Supporting Information

Photoredox-Catalyzed Generation of Sulfamyl Radicals: Sulfonamidation of Enol Silyl Ether with Chlorosulfonamide

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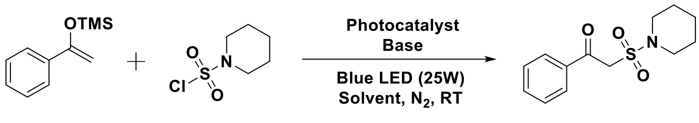
Contents

1. Reaction Optimization

Table S1. Screening of the Reaction Conditions[a]



1a 2a 3a

Entry	PC (mol%)	Base (mol%)	Ratio (**1a** : **2a**)	Solvent (mL)	Yield (%)[b]
1	$Ru(bpy)_3Cl_2$ (2)	K_2CO_3 (100)	2:1	DMSO (2)	NR
2	$Ru(bpy)_3Cl_2$ (2)	K_2CO_3 (100)	2:1	DMF (2)	NR
3	$Ru(bpy)_3Cl_2$ (2)	K_2CO_3 (100)	2:1	DCE (2)	Trace
4	$Ru(bpy)_3Cl_2$ (2)	K_2CO_3 (100)	2:1	Acetone (2)	NR
5	$Ru(bpy)_3Cl_2$ (2)	K_2CO_3 (100)	2:1	Dioxane (2)	NR
6	$Ru(bpy)_3Cl_2$ (2)	K_2CO_3 (100)	2:1	CH_3CN (2)	23
7[c]	$Ru(bpy)_3Cl_2$ (2)	K_2CO_3 (100)	2:1	CH_3CN (2)	NR
8	$Ru(bpy)_3Cl_2$ (2)	——	2:1	CH_3CN (2)	NR
9	——	K_2CO_3 (100)	2:1	CH_3CN (2)	NR
10	*fac*-$Ir(ppy)_3$ (2)	K_2CO_3 (100)	2:1	CH_3CN (2)	17
11	Eosin Y (2)	K_2CO_3 (100)	2:1	CH_3CN (2)	12
12	Rhodamine B (2)	K_2CO_3 (100)	2:1	CH_3CN (2)	NR
13	Basic Red 1 (2)	K_2CO_3 (100)	2:1	CH_3CN (2)	NR
14	$Ru(bpy)_3Cl_2$ (2)	K_2CO_3 (100)	3:1	CH_3CN (2)	26
15	$Ru(bpy)_3Cl_2$ (2)	K_2CO_3 (100)	4:1	CH_3CN (2)	33
16	$Ru(bpy)_3Cl_2$ (2)	K_2CO_3 (100)	5:1	CH_3CN (2)	45
17	$Ru(bpy)_3Cl_2$ (2)	Et_3N (100)	5:1	CH_3CN (2)	67
18	$Ru(bpy)_3Cl_2$ (2)	Bpy (100)	5:1	CH_3CN (2)	NR
19	$Ru(bpy)_3Cl_2$ (2)	CH_3COOK (100)	5:1	CH_3CN (2)	25
20	$Ru(bpy)_3Cl_2$ (2)	CsF (100)	5:1	CH_3CN (2)	19
21	$Ru(bpy)_3Cl_2$ (2)	DABCO	5:1	CH_3CN (2)	48
22	$Ru(bpy)_3Cl_2$ (2)	DIPEA (100)	5:1	CH_3CN (2)	63
23	$Ru(bpy)_3Cl_2$ (2)	Et_3N (50)	5:1	CH_3CN (2)	45
24	$Ru(bpy)_3Cl_2$ (2)	Et_3N (200)	5:1	CH_3CN (2)	53
25	$Ru(bpy)_3Cl_2$ (2)	Et_3N (100)	5:1	CH_3CN (1)	53
26	$Ru(bpy)_3Cl_2$ (2)	Et_3N (100)	5:1	CH_3CN (1.5)	61
27	$Ru(bpy)_3Cl_2$ (2)	Et_3N (100)	5:1	CH_3CN (3)	60
28	$Ru(bpy)_3Cl_2$ (3)	Et_3N (100)	5:1	CH_3CN (2)	75
29	$Ru(bpy)_3Cl_2$ (4)	Et_3N (100)	5:1	CH_3CN (2)	90(86[d])
30[e]	$Ru(bpy)_3Cl_2$ (4)	Et_3N (100)	5:1	CH_3CN (2)	78
31[f]	$Ru(bpy)_3Cl_2$ (4)	Et_3N (100)	5:1	CH_3CN (2)	91
32[g]	$Ru(bpy)_3Cl_2$ (4)	Et_3N (100)	5:1	CH_3CN (2)	10
33[h]	$Ru(bpy)_3Cl_2$ (4)	Et_3N (100)	5:1	CH_3CN (2)	68

[a] Reaction conditions: **1a**, **2a** (0.2 mmol), PC, base, CH_3CN, blue LED (25 W), N_2, rt, 24 h; [b] HPLC yield; [c] No light; [d] Yield based on **2a**; [e] 16 h; [f] 48 h; [g] 5 W blue LED; [h] 15 W blue LED.

2. Quantum Yield Measurement

A screw-top 1.0 cm quartz cuvette was charged with $Ru(bpy)_3Cl_2$ (4.0 mol%, 0.008 mmol), **1a** (5.0 equiv, 1.0 mmol), **2a** (1.0 equiv, 0.2 mmol), and 2mL CH_3CN, degassed with N_2. The sample was stirred under 25 W blue LED for 7200 s (2 h). The yield of product was determined by HPLC to be 1.5%. FZ-A irradiatometer was used to separately measure the irradiance of the light penetrating the mixture (***I***, 3.47 μw/cm^2) and CH_3CN (***I₀***→$\boldsymbol{I_0}$, 4.78 μw/cm^2). Light exposure area (**S**) of the cuvette containing 2 ml of solution was 2 cm^2, and the wavelength of 25 W blue LED is 460 nm. The photon number was calculated by equation (**i**) and the quantum yield was determined using equation (**ii**).

$$N_{photon} = \frac{E\lambda}{hcN_A} = \frac{(I_0 - I)St\lambda}{hcN_A}$$

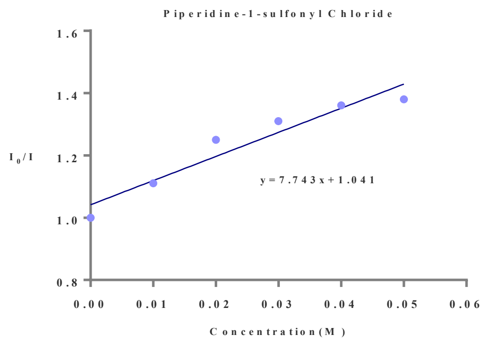
$$= \frac{(4.78 - 3.47) \times 100 \ \frac{\mu w}{cm^2} \times 2 \ cm^2 \times 7200 \ s \times 10^{-6} \times 460 \times 10^{-9} \ m}{6.626 \times 10^{-34} \ J \cdot s \times 3 \times 10^8 \ \frac{m}{s} \times 6.02 \times 10^{23} \ mol^{-1}} = 7.28\times10^{-6} \ mol \quad \textbf{(i)}$$

$$\phi = \frac{N_{product}}{N_{photon}} = \frac{0.2 \ mmol \times 1.5\% \times 10^{-3}}{7.28\times10^{-6} \ mol} = 41\% \quad \textbf{(ii)}$$

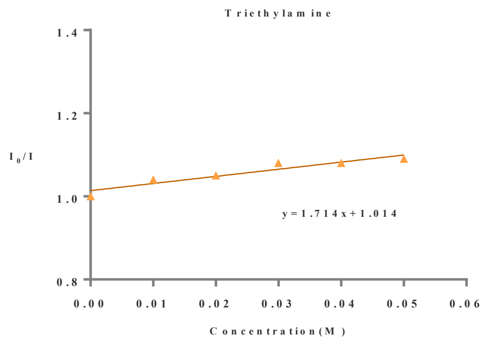
3. The Luminescence Quenching Experiment

Emission intensities were recorded using F98 Fluorospectrophotometer for all experiments. All $Ru(bpy)_3(Cl)_2$ solutions were excited at 460 nm and the emission intensity at 615 nm was observed. In a typical experiment, the CH_3CN solution of $Ru(bpy)_3(Cl)_2$ (36 μM) was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing with nitrogen for 10 min, the emission spectra of the samples were collected.

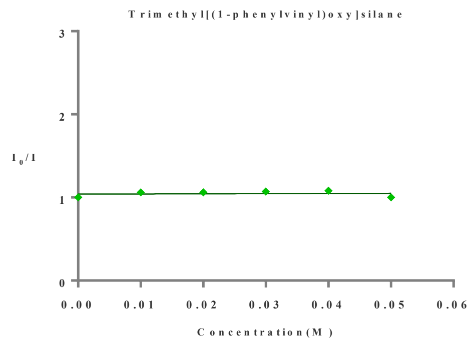
Scheme S1. $Ru(bpy)_3(Cl)_2$ Emission Quenching by Piperidine-1-sulfonyl Chloride (2a)



Scheme S2. $Ru(bpy)_3(Cl)_2$ Emission Quenching by Triethylamine

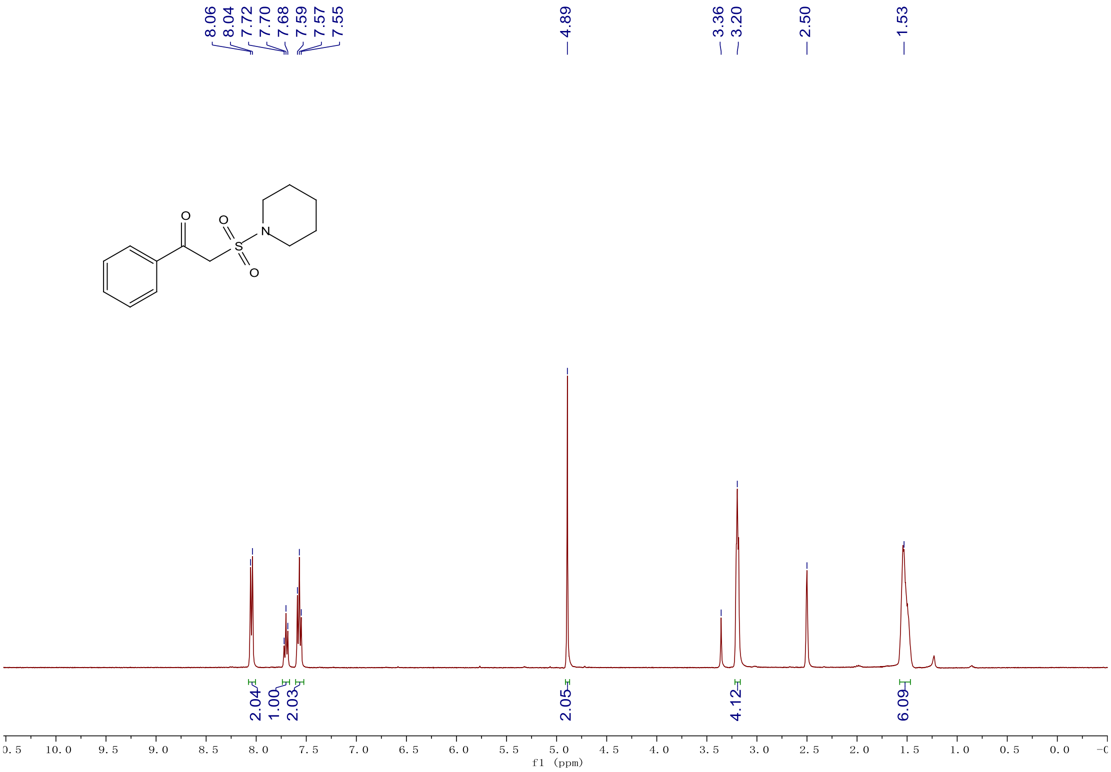


Scheme S3. $Ru(bpy)_3(Cl)_2$ Emission Quenching by Trimethyl[(1-phenylvinyl) oxy] silane (1a)

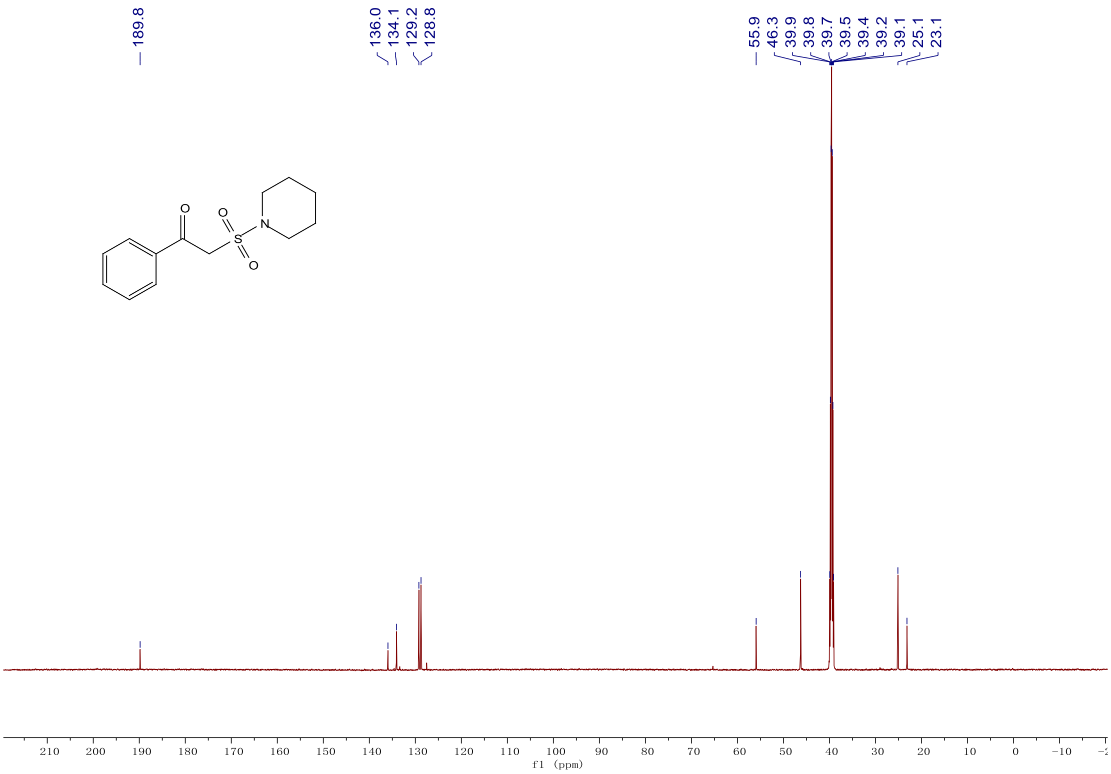


4. NMR Spectra

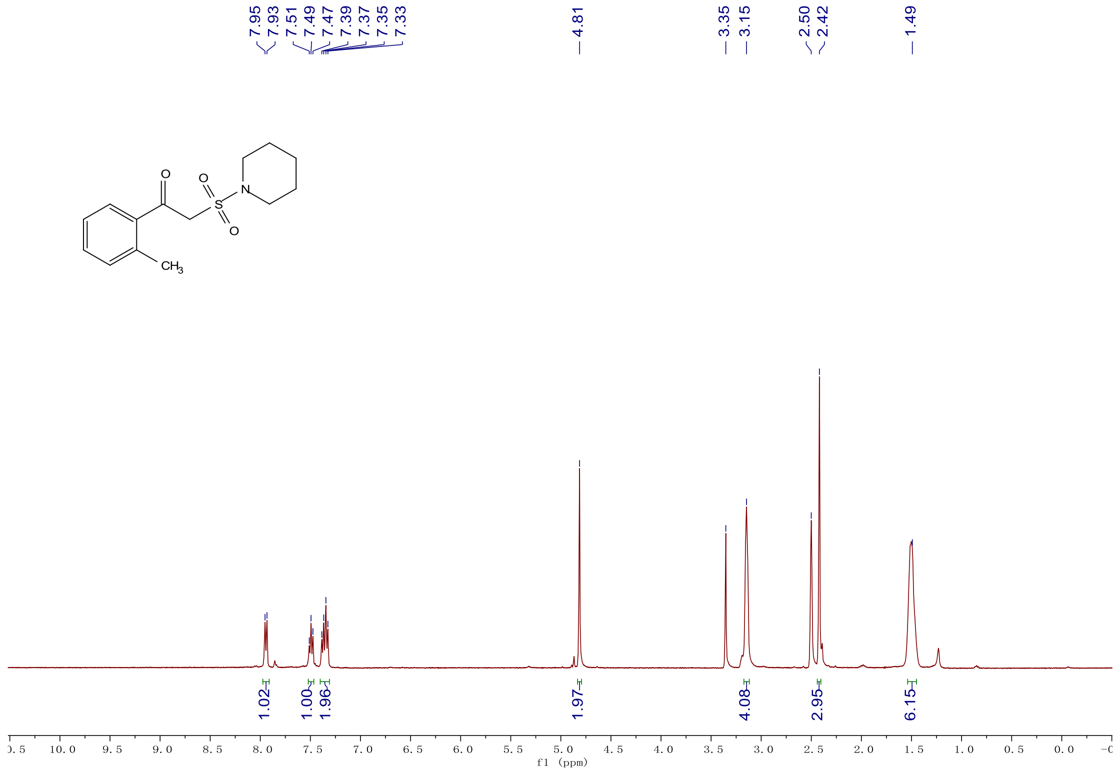
^{1}H NMR (400 MHz, DMSO-d_6) of **3a**



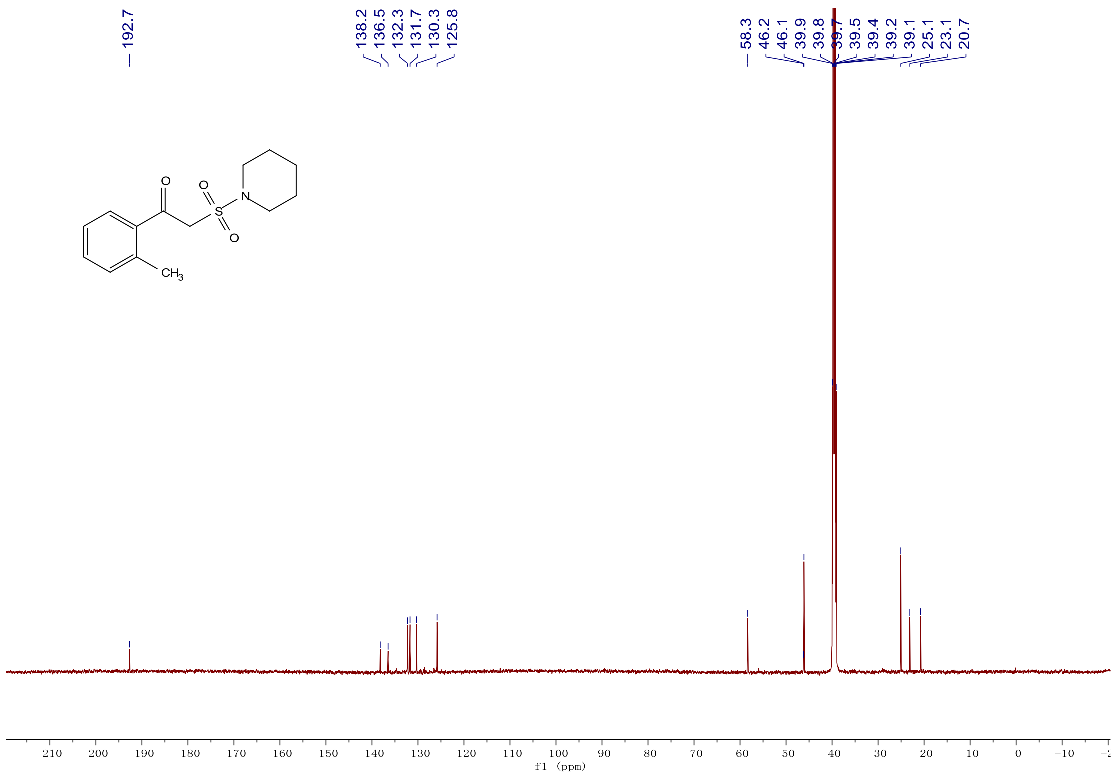
^{13}C NMR (150 MHz, DMSO-d_6) of **3a**



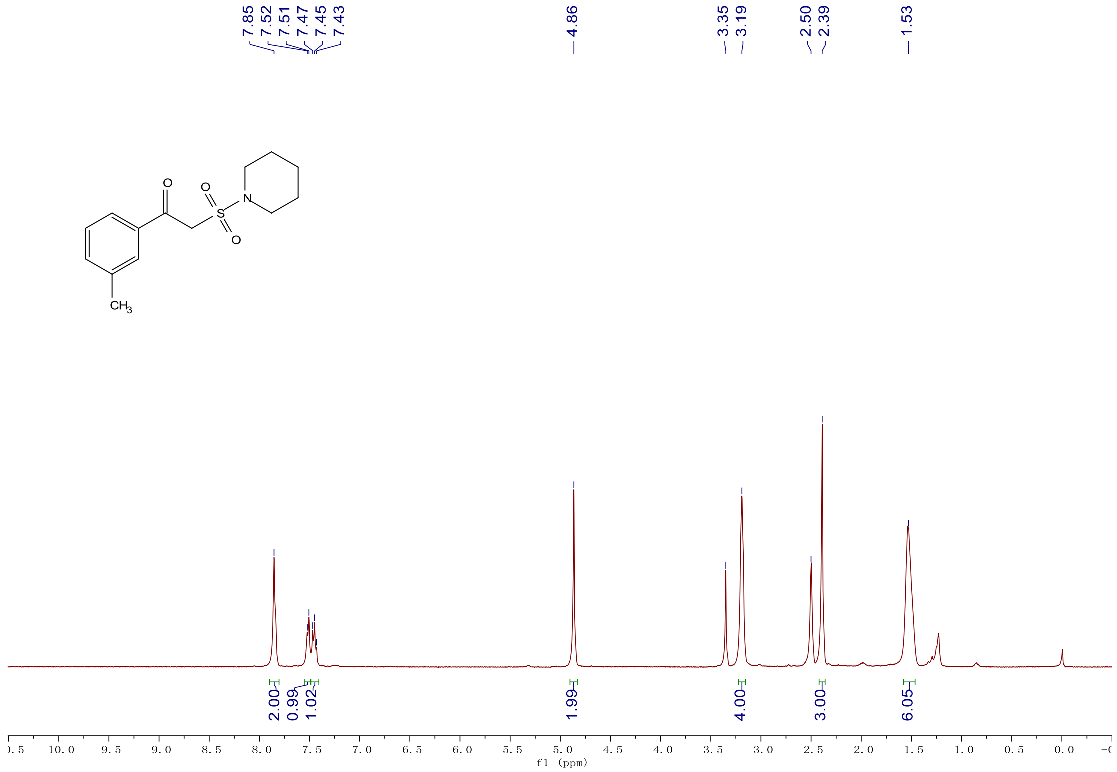
^{1}H NMR (400 MHz, DMSO-d_6) of **3b**



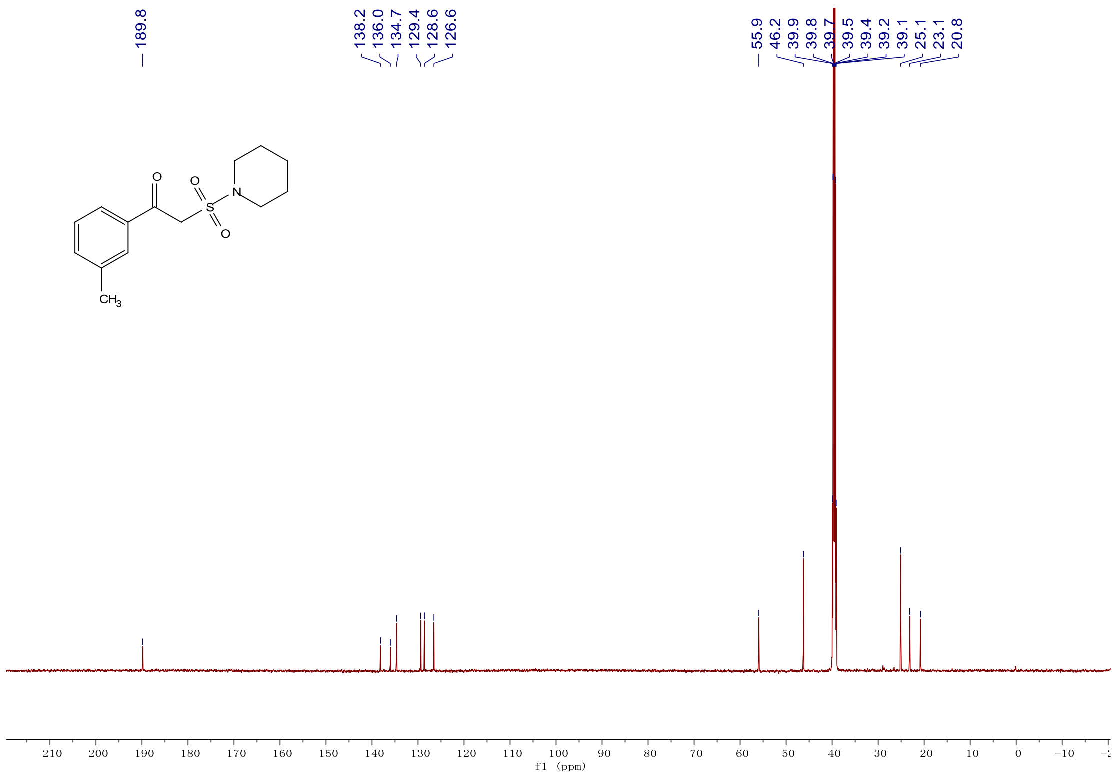
^{13}C NMR (150 MHz, DMSO-d_6) of **3b**



