Electronic Supplementary Information

An Efficient Chromium(III)-Catalyzed Aerobic Oxidation of Methylarenes in Water for the Green Preparation of Corresponding Acids

Feng Jiang,[‡a,e] Shanshan Liu,[‡b] Wenshu Zhao,[‡c] Han Yu,*[b,e] Likai Yan,*[d] and Yongge Wei*[e]

[a] Key Laboratory of Cardiovascular and Cerebrovascular Disease Prevention and Control, Ministry of Education, Gannan Medical University, Ganzhou, Jiangxi 341000, P.R. China. E-mail: jiangfenghz@163.com

[b] School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, P.R. China. E-mail: 798990721@qq.com, hanyu0220@tsinghua.edu.cn

[c] Longhua Hospital, Shanghai University of Traditional Chinese Medicine, Shanghai 200032, P.R. China. E-mail: Wenshuzhao005@163.com

[d] Faculty of Chemistry, Northeast Normal University, Changchun, 130024, P.R. China. E-mail: yanlk924@nenu.edu.cn

[e] Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China. E-mail: jiangfenghz@163.com, hanyu0220@ tsinghua.edu.cn, yonggewei@tsinghua.etu.cn

[‡] These authors contributed equally to this work.

* All correspondences should be addressed.

[†] Electronic Supplementary Information (ESI) available: experimental conditions, supplementary table and NMR spectra. See DOI: 10.1039/x0xx00000x

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I. General information

The catalyst was prepared according to published literature methods.[1] All reagents were purchased from Sigma-Aldrich or Adamas-beta, which were used without further purification. FT-IR spectra were recorded on a Thermo Fisher Nicolet 6700. XRD were explored on Rigaku D/Max 2200PC diffractometer using Cu Kα radiation. GC analyses were performed on Shimadzu GC-2014 with flame ionization detector equipped with Rtx-1 capillary column (internal diameter = 0.25 mm, length = 30 m) or Stabil wax capillary column (internal diameter = 0.25 mm, length = 30 m). GC-MS spectra were recorded on Shimadzu GCMS-QP 2010 with RTX-5MS column (0.25 mm× 30 m). ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker AVANCE III 500 MHz (500 MHz for proton, 125MHz for carbon) spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ or DMSO-d6 as solvent in all cases, and chemical shifts were reported in parts per million (ppm, δ). Column chromatography was performed using 200-300 mesh silica gel.

II. Preparation and Characterizations of catalyst

$[NH_4]_3[CrMo_6O_{18}(OH)_6]$ was prepared according to the published literature methods.[1-5] Firstly, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (5.0 g, 4 .0 mmol) was dissolved in water (80 mL) under stirring in an oil bath at 100 °C. Then, $Cr(NO_3)_3{\cdot}9H_2O$ (2.3 g, 5.8 mmol) was dissolved in water (80 mL), which was slowly added dropwise into the solution under stirring. The mixture was still stirring for 1 hour after complete adding. And then, filtering the yellow insoluble precipitate produced out, cooling the filtrate, and adding excess amounts of acetonitrile. After a few days, the purple crystals product (4.9 g) was collected. IR: 3197.39 (vas NH, m), 1638.23 (δ OH, m), 1401.23 (δ NH, s), 943.50 (ν Mo=O, vs), 893.36 (ν Mo=O, vs), 653.75 (ν Mo-O-Mo, vs), 577.56 (ν M-O-Mo, w) cm^{-1}.

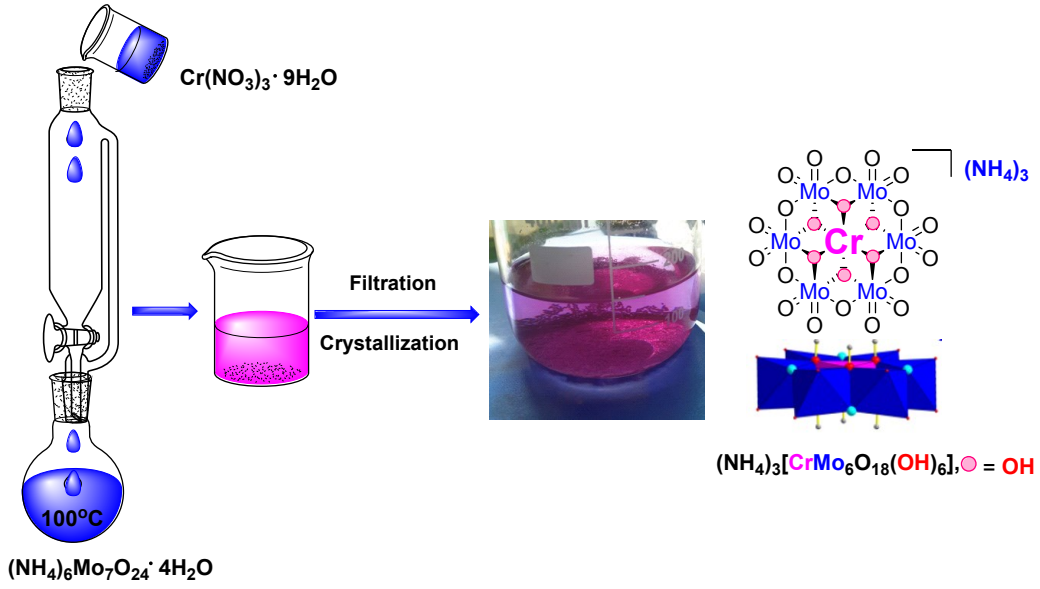


Figure S1. $[NH_4]_3[CrMo_6O_{18}(OH)_6]$

III. FT-IR and XRD spectra of catalyst 1

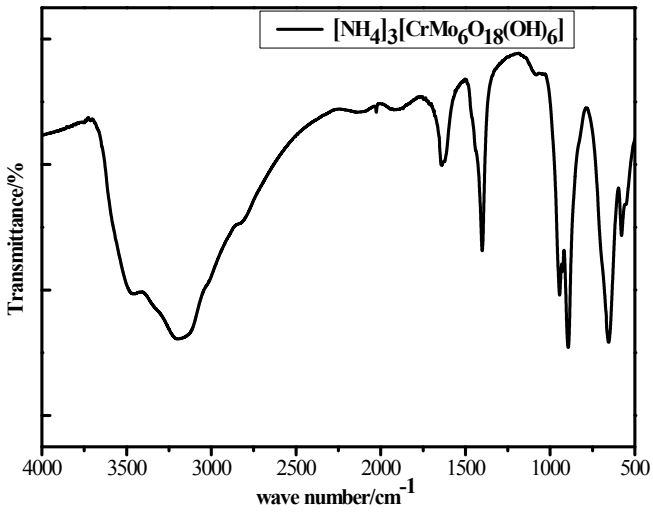


Figure S2. The FT-IR spectra of catalyst **1**

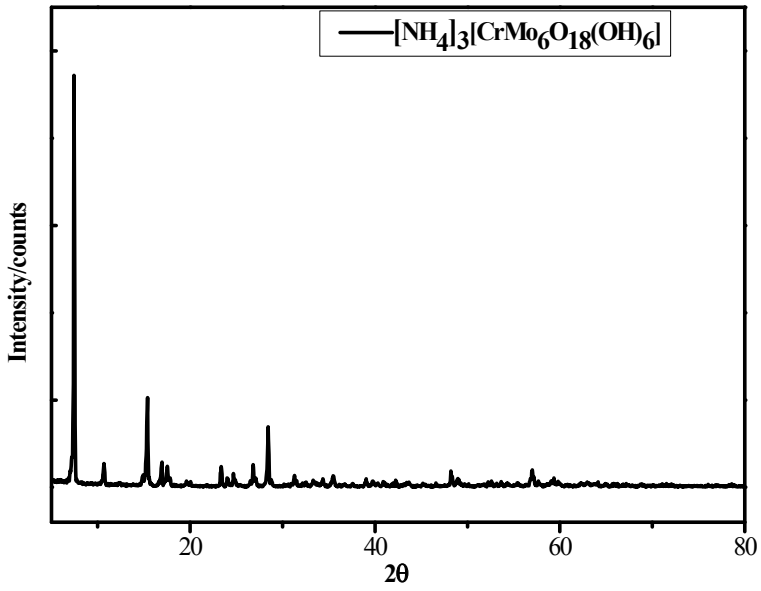


Figure S3. The XRD spectra of catalyst **1**

IV. General procedure for catalytic oxidative of methylarenes

The catalyst 1 (1.0 mol%), methylarenes (1.0 mmol), $K_2S_2O_8$ (1.0 mmol)/O_2 (1 atm), H_2O (2.0 mL) stirring at a reaction tube at 50 ^oC for 24 h. Reaction mixture was analyzed by GC-MS analysis. Following completion of the reaction, the product was extracted by adding 2.0 mL ethyl acetate or ether, the catalyst 1 were suspended in the water and could be easily recovered by filtration. Finally, the solvent was removed in vacuo, and the corresponding benzoic acid derivatives were isolated and purified by silica gel column.

V. Recycling experiments of catalyst 1

Following completion of the reaction, the product was extracted by adding ethyl acetate, the catalyst **1** were suspended in the water and could be easily recovered by filtration, washed in turn with water, acetone and ethyl acetate. Then, the dried catalyst was reused without any further purification.

The recovered catalyst was characterized by FTIR and XRD. The infrared image contains a new catalyst and the sixth catalyst.

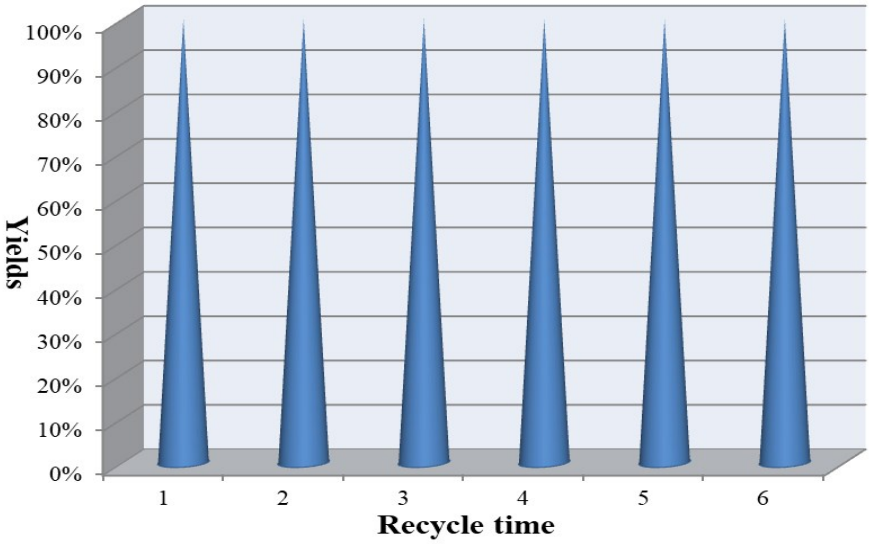


Figure S4. Recycling experiments for the catalyst **1**

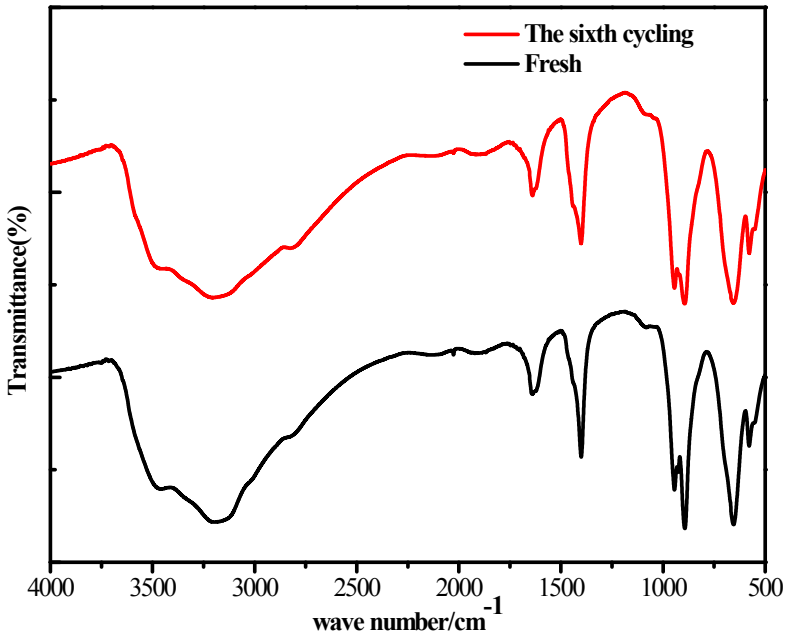


Figure S5. Recycling experiments for the catalyst **1**

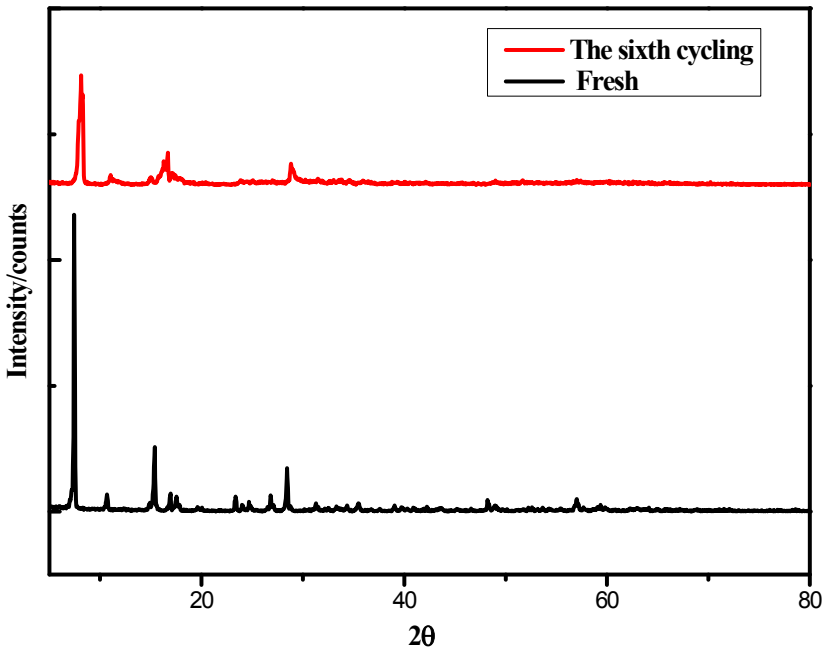


Figure S6. XRD of catalyst 1 before and after reaction

VI. GC-MS studies for the progress of the toluene oxidation

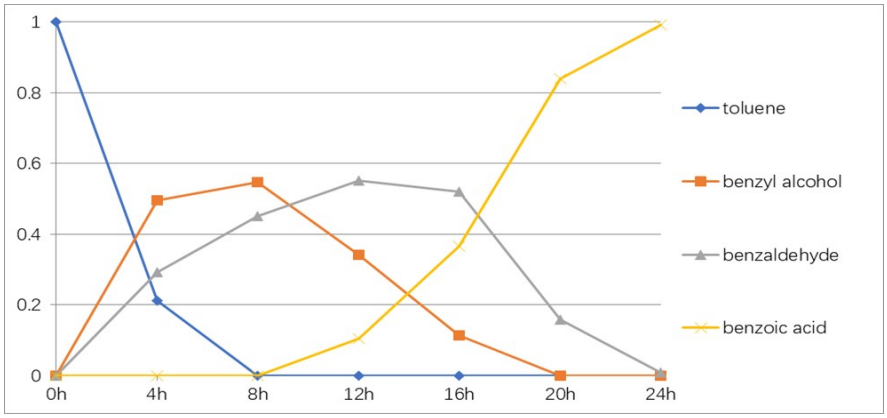


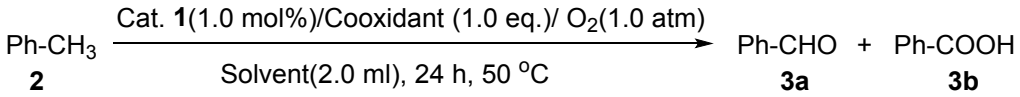
Figure S7. GC-MS studies for the progress of the toluene oxidation

VII. DFT computational details

All geometries were optimized without symmetry constraints in the gas phase by means of Gaussian 09 package[6] at (U)B3LYP[7,8] /6-31G(d,p) /LanL2DZ[9] (Cr, Mo) level. The vibrational frequency was calculated to check the nature of each stationary structure at the same theoretical level with optimization. Only one imaginary frequency was characterized for transition states, while no imaginary frequency was found for reactants, intermediates, and products. Moreover, the electronic energies were evaluated at the SMD[10] (water)/(U)B3LYP/6-311++G(d, p)/SDD(Cr, Mo) level.

VIII. Optimization of reaction conditions

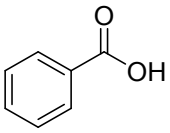
Table S1： Optimization of reaction conditions[a,b]



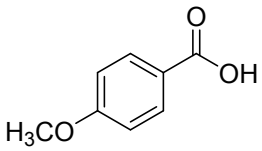
Entry	Solvent (ml)	Cooxidant (equiv.)	Yield (**3a**/**3b**)[b]
1	H_2O	$K_2S_2O_8$	1/99
2	CH_3CN	$K_2S_2O_8$	53/37
3	DMF	$K_2S_2O_8$	32/60
4	1,4-dioxane	$K_2S_2O_8$	29/65
5	DCE	$K_2S_2O_8$	72/16
6	Acetone	$K_2S_2O_8$	59/18
7	CH_3CN/ H_2O(1.0/1.0)	$K_2S_2O_8$	33/59
8	DMF/H_2O (1.0/1.0)	$K_2S_2O_8$	25/73
9	H_2O	$K_2S_2O_8$ (2.0)	2/93
10	H_2O	*m*-CPBA	<10/-
11	H_2O	DTBP	<10/-
12	H_2O	TBHP	<10/-
13[c]	H_2O	$K_2S_2O_8$	19/80
14[d]	H_2O	$K_2S_2O_8$	2/94
15[e]	H_2O	$K_2S_2O_8$	29/69
15[f]	H_2O	$K_2S_2O_8$	2/96

[a] Reaction conditions: Cat. **1** (1.0 mol%), Toluene (1.0 mmol), Cooxidant (1.0 equiv.)/O_2 (1 atm), H_2O (2.0 mL), at 50 °C, 24 h. [b] The Selectivity and yield were detemained by GC-MS. [c] at 40 °C, [d] at 60 °C, [e] Cat.**1** (0.5 mol%), [f] Cat. **1** (2.0 mol%).

