Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary information for:

"Direct Alkenyl C-H Functionalization of Cyclic Enamines with Carboxylic Acids via Rh Catalysis Assisted by Hydrogen Bonding"

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Table of Contents

General Experimental Section

Analytic methods.

^{1}H NMR, ^{13}C NMR data were obtained on Bruker 400 M nuclear resonance spectrometers unless otherwise specified, respectively. $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. Flash chromatography was performed using 200‐300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin‐layer chromatography (TLC) was performed on pre‐coated, glass‐backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). HRMS (ESI) analysis was performed by Analytical Instrumentation Center, Chengdu Institute of Biology, Chinese Academy of Sciences.

General preparation for chemicals.

Dicarbonylacetylacetonato rhodium(I) (99%), Chloro(1,5-cyclooctadiene)rhodium(I)(97%) dimer, Hydroxy(1,5-cyclooctadiene)rhodium(I)dimer,min.(97%), and Dicarbonylchlororhodium(I) dimer (97%)were purchased from Alfa Aesar. All the acids were purchased from Alfa Aesar. All the solvents were directly used from purchased without any further purification unless otherwise specified.

General Experimental Procedures

General procedure for preparation of enamine substrates 1

The substituted 2-aminepyridines were prepared as equtions (S1-S3)below.

(Eqution S1)3-Hydropyridine (78.5 mmol, 7.46g) was added to ice cold H_2SO_4 (42 ml), concentrated HNO_3 (4 ml) was added dropwise while maintaining the temperature below 10 ^oC.[1] After addition, the reaction was monitored by TLC until disappear of the started material in about 4 h. The ice cold water was addition by caution and then it was neutralized to pH=6 by saturated potassium carbonate. It was cooled and then solid precipitated, it was filtered and washed with petroleum ether/EtOAc =10/1. Recrystal in petroleum ether/EtOAc and afford yellow solid. The aqueous phase was extracted by EtOAc and combined with the mother solution and purified by flash chromatography on silica gel with petroleum ether/EtOAc (5:1). The two parts were combined to give g desired product 8.25g.

2-Nitro-3-hydropyridine (20 mmol, 2.82g) and potassium carbonate (40 mmol, 5.52g) were half-dissolved in acetone (150 ml), Me_2SO_4[2] (26 mmol, 2.46 ml) or BnBr[3] (26 mmol, 3.09 ml) was added dropwise at 0 ^oC and stirred at room until disappear of the started material. It was quenched by water and the solvent was removed and extracted by EtOAc, dried over Na_2SO_4, evaporated in vacuum to afford crude product which was purified by flash chromatography on silica gel with ether/EtOAc (10:1) to produce the desired product. And finally the methyl ether was reduction by Pd/C, H_2 and benzyl ether was reduction by Fe/AcOH.

(Eqution S2)The new prepared sodium methoxide (200 mmol, 10.8g) was mixed with 3,5-dichloropyridine (20 mmol, 2.96g) and dissolved in DMF (60 ml) in the atmosphere of N_2, it was heated to 80 ^oC for 36 h and then cooled to room temperature.[4] The DMF was removed under reduced pressure and washed with water (20 ml), extracted by EtOAc, dried over Na_2SO_4, evaporated in vacuum to afford product which was purified by flash chromatography on silica gel with petroleum ether/EtOAc (10:1) to produce the desired product 1.81g.

3,5-Dimethoxypyridine (10 mmol, 1.39g) was dissolved in concentrated H_2SO_4 (20 ml), HNO_3 (10.5 mmol, 0.675 ml) and H_2SO_4 (20 ml) were mixed and was added dropwise at 0 ^oC.[5] It was stirred for 5 minutes and quenched by ice and extracted by

EtOAc, dried over Na_2SO_4, evaporated in vacuum to afford crude product which was purified by flash chromatography on silica gel with petroleum ether/EtOAc (4:1) to produce the desired product 1.57 g. And finally it was reduction by Pd/C, H_2 in at room temperature.

(Eqution S3)Br_2 (107.26 mmol, 5.50 ml) was added to 10% NaOH solution 50 ml 5-10 ^oC. This sodium hypobromide solution was added over 2 h to a solution of 3-hydropyridine (105.15 mmol, 10 g) in 10% NaOH (50 ml).[6] The mixture was for additional 2 h. Acetic acid was added to bring the pH of the solution to between 6 and 7. The mixture was cooled to 5 ^oC for 1 h, and product was filtered off. It was washed with water and dried in vacuo at 85 ^oC to give the product 6.4 g as white solid. The methylation[2, 7], nitration[1, 8], debromide and reduction[8] to afford the desired product.

Substrates **1a-1j** was prepared by condensation of 1,2-ketones with substituted arylamine or acetamide as eqution below.[9]

(Equtuion S4)In a 50 mL round bottom flask, equipped with a condenser, 1,2-dione (10mmol) , arylamine or acetic amide (10 mmol), alumina (10 g) and toluene (30mL) was stirred and heated to reflux for 36 h. Upon reaction completion, alumina was removed by filtration and washed with EtOAc. The organic phases were combined and concentrated under vacuum and the residue was purified by flash chromatography eluting with petroleum ether/EtOAc (20:1-4:1) to give substrates **1a-1j**.

General Experimental Procedures and Characterizations

$[Rh(cod)Cl]_2$ (0.005 mmol, 2.4 mg) or $[Rh(CO)_2Cl]_2$ (0.005 mmol, 1.9 mg), enamine **1** (0.2 mmol), and carboxylic acid (0.24 mmol) were added to a Schlenk flask, which was then degassed with N_2 for three times. $(^tBuCO)_2O$ (0.3 mmol) and 2 mL of anhydrous toluene were added, and the reaction mixture was subsequently heated and kept at 140^{o}C in oil bath for the indicated time with stirring. After cooling to room temperature, 1 mL of a concentrated ammonia solution was added. The mixture was directly subjected to column chromatograph on silica gel with petroleum ether/EtOAc (12:1-5:1) as eluent to afford the desired product **2** or **3**.

General Experimental Procedures for 1 mmol scale

$[Rh(cod)Cl]_2$ (0.025 mmol, 12 mg) enamine **1c** (1 mmol, 218.3 mg), and carboxylic acid (0.24 mmol) were added to a Schlenk flask, which was then degassed with N_2 for three times. $(^tBuCO)_2O$ (3 mmol, 0.305) and 10 mL of anhydrous toluene were added, and the reaction mixture was subsequently heated and kept at 140^{o}C in oil bath for the indicated time with stirring. After cooling to room temperature, 4 mL of a concentrated ammonia solution was added. The mixture was directly subjected to column chromatograph on silica gel with petroleum ether/EtOAc (12:1-5:1) as eluent to afford the desired product **2** or **3**.

The hydrolysis of enamine product

(Equtuion S5)In a sealed tube, substrate **2a** (0.2 mmol, 58.8 mg), TsOH (0.8 mmol, 137.8 mg) and toluene/H_2O (1/1, 4 ml) were stirred at 140^oC for 36 h. After reaction completed, the mixture was extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with sat. $NaHCO_3$ (10 mL) and brine (10 mL) and dried over The solvent was removed under vacuum and the residue was purified by flash chromatography eluting with petroleum ether/EtOAc (10:1) to give product **4a** (24.5 mg, 65%) as white solid, part of **2a** was recovered (14.7 mg, 25%).

(Eqution S6)In a sealed tube, substrate **2w** (0.2 mmol), TsOH (0.8 mmol, 137.8 mg) and toluene/H_2O (1/1, 4 ml) were stirred at 140^oC for 24 h. After reaction completed, the mixture was diluted with 10 mL water and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with sat. $NaHCO_3$ (30 mL) and brine (30 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash chromatography eluting with petroleum ether/EtOAc (10:1) to give product **4w** (21.0 mg, 75%) as pale oil.

Characterization of Enamine Substrates 1 in Details

5-methyl-2-(pyridin-2-ylamino)cyclopent-2-enone

Compound **1a**[9] was obtained as amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.67 (t, *J* = 3.2 Hz, 1H), 7.51 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 6.78-6.75 (m, 2H), 6.70 (d, *J* = 8.4 Hz, 1H), 2.95 (ddd, *J* = 18.4, 6.4, 3.2 Hz, 1H), 2.50-2.42 (m, 1H), 2.27 (ddd, *J* = 18.4, 3.2, 2.0 Hz, 1H), 1.23 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.25, 154.33, 147.88, 137.33, 137.05, 131.27, 115.39, 110.63, 37.83, 33.86, 16.36.

5-methyl-2-((3-methylpyridin-2-yl)amino)cyclopent-2-enone

Compound **1b** was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 4.0 Hz, 1H), 7.83 (t, *J* = 2.8 Hz, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 6.72 (dd, *J* = 7.2, 5.2 Hz, 1H), 6.66 (br, 1H), 2.96 (ddd, *J* = 18.0, 6.4, 3.2 Hz, 1H), 2.51-2.43 (m, 1H), 2.31-2.27 (m, 1H), 2.25 (s, 3H), 1.24 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.50, 152.77, 145.29, 137.53, 136.88, 132.09, 118.33, 115.40, 37.80, 33.93, 16.82, 16.40.

HRMS: m/z: $[M + H]^+$ calculated for $C_{15}H_{15}N_2O$: 203.1179; found 203.1181.

2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Compound **1c** was obtained as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.82 (m, 2H), 7.34 (br, 1H), 6.95 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.72 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.87 (s, 3H), 2.94 (ddd, *J* = 18.4, 6.4, 3.2 Hz, 1H), 2.48-2.40 (m, 1H), 2.26 (ddd, *J* = 18.2, 3.2, 2.0 Hz, 1H), 1.23 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.27, 145.53, 142.95, 138.25, 136.75, 131.88, 114.73, 114.62, 55.26, 37.81, 33.90, 16.44.

HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{15}N_2O_2$: 219.1128; found 219.1132.

2-((3-(benzyloxy)pyridin-2-yl)amino)-5-methylcyclopent-2-enone

Compound **1d** was obtained as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.84 (m, 2H), 7.47 (br, 1H), 7.43-7.33 (m, 5H), 6.99 (d, *J* =8.0 Hz, 1H), 6.67 (dd, *J* = 7.6, 5.2 Hz, 1H), 5.14 (s, 2H), 2.95 (ddd, *J*=18.4, 6.4, 3.2 Hz, 1H), 2.48-2.41 (m, 1H), 2.27 (d, *J* = 18.4 Hz, 1H), 1.24 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.17, 145.74, 141.84, 138.63, 136.69, 135.89, 131.89, 128.67, 128.14, 127.03, 116.48, 114.65, 70.21, 37.78, 33.88, 16.36.

HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{19}N_2O_2$: 295.1441; found 295.1447.

2-((3,5-dimethoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Compound **1e** was obtained as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.72 (m, 1H), 7.48 (s, 1H), 7.11 (br, 1H), 6.65 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.94-2.87 (m, 1H), 2.43-2.38 (m, 1H), 2.23 (d, *J* = 18.0 Hz, 1H), 1.20 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.31, 150.25, 143.54, 140.06, 136.94, 130.00, 120.82, 105.82, 56.18, 55.38, 37.80, 33.78, 16.41.

HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{17}N_2O_3$: 249.1234; found 249.1237.

2-((5-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Compound **1f** was obtained as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.8 Hz, 1H), 7.54 (t, *J* = 3.2 Hz, 1H), 7.17 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 1H), 6.62 (br, 1H), 3.81 (s, 3H), 2.93 (ddd, *J* = 18.0, 6.4, 3.2 Hz, 1H), 2.49-2.41 (m, 1H), 2.26 (ddd, *J*=18.4, 2.8, 2.0 Hz, 1H), 1.23 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.34, 150.05, 148.71, 137.41, 132.81, 129.24, 125.17, 111.13, 56.10, 37.85, 33.73, 16.36.

HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{15}N_2O_2$: 219.1128; found 219.1133.

N-(4-methyl-5-oxocyclopent-1-en-1-yl)acetamide

Compound **1g** was obtained as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 2.87 (ddd, *J*=18.8, 6.0, 4.7Hz, 1H), 2.40-2.32 (m, 1H), 2.23-2.17 (m, 1H), 2.12 (s, 3H), 1.15 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100MHz, $CDCl_3$) δ 206.45, 168.80, 139.23, 135.67, 37.72, 34.03, 23.60, 15.99.

HRMS: m/z: [M + H]+ calculated for $C_8H_{12}NO_2$: 154.0863; found 154.0868.

2-((2-methoxyphenyl)amino)-5-methylcyclopent-2-enone

Compound **1h** was obtained as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.6 Hz, 1H), 6.95- 6.90 (m, 1H), 6.87-6.86 (d, *J* = 4.0 Hz, 2H), 6.84 (br, 1H), 6.68 (t, *J* = 3.2 Hz, 1H), 3.88 (s, 3H), 2.91 (ddd, *J* = 18.0, 6.4, 3.2 Hz, 1H), 2.50-2.42 (m, 1H), 2.26-2.20 (m, 1H), 1.24 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 207.31, 147.96, 138.66, 131.52, 122.91, 120.69, 120.08, 114.17, 110.07, 55.49, 37.77, 33.30, 16.42.

HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{16}NO_2$: 218.1176; found 218.1180.

2-((3-methoxypyridin-2-yl)amino)cyclopent-2-enone

Compound **1i** was obtained as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, *J* = 2.8 Hz, 1H), 7.83 (d, *J* = 5.2 Hz, 1H), 7.37 (br, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.72 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.87 (s, 3H), 2.69 (dd, *J* = 7.6, 3.2 Hz, 2H), 2.45-2.43(m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 204.69, 145.44, 142.96, 138.26, 137.90, 133.44, 114.64, 114.18, 55.27, 32.37, 24.57.

HRMS: m/z: $[M + H]^+$ calculated for $C_{11}H_{13}N_2O_2$: 205.0972; found 205.0978.

2-((3-methoxypyridin-2-yl)amino)cyclohex-2-enone

Compound **1j** was obtained as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (t, *J* = 4.8 Hz, 1H), 7.86 (br, 1H), 7.77 (d, *J* = 4.8 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.87 (s, 3H), 2.59-2.52 (m, 4H), 2.02 (q, *J*=6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.12, 146.48, 143.11, 137.78, 133.80, 123.76, 114.17, 113.91, 55.31, 37.60, 24.87, 22.80.

HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{15}N_2O_2$: 219.1128; found 219.1130.

Characterization of Products in Details

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-phenylcyclopent-2-enone

Petroleum ether/EtOAc =4/1 as eluate and **2a** was obtained as yellow solid (55.3 mg, 94%, condition A; 279.6 mg, 95%, 1mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.47 (m, 2H), 7.36 (d, *J* = 4.0 Hz, 1H), 7.28-7.21 (m, 3H), 6.94-6.91 (m, 2H), 6.56 (dd, *J* = 8.0, 5.2Hz, 1H), 3.88 (s, 3H), 3.33 (dd, *J* = 17.2, 6.8 Hz, 1H), 2.72-2.62 (m, 2H), 1.32 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.65, 149.12, 144.47, 143.65, 137.94, 136.53, 132.90, 128.78, 127.62, 127.55, 114.80, 114.52, 55.22, 37.87, 36.29, 16.42.

HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{19}N_2O_2$: 295.1441; found 295.1442.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(p-tolyl)cyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **2b** was obtained as yellow solid (55.5 mg, 90%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.84 (br, 1H), 6.57 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.89 (s, 3H), 3.31 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.70-2.61 (m, 2H), 2.32 (s, 3H), 1.31 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.63, 150.38, 144.85, 143.56, 139.17, 138.05, 133.33, 132.49, 128.34, 127.66, 114.73, 114.36, 55.19, 37.74, 36.15, 21.36, 16.40.

HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{21}N_2O_2$: 309.1598; found 309.1609.

3-(4-methoxyphenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Petroleum ether/EtOAc =3/1 as eluate and **2c** was obtained as yellow solid (59.0 mg, 91%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.43-7.42 (m, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.81 (br, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.57 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.31 (dd, *J* = 16.9, 7.2 Hz, 1H), 2.68 – 2.59 (m, 2H), 1.29 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.55, 160.23, 150.71, 145.01, 143.56, 138.12, 131.76, 129.54, 128.66, 114.69, 114.26, 113.01, 55.20, 55.14, 37.63, 36.06, 16.50.

HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{21}N_2O_3$: 325.1547; found 325.1554.

3-(4-fluorophenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **2d** was obtained as yellow solid (55.8 mg, 89%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.36 (dd, *J* = 4.2, 1.2 Hz, 1H), 6.95-6.89 (m, 4H), 6.58 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.89 (s, 3H), 3.30 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.70-2.61 (m, 2H), 1.31 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.49, 162.71 (d, *J*=248.3 Hz), 147.81, 144.30, 143.68, 137.85, 132.74 (d, *J*=3.3 Hz), 132.56, 129.67 (d, *J* = 8.3 Hz), 114.71 (d, *J* = 24.2 Hz), 114.66, 114.59, 55.20, 37.73, 36.25, 16.40.

HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{18}FN_2O_2$: 313.1347; found 313.1358.

3-(4-chlorophenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **2e** was obtained as yellow solid (59.8 mg, 91%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.99 (br, 1H), 6.94 (dd, *J* = 8, 0.8 Hz,1H), 6.58 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.89 (s, 3H), 3.29 (dd, *J* = 17.6, 7.2 Hz, 1H), 2.68-2.61(m, 2H), 1.31 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.44, 146.82, 144.08, 143.71, 137.87, 135.16, 134.39, 132.92, 129.00, 127.65, 114.89, 114.83, 55.24, 37.78, 36.18, 16.41.

HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{18}ClN_2O_2$: 329.1051; found 329.1065.

3-(4-bromophenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **2f** was obtained as yellow solid (47.0 mg, 63%, condition A; 59.0 mg, 79%, condition B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H), 6.99 (br, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.59 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.89 (s, 3H), 3.29 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.69-2.61 (m, 2H), 1.31 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.48, 146.82, 144.05, 143.73, 137.89, 135.63, 132.97, 130.62, 129.24, 122.79, 114.93, 114.88, 55.26, 37.80, 36.14, 16.40.

HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{18}BrN_2O_2$: 373.0546; found 373.0555.

4-(2-((3-methoxypyridin-2-yl)amino)-4-methyl-3-oxocyclopent-1-en-1-yl)benzonitrile

Petroleum ether/EtOAc =4/1 as eluate and **2g** was obtained as yellow solid (33.2 mg, 52%, condition A; 58.8 mg, 92%, condition B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49p-7.43 (m, 4H), 7.25 d, *J*=5.2 Hz, 1H), 7.18 (br, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.91 (s, 3H), 3.30 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.71-2.65 (m, 2H), 1.33 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.28, 143.92, 143.25, 143.12, 141.83, 137.51, 133.92, 131.02, 128.03, 118.92, 115.43, 115.17, 111.13, 55.32, 37.95, 36.13, 16.37.
HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{18}N_3O_2$: 320.1394; found 320.1399.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(4-(trifluoromethyl)phenyl)cyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **2h** was obtained as yellow solid (29.0 mg, 40%, condition A; 52.2 mg, 72%, condition B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 4H), 7.27 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.09 (br, 1H), 6.95 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.58 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.90 (s, 3H), 3.32 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.75-2.64 (m, 2H), 1.33 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.49, 145.03, 143.84, 143.68, 140.56, 137.68, 133.68, 129.87 (q, *J* = 32.1 Hz), 127.77, 124.25 (q, *J* = 3.8 Hz), 124.02 (q, *J* = 270.6 Hz), 115.14, 114.05, 55.28, 37.94, 36.31, 16.38.
HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{18}F_3N_2O_2$: 363.1315; found 363.1318.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(m-tolyl)cyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **2i** was obtained as yellow solid (56.7 mg, 92%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.8 Hz, 1H), 7.29-7.28 (m, 2H), 7.14-7.07 (m, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.88 (br, 1H), 6.57 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.90 (s, 3H), 3.32 (dd, *J* = 17.2, 6.8 Hz, 1H), 2.71-2.61 (m, 2H), 2.24 (s, 3H), 1.32 (d, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.61, 149.15, 144.54, 143.67, 137.99, 137.00, 136.30, 132.89, 129.55, 128.25, 127.41, 124.91, 114.78, 114.45, 55.22, 37.84, 36.29, 21.26, 16.40.
HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{21}N_2O_2$: 309.1598; found 309.1613.

3-(3-methoxyphenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc =3/1 as eluate and 2j was obtained as faint yellow solid (59.7 mg, 92%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 4.8 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.89 (br, 1H), 6.82 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.58 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.87 (s, 3H), 3.57 (s, 3H), 3.31 (dd, *J* = 17.2, 6.8 Hz, 1H), 2.71-2.62 (m, 2H), 1.31 (d, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.64, 158.81, 148.84, 144.47, 143.70, 138.02, 137.68, 133.04, 128.49, 120.19, 115.17, 114.85, 114.62, 112.80, 55.25, 54.89, 37.85, 36.32, 16.38.
HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{21}N_2O_3$: 325.1547; found 325.1549.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(3-nitrophenyl)cyclopent-2-enone
Petroleum ether/EtOAc =3/1 as eluate and **2k** was obtained as yellow solid (29.2 mg, 43%, condition B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.18 (m, 1H), 8.08 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.23-7.21 (m, 2H), 6.96 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.58 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.93 (s, 3H), 3.36 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.77-2.67 (m, 2H), 1.33 (d, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.32, 147.42, 144.13, 143.36, 142.59, 138.79, 137.44, 133.78, 133.52, 128.04, 122.68, 122.52, 115.44, 115.30, 55.40, 37.94, 36.18, 16.43.
HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{18}N_3O_4$: 340.1292; found 340.1295.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(o-tolyl)cyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **2l** was obtained as yellow solid (20.4 mg, 33%, condition B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.30 (m, 1H), 7.19-7.12 (m, 2H), 7.10 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.01 (d, *J* = 6.8 Hz, 1H), 6.87 (br, 1H), 6.82 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.47 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.81 (s, 3H), 3.20 (dd, *J* = 17.6, 6.8 Hz, 1H), 2.71-2.58 (m, 2H), 2.06 (s, 3H), 1.33 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.14, 148.48, 143.86, 142.99, 138.94, 137.48, 135.30, 134.14, 129.53, 127.56, 126.43, 124.99, 114.69, 114.64, 55.15, 39.02, 38.46, 19.83, 16.50.

HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{21}N_2O_2$: 309.1598; found 309.1613.

3-(2-methoxyphenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Petroleum ether/EtOAc =4/1 as eluate and **2m** was obtained as faint yellow solid (58.4 mg, 90%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.28-7.23 (m, 2H), 7.08 (br, 1H), 6.91 (td, *J* = 7.6, 0.4 Hz, 1H), 6.84 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.48 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.83 (s, 3H), 3.54 (s, 3H), 3.28 (dd, *J* = 17.6, 7.2 Hz, 1H), 2.71-2.63 (m, 2H), 1.31 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.07, 156.25, 144.60, 144.29, 142.98, 137.74, 134.35, 129.63, 127.65, 127.45, 119.93, 114.36, 113.96, 110.19, 55.13, 54.62, 38.34, 37.74, 16.14.

HRMS: m/z: [M + H]+ calculated for $C_{19}H_{21}N_2O_3$: 325.1547; found 325.1551.

3-(2-fluorophenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **2n** was obtained as yellow solid (57.5 mg, 92%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (td, *J* = 7.6, 1.6 Hz, 1H), 7.25-7.19(m, 1H), 7.15(dd, *J*=5.2, 1.6 Hz, 1H), 7.13 (br, 1H), 7.03 (td, *J* = 7.6, 0.8 Hz, 1H), 6.88-6.83 (m, 2H), 6.51 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.85 (s, 3H), 3.28 (dd, *J* = 17.2, 6.8 Hz, 1H), 2.73-2.61 (m, 2H), 1.32 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.14, 160.46 (d, *J*=249.0 Hz), 143.93, 143.29, 140.04, 137.35, 134.06, 129.71 (d, *J* = 8.5 Hz), 128.08 (d, *J* = 4.2 Hz), 126.85 (d, *J* = 14.7 Hz), 123.14 (d, *J* = 3.3 Hz), 115.03, 114.92 (d, *J* = 22.1 Hz), 114.74, 114.66, 55.19, 38.10, 37.43, 16.28.

HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{18}FN_2O_2$: 313.1347; found 313.1357.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(thiophen-2-yl)cyclopent-2-enone

Petroleum ether/EtOAc =4/1 as eluate and **2o** was obtained as yellow solid (57.1 mg, 95%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.45 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.33 (dd, *J*=3.6, 0.8 Hz, 1H), 7.05 (dd, *J* = 5.2, 4.0 Hz, 1H), 6.98 (dd, *J*=8.0, 1.2 Hz, 1H), 6.65 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.51 (br, 1H), 3.90 (s, 3H), 3.39 (dd, *J* = 17.2, 7.6 Hz, 1H), 2.74-2.66 (m, 2H), 1.31 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.73, 149.36, 145.80, 143.61, 138.42, 137.71, 131.69, 130.13, 128.78, 126.93, 115.09, 114.64, 55.35, 37.98, 35.74, 16.53.

HRMS: m/z: $[M + H]^+$ calculated for $C_{16}H_{17}N_2O_2S$: 301.1005; found 301.1008.

3-(furan-2-yl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Petroleum ether/EtOAc =6/1 as eluate and **2p** was obtained as brown oil (54.0 mg, 95%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.43 (s, 1H), 6.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.85 (br, 1H), 6.66 (dd, *J* = 8.0, 5.2 Hz, 1H), 6.44-6.42 (m, 2H), 3.88 (s, 3H), 3.29 (dd, *J* = 17.2, 6.8 Hz, 1H), 2.69-2.57 (m, 2H), 1.29 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 206.20, 150.74, 145.05, 143.85, 143.62, 139.29, 138.19, 130.89, 115.00, 114.81, 114.15, 112.01, 55.23, 37.70, 33.41, 16.39.
HRMS: m/z: $[M + H]^+$ calculated for $C_{16}H_{17}N_2O_3$: 285.1234; found 285.1238.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(pyridin-3-yl)cyclopent-2-enone

Petroleum ether/EtOAc =3/1 as eluate and **2q** was obtained as yellow solid (29.5 mg, 50%, condition A; 53.2 mg, 90%, condition B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.6 Hz, 1H), 8.44 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.66 (dt, *J*=8.0, 2.0 Hz, 1H), 7.28 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.17-7.13 (m, 2H), 6.94 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.58 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.90 (s, 3H), 3.34 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.73-2.64 (m, 2H), 1.33 (d, *J* = 7.2Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.23, 148.89, 148.74, 143.91, 143.61, 143.37, 137.64, 134.58, 133.46, 132.96, 122.34, 115.16, 115.09, 55.29, 37.84, 35.85, 16.42.
HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{18}N_3O_2$: 296.1394; found 296.1399.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(pyridin-4-yl)cyclopent-2-enone

Petroleum ether/EtOAc =4/1 as eluate and **2r** was obtained as yellow solid (33.1 mg, 56%, condition B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 6.0 Hz, 2H), 7.28 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.20 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.15 (br, 1H), 6.96 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.59 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.90 (s, 3H), 3.29 (dd, *J* = 17.6, 7.2 Hz, 1H), 2.71-2.63 (m, 2H), 1.32 (d, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.38, 149.01, 144.57, 143.86, 143.27, 142.40, 137.61, 134.40, 121.66, 115.48, 115.21, 55.31, 37.95, 35.84, 16.32.
HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{18}N_3O_2$: 296.1394; found 296.1401.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(naphthalen-2-yl)cyclopent-2-enone
Petroleum ether/EtOAc =6/1 as eluate and **2s** was obtained as yellow solid (57.9 mg, 84%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.76 (d, *J* = 9.2 Hz, 2H), 7.61 (s, 2H), 7.48-7.43 (m, 2H), 7.25 (d, *J* = 4.8 Hz, 1H), 7.04 (br, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.52 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.91 (s, 3H), 3.45 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.83 (dd, *J* = 17.2, 2.0 Hz, 1H), 2.75-2.68 (m, 1H), 1.36 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.62, 148.59, 144.56, 143.64, 137.99, 134.26, 133.28, 133.15, 132.63, 128.57, 127.44, 126.98, 126.67, 126.60, 126.03, 125.57, 114.84, 114.62 , 55.26, 37.91, 36.44, 16.49.
HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{21}N_2O_2$: 345.1598; found 345.1603.

(E)-2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(prop-1-en-1-yl)cyclopent-2-enone
Petroleum ether/EtOAc =6/1 as eluate and **2t** was obtained as brown oil (43.9 mg, 85%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 5.2 Hz, 1H), 6.96-6.93 (m, 2H), 6.78 (br, 1H), 6.68 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.19-6.10 (m, 1H), 3.87 (s, 3H), 3.03 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.58-2.50 (m, 1H), 2.34 (dd, *J* = 17.2, 2.4 Hz, 1H), 1.88 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.09, 148.30, 145.63, 143.18, 138.08, 131.76, 131.54, 128.75, 114.84, 114.71, 55.27, 37.60, 33.15, 19.14, 16.69.
HRMS: m/z: $[M + H]^+$ calculated for $C_{15}H_{19}N_2O_2$: 259.1441; found 259.1441.

(E)-2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-styrylcyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **2u** was obtained as yellow solid (55.1 mg, 86%, condition A; 285.1 mg, 89%, 1 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 16.4 Hz, 1H), 7.79 (d, *J* = 5.2 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.27-7.23 (m, 1H), 7.15 (br, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 16.4 Hz, 1H), 6.76 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.90 (s, 3H), 3.19 (dd, *J* = 16.4, 6.8 Hz, 1H), 2.66-2.58 (m, 1H), 2.49 (dd, *J* = 16.4, 2.0 Hz, 1H), 1.30 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.71, 144.95, 144.44, 143.39, 138.01, 137.16, 133.28, 131.53, 128.65, 128.27, 127.12, 126.27, 115.35, 115.11, 55.34, 37.63, 33.06, 16.75.

HRMS: m/z: [M + H]+ calculated for $C_{20}H_{21}N_2O_2$: 321.1598; found 321.1607.

2-((3-methoxypyridin-2-yl)amino)-3,5-dimethylcyclopent-2-enone

Petroleum ether/EtOAc =7/1 as eluate and **2v** was obtained as pale oil (44.1 mg, 95%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 4.8 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.66 (dd, *J* = 8.0, 5.2 Hz, 1H), 6.56 (br, 1H), 3.88 (s, 3H), 2.91 (dd, *J* = 18.0, 6.8 Hz, 1H), 2.55-2.48 (m, 1H), 2.26 (d, *J* = 18.0 Hz, 1H), 2.17 (s, 3H), 1.23 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.43, 156.93, 146.17, 143.09, 138.07, 134.37, 114.64, 114.18, 55.19, 39.30, 38.32, 19.44, 16.34.

HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{17}N_2O_2$: 233.1285; found 233.1278.

3-ethyl-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Petroleum ether/EtOAc =7/1 as eluate and **2w** was obtained as pale oil (44.8 mg, 91%, condition A; 234.0 mg, 95%, 1.0 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* =

5.2, 0.8 Hz, 1H), 6.90 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.64 (dd, *J* = 8.0, 5.2 Hz, 1H), 6.50 (br, 1H), 3.85 (s, 3H), 2.90 (dd, *J* = 18.0, 6.8 Hz, 1H), 2.59 (q, *J* = 7.6 Hz, 2H), 2.52-2.45 (m, 1H), 2.23 (d, *J* = 18.0 Hz, 1H), 1.21 (d, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.78, 162.27, 146.17, 143.04, 138.04, 133.38, 114.64, 114.18, 55.19, 38.15, 36.16, 25.81, 16.43, 11.08.
HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{19}N_2O_2$: 247.1441; found 247.1450.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-tridecylcyclopent-2-enone
Petroleum ether/EtOAc =7/1 as eluate and **2x** was obtained as pale oil (51.0 mg, 64%, condition A; 66.2 mg, 83%, condition B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.64 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.51 (br, 1H), 3.86 (s, 3H), 2.89 (dd, *J* = 18.4, 6.8 Hz, 1H), 2.57 (t, *J*=7.6 Hz, 2H), 2.52-2.45 (m, 1H), 2.23 (d, *J* = 18.0 Hz, 1H), 1.56-1.51 (m, 2H), 1.24-1.2 (m, 23H), 0.87 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.74, 161.24, 146.17, 143.06, 138.07, 133.76, 114.61, 114.15, 55.19, 38.19, 36.87, 32.76, 31.87, 29.74, 29.64, 29.60(s, 2C), 29.58, 29.47, 29.37, 29.31, 26.80, 22.64, 16.49, 14.07.
HRMS: m/z: $[M + H]^+$ calculated for $C_{25}H_{41}N_2O_2$: 401.3163; found 401.3177.

3-Benzyl-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc =6/1 as eluate and **2y** was obtained as brown oil (51.8 mg, 84%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 4.8 Hz, 1H), 7.29-7.25 (m, 2H), 7.22 (m, 3H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.69-6.66 (m, 2H), 4.03 (s, 2H), 3.88 (s, 3H), 2.74 (dd, *J* = 18.0, 6.8 Hz, 1H), 2.48-2.42 (m, 1H), 2.08 (d, *J* = 18.0 Hz, 1H), 1.16 (d, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.84, 157.38, 146.01, 143.23, 138.47, 138.03, 134.05, 129.15, 128.43, 126.29, 114.84, 114.50, 55.29, 39.14, 38.27, 36.58, 16.33.
HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{21}N_2O_2$: 309.1598; found 309.1604.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-phenethylcyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **2z** was obtained as pale oil (48.4 mg, 75%, condition A; 54.8 mg, 85%, condition B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.26-7.23 (m, 2H), 7.19-7.13 (m, 3H), 6.93 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.68 (dd, *J* = 8.0, 5.2 Hz, 1H), 6.59 (br, 1H), 3.87 (s, 3H), 2.98-2.86 (m, 5H), 2.54-2.44 (m, 1H), 2.21 (dd, *J* = 18.0, 1.6 Hz, 1H), 1.19 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.58, 158.40, 146.02, 143.08, 141.59, 138.03, 134.04, 128.28, 128.21, 125.89, 114.71, 114.38, 55.19, 38.15, 37.38, 34.72, 32.80, 16.40.

HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{23}N_2O_2$: 323.1754; found 323.1768.

5-methyl-3-phenyl-2-(pyridin-2-ylamino)cyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **3a** was obtained as yellow solid (21.1 mg, 40%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 4.4 Hz, 1H), 7.52-7.49 (m, 2H), 7.30-7.24 (m, 4H), 6.76 (br, 1H), 6.76 (dd, *J* = 5.6, 6.8 Hz, 1H), 6.13 (d, *J* = 8.4 Hz, 1H), 3.31 (dd, *J* = 17.6, 7.2 Hz, 1H), 2.70-2.63 (m, 2H), 1.33 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.28, 153.42, 148.03, 147.11, 136.94, 135.48, 133.39, 129.42, 128.25, 127.63, 115.57, 109.90, 37.82, 36.08, 16.57.

HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{17}N_2O$: 265.1335; found 265.1340.

5-methyl-2-((3-methylpyridin-2-yl)amino)-3-phenylcyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **3b** was obtained as yellow solid (10.0 mg, 18%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 3.6 Hz, 1H), 7.40-7.38 (m, 2H), 7.32 (dd, *J*= 7.2, 1.8 Hz, 1H), 7.24-7.18 (m, 3H), 6.57 (dd, *J* = 7.2, 5.2 Hz, 1H), 6.27 (br, 1H), 3.35 (dd, *J* = 17.6, 7.6 Hz, 1H), 2.73-2.65 (m, 2H), 2.30 (s, 3H), 1.34 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.73, 151.99, 147.48, 144.93, 137.66, 136.61, 133.51, 128.70, 127.59, 127.50, 119.99, 115.76, 37.90, 36.31, 17.34, 16.47.

HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{19}N_2O$: 279.1492; found 279.1495.

2-((3-(benzyloxy)pyridin-2-yl)amino)-5-methyl-3-phenylcyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and **3d** was obtained as yellow oil (42.2 mg, 57%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.2, 5.2 Hz, 4H), 7.43-7.36 (m, 4H), 7.27-7.22 (m, 3H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.96 (br, 1H), 6.55 (dd, *J* = 8.0, 5.2 Hz, 1H), 5.14 (s, 2H), 3.33 (dd, *J* = 17.6, 7.2 Hz, 1H), 2.72-2.62 (m, 2H), 1.32 (d, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.62, 149.42, 144.93, 142.76, 138.46, 136.47, 136.06, 133.06, 128.85, 128.71, 128.28, 127.63, 127.54, 116.71, 114.52, 70.37, 37.92, 36.29, 16.41.
HRMS: m/z: $[M + H]^+$ calculated for $C_{24}H_{23}N_2O_2$: 371.1754; found 371.1755.

2-((3,5-dimethoxypyridin-2-yl)amino)-5-methyl-3-phenylcyclopent-2-enone

Petroleum ether/EtOAc =3/1 as eluate and **3e** was obtained as yellow solid (48.7 mg, 75%, condition A). ^{1}H NMR (400 MHz, CDCl3) δ 7.46-7.44 (m, 2H), 7.25-7.22 (m, 3H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.72 (br, 1H), 6.65 (d, *J* = 2.4 Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H), 3.31 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.71-2.61 (m, 2H), 1.31 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100MHz, $CDCl_3$) δ 207.80, 150.29, 147.29, 144.41, 138.74, 136.63, 133.21, 128.57, 127.63, 127.51, 120.74, 105.92, 56.12, 55.41, 37.84, 36.21, 16.45.
HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{21}N_2O_3$: 325.1547; found 325.1547.

2-((5-methoxypyridin-2-yl)amino)-5-methyl-3-phenylcyclopent-2-enone

Petroleum ether/EtOAc =4/1 as eluate and **3f** was obtained as yellow solid (8.8 mg, 15%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.8 Hz, 1H), 7.47-7.44 (m, 2H),

7.28-7.27 (m, 3H), 6.87 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.64 (br, 1H), 6.10 (d, *J* = 8.8 Hz, 1H), 3.72 (s, 3H), 3.28 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.68-2.62 (m, 2H), 1.33 (d, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.42, 150.33, 147.44, 144.59, 135.68, 133.88, 133.84, 129.10, 128.14, 127.59, 123.62, 110.71, 56.05, 37.79, 36.04, 16.60.
HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{19}N_2O_2$: 295.1441; found 295.1447.

2-((3-methoxypyridin-2-yl)amino)-3-phenylcyclopent-2-enone

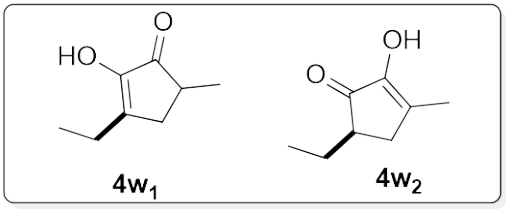
Petroleum ether/EtOAc =5/1 as eluate and **3i** was obtained as yellow solid (54.4 mg, 97%, condition A). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.8 Hz, 2H), 7.35 (d, *J* = 4.8 Hz, 1H), 7.24-7.23 (m, 3H), 6.93-6.90 (m, 2H), 6.56 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.87 (s, 3H), 3.08 (t, *J*=4.4 Hz, 2H), 2.62 (t, *J*=4.4 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 204.94, 151.08, 144.39, 143.59, 137.87, 136.42, 134.04, 128.82, 127.55, 127.46, 114.79, 114.53, 55.16, 32.36, 26.96.
HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{17}N_2O_2$: 281.1285; found 281.1286.

2-((3-methoxypyridin-2-yl)amino)-[1,1'-biphenyl]-3-ol

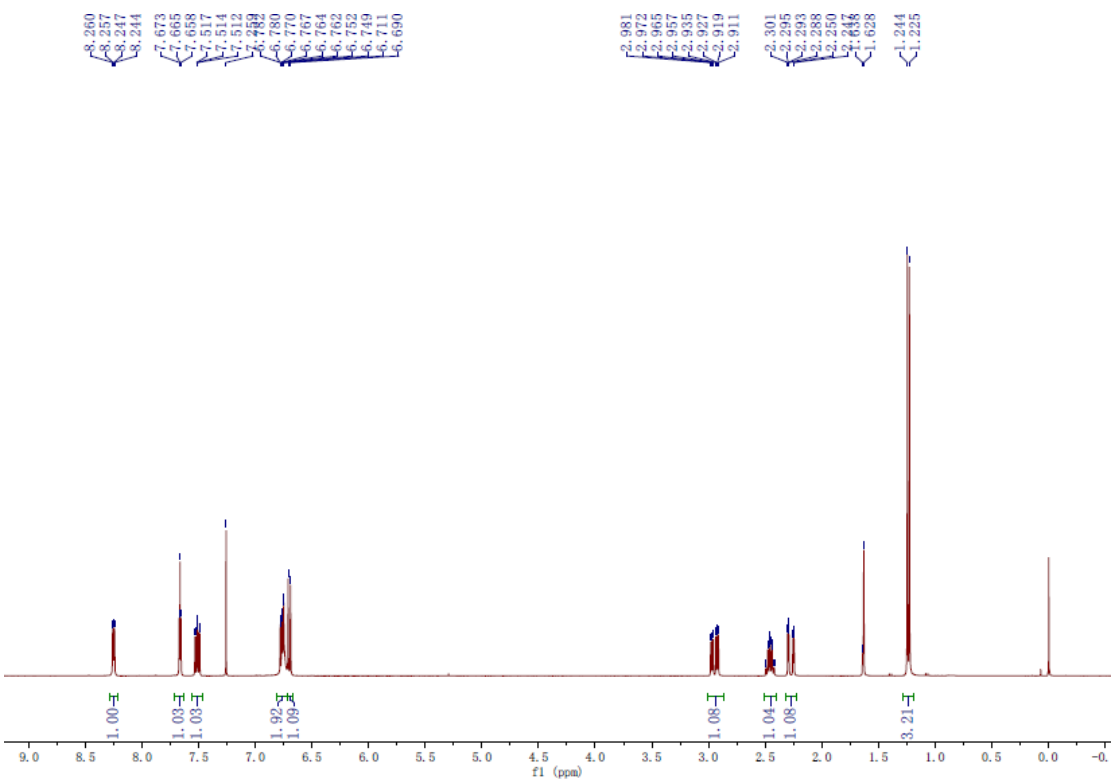
Petroleum ether/EtOAc =5/1 as eluate and **3j** was obtained as pale oil (21.6 mg, 37%, condition B). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.10 (m, 3H), 7.82 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.66 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.53-7.49 (m, 2H), 7.44 (t, *J*=7.6 Hz, 1H), 7.39-7.35 (m, 1H), 6.79-6.75 (m, 1H), 6.66 (d, *J* = 7.2 Hz, 1H), 4.05 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.19, 143.38, 141.85, 138.40, 133.21, 130.03, 129.41, 128.43, 127.29, 124.67, 121.55, 117.65, 110.29, 109.45, 103.95, 55.94.
HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{17}N_2O_2$: 293.1285; found 293.1287.

2-hydroxy-5-methyl-3-phenylcyclopent-2-enone

Petroleum ether/EtOAc =15/1 as eluate and **4a** was obtained as white solid (24.5 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.47-7.43 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 6.20 (br, 1H), 3.16 (dd, *J* = 16.8, 6.4 Hz, 1H), 2.65-2.57 (m, 1H), 2.47 (dd, *J* = 16.8, 1.6 Hz, 1H), 1.30 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 205.66, 146.92, 136.43, 133.82, 129.43, 128.61, 127.77, 36.61, 32.71, 16.62.
HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{13}O_2$: 189.0910; found 189.0913.



