Electronic Supplementary Information

Oxidative Carbon–Carbon Bond Cleavage of 1,2-Diols to Carboxylic Acids/Ketones by an Inorganic-Ligand Supported Iron Catalyst

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† Electronic Supplementary Information (ESI) available: experimental conditions, supplementary table and NMR spectra. See DOI: 10.1039/d1gc02641k

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1. General information

All commercially available materials and solvents were used directly without further purification unless otherwise noted. ^{1}H NMR and ^{13}C NMR data were recorded with a Bruker spectrometer (400 MHz) using TMS as internal standard and reported relative to residual solvent signals as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. The multiplicities are denoted as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. For diol substrates, the ratio of *meso*- to *dl*-configuration diols were confirmed by ^{1}H NMR and the two diastereoisomers were marked in ^{1}H NMR and ^{13}C NMR data if they could be distinguished. The mass spectra were determined on a THERMO LTQ. HPLC was recorded on Waters e2695 and the method is showed in section 3. FT-IR spectra were recorded on a Thermo fisher Nicolet 6700. XRPD were explored on D/max 2200PC of Japan. Column chromatography was performed using 200-300 mesh base-washed silica gel.

2. Preparation of inorganic-ligand supported iron catalyst 1

The inorganic-ligand supported iron catalyst **1** $[NH_4]_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$ was prepared according to the published methods.[1-3] $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (10 g, 8.0 mmol) was added into water (160 mL) under stirring at 100 °C. Then, an aqueous solution of $Fe_2(SO4)_3$ (4.6 g, 11.5 mmol) dissolved in 40 mL water was added drop-wise to the above solution. After the addition was completed, the mixed solution was further stirred at 100 °C for 2 hour. The solution was filtered and the filtrate was cooled at room temperature for over 12 hours and precipitated as a white crystal. After re-crystallized, filtered and vacuum dried, the white crystalline catalyst **1** (8.1 g) was obtained.[1]

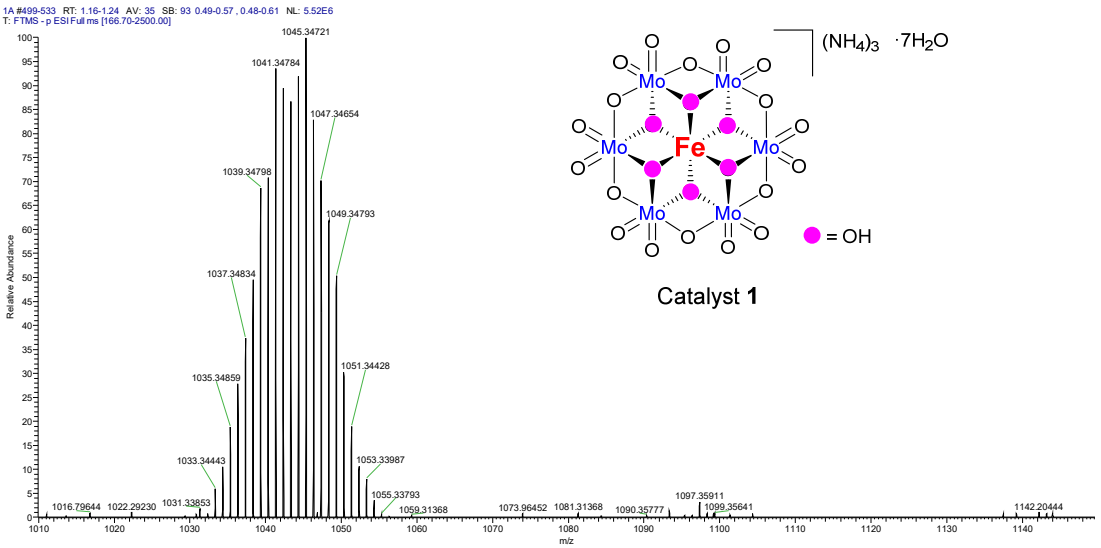


Figure S1. Zoom the area of ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$, (m/z = 1010-1150, $\{NH_4H[FeMo_6O_{24}H_6]\}^{1-}$ = 1043.34 g/mol)

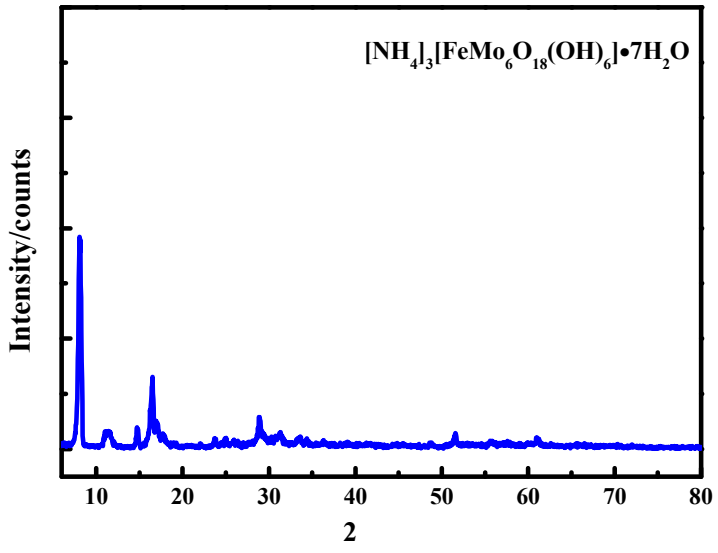


Figure S2. XRPD spectra of $(NH_4)_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$

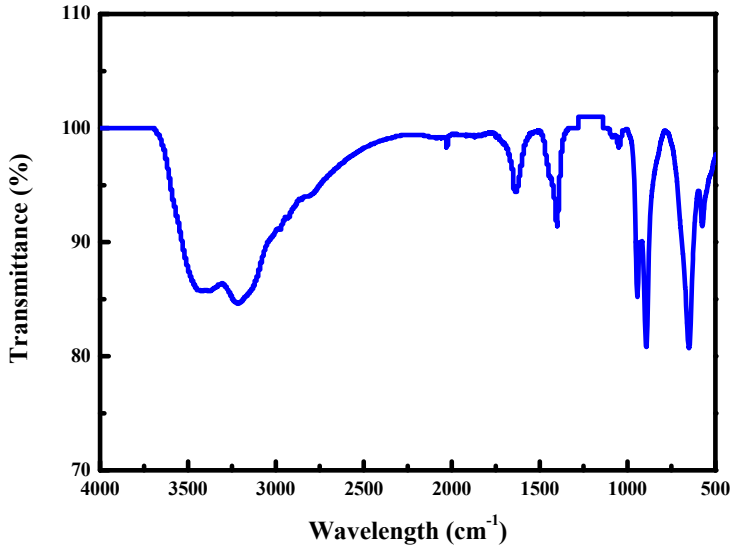


Figure S3. FT-IR spectra of $(NH_4)_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$

3. Reactions condition screening experiments

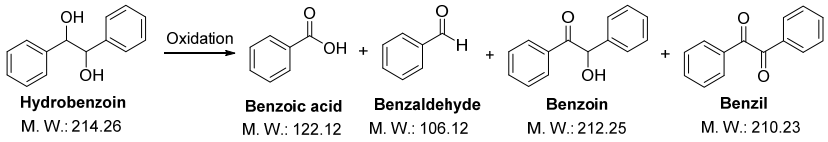


Figure S4. Screening experiments of oxidation of hydrobenzoin

1) General reaction conditions

Unless otherwise mentioned, general procedure was as follows. The catalyst **1** (including salt catalyst**,** 0.015 equiv.) and 30% H_2O_2 (0.53 mL) were added into the solution of hydrobenzoin (107 mg, 0.47 mmol) in 2 mL solvent. The mixture was heated at 80 °C for 18 hours and monitored by TLC (PE / EA = 3:1) or HPLC.

2) HPLC test of reaction mixtures

a) Samples preparation:

Standard sample: Five materials [216 mg hydrozoin (1.008 mmol), 121 mg benzoic acid (0.991 mmol), 118.1 mg benzaldehyde (1.113 mmol), 214 mg benzoin (1.008 mmol), and 213.3 mg benzil (1.015 mmol)] were mixed in 50 mL acetonitrile to obtain a solution with about 1 mmol/50 mL concentration for any component. Took 0.3 mL of above mixed solution and diluted with acetonitrile to 1.5 mL, which was stored to be used.

Reaction sample: about 0.1 mL of reaction mixture was diluted with about 5.0 mL acetonitrile. After filtration, HPLC test was performed as following methods.

b) HPLC method:

Equipment: Waters e2695 Separation Module

Column: Symetry ShieldRP™ 18.5 μm, 4.6×250 mm

Mobile A: 0.1% TFA; Mobile B: acetonitrile

Dilute: acetonitrile

Flow: 1 mL/min:

Wavelength: 230 nm

Column Temp: 25°C

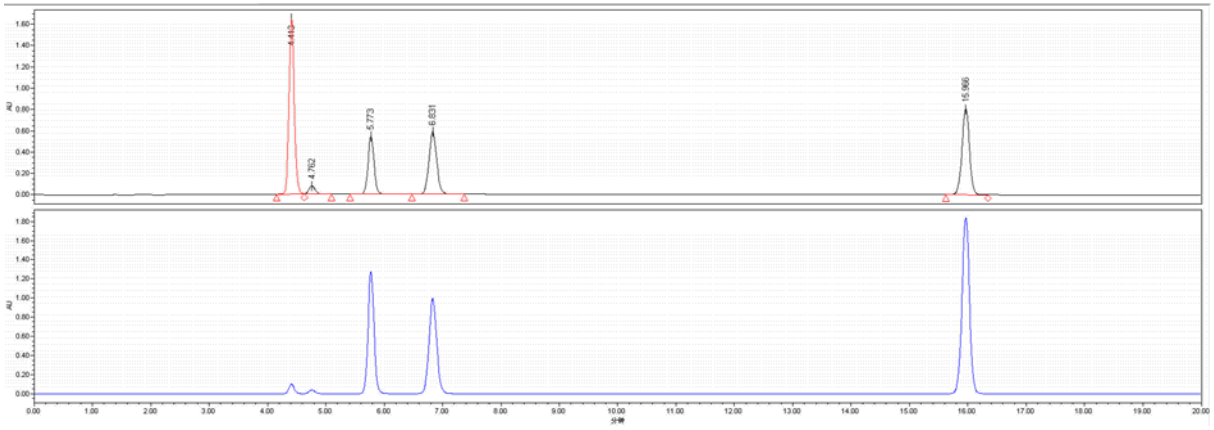
Volume: 5 μL

Time: 25 min

Time，min	A%	B%
0	50	50
15	50	50
20	30	70
25	20	80

3) Data Treatment

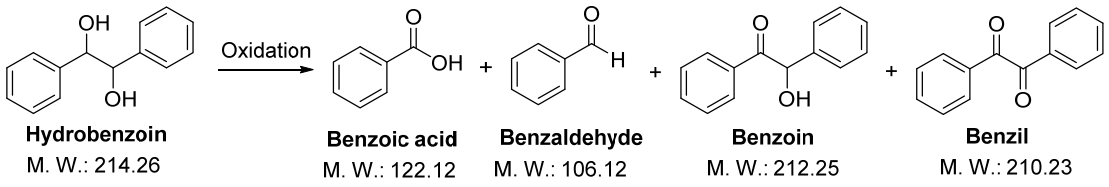
Standard sample: the results were calculated as area percentage in 230 nm, which is the maximum absorption wavelength of benzoic acid. Retention time: benzoic acid 4.413 min, hydrobenzoin 4.762 min, benzaldehyde 5.773 min, benzoin 6.831 min, benzil 15.966 min.



Note: Top 230 nm, down 254 nm.

Figure S5. HPLC spectra in different wavelengths

To calculate the conversion rate and mol yield, HPLC area percentages should be transferred the mol ratio as follows, which afforded the absorption factor based on mole ratio.



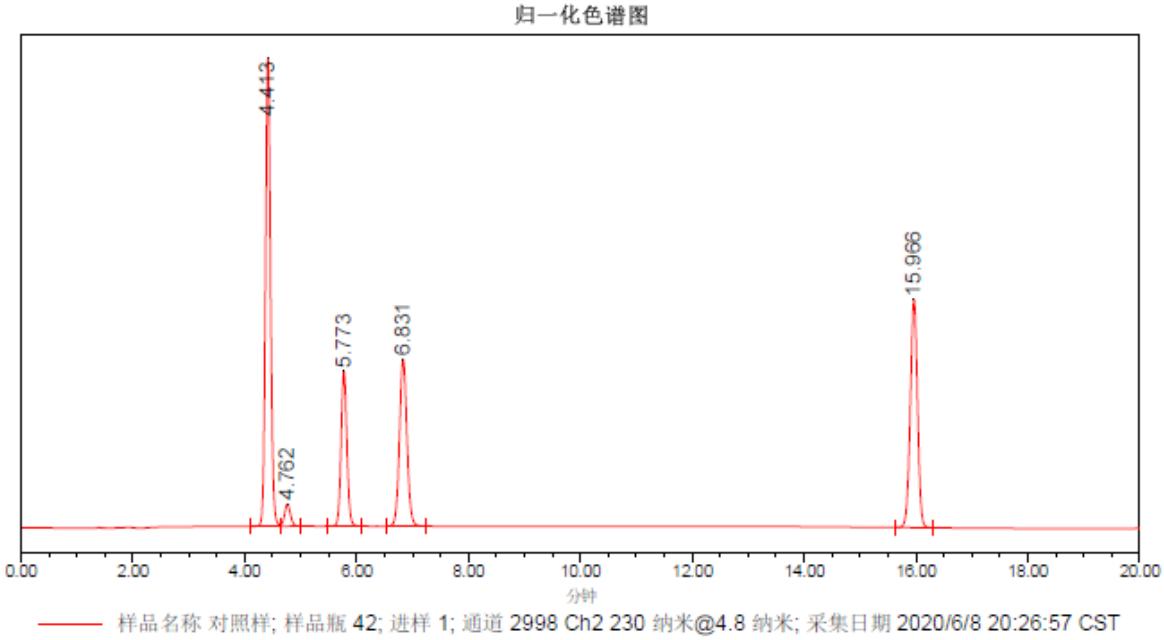
Hydrobenzoin
M. W.: 214.26

Benzoic acid
M. W.: 122.12

Benzaldehyde
M. W.: 106.12

Benzoin
M. W.: 212.25

Benzil
M. W.: 210.23



名称:

	进样	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)
1	1	4.413	10366131	37.73	1646503
2	1	4.762	575253	2.09	78033
3	1	5.773	3915206	14.25	545393
4	1	6.831	5446622	19.82	587570
5	1	15.966	7174151	26.11	802556

Figure S6. Typical HPLC spectra in 230 nm

a) Calculated Absorption Factor of five compounds:

	Hydrobenzoin	Benzoic acid	Benzaldehyde	Benzoin	Benzil
Sample quantity (M, mg)	216	121	118.1	214	213.3
Tested area percentage (A, %)	2.09	37.73	14.25	19.82	26.11
Mol. Weight (MW)	214.26	122.12	106.12	212.25	210.23
Calculated Absorption Factor based on Mole ratio (AFM*) [a]	**2.13**	**38.11**	**12.80**	**19.63**	**25.68**

Notes: [a] AFM = A/(M/MW)

b) HPLC mol percentages of reaction samples:

HPLC mol percentages were calculated based on above AFM value. The calculated method was showed as following table. **NOTE:** Since 1 mol hydrobenzoin generates 2 mol benzoic acid or benzaldehyde, mol% in reaction mixture should be divided by two.

	Hydrobenzoin	Benzoic acid	Benzaldehyde	Benzoin	Benzil
Tested area percentage (A_{sample}, %)	$A_{hydrobenzoin}$	$A_{benzoic\ acid}$	$A_{benzaldehyde}$	$A_{benzoin}$	A_{benzil}
Calculated AFM value	2.13	38.11	12.80	19.63	25.68
Calculated Mol Ratio (MR)[a]	$A_{hydrobenzoin}$ /AFM	$A_{benzoic\ acid}$/AFM	$A_{benzaldehyde}$/AFM	$A_{benzoin}$/AFM	A_{benzil}/AFM
Calculated Mol % based on MR	**$MR_{hydrobenzoin}$ /(M_{total})** [a]	**1/2 $MR_{benzoic\ acid}$ /(M_{total})**	**1/2 $MR_{benzaldehyde}$ /(M_{total})**	**$MR_{benzoin}$ /(M_{total})**	**MR_{benzyl} /(M_{total})**

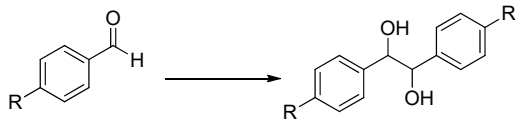
Notes: [a] $M_{total} = MR_{hydrobenzoin} + 1/2MR_{benzoic\ acid} + 1/2MR_{benzaldehyde} + MR_{benzoin} + MR_{benzil}$

4. Preparation of substrates (1,2-diols)

The substrates **2d, 2j, 2k, 2n, 2o**, **2p**, **4a**, **4b,** and **4f** were purchased from Whmall Shanghai Co., Ltd., Leyan Shanghai Co., Ltd., and Aladdin-E Shanghai Co., Ltd.. The others were prepared as following procedures.

Procedure A: Reduction-coupling of aldehyde by transition metal. For **2a** and **2b**, they were prepared using magnesium/iodine. After the starting material (ketone or aldehyde. 1 g, 1.0 equiv.) was added into 10 mL NH_4Cl solution (1 mol/L), Mg (20 equiv.) was added into with stirring overnight. The reactant was quenched carefully with 1 mol/L hydrochloric acid under 10 °C, and extracted with dichloromethane or ethyl acetate. The resulted organic phase was washed with water and brine, drive over anhydrous Na_2SO_4, and concentrated to obtain the crude diols. After purification was executed by column chromatography, pure diols were obtained as solid.

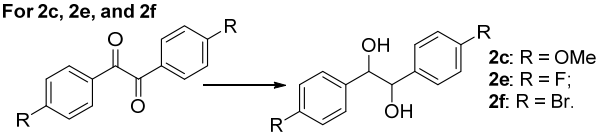
For 2a and 2b



2a: R_1 = Me;
2b: R_1 = Et.

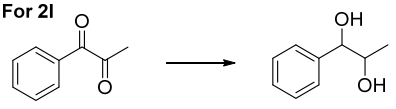
Procedure B: Reduction of acyloin and 1,2-diketone by $NaBH_4$. Starting material (acyloin or 1,2-diketone, 1.0 equiv.) was added into methanol (10 V) with stirring. After the mixture was cooled below 0 °C, $NaBH_4$ (2.0 equiv. for acyloin; 4.0 equiv. for 1,2-diketone) was added in portions under 0 °C. The mixture was stirred for 30–60 minutes and monitored by TLC. Then the reactant was extracted with dichloromethane or ethyl acetate and water. The resulted organic phase was washed with water and brine, drive over anhydrous Na_2SO_4, and concentrated to obtain the 1,2-diol. If necessary, purification was conducted by column chromatography. The materials **hydrobenzoin, 2c**, **2e, 2f, 2h, 2i, 2l**, and **2m** were obtained by this method.

For 2c, 2e, and 2f

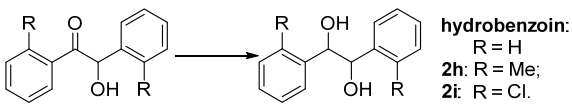


2c: R = OMe
2e: R = F;
2f: R = Br.

For 2l

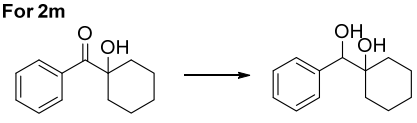


For hydrobenzoin, 2h, and 2i

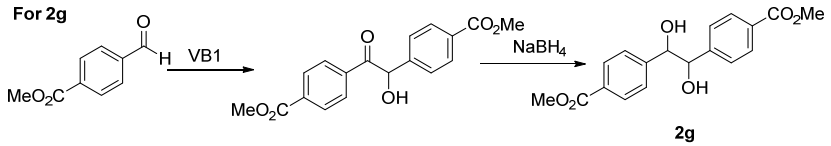


hydrobenzoin: R = H
2h: R = Me;
2i: R = Cl.

For 2m

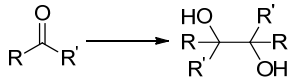


For **2g**, the benzoin intermediate was prepared according to the reference (Bingbing Guo, Fugang Li, Chiming Wang, Liangliang Zhang, and Daofeng Sun, A Rare (3,12)-Connected Zirconium Meta-Organic Framework with Efficient Iodine Adsorption Capacity and pH Sensing, *Journal of Materials Chemistry A*, 2019, 7: 13173-13179.). Then **2g** was obtained by reduction with $NaBH_4$ as procedure B.

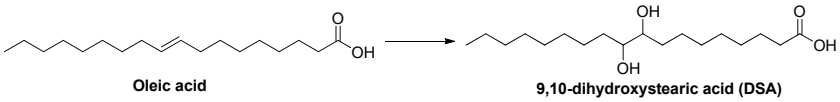


Procedure C: Reduction-coupling of ketone. For **4c**, **4d** and **4e**, they were prepared using zinc/zinc dichloride system. After the material (ketone. 1 g, 1.0 equiv.) was added into 10 mL THF/H_2O solution (1 mol/L), Zn (5 equiv.) and $ZnCl_2$ (5 equiv.) were added into with stirring overnight. After work-up as above procedure and purification by column chromatography, pure diols were obtained.

For 4c, 4d and 4e



Procedure D: Preparation of 9,10-dihydroxystearic acid (DSA). The substrate was prepared from natural oleic acid. Oleic acid (2.8 g) was mixed with formic acid 10 mL, and 30% hydrogen peroxide (1.2 g) was added by a dropping funnel under vigorous stirring. A homogeneous solution was obtained in about 30 minute and reacted at 40 °C for 3 h. The reaction mixture was extracted with ethyl acetate and quenched with $Na_2S_2O_3$. Sodium hydroxide solution was added and refluxed for 1 h. After cooling, the solution was poured into excessive 3 mol/L hydrochloric acid under full stirring. The organic layer is separated and soon solidified. After filtration, crude product was re-crystallized with ethanol and gave 1.4 g of 9,10-dihydroxystearic acid.



5. Oxidative carbon–carbon bond cleavage of 1,2-diols

Unless otherwise mentioned, general procedure was as follows.

Vinical diols (1-5 mmol, 1.0 equiv.) was added into the mixture of catalyst **1** (0.015 equiv.) in acetic acid (4 mL for 1 mmol diol). 30% H_2O_2 (1.2 mL for 1 mmol diol. If tetra-substituted diols were used as the substrates, 0.7 mL for 1 mmol diol was added.) was added in 3 portions per 3 hours. After the addition was finished, the reaction mixture was stirred for additional 3 hours, which was monitored by TLC prior to HPLC test. If the reaction was not completed, more H_2O_2 should be added to promote the cleavage.

The reaction mixture was filtered and/or added into water. The crude product was obtained by filtration or extracted with ethyl acetate if no obvious precipitate. If necessary, purification was performed by column chromatography to obtain the cleavage product.

In particular, 9,10-dihydroxystearic acid (DSA) was used for the oxidation as follows. 1.0 g 9,10-dihydroxystearic acid (3.16 mmol) was added into the mixture of catalyst **1** (60 mg, 0.015 equiv.) in acetic acid (12 mL). 30% H_2O_2 (5 mL) was added in 3 portions per 3 hours. The reaction was monitored by TLC. After the addition was finished, the reaction mixture was stirred for additional 3 hours. The reaction mixture was quenched with $Na_2S_2O_3$, and extracted with ethyl acetate to obtain the crude product. After column chromatography, pelargonic acid (0.36 g) was obtained in 72% yield as a light-yellow liquid, and azelaic acid (0.44 g) was obtained in 74% yield as a white solid with low solubility.

6. Scale-up experiments and catalyst recovery experiments

Scale-up experiments was performed on a 3.8 g scale of hydrobenzoin as general procedure as item 5.

After the oxidation was finished, the reaction mixture was quenched by sodium thiosulfate, concentrated, and dispersed into ethyl acetate and water. The organic phase was collected to afford product. The aqueous phase was basified with ammonia water, and the precipitate was collected by adding acetonitrile to the above aqueous phase. After filtration, the catalyst could be separated and directly used for the subsequent oxidation without further purification.

The recovered catalyst was used for the oxidation on a 1 mmol scale and monitored by HPLC. After recovered for 6 times, the yields were showed as follows, and the recovered catalyst was tested by FT-IR and XRPD, which indicated no obvious change and could give similar results for oxidation reaction.

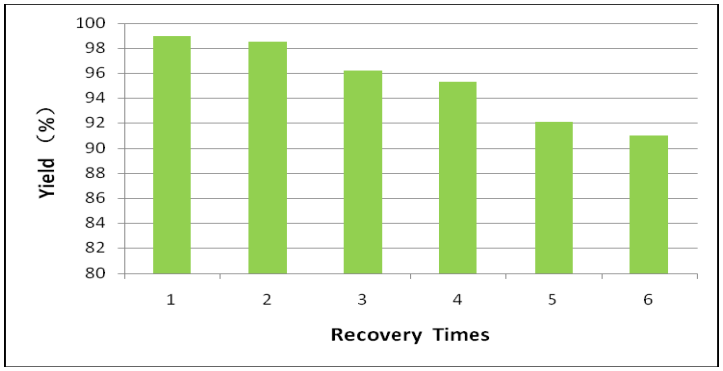


Figure S7. Catalyst recovery experiment of carbon–carbon bond cleavage of hydrobenzoin

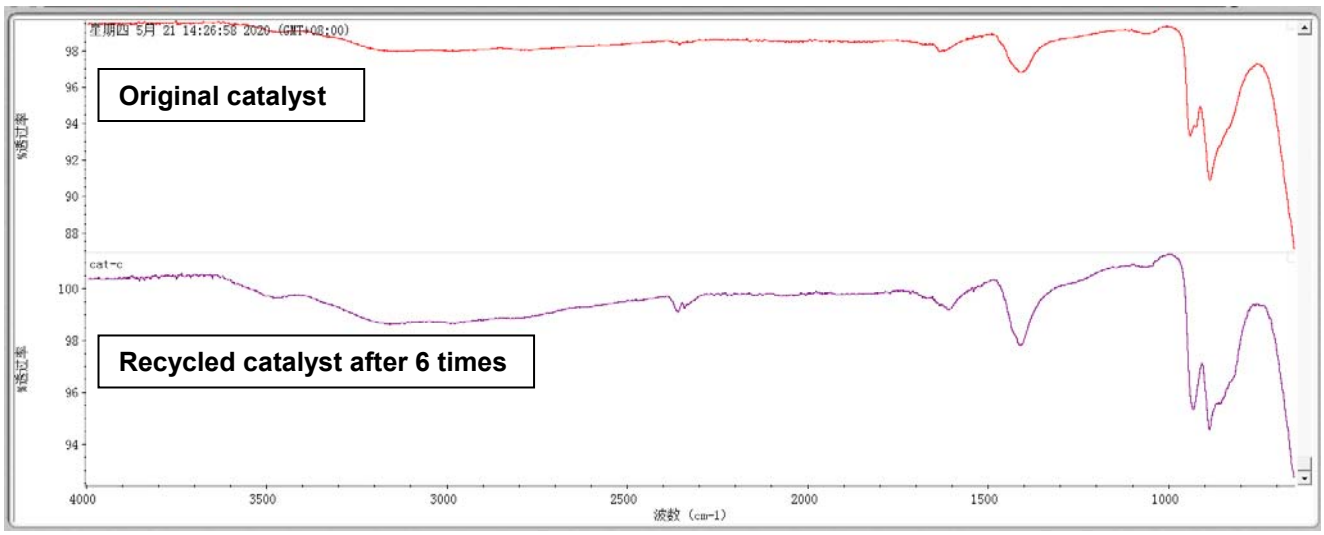


Figure S8. FT-IR spectra of catalyst **1** before and after reaction.

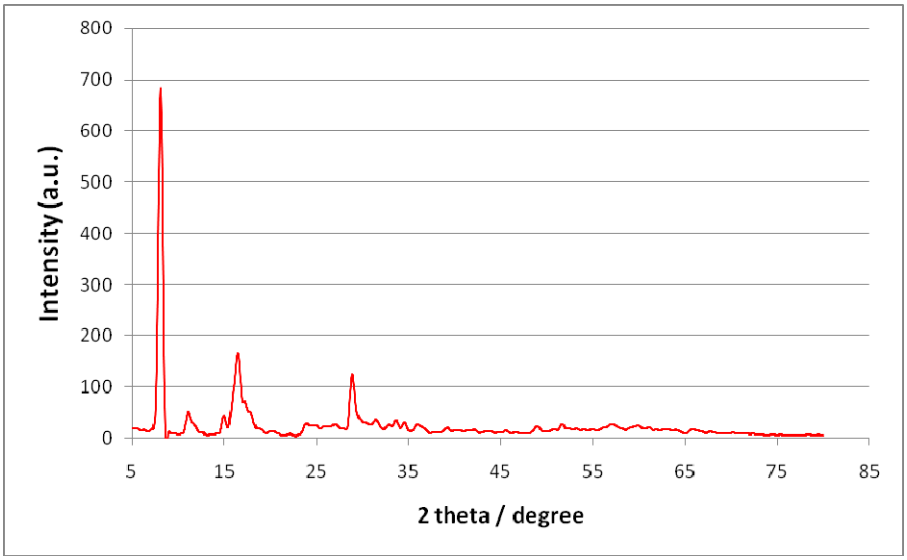
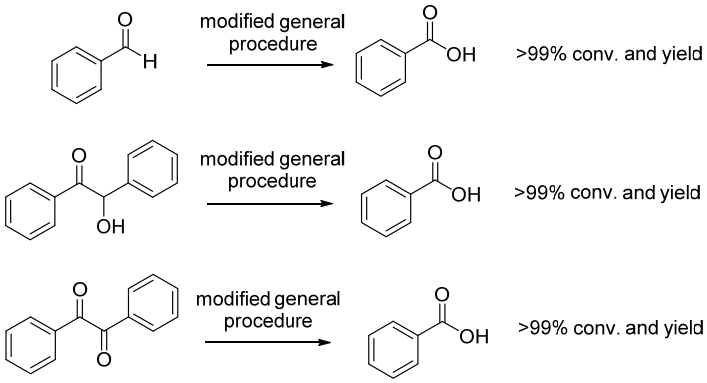


Figure S9. XRPD spectra of catalyst **1** after reaction.

7. Control experiments of mechanism study

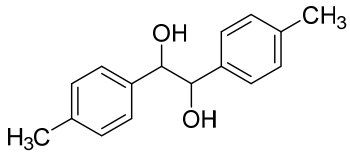
According to the screening experiments, possible intermediates (benzaldehyde, benzoin, and benzil) might generate with benzoic acid. They were used for the oxidative reaction as modified general procedure.

Benzaldehyde, benzoin or benzil (1 mmol, 1.0 equiv.) was added into the mixture of catalyst **1** (0.015 equiv.) in acetic acid (4 mL for 1 mmol substrate). 30% H_2O_2 (0.7 mL for 1 mmol diol) was added in two portions per 3 hours and stirred at 80 °C. After the addition was finished, the reaction mixture was monitored by TLC and stirred for additional 3 hours if necessary, which was monitored by TLC prior to HPLC test. The results indicated quantitative conv. rate and yield.

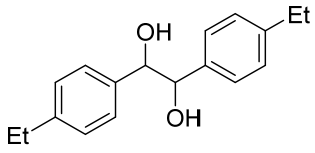


8. NMR spectra of substrates (1,2-diols) and products (carboxylic acids and ketones)

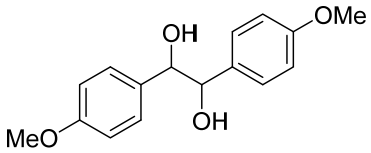
8.1 NMR spectra of substrates



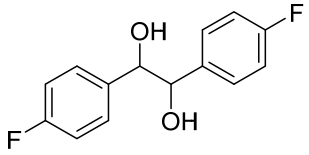
Compound **2a**[4]**.** ^{1}H NMR (400 MHz, DMSO-d_6, *meso: dl* = 3.4 : 1) δ 7.18 – 6.89 (m, 8H), 5.25 (dd, 0.5H, *dl*), 5.08 (dd, *J* = 3.1, 1.5 Hz, 1.5H, *meso*), 4.56 – 4.47 (m, 2H), 2.26 (s, 4.5H,*meso*), 2.22 (s, 1.5H,*dl*). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.73, 139.79 (*dl*), 136.00 (*dl*), 135.87, 128.38(*dl*), 128.30, 127.75, 127.61(*dl*), 78.01, 77.32, 21.21, 21.17(*dl*).



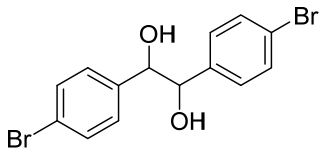
Compound **2b**[5]**.** ^{1}H NMR (400 MHz, DMSO-d_6, *meso: dl* = 0.7 : 1) δ 7.17 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (s, 5H), 5.23 (dd, *J* = 2.8, 1.5 Hz, 1.2H, *dl*), 5.14 – 5.00 (m, 0.8H, *meso*), 4.61 – 4.40 (m, 2H), 2.61 – 2.51 (m, 4H), 1.15 (dt, *J* = 15.1, 7.6 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.45, 142.39, 141.37, 140.25, 127.84, 127.64, 127.19, 127.15, 77.88 (*dl*), 77.35(*meso*), 28.36 (*meso*), 28.29 (*meso*), 16.26 (*dl*), 16.15 (*dl*).



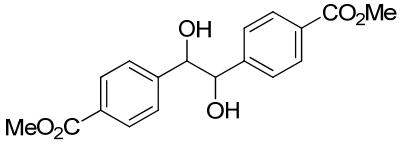
Compound **2c**[6,7]**.** ^{1}H NMR (400 MHz, DMSO-d_6, only *meso*-form after recrystallization.) δ 7.13 (d, *J* = 8.7 Hz, 4H), 6.80 (d, *J* = 8.7 Hz, 4H), 5.05 (dd, *J* = 3.0, 1.5 Hz, 2H), 4.48 (dd, *J* = 3.0, 1.4 Hz, 2H), 3.72 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.47, 135.79, 128.85, 113.12, 77.06, 55.40.



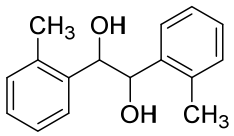
Compound **2e**[7]. ^{1}H NMR (400 MHz, DMSO-d_6, *meso: dl* = 5.3 : 1) δ 7.23 (ddd, *J* = 8.8, 5.5, 2.5 Hz, 3H), 7.12 – 6.93 (m, 5H), 5.34 (dd, *J* = 3.2, 1.5 Hz, 2H), 4.56 (dd, *J* = 3.2, 1.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.61 (d, *J* = 241.6 Hz, recorded as 162.82 and 160.41), 139.62 (d, *J* = 3.0 Hz, recorded as 139.64 and 139.61. *meso*), 138.72(d, *J* = 3.0 Hz, recorded as 138.73 and 138.70. *dl*), 129.54 (d, *J* = 8.0 Hz, recorded as 129.58 and 129.50. *meso*), 129.38 (d, *J* = 8.0 Hz, recorded as 129.42 and 129.34. *dl*),114.42 (d, *J* = 21.0 Hz, recorded as 114.53 and 114.32. *meso*), 114.40 (d, *J* = 21.0 Hz, recorded as 114.50 and 114.29. *dl)*, 77.07(*dl*), 76.64 (*meso*).



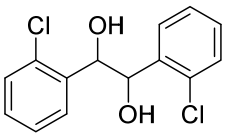
Compound **2f**[8]**.** ^{1}H NMR (400 MHz, DMSO-d_6, *meso: dl* = 6.7 : 1) δ 7.47 – 7.41 (m, 4H), 7.38 (d, *J* = 8.4 Hz, 0.6H), 7.20 – 7.14 (m, 4H), 7.06 (d, *J* = 8.4 Hz, 0.6H), 5.43 (dd, *J* = 3.2, 1.5 Hz, 2H), 4.53 (dd, *J* = 3.1, 1.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.83 (*meso*), 141.98 (*dl*), 130.67(*meso*), 130.60(*dl*), 130.00(*meso*), 129.79(*dl*), 120.25, 76.73(*dl*), 76.58(*meso*).



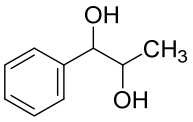
Compound **2g**[9]**.** ^{1}H NMR (400 MHz, DMSO-d_6, *meso: dl* = 5.8 : 1) δ 7.85 (d, *J* = 8.4 Hz, 4H), 7.77 (d, *J* = 8.4 Hz, 0.7H. *dl*), 7.36 (d, *J* = 8.3 Hz, 4H), 7.25 (d, *J* = 8.3 Hz, 0.7H. *dl*), 5.56 (dd, *J* = 3.2, 1.5 Hz, 2H), 4.68 (dd, *J* = 3.1, 1.5 Hz, 2H), 3.83 (d, J = 7.9 Hz, 6H).. ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.74, 148.95, 148.16 (*dl*), 128.77, 128.65 (*dl*), 128.55, 128.08, 127.82 (*dl*), 76.88, 52.48..



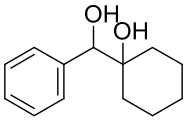
Compound **2h**[7]**.** ^{1}H NMR (400 MHz, DMSO-d_6, *meso: dl* = 1 : 1) δ 7.50 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.39 – 7.28 (m, 1H), 7.20 – 6.97 (m, 5H), 6.88 (dd, *J* = 7.2, 1.2 Hz, 1H), 5.35 (t, *J* = 1.8 Hz, 1H, *dl*), 5.08 (dd, *J* = 2.7, 1.5 Hz, 1H, *meso*), 4.90 (dd, *J* = 2.9, 1.3 Hz, 1H, *meso*), 4.75 (t, *J* = 1.6 Hz, 1H, *dl*), 2.14 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.10, 140.74, 135.88, 135.35, 129.89, 129.56, 128.39, 127.82, 127.15, 126.78, 125.67, 125.58, 74.00 (*dl*), 72.93 (*meso*), 19.48 (*meso*), 19.10 (*dl*).



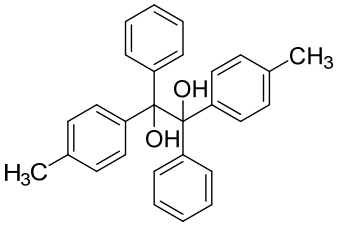
Compound **2i**[10]**.** ^{1}H NMR (400 MHz, DMSO-d_6, *meso: dl* = 1 : 1) δ 7.72 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.37 – 7.14 (m, 7H), 5.63 (dd, *J* = 3.2, 1.3 Hz, 1H, *dl*), 5.53 – 5.45 (m, 1H, *meso*), 5.25 (dd, *J* = 3.3, 1.2 Hz, 1H), 5.08 (dd, *J* = 4.4, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.60, 139.37, 132.75, 131.35, 131.01, 130.25, 128.95, 128.84, 128.50, 126.87, 126.71, 71.80, 71.69.



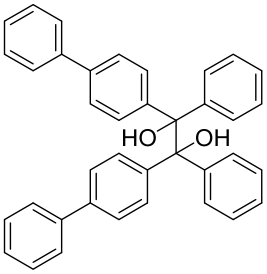
Compound **2l**[11]**.** ^{1}H NMR (400 MHz, DMSO-d_6, *meso: dl* = 3 : 1) δ 7.39 – 7.15 (m, 5H), 5.16 (dd, *J* = 16.8, 4.2 Hz, 1H), 4.60 (d, *J* = 5.5 Hz, 0.25H, *dl*), 4.46 (d, *J* = 5.5 Hz, 0.75H, *meso*), 4.36 (t, *J* = 4.8 Hz, 0.75H, *meso*), 4.29 (t, *J* = 4.8 Hz, 0.25H, *dl*), 3.66 (q, *J* = 5.8 Hz, 1H), 1.00 (d, *J* = 6.3 Hz, 2.25H, *meso*), 0.84 (d, *J* = 6.3 Hz, 0.75H, *dl*). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.13 (*meso*), 143.46 (*dl*), 128.07, 127.98, 127.51, 127.32, 126.95, 78.00 (*dl*), 77.41 (*meso*), 71.07 (*dl*), 71.04 (*meso*), 19.24 (*dl*), 18.92 (*meso*).



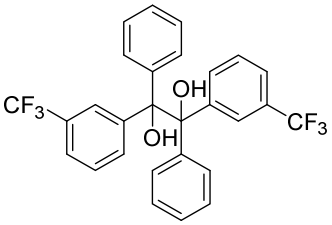
Compound **2m**[12]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 – 7.16 (m, 5H), 5.25 – 5.05 (m, 1H), 4.35 – 4.16 (m, 1H), 3.86 (d, *J* = 2.0 Hz, 1H), 1.64 – 0.84 (m, 10H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.05, 128.56, 127.40, 126.91, 80.07, 72.60, 33.37, 32.84, 26.14, 21.58, 21.55.



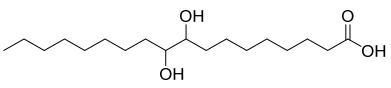
Compound **4c**[7]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 – 7.13 (m, 9H), 7.06 (dt, *J* = 8.5, 4.0 Hz, 6H), 6.88 (t, *J* = 8.6 Hz, 4H), 5.77 (d, *J* = 1.8 Hz, 2H), 2.20 (t, *J* = 2.4 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.17, 147.00, 144.24, 144.07, 134.94, 134.91, 129.64, 129.62, 129.54, 127.31, 127.19, 126.49, 126.36, 126.14, 83.07, 21.00.



