Supporting Information

Chromium-Catalysed Efficient *N*-formylation of Amines with a Recyclable Polyoxometalate-supported Green Catalyst

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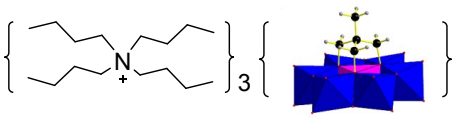
1. Chemicals

The Cr-Anderson POM catalyst was synthesized using the previously published literature method[1], and all the materials used in the experiment were purchased from Sigma-Aldrich and Adamas-beta, and they were used directly without further purification. ^{1}H-NMR ^{13}C-NMR experiments were acquired on Bruker AVANCE III 500 MHz (500 MHz for proton, 125MHz for carbon) spectrometer by using tetramethylsilane as the internal reference and DMSO-d_6 or $CDCl_3$ as solvent. FT-IR Spectrometer were recorded on a Thermo fisher Nicolet 6700 using potassium bromide tableting method. XRD were tested on D/max 2200PC of Japan. GCMS-QP2010 with RTX-5MS capillary column(0.25mm×30m). Column chromatography was used 300-400 mesh.

2. Preparation and Characterizations of Catalyst



$[NH_4]_3[CrMo_6O_{18}(OH)_6]$ •$7H_2O$ was synthesized that depicted in earlier works[1-2]. Firstly, $[NH_4]_6Mo_7O_{24}$ •$4H_2O$ weighed a certain amount (5.0 g) was dissolved in 100 mL water, then stirring at 100 ℃ in oil-filled magnetic stirrer. Secondly, $Cr(NO_3)_3 \cdot 9H_2O$ (2.3 g) was dissolved in 20 mL water, then added into the above solution drop by drop. Finally, the mixed solution was extracted and filtered, and the filtrate was placed at room temperature for 72 hs, after the crude samples were crystallized and dried obtaining purplish crystals. It is worth mentioning that the hydrogen ion concentration (pH) of the mixed solution was conducting in *ca* 2.5, using nitric acid to adjust by pH indicator paper to monitor.

$(NH_4)_3[CrMo_6O_{24}H_6]$ ·$7H_2O$ (2.4 g, 2.0 mmol), $CH_3C(CH_2OH)_3$ (0.36 g, 3.0 mmol） and H_2O (20 mL) was refluxed for 24 hs. After the solution was cooled to room temperature and the tetrabutyl ammonium bromide (2.0 g, 6.2 mmol) was added and still stirred for 1h. Then the large pink-purple solid appeared and filtered off.

3. FT-IR spectra of catalysts 1

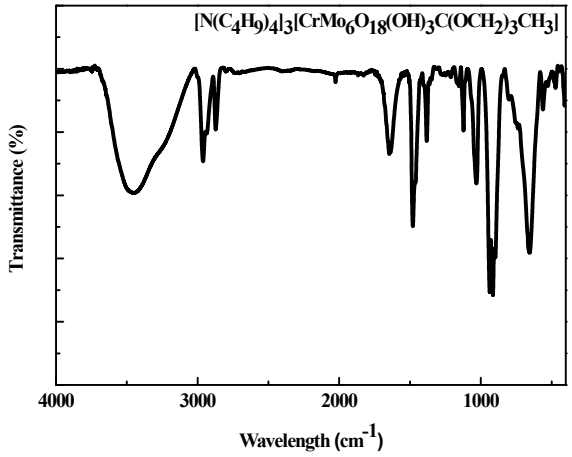


Figure S1. FT-IR spectra of Cat.1

4. XRD spectra of catalysts 1

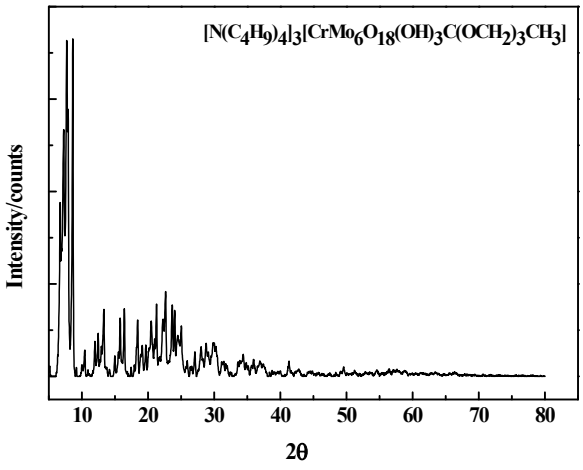


Figure S2. XRD spectra of Cat.**1**

5. ^{1}C-NMR spectra of catalysts 1

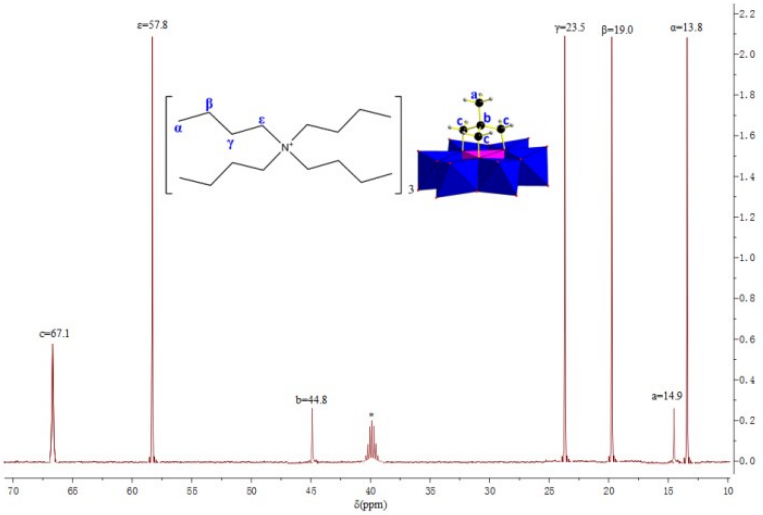
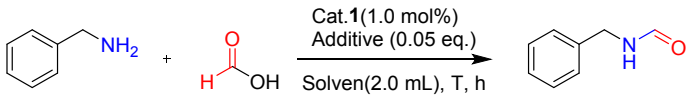


Figure S3. ^{1}C-NMR spectra of Cat.1

6. Reaction Optimization

Table S1. The effect of temperature, time, additive and solvent on *N*-formylation of amines [a]

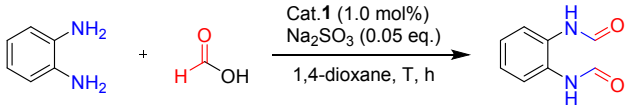


Entry	T (°C)	Time (h)	Additive	Solvent	Yield [b] (%)
1	30	2	Na_2SO_3	1,4-dioxane	34
2	40	2	Na_2SO_3	1,4-dioxane	57
3	50	2	Na_2SO_3	1,4-dioxane	72
4	60	2	Na_2SO_3	1,4-dioxane	80
5	70	2	Na_2SO_3	1,4-dioxane	89
6	80	2	Na_2SO_3	1,4-dioxane	92
7	90	2	Na_2SO_3	1,4-dioxane	78
8	**80**	**4**	Na_2SO_3	1,4-dioxane	**>99**
9	80	6	Na_2SO_3	1,4-dioxane	91
10	80	4	CH_3COONa	1,4-dioxane	64
11	80	4	Na_2CO_3	1,4-dioxane	75
12	80	4	Na_2SO_4	1,4-dioxane	33
13	80	4	K_2SO_4	1,4-dioxane	33
14	80	4	KBr	1,4-dioxane	24
15	80	4	KCl	1,4-dioxane	15
16	80	4	Na_2SO_3	Toluene	84

17	80	4	Na_2SO_3	THF	71
18	80	4	Na_2SO_3	DMF	81
19	80	4	Na_2SO_3	CH_2Cl_2	73

[a] Reaction conditions: Cat.**1** (1.0 mol%), benzylamine (1.0 mmol), formic acid (2.0 mmol), solvent (2.0 mL), Na_2SO_3 (0.05 eq.) stirring at 80 °C for 2 h. [b] Substrate conversion and yields were determined by GC-MS analysis (The external standard is toluene).

Table S2: Effect of temperature, time and amount of formic acid of *N*-formylation on diamine[a]



Entry	T (°C)	HCOOH (mmol)	T (h)	Yield [b] (%)
1	60	2	24	42
2	70	2	24	49
3	75	2	24	65
4	80	2	24	73
5	85	2	24	60
6	90	2	24	56
7	95	2	24	43
7	80	2.5	24	61
8	80	3	24	72
9	80	3.5	24	79
10	**80**	**4**	**24**	**86**
11	80	4.5	24	74
12	80	5	24	67
13	80	4	12	61
15	80	4	36	76

[a] Reaction conditions: Cat.**1** (1.0 mol%), phenylenediamine (1.0 mmol), 1,4-dioxane (2.0 mL), Na_2SO_3 (0.05 eq.) stirring at 80 °C for 24 h. [b] Yields were determined by ^{1}H-NMR, values in parentheses are the isolated yield.

7. Recycling experiments

The Catalyst **1** was precipitated after the cross-coupling reaction by adding organic solvent(ethyl acetate or anhydrous ether),and then recovered for reusing for the next catalytic reaction (Figure S2). The recovered catalyst was characterized by FTIR (Figure S3).

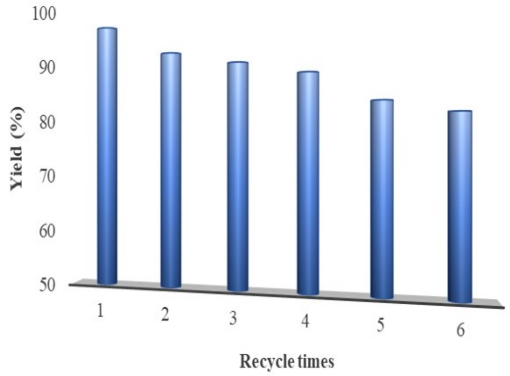


Figure S4. Recycling experiments for the cat. 1.

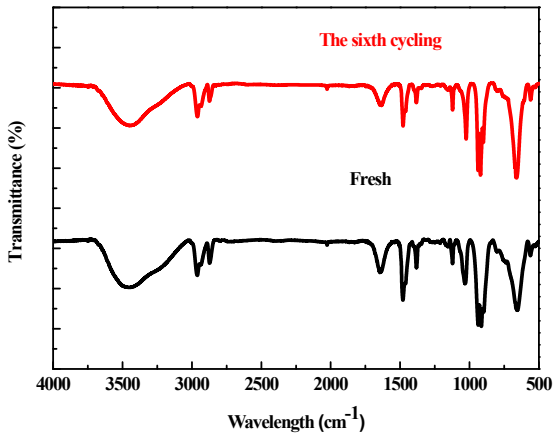
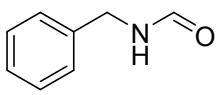
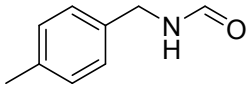


Figure S5. FT-IR spectra of Cat. 1 before and after reaction.

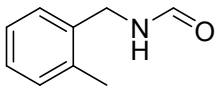
8. NMR data of products and spectra



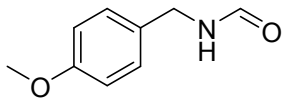
***N*-benzylformamide(2)[3-7]:** ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.33 – 7.28 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.22 (s, 1H), 4.37 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.83 (s), 137.75 (s), 128.08 (s), 127.04 (s), 42.37 (s).



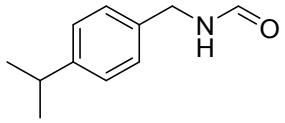
***N*-(4-methylbenzyl)formamide(3)[3-7]:** ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.28 (s, 1H), 7.20 (s, 2H), 7.18 (s, 2H), 4.43 (s, 2H), 2.35 – 2.34 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.06 (s), 137.43 (s), 134.59 (s), 129.45 (s), 127.81 (s), 41.95 (s), 21.10 (s).



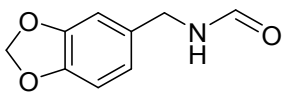
***N*-(2-methylbenzyl)formamide(4)[3-7]:** ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.17 (s, 1H), 7.37 (s, 4H), 4.83 (s, 2H), 1.54 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.38 (s), 142.51 (s), 128.79 (s), 127.60 (s), 126.17 (s), 125.80 (s), 47.65 (s), 21.74 (s).



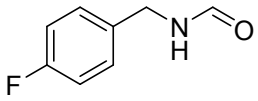
***N*-(4-methoxybenzyl)formamide(5)[3-7]:** ^{1}H NMR (501 MHz, DMSO) δ 8.45 (s, 1H), 8.22 (s, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 4.34 (d, *J* = 6.0 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 163.34 (s), 158.88 (s), 131.30 (s), 129.10 (s), 114.10 (s), 55.24 (s), 40.82 (s).



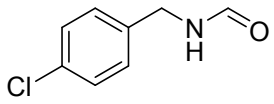
***N*-(4-isopropylbenzyl)formamide(6)[3-7]:** ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.20 (d, *J* = 5.8 Hz, 4H), 4.40 (d, *J* = 5.6 Hz, 2H), 2.89 (d, *J* = 6.8 Hz, 1H), 1.26 – 1.22 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.40 (s), 148.39 (s), 134.95 (s), 127.86 (s), 127.33 (d, *J* = 129.7 Hz), 41.91 (s), 33.82 (s), 23.85 (s).



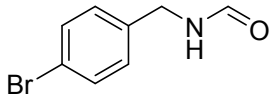
***N*-(benzo[d][1,3]dioxol-5-ylmethyl)formamide(7)[3-7]:** ^{1}H NMR (501 MHz, DMSO) δ 8.44 (s, 1H), 8.12 (s, 1H), 6.90 – 6.82 (m, 3H), 5.99 (d, *J* = 5.2 Hz, 2H), 4.22 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 161.73 (s), 148.02 (s), 146.88 (s), 133.60 (s), 121.26 (s), 108.72 (d, *J* = 5.9 Hz), 101.59 (s), 41.27 (s).



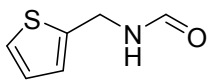
***N*-(4-fluorobenzyl)formamide(8)[3-7]:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.12 (s, 1H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.98 (s, 2H), 4.22 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.04 (s), 129.49 (d, *J* = 8.1 Hz), 115.71 (s), 115.54 (s), 41.46 (s).



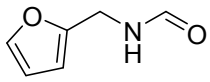
***N*-(4-chlorobenzyl)formamide(9)[3-7]:** ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.31 (t, *J* = 13.6 Hz, 4H), 5.96 (s, 1H), 4.47 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.96 (s), 136.14 (s), 133.58 (s), 129.14 (s), 128.93 (s), 128.31 (s), 41.50 (s).



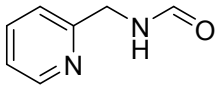
***N*-(4-bromobenzyl)formamide(10)[3-7]:** ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.96 (s, 1H), 4.46 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.03 (s), 136.65 (s), 131.90 (s), 129.49 (s),121.63(s), 41.56 (s).



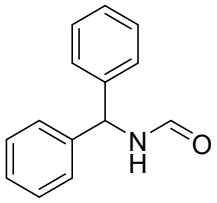
***N*-(thiophen-2-ylmethyl)formamide(11)[3-7]:** ^{1}H NMR (501 MHz, DMSO) δ 8.52 (s, 1H), 8.02 (s, 1H), 7.29 (s, 1H), 6.90 (d, *J* = 3.6 Hz, 2H), 4.40 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 161.40 (s), 142.30 (s), 127.18 (s), 126.05 (s), 125.55 (s), 36.20 (s).



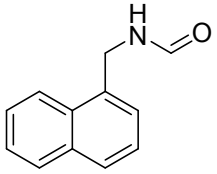
***N*-(furan-2-ylmethyl)formamide(12)[3-7]:** ^{1}H NMR (501 MHz, DMSO) δ 8.38 (s, 1H), 7.98 (s, 1H), 7.47 (s, 1H), 6.29 (s, 1H), 6.16 (s, 1H), 4.21 (d, *J* = 5.1 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 161.38 (s), 152.26 (s), 142.63 (s), 110.89 (s), 34.43 (s).



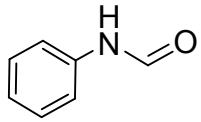
***N*-(pyridin-2-ylmethyl)formamide(13)[3-7]:** ^{1}H NMR (501 MHz, $CDCl_3$) δ 11.58 (s, 1H), 8.57 (s, 1H), 8.21 (s, 1H), 7.69 (s, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 4.83 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.65 (s), 156.97 (s), 148.29 (s), 137.35 (s), 123.77 (s), 120.72 (s), 44.69 (s).



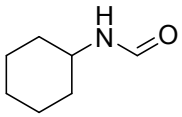
***N*-benzhydrylformamide(14)[3-7]:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.37 – 7.34 (m, 4H), 7.31 (d, *J* = 7.1 Hz, 2H), 7.26 (d, *J* = 7.1 Hz, 4H), 6.39 (s, 1H), 6.35 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.22 (s), 140.93 (s), 128.97 (s), 128.76 (s), 128.03 (s), 127.66 (s), 127.32 (d, *J* = 18.7 Hz), 55.72 (s).



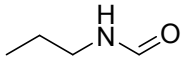
***N*-(naphthalen-1-ylmethyl)formamide(15)[3-7]:** ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.99 (s, 1H), 7.92 – 7.76 (m, 3H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.43 (s, 2H), 4.90 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.94 (s), 133.88 (s), 132.83 (s), 128.84 (s), 126.78 (d, *J* = 8.1 Hz), 126.12 (s), 125.41 (s), 123.36 (s), 40.29 (s).



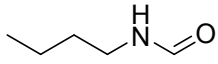
***N*-phenylformamide(16)[3-7]:** ^{1}H NMR (501 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.33 (d, *J* = 1.9 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.11 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.88 (s), 130.41 (s), 129.06 (s), 128.39 (s), 120.94 (s).



***N*-(cyclohexyl)formamide(17)[3-7]:** ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.01 (s, 1H), 6.80 – 6.79 (m, 1H), 3.69 (s, 1H), 1.75 (s, 4H), 1.48 (s, 2H), 1.25 (d, *J* = 12.1 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.67 (s), 49.95 (s),32.70 (s), 25.67 (s), 24.62 (s).

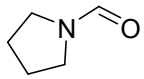


***N*-propylformamide(18)[3-7]:** ^{1}H NMR (501 MHz, DMSO) δ 7.90 (s, 1H), 3.43 (s, 1H), 2.93 (d, *J* = 3.9 Hz, 2H), 1.31 (d, *J* = 10.6 Hz, 2H), 0.74 (d, *J* = 10.7 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 161.46, 39.33, 22.69, 11.69.

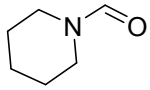


***N*-butylformamide(19)[3-7]:** ^{1}H NMR (501 MHz, DMSO) δ 8.85 (s, 1H), 8.00 (s, 1H), 3.37 (d, *J* = 7.2 Hz, 2H), 1.29 (s, 2H), 1.28 (s, 2H), 0.77 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 161.30 (s), 37.18 (s),

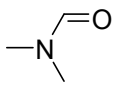
31.52 (s), 19.91 (s), 13.79 (s).



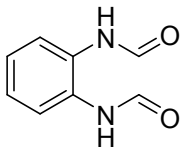
pyrrolidine-1-carbaldehyde(20)[3-7]: ^{1}H NMR (501 MHz, DMSO) δ 8.06 (s, 1H), 3.31 (d, *J* = 18.9 Hz, 4H), 1.69 (s, 4H). ^{13}C NMR (126 MHz, DMSO) δ 161.13 (s), 45.84 (s), 43.11 (s), 24.87 (s), 24.19 (s).



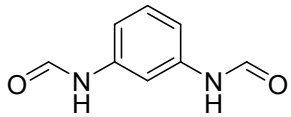
piperidine-1-carbaldehyde(21)[3-7]: ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.02 (s, 1H), 3.41 (dd, *J* = 84.7, 3.4 Hz, 4H), 1.57 (d, *J* = 4.2 Hz, 4H), 1.45 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.09 (s), 47.02 (s), 25.09 (s), 24.68 (s).



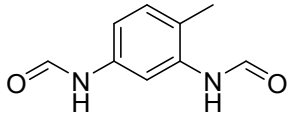
***N, N*-dimethylformamide(22)[3-7]:** ^{1}H NMR (501 MHz, DMSO) δ 7.88 (s, 1H), 2.80 (s, 6H). ^{13}C NMR (126 MHz, DMSO) δ 162.46 (s), 35.78 (s).



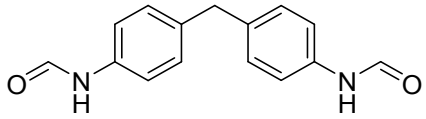
***N, N'*-(1,2-phenylene)diformamide(23):** ^{1}H NMR (501 MHz, DMSO) δ 8.22 (d, *J* = 59.5 Hz, 2H), 7.61 (s, 2H), 7.20 (d, *J* = 2.4 Hz, 2H), 6.44 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 163.56 (s), 122.39 (s), 115.74 (s).



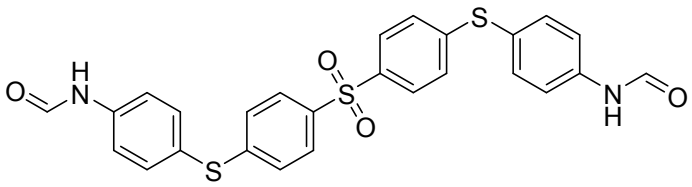
***N, N'*-(1,3-phenylene)diformamide(24):** ^{1}H NMR (501 MHz, DMSO) δ 10.04 (s, 2H), 8.27 (s, 2H), 7.98 (s, 1H), 7.51 (s, 1H), 7.31 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 160.21 (s), 138.82 (s), 129.60 (s), 115.31 (s), 110.90 (s).



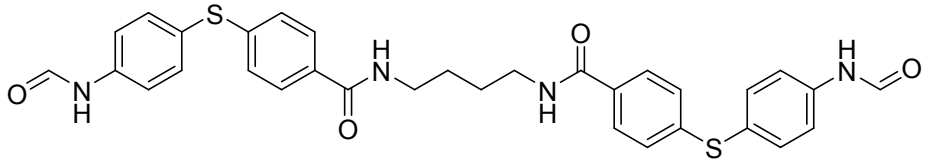
***N, N'*-(4-methyl-1,3-phenylene)diformamide(25):** ^{1}H NMR (501 MHz, DMSO) δ 10.16 (s, 1H), 9.57 (s, 1H), 8.22 (s, 2H), 7.63 (s, 1H), 7.44 (s, 1H), 7.38 (s, 1H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 160.22 (s), 136.21 (s), 131.51 (s), 130.91 (s), 116.10 (s), 114.13 (s), 17.79 (s).



