Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

O-Methylation of carboxylic acids with streptozotocin

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Supporting information

Contents

1 General information：

All of the reagents were obtained from commercial suppliers and used without further purification. All compounds were structurally verified by ^{1}H NMR and ^{13}C NMR. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker Advance drx 400 spectrometer operating at 400MHz, and the chemical shifts are reported in ppm and the coupling constant in Hz.

2 General experimental details

The methyl esterification of carboxyl acid:

To a vial, carboxylic acid substrate (0.1 mmol), and sodium carbonate (0.4 mmol) were added followed by dioxane (0.95 mL) and water (0.05 mL). Stir the mixture for 2 mins, then add STZ (0.2 mmol). The reaction mixture was stirred at room temperature in open container. After 4 h, the reaction was stopped and the solvent was removed. The residue was dissolved in ethyl acetate, then washed by water, and dried following by removing ethyl acetate on vacuum distiller to afford the pure methyl ester product.

The methyl esterification of sulfonic acid:

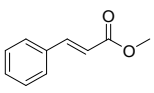
To a vial, sulfonic acid substrate (0.1 mmol), and sodium carbonate (0.4 mmol) were added followed by dioxane (0.95 mL) then water (0.05 mL). Stir the mixture for 2 mins, then add STZ (0.2 mmol). The reaction mixture was stirred at room temperature in open container. After 4 h, the reaction was stopped and the solvent was removed. The residue was dissolved in ethyl acetate, then washed by water, and dried following by removing ethyl acetate on rotoevaporator to afford the pure methyl ester product.

The methyl esterification of phosphonic acid:

To a vial, phosphoric acid substrate (0.1 mmol), and sodium carbonate (0.4 mmol) were added followed by dioxane (0.95 mL) then water (0.05 mL). Stir the mixture for 2 mins, then add STZ (0.2 mmol). The reaction mixture was stirred at room temperature in open container. After 4 h, the reaction was stopped and the solvent was removed. The residue was dissolved in ethyl acetate, then washed by water, and dried following by removing ethyl acetate on rotoevaporator to afford the pure methyl ester product.

3 Analytical Data:

Methyl cinnamate(2a)



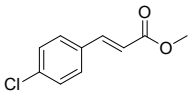
yield 83%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.55 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.46 - 7.37 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.37, 144.82, 134.35, 130.23, 128.83, 128.01, 117.77, 51.63.

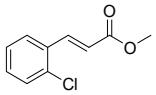
(E)-methyl 3-(4-chlorophenyl)acrylate(2b)

yield 85%



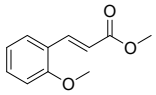
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.12, 143.36, 136.16, 132.83, 129.15 (d, *J* = 3.9 Hz), 118.34, 51.73.

(E)-methyl 3-(2-chlorophenyl)acrylate(2c)
yield 85%



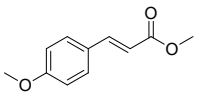
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 16.0 Hz, 1H), 7.66 - 7.59 (m, 1H), 7.49 - 7.40 (m, 1H), 7.33 (dt, *J* = 7.4, 5.8 Hz, 2H), 6.46 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.85, 140.58, 134.90, 132.64, 130.99, 130.12, 127.57, 127.02, 120.43, 51.79.

(E)-methyl 3-(2-methoxyphenyl)acrylate(2d)
yield 79%



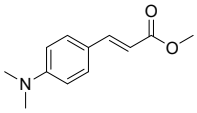
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 16.2 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.03 - 6.89 (m, 2H), 6.56 (d, *J* = 16.2 Hz, 1H), 3.91 (s, 3H), 3.83 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.88, 158.31, 140.22, 131.42, 128.87, 123.34, 120.65, 118.28, 111.09, 55.42, 51.52.

(E)-methyl 3-(4-methoxyphenyl)acrylate(2e)
yield 63%



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.71, 161.35, 144.47, 129.67, 127.08, 115.23, 114.28, 55.32, 51.52.

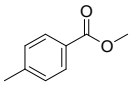
(E)-methyl 3-(4-(dimethylamino)phenyl)acrylate(2f)
yield 92%



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 3.06 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.45, 153.25, 131.19, 116.92, 110.64, 51.41, 39.98.

Methyl 4-methylbenzoate(2g)

yield 84%

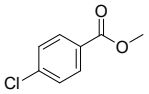


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 3.93 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.14, 143.49, 129.54, 129.01, 127.39, 51.88, 21.59.

Methyl 4-chlorobenzoate(2h)

yield 89%

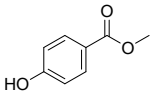


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 3.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.17, 139.32, 130.92, 128.60 (d, *J* = 10.9 Hz), 52.20.

Methyl 4-hydroxybenzoate(2i)

yield 74%

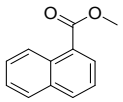


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.32 (s, 1H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.25, 160.14, 131.89, 122.34, 115.21, 51.98.

Methyl 1-naphthoate(2j)

yield 94%

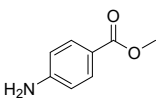


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.09 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.64 - 7.53 (m, 2H), 4.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.24, 135.48, 132.45, 131.02, 129.30, 128.14 (d, *J* = 8.3 Hz), 127.71, 127.35, 126.58, 125.17, 52.17.

Methyl 4-aminobenzoate(2k)

yield 12%

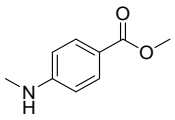


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 4.06 (s, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.09, 150.71, 131.55, 119.76, 113.75, 51.55.

Methyl 4-(methylamino)benzoate(byproduct of 2k)

yield 8%

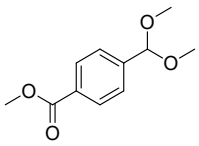


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 4.19 (s, 1H), 3.88 (s, 3H), 2.92 (d, *J* = 2.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.30, 152.62, 131.46, 118.39, 111.21, 51.48, 30.21.

4-(dimethoxymethyl)benzoic acid(2l)

yield 95%

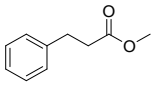


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 5.46 (s, 1H), 3.93 (s, 3H), 3.34 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.84, 142.85, 130.14, 129.47, 126.74, 102.29, 77.30, 76.98, 76.66, 52.61, 52.08.

Methyl 3-phenylpropanoate(2m)

yield 67%

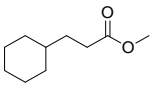


^{1}H NMR (400 MHz, DMSO) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.20 (dd, *J* = 16.1, 7.4 Hz, 3H), 3.59 (s, 3H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 173.06, 140.91, 128.67 (d, *J* = 12.0 Hz), 126.48, 51.67, 35.27, 30.64.

Methyl 3-cyclohexylpropanoate(2n)

yield 78%

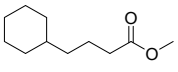


^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 2.38 - 2.28 (m, 2H), 1.69 (t, *J* = 16.1 Hz, 5H), 1.54 (dd, *J* = 15.4, 7.2 Hz, 2H), 1.30 - 1.16 (m, 4H), 0.90 (dd, *J* = 21.7, 11.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.61, 51.41, 37.15, 32.89, 32.27, 31.63, 26.46, 26.15.

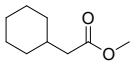
Methyl 4-cyclohexylbutanoate(2o)

yield 82%



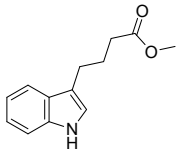
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.76 - 1.59 (m, 7H), 1.20 (dq, *J* = 24.5, 12.4 Hz, 6H), 0.88 (dd, *J* = 20.8, 10.6 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.33, 51.37, 37.31, 36.84, 34.34, 33.17, 26.59, 26.27, 22.29.

Methyl 2-cyclohexylacetate(2p)
yield 73%



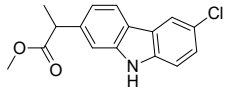
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 2.21 (d, *J* = 7.0 Hz, 2H), 1.72 (dt, *J* = 26.4, 15.8 Hz, 5H), 1.25 (ddd, *J* = 40.1, 18.6, 8.0 Hz, 4H), 1.04 - 0.93 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.58, 51.28, 41.92, 34.82, 32.97, 26.01 (d, *J* = 11.7 Hz).

Methyl 4-(1H-indol-3-yl)butanoate(2q)
yield 74%



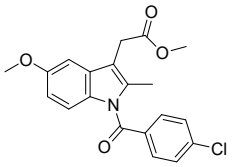
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.03 - 6.99 (m, 1H), 3.70 (s, 3H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 2.14 - 2.05 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.20, 136.34, 127.40, 121.90, 121.42, 119.16, 118.84, 115.55, 111.04, 51.43, 33.65, 25.30, 24.46.

Methyl 2-(6-chloro-9H-carbazol-2-yl)propanoate(2r)
yield 88%



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.95 (d, *J* = 1.6 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.34 - 7.28 (m, 2H), 7.24 (s, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 3.87 (q, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 1.57 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.41, 140.33, 139.11, 138.04, 125.75, 124.84, 124.21, 121.60, 120.56, 119.88, 119.54, 111.54, 109.51, 52.14, 45.78, 18.90.

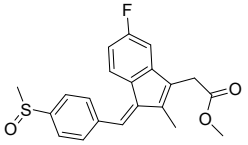
Methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate(2s)
yield 92%



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.86 (s, 3H), 3.73 (s, 3H), 3.69 (s, 2H), 2.41 (s, 3H).

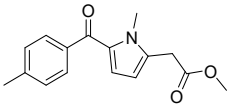
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.30, 168.24, 156.01, 139.20, 135.91, 133.86, 131.12, 130.68 (d, *J* = 16.2 Hz), 129.06, 114.90, 112.46, 111.55, 101.29, 55.66, 52.10, 30.07, 13.27.

(Z)-methyl 2-(5-fluoro-2-methyl-1-(4-(methylsulfinyl)benzylidene)-1H-inden-3-yl)acetate(2t)
yield 79%



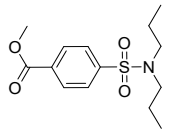
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.16 (dd, *J* = 7.6, 4.3 Hz, 2H), 6.89 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.57 (td, *J* = 9.1, 2.3 Hz, 1H), 3.72 (s, 3H), 3.58 (s, 2H), 2.82 (s, 3H), 2.22 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.63, 164.53, 162.08, 146.65 (d, *J* = 8.8 Hz), 145.44, 141.59, 139.62, 138.14, 131.71 (d, *J* = 2.5 Hz), 130.18, 129.44 (d, *J* = 2.9 Hz), 128.15 (d, *J* = 1.7 Hz), 123.86 - 123.35 (m), 110.83, 110.60, 106.16, 105.93, 52.18, 43.83, 31.51, 10.46.

Methyl 2-(1-methyl-5-(4-methylbenzoyl)-1H-pyrrol-2-yl)acetate(2u)
yield 97%



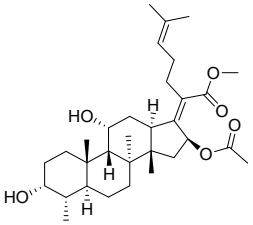
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.67 (d, *J* = 4.0 Hz, 1H), 6.10 (d, *J* = 4.0 Hz, 1H), 3.94 (s, 3H), 3.74 (s, 3H), 3.72 (s, 2H), 2.41 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.84, 169.76, 141.84, 137.27, 134.32, 131.40, 129.38, 128.63, 122.18, 109.38, 52.39, 33.12, 32.66, 21.47.

Methyl 4-(N,N-dipropylsulfamoyl)benzoate(2v)
yield 89%



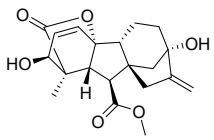
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 2H), 7.89 (d, *J* = 8.3 Hz, 2H), 3.97 (s, 3H), 3.16 - 3.05 (m, 4H), 1.61 - 1.50 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.68, 144.23, 133.36, 130.15, 126.93, 52.52, 49.83, 21.84, 11.07.

(Z)-methyl 2-((3R,4S,5S,8S,9S,10S,11R,13R,14S,16S)-16-acetoxy-3,11-dihydroxy-4,8,10,14-tetramethyldodecahydro-1H-cyclopenta[a]phenanthren-17(2H,10H,14H)-ylidene)-6-methylhept-5-enoate(2w)
yield 93%



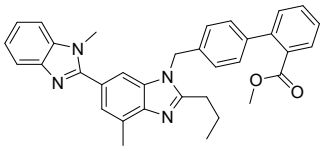
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.14 (dd, *J* = 7.6, 4.3 Hz, 2H), 6.88 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.56 (td, *J* = 9.1, 2.3 Hz, 1H), 3.71 (s, 3H), 3.57 (s, 2H), 2.81 (s, 3H), 2.21 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.63, 164.53, 162.08, 146.65 (d, *J* = 8.8 Hz), 145.44, 141.59, 139.62, 138.14, 131.71 (d, *J* = 2.5 Hz), 130.18, 129.44 (d, *J* = 2.9 Hz), 128.15 (d, *J* = 1.7 Hz), 123.86 - 123.35 (m), 110.83, 110.60, 106.16, 105.93, 52.18, 43.83, 31.51, 10.46.

(1S,2S,4aR,4bR,7S,9aS,10S,10aR)-methyl 2,7-dihydroxy-1-methyl-8-methylene-13-oxo-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[a]azulene-10-carboxylate(2x)
yield 84%



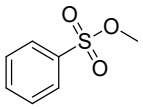
^{1}H NMR (400 MHz, DMSO) δ 6.34 (d, *J* = 9.3 Hz, 1H), 5.81 (dd, *J* = 9.3, 3.6 Hz, 1H), 5.60 (d, *J* = 6.7 Hz, 1H), 5.14 (s, 1H), 4.87 (d, *J* = 5.6 Hz, 2H), 3.89 (dd, *J* = 6.5, 3.6 Hz, 1H), 3.67 (d, *J* = 8.3 Hz, 3H), 3.14 (d, *J* = 10.7 Hz, 1H), 2.61 (d, *J* = 10.8 Hz, 1H), 2.16 (d, *J* = 15.6 Hz, 1H), 2.03 - 1.97 (m, 1H), 1.91 (dd, *J* = 16.9, 9.8 Hz, 2H), 1.76 (dd, *J* = 10.7, 1.7 Hz, 1H), 1.69 - 1.58 (m, 4H), 1.05 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 178.89, 172.54, 157.86, 133.73, 131.79, 106.85, 90.88, 76.98, 68.85, 53.42, 52.56, 52.31, 50.83 (d, *J* = 18.1 Hz), 50.21, 44.67, 43.15, 16.94, 14.85.

Methyl 4'-((1,7'-dimethyl-2'-propyl-1H,3'H-[2,5'-bibenzo[d]imidazol]-3'-yl)methyl)-[1,1'-biphenyl]-2-carboxylate(2y)
yield 89%



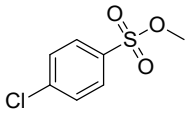
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.47 (dd, *J* = 18.5, 10.1 Hz, 3H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.33 - 7.22 (m, 6H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.43 (s, 2H), 3.76 (s, 3H), 3.56 (s, 3H), 2.99 - 2.88 (m, 2H), 2.77 (s, 3H), 1.93 - 1.79 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.60, 156.44, 154.57, 143.09, 142.74, 141.67, 141.08, 136.58, 134.99, 134.72, 131.32, 130.63, 130.52, 129.86, 129.39, 128.95, 127.33, 125.90, 123.79, 123.75, 122.46, 122.28, 119.41, 109.48, 108.94, 51.81, 47.05, 31.75, 29.77, 21.79, 16.85, 14.04.

Methyl benzenesulfonate(4a)
yield 30%



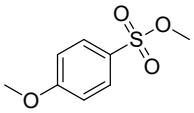
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 - 7.91 (m, 2H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 3.80 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 133.82, 129.25, 128.03, 56.27, 29.70.

Methyl 4-chlorobenzenesulfonate(4b)
yield 24%



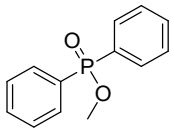
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.57, 133.75, 129.49 (d, *J* = 16.8 Hz), 56.36, 29.63.

Methyl 4-methoxybenzenesulfonate(4c)
yield 38%



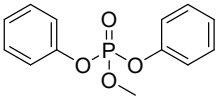
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.92 (s, 3H), 3.76 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.78, 130.21, 126.59, 114.39, 55.92, 55.65.

Methyl diphenylphosphinate(6a)
yield 62%



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.77 (m, 4H), 7.60 - 7.39 (m, 6H), 3.79 (d, *J* = 11.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.16 (d, *J* = 2.8 Hz), 131.63 (d, *J* = 10.1 Hz), 130.34, 128.52 (d, *J* = 13.1 Hz), 51.49 (d, *J* = 6.0 Hz).

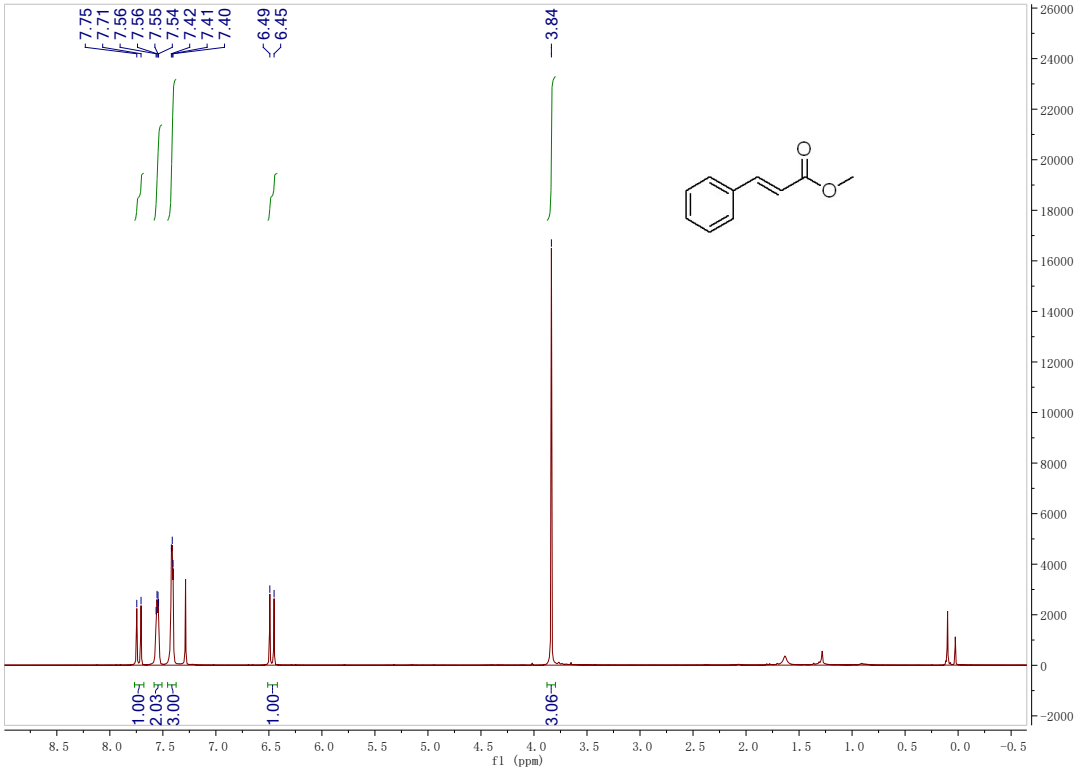
Methyl diphenyl phosphate(6b)
yield 42%

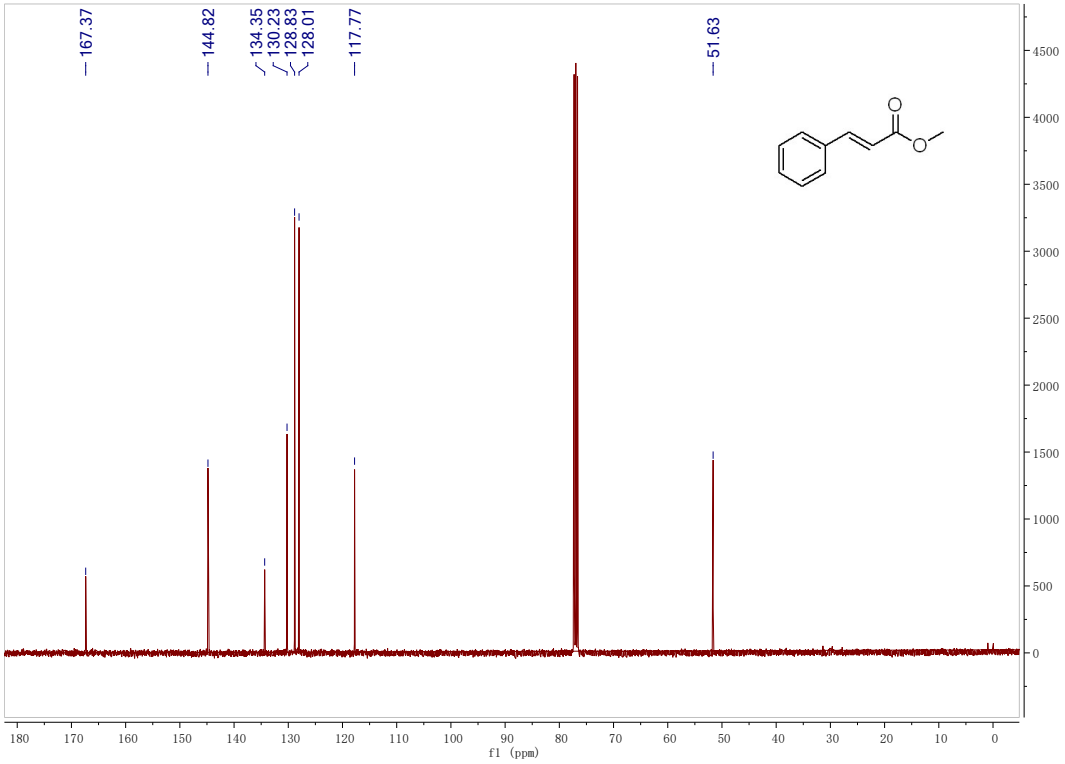


^{1}H NMR (400 MHz, DMSO) δ 7.45 (t, *J* = 7.6 Hz, 4H), 7.27 (t, *J* = 9.8 Hz, 6H), 3.94 (d, *J* = 11.6 Hz, 3H).
^{13}C NMR (101 MHz, DMSO) δ 150.43 (d, *J* = 7.0 Hz), 130.53, 126.01, 120.29 (d, *J* = 4.8 Hz), 56.07 (d, *J* = 6.6 Hz).

