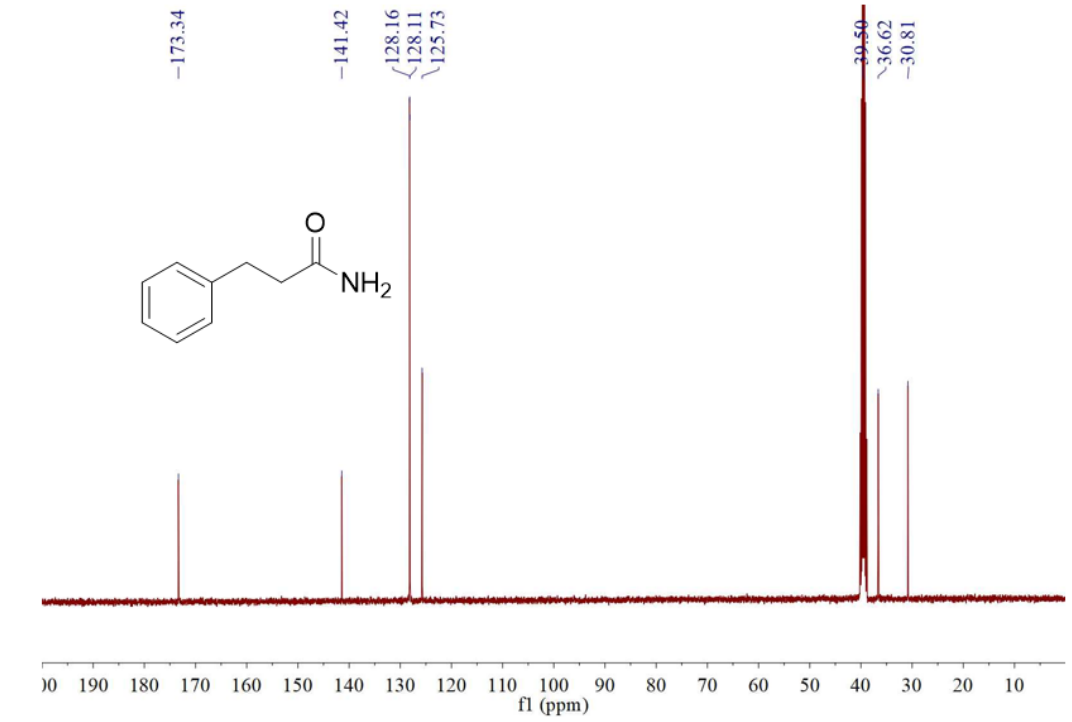

7.88
7.78
7.76
7.25
7.23
3.33
2.50
2.34
O
NH2
0.90
2.05
2.90
3.00
f1 (ppm)

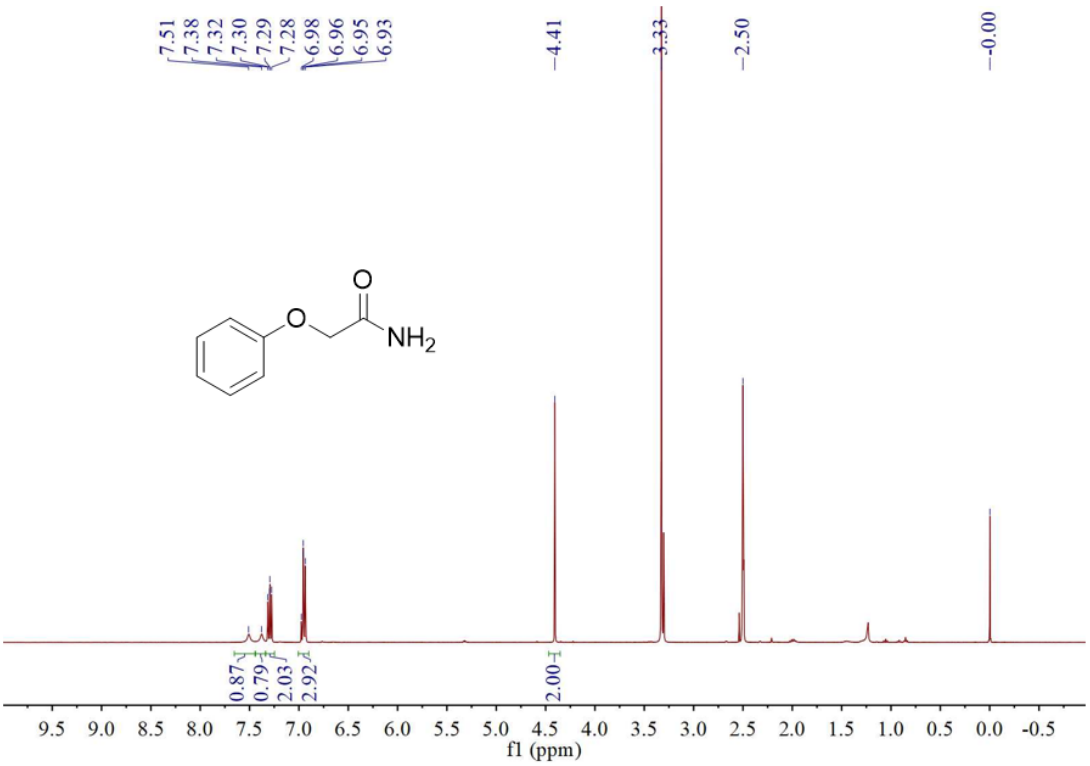

167.71
140.94
131.45
128.63
127.42
39.50
20.85
O
NH2
f1 (ppm)

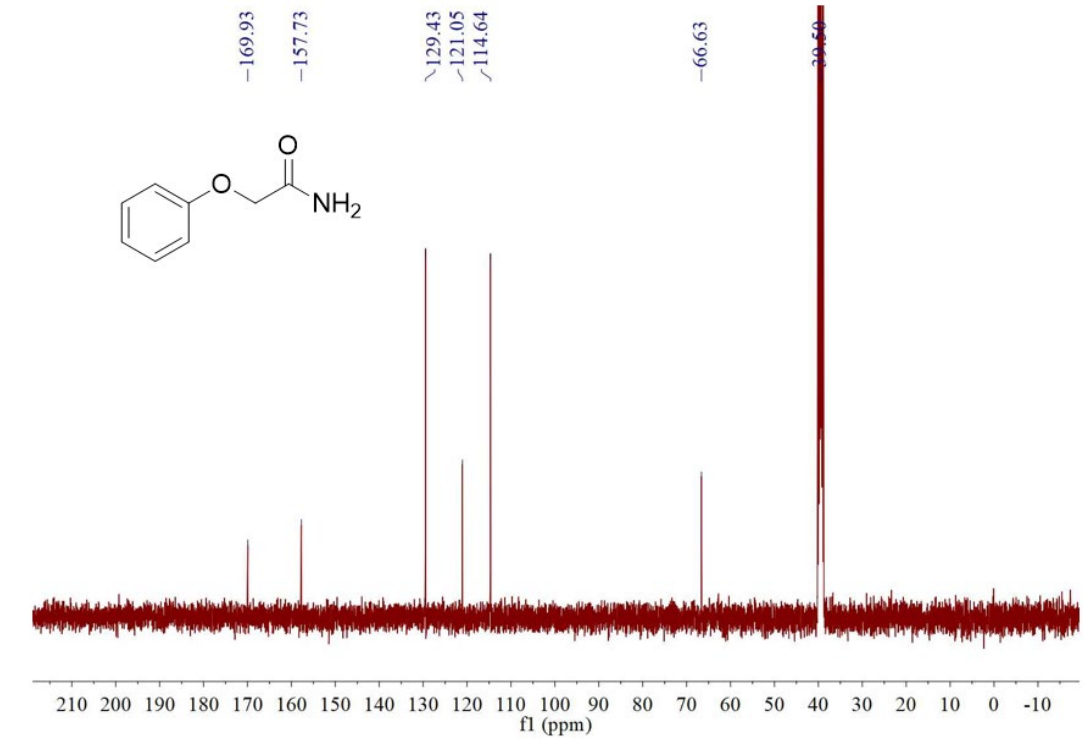

7.36
7.32
7.30
7.30
7.29
7.27
7.22
7.22
7.21
7.20
7.19
7.18
6.79
3.56
3.32
2.50
1.31
1.29
0.00
NH2
O
0.86
3.96
1.02
1.00
3.00
fl (ppm)

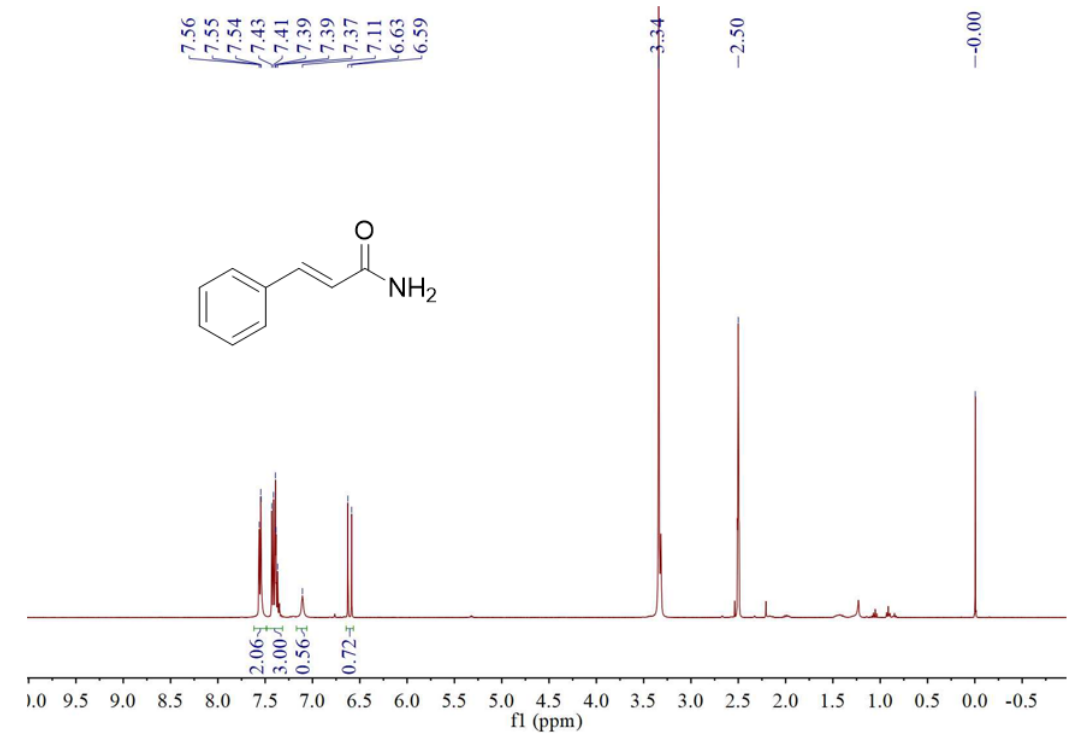

175.21
142.39
128.13
127.23
126.37
44.88
39.50
18.44
NH2
O
fl (ppm)

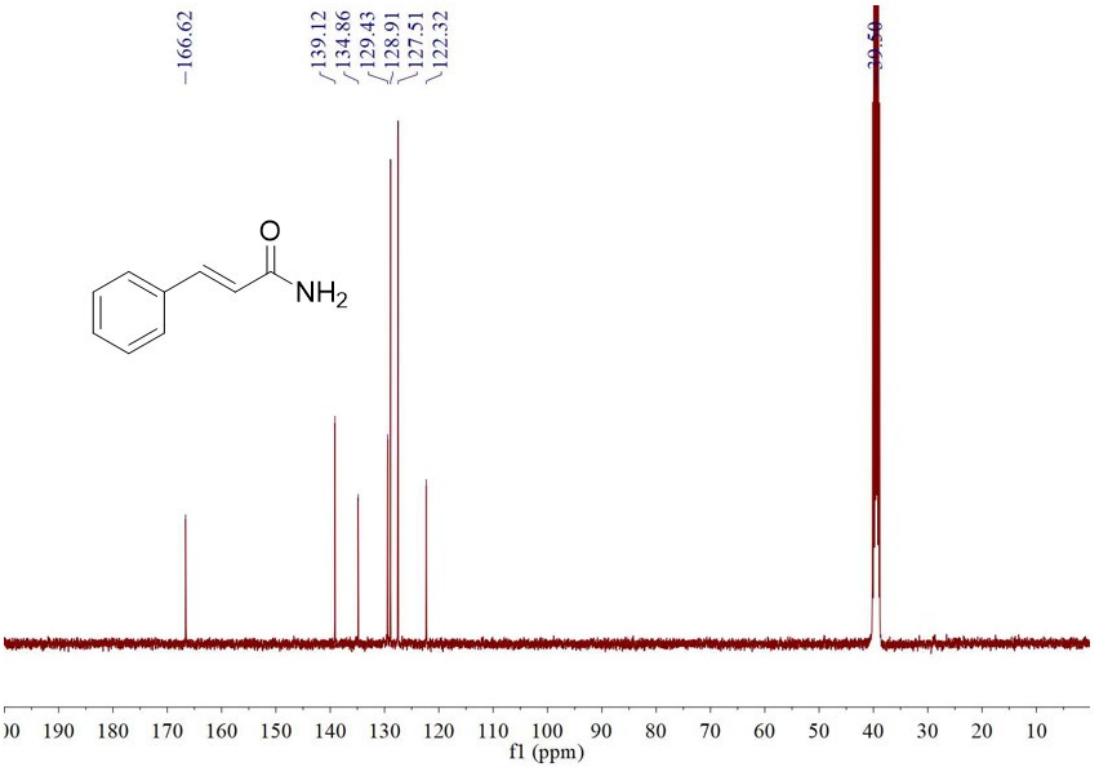

7.28
7.27
7.25
7.21
7.19
7.17
7.15
6.74
3.32
2.81
2.79
2.77
2.50
2.36
2.34
2.32
O
NH2
5.89
1.04
2.00
2.00
f1 (ppm)

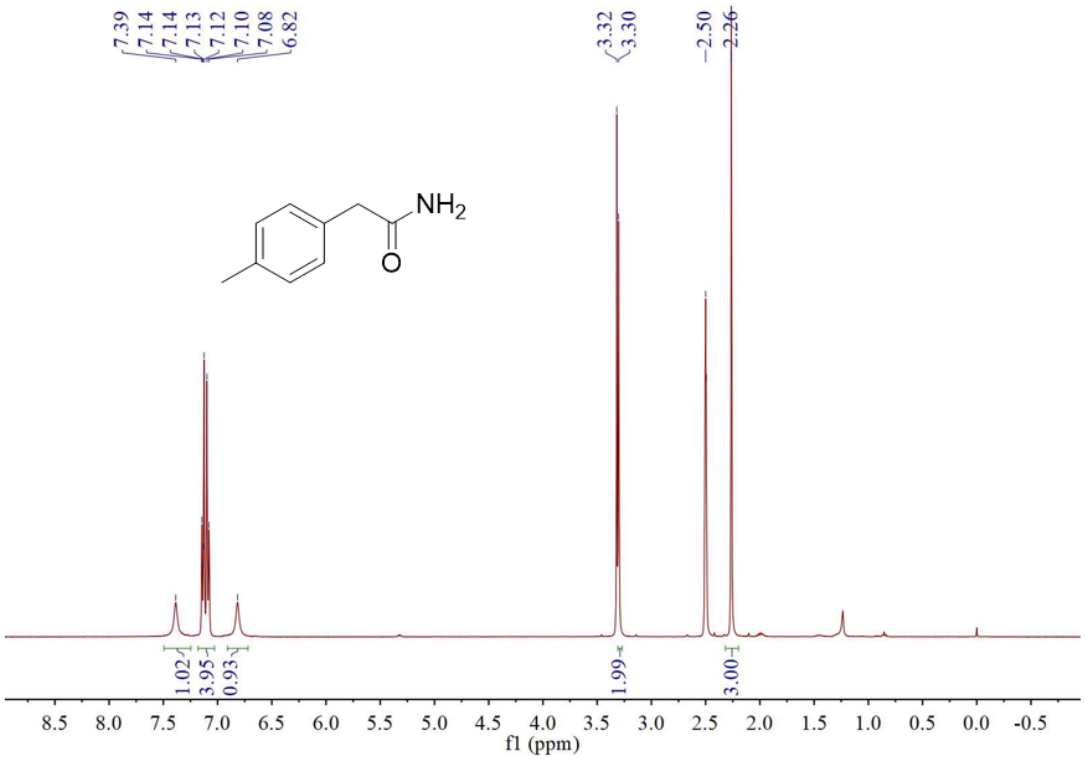

173.34
141.42
128.16
128.11
125.73
39.50
36.62
30.81
O
NH2
f1 (ppm)