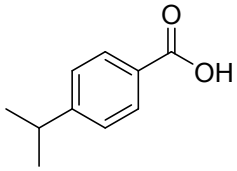
IX. NMR data and spectra of products



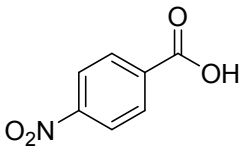
benzoic acid[11] **(3):** ^{1}H NMR (500 MHz, DMSO-d6) δ 12.97 (s, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d6) δ 167.79, 133.30, 131.24, 129.73, 129.01.



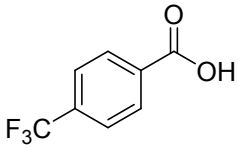
4-methoxybenzoic acid[11] **(4):** ^{1}H NMR (500 MHz, DMSO-d6) δ 12.59 (s, 1H), 7.85 (d, *J*=8.9, 2H), 6.97 (d, *J*=9.0, 2H), 3.78 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d6) δ 167.54, 163.36, 131.87, 123.48, 114.33, 55.95.



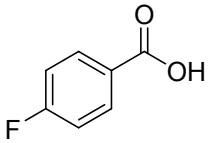
4-isopropylbenzoic acid[12] **(5):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J*=8.4, 2H), 7.32 (d, *J*=8.1, 2H), 2.98 (dt, *J*=13.8, 6.9, 1H), 1.27 (d, *J*=6.9, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.51, 155.48, 130.50, 126.72, 125.65, 34.44, 23.77.



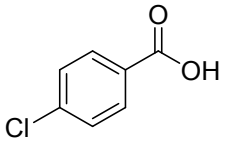
4-nitrobenzoic acid[11] **(6):** ^{1}H NMR (500 MHz, DMSO-d6) δ 13.63 (s, 1H), 8.27 (d, *J*=8.8, 2H), 8.11 (d, *J*=8.8, 2H). ^{13}C NMR (125 MHz, DMSO-d6) δ 166.34, 150.58, 136.90, 131.24, 124.28.



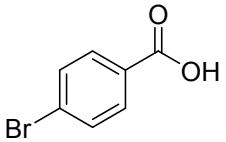
4-(trifluoromethyl)benzoic acid[12] **(7):** ^{1}H NMR (500 MHz, DMSO-d6) δ 13.49 (s, 1H), 8.14 (d, *J*=8.4, 2H), 7.87 (d, *J*=8.2, 2H). ^{13}C NMR (125 MHz, DMSO-d6) δ 166.65, 135.05, 132.81, 130.55, 126.05, 125.34.



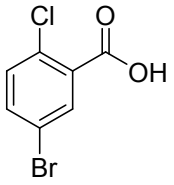
4-fluorobenzoic acid[12] **(8):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, *J*=8.9, 5.4, 2H), 7.14 (t, *J*=8.6, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 166.89, 132.68, 132.58, 116.27, 116.05.



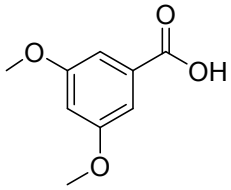
4-chlorobenzoic acid[11] **(9):** ^{1}H NMR (500 MHz, DMSO-d6) 13.16 (s, 1H), 7.93 (d, *J*=8.6, 2H), 7.52 (d, *J*=8.6, 2H). ^{13}C NMR (125 MHz, DMSO-d6) δ 166.91, 138.25, 131.55, 130.07, 129.10.



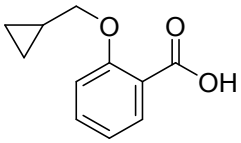
4-bromobenzoic acid[11] **(10):** ^{1}H NMR (500 MHz, DMSO-d6) δ 13.19 (s, 1H), 7.85 (s, 2H), 7.71 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d6) δ 167.07, 132.85, 131.48, 131.13, 130.47.



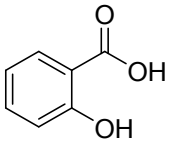
5-bromo-2-chlorobenzoic acid[12] **(11):** ^{1}H NMR (500 MHz, DMSO-d6) δ 13.73 (s, 1H), 7.94 (d, *J*=2.3, 1H), 7.74 (dd, *J*=8.6, 2.5, 1H), 7.52 (d, *J*=8.6, 1H). ^{13}C NMR (125 MHz, DMSO-d6) δ 165.72, 135.57, 133.86, 133.48, 133.05, 131.33, 120.32.



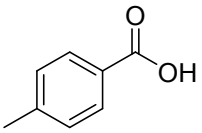
3,5-dimethoxybenzoic acid[12] **(12):** ^{1}H NMR (500 MHz, DMSO-d6) δ 12.94 (s, 1H), 6.97 (d, *J*=2.3, 2H), 6.64 (t, *J*=2.2, 1H), 3.69 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d6) δ 167.43, 160.83, 133.30, 107.29, 105.33, 5.86.



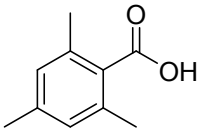
2-(cyclopropylmethoxy)benzoic acid[13] **(13):** ^{1}H NMR (500 MHz, DMSO-d6) δ 12.54 (s, 1H), 7.63 (dd, *J*=7.6, 1.7, 1H), 7.50 – 7.39 (m, 1H), 7.06 (d, *J*=8.4, 1H), 6.98 (t, *J*=7.5, 1H), 3.89 (d, *J*=6.6, 3H), 1.21 (s, 1H), 0.53 (dd, *J*=8.1, 1.8, 3H), 0.35 (d, *J*=6.2, 3H). ^{13}C NMR (125 MHz, DMSO-d6) δ 167.91, 157.80, 133.25, 130.97, 122.33, 120.57, 114.36, 73.08, 10.47, 3.26.



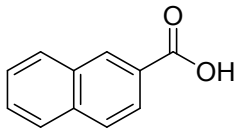
2-hydroxybenzoic acid[12] **(14):** ^{1}H NMR (500 MHz, DMSO-d6) δ 13.76 (s, 1H), 11.37 (s, 1H), 7.75 (dd, *J*=7.9, 1.7, 1H), 7.48 – 7.44 (m, 1H), 6.92 – 6.85 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d6) δ 172.48, 161.68, 136.17, 130.79, 119.69, 117.61, 113.40.



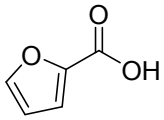
4-methylbenzoic acid[11] **(15):** ^{1}H NMR (500 MHz, DMSO-d6) δ 12.75 (s, 1H), 7.80 (d, *J*=8.1, 2H), 7.24 (d, *J*=8.1, 2H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d6) δ 167.84, 143.52, 129.85, 129.62, 128.55, 21.62.



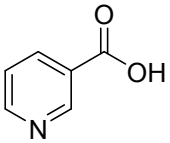
2,4,6-trimethylbenzoic acid[12] **(16):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 2H), 4.31 (s, 6H), 4.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.29, 142.14, 137.89, 131.31, 130.65, 22.86, 21.94.



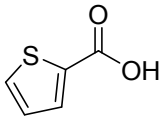
2-naphthoic acid[11] **(17):** ^{1}H NMR (500 MHz, DMSO-d6) δ 13.05 (s, 1H), 8.58 (s, 1H), 8.10 – 7.93 (m, 4H), 7.64 – 7.52 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.98, 135.46, 132.67, 131.05, 129.80, 128.85, 128.69, 128.59, 128.18, 127.33, 125.69.



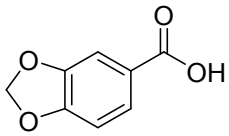
furan-2-carboxylic acid[12] **(18):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.32 (s, 1H), 7.66 – 7.61 (m, 1H), 7.35 – 7.30 (m, 1H), 6.55 (dd, *J*=3.6, 1.8, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.73, 147.54, 143.88, 120.28, 112.38.



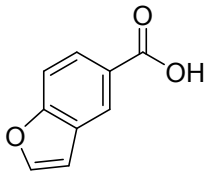
picolinic acid[12] **(19):** ^{1}H NMR (500 MHz, DMSO-d6) δ 13.13 (s, 1H), 8.66 (d, *J*=4.6, 1H), 8.01 – 7.92 (m, 2H), 7.58 (ddd, *J*=7.5, 4.7, 1.2, 1H). ^{13}C NMR (125 MHz, DMSO-d6) δ 166.70, 149.96, 148.86, 138.04, 127.62, 125.18.



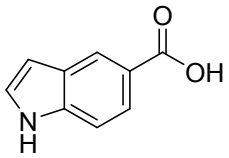
thiophene-2-carboxylic acid[12] **(20):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J*=3.7, 1.2, 1H), 7.64 (dd, *J*=4.9, 1.1, 1H), 7.14 (dd, *J*=4.9, 3.8, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.74, 135.13, 134.13, 132.92, 128.17.



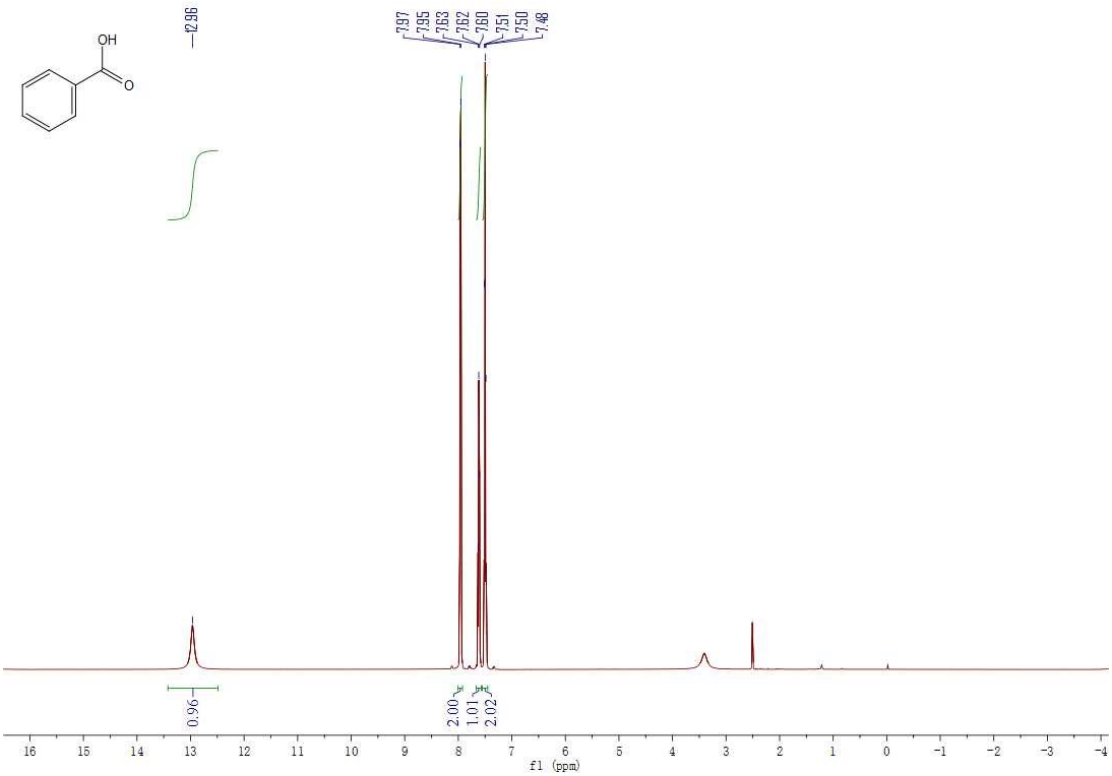
benzo[d][1,3]dioxole-5-carboxylic acid[12] **(21):** ^{1}H NMR (500 MHz, DMSO-d6) δ 12.77 (s, 1H), 7.55 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.36 (d, *J* = 1.3 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.13 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d6) δ 167.08, 151.60, 147.94, 125.42, 125.12, 109.25, 108.53, 102.40.



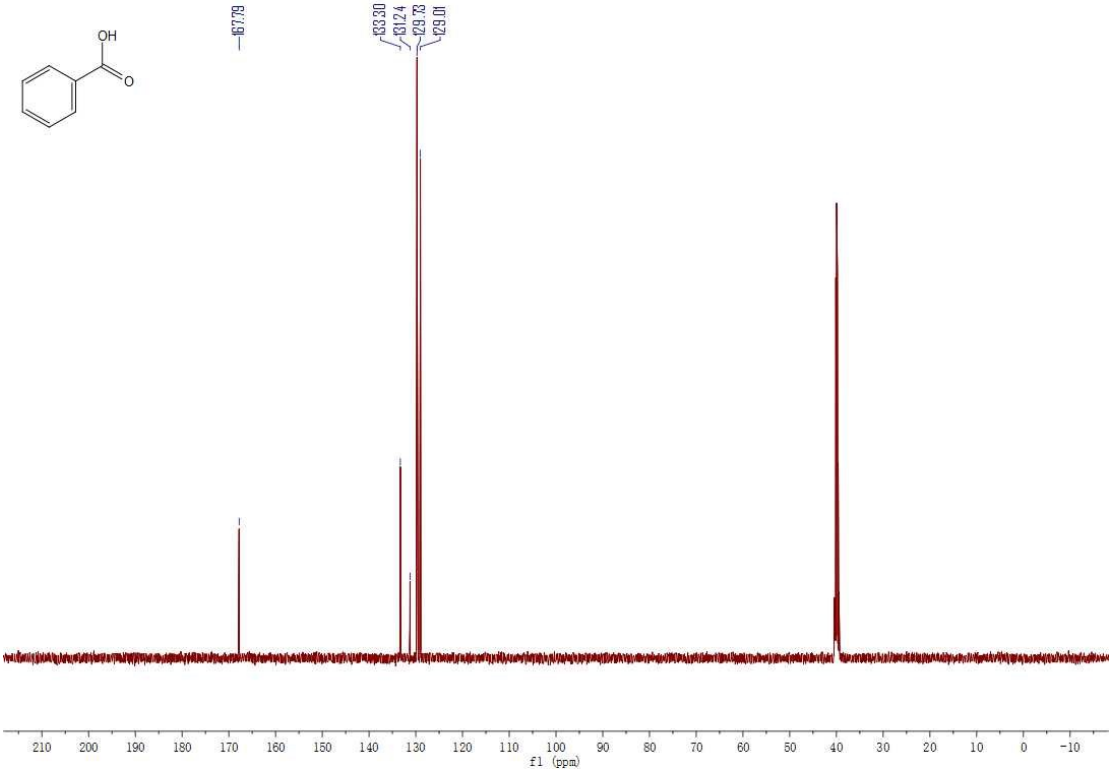
benzofuran-5-carboxylic acid[14] **(22):** ^{1}H NMR (500 MHz, DMSO-d6) δ 12.78 (s, 1H), 8.21 (m, 1H), 8.01 (s, 1H), 7.84 - 7.82 (m, 1H), 7.60 - 7.58 (m, 1H), 6.99 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d6) δ 167.86, 157.15, 147.86, 127.83, 126.31, 126.24, 123.88, 111.74, 107.77.



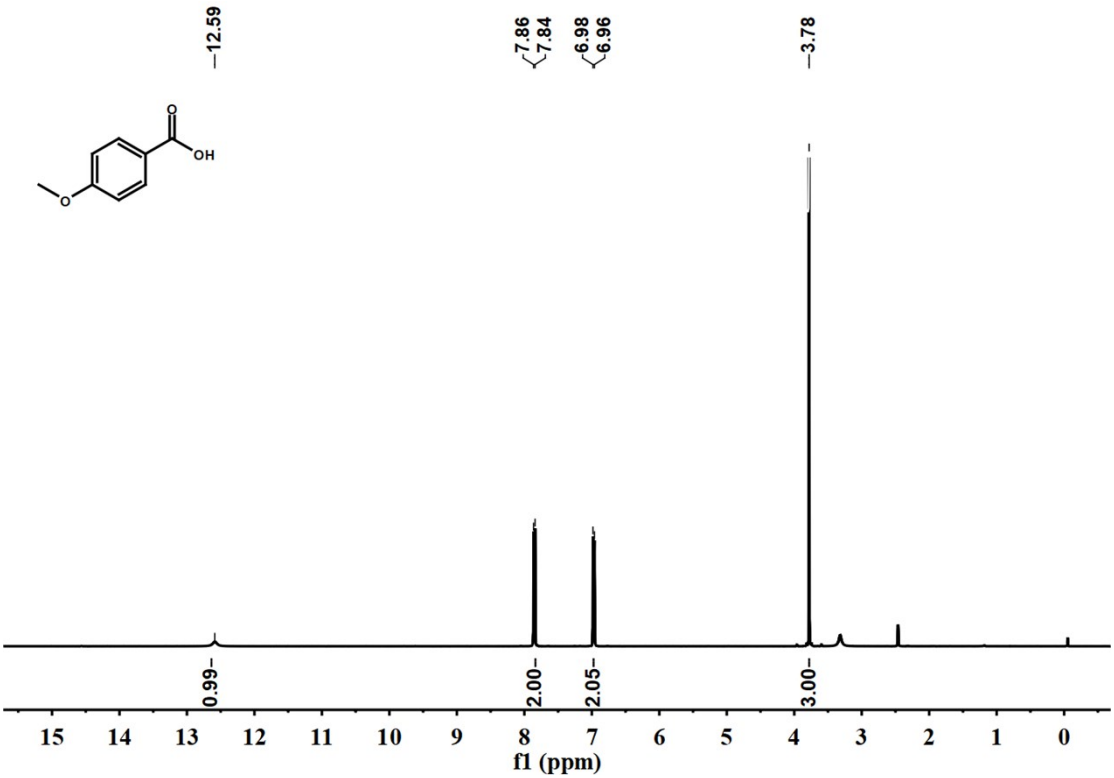
1H-indole-5-carboxylic acid[15] **(23):** ^{1}H NMR (500 MHz, DMSO-d6) δ 12.38 (s, 1H), 11.43 (s, 1H), 8.24 (d, *J*=0.6, 1H), 7.71 (dd, *J*=8.5, 1.5, 1H), 7.49 – 7.41 (m, 2H), 6.61 – 6.55 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d6) δ 168.88, 138.78, 127.64, 127.37, 123.26, 122.66, 121.85, 111.55, 102.94.