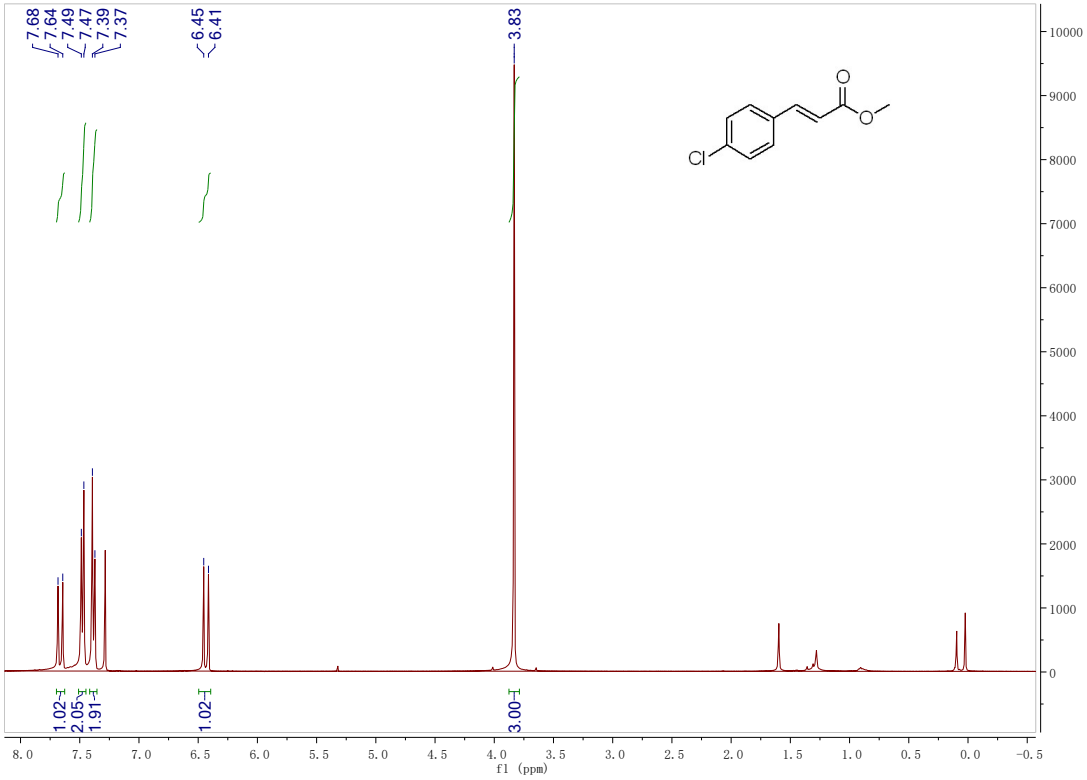
4 ^{1}H, ^{13}C NMR spectra

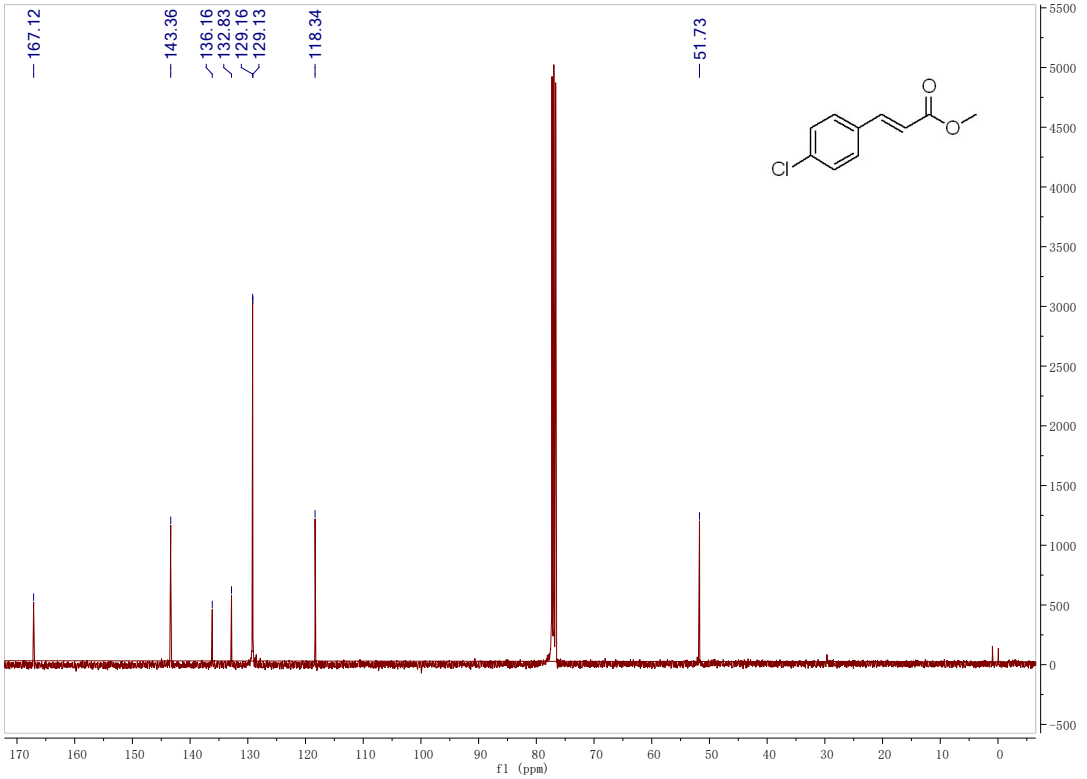
2a



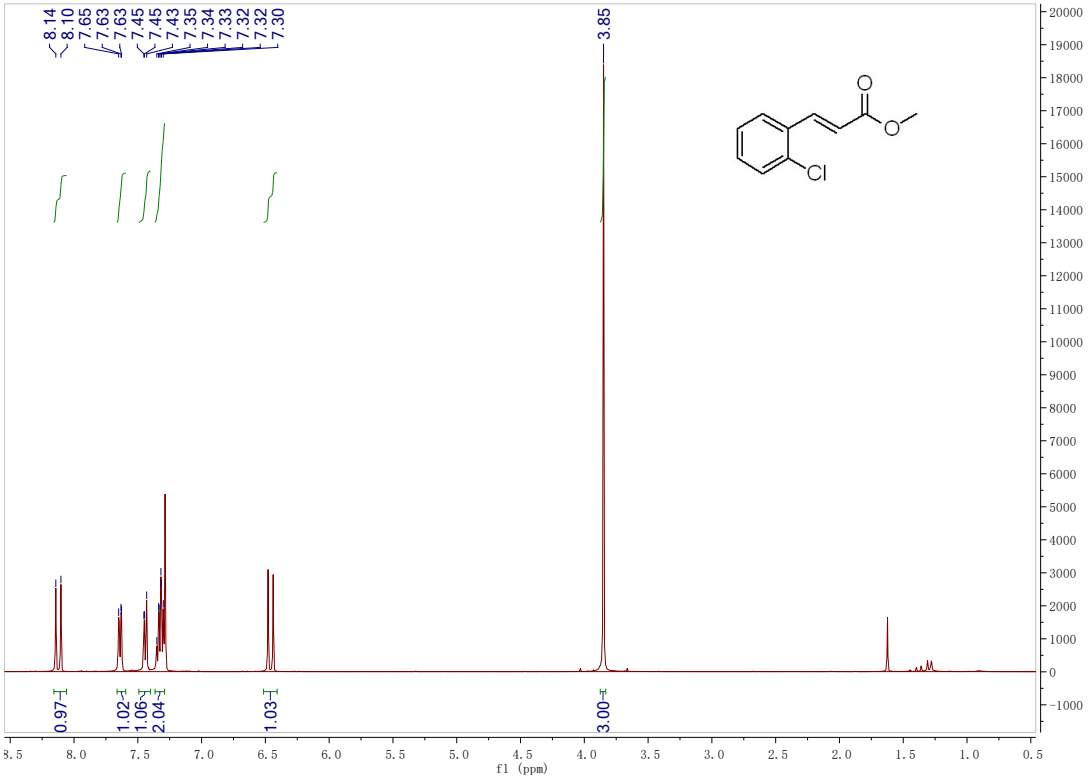


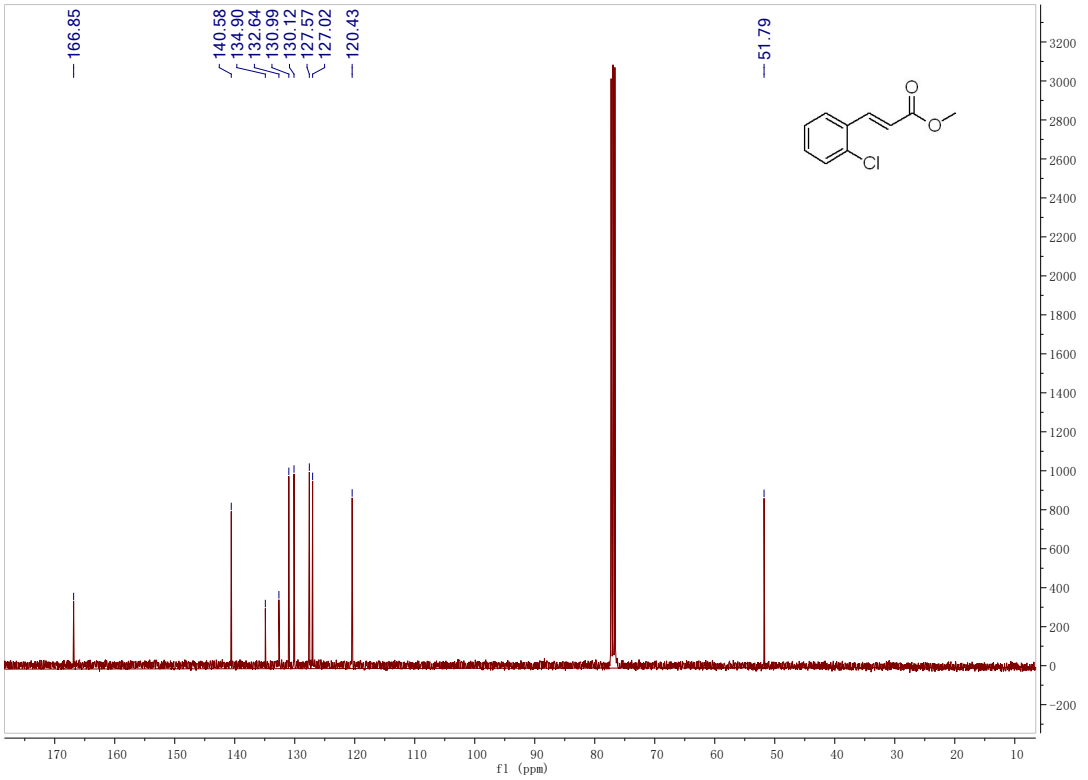
2b


7.68
7.64
7.49
7.47
7.39
7.37
6.45
6.41
3.83
1.02
2.05
1.91
1.02
3.00
Cl
O
O
f1 (ppm)

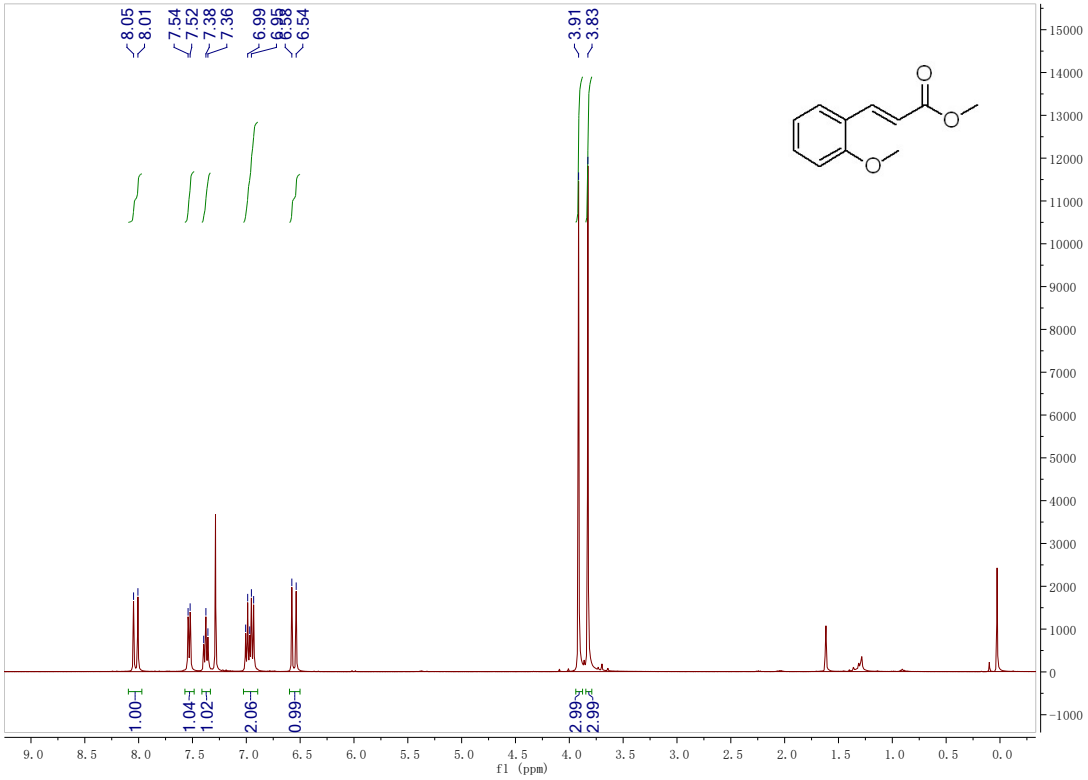

167.12
143.36
136.16
132.83
129.16
129.13
118.34
51.73
Cl
O
O
f1 (ppm)

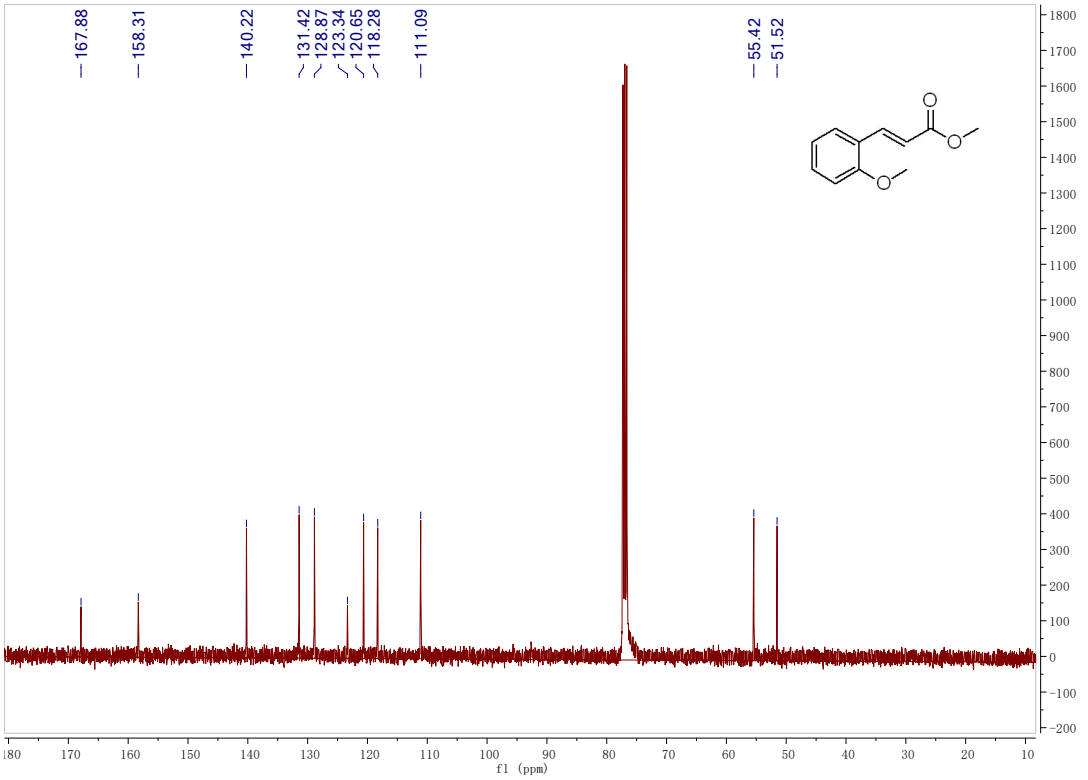
2c


8.14
8.10
7.65
7.63
7.63
7.45
7.45
7.43
7.35
7.34
7.33
7.32
7.32
7.30
3.85
0.97
1.02
1.06
2.04
1.03
3.00
f1 (ppm)

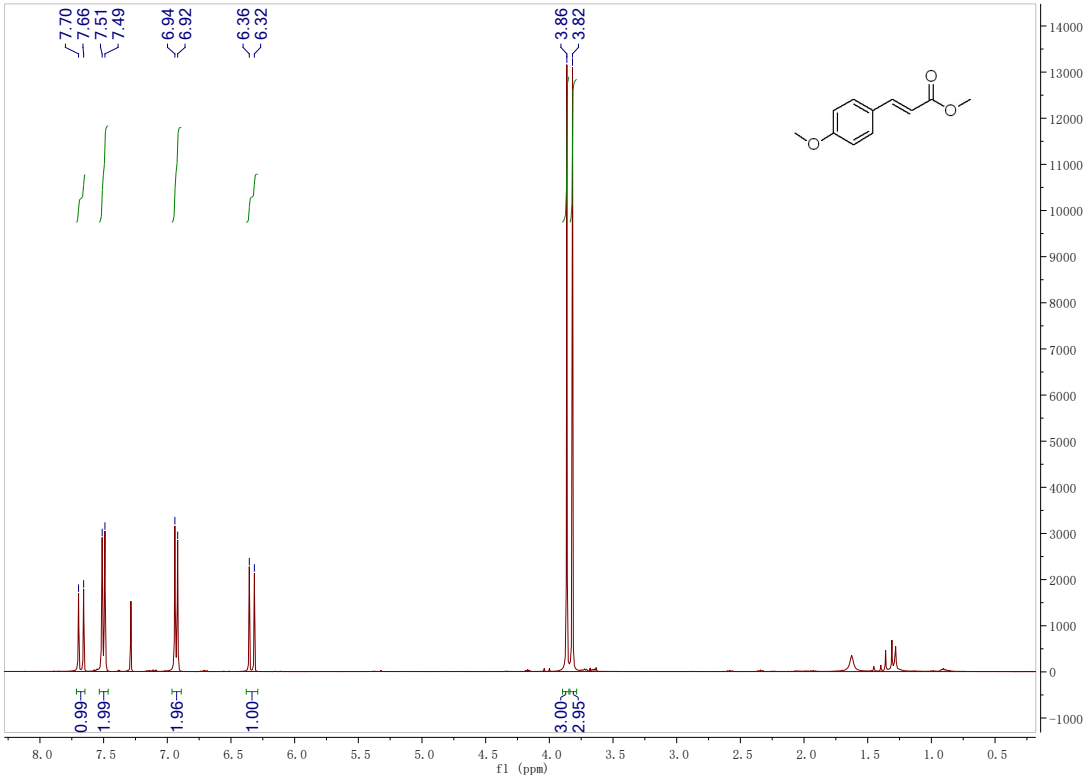

166.85
140.58
134.90
132.64
130.99
130.12
127.57
127.02
120.43
51.79
f1 (ppm)

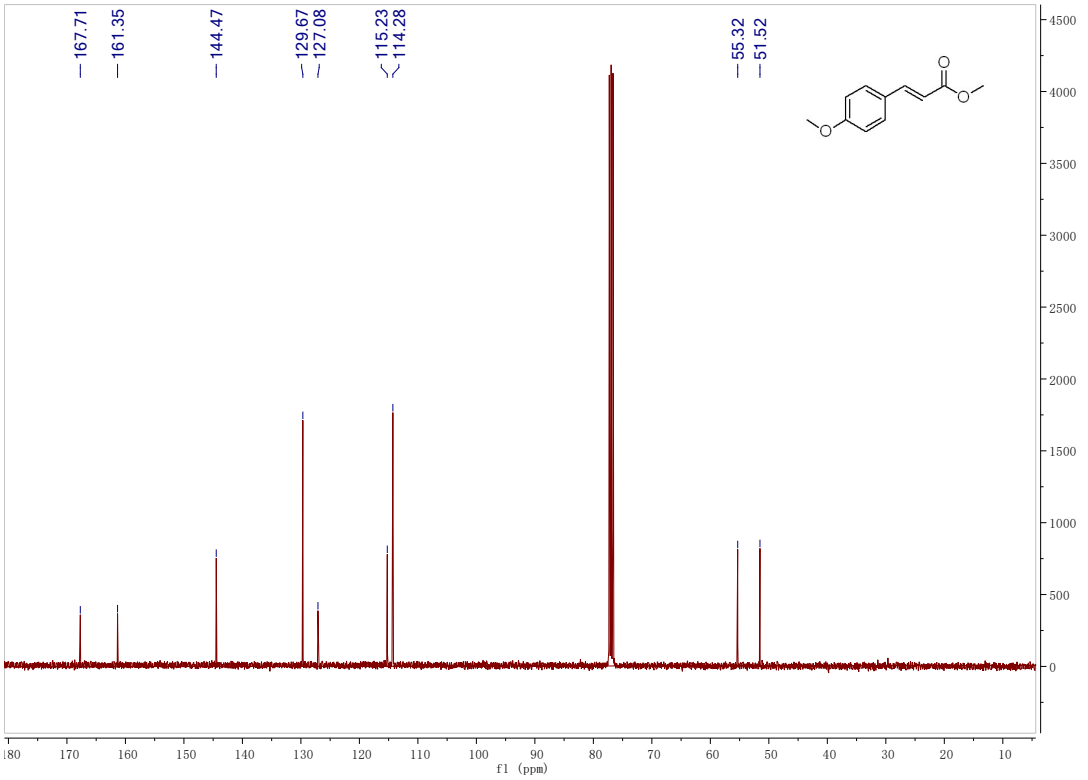
2d


8.05
8.01
7.54
7.52
7.38
7.36
6.99
6.95
6.58
6.54
3.91
3.83
1.00
1.04
1.02
2.06
0.99
2.99
2.99
f1 (ppm)

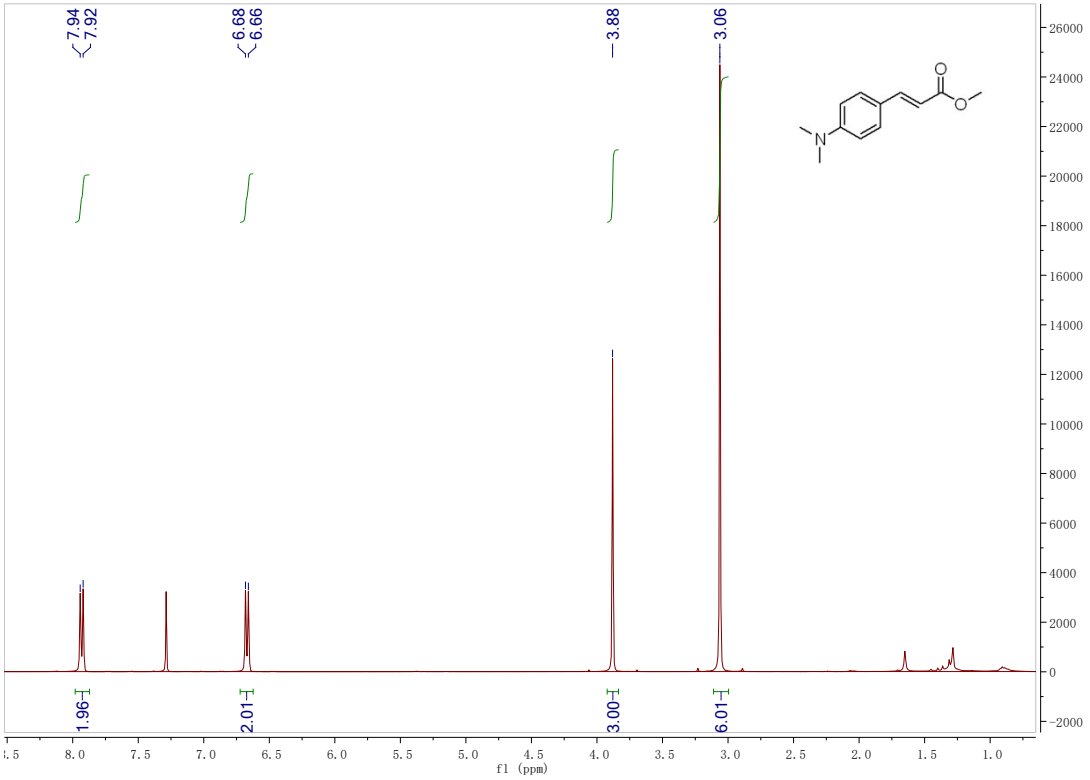

167.88
158.31
140.22
131.42
128.87
123.34
120.65
118.28
111.09
55.42
51.52
f1 (ppm)