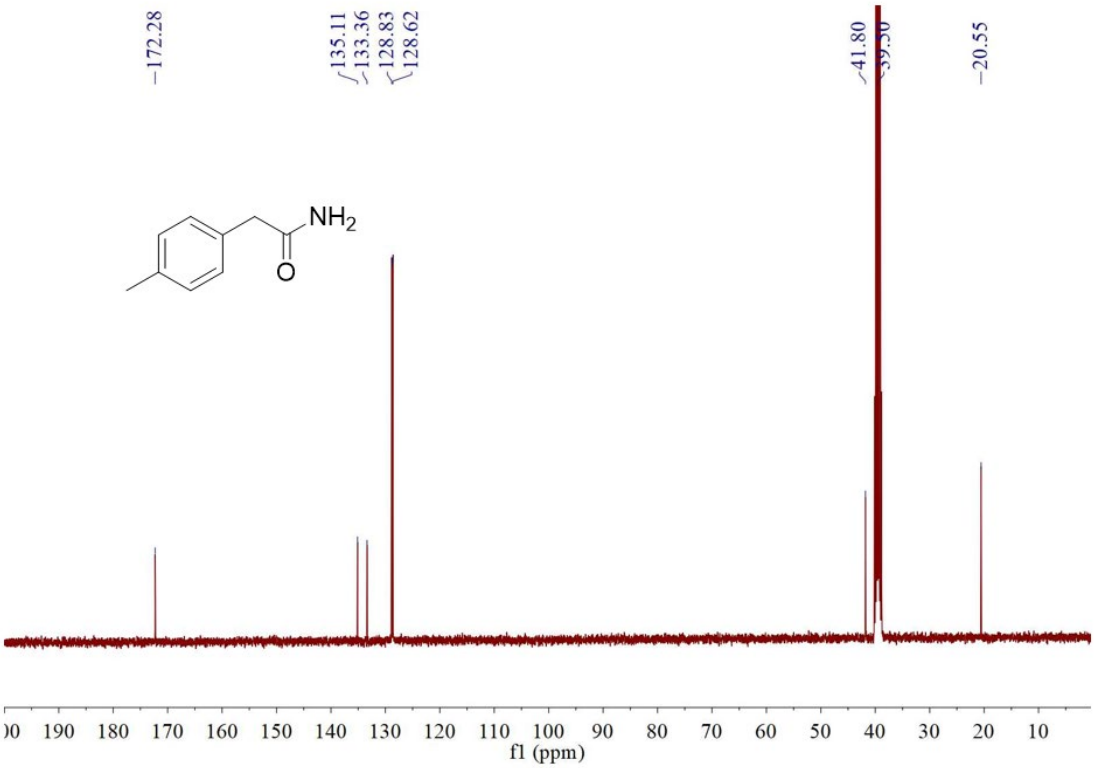

7.51
7.38
7.32
7.30
7.29
7.28
6.98
6.96
6.95
6.93
4.41
3.33
2.50
0.00
O
O
NH2
0.87
0.79
2.03
2.92
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

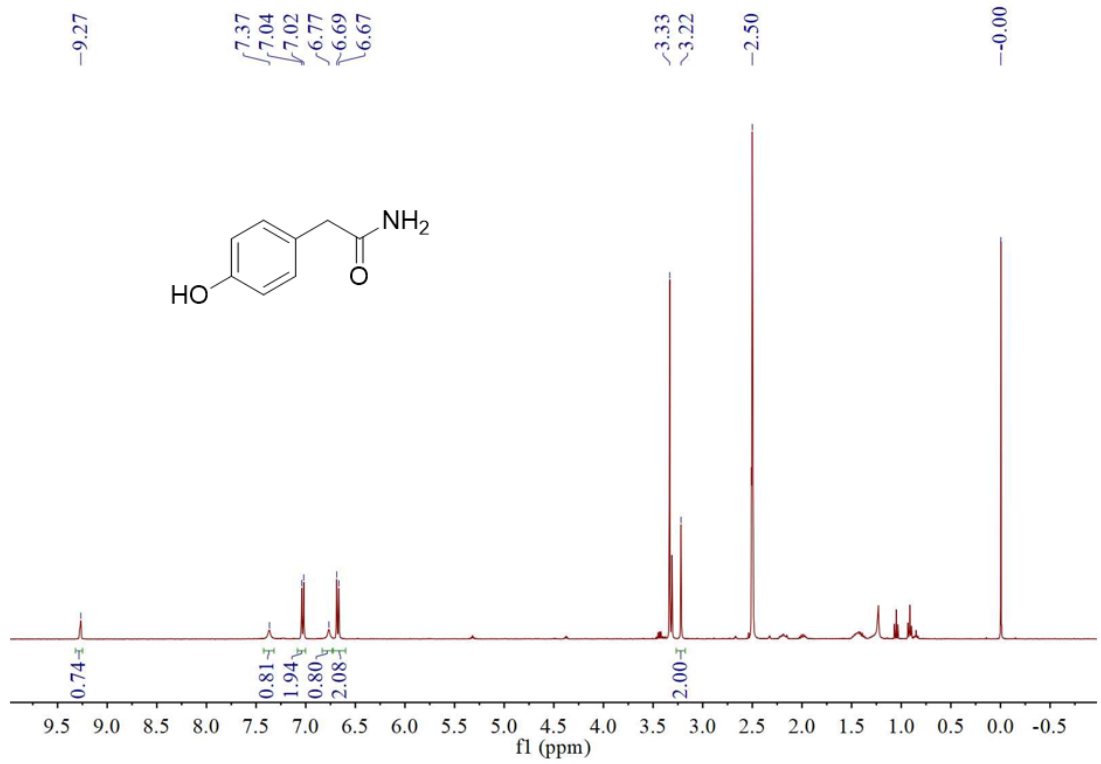

169.93
157.73
129.43
121.05
114.64
66.63
39.58
O
O
NH2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

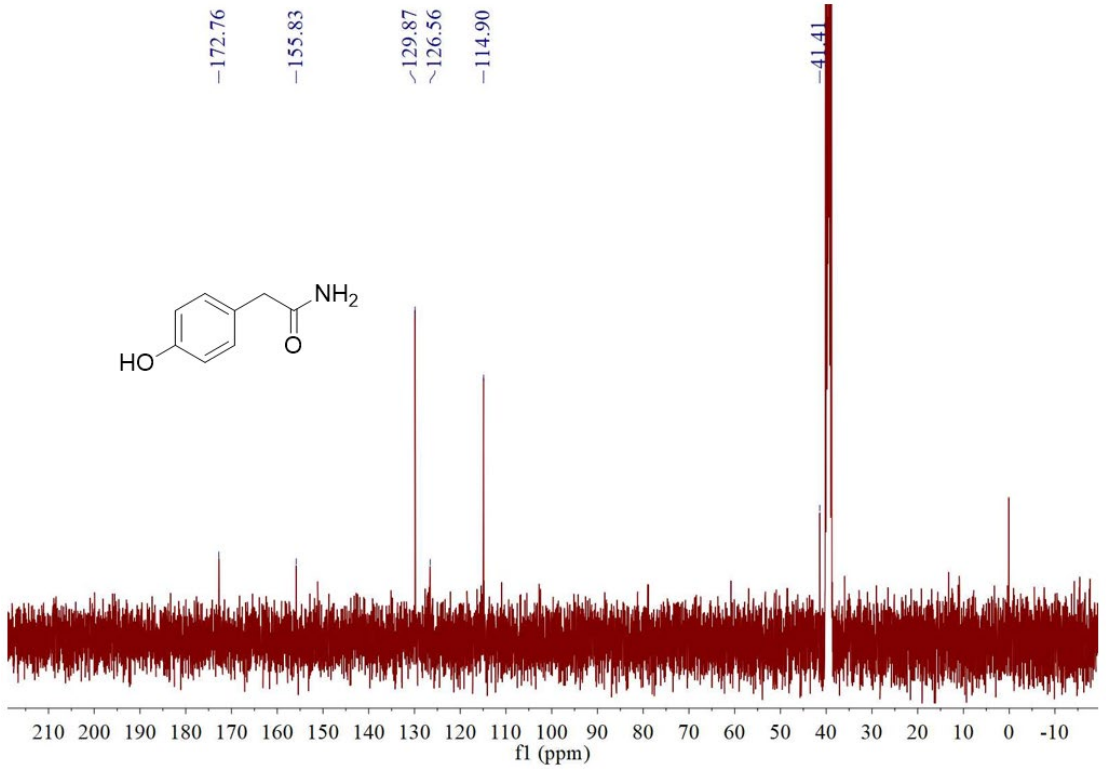

7.56
7.55
7.54
7.43
7.41
7.39
7.39
7.37
7.11
6.63
6.59
3.34
2.50
0.00
O
NH2
2.06
3.00
0.56
0.72
f1 (ppm)

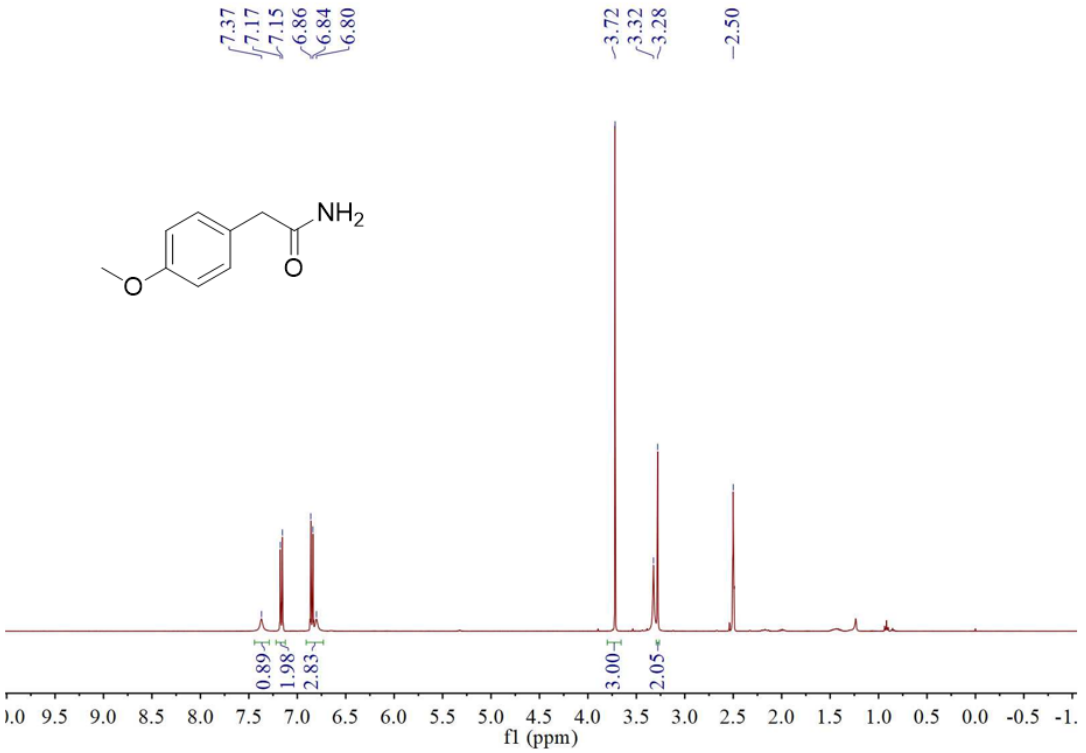

166.62
139.12
134.86
129.43
128.91
127.51
122.32
39.50
O
NH2
f1 (ppm)

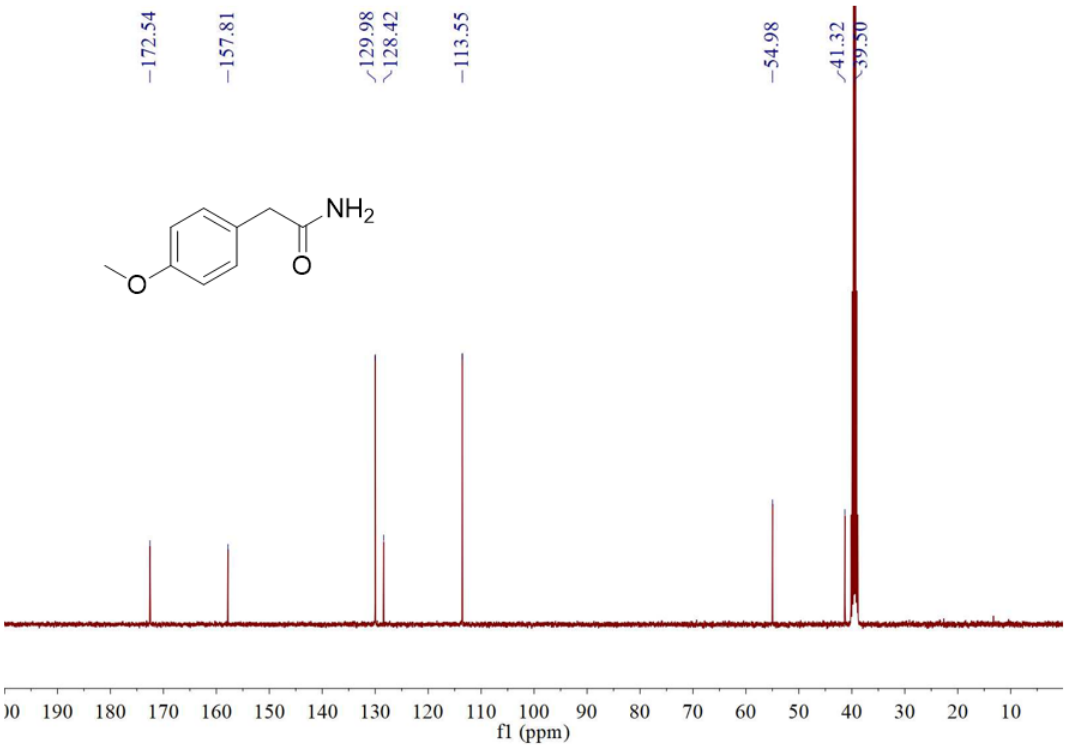

7.39
7.14
7.14
7.13
7.12
7.10
7.08
6.82
3.32
3.30
2.50
2.26
NH2
O
1.02
3.95
0.93
1.99
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


172.28
135.11
133.36
128.83
128.62
41.80
39.50
20.55
NH2
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


9.27
7.37
7.04
7.02
6.77
6.69
6.67
3.33
3.22
2.50
0.00
NH2
O
HO
0.74
0.81
1.94
0.80
2.08
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


172.76
155.83
129.87
126.56
114.90
41.41
NH2
O
HO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.37
7.17
7.15
6.86
6.84
6.80
3.72
3.32
3.28
2.50
NH2
O
O
0.89
1.98
2.83
3.00
2.05
f1 (ppm)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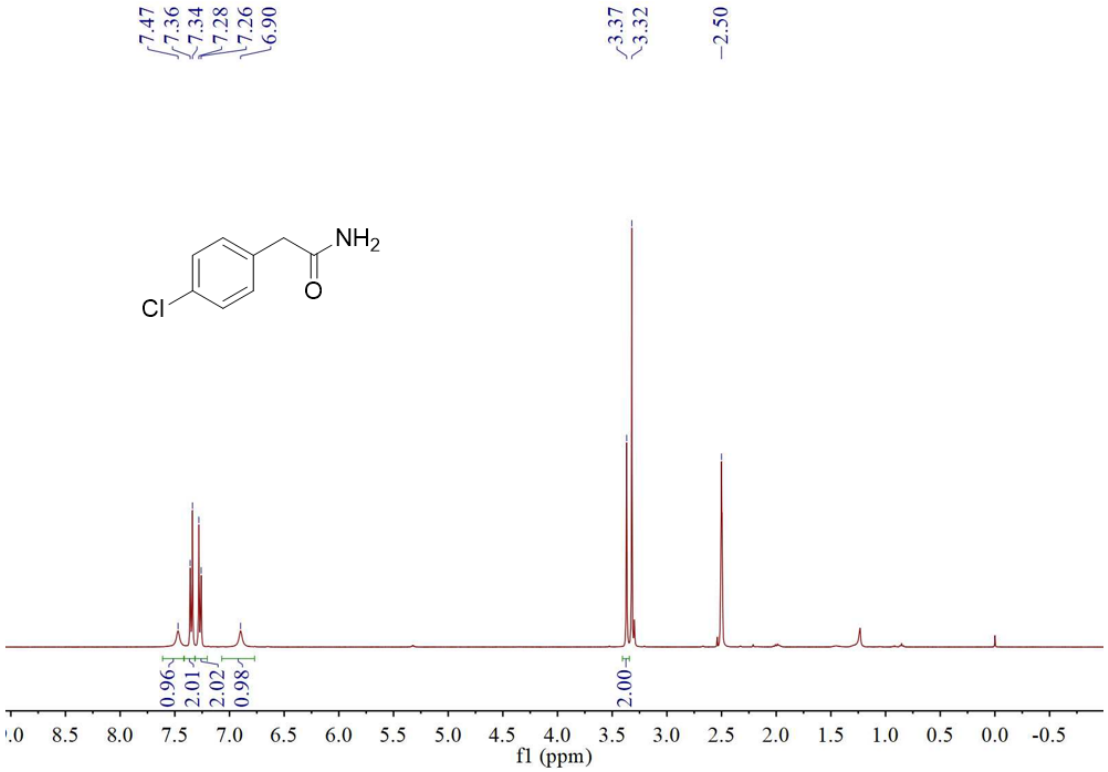
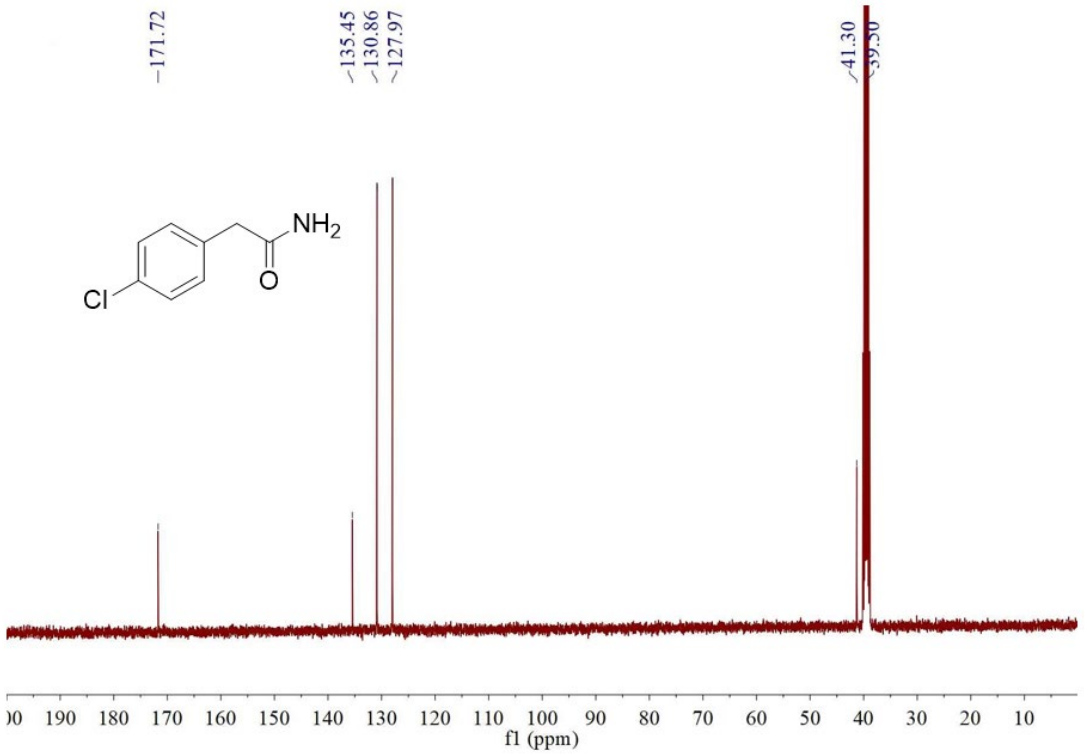
157.81
129.98
128.42
113.55
54.98
41.32
39.50
NH2
O
O
f1 (ppm)


