Supporting Information

Selective synthesis of THF-derived amines from biomass-derived carbonyl compounds

Shi Jiang,[†] Changru Ma,[‡] Eric Muller,[§] Marc Pera-Titus,*[,‡] François Jerôme[†] and Karine De Oliveira Vigier*[,†]

[†] *IC2MP UMR CNRS_Université de Poitiers 7285, ENSIP 1 rue Marcel Doré, TSA 41195, 86073 Poitiers Cedex 9, France, mail: karine.vigier@univ-poitiers.fr*

[‡] *Eco-Efficient Products and Processes Laboratory (E2P2L), UMI 3464 CNRS – Solvay, 3966 Jin Du Road, Xin Zhuang Ind. Zone, 201108 Shanghai, China, mail: marc.pera-titus-ext@solvay.com*

[§] *SOLVAY-Advanced Organic Chemistry & Molecule Design Laboratory, Recherche & Innovation Centre de Lyon, 85 Avenue des Frères Perret, 69192 Saint Fons, France*

[*] *Corresponding author: karine.vigier@univ-poitiers.fr*

Experimental Section

Chemicals

Pd(5%)/Al_2O_3 (Johnson Matthey), Pd(5%)/C (Johnson Matthey), Ru(5%)/Al_2O_3 (Alfa Aesar), Pt(5%)/Al_2O_3 (Johnson Matthey), Rh(5%)/Al_2O_3 (Johnson Matthey), Amberlyst® A26 hydroxide form (Moisture 66-75%, Sigma-Aldrich), Furfural (99%, Sigma-Aldrich), Methyl isobutyl ketone (≥ 99%, Sigma-Aldrich), EtOH (99.5%, J&K), 2-Pentanone (≥ 99%, Sigma-Aldrich), 2-Heptanone (≥ 98%, Sigma-Aldrich), Butylamine (≥ 99.5%, Sigma-Aldrich), Ethylenediamine (≥ 99.5%, Sigma-Aldrich)

Analysis

The analysis of reactants and products was carried out by gas chromatography on a Varian Bruker 450 GC equipped with a flame ionization detector (FID) and a HP-5MS column (L = 30m, Ø = 0.25mm, e = 0.25µm, temperature from 80 °C to 250 °C). The analytical methods were adjusted for the different mixtures depending on the boiling point and polarity of the different compounds. In all the methods, the injector temperature was set at 250 °C, the detector temperature was 300 °C and the sample injection volume was 2 µL. The calibration was performed using n-dodecane as internal standard.

Nuclear magnetic resonance spectroscopy (NMR) is a technique for determining the structure of organic compounds. Each compound can be characterized using several descriptors including the chemical shift, spin multiplicity, coupling constants, and integration. In this study, liquid NMR analysis was used to identify the structure of the products generated in the different reactions. The NMR spectra were recorded on 300 MHz or 400 MHz Bruker spectrometers.

Density functional theory (DFT) calculations

The free energy of reaction, ΔG at 120 °C, was calculated at the CCSD (T)/cc-pVTZ level and was implemented in Turbomole v7.1. The structures were optimized with the B3LYP/def2-TZVP approach, and the ethanol solvent effect was corrected with COSMO model (ε=24.3). The optimized structures were characterized by the absence of imaginary frequency.

X-Ray Diffraction analysis

X-ray diffraction (XRD) patterns were recorded on a PanAnytical Empyrean X-ray diffractometer, Bragg Benttano configuration, with CuKα radiation (λ = 1.54184 Å) as X-ray source. The data were collected in the 2θ range from 10^o to 80^o with a step of 0.05^o (step time of 120 s).

X-Ray Photoelectron spectrometry

X-ray photoelectron spectrometry (XPS) was performed by Thermo Fisher ESCALAB 250Xi photoelectron spectrometer with Al Kα radiation (*hv* = 1486.7 eV).

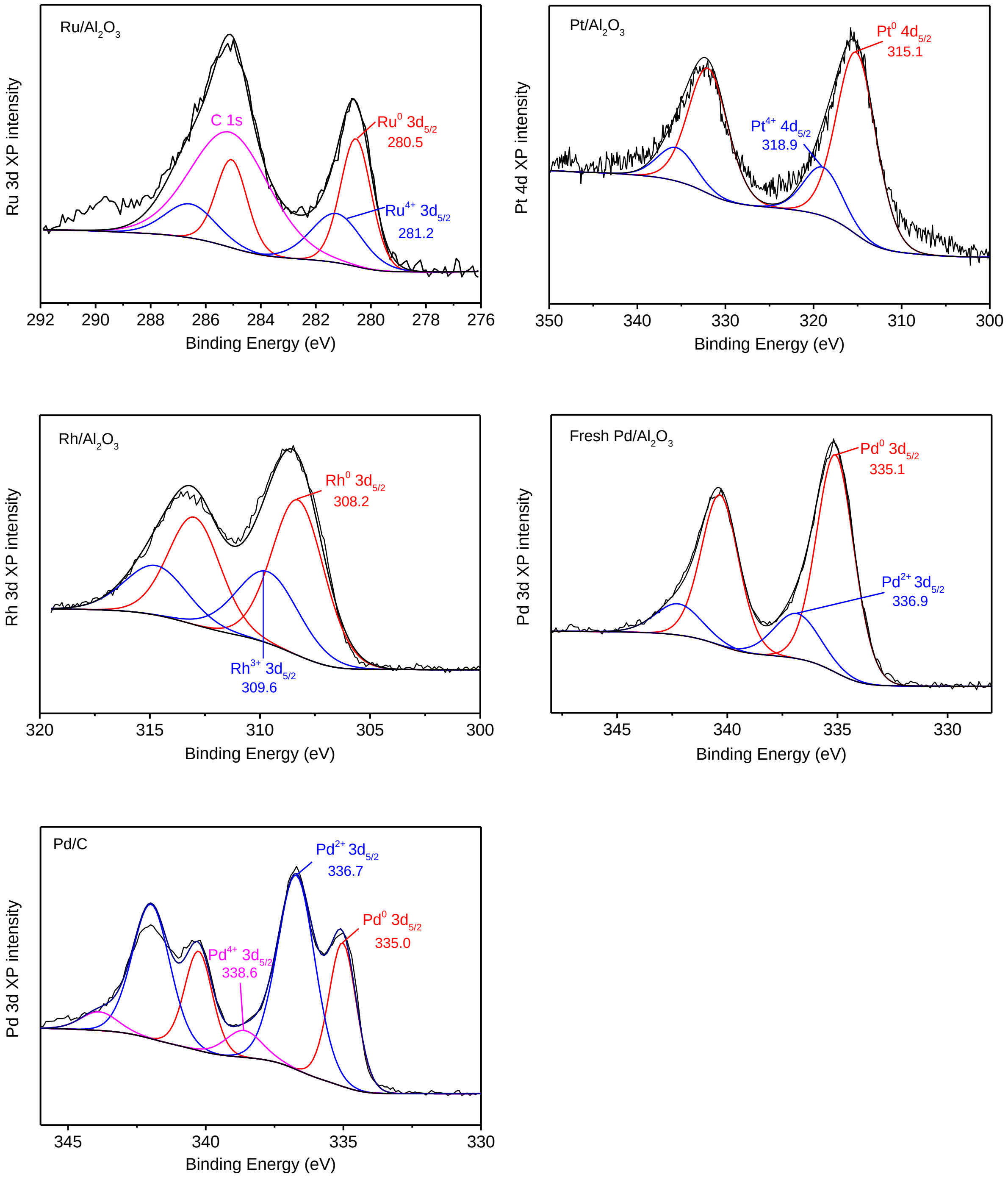


Figure S1. Normalized XPS spectra of Ru/Al$_2$O$_3$, Pt/Al$_2$O$_3$, Rh/Al$_2$O$_3$, Pd/Al$_2$O$_3$ and Pd/C before reaction.

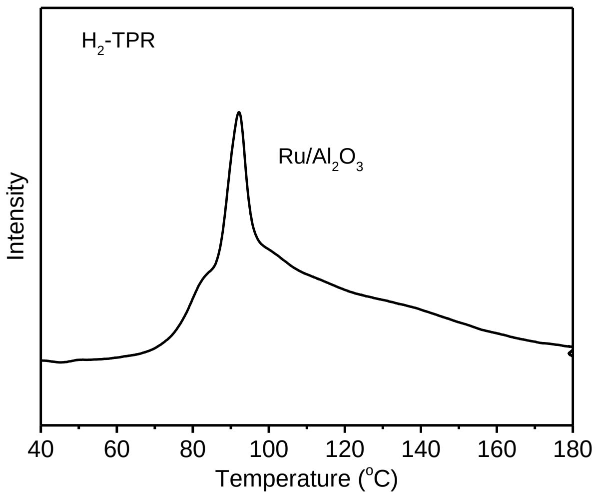


Figure S2. H_2-TPR profile of Ru on Al_2O_3.

Specific area measurement (BET)

The measurement of the specific surface area by gas adsorption involves the determination of the volume of an inert gas (typically N_2) adsorbed on a solid surface at low temperature as a function of pressure. When the pressure is reduced back to zero, a possible hysteresis can be revealed by comparing the values of desorption and adsorption. N_2 adsorption/desorption isotherms were obtained at -196 °C (77.2 K) using a Micromeritics TriStar instrument after degassing the sample overnight at 100 °C. The specific area was calculated using the Brunauer-Emmett-Teller (BET) equation in the P/P_0 range 0.05-0.25, while the pore size distribution was measured from the desorption branch using the Barrett-Joyner-Halenda (BJH) method using the following equation

$$\frac{1}{\left[V_a\left(\frac{P_0}{P}-1\right)\right]}=\frac{C-1}{V_m C}*\frac{P}{P_0}+\frac{1}{V_m C}$$

where P is the partial pressure of the gas in equilibrium with the surface (Pa), P_0 is the saturation pressure (Pa), V_a is the volume of gas adsorbed at standard temperature and pressure (mL), V_m is the volume of gas adsorbed at STP producing an apparent monolayer (mL), and C is the dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

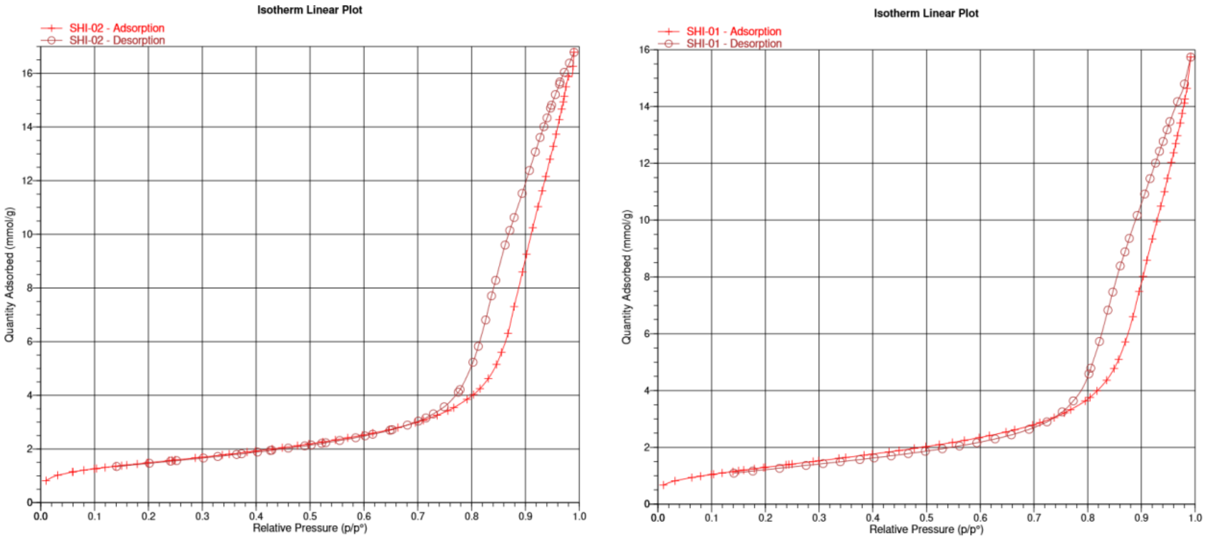


Figure S3. N_2 adsorption/desorption isotherm at 77 K of the fresh (left) and spent (right) Pd/Al_2O_3.

Transmission Electron Microscopy (TEM)

A JEOL 2100 instrument with Filament LaB6 having an acceleration voltage of 200 kV equipped with a Gatan 832 CCD camera was used for visualizing the catalyst surface. Prior to characterization, the samples were dispersed in ethanol with in an ultrasound bath for 5 min, and then dropped onto a carbon film on a copper grid. The particle size distribution was measured by manual analysis of micrographs using ImageJ software.

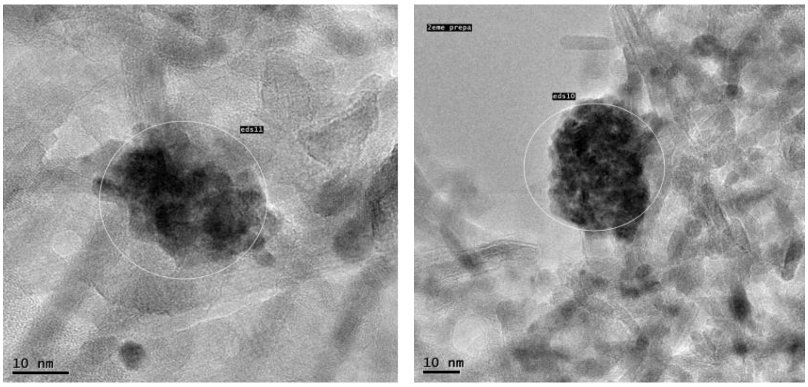


Figure S4. TEM micrographs of the recycled Pd/Al_2O_3.

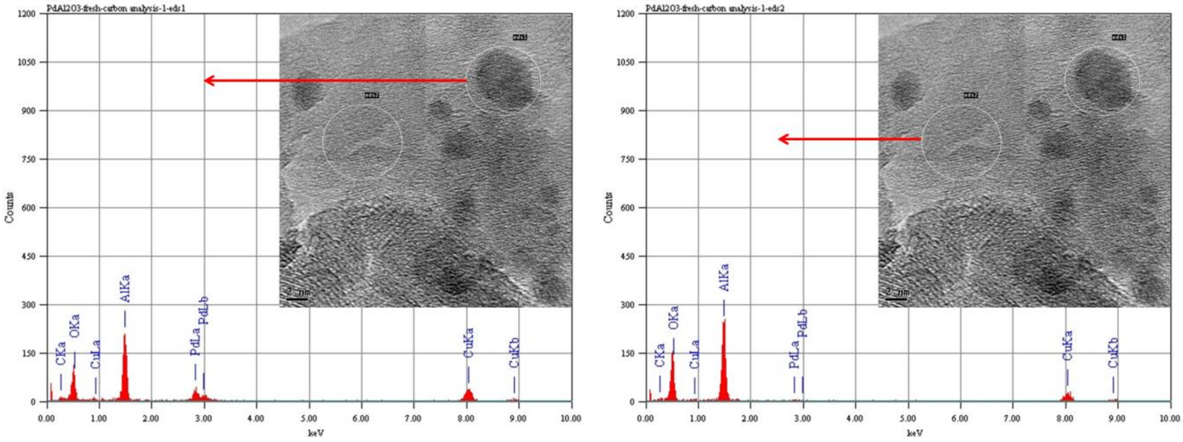


Figure S5. Element distribution in the fresh Pd/Al_2O_3 measured by EDS.