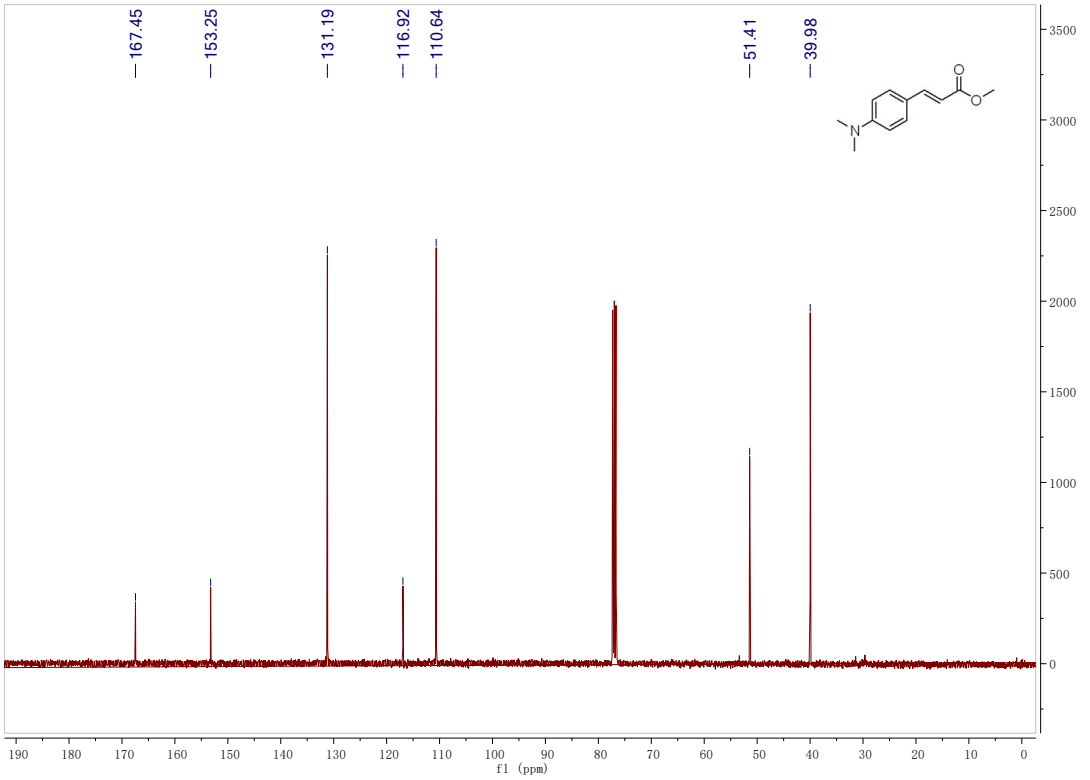
2e


7.70
7.66
7.51
7.49
6.94
6.92
6.36
6.32
3.86
3.82
0.99
1.99
1.96
1.00
3.00
2.95
f1 (ppm)

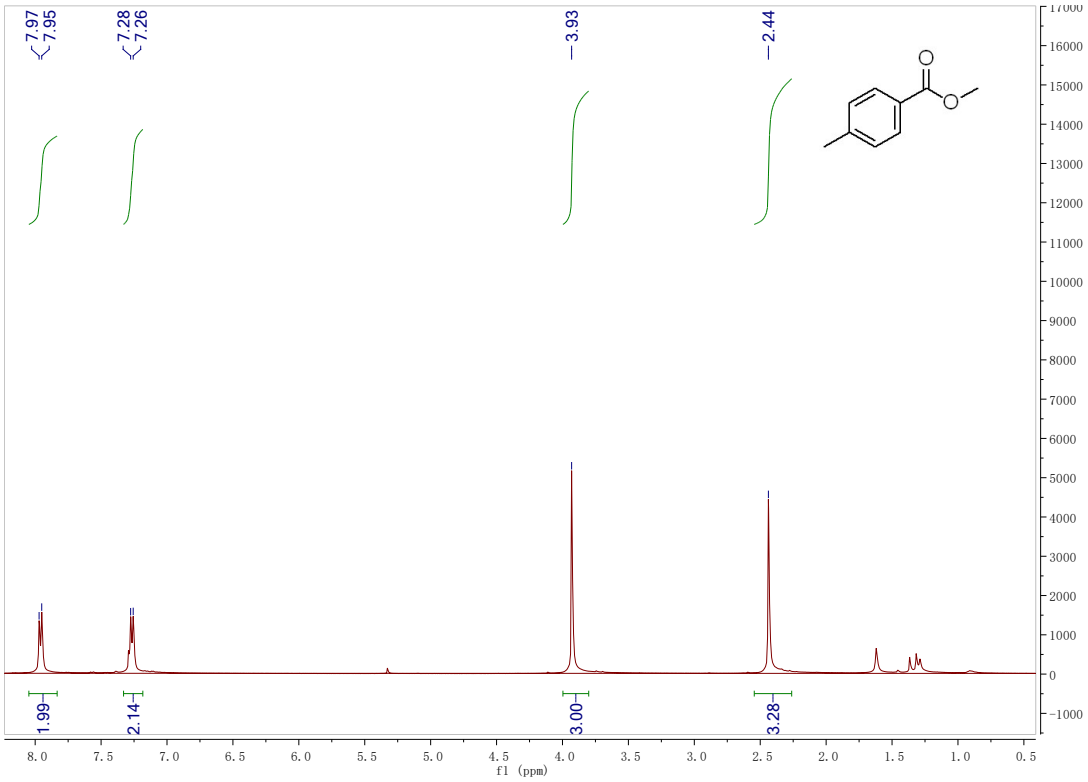

167.71
161.35
144.47
129.67
127.08
115.23
114.28
55.32
51.52
f1 (ppm)

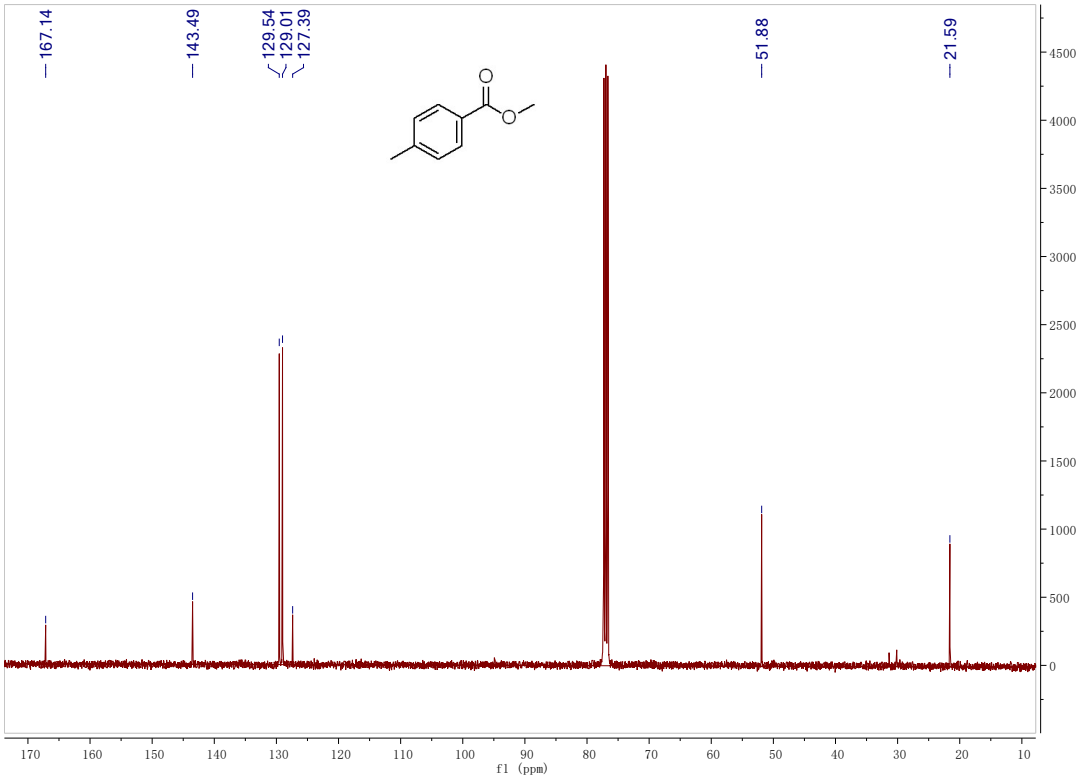
2f


7.94
7.92
6.68
6.66
3.88
3.06
1.96
2.01
3.00
6.01
f1 (ppm)

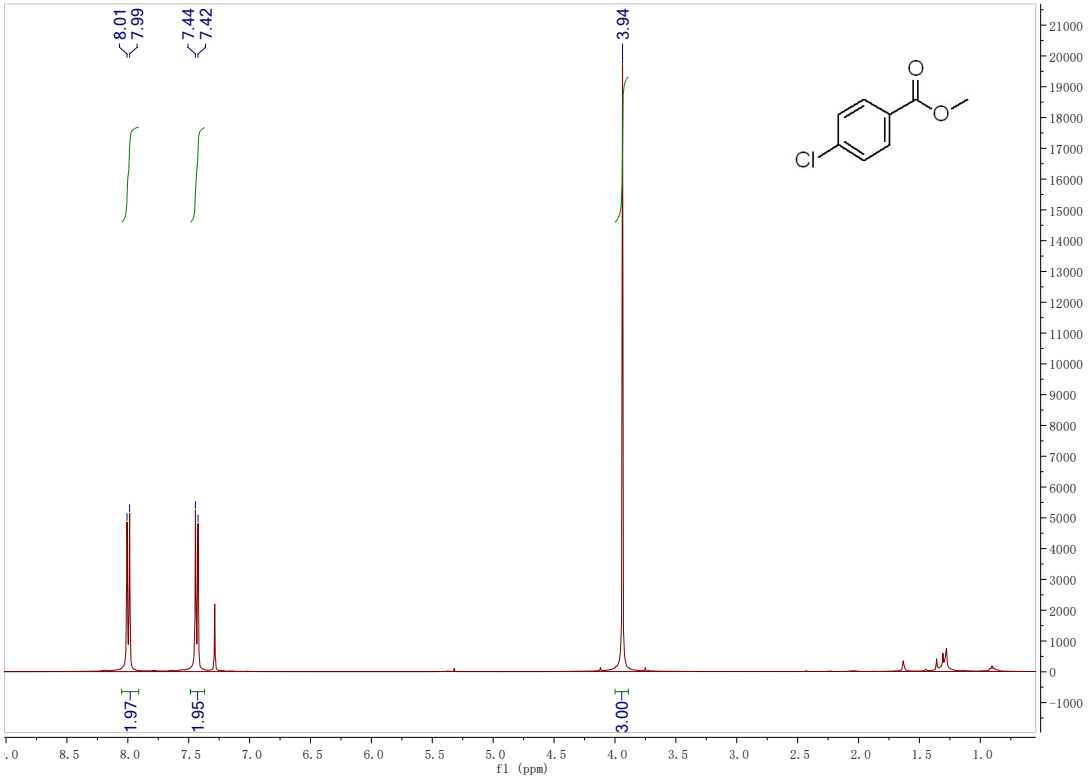

167.45
153.25
131.19
116.92
110.64
51.41
39.98
f1 (ppm)

2g


7.97
7.95
7.28
7.26
3.93
2.44
1.99
2.14
3.00
3.28
f1 (ppm)


167.14
143.49
129.54
129.01
127.39
51.88
21.59
f1 (ppm)

2h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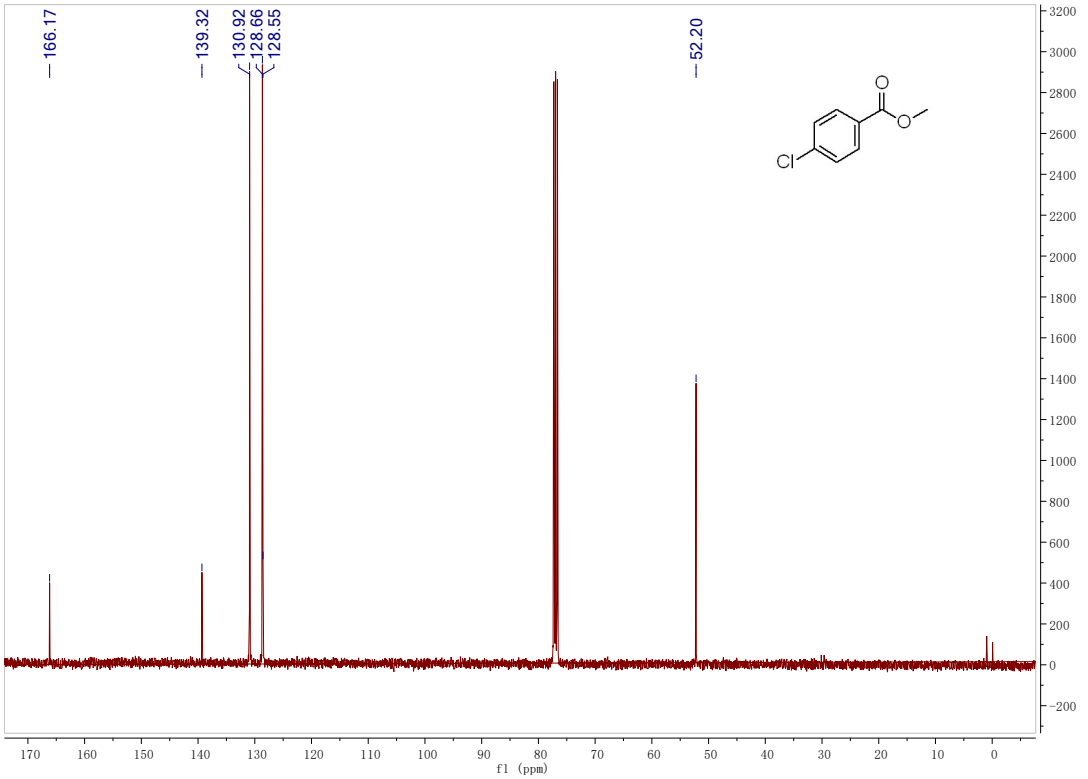
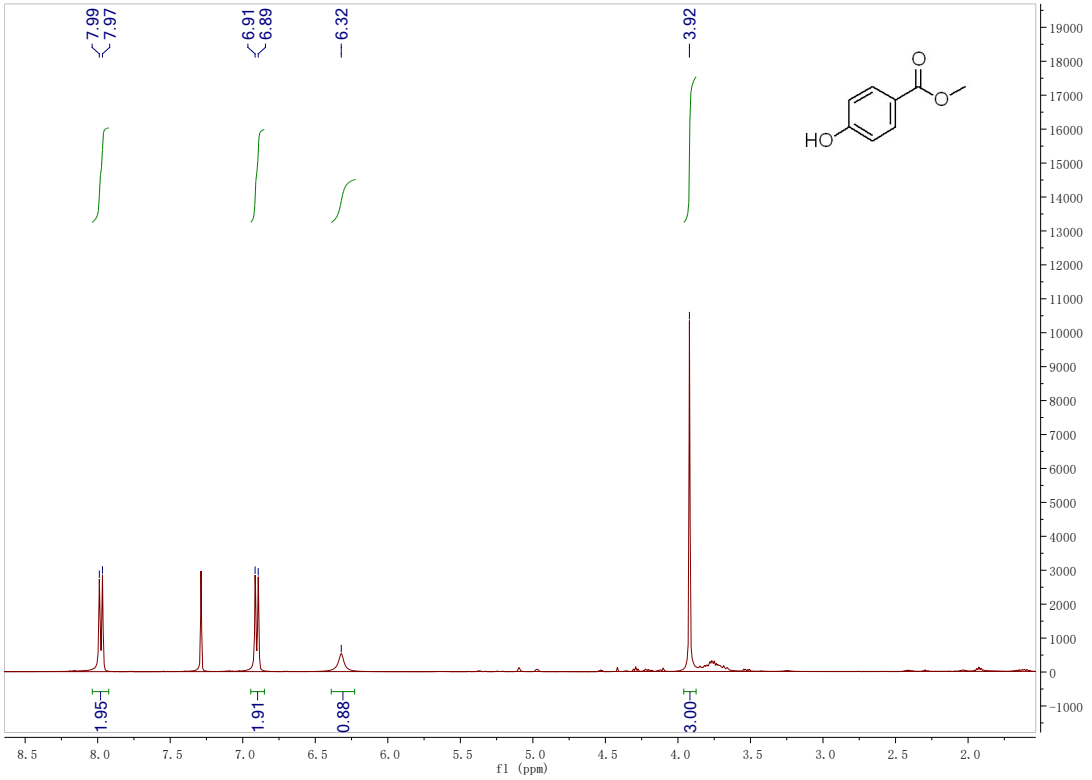
7.44
7.42
3.94
1.97
1.95
3.00
f1 (ppm)


166.17
139.32
130.92
128.66
128.55
52.20
f1 (ppm)

2i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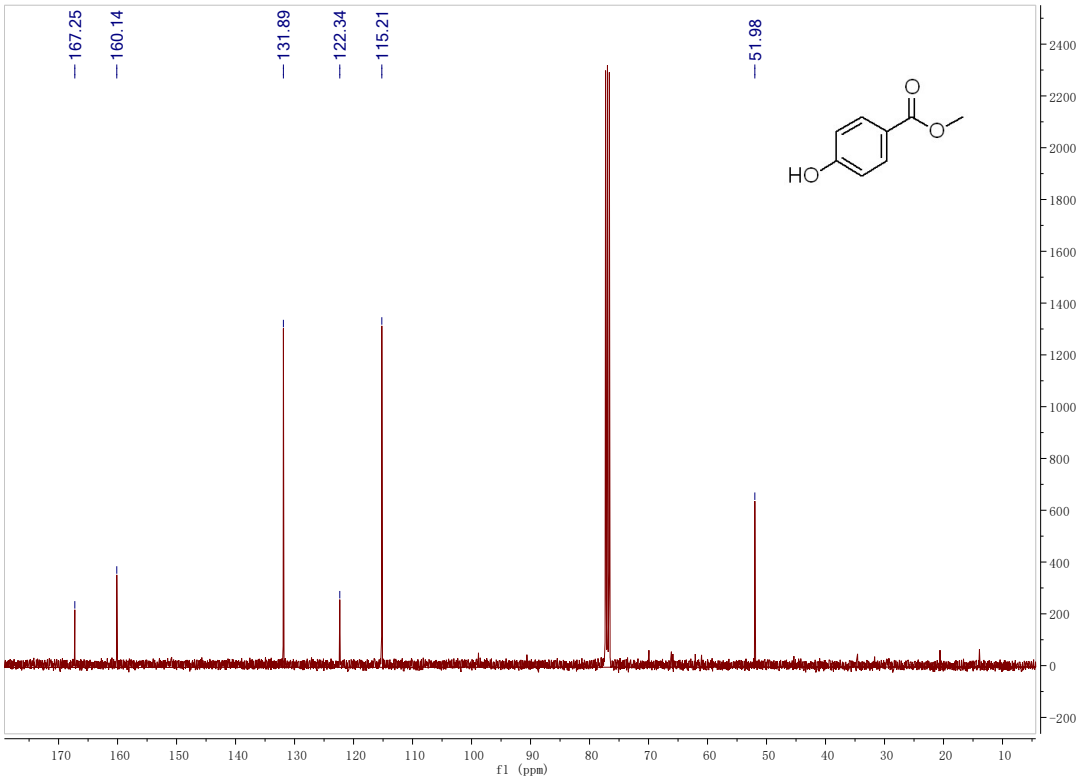
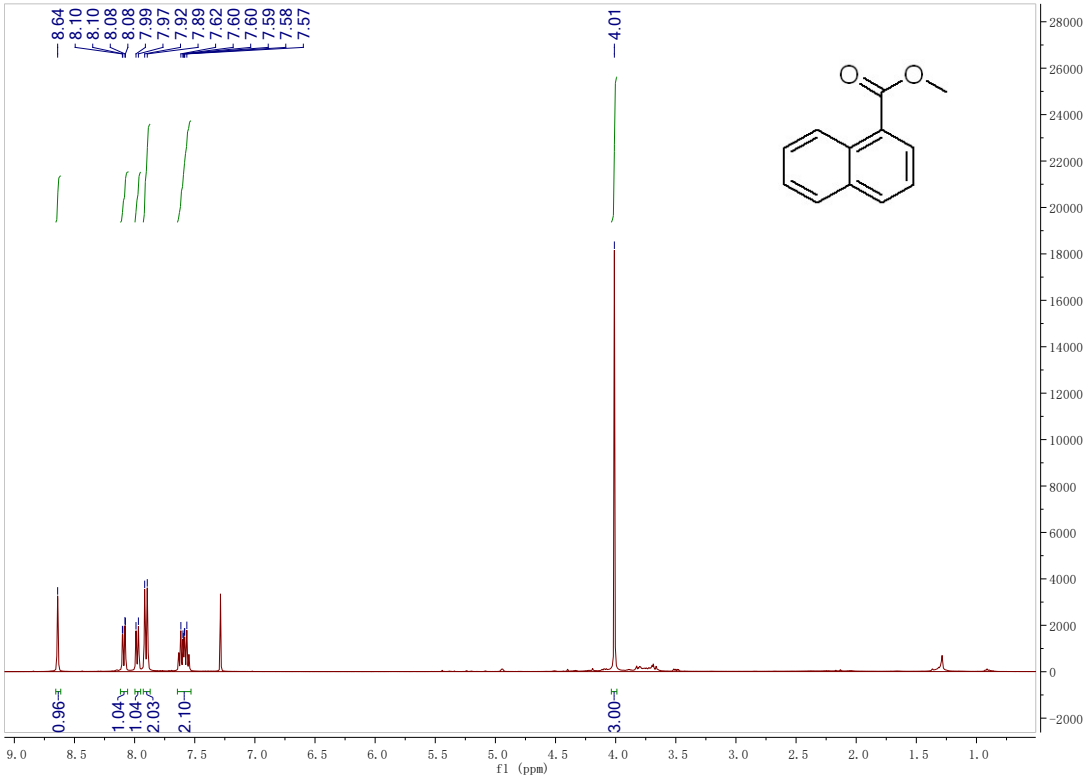
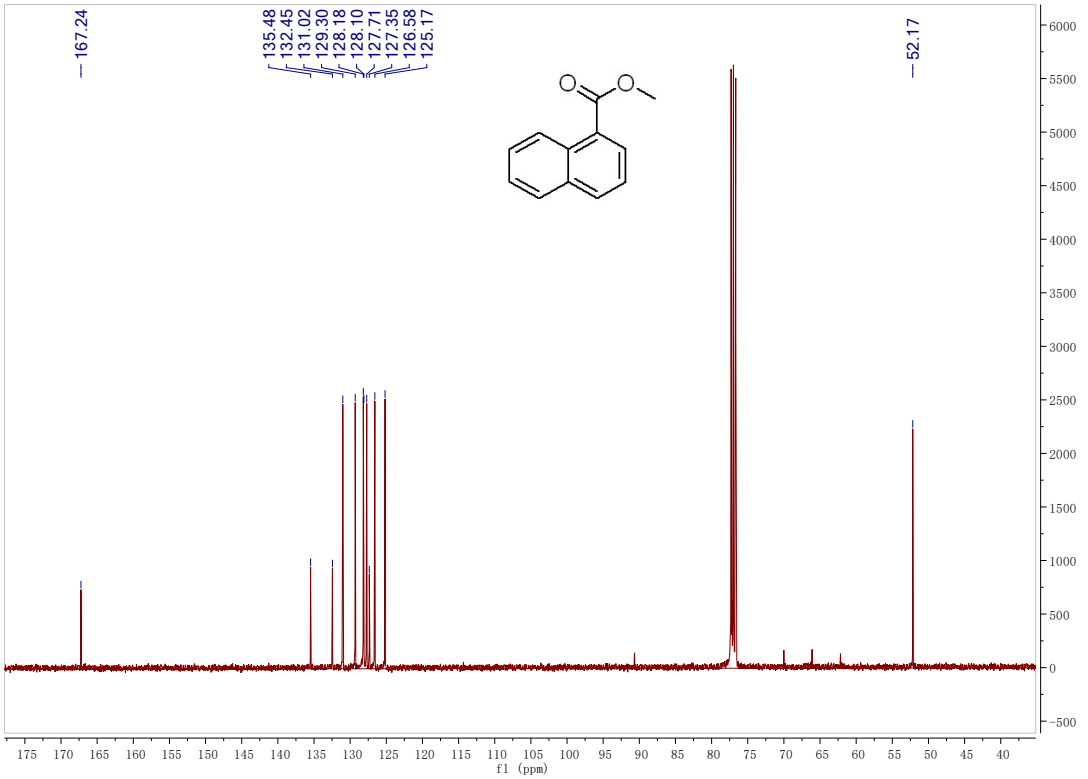
6.91
6.89
6.32
3.92
HO
O
O
1.95
1.91
0.88
3.00
f1 (ppm)