7.47
7.36
7.34
7.28
7.26
6.90
3.37
3.32
2.50
NH2
O
Cl
0.96
2.01
2.02
0.98
2.00
fl (ppm)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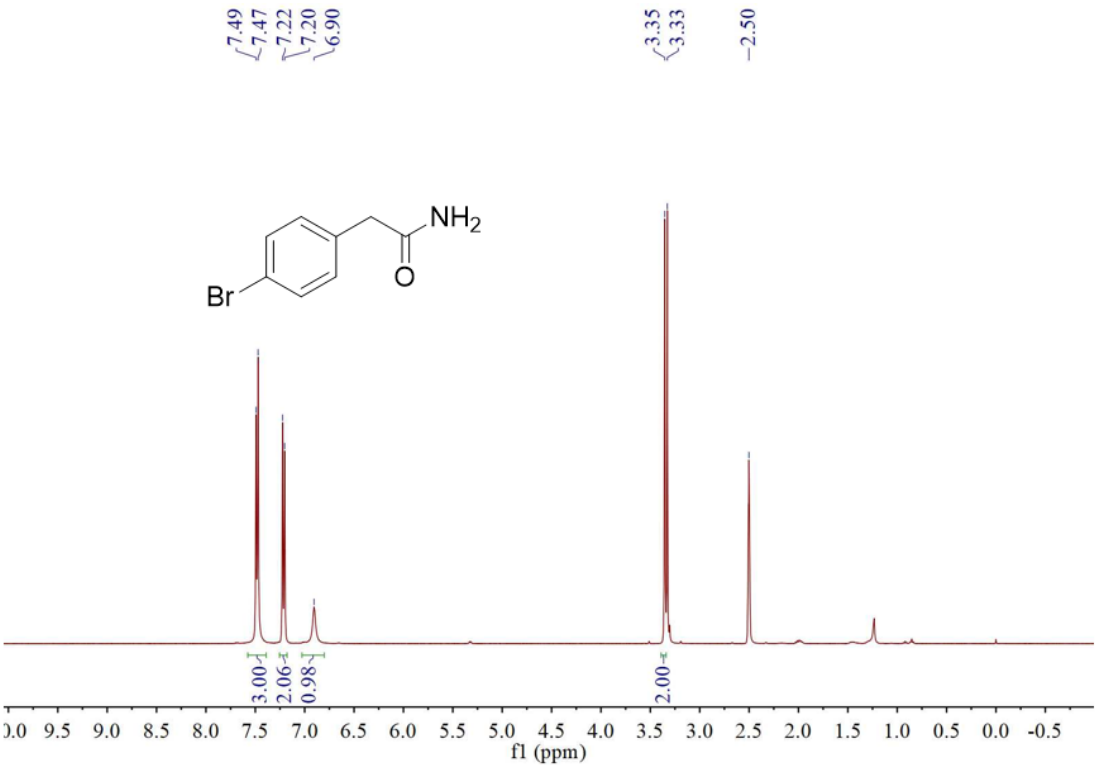
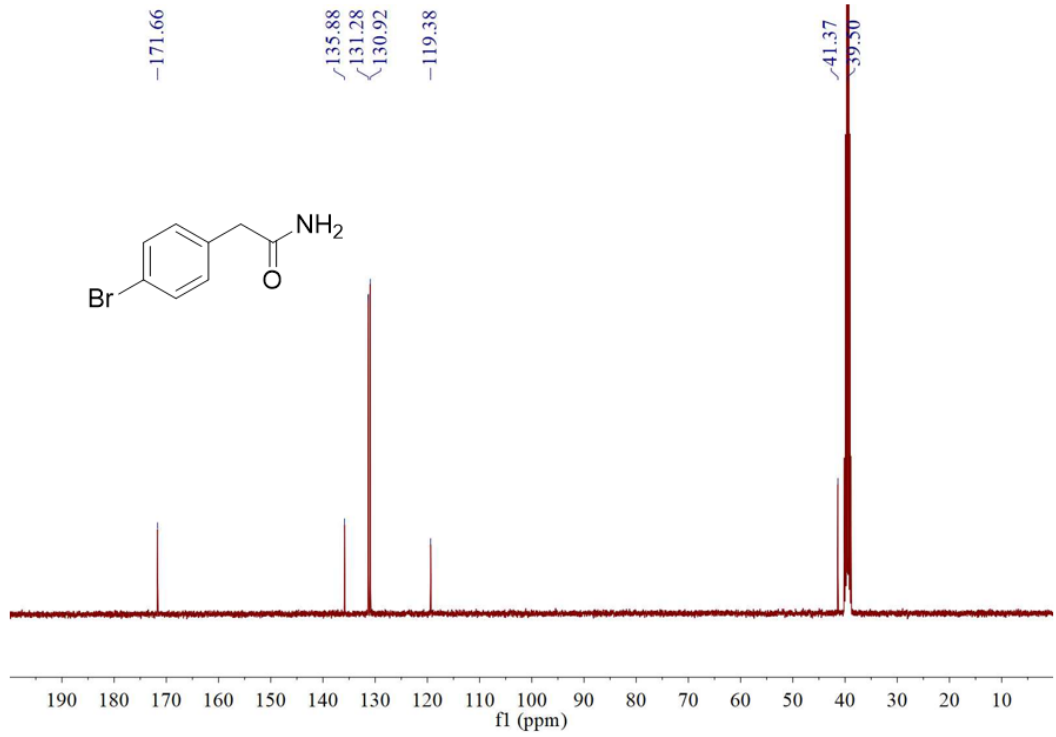
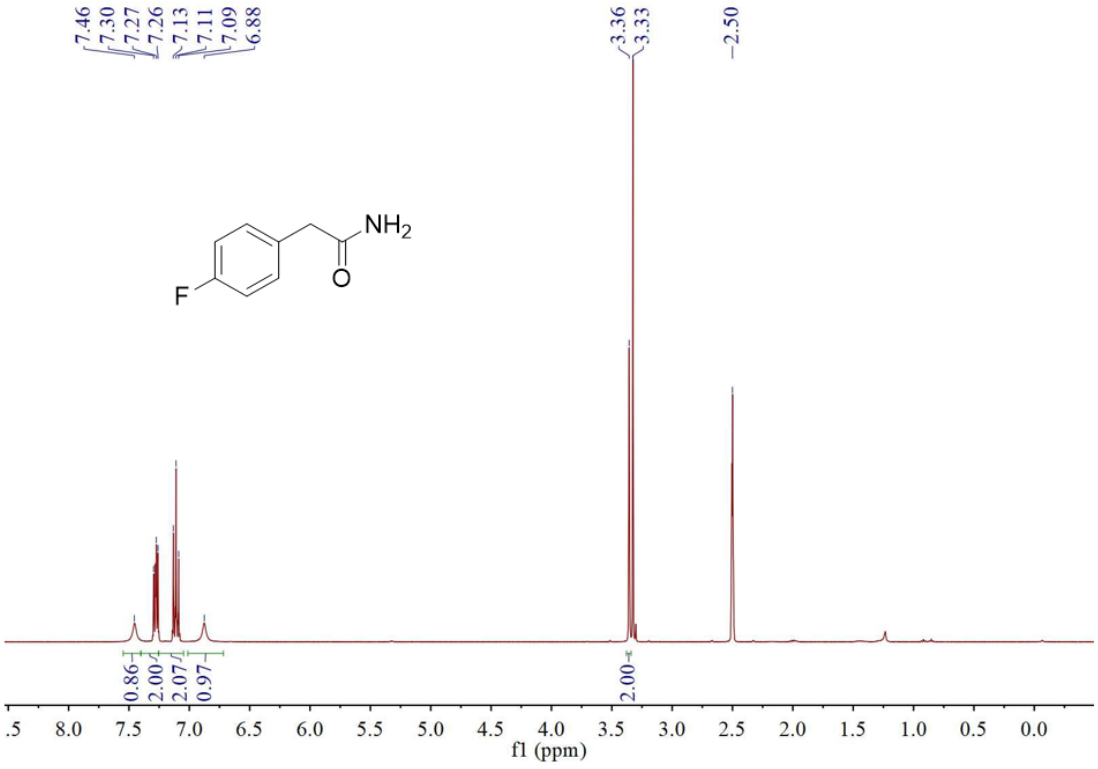
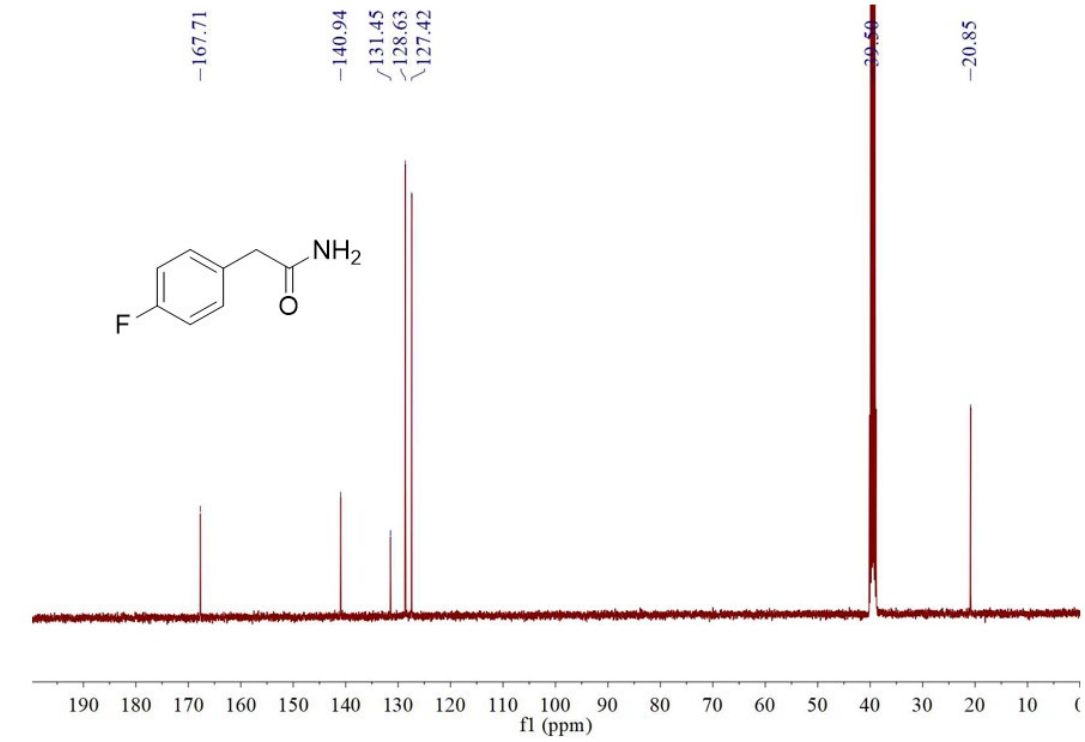
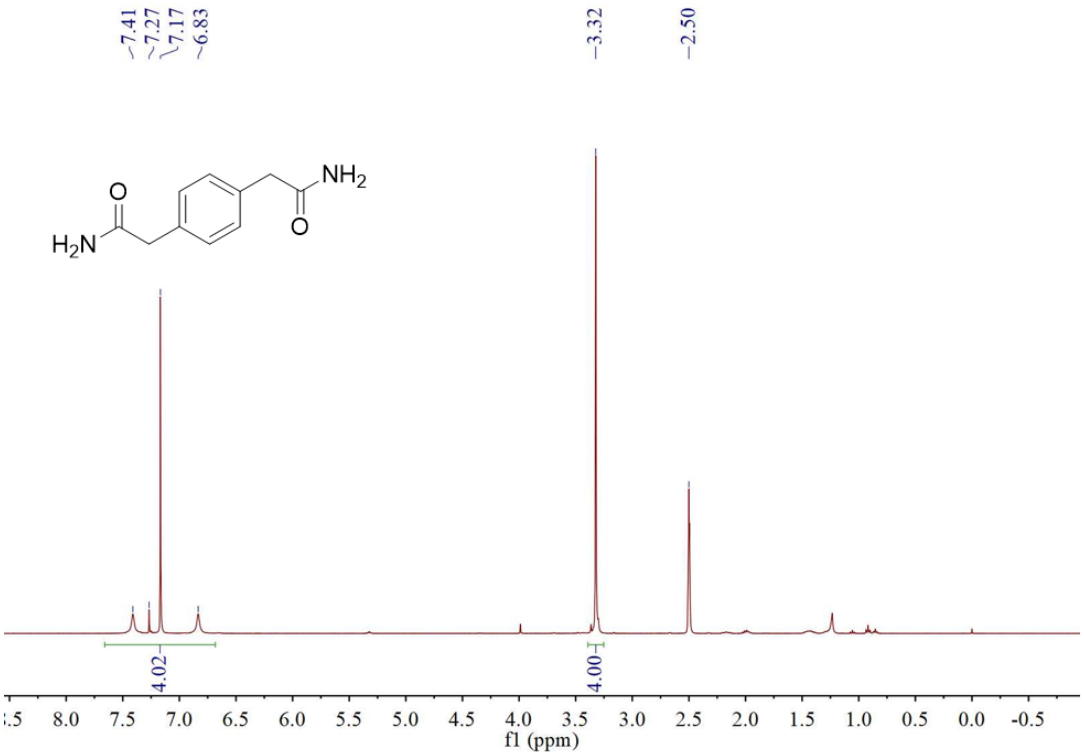
135.45
130.86
127.97
41.30
39.50
NH2
O
Cl
fl (ppm)

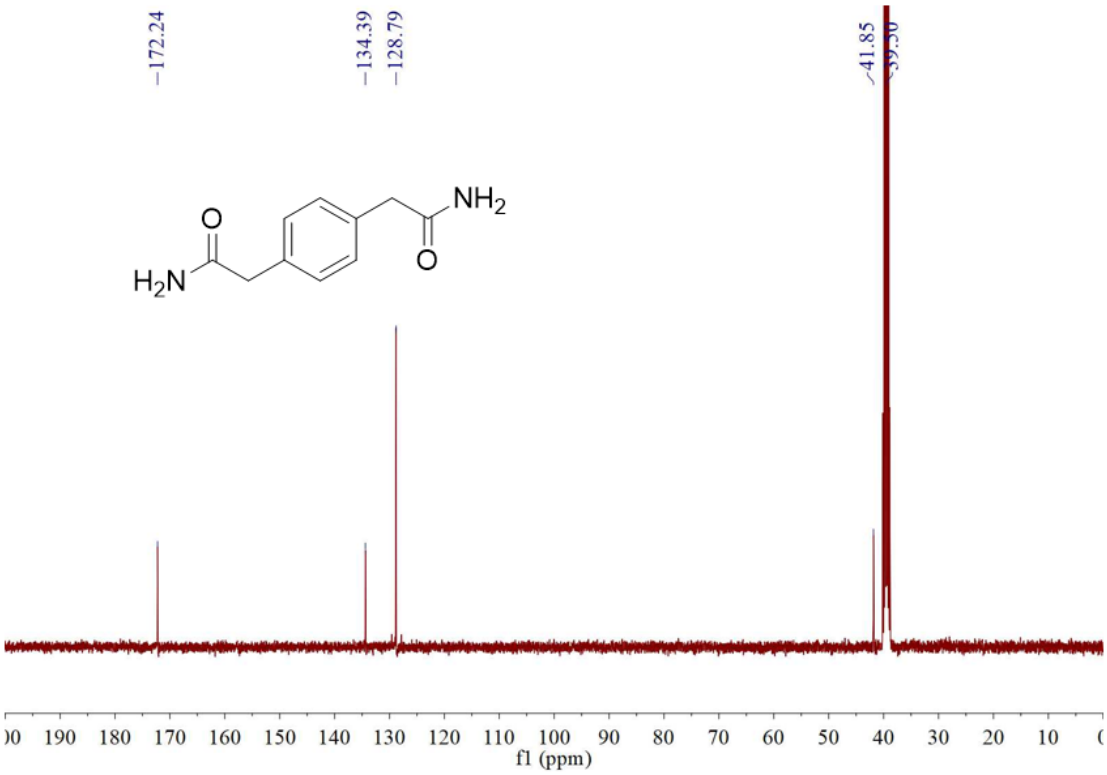

7.49
7.47
7.22
7.20
6.90
3.35
3.33
2.50
NH2
O
Br
3.00
2.06
0.98
2.00
f1 (ppm)