Compound **4d**[13]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70 – 7.25 (m, 23H), 7.10 (q, *J* = 5.1, 2.8 Hz, 6H), 6.08 (d, *J* = 1.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.79, 146.36, 140.22, 137.74, 137.69, 130.32, 130.24, 129.66, 129.59, 129.31, 127.66, 126.90, 126.69, 126.60, 126.34, 124.83, 124.73, 83.21.

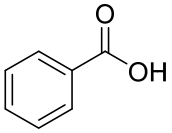


Compound **4e**[14]**.** ^{1}H NMR (400 MHz, DMSO-d_6, *meso: dl* = 2.6 : 1) δ 7.71 – 6.99 (m, 18H), 6.50 (dd, *J* = 6.6, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.74 (*dl*), 147.54(*meso*), 145.73(*meso*), 145.42(*dl*), 133.96 (*meso*), 133.77(*dl*), 129.52 (*meso*), 129.41(*dl*), 127.62, 127.51, 127.42, 127.17, 126.93, 126.84, 126.21, 125.49, 123.50, 123.27, 83.06 (*dl*), 82.93 (*meso*).

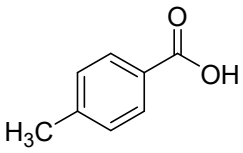


9,10-dihydroxystearic acid (**DSA**)[15]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41 (s, 1H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.78 – 1.12 (m, 28H), 0.88 (t, *J* = 6.5 Hz, 3H). ESI-MS: 315.2 $[M-H]^-$

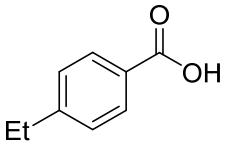
8.2 NMR spectra of products



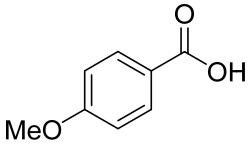
Benzoic acid, compound **3k, 3l,** and **3m**[16]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.94 (s, 1H), 8.00 – 7.87 (m, 2H), 7.66 – 7.58 (m, 1H), 7.50 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.80, 133.33, 131.20, 129.73, 129.03.



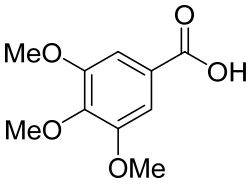
Compound **3a**[17]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.76 (brs, 1H), 7.96 – 7.69 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.81, 143.49, 129.80, 129.59, 128.50, 21.58.



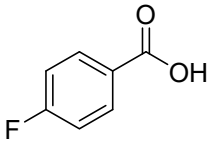
Compound **3b**[17]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.43 (s, 1H), 7.94 – 7.78 (m, 2H), 7.44 – 7.19 (m, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.80, 149.54, 129.89, 128.82, 128.41, 28.61, 15.68.



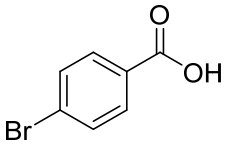
Compound **3c**[17]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.62 (s, 1H), 8.02 – 7.79 (m, 2H), 7.07 – 6.88 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.48, 163.30, 131.81, 123.42, 114.28, 55.90.



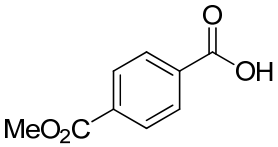
Compound **3d**[18]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.92 (s, 1H), 7.23 (s, 2H), 3.82 (s, 6H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.39, 153.11, 141.80, 126.37, 106.98, 60.58, 56.38.



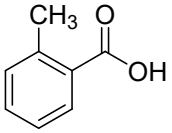
Compound **3e**[18]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.05 (s, 1H), 8.01 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.32 (t, *J* = 8.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.85, 165.38 (d, *J* = 250.4 Hz, recorded as 166.62 and 164.13), 132.57 (d, *J* = 9.5 Hz, recorded as 132.62 and 132.53), , 127.82 (d, *J* = 2.8 Hz, recorded as 127.83 and 127.81), 116.10 (d, *J* = 21.9 Hz, recorded as 116.20 and 115.99).



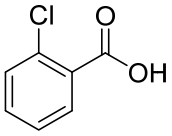
Compound **3f**[17]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.15 (brs, 1H), 7.94 – 7.82 (m, 2H), 7.76 – 7.62 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.10, 132.18, 131.77, 130.48, 127.35.



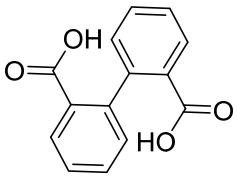
Compound **3g**[19]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.37 (s, 1H), 8.07 (s, 4H), 3.89 (s, 3H).. ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.00, 166.02, 135.22, 133.56, 129.99, 129.74, 52.84.



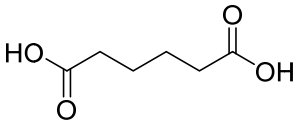
Compound **3h**[18]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.81 (s, 1H), 7.82 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.44 (td, *J* = 7.5, 1.5 Hz, 1H), 7.28 (td, *J* = 8.1, 7.3, 1.5 Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.15, 139.45, 132.18, 131.97, 130.89, 130.63, 126.30, 21.70.



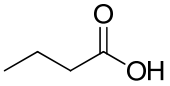
Compound **3i**[20]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.11 (s, 1H), 7.82 – 7.74 (m, 1H), 7.58 – 7.47 (m, 2H), 7.43 (ddd, *J* = 7.6, 5.7, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.22, 133.04, 132.02, 131.93, 131.26, 131.07, 127.69.



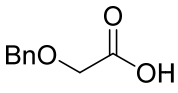
Compound **3m**[21]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.43 (s, 2H), 7.88 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.54 (td, *J* = 7.5, 1.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.31, 143.49, 131.50, 130.80, 130.76, 129.94, 127.37.



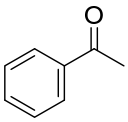
Compound **3n**[22]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.02 (s, 2H), 2.30 – 2.11 (m, 4H), 1.57 – 1.42 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.81, 33.84, 24.48.



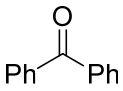
Compound **3o**[23]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.98 (s, 1H), 2.17 (t, *J* = 7.3 Hz, 2H), 1.51 (q, *J* = 7.3 Hz, 2H), 0.88 (dd, *J* = 7.8, 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ174.82, 36.01, 18.38, 13.96.



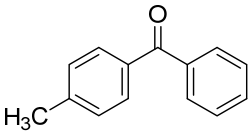
Compound **3p**[24]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.67 (s, 1H), 7.43 – 7.24 (m, 5H), 4.54 (s, 2H), 4.06 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.03, 138.33, 128.72, 128.15, 128.05, 72.49, 67.30.



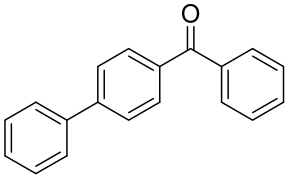
Compound **5a**[25]**.**^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 – 7.92 (m, 2H), 7.69 – 7.61 (m, 1H), 7.53 (dd, *J* = 8.4, 7.0 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 198.46, 137.26, 133.66, 129.15, 128.62, 27.18.



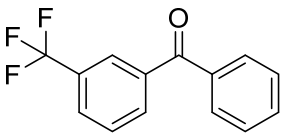
Compound **5b**[21]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78 – 7.70 (m, 2H), 7.72 – 7.63 (m, 2H), 7.56 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.31, 137.46, 133.17, 130.08, 129.04.



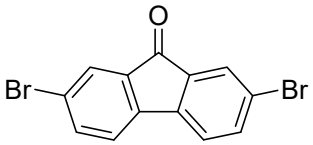
Compound **5c**[24]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 – 7.61 (m, 5H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 195.93, 143.63, 137.81, 134.75, 132.90, 130.32, 129.92, 129.60, 129.30, 128.97, 21.62.



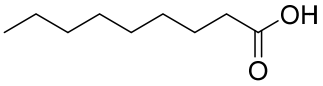
Compound **5d**[26]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 – 7.81 (m, 4H), 7.80 – 7.73 (m, 4H), 7.73 – 7.66 (m, 1H), 7.59 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.52 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.48 – 7.40 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 195.85, 144.66, 139.36, 137.62, 136.19, 133.12, 130.93, 130.03, 129.61, 129.07, 128.89, 127.48, 127.27.



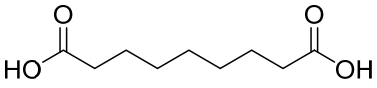
Compound **5e**[27]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11 – 7.96 (m, 3H), 7.88 – 7.67 (m, 4H), 7.59 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 195.02, 138.41, 136.67, 134.02, 133.71, 130.39, 130.23, 130.15 (q, J= 32.3 Hz, recorded as 130.63, 130.31,129.99, and 129.66) 129.43 (q, J= 273.5 Hz, recorded as 131.04, 128.33, 125.62, and 122.91), 129.43 (q, J= 3.6 Hz, recorded as 129.53, 129.49, 129.45, and 129.41) 129.23, 126.13 (q, J= 3.9 Hz, recorded as 126.19, 126.15, 126.11, and 126.07).



Compound **5f**[28]**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 – 7.73 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 190.84, 142.59, 138.34, 135.27, 127.36, 123.99, 123.13, 40.56, 40.36, 40.15, 39.94, 39.73, 39.52, 39.31.

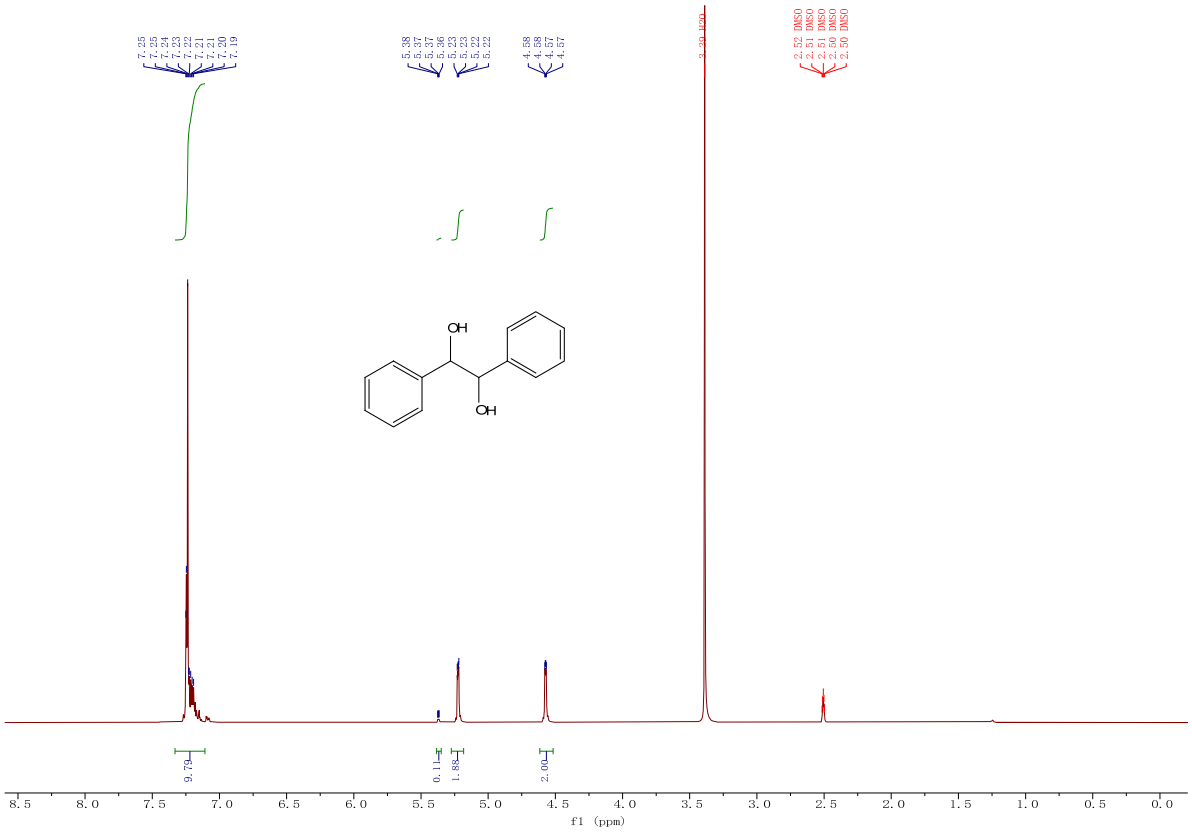


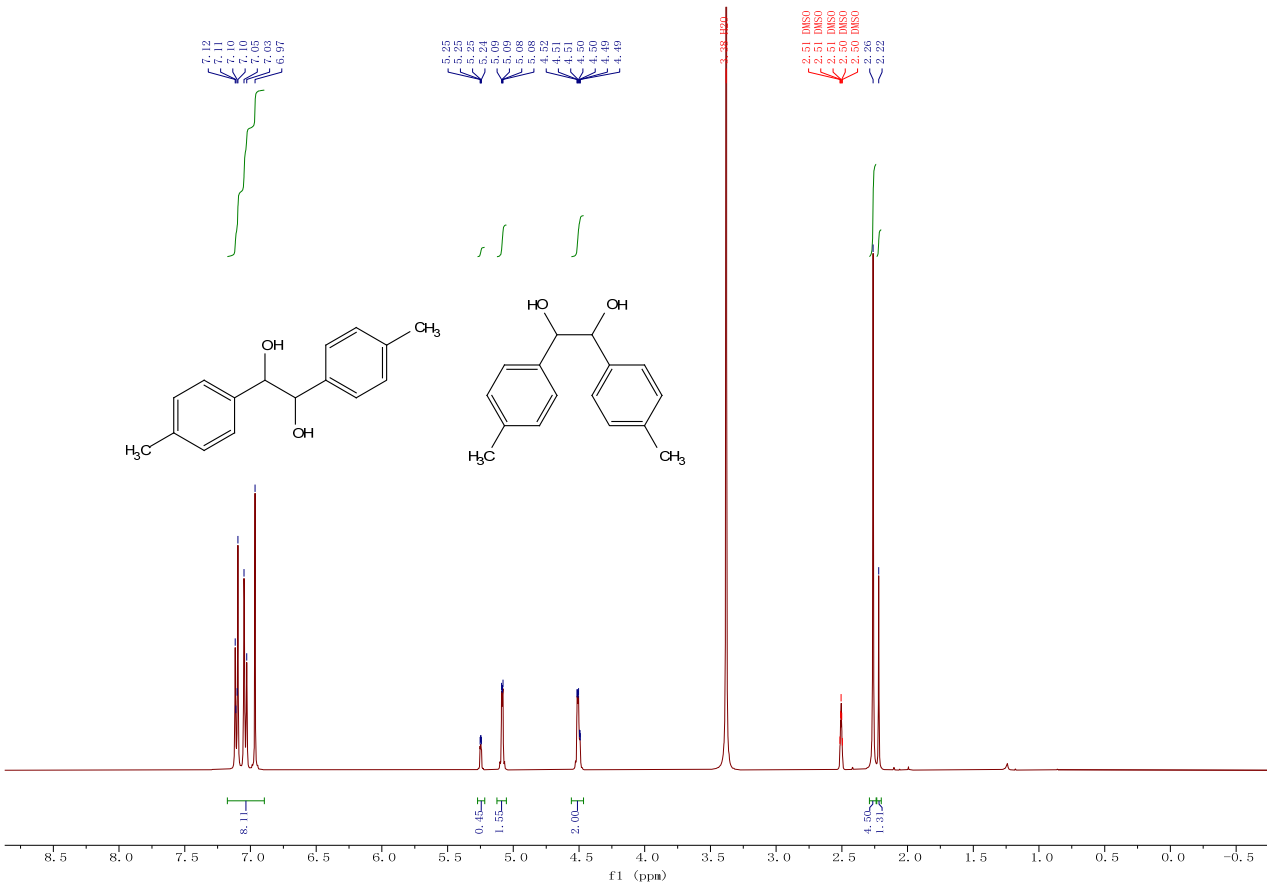
Pelargonic acid [29]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (t, *J* = 7.5 Hz, 2H), 1.69-1.53 (m, 2H), 1.42-1.19 (m, 10H), 0.87 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.29, 34.09, 31.81, 29.21, 29.10, 29.07, 24.68, 22.65, 14.10.



Azelaicacid [30]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.99 (s, 2H), 2.18 (t, J = 7.4 Hz, 4H), 1.48 (p, *J* = 7.2 Hz, 4H), 1.25 (d, *J* = 4.2 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.99, 34.09, 28.90, 28.86, 24.90.

Attachments: spectra of diols and products.

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4.50
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4.49
3.38
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H3C
HO
OH
H3C
CH3
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2.00
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1.31
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
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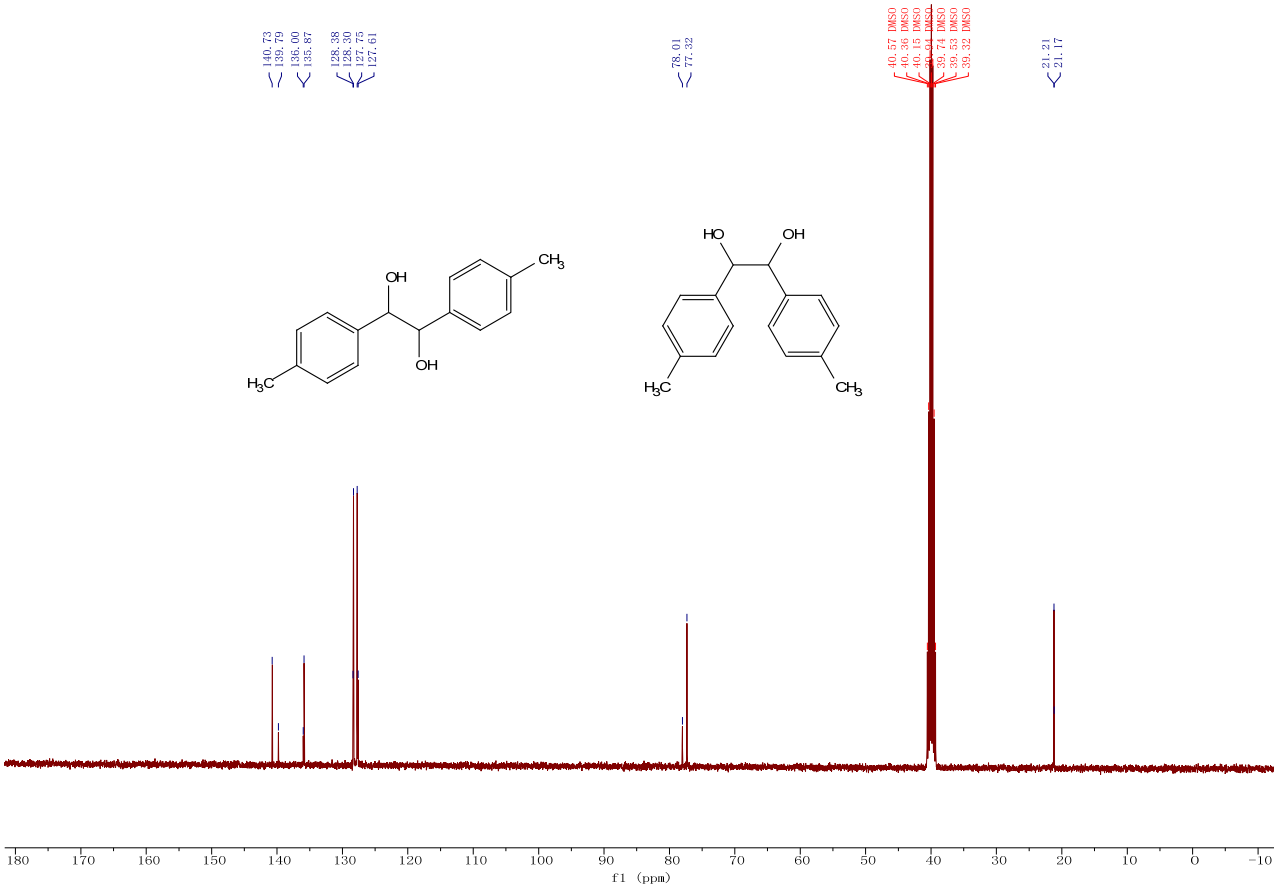
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39.94 DMSO
39.74 DMSO
39.53 DMSO
39.32 DMSO
21.21
21.17
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OH
CH3
H3C
HO
OH
H3C
CH3
180
170
160
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40
30
20
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0
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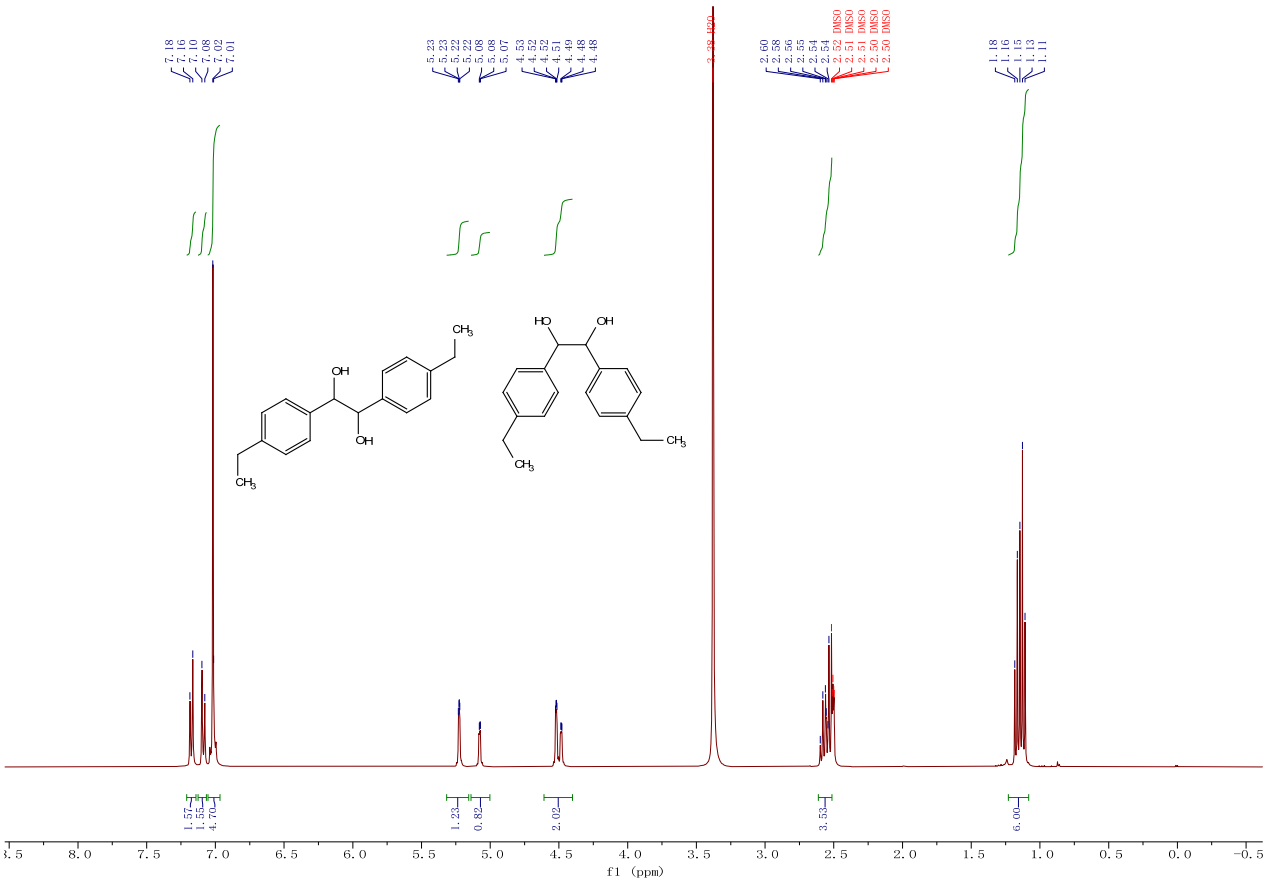
f1 (ppm)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5.22
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5.07
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4.51
4.49
4.48
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2.58
2.56
2.55
2.54
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2.51 DMSO
2.50 DMSO
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1.16
1.15
1.13
1.11
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CH3
HO
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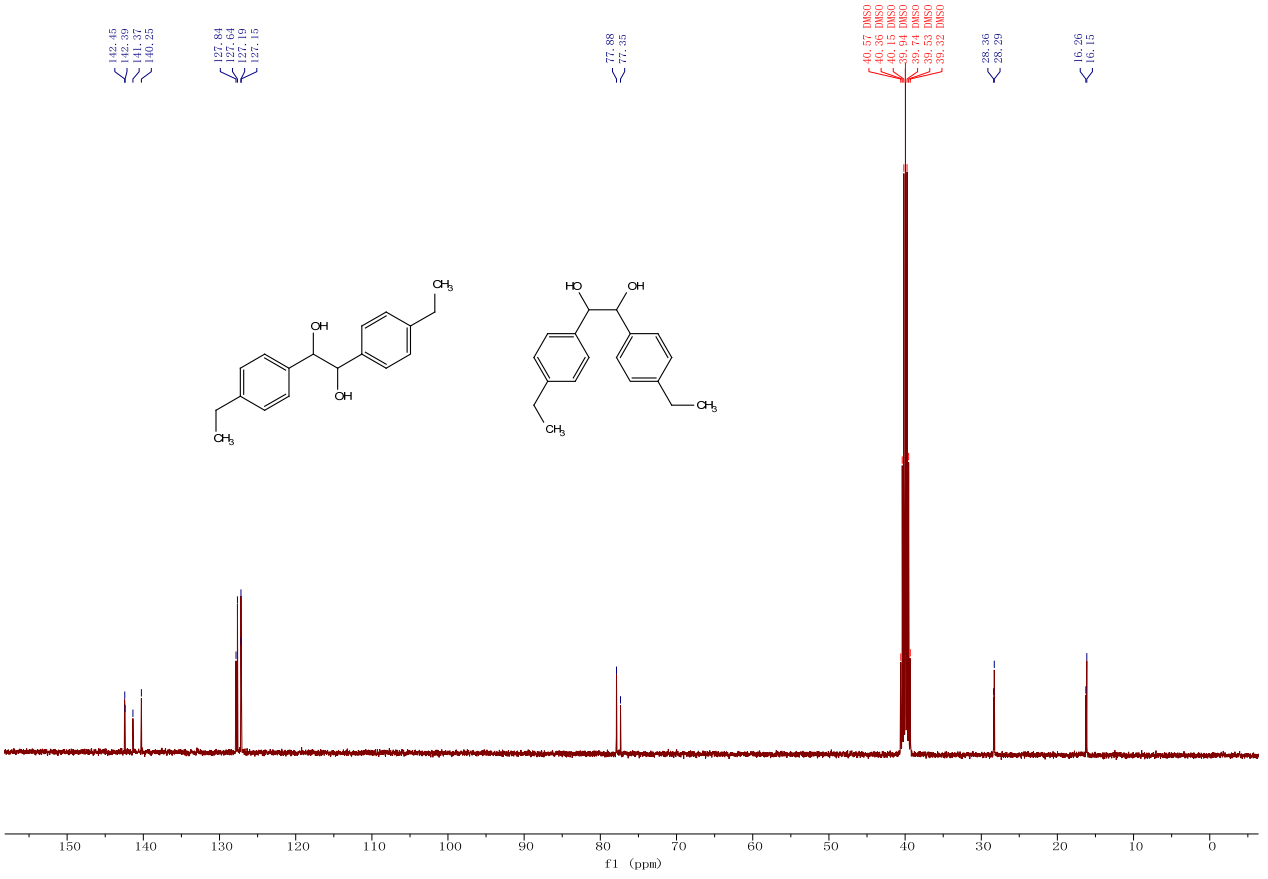
6.00
f1 (ppm)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77.35
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39.94 DMSO
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28.29
16.26
16.15
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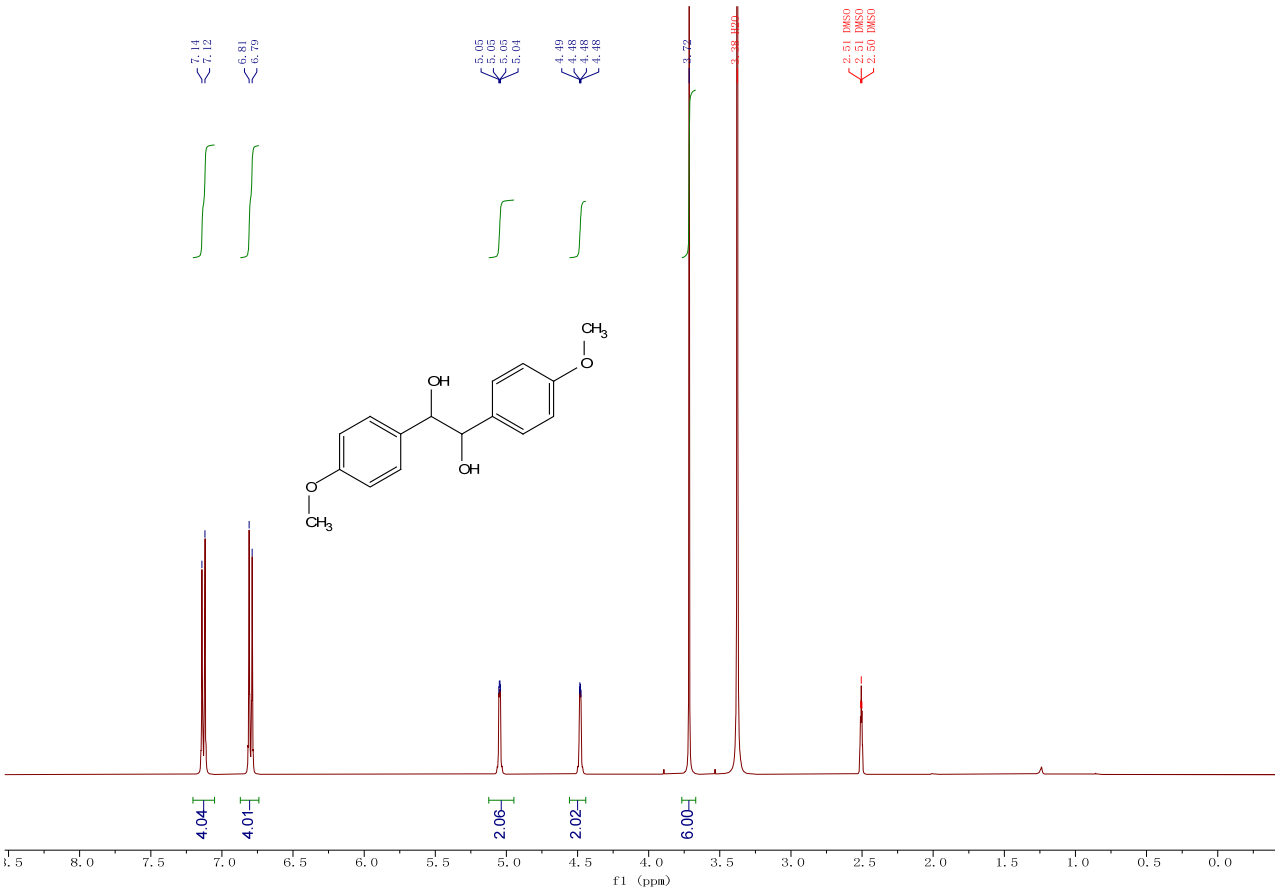
CH3
CH3
HO
OH
CH3
f1 (ppm)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5.04
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4.48
3.72
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2.51 DMSO
2.50 DMSO
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OH
OH
O
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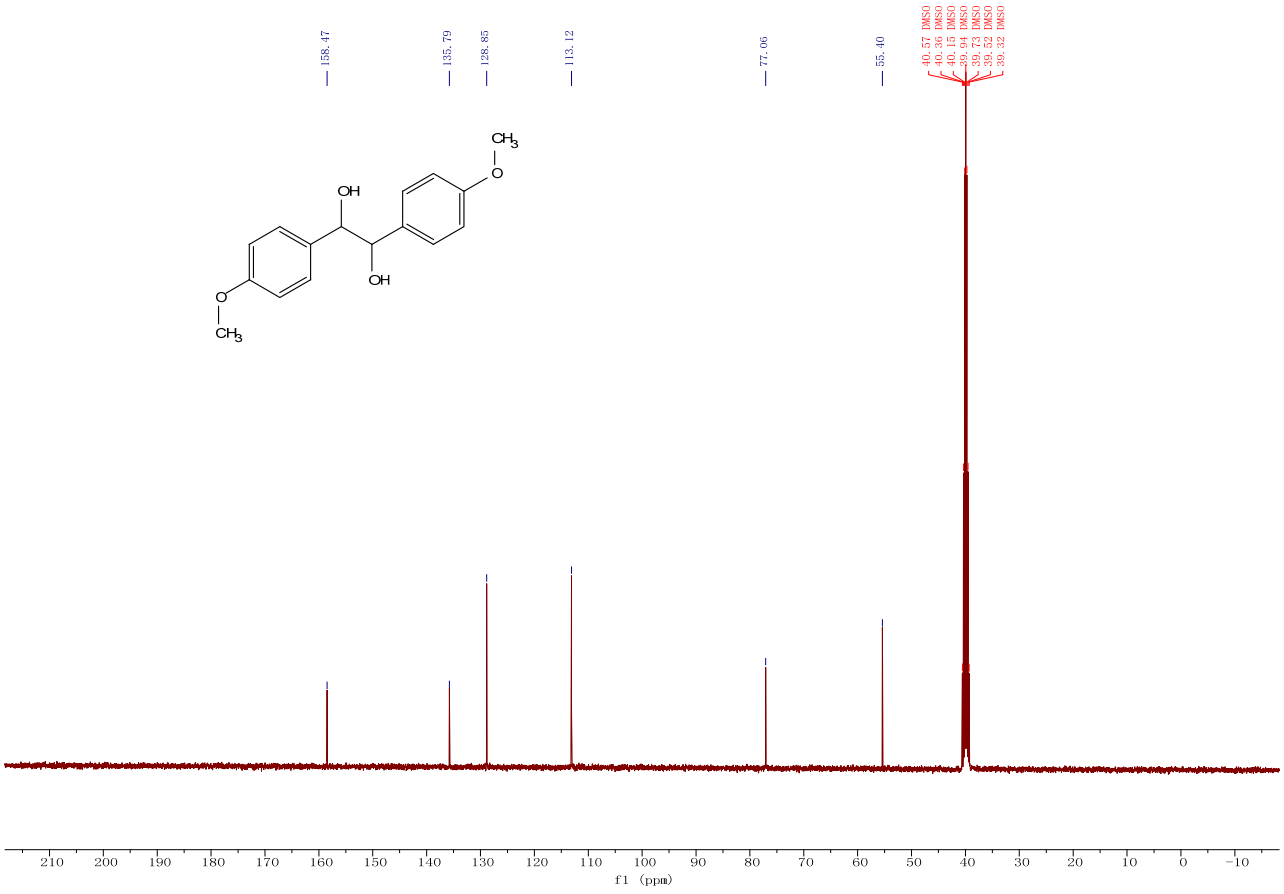
2.06
2.02
6.00
f1 (ppm)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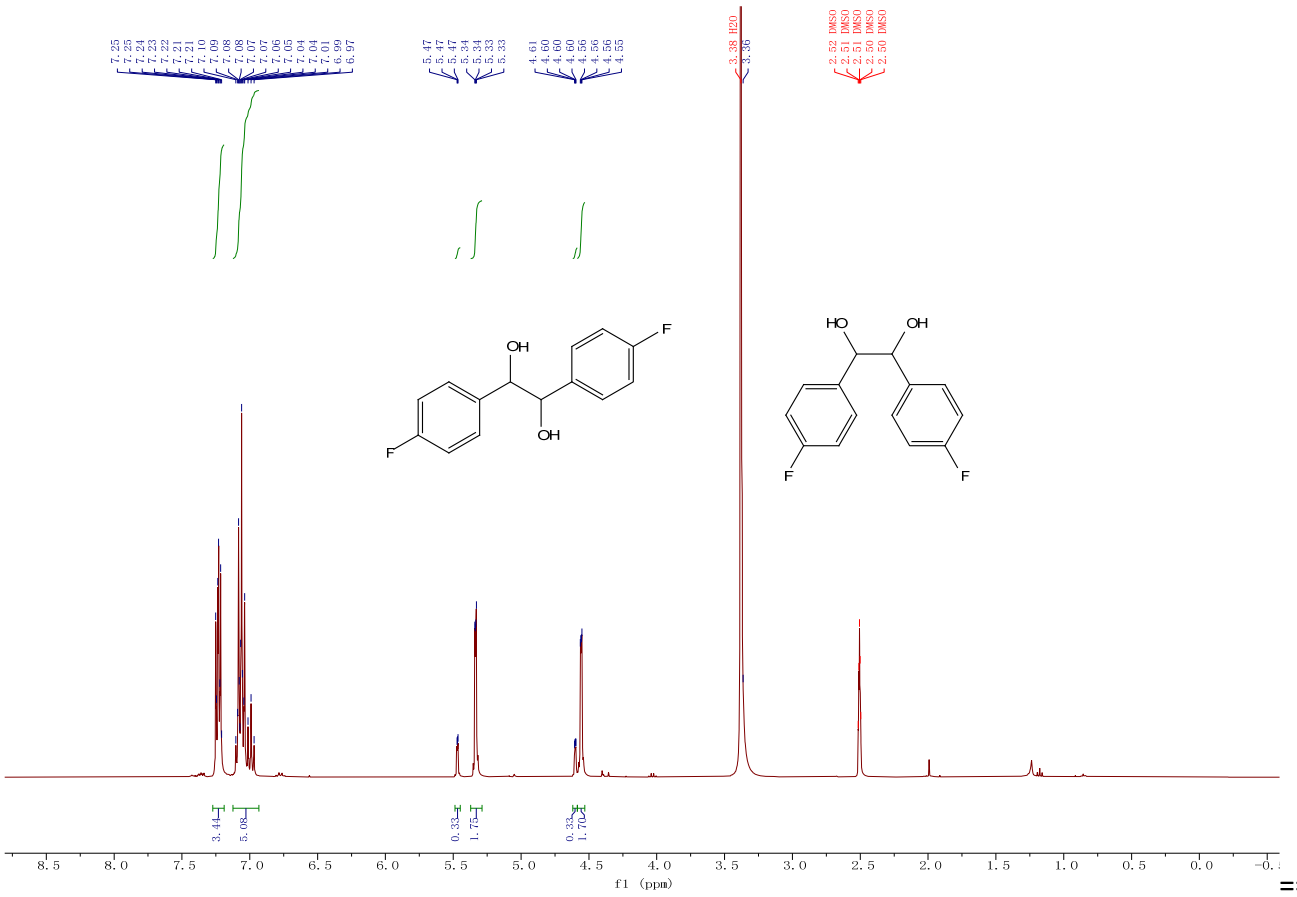
CH3
f1 (ppm)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4.61 4.60 4.60 4.56 4.56 4.55 4.55
3.38 H2O 3.35
2.52 DMSO 2.51 DMSO 2.51 DMSO 2.50 DMSO 2.50 DMSO
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HO OH F F
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f1 (ppm)