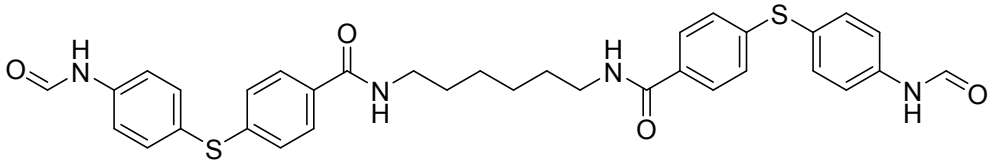
***N, N'*-(methylenebis(1,4-phenylene))diformamide(26):** ^{1}H NMR (501 MHz, DMSO) δ 10.09 (d, *J* = 19.3 Hz, 2H), 8.24 (d, *J* = 1.4 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 4H), 7.15 (d, *J* = 8.1 Hz, 4H), 3.84 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 159.86 (s), 136.71 (s), 129.99 (s), 129.46 (s), 119.75 (s).



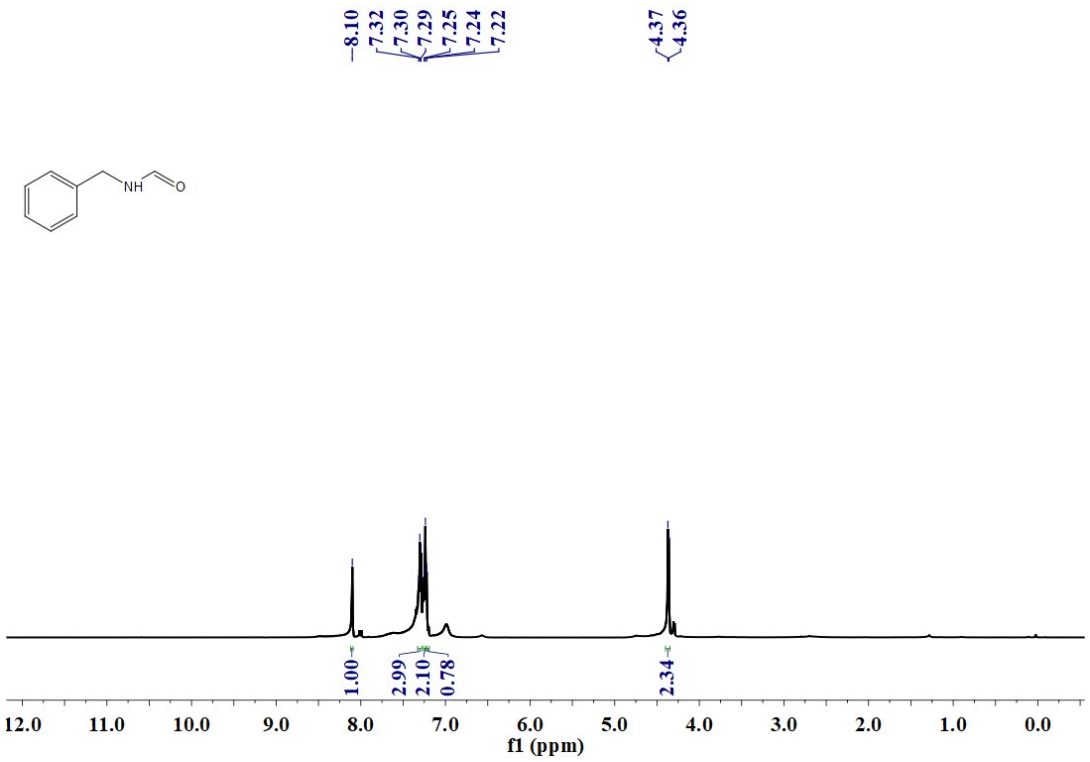
***N, N'*-(((sulfonylbis(1,4-phenylene))bis(sulfanediyl))bis(1,4-phenylene))diformamide(27):** ^{1}H NMR (500 MHz, DMSO) δ 10.47 (s, 2H), 8.34 (s, 2H), 7.77 (d, J = 8.5 Hz, 4H), 7.73 (d, J = 8.4 Hz, 4H), 7.51 (d, J = 8.4 Hz, 4H), 7.19 (d, J = 8.5 Hz, 4H). ^{13}C NMR (125 MHz, DMSO) δ 160.46 (s), 146.66 (s), 140.17 (s), 138.24 (s), 136.29 (s), 128.48 (s), 127.01 (s), 121.01 (s).



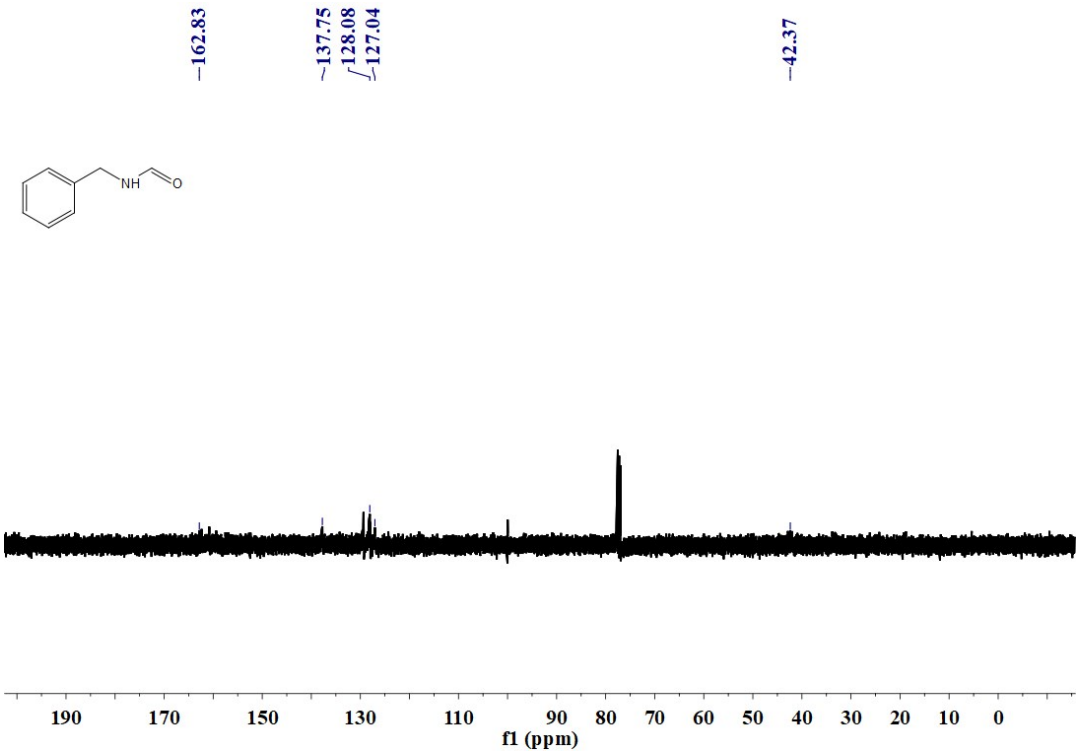
***N, N'*-(butane-1,4-diyl)bis(4-((4-formamidophenyl)thio)benzamide) (28):** ^{1}H NMR (500 MHz, DMSO) δ 10.38 (d, *J* = 35.6 Hz, 2H), 8.44 (d, *J* = 4.8 Hz, 2H), 8.33 (s, 2H), 7.76 (d, *J* = 8.2 Hz, 4H), 7.69 (d, *J* = 8.4 Hz, 3H), 7.46 (d, *J* = 8.3 Hz, 4H), 7.18 (d, *J* = 8.2 Hz, 4H), 3.26 (s, 4H), 1.54 (s, 4H). ^{13}C NMR (125 MHz, DMSO) δ 165.93 (s), 160.35 (s), 141.53 (s), 139.36 (s), 134.95 (s), 128.52 (s), 127.58 (s), 120.82 (s), 39.51 (s), 27.17 (s).



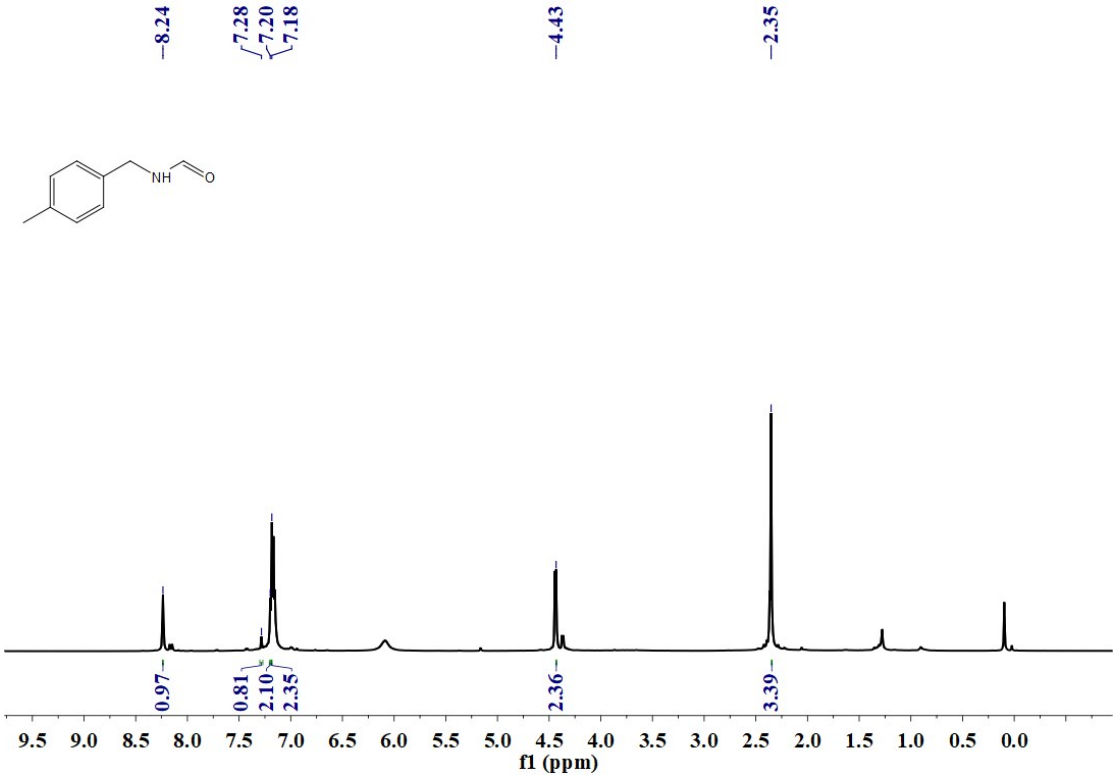
***N, N'*-(hexane-1,6-diyl)bis(4-((4-formamidophenyl)thio)benzamide) (29):** ^{1}H NMR (500 MHz, DMSO) δ 10.37 (d, J = 35.8 Hz, 2H), 8.39 (s, 2H), 8.32 (s, 2H), 7.75 (d, J = 8.2 Hz, 4H), 7.69 (d, J = 8.3 Hz, 4H), 7.46 (d, J = 8.1 Hz, 4H), 7.18 (d, J = 8.2 Hz, 4H), 3.35 (s, 4H), 1.48 (s, 4H), 1.25 (s, 4H).^{13}C NMR (125 MHz, DMSO) δ 165.86 (s), 160.35 (s), 141.49 (s), 139.36 (s), 134.96 (s), 128.51 (s), 127.56 (s), 120.80 (s), 40.51 (s), 29.49 (d, J = 17.0 Hz), 29.24 (s), 26.95 (s).



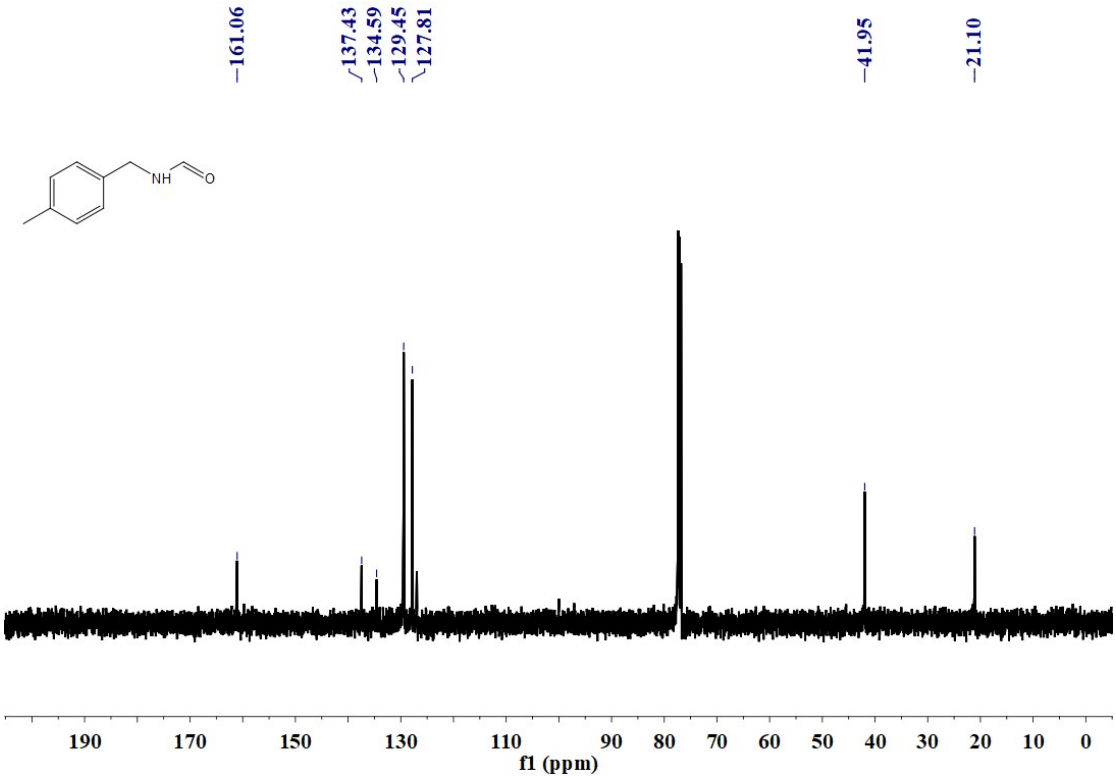
^{1}H NMR spectra of **2** (500 MHz, $CDCl_3$)



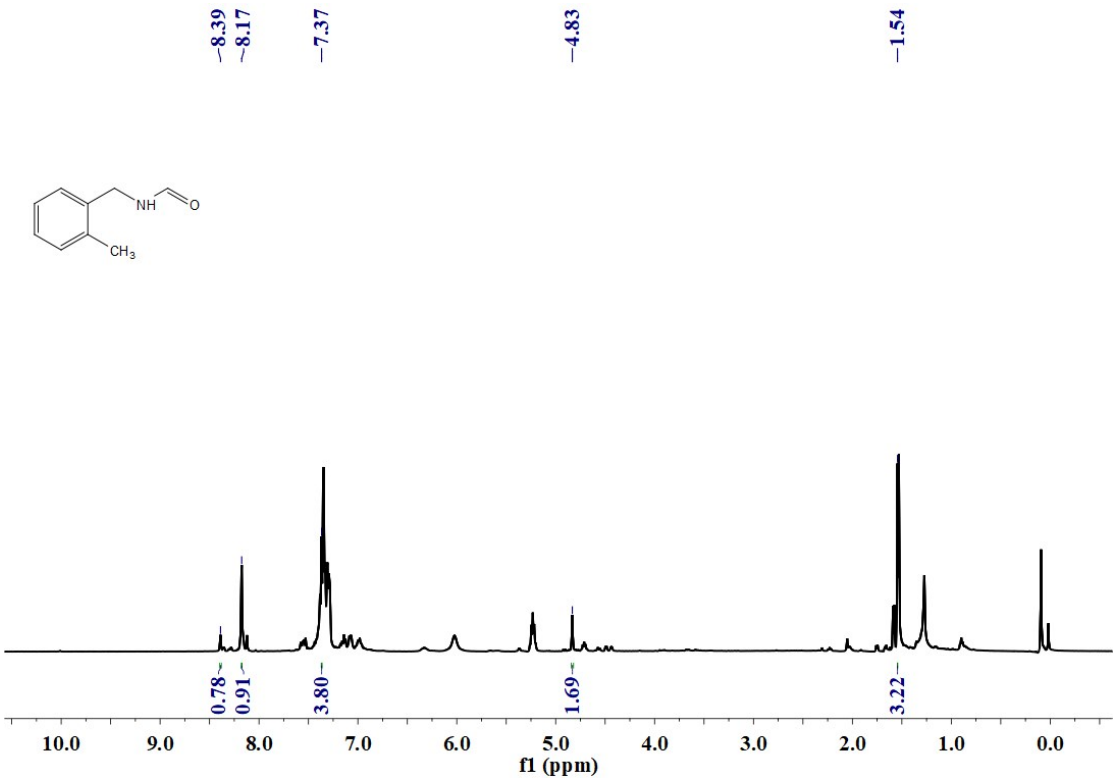
^{1}C NMR spectra of **2** (125 MHz, $CDCl_3$)



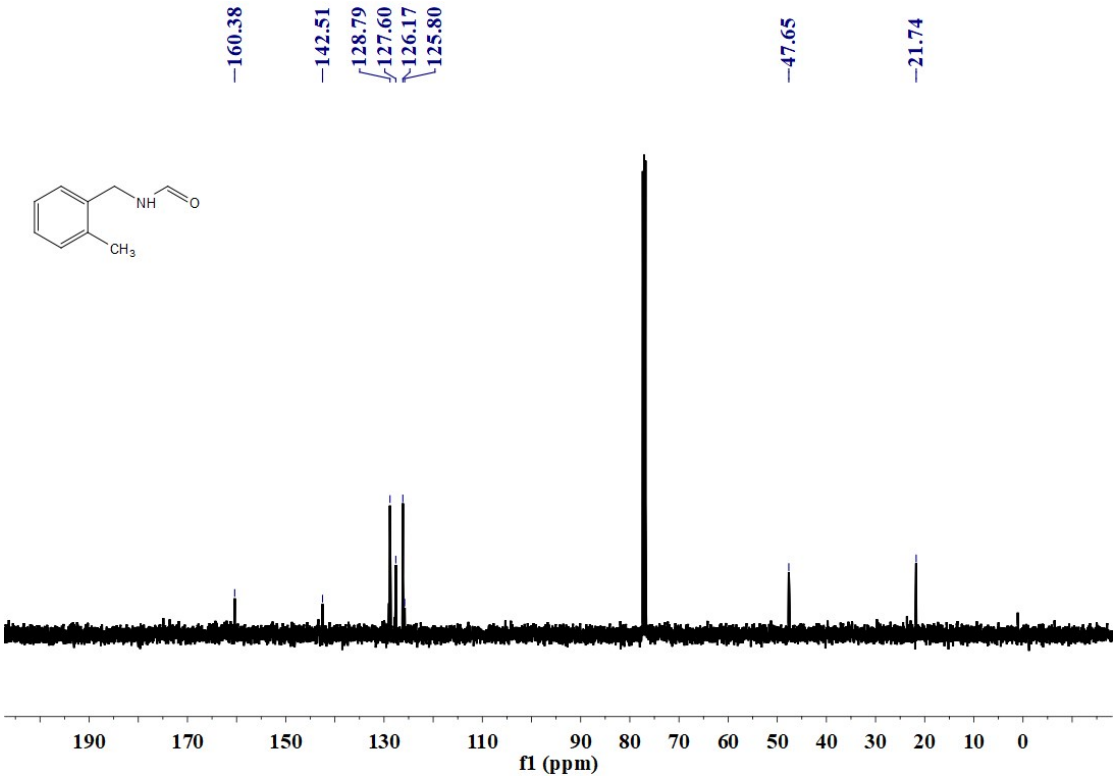
^{1}H NMR spectra of **3** (500 MHz, $CDCl_3$)



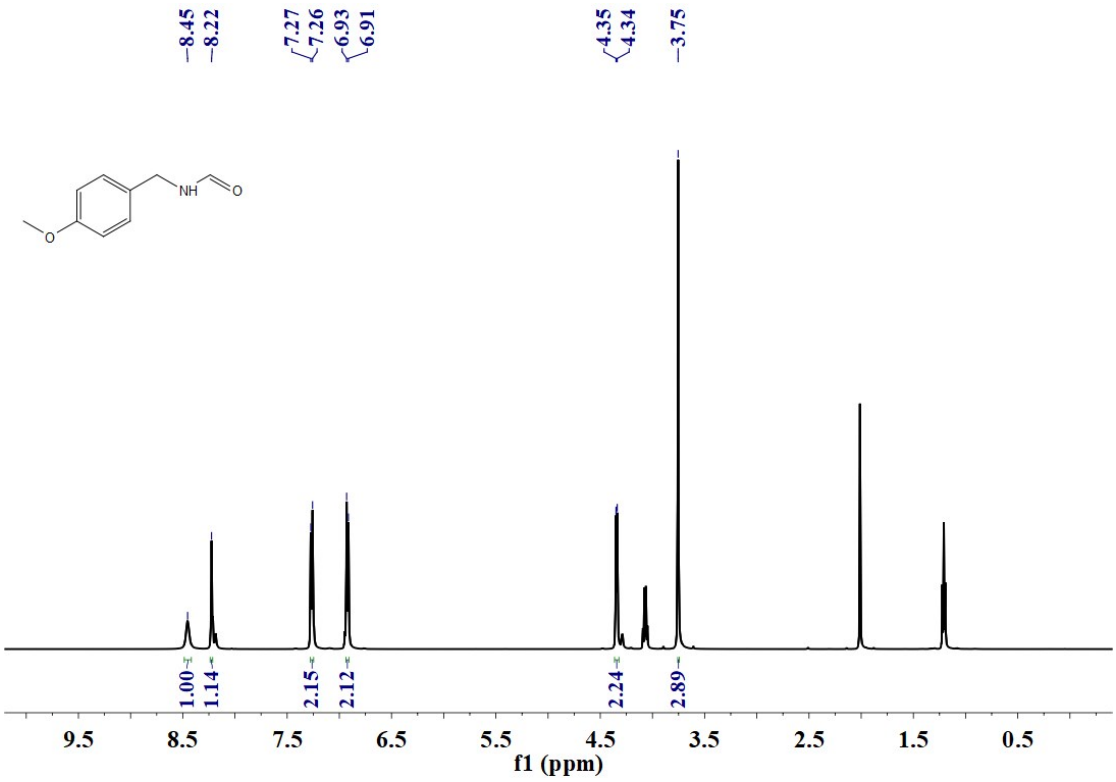
^{1}C NMR spectra of **3** (125 MHz, $CDCl_3$)