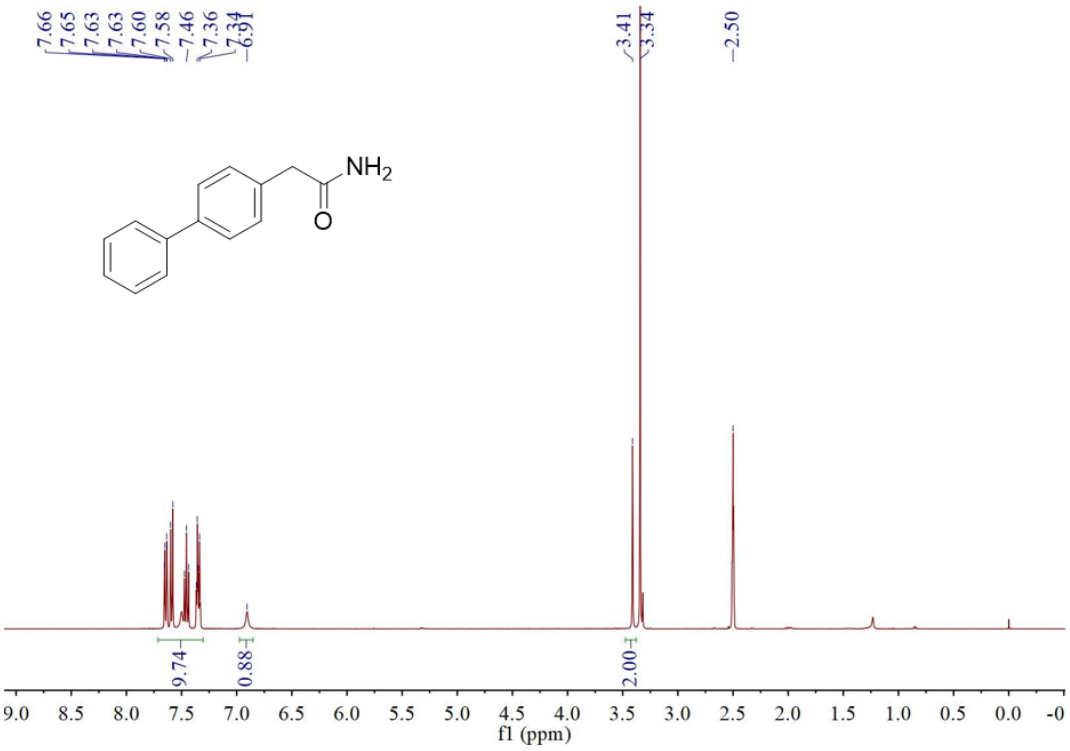

171.66
135.88
131.28
130.92
119.38
41.37
39.50
NH2
O
Br
f1 (ppm)

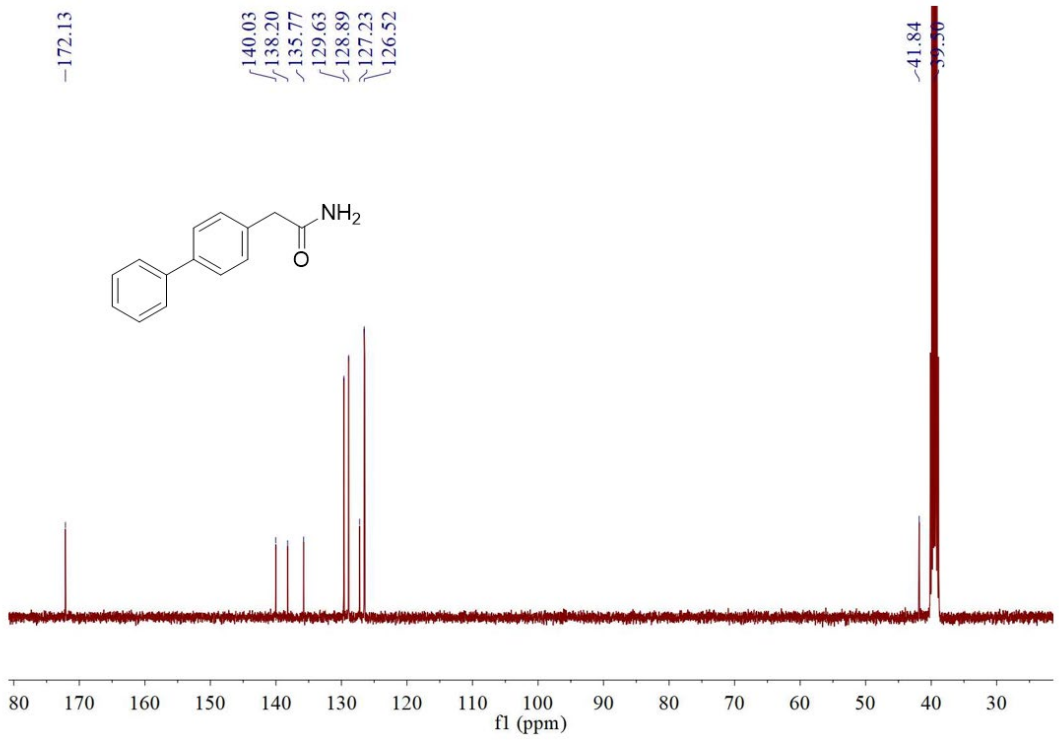

7.46
7.30
7.27
7.26
7.13
7.11
7.09
6.88
3.36
3.33
2.50
NH2
O
F
0.86
2.00
2.07
0.97
2.00
f1 (ppm)

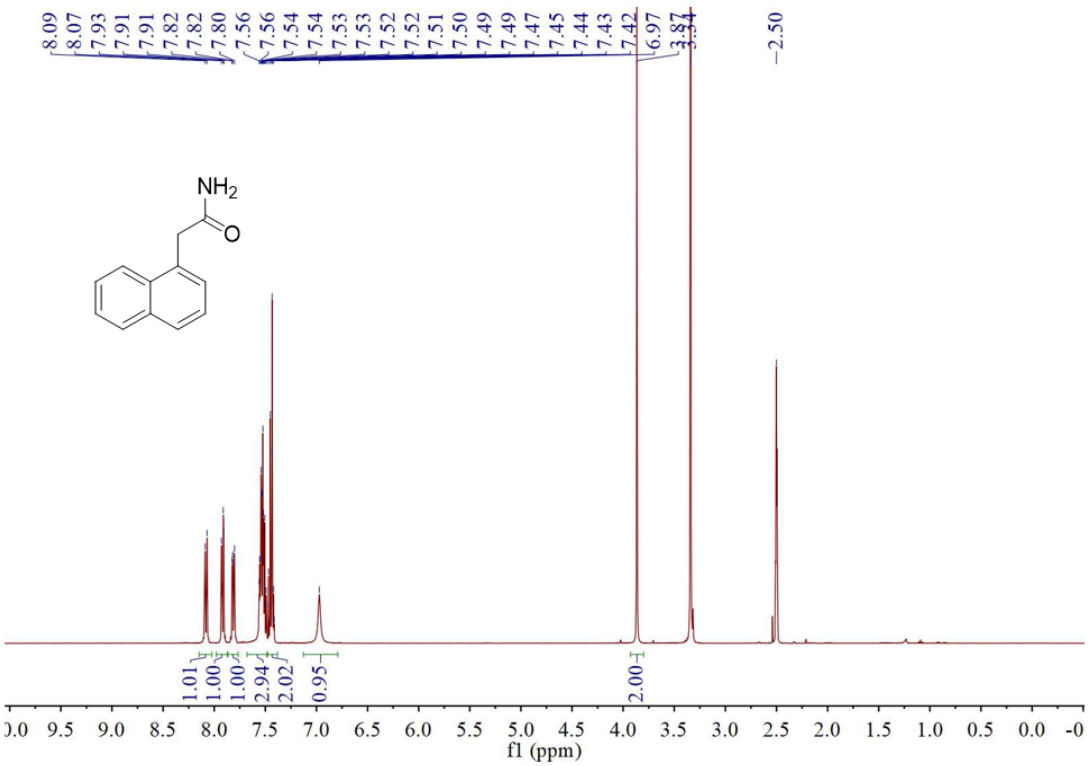

167.71
140.94
131.45
128.63
127.42
39.50
20.85
NH2
O
F
f1 (ppm)

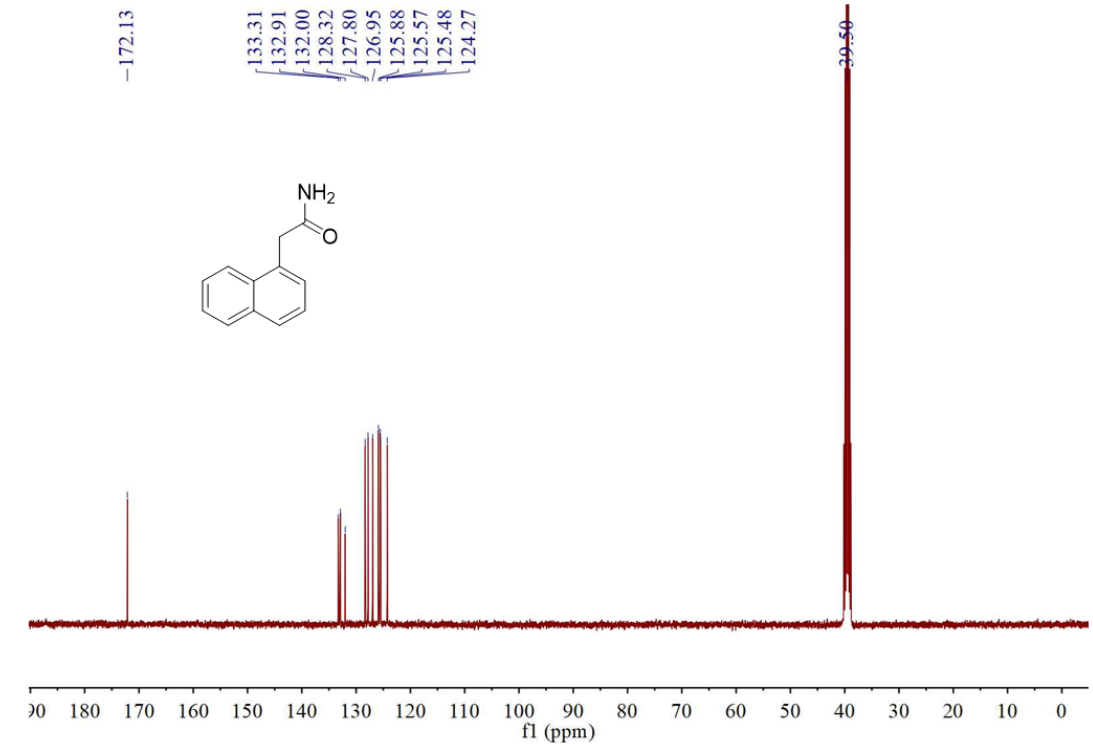

7.41
7.27
7.17
6.83
3.32
2.50
O
NH2
H2N
O
4.02
4.00
f1 (ppm)


172.24
134.39
128.79
41.85
39.50
O
NH2
H2N
O
f1 (ppm)


7.66
7.65
7.63
7.63
7.60
7.58
7.46
7.36
7.34
6.91
3.41
3.34
2.50
NH2
O
9.74
0.88
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


172.13
140.03
138.20
135.77
129.63
128.89
127.23
126.52
41.84
39.50
NH2
O
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)


8.09
8.07
7.93
7.91
7.91
7.82
7.82
7.80
7.56
7.56
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.49
7.49
7.47
7.45
7.44
7.43
7.42
6.97
3.87
3.54
2.50
NH2
O
1.01
1.00
1.00
2.94
2.02
0.95
2.00
f1 (ppm)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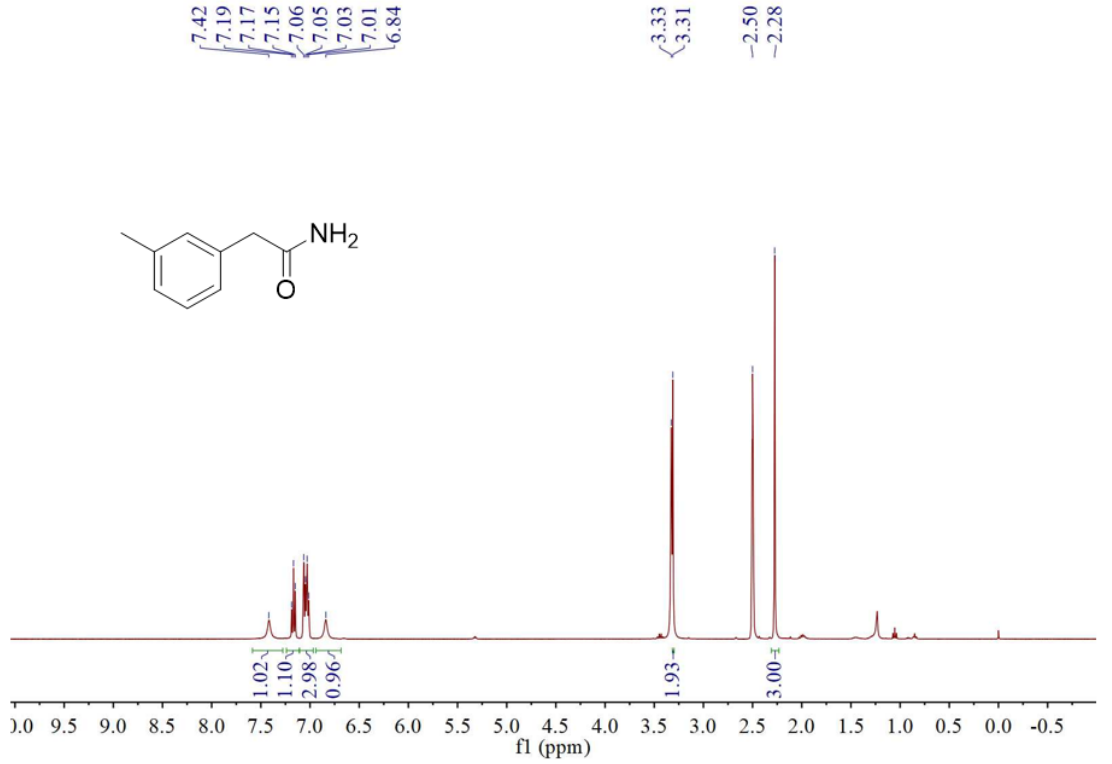
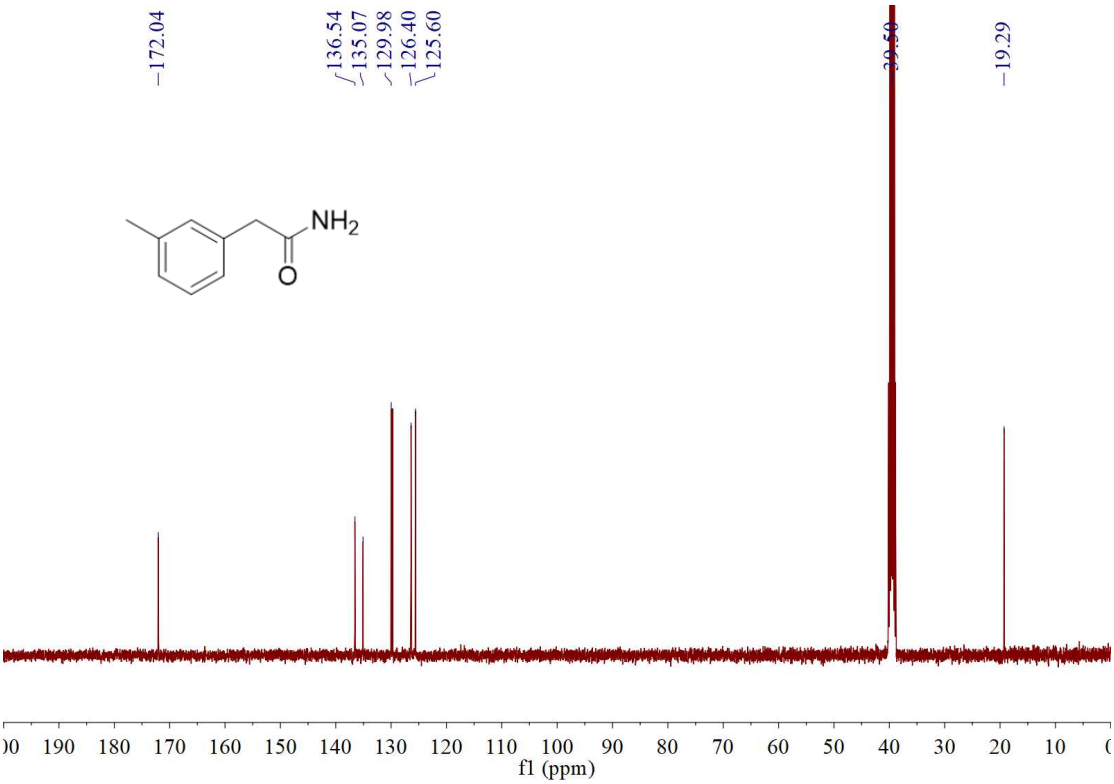
133.31
132.91
132.00
128.32
127.80
126.95
125.88
125.57
125.48
124.27
39.50
NH2
O
f1 (ppm)