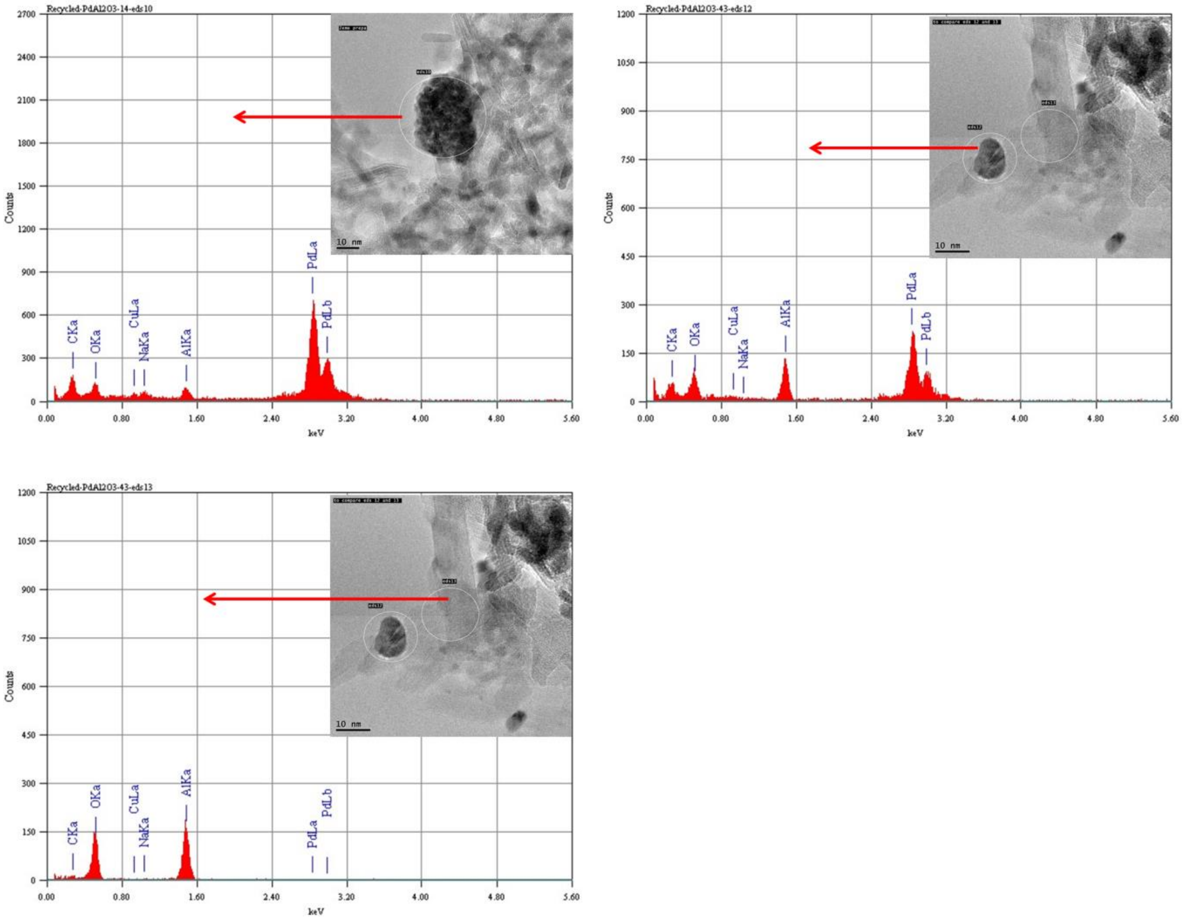
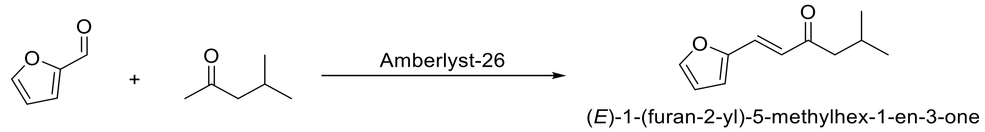


Figure S6. Element distribution in the recycled Pd/Al_2O_3 measured by EDS.

General procedure for aldol condensation reactions



The catalytic reaction was performed in a 30-mL tubular glass reactor with a sealable arrangement on top. The reaction was performed using 1 g of furfural and 10 g of MIBK in the presence of 0.2 g Amberlyst-26 in a glass tube placed in a preheated oil bath (120 °C) for 2 h at 600 rpm. The solvent was evaporated and a brown liquid was obtained with 96% yield. The product was analyzed and quantified on an Agilent 7890 GC equipped with a HP-5 capillary column with 5 wt% phenyl groups using n-dodecane as internal standard, a FID detector, and a split/splitless injection. ^{1}H&1^{3}C NMR and GCMS analysis were also performed. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.82 (d, *J* = 1.7 Hz, 1H), 7.38 (d, *J* = 16.0 Hz, 1H), 6.93 (d, *J* = 3.4 Hz, 1H), 6.61 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 2.46 (d, *J* = 6.9 Hz, 2H), 2.11-1.97 (m, 1H), 0.85 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 199.59, 151.04, 146.39, 129.18, 123.97, 116.87, 113.36, 49.28, 25.14, 22.84.

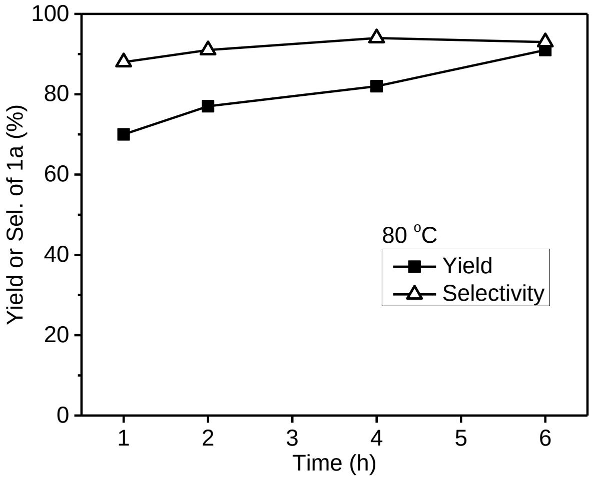
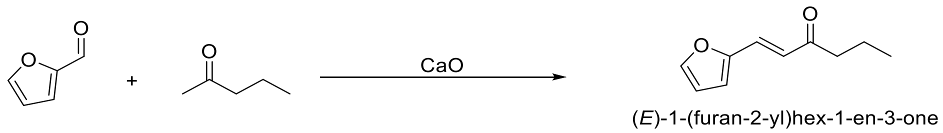
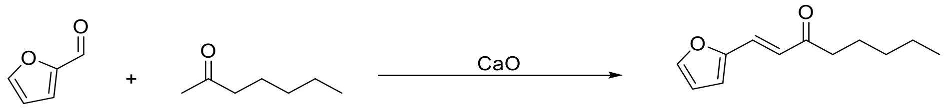


Figure S7: Kinetic profiles of aldol condensation between furfural and MIBK over Amberlyst-26 at 80 °C; Reaction conditions: furfural (108 mg, 1.125 mmol), MIBK (112.5 mg, 1.125 mmol), ethanol (2 g) and catalyst (43 mg); After 6 h, the conversion of furfural was over 98%.



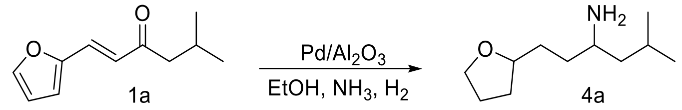
The aldol condensation of furfural with 2-pentanone was carried out in a closed reactor. Typically, 0.96 g (10 mmol) furfural, 15 mmol 2-pentanone, 10 g EtOH and 0.384 g CaO were put into the reactor. Before the reaction, the reactor was purged with Ar. The mixture was stirred at 80 °C for 6 h. After cooling down to room temperature, the liquid was filtered /evaporated under vacuum and 95% yield of **(*E*)-1-(furan-2-yl)hex-1-en-3-one** was obtained. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.84 (d, *J* = 1.8 Hz, 1H), 7.41 (d, *J* = 16.1 Hz, 1H), 6.95 (d, *J* = 3.4 Hz, 1H), 6.63 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 2.60 (t, *J* = 7.2 Hz, 2H), 1.60-1.48 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 199.87, 151.02, 146.40, 129.09, 123.70, 116.82, 113.38, 42.23, 17.75, 14.09.



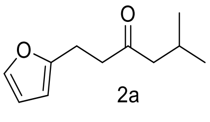
(*E*)-1-(furan-2-yl)oct-1-en-3-one

Following the same procedure of **(*E*)-1-(furan-2-yl)hex-1-en-3-one**, furfural and 2-heptanone gave **(*E*)-1-(furan-2-yl)oct-1-en-3-one** product as a brown solid with a yield of 95%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.83 (d, *J* = 1.8 Hz, 1H), 7.40 (d, *J* = 16.1 Hz, 1H), 6.94 (d, *J* = 3.4 Hz, 1H), 6.62 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.52 (d, *J* = 16.1 Hz, 1H), 2.60 (t, *J* = 7.3 Hz, 2H), 1.56-1.46 (m, 2H), 1.30-1.16 (m, 4H), 0.83 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 199.94, 151.02, 146.40, 129.07, 123.66, 116.83, 113.37, 40.30, 31.34, 23.99, 22.44, 14.32.

General procedure for synthesis of THF-derived amines



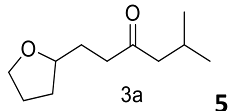
The catalytic tests were carried out in 20-mL stainless steel reactor equipped with pressure gauge and a safety rupture disk. In a given experiment, the reactor was charged with a mixture of **1a** (0.2 g), EtOH (2 g) and the pre-reduced catalyst (10 mg). The reactor was sealed and flushed with N_2 three times, and then NH_3 (5 bar) and H_2 (20 bar) were added to the reactor. The reactor was heated at 120 °C for 20 h under stirring. At the end of the reaction, the reactor was cooled down to room temperature and the reaction mixture was analyzed by a gas chromatography using an Agilent 7890 GC equipped with a HP-5MS capillary column with 5wt% phenyl groups and a FID detector using n-dodecane as internal standard. At the end of the reaction, the reactor was cooled down to room temperature and filtered, dried to give a colorless liquid with a yield of 98%. **5-methyl-1-(tetrahydrofuran-2-yl)hexan-3-amine** ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93-3.59 (m, 3H), 2.87-2.65 (m, 1H), 2.10-1.79 (m, 3H), 1.78-1.58 (m, 2H), 1.57-1.28 (m, 6H), 1.24-1.11 (m, 2H), 0.87 (t, J = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (79.58, 79.38), (67.66, 67.64), 48.96, (47.52, 47.48), (35.24, 35.06), (32.28, 32.12), (31.46, 31.37), (25.72, 25.69), (24.77, 24.76), (23.49, 23.48), (22.07, 22.04). HRMS (ESI-TOF, m/z): Calcd for $C_{11}H_{24}NO$ [M+H]+ 186.1852; found 186.1857



1-(furan-2-yl)-5-methylhexan-3-one

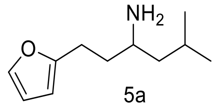
^{1}H NMR (300 MHz, DMSO-d_6): δ 7.48 (d, *J* = 1.0 Hz, 1H), 6.32 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.06 (dd, *J* = 3.1, 0.8 Hz, 1H), 2.84-2.66 (m, 4H), 2.32 (d, *J* = 6.9 Hz, 2H), 2.08-1.95 (m, 1H), 0.84 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (75 MHz, DMSO-d_6): δ 209.18, 155.04, 141.67, 110.76, 105.49, 51.24, 40.71, 24.34, 22.77, 21.98.

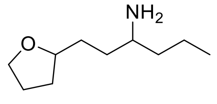

3a **5-methyl-1-(tetrahydrofuran-2-yl)hexan-3-one**

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.75-3.63 (m, 2H), 3.61-3.50 (m, 1H), 2.47-2.41 (m, 2H), 2.30 (d, *J* = 6.9 Hz, 2H), 2.08-1.96 (m, 1H), 1.95-1.70 (m, 3H), 1.68-1.53 (m, 2H), 1.45-1.30 (m, 1H), 0.85 (d, *J* = 6.6 Hz, 6H).

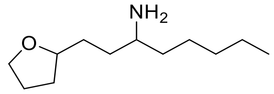
^{13}C NMR (75 MHz, DMSO-d_6): δ 210.26, 78.11, 67.19, 51.34, 39.60, 31.20, 29.52, 25.70, 24.38, 22.80, 22.79.


5a **1-(furan-2-yl)-5-methylhexan-3-amine**

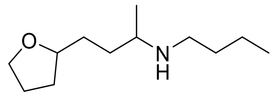
^{1}H NMR (300 MHz, DMSO-d_6): δ 7.47 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.31 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.05 (dd, *J* = 3.1, 0.9 Hz, 1H), 2.77-2.53 (m, 3H), 1.83-1.53 (m, 3H), 1.48-1.20 (m, 2H), 1.12 (t, *J* = 6.9 Hz, 2H), 0.83 (dd, *J* = 7.9, 6.6 Hz, 6H). 13C NMR (75 MHz, DMSO-d_6): δ 156.48, 141.42, 110.64, 105.11, 48.32, 47.88, 37.12, 24.61, 24.60, 23.83, 22.52.


1-(tetrahydrofuran-2-yl)hexan-3-amine

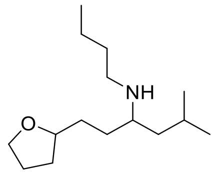
1-(tetrahydrofuran-2-yl)hexan-3-amine was synthesized by the same procedure of **4a**. It was obtained as colourless liquid with a yield of 94%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.98-3.52 (m, 3H), 2.88-2.56 (m, 1H), 2.14-1.04 (m, 14H), 0.99-0.81 (m, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 79.61, 79.39, 67.68, 67.67, 51.03, 51.00, 40.20, 40.19, 34.69, 34.53, 31.47, 31.39, 25.72, 25.69, 19.26, 19.25, 14.19. HRMS (ESI-TOF, m/z): Calcd for $C_{10}H_{22}NO$ [M+H]+ 172.1696; found 172.1705


1-(tetrahydrofuran-2-yl)octan-3-amine

1-(tetrahydrofuran-2-yl)octan-3-amine was synthesized by the same procedure of **4a** and it was obtained as colourless liquid with a yield of 96%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.93-3.60 (m, 3H), 2.81-2.51 (m, 1H), 2.09-1.13 (m, 18H), 0.98-0.80 (m, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (79.61, 79.39), (67.69, 67.67), (51.36, 51.31), 37.86, (34.60, 34.47), (32.29, 32.22), 31.99, (31.48, 31.40), (25.79, 25.72), 25.69, 22.65, 14.06. HRMS (ESI-TOF, m/z): Calcd for $C_{12}H_{26}NO$ [M+H]+ 200.2009; found 200.2015

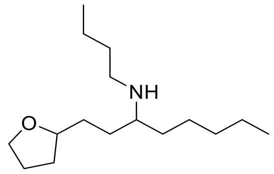

***N*-(4-(tetrahydrofuran-2-yl)butan-2-yl)butan-1-amine**

***N*-(4-(tetrahydrofuran-2-yl)butan-2-yl)butan-1-amine** was synthesized by the same procedure of **4a** (the molar ratio between (*E*)-4-(furan-2-yl)but-3-en-2-one and butylamine was 3/1) and It was obtained as colourless liquid with a yield of 96%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.90-3.62 (m, 3H), 2.70-2.43 (m, 3H), 2.03-1.73 (m, 3H), 1.67-1.15 (m, 10H), 1.01 (d, J = 6.3 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (79.50, 79.47), 67.62, (53.21, 53.19), (47.00, 46.97), (33.62, 33.59), 32.55, (32.09, 32.05), 31.35, 25.69, 20.55, (20.36, 20.30), 14.00. HRMS (ESI-TOF, m/z): Calcd for $C_{12}H_{26}NO$ [M+H]+ 200.2009; found 200.2012