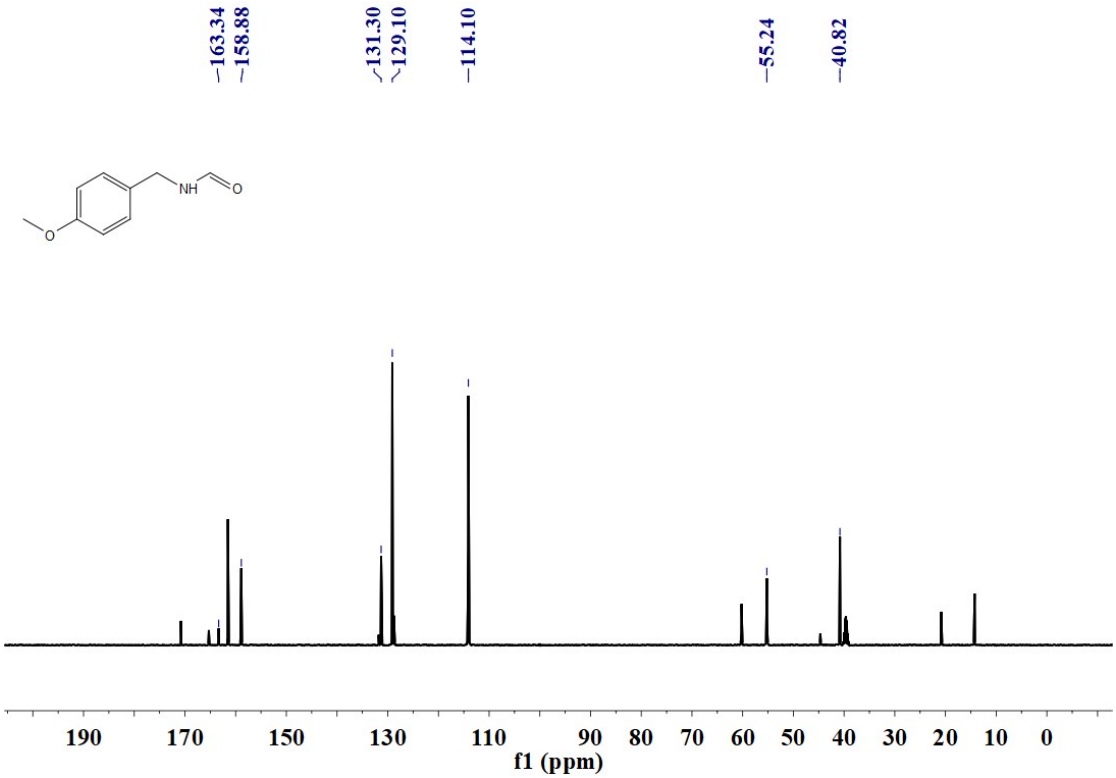
^{1}H NMR spectra of **4** (500 MHz, $CDCl_3$)



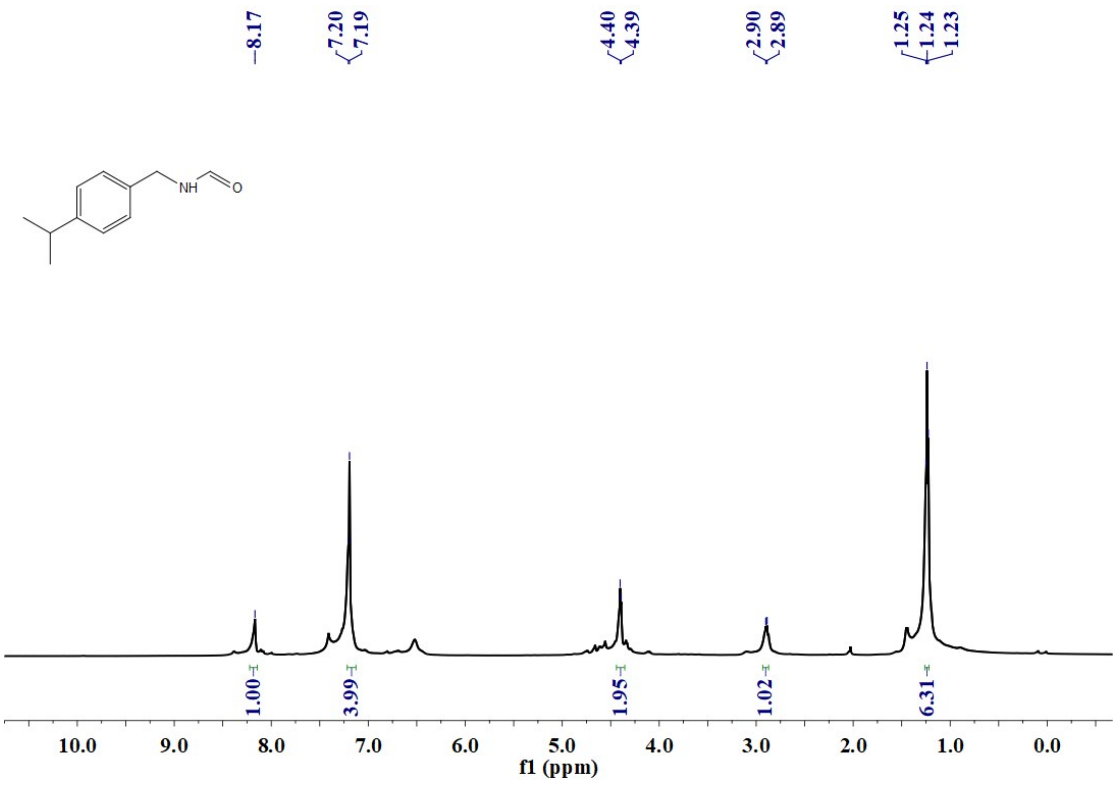
^{1}C NMR spectra of **4** (125 MHz, $CDCl_3$)



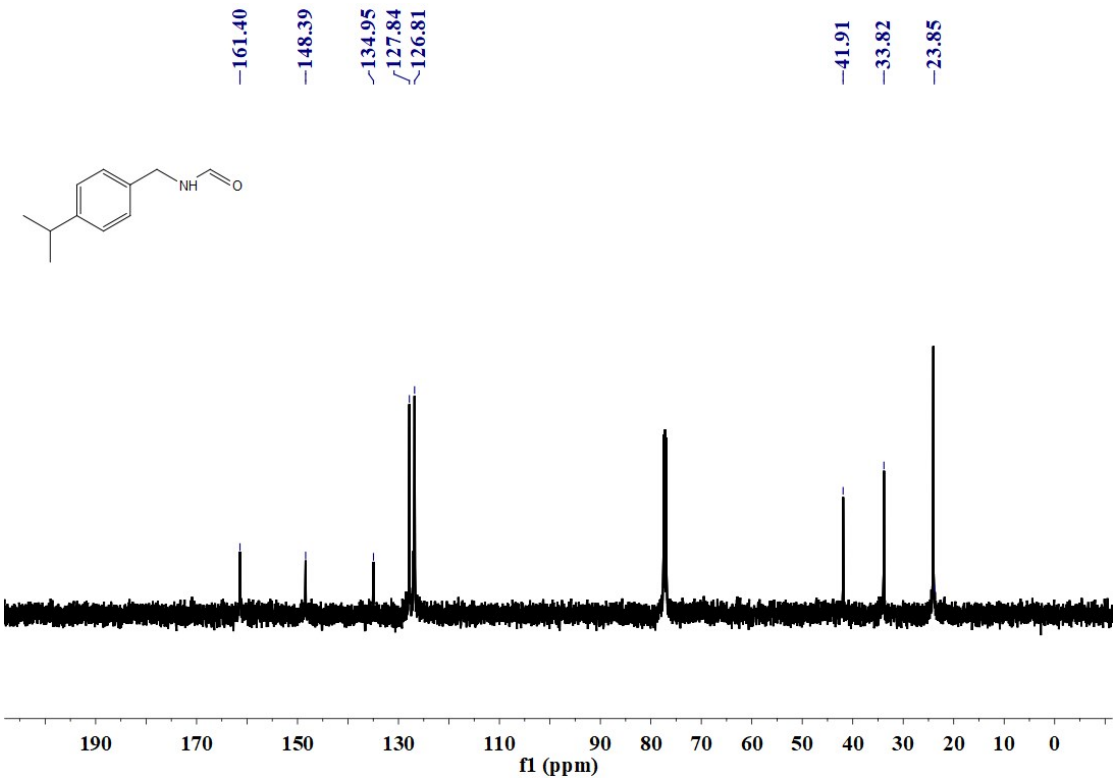
^{1}H NMR spectra of **5** (500 MHz, DMSO)



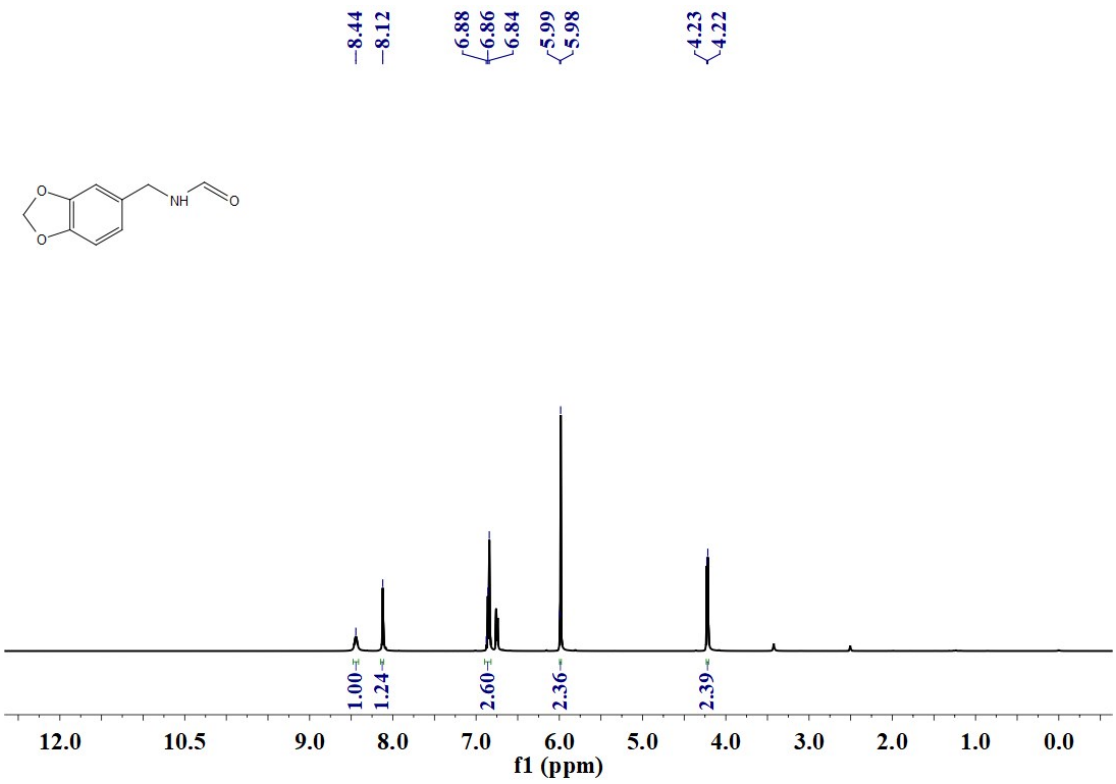
^{1}C NMR spectra of **5** (125 MHz, DMSO)



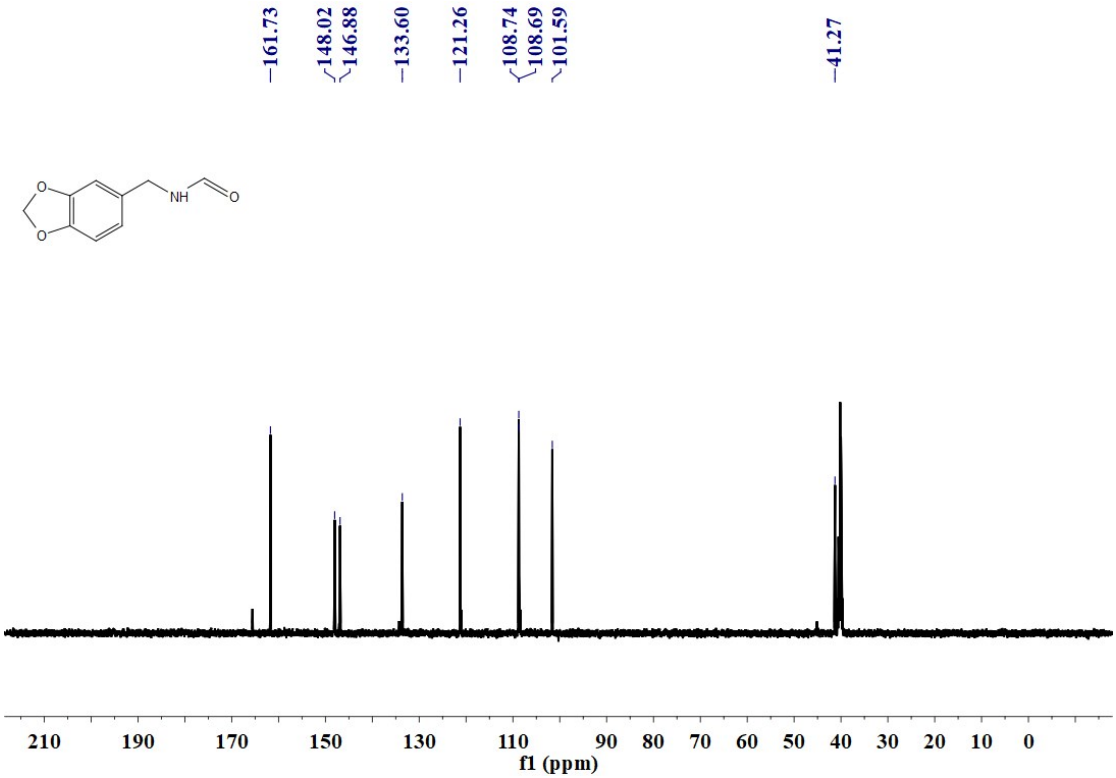
^{1}H NMR spectra of **6** (500 MHz, $CDCl_3$)



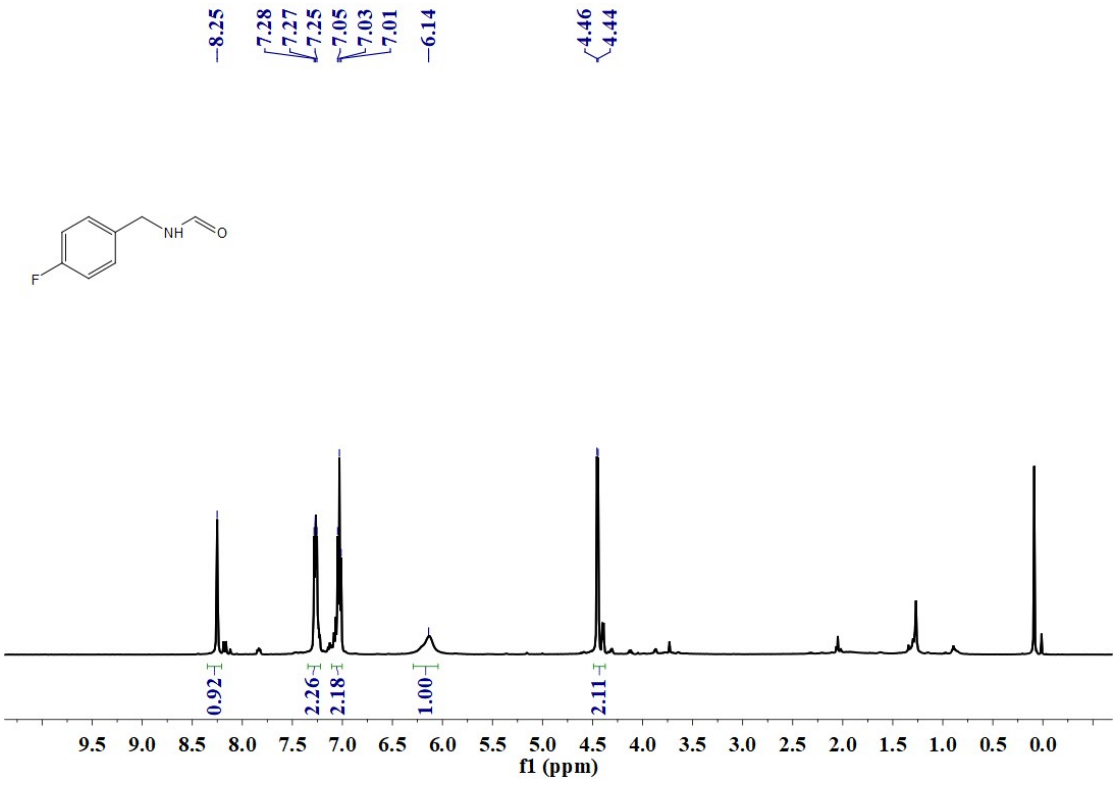
^{1}C NMR spectra of **6** (125 MHz, $CDCl_3$)



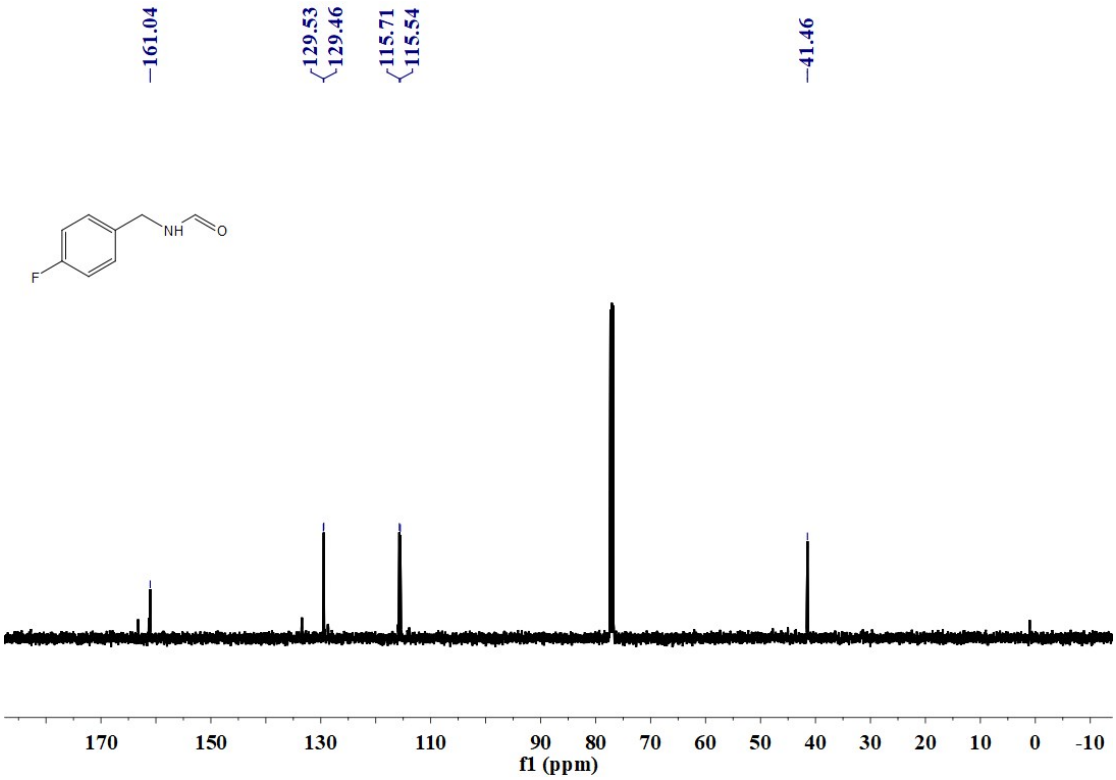
^{1}H NMR spectra of **7** (500 MHz, DMSO)



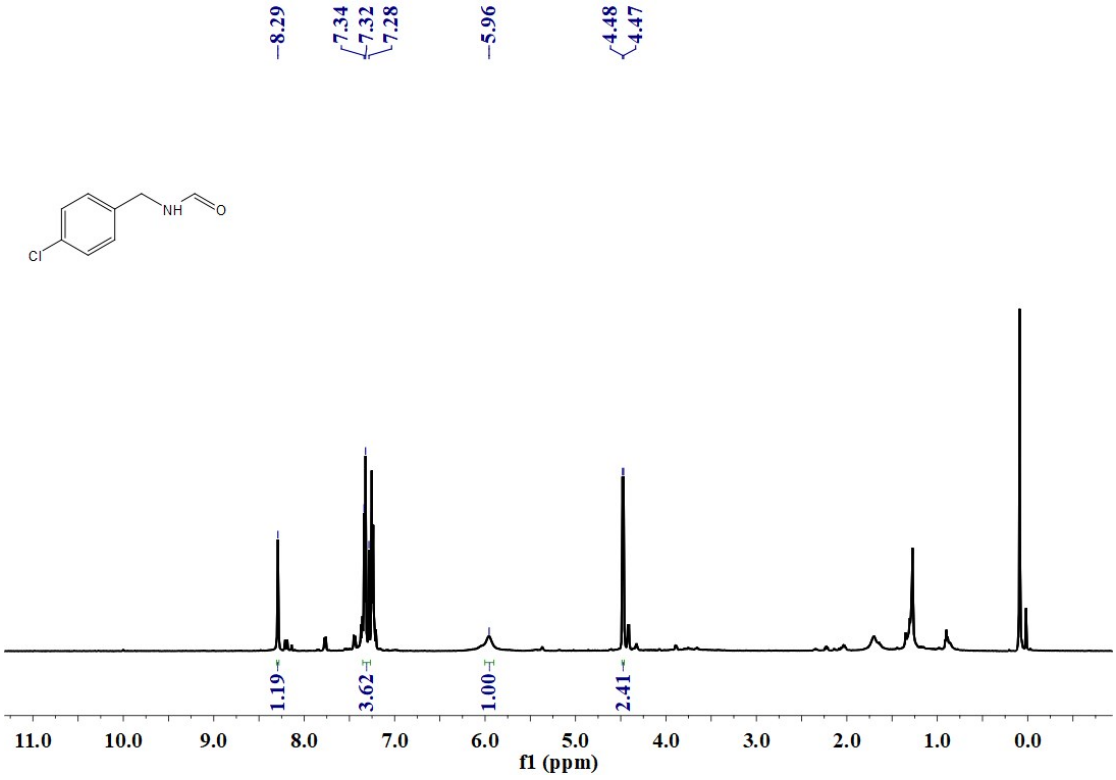
^{1}C NMR spectra of **7** (125 MHz, DMSO)