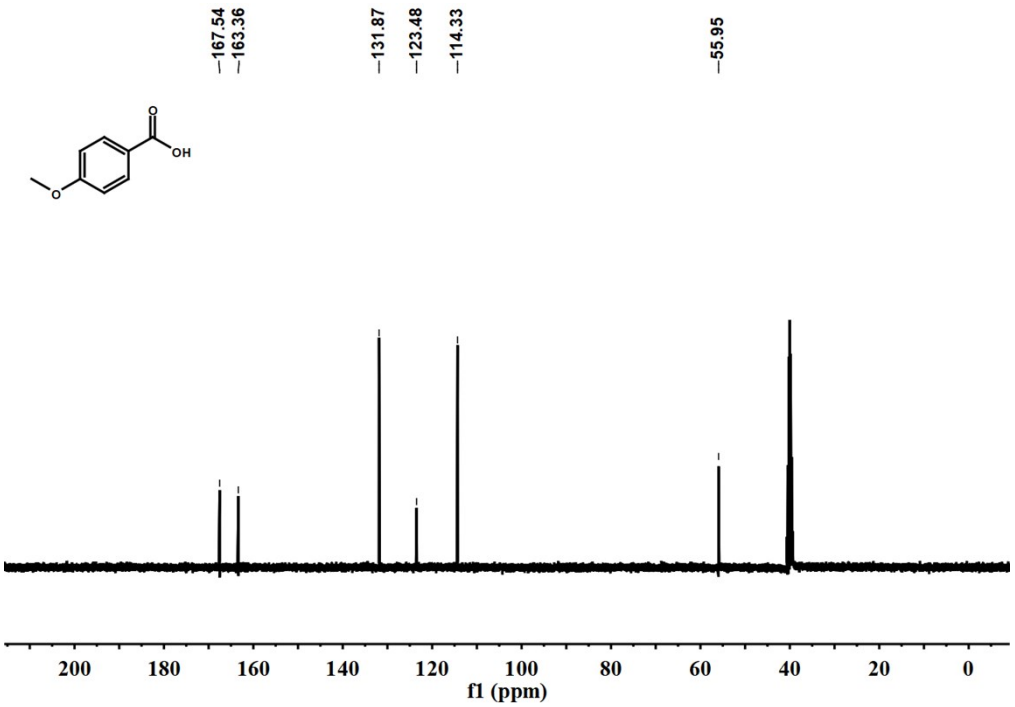
^{1}H NMR spectra of **3** (500 MHz, DMSO-d6)



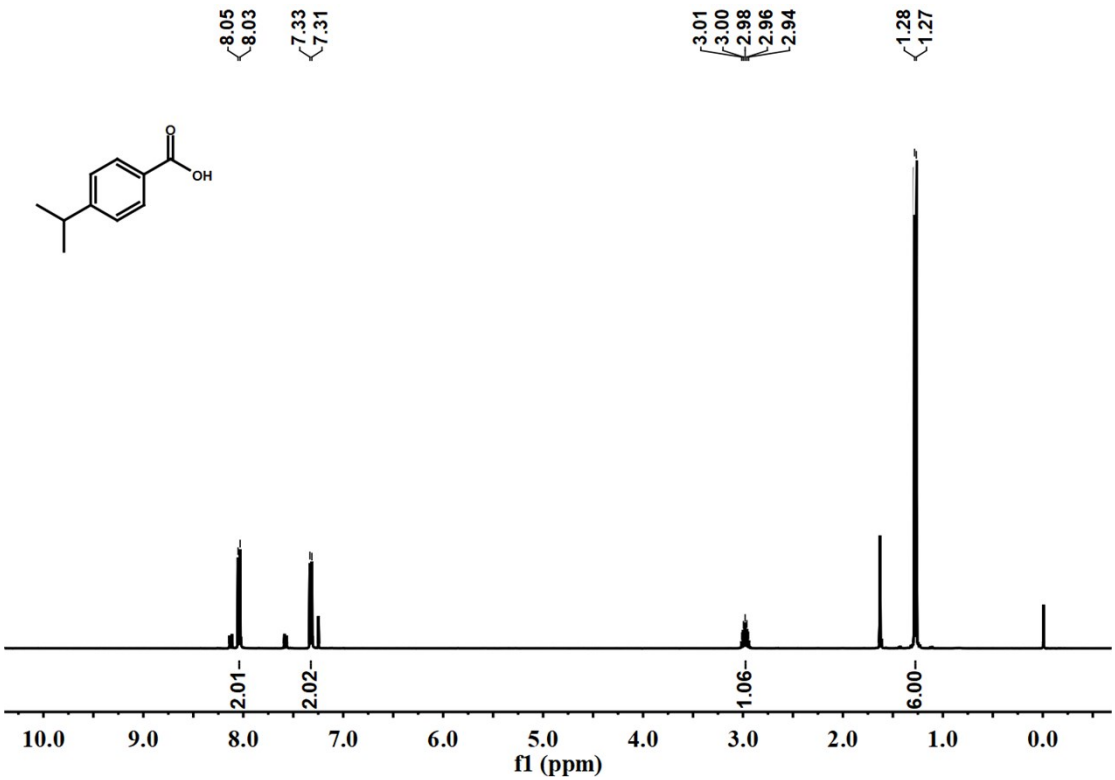
^{13}C NMR spectra of **3** (125 MHz, DMSO-d6)



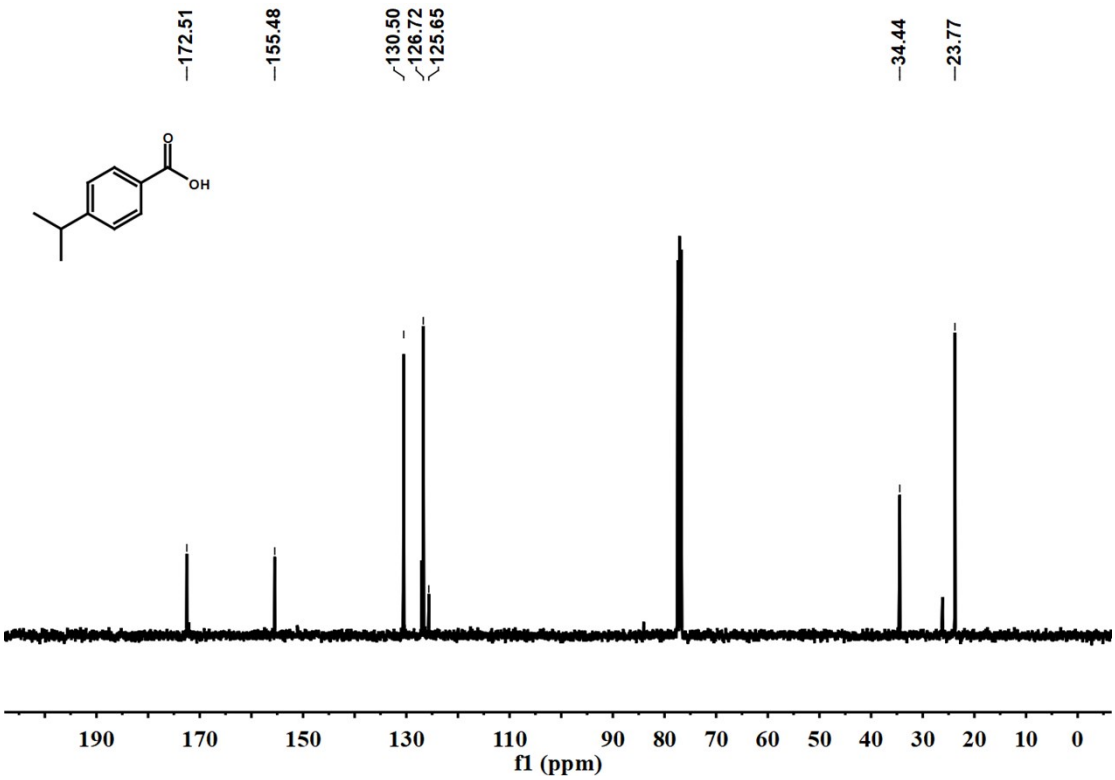
^{1}H NMR spectra of **4** (500 MHz, DMSO-d6)



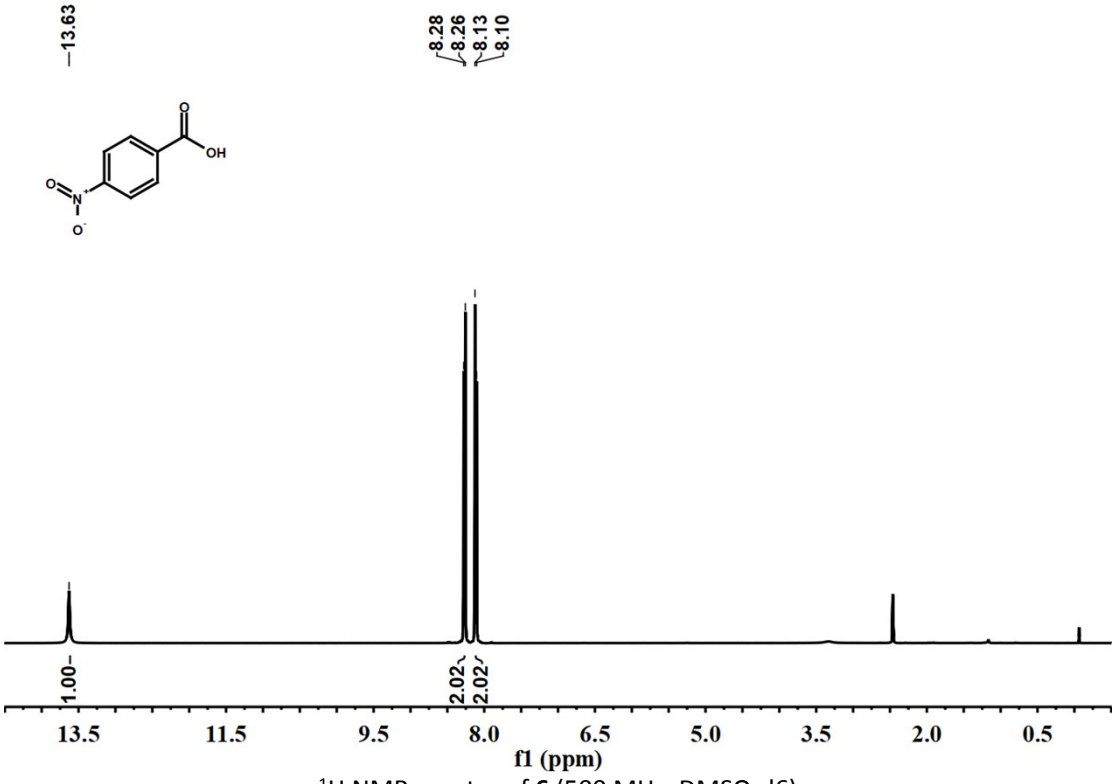
^{13}C NMR spectra of **4** (125 MHz, DMSO-d6)



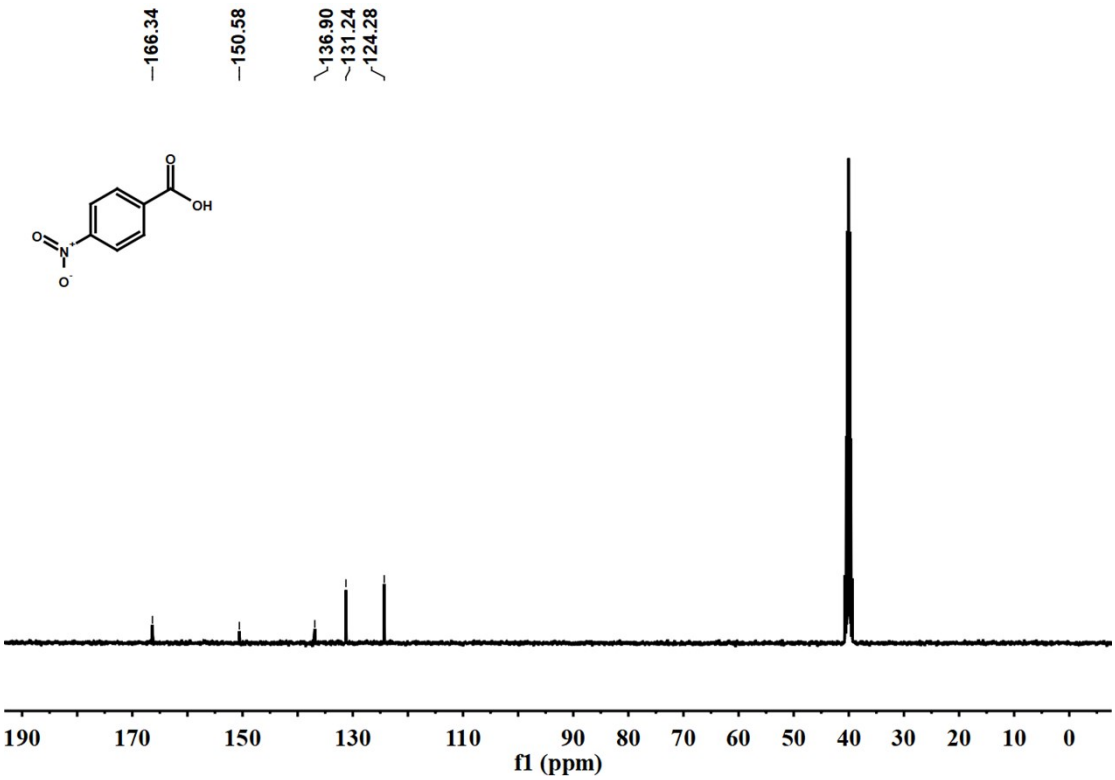
^{1}H NMR spectra of **5** (500 MHz, $CDCl_3$)



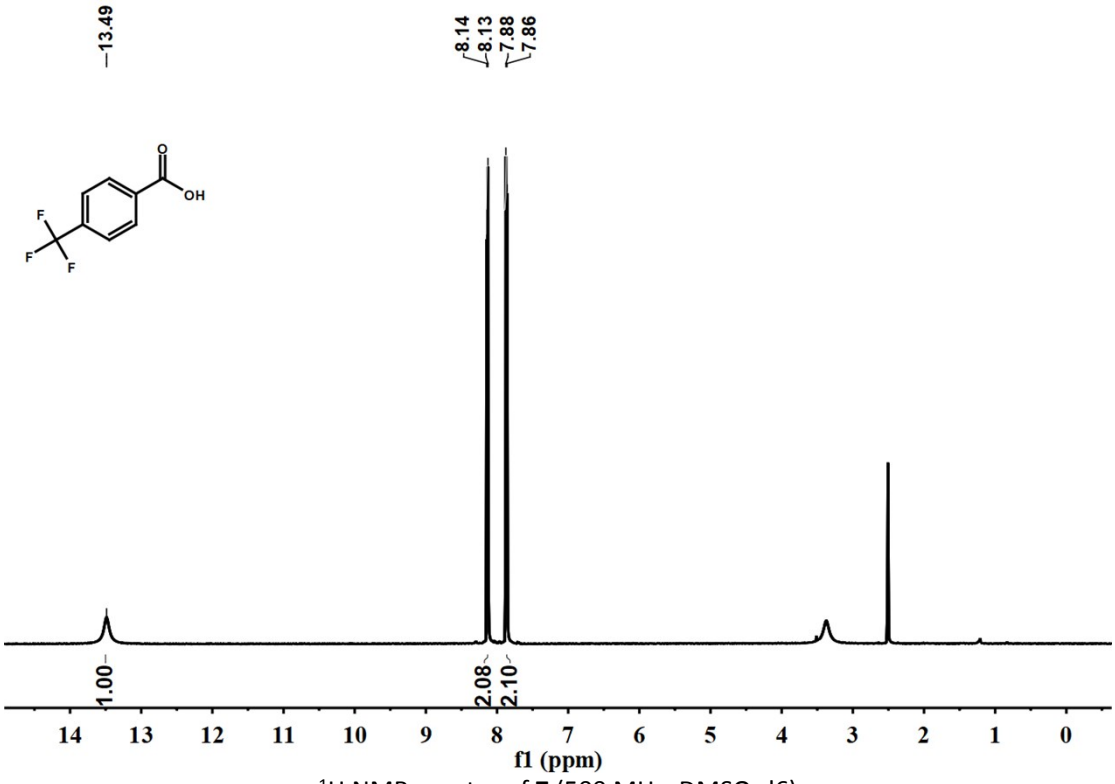
^{13}C NMR spectra of **5** (125 MHz, $CDCl_3$)



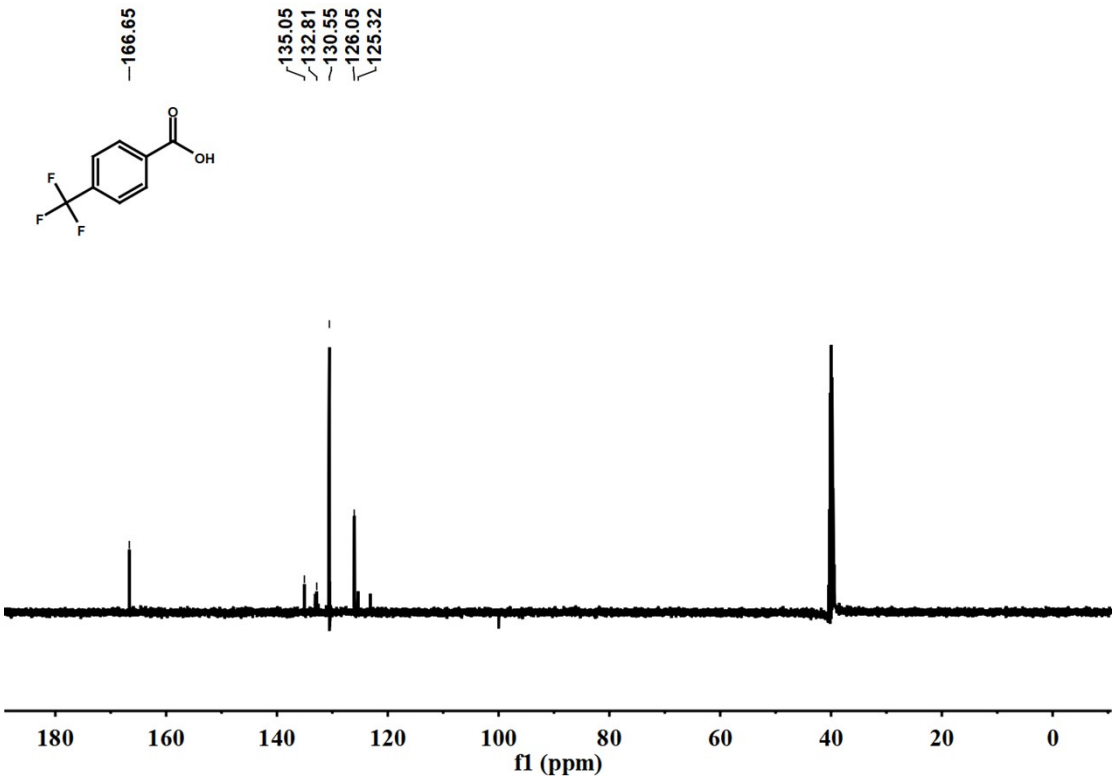
^{1}H NMR spectra of **6** (500 MHz, DMSO-d6)