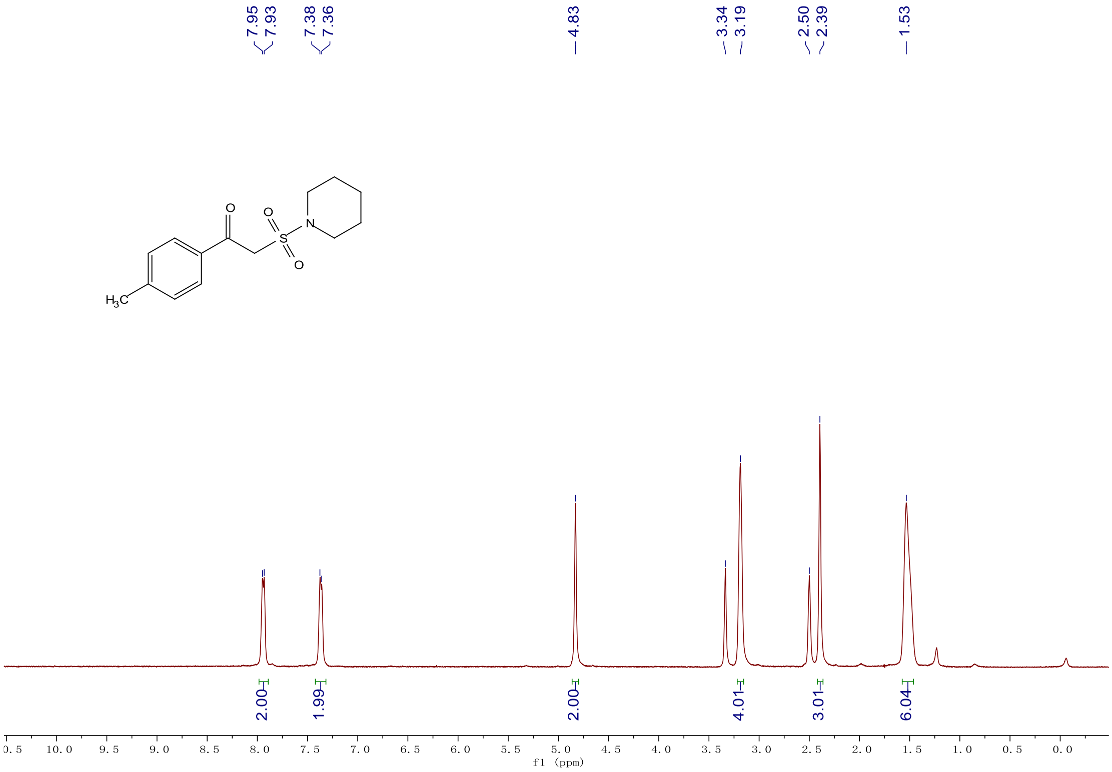
^{1}H NMR (400 MHz, DMSO-d_6) of **3c**



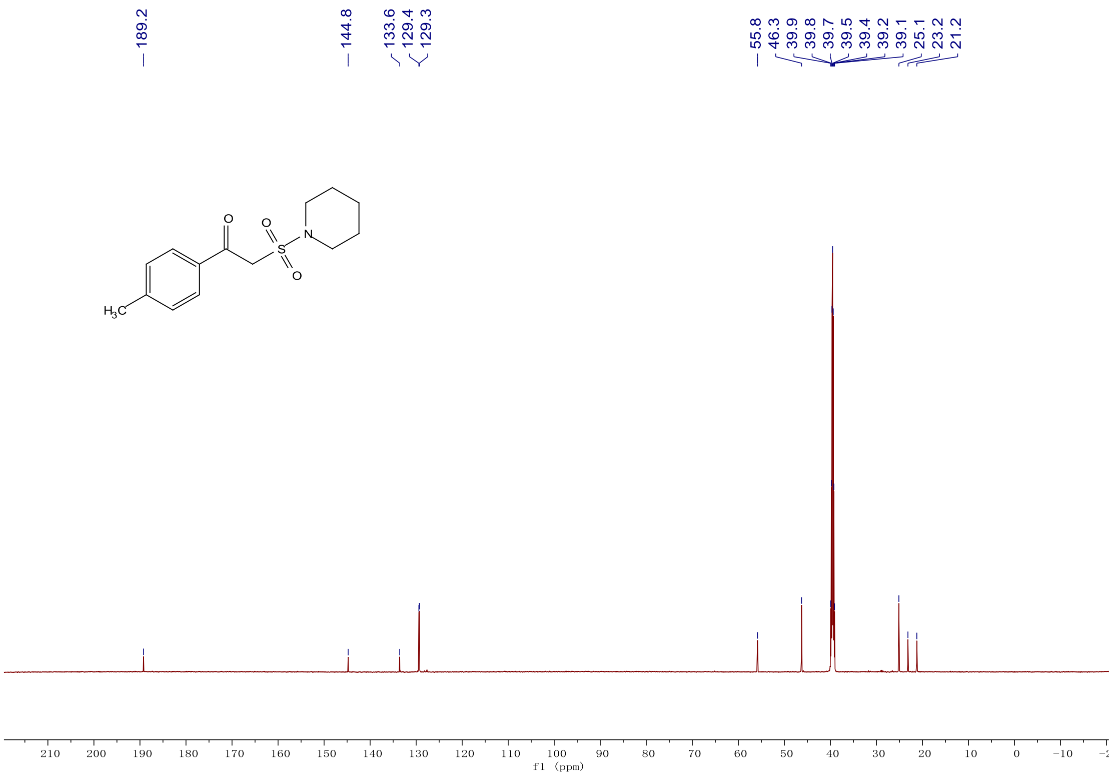
^{13}C NMR (150 MHz, DMSO-d_6) of **3c**



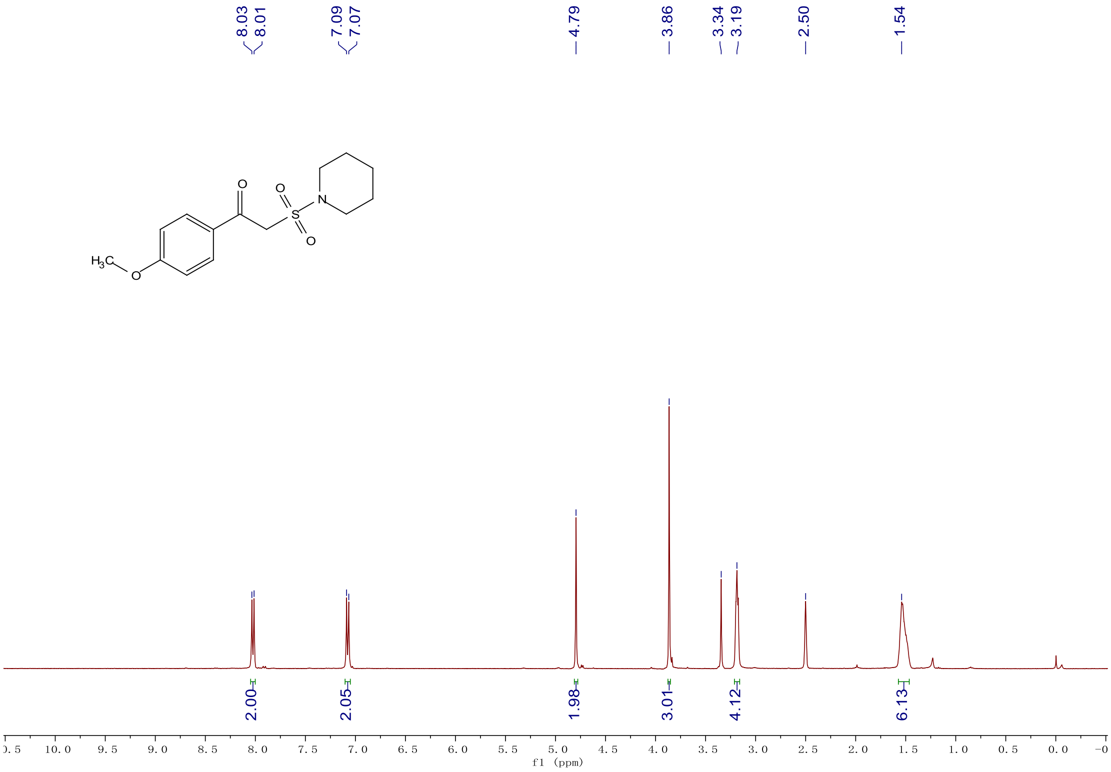
^{1}H NMR (400 MHz, DMSO-d_6) of **3d**



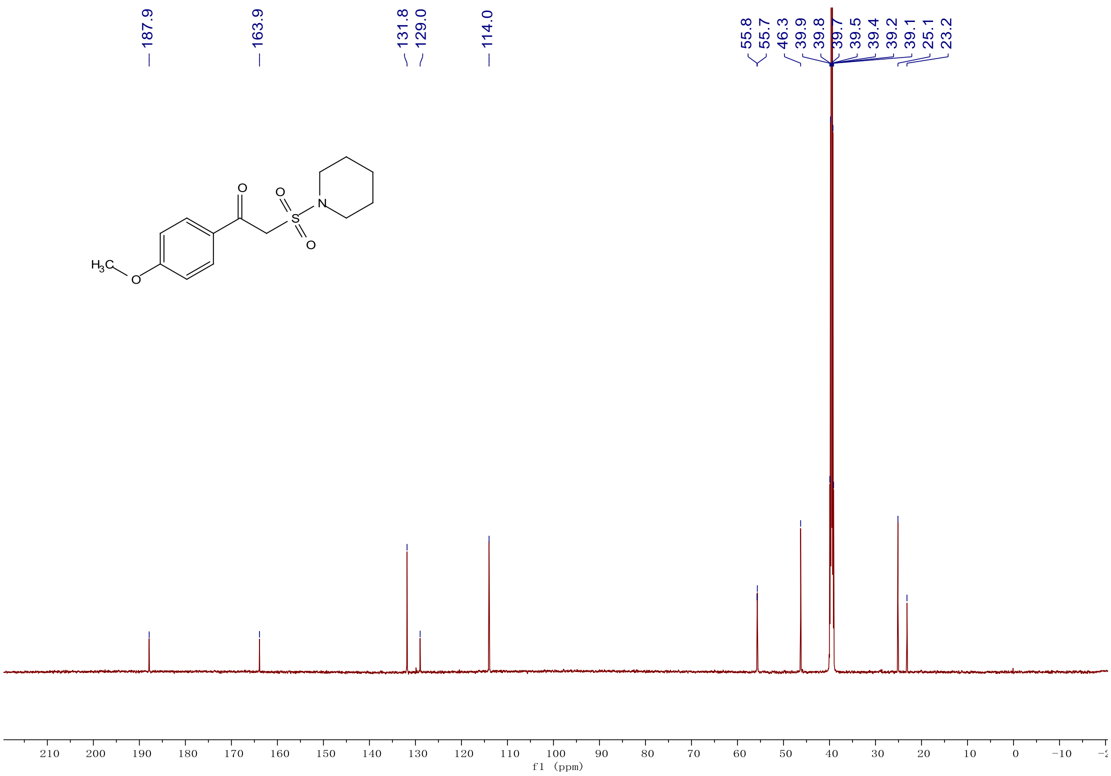
^{13}C NMR (150 MHz, DMSO-d_6) of **3d**



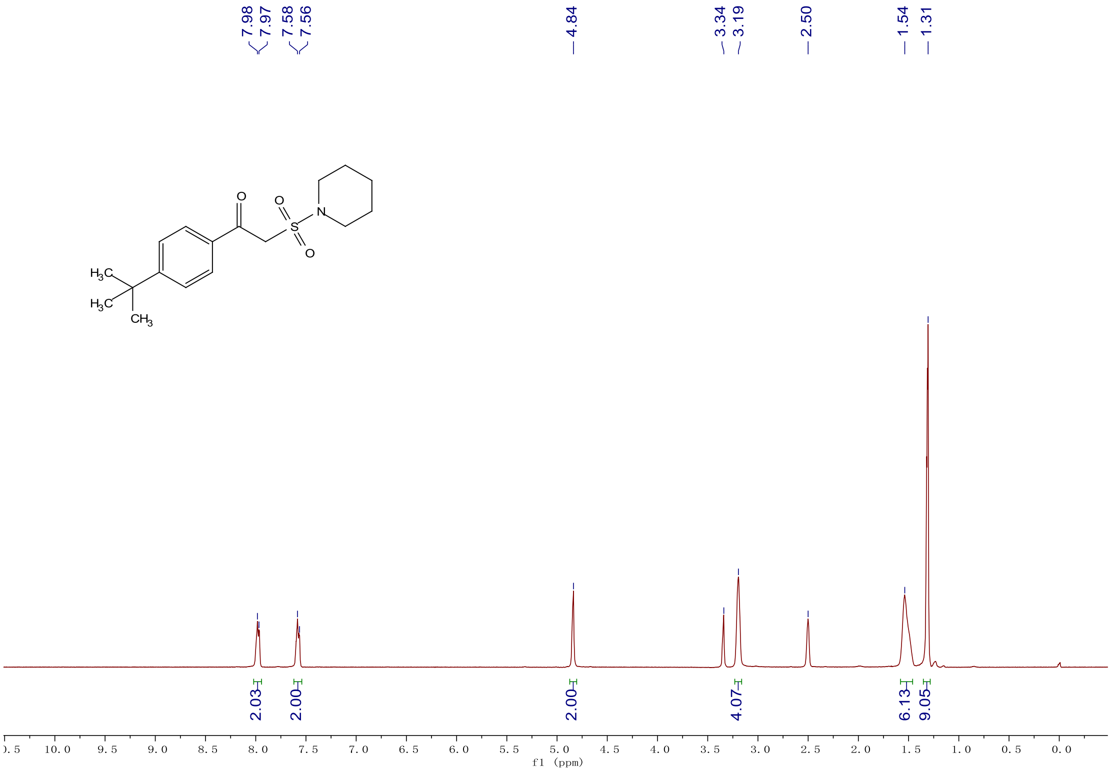
^{1}**H NMR** (400 MHz, DMSO-d_6) of **3e**



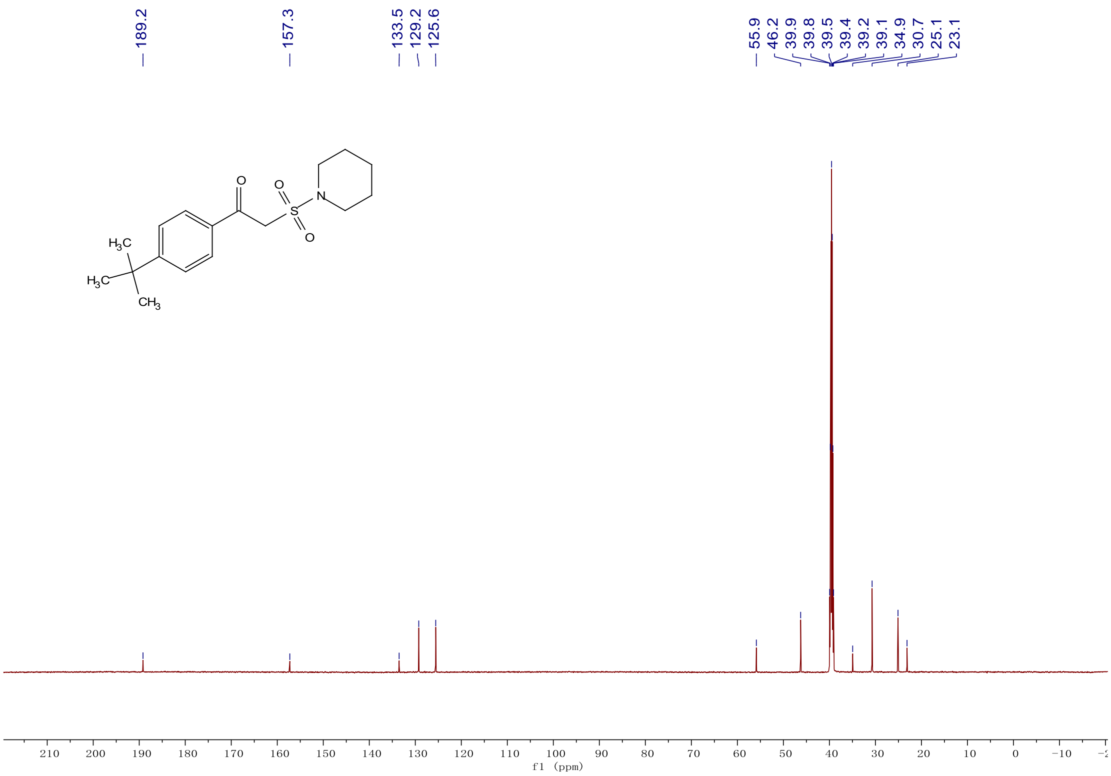
^{13}**C NMR** (150 MHz, DMSO-d_6) of **3e**



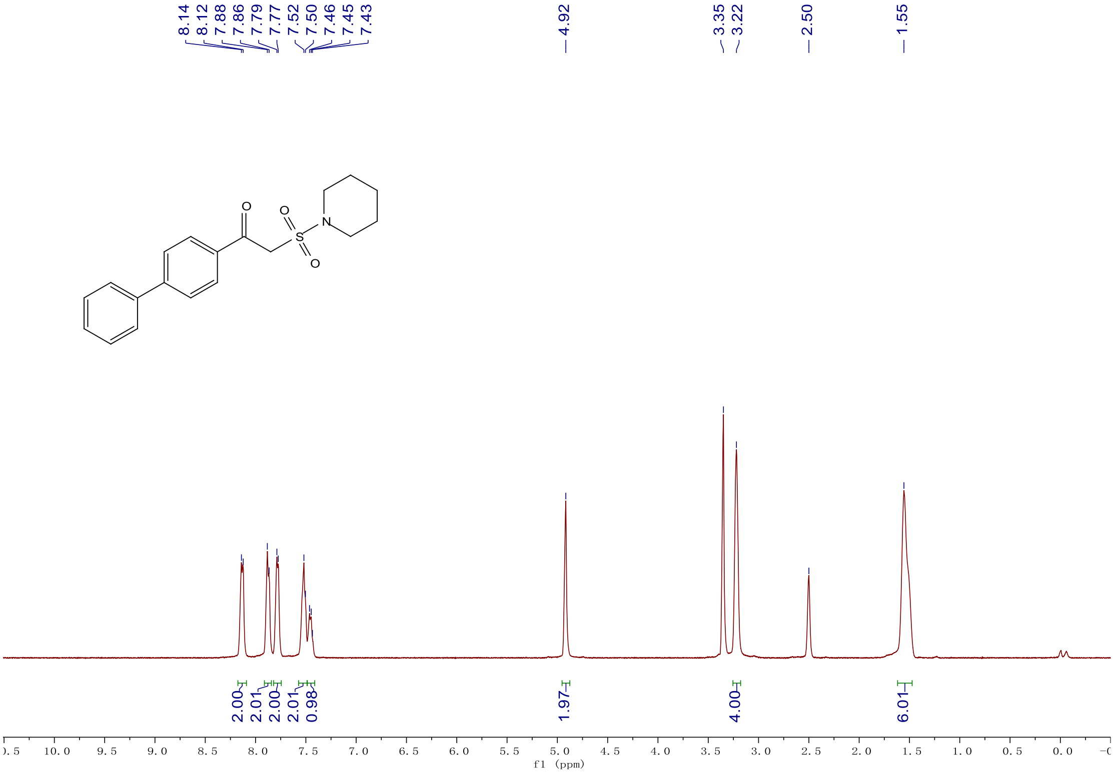
[1]H NMR (400 MHz, DMSO-*d*$_6$) of **3f**



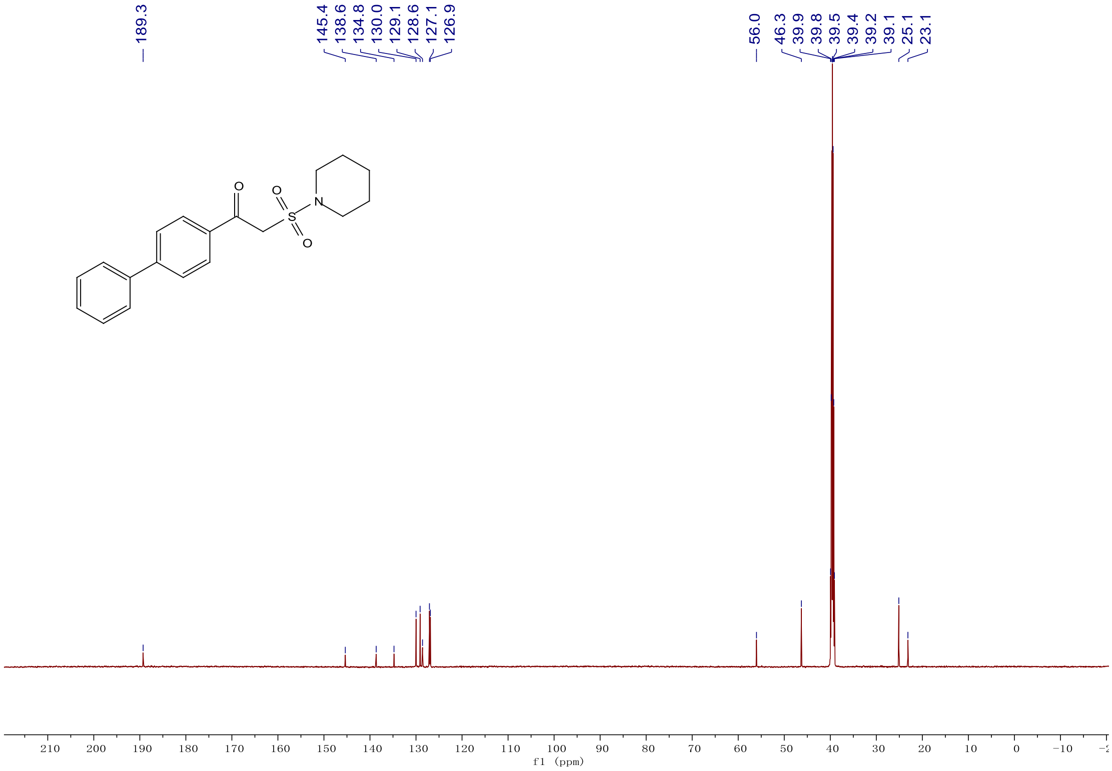
[13]C NMR (150 MHz, DMSO-*d*$_6$) of **3f**



^{1}H NMR (400 MHz, DMSO-d_6) of **3g**

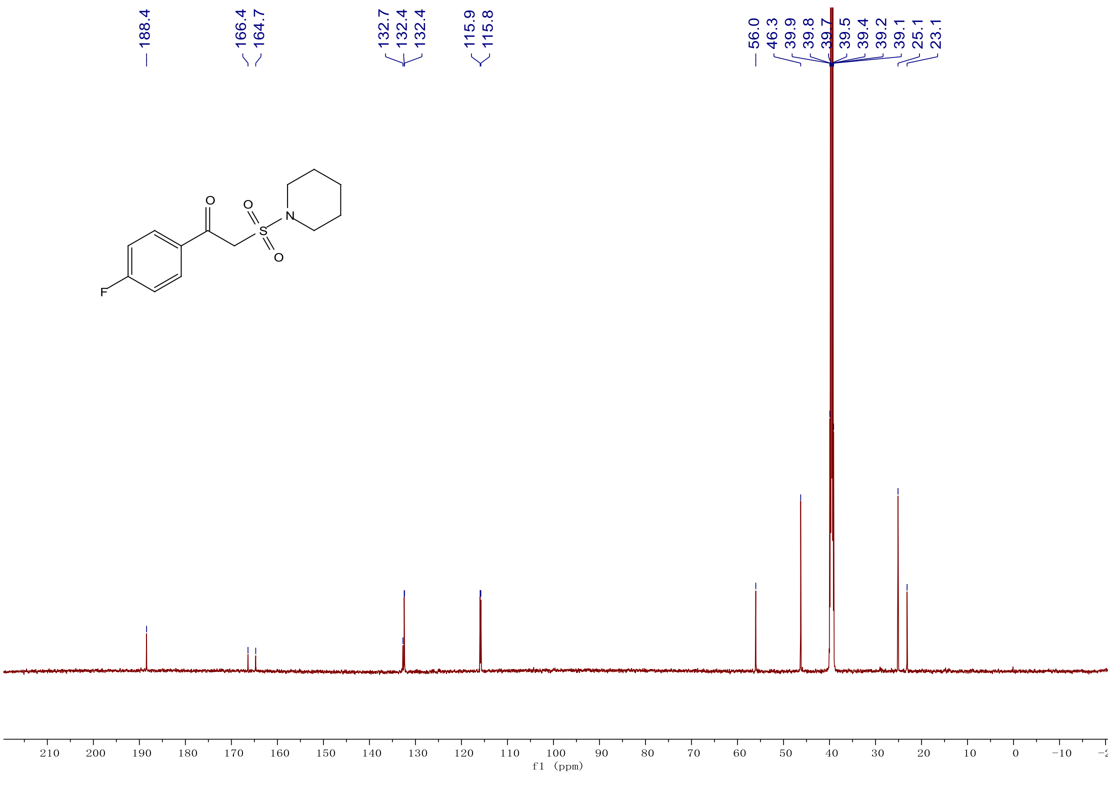


^{13}C NMR (150 MHz, DMSO-d_6) of **3g**

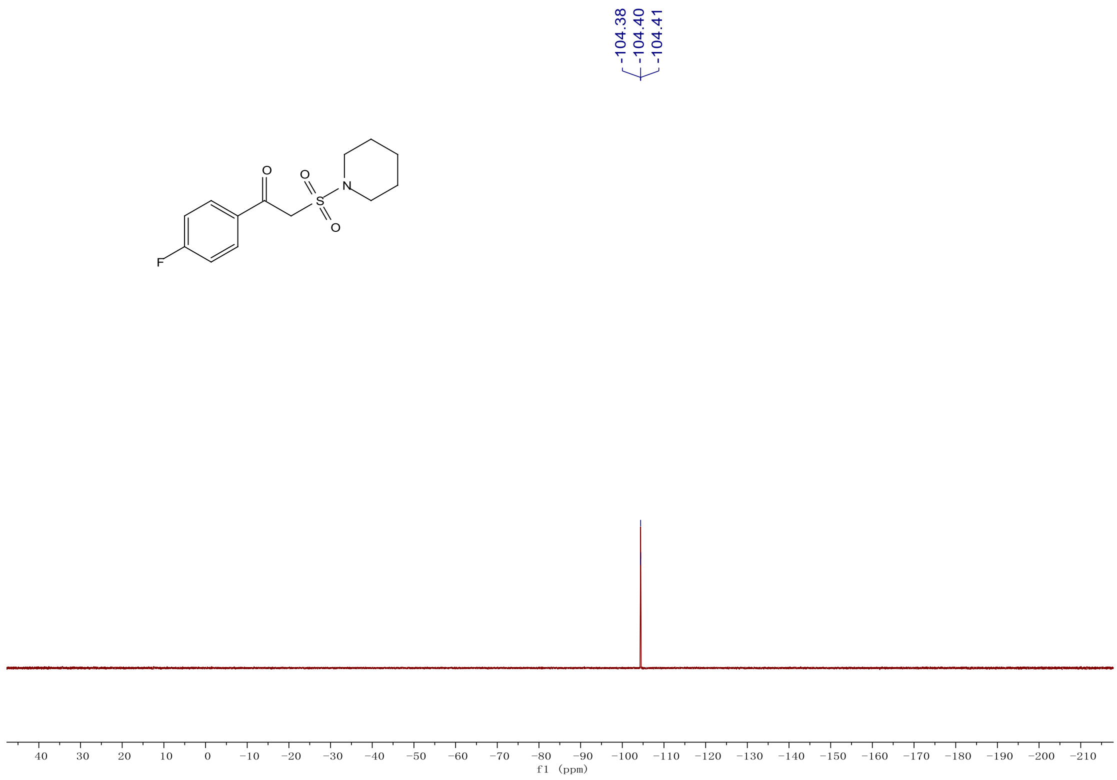


^{1}H NMR (400 MHz, DMSO-d_6) of **3h**

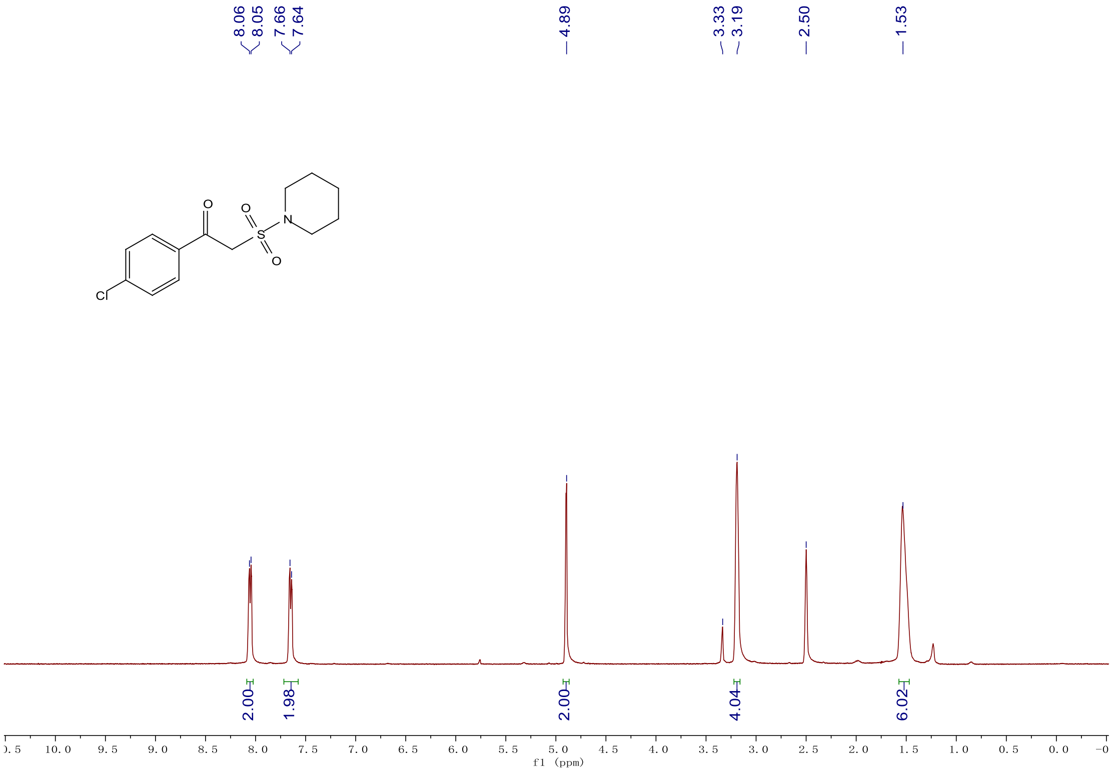
^{13}C NMR (150 MHz, DMSO-d_6) of **3h**