167.25
160.14
131.89
122.34
115.21
51.98
HO
O
O
f1 (ppm)

2j


8.64
8.10
8.10
8.08
8.08
7.99
7.97
7.92
7.89
7.62
7.60
7.60
7.59
7.58
7.57
4.01
0.96
1.04
1.04
2.03
2.10
3.00
f1 (ppm)


167.24
135.48
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128.10
127.71
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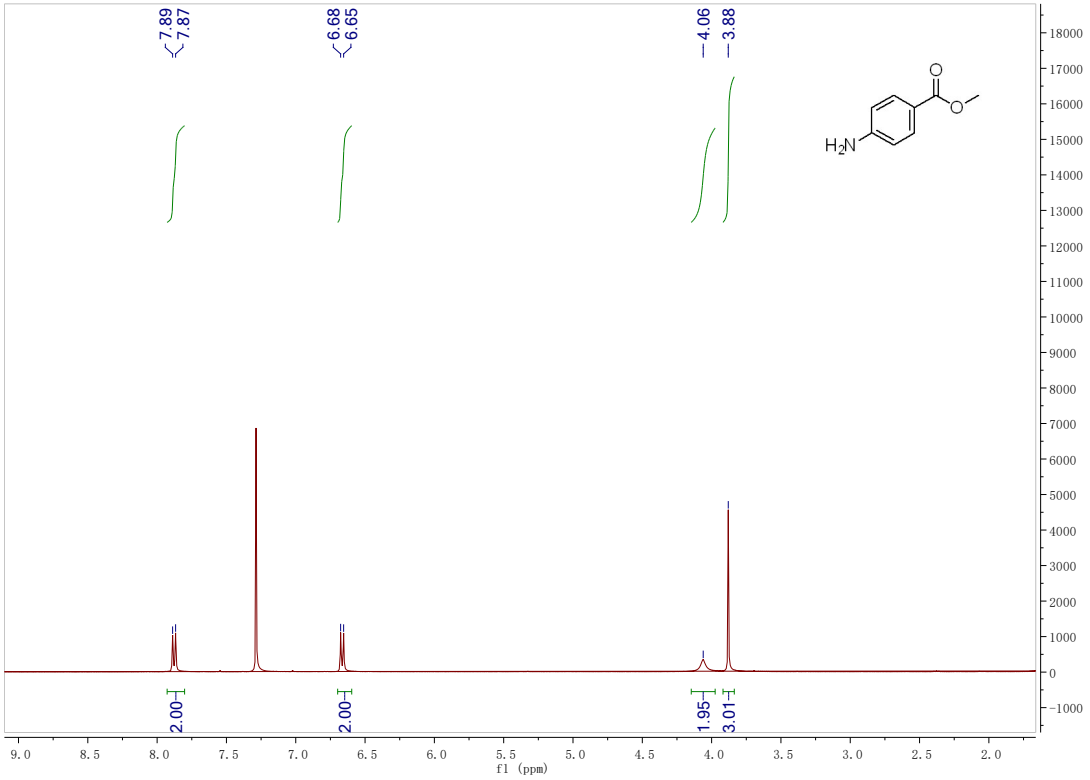
126.58
125.17
52.17
f1 (ppm)

2k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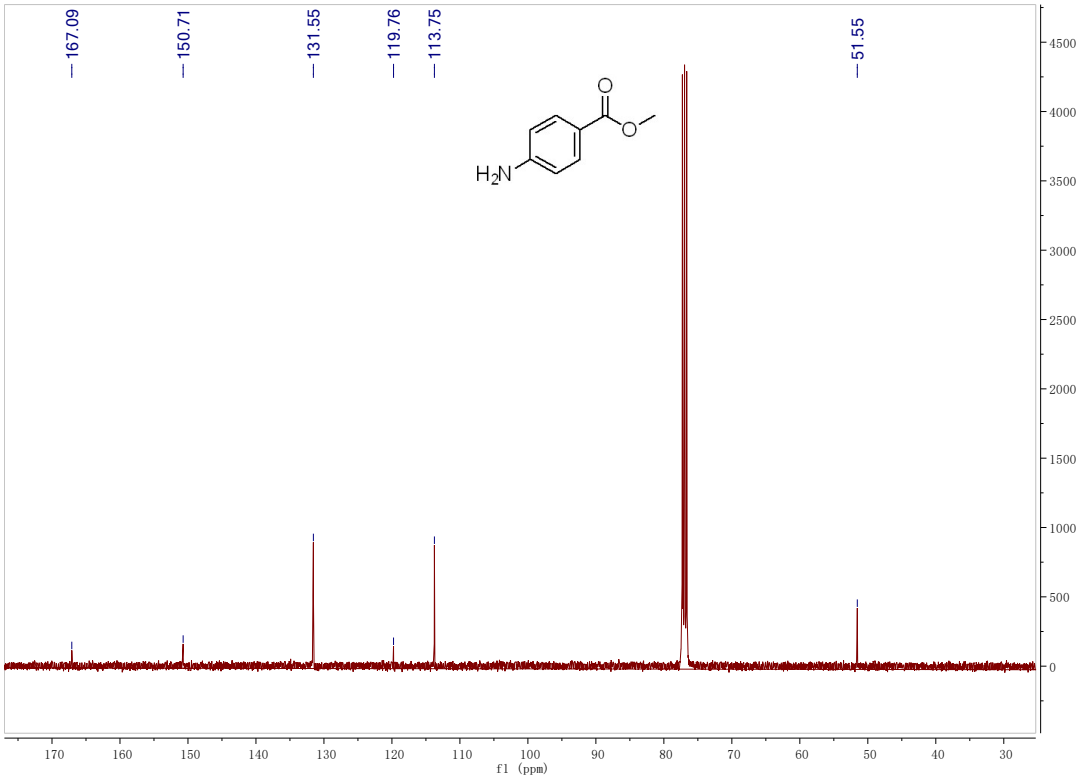
2.00
1.95
3.01
f1 (ppm)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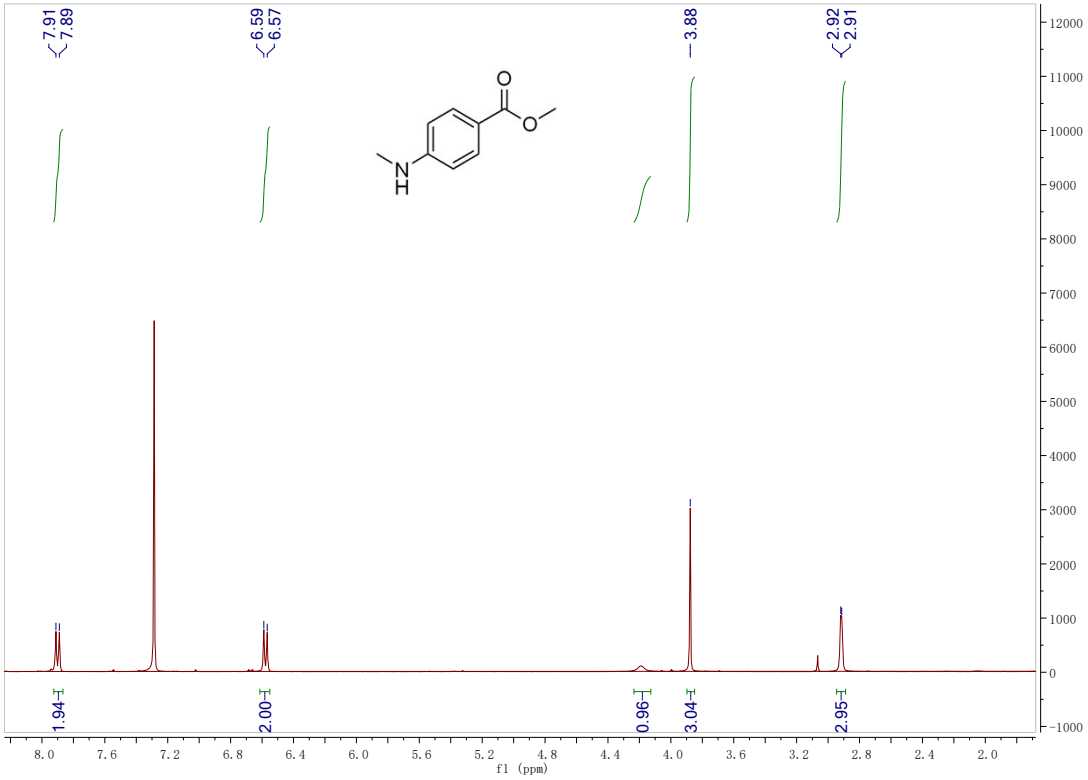
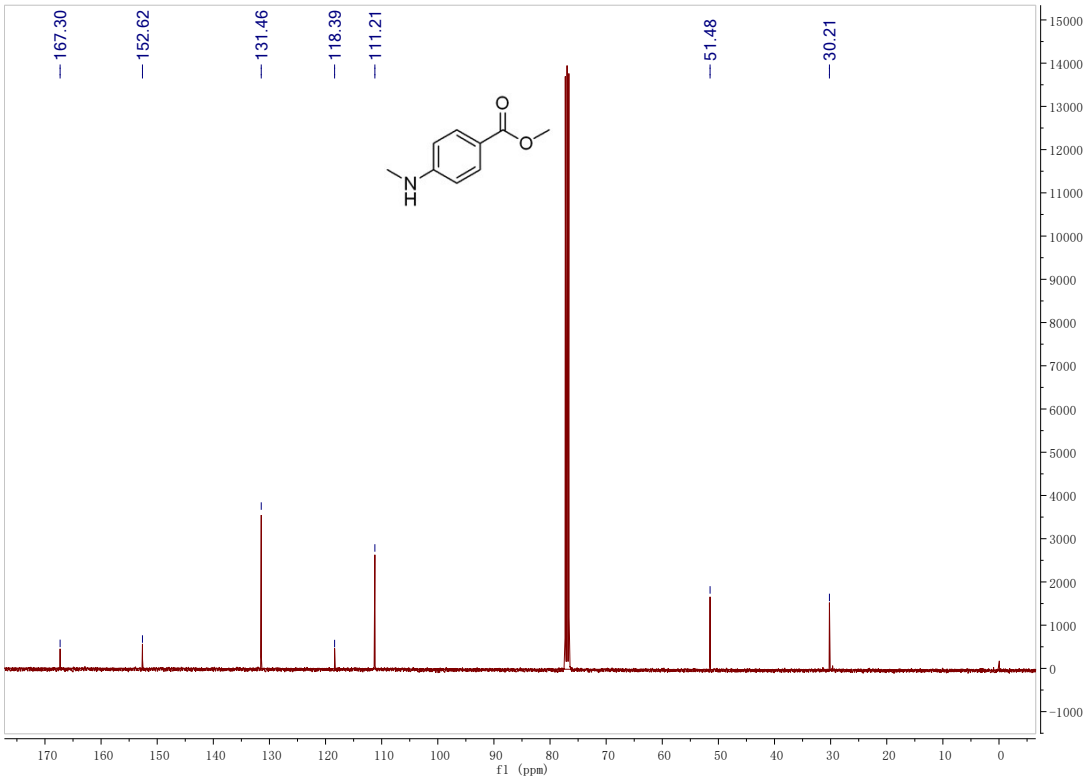
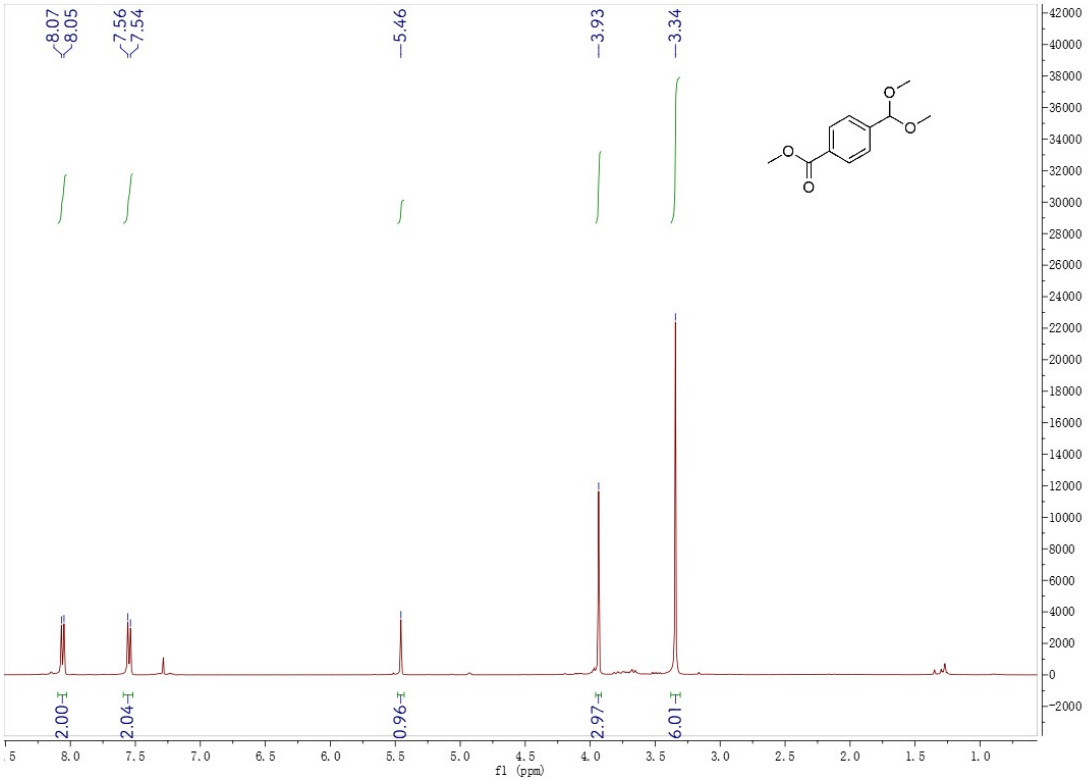
113.75
51.55
f1 (ppm)

byproduct of 2k





2l


8.07
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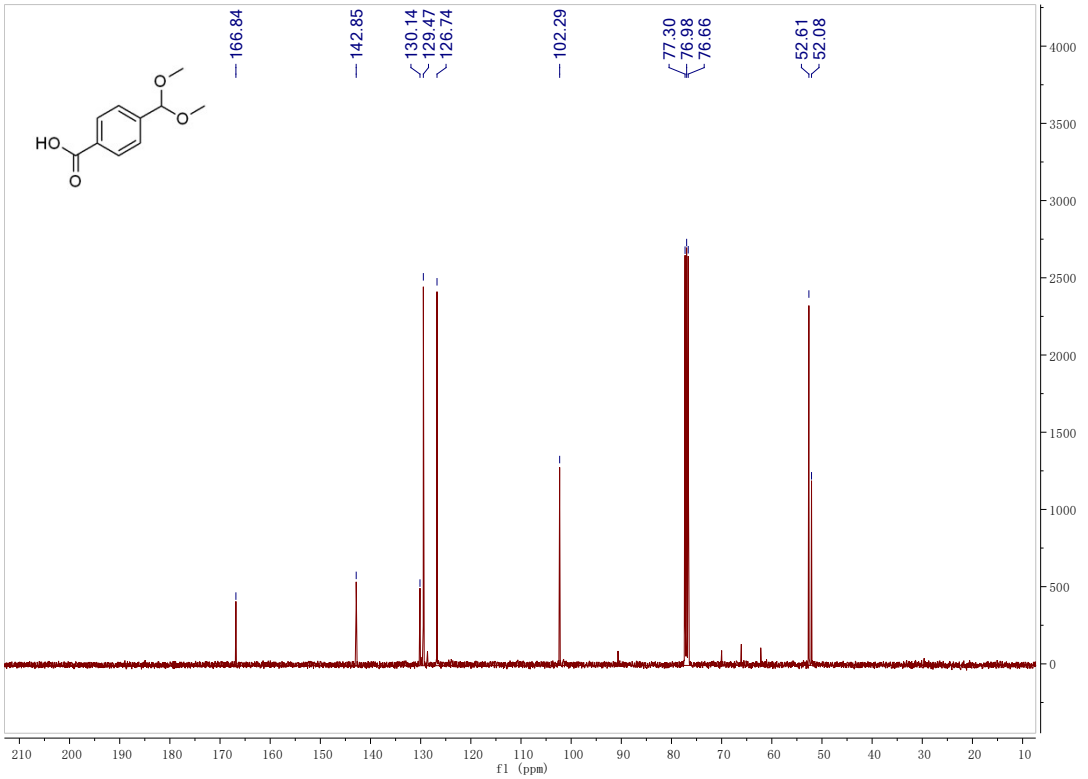
3.34
2.00
2.04
0.96
2.97
6.01
f1 (ppm)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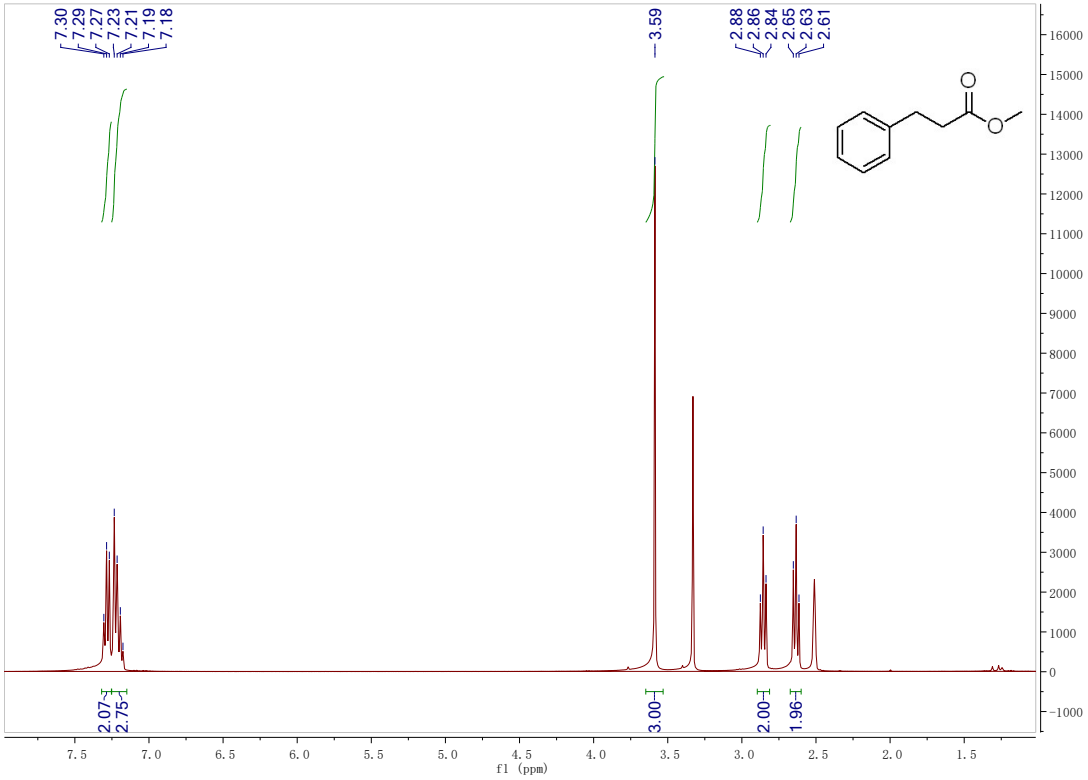
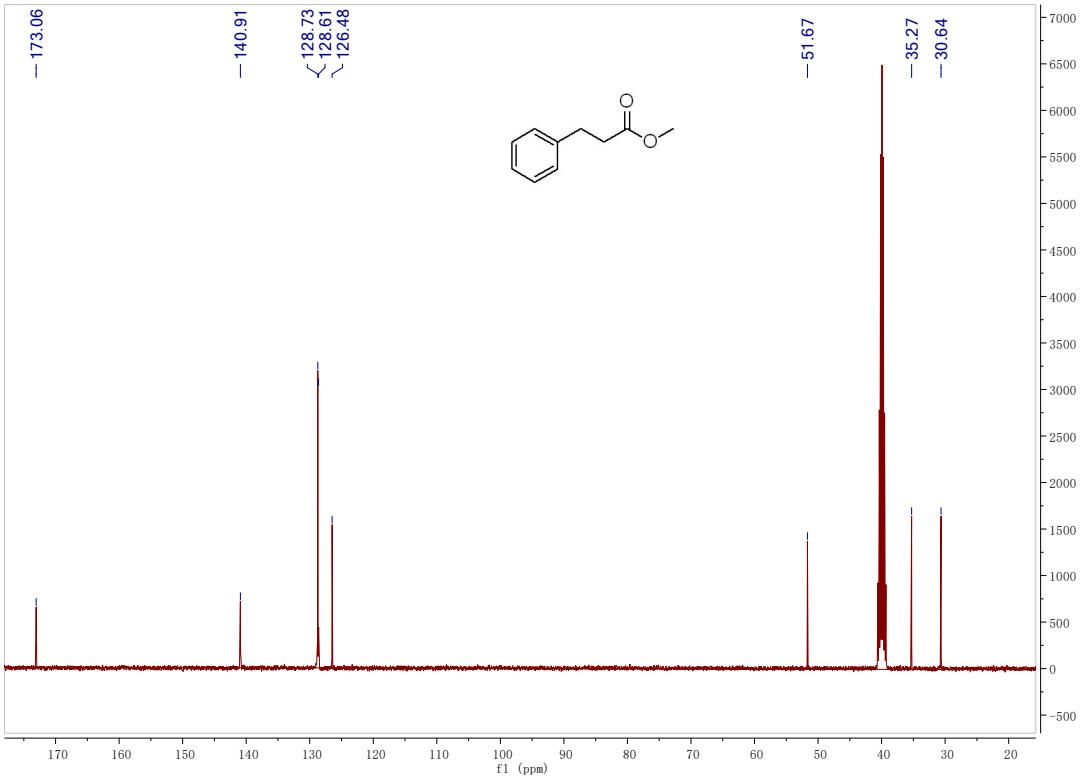
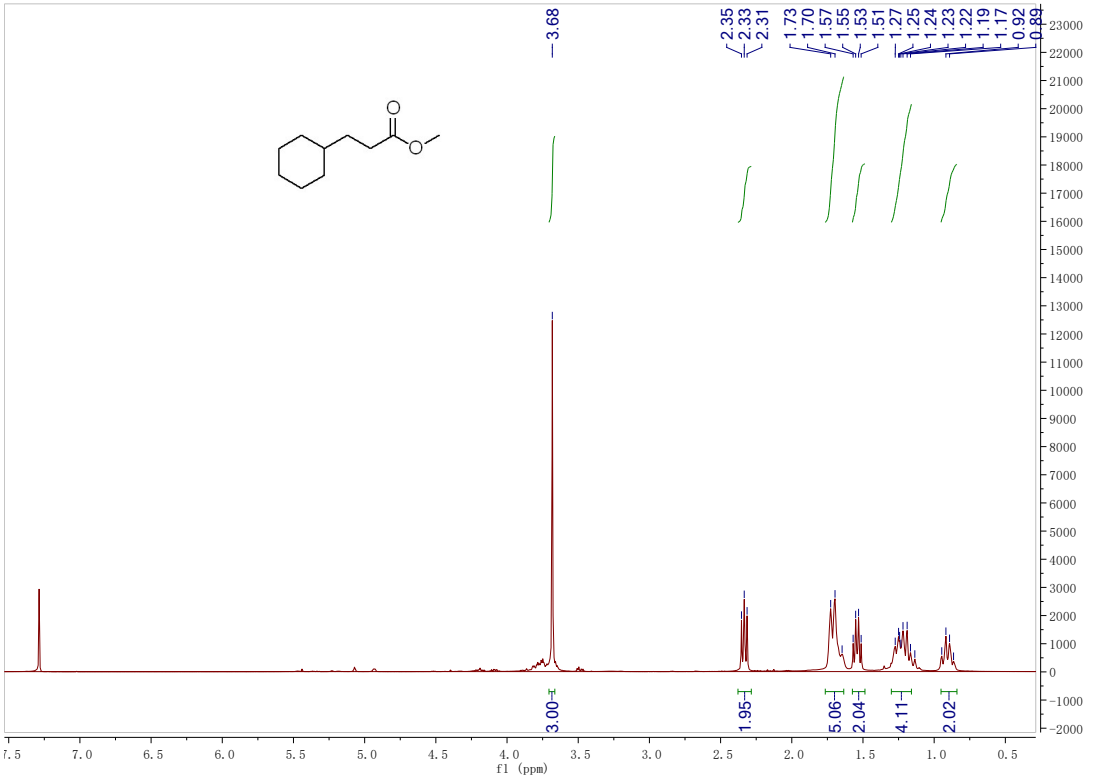
129.47
126.74
102.29
77.30
76.98
76.66
52.61
52.08
HO
f1 (ppm)