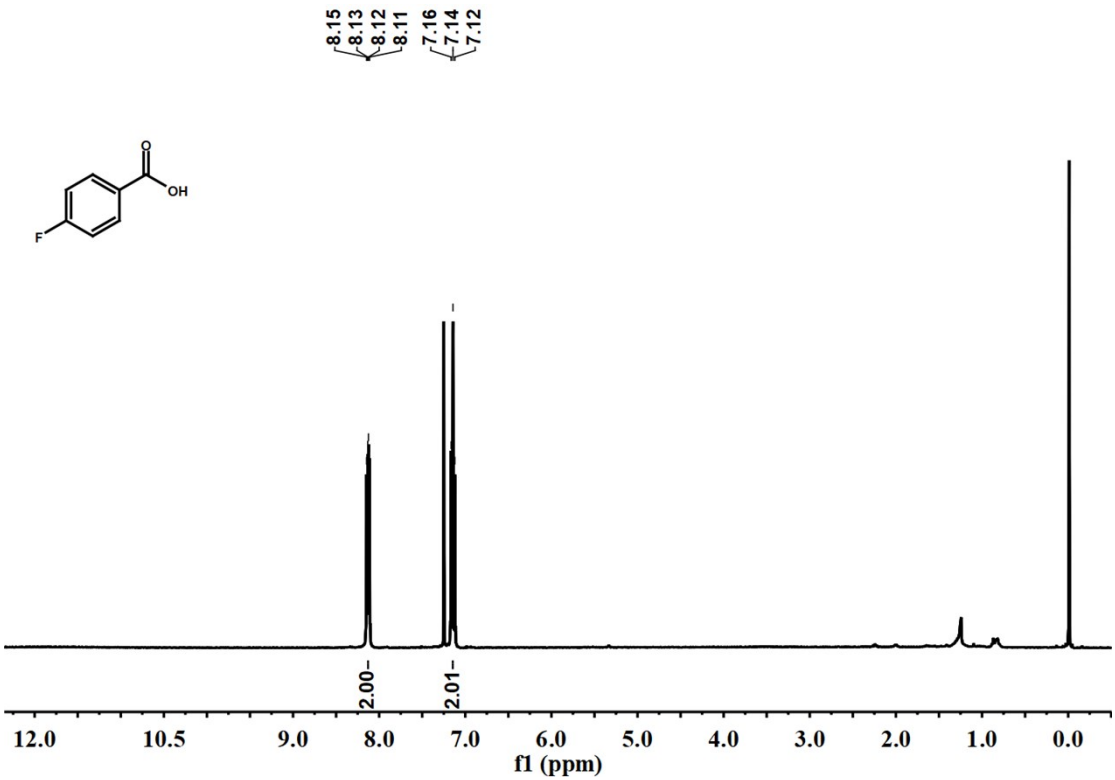
^{13}C NMR spectra of **6** (125 MHz, DMSO-d6)



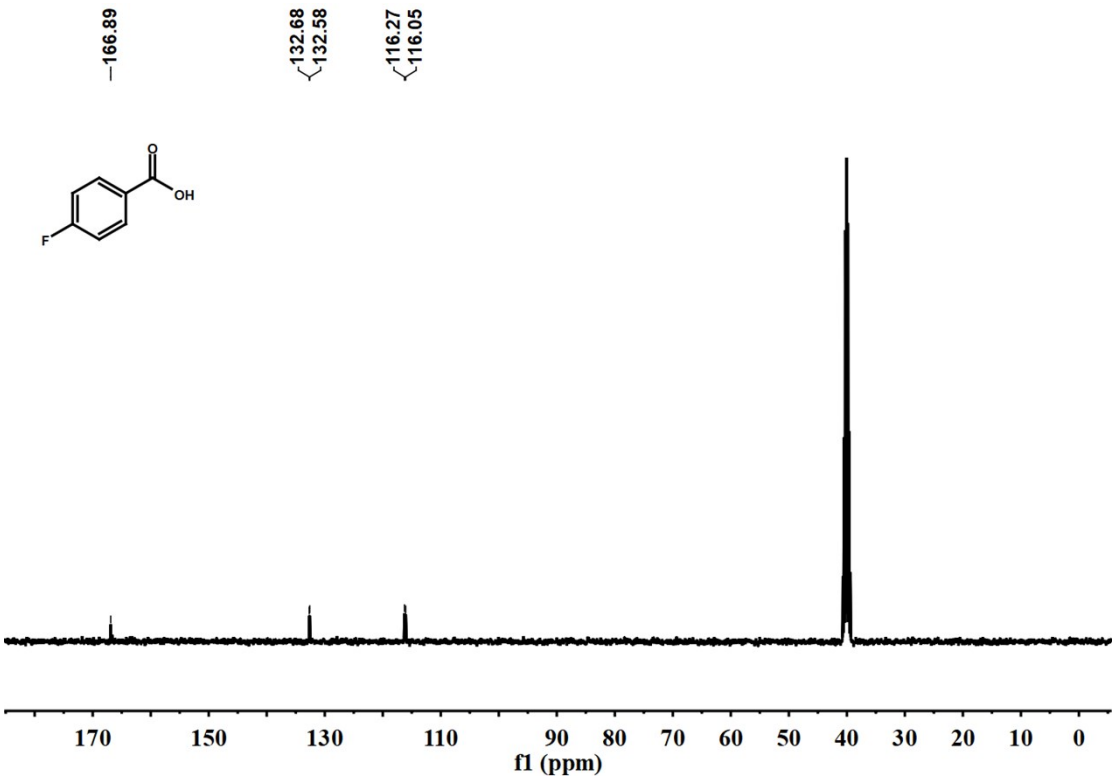
^{1}H NMR spectra of **7** (500 MHz, DMSO-d6)



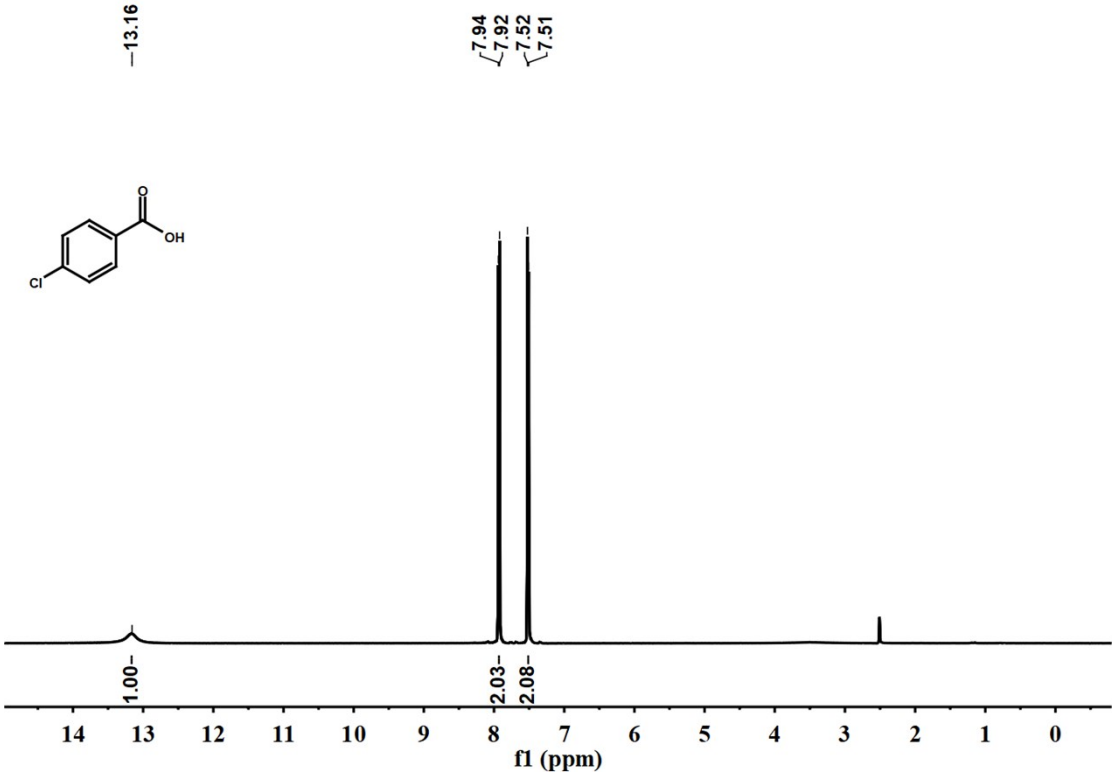
^{13}C NMR spectra of **7** (125 MHz, DMSO-d6)



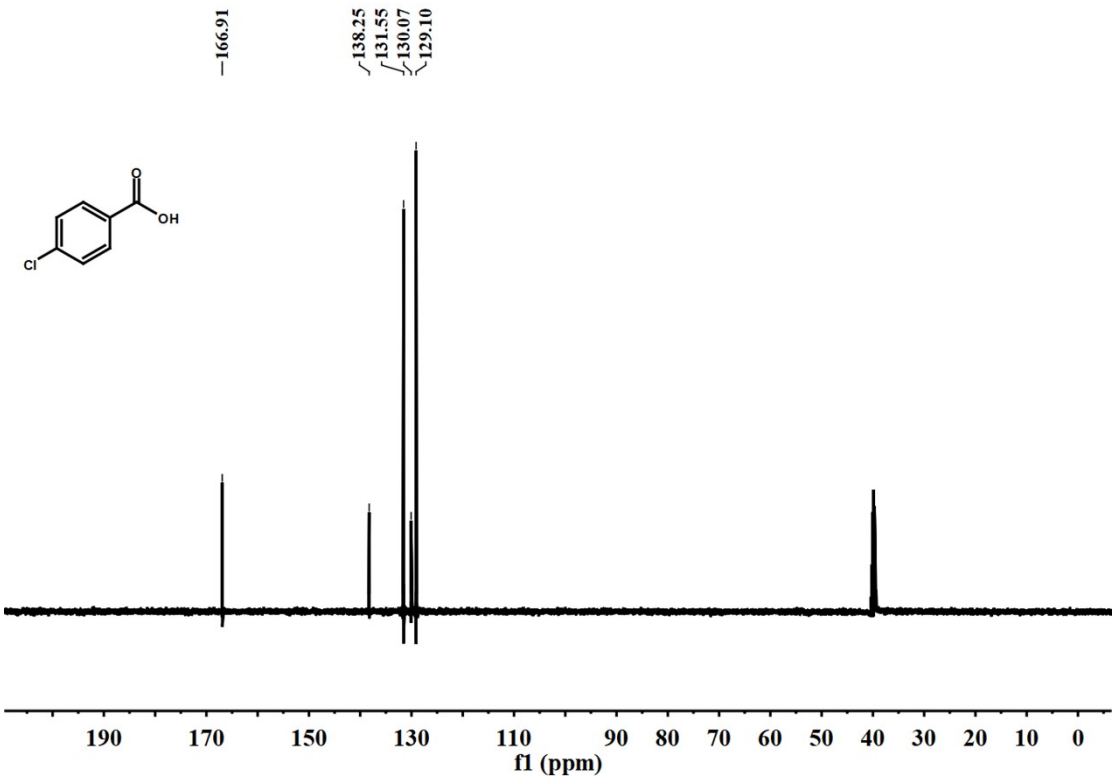
^{1}H NMR spectra of **8** (500 MHz, $CDCl_3$)



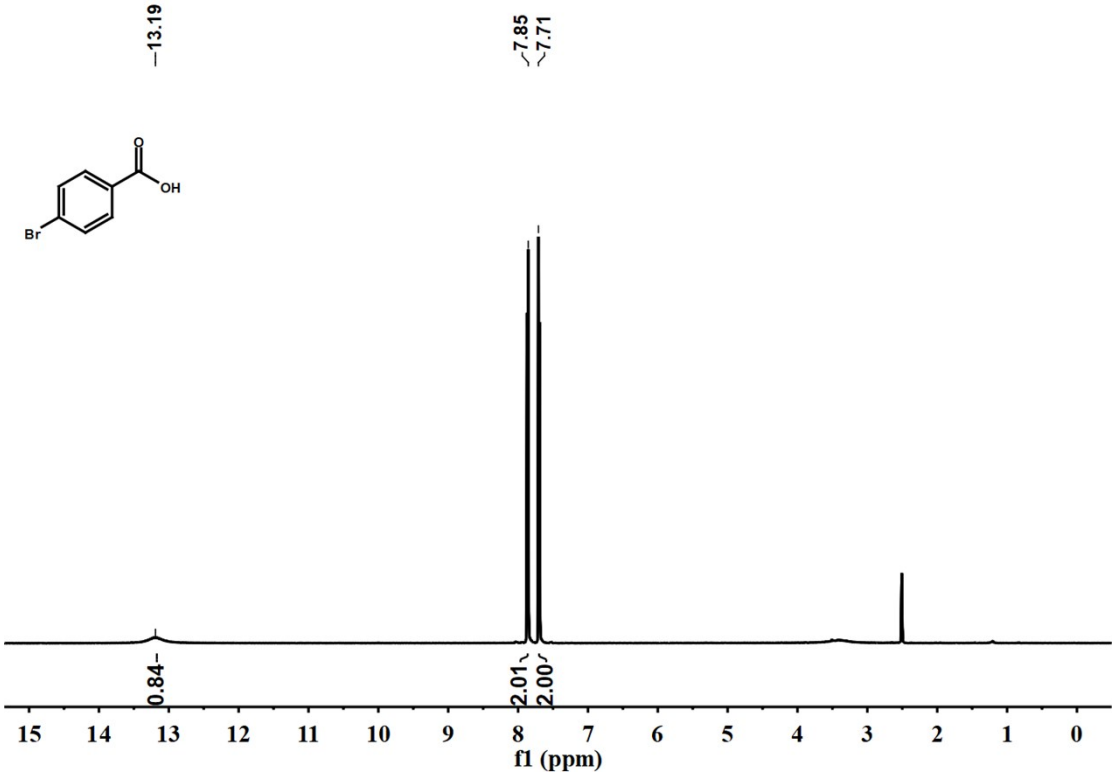
^{13}C NMR spectra of **8** (125 MHz, $CDCl_3$)



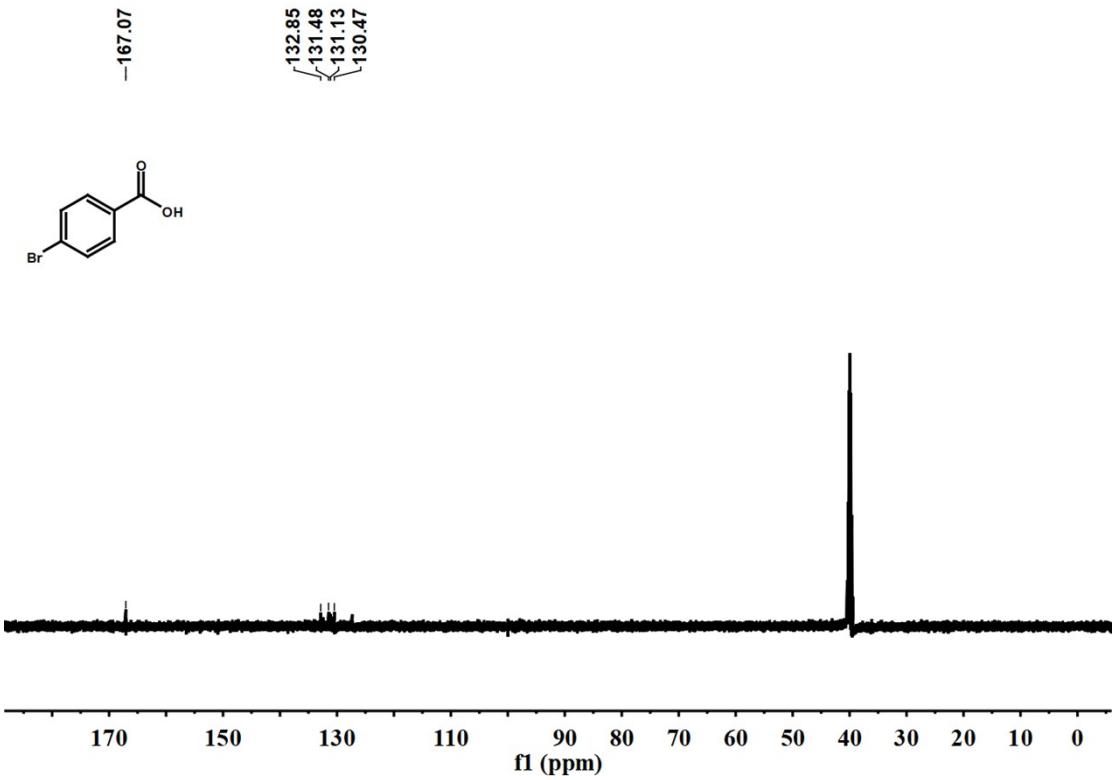
^{1}H NMR spectra of **9** (500 MHz, DMSO-d6)