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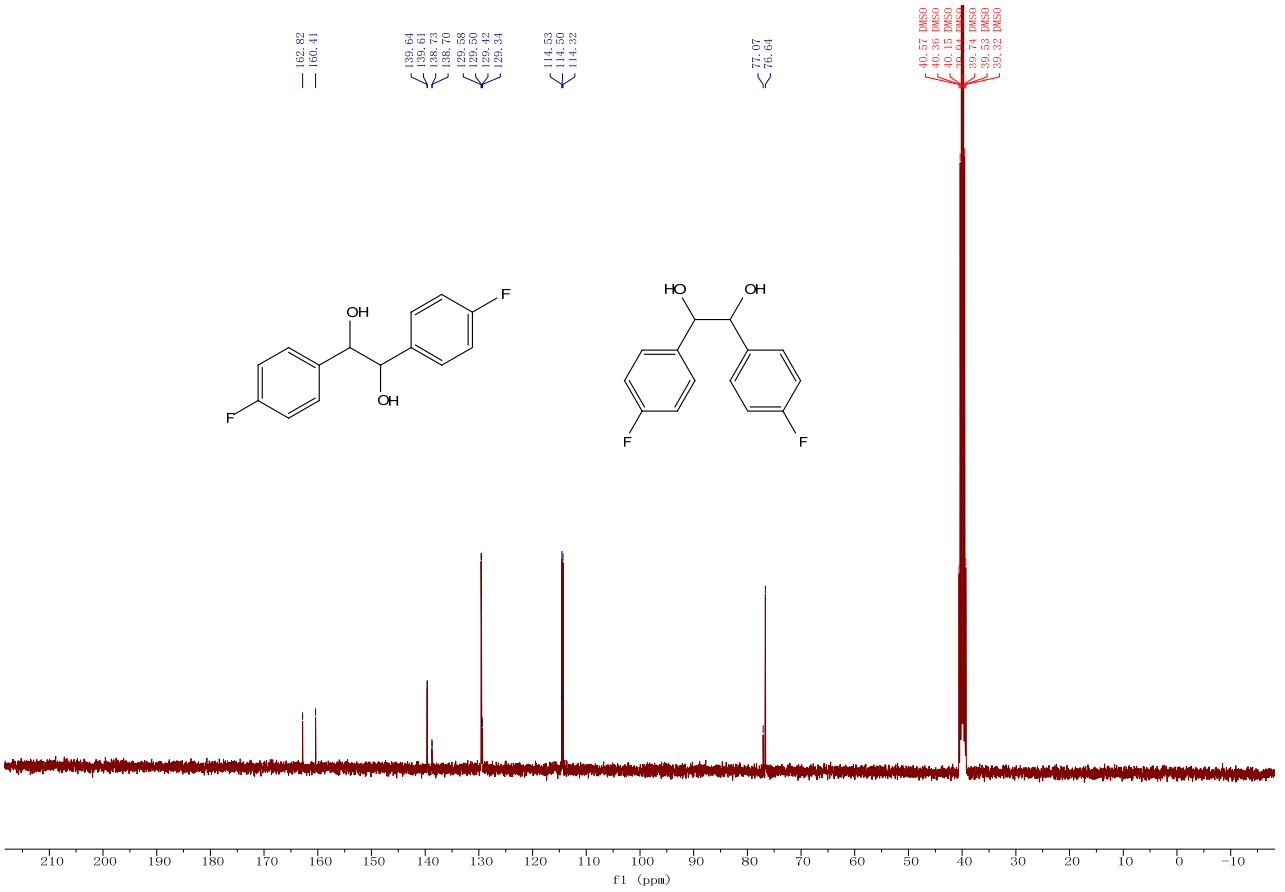
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114.53 114.50 114.32
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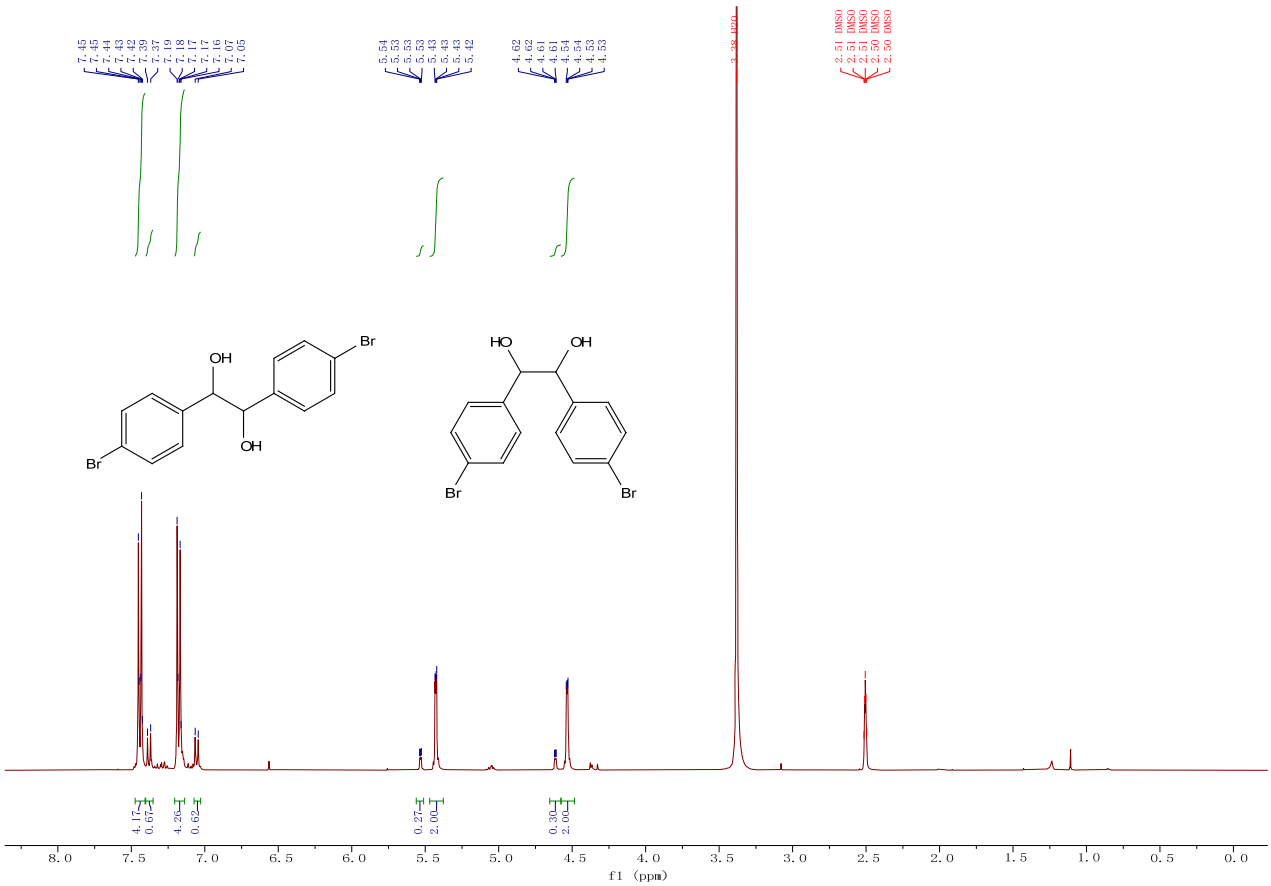
HO OH F F
f1 (ppm)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7.07
7.05
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5.53
5.53
5.43
5.43
5.42
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4.62
4.61
4.61
4.54
4.54
4.53
4.53
3.38 H2O
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2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
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OH
Br
Br
HO
OH
Br
Br
4.17
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4.26
0.62
0.27
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0.30
2.00
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7.0
6.5
6.0
5.5
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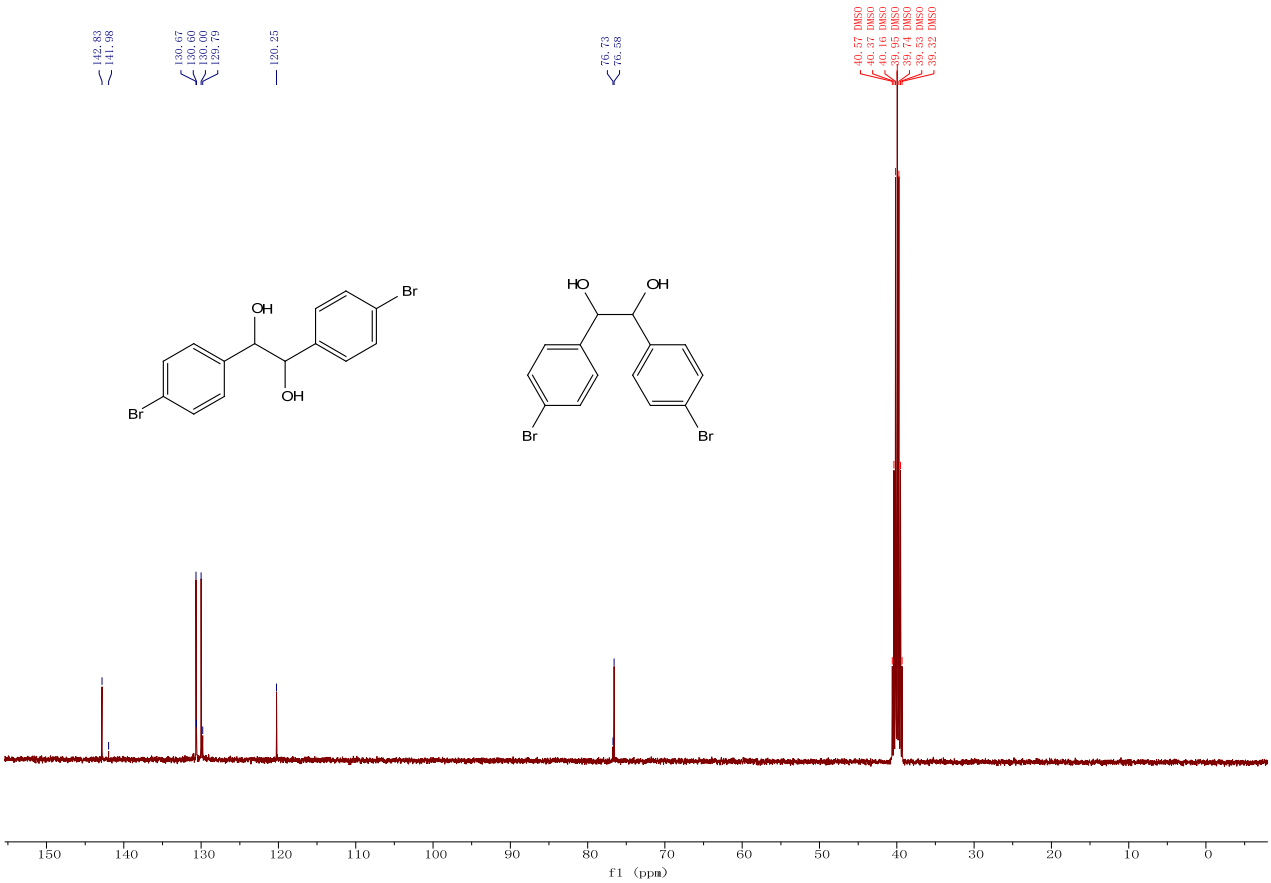
f1 (ppm)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39.32 DMSO
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OH
Br
Br
HO
OH
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50
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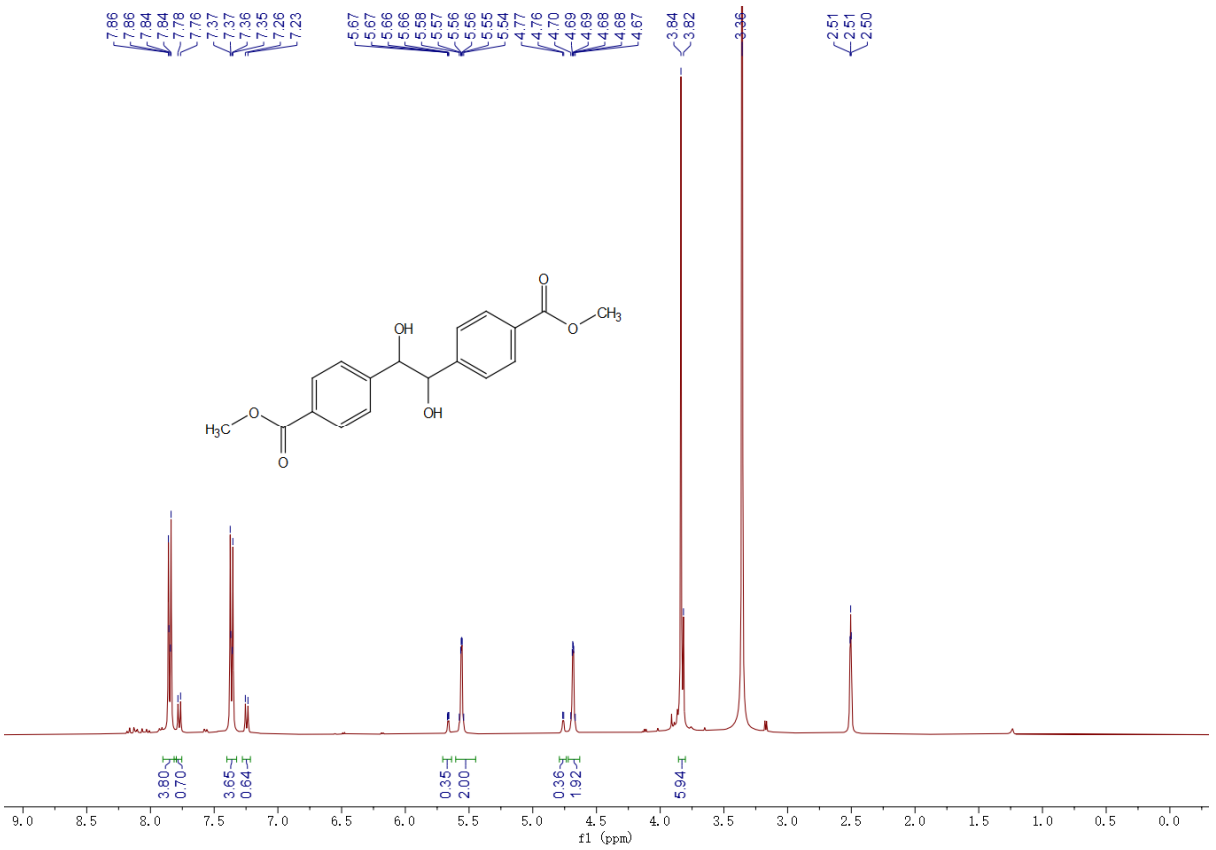
f1 (ppm)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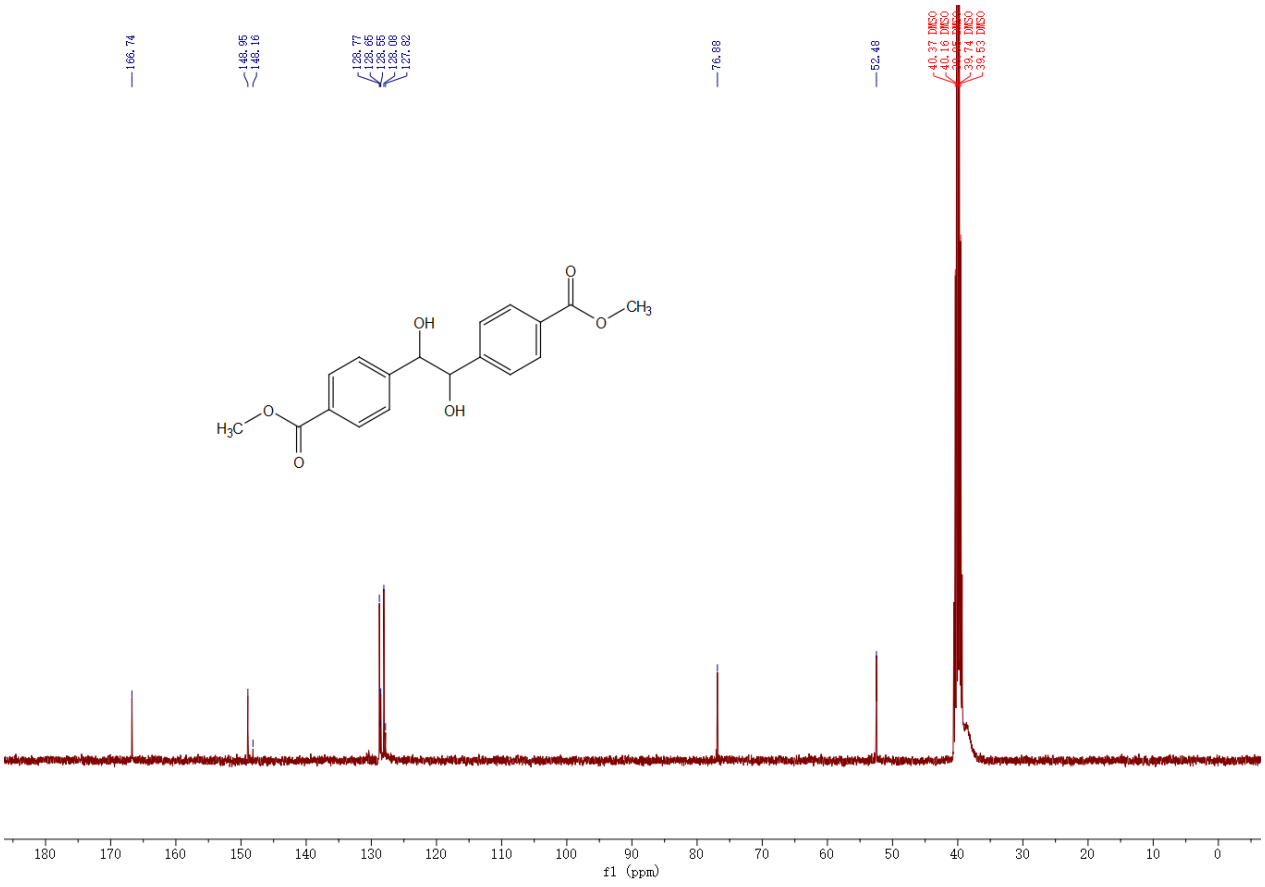
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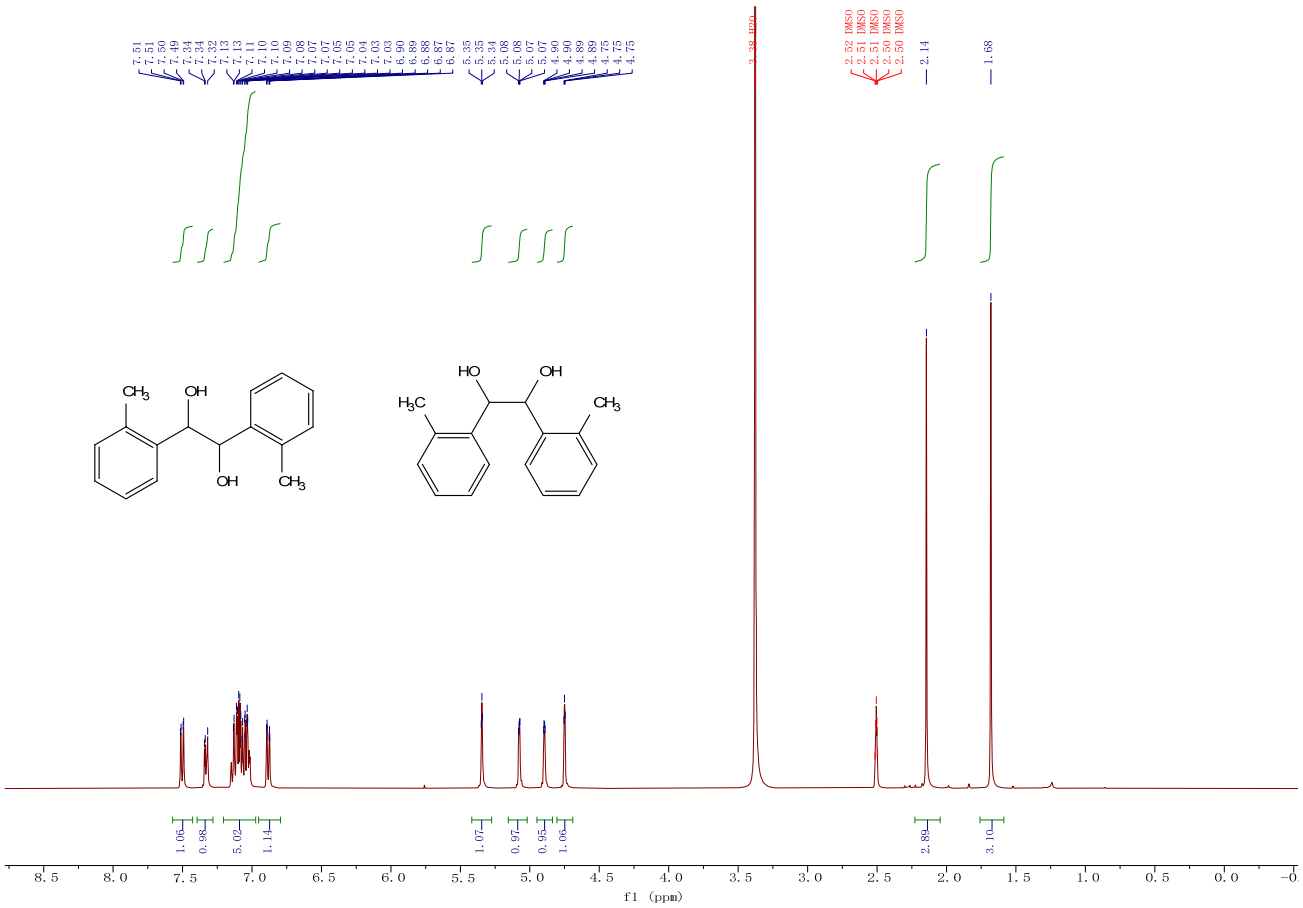
f1 (ppm)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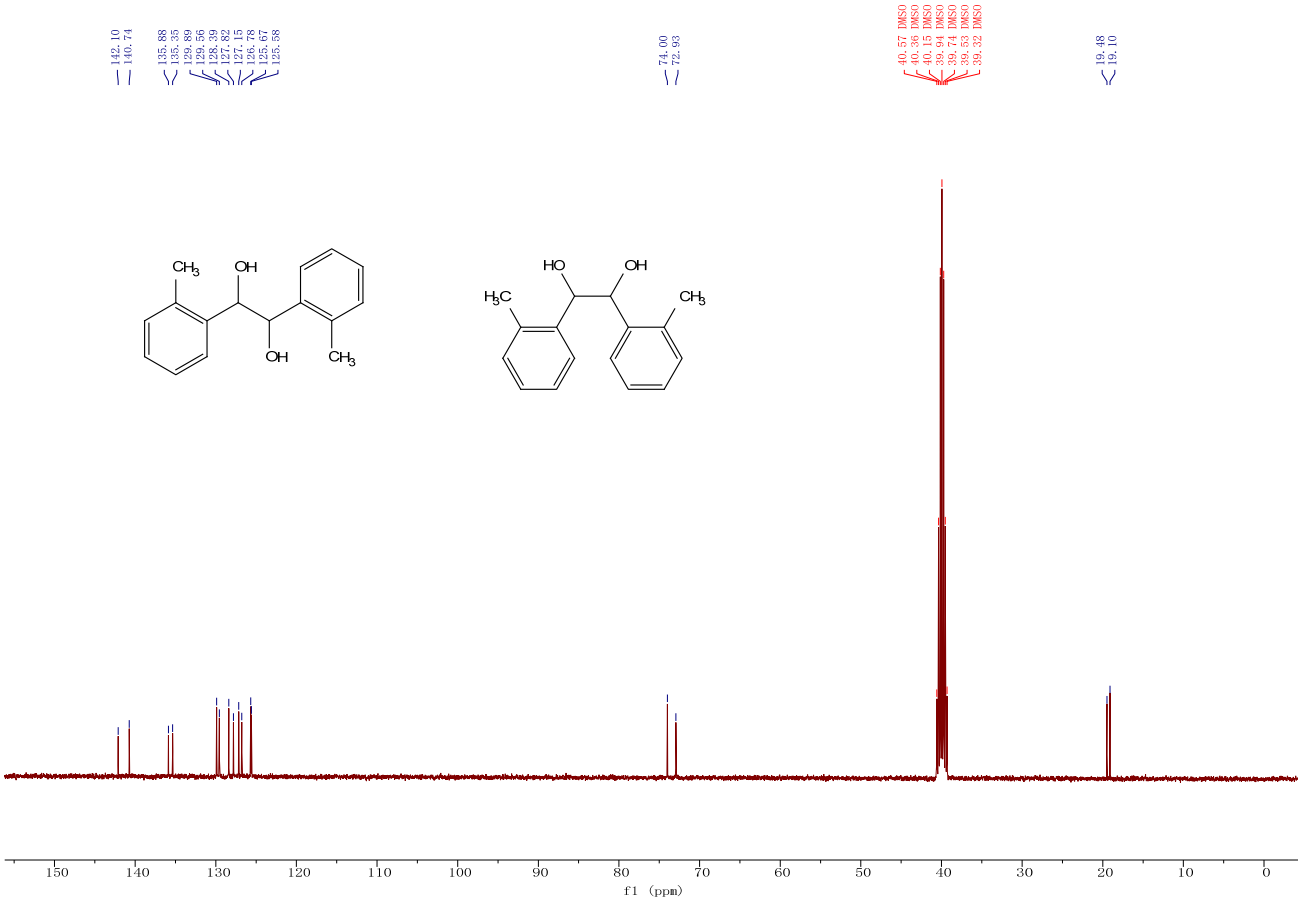
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39.94 DMSO
39.74 DMSO
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39.32 DMSO
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19.10
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OH
CH3
HO
OH
H3C
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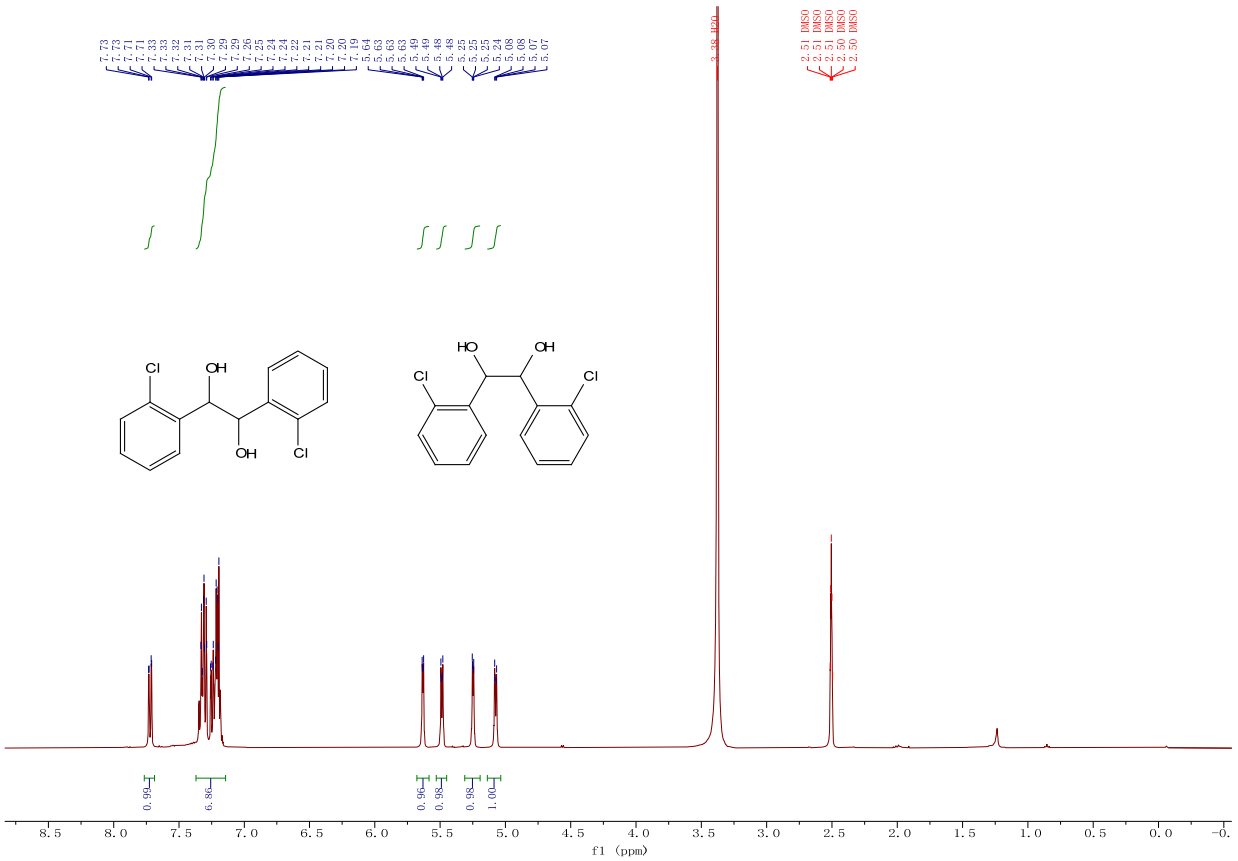
f1 (ppm)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Cl
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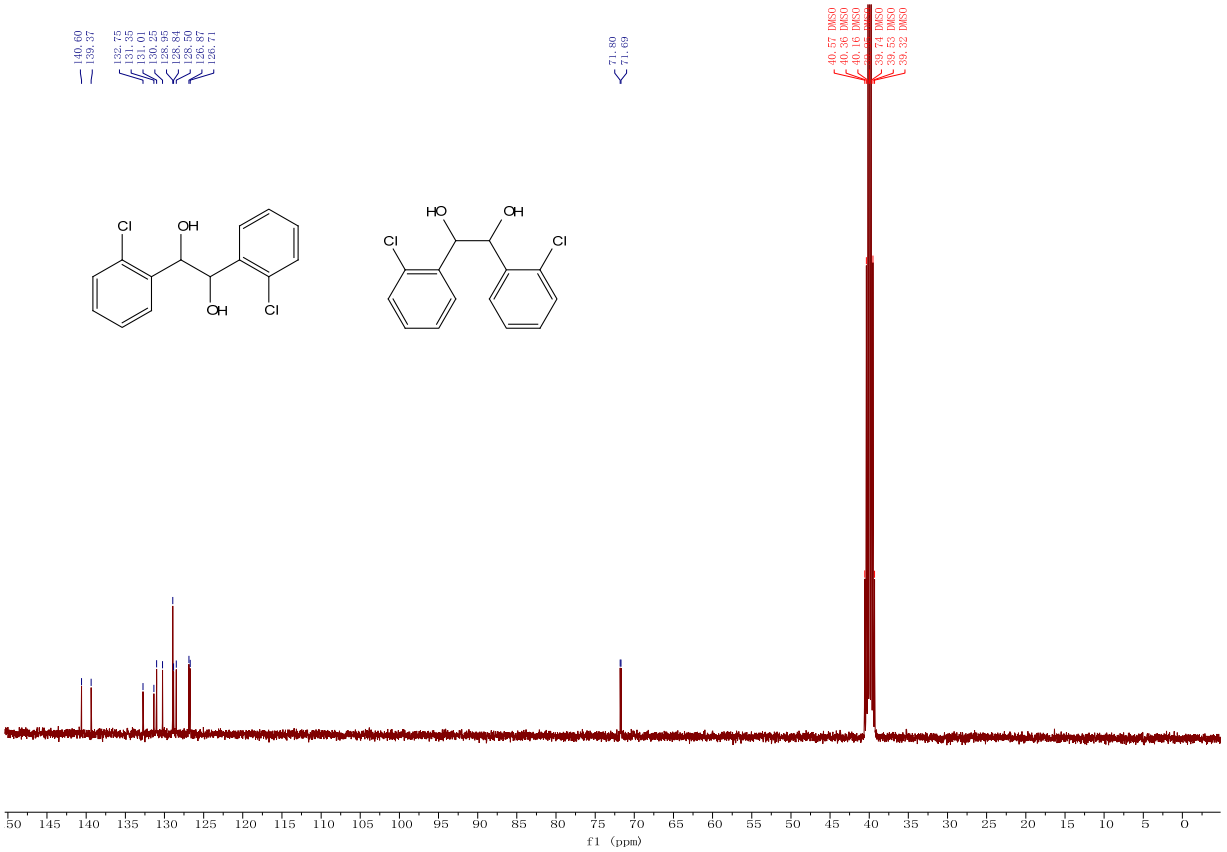
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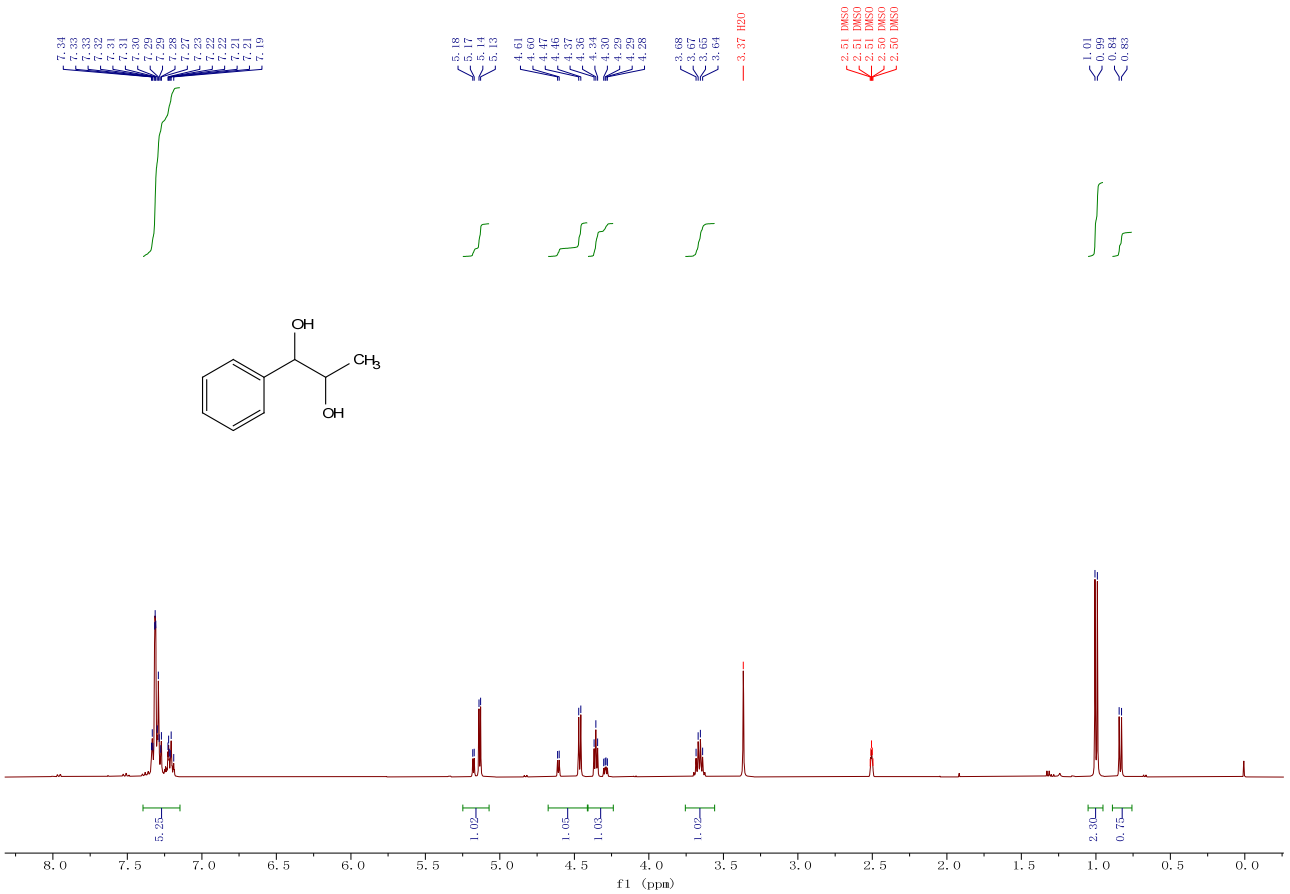
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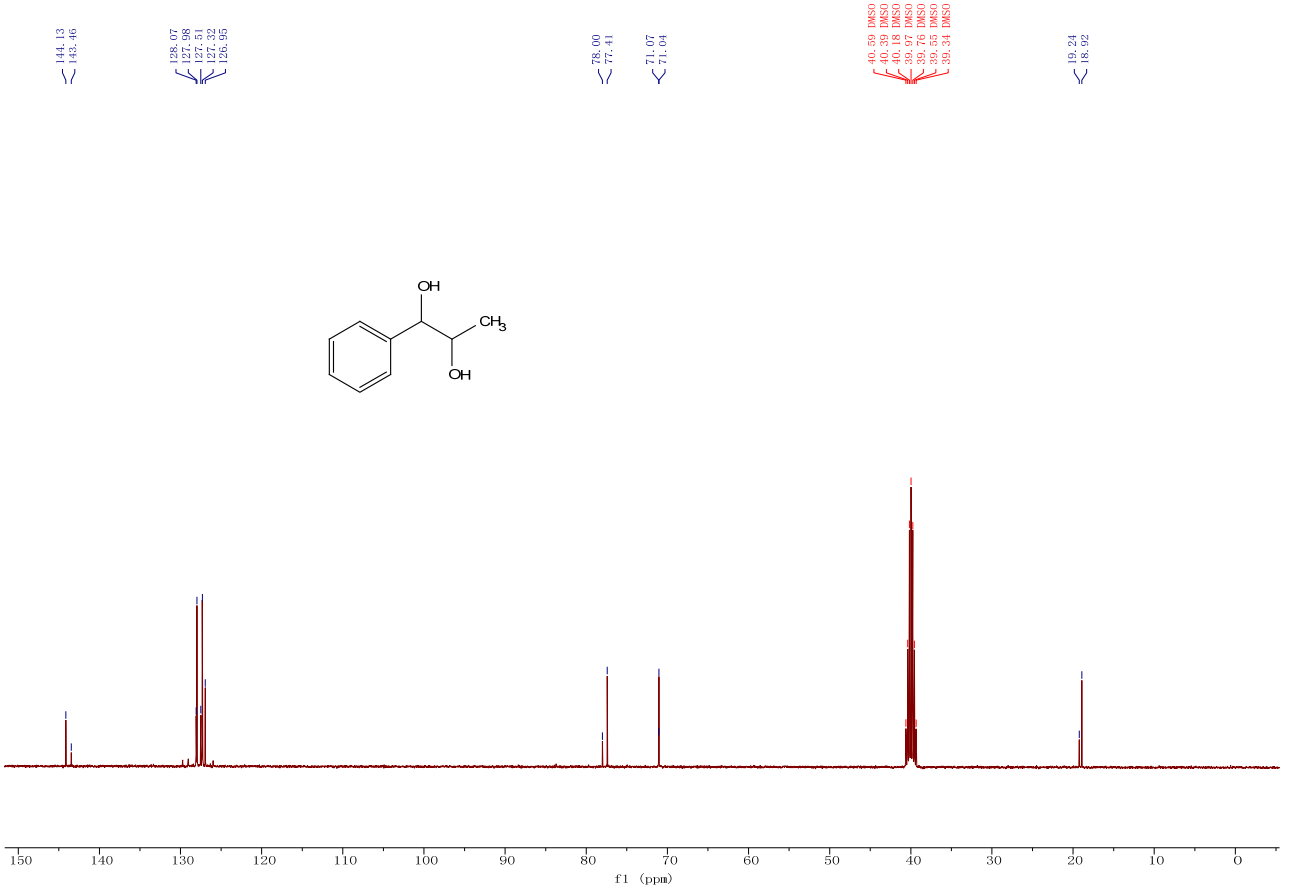
f1 (ppm)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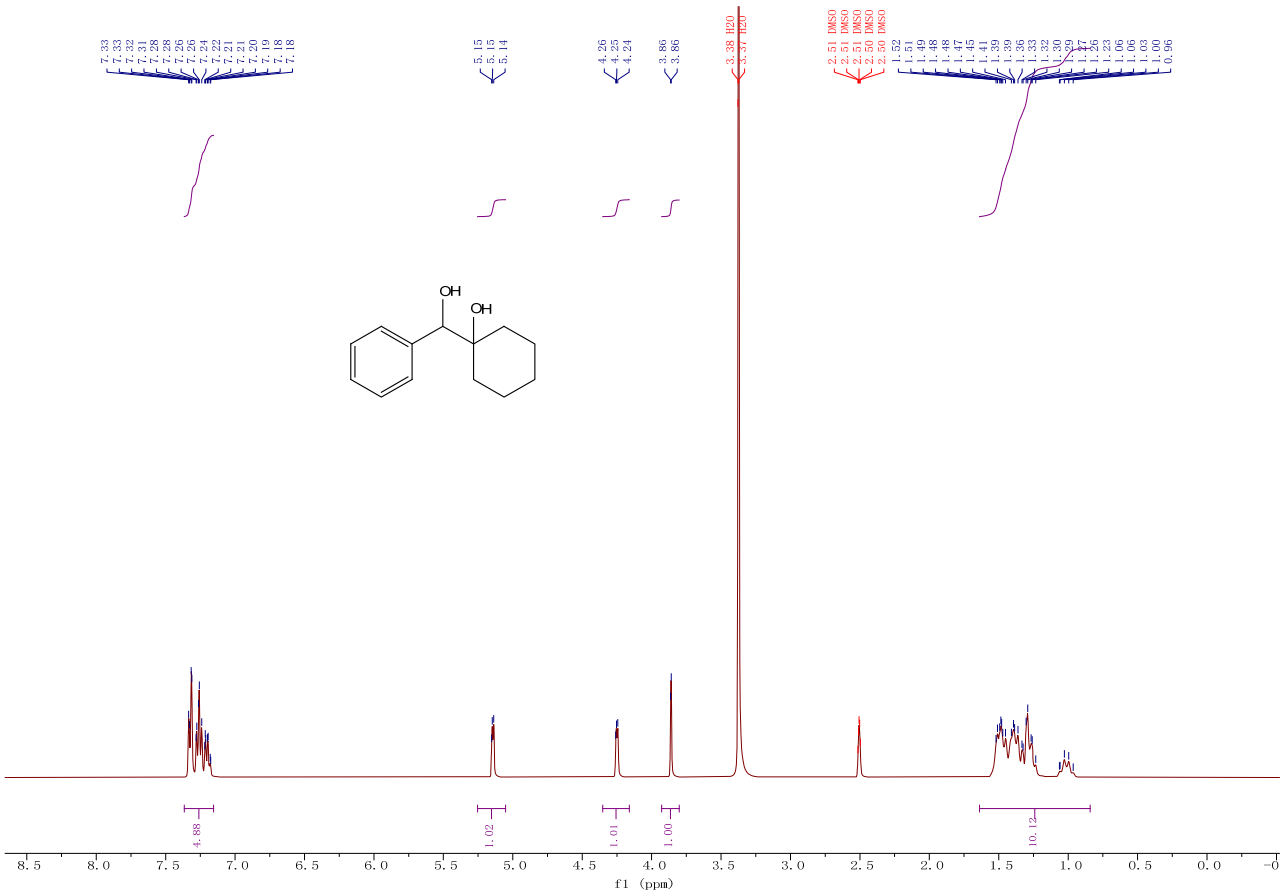
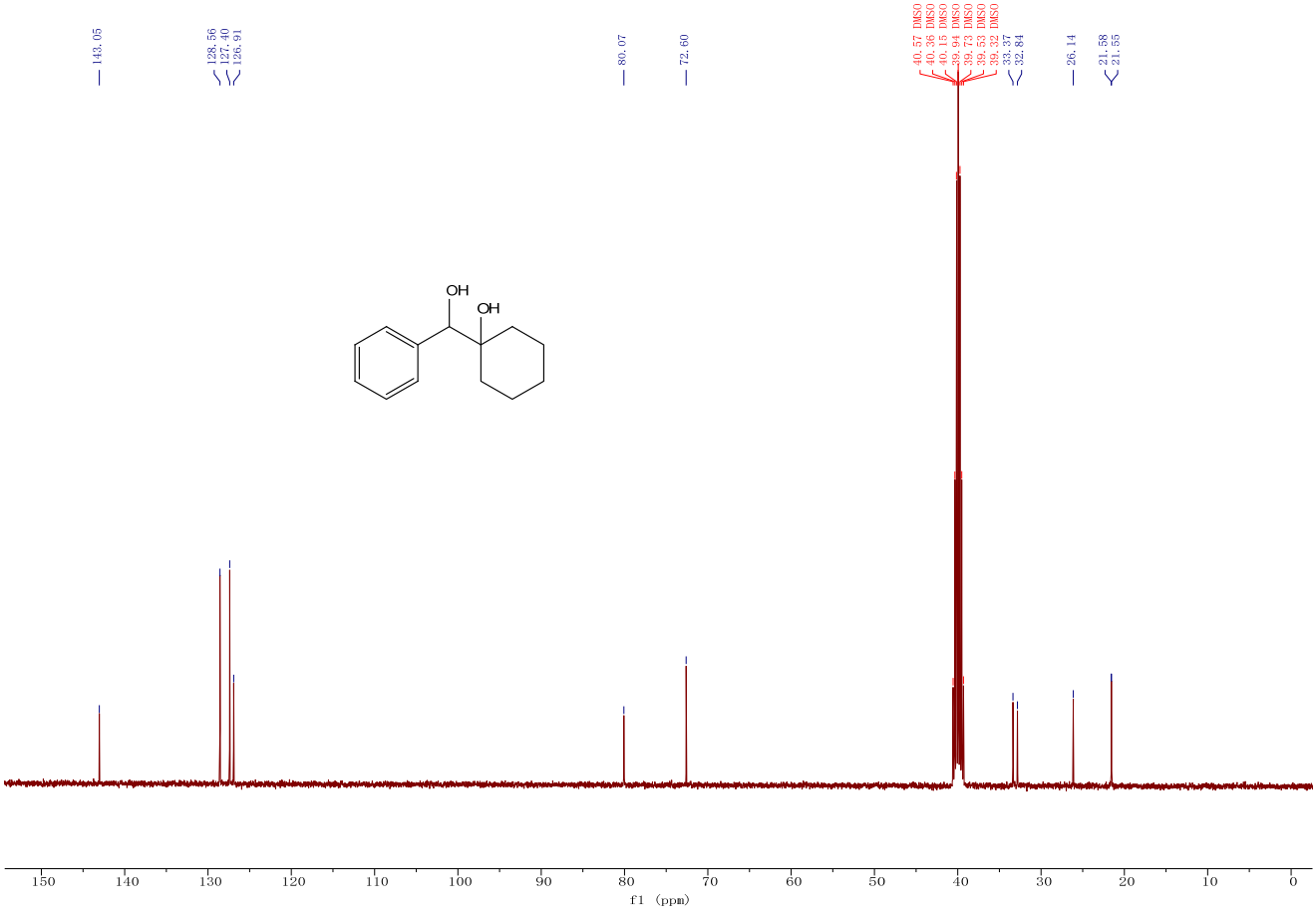
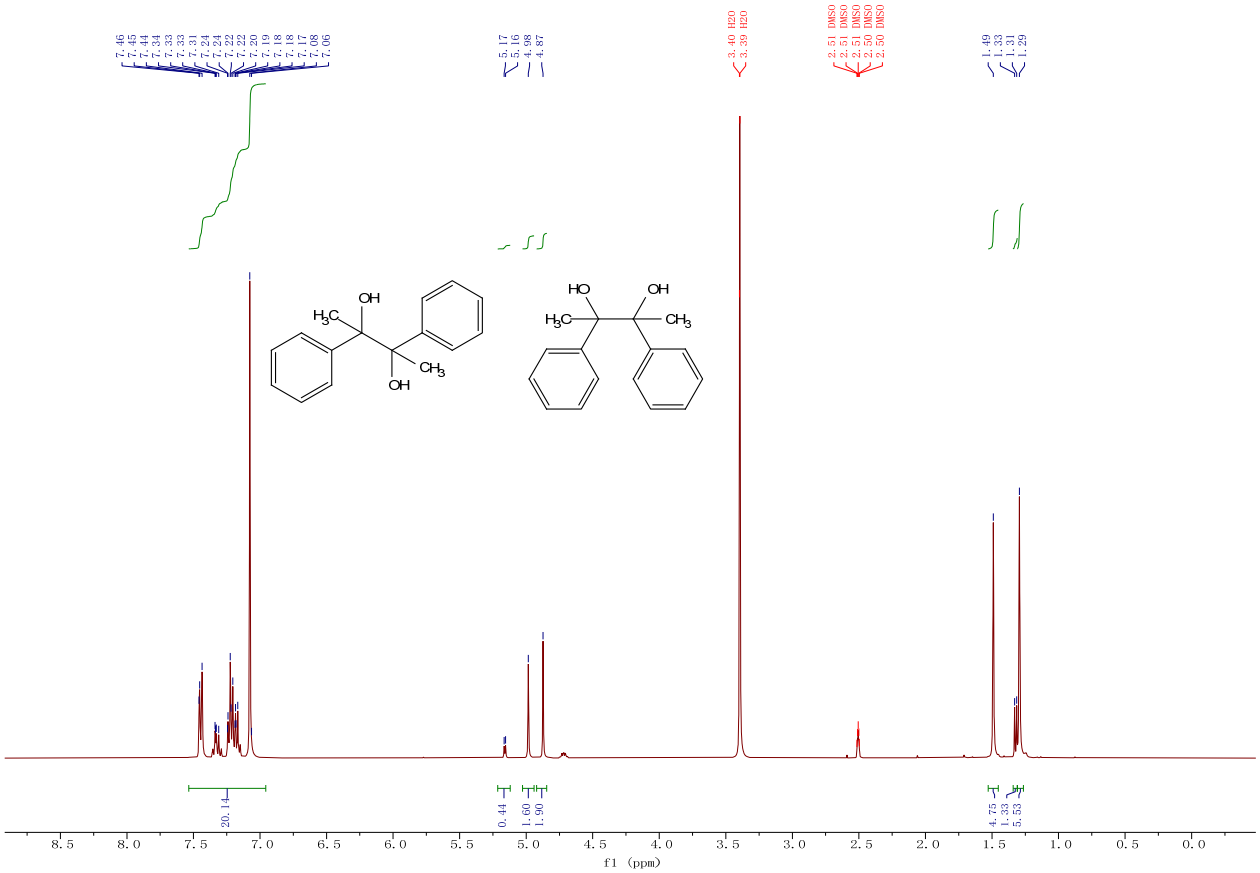
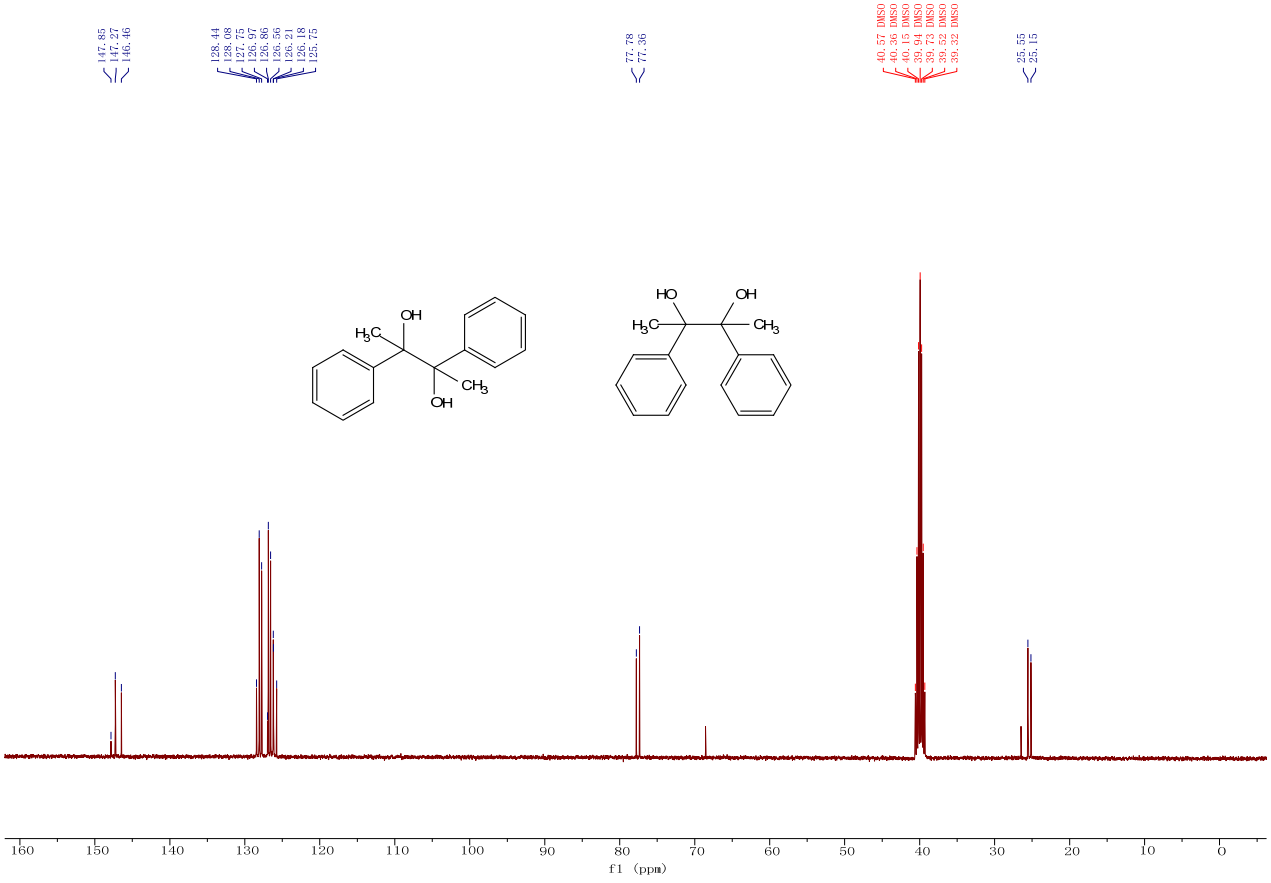
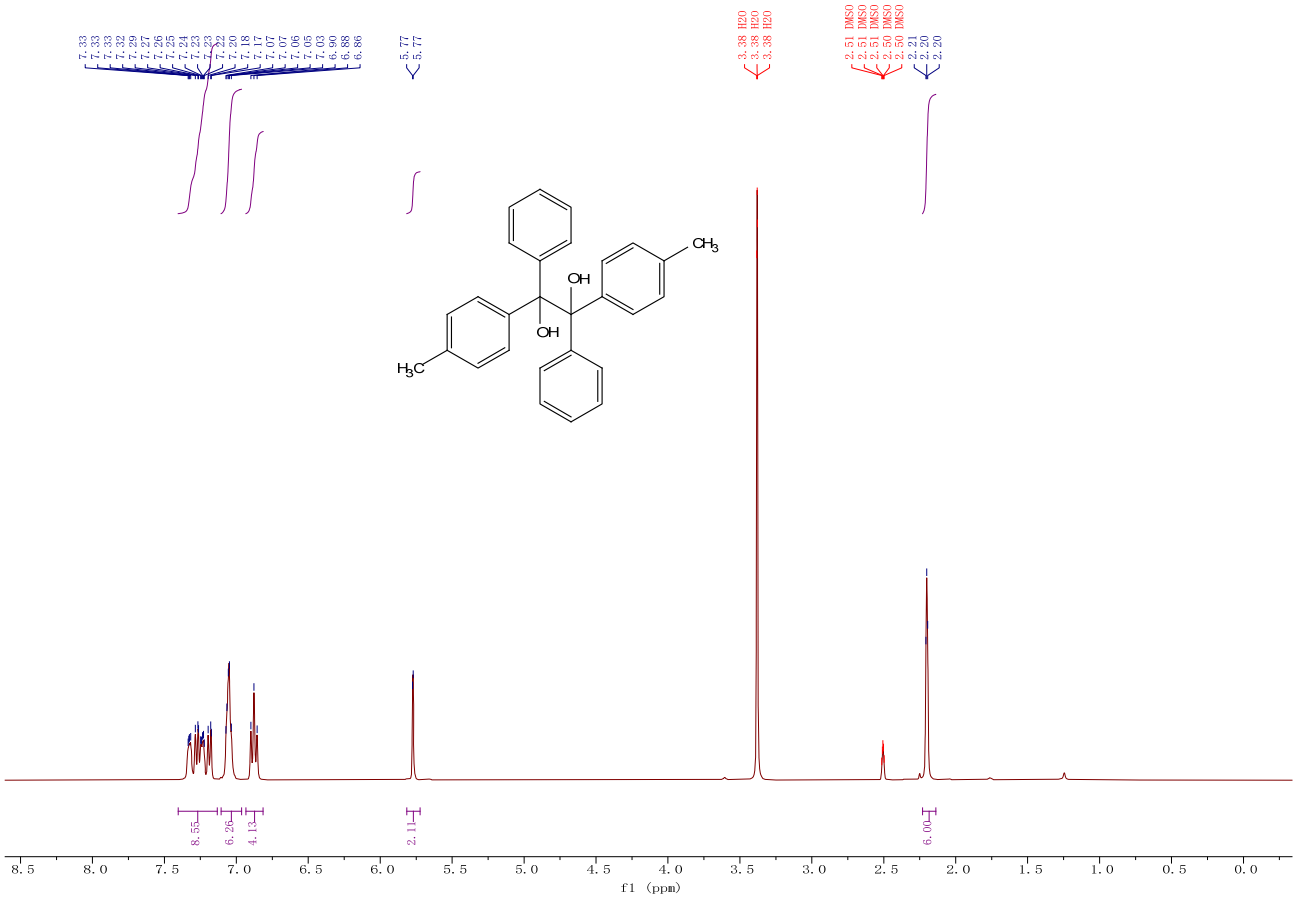
39.34 DMSO
19.24
18.92
OH
CH3
OH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