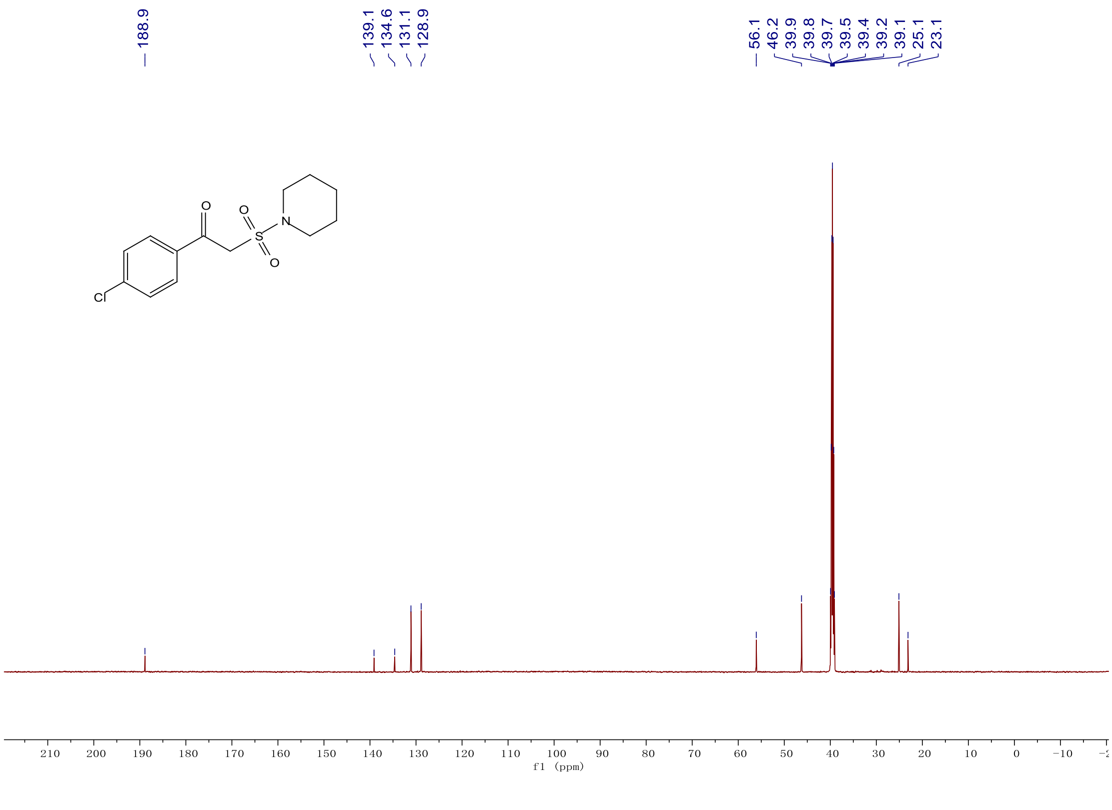
^{19}F NMR (376 MHz, DMSO-d_6) of **3h**



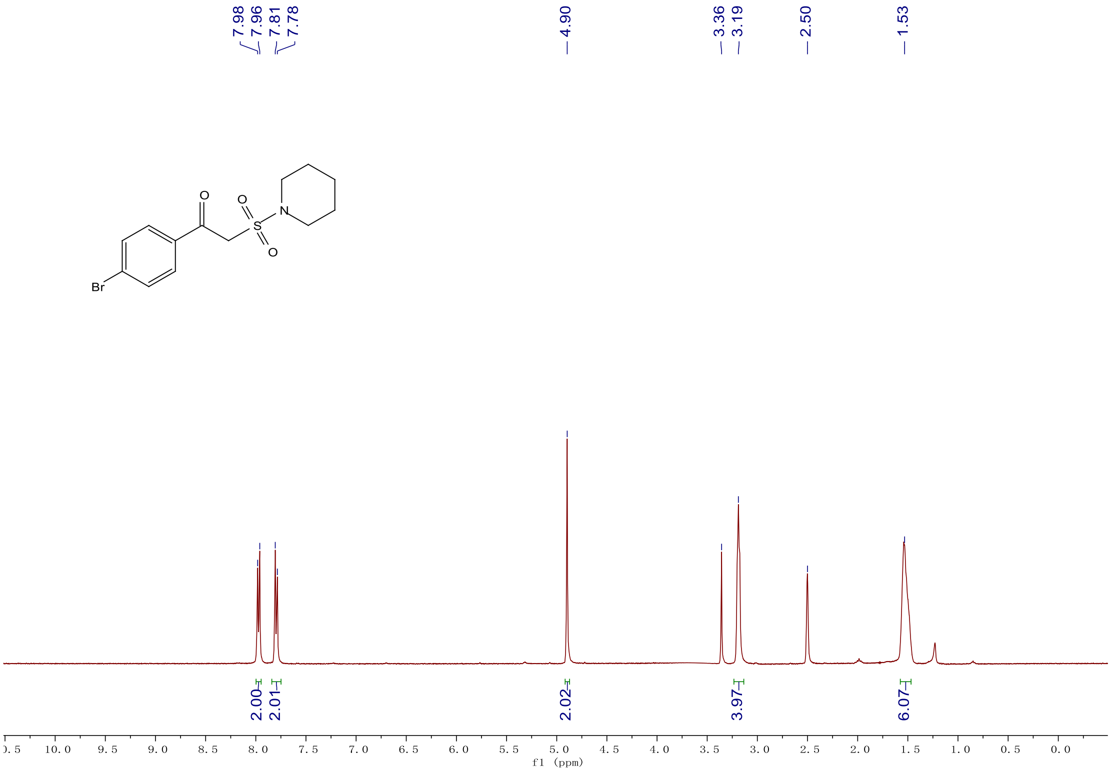
^{1}H NMR (400 MHz, DMSO-d_6) of **3i**



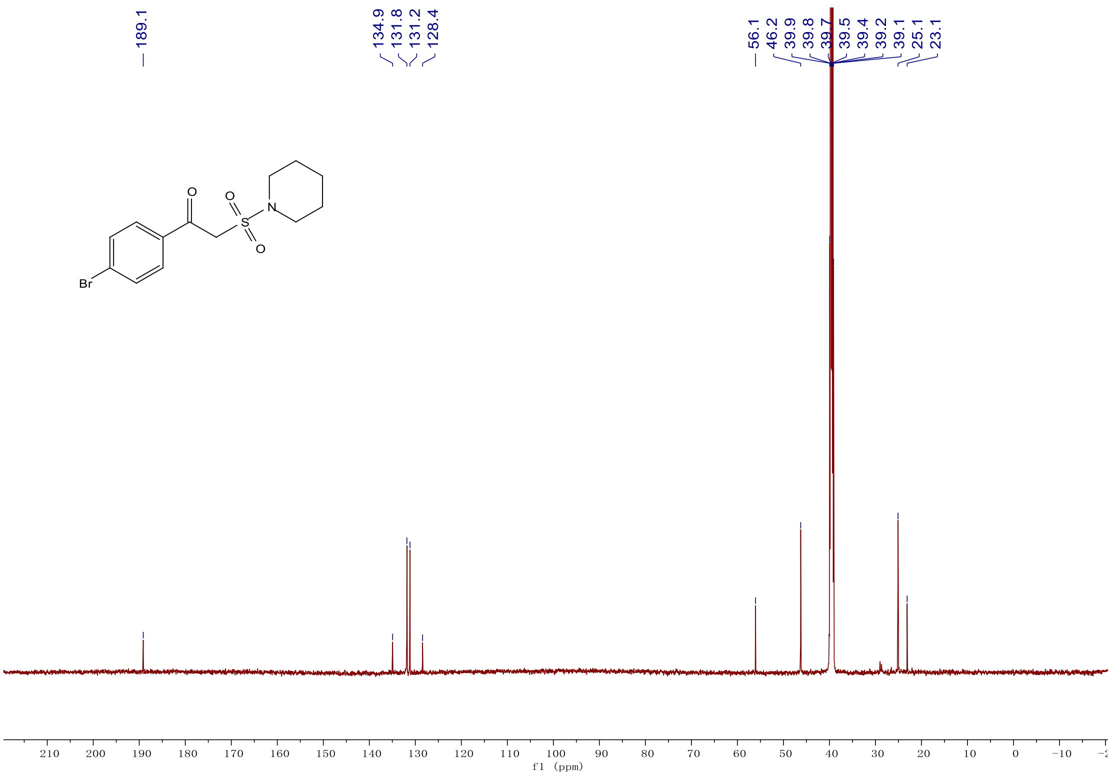
^{13}C NMR (150 MHz, DMSO-d_6) of **3i**



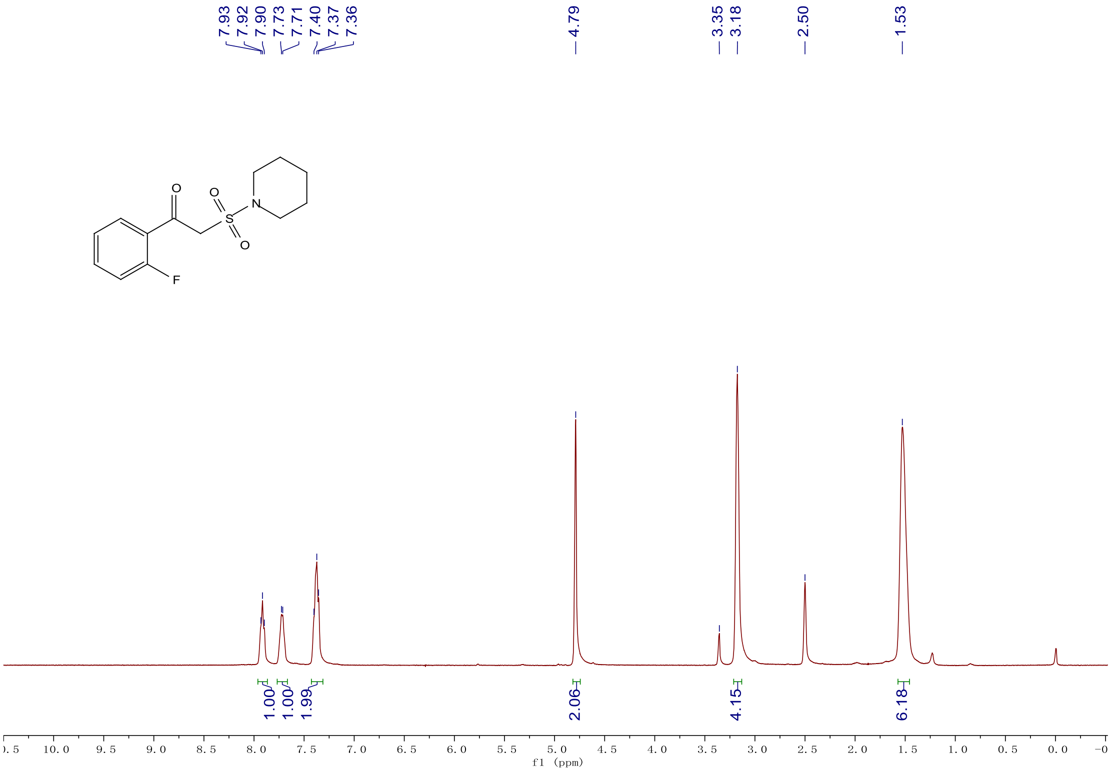
[1]H NMR (400 MHz, DMSO-d_6) of **3j**



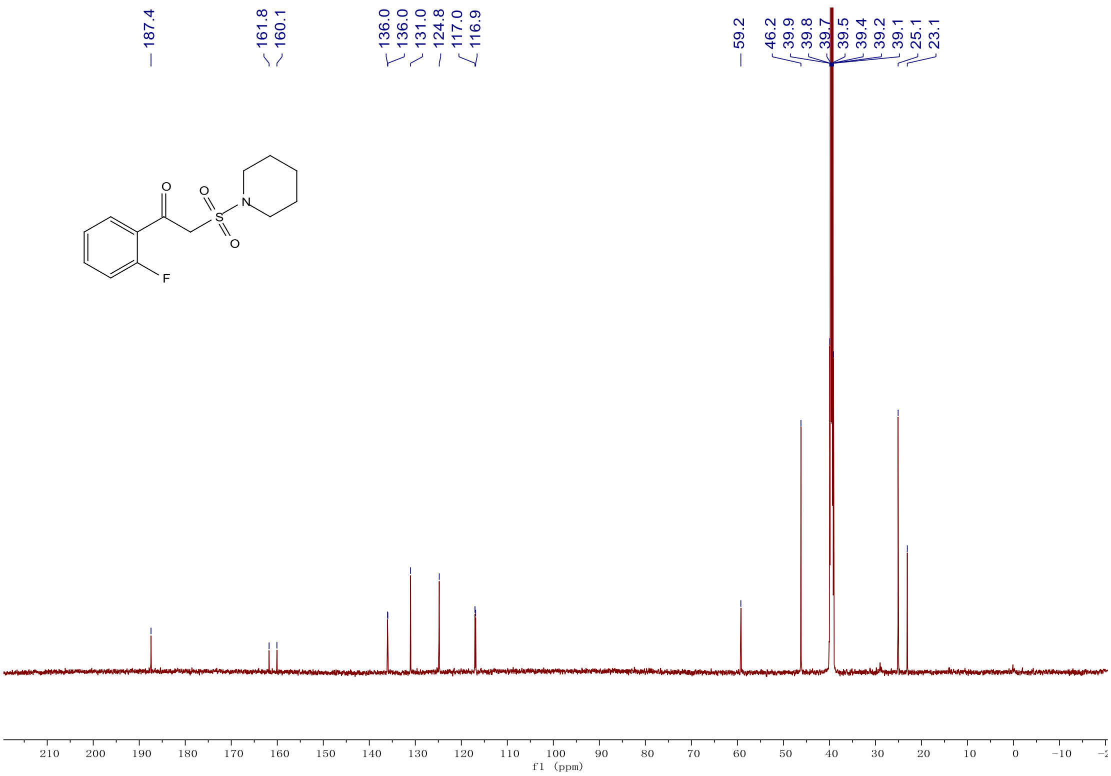
[13]C NMR (150 MHz, DMSO-d_6) of **3j**



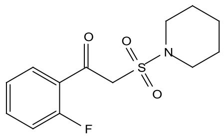
^{1}H NMR (400 MHz, DMSO-d_6) of **3k**

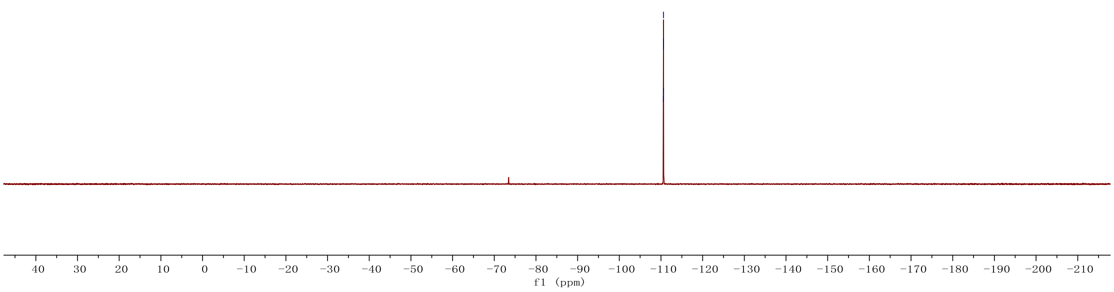


^{13}C NMR (150 MHz, DMSO-d_6) of **3k**

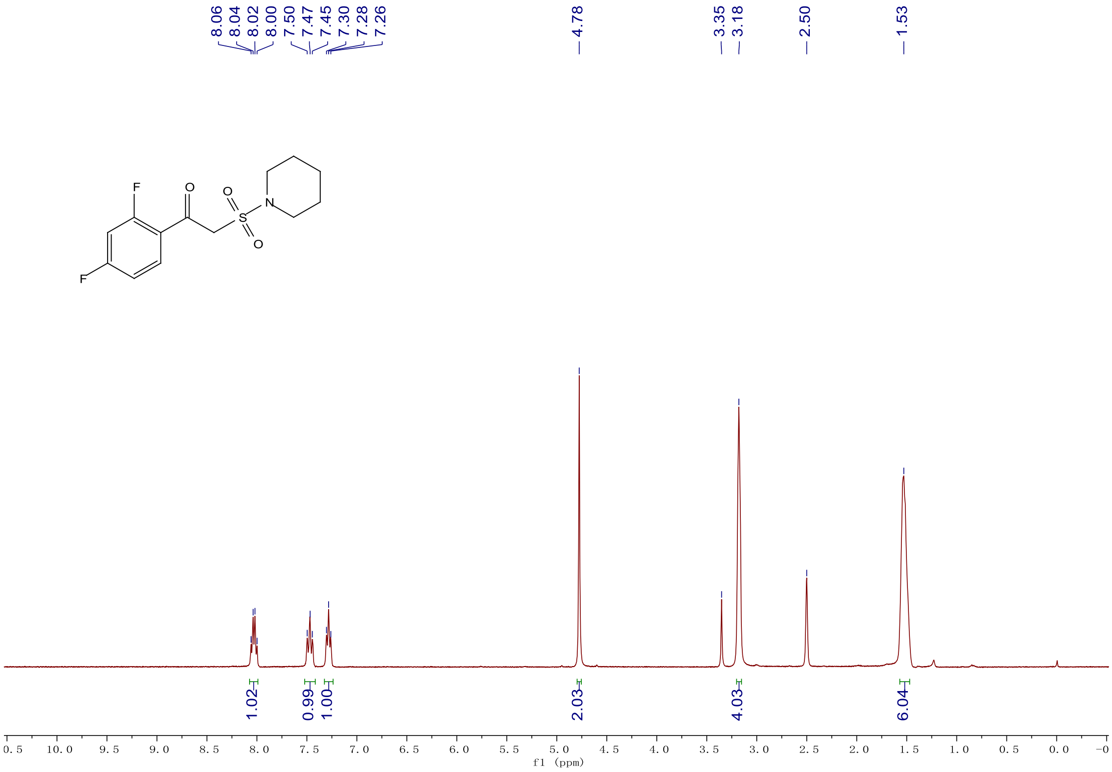


^{19}F NMR (376 MHz, DMSO-*d*$_6$) of **3k**

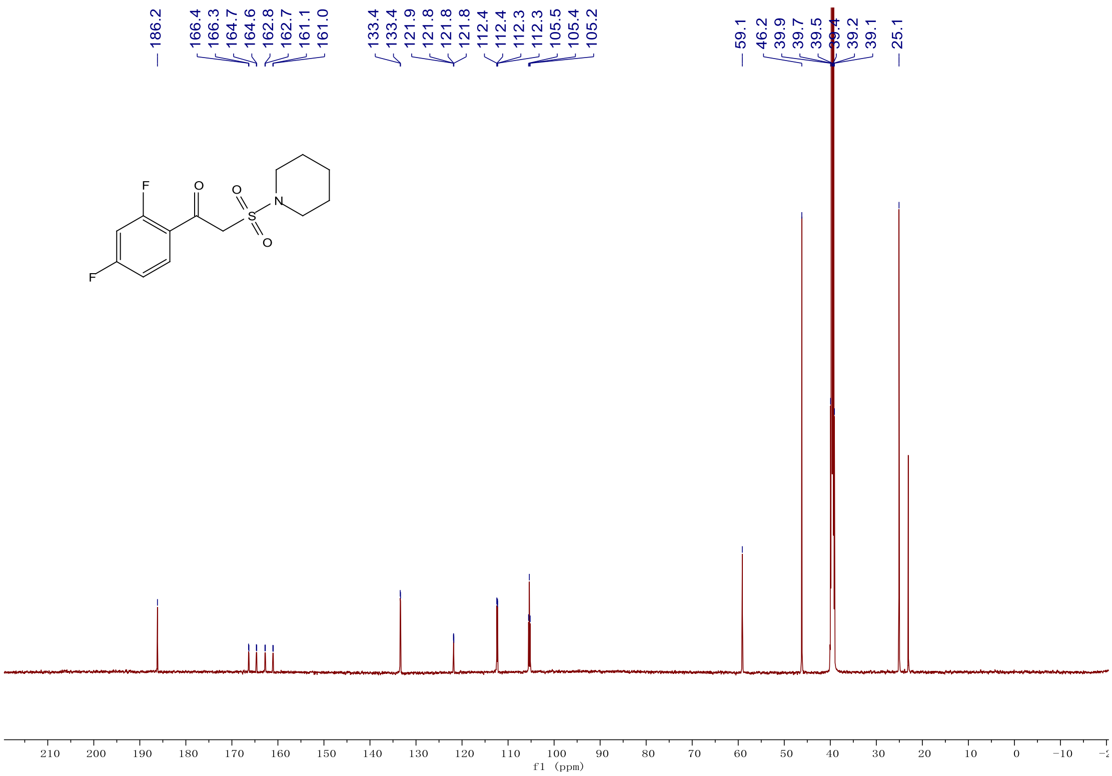




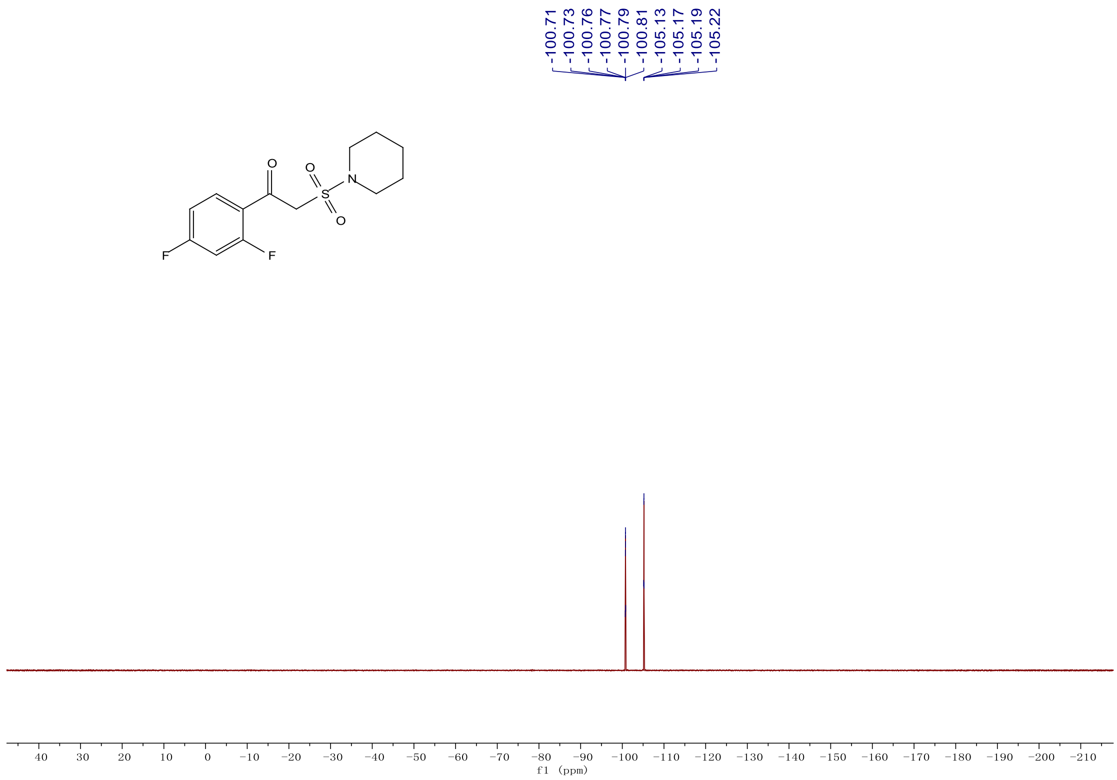
^{1}H NMR (400 MHz, DMSO-d_6) of **3l**



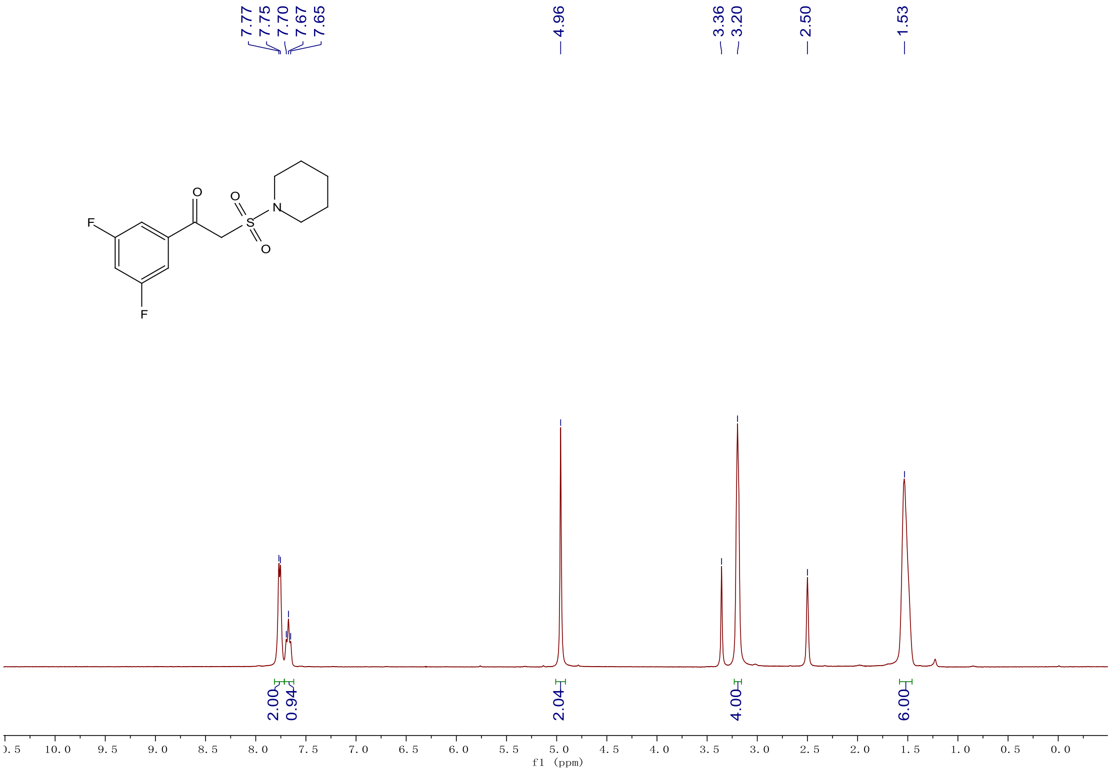
^{13}C NMR (150 MHz, DMSO-d_6) of **3l**