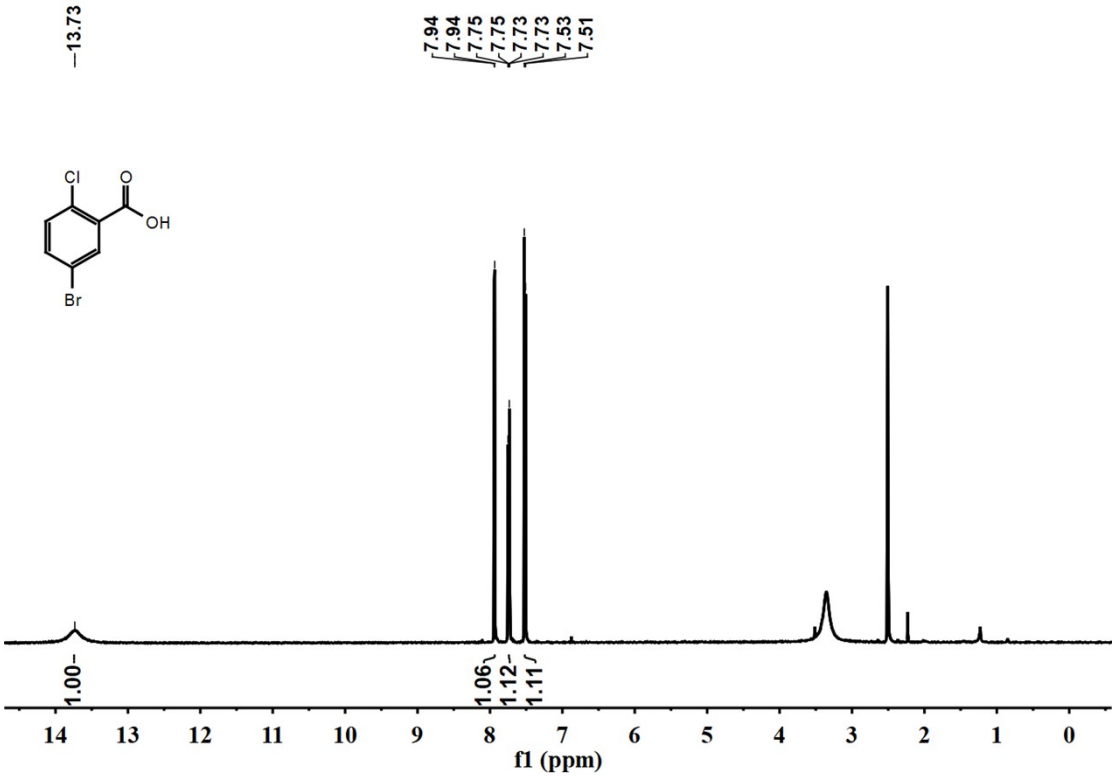
^{13}C NMR spectra of **9** (125 MHz, DMSO-d6)



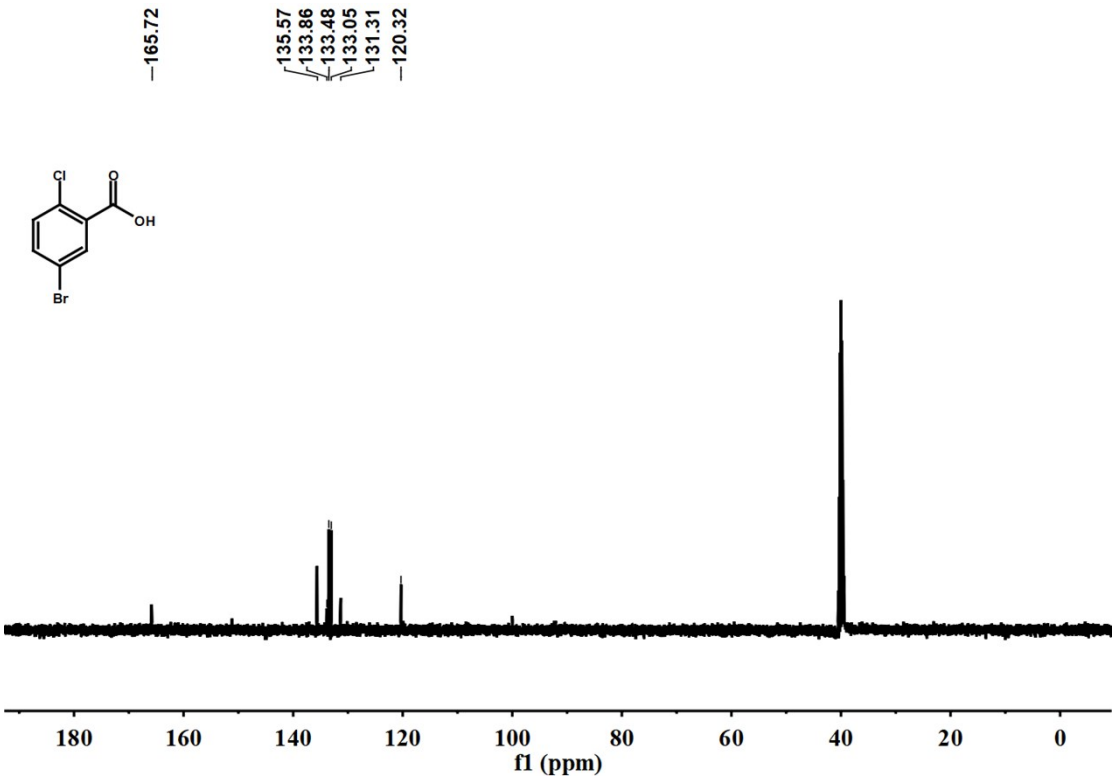
^{1}H NMR spectra of **10** (500 MHz, DMSO-d6)



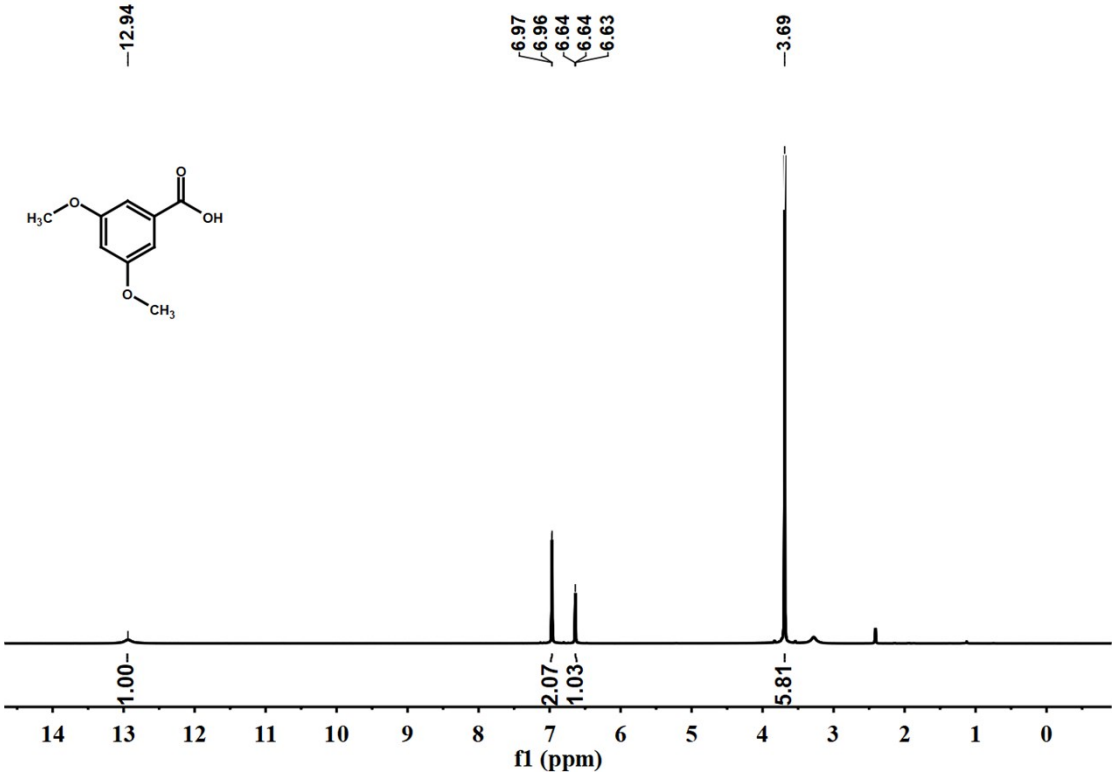
^{13}C NMR spectra of **10** (125 MHz, DMSO-d6)



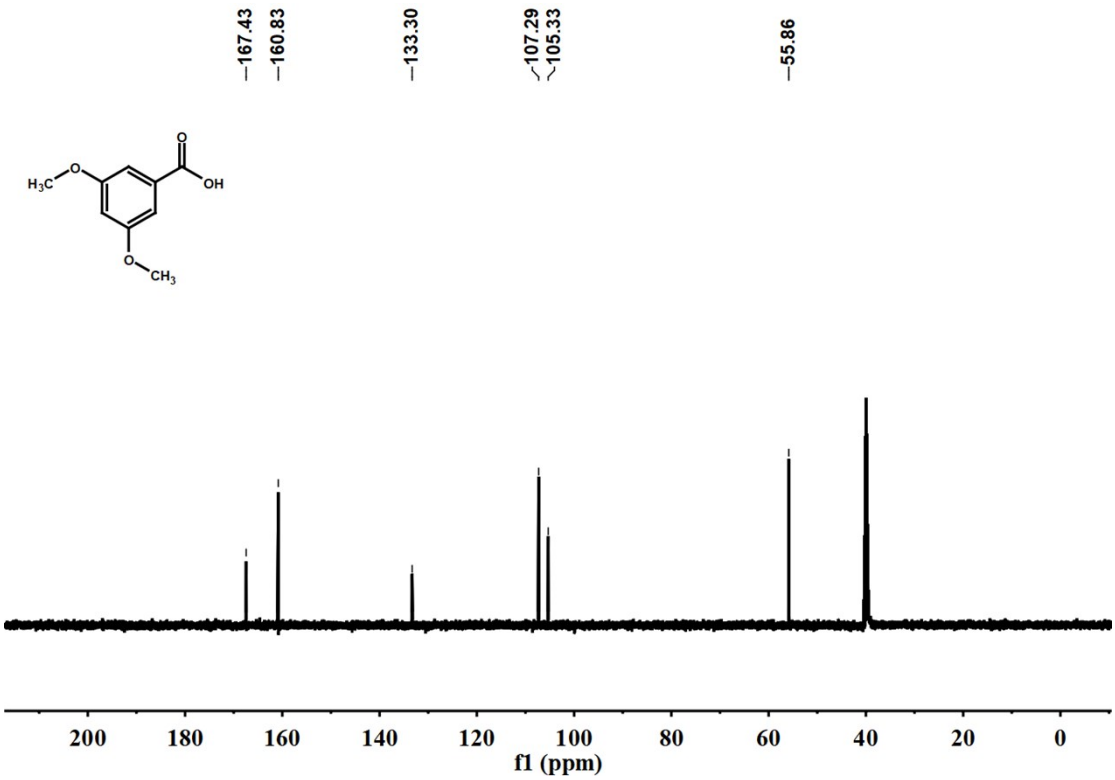
^{1}H NMR spectra of **11** (500 MHz, DMSO-d6)



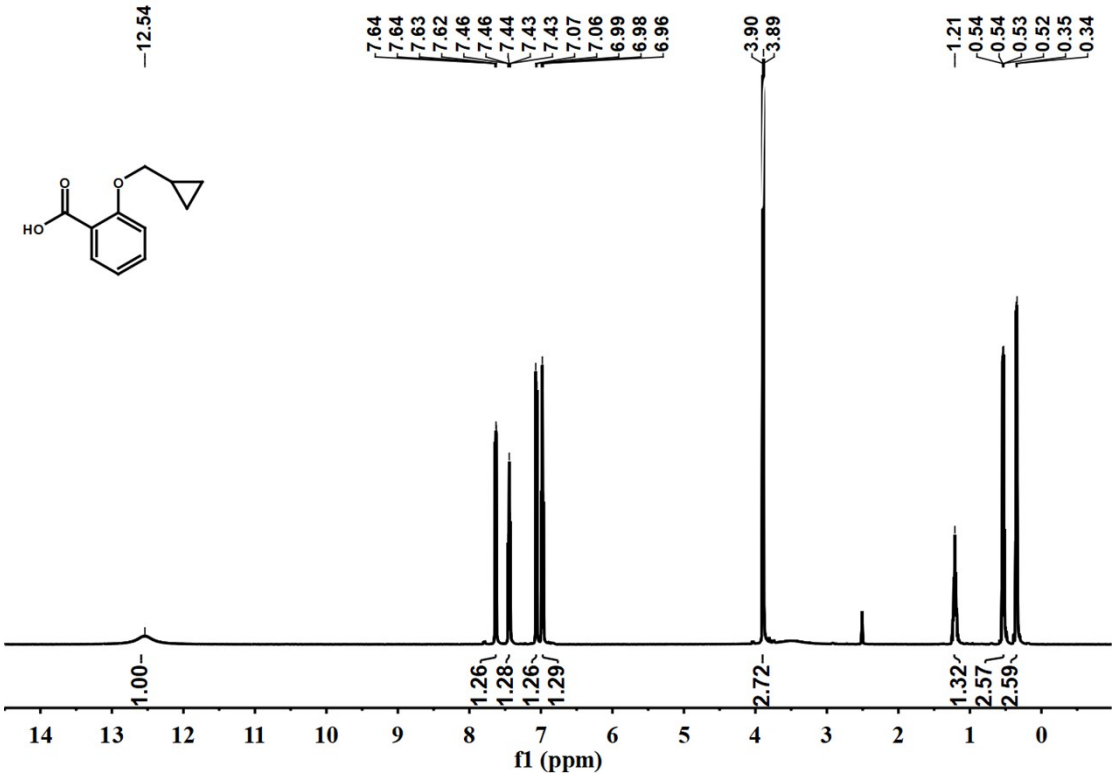
^{13}C NMR spectra of **11** (125 MHz, DMSO-d6)



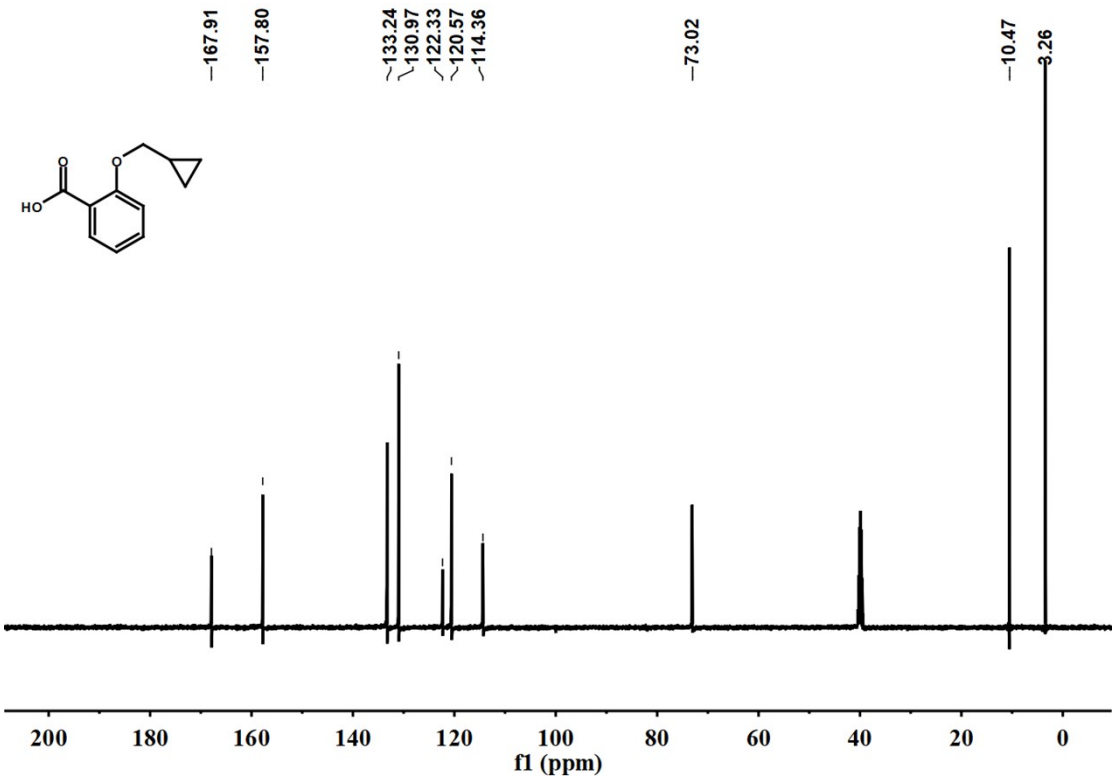
^{1}H NMR spectra of **12** (500 MHz, DMSO-d6)



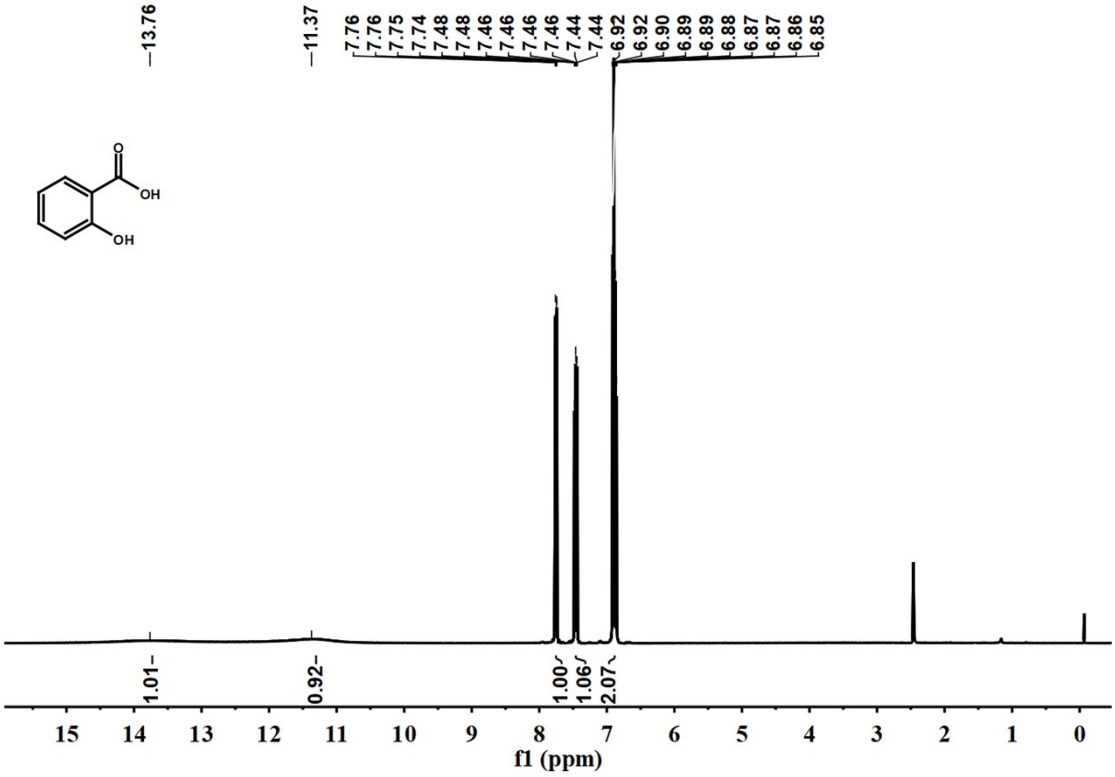
^{13}C NMR spectra of **12** (125 MHz, DMSO-d6)