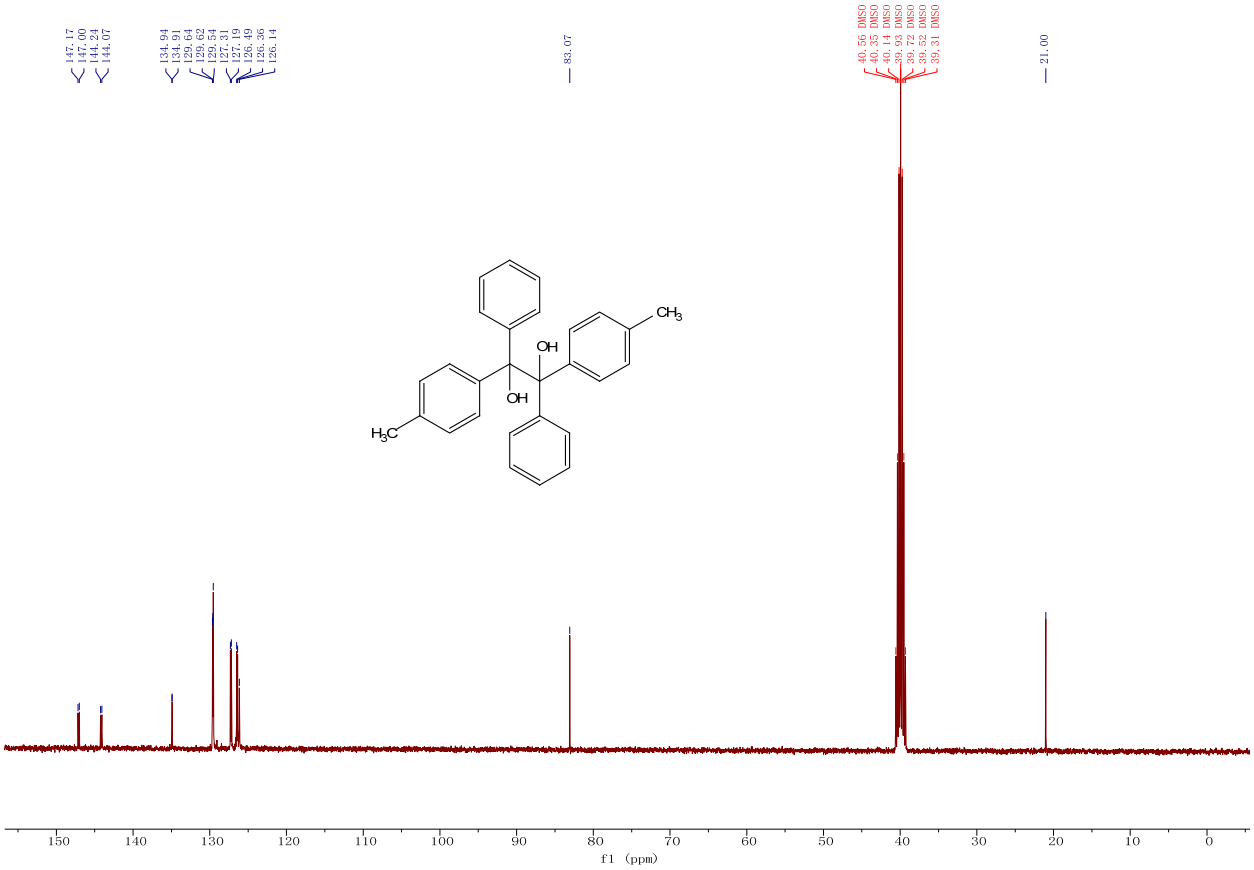

OH
OH
4.88
1.02
1.01
1.00
10.12
f1 (ppm)

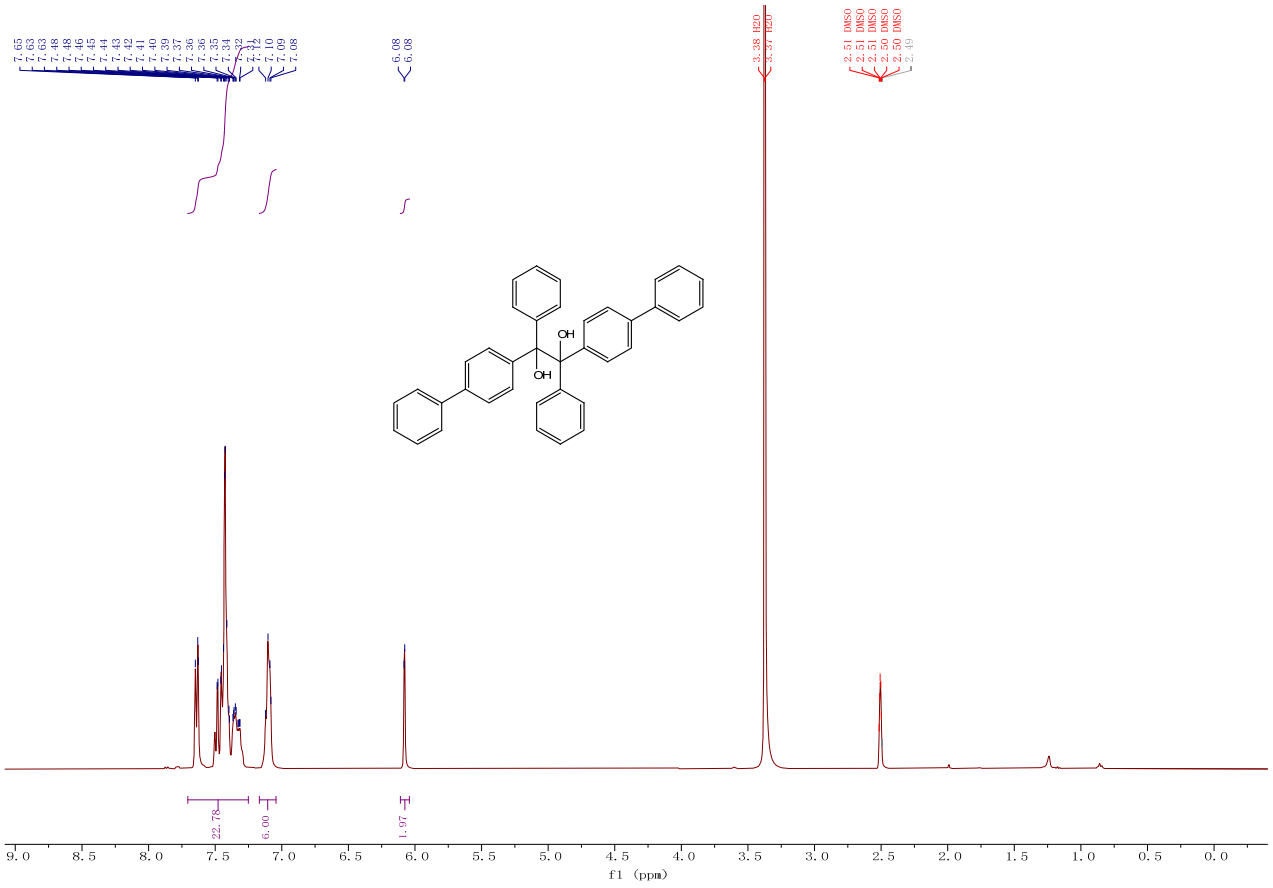

OH
OH
f1 (ppm)

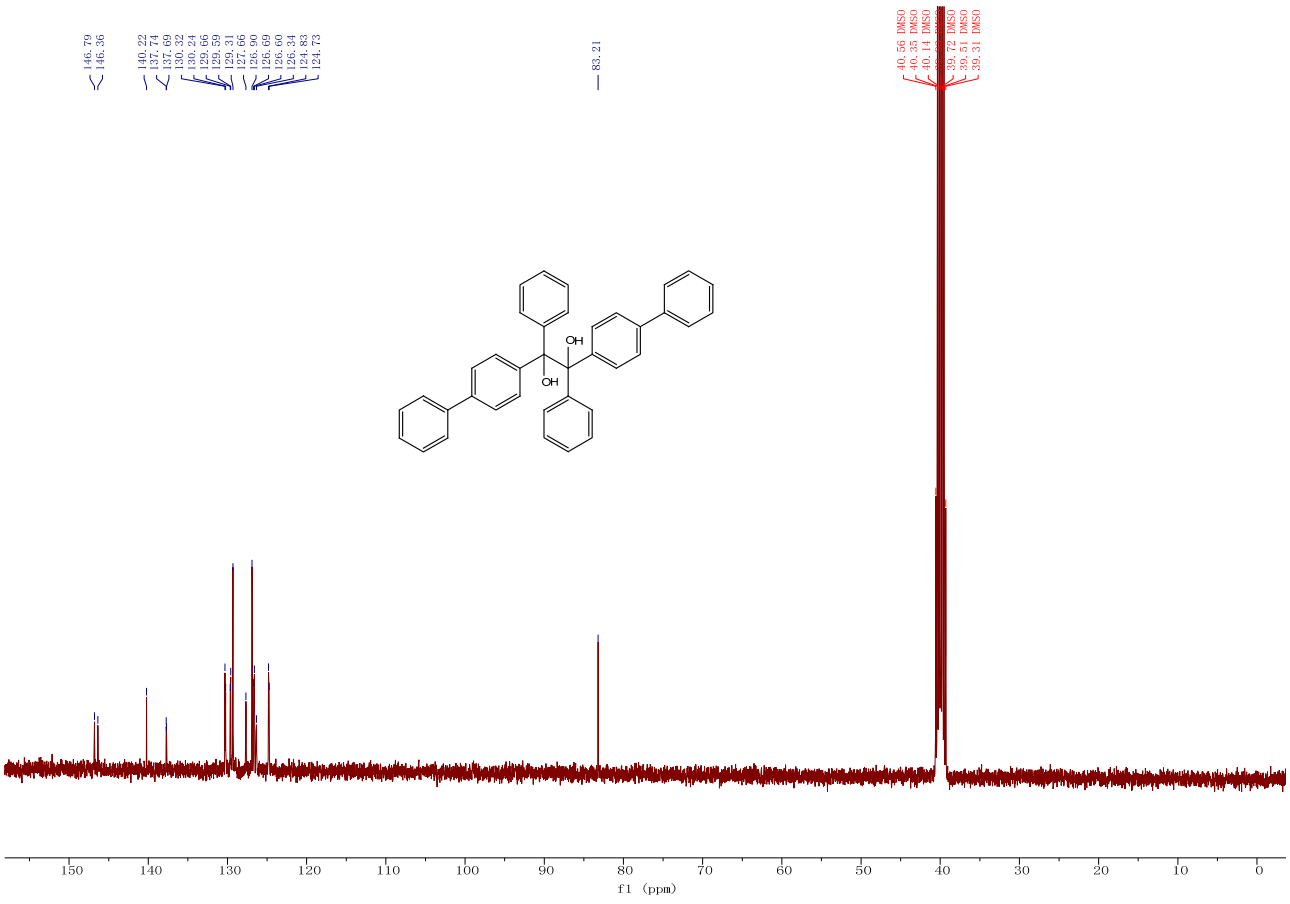

7.46
7.45
7.44
7.34
7.33
7.33
7.31
7.24
7.24
7.22
7.22
7.20
7.19
7.18
7.18
7.17
7.08
7.06
5.17
5.16
4.98
4.87
3.40 H2O
3.39 H2O
2.51 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
1.49
1.33
1.31
1.29
OH
H3C
CH3
OH
HO
OH
H3C
CH3
20.14
0.44
1.60
1.90
4.75
1.33
5.53
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

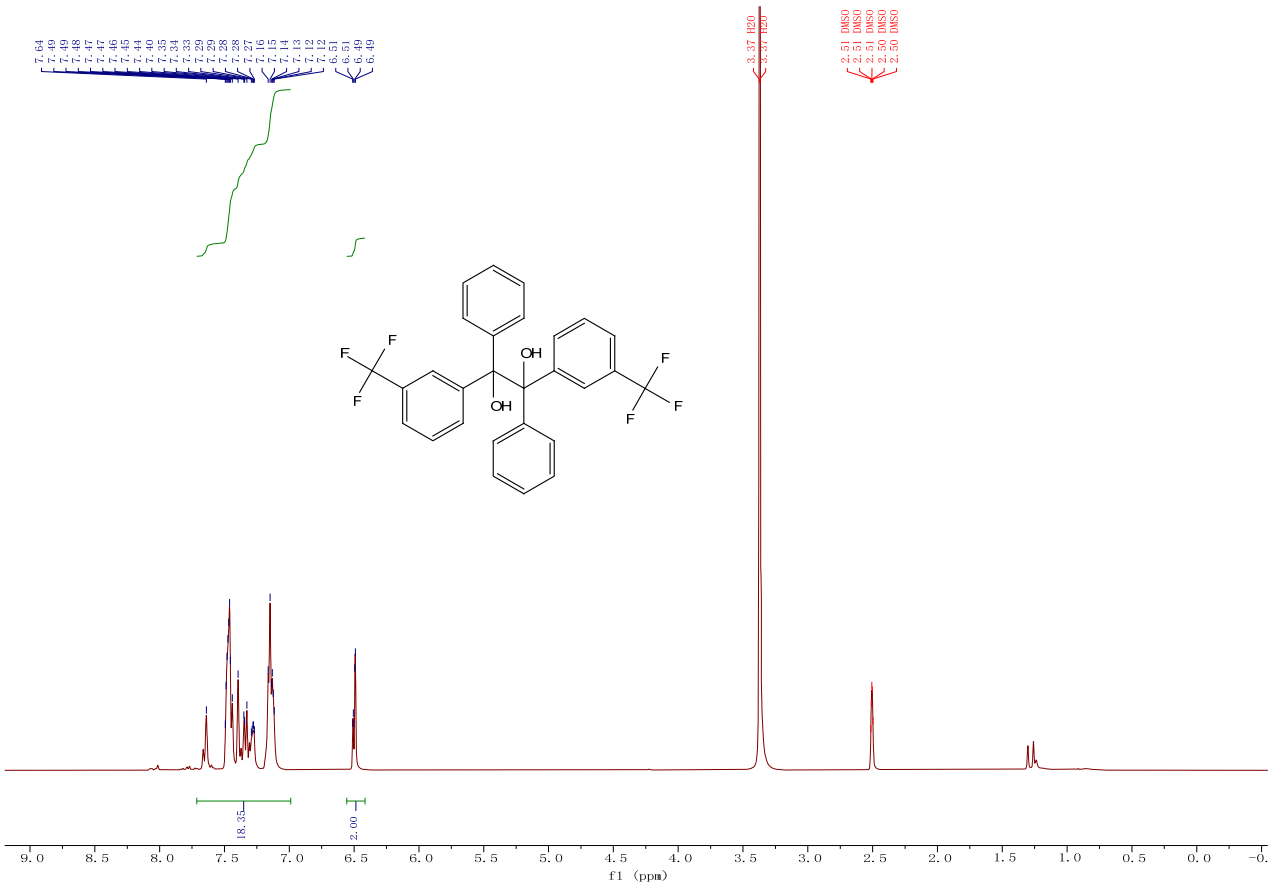

147.85
147.27
146.46
128.44
128.08
127.75
126.97
126.86
126.56
126.21
126.18
125.75
77.78
77.36
40.57 DMSO
40.36 DMSO
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.32 DMSO
25.55
25.15
OH
H3C
CH3
OH
HO
OH
H3C
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

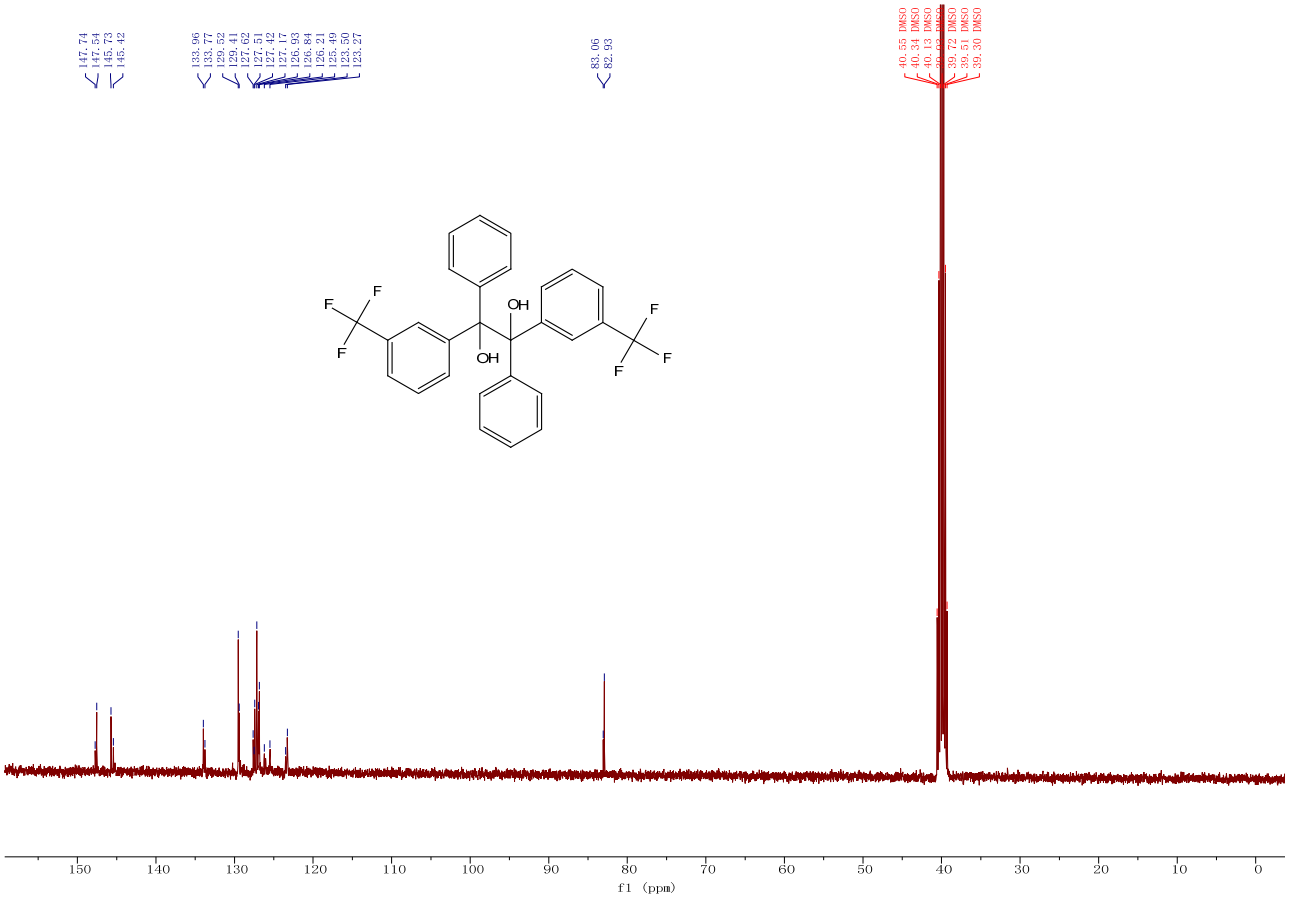

7.33
7.33
7.33
7.32
7.29
7.27
7.26
7.25
7.24
7.23
7.23
7.22
7.20
7.18
7.17
7.07
7.07
7.06
7.05
7.03
6.90
6.88
6.86
5.77
5.77
3.38 H2O
3.38 H2O
3.38 H2O
2.51 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.21
2.20
2.20
CH3
OH
OH
H3C
8.55
6.26
4.13
2.11
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

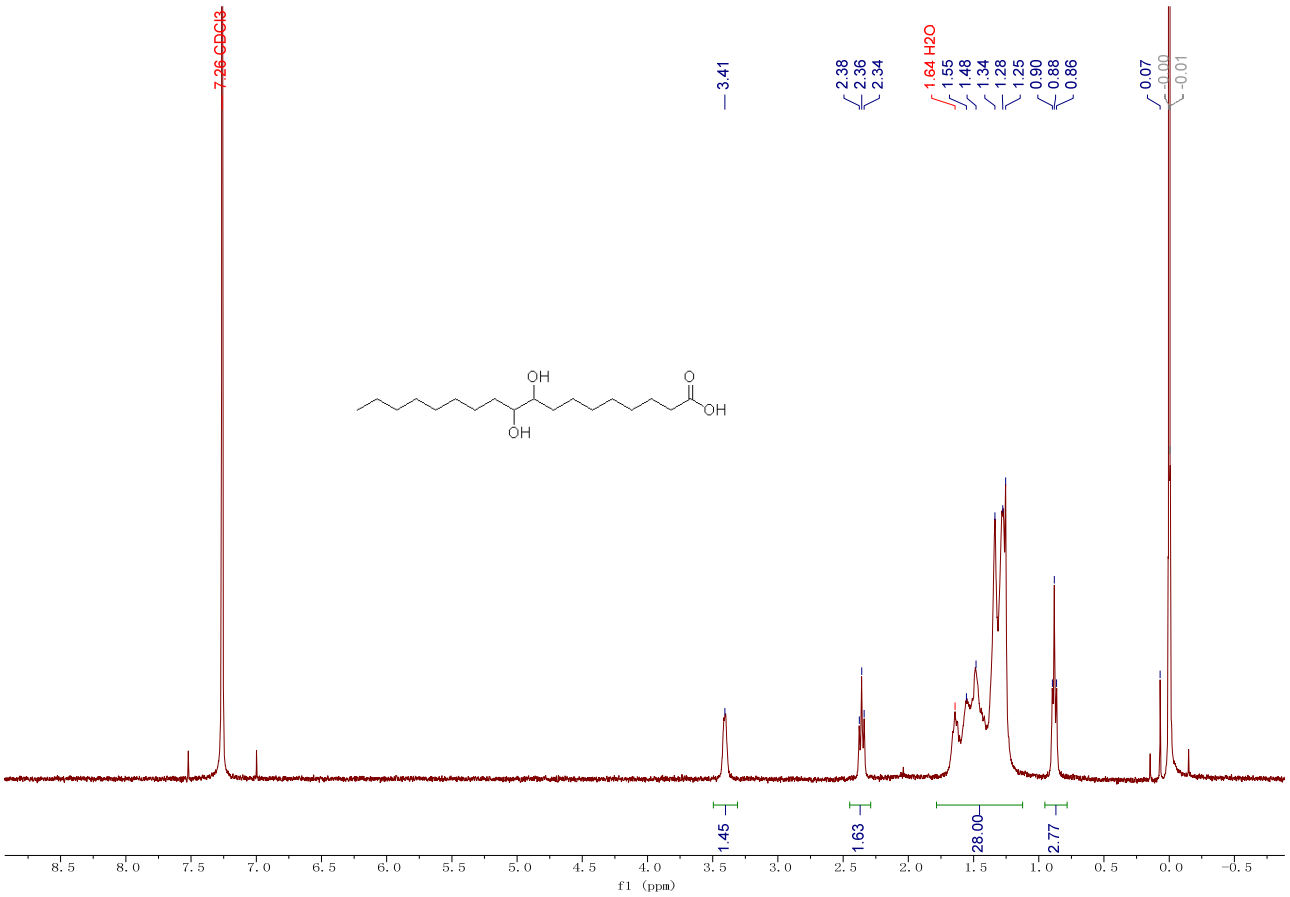

147.17
147.00
144.24
144.07
134.94
134.91
129.64
129.62
129.54
127.31
127.19
126.49
126.36
126.14
83.07
40.56 DMSO
40.35 DMSO
40.14 DMSO
39.93 DMSO
39.72 DMSO
39.52 DMSO
39.31 DMSO
21.00
CH3
OH
OH
H3C
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.65
7.63
7.63
7.48
7.48
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.37
7.36
7.35
7.34
7.32
7.31
7.10
7.09
7.08
6.08
6.08
3.38 H2O
3.37 H2O
2.51 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49
OH
OH
22.78
6.00
1.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

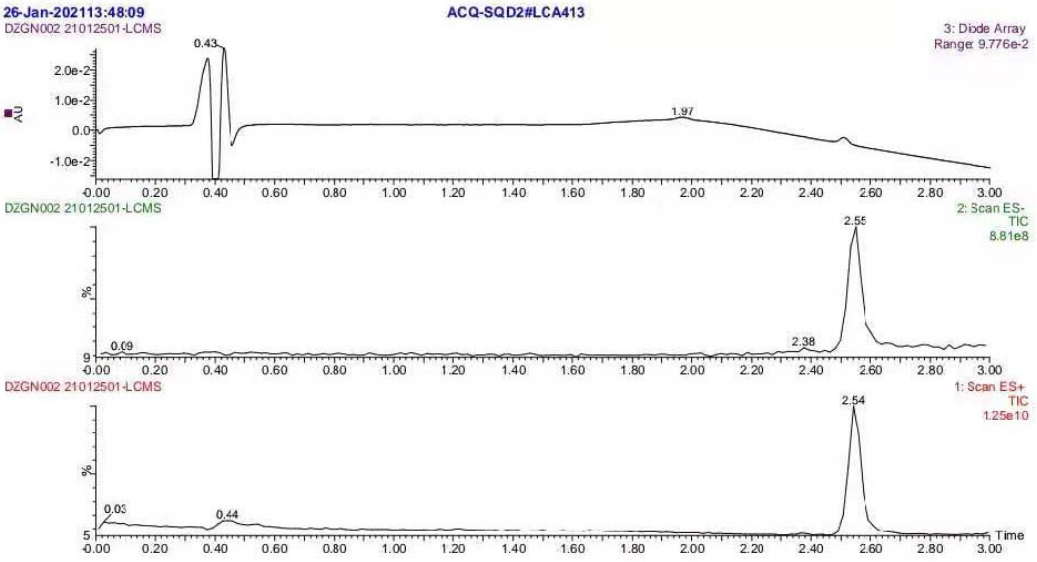

146.79
146.36
140.22
137.74
137.69
130.32
130.24
129.66
129.59
129.31
127.66
126.90
126.69
126.60
126.34
124.83
124.73
83.21
40.56 DMSO
40.35 DMSO
40.14 DMSO
39.72 DMSO
39.51 DMSO
39.31 DMSO
OH
OH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

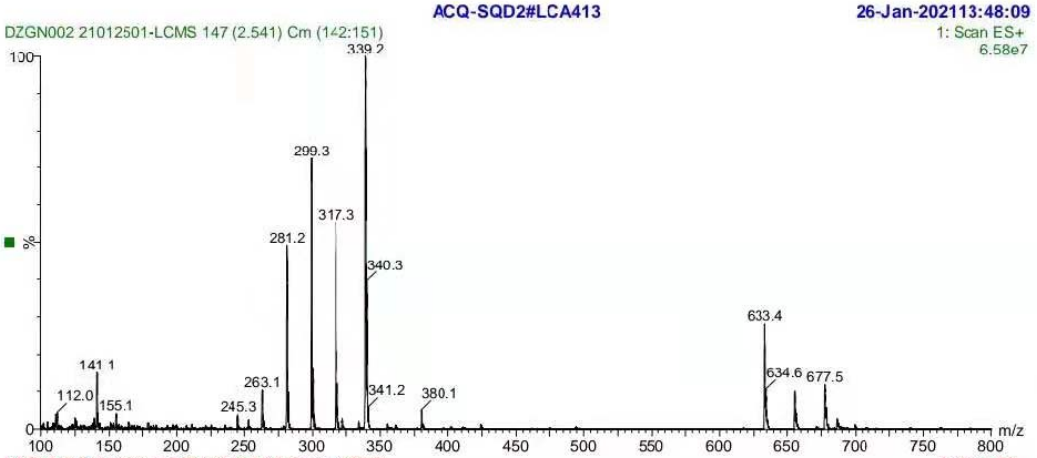

7.64
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.44
7.40
7.35
7.34
7.33
7.29
7.29
7.28
7.28
7.27
7.16
7.15
7.14
7.13
7.12
7.12
6.51
6.51
6.49
6.49
3.37 H2O
3.37 H2O
2.51 DMSO
2.51 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
F
F
F
OH
OH
F
F
F
18.35
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