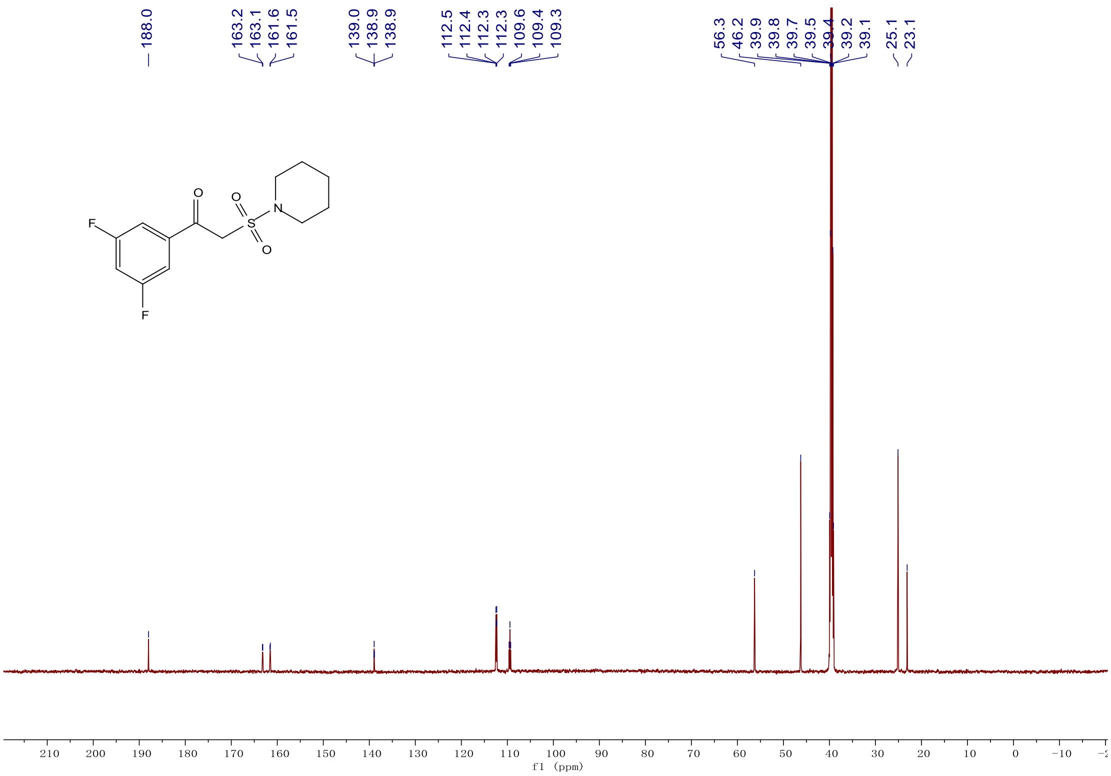
^{19}**F NMR** (376 MHz, DMSO-d_6) of **3l**



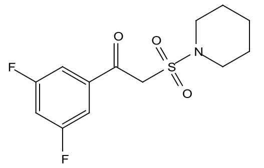
[1]H NMR (400 MHz, DMSO-d_6) of **3m**

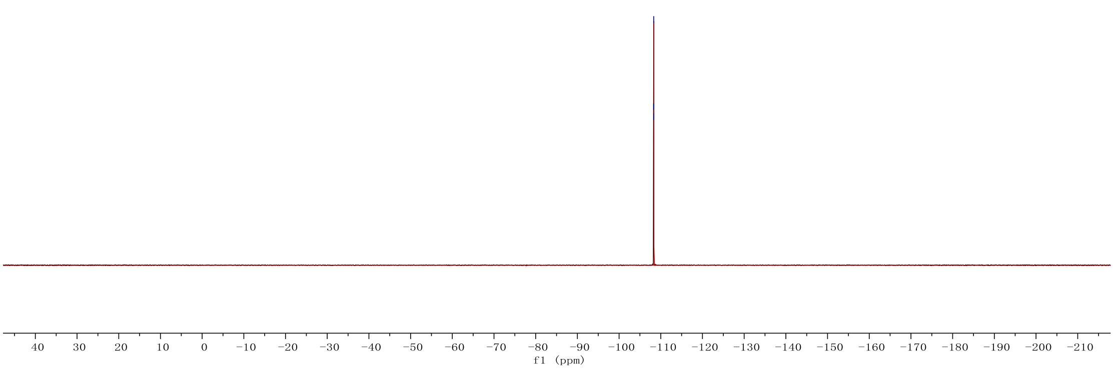


[13]C NMR (150 MHz, DMSO-d_6) of **3m**

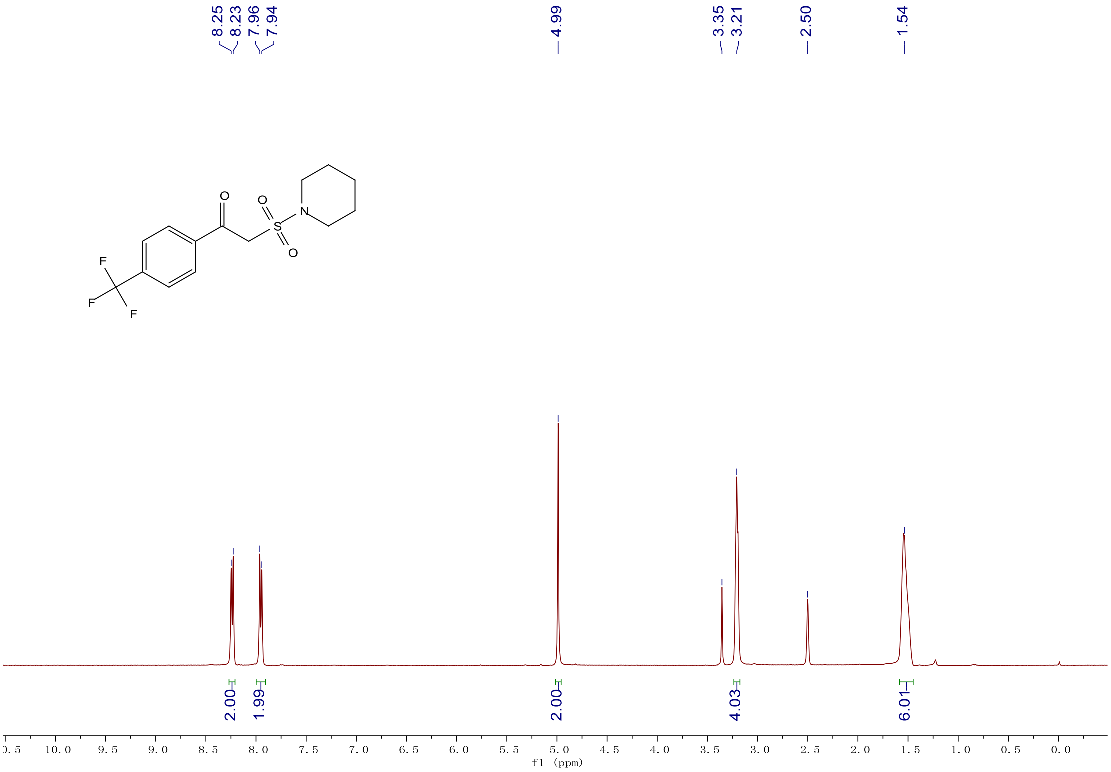


^{19}F NMR (376 MHz, DMSO-d_6) of **3m**



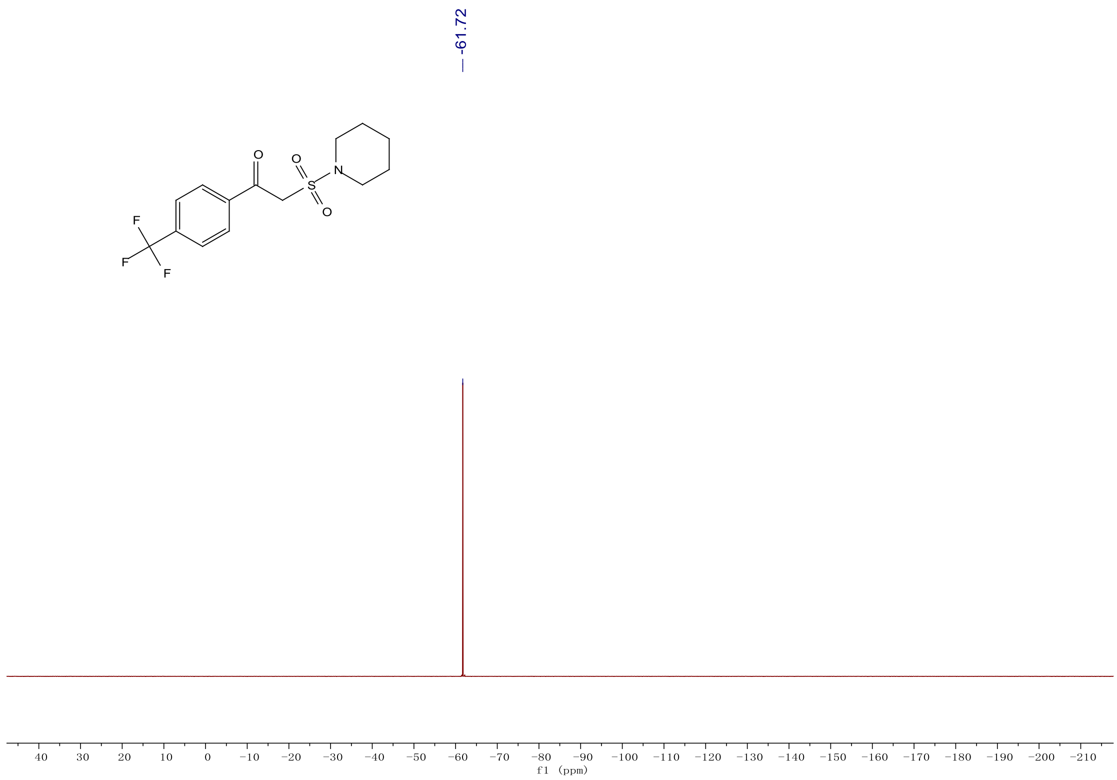


^{1}H NMR (400 MHz, DMSO-d_6) of **3n**



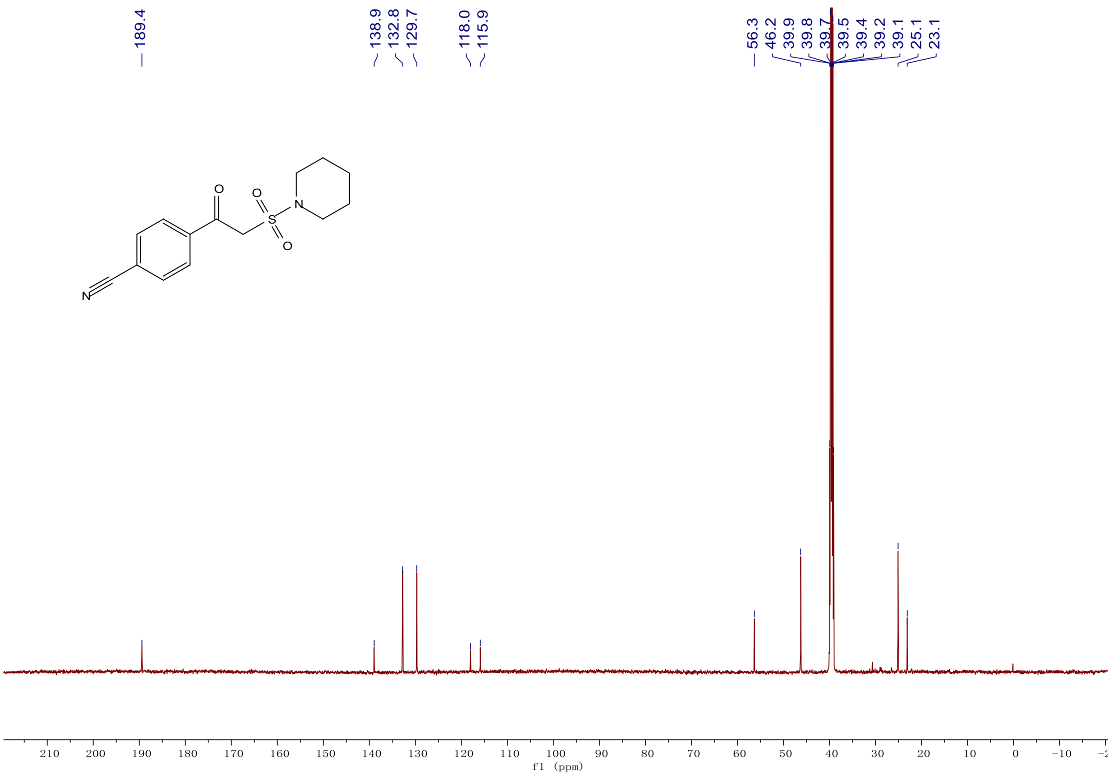
^{13}C NMR (150 MHz, DMSO-d_6) of **3n**

^{19}F NMR (376 MHz, DMSO-d_6) of **3n**



^{1}H NMR (400 MHz, DMSO-d_6) of **3o**

^{13}C NMR (150 MHz, DMSO-d_6) of **3o**



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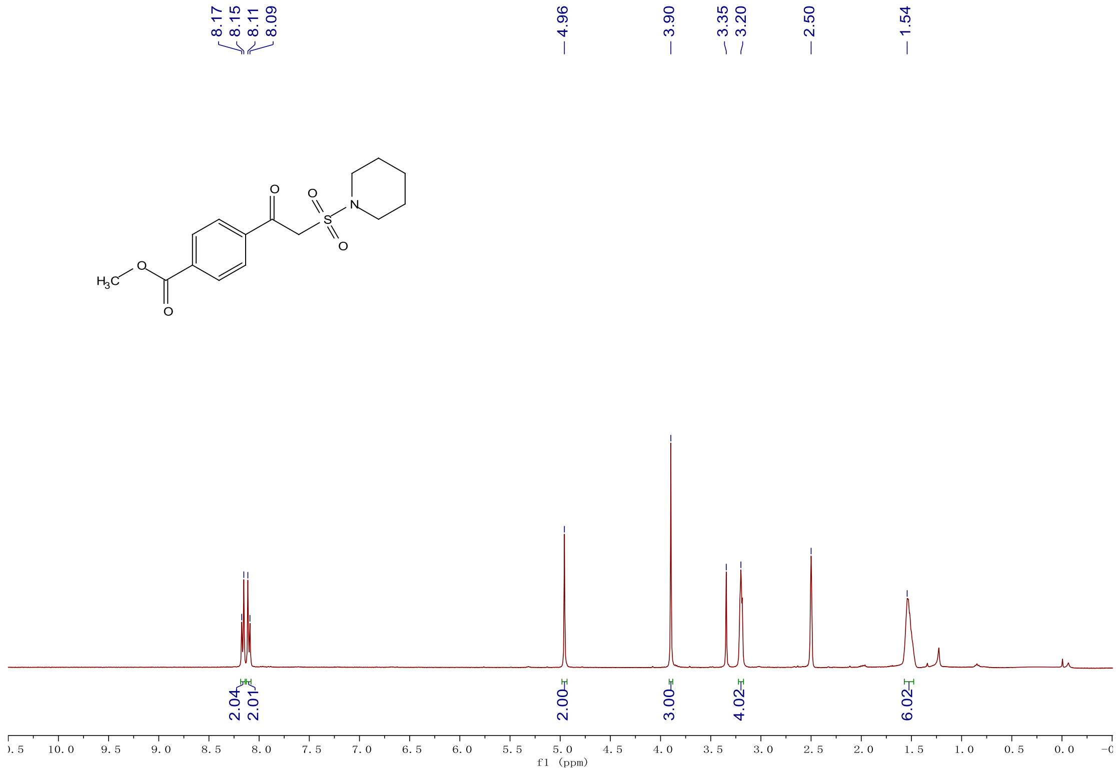
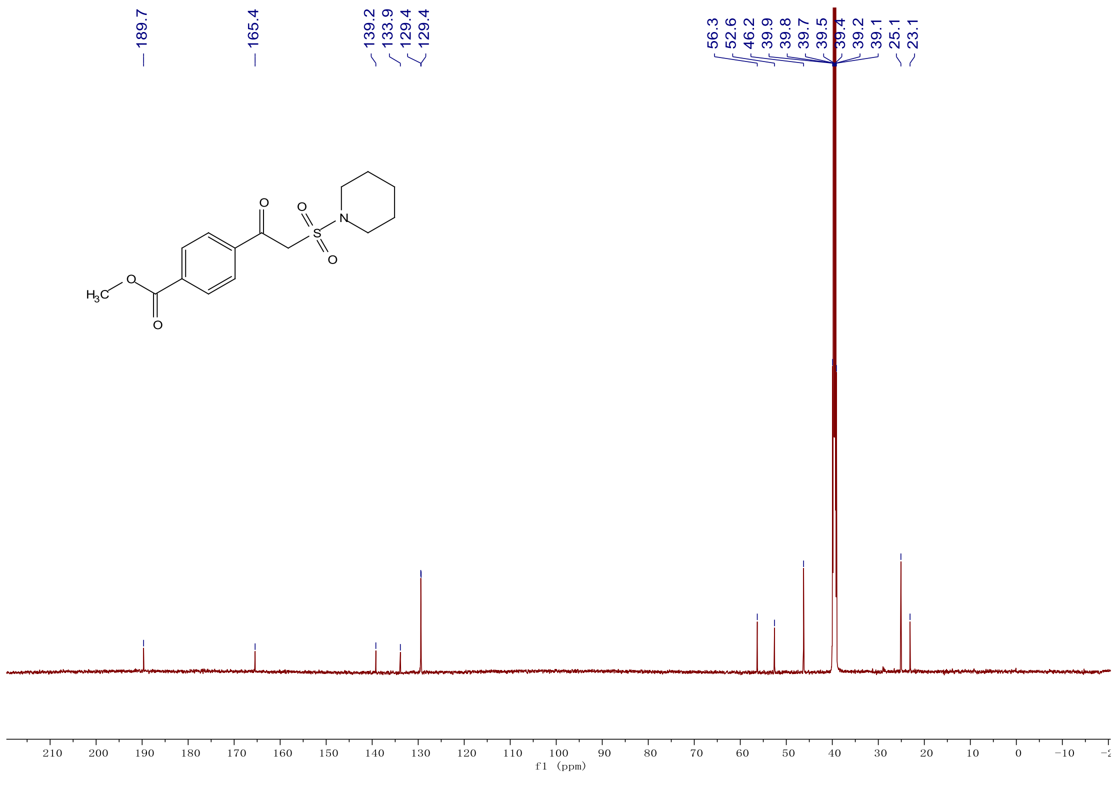
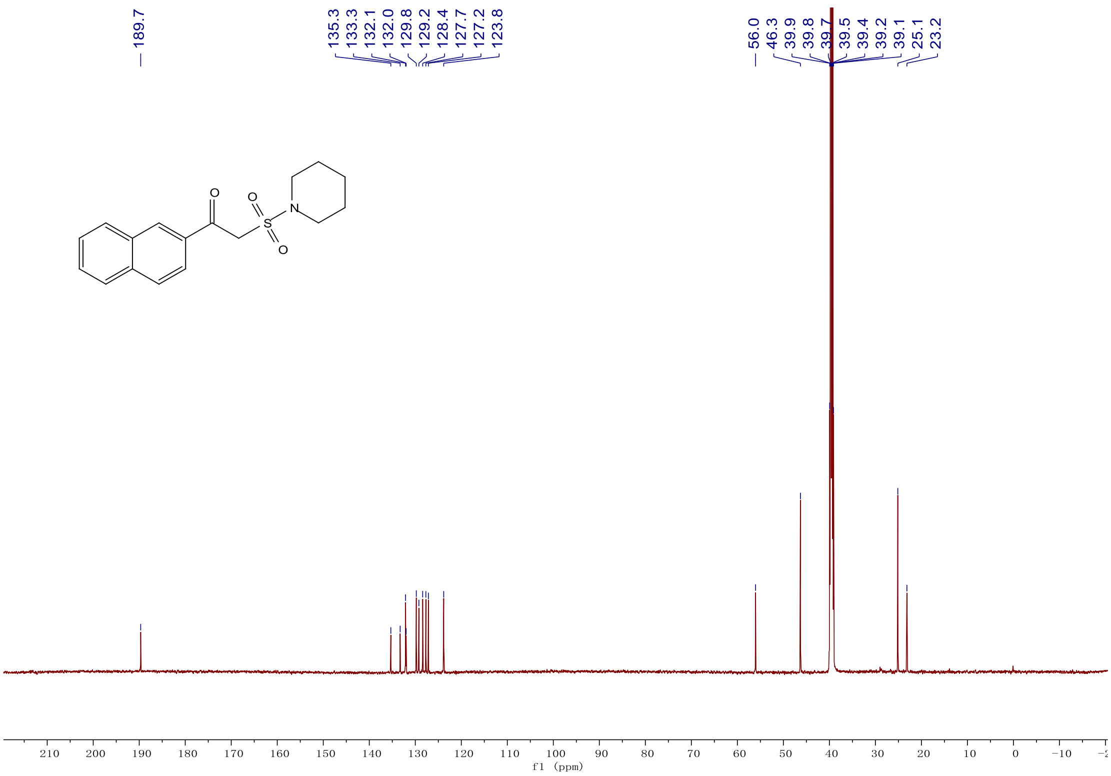


[13]C NMR (150 MHz, DMSO-d_6) of **3p**

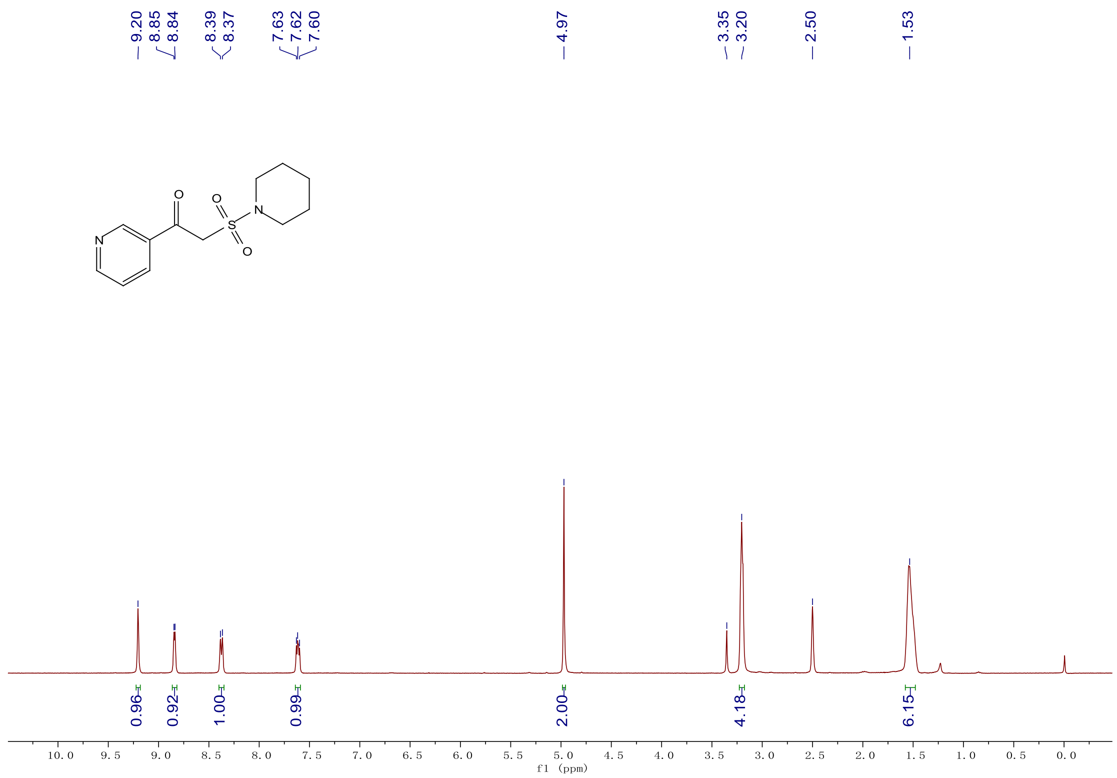


^{1}H NMR (400 MHz, DMSO-d_6) of **3q**

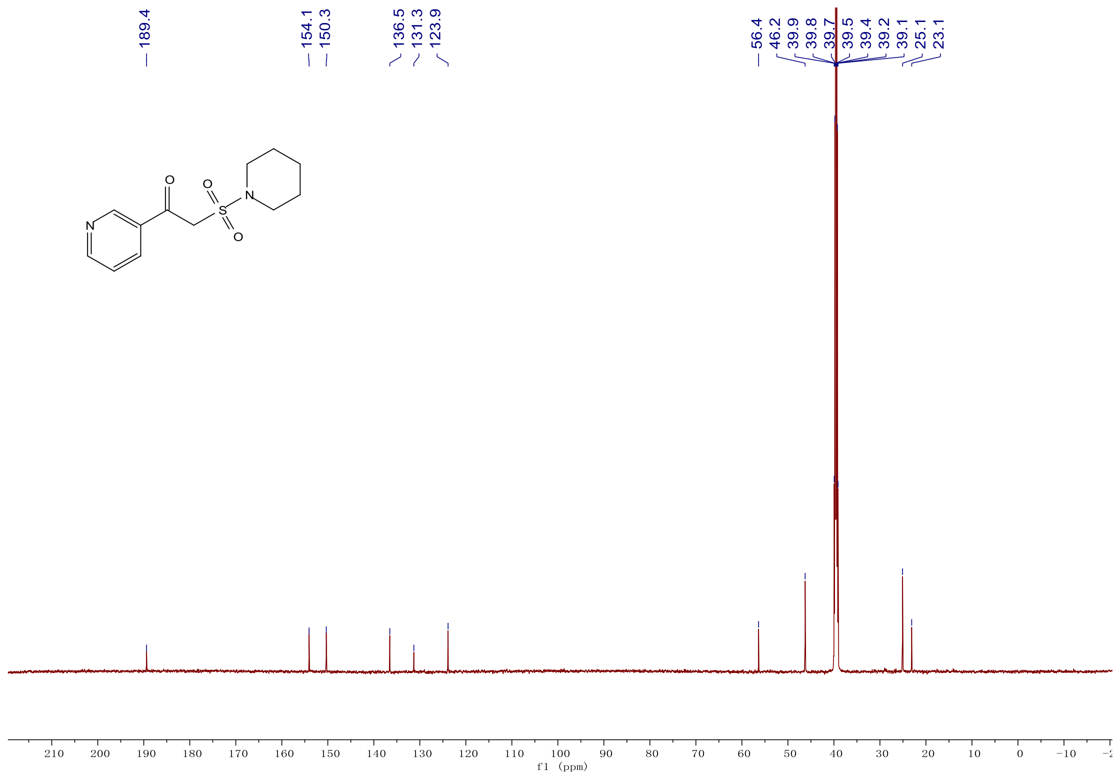
^{13}C NMR (150 MHz, DMSO-d_6) of **3q**