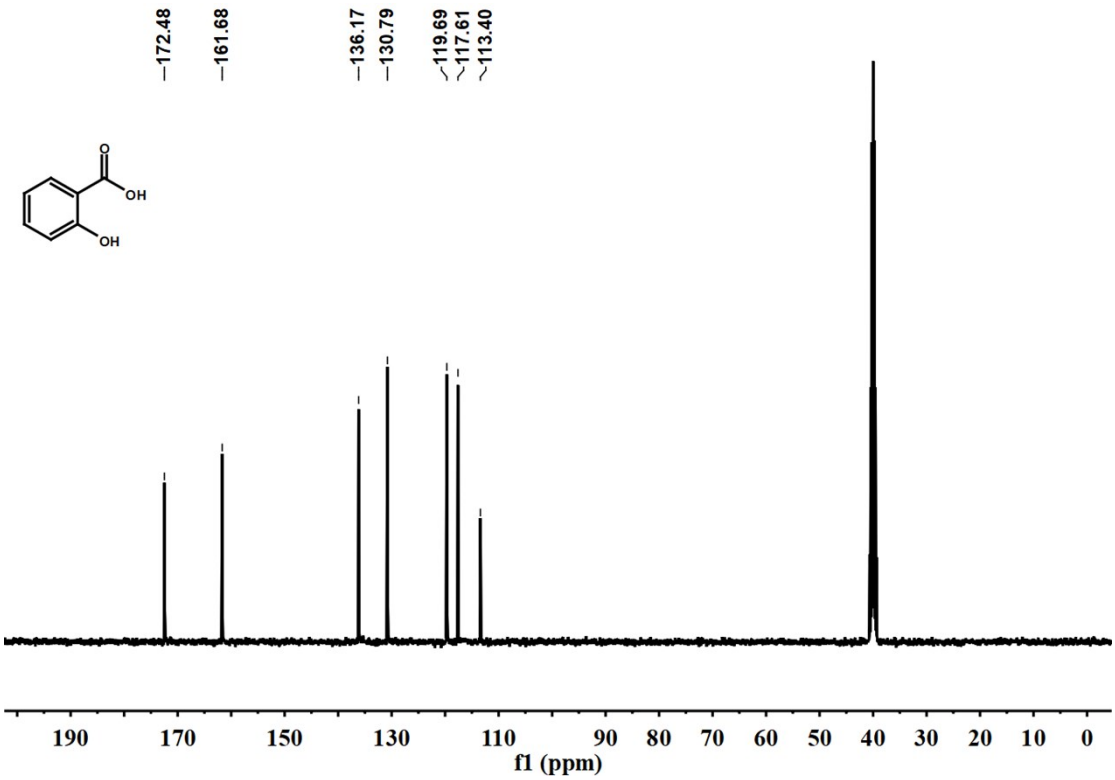
^{1}H NMR spectra of **13** (500 MHz, DMSO-d6)



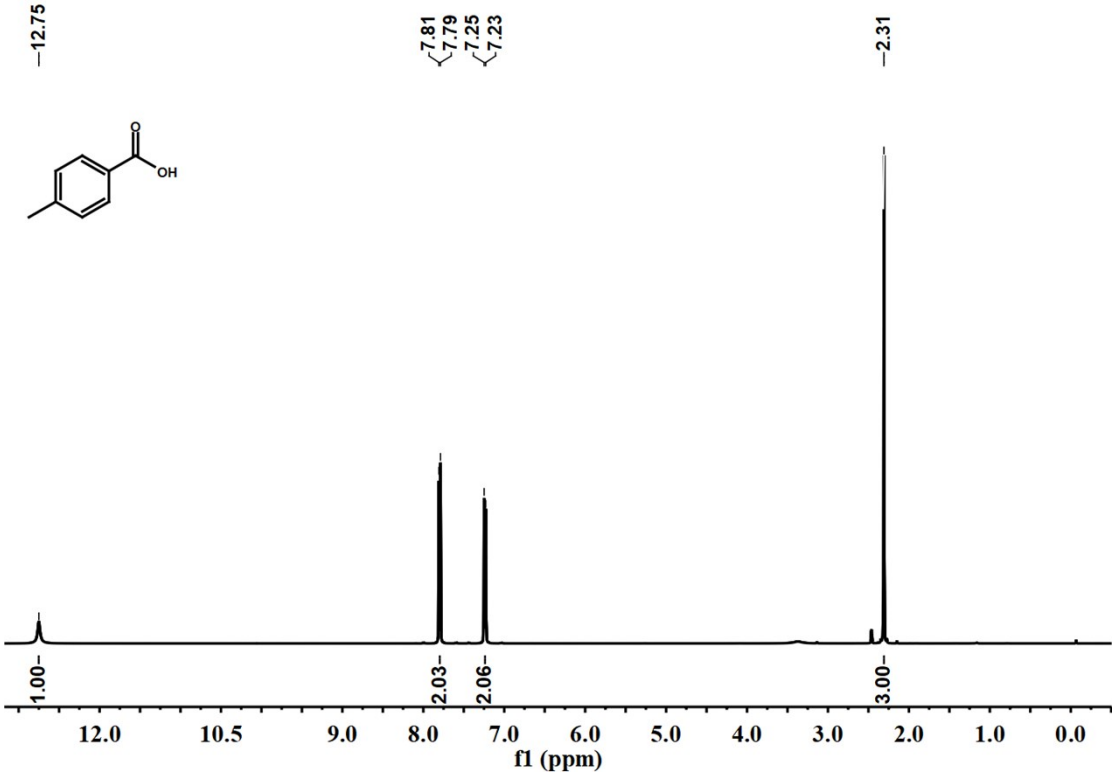
^{13}C NMR spectra of **13** (125 MHz, DMSO-d6)



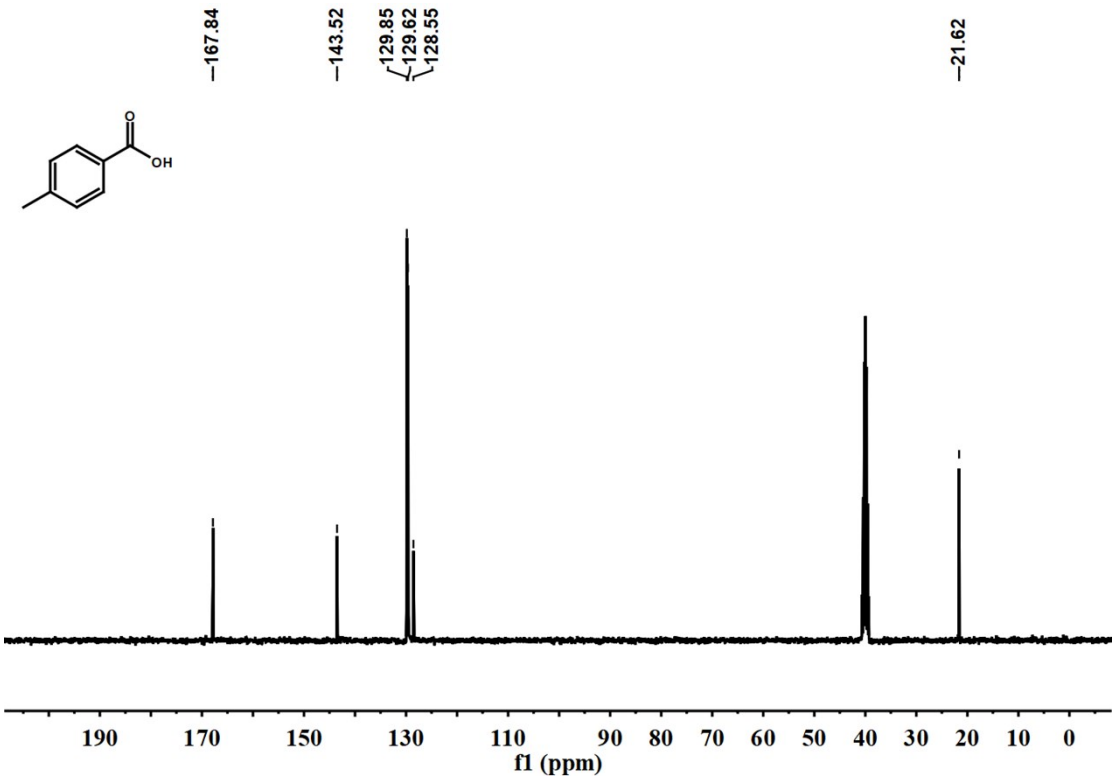
^{1}H NMR spectra of **14** (500 MHz, DMSO-d6)



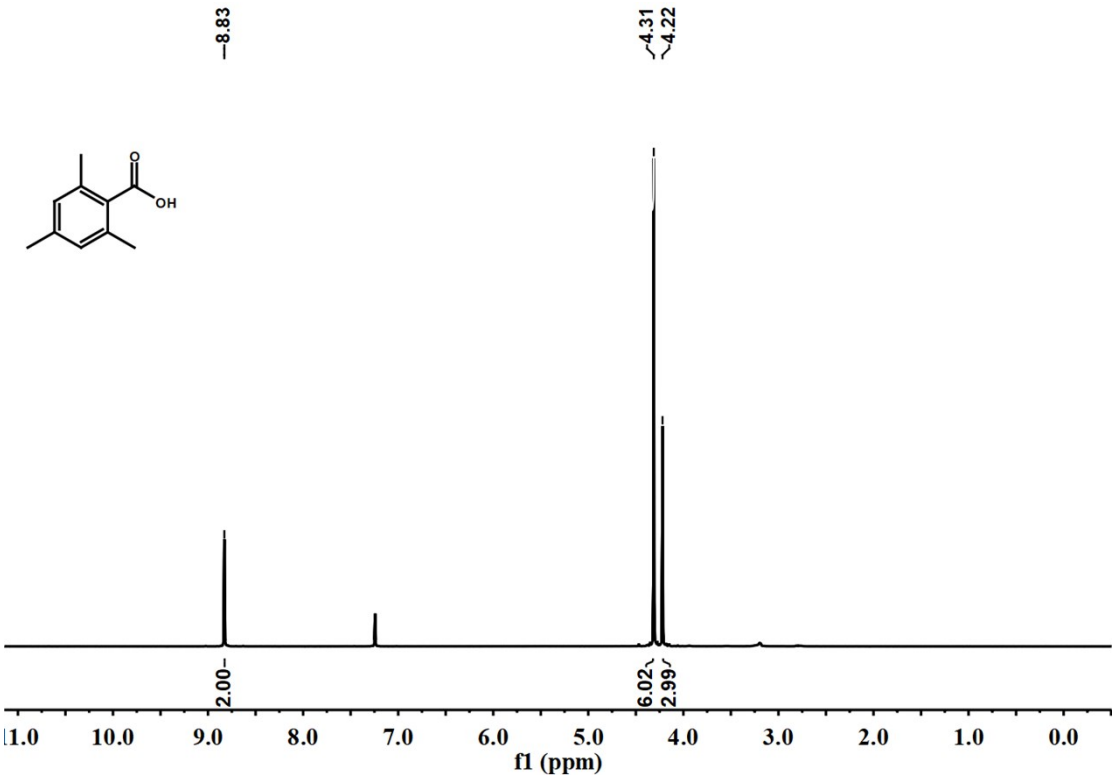
^{13}C NMR spectra of **14** (125 MHz, DMSO-d6)



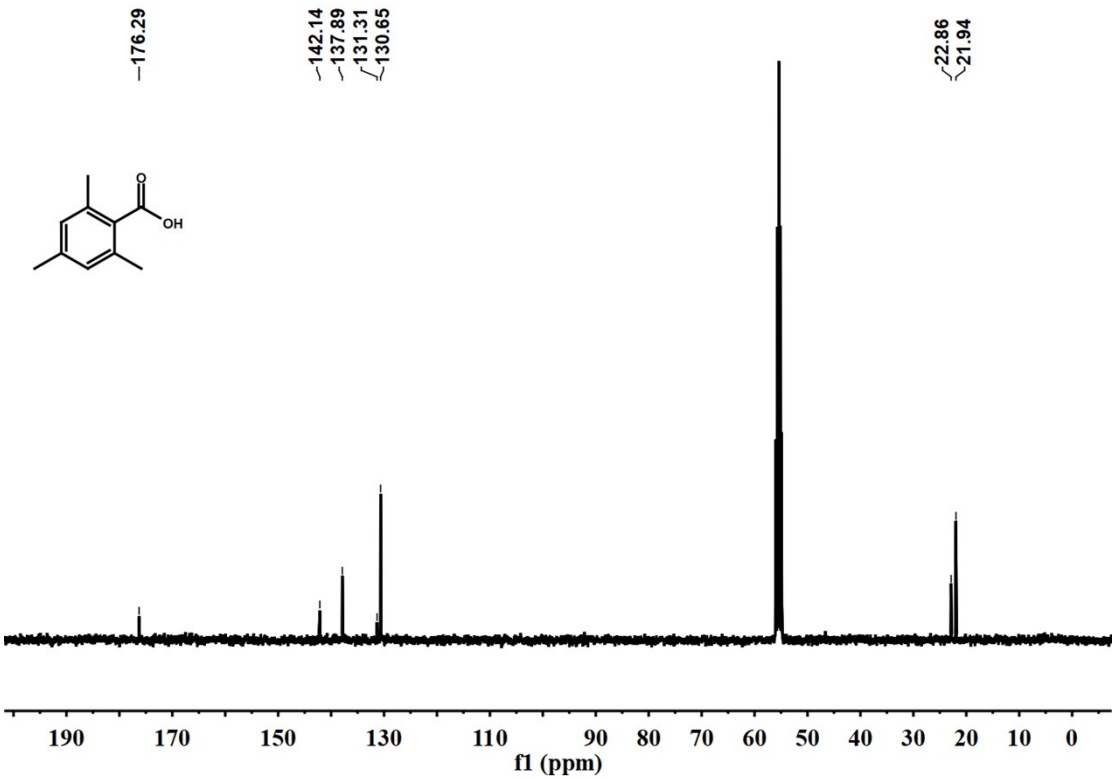
^{1}H NMR spectra of **15** (500 MHz, DMSO-d6)



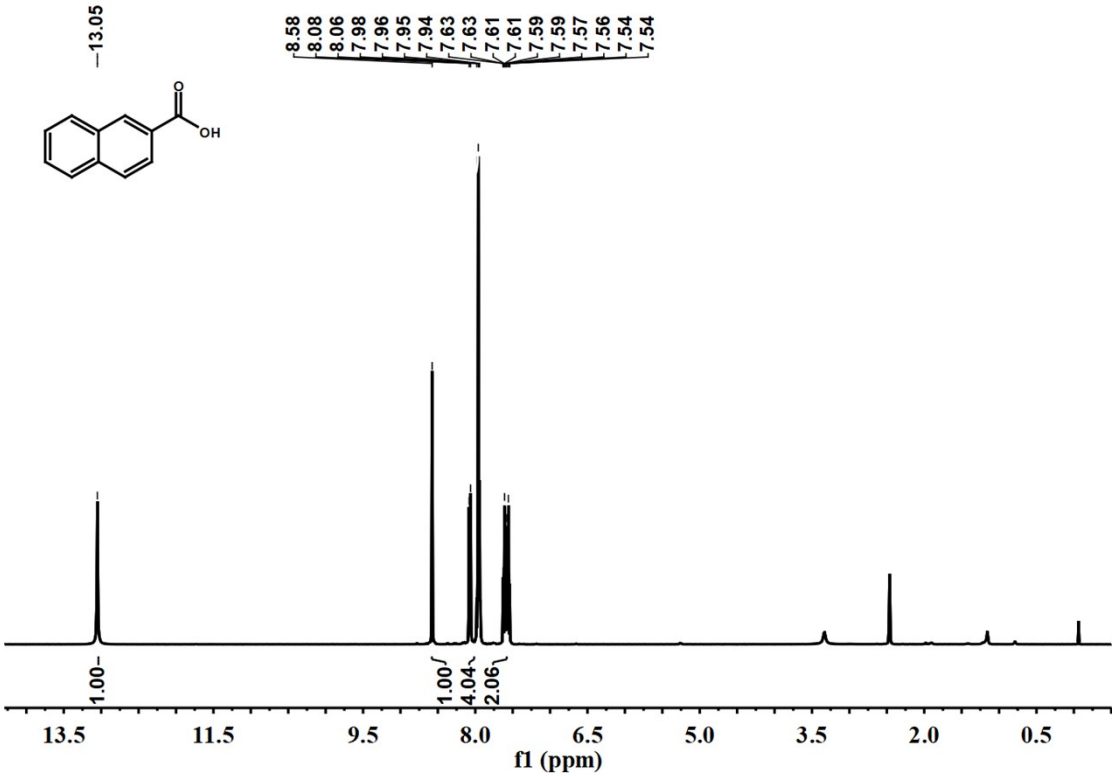
^{13}C NMR spectra of **15** (125 MHz, DMSO-d6)