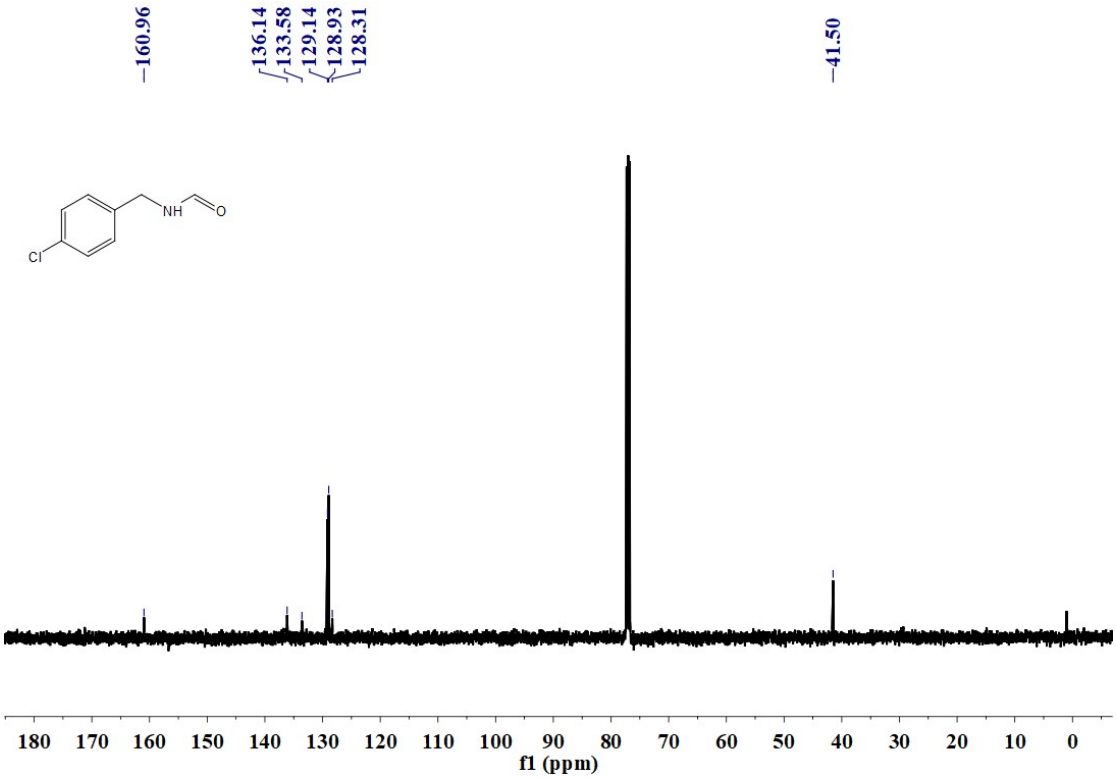
^{1}H NMR spectra of **8** (500 MHz, $CDCl_3$)



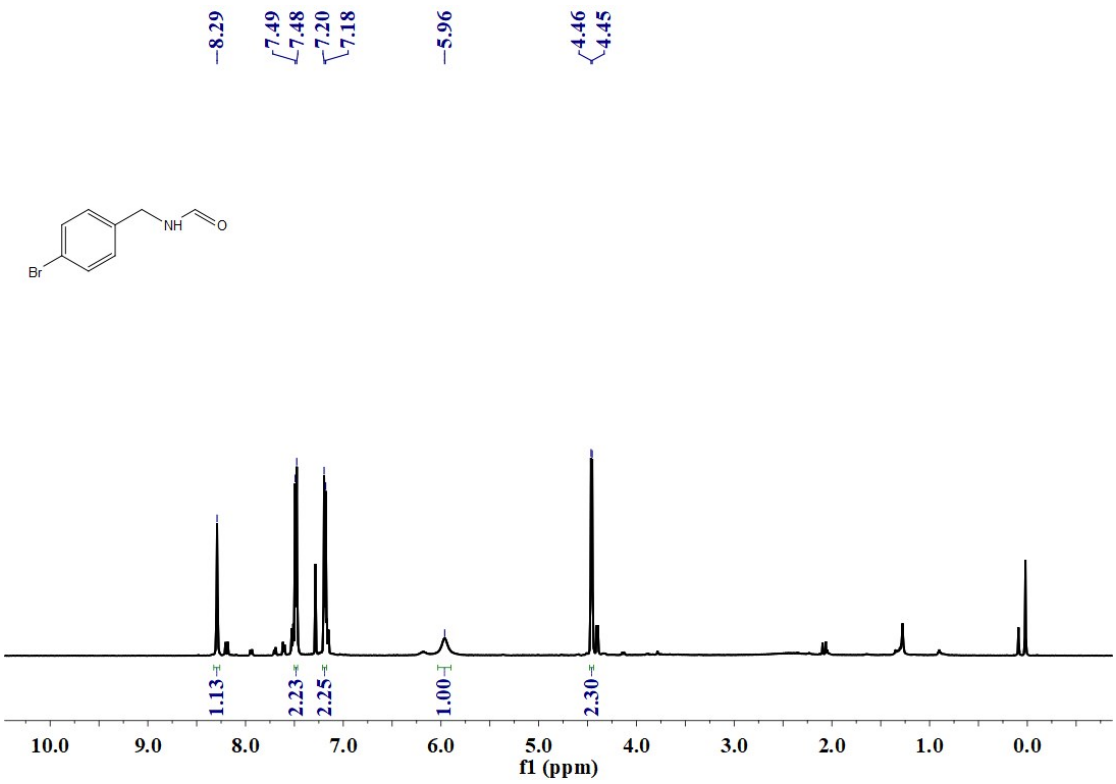
^{1}C NMR spectra of **8** (125 MHz, $CDCl_3$)



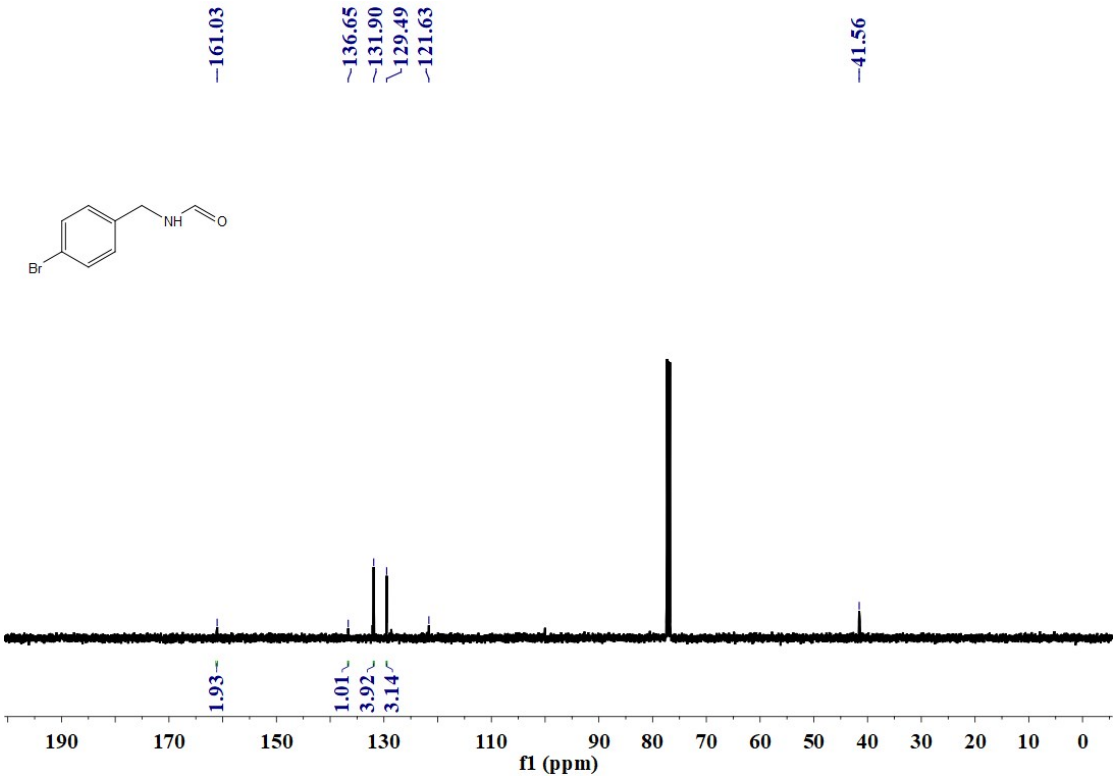
^{1}H NMR spectra of **9** (500 MHz, $CDCl_3$)



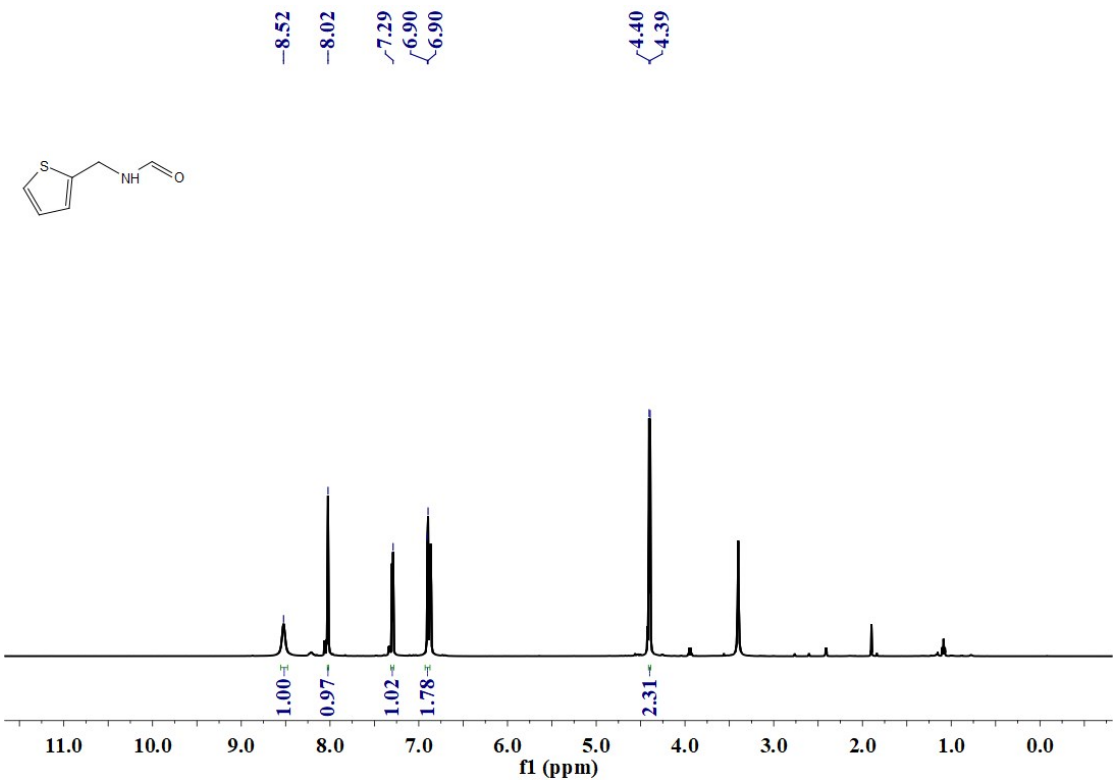
^{1}C NMR spectra of **9** (125 MHz, $CDCl_3$)



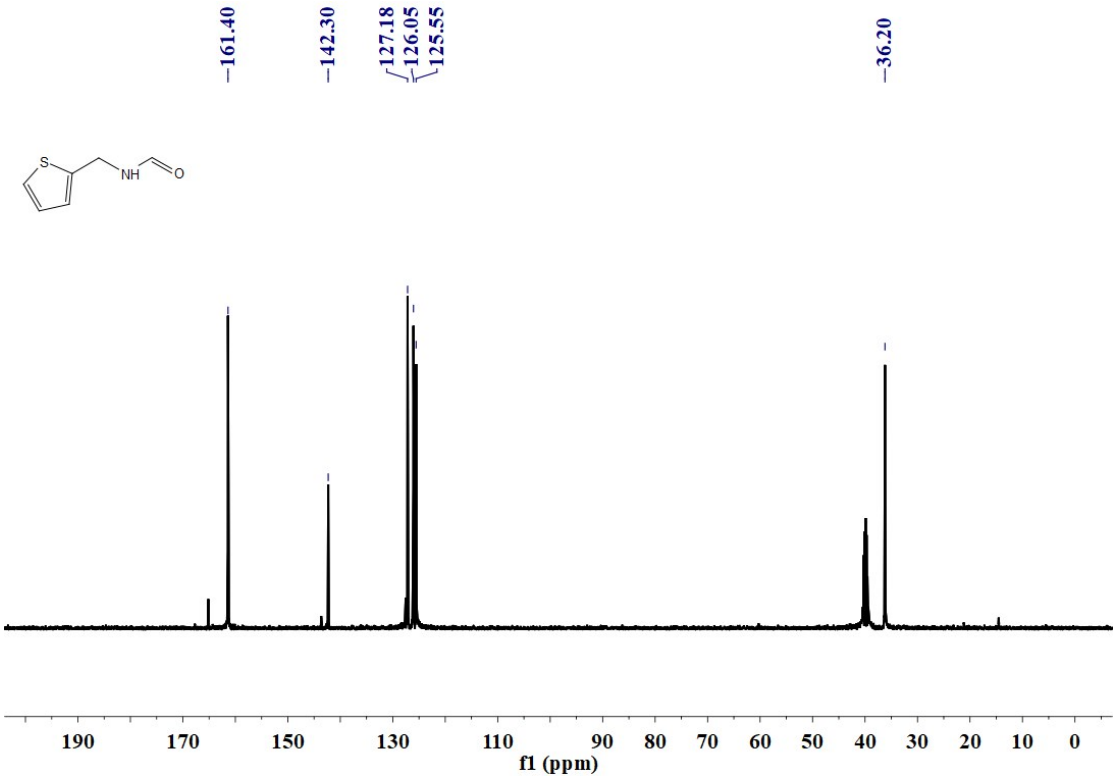
^{1}H NMR spectra of **10** (500 MHz, $CDCl_3$)



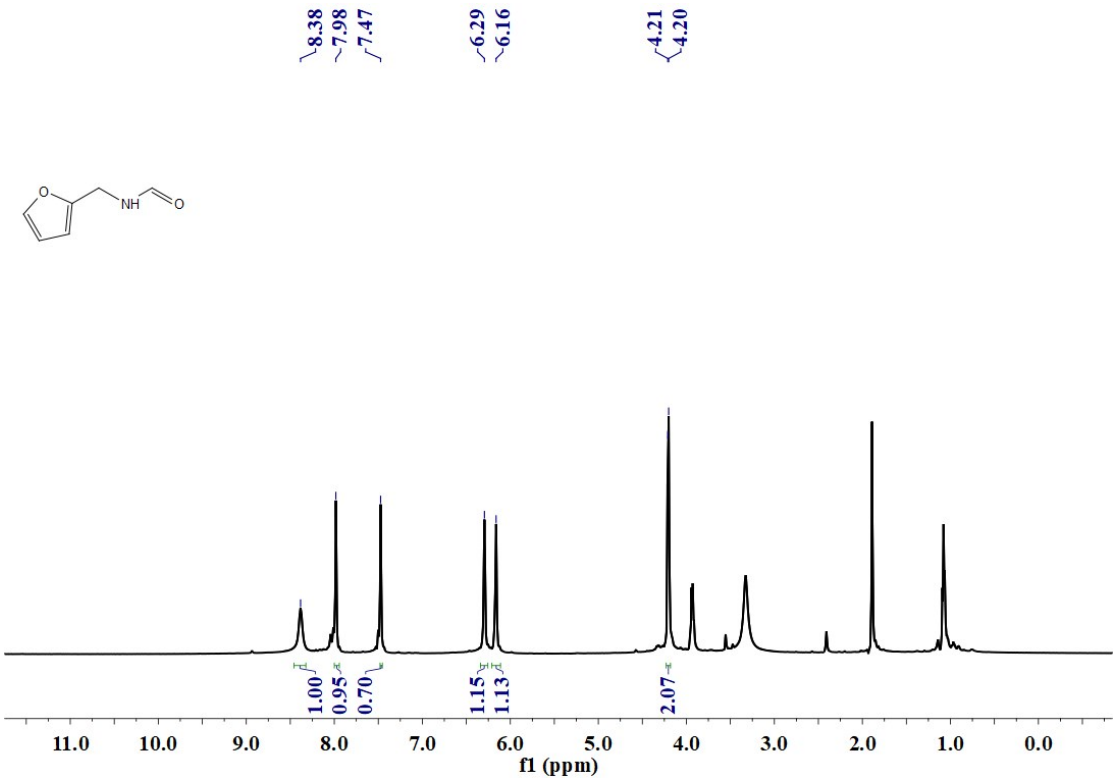
^{1}C NMR spectra of **10** (125 MHz, $CDCl_3$)



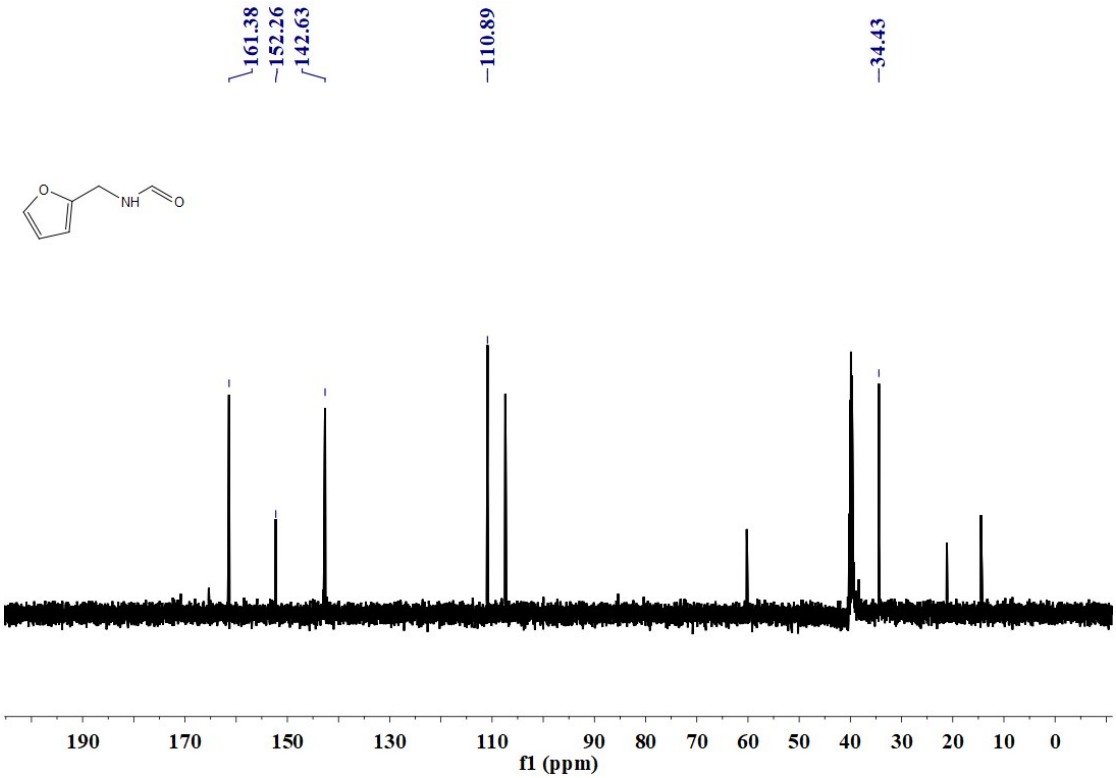
^{1}H NMR spectra of **11** (500 MHz, DMSO)



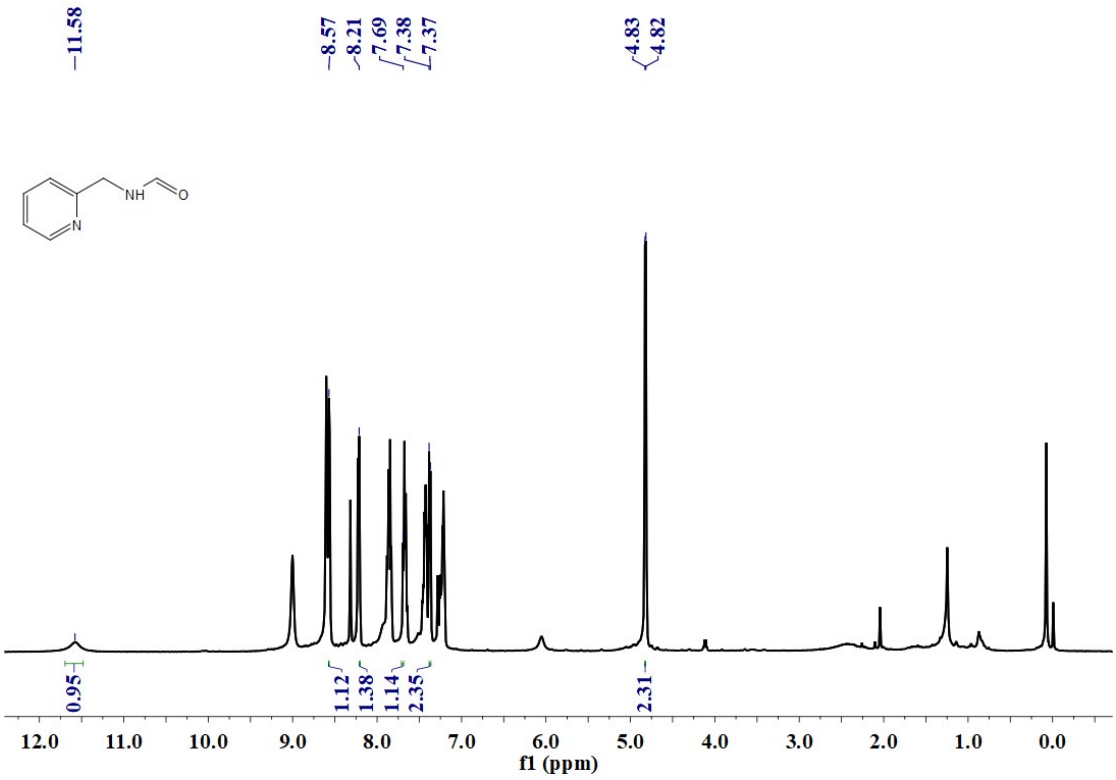
[1]C NMR spectra of **11** (125 MHz, DMSO)



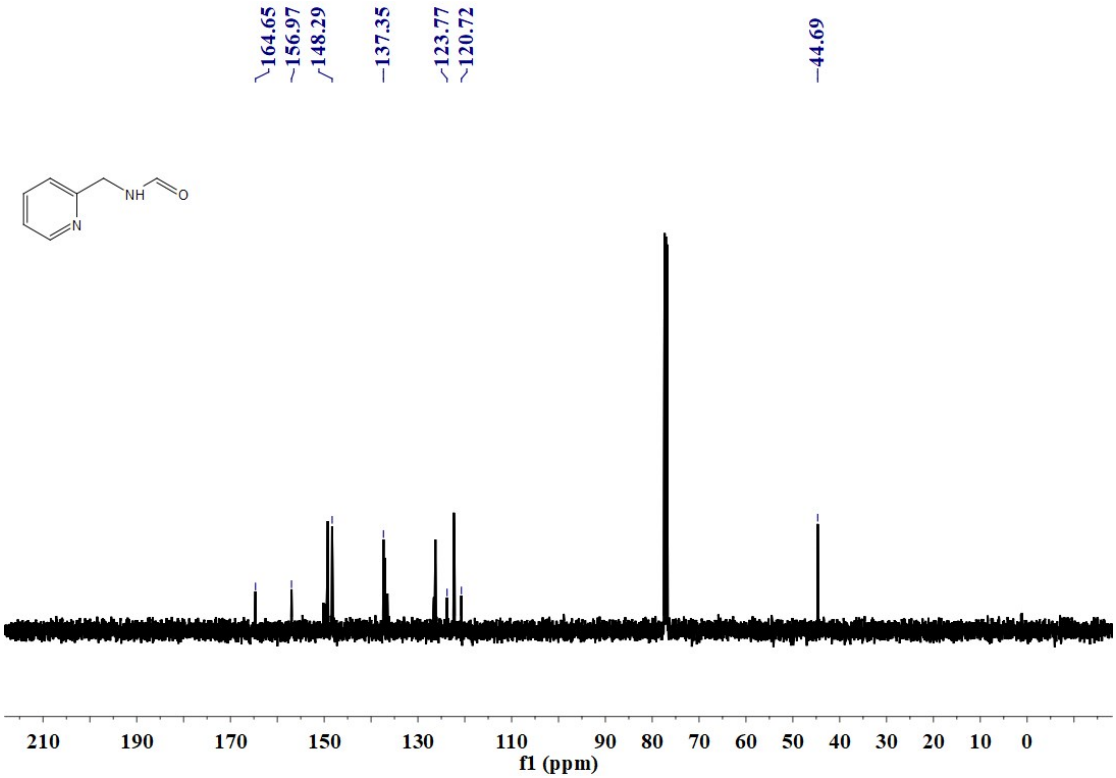
[1]H NMR spectra of **12** (500 MHz, DMSO)