Petroleum ether/EtOAc =15/1 as eluate and **4w**[9] was obtained as pale oil (21.0 mg, 75%). **4w$_1$**:**4w$_2$**=0.57:1. 1H NMR (400 MHz, $CDCl_3$) δ **4w$_1$**) 6.09 (br, 1H), 2.69 (dd, *J* = 17.6, 6.4 Hz, 1H), 2.46-2.38 (m, 3H), 2.07-2.04(m, 1H), 1.18 (d, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.6 Hz, 3H); **4w$_2$**) 6.12 (br, 1H), 2.59 (dd, *J* = 17.6, 6.0 Hz, 1H), 2.35-2.30 (m, 1H), 2.12-2.07 (m, 1H), 2.00 (s, 3H), 1.86-1.76 (m, 1H), 1.46-1.35 (m, 1H), 0.93 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ**4w$_1$**) 206.22, 148.06, 146.93, 37.34, 33.98, 21.59, 16.43, 11.23; **4w$_2$**) 205.25, 148.30, 143.34, 44.17, 33.95, 24.33, 14.22, 11.13.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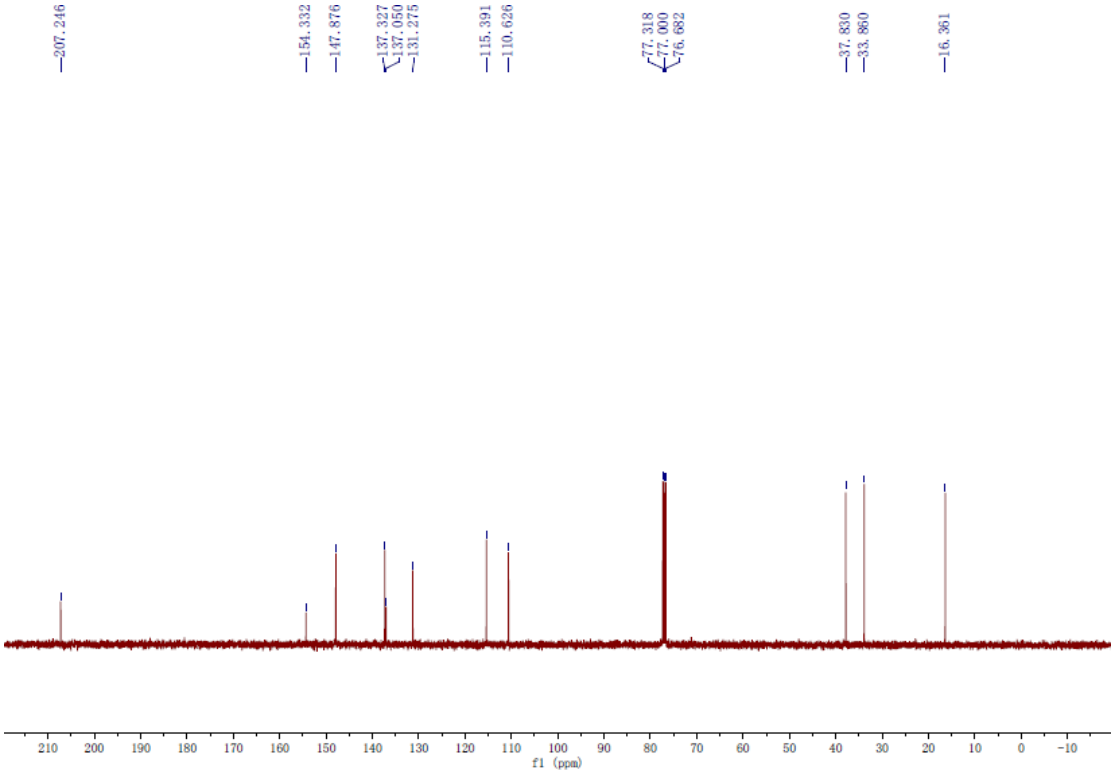
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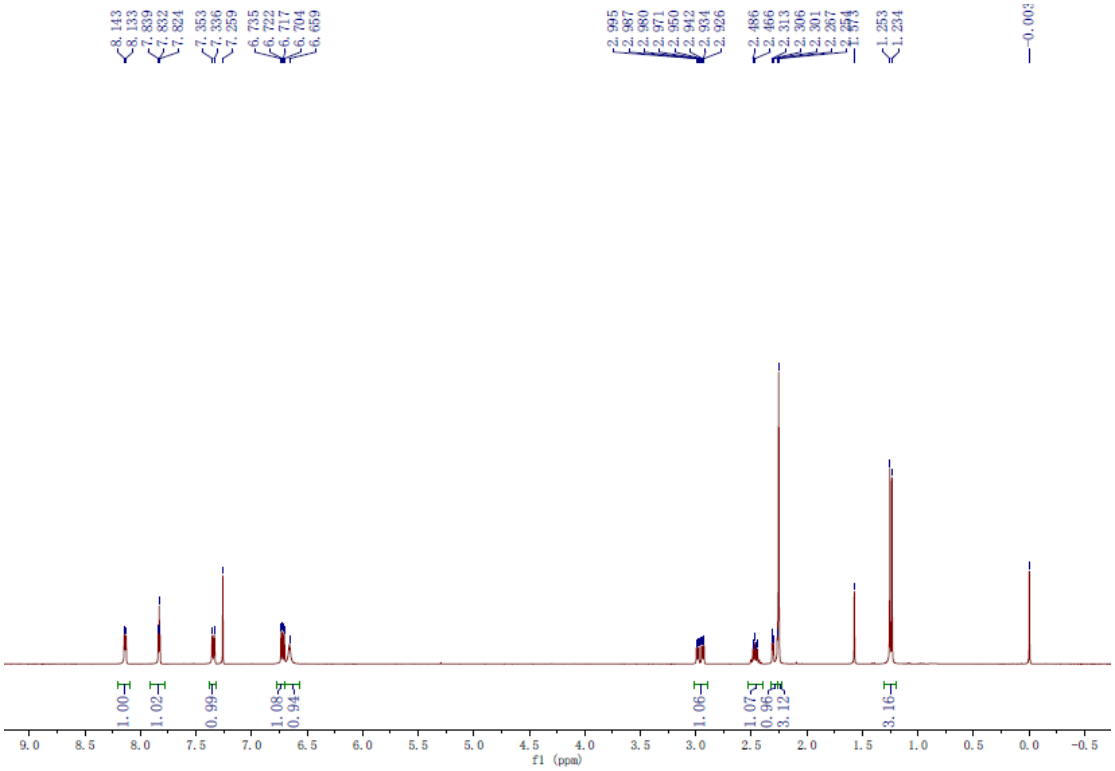
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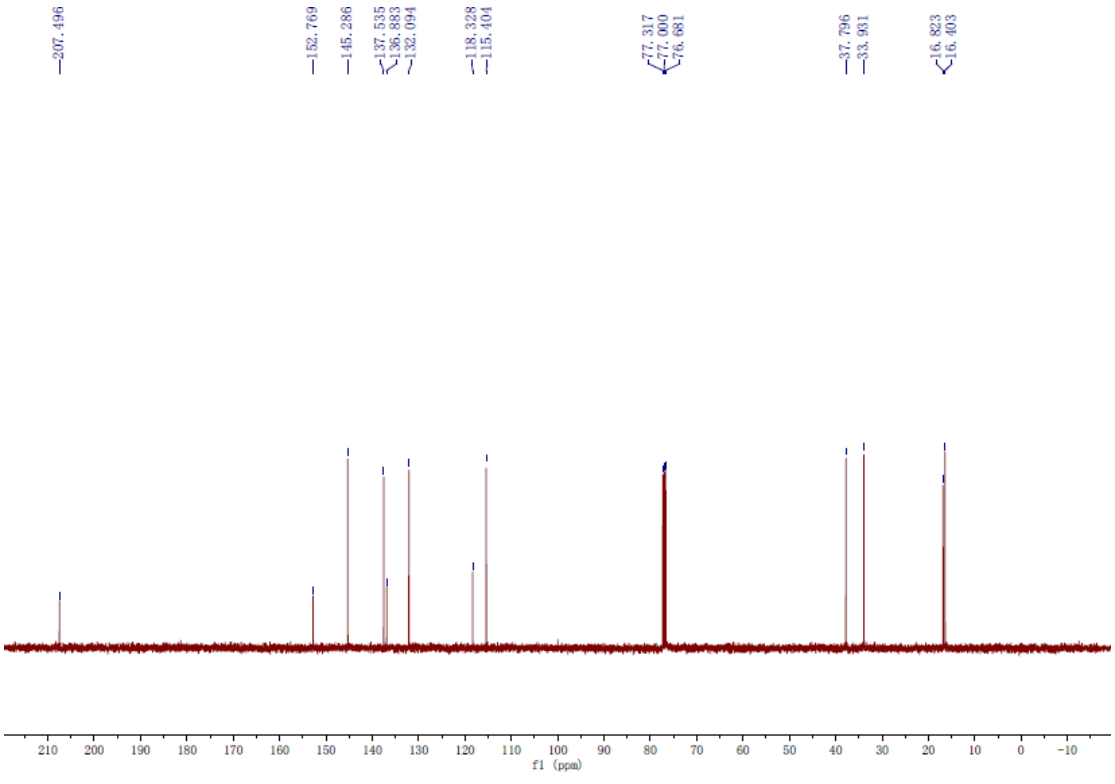
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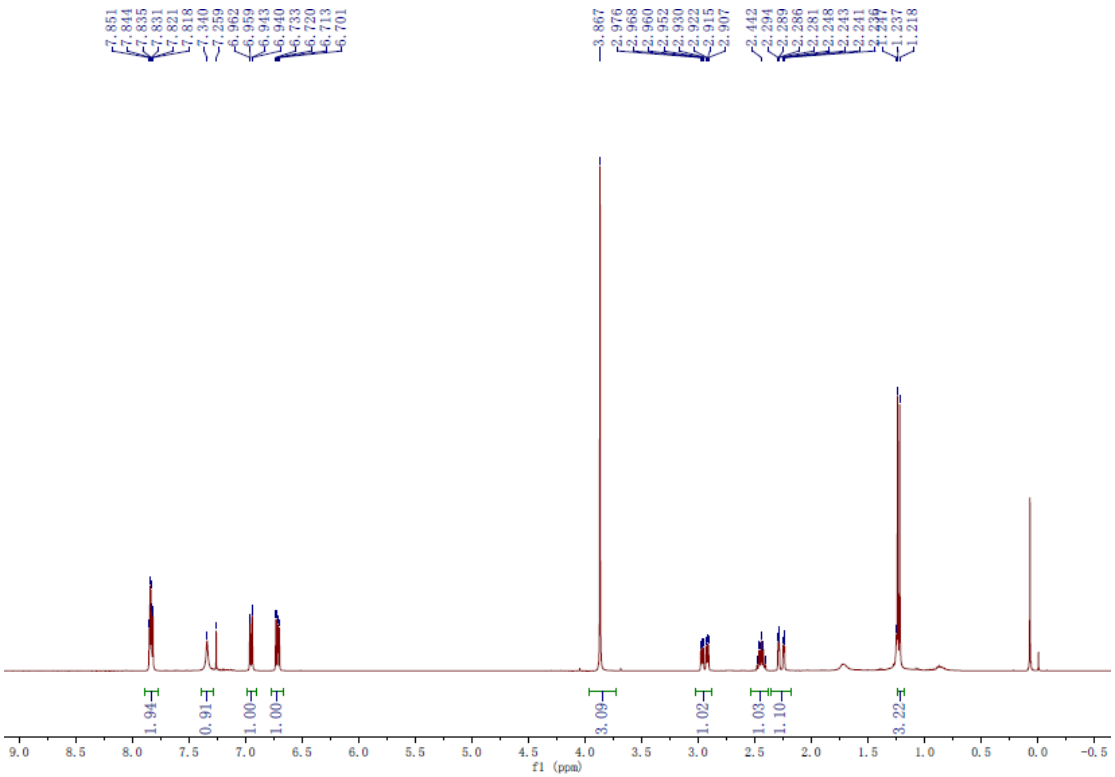
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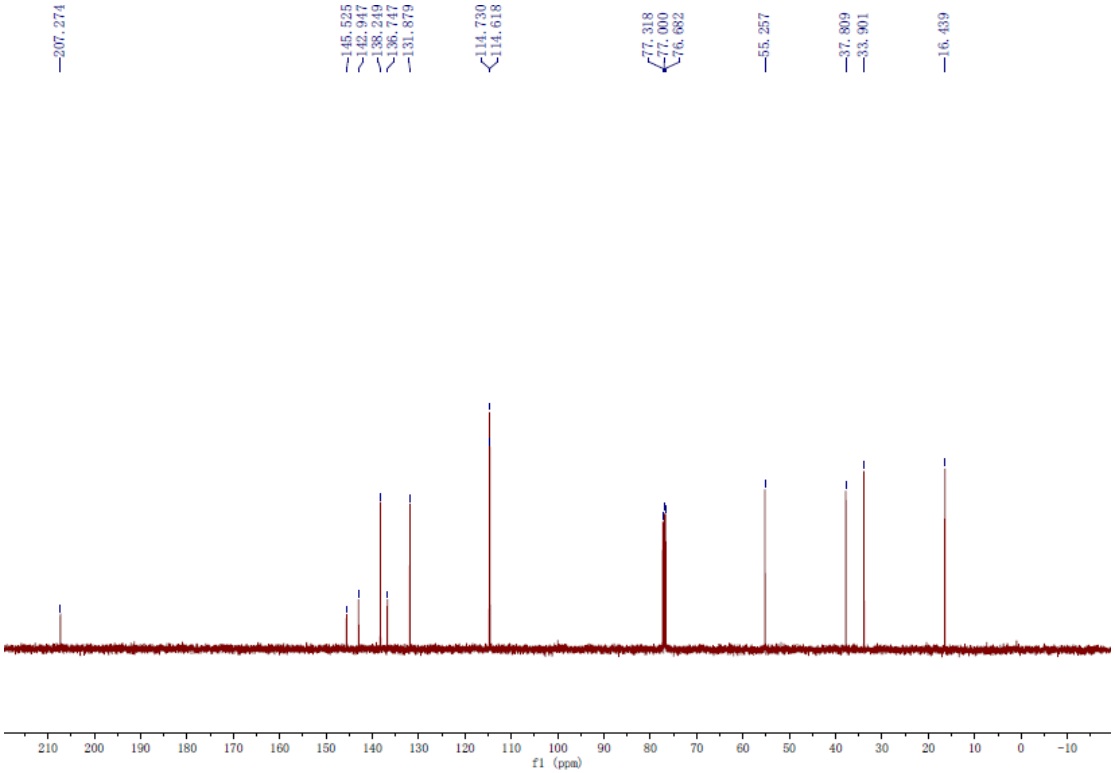
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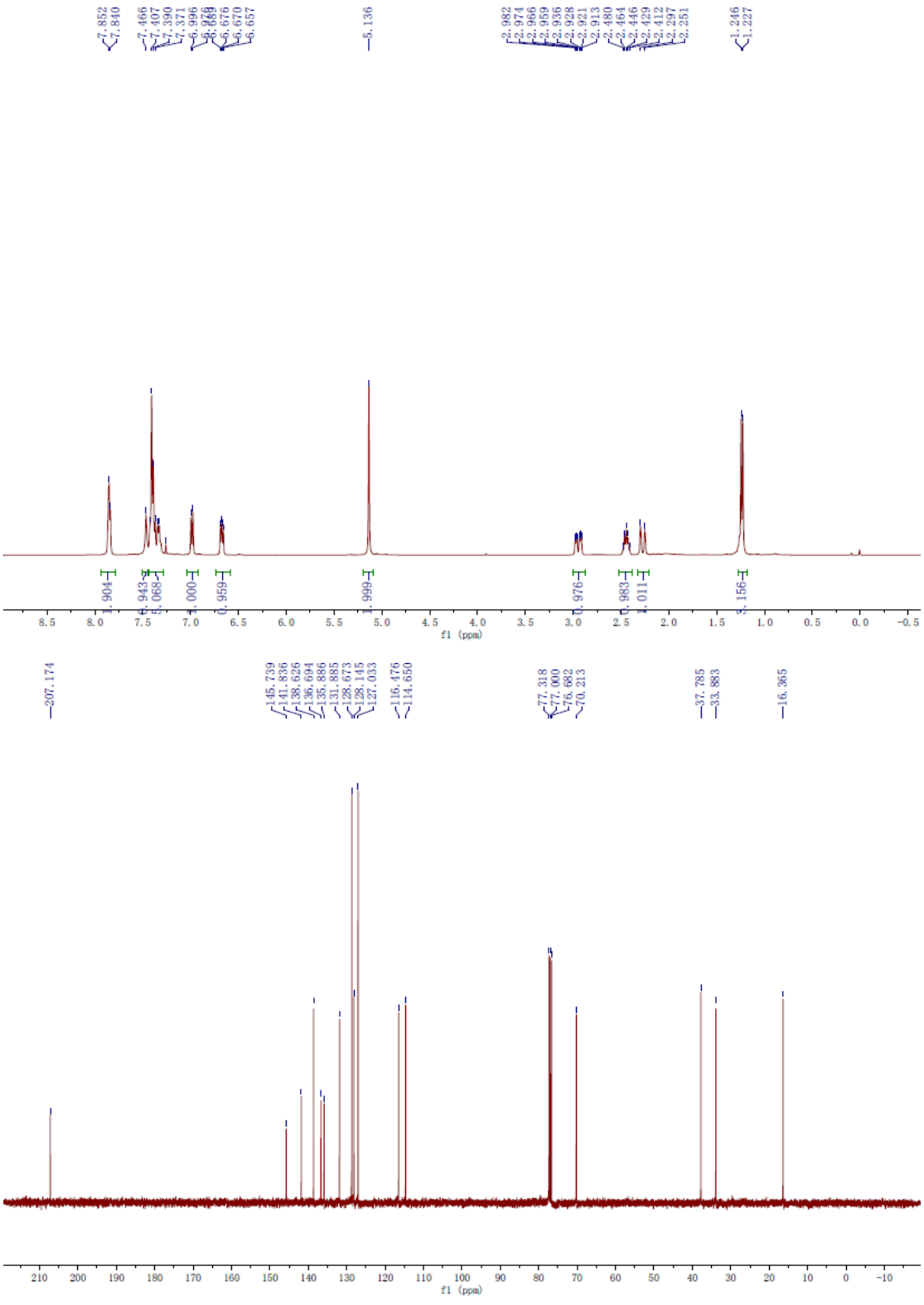
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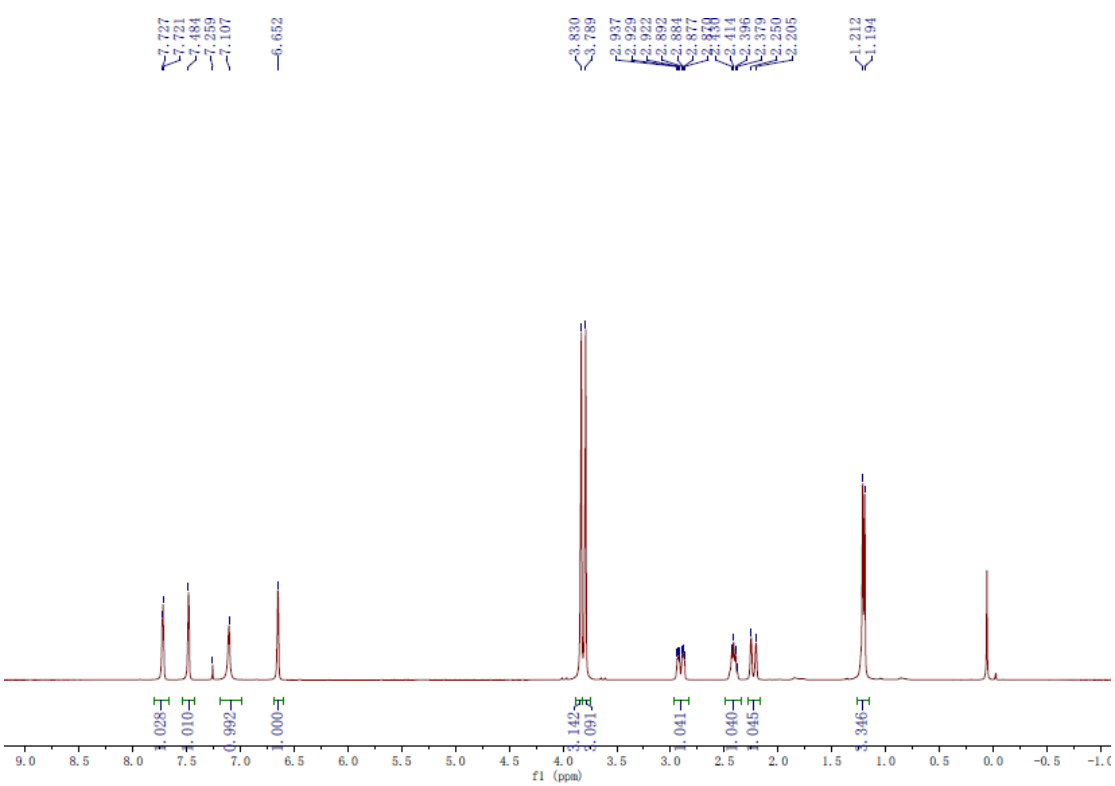
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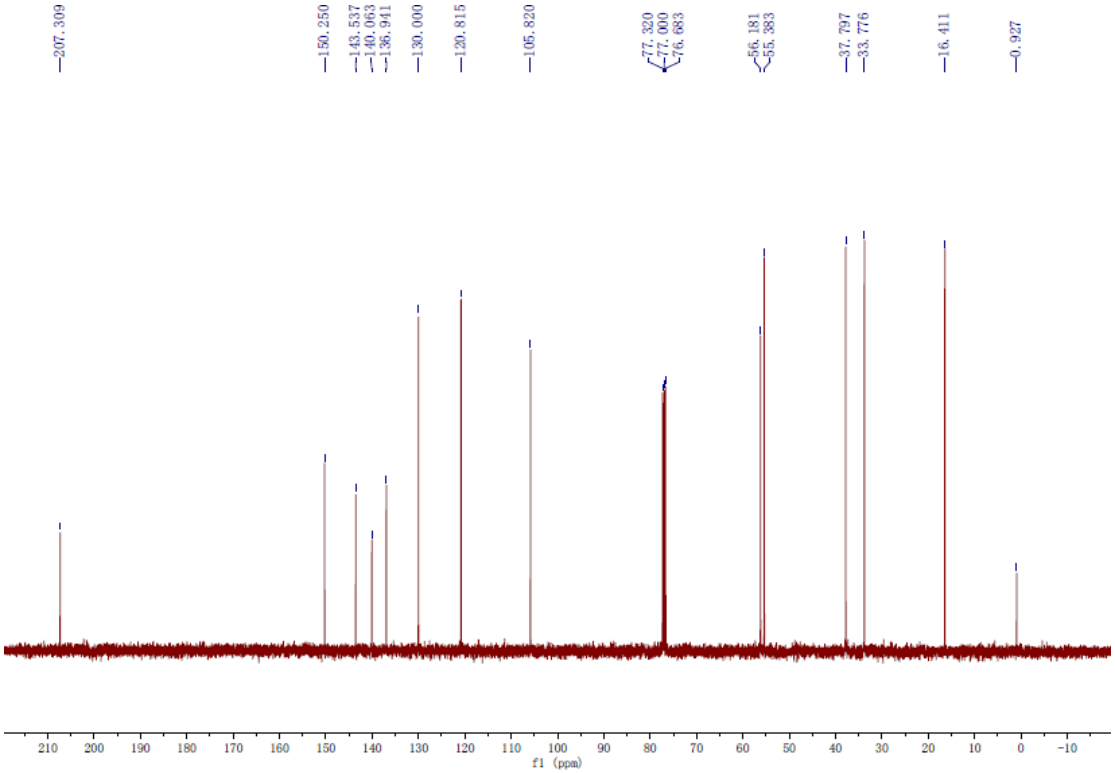
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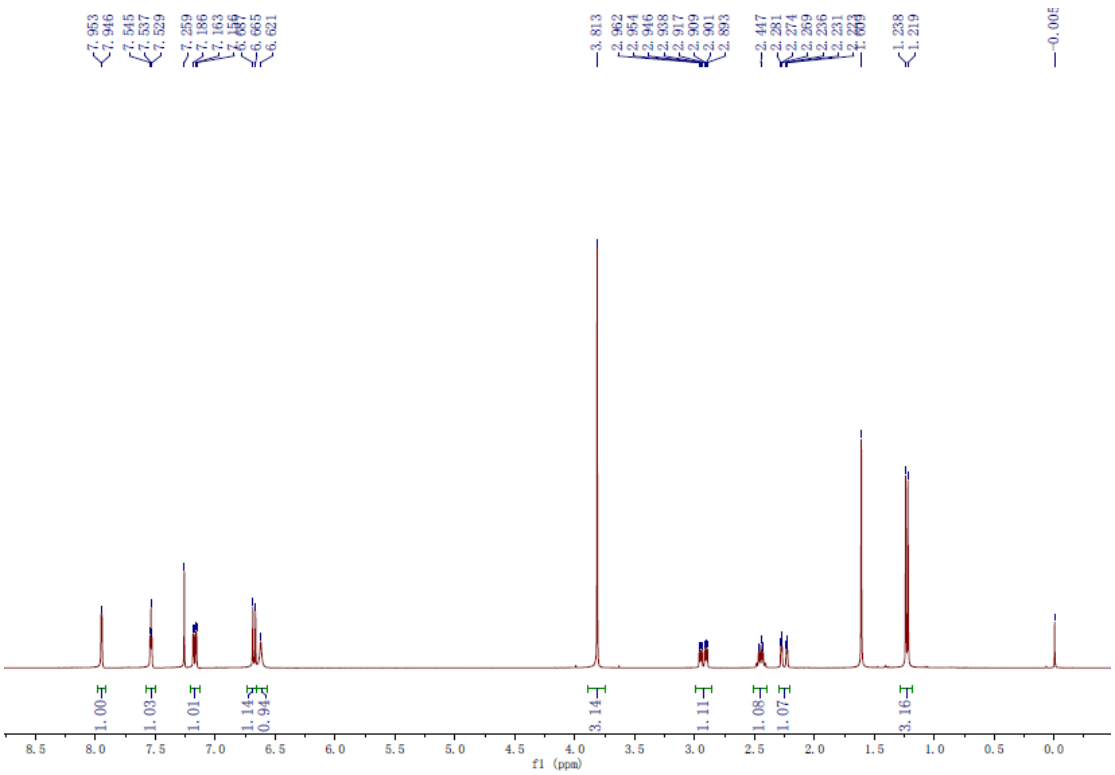
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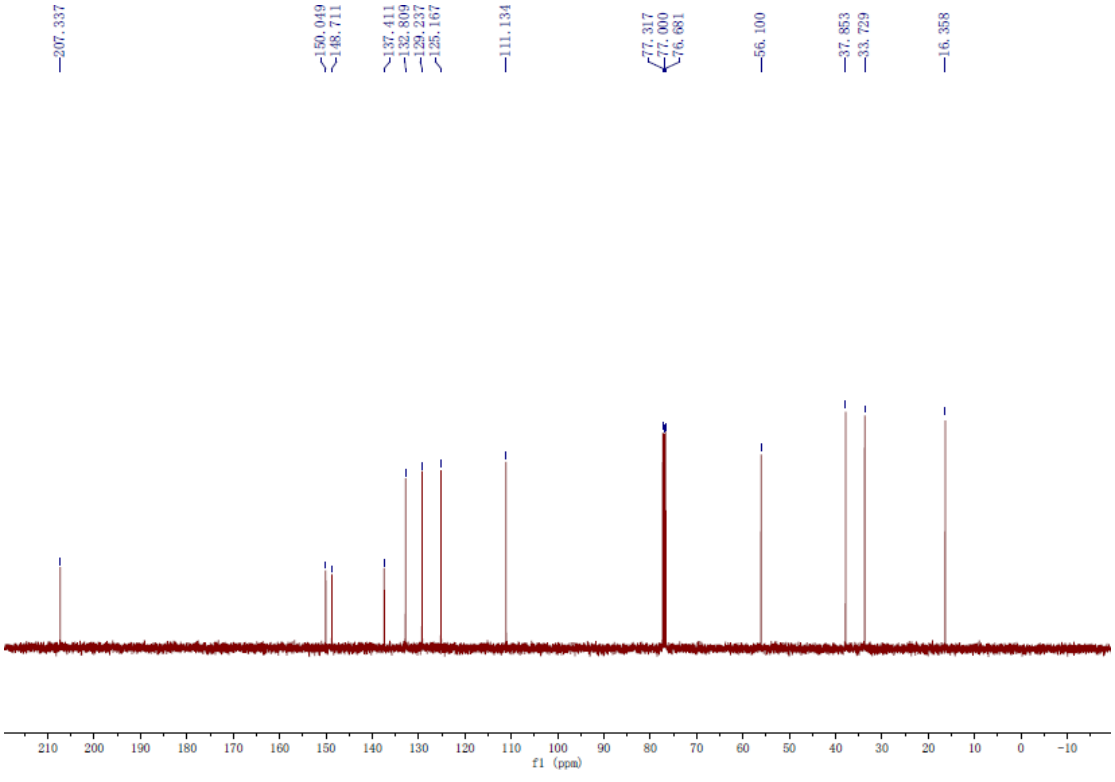
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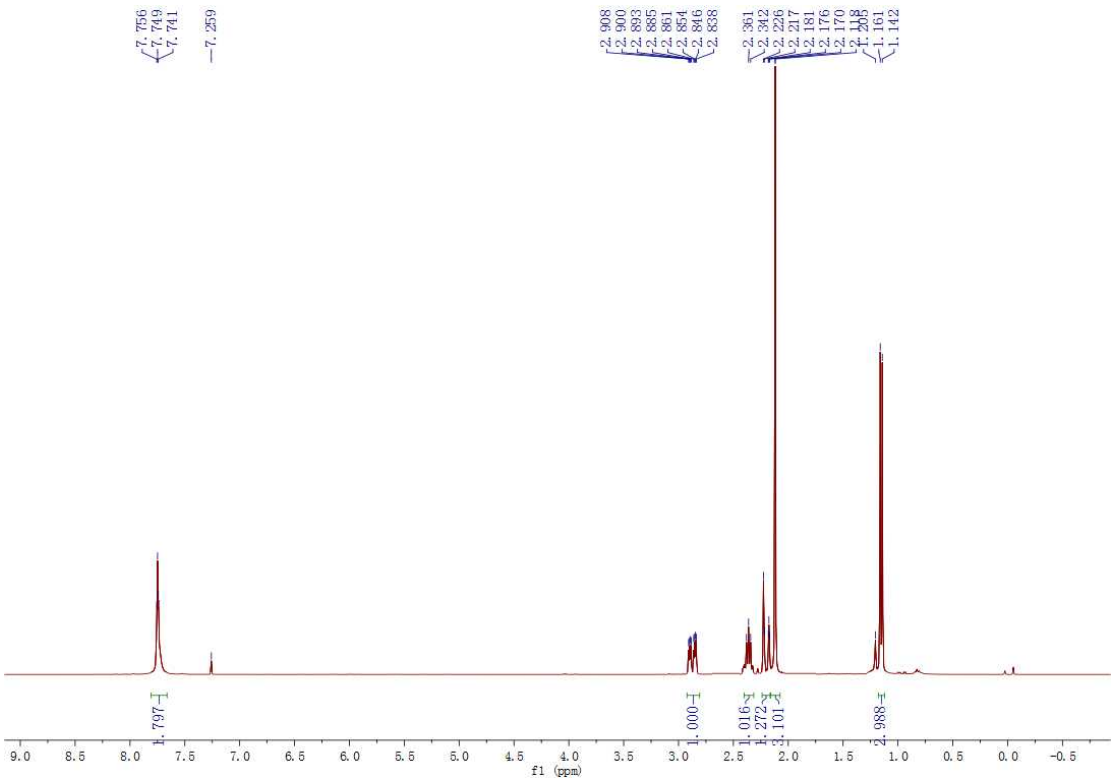
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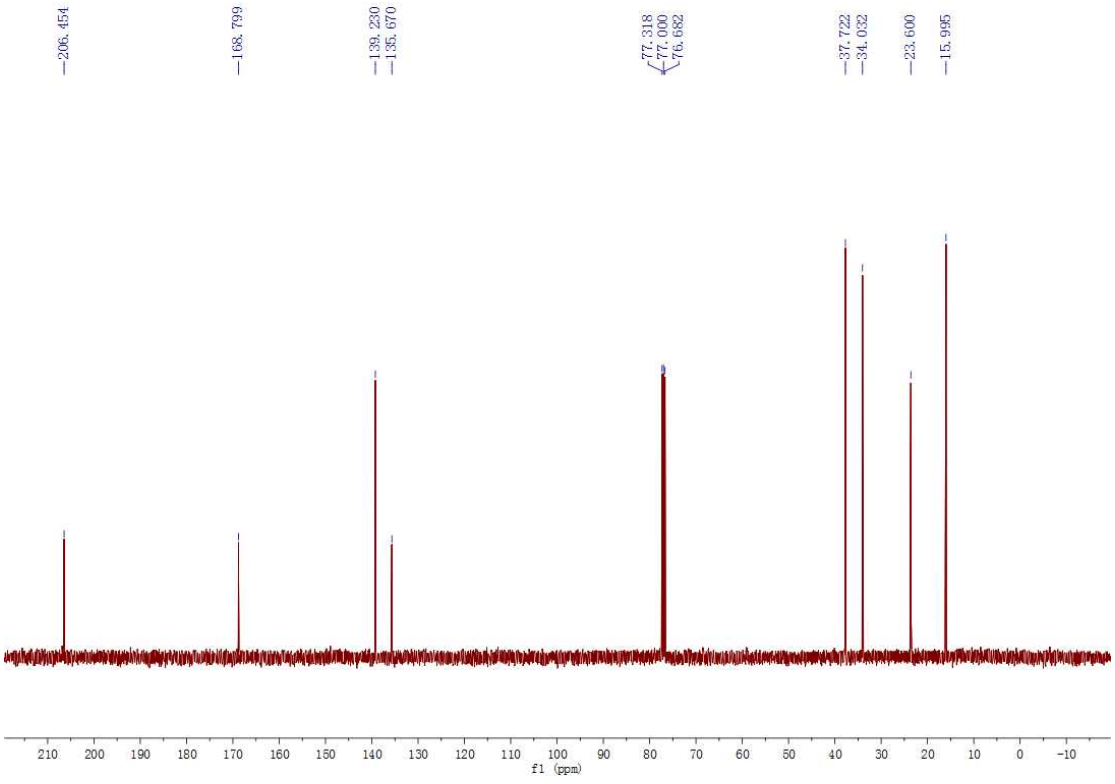
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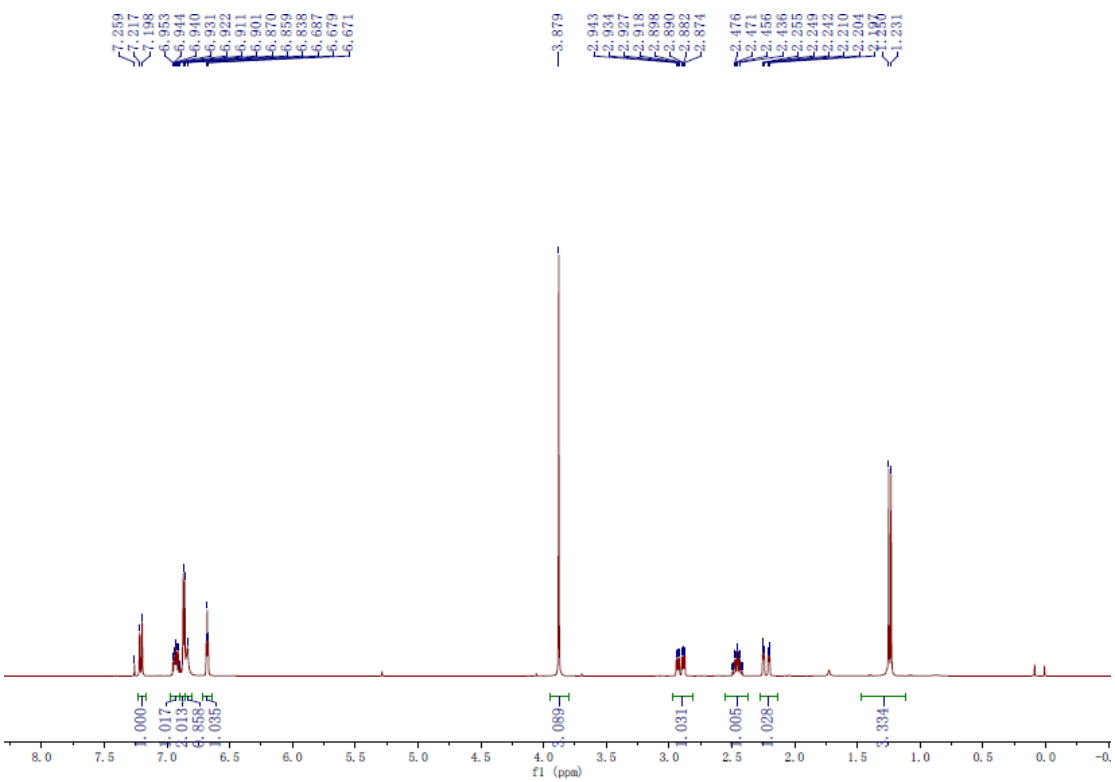
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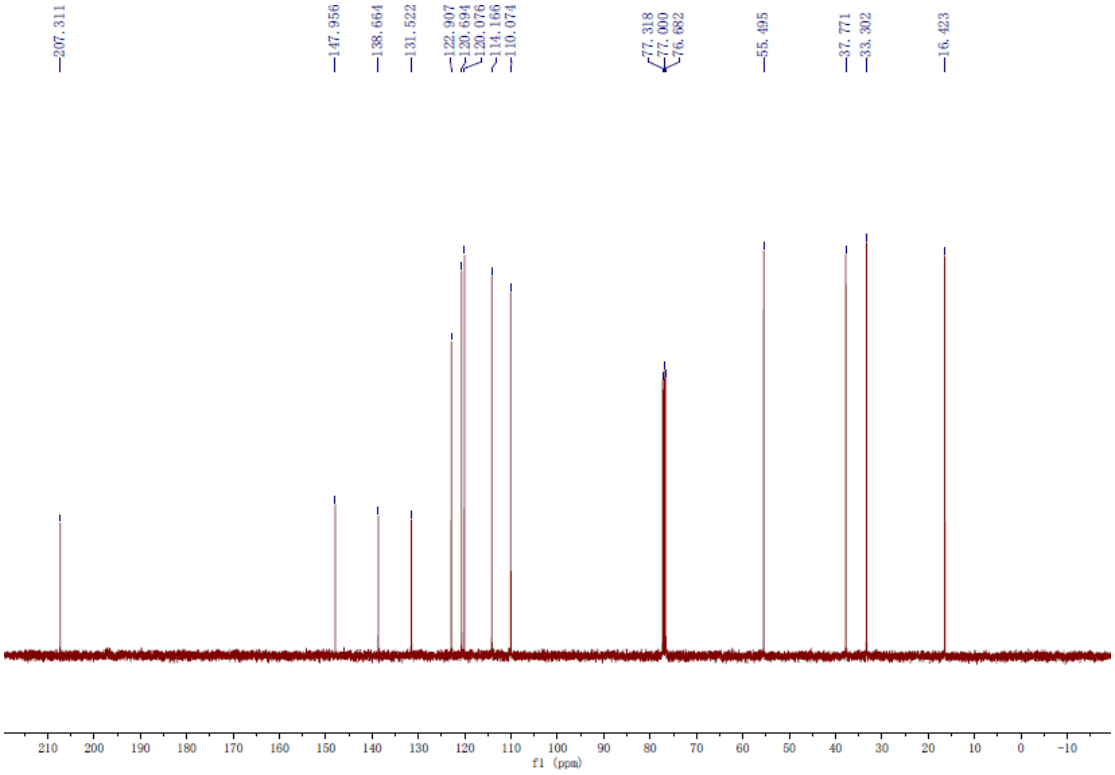
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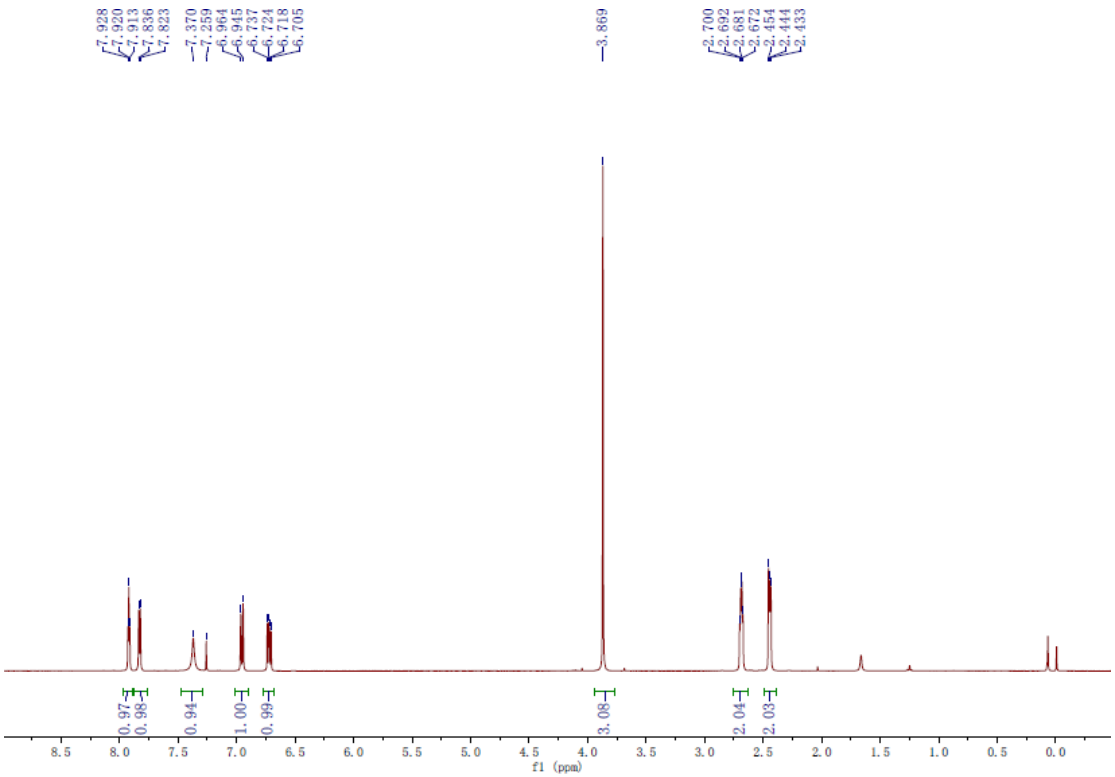
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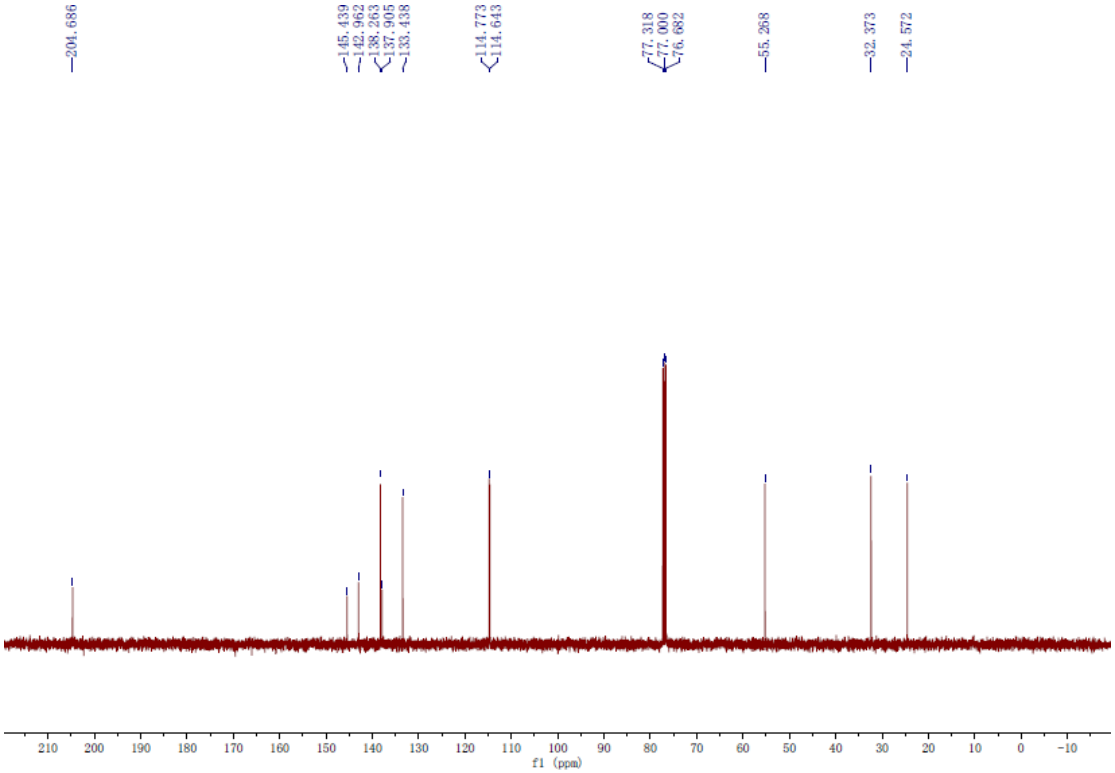
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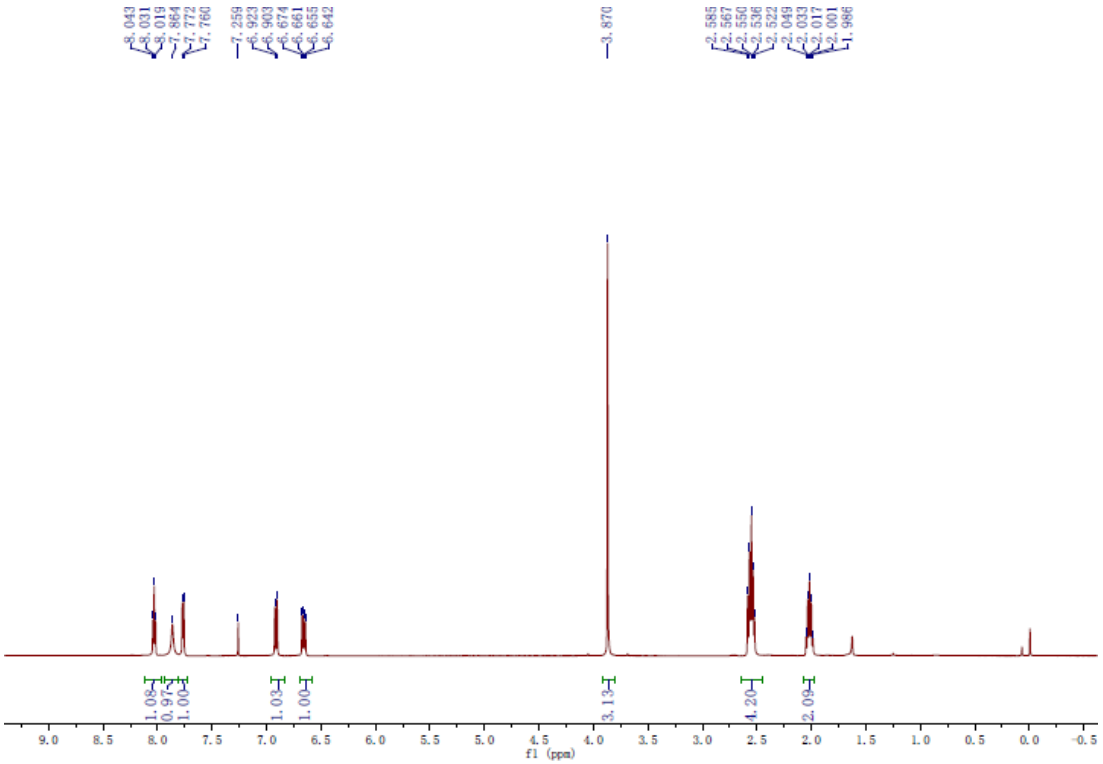
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6.642
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2.567
2.550
2.536
2.522
2.049
2.033
2.017
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1.00
1.03
1.00
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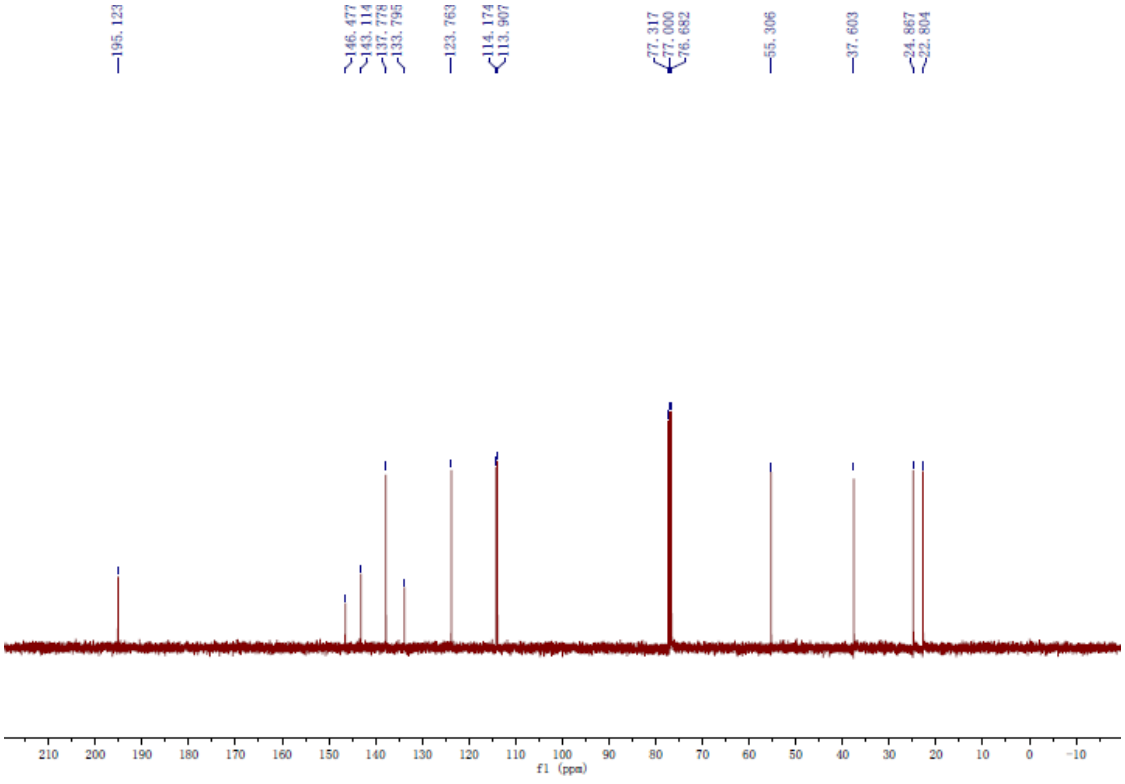
f1 (ppm)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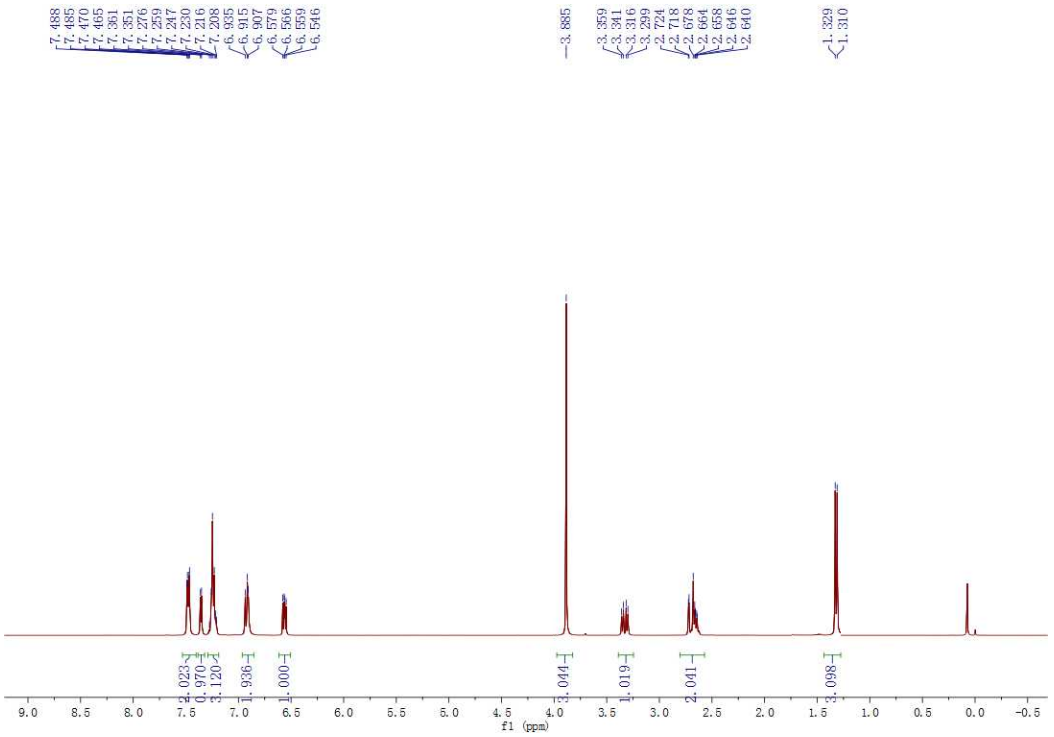
22.804
f1 (ppm)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6.559
6.546
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3.341
3.316
3.299
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2.718
2.678
2.664
2.658
2.646
2.640
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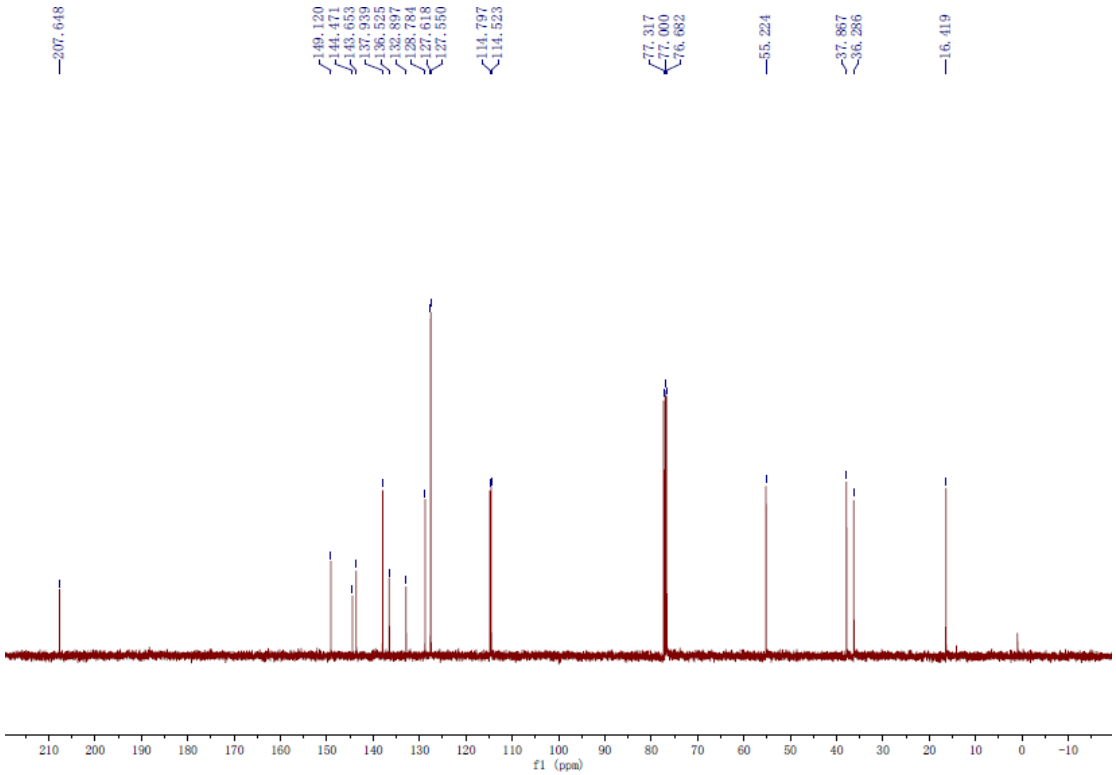
f1 (ppm)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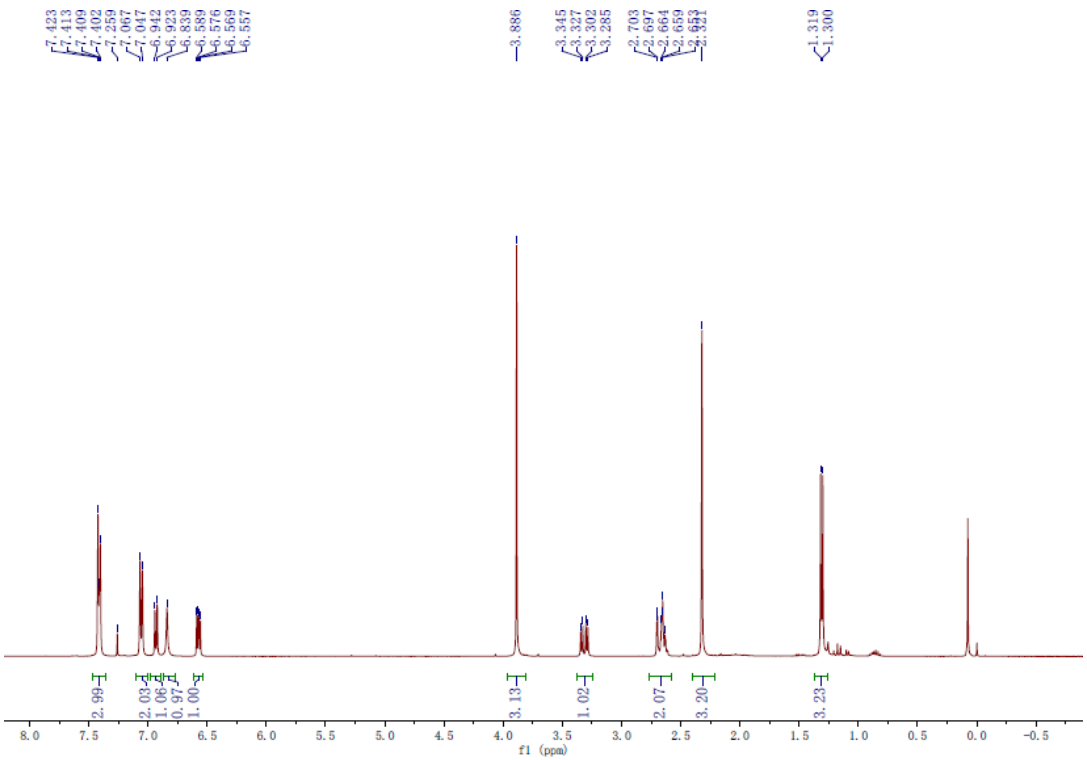
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2.697
2.664
2.659
2.653
2.621
1.319
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1.02
2.07
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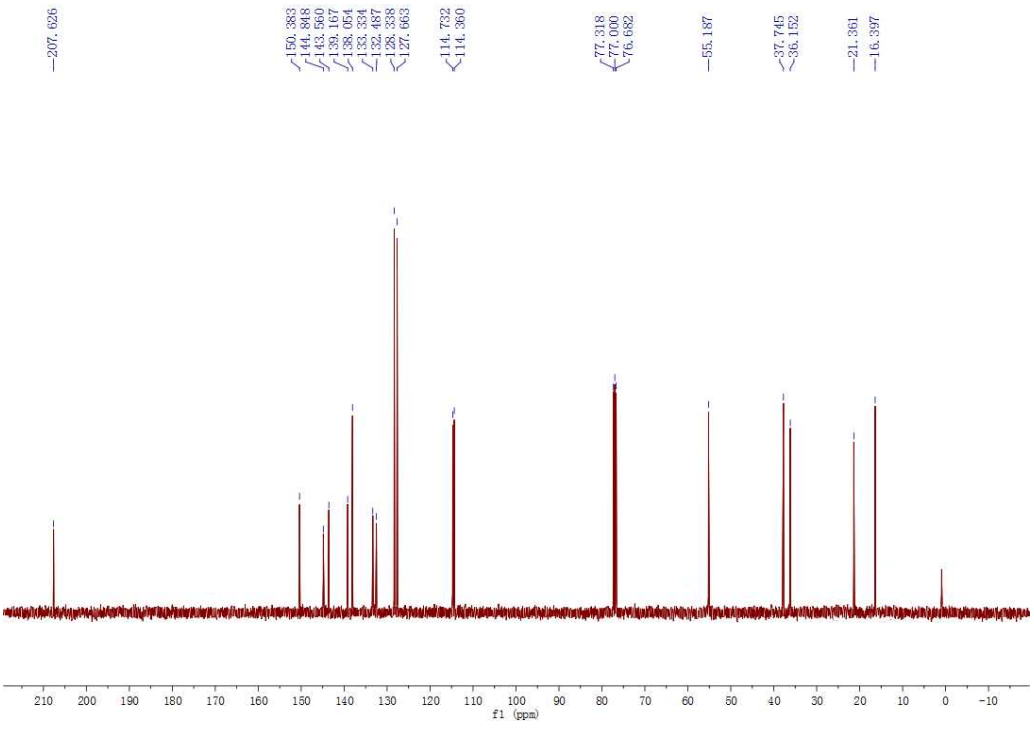
3.23
f1 (ppm)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76.682
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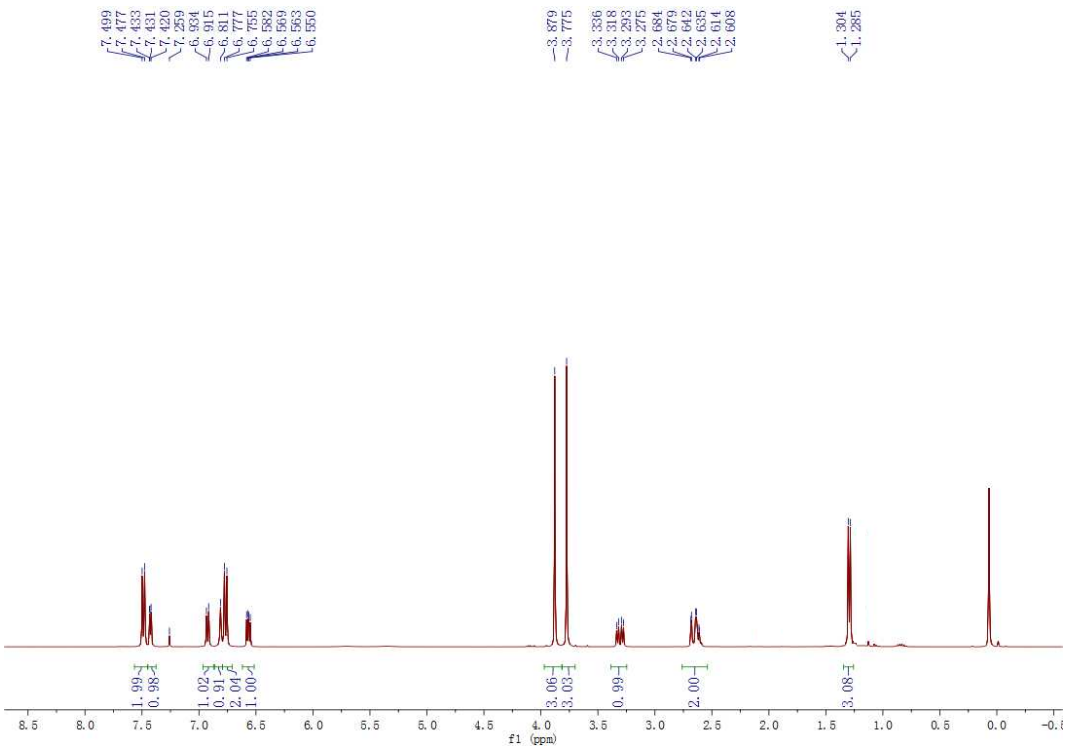
f1 (ppm)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6.915
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6.755
6.582
6.569
6.563
6.550
3.879
3.775
3.336
3.318
3.293
3.275
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2.679
2.642
2.635
2.614
2.608
1.304
1.285
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0.98
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1.00
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0.99