7.42
7.19
7.17
7.15
7.06
7.05
7.03
7.01
6.84
3.33
3.31
2.50
2.28
NH2
O
1.02
1.10
2.98
0.96
1.93
3.00
fl (ppm)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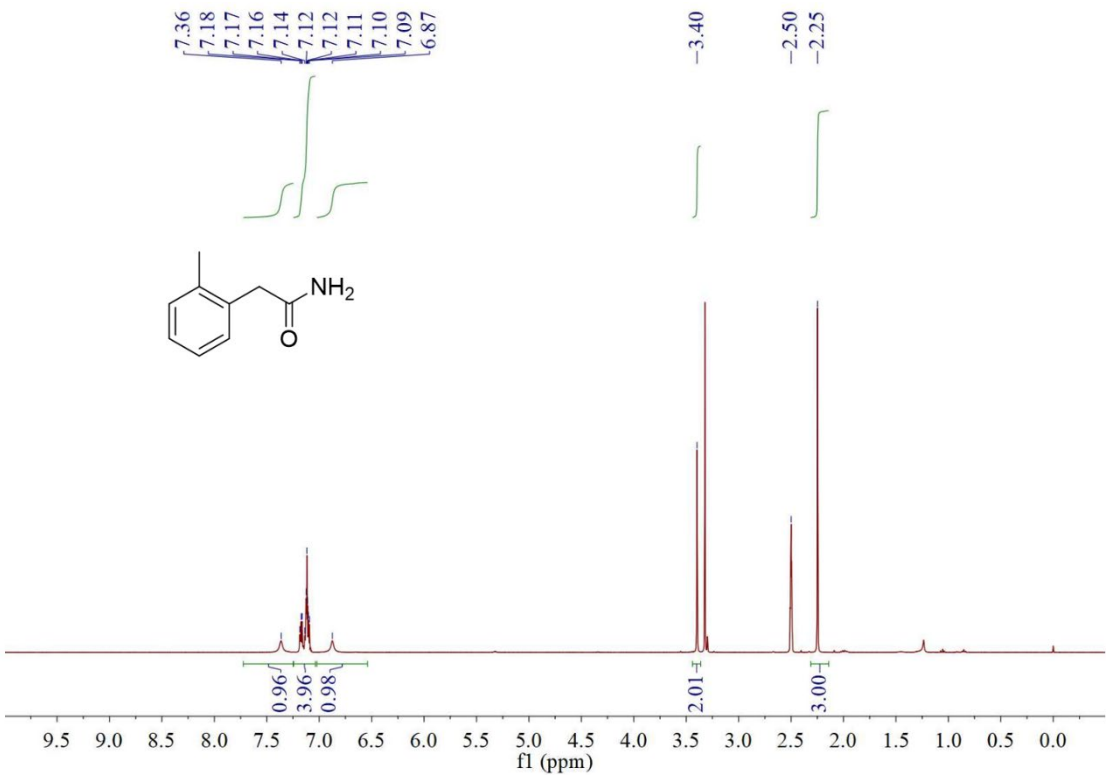
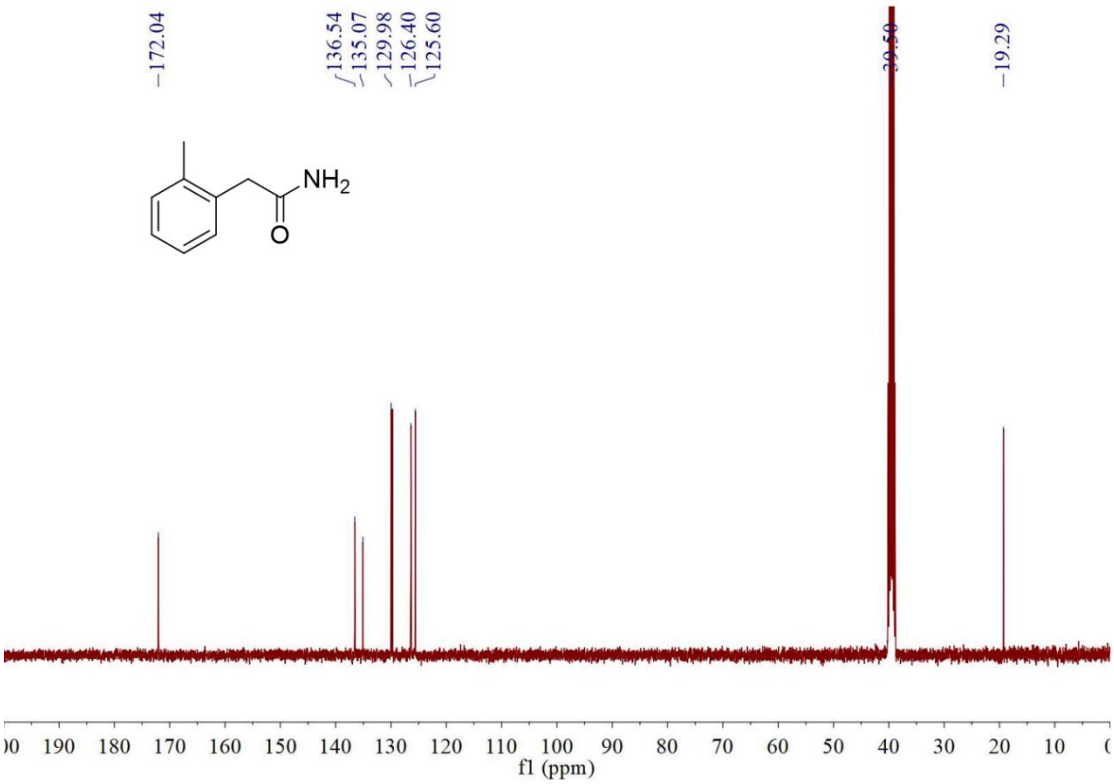
136.54
135.07
129.98
126.40
125.60
39.50
19.29
NH2
O
fl (ppm)