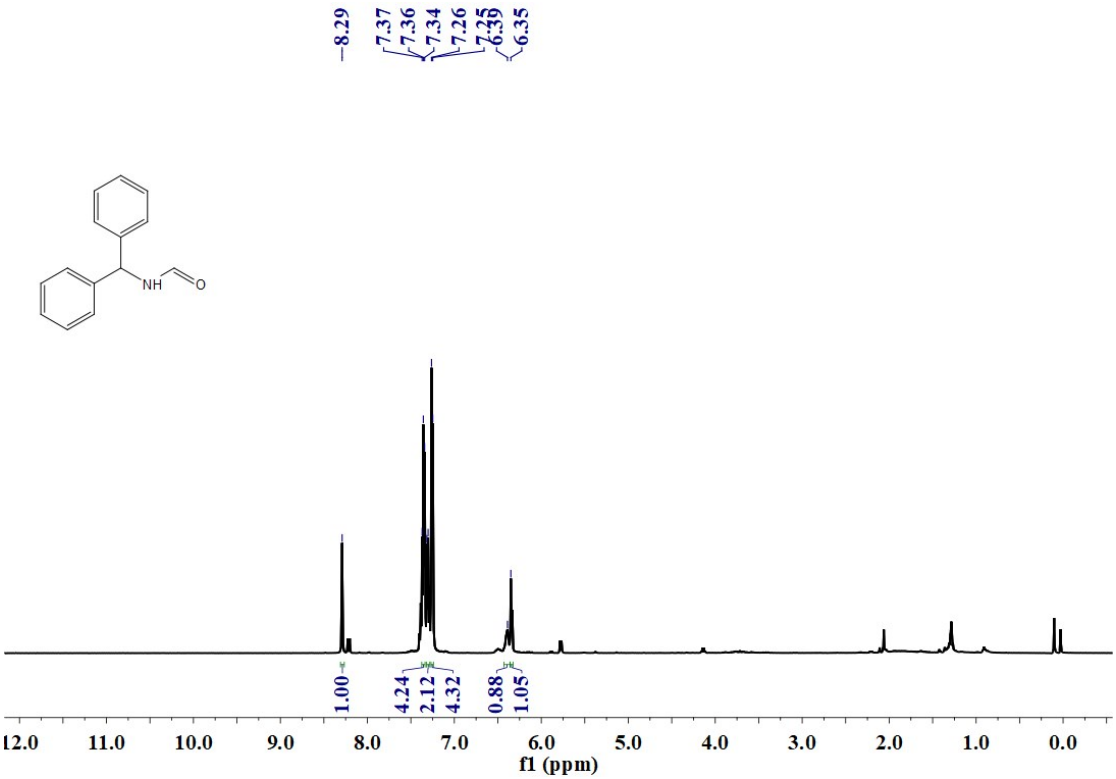
^{1}C NMR spectra of **12** (125 MHz, DMSO)



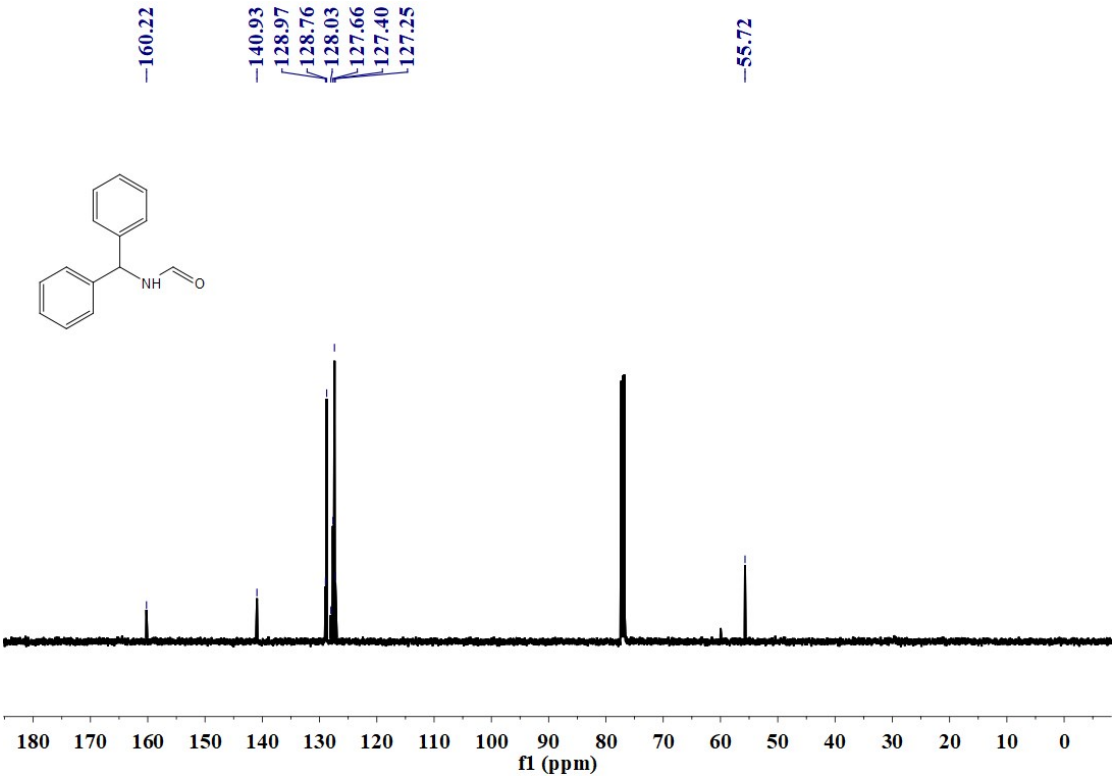
^{1}H NMR spectra of **13** (500 MHz, $CDCl_3$)



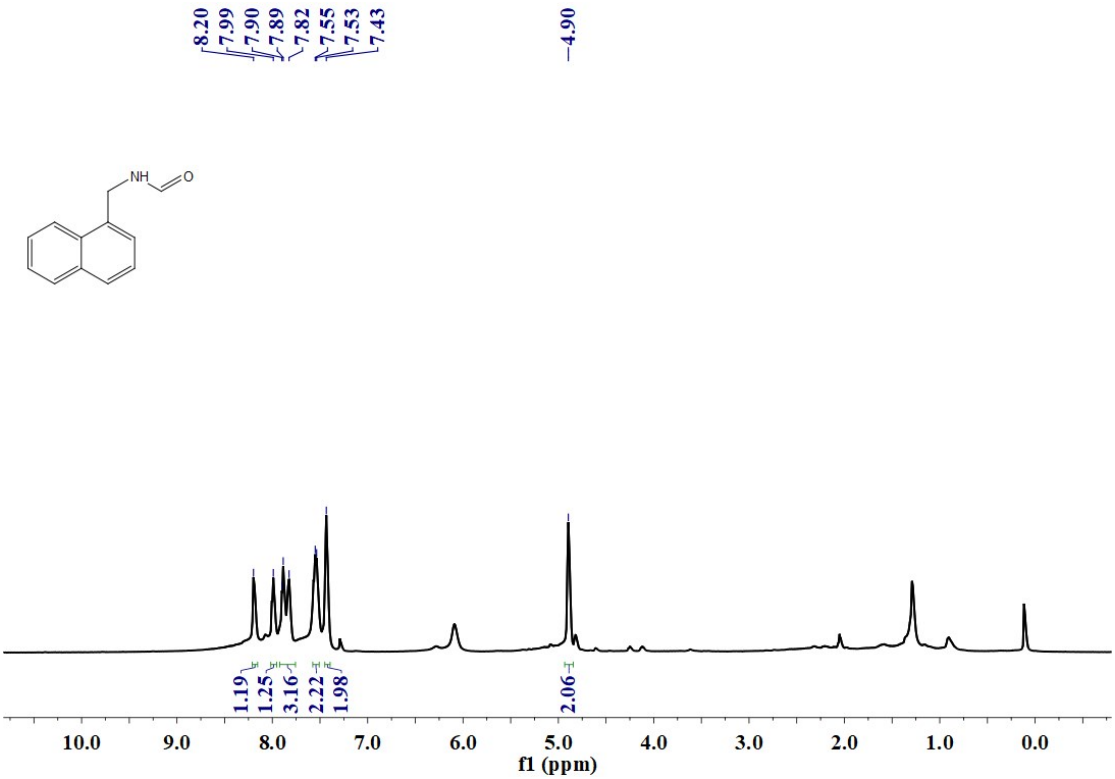
^{1}C NMR spectra of **13** (125 MHz, $CDCl_3$)



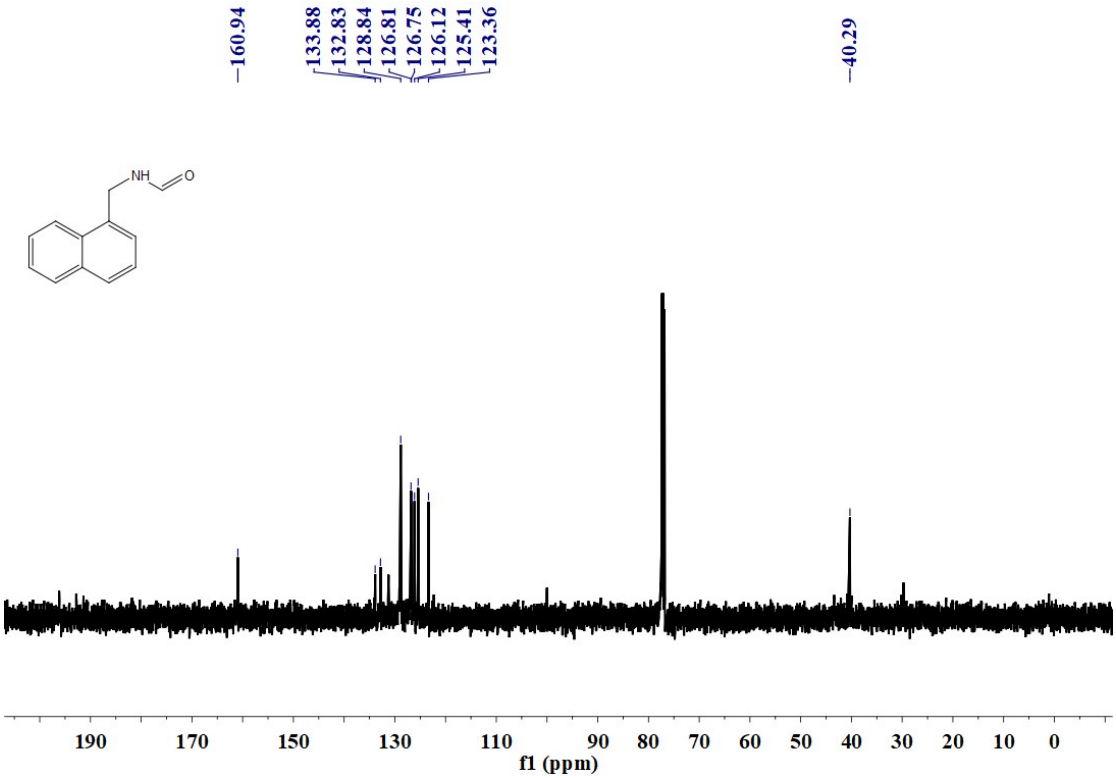
^{1}H NMR spectra of **14** (500 MHz, $CDCl_3$)



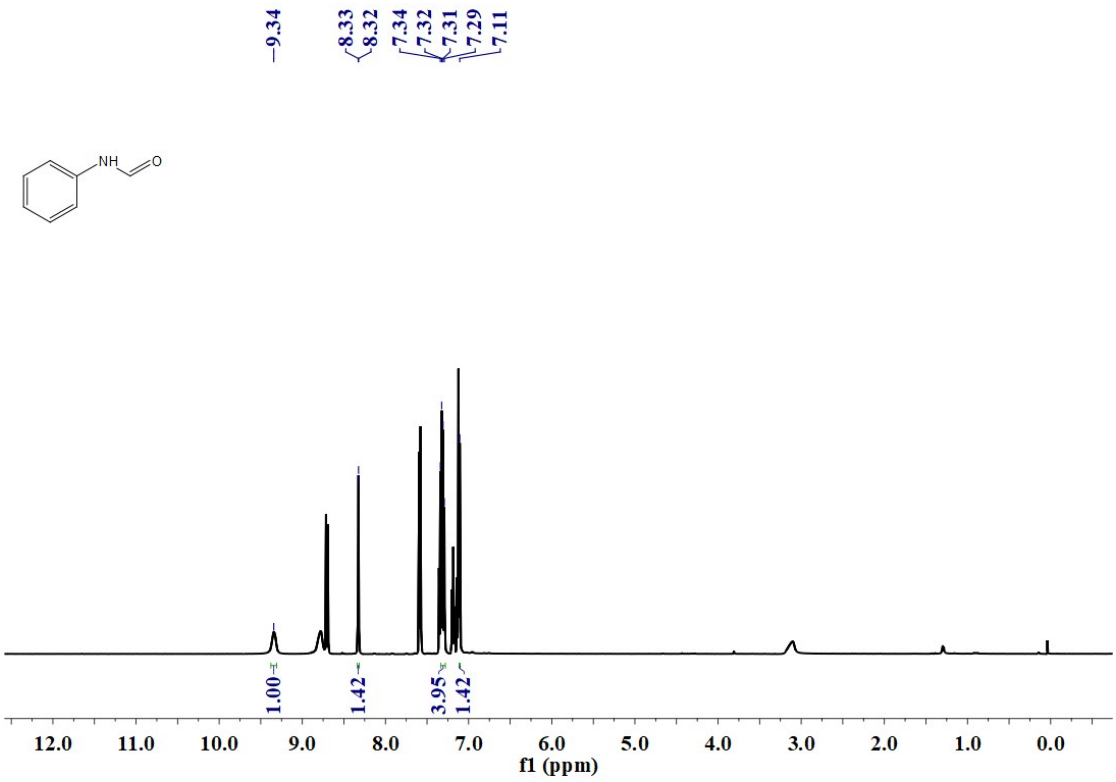
^{1}C NMR spectra of **14** (125 MHz, $CDCl_3$)



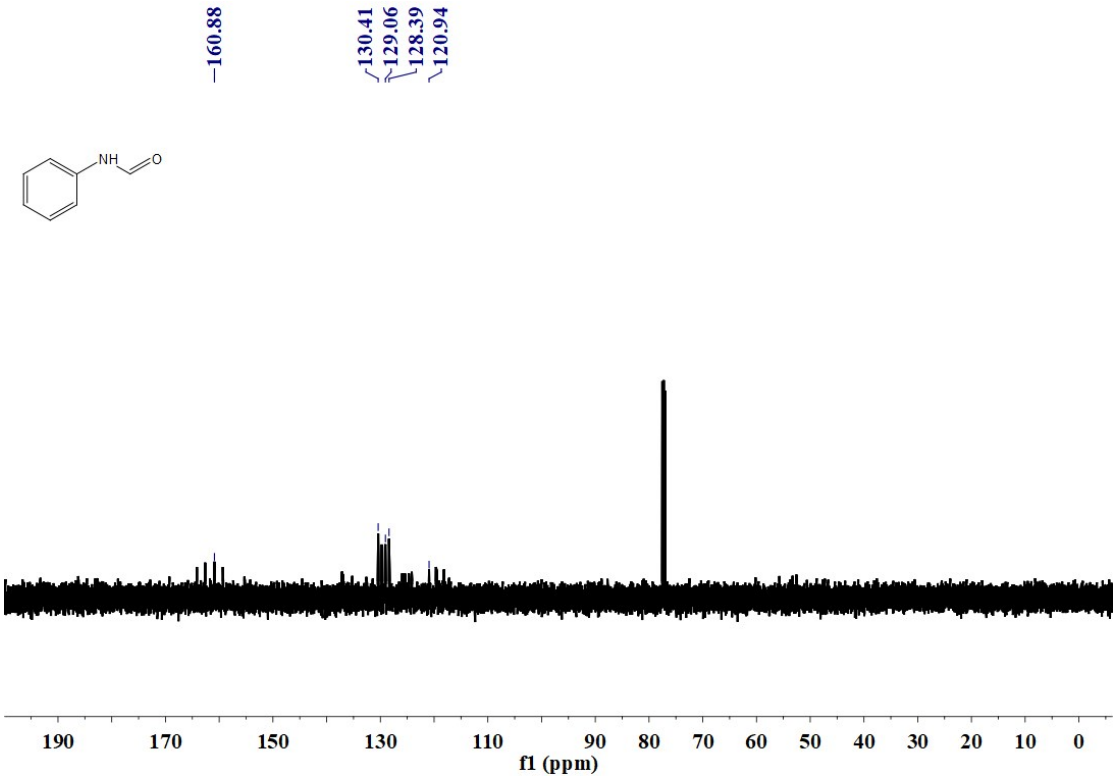
^{1}H NMR spectra of **15** (500 MHz, $CDCl_3$)



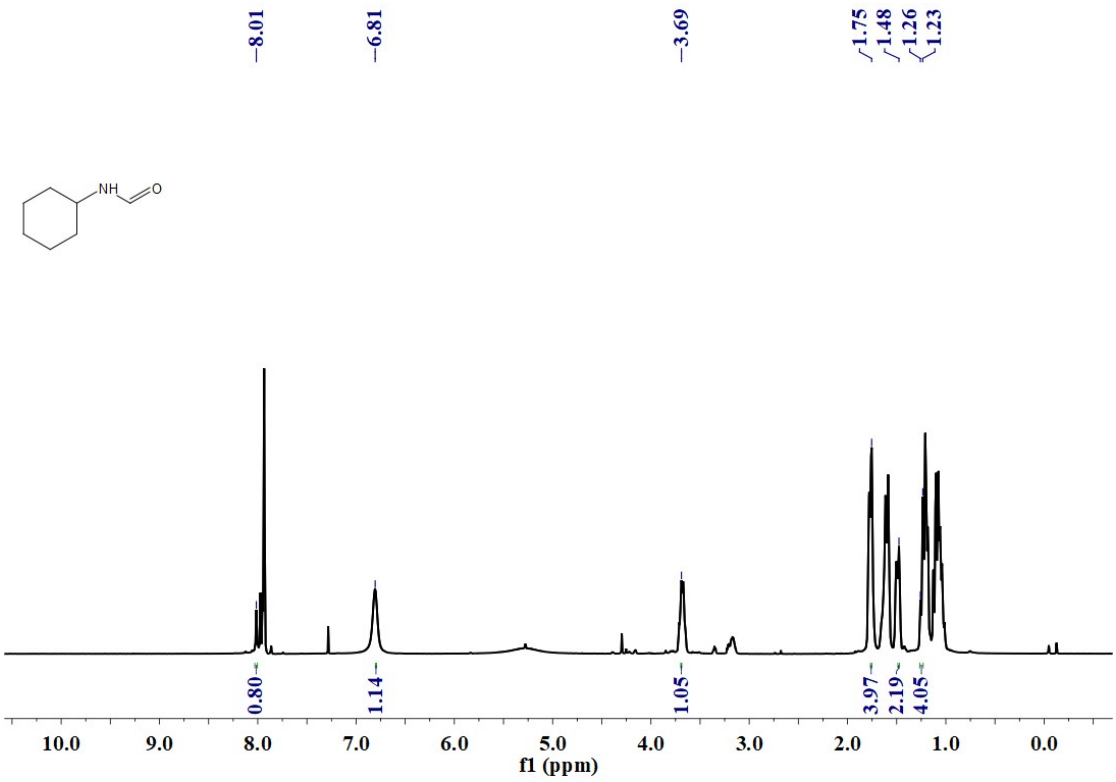
^{1}C NMR spectra of **15** (125 MHz, $CDCl_3$)



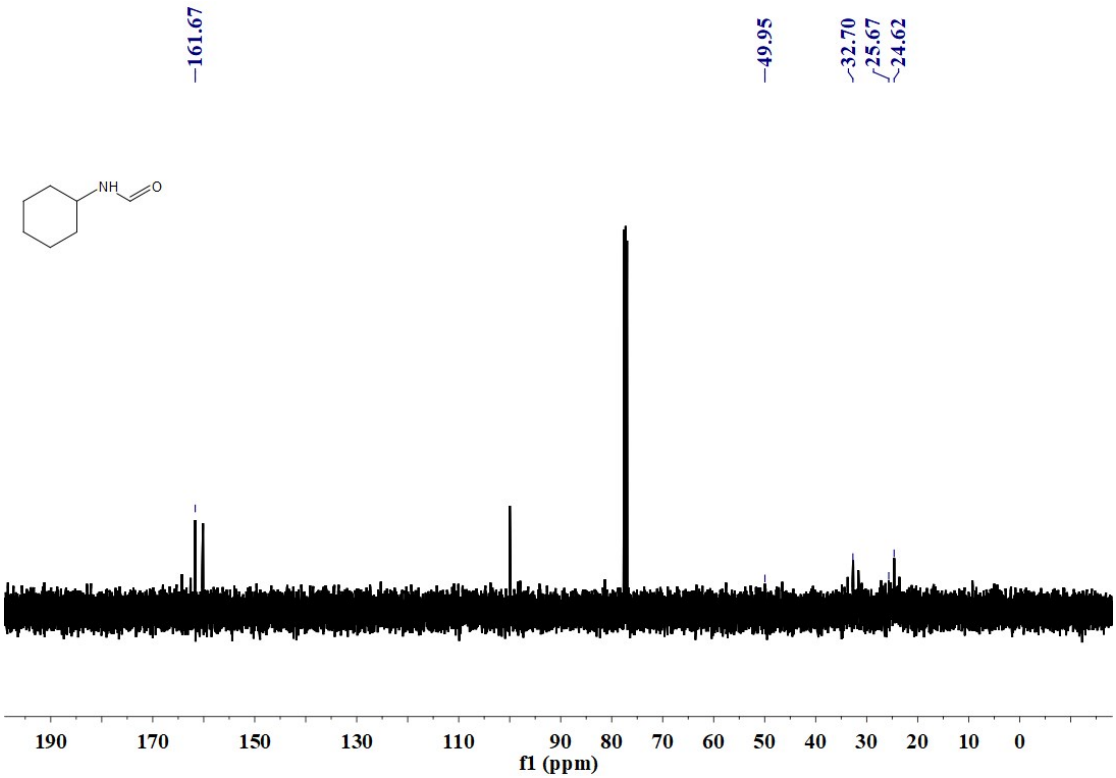
^{1}H NMR spectra of **16** (500 MHz, $CDCl_3$)