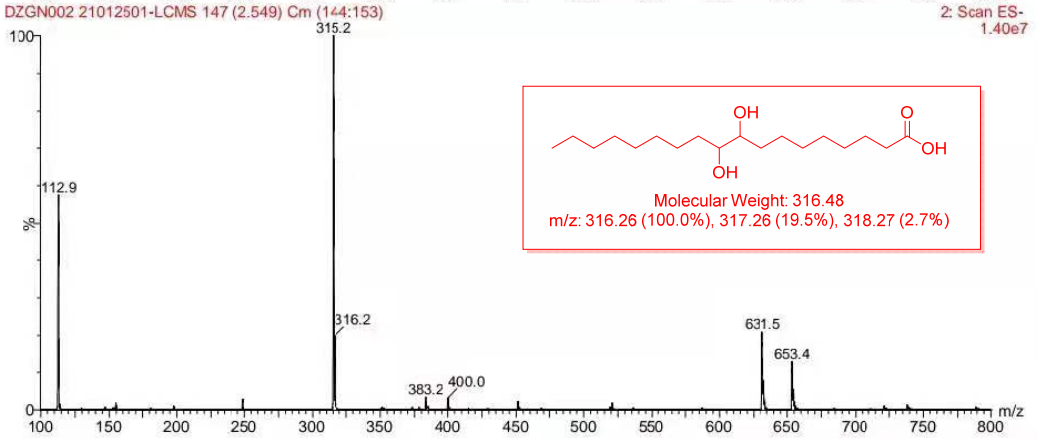

147.74
147.54
145.73
145.42
133.96
133.77
129.52
129.41
127.62
127.51
127.42
127.17
126.93
126.84
126.21
125.49
123.50
123.27
83.06
82.93
40.55 DMSO
40.34 DMSO
40.13 DMSO
39.72 DMSO
39.51 DMSO
39.30 DMSO
F
F
F
OH
OH
F
F
F
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 CDCl3
3.41
2.38
2.36
2.34
1.64 H2O
1.55
1.48
1.34
1.28
1.25
0.90
0.88
0.86
0.07
-0.00
-0.01
OH
OH
O
OH
1.45
1.63
28.00
2.77
f1 (ppm)

DZGN002 21012501-LCMS 50_100 03ML_MIN

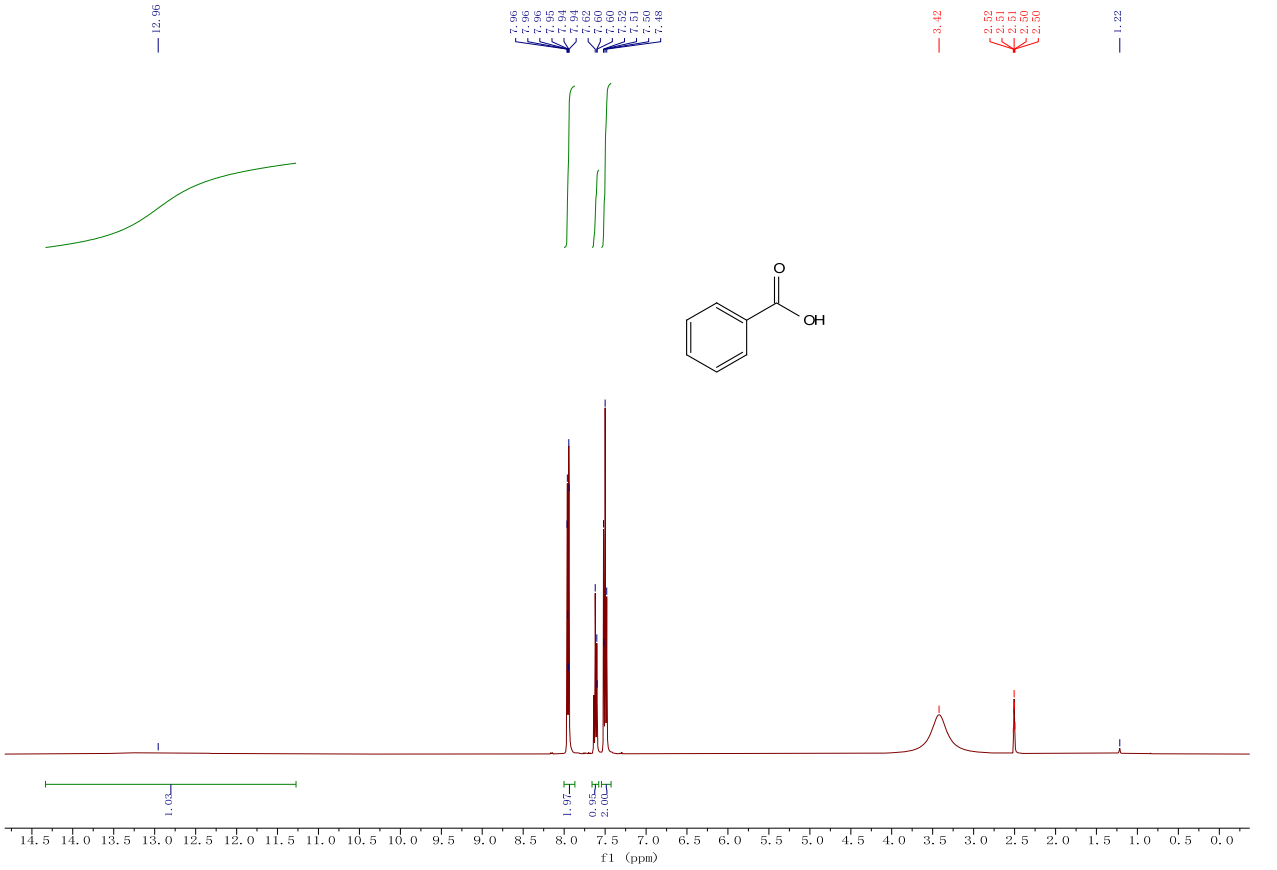


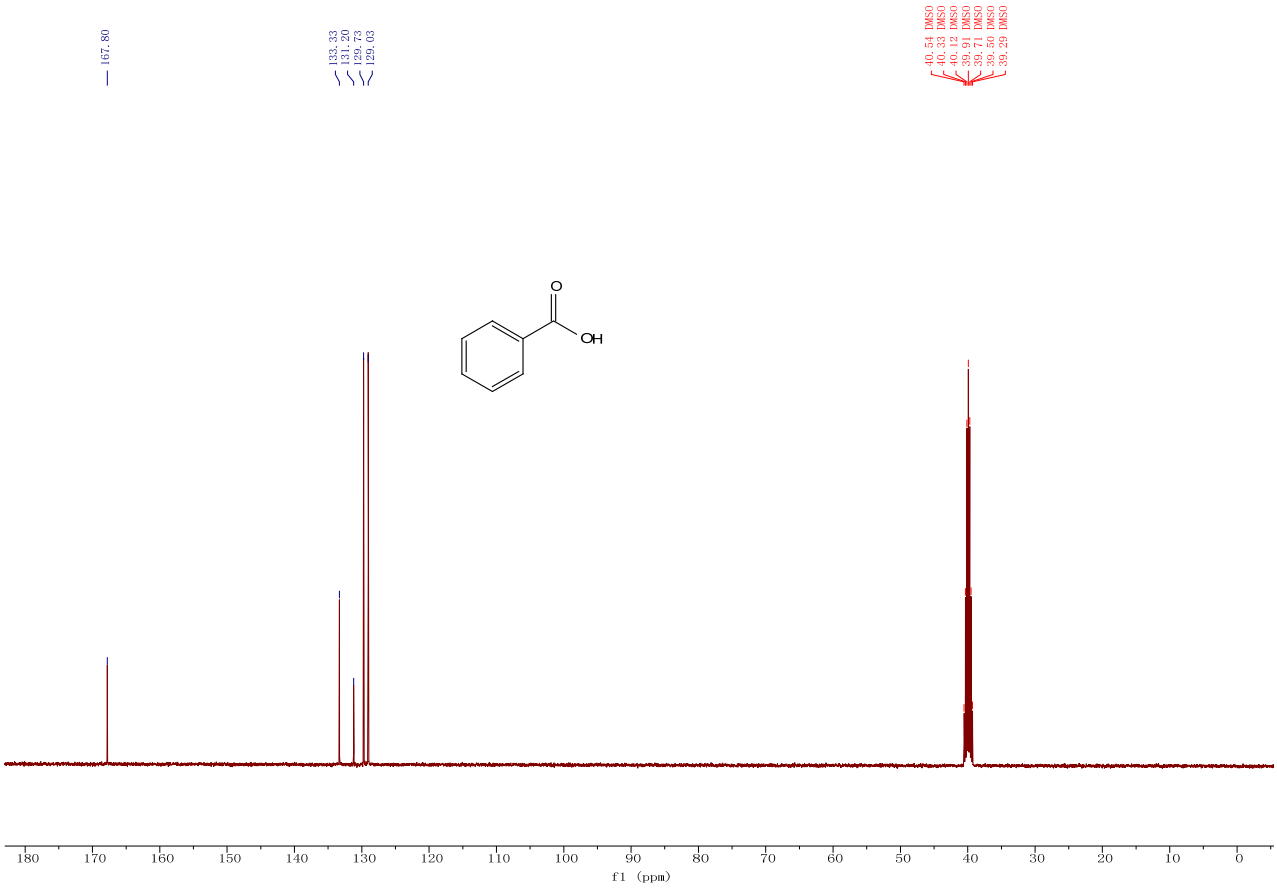


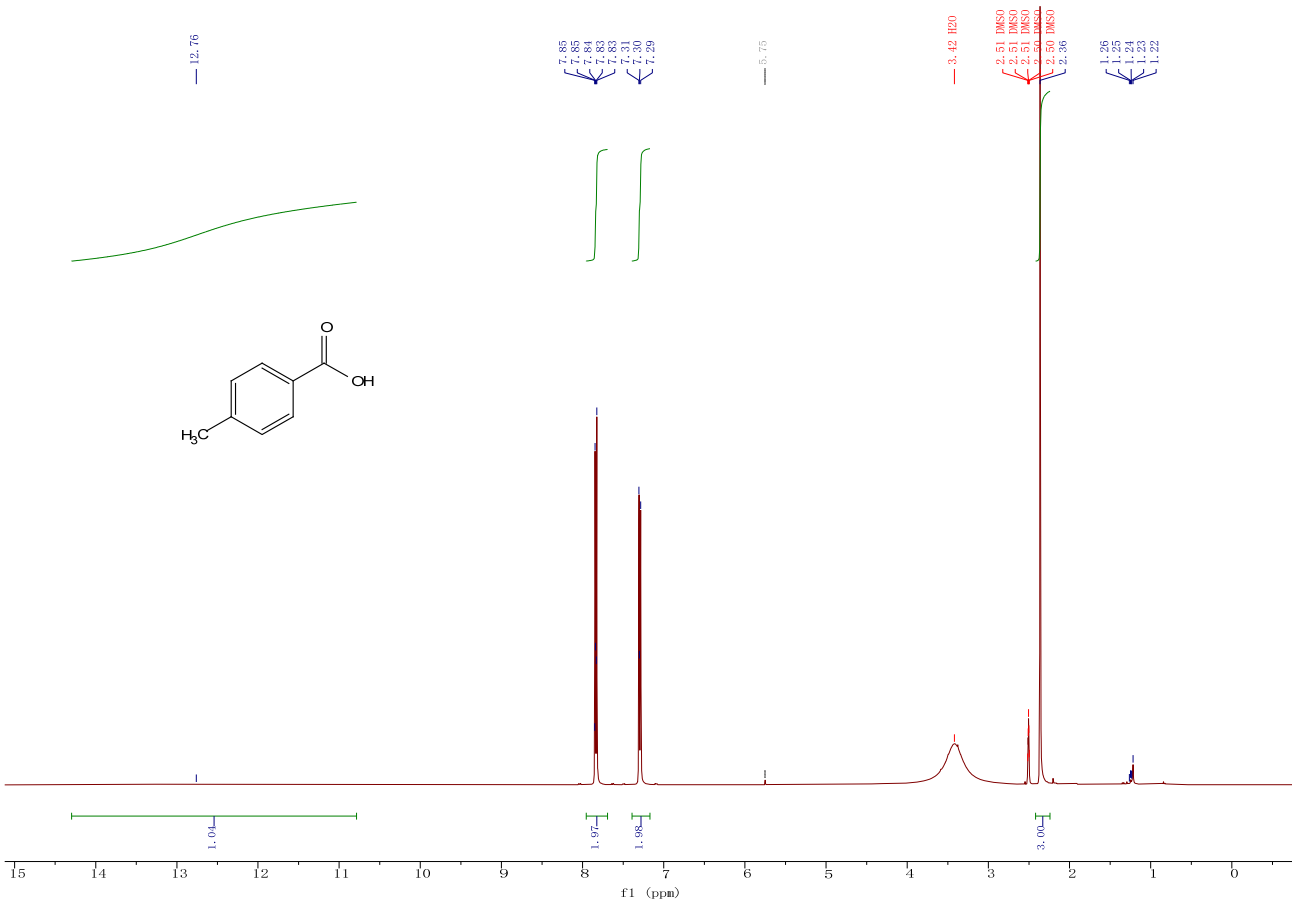


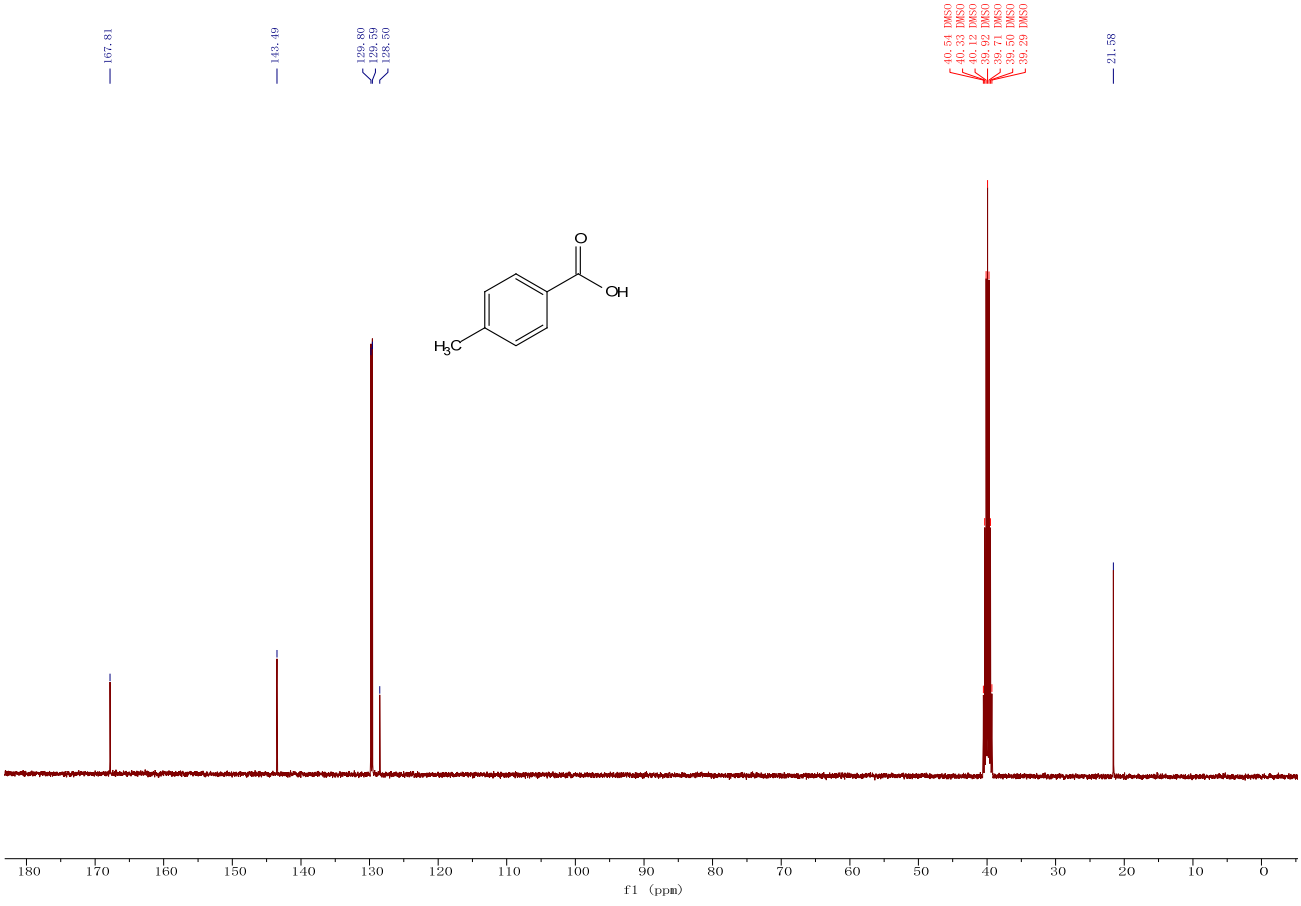
Molecular Weight: 316.48
m/z: 316.26 (100.0%), 317.26 (19.5%), 318.27 (2.7%)

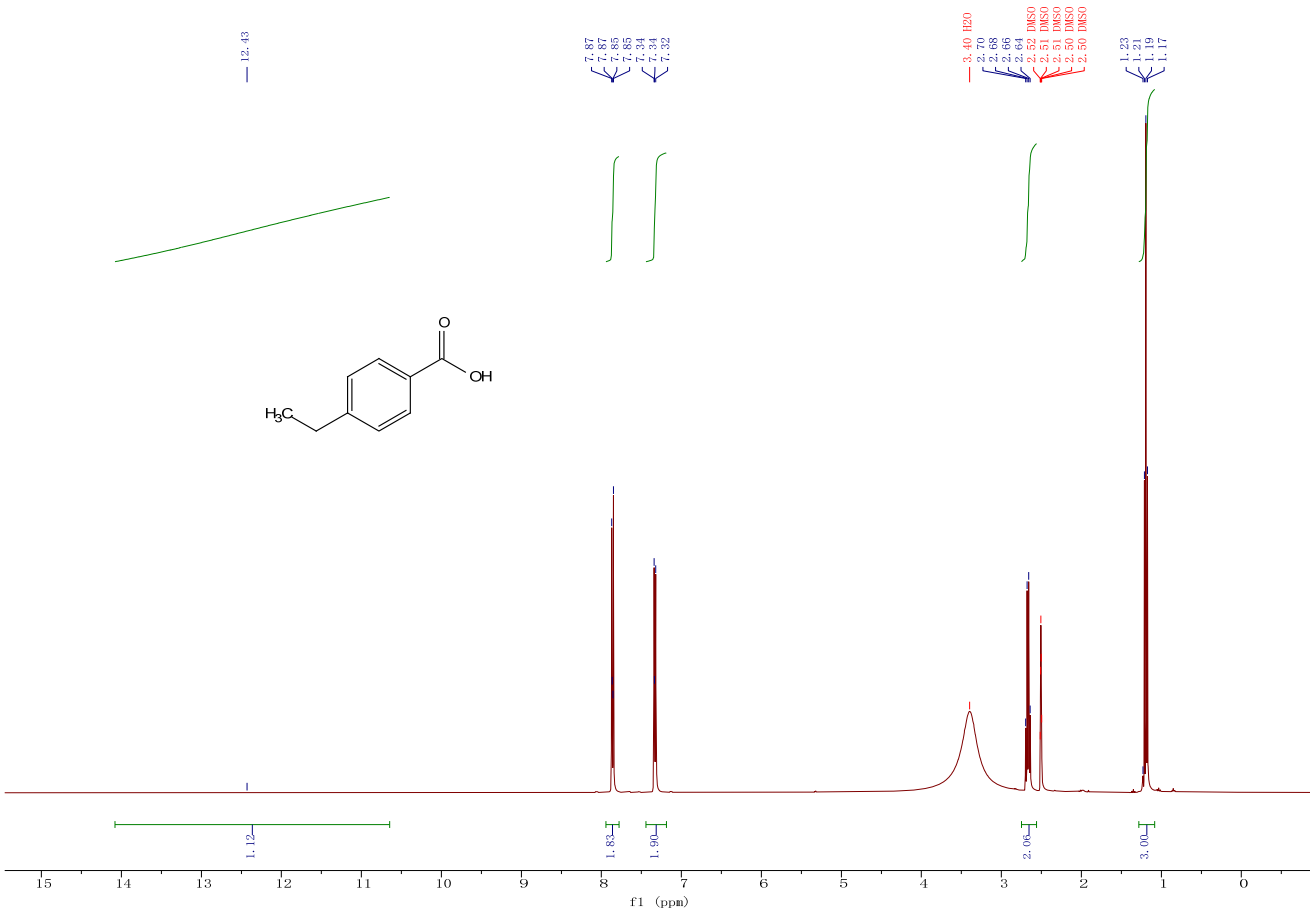
Oxidative products: carboxylic acid and ketones

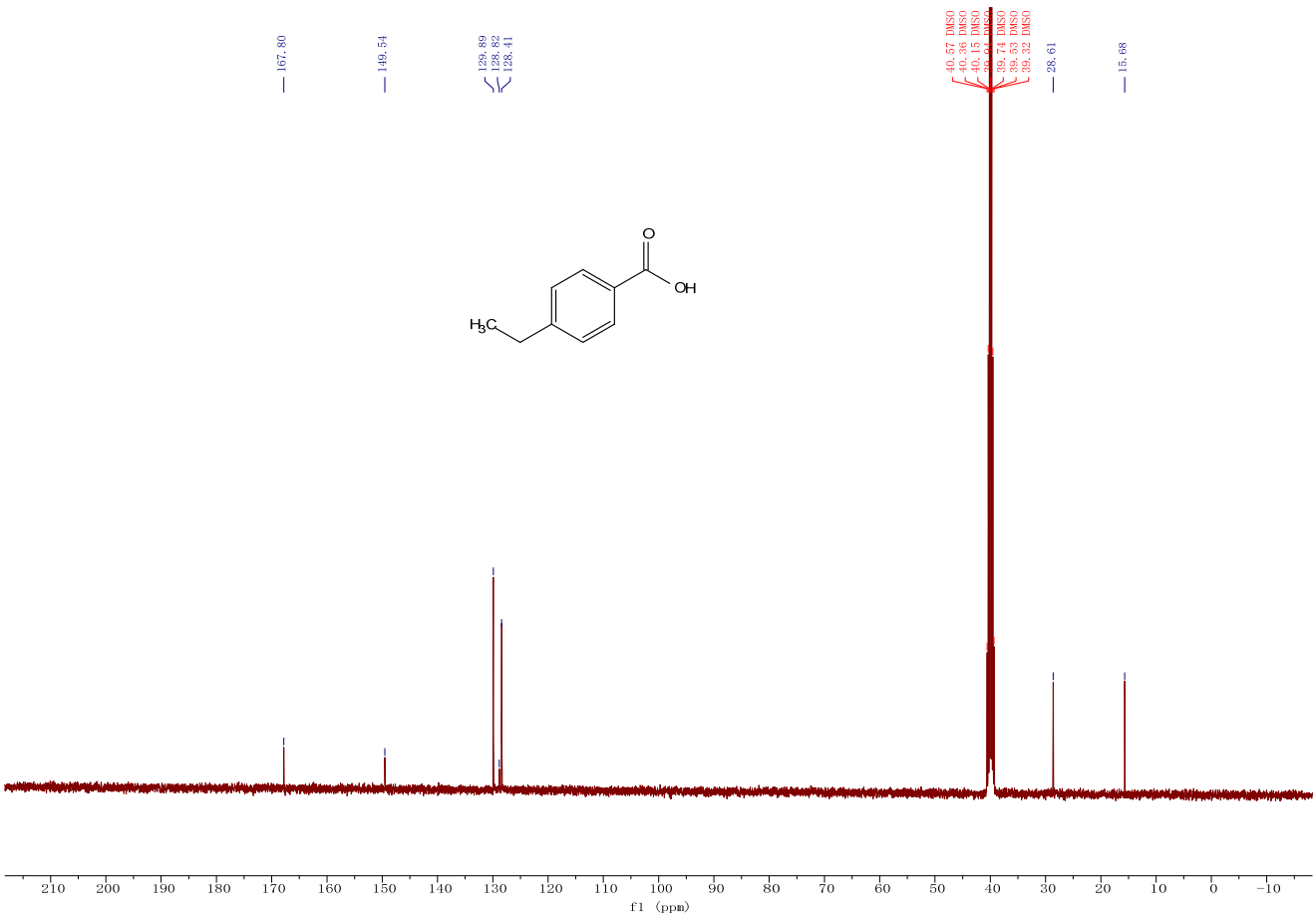


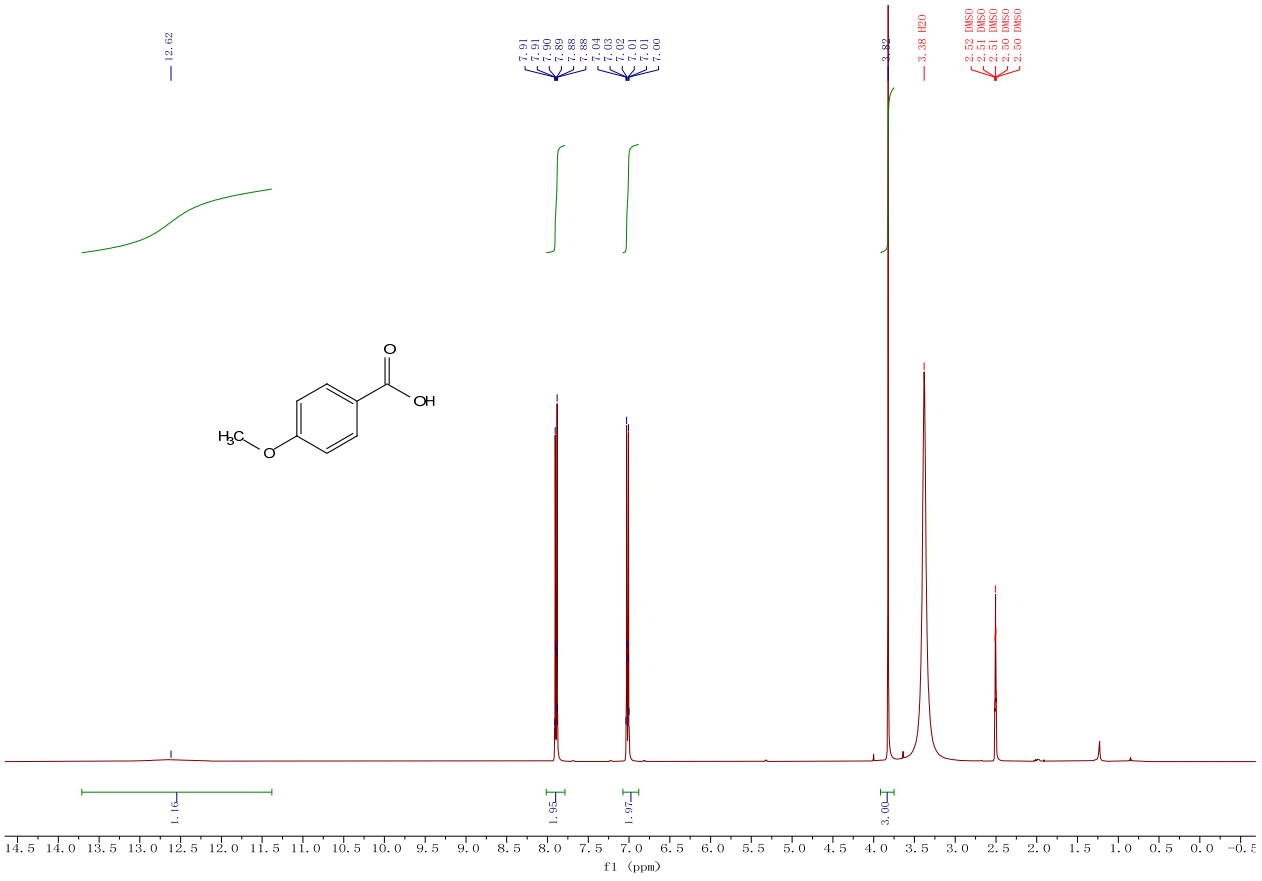


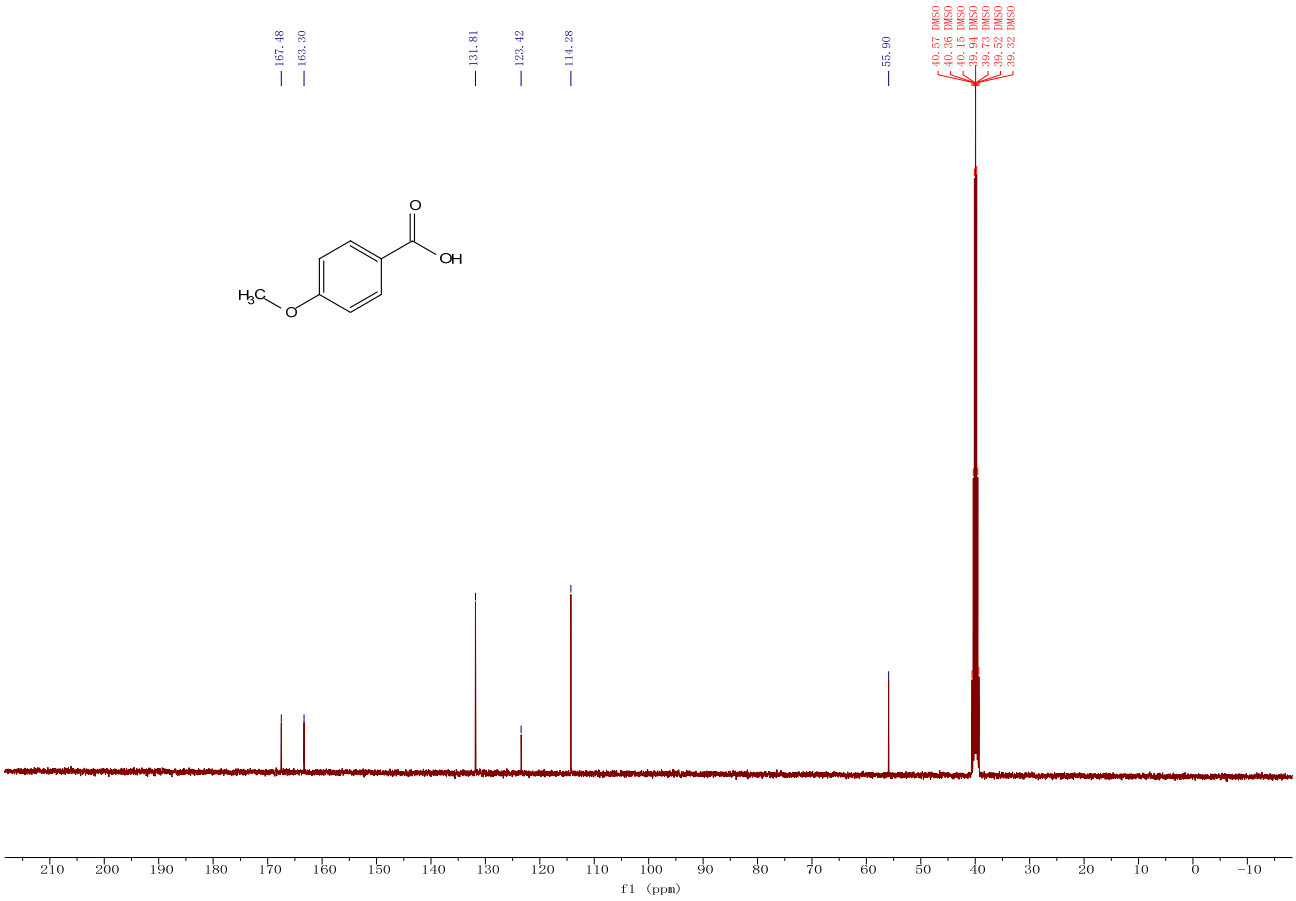

12.76
7.85
7.85
7.84
7.83
7.83
7.31
7.30
7.29
5.75
3.42 H2O
2.51 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.36
1.26
1.25
1.24
1.23
1.22
O
OH
H3C
1.04
1.97
1.98
3.00
f1 (ppm)

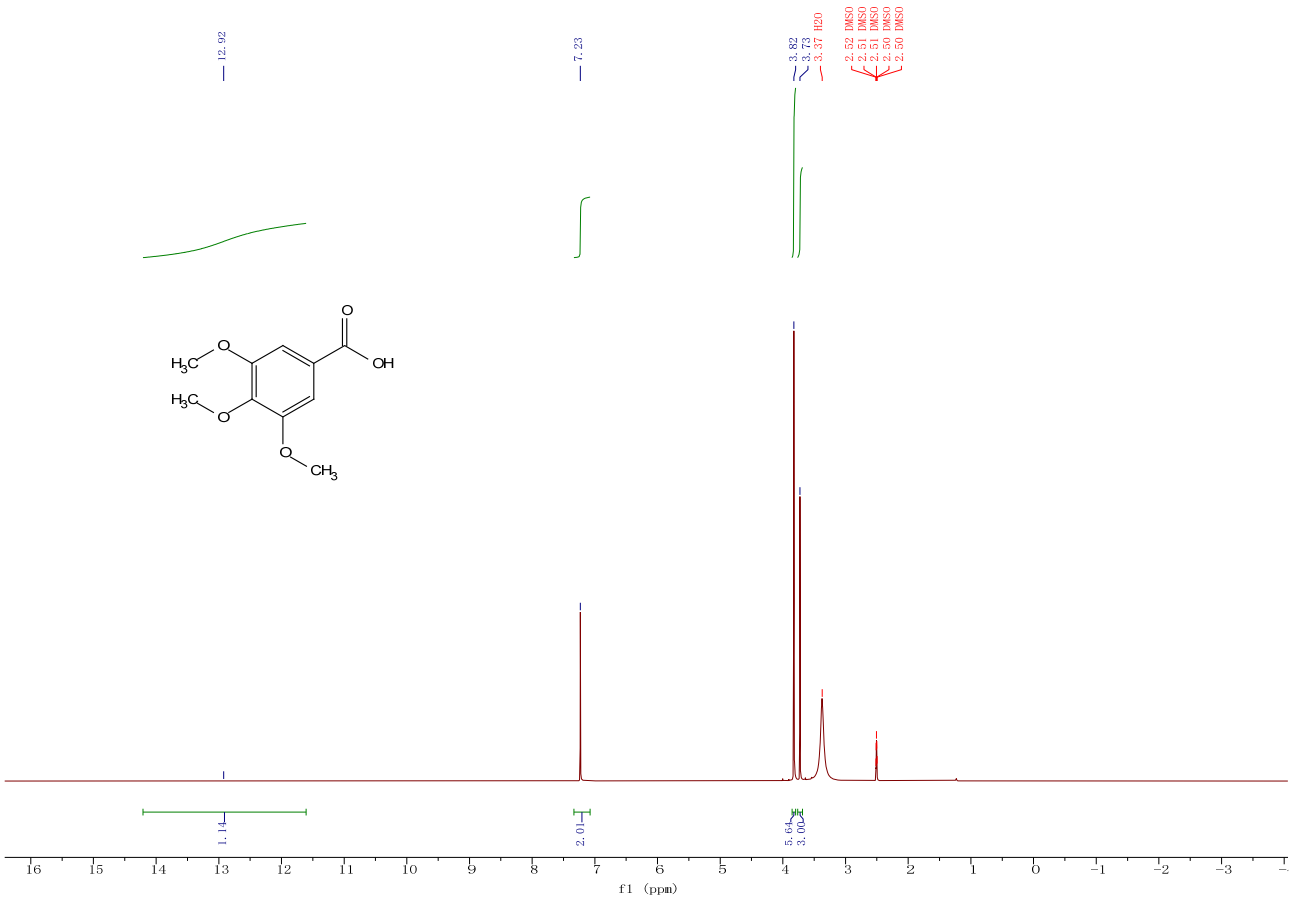

167.81
143.49
129.80
129.59
128.50
40.54 DMSO
40.33 DMSO
40.12 DMSO
39.92 DMSO
39.71 DMSO
39.50 DMSO
39.29 DMSO
21.58
O
OH
H3C
f1 (ppm)

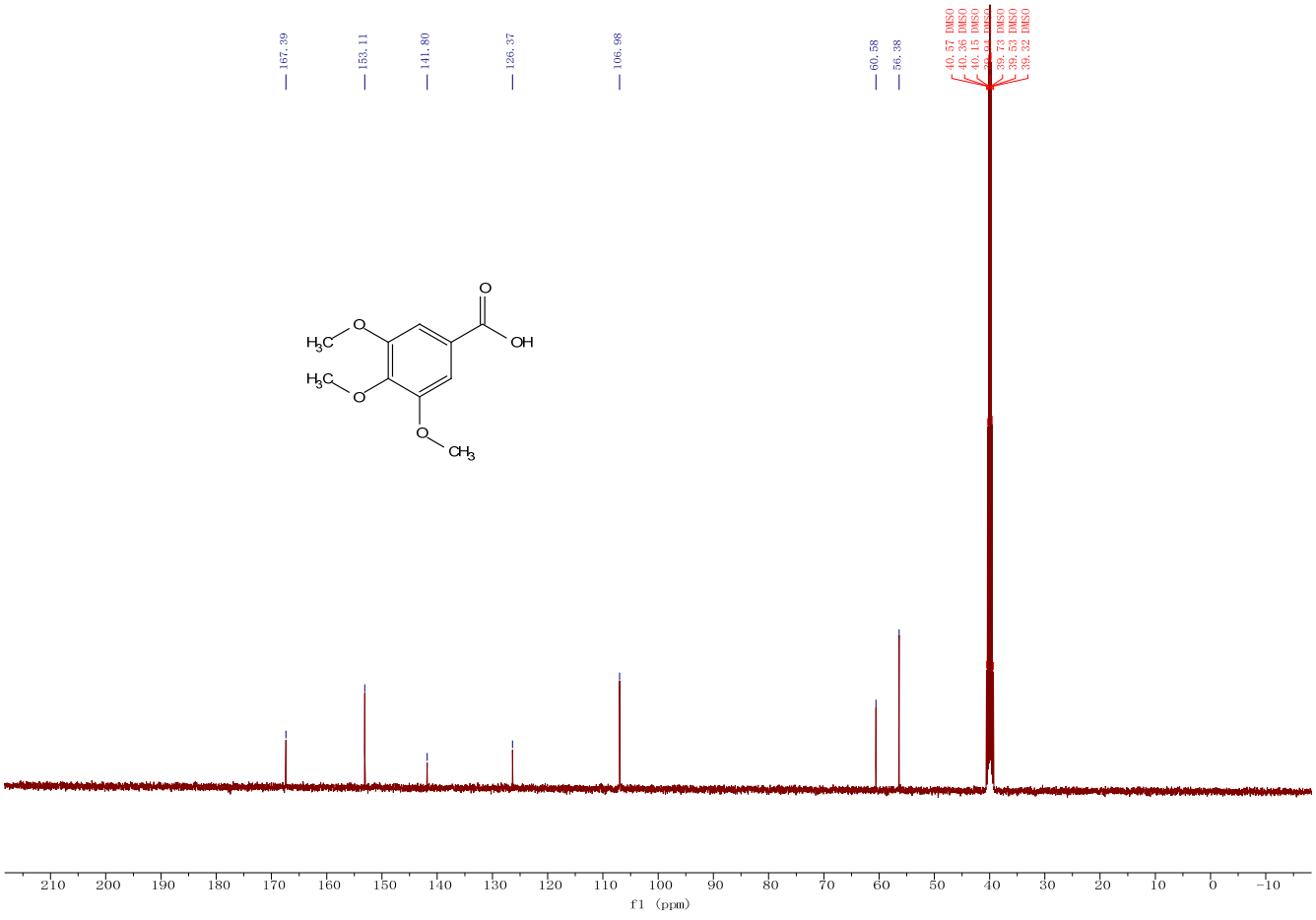

12.43
7.87
7.87
7.85
7.85
7.34
7.34
7.32
3.40 H2O
2.70
2.68
2.66
2.64
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
1.23
1.21
1.19
1.17
O
OH
H3C
1.12
1.83
1.90
2.06
3.00
f1 (ppm)

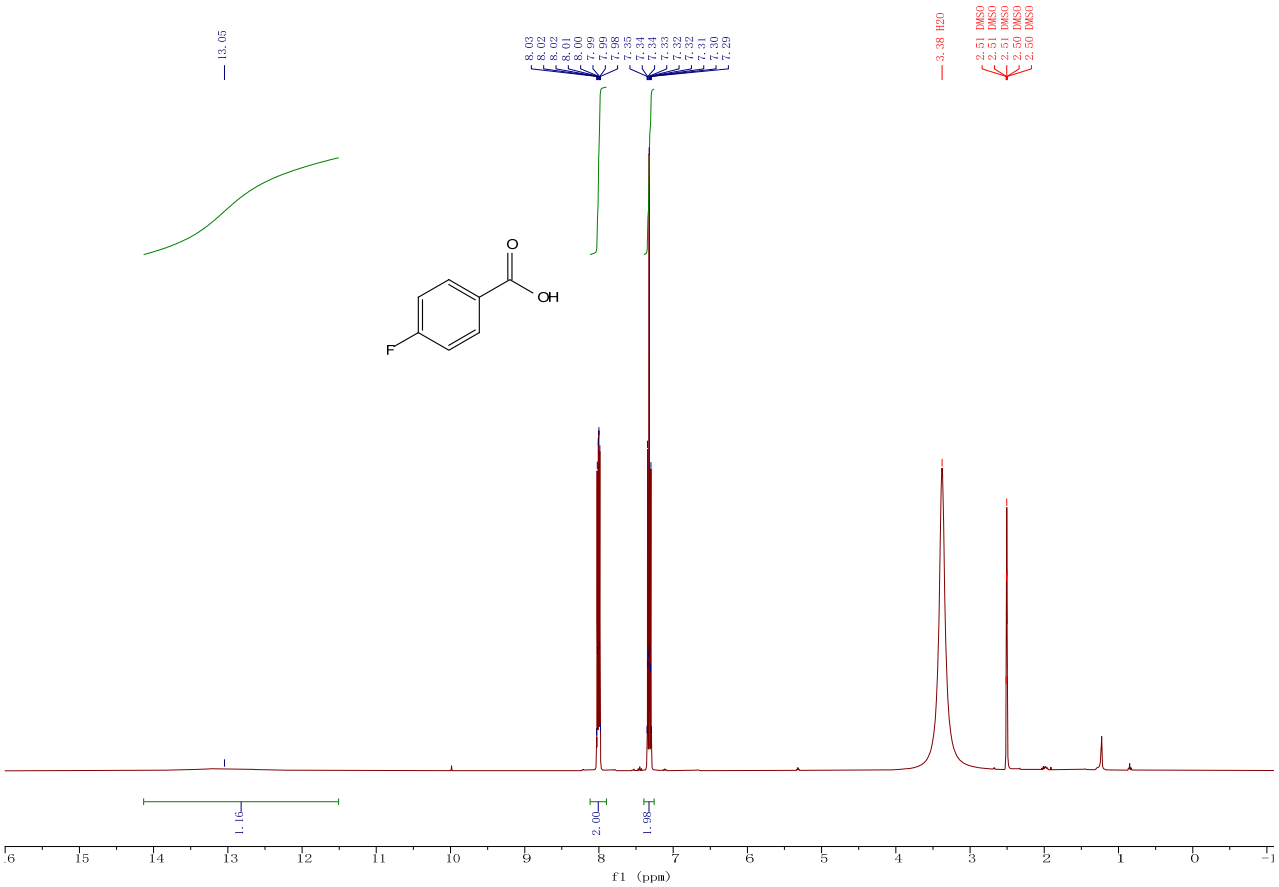

167.80
149.54
129.89
128.82
128.41
40.57 DMSO
40.36 DMSO
40.15 DMSO
39.74 DMSO
39.53 DMSO
39.32 DMSO
28.61
15.68
O
OH
H3C
f1 (ppm)