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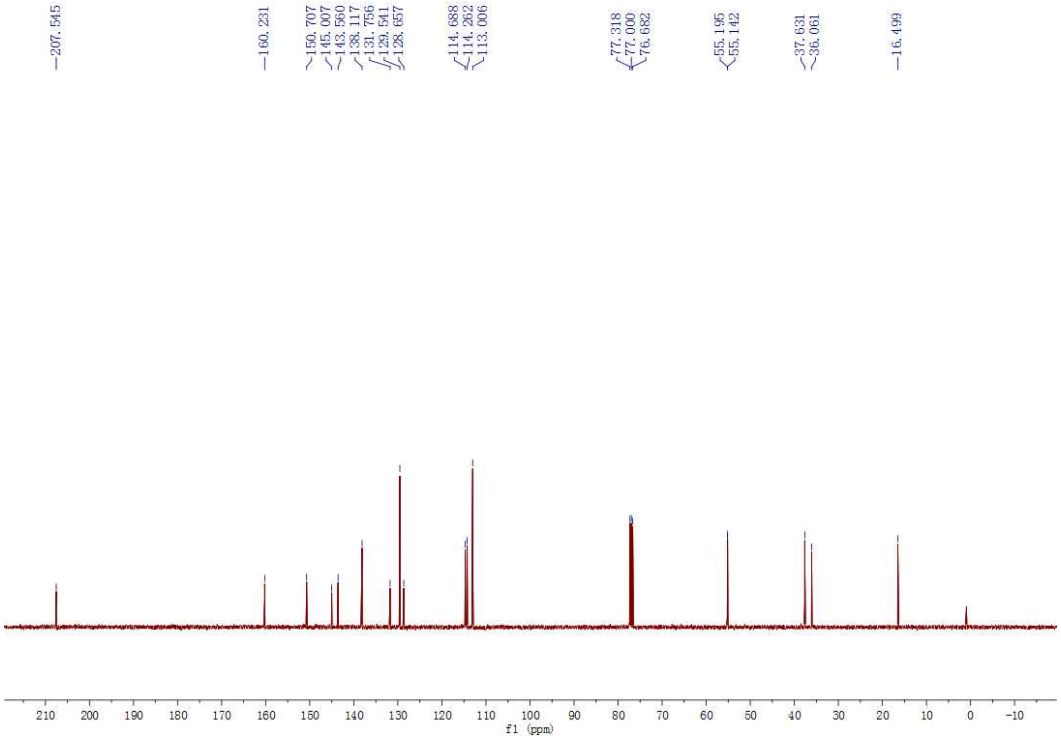
3.08
f1 (ppm)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128.657
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77.000
76.682
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37.631
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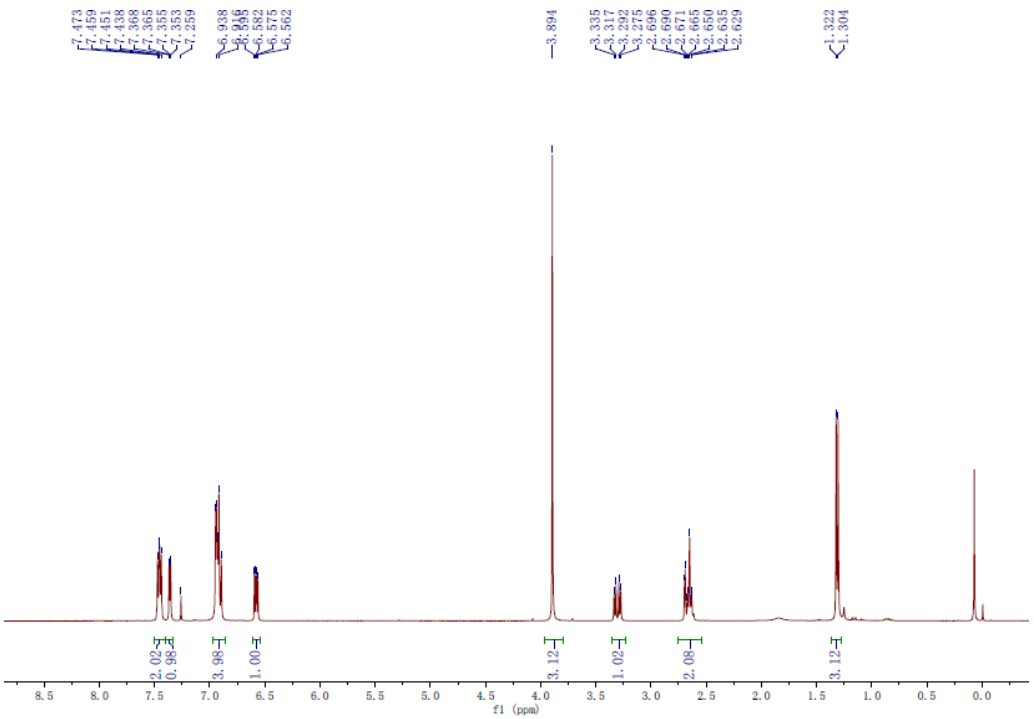
16.499
f1 (ppm)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6.575
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3.317
3.292
3.275
2.696
2.690
2.671
2.665
2.650
2.635
2.629
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1.304
2.02
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3.98
1.00
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1.02
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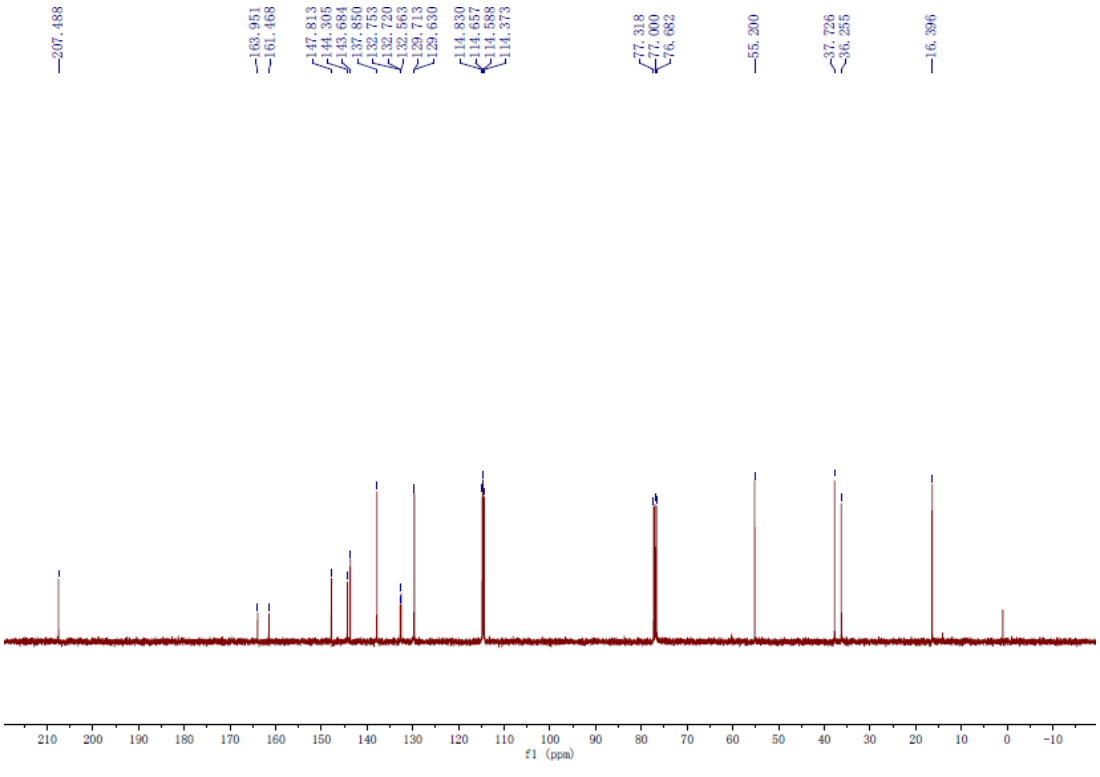
3.12
f1 (ppm)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129.713
129.630
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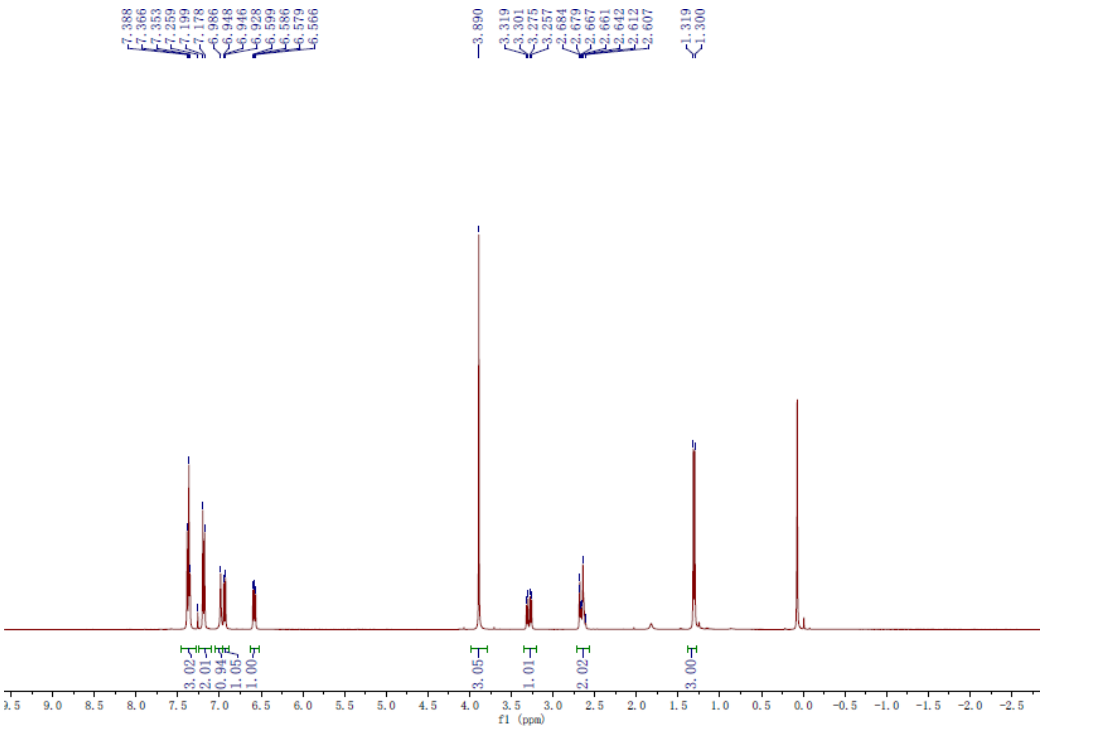
16.396
f1 (ppm)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6.566
3.890
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3.301
3.275
3.257
2.684
2.679
2.667
2.661
2.642
2.612
2.607
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1.300
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2.01
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1.00
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1.01
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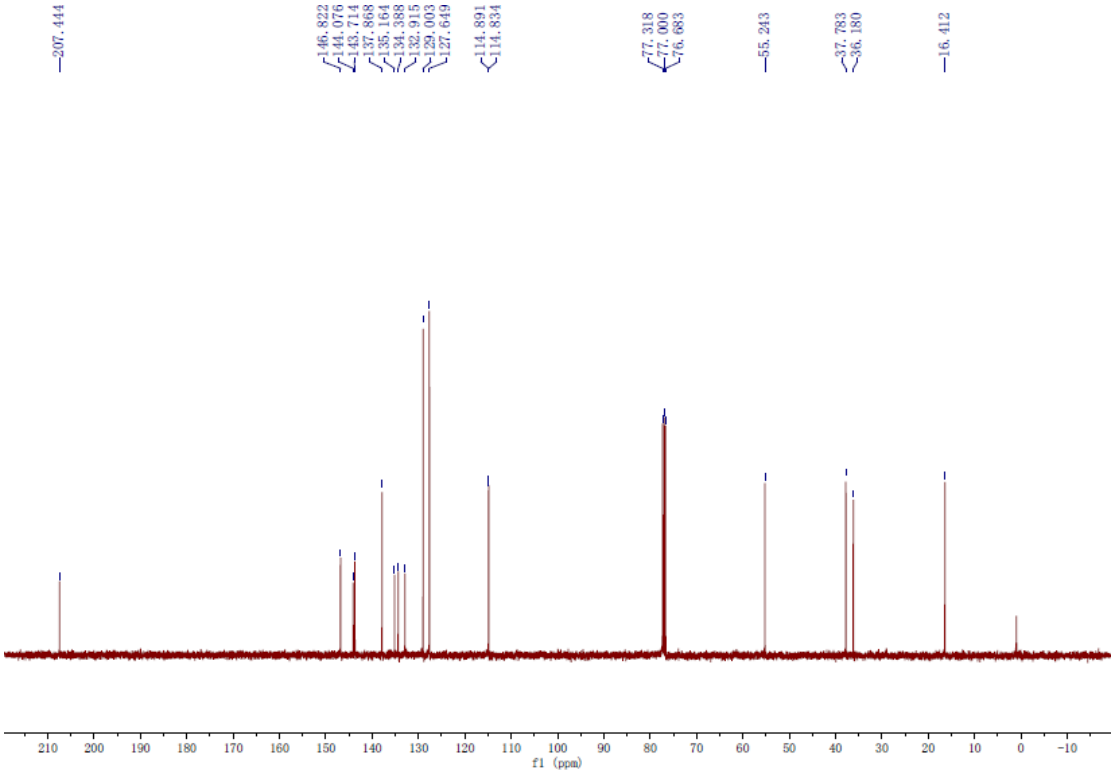
3.00
f1 (ppm)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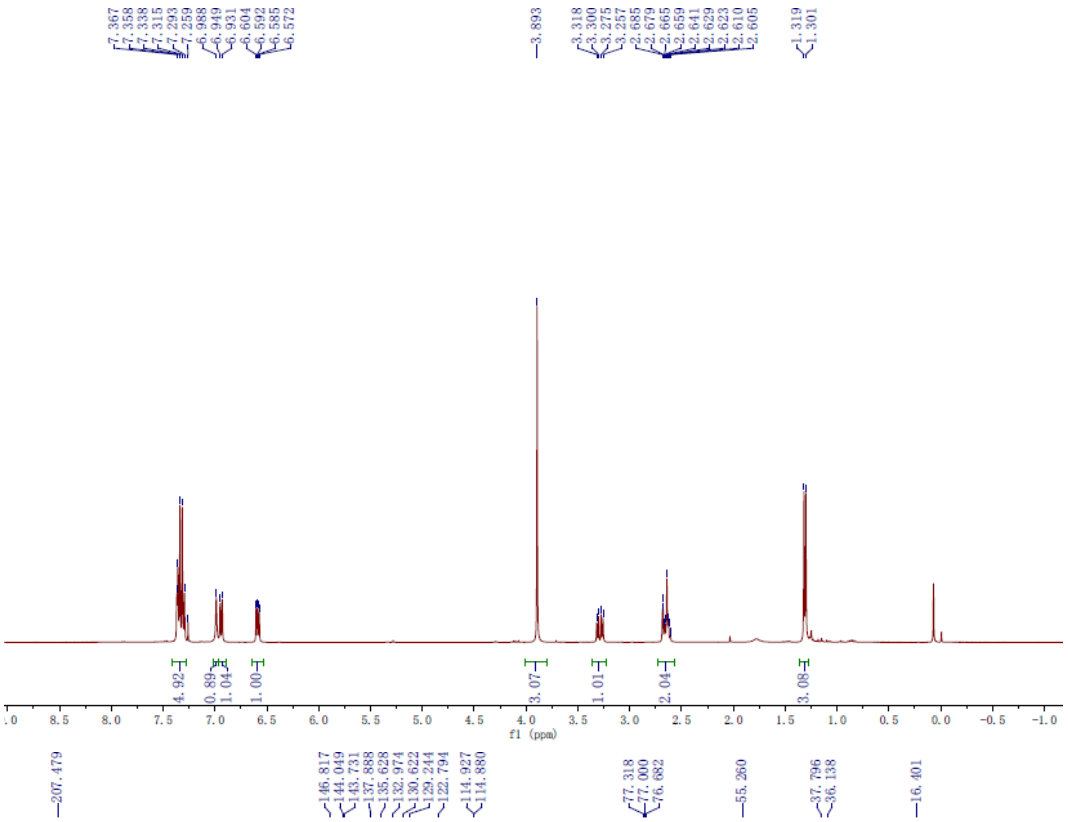
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6.572
3.893
3.318
3.300
3.275
3.257
2.685
2.679
2.665
2.659
2.641
2.629
2.623
2.610
2.605
1.319
1.301
4.92
0.89
1.04
1.00
3.07
1.01
2.04
3.08
f1 (ppm)
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130.622
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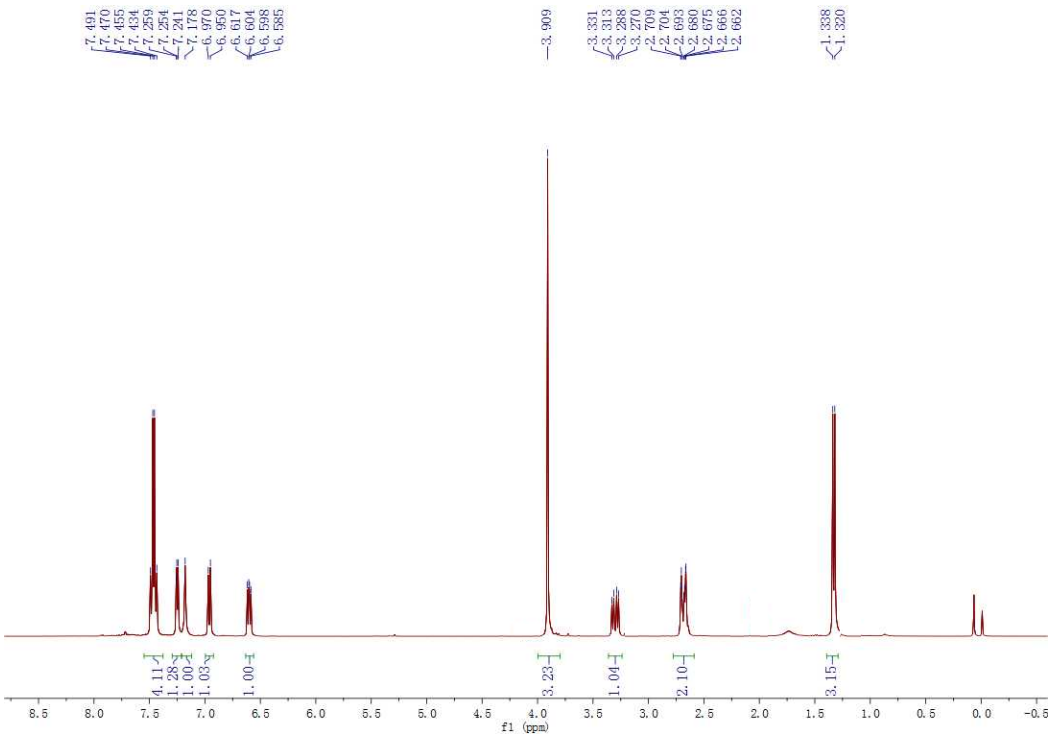
16.401
f1 (ppm)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6.585
3.909
3.331
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3.288
3.270
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2.704
2.693
2.680
2.675
2.666
2.662
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1.04
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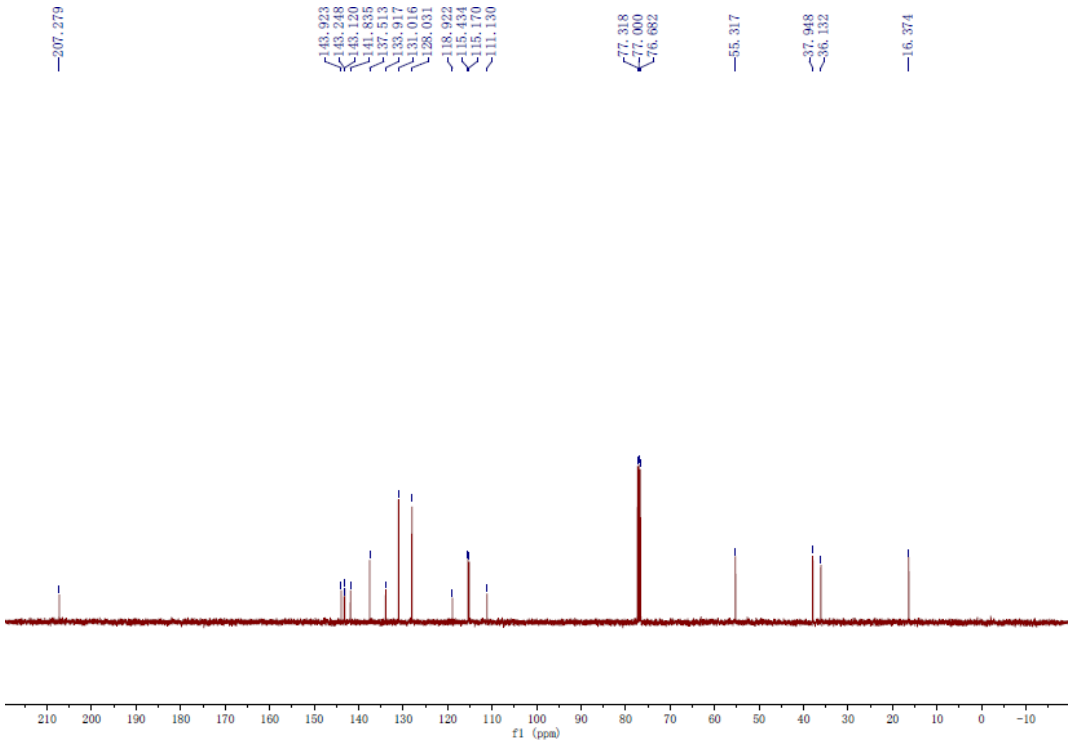
3.15
f1 (ppm)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128.031
118.922
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77.000
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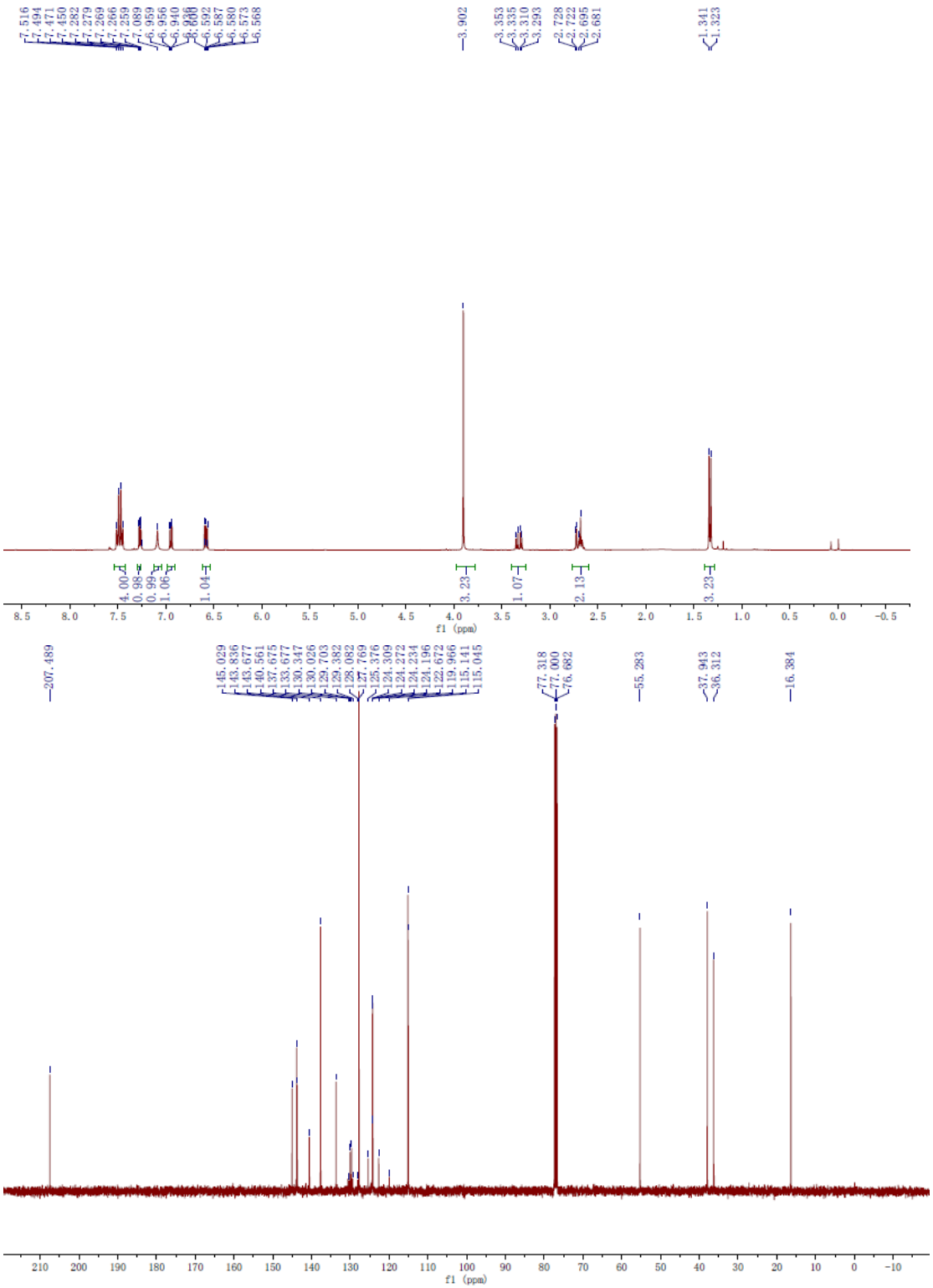
16.374
f1 (ppm)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6.936
6.592
6.587
6.580
6.573
6.568
3.902
3.353
3.335
3.310
3.293
2.728
2.722
2.695
2.681
1.341
1.323
4.00
0.98
0.99
1.06
1.04
3.23
1.07
2.13
3.23
f1 (ppm)
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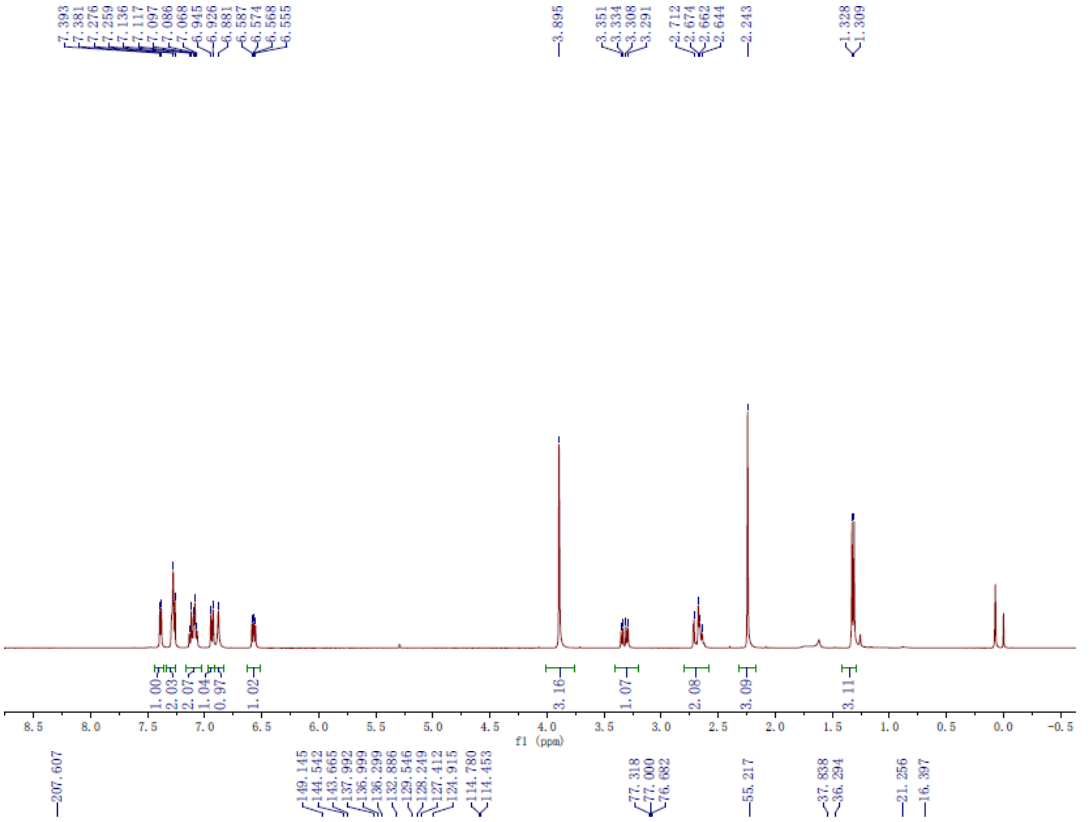
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6.574
6.568
6.555
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3.308
3.291
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2.674
2.662
2.644
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1.309
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2.03
2.07
1.04
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1.02
3.16
1.07
2.08
3.09
3.11
f1 (ppm)
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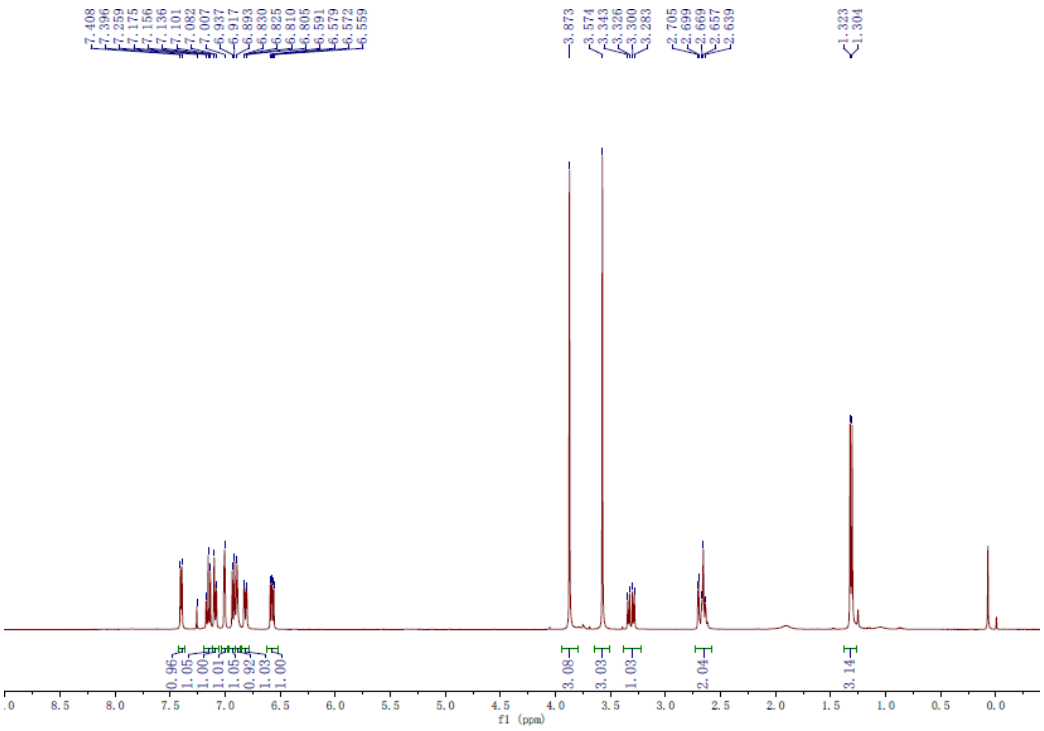
f1 (ppm)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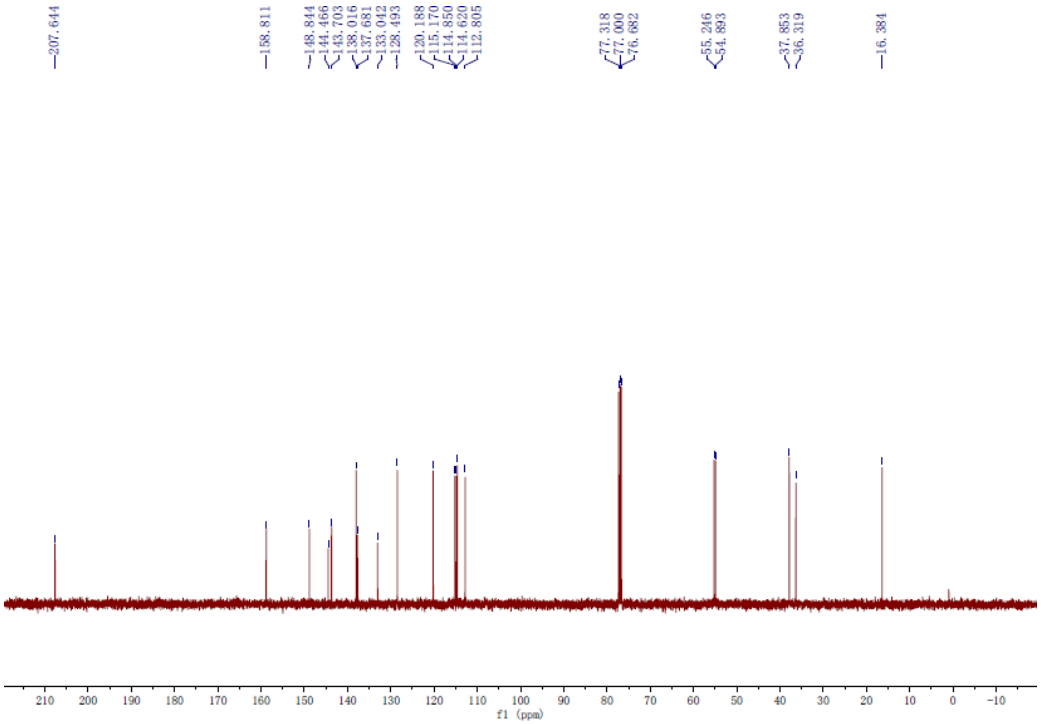
f1 (ppm)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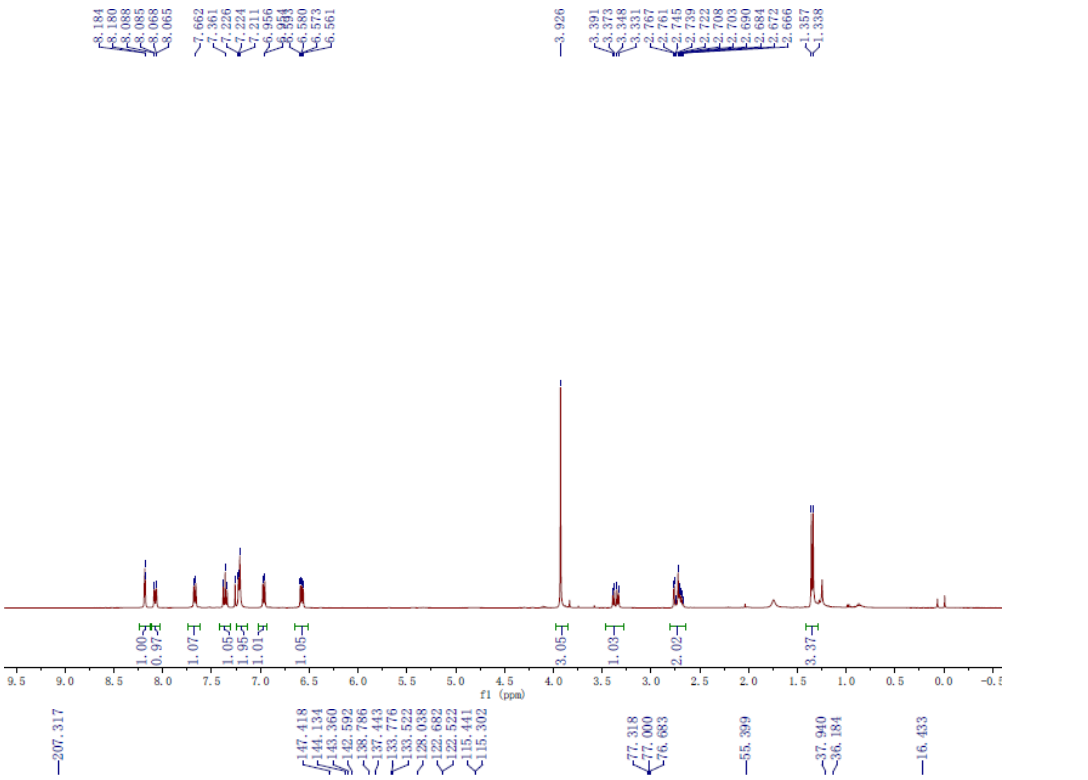
16.384
f1 (ppm)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6.573
6.561
3.926
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2.708
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1.05
3.05
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2.02
3.37
f1 (ppm)
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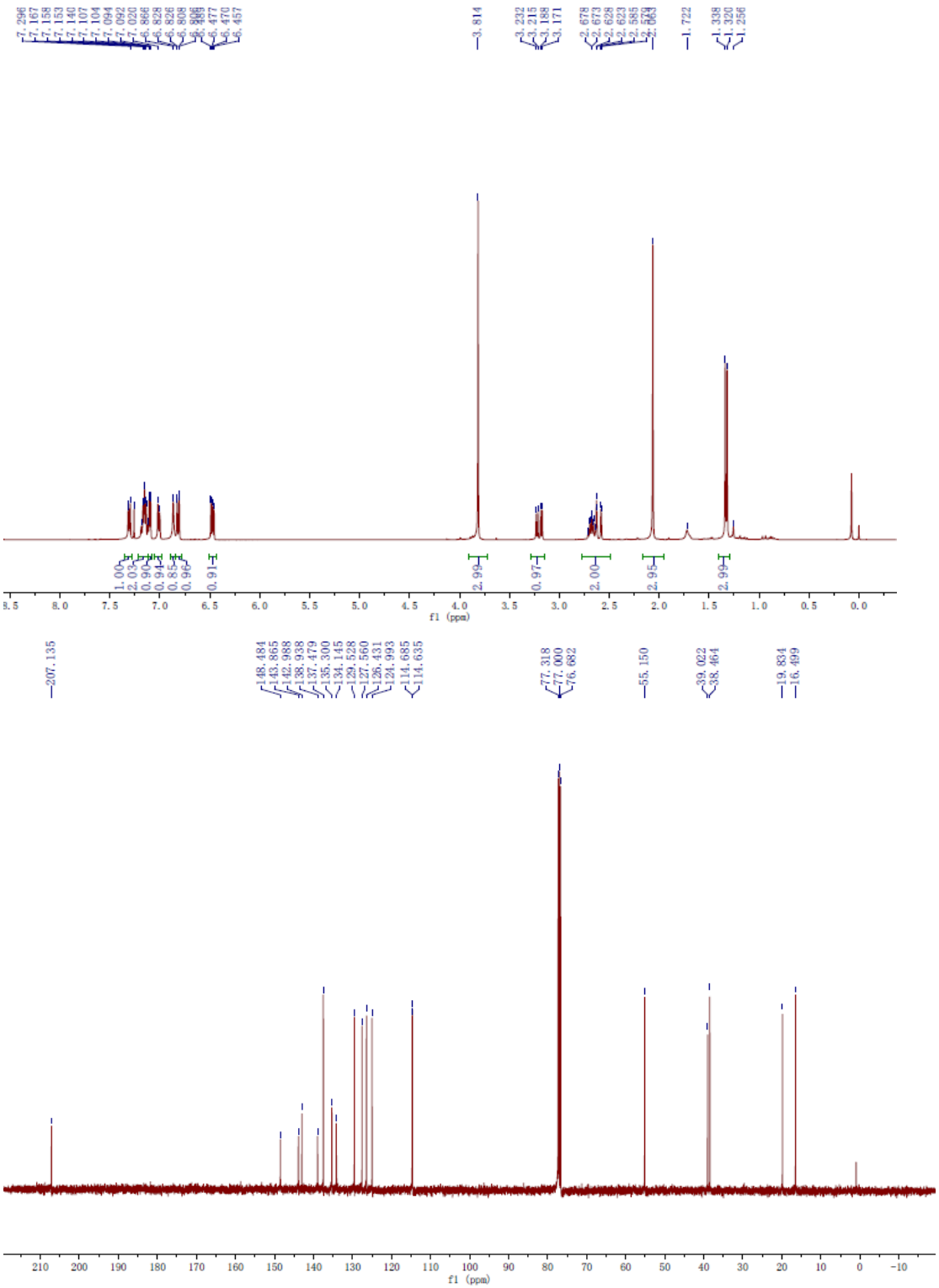