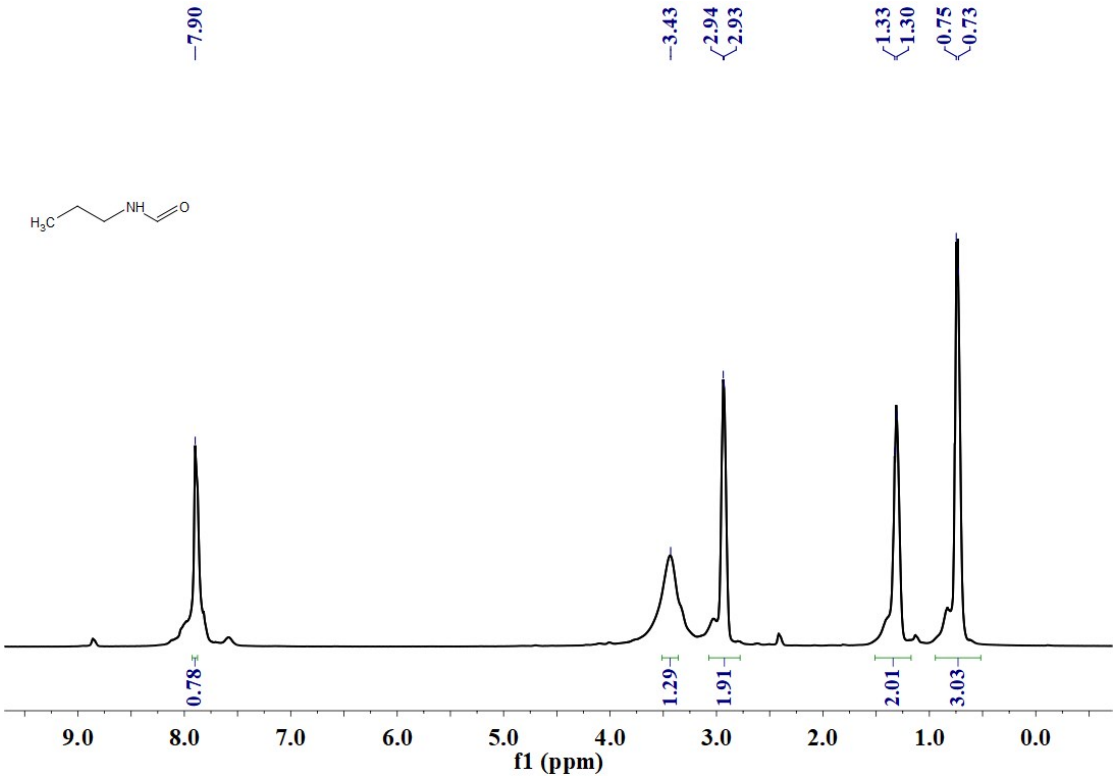
^{1}C NMR spectra of **16** (125 MHz, $CDCl_3$)



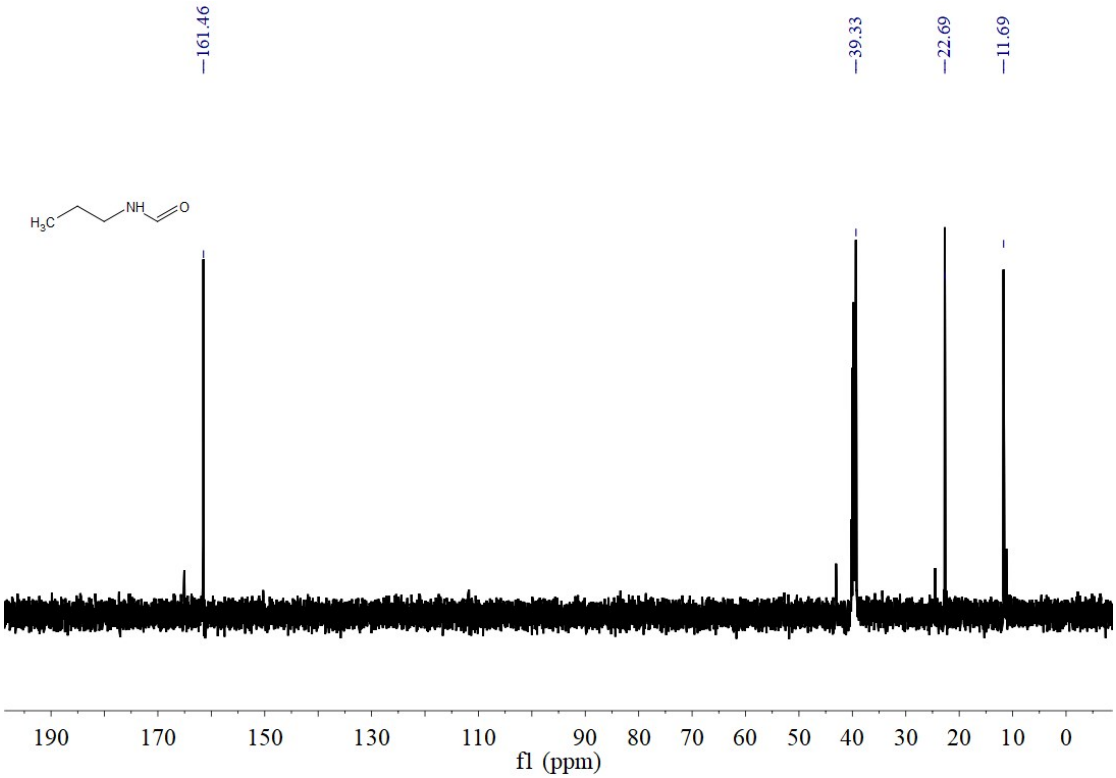
^{1}H NMR spectra of **17** (500 MHz, $CDCl_3$)



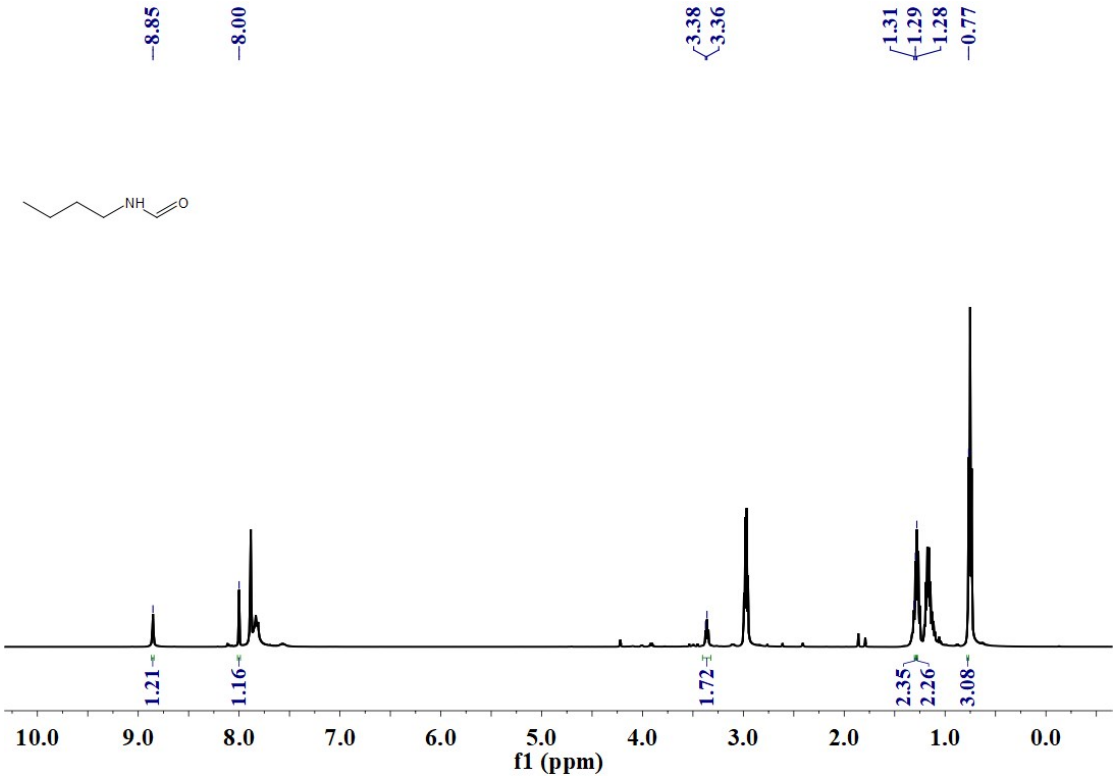
^{1}C NMR spectra of **17** (125 MHz, $CDCl_3$)



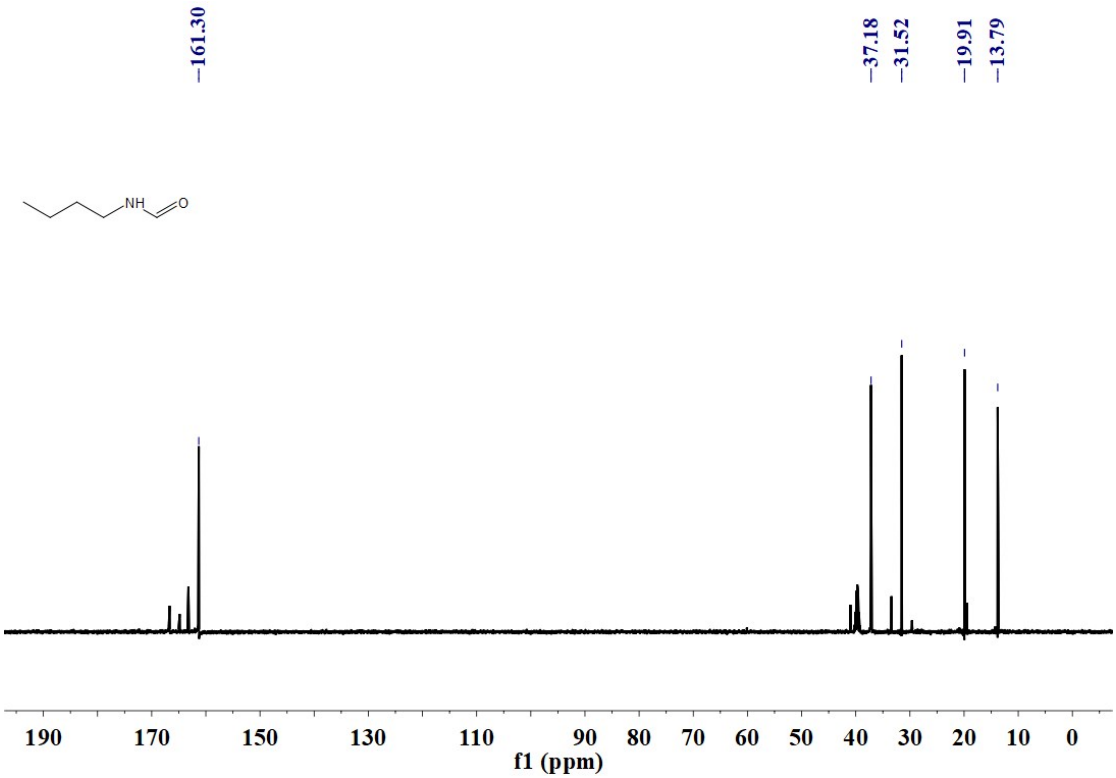
^{1}H NMR spectra of **18** (500 MHz, DMSO)



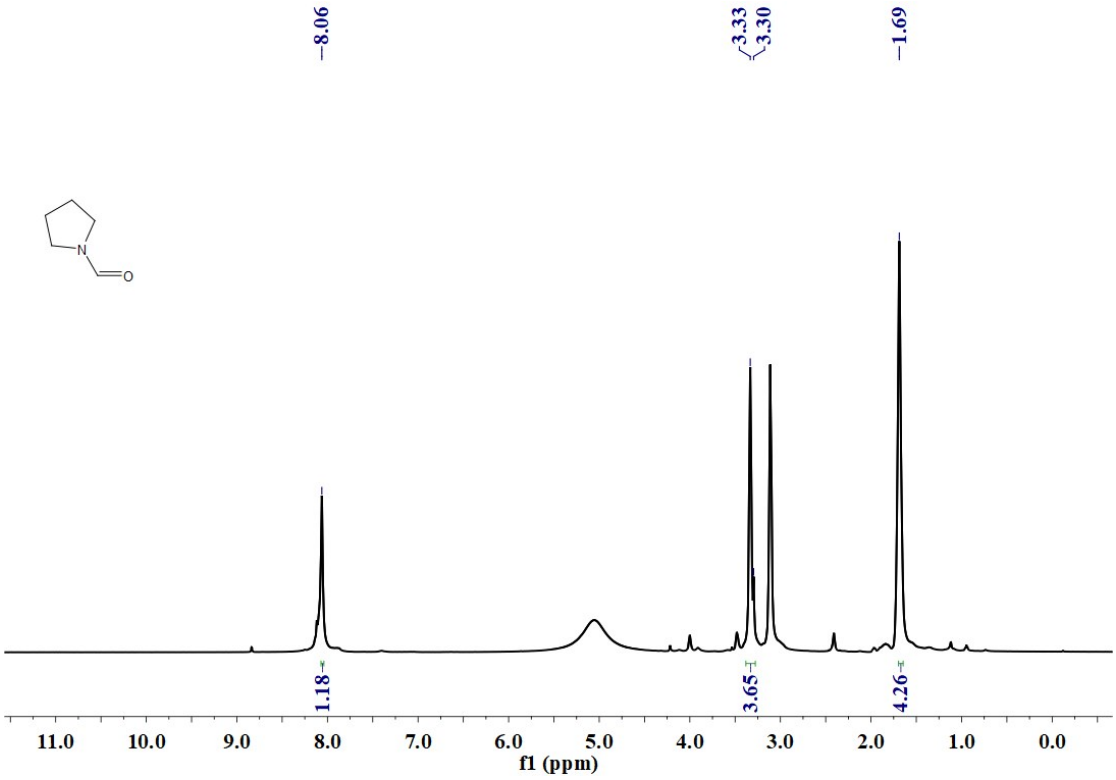
[1]C NMR spectra of **18** (125 MHz, DMSO)



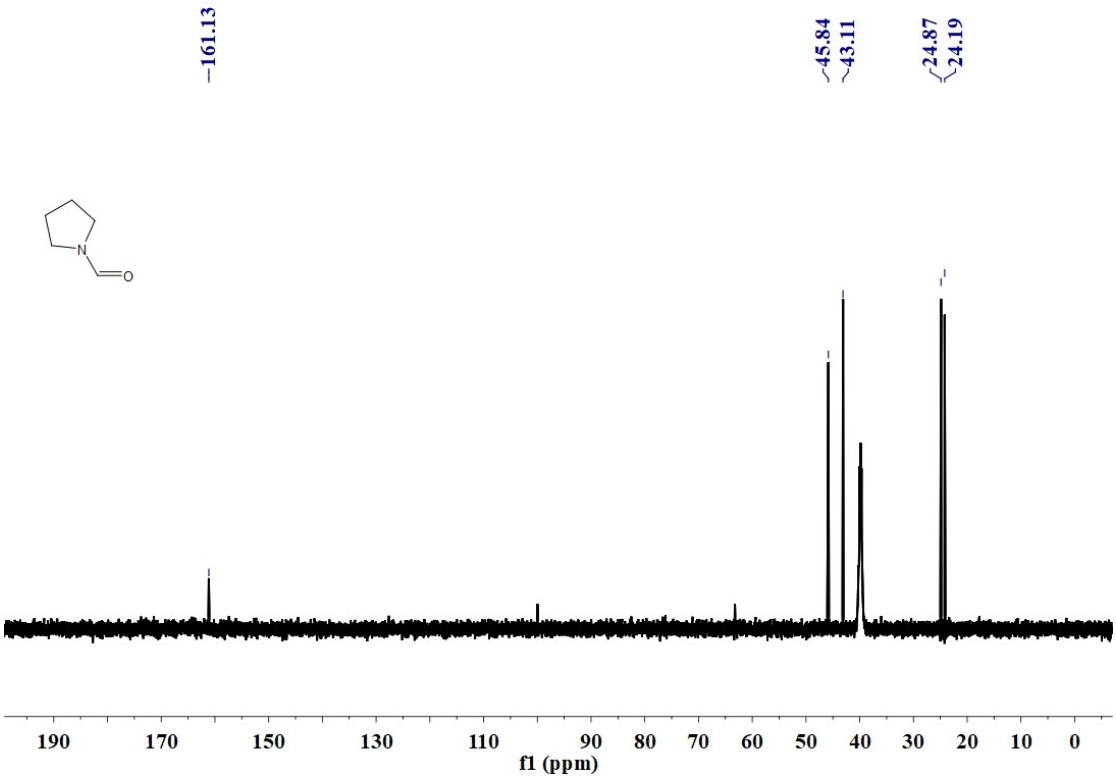
[1]H NMR spectra of **19** (500 MHz, DMSO)



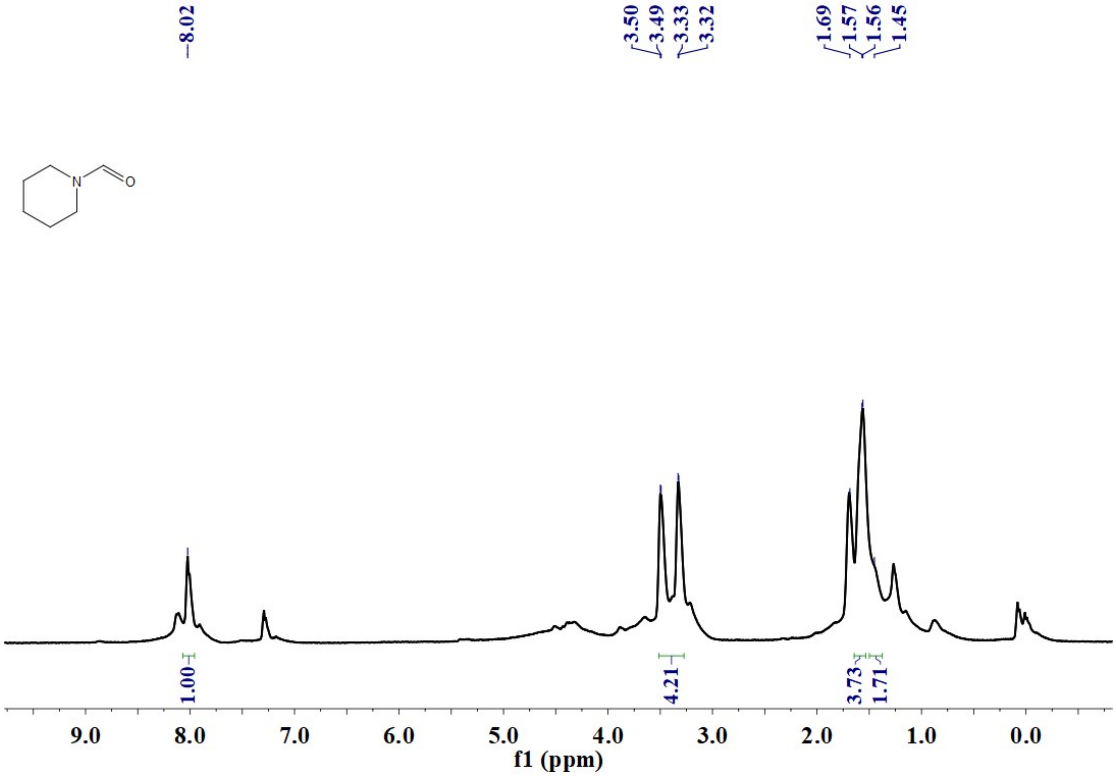
^{1}C NMR spectra of **19** (125 MHz, DMSO)



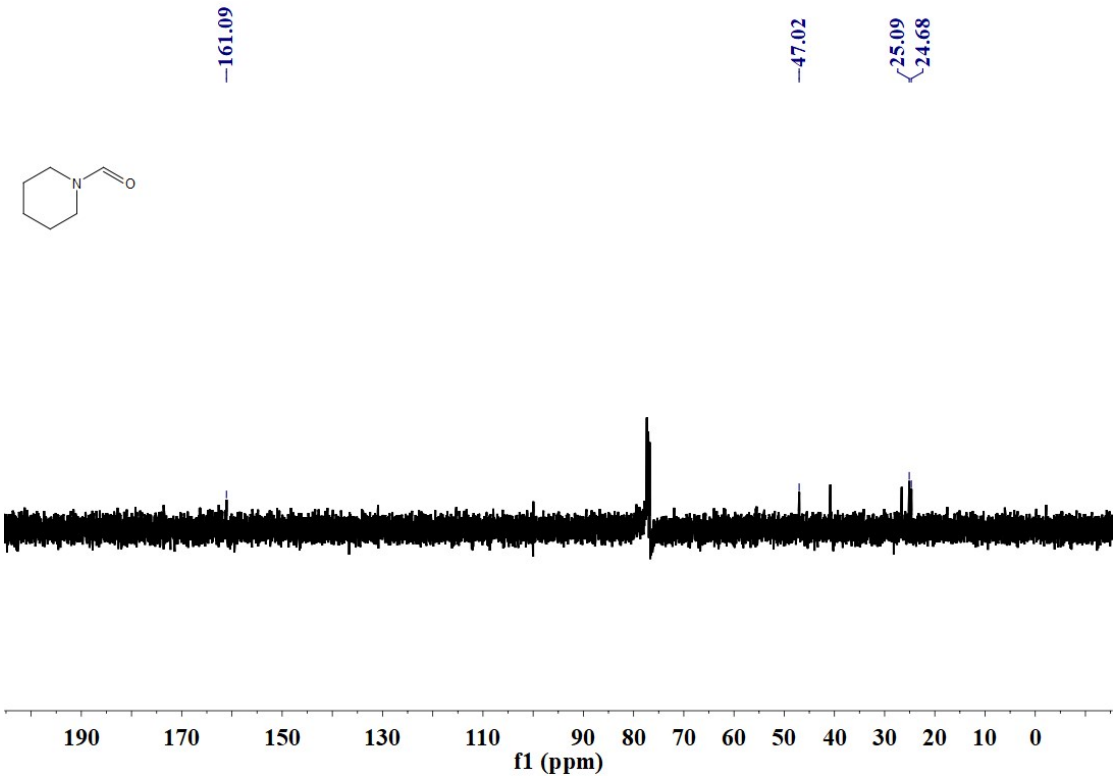
^{1}H NMR spectra of **20** (500 MHz, DMSO)