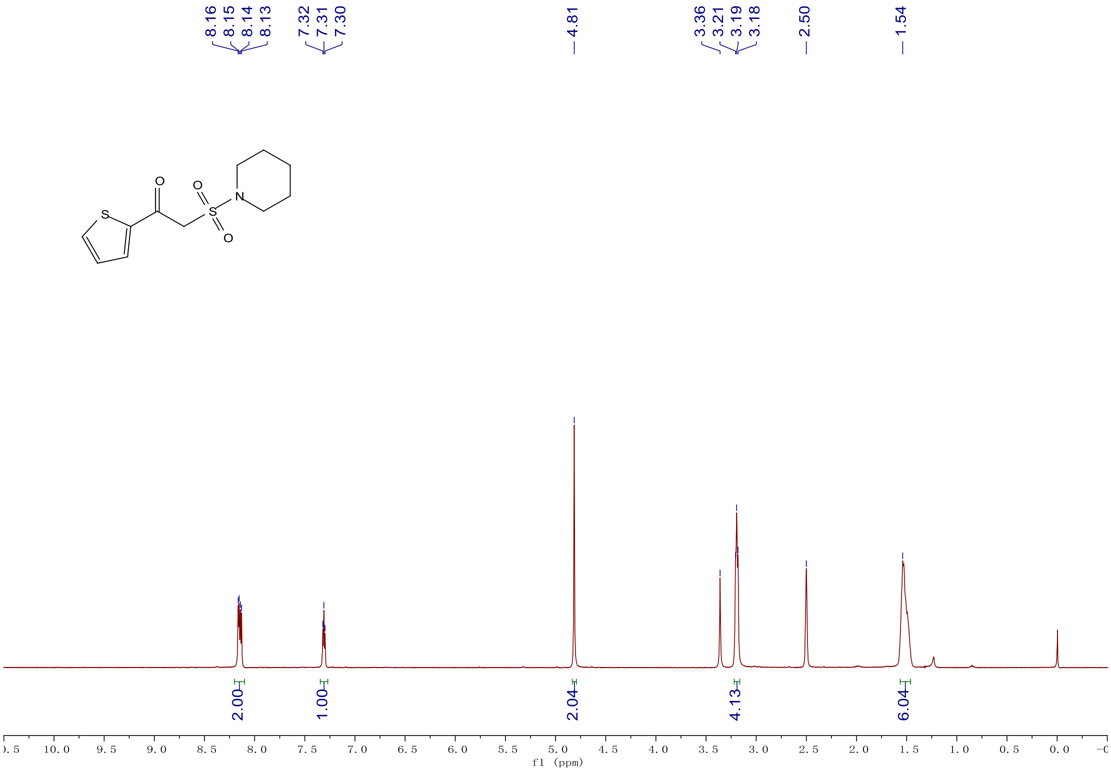
^{1}H NMR (400 MHz, DMSO-d_6) of **3r**



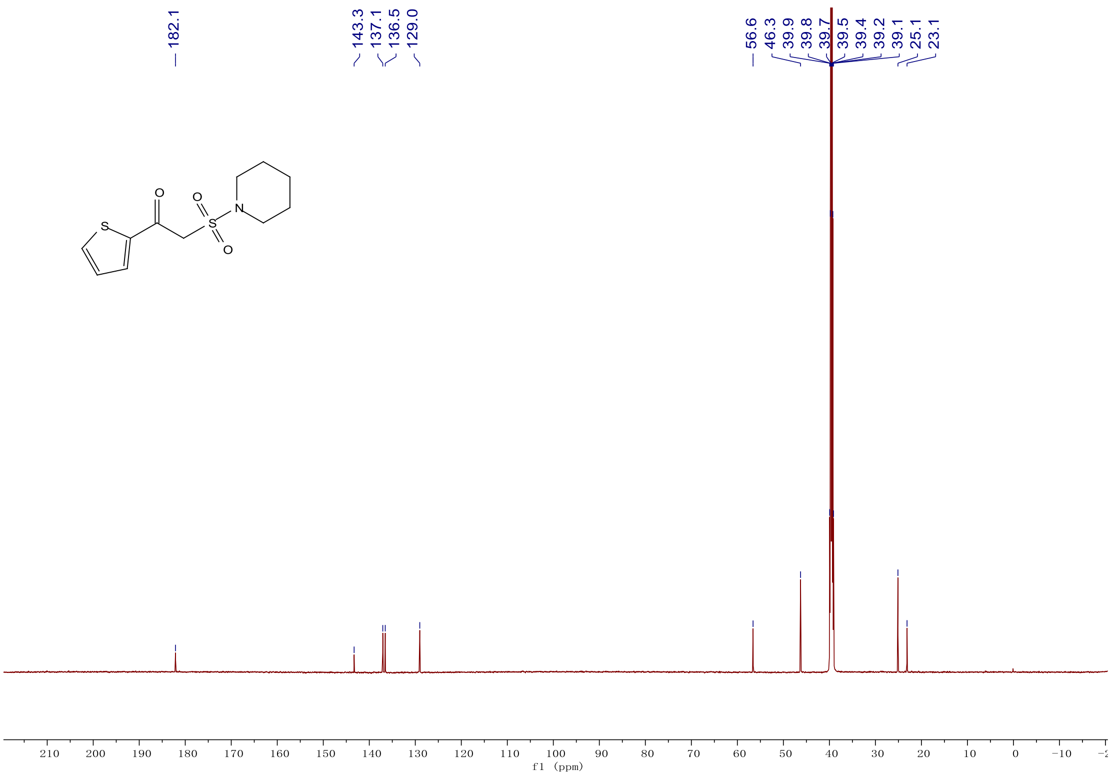
^{13}C NMR (150 MHz, DMSO-d_6) of **3r**



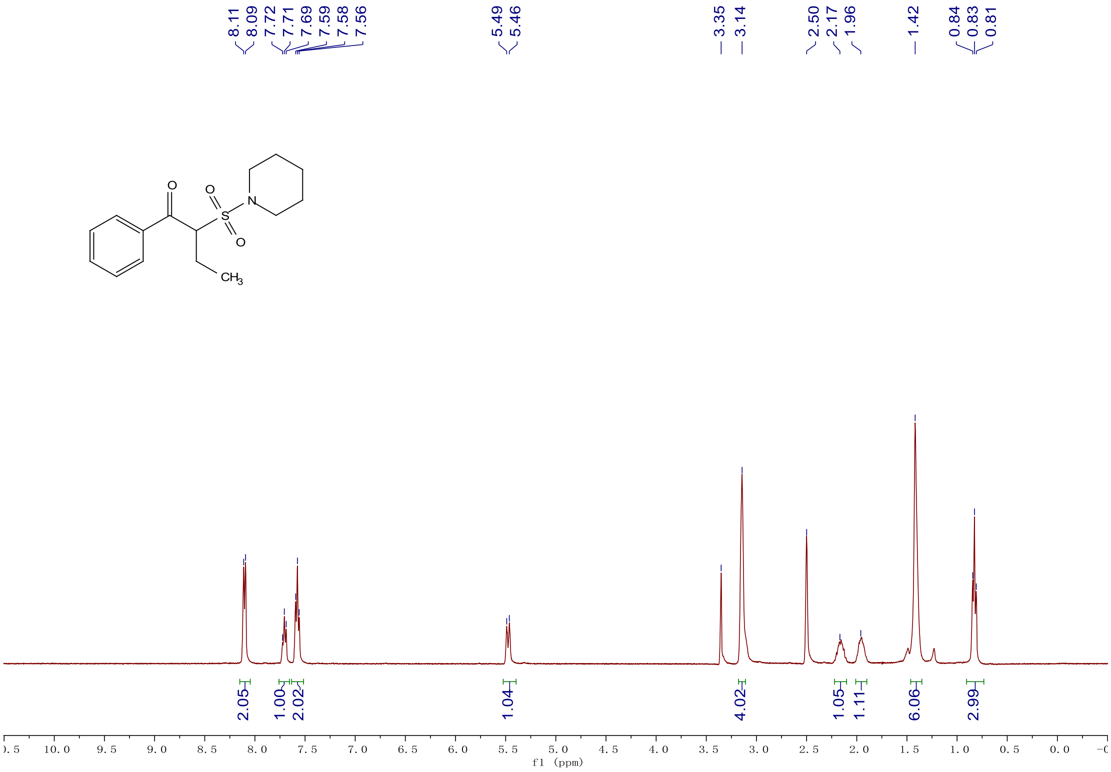
^{1}H NMR (400 MHz, DMSO-d_6) of **3s**



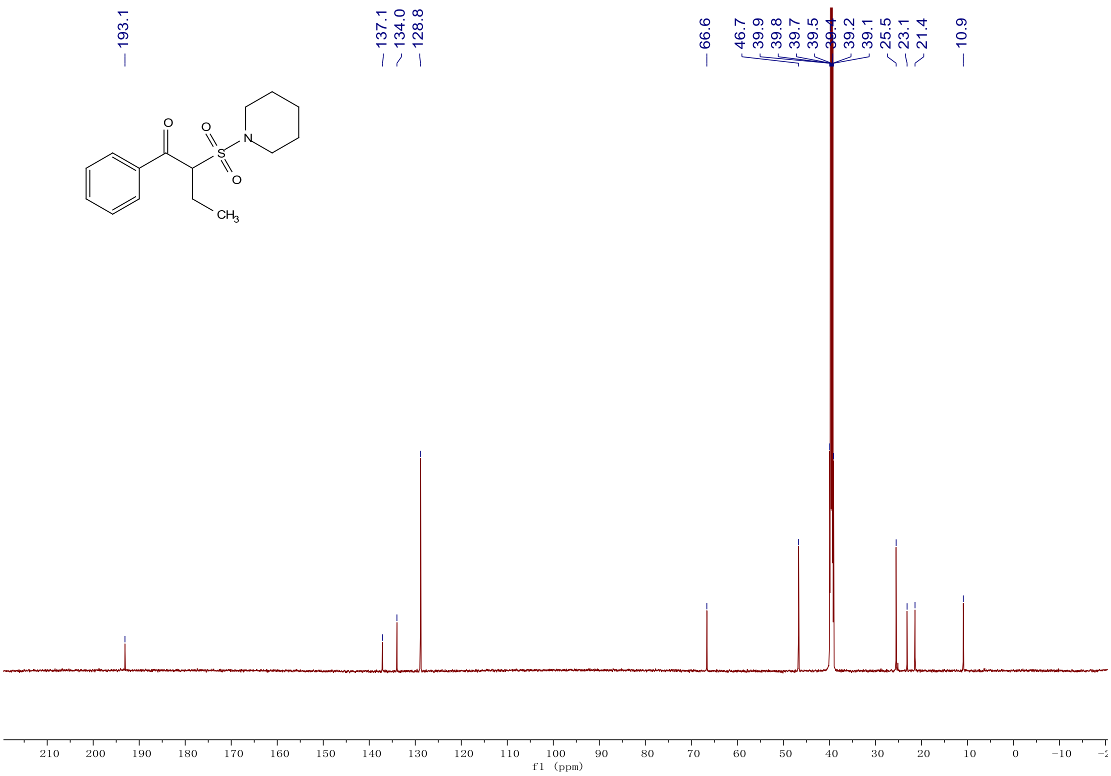
^{13}C NMR (150 MHz, DMSO-d_6) of **3s**



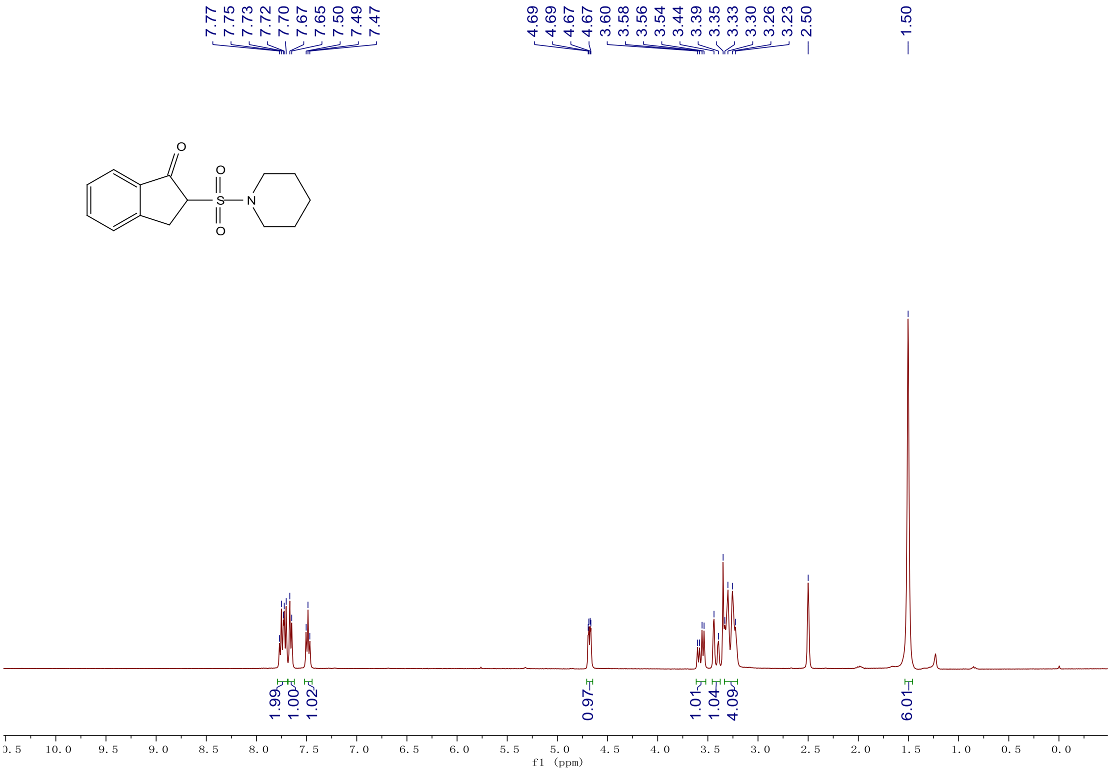
^{1}H NMR (400 MHz, DMSO-d_6) of **3t**



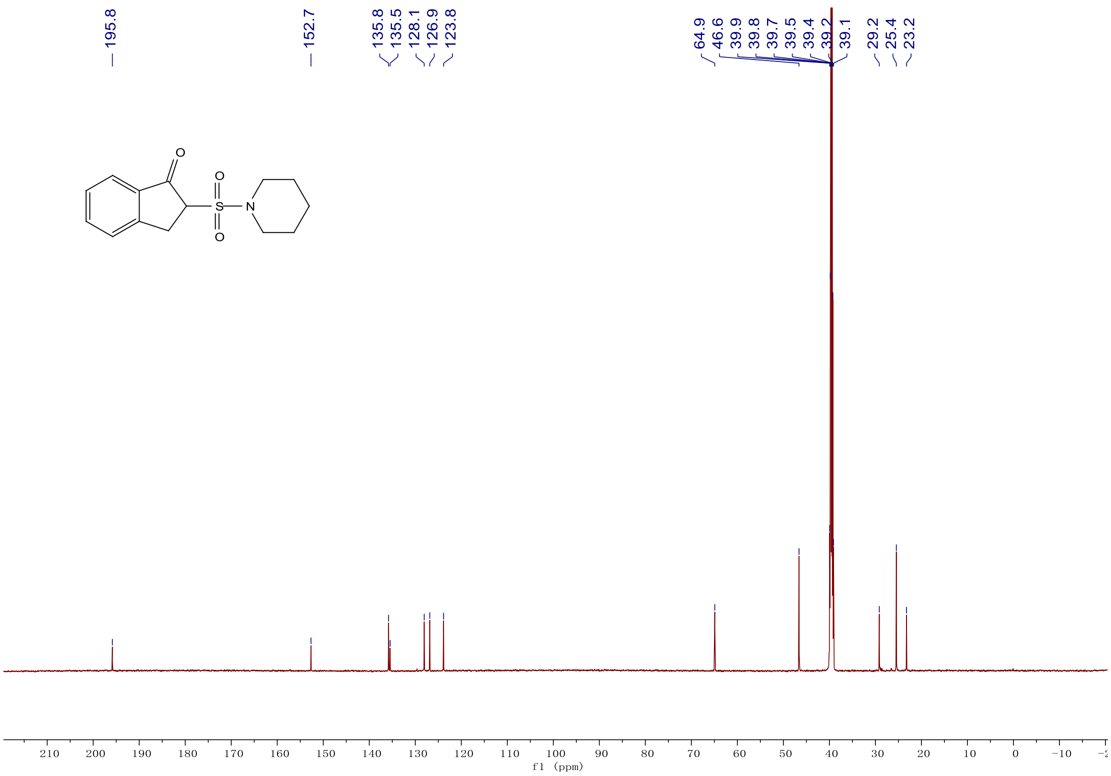
^{13}C NMR (150 MHz, DMSO-d_6) of **3t**



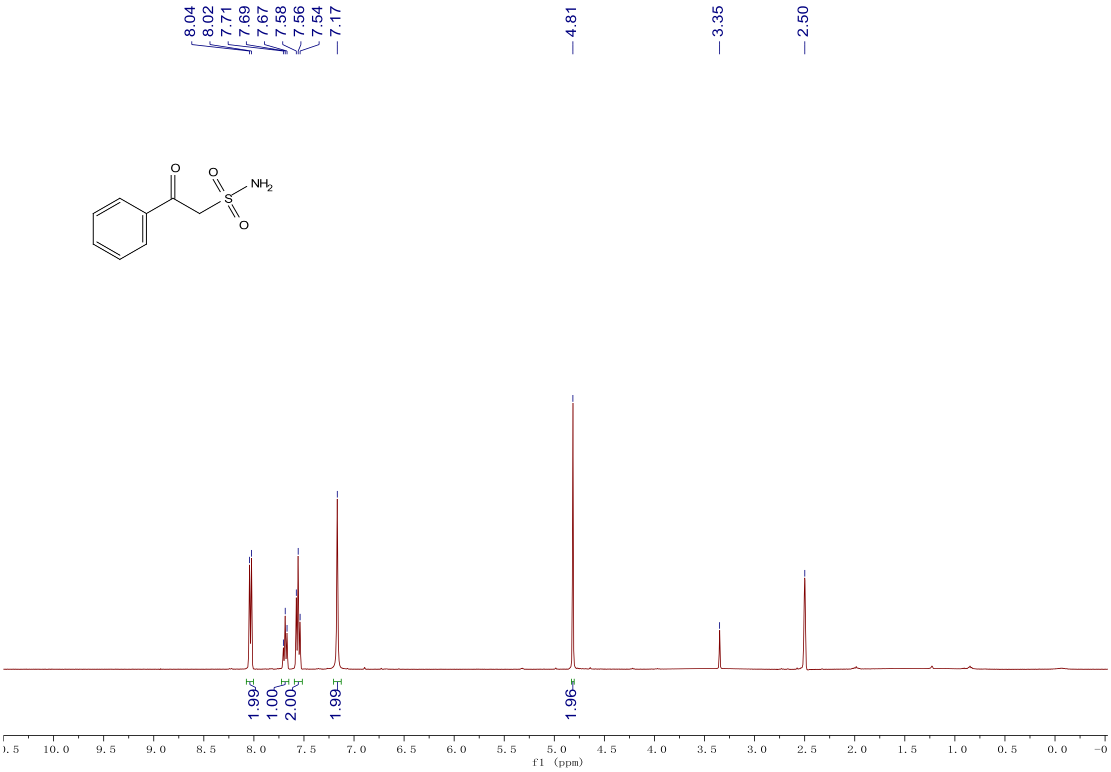
^{1}H NMR (400 MHz, DMSO-d_6) of **3v**



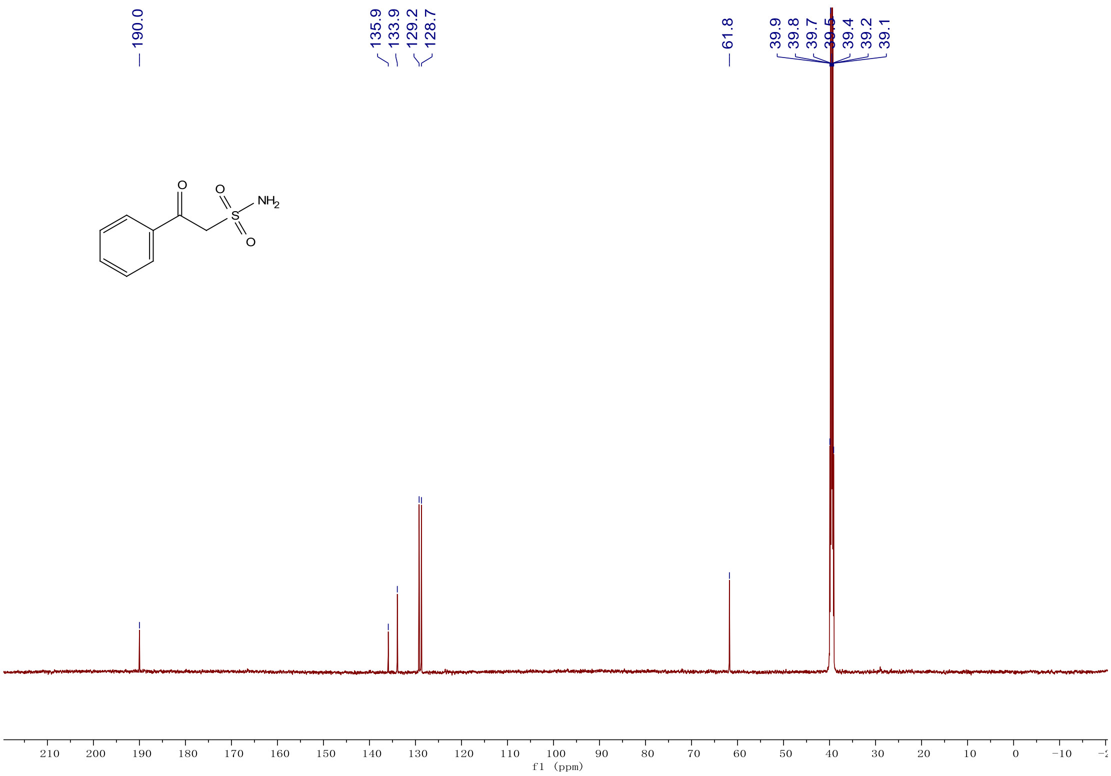
^{13}C NMR (150 MHz, DMSO-d_6) of **3v**



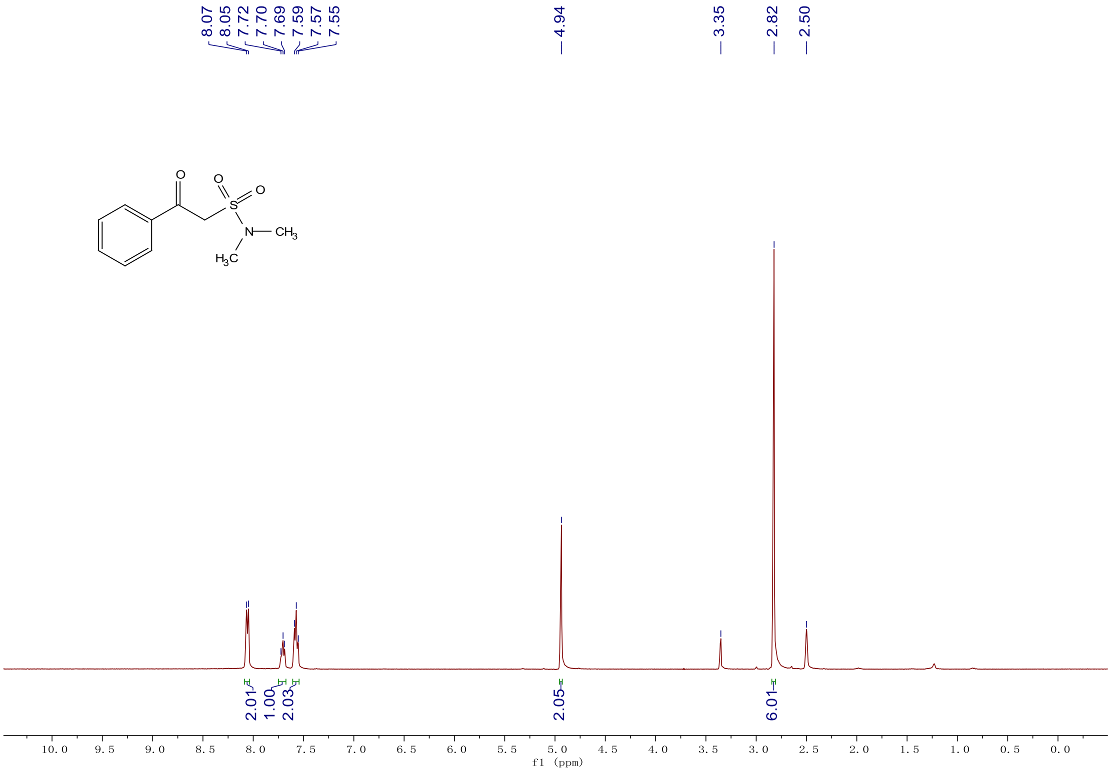
[1]**H NMR** (400 MHz, DMSO-d_6) of **4a**



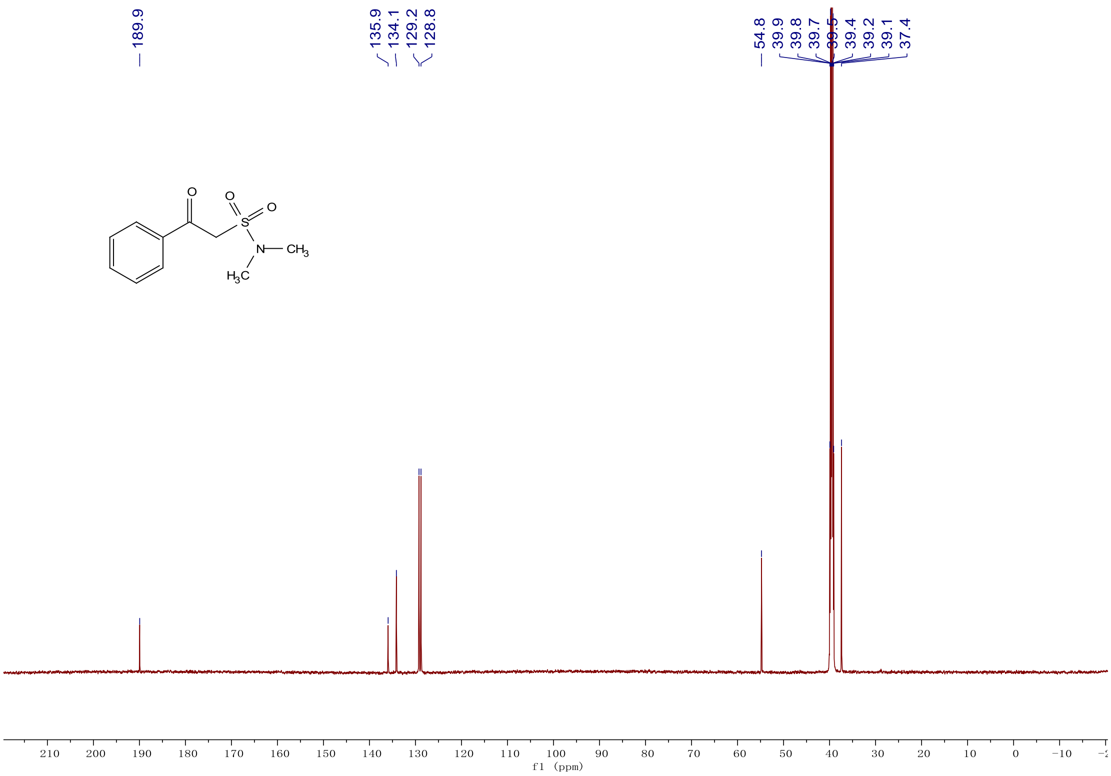
[13]**C NMR** (150 MHz, DMSO-d_6) of **4a**