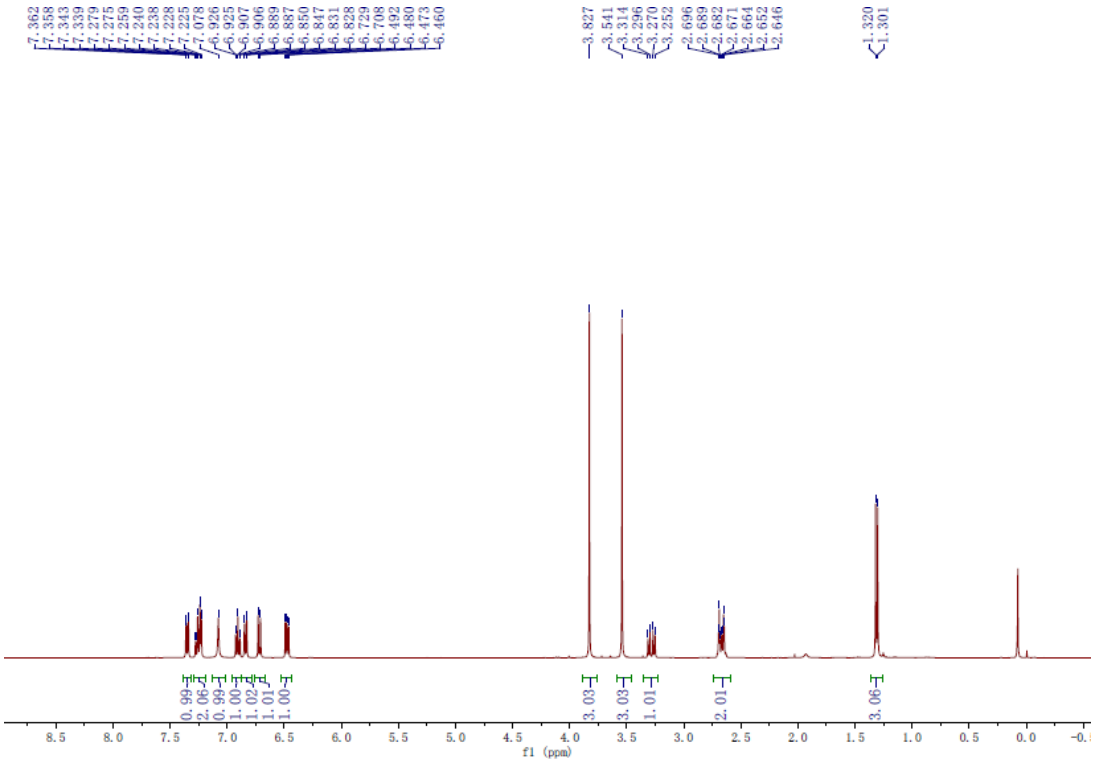
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2.689
2.682
2.671
2.664
2.652
2.646
1.320
1.301
0.99
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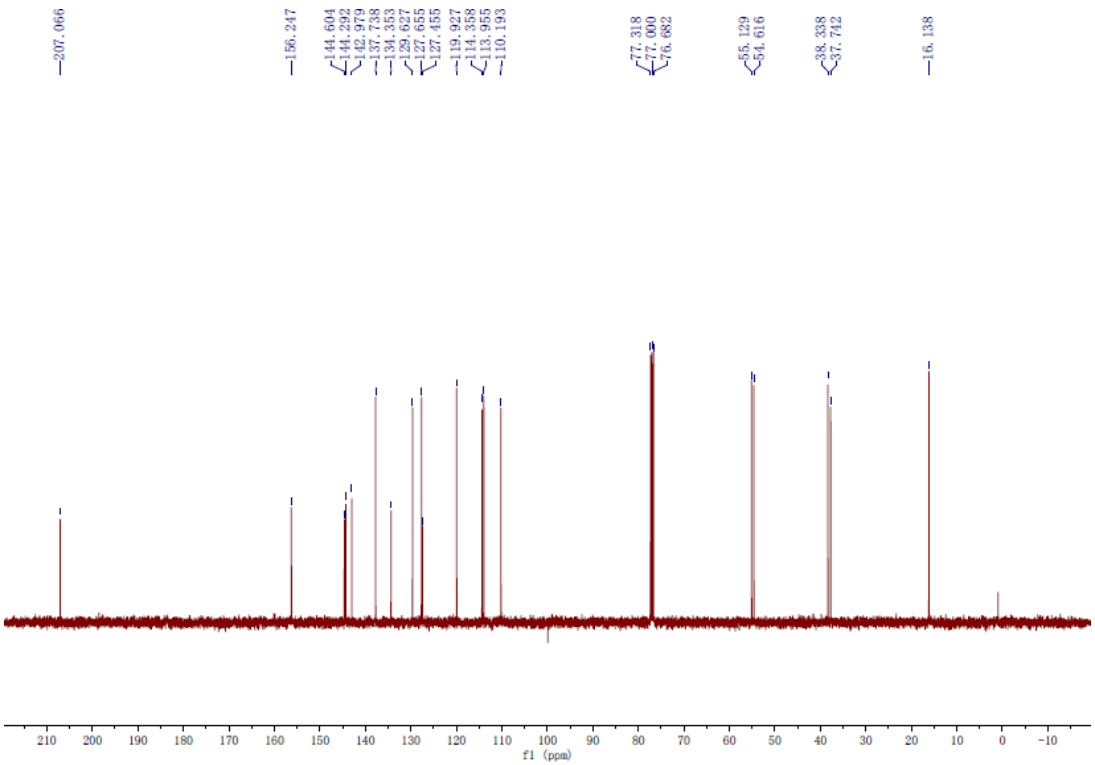
3.06
f1 (ppm)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38.338
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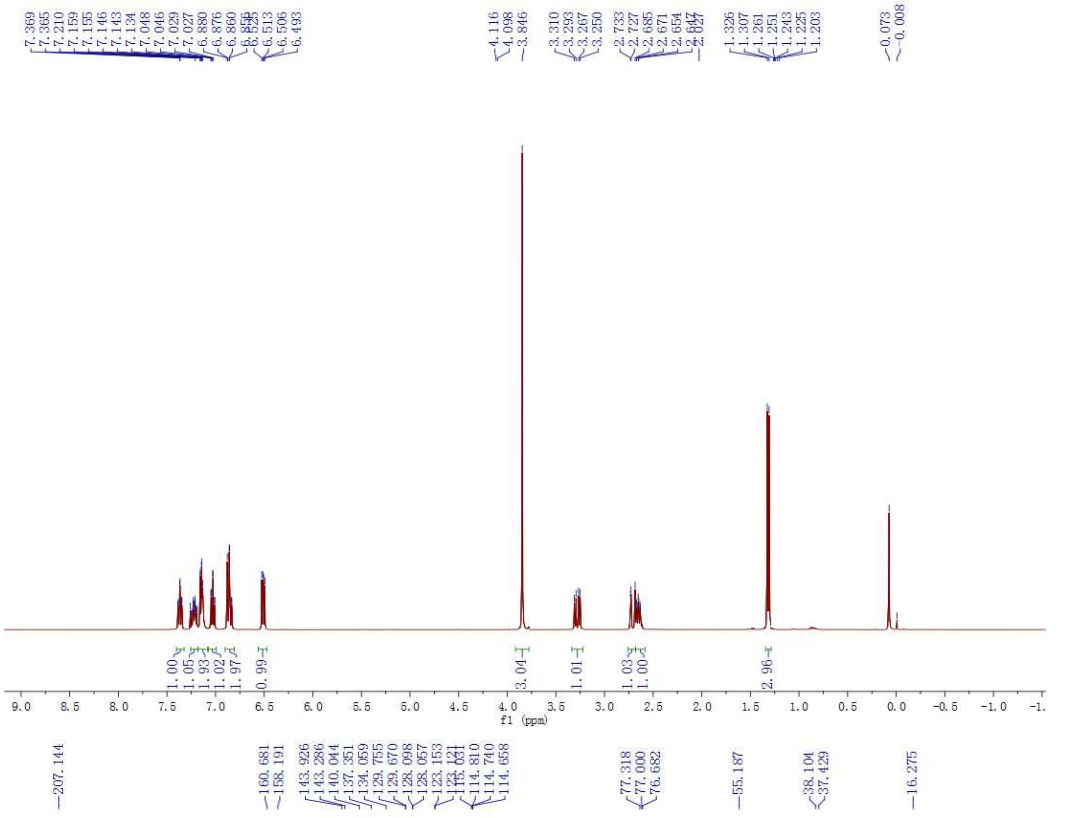
16.138
f1 (ppm)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1.307
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1.243
1.225
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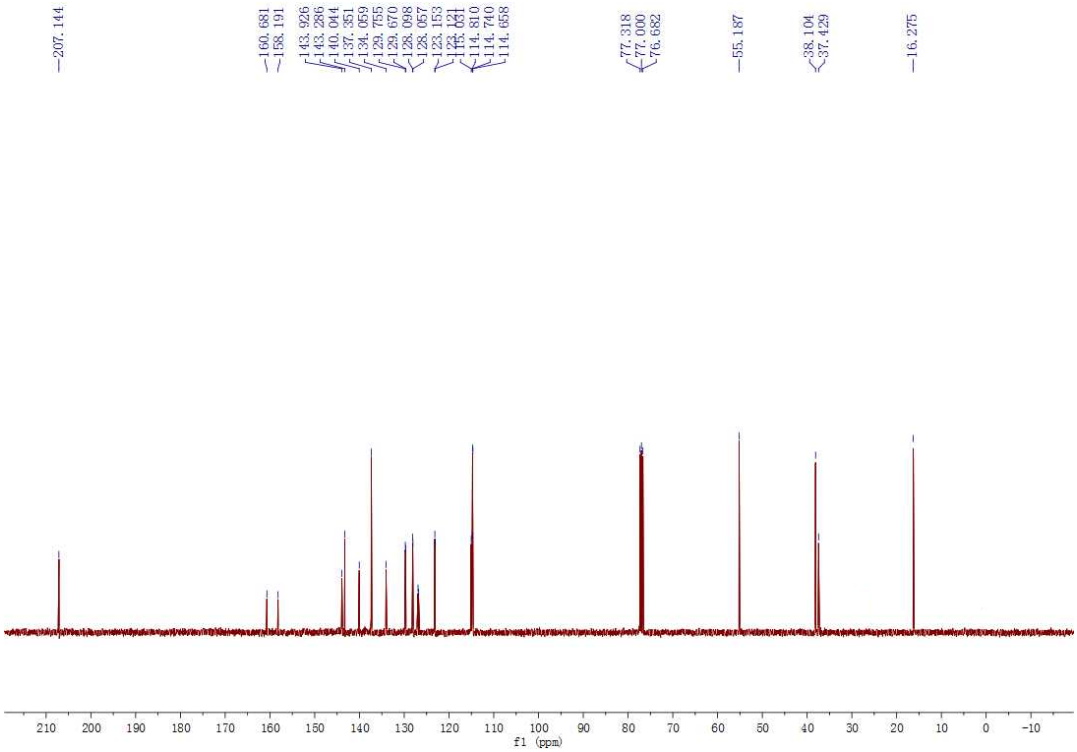
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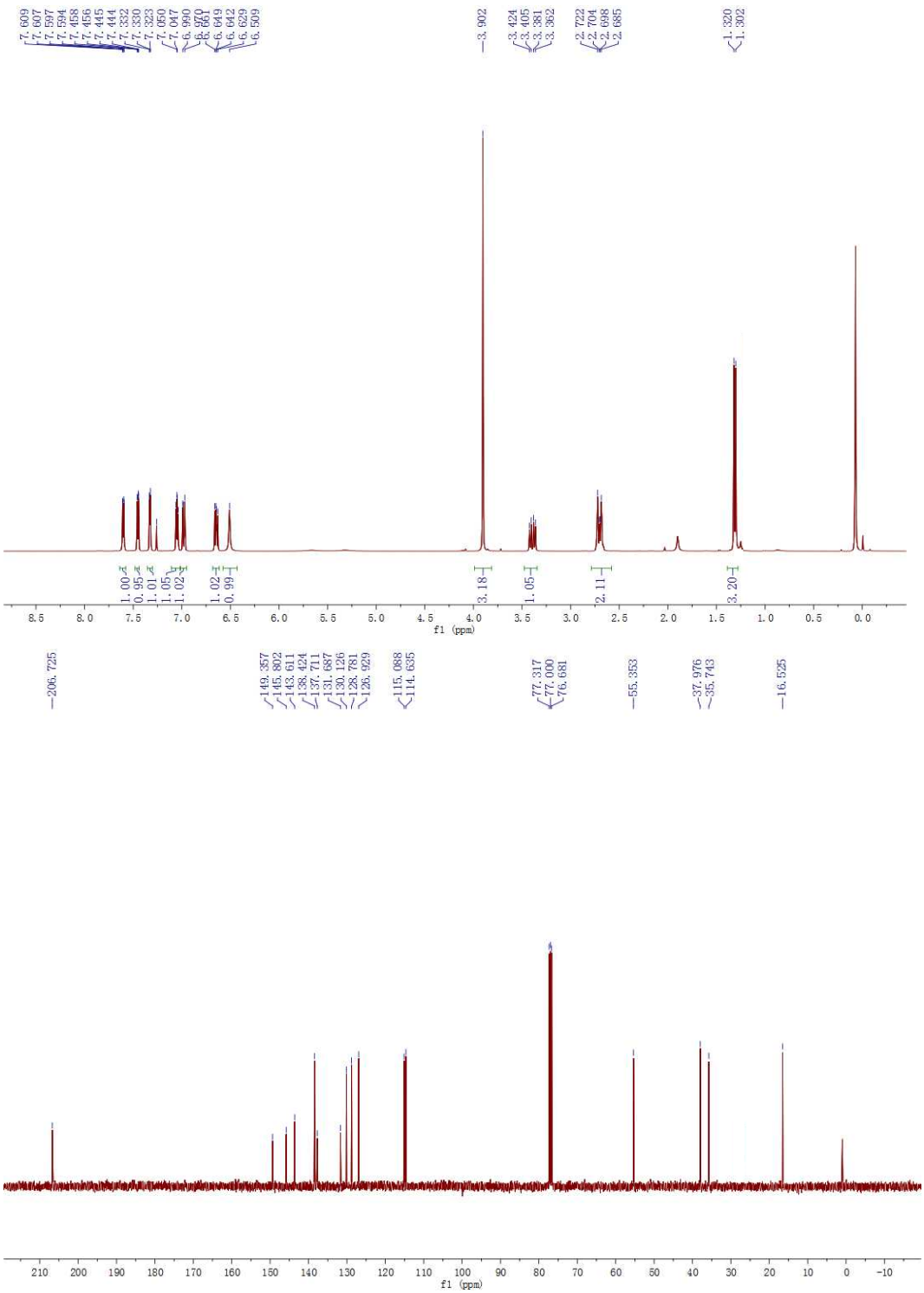
f1 (ppm)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6.649
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3.424
3.405
3.381
3.362
2.722
2.704
2.698
2.685
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1.302
1.00
0.95
1.01
1.05
1.02
1.02
0.99
3.18
1.05
2.11
3.20
f1 (ppm)
206.725
149.357
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138.424
137.711
131.687
130.126
128.781
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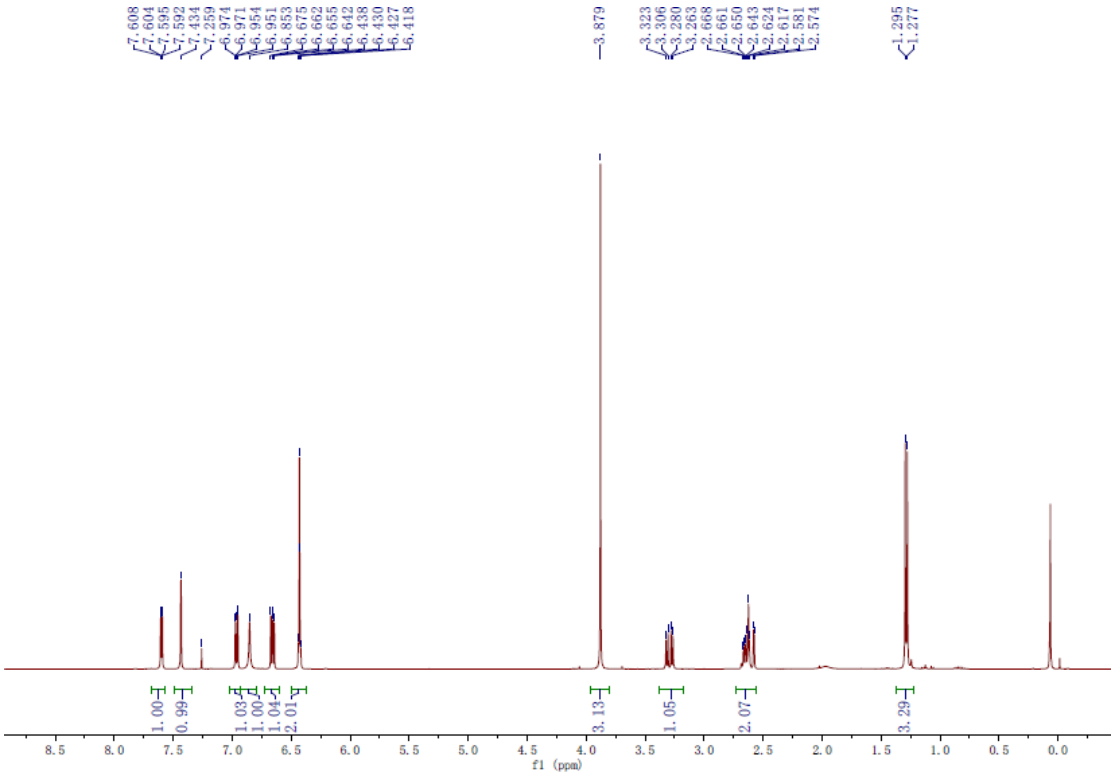
f1 (ppm)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6.642
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6.430
6.427
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2.661
2.650
2.643
2.624
2.617
2.581
2.574
1.295
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1.04
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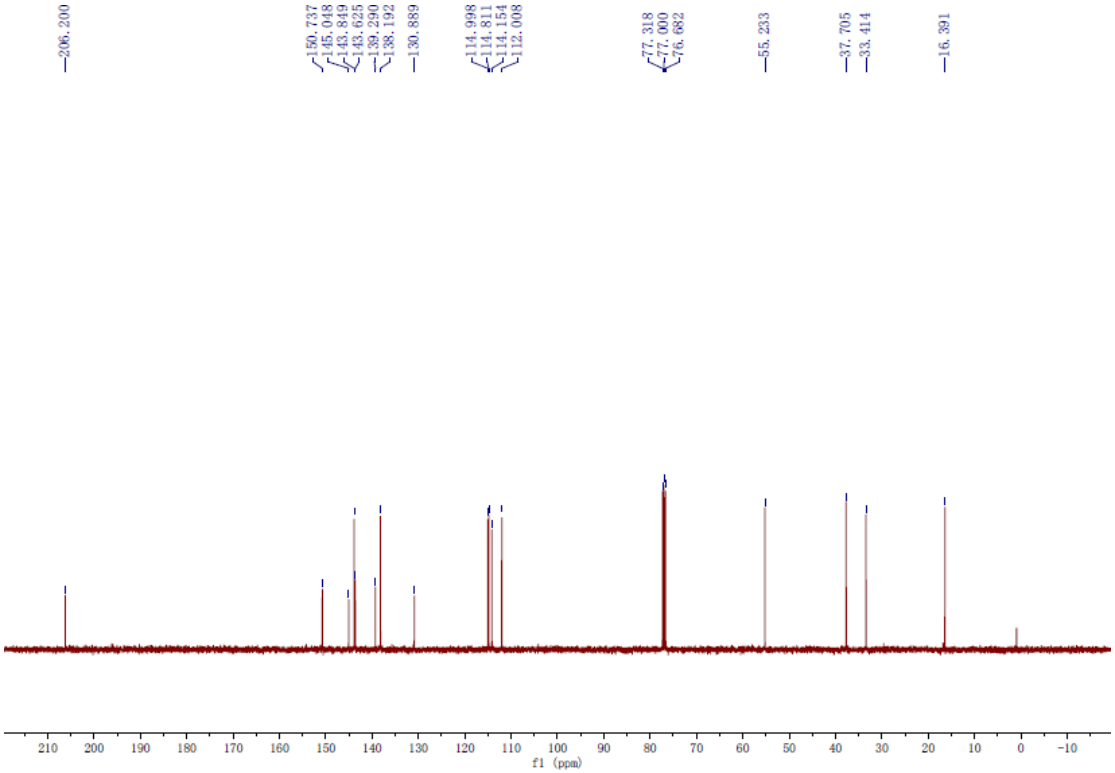
f1 (ppm)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37.705
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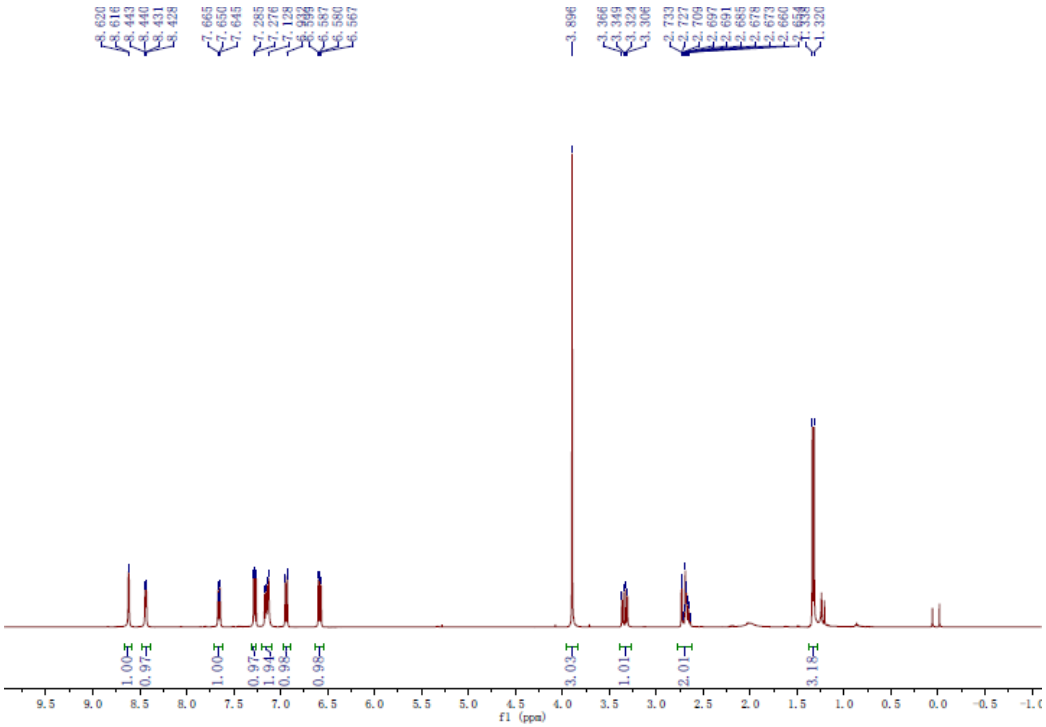
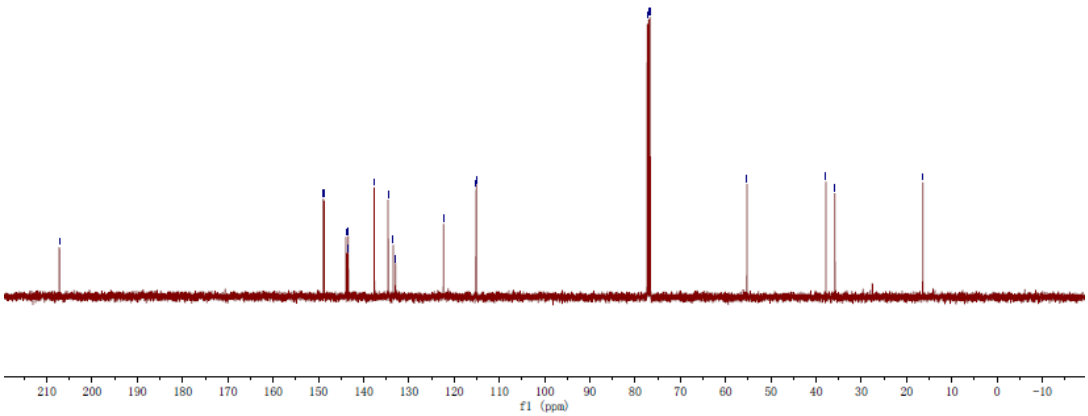
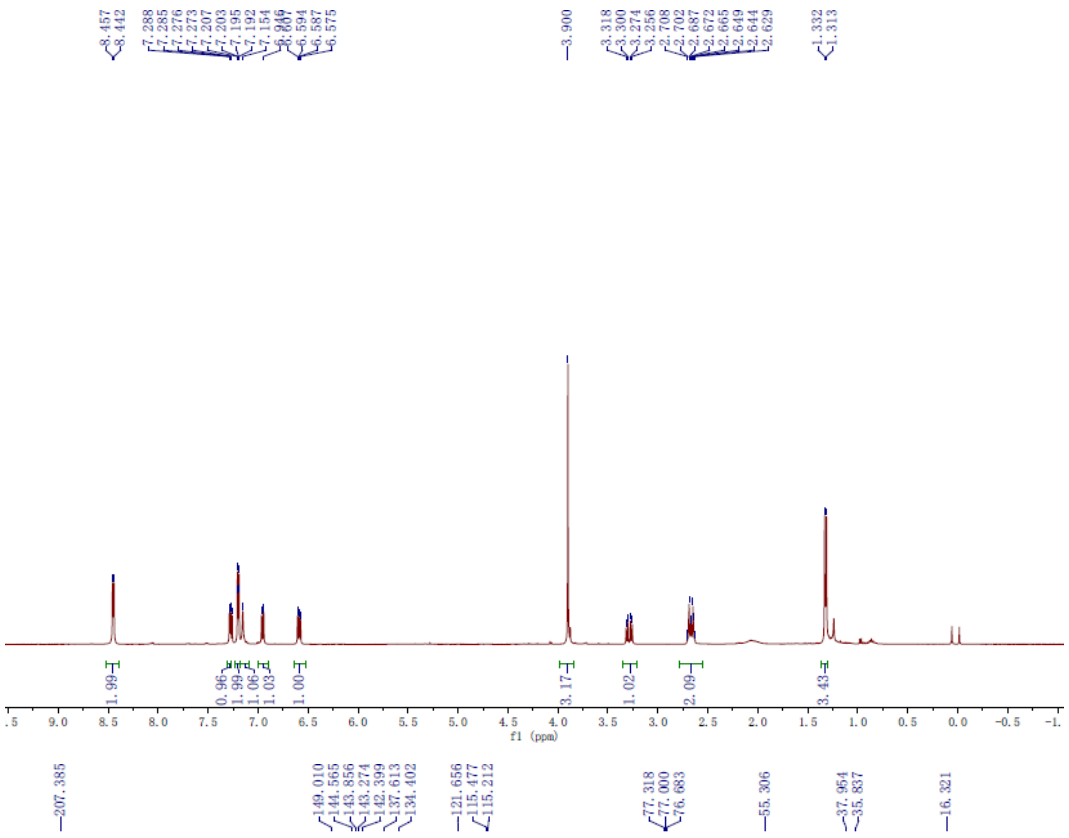
16.391
f1 (ppm)