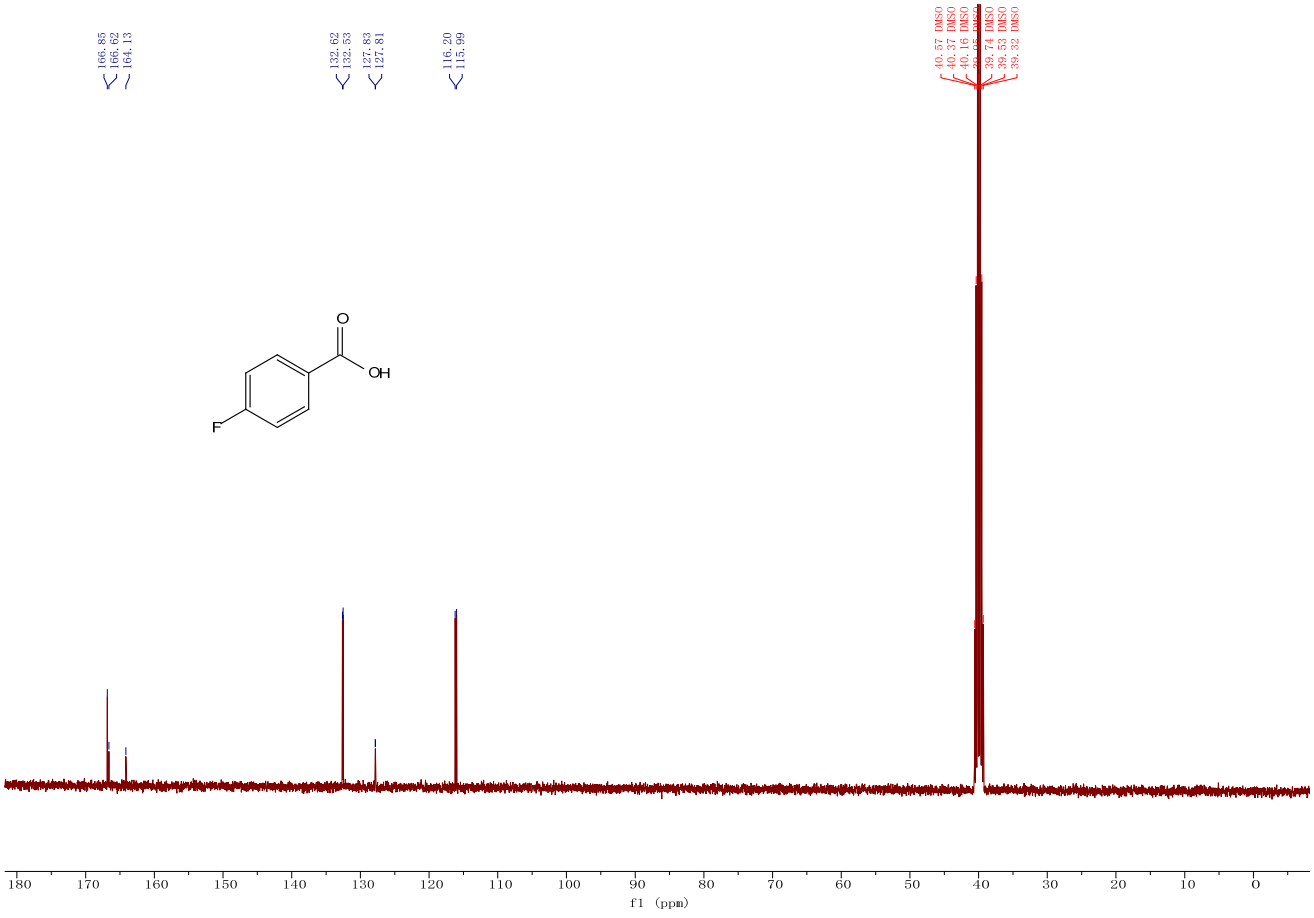

12.62
7.91
7.91
7.90
7.89
7.88
7.88
7.04
7.03
7.02
7.01
7.01
7.00
3.82
3.38 H2O
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
O
OH
H3C
O
1.16
1.95
1.97
3.00
f1 (ppm)

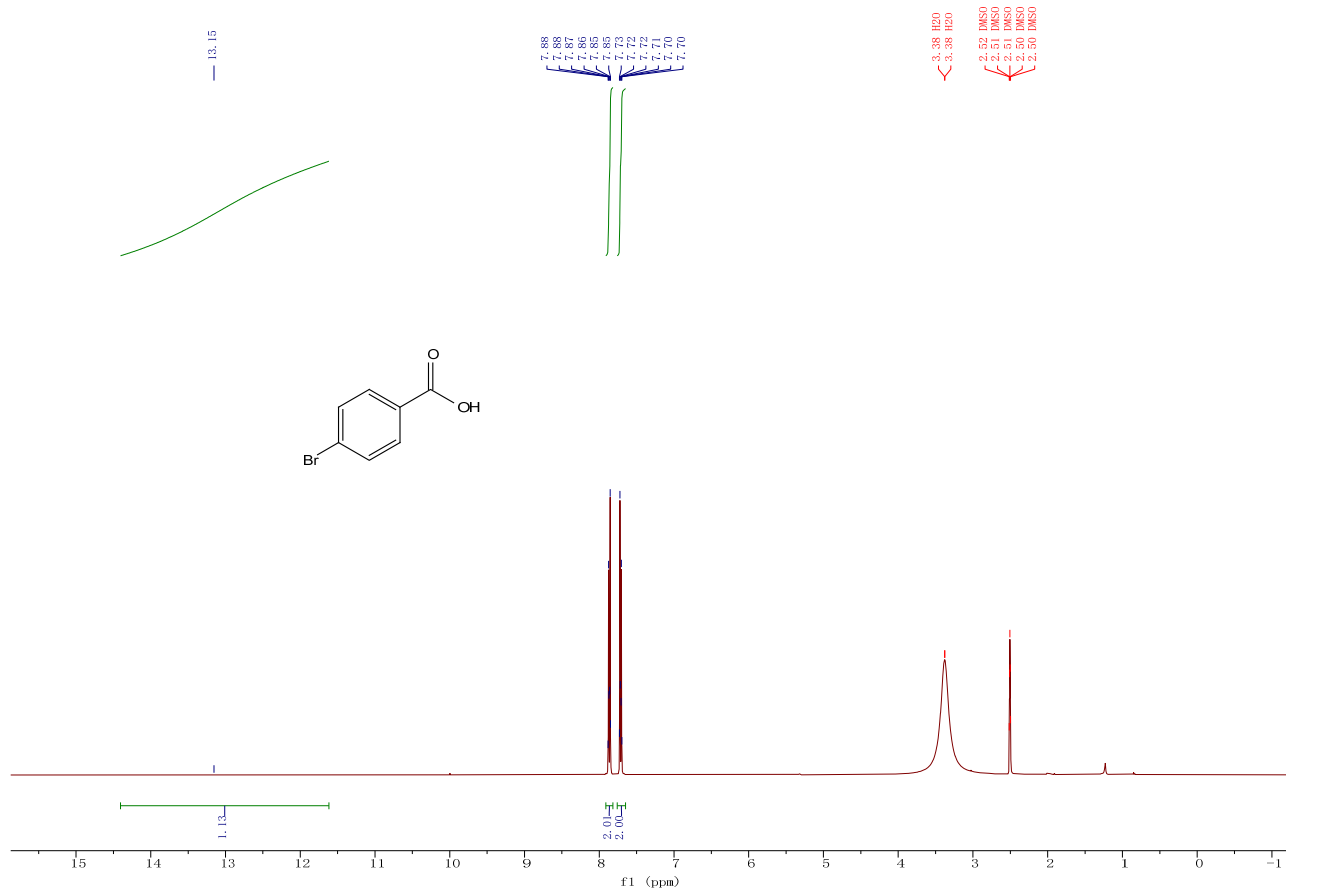

167.48
163.30
131.81
123.42
114.28
55.90
40.57 DMSO
40.36 DMSO
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.32 DMSO
O
OH
H3C
O
f1 (ppm)

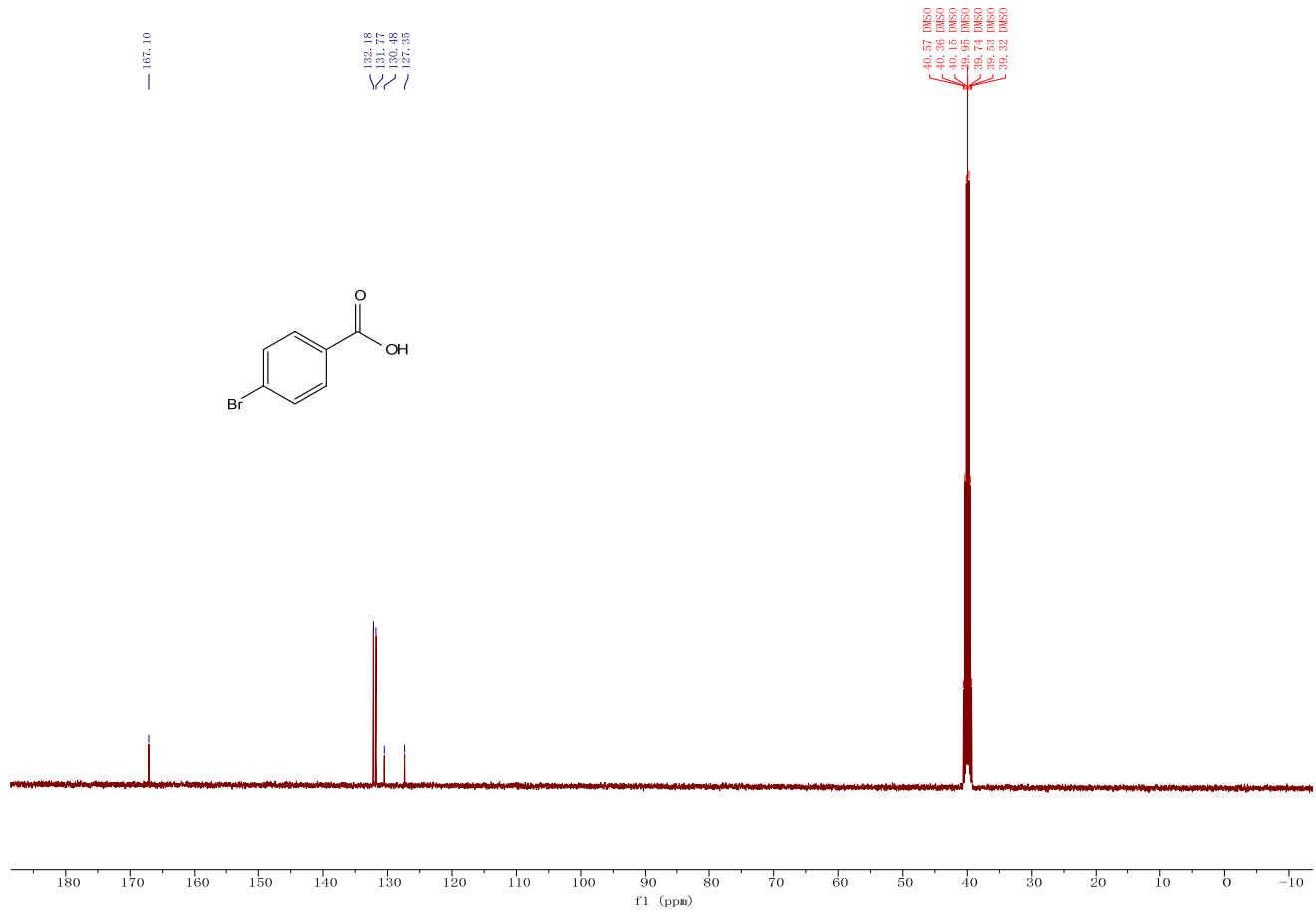

12.92
7.23
3.82
3.73
3.37 H2O
2.52 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
O
OH
H3C
O
H3C
O
O
CH3
1.14
2.01
5.64
3.00
f1 (ppm)

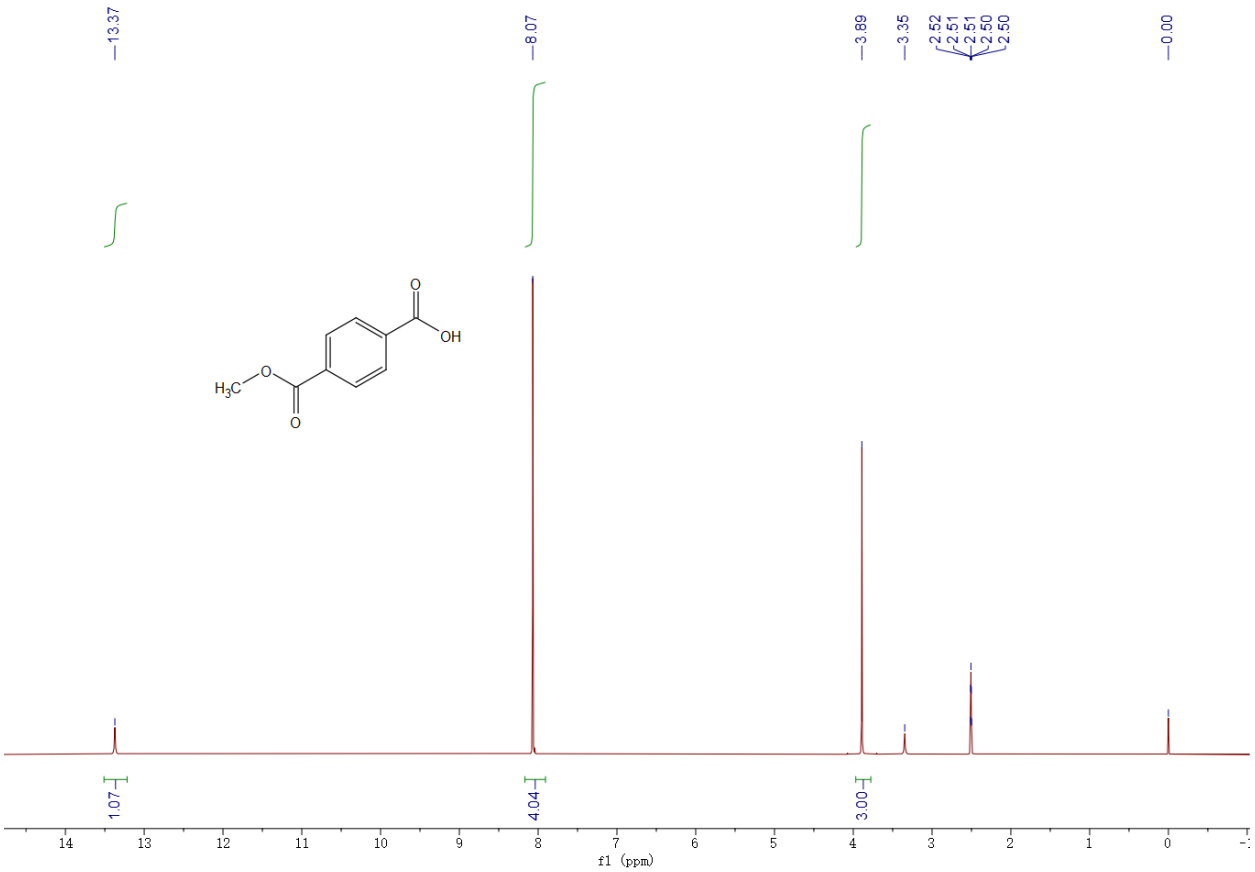

167.39
153.11
141.80
126.37
106.98
60.58
56.38
40.57 DMSO
40.36 DMSO
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.53 DMSO
39.32 DMSO
O
OH
H3C
O
H3C
O
O
CH3
f1 (ppm)

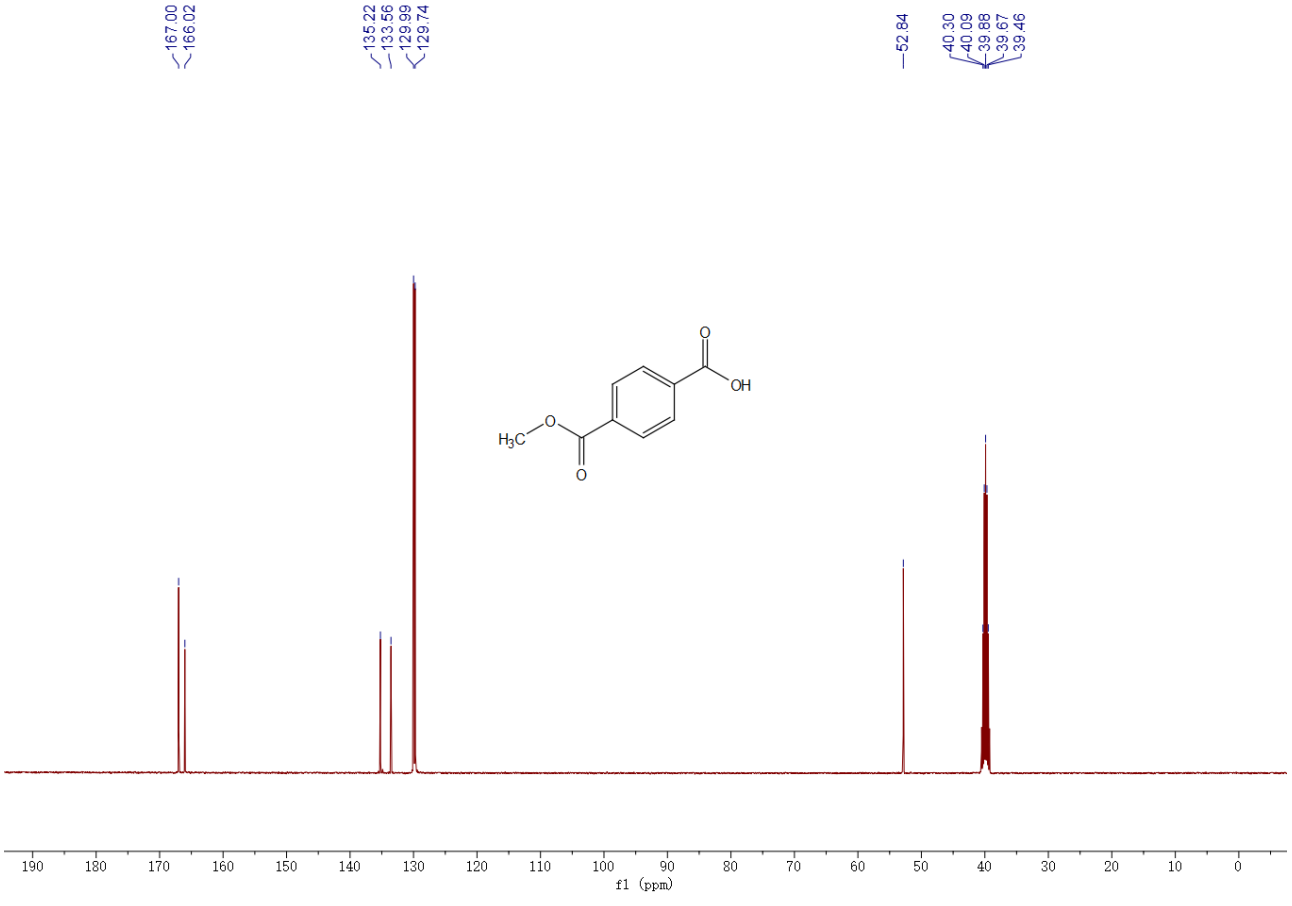

13.05
8.03
8.02
8.02
8.01
8.00
7.99
7.98
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.29
3.38 H2O
2.51 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
O
OH
F
1.16
2.00
1.98
f1 (ppm)

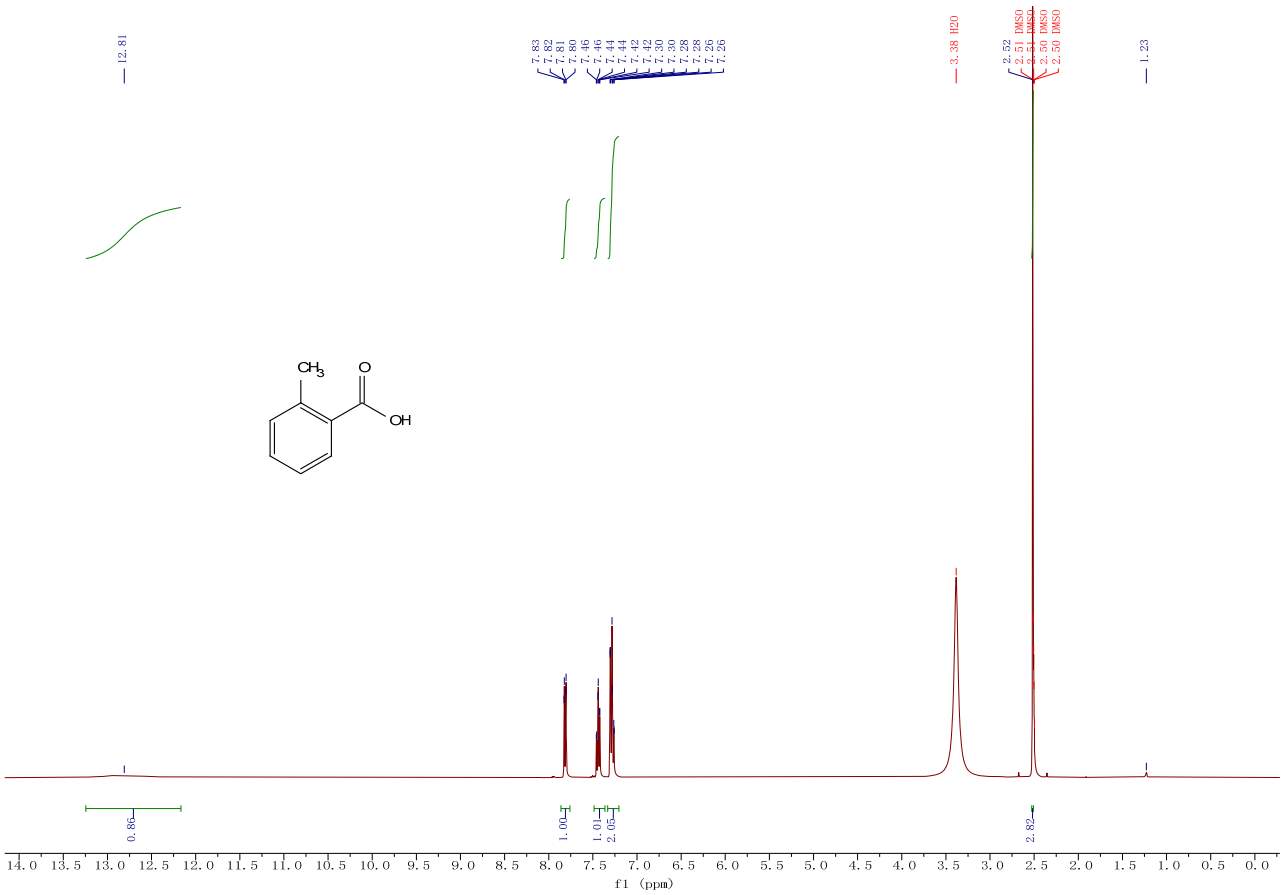

166.85
166.62
164.13
132.62
132.53
127.83
127.81
116.20
115.99
40.57 DMSO
40.37 DMSO
40.16 DMSO
39.74 DMSO
39.53 DMSO
39.32 DMSO
O
OH
F
f1 (ppm)

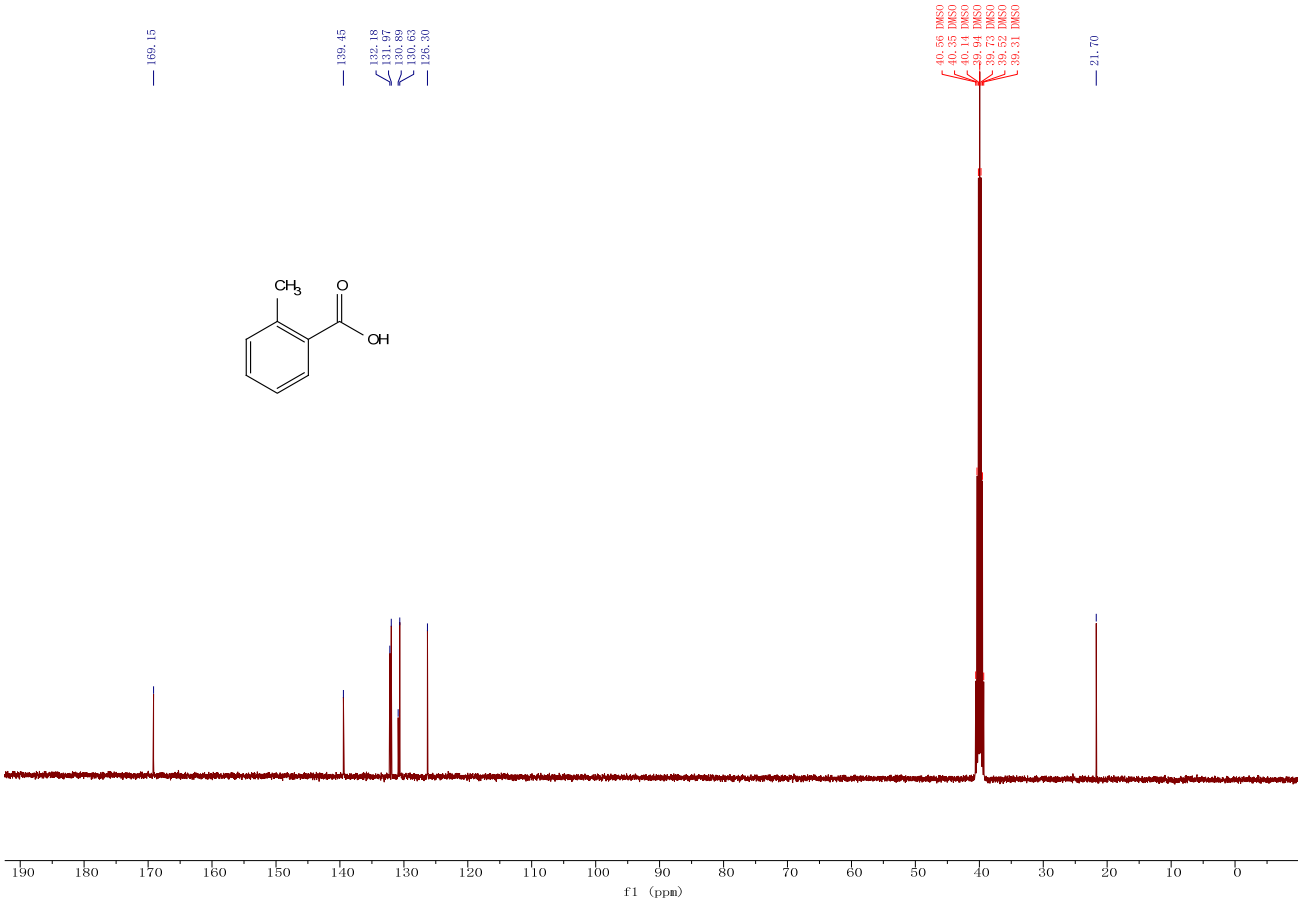

13.15
7.88
7.88
7.87
7.86
7.85
7.85
7.73
7.72
7.72
7.71
7.70
7.70
3.38 H2O
3.38 H2O
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
O
OH
Br
1.13
2.01
2.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

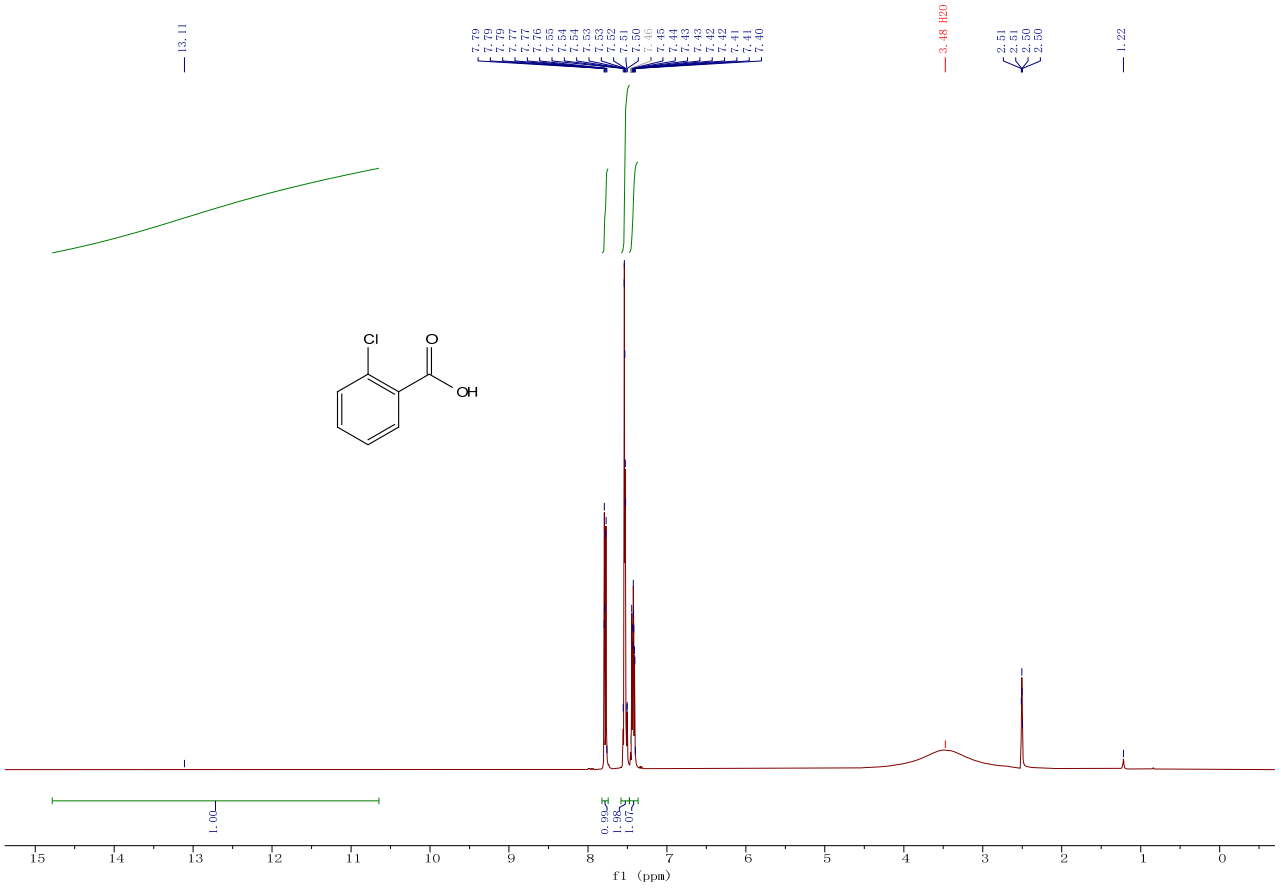

167.10
132.18
131.77
130.48
127.35
40.57 DMSO
40.36 DMSO
40.15 DMSO
39.95 DMSO
39.74 DMSO
39.53 DMSO
39.32 DMSO
O
OH
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

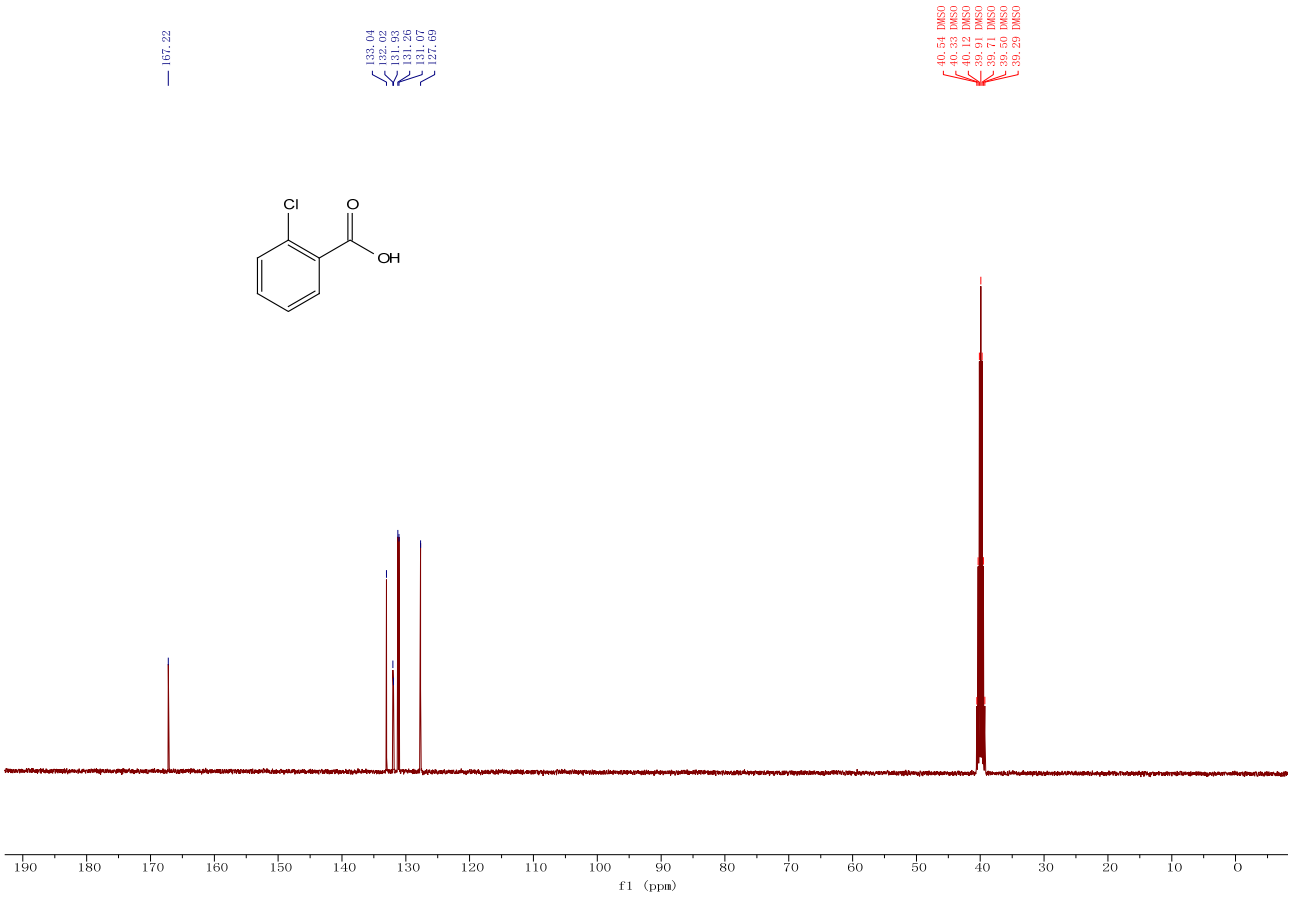

13.37
8.07
3.89
3.35
2.52
2.51
2.51
2.50
2.50
0.00
O
OH
H3C
O
O
1.07
4.04
3.00
f1 (ppm)

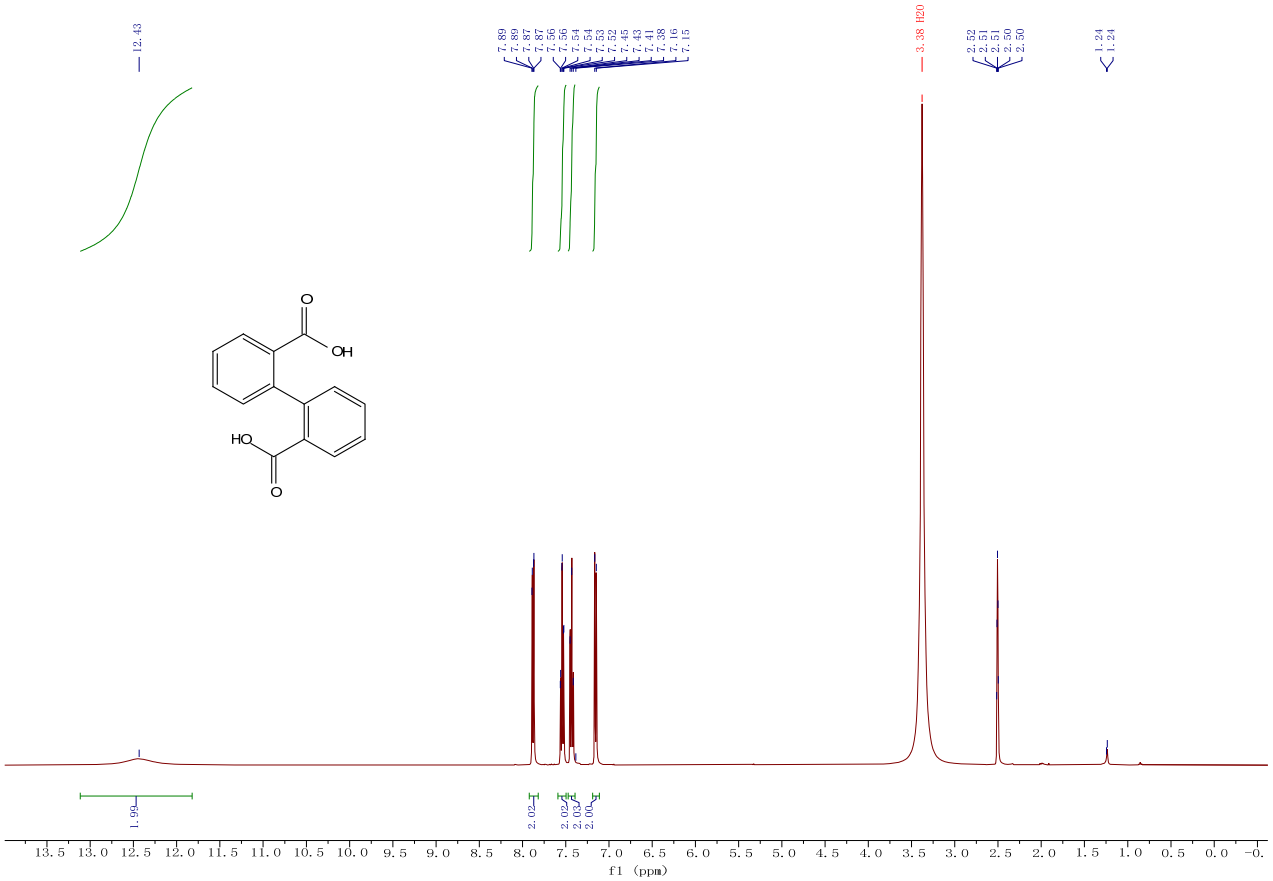

167.00
166.02
135.22
133.56
129.99
129.74
52.84
40.30
40.09
39.88
39.67
39.46
O
OH
H3C
O
O
f1 (ppm)