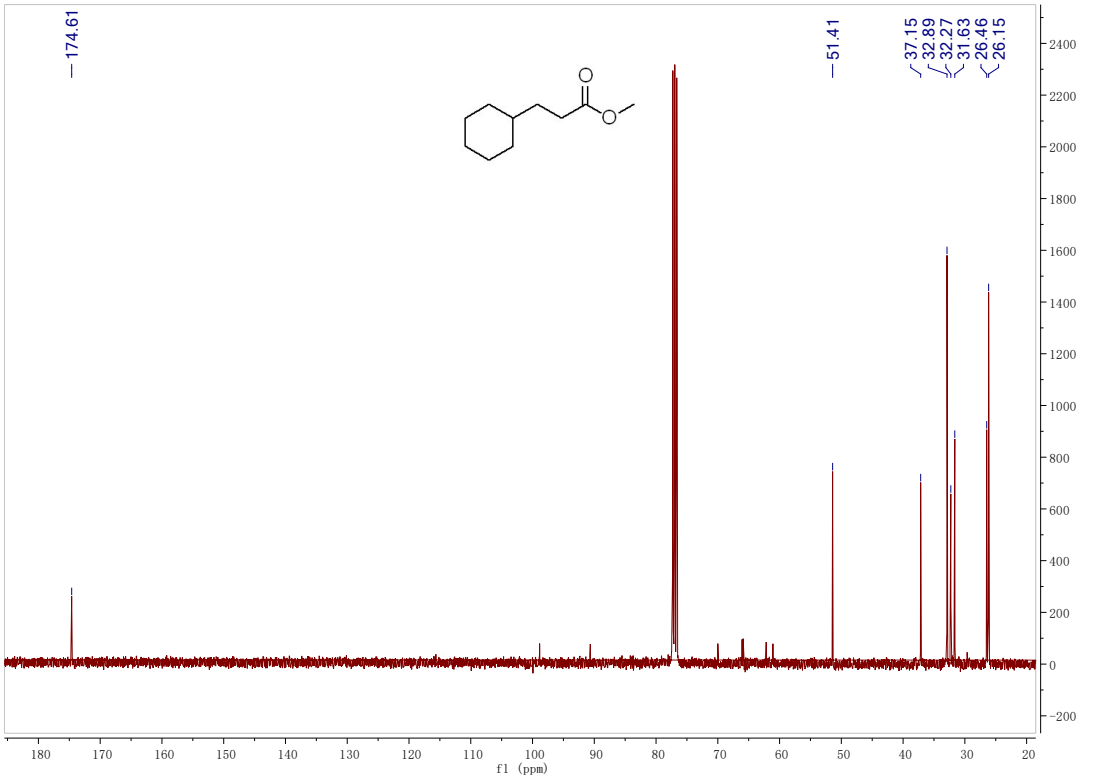
2m


7.30
7.29
7.27
7.23
7.21
7.19
7.18
3.59
2.88
2.86
2.84
2.65
2.63
2.61
2.07
2.75
3.00
2.00
1.96
f1 (ppm)

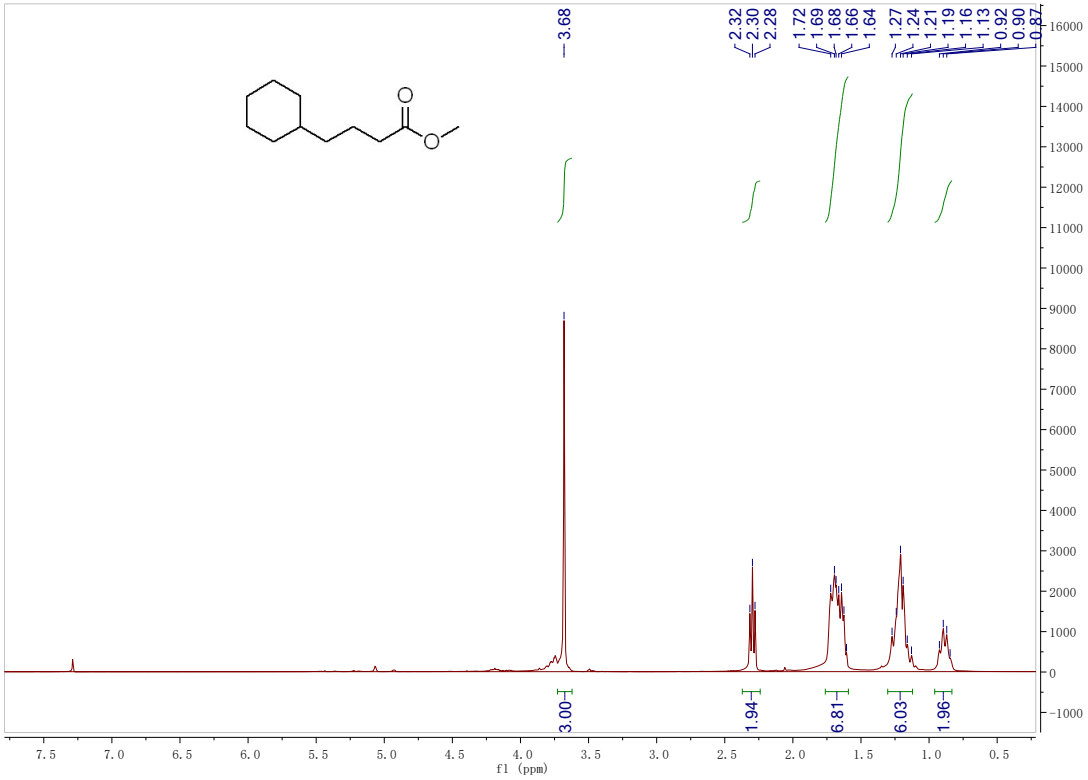

173.06
140.91
128.73
128.61
126.48
51.67
35.27
30.64
f1 (ppm)

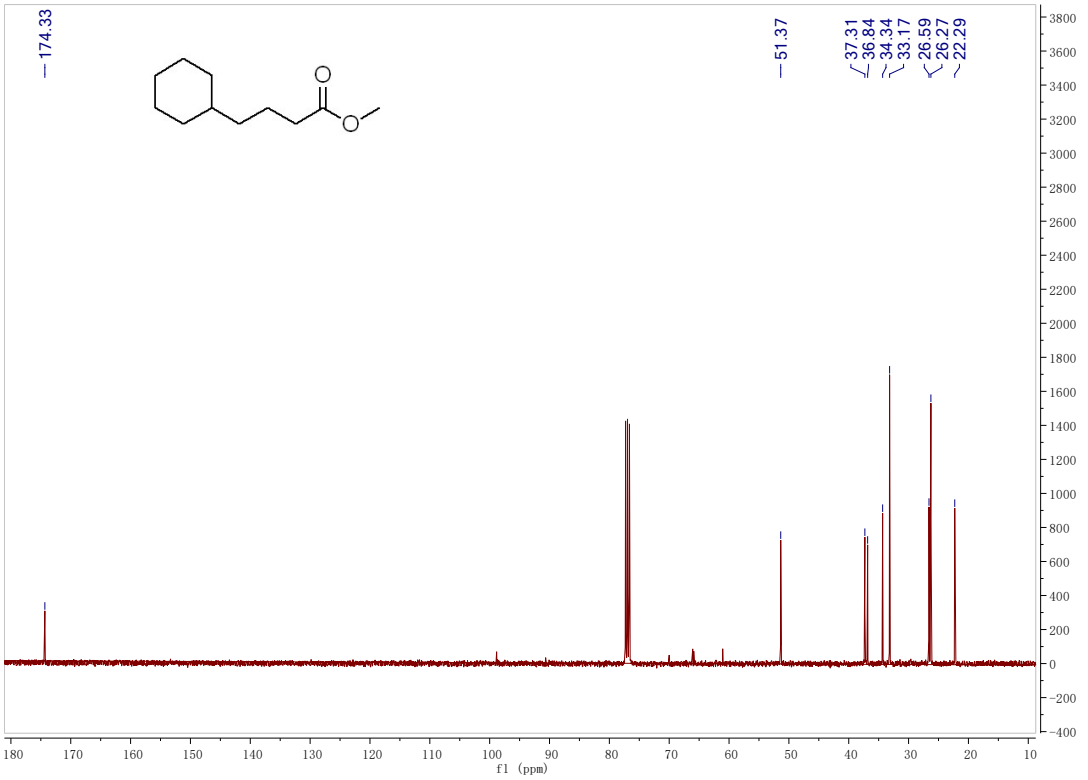
2n


3.68
2.35
2.33
2.31
1.73
1.70
1.57
1.55
1.53
1.51
1.27
1.25
1.24
1.23
1.22
1.19
1.17
0.92
0.89
3.00
1.95
5.06
2.04
4.11
2.02
f1 (ppm)

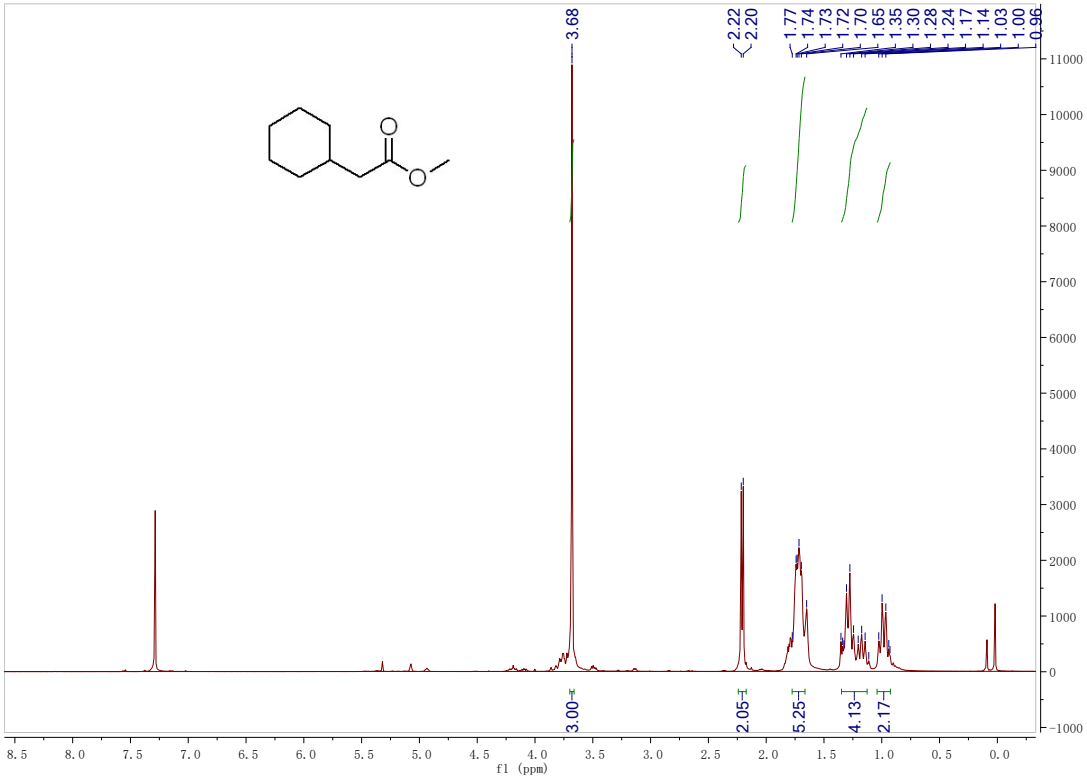

174.61
51.41
37.15
32.89
32.27
31.63
26.46
26.15
f1 (ppm)

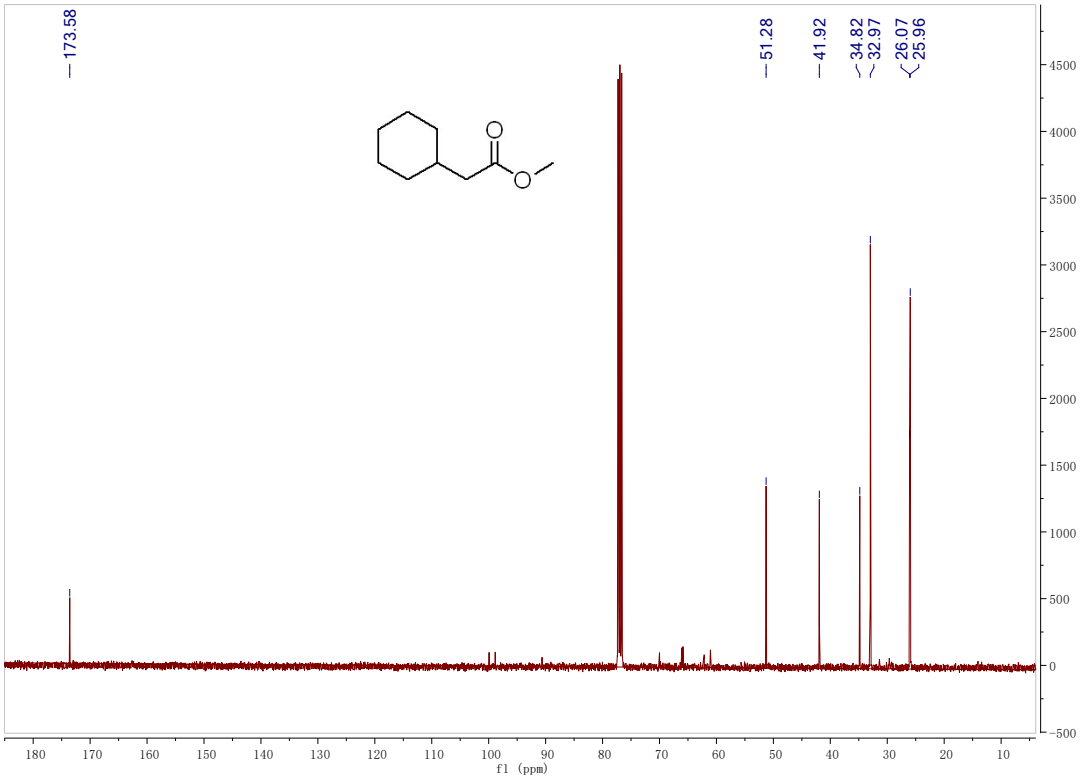
2o


3.68
2.32
2.30
2.28
1.72
1.69
1.68
1.66
1.64
1.27
1.24
1.21
1.19
1.16
1.13
0.92
0.90
0.87
3.00
1.94
6.81
6.03
1.96
f1 (ppm)

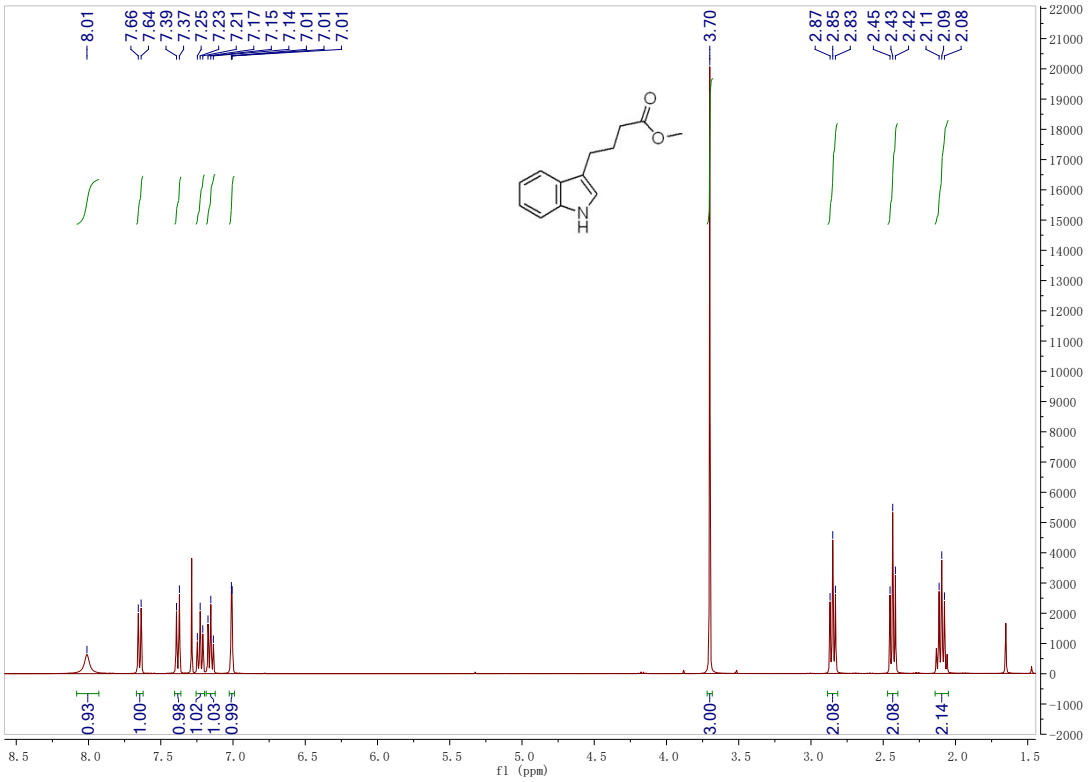

174.33
51.37
37.31
36.84
34.34
33.17
26.59
26.27
22.29
f1 (ppm)

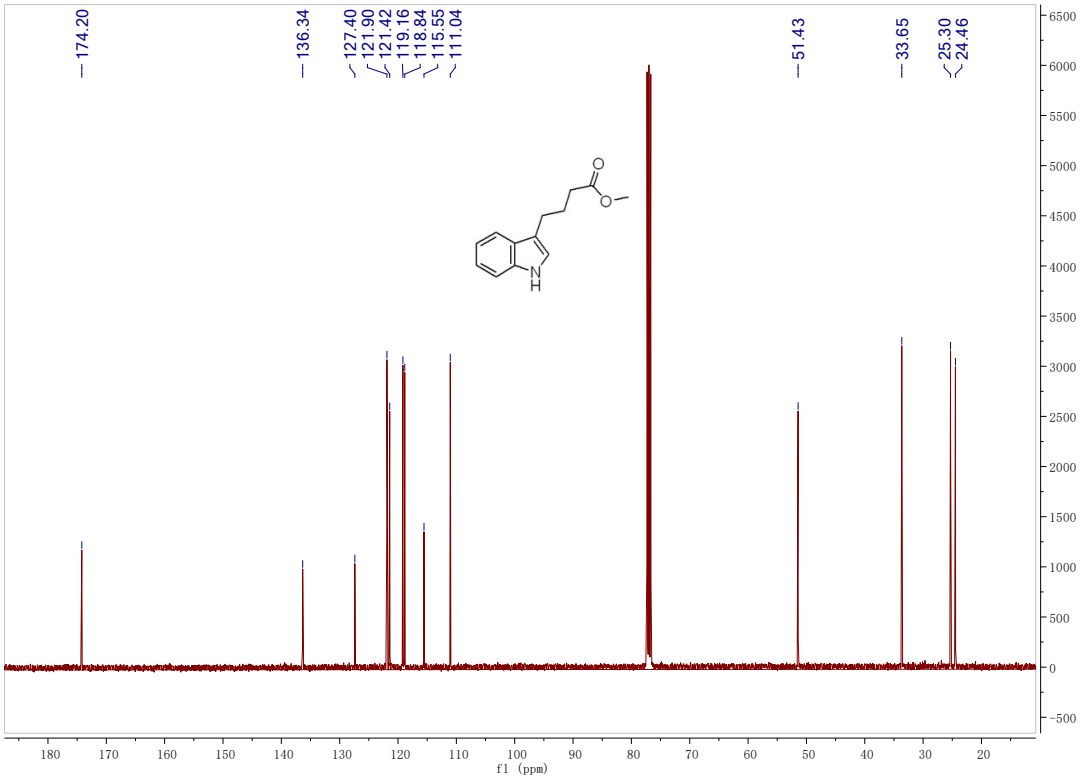
2p


3.68
2.22
2.20
1.77
1.74
1.73
1.72
1.70
1.65
1.35
1.30
1.28
1.24
1.17
1.14
1.03
1.00
0.96
3.00
2.05
5.25
4.13
2.17
f1 (ppm)

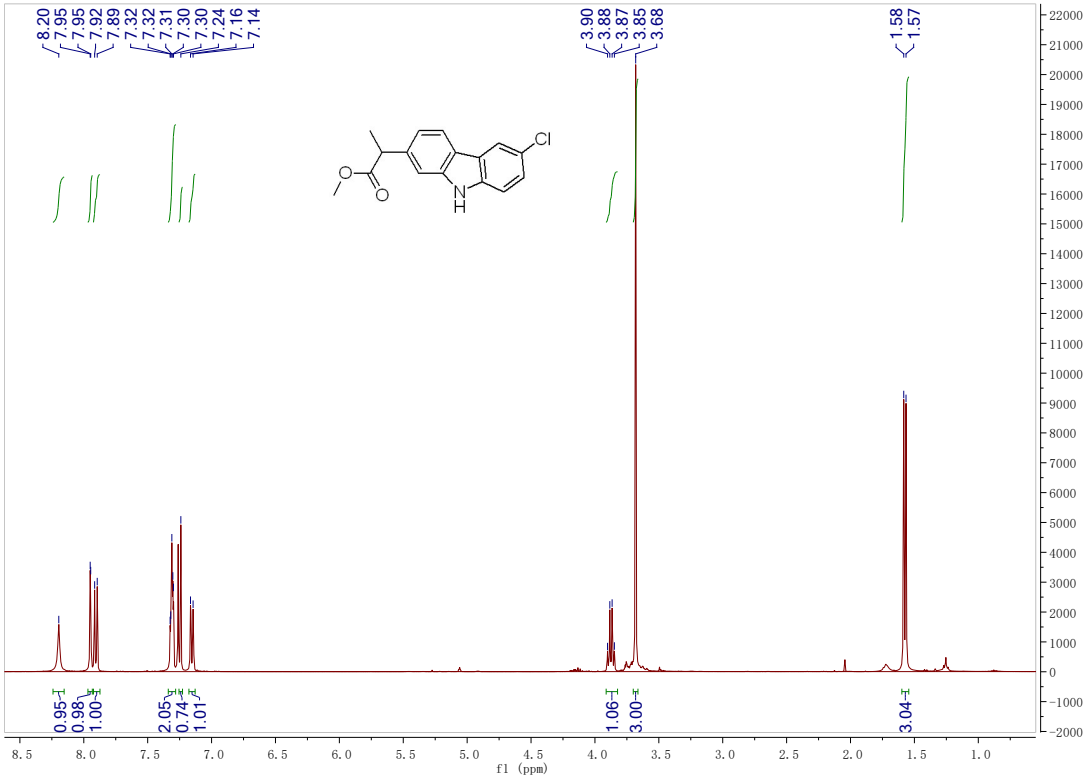

173.58
51.28
41.92
34.82
32.97
26.07
25.96
f1 (ppm)