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3.900
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3.274
3.256
2.708
2.702
2.687
2.672
2.665
2.649
2.644
2.629
1.332
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1.03
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1.02
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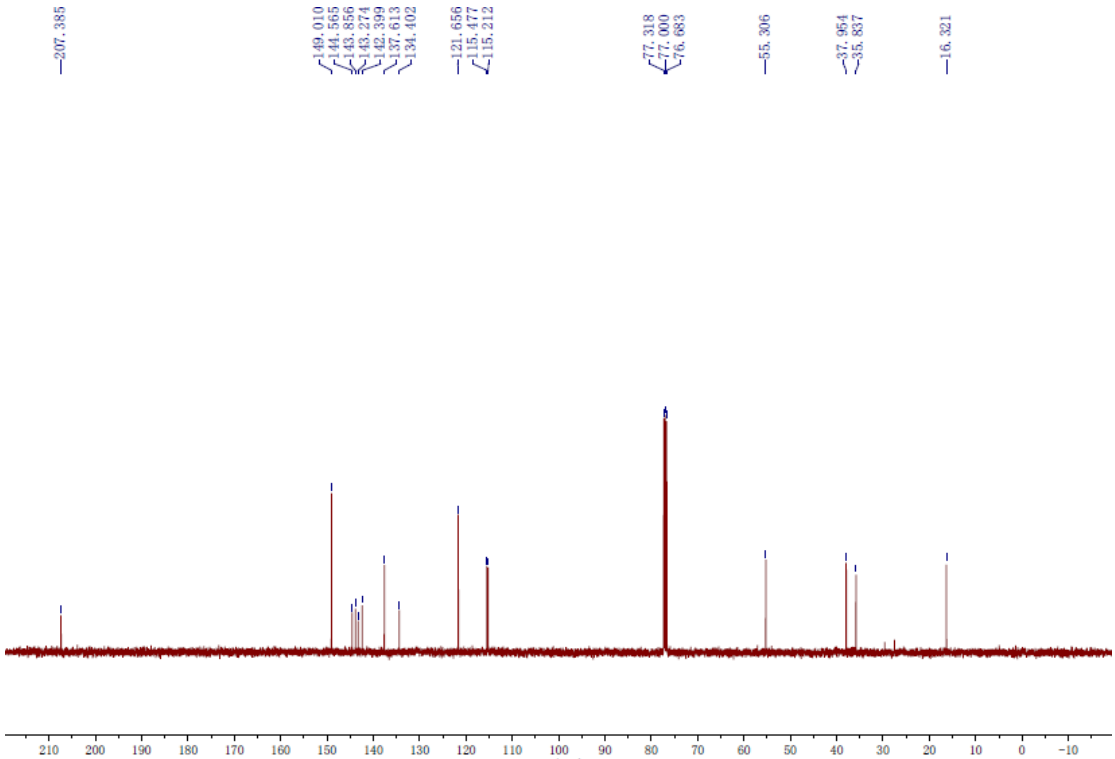
3.43
f1 (ppm)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77.000
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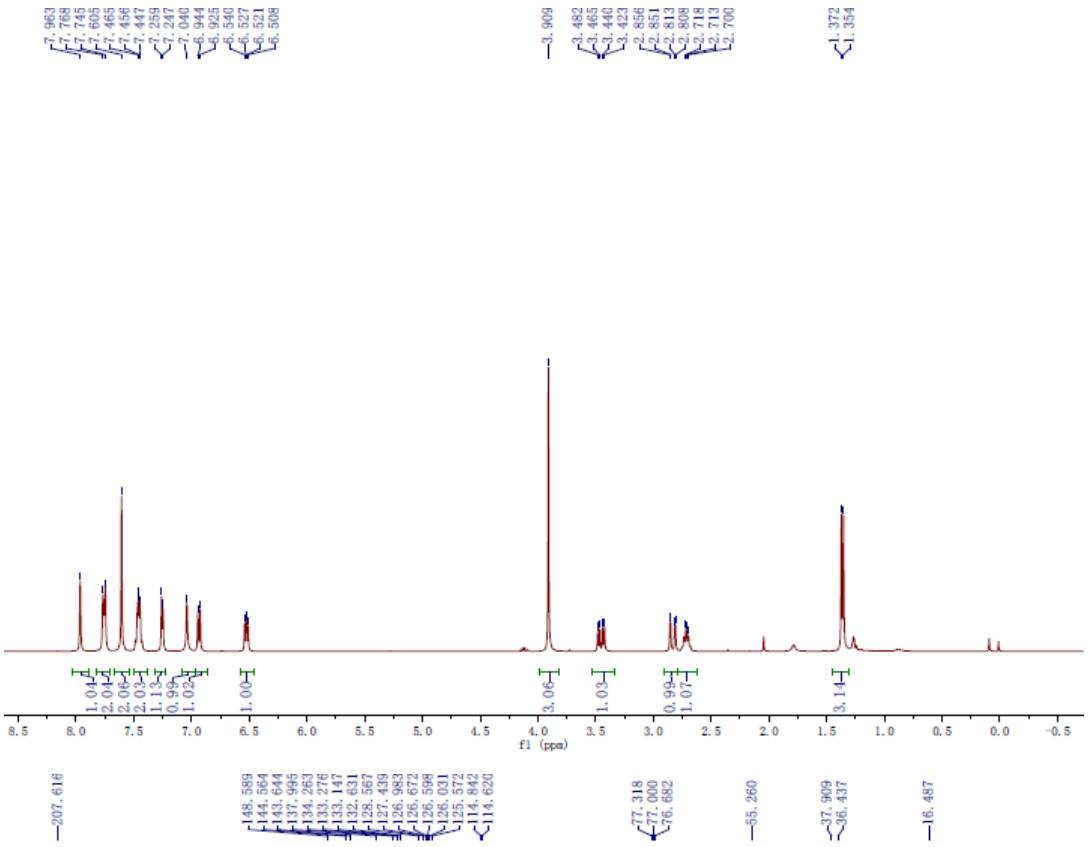
16.321
f1 (ppm)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6.540
6.527
6.521
6.508
3.909
3.482
3.465
3.440
3.423
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2.851
2.813
2.808
2.718
2.713
2.700
1.372
1.354
1.04
2.04
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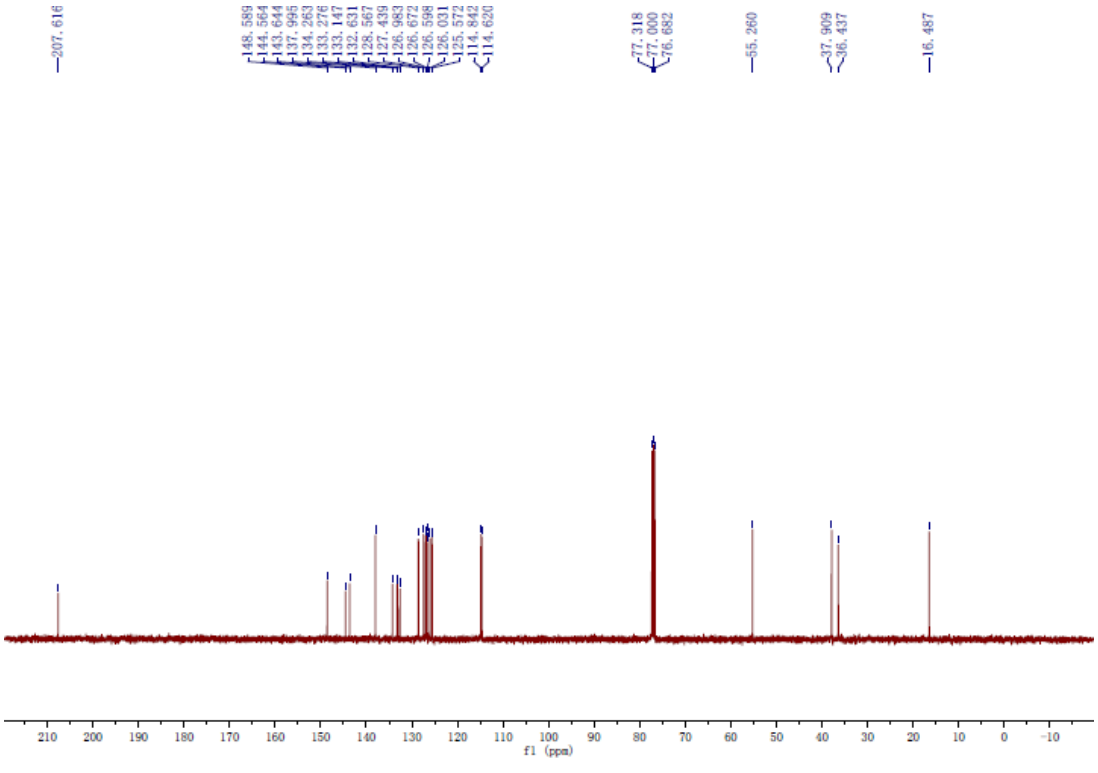
3.14
f1 (ppm)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126.672
126.598
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125.572
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114.620
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77.000
76.682
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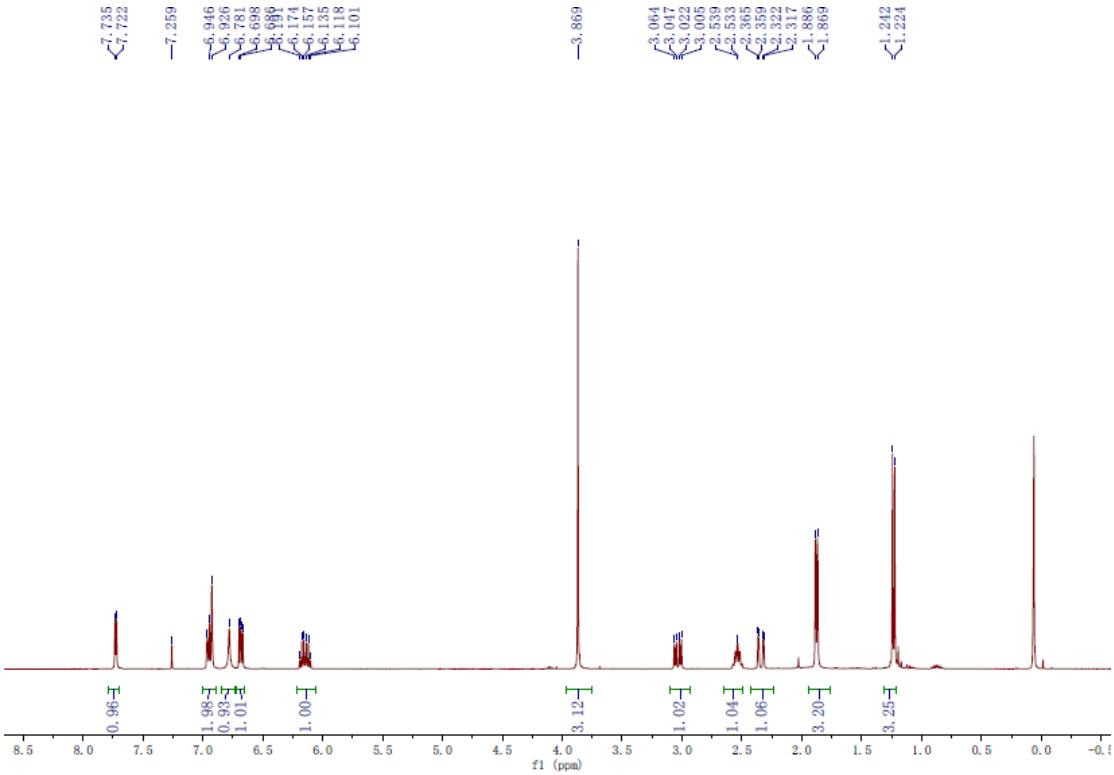
37.909
36.437
16.487
f1 (ppm)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6.118
6.101
3.869
3.064
3.047
3.022
3.005
2.539
2.533
2.365
2.359
2.322
2.317
1.886
1.869
1.242
1.224
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1.00
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1.02
1.04
1.06
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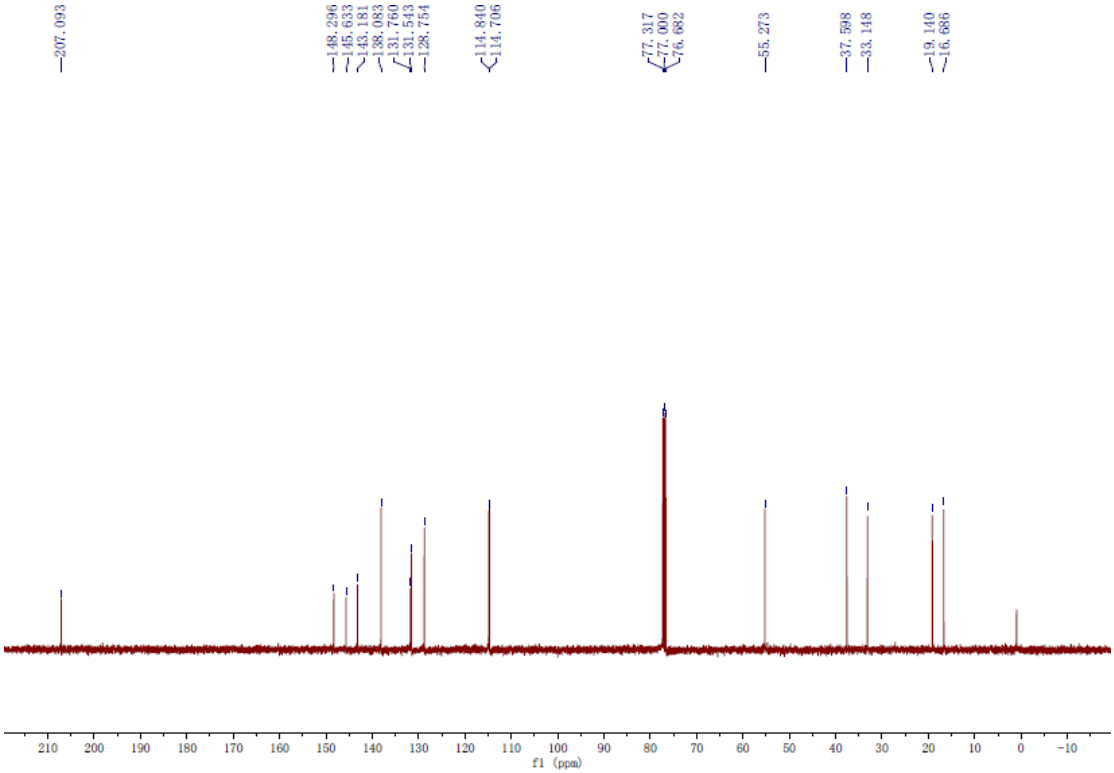
3.25
f1 (ppm)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131.760
131.543
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76.682
55.273
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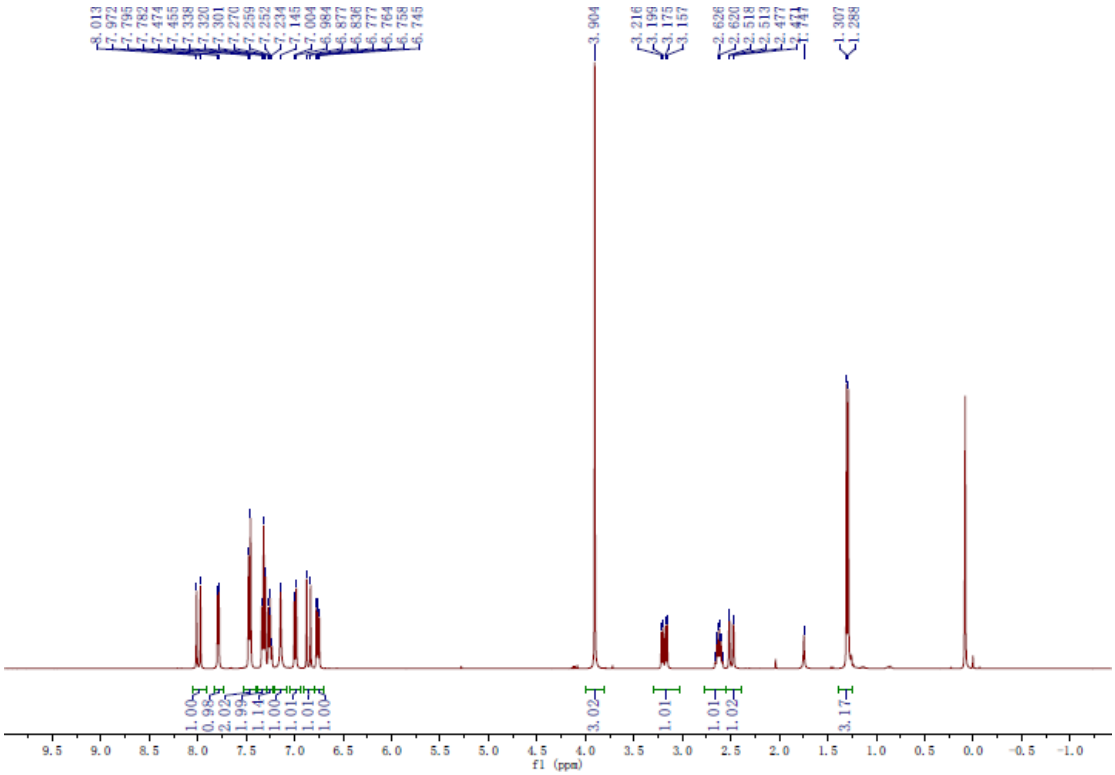
33.148
19.140
16.686
f1 (ppm)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7.234
7.145
7.004
6.984
6.877
6.836
6.777
6.764
6.758
6.745
3.904
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3.199
3.175
3.157
2.626
2.620
2.518
2.513
2.477
2.471
1.741
1.307
1.288
1.00
0.98
2.02
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1.14
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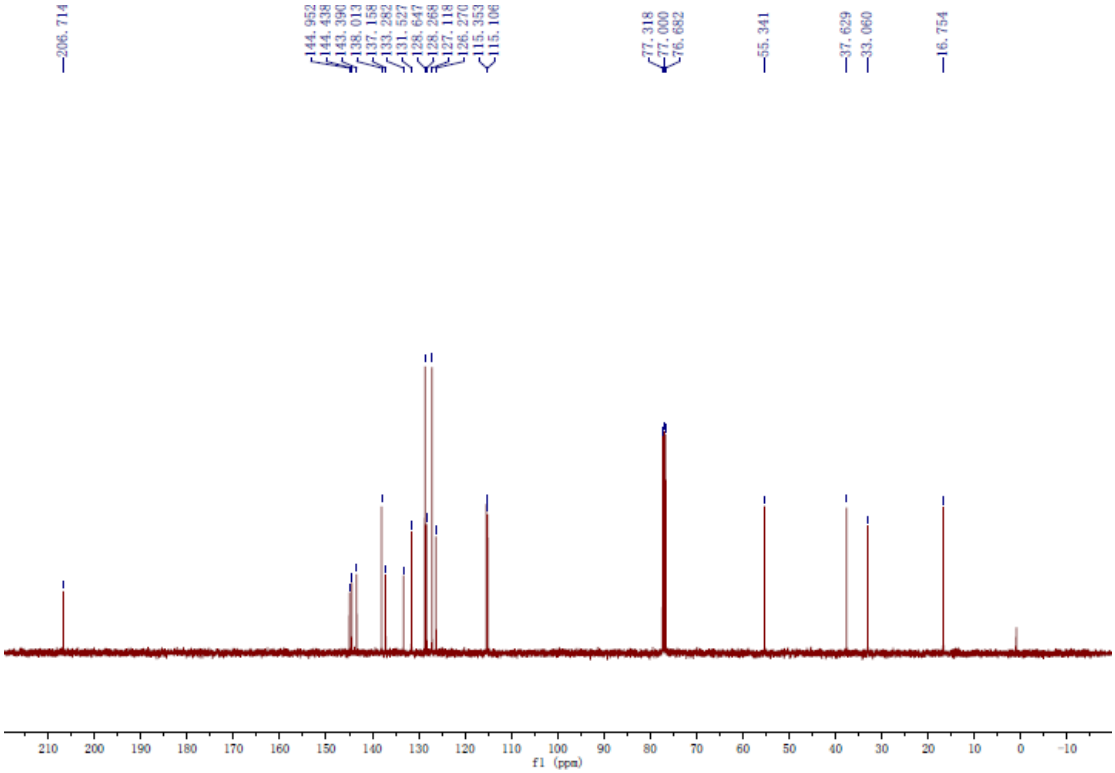
1.01
1.00
3.02
1.01
1.01
1.02
3.17
f1 (ppm)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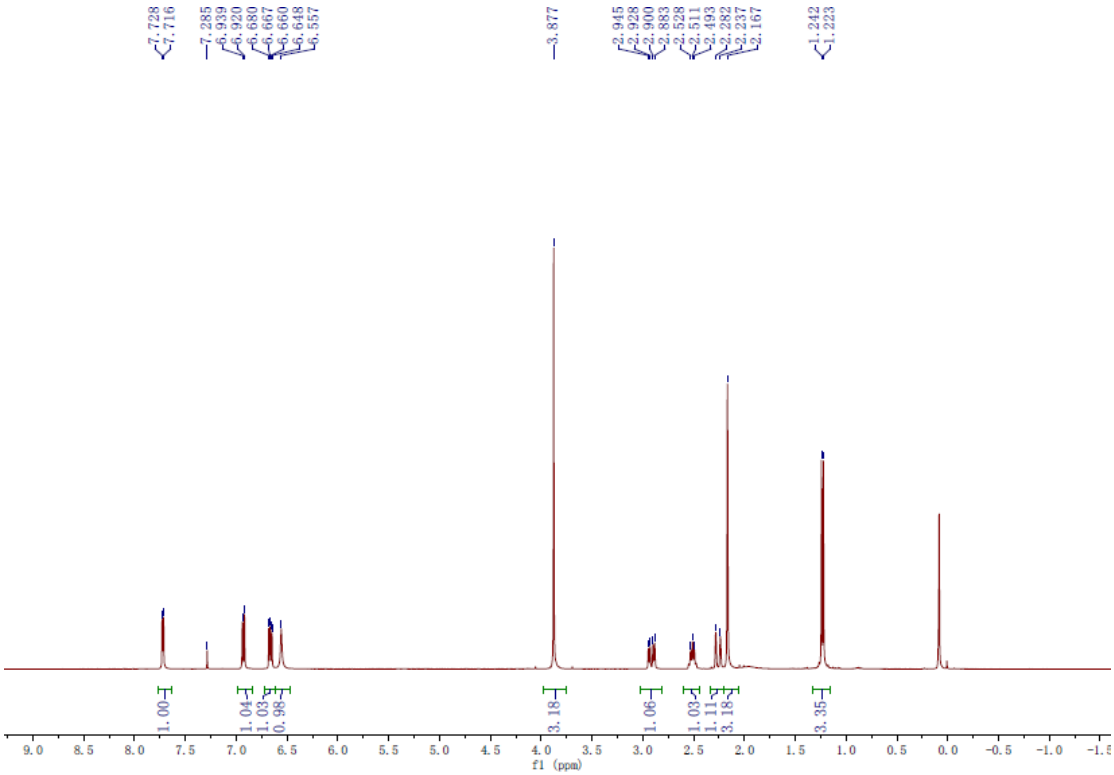
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6.660
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6.557
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2.900
2.883
2.528
2.511
2.493
2.282
2.237
2.167
1.242
1.223
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1.03
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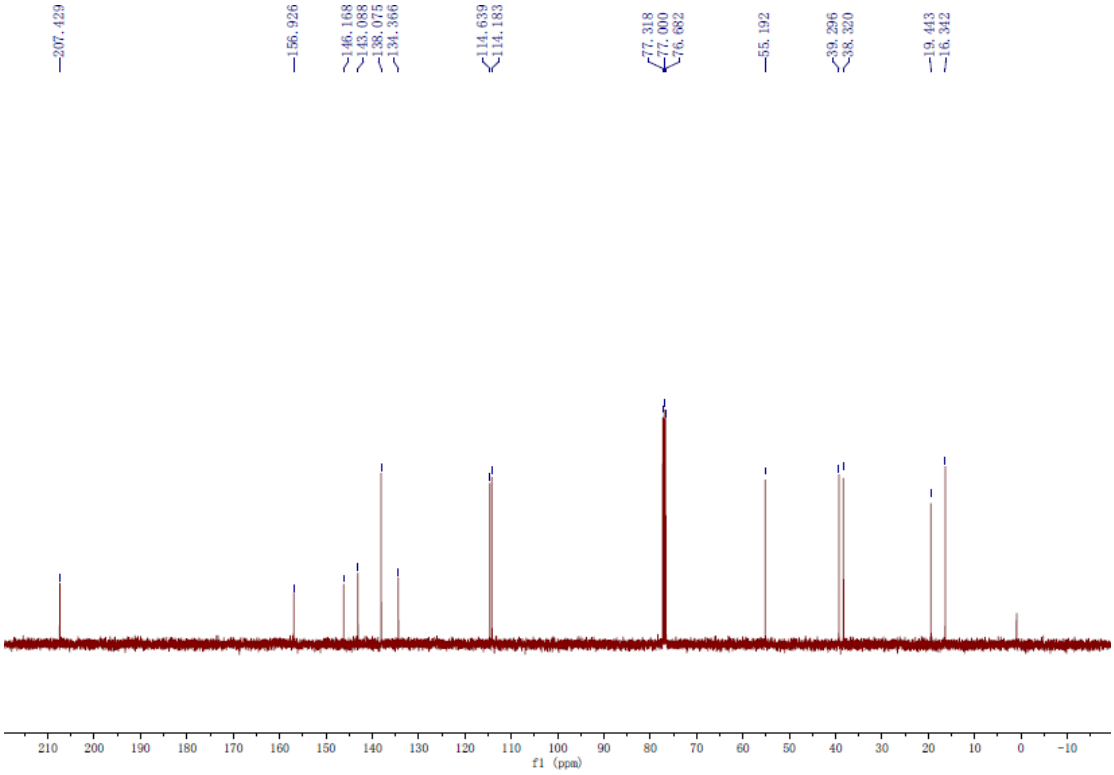