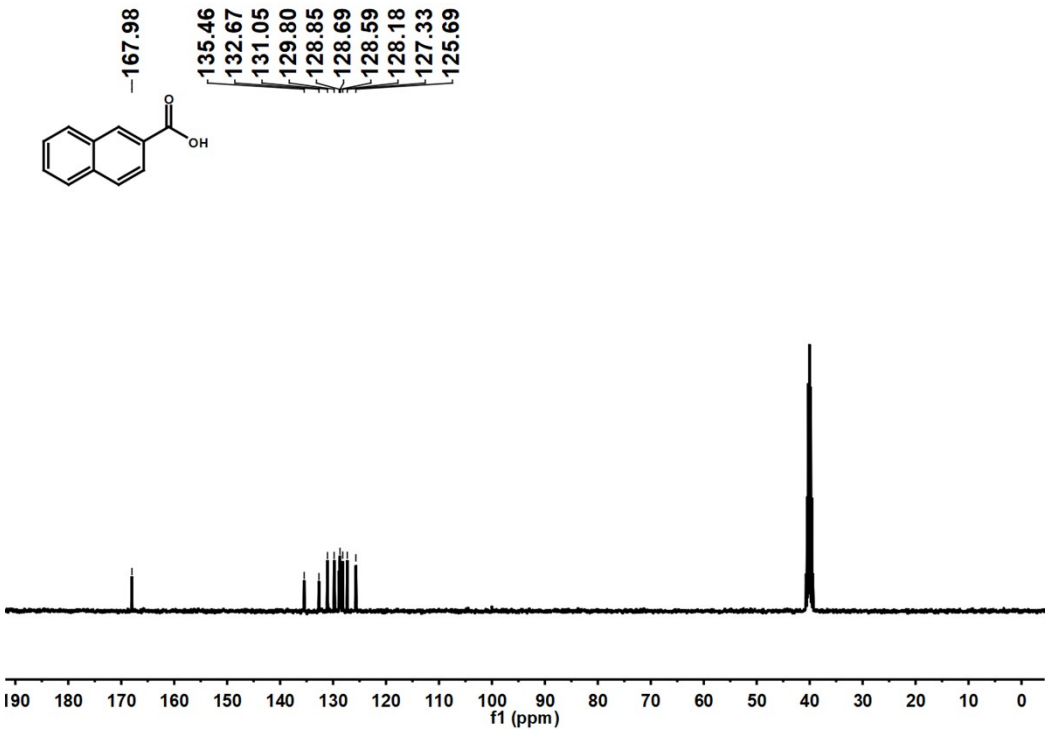
^{1}H NMR spectra of **16** (500 MHz, $CDCl_3$)



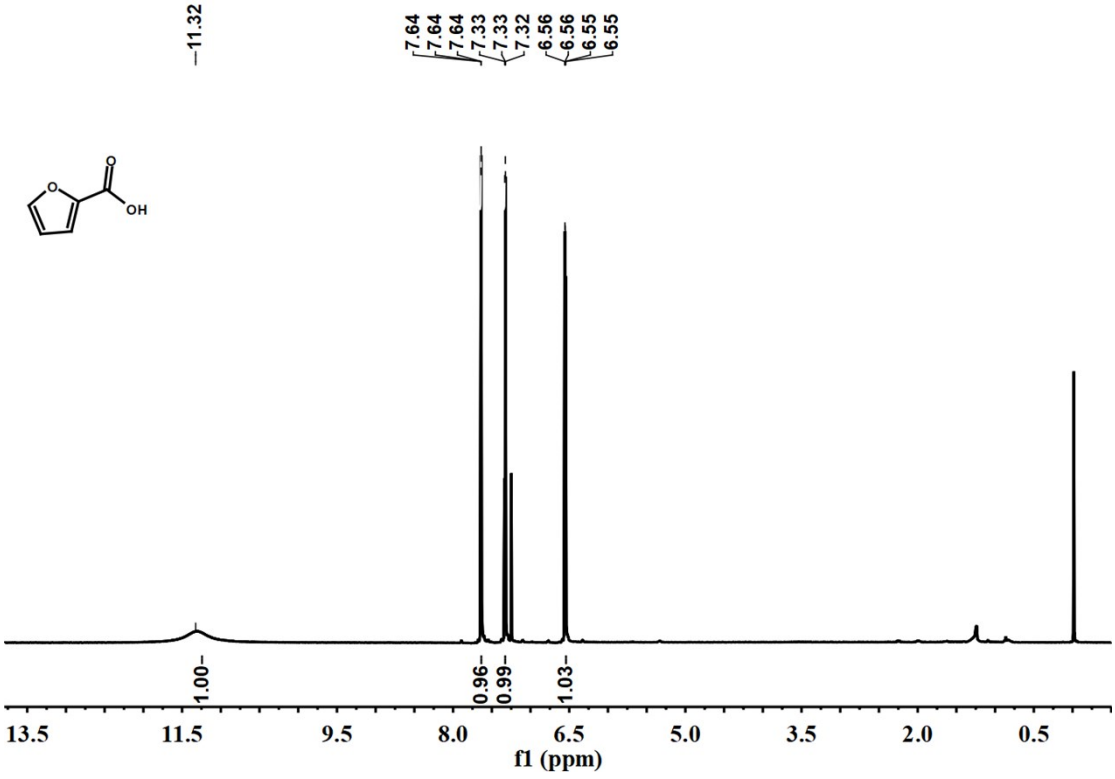
^{13}C NMR spectra of **16** (125 MHz, $CDCl_3$)



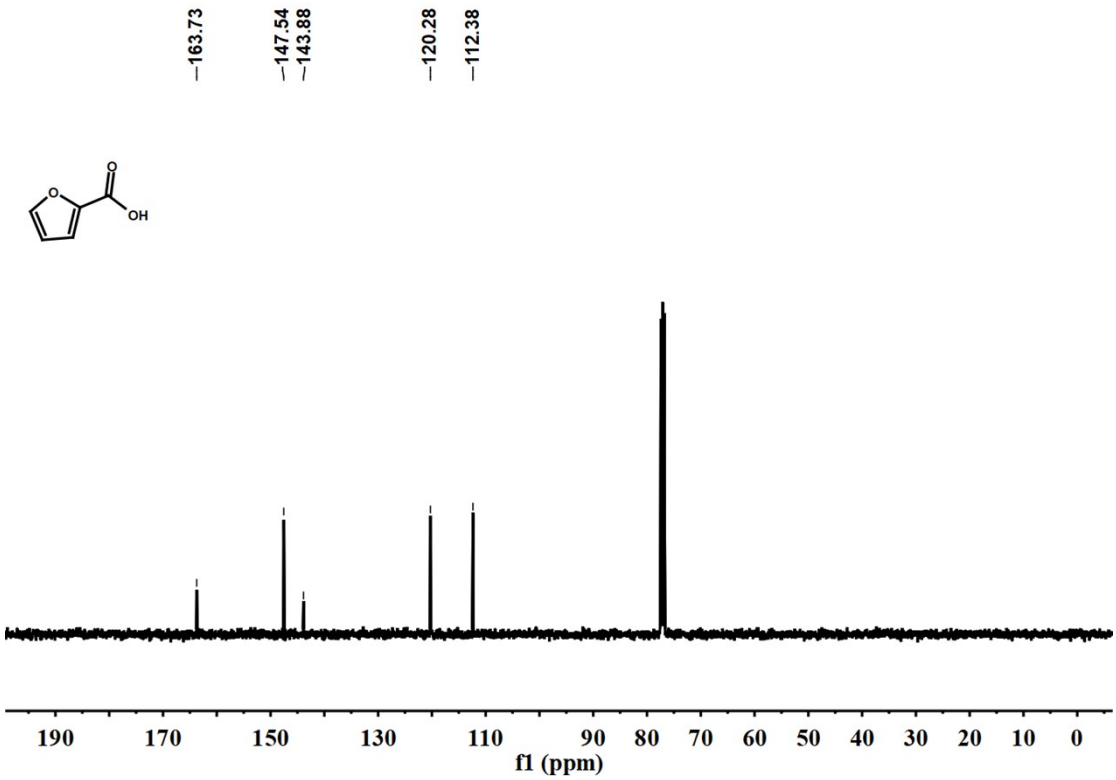
^{1}H NMR spectra of **17** (500 MHz, DMSO-d6)



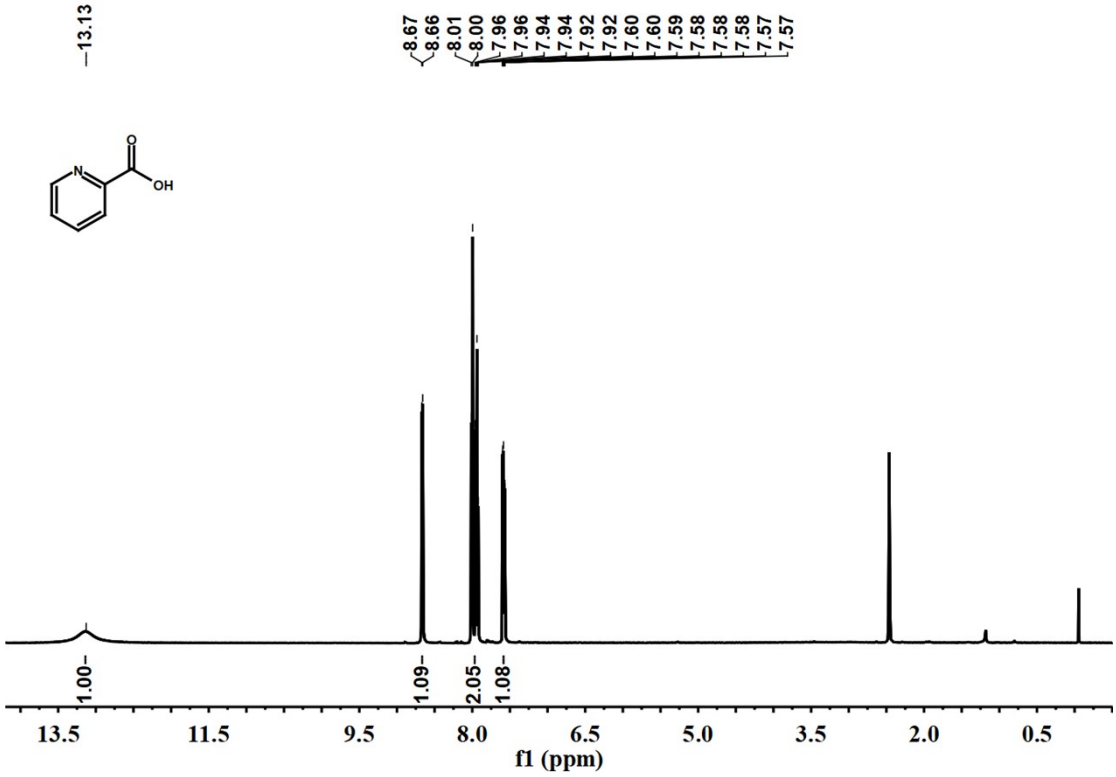
^{13}C NMR spectra of **17** (125 MHz, $CDCl_3$)



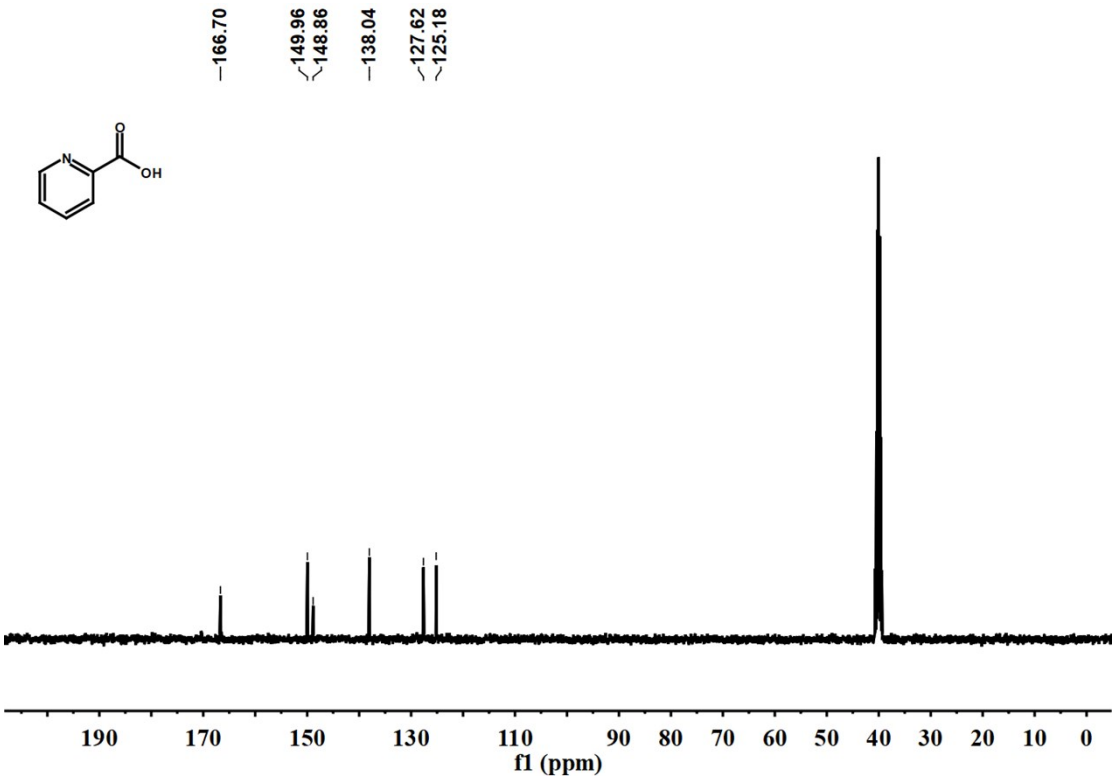
^{1}H NMR spectra of **18** (500 MHz, $CDCl_3$)



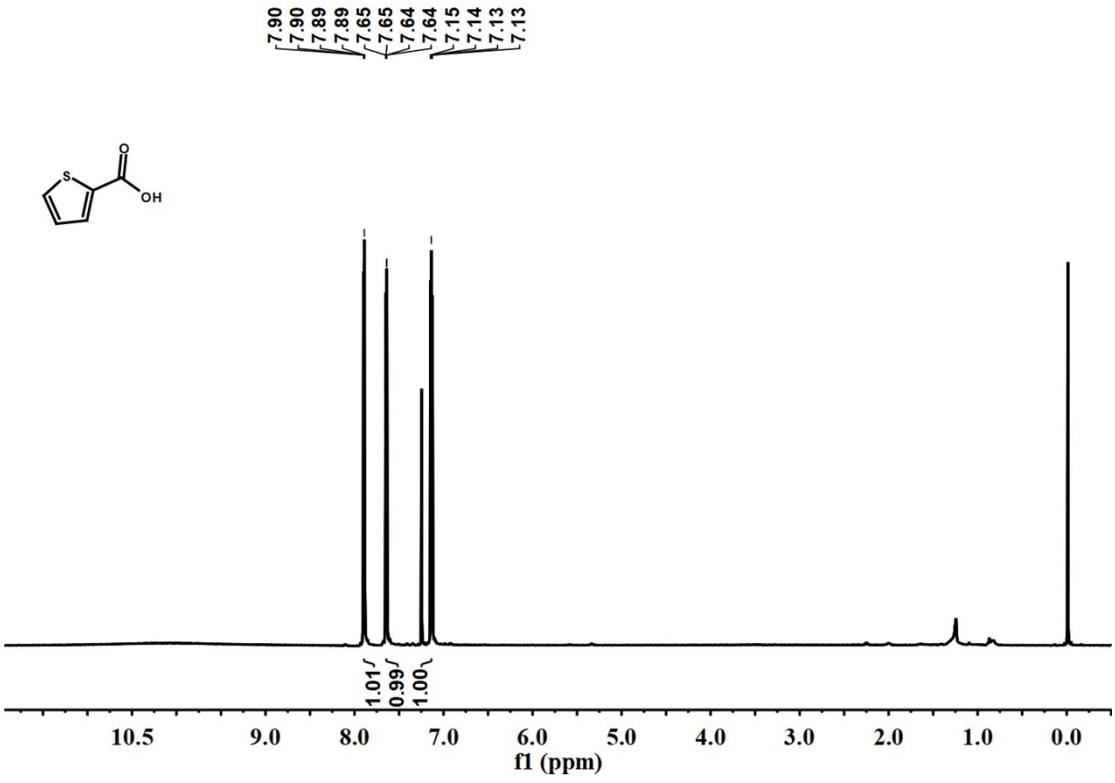
^{13}C NMR spectra of **18** (125 MHz, $CDCl_3$)



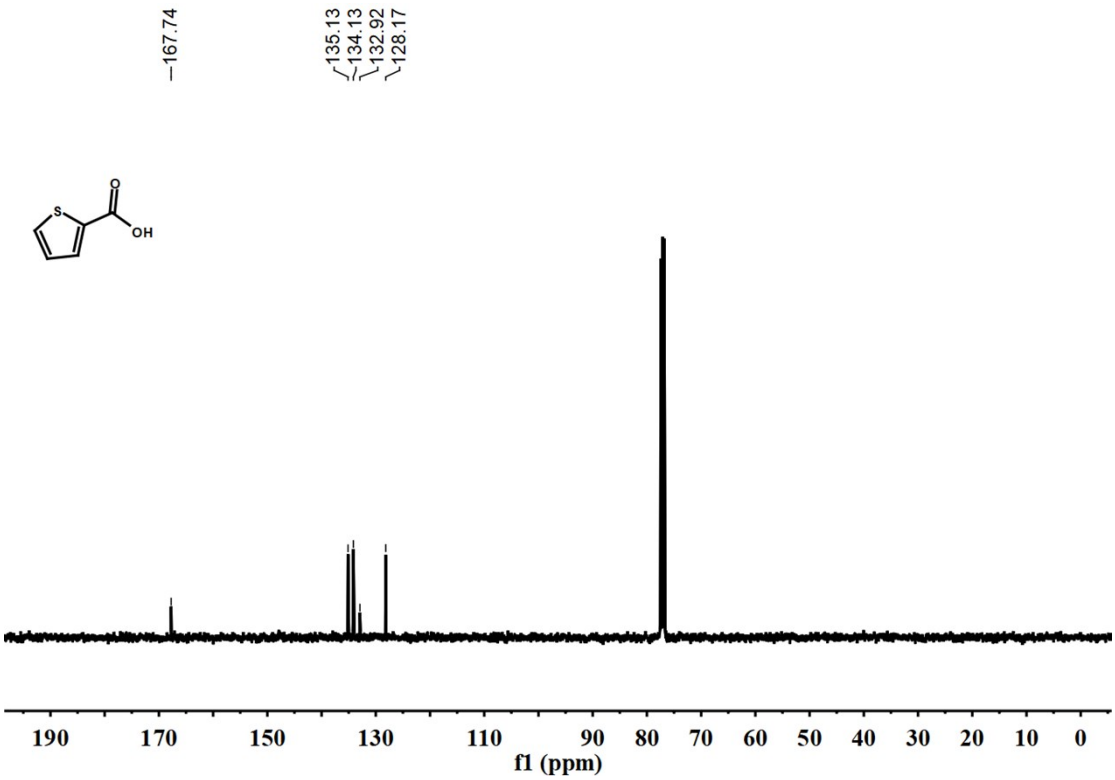
^{1}H NMR spectra of **19** (500 MHz, DMSO-d6)