7.36
7.18
7.17
7.16
7.14
7.12
7.12
7.11
7.10
7.09
6.87
3.40
2.50
2.25
NH2
O
0.96
3.96
0.98
2.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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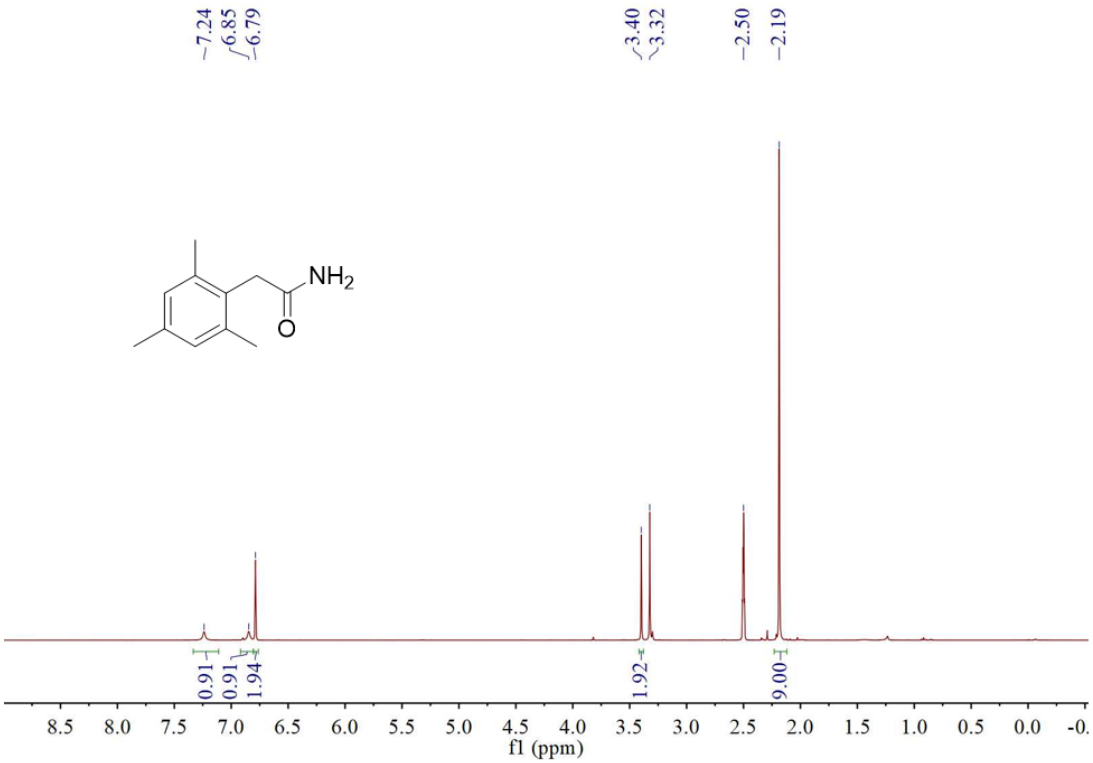
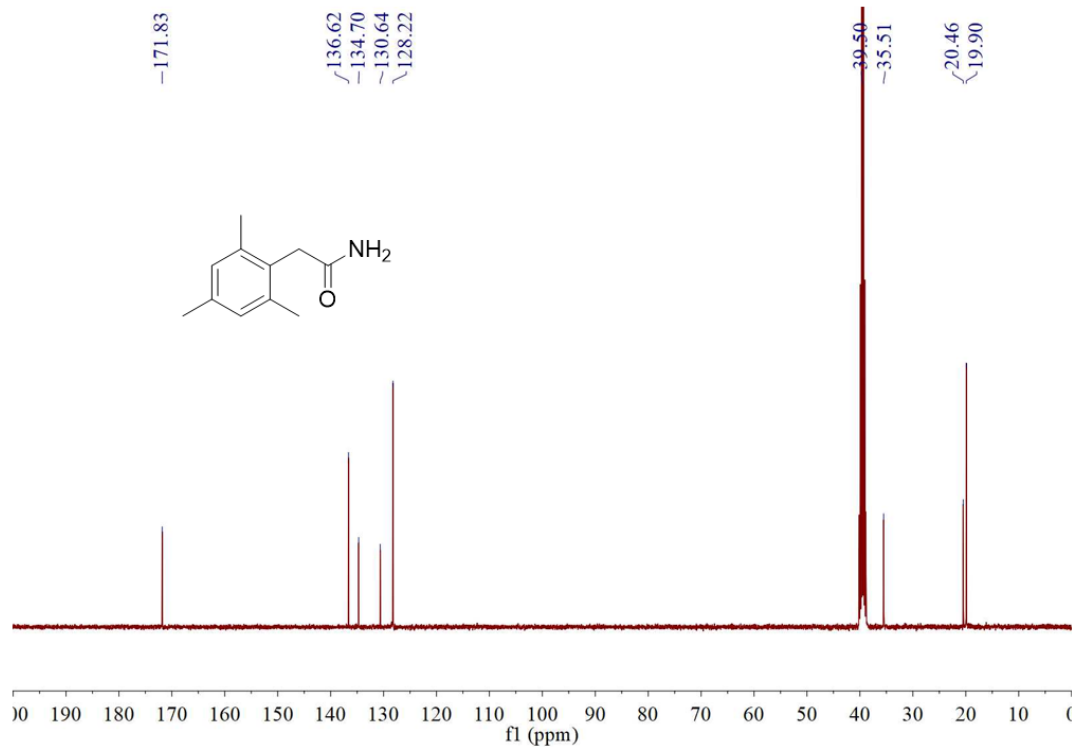
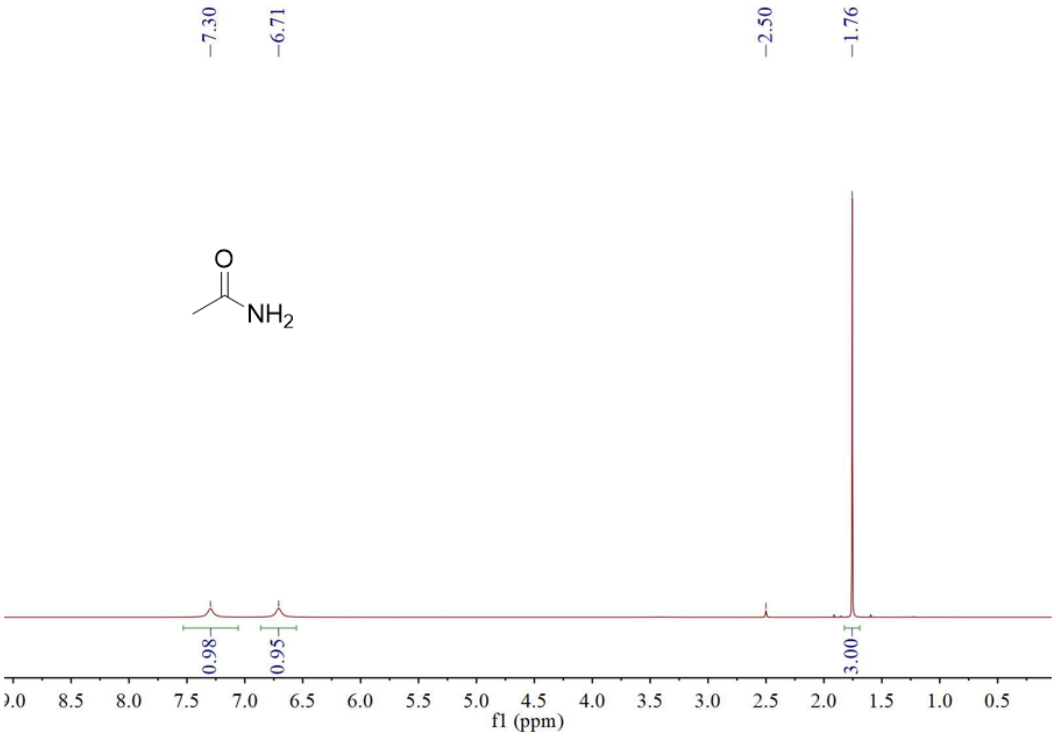
136.54
135.07
129.98
126.40
125.60
39.50
19.29
NH2
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.24
6.85
6.79
3.40
3.32
2.50
2.19
NH2
O
0.91
0.91
1.94
1.92
9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.83
136.62
134.70
130.64
128.22
39.50
35.51
20.46
19.90
NH2
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.30
6.71
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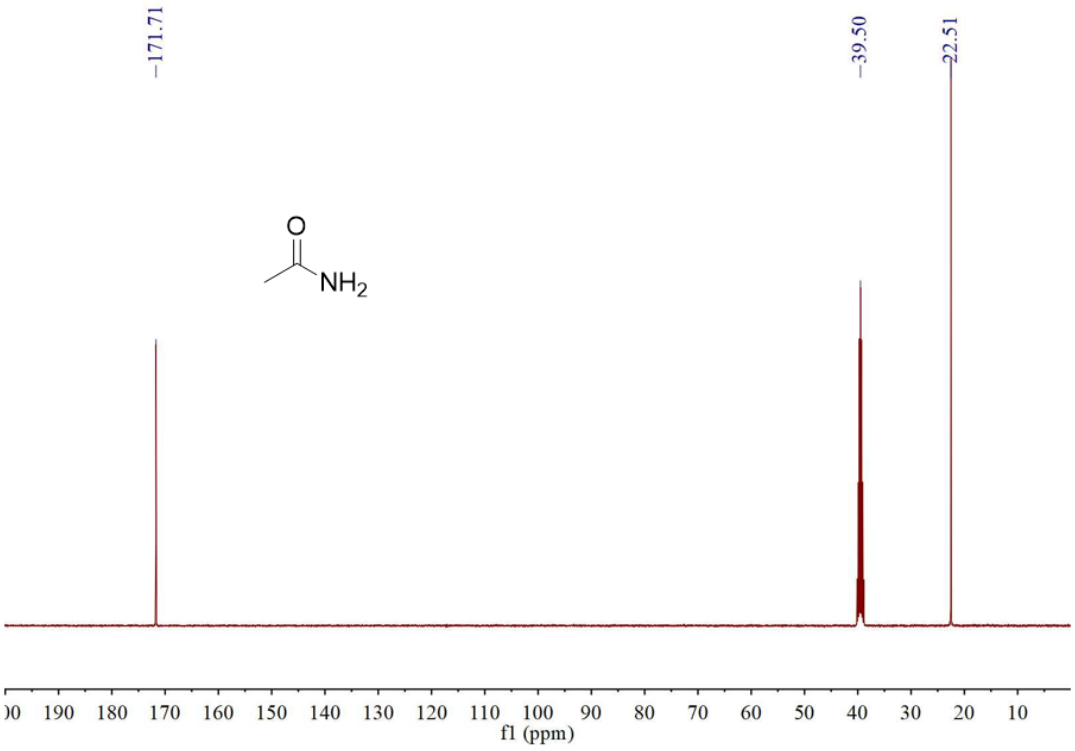
1.76
O
NH2
0.98
0.95
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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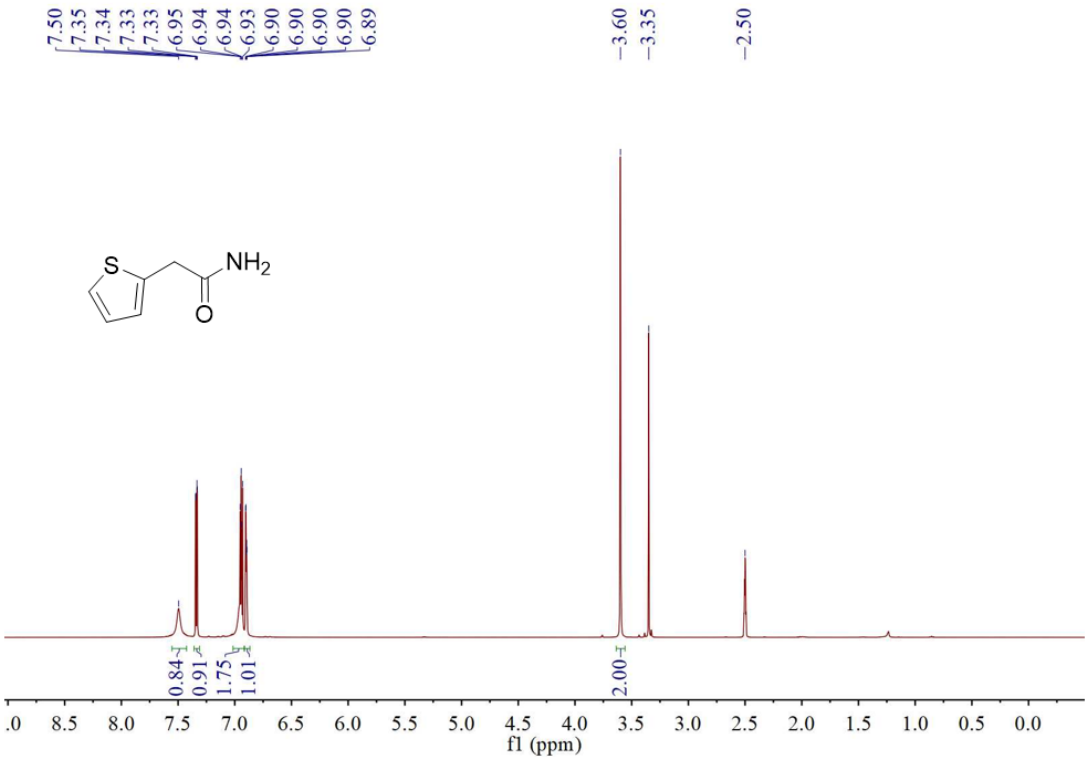
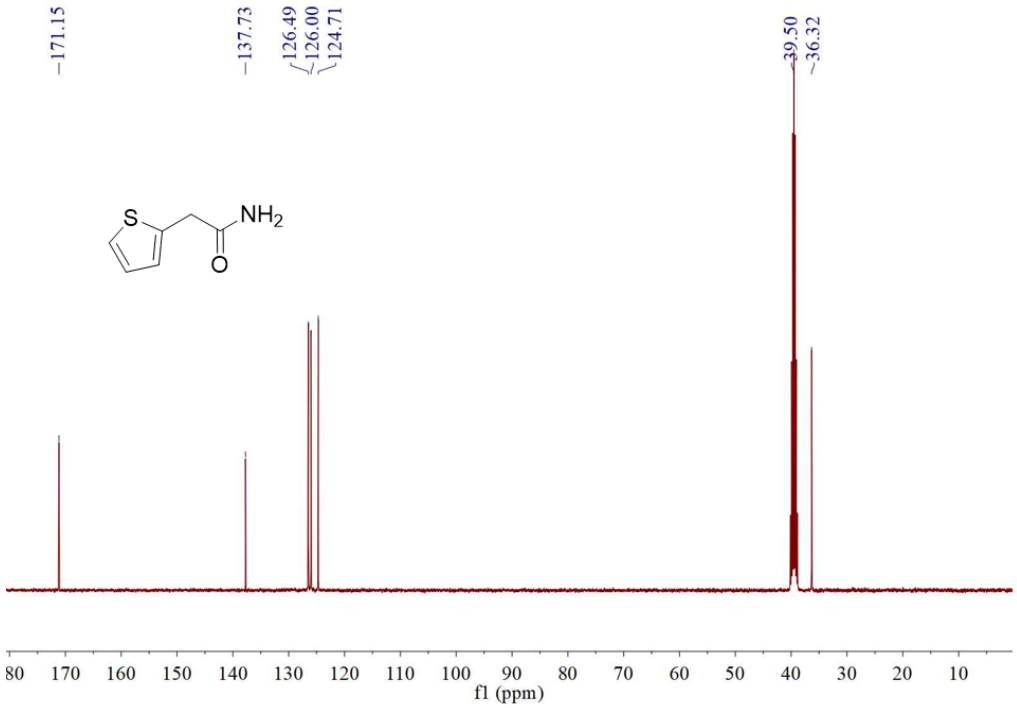
39.50
22.51
O
NH2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.50
7.35
7.34
7.33
7.33
6.95
6.94
6.94
6.93
6.90
6.90
6.90
6.90
6.89
3.60
3.35
2.50
S
NH2
O
0.84
0.91
1.75
1.01
2.00
f1 (ppm)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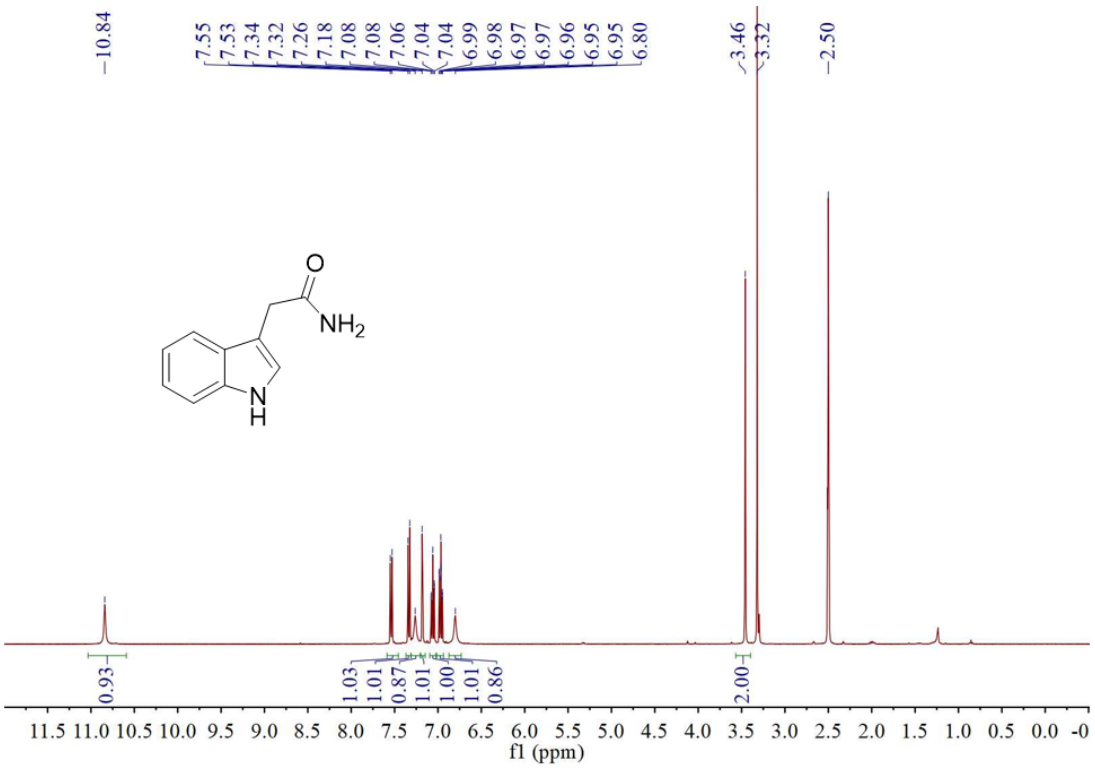
126.00
124.71
39.50
36.32
S
NH2
O
f1 (ppm)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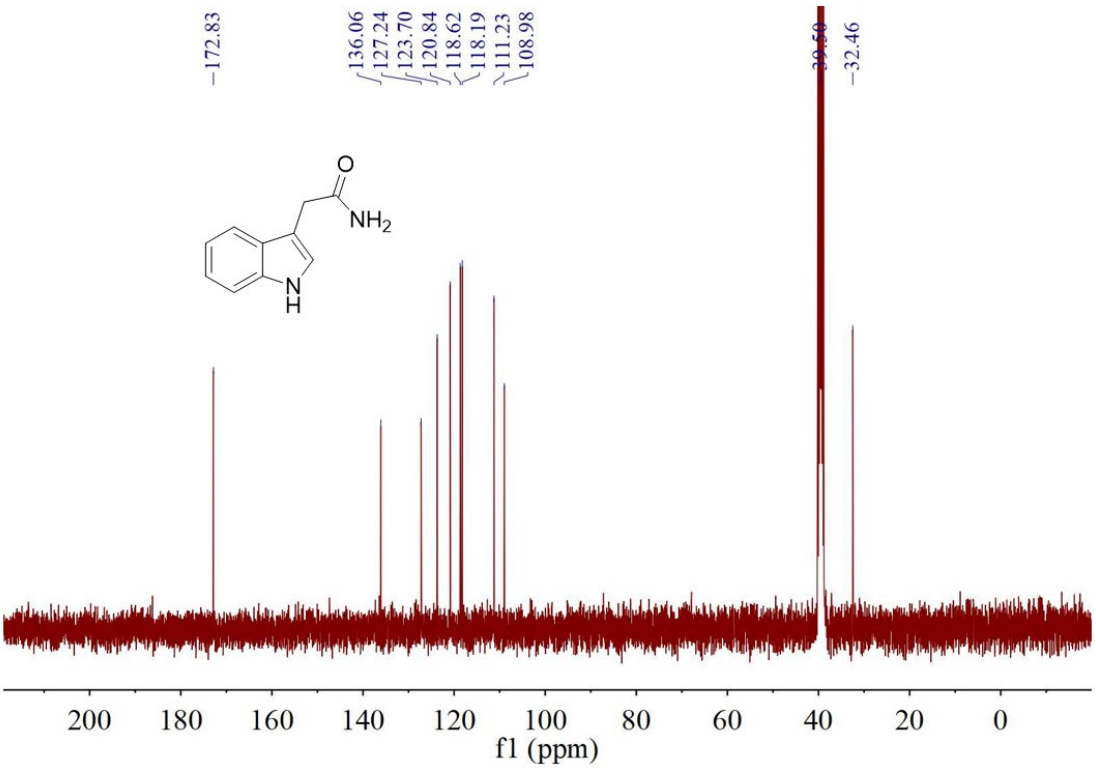
7.55
7.53
7.34
7.32
7.26
7.18
7.08
7.08
7.06
7.04
7.04
6.99
6.98
6.97
6.97
6.96
6.95
6.95
6.80
3.46
3.32
2.50
O
NH2
N
H
0.93
1.03
1.01
0.87
1.01
1.00
1.01
0.86
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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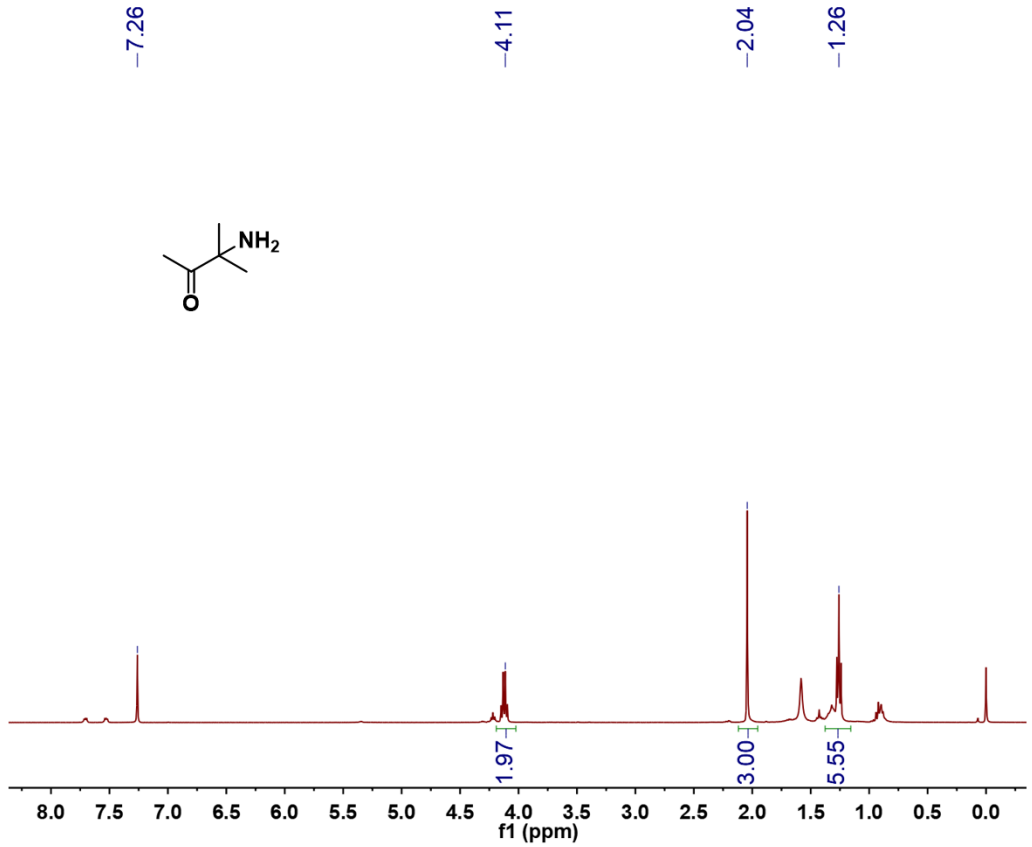
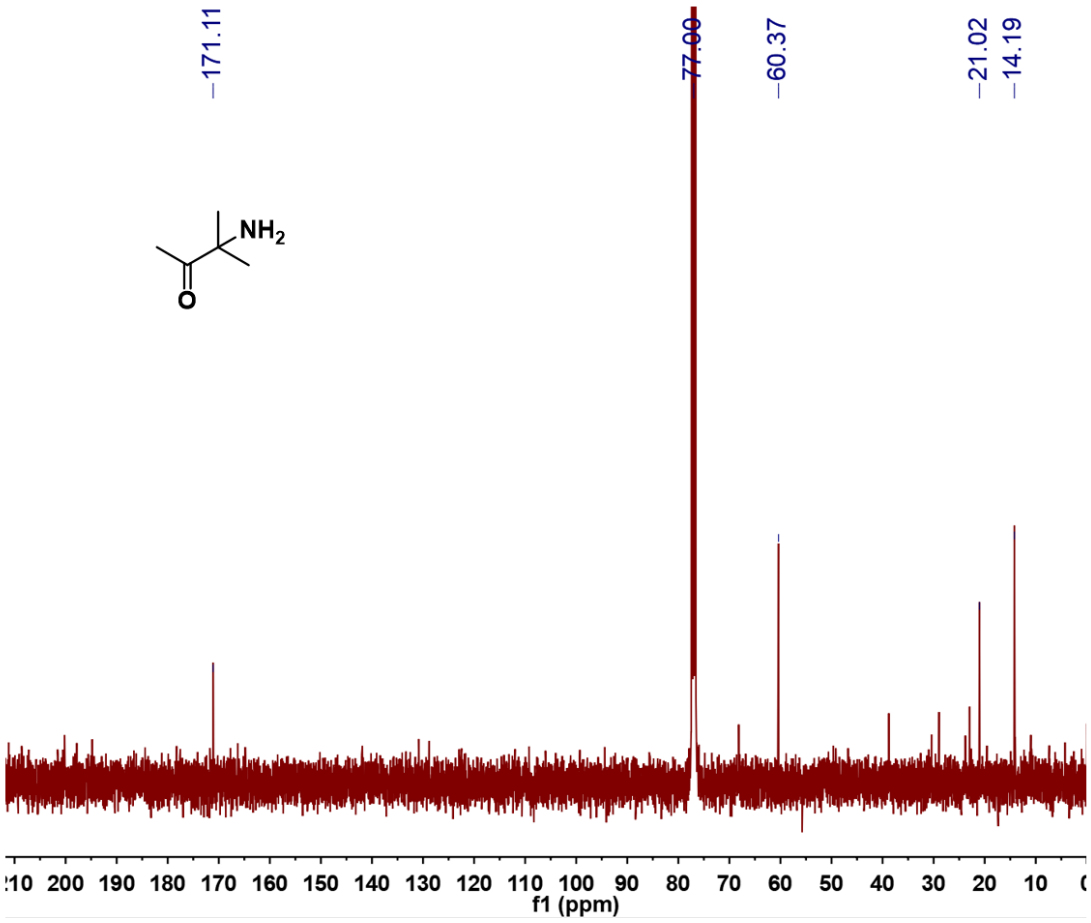
136.06
127.24
123.70
120.84
118.62
118.19
111.23
108.98
39.50
32.46
O
NH2
N
H
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