1.06
1.03
1.11
3.18
3.35
f1 (ppm)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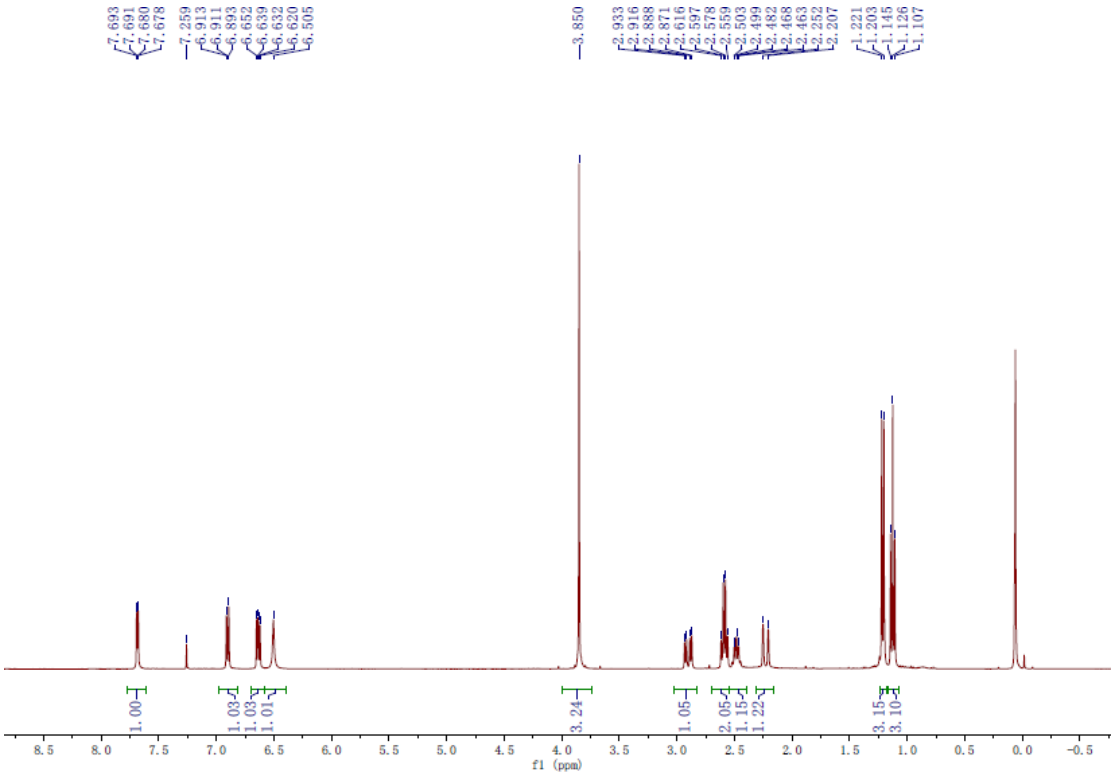
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3.850
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2.916
2.888
2.871
2.616
2.597
2.578
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2.503
2.499
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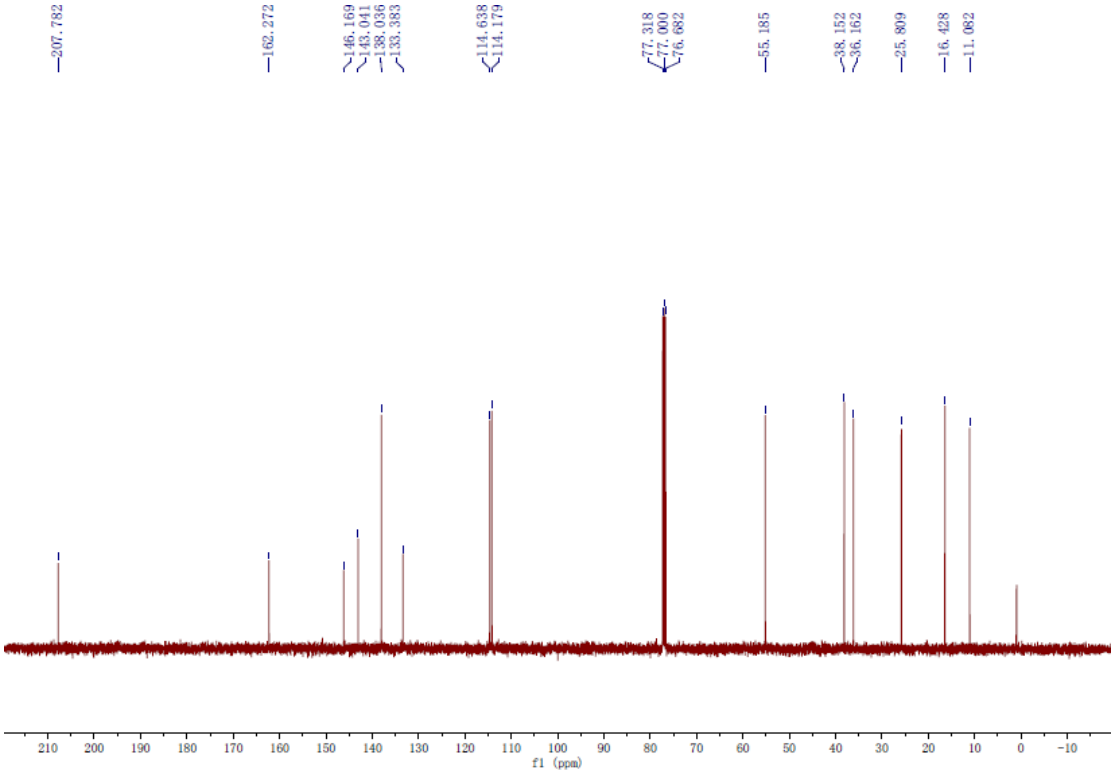
3.10
f1 (ppm)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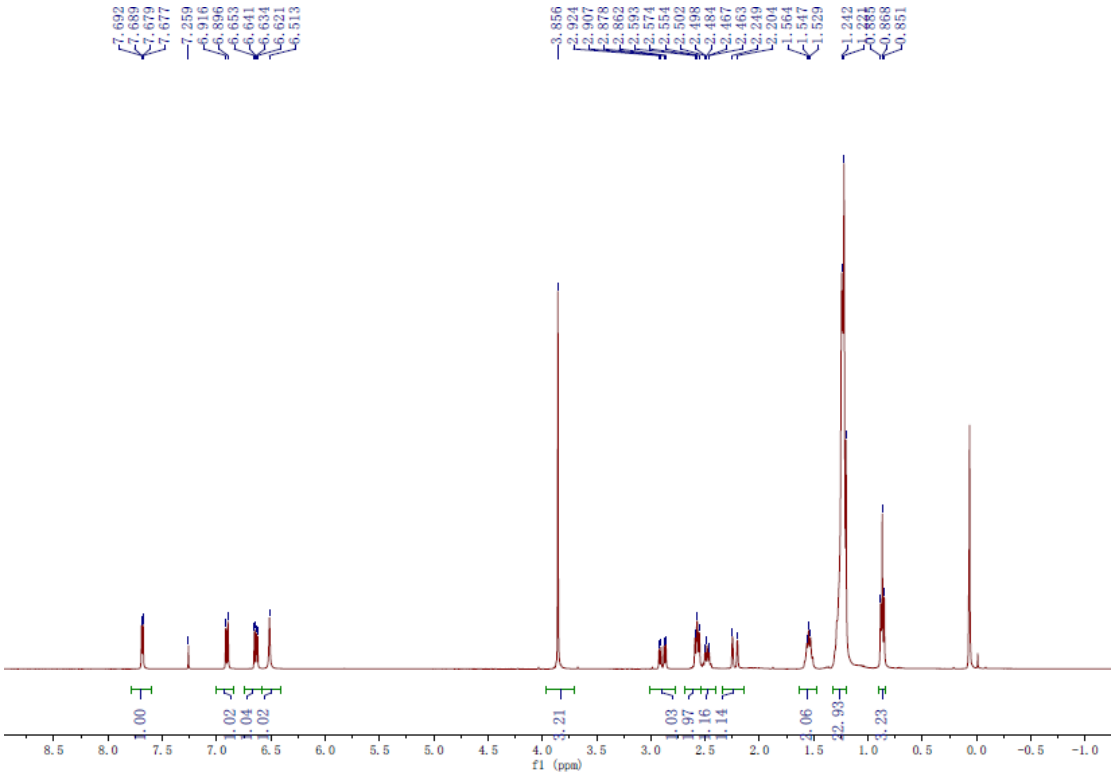
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2.574
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2.467
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2.249
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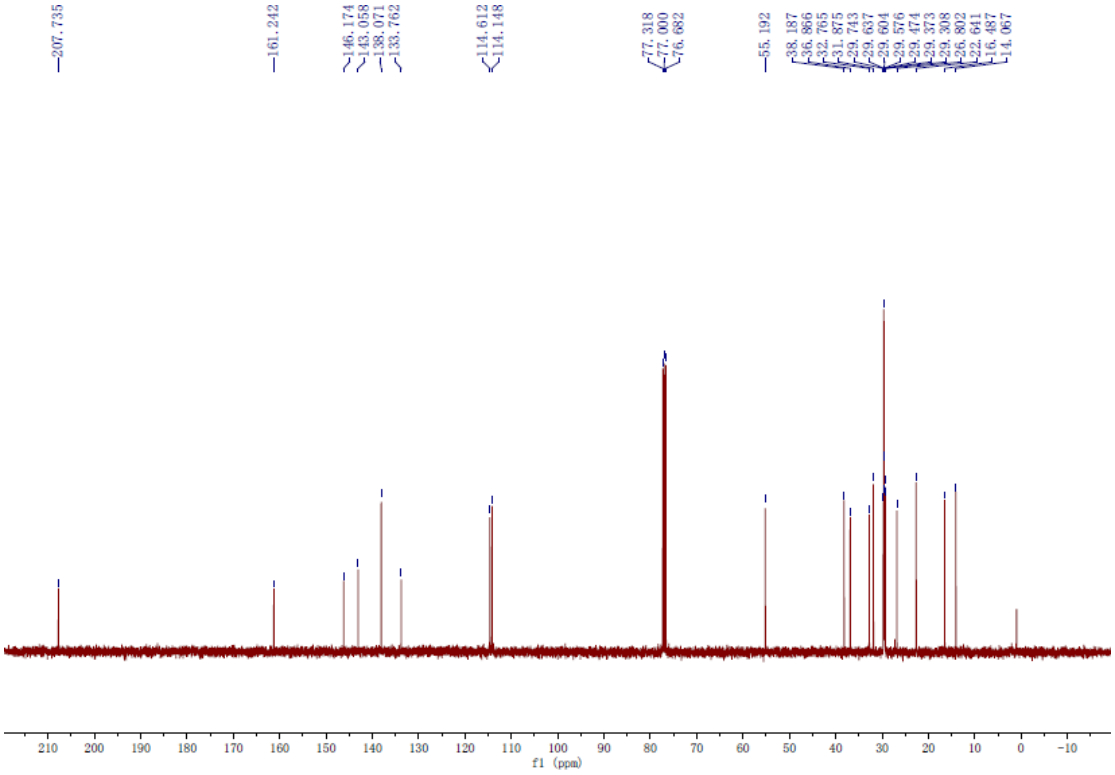
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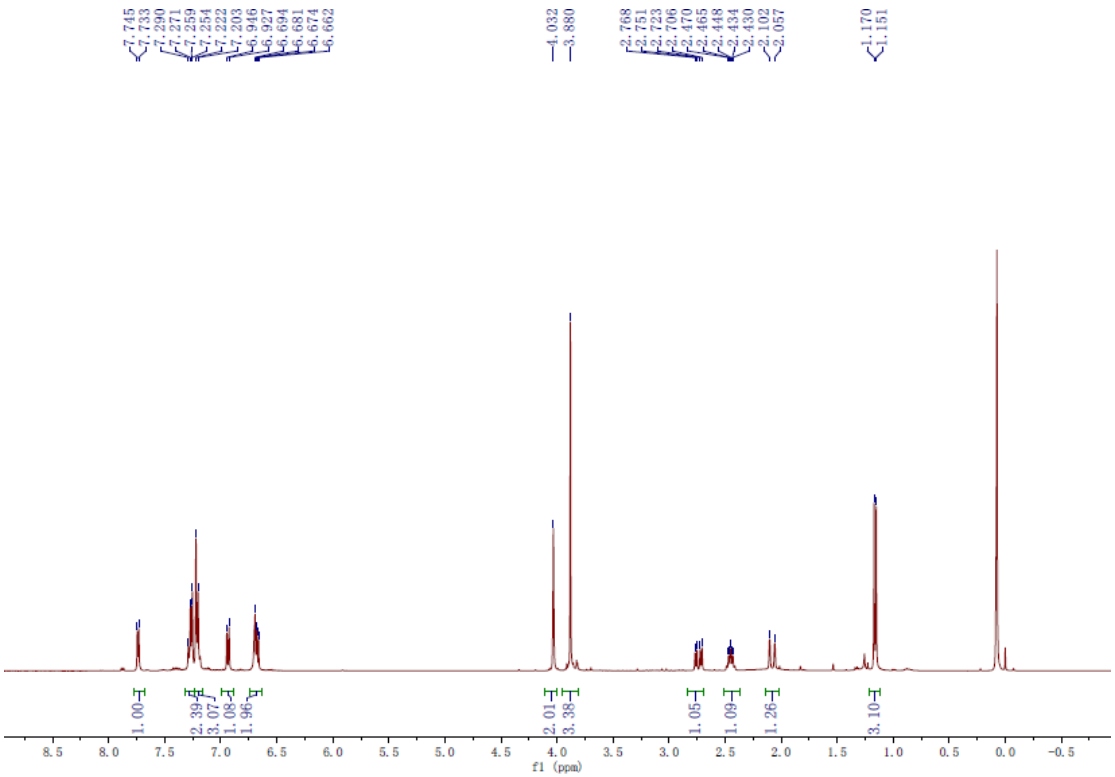
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2.430
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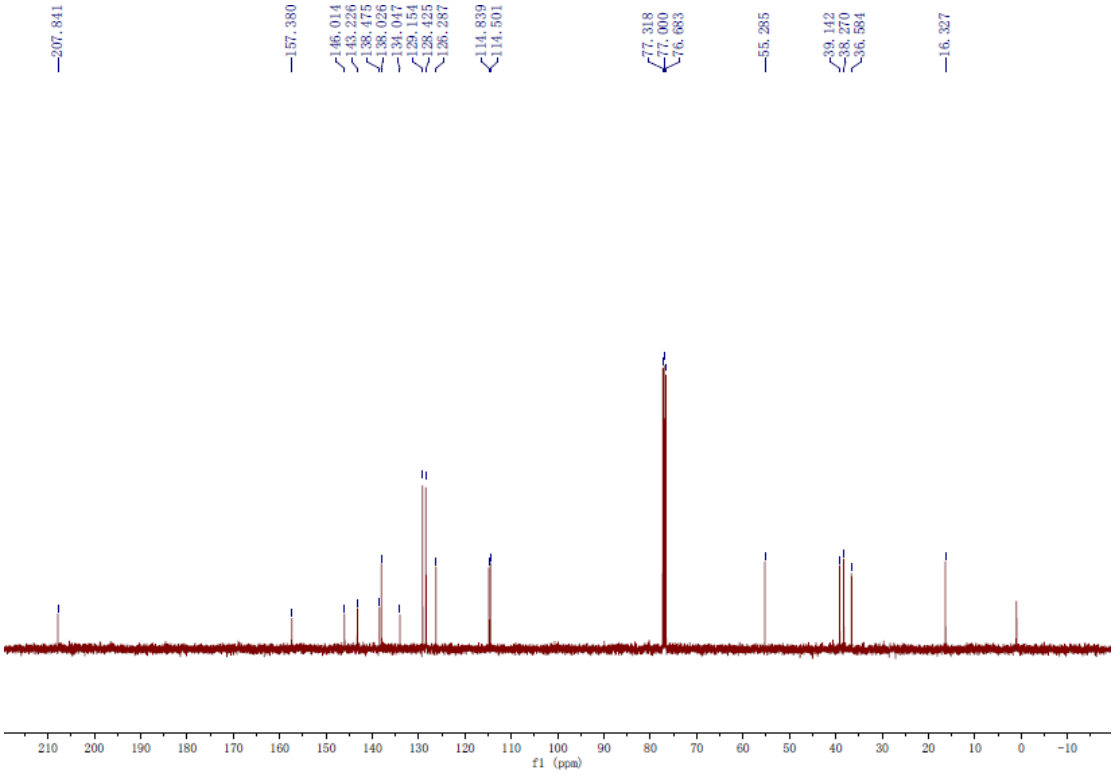
f1 (ppm)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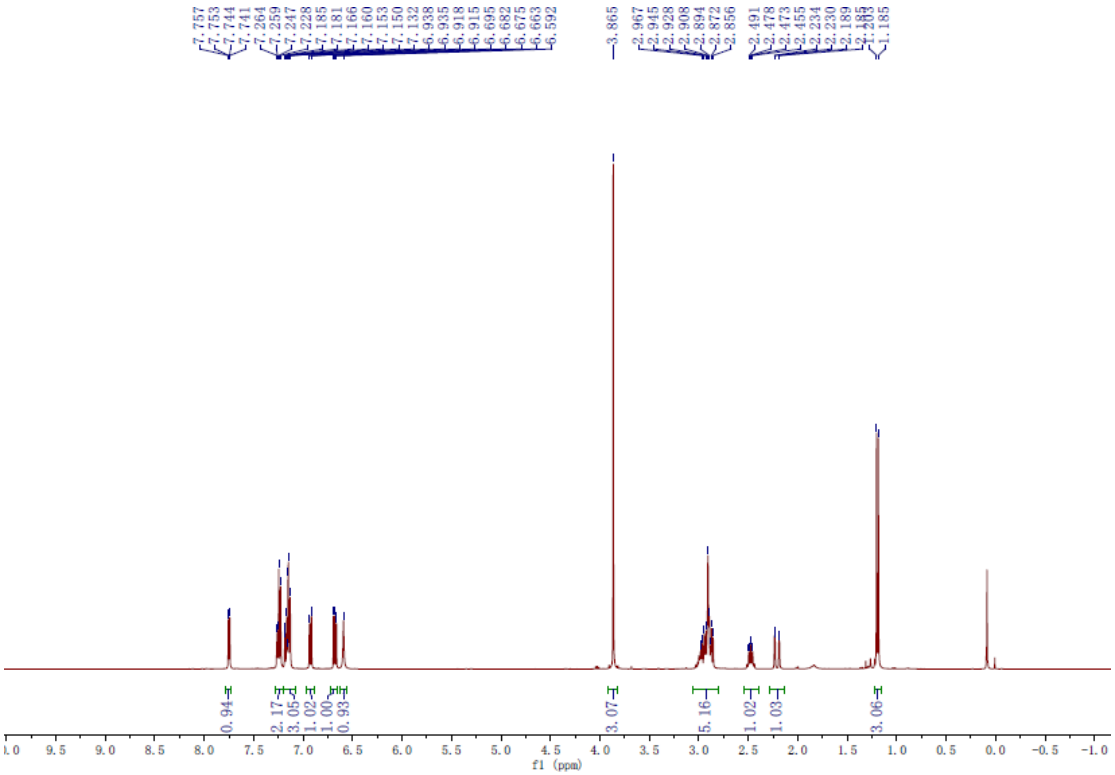
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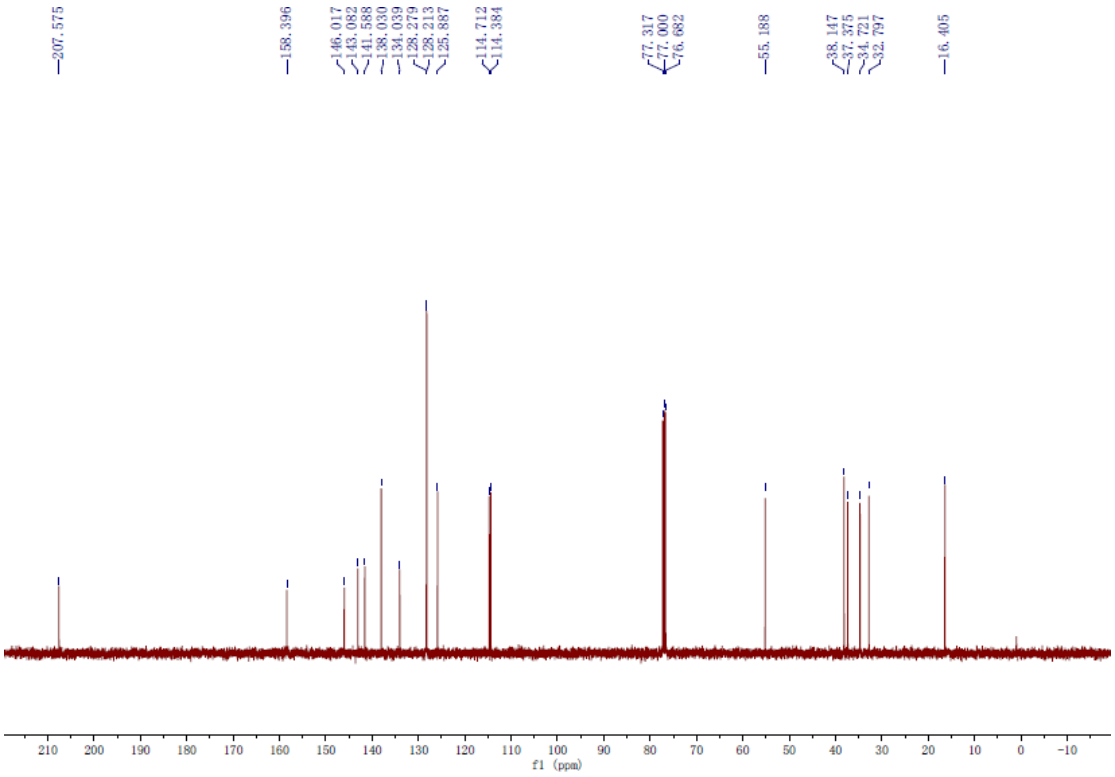
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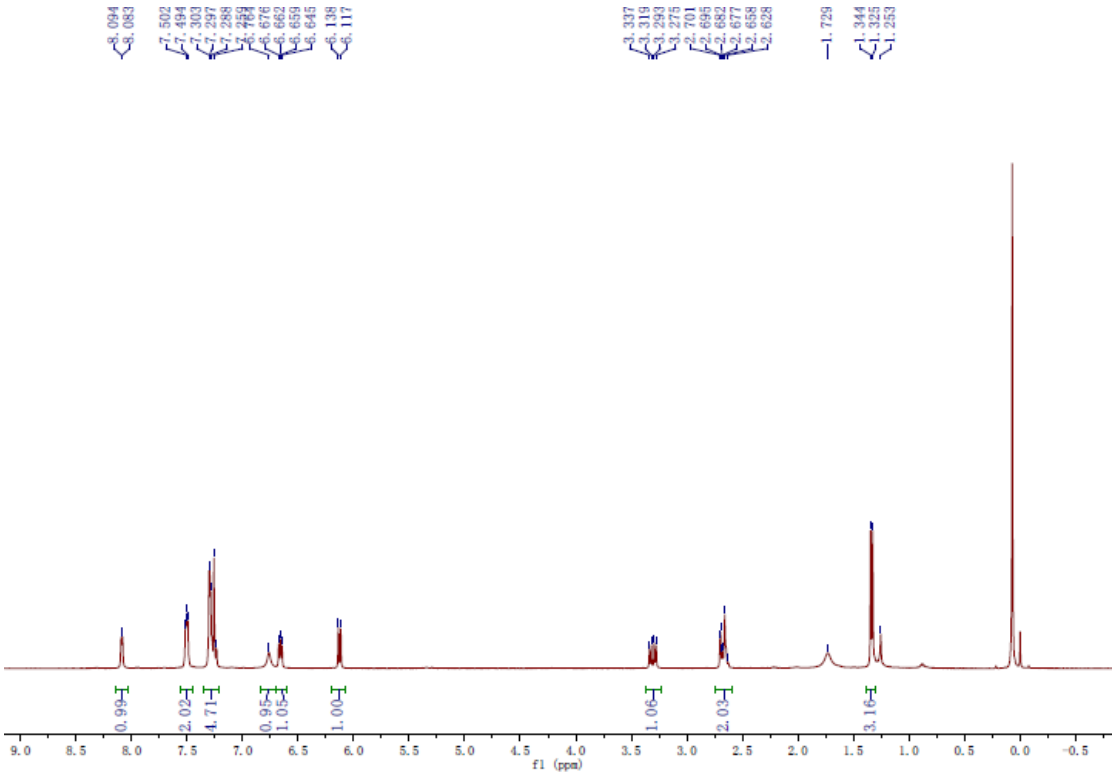
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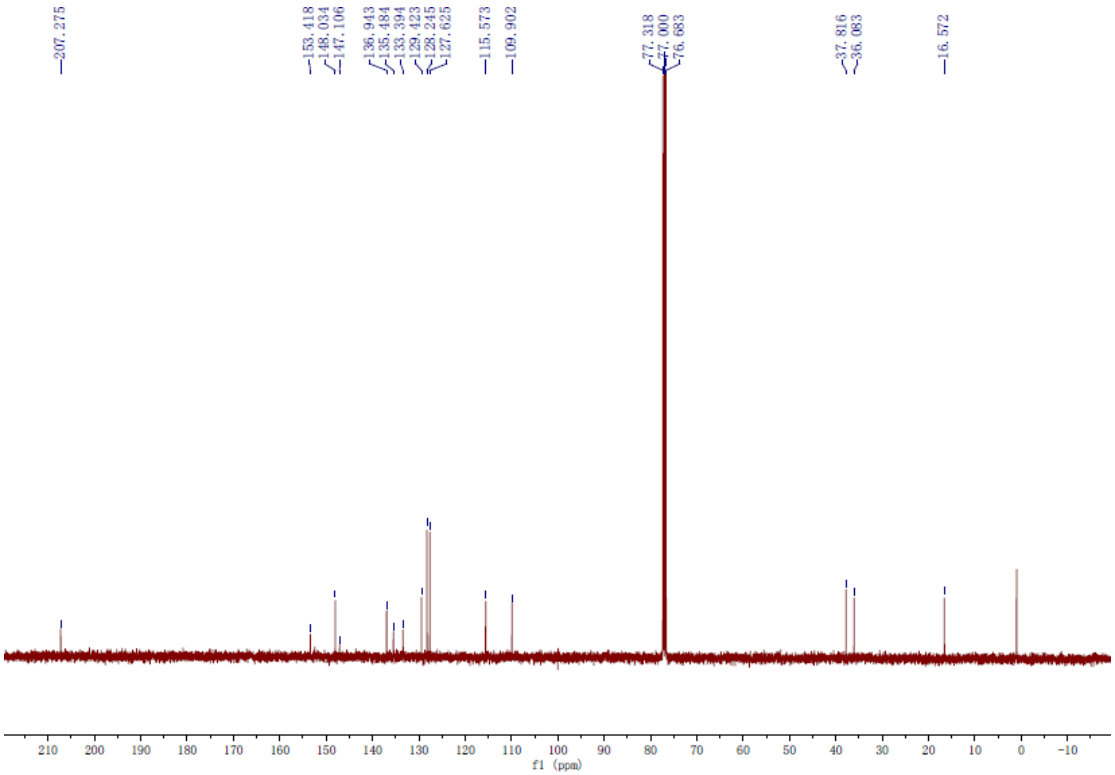
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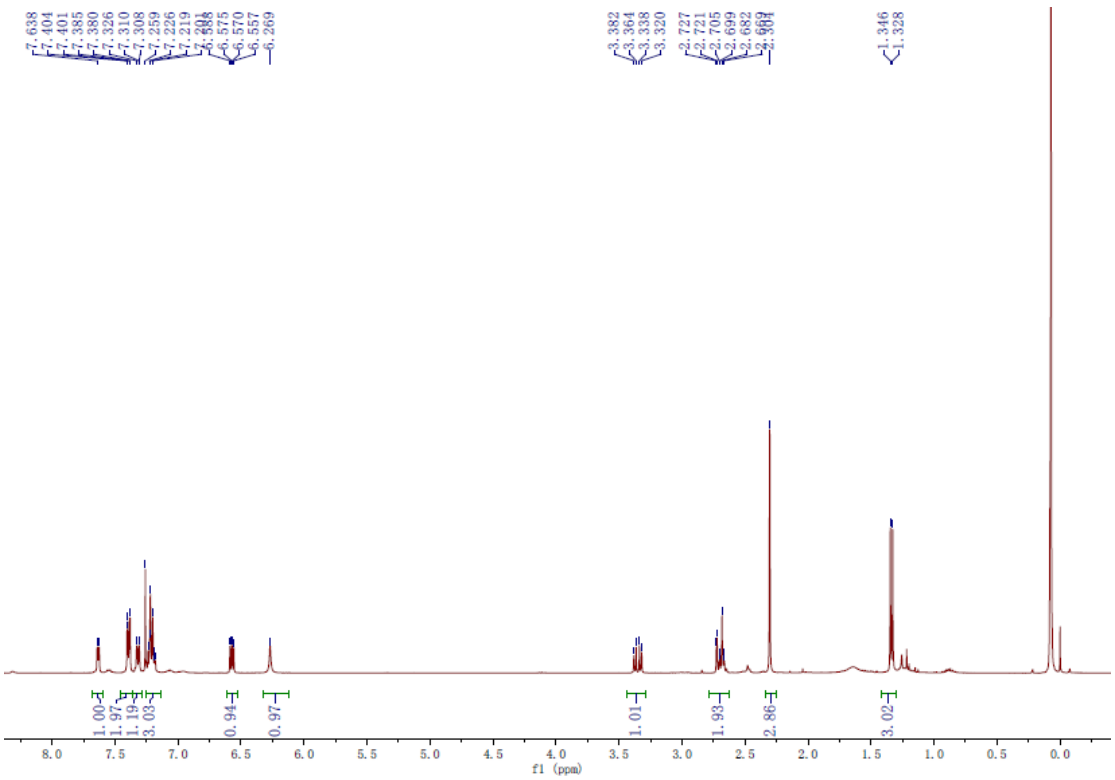
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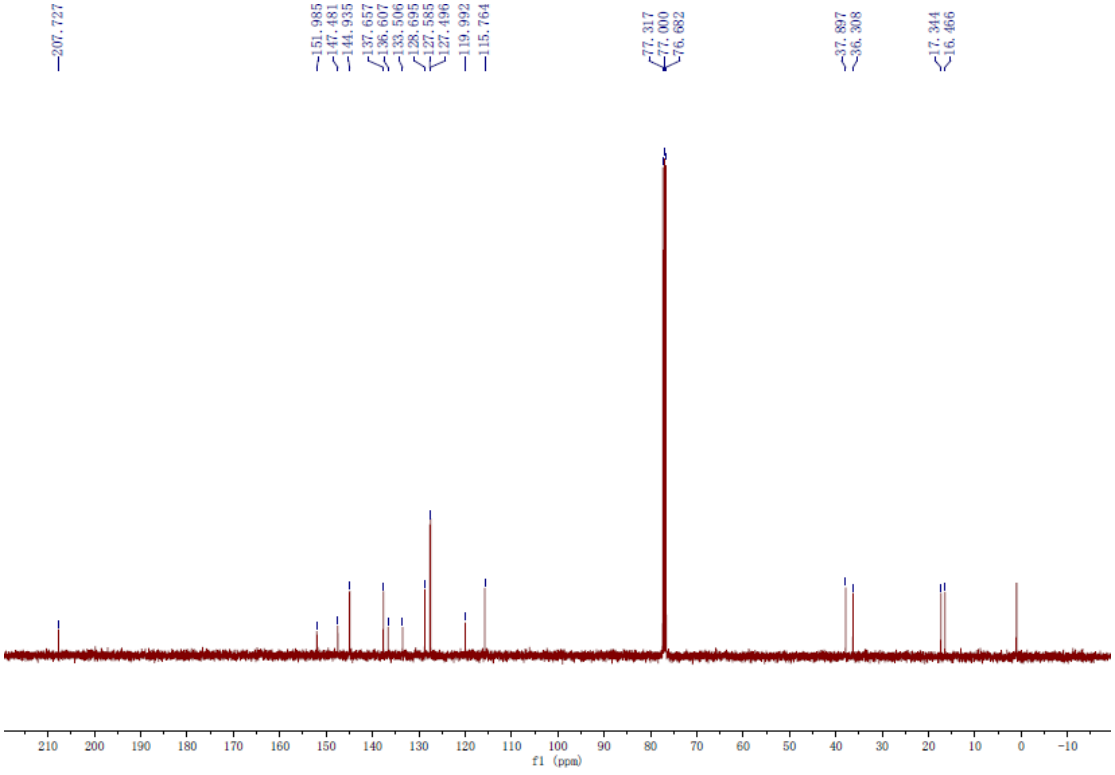
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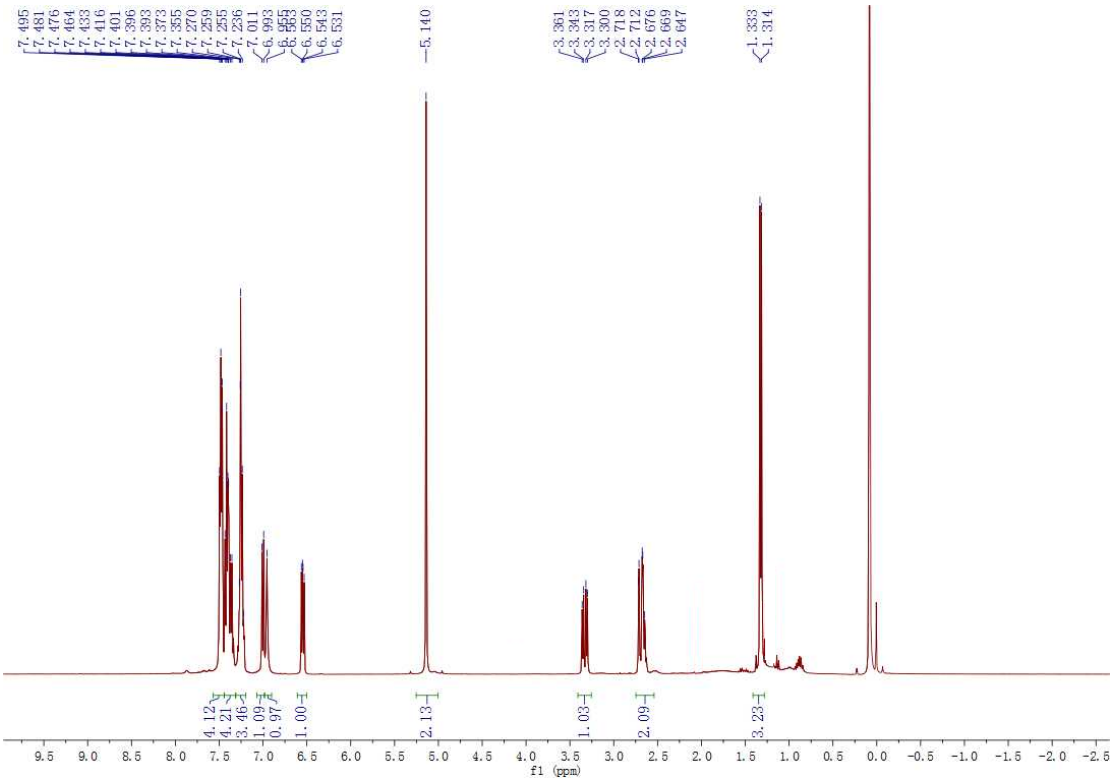
f1 (ppm)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3.343
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3.300
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2.712
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2.647
1.333
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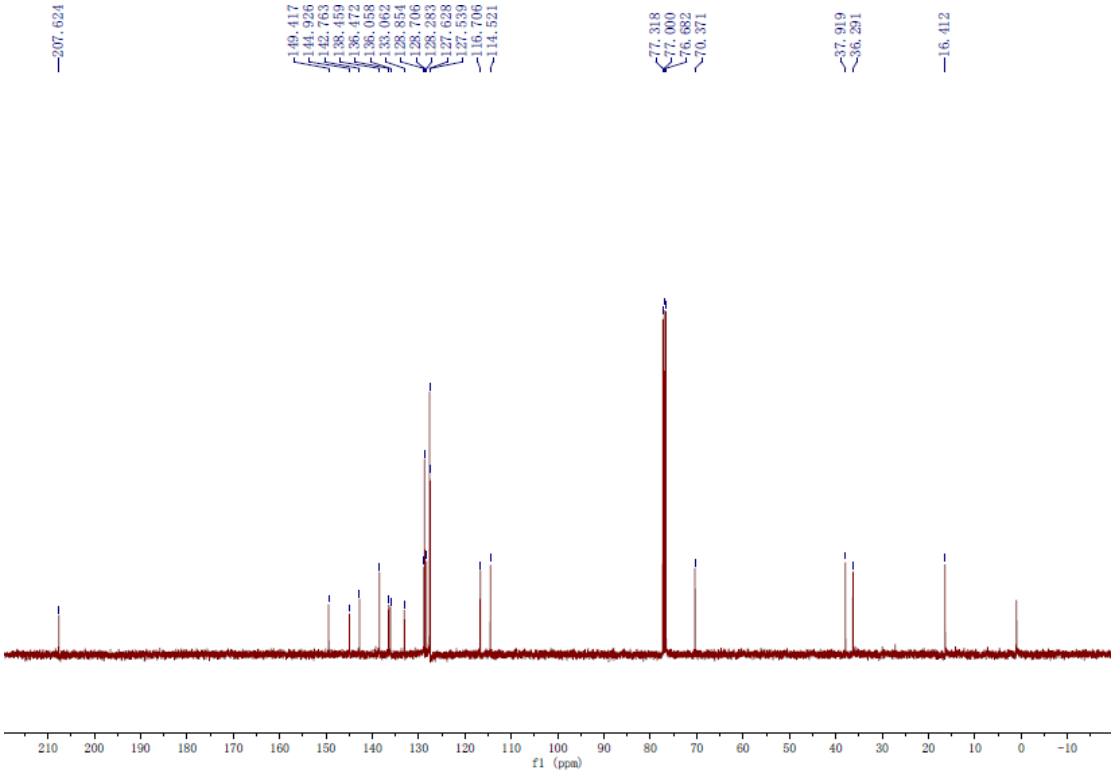
f1 (ppm)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76.682
70.371
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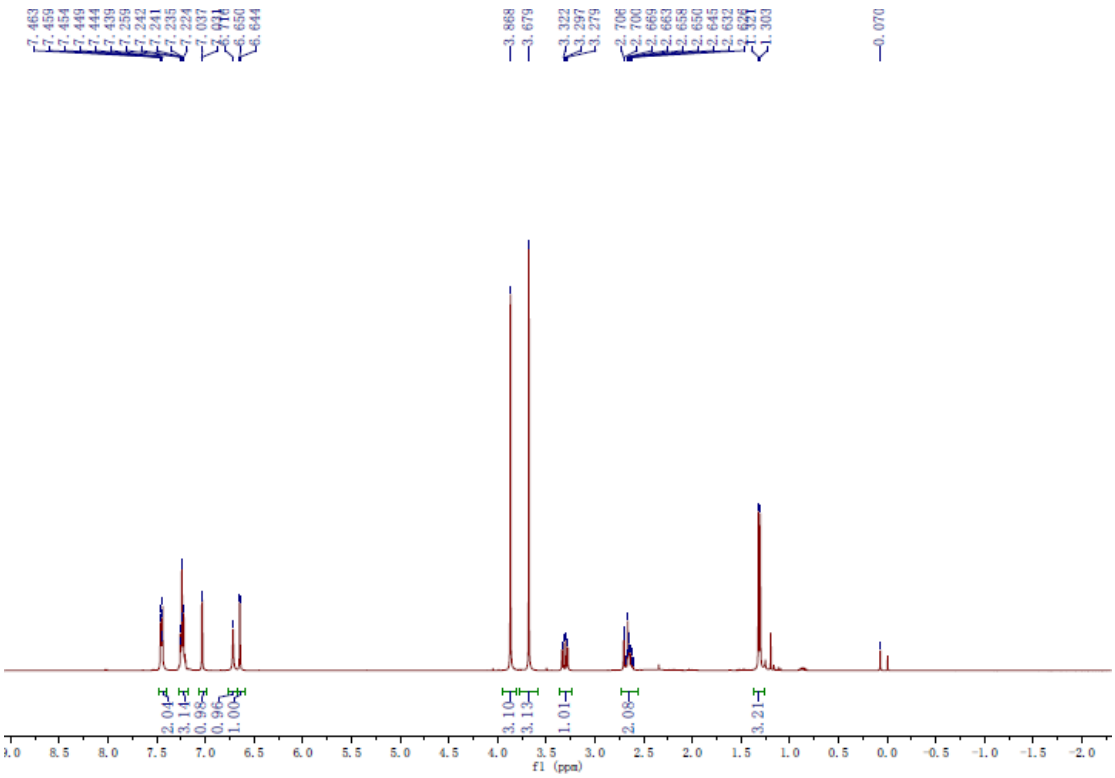
36.291
16.412
f1 (ppm)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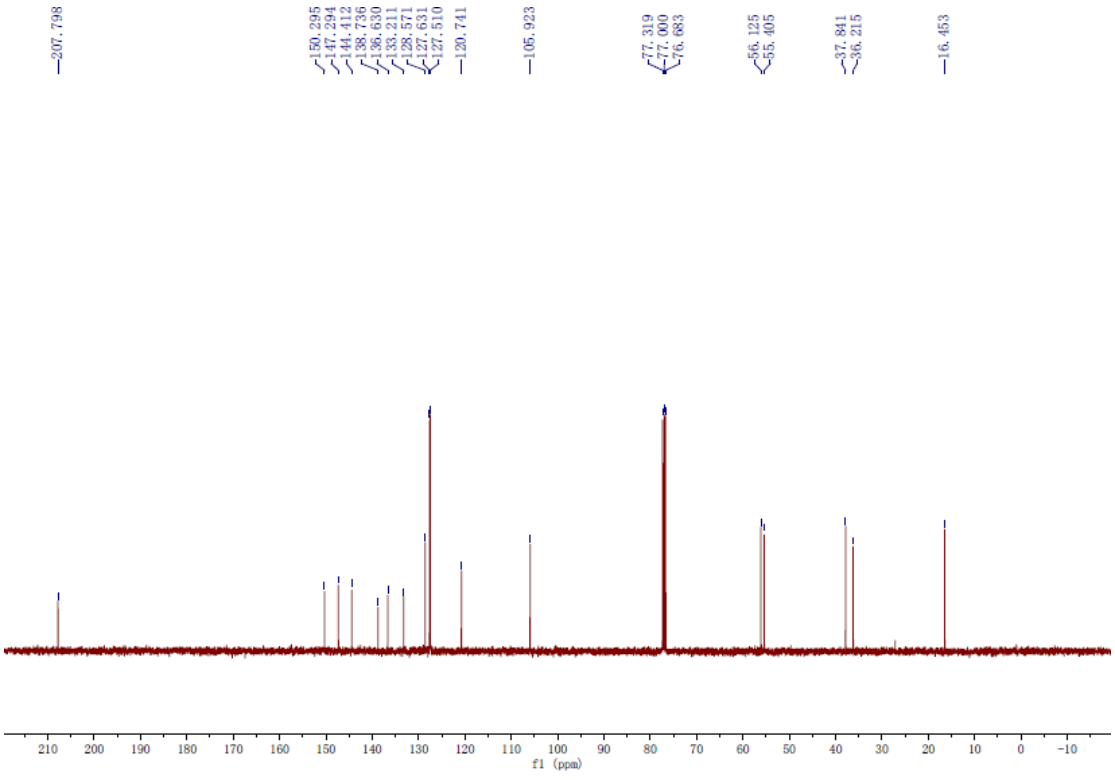
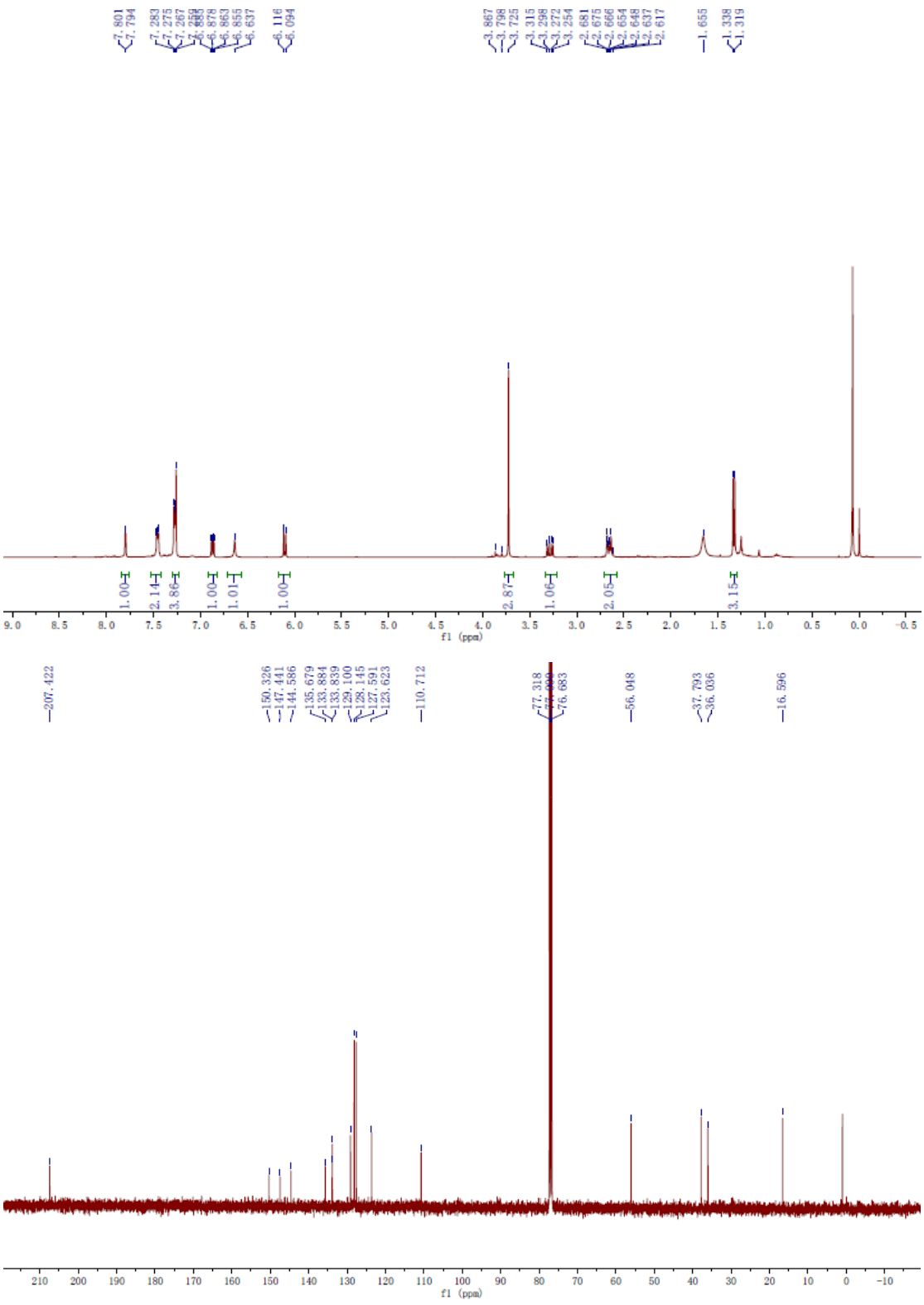
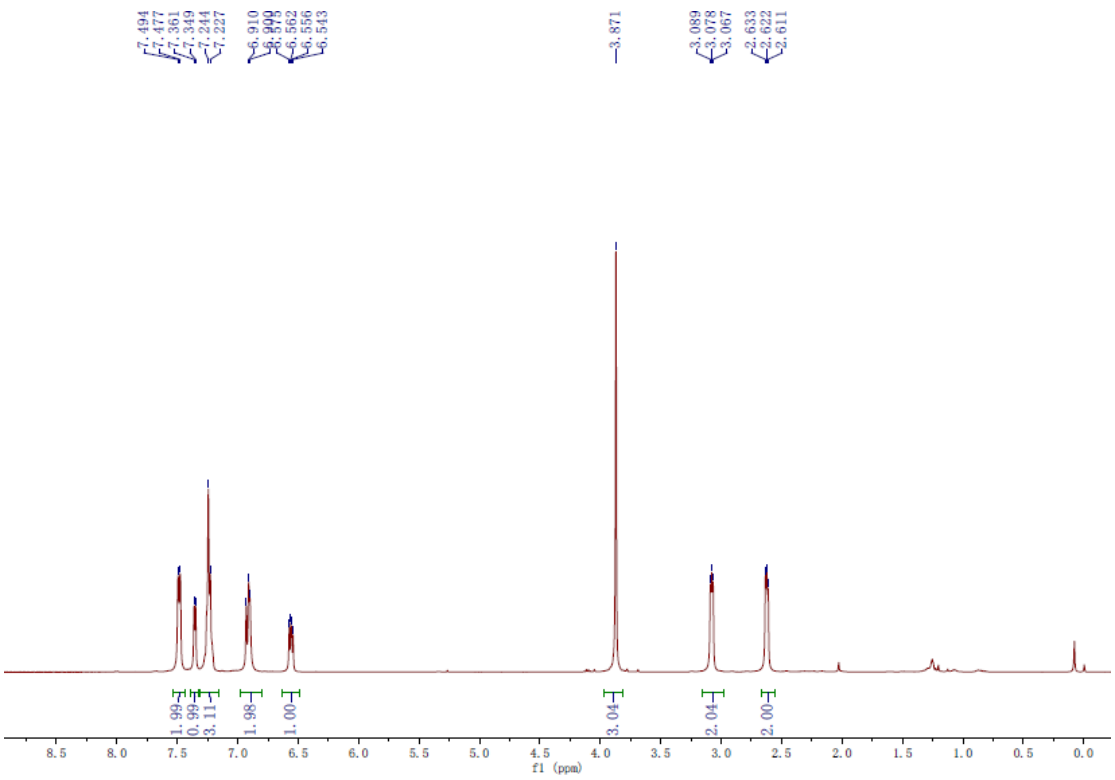
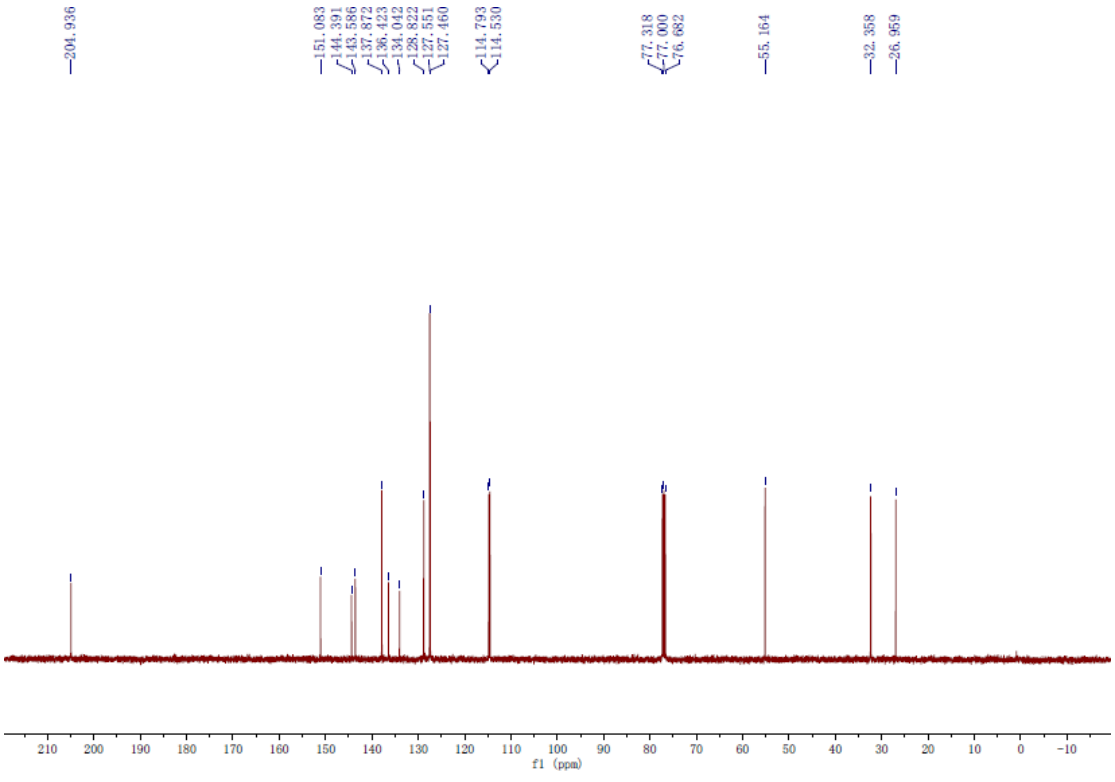
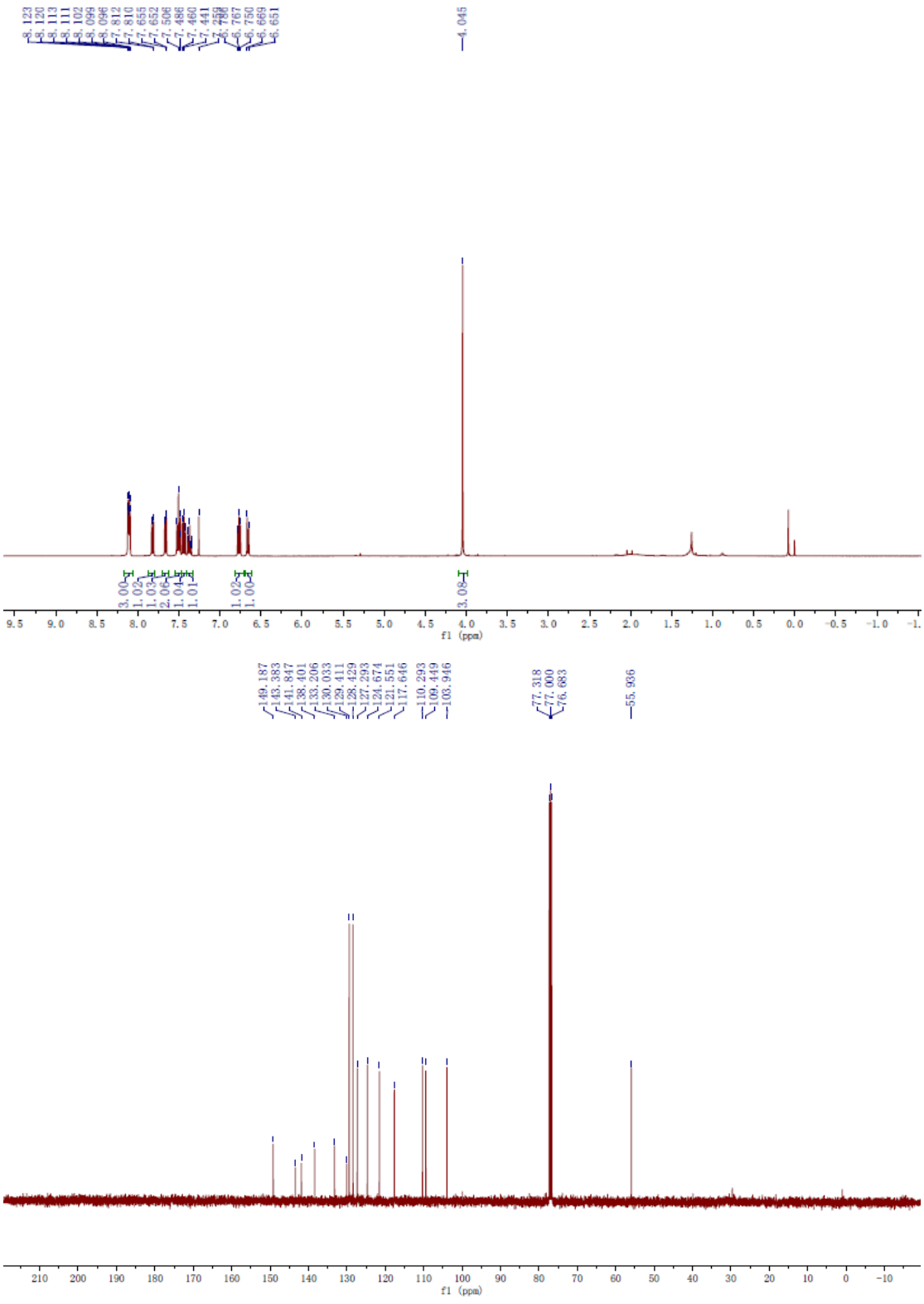
7.459
7.454
7.449
7.444
7.439
7.259
7.242
7.241
7.235
7.224
7.037
6.971
6.650
6.644
3.868
3.679
3.322
3.297
3.279
2.706
2.700
2.669
2.663
2.658
2.650
2.645
2.632
2.626
1.327
1.303
0.070
2.04
3.14
0.98
0.96
1.00
3.10
3.13
1.01
2.08
3.21
f1 (ppm)