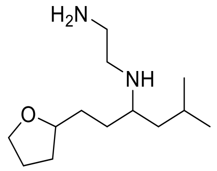
***N*-butyl-5-methyl-1-(tetrahydrofuran-2-yl)hexan-3-amine**

***N*-butyl-5-methyl-1-(tetrahydrofuran-2-yl)hexan-3-amine** was synthesized by the same procedure of **4a** (the molar ratio between (*E*)-1-(furan-2-yl)-5-methylhex-1-en-3-one and butylamine was 3/1) and It was obtained as colourless liquid with a yield of 98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.00-3.59 (m, 3H), 2.71-2.42 (m, 3H), 2.05-1.76 (m, 3H), 1.72-0.95 (m, 13H), 0.93-0.60 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (79.69, 79.67), 67.62, 55.31, (46.70, 46.64), (44.09, 44.00), 32.68, (31.56, 31.44), 31.39, (30.85, 30.76), 25.69, 24.91, (23.12, 23.05), (22.85, 22.75), 20.56, 14.02. HRMS (ESI-TOF, m/z): Calcd for $C_{15}H_{32}NO$ [M+H]+ 242.2478; found 242.2478



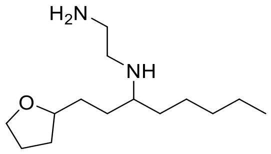
***N*-butyl-1-(tetrahydrofuran-2-yl)octan-3-amine**

***N*-butyl-1-(tetrahydrofuran-2-yl)octan-3-amine** was synthesized by the same procedure of **4a** (the molar ratio between (*E*)-1-(furan-2-yl)oct-1-en-3-one and butylamine was 3/1) and It was obtained as colourless liquid with a yield of 97%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.05-3.55 (m, 3H), 2.77-2.51 (m, 2H), 2.51-2.40 (m, 1H), 2.13-1.75 (m, 4H), 1.73-1.04 (m, 17H), 0.88 (q, J = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (79.68, 79.64), (67.63, 67.61), 57.54, (46.78, 46.73), (34.01, 33.96), 32.62, 32.17, (31.80, 31.69), (31.40, 31.38), (30.60, 30.49), 25.70, 25.42, 22.64, 20.56, 14.06, 14.01. HRMS (ESI-TOF, m/z): Calcd for $C_{16}H_{34}NO$ [M+H]+ 256.2635; found 256.2648



N^1-(5-methyl-1-(tetrahydrofuran-2-yl)hexan-3-yl)ethane-1,2-diamine

N^1-(5-methyl-1-(tetrahydrofuran-2-yl)hexan-3-yl)ethane-1,2-diamine was synthesized by the same procedure of **4a** (the molar ratio between (*E*)-1-(furan-2-yl)-5-methylhex-1-en-3-one and ethylenediamine was 3/1) and It was obtained as colourless liquid with a yield of 91%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.02-3.51 (m, 3H), 2.90-2.73 (m, 2H), 2.72-2.47 (m, 3H), 2.04-1.14 (m, 14H), 0.95-0.83 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (79.66, 79.63), (67.64, 67.62), (55.15, 55.13), (49.40, 49.32), (44.11, 44.07), (42.26, 42.22), 31.53, (31.43, 31.39), (30.94, 30.85), 25.69, 24.89, (23.11, 23.05), (22.81, 22.74). HRMS (ESI-TOF, m/z): Calcd for $C_{13}H_{29}NO$ [M+H]+ 229.2274; found 229.2281



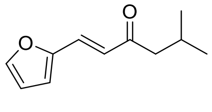
N^1-(1-(tetrahydrofuran-2-yl)octan-3-yl)ethane-1,2-diamine

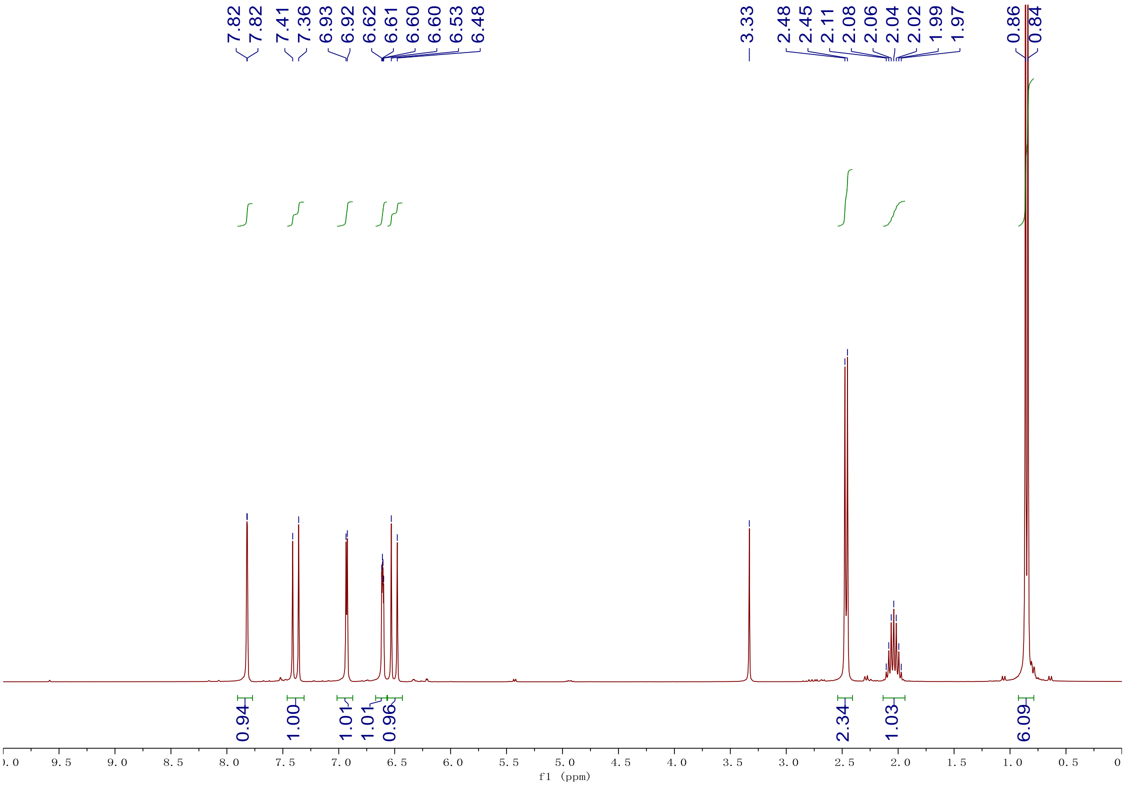
N^1-(1-(tetrahydrofuran-2-yl)octan-3-yl)ethane-1,2-diamine was synthesized by the same procedure of **4a** (the molar ratio between (*E*)-1-(furan-2-yl)oct-1-en-3-one and ethylenediamine was 3/1) and It was obtained as colourless liquid with a yield of 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93-3.54 (m, 3H), 2.93-2.69 (m, 2H), 2.69-2.53 (m, 2H), 2.53-2.34 (m, 1H), 2.01-1.75 (m, 3H), 1.74-1.01 (m, 16H), 0.93-0.77 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (79.60, 79.55), (67.58, 67.57), (57.31, 57.29), (49.50, 49.44), (42.21, 42.19), (34.10, 34.05), 32.10, (31.75, 31.65), (31.38, 31.34), (30.69, 30.58), 25.65, 25.37, 22.59, 14.01.

General procedure for catalyst recycling and reuse

In a typical catalytic test, 0.4 g of the aldol-condensation product (**1a**), 20 mg of Pd/Al_2O_3 and 4 g of EtOH were added to a 20-mL stainless steel reactor. Then, the reactor was sealed and flushed with N_2 three times, NH_3 (5 bar) and H_2 (20 bar) were introduced, and the reactor was heated to 120 °C for 20 h under stirring. The conversion and product yield were measured by GC using *n*-dodecane as internal standard. For the recycling procedure, the catalyst was separated by centrifugation and washed with EtOH three times, the new reagent solution was added, and the reaction procedure was repeated as illustrated above.

NMR Spectral data of starting materials and products





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3.33
2.48
2.45
2.11
2.08
2.06
2.04
2.02
1.99
1.97
0.86
0.84
0.94
1.00
1.01
1.01
0.96
2.34
1.03
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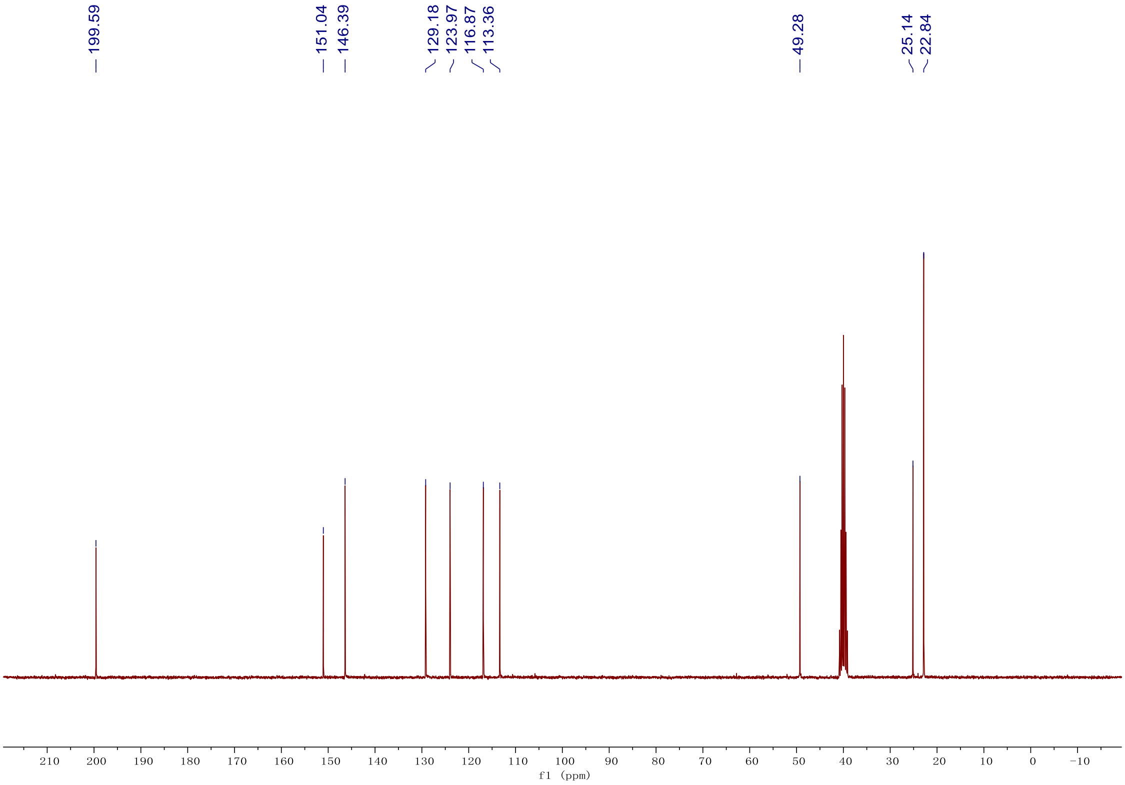

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200
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180
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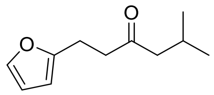
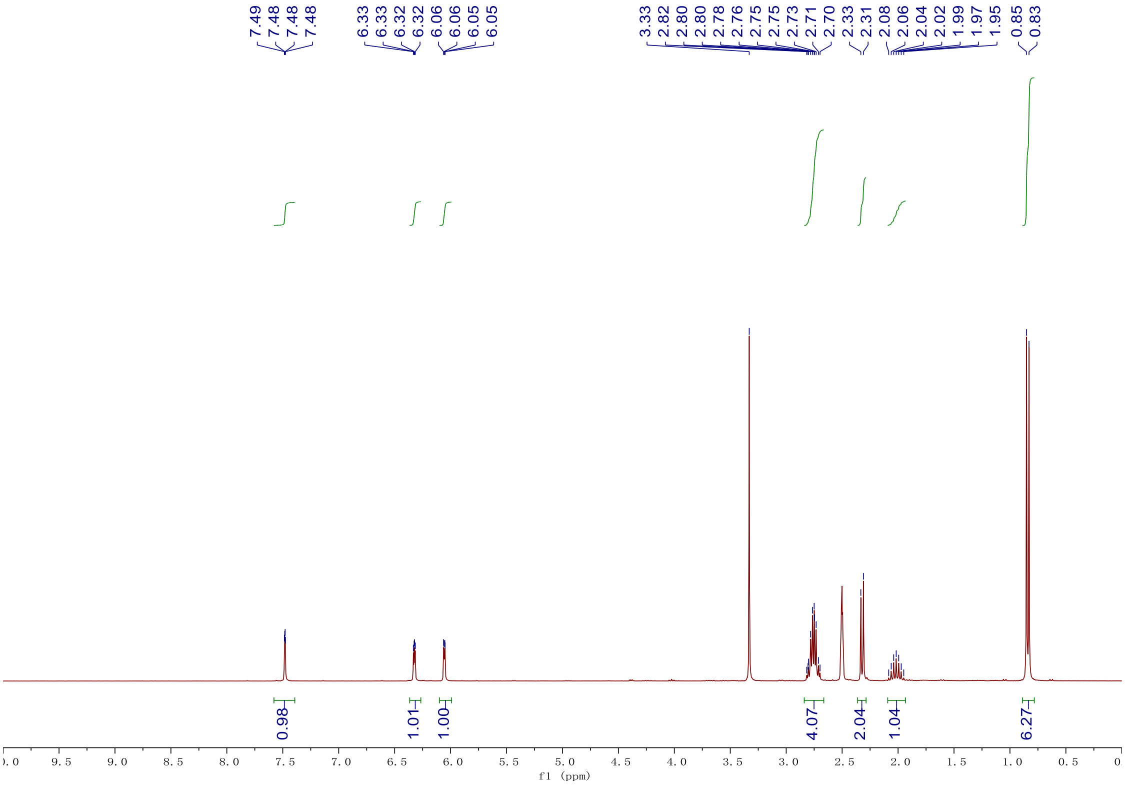
−10
f1 (ppm)