7.26
4.11
2.04
1.26
NH2
O
1.97
3.00
5.55
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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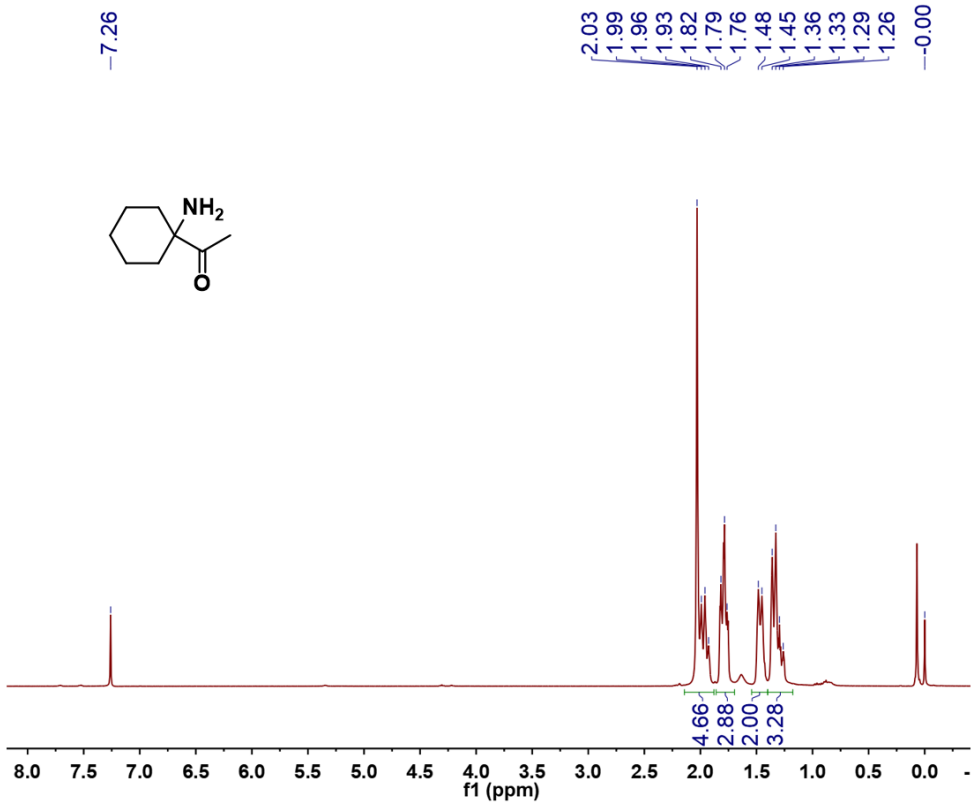
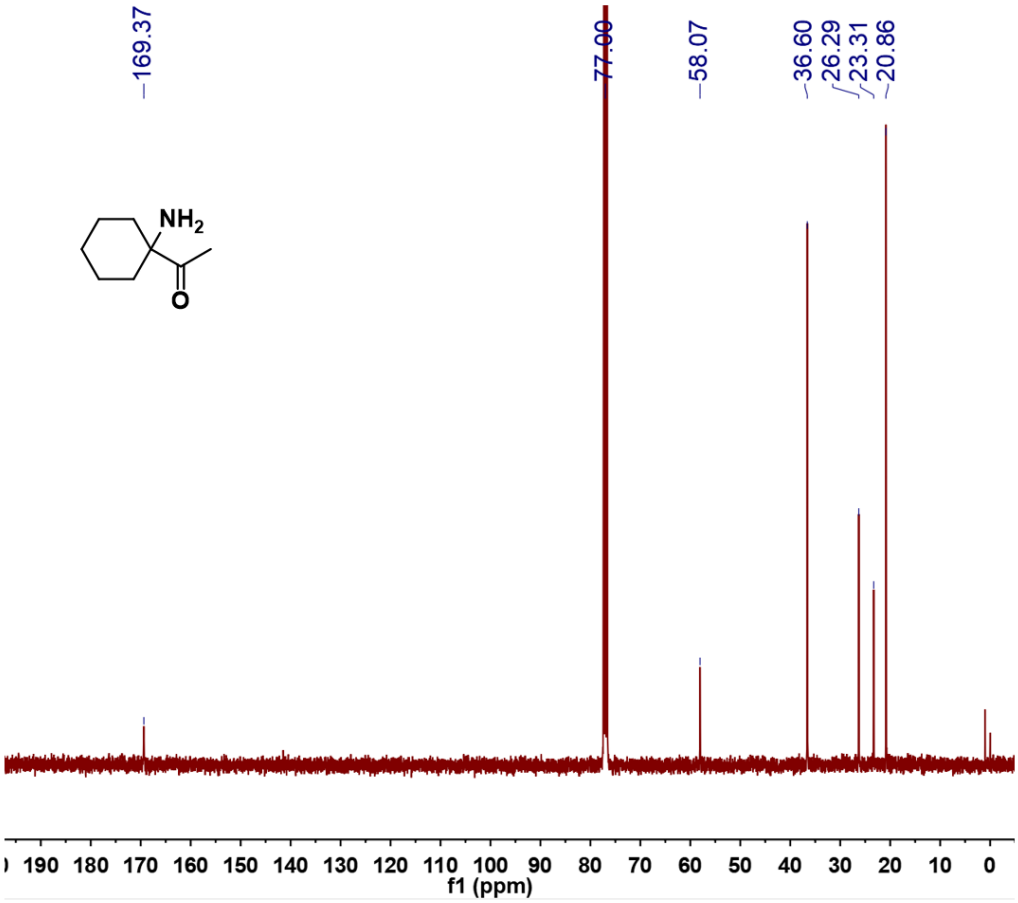
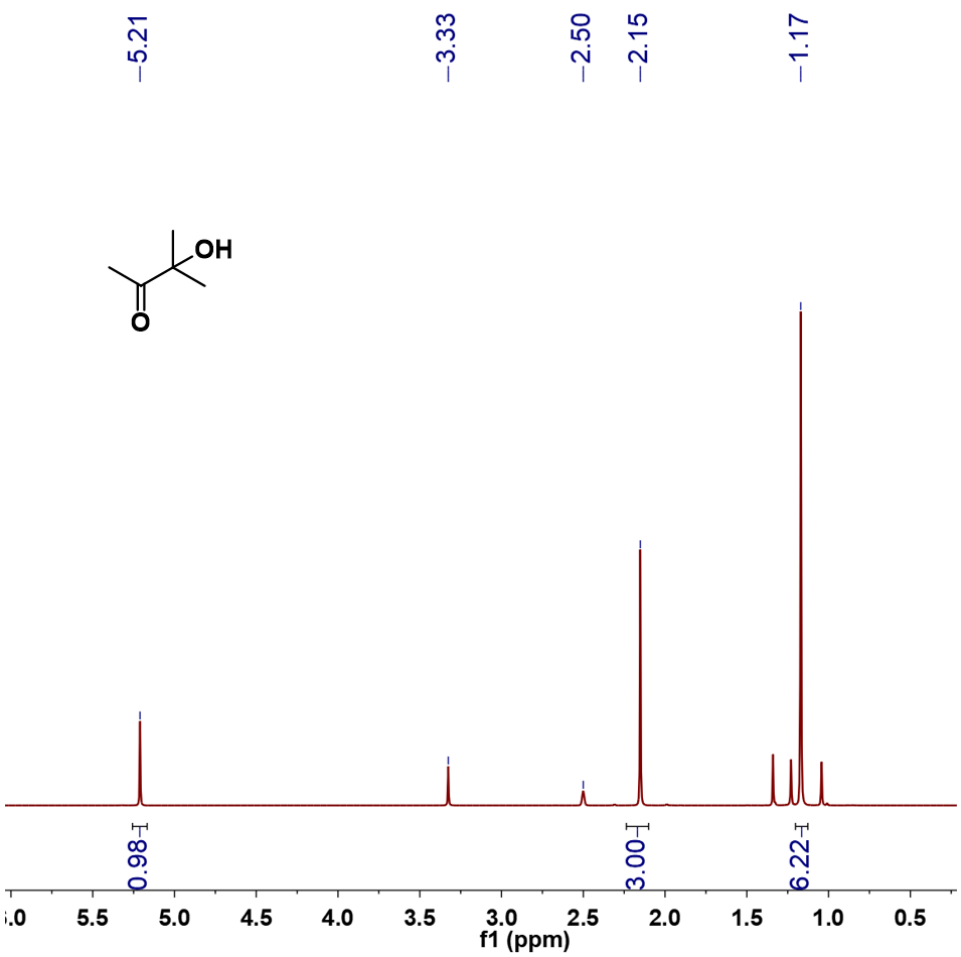
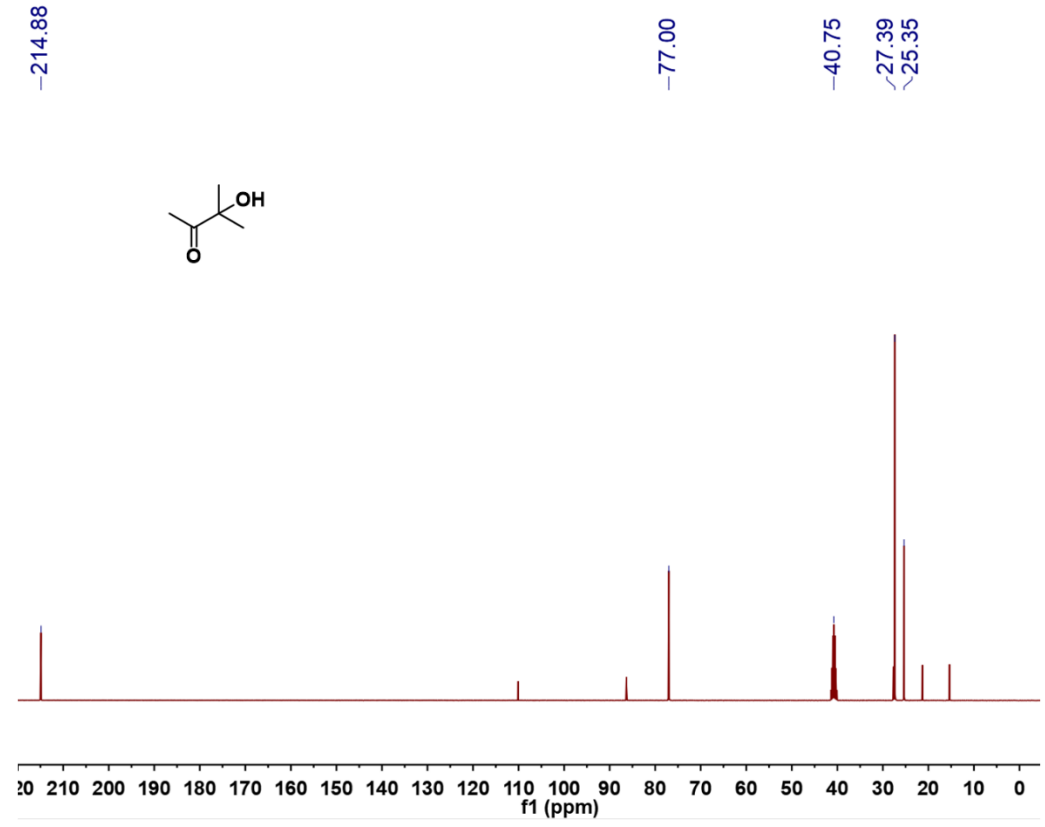
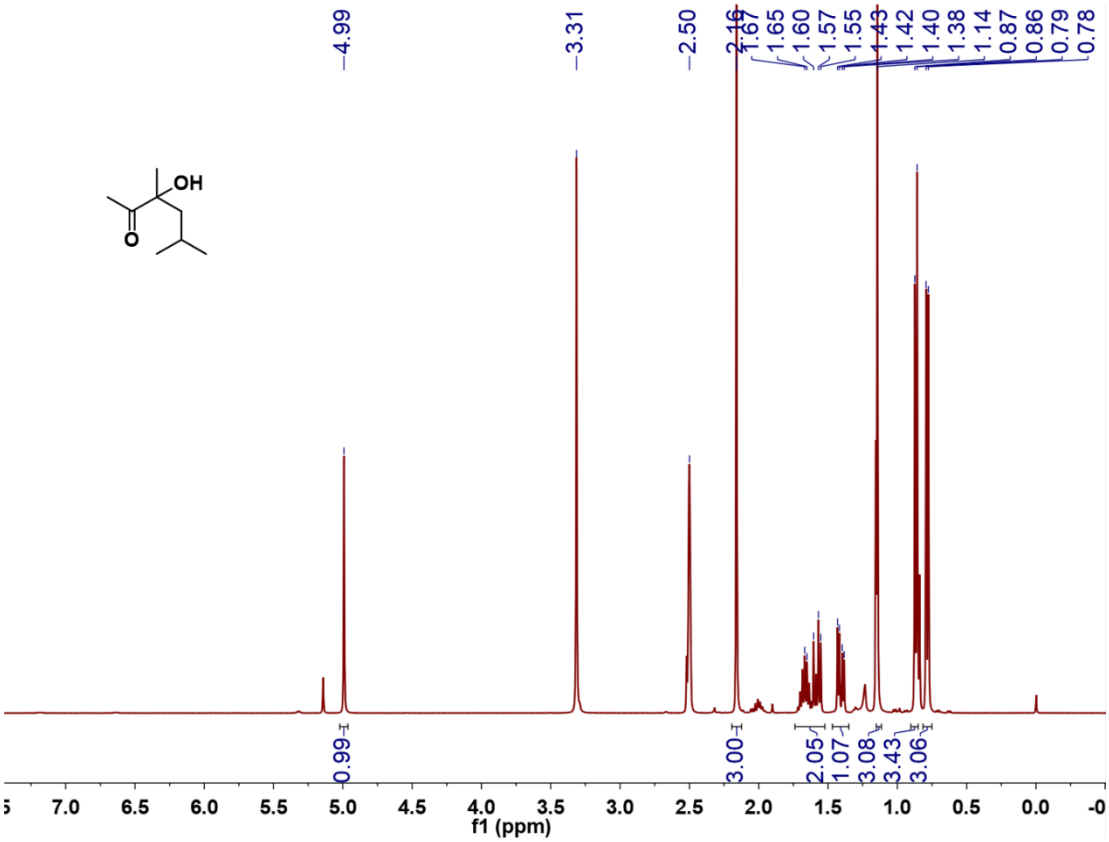
77.00
60.37
21.02
14.19
NH2
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

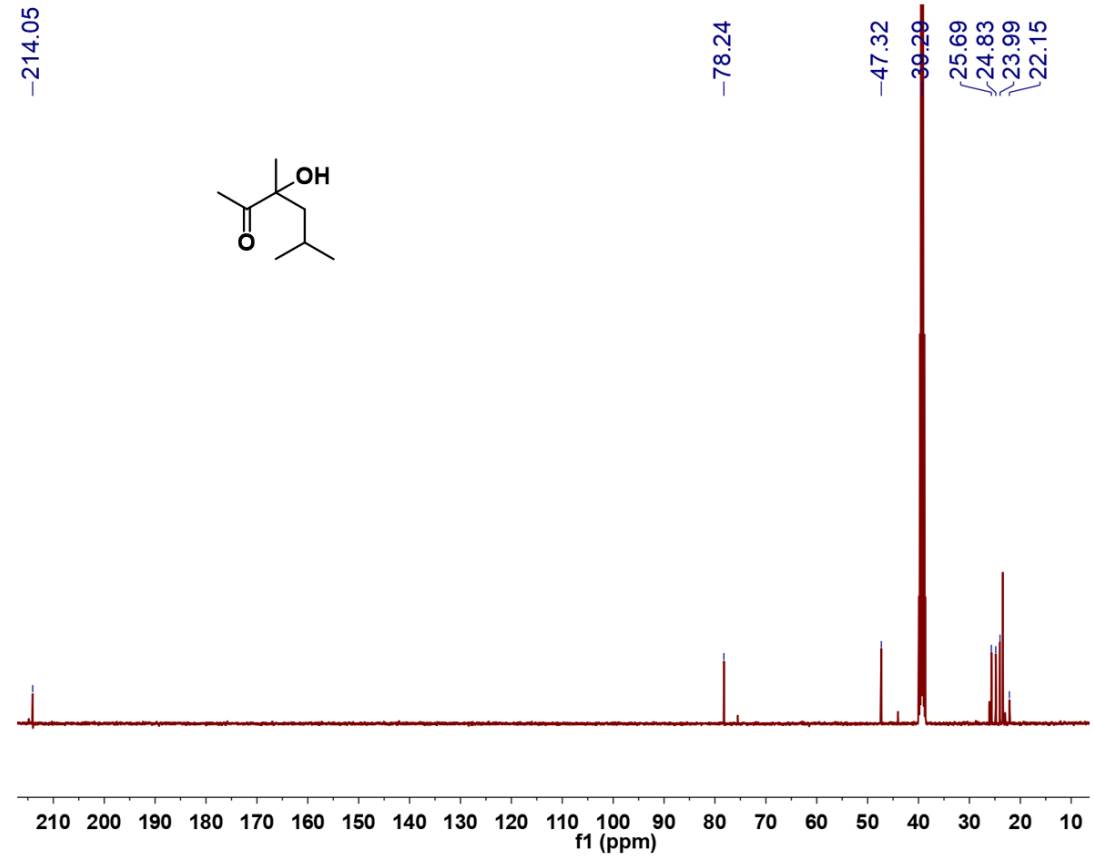

7.26
2.03
1.99
1.96
1.93
1.82
1.79
1.76
1.48
1.45
1.36
1.33
1.29
1.26
0.00
NH2
O
4.66
2.88
2.00
3.28
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

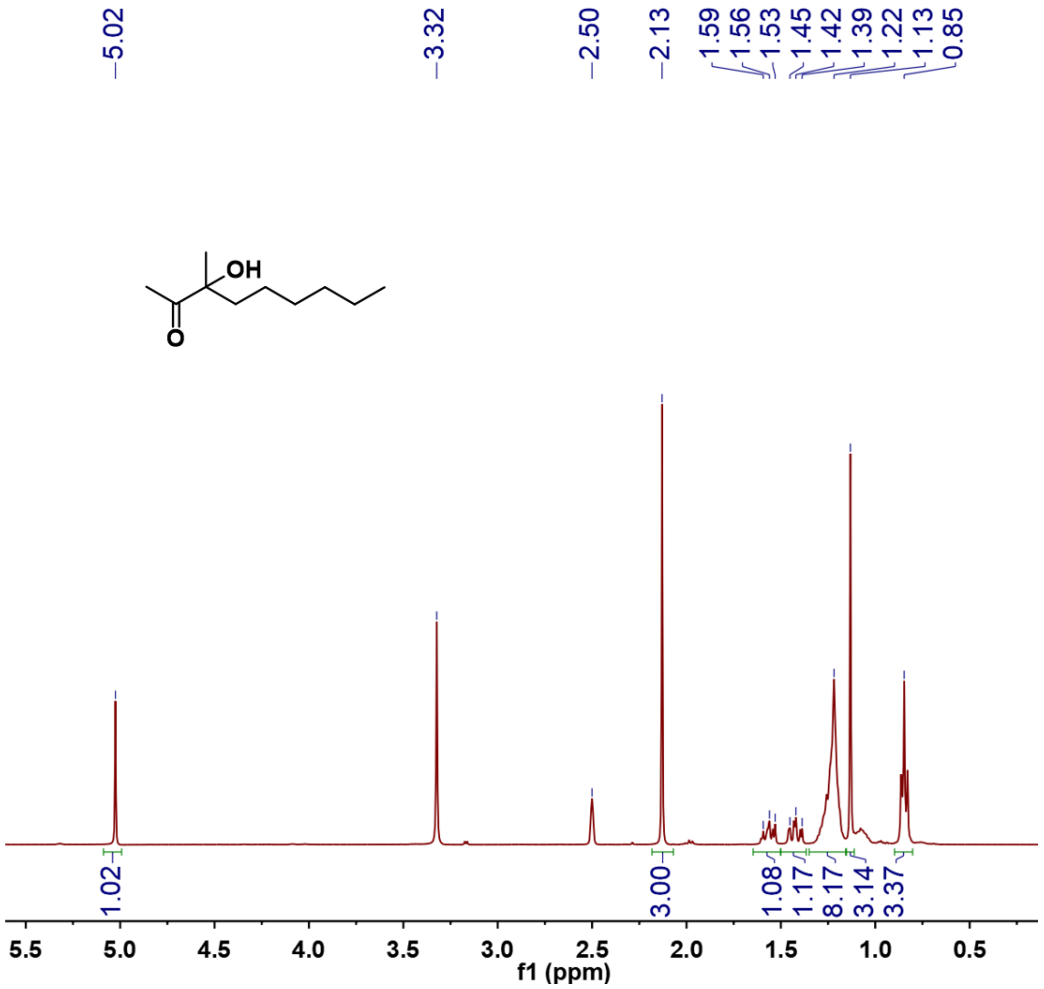

169.37
77.00
58.07
36.60
26.29
23.31
20.86
NH2
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