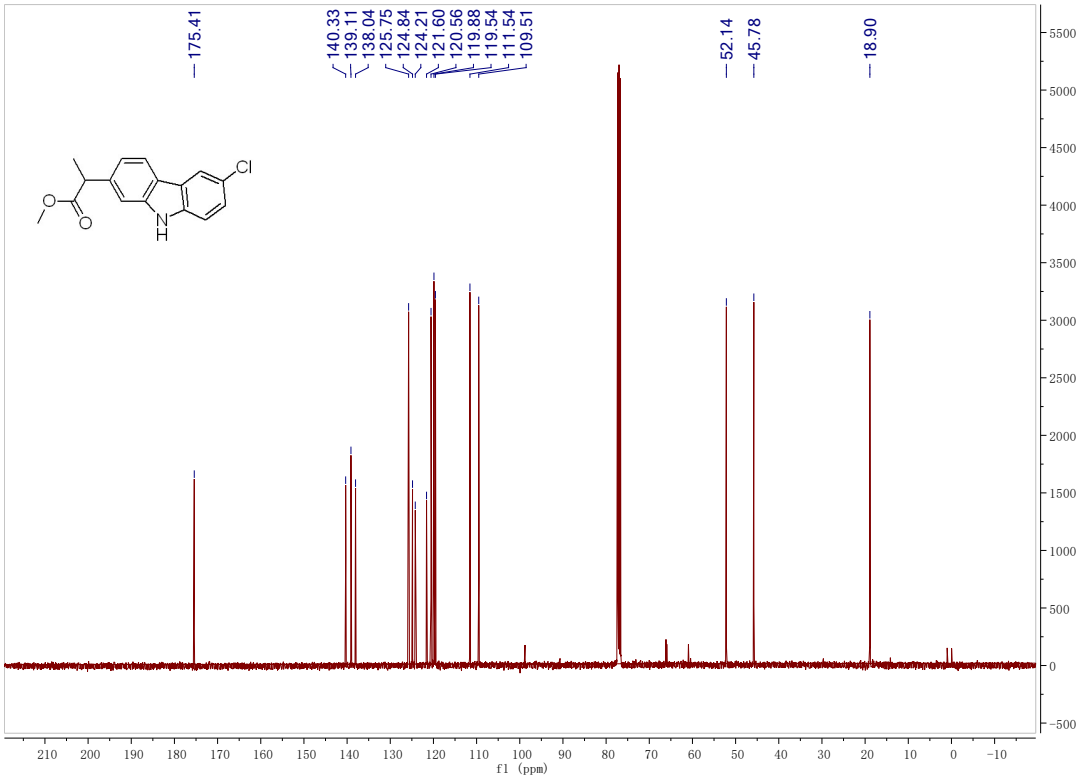
2q


8.01
7.66
7.64
7.39
7.37
7.25
7.23
7.21
7.17
7.15
7.14
7.01
7.01
7.01
3.70
2.87
2.85
2.83
2.45
2.43
2.42
2.11
2.09
2.08
0.93
1.00
0.98
1.02
1.03
0.99
3.00
2.08
2.08
2.14
f1 (ppm)

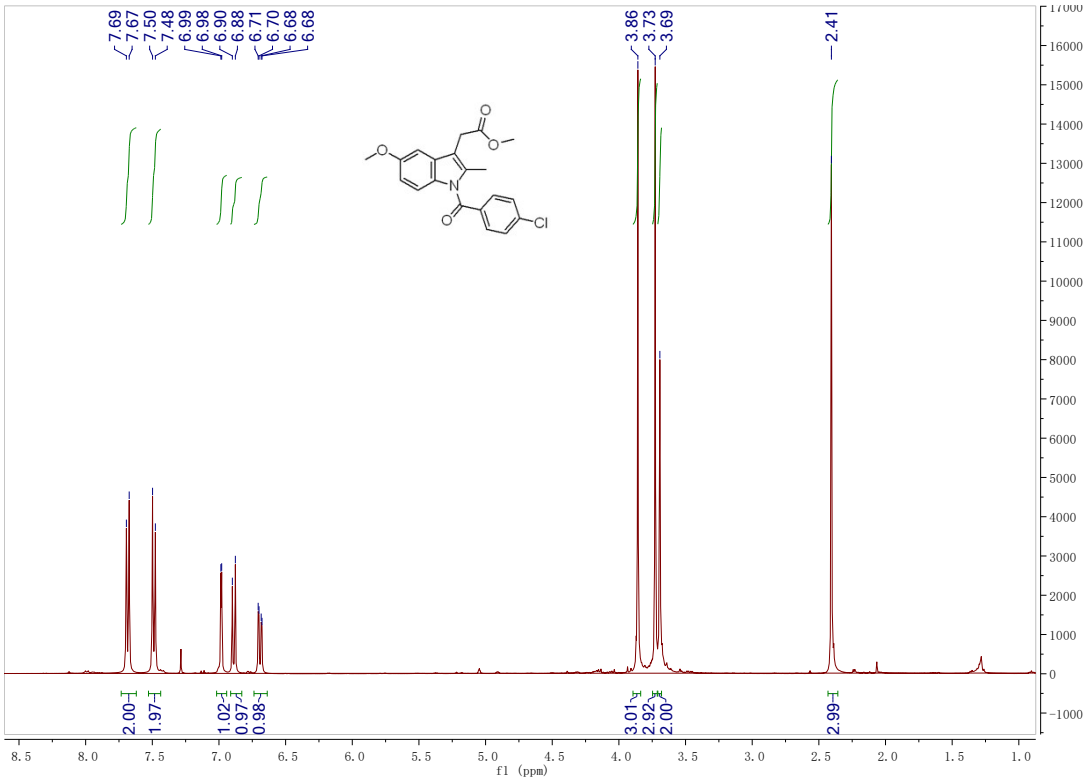

174.20
136.34
127.40
121.90
121.42
119.16
118.84
115.55
111.04
51.43
33.65
25.30
24.46
f1 (ppm)

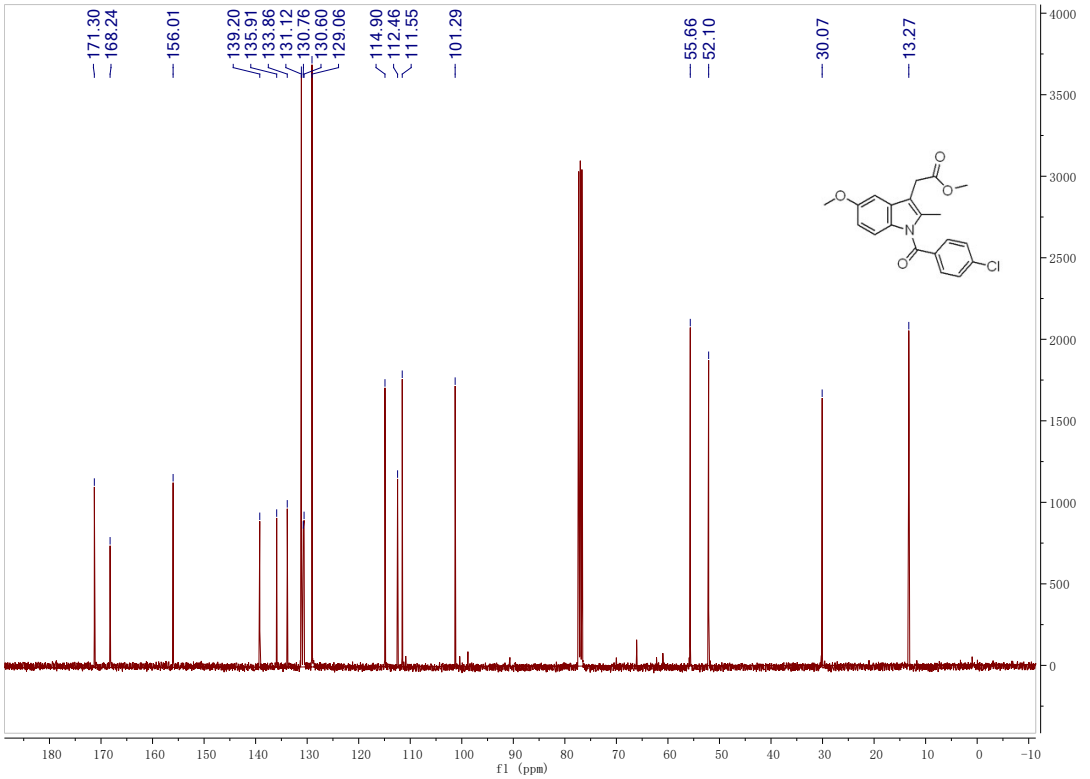
2r


8.20
7.95
7.95
7.92
7.89
7.32
7.32
7.31
7.30
7.30
7.24
7.16
7.14
3.90
3.88
3.87
3.85
3.68
1.58
1.57
Cl
O
O
N
H
0.95
0.98
1.00
2.05
0.74
1.01
1.06
3.00
3.04
f1 (ppm)

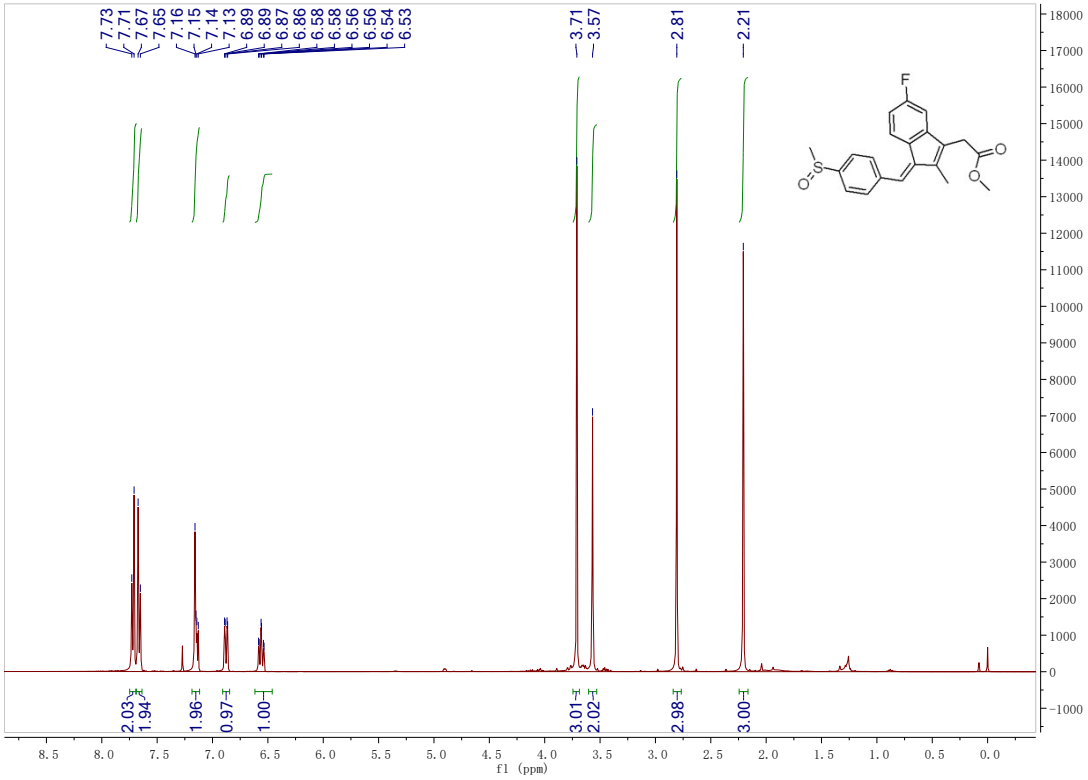

175.41
140.33
139.11
138.04
125.75
124.84
124.21
121.60
120.56
119.88
119.54
111.54
109.51
52.14
45.78
18.90
Cl
O
O
N
H
f1 (ppm)

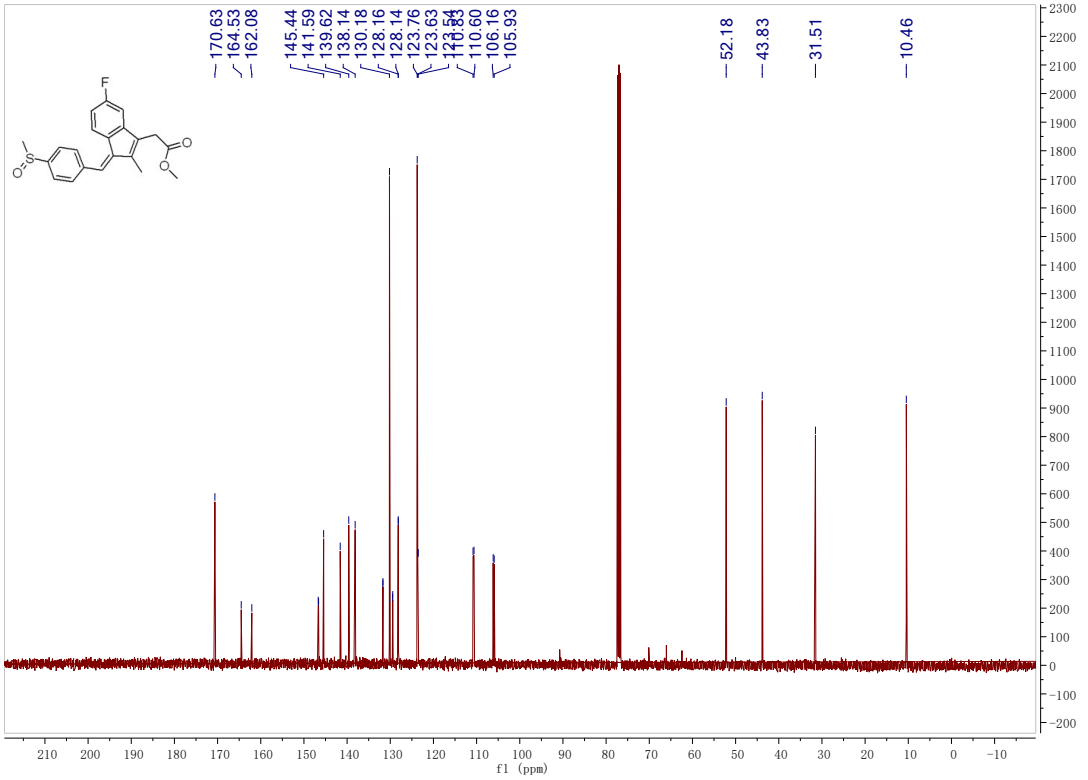
2s


7.69
7.67
7.50
7.48
6.99
6.98
6.90
6.88
6.71
6.70
6.68
6.68
3.86
3.73
3.69
2.41
2.00
1.97
1.02
0.97
0.98
3.01
2.92
2.00
2.99
f1 (ppm)

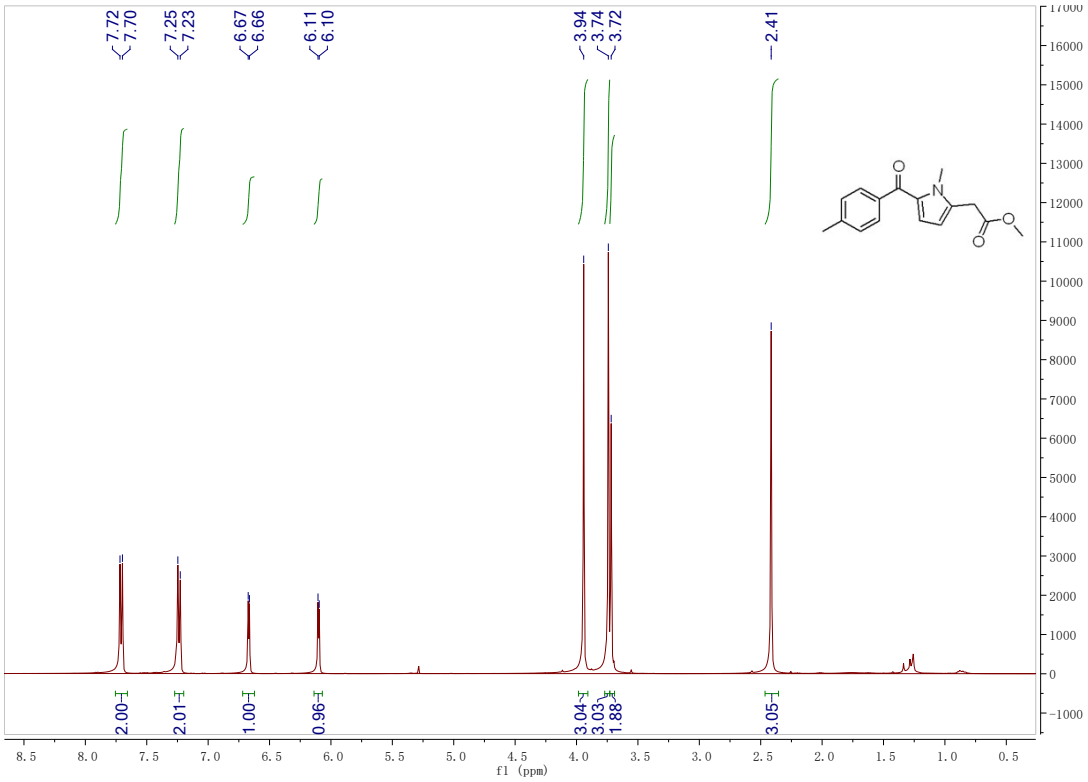

171.30
168.24
156.01
139.20
135.91
133.86
131.12
130.76
130.60
129.06
114.90
112.46
111.55
101.29
55.66
52.10
30.07
13.27
f1 (ppm)

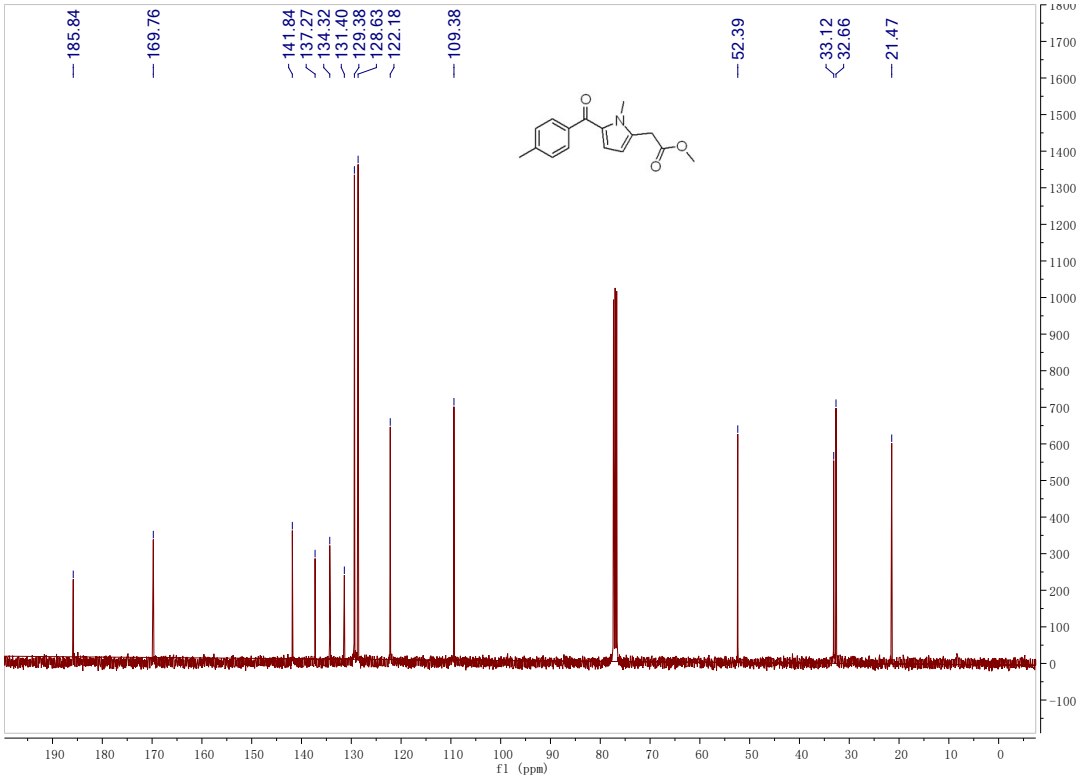
2t


7.73
7.71
7.67
7.65
7.16
7.15
7.14
7.13
6.89
6.89
6.87
6.86
6.58
6.58
6.56
6.56
6.54
6.53
3.71
3.57
2.81
2.21
F
O=S
O
O
2.03
1.94
1.96
0.97
1.00
3.01
2.02
2.98
3.00
f1 (ppm)

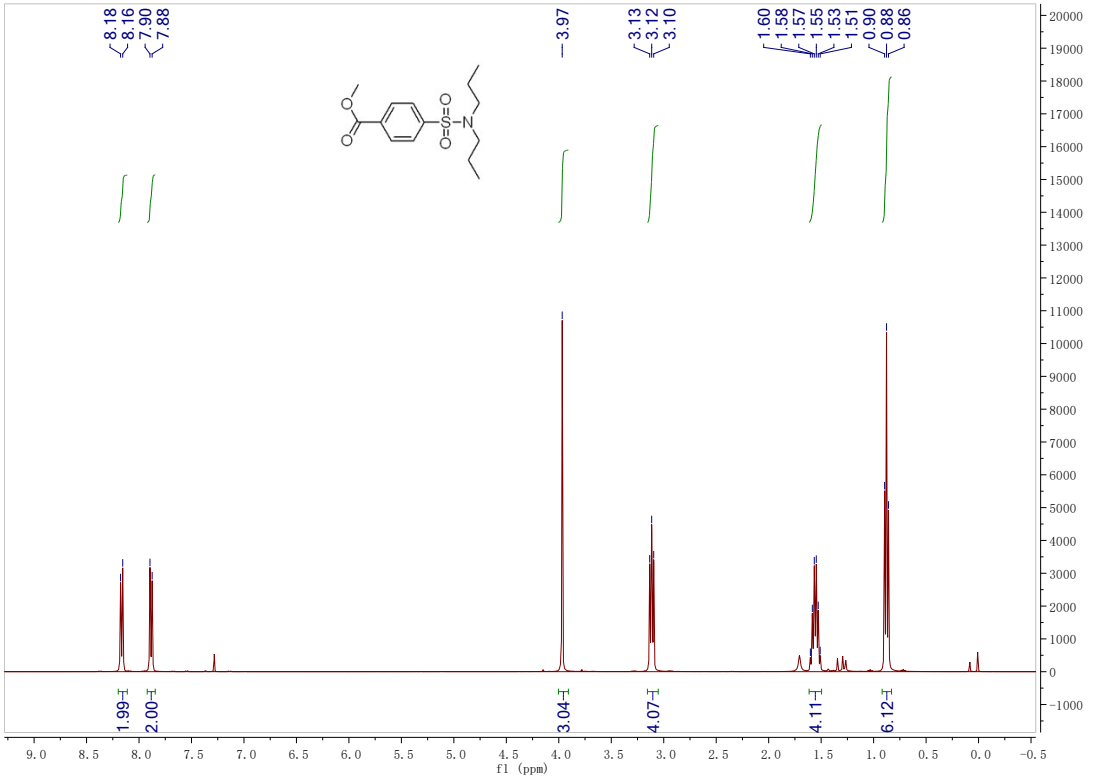

170.63
164.53
162.08
145.44
141.59
139.62
138.14
130.18
128.16
128.14
123.76
123.63
110.60
106.16
105.93
52.18
43.83
31.51
10.46
F
O=S
O
O
f1 (ppm)

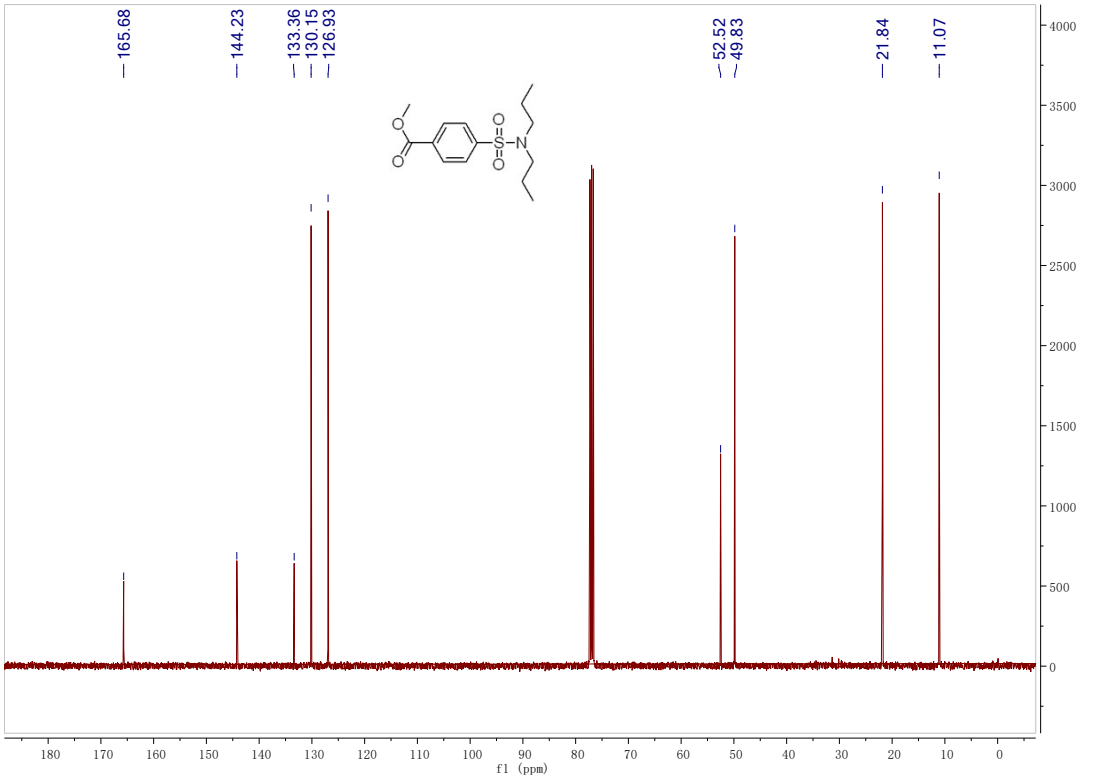
2u


7.72
7.70
7.25
7.23
6.67
6.66
6.11
6.10
3.94
3.74
3.72
2.41
2.00
2.01
1.00
0.96
3.04
3.03
1.88
3.05
f1 (ppm)