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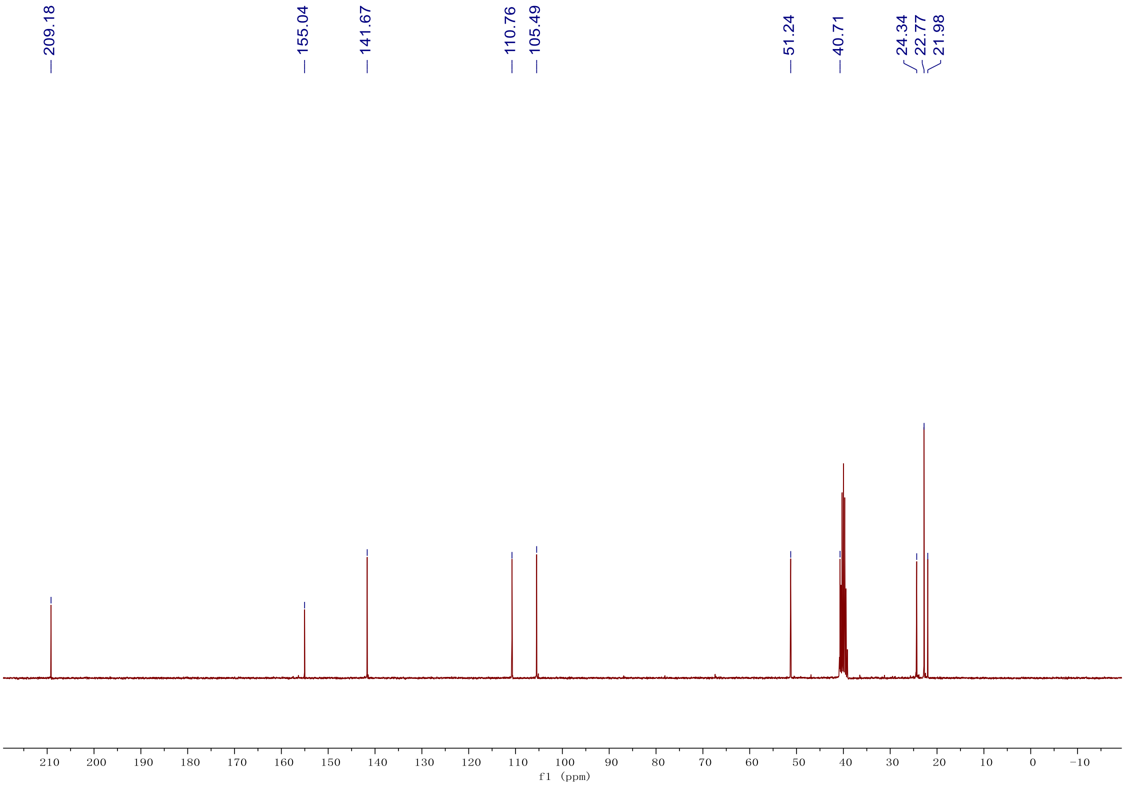
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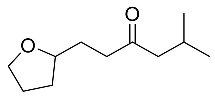
f1 (ppm)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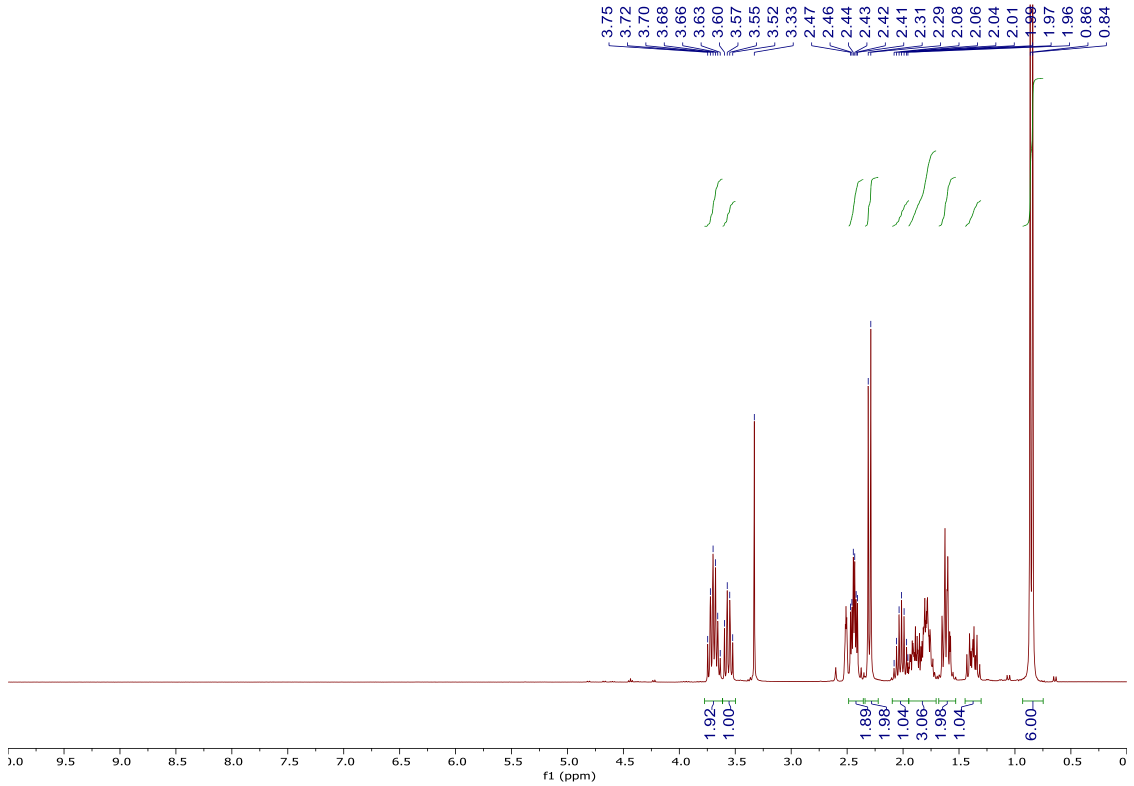
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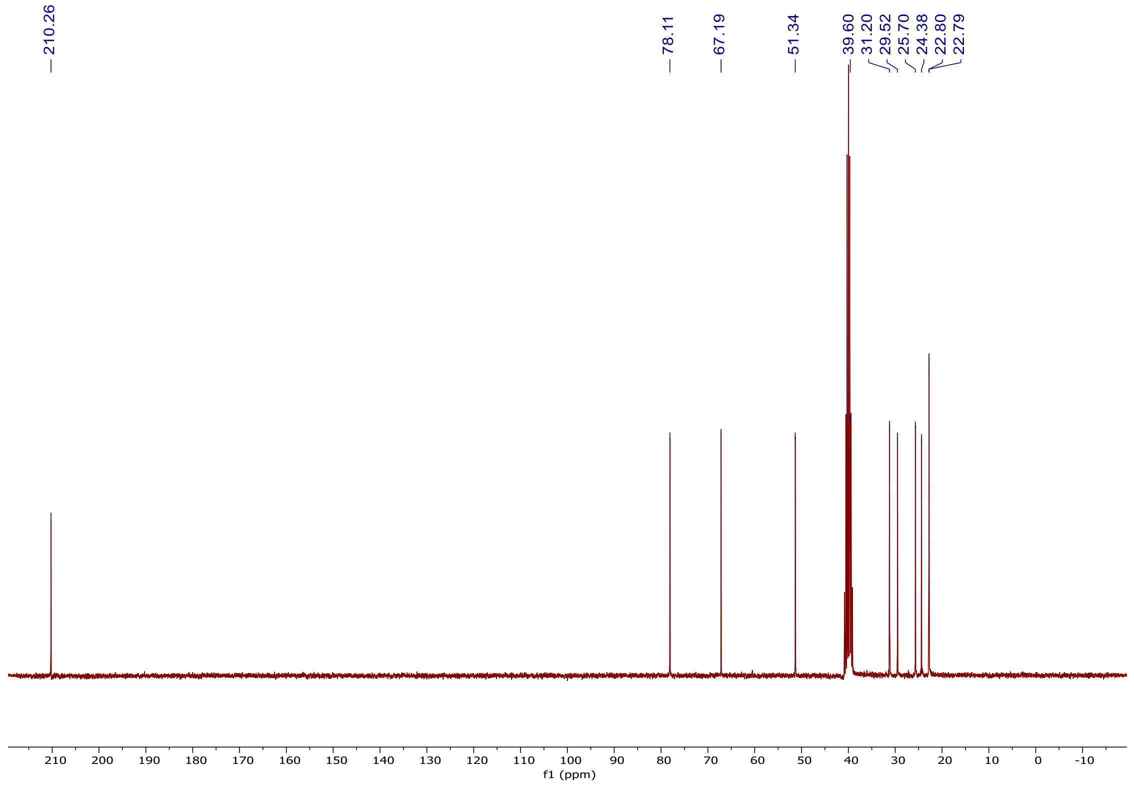
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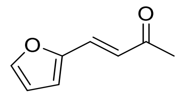
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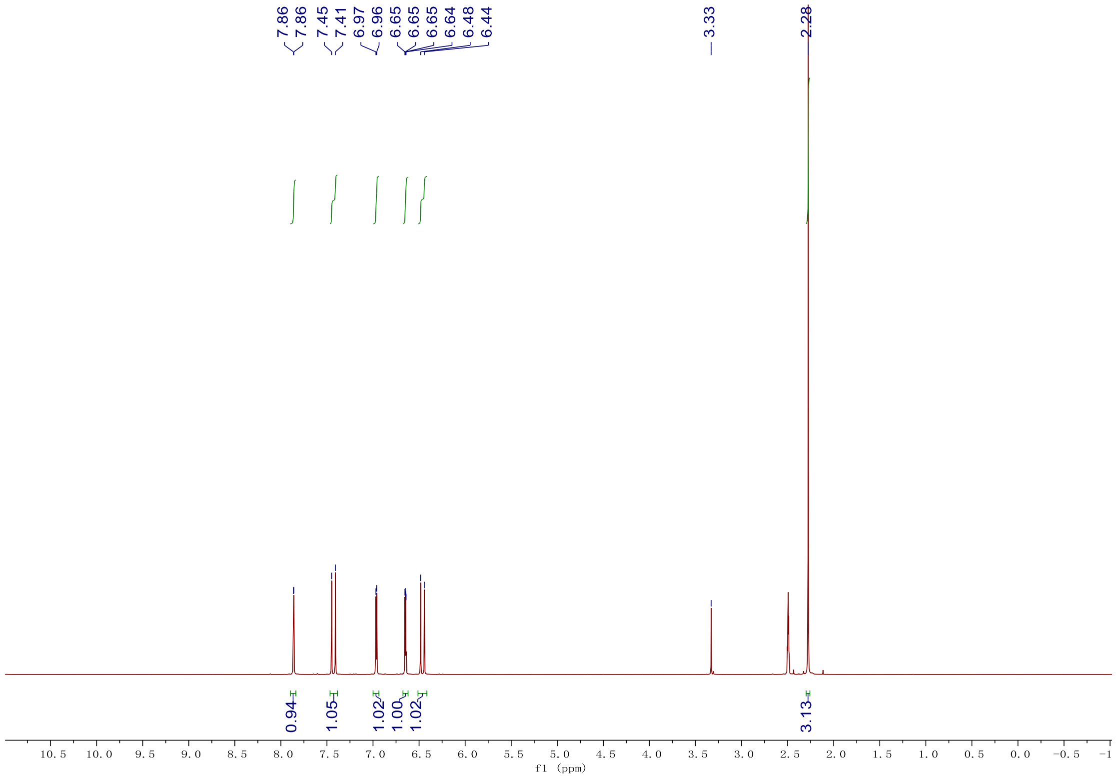
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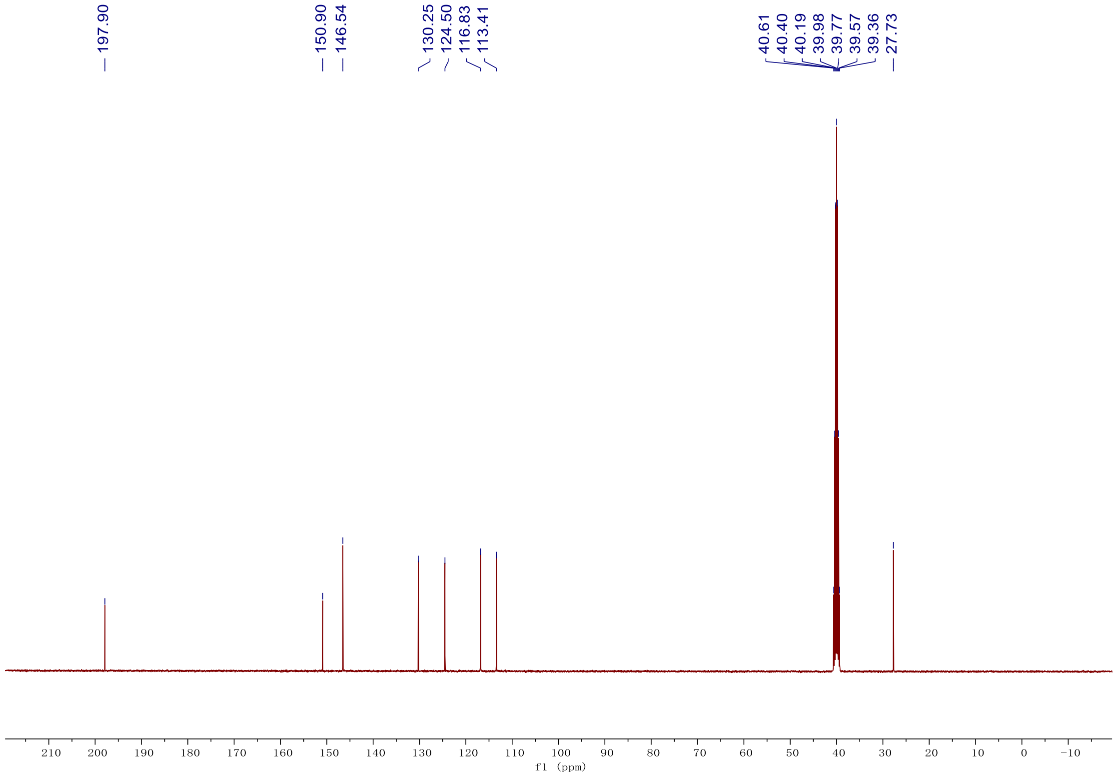
f1 (ppm)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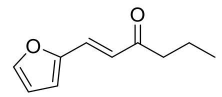
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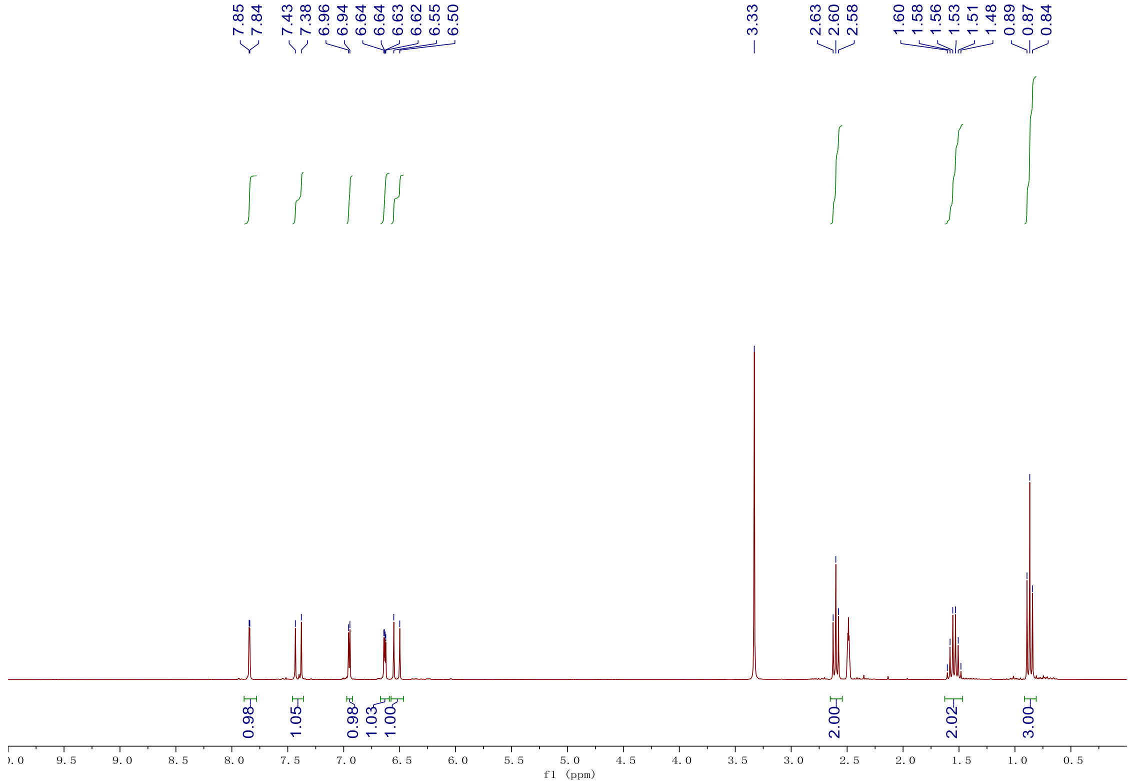
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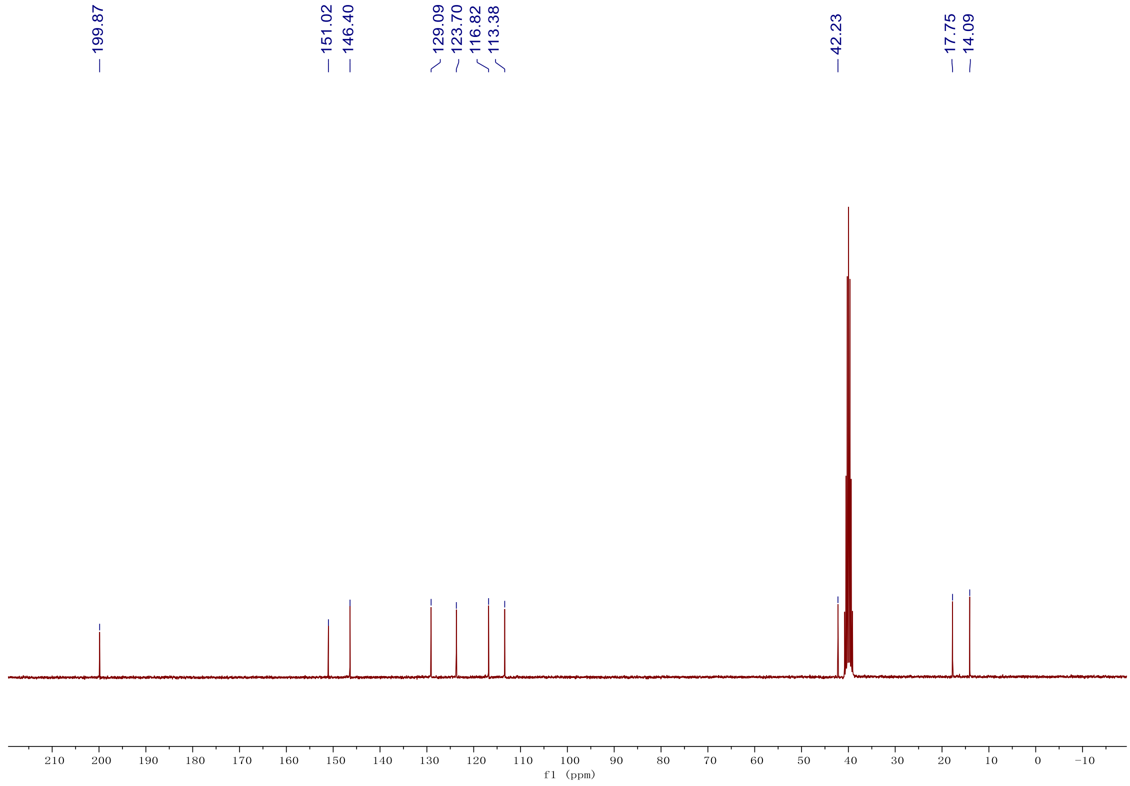
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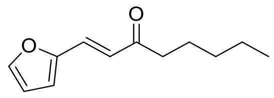
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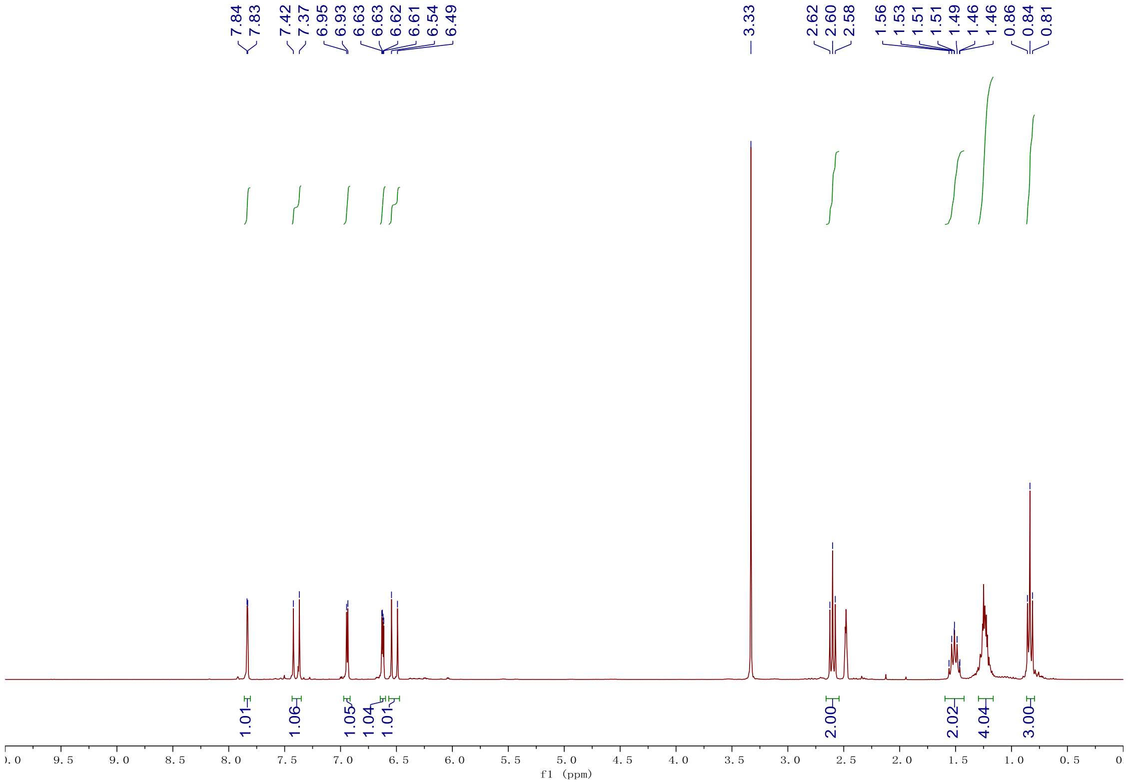
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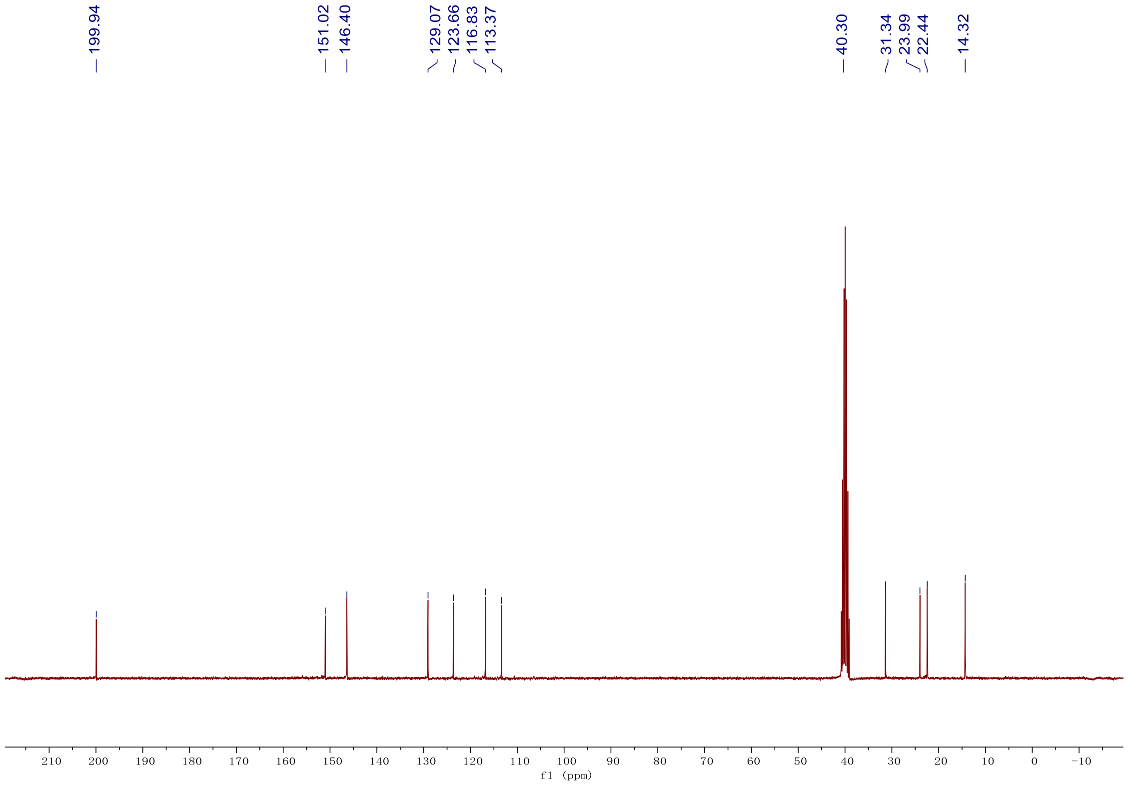
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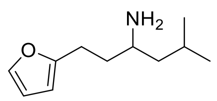
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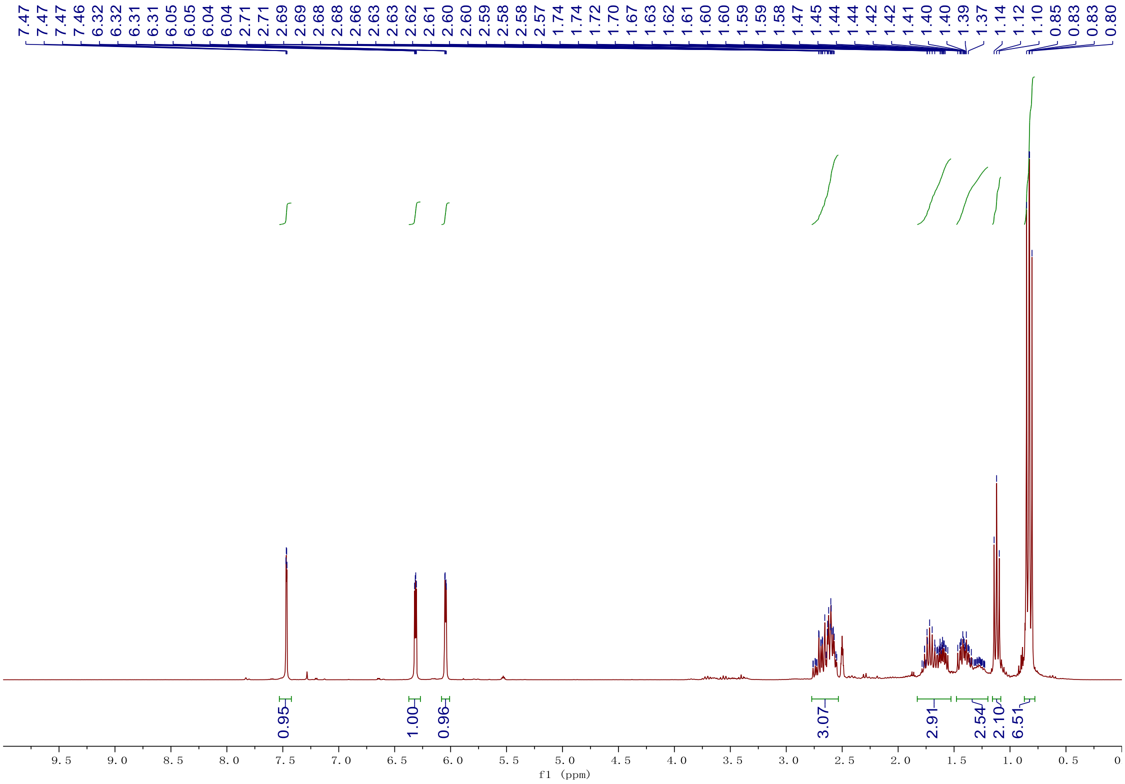
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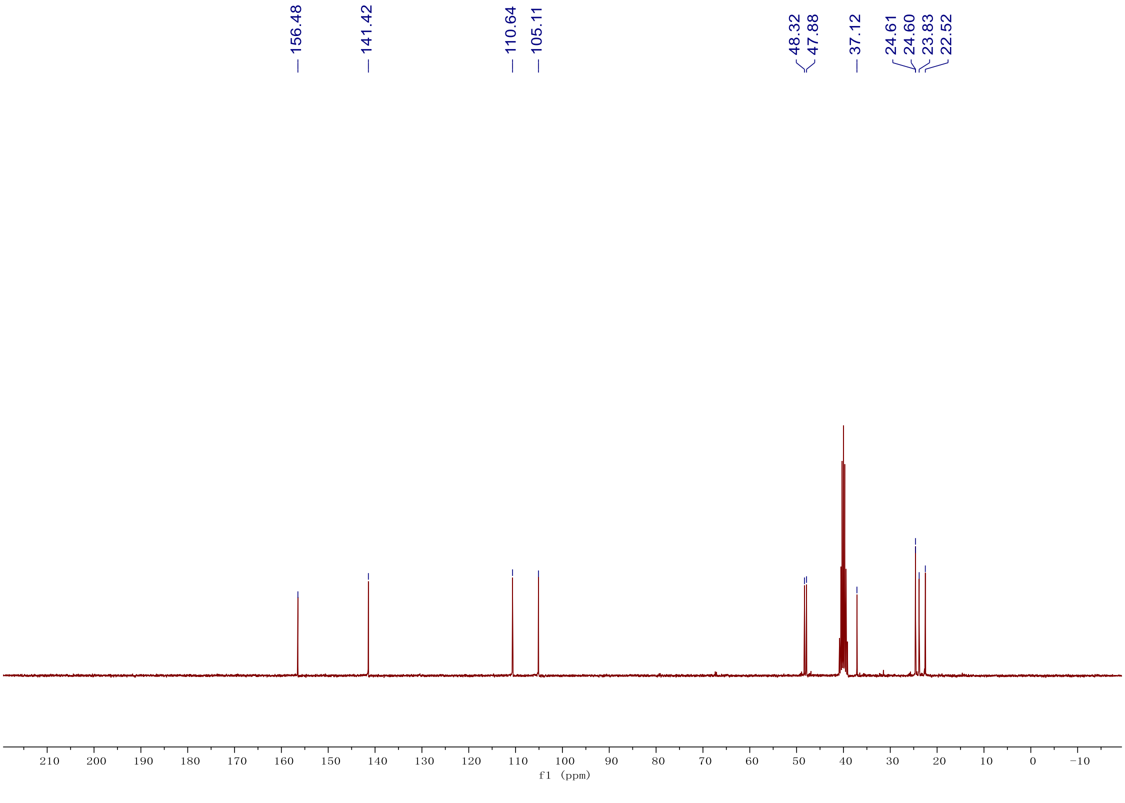
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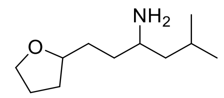
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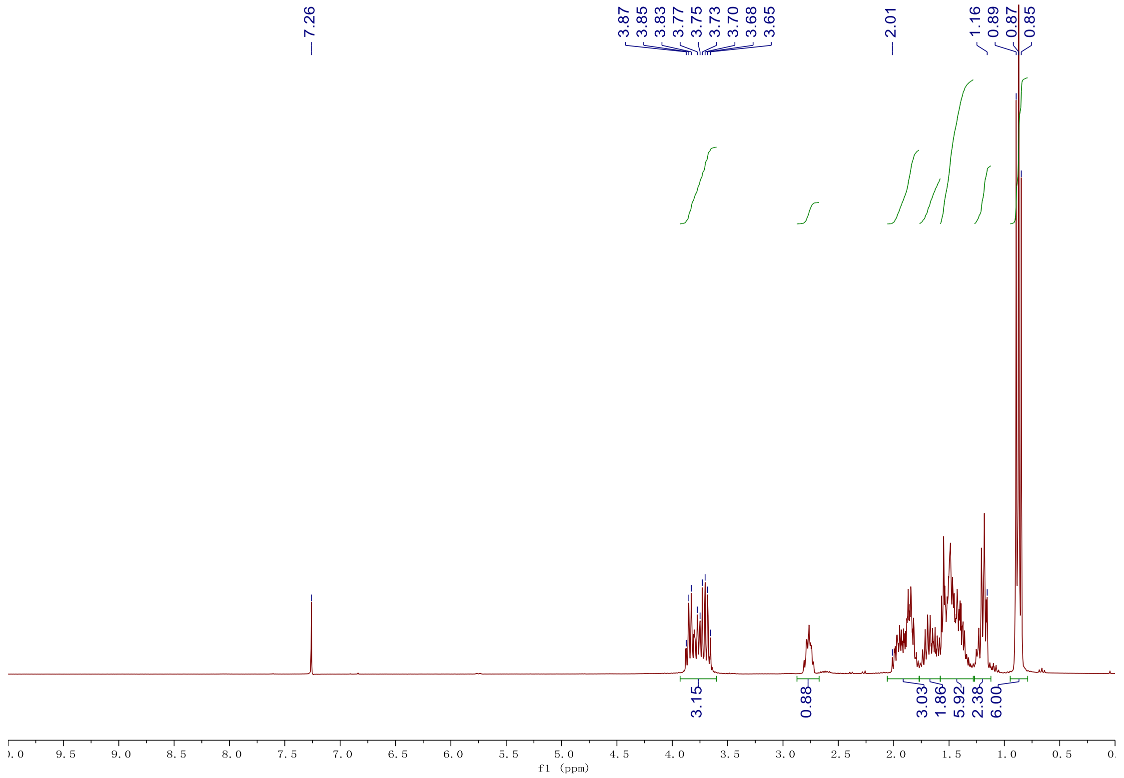
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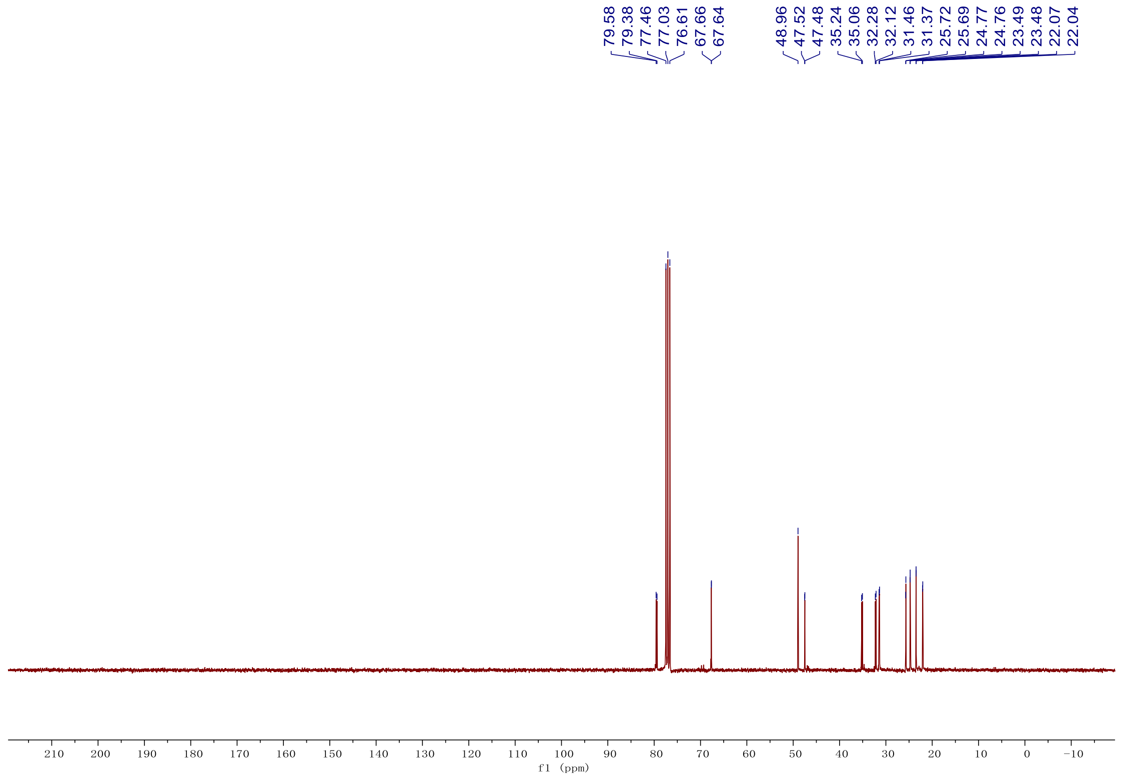
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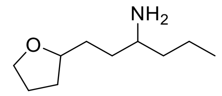
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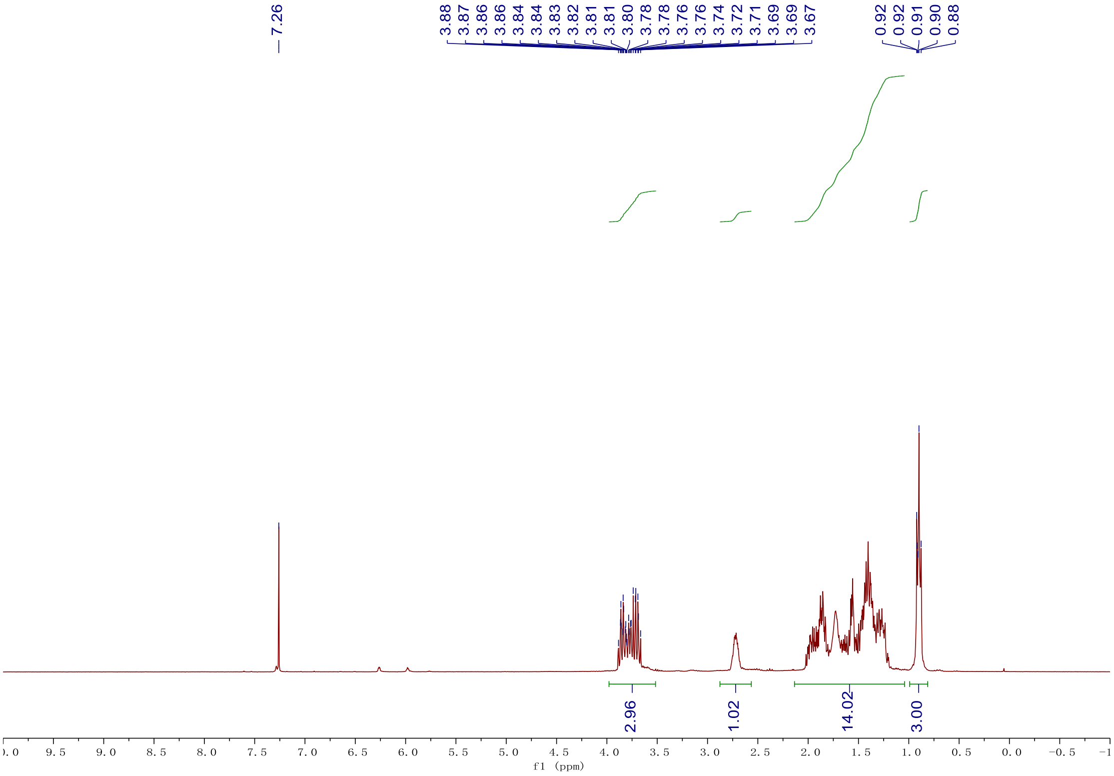
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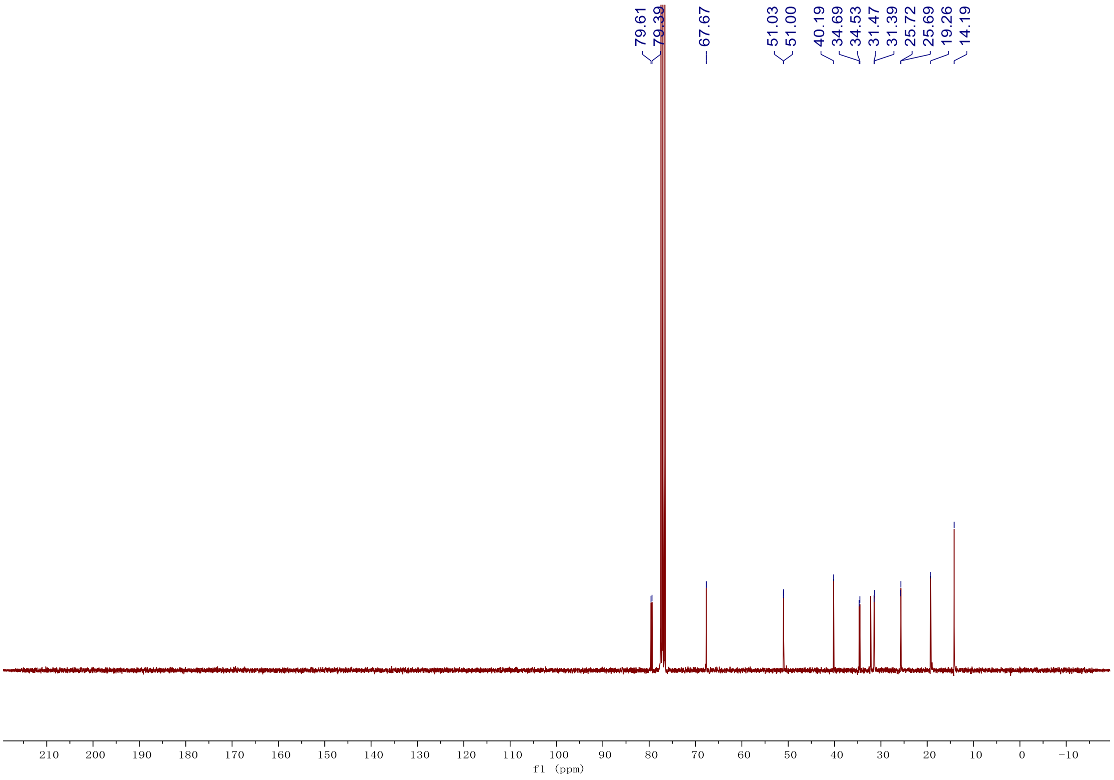
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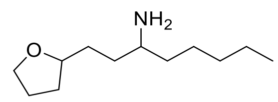
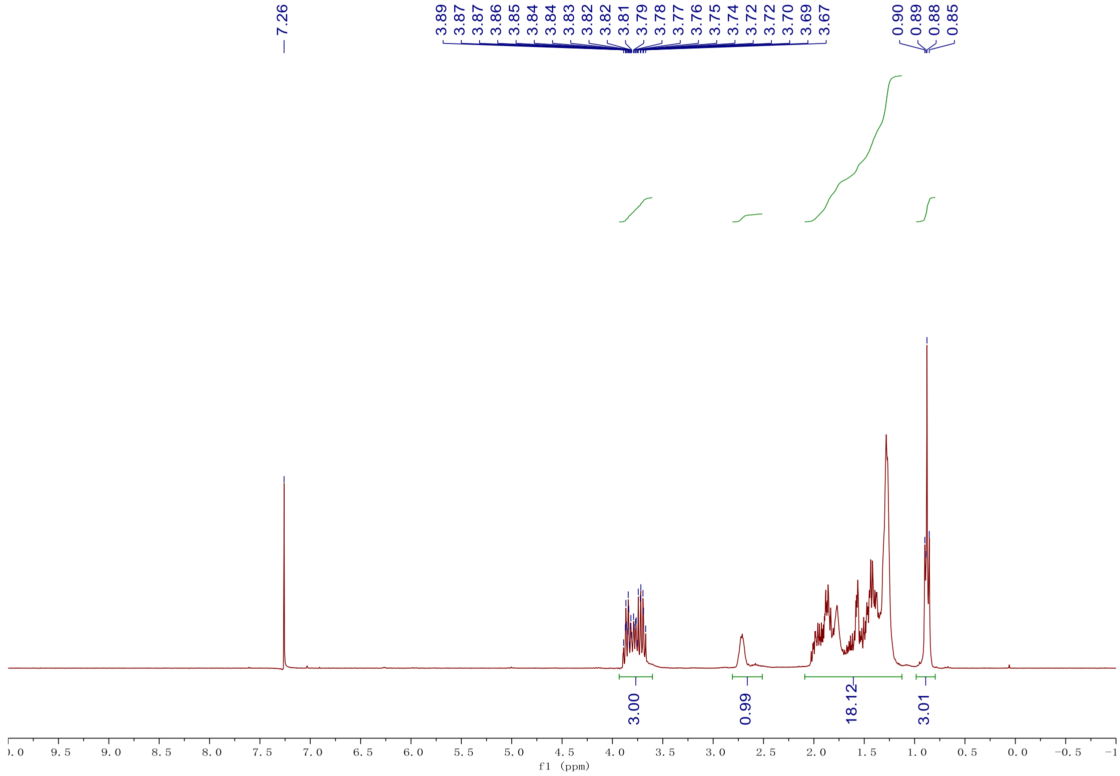