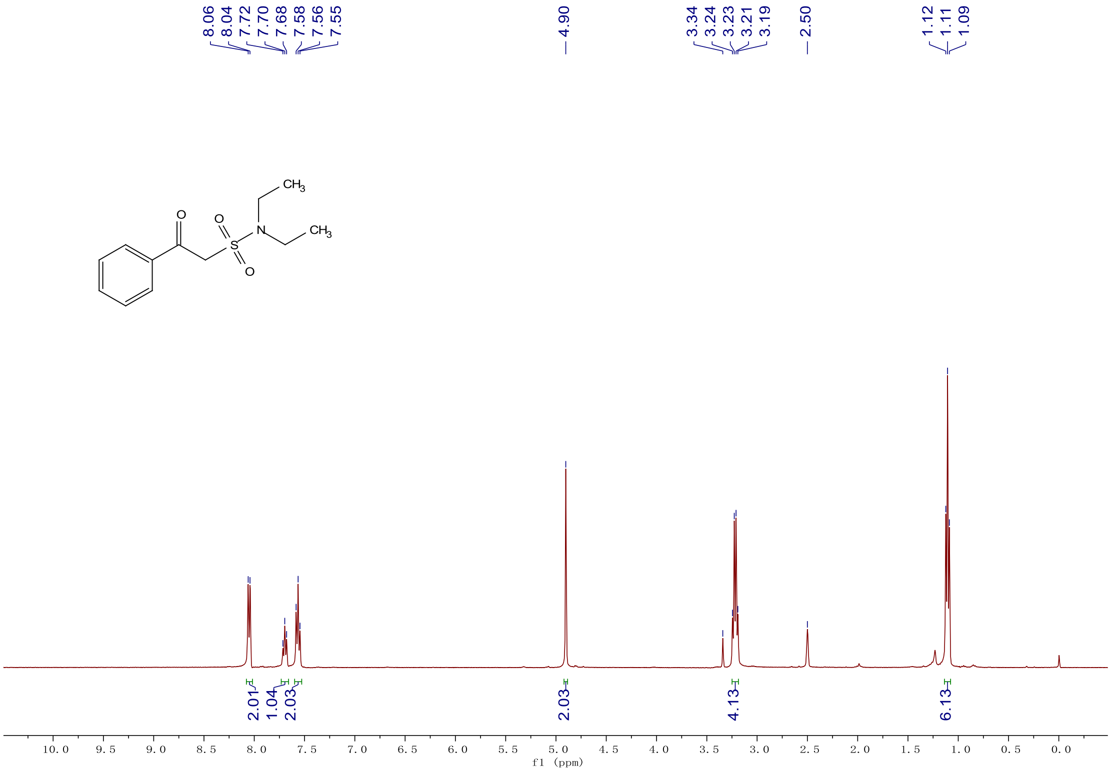
^{1}H NMR (400 MHz, DMSO-d_6) of **4b**



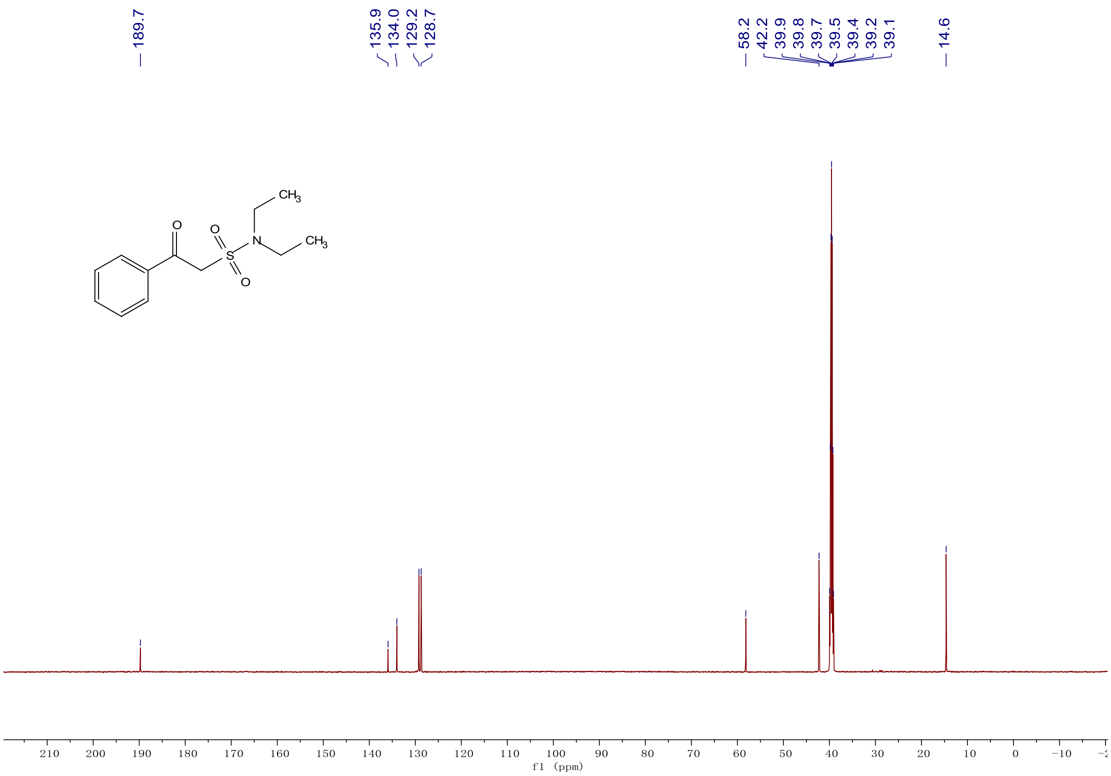
^{13}C NMR (150 MHz, DMSO-d_6) of **4b**



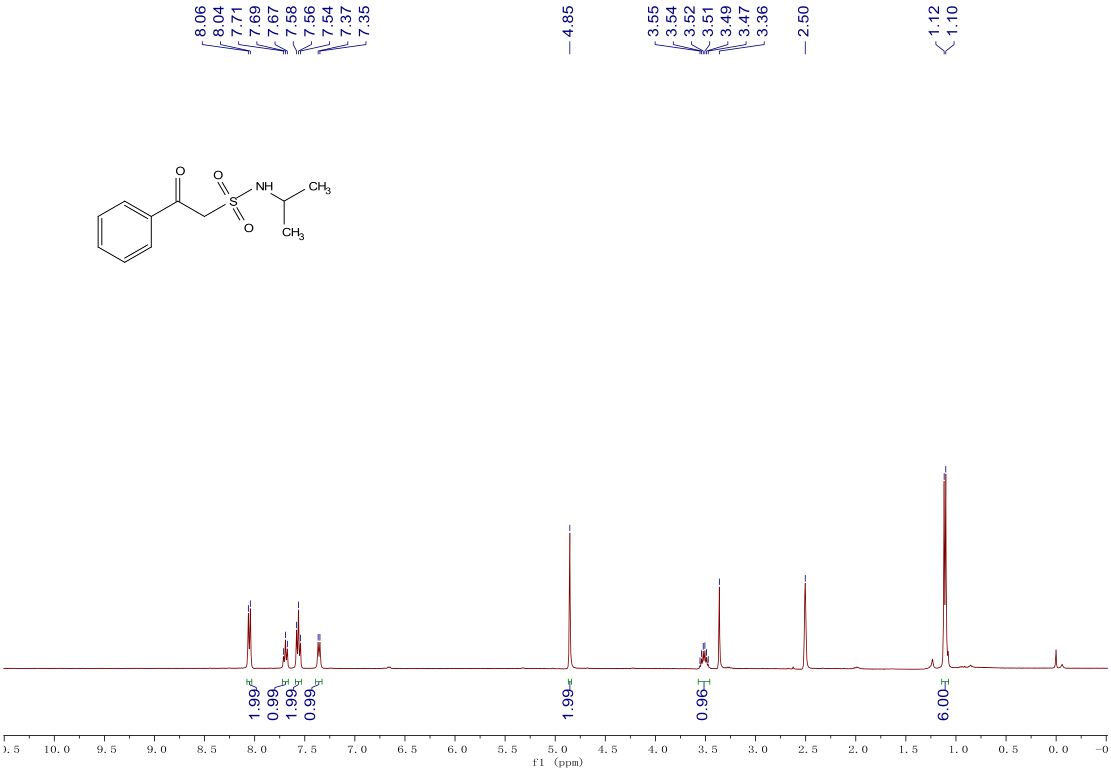
[1]H NMR (400 MHz, DMSO-d_6) of **4c**



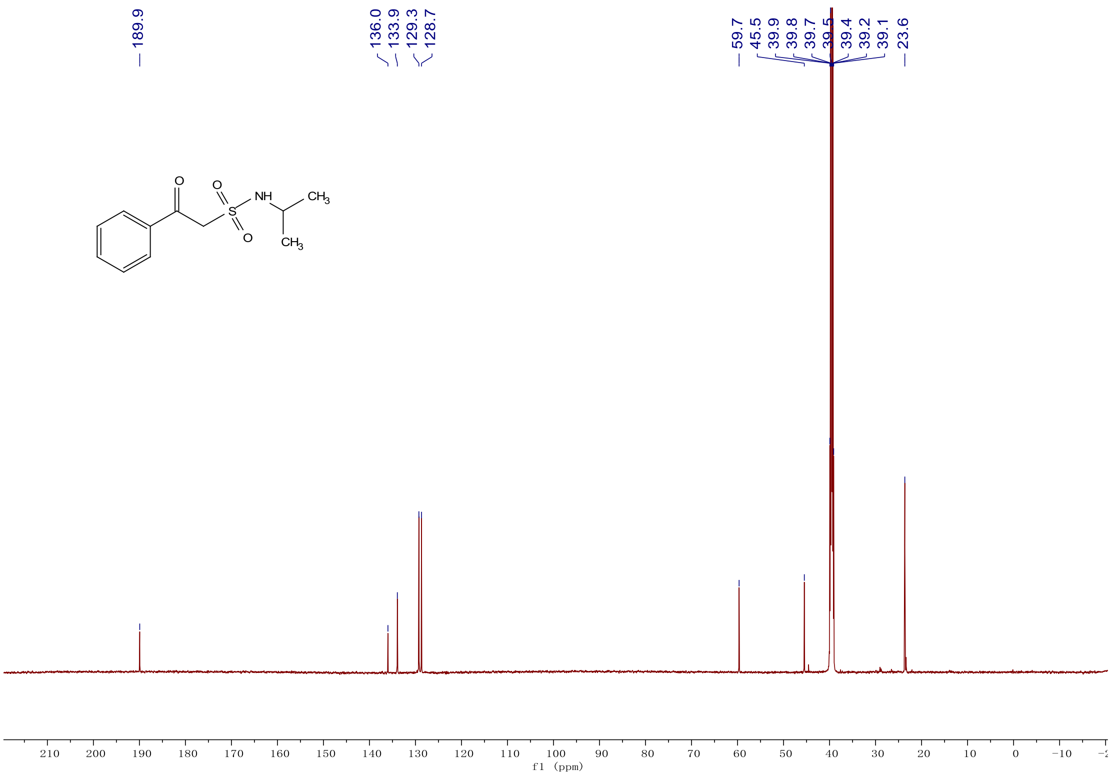
[13]C NMR (150 MHz, DMSO-d_6) of **4c**



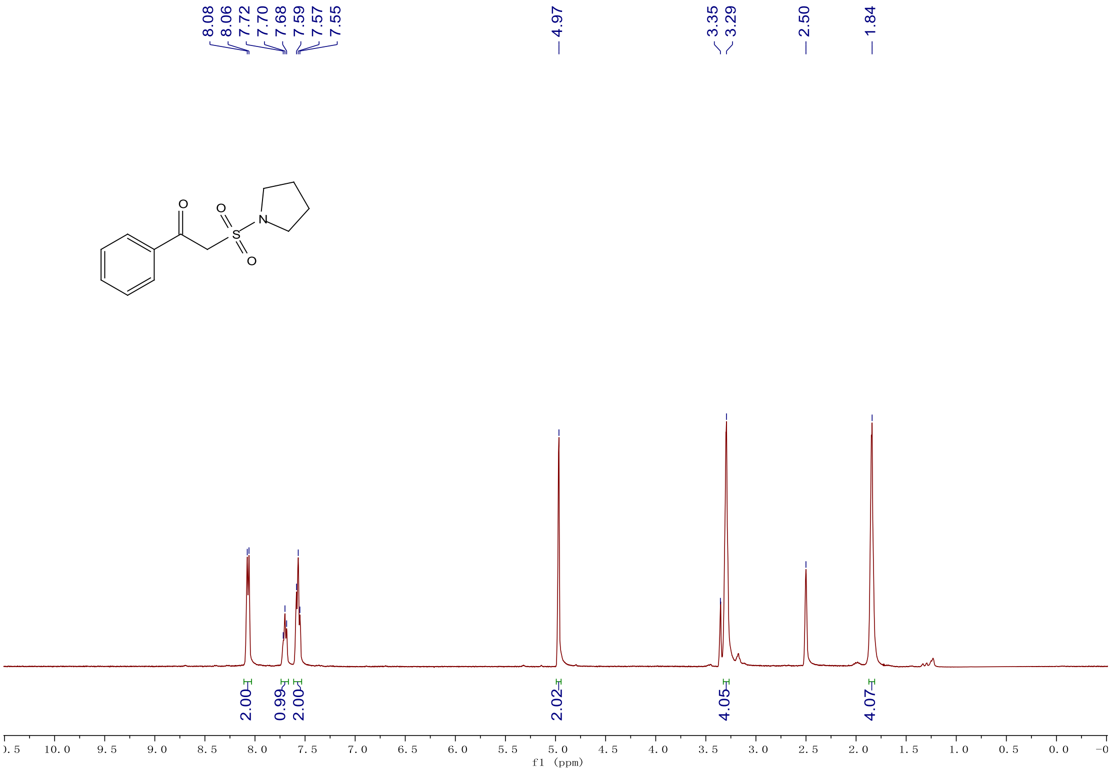
^{1}H NMR (400 MHz, DMSO-d_6) of **4d**



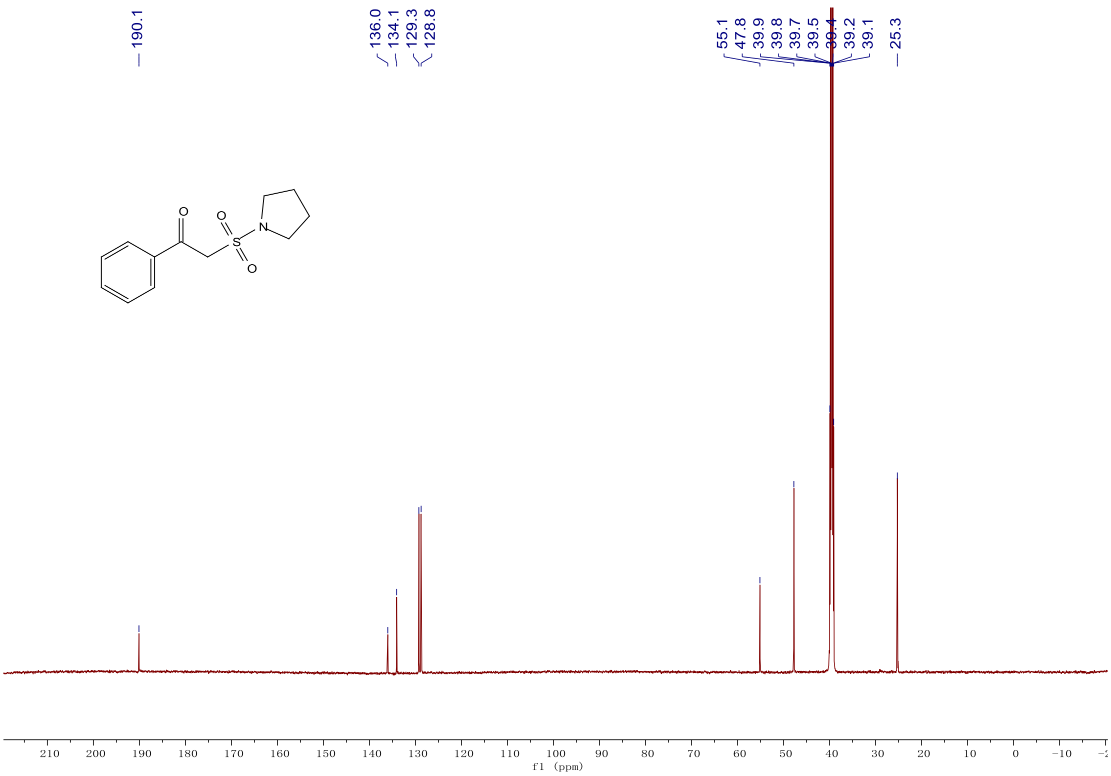
^{13}C NMR (150 MHz, DMSO-d_6) of **4d**



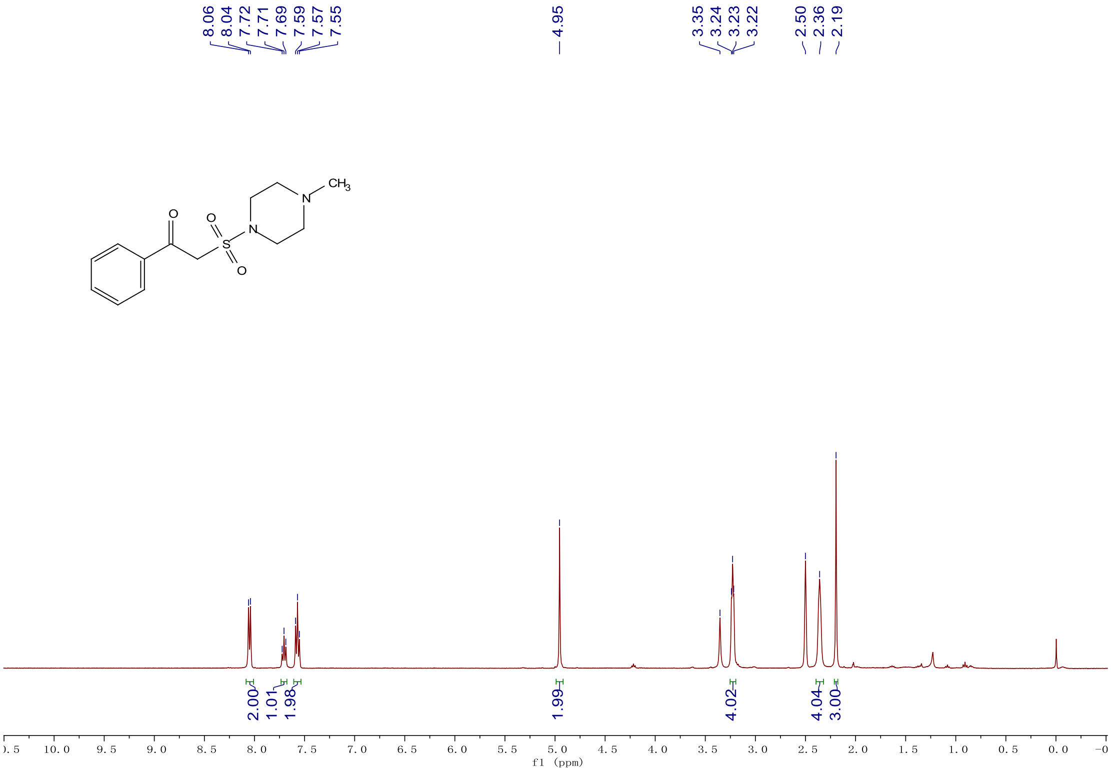
[1]H NMR (400 MHz, DMSO-d_6) of **4e**



[13]C NMR (150 MHz, DMSO-d_6) of **4e**

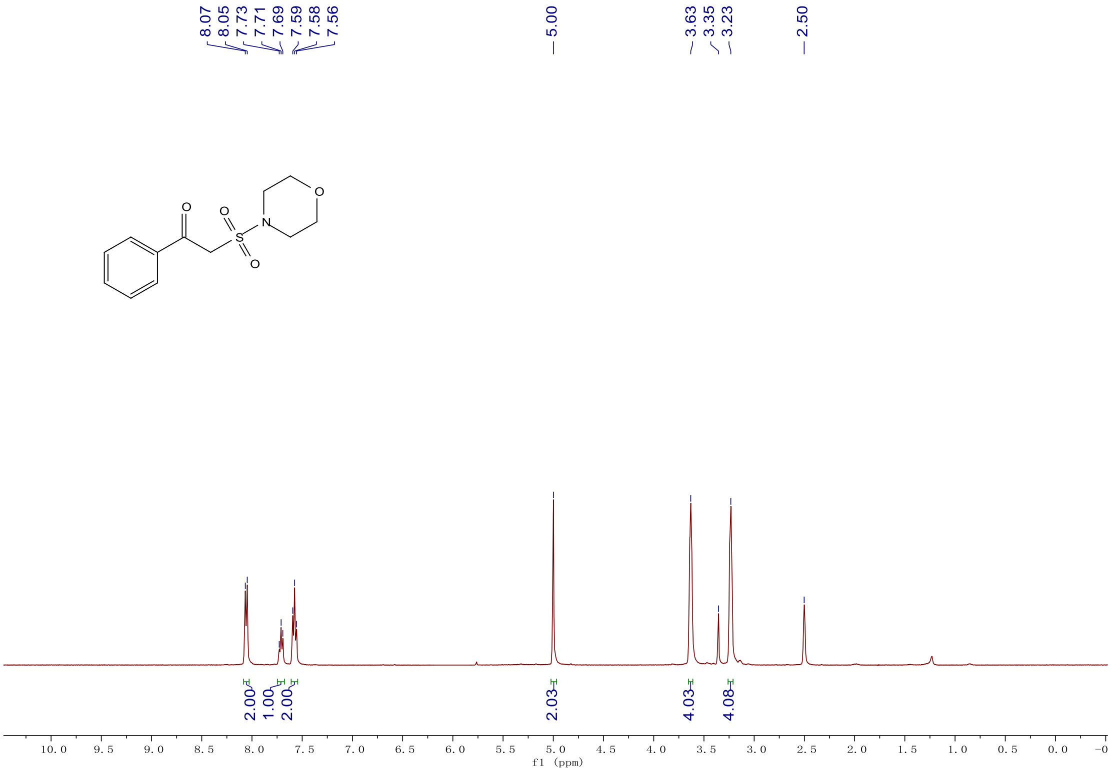


^{1}H NMR (400 MHz, DMSO-d_6) of **4f**

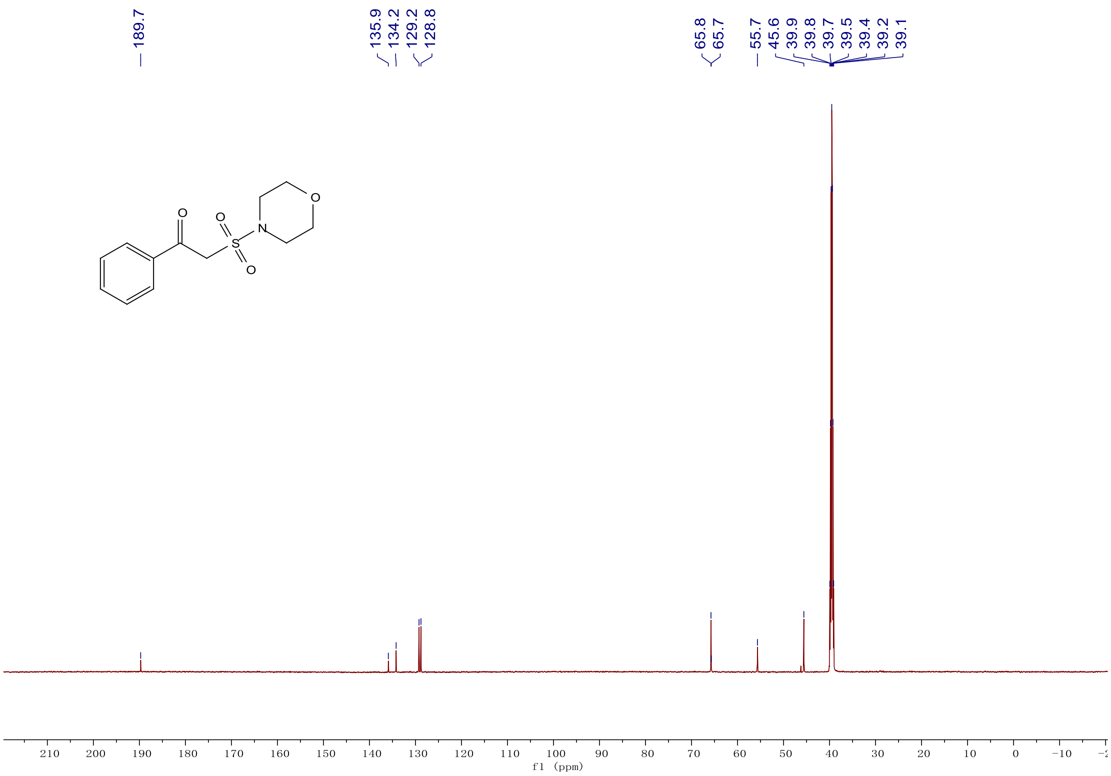


^{13}C NMR (150 MHz, DMSO-d_6) of **4f**

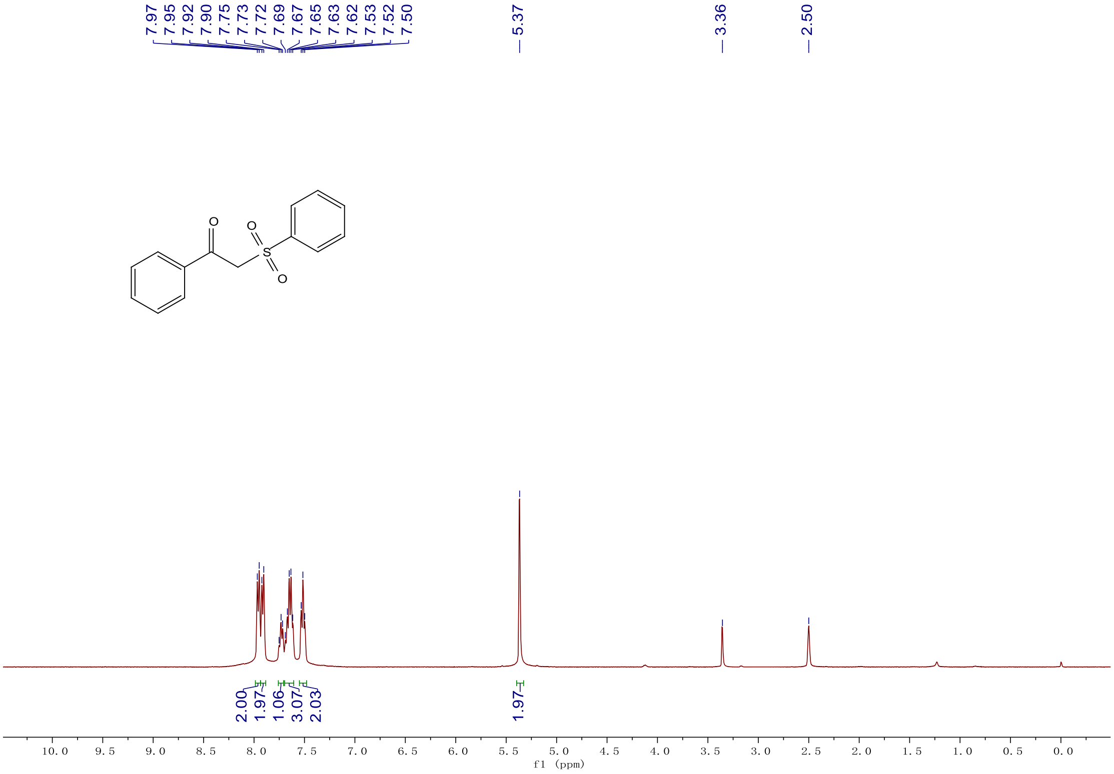
^{1}H NMR (400 MHz, DMSO-d_6) of **4g**



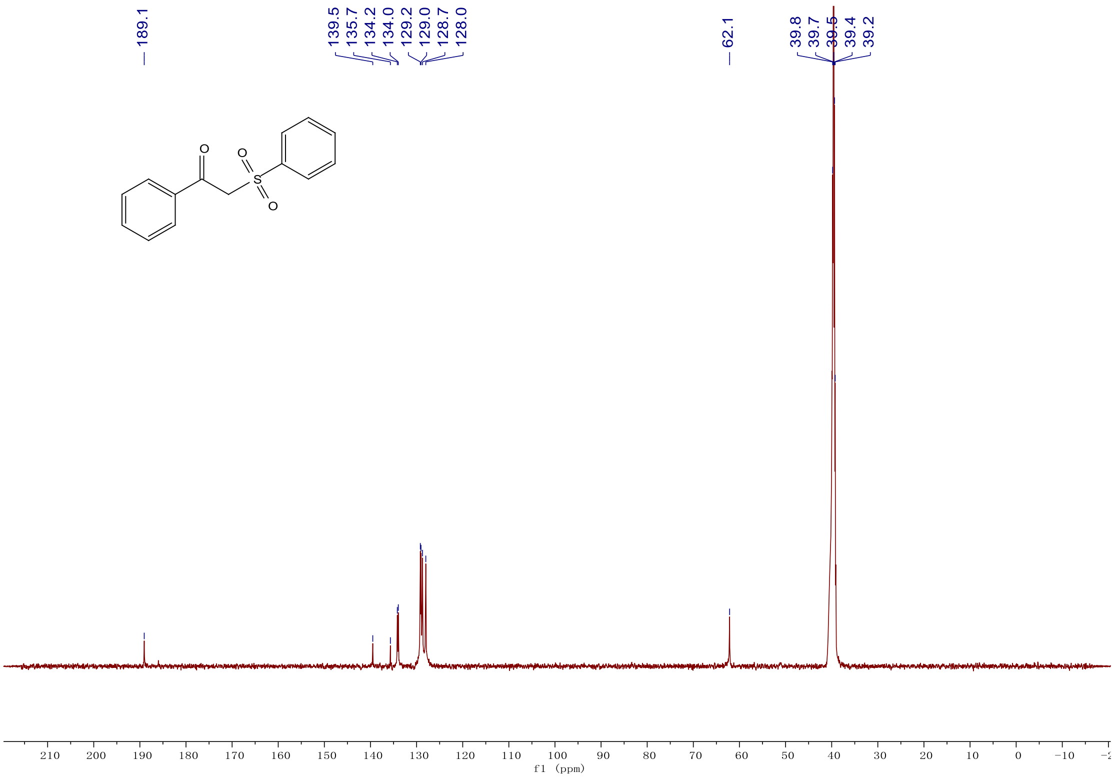
^{13}C NMR (150 MHz, DMSO-d_6) of **4g**