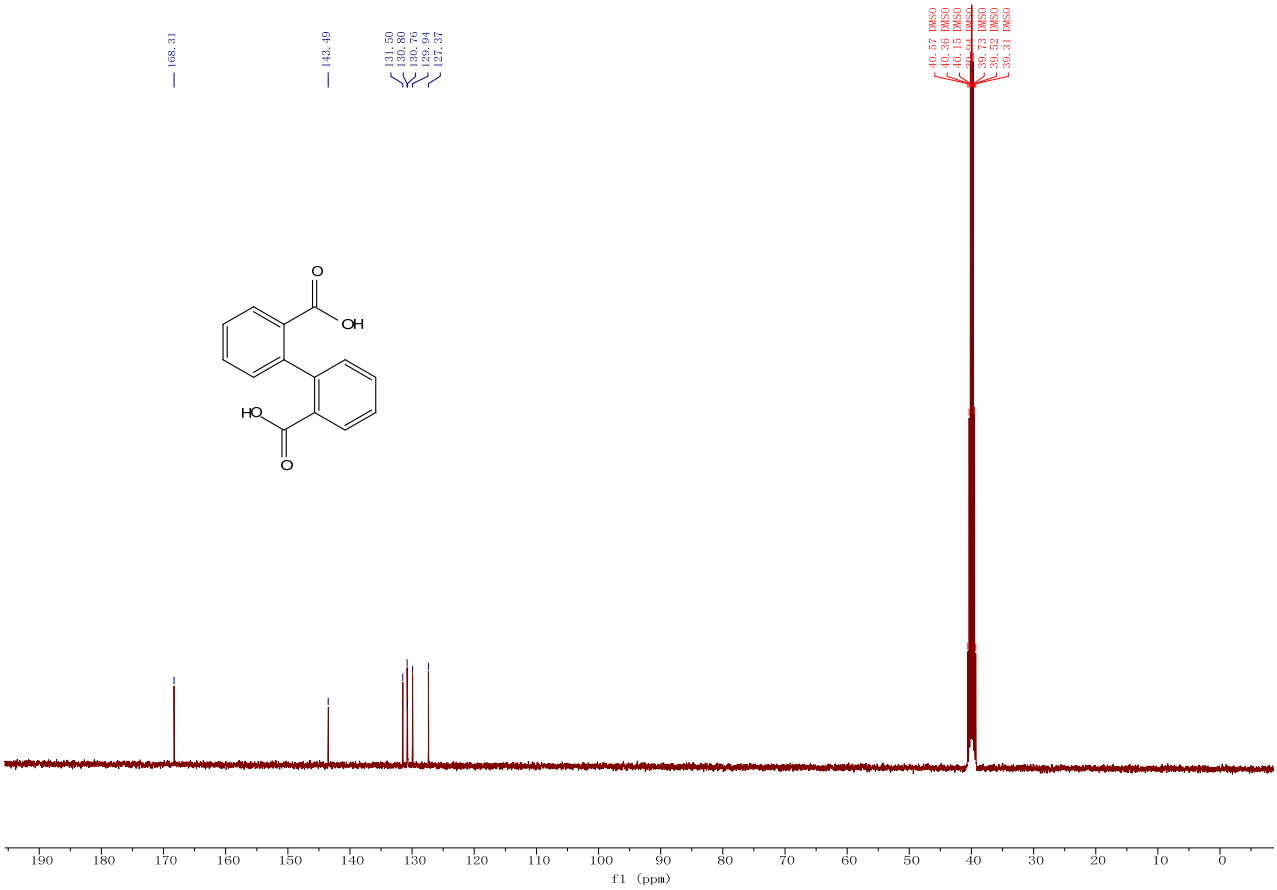

12.81
7.83
7.82
7.81
7.80
7.46
7.46
7.44
7.44
7.42
7.42
7.30
7.30
7.28
7.28
7.26
7.26
3.38 H2O
2.52
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
1.23
CH3
O
OH
0.86
1.00
1.01
2.05
2.82
f1 (ppm)

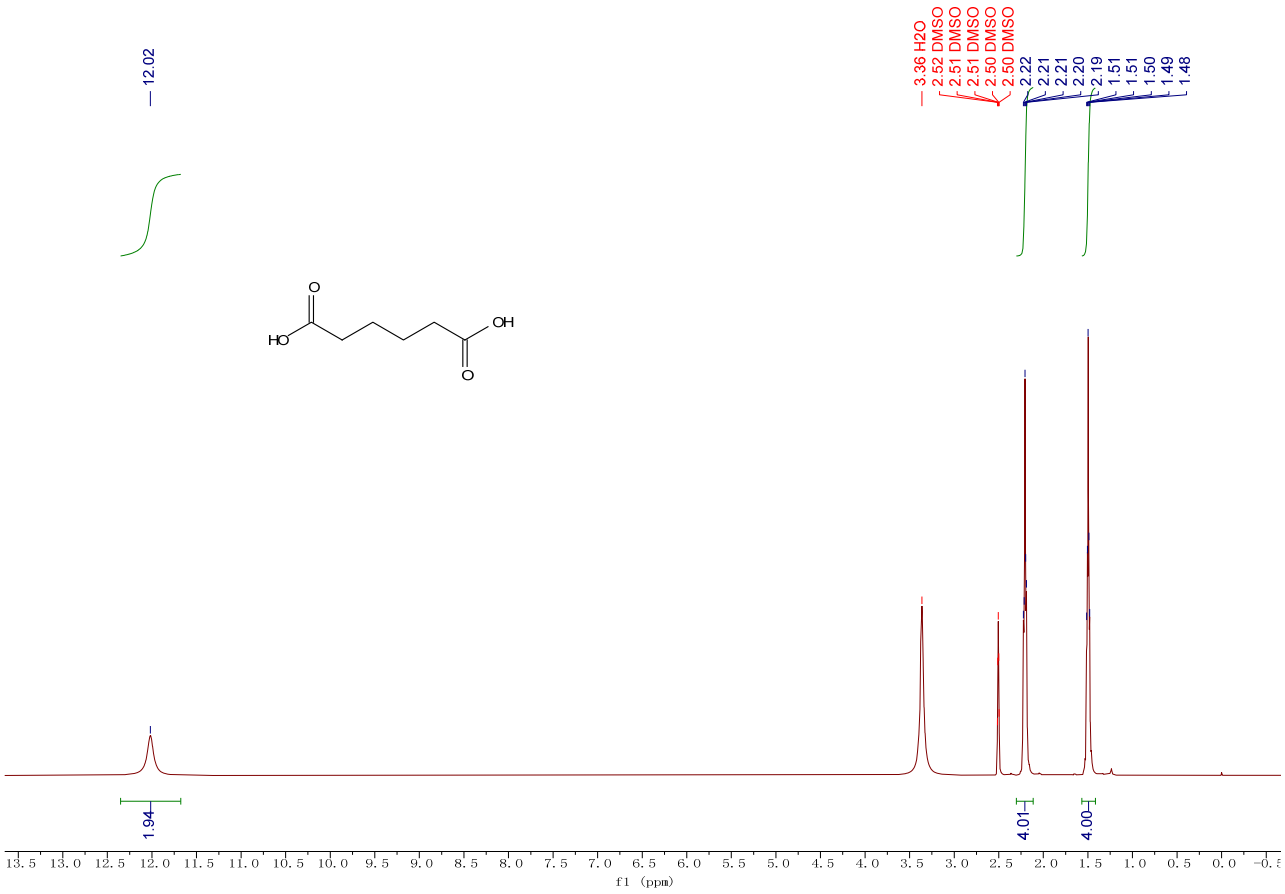

169.15
139.45
132.18
131.97
130.89
130.63
126.30
40.56 DMSO
40.35 DMSO
40.14 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
21.70
CH3
O
OH
f1 (ppm)

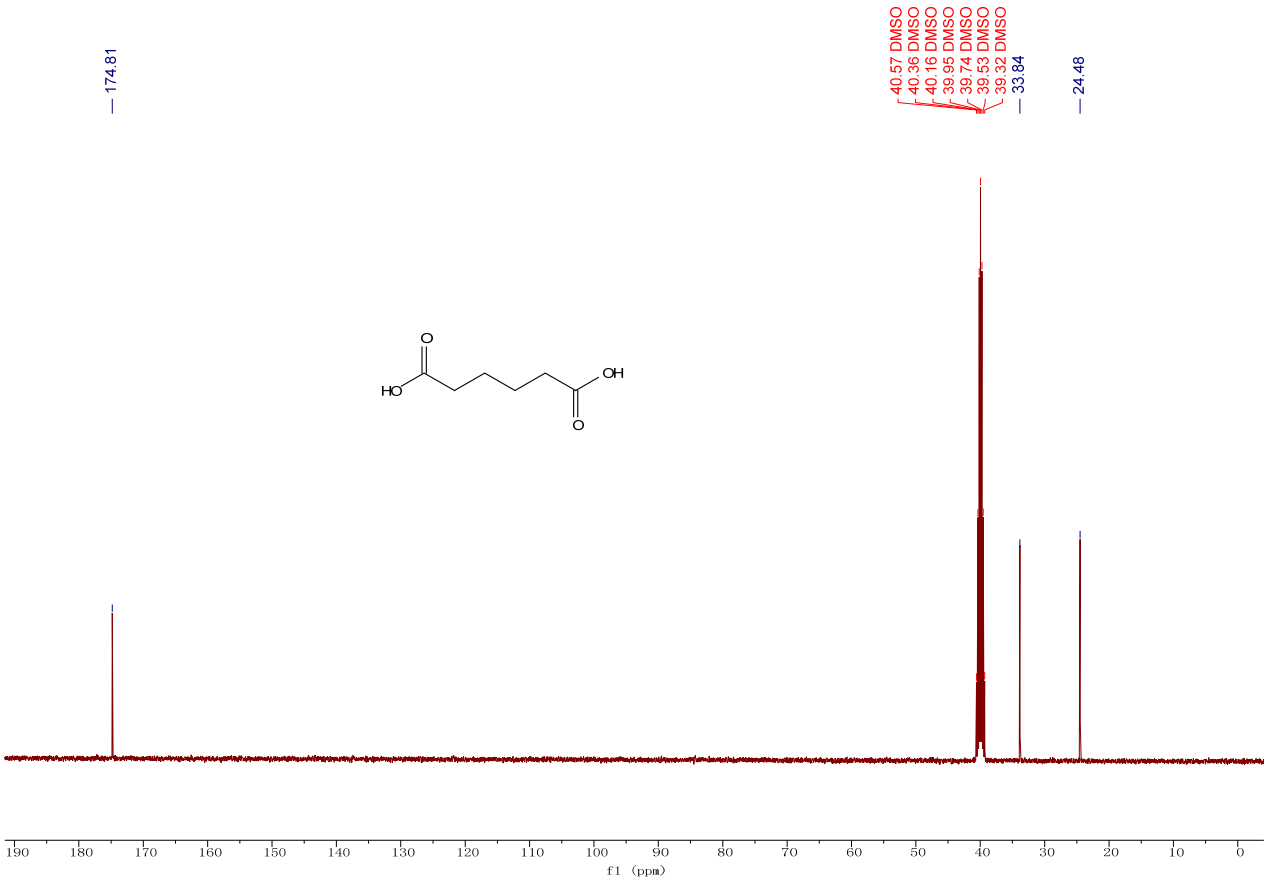

13.11
7.79
7.79
7.79
7.77
7.77
7.77
7.76
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.50
7.46
7.45
7.44
7.43
7.42
7.42
7.41
7.41
7.40
3.48 H2O
2.51
2.51
2.50
2.50
1.22
Cl
O
OH
1.00
0.99
1.98
1.07
f1 (ppm)

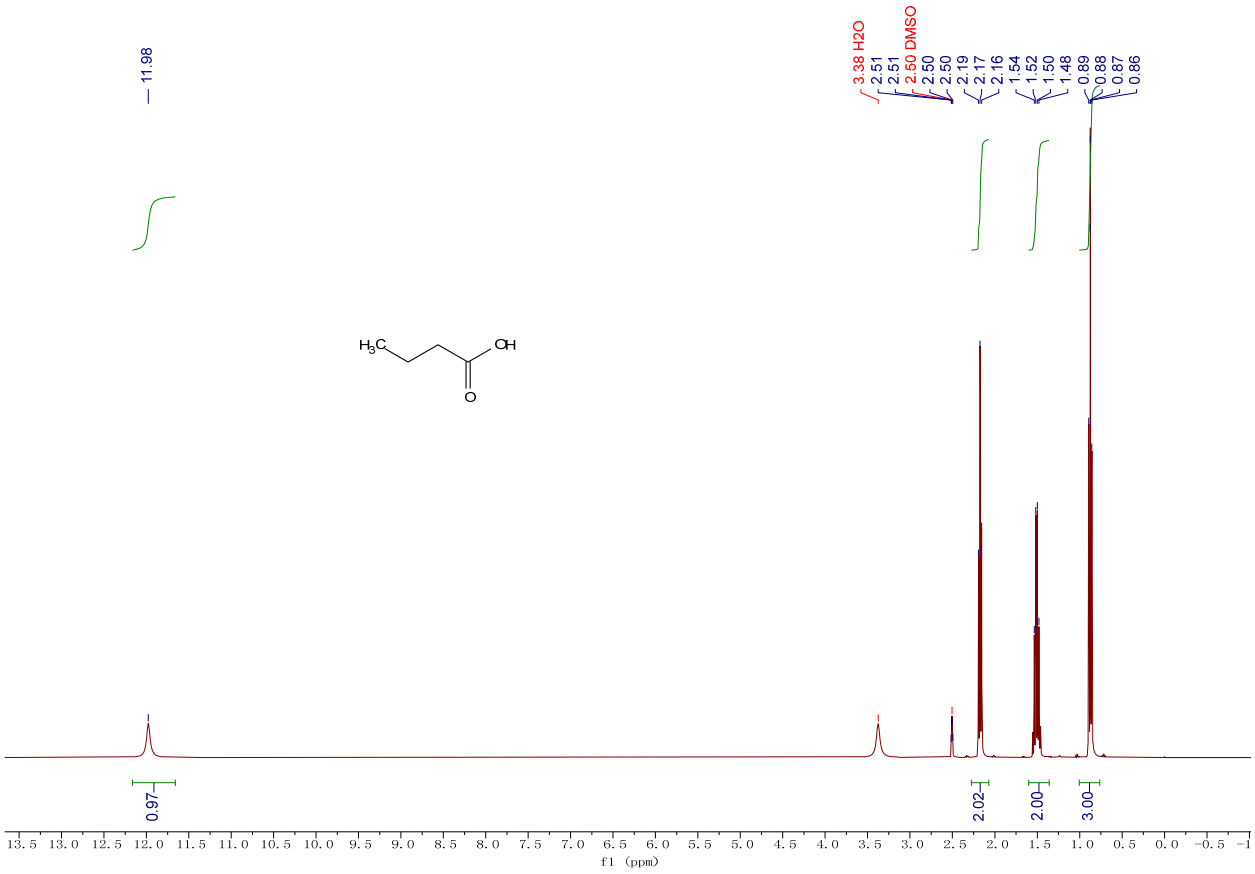

167.22
133.04
132.02
131.93
131.26
131.07
127.69
40.54 DMSO
40.33 DMSO
40.12 DMSO
39.91 DMSO
39.71 DMSO
39.50 DMSO
39.29 DMSO
Cl
O
OH
f1 (ppm)


12.43
7.89
7.89
7.87
7.87
7.56
7.56
7.54
7.54
7.53
7.52
7.45
7.43
7.41
7.38
7.16
7.15
3.38 H2O
2.52
2.51
2.51
2.50
2.50
1.24
1.24
O
OH
HO
O
1.99
2.02
2.02
2.03
2.00
f1 (ppm)

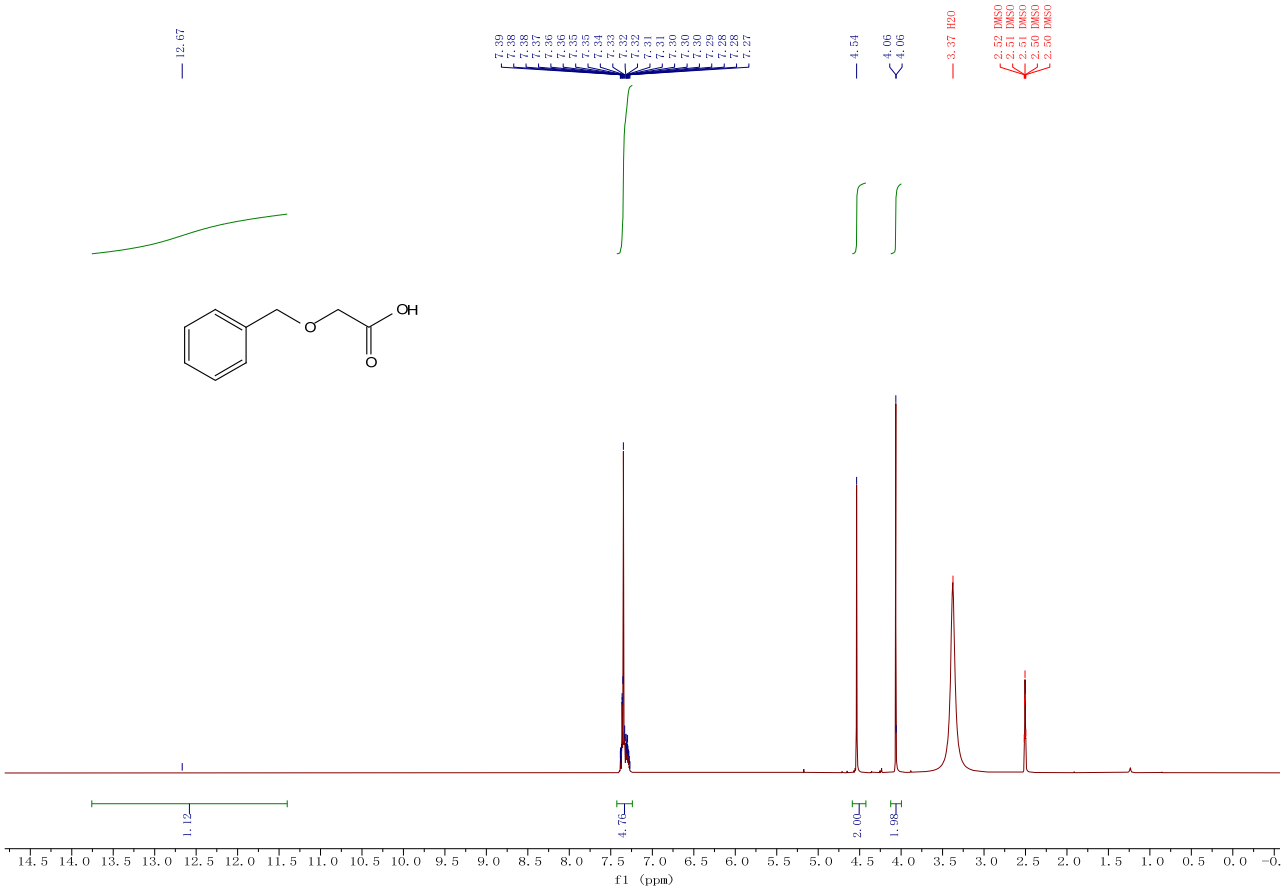

168.31
143.49
131.50
130.80
130.76
129.94
127.97
40.57 DMSO
40.36 DMSO
40.15 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
O
OH
HO
O
f1 (ppm)

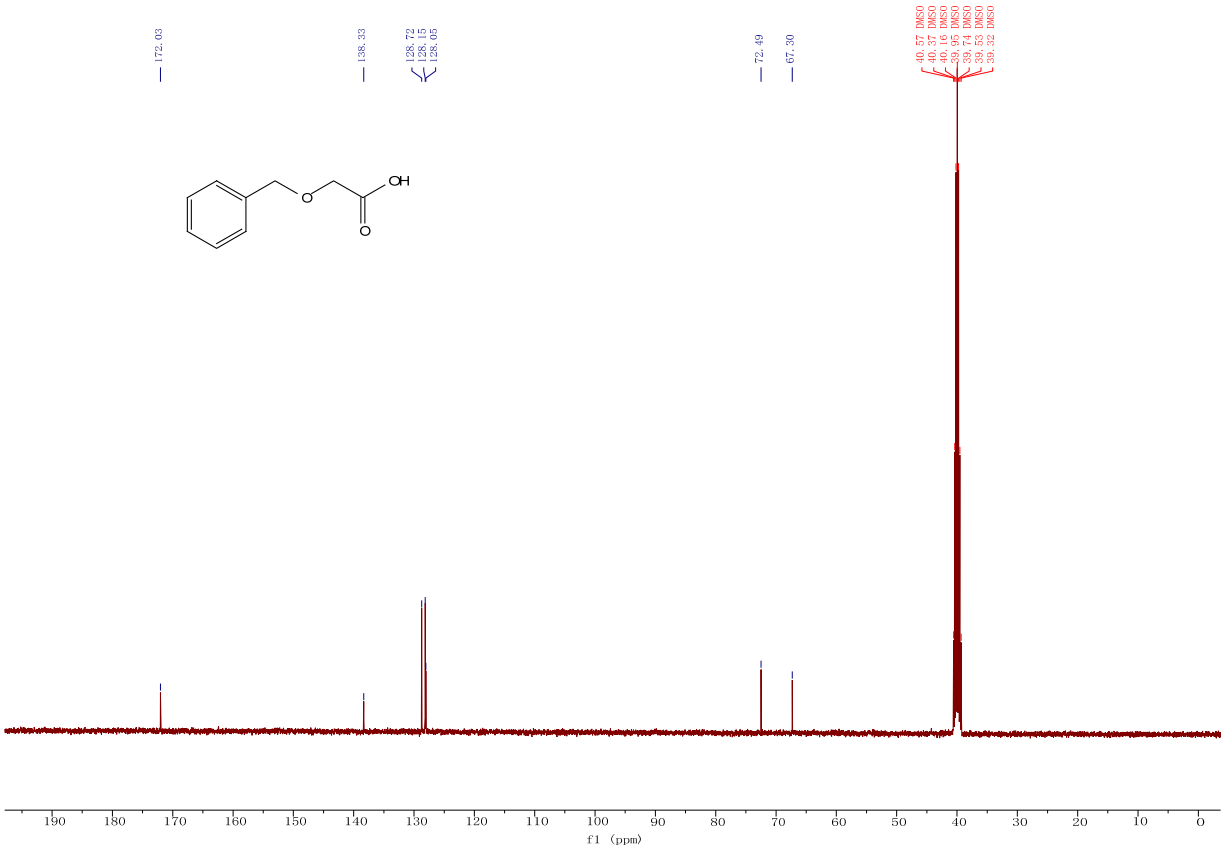

12.02
3.36 H2O
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.22
2.21
2.21
2.20
2.19
1.51
1.51
1.50
1.49
1.48
HO
O
OH
O
1.94
4.01
4.00
f1 (ppm)

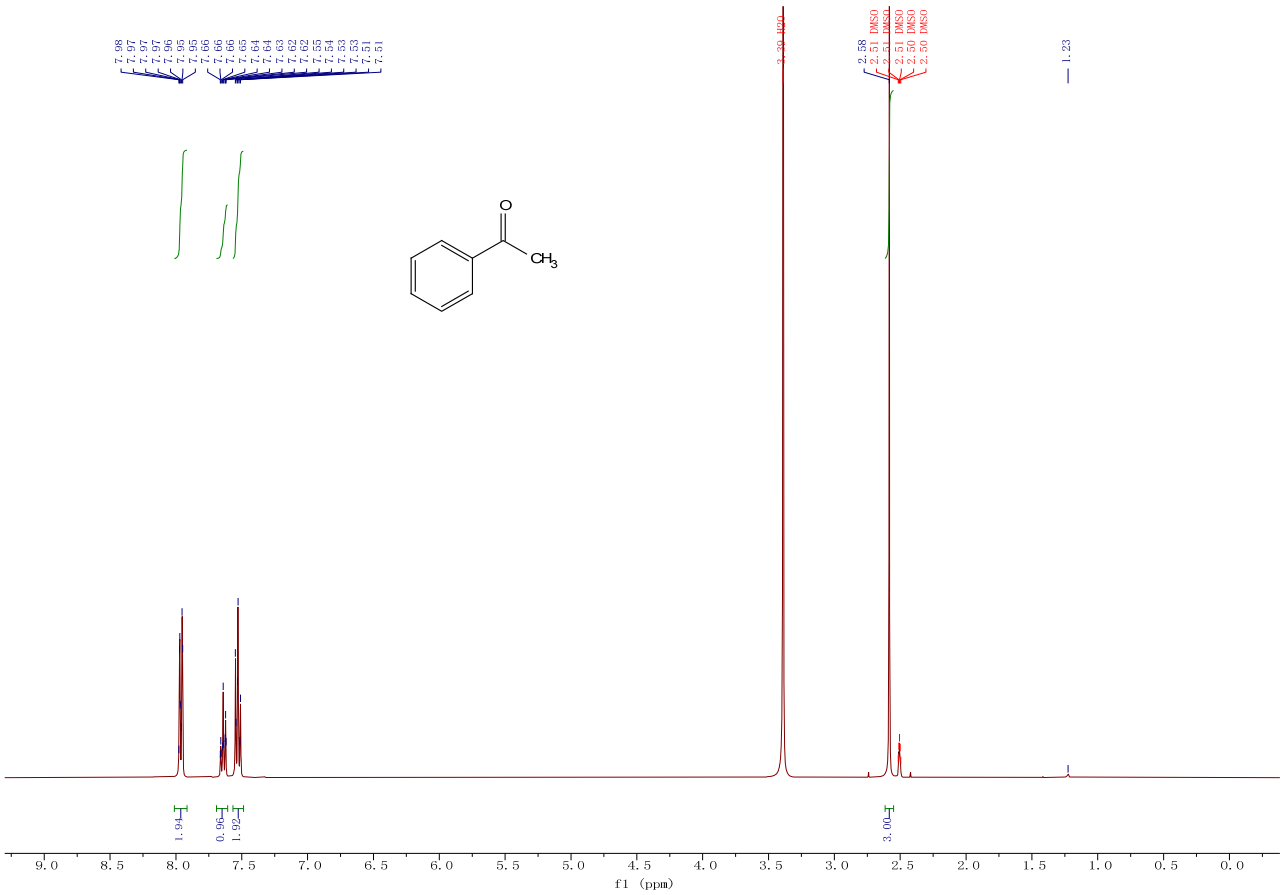

174.81
40.57 DMSO
40.36 DMSO
40.16 DMSO
39.95 DMSO
39.74 DMSO
39.53 DMSO
39.32 DMSO
33.84
24.48
HO
O
OH
O
f1 (ppm)

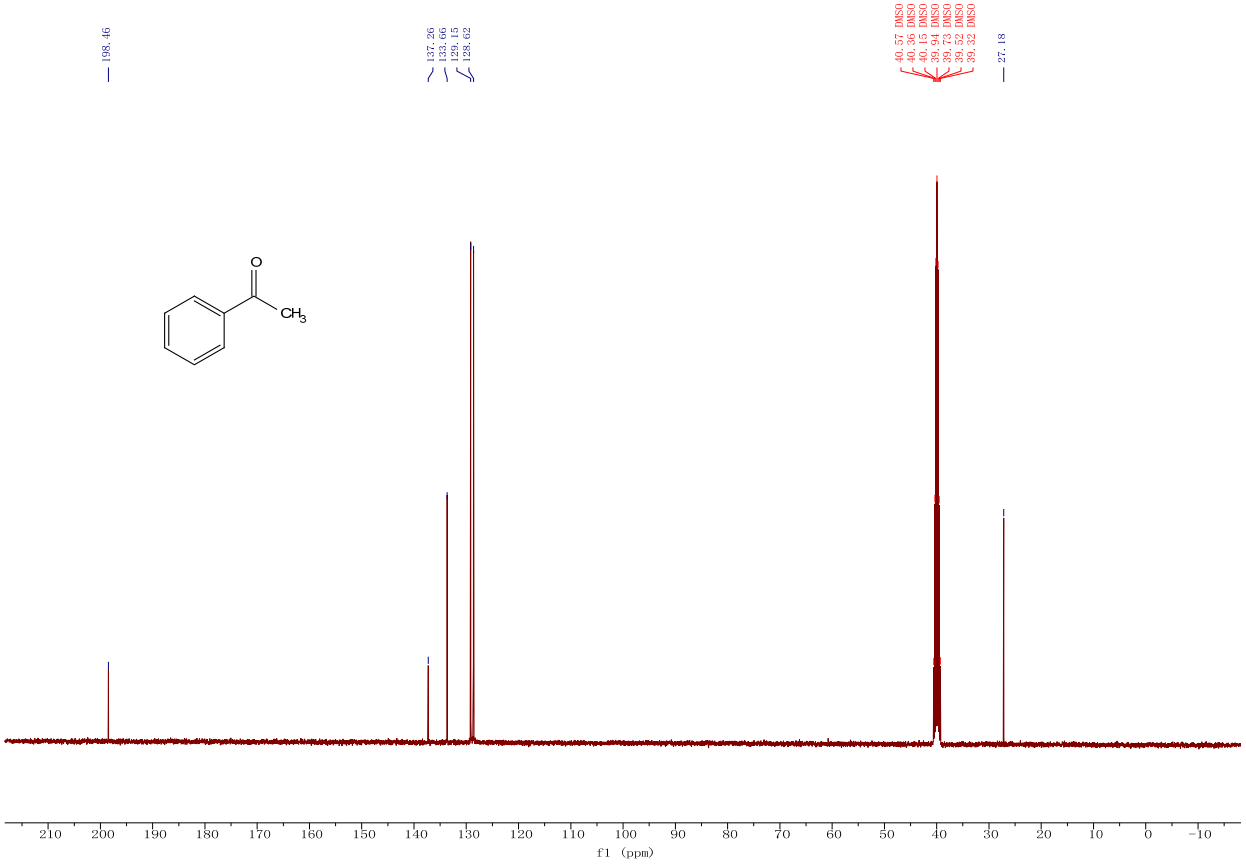

11.98
3.38 H2O
2.51
2.51
2.50 DMSO
2.50
2.50
2.19
2.17
2.16
1.54
1.52
1.50
1.48
0.89
0.88
0.87
0.86
H3C
OH
O
0.97
2.02
2.00
3.00
f1 (ppm)

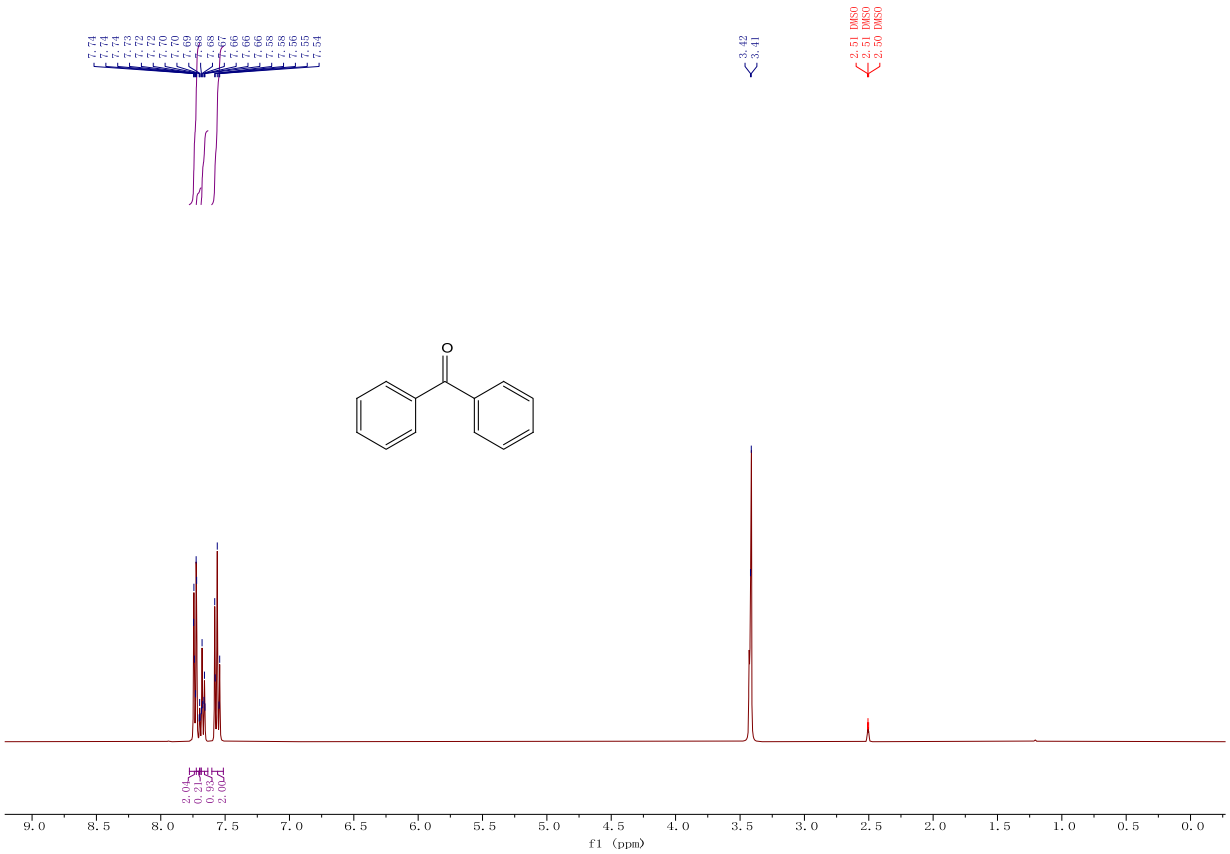

174.82
40.55 DMSO
40.34 DMSO
40.13 DMSO
39.92 DMSO
39.71 DMSO
39.51 DMSO
39.30 DMSO
36.01
18.38
13.96
H3C
OH
O
f1 (ppm)

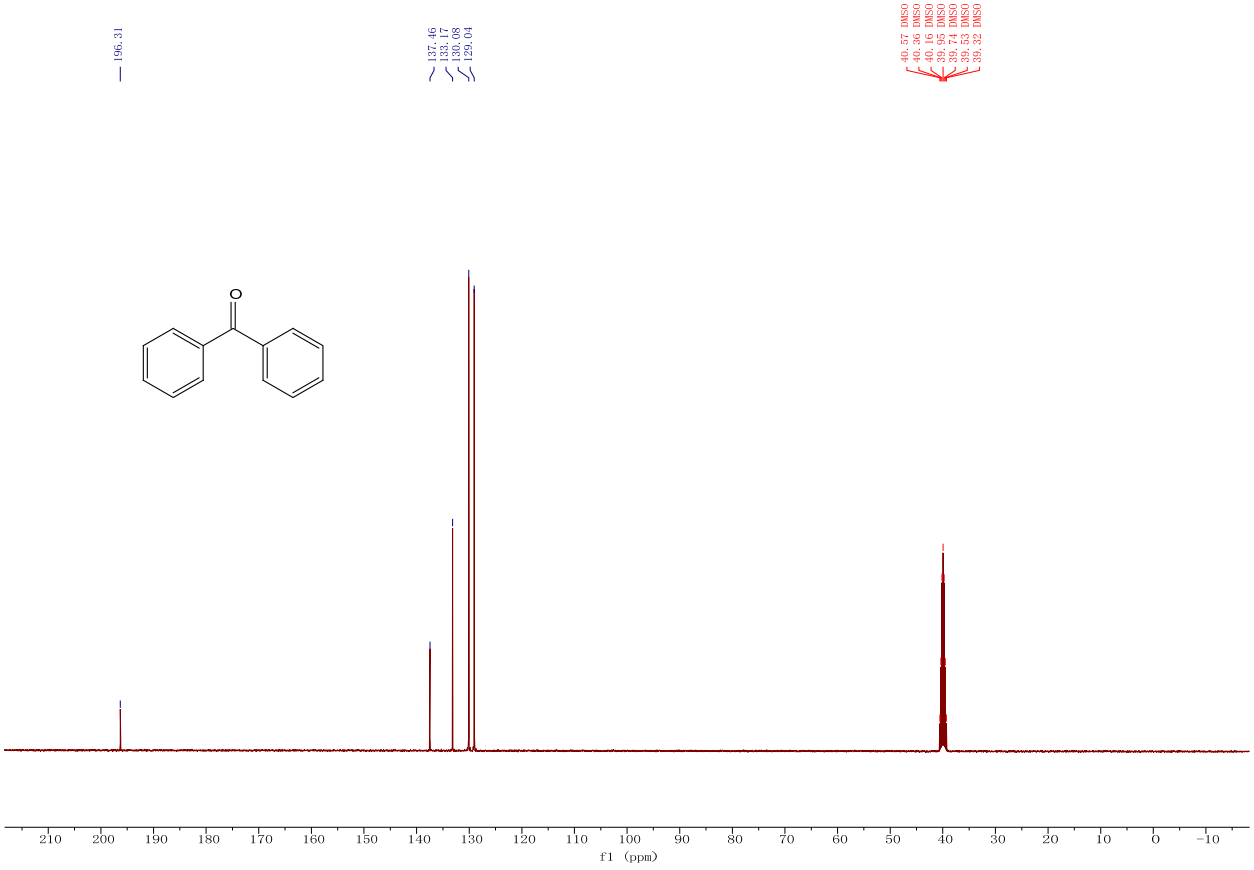

12.67
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.28
7.28
7.27
4.54
4.06
4.06
3.37 H2O
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
OH
O
O
1.12
4.76
2.00
1.98
f1 (ppm)

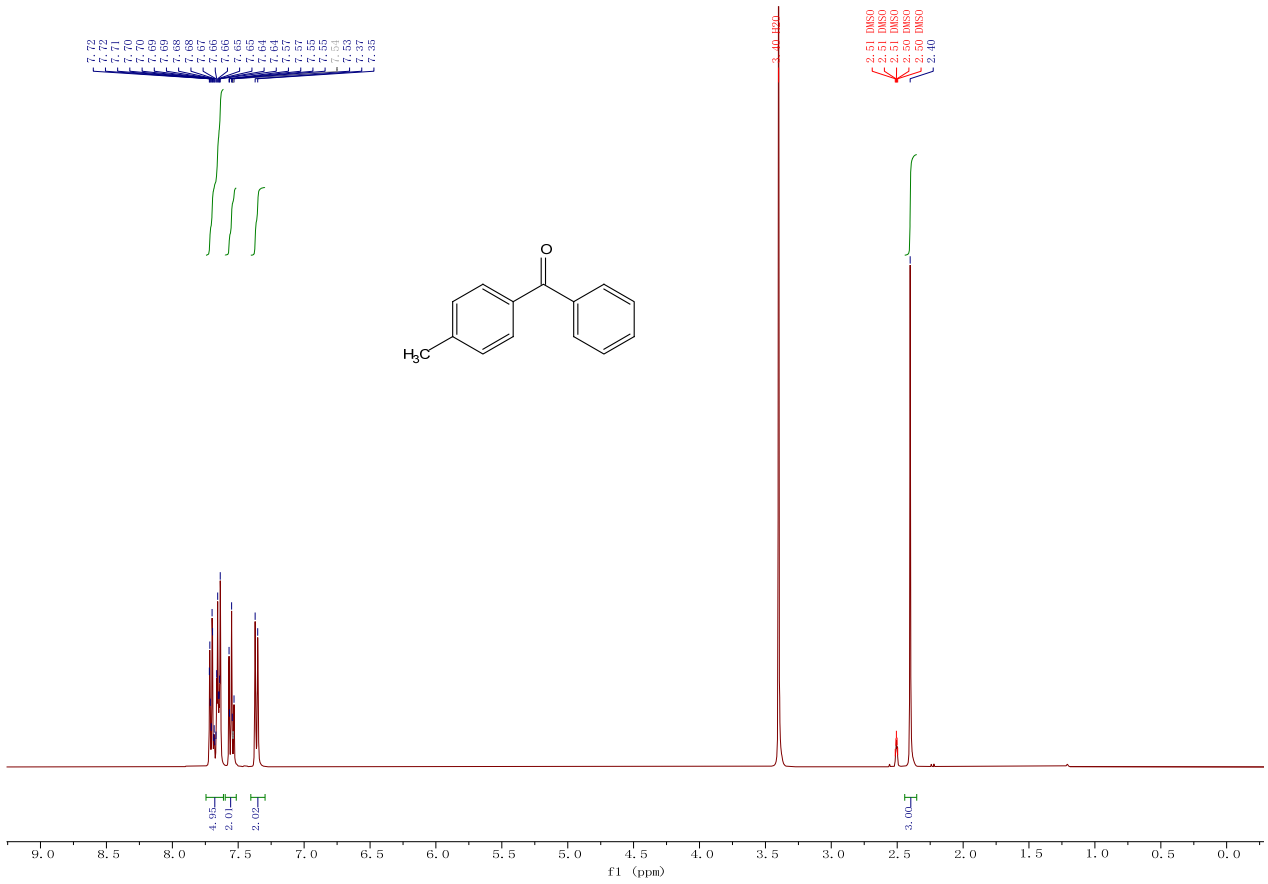

172.03
138.33
128.72
128.15
128.05
72.49
67.30
40.57 DMSO
40.37 DMSO
40.15 DMSO
39.95 DMSO
39.74 DMSO
39.53 DMSO
39.32 DMSO
OH
O
O
f1 (ppm)

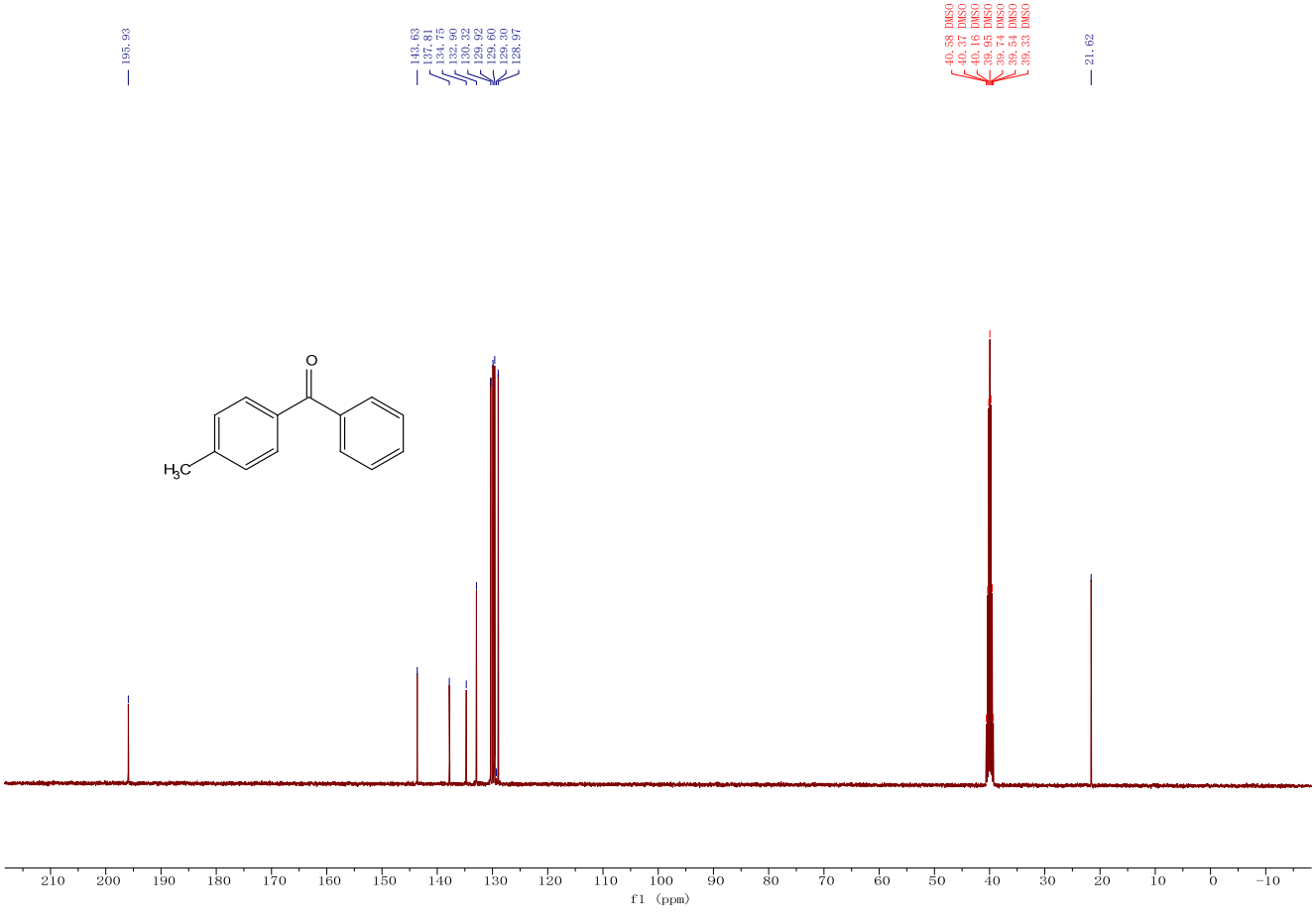

7.98
7.97
7.97
7.96
7.95
7.95
7.66
7.66
7.65
7.64
7.64
7.63
7.62
7.62
7.55
7.54
7.53
7.53
7.51
7.51
3.39 H2O
2.58 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
1.23
O
CH3
1.94
0.96
1.92
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