NH2
O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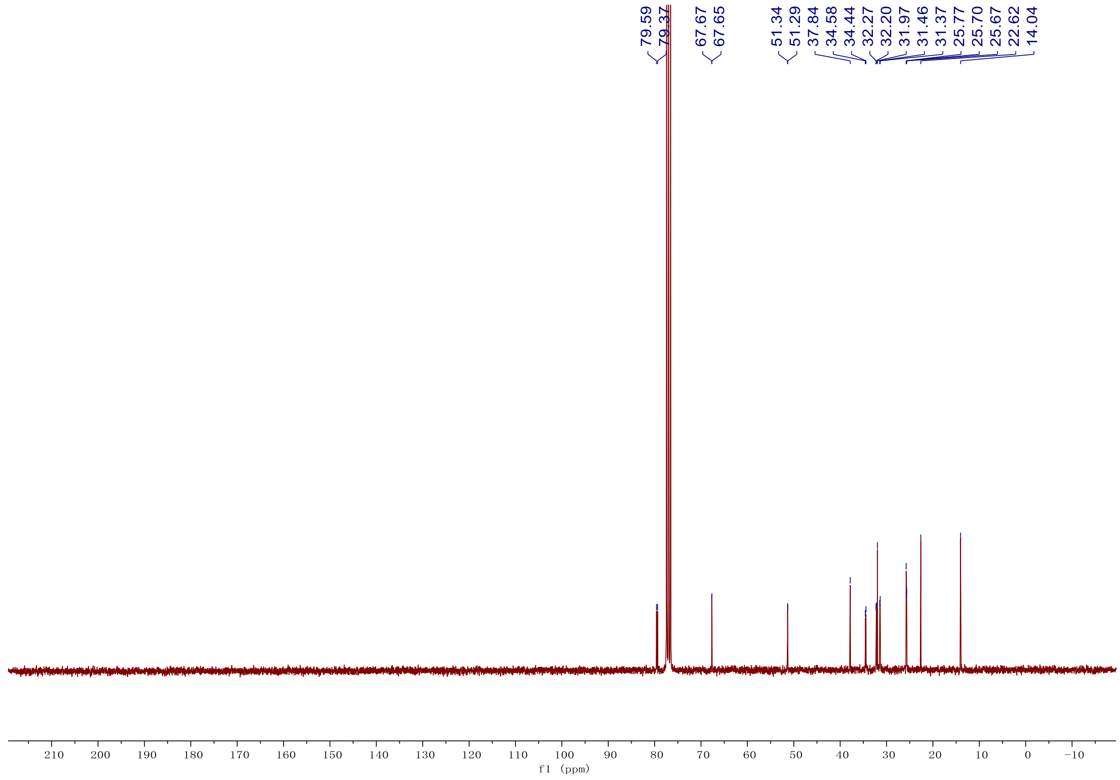
f1 (ppm)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200
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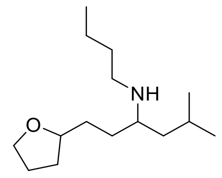
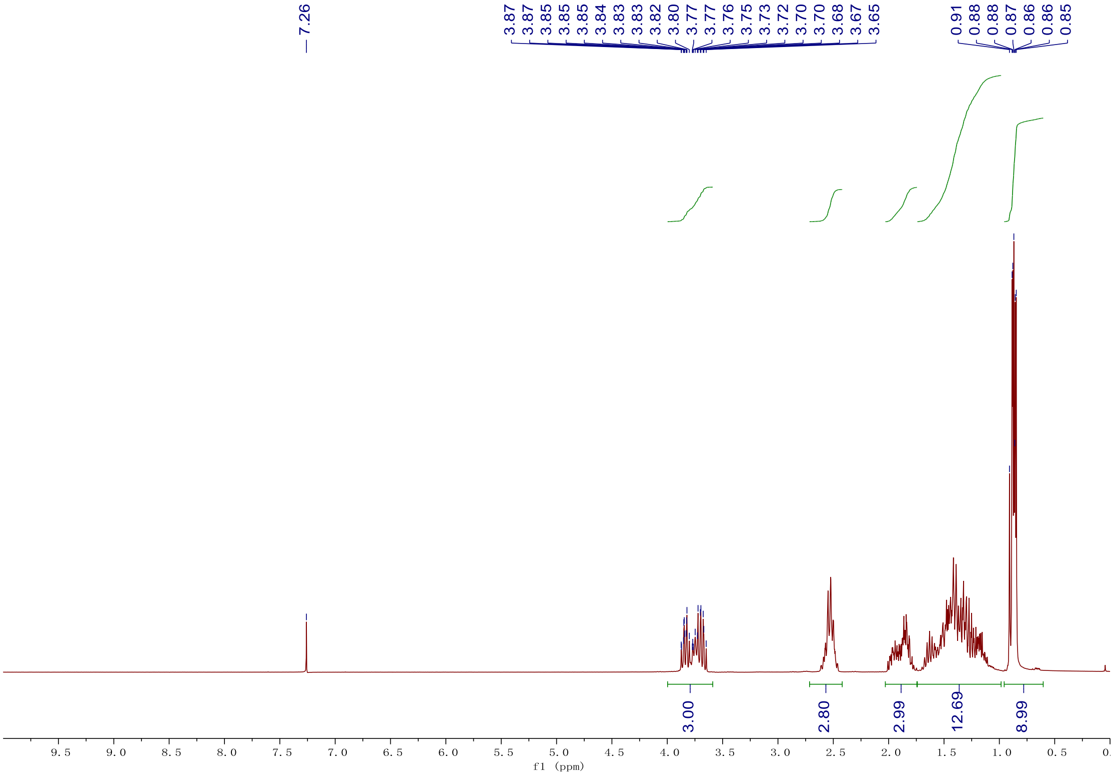
f1 (ppm)