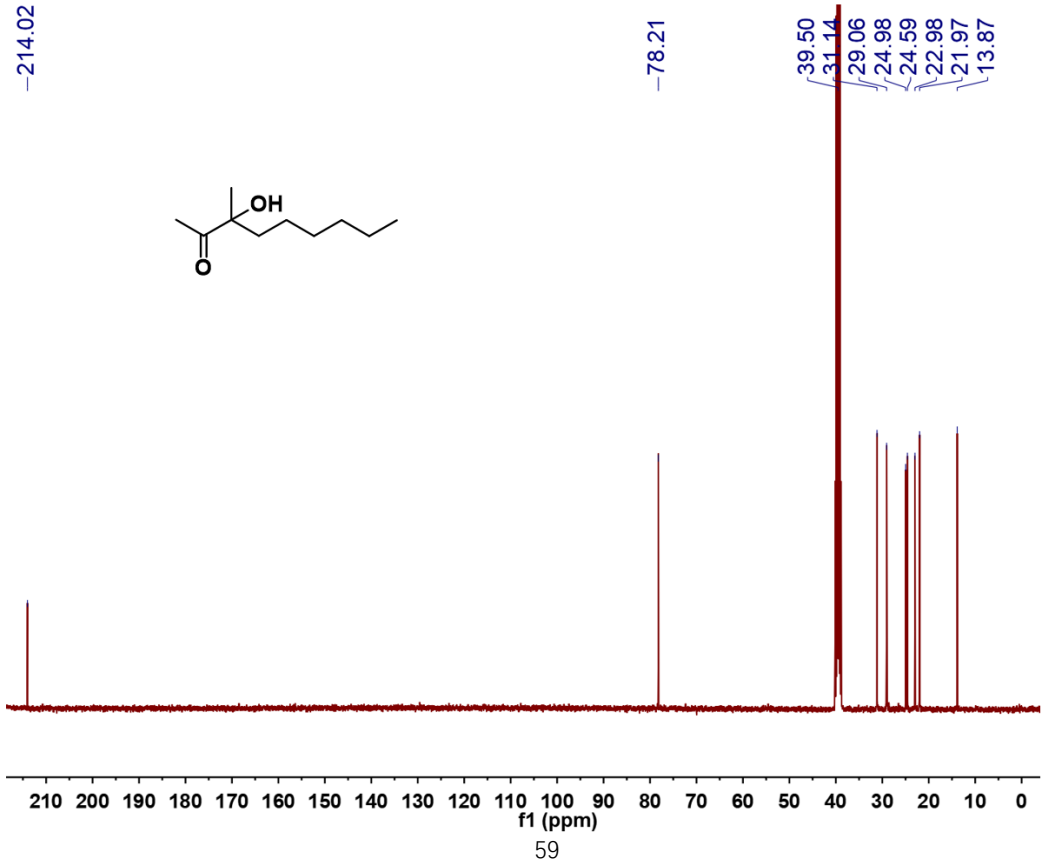

5.21
3.33
2.50
2.15
1.17
OH
O
0.98
3.00
6.22
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

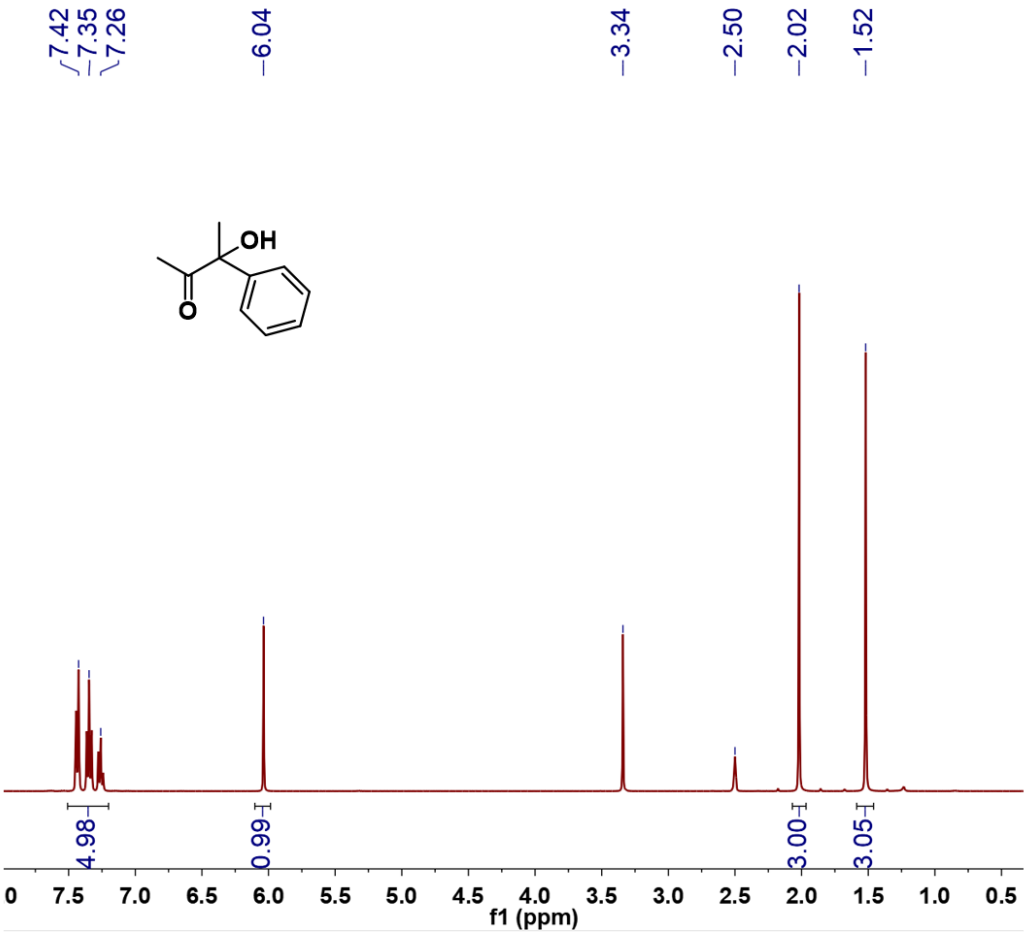

214.88
77.00
40.75
27.39
25.35
OH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

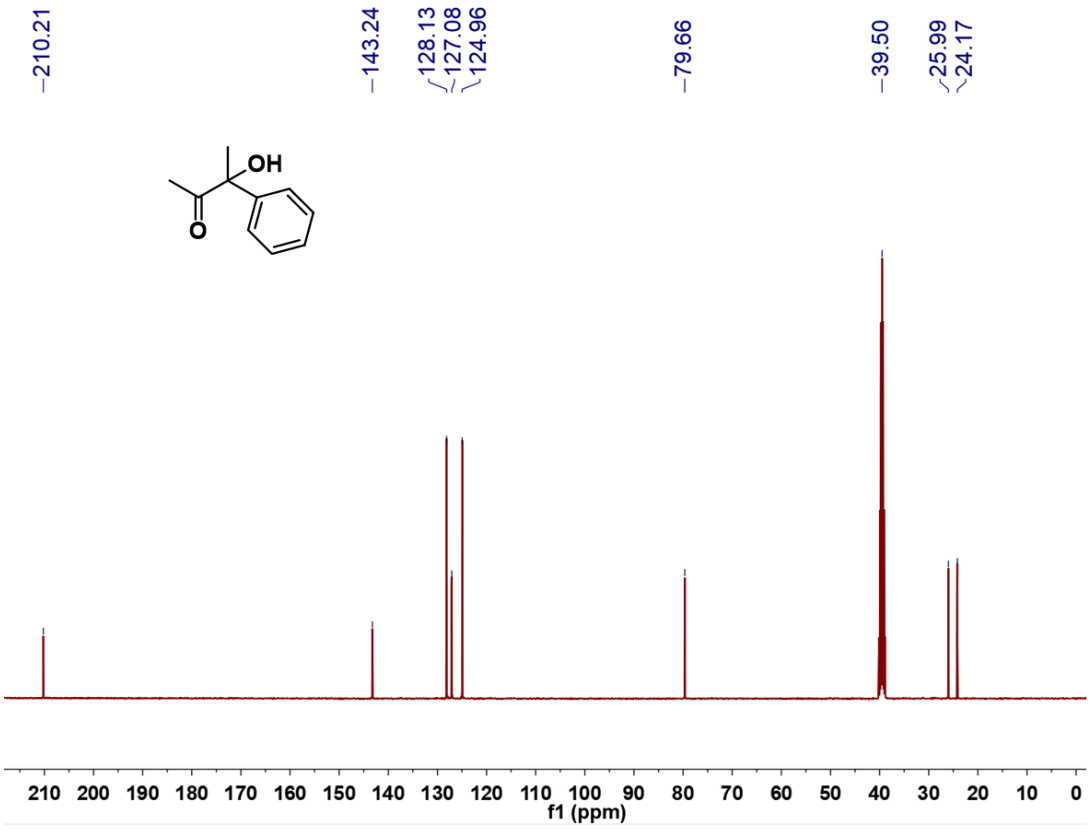

4.99
3.31
2.50
2.16
1.67
1.65
1.60
1.57
1.55
1.43
1.42
1.40
1.38
1.14
0.87
0.86
0.79
0.78
OH
O
0.99
3.00
2.05
1.07
3.08
3.43
3.06
f1 (ppm)

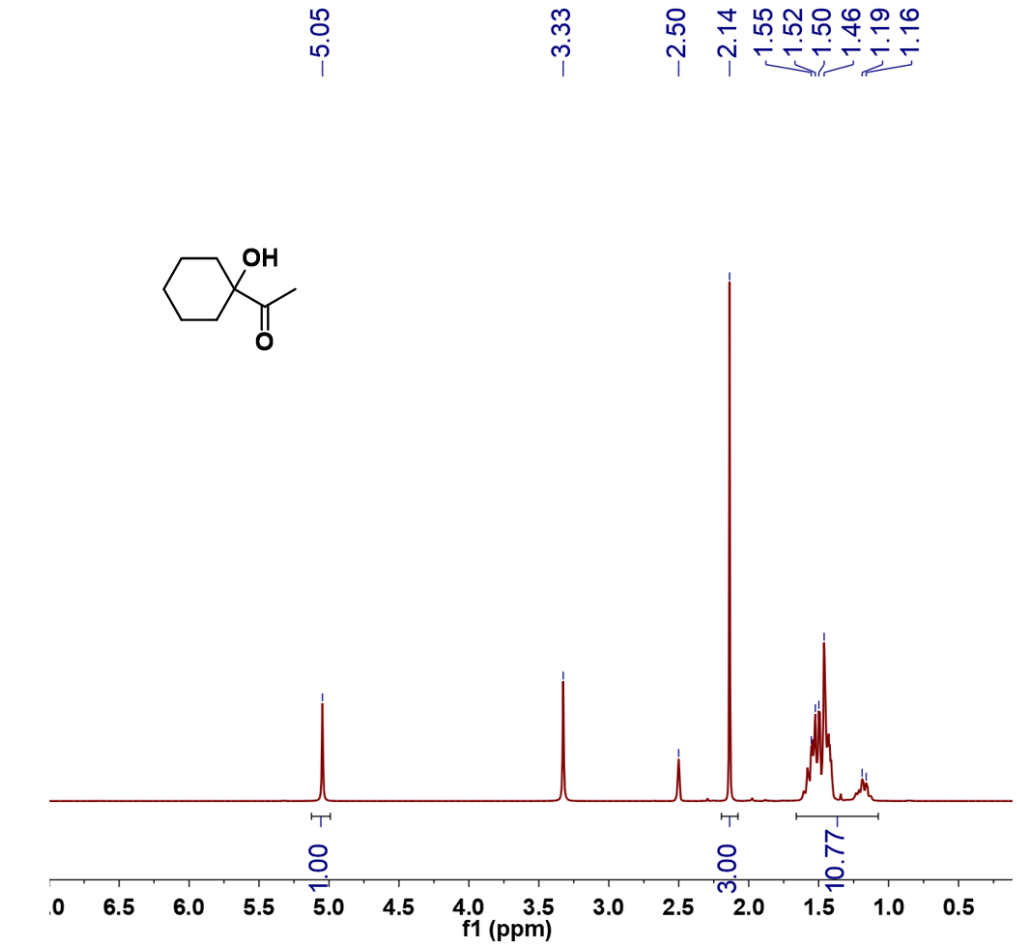

214.05
78.24
47.32
30.29
25.69
24.83
23.99
22.15
OH
O
f1 (ppm)

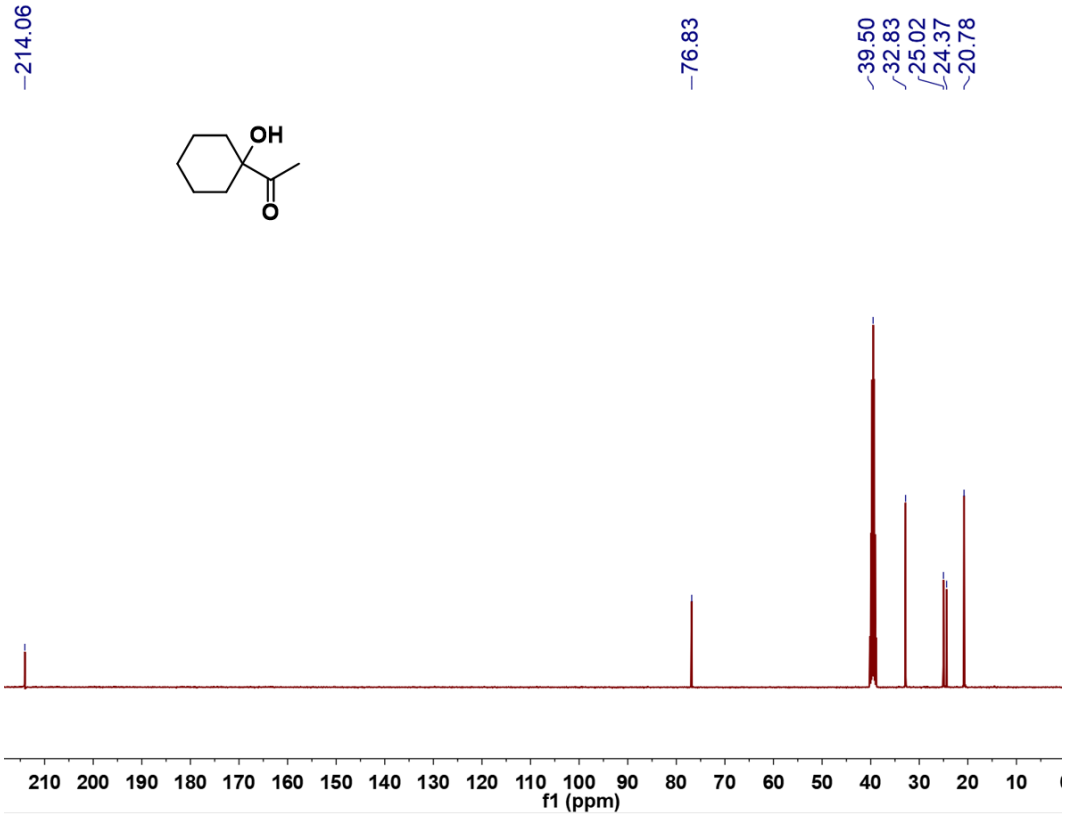

5.02
3.32
2.50
2.13
1.59
1.56
1.53
1.45
1.42
1.39
1.22
1.13
0.85
OH
O
1.02
3.00
1.08
1.17
8.17
3.14
3.37
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


214.02
78.21
39.50
31.14
29.06
24.98
24.59
22.98
21.97
13.87
OH
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.42
7.35
7.26
6.04
3.34
2.50
2.02
1.52
OH
O
4.98
0.99
3.00
3.05
0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


210.21
143.24
128.13
127.08
124.96
79.66
39.50
25.99
24.17
OH
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


5.05
3.33
2.50
2.14
1.55
1.52
1.50
1.46
1.19
1.16
OH
O
1.00
3.00
10.77
f1 (ppm)


214.06
76.83
39.50
32.83
25.02
24.37
20.78
OH
O
f1 (ppm)

11. References

1. (a) C. Wang, H. Luo, D.-e. Jiang, H. Li and S. Dai, *Angew. Chem. Int. Edit.*, 2010, **49**, 5978-5981. (b) Y. Tsuji, T. Mizumo and H. Ohno, *Chem. Commun.*, 2011, **47**, 3132-3134.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
3. E. Caldeweyher, C. Bannwarth and S. Grimme, *J. Chem. Phys.*, 2017, **147**, 034112.
4. T. Lu and Q. Chen, *Shermo: A General Code for Calculating Molecular Thermochemistry Properties*, 2020.
5. (a) W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graph.*, 1996, **14**, 33-38. (b) T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.