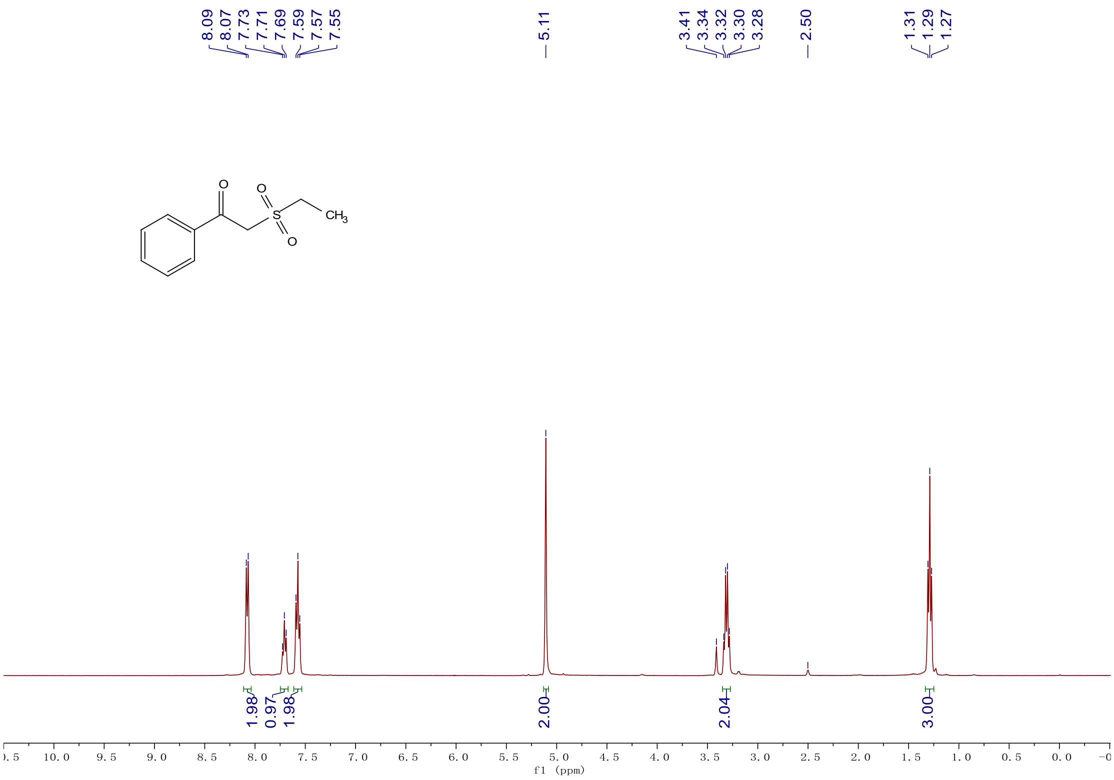
^{1}H NMR (400 MHz, DMSO-d_6) of **4h**



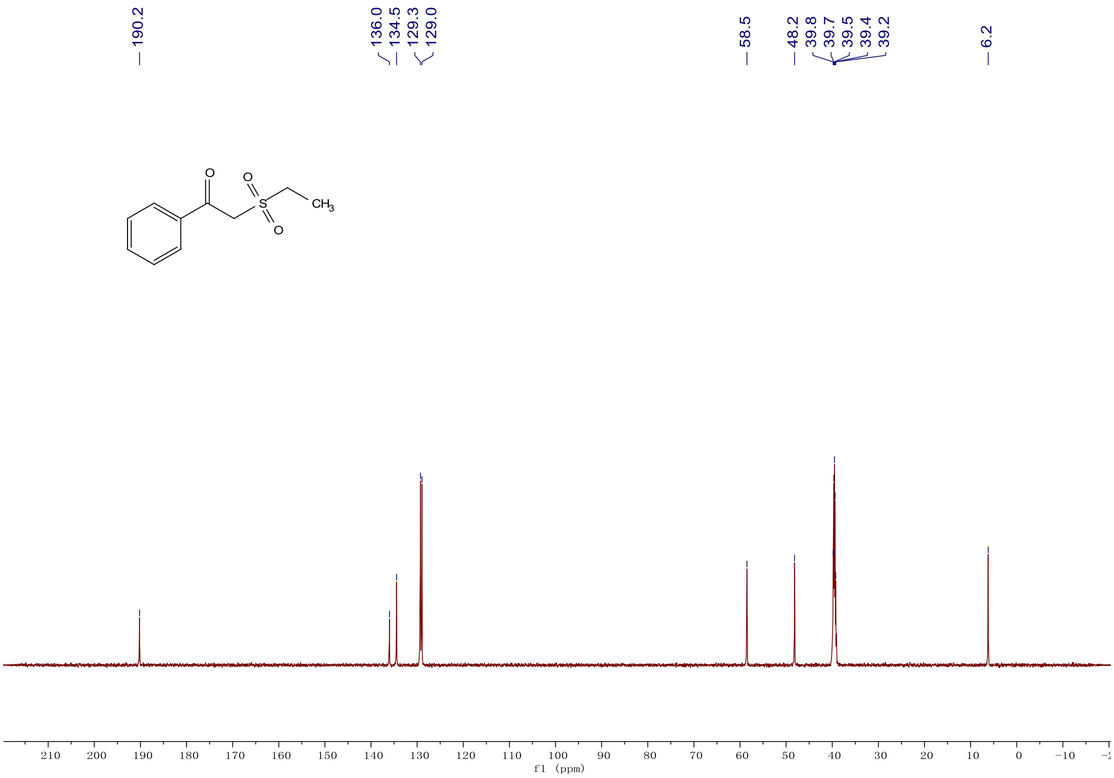
^{13}C NMR (150 MHz, DMSO-d_6) of **4h**



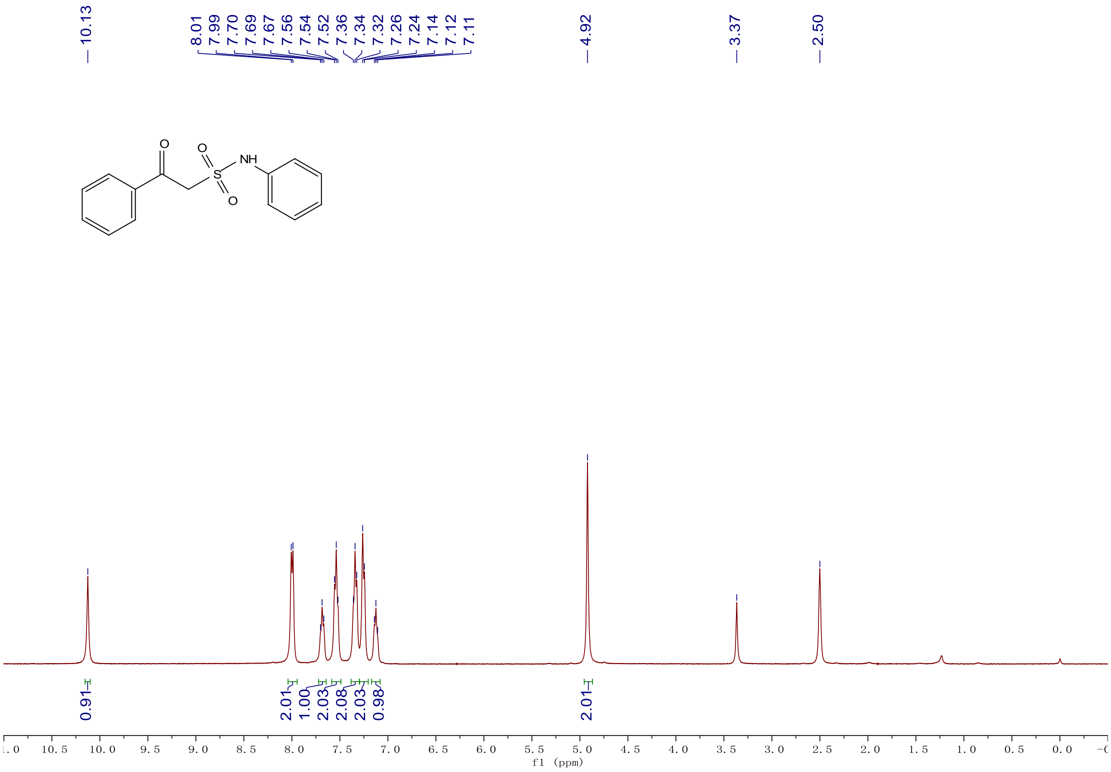
^{1}H NMR (400 MHz, DMSO-d_6) of **4i**



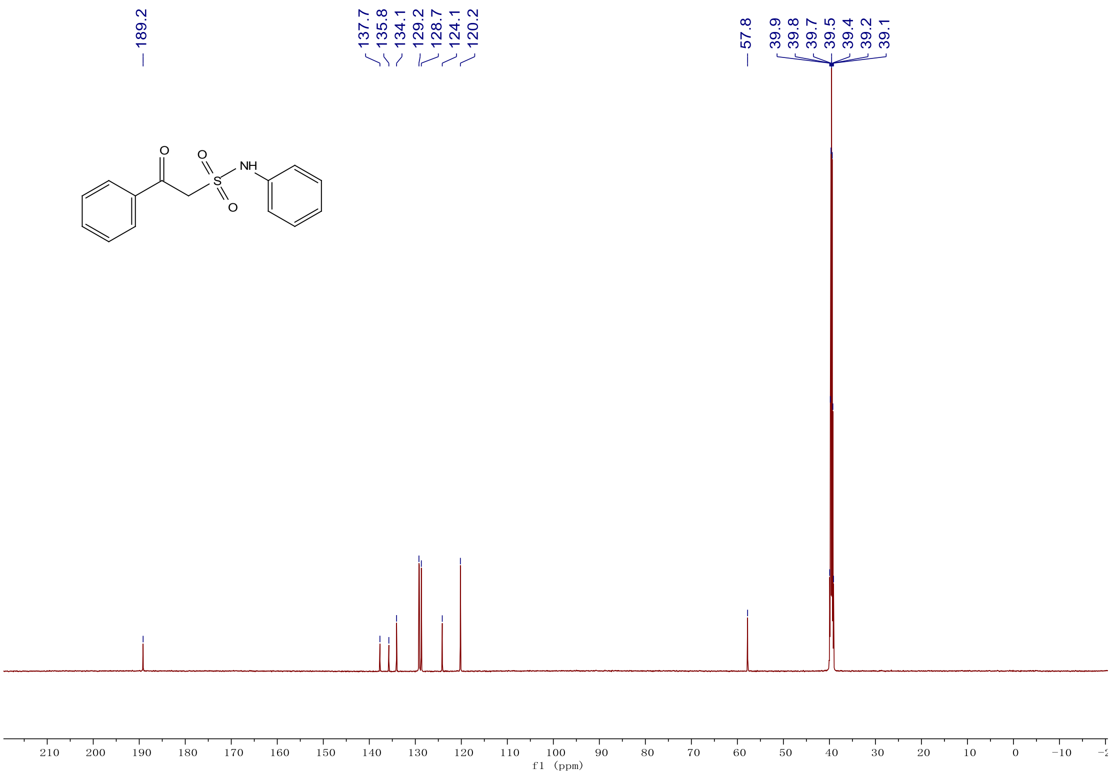
^{13}C NMR (150 MHz, DMSO-d_6) of **4i**