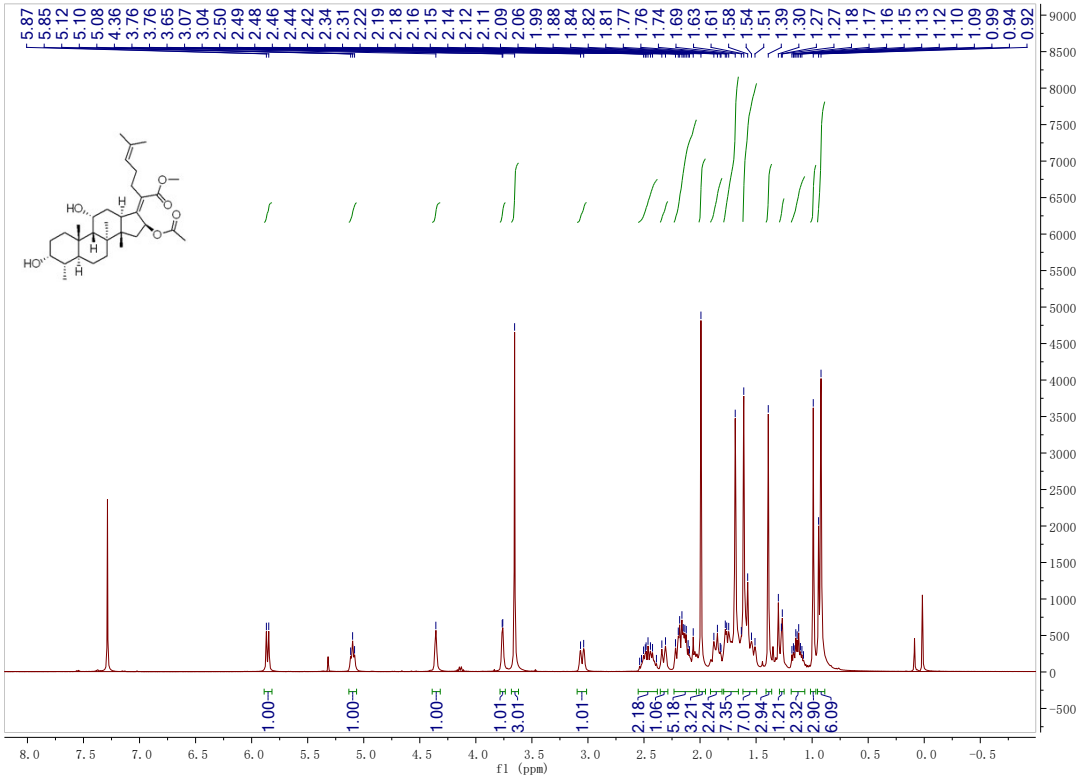

185.84
169.76
141.84
137.27
134.32
131.40
129.38
128.63
122.18
109.38
52.39
33.12
32.66
21.47
f1 (ppm)

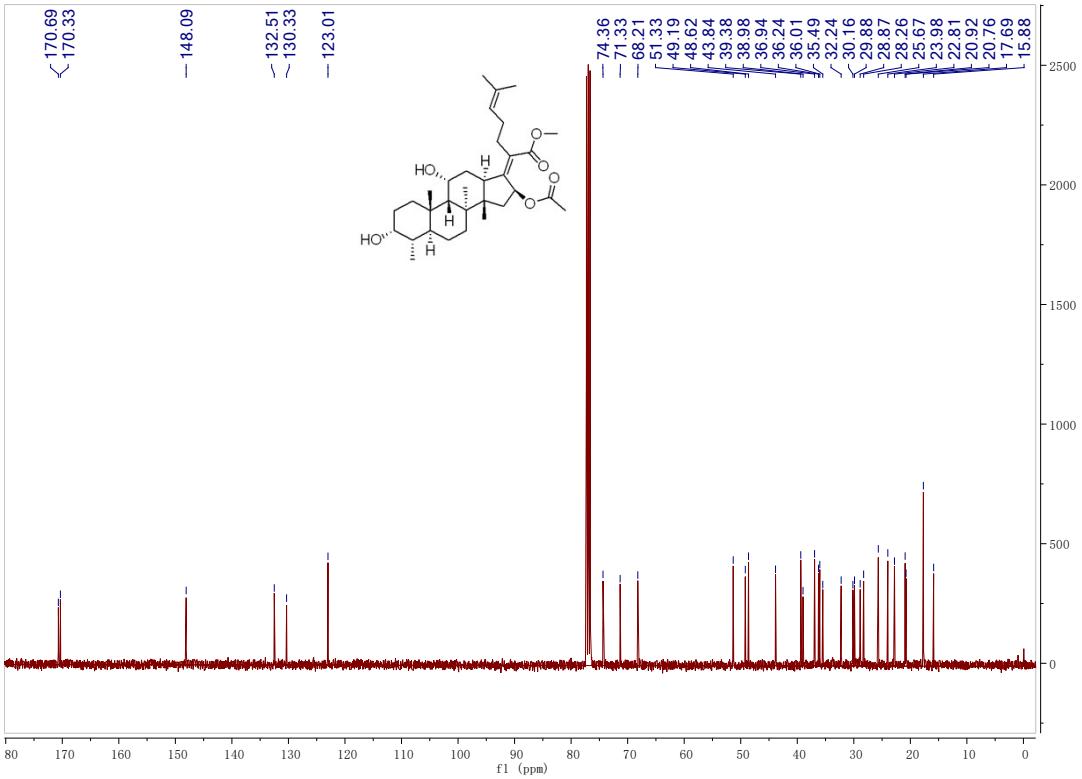
2v


8.18
8.16
7.90
7.88
3.97
3.13
3.12
3.10
1.60
1.58
1.57
1.55
1.53
1.51
0.90
0.88
0.86
1.99
2.00
3.04
4.07
4.11
6.12
f1 (ppm)

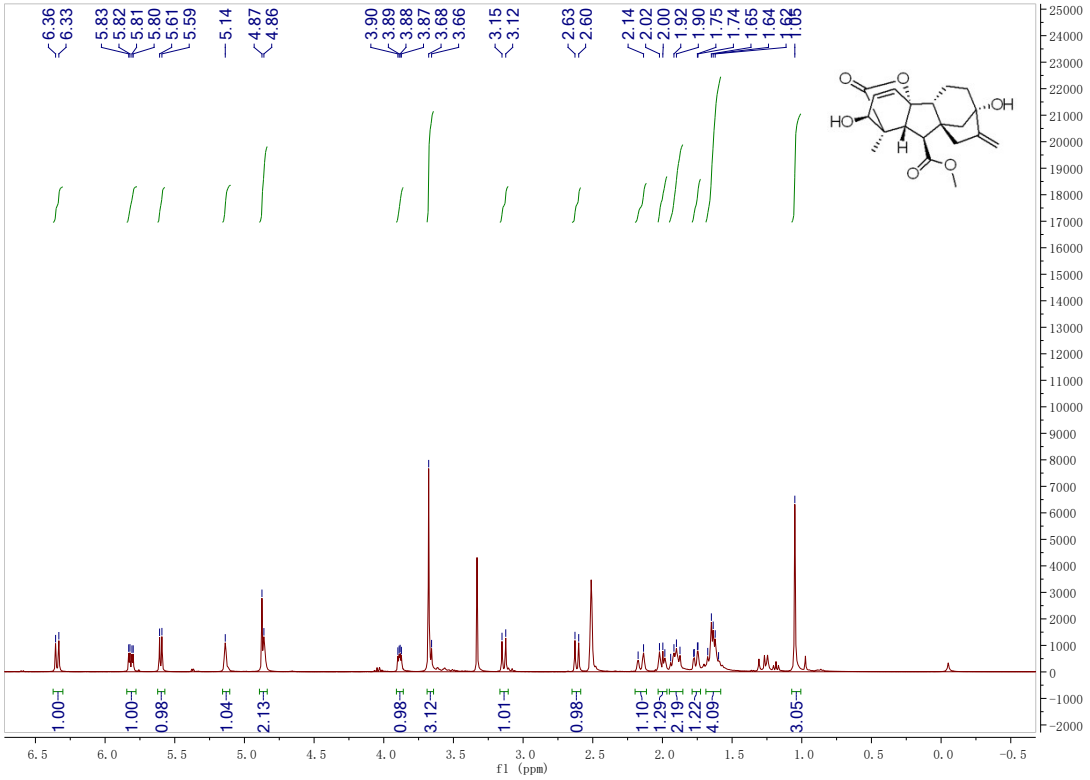

165.68
144.23
133.36
130.15
126.93
52.52
49.83
21.84
11.07
f1 (ppm)

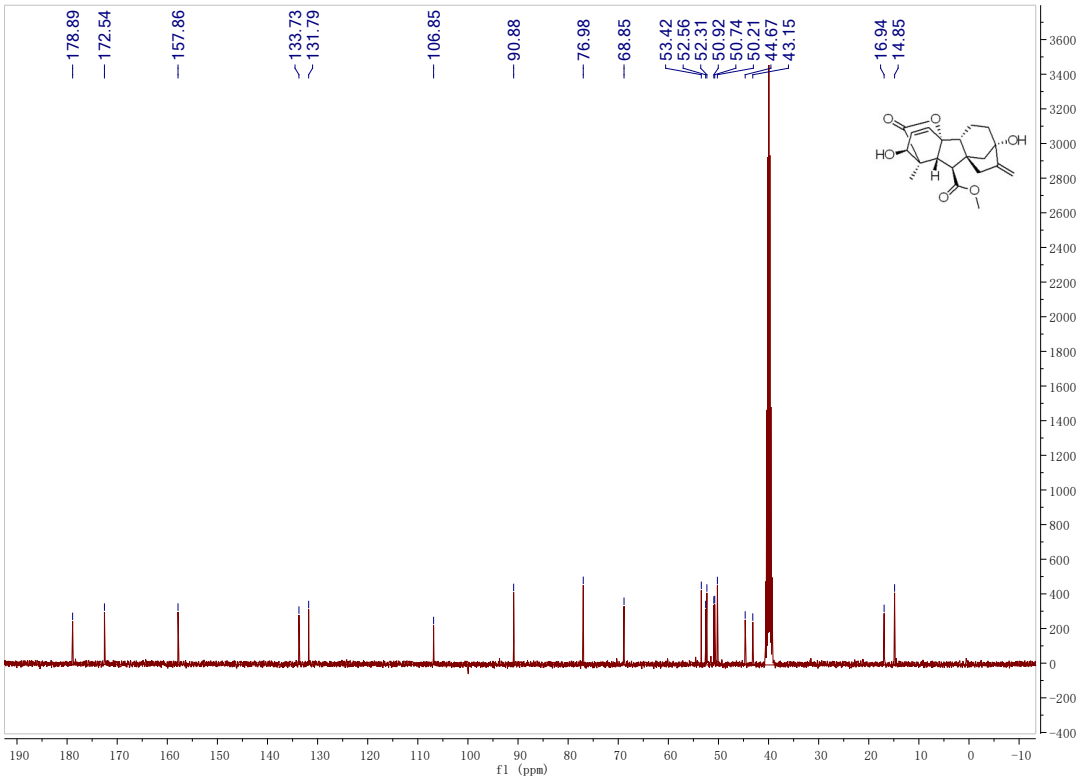
2w


5.87 5.85 5.12 5.10 5.08 4.36 3.76 3.76 3.65 3.07 3.04 2.50 2.49 2.48 2.46 2.44 2.42 2.34 2.31 2.22 2.19 2.18 2.16 2.15 2.14 2.12 2.11 2.09 2.06 1.99 1.88 1.84 1.82 1.81 1.77 1.76 1.74 1.69 1.63 1.61 1.58 1.54 1.51 1.39 1.30 1.27 1.27 1.18 1.17 1.16 1.15 1.13 1.12 1.10 1.09 0.99 0.94 0.92
1.00 1.00 1.00 1.01 3.01 1.01 2.18 1.06 5.18 3.21 2.24 7.35 7.01 2.94 1.21 2.32 2.90 6.09
f1 (ppm)

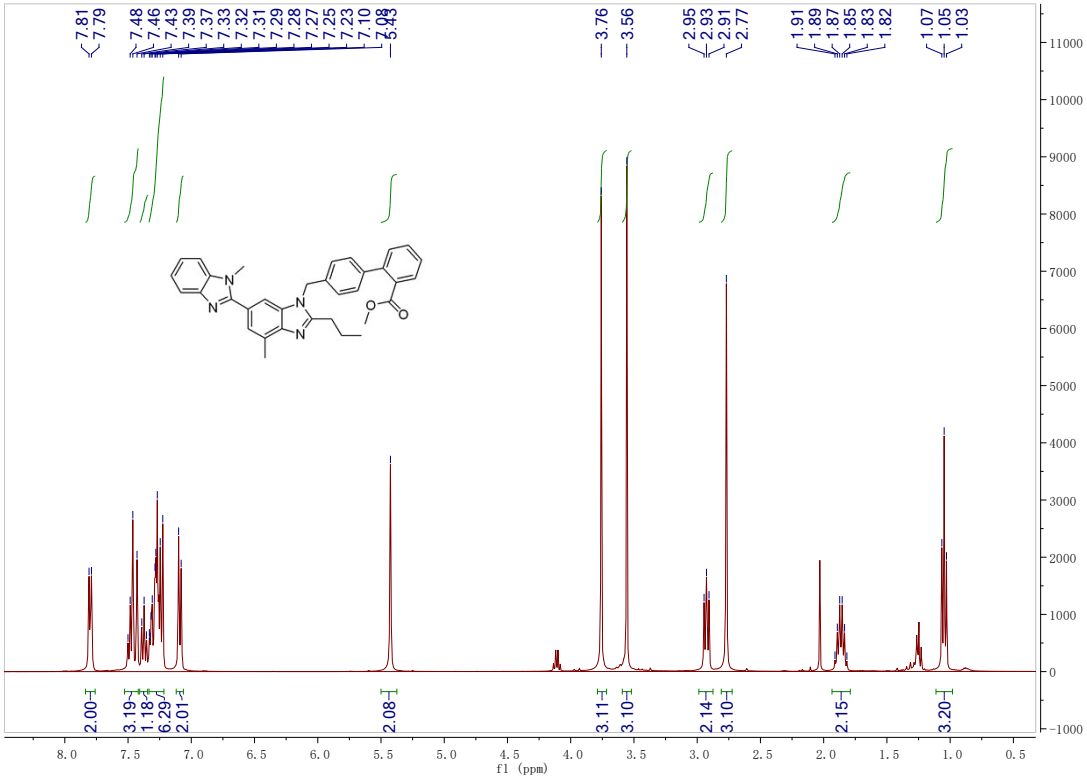

170.69 170.33 148.09 132.51 130.33 123.01 74.36 71.33 68.21 51.33 49.19 48.62 43.84 39.38 38.98 36.94 36.24 36.01 35.49 32.24 30.16 29.88 28.87 28.26 25.67 23.98 22.81 20.92 20.76 17.69 15.88
f1 (ppm)

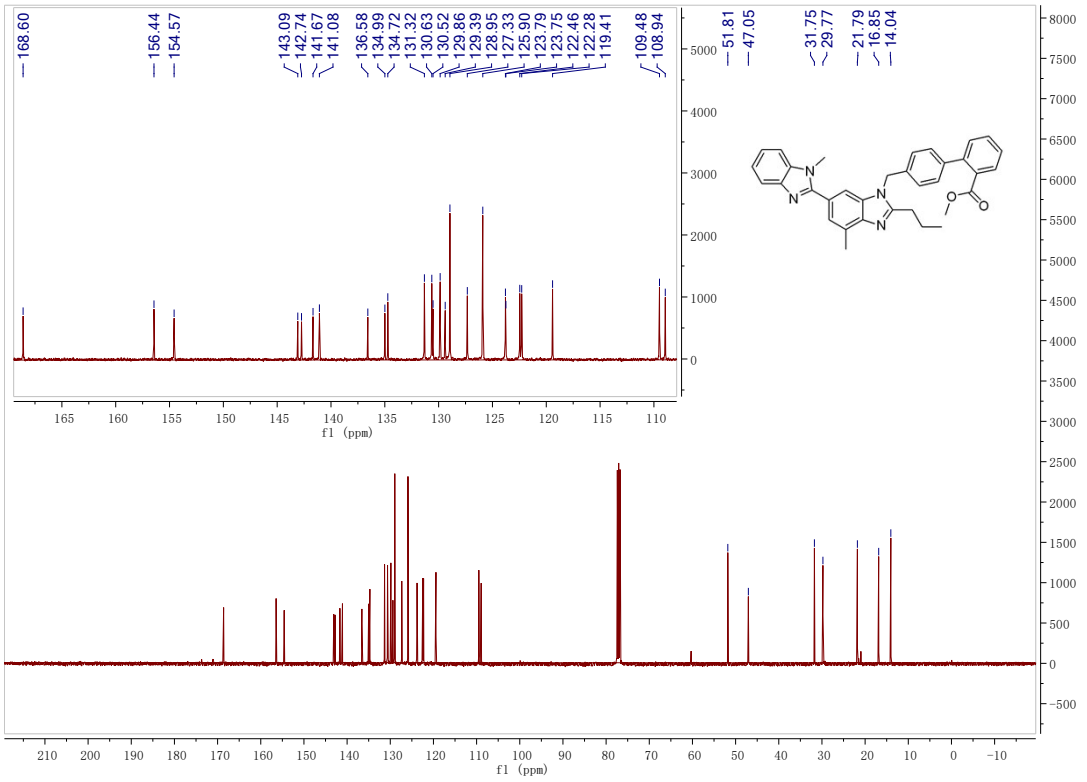
2x


6.36
6.33
5.83
5.82
5.81
5.80
5.61
5.59
5.14
4.87
4.86
3.90
3.89
3.88
3.87
3.68
3.66
3.15
3.12
2.63
2.60
2.14
2.02
2.00
1.92
1.90
1.75
1.74
1.65
1.64
1.63
1.62
1.00
1.00
0.98
1.04
2.13
0.98
3.12
1.01
0.98
1.10
1.29
2.19
1.22
4.09
3.05
f1 (ppm)

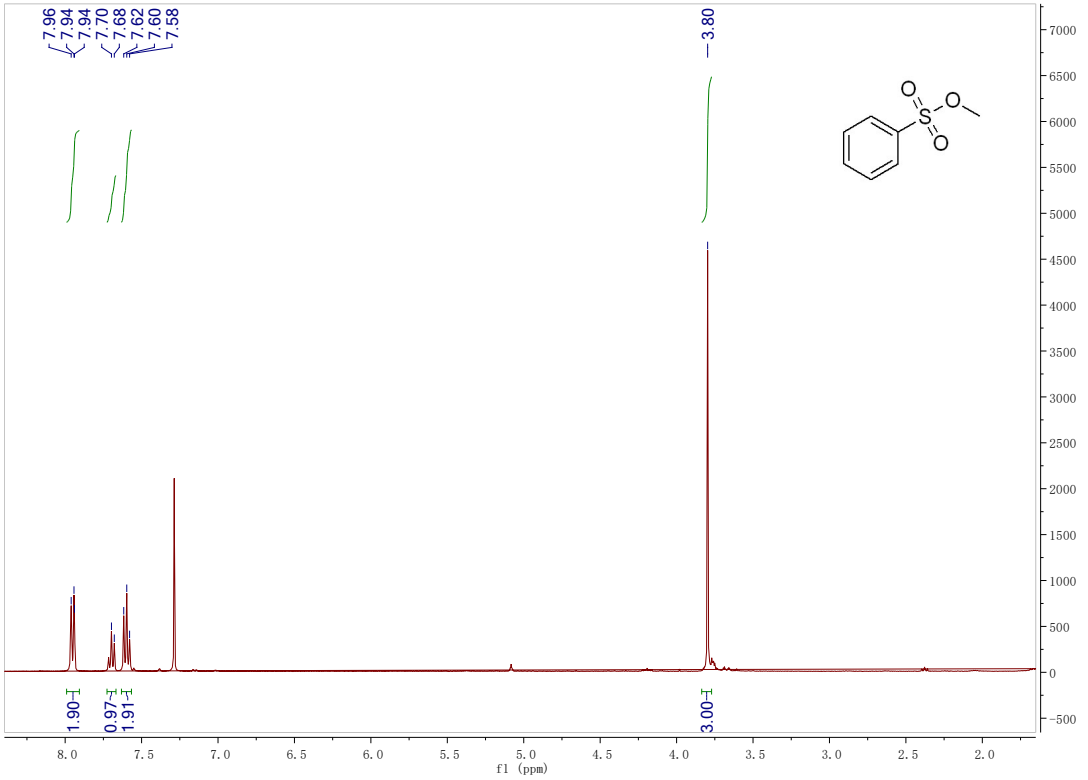

178.89
172.54
157.86
133.73
131.79
106.85
90.88
76.98
68.85
53.42
52.56
52.31
50.92
50.74
50.21
44.67
43.15
16.94
14.85
f1 (ppm)

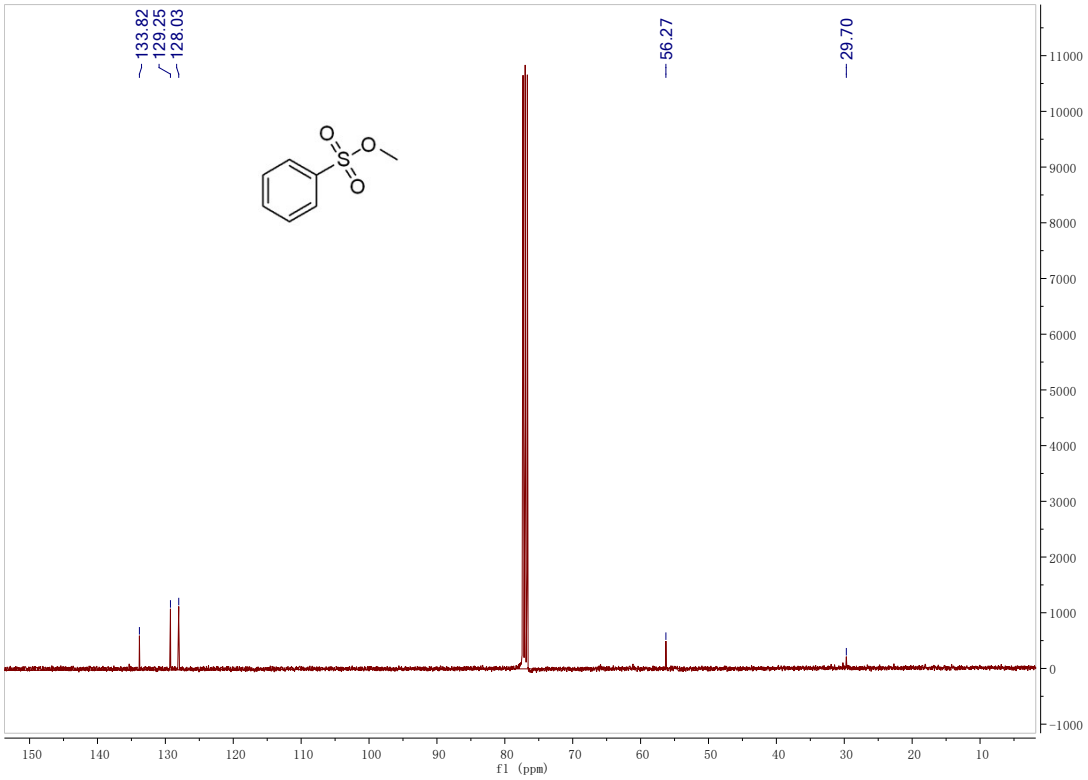
2y


7.81
7.79
7.48
7.46
7.43
7.39
7.37
7.33
7.32
7.31
7.29
7.28
7.27
7.25
7.23
7.10
7.08
7.03
3.76
3.56
2.95
2.93
2.91
2.77
1.91
1.89
1.87
1.85
1.83
1.82
1.07
1.05
1.03
2.00
3.19
1.18
6.29
2.01
2.08
3.11
3.10
2.14
3.10
2.15
3.20
f1 (ppm)