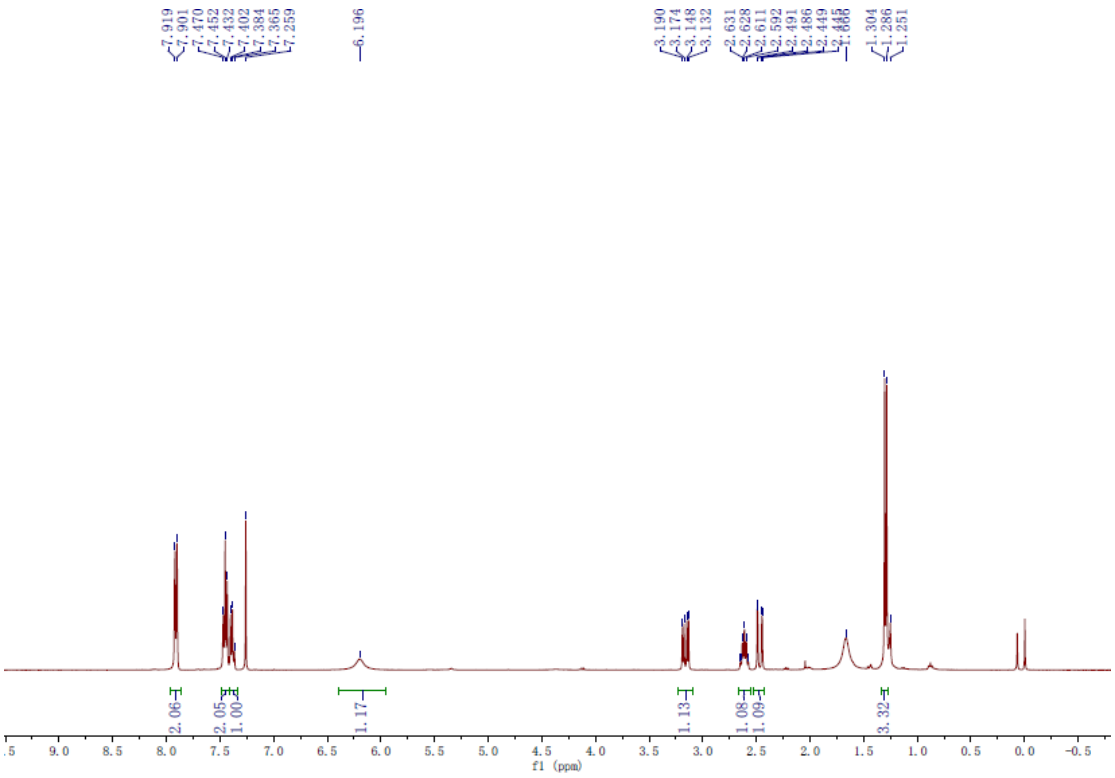

207.798
150.295
147.294
144.412
138.736
136.630
133.211
128.571
127.631
127.510
120.741
105.923
77.319
77.000
76.683
56.125
55.405
37.841
36.215
16.453
f1 (ppm)

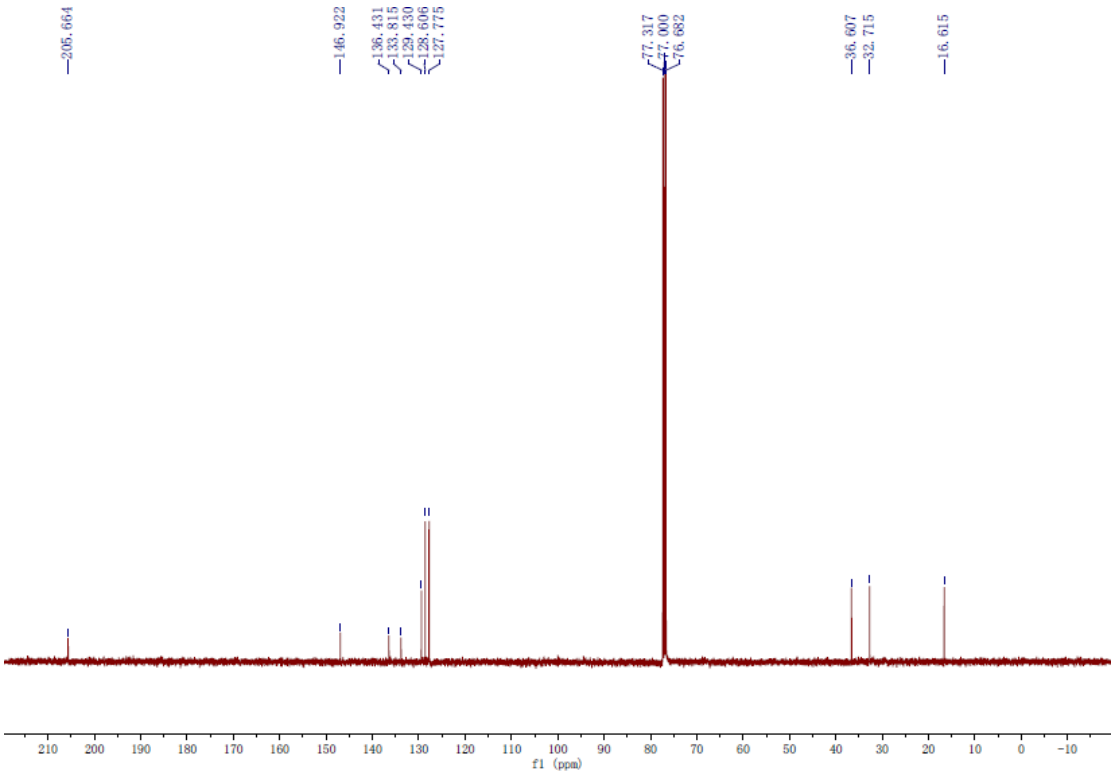

7.801
7.794
7.283
7.275
7.267
6.878
6.863
6.855
6.637
6.116
6.094
3.867
3.798
3.725
3.315
3.298
3.272
3.254
2.681
2.675
2.666
2.654
2.648
2.637
2.617
1.655
1.338
1.319
1.00
2.14
3.86
1.00
1.01
1.00
2.87
1.06
2.05
3.15
f1 (ppm)
207.422
150.326
147.441
144.586
135.679
133.884
133.839
129.100
128.145
127.591
123.623
110.712
77.318
76.683
56.048
37.793
36.036
16.596
f1 (ppm)

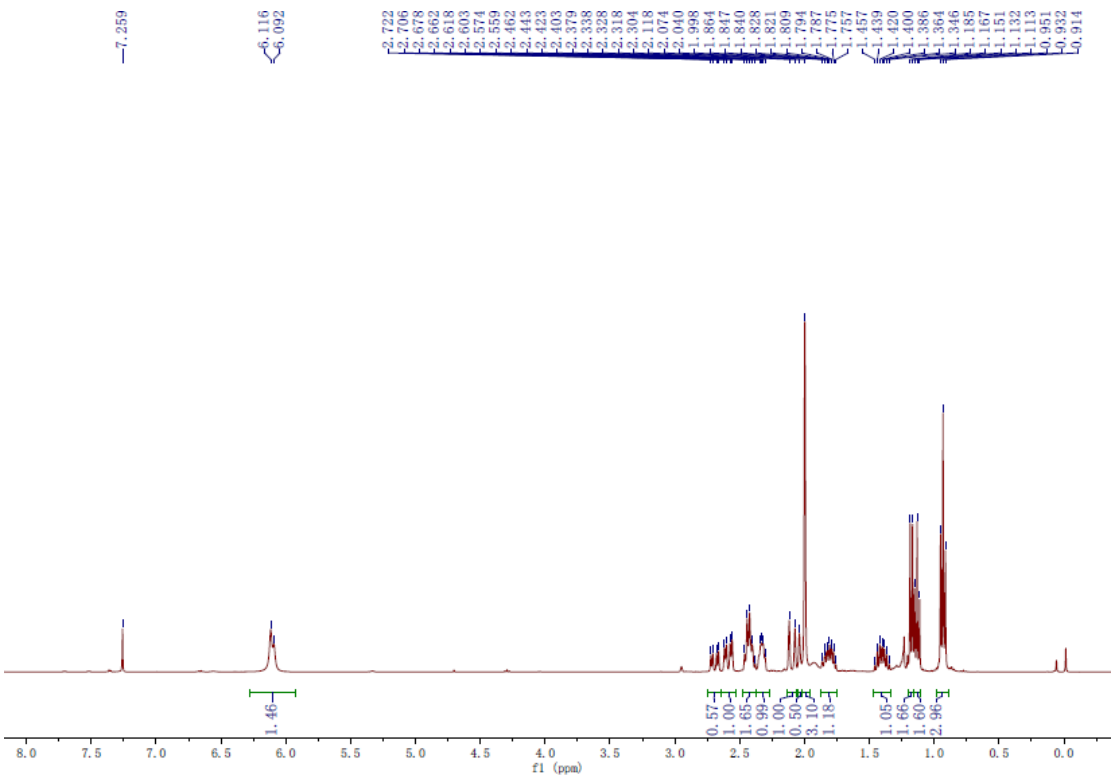

7.494
7.477
7.361
7.349
7.244
7.227
6.910
6.562
6.556
6.543
3.871
3.089
3.078
3.067
2.633
2.622
2.611
1.99
0.99
3.11
1.98
1.00
3.04
2.04
2.00
f1 (ppm)

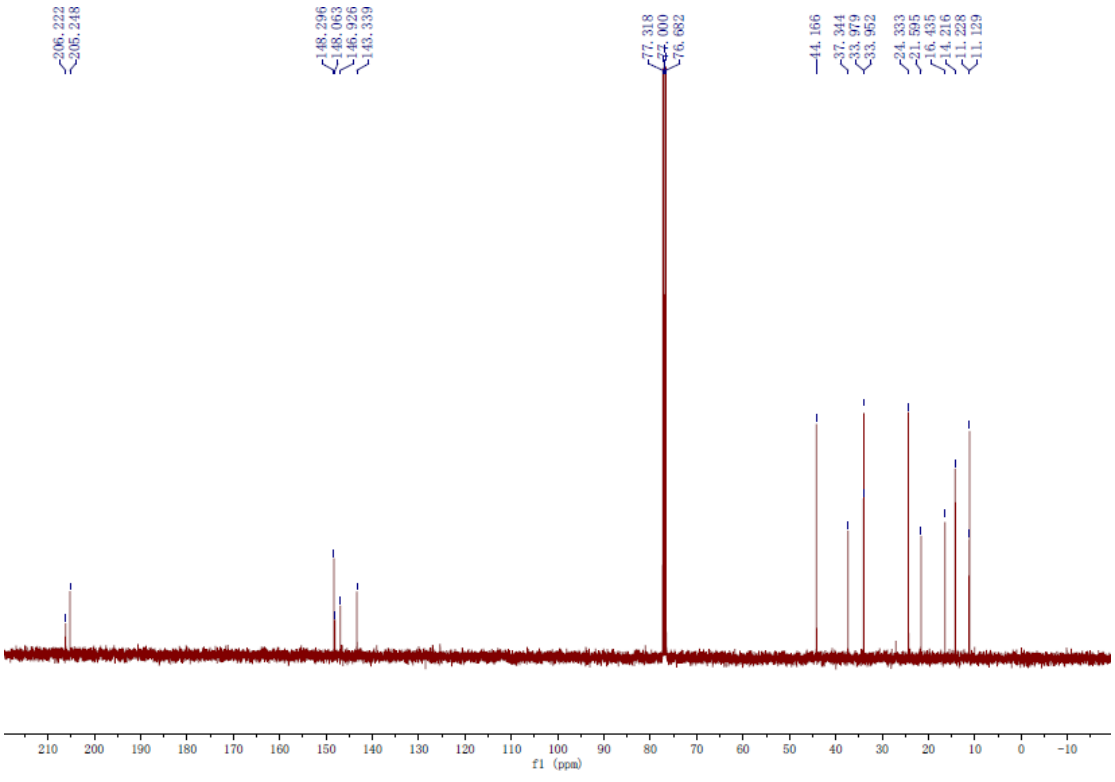

204.936
151.083
144.391
143.586
137.872
136.423
134.042
128.822
127.551
127.460
114.793
114.530
77.318
77.000
76.682
55.164
32.358
26.959
f1 (ppm)


8.123
8.120
8.113
8.111
8.102
8.099
8.096
7.812
7.810
7.655
7.652
7.506
7.488
7.460
7.441
6.767
6.750
6.669
6.651
4.045
3.00
1.02
1.03
2.06
1.04
1.01
1.02
1.00
3.08
f1 (ppm)
149.187
143.383
141.847
138.401
133.206
130.033
129.411
128.429
127.293
124.674
121.551
117.646
110.293
109.449
103.946
77.318
77.000
76.683
55.936
f1 (ppm)


7.919
7.901
7.470
7.452
7.432
7.402
7.384
7.365
7.259
6.196
3.190
3.174
3.148
3.132
2.631
2.628
2.611
2.592
2.491
2.486
2.449
1.304
1.286
1.251
2.06
2.05
1.00
1.17
1.13
1.08
1.09
3.32
f1 (ppm)


205.664
146.922
136.431
133.815
129.430
128.606
127.775
77.317
77.000
76.682
36.607
32.715
16.615
f1 (ppm)


7.259
6.116
6.092
2.722
2.706
2.678
2.662
2.618
2.603
2.574
2.559
2.462
2.443
2.423
2.403
2.379
2.338
2.328
2.318
2.304
2.118
2.074
2.040
1.998
1.864
1.847
1.840
1.828
1.821
1.809
1.794
1.787
1.775
1.757
1.457
1.439
1.420
1.400
1.386
1.364
1.346
1.185
1.167
1.151
1.132
1.113
0.951
0.932
0.914
1.46
0.57
1.00
1.65
0.99
1.00
0.50
3.10
1.18
1.05
1.66
1.60
2.96
f1 (ppm)


206.222
205.248
148.296
148.063
146.926
143.339
77.318
77.000
76.682
44.166
37.344
33.979
33.952
24.333
21.595
16.435
14.216
11.228
11.129
f1 (ppm)

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