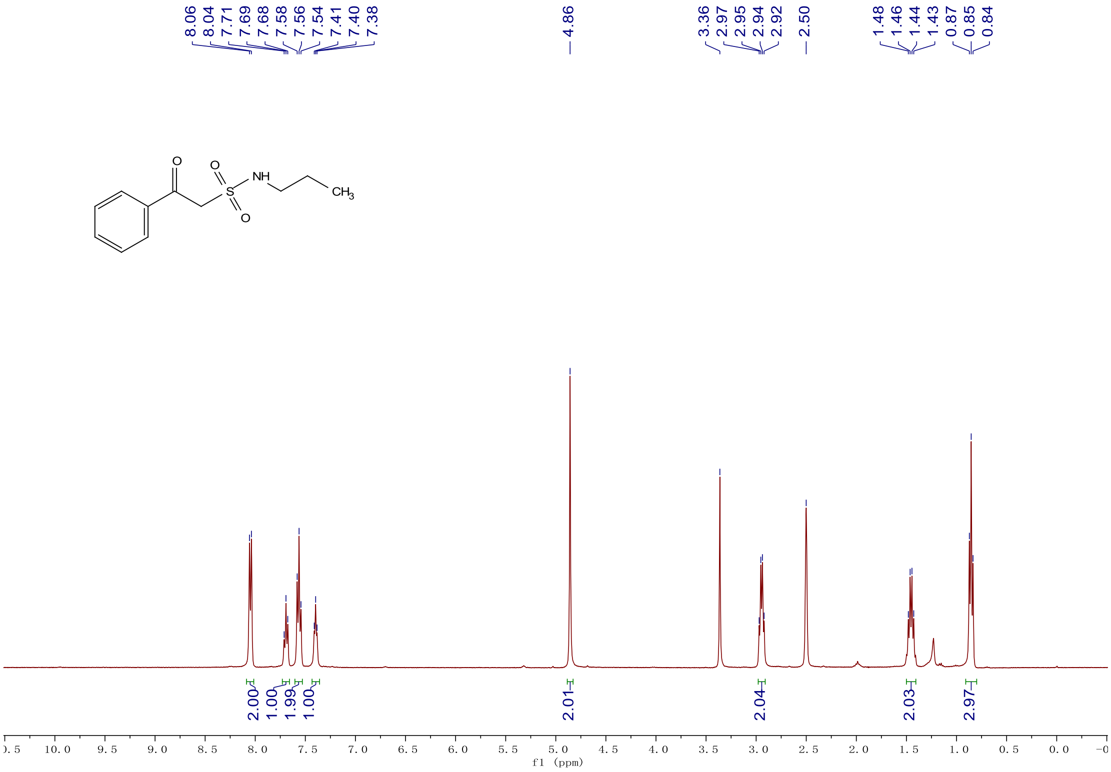
[1]H NMR (400 MHz, DMSO-d_6) of **5**



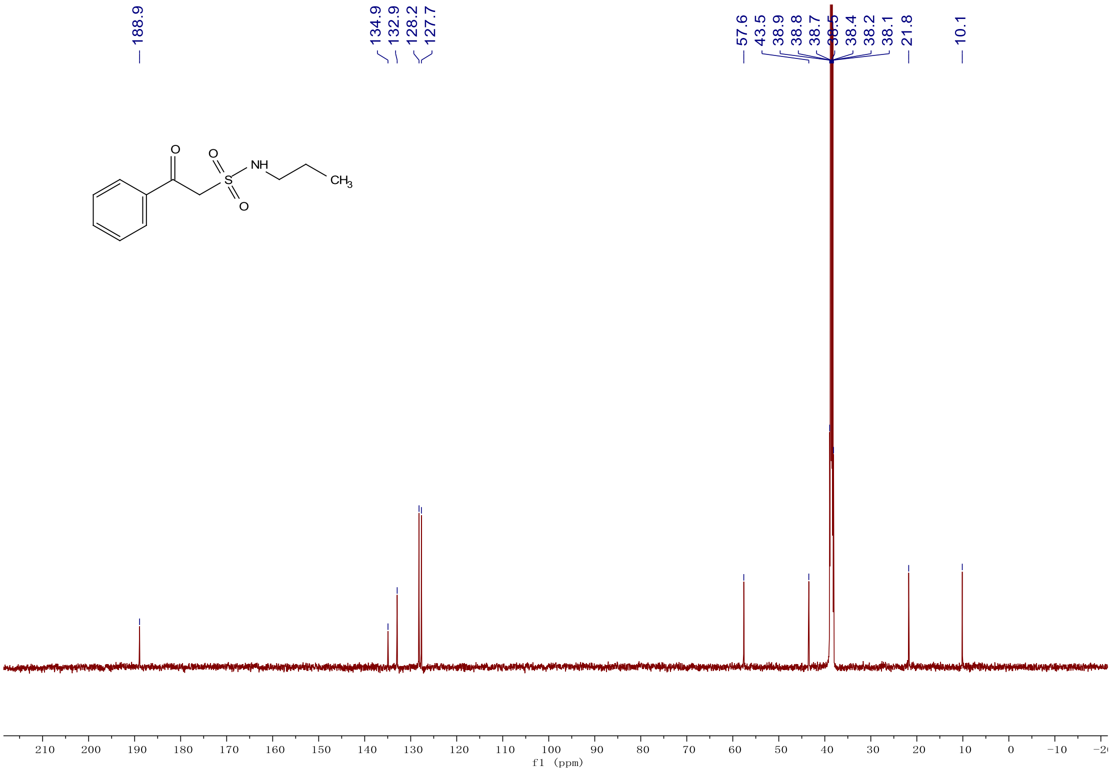
[13]C NMR (150 MHz, DMSO-d_6) of **5**



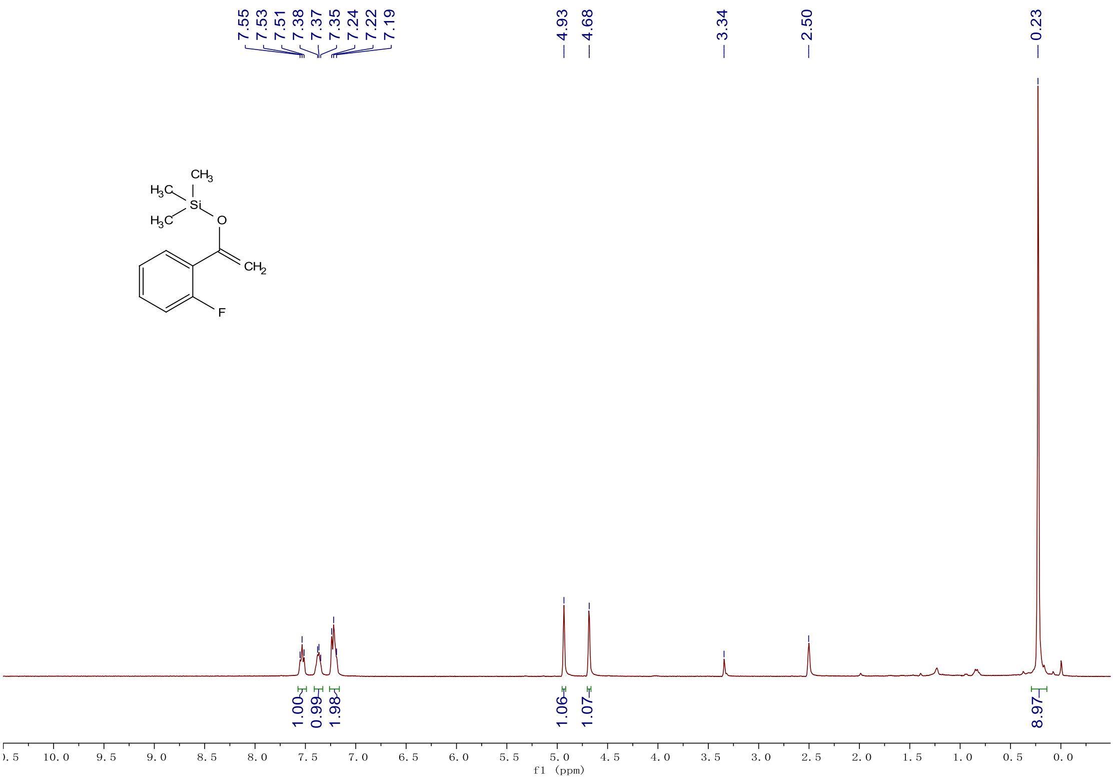
^{1}H NMR (400 MHz, DMSO-d_6) of **6**



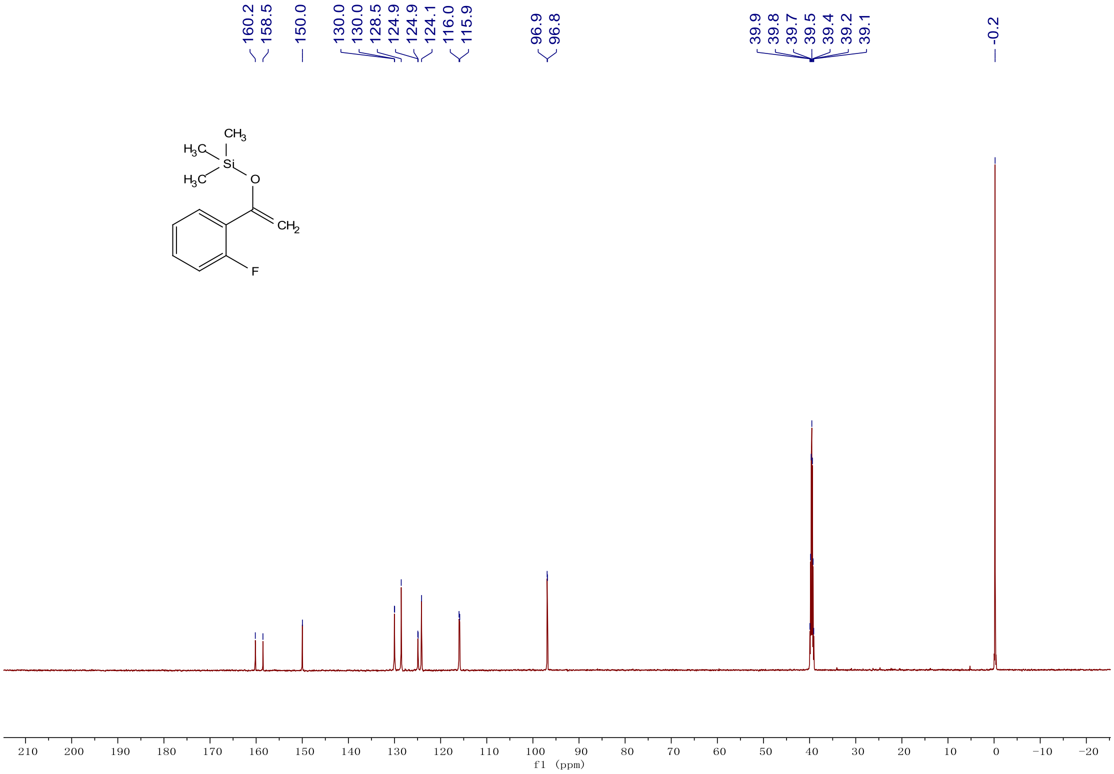
^{13}C NMR (150 MHz, DMSO-d_6) of **6**



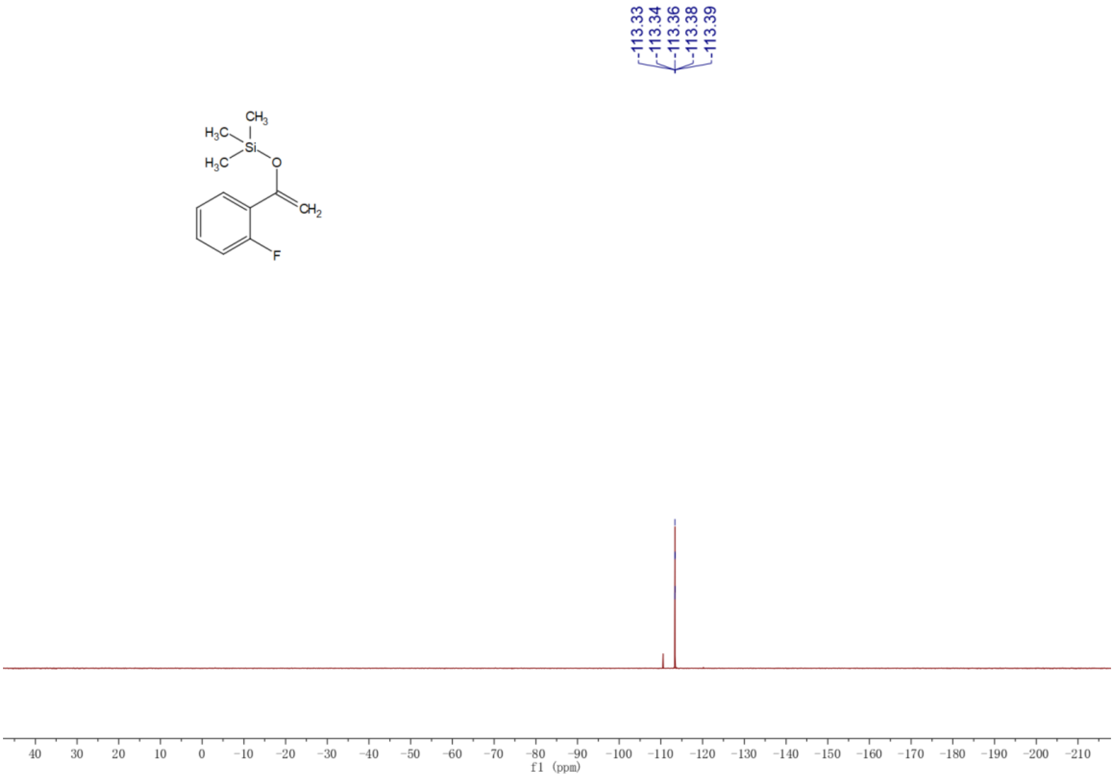
¹H NMR (400 MHz, DMSO-d_6) of **7b**



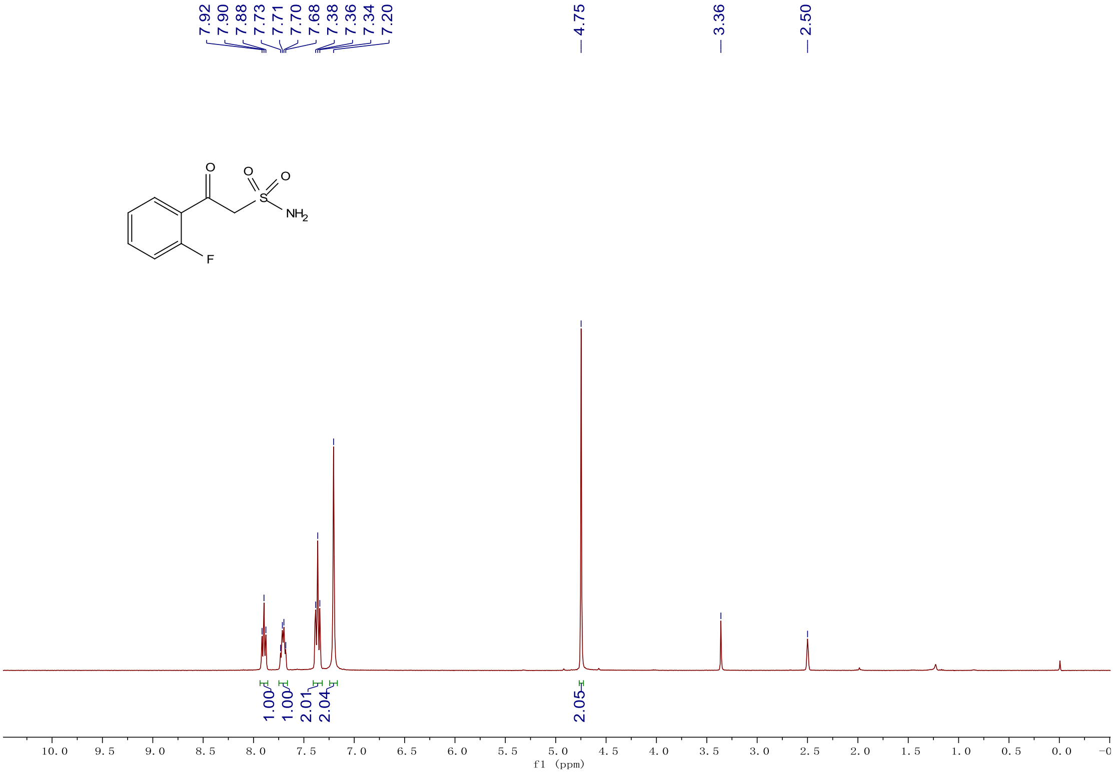
¹³C NMR (150 MHz, DMSO-d_6) of **7b**



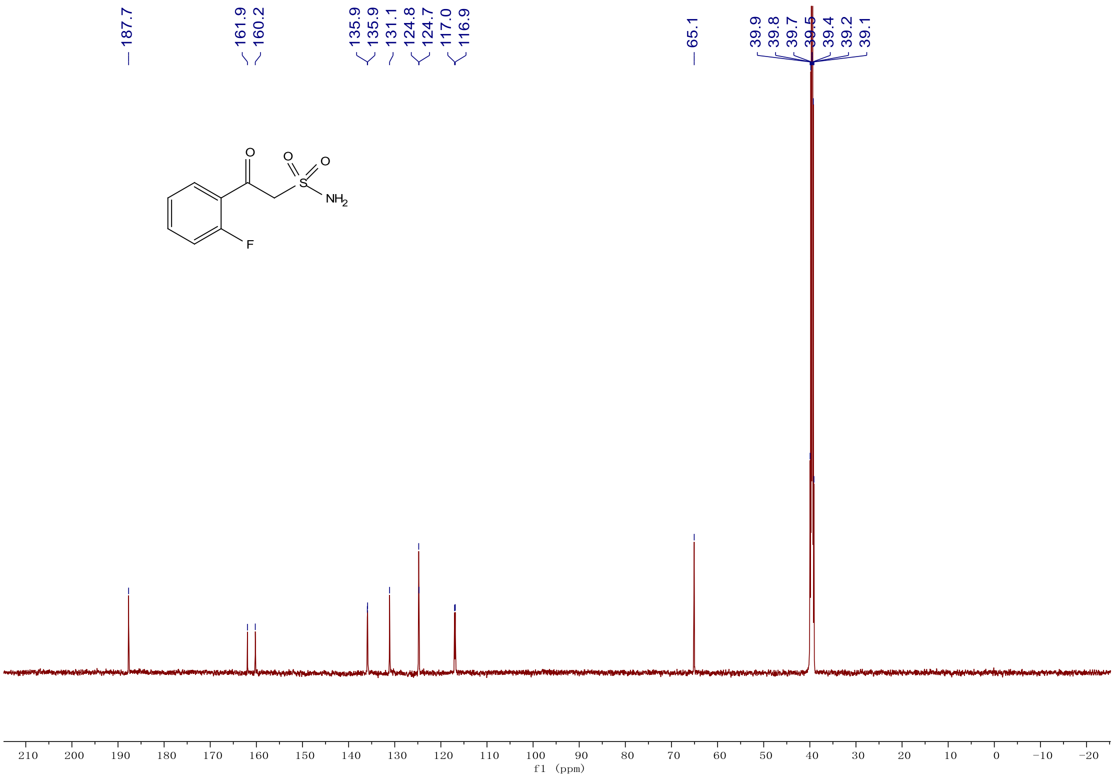
^{19}F NMR (376 MHz, DMSO-d_6) of **7b**



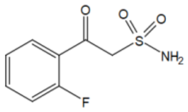
[1]H NMR (400 MHz, DMSO-d_6) of **7c**

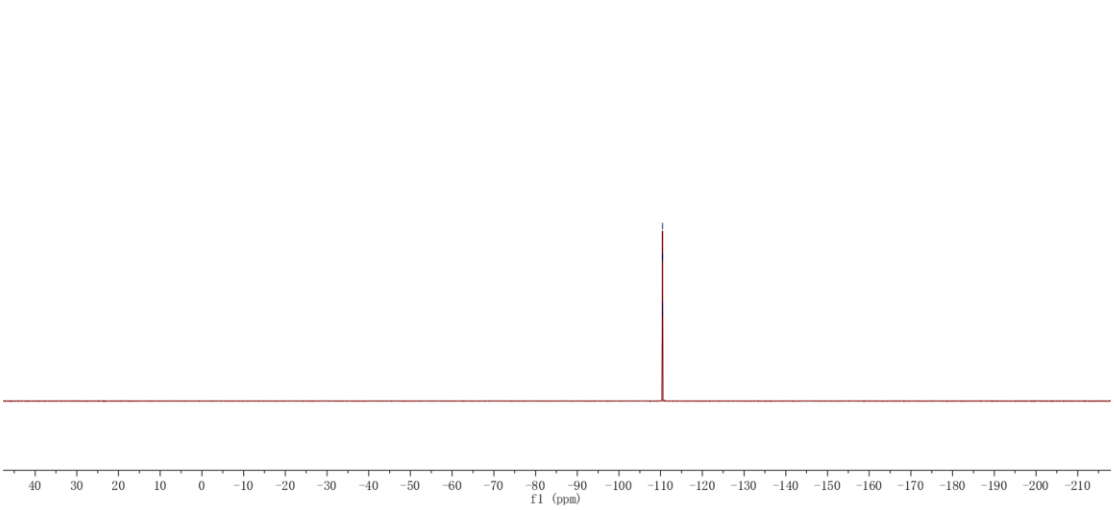


[13]C NMR (150 MHz, DMSO-d_6) of **7c**

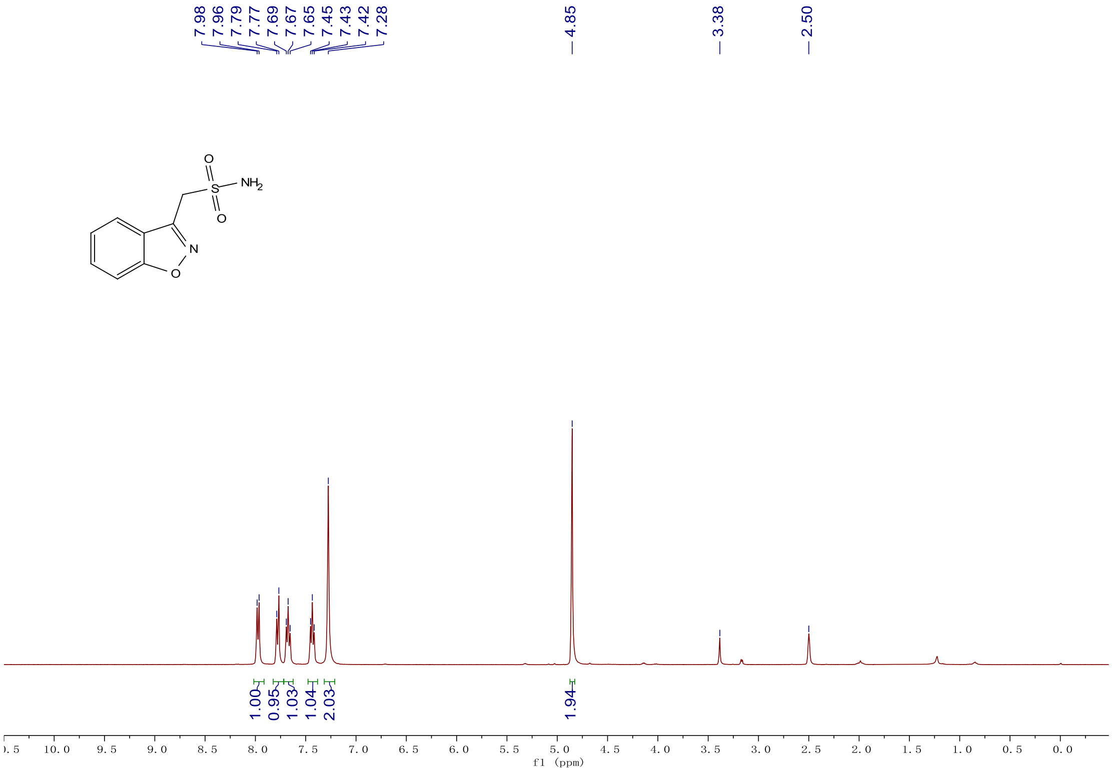


^{19}F NMR (376 MHz, DMSO-d_6) of **7c**

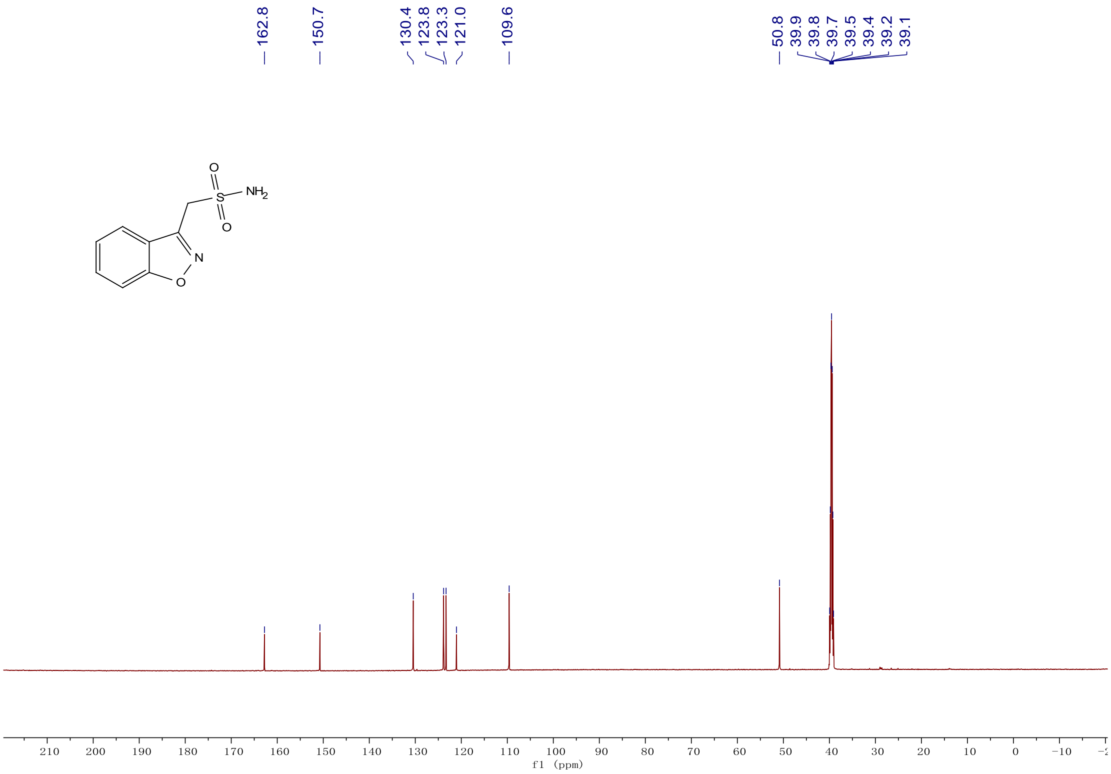




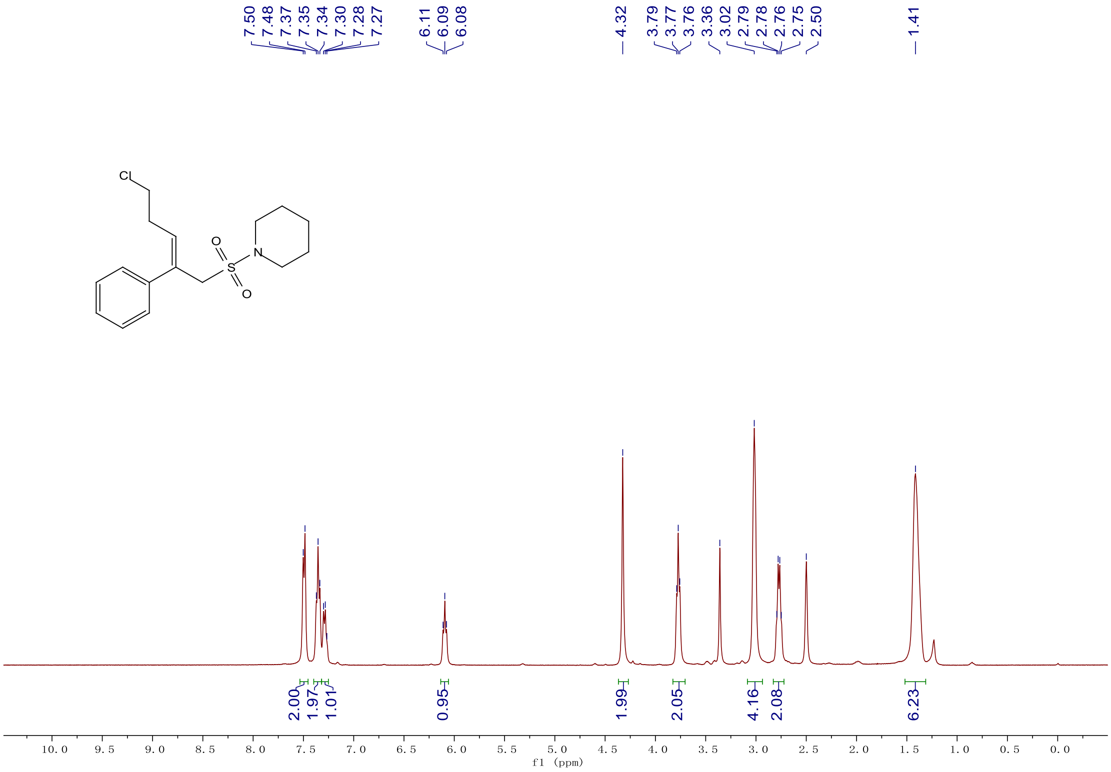
^{1}H NMR (400 MHz, DMSO-d_6) of **7**



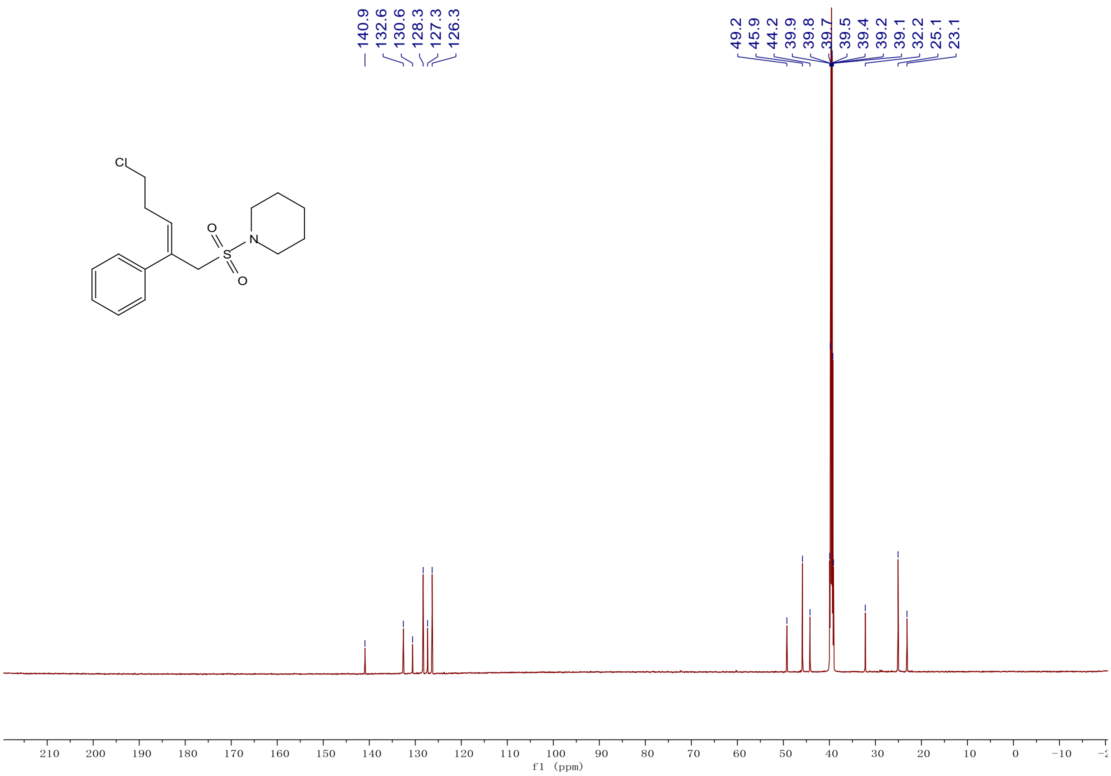
^{13}C NMR (150 MHz, DMSO-d_6) of **7**



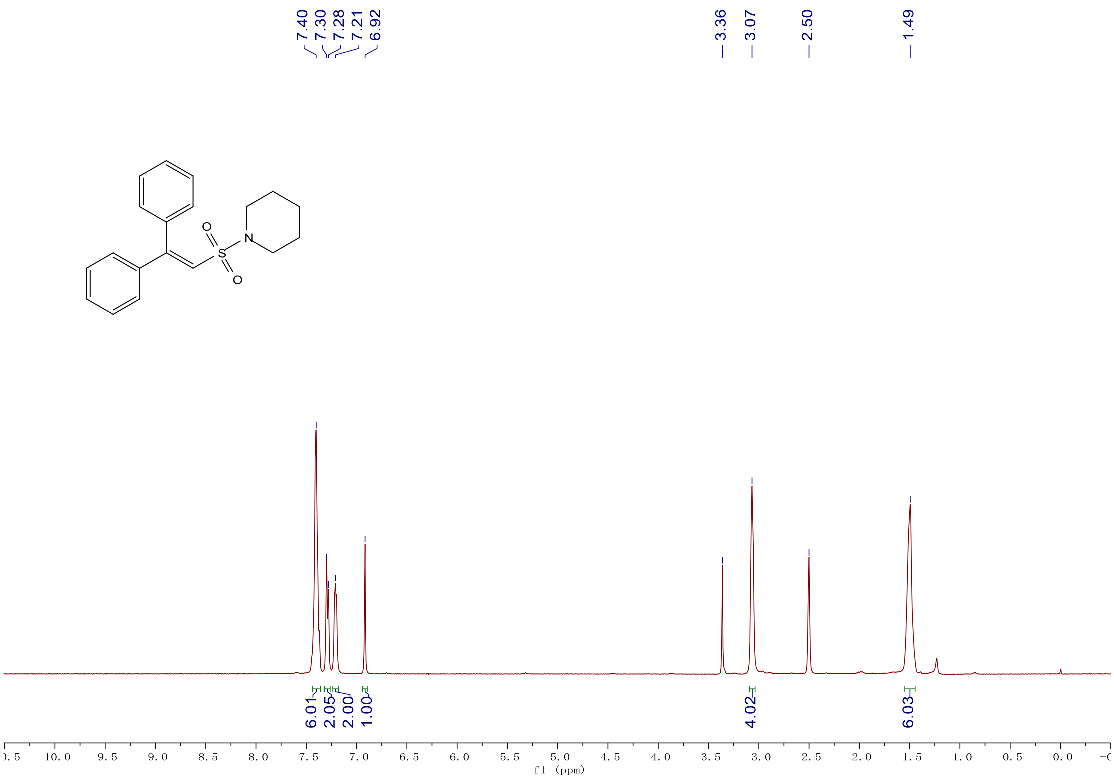
¹H NMR (400 MHz, DMSO-d_6) of **8**



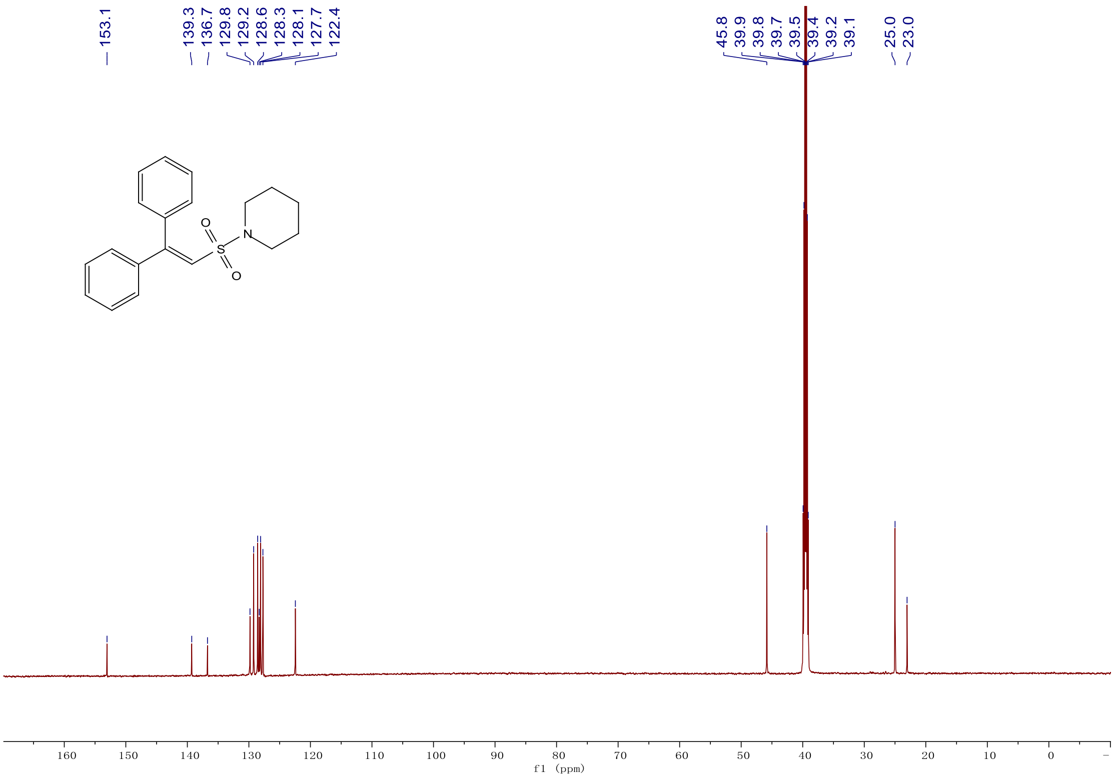
¹³C NMR (150 MHz, DMSO-d_6) of **8**



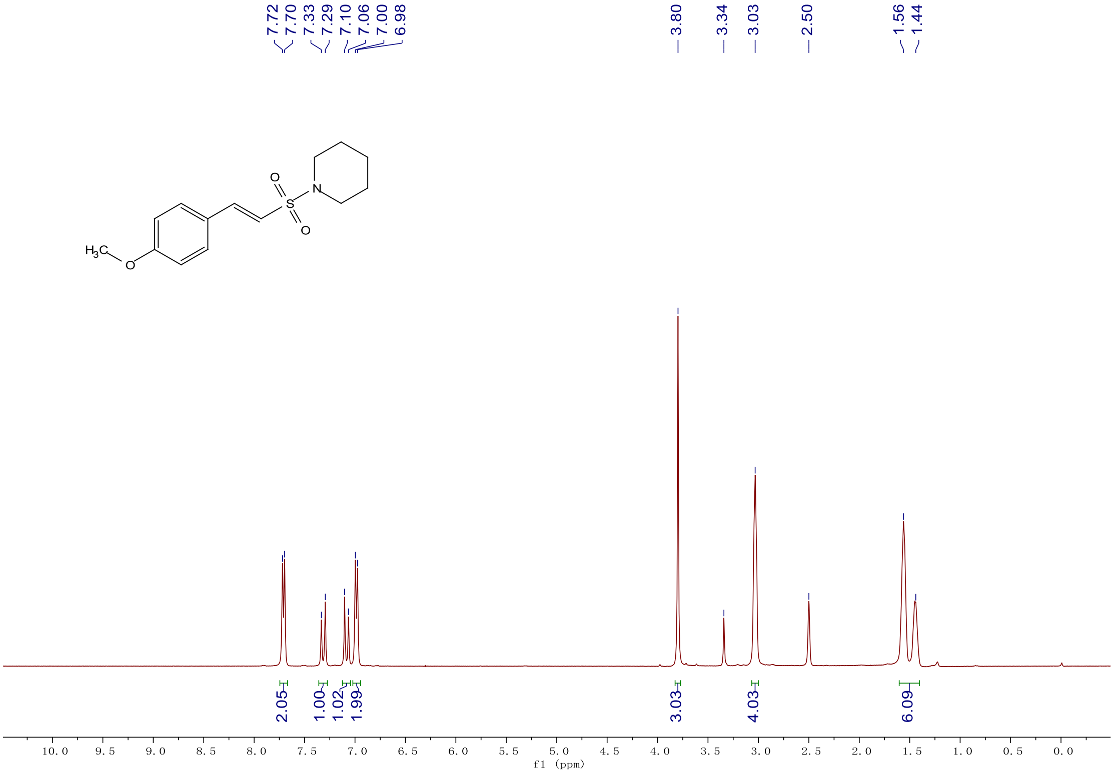
^{1}H NMR (400 MHz, DMSO-d_6) of **9**



^{13}C NMR (150 MHz, DMSO-d_6) of **9**



¹H NMR (400 MHz, DMSO-d_6) of **10**



¹³C NMR (150 MHz, DMSO-d_6) of **10**