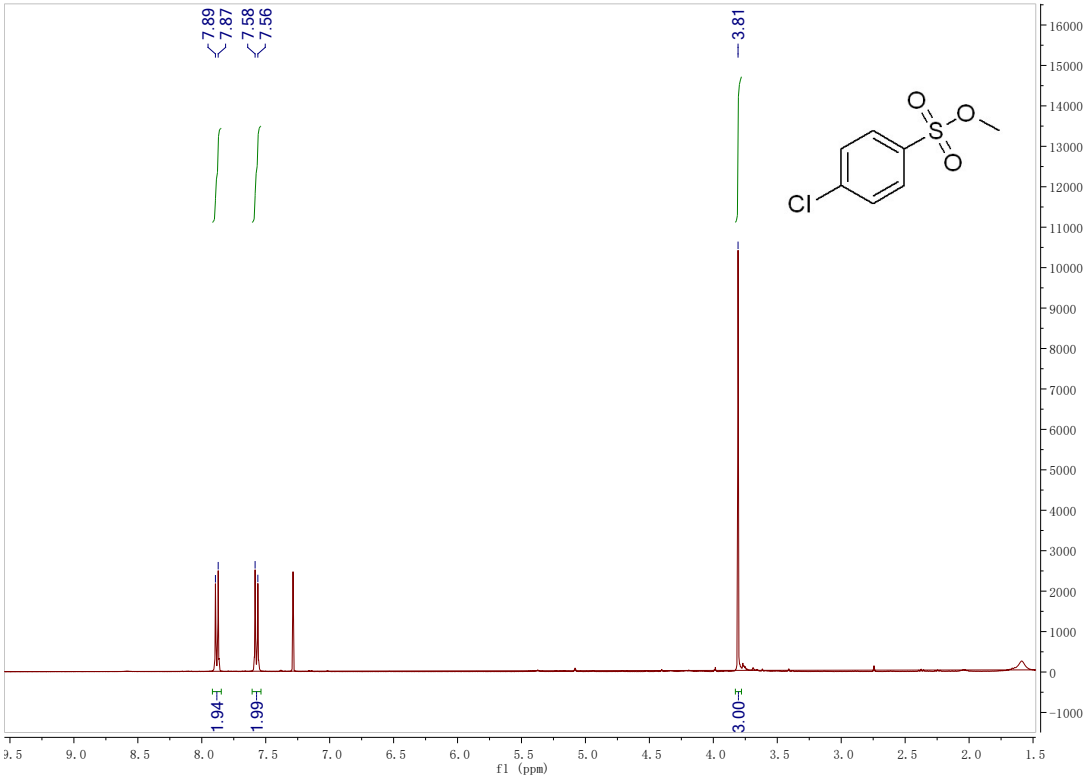

168.60
156.44
154.57
143.09
142.74
141.67
141.08
136.58
134.99
134.72
131.32
130.63
130.52
129.86
129.39
128.95
127.33
125.90
123.79
123.75
122.46
122.28
119.41
109.48
108.94
51.81
47.05
31.75
29.77
21.79
16.85
14.04
f1 (ppm)

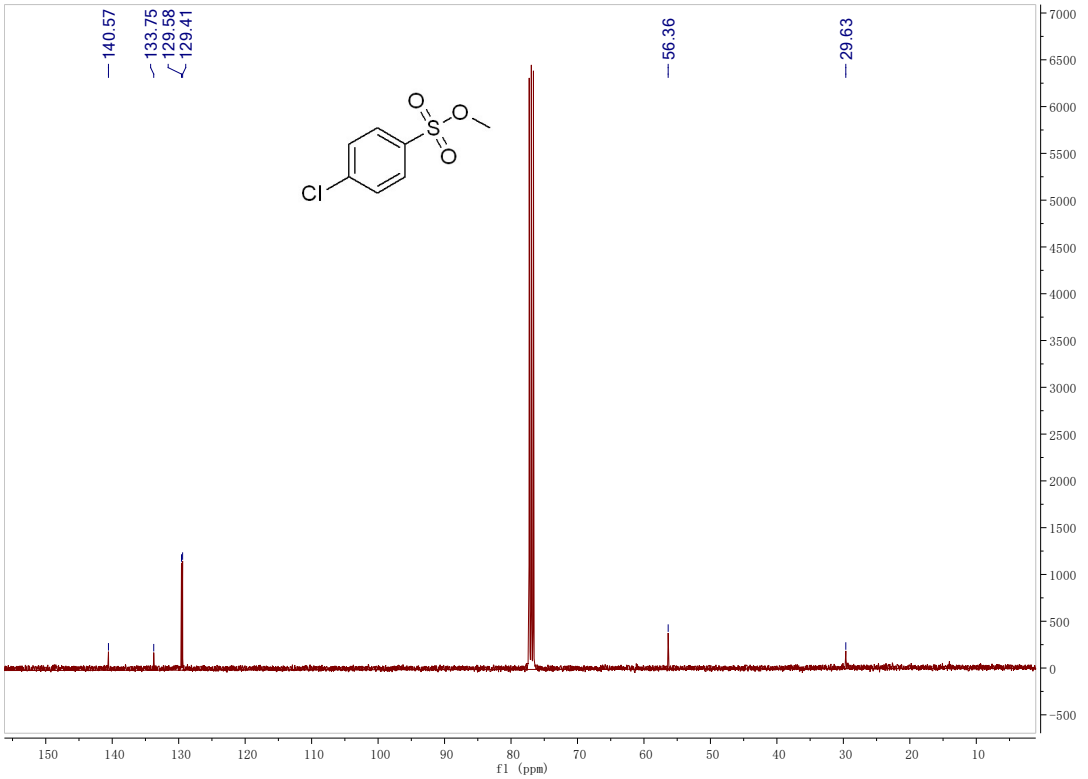
4a


7.96
7.94
7.94
7.70
7.68
7.62
7.60
7.58
3.80
1.90
0.97
1.91
3.00
f1 (ppm)

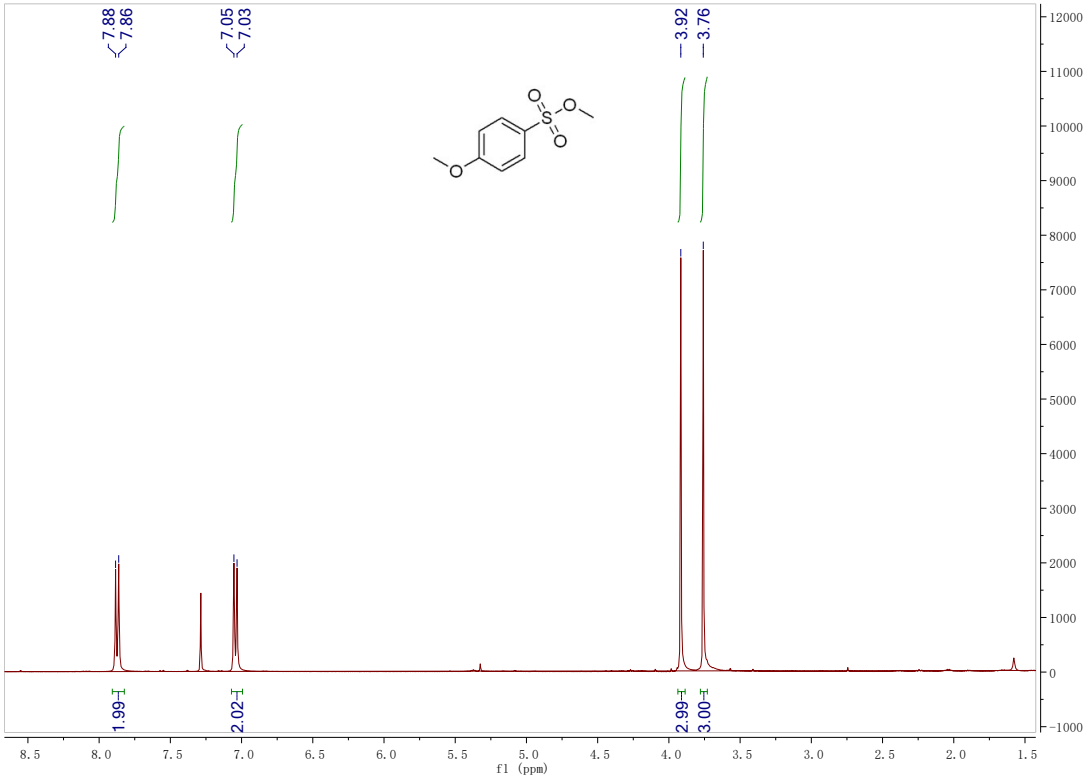

133.82
129.25
128.03
56.27
29.70
f1 (ppm)

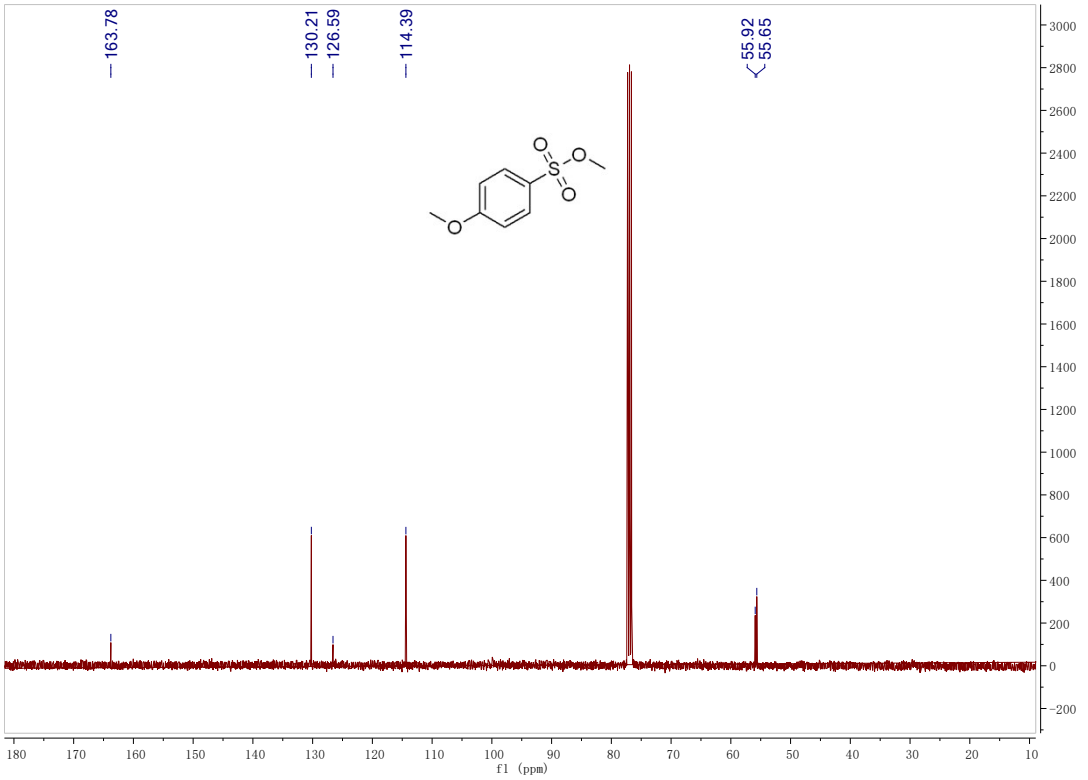
4b


7.89
7.87
7.58
7.56
3.81
1.94
1.99
3.00
f1 (ppm)

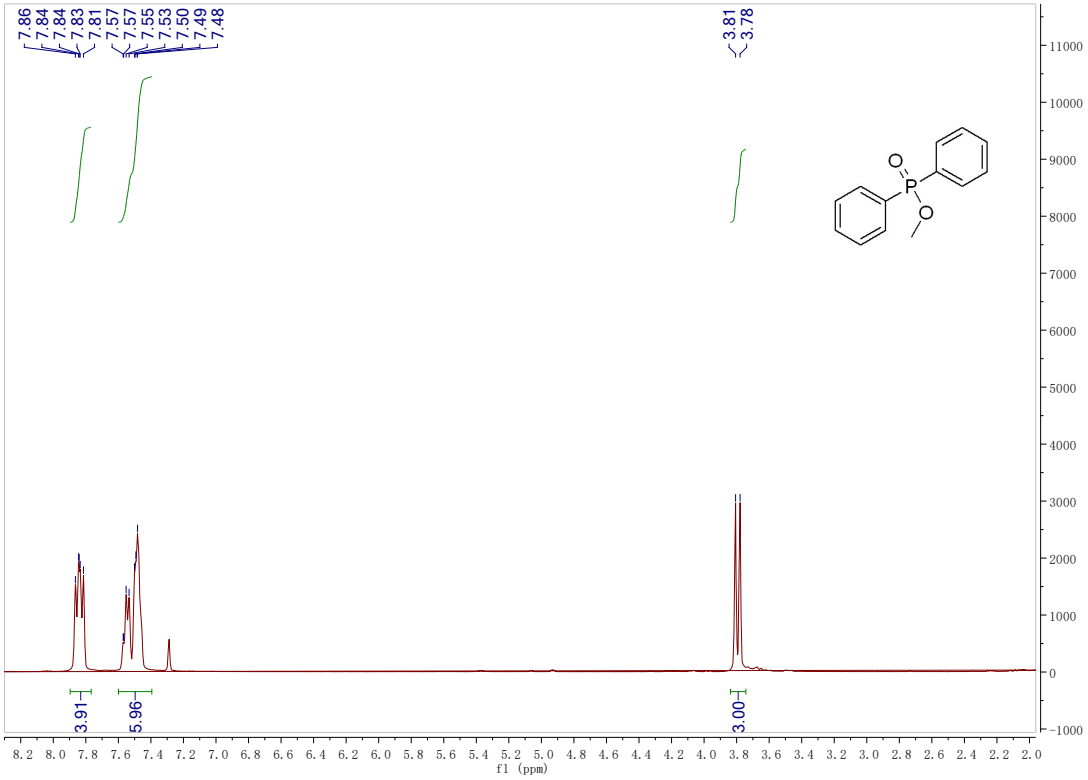

140.57
133.75
129.58
129.41
56.36
29.63
f1 (ppm)

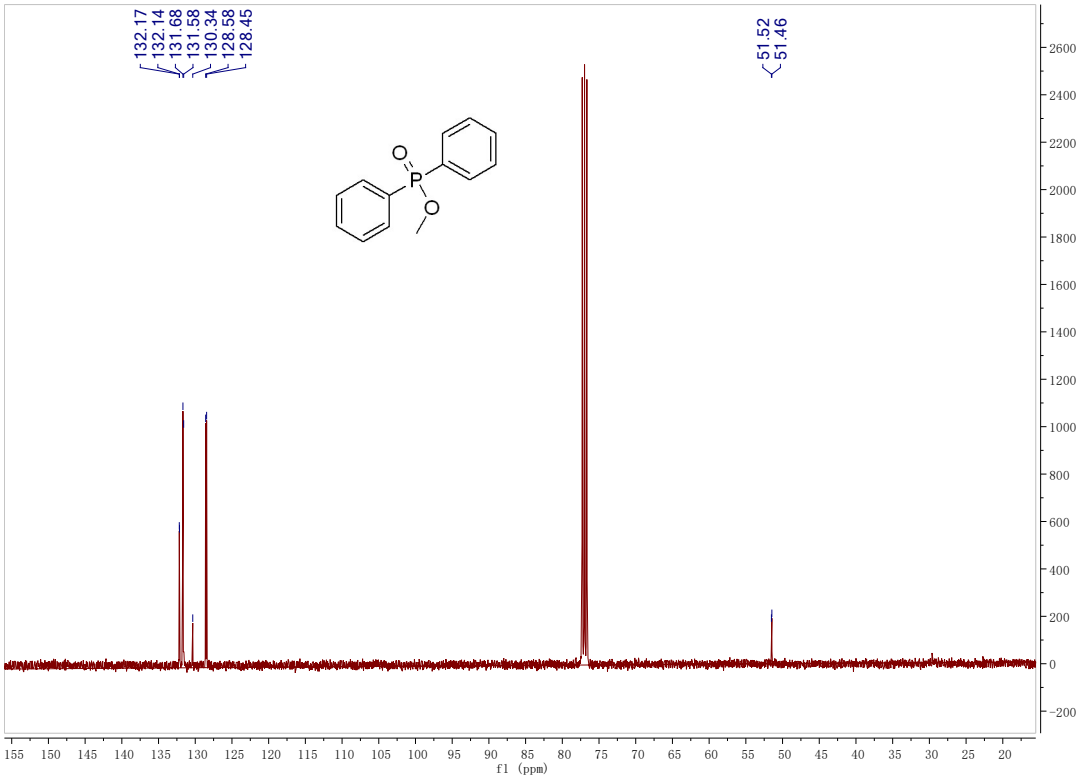
4c


7.88
7.86
7.05
7.03
3.92
3.76
1.99
2.02
2.99
3.00
f1 (ppm)

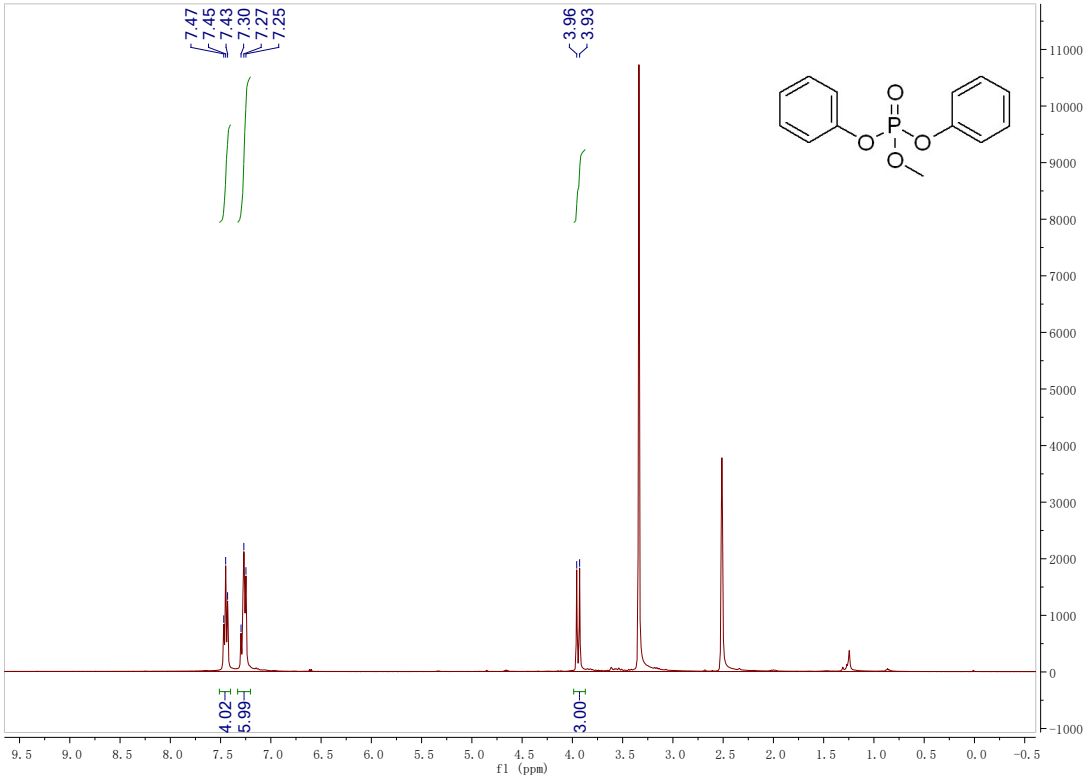

163.78
130.21
126.59
114.39
55.92
55.65
f1 (ppm)

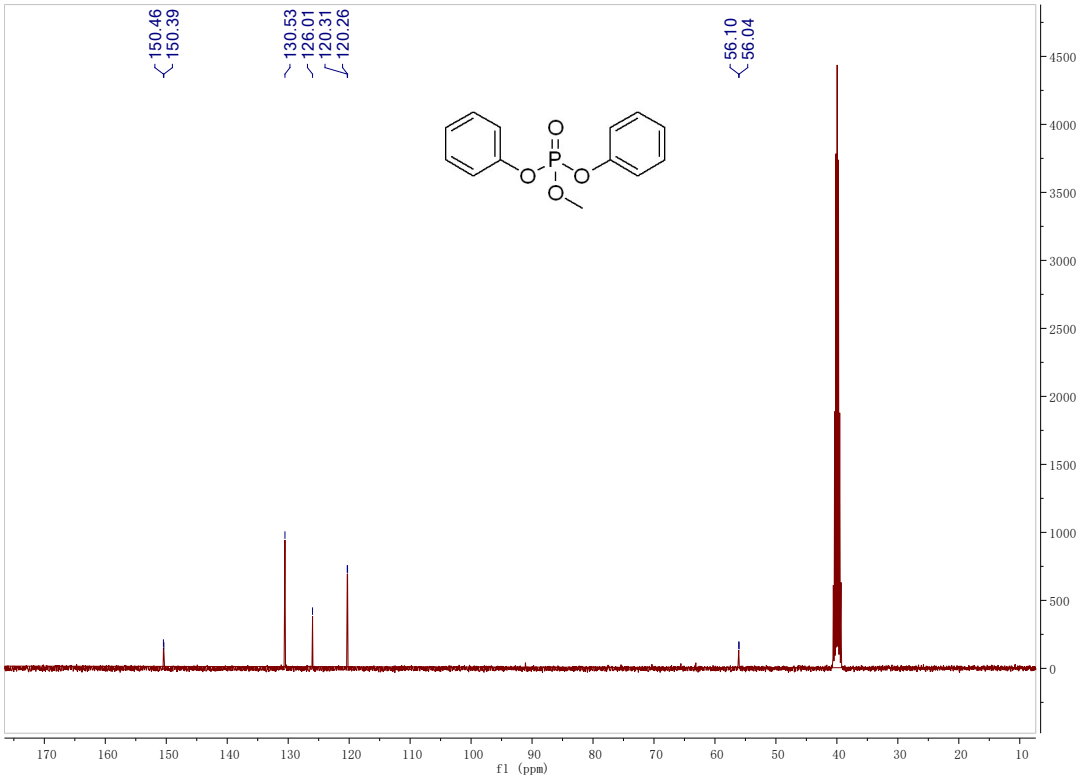
6a


7.86
7.84
7.84
7.83
7.81
7.57
7.57
7.55
7.53
7.50
7.49
7.48
3.81
3.78
3.91
5.96
3.00
f1 (ppm)


132.17
132.14
131.68
131.58
130.34
128.58
128.45
51.52
51.46
f1 (ppm)

6b


7.47
7.45
7.43
7.30
7.27
7.25
3.96
3.93
4.02
5.99
3.00
f1 (ppm)


150.46
150.39
130.53
126.01
120.31
120.26
56.10
56.04
f1 (ppm)