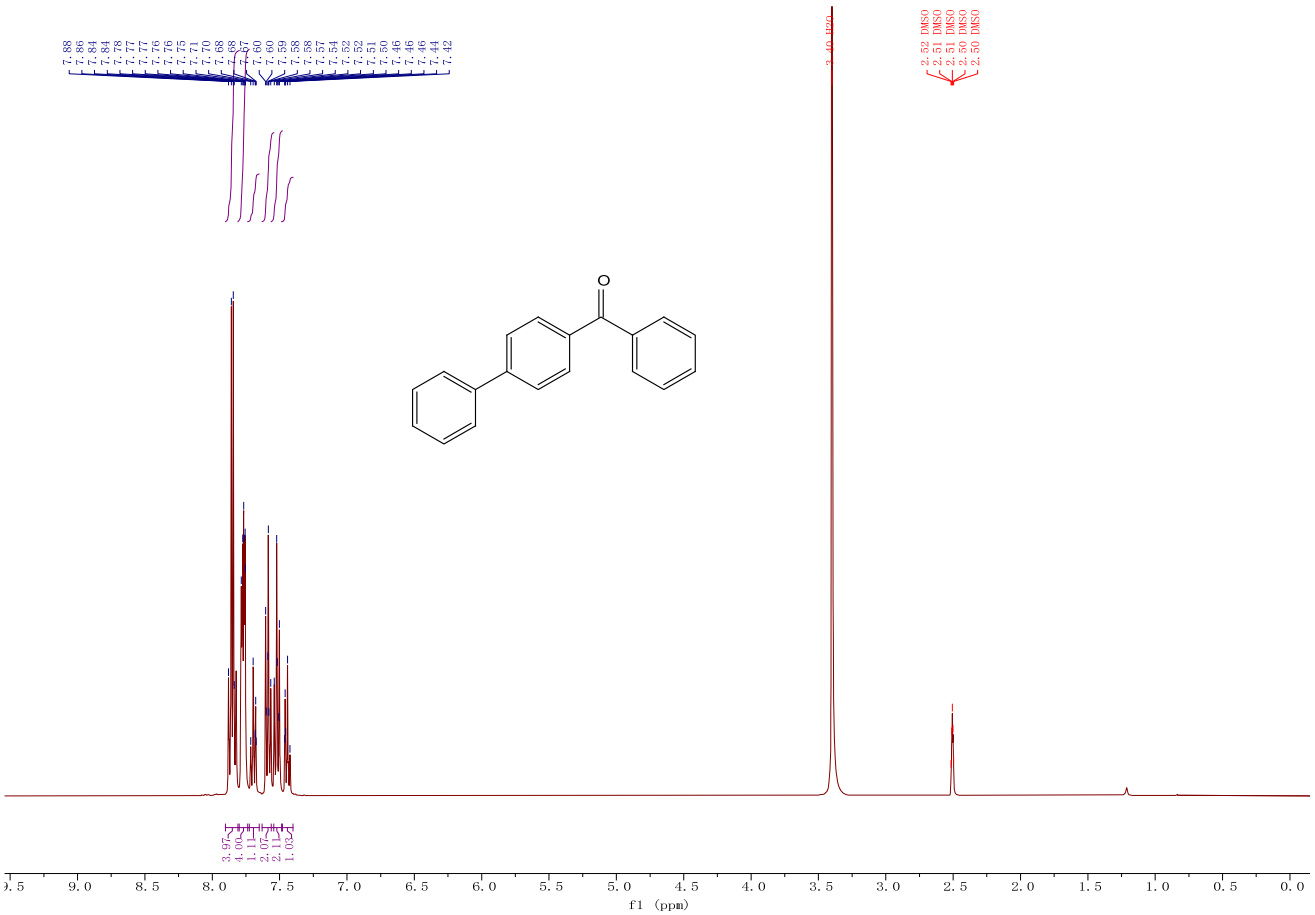

198.46
137.26
133.66
129.15
128.62
40.57 DMSO
40.36 DMSO
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.32 DMSO
27.18
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

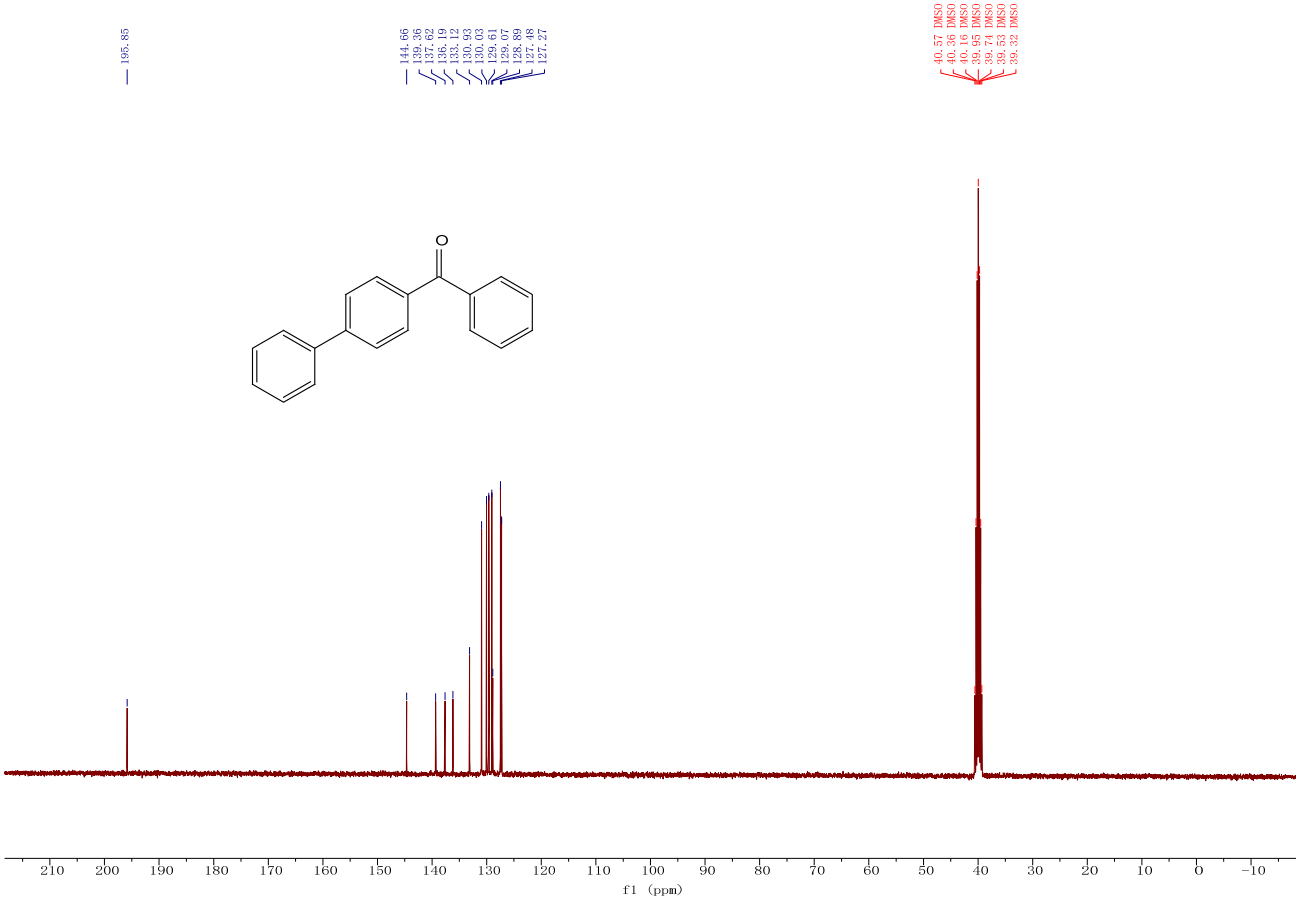

7.74
7.74
7.74
7.73
7.72
7.72
7.70
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.66
7.58
7.58
7.56
7.55
7.54
3.42
3.41
2.51 DMSO
2.51 DMSO
2.50 DMSO
O
2.04
2.21
0.93
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

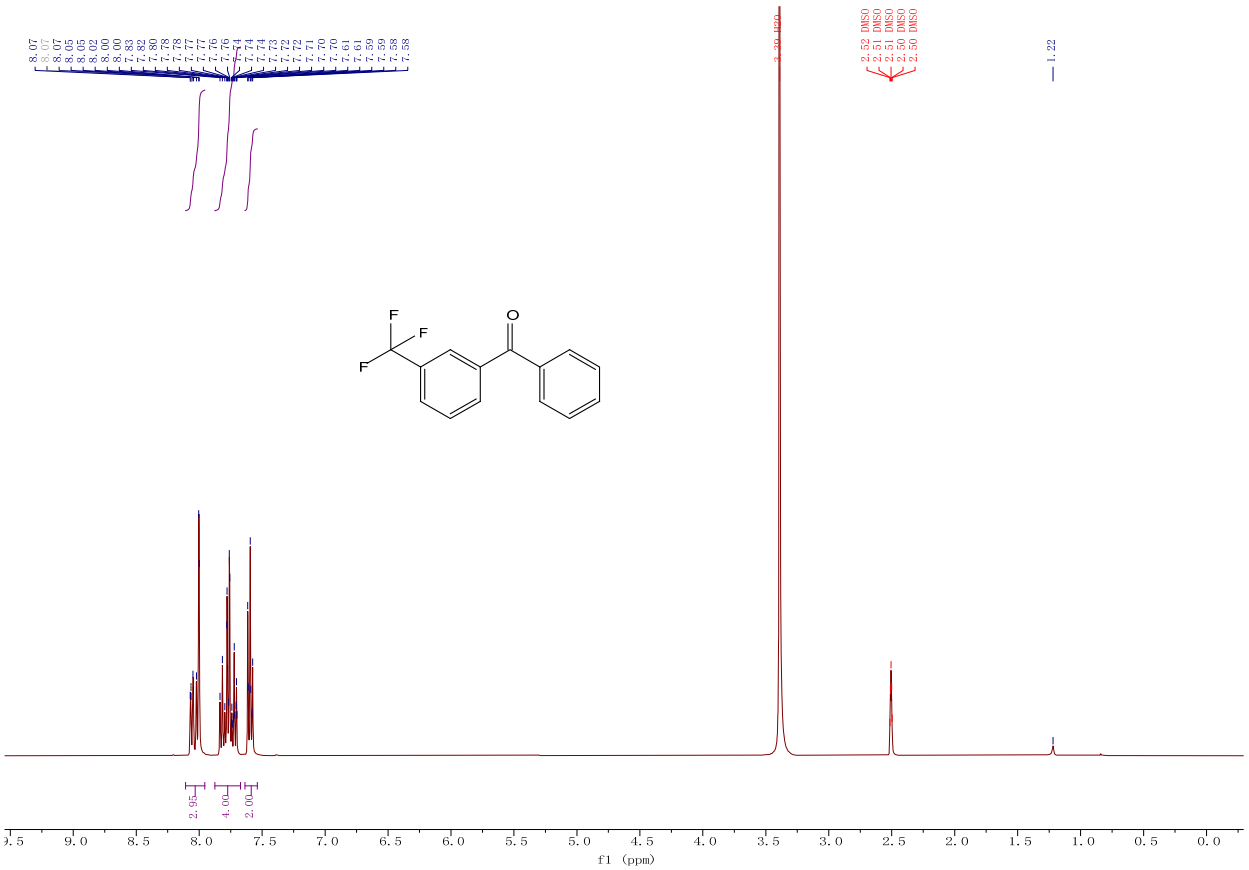

196.31
137.46
133.17
130.08
129.04
40.57 DMSO
40.36 DMSO
40.15 DMSO
39.95 DMSO
39.74 DMSO
39.53 DMSO
39.32 DMSO
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

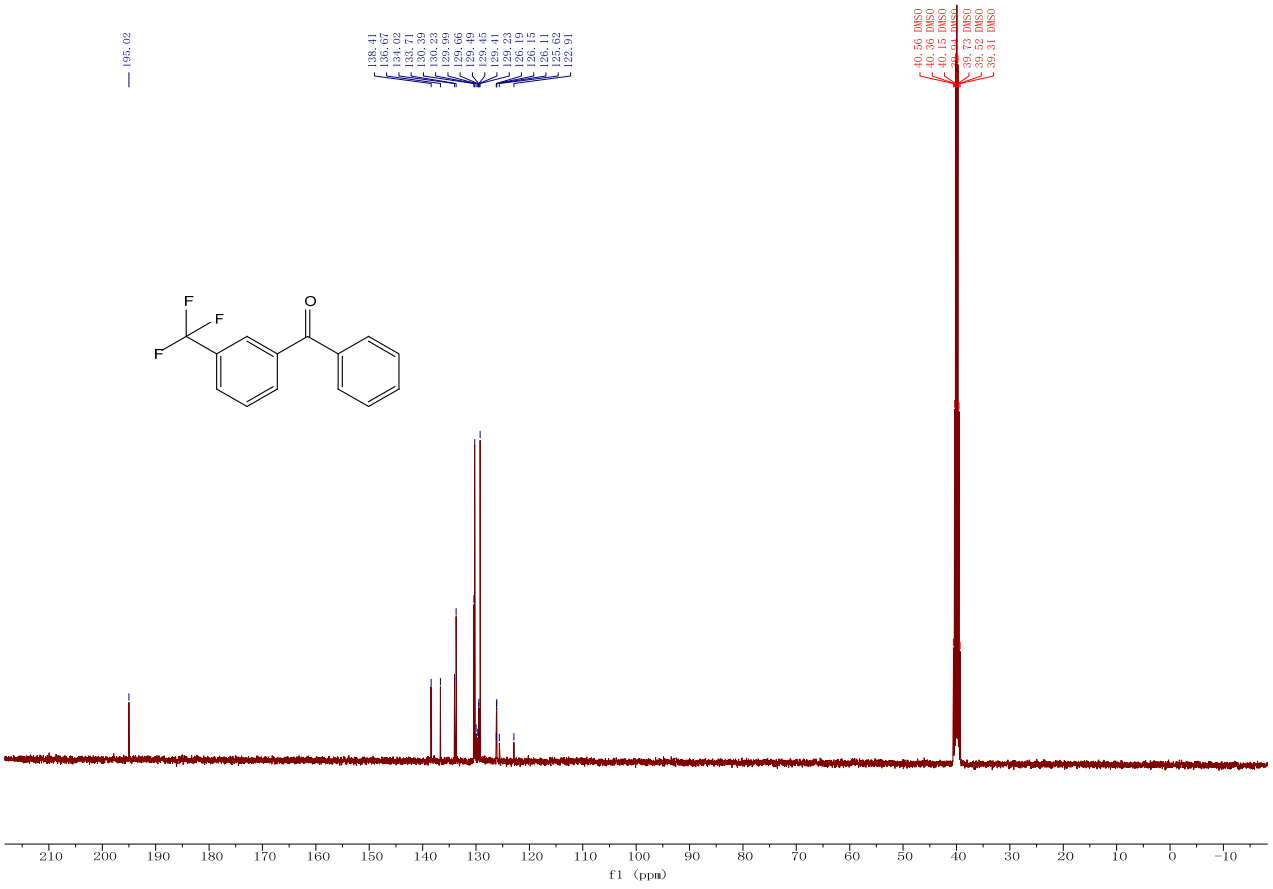

7.72
7.72
7.71
7.70
7.70
7.69
7.69
7.68
7.68
7.67
7.66
7.66
7.65
7.65
7.64
7.64
7.57
7.57
7.55
7.55
7.54
7.53
7.37
7.35
3.40 H2O
2.51 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.40
O
H3C
4.95
2.01
2.02
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

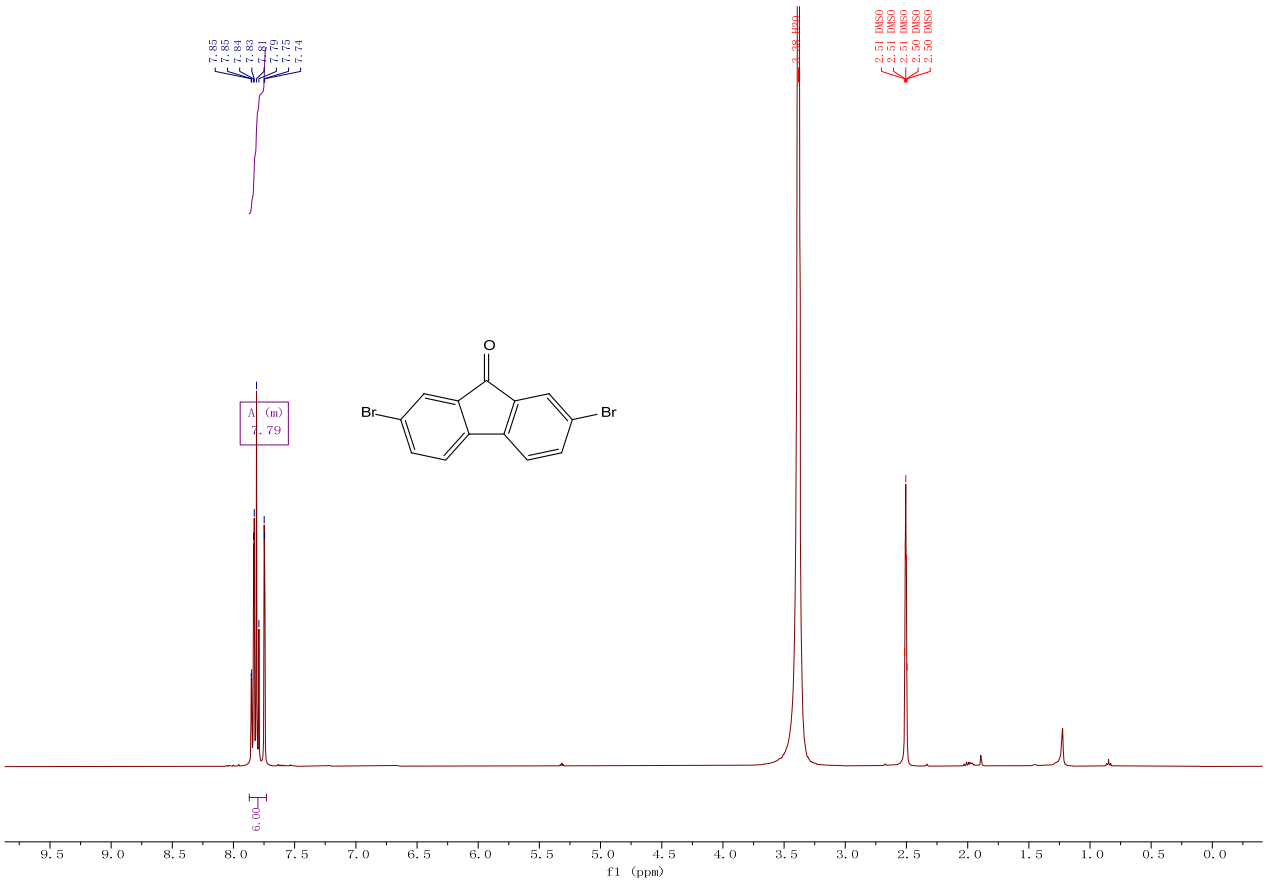

195.93
143.63
137.81
134.75
132.90
130.32
129.82
129.66
128.30
128.97
40.58 DMSO
40.37 DMSO
40.16 DMSO
39.95 DMSO
39.74 DMSO
39.54 DMSO
39.33 DMSO
21.62
O
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

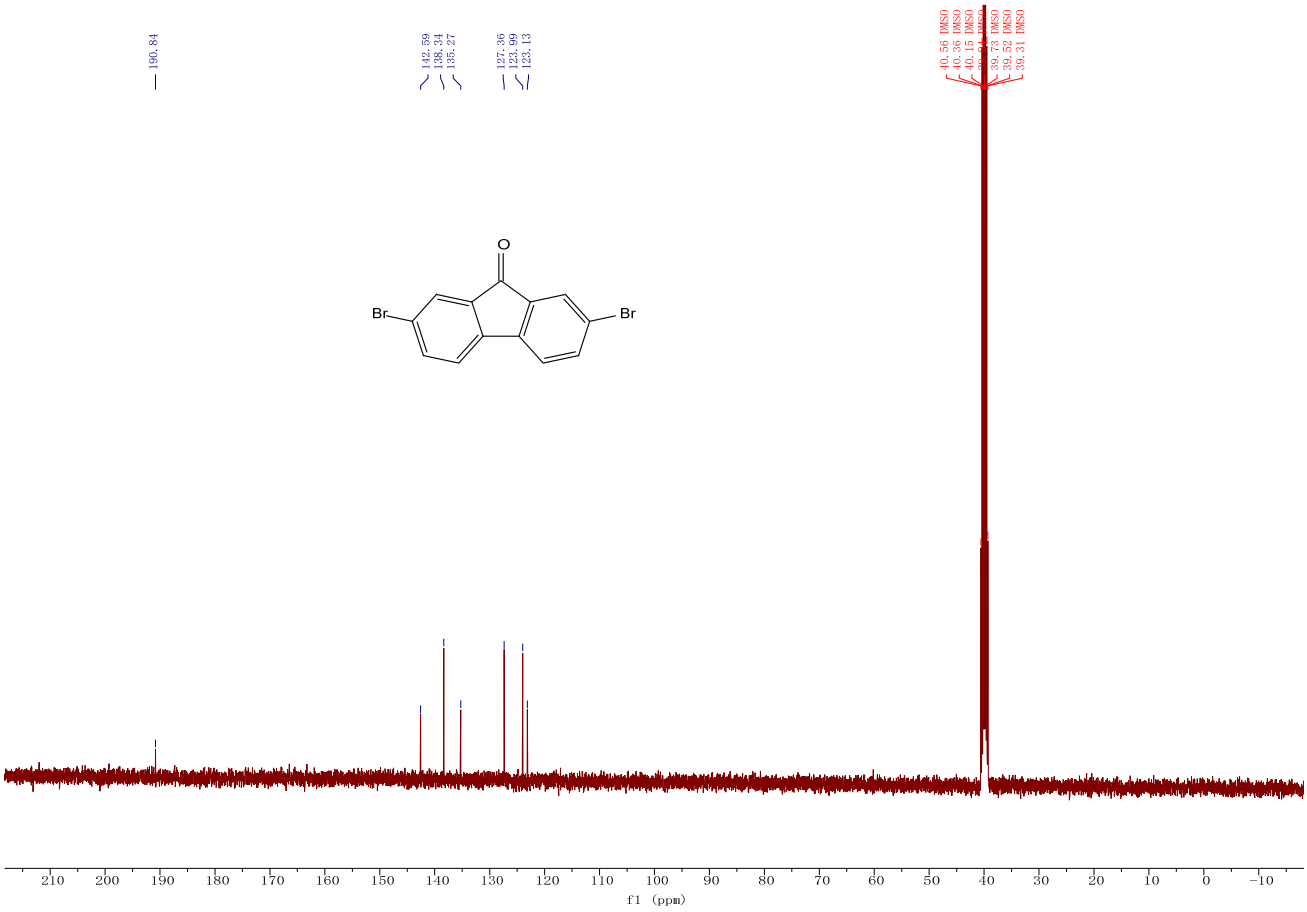

7.88
7.86
7.84
7.84
7.78
7.77
7.77
7.76
7.76
7.75
7.71
7.70
7.68
7.68
7.67
7.60
7.59
7.59
7.58
7.58
7.57
7.54
7.52
7.52
7.51
7.50
7.46
7.46
7.44
7.42
3.40 H2O
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
O
3.97
4.00
1.11
2.07
2.11
1.03
f1 (ppm)

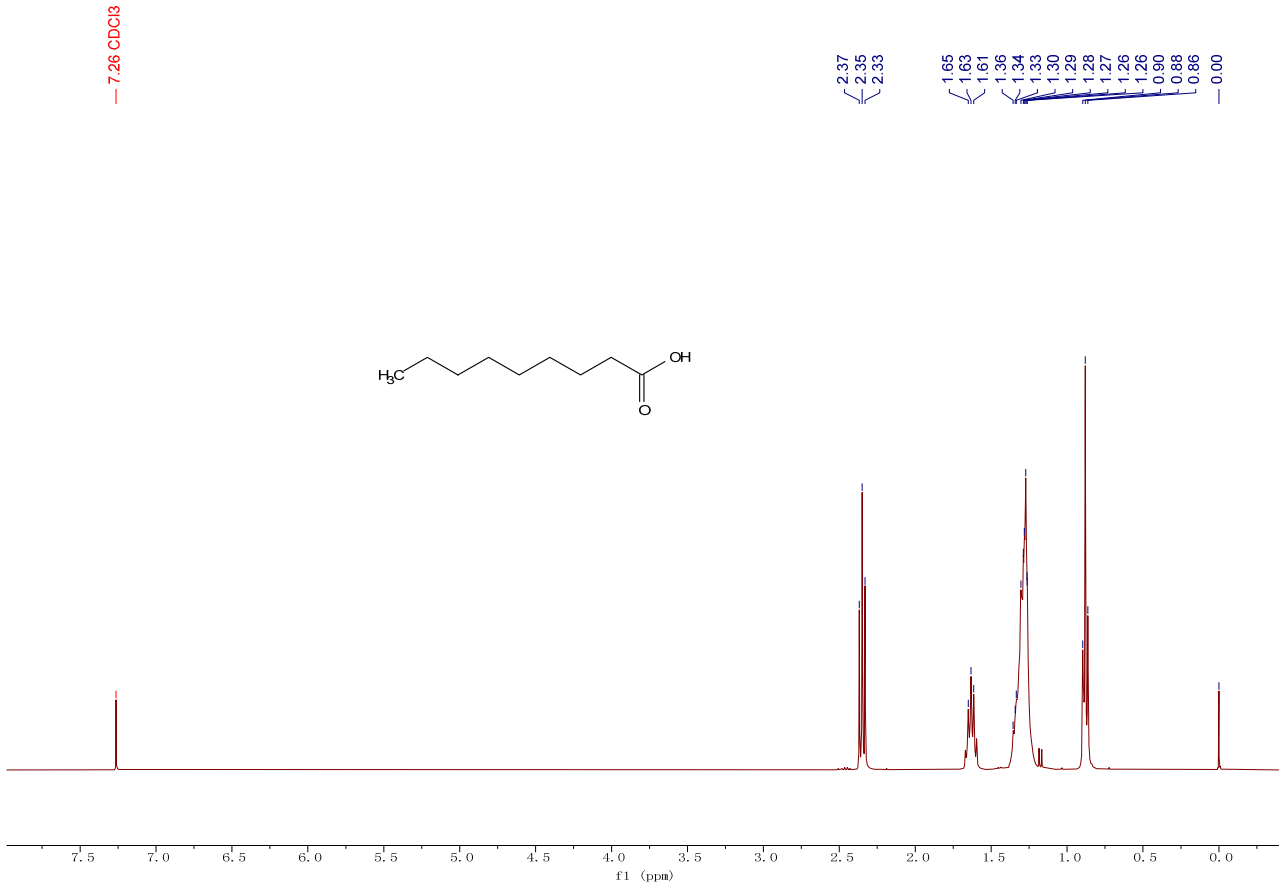

196.85
144.66
139.36
137.62
136.19
133.12
130.93
130.03
129.61
129.07
128.89
127.48
127.27
40.57 DMSO
40.36 DMSO
40.16 DMSO
39.95 DMSO
39.74 DMSO
39.53 DMSO
39.32 DMSO
O
f1 (ppm)

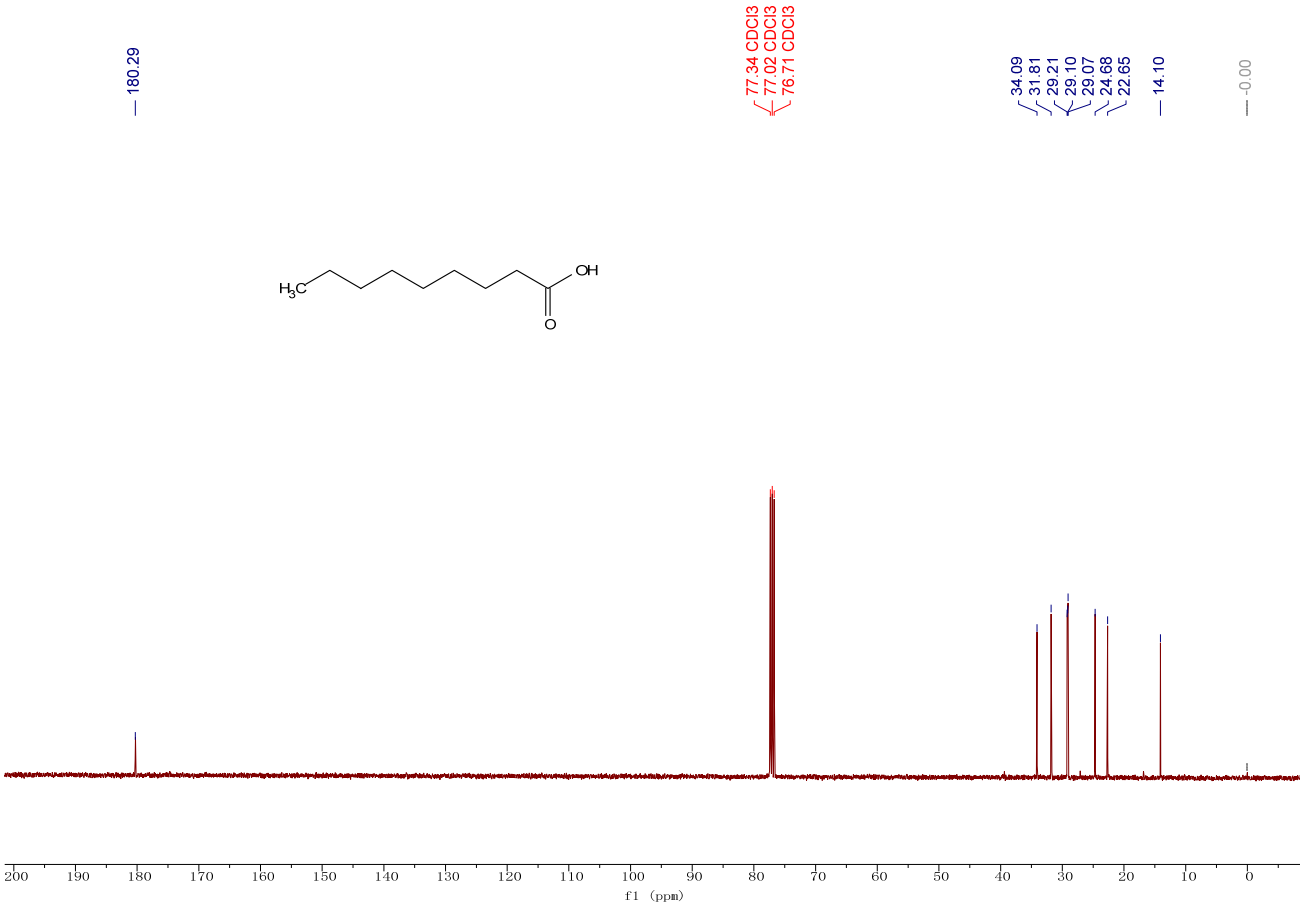

8.07
8.07
8.05
8.05
8.02
8.00
8.00
7.83
7.80
7.78
7.78
7.77
7.77
7.76
7.74
7.74
7.74
7.73
7.72
7.72
7.71
7.70
7.70
7.61
7.59
7.59
7.58
3.39 H2O
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
1.22
F
F
F
O
2.95
4.00
2.00
f1 (ppm)

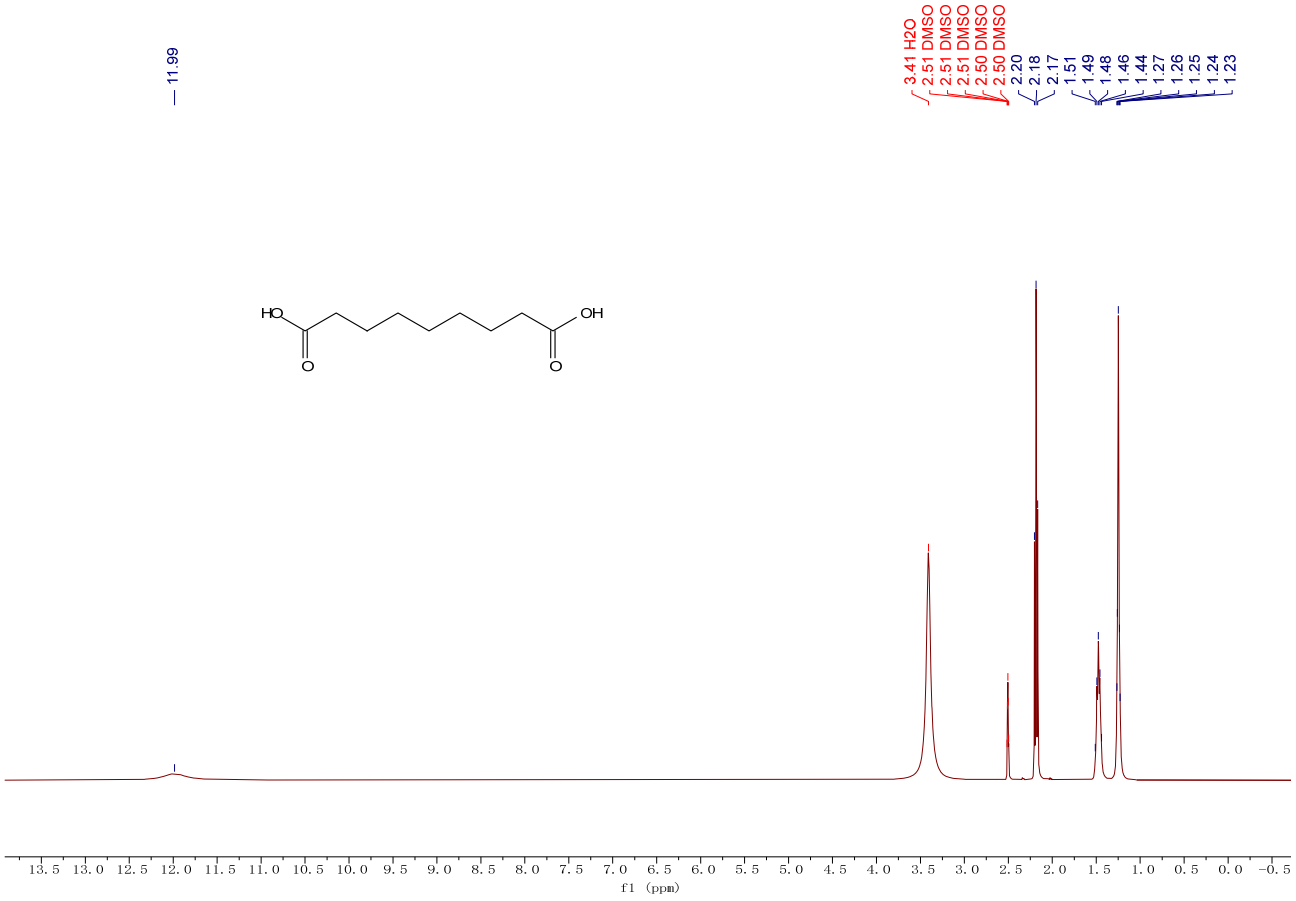

195.02
138.41
136.67
134.02
131.71
130.39
130.23
129.99
129.66
129.49
129.45
129.41
129.23
126.19
126.15
126.11
125.62
122.91
40.55 DMSO
40.35 DMSO
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
F
F
F
O
f1 (ppm)

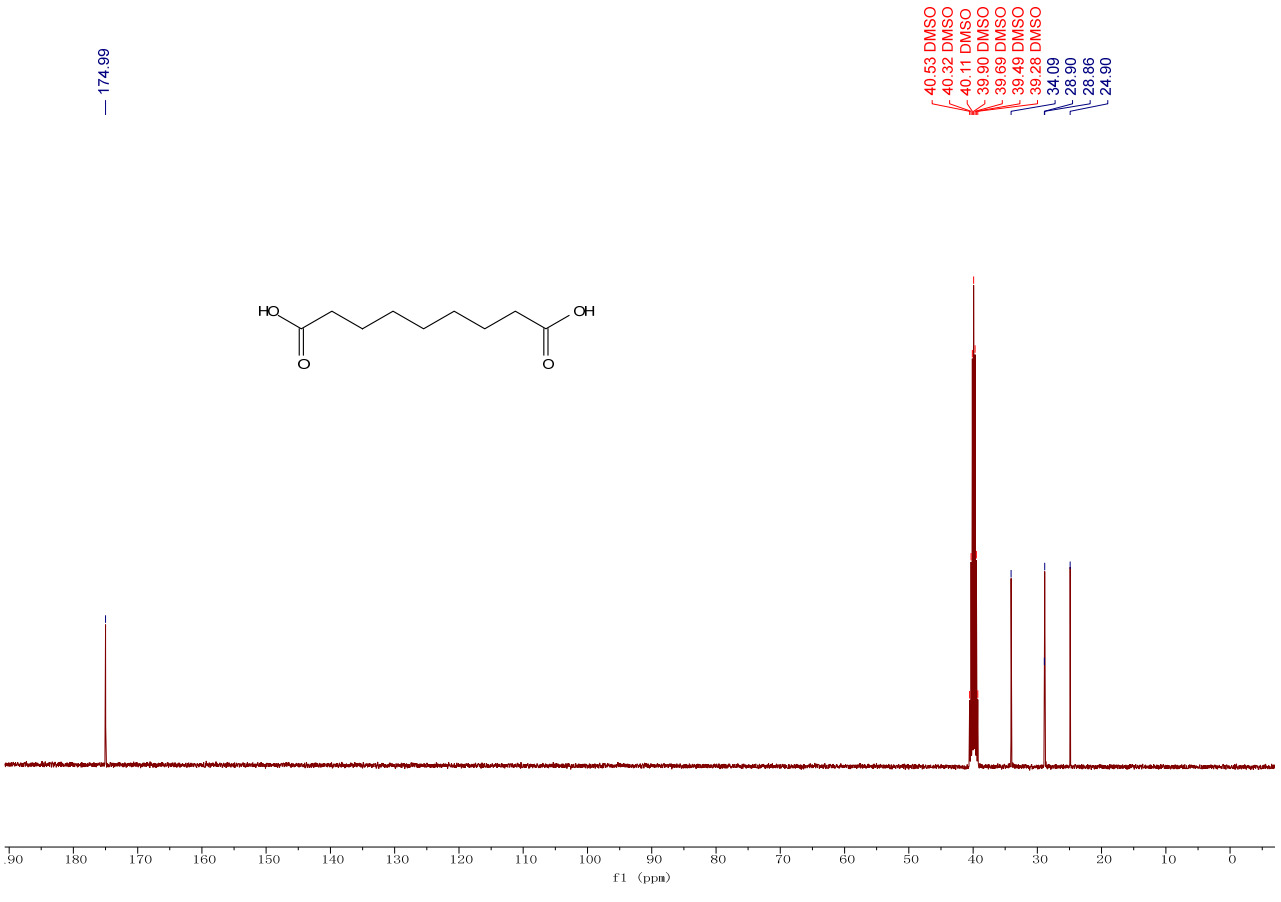

7.85
7.85
7.84
7.83
7.81
7.79
7.75
7.74
3.48 H2O
2.51 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
A (m)
7.79
6.00
O
Br
Br
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.84
142.59
138.94
135.27
127.36
123.99
123.13
40.56 DMSO
40.35 DMSO
40.15 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
O
Br
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 CDCl3
2.37
2.35
2.33
1.65
1.63
1.61
1.36
1.34
1.33
1.30
1.29
1.28
1.27
1.26
1.26
0.90
0.88
0.86
0.00
OH
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


180.29
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
34.09
31.81
29.21
29.10
29.07
24.68
22.65
14.10
-0.00
OH
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.99
3.41 H2O
2.51 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.20
2.18
2.17
1.51
1.49
1.48
1.46
1.44
1.27
1.26
1.25
1.24
1.23
HO
O
OH
O
f1 (ppm)


174.99
40.53 DMSO
40.32 DMSO
40.11 DMSO
39.90 DMSO
39.69 DMSO
39.49 DMSO
39.28 DMSO
34.09
28.90
28.86
24.90
HO
O
OH
O
f1 (ppm)

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