NH
O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3.80
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3.76
3.75
3.73
3.72
3.70
3.70
3.68
3.67
3.65
0.91
0.88
0.88
0.87
0.86
0.86
0.85
3.00
2.80
2.99
12.69
8.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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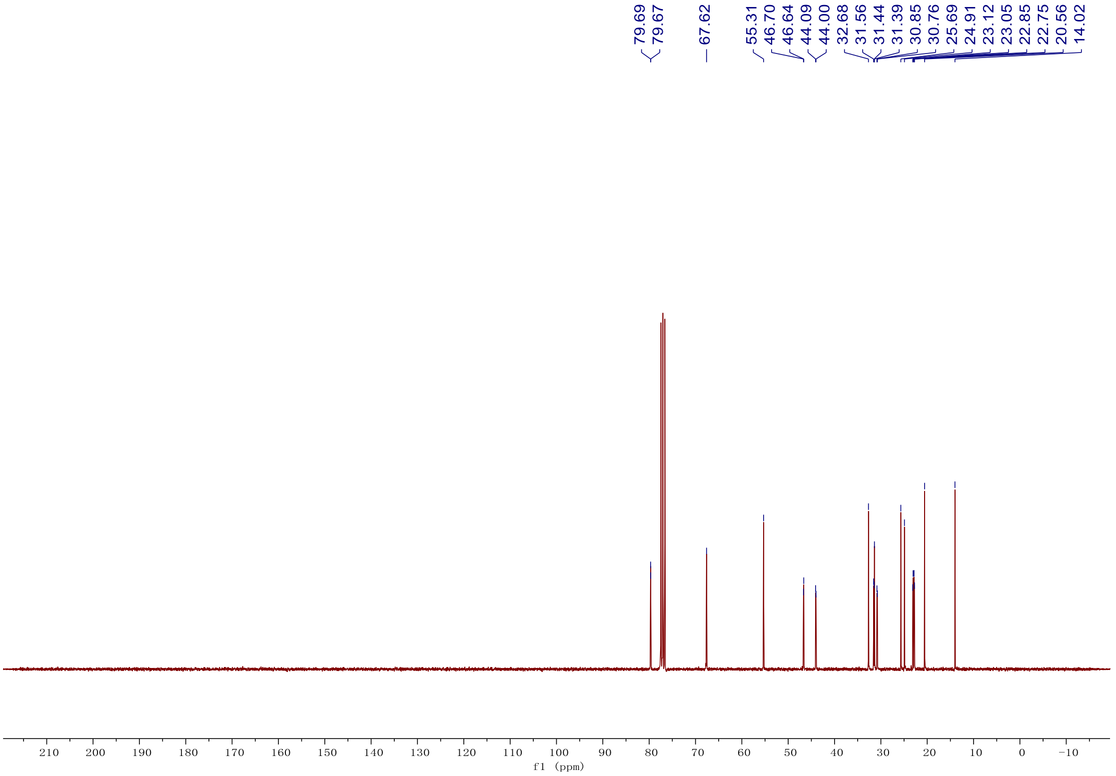
0.
f1 (ppm)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25.69
24.91
23.12
23.05
22.85
22.75
20.56
14.02
210
200
190
180
170
160
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100
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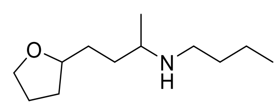
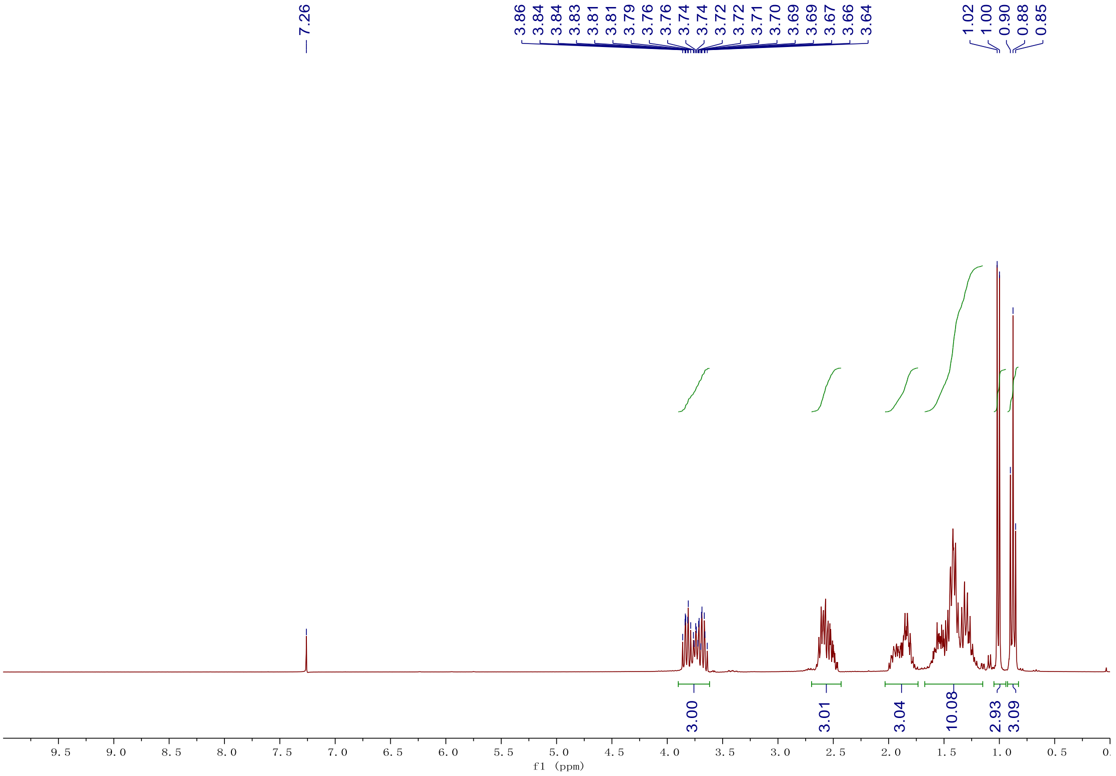
-10
f1 (ppm)