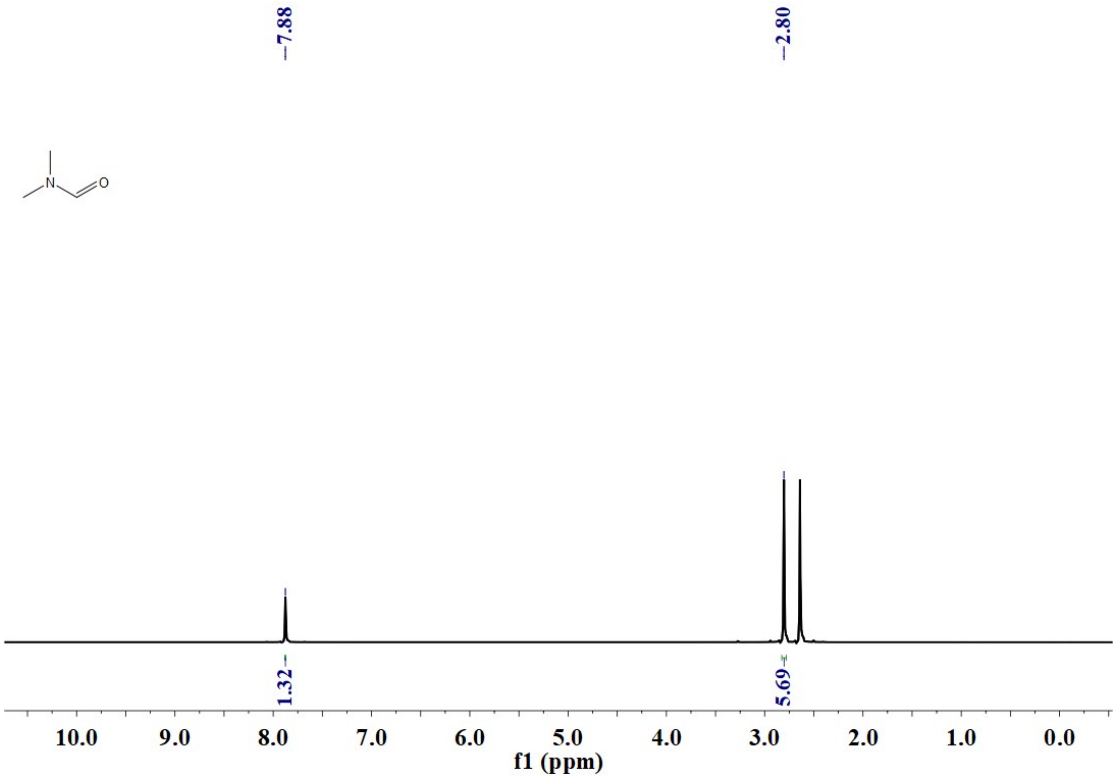
^{1}C NMR spectra of **20** (125 MHz, DMSO)



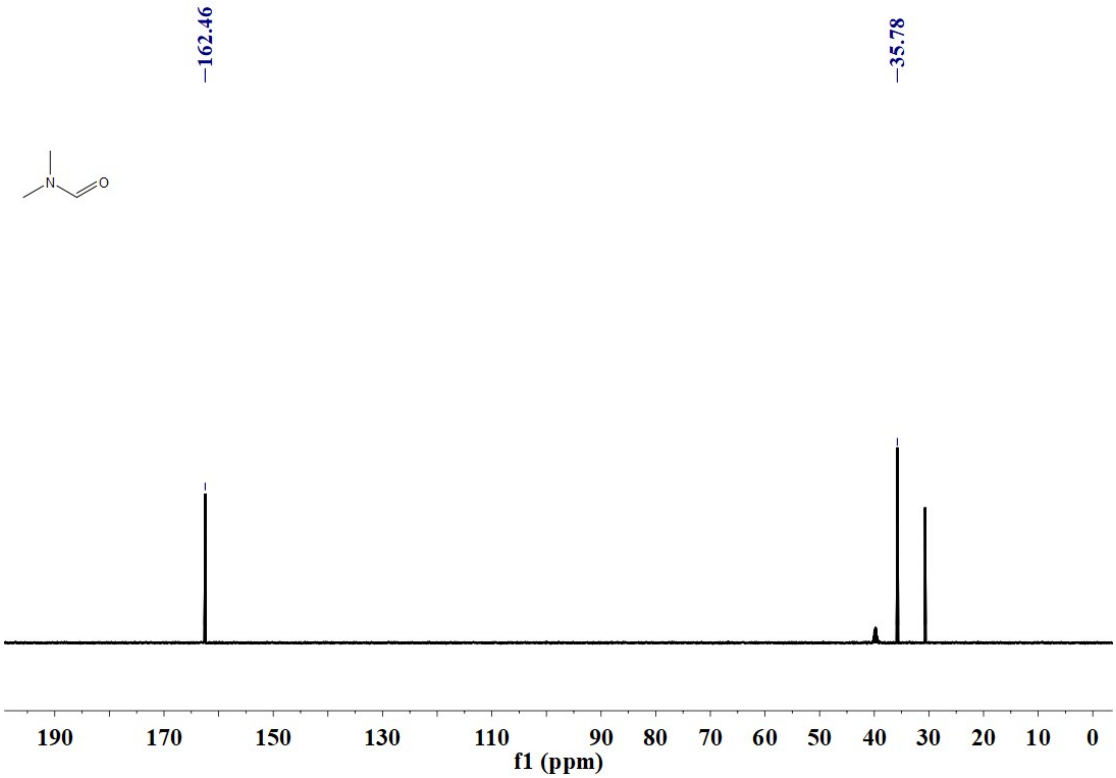
^{1}H NMR spectra of **21** (500 MHz, $CDCl_3$)



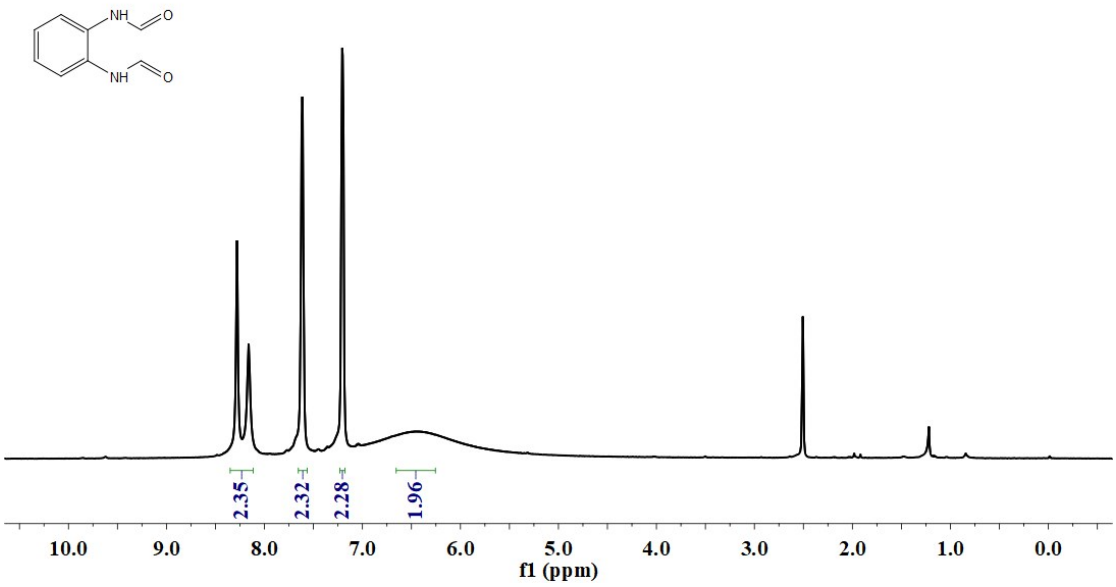
^{1}C NMR spectra of **21** (125 MHz, $CDCl_3$)



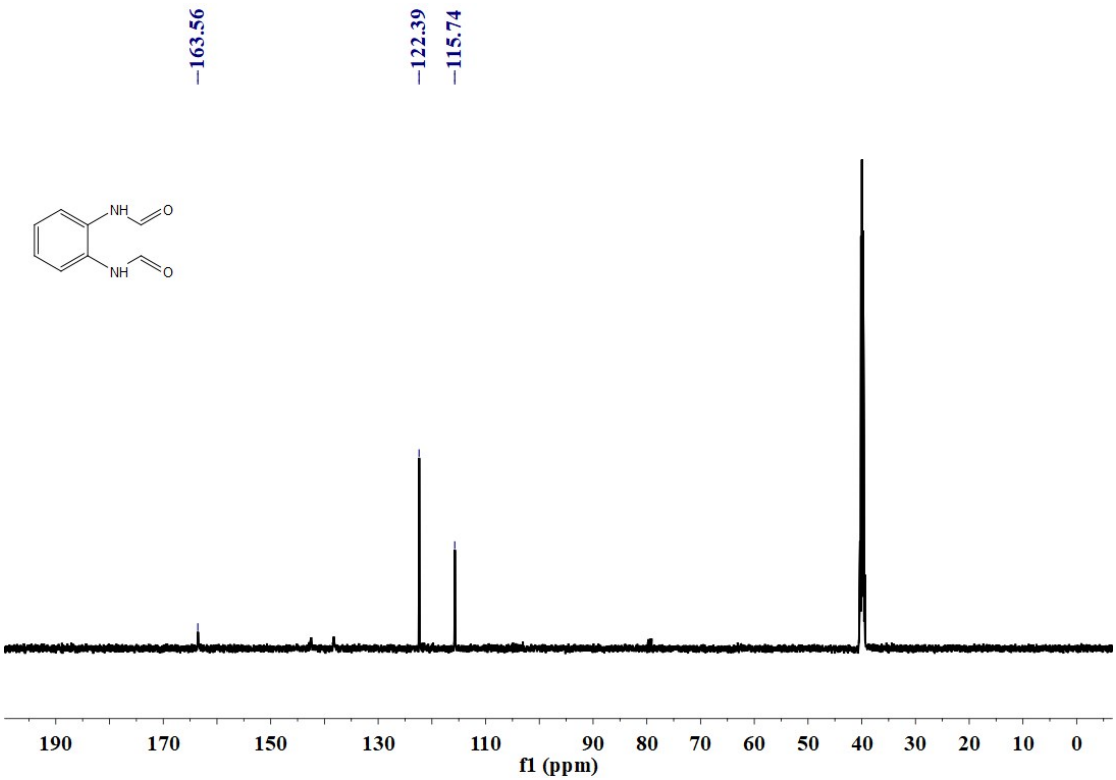
^{1}H NMR spectra of **22** (500 MHz, DMSO)



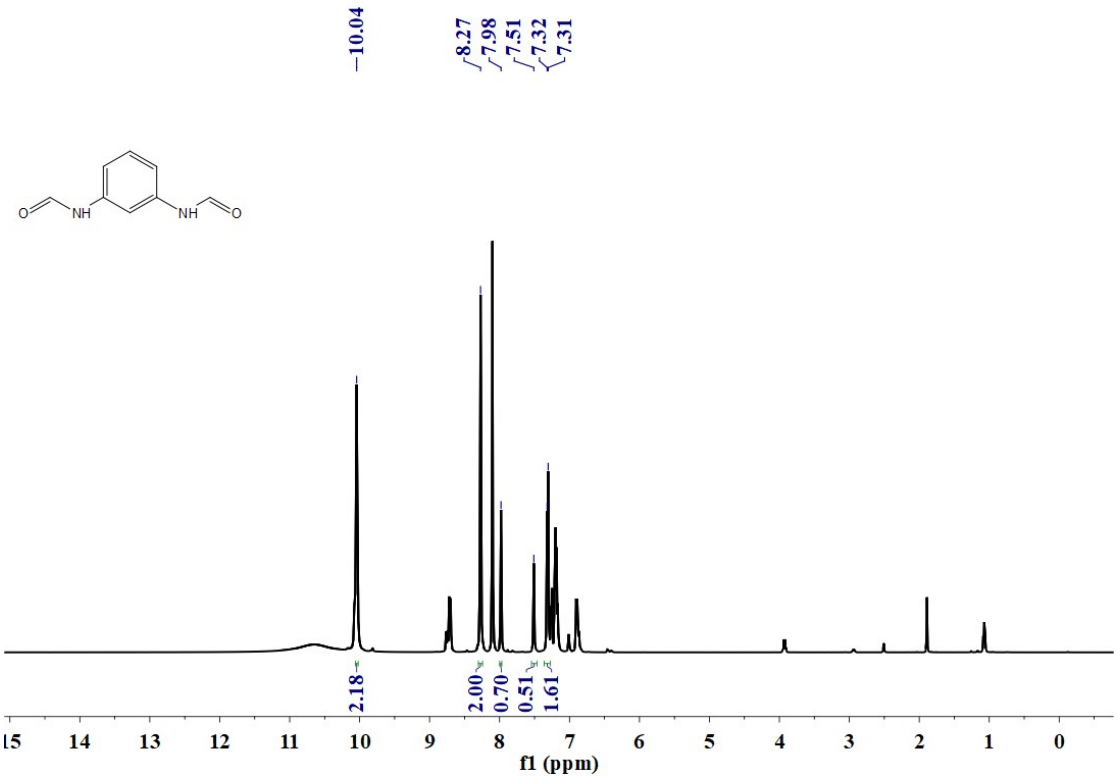
[1]C NMR spectra of **22** (125 MHz, DMSO)



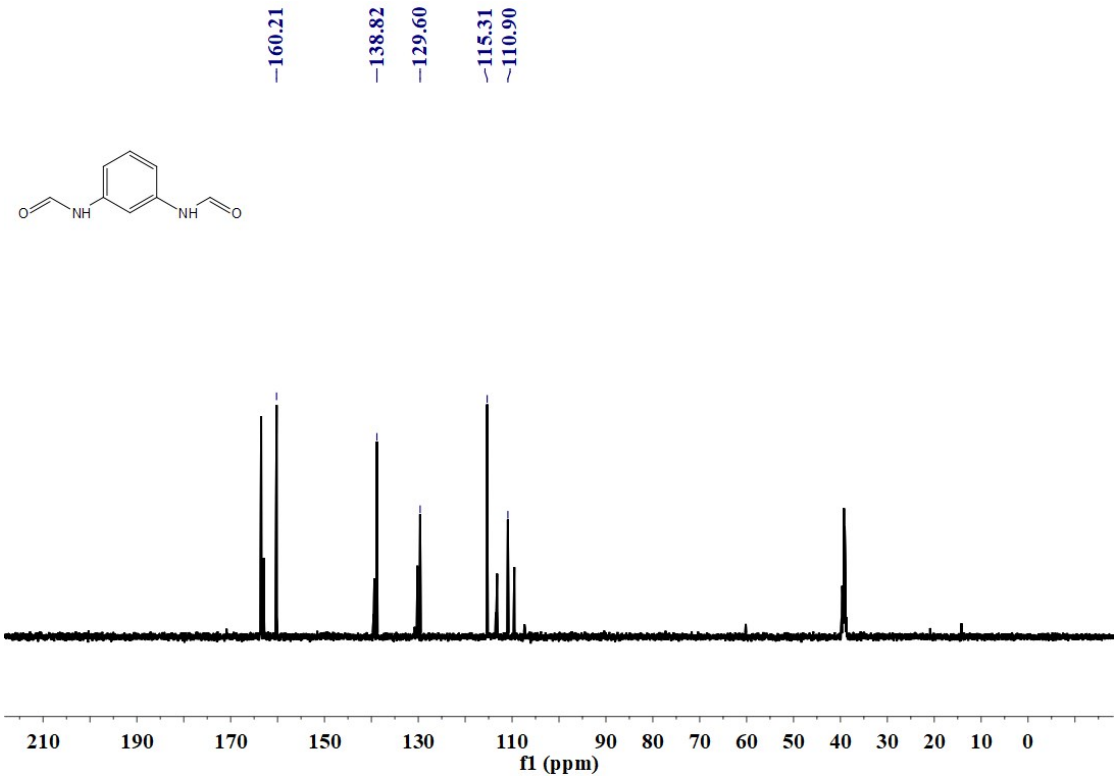
[1]H NMR spectra of **23** (500 MHz, DMSO)



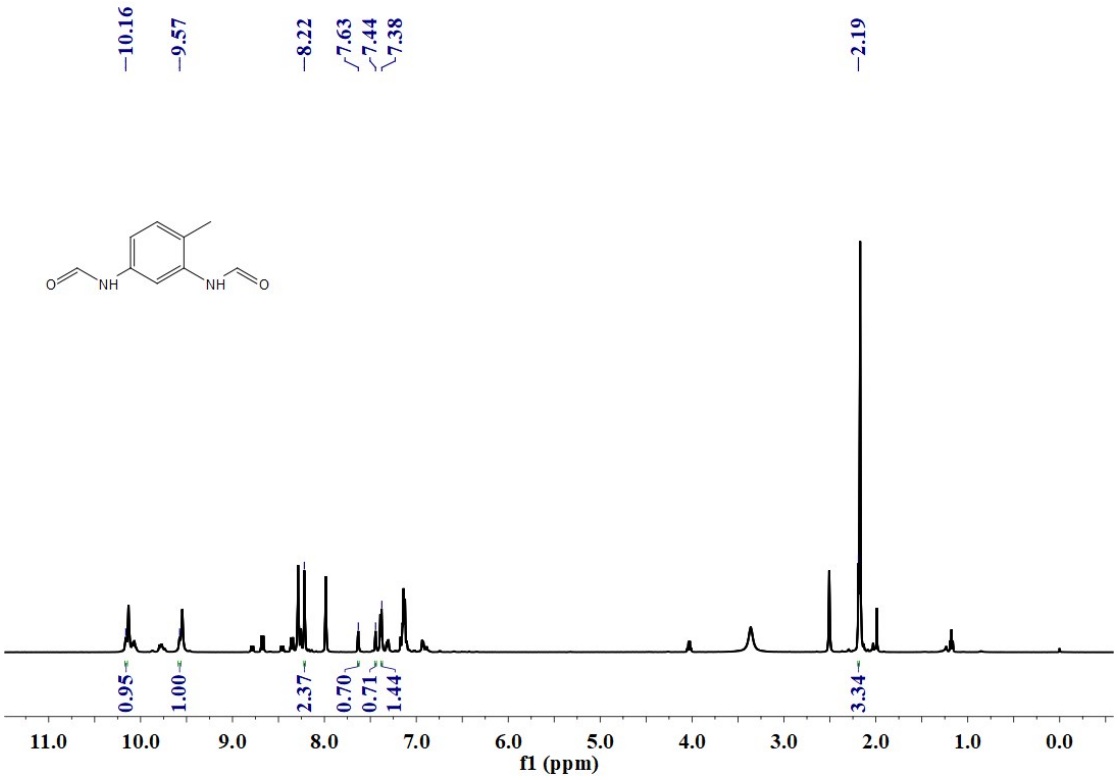
^{1}C NMR spectra of **23** (125 MHz, DMSO)



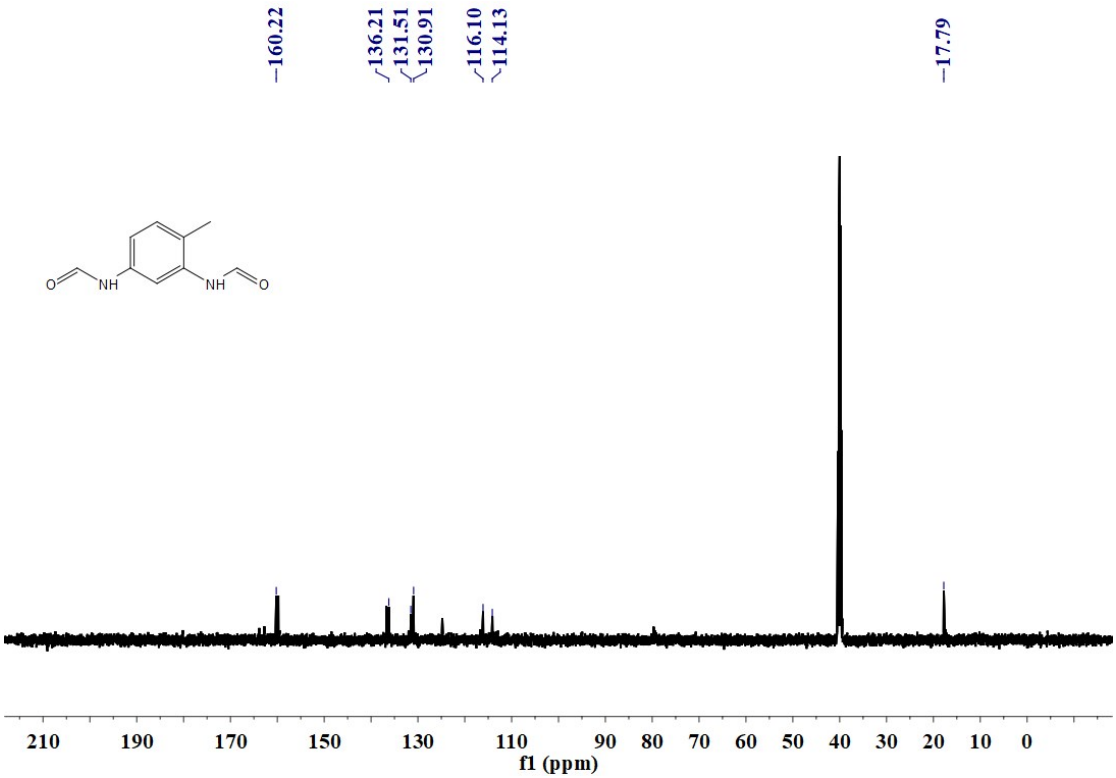
^{1}H NMR spectra of **24** (500 MHz, DMSO)



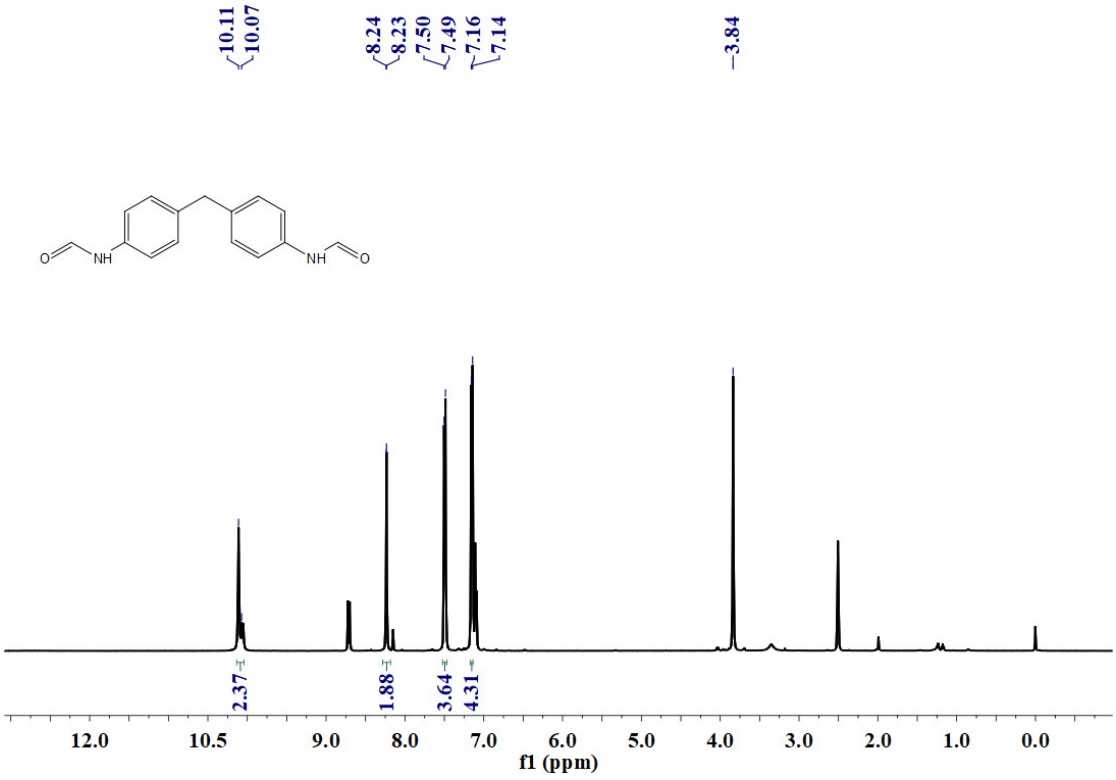
^{1}C NMR spectra of **24** (125 MHz, DMSO)