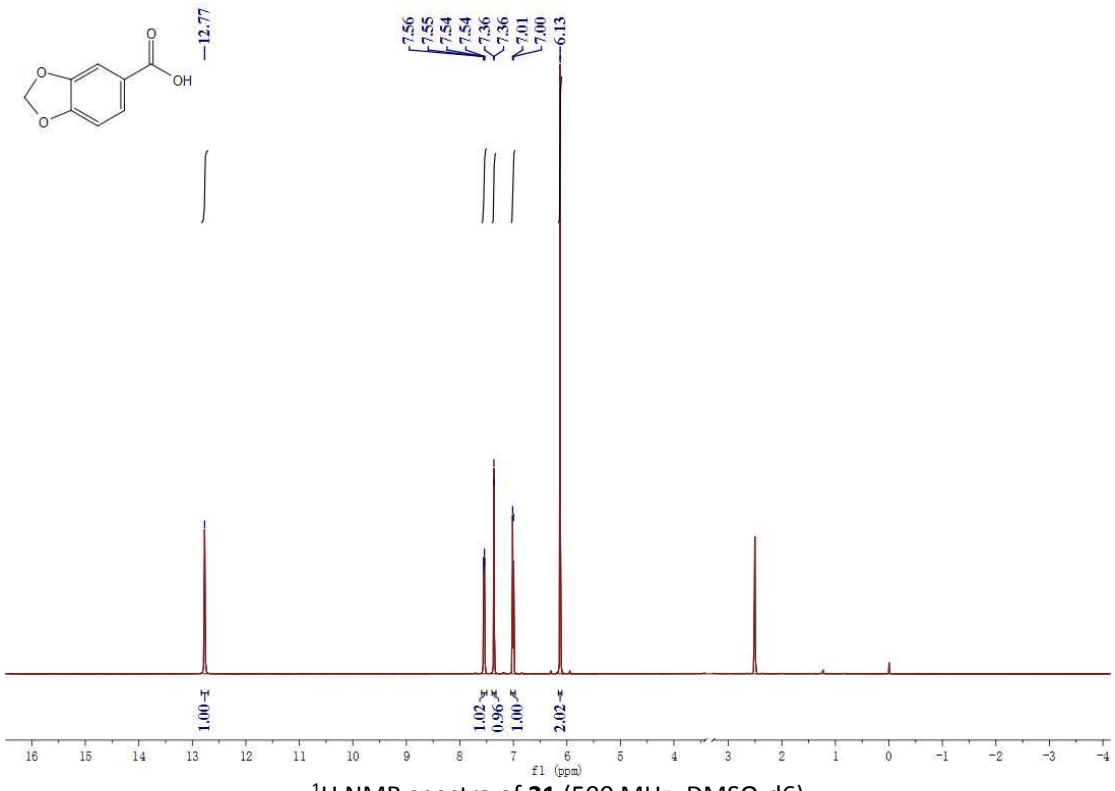
^{13}C NMR spectra of **19** (125 MHz, DMSO-d6)



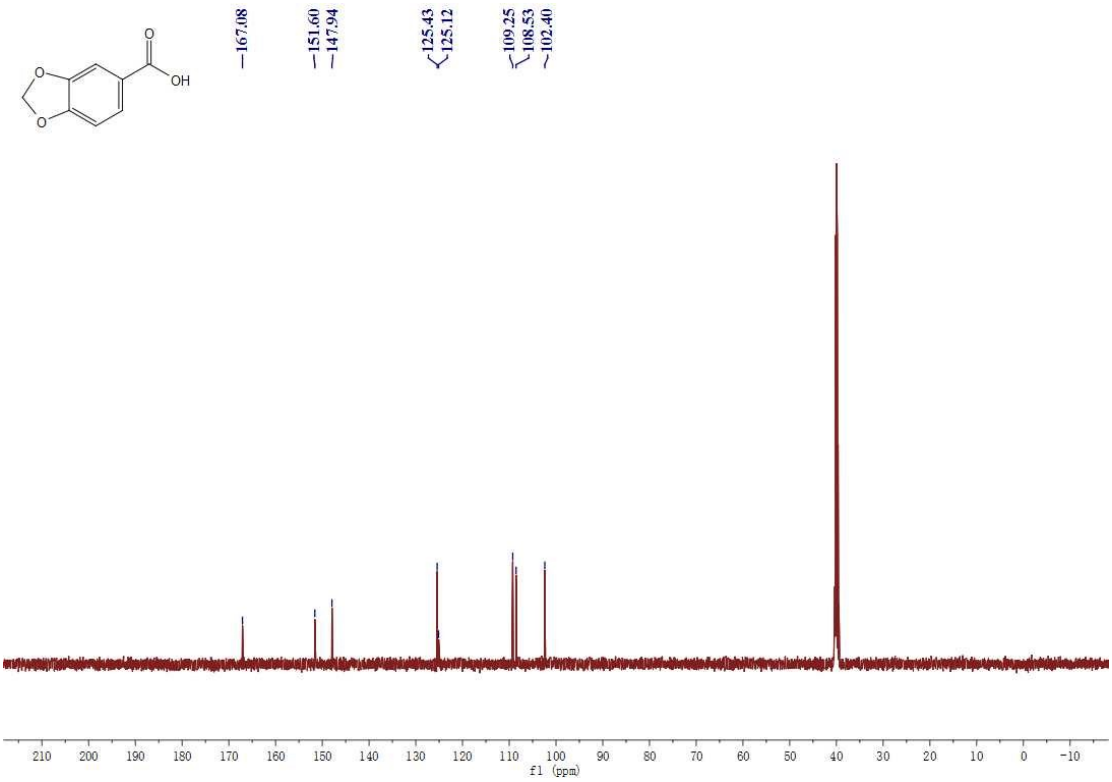
^{1}H NMR spectra of **20** (500 MHz, $CDCl_3$)



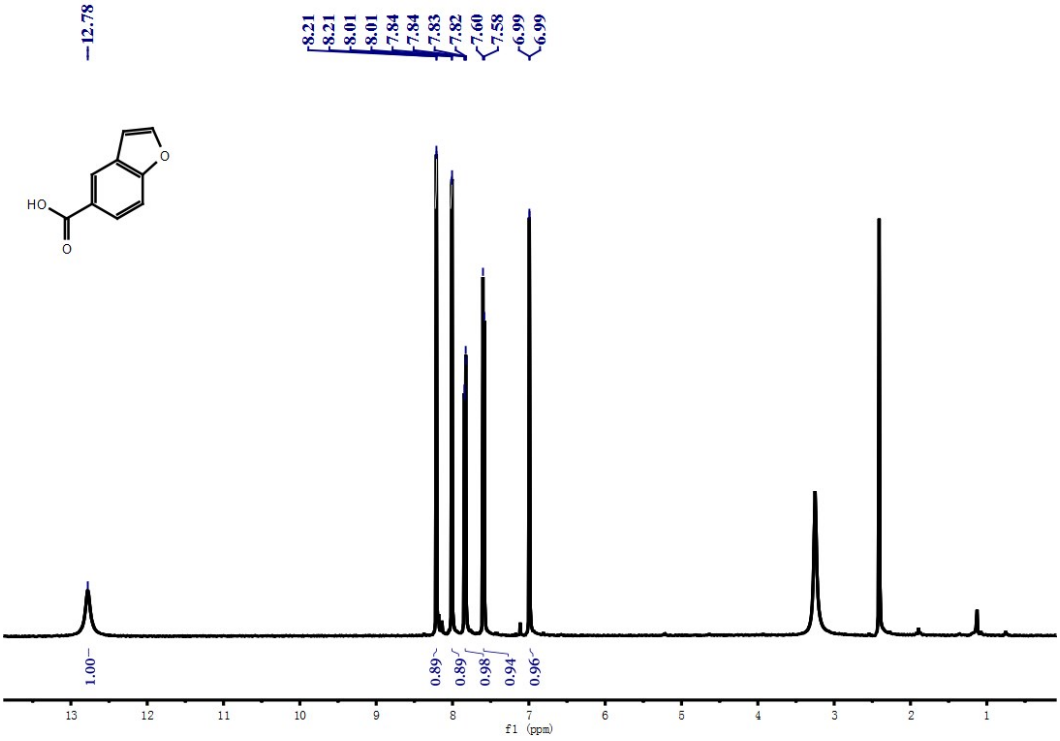
^{13}C NMR spectra of **20** (125 MHz, $CDCl_3$)



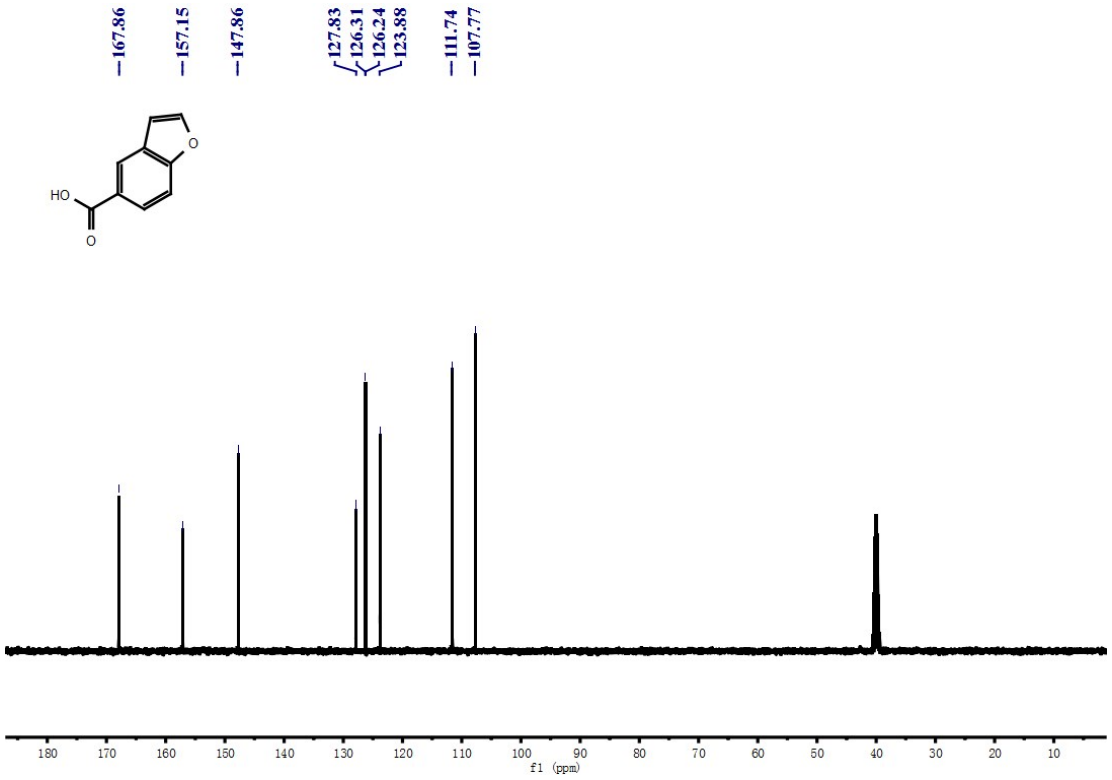
^{1}H NMR spectra of **21** (500 MHz, DMSO-d6)



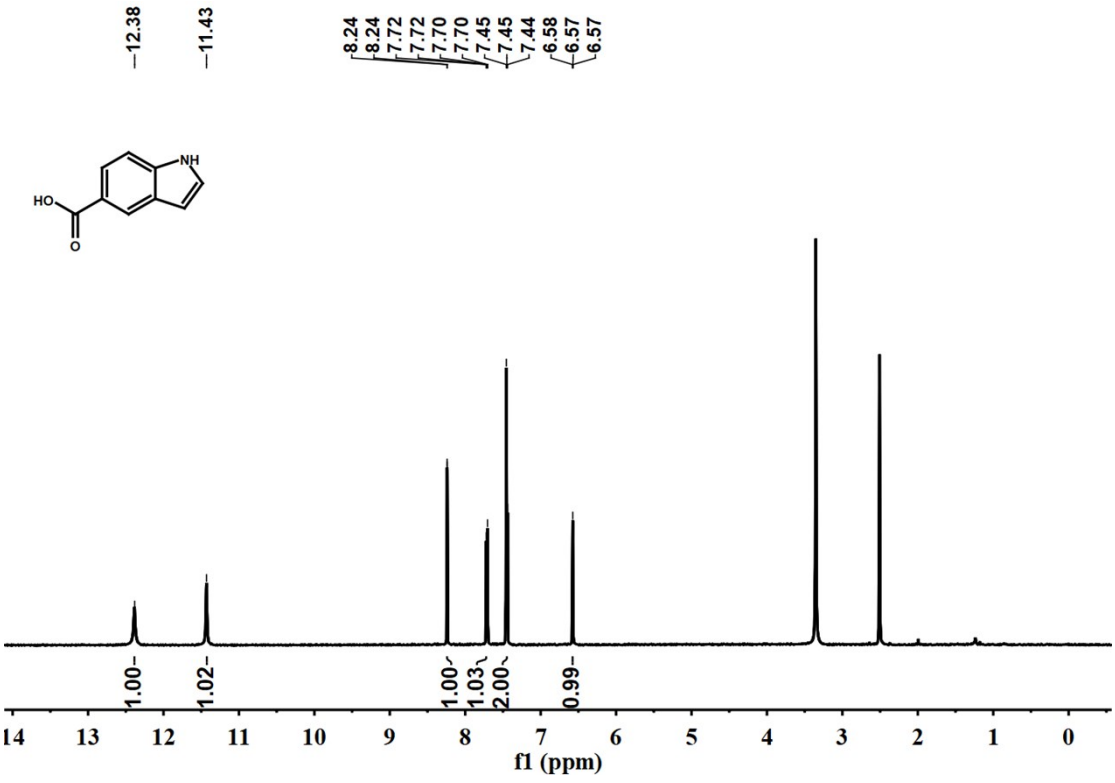
^{13}C NMR spectra of **21** (125 MHz, DMSO-d6)



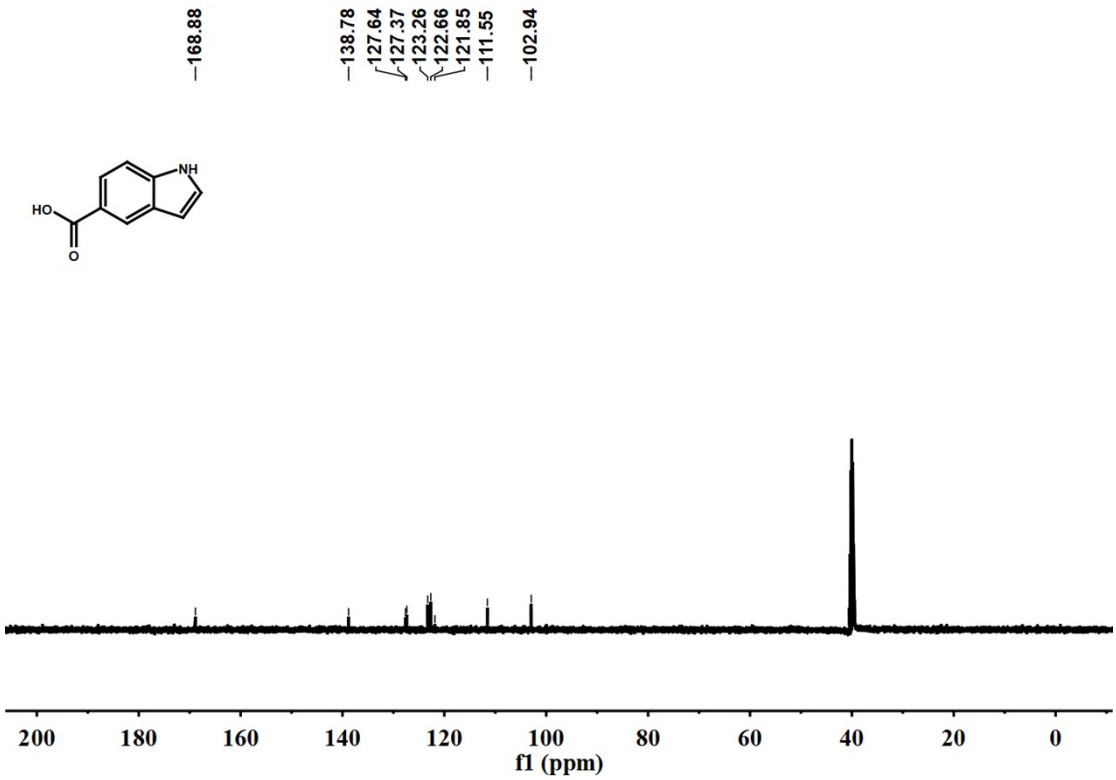
^{1}H NMR spectra of **22** (500 MHz, DMSO-d6)



^{13}C NMR spectra of **22** (125 MHz, DMSO-d6)



^{1}H NMR spectra of **23** (500 MHz, DMSO-d6)



^{13}C NMR spectra of **23** (125 MHz, DMSO-d6)

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