O
N
H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3.84
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3.79
3.76
3.76
3.74
3.74
3.72
3.72
3.71
3.70
3.69
3.67
3.66
3.64
1.02
1.00
0.90
0.88
0.85
3.00
3.01
3.04
10.08
2.93
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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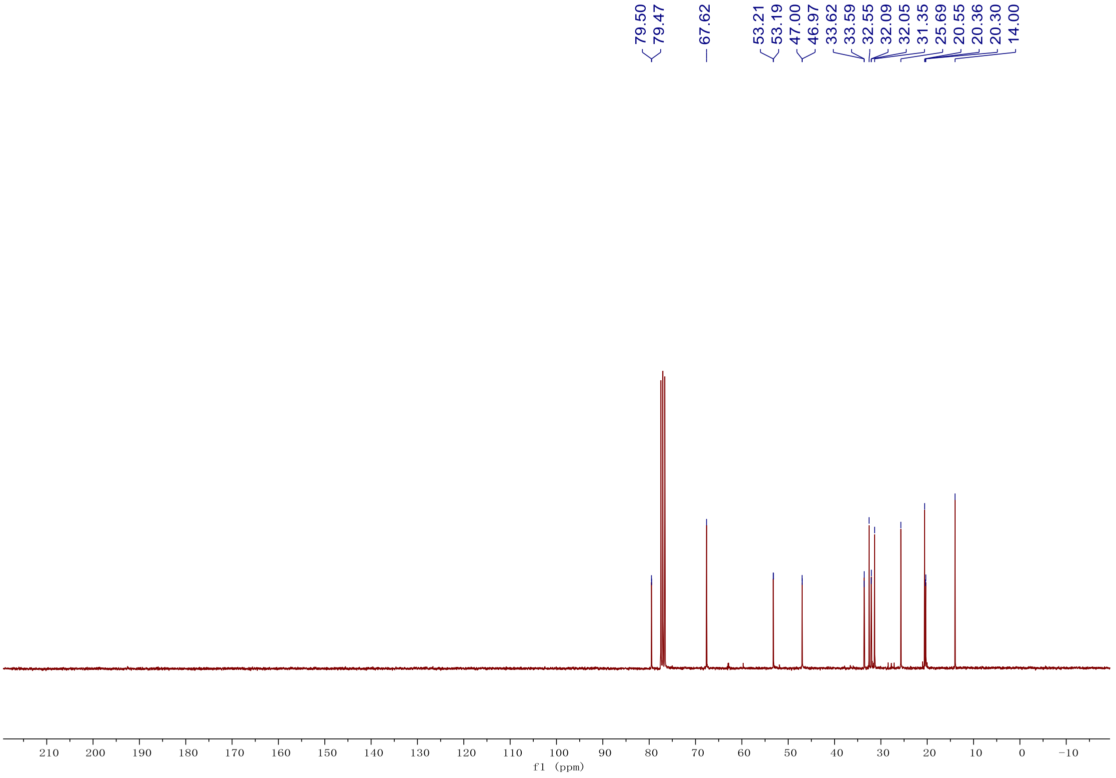
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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32.09
32.05
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25.69
20.55
20.36
20.30
14.00
210
200
190
180
170
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100
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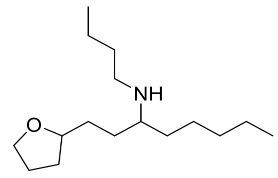
f1 (ppm)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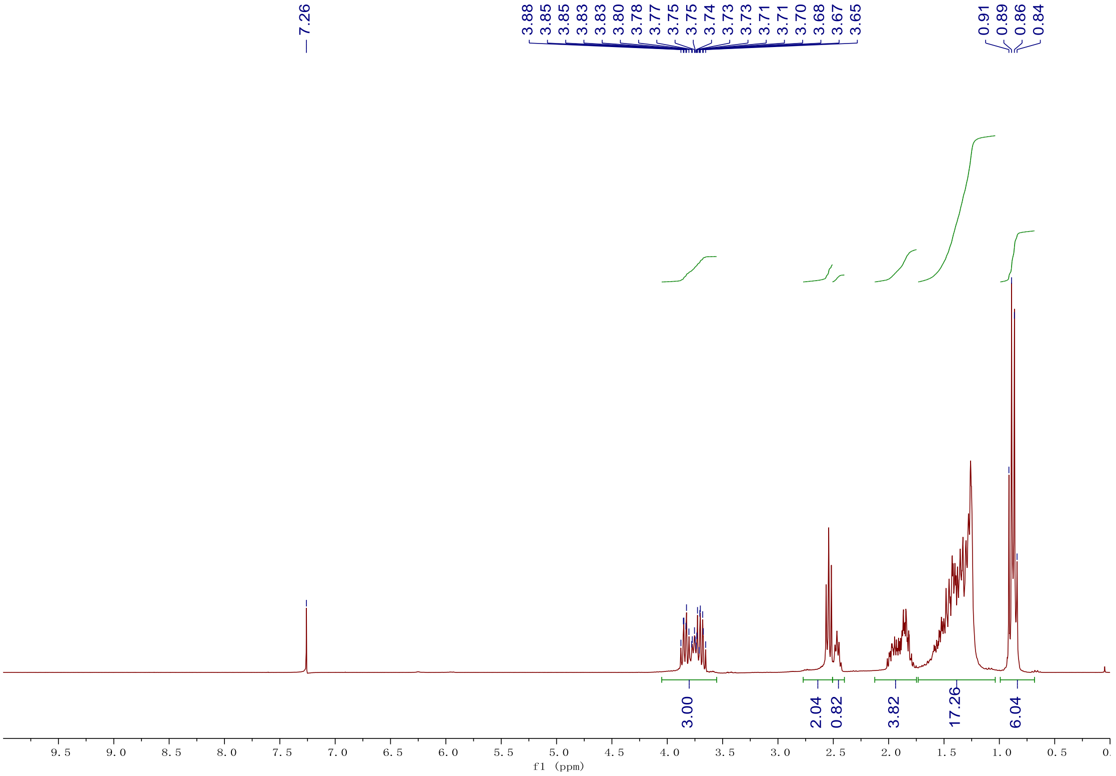
NH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3.73
3.71
3.71
3.70
3.68
3.67
3.65
0.91
0.89
0.86
0.84
3.00
2.04
0.82
3.82
17.26
6.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
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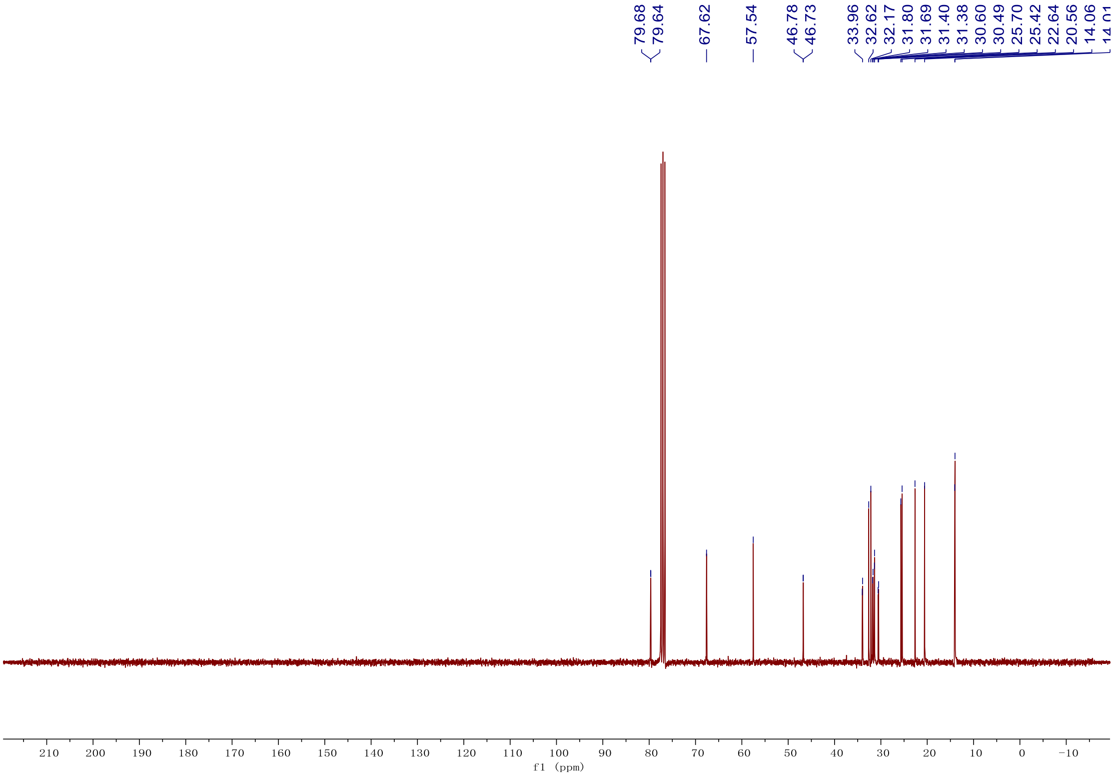
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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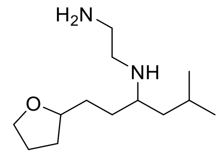
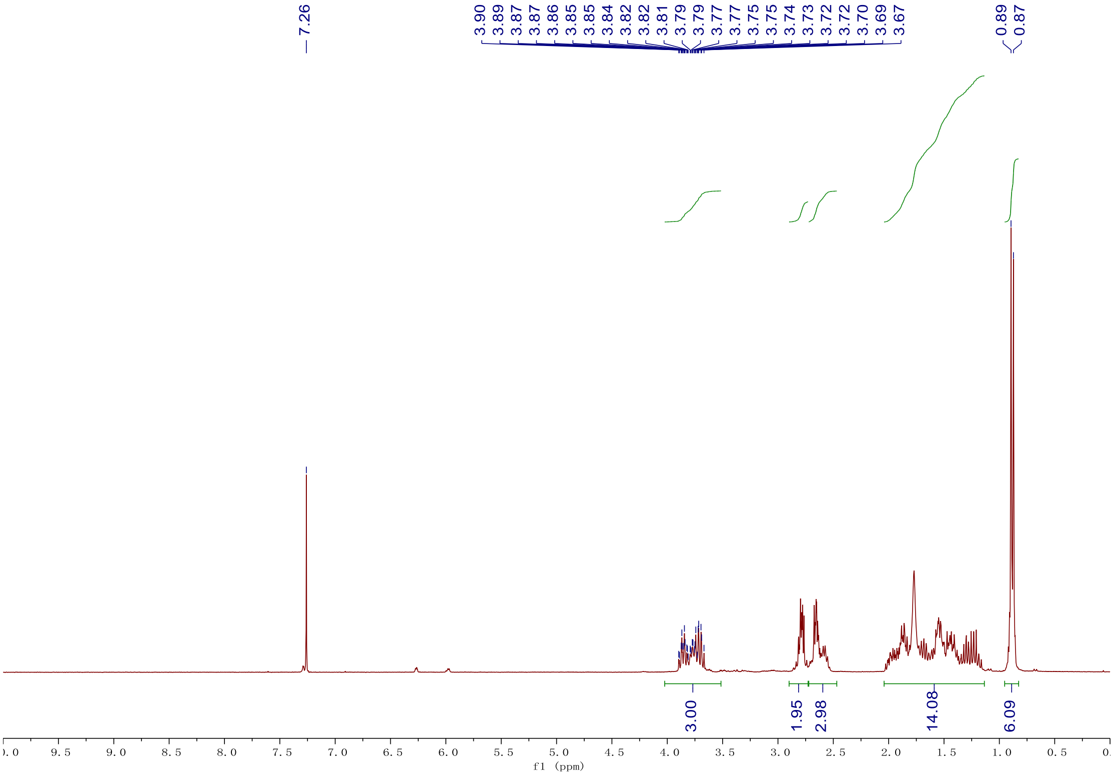
31.38
30.60
30.49
25.70
25.42
22.64
20.56
14.06
14.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