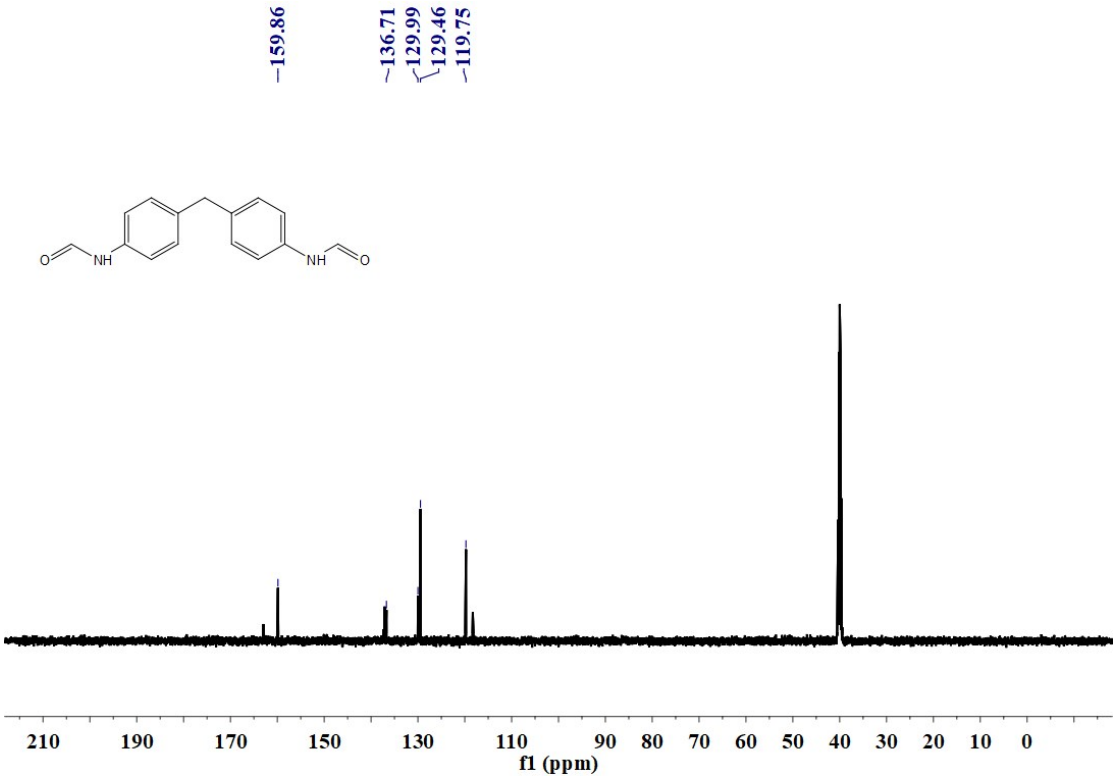
^{1}H NMR spectra of **25** (500 MHz, DMSO)



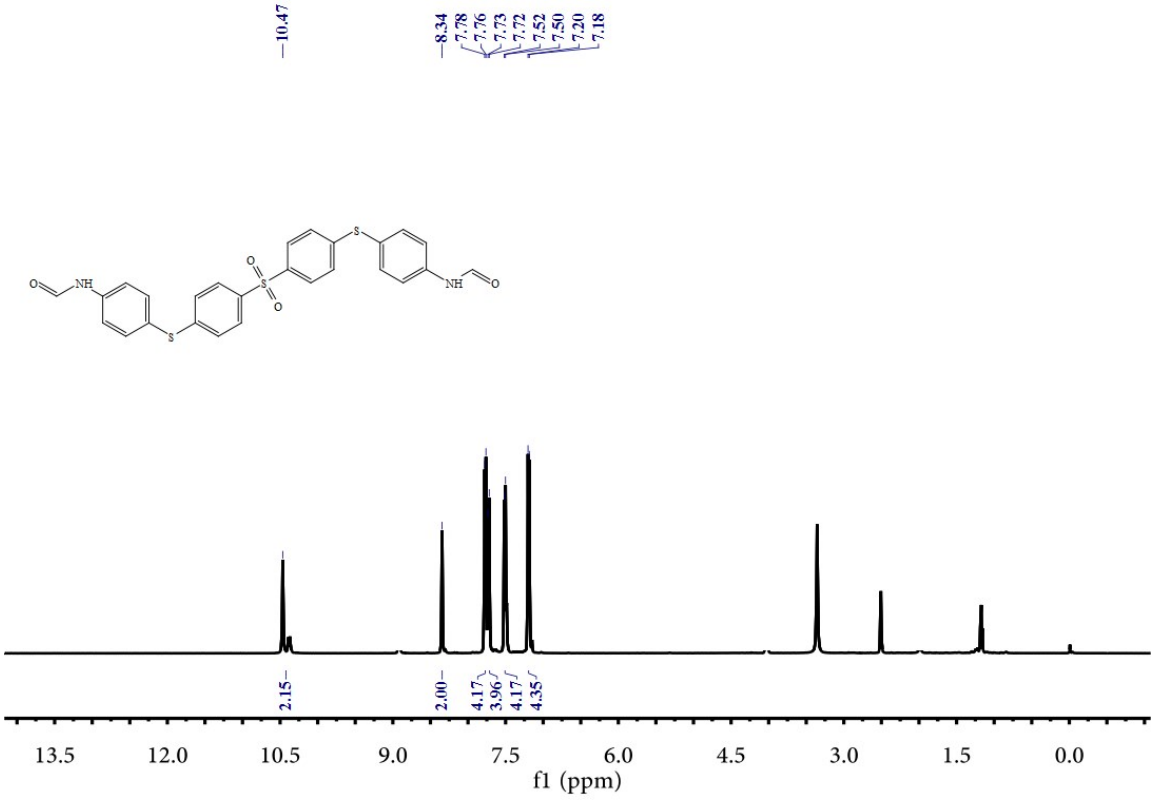
^{1}C NMR spectra of **25** (125 MHz, DMSO)



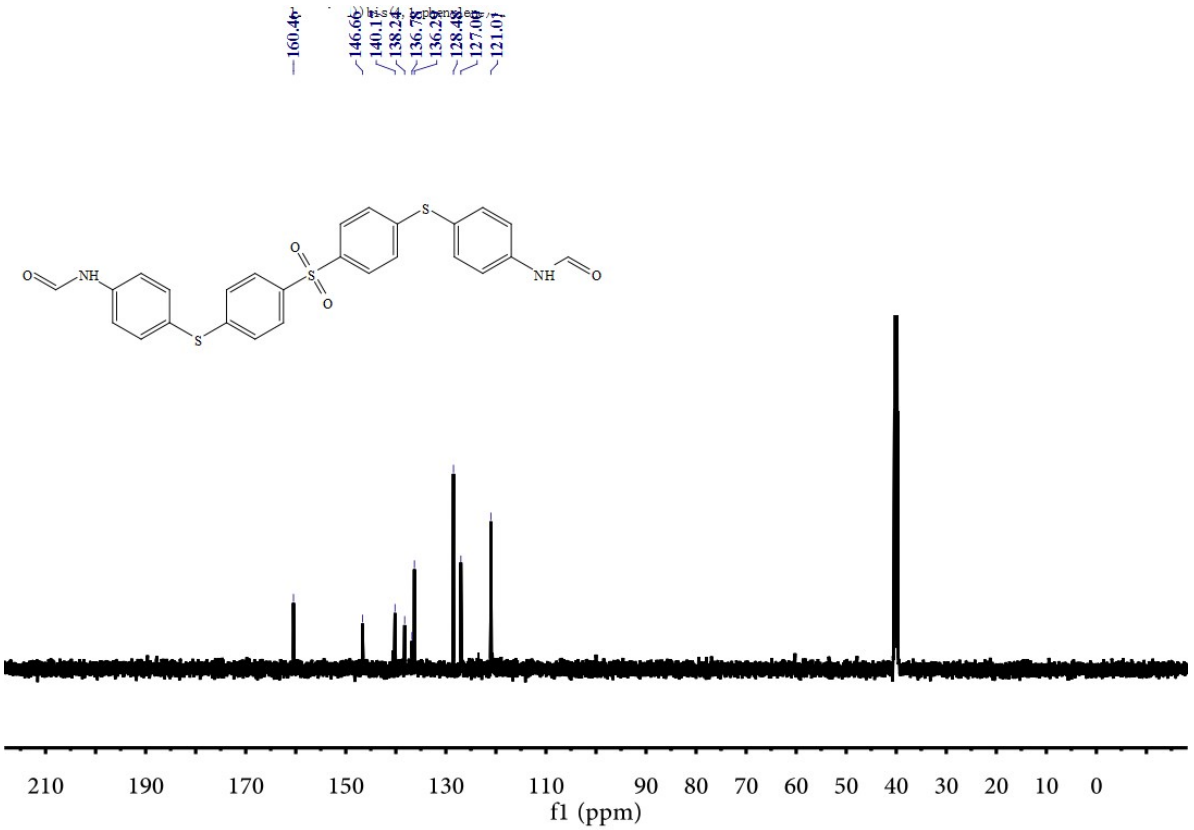
^{1}H NMR spectra of **26** (500 MHz, DMSO)



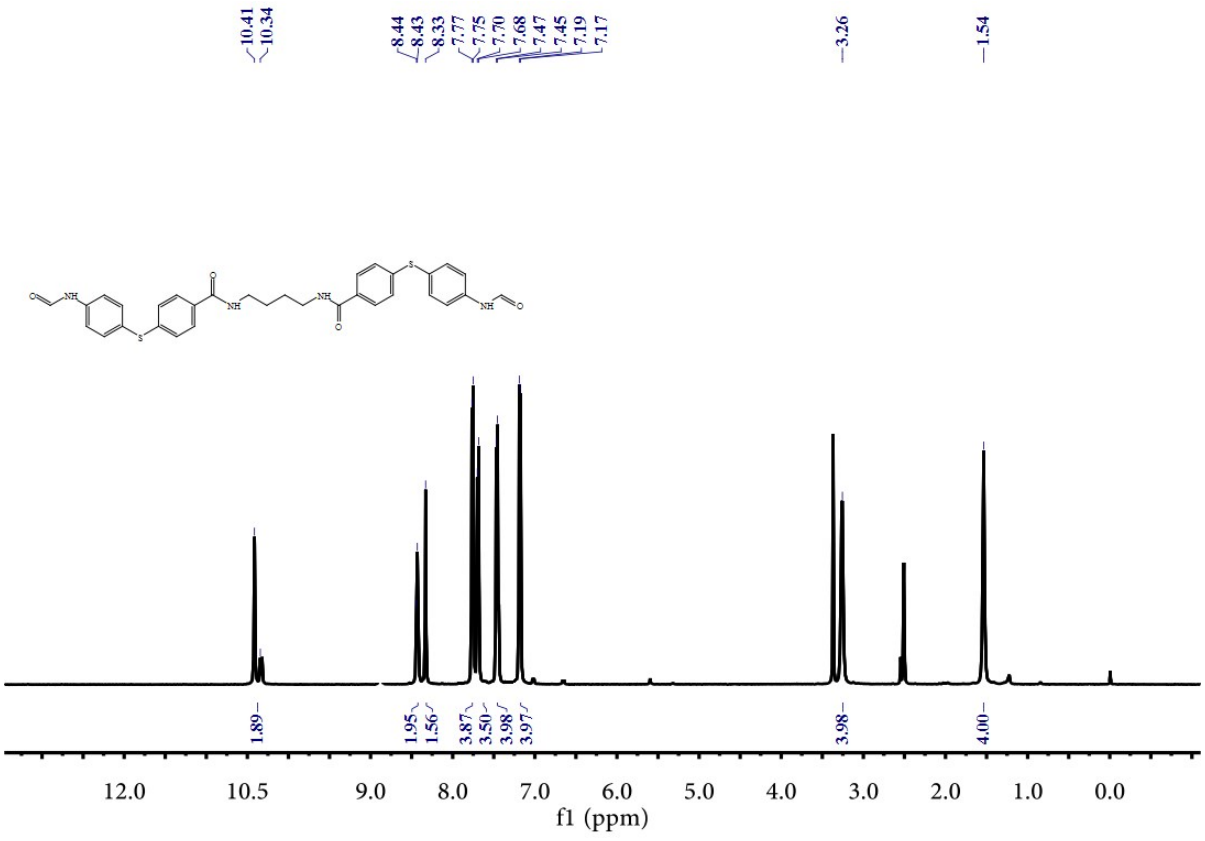
^{1}C NMR spectra of **26** (125 MHz, DMSO)



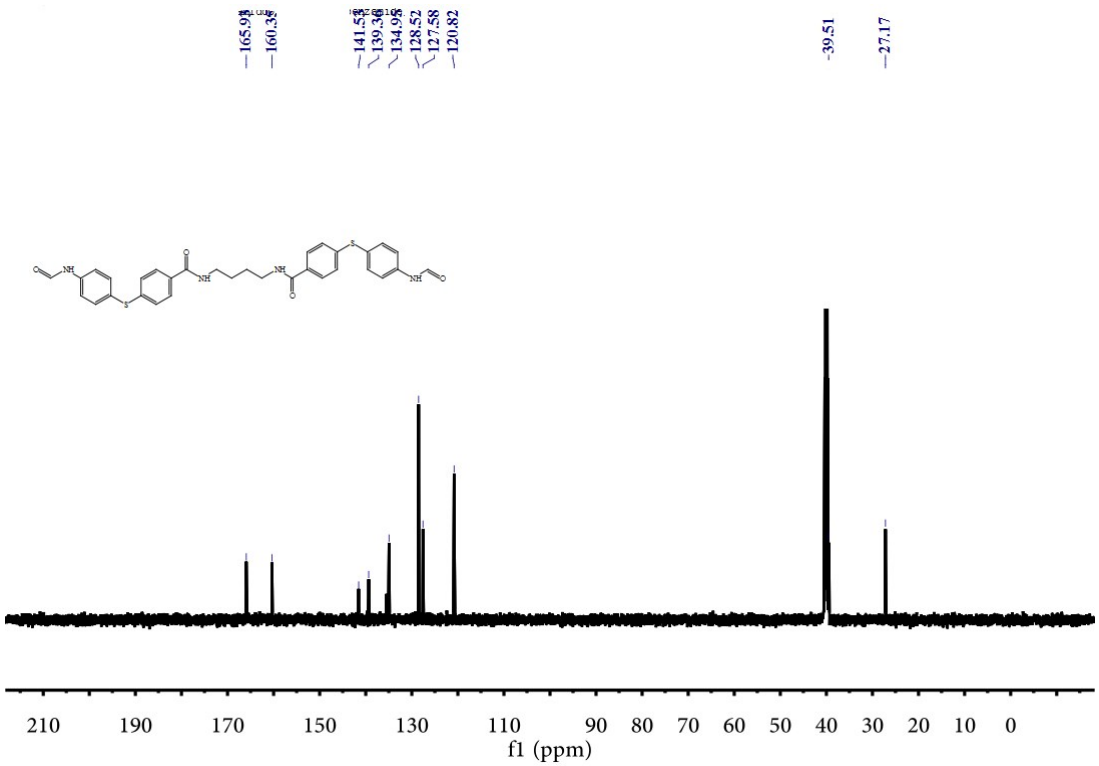
^{1}H NMR spectra of **27** (500 MHz, DMSO)



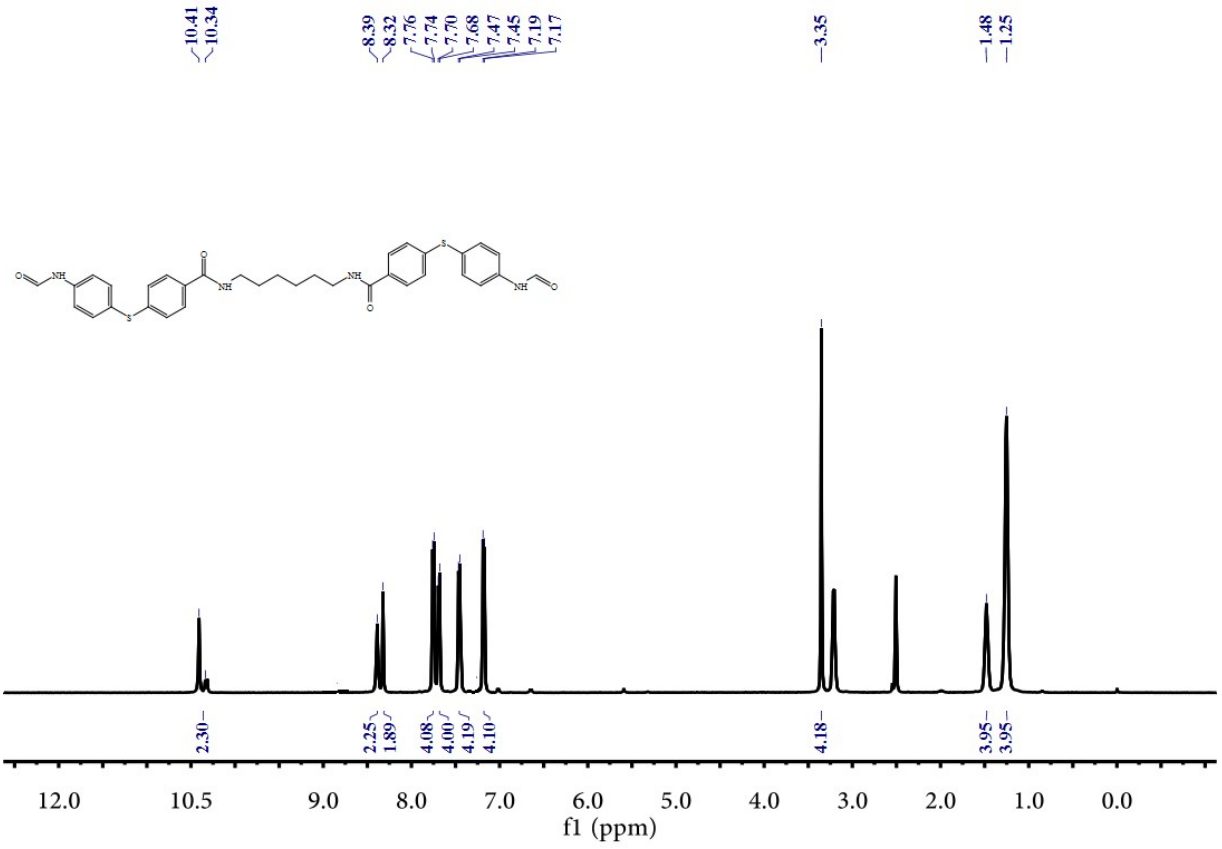
^{13}C NMR spectra of **27** (125 MHz, DMSO)



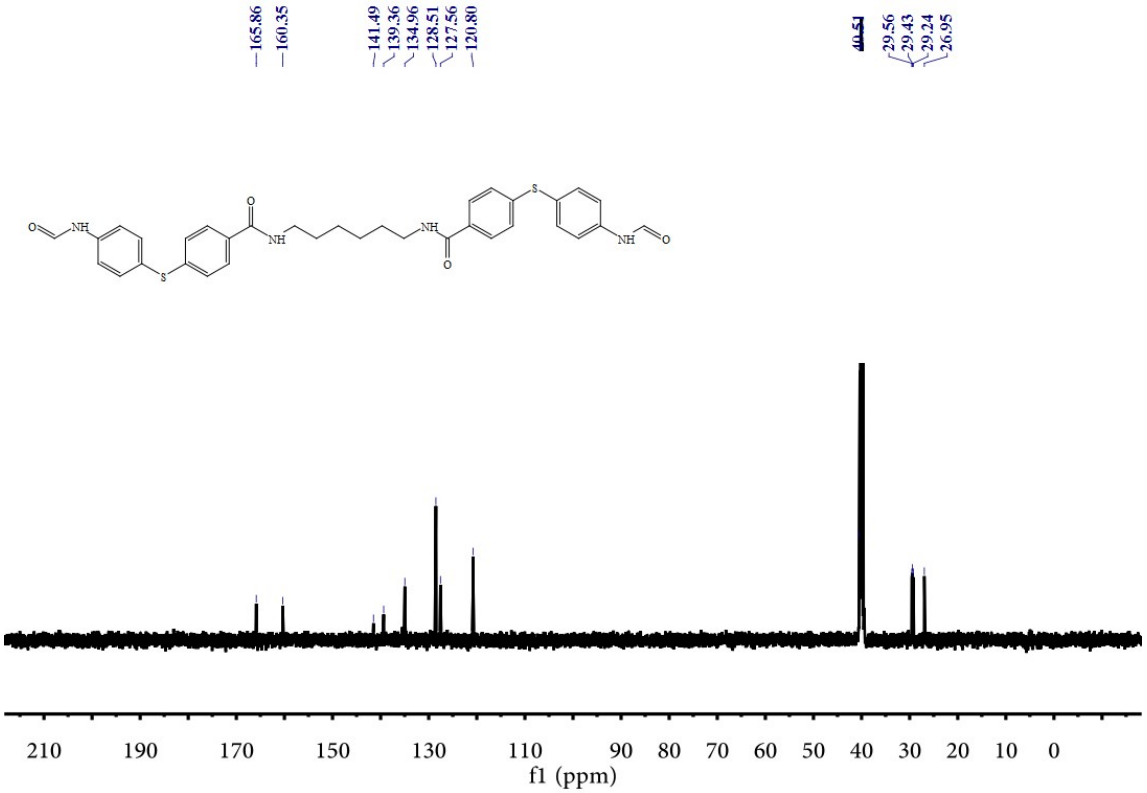
^{1}H NMR spectra of **28** (500 MHz, DMSO)



^{13}C NMR spectra of **28** (125 MHz, DMSO)



^{1}H NMR spectra of **29** (500 MHz, DMSO)



^{13}C NMR spectra of **29** (125 MHz, DMSO)

9. Supplementary Reference

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