H2N
NH
O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3.89
3.87
3.87
3.86
3.85
3.85
3.84
3.82
3.82
3.81
3.79
3.79
3.77
3.77
3.75
3.75
3.74
3.73
3.72
3.72
3.70
3.69
3.67
0.89
0.87
3.00
1.95
2.98
14.08
6.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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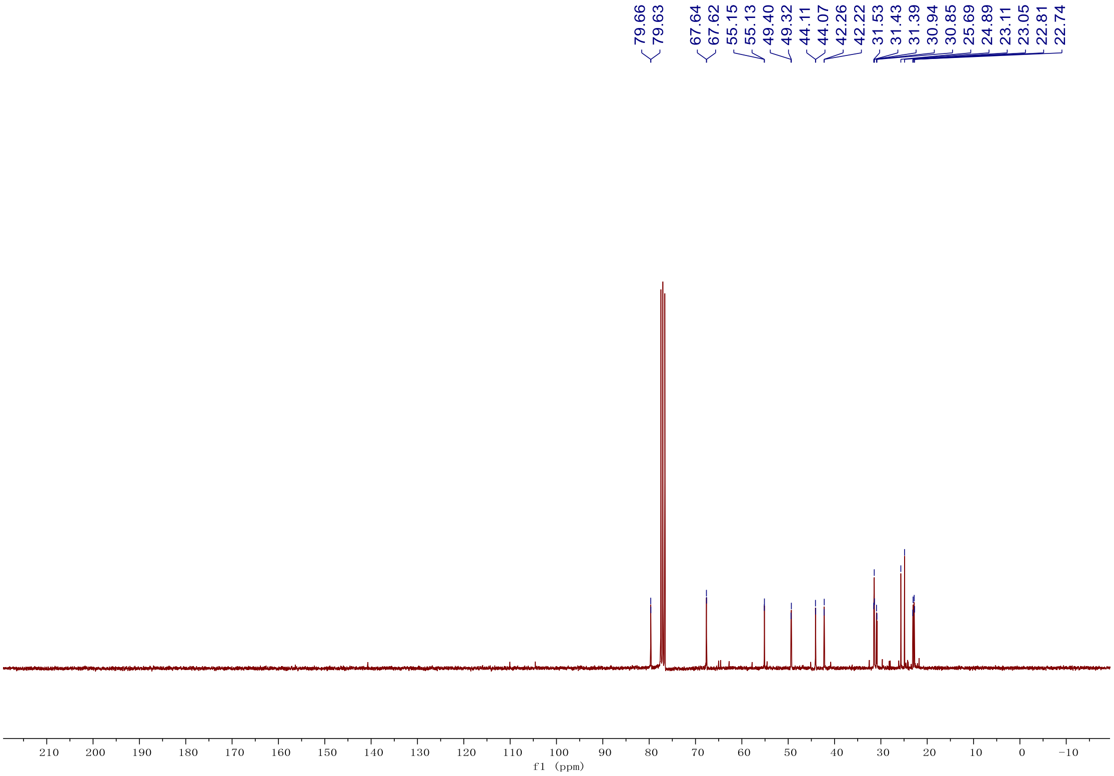
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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42.22
31.53
31.43
31.39
30.94
30.85
25.69
24.89
23.11
23.05
22.81
22.74
210
200
190
180
170
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140
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100
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80
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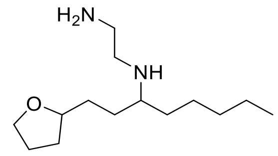
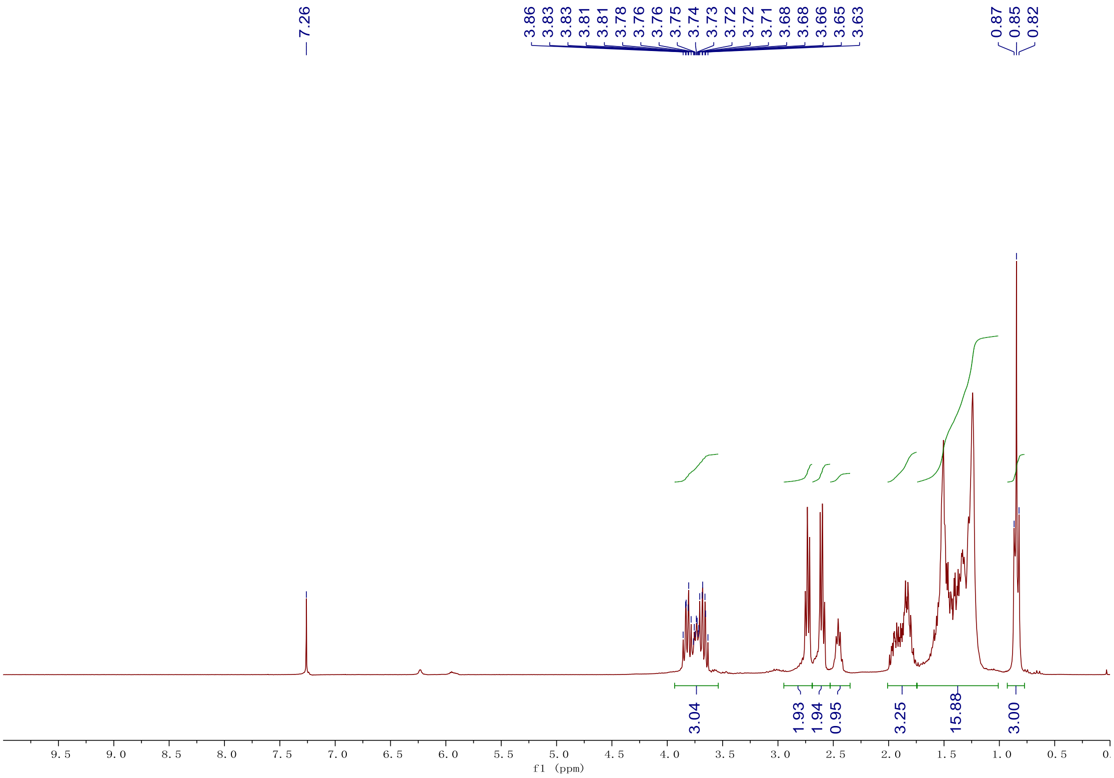
0
-10
f1 (ppm)


H2N
NH
O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3.83
3.83
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3.78
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3.76
3.75
3.74
3.73
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3.72
3.71
3.68
3.68
3.66
3.65
3.63
0.87
0.85
0.82
3.04
1.93
1.94
0.95
3.25
15.88
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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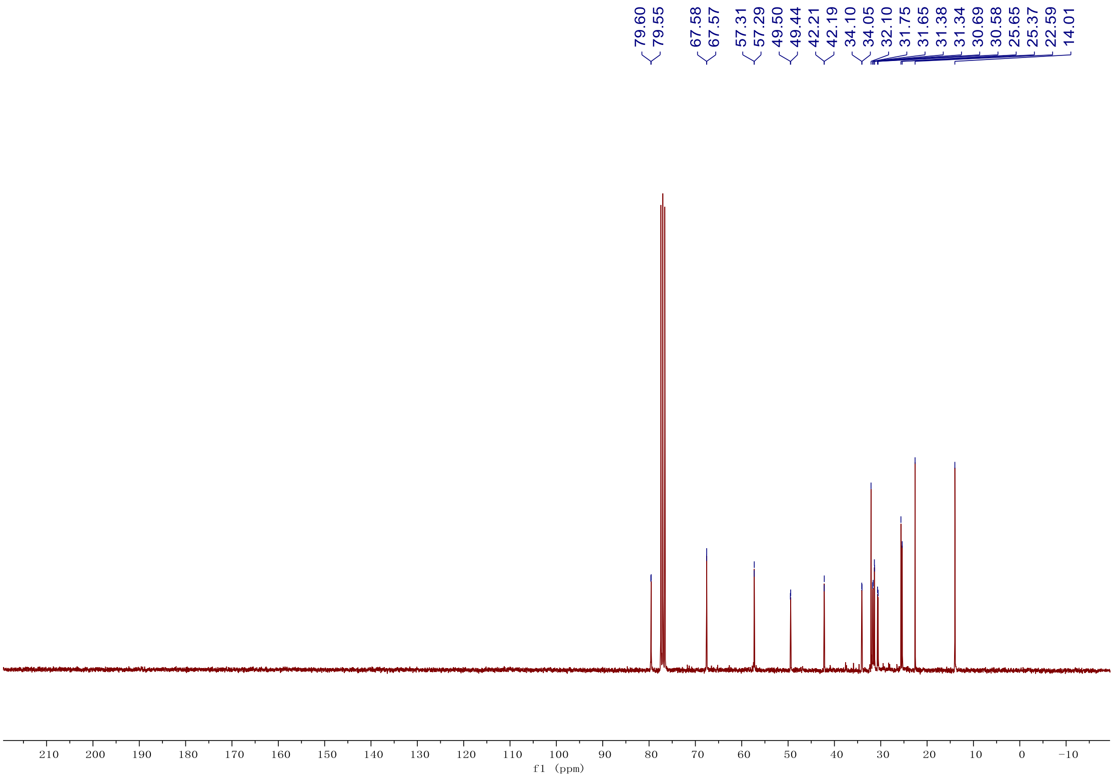
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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32.10
31.75
31.65
31.38
31.34
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30.58
25.65
25.37
22.59
14.01
210
200
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180
170
160
150
140
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120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)